ChemInform Abstract: Trapping the Lewis Acid Generated Transient Species from Pentafulvene Derived Diazanorbornenes with ortho-Functionalized Aryl Iodides and Aliphatic Alcohols.

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Trapping the Lewis acid generated transient species from pentafulvene derived diazanorbornenes with *ortho*-functionalized aryl iodides and aliphatic alcohols†

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Herein we describe our efforts on the Lewis acid catalyzed stereoselective ring-opening of pentafulvene derived diazabicyclic olefins using various *ortho*-functionalized aryl iodides such as 2-iodoanilines, 2-iodophenols and 2-iodobenzene thiols to access *trans*-1,2 disubstituted alkylidenecyclopentenes. The scope of the reaction was also explored with a range of easily available aromatic and aliphatic alcohols. Furthermore, the palladium catalyzed intramolecular Heck cyclization of *trans*-1,2 disubstituted alkylidenecyclopentenes would provide an easy approach for the synthesis of highly functionalized spiropentacyclic frameworks consisting of a cyclopentene fused to an indoline/benzothiophene and pyrazolidine.

Introduction

Diazabicyclic olefins have gained much attention in synthetic organic chemistry as a versatile candidate with great synthetic potential.[1] Desymmetrization of strained diazanorbornenes would provide a step-economical access to a wide variety of biologically relevant complex carbocycles and heterocycles. Synthetic modifications of these strained alkenes have been extensively studied by Micouin *et al.*,[2] Kaufmann *et al.*,[3] Pineschi *et al.*,[4] Lautens *et al.*[5] and our research group.[6] Transition metal catalyzed ring-opening of diazabicyclic olefins with various organometallic reagents, soft nucleophiles and aryl iodides represents an efficient method for the preparation of disubstituted cyclopentenes.[2–6] Similarly, highly efficient one-pot strategies have been developed for the carboannulation or heteroannulation reaction of diazabicyclic alkenes with bifunctionalized reactive species for the construction of functionalized polycyclic molecules.[7]

Synthesis of oxadiazenes was described earlier by the thermal or Lewis acid-catalyzed rearrangement of diazabicyclic olefins, especially *N*,*N*-acyloxy-2,3-diazabicyclo[2.2.1]-heptenes.[8] The reaction pathway was explained on the basis of a [3,3]-sigmatropic rearrangement or an intermediate allylic cation. In 2003, Micouin *et al.* reported a diastereoselective synthesis of bicyclic cyclopentenes by a protic or Lewis acid catalyzed intramolecular ring-opening of carbobenzyloxy-protected bicyclic [2.2.1] hydrazine through the formation of an allylic cation.[9] Later, Lautens *et al.* reassigned the structure of bicyclic cyclopentenes through X-ray crystallography and suggested a modified mechanism involving a 5-*exo*-trig cyclization for the ring-forming step.[10] They have also developed a one-pot protocol towards a variety of *N*′-arylaminooxazolidinones by a Lewis acid catalyzed rearrangement followed by an N-arylation reaction. During the same time Pineschi *et al.* achieved a regioselective synthesis of *trans*-1,4-disubstituted hydrazino- and aminocyclopentenes by a sequential copper-catalyzed rearrangement–allylic alkylation of N-Cbz protected and N-Boc protected Diels–Alder adducts.[11] A concerted cyclic mechanism, [3,4]-sigmatropic rearrangement, was put forward for the intramolecular ring-opening of N-Boc protected derivatives. Apart from these reports on the Lewis acid catalyzed intramolecular rearrangement of diazabicyclic olefins, there has been no detailed investigation on the Lewis acid catalyzed intermolecular ring-opening reaction. Very recently, we have described for the first time a Lewis acid catalyzed stereoselective ring-opening of pentafulvene derived diazabicyclic olefins by trapping the transient allylic cation with 2-iodoanilines.[12] In the same report, we have also demonstrated both step-wise and one-pot Lewis acid/palladium mediated synthesis of novel polycyclic motifs with a cyclopentene fused to an indoline and pyrazolidine.

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Cycloaddition chemistry of pentafulvenes is well utilized by various research groups including our own laboratory as an attractive and valuable synthetic tool for the construction of many natural products and pharmaceuticals.[13] However, the studies on pentafulvene derived diazabicyclic olefins are limited to a few reports on transition metal mediated synthesis of functionalized alkylidenecyclopentenes and heterocycle fused diazabicycles.[14] Our success in the Lewis acid catalyzed desymmetrization of diazabicyclic olefins with 2-iodoanilines prompted us to elaborate the developed chemistry for other aryl iodides containing hydroxyl or thiol functional groups at the *ortho* position as well as for various aliphatic alcohols. Herein, we wish to discuss all our efforts on the Lewis acid catalyzed ring-opening of pentafulvene derived diazabicyclic olefins towards *trans*-1,2 disubstituted alkylidenecyclopentenes, in cooperation with the palladium catalyzed intramolecular Heck cyclization to access complex heterocyclic scaffolds.

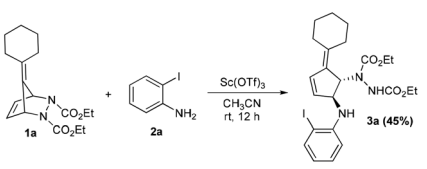
Results and discussion

The bicyclic olefins required for our studies were prepared by the Diels–Alder cycloaddition of various pentafulvenes with azodicarboxylates.[1] We started our investigations with the reaction of diazabicyclic olefin **1a** and 2-iodoaniline **2a** in the presence of $Sc(OTf)_3$ in CH_3CN at room temperature for 12 hours (Scheme 1). The desired 1,2-disubstituted alkylidenecyclopentene **3a** was obtained in 45% yield and the structure of the product was established by various spectroscopic techniques.

We have carried out detailed optimization studies to obtain the best conditions for the transformation (Table 1). Screening of a range of Lewis acids in different solvents proved that the reaction in the presence of $Sc(OTf)_3$ in toluene at room temperature for 30 minutes is the optimal catalytic condition for the formation of **3a** in 93% yield (Entry 4).

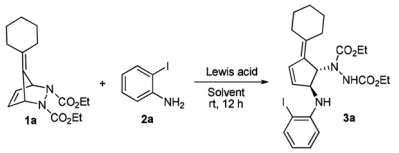
To test the scope and generality of both the reaction partners, a variety of bicyclic olefins were treated with different 2-iodoanilines under the optimized conditions (Fig. 1). All reactions proceeded very smoothly and provided the corresponding alkylidenecyclopentene derivatives in good to excellent yields. The structure and stereochemistry of the compound was unambiguously confirmed by single crystal X-ray analysis of **3a**.[15]

After accomplishing the promising results with 2-iodoanilines, we were interested in trapping the transient species from pentafulvene derived diazanorbornenes with other nucleophiles. With this idea in mind, the diazabicyclic olefin **1a** was



Scheme 1 Ring-opening of fulvene derived azabicyclic olefin with 2-iodoaniline.

Table 1 Optimization studies for a suitable catalyst system[a]



Entry	Lewis acid	Solvent	Yield (%)
1	$Sc(OTf)_3$	CH_3CN	45
2	$Sc(OTf)_3$	DMF	29
3	$Sc(OTf)_3$	THF	48
4	$Sc(OTf)_3$	Toluene	93
5	$Yb(OTf)_3$	Toluene	85
6	$Zn(OTf)_2$	Toluene	80
7	$La(OTf)_3$	Toluene	83
8	$Cu(OTf)_2$	Toluene	27
9	$AlCl_3$	Toluene	49

[a] Reaction conditions: alkene (3 equiv.), 2-iodoaniline (1 equiv.), catalyst (2 mol%), solvent (2 ml), at rt.

treated with 2-iodophenol **4a** under the same optimal reaction conditions employed in the case of 2-iodoanilines. As expected, 1,2-disubstituted alkylidenecyclopentene **5a** was formed in 43% yield (Scheme 2).

Detailed screening studies were performed by choosing **2a** and **4a** as the model substrates to accomplish the optimal reaction conditions and our efforts are summarized in Table 2. Among the various Lewis acids surveyed, AgOTf gave better yield compared to other Lewis acids such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Cu(OTf)_2$, $Sn(OTf)_2$, BF_3Et_2O and $B(C_6F_5)_3$. An extensive screening of the solvents revealed that CH_3CN was more proficient than toluene, DMF, acetone and DCM. The role of various bases in the Lewis acid catalyzed ring-opening was next examined and perceived that Na_2CO_3 was superior to other bases such as K_2CO_3, Cs_2CO_3 and Et_3N. Eventually, diazabicyclic olefin **1a** and 2-iodophenol **4a** in the presence of AgOTf and Na_2CO_3 in acetonitrile at room temperature for 4 hours was found to be the best reaction condition (entry 16).

With the optimal catalytic conditions in hand, we explored the ring-opening of various pentafulvene derived diazabicyclic olefins with different 2-iodophenols (Fig. 2). It is to be noted that 2-iodophenols bearing different functional groups such as NO_2, CO_2Me and phenyl were successfully employed in the developed method. The corresponding functionalized alkylidenecyclopentenes were formed in moderate to good yields through the ring-opening of diazabicyclic olefins.

In the next stage we have elaborated the scope of *ortho*-substituted aryl iodides to another class of nucleophiles, 2-iodobenzene thiols. We initiated our studies with the reaction of diazabicyclic olefin **1a** and 2-iodobenzene thiol **6a** in the presence of $Sc(OTf)_3$ in toluene at room temperature for 2 hours. The reaction afforded the desired 1,2-disubstituted alkylidenecyclopentene **7a** in 66% yield (Scheme 3).

To obtain the best catalyst system for the transformation, a detailed investigation on various reaction parameters was performed (Table 3). Initially a thorough screening of Lewis acids

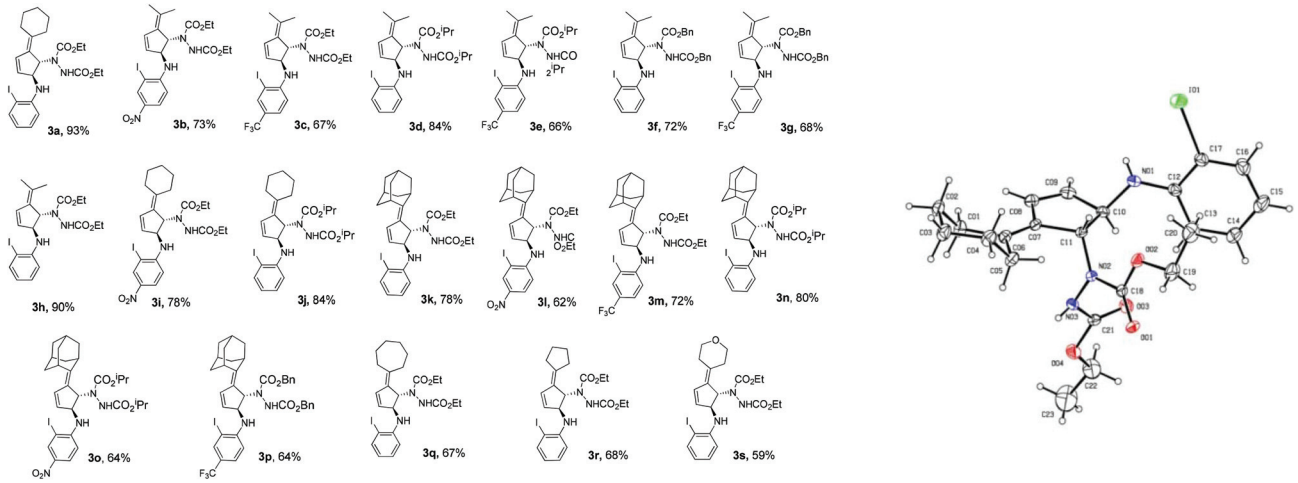
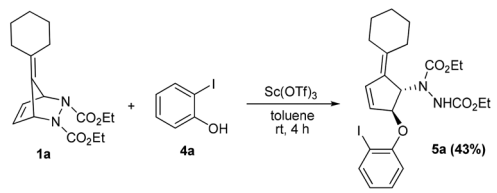
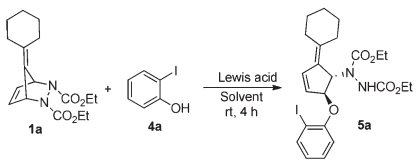


Fig. 1 (Left) Substrate scope of various diazabicyclic olefins and 2-iodoanilines. (Right) The single crystal X-ray structure of **3a**.



Scheme 2 Lewis acid catalyzed desymmetrization of fulvene derived diazabicyclic olefin with 2-iodophenol.

Table 2 Optimization data for the ring-opening of diazabicyclic olefin with 2-iodophenol[a]



Entry	Lewis acid	Solvent	Base	Yield (%)
1	$Sc(OTf)_3$	Toluene	—	43%
2	$Yb(OTf)_3$	Toluene	—	24%
3	$Cu(OTf)_2$	Toluene	—	29%
4	$Sn(OTf)_2$	Toluene	—	16%
5	$BF_3{\cdot}Et_2O$	Toluene	—	25%
6	$B(C_6F_5)_3$	Toluene	—	18%
7	AgOTf	Toluene	—	52%
8	AgOTf	DMF	—	20%
9	AgOTf	Acetone	—	20%
10	AgOTf	DCM	—	17%
11	AgOTf	Toluene	—	37%
12	AgOTf	CH_3CN	—	54%
13	AgOTf	CH_3CN	Cs_2CO_3	20%
14	AgOTf	CH_3CN	K_2CO_3	52%
15	AgOTf	CH_3CN	Et_3N	30%
16	AgOTf	CH_3CN	Na_2CO_3	63%

[a] Reaction conditions: alkene (3 equiv.), 2-iodophenol (1 equiv.), catalyst (2 mol%), base (1.5 equiv.), solvent (2 ml), at rt.

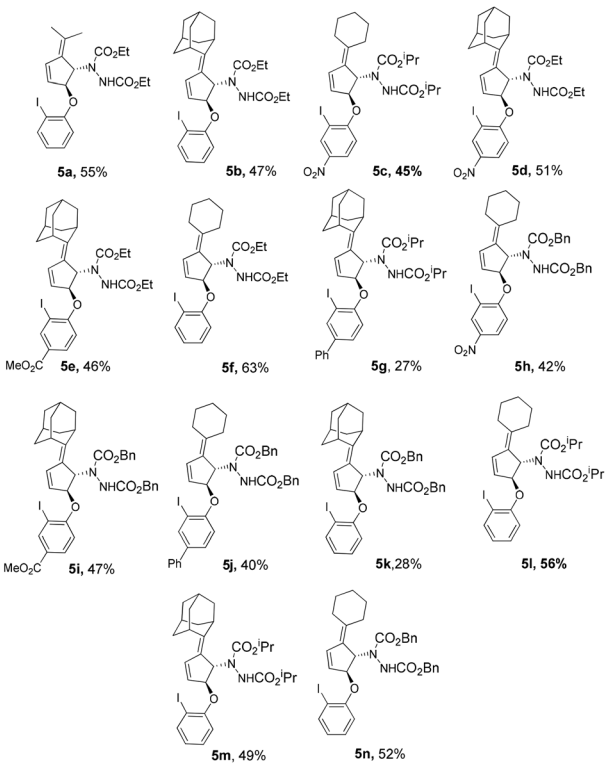
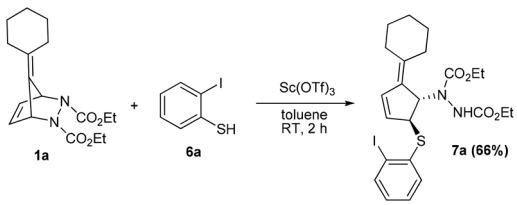
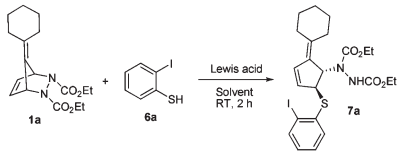


Fig. 2 Substrate scope of 2-iodophenols.



Scheme 3 Lewis acid catalyzed desymmetrization of fulvene derived diazabicyclic olefin with 2-iodobenzene thiol.

Table 3 Optimization studies for the best reaction conditions[a]



Entry	Lewis acid	Solvent	Yield (%)
1	$Sc(OTf)_3$	Toluene	66
2	$Zn(OTf)_2$	Toluene	70
3	$Yb(OTf)_3$	Toluene	53
4	$Cu(OTf)_2$	Toluene	39
5	AgOTf	Toluene	37
6	$BF_3{\cdot}Et_2O$	Toluene	36
7	$Fe(OTf)_3$	Toluene	45
8	$Zn(OTf)_2$	THF	76
9	$Zn(OTf)_2$	DCM	67
10	$Zn(OTf)_2$	CH_3CN	69

[a] Reaction conditions: alkene (3 equiv.), 2-iodobenzene thiol (1 equiv.), catalyst (2 mol%), solvent (2 ml), at rt, 2 h.

was carried out and $Zn(OTf)_2$ was found to be the most effective catalyst. Examination of the role of solvents revealed toluene as the favourable reaction medium than THF, DCM and CH_3CN. Finally, the optimized reaction conditions were obtained as: **1a** and **6a** in the presence of $Zn(OTf)_2$ as a Lewis acid in toluene at room temperature for 2 hours.

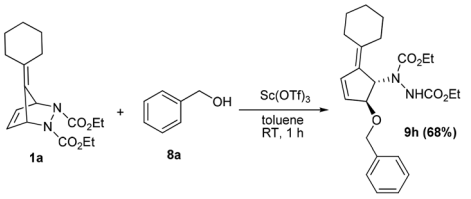
The reaction was found to be compatible with a range of diazabicyclic olefins and 2-iodobenzene thiols under the optimal conditions. Diazabicyclic olefins smoothly reacted with a range of 2-iodobenzene thiols and afforded the functionalized alkylidenecyclopentenes in moderate to good yields (Fig. 3).

Finally, we have expanded our studies to the ring-opening of diazabicyclic olefins with simple aliphatic and aromatic alcohols under Lewis acid catalysis. In a pilot experiment, bicyclic alkene **1a** was treated with benzyl alcohol **8a** in the presence of $Sc(OTf)_3$ in toluene at room temperature for 1 hour and the reaction afforded the ring-opened product **9h** in 68% yield (Scheme 4).

After an extensive screening of Lewis acids and solvents, $Cu(OTf)_2$ in toluene was found to be the most suitable catalyst system for the ring-opening of bicyclic olefins with alcohols (Table 4).

A variety of alcohols were applied in the developed method for the ring-opening of diazabicyclic olefins. The reaction was also found to proceed well with 2-iodobenzyl alcohol and produced the desired alkylidenecyclopentene **9i** in 55% yield. Interestingly, the reaction is tolerant of different aliphatic alcohols such as methanol, ethanol, propargyl alcohol, *etc*., under the optimal catalytic conditions. Ring-opening of bicyclic olefins took place very efficiently with various substituted aliphatic alcohols and afforded the corresponding alkylidenecyclopentene derivatives in moderate to good yields (Fig. 4).

Based on these results we propose a plausible mechanism for the Lewis acid catalyzed ring-opening of diazabicyclic olefins (Scheme 5). In the first step, the Lewis acid is co-ordinated to



Scheme 4 Lewis acid catalyzed desymmetrization of fulvene derived diazabicyclic olefin with benzyl alcohol.

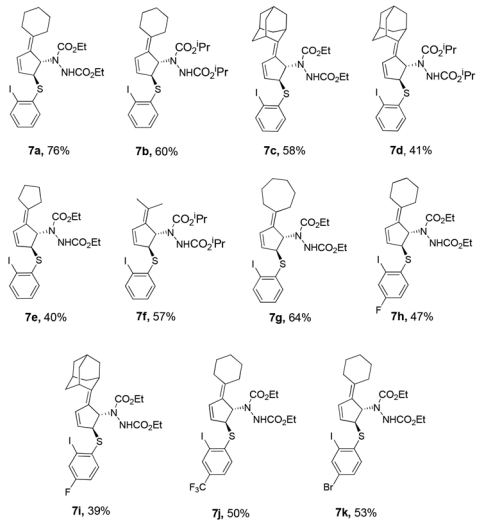
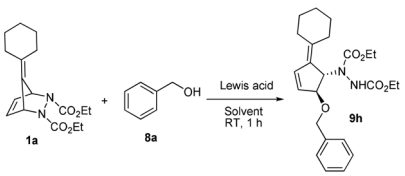


Fig. 3 Substrate scope of 2-iodobenzene thiols.

Table 4 Screening of various Lewis acids and different solvents towards ring-opening of diazabicyclic olefin[a]



Entry	Lewis acid	Solvent	Yield (%)
1	$Sc(OTF)_3$	Toluene	68
2	$Yb(OTf)_3$	Toluene	33
3	$Zn(OTf)_2$	Toluene	43
4	$La(OTf)_3$	Toluene	66
5	$Cu(OTf)_2$	Toluene	72
6	$Fe(OTf)_3$	Toluene	35
7	AgOTf	Toluene	45
8	$Cu(OTf)_2$	THF	29
9	$Cu(OTf)_2$	CH_3CN	NR
10	$Cu(OTf)_2$	DCM	NR

[a] Reaction conditions: azabicyclic olefin (3.0 equiv.), alcohol (1.0 equiv.), Lewis acid (5 mol%), solvent (2.5 ml), rt, 1 hour.

the carbonyl group of diazabicyclic olefin. The subsequent cleavage of the C–N bond leads to a transient allylic cation species **B**. Attack of the incoming nucleophile from the opposite face furnishes *trans*-1,2-disubstituted alkylidenecyclopentenes.

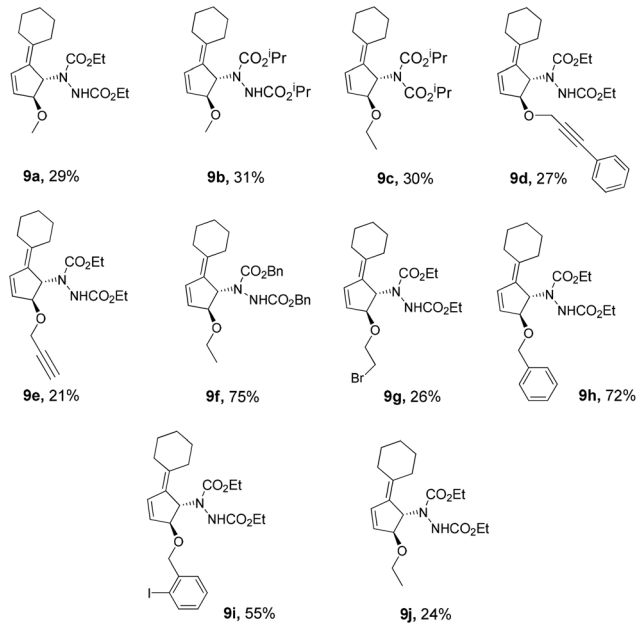
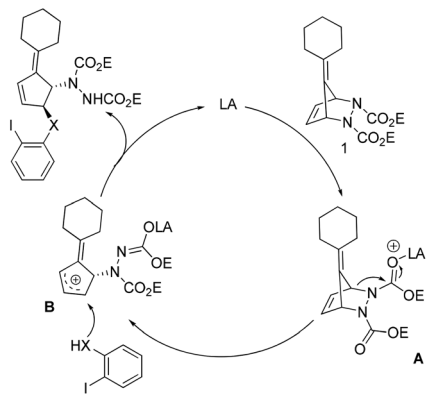
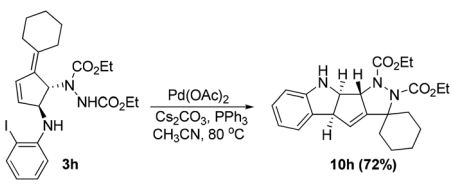


Fig. 4 Substrate scope of aliphatic and aromatic alcohols.



Scheme 5 Plausible mechanism.

To further explore the synthetic utility of the synthesized 1,2-disubstituted alkylidenecyclopentenes derived by the ring-opening with 2-iodoanilines, we have carried out an intramolecular Heck cyclization. Our attempts commenced with the treatment of an alkylidenecyclopentene with $Pd(OAc)_2$, PPh_3 and Cs_2CO_3 in CH_3CN at 80 °C (Scheme 6). To our delight, instead of the usual Heck cyclized product, a novel spiropentacyclic motif with a cyclopentene fused to an indoline and pyrazolidine **10h** was formed in 72% yield. The reaction proceeds through the intramolecular Heck reaction followed by the generation of a π-allyl palladium complex and the subsequent intramolecular nucleophilic attack by the hydrazine –NH.

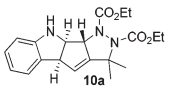
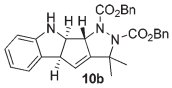
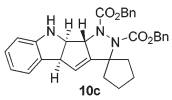
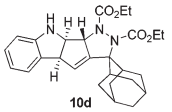
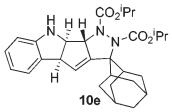
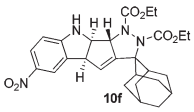
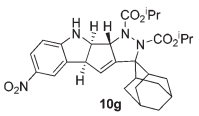
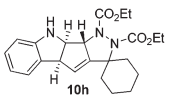
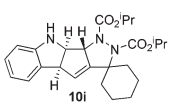


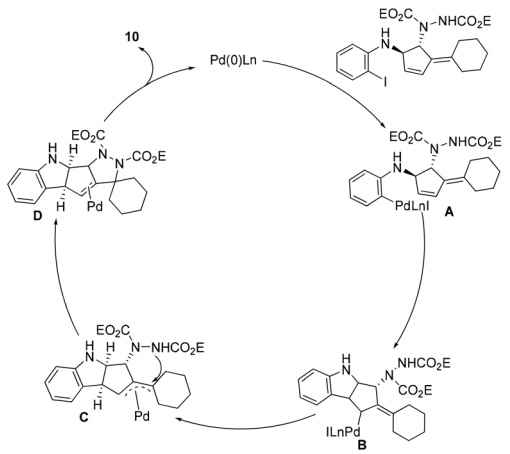
Scheme 6 Synthesis of an indoline derivative by the intramolecular Heck cyclization.

Owing to the prominence of indoline and pyrazolidine motifs, the generality of the intramolecular Heck cyclization was proved by the reaction of various alkylidenecyclopentenes and the results are depicted in Table 5. 1,2-Disubstituted alkylidene cyclopentenes derived from various diazabicyclic olefins and 2-iodoanilines smoothly underwent the intramolecular Heck cyclization and produced the corresponding spiropentacyclic motifs in good yields.

A plausible mechanism is shown in Scheme 7 for the formation of indoline–pyrazolidine fused cyclopentene. Initially, the oxidative addition of Pd(0) to the aryl iodide leads to the formation of **A**. Intermediate **A** thus formed is coordinated to the double bond of cyclopentene followed by the generation of a π-allylpalladium complex, the key intermediate **C**. The intra-

Table 5 Substrate scope for the intramolecular Heck cyclization

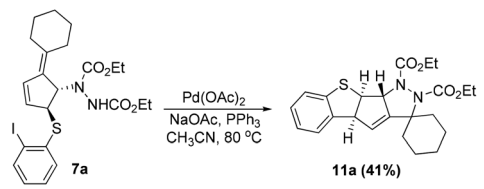
Entry	Substrate	Product	Yield (%)
1	**3a**	 **10a**	54%
2	**3b**	 **10b**	74%
3	**3c**	 **10c**	65%
4	**3a**	 **10d**	72%
5	**3b**	 **10e**	69%
6	**3c**	 **10f**	46%
7	**3a**	 **10g**	42%
8	**3b**	 **10h**	72%
9	**3c**	 **10i**	63%



Scheme 7 Proposed catalytic cycle for the intramolecular Heck cyclization.

molecular nucleophilic attack of the hydrazine moiety to the π-allylpalladium complex provides the polycycle.

In the next stage, we envisaged the synthesis of a highly functionalized spiropentacyclic framework consisting of a cyclopentene fused to a benzothiophene and pyrazolidine. With this objective, we have applied the intramolecular Heck cyclization strategy to the alkylidinecyclopentene derivative formed by the ring-opening of diazanorbornene **2a** with 2-iodobenzene thiol. The reaction resulted in the formation of a polycyclic scaffold with a cyclopentene fused to a benzothiophene and pyrazolidine **11a** in 34% yield. Screening studies showed that NaOAc provided the product in 41% yield (Scheme 8). Unfortunately, our efforts on the intramolecular cyclization of alkylidenecyclopentenes formed through the ring opening of diazabicyclic olefins with 2-iodophenols have not been successful so far.



Scheme 8 Synthesis of the derivatized dihydrobenzothiophene by the intramolecular Heck cyclization.

Ultimately, we have performed the tandem reactions to investigate the one-pot synthesis of spiropentacyclic motifs with a cyclopentene fused to an indoline and pyrazolidine. In an initial endeavour, the treatment of pentafulvene derived diazabicyclic olefin **1a** with 2-iodoaniline **2a** in the presence of $Sc(OTf)_3$, $Pd(OAc)_2$, PPh_3 and Cs_2CO_3 in CH_3CN afforded the functionalized polycycle in 28% yield along with alkylidenecyclopentene in 20% yield. The best catalytic system for the one-pot transformation was achieved after an extensive screening of various reaction parameters (Table 6). The reaction of **1a** and **2a** in the presence of $[Pd(allyl)Cl]_2$ (5 mol%), $Sc(OTf)_3$ (2 mol%), PPh_3 (10 mol%) and Cs_2CO_3 (1.5 equiv.) in a 2 : 0.5 mixture of acetonitrile–toluene led to the exclusive formation of spiropentacyclic molecules in 58% yield (Scheme 9).

Under the optimized reaction conditions various pentafulvene derived bicyclic olefins and 2-iodo anilines were successfully employed for the synthesis of the corresponding spiropentacyclic motifs in good yields (Table 7).

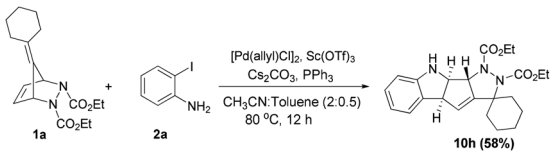
Conclusions

In summary, we have demonstrated a Lewis acid catalyzed stereoselective ring-opening of pentafulvene derived diazabicyclic olefins using various *ortho*-functionalized aryl iodides and aliphatic alcohols to access *trans*-1,2 disubstituted alkylidenecyclopentenes. The palladium catalyzed intramolecular Heck cyclization of *trans*-1,2 disubstituted alkylidenecyclopen-

Table 6 Optimization studies for the one pot synthesis of indoline–pyrazolidine fused cyclopentenes

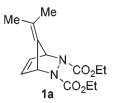
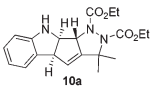
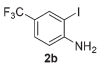
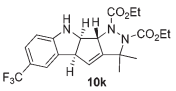
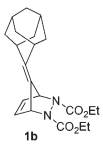
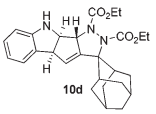
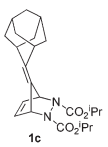
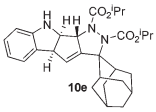
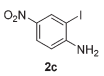
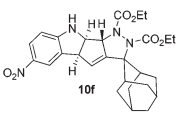
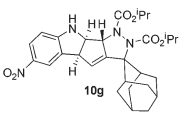
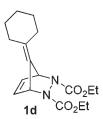
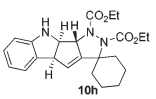
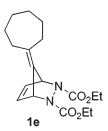
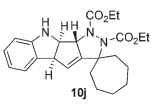
							Yield %	
Entry	Lewis acid	Pd catalyst	Ligand	Base	Solvent	Temperature °C	3	4
1	$Sc(OTf)_3$	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	CH_3CN	80	20	28
2	$Sc(OTf)_3$	$Pd(OAc)_2$	PPh_3	K_2CO_3	CH_3CN	80	10	21
3	$Sc(OTf)_3$	$Pd(OAc)_2$	PPh_3	KOAc	CH_3CN	60	Trace amount	
4	$Sc(OTf)_3$	$Pd(OAc)_2$	PPh_3	Et_3N	CH_3CN	60	15	Trace
5	$Sc(OTf)_3$	$PdCl_2$	PPh_3	Cs_2CO_3	CH_3CN	60	25	Trace
6	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	PPh_3	Cs_2CO_3	CH_3CN	60	—	28
7	$Sc(OTf)_3$	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	CH_3CN	80	Trace	42
8	$Sc(OTf)_3$	$PdCl_2$	PPh_3	Cs_2CO_3	CH_3CN	80	Trace amount	
9	$Sc(OTf)_3$	$Pd(PPh_3)_4$	PPh_3	Cs_2CO_3	CH_3CN	80	Trace amount	
10	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	PPh_3	Cs_2CO_3	CH_3CN	80	—	51
11	$Sc(OTf)_3$	$Pd(dba)_3CHCl_2$	PPh_3	Cs_2CO_3	CH_3CN	80	—	12
12	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	PPh_3	Cs_2CO_3	CH_3CN	80	—	55
13[a]	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	PPh_3	Cs_2CO_3	CH_3CN + toluene	80	—	58
14[a]	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	PPh_3	Cs_2CO_3	CH_3CN + toluene	70	—	14
15[a]	$Sc(OTf)_3$	$[Pd(allyl)Cl]_2$	dppe	Cs_2CO_3	CH_3CN + toluene	70	—	18

Reaction conditions: alkene (3 equiv.), 2-iodoaniline (1 equiv.), catalyst (5 mol%), base (1.5 equiv.), ligand (10 mol%), Lewis acid (2 mol%), solvent (2.5 ml) at 80 °C. [a] CH_3CN : toluene (2 : 0.5).



Scheme 9 One pot synthesis of the indoline derivative.

Table 7 Substrate scope for the one pot strategy

Entry	Bicyclic olefin	*o*-Iodoaniline	Product	Yield (%)
1				60
2	**1a**			41
3		**2a**		72
4		**2a**		75
5	**1b**			46
6	**1c**	**2c**		72
7		**2a**		58
8		**2a**		40

tenes provides an efficient method for the synthesis of highly functionalized spiropentacyclic frameworks consisting of cyclopentene fused to an indoline/benzothiophene and pyrazolidine. The developed strategy is an integration of the transient species generated by the Lewis acid and π-allyl palladium complex. Both one-pot and step-wise synthetic strategies toward functionalized heterocyclic scaffolds are discussed in detail. Further studies to explore the scope of other nucleophiles in trapping the transient species from diazabicyclic olefins and synthesis of other polycyclic scaffolds are in progress.

Experimental

General

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to the standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing the calcium sulfate binder. Gravity column chromatography was performed using 60–120 or 100–200 mesh silica gel and mixtures of hexane–ethyl acetate were used for elution.

Melting points were determined on Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker Avance DPX 300 and Bruker AMX 500 spectrophotometers ($CDCl_3$ as a solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.25, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quadret); dd (double doublet); m (multiplet). Coupling constants are reported as J values in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). Mass spectra were recorded by EI/HRMS at 60 000 resolution using a Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on a Bruker FT-IR spectrometer.

Characterization data of the compounds

General procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines with 2-iodoaniline. A mixture of pentafulvene derived diazabicyclic olefin (3.0 equiv.), *o*-iodoaniline (1.0 equiv.) and $Sc(OTf)_3$ (2 mol%) was weighed in a Schlenk tube and degassed for 10 minutes. Dry toluene (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 30 minutes. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidene cyclopentene.

Diethyl 1-(-2-cyclohexylidene-5-(2-iodophenylamino)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3a). Yield: 93% as a pale yellow coloured solid (m.p. = 132–134 °C); R_f : 0.46 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3387, 3284, 3063, 2980, 2928, 2853, 1709, 1586, 1499, 1449, 1410, 1381, 1313, 1281, 1228, 1171, 1123, 1061, 1007, 928, 741 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.64 (s, 1H), 7.22 (s, 1H), 7.00–6.84 (m, 1H), 6.65 (d, J = 5 Hz, 1H), 6.44 (t, J = 7 Hz, 1H), 6.21–6.17 (m, 1H), 5.95 (s, 1H), 5.10–4.92 (m, 2H), 4.23–4.08 (m, 5H), 2.33 (t, J = 5.5 Hz, 2H), 2.07 (s, 2H), 1.66–1.44 (m, 6H), 1.29–1.12 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.4, 155.2, 146.1, 138.8, 134.2, 132.3, 132.1, 129.5, 119.5, 112.9, 112.3, 85.5, 64.7, 63.4, 62.8, 62.1, 31.8, 31.4, 28.2, 28.0, 26.4, 14.5. MS (ESI): calcd for $C_{23}H_{30}IN_3O_4Na$: 562.11787; found: 562.11481 ($C_{23}H_{30}IN_3O_4Na$).

Diethyl 1-(-2-(2-iodo-4-nitrophenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3b). Yield: 73% as a pale yellow viscous liquid; R_f: 0.43 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3369, 3258, 2921, 1731, 1560, 1418, 1375, 1280, 1213, 1112, 1054, 1002, 751 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.56 (d, J = 10 Hz, 1H), 8.17 (d, J = 9 Hz, 1H), 7.05 (m, 1H), 6.67 (d, J = 5 Hz, 1H), 6.27–6.19 (m, 1H), 5.92 (s, 1H), 5.01–4.79 (m, 2H), 4.27–4.09 (m, 5H), 1.89 (s, 3H), 1.69 (s, 3H), 1.29 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.6, 154.7, 151.0, 138.6, 135.1, 134.8, 130.4, 126.2, 125.9, 112.2, 110.4, 82.4, 65.6, 64.1, 63.3, 62.2, 21.5, 20.9, 14.6, 14.1. MS (ESI): calcd for $C_{20}H_{25}IN_4O_6Na$: 567.07165; found: 567.07123 ($C_{20}H_{25}IN_4O_6Na$).

Diethyl 1-(-2-(2-iodo-4-(trifluoromethyl)phenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2 dicarboxylate (3c). Yield: 67% as a colourless viscous liquid; R_f: 0.40 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3379, 3280, 2988, 2920, 2868, 1714, 1580, 1478, 1450, 1368, 1301, 1224, 1129, 931, 749 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.85 (d, J = 13 Hz, 1H), 7.48 (s, 1H), 7.12–7.02 (m, 1H), 6.63 (s, 1H), 6.19–6.14 (m, 1H), 5.93 (s, 1H), 5.05 (d, J = 15.5 Hz, 1H), 4.87 (s, 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.23–4.11 (m, 4H), 1.99 (s, 3H), 1.68 (s, 3H), 1.32–1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): 156.4, 155.1, 148.5, 135.8, 135.2, 134.8, 131.0, 127.0, 126.7, 120.5, 111.6, 83.7, 63.9, 63.3, 62.9, 62.2, 21.4, 20.5, 14.5. MS (ESI): calcd for $C_{21}H_{25}F_3$ IN_3O_4Na: 590.07395; found: 590.07257 ($C_{21}H_{25}F_3$ IN_3O_4Na).

Diisopropyl 1-(-2-(2-iodophenylamino)-5-(propan-2-ylidene)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3d). Yield: 84% as a colourless viscous liquid; R_f: 0.45 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3375, 3280, 2979, 2934, 2850, 1730, 1580, 1490, 1446, 1403, 1314, 1280, 1220, 1120, 1060, 1000, 931, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.61 (d, J = 8 Hz, 1H), 7.23–7.19 (m, 1H), 7.02 (brs, 1H), 6.59 (d, J = 5.5 Hz, 1H), 6.65–6.41 (m, 1H), 6.16–6.05 (m, 1H), 5.94 (s, 1H), 5.05–4.89 (m, 4H), 4.05 (s, 1H), 1.87 (s, 3H), 1.68 (s, 3H), 1.28–1.09 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.1, 154.8, 146.1, 138.9, 135.6, 131.8, 129.7, 127.2, 125.3, 118.8, 112.9, 85.4, 70.8, 70.0, 65.1, 63.6, 26.9, 25.3, 22.1, 21.9, 21.5, 20.7. MS (ESI): calcd for $C_{22}H_{30}IN_3O_4Na$: 550.11787; found: 550.11633 ($C_{22}H_{30}IN_3O_4Na$).

Diisopropyl 1-(-2-(2-iodo-4-(trifluoromethyl) phenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3e). Yield: 66% as a colourless viscous liquid; R_f: 0.43 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3295, 2940, 2850, 1713, 1580, 1481, 1411, 1281, 1220, 1123, 1061, 1001, 920, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.84 (d, J = 11 Hz, 1H), 7.48 (d, J = 8 Hz, 1H), 7.16–7.06 (m, 1H), 6.63 (s, 1H), 6.14–6.06 (m, 1H), 5.92 (s, 1H), 5.05–4.87 (m, 4H), 4.43–4.38 (m, 1H), 1.88 (s, 3H), 1.68 (s, 3H), 1.32–1.03 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.8, 154.7, 148.4, 136.1, 135.9, 134.8, 130.7, 128.9, 126.9, 125.2, 120.2, 113.4, 111.6, 83.7, 70.2, 65.4, 63.7, 63.1, 26.9, 25.2, 22.6, 21.9, 21.4, 20.7. MS (ESI): calcd for $C_{23}H_{29}F_3IN_3O_4Na$: 618.10525; found: 618.10495 ($C_{23}H_{29}F_3IN_3O_4Na$).

Dibenzyl 1-(-2-(2-iodophenylamino)-5-(propan-2-ylidene)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3f). Yield: 72% as a colourless viscous liquid; R_f: 0.48 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3386, 3287, 3063, 3032, 2926, 2852, 1716, 1586, 1489, 1450, 1402, 1313, 1283, 1128, 1077, 1050, 1004, 894, 743, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.60 (d, J = 6.5 Hz, 1H), 7.52–7.04 (m, 12H), 6.79 (s, 1H), 6.55–6.32 (m, 3H), 5.92–5.86 (m, 1H), 5.29–4.85 (m, 5H), 4.05 (brs, 1H), 1.81 (s, 3H), 1.58 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.6, 155.2, 145.9, 145.3, 138.9, 137.4, 135.7, 135.4, 134.2, 131.7, 129.7, 128.6, 128.4, 128.2, 128.1, 119.0, 112.7, 85.5, 68.2, 67.7, 65.8, 63.5, 21.8, 21.4. MS (ESI): calcd for $C_{30}H_{30}IN_3O_4$, M^+: 623.12810; found: (M + 1) 624.13416.

Dibenzyl 1-(-2-(2-iodo-4-(trifluoromethyl)phenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3g). Yield: 68% as a colourless viscous liquid; R_f: 0.51 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3084, 2385, 3060, 3038, 2932, 2850, 1718, 1586, 1494, 1451, 1402, 1284, 1403, 1311, 1280, 1210, 1124, 1051, 1010, 916, 741, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.81 (s, 1H), 7.32–7.10 (m, 12H), 6.58 (d, J = 6 Hz, 1H), 6.36 (s, 1H), 5.87 (d, J = 12 Hz, 1H), 5.18–4.92 (m, 6H), 4.39 (brs, 1H), 1.83 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.9, 155.2, 148.3, 135.8, 135.1, 128.6, 128.5, 128.1, 127.1, 120.2, 111.5, 83.8, 68.4, 67.8, 64.1, 63.2, 21.5, 20.6. MS (ESI): calcd for $C_{31}H_{29}$ $F_3IN_3O_4Na$: 714.10325: found: 714.10339 ($C_{31}H_{29}$ $F_3IN_3O_4Na$).

Diethyl 1-(-2-(2-iodophenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3h). Yield: 90% as a colourless viscous liquid; R_f: 0.31 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3383, 3280, 3054, 2976, 2928, 2853, 1709, 1586, 1499, 1149, 1410, 1330, 1220, 1120, 1052, 1011, 920, 745 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): 7.61 (s, 1H), 7.20 (s, 1H), 6.99–6.80 (brs, 1H), 6.59 (d, J = 3.5 Hz, 1H), 6.42 (t, J = 7.5 Hz, 1H), 6.30–6.16 (m, 1H), 5.94 (s, 1H), 5.07–4.80 (m, 2H), 4.22–4.05 (m, 5H), 1.87 (s, 3H), 1.68 (s, 3H), 1.28–1.11 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): 156.8, 155.2, 146.0, 138.8, 135.5, 134.2, 131.9, 129.4, 118.9, 112.8, 85.5, 65.3, 63.8, 62.8, 62.0, 21.4, 20.6, 14.5. MS (ESI): calcd for $C_{20}H_{26}IN_3O_4Na$: 522.08657; found: 522.08608 ($C_{20}H_{26}IN_3O_4Na$).

Diethyl 1-(-2-cyclohexylidene-5-(2-iodo-4-nitrophenylamino)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3i). Yield: 78% as a yellow viscous liquid; R_f: 0.53 (hexane–ethyl acetate = 6 : 4). IR (neat) ν_{max}: 3464, 3365, 3071, 2920, 2852, 1705, 1623, 1582, 1469, 1410, 1380, 1318, 1173, 1115, 1058, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.59–8.57 (m, 1H), 8.19–8.15 (m, 1H), 7.07–7.01 (m, 1H), 6.74–6.69 (m, 1H), 6.24–6.19 (m, 1H), 5.93 (s, 1H), 5.10–4.83 (m, 3H), 4.26–4.12 (m, 4H), 2.39–2.34 (m, 2H), 2.07–2.05 (m, 2H), 1.59 (brs, 6H), 1.30–1.16 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.8, 154.8, 150.9, 138.5, 135.2, 131.7, 130.5, 126.3, 125.7, 112.3, 110.4, 82.5, 64.9, 63.5, 62.9, 62.4, 31.9, 30.9, 29.7, 28.3, 26.3, 14.6, 14.1. MS (ESI): calcd for $C_{23}H_{29}IN_4O_6Na$: 607.10295; found: 607.10139 ($C_{23}H_{29}IN_4O_6Na$).

Diisopropyl 1-(-2-cyclohexylidene-5-(2-iodophenylamino)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3j). Yield: 84% as a colourless viscous liquid; R_f: 0.48 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3387, 3285, 2979, 2927, 2853, 1721, 1706, 1587, 1497, 1451, 1384, 1316, 1282, 1107, 1037, 1005,

743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.61 (d, J = 7.5 Hz, 1H), 7.23–7.16 (m, 1H), 7.04–6.84 (m, 1H), 6.64 (d, J = 5.5 Hz, 1H), 6.42 (t, J = 7.5 Hz, 1H), 6.11–6.03 (m, 1H), 5.95 (s, 1H), 5.07–4.82 (m, 4H), 4.07 (brs, 1H), 2.34 (brs, 2H), 2.09 (s, 2H), 1.57 (brs, 6H), 1.28–1.17 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.9, 154.5, 146.0, 138.7, 133.7, 132.8, 129.7, 129.4, 118.8, 118.3, 110.3, 85.4, 70.7, 69.9, 63.8, 58.0, 32.1, 31.9, 28.2, 27.8, 26.4, 22.7, 22.2, 22.1, 21.9. MS (ESI): calcd for $C_{25}H_{34}IN_3O_4Na$: 590.14917: found: 590.14721 ($C_{25}H_{34}IN_3O_4Na$).

Compound 3k. Yield: 78% as a colourless viscous liquid; R_f: 0.48 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3389, 3293, 3062, 2912, 2849, 1750, 1712, 1586, 1498, 1449, 1406, 1316, 1281, 1220, 1116, 1061, 929, 802, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.62 (s, 1H), 7.24–7.21 (m, 1H), 6.99 (d, J = 14 Hz, 1H), 6.64 (d, J = 5 Hz, 1H), 6.43 (t, J = 5 Hz, 1H), 6.15–6.11 (m, 1H), 5.94 (s, 1H), 5.08–4.83 (m, 2H), 4.23–4.09 (m, 5H), 2.98 (s, 1H), 2.55 (d, J = 16.5 Hz, 1H), 1.98–1.74 (m, 12H), 1.29–1.14 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 156.2, 154.6, 147.2, 146.1, 138.8, 133.4, 131.9, 129.5, 128.5, 118.9, 112.9, 85.5, 64.2, 63.2, 62.6, 62.1, 40.3, 39.6, 38.9, 38.8, 36.9, 35.1, 34.5, 28.0, 27.9, 14.6, 14.5. MS (ESI): calcd for $C_{27}H_{34}IN_3O_4Na$: 614.14917: found: 614.14694 ($C_{27}H_{34}IN_3O_4Na$).

Compound 3l. Yield: 62% as a colourless viscous liquid; R_f: 0.51 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3382, 2955, 2919, 2851, 1736, 1654, 1584, 1499, 1463, 1379, 1324, 1183, 1116, 1054, 853 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 8.54 (s, 1H), 8.16 (d, J = 14 Hz, 1H), 7.03–7.00 (m, 1H), 6.72 (d, J = 9 Hz, 1H), 6.14 (s, 1H), 5.90 (s, 1H), 5.07–4.82 (m, 2H), 4.23–4.14 (m, 5H), 2.98 (s, 1H), 2.51 (s, 1H), 2.03–1.84 (m, 12H), 1.31–1.14 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 154.6, 150.9, 138.7, 134.7, 130.1, 129.0, 128.2, 126.2, 110.6, 82.5, 63.1, 62.9, 62.3, 40.4, 39.7, 38.9, 36.8, 35.2, 34.6, 31.6, 28.0, 26.9, 22.7, 14.7, 14.5. MS (ESI): calcd for $C_{27}H_{33}IN_4O_6Na$: 659.13425: found: 659.13192 ($C_{27}H_{33}IN_4O_6Na$).

Compound 3m. Yield: 72% as a colourless viscous liquid; R_f: 0.51 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3380, 3280, 2981, 2924, 2853, 1718, 1601, 1583, 1490, 1450, 1412, 1228, 1120, 1062, 1004, 928, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.87 (d, J = 14.5 Hz, 1H), 7.49 (d, J = 9 Hz, 1H), 7.11–7.00 (m, 1H), 6.68 (s, 1H), 6.13 (d, J = 5 Hz, 1H), 5.92 (s, 1H), 5.07–5.00 (m, 1H), 4.86 (s, 1H), 4.44–4.38 (m, 1H), 4.24–4.14 (m, 4H), 2.98 (s, 1H), 2.53 (d, J = 17.5 Hz, 1H), 1.99–1.76 (m, 12H), 1.33–1.12 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.4, 154.8, 148.4, 136.1, 135.8, 134.0, 131.1, 128.2, 127.0, 126.8, 120.5, 111.6, 83.7, 63.1, 62.8, 62.7, 62.2, 40.2, 39.7, 38.9, 36.8, 35.1, 34.6, 29.7, 29.4, 28.0, 27.8, 14.6, 14.5. MS (ESI): calcd for $C_{28}H_{33}F_3IN_3O_4Na$: 682.13655; found: 682.13652 ($C_{28}H_{33}F_3IN_3O_4Na$).

Compound 3n. Yield: 80% as a colourless viscous liquid; R_f: 0.46 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3297, 3032, 2920, 2856, 1736, 1601, 1498, 1453, 1400, 1314, 1280, 1214, 1124, 1046, 1014, 848, 749, 697, 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.62 (s, 1H), 7.22 (brs, 1H), 7.11 (brs, 1H), 6.74–6.64 (m, 1H), 6.43 (t, J = 11.5 Hz, 1H), 6.07–5.94 (m, 2H), 5.06–4.88 (m, 4H), 4.07 (s, 1H), 2.97 (s, 1H), 2.57 (s, 1H), 1.98–1.83 (m, 1H), 1.25–1.16 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.1, 154.5, 146.2, 138.9, 133.9, 131.8, 129.7, 128.7, 118.9, 114.7, 112.5, 85.4, 70.4, 69.8, 63.9, 63.1, 40.3, 39.7, 38.8, 36.9, 35.1, 34.5, 28.0, 27.9, 22.1, 21.9. MS (ESI): calcd for $C_{29}H_{38}IN_3NaO_4$: 642.18047; found: 642.18722 ($C_{29}H_{38}IN_3NaO_4$).

Compound 3o. Yield: 64% as a yellow viscous liquid; R_f: 0.54 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3389, 3285, 3059, 2990, 2926, 2850, 1718, 1583, 1492, 1443, 1410, 1380, 1281, 1227, 1170, 1120, 1059, 1014, 928, 741, 689 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.53 (s, 1H), 8.16 (d, J = 15 Hz, 1H), 7.15–7.04 (m, 1H), 6.72 (d, J = 9 Hz, 1H), 6.09–6.04 (m, 1H), 5.89 (s, 1H), 5.06–4.83 (m, 5H), 2.97 (s, 1H), 2.61 (s, 1H), 1.98–1.42 (m, 12H), 1.30–1.11 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.4, 154.1, 150.9, 148.1, 138.7, 134.8, 129.0, 128.2, 126.2, 110.7, 82.4, 70.4, 70.1, 63.0, 40.4, 39.7, 38.8, 36.8, 35.2, 34.6, 29.3, 28.0, 27.8, 26.9, 22.1, 22.0. MS (ESI): calcd for $C_{29}H_{37}IN_4O_6Na$: 687.16555: found: 687.16336 ($C_{29}H_{37}IN_4O_6Na$).

Compound 3p. Yield: 64% as a yellow viscous liquid; R_f: 0.46 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3378, 3281, 3059, 3027, 2920, 2858, 1719, 1580, 1489, 1449, 1400, 1311, 1281, 1050, 1000, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.83 (s, 1H), 7.35–7.29 (m, 11H), 6.96–6.94 (m, 1H), 6.65–6.63 (m, IH), 6.28–6.24 (m, 1H), 5.83 (brs, 1H), 5.29–4.99 (m, 6H), 4.40–4.37 (m, 1H), 2.93 (brs, 1H), 2.49 (s, 1H), 2.30 (brs, 1H), 1.97–1.66 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.2, 154.4, 148.4, 135.8, 135.4, 134.1, 128.6, 128.5, 128.2, 111.5, 83.7, 68.4, 67.9, 63.0, 62.8, 40.3, 40.1, 39.5, 38.7, 36.7, 35.1, 34.6, 34.1, 31.9, 29.7, 27.7. MS (ESI): calcd for $C_{38}H_{37}F_3IN_3O_4Na$: 806.16785: found: 806.16628 ($C_{38}H_{37}F_3IN_3O_4Na$).

Diethyl 1-(-2-cycloheptylidene-5-(2-iodophenylamino)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3q). Yield: 67% as a colourless viscous liquid; R_f: 0.40 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3384, 3295, 3062, 2979, 2928, 2855, 1745, 1710, 1586, 1500, 1409, 1228, 1124, 1061, 1008, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.65 (s, 1H), 7.24 (brs, 1H), 7.07 (s, 1H), 6.65 (d, J = 10 Hz, 1H), 6.48 (d, J = 11 Hz, 1H), 6.25 (brs, 1H), 5.98 (s, 1H), 5.11–4.70 (m, 2H), 4.25–4.11 (m, 5H), 2.49 (s, 2H), 2.23 (s, 2H), 1.85–1.14 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.4, 155.1, 146.0, 140.4, 138.7, 135.0, 134.1, 131.9, 129.4, 118.8, 112.3, 85.4, 64.9, 63.3, 62.7, 62.0, 32.5, 32.3, 29.7, 29.1, 27.8, 27.4, 26.8, 14.4. MS (ESI): calcd for $C_{24}H_{32}IN_3O_4Na$: 576.13352; found: 576.13131 ($C_{24}H_{32}IN_3O_4Na$).

Diethyl 1-(-2-cyclopentylidene-5-(2-iodophenylamino)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3r). Yield: 68% as a colourless viscous liquid; R_f: 0.37 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3388, 3289, 2978, 2955, 2926, 2869, 1714, 1587, 1499, 1453, 1385, 1315, 1280, 1231, 1180, 1107, 1037, 956, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.60 (s, 1H), 7.20 (brs, 1H), 7.08 (brs, 1H), 6.43 (d, J = 10 Hz, 2H), 6.18 (brs, 1H), 5.93 (s, 1H), 5.05 (m, 2H), 4.17 (m, 5H), 2.43 (s, 2H), 2.15–2.06 (m, 2H), 1.75–1.57 (m, 4H), 1.30–1.10 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.7, 155.6, 146.1, 140.7, 138.8, 134.9, 131.8, 129.5, 118.9, 112.9, 85.4, 66.2, 65.0, 63.3, 62.7,

31.9, 31.6, 30.5, 26.7, 26.4, 14.5. MS (ESI): calcd for $C_{22}H_{28}IN_3O_4Na$: 548.10222; found: 548.09994 ($C_{22}H_{28}IN_3O_4Na$).

Diethyl 1-(2-(2-iodophenylamino)-5-(2*H*-pyran-4(3*H*, 5*H*, 6*H*)-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (3s). Yield: 59% as a pale yellow viscous liquid; R_f: 0.48 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3369, 3291, 3048, 2980, 2931, 2872, 1711, 1601, 1491, 1452, 1414, 1381, 1281, 1228, 1171, 1123, 1009, 930, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.64 (s, 1H), 7.22 (s, 1H), 6.96 (s, 1H), 6.80 (s, 1H), 6.61 (d, J = 5 Hz, 1H), 6.46–6.34 (m, 1H), 6.03 (s, 1H), 5.11–4.92 (m, 2H), 4.24–4.18 (m, 5H), 3.83–3.59 (m, 4H), 2.51–2.21 (m, 6H), 1.29–1.11 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.8, 154.9, 145.9, 145.3, 138.9, 137.5, 135.8, 133.1, 127.3, 119.1, 112.7, 85.5, 68.5, 68.2, 63.6, 63.3, 62.7, 62.1, 31.9, 31.4, 14.4. MS (ESI): calcd for $C_{22}H_{28}IN_3O_5Na$: 564.09713; found: 564.01004 ($C_{22}H_{28}IN_3O_5Na$).

General procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines with 2-iodophenol

A mixture of pentafulvene derived diazabicyclic olefin (3.0 equiv.), *o*-iodoaniline (1.0 equiv.), AgOTf (3 mol%) and Na_2CO_3 (1.5 equiv.) was weighed in a Schlenk tube and degassed for 10 minutes. Dry acetonitrile (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 2 hours. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidene cyclopentene.

Diethyl 1-(2-(2-iodophenoxy)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5a). Yield: 55% as a yellow viscous liquid R_f = 0.60 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3357, 3064, 2958, 2921, 2854, 1715, 1578, 1467, 1411, 1379, 1307, 1280, 1236, 1167, 1122, 1058, 752 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.75 (d, J = 7.5 Hz, 1H), 7.30–7.27 (m, 1H), 6.93–6.87 (m, 2H), 6.73–6.68 (m, 2H), 5.95 (d, J = 5.5 Hz, 1H), 5.74 (d, J = 7 Hz, 1H), 5.48 (d, J = 7 Hz, 1H), 4.12–4.02 (m, 4H), 1.95–1.84 (m, 3H), 1.84 (s, 3H), 1.24–1.11 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.1, 155.9, 139.3, 135.8, 133.3, 132.6, 129.6, 128.1, 123.0, 113.0, 80.6, 62.4, 61.2, 57.8, 21.7, 21.1, 14.5. HRMS (ESI): calcd for $C_{20}H_{25}IN_2O_5Na$ [M + Na]: 523.07058; found: 523.07117.

Compound 5b. Yield: 47% as a colourless viscous liquid; R_f = 0.67 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3355, 3063, 2915, 2852, 1715, 1577, 1467, 1410, 1379, 1303, 1219, 1124, 1058, 1022, 73, 873, 746 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.77–7.73 (m, 1H), 7.31–7.28 (m, 1H), 6.93–6.88 (m, 1H), 6.85 (s, 1H), 6.73–6.70 (m, 2H), 5.93 (d, J = 5.5 Hz, 1H), 5.74 (d, J = 7.5 Hz, 1H), 5.49 (d, J = 7 Hz, 1H), 4.15–3.95 (m, 4H), 2.89 (d, J = 15.5 Hz, 2H), 2.43 (d, J = 12 Hz, 1H), 1.97–1.72 (m, 11H), 1.24 (t, J = 7 Hz, 3H), 1.08 (t, J = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.0, 155.1, 148.6, 139.3, 134.8, 129.6, 129.1, 127.8, 126.1, 123.0, 113.0, 80.8, 62.3, 61.1, 57.1, 40.1, 40.0, 38.2, 37.3, 37.2, 35.1, 35.0, 28.4, 28.0, 14.6, 14.3. HRMS (ESI): calcd for $C_{27}H_{33}IN_2O_5Na$ [M + Na]: 615.13318; found: 615.13287.

Diisopropyl 1-(2-cyclohexylidene-5-(2-iodo-4-nitrophenoxy)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5c). Yield: 45% as a yellow viscous liquid; R_f = 0.69 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3376, 3062, 2921, 2853, 1757, 1710, 1657, 1577, 1517, 1468, 1411, 1380, 1341, 1305, 1267, 1216, 1119, 1037, 894, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.64 (d, J = 2 Hz, 1H), 8.24 (m, 1H), 6.99 (d, J = 9.5 Hz, 1H), 6.79 (d, J = 5.5 Hz, 1H), 6.53 (s, 1H), 5.94–5.91 (m, 1H), 5.81 (d, J = 7 Hz, 1H), 5.57 (d, J = 6.5 Hz, 1H), 4.85–4.82 (m, 1H), 4.73–4.70 (m, 1H), 2.45–2.43 (m, 2H), 1.90–1.42 (m, 8H), 1.29–1.16 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): 160.9, 155.1, 154.8, 142.2, 141.9, 136.3, 134.8, 129.5, 126.9, 125.6, 111.7, 82.0, 70.1, 68.9, 56.8, 31.9, 31.5, 27.8, 27.2, 26.4, 22.1, 22.0, 21.8. HRMS (ESI): calcd for $C_{25}H_{32}IN_3O_7Na$ [M + Na]: 636.11826; found: 636.11866.

Compound 5d. Yield: 51% as a yellow viscous liquid; R_f = 0.69 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3362, 2909, 2851, 1759, 1719, 1591, 1481, 1438, 1407, 1386, 1301, 1257, 1215, 1116, 1048, 875, 761, 668, 611, 556 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.65 (s, 1H), 8.25 (d, J = 9.5 Hz, 1H), 6.99 (d, J = 9 Hz, 1H), 6.79 (d, J = 5.5 Hz, 1H), 6.62 (s, 1H), 5.89 (d, J = 5.5 Hz, 1H), 5.78 (d, J = 7 Hz, 1H), 5.58 (d, J = 7 Hz, 1H), 4.14–3.94 (m, 4H), 2.88 (s, 2H), 2.42 (d, J = 12 Hz, 1H), 1.98–1.80 (m, 11H), 1.25 (t, J = 7 Hz, 3H), 1.08 (t, J = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 160.4, 155.2, 153.2, 142.6, 140.4, 136.3, 134.9, 133.9, 126.3, 125.7, 82.1, 62.5, 61.4, 59.1, 57.1, 40.1, 38.6, 37.1, 35.2, 28.3, 27.9, 14.6, 14.3, 10.4. HRMS (ESI): calcd for $C_{27}H_{32}IN_3O_7Na$ [M + Na]: 660.11826; found: 660.11799.

Diisopropyl 1-(-2-(2-iodo-4-(trifluoromethyl)phenylamino)-5-(propan-2-ylidene)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5e). Yield: 46% as a colourless viscous liquid; R_f = 0.73 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3370, 2913, 2850, 1760, 1719, 1591, 1567, 1480, 1439, 1407, 1385, 1301, 1256, 1214, 1117, 1046, 972, 942, 876, 838, 803, 760, 728, 698, 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.43 (d, J = 1.5 H z, 1H), 8.01–7.99 (m, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.76 (s, 2H), 5.91 (d, J = 6 Hz, 1H), 5.76 (d, J = 6.5 Hz, 1H), 5.56 (d, J = 7 Hz, 1H), 4.12–3.94 (m, 4H), 3.89 (s, 3H), 2.89 (s, 2H), 2.42 (d, J = 11.5 Hz, 1H), 1.97–1.72 (m, 1H), 1.24 (t, J = 7 Hz, 3H), 1.08 (t, J = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 165.1, 159.1, 156.1, 155.2, 140.9, 140.4, 131.7, 125.8, 124.9, 124.7, 114.6, 112.0, 81.1, 62.5, 61.4, 52.1, 40.1, 37.2, 35.2, 28.4, 28.0, 14.7, 14.4. HRMS (ESI): calcd for $C_{29}H_{35}IN_2O_7Na$ [M + Na]: 673.13866; found: 673.13855.

Diethyl 1-(-2-cyclohexylidene-5-(2-iodophenoxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5f). Yield: 63% as a yellow viscous liquid; R_f = 0.67 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3385, 3052, 2925, 2855, 1763, 1718, 1596, 1478, 1462, 1409, 1379, 1309, 1277, 1218, 1129, 1097, 1065, 924, 838, 752 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.74 (d, J = 8 Hz, 1H), 7.29–7.26 (m, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6. 85 (s, 1H), 6.73–6.69 (m, 2H), 5.95 (d, J = 5.5 Hz, 1H), 5.76 (d, J = 7.5 Hz, 1H), 5.48 (d, J = 7 Hz, 1H), 4.11–4.01 (m, 4H), 2.43–2.35 (m, 2H), 2.16–2.12 (m, 1H), 1.88–1.42 (m, 7H), 1.23 (t, J = 7 Hz, 3H), 1.10 (t, J = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS):

δ 156.0, 155.3, 140.9, 139.4, 135.3, 129.9, 129.7, 128.3, 123.5, 113.0, 80.6, 62.4, 61.2, 58.4, 31.9, 31.5, 27.8, 27.2, 26.5, 14.6, 14.4. HRMS (ESI): calcd for $C_{23}H_{29}IN_2O_5Na$ [M + Na]: 563.10188; found: 563.10076.

Compound 5g. Yield: 27% as a yellow viscous liquid; R_f = 0.73 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3365, 3062, 3029, 2979, 2908, 2849, 1757, 1710, 1660, 1595, 1555, 1473, 1404, 1385, 1302, 1241, 1218, 1179, 1110, 1045, 974, 955, 921, 876, 808, 760, 739, 699, 664, 640, 603, 555 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.97 (s, 1H), 7.53–7.48 (m, 3H), 7.42–7.39 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.76–6.72 (m, 2H), 5.95 (d, *J* = 5.5 Hz, 1H), 5.78 (d, *J* = 7 Hz, 1H), 5.52 (d, *J* = 7 Hz, 1H), 4.88–4.84 (m, 1H), 4.74–4.69 (m, 1H), 2.94–2.89 (m, 3H), 2.43 (d, *J* = 12 Hz, 1H), 1.96–1.73 (m, 10H), 1.26–1.22 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.4, 154.8, 148.5, 139.2, 137.8, 136.4, 134.8, 128.8, 128.2, 127.9, 127.2, 126.7, 126.3, 113.0, 81.2, 69.9, 68.5, 56.9, 40.1, 38.3, 37.3, 35.1, 35.0, 28.4, 28.0, 22.1, 22.0. HRMS (ESI): calcd for $C_{35}H_{41}IN_2O_5Na$ [M + Na]: 719.19579: found: 719.19532.

Dibenzyl 1-(-2-cyclohexylidene-5-(2-iodo-4-nitrophenoxy)-cyclopent-3enyl)hydrazine-1,2-dicarboxylate (5h). Yield: 42% as a yellow viscous liquid R_f = 0.67 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3360, 2910, 2854, 1759, 1715, 1598, 1479, 1438, 1405, 1387, 1298, 1257, 1215, 1118, 1045, 924, 836, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.45 (d, *J* = 2 Hz, 1H), 8.14 (m, 1H), 7.32–7.14 (m, 10H), 6.89 (d, *J* = 9 Hz, 1H), 6.76–6.74 (m, 2H), 5.90 (d, *J* = 5.5 Hz, 1H), 5.82 (d, *J* = 7 Hz, 1H), 5.52 (d, *J* = 7 Hz, 1H), 5.14–5.06 (m, 4H), 2.41–2.37 (m, 2H), 2.10–2.05 (m, 1H), 1.89–1.88 (m, 1H), 1.67–1.62 (m, 3H), 1.44–1.39 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 160.6, 155.4, 155.0, 142.4, 142.2, 136.4, 136.3, 135.7, 134.9, 129.9, 129.6, 129.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7 (2), 126.8, 125.5, 111.5, 81.8, 68.0, 66.9, 57.4, 31.9, 31.4, 27.7, 27.1, 26.4. HRMS (ESI): calcd for $C_{33}H_{32}IN_3O_7Na$ [M + Na]: 732.11826; found: 732.11755.

Compound 5i. Yield: 47% as a yellow viscous liquid; R_f = 0.67 (hexane–ethyl acetate; 7 : 3). IR (neat) ν_{max}: 3366, 2920, 2854, 1760, 1718, 1654, 1592, 1483, 1446, 1406, 1300, 1258, 1214, 1117, 1046, 756, 698, 611 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.35 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.32–7.21 (m, 10H), 6.99 (s, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 5.5 Hz, 1H), 5.89 (d, *J* = 6 Hz, 1H), 5.80 (d, *J* = 7.5 Hz, 1H), 5.55 (d, *J* = 6.5 Hz, 1H), 5.16–5.03 (m, 4H), 3.89 (s, 3H), 2.91–2.83 (m, 2H), 2.44 (d, *J* = 11.5 Hz, 1H), 1.95–1.68 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 165.1, 155.8, 155.0, 149.4, 140.9, 140.4, 136.4, 135.8, 135.5, 131.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 127.4, 126.8, 125.5, 124.8, 111.8, 81.0, 67.9, 66.7, 57.2, 52.1, 40.0, 37.9, 37.1, 35.1(2), 28.3, 27.9. HRMS (ESI): calcd for $C_{39}H_{39}IN_2O_7Na$ [M + Na]: 797.16996; found: 797.16933.

Dibenzyl 1-(-2-cyclohexylidene-5-(3-iodobiphenyl-4-yloxy)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5j). Yield: 40% as a yellow viscous liquid; R_f = 0.64 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3382, 3053, 2925, 2855, 1761, 1715, 1596, 1476, 1461, 1408, 1378, 1310, 1279, 1217, 1130, 1097, 1066, 924, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.9 (s, 1H), 7.49–7.19 (m, 16H), 7.05 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.70 (d, *J* = 6 Hz, 1H), 5.97 (d, *J* = 5.5 Hz, 1H), 5.81 (d, *J* = 7.5 Hz, 1H), 5.50 (d, *J* = 7.5 Hz, 1H), 5.11–4.99 (m, 4H), 2.45–2.38 (m, 3H), 2.11–2.07 (m, 1H), 1.89–1.85 (m, 1H), 1.64–1.41 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.9, 155.4, 155.2, 141.2, 139.1, 137.8, 136.5, 136.4, 136.0, 135.5, 129.0, 128.8 (2), 128.4, 128.3(2), 128.2 (2), 128.1, 128.0, 127.9, 127.7, 127.5, 127.3 (2), 126.7, 113.1, 80.9, 67.8, 66.7, 57.6, 31.9, 31.4, 29.7, 27.7, 27.2, 22.7, 14.2. HRMS (ESI): calcd for $C_{39}H_{37}IN_2O_5Na$ [M + Na]: 763.16448: found: 763.16501.

Compound 5k. Yield: 28% as a yellow viscous liquid; R_f = 0.71 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3368, 3063, 3032, 2960, 2960, 2908, 2848, 1762, 91, 1467, 1716, 1609, 1578, 1491, 1467, 1444, 1407, 1359, 1300, 1262, 1238, 1211, 1100, 1050, 871, 801, 748, 697, 657, 602, 556 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.33–7.21 (m, 11H), 7.10 (s, 1H), 6.90 (d, *J* = 8 Hz, 1H), 6.71–6.67 (m, 2H), 5.92 (d, *J* = 6 Hz, 1H), 5.79 (d, *J* = 7 Hz, 1H), 5.49 (d, *J* = 7 Hz, 1H), 5.16–5.04 (m, 4H), 3.04–2.83 (m, 3H), 2.46–2.43 (m, 1H), 1.95–1.66 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 156.0, 155.9, 155.1, 148.8, 139.3, 136.5, 136.1, 135.0, 128.4(3), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 123.1, 113.1, 80.7, 68.1, 67.8, 67.7, 66.7, 57.4, 40.0, 38.0, 37.2, 37.1, 35.1, 35.0, 28.4, 27.9. HRMS (ESI): calcd for $C_{37}H_{37}IN_2O_5Na$ [M + Na]: 739.16448: found: 739.16400.

Diisopropyl 1-(-2-cyclohexylidene-5-(2-iodophenoxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5l). Yield: 56% as a white solid; Mp: 138 °C; R_f = 0.73 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3367, 3066, 2977, 2926, 2853, 1756, 1710, 1577, 1468, 1443, 1404, 1382, 1300, 1220, 1177, 1110, 1043, 961, 936, 874, 854, 806, 749 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): 7.73 (d, *J* = 8 Hz, 1H), 7.30–7.26 (m, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.73–6.69 (m, 3H), 5.95 (d, *J* = 6 Hz, 1H), 5.77 (d, *J* = 7 Hz, 1H), 5.47 (d, *J* = 7 Hz, 1H), 4.85–4.71 (m, 2H), 2.64–2.59 (m, 1H), 2.45–2.34 (m, 2H), 2.15–2.10 (m, 1H), 1.87 (d, *J* = 6 Hz, 1H), 1.68–1.38 (m, 4H), 1.23–0.95 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 155.4, 155.1, 140.7, 139.3, 135.2, 130.1, 129.6, 129.5, 128.4, 122.9, 113.0, 80.6, 69.9, 68.6, 57.0, 31.8, 31.4, 27.8, 27.3, 26.5, 22.2, 22.0. HRMS (ESI): calcd for $C_{25}H_{33}IN_2O_5Na$ [M + Na]: 591.13318: found: 591.13366.

Compound 5m. Yield: 49% as a white solid; Mp: 154 °C; R_f = 0.69 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3366, 3065, 2979, 2908, 2850, 1757, 1709, 1661, 1577, 1468, 1404, 1381, 1301, 1217, 1178, 1110, 1046, 1025, 974, 942, 870, 806, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.31–7.26 (m, 1H), 6.93 (d, *J* = 8 Hz, 1H), 6.75–6.69 (m, 3H), 5.93 (d, *J* = 6.5 Hz, 1H), 5.75 (d, *J* = 7 Hz, 1H), 5.48 (d, *J* = 7 Hz, 1H), 4.86–4.69 (m, 2H), 2.93–2.87 (m, 2H), 2.42 (d, *J* = 12 Hz, 1H), 1.97–1.79 (m, 11H), 1.25–0.94 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.4, 154.8, 148.3, 139.3, 134.7, 129.6, 128.0, 126.3, 113.0, 80.9, 69.9, 68.5, 56.9, 40.0(2), 38.3, 37.3, 35.0(2), 28.4, 28.0, 22.1, 22.0. HRMS (ESI): calcd for $C_{29}H_{37}IN_2O_5Na$ [M + Na]: 643.16448; found: 643.16521.

Dibenzyl 1-(-2-cyclohexylidene-5-(2-iodophenoxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (5n). Yield: 52% as a yellow viscous liquid; R_f = 0.67 (hexane–ethyl acetate, 7 : 3). IR (neat)

ν_{max}: 3366, 3064, 3032, 2925, 2852, 1762, 1716, 1660, 1578, 1491, 1467, 1443, 1407, 1302, 1237, 1211, 1125, 1050, 1023, 974, 928, 875, 851, 806, 748, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.67 (d, J = 7.5 Hz, 1H), 7.31–7.19 (m, 12H), 7.04 (s, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.70–6.67 (m, 2H), 5.94 (d, J = 5.5 Hz, 1H), 5.79 (d, J = 7.5 Hz, 1H), 5.47 (d, J = 7.5 Hz, 1H), 5.12–4.97 (m, 4H), 2.42–2.32 (m, 2H), 2.10–2.08 (m, 1H), 1.63–1.40 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.9, 155.2, 141.1, 139.4, 136.5, 136.1, 135.4, 129.7, 129.6, 128.6, 128.4, 128.3 (2), 128.2, 127.9 (2), 127.7, 127.5, 127.4, 123.1, 113.1, 80.6, 67.8, 66.7, 57.6, 31.4, 29.7, 29.5, 29.4, 27.7, 27.2. HRMS (ESI): calcd for $C_{33}H_{33}IN_2O_5Na$ [M + Na]: 687.13318; found: 687.13368.

General procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines with 2-iodobenzenethiol

A mixture of pentafulvene derived diazabicyclic olefin (2.0 equiv.), 2-iodobenzenethiol (1.0 equiv.) and $Zn(OTf)_2$ (5 mol%) was weighed in a Schlenk tube and degassed for 10 minutes. Dry THF (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 2 hours. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidenecyclopentene.

Diethyl 1-(-2-cyclohexylidene-5-(2-iodophenylthio)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7a). Yield: 76% as a yellow viscous liquid; R_f = 0.39 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3728, 3294, 3058, 2927, 2853, 1709, 1562, 1440, 1410, 1301, 1225, 1115, 1060, 1013, 933, 863, 750, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (brs, 1H), 7.32–7.27 (m, 2H), 6.85 (d, J = 7 Hz, 1H), 6.55 (d, J = 6 Hz, 1H), 6.26–6.16 (m, 1H), 5.92–5.87 (m, 1H), 5.44–5.26 (m, 1H), 4.78 (brs, 1H), 4.20–4.14 (m, 4H), 2.31–2.28 (m, 2H), 2.16–2.08 (m, 2H), 1.57–1.43 (m, 6H), 1.27–1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 154.6, 140.8, 139.2, 133.2, 132.5, 130.5, 128.9, 128.5, 128.1, 127.1, 126.7, 81.4, 65.0, 62.6, 62.0, 56.0, 31.9, 31.4, 29.6, 28.1, 27.9, 26.3, 14.5. HRMS (ESI): calcd for $C_{23}H_{29}IN_2NaO_4S$ [M + Na]: 579.07904; found: 579.07955.

Diisopropyl 1-(-2-cyclohexylidene-5-(2-iodophenylthio)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7b). Yield: 60% as a yellow viscous liquid; R_f = 0.48 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3727, 3292, 2925, 2855, 2309, 1704, 1608, 1503, 1446, 1392, 1299, 1174, 1109, 1032, 754, 670, 613, 560 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 8 Hz, 1H), 7.42 (d, J = 6.5 Hz, 1H), 7.30–7.27 (m, 2H), 6.90–6.83 (m, 1H), 6.50 (d, J = 5.5 Hz, 1H), 5.98–5.92 (m, 2H), 5.29 (m, 1H), 5.00–4.90 (m, 2H), 4.75 (brs, 1H), 2.29–2.11 (m, 4H), 1.63–1.57 (m, 6H), 1.29–1.22 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 154.8, 139.8, 139.3, 134.5, 133.0, 131.3, 130.6, 129.1, 128.6, 128.1, 127.6, 83.5, 70.1, 69.4, 62.8, 32.9, 32.0, 31.6, 28.2, 27.9, 26.9, 26.4, 22.2, 22.0. HRMS (ESI): calcd for $C_{25}H_{33}IN_2NaO_4S$ [M + Na]: 607.11034; found: 607.11096.

Compound 7c. Yield: 58% as a yellow viscous liquid; R_f = 0.43 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3297, 3059, 2976, 2912, 2851, 1710, 1565, 1443, 1411, 1299, 1222, 1172, 1110, 1061, 1015, 867, 749, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.85–7.79 (m, 1H), 7.32–7.28 (m, 2H), 6.90–6.85 (m, 1H), 6.54 (d, J = 5.5 Hz, 1H), 6.12–5.85 (m, 2H), 5.45–5.25 (m, 1H), 4.76 (brs, 1H), 4.24–4.19 (m, 4H), 2.92 (s, 1H), 2.56 (brs, 1H), 1.96–1.72 (m, 12 H), 1.29–1.26 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 155.0, 140.8, 139.4, 130.4, 128.6, 128.5, 128.4, 127.5, 121.6, 85.1, 64.8, 62.8, 60.9, 53.3, 38.8, 36.8, 35.6, 35.6, 35.1, 34.7, 27.8, 27.7, 27.6, 14.7, 14.6, 14.5. HRMS (ESI): calcd for $C_{27}H_{33}IN_2NaO_4S$ [M + Na]: 631.11034; found: 631.11102.

Compound 7d. Yield: 41% as a yellow viscous liquid; R_f = 0.48 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3727, 3307, 3060, 2978, 2914, 2853, 1711, 1627, 1565, 1449, 1388, 1299, 1231, 1178, 1109, 1035, 946, 837, 750, 558 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (m, 1H), 7.26–7.14 (m, 2H), 6.85–6.83 (m, 1H), 6.54 (d, J = 5.1 Hz, 1 H), 6.00–5.89 (m, 2H), 5.43–5.27 (m, 1H), 4.95 (m, 2H), 4.73 (brs, 1H), 2.92 (s, 1H), 2.72–2.59 (m, 1H), 1.95–1.82 (m, 12H), 1.26–1.07 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 155.5, 139.7, 139.3, 137.7, 132.9, 129.0, 128.5, 128.2, 126.6, 125.3, 81.2, 70.1, 69.8, 64.7, 55.5, 38.8, 36.9, 35.1, 34.7, 34.5, 31.6, 28.2, 28.0, 27.8, 26.9, 22.1, 22.0, 14.2. HRMS (ESI): calcd for $C_{29}H_{37}IN_2NaO_4S$ [M + Na]: 659.14164; found: 659.14270.

Diethyl 1-(-2-cyclopentylidene-5-(2-iodophenylthio)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7e). Yield: 40% as a yellow viscous liquid; R_f = 0.35 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3728, 3298, 2925, 2862, 1710, 1602, 1416, 1384, 1304, 1231, 1166, 1108, 1060, 753, 666, 612, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.25–7.19 (m, 1H), 6.84–6.81 (m, 1H), 6.33–6.30 (m, 1H), 6.11–5.82 (m, 2H), 5.31–5.14 (m, 1H), 4.74 (brs, 1H), 4.14–4.10 (m, 4H), 2.34–2.22 (m, 4H), 1.67–1.57 (m, 4H), 1.23–1.19 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 154.9, 139.8, 139.3, 131.3, 130.1, 129.8, 129.1, 128.6, 128.4, 128.0, 126.5, 83.2, 62.8, 62.4, 61.7, 55.4, 26.7, 26.4, 25.7, 24.6, 14.6, 14.4. HRMS (ESI): calcd for $C_{22}H_{27}IN_2NaO_4S$ [M + Na]: 565.06339; found: 607.06390.

Diisopropyl 1-(-2-(2-iodophenylthio)-5-(propan-2-ylidene)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7f). Yield: 57% as a yellow viscous liquid; R_f = 0.36 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3728, 3336, 2920, 2854, 2393, 2311, 1733, 1603, 1457, 1377, 1303, 1245, 1171, 1108, 1053, 743, 666, 612, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (m, 1H), 7.40–7.37 (m, 2H), 6.92–6.90 (m, 1H), 6.78 (d, J = 5.5 Hz, 1H), 6.19 (d, J = 5 Hz, 1H), 5.32–5.31 (m, 1H), 5.23 (d, J = 6 Hz, 1H), 5.04–4.92 (m, 2H), 4.67 (brs, 1H), 1.96 (s, 3H), 1.87 (s, 3H), 1.31–1.28 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 154.9, 139.2, 138.1, 135.8, 132.7, 130.0, 129.0, 128.7, 127.4, 80.9, 70.3, 70.1, 69.7, 64.3, 22.1, 22.0, 21.8, 21.4. HRMS (ESI): calcd for $C_{22}H_{29}IN_2NaO_4S$ [M + Na]: 567.07904; found: 567.07934.

Diethyl 1-(-2-cycloheptylidene-5-(2-iodophenylthio)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7g). Yield: 64% as a yellow viscous liquid; R_f = 0.4 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3729, 3300, 2977, 2925, 2857, 2390, 2312, 1712, 1560, 1441, 1413, 1383, 1304, 1227, 1171, 1117, 1060, 1015, 865, 752, 611, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ

7.87–7.81 (m, 1H), 7.37–7.31 (m, 1H), 6.92–6.86 (m, 2H), 6.54 (d, J = 5.5 Hz, 1H), 6.13–5.94 (m, 2H), 5.44–5.27 (m, 1H), 4.78 (brs, 1H), 4.31–4.21 (m, 4H), 2.49–2.27 (m, 4H), 1.69–1.44 (m, 8H), 1.32–1.27 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 154.9, 147.3, 141.2, 139.8, 135.9, 134.0, 129.0, 128.5, 128.2, 121.8, 82.0, 65.8, 62.6, 61.7, 55.1, 32.7, 29.9, 29.1, 28.3, 27.9, 27.6, 14.5. HRMS (ESI): calcd for $C_{24}H_{31}IN_2NaO_4S$ [M + Na]: 593.09469; found: 593.09418.

Diethyl 1-(-2-cyclohexylidene-5-(4-fluoro-2-iodophenylthio)-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7h). Yield: 47% as a yellow viscous liquid; R_f = 0.43 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3725, 3292, 2927, 2857, 2315, 1709, 1578, 1453, 1412, 1383, 1303, 1252, 1168, 1113, 1061, 863, 768, 722, 666, 614, 560 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.47 (m, 2H), 7.06–7.04 (m, 1H), 6.54 (d, J = 6 Hz, 1H), 6.33–6.21 (m, 1H), 5.91–5.89 (m, 1H), 5.45–5.26 (m, 1H), 4.77 (brs, 1H), 4.23–4.11 (m, 4H), 2.32–2.15 (m, 4H), 1.55–1.27 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 155.2, 140.0, 135.9, 129.0, 128.2, 126.9, 126.8, 125.3, 81.0, 65.0, 62.4, 61.7, 54.8, 34.7, 31.9, 31.6, 26.9, 26.4, 22.8, 14.7, 14.5. HRMS (ESI): calcd for $C_{23}H_{28}FIN_2NaO_4S$ [M + Na]: 597.06962; found: 597.06993.

Compound 7i. Yield: 39% as a yellow viscous liquid; R_f = 0.5 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3730, 3327, 2917, 2854, 2391, 2304, 1729, 1651, 1583, 1511, 1457, 1381, 1312, 1257, 1168, 1114, 1056, 724, 667, 613, 558 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.56 (m, 2H), 7.07–7.04 (m, 1H), 6.53 (d, J = 6 Hz, 1H), 6.11 (s, 1H), 5.90 (d, J = 2.5 Hz, 1H), 5.45–5.26 (m, 1H), 4.69 (brs, 1H), 4.20–4.01 (m, 4H), 2.90 (s, 1H), 2.57 (s, 1H), 1.97–1.84 (m, 12H), 1.29–1.22 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 154.7, 147.6, 135.8, 132.9, 130.6, 130.1, 129.1, 128.5, 128.2, 126.5, 125.4, 81.7, 64.4, 62.8, 62.2, 57.0, 39.7, 39.3, 38.8, 36.9, 36.8, 35.8, 35.1, 34.7, 28.1, 27.8, 14.6. HRMS (ESI): calcd for $C_{27}H_{32}FIN_2NaO_4S$ [M + Na]: 649.10092; found: 649.10101.

Diethyl 1-(-2-cyclohexylidene-5-(2-iodo-4-(trifluoromethyl)-phenylthio)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7j). Yield: 50% as a yellow viscous liquid; R_f = 0.43 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3728, 3290, 2928, 2859, 2358, 2325, 1711, 1595, 1512, 1415, 1382, 1319, 1258, 1169, 1126, 1065, 723, 667, 612, 558 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.17–7.15 (m, 1H), 6.37 (s, 1H), 6.17–5.57 (m, 3H), 4.23–4.19 (m, 5H), 2.24–2.06 (m, 4H), 1.66–1.59 (m, 6H), 1.28–1.27 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 153.5, 141.7, 136.2, 132.0, 131.4, 129.1, 128.5, 128.2, 125.4, 122.4, 121.7, 82.9, 63.4, 62.7, 62.3, 55.1, 26.9, 26.0, 25.1, 22.9, 22.4, 19.8, 14.4. HRMS (ESI): calcd for $C_{24}H_{28}F_3IN_2NaO_4S$ (M + Na): 647.06643; found: 647.06598.

Diethyl 1-(-2-(4-bromo-2-iodophenylthio)-5-cyclohexylidene cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (7k). Yield: 53% as a yellow viscous liquid; R_f = 0.48 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 3724, 3296, 2927, 2855, 2392, 1715, 1605, 1549, 1443, 1380, 1315, 1221, 1167, 1114, 1057, 763, 668, 613, 558 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (brs, 1H), 7.48–7.45 (m, 2H), 6.57 (d, J = 6 Hz, 1H), 6.13 (brs, 1H), 5.91 (s, 1H), 5.42–5.22 (m, 1H), 4.78 (m, 1H), 4.34–4.17 (m, 4H), 2.29–2.27 (m, 2H), 2.12–2.05 (m, 2H), 1.59–1.52 (m, 6H), 1.30–1.27 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 154.3, 142.6, 141.1, 132.1, 130.5, 129.0, 127.5, 126.0, 125.3, 120.0, 81.1, 63.6, 62.7, 62.5, 55.1, 32.1, 32.0, 28.3, 27.9, 26.4, 14.5, 14.4. HRMS (ESI): calcd for $C_{23}H_{28}BrIN_2NaO_4S$ [M + Na]: 656.98955; found: 656.98834.

General procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines with alcohols

A mixture of pentafulvene derived diazabicyclic olefin (3.0 equiv.), alcohol (1.0 equiv.) and $Cu(OTf)_2$ (5 mol%) was weighed in a Schlenk tube and degassed for 10 minutes. Dry toluene (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 1 hour. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidenecyclopentene.

Diethyl-1-(2-cyclohexylidene-5-methoxycyclopent-3-enyl)-hydrazine-1,2-dicarboxylate (9a). Yield: 29% as a pale yellow liquid; R_f : 0.55 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3297, 2927, 2852, 1715, 1416, 1383, 1227, 1061, 760 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.61 (s, 1H), 6.35–6.21 (m, 1H), 5.93 (s, 1H), 5.13–4.98 (m, 1H), 4.63–4.52 (m, 1H), 4.29–4.10 (m, 4H), 3.47 (s, 3H), 2.39–2.36 (m, 1H), 2.16–2.07 (m, 3H), 1.59–1.54 (m, 6H), 1.26–1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 154.6, 137.8, 135.0, 134.3, 131.5, 88.5, 62.5, 62.3, 61.8, 56.8, 31.5, 31.1, 27.9, 26.4, 24.6, 14.4. HRMS (ESI): calcd for $C_{18}H_{29}N_2O_5$ (M + 1): 353.20765; found: 353.20721.

Diisopropyl-1-(2-cyclohexylidene-5-methoxycyclopent-3-enyl)-hydrazine-1,2-dicarboxylate (9b). Yield: 31% as a colourless viscous liquid; R_f : 0.60 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3441, 3301, 2935, 1719, 1468, 1376, 1297, 1238 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (d, 1H, J = 5.5 Hz), 6.07–6.00 (m, 1H), 5.92 (s, 1H), 5.13–4.89 (m, 3H), 4.63–4.55 (m, 1H), 3.49 (s, 3H), 2.35–2.26 (m, 2H), 2.13–2.08 (m, 2H), 1.58–1.54 (m, 6H), 1.26–1.22 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 154.5, 137.8, 134.1, 132.0, 129.9, 88.5, 70.1, 69.5, 61.7, 57.0, 31.6, 31.0, 28.1, 27.9, 26.4, 22.1, 21.8. HRMS (ESI): calcd for $C_{20}H_{32}N_2O_5$ (M + Na): 403.22089; found: 403.22098.

Diisopropyl-1-(2-cyclohexylidene-5-ethoxycyclopent-3-enyl)-hydrazine-1,2-dicarboxylate (9c). Yield: 31% as a pale yellow viscous liquid; R_f : 0.66 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3303, 2935, 1715, 1411, 1232, 1101, 1061 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.59 (d, 1H, J = 5 Hz), 6.06–5.98 (m, 1H), 5.92 (s, 1H), 5.12–4.89 (m, 3H), 4.74–4.63 (m, 1H), 3.88–3.80 (m, 1H), 3.60 (brs, 1H), 2.35–2.26 (m, 2H), 2.12–2.04 (m, 2H), 1.76–1.58 (m, 6H), 1.25–1.22 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 154.6, 137.4, 133.9, 132.8, 132.1, 86.8, 69.9, 69.5, 64.8, 62.1, 34.7, 31.6, 31.0, 28.1, 26.9, 26.6, 25.2, 22.2, 22.0, 15.5. HRMS (ESI): calcd for $C_{21}H_{34}N_2O_5$ (M^+): 395.24677; found: 395.14380.

Diethyl-1-(-2-cyclohexylidene-5-(3-phenylprop-2-ynyloxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9d). Yield: 27% as a colourless liquid; R_f : 0.55 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3316, 3059, 2935, 2861, 2223, 1712, 1603, 1413, 1380, 1232, 1173, 1062 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.28 (m, 5H), 6.63 (d, 1H, J = 4.5 Hz), 6.28–6.16 (m, 1H),

5.99 (d, 1H, J = 3.5 Hz), 5.15–5.12 (m, 1H), 5.08–5.05 (m, 1H), 4.66–4.49 (m, 2H), 4.23–4.06 (m, 4H), 2.40–2.35 (m, 1H), 2.24–2.03 (m, 3H), 1.61–1.54 (m, 6H), 1.25–1.23 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 155.1, 134.7, 131.8, 131.2, 129.0, 128.1, 122.9, 99.1, 87.0, 85.7, 62.5, 61.8, 57.5, 31.6, 31.2, 30.8, 28.0, 26.4, 14.6, 14.4. HRMS (ESI): calcd for $C_{26}H_{32}N_2NaO_5$ (M + Na): 475.22089; found: 475.22125.

Diethyl-1-(-2-cyclohexylidene-5-(prop-2-ynyloxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9e). Yield: 21% as a colourless liquid; R_f: 0.53 (Hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3292, 2922, 2854, 1714, 1414, 1232, 1061 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.62 (d, 1H, J = 4.5 Hz), 6.07 (brs, 1H), 5.95 (s, 1H), 5.08 (brs, 1H), 4.88 (s, 1H), 4.42–4.10 (m, 6H), 2.40–2.35 (m, 2H), 2.24–2.06 (m, 3H), 1.66–1.55 (m, 6H), 1.28–1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 154.4, 136.8, 134.3, 132.0, 129.4, 87.8, 74.5, 65.2, 62.5, 57.3, 31.7, 31.3, 29.7, 26.8, 25.7, 20.8, 14.6, 14.1. HRMS (ESI): calcd for $C_{20}H_{28}N_2NaO_5$ (M + Na): 399.18959; found: 399.19028.

Dibenzyl-1-(2-cyclohexylidene-5-ethoxycyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9f). Yield: 40% as a pale yellow liquid; R_f: 0.64 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3287, 3033, 2933, 2860, 1718, 1498, 1454, 1408, 1220, 1127, 1084 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.24 (m, 10H), 6.55 (s, 1H), 6.29–6.21 (m, 1H), 5.90 (s, 1H), 5.26–4.72 (m, 7H), 3.59–3.48 (m, 1H), 2.32–2.18 (m, 1H), 2.11–1.96 (m, 3H), 1.70–1.40 (m, 6H), 1.25–1.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 154.7, 135.1, 134.0, 132.7, 131.5, 128.5, 128.1, 127.9, 127.8, 127.6, 87.2, 68.1, 67.6, 65.0, 62.5, 31.5, 31.1, 27.9, 26.4, 25.6, 15.3. HRMS (ESI): calcd for $C_{29}H_{34}N_2O_5Na$, (M + Na): 513.23654; found: 513.23627.

Diethyl-1-(-2-(2-bromoethoxy)-5-cyclohexylidenecyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9g). Yield: 26% as a colourless liquid; R_f: 0.63 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3320, 2931, 1711, 1414, 1379, 1234, 1061 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.61 (d, 1H, J = 5.5 Hz), 6.15–6.07 (m, 1H), 5.93 (s, 1H), 5.12–5.01 (m, 1H), 4.80–4.69 (m, 1H), 4.31–4.00 (m, 5H), 3.90–3.83 (m, 1H), 3.49 (brs, 2H), 2.39–2.36 (m, 1H), 2.26–2.05 (m, 3H), 1.67–1.50 (m, 6H), 1.39–1.22 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 155.1, 138.3, 134.5, 131.7, 128.3, 87.5, 69.9, 69.3, 62.7, 62.0, 32.0, 31.6, 29.7, 28.1, 27.9, 26.4, 14.4. HRMS (ESI): calcd for $C_{19}H_{29}BrN_2O_5$, (M + Na): 467.11575; found: 467.11561.

Diethyl 1-((1S, 2S)-2-(benzyloxy)-5-cyclohexylidenecyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9h). Yield: 72% as a pale yellow liquid; R_f: 0.64 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3296, 2923, 2855, 1711, 1414, 1376, 1267, 1225, 1063 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (m, 5H), 6.60 (d, 1H, J = 5 Hz), 6.05–5.94 (m, 1H), 5.84 (s, 1H), 5.24–5.10 (m, 1H), 4.85–4.7 0 (m, 2H), 4.62–4.60 (m, 1H), 4.24–4.10 (m, 4H), 2.39–2.36 (m, 1H), 2.26–2.05 (m, 3H), 1.59–1.53 (m, 6H), 1.28–1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 155.1, 138.6, 134.3, 132.5, 130.9, 129.9, 128.5, 128.2, 127.4, 126.9, 88.1, 71.8, 62.5, 62.0, 53.3, 31.6, 30.6, 28.0, 27.8, 26.4, 14.6, 14.4. HRMS (ESI): calcd for $C_{24}H_{32}N_2O_5$ (M + Na): 451.22089; found: 451.22040.

Diethyl-1-(-2-cyclohexylidene-5-(2-iodobenzyloxy)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9i). Yield: 55% as a pale yellow liquid; R_f: 0.61 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 3296, 2923, 2855, 1711, 1414, 1376, 1267, 1225, 1063 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, 1H, J = 7.5 Hz), 7.48 (d, 1H, J = 7 Hz), 7.34 (dd, 1H, J_1 = 14 Hz, J_2 = 5 Hz), 6.96 (brs, 1H), 6.66 (d, 1H, J = 5.5 Hz), 6.10 (brs, 1H), 6.02–5.94 (m, 1H), 5.32–5.17 (m, 1H), 4.93–4.80 (m, 2H), 4.61–4.58 (m, 1H), 4.37–4.12 (m, 4H), 2.42–2.39 (m, 1H), 2.28–2.10 (m, 3H), 1.64–1.58 (m, 6H), 1.30–1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 155.0, 140.9, 139.0, 137.9, 134.7, 131.7, 129.0, 128.1, 87.6, 75.0, 62.8, 62.6, 61.9, 31.6, 31.2, 28.1, 27.9, 26.4, 14.5. HRMS (ESI): calcd for $C_{24}H_{31}IN_2O_5$ (M + Na): 577.11753; found: 577.11853.

Diethyl-1-(2-cyclohexylidene-5-ethoxycyclopent-3-enyl)hydrazine-1,2-dicarboxylate (9j). Yield: 24% as a pale yellow liquid; R_f: 0.51 (hexane–ethyl acetate = 7 : 3). IR (neat) ν_{max}: 2923, 2855, 2355, 1711, 1411, 1232, 1101, 1061 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (d, 1H, J = 5 Hz), 6.06 (brs, 1H), 5.93–5.89 (m, 1H)), 5.13–4.98 (m, 1H), 4.72–4.61 (m, 1H), 4.29–4.10 (m, 4H), 3.87–3.78 (m, 1H), 3.59–3.54 (m, 1H), 2.38–2.35 (m, 1H), 2.25–2.05 (m, 3H), 1.63–1.53 (m, 6H), 1.27–1.22 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 155.5, 134.5, 133.0, 131.7, 130.5, 87.2, 70.1, 65.2, 62.9, 62.6, 32.0, 31.5, 30.1, 28.2, 26.8, 26.0, 15.8, 14.8. HRMS (ESI): calcd for $C_{19}H_{30}N_2O_5$, (M + Na): 389.20524, found: 389.20565.

General procedure for the intramolecular Heck reaction

A mixture of *trans*-3,4-disubstituted alkylidenecyclopentene (1.0 equiv.), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) and Cs_2CO_3 (1.5 equiv.) was weighed in a Schlenk tube and degassed for 10 minutes. Dry acetonitrile (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at 80 °C for 12 hours. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded indoline–pyrazolidine fused cyclopentene.

General procedure for the one-pot synthesis of indoline–pyrazolidine fused cyclopentene

A mixture of pentafulvene derived diazabicyclic olefin (3.0 equiv.), *o*-iodoaniline (1.0 equiv.), $[Pd(allyl)Cl]_2$ (5 mol%), PPh_3 (10 mol%), $Sc(OTf)_3$ (2 mol%) and Cs_2CO_3 (1.5 equiv.) was weighed in a Schlenk tube and degassed for 10 minutes. Dry acetonitrile (2 ml) and toluene (0.5 ml) were added and the reaction mixture was purged with argon and allowed to stir at 80 °C for 12 hours. The solvent was evaporated *in vacuo* and the residue on silica gel (100–200 mesh) column chromatography yielded indoline–pyrazolidine fused cyclopentene.

Compound 10a. Yield: 54% as a colourless viscous liquid; R_f: 0.31 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3388, 3263, 2969, 2919, 2848, 1708, 1605, 1558, 1490, 1410, 1389, 1313, 1289, 1218, 1120, 1071, 938, 731 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.07–7.00 (m, 2H), 6.74–6.67 (m, 2H), 5.91 (t, J = 3 Hz, 1H), 4.69 (s, 1H), 4.55 (s, 1H), 4.54 (brs, 1H), 4.27–4.11 (m, 5H), 1.71 (s, 3H), 1.32–1.24 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.6, 154.8, 148.9, 139.8,

127.5, 126.9, 125.9, 123.2, 118.0, 109.2, 64.4, 61.4, 61.0, 56.1, 21.4, 20.9, 14.5, 14.1. MS (ESI): calcd for $C_{20}H_{25}N_3O_4$, M^+: 371.18451; found, (M + 1): 372.19001.

Compound 10b. Yield: 74% as a colourless viscous liquid; R_f: 0.54 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3390, 3288, 3060, 3038, 297, 2849, 1717, 1594, 1498, 1454, 1404, 1318, 1279, 1218, 1131, 1056, 1011, 916, 748, 670 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.34–7.25 (m, 12H), 7.02–6.97 (m, 2H), 6.69 (t, J = 7 Hz, 1H), 5.85 (s, 1H), 5.17–5.09 (m, 4H), 4.69 (brs, 1H), 4.49 (brs, 1H), 4.40 (brs, 1H), 1.79–1.552 (m, 3H), 1.25–1.20 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 157.7, 156.1, 149.8, 136.0, 128.6, 128.5, 128.1, 127.9, 127.7, 127.3, 126.9, 124.3, 119.0, 70.1, 68.2, 57.2, 39.4, 23.3, 23.2. MS (ESI): calcd for $C_{30}H_{29}N_3O_4Na$: 518.20558; found: 518.20322 ($C_{30}H_{29}N_3O_4Na$).

Compound 10c. Yield: 65% as a colourless viscous liquid; R_f: 0.31 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3377, 3058, 2918, 2851, 1729, 1604, 1461, 1403, 1118, 1050, 740, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.36–7.31 (m, 12H), 7.00 (t, J = 12.5 Hz, 1H), 6.69 (t, J = 12 Hz, 1H), 5.89 (s, 1H), 5.20–5.12 (m, 4H), 4.69 (s, 2H), 4.46 (brs, 1H), 4.35 (brs, 1H), 2.71 (brs, 1H), 2.48 (brs, 1H), 1.97–1.54 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 154.9, 152.1, 149.8, 136.0, 128.6, 128.5, 128.1, 127.9, 127.7, 127.3, 126.9, 124.3, 119.0, 76.1, 67.8, 65.2, 56.9, 46.2, 31.9, 29.3, 27.4, 23.9. MS (ESI): calcd for $C_{32}H_{31}N_3O_4$, M^+: 521.23146; found (M + 1): 522.23688 ($C_{32}H_{32}N_3O_4$).

Compound 10d. Yield: 72% as a pale yellow solid, Mp = 136–139 °C; R_f: 0.31 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3368, 3268, 2990, 2931, 2860, 1718, 1588, 1410, 1282, 1228, 1124, 1056, 1016, 746, 694 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.05 (m, 2H), 6.73–6.66 (m, 2H), 6.11 (s, 1H), 4.64 (brs, 1H), 4.48 (brs, 1H), 4.37–4.35 (m, 1H), 4.23–4.12 (m, 5H), 2.80 (s, 1H), 2.55–2.51 (m, 1H), 2.21–2.12 (m, 2H), 1.90–1.54 (m, 6H), 1.59–1.54 (m, 4H), 1.29–1.22 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 157.9, 157.1, 154.5, 149.5, 127.9, 124.2, 123.8, 119.3, 119.0, 110.2, 109.9, 71.4, 62.1, 57.0, 37.2, 35.7, 35.4, 34.6, 32.5, 32.2, 32.0, 27.1, 27.0, 14.7, 14.5. MS (ESI): calcd for $C_{27}H_{33}N_3O_4$, M^+: 463.24711; found, (M + 1): 464.25262 ($C_{27}H_{34}N_3O_4$).

Compound 10e. Yield: 69% as a colourless viscous liquid; R_f: 0.36 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3380, 3051, 2978, 2920, 2856, 2666, 1704, 1683, 1606, 1460, 1277, 1106, 956, 912, 746 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.06–7.02 (m, 2H), 6.72–6.65 (m, 2H), 6.10 (d, J = 5.5 Hz, 1H), 5.02–4.87 (m, 2H), 4.62–4.06 (m, 4H), 2.83 (brs, 1H), 2.61–2.51 (m, 1H), 2.35–2.11 (m, 2H), 1.89–1.37 (m, 10H), 1.25–1.21 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 157.4, 156.8, 149.8, 129.0, 128.2, 127.9, 125.3, 124.2, 118.9, 110.1, 75.6, 71.4, 69.5, 56.9, 37.2, 35.8, 35.4, 34.6, 32.6, 32.3, 32.0, 27.2, 22.2, 22.1. MS (ESI): calcd for $C_{29}H_{37}N_3O_4$, (M^+): 491.27841; found (M + 1): 492.28394 ($C_{29}H_{38}N_3O_4$).

Compound 10f. Yield: 46% as a colourless viscous liquid; R_f: 0.37 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3381, 980, 2938, 2861, 1738, 1712, 1594, 1499, 1451, 1410, 1284, 1230, 1126, 1062, 1007, 746, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.03 (d, J = 14.5 Hz, 1H), 7.95 (s, 1H), 6.57 (d, J = 14.5 Hz, 1H), 6.09 (s, 1H), 5.33 (s, 1H), 4.62–4.56 (m, 2H), 4.23–4.12 (m, 5H), 2.76 (s, 1H), 2.50–2.03 (m, 4H), 1.91–1.42 (m, 9H), 1.29–1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.9, 154.3, 147.2, 138.8, 133.4, 131.9, 129.5, 128.5, 118.9, 112.9, 75.6, 64.3, 63.3, 62.4, 56.1, 40.1, 39.5, 38.9, 38.8, 36.8, 35.0, 34.5, 28.1, 27.9, 14.6, 14.4. MS (ESI): calcd for $C_{27}H_{32}N_4O_6$, M^+: 508.23218; found (M + 1): 509.23765 ($C_{27}H_{33}N_4O_6$).

Compound 10g. Yield: 42% as a colourless viscous liquid; R_f: 0.40 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3293, 2922, 2852, 1716, 1587, 1499, 1456, 1381, 1316, 1282, 1178, 1109, 1038, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.05 (d, J = 9 Hz, 1H), 7.95 (s, 1H), 6.57 (d, J = 8.5 Hz, 1H), 6.10 (s, 1H), 5.01–4.89 (m, 2H), 4.62 (s, 1H), 4.57–4.52 (m, 3H), 2.80 (s, 1H), 2.53 (d, J = 13.5 Hz, 1H), 2.21–2.11 (m, 2H), 1.92–1.53 (m, 10H), 1.31–1.24 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.6, 155.1, 153.3, 148.9, 138.1, 126.2, 124.7, 121.2, 119.3, 105.7, 69.8, 68.2, 68.1, 54.5, 35.4, 34.0, 33.6, 32.5, 30.9, 30.7, 30.3, 27.7, 25.4, 25.2, 20.5, 20.4. MS (ESI): calcd for $C_{29}H_{36}N_4O_6$, (M^+): 536.26348; found (M + 1): 537.26905 ($C_{29}H_{37}N_4O_6$).

Compound 10h. Yield: 72% as a colourless viscous liquid; R_f: 0.34 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3375, 3051, 2933, 2861, 1698, 1605, 1459, 1407, 1377, 1334, 1287, 1171, 1131, 1098, 1032, 897, 870, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.71–7.04 (m, 2H), 6.74–6.68 (m, 2H), 6.06 (s, 1H), 4.66 (s, 1H), 4.54 (d, J = 6.5 Hz, 1H), 4.37 (brs, 1H), 4.23–4.13 (m, 5H), 2.46 (t, J = 10 Hz, 1H), 2.36 (s, 1H), 1.97 (d, J = 10.5 Hz, 2H), 1.63–1.20 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.6, 154.9, 148.8, 139.9, 128.4, 127.5, 126.1, 125.9, 123.3, 122.7, 118.0, 109.2, 64.3, 61.3, 56.0, 32.1, 30.4, 28.7, 24.5, 22.9, 22.0, 13.6, 13.4. MS (ESI): calcd for $C_{23}H_{29}N_3O_4Na$: 434.20558; found: 434.20336 ($C_{23}H_{29}N_3O_4Na$).

Compound 10i. Yield: 63% as a colourless viscous liquid; R_f: 0.43 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3377, 3051, 2928, 2856, 2670, 1708, 1694, 1606, 1462, 1379, 1232, 1107, 1022, 916, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.08–7.03 (m, 2H), 6.75–6.68 (m, 2H), 6.03 (s, 1H), 4.99–4.86 (m, 2H), 6.46 (s, 1H), 4.50 (s, 1H), 4.36 (s, 1H), 2.43 (m, 1H), 2.17 (brs, 1H), 1.99–1.91 (m, 2H), 1.60–1.25 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 156.1, 154.7, 145.9, 138.7, 133.6, 132.8, 129.6, 129.3, 118.8, 118.2, 110.2, 69.9, 63.2, 57.8, 32.0, 31.8, 28.2, 27.8, 26.4, 22.6, 22.1. MS (ESI): calcd for $C_{25}H_{33}N_3O_4$, M^+: 439.24711; found, (M + 1): 440.25259 ($C_{25}H_{34}N_3O_4$).

Compound 10j. Yield: 40% as a colourless viscous liquid; R_f: 0.34 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3376, 2983, 2924, 2857, 2359, 1706, 1597, 1468, 1410, 1379, 1307, 1230, 1172, 1132, 1061, 939, 868 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.07–7.02 (m, 2H), 6.74–6.67 (m, 2H), 5.95 (t, J = 3 Hz, 1H), 4.64 (s, 1H), 4.52 (s, 1H), 4.39–4.38 (m, 1H), 4.22–4.17 (m, 5H), 2.52–2.46 (m, 2H), 2.19–2.16 (m, 2H), 1.59 (m, 8H), 1.29–1.26 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 155.5, 155.2, 145.2, 135.5, 128.0, 127.9, 124.4, 122.7, 119.1, 110.6, 62.4, 62.0, 61.9, 56.8, 34.6, 32.3, 29.8, 29.1, 24.5, 14.5. MS (ESI): calcd for $C_{24}H_{31}N_3NaO_4$: 448.22123; found: 448.22079 ($C_{23}H_{29}N_3O_4Na$).

Compound 10k. Yield: 41% as a colourless viscous liquid; R_f: 0.45 (hexane–ethyl acetate = 3 : 1). IR (neat) ν_{max}: 3376, 3261, 2971, 2942, 2858, 1712, 1600, 1541, 1501, 1400, 1395, 1321, 1282, 1223, 1110, 1071, 929, 731 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.32 (d, J = 8.1 Hz, 1H), 7.24 (s, 1H), 6.68 (d, J = 8.1 Hz, 1H), 5.91 (s, 1H), 4.67–4.56 (m, 4H), 4.26–4.14 (m, 4H), 1.72 (s, 3H), 1.34–1.26 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 155.3, 154.9, 147.9, 140.2, 127.4, 126.2, 125.1, 121.5, 108.9, 65.5, 62.6, 62.0, 56.5, 24.7, 23.0, 14.7, 14.5. MS (ESI): calcd for $C_{21}H_{24}F_3N_3O_4$, M^+: 439.17189; found, (M + 1): 440.17828.

Compound 11a. Yield: 41% as a yellow viscous liquid; R_f = 0.43 (hexane–ethyl acetate, 7 : 3). IR (neat) ν_{max}: 2929, 2859, 2312, 1711, 1591, 1452, 1404, 1377, 1323, 1277, 1211, 1130, 1032, 899, 792, 746, 662, 612 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.21–7.14 (m, 2H), 7.07–7.02 (m, 2H), 6.14–6.13 (m, 1H), 4.93 (brs, 1H), 4.84 (d, J = 7 Hz, 1H), 4.24–4.13 (m, 5H), 2.51–2.47 (m, 2H), 2.00–1.98 (m, 2H), 1.63–1.57 (m, 6H), 1.31–1.20 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 155.4, 141.1, 138.5, 131.5, 127.9, 124.5, 124.4, 123.2, 122.7, 83.9, 63.6, 62.4, 62.0, 53.3, 31.5, 29.7, 26.9, 25.6, 24.0, 23.1, 14.6, 14.5. HRMS (ESI): calcd for $C_{23}H_{28}N_2NaO_4S$ [M + Na]: 451.16675; found: 451.16537.

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