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# Synthesis of Diiodinated All-Carbon 3,3'-Diphenyl-1,1'-spirobiindene Derivatives *via* a Cascade Enyne Cyclization and Electrophilic Aromatic Substitution

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Cascade Enyne Cyclization and Electrophilic Aromatic Substitution

**Abstract**: A synthetic method for the construction of diiodinated all-carbon spirobiindene derivatives has been developed from the reaction of propargyl alcohol-tethered alkylidenecyclopropanes with iodine. The reaction proceeded through an iodination-initiated cascade intramolecular enyne cyclization and electrophilic aromatic substitution reaction process in DCE upon heating, giving the desired spirocyclic products in moderate to excellent yields. The further transformation of the obtained products has been also presented.

#### Introduction

Spirocyclic frameworks as key structural subunits exist in a wide range of functional materials,<sup>1</sup> chiral ligands,<sup>2</sup> and bioactive compounds (Scheme 1).<sup>3</sup> Moreover, their inherent characteristic with the spirocyclic skeleton and functional groups render them to be a class of synthetically useful building blocks in the organic syntheses.<sup>4</sup> Among those spirocyclic scaffolds, spirobiindanes are fascinating and versatile examples with broad pharmaceutical and synthetic activities including ligands,<sup>2a,2c</sup> drug candidates<sup>3c,5</sup> and catalysts.<sup>6</sup> Recently, spirocyclizations have witnessed significant progress upon transition metal catalysis<sup>7</sup> or under metal free conditions<sup>8</sup> through intermolecular or intramolecular manner. Although the 1,1'-spirobi[indene] cores have been reported previously,<sup>9</sup> the construction of iodinated and diiodinated derivatives of 1,1'-spirobi[indene] skeleton is a challenging work. In this aspect, substantial efforts have been focused on the development of practical method using easily

available starting material and reagent as a key part for the construction of all-carbon spirobiindene.

Iodine and its derivatives are an easy to handle solid with excellent solubility in many organic solvents; thus, it is frequently employed both as a stoichiometric reagent and as a catalyst reactions<sup>10</sup> in many different organic affording iodocyclization products.11 Methylenecyclopropanes (MCPs), containing the smallest carbocycle with an exo-methylene moiety.<sup>12</sup> are useful building blocks in the field of organic synthesis due to their high ring strain and high reactivity.<sup>13</sup> MCPs can undergo various ring-opening reactions because of a thermodynamic driving force derived from the release of the cyclopropyl ring strain (40 kcal/mol)<sup>14</sup> and the kinetic opportunity originating from the  $\pi$ -character of the ring bonds of the cyclopropane to initiate the unleashing of the strain.<sup>15</sup> To design a novel cascade reaction under mild conditions, we considered to apply iodine as initiator to promote an intermolecular cascade reaction of MCPs having a propargyl alcohol moiety.

Scheme 1 Representative examples containing spiro-bicyclic skeleton.



OS-689;(+)-enantiomer Nonsteroidal Estrogen Receptor Agonist for Hot Flush

Scheme 2 Previous work<sup>9d,16,17</sup> and this work.





In 2011, Liang and co-workers reported a new cascade cyclization reaction of propargyl alcohols in the presence of iodine to afford a series of carbocyclization products in good yields (Scheme 2, eq 1).<sup>16</sup> Xu and co-workers reported an expedient and divergent tandem one-pot synthesis of spiro[indene-1,3'-pyrrole] derivatives from alkyne-tethered chalcones/cinnamates and tosylmethyl isocyanide (TosMIC), giving the corresponding nitrogen-containing spiroindene products in 47-62% yields (Scheme 2, eq 2).<sup>17</sup> In 1972, Hill and co-workers reported the synthetic method of 1,1'-spirobi[indene] using 3,3-diphenylpentanedioic acid with PPA to afford 1,1'-spirobi-3-indanone, followed by reduction and dehydration to obtain 1,1'-spirobi[indene].<sup>9d</sup> As part of our continuing interest in the formation of all-carbon spirobiindene skeleton, we herein wish to report a novel cascade process for the synthesis of 3,3'-diphenyl-1,1'-spirobi[indene] derivatives from propargyl alcohol-tethered alkylidenecyclopropanes in the presence of I<sub>2</sub>. To our knowledge, this is the first example for the construction of diiodinated all-carbon spirobiindene skeleton, which can be used for further transformation.

### **Results and Discussion**

We initially investigated the reaction outcome using **1a** as a model substrate in the presence of iodine (1.0 equiv), and found that the desired cyclized product was obtained in only 10% yield at 80 °C in 1,2-dichloroethane (DCE) (Table 1, entry 1). Increasing the amount of  $I_2$  to 1.5 and 2.0

equivalent produced **2a** in 82% and 98% yield, respectively (Table 1, entries 2-3). Further increasing the amount of  $I_2$  to 5.0 equivalent did not improve the yield of **2a** (Table 1, entry 4). The study on the solvent effect indicated that DCE is the best one, giving product **2a** in the highest yield (Table 1, entries 5-8). The examination of reaction temperature revealed that this cascade cyclization should be carried out at 80 °C (Table 1, entries 9-12) (for more details, see Table S1 in the Supporting Information). The structure of **2a** has been unambiguously established by X-ray diffraction. The ORTEP drawing of **2a** is shown in Table 1 and the corresponding CIF data are presented in the Supporting Information.

Table 1 Optimization of the reaction conditions for the synthesis of 2a.



entry <sup>[a]</sup>	temp (°C)	solvent	$I_2$ (equiv)	yield (%) <sup>[b]</sup>
1	80	DCE	1.0	10
2	80	DCE	1.5	82
3	80	DCE	2.0	98
4	80	DCE	5.0	98
5 <sup>d</sup>	80	CHCl <sub>3</sub>	2.0	81
6	80	toluene	2.0	34
7e	80	THF	2.0	89
8	80	MeCN	2.0	89
9	r.t.	DCE	2.0	83
10	40	DCE	2.0	86
11 <sup>[c]</sup>	60	DCE	2.0	96
12 <sup>[c]</sup>	r.t.	DCE	2.0	85

<sup>a</sup> The reaction was conducted with **1a** (0.2 mmol) and I<sub>2</sub> in DCE (2 mL) for 2 hours. <sup>b</sup> Yield of isolated product purified by a column chromatography on silica gel. <sup>c</sup> The reaction was conducted with **1a** (0.2 mmol) and I<sub>2</sub> in DCE (2 mL) for 10 hours. <sup>d</sup> The reaction was conducted with **1a** (0.2 mmol) and I<sub>2</sub> in CHCl<sub>3</sub> (2 mL) in sealed tube for 2 hours. <sup>e</sup> The reaction was conducted with **1a** (0.2 mmol) and I<sub>2</sub> in THF in sealed tube (2 mL) for 2 hours.

With the optimized reaction condition in hand, we next turned our attention towards the examination of substrate scope, and the results are summarized in Scheme 3. All of the reactions proceeded efficiently under the optimal condition, furnishing the desired products in moderate to excellent yields except for substrates **10**, **1ab**, **1ac** and **1ad**. As can be seen, the desired products **2b-2j** were afforded in good yields ranging from 89% to 98% for both electron-donating substituent and electron-withdrawing substituent incorporated substrates, suggesting that the electronic property of these substituents did not have a significant impact on the reaction outcomes. For substrate **1k** having an aliphatic methyl group, the reaction proceeded smoothly, delivering the corresponding product **2k** in 79%. For substrates **1l-1s**, similar results were obtained, affording the desired products **2l-2s** in good to excellent yields. In the case of **10**, the reaction could not deliver

the desired product **2o** under the optimized reaction condition and gave a complex mixture. After raising reaction temperature to 100 °C in a sealed tube, we could obtain the desired product **2o** in 93% yield (for details, see Table S2 in the Supporting Information). For substrates **2t** to **2v**, in which the propargyl alcohol moiety contained two different aromatic rings, we found that the carbocyclization took place exclusively at the electron-rich aromatic ring, suggesting that the cyclization proceeded through an electrophilic aromatic substitution reaction pathway. In the case of substrate **1w**, the corresponding product **2w** was formed in 90% yield. Substrate **1x** containing a naphthyl ring produced the corresponding monoiodinated product **2x** in 55% yield, probably due to the steric hinderance effect and lower aromaticity of the naphthyl ring. Thus, it tended to react with a proton rather than I<sub>2</sub> during the electrophilic aromatic substitution process. Substrate **1y** with heteroaromatic rings produced the desired **2y** in 78% yield under the standard conditions. Using **1a** as substrate, the similar result could be obtained when I<sub>2</sub> was replaced by ICl and Br<sub>2</sub>, giving the desired product **2z** and **2aa** in 56% and 64% yield, respectively. Unfortunately, we failed to get the desired products **2ab**, **2ac** and **2ad** after examining several reaction conditions.

Scheme 3 Reaction scope of substrates 1.



<sup>a</sup> The reaction was conducted with **1** (0.2 mmol),  $I_2$  (0.4 mmol) in DCE (2 mL) at 80 °C in 2 hours. <sup>b</sup> Yield of isolated product purified by a column chromatography on silica gel. <sup>c</sup> The reaction was conducted with **1** (0.2 mmol),  $I_2$  (0.4 mmol) in DCE (2 mL) at 100 °C in 2 hours. <sup>d</sup> The reaction was conducted with **1a** (0.2 mmol), ICl (0.4 mmol) in DCE (2 mL) at 80 °C in 2 hours. <sup>e</sup> The reaction was conducted with **1a** (0.2 mmol), Br<sub>2</sub> (0.4 mmol) in DCE (2 mL) at 80 °C in 2 hours. <sup>e</sup> The reaction was conducted with **1a** (0.2 mmol), Br<sub>2</sub> (0.4 mmol) in DCE (2 mL) at 80 °C in 2 hours.

During our exploration of the optimal conditions for the iodine-initiated cyclization of 10 and

 **1ab** bearing a thiophene moiety, we found that the ring-opening product **3o** was obtained in 63% yield (Scheme 4, eq 1) at 80 °C and **3ab** was obtained in 49% yield at -78 °C (Scheme 4, eq 2) in dark condition, suggesting that sterically bulky aromatic ring containing substrate and electron-rich heteroaromatic ring containing substrate did not facilitate the enyne cyclization process (for more details, see Table S3 in the Supporting Information). It should be clarified that only the ring-opening reaction of **1o** and **1ab** should be processed in dark condition and the products **3o** and **3ab** probably decomposed under the light condition. For product **3ab**, it is not stable at high temperature; thus, the reaction was carried out at -78 °C. The structure of **3ab** has been confirmed by X-ray diffraction. The ORTEP drawing of **3ab** is shown in Scheme 4, and the CIF data are presented in the Supporting Information. We also successfully isolated the corresponding product **3a** when using substrate **1a** as substrate, which means the reaction first undergoes a ring-opening process to get the intermediate **3a** (Scheme 4, eq 3).

Scheme 4 Iodine-initiated reaction of 1a, 1o and 1ab.



<sup>a</sup> The reaction was conducted with **1o** (0.2 mmol),  $I_2$  (0.4 mmol), without light in DCE (2 mL). <sup>b</sup> The reaction was conducted with **1ab** (0.2 mmol),  $I_2$  (0.4 mmol), without light in DCM (2 mL). <sup>c</sup> The reaction was conducted with **1a** (0.2 mmol),  $I_2$  (0.4 mmol), without light in CDCl<sub>3</sub> (2 mL). <sup>d</sup> Yield of isolated product purified by column chromatography on silica gel.

Furthermore, we conducted a series of control experiments to explore reaction process using **3a** and **3o** as substrates (Scheme 5). Interestingly, we successfully obtained the products **2a**, **2o**, and **8a** in 93%, 82% and 80% yields respectively using  $I_2$  or HI as initiator, which indicates that the cyclopropane moiety probably opens first and  $I_2$  as initiator promotes the leaving process of hydroxyl group and the subsequent electrophilic aromatic substitution step (for more details, see Table S4 in the Supporting Information).

Scheme 5 Thermal cyclization reaction of **3a** and **3o**.



The further transformation of product **2a** could be exploited by using palladium-catalyzed cross-coupling reaction processes (Scheme 6). For example, the Sonagashira<sup>18</sup> and Suzuki<sup>19</sup> coupling of **2a** afforded the corresponding products **4** and **6** in 88% and 57%, respectively, which afforded the corresponding products **5** and **7** in 92% and 98% upon further treatment with *t*-BuOK in *t*-BuOH at 80 °C. The photonic properties of products **5** and **7** were investigated, and were compared to those of products **4** and **6**. Their emission spectra were measured under the concentration  $1.0 \times 10^{-3}$  mmol/ml in DCM and plotted in Figure 1. The  $\lambda_{max}$  emission at 445 nm for **5** and 450 nm for **7** were identified, respectively, indicating a wavelength redshift because of the larger conjugated system as compared with those of **4** and **6**, which may indicate their

potential application in fluorescent material (for their absorption spectra, see Figure S1 in Supporting Information).<sup>20</sup> Furthermore, the large-scale synthesis of 2a (1.231 g) using 2 mmol of 1a was conducted to show the practical utility of this work (Scheme 7).

Scheme 6 Pd-catalyzed cross-coupling of 2a for further transformations.



Figure 1 Emission spectra of products 4, 5, 6 and 7 ( $\lambda_{\text{excitation}} = 250$ nm) in DCM (b = 1cm, c = 10 x 10<sup>-5</sup> mol/L, 25 °C).

In order to investigate whether this is a HI-promoted reaction, we carried out a series of control experiments; the results are summarized in Table 2. We used **1a** as a model substrate in optimized reaction condition with HI solution (0.2 equiv), and found that the desired cyclized product **2a** was obtained in only 38% yield (Table 2, entry 1). This result indicates that the HI cannot promote this reaction. HI probably hindered the progress of the reaction because of competitive reaction during electrophilic aromatic substitution process. Increasing the amount of HI while decreasing the amount of I<sub>2</sub>, 40% of **8a** was obtained without **2a** (Table 2, entry 3). We failed to get **8a** while I<sub>2</sub> was replaced by HI (0.5 equiv) (Table 2, entry 4). Further increasing the amount of HI to 2 equivalents improved the yield of **8a** up to 61% (Table 2, entries 5-7).





Table 2 Investigation on the effect of proton affording 2a and 8a.

	1a OH	HI, I <sub>2</sub> DCE, 80 °C	2a 8	Ba
entry <sup>[a]</sup>	HI (equiv)	I <sub>2</sub> (equiv)	2a yield (%) <sup>[b]</sup>	8a yield (%) <sup>[b]</sup>
1	0.2	2.0	38	-
2	0.5	1.0	-	-
3	1.0	1.0	-	40
4	0.5	-	-	-
5	1.0	-	-	45
6	1.5	-	-	50
7	2.0	-	-	61

 $^{a}$  The reaction was conducted with **1a** (0.2 mmol) and I<sub>2</sub> in DCE (2 mL) for 2 hours.  $^{b}$  NMR yield.

A plausible mechanism for this iodine-initiated cascade cyclization is proposed in Scheme 8 using 1a as the model substrate. First, the  $I_2$  is associated with the alkene moiety in 1a to give a complex A, which subsequently generates a zwitterionic intermediate B. The intermediate B undergoes the ring-opening to afford an intermediate  $C^{21}$  The intermediate C may go through two possible pathways to generate an intermediate F. In Path A, the intramolecular iodination of the intermediate C gives an intermediate D. Another molecular  $I_2$  activates the hydroxyl group<sup>22</sup> in intermediate D to promote an intramolecular enyne cyclization, giving an intermediate E along with the release of HOI.<sup>23</sup> With the elimination of Iodine cation in intermediate  $\mathbf{E}$ , an intermediate **F** is generated. In Path B, it is also possible that the trace amount of  $H^+$  in the reaction could trigger the hydroxy group leaving process in the intermediate H to facilitate an intramolecular envne cyclization to afford an intermediate I. In the presence of another molecule I2, the intermediate F can also be generated. An intermediate G is then formed through an intramolecular electrophilic aromatic substitution<sup>24</sup> of the intermediate F, which releases a molecule of HI to deliver the desired product 2a. The synthesis of products 2z and 2aa using ICl and Br<sub>2</sub> to react with 1a also prove that these two proposed mechanisms are reasonable (for more details, see Scheme S1 in the Supporting Information).



Scheme 8 The proposed reaction mechanism.



#### Conclusion

In summary, we have developed a novel protocol for the synthesis of all-carbon spirobiindene scaffold from a class of well designed propargyl alcohol-tethered alkylidenecyclopropane substrates 1 in good moderate to excellent yields under mild reaction conditions with a broad substrate scope. The diiodinated moiety can be readily used for further transformation. In this transformation, ICl and  $Br_2$  can be used as well to give the corresponding spirobiindene derivative. Further investigations on expanding this cascade cyclization and its asymmetric version as well as application of this method for the synthesis of bidentate ligands are undergoing in our laboratory.

# **Experimental Section**

**General information.** <sup>1</sup>H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. <sup>13</sup>C NMR spectra were recorded on a Varian

Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers (CDCl<sub>3</sub>: 77.0 ppm). Mass and HRMS spectra were recorded by MALDI, DART or ESI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm<sup>-1</sup>. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Fluorescence spectra for emission and excitation were obtained on a Hitachi F-2700 FL Spectrophotometer. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

Precursors  $S_2$  and  $S_4$  were prepared according to the previous literature.  $^{\rm 25}$ 

Precursors  $S_5$  and  $S_6$  were prepared according to the previous literature.<sup>26</sup>

General procedure for the preparation of precursor  $S_2$  of 1b: To a stirred solution of commercially available  $S_1$  of 1b (7.55 g, 1.0 equiv) in anhydrous THF (80 mL, 0.625 mol/L) was added 1,1'-carbonyldiimidazole (8.1 g, 1.0 equiv) at 0 °C under argon atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then a suspension of N,O-dimethylhydroxylamine hydrochloride (4.85 g, 1.0 equiv) and Et<sub>3</sub>N (5.35 g, 1.0 equiv) in THF (80 mL, 0.625 mol/L) was added, and the reaction mixture was stirred overnight. The residue was poured into H<sub>2</sub>O (100 mL). The mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 50:50) to yield 2-amino-N-methoxy-N,3-dimethylbenzamide  $S_2$  of 1b as a colorless solid in 82% yield (8.240 g).

General procedure for the preparation of precursor  $S_4$  of 1b: To a solution of 2-amino-N-methoxy-N,3-dimethylbenzamide  $S_2$  of 1b (6.606 g, 1.0 equiv.) in 100 mL of freshly distilled anhydrous THF (0.34 mol/L) was added bromobenzene  $S_3$  (5.304 g, 1.0 equiv.) and n-butyllithium (68 mmol, 2.0 equiv.) by dropwise at -78 °C. The reaction mixture was capped under argon atmosphere. The mixture was poured into 5% HCl in ethanol at -0 °C and the mixture was partitioned between brine and a 1:1 mixture of ether and methylene chloride. The organic extract was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 30 / 1) to afford (2-amino-3-methylphenyl)(phenyl)methanone  $S_4$  of 1b as yellow solid in 78% yield (5.600 g).

General procedure for the preparation of precursor  $S_5$  of 1b: To a 150 mL flask charged with (2-amino-3-methylphenyl)(phenyl)methanone  $S_4$  of 1b (5.600 g, 1.0 equiv) and TsOH (15.200 g, 3.0 equiv) in MeCN (100 mL, 0.265 mol/mL) was added NaNO<sub>2</sub> (3.657 g, 2.0 equiv) and KI (11.006g, 2.5 equiv) dissolved in H<sub>2</sub>O (100 mL) dropwise at room temperature and the resulting solution was stirred at room temperature for another 2 h. Upon completion, saturated aqueous sodium sulfite was added to the solution to quench the reaction until the reaction mixture turned to be yellow. After removal of the most of MeCN solvent under reduced pressure, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 50 / 1) to afford (2-iodo-3-methylphenyl)(phenyl)methanone  $S_5$  of 1b as a white solid in 61% yield (5.505 g).

General procedure for the preparation of precursor  $S_6$  of 1b: A solution of 3-bromopropyltriphenylphosphonium bromide (8.908 g, 1.2 equiv) and NaH (2.048g, 3.2 equiv) in THF (50 mL) was stirred at 80 °C in oil bath under Ar for 8 h. Afterwards compound

(2-iodo-3-methylphenyl)(phenyl)methanone  $S_5$  of 1b (5.505 g, 1.0 equiv) in THF (50 mL, 0.342 mol/L) was added and the reaction solution was stirred at 80 °C in oil bath for another 8 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether) to afford 1-(cyclopropylidene(phenyl)methyl)-2-iodo-3-methylbenzene  $S_6$  of 1b as colorless oil in 86% (5.010 g).

General procedure for the preparation of compound 1b: To a stirred solution of iodine-tethered 1-(cyclopropylidene(phenyl)methyl)-2-iodo-3-methylbenzene  $S_6$  of 1b (5.010 g, 1.1 equiv) and 1,1-diphenylprop-2-yn-1-ol (2.590 g, 1.0 equiv) in Et<sub>3</sub>N (50 mL, 0.290 mol/L) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (192 mg, 2 mol%) and CuI (52 mg, 2 mol%) in Ar atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the separation of solid by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 20 / 1) to afford the corresponding compound 1b as a white solid in 74% yield (4.601 g).

**3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (1a). A white solid. 1627 mg, 79% yield. m.p. 115-117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 1H), 7.16-7.20 (m, 6H), 7.21-7.30 (m, 4H), 7.31-7.38 (m, 6H), 7.39-7.43 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 74.5, 86.3, 94.8, 122.2, 125.8, 125.9, 126.7, 126.8, 126.9, 127.3, 128.0, 128.1, 128.6, 128.9, 130.1, 132.3, 140.1, 144.1, 144.8 IR (neat) 3549, 3089, 3058, 3029, 1492, 1447, 1160, 1030, 992, 770, 762, 751 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{31}H_{24}O]^+$  Calcd for  $C_{31}H_{24}O^+$  412.1822; Found 412.1821.

**3-(2-(cyclopropylidene(phenyl)methyl)-6-methylphenyl)-1,1-diphenylprop-2-yn-1-ol (1b).** A white solid. 4601 mg, 74% yield. m.p. 170-172 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.12 (t, J = 8.0 Hz, 2H), 1.46 (t, J = 7.6 Hz, 2H), 2.24 (s, 1H), 2.47 (s, 3H), 7.14-7.19 (m, 7H), 7.19-7.27 (m, 2H), 7.24-7.29 (m, 3H), 7.34-7.41 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.6, 5.4, 21.1, 74.8, 85.5, 99.3, 122.1, 125.4, 125.9, 126.2, 126.6, 126.8, 127.3, 127.5, 128.0, 128.1, 128.2, 129.3, 140.4, 140.7, 144.4, 144.9. IR (neat) 3530, 3089, 3050, 3029, 1490, 1449, 1159, 1037, 1088, 945, 789, 779, 669 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>32</sub>H<sub>26</sub>ONa] [M+Na]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>26</sub>ONa<sup>+</sup> 449.1876; found 449.1857.

**3-(2-(cyclopropylidene(phenyl)methyl)-5-methylphenyl)-1,1-diphenylprop-2-yn-1-ol (1c)**. A white solid. 1470 mg, 69% yield. m.p. 117-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.12 (t, J = 7.6 Hz, 2H), 1.46 (t, J = 7.6 Hz, 2H), 2.30 (s, 1H), 2.35 (s, 3H), 7.14-7.19 (m, 7H), 7.19-7.23 (m, 2H), 7.23-7.29 (m, 2H), 7.32-7.37 (m, 5H), 7.41 (d, J = 7.6 Hz, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.3, 20.9, 74.5, 86.9, 94.5, 122.0, 125.6, 125.9, 126.6, 126.9, 127.3, 128.0, 128.1, 128.8, 129.5, 130.0, 132.8, 136.6, 140.4, 141.2, 144.9. IR (neat) 3530, 3026, 2966, 2920, 2207, 1597, 1596, 1490, 1447, 1184, 1044, 733 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>32</sub>H<sub>26</sub>ONa] [M+Na]<sup>+</sup>C alcd for C<sub>32</sub>H<sub>26</sub>ONa<sup>+</sup> 449.1876; found 449.1859.

**3-(2-(cyclopropylidene(phenyl)methyl)-5-methoxyphenyl)-1,1-diphenylprop-2-yn-1-ol** (1d). A white solid. 2100 mg, 79% yield. m.p. 112-114 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 7.6 Hz, 2H), 1.47 (m, J = 7.6 Hz, 2H), 2.33 (s, 1H), 3.83 (s, 3H), 6.92-6.97 (m, 1H), 7.05-7.08 (m, 1H), 7.17-7.22 (m, 6H), 7.21-7.30 (m, 4H), 7.31-7.36 (m, 4H), 7.40-7.44 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 55.4, 74.5, 86.6, 94.6, 115.4, 116.6, 123.1,

125.6, 125.9, 126.6, 126.9, 127.4, 128.0, 128.1, 128.5, 131.2, 136.7, 140.5, 144.8, 158.2. IR (neat) 3338, 3055, 2961, 1599, 1491, 1447, 1218, 1034, 859, 764, 757, 728 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z:  $[C_{32}H_{26}O_2Na]$  [M+Na]<sup>+</sup> Calcd for  $C_{32}H_{26}O_2Na^+$  465.1825; found 465.1809.

**3-(2-(cyclopropylidene(phenyl)methyl)-5-(trifluoromethyl)phenyl)-1,1-diphenylprop-2-yn-1** -ol (1e). A white solid. 3700 mg, 77% yield. m.p. 126-128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.14 (t, J = 8.0 Hz, 2H), 1.51 (t, J = 8.0 Hz, 2H), 2.34 (s, 1H), 7.18-7.23 (m, 6H), 7.23-7.30 (m, 3H), 7.30-7.34 (m, 4H), 7.35-7.39 (m, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.4, 74.5, 85.2, 96.4, 124.2 (q, J = 272.6Hz), 125.1 (q, J = 3.8 Hz), 125.8, 126.0, 127.0, 127.1, 127.5, 128.0, 128.3, 129.2 (q, J = 3.6 Hz), 129.4 (q, J = 32.2 Hz), 130.7, 139.3, 144.5, 147.7. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) -62.63 (s). IR (neat) 3555, 3050, 2974, 2157, 1450, 1329, 1167, 1119, 1082, 767, 693, cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>] [M-OH]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>22</sub>F<sub>3</sub><sup>+</sup> 463.1668; found 463.1666.

**3-(5-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (**1f**). A white solid. 2420 mg, 74% yield. m.p. 130-132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.11 (t, J = 8.0 Hz, 2H), 1.47 (t, J = 7.6 Hz, 2H), 2.35 (s, 1H), 7.14-7.19 (m, 6H), 7.21-7.27 (m, 4H), 7.27-7.35 (m, 5H), 7.36-7.40 (m, 2H), 7.51-7.53 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.4, 74.5, 85.3, 96.0, 123.9, 125.8, 126.5, 126.8, 126.9, 127.5, 128.00, 128.03, 128.2, 128.8, 131.4, 132.0, 133.0, 139.7, 142.5, 144.5. IR (neat) 3517, 3056, 2974, 2170, 1591, 1482, 1446, 1390, 1088, 1029, 883, 766, 720, 691 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>31</sub>H<sub>23</sub>OClNa<sup>+</sup> 469.1330; found 469.1314.

**3-(2-(cyclopropylidene(phenyl)methyl)-4-methylphenyl)-1,1-diphenylprop-2-yn-1-ol (1g)**. A white solid. 3453 mg, 49% yield. m.p. 120-122 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 7.6 Hz, 2H), 1.46 (t, J = 7.6 Hz, 2H), 2.37 (s, 4H), 7.08-7.14 (m, 2H), 7.16-7.18 (m, 6H), 7.20-7.24 (m, 1H), 7.24-7.30 (m, 2H), 7.32-7.35 (m, 4H), 7.39-7.47 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.3, 21.5, 74.6, 86.8, 94.0, 119.3, 125.5, 125.9, 126.6, 126.9, 127.3, 127.8, 128.0, 128.1, 128.9, 130.7, 132.2, 138.7, 140.3, 144.1, 145.0. IR (neat) 2956, 2924, 2845, 2237, 1700, 1595, 1488, 1359, 1169, 1089, 811, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>30</sub>ON] [M+NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>30</sub>ON<sup>+</sup> 444.2322; found 444.2321.

**3-(2-(cyclopropylidene(phenyl)methyl)-4-methoxyphenyl)-1,1-diphenylprop-2-yn-1-ol** (1h). A white solid. 663 mg, 75% yield. m.p. 127-129 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.15 (t, J = 8.0 Hz, 2H), 1.47 (t, J = 8.0 Hz, 2H), 2.30 (s, 1H), 3.81 (s, 3H), 6.82-6.87 (m, 2H), 7.15-7.20 (m, 6H), 7.21-7.35 (m, 7H), 7.42 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 55.3, 74.6, 86.6, 93.4, 112.7, 114.6, 115.6, 125.7, 125.9, 126.7, 126.8, 127.3, 128.0, 128.2, 128.9, 133.7, 139.9, 145.0, 145.8, 159.7. IR (neat) 3465, 3084, 3055, 2971, 2223, 1596, 1488, 1225, 1197, 1040, 1021, 893, 780, 692 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>O] [M-OH]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>O<sup>+</sup> 425.1900; found 425.1899.

**3-(4-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1i)**. A white solid. 694 mg, 57% yield. m.p. 155-157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.14 (t, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 1H), 7.15-7.28 (m, 10H), 7.28-7.33 (m, 5H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.4, 74.5, 85.5, 95.7, 120.9, 125.8, 126.7, 126.8, 126.9, 127.2, 127.4, 127.98, 128.02, 128.2, 130.2, 133.5, 134.4, 139.5, 144.6, 145.8. IR (neat) 3555, 3084, 3063, 3023, 2971, 1581, 1490, 1445, 1162, 1029, 969, 762, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>23</sub>OCl] [M]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>23</sub>OCl<sup>+</sup> 446.1432; found 446.1432.

**3-(2-(cyclopropylidene(phenyl)methyl)-4-fluorophenyl)-1,1-diphenylprop-2-yn-1-ol** (**1j**). A white solid. 1300 mg, 63% yield. m.p. 95-97°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.15 (t, J = 7.6 Hz, 2H), 1.48 (t, J = 8.0 Hz, 2H), 2.32 (s, 1H), 6.97-7.06 (m, 2H), 7.15-7.22 (m, 6H), 7.29-7.35 (m, 7H), 7.37-7.41 (m, 2H), 7.48-7.53 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>, TMS) 1.9, 5.4, 74.5, 85.6, 94.6, 114.3 (d, J = 22.2 Hz), 117.2 (d, J = 22.2 Hz), 118.5 (d, J = 3.9 Hz), 125.9, 126.6, 126.8, 126.9, 127.4, 128.0, 128.2, 128.3, 134.1 (d, J = 8.4 Hz), 139.6, 144.7, 146.6 (d, J = 7.7 Hz), 162.5 (d, J = 249 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) -110.78 (s). IR (neat) 3543, 3058, 3034, 1601, 1488, 1448, 1265, 1166, 1030, 882, 782, 776, 702 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{31}H_{24}OF]$  [M+H]<sup>+</sup> Calcd for  $C_{31}H_{24}OF^+$  431.1806; found 431.1804.

**3-(2-(1-cyclopropylideneethyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1k)**. A white solid. 3510 mg, 77% yield. m.p. 71-73°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.05 (s, 4H), 2.21 (s, 3H), 2.80 (s, 1H), 7.18-7.33 (m, 9H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.57-7.62 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.2, 4.3, 22.0, 74.9, 87.4, 93.8, 120.6, 122.9, 124.2, 126.1, 126.3, 127.6, 128.0, 128.1, 128.4, 132.9, 145.0, 146.2. IR (neat) 3516, 3060, 2968, 2921, 2843, 2230, 1594, 1487, 1449, 1071, 1042, 1001, 990, 784, 750, 700 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>26</sub>H<sub>21</sub>] [M-OH]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>21</sub><sup>+</sup> 333.1640; found 333.1640.

**3-(2-(cyclopropylidene(m-tolyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (**1**). A white solid. 3290 mg, 52% yield. m.p. 99-101 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 2H), 2.24 (s, 3H), 2.36 (s, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.14-7.24 (m, 9H), 7.27-7.39 (m, 7H), 7.53 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 21.5, 74.6, 86.7, 94.9, 122.2, 124.1, 125.7, 125.9, 126.9, 127.4, 127.5, 127.6, 128.0, 128.1, 128.6, 129.0, 130.1, 133.0, 137.7, 140.2, 144.3, 144.9. IR (neat) 3547, 3057, 3026, 2963, 1601, 1483, 1445, 1184, 1046, 1031, 796, 789, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>O] [M-H]<sup>-</sup>Calcd for C<sub>32</sub>H<sub>25</sub>O<sup>-</sup> 425.1911; found 425.1916.

**3-(2-(cyclopropylidene(3-(trifluoromethyl)phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1ol (1m)**. A yellow oil. 1770 mg, 65% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 8.0 Hz, 2H), 1.47 (t, J = 8.0 Hz, 2H), 2.49 (s, 1H), 7.14-7.19 (m, 5H), 7.25-7.38 (m, 9H), 7.44 (d, J = 8.0 Hz, 1H), 7.48-7.53 (m, 1H), 7.55-7.59 (m, 1H), 7.65-7.71 (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.4, 74.6, 86.4, 95.0, 122.4, 123.1 (q, J = 3.8 Hz), 123.3 (q, J = 3.9 Hz), 124.2 (q, J = 270.4 Hz), 125.6, 127.3, 127.5, 127.8, 127.99, 128.03, 128.6, 128.8, 129.9, 130.0, 130.5 (q, J = 32.2 Hz), 132.6, 140.8, 143.1, 144.7. <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -62.46 (s). IR (neat) 3502, 3060, 2927, 2848, 1489, 1448, 1332, 1165, 1124, 800, 757, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>24</sub>OF<sub>3</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>24</sub>OF<sub>3</sub><sup>+</sup> 481.1774; found 481.1773.

**3-(2-(cyclopropylidene(3,5-dimethylphenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1n)**. A white solid. 930 mg, 75% yield. m.p. 101-103 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 7.6 Hz, 2H), 1.48 (t, J = 7.6 Hz, 2H), 2.21 (s, 6H), 2.32 (s, 1H), 6.86 (s, 1H), 7.00 (s, 2H), 7.17-7.23 (m, 6H), 7.26-7.40 (m, 7H), 7.51-7.54 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.4, 21.4, 74.5, 86.7, 95.0, 122.2, 124.8, 125.5, 125.9, 126.8, 127.3, 128.0, 128.4, 128.5, 129.1, 130.1, 132.2, 137.6, 140.3, 144.5, 144.9. IR (neat) 3527, 3057, 3018, 2958, 1599, 1488, 1449, 1333, 1161, 1031, 987, 757, 702 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>33</sub>H<sub>28</sub>ONa] [M+Na]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>28</sub>ONa<sup>+</sup> 463.2032; found 463.2031.

**3-(2-(cyclopropylidene(4-isopropylphenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (10). A yellow oil. 450 mg, 40% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.09 (t, *J* = 7.6 Hz, 2H), 1.21 (d, *J* = 7.6 Hz, 6H), 1.44 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 1H), 2.78-2.92 (m, 1H), 7.09-7.19 (m, 7H), 7.20-7.28 (m, 2H), 7.28-7.38 (m, 8H), 7.49-7.58 (m, 1H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_C$  1.6, 5.3, 23.9, 33.7, 74.5, 86.7, 94.8, 122.2, 124.8, 125.9, 126.1, 126.8, 127.3, 127.9, 128.1, 128.5, 128.8, 130.1, 132.2, 137.7, 144.3, 144.9, 147.3. IR (neat) 3542, 3081, 3060, 3023, 2959, 2929, 2866, 2220, 1594, 1510, 1448, 1045, 1031, 753, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>34</sub>H<sub>31</sub>O] [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>31</sub>O<sup>+</sup> 455.2369; found 455.2369.

**3-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (1**p**). A yellow oil. 1930 mg, 58% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.11 (t, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 2H), 2.48 (s, 1H), 3.76 (s, 3H), 6.79-6.84 (m, 2H), 7.15-7.23 (m, 6H), 7.25-7.32 (m, 2H), 7.32-7.38 (m, 7H), 7.51-7.55 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.6, 5.2, 55.2, 74.6, 86.7, 94.7, 113.5, 122.3, 123.4, 125.9, 126.9, 127.4, 127.9, 128.0, 128.4, 128.6, 130.1, 132.3, 140.0, 144.4, 144.9, 158.5. IR (neat) 2974, 2922, 2853, 2235, 1597, 1488, 1364, 1169, 1088, 1007, 813, 748, 663 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>27</sub>O<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>27</sub>O<sub>2</sub><sup>+</sup> 443.2006; found 443.2002.

**3-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1ol** (**1q**). A white solid. 4080 mg, 76% yield. m.p. 98-100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 8.0 Hz, 2H), 1.46 (t, J = 8.0 Hz, 2H), 2.53 (s, 1H), 7.13-7.17 (m, 6H), 7.24-7.28 (m, 1H), 7.28-7.35 (m, 4H), 7.35-7.39 (m, 1H), 7.44-7.52 (m, 4H), 7.52-7.77 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.9, 5.5, 74.6, 86.3, 95.0, 122.4, 124.3 (q, J = 269.6 Hz), 125.0 (q, J =3.1 Hz), 126.8, 127.3, 127.5, 128.0, 128.4 (q, J = 3.1 Hz), 128.7, 128.8, 130.0, 132.5, 143.3, 143.4, 144.7. <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -62.14 (s). IR (neat) 3537, 3065, 3021, 2974, 1611, 1488, 1449, 1324, 1110, 1068, 1057, 918, 760, 750, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>24</sub>OF<sub>3</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>24</sub>OF<sub>3</sub><sup>+</sup> 481.1774; found 481.1775.

**3-(2-((4-(benzyloxy)phenyl)(cyclopropylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (**1r**). A yellow oil. 1730 mg, 67% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.09 (t, *J* = 7.6 Hz, 2H), 1.45 (t, *J* = 7.6 Hz, 2H), 2.48 (s, 1H), 5.00 (s, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.14-7.20 (m, 6H), 7.20-7.30 (m, 3H), 7.30-7.38 (m, 9H), 7.38-7.42 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.6, 5.2, 69.9, 74.6, 86.7, 94.7, 114.4, 122.3, 123.5, 125.9, 126.9, 127.3, 127.4, 127.90, 127.93, 128.0, 128.3, 128.5, 130.0, 132.3, 133.1, 137.0, 144.3, 144.9, 157.7. IR (neat) 3431, 3059, 3031, 2968, 2921, 1773, 1602, 1507, 1488, 1449, 1240, 1174, 1025, 750, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>38</sub>H<sub>31</sub>O<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>31</sub>O<sub>2</sub><sup>+</sup> 519.2319; found 519.2316.

**3-(2-((4-chlorophenyl)(cyclopropylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1s)**. A white solid. 1030 mg, 70% yield. m.p. 129-131 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, J = 7.6 Hz, 2H), 1.47 (t, J = 7.6 Hz, 2H), 2.47 (s, 1H), 7.18-7.24 (m, 8H), 7.26-7.34 (m, 8H), 7.35-7.40 (m, 1H), 7.54 (d, J = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 74.6, 86.5, 94.9, 122.3, 125.9, 126.4, 127.2, 127.5, 128.0, 128.1, 128.3, 128.7, 130.0, 132.42, 132.44, 138.5, 143.6, 144.7. IR (neat) 3537, 3052, 3018, 2979, 2236, 1485, 1449, 1397, 1085, 1046, 992, 858, 763, 714, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>22</sub>OCl] [M-H]<sup>-</sup> Calcd for C<sub>31</sub>H<sub>22</sub>OCl<sup>-</sup> 445.1365; found 445.1368.

**3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1-(4-fluorophenyl)-1-(4-methoxyphenyl)pro p-2-yn-1-ol (1t)**. A white solid. 1590 mg, 79% yield. m.p. 126-128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.14 (t, J = 7.6 Hz, 2H), 1.50 (t, J = 7.6 Hz, 2H), 2.39 (s, 1H), 3.75 (s, 3H), 6.68-6.73 (m, 2H), 6.81-6.87 (m, 2H), 7.19-7.34 (m, 9H), 7.35-7.43 (m, 3H), 7.53 (d, J = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 55.2, 73.8, 86.3, 94.8, 113.3, 114.1 (d, J

= 21.4 Hz), 122.2, 125.8, 126.8, 127.0, 127.2, 127.7 (d, J = 8.4 Hz), 127.73, 128.2, 128.7, 128.9, 130.1, 132.3, 137.1, 140.1, 140.3 (d, J = 3.1 Hz), 144.1, 158.9, 161.9 (d, J = 245.1 Hz). <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -115.61 (s). IR (neat) 3434, 3081, 2966, 2835, 1602, 1507, 1411, 1215, 1173, 1028, 844, 787, 777, 766, 758, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>26</sub>O<sub>2</sub>F] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>26</sub>O<sub>2</sub>F<sup>+</sup> 461.1911; found 461.1912.

**3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-o I** (1u). A white solid. 690 mg, 64% yield. m.p. 75-77 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$ 1.13 (t, J = 8.0 Hz, 2H), 1.49 (t, J = 7.6 Hz, 2H), 2.32 (s, 1H), 3.74 (s, 3H), 6.67-6.71 (m, 2H), 7.17-7.31 (m, 9H), 7.31-7.43 (m, 6H), 7.52-7.55 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 55.2, 74.2, 86.5, 95.0, 113.3, 122.4, 125.8, 126.7, 126.9, 127.0, 127.3, 128.0, 128.2, 128.5, 128.9, 130.1, 132.3, 137.2, 140.2, 144.1, 145.1, 158.8. IR (neat) 3447, 3057, 2970, 2835, 1606, 1492, 1446, 1247, 1031, 831, 797, 786, 724, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>O] [M-OH]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>O<sup>-</sup> 425.1900; found 425.1896.

**3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1-(4-fluorophenyl)-1-phenylprop-2-yn-1-ol** (**1v**). A white solid. 573 mg, 61% yield. m.p. 105-107 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$ 1.27 (t, *J* = 8.0 Hz, 2H), 1.48 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 1H), 6.80-6.86 (m, 2H), 7.16-7.23 (m, 4H), 7.24-7.34 (m, 8H), 7.34-7.42 (m, 3H), 7.51-7.54 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 74.1, 86.8, 94.6, 114.7 (d, *J* = 21.4 Hz), 122.1, 125.8, 125.9, 126.7, 126.8, 127.0, 127.5, 127.8 (d, *J* = 7.7 Hz), 128.1, 128.2, 128.7, 128.9, 130.2, 132.3, 140.1, 140.7 (d, *J* = 3.1 Hz), 144.1, 144.7, 162.0 (d, *J* = 245.2 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz, CFCl<sub>3</sub>)  $\delta$  -115.25 (s). IR (neat) 3549, 3047, 2976, 1596, 1503, 1491, 1216, 1161, 1048, 833, 766, 758, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>22</sub>F] [M-OH]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>22</sub>F<sup>+</sup> 413.1700; found 413.1699.

**3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-di-p-tolylprop-2-yn-1-ol (1w)**. A yellow oil. 1850 mg, 84% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.15 (t, *J* = 7.6 Hz, 2H), 1.50 (t, *J* = 7.6 Hz, 2H), 2.26 (s, 1H), 2.28 (s, 6H), 6.98 (d, *J* = 8.0 Hz, 4H), 7.19-7.25 (m, 5H), 7.27-7.43 (m, 7H), 7.53 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 21.0, 74.3, 86.3, 95.1, 122.4, 125.7, 125.8, 126.6, 126.86, 126.89, 128.1, 128.4, 128.6, 129.0, 130.1, 132.3, 136.9, 140.2, 142.2, 144.1. IR (neat) 3536, 3081, 3052, 3021, 2974, 2924, 2851, 1508, 1493, 1480, 1053, 1021, 824, 758, 693 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>33</sub>H<sub>29</sub>O] [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>29</sub>O<sup>+</sup> 441.2213; found 441.2213.

**3-(2-(cyclopropylidene(naphthalen-2-yl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1x)**. A yellow oil. 1510 mg, 56% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.15 (t, J = 8.0 Hz, 2H), 1.57 (t, J = 7.6 Hz, 2H), 2.35 (s, 1H), 6.95-7.02 (m, 4H), 7.03-7.11 (m, 2H), 7.21 (d, J = 7.6 Hz, 4H), 7.28-7.44 (m, 5H), 7.55-7.61 (m, 2H), 7.63-7.68 (m, 1H), 7.73-7.80 (m, 2H), 7.81-7.88 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.7, 74.5, 86.6, 94.8, 122.4, 124.9, 125.68, 125.73, 125.8, 126.0, 126.4, 127.0, 127.3, 127.5, 127.7, 127.9, 128.3, 128.6, 129.1, 130.1, 132.39, 132.42, 133.4, 137.5, 144.1, 144.7. IR (neat) 3374, 3057, 3023, 2971, 2916, 1773, 1597, 1505, 1488, 1044, 1002, 992, 749, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>35</sub>H<sub>27</sub>O] [M+H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>27</sub>O<sup>+</sup> 463.2056; found 463.2054.

**3-(2-(benzo[b]thiophen-5-yl(cyclopropylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (**1y**) A white solid. 1010 mg, 71% yield. m.p. 83-85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$ 1.16 (t, *J* = 7.6 Hz, 2H), 1.54 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 1H), 7.04-7.26 (m, 11H), 7.31-7.42 (m, 4H), 7.55-7.61 (m, 2H), 7.66-7.69 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.8, 5.6, 74.6, 86.6, 94.8, 121.9, 122.0, 122.4, 123.4, 124.2, 125.4, 125.8, 126.6, 127.0, 127.4, 127.9, 128.7, 129.0, 130.2, 132.4, 136.6, 138.2, 139.8, 144.3, 144.7. IR (neat) 3549, 3057, 3031, 2963, 2228, 1605, 1487, 1448, 1158, 1029, 891, 751, 698 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>33</sub>H<sub>24</sub>ONaS] [M+Na]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>24</sub>ONaS<sup>+</sup> 491.1440; found 491.1424.

**3-(2-(cyclopropylidene(thiophen-3-yl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (1ab)**. A yellow oil. 750 mg, 69% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.6 Hz, 2H), 2.55 (s, 1H), 6.88-6.91 (m, 1H), 7.16-7.27 (m, 6H), 7.28-7.31 (m, 2H), 7.31-7.42 (m, 7H), 7.53 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.4, 5.1, 74.7, 86.7, 94.6, 121.4, 122.2, 124.4, 125.1, 125.2, 126.0, 126.4, 127.1, 127.5, 128.2, 128.6, 129.7, 132.4, 142.5, 144.2, 145.0. IR (neat) 3438, 3058, 3026, 2925, 2848, 2223, 1773, 1597, 1488, 1448, 1334, 1162, 1030, 783, 755, 698, 669 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>29</sub>H<sub>22</sub>OS] [M]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>22</sub>OS<sup>+</sup> 418.1386; found 418.1382.

**3-(4-chloro-2-((2-chlorophenyl)(cyclopropylidene)methyl)phenyl)-1,1-diphenylprop-2-yn-1ol (1ac)**. A yellow oil. 2840 mg, 75% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.15 (t, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 2H), 2.62 (s, 1H), 7.07-7.16 (m, 2H), 7.16-7.19 (m, 1H), 7.19-7.22 (m, 2H), 7.22-7.33 (m, 6H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.46-7.68 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.3, 5.2, 74.7, 86.1, 95.8, 120.0, 126.2, 126.5, 126.7, 127.0, 127.7, 128.3, 128.5, 129.3, 130.1, 131.8, 132.9, 133.4, 134.3, 134.6, 139.9, 144.9, 145.3. IR (neat) 3549, 3063, 3026, 2961, 2924, 2853, 1584, 1477, 1449, 1390, 1155, 1031, 751, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>23</sub>OCl<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>23</sub>OCl<sub>2</sub><sup>+</sup> 481.1120; found 481.1120.

**3-(2-(cyclopropylidene(3-methoxyphenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol** (1ad). A yellow oil. 890 mg, 34% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.13 (t, *J* = 8.0 Hz, 2H), 1.48 (t, *J* = 8.0 Hz, 2H), 2.43 (s, 1H), 3.68 (s, 3H), 6.77 (d, *J* = 8.8 Hz, 1H), 7.00-7.01 (m, 2H), 7.17-7.24 (m, 7H), 7.28-7.45 (m, 7H), 7.53 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  1.7, 5.4, 55.1, 74.6, 86.6, 94.8, 112.0, 112.7, 119.6, 122.3, 125.9, 126.1, 126.9, 127.4, 128.0, 128.6, 128.8, 129.0, 130.1, 132.3, 141.6, 144.0, 144.9, 159.5. IR (neat) 3433, 3287, 3059, 3023, 1597, 1488, 1448, 1162, 1031, 1002, 756, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>O] [M-OH]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>O<sup>+</sup> 425.1900; found 425.1900.

General procedure for the preparation of compounds 2b: To a stirred solution of **3-(2-(cyclopropylidene(phenyl)methyl)-4-methylphenyl)-1,1-diphenylprop-2-yn-1-ol 1b** (93 mg, 1.0 equiv) in DCE (2 mL, 0.1mol/L) was added I<sub>2</sub> (101 mg, 2 equiv). The resulting mixture was stirred at 80 °C in oil bath for 2 h. After quenching the remaining I<sub>2</sub> by Na<sub>2</sub>SO<sub>3</sub> solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding products **2b** as white solid in 93% (123 mg).

**2-iodo-2'-(2-iodoethyl)-3,3'-diphenyl-1,1'-spirobi[indene]** (**2a**). A white solid. 127 mg, 98% yield. m.p. 195-197 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.55-2.64 (m, 1H), 2.66-2.77 (m, 2H), 2.79-2.88 (m, 1H), 6.82 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 7.08-7.17 (m, 2H), 7.22-7.25 (m, 1H), 7.26-7.35 (m, 3H), 7.43-7.51 (m, 2H), 7.52-7.58 (m, 6H), 7.59-7.64 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.2, 31.9, 75.7, 105.0, 120.5, 122.3, 123.2, 126.2, 126.4, 127.8, 127.9, 128.1, 128.5, 128.6, 128.7, 128.8, 130.0, 134.4, 134.8, 143.0, 143.7, 144.7, 145.2, 145.6, 146.4, 151.7. IR (neat) 3073, 3065, 3052, 3005, 2919, 1589, 1565, 1450, 1166, 1071, 802, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>23</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>23</sub>I<sub>2</sub><sup>+</sup> 648.9884;

# found 648.9883.

**2'-iodo-2-(2-iodoethyl)-7-methyl-3,3'-diphenyl-1,1'-spirobi[indene]** (**2b**). A white solid. 123 mg, 93% yield. m.p. 165-167 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.69 (s, 3H), 2.44-2.54 (m, 1H), 2.55-2.67 (m, 2H), 2.76-2.86 (m, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.00-7.08 (m, 2H), 7.08-7.14 (m, 1H), 7.19-7.24 (m, 1H), 7.24-7.29 (m, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.39-7.48 (m, 2H), 7.48-7.53 (m, 4H), 7.53-7.61 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.3, 16.5, 31.3, 76.0, 103.2, 118.0, 120.5, 123.2, 126.3, 127.7, 128.0, 128.1, 128.4, 128.6, 128.67, 128.70, 128.8, 133.9, 134.7, 134.9, 140.9, 143.1, 143.4, 145.2, 145.5, 146.9, 152.1. IR (neat) 3068, 3015, 2916, 2843, 1647, 1592, 1149, 1140, 1169, 1082, 974, 799, 759, 714, 701, 668 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>I<sub>2</sub><sup>+</sup> 663.0040; found 663.0034.

**2'-iodo-2-(2-iodoethyl)-6-methyl-3,3'-diphenyl-1,1'-spirobi[indene]** (**2c**). A white solid. 118 mg, 89% yield. m.p. 156-158 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.26 (s, 3H), 2.52-2.63 (m, 1H), 2.64-2.75 (m, 2H), 2.78-2.88 (m, 1H), 6.63 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.06-7.15 (m, 3H), 7.20-7.27 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.40-7.57 (m, 8H), 7.63 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 21.4, 31.9, 75.6, 105.6, 120.2, 120.5, 123.0, 123.3, 126.2, 127.7, 128.0, 128.5, 128.60, 128.64, 128.8, 130.0, 134.6, 134.8, 136.3, 142.0, 143.8, 144.6, 145.4, 145.5, 151.5. IR (neat) 3065, 3034, 2955, 2921, 2845, 1644, 1594, 1571, 1489, 1451, 1441, 1173, 1071, 818, 775, 7657, 750, 740, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>I<sub>2</sub><sup>+</sup> 663.0040; found 663.0039.

**2'-iodo-2-(2-iodoethyl)-6-methoxy-3,3'-diphenyl-1,1'-spirobi[indene]** (**2d**). A white solid. 133 mg, 98% yield. m.p. 133-135 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.53-2.61 (m, 1H), 2.61-2.74 (m, 2H), 2.78-2.87 (m, 1H), 3.68 (s, 3H), 6.39-6.40 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.07-7.16 (m, 2H), 7.20-7.27 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.39-7.56 (m, 8H), 7.61 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.6, 31.9, 55.5, 75.6, 105.4, 109.1, 112.7, 120.5, 120.9, 123.3, 126.2, 127.7, 128.0, 128.5, 128.6, 128.8, 129.0, 134.66, 134.71, 139.3, 140.8, 144.5, 145.1, 145.46, 145.52, 151.5, 159.0. IR (neat) 3060, 2995, 2961, 2937, 2937, 2832, 1607, 1594, 1576, 1477, 1441, 1346, 1268, 1141, 1024, 815, 788, 753, 736, 707, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub><sup>+</sup> 678.9989; found 678.9990.

**2'-iodo-2-(2-iodoethyl)-3,3'-diphenyl-6-(trifluoromethyl)-1,1'-spirobi[indene]** (2e). A white solid. 140 mg, 98% yield. m.p. 124-126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.55-2.66 (m, 1H), 2.67-2.75 (m, 2H), 2.76-2.83 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 7.03-7.06 (m, 1H), 7.11-7.17 (m, 1H), 7.28-7.38 (m, 3H), 7.45-7.59 (m, 9H), 7.61-7.65 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.2, 31.8, 75.7, 103.0, 119.1 (q, J = 3.8 Hz), 120.6, 120.9, 123.3, 124.4 (q, J = 270.3 Hz), 125.5 (q, J = 3.8 Hz), 126.5, 128.1 (q, J = 32.2 Hz), 128.2, 128.5, 128.6, 128.7, 128.8, 128.96, 129.03, 133.7, 134.4, 143.9, 144.4, 144.7, 144.8, 146.4, 149.8, 152.6. <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -61.08 (s). IR (neat) 3073, 3031, 2963, 2919, 2851, 1322, 1262, 1161, 1117, 775, 766, 751, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub><sup>+</sup> 716.9757; found 716.9760.

**6-chloro-2'-iodo-2-(2-iodoethyl)-3,3'-diphenyl-1,1'-spirobi[indene]** (**2f**). A white solid. 134 mg, 98% yield. m.p. 203-205 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.53-2.62 (m, 1H), 2.65-2.74 (m, 2H), 2.75-2.84 (m, 1H), 6.79-6.81 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.09-716 (m, 2H), 7.21-7.30 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.41-7.49 (m, 2H), 7.49-7.57 (m, 6H), 7.61 (d, *J* = 7.2 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.7, 31.8, 75.5, 103.7, 120.7, 121.3,

122.7, 123.3, 126.4, 128.0, 128.1, 128.3, 128.6, 128.7, 128.90, 128.93, 132.3, 134.0, 134.5, 143.5, 144.4, 144.6, 144.77, 144.84, 145.5, 152.2. IR (neat) 3065, 3023, 2942, 1597, 1563, 1465, 1440, 1168, 957, 775, 759, 725, 704 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{31}H_{22}CII_2]$  [M+H]<sup>+</sup> Calcd for  $C_{31}H_{22}CII_2^+$  682.9494; found 682.9498.

**2'-iodo-2-(2-iodoethyl)-5-methyl-3,3'-diphenyl-1,1'-spirobi[indene]** (**2g**). A white solid. 118 mg, 89% yield. m.p. 135-137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.33 (s, 3H), 2.53-2.63 (m, 1H), 2.64-2.75 (m, 2H), 2.78-2.87 (m, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.94-7.02 (m, 2H), 7.03 (s, 1H), 7.06-7.12 (m, 1H), 7.21-7.26 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.41-7.49 (m, 2H), 7.50-7.56 (m, 6H), 7.59-7.63 (m, J = 7.2 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.3, 21.6, 32.0, 75.4, 105.5, 120.5, 121.3, 122.0, 123.2, 126.2, 127.2, 127.7, 128.0, 128.5, 128.6, 128.7, 128.8, 129.0, 134.6, 134.8, 137.8, 140.6, 143.3, 144.6, 145.4, 145.6, 146.5, 151.5. IR (neat) 3063, 3023, 2958, 2916, 2851, 1492, 1471, 1458, 1443, 1172, 1072, 795, 782, 729, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>I<sub>2</sub><sup>+</sup> 663.0039; found 663.0035.

**2'-iodo-2-(2-iodoethyl)-5-methoxy-3,3'-diphenyl-1,1'-spirobi[indene]** (**2h**). A white solid. 133 mg, 98% yield. m.p. 156-158 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.53-2.62 (m, 1H), 2.63-2.74 (m, 2H), 2.78-2.86 (m, 1H), 3.74 (s, 3H), 6.66-6.70 (m, 1H), 6.71-6.75 (m, 1H), 6.77-6.80 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.21-7.27 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.40-7.48 (m, 2H), 7.49-7.56 (m, 6H), 7.58-7.62 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.1, 32.0, 55.4, 75.1, 105.8, 106.6, 116.7, 120.4, 122.9, 123.2, 126.2, 127.7, 128.1, 128.5, 128.58, 128.64, 128.8, 129.0, 134.3, 134.8, 135.1, 144.3, 144.5, 145.3, 145.4, 147.8, 151.4, 160.0. IR (neat) 3063, 3005, 2947, 2927, 2819, 1594, 1490, 1475, 1231, 1170, 1022, 786, 770, 730, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub><sup>+</sup> 678.9989; found 678.9987.

**5'-chloro-2-iodo-2'-(2-iodoethyl)-3,3'-diphenyl-3a,7a-dihydro-1,1'-spirobi[indene]** (2i). A white solid. 134 mg, 98% yield. m.p. 166-168 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.54-2.65 (m, 1H), 2.67-2.75 (m, 2H), 2.77-2.87 (m, 1H), 6.71-6.78 (m, 1H), 6.97-7.05 (m, 1H), 7.08-7.15 (m, 2H), 7.19-7.36 (m, 3H), 7.42-7.65 (m, 10H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.6, 31.9, 75.3, 103.9, 120.7, 120.8, 123.2, 123.3, 126.3, 126.4, 128.0, 128.4, 128.6, 128.7, 128.9, 129.0, 133.8, 133.9, 134.5, 142.0, 144.5, 144.6, 144.7, 144.9, 148.1, 152.1. IR (neat) 3068, 3026, 2916, 2845, 1647, 1049, 1264, 1194, 876, 775, 752, 728, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{31}H_{22}CII_2]$  [M+H]<sup>+</sup> Calcd for  $C_{31}H_{22}CII_2^+$  682.9494; found 682.9487.

**5-fluoro-2'-iodo-2-(2-iodoethyl)-3,3'-diphenyl-1,1'-spirobi[indene]** (**2j**). A white solid. 130 mg, 95% yield. m.p. 163-166 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.52-2.63 (m, 1H), 2.65-2.75 (m, 2H), 2.76-2.85 (m, 1H), 6.73-6.78 (m, 1H), 6.79-6.86 (m, 1H), 6.90-6.95 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.09-7.14 (m, 1H), 7.22-7.29 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.42-7.49 (m, 2H), 7.49-7.57 (m, 6H), 7.58-7.63 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.6, 32.0, 75.1, 104.5, 108.0 (d, *J* = 23.8 Hz), 113.0 (d, *J* = 22.9 Hz), 120.6, 123.3 (d, *J* = 9.2 Hz), 123.4, 126.3, 127.9, 128.3, 128.6 (d, *J* = 7.7 Hz), 128.6, 128.9, 129.0, 133.9, 134.6, 138.7 (d, *J* = 3.0 Hz), 144.5 (d, *J* = 3.1 Hz), 144.6, 144.7, 145.2, 148.4, 148.5, 151.9, 163.2 (d, *J* = 243.7 Hz), <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz) δ -114.33 (s). IR (neat) 3063, 3026, 2961, 2911, 2843, 1604, 1470, 1408, 1330, 1139, 865, 775, 753, 714, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>25</sub>NFI<sub>2</sub>] [M+NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>25</sub>NFI<sub>2</sub><sup>+</sup> 684.0055; found 684.0048.

**2-iodo-2'-(2-iodoethyl)-3'-methyl-3-phenyl-3a,7a-dihydro-1,1'-spirobi[indene]** (2k). A white solid. 93 mg, 79% yield. m.p. 135-137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.23 (s, 3H),

2.52-2.69 (m, 2H), 2.80-2.89 (m, 2H), 6.75 (d, J = 7.6 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.99-7.04 (m, 1H), 7.07-7.12 (m, 1H), 7.15-7.22 (m, 2H), 7.26-7.37 (m, 3H), 7.40-7.45 (m, 1H), 7.47-7.53 (m, 2H), 7.56-7.60 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.2, 11.5, 31.1, 75.7, 105.5, 119.0, 120.3, 121.9, 123.0, 126.0, 126.1, 127.5, 127.8, 128.4, 128.5, 128.9, 134.8, 140.2, 140.6, 143.7, 144.4, 145.6, 146.9, 151.4. IR (neat) 3070, 3055, 3018, 2961, 2916, 2848, 1449, 1442, 1169, 1011, 869, 765, 754, 742, 731, 693 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>26</sub>H<sub>21</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>21</sub>I<sub>2</sub><sup>+</sup> 586.9727; found 586.9727.

**2-iodo-2'-(2-iodoethyl)-3-phenyl-3'-(m-tolyl)-1,1'-spirobi[indene]** (**2l**). A white solid. 103 mg, 78% yield. m.p. 122-124 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.46 (s, 3H), 2.54-2.62 (m, 1H), 2.65-2.77 (m, 2H), 2.81-2.90 (m, 1H), 6.81 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 7.07-7.16 (m, 2H), 7.22-7.29 (m, 4H), 7.30-7.35 (m, 3H), 7.38-7.44 (m, 1H), 7.44-7.50 (m, 1H), 7.51-7.56 (m, 2H), 7.59-7.64 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.3, 21.6, 32.0, 75.7, 105.1, 120.5, 120.6, 122.3, 123.2, 125.7, 126.2, 126.3, 127.7, 127.9, 128.5, 128.6, 128.7, 128.8, 129.0, 129.2, 134.4, 134.8, 138.4, 142.9, 143.7, 144.7, 145.3, 145.7, 146.4, 151.7. IR (neat) 3068, 3057, 3031, 2913, 2851, 1451, 1440, 1175, 764, 756, 744, 715, 704, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>I<sub>2</sub><sup>+</sup> 663.0040; found 663.0042.

**2-iodo-2'-(2-iodoethyl)-3-phenyl-3'-(3-(trifluoromethyl)phenyl)-1,1'-spirobi[indene]** (**2m**). A white solid. 122 mg, 85% yield. m.p. 134-136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.55-2.66 (m, 1H), 2.67-2.80 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.10-7.21 (m, 3H), 7.23-7.36 (m, 3H), 7.45-7.58 (m, 3H), 7.59-7.77 (m, 5H), 7.82 (s, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.7, 31.8, 75.7, 120.0, 120.2, 120.6, 122.5, 123.4, 124.0 (q, *J* = 271.2 Hz), 124.9 (q, *J* = 3.8 Hz), 125.6 (q, *J* = 3.8 Hz), 126.4, 126.8, 127.9, 128.1, 128.6, 128.7, 129.0, 129.4, 131.3 (q, *J* = 32.1 Hz), 132.3, 134.7, 135.3, 143.8, 144.2, 144.3, 144.6, 144.8, 145.7, 152.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -62.48 (s). IR (neat) 3065, 3021, 2953, 2924, 2853, 1594, 1487, 1453, 1320, 1168, 1119, 1069, 802, 765, 756, 717, 693 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub><sup>+</sup> 716.9757; found 716.9767.

**3-(3,5-dimethylphenyl)-2'-iodo-2-(2-iodoethyl)-3'-phenyl-1,1'-spirobi[indene]** (**2n**). A yellow oil. 103 mg, 76% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.42 (s, 6H), 2.54-2.63 (m, 1H), 2.63-2.79 (s, 2H), 2.80-2.94 (m, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 7.06-7.15 (m, 5H), 7.22-7.29 (m, 3H), 7.30-7.35 (m, 1H), 7.44-7.49 (m, 1H), 7.52-7.57 (m, 2H), 7.59-7.64 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 21.4, 32.1, 75.7, 105.2, 120.5, 120.6, 122.2, 123.2, 126.2, 126.29, 126.32, 127.7, 127.8, 128.5, 128.6, 128.0, 129.7, 134.3, 134.8, 138.3, 142.7, 143.7, 144.7, 145.3, 145.8, 146.5, 151.7. IR (neat) 3063, 3018, 2920, 2851, 1599, 1452, 1296, 1170, 1020, 855, 754, 742, 715, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>33</sub>H<sub>27</sub>I<sub>2</sub><sup>+</sup> 677.0197; found 677.0192.

**2-iodo-2'-(2-iodoethyl)-3'-(4-isopropylphenyl)-3-phenyl-1,1'-spirobi[indene]** (**2o**). A white solid. 129 mg, 93% yield. m.p. 125-127 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.34 (d, J = 6.8 Hz, 6H), 2.57-2.64 (m, 1H), 2.65-2.77 (m, 2H), 2.84-2.91 (m, 1H), 2.96-3.04 (m, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 7.07-7.17 (m 2H), 7.22-7.30 (m, 3H), 7.32 (d, J = 7.2 Hz, 1H), 7.35-7.41 (m, 2H), 7.43-7.51 (m, 3H), 7.52-7.57 (m, 2H), 7.59-7.64 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 24.0, 32.1, 34.0, 75.7, 105.3, 120.5, 120.7, 122.2, 123.3, 126.2, 126.3, 126.9, 127.7, 127.8, 128.5, 128.60, 128.62, 129.0, 131.7, 134.8, 142.7, 143.7, 144.7, 145.4, 145.5, 146.5, 148.7, 151.7. IR (neat) 3060, 3010, 2955, 2916, 2843, 1490, 1451, 1440, 1262, 1171, 1071, 1020, 834, 752, 740, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>34</sub>H<sub>29</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for

#### $C_{34}H_{29}I_2^+$ 691.0353; found 691.0355.

**2-iodo-2'-(2-iodoethyl)-3'-(4-methoxyphenyl)-3-phenyl-1,1'-spirobi[indene]** (**2p**). A white solid. 77 mg, 5% yield. m.p. 208-209 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.54-2.64 (m, 1H), 2.65-2.78 (m, 2H), 2.80-2.90 (m, 1H), 3.90 (s, 3H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 7.04-7.17 (m, 4H), 7.23-7.34 (m, 4H), 7.44-7.51 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.59-7.64 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 32.0, 55.3, 75.7, 105.3, 114.3, 120.5, 122.3, 123.3, 126.2, 126.3, 126.7, 127.7, 127.9, 128.5, 128.6, 129.0, 129.9, 134.8, 142.6, 143.7, 144.7, 145.3, 146.6, 151.7, 159.4. IR (neat) 3063, 3039, 2987, 2942, 2911, 2851, 2827, 1507, 1451, 1441, 1245, 1174, 1038, 836, 772, 764, 756, 744, 729, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub><sup>+</sup> 678.9989; found 678.9983.

**2-iodo-2'-(2-iodoethyl)-3-phenyl-3'-(4-(trifluoromethyl)phenyl)-1,1'-spirobi[indene]** (**2q**). A white solid. 113 mg, 79% yield. m.p. 205-207 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.56-2.81 (m, 4H), 6.84 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 7.09-7.20 (m, 3H), 7.25-7.36 (m, 3H), 7.45-7.51 (m, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.59-7.63 (m, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.7, 31.8, 75.8, 104.5, 120.3, 120.6, 122.5, 123.4, 124.0 (q, J = 270.4 Hz), 125.9 (q, J = 3.9 Hz), 126.4, 126.8, 128.0, 128.1, 128.66, 128.68, 129.0, 129.3, 130.2 (q, J = 32.1 Hz), 134.7, 138.3, 143.7, 144.2, 144.4, 144.6, 144.8, 145.7, 152.0. <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -62.53 (s). IR (neat) 3070, 3036, 2919, 2845, 1647, 1626, 1445, 1398, 1322, 1165, 1124, 1065, 845, 773, 765, 716, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>22</sub>F<sub>3</sub>I<sub>2</sub><sup>+</sup> 716.9757; found 716.9768.

**3-(4-(benzyloxy)phenyl)-2'-iodo-2-(2-iodoethyl)-3'-phenyl-1,1'-spirobi[indene]** (**2r**). A white solid. 127 mg, 84% yield. m.p. 148-150 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.54-2.64 (m, 1H), 2.66-2.78 (m, 2H), 2.80-2.89 (m, 1H), 5.14 (s, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.06-7.15 (m, 4H), 7.20-7.29 (m, 3H), 7.29-7.37 (m, 2H), 7.38-7.56 (m, 9H), 7.59-7.63 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.3, 32.0, 70.1, 75.7, 105.2, 115.2, 120.46, 120.48, 122.2, 123.2, 126.2, 126.3, 126.9, 127.6, 127.7, 127.8, 128.0, 128.5, 128.60, 128.61, 129.0, 129.9, 134.8, 136.8, 142.6, 143.7, 144.6, 145.1, 145.3, 146.5, 151.6, 158.6. IR (neat) 3068, 3031, 2953, 2924, 2898, 2848, 1508, 1452, 1245, 1173, 1040, 837, 765, 739, 711, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>38</sub>H<sub>29</sub>OI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>29</sub>OI<sub>2</sub><sup>+</sup> 755.0302; found 755.0300.

**3-(4-chlorophenyl)-2'-iodo-2-(2-iodoethyl)-3'-phenyl-1,1'-spirobi[indene]** (2s). A white solid. 134 mg, 98% yield. m.p. 211-213 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.53-2.63 (m, 1H), 2.64-2.75 (m, 2H), 2.75-2.83 (m, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.08-7.13 (m, 1H), 7.14-7.22 (m, 2H), 7.24-7.30 (m, 2H), 7.30-7.35 (m, 1H), 7.45-7.51 (m, 5H), 7.51-7.57 (m, 2H), 7.58-7.63 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  2.9, 31.8, 75.7, 104.7, 120.3, 120.6, 122.4, 123.3, 126.3, 126.6, 127.9, 128.0, 128.60, 128.64, 129.0, 129.1, 130.1, 132.9, 134.0, 134.7, 143.6, 143.7, 144.5, 144.6, 144.9, 146.0, 151.9. IR (neat) 3060, 3034, 3018, 2958, 1487, 1450, 1348, 1084, 1012, 836, 786, 768, 749, 730, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{31}H_{22}CII_2]$  [M+H]<sup>+</sup> Calcd for  $C_{31}H_{22}CII_2^+$  682.9494; found 682.9495.

**3-(4-fluorophenyl)-2-iodo-2'-(2-iodoethyl)-6-methoxy-3'-phenyl-1,1'-spirobi[indene]** (2t). A white solid. 121 mg, 87% yield. m.p. 144-146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.56-2.65 (m, 1H), 2.68-2.88 (m, 3H), 3.70 (s, 3H), 6.58-6.61 (m, 1H), 6.77-6.85 (m, 2H), 7.10-7.31 (m, 6H), 7.40-7.62 (m, 7H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 31.8, 55.5, 75.3, 101.6, 109.9, 113.0, 115.6 (d, *J* = 21.5 Hz), 120.5, 120.9, 122.3, 126.4, 127.9, 128.1, 128.7, 128.8, 130.8 (d, *J* = 8.4 Hz), 130.9 (d, *J* = 3.8 Hz), 134.3, 137.5, 142.9, 143.9, 145.6, 146.2, 146.8, 150.2, 158.7, 162.5

(d, J = 246.7 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -112.37 (s). IR (neat) 3050, 3018, 2958, 2924, 2851, 2830, 1613, 1474, 1274, 1170, 1156, 1028, 840, 792, 714, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>24</sub>OFI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>24</sub>OFI<sub>2</sub><sup>+</sup> 696.9895; found 696.9894.

**2-iodo-2'-(2-iodoethyl)-6-methoxy-3,3'-diphenyl-1,1'-spirobi[indene]** (**2u**). A white solid. 117 mg, 86% yield. m.p. 144-146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.64-2.88 (m, 4H), 3.74 (s, 3H), 6.55-6.62 (m, 1H), 6.77-6.87(m, 2H), 7.12-7.19 (m, 1H), 7.22-7.32 (m, 3H), 7.43-7.63 (m, 10H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.5, 31.9, 55.5, 75.4, 101.2, 109.8, 112.9, 120.5, 121.1, 122.4, 126.4, 127.9, 128.0, 128.5, 128.6, 128.7, 128.8, 128.9, 134.4, 135.0, 137.8, 143.1, 144.1, 145.5, 146.8, 151.2, 158.7. IR (neat) 3057, 2953, 2921, 2850, 1644, 1608, 1474, 1462, 1277, 1169, 1094, 1027, 870, 816, 762, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>25</sub>OI<sub>2</sub><sup>+</sup> 678.9989; found 678.9988.

**3-(4-fluorophenyl)-2-iodo-2'-(2-iodoethyl)-3'-phenyl-1,1'-spirobi[indene]** (**2v**). A white solid. 130 mg, 97% yield. m.p. 201-203 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.53-2.62 (m, 1H), 2.65-2.75 (m, 2H), 2.77-2.86 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.08-7.17 (m, 2H), 7.21-7.32 (m, 6H), 7.42-7.48 (m, 1H), 7.50-7.56 (m, 4H), 7.57-7.63 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.0, 31.9, 75.7, 105.5, 115.7 (d, *J* = 21.5 Hz), 120.3, 120.6, 122.3, 123.3, 126.37, 126.43, 127.8, 128.0, 128.1, 128.7, 128.8, 130.7 (d, *J* = 3.9 Hz), 130.9 (d, *J* = 7.7 Hz), 134.4, 142.9, 143.5, 144.5, 145.1, 145.7, 146.4, 150.8, 162.7 (d, *J* = 246.7 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -112.36 (s). IR (neat) 3050, 3026, 2966, 2919, 2830, 1449, 1474, 1275, 1221, 1156, 1094, 840, 754, 742, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>22</sub>FI<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>22</sub>FI<sub>2</sub><sup>+</sup> 666.9789; found 666.9797.

**2-iodo-2'-(2-iodoethyl)-6-methyl-3'-phenyl-3-(p-tolyl)-1,1'-spirobi[indene]** (**2w**). A white solid. 122 mg, 90% yield. m.p. 193-195 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.26 (s, 3H), 2.45 (s, 3H), 2.57-2.72 (m, 2H), 2.72-2.86 (m, 2H), 6.80-6.85 (m, 2H), 7.03-7.07 (m, 1H), 7.12-7.17 (m, 1H), 7.19-7.36 (m, 5H), 7.41-7.57 (m, 7H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.5, 21.3, 21.5, 31.9, 75.4, 103.0, 120.2, 120.4, 122.4, 124.0, 126.3, 127.8, 128.0, 128.4, 128.76, 128.77, 128.82, 129.3, 131.9, 134.5, 136.2, 138.3, 142.2, 143.3, 144.1, 145.2, 145.4, 146.3, 151.5. IR (neat) 3076, 3055, 3021, 2932, 2911, 2856, 1505, 1466, 1440, 1301, 1172, 1002, 909, 821, 799, 742, 734, 699 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>33</sub>H<sub>27</sub>I<sub>2</sub>] [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>27</sub>I<sub>2</sub><sup>+</sup> 677.0197; found 677.0191.

**2-(2-iodoethyl)-3-(naphthalen-2-yl)-3'-phenyl-1,1'-spirobi[indene]** (**2x**). A yellow oil. 63 mg, 55% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.51-2.62 (m, 1H), 2.79-2.96 (m, 3H), 6.37 (s, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.07-7.12 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.20-7.30 (m, 2H), 7.32-7.38 (m, 1H), 7.39-7.45 (m, 1H), 7.48-7.57 (m, 4H), 7.62-7.68 (m, 2H), 7.70-7.76 (m, 2H), 7.88-7.95 (m, 2H), 7.97-8.04 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.5, 31.4, 70.6, 120.5, 121.1, 122.2, 122.6, 125.9, 126.26, 126.34, 126.4, 126.8, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.4, 128.8, 132.2, 132.9, 133.5, 134.4, 135.2, 143.7, 143.9, 144.3, 145.9, 146.0, 147.0. IR (neat) 3060, 3015, 1598, 1489, 1452, 1264, 1170, 1020, 857, 755, 740, 716, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>35</sub>H<sub>26</sub>I] [M+H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>26</sub>I<sup>+</sup> 573.1074; found 573.1070.

**5-(2'-iodo-2-(2-iodoethyl)-3'-phenyl-1,1'-spirobi[inden]-3-yl)benzo[b]thiophene** (2y). A white solid. 110 mg, 78% yield. m.p. 180-182 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.58-2.68 (m, 1H), 2.69-2.79 (m, 2H), 2.82-2.87 (m, 1H), 6.84 (d, J = 7.2 Hz, 1H), 7.02-7.07 (m, 1H), 7.10-7.18 (m, 2H), 7.23-7.31 (m, 3H), 7.34 (d, J = 7.6 Hz, 1H), 7.41-7.45 (m, 1H), 7.45-7.58 (m,

5H), 7.60-7.65 (m, 2H), 7.97-8.05 (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.2, 32.0, 75.8, 105.1, 120.5, 120.6, 122.3, 122.9, 123.3, 123.7, 124.0, 125.0, 126.3, 126.4, 127.3, 127.8, 127.9, 128.56, 128.64, 129.0, 130.5, 134.8, 139.4, 140.0, 143.2, 143.7, 144.7, 145.2, 145.6, 146.6, 151.8. IR (neat) 3070, 3050, 3021, 2961, 2921, 2840, 1600, 1451, 1257, 1174, 1047, 814, 752, 745, 712, 697, 673 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>33</sub>H<sub>23</sub>I<sub>2</sub>S] [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>23</sub>I<sub>2</sub>S<sup>+</sup> 704.9604; found 704.9600.

**2-(2-chloroethyl)-2'-iodo-3,3'-diphenyl-1,1'-spirobi[indene]** (**2z**). A white solid. 62 mg, 56% yield. m.p. 187-189 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.72-3.16 (m, 2H), 3.58-3.87 (m, 2H), 6.94-7.05 (m, 1H), 7.10-7.17 (m, 2H), 7.17-7.24 (m, 4H), 7.24-7.37 (m, 9H), 7.40-7.45 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  43.8, 45.0, 68.9, 104.1, 118.2, 124.8, 127.4, 127.58, 127.61, 127.7, 128.1, 128.3, 128.48, 128.53, 128.8, 128.9, 129.1, 132.7, 134.8, 137.7, 140.8, 141.1, 144.9, 145.9, 152.3. IR (neat) 3057, 3031, 2966, 2916, 2848, 1538, 1489, 1440, 1260, 1164, 1031, 1019, 798, 775, 761, 748, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>23</sub>ClI] [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>23</sub>ClI<sup>+</sup> 557.0527; found 557.0526.

**2-bromo-2'-(2-bromoethyl)-3,3'-diphenyl-1,1'-spirobi[indene]** (**2aa**). A white solid. 71 mg, 64% yield. m.p. 158-160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.82-2.92 (m, 2H), 3.48-3.66 (m, 2H), 7.04-7.08 (m, 1H), 7.14-7.23 (m, 6H), 7.26-7.36 (m, 9H), 7.48 (d, J = 7.6 Hz, 2H) <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  30.3, 42.0, 69.1, 121.5, 124.5, 124.6, 127.3, 127.6, 127.7, 127.9, 128.4, 128.5, 128.6, 129.4, 129.9, 133.8, 135.6, 139.2, 140.5, 140.6, 140.8, 141.4, 150.7. IR (neat) 3086, 3057, 3031, 2963, 2245, 1597, 1490, 1465, 1441, 1411, 1270, 1214, 1151, 1033, 905, 750, 721, 696 cm<sup>-1</sup>. HRMS (EI-TOF) m/z: [C<sub>31</sub>H<sub>22</sub>Br<sub>3</sub>] [M+Br]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>22</sub>Br<sub>3</sub><sup>+</sup> 630.9266; found 630.9272.

General procedure for the preparation of compound 3a: To a stirred solution of 3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1a (82 mg, 1.0 equiv) in CDCl<sub>3</sub> (2 mL, 0.1mol/L) was added I<sub>2</sub> (101 mg, 2 equiv). The resulting mixture was stirred at -10 °C for 4 h. After quenching the remaining I<sub>2</sub> by Na<sub>2</sub>SO<sub>3</sub> solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 20 / 1) to afford the corresponding product 3a in 88% yield (124 mg).

**3-(2-(2,4-diiodo-1-phenylbut-1-en-1-yl)phenyl)-1,1-diphenylprop-2-yn-1-ol (3a)**. A yellow oil. 117 mg, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.84-2.90 (m, 3H), 3.18-3.24 (m, 2H), 7.05-7.09 (m, 0.4H), 7.13-7.18 (m, 0.6H), 7.20-7.30 (m, 11.04H), 7.32-7.38 (m, 4.67H), 7.51-7.55 (m, 1.22H), 7.60-7.67 (m, 4.43H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.8, 5.4, 44.3, 44.8, 74.8, 74.9, 85.9, 86.1, 94.4, 95.0, 107.7, 108.8, 120.5, 120.8, 126.7, 127.45, 127.49, 127.6, 127.8, 128.1, 128.25, 128.27, 128.30, 128.40, 128.43, 128.5, 128.9, 129.0, 129.1, 132.8, 138.6, 142.3, 144.5, 144.6, 144.8, 145.1, 148.1, 149.0, 149.2. IR (neat) 3565, 3058, 3021, 2958, 1489, 1448, 1248, 1169, 1137, 1029, 986, 888, 732, 697 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>24</sub>OI] [M-I]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>24</sub>OI<sup>+</sup> 539.0866; found 539.0861.

**3-(2-(2,4-diiodo-1-(4-isopropylphenyl)but-1-en-1-yl)phenyl)-1,1-diphenylprop-2-yn-1-ol (30)**. A yellow oil. 89 mg, 63% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  1.21 (d, *J* = 6.8 Hz, 6H), 2.86 (m, 4H), 3.21 (t, *J* = 7.6 Hz, 2H), 7.07 (m, *J* = 7.6 Hz, 2H), 7.17-7.26 (m, 4H), 7.26-7.31 (m, 3H), 7.31-7.39 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.63 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  5.4, 23.8, 33.7, 45.0, 74.9, 86.2, 94.9, 107.1, 120.9, 126.0, 126.27, 126.30, 127.4, 127.8,

128.38, 128.44, 128.9, 129.1, 132.8, 142.2, 142.6, 144.5, 144.6, 148.1, 148.2. IR (neat) 3421, 3081, 3060, 3015, 2961, 2919, 2869, 1492, 1476, 1137, 1029, 805, 753, 696 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{34}H_{29}I_2]$  [M-OH]<sup>+</sup> Calcd for  $C_{34}H_{29}I_2^+$  691.0345; found 691.0349.

**3-(2-(2,4-diiodo-1-(thiophen-3-yl)but-1-en-1-yl)phenyl)-1,1-diphenylprop-2-yn-1-ol (3ab)**. A white solid. 65 mg, 49% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.80 (s, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 7.03-7.06 (m, 1H), 7.14-7.19 (m, 2H), 7.22-7.31 (m, 4H), 7.31-7.39 (m, 5H), 7.51-7.62 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.5, 45.7, 74.8, 85.8, 95.2, 106.4, 121.0, 124.5, 124.8, 126.2, 127.7, 127.8, 128.1, 128.4, 128.5, 128.9, 129.0, 132.9, 142.7, 143.5, 143.9, 144.5, 144.6. IR (neat) 3544, 3112, 3063, 2955, 2921, 2843, 1647, 1592, 1446, 1434, 1154, 1039, 992, 882, 791, 746, 695 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>29</sub>H<sub>21</sub>I<sub>2</sub>S] [M-OH]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>21</sub>I<sub>2</sub>S<sup>+</sup> 654.9448; found 654.9450.

General procedure for the preparation of compound 4: To a stirred solution of 2a (160 mg, 1.0 equiv) and phenylacetylene (43 mg, 1.1 equiv) in i-Pr<sub>2</sub>NH (10 mL, 0.025 mol/L) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mg, 2 mol%) and CuI (3 mg, 2 mol%) under argon atmosphere. The resulted mixture was stirred at 80 °C in oild bath for 8 h. After the separation of solid by filtration and the removal of solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 100 / 1) to afford the corresponding compound 4 as a white solid in 88% yield (135 mg).

**2-(2-iodoethyl)-3,3'-diphenyl-2'-(phenylethynyl)-1,1'-spirobi[indene]** (**4**). A white solid. 135 mg, 88% yield. m.p. 142-144 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.60-2.70 (m, 1H), 2.72-2.86 (m, 2H), 2.91-3.00 (m, 1H), 6.88 (d, J = 7.2 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 7.07-7.13 (m, 3H), 7.15-7.28 (m, 6H), 7.33-7.39 (m, 1H), 7.42-7.50 (m, 2H), 7.51-7.59 (m, 6H), 7.64 (d, J = 7.6 Hz, 1H), 7.89-7.93 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.4, 32.0, 73.4, 84.6, 97.7, 120.2, 121.7, 122.1, 123.1, 126.2, 127.1, 127.2, 127.5, 127.9, 128.0, 128.2, 128.5, 128.6, 128.77, 128.80, 128.83, 131.4, 134.0, 134.7, 143.4, 144.01, 144.04, 144.68, 144.70, 146.2, 148.9. IR (neat) 3060, 3013, 2961, 2934, 2911, 2191, 1597, 1485, 1462, 1441, 1348, 1171, 1068, 1029, 932, 776, 749, 737, 683 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>39</sub>H<sub>28</sub>I] [M+H]<sup>+</sup> Calcd for C<sub>39</sub>H<sub>28</sub>I<sup>+</sup> 623.1230; found 623.1225.

General procedure for the preparation of compound 5: To a stirred solution of 4 (124 mg, 1.0 equiv) was added t-BuOK (45 mg, 1.5 equiv) in t-BuOH (3.0 mL, 0.066 mol/L) under argon atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the removal of solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 100 / 1) to afford the corresponding compound 5 as a white solid in 92% yield (91 mg).

**3,3'-diphenyl-2-(phenylethynyl)-2'-vinyl-1,1'-spirobi[indene]** (**5**). A white solid. 91 mg, 92% yield. m.p. 162-164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  4.63 (d, J = 18.0 Hz, 1H), 4.84 (d, J = 9.6 Hz, 1H), 6.54-6.63 (m, 1H), 6.83 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 7.07-7.12 (m, 3H), 7.15-7.21 (m, 3H), 7.23-7.25 (m, 1H), 7.32-7.38 (m, 2H), 7.42-7.62 (m, 8H), 7.67 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  71.4, 84.6, 97.4, 115.9, 120.7, 121.6, 121.7, 122.8, 123.4, 126.7, 127.3, 127.4, 127.5, 127.9, 128.0, 128.1, 128.4, 128.5, 128.6, 128.8, 128.9, 129.7, 129.9, 131.5, 134.3, 134.6, 140.2, 143.5, 145.3, 145.67, 145.74, 147.0, 147.5. IR (neat) 2990, 2903, 2160, 1496, 1444, 1294, 1254, 1075, 1066, 1025, 898, 774,

748, 734, 696, 660 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z:  $[C_{39}H_{27}]$  [M+H]<sup>+</sup> Calcd for  $C_{39}H_{27}^+$  495.2107; found 495.2108.

General procedure for the preparation of compound 6: To a stirred solution of 2a (200 mg, 1.0 equiv.) and 4-MeOPhB(OH)<sub>2</sub> (68 mg, 1.5 equiv.) in a mixing solvent of toluene : EtOH : H<sub>2</sub>O = 2 : 2 : 1 (5.0 mL, 0.064 mol/L) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 2 mol%) and Na<sub>2</sub>CO<sub>3</sub> (64 mg, 2 equiv.) under argon atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the removal of solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 100 / 1) to afford the corresponding compound 6 as a yellow oil in 57% yield (110 mg).

**2-(2-iodoethyl)-2'-(4-methoxyphenyl)-3,3'-diphenyl-1,1'-spirobi[indene]** (6). A yellow oil. 110 mg, 57% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.52-2.64 (m, 4H), 3.65 (s, 3H), 6.49 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 7.05-7.14 (m, 2H), 7.23-7.29 (m, 3H), 7.33-7.51 (m, 11H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  3.1, 32.4, 55.0, 73.3, 113.2, 120.6, 120.8, 121.9, 122.1, 126.0, 126.3, 127.2, 127.3, 127.5, 127.6, 127.9, 128.6, 128.8, 128.9, 129.5, 134.7, 135.7, 142.3, 142.7, 143.9, 145.0, 145.6, 145.7, 146.0, 146.1, 158.5. IR (neat) 3063, 3012, 2953, 2928, 2897, 2832, 1605, 1509, 1490, 1459, 1441, 1290, 1248, 1176, 1030, 836, 773, 735, 699 cm<sup>-1</sup>. HRMS (MALDI-TOF) m/z: [C<sub>38</sub>H<sub>29</sub>OI] [M]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>29</sub>OI<sup>+</sup> 628.1258; found 628.1278.

General procedure for the preparation of compound 7: To a stirred solution of 6 (100 mg, 1.0 equiv) was added t-BuOK (27 mg, 1.5 equiv) in t-BuOH (3.0 mL, 0.053 mol/L) under argon atmosphere. The resulted mixture was stirred at 80 °C in oil bath for 8 h. After the removal of solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 100 / 1) to afford the corresponding compound 7 as a white solid in 98% yield (78 mg).

**2-(4-methoxyphenyl)-3,3'-diphenyl-2'-vinyl-1,1'-spirobi[indene]** (7). A white solid. 78 mg, 98% yield. m.p. 141-143 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  3.63 (s, 3H), 4.86 (dd,  $J_I$  = 1.2 Hz,  $J_2$  = 4.8 Hz, 1H), 4.90 (dd,  $J_I$  = 1.6 Hz,  $J_2$  = 10.8 Hz, 1H), 6.47-6.56 (m, 3H), 6.69-6.73 (m, 2H), 6.86 (d, J = 7.2 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.05-7.12 (m, 2H), 7.18-7.23 (m, 1H), 7.24-7.30 (m, 2H), 7.31-7.36 (m, 1H), 7.38-7.43 (m, 4H), 7.45-7.52 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  54.9, 71.4, 112.9, 116.3, 120.9, 121.0, 121.5, 121.6, 126.1, 126.7, 127.1, 127.2, 127.3, 127.4, 127.9, 128.5, 128.6, 129.3, 129.5, 129.8, 134.5, 135.7, 141.1, 141.3, 145.2, 145.4, 145.9, 146.9, 147.3, 158.4. IR (neat) 3060, 3021, 2950, 2928, 2905, 2835, 1606, 1509, 1490, 1454, 1442, 1291, 1247, 1176, 1030, 906, 837, 773, 733, 698 cm<sup>-1</sup>. HRMS (ESI-TOF) m/z: [C<sub>38</sub>H<sub>29</sub>O] [M+H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>29</sub>O<sup>+</sup> 501.2212; found 501.2212.

General procedure for the preparation of compound 8a: To a stirred solution of 3-(2-(cyclopropylidene(phenyl)methyl)phenyl)-1,1-diphenylprop-2-yn-1-ol 1a (82 mg, 1.0 equiv) in DCE (2 mL, 0.1 mol/L) was added 45% HI (113 mg, 2 equiv). The resulting mixture was stirred at 80 °C for 2 h. After quenching the remaining I<sub>2</sub> by Na<sub>2</sub>SO<sub>3</sub> solution and removing solvent under reduced pressure, the residue was purified by a column chromatography on silica gel (petroleum ether / ethyl acetate = 200 / 1) to afford the corresponding products 8a as a white solid in 60% (63 mg).

**2-(2-iodoethyl)-3,3'-diphenyl-1,1'-spirobi[indene] (8a).** A white solid. 63 mg, 60% yield. m.p. 151-153 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm H}$  2.47-2.56 (m, 1H), 2.74-2.94 (m, 3H), 6.32 (s, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 7.05-7.16 (m, 2H), 7.20-7.25 (m, 2H), 7.30-7.36 (m, 1H), 7.39-7.44 (m, 2H), 7.47-7.53 (m, 6H), 7.64 (d, J = 7.6 Hz, 1H), 7.69-7.73 (m, 2H) <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta_{\rm C}$  4.3, 31.4, 70.5, 120.4, 121.1, 122.1, 122.6, 125.9, 126.3, 127.3, 127.5, 127.6, 127.8, 128.1, 128.76, 128.82, 134.4, 134.6, 135.2, 143.7, 143.8, 143.9, 144.2, 145.9, 145.9, 146.9. IR (neat) 3060, 3026, 2921, 2845, 1595, 1491, 1452, 1443, 1345, 1264, 1167, 1072, 910, 833, 734, 698 cm<sup>-1</sup>. HRMS (DART-FTICR) m/z: [C<sub>31</sub>H<sub>24</sub>I] [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>24</sub>I<sup>+</sup> 523.0917; found 523.0919.

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**Supporting Information Available:** Reaction optimization, NMR spectra, general Scheme for preparation of compound **1**, another possible reaction mechanism, absorption spectra, and CIF files for compounds for **1a**, **2a** and **3ab** are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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