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Highly efficient synthesis of functionalized dihydronaphthalenes, tetrahydronaphthalenes, and tetrahydroisoquinolines by iron-catalyzed intramolecular Friedel–Crafts reaction of aryl-containing propargylic alcohols

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ABSTRACT

An efficient, convenient, and one-pot procedure for the synthesis of a series of new dihydro- and tetrahydronaphthalenes as well as tetrahydroisoquinolines has been established through Lewis acid-catalyzed intramolecular Friedel–Crafts reaction of aryl-substituted propargylic alcohols.

1. Introduction

The presence of hydrogenated naphthalene and isoquinoline ring skeletons in a number of naturally occurring compounds and synthetic materials, coupled with their role in the fine-tuning of the biological and/or physical properties of the compounds for final application, illustrates the need for the development of new functionalized dihydronaphthalene, tetrahydronaphthalene, and tetrahydroisoquinoline-based structures and new methods for their construction.[1,2] The intramolecular Friedel–Crafts (IFC) reaction[3] is an attractive method for the formation of these types of compounds. However, one of the challenging problems in such process is the introduction of appropriate substituents during cyclization because the presence of functional substituents often prevents the desired IFC reaction in some cases.[4–9]

In conjunction with our previous research toward the development of new methods for the synthesis of biologically active hydrogenated naphthalenes, spiroindenes, and isoquinolines,[10] we become interested in extending the IFC reaction to other propargylic alcohol substrates, especially, we want to investigate how the donating substituent at the benzyl position affects the IFC reaction. Herein, we wish to report the results. The system allows the desired IFC reaction of a wide range of applicable substrates under mild conditions.

2. Results and discussion

We have previously reported that aryl-substituted propargylic alcohols can serve as new precursors for synthesis of functionalized spirocyclics, di- and tetrahydronaphthalenes via an intramolecular Friedel–Crafts reaction.[10b] However, the method has been limited to synthesize di- and tetrahydronaphthalenes containing the electron-withdrawing substituents (ester group) on the non-aromatic ring. To understand the influence of the substituents better and to develop the method further, in this work we firstly made an extension of this reaction to synthesize di- and tetrahydronaphthalenes bearing the electron-donating substituents such as $-CH_2OCH_3$ and $-CH_2OCH_2CH_3$. The starting materials (**1**) were synthesized by the following five-step reactions:[11] reaction of benzyl halides with sodium diethyl malonate in ethanol gave compounds **I**, and treatment of **I** with sodium hydride in THF followed by reacting with propargylic bromide led to the formation of compounds **II**; reduction of **II** with $LiAlH_4$ yielded **III**; the compounds **IV** were obtained from reaction of **III** with methyl iodine or ethyl iodine in the presence of excess KOH; treatment of **IV** with

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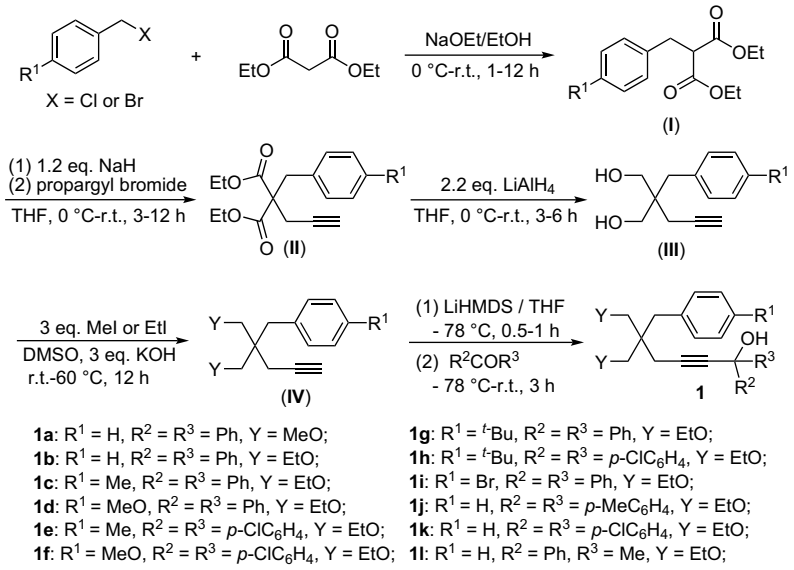
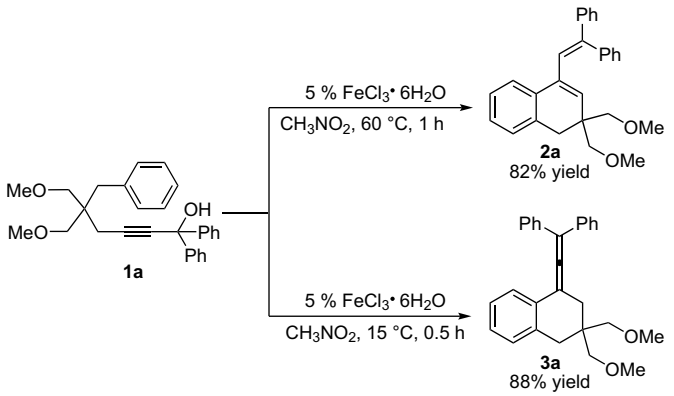


1a: R^1 = H, R^2 = R^3 = Ph, Y = MeO;
1b: R^1 = H, R^2 = R^3 = Ph, Y = EtO;
1c: R^1 = Me, R^2 = R^3 = Ph, Y = EtO;
1d: R^1 = MeO, R^2 = R^3 = Ph, Y = EtO;
1e: R^1 = Me, R^2 = R^3 = *p*-ClC_6H_4, Y = EtO;
1f: R^1 = MeO, R^2 = R^3 = *p*-ClC_6H_4, Y = EtO;
1g: R^1 = ^{t}Bu, R^2 = R^3 = Ph, Y = EtO;
1h: R^1 = ^{t}Bu, R^2 = R^3 = *p*-ClC_6H_4, Y = EtO;
1i: R^1 = Br, R^2 = R^3 = Ph, Y = EtO;
1j: R^1 = H, R^2 = R^3 = *p*-MeC_6H_4, Y = EtO;
1k: R^1 = H, R^2 = R^3 = *p*-ClC_6H_4, Y = EtO;
1l: R^1 = H, R^2 = Ph, R^3 = Me, Y = EtO;

Scheme 1. Synthesis of carbon-centered propargylic alcohols **1a**–**l**.

LiHMDS and sequent reaction with ketones gave the propargylic alcohols **1** (Scheme 1).

With the starting materials in hand, we initially studied the cyclization reaction of propargylic alcohol **1a**. Treatment of a nitromethane solution of **1a** with $FeCl_3 \cdot 6H_2O$ (5 mol %) at 80 °C for 15 h yielded dihydronaphthalene **2a** in 62% yield along with some byproducts. Reducing the reaction temperature to 60 °C cleanly gave **2a** in 82% isolated yield after 1 h. However, when the reaction temperature was further lowered to 10–15 °C, tetrahydronaphthalene product **3a** rather than **2a** was selectively obtained in 88% yield (Scheme 2). In contrast to the reaction of the corresponding propargylic alcohols containing ester groups that give spirocycle compounds at 80 °C, attempts to transform **1a** or **2a** into a spirocyclization product were unsuccessful under the similar conditions. These results indicate that the nature of substituents located at the dihydronaphthalene ring might play an important role in controlling the spirocyclization reaction.



Scheme 2.

With the strategy of controlling selective transformation of aryl-substituted propargylic alcohols in hand, we firstly explored the use of the reaction in synthesis of dihydronaphthalene derivatives. A variety of aryl-substituted propargylic alcohol substrates were examined. As shown in Table 1, the results demonstrated good compatibility with various functional groups, including alkyl, alkoxy, and halide. For instance, the introduction of the electron-donating groups such as methyl and methoxy at the *para*-position of the nucleophilic benzene ring had only a slight influence on the reactivity compared with **1a** (Table 1, entries 3 and 4). Notably, the sterically demanding *tert*-butylphenyl ring also displayed a high reactivity (Table 1, entries 7 and 8). Even with the presence of an electron-withdrawing bromide group on the aromatic ring, the cyclization reaction process was also smooth to give dihydronaphthalene **2i** in moderate yield (Table 1, entry 9).

Then, the present method was applied to the synthesis of tetrahydronaphthalene derivatives under the optimized reaction conditions. Table 2 illustrates the generality of this reaction. Treatment of a variety of aryl-substituted propargylic alcohols with 5 mol % $FeCl_3 \cdot 6H_2O$ in CH_3NO_2 at 10–15 °C afforded the corresponding tetrahydronaphthalenes products in moderate to good yields, which depends on the nucleophilicity of the aryl nucleus involved and the nature of substituents at the propargylic position. It was found that the substrate containing an electron-withdrawing chloride at the *para*-position of the benzene rings located at the propargylic position gave the corresponding tetrahydronaphthalene in a higher yield compared with that bearing an electron-donating methyl in the same position (Table 2, entries 7 and 8). Furthermore, substitution of one phenyl at the propargylic position by methyl led to the decrease of yield (Table 2, entry 9). The results described above have demonstrated that the nature of substituents at the propargylic position plays an important role in determining the behavior of a propargylic cation intermediate. The conjugative effect of aryl groups is likely to assist the isomerization of propargyl to allenyl. On the other hand, the strong electron-donating ability of aryl groups should offer a good stabilizing environment for propargylium and/or allenylium, and thus may impair the Friedel–Crafts reaction.

Examples of the direct construction of tetrahydroisoquinoline frameworks by the IFC reaction are very scarce.[5b,12] With the aim of establishing whether the nature of *N*-substituents would affect the cyclization reaction of benzylamino-substituted propargylic alcohols as observed above in synthesis of tetrahydronaphthalenes,[10a] we decided to extend our study on the reaction of benzylamino-substituted propargylic alcohols that were synthesized by N-sulfonylation of benzylamine followed by N-propargylation, deprotonation, and sequent addition with ketones (Scheme 3).

Table 1
Synthesis of dihydronaphthalenes[a]

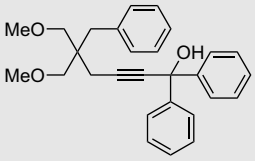
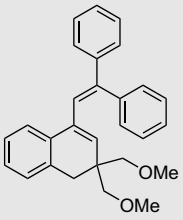
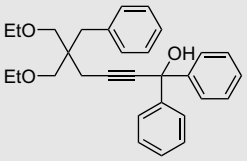
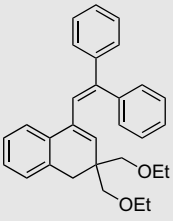
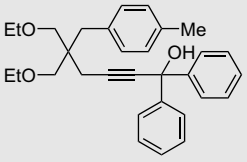
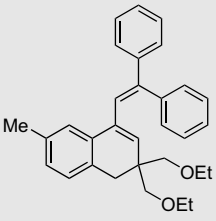
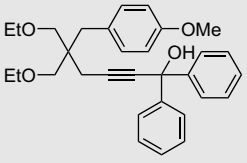
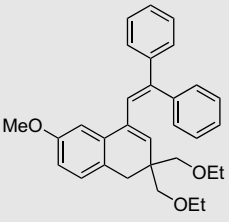
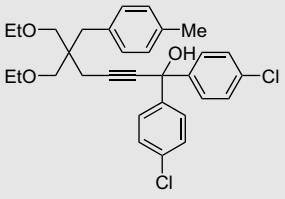
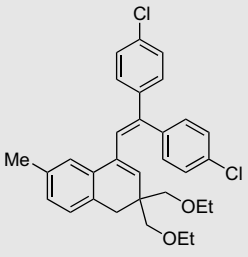
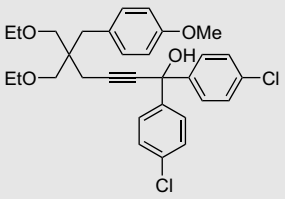
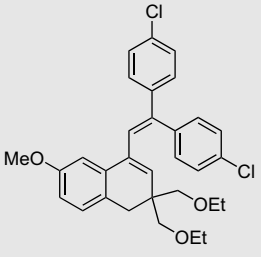
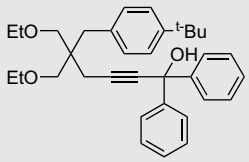
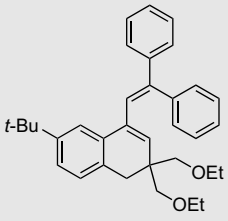
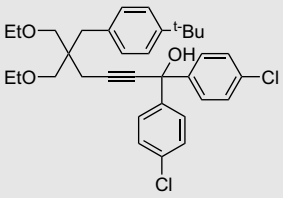
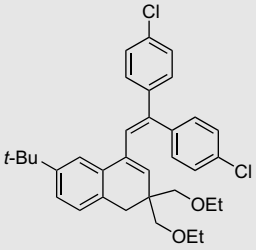
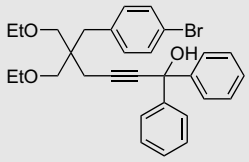
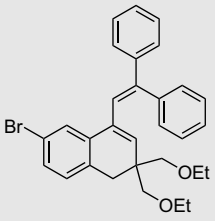
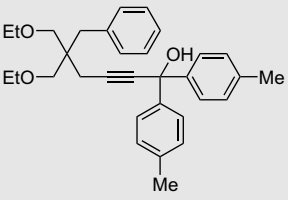
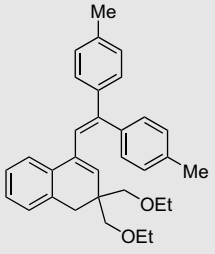
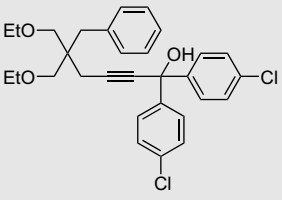
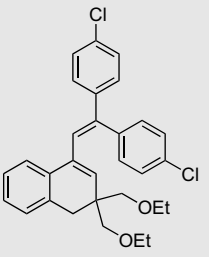
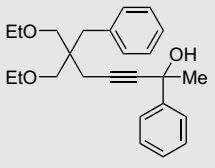
Entry	Substrate	Product	Yield[b] (%)
1	 **1a**	 **2a**	82 62[c] 78[d]
2	 **1b**	 **2b**	81
3	 **1c**	 **2c**	87
4	 **1d**	 **2d**	80
5[e]	 **1e**	 **2e**	81
6[e]	 **1f**	 **2f**	76

Table 1 (*continued*)

Entry	Substrate	Product	Yield[b] (%)
7	 **1g**	 **2g**	81
8[e]	 **1h**	 **2h**	89
9[f]	 **1i**	 **2i**	66
10	 **1j**	 **2j**	72
11[e]	 **1k**	 **2k**	85
12[g]	 **1l**		

[a] General reaction conditions: 0.2–0.3 mmol substrate, 5 mol% of $FeCl_3 \cdot 6H_2O$ in 3 mL of CH_3NO_2 at 60 °C for 1–3 h.
[b] Isolated yield.
[c] The reaction was carried out at 80 °C for 15 h.
[d] Using $Yb(OTf)_3$ as a catalyst and the reaction was carried out at 80 °C for 3 h.
[e] 1 mL of CH_2Cl_2 was added to the reaction mixture in order to increase the solubility.
[f] The reaction time was 24 h.
[g] The reaction gave a complex mixture.

Table 2
Synthesis of tetrahydronaphthalenes[a]

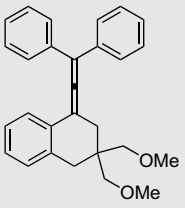
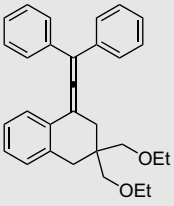
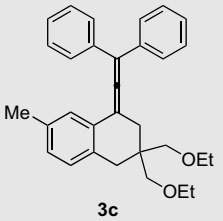
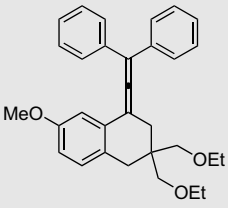
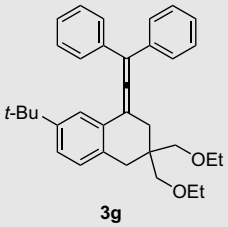
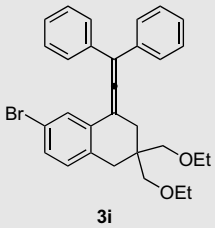
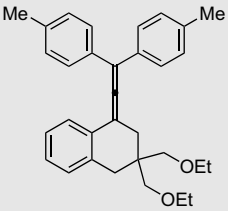
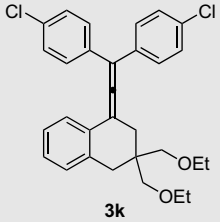
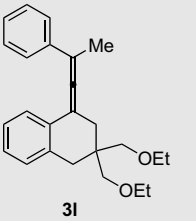
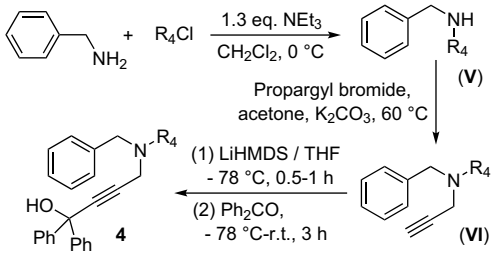
Entry	Substrate	Product	Yield[b] (%)
1	**1a**	 **3a**	88 92[c]
2	**1b**	 **3b**	90
3	**1c**	 **3c**	89
4	**1d**	 **3d**	85
5	**1g**	 **3g**	83
6	**1i**	 **3i**	38
7	**1j**	 **3j**	61

Table 2 (*continued*)

Entry	Substrate	Product	Yield[b] (%)
8[d]	**1k**	 **3k**	82
9	**1l**	 **3l**	67

[a] General reaction conditions: 0.2–0.3 mmol substrate, 5 mol % of $FeCl_3 \cdot 6H_2O$ in 3 mL of CH_3NO_2 at 10–15 °C for 0.2–3 h.
[b] Isolated yield.
[c] Using $Yb(OTf)_3$ as a catalyst and the product along with about 5% product **2a**.
[d] 1 mL of CH_2Cl_2 was added to the reaction mixture in order to increase the solubility.



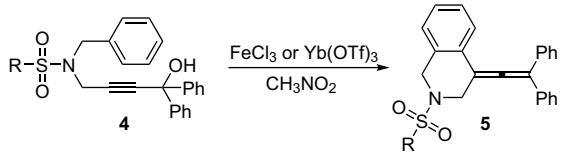
Scheme 3. Synthesis of nitrogen-centered propargylic alcohols.

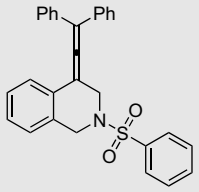
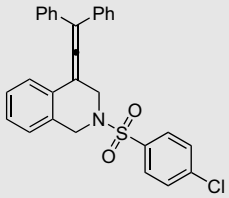
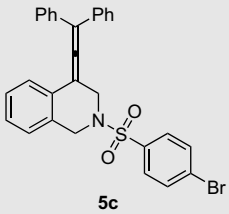
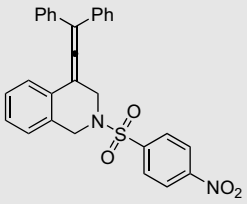
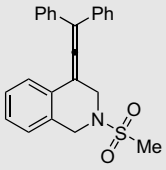
Table 3 summarizes some representative results of the $FeCl_3 \cdot 6H_2O$ (Table 3, Condition A) and $Yb(OTf)_3$ (Table 3, Condition B) catalyzed reaction of benzylamino-substituted propargylic alcohols having various *N*-substituents. All propargylic substrates (**4**) gave the corresponding substituted tetrahydroisoquinolines (**5**) in moderate to good yields in the presence of $FeCl_3 \cdot 6H_2O$ or $Yb(OTf)_3$ (Table 3, entries 1–5). The reaction was not significantly affected by the nature of sulfonyl substituents. The methylsulfonyl-substituted substrate gave the corresponding tetrahydroisoquinoline in a higher yield compared to the benzylamino-substituted propargylic alcohol containing phenylsulfonyl group (Table 3, entries 1 and 5). Notably, although $FeCl_3$ as a catalyst is cheaper, even more active than $Yb(OTf)_3$, its reaction conditions such as reaction time and moisture must be carefully controlled. For the large scales synthesis of this type of products, $Yb(OTf)_3$ was the better choice as a catalyst. The structure of **5d** was further confirmed by X-ray diffraction analysis, the crystal data clearly demonstrate the isomerization of the propargyl cation to allenyl cation in the intramolecular Friedel–Crafts reaction process (Fig. 1).[13]

3. Conclusion

In summary, experimentally convenient and cheap catalytic processes for regioselective synthesis of a series of new multi-substituted di- and tetrahydronaphthalenes as well as tetrahydroisoquinoline derivatives from the corresponding aryl-containing propargylic alcohols via an intramolecular Friedel–Crafts reaction have been established. Significant substrate flexibility and excellent control of the double bond

Table 3
Synthesis of tetrahydroisoquinolines[a]



Entry	Substrate R **4**	Product	Con. A, yield[b] (%)	Con. B, yield[b] (%)
1	C_6H_5 **4a**	 **5a**	75	79
2	*p*-ClC_6H_4 **4b**	 **5b**	80	82
3	*p*-BrC_6H_4 **4c**	 **5c**	77	83
4[c]	*p*-$NO_2C_6H_4$ **4d**	 **5d**	86	88
5	Me **4e**	 **5e**	84	90

[a] Condition A: 0.2 mmol substrate, 2 mL of CH_3NO_2, 20 mol % of $FeCl_3 \cdot 6H_2O$, rt, 0.2–3 h. Condition B: 0.2 mmol substrate, 2 mL of CH_3NO_2, 5 mol % of $Yb(OTf)_3$, 70 °C, 0.5–3 h.
[b] Isolated yield.
[c] The structure of product was further confirmed by X-ray diffraction analysis.

and substituent positions render this an attractive method for synthesis of versatile hydrogenated naphthalenes and isoquinolines.

4. Experimental

4.1. General

All reactions and manipulations were performed in air unless otherwise indicated. Melting points are uncorrected. NMR spectra were recorded at 400 or 500 MHz instrument using tetramethylsilane (TMS) as the internal standard. High resolution mass spectra (HRMS) were recorded using EI or ESI ionization sources. Infrared spectra were recorded on a FTIR spectrometer. X-ray structural analysis was carried out using graphite-monochromated Mo Kα (λ=0.71073 Å) radiation. Organic solvents used were dried by standard methods. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC or NMR experiments. Flash column chromatography was carried out using 300–400 mesh silica gel.

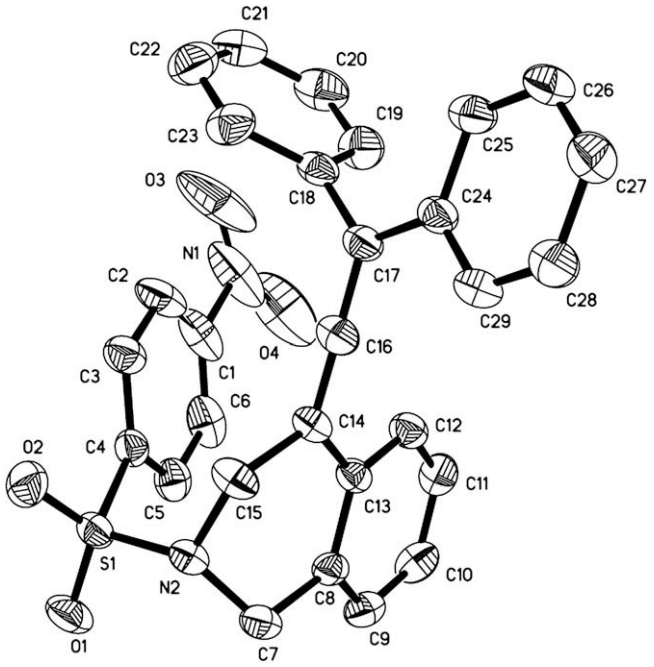


Figure 1. ORTEP diagram of the single-crystal X-ray structure of **5d**.

4.2. Typical procedure for synthesis of dihydronaphthalenes 2 from propargylic alcohols 1

To a stirred solution of propargylic alcohol **1a** (0.2 mmol) in nitromethane (3 mL) at 60 °C was added 5 mol % $FeCl_3 \cdot 6H_2O$, and then the reaction mixture was stirred at this temperature until the completion of the reaction (monitored by TLC or NMR). The crude mixture was purified by silica gel column chromatography to provide the dihydronaphthalene product **2a**.

4.3. Typical procedure for synthesis of tetrahydronaphthalenes 3 from propargylic alcohols 1

To a stirred solution of propargylic alcohol **1a** (0.2 mmol) in nitromethane (3 mL) at 15 °C was added 5 mol % $FeCl_3 \cdot 6H_2O$. TLC analysis showed that the reaction was completed in about 5–30 min. The crude mixture was directly purified by silica gel column chromatography to provide the desired product **3a**.

4.4. Characterization data

*4.4.1. 4-(2,2-Diphenylvinyl)-2,2-bis(methoxymethyl)-1,2-dihydronaphthalene (**2a**)*

Yellow liquid; IR: 3052, 2974, 2932, 2881, 2827, 1596, 1487, 1440, 1196, 1110, 768, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.73 (s, 2H), 2.89 (d, J=9.2 Hz, 2H), 3.02 (d, J=8.7 Hz, 2H), 3.2 (s, 6H), 5.38 (d, J=0.9 Hz, 1H), 6.72 (d, J=0.9 Hz, 1H), 7.13–7.19 (m, 8H), 7.23–7.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.2,

143.0, 140.7, 136.1, 134.5, 134.2, 132.2, 130.1, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.1, 126.6, 124.3, 74.4, 59.4, 41.1, 32.3; HRMS-ESI-TOF: calcd for $C_{28}H_{28}O_2Na$ ([M+Na]$^+$): 419.1987, found: 419.1961.

4.4.2. 4-(2,2-Diphenylvinyl)-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2b**)

Yellow liquid; IR: 3052, 3017, 2970, 2866, 1596, 1491, 1440, 1110, 1025, 768, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, J=6.9 Hz, 6H), 2.73 (s, 2H), 2.92 (d, J=9.2 Hz, 2H), 3.05 (d, J=9.2 Hz, 2H), 3.30–3.33 (m, 4H), 5.42 (s, 1H), 6.73 (d, J=0.9 Hz, 1H), 7.10–7.15 (m, 5H), 7.17–7.20 (m, 3H), 7.27–7.33 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.8, 142.8, 140.6, 135.5, 134.6, 134.2, 132.7, 130.0, 128.4, 128.1, 127.9, 127.8, 127.5, 127.3, 127.0, 126.8, 126.3, 124.0, 71.6, 66.6, 40.9, 32.3, 15.0; HRMS-EI-TOF: calcd for $C_{30}H_{32}O_2$ (M$^+$): 424.2402, found: 424.2401.

4.4.3. 4-(2,2-Diphenylvinyl)-2,2-bis(ethoxymethyl)-6-methyl-1,2-dihydronaphthalene (**2c**)

White solid; mp: 87–88 °C; IR: 3009, 2974, 2862, 1631, 1495, 1444, 1386, 1118, 765, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.06 (t, J=6.9 Hz, 6H), 2.28 (s, 3H), 2.68 (s, 2H), 2.91 (d, J=9.2 Hz, 2H), 3.05 (d, J=9.2 Hz, 2H), 3.19–3.32 (m, 4H), 5.42 (s, 1H), 6.73 (d, J=0.9 Hz, 1H), 6.94–7.01 (m, 2H), 7.12–7.20 (m, 6H), 7.26–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.6, 142.9, 140.6, 135.6, 135.5, 134.0, 132.8, 131.5, 130.0, 128.3, 128.1, 127.9, 127.8, 127.4, 127.2, 126.8, 124.8, 71.6, 66.5, 40.9, 31.8, 21.1, 15.0; HRMS-EI-TOF: calcd for $C_{31}H_{34}O_2$ (M$^+$): 438.2559, found: 438.2560.

4.4.4. 4-(2,2-Diphenylvinyl)-2,2-bis(ethoxymethyl)-6-methoxy-1,2-dihydronaphthalene (**2d**)

Yellow viscous liquid; IR: 3017, 2866, 1603, 1483, 1382, 1114, 765, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, J=6.9 Hz, 6H), 2.65 (s, 2H), 2.91 (d, J=9.2 Hz, 2H), 3.05 (d, J=9.2 Hz, 2H), 3.30–3.33 (m, 4H), 3.75 (s, 3H), 5.46 (s, 1H), 6.67–6.71 (m, 2H), 6.90 (d, J=2.7 Hz, 1H), 7.02 (d, J=8.2 Hz, 1H), 7.12–7.28 (m, 5H), 7.27–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.3, 144.9, 142.8, 140.5, 135.5, 135.2, 133.5, 130.0, 129.0, 128.1, 127.9, 127.8, 127.4, 126.9, 126.8, 126.6, 111.8, 110.5, 71.5, 66.6, 55.3, 41.2, 31.4, 15.0; HRMS-EI-TOF: calcd for $C_{31}H_{34}O_3$ (M$^+$): 454.2508, found: 454.2507.

4.4.5. 4-(2,2-Bis(4-chlorophenyl)vinyl)-2,2-bis(ethoxymethyl)-6-methyl-1,2-dihydronaphthalene (**2e**)

Yellow viscous liquid; IR: 3048, 2970, 2850, 1634, 1487, 1378, 1106, 1013, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.08 (t, J=7.3 Hz, 6H), 2.28 (s, 3H), 2.68 (s, 2H), 2.96 (d, J=9.2 Hz, 2H), 3.08 (d, J=9.2 Hz, 2H), 3.32 (q, J=7.3 Hz, 4H), 5.42 (s, 1H), 6.72 (s, 1H), 6.96–7.07 (m, 5H), 7.17–7.19 (m, 2H), 7.23–7.31 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3, 141.0, 138.6, 135.7, 135.2, 133.6, 133.4, 133.0, 131.5, 131.3, 129.6, 129.1, 128.6, 128.4, 128.2, 128.1, 124.6, 71.6, 66.6, 41.0, 32.0, 21.2, 15.0; HRMS-EI-TOF: calcd for $C_{31}H_{32}Cl_2O_2$ (M$^+$): 506.1779, found: 506.1782.

4.4.6. 4-(2,2-Bis(4-chlorophenyl)vinyl)-2,2-bis(ethoxymethyl)-6-methoxy-1,2-dihydronaphthalene (**2f**)

White solid; mp: 108–109 °C; IR: 3021, 2974, 2866, 1572, 1483, 1099, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.08 (t, J=7.3 Hz, 6H), 2.66 (s, 2H), 2.96 (d, J=9.2 Hz, 2H), 3.08 (d, J=9.2 Hz, 2H), 3.32 (q, J=7.3 Hz, 4H), 3.76 (s, 3H), 5.46 (s, 1H), 6.69 (s, 1H), 6.71 (d, J=2.3 Hz, 1H), 6.83 (d, J=2.3 Hz, 1H), 7.03–7.07 (m, 3H), 7.17–7.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.3, 142.7, 140.8, 138.5, 135.1, 134.8, 134.0, 133.6, 133.0, 131.3, 129.2, 129.1, 128.4, 128.2, 127.8, 126.6, 111.8, 110.6, 71.6, 66.6, 55.3, 41.2, 31.5, 15.0; HRMS-EI-TOF: calcd for $C_{31}H_{32}Cl_2O_3$ (M$^+$): 522.1729, found: 522.1729.

4.4.7. 6-tert-Butyl-4-(2,2-diphenylvinyl)-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2g**)

Colorless viscous liquid; IR: 3048, 2970, 2873, 1596, 1491, 1122, 1095, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, J=6.9 Hz, 6H), 1.27 (s, 9H), 2.68 (s, 2H), 2.95 (d, J=8.7 Hz, 2H), 3.08 (d, J=9.2 Hz, 2H), 3.27–3.33 (m, 4H), 5.49 (s, 1H), 6.78 (s, 1H), 7.02 (d, J=7.8 Hz, 1H), 7.13–7.16 (m, 6H), 7.27–7.38 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.0, 144.7, 143.0, 140.7, 135.9, 133.5, 132.8, 131.5, 130.0, 128.1, 128.0, 127.9, 127.7, 127.3, 127.0, 126.8, 124.0, 121.0, 71.6, 66.6, 41.0, 34.4, 32.0, 31.4, 15.0; HRMS-EI-TOF: calcd for $C_{34}H_{40}O_2$ (M$^+$): 480.3028, found: 480.3028.

4.4.8. 4-(2,2-Bis(4-chlorophenyl)vinyl)-6-tert-butyl-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2h**)

Yellow liquid; IR: 3060, 2970, 2866, 1638, 1491, 1382, 1102, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (t, J=7.3 Hz, 6H), 1.27 (s, 9H), 2.68 (s, 2H), 3.00 (d, J=9.2 Hz, 2H), 3.10 (d, J=9.2 Hz, 2H), 3.32–3.35 (m, 4H), 5.48 (s, 1H), 6.75 (s, 1H), 7.03–7.08 (m, 3H), 7.15–7.18 (m, 3H), 7.22–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.1, 142.1, 141.0, 138.7, 135.5, 133.6, 133.3, 133.1, 133.0, 131.5, 131.3, 129.3, 128.5, 128.2, 128.1, 124.3, 120.8, 71.7, 66.6, 41.0, 34.4, 32.1, 31.4, 15.0; HRMS-EI-TOF: calcd for $C_{34}H_{38}Cl_2O_2$ (M$^+$): 548.2249, found: 548.2252.

4.4.9. 6-Bromo-4-(2,2-diphenylvinyl)-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2i**)

Yellow viscous liquid; IR: 3075, 2970, 2862, 1642, 1386, 1118, 761, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, J=7.3 Hz, 6H), 2.66 (s, 2H), 2.91 (d, J=9.2 Hz, 2H), 3.01 (d, J=9.2 Hz, 2H), 3.30 (q, J=7.3 Hz, 4H), 5.50 (s, 1H), 6.66 (d, J=0.9 Hz, 1H), 6.97 (d, J=7.8 Hz, 1H), 7.11–7.13 (m, 2H), 7.18–7.25 (m, 4H), 7.28–7.35 (m, 5H), 7.41 (d, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.5, 142.5, 140.3, 136.2, 134.7, 134.3, 133.5, 129.8, 128.0, 127.8, 127.6, 127.0, 126.9, 125.9, 120.0, 71.4, 66.6, 40.9, 31.7, 15.0; HRMS-EI-TOF: calcd for $C_{30}H_{31}BrO_2$ (M$^+$): 502.1507, found: 052.1508.

4.4.10. 4-(2,2-Di-p-tolylvinyl)-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2j**)

Yellow liquid; IR: 3017, 2970, 2866, 1603, 1506, 1110, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.07 (t, J=6.9 Hz, 6H), 2.29 (s, 3H), 2.34 (s, 3H), 2.73 (s, 2H), 2.93 (d, J=9.2 Hz, 2H), 3.06 (d, J=9.2 Hz, 2H), 3.29–3.32 (m, 4H), 5.41 (s, 1H), 6.66 (s, 1H), 6.98–7.03 (m, 4H), 7.09–7.14 (m, 5H), 7.23–7.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.6, 140.2, 137.7, 137.2, 136.2, 135.6, 134.6, 134.3, 132.4, 129.8, 128.8, 128.4, 128.3, 127.8, 127.2, 126.2, 125.9, 124.0, 71.7, 66.5, 40.9, 32.3, 21.1, 21.0, 15.0; HRMS-EI-TOF: calcd for $C_{32}H_{36}O_2$ (M$^+$): 452.2715, found: 452.2715.

4.4.11. 4-(2,2-Bis(4-chlorophenyl)vinyl)-2,2-bis(ethoxymethyl)-1,2-dihydronaphthalene (**2k**)

Yellow liquid; IR: 2970, 2862, 1631, 1483, 1382, 1091, 831, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.08 (t, J=6.9 Hz, 6H), 2.73 (s, 2H), 2.97 (d, J=8.7 Hz, 2H), 3.08 (d, J=9.2 Hz, 2H), 3.32 (q, J=6.9 Hz, 4H), 5.43 (s, 1H), 6.72 (s, 1H), 7.05 (d, J=8.2 Hz, 2H), 7.10–7.19 (m, 5H), 7.21–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3, 140.8, 138.6, 135.1, 134.6, 133.8, 133.6, 133.2, 133.0, 131.3, 129.1, 128.5, 128.4, 128.2, 128.0, 127.5, 126.3, 123.8, 71.6, 66.6, 41.0, 32.4, 15.0; HRMS-EI-TOF: calcd for $C_{30}H_{30}Cl_2O_2$ (M$^+$): 492.1623, found: 492.1627.

4.4.12. 1-(2,2-Diphenylvinylidene)-3,3-bis(methoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3a**)

White solid; mp: 128–129 °C; IR: 2986, 2928, 2885, 2811, 1926, 1596, 1448, 1382, 1114, 768, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.68 (s, 2H), 2.78 (s, 2H), 3.28–3.36 (m, 10H), 7.10–7.11 (m, 3H), 7.22–7.32 (m, 6H), 7.39–7.42 (m, 4H), 7.56–7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.7, 137.2, 134.6, 130.7, 130.2, 128.6, 128.5,

127.5, 127.4, 126.6, 126.3, 112.8, 102.9, 75.7, 59.5, 38.8, 34.9, 32.9; HRMS-ESI-TOF: calcd for $C_{28}H_{28}O_2Na$ ([M+Na]$^+$): 419.1987, found: 419.1991.

*4.4.13. 1-(2,2-Diphenylvinylidene)-3,3-bis(ethoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3b**)*

White solid; mp: 85–87 °C; IR: 3017, 2974, 2862, 1926, 1487, 1382, 1102, 776, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=7.3 Hz, 6H), 2.70 (s, 2H), 2.80 (s, 2H), 3.34–3.44 (m, 8H), 7.09–7.11 (m, 3H), 7.19–7.32 (m, 6H), 7.40–7.43 (m, 4H), 7.55–7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.6, 137.1, 134.8, 130.6, 130.0, 128.4, 128.3, 127.3, 127.2, 126.4, 126.0, 112.6, 103.0, 73.3, 66.8, 38.7, 34.7, 32.7, 15.0; HRMS-EI-TOF: calcd for $C_{30}H_{32}O_2$ (M$^+$): 424.2402, found: 424.2400.

*4.4.14. 1-(2,2-Diphenylvinylidene)-3,3-bis(ethoxymethyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (**3c**)*

Yellow sticky liquid; IR: 3056, 2970, 2866, 1926, 1596, 1483, 1382, 1130, 765, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=6.9 Hz, 6H), 2.26 (s, 3H), 2.68 (s, 2H), 2.76 (s, 2H), 3.33–3.43 (m, 8H), 6.94 (d, J=7.8 Hz, 1H), 7.01 (d, J=7.8 Hz, 1H), 7.21–7.36 (m, 7H), 7.41–7.43 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.6, 137.2, 135.5, 131.8, 130.2, 129.8, 128.5, 128.4, 128.3, 127.2, 126.7, 112.4, 103.1, 73.3, 66.7, 38.8, 34.3, 32.8, 21.1, 15.1; HRMS-EI-TOF: calcd for $C_{31}H_{34}O_2$ (M$^+$): 438.2559, found: 438.2559.

*4.4.15. 1-(2,2-Diphenylvinylidene)-3,3-bis(ethoxymethyl)-7-methoxy-1,2,3,4-tetrahydronaphthalene (**3d**)*

Yellow viscous liquid; IR: 3001, 2970, 2873, 1930, 1603, 1491, 1386, 1269, 1091, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=6.9 Hz, 6H), 2.68 (s, 2H), 2.73 (s, 2H), 3.32–3.43 (m, 8H), 3.71 (s, 3H), 6.71–6.74 (m, 1H), 7.03 (d, J=8.7 Hz, 1H), 7.10–7.11 (m, 1H), 7.24–7.33 (m, 6H), 7.40–7.43 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.5, 157.7, 137.1, 131.5, 130.8, 128.4, 128.3, 127.2, 127.1, 113.9, 112.7, 110.5, 103.1, 73.2, 66.7, 55.1, 38.8, 33.9, 32.6, 15.1; HRMS-EI-TOF: calcd for $C_{31}H_{34}O_3$ (M$^+$): 454.2508, found: 454.2505.

*4.4.16. 7-tert-Butyl-1-(2,2-diphenylvinylidene)-3,3-bis(ethoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3g**)*

Yellow liquid; IR: 3013, 2974, 2869, 1933, 1491, 1110, 912, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 (t, J=6.9 Hz, 6H), 1.26 (s, 9H), 2.68 (s, 2H), 2.76 (s, 2H), 3.34–3.45 (m, 8H), 7.05 (d, J=7.8 Hz, 1H), 7.16–7.33 (m, 7H), 7.41–7.43 (m, 4H), 7.60 (d, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.4, 148.7, 137.4, 131.8, 129.9, 129.6, 128.4, 128.3, 127.1, 124.7, 123.0, 112.5, 103.3, 73.3, 66.7, 38.8, 34.3, 34.2, 32.7, 31.3, 15.1; HRMS-EI-TOF: calcd for $C_{34}H_{40}O_2$ (M$^+$): 480.3028, found: 480.3028.

*4.4.17. 7-Bromo-1-(2,2-diphenylvinylidene)-3,3-bis(ethoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3i**)*

Yellow viscous liquid; IR: 2974, 1926, 1491, 1386, 1099, 772, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=6.9 Hz, 6H), 2.68 (s, 2H), 2.73 (s, 2H), 3.31–3.42 (m, 8H), 6.97 (d, J=7.8 Hz, 1H), 7.21–7.24 (m, 1H), 7.25–7.43 (m, 10H), 7.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.3, 136.6, 133.6, 132.9, 131.5, 130.2, 128.9, 128.4, 128.3, 127.4, 119.7, 113.1, 102.2, 73.1, 66.7, 38.5, 34.1, 32.5, 15.0; HRMS-EI-TOF: calcd for $C_{30}H_{31}BrO_2$ (M$^+$): 502.1507, found: 502.1508.

*4.4.18. 1-(2,2-Di-p-tolylvinylidene)-3,3-bis(ethoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3j**)*

White solid; mp: 109–111 °C, IR: 3021, 2920, 2850, 1926, 1506, 1479, 1110, 823, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=7.3 Hz, 6H), 2.34 (s, 6H), 2.68 (s, 2H), 2.79 (s, 2H), 3.32–3.44 (m, 8H), 7.06–7.12 (m, 7H), 7.27–7.32 (m, 4H), 7.53–7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.2, 136.9, 134.7, 134.3, 130.8, 129.9, 129.0, 128.3, 127.1, 126.4, 126.0, 112.2, 102.6, 73.3, 66.8, 38.7, 34.6, 32.7, 21.1, 15.1; HRMS-EI-TOF: calcd for $C_{32}H_{36}O_2$ (M$^+$): 452.2715, found: 452.2716.

*4.4.19. 1-(2,2-Bis(4-chlorophenyl)vinylidene)-3,3-bis(ethoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3k**)*

White solid; mp: 145–146 °C; IR: 3048, 2974, 2866, 1926, 1483, 1390, 1106, 831, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, J=7.3 Hz, 6H), 2.69 (s, 2H), 2.80 (s, 2H), 3.33–3.44 (m, 8H), 7.10–7.14 (m, 3H), 7.26–7.32 (m, 8H), 7.48 (d, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.5, 135.3, 135.0, 133.2, 130.1, 130.0, 129.6, 128.6, 127.6, 126.3, 126.1, 110.8, 103.9, 73.2, 66.8, 38.7, 34.6, 32.5, 15.1; HRMS-EI-TOF: calcd for $C_{30}H_{30}Cl_2O_2$ (M$^+$): 492.1623, found: 492.1625.

*4.4.20. 3,3-Bis(ethoxymethyl)-1-(2-phenylprop-1-enylidene)-1,2,3,4-tetrahydronaphthalene (**3l**)*

Yellow liquid; IR: 3060, 2966, 2866, 1930, 1596, 1487, 1106, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12–1.21 (m, 6H), 2.19 (s, 3H), 2.56 (d, J=14.2 Hz, 1H), 2.61 (d, J=14.2 Hz, 1H), 2.79 (s, 2H), 3.36–3.48 (m, 8H), 7.05–7.21 (m, 4H), 7.25–7.31 (m, 2H), 7.39–7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.5, 137.4, 134.6, 131.2, 129.9, 128.3, 126.9, 126.6, 126.5, 125.9, 125.8, 103.2, 101.7, 73.5, 66.8, 38.6, 34.5, 32.8, 16.9, 15.1, 15.0; HRMS-EI-TOF: calcd for $C_{25}H_{30}O_2$ (M$^+$): 362.2246, found: 362.2245.

*4.4.21. 4-(2,2-Diphenylvinylidene)-2-(phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (**5a**)*

Brown liquid; IR: 3052, 3013, 1930, 1487, 1440, 1168, 1087, 726, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.36 (s, 2H), 4.47 (s, 2H), 7.02–7.09 (m, 3H), 7.17–7.21 (m, 2H), 7.27–7.36 (m, 12H), 7.67–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.5, 137.3, 136.1, 132.9, 130.8, 129.0, 128.8, 128.7, 128.6, 128.1, 127.9, 127.8, 127.6, 126.8, 126.6, 116.0, 99.9, 48.6, 47.3; HRMS-ESI-TOF: calcd for $C_{29}H_{24}NO_2S$ ([M+H]$^+$): 450.1528, found: 450.1537.

*4.4.22. 2-(4-Chlorophenylsulfonyl)-4-(2,2-diphenylvinylidene)-1,2,3,4-tetrahydroisoquinoline (**5b**)*

Brown viscous liquid; IR: 3013, 2924, 1938, 1448, 1382, 1343, 1165, 1091, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.45 (s, 2H), 4.56 (s, 2H), 7.02–7.15 (m, 5H), 7.30–7.37 (m, 11H), 7.52–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.1, 139.1, 136.3, 136.0, 130.4, 129.1, 129.0, 128.7, 128.6, 128.5, 128.1, 127.8, 127.6, 126.7, 126.6, 115.8, 99.3, 48.7, 47.2; HRMS-ESI-TOF: calcd for $C_{29}H_{22}ClNO_2SNa$ ([M+Na]$^+$): 506.0957, found: 506.0981.

*4.4.23. 2-(4-Bromophenylsulfonyl)-4-(2,2-diphenylvinylidene)-1,2,3,4-tetrahydroisoquinoline (**5c**)*

Brown solid; mp: 149–151 °C; IR: 3023, 1933, 1568, 1436, 1347, 1157, 932 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.44 (s, 2H), 4.54 (s, 2H), 7.03–7.22 (m, 5H), 7.28–7.39 (m, 11H), 7.45 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.1, 136.8, 136.0, 132.0, 130.4, 129.2, 128.8, 128.6, 128.5, 128.1, 127.9, 127.7, 126.8, 126.6, 115.8, 99.3, 48.7, 47.2; HRMS-ESI-TOF: calcd for $C_{29}H_{23}BrNO_2S$ ([M+H]$^+$): 528.0633, found: 528.0643.

*4.4.24. 4-(2,2-Diphenylvinylidene)-2-(4-nitrophenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (**5d**)*

Yellow solid; mp: 181–183 °C; IR: 3027, 1928, 1527, 1446, 1347, 1311, 1168, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.57 (s, 2H), 4.67 (s, 2H), 7.01–7.05 (m, 2H), 7.09–7.11 (m, 1H), 7.20–7.22 (m, 1H), 7.27–7.30 (m, 4H), 7.35–7.40 (m, 6H), 7.65–7.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.7, 149.7, 144.2, 135.8, 130.0, 128.9, 128.8, 128.6, 128.4, 128.0, 127.9, 126.8, 126.5, 123.6, 116.2, 98.6, 48.9, 47.4. Anal. Calcd for $C_{29}H_{22}N_2O_4S$: C, 70.43; H, 4.48; N, 5.66. Found: C, 70.35; H, 4.52; N, 5.64. HRMS-ESI-TOF: calcd for $C_{29}H_{22}N_2O_4SNa$ ([M+Na]$^+$): 517.1198, found: 517.1216.

*4.4.25. 4-(2,2-Diphenylvinylidene)-2-(methylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (**5e**)*

Brown solid; mp: 191–193 °C; IR: 3017, 2823, 1930, 1487, 1351, 1157, 947, 780, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.63 (s, 3H), 4.55 (s, 2H), 4.68 (s, 2H), 7.14–7.17 (m, 1H), 7.23–7.25 (m, 2H), 7.28–7.40 (m, 10H), 7.61–7.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.8, 136.1, 130.9, 128.9, 128.8, 128.6, 128.3, 128.2, 128.0, 127.1, 126.8, 116.2, 98.9, 48.3, 47.3, 38.8; HRMS-ESI-TOF: calcd for $C_{24}H_{21}NO_2SNa$ ($[M+Na]^+$): 410.1191, found: 410.1211.

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13. CCDC 715241 (**5d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 (0)1223 336033, or e-mail: deposit@ccdc.cam.ac.uk.