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Montmorillonite K-10-catalyzed intramolecular rearrangement of vinylidenecyclopropanes

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Abstract—A series of naphthalene, indene, and 6a*H*-benzo[*c*]fluorene derivatives are synthesized by intramolecular rearrangement of vinylidenecyclopropanes using a heterogeneous solid acid catalyst, montmorillonite K-10, under mild reaction conditions in good to excellent yields. The solid acidic catalyst, montmorillonite K-10, can be recovered and reused.
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1. Introduction

Polysubstituted aromatic compounds have played an important role in the chemical and pharmaceutical industries as well as in the fields of optical and electronic materials. Recently, there has been a considerable interest in synthesizing naphthalene derivatives and other extended aromatic systems, which are extremely useful benzenoid compounds for biological studies and material applications. The most important methods for these compounds include annulation via Fisher carbenes (the Dotz reaction)[1] and palladium-catalyzed cyclization of alkynes with arylsilyl triflate via highly reactive benzynes (generated in situ).[2] Another method for naphthalene derivatives is cyclization reactions between alkynes and carbonyl or epoxide compounds catalyzed by gallium trichloride.[3] Very recently, we reported novel Lewis acids or Brønsted acids-catalyzed rearrangement of vinylidenecyclopropanes **1** having three substituents at the cyclopropyl ring to provide easy access to naphthalene, indene, and 6a*H*-benzo[*c*]fluorene derivatives via intramolecular Friedel–Crafts reaction under mild conditions in good to high yields.[4]

In recent years, the use of solid acidic catalysts such as clays and zeolites has attracted significant attention in different areas of organic synthesis.[5] In fact, solid acids are advantageous as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation, thereby making the process economically viable. Among various heterogeneous catalysts, clays are the most attractive because of their reusability, environmental compatibility, high selectivity, low cost, non-toxicity, and operational simplicity. Herein we wish to report a simple and an efficient synthetic method for naphthalene, indene, and 6a*H*-benzo[*c*]fluorene derivatives by intramolecular rearrangement of vinylidenecyclopropanes using a heterogeneous solid acid catalyst, montmorillonite K-10, under mild reaction conditions.

2. Results and discussion

An initial examination was carried out using vinylidenecyclopropane **1a** as a substrate in the presence of a variety of solid acids. We found that the intramolecular rearrangement reaction took place smoothly to give 2-methyl-1,4-diphenylnaphthalene **2a** in 86% and 92% yields, respectively, when montmorillonite KSF and K-10 (from Aldrich) were used as the catalysts at 80 °C in 1,2-dichloroethane (DCE) (Table 1, entries 1 and 2). The other solid acid catalysts such as silica gel (SiO_2), neutral Al_2O_3, and zeolite[6] showed no catalytic abilities for this intramolecular rearrangement (Table 1, entries 3–5). The examination of solvent effects revealed that DCE is the best solvent of choice for the reaction (Table 1, entries 7–12), although the reaction could also proceed to give **2a** in 46% yield without solvent under otherwise identical conditions (Table 1, entry 6).

Under these optimized reaction conditions, we next examined a variety of vinylidenecyclopropanes **1a**–**h** (R^1, R^3=aryl, R^2=alkyl, R^4=H, R^5=H or alkyl or R^1, R^2, R^3=aryl; R^4=H, R^5=H or alkyl) in the presence of montmorillonite K-10. The results are summarized in Table 2. As can

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Keywords: Vinylidenecyclopropane; Naphthalene; Indene; 6a*H*-Benzo[*c*]fluorene; Intramolecular rearrangement; Solid acid; Montmorillonite K-10.

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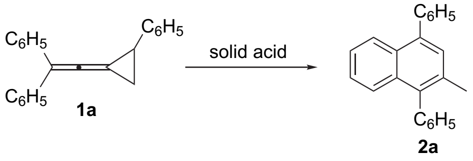
Table 1. Effects of various catalysts and solvents in the rearrangement of vinylidenecyclopropane **1a**



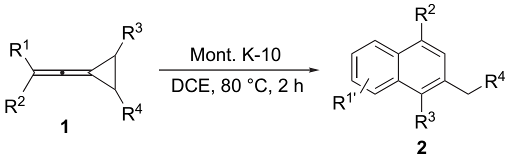
Entry[a]	Solvent	Catalyst	*T* [°C]	*t* [h]	Yield[b] [%]
1	DCE	KSF	80	6	86
2	DCE	K-10	80	2	92
3	DCE	SiO_2	80	24	Trace
4	DCE	Neutral Al_2O_3	80	24	Trace
5	DCE	Zeolite	80	24	Trace
6	Neat	K-10	80	1.5	46
7	THF	K-10	66	24	N.R
8	Acetone	K-10	56	24	N.R
9	Toluene	K-10	80	3	73
10	Et_2O	K-10	35	24	N.R
11	CH_3CN	K-10	80	24	N.R
12	EtOH	K-10	78	24	N.R

[a] All reactions were carried out using **1a** (0.2 mmol), catalyst (50 mg), and solvent (2.0 mL).

[b] Isolated yield.

be seem from Table 2, the corresponding naphthalene derivatives **2** were obtained in good yields (Table 2). It should be noted that the montmorillonite K-10 catalyst could be recovered after reaction just by filtration. The recovered solid acid catalyst K-10 can be reused in the next reaction to give **2a** in very similar yields after drying at 120 °C for 2 h in an oven (Table 2, entries 1–3). The solvent DCE can be also collected by evaporation with a condenser.

Table 2. Montmorillonite K-10-catalyzed rearrangement of vinylidenecyclopropanes **1a**–**h** to naphthalene derivatives **2** in DCE at 80 °C



Entry[a]	**1** ($R^1/R^2/R^3/R^4$)	Yield[b] [%]
1[c]	**1a** ($C_6H_5/C_6H_5/C_6H_5$/H)	**2a** (89)[d]
2[c]	**1a** ($C_6H_5/C_6H_5/C_6H_5$/H)	**2a** (90)[d]
3[c]	**1a** ($C_6H_5/C_6H_5/C_6H_5$/H)	**2a** (86)[d]
4	**1b** (p-$CH_3C_6H_4$/p-$CH_3C_6H_4/C_6H_5$/H)	**2b** (88)
5	**1c** (p-$CH_3OC_6H_4$/p-$CH_3OC_6H_4/C_6H_5$/H)	**2c** (87)
6	**1d** (p-FC_6H_4/p-FC_6H_4/C_6H_5/H)	**2d** (88)
7	**1e** (C_6H_5/C_6H_5/p-$CH_3C_6H_4$/H)	**2e** (82)
8	**1f** (C_6H_5/C_6H_5/p-$CH_3OC_6H_4$/H)	**2f** (60)
9	**1g** ($C_6H_5/CH_3/C_6H_5$/H)[e]	**2g** (57)
10	**1h** ($C_6H_5/C_6H_5/C_6H_5/CH_3$)[f]	**2h** (84)

[a] All reactions were carried out using **1** (0.2 mmol) and K-10 (50 mg) in DCE (2.0 mL) at 80 °C for 2 h.

[b] Isolated yields.

[c] The catalyst K-10 was recovered by filtration from the reaction mixture and used as the catalyst after drying at 120 °C for 2 h in an oven.

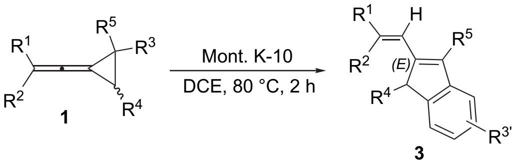
[d] Isolated yields when the recovered catalyst K-10 was used.

[e] *E*/*Z*=1:1.

[f] *syn*/*anti*=1:1.

On the other hand, using vinylidenecyclopropanes **1i** and **1j** (R^1, R^2, R^3, R^5=aryl; R^4=alkyl or H) and **1k** and **1l** (R^1, R^2, R^3=aryl; R^4, R^5=alkyl and at least one of aromatic groups of R^1, R^2 or R^3 has electron-withdrawing substituents) as substrates in the presence of montmorillonite K-10, the corresponding indene derivatives **3a–d** were obtained in good to high yields under identical conditions (Table 3).

Table 3. Montmorillonite K-10-catalyzed rearrangement of vinylidenecyclopropanes **1i–l** to indene derivatives **3** in DCE at 80 °C



Entry[a]	**1** ($R^1/R^2/R^3/R^4/R^5$)	Yield[b] [%]
1	**1i** ($C_6H_5/C_6H_5/C_6H_5$/H/C_6H_5)	**3a** (78)
2	**1j** ($C_6H_5/C_6H_5/C_6H_5/CH_3/C_6H_5$)	**3b** (97)
3	**1k** (C_6H_5/C_6H_5/p-$ClC_6H_4/CH_3/CH_3$)[c]	**3c** (93)
4	**1l** (p-FC_6H_4/p-$FC_6H_4/C_6H_5/CH_3/CH_3$)[d]	**3d** (89)

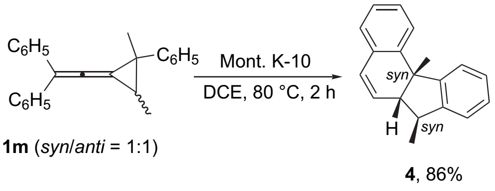
[a] All reactions were carried out using **1** (0.2 mmol) and K-10 (50 mg) in DCE (2.0 mL) at 80 °C for 2 h.

[b] Isolated yields.

[c] *syn*/*anti*=2:3.

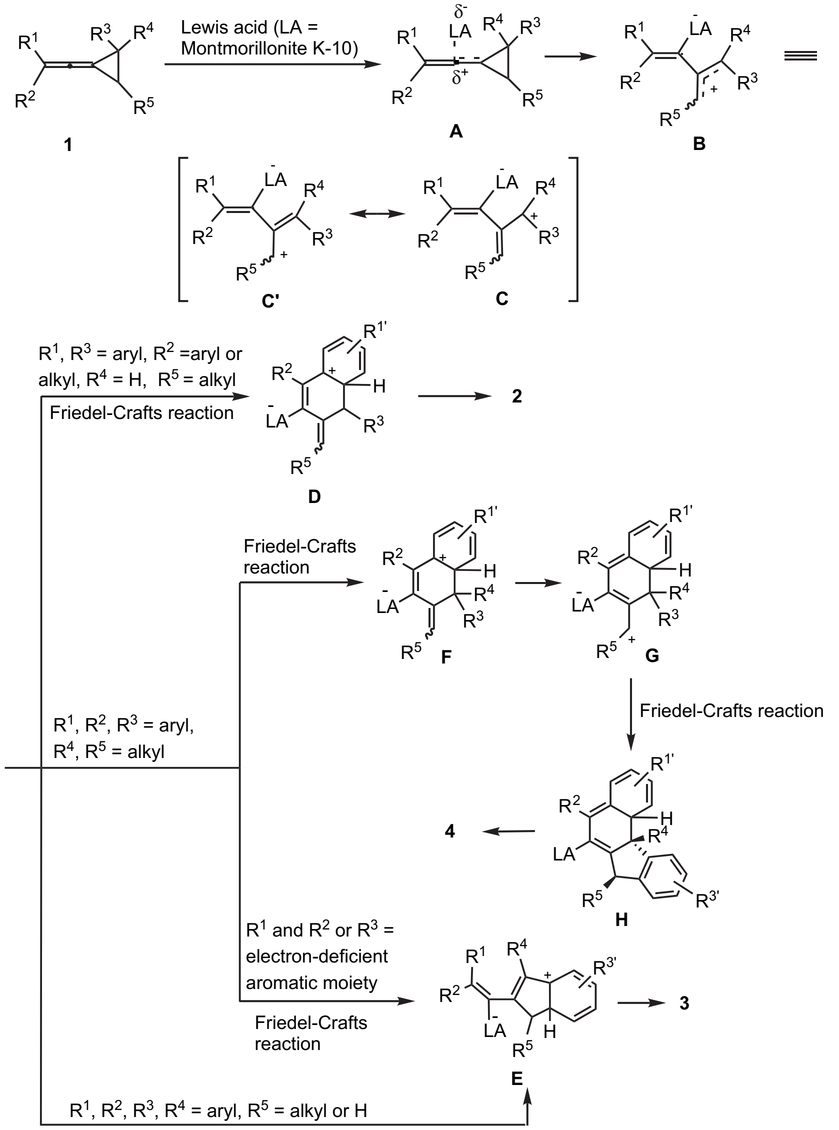
[d] *syn*/*anti*=2:3.

Next, for vinylidenecyclopropane **1m** (R^1=R^2=R^3=phenyl; R^4=R^5=methyl), 6a*H*-benzo[*c*]fluorene derivative **4** was formed in good yield under identical conditions (Scheme 1).



Scheme 1. Montmorillonite K-10-catalyzed rearrangement of vinylidenecyclopropanes **1m**.

The reaction mechanism for the formation of naphthalene, indene, and 6a*H*-benzo[*c*]fluorene derivatives **2**, **3**, and **4** is outlined in Scheme 2. The coordination of **1** to Lewis acid (montmorillonite K-10) initially gives zwitterionic intermediate **A**, which results in the formation of cyclopropane ring-opening zwitterionic intermediate **B** or the resonance-stabilized zwitterionic intermediates **C** and **C′**. Intramolecular Friedel–Crafts reaction takes place from zwitterionic intermediate **C** with the aromatic R^1 group to give the corresponding naphthalene derivative **2** via intermediate **D** when R^1 and R^3 are aryl groups, R^2 is aryl or alkyl group, R^4 is H group, and R^5 is H or alkyl group. When R^1, R^2, R^3, and R^5 are aryl groups, R^4 is alkyl or H group or R^1, R^2, and R^3 are aryl groups, R^4 and R^5 are alkyl groups and at least one of aromatic groups of R^1, R^2 or R^3 has electron-withdrawing substituents, intramolecular Friedel–Crafts reaction takes place from zwitterionic intermediate **C′** with the aromatic R^3 group to produce the corresponding indene derivative **3** via intermediate **E**. Double intramolecular Friedel–Crafts reaction takes place to produce 6a*H*-benzo[*c*]fluorene derivatives **4** from intermediate **C** via intermediates **F**, **G**, and **H** when R^1, R^2, and R^3 are aryl groups, R^4 and R^5 are alkyl groups (Scheme 2). The spectroscopic data of products **2–4** and the more detailed mechanism have been reported in our previous work.[4]



Scheme 2. Lewis acid (montmorillonite K-10)-catalyzed rearrangement of arylvinylidenecyclopropanes **1**.

3. Conclusion

We have disclosed a simple and an efficient method for the preparation of naphthalene, indene, and 6a*H*-benzo[*c*]fluorene derivatives by intramolecular rearrangement of vinylidenecyclopropanes **1** using a heterogeneous solid acid catalyst, montmorillonite K-10, under mild reaction conditions. The obvious advantages of the catalyst are easy and simple operation in the workup in an inexpensive, non-toxic, non-corrosive, recyclable, more economical, and environmentally friendly procedure. Efforts are underway to elucidate the further mechanistic details of this reaction and to identify systems enabling the similar reactions of other substrates and subsequent transformations thereof.

4. Experimental procedures

4.1. General methods

^{1}H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Montmorillonite K-10 was purchased from Aldrich, CAS: 1318-93-0, Lot. S20698-184. Flash column chromatography was carried out using 300–400 mesh silica gel.

4.1.1. General procedure for palladium-catalyzed reaction of vinylidenecyclopropanes with acetic acid. Under an argon atmosphere, vinylidenecyclopropanes **1** (0.2 mmol), montmorillonite K-10 (50 mg), and DCE (2.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 80 °C for 2 h. The reaction mixture was filtered off and the solid was washed with dimethoxyethylene (DME). The obtained solid acid catalyst (K-10) was dried at 120 °C in an oven for 2 h, the recovered solid can directly used. The solvent can also be recovered by evaporation and the residue was purified by a flash column chromatography.

4.1.1.1. 2-Methyl-1,4-diphenylnaphthalene (2a). A white solid, mp 129–130 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.27 (3H, s, CH$_3$), 7.30–7.57 (14H, m, Ar), 7.88–7.91 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.8, 124.8, 125.6, 125.8, 126.5, 127.0, 127.2, 128.2, 128.4, 129.7, 130.1, 130.2, 132.6, 133.3, 137.8, 139.4, 139.8, 140.8; IR (CH$_2$Cl$_2$): ν 3056, 3025, 2920, 2859, 1591, 1496, 1441, 1387, 1373, 1072, 1030, 886, 774, 744, 702, 540 cm^{-1}; MS (EI) *m/z* (%): 294 (100) [M$^+$], 279 (29.7), 217 (8.9), 215 (24.1), 202 (14.6), 77 (9.7). Anal. Calcd for C$_{23}$H$_{18}$ requires C, 93.84; H, 6.16%. Found: C, 93.55; H, 6.43%.

4.1.1.2. 2-Methyl-1-phenyl-4-(*p*-methylphenyl)-7-methylnaphthalene (2b). A colorless oil, ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.22 (3H, s, CH$_3$), 2.34 (3H, s, CH$_3$), 2.45 (3H, s, CH$_3$), 7.15–7.22 (2H, m, Ar), 7.28–7.31 (5H, m, Ar), 7.40–7.53 (5H, m, Ar), 7.82 (1H, d, J=8.7 Hz, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.9, 21.3, 21.8, 125.4, 125.8, 126.9, 126.9, 128.4, 128.4, 128.8, 128.9, 130.0, 130.2, 132.7, 133.4, 135.2, 136.8, 137.0, 138.0, 139.2, 140.0; IR (CH$_2$Cl$_2$): ν 3053, 3023, 2954, 2923, 2855, 1620, 1600, 1516, 1507, 1440, 1381, 1362, 1029, 883, 824, 760, 703, 526 cm^{-1}; MS (EI) *m/z* (%): 322 (100) [M$^+$], 307 (10.3), 292 (7.6), 229 (3.8), 215 (5.1), 91 (1.7); HRMS (MALDI) Calcd for C$_{25}$H$_{23}$ (M$^+$+H) requires 323.1794, found: 323.1786.

4.1.1.3. 2-Methyl-1-phenyl-4-(*p*-methoxylphenyl)-7-methoxylnaphthalene (2c). A white solid, mp 135.9–136.2 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.22 (3H, s, CH$_3$), 3.65 (3H, s, OCH$_3$), 3.88 (3H, s, OCH$_3$), 6.76–6.77 (1H, m, Ar), 6.99–7.04 (3H, m, Ar), 7.21 (1H, s, Ar), 7.30–7.33 (2H, m, Ar), 7.42–7.53 (5H, m, Ar), 7.81–7.85 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.9, 55.0, 55.3, 105.3, 113.7, 116.7, 125.7, 127.0, 127.5, 127.6, 128.5, 130.1, 131.1, 133.2, 133.3, 134.6, 136.5, 139.0, 140.0, 157.3, 158.8; IR (CH$_2$Cl$_2$): ν 3060, 2953, 2926, 2853, 2834, 1618, 1517, 1507, 1440, 1380, 1247, 1226, 1034, 833, 704, 535 cm^{-1}; MS (EI) *m/z* (%): 354 (100) [M$^+$], 339 (12.2), 324 (5.2), 309 (3.1), 293 (1.0), 277 (1.3), 202 (1.7); HRMS (EI) Calcd for C$_{25}$H$_{22}$O$_2$ (M$^+$) requires 354.1620, found: 354.1604.

4.1.1.4. 2-Methyl-1-phenyl-4-(*p*-fluorophenyl)-7-fluoronaphthalene (2d). A white solid, mp 95.9–96.4 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.25 (3H, s, CH$_3$), 7.05–7.29 (7H, m, Ar), 7.44–7.54 (5H, m, Ar), 7.79–7.84 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.8, 110.0 (d, $J_{\mathrm{C-F}}$=21.2 Hz), 115.0 (d, $J_{\mathrm{C-F}}$=24.6 Hz), 115.3 (d, $J_{\mathrm{C-F}}$=21.2 Hz), 127.2, 127.4, 128.2 (d, $J_{\mathrm{C-F}}$=9.2 Hz), 128.6, 129.0 (d, $J_{\mathrm{C-F}}$=1.6 Hz), 130.0, 131.5 (d, $J_{\mathrm{C-F}}$=8.0 Hz), 134.0, 134.5 (d, $J_{\mathrm{C-F}}$=8.9 Hz), 136.4 (d, $J_{\mathrm{C-F}}$=3.7 Hz), 137.5 (d, $J_{\mathrm{C-F}}$=6.2 Hz), 138.4, 139.2, 160.6 (d, $J_{\mathrm{C-F}}$=243.4 Hz), 162.3 (d, $J_{\mathrm{C-F}}$=244.4 Hz); IR (CH$_2$Cl$_2$): ν 3056, 2925, 2855, 1623, 1607, 1519, 1507, 1441, 1424, 1384, 1223, 1198, 1158, 978, 834, 760, 703, 530 cm^{-1}; MS (EI) *m/z* (%): 330 (100) [M$^+$], 315 (11.7), 295 (2.9), 235 (2.3), 233 (8.0), 220 (3.2), 215 (1.5); HRMS (EI) Calcd for C$_{23}$H$_{16}$F$_2$ (M$^+$) requires 330.1220, found: 330.1225.

4.1.1.5. 2-Methyl-1-(*p*-methylphenyl)-4-phenylnaphthalene (2e). A white solid, mp 97.7–98.5 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.26 (3H, s, CH$_3$), 2.46 (3H, s, CH$_3$), 7.18–7.21 (2H, m, Ar), 7.28–7.55 (11H, m, Ar), 7.87–7.90 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.8, 21.3, 124.8, 125.6, 125.8, 126.5, 127.1, 128.2, 129.1, 129.7, 130.1, 130.1, 132.7, 133.4, 136.5, 136.7, 137.8, 139.3, 140.8; IR (CH$_2$Cl$_2$): ν 3055, 3024, 2922, 2855, 1592, 1516, 1508, 1441, 1387, 1374, 819, 775, 766, 701, 532 cm^{-1}; MS (EI) *m/z* (%): 308 (100) [M$^+$], 293 (15.7), 278 (6.8), 231 (1.8), 217 (1.5), 215 (9.5), 202 (2.5), 91 (1.3); HRMS (EI) Calcd for C$_{24}$H$_{20}$ (M$^+$) requires 308.1565, found: 308.1559.

4.1.1.6. 2-Methyl-1-(*p*-methoxylphenyl)-4-phenylnaphthalene (2f). A white solid, mp 120.7–121.1 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.27 (3H, s, CH$_3$), 3.91 (3H, s, OCH$_3$), 7.05–7.08 (2H, m, Ar), 7.21–7.56 (11H, m, Ar), 7.87–7.91 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 20.9, 55.3, 113.8, 124.7, 125.6, 125.8, 126.5, 127.2, 128.2, 129.7, 130.1, 131.2, 131.9, 133.0, 133.6, 137.5, 139.2, 140.8, 158.6; IR (CH$_2$Cl$_2$): ν 3062, 3032, 2953, 2925, 2834, 1609, 1515, 1508, 1441, 1386, 1373, 1243, 1035, 831, 775, 702 cm^{-1}; MS (EI) *m/z* (%): 324 (100) [M$^+$], 309 (31.2), 294 (5.9), 293 (6.1), 278 (4.7), 266 (9.6), 215 (6.8), 202 (5.9), 77 (1.6); HRMS (EI) Calcd for C$_{24}$H$_{20}$O (M$^+$) requires 324.1514, found: 324.1471.

4.1.1.7. 2,4-Dimethyl-1-phenylnaphthalene (2g). A white solid, mp 75.7–76.5 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.20 (3H, s, CH$_3$), 2.72 (3H, s, CH$_3$), 7.23–7.51 (9H, m, Ar), 7.99 (1H, d, J=9.0 Hz, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 19.4, 20.7, 123.9, 124.6, 125.4, 126.7, 126.8, 128.3, 129.4, 130.3, 131.0, 132.7, 133.0, 133.3, 136.5, 140.0; IR (CH$_2$Cl$_2$): ν 3061, 3025, 2924, 2854, 1601, 1512, 1493, 1442, 1388, 1379, 1033, 874, 776, 757, 703 cm^{-1}; MS (EI) *m/z* (%): 232 (100) [M$^+$], 217 (46.6), 215 (25.7), 202 (20.7), 77 (1.3); HRMS (EI) Calcd for C$_{18}$H$_{16}$ (M$^+$) requires 232.1252, found: 232.1216.

4.1.1.8. 2-Ethyl-1,4-diphenylnaphthalene (2h). A white solid, mp 109.7–110.6 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 1.13 (3H, t, J=7.5 Hz, CH$_3$), 2.56 (2H, q, J=7.5 Hz, CH$_2$), 7.29–7.35 (4H, m, Ar), 7.40–7.57 (10H, m, Ar), 7.89–7.92 (1H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ 16.0, 27.0, 124.9, 125.6, 125.8, 126.8, 127.0, 127.2, 128.2, 130.0, 130.1, 130.4, 133.4, 137.2, 138.8, 139.5, 139.8, 140.9; IR (CH$_2$Cl$_2$): ν 3058, 3025, 2959, 2925, 2854, 1601, 1496, 1456, 1441, 1381, 1289, 1244, 891, 773, 760, 741, 701 cm^{-1}; MS (EI) *m/z* (%): 308 (100) [M$^+$], 293 (15.0), 279 (8.5), 217 (1.6), 215 (20.5), 202 (4.4), 77 (1.2). Anal. Calcd for C$_{24}$H$_{20}$ requires C, 93.46; H, 6.54%. Found: C, 93.07; H, 6.69%.

4.1.1.9. 2-(2,2-Diphenylpvinyl)-3-phenyl-1*H*-indene (3a). A white solid, mp 140–141 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ 2.96 (2H, s, CH$_2$), 7.09–7.33 (12H, m, ArH+=CH), 7.39–7.53 (8H, m, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): δ 39.7, 120.2, 123.1, 123.4, 125.3, 126.2, 127.1, 127.6, 128.1, 128.5, 128.6, 129.8, 130.4, 135.1, 140.3, 141.0, 141.7, 142.6, 143.3, 144.7, 145.1; IR (CH$_2$Cl$_2$): ν 3056, 3023, 2921, 2850, 1599, 1485, 1460, 1442, 1387, 1264, 1073, 1029, 946, 775, 764 cm^{-1}; MS (EI) *m*/*z* (%): 370 (100) [M$^+$]; HRMS (EI) Calcd for $C_{29}H_{22}$ (M$^+$) requires 370.1722, found: 370.1718.

4.1.1.10. 1-Methyl-3-phenyl-2-(2,2-diphenylvinyl)-1*H*-indene (3b). A green solid, mp 138.8–139.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.05 (3H, d, *J*=7.5 Hz, CH_3), 3.09 (1H, q, *J*=7.2 Hz, CH), 6.80 (1H, s, $Ar_2C{=}CH$), 7.13–7.54 (19H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.5, 43.8, 120.1, 122.8, 123.0, 125.4, 126.3, 127.4, 127.5, 127.7, 127.9, 128.0, 128.1, 128.4, 129.7, 131.1, 135.0, 140.8, 142.1, 143.3, 143.4, 143.6, 146.6, 149.2; IR (CH_2Cl_2): ν 3054, 3020, 2962, 2926, 2851, 1598, 1492, 1461, 1443, 1369, 1265, 1075, 1030, 778, 740, 701, 590 cm^{-1}; MS (EI) *m*/*z* (%): 384 (100) [M$^+$], 369 (16.4), 292 (12.0), 291 (47.1), 229 (4.3), 215 (5.3), 202 (3.2), 165 (5.4). Anal. Calcd for $C_{30}H_{24}$ requires C, 93.71; H, 6.29%. found: C, 93.64; H, 6.30%.

4.1.1.11. 6-Chloro-2-(2,2-diphenylvinyl)-1,3-dimethyl-1*H*-indene (3c). A yellow solid, mp 134–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.97 (3H, d, *J*=7.5 Hz, CH_3), 2.05 (3H, d, *J*=1.2 Hz, CH_3), 3.01 (1H, q, *J*=7.5 Hz, CH), 6.88 (1H, s, $=$CH), 7.11–7.32 (13H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 17.1, 43.8, 119.5, 122.0, 122.8, 126.4, 127.5, 127.6, 127.9, 128.1, 130.9, 131.0, 137.0, 140.7, 142.2, 143.1, 143.4, 143.6, 145.2, 150.6; IR (CH_2Cl_2): ν 3077, 3051, 3026, 2962, 2923, 2865, 1594, 1491, 1459, 1443, 1412, 1380, 1261, 1076, 1021, 817, 762 cm^{-1}; MS (EI) *m*/*z* (%): 356 (100) [M$^+$], 358 (28), 341 (39), 306 (20), 291 (30), 263 (19), 191 (31); HRMS (EI) Calcd for $C_{25}H_{21}Cl$ (M$^+$) requires 356.1332, found: 356.1317.

4.1.1.12. 2-[2,2-Bis(4-fluorophenyl)-vinyl]-1,3-dimethyl-1*H*-indene (3d). A colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.00 (3H, d, *J*=7.5 Hz, CH_3), 2.07 (3H, d, *J*=1.2 Hz, CH_3), 3.05 (1H, q, *J*=7.5 Hz, CH), 6.84 (1H, s, $=$CH), 6.97–7.03 (4H, m, ArH), 7.12–7.28 (7H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 11.2, 17.1, 43.8, 115.0 (d, $J_{C\text{–}F}$=14.7 Hz), 115.2, 115.5 (d, $J_{C\text{–}F}$=12.9 Hz), 118.8, 122.5 (d, $J_{C\text{–}F}$=12 Hz), 125.4, 126.4, 129.4 (d, $J_{C\text{–}F}$=7.7 Hz), 132.6 (d, $J_{C\text{–}F}$=7.5 Hz), 136.7 (d, $J_{C\text{–}F}$=3.5 Hz), 138.2, 139.8, 140.4, 144.2, 144.8, 148.7, 162.2 (d, $J_{C\text{–}F}$=246.2 Hz), 162.4 (d, $J_{C\text{–}F}$=245.6 Hz); IR (CH_2Cl_2): ν 3064, 3042, 2962, 2926, 2854, 1601, 1507, 1466, 1384, 1224, 1157, 1015, 838, 761 cm^{-1}; MS (EI) *m*/*z* (%): 358 (75) [M$^+$], 343 (19), 203 (100), 183 (18); HRMS (EI) Calcd for $C_{25}H_{20}F_2$ (M$^+$) requires 358.1533, found: 358.1518.

4.1.1.13. 7,11b-Dihydro-7,11b-dimethyl-5-phenyl-6a*H*-benzo[*c*]fluorene (4). A white solid, mp 126.6–127.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.43 (3H, d, *J*=6.6 Hz, CH_3), 1.58 (3H, s, CH_3), 2.46–2.52 (1H, m, CH), 2.91–2.97 (1H, m, CH), 6.19 (1H, d, *J*=6.6 Hz, $Ar_2C{=}CH$), 7.00–7.44 (12H, m, ArH), 7.61 (1H, d, *J*=7.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 16.5, 27.4, 43.9, 48.3, 57.5, 122.5, 124.7, 125.8, 125.8, 126.3, 126.5, 126.9, 127.1, 127.3, 127.7, 128.2, 129.0, 132.6, 139.2, 140.2, 140.9, 147.6, 149.2; IR (CH_2Cl_2): ν 3059, 3022, 2956, 2922, 2869, 1597, 1493, 1478, 1443, 1369, 1265, 1028, 778, 763, 754, 741, 704, 582 cm^{-1}; MS (EI) *m*/*z* (%): 322 (84.1) [M$^+$], 307 (100), 292 (20.1), 229 (54.9), 215 (27.1), 202 (6.6), 115 (2.3). Anal. Calcd for $C_{25}H_{22}$ requires C, 93.12; H, 6.88%. Found: C, 92.96; H, 6.72%.

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6. The silica gel (SiO_2, 100–200 mesh) was purchased from Huanghai Chemical Reagent Company; neutral Al_2O_3 (Q/BKUS5-91) was purchased from Shanghai Wu Si Chemistry Reagent Company. The zeolite was made from glass capillary.