Brønsted Acid Mediated Double Friedel–Crafts Reaction of Methylenecyclopropanes with Arenes

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This paper describes the Brønsted acid mediated reaction of methylenecyclopropanes with various arenes to give the corresponding double Friedel–Crafts reaction products (cyclized products) under mild conditions. A plausible reaction mechanism is discussed on the basis of deuterium labeling and control experiments.

Introduction

Methylenecyclopropanes (MCPs, **1**) are highly strained but readily accessible molecules that serve as useful building blocks in organic synthesis. MCPs undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1]

Transition-metal-catalyzed reactions (for example with Pd, Rh, Ru, and Pt) of MCPs with various reactants have attracted much attention.[2,3] In the field of Lewis acid catalyzed ring-opening reactions of MCPs in this laboratory, we have found that the cyclopropane ring of MCPs can be opened by alcohols and other nucleophiles in a different, novel manner to give the corresponding homoallylic derivatives in good yields under mild conditions.[4] Previously, we reported that methylenecyclopropanes react with various arenes to give the corresponding Friedel–Crafts reaction products in good yields in the presence of the Lewis acid $BF_3 \cdot OEt_2$ (1.0 equiv.) at 60 °C within 5 h.[5] In this paper, we wish to report an interesting Brønsted acid mediated reaction of MCPs with various arenes to give the corresponding double Friedel–Crafts reaction products (cyclized products) exclusively under mild conditions.

Results and Discussion

In our ongoing investigation on Brønsted acids such as trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H; TfOH), sulfuric acid (H_2SO_4), and 4-methylbenzenesulfonic acid (TsOH) as catalysts for the transformation of MCPs, we found that in the presence of TfOH (1.0 equiv.), (diphenylmethylene)cyclopropane (**1a**; 0.4 mmol) reacts with toluene (2.0 mL) to give the cyclized products **2a-1** and **2a-2** as mixtures of regioisomers (Table 1). The reaction temperature significantly affects the yields of **2a-1** and **2a-2** (Table 1, Entries 1–4). At 0 °C, the reaction is sluggish (Table 1, Entry 1), whereas at room temperature (27 °C) and 55 °C the cyclized products were obtained in 70 and 96% yields after 8 and 6 h, respectively (Table 1, Entries 2 and 3). At higher temperature (80 °C), the reaction was greatly accelerated but the cyclized products were obtained in only 76% yield after 2 h (Table 1, Entry 4). The best reaction temperature is therefore 55 °C since at this temperature the cyclized products were isolated in 96% yield after 6 h (Table 1, Entry 3). It should be noted that in order to obtain the cyclized products in high yield in this reaction, 1.0 equiv. of TfOH is required because in the presence of 0.1 equiv. of TfOH, the cyclized products were isolated in only 10% yield even after a prolonged reaction time (Table 1, Entry 5).

Other Brønsted and Lewis acids were examined in this reaction under identical conditions. The results are summarized in Table 2. The Brønsted acids H_2SO_4 and TsOH gave the cyclized products in low yields (Table 2, Entries 1 and 2) and, in addition, the Brønsted acids CF_3CO_2H and acetic acid (AcOH) did not catalyze this reaction at all (Table 2, Entries 3 and 4). However, in the presence of 1.0 equiv. of $BF_3 \cdot OEt_2$ the cyclized products were still obtained in moderate yield (40%) after a prolonged reaction time (30 h; Table 2, Entry 5). It should be emphasized here that within a short reaction time (1–2 h) only the corresponding Friedel–Crafts reaction products were formed.[5] Other Lewis acids such as $Yb(OTf)_3$ and $Sc(OTf)_3$ showed no catalytic activity for this reaction under the same conditions (Table 2, Entries 6 and 7). The best conditions for the

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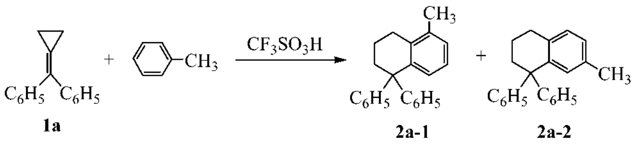
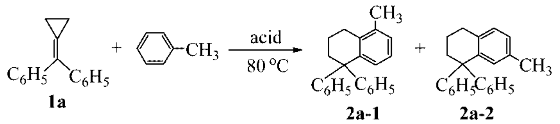
Table 1. Triflic-acid-mediated double Friedel–Crafts reactions of **1a** with toluene.



Entry	Temp. [°C]	Time [h]	Yield [%][a] **(2a-1/2a-2)**
1	0	24	20 (1:0.35)
2	27	8	70 (1:0.25)
3	55	6	96 (1:0.25)
4	80	2	76 (1:0.3)
5	80	48	10 (1:04)[b]

[a] Isolated yields of **2a-1** and **2a-2** in the presence of toluene (2.0 mL) and triflic acid (1.0 equiv.). [b] Triflic acid (0.1 equiv.).

Table 2. The effects of various acids in the double Friedel–Crafts reaction of MCP **1a** with toluene.

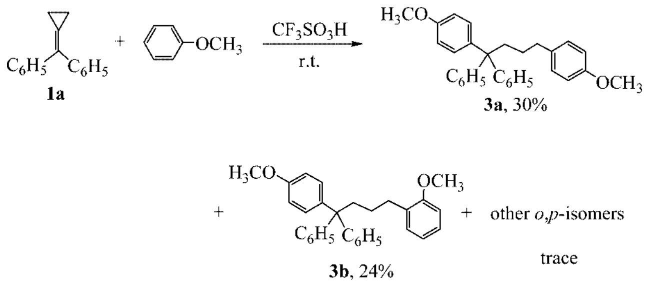


Entry	Acid	Time [h]	Yield [%][a] **(2a-1/2a-2)**
1	H_2SO_4	30	30 (1:0.35)
2	TsOH	12	<3
3	CF_3CO_2H	8	0
4	AcOH	24	0
5	$BF_3{\cdot}OEt_2$	30	40 (1:05)
6	$Yb(OTf)_3$	24	no reaction
7	$Sc(OTf)_3$	24	no reaction

[a] Isolated yields, all reactions were carried out with 1.0 equiv. of the acid in 2.0 mL of toluene.

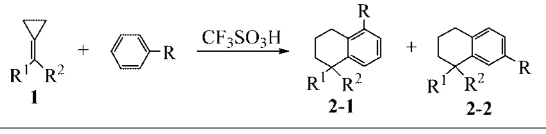
formation of the corresponding cyclized products were found to be in toluene at 55 °C with 1.0 equiv. of the strong Brønsted acid TfOH.

With benzene, toluene, and anisole as substrates, we examined the double Friedel–Crafts reaction with a variety of MCPs **1** under the optimized reaction conditions. The results are shown in Table 3 and Scheme 1. With benzene as substrate, the double Friedel–Crafts reaction was carried out at 80 °C because it is less reactive toward electrophiles in Friedel–Crafts reactions (Table 3, Entries 1, 2, 4, and 6). In fact, electron-rich aromatic compounds are usually more easily able to undergo Friedel–Crafts reactions. In general, the corresponding double Friedel–Crafts reaction products **2** were obtained in moderate to high yields (Table 3, Entries 1–7). The substituents on the aromatic rings of the MCPs significantly affect their reactivities. For MCPs having an electron-withdrawing group, such as a chlorine atom, or a moderately electron-donating group, such as a methyl group, the reaction proceeded smoothly to give the corresponding double Friedel–Crafts reaction products **2c**–**2h** in good to excellent yields (Table 3, Entries 2–7). However, if the MCPs have a strongly electron-donating group, such as a methoxy group, on the aromatic ring, i.e. [bis(4-methoxyphenyl)methylene]cyclopropane (**1e**), we found that the reaction solution immediately became dark and that, although the starting material was consumed quickly, the cyclized product **2** was not formed (Table 3, Entry 8). The same results were obtained even when the reactions were carried out at lower temperature (room temperature and 0 °C). We believe that since the *p*-methoxyphenyl group is a more active moiety for the Friedel–Crafts reaction, a self Friedel–Crafts reaction takes place to give more complex



Scheme 1. Double Friedel–Crafts reaction of **1a** with 2.0 mL of anisole in the presence of triflic acid (1.0 equiv.).

Table 3. Double Friedel–Crafts reactions of various MCPs with toluene or benzene in the presence of triflic acid.



Entry[a]	R^1	R^2		R	Temp. [°C]	Time [h]		Yield [%][b] **(2a-1/2a-2)**
1	C_6H_5	C_6H_5	**1a**	H	80	8	**2b**	70
2	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	H	80	4	**2c**	55
3	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	Me	55	5	**2d**	73 (1:0.7)[c]
4	*p*-ClC_6H_4	*p*-ClC_6H_4	**1c**	H	80	5	**2e**	81
5	*p*-ClC_6H_4	*p*-ClC_6H_4	**1c**	Me	60	8	**2f**	97 (1:0.6)[c]
6	*p*-MeC_6H_4	*p*-MeC_6H_4	**1d**	H	80	3	**2g**	30
7	*p*-MeC_6H_4	*p*-MeC_6H_4	**1d**	Me	55	1.5	**2h**	54 (1:0.5)[c]
8	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**1e**	Me	30	24	–	

[a] All reactions were carried out with MCP (0.4 mmol) and triflic acid (0.4 mmol) in 2.0 mL of toluene or benzene. [b] Isolated yields. [c] The ratios were determined by ^1H NMR spectroscopy.

products when **1e** is used as the substrate. In addition, it should be noted that for electron-deficient aromatic compounds such as chlorobenzene and bromobenzene no reaction occurred under identical conditions.

Interestingly, in the reaction of **1a** (0.4 mmol) with anisole (2.0 mL) mediated by TfOH (1.0 equiv.) at room temperature, the double Friedel–Crafts reaction products **3a** and **3b** were isolated as major products along with a trace of the other two regioisomers, derived from **1a** with two molecules of anisole, rather than the cyclized product (Scheme 1). This is because anisole is more reactive in the Friedel–Crafts reaction. The Friedel–Crafts reaction product formed in situ can react with another molecule of anisole to give the double Friedel–Crafts reaction product **3** in the presence of TfOH. However, in the reaction of **1a** (0.4 mmol) with anisole (1.0 equiv.) mediated by TfOH (1.0 equiv.) in 2.0 mL of dichloromethane (DCM) at room temperature, the reaction was sluggish and the products were complex.

The structures of **2a**–**2h** and **3a** and **3b** were determined by ^{1}H and ^{13}C NMR spectroscopy and a NOESY spectroscopic analysis (see Supporting Information). An X-ray diffraction study of the cyclized product **2a-1** was also carried out. The X-ray crystal structure of **2a-1** is shown in Figure 1.[6]

With 1,4-dimethylbenzene as the substrate, the corresponding double Friedel–Crafts reactions with a variety of MCPs were examined as well. The results are summarized in Table 4. For many MCPs, these reactions proceeded smoothly to give the corresponding cyclized products **2i**–**2p** in moderate to good yields at room temperature under otherwise identical conditions (Table 4, Entries 1–4, 6, and7). For the unsymmetrical MCPs **1f**–**1h**, the corresponding double Friedel–Crafts reaction products **2m**–**2o** were obtained in moderate to good yields (Table 4, Entries 5–7). Moreover, for the aliphatic MCP **1i** ($R^1 = R^2 =$ Bu), the corresponding cyclized product **2p** was formed in 25% yield under identical conditions (Table 4, Entry 8).

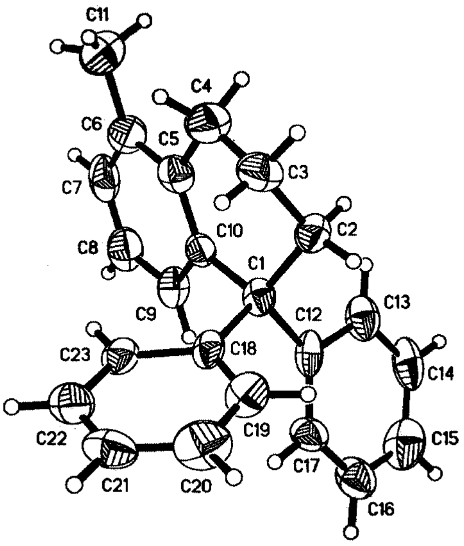
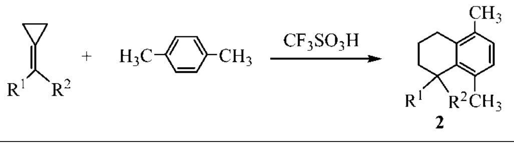


Figure 1. ORTEP drawing of **2a-1**.

A plausible mechanism for this novel double Friedel–Crafts reaction of MCPs with aromatic compounds mediated by the Brønsted acid TfOH is shown in Scheme 2. The MCPs are first protonated by TfOH to give the cationic intermediate **A** (initiation).[7] Then, nucleophilic attack by the arene produces the cationic intermediate **B** and the subsequent release of the proton gives the Friedel–Crafts reaction intermediate **C**. In the presence of Brønsted acid, reprotonation of **C** affords the cationic intermediate **D**. The intramolecular Friedel–Crafts reaction affords the cyclized cationic intermediate **E**, and the release of a proton produces the final product **2** (double Friedel–Crafts reaction). A control experiment showed that the Friedel–Crafts reaction intermediate **C**, derived from the Lewis acid ($BF_3{\cdot}OEt_2$) catalyzed the reaction of **1a** with toluene within a short reaction time,[5] can be transformed into the corresponding cyclized products **2a-1** and **2a-2** in 83% yield in

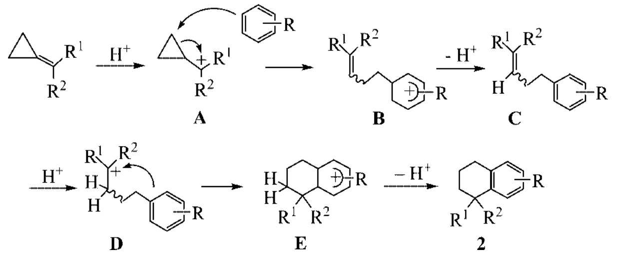
Table 4. Double Friedel–Crafts reactions of various MCPs with xylene in the presence of triflic acid.



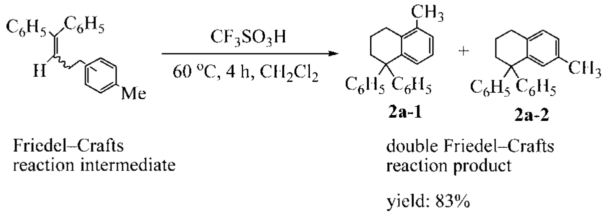
Entry[a]	R1	R2		Temp.	Time [h]	Yield [%][b]
1	C_6H_5	C_6H_5	**1a**	room temp.	2	**2i**, 81
2	p-FC_6H_4	p-FC_6H_4	**1b**	room temp.	2	**2j**, 88
3	p-ClC_6H_4	p-ClC_6H_4	**1c**	room temp.	2	**2k**, 81
4	p-MeC_6H_4	p-MeC_6H_4	**1d**	room temp.	2	**2l**, 70
5	C_6H_5	H	**1f**	room temp.	2	**2m**, 55
6	p-ClC_6H_4	C_6H_5	**1g**	room temp.	2	**2n**, 80
7	p-$MeOC_6H_4$	C_6H_5	**1h**	room temp.	2	**2o**, 50
8	Bu	Bu	**1i**	room temp.	2	**2p**, 25

[a] All reactions were carried out with MCPs **1** (0.4 mmol) and CF_3SO_3H (0.4 mmol) in 2.0 mL of 1,4-dimethylbenzene. [b] Isolated yields.

the presence of TfOH (1.0 equiv.) in dichloromethane under similar conditions to those described above (Scheme 3).

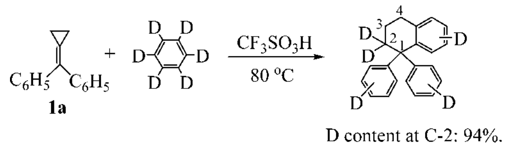


Scheme 2. Proposed mechanism of the ring-opening reactions of MCPs mediated by triflic acid.

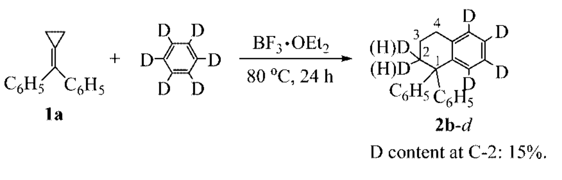


Scheme 3. Control experiment.

To identify the proton source in this reaction, we used [D$_6$]benzene as a substrate to examine its reaction with **1a** in the presence of TfOH (Scheme 4). However, we found that deuterium scrambling occurred at the benzene ring of **1a** under the standard conditions, although the D content at C-2 is 94% (Scheme 4).[8] Next, we used the Lewis acid $BF_3{\cdot}OEt_2$ as the catalyst for this reaction for a prolonged reaction time. We found that the corresponding double Friedel–Crafts reaction product was obtained in 20% yield with a D content at C-2 of 15% (see Supporting Information and Scheme 5).[9] Deuterium incorporation did not occur at the other carbon atoms of **2b**, which is in agreement with the proposed mechanism.



Scheme 4. Deuterium labeling experiment.



Scheme 5. Deuterium labeling experiment.

Conclusion

We have disclosed an interesting transformation involving MCPs and aromatic compounds in the presence of the Brønsted acid TfOH. In this transformation, the double Friedel–Crafts products **2** can be obtained in moderate to good yields, depending on the substituents of the MCPs and aromatic substrates. A wide range of aromatic compounds and MCPs have been examined. The supposed reaction has been discussed on the basis of a deuterium-labeling and a control experiment. This process provides a novel and efficient route for the synthesis of naphthalene derivatives. Efforts are in progress to further elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded with a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured with a Perkin–Elmer 983 spectrometer. Mass spectra were recorded with an HP-5989 instrument and HR mass spectra were measured with a Finnigan MA$^+$ mass spectrometer. C,H,N 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. Flash column chromatography was carried out using 300–400 mesh silica gel.

General Procedure for the Triflic-Acid-Catalyzed Double Friedel–Crafts Reaction of Methylenecyclopropanes with Arenes: A mixture of MCP **1** (0.4 mmol), TfOH (CF_3SO_3H) (0.4 mmol), and arene (2.0 mL) was stirred at 30–80 °C for 1.5–8 h. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using petroleum ether as eluent to give the product.

5-Methyl-1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (2a-1) and 7-Methyl-1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (2a-2). Compound **2a** was obtained as a colorless solid (114 mg, 96%) as a mixture of **2a-1** and **2a-2** (**2a-1**/**2a-2** = 1:0.25). M.p. 112–118 °C. IR (KBr): $\tilde{\nu}$ = 700, 758, 1032, 1444, 1491, 1594, 2867, 2933, 3015, 3052 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): **2a-1**: δ = 1.67–1.68 (m, 2 H, CH_2), 2.28 (s, 3 H, CH_3), 2.62–2.63 (m, 2 H, CH_2), 2.72–2.74 (m, 2 H, CH_2), 6.51–6.54 (m, 1 H, ArH), 6.93–6.98 (m, 1 H, ArH), 7.05–7.28 (m, 11 H, ArH) ppm; **2a-2**: δ = 1.67–1.68 (m, 2 H, CH_2), 2.16 (s, 3 H, CH_3), 2.62–2.63 (m, 2 H, CH_2), 2.84–2.86 (m, 2 H, CH_2), 6.51–6.54 (m, 1 H, ArH), 6.93–6.98 (m, 1 H, ArH), 7.05–7.28 (m, 11 H, ArH) ppm. MS (EI): *m*/*z* = 91 (42), 178 (35), 192 (41), 221 (99), 255 (33), 269 (57), 298 (100) [M$^+$]. $C_{23}H_{22}$ (298.17): calcd. C 92.57, H 7.43; found C 92.60, H 7.24.

1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (2b): This compound was obtained as a colorless solid (80 mg, 70%). M.p. 93–95 °C. IR (KBr): $\tilde{\nu}$ = 700, 756, 1444, 1490, 1594, 2859, 2933, 3007, 3059 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.58–1.66 (m, 2 H, CH_2), 2.58–2.62 (m, 2 H, CH_2), 2.82–2.87 (t, *J* = 6.9 Hz, 2 H, CH_2), 6.65 (d, *J* = 7.8 Hz, 1 H, ArH), 6.95–7.00 (m, 1 H, ArH), 7.05–7.26 (m, 12 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 19.1, 29.3, 38.3, 53.7, 125.1, 125.9, 126.1, 127.7, 129.2, 129.4, 131.5, 137.2, 142.8, 148.3 ppm. MS (EI): *m*/*z* = 77 (100), 91 (57), 115 (18), 128 (16), 165 (20), 178 (46), 207 (14), 255 (8), 284 (14) [M$^+$]. $C_{22}H_{20}$ (284.16): calcd. C 92.91, H 7.09; found C 92.70, H 7.16.

1,1-Bis(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene (2c): This compound was obtained as a colorless solid (71 mg, 55%). M.p. 153–155 °C. IR (KBr): $\tilde{\nu}$ = 570, 758, 830, 1163, 1226, 1505, 1602, 2830, 2867, 2941, 3067 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.54–1.66 (m, 2 H, CH_2), 2.63–2.67 (m, 2 H, CH_2), 2.87 (t, *J* = 6.9 Hz, 2 H, CH_2), 6.61 (d, *J* = 7.5 Hz, 1 H, ArH), 6.90–7.15 (m, 12 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 19.0, 29.1, 38.6, 52.7, 114.5 (d, $J_{C,F}$ = 20.9 Hz), 125.3, 126.4, 129.4, 130.8 (d, $J_{C,F}$ = 8.3 Hz), 131.1, 137.1, 142.4, 143.8 (d, $J_{C,F}$ = 2.8 Hz), 161.1 (d, $J_{C,F}$ = 244.7 Hz) ppm. MS (EI): *m/z* = 75 (52), 96 (100), 109 (41), 128 (14), 196 (33), 224 (13), 320 (7) [M$^+$]. $C_{22}H_{18}F_2$ (320.14): calcd. C 82.48, H 5.66; found C 82.49, H 5.56.

1,1-Bis(4-fluorophenyl)-5-methyl-1,2,3,4-tetrahydronaphthalene (2d-1) and 1,1-Bis(4-fluorophenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (2d-2): Compound **2d** was obtained as a colorless solid (98 mg, 73%) as a mixture of **2d-1** and **2d-2** (**2d-1**/**2d-2** = 1:0.7). M.p. 157–165 °C. IR (KBr): ṽ = 808, 830, 1015, 1162, 1228, 1506, 1601, 2874, 2941, 3052 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): **2d-1**: δ = 1.57–1.67 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.51–2.55 (m, 2 H, CH$_2$), 2.69 (t, *J* = 6.9 Hz, 2 H, CH$_2$), 6.40–6.50 (m, 1 H, ArH), 6.88–7.04 (m, 10 H, ArH) ppm; **2d-2**: δ = 1.57–1.67 (m, 2 H, CH$_2$), 2.14 (s, 3 H, CH$_3$), 2.51–2.55 (m, 2 H, CH$_2$), 2.80 (t, *J* = 6.9 Hz, 2 H, CH$_2$), 6.40–6.50 (m, 1 H, ArH), 6.88–7.04 (m, 10 H, ArH) ppm. MS (EI): *m/z* = 96 (78), 109 (100), 210 (67), 238 (89), 291 (35), 305 (50), 334 (79) [M$^+$]. $C_{23}H_{20}F_2$ (334.15): calcd. C 82.61, H 6.03; found C 82.72, H 6.08.

1,1-Bis(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalene (2e): This compound was obtained as a colorless solid (114 mg, 81%). M.p. 155–157 °C. IR (KBr): ṽ = 758, 820, 1012, 1096, 1398, 1449, 1488, 2867, 2933, 3052 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.59–1.63 (m, 2 H, CH$_2$), 2.51–2.55 (m, 2 H, CH$_2$), 2.85 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.60 (d, *J* = 8.1 Hz, 1 H, ArH), 6.94–7.22 (m, 11 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 18.9, 29.1, 38.4, 53.0, 125.3, 126.5, 128.0, 129.5, 130.7, 131.1, 132.0, 137.1, 141.7, 146.4 ppm. MS (EI): *m/z* = 112(95), 125 (100), 178 (61), 212 (41), 240 (46), 252 (56), 289 (33), 317 (23), 352 (29) [M$^+$]. $C_{22}H_{18}Cl_2$ (352.08): calcd. C 74.79, H 5.14; found C 74.94, H 5.09.

1,1-Bis(4-chlorophenyl)-5-methyl-1,2,3,4-tetrahydronaphthalene (2f-1) and 1,1-Bis(4-chlorophenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (2f-2): Compound **2f** was obtained as a colorless solid (142 mg, 97%) as a mixture of **2f-1** and **2f-2** (**2f-1**/**2f-2** = 1:0.6). M.p. 122–135 °C. IR (KBr): ṽ = 557, 739, 782, 820, 1012, 1096, 1264, 1398, 1455, 1470, 1489, 2859, 2933, 2941, 3030, 3067 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): **2f-1**: δ = 1.55–1.65 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.50–2.51 (m, 2 H, CH$_2$), 2.66–2.71 (m, 2 H, CH$_2$), 6.39–6.37 (m, 1 H, ArH), 6.89–7.21 (m, 10 H, ArH) ppm; **2f-2**: δ = 1.55–1.65 (m, 2 H, CH$_2$), 2.14 (s, 3 H, CH$_3$), 2.50–2.51 (m, 2 H, CH$_2$), 2.76–2.83 (m, 2 H, CH$_2$), 6.39–6.37 (m, 1 H, ArH), 6.89–7.21 (m, 10 H, ArH) ppm. MS (EI): *m/z* = 112 (57), 125 (90), 226 (28), 254 (93), 303 (56), 331 (31), 366 (100) [M$^+$]. HRMS (EI): calcd. for $C_{23}H_{20}Cl_2$ 366.0942; found 366.0920.

1,1-Di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene (2g): This compound was obtained as a colorless solid (37 mg, 30%). M.p. 130–132 °C. IR (KBr): ṽ = 753, 810, 1021, 1039, 1190, 1448, 1487, 1510, 2868, 2940, 3020, 3053 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.58–1.67 (m, 2 H, CH$_2$), 2.31 (s, 6 H, CH$_3$), 2.54–2.58 (m, 2 H, CH$_2$), 2.85 (t, *J* = 6.9 Hz, 2 H, CH$_2$), 6.66 (d, *J* = 7.8 Hz, 1 H, ArH), 6.93–7.13 (m, 11 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 19.1, 20.9, 29.3, 38.4, 53.0, 125.0, 125.9, 128.4, 129.2, 129.3, 131.4, 135.3, 137.1, 143.1, 145.5 ppm. MS (EI): *m/z* = 91 (100), 105 (31), 129 (12), 192 (19), 220 (13), 312 (6) [M$^+$]. $C_{24}H_{24}$ (312.19): calcd. C 92.26, H 7.74; found C 92.54, H 7.78.

5-Methyl-1,1-di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene (2h-1) and 7-Methyl-1,1-di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene (2h-2): Compound **2h** was obtained as a colorless solid (70 mg, 54%) as a mixture of **2h-1** and **2h-2** (**2h-1**/**2h-2** = 1:0.5). M.p. 80–100 °C. IR (KBr): ṽ = 563, 766, 810, 1020, 1035, 1109, 1190, 1451, 1500, 2867, 2941, 3022, 3044 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): **2h-1**: δ = 1.50–1.68 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.31 (s, 6 H, CH$_3$), 2.53–2.57 (m, 2 H, CH$_2$), 2.68 (t, *J* = 6.9 Hz, 2 H, CH$_2$), 6.47–6.56 (m, 1 H, ArH), 6.88–7.06 (m, 10 H, ArH) ppm; **2h-2**: δ = 1.50–1.68 (m, 2 H, CH$_2$), 2.13 (s, 3 H, CH$_3$), 2.31 (s, 6 H, CH$_3$), 2.53–2.57 (m, 2 H, CH$_2$), 2.79 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.47–6.56 (m, 1 H, ArH), 6.88–7.06 (m, 10 H, ArH) ppm. MS (EI): *m/z* = 91 (29), 105 (44), 206 (34), 234 (71), 283 (50), 311 (19), 326 (100) [M$^+$]. HRMS (EI): calcd. for $C_{25}H_{26}$ 326.2034; found 326.2048.

5,8-Dimethyl-1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (2i): This compound was obtained as a colorless solid (101 mg, 81%). M.p. 109–111 °C. IR (KBr): ṽ = 571, 739, 810, 1031, 1170, 1187, 1213, 1265, 1380, 1447, 1460, 1492, 1571, 1598, 2868, 2937, 3056 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.32 (s, 3 H, CH$_3$), 1.42–1.45 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.43–2.45 (m, 2 H, CH$_2$), 2.70 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.79 (d, *J* = 7.2 Hz, 1 H, ArH), 7.01 (d, *J* = 7.8 Hz, 1 H, ArH), 7.14–7.25 (m, 10 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.2, 20.3, 23.4, 28.7, 44.9, 54.6, 125.5, 127.6, 128.1, 129.3, 129.5, 134.4, 137.0, 137.1, 141.1 146.8 ppm. MS (EI): *m/z* = 78 (100.00), 91 (55.25), 165 (22.97), 206 (21.03), 283 (13.07), 312 (24.46) [M$^+$]. $C_{24}H_{24}$ (312.19): calcd. C 92.26, H 7.74; found C 92.35, H 7.79.

1,1-Bis(4-fluorophenyl)-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (2j): This compound was obtained as a colorless solid (122 mg, 88%). M.p. 130–132 °C. IR (KBr): ṽ = 568, 740, 806, 1034, 1163, 1231, 1265, 1381, 1410, 1462, 1505, 1600, 2870, 2938, 3056 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.32 (s, 3 H, CH$_3$), 1.41–1.45 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.37–2.40 (m, 2 H, CH$_2$), 2.70 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.79–7.20 (m, 10 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.1, 20.2, 23.5, 28.6, 45.1, 53.6, 114.4 (d, $J_{C,F}$ = 20.8 Hz), 128.4, 129.5, 130.9 (d, $J_{C,F}$ = 7.3 Hz), 134.6, 136.68, 136.70, 140.7, 142.4 (d, $J_{C,F}$ = 3.0 Hz), 160.8 (d, $J_{C,F}$ = 244.6 Hz) ppm. MS (EI): *m/z* = 109 (47.96), 210 (42.53), 225 (82.42), 305 (59.52), 319 (71.03), 333 (15.95), 348 (100.00) [M$^+$]. $C_{24}H_{22}F_2$ (348.17): calcd. C 82.76, H 6.36; found C 82.87, H 6.65.

1,1-Bis(4-chlorophenyl)-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (2k): This compound was obtained as a colorless solid (123 mg, 81%). M.p. 162–164 °C. IR (KBr): ṽ = 568, 740, 818, 1050, 1096, 1165, 1209, 1376, 1403, 1460, 1489, 1571, 2869, 2938, 3055 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.32 (s, 3 H, CH$_3$), 1.41–1.45 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.34–2.38 (m, 2 H, CH$_2$), 2.69 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.80 (d, *J* = 7.5 Hz, 1 H, ArH), 7.03 (d, *J* = 7.8 Hz, 1 H, ArH), 7.12–7.23 (m, 8 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.0, 20.2, 23.5, 28.5, 44.9, 53.8, 127.8, 128.5, 129.5, 130.8, 131.5, 134.7, 136.6, 136.7, 140.0, 145.0 ppm. MS (EI): *m/z* = 125 (26.90), 206 (21.42), 240 (31.44), 302 (24.51), 317 (59.45), 351 (38.93), 380 (100.00) [M$^+$]. $C_{24}H_{22}Cl_2$ (380.11): calcd. C 75.59, H 5.81; found C 75.61, H 5.94.

5,8-Dimethyl-1,1-di-*p*-tolyl-1,2,3,4-tetrahydronaphthalene (2l): This compound was obtained as a yellow liquid (95 mg, 70%). IR (KBr): ṽ = 569, 734, 811, 1020, 1034, 1168, 1211, 1379, 1460, 1509, 1608, 2855, 2925, 3051 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.33 (s, 3 H, CH$_3$), 1.43–1.45 (m, 2 H, CH$_2$), 2.24 (s, 3 H, CH$_3$), 2.31 (s, 6 H, 2CH$_3$), 2.38–2.42 (m, 2 H, CH$_2$), 2.69 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 6.77–7.13 (m, 10 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.3, 20.3, 20.9, 23.5, 28.7, 44.9, 53.9, 128.0, 128.3, 129.2, 129.4, 134.2, 134.9, 136.8, 137.2, 141.4, 144.0 ppm. MS (EI): *m/z* = 105 (19.26), 206 (15.77), 220 (42.98), 249 (15.51), 297 (38.93), 311 (38.74), 340 (100.00) [M$^+$]. HRMS (EI): calcd. for $C_{26}H_{28}$ 340.2191; found 340.2212.

5,8-Dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (2m): This compound was obtained as a yellow liquid (52 mg, 55%). IR (KBr): ṽ = 559, 754, 809, 1030, 1163, 1379, 1460, 1492, 1601, 2866, 2932, 3059 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.63–1.68 (m, 2 H, CH$_2$), 1.91 (s, 3 H, CH$_3$), 1.98–2.00 (m, 2 H, CH$_2$), 2.18 (s, 3 H, CH$_3$), 2.51–2.82 (m, 2 H, CH$_2$), 4.22–4.24 (m, 1 H, CH), 6.88–7.24 (m, 7 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 17.2, 19.4, 19.7, 27.1, 31.6, 41.9, 125.5, 127.4, 127.5, 127.9, 128.5, 133.9, 134.7, 136.1, 136.4, 146.3 ppm. MS (EI): *m/z* = 91 (35.84), 143 (35.82), 158 (40.76), 193 (24.83), 221 (56.23), 236 (100.00) [M$^+$]. HRMS (MALDI): calcd. for C$_{18}$H$_{20}$ [M$^+$ + 23] 259.1460; found 259.1457.

1-(4-Chlorophenyl)-5,8-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (2n): This compound was obtained as a colorless solid (111 mg, 80%). M.p. 132–134 °C. IR (KBr): $\tilde{\nu}$ = 570, 740, 826, 1013, 1050, 1096, 1165, 1213, 1380, 1398, 1460, 1490, 1598, 2868, 2937, 3055 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.32 (s, 3 H, CH$_3$), 1.42–1.46 (m, 2 H, CH$_2$), 2.26 (s, 3 H, CH$_3$), 2.37–2.43 (m, 2 H, CH$_2$), 2.71 (t, *J* = 6.8 Hz, 2 H, CH$_2$), 6.81 (d, *J* = 7.2 Hz, 1 H, ArH), 7.04 (d, *J* = 8.1 Hz, 1 H, CH), 7.16–7.29 (m, 9 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.1, 20.3, 23.5, 28.6, 44.9, 54.2, 125.7, 127.69, 127.73, 128.3, 129.4, 130.9, 131.3, 134.5, 136.8, 136.9, 140.6, 145.6, 146.2 ppm. MS (EI): *m/z* = 91 (14.83), 165 (16.54), 206 (32.94), 268 (27.77), 283 (35.37), 317 (59.34), 346 (100.00) [M$^+$]. C$_{24}$H$_{23}$Cl (346.1488): calcd. C 83.10, H 6.68; found C 82.81, H 6.72.

1-(4-Methoxyphenyl)-5,8-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (2o): This compound was obtained as a yellow liquid (68 mg, 50%). IR (KBr): $\tilde{\nu}$ = 572, 733, 809, 1034, 1183, 1206, 1380, 1461, 1508, 1607, 2868, 2935, 3055 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.33 (s, 3 H, CH$_3$), 1.42–1.48 (m, 2 H, CH$_2$), 2.25 (s, 3 H, CH$_3$), 2.41 (t, *J* = 5.4 Hz, 2 H, CH$_2$), 2.71 (t, *J* = 6.6 Hz, 2 H, CH$_2$), 3.79 (s, 3 H, CH$_3$), 6.78–7.25 (m, 11 H, ArH) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 19.2, 20.3, 23.5, 28.7, 44.9, 53.9, 55.2, 112.9, 125.4, 127.6, 128.1, 129.3, 129.4, 130.7, 134.4, 136.8, 137.1, 138.4, 141.3, 147.6, 157.3 ppm. MS (EI): *m/z* = 121 (13.64), 206 (25.96), 234 (55.91), 265 (18.28), 299 (19.49), 313 (35.26), 342 (100.00) [M$^+$]. HRMS (EI): calcd. for C$_{25}$H$_{26}$O 342.1984; found 342.1957.

1,1-Dibutyl-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (2p): This compound was obtained as a colorless liquid (27 mg, 25%). IR (KBr): $\tilde{\nu}$ = 805, 1378, 1459, 2870, 2929, 2955 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 0.82–0.91 (m, 6 H, CH$_3$), 1.18–1.30 (m, 12 H), 1.72–1.73 (m, 2 H, CH$_2$), 2.17 (s, 3 H, CH$_3$), 2.41 (s, 3 H, CH$_3$), 2.26–2.28 (m, 2 H, CH$_2$), 2.51–2.58 (m, 2 H, CH$_2$), 6.80–6.89 (m, 2 H, ArH) ppm. MS (EI): *m/z* = 84 (74), 145 (57), 159 (75), 215 (100), 229 (15), 272 (11) [M$^+$]. HRMS (MALDI):calcd. for C$_{20}$H$_{33}$ [M$^+$ + 1] 273.2577; found 273.2588.

3a: This compound was obtained as a colorless liquid (50 mg, 30%). IR (KBr): $\tilde{\nu}$ = 703, 748, 828, 1034, 1182, 1248, 1298, 1442, 1463, 1493, 1511, 1582, 1610, 2834, 2948, 2998, 3031, 3055 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.40–1.43 (m, 2 H, CH$_2$), 2.53–2.58 (m, 4 H, CH$_2$), 3.77 (s, 3 H, OCH$_3$), 3.78 (s, 3 H, OCH$_3$), 6.76–6.82 (m, 4 H, ArH), 7.03 (d, *J* = 8.7 Hz, 2 H, ArH), 7.11 (d, *J* = 8.7 Hz,, 2 H, ArH), 7.10–7.24 (m, 10 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 27.5, 35.4, 39.7, 55.1, 55.2, 55.8, 113.0, 113.6, 125.6, 127.7, 129.1, 129.3, 130.2, 134.2, 139.5, 147.7, 157.3, 157.6 ppm. MS (EI): *m/z* = 121 (19), 165 (10), 195 (6), 229 (3), 273 (100), 422 (1) [M$^+$]. HRMS (MALDI): calcd. for C$_{30}$H$_{30}$O$_2$ [M$^+$ + 23] 445.2138; found 445.2159.

3b: This compound was obtained as a colorless liquid (40 mg, 24%). IR (KBr): $\tilde{\nu}$ = 703, 753, 829, 1035, 1113, 1183, 1245, 1291, 1441, 1463, 1493, 1510, 1601, 2834, 2936, 2951, 3037, 3067 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.37–1.42 (m, 2 H, CH$_2$), 2.57–2.64 (m, 4 H, CH$_2$), 3.75 (s, 3 H, OCH$_3$), 3.75 (s, 3 H, OCH$_3$), 6.73 (d, *J* = 7.2 Hz, 2 H, ArH), 6.74–6.83 (m, 2 H, ArH), 7.02 (d, *J* = 7.2 Hz, 2 H, ArH), 7.09–7.25 (m, 12H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 25.7, 30.7, 40.2, 55.1, 55.15, 55.8, 110.1, 112.9, 120.2, 125.6, 126.9, 127.6, 129.1, 129.8, 130.2, 130.6, 139.7, 147.9, 157.3, 157.4 ppm. MS (EI): *m/z* = 91 (25), 121 (19), 165 (12), 195 (8), 229 (6), 273 (100), 422 (1) [M$^+$]. HRMS (MALDI): calcd. for C$_{30}$H$_{30}$O$_2$ [M$^+$ + 23] 445.2138; found 445.2153.

Supporting Information (see on the first page of this article): ^{1}H and ^{13}C NMR spectra for double Friedel–Crafts reaction products and X-ray crystal data for **2a-1**.

Acknowledgments

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