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$AlCl_3$-mediated tandem Friedel–Crafts reactions of vinylidenecyclopropanes with acyl chlorides: a facile synthetic method for the construction of 1-[2-(2,2-diarylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone derivatives

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Abstract

$AlCl_3$-mediated tandem Friedel–Crafts reaction of vinylidenecyclopropanes with acyl chlorides produced the corresponding 1-[2-(2,2-diarylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone derivatives in moderate to good yields under mild conditions within short reaction time.

Keywords: $AlCl_3$; Friedel–Crafts reaction; Vinylidenecyclopropanes; Acyl chlorides; 1-[2-(2,2-Diarylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone derivatives; Tandem reaction

1. Introduction

Skeleton rearrangements of highly strained small rings with multiple bonds and functional groups have attracted much attention from both synthetic and mechanistic viewpoints.[1] Among these interesting substances, vinylidenecyclopropanes (VDCPs) are highly strained but readily accessible and stable molecules that serve as useful building blocks in organic synthesis.[1] Thus far, it has been known that VDCPs can undergo a variety of ring-opening/cycloaddition reactions upon heating or photoirradiation as well as in the presence of Lewis acids because the relief of ring strain can provide a powerful thermodynamic driving force.[2,3] As an interesting example, recently we have found a novel *intramolecular* rearrangement of diarylvinylidenecyclopropanes having three substituents at the 1- and 2-positions of the corresponding cyclopropane catalyzed by Lewis acids to give 6a*H*-benzo[*c*]fluorine derivatives via a double intramolecular Friedel–Crafts reaction or to give an indene derivative via an intramolecular Friedel–Crafts reaction.[3a] These results stimulated us to further explore the transformation of VDCPs under mild conditions. Herein, we wish to report an interesting $AlCl_3$-mediated tandem *intermolecular* Friedel–Crafts reaction of VDCPs **1** with acyl chlorides **2** that effectively produces 1-[2-(2,2-diarylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone derivatives **3** in good to high yields under mild conditions.[4]

2. Results and discussion

Initial examinations using diphenylvinylidenecyclopropane (**1a**, 0.2 mmol) having two phenyl groups at the 1-position and acetyl chloride (**2a**, 0.16–0.3 mmol) as the substrates in the presence of $AlCl_3$ (0.1–0.3 mmol, 0.5–1.5 equiv) in 1,2-dichloroethane (DCE, 2.0 mL) were aimed at determining the best conditions for this intermolecular Friedel–Crafts reaction and the results of these experiments are summarized in Table 1. We found that using $AlCl_3$ (1.0 equiv) as a Lewis acid, 1-[2-(2,2-diphenylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone **3a** was formed in 50% yield at room temperature (20 °C) from

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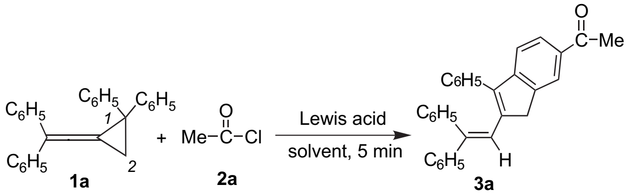
Table 1
Optimization of the reaction conditions



Entry[a]	Lewis acid	**1a**:**2a**	Solvent	Temp (°C)	Yield of **3a**[b] [%]
1	$AlCl_3$ (1.0 equiv)	1:1.5	DCE	rt	44
2	$AlCl_3$ (0.5 equiv)	1:1	DCE	rt	26
3	$AlCl_3$ (1.0 equiv)	1:1	DCE	rt	50
4	$AlCl_3$ (1.5 equiv)	1:1	DCE	rt	Complex
5	$AlCl_3$ (1.0 equiv)	1:0.8	DCE	rt	16
6	$AlCl_3$ (1.0 equiv)	1:1	DCE	−8	Complex
7	$AlCl_3$ (1.0 equiv)	1:1	DCE	55	Complex
8	$AlCl_3$ (1.0 equiv)	1:1	DCE	rt	Complex[c]
9	$AlCl_3$ (1.0 equiv)	1:1	CS_2	rt	Complex
10	*$AlCl_3$ (1.0 equiv)*	*1:1*	*DCM*	*rt*	*70*
11	$AlCl_3$ (1.0 equiv)	1:1	THF	rt	Trace
12	$AlCl_3$ (1.0 equiv)	1:1	$MeNO_2$	rt	Complex
13	$AlCl_3$ (1.0 equiv)	1:1	$Cl_2CHCHCl_2$	rt	67
14	$AlCl_3$ (1.0 equiv)	1:1	DCM	−8	53
15	$AlCl_3$ (1.0 equiv)	1:1	DCM	−78	Complex
16	$AlCl_3$ (1.0 equiv)	1:1	DCM	rt	61[d]
17	$AlCl_3$ (1.5 equiv)	1:1.5	DCM	−78	26
18	$AlCl_3$ (3.0 equiv)	1:3.0	DCM	rt	Complex
19	$ZnCl_2$ (1.0 equiv)	1:1	DCM	rt	Trace
20	$FeCl_3$ (1.0 equiv)	1:1	DCM	rt	Trace
21	$ZrCl_4$ (1.0 equiv)	1:1	DCM	rt	18
22	$Yb(OTf)_3$ (1.0 equiv)	1:1	DCM	rt	Trace
23	$Zr(OTf)_4$ (1.0 equiv)	1:1	DCM	rt	Trace

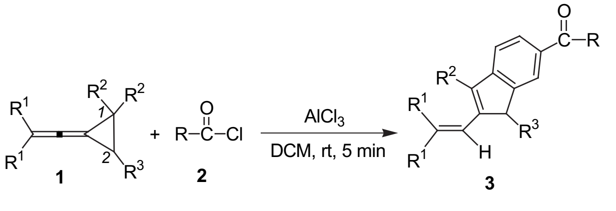
[a] All reactions were carried out using **1a** (0.20 mmol), **2a** (0.20 mmol), and $AlCl_3$ (0.20 mmol, 1.0 equiv) in solvent (2.0 mL) unless otherwise specified.
[b] Isolated yields.
[c] DBU (0.20 mmol) was added.
[d] DCM: 1.0 mL was employed.

the reaction of **1a** (0.2 mmol) with **2a** (0.2 mmol) (Table 1, entry 3). In the presence of excess amounts of $AlCl_3$ (1.5 equiv), complex product mixtures were obtained, although 26% of **3a** was formed using $AlCl_3$ (0.5 equiv) as a Lewis acid (Table 1, entries 2 and 4). Increasing and decreasing the amounts of **2a** did not improve the yields of **3a** (Table 1, entries 1 and 5). Raising and lowering the reaction temperatures, complex product mixtures were formed (Table 1, entries 6 and 7). In order to get rid of the in situ formed HCl, DBU was added into the reaction system, but leading to the formation of complex product mixtures (Table 1, entry 8). Examination of the solvent effects revealed that dichloromethane (DCM) is the solvent of choice to afford **3a** in 70% yield at room temperature (Table 1, entries 9–13). Raising and lowering the reaction temperatures as well as changing the ratios of reactants in DCM did not improve the yield of **3a** either (Table 1, entries 14–18). In higher concentration of the reaction solution (1.0 mL of DCM), **3a** was formed in 61% yield (Table 1, entry 16). Other Lewis acids such as $ZnCl_2$, $FeCl_3$, $ZrCl_4$, $Yb(OTf)_3$, and $Zr(OTf)_4$ are not as effective as $AlCl_3$ under identical conditions (Table 1, entries 17–21). Therefore, the best reaction conditions are to carry out the reaction in 2.0 mL (or 1.0 mL) of DCM at room temperature using $AlCl_3$ (0.2 mmol, 1.0 equiv) as a Lewis acid with **1a** (0.2 mmol, 1.0 equiv) and **2a** (0.2 mmol, 1.0 equiv). Under these optimal conditions, these reactions generally completed within 5 min.

With these optimal reaction conditions identified, we next carried out this interesting (1-phenyl-3*H*-inden-5-yl)ethanone derivative forming reaction using a variety of starting materials **1** and **2**. The results of these experiments are summarized in Table 2. As can be seen from Table 2, the corresponding (1-phenyl-3*H*-inden-5-yl)ethanone derivatives **3** were obtained in 23–80% yields (Table 2, entries 1–11). Adding moderately electron-donating substituents, such as a methyl group, on the aromatic rings of **1** afforded the corresponding 1-[2-(2,2-di-*p*-tolylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone **3d** in 23% yield (Table 2, entry 3). The reaction of VDCP **1d** with benzoyl chloride produced the corresponding product **3j** in 80% yield (Table 2, entry 9). When the reaction was carried out in 1.0 mL of DCM, the corresponding products were obtained in slightly lower yields (the results shown in brackets). Product structures were determined by ^{1}H and ^{13}C NMR spectroscopic data, HRMS, microanalysis. Furthermore, the X-ray crystal structures of **3a** and **3e** were determined and their CIF data are presented in the Supplementary data (Figs. 1 and 2).[5]

Interestingly, introducing electron-withdrawing group, such as a chloro or fluoro atom, on the aromatic ring of R^2 of VDCPs **1f** and **1g** furnished the corresponding indene derivatives **4**, (1-(4-{2-[6-chloro-3-(4-chlorophenyl)-1*H*-inden-2-yl]-1-phenylvinyl}phenyl)-ethanone **4a** and 1-(4-{2-[6-fluoro-3-(4-fluorophenyl)-1*H*-inden-2-yl]-1-phenylvinyl}-phenyl)-ethanone **4b**, R=Me), in moderate yields as mixtures of *E*- and *Z*-isomers under the standard conditions (Table 3, entries 1 and 2). The crystal structure of *trans*-**4a** has been unambiguously determined by X-ray diffraction (Fig. 3).[6] Using benzoyl chloride,

Table 2
$AlCl_3$-mediated Friedel–Crafts reactions of **1** with **2** under these optimized reaction conditions



Entry	$R^1/R^2/R^3$	R	Yield of **3**[a] [%]
1	C_6H_5/C_6H_5/H, **1a**	Et	**3b**, 64 (44)[b]
2	**1a**	C_6H_5	**3c**, 46 (34)[b]
3	*p*-MeC_6H_4/C_6H_5/H, **1b**	Me	**3d**, 23
4	*p*-FC_6H_4/C_6H_5/H, **1c**	Me	**3e**, 60 (50)[b]
5	**1c**	C_6H_5	**3f**, 70
6	**1c**	*p*-$MeOC_6H_4$	**3g**, 64
7	**1c**	*p*-ClC_6H_4	**3h**, 61
8	*p*-ClC_6H_4/C_6H_5/H, **1d**	Me	**3i**, 61 (42)[b]
9	**1d**	C_6H_5	**3j**, 80
10	**1d**	*p*-$MeOC_6H_4$	**3k**, 50
11	C_6H_5/C_6H_5/Me, **1e**	Me	**3l**, 77

[a] Isolated yields.
[b] DCM: 1.0 mL was employed.

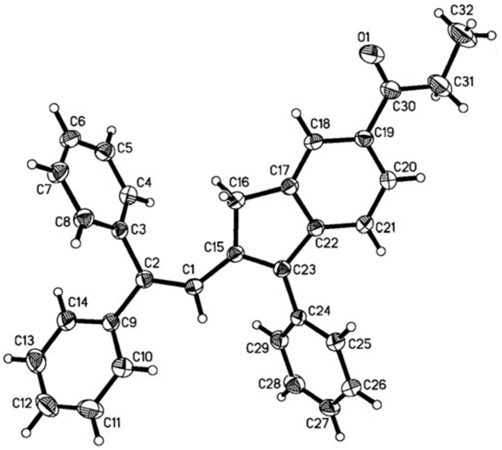


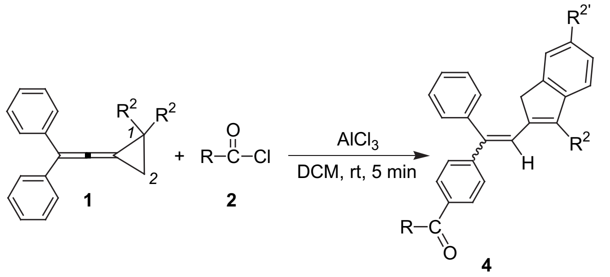
Figure 1. ORTEP drawing of **3a**.

p-chlorobenzoyl chloride, and *p*-methoxybenzoyl chloride as acyl reagents under identical conditions, similar results were obtained (Table 3, entries 3–5).

Since VDCP **1a** can rearrange to the corresponding indene derivative in the presence of Lewis acid,[3] a control experiment of indene **5a**, derived from **1a** in the presence of $Yb(OTf)_3$, with acetyl chloride was carried out under the standard conditions (Scheme 1). We found that the reaction became sluggish to give **3a** in 50% yield after 24 h, suggesting that the reaction of **1** with acyl chloride indeed can be accelerated by release of cyclopropyl ring strain (27 kcal/mol)[7] to provide a thermodynamic driving force and by the π-character of the ring bonds of a cyclopropane affording the kinetic opportunity to initiate the unleashing of the strain.[8]

Table 3

$AlCl_3$-mediated Friedel–Crafts reactions of **1** with **2** under these optimized reaction conditions



mixtures of cis- and trans-isomers

Entry	R^2	R	Yield of **3** [%] (trans:cis)[a]
1	*p*-ClC_6H_4, **1f**	Me	**4a**, 50 (9:1) [23 (9:1)][b]
2	*p*-FC_6H_4, **1g**	Me	**4b**, 34 (5:1)
3	**1f**	C_6H_5	**4c**, 33 (40:1)
4	**1f**	*p*-ClC_6H_4	**4d**, 32 (100:1)
5	**1f**	*p*-$CH_3OC_6H_4$	**4e**, 35 (5:1)

[a] Isolated yields.

[b] DCM: 1.0 mL was employed.

On the basis of above results, a plausible mechanism for this interesting $AlCl_3$-mediated tandem Friedel–Crafts reaction is tentatively outlined in Scheme 2 using **1a** as a model. The coordination of **1a** with $AlCl_3$ produces the initial zwitterionic intermediate **A**, from which the corresponding cyclopropyl ring-opened zwitterionic intermediate **B** is formed. Intramolecular Friedel–Crafts reaction with the aromatic group at the C-1 position and the intermolecular Friedel–Crafts reaction with the in situ generated acyl cation in the presence of $AlCl_3$ take place at the same time to produce zwitterionic intermediate **C**, which affords the corresponding zwitterionic intermediate **D** via an allylic rearrangement. Subsequent twice 1,3-proton shift along with the release of Lewis acid via zwitterionic intermediate **E** produces the corresponding indene derivative **3a**. At the present stage, we do not exactly understand which step is responsible to the intermolecular Friedel–Crafts reaction with acyl cation in the presence of $AlCl_3$. We believe that the ring-opening process provides a driving force to accelerate

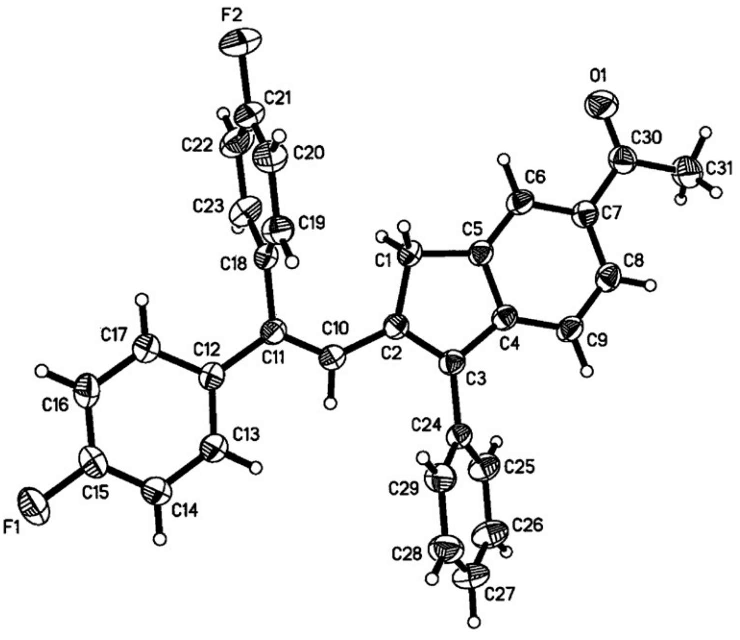


Figure 2. ORTEP drawing of **3e**.

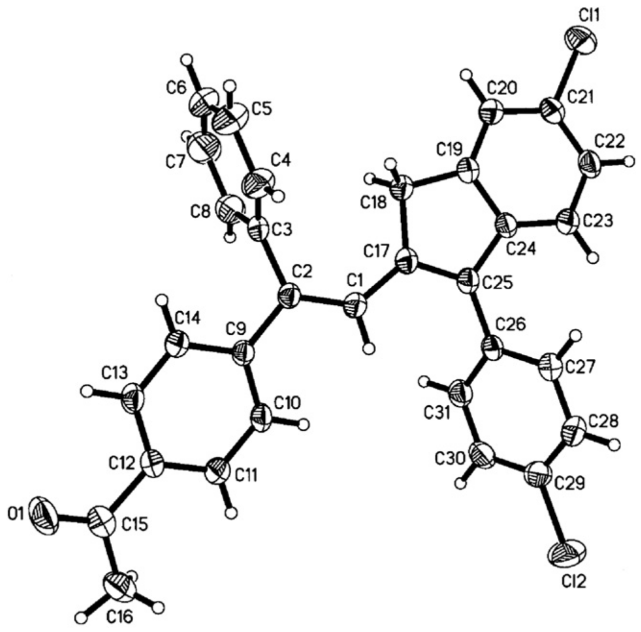
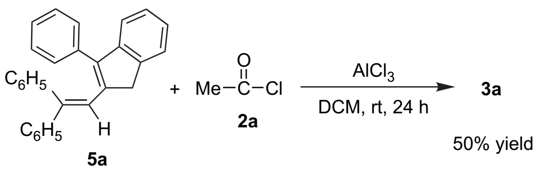


Figure 3. ORTEP drawing of **4a**.



Scheme 1. A control experiment.

the intermolecular Friedel–Crafts reaction. This is why these transformations complete within shorter reaction time.

In conclusion, we have identified an interesting $AlCl_3$-mediated tandem Friedel–Crafts reaction of vinylidenecyclopropanes with acyl chlorides that produced the corresponding 1-[2-(2,2-diarylvinyl)-1-phenyl-3*H*-inden-5-yl]ethanone derivatives in moderate to good yields under the optimized conditions. Adding electron-withdrawing group on the aromatic ring of R^2 in VDCPs afforded another type of indene derivatives **4** as mixtures of *E*- and *Z*-isomers in moderate yields under mild conditions. Efforts are underway to further elucidate the reaction mechanism and to understand the scope and limitations of this process.

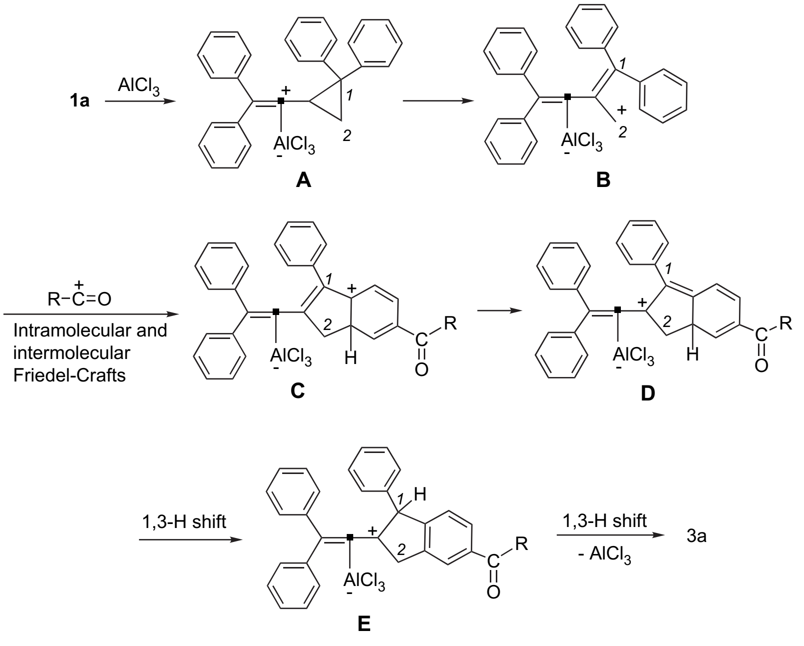
3. Experimental section

3.1. General remarks

^1H NMR spectra were recorded on a Varian Mercury vx 300 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are in hertz. Mass spectra were recorded with an HP-5989 instrument. Organic solvents used were dried by standard methods when necessary. Part of solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. X-ray diffraction analysis was performed on a Rigaku AFC7R X-ray diffractometer. Commercially obtained reagents were used without further purification. 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 at increased pressure.

3.2. General procedure for Lewis acid-catalyzed reaction of arylvinylidenecyclopropanes with acyl chlorides

Under an argon atmosphere, arylvinylidenecyclopropane **1** (0.2 mmol) and $AlCl_3$ (0.2 mmol) were added into a Schlenk tube, and then the solvent CH_2Cl_2 (1.0 mL) was added. The



Scheme 2. A plausible reaction mechanism.

reaction mixture was stirred at room temperature for a while, then acyl chloride **2** (0.2 mmol) was added. The reaction was quenched after 5 min by addition of water. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

3.3. Analytical data of the products

Compound ***3a***. A yellow solid, mp: 182–184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.55 (s, 3H, CH_3), 3.00 (s, 2H, CH_2), 7.13 (s, 1H), 7.21–7.23 (m, 5H, Ar), 7.30–7.32 (m, 3H, Ar), 7.46–7.52 (m, 8H, Ar), 7.77–7.83 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.6, 39.7, 119.7, 122.5, 123.1, 127.2, 127.3, 127.5, 127.9, 128.2, 128.6, 128.7, 129.7, 130.1, 134.0, 134.4, 140.6, 142.2, 143.2, 143.6, 144.3, 149.4, 197.9. IR (CH_2Cl_2) ν 3076, 3056, 3026, 2924, 1676, 1599, 1492, 1443, 1356, 1256, 1161, 1074, 944, 765, 702 cm^{-1}. MS (%) *m*/*e* 412 (M^+, 14), 335 (13), 313 (10), 285 (12), 169 (62), 147 (38), 119 (35), 105 (16), 97 (22), 77 (15), 69 (100), 57 (12), 55 (15), 51 (18), 44 (73), 43 (42). Anal. Calcd for $C_{31}H_{24}O$ requires C, 90.26%; H, 5.86%. Found: C, 90.22%; H, 5.88%.

Compound ***3b***. A yellow solid, mp: 161–163 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.19 (t, J=7.5 Hz, 3H, CH_3), 2.94 (q, J=7.5 Hz, 2H, CH_2), 3.00 (s, 2H, CH_2), 7.13 (s, 1H), 7.19–7.24 (m, 5H, Ar), 7.30–7.32 (m, 3H, Ar), 7.42–7.54 (m, 8H, Ar), 7.78–7.85 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 8.5, 31.7, 39.7, 119.8, 122.6, 122.8, 126.9, 127.2, 127.5, 127.9, 128.2, 128.6, 128.7, 129.7, 130.1, 133.8, 134.4, 140.7, 142.2, 143.2, 143.6, 144.2, 144.4, 149.2, 200.6. IR (CH_2Cl_2) ν 3056, 3027, 2934, 1678, 1599, 1492, 1444, 1376, 1228, 1153, 1075, 1110, 944, 802, 765, 702, 588 cm^{-1}. MS (%) *m*/*e* 426 (M^+, 100), 397 (61), 369 (12), 291 (53), 289 (31), 276 (14), 165 (14), 145 (19), 91 (18), 57 (39). Anal. Calcd for $C_{32}H_{26}O$ requires C, 90.11%; H, 6.14%. Found: C, 90.28%; H, 6.32%.

Compound ***3c***. A yellow solid, mp: 138–139 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.02 (s, 2H, CH_2), 7.14 (s, 1H, Ar), 7.19–7.25 (m, 5H, Ar), 7.30–7.35 (m, 3H, Ar), 7.42–7.56 (m, 11H, Ar), 7.66–7.76 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 119.6, 122.6, 125.1, 127.3, 127.6, 128.0, 128.1, 128.2, 128.6, 128.8, 129.4, 129.77, 129.83, 130.2, 131.9, 134.3, 134.5, 138.4, 140.7, 142.3, 143.1, 143.6, 144.2, 144.5, 149.1, 196.7. IR (CH_2Cl_2) ν 3056, 3026, 2911, 1652, 1599, 1277, 1102, 769, 701 cm^{-1}. MS (%) *m*/*e* 474 (M^+, 40), 346 (15), 335 (10), 291 (18), 169 (44), 147 (27), 119 (22), 105 (100), 97 (19), 91 (19), 77 (55), 69 (59), 57 (29), 55 (30), 51 (19), 44 (29), 43 (66). Anal. Calcd for $C_{36}H_{26}O$ requires C, 91.11%; H, 5.52%. Found: C, 90.81%; H, 5.76%.

Compound ***3d***. A yellow solid, mp: 182–185 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.30 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.03 (s, 2H, CH_2), 7.07 (d, 2H, J=7.8 Hz, Ar), 7.18 (d, 2H, J=7.8 Hz, Ar), 7.27 (d, 2H, J=8.4 Hz, Ar), 7.30–7.52 (m, 7H, Ar), 7.50 (s, 1H), 7.51 (s, 1H, Ar), 7.82 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.1, 21.4, 26.7, 39.8, 119.6, 121.7, 123.1, 125.7, 127.2, 127.4, 127.8, 128.6, 128.9, 129.4, 129.7, 130.0, 133.9, 134.5, 137.5, 137.6, 139.8, 143.3, 143.7, 143.9, 144.9, 149.6, 198.1. IR (CH_2Cl_2) ν 3023, 2923, 2853, 1731, 1676, 1604, 1508, 1428, 1356, 1257, 1172, 820, 703, 527 cm^{-1}. MS (%) *m*/*e* 440 (M^+, 100), 397 (11), 347 (12), 305 (21), 289 (9). HRMS (EI) calcd for $C_{33}H_{28}O$: 440.2140. Found: 440.2140.

Compound ***3e***. A yellow solid, mp: 216–219 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.57 (s, 3H, CH_3), 3.01 (s, 2H, CH_2), 6.90–6.95 (m, 2H, Ar), 7.03 (s, 1H), 7.10–7.21 (m, 4H, Ar), 7.25–7.33 (m, 3H, Ar), 7.41–7.55 (m, 5H, Ar), 7.83–7.86 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.7, 39.8, 115.2 (d, J_{C-F}=21.8 Hz), 115.9 (d, J_{C-F}=21.2 Hz), 119.9, 122.9, 123.3, 127.4, 128.0, 128.7, 128.8 (d, J_{C-F}=8.0 Hz), 129.6, 131.8 (d, J_{C-F}=8.0 Hz), 134.3, 136.4 (d, J_{C-F}=2.9 Hz), 138.4 (d, J_{C-F}=2.9 Hz), 141.4, 143.0, 143.7, 144.9, 149.3, 162.4 (d, J_{C-F}=247.2 Hz), 162.6 (d, J_{C-F}=246.6 Hz), 197.9. IR (CH_2Cl_2) ν 3052, 1673, 1608, 1505, 1428, 1355, 1280, 1254, 1221, 1159, 1125, 973, 944, 911, 832, 819, 705, 651, 566, 507, 483 cm^{-1}. MS (%) *m*/*e* 448 (M^+, 100), 433 (12), 405 (12), 327 (30), 309 (38), 307 (16), 109 (10), 91 (7), 69 (8), 43 (71). HRMS (EI) calcd for $C_{31}H_{22}F_2O$: 448.1639. Found: 448.1639.

Compound ***3f***. A yellow solid, mp: 194–196 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.03 (s, 2H, CH_2), 6.89–6.94 (m, 2H, Ar), 7.05 (s, 1H), 7.10–7.18 (m, 4H, Ar), 7.23–7.29 (m, 2H, Ar), 7.33–7.36 (m, 1H, Ar), 7.42–7.57 (m, 8H, Ar), 7.69–7.76 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 115.1 (d, J_{C-F}=21.6 Hz), 115.9 (d, J_{C-F}=21.3 Hz), 119.7, 122.9, 125.2, 128.2 (d, J_{C-F}=8.1 Hz), 128.7, 128.8 (d, J_{C-F}=8.0 Hz), 129.4, 129.7, 129.8, 131.7, 131.9, 132.0, 134.3, 134.5, 136.3 (d, J_{C-F}=3.0 Hz), 138.2, 138.4 (d, J_{C-F}=2.7 Hz), 141.3, 142.8, 143.5, 144.9, 148.9, 162.3 (d, J_{C-F}=246.9 Hz), 162.5 (d, J_{C-F}=246.2 Hz), 196.6. IR (CH_2Cl_2) ν 3058, 2925, 1652, 1605, 1507, 1233, 1159, 836, 704, 567 cm^{-1}. MS (%) *m*/*e* 510 (M^+, 65), 309 (13), 169 (31), 147 (16), 119 (23), 105 (100), 97 (16), 91 (9), 77 (30), 69 (47), 57 (12), 51 (11), 47 (10), 44 (34), 43 (17). HRMS (EI) calcd for $C_{36}H_{24}F_2O$: 510.1795. Found: 510.1789.

Compound ***3g***. A yellow solid, mp: 195–197 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.03 (s, 2H, CH_2), 3.86 (s, 3H, CH_3), 6.89–6.96 (m, 4H, Ar), 7.05 (s, 1H, CH), 7.11–7.19 (m, 4H, Ar), 7.24–7.35 (m, 3H, Ar), 7.42–7.53 (m, 5H, Ar), 7.66–7.67 (m, 2H, Ar), 7.76–7.79 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 55.4, 113.4, 115.1 (d, J_{C-F}=21.2 Hz), 115.9 (d, J_{C-F}=21.2 Hz), 119.6, 123.0, 124.9, 128.0, 128.7, 128.8 (d, J_{C-F}=8.0 Hz), 129.0, 129.7, 130.7, 131.8 (d, J_{C-F}=8.0 Hz), 132.3, 134.4, 135.2, 136.4 (d, J_{C-F}=3.4 Hz), 138.4 (d, J_{C-F}=2.9 Hz), 141.1, 142.7, 143.1, 145.0, 148.4, 162.4 (d, J_{C-F}=247.3 Hz), 162.5 (d, J_{C-F}=246.2 Hz), 162.8, 195.4. IR (CH_2Cl_2) ν 3052, 2926, 1647, 1601, 1508, 1255, 1167, 836, 777, 703, 566 cm^{-1}. MS (%) *m*/*e* 540 (M^+, 27), 335 (14), 313 (13), 285 (10), 169 (72), 147 (33), 135 (46), 119 (35), 105 (18), 97 (23), 91 (14), 77 (25), 69 (100), 57 (19), 55 (23), 51 (20), 44 (51), 43 (30). Anal. Calcd for $C_{37}H_{26}F_2O_2$ requires C, 82.20%; H, 4.85%. Found: C, 82.10%; H, 4.88%.

Compound ***3h***. A yellow solid, mp: 169–170 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.03 (s, 2H, CH_2), 6.89–6.95 (m, 2H, Ar), 7.05 (s, 1H, CH), 7.11–7.20 (m, 4H, Ar), 7.25–7.36

(m, 3H, Ar), 7.41–7.53 (m, 7H, Ar), 7.66–7.71 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 115.2 (d, J_{C-F}=21.7 Hz), 116.0 (d, J_{C-F}=21.1 Hz), 119.8, 122.9, 125.0, 128.1, 128.5, 128.7, 128.9 (d, J_{C-F}=8.0 Hz), 129.3, 129.6, 131.2, 131.8 (d, J_{C-F}=8.4 Hz), 134.1, 134.2, 136.3 (d, J_{C-F}=3.4 Hz), 136.5, 138.4, 141.5, 142.9, 143.7, 144.9, 149.1, 162.4 (d, J_{C-F}=251.8 Hz), 162.7 (d, J_{C-F}=253.3 Hz), 195.3. IR (CH_2Cl_2) ν 3056, 2925, 1654, 1606, 1508, 1234, 1159, 835, 737, 704, 566 cm^{-1}. MS (%) *m*/*e* 544 (M^+, 12), 335 (14), 169 (60), 147 (33), 131 (11), 119 (42), 105 (23), 100 (17), 97 (22), 91 (13), 77 (24), 69 (100), 55 (24), 51 (21), 44 (79), 43 (25). Anal. Calcd for $C_{36}H_{23}ClF_2O$ requires C, 79.34%; H, 4.25%. Found: C, 79.34%; H, 4.32%.

Compound **3i**. A yellow solid, mp: 214–217 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.48 (s, 3H, CH_3), 2.94 (s, 2H, CH_2), 6.96–7.00 (m, 3H, Ar), 7.08–7.15 (m, 4H, Ar), 7.24 (d, *J*=8.4 Hz, Ar), 7.35–7.43 (m, 7H, Ar), 7.74–7.76 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.7, 39.8, 120.0, 123.3, 123.5, 127.4, 128.1, 128.4, 128.7, 129.2, 129.6, 131.5, 133.6, 134.1, 134.2, 134.4, 138.6, 140.4, 140.9, 143.0, 143.3, 145.4, 149.1, 197.9. IR (CH_2Cl_2) ν 3055, 2919, 1713, 1676, 1606, 1491, 1356, 1258, 1090, 1014, 829, 703, 528 cm^{-1}. MS (%) *m*/*e* 480 (M^+, 17), 335 (12), 169 (43), 149 (27), 147 (17), 119 (26), 97 (29), 91 (15), 86 (21), 71 (27), 69 (100), 57 (41), 51 (29), 49 (42), 44 (52), 43 (63). Anal. Calcd for $C_{31}H_{22}Cl_2O$ requires C, 77.34%; H, 4.61%. Found: C, 77.58%; H, 4.80%.

Compound **3j**. A yellow solid, mp: 201–204 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.06 (s, 2H, CH_2), 7.06–7.09 (m, 3H, Ar), 7.18–7.25 (m, 4H, Ar), 7.35 (d, 1H, *J*=8.1 Hz, Ar), 7.43–7.59 (m, 10H, Ar), 7.70–7.77 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 119.9, 123.5, 125.2, 128.2, 128.4, 128.7, 129.2, 129.4, 129.7, 129.8, 131.5, 132.0, 133.6, 134.2, 134.6, 138.2, 138.6, 140.5, 140.8, 142.8, 143.1, 145.5, 148.7, 196.6. IR (CH_2Cl_2) ν 3057, 2924, 1652, 1606, 1491, 1280, 1101, 1014, 829, 709 cm^{-1}. MS (%) *m*/*e* 543 ($M-1^+$, 41), 289 (13), 105 (100), 77 (36). Anal. Calcd for $C_{36}H_{24}Cl_2O$ requires C, 79.57%; H, 4.45%. Found: C, 79.41%; H, 4.40%.

Compound **3k**. A yellow solid, mp: 182–185 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.06 (s, 2H, CH_2), 3.86 (s, 3H, CH_3), 6.94 (d, 2H, *J*=8.7 Hz, Ar), 7.07 (d, 3H, *J*=8.4 Hz, Ar), 7.18–7.24 (m, 4H, Ar), 7.35 (d, 2H, *J*=8.7 Hz, Ar), 7.43–7.53 (m, 7H, Ar), 7.65–7.67 (m, 2H, Ar), 7.78 (d, 2H, *J*=9.0 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.8, 55.4, 113.4, 119.8, 123.6, 125.0, 128.1, 128.4, 128.7, 129.0, 129.1, 129.7, 130.6, 131.5, 132.3, 133.5, 134.1, 134.2, 135.3, 138.7, 140.5, 140.6, 142.7, 142.8, 145.5, 148.2, 162.8, 195.4. IR (CH_2Cl_2) ν 3059, 2919, 1647, 1601, 1508, 1491, 1255, 1167, 830, 777, 702 cm^{-1}. MS (%) *m*/*e* 574 (M^+, 14), 572 (23), 289 (8), 135 (100), 107 (13), 85 (12), 77 (20), 71 (16), 57 (23), 43 (14). Anal. Calcd for $C_{37}H_{26}Cl_2O_2$ requires C, 77.49%; H, 4.57%. Found: C, 79.20%; H, 4.69%.

Compound **3l**. A yellow solid, mp: 110–112 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.09 (d, 3H, *J*=7.5 Hz, CH_3), 2.57 (s, 3H, CH_3), 3.12 (q, 1H, *J*=7.5 Hz), 6.81 (d, 1H, *J*=1.2 Hz), 7.24–7.52 (m, 16H, Ar), 7.81–7.85 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.3, 26.7, 43.9, 119.8, 122.3, 122.4, 127.6, 127.76, 127.84, 127.9, 128.0, 128.1, 128.2, 128.5, 129.6, 131.1, 134.2, 134.3, 140.3, 142.2, 142.8, 145.3, 148.2, 149.1, 150.7, 198.1. IR (CH_2Cl_2) ν 3056, 3026, 2965, 2927, 1676, 1605, 1492, 1443, 1423, 1355, 1253, 1164, 1075, 943, 828, 775, 700, 656 cm^{-1}. MS (%) *m*/*e* 426 (M^+, 100), 411 (15), 383 (9), 333 (15), 305 (28), 291 (15), 289 (13). HRMS (EI) calcd for $C_{32}H_{26}O$: 426.1984. Found: 426.1984.

Compound **4a**. A yellow solid, mp: 189–192 °C. (*E*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.55 (s, 3H, CH_3), 2.93 (s, 2H), 7.11–7.19 (m, 4H, Ar), 7.24–7.30 (m, 4H, Ar), 7.41 (d, 2H, *J*=8.4 Hz, Ar), 7.40–7.51 (m, 5H, Ar), 7.83 (d, 2H, *J*=8.4 Hz, Ar). (*Z*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.70 (s, 3H, CH_3), 2.93 (s, 2H), 7.11–7.19 (m, 4H, Ar), 7.24–7.30 (m, 4H, Ar), 7.40–7.51 (m, 7H, Ar), 8.06 (d, 2H, *J*=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.6, 39.4, 120.9, 124.0, 124.3, 126.6, 127.1, 128.2, 128.3, 129.0, 130.1, 131.0, 131.8, 132.8, 134.0, 135.6, 140.0, 140.6, 141.5, 142.6, 144.3, 144.9, 146.8, 197.5. IR (CH_2Cl_2) ν 3052, 2924, 2852, 1682, 1602, 1564, 1357, 1266, 1165, 1091, 939, 825, 736 cm^{-1}. MS (%) *m*/*e* 480 (M^+, 48), 325 (34), 289 (22), 69 (12), 43 (100). HRMS (EI) calcd for $C_{31}H_{22}Cl_2O$: 480.1048. Found: 480.1048.

Compound **4b**. A yellow solid, mp: 216–218 °C. (*E*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.54 (s, 3H, CH_3), 2.93 (s, 2H, CH_2), 6.92 (d, 2H, *J*=9.3 Hz, Ar), 7.04–7.31 (m, 8H, Ar), 7.42–7.49 (m, 5H, Ar), 7.82 (d, 2H, *J*=8.7 Hz, Ar). (*Z*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.70 (s, 3H, CH_3), 2.93 (s, 2H, CH_2), 6.87 (d, 2H, *J*=9.4 Hz, Ar), 7.04–7.31 (m, 8H, Ar), 7.42–7.49 (m, 5H, Ar), 8.06 (d, 2H, *J*=8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.5, 39.5, 111.2 (d, *J*=23.0 Hz), 113.4 (d, *J*=23.0 Hz), 115.7 (d, *J*=21.2 Hz), 120.9 (d, *J*=9.2 Hz), 124.6, 127.0, 127.1, 127.6, 128.1, 128.3, 128.7, 128.9, 130.2, 130.6 (d, *J*=10.8 Hz), 131.4 (d, *J*=8.0 Hz), 135.5, 139.9 (d, *J*=30.4 Hz), 140.1 (d, *J*=42.9 Hz), 140.7, 144.6, 145.4, 145.5, 147.0, 161.9 (d, *J*=243.1 Hz), 162.4 (d, *J*=246.6 Hz), 197.4. IR (CH_2Cl_2) ν 3052, 2919, 1683, 1603, 1268, 1095, 956, 838, 702, 550 cm^{-1}. MS (%) *m*/*e* 448 (M^+, 8), 335 (13), 313 (15), 169 (56), 147 (29), 119 (33), 97 (23), 69 (100), 51 (16), 50 (14), 44 (38), 43 (21). Anal. Calcd for $C_{31}H_{22}F_2O$ requires C, 83.02; H, 4.94%. Found: C, 83.05%; H, 5.00%.

Compound **4c**. A yellow solid, mp: 152–155 °C. (*E*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.94 (s, 2H, CH_2), 7.14–7.20 (m, 4H, Ar), 7.25–7.32 (m, 4H, Ar), 7.41–7.59 (m, 10H, Ar), 7.69–7.79 (m, 4H, Ar). (*Z*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 3.00 (s, 2H, CH_2), 7.14–7.20 (m, 4H, Ar), 7.25–7.32 (m, 4H, Ar), 7.41–7.59 (m, 10H, Ar), 7.88–7.94 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 39.4, 120.9, 124.0, 124.2, 126.6, 126.8, 128.2, 129.0, 129.9, 130.17, 130.21, 131.0, 131.8, 132.3, 132.9, 134.0, 136.0, 137.6, 140.0, 140.7, 141.6, 142.6, 144.2, 144.9, 146.2, 196.0. IR (CH_2Cl_2) ν 3057, 2925, 1658, 1599, 1577, 1481, 1445, 1315, 1276, 1140, 1091, 938, 829, 700, 534 cm^{-1}. MS (%) *m*/*e* 542 (M^+, 100), 402 (7), 327 (11), 325 (28), 289 (16), 105 (67), 77 (15). HRMS (EI) calcd for $C_{36}H_{24}Cl_2O$: 542.1204. Found: 542.1204.

Compound **4d**. A yellow solid, mp: 218–221 °C. (*E*-isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.94 (s, 2H, CH_2), 7.13–7.21 (m, 4H, Ar), 7.26–7.32 (m, 5H, Ar), 7.41–7.52 (m, 9H, Ar), 7.66–7.74 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 39.4, 120.9, 124.0, 124.4, 126.7, 126.9, 128.2, 128.6, 129.0, 130.1, 130.2, 131.0, 131.3, 131.82, 131.85, 132.8, 134.0, 135.6, 135.9, 138.7, 139.9, 140.6, 141.5, 142.6, 144.4, 145.0, 146.5, 194.7. IR (CH$_2$Cl$_2$) ν 2955, 2925, 2854, 1714, 1660, 1600, 1486, 1455, 1274, 1091, 1017, 927, 858, 830, 762 cm^{-1}. MS (%) *m/e* 578 (M$^+$, 10), 325 (6), 139 (24), 111 (8), 91 (8), 77 (8), 69 (11), 55 (8), 44 (100), 43 (21). Anal. Calcd for C$_{36}$H$_{23}$Cl$_3$O requires C, 74.82%; H, 4.01%. Found: C, 74.55%; H, 4.18%.

*Compound **4e***. A yellow solid, mp: 117–120 °C. (*E*-isomer) ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 2.94 (s, 2H, CH$_2$), 3.88 (s, 3H, OCH$_3$), 6.95 (d, 2H, J=8.4 Hz, Ar), 7.12–7.20 (m, 5H, Ar), 7.20–7.33 (m, 4H, Ar), 7.41–7.52 (m, 6H, Ar), 7.66 (d, 2H, J=8.4 Hz, Ar), 7.81 (d, 2H, J=8.4 Hz, Ar). (*Z*-isomer) ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 3.01 (s, 2H, CH$_2$), 3.92 (s, 3H, OCH$_3$), 7.03 (d, 2H, J=8.4 Hz, Ar), 7.12–7.33 (m, 9H, Ar), 7.41–7.52 (m, 6H, Ar), 7.90 (d, 2H, J=8.4 Hz, Ar), 7.92 (d, 2H, J=8.4 Hz, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 39.4, 55.5, 113.5, 113.7, 120.8, 124.0, 126.7, 126.8, 127.2, 127.8, 128.2, 128.4, 129.0, 129.9, 130.2, 131.0, 131.7, 132.4, 132.5, 132.9, 133.9, 136.8, 140.1, 140.7, 141.8, 144.9, 145.8, 163.1, 199.4. IR (CH$_2$Cl$_2$) ν 3056, 3030, 2956, 2926, 2853, 1727, 1650, 1601, 1509, 1481, 1461, 1418, 1313, 1281, 1256, 1171, 1152, 1091, 928, 853, 832, 771, 700, 621, 594, 534 cm^{-1}. MS (%) *m/e* 572 (M$^+$, 29), 572 (29), 289 (10), 136 (8), 135 (100), 77 (21), 44 (57). HRMS (EI) calcd for C$_{37}$H$_{26}$Cl$_2$O$_2$: 572.1310. Found: 572.1310.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.02.003.

References and notes

1. (a) For recent review, see: Maeda, H.; Mizuno, K. *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 1014–1025; For the synthesis of vinylidenecyclopropanes, see: (b) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283–2285 and references therein; (c) Al-Dulayymi, J. R.; Baird, M. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1547–1548.
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4. (a) For a review, see: Fleming, I. *Chemtracts: Org. Chem.* **2001**, *14*, 405–406; (b) For the reaction of methylenecyclopropanes with acyl chloride in the presence of AlCl$_3$, see: Huang, X.; Yang, Y.-W. *Org. Lett.* **2007**, *9*, 1667–1670.
5. The crystal data of **3a** have been deposited in CCDC with number 664633. Empirical formula: C$_{32}$H$_{26}$O; formula weight: 426.53; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=9.661(5) Å, b=10.626(5) Å, c=22.961(11) Å, α=90°, β=95.370(9)°, γ=90°, V=2347(2) Å^3; space group: $P2(1)/n$; Z=4; D_{calcd}=1.207 g/cm^3; F_{000}=904; diffractometer: Rigaku AFC7R; residuals: *R*; *Rw*: 0.0583, 0.1247.

   The crystal data of **3e** have been deposited in CCDC with number 665675. Empirical formula: C$_{31}$H$_{22}$F$_2$O; formula weight: 448.49; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=8.0477(8) Å, b=28.566(3) Å, c=10.6859(10) Å, α=90°, β=111.070(2)°, γ=90°, V=2292.3(4) Å^3; space group: $P2(1)/c$; Z=4; D_{calcd}=1.300 g/cm^3; F_{000}=936; diffractometer: Rigaku AFC7R; residuals: *R*; *Rw*: 0.0534, 0.1149.
6. The X-ray crystal data of **4a** have been deposited in CCDC with number 663279. Empirical formula: C$_{31}$H$_{22}$Cl$_2$O; formula weight: 481.39; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=22.321(2) Å, b=15.0593(14) Å, c=7.3913(7) Å, α=90°, β=97.347(2)°, γ=90°, V=2464.1(4) Å^3; space group: $P2(1)/c$; Z=4; D_{calcd}=1.298 g/cm^3; F_{000}=1000; diffractometer: Rigaku AFC7R; residuals: *R*; *Rw*: 0.0526, 0.1125.
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