A Concise Synthesis of Indene-based Polycyclic Compounds via FeCl₃-Catalyzed Cascade Cyclization

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I. General Information

All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using dry solvents. Flash column chromatography was performed over silica gel (200-400 mesh) purchased from Ocean Chemical Factory of Qingdao, China. FeCl$_3$ was purchased from Alfa Aesar (98% purity) and used as supplied. All of solvents were dried with activated molecule sieve, and CHCl$_3$ was purified with H$_2$SO$_4$(c) and freshly distilled over CaH$_2$ to remove H$_2$O and ethanol before use. $^1$H and $^{13}$C NMR spectra were collected on a JEOL AL-300MHz, AL-400MHz or AL-600MHz spectrometer with residue solvent peaks as an internal standard ($^1$H NMR: CDCl$_3$ at 7.26 ppm, $^{13}$C NMR: CDCl$_3$ at 77.16 ppm). Mass spectra were collected on GCMS-QP2010 SE.
II. Synthesis of Propargylic Alcohols

Propargylic alcohols 1a were purchased from commercial suppliers. Propargylic alcohols 1b-1f, 1h-1k were prepared following the Method A. \[1\] Propargylic alcohol 1g and 1l were prepared following the Method B\[2\] and Method C\[3\].

**Method A:**
To a solution of alkyne (8 mmol, 1.0 eq.) in THF was added LDA (2.0 M in THF, 1.5 equiv.) at -78 °C. The resulting solution was allowed to warm to room temperature and stirred for a further 1 h. Then corresponding ketones were slowly added at -78 °C. The resulting reaction mixture was warmed up to room temperature and stirred for a further 12 h. On completion, the reaction mixture was quenched by addition of saturated NH\(_4\)Cl and extracted with ethyl acetate. The combined organic layers were dried over Mg\(_2\)SO\(_4\), concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: n-hexane: ethyl acetate = 10: 1) to give the titled compounds.

Spectra datas of alkynes 1b-1e, 1h-1k are consistent with the literatures.\[1,4\]

![Chemical structure of 6-methoxy-1,1-diphenylhex-2-yn-1-ol (1f)]

**6-methoxy-1,1-diphenylhex-2-yn-1-ol (1f):** white solid, 65% yield.

1H NMR (400 MHz, CHLOROFORM-D) \(\delta\) 7.63 – 7.56 (m, 4H), 7.33 – 7.26 (m, 4H), 7.25 – 7.20 (m, 2H), 3.45 (t, \(J = 6.2\) Hz, 2H), 3.29 (s, 3H), 2.41 (t, \(J = 7.1\) Hz, 2H), 1.82 (p, \(J = 6.7\) Hz, 2H).

13C NMR (101 MHz, CHLOROFORM-D) \(\delta\) 145.66, 128.23 (CH×4), 127.57 (CH×2), 126.10 (CH×4), 87.46, 83.62, 74.47, 71.33, 58.71, 28.65, 15.82.

**Method B:**
In a sealable tube Pd(OAc)\(_2\) (28 mg, 0.125 mmol) and PPh\(_3\) (65.6 mg, 0.25 mmol) are dissolving anhydrous CH\(_3\)CN (3.75 mL ). The yellow suspension is stirred at r.t. under N\(_2\) atmosphere until the solution becomes dark red (usually in less than 2h). This color change indicates that the formation of the catalyst is completed. Then, finely ground K\(_3\)PO\(_4\) (1.0 g, 5.0 mmol), Et\(_3\)N (12.5 mmol), 1,1-diphenylprop-2-yn-1-ol (1.0 g, 5.0 mmol) and 2-bromothiophene (897 mg, 5.5 mmol) were added. The reaction can be heated at 100 °C for 12 h. On completion, the reaction mixture was quenched by saturated NH\(_4\)Cl solution and extracted with ethyl acetate. The combined organic layers were dried over Mg\(_2\)SO\(_4\),
concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: n-hexane: ethyl acetate = 20:1) to give the compound 1g\textsuperscript{[2]}.

![Image of 1,1-diphenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (1g)]

**1,1-diphenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (1g):** yellow liquid, 62% yield.

\[
\begin{align*}
\text{Ph} & \quad \equiv \quad \text{Ph} \\
\text{S} & \quad \text{OH}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta\) 7.68 - 7.62 (m, 3H), 7.41 - 7.33 (m, 5H), 7.31 - 7.27 (m, 3H), 7.00 (dd, \(J = 8.4, 4.4\) Hz, 1H), 2.95 (s, 1H).

\(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \(\delta\) 165.31, 144.80, 132.71, 128.46, 128.16, 127.93, 127.72, 127.14, 126.17, 122.32, 95.46, 80.68, 75.12.

**Method C:**

A sealed tube charged with PdCl\(_2\) (44 mg, 0.25 mmol), triphenylphosphine (131 mg, 0.5 mmol) and copper(I) iodide (100 mg, 0.5 mmol) in 3 mL of dry DMF was barbotated with \(\text{N}_2\) for 15 min at 40 °C. Then solution of 2-bromopyridine (790 mg, 5 mmol) and 1,1-diphenylprop-2-yn-1-ol (1.35 g, 6.5 mmol) in dry DMF (5 mL) and diisopropylamine (3 mL) was added to the reaction mixture. After 12 h of heating at 80 °C to the reaction mixture was added ethyl acetate (20 mL) and saturated NH\(_4\)Cl solution (10 mL). The organic layers was washed with water (20 mL×3) and dried over Mg\(_2\)SO\(_4\), concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: n-hexane:ethyl acetate:DCM:Et\(_3\)N= 50:20:20:1) to give the desired product 1l\textsuperscript{[3]}.

![Image of 1,1-diphenyl-3-(pyridin-2-yl)prop-2-yn-1-ol (1l)]

**1,1-diphenyl-3-(pyridin-2-yl)prop-2-yn-1-ol (1l):** white solid, 60% yield.

\[^1\text{H}\text{ NMR (400 MHz, CHLOROFORM-D)} \delta 8.42 \text{ (s, 1H), 7.70 (d, } J = 7.4 \text{ Hz, 4H), 7.58 (t, } J = 6.4 \text{ Hz, 1H), 7.40 (d, } J = 6.6 \text{ Hz, 1H), 7.34 – 7.24 \text{ (m, 6H), 7.17 (d, } J = 4.9 \text{ Hz, 1H).} \]

\(^{13}\text{C NMR (101 MHz, CHLOROFORM-D)} \delta 149.93, 144.87, 142.81, 136.36, 128.41, 127.83, 127.47, 126.34, 123.24, 92.22, 86.18, 74.68.
III. Synthesis of Alkene Substrates

Alkenes 2a-2c, 2f-2h, 2j, 2l-2m were purchased from commercial suppliers. Alkenes 2d-2e, 2k were known compounds and prepared according to the literature procedures. Alkene 2i was synthesized with the following procedures.

\[
\text{OTs} + \text{TMS} \xrightarrow{\text{CuCl 5 mol\%}} \text{TMS}
\]

A solution of ((trimethylsilyl)methyl)magnesium chloride (6 mmol) was added to a 10 mL of THF solution containing CuCl (24.7 mg, 0.25 mmol) and 3-methylbut-3-en-1-yl 4-methylbenzenesulfonate (5 mmol, 1.2 g) under N\textsubscript{2} atmosphere. The reaction mixture was stirred at room temperature for 3 h and then quenched by saturated NH\textsubscript{4}Cl aqueous solution and extracted with ether. The combined organic layers were dried over MgSO\textsubscript{4}, evaporated under a reduced pressure and purified by flash column chromatography on silica gel (eluent: n-hexane) to give the product 2i.

**trimethyl(4-methylpent-4-en-1-yl)silane (2i):** colorless liquid, 70% yield

\[\text{1H NMR (400 MHz, CHLOROFORM-D) } \delta 4.72 - 4.64 (m, 2H), 2.03 (t, J = 7.4 Hz, 2H), 1.70 (s, 3H), 1.49 - 1.39 (m, 2H), 0.51 - 0.44 (m, 2H), -0.02 (s, 9H).\]

\[\text{13C NMR (101 MHz, CHLOROFORM-D) } \delta 146.27, 110.00, 41.84, 22.43, 22.18, 16.42, -1.52 (CH\textsubscript{3}\times3).\]
IV. Synthesis of the Desired Products

General Procedure:
To an oven-dried 4-mL vial or screw-capped tube was added FeCl₃ (1.6 mg, 0.01 mmol, or otherwise noted), DCE (1 mL), Propargylic alcohols (0.1 mmol) and alkenes (0.12 mmol) sequentially under N₂ atmosphere. The reaction mixture was stirred at 60 °C (or otherwise noted) for 12 h. Upon completion, the reaction mixture was cooled to room temperature, extracted with ether. The organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (eluent: hexanes/DCM= 50:1 to 25:1) to give the desired products.

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<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp.(°C)</th>
<th>Yield³</th>
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<th>4aa</th>
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ᵃDetermined by ¹H NMR versus an internal standard
ᵇAmount of acid catalyst: 20 mol%
ᶜIsolated yield
3'-phenyl-2'-(1-phenylvinyl)spiro[cyclohexane-1,1'-indene] (3aa): colorless liquid, 28.9 mg, 80% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4mg, 0.1 mmol) and alkene 2a (14 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.88 (d, $J = 7.4$ Hz, 1H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.46 – 7.41 (m, 2H), 7.38 – 7.22 (m, 9H), 5.79 (s, 1H), 5.12 (s, 1H), 2.03 – 1.91 (m, 2H), 1.85 (d, $J = 13.3$ Hz, 1H), 1.80 – 1.65 (m, 4H), 1.38 – 1.24 (m, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 153.32, 152.09, 143.84, 143.59, 140.49, 139.11, 135.48, 129.26 (CH×2), 128.22 (CH×2), 128.19 (CH×2), 127.62, 127.20, 126.75 (CH×2), 126.54, 124.84, 124.57, 120.92, 118.46, 55.00, 32.95 (CH$_2$×2), 25.32, 22.50 (CH$_2$×2).

GC-MS: m/z calced for C$_{28}$H$_{26}$: 362, found: 362.

10'-methyl-10'-phenyl-10'H-spiro[cyclohexane-1,9'-indenol1,2-a]indene (4aa): white solid, 25.3 mg, 70% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-l-ol 1a (28.4mg, 0.1 mmol) and alkene 2a (14 μL, 0.12 mmol) with AgSbF$_6$ (3.5 mg, 0.01 mmol) in CHCl$_3$ at 60 °C.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.80 – 7.71 (m, 3H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.33 – 7.28 (m, 1H), 7.22 – 7.11 (m, 7H), 7.02 (d, $J = 7.5$ Hz, 1H), 2.13 (td, $J = 12.8$, 4.1 Hz, 1H), 1.94 (s, 3H), 1.82 – 1.68 (m, 3H), 1.54 – 1.46 (m, 1H), 1.35 – 1.23 (m, 2H), 1.14 – 0.98 (m, 2H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 170.66, 160.68, 156.94, 142.78, 142.25, 137.69, 137.29, 128.22 (CH×2), 126.84 (CH×2), 126.76, 126.66, 126.48, 125.80, 125.67, 124.45, 122.97, 120.25, 119.94, 54.57, 52.88, 33.59, 32.96, 25.39, 22.81, 22.43, 21.93.

GC-MS: m/z calced for C$_{28}$H$_{26}$: 362, found: 362.
4b-methyl-9,10-diphenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3ab): white solid, 28.2 mg, 81% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.39 (m, 1H), 7.36 – 7.32 (s, 1H), 7.29 – 7.19 (m, 4H), 7.13 – 6.98 (m, 5H), 6.95 – 6.89 (m, 3H), 6.41 – 6.36 (m, 1H), 2.54 - 2.45 (m, 1H), 2.39 – 2.26 (m, 2H), 2.01 (q, $J = 12.0$ Hz, 1H), 1.85 – 1.77 (m, 1H), 1.62 (t, $J = 12.9$ Hz, 1H), 1.53 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 155.15, 151.62, 142.71, 142.08, 140.07, 139.63, 135.48, 131.71, 129.18 (CH×2), 127.69 (CH×2), 127.43 (CH×2), 127.17 (CH×2), 126.96, 126.58, 126.21, 125.52, 121.48, 120.57, 51.66, 42.57, 30.33, 25.19, 20.94.
GC-MS: m/z calced for C27H24: 348, found: 348.

(Z)-4b-methyl-10,11-diphenyl-4b,6,7,8-tetrahydro-5H-cycloocta[a]indene (3ac): white solid, 27.5 mg, 76% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2c (14 μL, 0.12 mmol) with AgSbF$_6$ (3.5 mg, 0.01 mmol) in CHCl$_3$ at 60 °C.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.58 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 7.5$ Hz, 1H), 7.41 – 7.26 (m, 8H), 7.22 – 7.13 (m, 3H), 6.46 (t, $J = 7.3$ Hz, 1H), 2.35 – 2.18 (m, 2H), 2.12 – 2.04 (m, 1H), 2.00 – 1.91 (m, 1H), 1.76 – 1.67 (m, 1H), 1.62 – 1.54 (m, 1H), 1.49 – 1.42 (m, 1H), 1.11 – 0.98 (m, 4H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 153.06, 150.21, 143.41, 140.20, 138.00, 137.01, 135.61, 129.97, 128.37 (CH×4), 128.16 (CH×2), 127.32, 126.84, 126.62, 126.13 (CH×2), 125.26, 121.55, 120.61, 56.45, 37.28, 28.69, 28.00, 25.37, 23.51.
GC-MS: m/z calced for C28H26: 362, found: 362.

(Z)-4b-methyl-11,12-diphenyl-4b,5,6,7,8,9-hexahydrocyclonona[a]indene (3ad): white solid, 28.2 mg, 75% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2d (13.2 μL, 0.12 mmol) in CHCl$_3$ at 60 °C.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 1H), 7.41 – 7.26 (m, 8H), 7.22 – 7.13 (m, 3H), 6.46 (t, $J = 7.3$ Hz, 1H), 2.35 – 2.18 (m, 2H), 2.12 – 2.04 (m, 1H), 2.00 – 1.91 (m, 1H), 1.76 – 1.67 (m, 1H), 1.62 – 1.54 (m, 1H), 1.49 – 1.42 (m, 1H), 1.11 – 0.98 (m, 4H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 153.06, 150.21, 143.41, 140.20, 138.00, 137.01, 135.61, 129.97, 128.37 (CH×4), 128.16 (CH×2), 127.32, 126.84, 126.62, 126.13 (CH×2), 125.26, 121.55, 120.61, 56.45, 37.28, 28.69, 28.00, 25.37, 23.51.
GC-MS: m/z calced for C28H26: 362, found: 362.
mg, 0.12 mmol) with AgSbF$_6$ (3.5 mg, 0.01 mmol) in CHCl$_3$ at 60 °C.

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.61 (d, $J$ = 8.1 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 3H), 7.37 (dd, $J$ = 11.1, 3.8 Hz, 2H), 7.32 – 7.20 (m, 7H), 6.07 (dd, $J$ = 10.7, 6.6 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.08 – 2.00 (m, 1H), 1.86 – 1.73 (m, 2H), 1.64 – 1.56 (m, 1H), 1.49 – 1.40 (m, 2H), 1.38 – 1.29 (m, 1H), 1.23 – 1.14 (m, 1H), 0.92 (s, 3H), 0.71 – 0.61 (m, 1H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 152.62, 149.11, 143.65, 141.88, 140.51, 136.47, 135.62, 133.12, 128.39 (CH×4), 128.22 (CH×2), 127.36, 127.06 (CH×2), 127.00, 126.52, 125.35, 121.60, 120.68, 56.09, 35.99, 27.47, 27.16, 25.50, 24.66, 19.05.

GC-MS: m/z calced for C$_{29}$H$_{28}$: 376, found: 376.

(Z)-4b-methyl-12,13-diphenyl-4b,6,7,8,9,10-hexahydro-5H-cyclodeca[a]indene (3ae):
white solid, 27.3 mg, 70% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2e (14.9 mg, 0.12 mmol) with AgSbF$_6$ (3.5 mg, 0.01 mmol) in CHCl$_3$ at 60 °C.

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.62 (d, $J$ = 7.0 Hz, 2H), 7.55 (d, $J$ = 7.4 Hz, 2H), 7.45 (d, $J$ = 7.0 Hz, 1H), 7.40 – 7.24 (m, 9H), 5.73 – 5.66 (m, 1H), 2.39 – 2.26 (m, 1H), 1.77 (dt, $J$ = 13.7, 8.9 Hz, 1H), 1.68 – 1.57 (m, 2H), 1.49 – 1.42 (m, 1H), 1.27 (dd, $J$ = 26.5, 13.9 Hz, 4H), 1.10 – 0.99 (m, 1H), 0.93 (s, 3H), 0.73 – 0.61 (m, 1H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 152.10, 148.49, 143.50, 142.81, 141.70, 137.30, 135.82, 133.78, 128.40 (CH×2), 128.35 (CH×2), 128.27 (CH×2), 127.65 (CH×2), 127.23, 127.13, 126.38, 125.39, 121.81, 120.61, 55.26, 32.77, 29.48, 28.89, 28.66, 27.99, 22.35, 20.88.

GC-MS: m/z calcd for C$_{30}$H$_{30}$: 390, found: 390.

(Z)-1,1,9b-trimethyl-4,5-diphenyl-1,1a,2,9b,10,10a-hexahydrocyclopropa[6,7]cycloocta[1,2-a]indene (3af): colorless liquid, 28.5 mg, 71% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2d (14 μL, 0.12 mmol) according to the General Procedure.
**1H NMR (600 MHz, CHLOROFORM-D)** \( \delta \) 7.45 – 7.43 (m, 1H), 7.39 – 7.36 (m, 2H), 7.33 – 7.31 (m, 1H), 7.29 – 7.27 (m, 2H), 7.22 (dd, \( J = 10.4, 4.7 \) Hz, 2H), 7.14 (ddd, \( J = 6.8, 4.0, 1.3 \) Hz, 1H), 7.11 – 7.08 (m, 1H), 7.00 – 6.96 (m, 3H), 6.32 (dd, \( J = 6.8, 2.8 \) Hz, 1H), 2.81 (ddd, \( J = 20.1, 6.7, 5.5 \) Hz, 1H), 2.35 – 2.26 (m, 2H), 1.66 (t, \( J = 13.0 \) Hz, 1H), 1.42 (s, 3H), 1.00 (s, 3H), 0.88 (s, 3H), -0.01 (ddd, \( J = 12.6, 8.9, 2.1 \) Hz, 1H).

**13C NMR (101 MHz, CHLOROFORM-D)** \( \delta \) 152.75, 151.99, 144.23, 143.56, 139.12, 135.96, 135.51, 131.78, 128.90 (CH\( \times 2 \)), 127.92 (CH\( \times 2 \)), 127.49 (CH\( \times 2 \)), 127.11 (CH\( \times 2 \)), 126.88, 126.67, 126.08, 125.17, 121.29, 119.99, 57.42, 34.77, 28.78, 27.28, 24.26, 23.41, 22.97, 17.83, 15.37.

GC-MS: m/z calced for C\(_{31}\)H\(_{30}\): 402, found: 402.

![Image of 3,3-dimethyl-3'-phenyl-2'-(1-phenylvinyl)spiro[cyclohexane-1,1'-indene] (3ag)](image)

3,3-dimethyl-3'-phenyl-2'-(1-phenylvinyl)spiro[cyclohexane-1,1'-indene] (3ag): colorless liquid, 22.6 mg, 58% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2e (15 mg, 0.12 mmol) according to the General Procedure.

**1H NMR (400 MHz, CHLOROFORM-D)** \( \delta \) 7.90 (d, \( J = 7.4 \) Hz, 1H), 7.43 (d, \( J = 7.7 \) Hz, 2H), 7.38 (dd, \( J = 7.0, 1.3 \) Hz, 2H), 7.31 (t, \( J = 7.5 \) Hz, 2H), 7.26 – 7.17 (m, 7H), 5.73 (s, 1H), 5.05 (s, 1H), 2.02 – 1.92 (m, 1H), 1.87 (d, \( J = 14.3 \) Hz, 1H), 1.58 – 1.41 (m, 5H), 1.12 – 1.08 (m, 4H), 0.85 (s, 3H).

**13C NMR (101 MHz, CHLOROFORM-D)** \( \delta \) 154.04, 153.07, 144.15, 143.65, 140.90, 139.37, 135.58, 129.27 (CH\( \times 2 \)), 128.22 (CH\( \times 2 \)), 128.16 (CH\( \times 2 \)), 127.61, 127.16, 126.81 (CH\( \times 2 \)), 126.35, 124.93, 124.61, 120.75, 119.40, 56.10, 44.38, 38.76, 35.73, 32.14, 30.86, 28.23, 20.30.

GC-MS: m/z calced for C\(_{30}\)H\(_{30}\): 390, found: 390.

![Image of 1-methyl-3-phenyl-2-(1-phenylvinyl)-1-propyl-1H-indene (3ah)](image)

1-methyl-3-phenyl-2-(1-phenylvinyl)-1-propyl-1H-indene (3ah): colorless liquid, 25.2 mg, 72% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2f (15 \( \mu \)L, 0.12 mmol) according to the General Procedure.
\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta\) 7.50 (d, \(J = 7.6\) Hz, 2H), 7.37 – 7.31 (m, 6H), 7.29 – 7.19 (m, 6H), 5.63 – 5.57 (m, 1H), 5.15 (s, 1H), 1.83 – 1.73 (m, 2H), 1.20 (s, 3H), 1.09 – 0.99 (m, 1H), 0.76 – 0.67 (m, 4H).

\(^1^3\)C NMR (101 MHz, CHLOROFORM-D) \(\delta\) 151.99, 150.54, 144.54, 143.79, 141.26, 140.50, 135.56, 129.23 (CH×2), 128.20 (CH×2), 128.05 (CH×2), 127.50, 127.28 (CH×2), 127.22, 126.50, 125.48, 121.69, 120.72, 118.06, 55.43, 40.70, 25.20, 17.50, 14.36.

GC-MS: m/z calced for C\(_{27}\)H\(_{26}\): 350, found: 350.

trimethyl(3-(1-methyl-3-phenyl-2-(1-phenylvinyl)-1H-inden-1-yl)propyl)silane (3ai): colorless liquid, 26.2 mg, 62% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2g (18.7 mg, 0.12 mmol) according to the General Procedure.

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta\) 7.49 – 7.44 (m, 2H), 7.35 – 7.18 (m, 12H), 5.57 (s, 1H), 5.10 (s, 1H), 1.86 – 1.69 (m, 2H), 1.17 (s, 3H), 1.05 (dtd, \(J = 13.6, 11.3, 5.2\) Hz, 1H), 0.80 – 0.68 (m, 1H), 0.28 – 0.22 (m, 2H), -0.14 (s, 9H).

\(^1^3\)C NMR (101 MHz, CHLOROFORM-D) \(\delta\) 151.95, 150.59, 144.60, 143.73, 141.27, 140.48, 135.63, 129.21 (CH×2), 128.24 (CH×2), 128.08 (CH×2), 127.51, 127.29 (CH×2), 127.21, 126.49, 125.48, 121.70, 120.73, 118.12, 55.57, 42.37, 25.16, 18.49, 17.13, -1.46 (CH×2).

GC-MS: m/z calced for C\(_{30}\)H\(_{34}\)Si: 422, found: 422.

1,1-dimethyl-2-(2-methyl-1-phenylprop-1-en-1-yl)-3-phenyl-1H-indene (3aj): colorless liquid, 30.8 mg, 88% yield.

Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2h (12 µL, 0.12 mmol) according to the General Procedure.

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta\) 7.65 (d, \(J = 7.8\) Hz, 2H), 7.42 (t, \(J = 7.7\) Hz, 3H), 7.38 – 7.21 (m, 9H), 1.69 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 0.74 (s, 3H).

\(^1^3\)C NMR (101 MHz, CHLOROFORM-D) \(\delta\) 154.26, 152.98, 142.49, 141.65, 138.12, 136.38, 134.21, 130.45 (CH×2), 130.21, 128.53 (CH×2), 128.37 (CH×2), 127.85 (CH×2), 127.12, 126.53, 126.45, 125.23, 121.37, 120.66, 51.93, 26.78, 24.49, 23.64, 21.99.
GC-MS: m/z calced for C_{27}H_{26}: 350, found: 350.

**Ph**<sup>Ph</sup>(E)-3'-phenyl-2'-(1-phenylprop-1-en-1-yl)spiro[cyclohexane-1,1'-indene] (3ak): white solid, 29.7 mg, 79% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2i (13.2 mg, 0.12 mmol) according to the General Procedure.

<sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 7.82 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 – 7.25 (m, 7H), 7.23 – 7.17 (m, 2H), 5.63 (q, J = 7.0 Hz, 1H), 1.97 – 1.80 (m, 3H), 1.72 (d, J = 7.2 Hz, 3H), 1.67 – 1.58 (m, 4H), 1.25 – 1.15 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 156.27, 151.98, 144.15, 139.61, 138.58, 136.14, 135.79, 129.97, 129.62 (CH×2), 129.52 (CH×2), 128.20 (CH×2), 127.92 (CH×2), 126.99, 126.75, 126.40, 124.85, 124.34, 120.85, 54.93, 32.92 (CH₂×2), 25.43, 22.54 (CH₂×2), 15.38.

GC-MS: m/z calced for C_{29}H_{28}: 376, found: 376.

**Ph**<sup>Ph</sup>CH<sub>2</sub>Cl

1-(4-chlorophenyl)-3-phenyl-2-(1-phenylvinyl)-1H-indene (3al): colorless liquid, 25.4 mg, 63% yield.
Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2j (14 μL, 0.12 mmol) according to the General Procedure.

<sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 7.45 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.32 (t, J = 6.3 Hz, 3H), 7.28 – 7.25 (m, 1H), 7.23 – 7.16 (m, 9H), 6.88 (d, J = 8.3 Hz, 2H), 5.33 (s, 1H), 5.00 (s, 1H), 4.83 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 147.76, 147.18, 145.00, 143.73, 142.16, 141.03, 138.17, 134.87, 132.44, 129.91 (CH×2), 129.22 (CH×2), 128.71 (CH×2), 128.31 (CH×2), 128.12 (CH×2), 127.49 (CH×4), 127.26, 126.11, 124.26, 120.95, 118.79, 57.41.

GC-MS: m/z calced for C_{29}H_{21}Cl: 404, found: 404.
3-phenyl-2-(1-phenylvinyl)-1-(p-tolyl)-1H-indene (3am): white solid, 23.8 mg, 62% yield. Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2k (16 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.43 (d, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 3H), 7.25 – 7.14 (m, 8H), 7.03 (d, $J = 7.7$ Hz, 2H), 6.87 (d, $J = 7.7$ Hz, 2H), 5.33 (s, 1H), 5.03 (s, 1H), 4.84 (s, 1H), 2.29 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 148.47, 147.63, 144.99, 143.99, 141.73, 141.20, 136.45, 136.22, 135.15, 129.28 (CH×3), 128.41 (CH×2), 128.18 (CH×2), 127.98 (CH×2), 127.55 (CH×2), 127.32 (CH×2), 126.95, 125.94, 124.30, 120.74, 118.58, 57.88, 21.26.

GC-MS: m/z calced for C$_{30}$H$_{24}$: 384, found: 384.

1-(4-(tert-butyl)phenyl)-3-phenyl-2-(1-phenylvinyl)-1H-indene (3an): white solid, 26.0 mg, 61% yield. Synthesized from 1,1,3-triphenylprop-2-yn-1-ol 1a (28.4 mg, 0.1 mmol) and alkene 2l (22 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.39 (d, $J = 7.6$ Hz, 2H), 7.34 (d, $J = 7.4$ Hz, 1H), 7.29 – 7.10 (m, 15H), 6.90 (d, $J = 8.2$ Hz, 2H), 5.32 (s, 1H), 5.04 (s, 1H), 4.84 (s, 1H), 1.26 (s, 9H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 149.36, 148.39, 147.64, 144.99, 144.02, 141.67, 141.23, 136.31, 135.21, 129.30 (CH×2), 128.14 (CH×2), 128.06 (CH×2), 127.92 (CH×2), 127.58 (CH×2), 127.27, 127.24, 126.92, 125.86, 125.39 (CH×2), 124.36, 120.72, 118.70, 57.88, 34.52, 31.51 (CH×3).

GC-MS: m/z calced for C$_{33}$H$_{30}$: 426, found: 426.
4b-methyl-10-phenyl-9-(p-tolyl)-4b,5,6,7-tetrahydrobenzo[a]azulene (3bb): white solid, 30.4 mg, 84% yield.
Synthesized from propargylic alcohol 1b (29.8 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.45 – 7.34 (m, 2H), 7.32 – 7.23 (m, 4H), 7.17 – 7.04 (m, 3H), 6.93 (d, $J = 8.1$ Hz, 2H), 6.75 (d, $J = 8.0$ Hz, 2H), 6.41 – 6.36 (m, 1H), 2.54 – 2.44 (m, 1H), 2.38 – 2.27 (m, 2H), 2.15 (s, 3H), 2.06 – 1.95 (m, 1H), 1.86 – 1.77 (m, 1H), 1.68 – 1.59 (m, 1H), 1.52 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 155.16, 151.70, 142.76, 139.78, 139.38, 139.04, 135.76, 135.53, 130.66, 129.12 (CH×2), 128.15 (CH×2), 127.69 (CH×2), 126.93, 126.88 (CH×2), 126.55, 125.44, 121.46, 120.54, 51.69, 42.71, 30.24, 25.16, 21.00, 20.79.
GC-MS: m/z calced for C$_{28}$H$_{26}$: 362, found: 362.

9-(4-bromophenyl)-4b-methyl-10-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3cb): white solid, 33.6 mg, 79% yield.
Synthesized from propargylic alcohol 1c (36.2 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.42 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.06 (m, 3H), 7.06 – 7.01 (m, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.37 (dd, $J = 8.4$, 4.3, 1H), 2.49 (dt, $J = 14.9$, 7.5 Hz, 1H), 2.37 – 2.24 (m, 2H), 2.00 (td, $J = 13.7$, 1.8 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.61 (t, $J = 12.9$ Hz, 1H), 1.49 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 155.04, 150.93, 142.47, 141.05, 139.99, 139.05, 135.25, 132.26, 130.47 (CH×2), 129.07 (CH×2), 128.68 (CH×2), 127.87 (CH×2), 127.27, 126.66, 125.71, 121.50, 120.67, 120.04, 51.62, 42.46, 30.31, 25.04, 20.85.
GC-MS: m/z calced for C$_{27}$H$_{23}$Br: 426, found: 426.
9-(4-methoxyphenyl)-4b-methyl-10-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3db): colorless liquid, 24.9 mg, 66% yield. Synthesized from propargylic alcohol 1d (31.4 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) according to the General Procedure.

\[
\begin{align*}
\text{^1H NMR (400 MHz, CHLOROFORM-D)} & \delta 7.43 – 7.32 (m, 2H), 7.31 – 7.21 (m, 4H), 7.16 – 7.09 (m, 2H), 7.08 – 7.02 (m, 1H), 6.98 – 6.91 (m, 2H), 6.51 – 6.45 (m, 2H), 6.31 (dt, J = 7.3, 3.7 Hz, 1H), 3.64 (s, 3H), 2.46 (dd, J = 14.8, 7.2 Hz, 1H), 2.36 – 2.23 (m, 2H), 1.99 (dd, J = 25.0, 12.6 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.60 (t, J = 13.0 Hz, 1H), 1.50 (s, 3H).
\end{align*}
\]

\[
\begin{align*}
\text{^13C NMR (101 MHz, CHLOROFORM-D)} & \delta 158.13, 155.15, 151.84, 142.74, 139.38, 135.51, 134.79, 129.94, 129.09 (CH×2), 128.13 (CH×2), 127.72 (CH×2), 127.00, 126.55, 125.45, 121.46, 120.53, 112.89 (CH×2), 55.27, 51.67, 42.68, 30.20, 25.26, 20.81.
\end{align*}
\]

GC-MS: m/z calced for C_{28}H_{26}O: 378, found: 378.

4b-methyl-10-phenyl-9-propyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3eb): colorless liquid, 21.0 mg, 67% yield. Synthesized from propargylic alcohol 1e (25.0 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) at 25 °C according to the General Procedure.

\[
\begin{align*}
\text{^1H NMR (400 MHz, CHLOROFORM-D)} & \delta 7.45 – 7.19 (m, 9H), 5.88 – 5.80 (m, 1H), 2.23 (dd, J = 12.6, 4.5 Hz, 2H), 2.14 (t, J = 12.7 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.74 – 1.62 (m, 3H), 1.49 (t, J = 13.0 Hz, 1H), 1.33 (s, 3H), 1.22 – 1.02 (m, 2H), 0.62 (t, J = 7.3 Hz, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{^13C NMR (101 MHz, CHLOROFORM-D)} & \delta 154.84, 153.10, 143.06, 139.62, 136.57, 136.39, 129.10, 128.98 (CH×2), 128.39 (CH×2), 127.39, 126.43, 125.08, 121.28, 120.03, 51.57, 42.54, 39.44, 29.76, 25.38, 21.99, 21.19, 14.12.
\end{align*}
\]

GC-MS: m/z calced for C_{24}H_{26}: 314, found: 314.
9-(3-methoxypropyl)-4b-methyl-10-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3fb):
colorless liquid, 19.9 mg, 58% yield.
Synthesized from propargylic alcohol 1f (28.0 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) at 25 °C according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.24 (m, 4H), 7.23 – 7.19 (m, 2H), 5.89 – 5.84 (m, 1H), 3.16 (s, 3H), 3.04 (t, $J = 6.0$ Hz, 2H), 2.26 – 2.08 (m, 3H), 1.94 – 1.84 (m, 1H), 1.79 – 1.62 (m, 4H), 1.51 – 1.41 (m, 2H), 1.32 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 154.81, 152.61, 142.92, 138.87, 136.86, 136.25, 129.61, 128.97 (CH×2), 128.44 (CH×2), 127.51, 126.46, 125.19, 121.30, 120.08, 72.73, 58.42, 51.58, 42.49, 33.43, 29.76, 28.77, 25.31, 21.23.

GC-MS: m/z calced for C$_{25}$H$_{28}$O: 344, found: 344.

2-(4b-methyl-10-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulen-9-yl)thiophene (3gb):
colorless liquid, 20.5 mg, 58% yield

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.47 – 7.37 (m, 4H), 7.32 – 7.27 (m, 2H), 7.22 (t, $J = 7.5$ Hz, 2H), 7.15 (t, $J = 7.3$ Hz, 1H), 6.82 (d, $J = 5.0$ Hz, 1H), 6.58 – 6.54 (m, 1H), 6.54 – 6.47 (m, 2H), 2.50 – 2.40 (m, 1H), 2.36 – 2.25 (m, 2H), 2.03 – 1.91 (m, 1H), 1.83 – 1.74 (m, 1H), 1.58 (td, $J = 13.2$, 2.7 Hz, 1H), 1.46 (s, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 155.05, 150.65, 145.56, 142.38, 139.55, 135.57, 133.68, 130.28, 128.91 (CH×2), 127.95 (CH×2), 127.25, 126.60, 126.56, 125.71, 124.53, 123.07, 121.51, 120.81, 51.77, 42.50, 29.96, 24.98, 20.40.

GC-MS: m/z calced for C$_{33}$H$_{22}$S: 354, found: 354.

4b,10-dimethyl-9-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3hb): colorless liquid, 20.3
mg, 71% yield.
Synthesized from propargylic alcohol 1g (22.0 mg, 0.1 mmol) and alkene 2b (13 µL, 0.12 mmol) at 25 °C according to the General Procedure.

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta 7.36 – 7.17 \text{ (m, 9H), 6.43 – 6.36 \text{ (m, 1H), 2.41 (dt, } J = 15.0, 7.5 \text{ Hz, 1H), 2.25 (dd, } J = 13.3, 4.9 \text{ Hz, 1H), 2.14 (t, } J = 13.3 \text{ Hz, 1H), 1.91 (dd, } J = 25.8, 12.1 \text{ Hz, 1H), 1.76 – 1.66 \text{ (m, 1H), 1.60 (s, 3H), 1.49 (t, } J = 13.0 \text{ Hz, 1H), 1.40 (s, 3H).}

\(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \(\delta 154.92, 149.50, 144.22, 143.24, 139.29, 134.86, 131.36, 128.32 (\text{CH} \times 2), 126.93 (\text{CH} \times 2), 126.69, 126.52, 125.26, 121.00, 119.08, 51.34, 42.03, 30.28, 24.98, 21.25, 12.28.

GC-MS: m/z calced for C\(_{22}\)H\(_{22}\): 286, found: 286.

3,4b,10-trimethyl-9-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3ib): colorless liquid, 18.0 mg, 60% yield.
Synthesized from propargylic alcohol 1h (23.6 mg, 0.1 mmol) and alkene 2b (13 µL, 0.12 mmol) at 25 °C according to the General Procedure.

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta 7.28 – 7.19 \text{ (m, 5H), 7.16 – 7.13 \text{ (m, 2H), 7.12 – 7.07 \text{ (m, 1H), 6.38 (dd, } J = 8.5, 4.2 \text{ Hz, 1H), 2.43 (s, 3H), 2.38 (dd, } J = 15.9, 7.9 \text{ Hz, 1H), 2.23 (dd, } J = 13.0, 5.7 \text{ Hz, 1H), 2.18 – 2.09 \text{ (m, 1H), 1.95 – 1.84 \text{ (m, 1H), 1.74 – 1.67 \text{ (m, 1H), 1.58 (s, 3H), 1.53 – 1.44 \text{ (m, 1H), 1.39 (s, 3H).}}

\(^{13}\)C NMR (101 MHz, CHLOROFORM-D) \(\delta 155.18, 148.50, 143.35, 141.65, 139.40, 134.97, 134.75, 131.09, 128.28 (\text{CH} \times 2), 127.19, 126.94 (\text{CH} \times 2), 126.64, 121.97, 118.82, 51.13, 42.14, 30.30, 24.95, 21.79, 21.31, 12.33.

GC-MS: m/z calced for C\(_{23}\)H\(_{24}\): 300, found: 300.

3-chloro-4b,10-dimethyl-9-phenyl-4b,5,6,7-tetrahydrobenzo[a]azulene (3jb): colorless liquid, 20.8 mg, 65% yield.
Synthesized from propargylic alcohol 1i (25.6 mg, 0.1 mmol) and alkene 2b (13 µL, 0.12 mmol) at 25 °C according to the General Procedure.

\(^1\)H NMR (400 MHz, CHLOROFORM-D) \(\delta 7.31 – 7.18 \text{ (m, 7H), 7.14 (d, } J = 8.1 \text{ Hz, 1H), 6.39 (dd, } J = 8.4, 4.3 \text{ Hz, 1H), 2.41 (dt, } J = 15.0, 7.5 \text{ Hz, 1H), 2.23 – 2.08 \text{ (m, 2H), 1.95 – } 818
1.83 (m, 1H), 1.74 – 1.65 (m, 1H), 1.56 (s, 3H), 1.52 – 1.44 (m, 1H), 1.39 (s, 3H).

$^1$C NMR (101 MHz, CHLOROFORM-D) δ 156.57, 149.96, 143.00, 142.72, 138.96, 134.20, 131.63, 131.22, 128.38 (CH×2), 126.87 (CH×2), 126.81, 126.63, 121.70, 120.00, 51.61, 41.81, 30.22, 24.81, 21.21, 12.25.

GC-MS: m/z calced for C$\text{22}$H$\text{21}$Cl: 320, found: 320.

4b,10-dimethyl-9-phenyl-3-(trifluoromethyl)-4b,5,6,7-tetrahydrobenzo[a]azulene (3kb): colorless liquid, 21.6 mg, 61% yield.

Synthesized from propargylic alcohol 1j (29.0 mg, 0.1 mmol) and alkene 2b (13 μL, 0.12 mmol) at 25 °C according to the General Procedure.

$^1$H NMR (400 MHz, CHLOROFORM-D) δ 7.54 (d, $J = 7.1$ Hz, 2H), 7.32 – 7.21 (m, 6H), 6.46 – 6.41 (m, 1H), 2.43 (dt, $J = 15.1$, 7.4 Hz, 1H), 2.26 (dd, $J = 13.7$, 5.6 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.92 (dd, $J = 24.1$, 11.9 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.60 (s, 3H), 1.54 – 1.49 (m, 1H), 1.42 (s, 3H).

$^1$C NMR (101 MHz, CHLOROFORM-D) δ 155.10, 152.66, 147.64, 142.80, 138.80, 134.23, 132.09, 128.45, 127.14 (q, $J = 31.8$ Hz), 126.91, 126.84, 125.12 (q, $J = 272.1$ Hz), 124.03 (q, $J = 3.5$ Hz), 119.08, 117.80 (q, $J = 3.6$ Hz), 51.79, 41.69, 30.23, 24.82, 21.13, 12.23.

GC-MS: m/z calced for C$\text{23}$H$\text{21}$F$_3$: 354, found: 354.
V. Product Structure Determination

The structure of products were determined by X-ray diffraction. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC). The structure of other products were assumed by analogy.

### Table S1. Crystal data and structure refinement for 3ab (CCDC: 1813668).

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<td>293 K</td>
</tr>
<tr>
<td>Volume</td>
<td>991.35(15)</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>Hall group</td>
<td>-P 1</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C27 H24</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C27 H24</td>
</tr>
<tr>
<td>Mr</td>
<td>348.46</td>
</tr>
<tr>
<td>Dx, g/cm³</td>
<td>1.167</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Mu (mm⁻¹)</td>
<td>0.493</td>
</tr>
<tr>
<td>F000</td>
<td>372.0</td>
</tr>
<tr>
<td>h, k, l max</td>
<td>11, 12, 13</td>
</tr>
<tr>
<td>Nref</td>
<td>3316</td>
</tr>
<tr>
<td>Tmin, Tmax</td>
<td>0.874, 1.000</td>
</tr>
<tr>
<td>Correction method</td>
<td># Reported T Limits: Tmin=0.874 Tmax=1.000</td>
</tr>
<tr>
<td>Data completeness</td>
<td>0.966</td>
</tr>
<tr>
<td>Theta(max)</td>
<td>65.647</td>
</tr>
<tr>
<td>R(reflections)</td>
<td>0.0516(2686)</td>
</tr>
<tr>
<td>wR2(reflections)</td>
<td>0.1400(3316)</td>
</tr>
<tr>
<td>S</td>
<td>1.035</td>
</tr>
<tr>
<td>Npar</td>
<td>245</td>
</tr>
</tbody>
</table>

### Table S2. Crystal data and structure refinement for 3ak (CCDC: 1813666).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Cell: a=15.1865(15)</td>
<td>b=11.8880(14)</td>
</tr>
<tr>
<td>c=23.645(3)</td>
<td></td>
</tr>
</tbody>
</table>
alpha=90                beta=95.227(10)         gamma=90
Temperature            100 K
Volume                  4251.0(8)
Space group             C2/c
Hall group              -C2yc
Moiety formula          C29 H28
Sum formula             C29 H28
Mr                      376.51
Dx,g/cm3                1.177
Z                       8
Mu (mm-1)               0.066
F000                    1616.0
h,k,lmax                18,14,28
Nref                    3732
Tmin,Tmax               0.370,1.000
Correction method= # Reported T Limits:  Tmin=0.370   Tmax=1.000
Data completeness= 0.997  Theta(max)= 25.005
R(reflections)= 0.0617( 2397)   wR2(reflections)= 0.1383( 3732)
S = 1.034               Npar= 263
References:
3al

Ph
Ph
CH₂
Cl

Ph

3al
3am