Supporting Information

FeCl₃ mediated intramolecular olefin-cation cyclisation of cinnamates for the synthesis of highly substituted indenes

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General Information

All reactions were carried out under nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. Anhydrous THF and diethyl ether were distilled from sodium-benzophenone and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure material, unless otherwise stated.

Reaction were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrine stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. 2-acetylbenzaldehyde was obtained from Aldrich and used as it is. NMR spectra were recorded on either a Bruker Avance 200 (\textsuperscript{1}H: 200 MHz, \textsuperscript{13}C: 50MHz), Bruker Avance 400 (\textsuperscript{1}H: 400 MHz, \textsuperscript{13}C: 100MHz), Bruker Avance 500 (\textsuperscript{1}H: 500 MHz, \textsuperscript{13}C: 125 MHz), JEOL ECX 500 (\textsuperscript{1}H: 500 MHz, \textsuperscript{13}C: 125 MHz) Mass spectrometric data were obtained using WATERS-Q-Tof Premier-ESI-MS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dm = doublet of a multiplet, m = multiplet, br = broad.
Compound 11g: To a magnetically stirred solution of the 11j (50 mg, 0.20 mmol) in CH₂Cl₂ (5 ml) was added pyridine (0.1 ml, 1 mmol) and benzoyl chloride (0.1 ml, 0.60 mmol). The reaction mixture was stirred for 6 h at RT then extracted with CH₂Cl₂, washed with brine, dil.HCl and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using EtOAc-hexane (5:95) as eluent furnished the compound 11g (60 mg, 85%) as a white crystalline solid. Rᵥ = 0.45 (EtOAc-hexane 5:95); IR (neat): v max/cm⁻¹ 1740, 1716, 1637, 1451, 1307, 1263; ¹H NMR (500 MHz, CDCl₃) δ 1.16 (t, J = 7.3 Hz, 3H), 2.04 (s, 3H), 2.20 (s, 3H), 4.10 (q, J = 7.3 Hz, 2H), 4.96 (s, 1H), 5.28 (br s, 1H), 6.40 (d, J = 16.4 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.53 (m, 2H), 7.67 (m, 2H), 8.21 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 14.1, 16.4, 24.4, 60.3, 117.5, 123.3, 125.6, 126.3, 128.7, 129.0, 130.1, 130.2, 131.4, 133.8, 139.2, 143.8, 144.2, 147.9, 164.3, 166.7; HRMS (C₂₂H₂₃O₄): Calc’d 351.1596 [(M+H)+], Found 351.1598.

Compound 11h: To a magnetically stirred solution of the 11j (45.0 mg, 0.18 mmol) in CH₂Cl₂ (5.0 ml), was added pyridine (0.1 ml, 0.36 mmol) and benzoyl chloride (66.6 mg, 0.36 mmol). The reaction mixture was stirred for 6 h at RT then extracted with CH₂Cl₂, washed with brine, dil.HCl and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using EtOAc-hexane (1:9) as eluent furnished the compound 11h (54 mg, 76%) as a white crystalline solid Rᵥ = 0.39 (EtOAc-hexane 5:95); IR (neat): v max/cm⁻¹ 1774, 1705, 1616, 1590, 1522, 1488, 1347, 1325, 1227; ¹H NMR (200 MHz, CDCl₃) δ 1.32 (t, J = 7.2 Hz, 3H), 2.04 (s, 3H), 2.32 (s, 3H), 4.26 (q, J = 7.2 Hz, 2H), 4.93 (br s, 1H), 5.31 (br s, 1H), 6.51 (d, J = 16.4 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 16.4 Hz, 1H), 8.30 (d, J = 9.0 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 14.3, 16.0, 24.4, 60.7, 118.1, 121.8, 123.5, 125.4, 126.9, 129.5,
HRMS (C_{22}H_{22}NO_{6}): Calc’d 396.1447 [(M+H)^+], Found 396.1442.

(a) PPh_{3}={CHCO_{2}Et, CH_{2}Cl_{2}, RT, 6 h, 95%; (b) CH_{3}P^{+}Ph_{3}Br^{-}, n-BuLi, THF, 0°C, 82%.

**Compound 14:** To a stirred solution of the aldehyde 13 (500 mg, 2.08 mmol) which was prepared according to reported literature procedure\(^1\) in CH_{2}Cl_{2} (15 ml) was added Ph_{3}P={CHCO_{2}Et (2.1 g, 6.25 mmol) and the reaction mixture was stirred for 6 h at RT. Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using EtOAc-hexane (2:8) as eluent furnished product 14 (614 mg, 95%) as a white solid. \(R_f = 0.3\) (EtOAc-hexane 2:8); IR (neat): \(\nu_{\text{max}}/\text{cm}^{-1} \) 2933, 1712, 1654, 1597, 1316, 1178; \(^{1}\)H NMR (500 MHz, CDCl_{3}) \(\delta \) 1.25 (t, \(J = 7.2\) Hz, 3H), 3.86 (s, 3H), 4.17 (q, \(J = 7.2\) Hz, 2H), 6.37 (d, \(J = 15.7\) Hz, 1H), 6.92 (d, \(J = 8.9\) Hz, 1H), 7.38 - 7.51 (m, 3H), 7.72 (d, \(J = 15.7\) Hz, 1H), 7.71 (d, \(J = 7.7\) Hz, 1H), 7.77 (d, \(J = 8.9\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl_{3}) \(\delta \) 14.2, 55.5, 60.5, 113.8, 120.7, 127.0, 128.7, 129.1, 130.2, 130.3, 132.8, 133.4, 140.0, 141.7, 164.0, 166.3, 195.8; HRMS: m/z calcd for C_{19}H_{19}O_{4} [(M+H)^+]: 311.1283; Found: 311.1289.

**Compound 11l:** To a cold (0°C) magnetically stirred solution of CH_{3}P^{+}Ph_{3}Br^{-} (921 mg, 2.5 mmol) in dry THF (10 ml) was added n-BuLi (1.6 M in hexane, 1.5 ml, 2.5 mmol) slowly and stirred for 30 min. Then 14 (400 mg, 1.29 mmol) was added slowly and stirred reaction mixture for 3h at 0°C. When completion of the reaction was noticed by TLC, the mixture was carefully quenched with saturated ammonium chloride at 0°C and the product was extracted with ether twice. The combined organic layers were dried over Na_{2}SO_{4}. The solvent was removed under vacuo and the residue was purified on a silica gel column using EtOAc-hexane to furnish product 11l (326 mg, 82%) as a
colourless liquid; \( R_f = 0.33 \) (EtOAc-hexane 5:95); \textbf{IR} (neat): \( v_{\text{max}}/\text{cm}^{-1} \) 2925, 1711, 1510, 1314, 1176; \textbf{\( ^1H \) NMR} (500 MHz, CDCl\(_3\)) \( \delta \) 1.27 (t, \( J = 7.0 \) Hz, 3H), 3.79 (s, 3H), 4.17 (q, \( J = 7.0 \) Hz, 2H), 5.08 (br s, 1H), 5.79 (br s, 1H), 6.33 (d, \( J = 16.2 \) Hz, 1H), 6.82 (d, \( J = 8.9 \) Hz, 2H), 7.18 (d, \( J = 8.9 \) Hz, 2H), 7.25 (m, 1H), 7.35 - 7.39 (m, 2H), 7.67 (m, 1H), 7.76 (d, \( J = 16.2 \) Hz, 1H); \textbf{\( ^13C \) NMR} (125 MHz, CDCl\(_3\)) \( \delta \) 14.3, 55.3, 60.3, 113.8, 115.4, 118.8, 126.4, 127.8, 128.2, 129.7, 130.6, 133.2, 133.5, 143.1, 143.3, 146.8, 159.4, 166.9; \textbf{HRMS}: \( m/z \) calcd for C\(_{20}\)H\(_{20}\)O\(_3\) [(M+H)+]: 309.1491; Found: 309.1490

(a) \( \text{PPh}_3=\text{CHCO}_2\text{Et}, \text{CH}_2\text{Cl}_2, \text{RT, 6 h, 93 \%} \); (b) \( \text{CH}_3\text{P}^+\text{Ph}_3\text{Br}^- , n\text{-BuLi, THF, 0}^\circ\text{C, 80\%} \).

\textbf{Compound 16:} According to the procedure of wittig reaction for the compound 14, compound 15 (860 mg, 2.97 mmol) which was prepared according to reported literature procedure\(^1\) and \( \text{PPh}_3=\text{CHCO}_2\text{Et} \) (3.1g, 8.9 mmol) were used to furnish product 16 (1 g, 93\%) as a yellow solid, \( R_f =0.33 \) (EtOAc-hexane 15:85); \textbf{IR} (neat): \( v_{\text{max}}/\text{cm}^{-1} \) 1704, 1660, 1582, 1366; \textbf{\( ^1H \) NMR} (500 MHz, CDCl\(_3\)) \( \delta \) 1.25 (t, \( J = 7.2 \) Hz, 3H), 4.17 (q, \( J = 7.2 \) Hz, 2H), 6.36 (d, \( J = 16.0 \) Hz, 1H), 7.37 - 7.44 (m, 2H), 7.51- 7.59 (m, 3H), 7.62 - 7.65 (m, 2H), 7.70 - 7.73 (m, 2H); \textbf{\( ^13C \) NMR} (125 MHz, CDCl\(_3\)) \( \delta \) 14.2, 60.5, 121.1, 127.3, 128.8, 129.1, 129.2, 130.9, 131.7, 131.8, 134.0, 136.0, 138.6, 141.4, 166.1, 196.0; \textbf{HRMS}: \( m/z \) calcd for C\(_{18}\)H\(_{16}\)BrO\(_3\) [(M+H)+]: 359.0283; Found: 359.0281.

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**Compound 11m:** According to the procedure of one carbon Wittig reaction for the compound 11l, compound 16 (200 mg, 0.55 mmol), CH$_3$P$^+$Ph$_3$Br$^-$ (398 mg, 1.1 mmol) and n- BuLi (1.6 M in hexane, 0.68 ml, 1.1 mmol) were used to furnish product 11m (156 mg, 80 %) as a white solid; $R_f$ = 0.3 (EtOAc- hexane 5:95); **IR** (neat): $v_{max}$/cm$^{-1}$ 2927, 1712, 1487, 1313, 1175; **$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 1.26 (t, $J$ = 7.0 Hz, 3H), 4.17 (q, $J$ = 7.0 Hz, 2H), 5.2 (br s, 1H), 5.9 (br s, 1H), 6.30 (d, $J$ = 15.8 Hz, 1H), 7.11 (d, $J$ = 8.5 Hz, 2H), 7.22 - 7.23 (m, 1H), 7.36 - 7.38 (m, 2H), 7.40 (d, $J$ = 8.5 Hz, 2H), 7.65 - 7.67 (m, 1H), 7.69 (d, $J$ = 15.8 Hz, 1H); **$^{13}$C NMR** (125 MHz, CDCl$_3$) $\delta$ 14.3, 60.4, 117.7, 119.2, 122.0, 126.6, 128.2, 128.5, 129.9, 130.6, 131.6, 133.2, 139.7, 142.1, 143.0, 146.5, 166.7; **HRMS:** m/z calcd for C$_{19}$H$_{18}$BrO$_2$ [(M+H)$^+$]: 357.0490; Found: 357.0493.

**General Procedure For The Preparation Of Amide:**

Step 1: To a solution of ester in EtOH was added NaOH (3eq. dissolve in water) at room temperature and reflux for 2h, the mixture was adjusted to pH 1.0 with 1N HCl, and then extracted with EtOAc. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo and crude acid was directly used for next step.

Step 2: To a solution of acid in CH$_2$Cl$_2$ were added Dimethylformamide (DMF) (1 drop) and oxalyl chloride at 0°C under argon atmosphere. After 40 min. of stirring, the mixture was concentrated in vacuo to afford the crude acid chloride as yellow oil and crude product was employed directly in the following reaction. A solution of the crude acid chloride in CH$_2$Cl$_2$ was poured into 28% aqueous NH$_3$ solution or NHMe$_2$ 1M solution in THF at 0°C under argon atmosphere. After 10 min of stirring, the mixture was extracted with CH$_2$Cl$_2$, washed with brine, dried over Na$_2$SO$_4$, filtered and the solvent was removed under vacuo and the residue was purified on a silica gel column using EtOAc-hexane to furnish product.
**Compound 11n:** According to the general procedure of amide preparation, Step 1: ester 11b (460 mg, 1.76 mmol) and NaOH (212 mg, 5.30 mmol), furnished acid. Step 2: crude acid (396 mg, 1.70 mmol) in CH₂Cl₂, Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.439 ml, 5.11 mmol), then 10 ml 28% aqueous NH₃ solution afforded product 11n (296 mg, 73%) as a white solid; $R_f = 0.33$ (EtOAc-hexane 50:50); IR (neat): $\nu_{\text{max}}$ cm⁻¹ 3367, 3190, 2928, 1666, 1608, 1390; $^1$H NMR (500 MHz, CDCl₃) $\delta$ 1.99 (s, 3H), 2.27 (s, 3H), 3.64 (s, 3H), 4.87 (br s, 1H), 5.21 (br s, 1H), 5.95 (br s, 1H), 6.45 (br s, 1H), 6.80 (d, $J = 15.7$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 15.7$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl₃) $\delta$ 15.9, 24.6, 59.7, 116.7, 124.0, 124.3, 125.3, 130.3, 131.6, 137.3, 144.4, 144.9, 157.5, 169.0; HRMS: m/z calcd for C₁₄H₁₇NNaO₂ [(M+Na)+]: 254.1157; Found: 254.1151.

**Compound 11o:** According to the general procedure of amide preparation, Step 1: ester 11b (180 mg, 0.69 mmol) and NaOH (83 mg, 2.07 mmol), furnished acid. Step 2: crude acid (155 mg, 0.66 mmol) in CH₂Cl₂, Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.172 ml, 2.00 mmol), then 10 ml NHMe₂ (1M solution in THF) afforded product 11o (126 mg, 71%) as a yellow liquid; $R_f = 0.4$ (EtOAc-hexane 50:50); IR (neat): $\nu_{\text{max}}$ cm⁻¹ 2930, 1651, 1613, 1476, 1396; $^1$H NMR (500 MHz, CDCl₃) $\delta$ 1.97 (s, 3H), 2.26 (s, 3H), 3.03 (s, 3H), 3.08 (s, 3H), 3.64 (s, 3H), 4.87 (br s, 1H), 5.18 (br s, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 7.21 (d, $J = 15.7$ Hz, 1H), 7.73 (d, $J = 15.7$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl₃) $\delta$ 15.8, 24.5, 35.7, 59.7, 116.3, 121.7, 124.3, 126.0, 130.2, 131.2, 137.2, 144.1, 145.2, 157.2, 167.4; HRMS: m/z calcd for C₁₆H₂₂O₂ [(M+H)+]: 260.1651; Found: 260.1650.

**Compound 11p:** According to the general procedure of amide preparation, Step 1: ester 11i (180 mg, 0.51 mmol) and NaOH (61 mg, 1.51 mmol), furnished acid. Step 2: crude acid (156 mg, 0.48 mmol) in CH₂Cl₂, Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.124 ml, 1.45 mmol), then 10 ml 28% aqueous NH₃ solution afforded product 11p (114 mg, 70%) as a white solid; $R_f = 0.4$ (EtOAc-hexane 50:50); IR (neat): $\nu_{\text{max}}$ cm⁻¹ 3330, 3184, 2929, 1666, 1593, 1374; $^1$H NMR (500 MHz, CDCl₃) $\delta$ 2.00 (s, 3H),
2.17 (s, 3H), 3.63 (s, 3H), 3.96 (s, 2H), 4.89 (br s, 1H), 5.22 (br s, 1H), 5.78 (br s, 1H), 6.06 (br s, 1H), 6.79 (d, J = 15.8 Hz, 1H), 6.80 (s, 1H), 7.12 - 7.30 (m, 5H), 7.76 (d, J = 15.8 Hz, 1H); ^13^C NMR (125 MHz, CDCl₃) δ 12.0, 24.7, 39.8, 60.0, 116.8, 123.2, 123.4, 126.1, 126.3, 128.5, 128.6, 129.4, 137.8, 139.7, 141.8, 143.9, 144.9, 157.9, 168.9; HRMS: m/z calcd for C₂₁H₂₄NO₂ [(M+H)^+]: 322.1807; Found: 322.1802.

General Procedure For The Wittig - Horner Reaction

To a cold (0°C) magnetically stirred solution of diethylcyanomethylphosphonate in dry THF was added NaH (60% suspension in mineral oil) and stirred for 30 min. at 0°C. Then aldehyde in THF was added slowly and stirred reaction mixture for 3h at 0°C. When completion of the reaction was noticed by TLC, the mixture was carefully quenched with water and the product was extracted with ether twice. The combined organic layers were dried over Na₂SO₄. The solvent was removed under vacuo and the residue was purified on a silica gel column using EtOAc-hexane to furnish product.

**Compound 11q:** According to the general procedure of Wittig-Horner reaction, diethylcyanomethylphosphonate (0.476 ml, 2.49 mmol), NaH (61 mg, 2.55 mmol) and aldehyde 17 (140 mg, 0.73 mmol), were used to furnish the product 11q (140 mg, 90%) as a yellow oil. \( R_f = 0.50 \) (EtOAc-hexane 5:95); IR (neat): ν max/cm⁻¹ 2937, 2215, 1613, 1477, 1217; ^1H NMR (500 MHz, CDCl₃) δ 2.0 (s, 3H), 2.30 (s, 3H), 3.67 (s, 3H), 4.87 (br s, 1H), 5.27 (br s, 1H), 5.27 (br s, 1H), 6.37 (d, J = 17.1 Hz, 1H), 6.89 (d, J = 17.1 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H); ^13^C NMR (125 MHz, CDCl₃) δ 15.8, 24.8, 59.7, 100.3, 117.5, 119.1, 123.9, 124.4, 130.7, 133.0, 144.1, 144.3, 146.2, 157.9; HRMS: m/z calcd for C₁₄H₁₅NNaO [(M+Na)^+]: 236.1051; Found: 236.1050.
**Compound 11r**: According to the general procedure of Wittig-Horner reaction, diethylcyanomethylphosphonate (0.202 ml, 1.14 mmol), NaH (23 mg, 0.98 mmol) and aldehyde 18 (80 mg, 0.28 mmol), were used to furnish the product 11r (78 mg, 92%) as a yellow oil. \( R' = 0.30 \) (EtOAc-hexane 5:95); \( \text{IR} \) (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 2934, 2214, 1590, 1452, 1313; \( \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 1.99 (s, 3H), 2.17 (s, 3H), 3.64 (s, 3H), 3.98 (s, 2H), 4.88 (br s, 1H), 5.26 (br s, 1H), 6.37 (d, \( J = 16.8 \) Hz, 1H), 6.80 (s, 1H), 7.10 – 7.30 (m, 5H), 7.53 (d, \( J = 16.8 \) Hz, 1H); \( \text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 12.0, 24.9, 39.9, 60.1, 99.7, 117.5, 119.4, 122.2, 126.3, 128.5, 128.6, 129.7, 139.3, 143.4, 143.8, 144.2, 146.2, 158.2; \( \text{HRMS:} \) m/z calcd for C\(_{21}\)H\(_{22}\)NO [(M+H)+]: 304.1701; Found: 304.1704.

**General Procedure For olefin-cation cyclization reaction:**

Under inert atmosphere of argon, to a stirred solution of ester in CH\(_2\)Cl\(_2\) and FeCl\(_3\) (2.0 eq) was added at 0°C and stirred for 1h at RT. The reaction progress was monitored by TLC and after completion the reaction was quenched by sodium bisulphate. The reaction mixture was extracted with CH\(_2\)Cl\(_2\) and the combined organic layers were washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography using EtOAc-hexane as an eluent to furnish the produc.
**Compound 12a:** According to the general procedure of cyclization, diene ester 11a (40 mg, 0.18 mmol) in 60 ml CH₂Cl₂ and FeCl₃ (58 mg, 0.36 mmol) were used to furnish product 12a (38 mg, 97%) as a yellow solid \( R_f = 0.4 \) (EtOAc-hexane 2.5:97.5); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 2934, 1714, 1435, 1313, 1175; **¹H NMR** (500 MHz, CDCl₃) \( \delta \) 1.37 (t, \( J = 7.0 \) Hz, 3H), 1.46 (s, 6H), 4.30 (q, \( J = 7.0 \) Hz, 2H), 7.27 - 7.39 (m, 3H), 7.47 (m, 1H), 7.62 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) \( \delta \) 14.4, 24.0, 50.0, 60.0, 121.7, 123.7, 127.0, 128.0, 139.3, 145.8, 156.7, 164.4; **HRMS** (C₁₄H₁₇O₂): Calc’d 217.1229 [(M+H)+], Found 217.1227.

**Compound 12b:** According to the general procedure of cyclization, diene ester 11b (33.0 mg, 0.12 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (38.9 mg, 0.24 mmol) were used to furnish product 12b (31.5 mg, 95%) as a yellow solid. \( R_f = 0.51 \) (EtOAc-hexane 3:97); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 2979, 2928, 1704, 1568, 1478, 1419, 1244; **¹H NMR** (200 MHz, CDCl₃) \( \delta \) 1.38 (t, \( J = 7.0 \) Hz, 3H), 1.44 (s, 6H), 2.29 (s, 3H), 3.94 (s, 3H), 4.3 (q, \( J = 7.0 \) Hz, 2H), 7.00 (d, \( J = 7.4 \) Hz, 1H), 7.17 (d, \( J = 7.4 \) Hz, 1H), 7.79 (s, 1H); **¹³C NMR** (50 MHz, CDCl₃) \( \delta \) 14.4, 15.8, 24.2, 49.8, 60.0, 61.5, 116.7, 128.5, 130.5, 131.3, 136.0, 145.0, 153.8, 157.0, 164.4; **HRMS** (C₁₆H₂₁O₃): Calc’d 261.1491 [(M+H)+], Found 261.1495.

**Compound 12c:** According to the general procedure of cyclization, diene ester 11c (50 mg, 0.18 mmol) in 60 ml CH₂Cl₂ and FeCl₃ (59 mg, 0.36 mmol) were used to furnish product 12c (48 mg, 96%) as a yellow solid. \( R_f = 0.4 \) (EtOAc-hexane 5:95); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 1703, 1557, 1463, 1410, 1252, 1210; **¹H NMR** (200 MHz, CDCl₃) \( \delta \) 1.38 (t, \( J = 7.0 \) Hz, 3H), 1.45 (s, 6H), 2.21 (s, 3H), 2.34 (s, 3H), 3.91 (s, 3H), 4.30 (q, \( J = 7.0 \) Hz, 2H), 6.96 (s, 1H), 7.78 (s, 1H); **¹³C NMR** (50 MHz, CDCl₃) \( \delta \) 12.1, 20.0, 24.22, 29.6, 59.7, 71.3, 115.3, 120.6, 125.1, 126.0, 128.6, 136.8, 141.3, 141.8, 146.4, 156.1; **HRMS** (C₁₇H₂₃O₃): Calc’d 275.1647 [(M+H)+], Found 275.1640.

**Compound 12d:** According to the general procedure of cyclization, diene ester 11d (40.0 mg, 0.13 mmol) in 60 ml CH₂Cl₂ and FeCl₃ (45.0 mg, 0.27 mmol) were used to furnish product 12d (38.0 mg, 95%) as a yellow solid \( R_f = 0.52 \) (EtOAc-hexane 1:9); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 1703, 1611, 1556, 1460, 1267; **¹H NMR** (400 MHz, CDCl₃) \( \delta \) 1.25 (t, \( J = 7.5 \) Hz, 3H), 1.38 (t, \( J = 7.0 \) Hz, 3H), 1.45 (s, 6H), 2.24 (s, 3H), 2.69 (q, \( J = 7.5 \) Hz, 2H), 3.91 (s,
3H), 4.30 (q, J = 7.0 Hz, 2H), 6.96 (s, 1H), 7.77 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.3, 14.4, 14.6, 24.3, 27.3, 49.9, 59.9, 61.7, 116.8, 126.6, 128.4, 136.2, 144.0, 145.1, 153.7, 156.2, 164.4; HRMS (C$_{18}$H$_{25}$O$_3$): Calc’d 289.1804 [(M+H)$^+$], Found 289.1808.

**Compound 12e:** According to the general procedure of cyclization, diene ester 11e (30 mg, 0.10 mmol) in 40 ml CH$_2$Cl$_2$ and FeCl$_3$ (34 mg, 0.20 mmol) were used to furnish product 12e (28 mg, 93%) as a yellow solid. $R_f$ = 0.35 (EtOAc-hexane 5:95); IR (neat): v max/cm$^{-1}$ 1702, 1461, 1319, 1276, 1202; $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ 1.34 (t, J = 7.0 Hz, 3H), 1.55 (s, 6H), 2.23 (s, 6H), 2.40 (s, 3H), 3.78 (s, 3H), 4.25 (q, J = 7.0 Hz, 2H), 7.66 (s, 1H); $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta$ 13.1, 15.1, 16.4, 16.8, 22.3, 52.7, 61.1, 63.0, 129.2, 130.9, 136.4, 139.8, 145.7, 153.2, 153.4, 165.2; HRMS (C$_{18}$H$_{25}$O$_3$): Calc’d 289.1804 [(M+H)$^+$], Found 289.1806.

**Compound 12f:** According to the general procedure of cyclization, diene ester 11f (50.0 mg, 0.15 mmol) in 60 ml CH$_2$Cl$_2$ and FeCl$_3$ (48.0 mg, 0.30 mmol) were used to furnish product 12f (47.0 mg, 94%) as a yellow solid. $R_f$ = 0.42 (EtOAc-hexane 5:95); IR (neat): v max/cm$^{-1}$ 1702, 1608, 1552, 1455, 1287, 1291, 1245; $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ 1.39 (t, J = 7.1 Hz, 3H), 1.46 (s, 6H), 2.19 (s, 3H), 3.99 (s, 3H), 4.31 (q, J = 7.1 Hz, 2H), 7.01 (s, 1H), 7.33 - 7.44 (m, 5H), 7.83 (s, 1H); $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta$ 14.2, 15.1, 24.9, 51.3, 61.3, 62.7, 119.9, 127.8, 128.5, 129.6, 130.6, 130.8, 136.8, 143.3, 145.5, 146.7, 155.5, 157.4, 165.3; HRMS (C$_{22}$H$_{25}$O$_3$): Calc’d 337.1804 [(M+H)$^+$], Found 337.1803.

**Compound 12g:** According to the general procedure of cyclization, diene ester 11g (50.0 mg, 0.14 mmol) in 60 ml CH$_2$Cl$_2$ and FeCl$_3$ (46.0 mg, 0.28 mmol) were stirred together for 3 h to furnish product 12g (46.0 mg, 92%) as a yellow solid. $R_f$ = 0.42 (EtOAc-hexane 5:95); IR (neat): v max/cm$^{-1}$ 1733, 1706, 1593, 1566, 1477, 1453, 1263; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.32 (t, J = 7.0 Hz, 3H), 1.48 (s, 6H), 2.26 (s, 3H), 4.25 (q, J = 7.0 Hz, 2H), 7.20 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.47 (s, 1H), 7.52 - 7.74 (m, 3H), 8.25 - 8.30 (m, 2H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 14.4, 16.0, 24.0, 50.5, 60.1, 119.4, 128.8, 129.1, 130.4, 131.2, 132.3, 133.8, 134.7, 144.2, 146.3, 156.2, 164.0, 164.5; HRMS (C$_{22}$H$_{25}$O$_4$): Calc’d 351.1596 [(M+H)$^+$], Found 351.1592.

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Compound 12h: According to the general procedure of cyclization, diene ester 11h (40.0 mg, 0.10 mmol) in 50 ml CH₂Cl₂ and FeCl₃ (32.5 mg, 0.20 mmol) were stirred together for 5 h to furnish product 12h (37.0 mg, 92%) as a yellow solid. \( R_f = 0.37 \) (EtOAc-hexane 2:8); IR (neat): \( \nu_{max}/\text{cm}^{-1} 1764, 1705, 1616, 1570, 1522, 1488, 1377, 1335; \) \(^1\)H NMR (200 MHz, CDCl₃) \( \delta \) 1.38 (t, \( J = 7.2 \) Hz, 3H), 1.48 (s, 6H), 2.34 (s, 3H), 4.31 (q, \( J = 7.2 \) Hz, 2H), 7.26 (d, \( J = 3.1 \) Hz, 2H), 7.53 (d, \( J = 9.2 \) Hz, 2H), 7.60 (s, 1H), 8.34 (d, \( J = 9.2 \) Hz, 2H); \(^{13}\)C NMR (50 MHz, CDCl₃) \( \delta \) 14.4, 15.7, 23.8, 50.6, 60.3, 120.2, 121.6, 125.5, 128.3, 131.4, 133.7, 143.7, 145.6, 147.1, 150.5, 155.3, 156.5, 163.8; HRMS (C₂₂H₂₂NO₆): Calc’d 396.1447 [(M+H)⁺], Found 396.1442.

Compound 12i: According to the general procedure of cyclization, diene ester 11i (60.0 mg, 0.17 mmol) in 60 ml CH₂Cl₂ and FeCl₃ (55.54 mg, 0.34 mmol) were used to furnish the product 12i (57.0 mg, 95%) as a yellow solid. \( R_f = 0.43 \) (EtOAc-hexane 5:95); IR (neat): \( \nu_{max}/\text{cm}^{-1} 1703, 1613, 1494, 1454, 1284, 1210 \) \(^1\)H NMR (500 MHz, CD₃CN) \( \delta \) 1.35 (t, \( J = 7.0 \) Hz, 3H), 1.41 (s, 6H), 2.17 (s, 3H), 3.87 (s, 3H), 4.07 (s, 2H), 4.27 (q, \( J = 7.0 \) Hz, 2H), 7.09 (s, 1H), 7.18 to 7.31 (m, 5H), 7.75 (s, 1H); \(^{13}\)C NMR (125 MHz, CD₃CN) 12.4, 15.0, 41.0, 51.0, 61.2, 62.7, 120.4, 127.3, 128.7, 129.8, 129.9, 130.1, 136.9, 141.9, 143.2, 145.9, 155.3, 157.4, 165.3; HRMS (C₂₃H₂₇O₃): Calc’d 351.1960 [(M+H)⁺], Found 351.1966.

Compound 12j: According to the general procedure of cyclization, diene ester 11j (30.0 mg, 0.12 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (40.0 mg, 0.24 mmol) were used to furnish product 12j (26 mg, 87%) as a yellow solid. \( R_f = 0.37 \) (EtOAc-hexane 10:90); IR (neat): \( \nu_{max}/\text{cm}^{-1} 3423, 2925, 1704, 1567, 1464, 1368, 1287, 1213; \) \(^1\)H NMR (500 MHz, CDCl₃) \( \delta \) 1.38 (t, \( J = 7.0 \) Hz, 3H), 1.43 (s, 6H), 2.28 (s, 3H), 4.31 (q, \( J = 7.3 \) Hz, 2H), 5.66 (br s, 1H), 6.86 (d, \( J = 7.6 \) Hz, 1H), 7.13 (d, \( J = 7.6 \) Hz, 1H), 7.93 (s, 1H); \(^{13}\)C NMR (125 MHz, CDCl₃) \( \delta \) 14.4, 15.5, 24.2, 50.6, 60.2, 113.9, 121.9, 126.0, 131.4, 135.8, 144.1, 149.4, 156.7, 164.8; HRMS (C₁₅H₁₉O₃): Calc’d 247.1334 [(M+H)⁺], Found 247.1339.
**Compound 12k:** According to the general procedure of cyclization, diene ester 11k (31 mg, 0.11 mmol) in 40 ml CH$_2$Cl$_2$ and FeCl$_3$ (35 mg, 0.22 mmol) were used to furnish product 12k (27 mg, 89%) as a yellow solid \( R' = 0.3 \) (EtOAc-hexane 5:95); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \): 2929, 1708, 1568, 1243, 1183; **$^1$H NMR** (500 MHz, CDCl$_3$) \( \delta \): 1.20 (t, \( J = 7.2 \) Hz, 3H), 1.88 (s, 3H), 4.13 (q, \( J = 7.2 \) Hz, 2H), 7.10 - 7.17 (m, 4H), 7.19 - 7.22 (m, 3H), 7.25 - 7.31 (m, 2H), 7.76 (s, 1H); **$^{13}$C NMR** (125 MHz, CDCl$_3$) \( \delta \): 14.2, 21.7, 56.8, 60.0, 123.1, 123.8, 126.0, 126.5, 127.1, 128.2, 128.7, 139.7, 140.3, 141.3, 146.8, 157.3, 163.8; **HRMS** (C$_{19}$H$_{18}$NaO$_2$): Calc’d 301.1204 [(M+Na)$^+$], Found 301.1205.

**Compound 12l:** According to the general procedure of cyclization, diene ester 11l (40 mg, 0.13 mmol) in 50 ml CH$_2$Cl$_2$ and FeCl$_3$ (42 mg, 0.26 mmol) were used to furnish product 12l (35 mg, 88%) as a yellow solid \( R' = 0.3 \) (EtOAc-hexane 5:95); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \): 2974, 1706, 1567, 1487, 1321, 1244, 1184; **$^1$H NMR** (500 MHz, CDCl$_3$) \( \delta \): 1.22 (t, \( J = 7.0 \) Hz, 3H), 1.86 (s, 3H), 3.75 (s, 3H), 4.15 (q, \( J = 7.0 \) Hz, 2H), 6.74 (d, \( J = 8.9 \) Hz, 2H), 7.04 (d, \( J = 8.9 \) Hz, 2H), 7.11 (m, 1H), 7.29 (m, 1H), 7.50 (m, 1H), 7.72 (s, 1H); **$^{13}$C NMR** (125 MHz, CDCl$_3$) \( \delta \): 14.2, 22.0, 55.2, 56.3, 60.1, 113.6, 123.0, 123.7, 127.1, 127.2, 128.6, 133.1, 139.6, 140.0, 146.8, 157.4, 158.1, 163.8; **HRMS** (C$_{20}$H$_{21}$O$_3$): Calc’d 309.1491 [(M+H)$^+$], Found 309.1495.

**Compound 12m:** According to the general procedure of cyclization, diene ester 11m (50 mg, 0.14 mmol) in 60 ml CH$_2$Cl$_2$ and FeCl$_3$ (45 mg, 0.28 mmol) were used to furnish product 12m (mg, 85%) as a yellow solid \( R' = 0.33 \) (EtOAc-hexane 5:95); **IR** (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \): 2976, 1706, 1567, 1487, 1321, 1244, 1184; **$^1$H NMR** (500 MHz, CDCl$_3$) \( \delta \): 1.22 (t, \( J = 7.0 \) Hz, 3H), 1.85 (s, 3H), 4.15 (q, \( J = 7.0 \) Hz, 2H), 7.01 (d, \( J = 8.8 \) Hz, 2H), 7.04 (d, \( J = 6.7 \) Hz, 1H), 7.28 - 7.32 (m, 5H), 7.51 (d, \( J = 6.7 \) Hz, 1H), 7.74 (s, 1H); **$^{13}$C NMR** (125 MHz, CDCl$_3$) \( \delta \): 14.2, 21.6, 56.4, 60.2, 120.4, 124.0, 127.4, 128.0, 128.8, 131.3, 139.6, 140.5, 140.6, 146.3, 156.7, 163.6; **HRMS** (C$_{19}$H$_{18}$BrO$_2$): Calc’d 357.0490 [(M+H)$^+$], Found 357.0497.
**Compound 12n:** According to the general procedure of cyclization, amide **11n** (30.0 mg, 0.13 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (42 mg, 0.26 mmol) were used to furnish product **12n** (23 mg, 78%) as a white solid. \( R_f = 0.51 \) (EtOAc-hexane 50:50); IR (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 3343, 3193, 2923, 1648, 1607, 1480; \(^1\text{H NMR}\) (400 MHz, CDCl₃) \( \delta \) 1.48 (s, 6H), 3.02 (s, 3H), 3.91 (s, 3H), 5.81 (br s, 1H), 7.01 (d, \( J = 7.7\) Hz, 1H), 7.15 (d, \( J = 7.7\) Hz, 1H), 7.42 (s, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \( \delta \) 15.8, 24.5, 40.8, 61.6, 61.5, 116.9, 128.7, 130.5, 130.9, 131.1, 147.7, 153.5, 156.4, 166.9; \( \text{HRMS} \) (C₁₄H₁₈NO₂): Calc’d 232.1338 [(M+H)+], Found 232.1331.

**Compound 12o:** According to the general procedure of cyclization, amide **11o** (32.0 mg, 0.12 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (40 mg, 0.24 mmol) were used to furnish product **12o** (24 mg, 76%) as a yellow oil, \( R_f = 0.50 \) (EtOAc-hexane 50:50); IR (neat): \( v_{\text{max}}/\text{cm}^{-1} \) 2924, 1629, 1574, 1460, 1389; \(^1\text{H NMR}\) (500 MHz, CDCl₃) \( \delta \) 1.43 (s, 6H), 2.29 (s, 3H), 3.09 (s, 6H), 3.87 (s, 3H), 6.85 (s, 1H), 6.98 (d, \( J = 7.3\) Hz, 1H), 7.08 (d, \( J = 7.3\) Hz, 1H); \(^{13}\text{C NMR}\) (125 MHz, CDCl₃) \( \delta \) 15.8, 24.7, 52.4, 61.4, 116.6, 125.6, 128.9, 129.4, 131.7, 148.5, 152.8, 154.0, 168.7; \( \text{HRMS} \) (C₁₆H₂₂NO₂): Calc’d 260.1651 [(M+H)+], Found 260.1652.

**Compound 12p:** According to the general procedure of cyclization, amide **11p** (25.0 mg, 0.07 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (25 mg, 0.15 mmol) were used to furnish product **12p** (20 mg, 80%) as a white solid. \( R_f = 0.4 \) (EtOAc-hexane 50:50); IR (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 3342, 3192, 2925, 1648, 1603, 1418; \(^1\text{H NMR}\) (400 MHz, CDCl₃) \( \delta \) 1.47 (s, 6H), 2.16 (s, 3H), 3.87 (s, 3H), 4.04 (s, 2H), 5.61 (br s, 2H), 6.93 (s, 1H), 7.11 - 7.29 (m, 5H), 7.39 (s, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \( \delta \) 11.9, 24.5, 40.4, 50.9, 61.9, 119.1, 126.1, 127.7, 128.2, 128.3, 128.5, 128.6, 130.6, 140.1, 141.0, 147.0, 153.6, 155.6, 166.8; \( \text{HRMS} \) (C₂₁H₂₃NO₂): Calc’d 322.1807 [(M+H)+], Found 322.1804.

**Compound 12q:** According to the general procedure of cyclization, compound **11q** (30.0 mg, 0.14 mmol) in 40 ml CH₂Cl₂ and FeCl₃ (45 mg, 0.28 mmol) were used to furnish product **12q** (24 mg, 80%) as a yellow oil, \( R_f = 0.4 \) (EtOAc-hexane 5:95); IR (neat): \( \nu_{\text{max}}/\text{cm}^{-1} \) 2927, 2211, 1480, 1256; \(^1\text{H NMR}\) (400 MHz, CDCl₃) \( \delta \) 1.40 (s, 6H), 2.29 (s, 3H), 3.91 (s, 3H), 7.0 (d, \( J = 7.7\) Hz, 1H), 7.20 (d, \( J = 7.7\) Hz, 1H), 7.56 (s, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \( \delta \)
15.8, 23.9, 52.1, 61.6, 116.2, 116.9, 126.1, 129.4, 130.1, 132.1, 139.0, 153.4, 153.6; **HRMS** (C_{14}H_{16}NO): Calc’d 214.1232 [(M+H)^+] , Found 214.1234.

**Compound 12r**: According to the general procedure of cyclization, compound 11r (35.0 mg, 0.11 mmol) in 50 ml CH_2Cl_2 and FeCl_3 (37 mg, 0.23 mmol) were used to furnish product 12r (27mg, 78%) as a yellow oil, Rf = 0.3 (EtOAc-hexane 5:95); **IR** (neat): ν_{max}/cm^{-1} 2920, 2211, 1602, 1453, 1300; **^{1}H NMR** (500 MHz, CDCl_3) δ 1.38 (s, 6H), 2.16 (s, 3H), 3.87 (s, 3H), 4.04 (s, 2H), 6.91 (s, 1H), 7.09 - 7.30 (m, 5H), 7.54 (s, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 40.4, 52.3, 61.9, 116.4, 118.3, 119.2, 125.5, 126.2, 128.5, 128.6, 139.0, 139.8, 142.3, 152.7, 153.8; **HRMS** (C_{21}H_{21}NNaO): Calc’d 326.1521 [(M+Na)^+] , Found 326.1521.
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