Supporting Information For

Palladium-Catalyzed Synthesis of Indene Derivatives via Propargylic Carbonates with in situ Organozinc Compounds

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General information:
Column chromatography was carried out on silica gel. \(^1\)H NMR spectra were recorded on 300 MHz or 400 MHz in CDCl\(_3\) and \(^{13}\)C NMR spectra were recorded on 75 MHz or 100 MHz in CDCl\(_3\) using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm\(^{-1}\). Melting points were determined on a microscopic apparatus and were uncorrected. All new compounds were further characterized by element analysis; copies of their \(^1\)H NMR and \(^{13}\)C NMR spectra are provided. Unless otherwise stated, all aryl halides were purchased from commercial suppliers and used without further purification. Propargylic carbonates were prepared according to the following literature:


Typical procedure for preparation of 5 and in synthesis of 3i

\[
\begin{align*}
\text{CO}_2\text{Et} & \quad + \quad \text{Zn} \cdot \text{LiCl} \\
\text{1a} & \quad \text{Pd(PPh}_3\text{)}_4, \text{ K}_2\text{CO}_3 \\
\text{DMSO, 50 °C, 12 h} & \quad \rightarrow \\
\text{CO}_2\text{Et} & \quad \text{EtO}_2\text{C} \\
\text{3i (68%)} & \quad \text{OCO}_2\text{Et}
\end{align*}
\]

Anhydrous LiCl (7 mmol) was placed in an Ar-flushed flask and dried for 20 min at 150 – 170 °C under high vacuum (1 mbar). Zinc powder (7 mmol, 1.4 equiv, 325 mesh, Strem) was added under Ar and the heterogeneous mixture of Zn and LiCl was dried again for 10 – 20 min at 150 – 170 °C under high vacuum (1 mbar). The reaction flask was evacuated and refilled with argon three times. THF (5 mL) was added and the Zn was activated with BrCH\(_2\)CH\(_2\)Br (5 mol%) and Me\(_3\)SiCl (1 mol%). 1-iodo-3-methylbenzene (5 mmol) was then added neat at room temperature. The insertion reaction was complete after 48 h and afforded the solution of 5.

The solution of 5 (0.3 mmol, 0.38 mL, titration with iodine) was carefully separated from the remaining zinc powder by using a syringe and transferred to the mixture of diethyl 2-(2-(3-(ethoxycarbonyloxy)prop-1-ynyl)phenyl)malonate 1a (36.2 mg, 0.10 mmol), Pd(PPh\(_3\))\(_4\) (2.3 mg, 0.002 mmol, 2 mol %), K\(_2\)CO\(_3\) (27.6 mg, 0.20 mmol) in DMSO (2.0 mL) under an argon atmosphere. The resulting mixture was stirred for 12 h at 50 °C. Then, the reaction mixture was allowed to cool to room temperature, quenched with water and extracted with EtOAc (2 mL*3). The combined organic extracts were washed with water and saturated brine. The organic layer was dried over Na\(_2\)SO\(_4\) and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding indene product 3i in 68% yield (hexanes/EtOAc 15:1).
Typical procedure for indenes synthesis via in situ organozinc compounds

\[
\begin{align*}
\text{CO}_2\text{Et} & \quad \text{E} \\
\text{CO}_2\text{Et} & \quad \text{OCO}_2\text{Et} \\
\text{1} & \quad \text{ArX} \\
\text{Zn, LiCl, DMSO, 50 °C} & \quad \text{Pd(PPh}_3\text{)}_4, \text{K}_2\text{CO}_3
\end{align*}
\]

The solution of the propargylic carbonate 1 (0.10 mmol), aryl iodine (0.15 mmol), Zn powder (19.5 mg, 0.30 mmol), anhydrous LiCl (12.8 mg, 0.30 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (2.3 mg, 0.002 mmol, 2 mol %), K\textsubscript{2}CO\textsubscript{3} (27.6 mg, 0.20 mmol) in DMSO (2.0 mL) was stirred under an argon atmosphere at 50 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was allowed to cool to room temperature, quenched with water and extracted with EtOAc (2 mL*3). The combined organic extracts were washed with water and saturated brine. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding indene product 3.

**Spectroscopic data for indene products 3**

\[\text{3a: } mp: 50-51 °C. \textsuperscript{1}H NMR (300 MHz, CDCl}_3 \delta 7.75-7.72 (m, 1H), 7.48-7.42 (m, 5H), 7.35-7.32 (m, 2H), 7.25-7.21 (m, 1H), 5.15 (s, 2H), 4.31-4.12 (m, 6H), 1.30-1.24 (m, 9H). \textsuperscript{13}C NMR (75 MHz, CDCl}_3 \delta 167.7, 154.8, 149.5, 143.9, 140.5, 133.5, 132.6, 128.9, 128.6, 127.2, 125.3, 121.5, 70.2, 63.8, 62.7, 62.2, 14.2, 13.8. IR (KBr, cm\textsuperscript{-1}) 2983, 1744, 1254, 1050. Anal.Calcd for C\textsubscript{25}H\textsubscript{26}O\textsubscript{7}: C 68.48, H 5.98; Found: C 68.27, H 5.69.

\[\text{3b: } mp: 80-80.5 °C. \textsuperscript{1}H NMR (300 MHz, CDCl}_3 \delta 7.74-7.71 (m, 1H), 7.36-7.22 (m, 7H), 5.14 (s, 2H), 4.30-4.12 (m, 6H), 2.42 (s, 3H), 1.30-1.25 (t, \textit{J} = 6.9 Hz, 9H). \textsuperscript{13}C NMR (75 MHz, CDCl}_3 \delta 167.8, 154.8, 149.6, 144.0, 140.6, 138.4, 133.1, 129.6,
129.3, 128.8, 128.5, 127.2, 125.3, 121.5, 70.2, 63.8, 62.8, 62.2, 21.3, 14.2, 13.8. IR (KBr, cm⁻¹) 2979, 1730, 1261, 1046. Anal. Calcd for C₂₆H₂₈O₇: C 69.01, H 6.24; Found: C 68.75, H 5.96.

3c: mp: 90.5-91 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.09-8.06 (d, J = 8.1 Hz, 2H), 7.75-7.72 (m, 1H), 7.55-7.57 (d, J = 8.1 Hz, 2H), 7.36-7.33 (m, 2H), 7.18-7.15 (m, 1H), 5.11 (s, 2H), 4.31-4.18 (m, 4H), 4.18-4.11 (q, J = 6.9 Hz, 2H), 2.66 (s, 3H), 1.30-1.24 (q, J = 6.9 Hz, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 197.6, 167.4, 154.7, 148.4, 143.4, 140.5, 137.6, 137.0, 134.6, 129.2, 128.7, 128.6, 127.6, 125.5, 121.3, 70.4, 63.9, 62.4, 62.3, 26.7, 14.2, 13.8. IR (KBr, cm⁻¹) 3428, 2992, 1742, 1261, 1046, 70.4, 63.9, 62.4, 62.3, 26.7, 14.2, 13.8. IR (KBr, cm⁻¹) 3428, 2992, 1742, 1261, 1046. Anal. Calcd for C₂₇H₂₉O₈: C 67.49, H 5.87; Found: C 67.64, H 5.66.

3d: mp: 77-78 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.74-7.71 (m, 1H), 7.48-7.45 (d, J = 8.4 Hz, 2H), 7.41-7.38 (d, J = 8.4 Hz, 2H), 7.36-7.33 (m, 2H), 7.18-7.16 (m, 1H), 5.11 (s, 2H), 4.31-4.12 (m, 6H), 1.32-1.25 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 167.5, 154.7, 148.4, 143.5, 140.4, 134.6, 134.0, 131.0, 130.3, 128.9, 128.7, 127.5, 125.4, 121.3, 70.3, 63.9, 62.5, 62.3, 14.3, 13.8. IR (KBr, cm⁻¹) 2978, 1727, 1261, 1044. Anal. Calcd for C₂₅H₂₅ClO₇: C 63.49, H 5.33; Found: C 63.37, H 5.38.

3e: mp: 87-88 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.75-7.72 (m, 1H), 7.64-7.61 (m, 2H), 7.37-7.32 (m, 4H), 7.19-7.16 (m, 1H), 5.11 (s, 2H), 4.31-4.12 (m, 6H), 1.30-1.25 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 167.5, 154.7, 148.3, 143.5, 140.4, 134.0, 131.8, 131.5, 130.6, 128.7, 127.5, 125.4, 122.8, 121.3, 70.3, 63.9, 62.5, 62.3, 14.2,
13.8. IR (KBr, cm$^{-1}$) 2978, 1745, 1725, 1260. Anal.Calcd for C$_{25}$H$_{25}$BrO$_7$: C 58.04, H 4.87; Found: C 58.01, H 5.01.

3f: mp: 94-95 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.74-7.71 (m, 1H), 7.42-7.39 (d, $J$ = 8.7 Hz, 2H), 7.35-7.32 (m, 2H), 7.27-7.24 (m, 1H), 7.03-7.00 (d, $J$ = 8.7 Hz, 2H), 5.14 (s, 2H), 4.31-4.13 (m, 6H), 3.86 (s, 3H), 1.30-1.25 (t, $J$ = 6.9 Hz, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.8, 159.7, 154.8, 149.3, 144.0, 140.5, 132.7, 130.2, 128.5, 127.2, 125.3, 124.8, 121.5, 114.0, 70.1, 63.8, 62.9, 62.2, 55.3, 14.3, 13.8. IR (KBr, cm$^{-1}$) 2994, 1741, 1241, 1044. Anal.Calcd for C$_{26}$H$_{28}$O$_8$: C 66.66, H 6.02; Found: C 66.38, H 5.75.

3g: mp: 91-92 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.77-7.74 (m, 3H), 7.60-7.57 (d, $J$ = 8.4 Hz, 2H), 7.37-7.34 (m, 2H), 7.17-7.14 (m, 1H), 5.12 (s, 2H), 4.32-4.11 (m, 6H), 1.31-1.24 (q, $J$ = 6.9 Hz, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.4, 154.7, 148.0, 143.4, 140.4, 136.4, 134.8, 129.4, 128.8, 127.6, 125.6, 125.5, 121.2, 70.4, 64.0, 62.4, 14.2, 13.8. IR (KBr, cm$^{-1}$) 2978, 1745, 1725, 1257, 1116. Anal.Calcd for C$_{26}$H$_{28}$F$_3$O$_7$: C 61.66, H 4.98; Found: C 61.47, H 4.68.

3h: mp: 71-72 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.18-8.15 (d, $J$ =8.1 Hz, 2H), 7.76-7.73 (m, 1H), 7.56-7.53, (d, $J$ = 8.4 Hz, 2H), 7.37-7.34 (m, 2H), 7.19-7.17 (m, 1H), 5.12 (s, 2H), 4.30-4.12 (m, 6H), 3.96 (s, 3H), 1.31-1.25 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.5, 166.7, 154.7, 148.5, 143.4, 140.5, 137.4, 134.6, 130.2, 129.9, 129.0, 128.7, 127.5, 125.5, 121.3, 70.4, 63.9, 62.5, 62.4, 52.3, 14.2, 13.9. IR (KBr, cm$^{-1}$) 2978, 1745, 1725, 1260.
cm\(^{-1}\)) 2923, 1739, 1258, 1046. Anal. Calcd for C\(_{27}\)H\(_{28}\)O\(_9\): C 65.31, H 5.68; Found: C 65.60, H 5.74.

![Chemical structure of compound 3i](image)

3i: mp: 102-103 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.74-7.71 (m, 1H), 7.39-7.30 (m, 3H), 7.25-7.21 (m, 4H), 5.14 (s, 2H), 4.31-4.12 (m, 6H), 2.41 (s, 3H), 1.30-1.25 (t, \(J = 7.5\) Hz, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.8, 154.8, 149.7, 144.0, 140.6, 138.2, 133.4, 132.5, 129.5, 129.3, 128.6, 128.5, 127.2, 126.0, 125.3, 121.6, 70.2, 63.8, 62.8, 62.2, 21.5, 14.3, 13.9. IR (KBr, cm\(^{-1}\)) 3001, 1735, 1255, 1044. Anal. Calcd for C\(_{26}\)H\(_{28}\)O\(_7\): C 69.01, H 6.24; Found: C 68.78, H 6.12.

![Chemical structure of compound 3j](image)

3j: mp: 70-70.5 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.75-7.72 (m, 1H), 7.45-7.42 (m, 3H), 7.37-7.32 (m, 3H), 7.20-7.17 (m, 1H), 5.13 (s, 2H), 4.29-4.13 (m, 6H), 1.31-1.26 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.4, 154.7, 148.0, 143.4, 140.4, 134.5, 134.4, 130.0, 128.9, 128.7, 127.5, 127.1, 125.4, 121.3, 70.3, 63.9, 62.4, 62.3, 14.2, 13.8. IR (KBr, cm\(^{-1}\)) 2987, 1735, 1255, 1043. Anal. Calcd for C\(_{25}\)H\(_{25}\)ClO\(_7\): C 63.49, H 5.33; Found: C 63.52, H 5.04.

![Chemical structure of compound 3k](image)

3k: oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.74-7.72 (m, 1H), 7.34-7.23 (m, 5H), 7.20-7.18 (m, 1H), 6.90-6.87 (m, 1H), 5.08-5.04 (d, \(J = 12.3\) Hz, 1H), 5.00-4.97 (d, \(J = 12.3\) Hz, 1H), 4.30-4.17 (m, 4H), 4.12-4.05 (q, \(J = 6.9\) Hz, 2H), 2.15 (s, 3H), 1.32-1.20 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.0, 167.5, 154.8, 149.3, 144.4, 140.4, 136.6, 134.6, 132.3, 130.1, 129.2, 128.6, 128.4, 127.1, 125.8, 125.0, 121.3, 70.2, 63.7, 62.8, 62.2, 19.5, 14.2, 13.9. IR (KBr, cm\(^{-1}\)) 2983, 1746, 1252, 1051.
Anal. Calcd for C$_{26}$H$_{28}$O$_7$: C 69.01, H 6.24; Found: C 68.83, H 5.98.

3i: oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11-8.09 (m, 1H), 7.73-7.70 (m, 1H), 7.63-7.59 (m, 1H), 7.54-7.50 (m, 1H), 7.36-7.34 (m, 1H), 7.30-7.26 (m, 2H), 6.84-6.82 (m, 1H), 5.10-5.07 (dd, $J_1 = 0.9$ Hz, $J_2 = 8.4$ Hz, 1H), 5.00-4.97 (dd, $J_1 = 0.9$ Hz, $J_2 = 8.4$ Hz, 1H), 4.31-4.20 (m, 4H), 4.11-4.06 (m, 2H), 3.48 (s, 3H), 1.32-1.21 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 167.6, 167.2, 154.8, 149.6, 145.0, 140.0, 133.7, 133.1, 132.2, 130.9, 130.6, 128.6, 128.6, 127.0, 125.1, 120.7, 70.4, 63.7, 62.7, 62.2, 51.9, 14.2, 13.9. IR (KBr, cm$^{-1}$) 2983, 1740, 1258, 1042.

Anal. Calcd for C$_{27}$H$_{29}$O$_9$: C 65.31, H 5.68; Found: C 65.29, H 5.92.

3m: oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.73-7.70 (m, 1H), 7.33-7.30 (m, 2H), 7.26-7.19 (m, 1H), 7.12-7.07 (m, 2H), 6.84-6.77 (m, 2H), 5.10 (s, 2H), 4.34-4.07 (m, 6H), 3.74 (s, 1H), 1.32-1.21 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.1, 167.3, 154.7, 146.5, 144.3, 143.6, 140.7, 136.1, 129.9, 129.7, 128.7, 127.4, 125.1, 121.7, 118.0, 117.4, 115.4, 70.2, 63.8, 63.0, 62.4, 62.3, 14.2, 13.9. IR (KBr, cm$^{-1}$) 3471, 3379, 2983, 1744, 1253. Anal. Calcd for C$_{25}$H$_{26}$O$_8$: C 66.07, H 5.77; Found: C 66.33, H 5.95.

3n: mp: 76-77 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.72-7.69 (m, 1H), 7.42-7.37 (m, 1H), 7.30-7.26 (m, 3H), 7.06-6.99 (m, 3H), 5.23-5.19 (d, $J = 12.3$ Hz, 1H), 5.01-4.97 (d, $J = 12.3$ Hz, 1H), 4.30-4.06 (m, 6H), 3.74 (s, 3H), 1.31-1.21 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.0, 167.7, 157.1, 154.8, 145.7, 144.3, 140.3, 134.8, 130.8, 130.0, 128.3, 126.7, 125.0, 121.6, 120.5, 111.3, 70.2, 63.7, 63.4, 62.2, 62.1, 55.5, 14.2, 13.9, 13.8. IR (KBr, cm$^{-1}$) 2927, 1741, 1247. Anal. Calcd for C$_{26}$H$_{28}$O$_8$: C 66.66, H 6.02; Found: C 66.59, H 5.83.
3o: mp:80-80.5 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.74-7.72 (m, 1H), 7.59-7.56 (m, 1H), 7.51-7.49 (m, 1H), 7.42-7.33 (m, 3H), 7.20-7.17 (m, 1H), 5.24 (s, 2H), 4.30-4.16 (m, 6H), 1.32-1.25 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.4, 154.8, 143.1, 142.5, 140.2, 134.1, 132.9, 128.7, 128.6, 127.5, 127.2, 125.4, 121.7, 70.4, 63.9, 62.7, 62.3, 14.3, 13.8. IR (KBr, cm$^{-1}$) 2983, 1742, 1251, 1043. Anal.Calcd for C$_{23}$H$_{24}$O$_7$S: C 62.15, H 5.44; Found: C 61.86, H 5.24.

3p: mp:78-80 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68-7.66 (m, 1H), 7.48-7.42 (m, 5H), 7.31-7.26 (m, 2H), 7.05-7.02 (m, 1H), 5.95-5.93 (m, 1H), 4.30-4.10 (m, 6H), 1.37-1.35 (m, 3H), 1.30-1.22 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.9, 167.8, 154.4, 147.5, 145.3, 140.0, 138.4, 134.0, 129.2, 128.6, 128.4, 128.2, 127.0, 124.7, 121.2, 71.4, 63.6, 62.1, 19.3, 14.3, 13.9, 13.8. IR (KBr, cm$^{-1}$) 2985, 1741, 1265, 1047. Anal.Calcd for C$_{26}$H$_{28}$O$_7$: C 69.01, H 6.24; Found: C 69.25, H 6.06.

3q: mp:85-86 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.10-8.05 (m, 2H), 7.74-7.68 (m, 1H), 7.60-7.57 (m, 2H), 7.32-7.27 (m, 2H), 6.99-6.97 (m, 1H), 5.95-5.92 (m, 1H), 4.32-4.10 (m, 6H), 2.67 (s, 3H), 1.37-1.25 (m, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.6, 167.6, 167.4, 154.2, 146.4, 144.7, 139.8, 139.2, 139.0, 136.7, 129.5, 128.9, 128.7, 128.3, 127.2, 124.9, 120.9, 71.3, 71.0, 63.6, 62.3, 26.6, 19.4, 14.2, 13.8, 13.7. IR (KBr, cm$^{-1}$) 2988, 1730, 1682, 1260. Anal.Calcd for C$_{28}$H$_{30}$O$_8$: C 68.00, H 6.11; Found: C 68.29, H 6.05.
3r: mp: 96-97 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69-7.66 (m, 1H), 7.47-7.45 (m, 2H), 7.42-7.39 (m, 2H), 7.33-7.29 (m, 2H), 7.01-6.99 (m, 1H), 5.94-5.89 (m, 1H), 4.32-4.09 (m, 6H), 1.41-1.35 (m, 3H), 1.33-1.20 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.8, 167.5, 154.3, 146.4, 145.0, 139.9, 138.9, 134.3, 132.4, 130.6, 128.7, 127.2, 124.9, 121.0, 109.8, 71.1, 63.6, 62.2, 19.4, 14.3, 13.9, 13.8. IR (KBr, cm$^{-1}$) 2984, 1743, 1260, 1048. Anal. Calcd for C$_{26}$H$_{27}$ClO$_7$: C 64.13, H 5.59; Found: C 64.43, H 5.68.

3s: mp: 66-67 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68-7.65 (m, 1H), 7.42-7.39 (d, $J = 8.7$ Hz, 2H), 7.31-7.28 (m, 2H), 7.09-7.06 (m, 1H), 7.02-7.00 (d, $J = 8.1$ Hz, 2H), 5.95-5.93 (m, 1H), 4.31-4.10 (m, 6H), 3.87 (s, 3H), 3.87 (s, 3H), 1.39-1.36 (d, $J = 6.9$ Hz, 3H), 1.31-1.23 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.0, 167.9, 159.6, 154.4, 147.3, 145.5, 140.0, 137.9, 130.4, 128.5, 126.9, 126.1, 124.7, 121.2, 113.9, 71.4, 63.5, 62.1, 55.2, 19.1, 14.3, 13.9, 13.8. IR (KBr, cm$^{-1}$) 2984, 1730, 1251, 1049. Anal. Calcd for C$_{27}$H$_{30}$O$_8$: C 67.21, H 6.27; Found: C 67.04, H 5.98.

3t: mp: 94-95 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68-7.65 (m, 1H), 7.36-7.21 (m, 6H), 7.05-7.02 (m, 1H), 5.94-5.92 (m, 1H), 4.31-4.09 (m, 6H), 2.41 (s, 3H), 1.39-1.37 (d, $J = 6.6$ Hz, 3H), 1.31-1.23 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.0, 167.8, 154.3, 147.6, 145.3, 139.9, 138.1, 137.9, 133.7, 129.7, 128.9, 128.5, 128.2, 126.9, 126.2, 124.6, 121.2, 71.4, 71.0, 63.5, 62.1, 21.4, 19.3, 14.3, 13.9, 13.8. IR (KBr, cm$^{-1}$) 2986, 1731, 1258, 1042. Anal. Calcd for C$_{27}$H$_{30}$O$_7$: C 69.51, H 6.48; Found: C 69.35, H 6.24.
3u: oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10-8.08 (d, $J = 7.6$ Hz, 1H), 7.98-7.96 (d, $J = 7.6$ Hz, 2H), 7.50-7.41 (m, 2H), 7.33-7.28 (m, 3H), 7.23-7.19 (m, 2H), 7.05-7.03 (d, $J = 8.0$ Hz, 2H), 6.77-6.75 (d, $J = 7.6$ Hz, 1H), 5.54-5.12 (d, $J = 12.8$ Hz, 1H), 5.08-5.05 (d, $J = 12.4$ Hz, 1H), 4.45-4.41 (m, 2H), 4.17-4.12 (q, $J = 7.2$ Hz, 2H), 2.63 (s, 3H), 1.41-1.38 (m, 3H), 1.29-1.25 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.3, 163.2, 151.5, 143.8, 137.2, 136.9, 136.7, 134.2, 133.8, 131.4, 130.0, 129.8, 128.6, 128.4, 127.9, 127.8, 127.5, 121.2, 74.2, 64.0, 63.4, 61.5, 26.6, 14.3, 13.9. IR (KBr, cm$^{-1}$) 3411, 2923, 1741, 1249. Anal.Calcd for C$_{30}$H$_{28}$O$_8$S: C 65.68, H 5.14; Found: C 65.78, H 5.37.