Rh(III)-Catalyzed Relay Carbenoid Functionalization of Aromatic C-H Bonds: Access to π-Conjugated Fused Heteroarenes

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Supporting Information

Table of Contents

1. General experimental information .................................................................2
   1.1. Table S1. Catalyst screening for Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds .................................................................3
   1.2. Table S2. The effect of the solvent on the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds .................................................................3
   1.3. Table S3. The effect of additives on the the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds .................................................................4
   1.4. Table S4. The effect of the reaction temperature on the the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds .................................................................4
   1.5. General procedure for the synthesis of ketoimines ........................................4
   1.6. General procedure for the synthesis of diazocarbony compounds ..................5
   1.7 General procedure for synthesis of polysubstituted 1-APLE derivatives (3a-3ad)........7
   1.8 Procedure for synthesis of π-conjugated organic molecules 5 and 7 ..................17
   1.9 The photophysical and electrochemical properties of the compound 5 and 7 ..........18

2. Preliminary mechanistic studies ..................................................................19

3. Single crystal data about 3k .........................................................................25

4. References ....................................................................................................28

5. 1H NMR and 13C NMR spectrum for all isolated products .........................29
1. General experimental information

1.1. General methods

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm⁻¹). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ¹H NMR and ¹³C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a platinum working electrode and a Pt wire counter electrode at a scanning rate of 100 mV s⁻¹ against a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate. UV-vis absorption spectra were recorded on a HP8453 spectrophotometer. Pholuminescence (PL) spectra were measured by using a Jobin-Yvon spectrofluorometer.
1.1. Table S1. Catalyst screening for Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds

| entry | catalyst                                      | yield (%) | b
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)$_2$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>CuI</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)$_2$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>[{RuCl$_2$(p-cymene)}$_2$]</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[Cp*RhCl$_2$]</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>RhCl$_3$</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Rh$_2$(COD)$_2$Cl$_2$</td>
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</tr>
<tr>
<td>8</td>
<td>[Cp*RhCl$_2$]</td>
<td>58</td>
</tr>
</tbody>
</table>

*All the reactions were carried out using ketoimine 1a (0.1 mmol), diazo compound 2a (0.3 mmol), catalyst (2.5 mol %), AgSbF$_6$ (10 mol %) in THF (2.0 mL) at 80 °C for 24 h in a sealed reaction tube, followed by flash chromatography on SiO$_2$. " Isolated yield.

1.2. Table S2. The effect of the solvent on the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds

| entry | solvent | yield (%) | b
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Dioxane</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$CN</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>26</td>
</tr>
</tbody>
</table>

*All the reactions were carried out using ketoimine 1a (0.1 mmol), diazo compound 2a (0.3 mmol), [Cp*RhCl$_2$]$_2$ (1.6 mg, 2.5 mol %), AgSbF$_6$ (10 mol %) in solvent (2.0 mL) at 80 °C for 8 h in a sealed reaction tube, followed by flash chromatography on SiO$_2$. " Isolated yield.

S-3
1.3. Table S3. The effect of additives on the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>AgBF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>AgNTf&lt;sub&gt;2&lt;/sub&gt;</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>AgOAc</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>AgSbF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>85</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were carried out using ketoimine 1a (0.1 mmol), diazo compound 2a (0.3 mmol), [Cp*RhCl<sub>2</sub>] (2.5 mol%), additive (10 mol%) in DCE (2.0 mL) at 80 °C for 8 h in a sealed reaction tube, followed by flash chromatography on SiO<sub>2</sub>.<sup>b</sup> Isolated yield.

1.4. Table S4. The effect of the reaction temperature on the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>82</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were carried out using ketoimine 1a (0.1 mmol), diazo compound 2a (0.3 mmol), [Cp*RhCl<sub>2</sub>] (2.5 mol%), AgSbF<sub>6</sub> (10 mol%) in DCE (2.0 mL) at the given temperature for 8 h in a sealed reaction tube, followed by flash chromatography on SiO<sub>2</sub>.<sup>b</sup> Isolated yield.

1.5. General procedure for the synthesis of ketoimines

The mixture of acetophenone derivatives (0.2 mmol, 1.0 equiv.) and substituted anilines (0.2 mmol, 1.0 equiv.) was stirred in toluene (3.0 mL) at 120 °C for 24 h in the presence of molecular...
sieve (4Å) (0.40 g) and a catalytic amount of concentrated H₂SO₄ (10 mol %). The mixture was then filtered and the solvent was removed under reduced pressure to produce crude ketoimines. The crude ketoimines could be directly used for synthetic purpose without further purification because these ketoimines are easily decomposed on silica gel. ¹H and ¹³C NMR spectral data for the rest of the imines showed good agreement with literature data. [¹]

\[
\begin{align*}
\text{d-1a-a} & \\
\text{The compound (d-1a-a) was prepared according to the above-mentioned procedure. The product was obtained as yellow oil in 75 % yield. ¹H NMR (400 MHz, CDCl₃) } & \\
\delta 7.97 (d, J = 6.5 \text{ Hz}, 1H), 7.44 (s, 3H), 7.33 (d, J = 7.3 \text{ Hz}, 2H), 7.07 (t, J = 7.3 \text{ Hz}, 1H), 6.79 (d, J = 7.7 \text{ Hz}, 2H), 2.22 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) & \\
\delta 165.45, 151.75, 139.47, 130.48, 128.98, 128.87, 128.39, 128.27, 127.19, 123.24, 119.40, 29.73, 17.37.
\end{align*}
\]

\[
\begin{align*}
\text{d-1a-b} & \\
\text{The compound (d-1a-b) was prepared according to the above-mentioned procedure. The product was obtained as yellow oil in 78 % yield. ¹H NMR (400 MHz, CDCl₃) } & \\
\delta 7.34 (t, J = 7.4 \text{ Hz}, 2H), 7.08 (t, J = 7.4 \text{ Hz}, 1H), 6.79 (d, J = 7.8 \text{ Hz}, 2H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) & \\
\delta 165.45, 151.74, 139.38, 128.96, 123.22, 119.39, 17.36.
\end{align*}
\]

1.6. General procedure for the synthesis of diazocompounds

\[
\begin{align*}
\text{Method A: To a solution of β-ketoester or β-diketone (1.0 equiv.) and 4-methylbenzenesulfonyl azide (1.2 equiv.) in CH₃CN at 0 °C was added triethylamine (1.2 equiv.). The resulting solution was stirred at 0 °C for 3 h and slowly brought to room temperature. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous MgSO₄. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silical gel using 20 % (v/v) ethyl acetate in petroleum ether as eluent to afford the desired diazocompounds.}
\end{align*}
\]
Ethyl 2-diazo-3-oxobutanoate (2a) [2]

The title compound (2a) was prepared according to Method A. The product was obtained as yellow oil in 91 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.31 (q, $J$ = 7.1 Hz, 2H), 2.48 (s, 3H), 1.34 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.2, 161.4, 61.4, 28.2, 14.3. IR (KBr): 2989, 2876, 2135, 1720, 1658, 1469, 1375, 1072 cm$^{-1}$.

Ethyl 2-diazo-3-oxopentanoate (2b) [2]

The title compound (2b) was prepared according to Method A. The product was obtained as yellow oil in 88 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.30 (q, $J$ = 6.9 Hz, 2H), 2.86 (q, $J$ = 7.2 Hz, 2H), 1.33 (t, $J$ = 7.0 Hz, 3H), 1.14 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.5, 161.4, 61.3, 33.7, 14.3, 8.2. IR (KBr): 2981, 2844, 2138, 1720, 1658, 1469, 1373, 1065 cm$^{-1}$.

Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (2d) [3]

The title compound (2d) was prepared according to Method A. The product was obtained as yellow oil in 81 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.30 (q, $J$ = 6.9 Hz, 2H), 3.32 (t, $J$ = 9.8 Hz, 1H), 1.80 (d, $J$ = 7.7 Hz, 4H), 1.69 (d, $J$ = 12.3 Hz, 1H), 1.46 - 1.38 (m, 2H), 1.37 - 1.30 (m, 5H), 1.24 (d, $J$ = 11.7 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 196.0, 161.2, 61.2, 46.7, 28.7, 25.7, 14.3. IR (KBr): 2979, 2856, 2138, 1715, 1651, 1371, 1318, 1146, 1077, 1044 cm$^{-1}$.

Methyl 2-diazo-4-methoxy-3-oxobutanoate (2g) [3]

The title compound (2g) was prepared according to Method A. The product was obtained as yellow oil in 86 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.53 (s, 2H), 3.85 (s, 3H), 3.47 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 188.7, 161.5, 75.7, 59.4, 52.3; IR (KBr): 2976, 2837, 2115, 1713, 1648, 1469, 1375, 1065 cm$^{-1}$.

Ethyl 2-diazo-3-oxohept-6-enoate (2f) [4]

The title compound (2f) was prepared according to Method A. The product was obtained as yellow oil in 78 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.92 - 5.77 (m, 1H), 5.03 (dd, $J$ = 29.0, 13.6 Hz, 2H), 4.30 (q, $J$ = 7.1 Hz, 2H), 2.96 (t, $J$ = 7.3 Hz, 2H), 2.43 - 2.34 (m, 2H), 1.33 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.0, 161.3, 136.9, 115.3, 61.3, 39.3, 28.1, 14.3; IR (KBr): 3061, 2980, 2930, 2136, 1718, 1657, 1434, 1370, 1050 cm$^{-1}$.
The title compound (2e) was prepared according to Method A. The product was obtained as yellow oil in 78 % yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (t, $J = 9.9$ Hz, 4H), 7.19 (d, $J = 5.5$ Hz, 1H), 4.28 (q, $J = 6.8$ Hz, 2H), 3.18 (t, $J = 7.2$ Hz, 2H), 2.96 (t, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 6.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.9, 161.3, 140.8, 128.4, 126.1, 61.4, 41.7, 30.2, 14.3. IR (KBr): 3011, 2983, 2140, 1714, 1651, 1454, 1374, 1313, 1052 cm$^{-1}$.

1.7 General procedure for synthesis of polysubstituted 1-APLE derivatives (3a-3ad)

A 10 mL of reaction tube was charged with [Cp*RhCl$_2$]$_2$ (1.6 mg, 2.5 mol %), AgSbF$_6$ (3.4 mg, 10 %), ketoimine 1 (0.1 mmol) and DCE (1.5 mL) under atmspher. Then diazo compound 2 (0.3 mmol) in DCE (0.5 mL) was added in one-pot under air and the mixture was stirred at 80 °C for 8 h. The corresponding reaction mixture was cooled to room temperature and the filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel using 30% (v/v) ethyl acetate in petroleum ether as eluent to afford the desired product 3.

Diethyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3a): Yellow oil; 35.0 mg, 85 % yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (t, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.23 (t, $J = 5.9$ Hz, 3H), 6.77 (d, $J = 7.3$ Hz, 1H), 5.34 (s, 1H), 4.39 (p, $J = 7.3$ Hz, 4H), 2.13 (s, 3H), 1.77 (s, 3H), 1.39 (dd, $J = 10.1$, 3.9 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.63, 168.46, 143.91, 140.73, 139.93, 136.10, 133.26, 131.17, 130.88, 129.66, 129.14, 128.92, 124.50, 119.81, 118.29, 112.22, 110.91, 107.27, 60.99, 60.67, 20.86, 19.20, 14.35, 14.27. HR-MS (ESI) caled for [M + 1]$^+$: C$_{25}$H$_{26}$NO$_4$, found: 416.1869; IR (KBr): 3480.74, 2981.85, 1702.63, 1342.22 cm$^{-1}$.
Diethyl 5-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3b): Yellow solid; 41.0 mg, 91 % yield; m.p. 168.9-169.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 7.3 Hz, 2H), 6.81 (s, 0H), 6.47 (s, 1H), 5.26 (s, 1H), 4.39 (dq, J = 14.2, 7.1 Hz), 3.82 (s, 3H), 2.13 (s, 3H), 1.78 (s, 3H), 1.39 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.69, 168.31, 160.14, 143.61, 141.36, 139.84, 137.27, 135.12, 132.47, 131.05, 129.64, 129.15, 120.09, 118.70, 110.48, 106.15, 103.09, 98.64, 61.03, 60.52, 54.98, 21.22, 19.29, 14.39, 14.28. HR-MS (ESI) calcd for [M + 1]+: C₂₇H₂₈NO₄ 446.1962, found: 446.1978; IR (KBr): 3485.74, 2981.85, 1712.63, 1347.22 cm⁻¹

3c

Diethyl 2,5,8-trimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3c): Yellow solid; 38.1 mg, 89 % yield; m.p. 161.5-162.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 7.3 Hz, 2H), 7.09 (s, 1H), 5.27 (s, 1H), 4.40 (dd, J = 14.2, 7.1 Hz), 2.33 (s, 3H), 2.11 (s, 3H), 1.76 (s, 3H), 1.39 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.80, 168.55, 143.77, 142.58, 139.96, 138.72, 136.06, 133.48, 131.08, 130.63, 129.72, 129.08, 122.80, 119.23, 117.83, 113.99, 110.69, 106.56, 60.96, 60.61, 22.34, 20.87, 19.22, 14.36, 14.27. HR-MS (ESI) calcd for [M + 1]+: C₂₇H₂₈NO₄ 430.2013, found: 430.2025; IR (KBr): 3659.72, 1712.56, 1582.33, 1286.02, 1120.09 cm⁻¹

3d

Diethyl 5-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3d): Yellow solid; 31.8 mg, 71 % yield; m.p. 198.5-199.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.31 (s, 1H), 7.22 (d, J = 7.3 Hz, 1H), 6.77 (s, 1H), 5.37 (s, 1H), 4.41 (dd, J = 13.8, 6.9 Hz, 4H), 2.14 (s, 3H), 1.80 (s, 3H), 1.39 (dd, J = 9.3, 4.7 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.04, 168.86, 143.55, 142.34, 139.56, 137.56, 137.53, 135.57, 134.18, 132.77, 131.26, 129.40, 122.84, 119.15, 117.13, 112.52, 110.80, 107.83, 61.20, 60.87, 21.08, 19.39, 14.33, 14.24. HR-MS (ESI) calcd for [M + 1]+: C₂₇H₂₆ClNO₄ 450.1467, found: 450.1478; IR (KBr): 2986.66, 1697.91, 1576.65, 1280.99, 1130.80, 740.72 cm⁻¹

3e

Diethyl 5-bromo-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3e): Yellow solid; 37.0 mg, 75 % yield; m.p. 182.3-182.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (t, J =
7.5 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.47 (s, 1H), 7.22 (d, J = 7.6 Hz, 2H), 6.90 (s, 1H), 5.38 (s, 1H), 4.41 (dd, J = 14.0, 6.9 Hz, 4H), 2.13 (s, 3H), 1.80 (s, 3H), 1.40 (t, J = 7.0 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.01, 167.84, 143.61, 142.31, 139.57, 137.45, 134.41, 132.79, 131.26, 129.41, 124.32, 123.03, 120.29, 119.06, 115.13, 109.95, 107.92, 61.20, 60.87, 21.06, 19.37, 14.32, 14.23. HR-MS (ESI) calcd for [M + 1]$^+$: C$_{26}$H$_{32}$BrNO$_4$ 494.0961, found: 494.0966; IR (KBr): 2976.06, 1897.91, 1476.65, 1280.99, 1130.80, 1040.72 cm$^{-1}$

![3f](image)

**Diethyl 5-fluoro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3f):**

Yellow solid; 29.4 mg, 68 % yield; m.p. 118.2-119.0 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 7.4 Hz, 2H), 7.01 (d, J = 11.6 Hz, 1H), 6.61 (d, J = 10.3 Hz, 1H), 5.34 (s, 1H), 4.43 – 4.36 (m, 4H), 2.14 (s, 3H), 1.81 (s, 3H), 1.39 (dd, J = 6.3, 4.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.14, 167.91, 163.42 (d, J = 243.5 Hz, J$_{CF}$), 143.63, 142.55, 139.61, 137.83, 135.05 (d, J = 11.4 Hz, J$_{CF}$), 133.87, 133.75, 131.24, 129.42, 129.37, 121.71, 119.40, 119.35, 110.40, 107.21, 102.43 (d, J = 24.4 Hz, J$_{CF}$), 101.63, 101.35, 61.17, 60.78, 21.17, 19.42, 14.33, 14.24. HR-MS (ESI) calcd for [M + 1]$^+$: C$_{26}$H$_{25}$BrNO$_4$ 434.1762, found: 434.1775; IR (KBr): 2986.52, 1709.73, 1580.22, 1282.47, 1128.67, 711.71 cm$^{-1}$

![3g-3h](image)

**Diethyl 6-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3g) and diethyl 4-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3h):**

Yellow oil; 21.8 mg, 49 % yield $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 (t, J = 7.5 Hz, 2H), 7.40 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 9.2 Hz, 1H), 7.15 (d, J = 7.5 Hz, 2H), 7.00 (d, J = 9.3 Hz, 1H), 5.18 (s, 1H), 4.34 – 4.21 (m, 4H), 3.70 (s, 3H), 2.02 (s, 3H), 1.60 (s, 3H), 1.29 (q, J = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.24, 169.60, 144.64, 144.04, 139.99, 138.45, 135.05, 131.09, 129.84, 129.22, 129.00, 125.56, 119.52, 119.09, 119.01, 117.83, 108.07, 106.79, 61.01, 60.61, 58.09, 20.86, 18.15, 14.36, 14.22. HR-MS (ESI) calcd for [M + 1]$^+$: C$_{26}$H$_{30}$NO$_5$ 446.1662, found: 446.1974; IR (KBr): 3853.86, 2986.76, 1714.77, 1266.76, 752.65 cm$^{-1}$

![3i](image)

**Diethyl 4-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3i):**

Yellow solid; 20.2 mg, 45 % yield; m.p. 187.6-188.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, J =
7.5 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.22 (dd, J = 14.7, 8.4 Hz, 4H), 5.47 (s, 1H), 4.45 – 4.30 (m, 4H),
2.13 (s, 3H), 1.79 (s, 3H), 1.37 (q, J = 7.5 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 169.59, 169.27, 142.90, 141.96, 139.72, 136.10, 131.81, 131.37, 131.23, 129.54, 129.33, 127.64, 125.81, 120.06, 119.74, 117.19, 108.91, 108.43, 61.43, 50.87, 20.77, 18.60, 14.32, 14.01. HR-MS (ESI) calcd for [M + H]+: C26H25ClNO4 450.1467, found: 450.1470; IR (KBr): 2984.63, 1715.37, 1272.76, 742.19, 630.32 cm⁻¹.

**3j**

Diethyl 2,8-dimethyl-5-nitro-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3j): Red solid; 30.0 mg, 65 % yield; m.p. 230.5-231.2 °C; 1H NMR (400 MHz, CDCl3) δ 8.26 (s, 1H), 7.65 (t, J = 7.3 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.27 – 7.22 (m, 2H), 5.59 (s, 1H), 4.50 – 4.42 (m, 4H), 2.20 (s, 3H), 1.86 (s, 3H), 1.44 (t, J = 6.8 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 168.34, 167.48, 148.34, 143.55, 143.39, 139.24, 133.31, 132.71, 129.69, 129.15, 126.53, 121.71, 114.31, 110.74, 110.54, 105.09, 61.44, 61.26, 21.14, 19.43, 14.33, 14.23. HR-MS (ESI) calcd for [M + H]+: C26H25NO6 461.1707, found: 461.1711; IR (KBr): 2987.84, 1706.35, 1336.70, 1282.67, 1113.37 cm⁻¹.

**3k**

3,7-Diethyl 5-methyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,5,7-tricarboxylate (3k): Yellow solid; 34.0 mg, 72 % yield; m.p. 190.5-190.9 °C; 1H NMR (400 MHz, CDCl3) δ 8.06 (s, 1H), 7.62 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (s, 1H), 7.23 (d, J = 7.4 Hz, 2H), 5.46 (s, 1H), 4.43 (dd, J = 15.1, 6.8 Hz, 4H), 3.91 (s, 3H), 2.16 (s, 3H), 1.80 (s, 3H), 1.43 (t, J = 7.0 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 169.04, 168.10, 167.54, 143.61, 141.74, 139.64, 137.05, 132.64, 131.43, 131.31, 130.04, 129.46, 129.35, 126.28, 121.01, 120.92, 111.74, 110.81, 109.26, 61.20, 60.96, 52.17, 20.90, 19.23, 14.32, 14.24. HR-MS (ESI) calcd for [M + H]+: C28H27NO6 474.1911, found: 474.1919; IR (KBr): 3748.24, 1711.83, 1263.29, 1109.79, 741.11 cm⁻¹.

**3l**

Diethyl 5-cyano-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3l): Yellow solid; 31.0 mg, 70 % yield; m.p. 160.4-161.8 °C; 1H NMR (400 MHz, CDCl3) δ 7.67 – 7.62 (m, 3H), 7.56 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 7.4 Hz, 2H), 6.92 (s, 1H), 5.54 (s, 1H), 4.42 (dq, J = 14.5, 7.2 Hz, 4H), 2.17 (s, 3H), 1.83 (s, 3H), 1.41 (t, J = 6.7 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 168.54, 167.54,
143.30, 143.06, 139.27, 138.06, 132.58, 132.44, 131.48, 129.64, 129.18, 125.52, 123.58, 120.26, 119.56, 112.69, 112.61, 110.12, 110.04, 61.40, 61.19, 21.11, 19.45, 14.32, 14.24.

HR-MS (ESI) calcd for \([M + 1]^+\): C_{27}H_{25}N_{2}O_{4} 441.1809, found: 441.1812; IR (KBr): 3456.26, 2984.46, 1705.05, 1285.80, 1115.96, 711.19 cm\(^{-1}\)

\(\text{3m} \)

Diethyl 1-(4-methoxyphenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3m): Yellow solid; 36.5 mg, 82 % yield; m.p. 177.2-178.0 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (t, \(J = 7.6\) Hz, 1H), 7.14 (t, \(J = 7.9\) Hz, 1H), 7.02 (q, \(J = 8.6\) Hz, 4H), 6.68 (d, \(J = 7.2\) Hz, 1H), 5.32 (s, 1H), 4.36 – 4.26 (m, 4H), 3.80 (s, 3H), 2.07 (s, 3H), 1.70 (s, 3H), 1.30 (t, \(J = 7.1\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.67, 168.52, 159.69, 144.24, 141.29, 136.15, 133.28, 132.45, 130.94, 130.58, 128.89, 124.54, 119.69, 118.20, 116.24, 112.09, 110.80, 107.25, 60.98, 60.67, 55.54, 29.70, 20.89, 19.21, 14.35, 14.27. HR-MS (ESI) calcd for \([M + 1]^+\): C_{27}H_{25}N_{2}O_{4} 446.1962, found: 446.1966; IR (KBr): 3748.74, 2983.05, 1711.60, 1509.19, 1253.01, 1096.72 cm\(^{-1}\)

\(\text{3n} \)

Diethyl 2,8-dimethyl-1-(p-tolyl)-1H-benzo[de]quinoline-3,7-dicarboxylate (3n): Yellow solid; 36.0 mg, 84 % yield; m.p. 181.2-181.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 (t, \(J = 7.5\) Hz, 1H), 7.27 (t, \(J = 10.6\) Hz, 2H), 7.09 (d, \(J = 7.1\) Hz, 2H), 6.75 (d, \(J = 6.9\) Hz, 1H), 5.37 (s, 1H), 4.42 – 4.36 (m, 4H), 2.46 (s, 3H), 2.15 (s, 3H), 1.77 (s, 3H), 1.38 (t, \(J = 6.2\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.70, 168.55, 144.03, 141.04, 139.12, 137.23, 136.14, 133.27, 131.77, 130.94, 129.25, 128.89, 124.53, 119.65, 118.18, 112.08, 110.76, 107.25, 60.98, 60.67, 55.54, 29.70, 20.89, 19.20, 14.35, 14.27. HR-MS (ESI) calcd for \([M + 1]^+\): C_{27}H_{28}NO_{5} 430.2013, found: 430.2010; IR (KBr): 3748.34, 1709.75, 1643.00, 1283.10, 1096.72 cm\(^{-1}\)

\(\text{3o} \)

Diethyl 1-(3,5-dimethylphenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3o): Yellow solid; 35.4 mg, 80 % yield; m.p. 160.3-161.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 (t, \(J = 7.5\) Hz, 1H), 7.24 (t, \(J = 7.9\) Hz, 1H), 7.14 (s, 1H), 6.85 (s, 2H), 6.78 (d, \(J = 7.2\) Hz, 1H), 5.43 (s, 1H), 4.47 – 4.35 (m, 4H), 2.40 (s, 3H), 2.18 (s, 3H), 1.82 (s, 3H), 1.40 (t, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.70, 168.55, 143.93, 141.06, 141.00, 139.71, 136.14, 133.27, 131.00, 130.71, 128.87, 126.81, 124.52, 119.57, 118.09, 111.98, 110.62, 107.31, 60.94, 60.64, 21.30, 20.92, 19.17,
14.36, 14.28. HR-MS (ESI) calcd for [M + 1]^+: C_{28}H_{30}NO_4 444.2169, found: 444.2173; IR (KBr): 3494.23, 2983.11, 1710.84, 1637.65, 1253.89, 1098.07 cm$^{-1}$

3p Diethyl 1-(4-fluorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3p):
Yellow solid; 31.1 mg, 72 % yield; m.p. 134.2-134.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.19 (m, 6H), 6.77 (d, J = 7.2 Hz, 1H), 5.33 (s, 1H), 4.39 (dt, J = 14.7, 7.2 Hz, 4H), 2.15 (s, 3H), 1.76 (s, 3H), 1.38 (s, J = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.55, 168.33, 162.47 (d, J = 250.7 Hz, J$_{CF}$), 143.87, 140.46, 136.06, 135.79, 133.21, 131.61 (d, J = 12 Hz, J$_{CF}$), 130.67, 128.98, 124.41, 120.08, 118.48, 118.41, 118.19, 112.44, 111.21, 107.16, 61.06, 60.73, 29.69, 20.84, 19.21, 14.34, 14.26. HR-MS (ESI) calcd for [M + 1]^+: C$_{26}$H$_{25}$FNO$_4$ 434.1762, found: 434.1753; IR (KBr): 3748.81, 2986.22, 1710.84, 1508.48, 1282.74, 1095.56, 742.20 cm$^{-1}$

3q Diethyl 1-(3-fluorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3q):
Yellow solid; 28.1 mg, 65 % yield; m.p. 131.2-131.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (dd, J = 14.6, 7.8 Hz, 2H), 7.31 (d, J = 8.3 Hz, 1H), 7.24 (t, J = 8.0 Hz, 2H), 7.06 (d, J = 7.9 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 7.2 Hz, 1H), 5.36 (s, 1H), 4.39 (dq, J = 14.2, 7.0 Hz, 4H), 2.15 (s, 3H), 1.79 (s, 3H), 1.39 (s, J = 7.0 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.54, 168.29, 143.45, 141.29, 141.20, 140.05, 136.06, 133.17, 132.53, 132.44, 130.56, 128.98, 125.67, 125.63, 124.32, 120.19, 118.56, 117.29 (d, J = 21.8 Hz, J$_{CF}$), 116.58 (d, J = 20.8 Hz, J$_{CF}$), 112.54, 111.26, 107.16, 61.09, 60.76, 20.85, 19.06, 14.35, 14.26. HR-MS (ESI) calcd for [M + 1]^+: C$_{26}$H$_{25}$FNO$_4$ 434.1762, found: 434.1760; IR (KBr): 3748.81, 2986.22, 1708.67, 1508.48, 1282.74, 1095.56, 742.20 cm$^{-1}$

3r Diethyl 1-(4-chlorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3r):
Yellow solid; 32.7 mg, 73 % yield; m.p. 135.3-135.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.76 (d, J = 7.0 Hz, 1H), 5.34 (s, 1H), 4.45 – 4.34 (m, 4H), 2.15 (s, 3H), 1.76 (s, 3H), 1.39 (s, J = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.56, 168.32, 143.63, 140.12, 138.39, 136.06, 135.13, 133.18, 131.58, 131.27, 130.58, 128.99, 124.36, 120.16, 118.53, 112.52, 111.30, 107.17, 61.10, 60.77, 20.82, 19.22, 14.34, 14.26. HR-MS (ESI)
calcd for [M + 1]+: C_{26}H_{25}ClNO_{4} 450.1467, found: 450.1459; IR (KBr): 3494.32, 1708.81, 1642.81, 1282.45, 1095.30, 715.97 cm⁻¹

3s

**Diethyl 1-(4-bromophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3s):**

Yellow solid; 39.0 mg, 79 % yield; m.p. 139.2-140.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 7.8 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.75 (s, 1H), 5.34 (s, 1H), 4.38 (dd, J = 15.9, 7.8 Hz, 4H), 2.15 (s, 3H), 1.76 (s, 3H), 1.39 (t, J = 6.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.56, 168.31, 143.56, 140.03, 138.92, 136.06, 134.59, 133.17, 131.61, 130.56, 129.00, 124.35, 123.18, 120.18, 118.54, 112.54, 111.31, 107.18, 60.77, 20.82, 19.23, 14.34, 14.26. HR-MS (ESI) calcd for [M + 1]+: C_{26}H_{25}BrNO_{4} 494.0961, found: 494.0964; IR (KBr): 2919.80, 1712.80, 1473.36, 1260.20, 1095.94, 1018.58, 754.96 cm⁻¹.

3u

**Diethyl 1-(4-acetamidophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3u):**

Yellow oil; 38 mg, 80% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.24 – 7.11 (m, 2H), 7.01 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 7.0 Hz, 1H), 5.28 (s, 1H), 4.32 (dq, J = 14.4, 7.1 Hz, 4H), 2.14 (s, 3H), 2.02 (s, 3H), 1.68 (s, 3H), 1.32 (td, J = 7.0, 2.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 170.14, 168.91, 168.59, 144.01, 143.15, 136.06, 135.64, 135.00, 129.36, 128.80, 124.44, 124.18, 119.74, 118.17, 112.23, 110.89, 107.19, 60.43, 24.53, 20.79, 19.23, 14.33, 14.25. HR-MS (ESI) calcd for [M + 1]+: C_{28}H_{29}N_{2}O_{5} 473.2071, found: 473.2074; IR (KBr): 3456.26, 2984.46, 1695.05, 1280.79, 1115.96, 748.19 cm⁻¹.

3w

**Diethyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3w):**

Yellow oil; 31.9 mg, 72 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 6.9 Hz, 1H), 7.28 (d, J = 7.4 Hz, 2H), 7.22 (s, 2H), 6.71 (s, 1H), 5.31 (s, 1H), 4.39 (d, J = 6.5 Hz, 4H), 2.40 (d, J = 7.0 Hz, 2H), 2.18 (d, J = 7.2 Hz, 2H), 1.40 – 1.36 (m, 6H), 0.98 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.78, 168.44, 145.87, 144.44, 141.89, 139.57, 133.10, 131.15, 130.95, 130.19, 129.15, 128.80, 124.58, 119.47, 118.27, 112.25, 110.47, 105.98, 60.93, 60.72, 27.67, 24.44, 15.56, 14.29, 14.25, 13.68. HR-MS
(ESI) calcd for [M + 1]⁺: C_{28}H_{30}NO_{4} 444.2169, found: 444.2176; IR (KBr): 1485.74, 2981.85, 1712.63, 1581.65, 1282.60, 1095.88, 743.10 cm⁻¹

Diethyl 2,8-dicyclohexyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3x): Yellow oil; 38.5 mg, 70 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.7 Hz, 2H), 7.14 (dd, J = 17.1, 7.9 Hz, 2H), 6.47 (d, J = 7.1 Hz, 1H), 5.33 (s, 1H), 4.44 – 4.35 (m, 4H), 2.46 (t, J = 11.6 Hz, 2H), 2.09 (t, J = 11.6 Hz, 2H), 1.75 – 1.60 (m, 12H), 1.40 (d, J = 9.6 Hz, 6H), 0.85 (dt, J = 35.6, 12.1 Hz, 8H);

¹³C NMR (100 MHz, CDCl₃) δ 170.15, 169.05, 145.90, 144.73, 144.52, 140.42, 132.56, 131.78, 131.00, 130.12, 128.98, 128.69, 124.26, 119.10, 118.15, 111.23, 103.65, 61.04, 60.67, 42.24, 30.54, 29.69, 27.04, 26.69, 25.97, 25.72, 14.35, 14.12. HR-MS (ESI) calcd for [M + 1]⁺: C_{36}H_{42}NO_{4} 552.3108, found: 552.3104; IR (KBr): 3749.49, 2922.39, 1715.09, 1267.06, 1092.21, 745.78 cm⁻¹

Dimethyl 2,8-bis(methoxymethyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3y): Yellow oil; 28.0 mg, 63 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 7.4 Hz, 2H), 7.25 (d, J = 9.3 Hz, 1H), 6.79 (d, J = 7.4 Hz, 1H), 5.61 (s, 1H), 4.30 (s, 2H), 3.89 (d, J = 7.6 Hz, 6H), 3.80 (s, 2H), 3.16 (s, 3H), 3.05 (d, J = 12.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.36, 168.15, 144.60, 139.64, 137.49, 133.41, 130.78, 130.42, 130.04, 129.32, 128.99, 125.98, 119.67, 113.15, 104.52, 99.99, 72.90, 68.37, 58.06, 52.13, 51.81. HR-MS (ESI) calcd for [M + 1]⁺: C_{26}H_{26}NO_{6} 448.1768, found: 448.1755; IR (KBr): 3748.97, 2990.40, 1717.27, 1345.04, 1100.27, 760.39 cm⁻¹

Diethyl 8-allyl-2-(but-3-en-1-yl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z): Yellow oil; 35.6 mg, 72 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (t, J = 7.1 Hz, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.30 – 7.19 (m, 4H), 6.73 (d, J = 6.7 Hz, 1H), 5.67 (dt, J = 16.0, 7.8 Hz, 1H), 5.49 (dd, J =
16.7, 9.9 Hz, 1H), 5.32 (s, 1H), 4.93 – 4.72 (m, 4H), 4.42 – 4.34 (m, 4H), 2.48 (t, J = 7.5 Hz, 2H), 2.25 – 2.10 (m, 6H), 1.38 (dd, J = 11.1, 5.3 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.61, 168.27, 144.18, 143.83, 139.55, 139.44, 137.90, 136.73, 133.15, 130.97, 130.16, 129.28, 128.82, 124.70, 119.92, 118.53, 115.17, 114.73, 112.57, 111.07, 106.63, 60.99, 60.76, 35.04, 33.82, 32.95, 30.74, 14.31, 14.26.

HR-MS (ESI) calcd for [M + 1]$^+$: C$_{32}$H$_{34}$NO$_4$ 496.2482, found: 496.2485; IR (KBr): 3749.08, 2983.61, 1712.45, 1286.21, 1099.10, 747.69, 710.40 cm$^{-1}$

3z-1

**Diethyl 2,8-diphenethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z-1):** Yellow solid; 30.9 mg, 52 % yield; m.p. 109.4-110.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (dd, J = 13.9, 7.0 Hz, 2H), 7.17 (dd, J = 16.4, 7.9 Hz, 10H), 7.00 (d, J = 6.3 Hz, 2H), 6.73 (dd, J = 15.0, 6.8 Hz, 3H), 5.20 (s, 1H), 4.46 – 4.37 (m, 4H), 2.72 (s, 6H), 2.41 (d, J = 7.9 Hz, 2H), 1.40 (dd, J = 13.9, 6.8 Hz, 6H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.65, 168.34, 143.54, 141.39, 140.70, 139.39, 139.20, 133.26, 131.06, 130.24, 129.24, 128.81, 128.42, 128.25, 127.98, 126.19, 125.80, 119.93, 118.66, 112.56, 111.14, 107.01, 61.13, 60.86, 37.25, 36.36, 35.24, 33.78, 14.37. HR-MS (ESI) calcd for [M + 1]$^+$: C$_{40}$H$_{38}$NO$_4$ 596.2795, found: 596.2774; IR (KBr): 3742.91, 2985.64, 1701.68, 1279.41, 742.49 cm$^{-1}$

3z-2

**Diethyl 2,8-bis(3-chloropropyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z-2):** Yellow oil; 35.7 mg, 70 % yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 6.9 Hz, 1H), 7.28 (d, J = 7.4 Hz, 2H), 7.22 (s, 2H), 6.71 (s, 1H), 5.31 (s, 1H), 4.39 (d, J = 6.5 Hz, 4H), 2.40 (d, J = 7.0 Hz, 2H), 2.18 (d, J = 7.2 Hz, 2H), 1.42 – 1.35 (m, 6H), 0.98 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.78, 168.44, 145.87, 144.44, 141.89, 139.57, 133.10, 131.15, 130.95, 130.19, 129.15, 128.80, 124.58, 119.47, 118.27, 112.25, 110.47, 105.98, 60.93, 60.72, 27.67, 24.44, 15.56, 14.29, 14.25, 13.68. HR-MS (ESI) calcd for [M + 1]$^+$: C$_{38}$H$_{32}$ClNO$_4$ 541.1736, found: 541.1709; IR (KBr): 3759.08, 2983.01, 1712.45, 1280.21, 1099.10, 747.69, 710.40 cm$^{-1}$
3aa+3ab=43% (3aa/3ab=0.6:1)

Diethyl 2-ethyl-8-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3aa) and diethyl 8-ethyl-2-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3ab): Yellow oil; 18.4 mg, 43 % yield; 1H NMR (400 MHz, CDCl₃) δ 7.61 (td, J = 7.6, 1.9 Hz, 4H), 7.28 (d, J = 1.2 Hz, 1H), 7.23 – 7.21 (m, 3H), 6.78 – 6.76 (m, 1H), 4.45 – 4.34 (m, 4H), 2.47 – 2.36 (m, 2H), 2.11 (s, 2H), 1.77 (s, 3H), 1.39 (dd, J = 7.1, 3.6, 2.1 Hz, 6H), 0.99 (ddd, J = 8.5, 7.6, 4.4 Hz, 3H); 13C NMR (101 MHz, CDCl₃) δ 169.52, 168.25, 144.03, 139.53, 138.88, 136.29, 133.25, 131.20, 130.70, 130.33, 130.18, 129.58, 129.20, 128.83, 125.01, 119.93, 119.34, 113.08, 112.95, 107.37, 68.37, 60.69, 57.99, 52.06, 22.64, 20.85, 19.16, 14.32. HR-MS (ESI) calcd for [M + 1]+: C₃₁H₂₈NO₄ 430.2013, found: 430.2018; IR (KBr): 3742.91, 2985.64, 1701.68, 1513.34, 1279.41, 742.49 cm⁻¹

7-Ethyl 3-methyl 2-(methoxymethyl)- 8-methyl- 1-phenyl-1H -benzo[de] quinoline-3,7 -dicarboxylate (3ac) and 3-ethyl 7-methyl 8-(methoxymethyl)- 2-methyl-1-phenyl-1H-benzo[de]quinoline-3,7- dicarboxylate (3ad): Yellow oil; 15.3 mg, 34 % yield; 1H NMR (400 MHz, CDCl₃) δ 7.60 (dd, J = 10.1, 4.8 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.23 (dd, J = 12.8, 5.4 Hz, 1H), 6.74 (d, J = 7.3 Hz, 1H), 5.36 (s, 1H), 4.43 – 4.37 (m, 2H), 3.90 (s, 3H), 3.79 (s, 2H), 3.03 (s, 3H), 2.12 (s, 3H), 1.40 – 1.34 (m, 3H); 13C NMR (100 MHz, CDCl₃) δ 169.52, 168.25, 144.03, 139.53, 138.88, 136.29, 133.25, 131.19, 130.70, 130.33, 130.18, 129.58, 129.20, 128.83, 125.01, 119.93, 119.34, 113.07, 112.95, 107.37, 72.93, 68.37, 60.69, 58.03, 57.99, 52.06, 29.68, 20.84, 14.32. HR-MS (ESI) calcd for [M + 1]+: C₃₈H₂₆NO₅ 432.1822, found: 432.1805; IR (KBr): 3616.23, 2988.46, 1644.21, 1274.37, 739.76 cm⁻¹
1.8 Procedure for synthesis of $\pi$-conjugated organic molecules 5 and 7

Preparation of carbazole-based 1-azaphenalene (5): The reaction was conducted in the presence of $\text{Pd(PPh}_3)_4$ (10 mol%), $\text{K}_2\text{CO}_3$ (69 mg, 0.5 mmol), diethyl 5-bromo-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (62 mg, 0.125 mmol), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)-9H-carbazole (24 mg, 0.05 mmol) in toluene (2 mL) at 120 °C for 24h. Then it was filtered through celite. The filtrate was evaporated under reduced pressure and the resulting was subjected to column chromatography on silica gel with petroleum ether to yield 43 mg of 5 (70% yield). Yellow solid; 43.0 mg, 70% yield; m.p. 166.8-167.4 °C; $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 8.16 (dd, $J = 12.7$, 8.1 Hz, 2H), 7.80 (s, 1H), 7.62 (t, $J = 7.8$ Hz, 7H), 7.55 – 7.49 (m, 4H), 7.27 (d, $J = 7.6$ Hz, 4H), 7.17 (d, $J = 2.1$ Hz, 2H), 5.38 (s, 2H), 4.73 – 4.63 (m, 1H), 4.47 – 4.40 (m, 8H), 2.42 – 2.33 (m, 2H), 2.18 (s, 6H), 2.05 – 1.96 (m, 2H), 1.83 (s, 6H), 1.43 (td, $J = 7.0$, 2.8 Hz, 12H), 1.26 – 1.11 (m, 20H), 0.89 – 0.83 (m, 4H), 0.79 (t, $J = 6.9$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) δ 169.68, 168.51, 143.79, 143.00, 142.76, 141.18, 139.96, 139.65, 139.22, 136.64, 133.65, 131.30, 131.17, 129.70, 129.19, 123.59, 121.78, 120.56, 120.28, 120.09, 118.76, 117.31, 112.49, 111.00, 110.44, 107.64, 107.31, 61.00, 60.67, 56.89, 34.02, 31.75, 29.59, 29.39, 29.17, 27.13, 22.58, 20.96, 19.28, 14.53, 14.46, 14.03. HR-MS (ESI) calcd for [M + 2H]$^{2+}$: $C_{39}H_{39}N_7O_8$ 616.8399, found: 616.8398; IR (KBr): 3749.48, 2898.58, 1643.57, 1272.97, 752.53 cm$^{-1}$
Preparation of dithiophene-based 1-azaphenalene (7): Diethyl 5-bromo-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (62 mg, 0.125 mmol) and (4,8-bis((2-ethylhexyl)oxy)benzo [1,2-b:4,5-b']dithiophene -2,6-diyl) bis(trimethylstannane) (35 mg, 0.05 mmol) were dissolved in dry toluene (2 mL) and deoxygenated with nitrogen for 15 min. Then Pd(PPh$_3$)$_4$ (12 mg, 10 mol%) was added under nitrogen. The mixture was stirred at reflux for 24 h. After the reaction mixture was cooled to room temperature, the mixture was evaporated under reduced pressure and the resulting was subjected to column chromatography on silica gel with (30%) petroleum ether in acetate to yield 56 mg of 7 (88% yield). Yellow solid; 56.0 mg, 88% yield; m.p. 165.6-166.4 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 – 7.69 (m, 4H), 7.64 (dd, $J = 13.0, 5.5$ Hz, 4H), 7.54 (t, $J = 7.4$ Hz, 2H), 7.27 (d, $J = 6.0$ Hz, 4H), 7.20 (d, $J = 1.3$ Hz, 2H), 5.40 (s, 2H), 4.47 (dq, $J = 14.5, 7.2$ Hz, 8H), 4.28 – 4.21 (m, 4H), 2.18 (s, 6H), 1.92 – 1.87 (m, 2H), 1.84 (s, 6H), 1.75 (dd, $J = 14.0, 6.8$ Hz, 2H), 1.63 (dt, $J = 12.1, 5.9$ Hz, 4H), 1.50 (q, $J = 6.0$ Hz, 12H), 1.44 – 1.38 (m, 6H), 1.06 (t, $J = 7.4$ Hz, 6H), 0.94 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.29, 168.26, 144.42, 144.18, 143.56, 141.86, 139.80, 137.27, 134.43, 133.49, 132.63, 131.66, 131.20, 129.57, 129.45, 129.27, 124.11, 120.10, 116.55, 116.45, 110.63, 110.56, 108.03, 76.31, 61.07, 60.79, 40.68, 30.43, 29.70, 29.22, 23.83, 23.12, 21.01, 19.32, 14.55, 14.47, 14.15, 11.28. HR-MS (ESI) calcd for [M + 2H]$^{2+}$: C$_{78}$H$_{86}$N$_2$O$_{10}$S$_6$ 637.2844, found: 637.2856; IR (KBr): 3492.48, 2924.58, 1710.29, 1285.20, 709.42 cm$^{-1}$.

1.9 The photophysical and electrochemical properties of the compounds 5 and 7.

Figure S1. UV-vis absorption spectra of the compounds 5 and 7 in chloroform solutions.
**Figure S2.** Photoluminescence spectra of the compounds 5 and 7 in chloroform solutions.

**Figure S3.** Cyclic voltammograms of the compounds 5 and 7 in thin solid films on the Pd/C electrode in an anhydrous acetonitrile solution of 0.1 mol L⁻¹ Bu₄NPF₆ with a scan rate of 100 mV s⁻¹.

**Table S5.** Energy levels of the compounds 5 and 7.

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<th>Compound</th>
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<th>E°_{onset}^{red} [b]</th>
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[a] Estimated from the oxidation onset of the CV (in CH₃CN); [b] Estimated from the reduction onset of the CV (in CH₃CN) [c] HOMO = -(4.40 + E°_{onset}^{ox}); [d] LUMO = -(4.40 + E°_{onset}^{red}).

2. Preliminary mechanistic studies

(1): Kinetic isotope effect of this transformation on monodeuterate ketoimine

A sample experimental set-up is shown as follows: Ketoimine (1a: 20 mg, 0.1 mmol; or d-1a: 20 mg, 0.1 mmol) were added to the solution of diazo compound 2a (0.3 mmol), [RhCp*Cl₂]₂ (2 mg, 2.5 mol %) and AgSbF₆ (5 mg, 10 mol%) in DCE (2.0 mL) under air atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube for 80 °C. When the reaction was stirred at 80 °C for 15 min, the mixtures were removed under pressure and analyzed by ¹H NMR spectrum (see Figure 4 and Figure 5).

![Chemical structures and reaction scheme](image-url)
Figure S4, The conversion of 1a was monitored by $^1$H NMR method.

$\text{Ph} - N - D + \text{O} - \text{O} - \text{Et} \xrightarrow{[\text{Cp}^*\text{RhCl}]_2 (2.5 \text{ mol } \%), \text{AgSbF}_6 (10 \text{ mol } \%)} 2a (3.0 \text{ equiv}), \text{DCE (2.0 mL), 80 }{^\circ}\text{C, 15 min}} \rightarrow \text{EtO}_2\text{C} - \text{N} - \text{Ph} - \text{CO}_2\text{Et}$
Figure S5. The conversion of d-1a-a was monitored by $^1$H NMR method

(2) Kinetic isotope effect of this transformation on pentadeuterate ketoimine
To a 15 mL of Schlenk tube, the catalyst \([\text{RhCp}^*\text{Cl}_2]\) (4 mg, 2.5 mol %), \(\text{AgSbF}_6\) (10 mg, 10 mol %), substrate \(\text{1a}\) (19 mg, 0.1 mmol), substrate \(d\text{-1a-b}\) (20 mg, 0.1 mmol)\(^{[4]}\) were added in sequence under air atmosphere. After the diazo compound \(\text{2a}\) (0.6 mmol) in DCE (2.0 mL) was added, the reaction mixture was sealed and stirred at 80 °C for 30 min. Then the product was isolated by column chromatography, afford \(3\text{a/d-3a}\) with ration 2.04/1, determined by \(^1\text{H}\) NMR

(3) Control experiments for mechanism studies

To the solution of \textit{ortho}-substituted aryketimine \(\text{1r}\) (0.1 mmol) in dry DCE (2.0 mL) were added diazo compound \(\text{2a}\) (0.3 mmol), \([\text{RhCp}^*\text{Cl}_2]\) (4 mg, 2.5 mol %) and \(\text{AgSbF}_6\) (10 mg, 10 mol%). The reaction mixture was stirred at 80 °C for 8 h. After the reaction mixture was cooled down to room temperature, and filtrated, the filtration was concentrated under vacuum and purified by flash chromatography on silica gel using 20% (v/v) ethyl acetate in petroleum ether as eluent to give the compound \(8\) (28 mg, 85% yield). \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (t, \(J = 7.6\) Hz, 2H), 7.51 – 7.46 (m, 1H), 7.25 (dd, \(J = 4.8, 3.6\) Hz, 2H), 7.17 – 7.10 (m, 2H), 6.94 – 6.90 (m, 1H), 6.86 (t, \(J = 7.9\) Hz, 1H), 6.74 (dd, \(J = 6.8, 1.6\) Hz, 1H), 5.48 (dd, \(J = 7.6, 0.8\) Hz, 1H), 4.37 (q, \(J = 7.1\) Hz, 3H), 1.76 (s, 3H), 1.39 (t, \(J = 7.1\) Hz, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.66, 143.00, 141.64, 140.31, 135.81, 131.26, 131.07, 129.91, 128.87, 127.87, 126.82, 126.39, 120.93, 117.67, 112.15, 109.96, 104.99, 60.79, 19.24, 14.28.

S-24
To the solution of (E)-N-(1-(o-tolyl)ethylidene)aniline 1w (0.1 mmol) in dry (2.0 mL) were added diazo compound 2a (0.3 mmol), [RhCp*RhCl2]2 (4 mg, 2.5 mol %) and AgSbF6 (10 mg, 10 mol %). The reaction mixture was stirred at 80 °C for 8 h. After the reaction mixture was cooled down to room temperature, and filtrated, the filtration was concentrated under vacuum and purified by flash chromatography on silica gel using 10% (v/v) ethyl acetate in petroleum ether as eluent to give the compound 9 (24 mg, 78% yield). 1H NMR (400 MHz, CDCl3) δ 7.65 (d, J = 8.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.26 – 7.19 (m, 2H), 7.14 (d, J = 6.5 Hz, 2H), 6.85 (dd, J = 18.9, 7.6 Hz, 3H), 5.96 (s, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.83 (s, 3H), 2.38 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 170.36, 145.36, 141.04, 133.92, 133.18, 133.07, 129.48, 129.10, 127.38, 127.20, 126.64, 123.59, 122.50, 120.00, 116.36, 61.30, 24.83, 19.74, 14.40. HR-MS (ESI) calcd for [M + 1]+: C21H22NO2, 320.1653, found: 320.1645; IR (KBr): 3450.13, 2927.25, 1704.10, 1601.48, 1499.89, 1382.08 cm⁻¹.

3. Single crystal data about 3k

Table S6. Crystal data and structure refinement for 3k

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Table S7. Atomic coordinates and equivalent isotropic displacement parameters for shelxl. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table S9. Anisotropic displacement parameters for shelxl.
Table S10. Hydrogen coordinates and isotropic displacement parameters for shelxl.

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4. References
5. $^1$H NMR and $^{13}$C NMR spectrum for all isolated products.

1) monodeuterated ketoimine ($d$-1a-a) (Using CDCl$_3$ as solvent)
2) Pentadeuterate ketoimine (d-1a-b)  (Using CDCl₃ as solvent)
3) Diethyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3a) (Using CDCl₃ as solvent)
4) Diethyl 5-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3b) (Using CDCl$_3$ as solvent)
5) Diethyl 2,5,8-trimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3c) (Using CDCl₃ as solvent)
6) Diethyl 5-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3d)
(Using CDCl₃ as solvent)
7) Diethyl 5-bromo-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3e) (Using CDCl₃ as solvent)
8) Diethyl 5-fluoro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3f) (Using CDCl$_3$ as solvent)
9) Diethyl 6-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3g) and diethyl 4-methoxy-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3h) (Using CDCl₃ as solvent)
10) Diethyl 6-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3i) (Using CDCl₃ as solvent)
11) Diethyl 2,8-dimethyl-5-nitro-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3j) (Using CDCl₃ as solvent)
12) 3,7-Diethyl 5-methyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,5,7-tricarboxylate (3k) (Using CDCl$_3$ as solvent)
13) Diethyl 5-cyano-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3l) (Using CDCl₃ as solvent)
14) Diethyl 1-(4-methoxyphenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3m) (Using CDCl₃ as solvent)
15) Diethyl 2,8-dimethyl-1-(p-tolyl)-1H-benzo[de]quinoline-3,7-dicarboxylate (3n) (Using CDCl₃ as solvent)
16) Diethyl 1-(3,5-dimethylphenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3o) (Using CDCl₃ as solvent)
17) Diethyl 1-(4-fluorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3p) (Using CDCl$_3$ as solvent)
18) Diethyl 1-(3-fluorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3q) (Using CDCl₃ as solvent)
19) Diethyl 1-(4-chlorophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3r) (Using CDCl₃ as solvent)
20) Diethyl 1-(4-bromophenyl)-2,8-dimethyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3s) (Using CDCl₃ as solvent)
21) Diethyl 1-(4-acetamidophenyl)-2,8-dimethyl-1\textit{H}-benzo[de]quinoline-3,7-dicarboxylate (3u)
(Using CDCl\textsubscript{3} as solvent)
22) Diethyl 2,8-diethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3w) (Using CDCl₃ as solvent)
23) Diethyl 2,8-dicyclohexyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate
(3x) (Using CDCl₃ as solvent)
24) Dimethyl 2,8-bis(methoxymethyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3y) 
(Using CDCl3 as solvent)
25) Diethyl 8-allyl-2-(but-3-en-1-yl)-1-phenyl-1H-benzo(de)quinoline-3,7-dicarboxylate (3z) (Using CDCl$_3$ as solvent)
26) Diethyl 2,8-diphenyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z-1) (Using CDCl₃ as solvent)
27) Diethyl 2,8-bis(3-chloropropyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z-2) 
(Using CDCl₃ as solvent)
28) Diethyl 2-ethyl-8-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3aa)
diethyl 8-ethyl-2-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3ab) (Using CDCl₃ as solvent)
29) 7-Ethyl 3-methyl 2-(methoxymethyl)-8-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3ac) and 3-ethyl 7-methyl 8-(methoxymethyl)-2-methyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3ad) (Using CDCl₃ as solvent)
30) Tetraethyl 5,5'-(9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate) (5) (Using CDCl₃ as solvent)
31) Tetraethyl 5,5'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl) bis(2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate) (7) (Using CDCl₃ as solvent)
32) Ethyl 2-methyl-1-phenyl-1H-benzo[de]quinoline-3-carboxylate (8) (Using CDCl₃ as solvent)
33) Ethyl 2,5-dimethyl-4-(phenylamino)-1-naphthoate (9) (Using CDCl₃ as solvent)