

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

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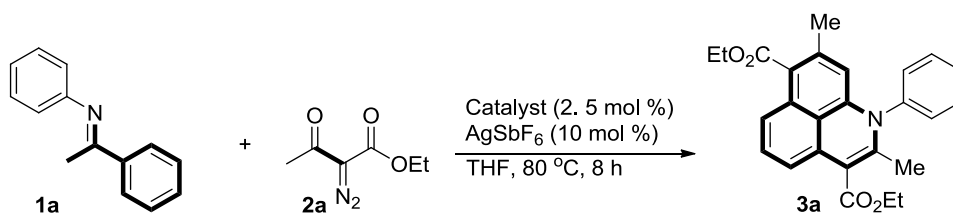
# 1. General experimental information

## 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 Bruker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers ( $\text{cm}^{-1}$ ). Infrared spectra were recorded by preparing a KBr pellet containing the title compound.  $^1\text{H}$  NMR and  $^{13}\text{C}$  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  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  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 -  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 (2) K and operating in the  $\phi$ - $\omega$ scan 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  $100 \text{ mV s}^{-1}$  against a  $\text{Ag}/\text{Ag}^+$  (0.1 M of  $\text{AgNO}_3$  in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile solution of  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate. UV-vis absorption spectra were recorded on a HP8453 spectrophotometer. Pholuminescence (PL) spectra were measured by using a Jobin-Yvon spectrofluorometer.

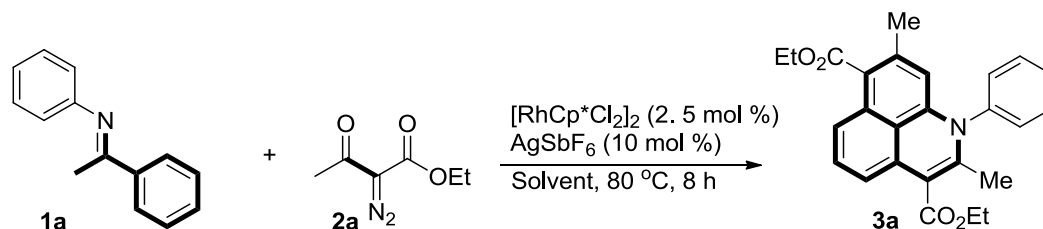
**1.1. Table S1. Catalyst screening for Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds<sup>a</sup>**



entry	catalyst	yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	0
2	CuI	0
3	Cu(OAc) <sub>2</sub>	0
4	[{RuCl <sub>2</sub> (p-cymene)} <sub>2</sub> ]	0
5	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	7
6	RhCl <sub>3</sub>	0
7	Rh <sub>2</sub> (COD) <sub>2</sub> Cl <sub>2</sub>	0
8	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	58

<sup>a</sup>All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.3 mmol), catalyst (2.5 mol %), AgSbF<sub>6</sub> (10 mol %) in THF (2.0 mL) at 80 °C for 24 h in a sealed reaction tube, followed by flash chromatography on SiO<sub>2</sub>. <sup>b</sup> Isolated yield.

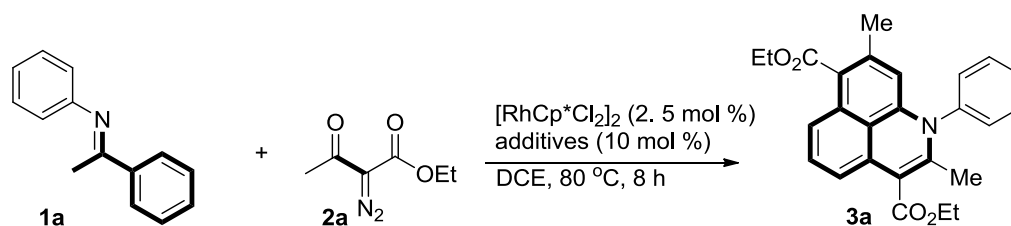
**1.2. Table S2. The effect of the solvent on the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds<sup>a</sup>**



entry	solvent	yield (%) <sup>b</sup>
1	THF	58
2	DMF	trace
3	DCE	85
4	Toluene	62
5	Dioxane	0
6	CH <sub>3</sub> CN	31
7	DMSO	26

<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>]<sub>2</sub> (1.6 mg, 2.5 mol %), AgSbF<sub>6</sub> (10 mol %) in solvent (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.

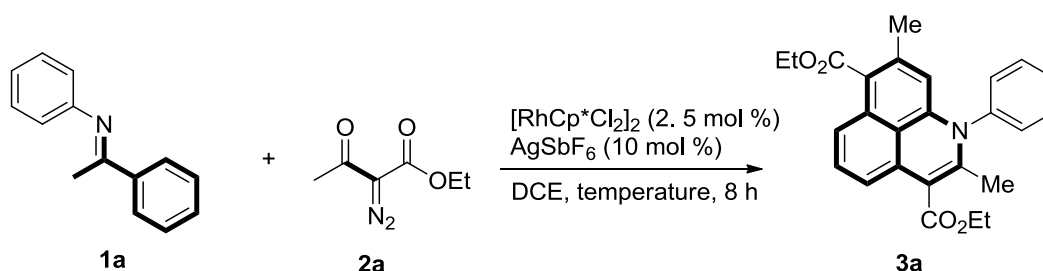
**1.3. Table S3. The effect of additives on the the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds <sup>a</sup>**



entry	additive	yield (%) <sup>b</sup>
1	AgClO <sub>4</sub>	38
2	AgBF <sub>4</sub>	64
3	AgNTf <sub>2</sub>	81
4	AgOAc	69
5	AgSbF <sub>6</sub>	85

<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>]<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.

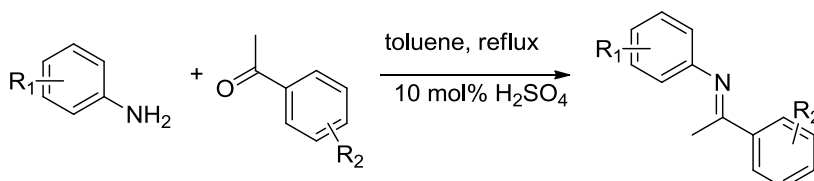
**1.4. Table S4. The effect of the reaction temperature on the the Rh(III)-catalyzed relay carbenoid functionalization of aromatic C-H bonds <sup>a</sup>**



Entry	Temp. (°C)	Yield (%) <sup>b</sup>
1	60	71
2	80	85
3	100	82

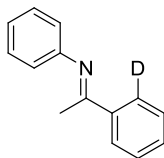
<sup>a</sup>All the reactions were carried out using ketoimine **1a** (0.1 mmol), diazo compound **2a** (0.3 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2.5 mol %), AgSbF<sub>6</sub> (10 mol %) in DCE (2.0 mL) at the given temperature for 8 h in a sealed reaction tube, followed by flash chromatography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

**1.5. General procedure for the synthesis of ketoimines**



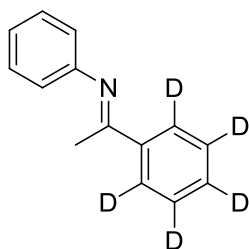
The mixture of acetophenone derivatives (0.2 mmol, 1.0 equiv.) and substituted anilines (0.2 mmol, 1.0 equiv.) was stirred in toluene (3.0 mL) at 120 °C for 24 h in the presence of molecular

sieve (4Å) (0.40 g) and a catalytic amount of concentrated H<sub>2</sub>SO<sub>4</sub> (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. <sup>1</sup>H and <sup>13</sup>C NMR spectral data for the rest of the imines showed good agreement with literature data.<sup>[1]</sup>



***d-1a-a***

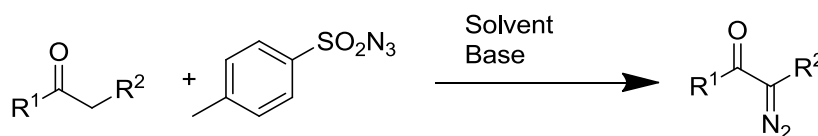
The compound (***d-1a-a***) was prepared according to the above-mentioned procedure. The product was obtained as yellow oil in 75 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 6.5 Hz, 1H), 7.44 (s, 3H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 2H), 2.22 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 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.



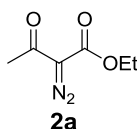
***d-1a-b***

The compound (***d-1a-b***) was prepared according to the above-mentioned procedure. The product was obtained as yellow oil in 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 2H), 2.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.45, 151.74, 139.38, 128.96, 123.22, 119.39, 17.36.

**1.6. General procedure for the synthesis of diazocompounds**

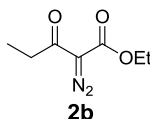


**Method A:** To a solution of β-ketoester or β-diketone (1.0 equiv.) and 4-methylbenzenesulfonyl azide (1.2 equiv.) in CH<sub>3</sub>CN at 0 °C was added triethylamine (1.2 equiv.). The resulting solution was stirred at 0 °C for 3 h and slowly brought to room temperature. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous MgSO<sub>4</sub>. 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.



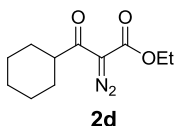
### Ethyl 2-diazo-3-oxobutanoate (**2a**)<sup>[2]</sup>

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



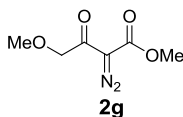
### Ethyl 2-diazo-3-oxopentanoate (**2b**)<sup>[2]</sup>

The title compound (**2b**) was prepared according to Method A. The product was obtained as yellow oil in 88 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.5, 161.4, 61.3, 33.7, 14.3, 8.2. IR (KBr): 2981, 2844, 2138, 1721, 1650, 1458, 1373, 1065 cm<sup>-1</sup>.



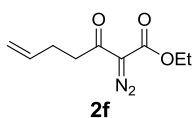
### Ethyl 3-cyclohexyl-2-diazo-3-oxopropanoate (**2d**)<sup>[3]</sup>

The title compound (**2d**) was prepared according to Method A. The product was obtained as yellow oil in 81 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>.



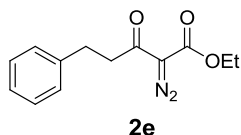
### Methyl 2-diazo-4-methoxy-3-oxobutanoate (**2g**)<sup>[3]</sup>

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



### Ethyl 2-diazo-3-oxohept-6-enoate (**2f**)<sup>[4]</sup>

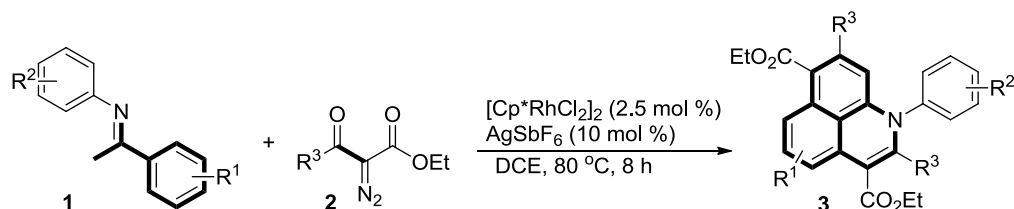
The title compound (**2f**) was prepared according to Method A. The product was obtained as yellow oil in 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.92 - 5.77 (m, 1H), 5.03 (dd, *J* = 29.0, 13.6 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.43 - 2.34 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>.



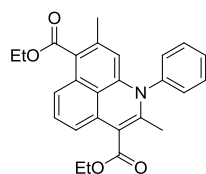
### Ethyl 2-diazo-3-oxo-5-phenylpentanoate (**2e**)<sup>[3]</sup>

The title compound (**2e**) was prepared according to Method A. The product was obtained as yellow oil in 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>.

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

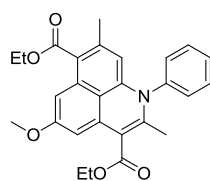


A 10 mL of reaction tube was charged with [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (1.6 mg, 2.5 mol %), AgSbF<sub>6</sub> (3.4 mg, 10 %), ketimine **1** (0.1 mmol) and DCE (1.5 mL) under atmosphere. Then diazo compound **2** (0.3 mmol) in DCE (0.5 mL) was added in one-pot under air and the mixture was stirred at 80 °C for 8 h. The corresponding reaction mixture was cooled to room temperature and filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using 30% (v/v) ethyl acetate in petroleum ether as eluent to afford the desired product **3**.



**3a**

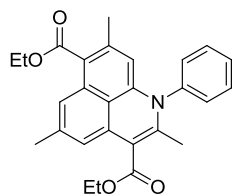
**Diethyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3a):** Yellow oil; 35.0 mg, 85 % yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 5.9 Hz, 3H), 6.77 (d, *J* = 7.3 Hz, 1H), 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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) calcd for [M + 1]<sup>+</sup>: C<sub>26</sub>H<sub>26</sub>NO<sub>4</sub> 416.1857, found: 416.1869; IR (KBr): 3480.74, 2981.85, 1702.63, 1342.22 cm<sup>-1</sup>.



**3b**

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

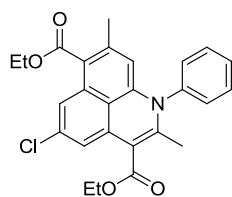
Yellow solid; 41.0 mg, 91 % yield; m.p. 168.9-169.8 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 6.81 (s, 0H), 6.47 (s, 1H), 5.26 (s, 1H), 4.39 (dq, *J* = 14.2, 7.1 Hz, 4H), 3.82 (s, 3H), 2.13 (s, 3H), 1.78 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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]<sup>+</sup>: C<sub>27</sub>H<sub>28</sub>NO<sub>5</sub> 446.1962, found: 446.1978; IR (KBr): 3485.74, 2981.85, 1712.63, 1347.22 cm<sup>-1</sup>



**3b**

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

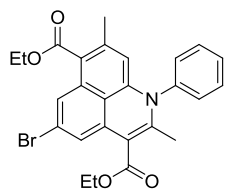
Yellow solid; 38.1 mg, 89 % yield; m.p. 161.5-162.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (t, *J* = 7.5 Hz, 2H), 7.48 (dd, *J* = 18.0, 10.6 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.09 (s, 1H), 6.61 (s, 1H), 5.27 (s, 1H), 4.40 (dd, *J* = 14.2, 7.1 Hz, 4H), 2.33 (s, 3H), 2.11 (s, 3H), 1.76 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.80, 168.55, 143.77, 140.58, 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]<sup>+</sup>: C<sub>27</sub>H<sub>28</sub>NO<sub>4</sub> 430.2013, found: 430.2025; IR (KBr): 3659.72, 1712.56, 1582.33, 1286.02, 1120.09 cm<sup>-1</sup>



**3c**

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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* = 7.5 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.04, 167.86, 143.55, 142.34, 139.56, 137.53, 135.57, 134.18, 132.77, 131.26, 129.40, 122.84, 119.15, 117.13, 112.52, 110.08, 107.83, 61.20, 60.87, 21.08, 19.39, 14.33, 14.24. HR-MS (ESI) calcd for [M + 1]<sup>+</sup>: C<sub>26</sub>H<sub>25</sub>ClNO<sub>4</sub> 450.1467, found: 450.1478; IR (KBr): 2986.66, 1697.91, 1576.65, 1280.99, 1130.80, 740.72 cm<sup>-1</sup>



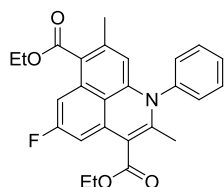
**3d**

**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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (t, *J* =



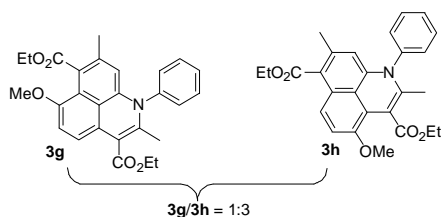
7.5 Hz, 2H), 7.53 (t,  $J = 7.2$  Hz, 1H), 7.47 (s, 1H), 7.22 (d,  $J = 7.6$  Hz, 2H), 6.90 (s, 1H), 5.38 (s, 1H), 4.41 (dd,  $J = 14.0, 6.9$  Hz, 4H), 2.13 (s, 3H), 1.80 (s, 3H), 1.40 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.01, 167.84, 143.61, 142.31, 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  $[\text{M} + 1]^+$ :  $\text{C}_{26}\text{H}_{24}\text{BrNO}_4$  494.0961, found: 494.0966; IR (KBr): 2976.06, 1897.91, 1476.65, 1280.99, 1130.80, 1040.72  $\text{cm}^{-1}$



**3f**

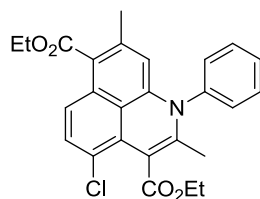
**Diethyl 5-fluoro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3f):**

Yellow solid; 29.4 mg, 68 % yield; m.p. 118.2-119.0  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.14, 167.91, 163.42 (d,  $J = 243.5$  Hz,  $J_{\text{CF}}$ ), 143.63, 142.55, 139.61, 137.83, 135.05 (d,  $J = 11.4$  Hz,  $J_{\text{CF}}$ ), 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,  $J_{\text{CF}}$ ), 101.63, 101.35, 61.17, 60.78, 21.17, 19.42, 14.33, 14.24. HR-MS (ESI) calcd for  $[\text{M} + 1]^+$ :  $\text{C}_{26}\text{H}_{25}\text{FNO}_4$  434.1762, found: 434.1775; IR (KBr): 2986.52, 1709.73, 1580.22, 1282.47, 1128.67, 711.71  $\text{cm}^{-1}$



**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  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{27}\text{H}_{28}\text{NO}_5$  446.1962, found: 446.1974; IR (KBr): 3853.86, 2986.76, 1714.77, 1266.76, 752.65  $\text{cm}^{-1}$

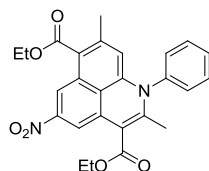


**3i**

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

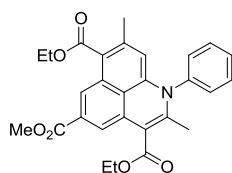
Yellow solid; 20.2 mg, 45 % yield; m.p. 187.6-188.9  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J =$

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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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, 60.87, 20.77, 18.60, 14.32, 14.01. HR-MS (ESI) calcd for  $[\text{M} + 1]^+$ :  $\text{C}_{26}\text{H}_{25}\text{ClNO}_4$  450.1467, found: 450.1470; IR (KBr): 2984.63, 1715.37, 1272.76, 742.19, 630.32  $\text{cm}^{-1}$



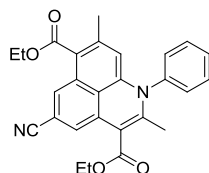
### 3j

**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  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.34, 167.48, 148.34, 143.55, 143.39, 139.24, 138.67, 133.31, 132.71, 131.51, 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  $[\text{M} + 1]^+$ :  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_6$  461.1707, found: 461.1711; IR (KBr): 2987.84, 1706.35, 1336.70, 1282.67, 1113.37  $\text{cm}^{-1}$



### 3k

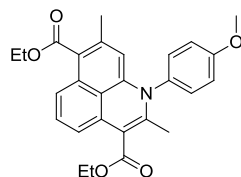
**3,7-Diethyl 5-methyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,5,7-tricarboxylate (3k):** Yellow solid; 34.0 mg, 72 % yield; m.p. 190.5-190.9  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.62 (t,  $J = 7.5$  Hz, 2H), 7.53 (t,  $J = 7.4$  Hz, 1H), 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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.04, 168.10, 167.35, 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  $[\text{M} + 1]^+$ :  $\text{C}_{28}\text{H}_{27}\text{NO}_6$  474.1911, found: 474.1919; IR (KBr): 3748.24, 1711.83, 1263.29, 1109.79, 741.11  $\text{cm}^{-1}$



### 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  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.54, 167.54,

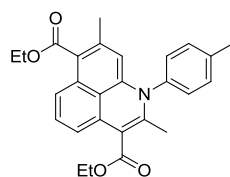
143.30, 143.06, 139.27, 138.06, 132.58, 132.44, 131.48, 129.64, 129.18, 125.52, 123.58, 120.26, 119.56, 112.69, 112.61, 110.12, 110.04, 61.40, 61.19, 21.11, 19.45, 14.32, 14.24. HR-MS (ESI) calcd for  $[M + 1]^+$ :  $C_{27}H_{25}N_2O_4$  441.1809, found: 441.1812; IR (KBr): 3456.26, 2984.46, 1705.05, 1285.80, 1115.96, 711.19  $cm^{-1}$



**3m**

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

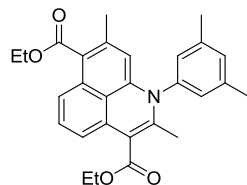
Yellow solid; 36.5 mg, 82 % yield; m.p. 177.2-178.0 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.20 (t,  $J = 7.6$  Hz, 1H), 7.14 (t,  $J = 7.9$  Hz, 1H), 7.02 (q,  $J = 8.6$  Hz, 4H), 6.68 (d,  $J = 7.2$  Hz, 1H), 5.32 (s, 1H), 4.36 – 4.26 (m, 4H), 3.80 (s, 3H), 2.07 (s, 3H), 1.70 (s, 3H), 1.30 (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  $[M + 1]^+$ :  $C_{27}H_{28}NO_5$  446.1962, found: 446.1966; IR (KBr): 3748.74, 2983.05, 1711.60, 1509.19, 1253.01, 1096.72  $cm^{-1}$



**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;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.38 (d,  $J = 7.1$  Hz, 2H), 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, 21.29, 20.86, 19.20, 14.35, 14.27. HR-MS (ESI) calcd for  $[M + 1]^+$ :  $C_{27}H_{28}NO_4$  430.2013, found: 430.2010; IR (KBr): 3748.34, 1709.75, 1643.00, 1283.10, 1096.74, 731.75  $cm^{-1}$

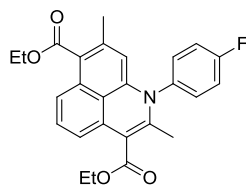


**3o**

**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;  $^1H$  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, 6H), 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,

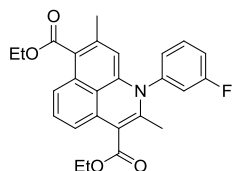
14.36, 14.28. HR-MS (ESI) calcd for  $[M + 1]^+$ :  $C_{28}H_{30}NO_4$  444.2169, found: 444.2173; IR (KBr): 3494.23, 2983.11, 1710.84, 1637.65, 1253.89, 1098.07  $cm^{-1}$



**3p**

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

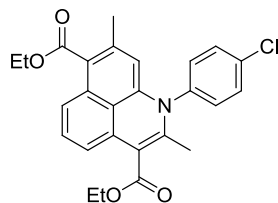
Yellow solid; 31.1 mg, 72 % yield; m.p. 134.2-134.8 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.32 – 7.19 (m, 6H), 6.77 (d,  $J = 7.2$  Hz, 1H), 5.33 (s, 1H), 4.39 (dt,  $J = 14.7, 7.2$  Hz, 4H), 2.15 (s, 3H), 1.76 (s, 3H), 1.38 (t,  $J = 7.1$  Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.55, 168.33, 162.47 (d,  $J = 250.0$  Hz,  $J_{CF}$ ), 143.87, 140.46, 136.06, 135.83, 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, 1708.67, 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;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.59 (dd,  $J = 14.6, 7.8$  Hz, 1H), 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 (t,  $J = 7.0$  Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.54, 168.29, 164.18 (d,  $J = 250.7$  Hz,  $J_{CF}$ ), 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  $cm^{-1}$

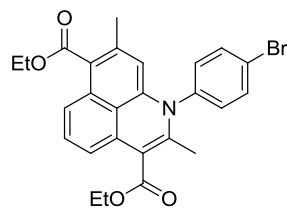


**3r**

**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;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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 (t,  $J = 6.8$  Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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)

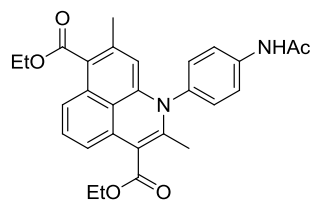
calcd for  $[M + 1]^+$ :  $C_{26}H_{25}ClNO_4$  450.1467, found: 450.1459; IR (KBr): 3494.32, 1708.81, 1642.81, 1282.45, 1095.30, 715.97  $cm^{-1}$



**3s**

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

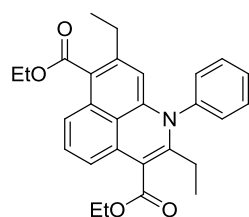
Yellow solid; 39.0 mg, 79 % yield; m.p. 139.2-140.2 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.74 (d,  $J$  = 7.8 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.13 (d,  $J$  = 7.9 Hz, 2H), 6.75 (s, 1H), 5.34 (s, 1H), 4.38 (dd,  $J$  = 15.9, 7.8 Hz, 4H), 2.15 (s, 3H), 1.76 (s, 3H), 1.39 (t,  $J$  = 6.9 Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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, 61.10, 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):**

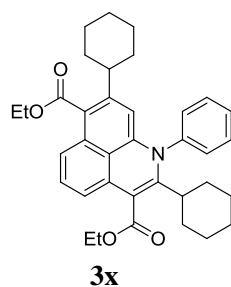
yellow oil; 38 mg, 80% yield;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.01 (s, 1H), 7.61 (d,  $J$  = 8.3 Hz, 2H), 7.24 – 7.11 (m, 2H), 7.01 (d,  $J$  = 8.3 Hz, 2H), 6.69 (d,  $J$  = 7.0 Hz, 1H), 5.28 (s, 1H), 4.32 (dq,  $J$  = 14.4, 7.1 Hz, 4H), 2.14 (s, 3H), 2.02 (s, 3H), 1.68 (s, 3H), 1.32 (td,  $J$  = 7.0, 2.8 Hz, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  170.14, 168.91, 168.59, 144.01, 140.98, 138.90, 136.10, 135.00, 133.18, 130.89, 130.04, 129.03, 124.44, 121.87, 119.74, 118.17, 112.23, 110.89, 107.19, 61.14, 60.93, 24.53, 20.79, 19.23, 14.33, 14.25. HR-MS (ESI) calcd for  $[M + 1]^+$ :  $C_{28}H_{29}N_2O_5$  473.2071, found: 473.2074; IR (KBr): 3456.26, 2984.46, 1695.05, 1280.79, 1115.96, 748.19  $cm^{-1}$ .



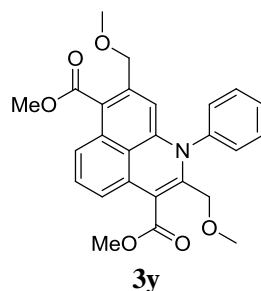
**3w**

**Diethyl 2,8-diethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3w):** Yellow oil; 31.9 mg, 72 % yield;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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

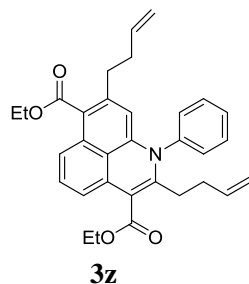
(ESI) calcd for  $[M + 1]^+$ :  $C_{28}H_{30}NO_4$  444.2169, found: 444.2176; IR (KBr): 1485.74, 2981.85, 1712.63, 1581.65, 1282.60, 1095.88, 743.10  $cm^{-1}$



**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,  $CDCl_3$ )  $\delta$  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);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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  $cm^{-1}$

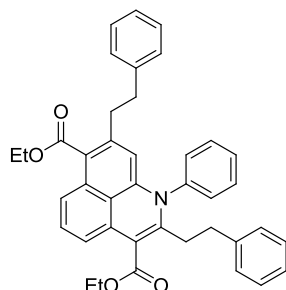


**Dimethyl 2,8-bis(methoxymethyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3y):** Yellow oil; 28.0 mg, 63 % yield;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.59 (t,  $J = 7.6$  Hz, 2H), 7.52 (t,  $J = 7.3$  Hz, 1H), 7.43 (d,  $J = 8.6$  Hz, 1H), 7.30 (d,  $J = 7.4$  Hz, 2H), 7.25 (d,  $J = 9.3$  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);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.36, 168.15, 144.60, 139.64, 138.73, 137.49, 133.41, 130.78, 130.42, 130.04, 129.32, 128.99, 125.98, 119.67, 118.48, 113.55, 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  $cm^{-1}$



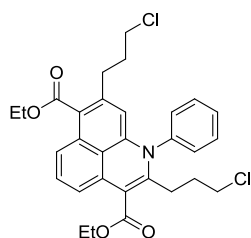
**Diethyl 8-allyl-2-(but-3-en-1-yl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z):** Yellow oil; 35.6 mg, 72 % yield;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.62 (t,  $J = 7.1$  Hz, 2H), 7.54 (d,  $J = 7.0$  Hz, 1H), 7.30 – 7.19 (m, 4H), 6.73 (d,  $J = 6.7$  Hz, 1H), 5.67 (dt,  $J = 16.0, 7.8$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{32}\text{H}_{34}\text{NO}_4$  496.2482, found: 496.2485; IR (KBr): 3749.08, 2983.61, 1712.45, 1286.21, 1099.10, 747.69, 710.40  $\text{cm}^{-1}$



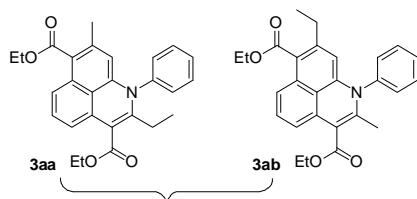
### 3z-1

**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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{40}\text{H}_{38}\text{NO}_4$  596.2795, found: 596.2774; IR (KBr): 3742.91, 2985.64, 1701.68, 1279.41, 742.49  $\text{cm}^{-1}$



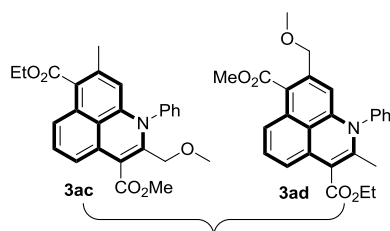
### 3z-2

**Diethyl 2,8-bis(3-chloropropyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3z-2):** Yellow oil; 35.7 mg, 70 % yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{30}\text{H}_{32}\text{ClNO}_4$  541.1736, found: 541.1709; IR (KBr): 3759.08, 2983.01, 1712.45, 1280.21, 1099.10, 747.69, 710.40  $\text{cm}^{-1}$



**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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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 (dtd,  $J = 7.1, 3.6, 2.1$  Hz, 6H), 0.99 (ddd,  $J = 8.5, 7.6, 4.4$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{27}\text{H}_{28}\text{NO}_4$  430.2013, found: 430.2018; IR (KBr): 3742.91, 2985.64, 1701.68, 1513.34, 1279.41, 742.49  $\text{cm}^{-1}$

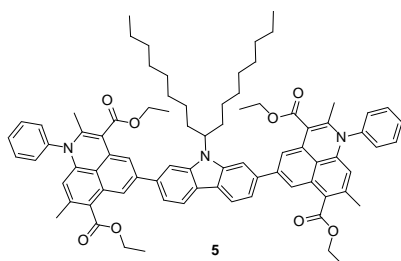
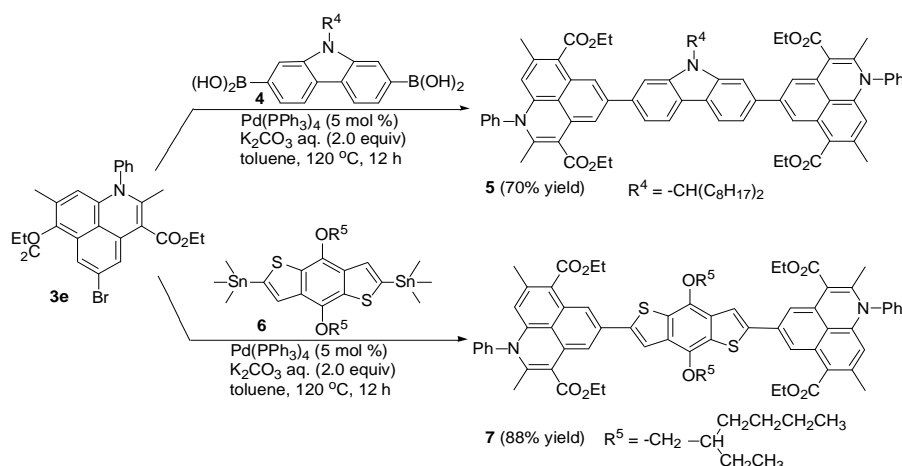


**3ac + 3ad = 34% (3ac/3ad = 3.5:1)**

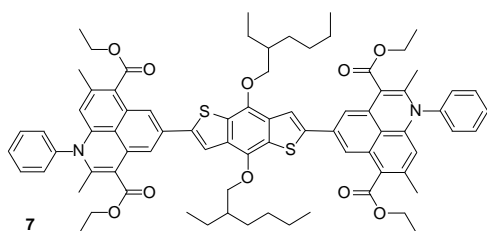
**7-Ethyl 3-methyl 2-(methoxymethyl)- 8-methyl- 1-phenyl-1H -benzo[de] quinoline-3,7 -dicarboxylate (3ac) and 3-ethyl 7-methyl 8-(methoxymethyl)- 2-methyl-1-phenyl-1H-benzo[de]quinoline-3,7- dicarboxylate (3ad):** Yellow oil; 15.3 mg, 34 % yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{26}\text{H}_{26}\text{NO}_5$  432.1822, found: 432.1805; IR (KBr): 3616.23, 2988.46, 1644.21, 1274.37, 739.76  $\text{cm}^{-1}$



## 1.8 Procedure for synthesis of $\pi$ -conjugated organic molecules 5 and 7

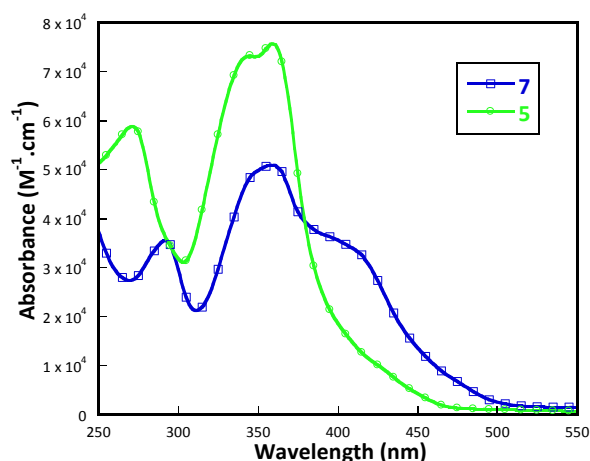


**Preparation of carbazole-based 1-azaphenylene (5):** The reaction was conducted in the presence of  $\text{Pd(PPh}_3)_4$  (10 mol%),  $\text{K}_2\text{CO}_3$  (69 mg, 0.5 mmol), diethyl 5-bromo-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (62 mg, 0.125 mmol), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (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,  $\text{CDCl}_3$ )  $\delta$  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,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 2\text{H}]^{2+}$ :  $\text{C}_{81}\text{H}_{91}\text{N}_3\text{O}_8$  616.8399, found: 616.8398; IR (KBr): 3749.48, 2898.58, 1643.57, 1272.97, 752.53  $\text{cm}^{-1}$

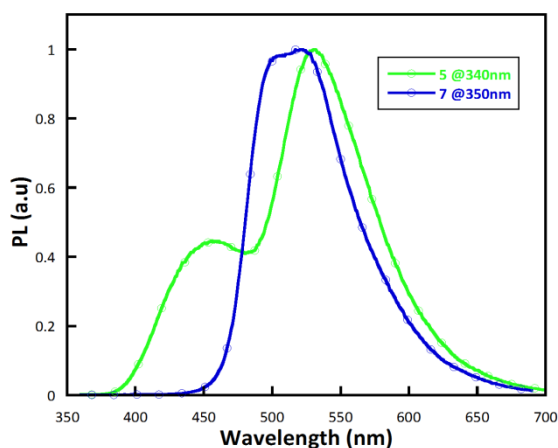


**Preparation of dithiophene-based 1-azaphenalene (7):** Diethyl 5-bromo-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (62 mg, 0.125 mmol) and (4,8-bis((2-ethylhexyl)oxy)benzo [1,2-*b*:4,5-*b'*]dithiophene -2,6-diyl) bis(trimethylstannane) (35 mg, 0.05 mmol) were dissolved in dry toluene (2 mL) and deoxygenated with nitrogen for 15 min. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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]<sup>2+</sup>: C<sub>78</sub>H<sub>86</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub> 637.2844, found: 637.2856; IR (KBr): 3492.48, 2924.58, 1710.29, 1285.20, 709.42 cm<sup>-1</sup>

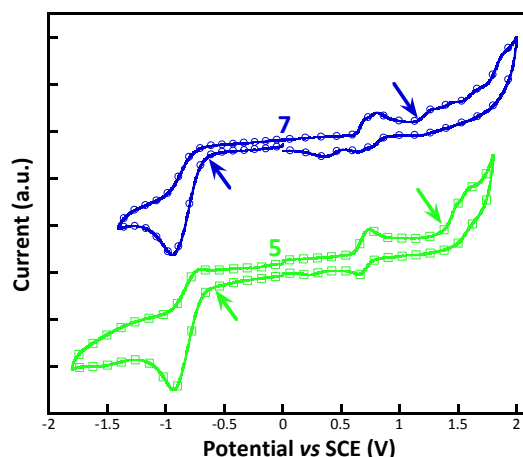
### 1.9 The photophysical and electrochemical properties of the compounds **5** and **7**.



**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<sup>-1</sup>Bu<sub>4</sub>NPF<sub>6</sub> with a scan rate of 100 mV s<sup>-1</sup>.

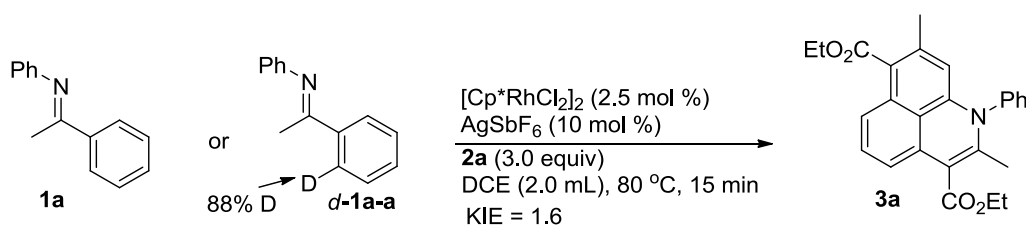
**Table S5.** Energy levels of the compounds **5** and **7**.

Compound	E <sub>onset</sub> <sup>ox</sup> [a]	E <sub>onset</sub> <sup>red</sup> [b]	HOMO (eV) [c]	LUMO (eV) [d]
<b>5</b>	1.36	-0.59	-5.76	-3.81
<b>7</b>	1.17	-0.61	-5.57	-3.79

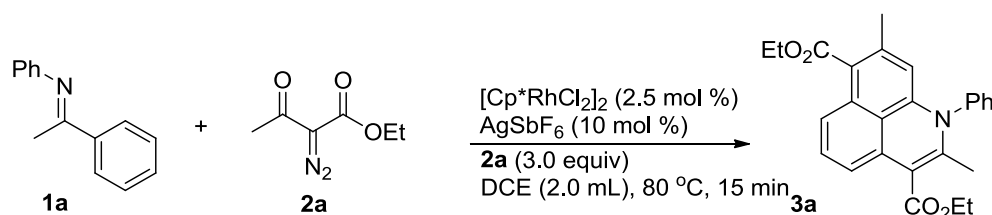
[a] Estimated from the oxidation onset of the CV (in CH<sub>3</sub>CN); [b] Estimated from the reduction onset of the CV (in CH<sub>3</sub>CN) [c] HOMO = -(4.40 + E<sub>onset</sub><sup>ox</sup>); [d] LUMO = -(4.40 + E<sub>onset</sub><sup>red</sup>).

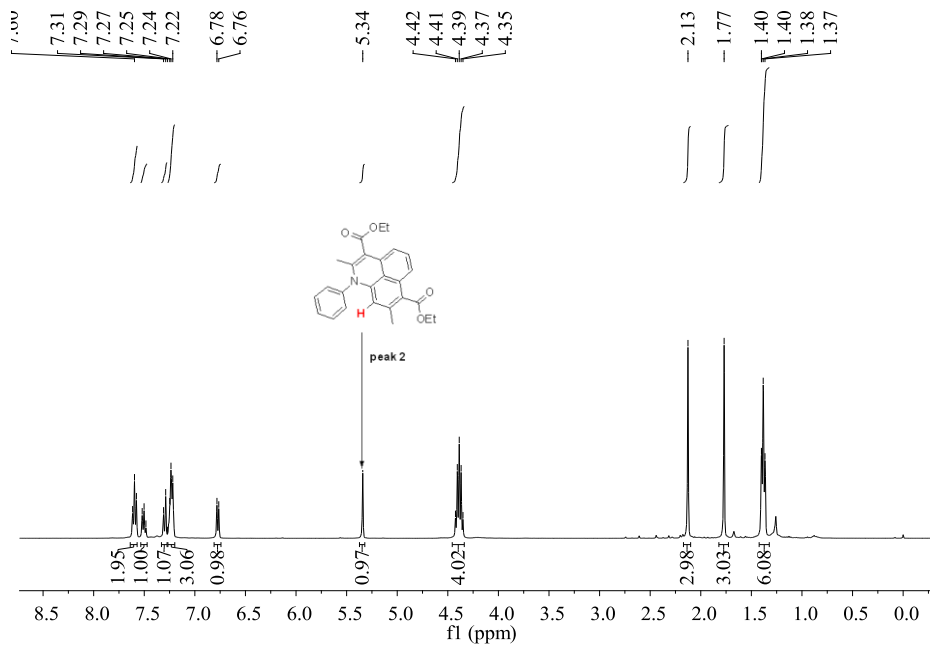
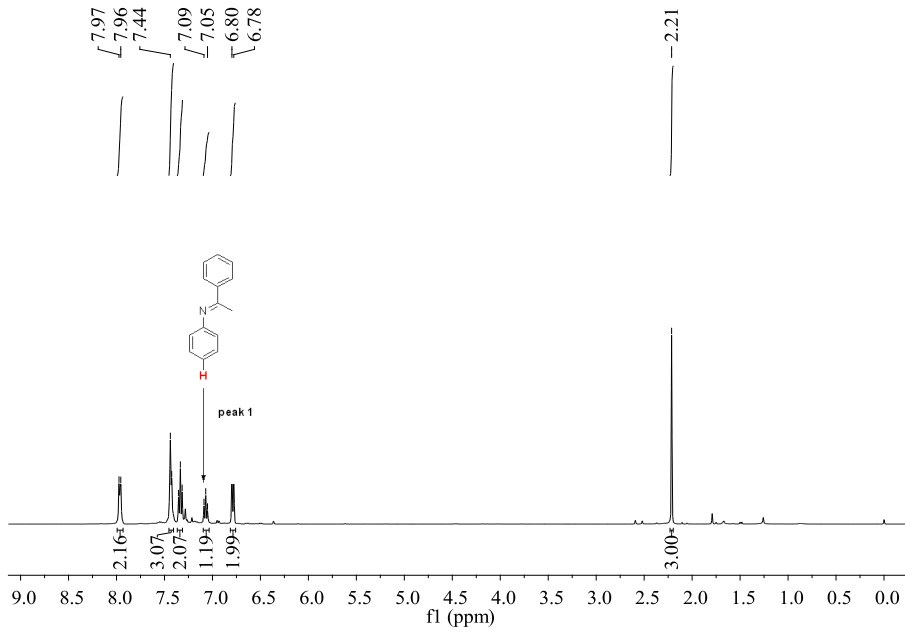
## 2. Preliminary mechanistic studies

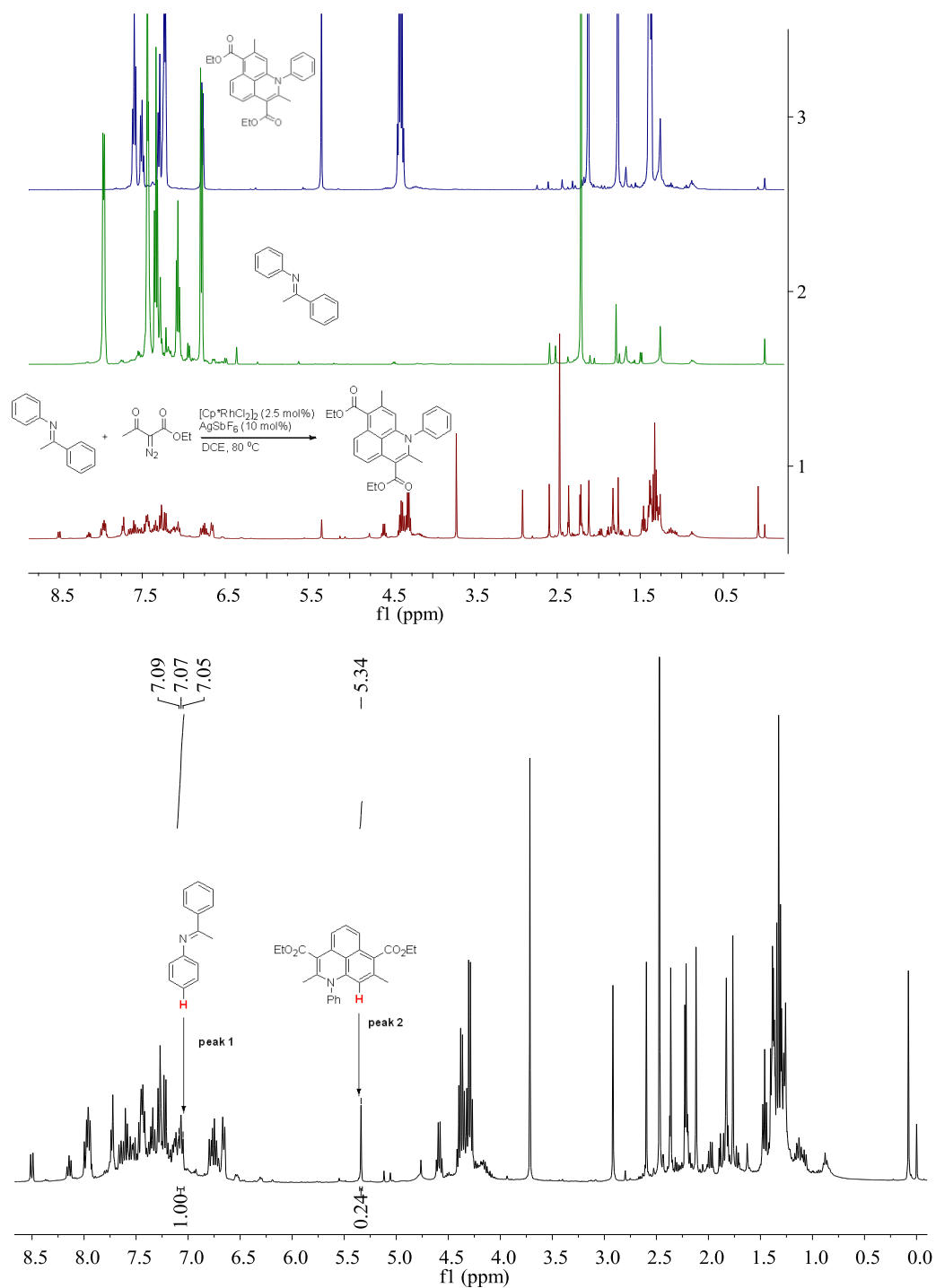
### (1): Kinetic isotope effect of this transformation on monodeuterate ketoimine



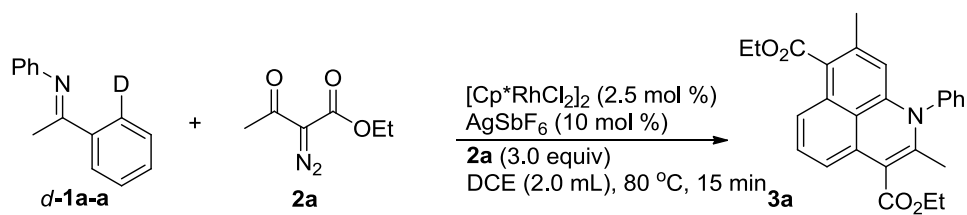
A sample experimental set-up is shown as follows: Ketoimine (**1a**: 20 mg, 0.1 mmol; or **d-1a**: 20 mg, 0.1 mmol) were added to the solution of diazo compound **2a** (0.3 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (2 mg, 2.5 mol %) and AgSbF<sub>6</sub> (5 mg, 10 mol%) in DCE (2.0 mL) under air atmosphere, 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 <sup>1</sup>H NMR spectrum (see **Figure 4** and **Figure 5**).

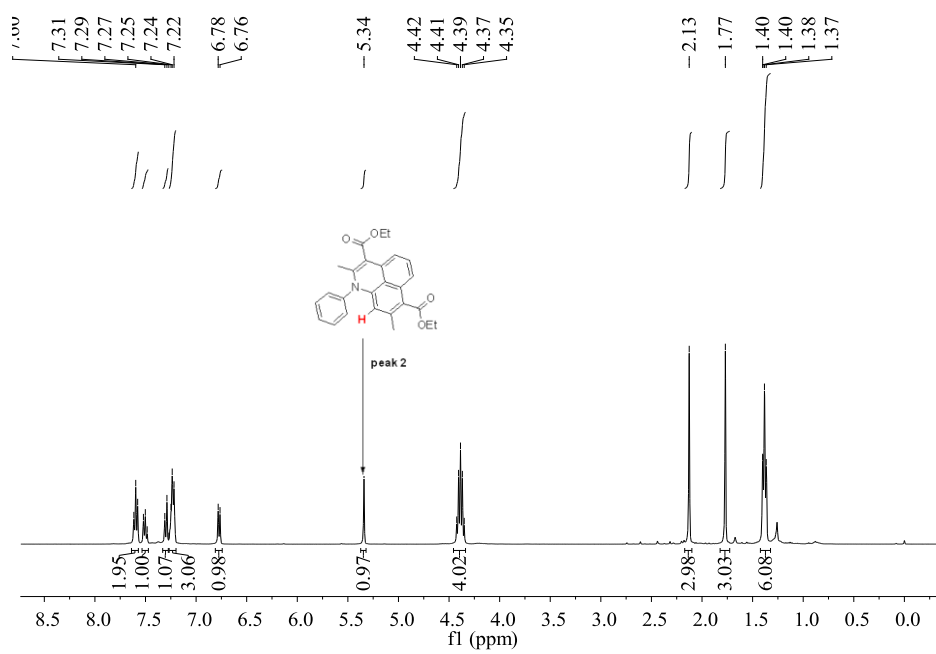
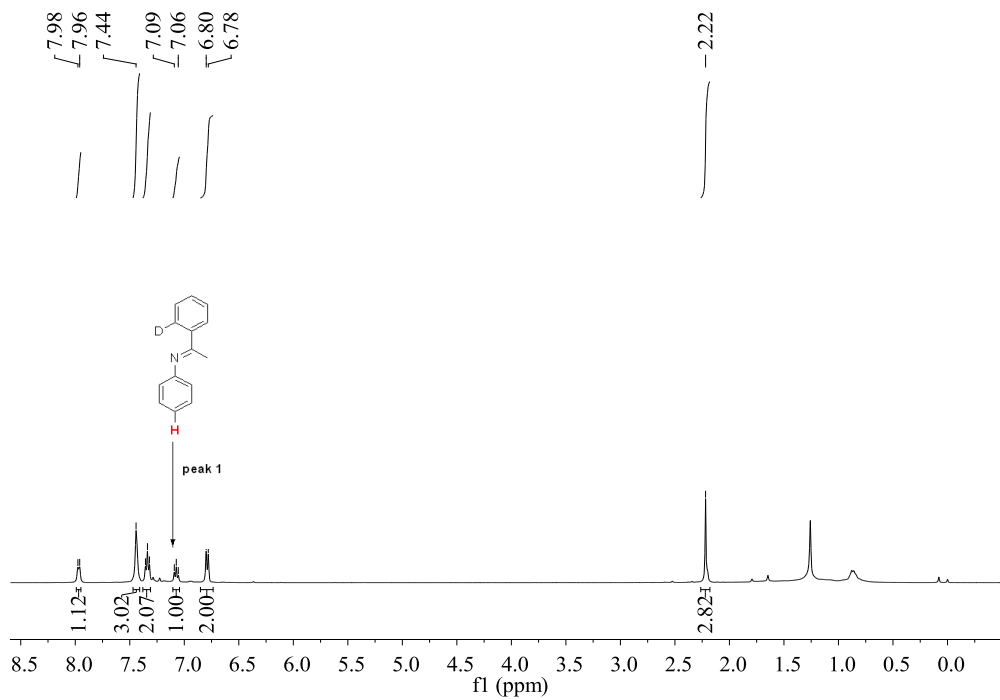


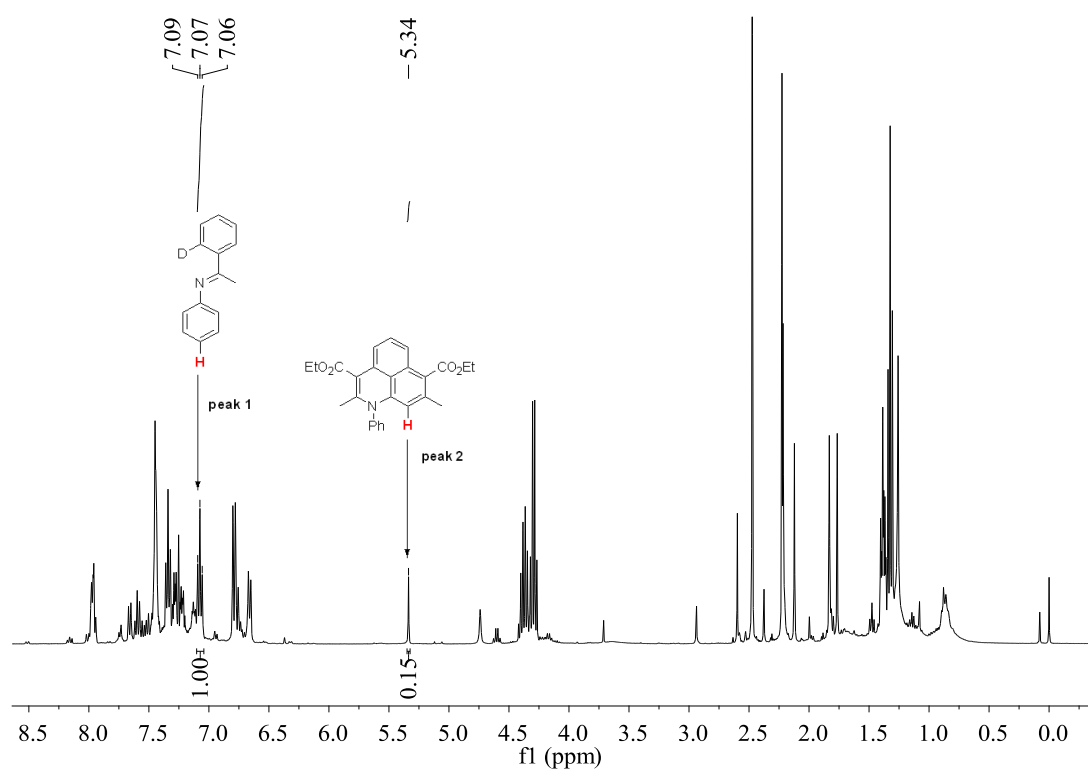
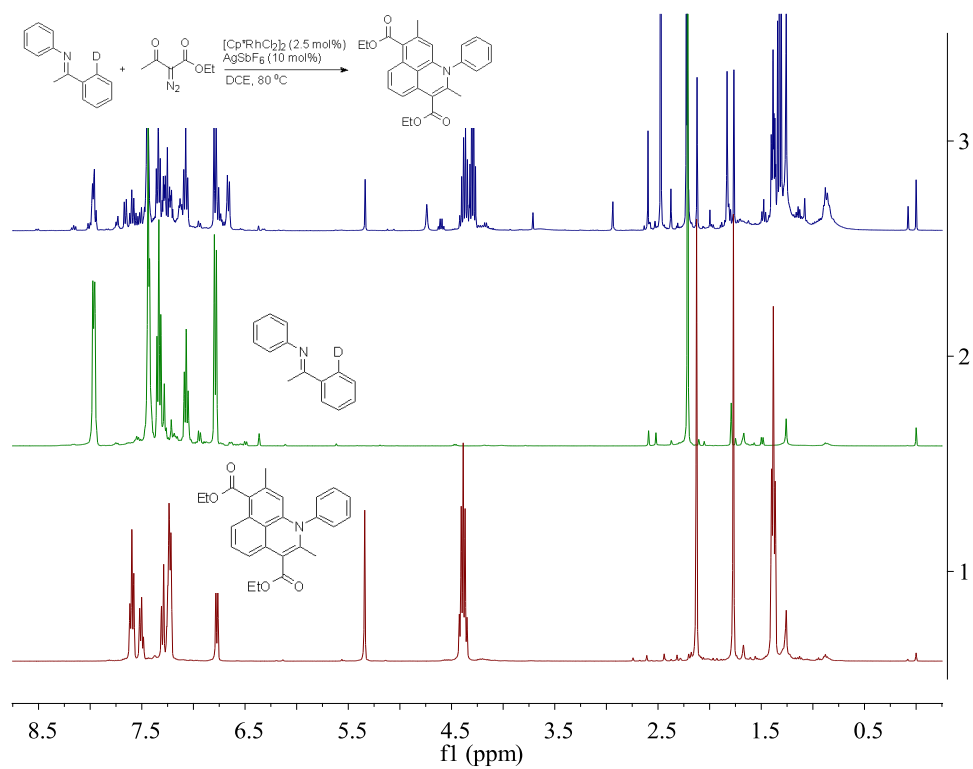




**Figure S4**, The conversion of **1a** was monitored by  $^1\text{H}$  NMR method

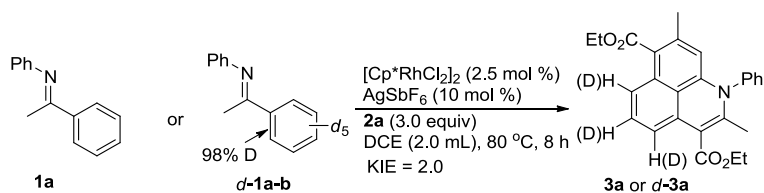




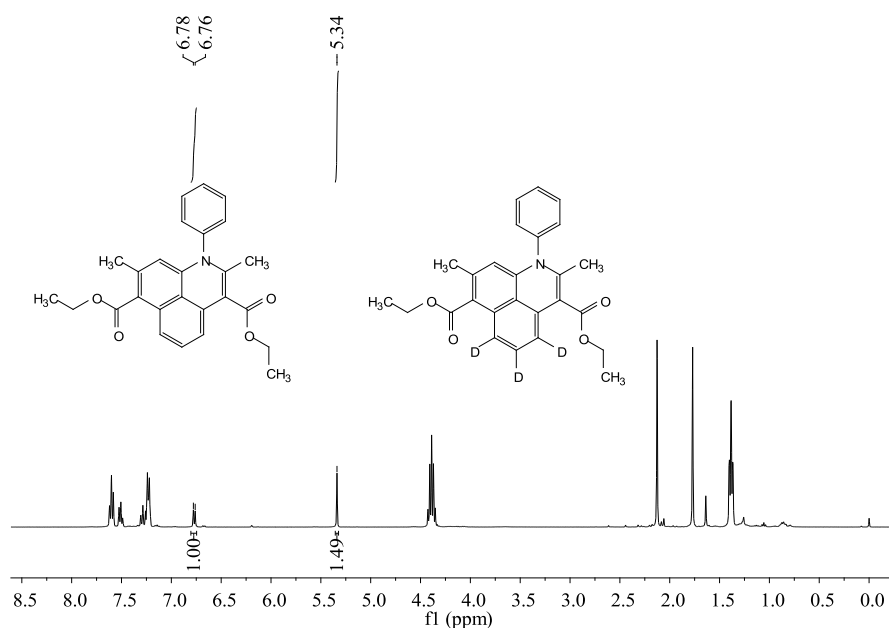


**Figure S5.** The conversion of *d*-1a-a was monitored by  $^1\text{H}$  NMR method

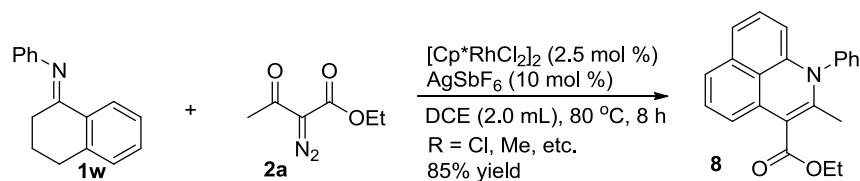
**(2) Kinetic isotope effect of this transformation on pentadeuterate ketimine**



To a 15 mL of Schlenk tube, the catalyst  $[\text{RhCp}^*\text{Cl}_2]_2$  (4 mg, 2.5 mol %),  $\text{AgSbF}_6$  (10 mg, 10 mol %), substrate  $\mathbf{1a}$  (19 mg, 0.1 mmol), substrate  $d\text{-1a-b}$  (20 mg, 0.1 mmol)<sup>[4]</sup> were added in sequence under air atmosphere. After the diazo compound  $\mathbf{2a}$  (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  $\mathbf{3a/d-3a}$  with ration 2.04/1, determined by  $^1\text{H}$  NMR

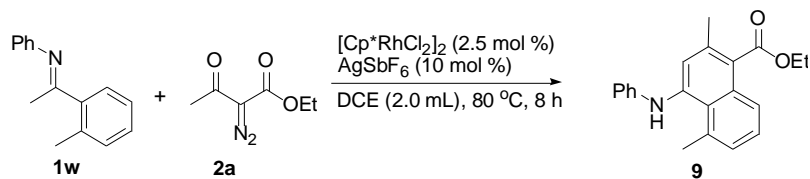


### (3) Control experiments for mechanism studies



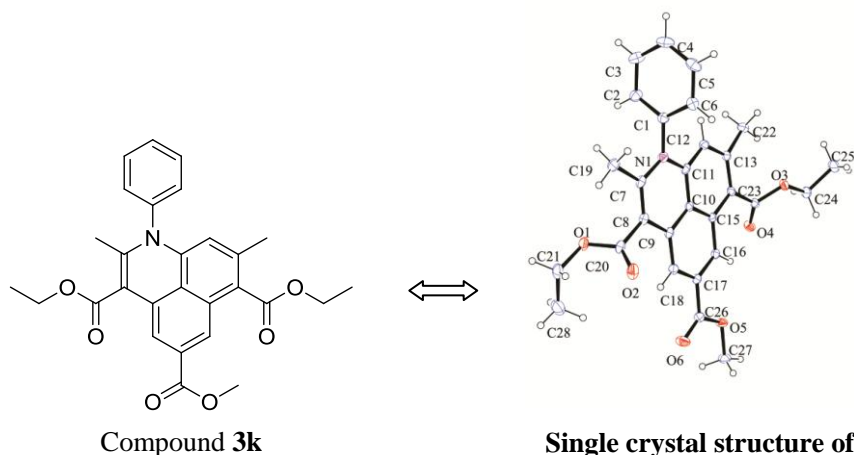
To the solution of *ortho*-substituted aryketoimine  $\mathbf{1r}$  (0.1 mmol) in dry DCE (2.0 mL) were added diazo compound  $\mathbf{2a}$  (0.3 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (4 mg, 2.5 mol %) and  $\text{AgSbF}_6$  (10 mg, 10 mol%). The reaction mixture was stirred at 80 °C for 8 h. After the reaction mixture was cooled down to room temperature, and filtrated, the filtration was concentrated under vacuum and urified by flash chromatography on silica gel using 20% (v/v) ethyl acetate in petroleum ether as eluent to give the compound  $\mathbf{8}$  (28 mg, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $\text{CDCl}_3$ )  $\delta$  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.





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),  $[\text{RhCp}^*\text{Cl}_2]_2$  (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 10% (v/v) ethyl acetate in petroleum ether as eluent to give the compound **9** (24 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $[\text{M} + 1]^+$ :  $\text{C}_{21}\text{H}_{22}\text{NO}_2$  320.1653, found: 320.1645; IR (KBr): 3450.13, 2927.25, 1704.10, 1601.48, 1499.89, 1382.08  $\text{cm}^{-1}$ .

### 3. Single crystal data about 3k



**Figure S6.** The single crystal structure of **3k** (the ellipsoid contour probability level is 30%)

**Table S6.** Crystal data and structure refinement for **3k**

Empirical formula	$\text{C}_{28}\text{H}_{27}\text{NO}_6$
Formula weight	437.51
Crystal system	Monoclinic
Temperature	571 K
Wavelength	1.54178 Å
Space group	P 21/c
a (Å)	12.3361(5)
b (Å)	16.8521(6)

c (Å)	12.0571(5)
$\alpha$ (°)	90
$\beta$ (°)	112.100(5)
$\gamma$ (°)	90
V (Å <sup>3</sup> )	2322.38(15)
Z	4
Dc (g cm <sup>-3</sup> )	1.354
Crystal size (mm)	0.28 x 0.21 x 0.18
F (000)	1000.0
Range / °	4.67 to 62.77
Reflections collected / unique	9906 / 3200 [R(int) = 0.0281]
Data / restraints / parameters	3646 / 0 / 316
Goodness-of-fit on F <sup>2</sup>	1.051
Rindices (all data)	R1 = 0.0513, wR2 = 0.1402

**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.**

	x	y	z	U(eq)
O(1)	0.73640(13)	-0.19366(10)	0.65160(13)	0.0326(4)
O(2)	0.65120(15)	-0.24642(11)	0.46877(15)	0.0410(4)
O(3)	1.09579(13)	0.02452(9)	0.16925(13)	0.0286(4)
O(4)	0.96591(13)	0.10140(9)	0.20627(14)	0.0302(4)
O(5)	0.60641(2)	0.05718(9)	0.13528(13)	0.0292(4)
O(6)	0.51074(13)	-0.01649(11)	0.22328(16)	0.0403(4)
N(1)	1.04455(15)	-0.19929(10)	0.56508(15)	0.0258(4)
C(1)	1.15476(18)	-0.24092(12)	0.6223(2)	0.0264(5)
C(2)	1.2261(2)	-0.22252(14)	0.7378(2)	0.0341(5)
C(3)	1.33102(2)	-0.26308(15)	0.7904(2)	0.0435(6)
C(4)	1.3636(2)	-0.32000(15)	0.7269(3)	0.0443(7)
C(5)	1.2919(2)	-0.33771(14)	0.6110(3)	0.0410(6)
C(6)	1.1860(2)	-0.29854(13)	0.5575(2)	0.0326(5)
C(7)	0.94669(19)	-0.22171(12)	0.58687(18)	0.0257(5)
C(8)	0.84069(18)	-0.18857(12)	0.52315(18)	0.0247(5)
C(9)	0.82746(18)	-0.12862(12)	0.43270(17)	0.0229(4)
C(10)	0.93126(17)	-0.10294(12)	0.41759(17)	0.0211(4)

C(11)	1.04103(18)	-0.13794(12)	0.48605(17)	0.0233(4)
C(12)	1.14173(18)	-0.11091(13)	0.47336(19)	0.0257(5)
C(13)	1.13972(18)	-0.05191(12)	0.39181(18)	0.0233(4)
C(14)	1.03322(17)	-0.01828(12)	0.31995(18)	0.0224(4)
C(15)	0.92704(17)	-0.04228(11)	0.33397(17)	0.0200(4)
C(16)	0.81645(17)	-0.00946(12)	0.26587(18)	0.0218(4)
C(17)	0.71657(17)	-0.03480(12)	0.28144(17)	0.0222(4)
C(18)	0.72137(18)	-0.09422(12)	0.36418(18)	0.0243(5)
C(19)	0.9641(2)	-0.28389(14)	0.6812(2)	0.0323(5)
C(20)	0.7339(2)	-0.21372(12)	0.54319(18)	0.0267(5)
C(21)	0.6337(2)	-0.21541(16)	0.6776(2)	0.0399(6)
C(22)	1.25641(18)	-0.02671(14)	0.3889(2)	0.0307(5)
C(23)	1.02653(17)	0.04263(12)	0.22928(18)	0.0228(4)
C(24)	1.1036(2)	0.08346(14)	0.0852(2)	0.0317(5)
C(25)	1.1977(2)	0.05585(17)	0.0420(2)	0.0420(6)
C(26)	0.60121(18)	0.00149(12)	0.21252(19)	0.0252(5)
C(27)	0.49695(19)	0.09563(14)	0.0671(2)	0.0338(5)
C(28)	0.5375(2)	-0.15596(18)	0.6273(3)	0.0509(7)

**Table S8. Bond lengths [Å] for shelxl**

Bond	Lengths [Å]
O(1)- C(20)	1.339(3)
O(1)- C(21)	1.462(3)
O(2)- C(20)	1.209(3)
O(3)- C(23)	1.346(2)
O(3)- C(24)	1.448(3)
O(4)- C(23)	1.209(3)
O(5)- C(26)	1.341(3)
O(5)- C(27)	1.444(3)
O(6)- C(26)	1.210(3)
N(1)- C(7)	1.381(3)
N(1)- C(11)	1.396(3)
N(1)- C(1)	1.453(3)
C(1)- C(2)	1.373(3)
C(1)- C(6)	1.389(3)
C(2)- C(1)	1.388(3)
C(3)- C(4)	1.378(4)

C(4)- C(5)	1.376(4)
C(5)- C(6)	1.388(3)
C(7)- C(8)	1.362(3)
C(7)- C(19)	1.501(3)
C(8)- C(9)	1.450(3)
C(8)- C(20)	1.487(3)
C(9)- C(18)	1.385(3)
C(9)- C(10)	1.427(3)
C(10)- C(11)	1.422(3)
C(10)- C(15)	1.423(3)
C(11)- C(12)	1.385(3)
C(15)- C(16)	1.414(3)
C(15)- C(14)	1.440(3)
C(17)- C(16)	1.382(3)
C(17)- C(18)	1.399(3)
C(17)- C(26)	1.483(3)
C(13)- C(12)	1.392(3)
C(13)- C(14)	1.393(3)
C(13)- C(22)	1.514(3)
C(14)- C(23)	1.479(3)
C(24)- C(25)	1.498(3)
C(21)- C(28)	1.496(4)

**Table S9. Anisotropic displacement parameters for shelxl.**

	U11	U22	U33	U23	U13	U12
O1	0.0359(9)	0.0415(9)	0.0219(8)	-0.0026(7)	0.0126(7)	-0.0078(7)
O2	0.0455(10)	0.0493(11)	0.0313(9)	-0.0121(8)	0.0180(8)	-0.0236(8)
O3	0.0318(8)	0.0309(8)	0.0295(8)	0.0022(6)	0.0189(7)	0.0030(6)
O4	0.0322(8)	0.0255(8)	0.0374(9)	0.0031(7)	0.0184(7)	0.0036(7)
O5	0.0208(7)	0.0322(8)	0.0327(8)	0.0116(6)	0.0078(6)	0.0045(6)
O6	0.0238(8)	0.0477(10)	0.0502(11)	0.0164(8)	0.0149(7)	0.0018(7)
N1	0.0275(9)	0.0258(9)	0.0229(9)	0.0021(7)	0.0082(7)	0.0020(7)
C1	0.0277(11)	0.0222(11)	0.0295(11)	0.0062(9)	0.0109(9)	0.0020(9)
C2	0.0373(13)	0.0294(12)	0.0316(12)	0.0000(10)	0.0085(10)	0.0026(10)
C3	0.0357(13)	0.0374(14)	0.0440(15)	0.0048(11)	-0.0002(11)	0.0028(11)
C4	0.0274(12)	0.0324(13)	0.0686(18)	0.0112(13)	0.0128(12)	0.0067(10)
C5	0.0398(13)	0.0273(12)	0.0635(17)	0.0014(12)	0.0281(13)	0.0050(10)
C6	0.0364(12)	0.0283(12)	0.0357(12)	-0.0009(10)	0.0168(10)	-0.0012(10)
C7	0.0349(12)	0.0213(10)	0.0193(10)	-0.0011(8)	0.0085(9)	-0.0014(9)
C8	0.0322(11)	0.0225(10)	0.0189(10)	-0.0014(8)	0.0090(9)	-0.0037(9)
C9	0.0287(11)	0.0206(10)	0.0185(10)	-0.0035(8)	0.0081(8)	-0.0025(8)
C10	0.0257(10)	0.0203(10)	0.0170(10)	-0.0052(8)	0.0078(8)	-0.0001(8)
C11	0.0306(11)	0.0201(10)	0.0170(10)	-0.0027(8)	0.0064(8)	0.0022(8)

C15	0.0228(10)	0.0195(10)	0.0172(9)	-0.0047(8)	0.0068(8)	0.0014(8)
C17	0.0230(10)	0.0225(10)	0.0204(10)	-0.0023(8)	0.0073(8)	-0.0011(8)
C16	0.0255(10)	0.0208(10)	0.0196(10)	-0.0009(8)	0.0089(8)	0.0008(8)
C18	0.0244(10)	0.0254(11)	0.0236(10)	-0.0017(8)	0.0095(9)	-0.0042(8)
C13	0.0239(10)	0.0245(11)	0.0220(10)	-0.0050(8)	0.0091(8)	0.0004(8)
C14	0.0229(10)	0.0230(10)	0.0228(10)	-0.0062(8)	0.0101(8)	-0.0003(8)
C12	0.0228(10)	0.0287(11)	0.0237(10)	-0.0038(9)	0.0068(8)	0.0044(9)
C23	0.0216(10)	0.0243(11)	0.0233(10)	-0.0051(8)	0.0091(8)	-0.0021(9)
C20	0.0372(12)	0.0220(10)	0.0208(10)	0.0006(8)	0.0107(9)	-0.0029(9)
C19	0.0373(12)	0.0298(12)	0.0284(12)	0.0066(9)	0.0107(10)	0.0001(10)
C22	0.0235(11)	0.0355(12)	0.0332(12)	0.0010(10)	0.0107(9)	0.0015(9)
C24	0.0336(12)	0.0353(12)	0.0298(12)	0.0056(10)	0.0161(10)	-0.0003(10)
C25	0.0387(13)	0.0564(16)	0.0403(14)	0.0129(12)	0.0255(11)	0.0052(12)
C26	0.0248(11)	0.0243(11)	0.0255(10)	0.0003(8)	0.0085(9)	-0.0016(9)
C27	0.0258(11)	0.0370(13)	0.0356(13)	0.0111(10)	0.0080(10)	0.0092(10)
C21	0.0469(14)	0.0479(15)	0.0307(12)	-0.0010(11)	0.0212(11)	-0.0113(12)
C28	0.0458(15)	0.0616(18)	0.0537(17)	-0.0065(14)	0.0282(14)	-0.0079(14)

**Table S10. Hydrogen coordinates and isotropic displacement parameters for shelxl.**

	x	y	z	U(eq)
H(2A)	1.2045	-0.1835	0.7800	0.041
H(3A)	1.3796	-0.2518	0.8689	0.052
H(4A)	1.4343	-0.3466	0.7626	0.053
H(5A)	1.3146	-0.3760	0.5684	0.049
H(6A)	1.1367	-0.3107	0.4796	0.039
H(16A)	0.8108	0.0298	0.2097	0.026
H(18A)	0.6532	-0.1106	0.3732	0.029
H(12A)	1.2132	-0.1330	0.5210	0.031
H(19A)	0.8907	-0.2948	0.6887	0.048
H(19B)	1.0193	-0.2651	0.7564	0.048
H(19C)	0.9933	-0.3316	0.6588	0.048
H(22A)	1.2442	0.0139	0.3296	0.046
H(22B)	1.2937	-0.0716	0.3692	0.046
H(22C)	1.3053	-0.0065	0.4660	0.046
H(24A)	1.1234	0.1349	0.1237	0.038
H(24B)	1.0296	0.0879	0.0178	0.038
H(25A)	1.2063	0.0933	-0.0121	0.063
H(25B)	1.1770	0.0049	0.0062	0.063
H(25C)	1.2703	0.0516	0.1117	0.063
H(27A)	0.5094	0.1343	0.0146	0.051
H(27B)	0.4671	0.1214	0.1207	0.051
H(27C)	0.4416	0.0567	0.0206	0.051
H(21A)	0.6553	-0.2189	0.7636	0.048

H(21B)	0.6059	-0.2672	0.6436	0.048
H(28A)	0.4713	-0.1718	0.6456	0.076
H(28B)	0.5150	-0.1531	0.5420	0.076
H(28C)	0.5643	-0.1048	0.6618	0.076

**Table S11. Bond angles [deg] for shelxl.**

<b>Bond</b>	<b>Bond angles [deg]</b>
C(20)- O(1 )-C(21)	116.27(17)
C(23)- O(3)- C(24)	116.37(16)
C(26)- O(5)- C(27)	115.53(16)
C(7 )-N(1)- C(11)	121.85(17)
C(7)- N(1)- C(1)	120.40(17)
C(11)- N(1)- C(1)	117.73(17)
C(2 )-C(1)- C(6)	121.4(2)
C(2)- C(1)- N(1)	120.06(19)
C(6)- C(1)- N(1)	118.6(2)
C(1)- C(2)- C(3)	118.9(2)
C(4)- C(3)- C(2)	120.4(2)
C(5)- C(4 )-C(3)	120.3(2)
C(4)- C(5)- C(6)	120.1(2)
C(5)- C(6)- C(1)	118.9(2)
C(8)- C(7)- N(1)	120.18(19)
C(8)- C(7)- C(19)	123.12(19)
N(1)- C(7)- C(19)	116.69(19)
C(7)- C(8)- C(9)	121.48(19)
C(7)- C(8)- C(20)	120.82(19)
C(9)- C(8)- C(20)	117.69(18)
C(18)- C(9)- C(10)	119.27(18)
C(18)- C(9)- C(8)	123.64(19)
C(10)- C(9)- C(8)	117.06(18)
C(11)- C(10)- C(15)	118.83(18)
C(11)- C(10)- C(9)	120.30(18)
C(15)- C(10)- C(9)	120.87(18)
C(12)- C(11)- N(1)	121.36(18)
C(12)- C(11)- C(10)	119.83(18)
N(1)- C(11)- C(10)	118.81(18)
C(16)- C(15)- C(10)	117.56(18)
C(16)- C(15)- C(14)	122.92(18)
C(10)- C(15)- C(14)	119.50(18)
C(16)- C(17)- C(18)	121.16(19)
C(16)- C(17)- C(26)	120.87(18)
C(18)- C(17)- C(26)	117.96(18)
C(17)- C(16)- C(15)	121.00(18)
C(9)- C(18)- C(17)	120.13(18)

C(12)- C(13)- C(14)	119.46(19)
C(12)- C(13)- C(22)	116.90(18)
C(14)- C(13)- C(22)	123.63(19)
C(13)- C(14)- C(15)	119.94(19)
C(13)- C(14)- C(23)	121.28(18)
C(15)- C(14)- C(23)	118.77(18)
C(11)- C(12)-C(13)	122.33(19)
O(4 )-C(23)- O(3)	121.69(19)
O(4 )-C(23)- C(14)	126.58(18)
O(3)- C(23)- C(14)	111.71(17)
O(2)- C(20)- O(1)	122.9(2)
O(2)- C(20)- C(8)	124.14(19)
O(1)- C(20)- C(8)	112.97(18)
O(3)- C(24)- C(25)	106.45(18)
O(6)- C(26)- O(5)	122.49(19)
O(6)- C(26)- C(17)	124.48(19)
O(5)- C(26)- C(17)	113.03(17)
O(1)- C(21)- C(28)	111.4(2)

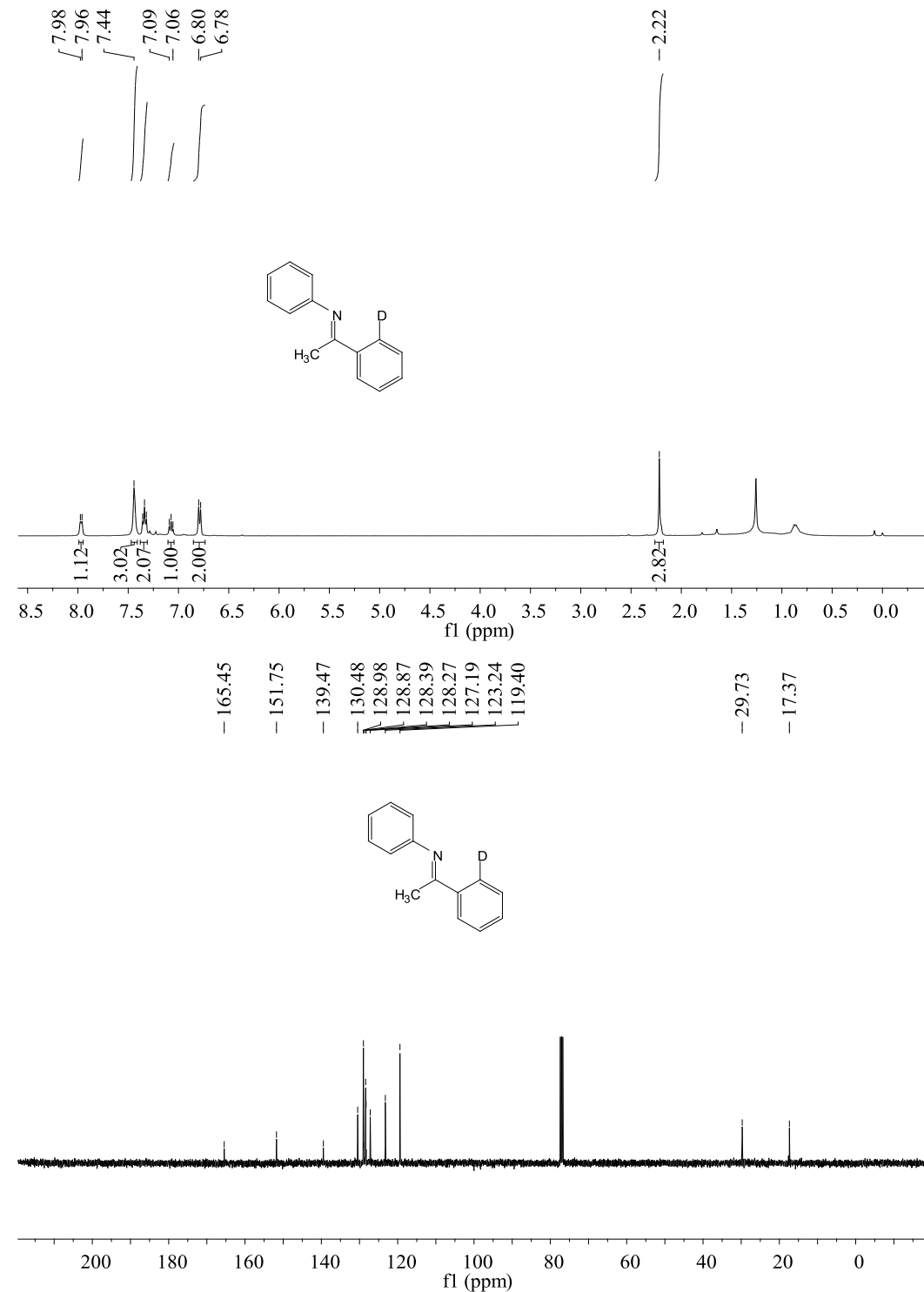
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#### 4. References

1. Ye, W.; Indubhusan, D.; Naohiko, Y. *J. Am. Chem. Soc.* **2012**, *134*, 9098.
2. Jiang, Y.; Khong, V. Z. Y.; Lourdusamy, E.; Park, C. M. *Chem. Commun.* **2012**, *48*, 3133.
3. Shi, Z.; Koester, D. C.; Boultadakis-Arapinis, M.; Glorious, F. *J. Am. Chem. Soc.* **2013**, *135*, 12204.
4. Chan, P. P.; Advait, N.; Cheol, H. Y.; Kyung, W. J. *J. Org. Chem.* **2009**, *74*, 6231.

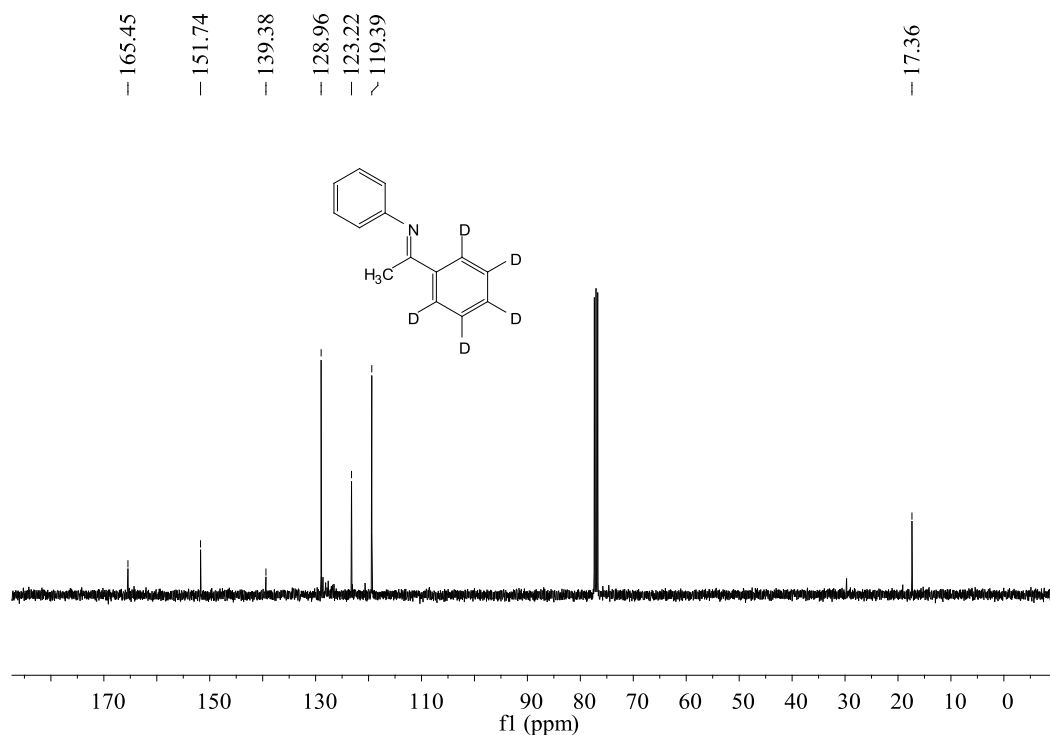
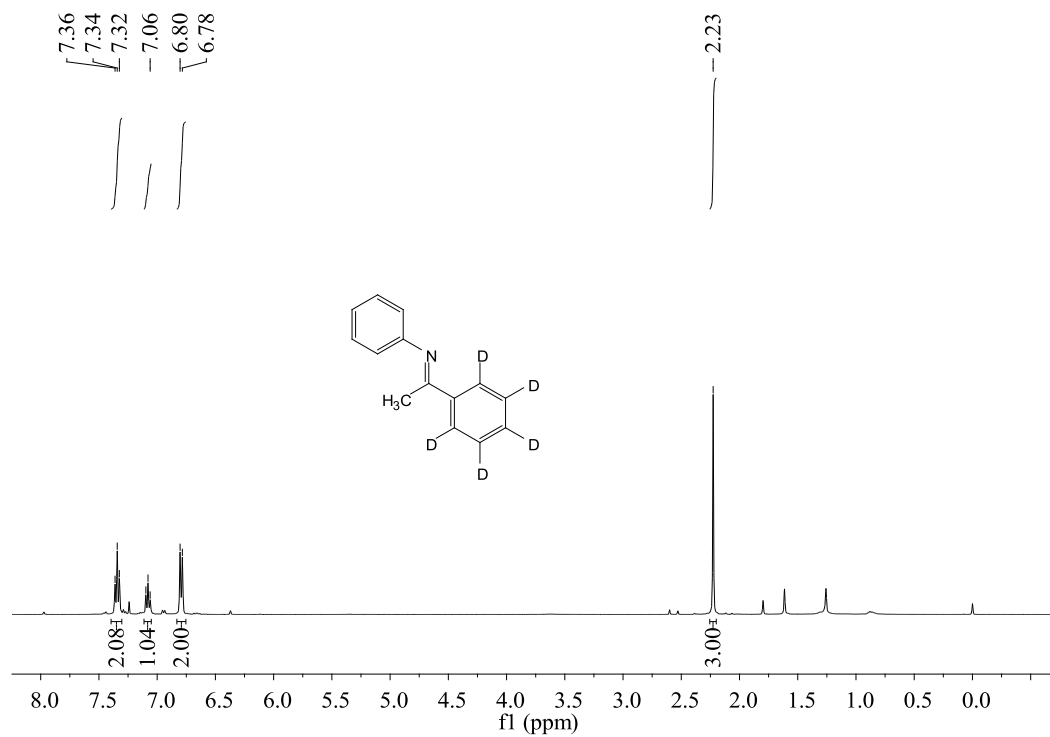
5.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for all isolated products.

1) monodeuterated ketimine (*d*-1a-a) (Using  $\text{CDCl}_3$  as solvent)

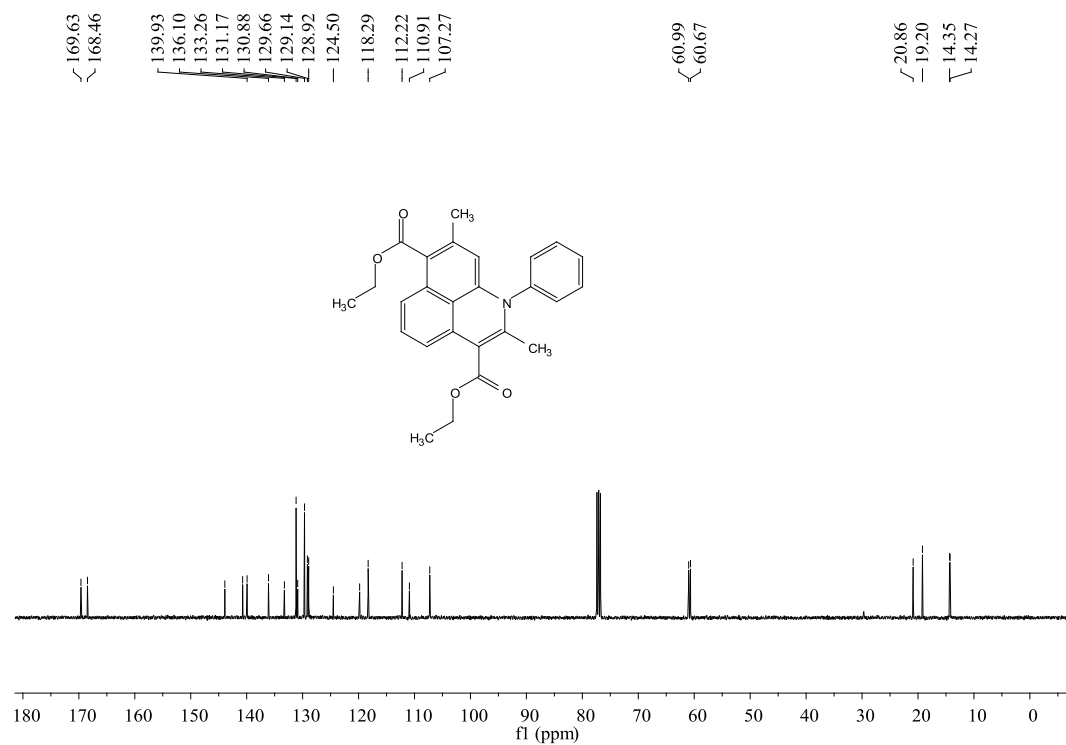
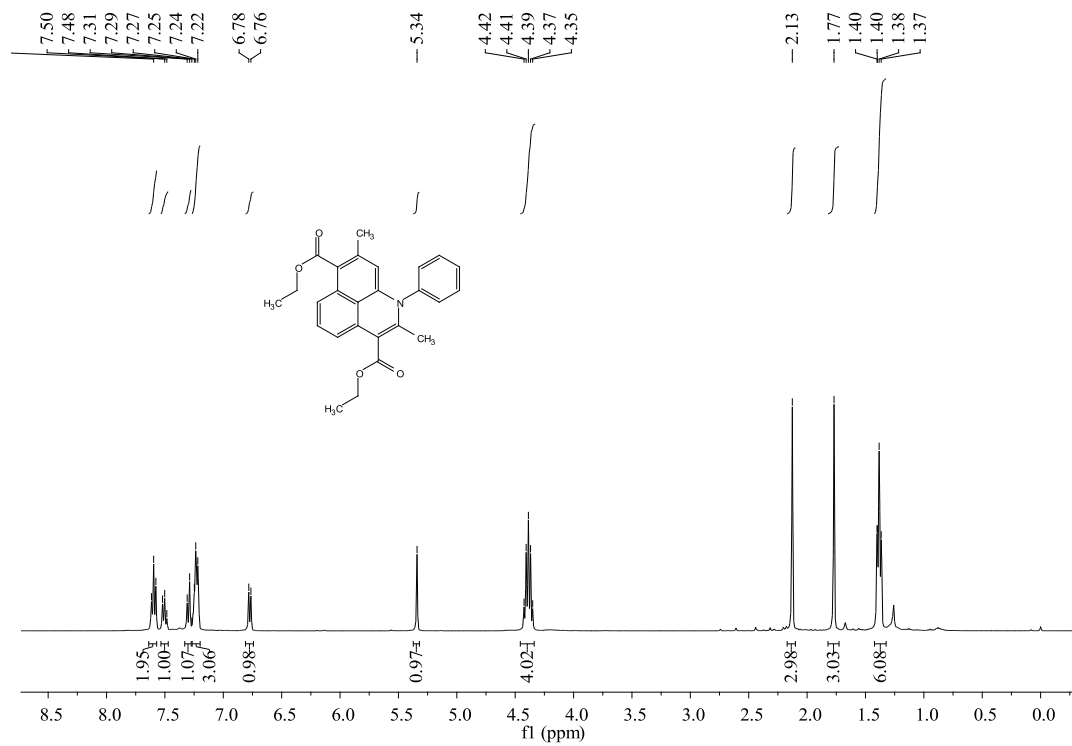




2) Pentadeuterate ketoimine (**d-1a-b**) (Using CDCl<sub>3</sub> as solvent)

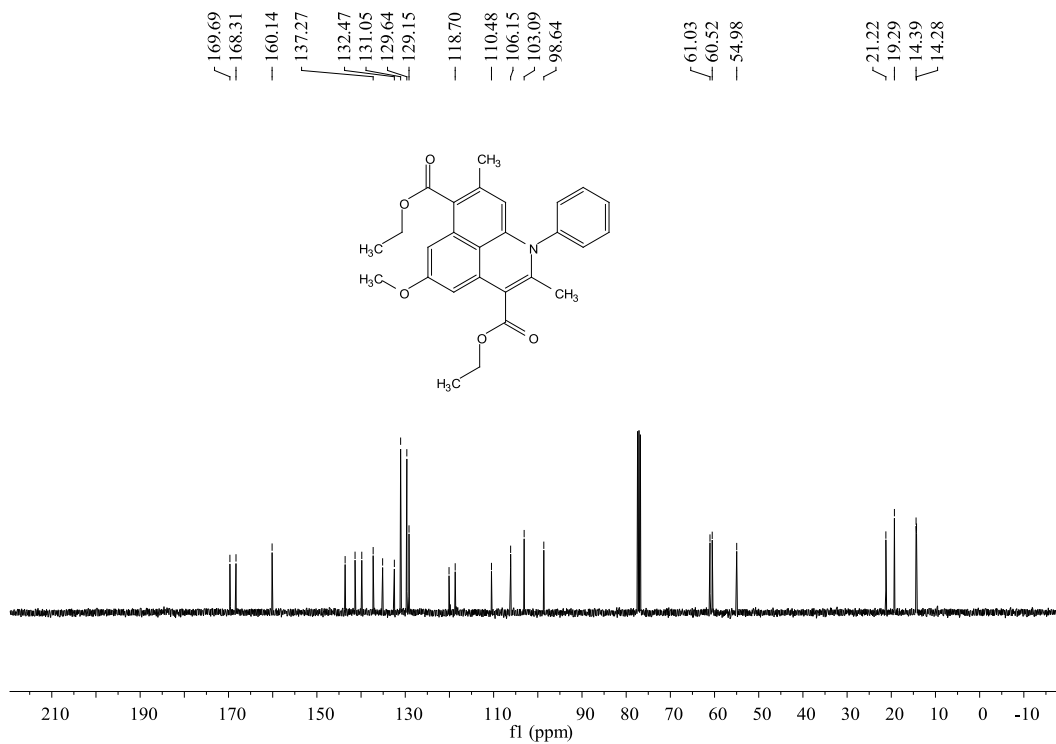
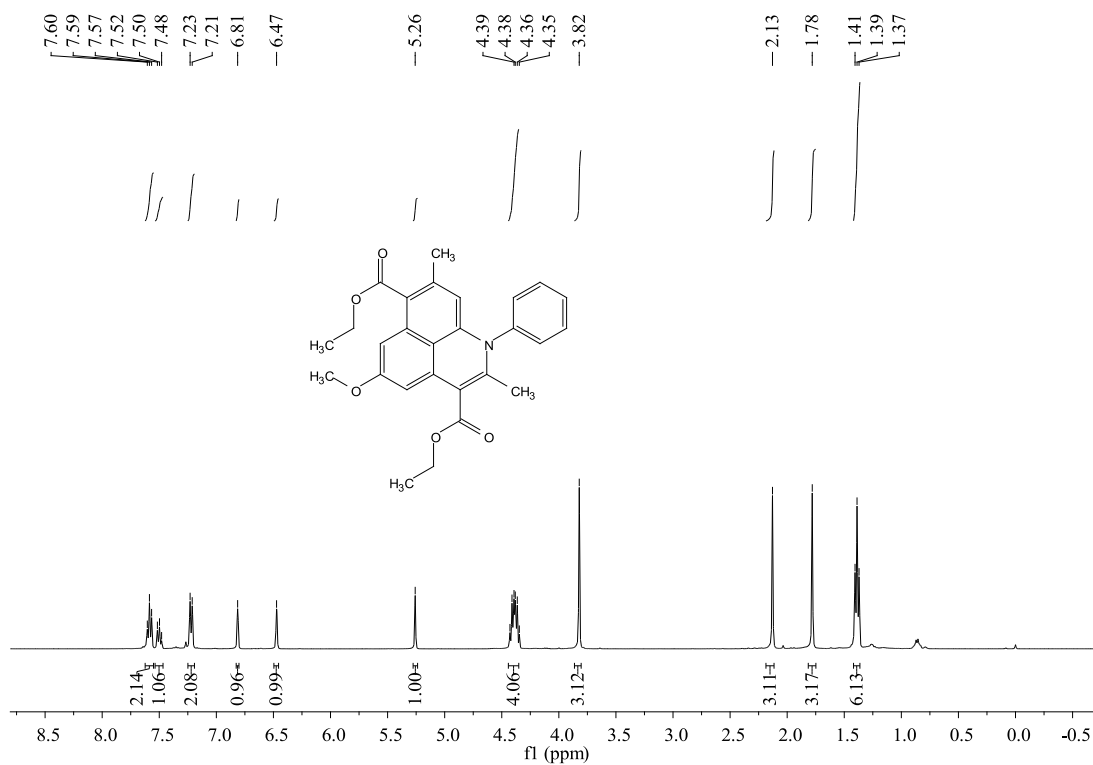


3) Diethyl 2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3a**) (Using CDCl<sub>3</sub> as solvent)

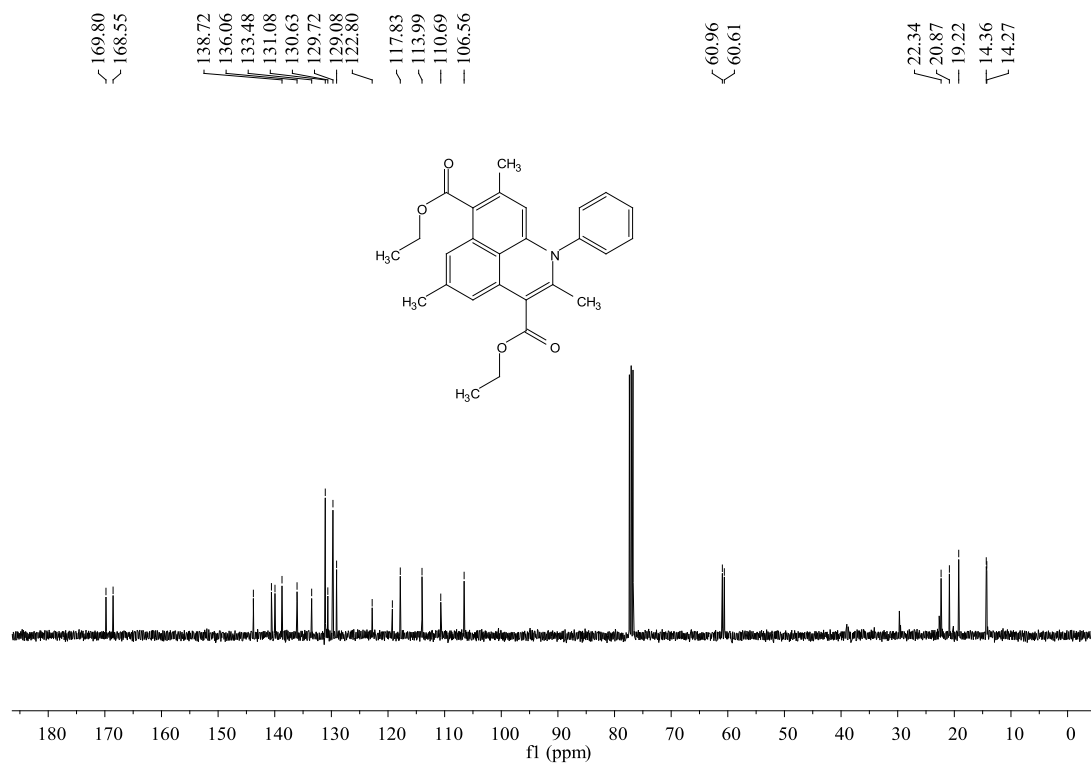
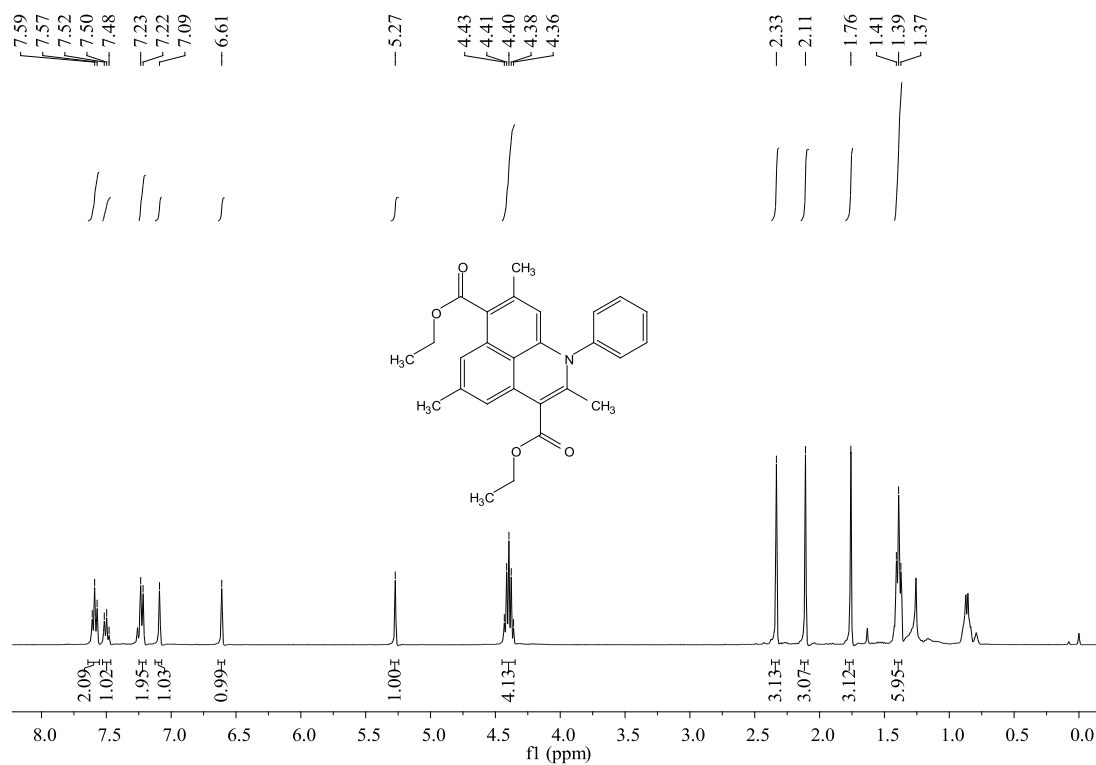


4) Diethyl 5-methoxy-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate

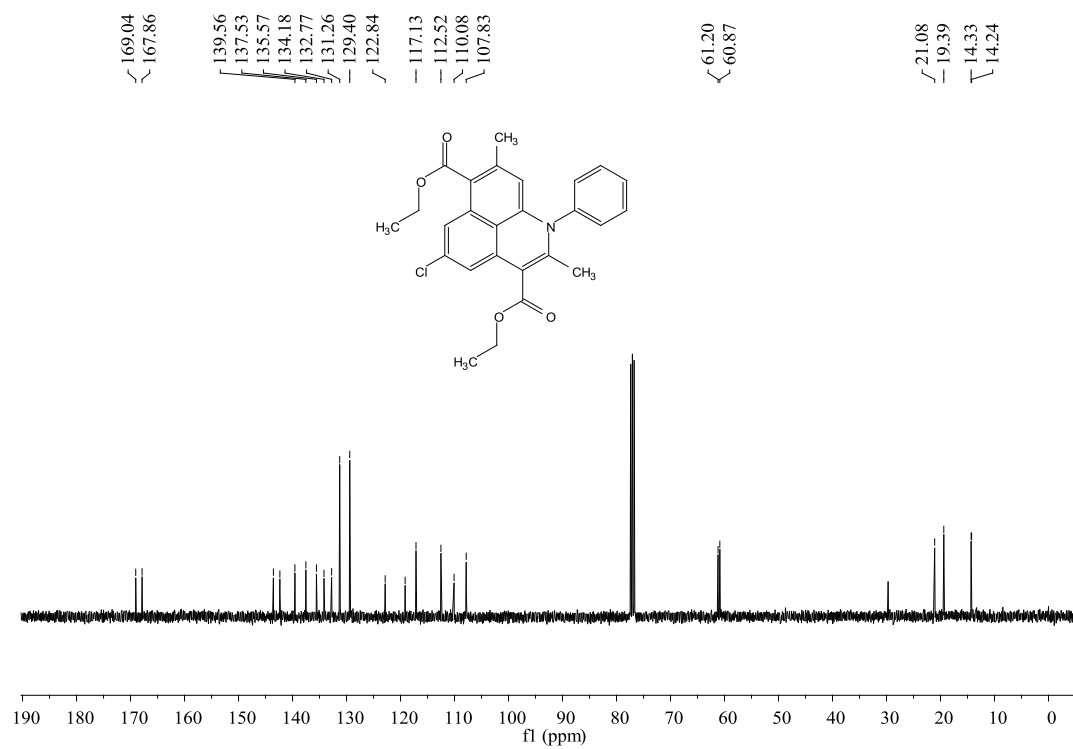
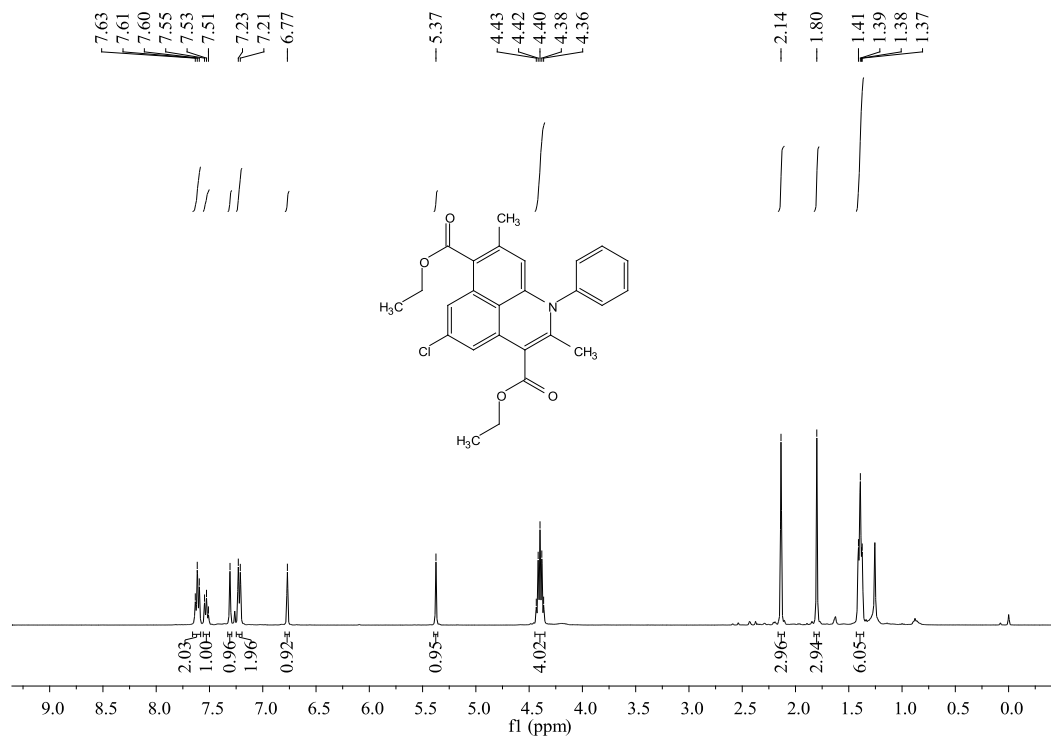
(3b) (Using CDCl<sub>3</sub> as solvent)



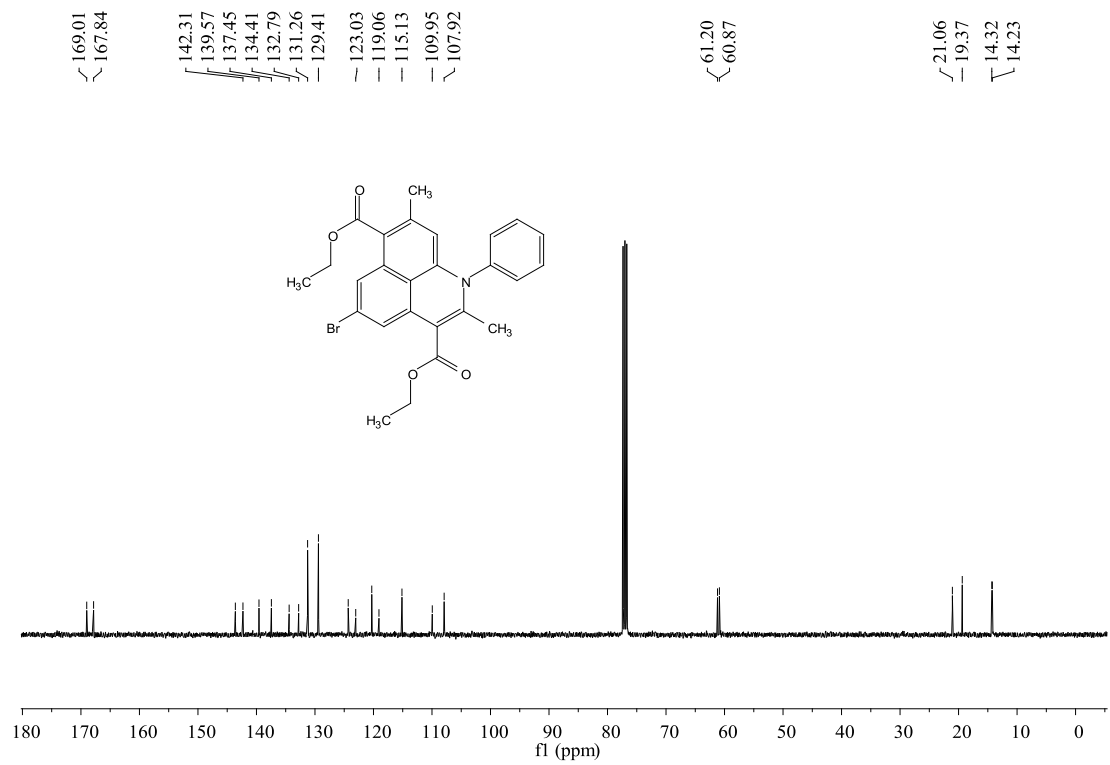
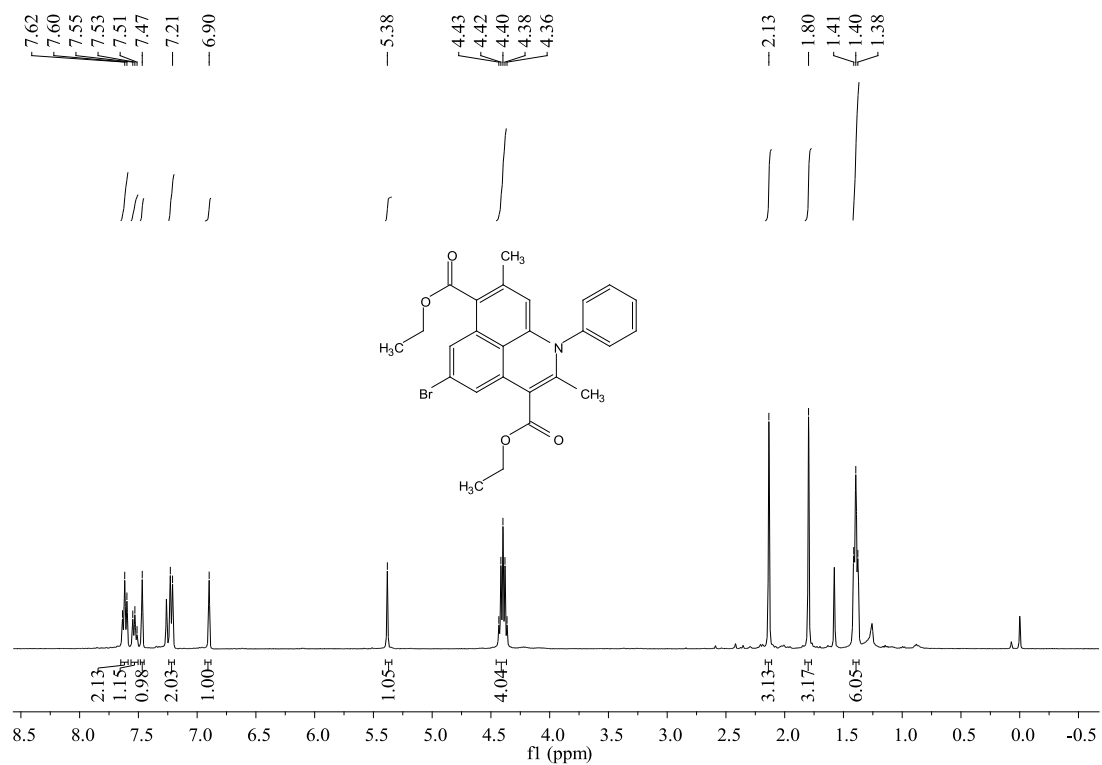
5) Diethyl 2,5,8-trimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3c**) (Using CDCl<sub>3</sub> as solvent)



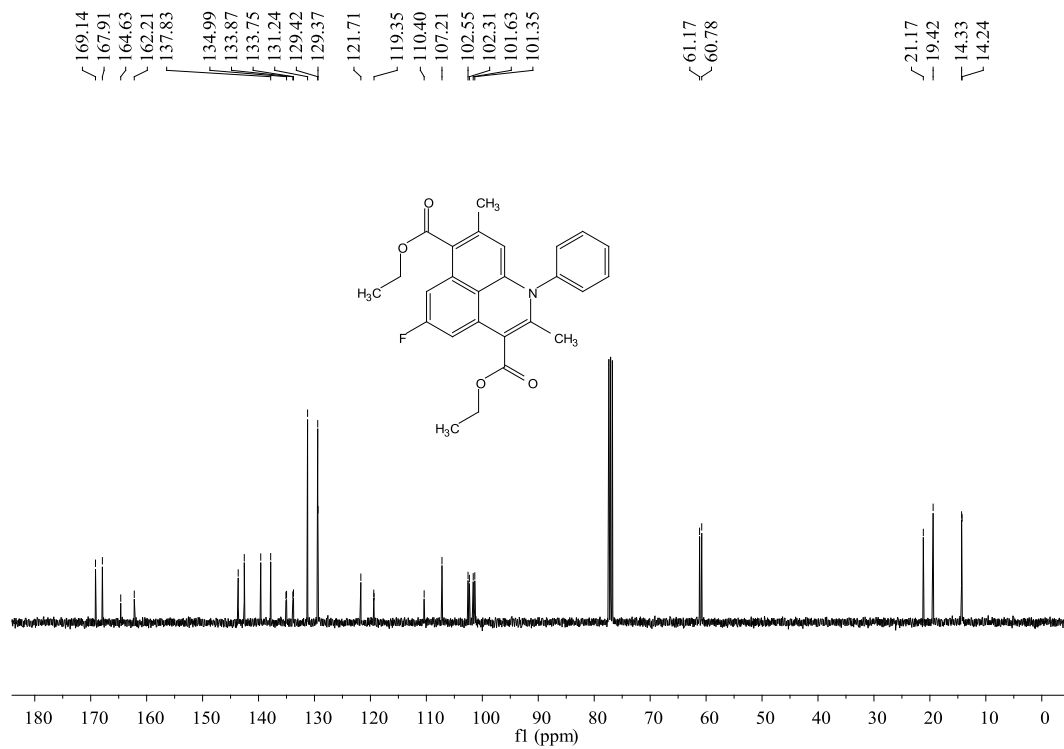
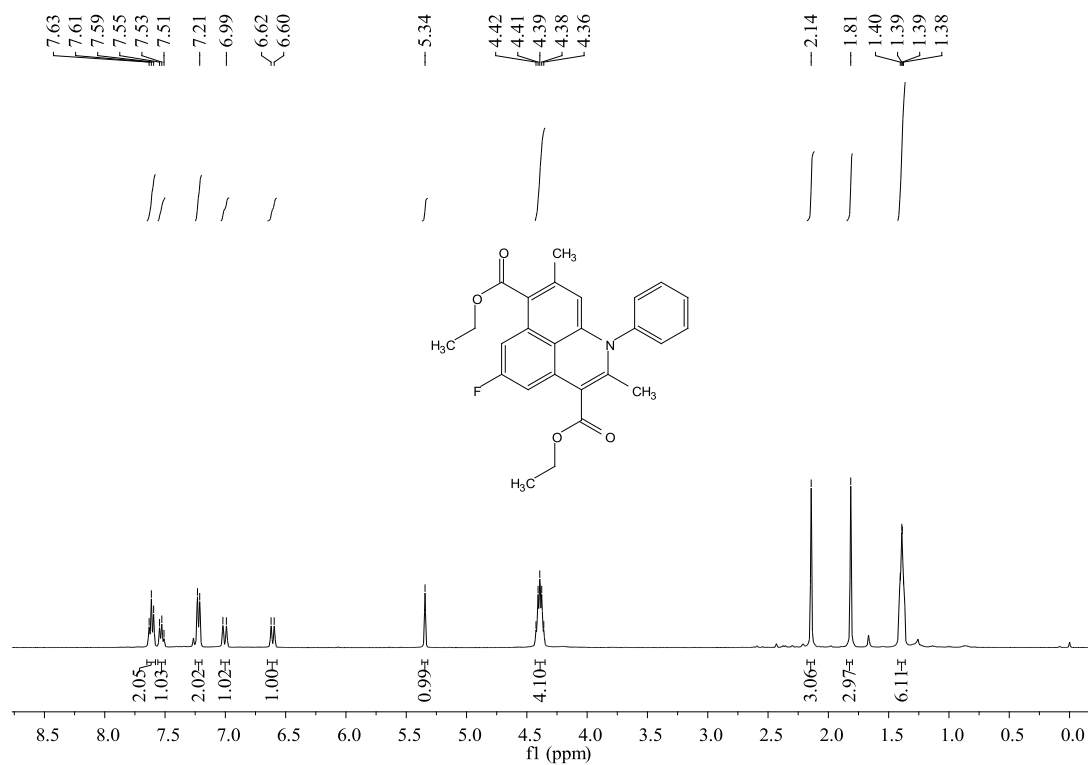
6) Diethyl 5-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (3d)  
 (Using CDCl<sub>3</sub> as solvent)



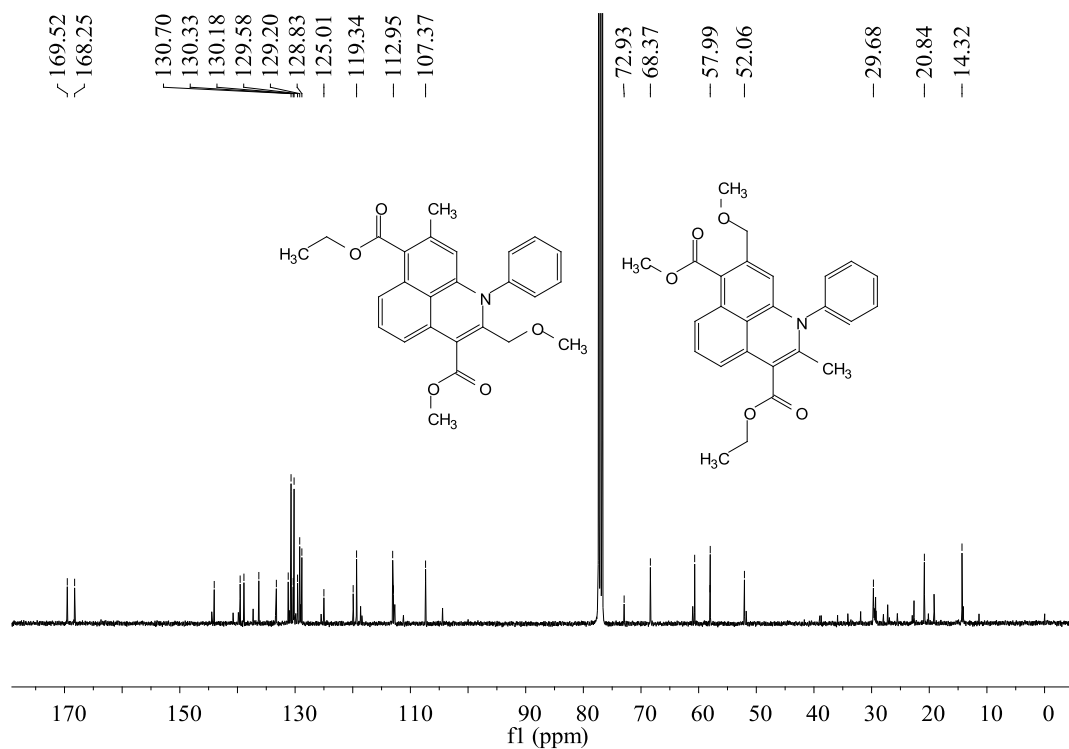
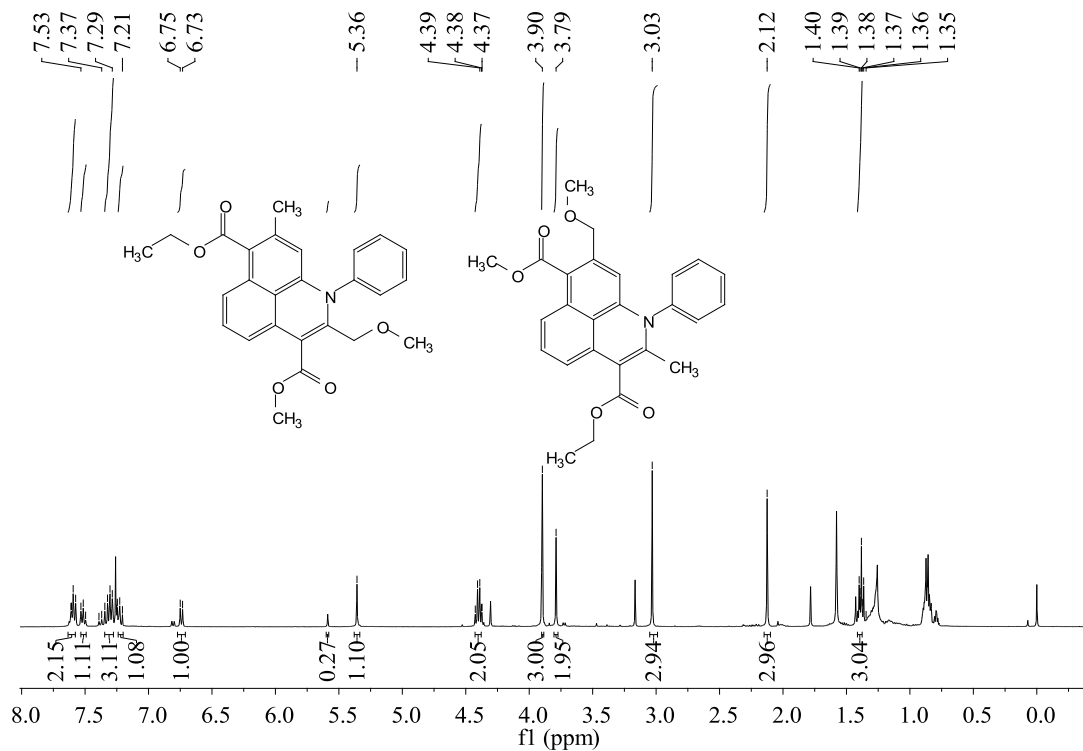
7) Diethyl 5-bromo-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate  
**(3e)** (Using CDCl<sub>3</sub> as solvent)



8) Diethyl 5-fluoro-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3f**) (Using CDCl<sub>3</sub> as solvent)



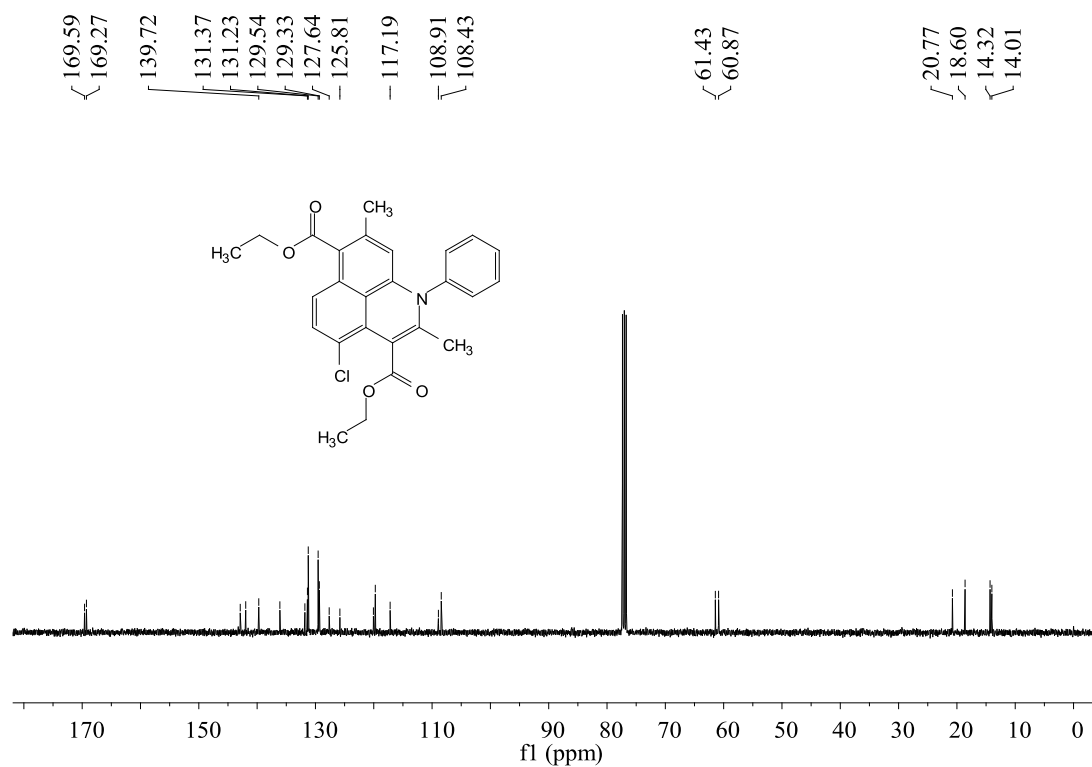
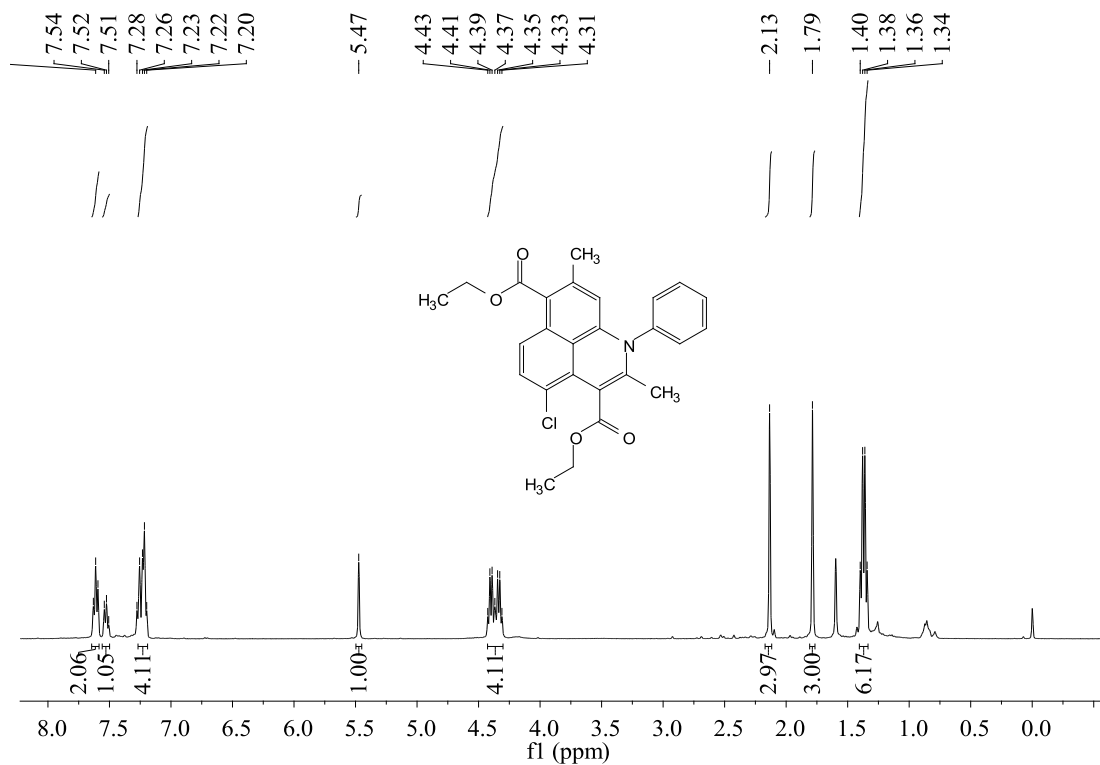
9) Diethyl 6-methoxy-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3g**) and diethyl 4-methoxy-2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3h**) (Using CDCl<sub>3</sub> as solvent)





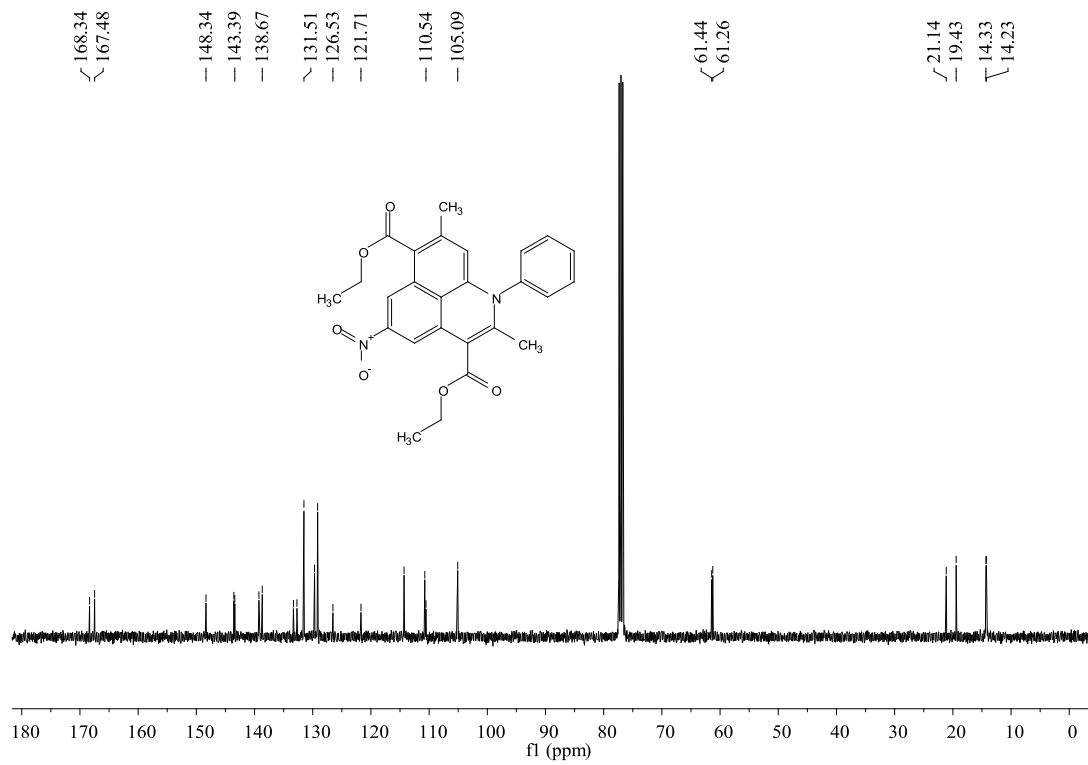
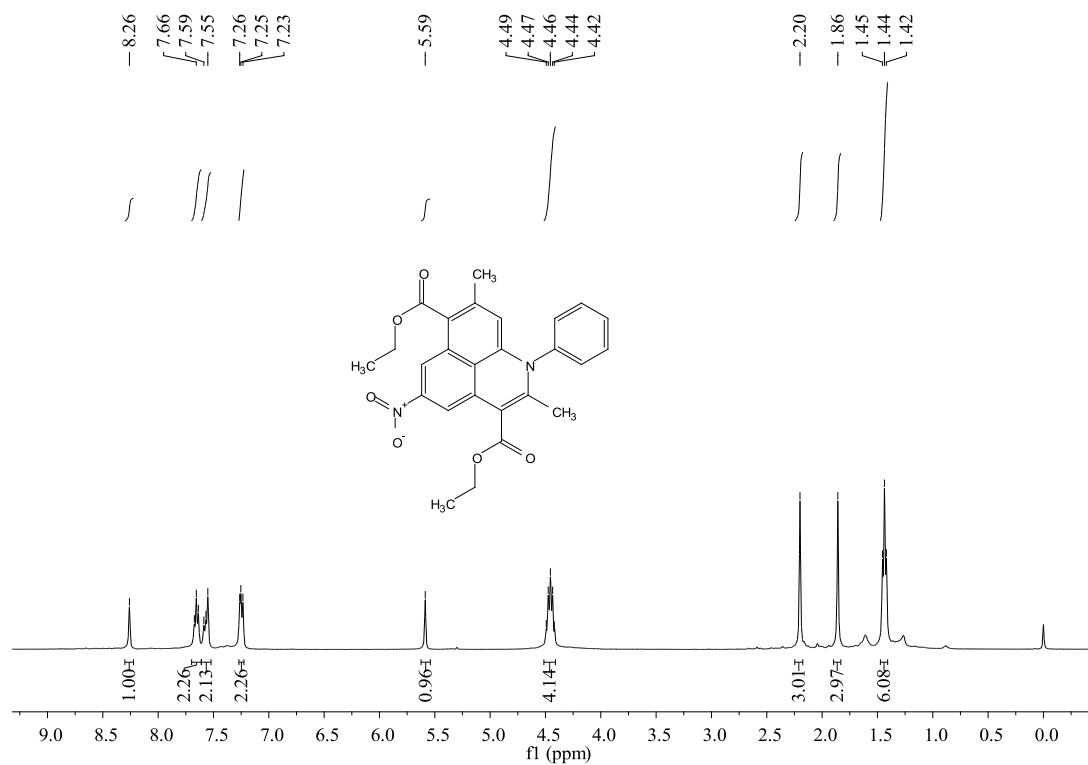
10) Diethyl 6-chloro-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate

(3i) (Using CDCl<sub>3</sub> as solvent)

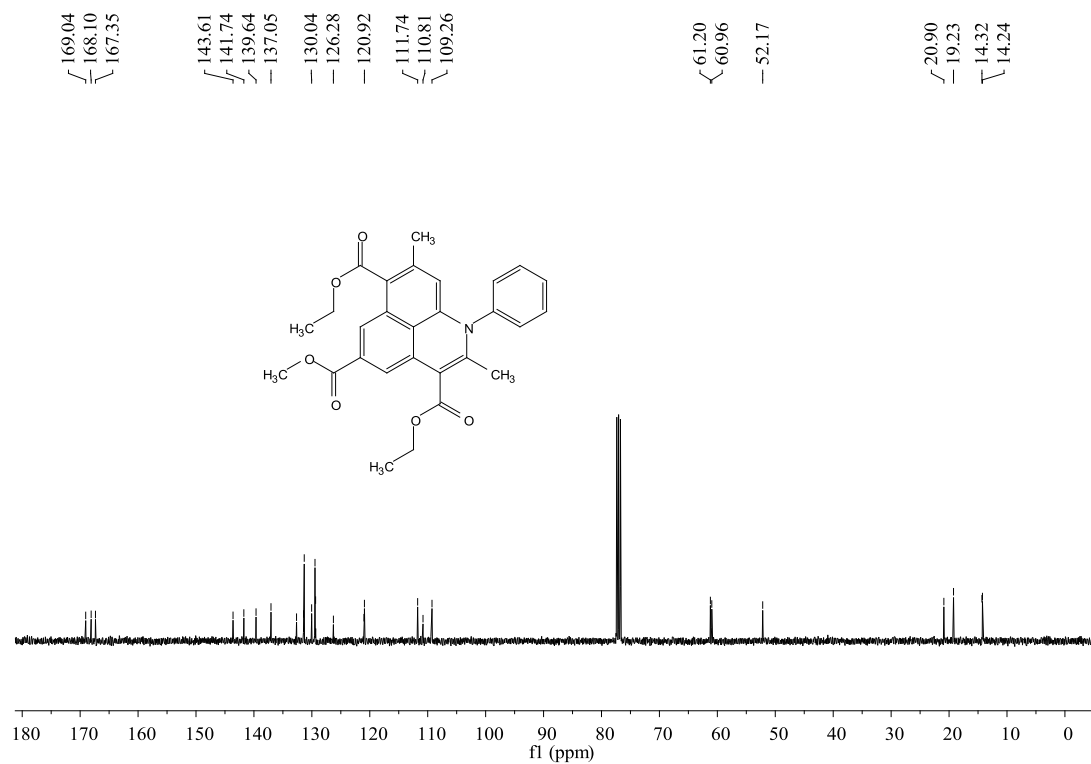
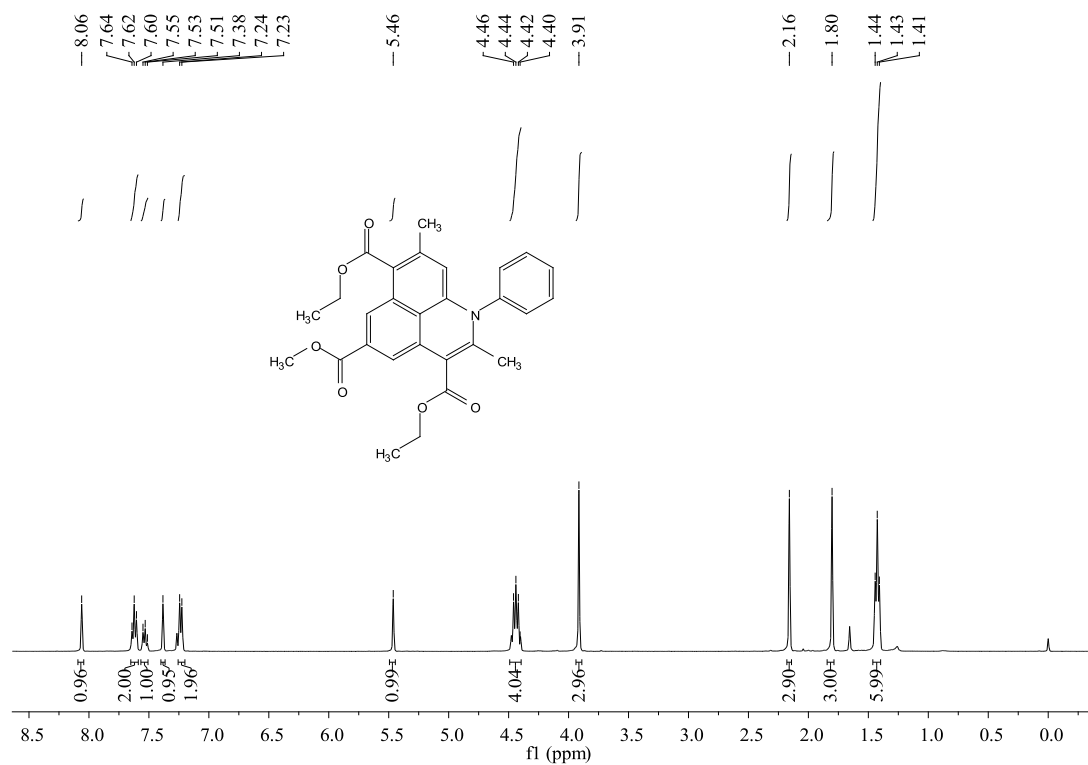


11) Diethyl 2,8-dimethyl-5-nitro-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate

(3j) (Using CDCl<sub>3</sub> as solvent)

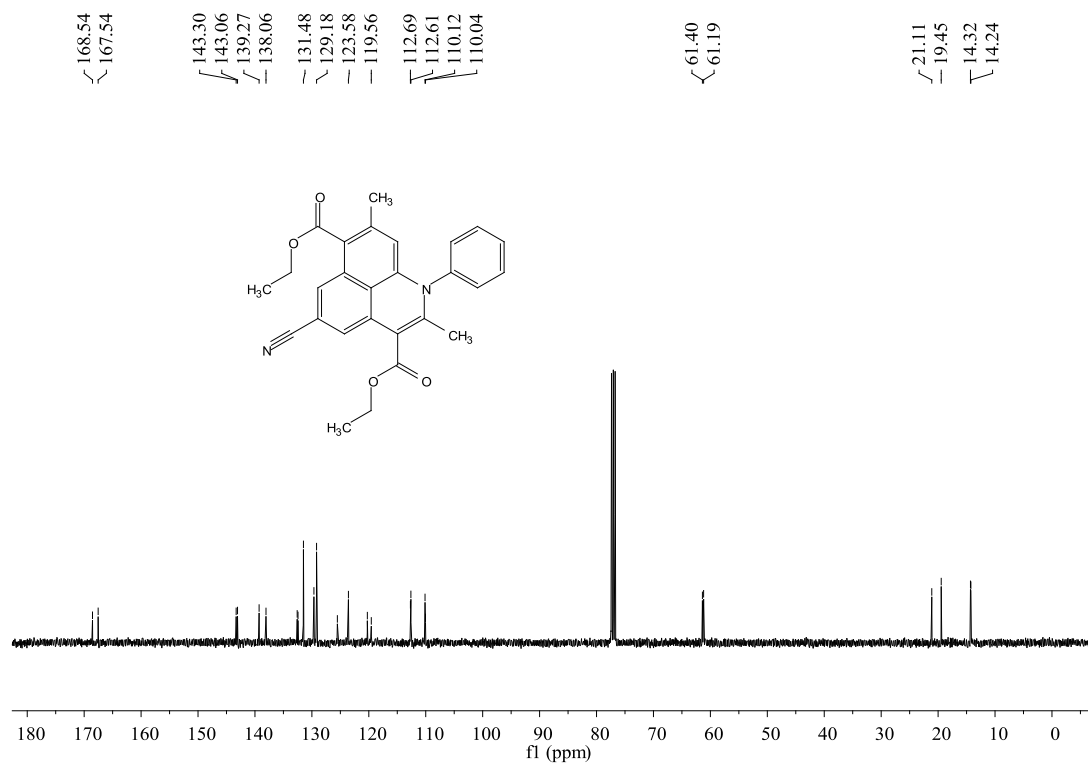
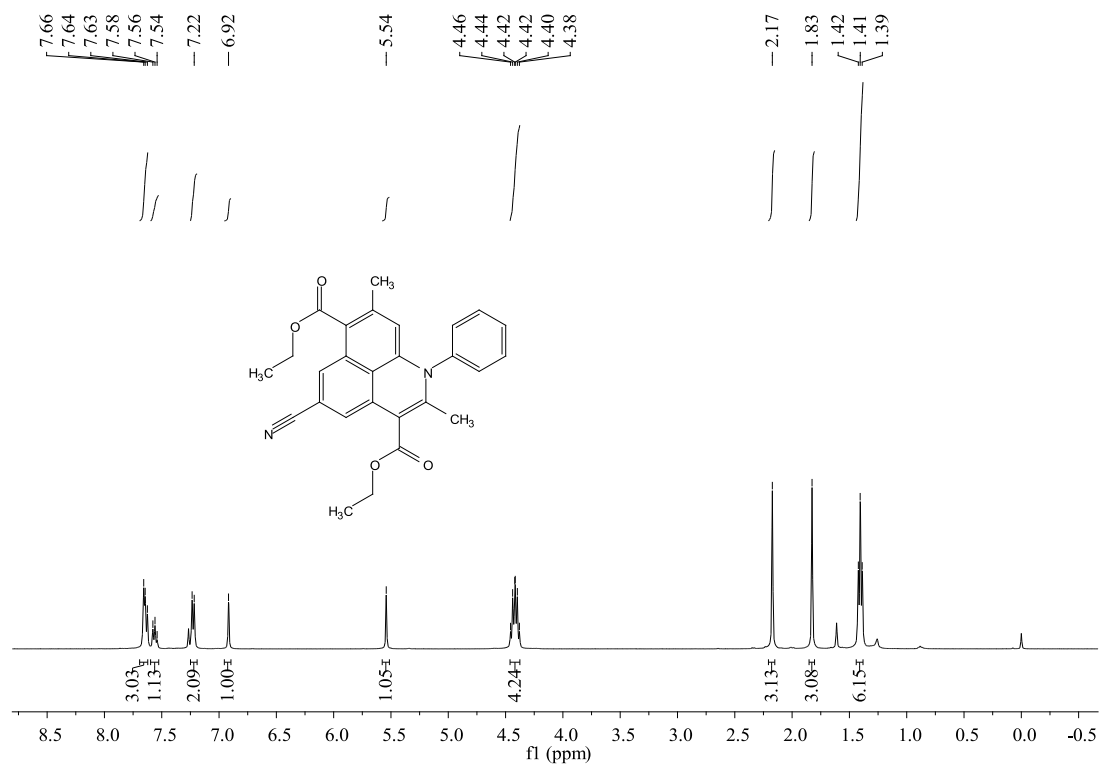


12) 3,7-Diethyl 5-methyl 2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,5,7-tricarboxylate (**3k**)  
 (Using CDCl<sub>3</sub> as solvent)

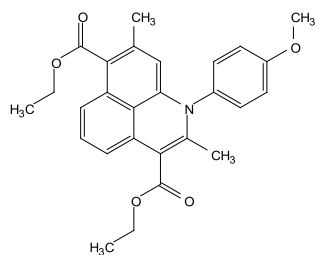
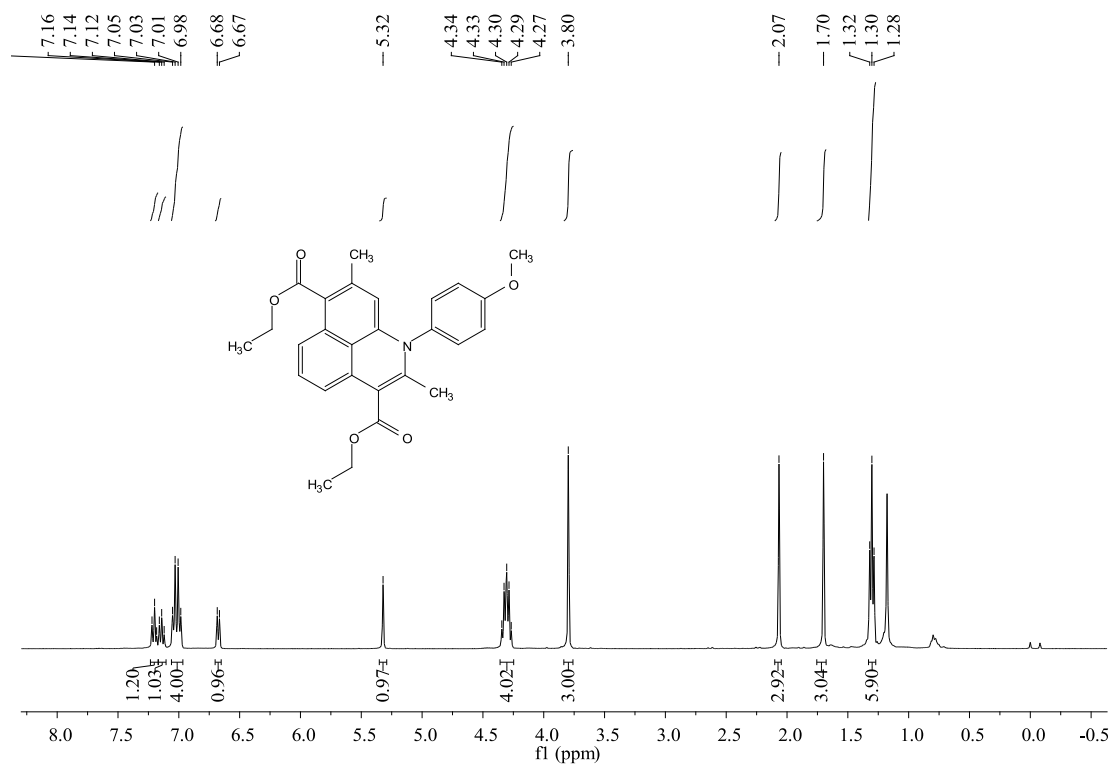


13) Diethyl 5-cyano-2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate

(31) (Using CDCl<sub>3</sub> as solvent)

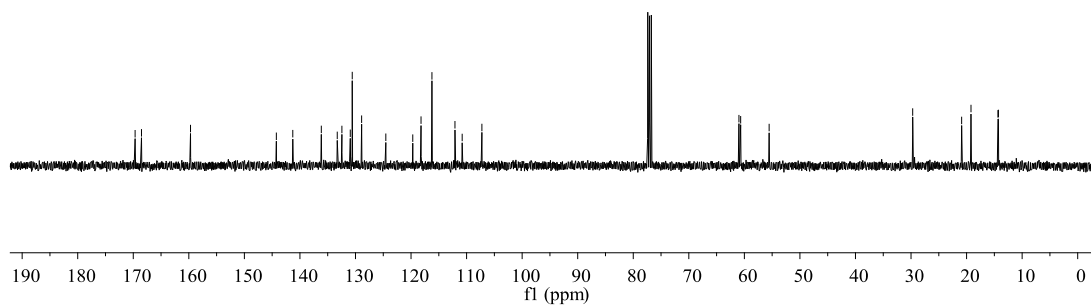
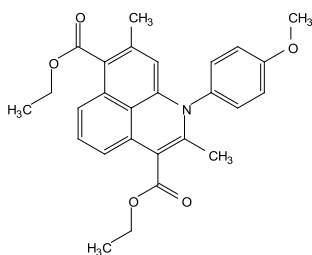


14) Diethyl 1-(4-methoxyphenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate  
**(3m)** (Using CDCl<sub>3</sub> as solvent)



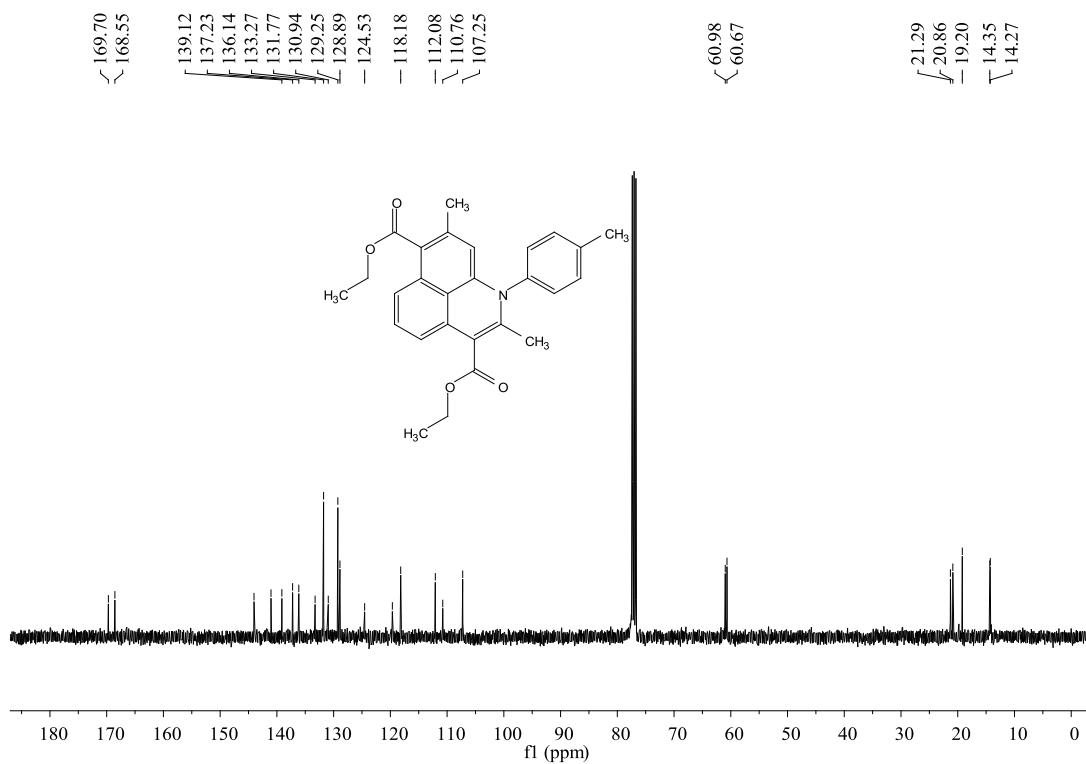
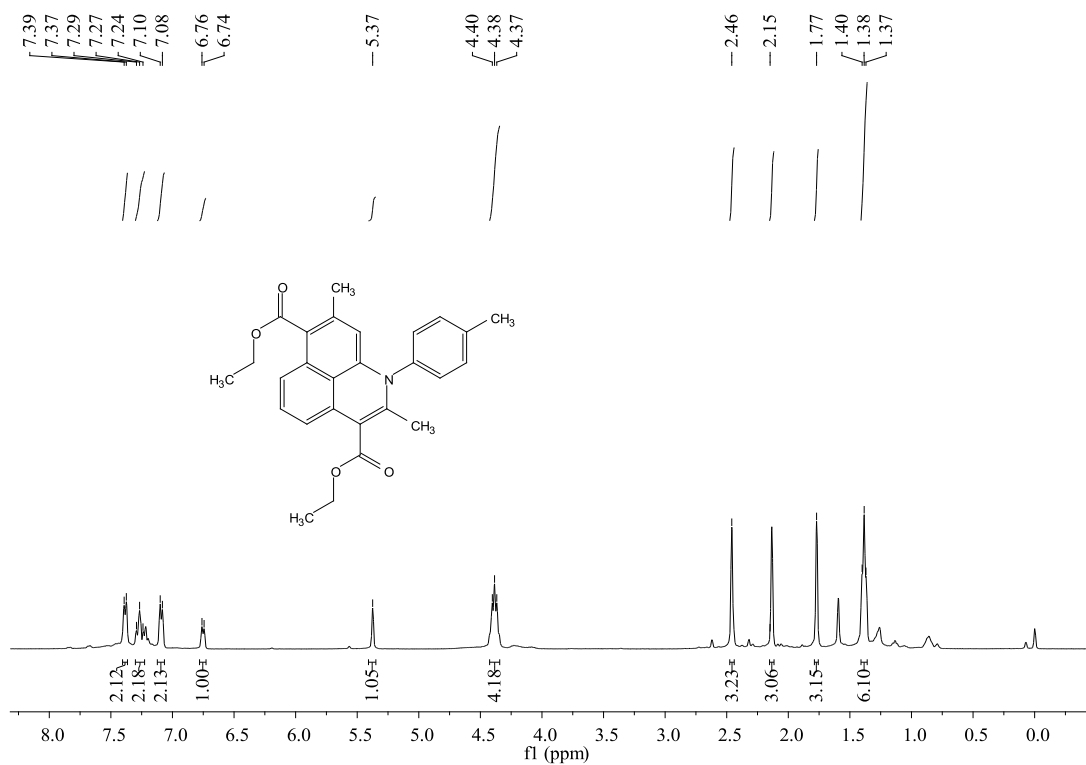
<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of compound **(3m)**. The x-axis represents chemical shift in ppm, ranging from 190 to 0. The spectrum shows several peaks in the carbonyl region (140-170 ppm), aromatic region (107-145 ppm), and aliphatic region (14-61 ppm).

Chemical Shift (ppm)
169.67, 168.52
159.69
144.24, 141.29
132.45, 128.89, 124.54
116.24, 112.09, 110.80, 107.25
60.98, 60.67, 55.54
29.70, 20.89, 19.21, 14.35, 14.27

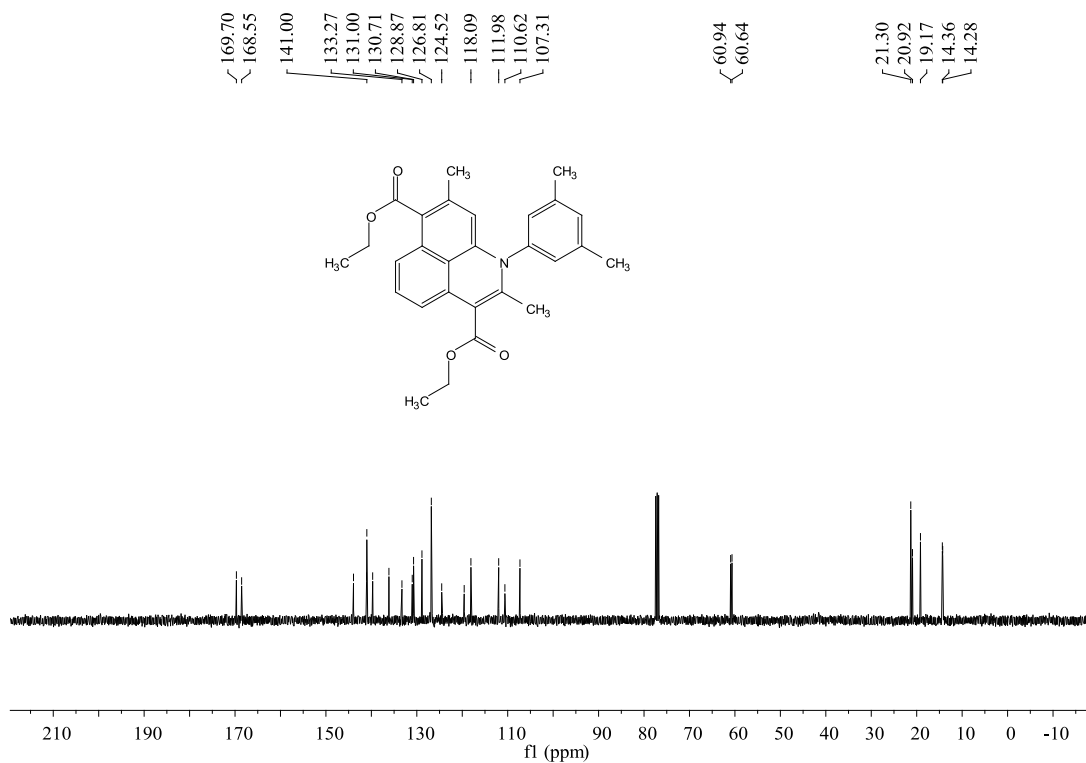
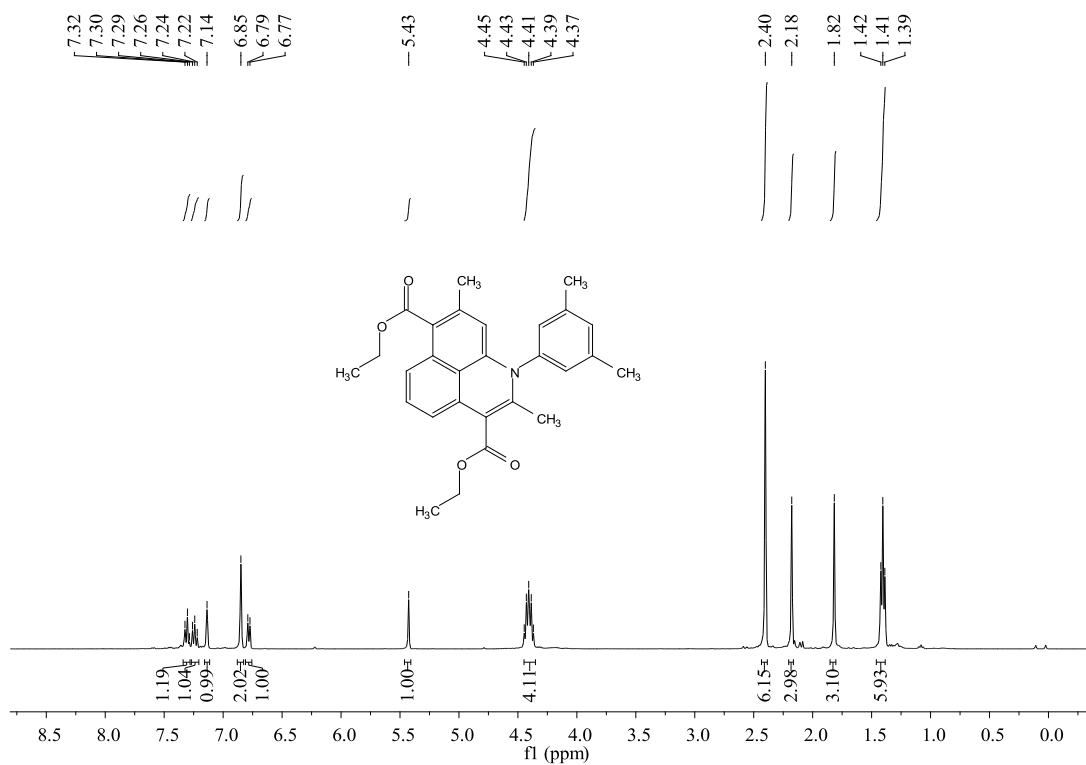


15) Diethyl 2,8-dimethyl-1-(p-tolyl)-1*H*-benzo[de]quinoline-3,7-dicarboxylate

(**3n**) (Using CDCl<sub>3</sub> as solvent)

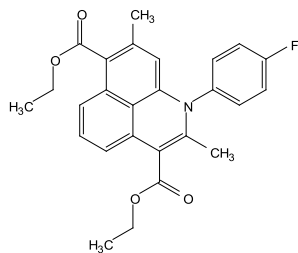
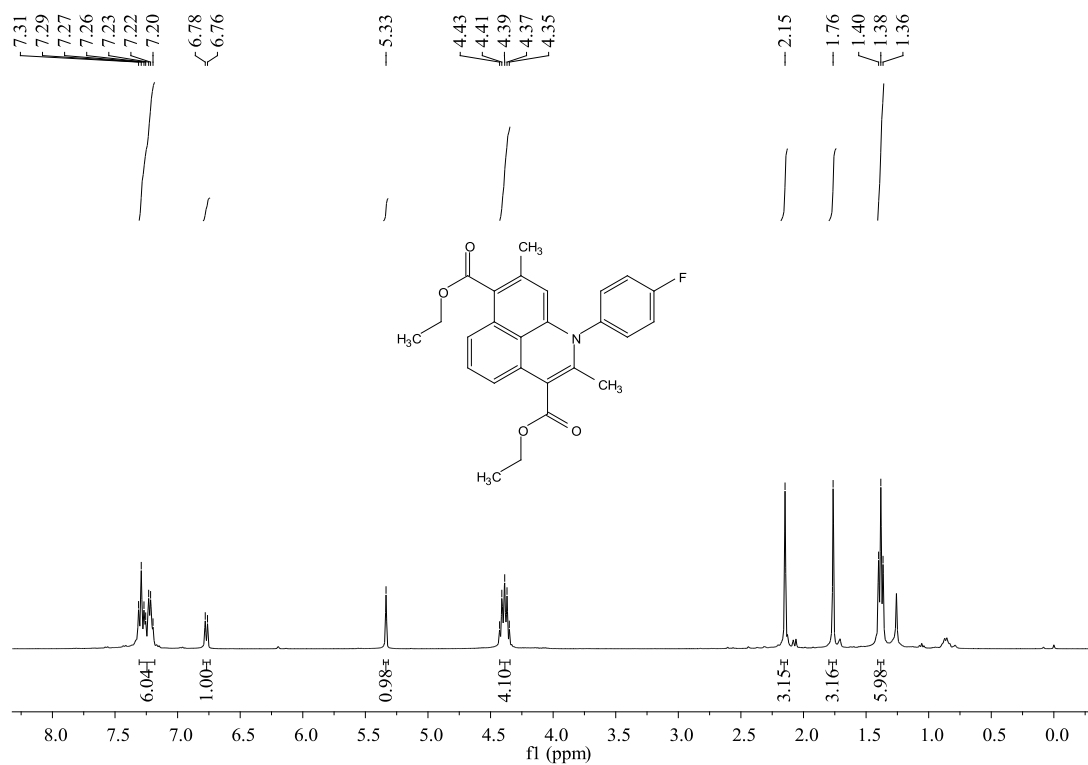


16) Diethyl 1-(3,5-dimethylphenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate  
**(3o)** (Using CDCl<sub>3</sub> as solvent)



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

**(3p)** (Using CDCl<sub>3</sub> as solvent)

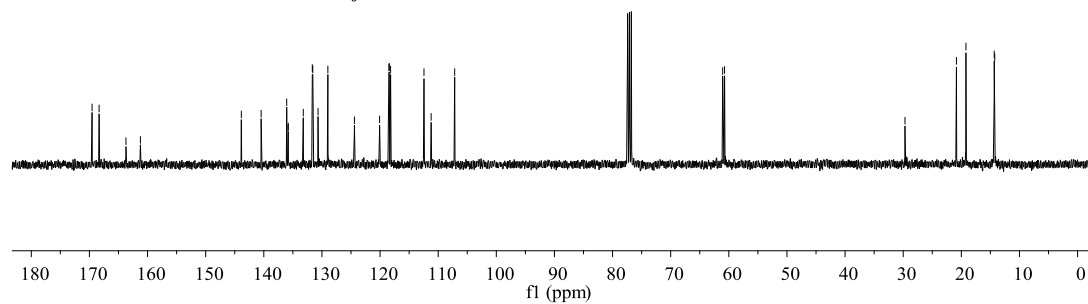
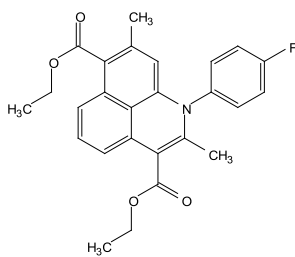


169.55  
168.33  
163.71  
161.23

143.87  
140.46  
133.21  
128.98  
124.41  
118.19  
111.21  
107.16

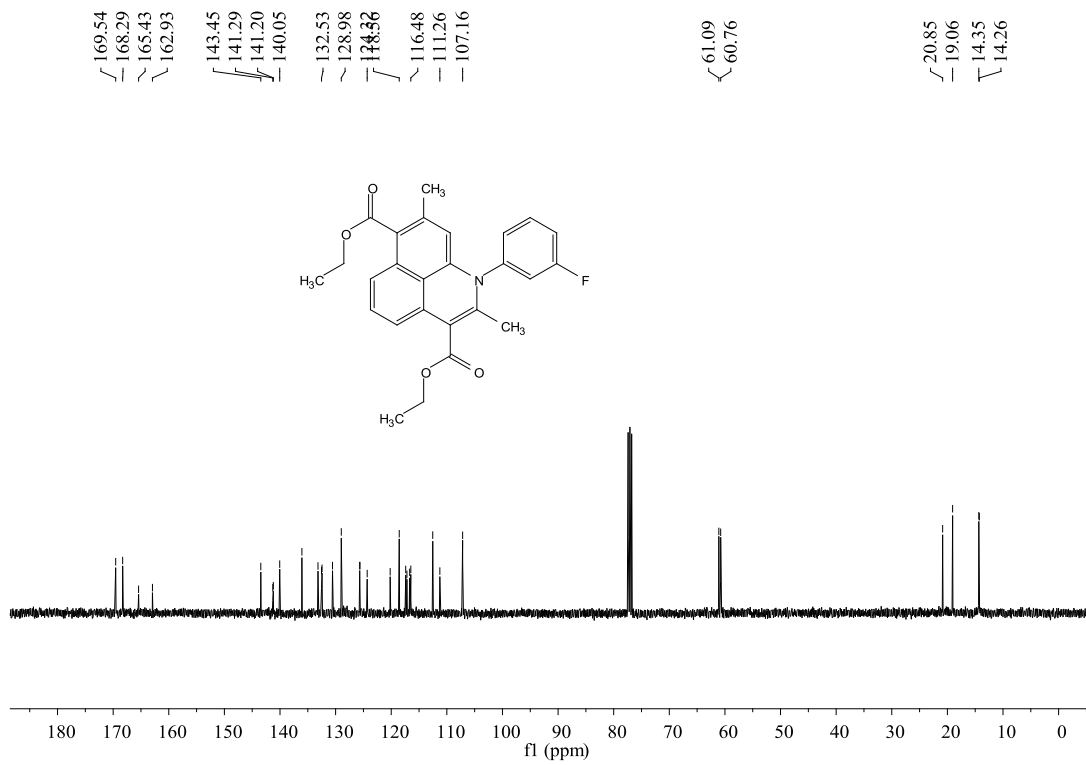
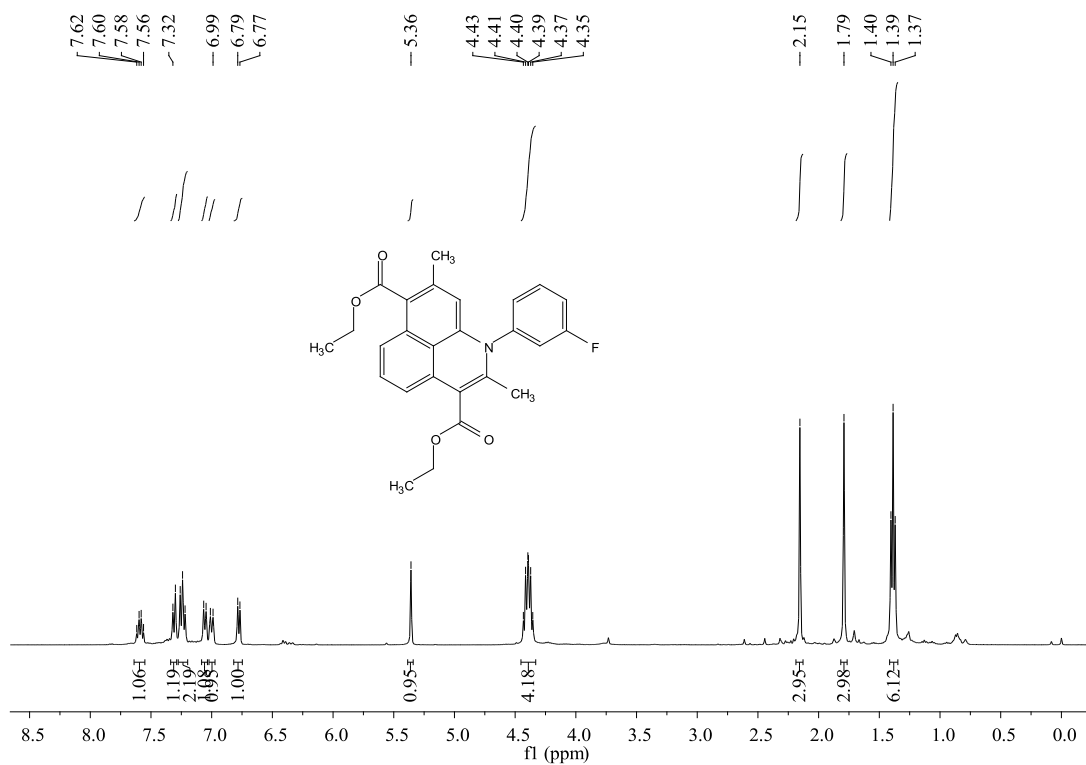
61.06  
60.73

29.69  
20.84  
19.21  
14.34  
14.26

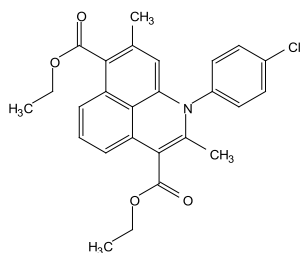
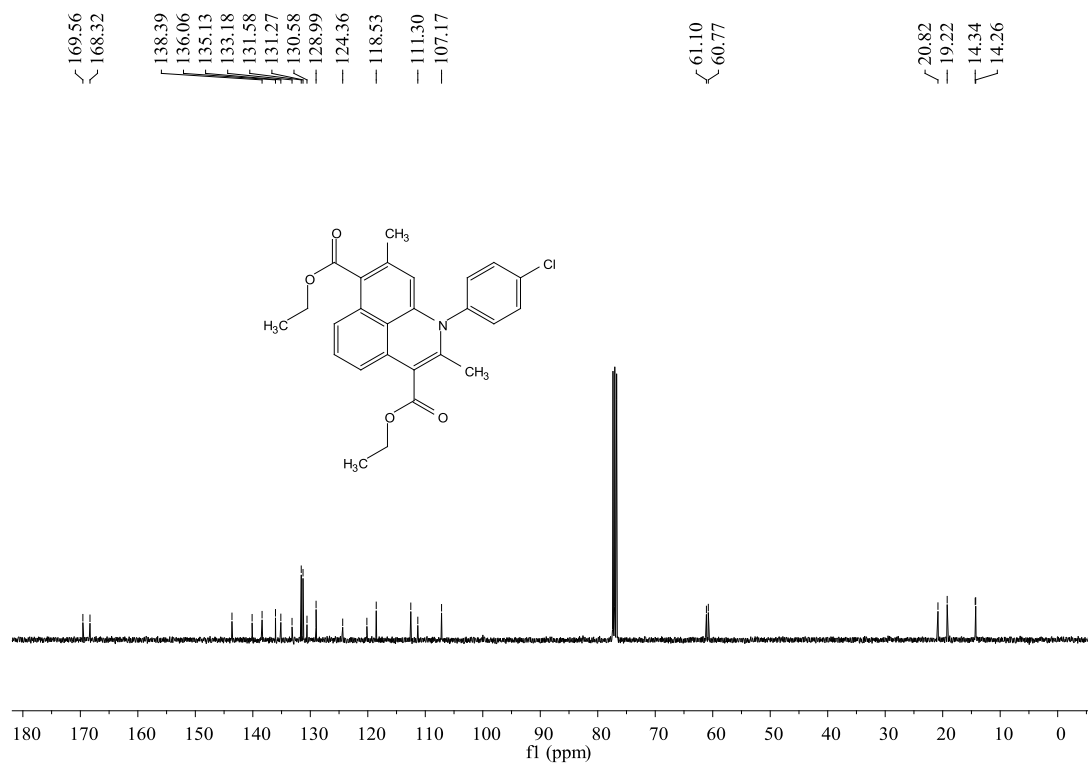
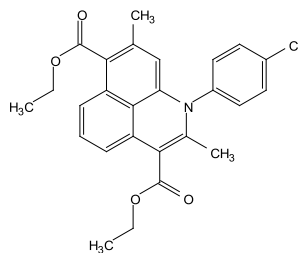
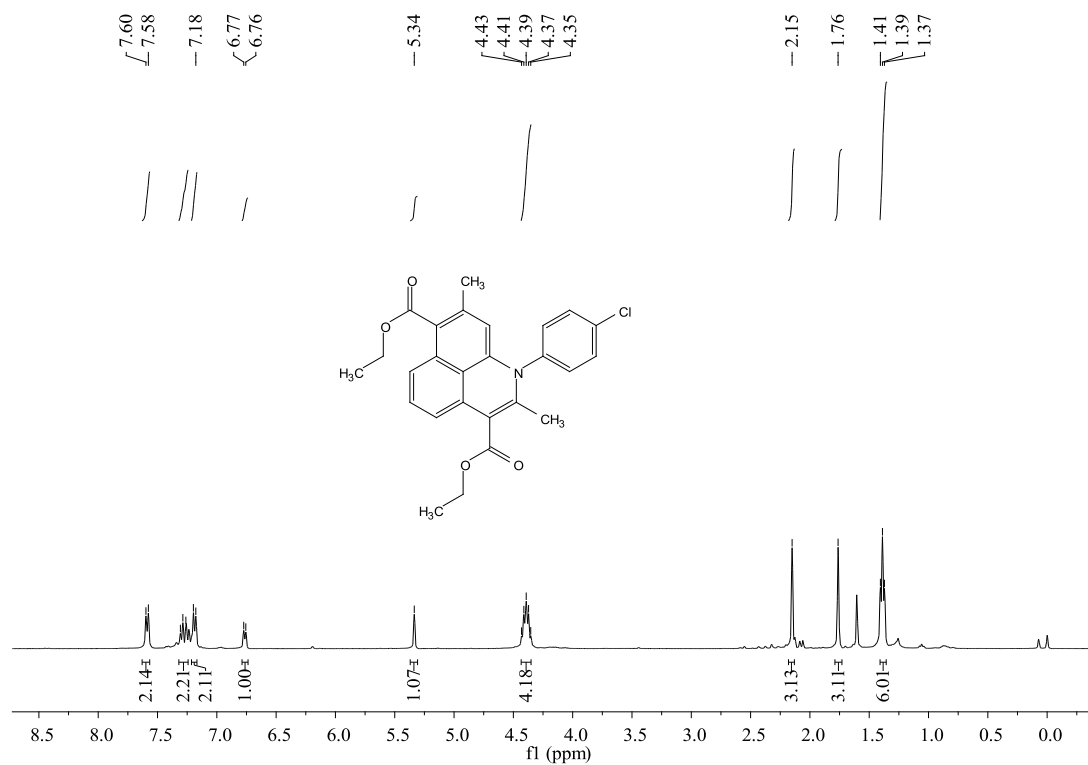




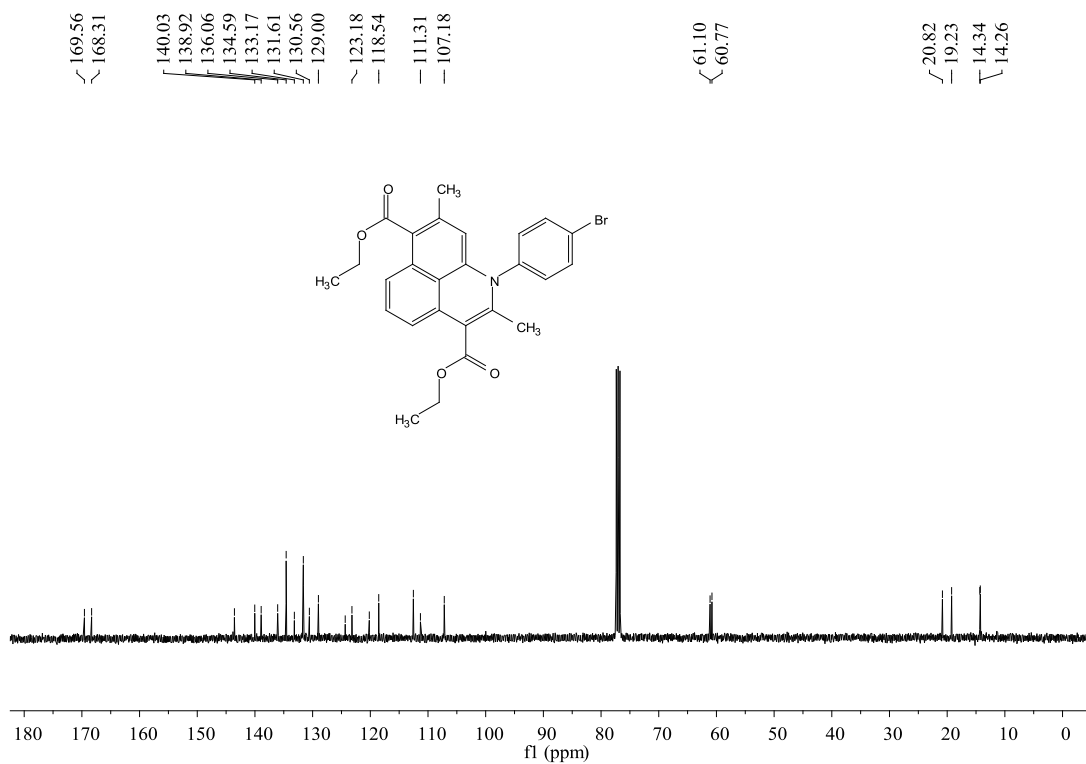
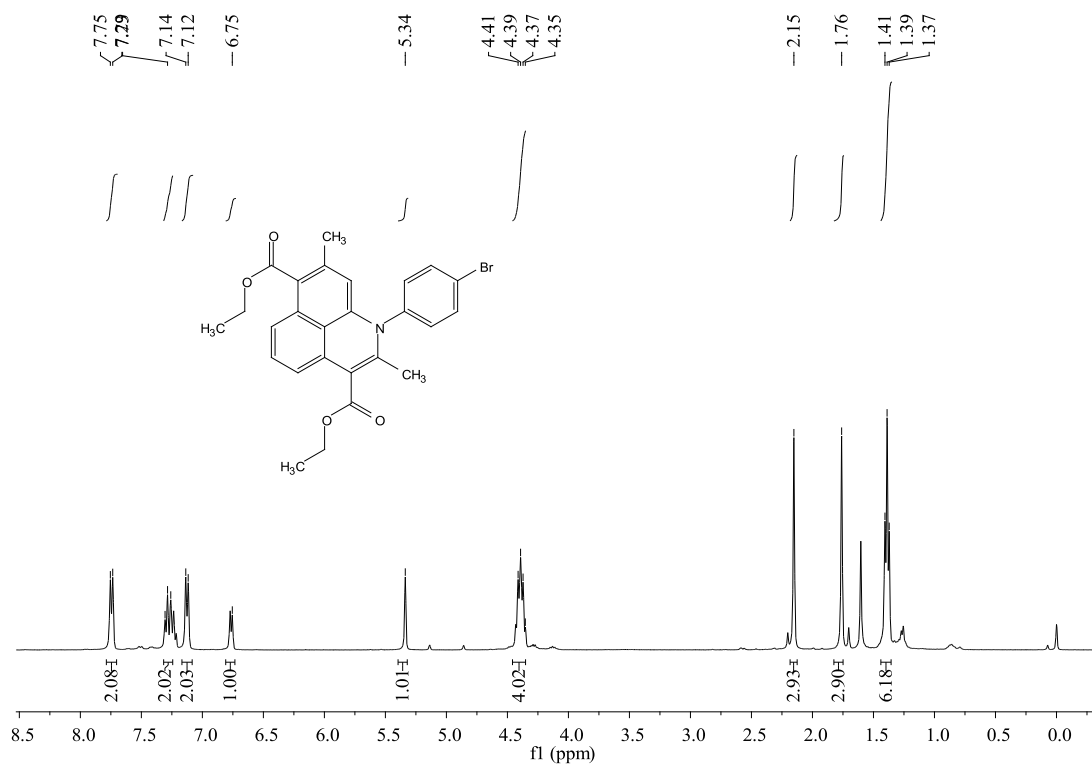
18) Diethyl 1-(3-fluorophenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate  
**(3q)** (Using CDCl<sub>3</sub> as solvent)



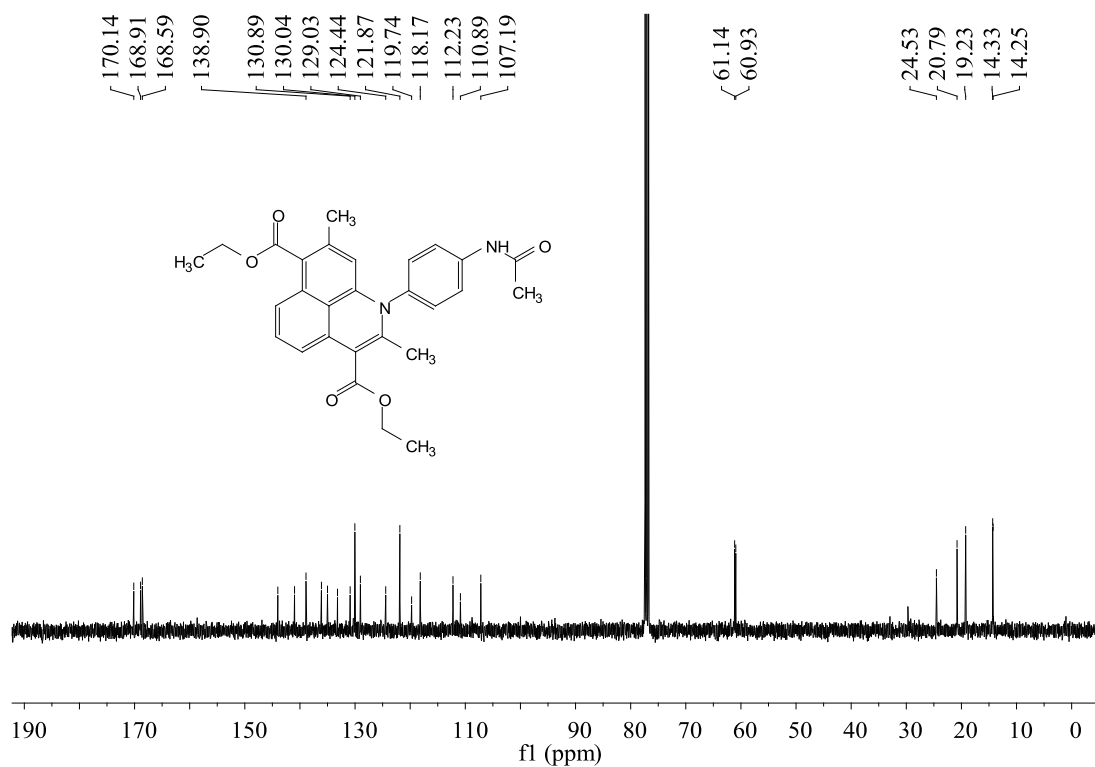
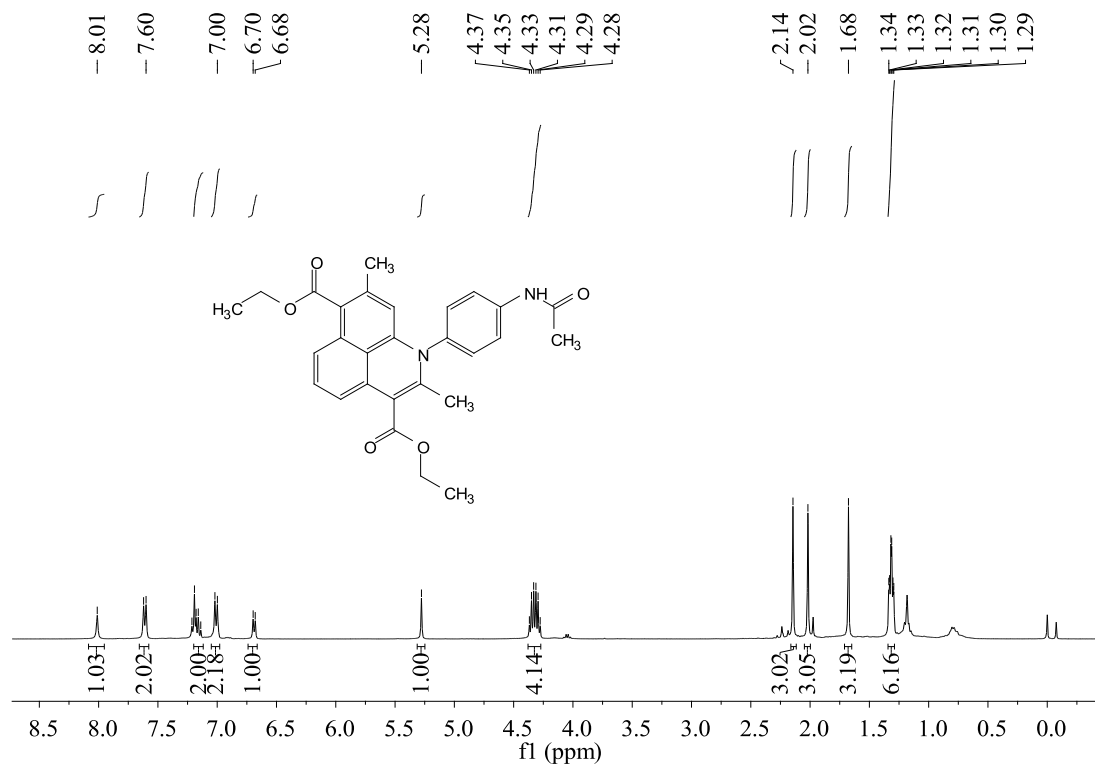
19) Diethyl 1-(4-chlorophenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate  
**(3r)** (Using CDCl<sub>3</sub> as solvent)



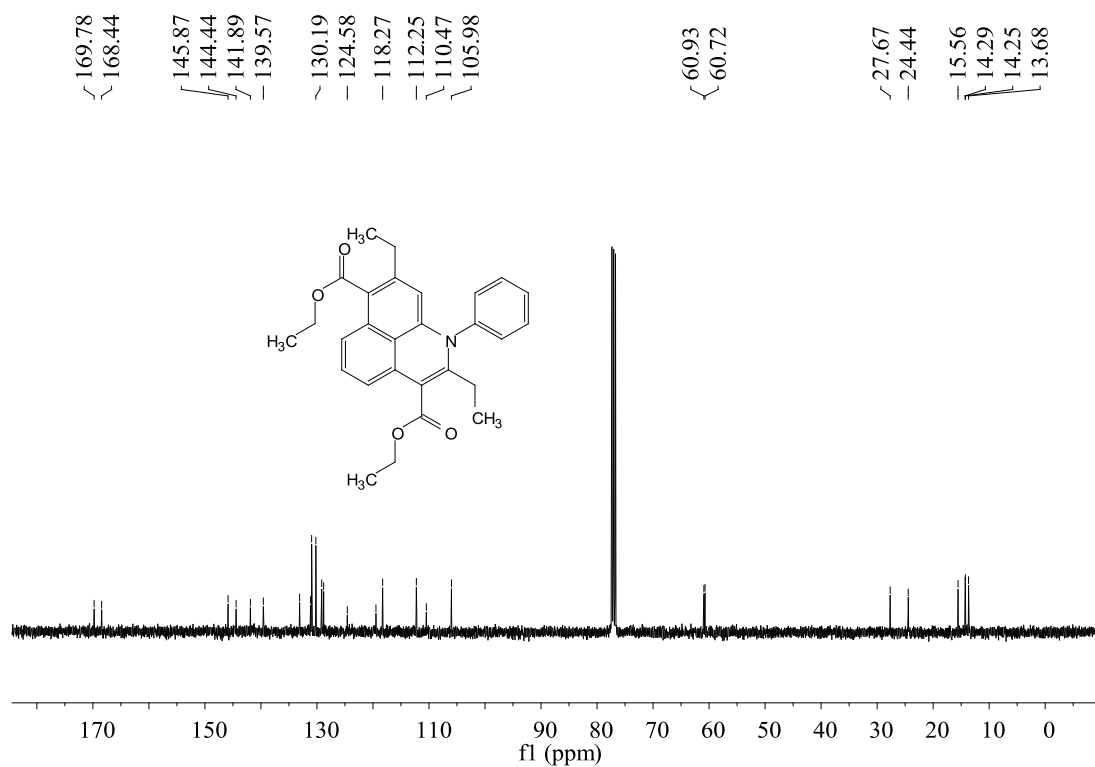
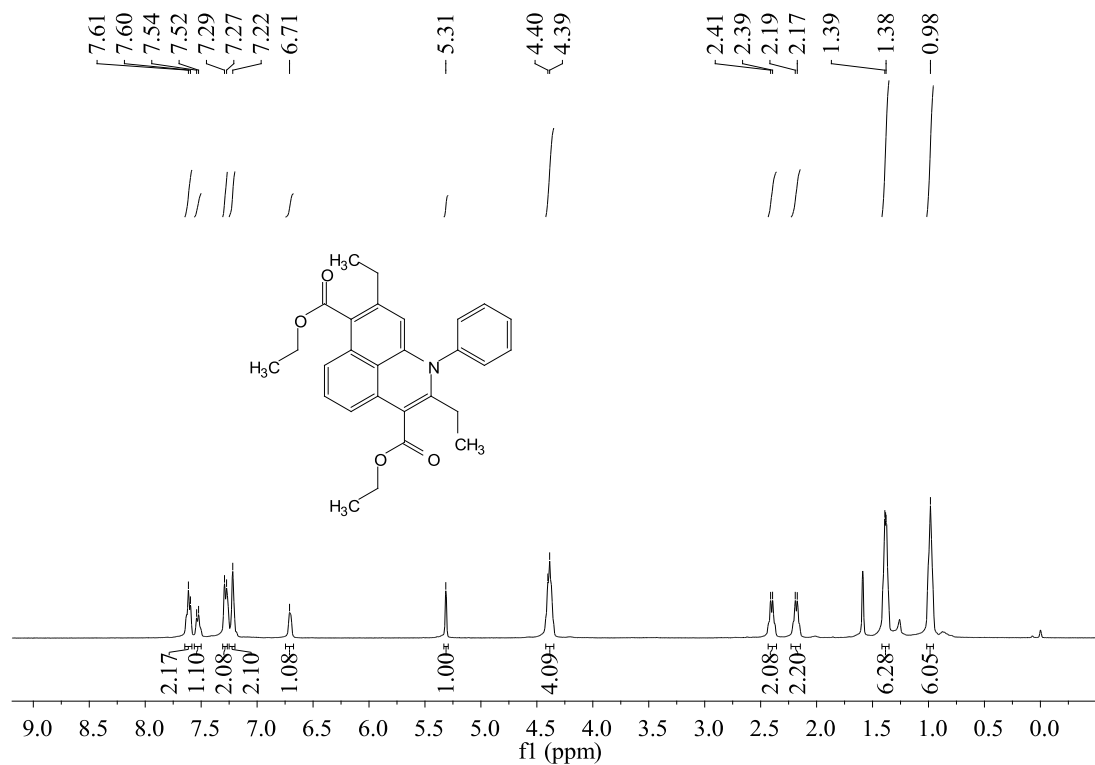
20) Diethyl 1-(4-bromophenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate  
**(3s)** (Using CDCl<sub>3</sub> as solvent)



21) Diethyl 1-(4-acetamidophenyl)-2,8-dimethyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (3u)  
 (Using CDCl<sub>3</sub> as solvent)

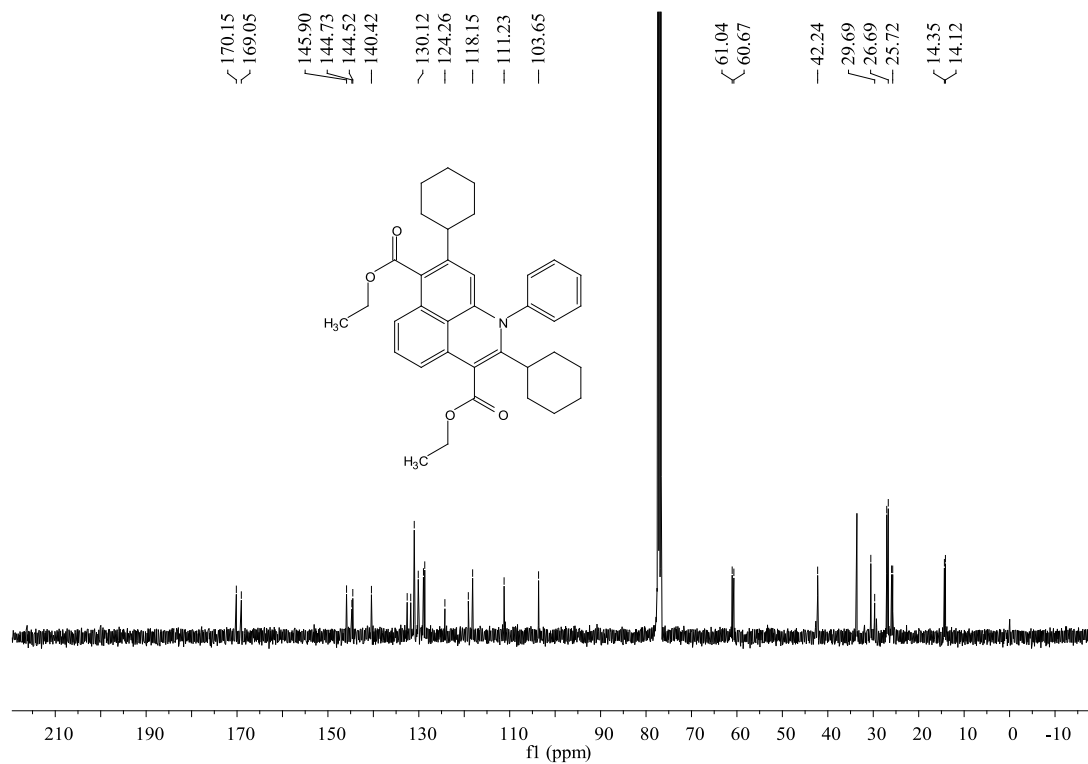
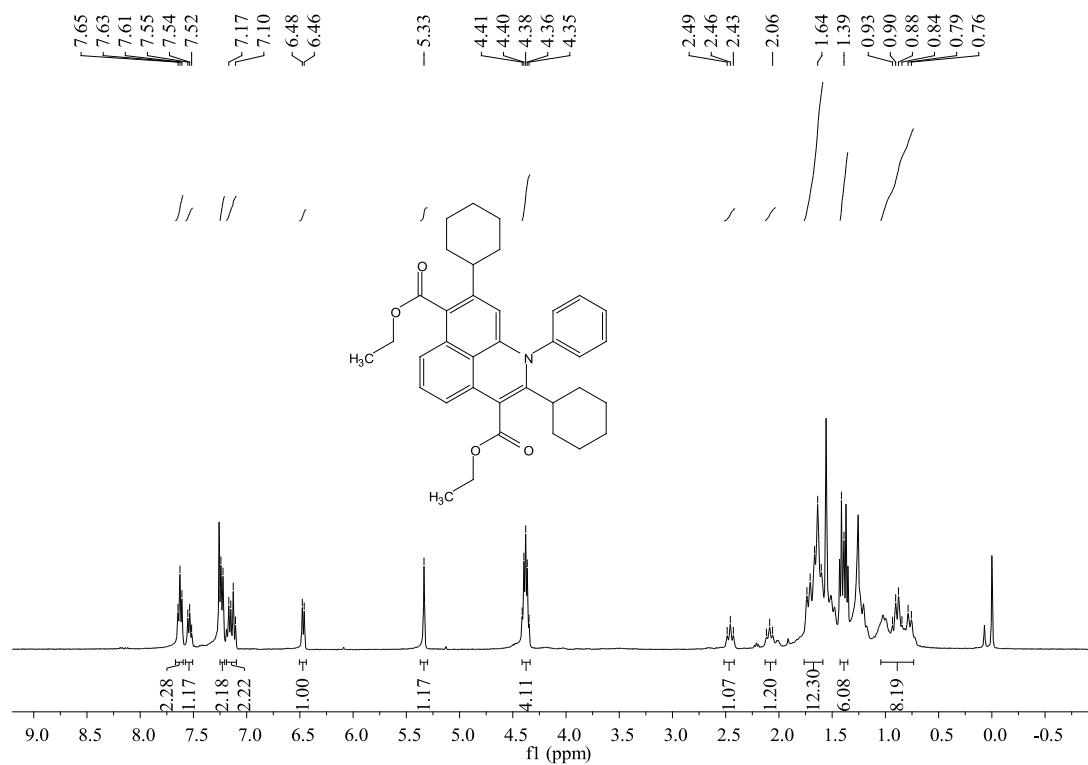


22) Diethyl 2,8-diethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3w**) (Using CDCl<sub>3</sub> as solvent)

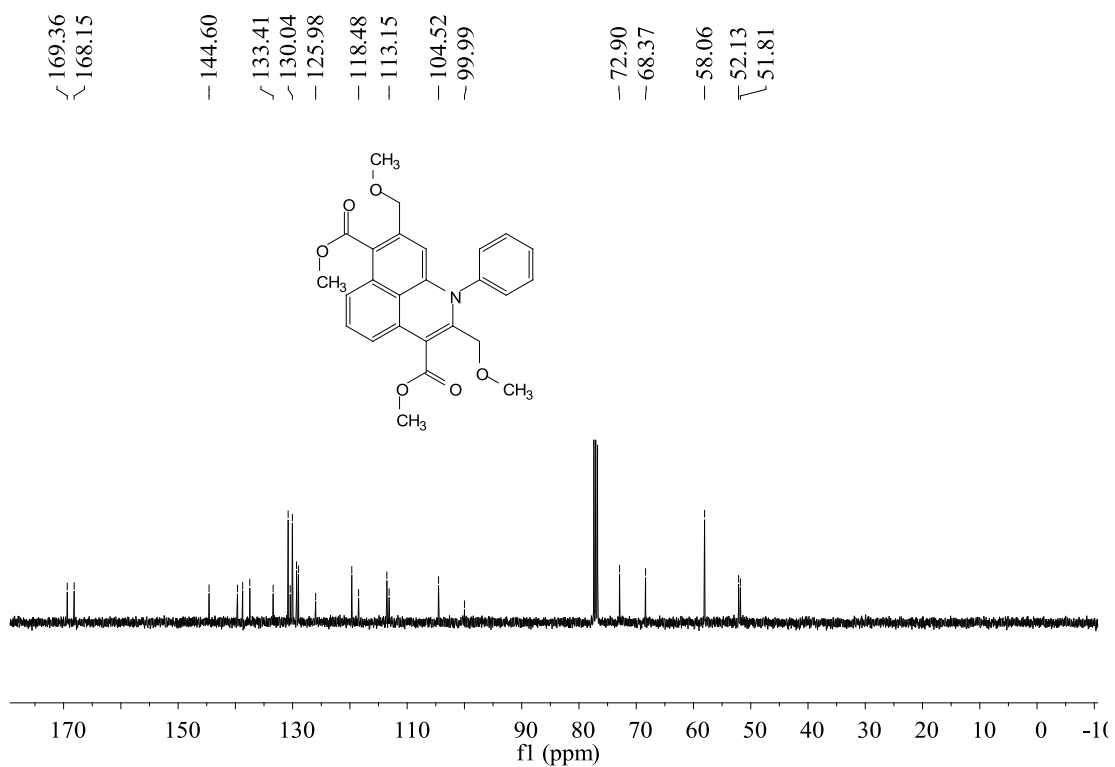
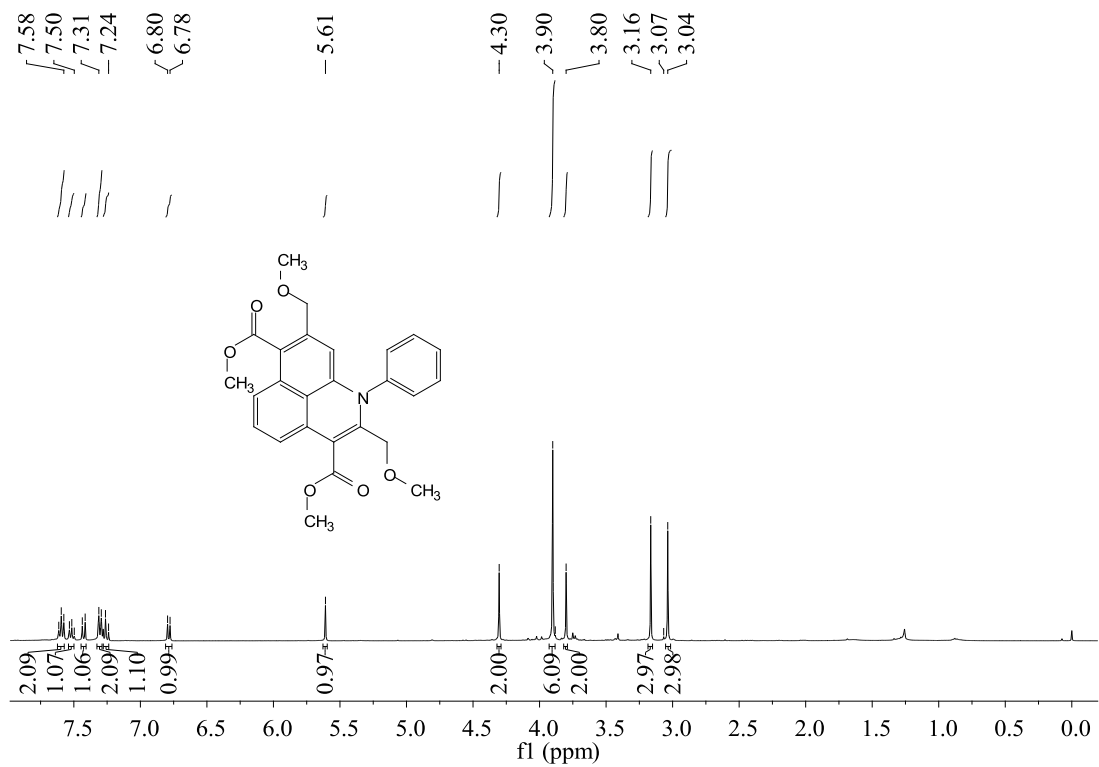


23) Diethyl 2,8-dicyclohexyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate

(**3x**) (Using CDCl<sub>3</sub> as solvent)

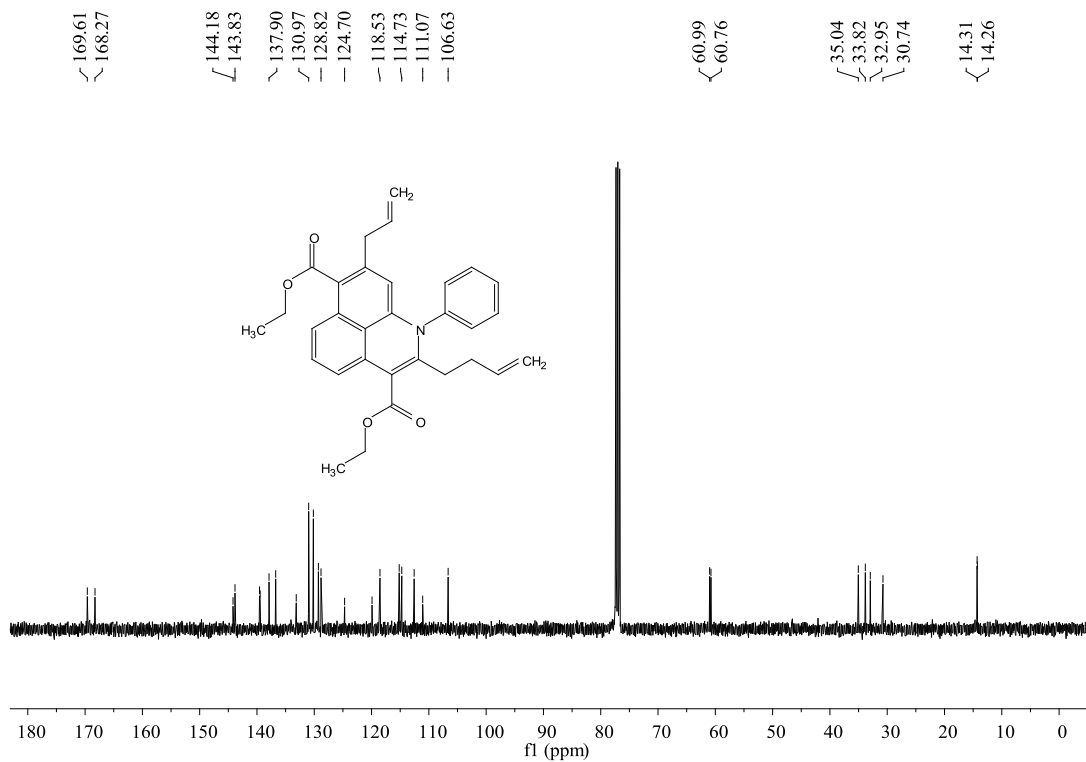
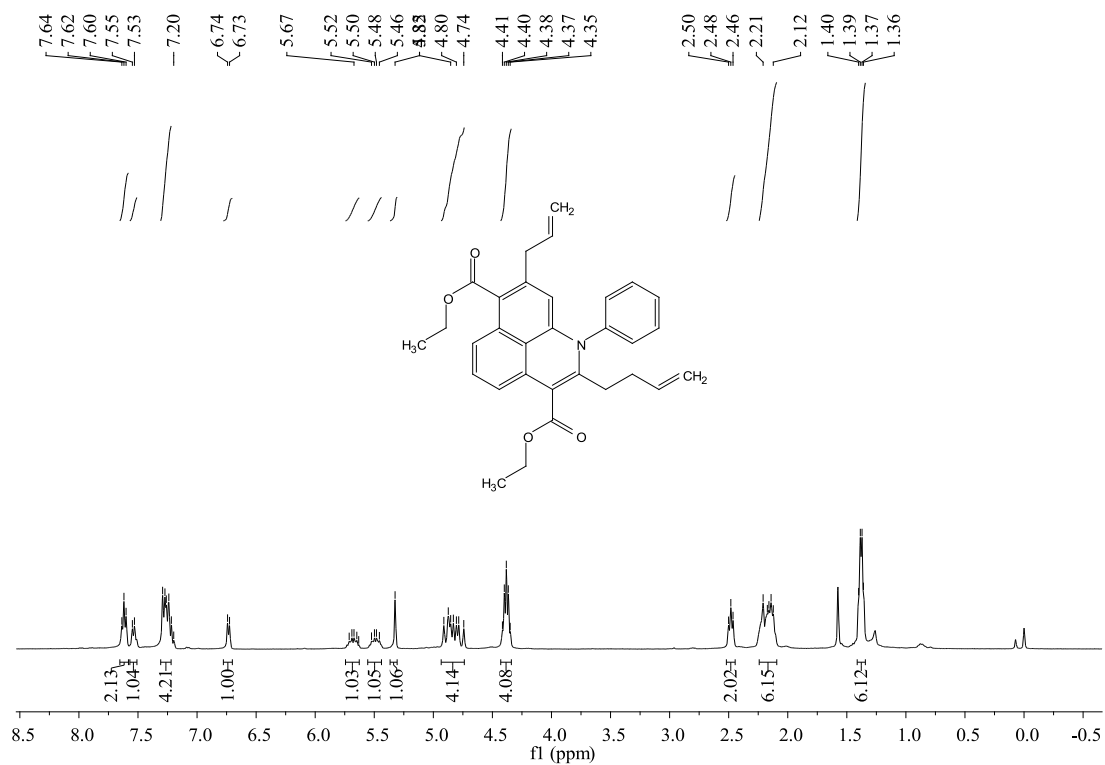


24) Dimethyl 2,8-bis(methoxymethyl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate (**3y**)  
 (Using CDCl<sub>3</sub> as solvent)



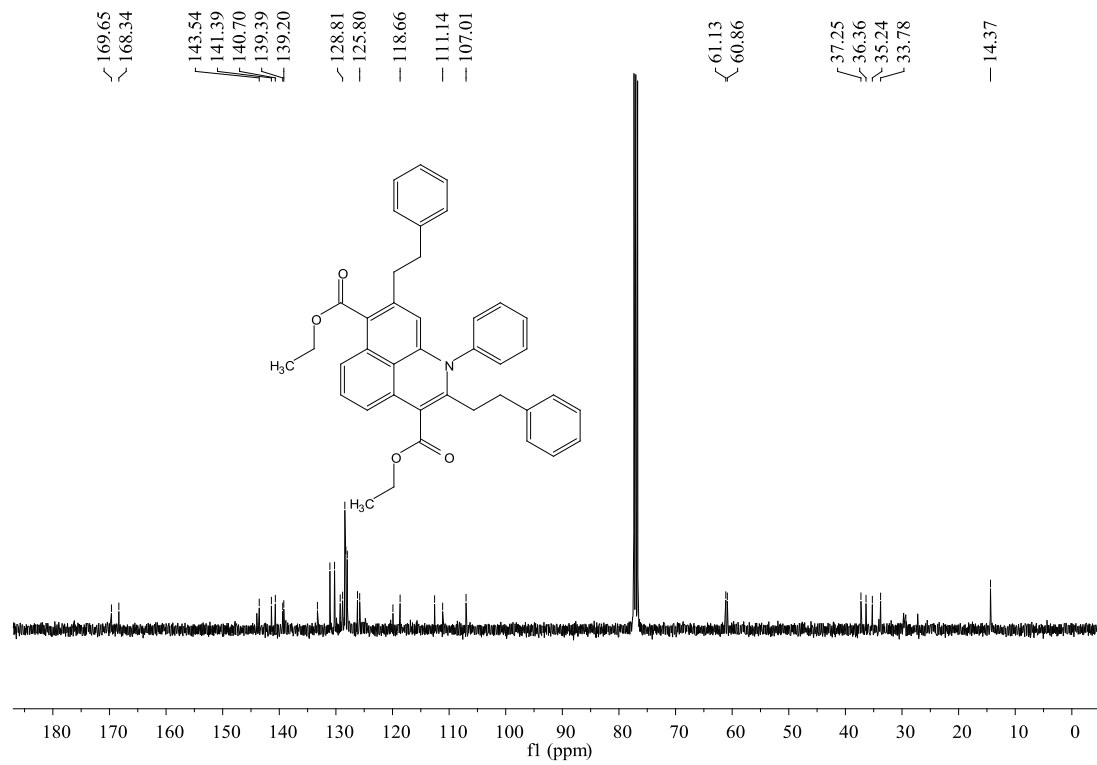
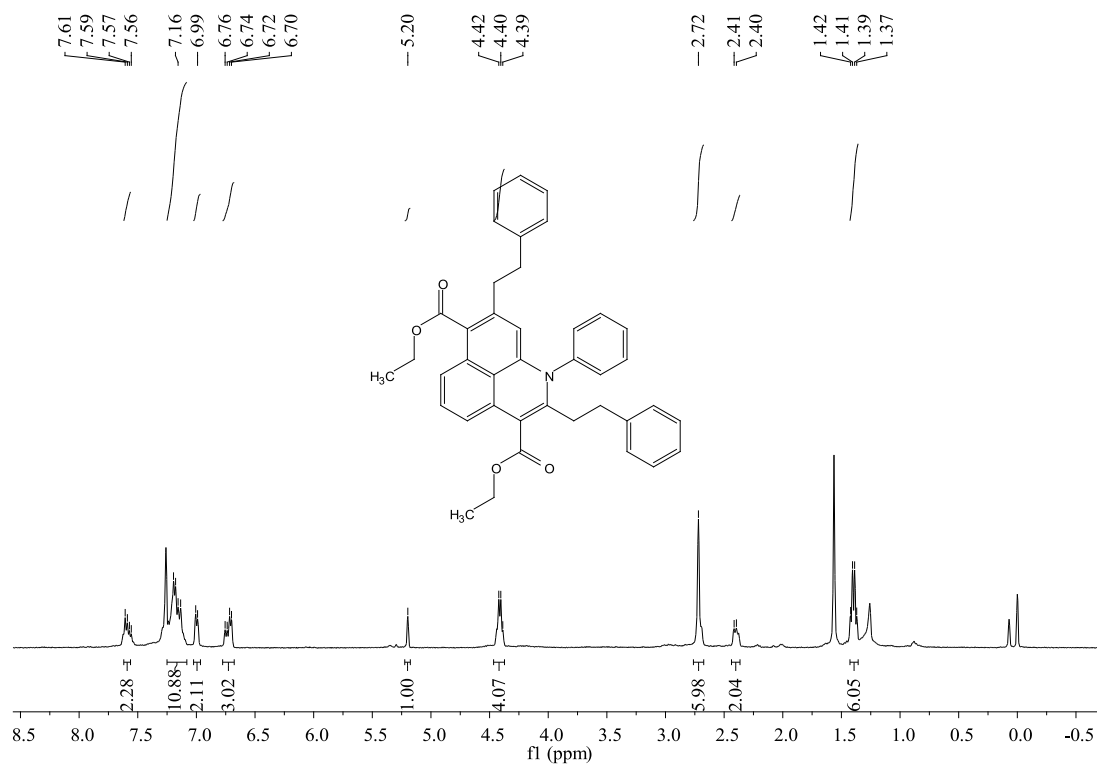
25) Diethyl 8-allyl-2-(but-3-en-1-yl)-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate

(3z) (Using CDCl<sub>3</sub> as solvent)

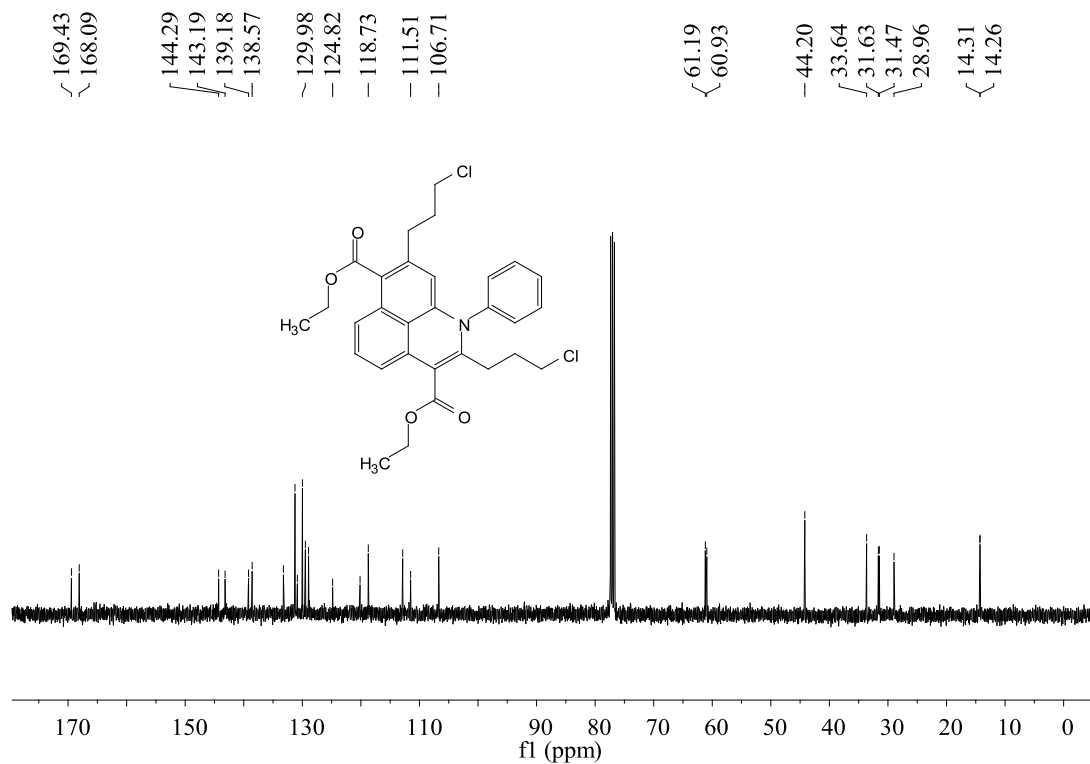
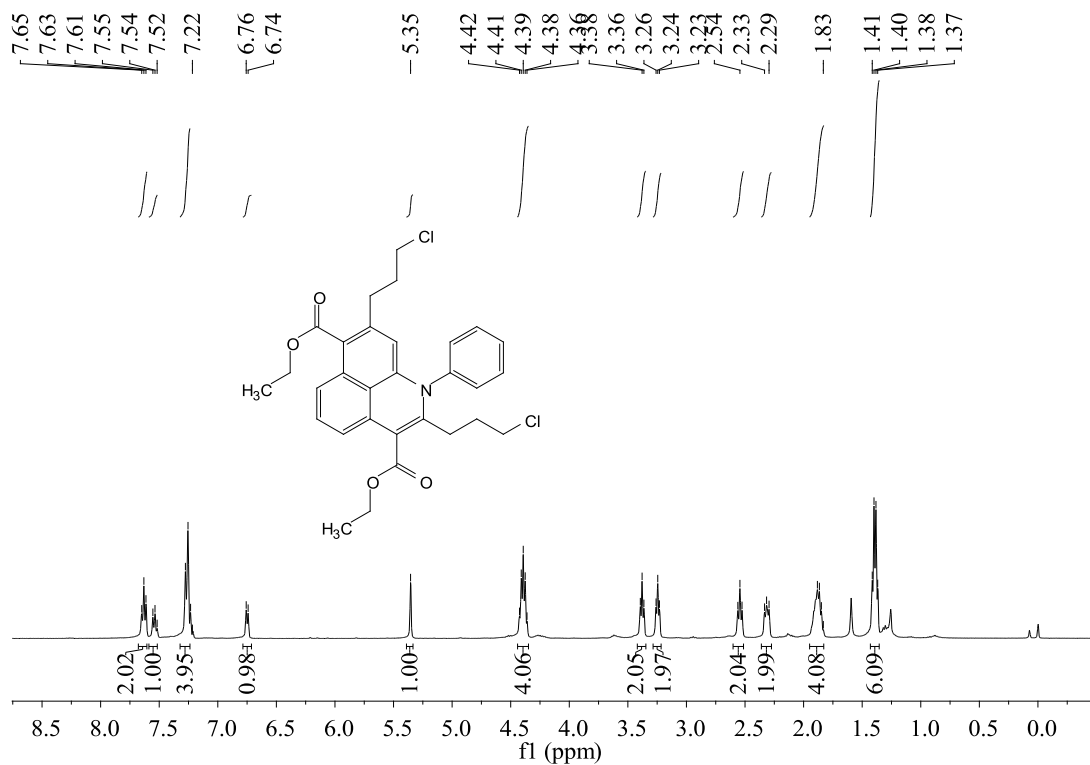




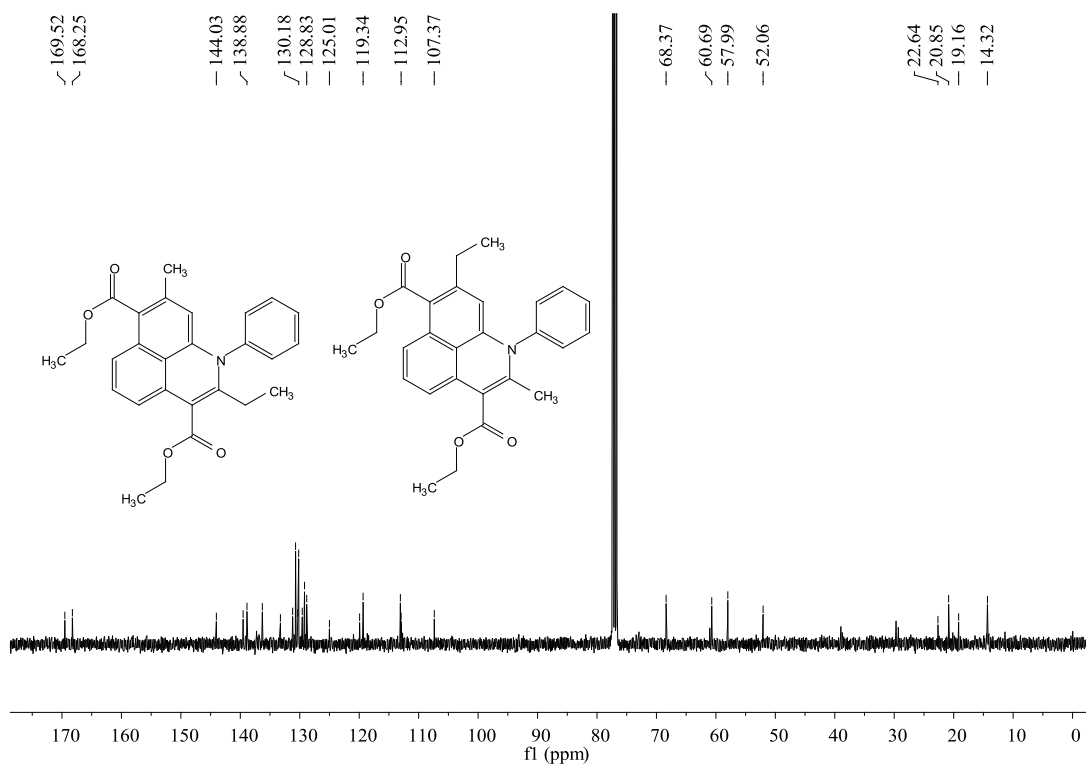
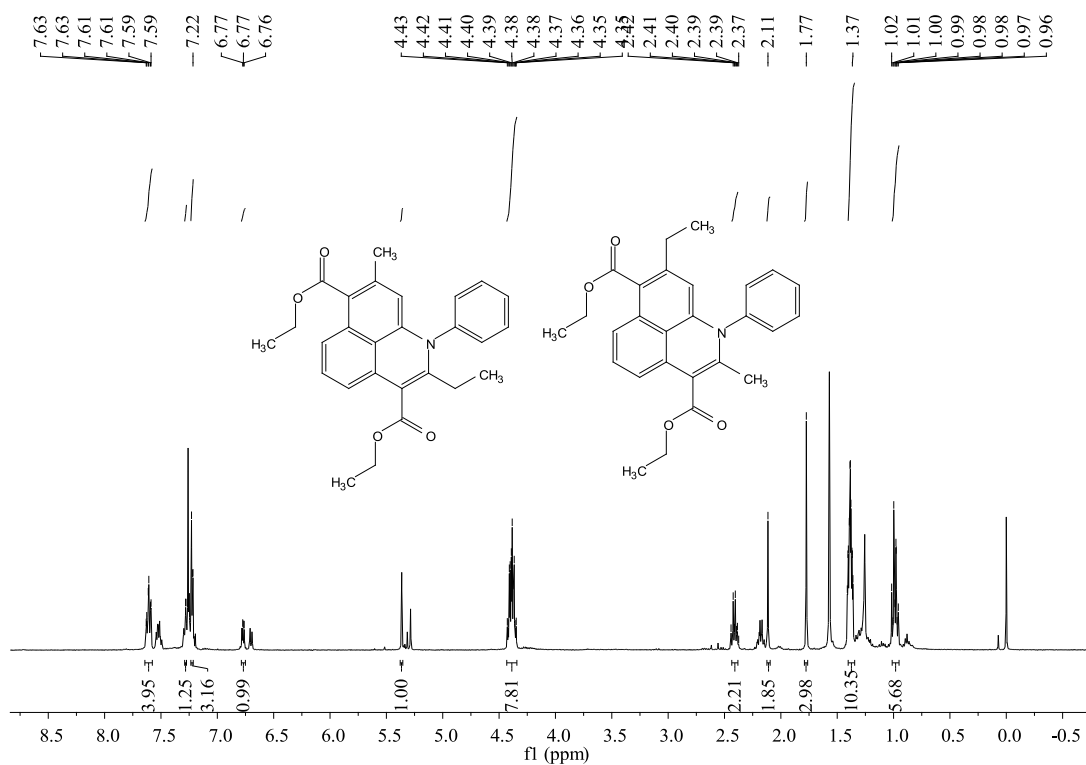
26) Diethyl 2,8-diphenethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3z-1**) (Using CDCl<sub>3</sub> as solvent)



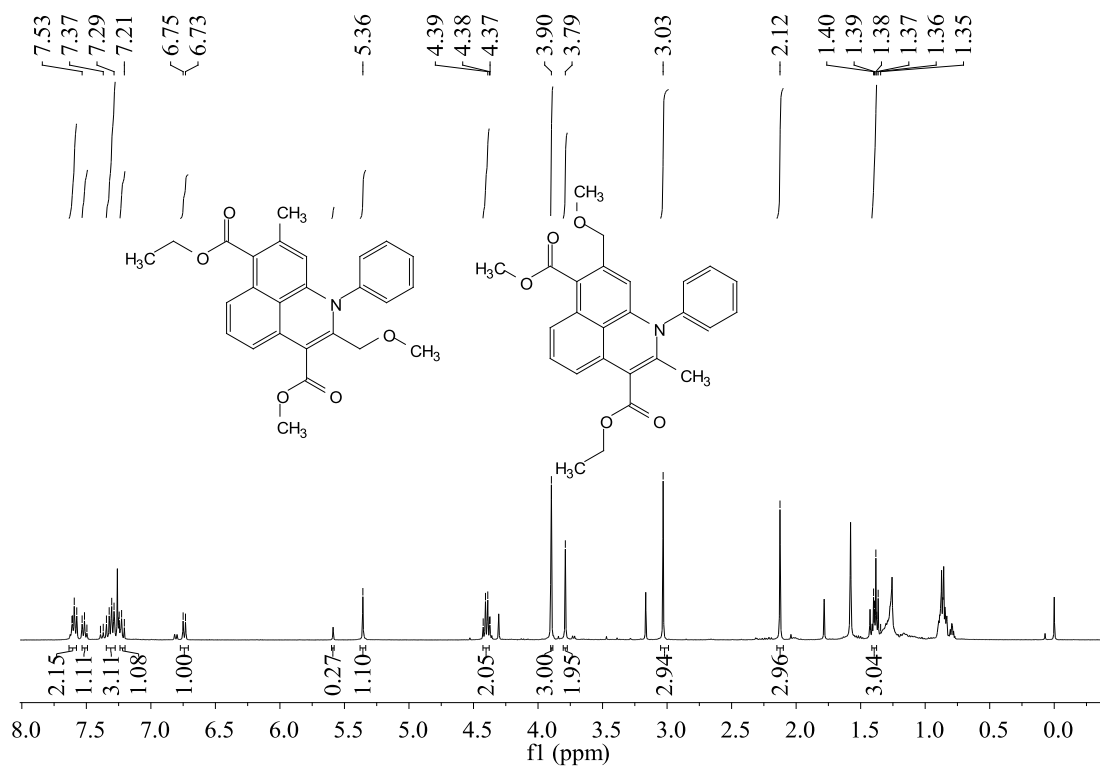
27) Diethyl 2,8-bis(3-chloropropyl)-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3z-2**)  
 (Using CDCl<sub>3</sub> as solvent)

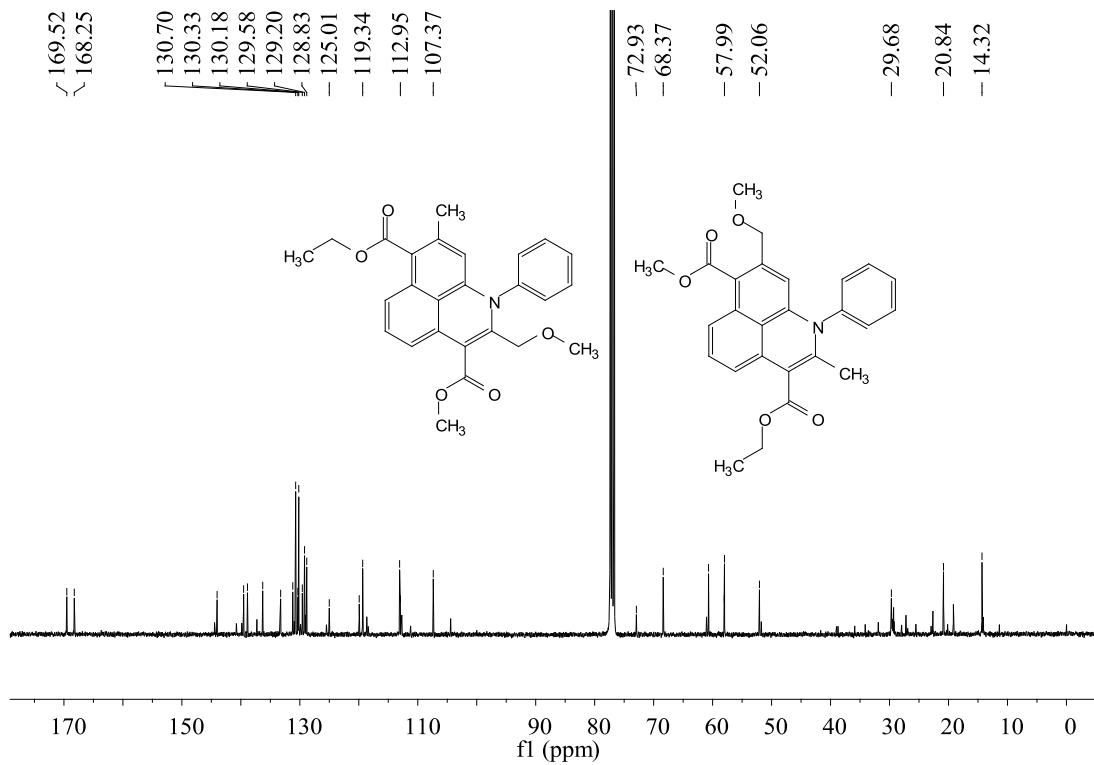


28) Diethyl 2-ethyl-8-methyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3aa**)  
 diethyl 8-ethyl-2-methyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3ab**) (Using CDCl<sub>3</sub>  
 as solvent)

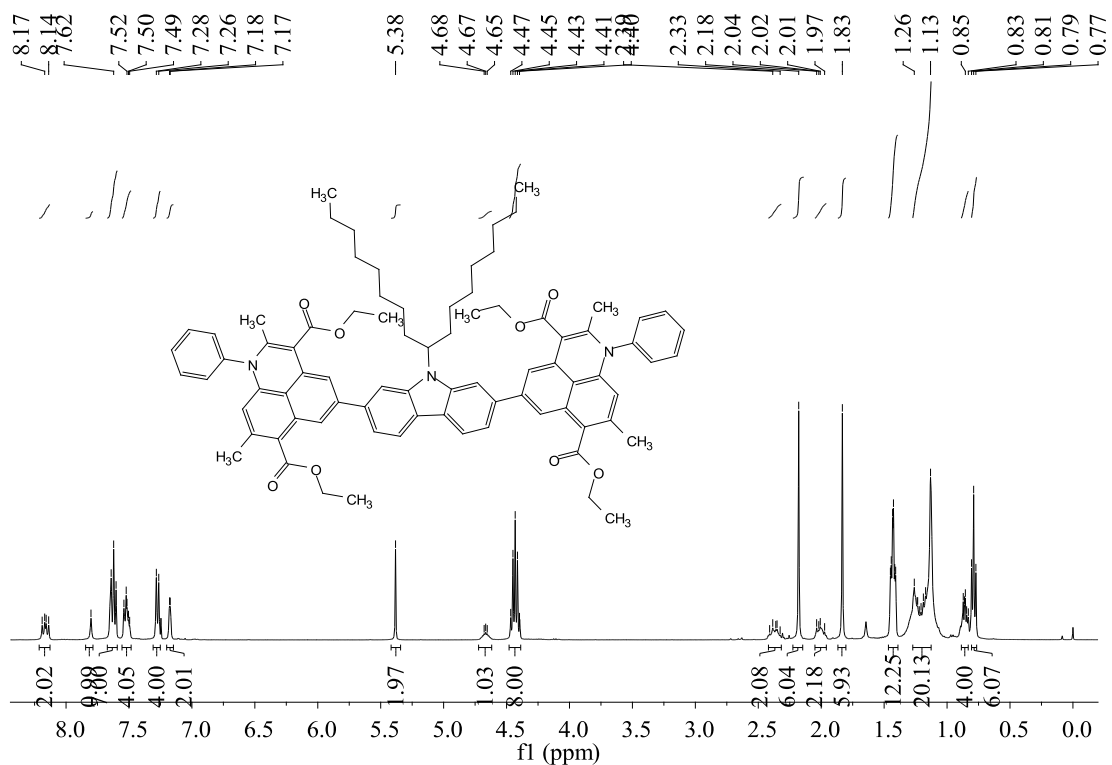


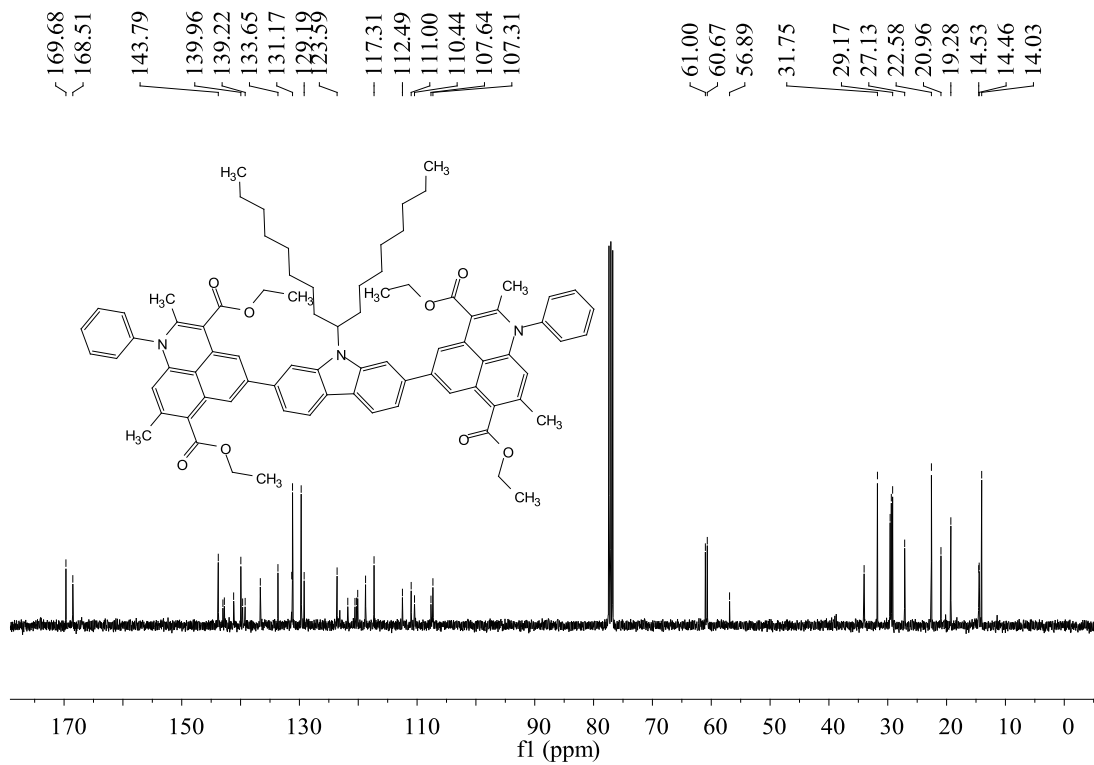
29) 7-Ethyl 3-methyl 2-(methoxymethyl)- 8-methyl-1-phenyl-1*H*- benzo[de]quinoline-3,7-dicarboxylate (**3ac**) and 3-ethyl 7-methyl 8-(methoxymethyl)-2-methyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate (**3ad**) (Using CDCl<sub>3</sub> as solvent)



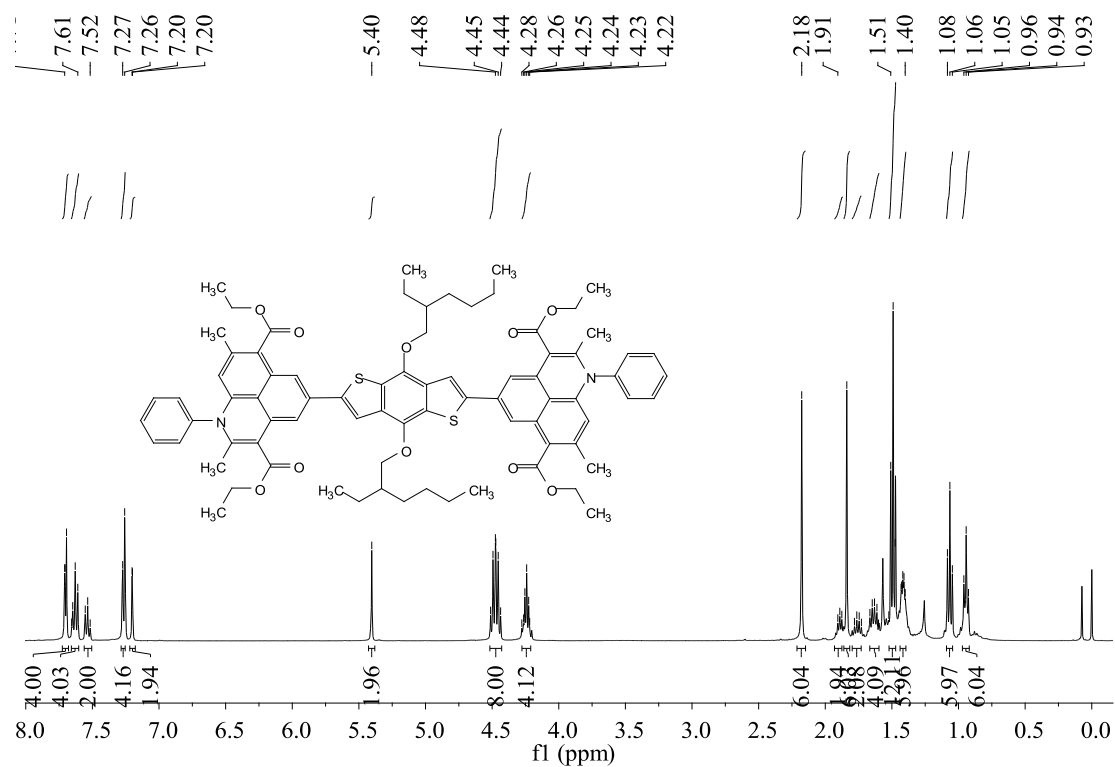


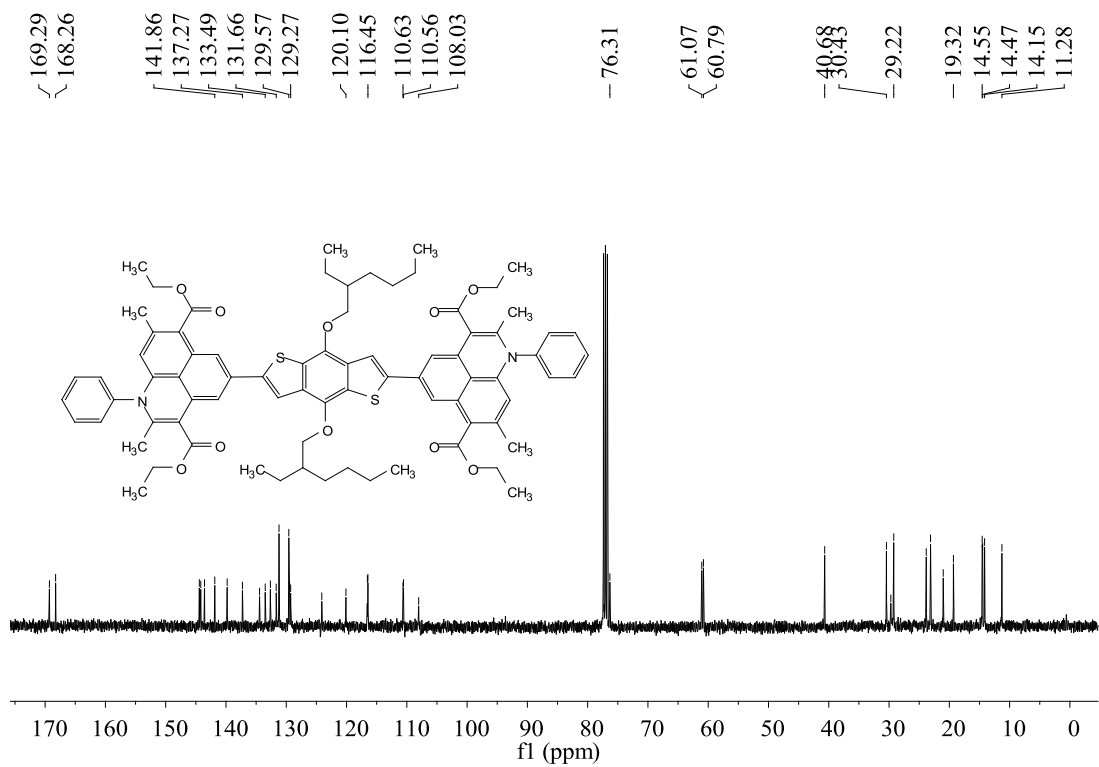
30) Tetraethyl 5,5'-(9-(heptadecan-9-yl)-9H-carbazole-2,7-diyl)bis(2,8-dimethyl-1-phenyl-1H-benzo[de]quinoline-3,7-dicarboxylate) (5) (Using CDCl<sub>3</sub> as solvent)



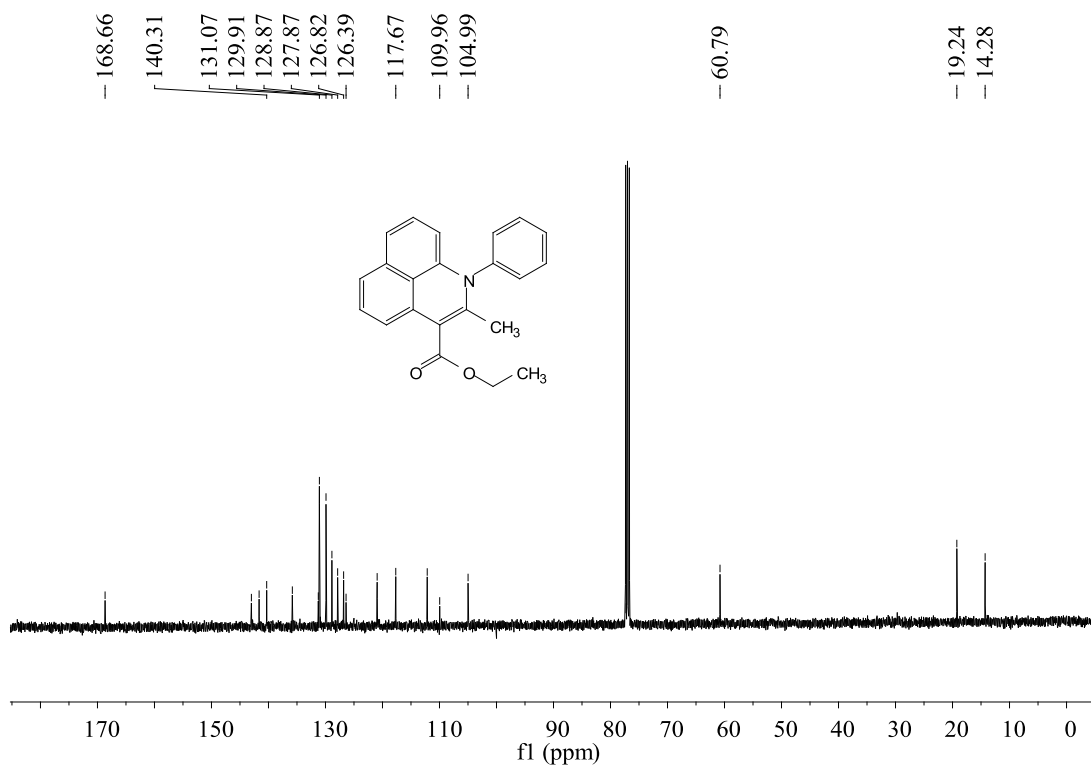
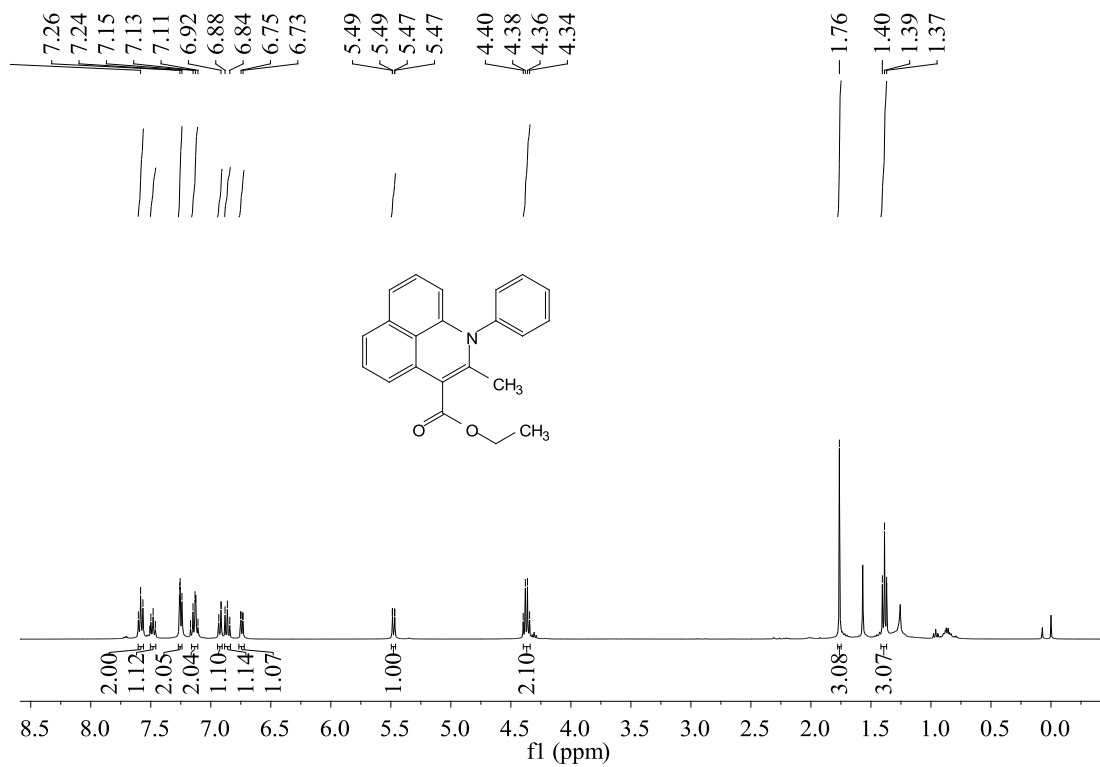


31) Tetraethyl 5,5'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophene-2,6- diyl) bis(2,8-dimethyl-1-phenyl-1*H*-benzo[de]quinoline-3,7-dicarboxylate) (**7**) (Using CDCl<sub>3</sub> as solvent)





32) Ethyl 2-methyl-1-phenyl-1*H*-benzo[de]quinoline-3-carboxylate (**8**) (Using CDCl<sub>3</sub> as solvent)





33) Ethyl 2,5-dimethyl-4-(phenylamino)-1-naphthoate (**9**) (Using CDCl<sub>3</sub> as solvent)

