Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrochemical Ruthenium-Catalyzed Alkyne Annulations by C−H/Het−H Activation of Aryl Carbamates or Phenols in Protic Media

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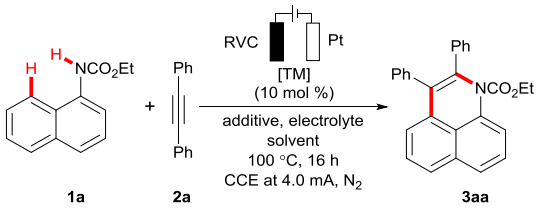
General Remarks

Catalytic reactions were carried out in undivided electrochemical cells under a N_2 atmosphere using pre–dried glassware, if not noted otherwise. Naphthalene carbamates **1**[1] and internal alkynes **2b-2h**[2] were synthesized according to previously described methods. All the other chemicals were used as obtained by commercial sources. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and RVC electrodes (10 mm × 15 mm × 6 mm, SIGRACELL®GFA 6 EA) were connected using stainless steel adapters. Electrolysis was conducted using an AXIOMET AX3003P potentiostat in constant current mode. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR. Chromatography: Merck silica gel 60 (40–63 μm). NMR: Spectra were recorded on a Varian Unity 300, Mercury 300, Inova 500 or Bruker Avance III 300, Bruker Avance III HD 400 and Bruker Avance III HD 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS- and ESI-MSspectra were recorded with Finnigan MAT 95, 70 eV and Finnigan LCQ; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected. Fluorescence excitation and emission data in solution were recorded on a Jasco® FP-8500 spectrofluorometer. The widths of excitation and emission slits were held constant at 2.5 and 5.0 nm, respectively. The scan speed was adjusted to 500 nm/min. The concentration in CH_3CN is given for each sample and the excitation wavelengths were selected at the strongest signal.

Optimization studies

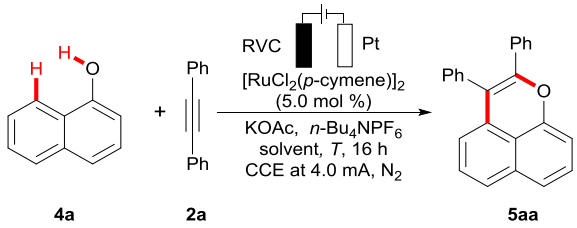
Table S-1 Optimization of the Electrooxidative Ruthenium-Catalyzed C–H/N–H Activation with Aryl Carbamates **1a**.



Entry	[TM]	Solvent	Electrolyte	Addtive	FE [%]	Yield
1	$[RuCl_2(p\text{-cymene})]_2$	DMF	$n\text{-Bu}_4NPF_6$	KOAc	9	35
2	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH	$n\text{-Bu}_4NPF_6$	KOAc	13	51
3	$[Cp^*RhCl_2]_2$	*t*-AmOH	$n\text{-Bu}_4NPF_6$	KOAc	---	<5
4	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH/H_2O (3/1)	$n\text{-Bu}_4NPF_6$	KOAc	15	61
5	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH/H_2O (3/1)	---	KOAc	7	27
6	$[RuCl_2(p\text{-cymene})]_2$	DMF/H_2O (3/1)	$n\text{-Bu}_4NPF_6$	KOAc	7	28
7	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NPF_6$	NaOPiv	14	57
8	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NPF_6$	Na_2CO_3	3	12
9	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NOAc$	KOAc	15	59
10	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NBF_4$	KOAc	15	58
11	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NCl$	KOAc	14	57
12	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	16	65
13	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NNO_3$	KOAc	12	47
14	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	Ferrocene	KOAc	11	43
15	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	23	36[b]
16	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	39	77[c]
17	**$[RuCl_2(p\text{-cymene})]_2$**	***t*-AmOH /H_2O (3/1)**	***n*-Bu_4NClO_4**	**KOAc**	**37**	**82[d]**
18	---	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	---	<5
19	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	---	31[e]
20	$[RuCl_2(p\text{-cymene})]_2$	*t*-AmOH /H_2O (3/1)	$n\text{-Bu}_4NClO_4$	KOAc	---	36[f]

[a] Reaction conditions: **1a** (0.60 mmol), **2a** (0.30 mmol), [TM] (10 mol %), additive (0.60 mmol), electrolyte (0.18 mmol), solvent (4.0 mL), 100 °C, 16 h, under N_2, constant current (CCE) at 4.0 mA, undivided cell, RVC anode (1.0 × 1.5 cm), Pt cathode (1.0 × 1.5 cm), isolated yield. [b] 10 mA. 2.5 h. [c] 2.0 mA, 16 h. [d] 1.5 mA, 24 h. [e] Without current, 24 h. [f] Without current, under air, 24 h.

Table S-2 Optimization of the Electrooxidative Ruthenium-Catalyzed C–H/O–H Activation with Naphthol **4a**.



Entry	[TM] (mol %)	Solvent	Electrolyte	T [°C]	FE [%]	Yield [%][a]
1	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*t*-AmOH/H_2O (3/1)	---	90	15	36
2	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*t*-AmOH	*n*-Bu_4NPF_6	90	25	59
3	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*p*-xylene	*n*-Bu_4NPF_6	90	28	68
4	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	CH_3CN	*n*-Bu_4NPF_6	90	14	33
5	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	GVL	*n*-Bu_4NPF_6	90	6	15
6	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	MeOH	---	70	5	11
7	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	TFE	---	70	---	<5
8	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*m*-xylene/*t*-AmOH (3/1)	*n*-Bu_4NPF_6	100	29	70
9	**$[RuCl_2(p\text{-cymene})]_2$ (5.0)**	***m*-xylene/*t*-AmOH (1/1)**	***n*-Bu_4NPF_6**	**100**	**35**	**84**
10	$[RuCl_2(p\text{-cymene})]_2$ (2.5)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	32	77
11	$[Ru(MesCO_2)_2(p\text{-cymene})]$ (5.0)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	32	76
12	$[Cp^*IrCl_2]_2$ (2.5)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	---	<5
13	$[Cp^*RhCl_2]_2$ (2.5)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	8	20
14	$Cp^*Co(CO)I_2$ (10)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	---	<5
15	---	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	---	<5
16	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	---	8[b]
17	$[RuCl_2(p\text{-cymene})]_2$ (5.0)	*m*-xylene/*t*-AmOH (1/1)	*n*-Bu_4NPF_6	100	---	29[c]

[a] Reaction conditions: **4a** (1.0 mmol), **2a** (0.50 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), KOAc (1.0 mmol), electrolyte (0.30 mmol), solvent (3.0 mL), 16 h, under N_2, constant current (CCE) at 4.0 mA, undivided cell, RVC anode (1.0 × 1.5 cm), Pt cathode (1.0 × 1.5 cm), isolated yield. [b] Without current. [c] Without current, under air.

General Procedures for the Electrooxidative Ruthenium(II)-Catalyzed C–H/Het–H Annulations

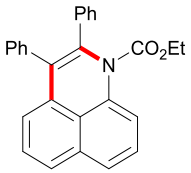
General Procedure (GP1) for the Ruthenium(II)-Catalyzed C–H/N–H Annulation with Aryl Carbamates 1.

The electrolysis was carried out in an undivided cell with a RVC anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Carbamate **1** (0.60 mmol, 2.0 equiv), alkyne **2** (0.30 mmol, 1.0 equiv), KOAc (59 mg, 0.60 mmol, 2.0 equiv), *n*-Bu_4NClO_4 (62 mg, 0.18 mmol, 0.60 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5.0 mol %) were dissolved in *t*-AmOH/H_2O (3/1, 4.0 mL) under a N_2 atmosphere. Electrolysis was performed at 100 °C with a constant current of 1.5 mA which was then maintained for 24 h. At ambient temperature, the mixture was transferred to a flask and the RVC anode was washed with acetone (3×10 mL) in an ultrasonic bath. Then, silica gel (1.0 g) was added and the combined solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane or *n*-heptane/EtOAc = 40/1 to 20/1) affording the corresponding products **3**.

General Procedure (GP2) for the Ruthenium(II)-Catalyzed C–H/O–H Annulation with Naphthalol 4a.

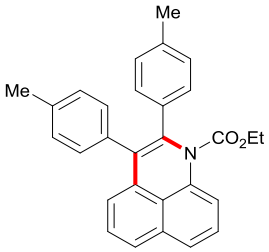
The electrolysis was carried out in an undivided cell with a RVC anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Naphthalen-1-ol (**4a**) (1.0 mmol, 2.0 equiv), alkyne **2** (0.50 mmol, 1.0 equiv), KOAc (98 mg, 1.0 mmol, 2.0 equiv), *n*-Bu_4NPF_6 (110 mg, 0.30 mmol, 0.60 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %) were dissolved in *t*-AmOH/*m*-xylene (1/1, 3.0 mL) under a N_2 atmosphere. Electrolysis was performed at 100 °C with a constant current of 4.0 mA which was then maintained for 16 h. At ambient temperature, the mixture was transferred to a flask and the RVC anode was washed with acetone (3×10 mL) in an ultrasonic bath. Then, silica gel (1.0 g) was added and the combined solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane or *n*-heptane/EtOAc = 40/1 to 30/1) affording the corresponding products **5**.

Characterization Data of Products 3 and 5



Ethyl 2,3-diphenyl-1*H*-benzo[de]quinoline-1-carboxylate (3aa)

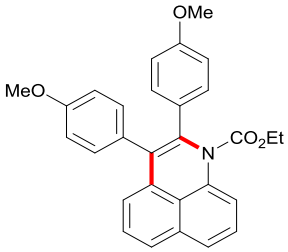
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3aa** (96.3 mg, 82%, FE: 37%) as a pale yellow solid. M. p. = 153−154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 5.5, 3.4 Hz, 1H), 7.54–7.44 (m, 3H), 7.33–7.20 (m, 4H), 7.19–7.14 (m, 4H), 7.13–7.05 (m, 3H), 6.74 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.83 (q, *J* = 7.1 Hz, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.3 (C_q), 139.2 (C_q), 136.6 (C_q), 136.6 (C_q), 136.5 (C_q), 133.7 (C_q), 131.9 (C_q), 131.0 (CH), 128.8 (CH), 128.4 (CH), 127.3 (CH), 127.1 (C_q), 126.9 (CH), 126.8 (CH), 126.6 (C_q), 126.5 (CH), 126.5 (CH), 125.1 (CH), 122.0 (CH), 119.8 (CH), 114.8 (CH), 62.7 (CH_2), 13.3 (CH_3). IR (neat): 3097, 2926, 1713, 1462, 1210, 1122, 1013, 828, 695 cm^{-1}. MS (EI) m/z (relative intensity) 392 (15) $[M+H]^+$, 391 (50) $[M+H]^+$, 347 (30), 318 (100). HR-MS (EI) m/z calcd for $C_{27}H_{21}NO_2$ $[M]^+$ 391.1572, found 391.1574. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-di-*p*-tolyl-1*H*-benzo[de]quinoline-1-carboxylate (3ab)

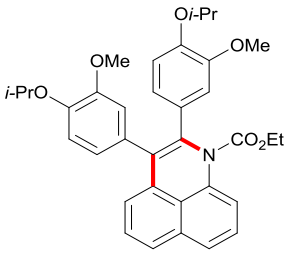
The general procedure **GP1** was followed using 1,2-di-*p*-tolylethyne (**2b**) (61.9 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ab** (91.9 mg, 73%, FE: 33%) as a pale yellow solid. M. p. = 176−177 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.50–7.43 (m, 3H), 7.19 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.72 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.83 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.24 (s, 3H),

0.77 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 154.3 (C_q), 136.6 (C_q), 136.5 (C_q), 136.3 (C_q), 136.3 (C_q), 136.3 (C_q), 133.7 (C_q), 133.6 (C_q), 132.3 (C_q), 130.8 (CH), 129.0 (CH), 128.6 (CH), 128.0 (CH), 126.6 (C_q), 126.6 (C_q), 126.5 (CH), 126.4 (CH), 124.7 (CH), 121.8 (CH), 119.6 (CH), 114.6 (CH), 62.7 (CH_2), 21.3 (CH_3), 21.2 (CH_3), 13.5 (CH_3). IR (neat): 2993, 1730, 1577, 1403, 1241, 1121, 1010, 771 cm^{-1}. MS (ESI) m/z (relative intensity) 420 (20) $[M+H]^+$, 419 (60) $[M+H]^+$, 375 (30), 346 (100), 331 (35). HR-MS (ESI) m/z calcd for $C_{29}H_{26}NO_2$ $[M+H]^+$ 420.1958, found 420.1956.



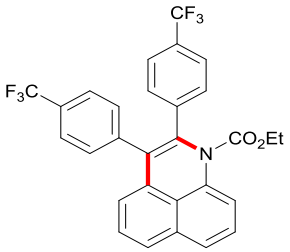
Ethyl 2,3-bis(4-methoxyphenyl)-1*H*-benzo[de]quinoline-1-carboxylate (3ac)

The general procedure **GP1** was followed using 1,2-bis(4-methoxyphenyl)ethyne (**2c**) (71.5 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3aa** (88.0 mg, 65%, FE: 29%) as a pale yellow solid. M. p. = 171−172 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 5.7, 3.1 Hz, 1H), 7.50–7.41 (m, 3H), 7.19 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.73 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.2 (C_q), 158.1 (C_q), 154.3 (C_q), 136.6 (C_q), 136.4 (C_q), 133.6 (C_q), 132.4 (C_q), 132.0 (CH), 131.6 (C_q), 129.9 (CH), 128.9 (C_q), 126.5 (C_q), 126.5 (CH), 126.3 (CH), 125.8 (C_q), 124.6 (CH), 121.8 (CH), 119.3 (CH), 114.4 (CH), 113.8 (CH), 112.7 (CH), 62.7 (CH_2), 55.1 (CH_3), 55.1 (CH_3), 13.5 (CH_3). IR (neat): 2954, 1712, 1607, 1508, 1284, 1241, 1172, 1022, 828 cm^{-1}. MS (ESI) m/z (relative intensity) 474 (100) $[M+Na]^+$, 452 (40) $[M+H]^+$. HR-MS (ESI) m/z calcd for $C_{29}H_{26}NO_4$ $[M+H]^+$ 452.1856, found 452.1854. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-bis(4-isopropoxy-3-methoxyphenyl)-1*H*-benzo[de]quinoline-1-carboxylate (3ad)

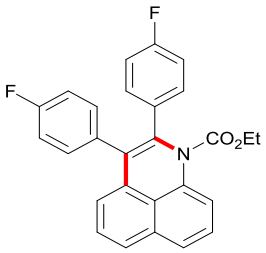
The general procedure **GP1** was followed using 1,2-bis(4-isopropoxy-3-methoxyphenyl)ethyne (**2d**) (106.3 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:1) yielded **3ad** (120.9 mg, 71%, FE: 32%) as a pale yellow solid. M. p. = 154−155 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.49–7.40 (m, 3H), 7.20 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.87–6.83 (m, 2H), 6.79 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.74 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 2.1 Hz, 1H), 6.58 (d, *J* = 1.9 Hz, 1H), 4.53–4.39 (m, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 3.52 (s, 3H), 1.35 (d, *J* = 6.1 Hz, 6H), 1.29 (d, *J* = 6.1 Hz, 6H), 0.78 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.5 (C_q), 150.5 (C_q), 149.3 (C_q), 146.1 (C_q), 146.0 (C_q), 136.6 (C_q), 136.5 (C_q), 133.8 (C_q), 132.5 (C_q), 132.1 (C_q), 129.8 (C_q), 126.6 (CH), 126.6 (C_q), 126.4 (CH), 125.8 (C_q), 124.7 (CH), 123.3 (CH), 121.9 (CH), 120.3 (CH), 119.4 (CH), 115.6 (CH), 114.8 (CH), 114.8 (CH), 114.3 (CH), 113.6 (CH), 71.3 (CH), 71.2 (CH), 62.7 (CH_2), 55.8 (CH_3), 55.6 (CH_3), 22.0 (CH_3), 21.9 (CH_3), 13.4 (CH_3). IR (neat): 2979, 2932, 1713, 1576, 1507, 1231, 1106, 1032, 829 cm^{-1}. MS (ESI) m/z (relative intensity) 590 (100) $[M+Na]^+$, 568 (60) $[M+H]^+$. HR-MS (ESI) m/z calcd for $C_{35}H_{38}NO_6$ $[M+H]^+$ 568.2694, found 568.2689.



Ethyl 2,3-bis{4-(trifluoromethyl)phenyl}-1*H*-benzo[de]quinoline-1-carboxylate (3ae)

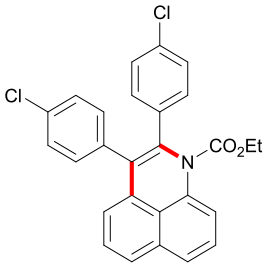
The general procedure **GP1** was followed using 1,2-bis{4-(trifluoromethyl)phenyl}ethyne (**2e**) (94.3 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ae** (63.3 mg, 40%, FE: 18%) as a pale yellow solid. M. p. = 141−142 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J* = 7.0, 1.9 Hz, 1H),

7.61–7.47 (m, 5H), 7.38 (d, J = 8.2 Hz, 2H), 7.30–7.18 (m, 5H), 6.66 (dd, J = 7.3, 1.0 Hz, 1H), 3.86 (q, J = 7.1 Hz, 2H), 0.76 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.7 (C_q), 142.5 (C_q), 139.9 (C_q), 135.9 (C_q), 135.4 (C_q), 133.6 (C_q), 131.3 (CH), 130.6 (C_q), 129.7 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, C_q), 129.1 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, C_q), 129.0 (CH), 127.7 (C_q), 126.6 (CH), 126.5 (C_q), 126.4 (CH), 126.1 (CH), 125.6 (q, $^3J_{C\text{-}F}$ = 3.5 Hz, CH), 124.5 (q, $^3J_{C\text{-}F}$ = 3.6 Hz, CH), 123.9 (q, $^1J_{C\text{-}F}$ = 271.7 Hz, C_q), 123.8 (d, $^1J_{C\text{-}F}$ = 271.6 Hz, C_q), 122.7 (CH), 120.4 (CH), 116.3 (CH), 63.0 (CH_2), 13.4 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.55 (s, 3F), -62.60 (s, 3F). IR (neat): 1726, 1616, 1578, 1405, 1321, 1245, 1167, 1106, 1014 cm^{-1}. MS (ESI) m/z (relative intensity) 550 (60) $[M+Na]^+$, 528 (10) $[M+H]^+$, 437 (30), 381 (100). HR-MS (ESI) m/z calcd for $C_{29}H_{20}F_6NO_2$ $[M+H]^+$ 528.1393, found 528.1389.



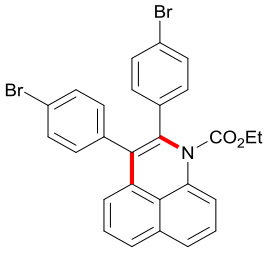
Ethyl 2,3-bis(4-fluorophenyl)-1*H*-benzo[de]quinoline-1-carboxylate (3af)

The general procedure **GP1** was followed using 1,2-bis(4-fluorophenyl)ethyne (**2f**) (64.3 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3af** (92.3 mg, 72%, FE: 32%) as a pale yellow solid. M. p. = 163−164 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (dd, J = 6.3, 2.6 Hz, 1H), 7.56–7.44 (m, 3H), 7.22 (dd, J = 8.3, 7.3 Hz, 1H), 7.17–7.07 (m, 4H), 7.05–6.98 (m, 2H), 6.89–6.81 (m, 2H), 6.70 (dd, J = 7.3, 1.0 Hz, 1H), 3.89 (q, J = 7.1 Hz, 2H), 0.84 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.8 (d, $^1J_{C\text{-}F}$ = 246.6 Hz, C_q), 161.5 (d, $^1J_{C\text{-}F}$ = 247.4 Hz, C_q), 154.1 (C_q), 136.4 (C_q), 136.0 (C_q), 135.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, C_q), 133.7 (C_q), 132.6 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, CH), 132.3 (d, $^4J_{C\text{-}F}$ = 3.6 Hz, C_q), 131.6 (C_q), 130.5 (d, $^3J_{C\text{-}F}$ = 8.1 Hz, CH), 126.6 (C_q), 126.6 (CH), 126.5 (CH), 126.4 (C_q), 125.3 (CH), 122.2 (CH), 119.8 (CH), 115.6 (d, $^2J_{C\text{-}F}$ = 21.5 Hz, CH), 115.2 (CH), 114.5 (d, $^2J_{C\text{-}F}$ = 21.6 Hz, CH), 62.9 (CH_2), 13.4 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -(114.15–114.05) (m, 1F), -(114.52–114.43) (m, 1F). IR (neat): 3054, 2985, 1720, 1577, 1505, 1403, 1366, 1247, 1213 cm^{-1}. MS (ESI) m/z (relative intensity) 450 (80) $[M+Na]^+$, 428 (30) $[M+H]^+$, 381 (100). HR-MS (ESI) m/z calcd for $C_{27}H_{20}F_2NO_2$ $[M+H]^+$ 428.1457, found 428.1456.



Ethyl 2,3-bis(4-chlorophenyl)-1*H*-benzo[de]quinoline-1-carboxylate (3ag)

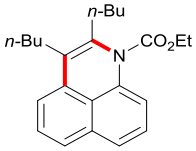
The general procedure **GP1** was followed using 1,2-bis(4-chlorophenyl)ethyne (**2g**) (74.1 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ag** (77.3 mg, 56%, FE: 25%) as a pale yellow solid. M. p. = 152−153 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.57–7.43 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, *J* = 8.3, 7.4 Hz, 1H), 7.14–7.03 (m, 6H), 6.68 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.88 (q, *J* = 7.1 Hz, 2H), 0.82 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.9 (C_q), 137.5 (C_q), 136.1 (C_q), 135.6 (C_q), 134.7 (C_q), 133.6 (C_q), 133.1 (C_q), 132.7 (C_q), 132.2 (CH), 131.2 (C_q), 130.0 (CH), 128.8 (CH), 127.7 (CH), 126.7 (C_q), 126.5 (CH), 126.5 (C_q), 126.4 (CH), 125.6 (CH), 122.4 (CH), 120.0 (CH), 115.6 (CH), 63.0 (CH_2), 13.6 (CH_3). IR (neat): 3054, 2985, 1720, 1631, 1574, 1487, 1397, 1365, 1242 cm^{-1}. MS (ESI) m/z (relative intensity) 482 (30) $[M+Na]^+$, 460 (10) $[M+H]^+$, 437 (20), 381 (100). HR-MS (ESI) m/z calcd for $C_{27}H_{20}{}^{35}Cl_2NO_2$ $[M+H]^+$ 460.0866, found 460.0862; $C_{27}H_{20}{}^{35}Cl^{37}ClNO_2$ $[M+H]^+$ 462.0838, found 462.0839. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-bis(4-bromophenyl)-1*H*-benzo[de]quinoline-1-carboxylate (3ah)

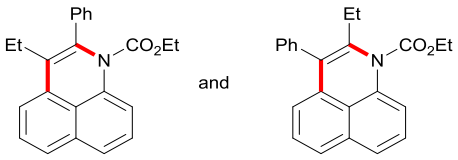
The general procedure **GP1** was followed using 1,2-bis(4-bromophenyl)ethyne (**2h**) (100.8 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ah** (117.0 mg, 71%, FE: 32%) as a pale yellow solid. M. p. = 174−175 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.55–7.42 (m, 5H), 7.30–7.26 (m, 2H), 7.21 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.08–6.98 (m, 4H), 6.69 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ =

153.9 (C_q), 138.0 (C_q), 136.1 (C_q), 135.6 (C_q), 135.2 (C_q), 133.6 (C_q), 132.6 (CH), 131.8 (CH), 131.1 (C_q), 130.7 (CH), 130.4 (CH), 126.8 (C_q), 126.6 (CH), 126.5 (C_q), 126.5 (CH), 125.6 (CH), 122.4 (CH), 121.3 (C_q), 121.0 (C_q), 120.0 (CH), 115.7 (CH), 62.9 (CH_2), 13.5 (CH_3). IR (neat): 3053, 2981, 1722, 1629, 1574, 1485, 1404, 1366, 1242, 1008 cm^{-1}. MS (ESI) m/z (relative intensity) 572 (80) $[M+Na]^+$, 550 (20) $[M+H]^+$, 450 (30), 381 (100). HR-MS (ESI) m/z calcd for $C_{27}H_{20}{}^{79}Br^{81}Br\ NO_2$ $[M+H]^+$ 549.9837, found 549.9826. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-dibutyl-1*H*-benzo[de]quinoline-1-carboxylate (3ai)

The general procedure **GP1** was followed using dec-5-yne (**2i**) (41.5 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ai** (54.8 mg, 52%, FE: 23%) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.46 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.42–7.38 (m, 1H), 7.38–7.34 (m, 1H), 7.18 (dd, *J* = 7.3, 1.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.80–2.74 (m, 2H), 2.58–2.53 (m, 2H), 1.57–1.42 (m, 6H), 1.40–1.30 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.2 (C_q), 137.1 (C_q), 136.2 (C_q), 133.2 (C_q), 130.7 (C_q), 127.0 (C_q), 126.4 (CH), 125.7 (CH), 125.1 (C_q), 124.6 (CH), 122.3 (CH), 117.4 (CH), 117.4 (CH), 62.7 (CH_2), 31.6 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 28.2 (CH_2), 23.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 14.0 (CH_3), 14.0 (CH_3). IR (neat): 2955, 2928, 1713, 1634, 1578, 1403, 1270, 763 cm^{-1}. MS (ESI) m/z (relative intensity) 374 (40) $[M+Na]^+$, 352 (100) $[M+H]^+$. HR-MS (ESI) m/z calcd for $C_{23}H_{30}NO_2$ $[M+H]^+$ 352.2271, found 352.2270.

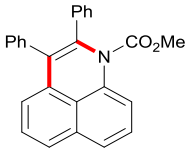


3aj/3aj´ (9/1)

Ethyl 3-ethyl-2-phenyl-1*H*-benzo[de]quinoline-1-carboxylate (**3aj**)

Ethyl 2-ethyl-3-phenyl-1*H*-benzo[de]quinoline-1-carboxylate (3aj´)

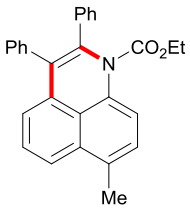
The general procedure **GP1** was followed using but-1-yn-1-ylbenzene (**2j**) (39.1 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3aj** and **3aj´** (62.8 mg, 9/1, 61%, FE: 27%) as a pale yellow solid. M. p. = 95−96 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.91 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.2 Hz, 0.11H), 7.56 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.50–7.46 (m, 3.33H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.43–7.38 (m, 3.33H), 7.35–7.31 (m, 1H), 7.28 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.27–7.25 (m, 0.22H), 7.20 (dd, *J* = 8.2, 7.3 Hz, 0.11H), 6.49 (dd, *J* = 7.3, 1.0 Hz, 0.11H), 4.33 (q, *J* = 7.2 Hz, 0.22H), 3.82 (q, *J* = 7.2 Hz, 2H), 2.57 (q, *J* = 7.5 Hz, 0.22H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 0.33H), 1.16 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 0.33H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.1 (C_q), 139.3 (C_q), 136.2 (C_q), 135.4 (C_q), 133.7 (C_q), 130.5 (C_q), 129.0 (CH), 127.7 (CH), 127.3 (CH), 127.0 (C_q), 126.5 (CH), 126.1 (CH), 125.1 (C_q), 124.9 (CH), 121.7 (CH), 117.5 (CH), 114.4 (CH), 62.5 (CH_2), 21.9 (CH_2), 14.2 (CH_3), 13.5 (CH_3). IR (neat): 3055, 2966, 1715, 1632, 1577, 1402, 1367, 1237, 1173, 1022 cm^{-1}. MS (ESI) m/z (relative intensity) 366 (100) $[M+Na]^+$, 344 (20) $[M+H]^+$, 305 (10), 261 (10). HR-MS (ESI) m/z calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$ 344.1645, found 344.1644.



Methyl 2,3-diphenyl-1*H*-benzo[de]quinoline-1-carboxylate (3ba)

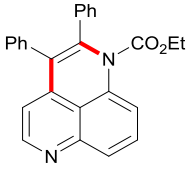
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1b** (121 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ba** (71.3 mg, 63%, FE: 28%) as a pale yellow solid. M. p. = 184−185 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.56–7.46 (m, 3H), 7.35–7.24 (m, 3H), 7.23–7.07 (m, 8H), 6.76 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.8 (C_q), 138.9 (C_q), 136.5 (C_q), 136.5 (C_q), 136.4 (C_q), 133.7 (C_q), 131.8 (C_q), 130.9 (CH),

128.6 (CH), 128.4 (CH), 127.4 (CH), 127.2 (C_q), 127.0 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 126.5 (C_q), 125.1 (CH), 122.1 (CH), 119.9 (CH), 114.8 (CH), 53.1 (CH_3). IR (neat): 3054, 1718, 1629, 1574, 1438, 1281, 1244, 1211, 697 cm^{-1}. MS (ESI) m/z (relative intensity) 400 (100) $[M+Na]^+$, 378 (30) $[M+H^+]$. HR-MS (ESI) m/z calcd for $C_{26}H_{20}NO_2$ $[M+H]^+$ 378.1489, found 378.1484. The analytical data correspond with those reported in the literature.[1]



Ethyl 7-methyl-2,3-diphenyl-1*H*-benzo[de]quinoline-1-carboxylate (3ca)

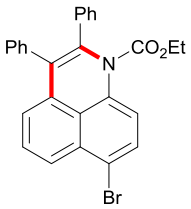
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1c** (137.6 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ca** (96.1 mg, 79%, FE: 35%) as a pale yellow solid. M. p. = 143−144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 7.9 Hz, 1H), 7.62 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.36 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.33–7.25 (m, 4H), 7.20–7.14 (m, 4H), 7.13–7.07 (m, 3H), 6.81 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4 (C_q), 139.4 (C_q), 136.8 (C_q), 136.8 (C_q), 136.5 (C_q), 134.7 (C_q), 132.4 (C_q), 132.2 (C_q), 131.1 (CH), 128.9 (CH), 128.5 (C_q), 128.3 (CH), 127.3 (C_q), 127.3 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.3 (CH), 121.8 (CH), 120.0 (CH), 115.2 (CH), 62.6 (CH_2), 19.0 (CH_3), 13.3 (CH_3). IR (neat): 3059, 2982, 1711, 1580, 1400, 1366, 1247, 1106, 1023 cm^{-1}. MS (EI) m/z (relative intensity) 406 (20) $[M+H]^+$, 405 (100) $[M]^+$, 361 (20), 332 (100), 317 (30). HR-MS (EI) m/z calcd for $C_{28}H_{23}NO_2$ $[M+H]^+$ 405.1729, found 405.1737. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-diphenyl-1*H*-benzo[ij][2,7]naphthyridine-1-carboxylate (3da)

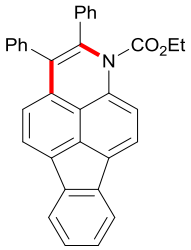
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1d** (130 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel

(*n*-hexane/EtOAc 20:1) yielded **3da** (74.2 mg, 63%, FE: 28%) as a pale yellow solid. M. p. = 101−102 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 4.8 Hz, 1H), 7.70 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.67–7.55 (m, 2H), 7.30–7.20 (m, 3H), 7.19–7.04 (m, 7H), 6.39 (d, *J* = 4.8 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.5 (C_q), 151.6 (CH), 148.5 (C_q), 141.1 (C_q), 140.4 (C_q), 137.0 (C_q), 136.0 (C_q), 135.0 (C_q), 130.8 (CH), 129.7 (CH), 128.9 (CH), 128.5 (CH), 127.9 (CH), 127.6 (CH), 127.2 (CH), 121.8 (C_q), 121.6 (CH), 121.0 (C_q), 111.0 (CH), 109.7 (CH), 63.8 (CH_2), 13.2 (CH_3). IR (neat): 3062, 2891, 1735, 1622, 1578, 1224, 1016, 835, 759 cm^{-1}. MS (ESI) m/z (relative intensity) 393 (100) $[M+H]^+$, 381 (10). HR-MS (ESI) m/z calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1598, found 393.1602. The analytical data correspond with those reported in the literature.[1]



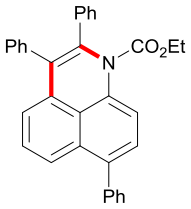
Ethyl 7-bromo-2,3-diphenyl-1*H*-benzo[de]quinoline-1-carboxylate (3ea)

The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1e** (176 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ea** (112.9 mg, 80%, FE: 36%) as a pale yellow solid. M. p. = 183−184 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.35–7.24 (m, 4H), 7.20–7.08 (m, 7H), 6.81 (dd, *J* = 7.4, 1.0 Hz, 1H), 3.83 (q, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.0 (C_q), 138.7 (C_q), 136.7 (C_q), 136.4 (C_q), 136.4 (C_q), 132.3 (C_q), 132.0 (C_q), 131.0 (CH), 130.2 (CH), 128.8 (CH), 128.5 (CH), 127.8 (CH), 127.7 (C_q), 127.4 (CH), 127.1 (CH), 127.0 (CH), 126.5 (C_q), 124.2 (CH), 120.4 (CH), 115.5 (C_q), 114.8 (CH), 63.0 (CH_2), 13.2 (CH_3). IR (neat): 3053, 1722, 1597, 1573, 1403, 1365, 1235, 1212, 1017, 685 cm^{-1}. MS (ESI) m/z (relative intensity) 492 (100) $[M+Na]^+$, 472 (30) $[M+H]^+$. HR-MS (ESI) m/z calcd for $C_{27}H_{21}{}^{79}BrNO_2$ $[M+H]^+$ 470.0750, found 470.0745. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3-diphenyl-1*H*-fluoreno[2,1,9-def]quinoline-1-carboxylate (3fa)

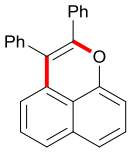
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1f** (174 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3fa** (75.4 mg, 54%, FE: 24%) as a light yellow solid. M. p. = 203−204 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.0 Hz, 1H), 8.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.13 (dd, *J* = 7.2, 1.0 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.33–7.30 (m, 2H), 7.29–7.23 (m, 3H), 7.22–7.14 (m, 5H), 7.04 (d, *J* = 7.4 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 154.2 (C_q), 137.8 (C_q), 137.7 (C_q), 137.2 (C_q), 136.5 (C_q), 136.5 (C_q), 135.9 (C_q), 131.8 (C_q), 131.1 (CH), 131.0 (C_q), 130.7 (C_q), 129.6 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 127.3 (C_q), 127.0 (CH), 126.2 (CH), 125.5 (CH), 123.4 (C_q), 122.2 (CH), 122.2 (CH), 121.3 (CH), 120.9 (CH), 120.3 (C_q), 117.4 (CH), 108.5 (CH), 63.9 (CH_2), 13.1 (CH_3). IR (neat): 3053, 1731, 1615, 1553, 1440, 1365, 1215, 1107, 1035, 750 cm^{-1}. MS (EI) m/z (relative intensity) 466 (20) $[M+H]^+$, 465 (50) $[M]^+$, 421 (20), 392 (100), 314 (20). HR-MS (EI) m/z calcd for $C_{33}H_{23}NO_2$ $[M]^+$ 465.1729, found 465.1742. UV-Vis λ_{max} (2.1 mg/L in CH_3CN) = 251 nm. $E_m\lambda_{max}$ (21 µg/L in CH_3CN) = 505 nm. The analytical data correspond with those reported in the literature.[1]



Ethyl 2,3,7-triphenyl-1*H*-benzo[de]quinoline-1-carboxylate (3ga)

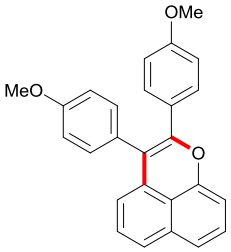
The general procedure **GP1** was followed using 1,2-diphenylethyne (**2a**) (53.5 mg, 0.30 mmol) and carbamate **1g** (175 mg, 0.60 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded **3ga** (85.6 mg, 61%, FE: 27%) as a pale yellow solid. M. p. = 175−176 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.54–7.46 (m, 5H), 7.44–7.40 (m, 1H), 7.34–7.30 (m, 2H), 7.29–7.25 (m, 1H), 7.23–7.17 (m, 5H), 7.15–7.08 (m, 3H), 6.81 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.1 Hz, 3H). **^{13}C**

NMR (125 MHz, $CDCl_3$) δ = 154.2 (C_q), 140.5 (C_q), 139.1 (C_q), 136.6 (C_q), 136.3 (C_q), 135.9 (C_q), 134.5 (C_q), 132.0 (C_q), 131.7 (C_q), 131.0 (CH), 129.8 (CH), 128.8 (CH), 128.3 (CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 127.2 (C_q), 127.0 (CH), 126.9 (CH), 126.8 (C_q), 126.7 (CH), 126.5 (CH), 123.4 (CH), 120.1 (CH), 114.9 (CH), 62.8 (CH_2), 13.4 (CH_3). IR (neat): 3056, 1720, 1628, 1575, 1411, 1256, 1104, 1014, 697 cm^{-1}. MS (ESI) m/z (relative intensity) 468(20) $[M+H]^+$, 467 (60) $[M]^+$, 423 (20), 394 (100), 317 (20). HR-MS (EI) m/z calcd for $C_{33}H_{25}NO_2$ $[M]^+$ 467.1885, found 467.1884.



2,3-Diphenylbenzo[de]chromene (5aa)

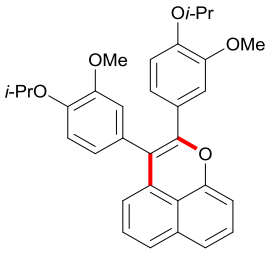
The general procedure **GP2** was followed using 1,2-diphenylethyne (**2a**) (89.1 mg, 0.50 mmol) and naphthalen-1-ol (**4a**) (144 mg, 1.0 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 40:1) yielded **5aa** (134.6 mg, 84%, FE: 35%) as a pale yellow solid. M. p. = 111−112 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.40–7.36 (m, 3H), 7.35–7.30 (m, 4H), 7.27 (ddd, *J* = 7.9, 7.9, 1.2 Hz, 3H), 7.23–7.17 (m, 3H), 7.15 (dd, *J* = 8.4, 7.3 Hz, 1H), 6.88 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.47 (dd, *J* = 7.3, 0.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 152.5 (C_q), 149.3 (C_q), 135.4 (C_q), 134.7 (C_q), 134.1 (C_q), 131.8 (C_q), 130.9 (CH), 128.9 (CH), 128.8 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 123.6 (CH), 122.8 (C_q), 119.1 (CH), 117.5 (C_q), 115.6 (CH), 106.9 (CH). IR (neat): 3053, 1633, 1577, 1488, 1441, 1362, 1105, 1030, 689 cm^{-1}. MS (ESI) m/z (relative intensity) 321 (40) $[M+H]^+$, 320 (100) $[M]^+$, 289 (30), 276 (10), 215 (20). HR-MS (EI) m/z calcd for $C_{24}H_{16}O$ $[M]^+$ 320.1201, found 320.1202. The analytical data correspond with those reported in the literature.[3]



2,3-Bis(4-methoxyphenyl)benzo[de]chromene (5ac)

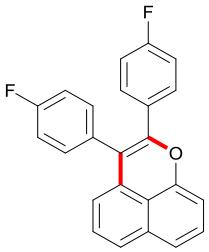
The general procedure **GP2** was followed using 1,2-bis(4-methoxyphenyl)ethyne (**2c**) (119.2 mg, 0.50 mmol) and naphthalen-1-ol (**4a**) (144 mg, 1.0 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 40:1) yielded **5ac** (110.3 mg, 58%, FE: 24%) as a pale

yellow solid. M. p. = 146−147 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.29 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.26–7.22 (m, 3H), 7.18–7.10 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.84 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.44 (dd, *J* = 7.3, 0.9 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.2 (C_q), 158.7 (C_q), 152.6 (C_q), 149.1 (C_q), 134.7 (C_q), 132.4 (C_q), 132.0 (CH), 130.1 (CH), 127.9 (C_q), 127.6 (CH), 127.2 (CH), 126.7 (C_q), 123.2 (CH), 122.7 (C_q), 118.9 (CH), 116.0 (C_q), 115.2 (CH), 114.5 (CH), 113.0 (CH), 106.7 (CH), 55.2 (CH_3), 55.2 (CH_3). IR (neat): 3113, 2978, 1649, 1607, 1509, 1463, 1169, 1126, 832 cm^{-1}. MS (ESI) m/z (relative intensity) 403 (70) $[M+Na]^+$, 381 (100) $[M+H]^+$, 353 (10), 305 (10). HR-MS (ESI) m/z calcd for $C_{26}H_{21}O_3$ $[M+H]^+$ 381.1485, found 381.1475; $C_{26}H_{20}O_3Na$ $[M+Na]^+$ 403.1305, found 403.1302. The analytical data correspond with those reported in the literature.[3]



2,3-Bis(4-iso-propoxy-3-methoxyphenyl)benzo[de]chromene (5ad)

The general procedure **GP2** was followed using 1,2-bis(4-iso-propoxy-3-methoxyphenyl)ethyne (**2d**) (177.2 mg, 0.50 mmol) and naphthalen-1-ol (**4a**) (144 mg, 1.0 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 40:1) yielded **5ad** (158.9 mg, 64%, FE: 27%) as a pale yellow solid. M. p. = 143−144 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.31–7.27 (m, 1H), 7.25–7.22 (m, 1H), 7.17–7.12 (m, 1H), 7.04 (ddd, *J* = 8.4, 2.2, 0.8 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.79–6.76 (m, 2H), 6.75–6.73 (m, 2H), 6.51 (dd, *J* = 7.3, 0.9 Hz, 1H), 4.56–4.47 (m, 2H), 3.72 (s, 3H), 3.52 (s, 3H), 1.42–1.29 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 152.5 (C_q), 150.9 (C_q), 148.8 (C_q), 148.8 (C_q), 147.2 (C_q), 146.5 (C_q), 134.7 (C_q), 132.2 (C_q), 128.7 (C_q), 128.7 (C_q), 127.6 (CH), 127.2 (CH), 126.7 (C_q), 123.2 (CH), 123.1 (CH), 122.7 (C_q), 121.2 (CH), 119.0 (CH), 116.2 (CH), 115.3 (CH), 114.6 (CH), 114.0 (CH), 112.7 (CH), 106.7 (CH), 71.3 (CH), 71.1 (CH) , 56.0 (CH_3), 55.5 (CH_3), 22.2 (CH_3), 22.1 (CH_3). IR (neat): 3113, 2973, 1647, 1608, 1507, 1462, 1262, 1215, 1133, 940 cm^{-1}. MS (ESI) m/z (relative intensity) 519 (60) $[M+Na]^+$, 497 (30) $[M+H]^+$, 379 (100), 357 (30). HR-MS (ESI) m/z calcd for $C_{32}H_{33}O_5$ $[M+H]^+$ 497.2323, found 497.2317.

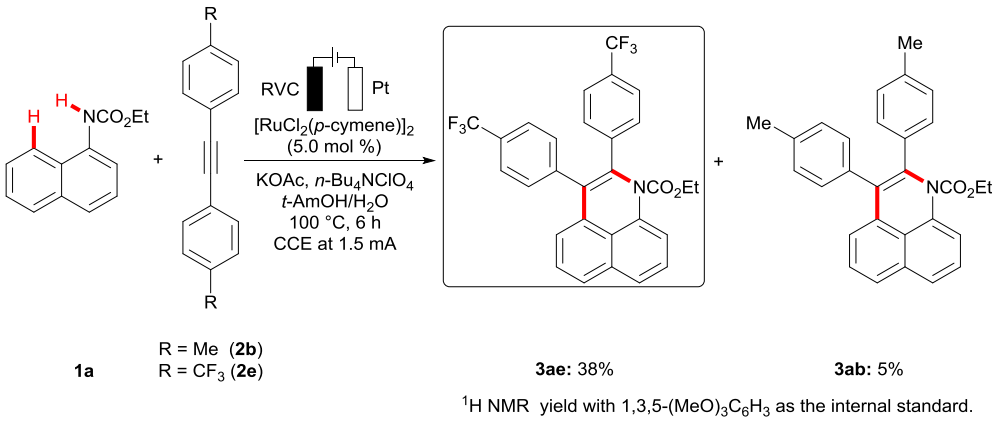


2,3-Bis(4-fluorophenyl)benzo[de]chromene (5ae)

The general procedure **GP2** was followed using 1,2-bis(4-fluorophenyl)ethyne (**2e**) (107.1 mg, 0.50 mmol) and naphthalen-1-ol (**4a**) (144 mg, 1.0 mmol, 2.0 equiv). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 40:1) yielded **5ae** (96.2 mg, 54%, FE: 23%) as a pale yellow solid. M. p. = 138−139 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.37 (dd, J = 8.4, 0.9 Hz, 1H), 7.31 (dd, J = 8.2, 7.5 Hz, 1H), 7.28–7.23 (m, 3H), 7.21–7.16 (m, 2H), 7.14 (dd, J = 8.3, 7.2 Hz, 1H), 7.09–7.05 (m, 2H), 6.91–6.86 (m, 2H), 6.85 (dd, J = 7.6, 1.2 Hz, 1H), 6.40 (dd, J = 7.3, 0.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 162.3 (d, $^{1}J_{C\text{-}F}$ = 249.2 Hz, C_q), 162.1 (d, $^{1}J_{C\text{-}F}$ = 246.7 Hz, C_q), 152.3 (C_q), 148.7 (C_q), 134.7 (C_q), 132.6 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz, CH), 131.5 (C_q), 131.2 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, C_q), 130.8 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz, CH), 130.1 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, C_q), 127.5 (CH), 127.4 (CH), 123.8 (CH), 122.7 (C_q), 119.3 (CH), 116.4 (C_q), 116.2 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz, CH), 115.5 (CH), 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz, CH), 107.0 (CH). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -(111.79–112.72) (m, 1F), -(113.90–113.82) (m, 1F). IR (neat): 3054, 2851, 1891, 1639, 1598, 1504, 1217, 1155, 1104, 1004 cm^{-1}. MS (EI) m/z (relative intensity) 357 (30) $[M+H]^+$, 356 (100) $[M]^+$, 325 (10), 307 (10), 233 (15). HR-MS (EI) m/z calcd for $C_{24}H_{14}F_2O$ $[M]^+$ 356.1013, found 356.1015. The analytical data correspond with those reported in the literature.[3a]

Mechanistic studies

Competition Experiments



^{1}H NMR yield with 1,3,5-$(MeO)_3C_6H_3$ as the internal standard.

The general procedure **GP1** was followed using alkyne **2b** (61.9 mg, 0.30 mmol), **2e** (94.3 mg, 0.30 mmol) and carbamate **1a** (129 mg, 0.60 mmol). Electrolysis was performed at 100 °C using a constant current of 1.5 mA which was maintained for 6 h. At ambient temperature, the reaction mixture was dry loaded onto silica gel and purified by column chromatography (*n*-hexane/EtOAc = 20:1) to afford a mixture of **3ae** and **3ab** (66.4 mg). This mixture was analyzed by ^{1}H-NMR using 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol) as internal standard, which showed a product distribution of 7.7/1 in favour of **3ae**.

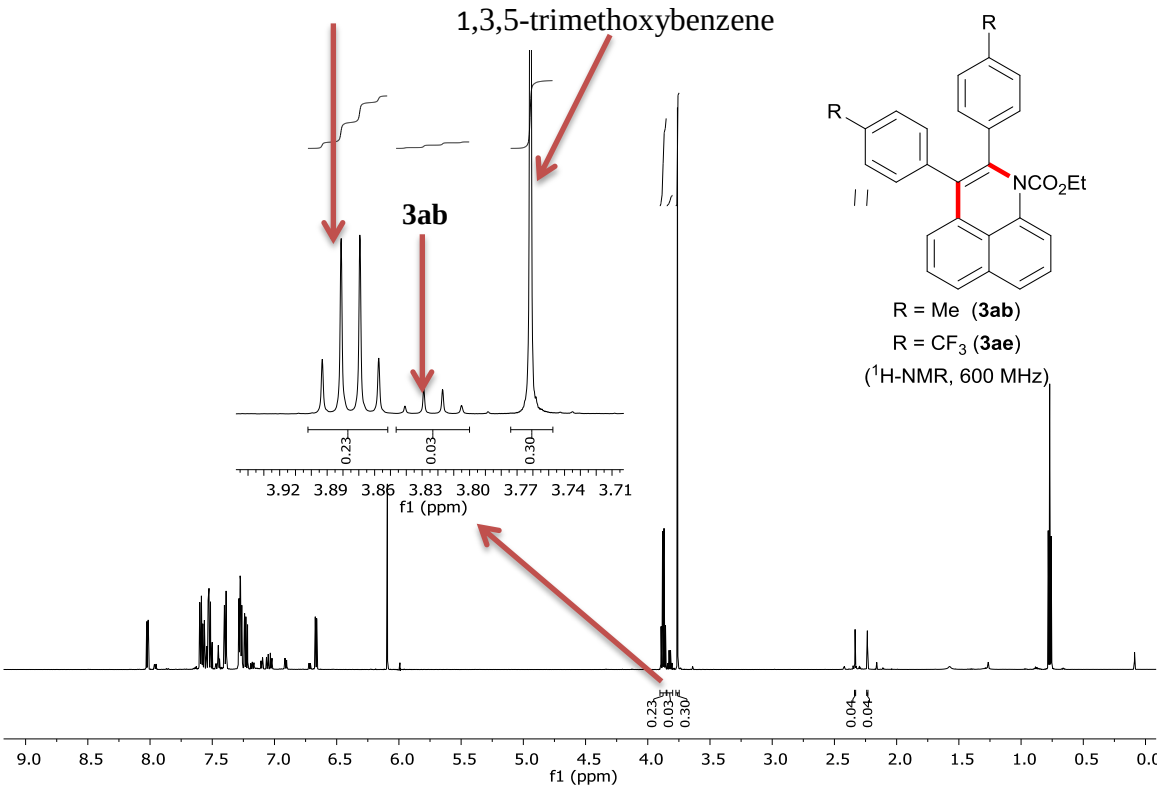
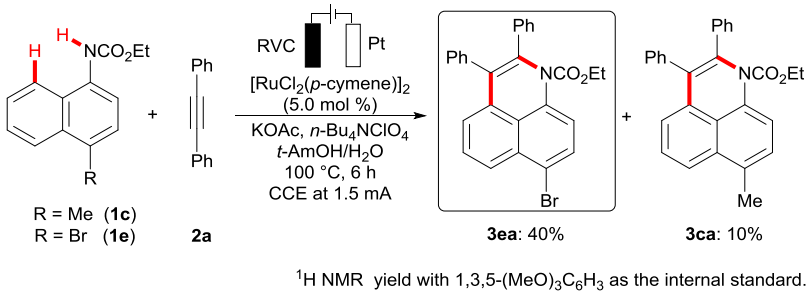


Figure S-1: ^{1}H-NMR spectra of the mixture of **3ab** and **3ae**.



^{1}H NMR yield with 1,3,5-$(MeO)_3C_6H_3$ as the internal standard.

The general procedure **GP1** was followed using carbamate **1c** (68.8 mg, 0.30 mmol), **1e** (88.2 mg, 0.30 mmol) and alkyne **2a** (53.4 mg, 0.30 mmol). Electrolysis was performed at 100 °C using a constant current of 1.5 mA which was maintained for 6 h. At ambient temperature, the reaction mixture was dry loaded onto silica gel and purified by column chromatography (*n*-hexane/EtOAc = 20:1) to afford a mixture of **3ea** and **3ca** (68.6 mg). This mixture was analyzed by ^{1}H-NMR using 1,3,5-trimethoxybenzene (16.8 mg, 0.10 mmol) as the internal standard, which showed a product distribution of 4/1 in favour of **3ea**.

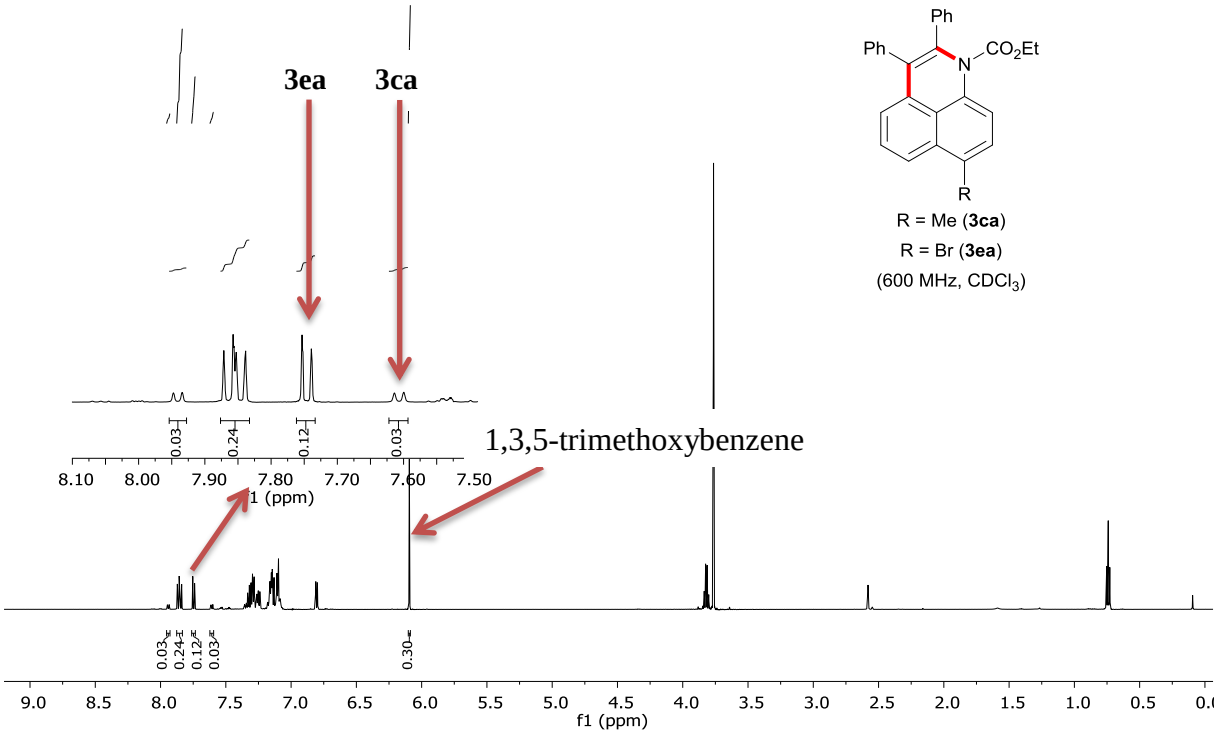
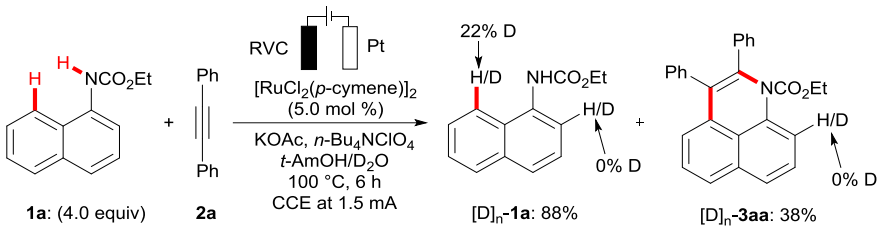


Figure S-2: ^{1}H-NMR spectra of the mixture of **3ca** and **3ea**.

Deuteration Experiment



The general procedure **I** was followed using alkyne **2a** (53.4 mg, 0.30 mmol) and carbamate **1a** (258 mg, 1.20 mmol). Electrolysis was performed at 100 °C and a constant current of 1.5 mA in a solvent mixture of *t*-AmOH/D_2O (3/1, 4.0 mL) for 6 h. At ambient temperature, the mixture was transferred to a flask and the electrodes were rinsed with acetone (3 × 5.0 mL). Then silica gel (1.0 g) was added and the combined solvent was removed under reduced pressure. The residue solid was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 30/1 to 15/1) yielding the desired product $[D]_n$-**3aa** (44.6 mg, 38%) as a pale yellow solid and the reisolated starting material $[D]_n$-**1a** (228 mg, 88%) as a white solid.

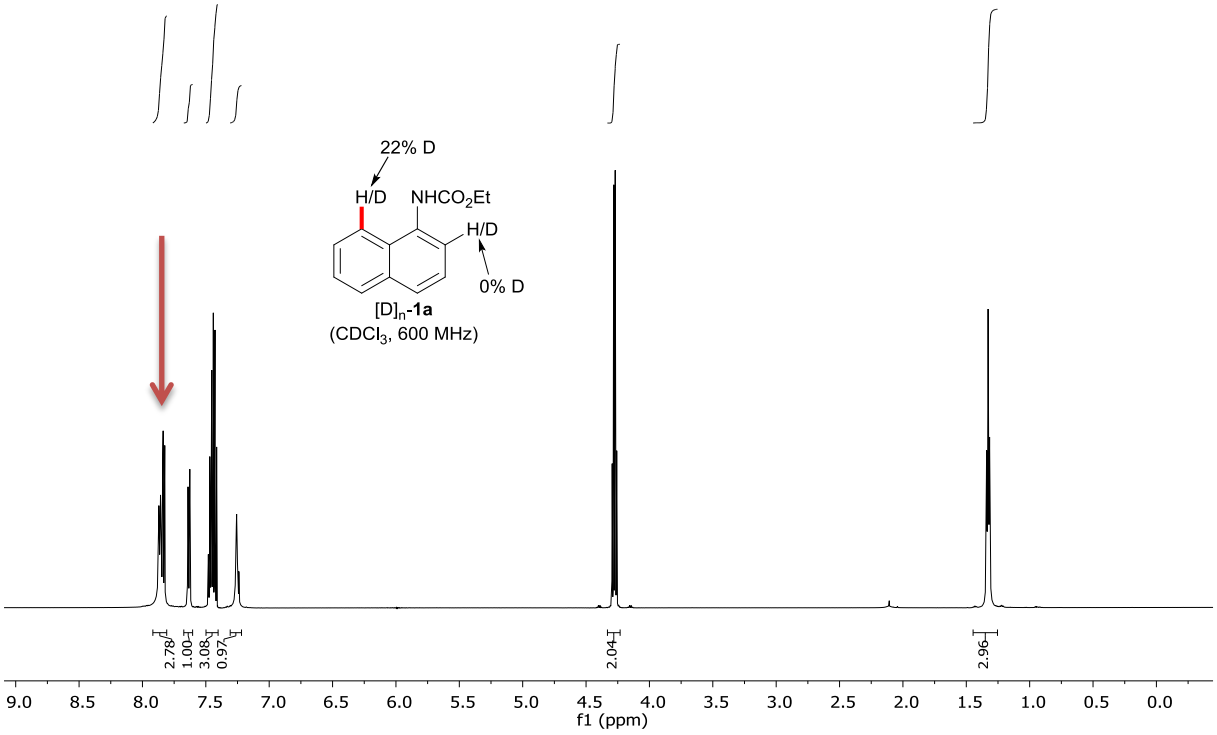


Figure S-3: ^{1}H-NMR spectra of $[D]_n$-**1a** from the deuteration study.

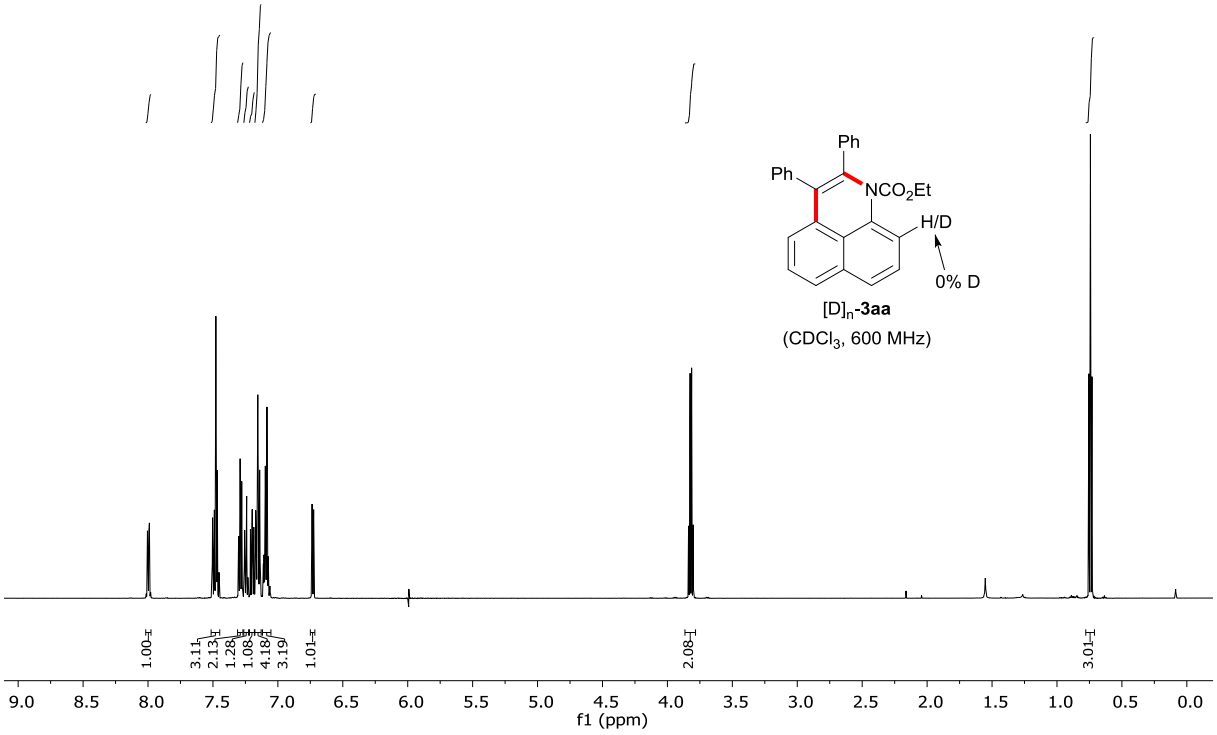


Figure S-4: ^{1}H-NMR spectra of $[D]_n$-**3aa** from the deuteration study.

KIE Studies

Preparation of $[D]_7$**-1a**[4]

$NaNO_3$ (570 mg, 6.7 mmol) was dissolved in TFA (28 mL), and $[D]_8$-naphthalene (99% D, 1.0 g, 7.35 mmol) was added in several portions at ambient temperature under air. The mixture was stirred for 5 h at the same temperature, cooled to 0 °C, and then neutralized with aq NaOH (6 M). The mixture was extracted with Et_2O (4 × 50 mL) and evaporated under reduced pressure. The crude $[D]_7$-1-nitronaphthalene obtained was used for the next step without further purification. To a mixture of the above $[D]_7$-1-nitronaphthalene and concentrated aq HCl (ca. 11.4 M, 7.0 mL) in EtOH (15 mL), Sn powder (3.50 g, 29.0 mmol) was added in several portions, and the resulting mixture was stirred at ambient temperature under air. After 6 h, volatile materials were evaporated *in vacuo*. The residue was dissolved in H_2O and Et_2O. The mixture was neutralized with saturated aq K_2CO_3 and then filtered through a pad of Celite. The filtrate was extracted with EtOAc (3 × 50 mL), concentrated under reduced pressure, and purified by column chromatography (*n*-hexane/EtOAc, 3/1) on silica gel to afford $[D]_7$-1-naphthylamine (751 mg, 68%) in a two-step sequence. The deuterium content at each position in the naphthalene ring was determined by ^1H and ^2H NMR analysis, as follows: 92% D at C_2; >95% D at all the other aromatic C−H bond. The attachment of the ethyl carbonochloridate to 1-naphthylamine-d_7 was performed according to a literature reported method,[1] and purification by chromatography (*n*-hexane/EtOAc, 15/1) furnished $[D]_7$-**1a** (1.02 g, 92%) as a white solid.

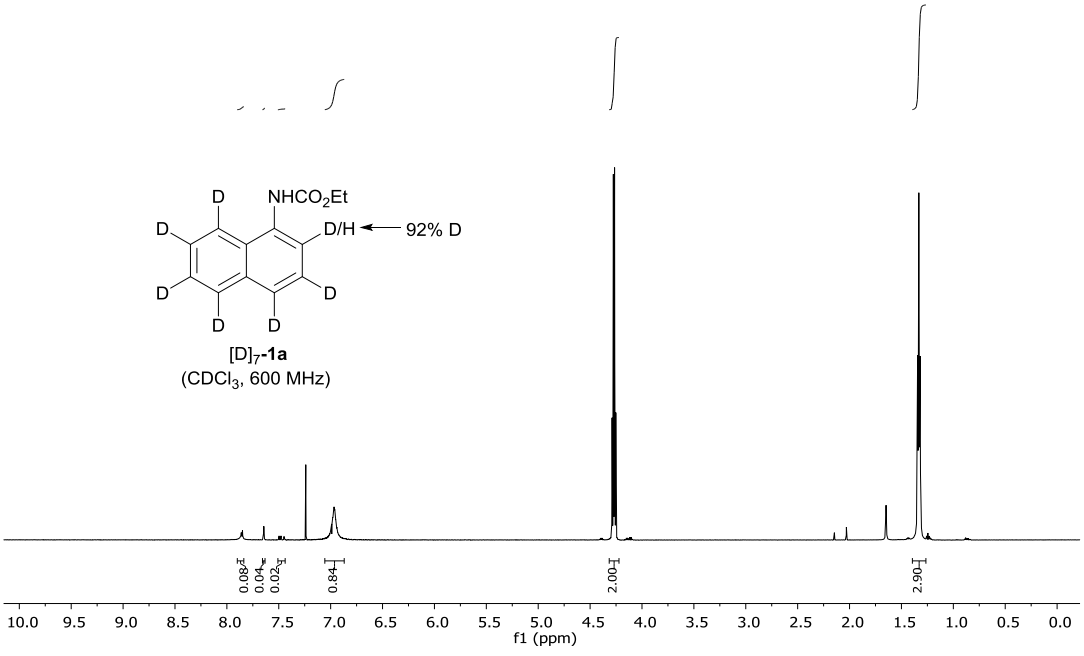
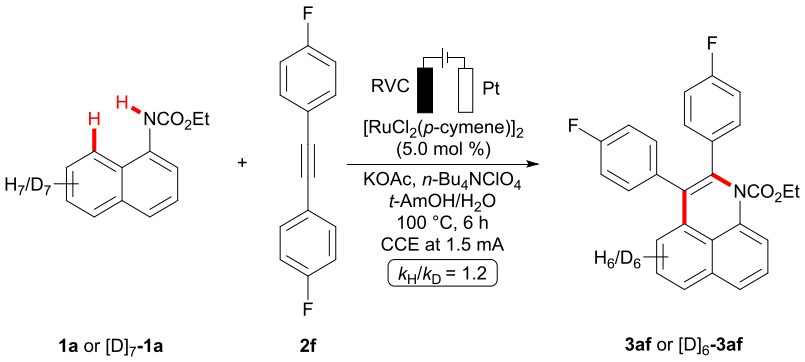


Figure S-5: ^1H-NMR spectra of $[D]_7$-**1a**.

Parallel experiment



Two independent reactions following the general procedure **GP1** were carried out. Carbamates **1a** (215 mg, 1.0 mmol) or [D]$_7$-**1a** (222 mg, 1.0 mmol), 1,2-bis(4-fluorophenyl)ethyne (**2f**) (107 mg, 0.50 mmol) and 4′-(trifluoromethyl)acetophenone (37.6 mg, 0.20 mmol, as the internal standard) were dissolved in *t*-AmOH/H_2O (6/2, 8.0 mL) under a N_2 atmosphere. After 10 minutes to reach a stable constant current of 1.5 mA, aliquots of 0.1 mL were removed from each cell every 10 minutes. The mixture was diluted immediately with EtOAc (3.0 mL) and filtered through a silica pad. After evaporation of the solvent, each sample was analyzed by ^{19}F-NMR.

Time [min]	10	20	30	40	50	60
3af [%]	5.2	6.9	9.2	12.1	14.3	15.8
[D]$_6$-**3af** [%]	4.2	6.1	7.8	10.0	11.2	13.2

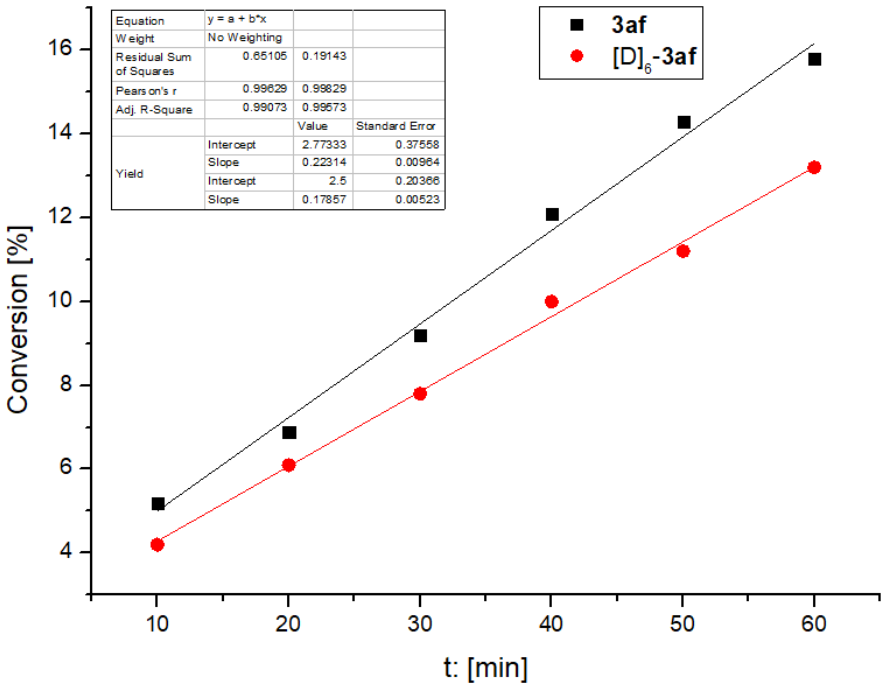


Figure S-6: Parallel experiment for KIE study.

References

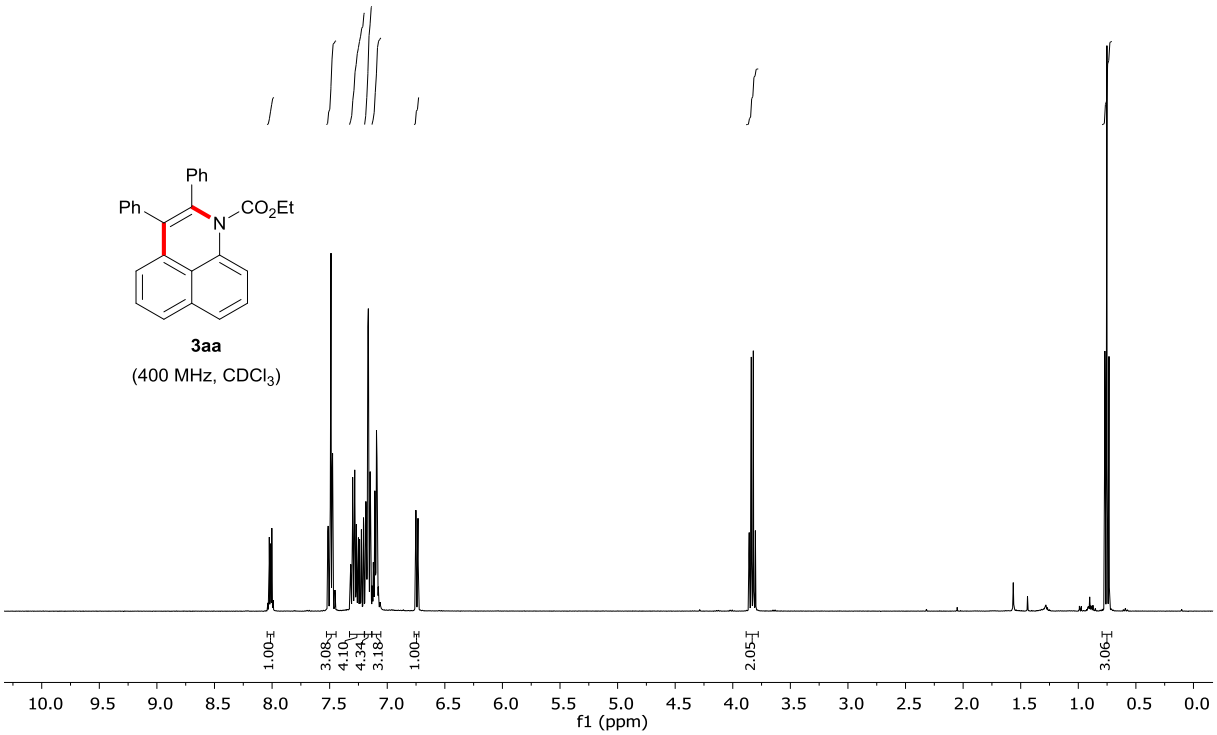
[1] X. Zhang, W. Si, M. Bao, N. Asao, Y. Yamamoto and T. Jin, *Org. Lett.*, 2014, **16**, 4830–4833.

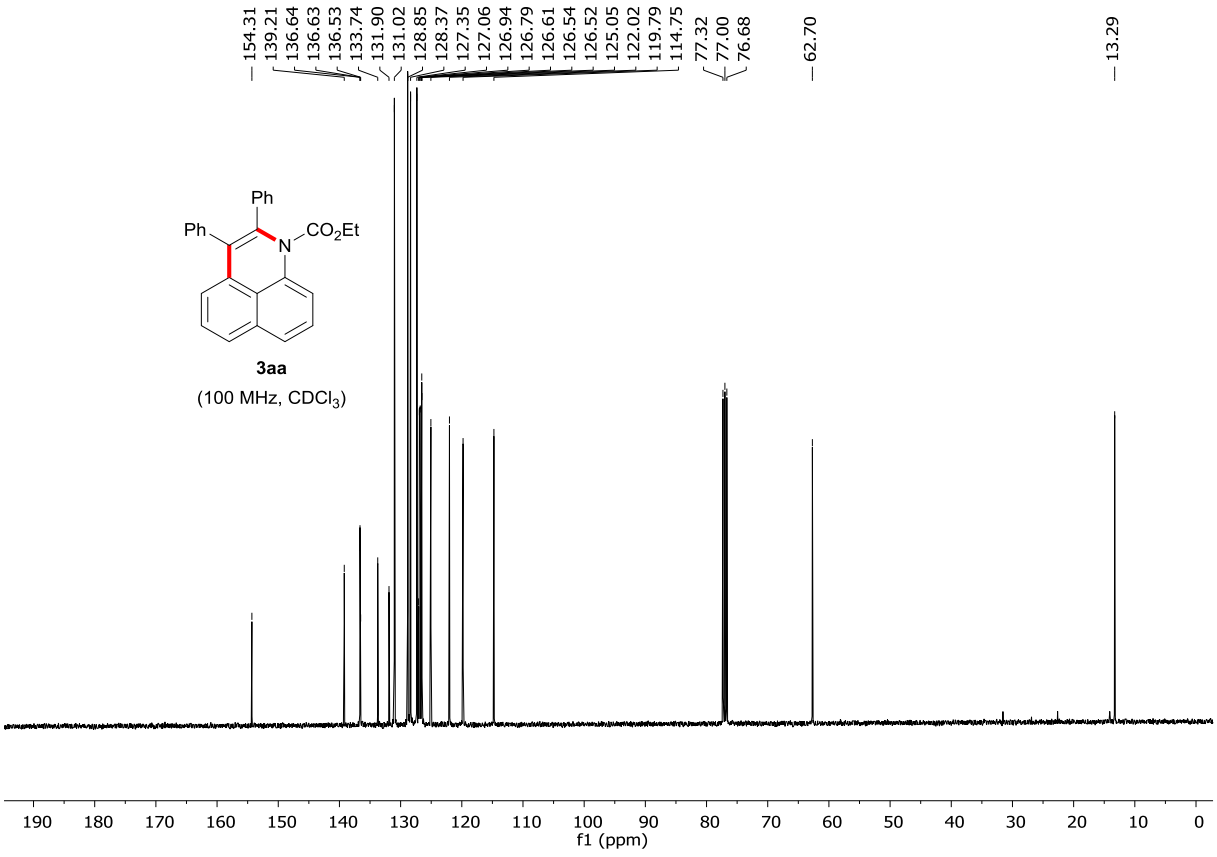
[2] (a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199–3202; (b) R. Mei, S.-K. Zhang and L. Ackermann, *Synlett*, 2017, **28**, 1715–1718.

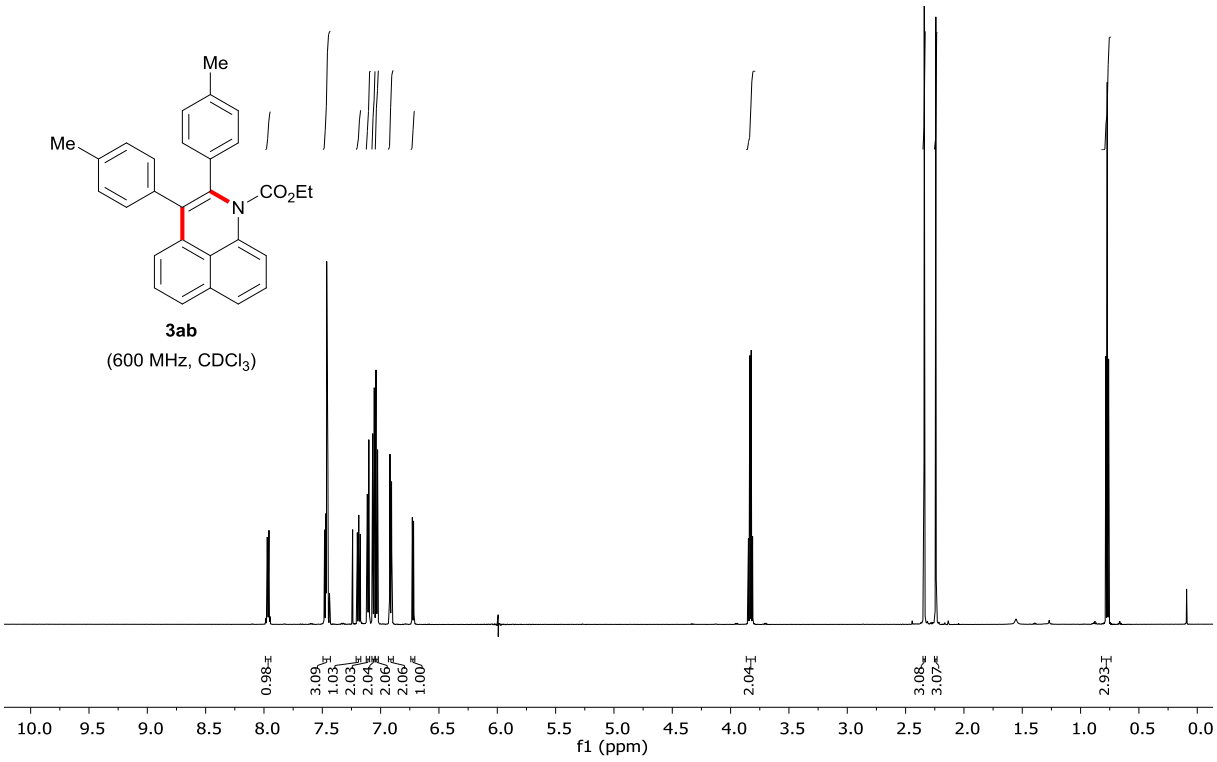
[3] (a) V. S. Thirunavukkarasu, M. Donati and L. Ackermann, *Org. Lett.*, 2012, **14**, 3416–3419; (b) S. Mochida, M. Shimizu, K. Hirano, T. Satoh and M. Miura, *Chem. Asian J.*, 2010, **5**, 847–851.

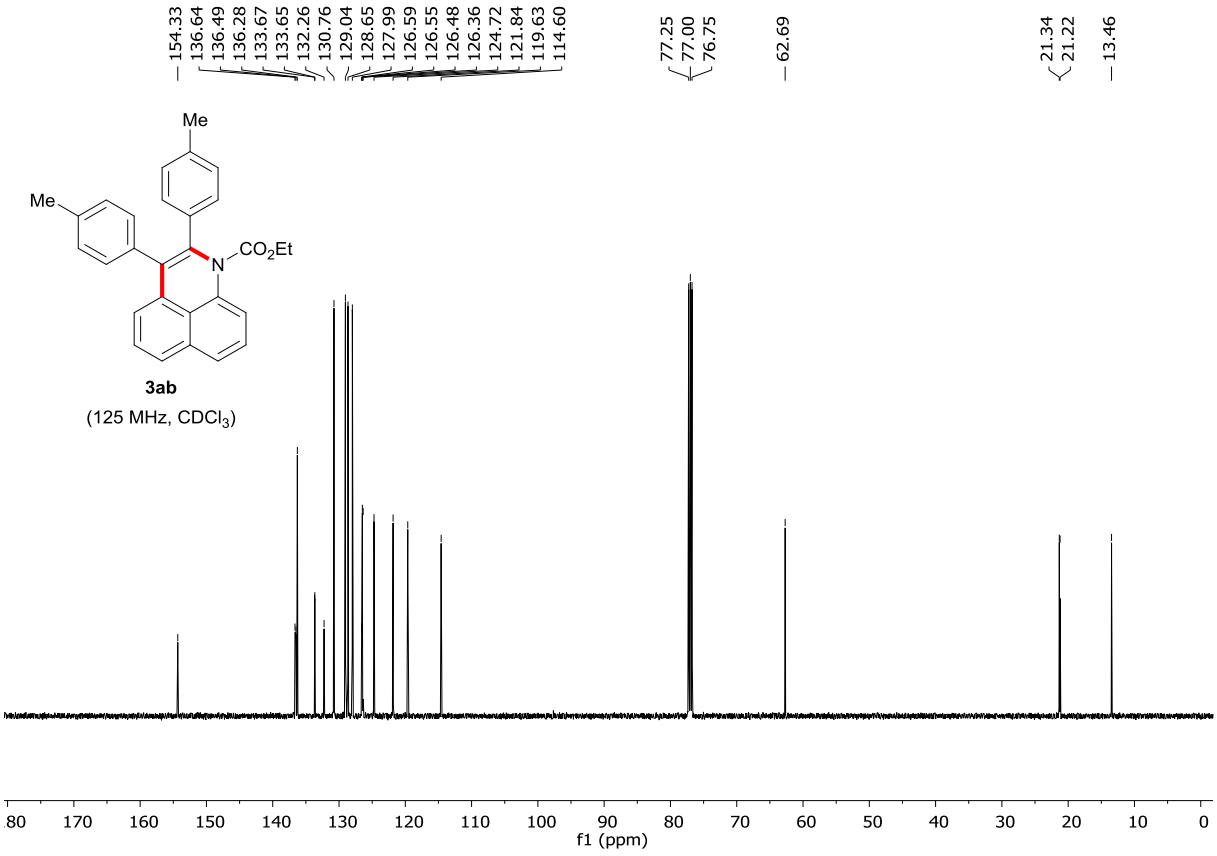
[4] R. Odani, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2013, **78**, 11045–11052.

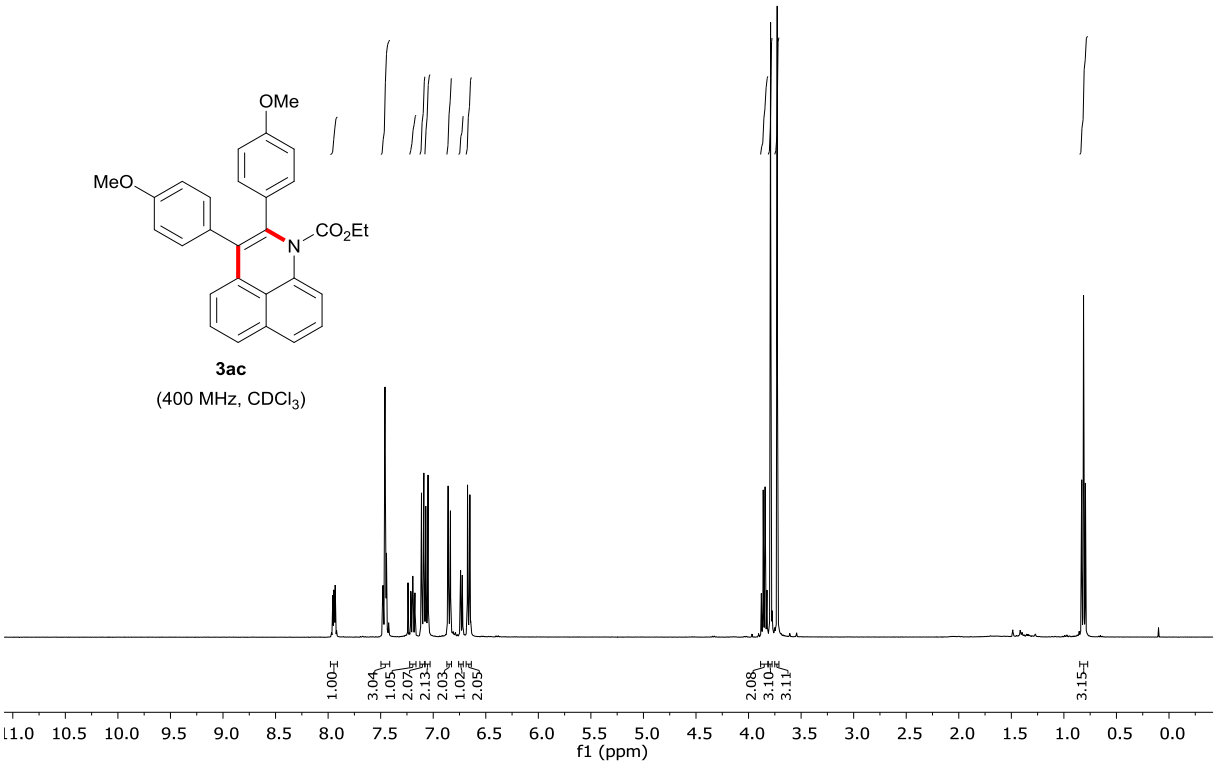
^{1}H-, ^{13}C- and ^{19}F-NMR Spectra





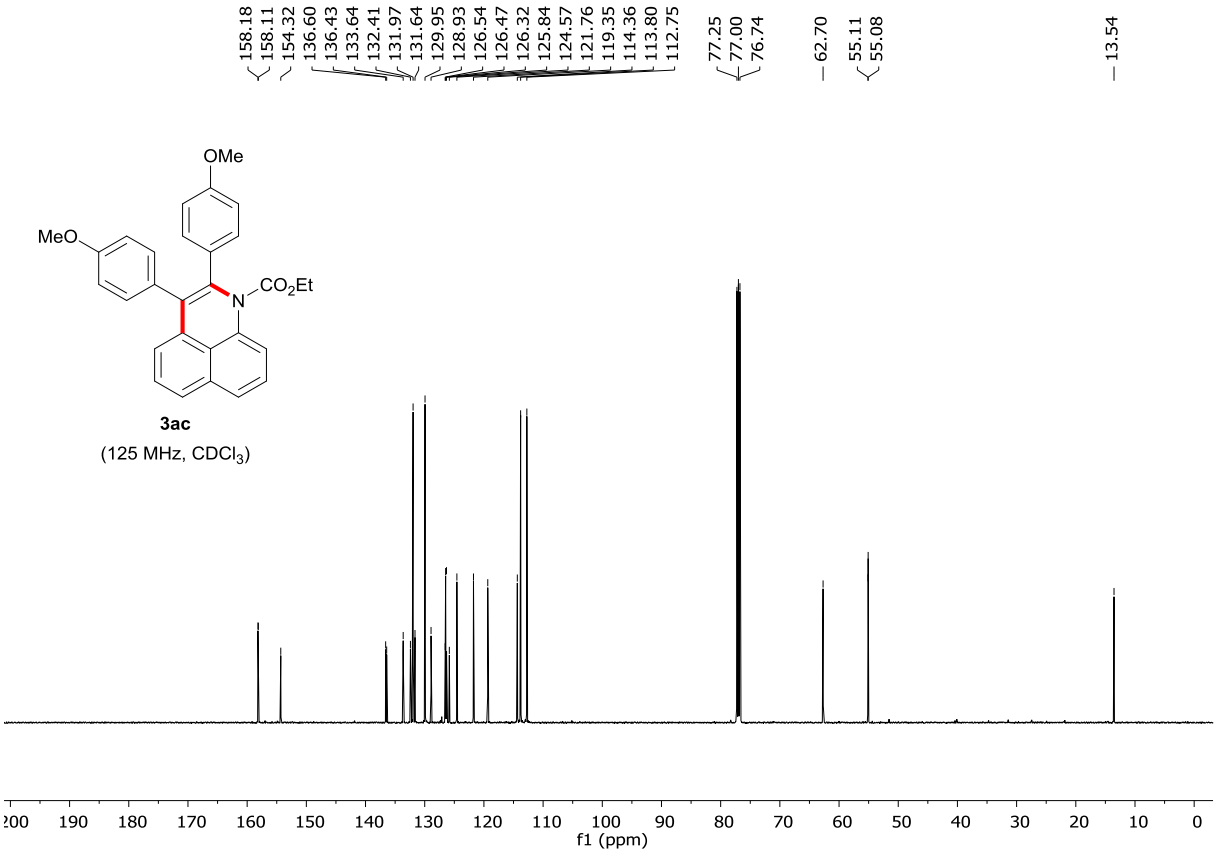

Me
Me
N
CO2Et
3ab
(600 MHz, CDCl3)
0.98
3.09
1.03
2.03
2.04
2.06
2.06
1.00
2.04
3.08
3.07
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.33
136.64
136.49
136.28
133.67
133.65
132.26
130.76
129.04
128.65
127.99
126.59
126.55
126.48
126.36
124.72
121.84
119.63
114.60
77.25
77.00
76.75
62.69
21.34
21.22
13.46
Me
Me
N
CO2Et
3ab
(125 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



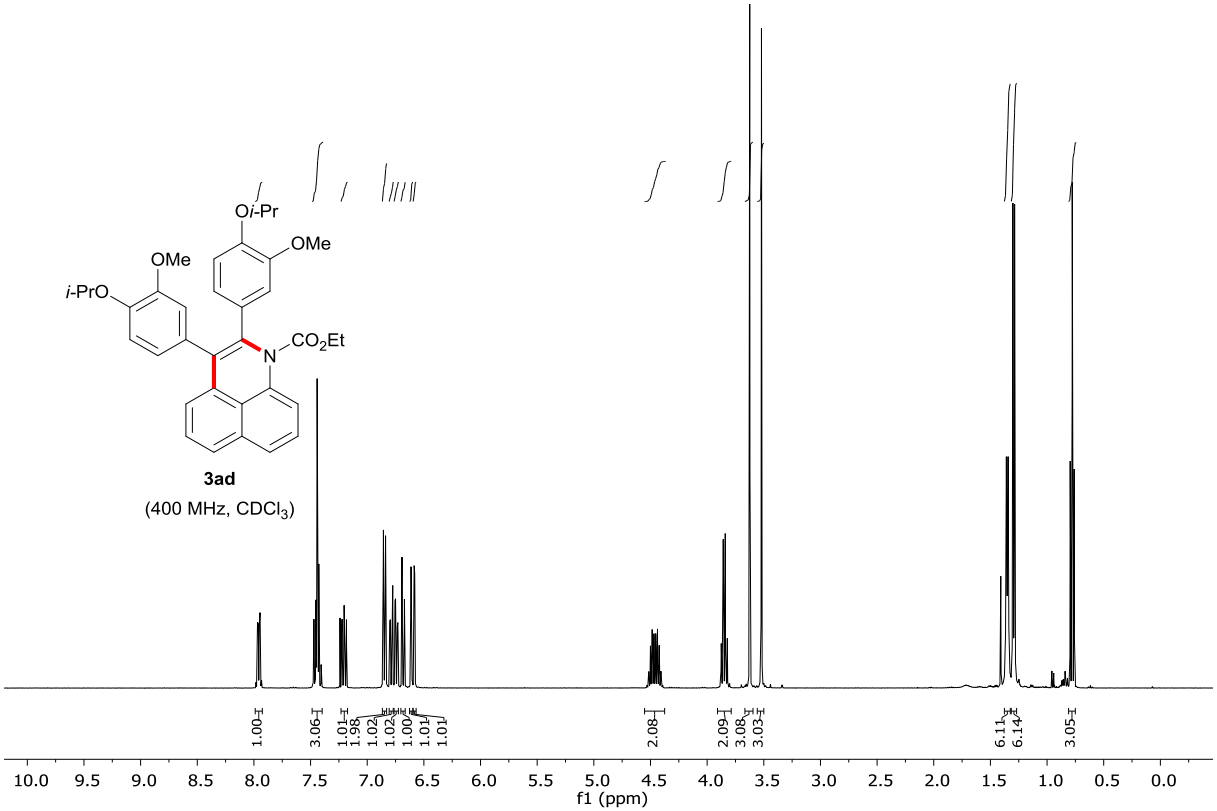
3ac

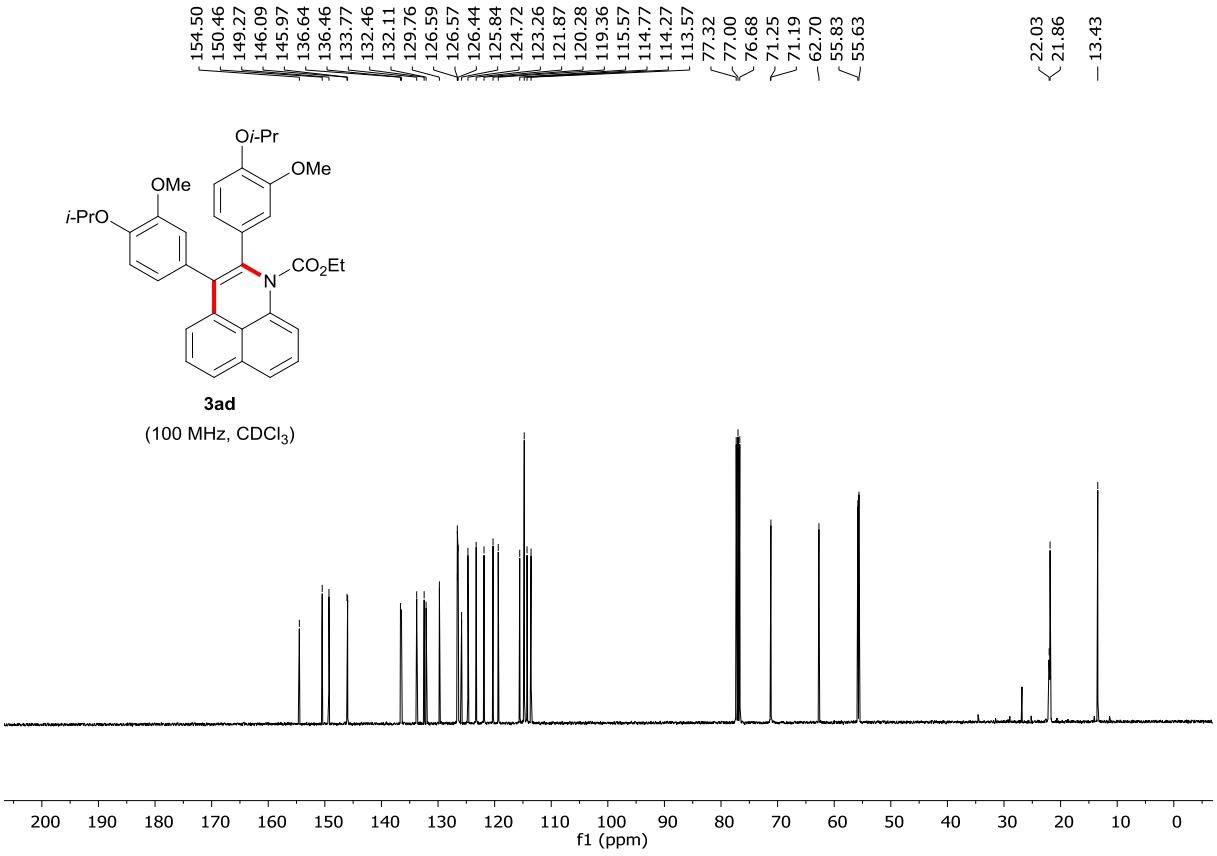
(400 MHz, $CDCl_3$)

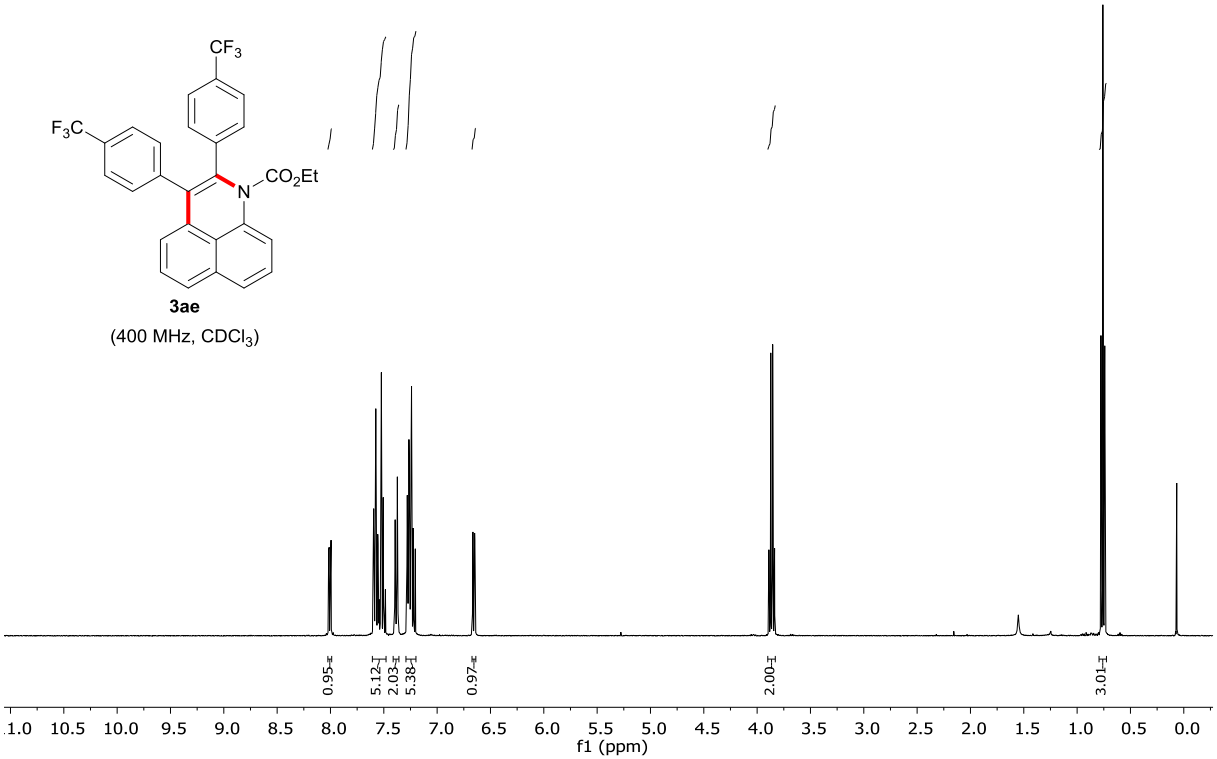


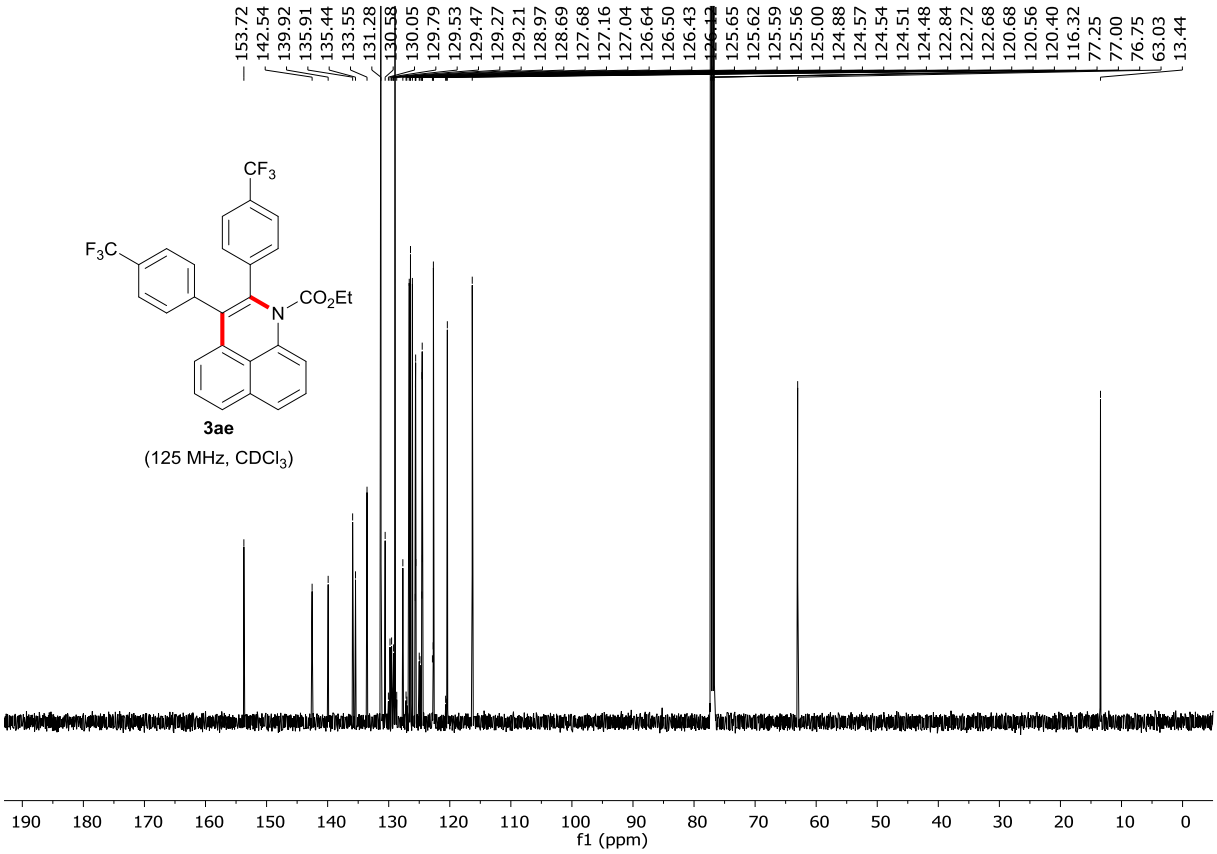
3ac

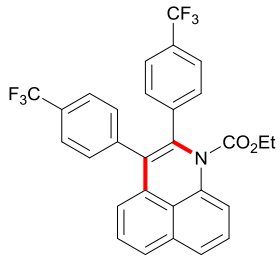
(125 MHz, $CDCl_3$)


Oi-Pr
OMe
OMe
i-PrO
CO2Et
N
3ad
(400 MHz, CDCl3)
1.00
3.06
1.01
1.98
1.02
1.02
1.00
1.01
1.01
2.08
2.09
3.08
3.03
6.11
6.14
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.50
150.46
149.27
146.09
145.97
136.64
136.46
133.77
132.46
132.11
129.76
126.59
126.57
126.44
125.84
124.72
123.26
121.87
120.28
119.36
115.57
114.77
114.27
113.57
77.32
77.00
76.68
71.25
71.19
62.70
55.83
55.63
22.03
21.86
13.43
Oi-Pr
OMe
OMe
i-PrO
CO2Et
N
3ad
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

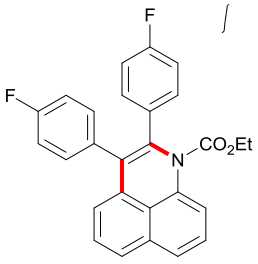

CF3
F3C
CO2Et
N
3ae
(400 MHz, CDCl3)
0.95
5.12
2.03
5.38
0.97
2.00
3.01
f1 (ppm)


153.72
142.54
139.92
135.91
135.44
133.55
131.28
130.58
130.05
129.79
129.53
129.47
129.27
129.21
128.97
128.69
127.68
127.16
127.04
126.64
126.50
126.43
125.65
125.62
125.59
125.56
125.00
124.88
124.57
124.54
124.51
124.48
122.84
122.72
122.68
120.68
120.56
120.40
116.32
77.25
77.00
76.75
63.03
13.44
CF3
F3C
CO2Et
N
3ae
(125 MHz, CDCl3)
f1 (ppm)



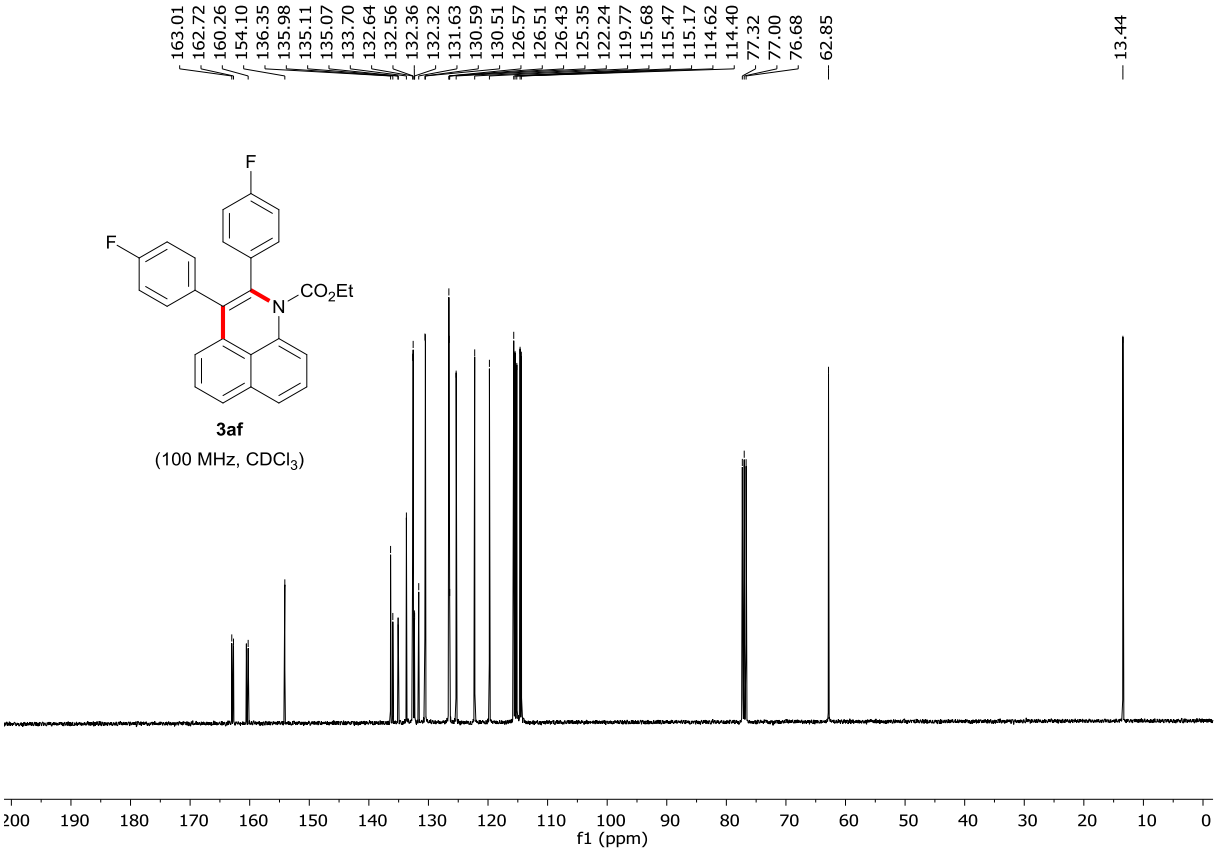
3ae

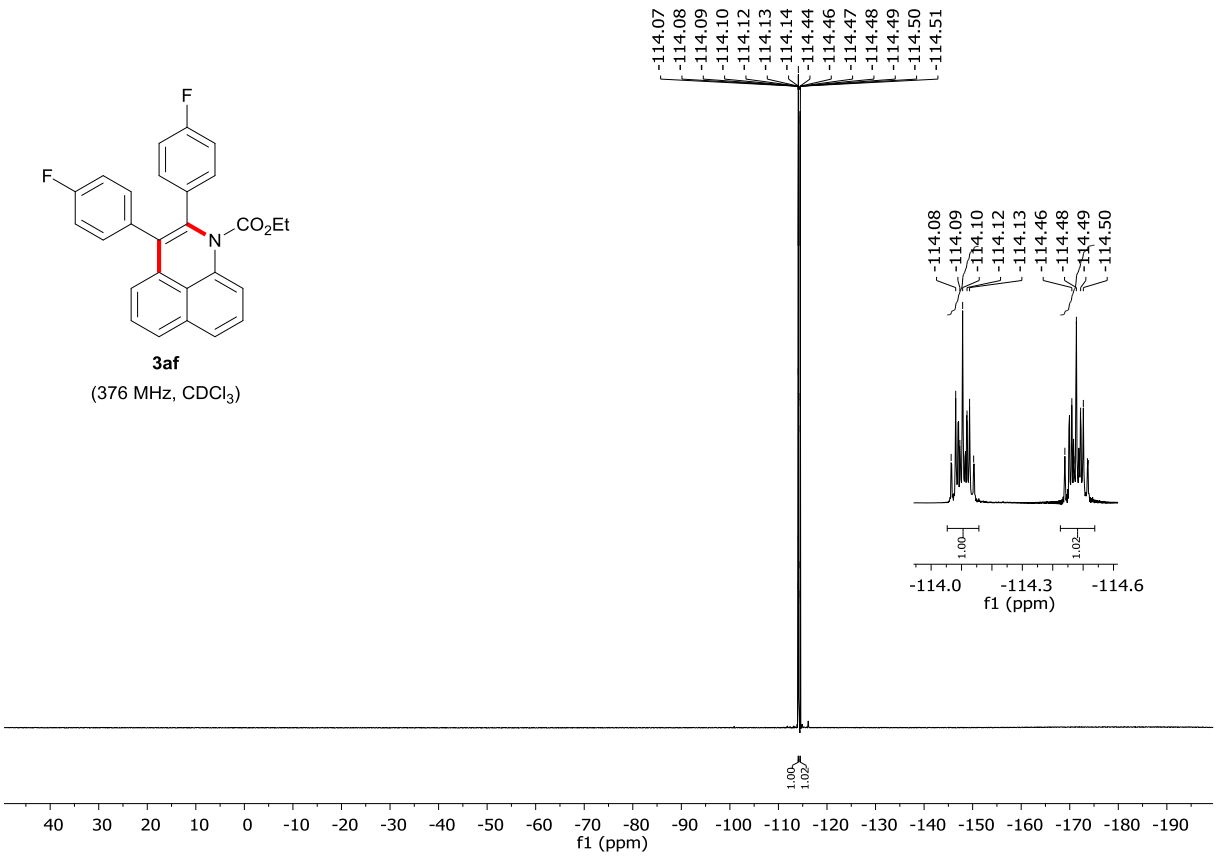
(376 MHz, $CDCl_3$)

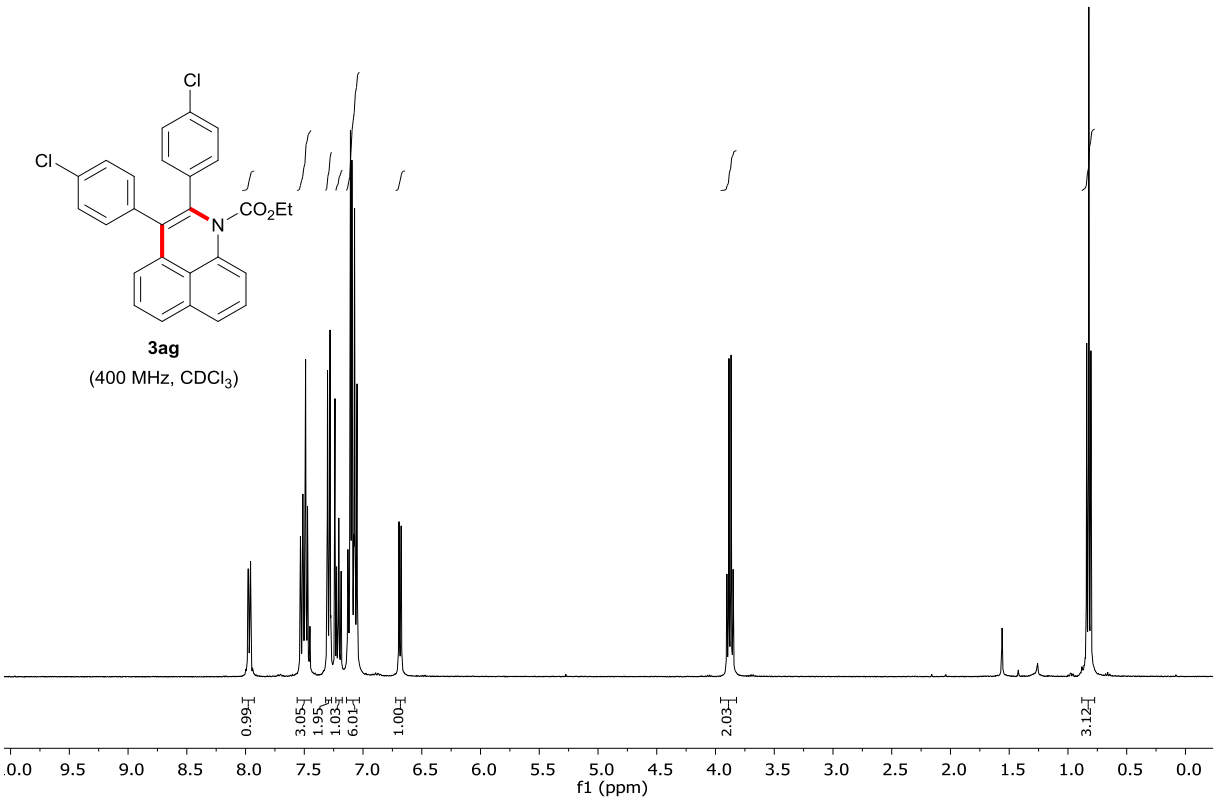


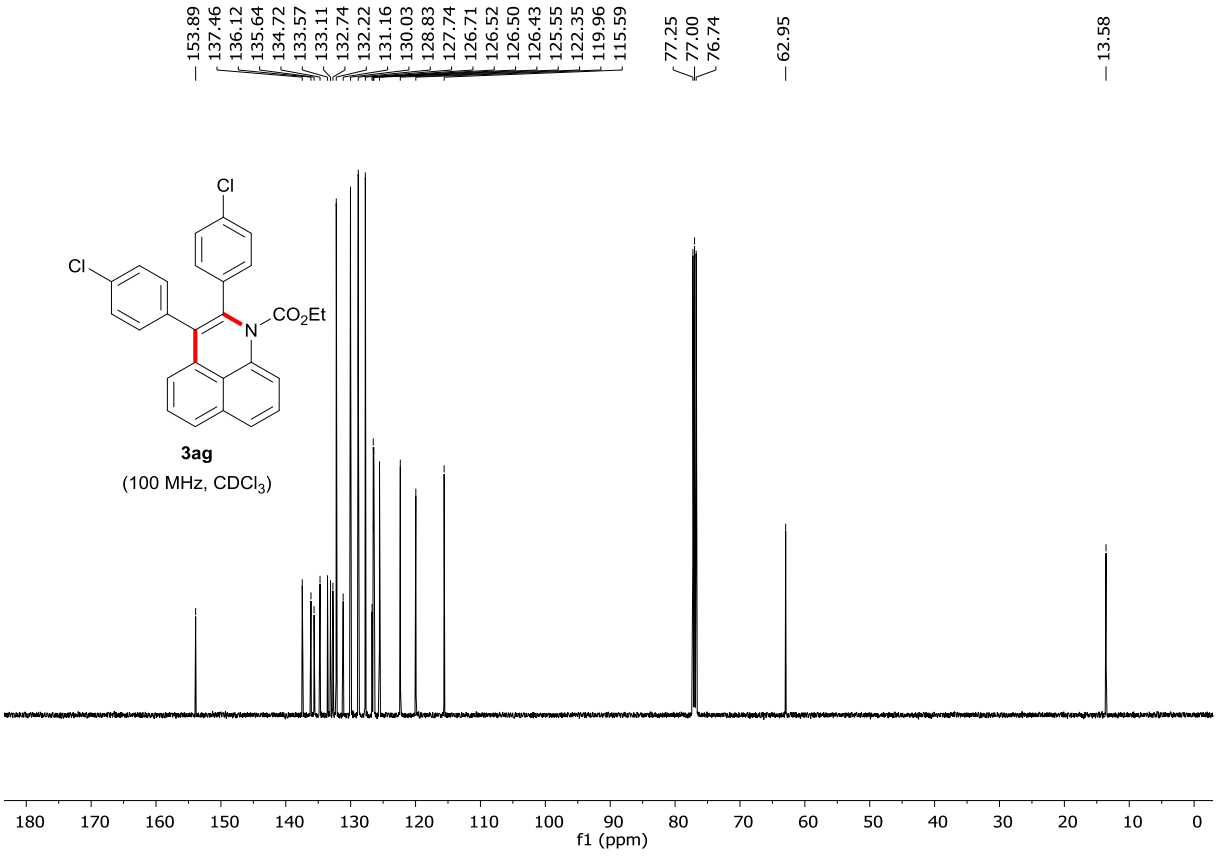
3af

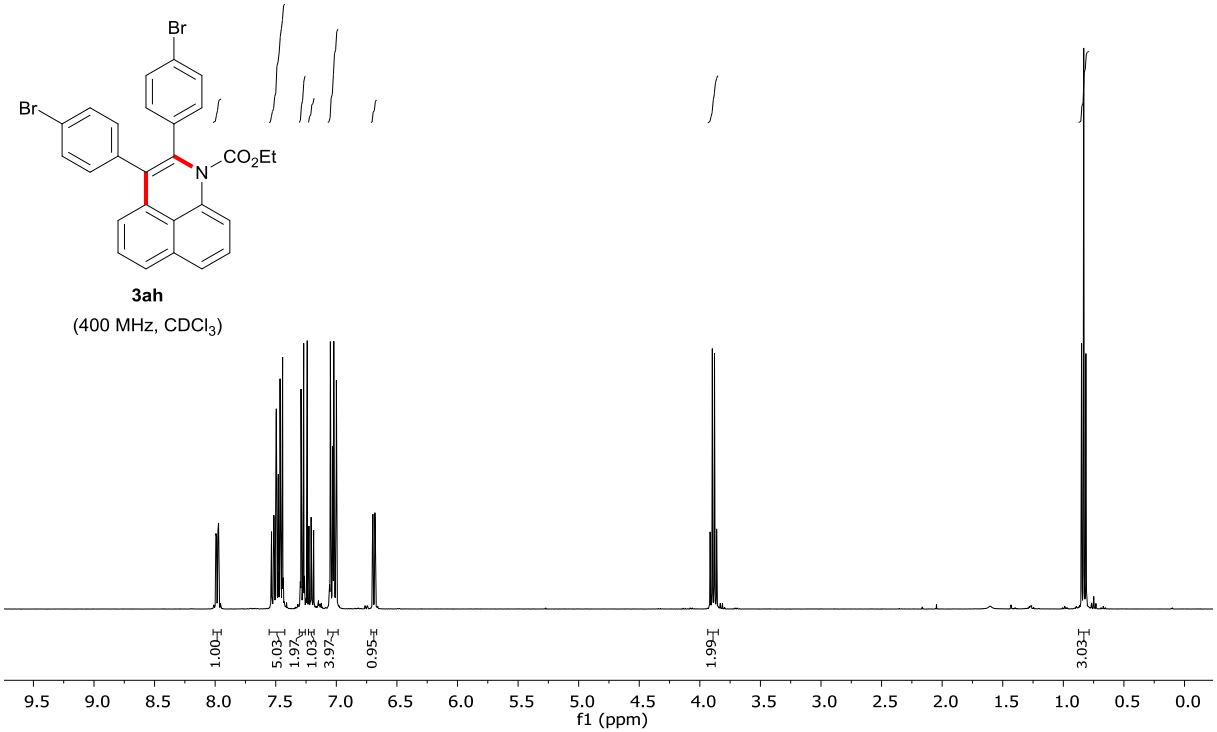
(400 MHz, $CDCl_3$)


163.01
162.72
160.26
154.10
136.35
135.98
135.11
135.07
133.70
132.64
132.56
132.36
132.32
131.63
130.59
130.51
126.57
126.51
126.43
125.35
122.24
119.77
115.68
115.47
115.17
114.62
114.40
77.32
77.00
76.68
62.85
13.44
F
F
N
CO2Et
3af
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-114.07
-114.08
-114.09
-114.10
-114.12
-114.13
-114.14
-114.44
-114.46
-114.47
-114.48
-114.49
-114.50
-114.51
F
F
N
CO2Et
3af
(376 MHz, CDCl3)
-114.08
-114.09
-114.10
-114.12
-114.13
-114.46
-114.48
-114.49
-114.50
1.00
1.02
-114.0
-114.3
-114.6
f1 (ppm)
1.00
1.02
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

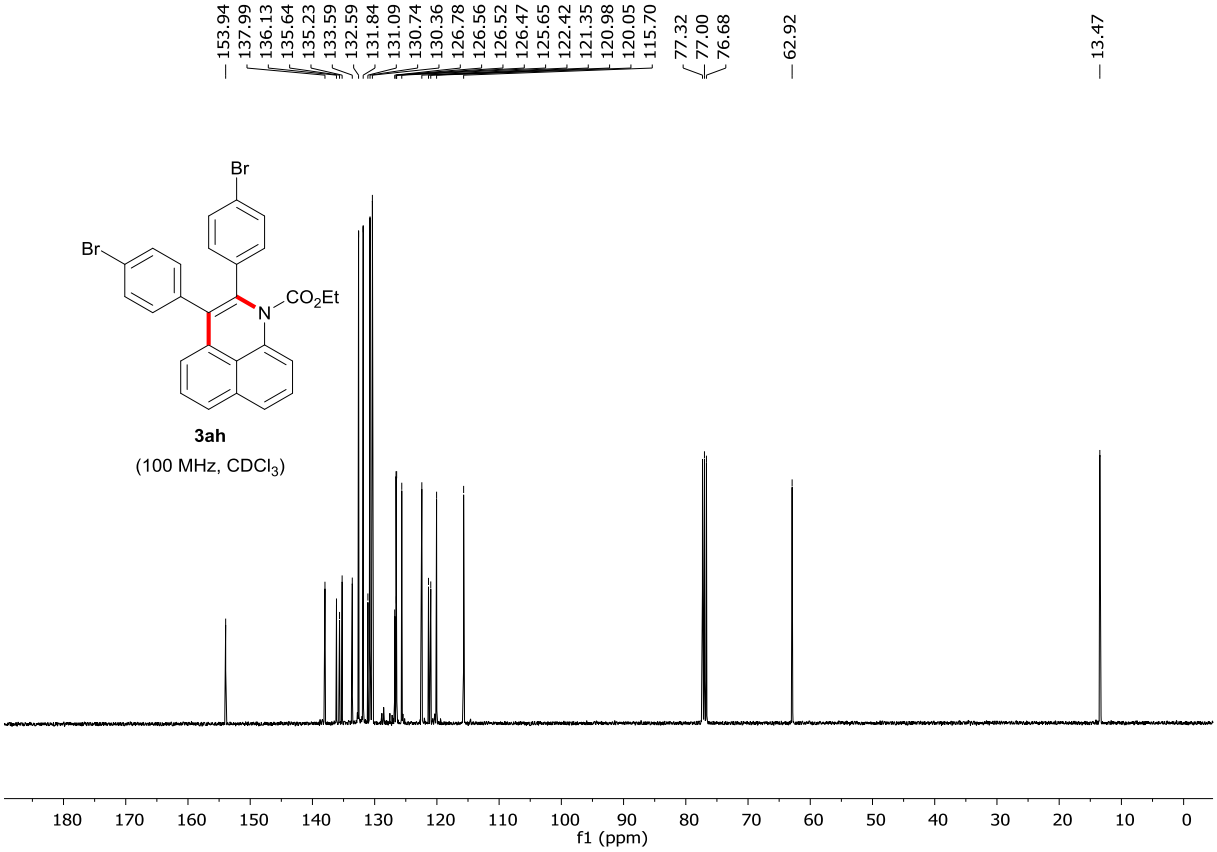

Cl
Cl
CO2Et
N
3ag
(400 MHz, CDCl3)
0.99
3.05
1.95
1.03
6.01
1.00
2.03
3.12
f1 (ppm)


153.89
137.46
136.12
135.64
134.72
133.57
133.11
132.74
132.22
131.16
130.03
128.83
127.74
126.71
126.52
126.50
126.43
125.55
122.35
119.96
115.59
77.25
77.00
76.74
62.95
13.58
Cl
Cl
CO2Et
N
3ag
(100 MHz, CDCl3)
f1 (ppm)



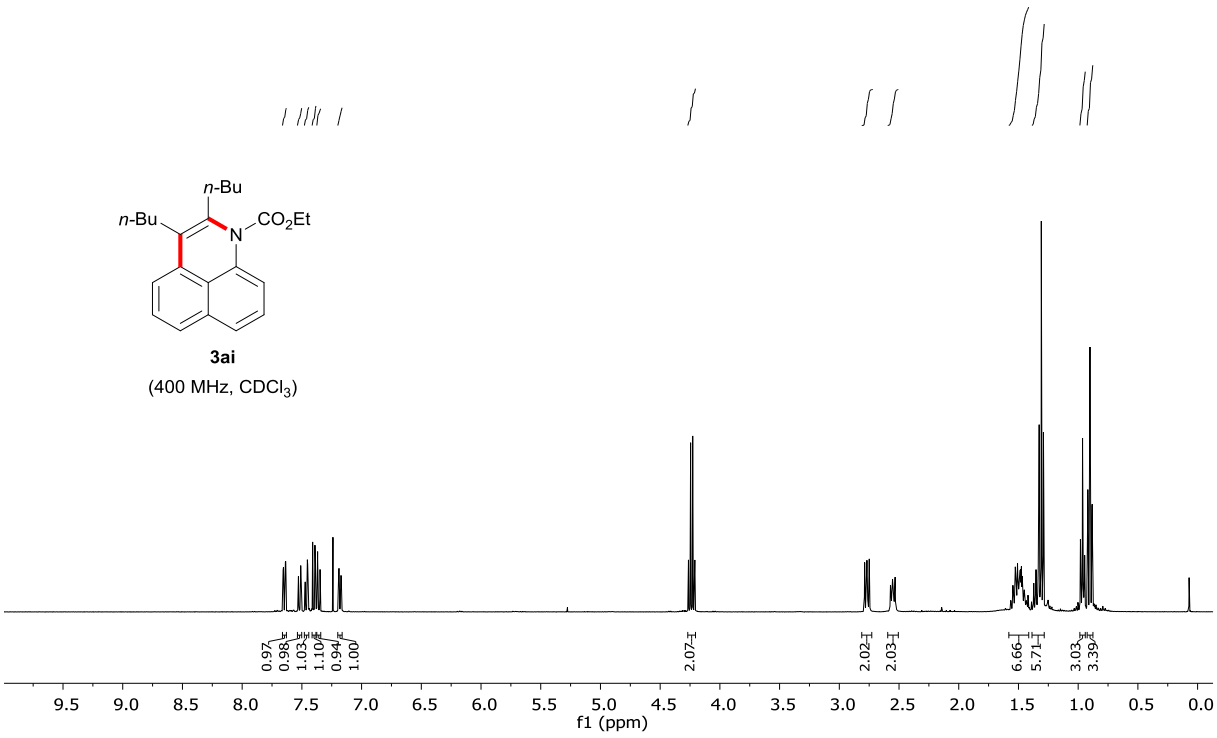
3ah

(400 MHz, $CDCl_3$)



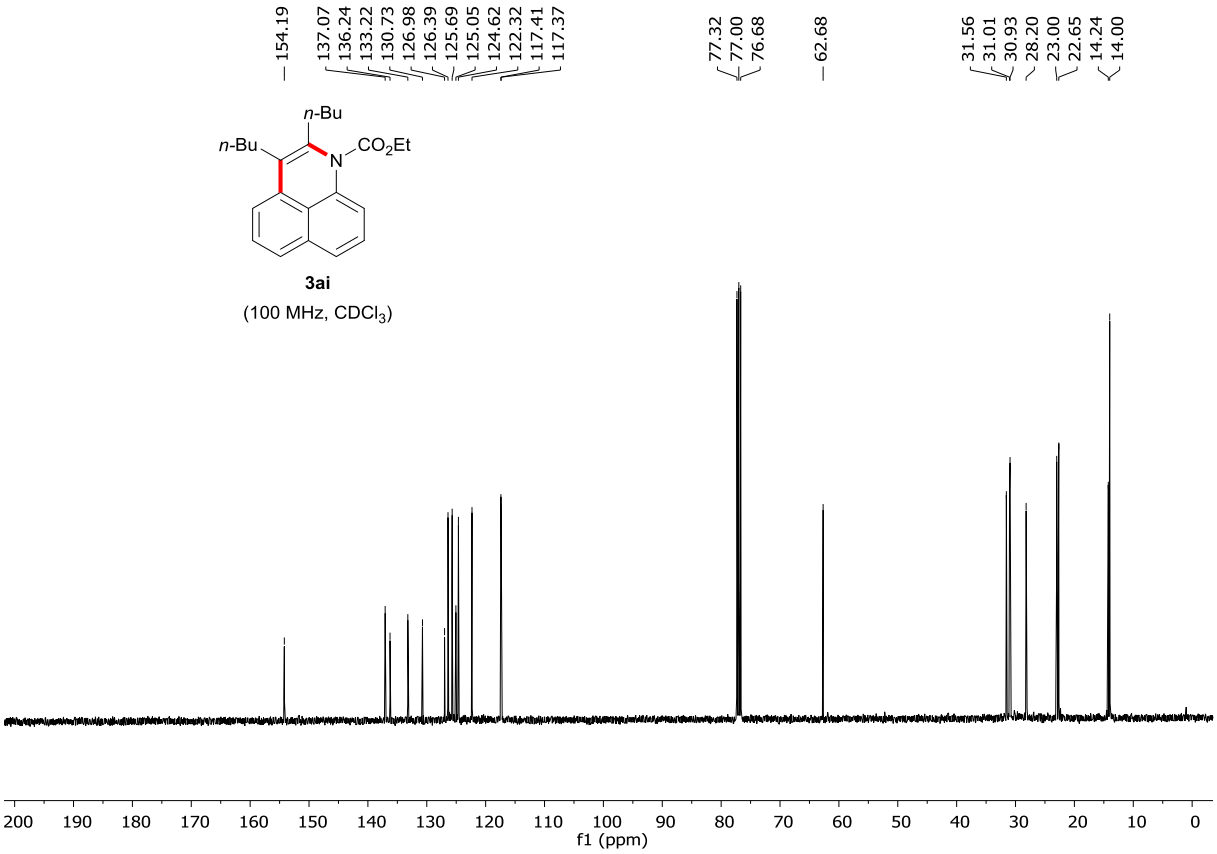
3ah

(100 MHz, $CDCl_3$)



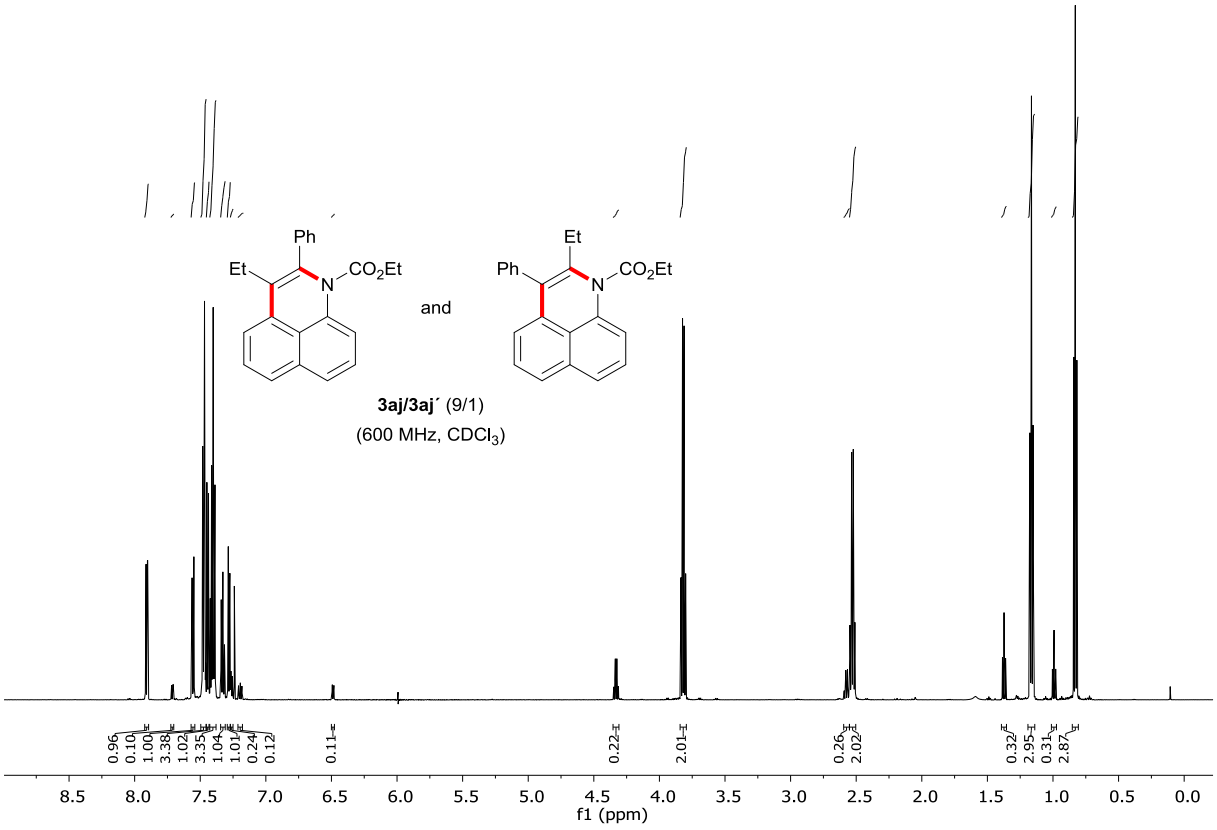
3ai

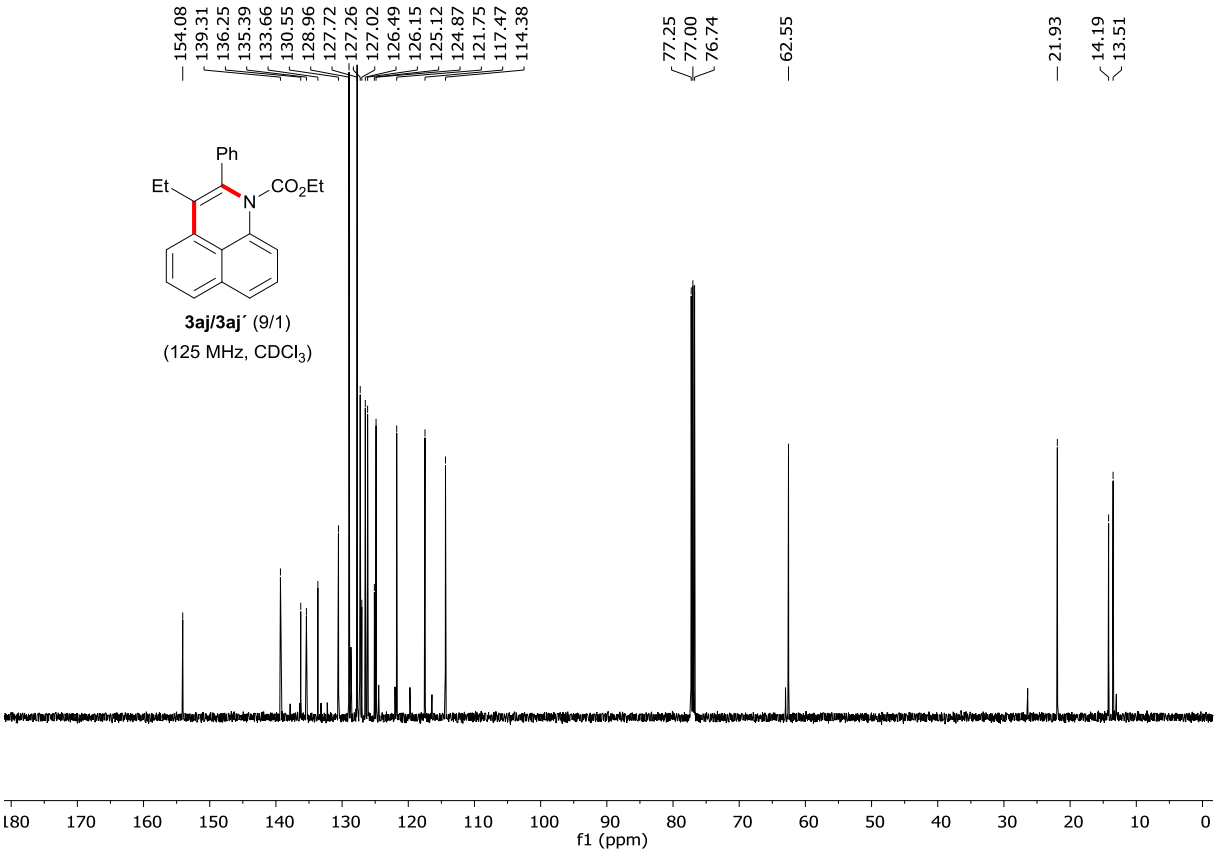
(400 MHz, $CDCl_3$)

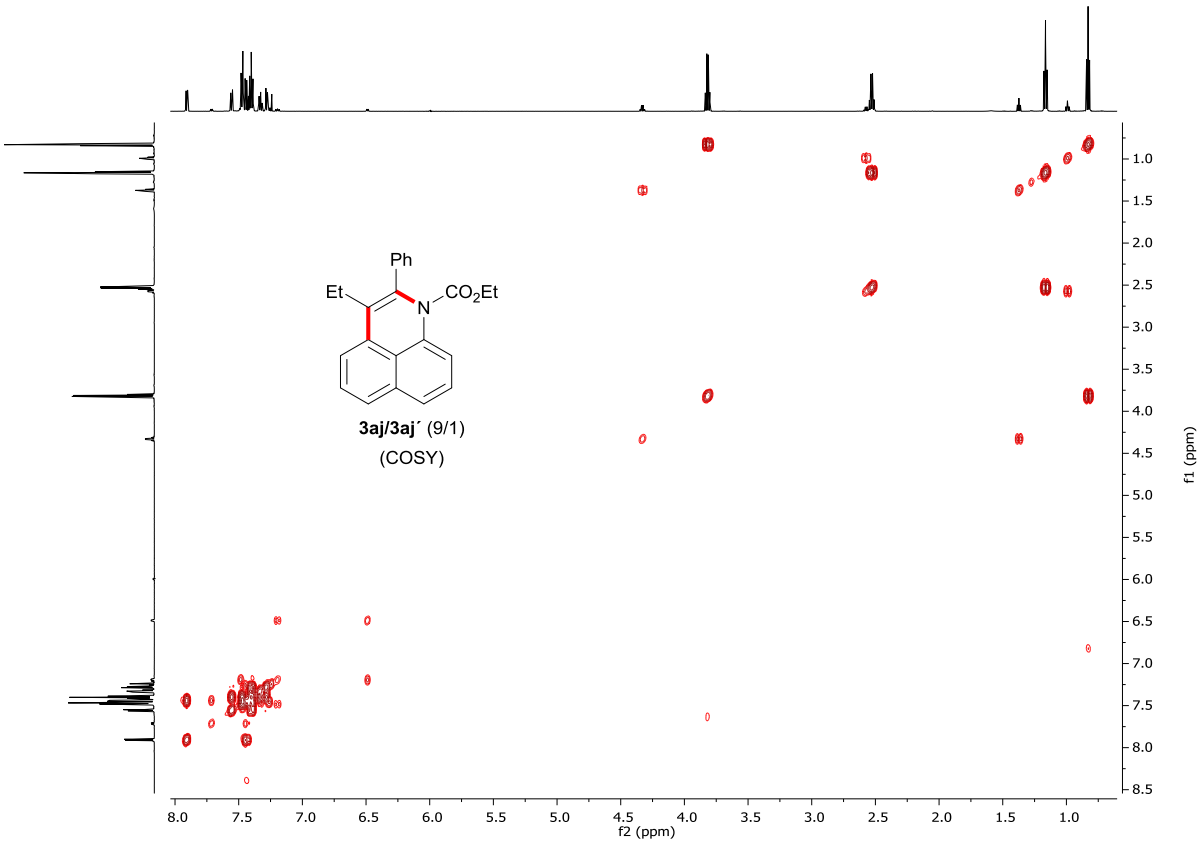


3ai

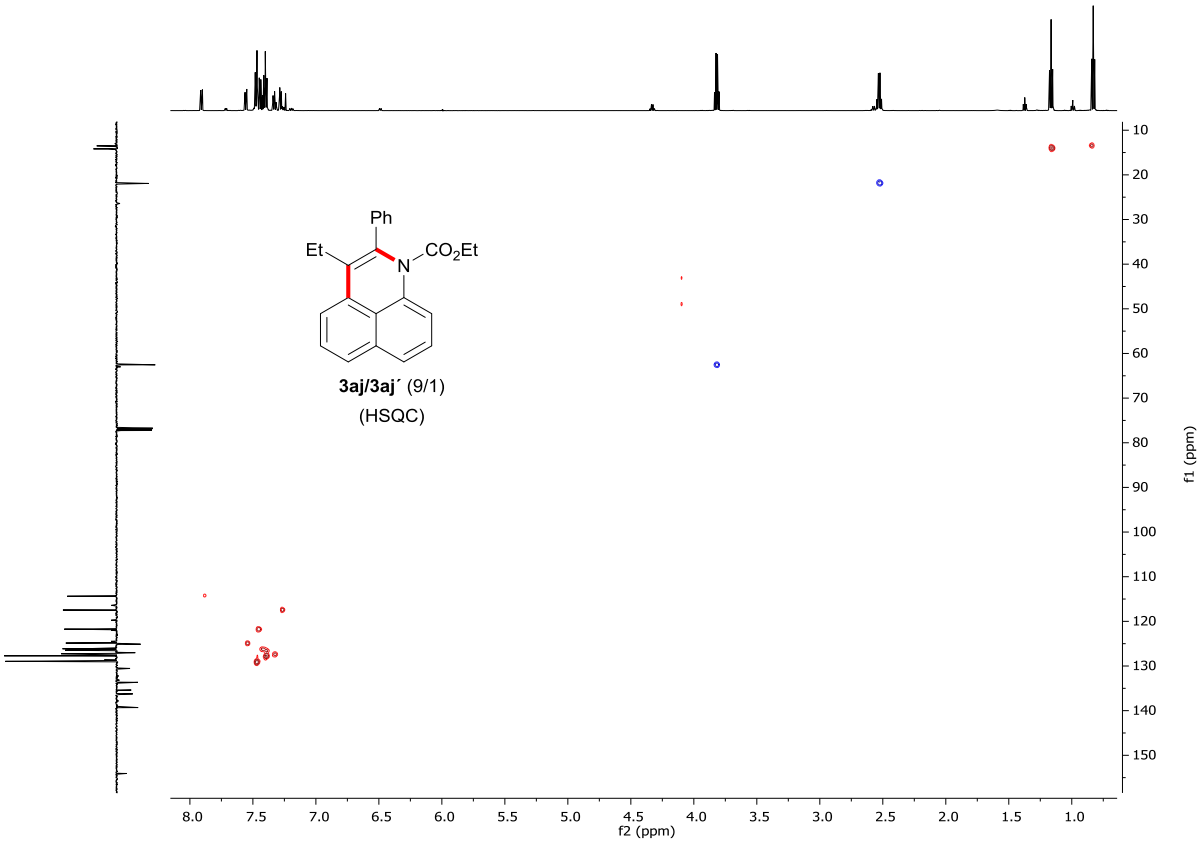
(100 MHz, $CDCl_3$)


Ph
Et
N
CO2Et
and
Et
Ph
N
CO2Et
3aj/3aj´ (9/1)
(600 MHz, CDCl3)
0.96
0.10
1.00
3.38
1.02
3.35
1.04
1.01
0.24
0.12
0.11
0.22
2.01
0.26
2.02
0.32
2.95
0.31
2.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

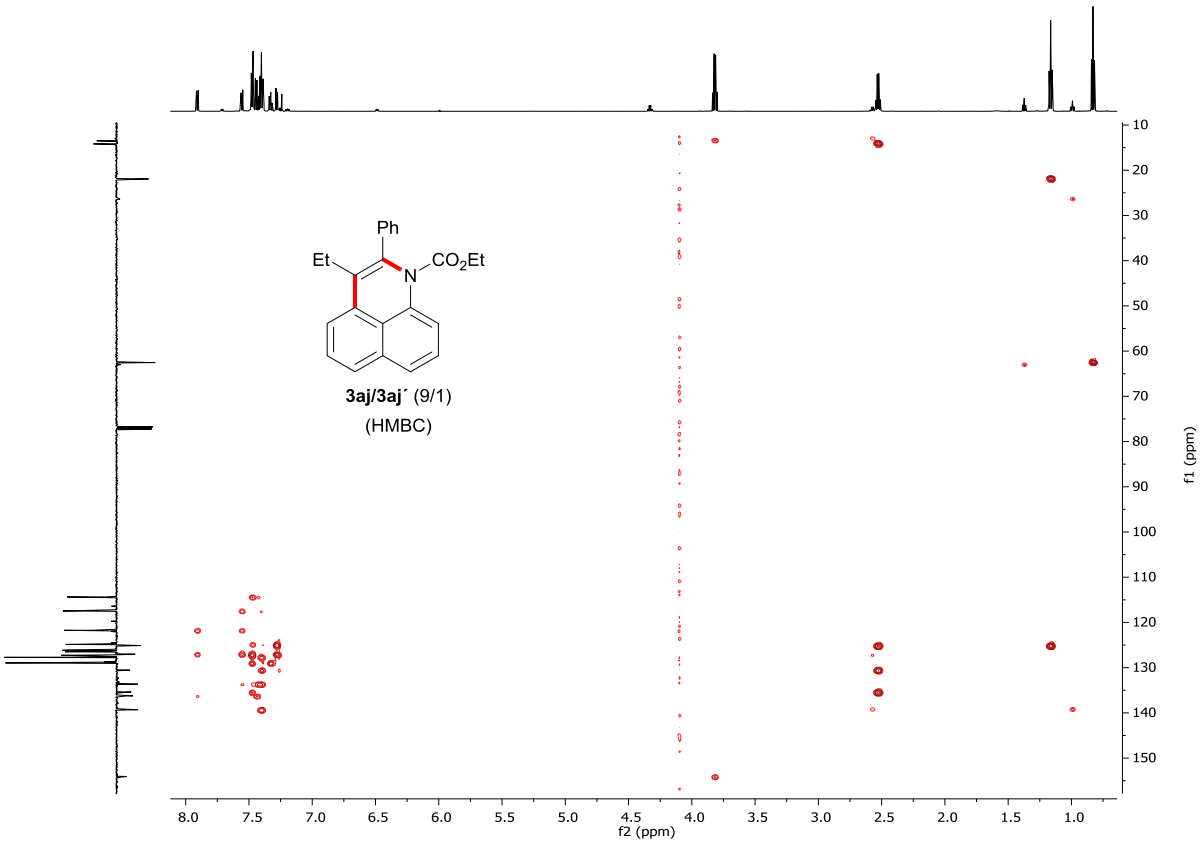

154.08
139.31
136.25
135.39
133.66
130.55
128.96
127.72
127.26
127.02
126.49
126.15
125.12
124.87
121.75
117.47
114.38
77.25
77.00
76.74
62.55
21.93
14.19
13.51
Ph
Et
N
CO2Et
3aj/3aj´ (9/1)
(125 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

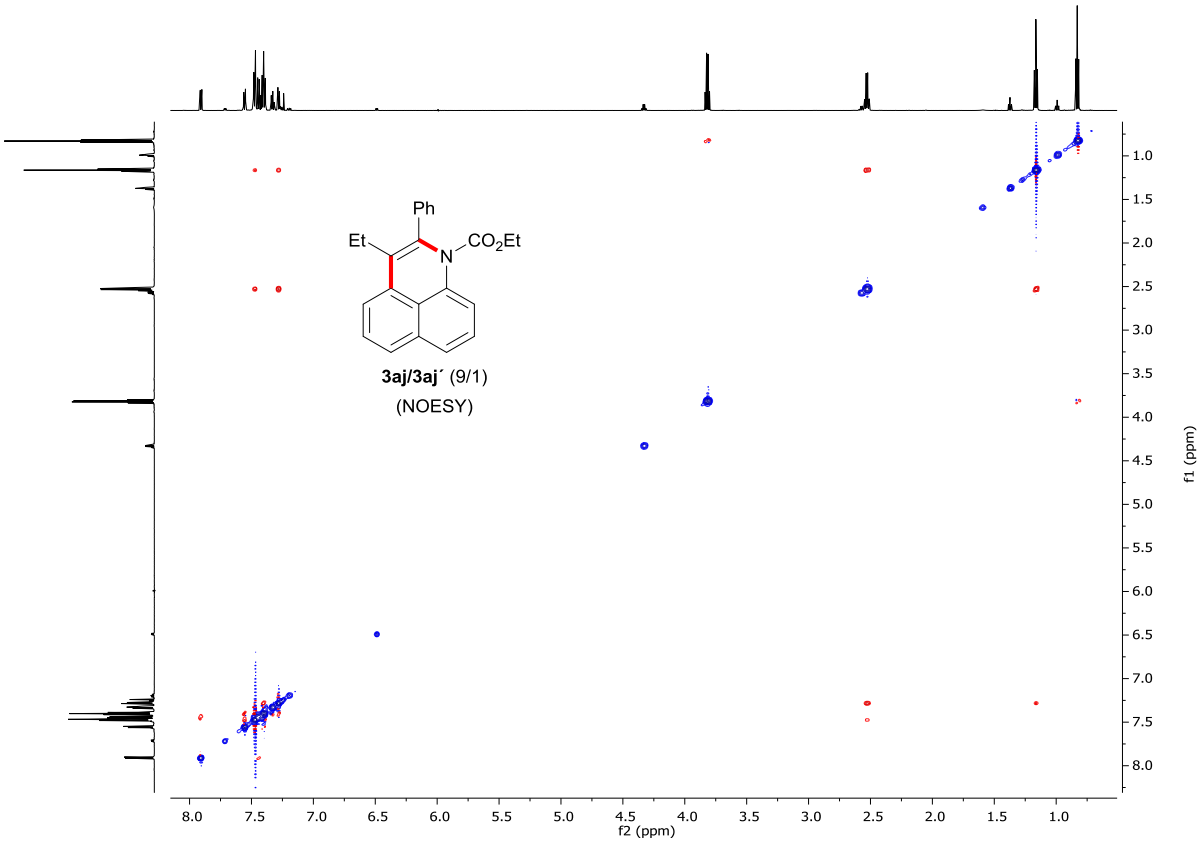


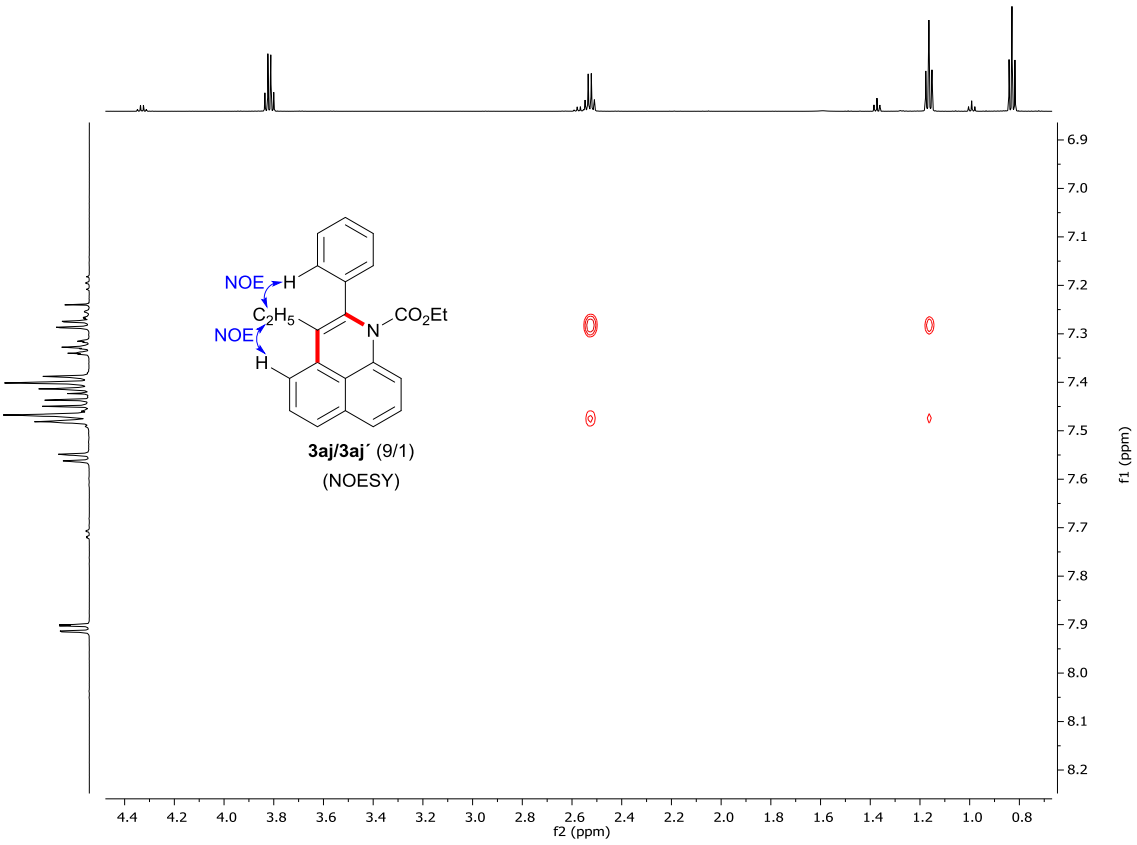
3aj/3aj´ (9/1)
(COSY)

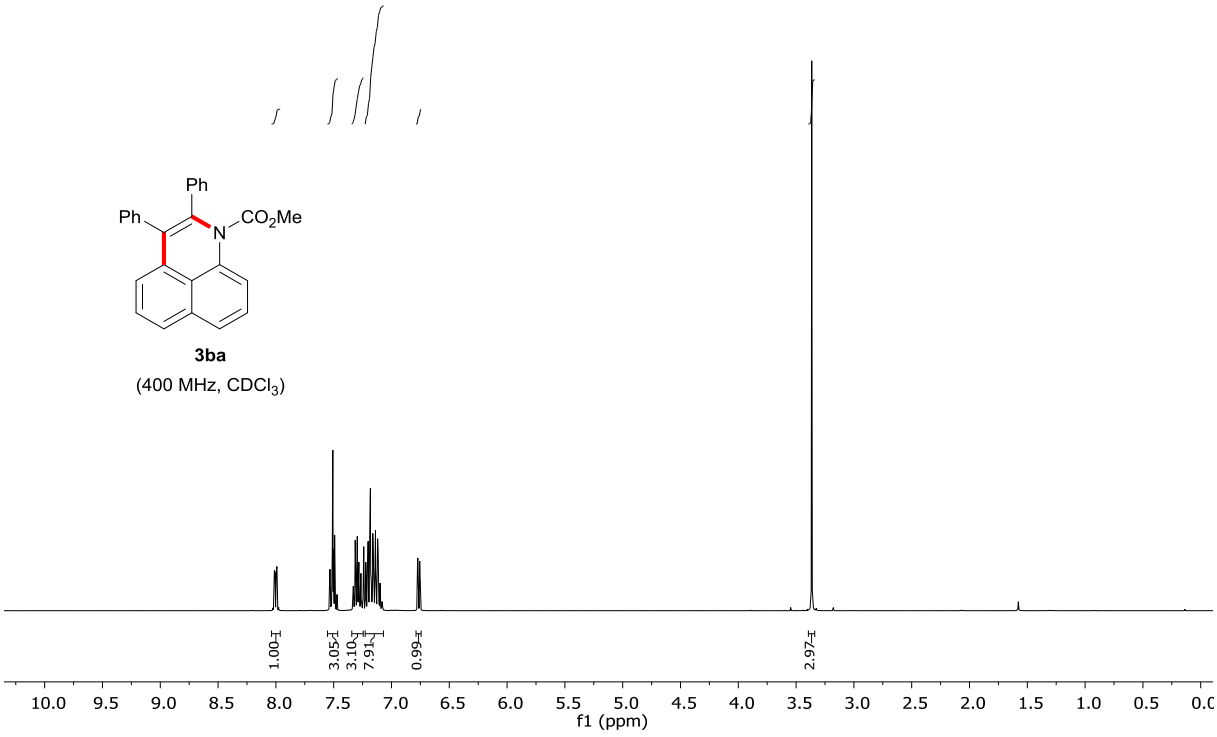


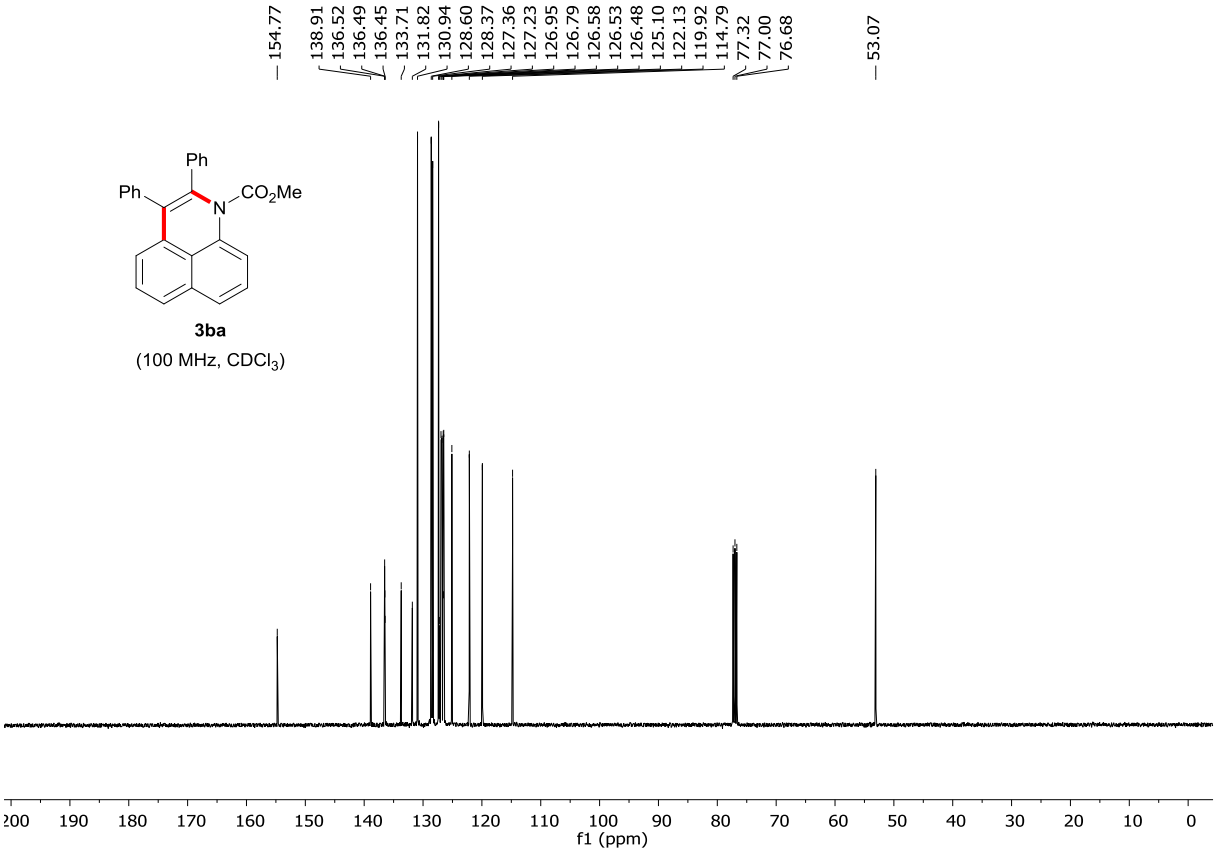
3aj/3aj´ (9/1)
(HSQC)

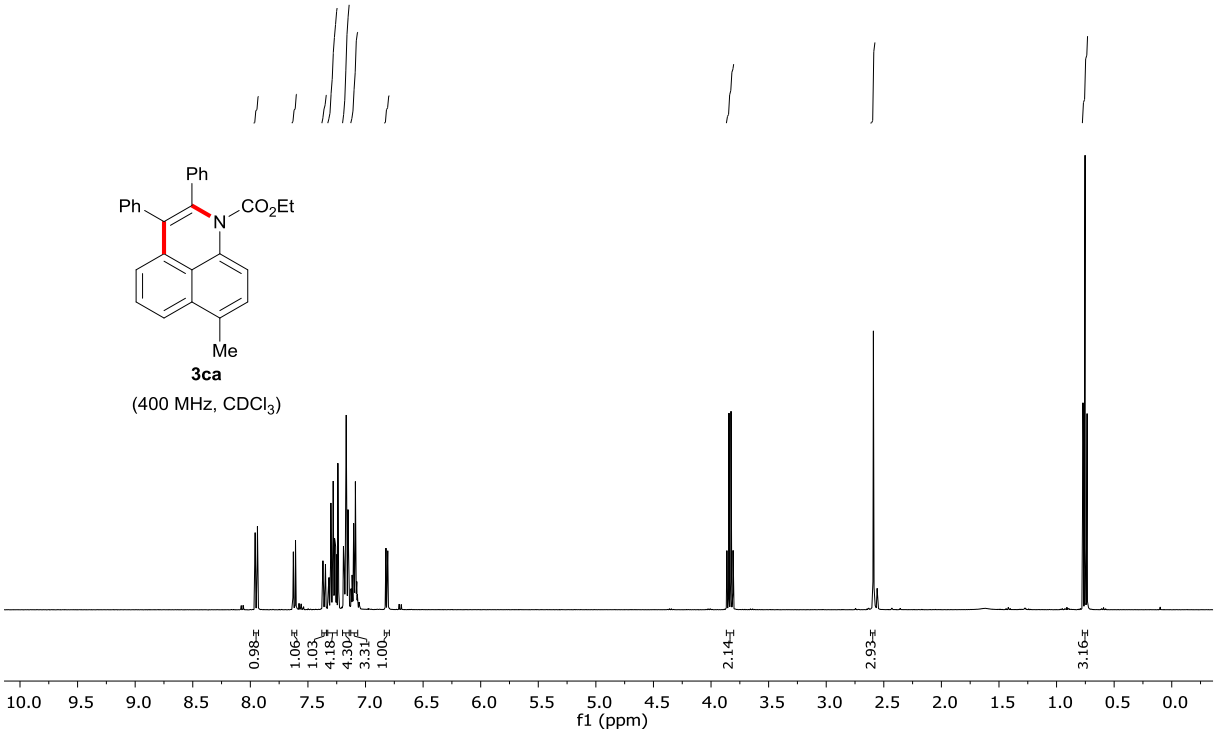

Ph
Et
N
CO2Et
3aj/3aj´ (9/1)
(HMBC)
f2 (ppm)
f1 (ppm)

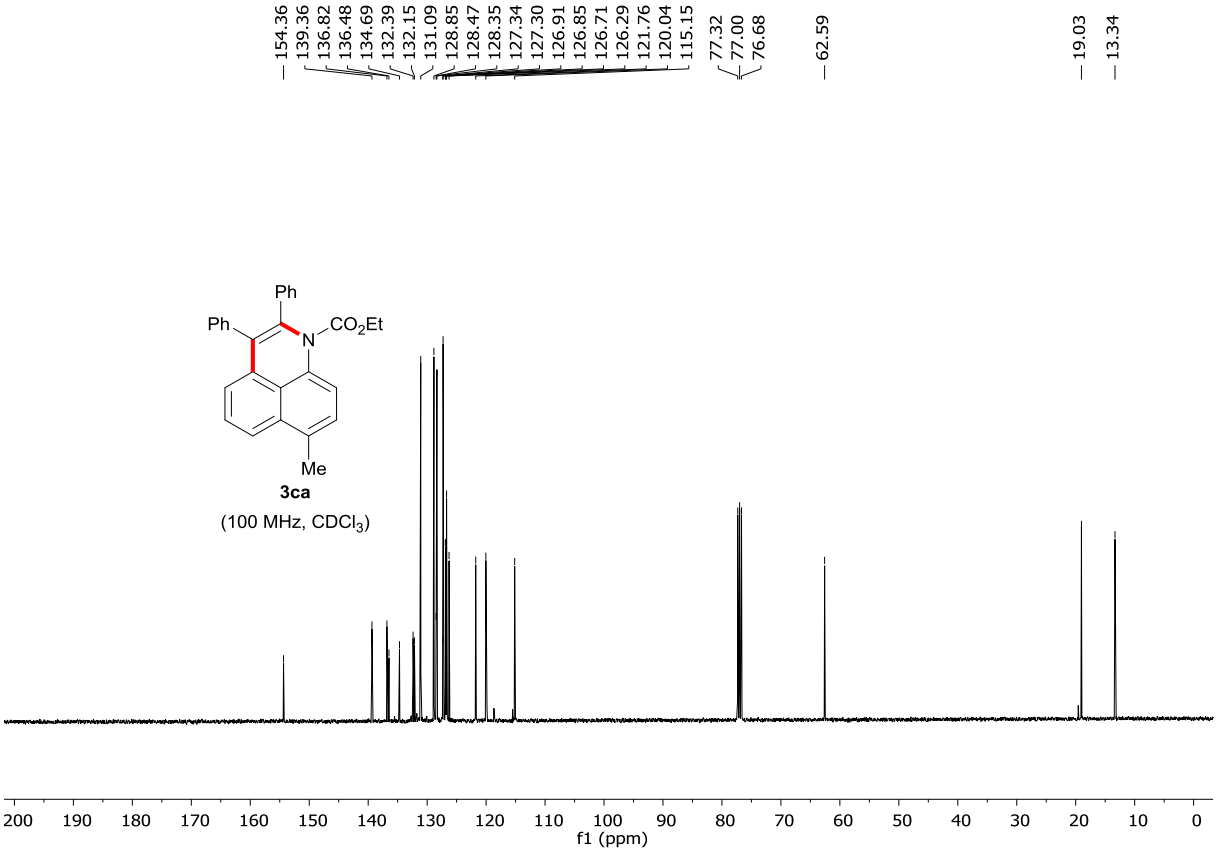

Ph
Et
N
CO2Et
3aj/3aj´ (9/1)
(NOESY)
f2 (ppm)
f1 (ppm)

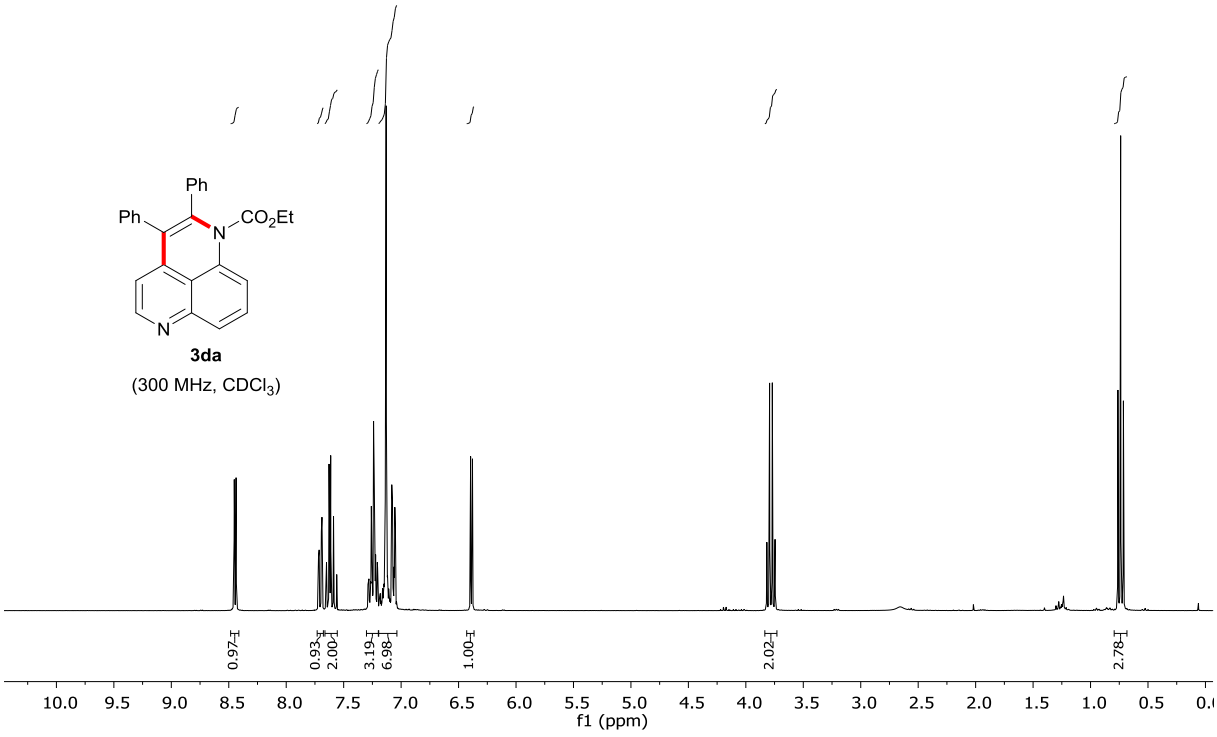

NOE
H
C2H5
NOE
H
N
CO2Et
3aj/3aj´ (9/1)
(NOESY)
f2 (ppm)
f1 (ppm)

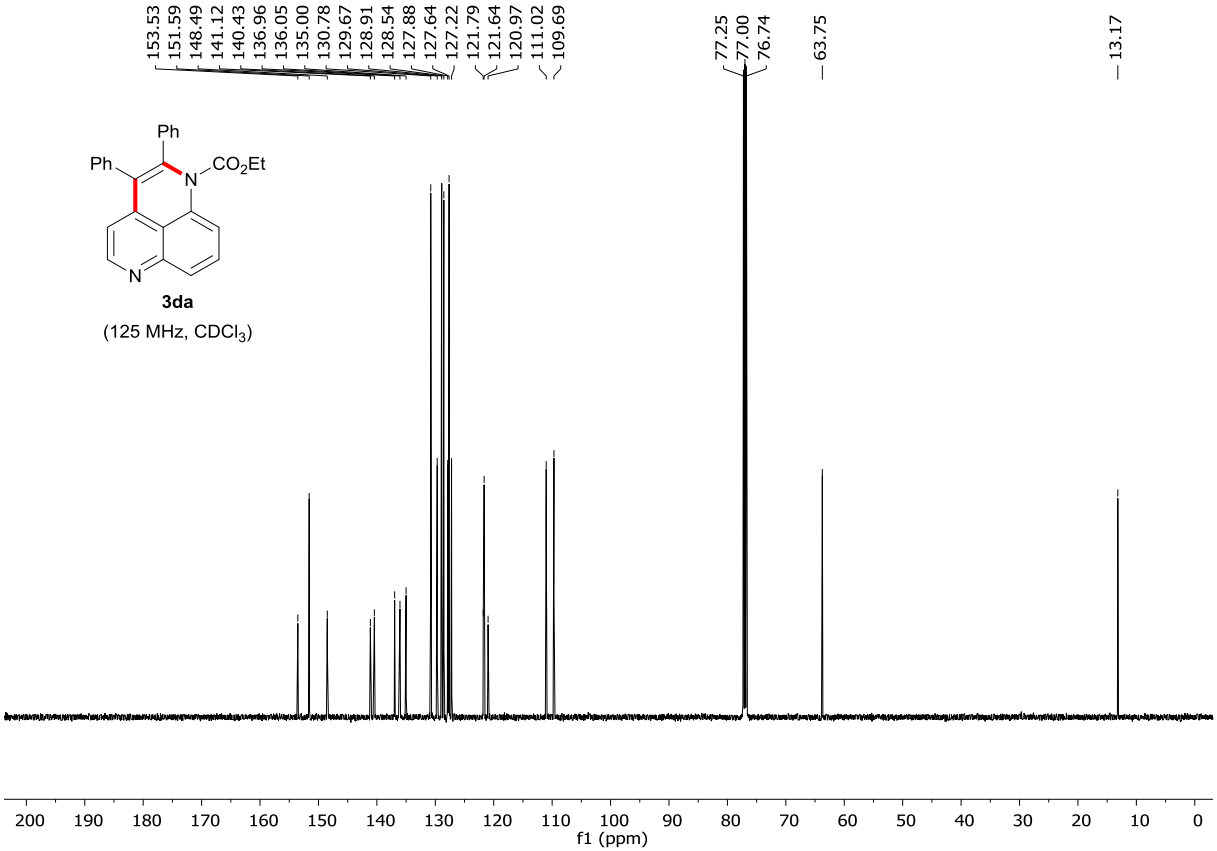

Ph
Ph
N
CO2Me
3ba
(400 MHz, CDCl3)
1.00
3.05
3.10
7.91
0.99
2.97
f1 (ppm)

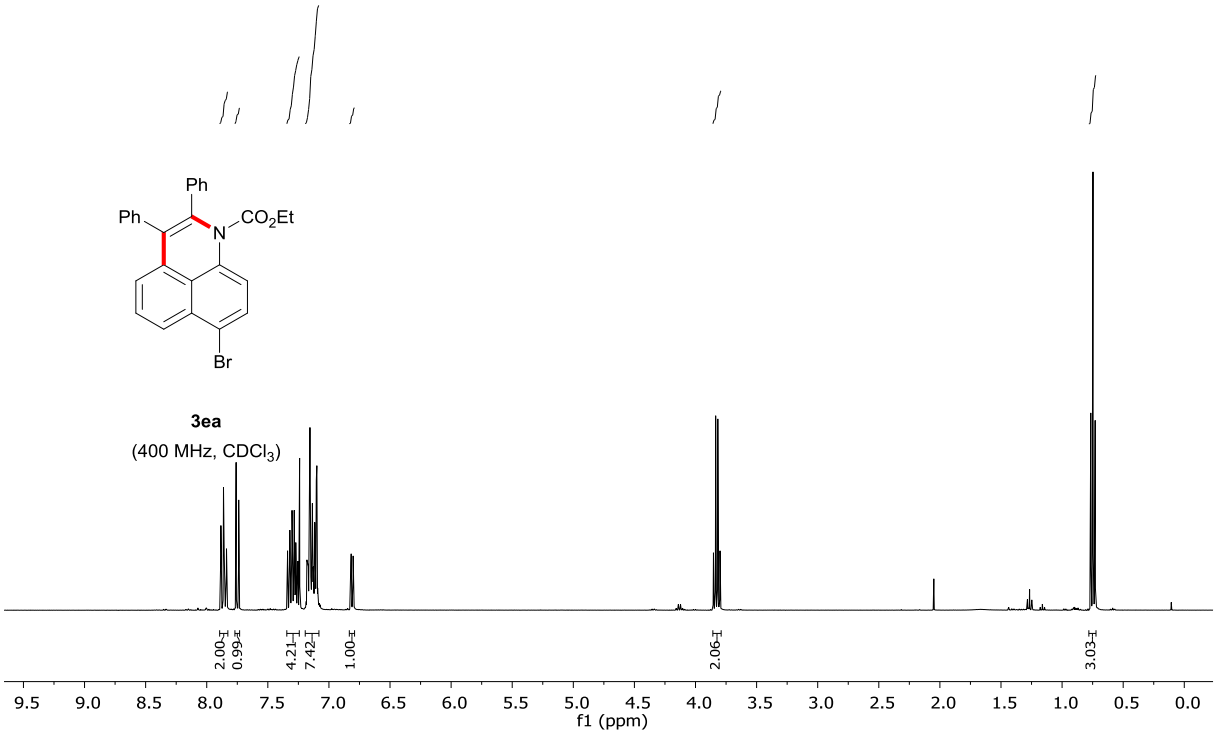

154.77
138.91
136.52
136.49
136.45
133.71
131.82
130.94
128.60
128.37
127.36
127.23
126.95
126.79
126.58
126.53
126.48
125.10
122.13
119.92
114.79
77.32
77.00
76.68
53.07
Ph
Ph
N
CO2Me
3ba
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

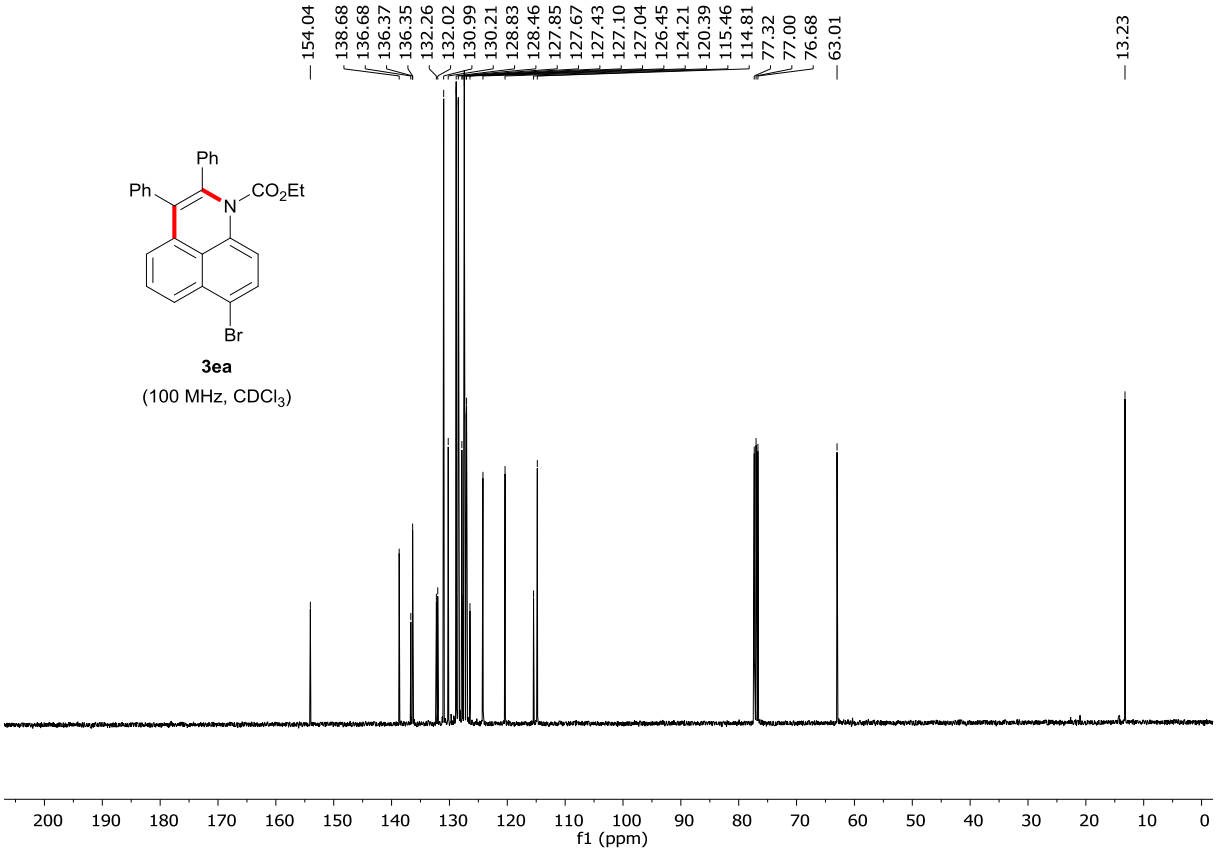

Ph
Ph
N
CO2Et
Me
3ca
(400 MHz, CDCl3)
0.98
1.06
1.03
4.18
4.30
3.31
1.00
2.14
2.93
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.36
139.36
136.82
136.48
134.69
132.39
132.15
131.09
128.85
128.47
128.35
127.34
127.30
126.91
126.85
126.71
126.29
121.76
120.04
115.15
77.32
77.00
76.68
62.59
19.03
13.34
Ph
Ph
N
CO2Et
Me
3ca
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
N
CO2Et
N
3da
(300 MHz, CDCl3)
0.97
0.93
2.00
3.19
6.98
1.00
2.02
2.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

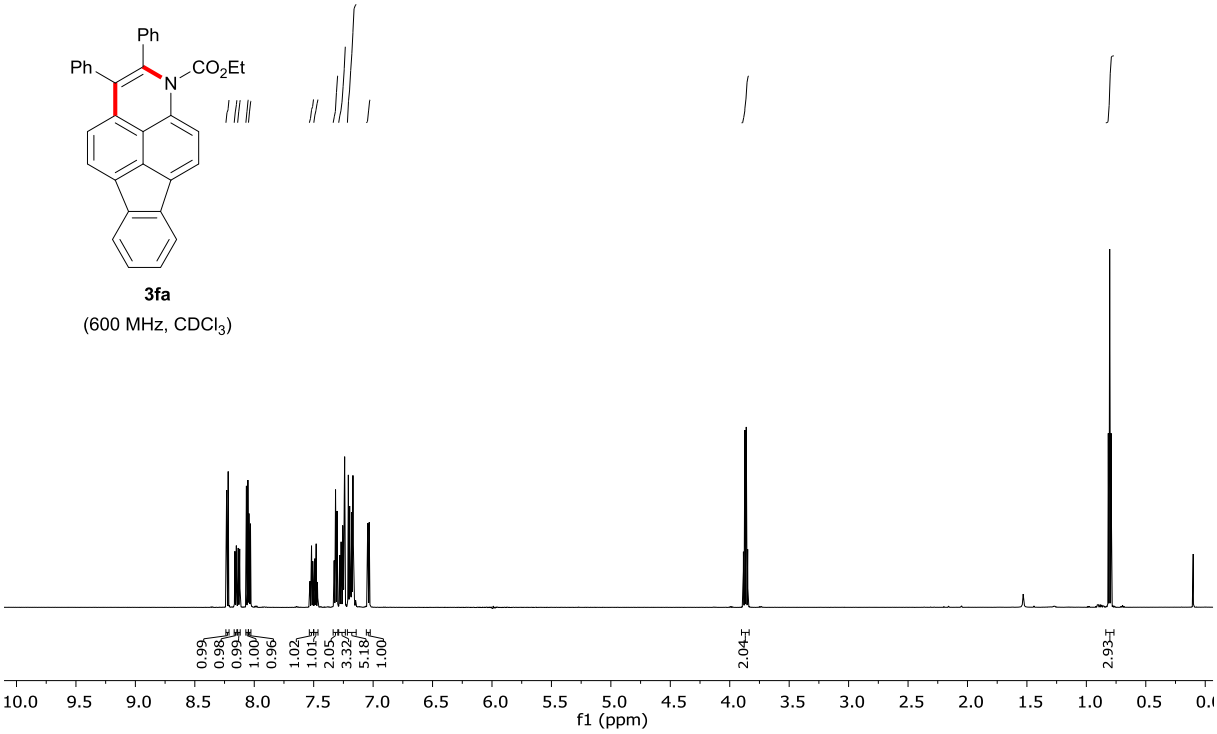

153.53
151.59
148.49
141.12
140.43
136.96
136.05
135.00
130.78
129.67
128.91
128.54
127.88
127.64
127.22
121.79
121.64
120.97
111.02
109.69
77.25
77.00
76.74
63.75
13.17
Ph
Ph
CO2Et
N
N
3da
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
CO2Et
N
Br
3ea
(400 MHz, CDCl3)
2.00
0.99
4.21
7.42
1.00
2.06
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



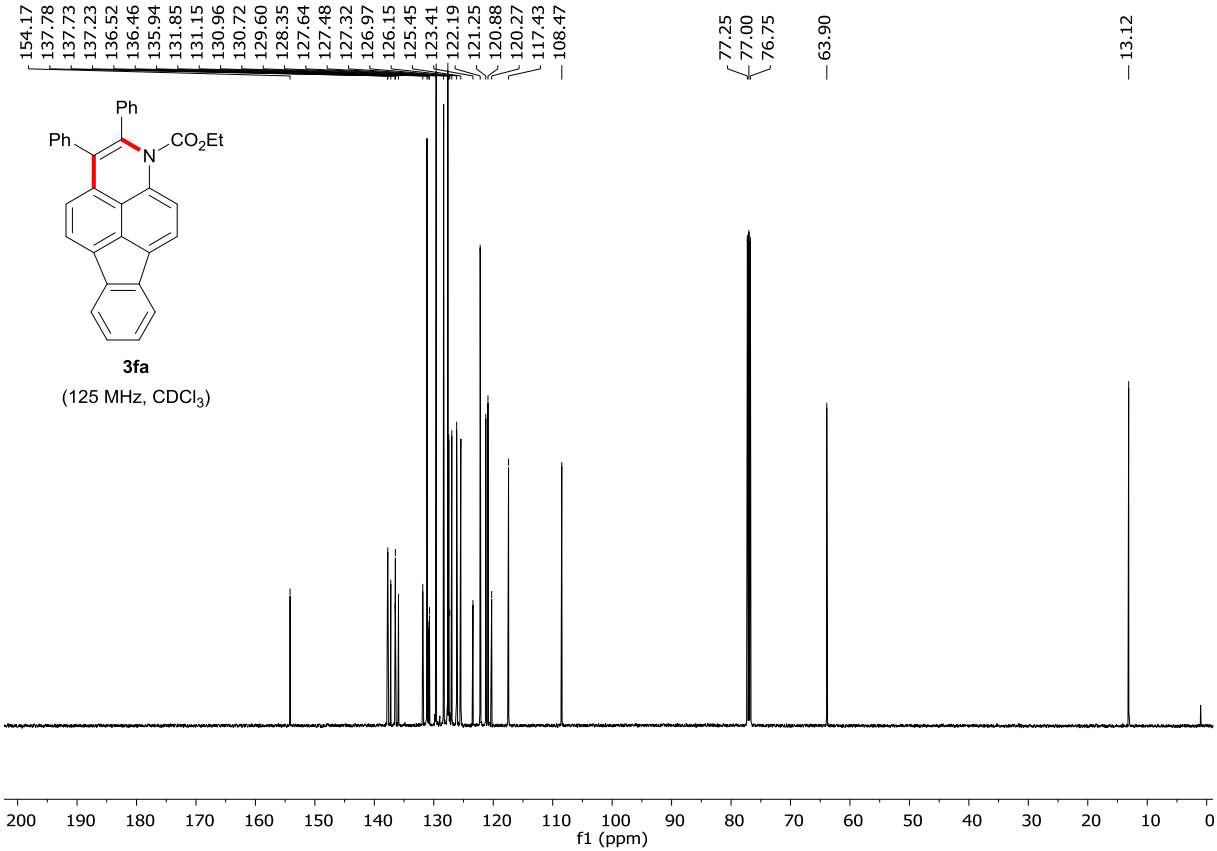
3ea

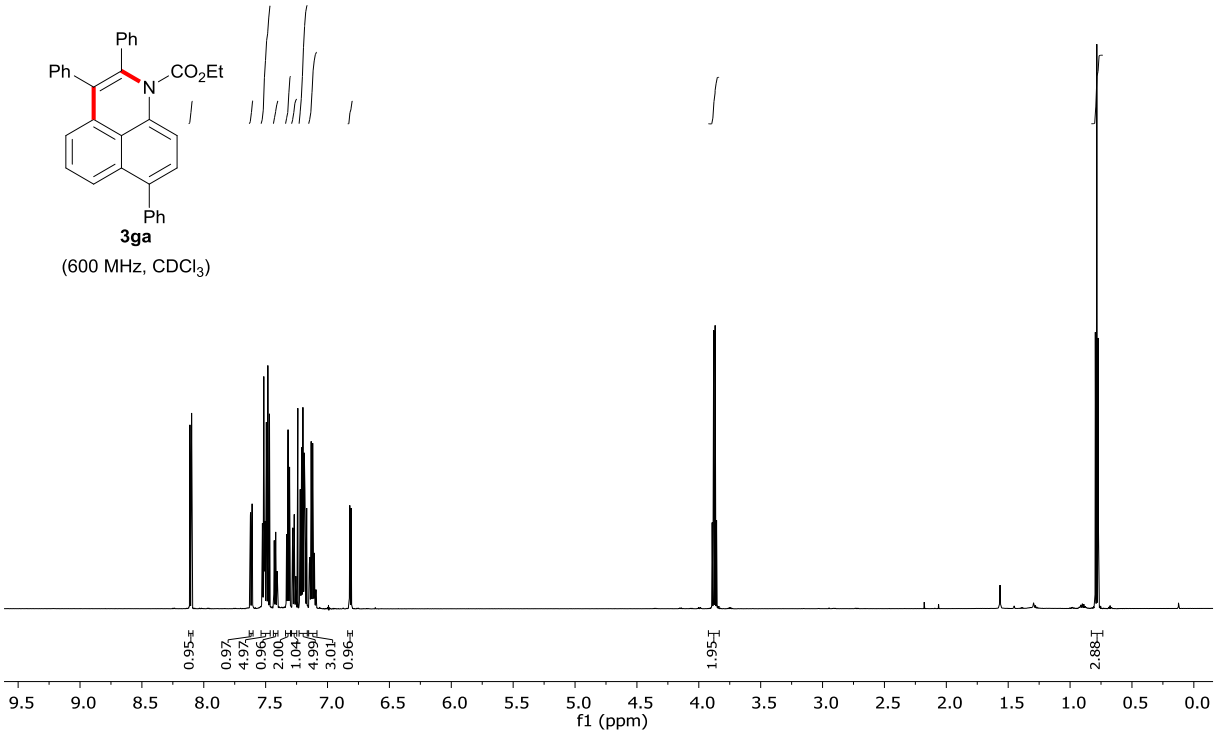
(100 MHz, $CDCl_3$)

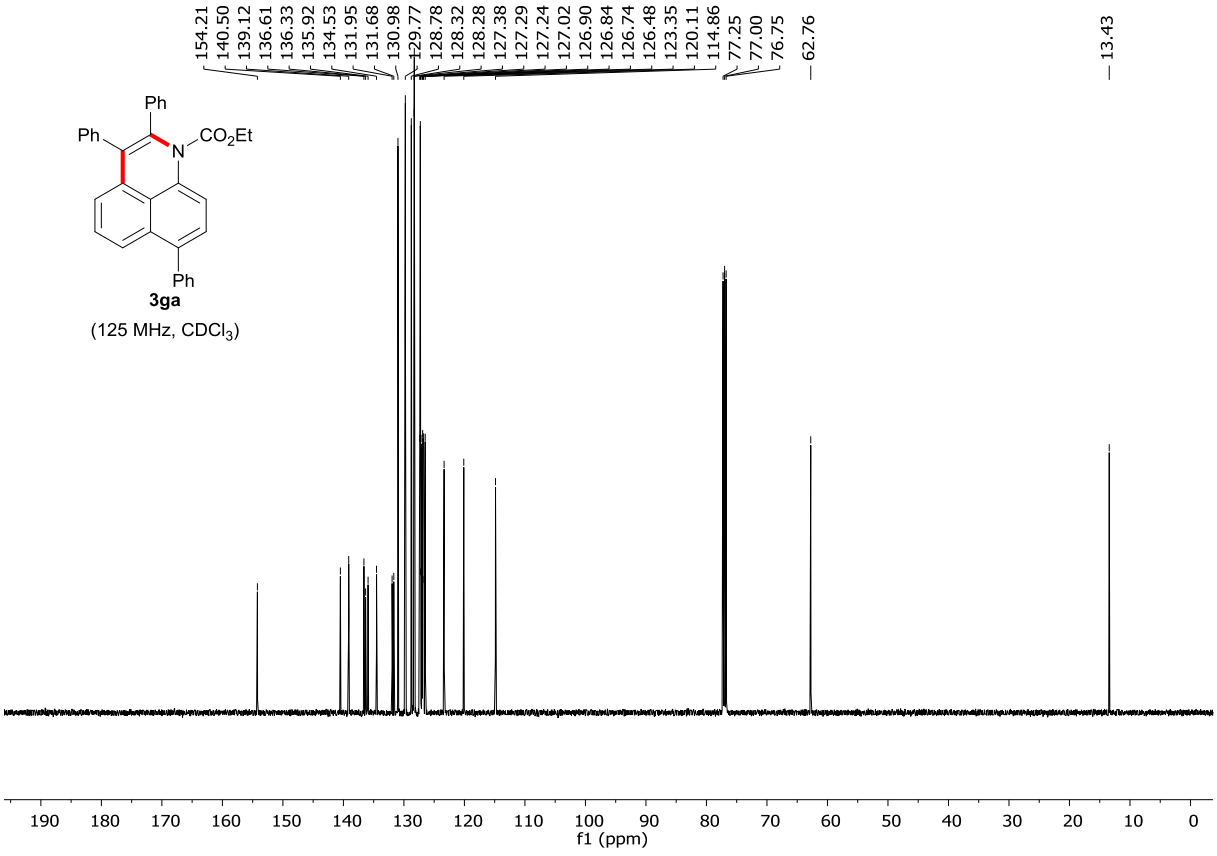


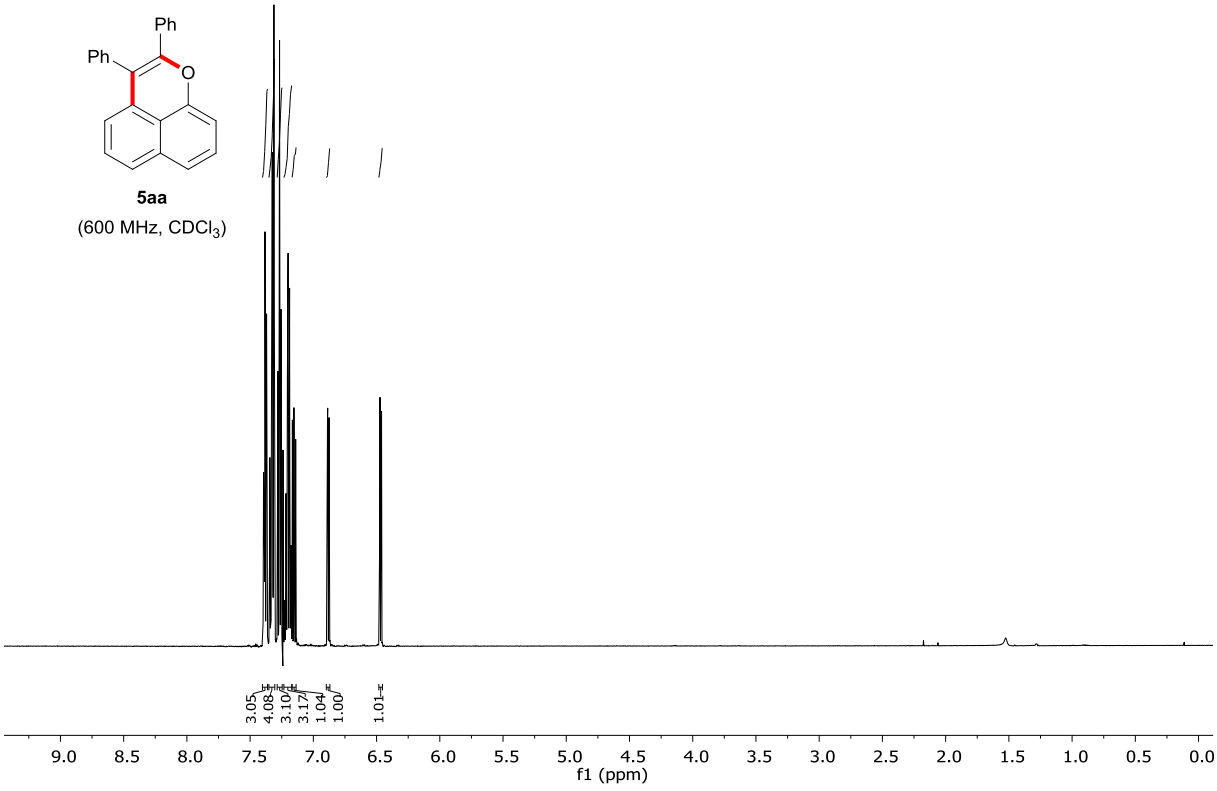
3fa

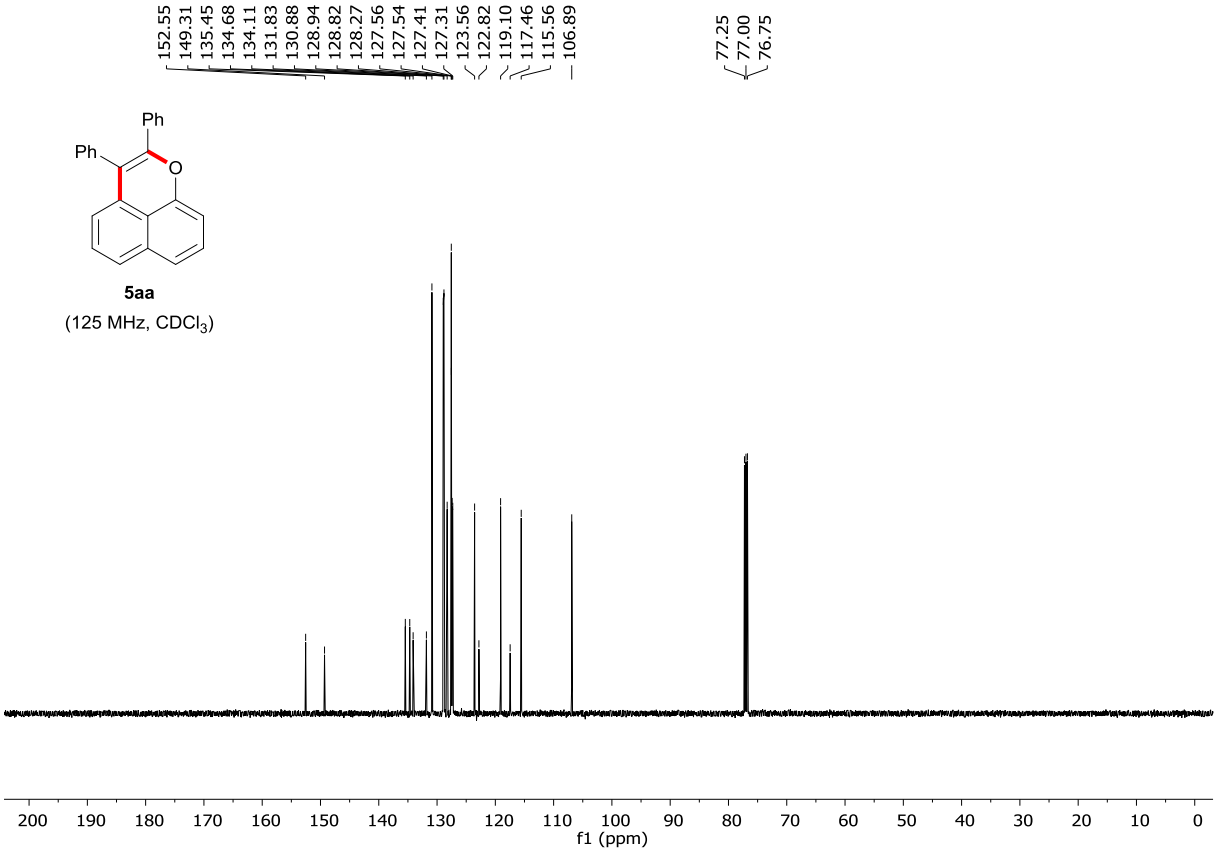
(600 MHz, $CDCl_3$)

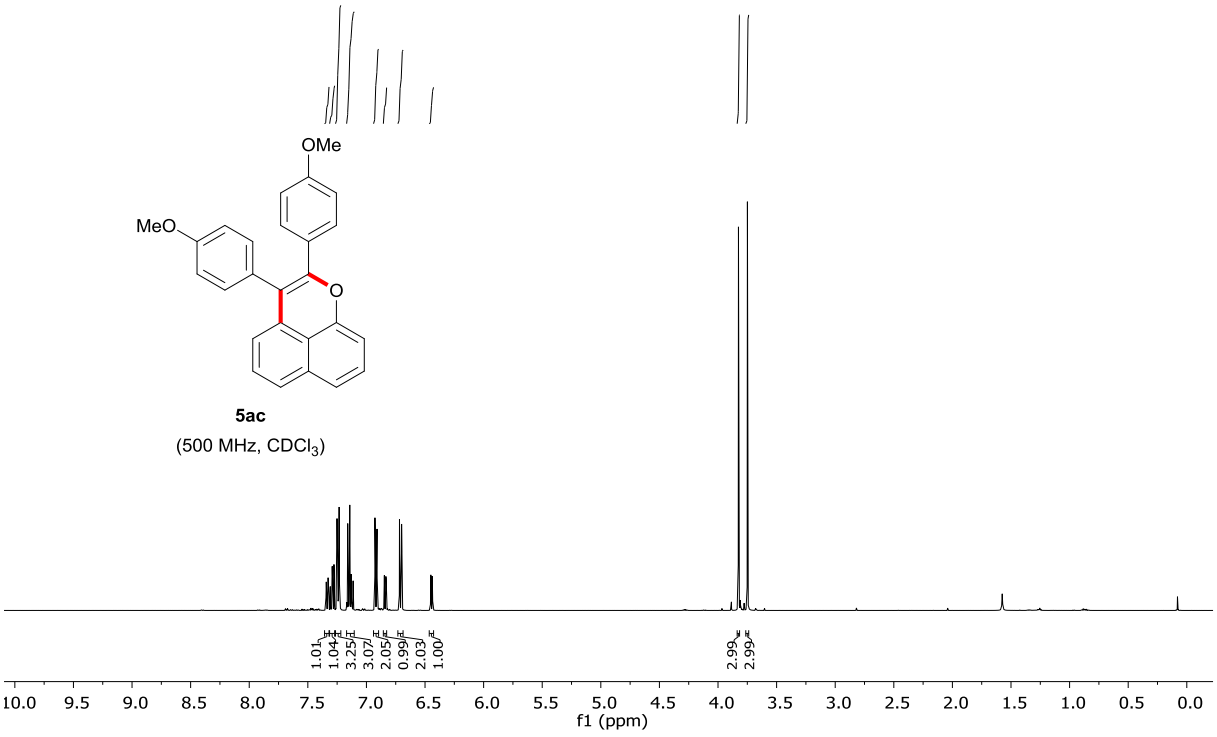

154.17
137.78
137.73
137.23
136.52
136.46
135.94
131.85
131.15
130.96
130.72
129.60
128.35
127.64
127.48
127.32
126.97
126.15
125.45
123.41
122.19
121.25
120.88
120.27
117.43
108.47
77.25
77.00
76.75
63.90
13.12
Ph
Ph
N
CO2Et
3fa
(125 MHz, CDCl3)
f1 (ppm)

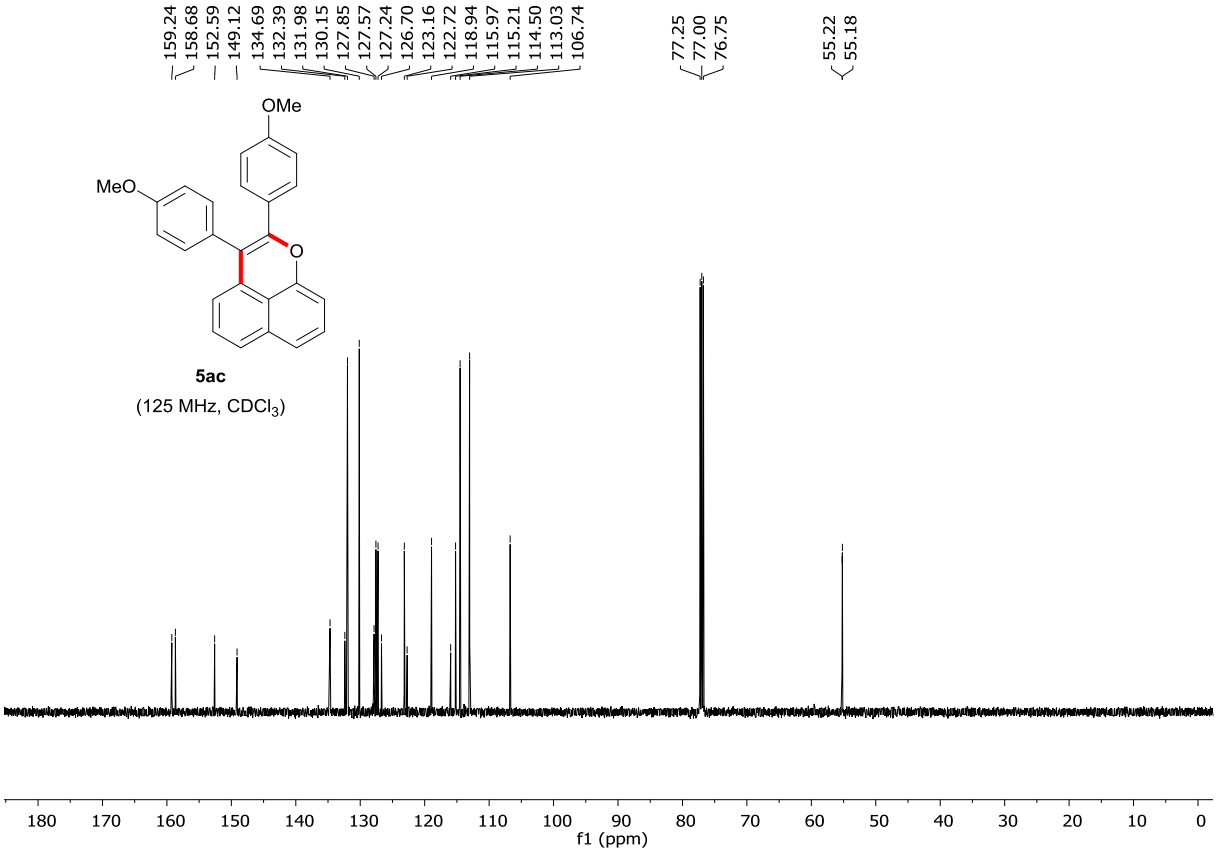

Ph
Ph
N
CO2Et
Ph
3ga
(600 MHz, CDCl3)
0.95
0.97
4.97
0.96
2.00
1.04
4.99
3.01
0.96
1.95
2.88
f1 (ppm)


154.21
140.50
139.12
136.61
136.33
135.92
134.53
131.95
131.68
130.98
129.77
128.78
128.32
128.28
127.38
127.29
127.24
127.02
126.90
126.84
126.74
126.48
123.35
120.11
114.86
77.25
77.00
76.75
62.76
13.43
Ph
Ph
N
CO2Et
Ph
3ga
(125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
O
5aa
(600 MHz, CDCl3)
3.05
4.08
3.10
3.17
1.04
1.00
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

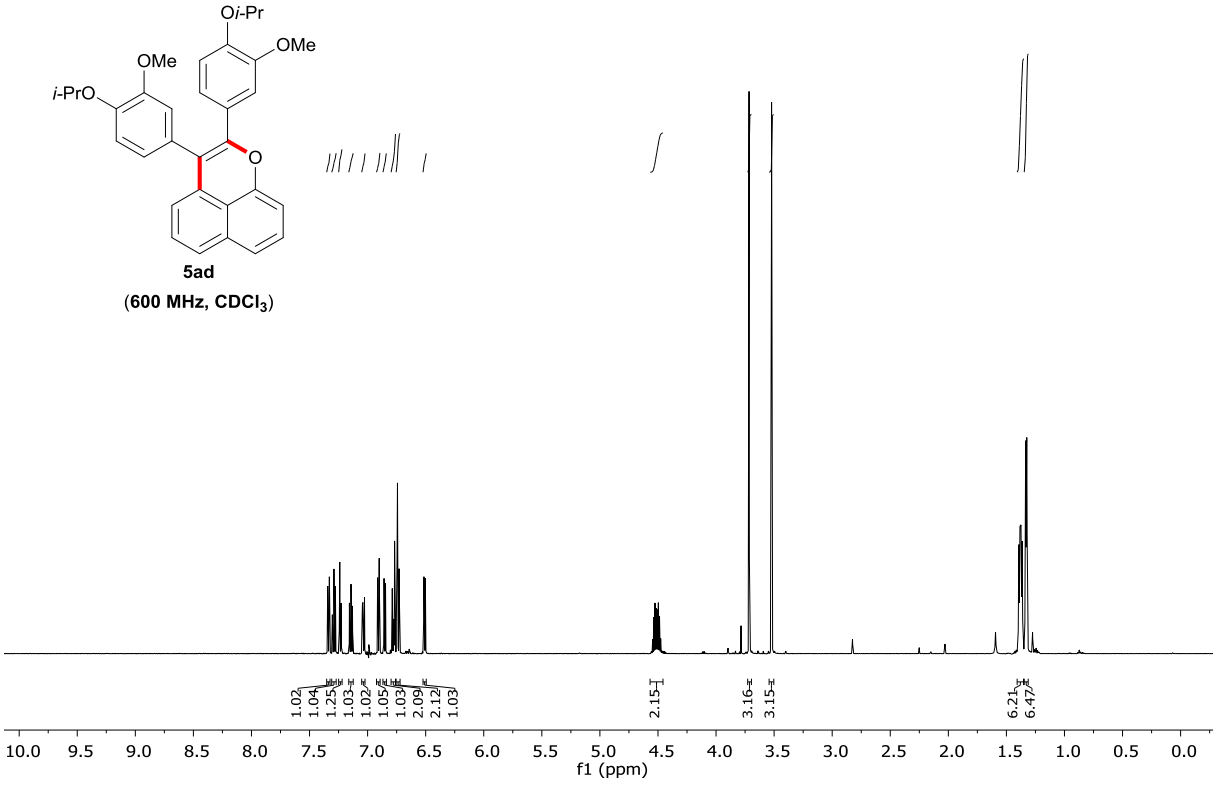

152.55
149.31
135.45
134.68
134.11
131.83
130.88
128.94
128.82
128.27
127.56
127.54
127.41
127.31
123.56
122.82
119.10
117.46
115.56
106.89
77.25
77.00
76.75
Ph
Ph
O
5aa
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
MeO
O
5ac
(500 MHz, CDCl3)
1.01
1.04
3.25
3.07
2.05
0.99
2.03
1.00
2.99
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



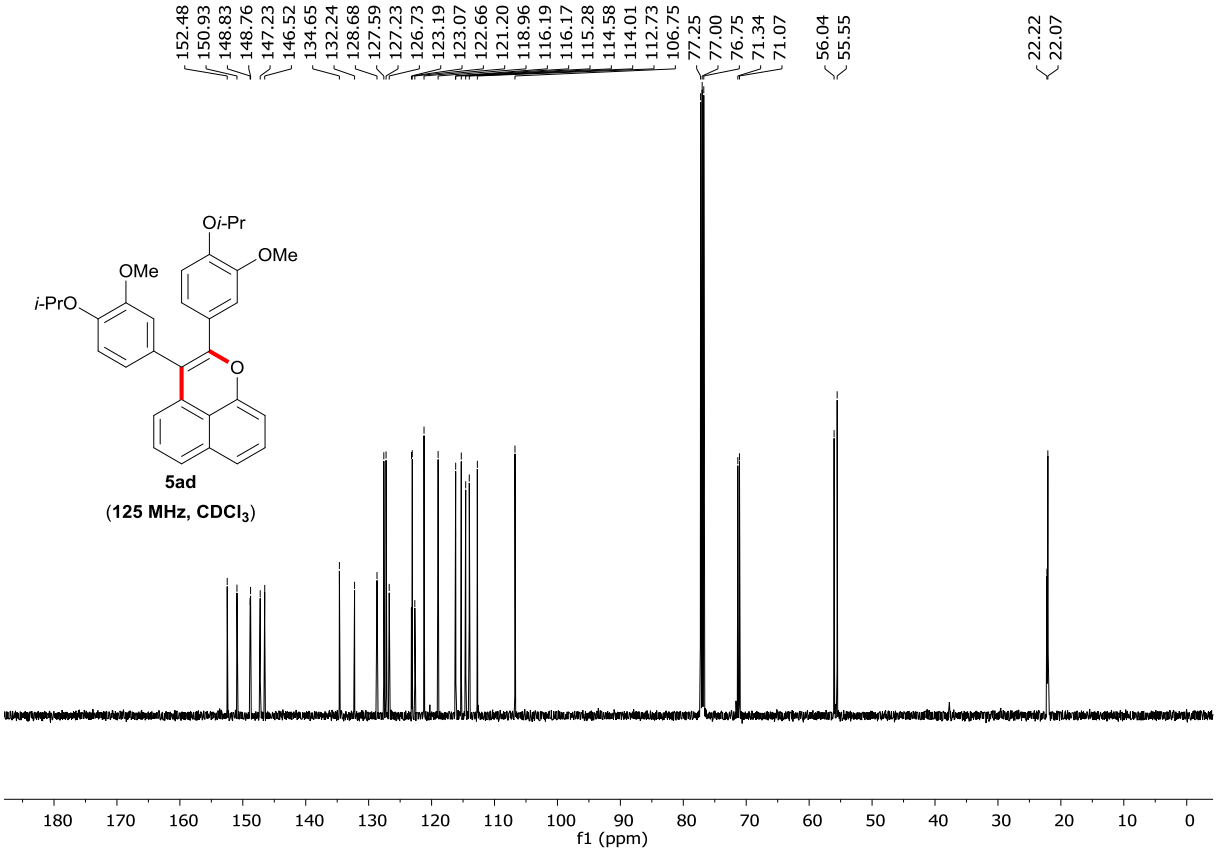
5ac

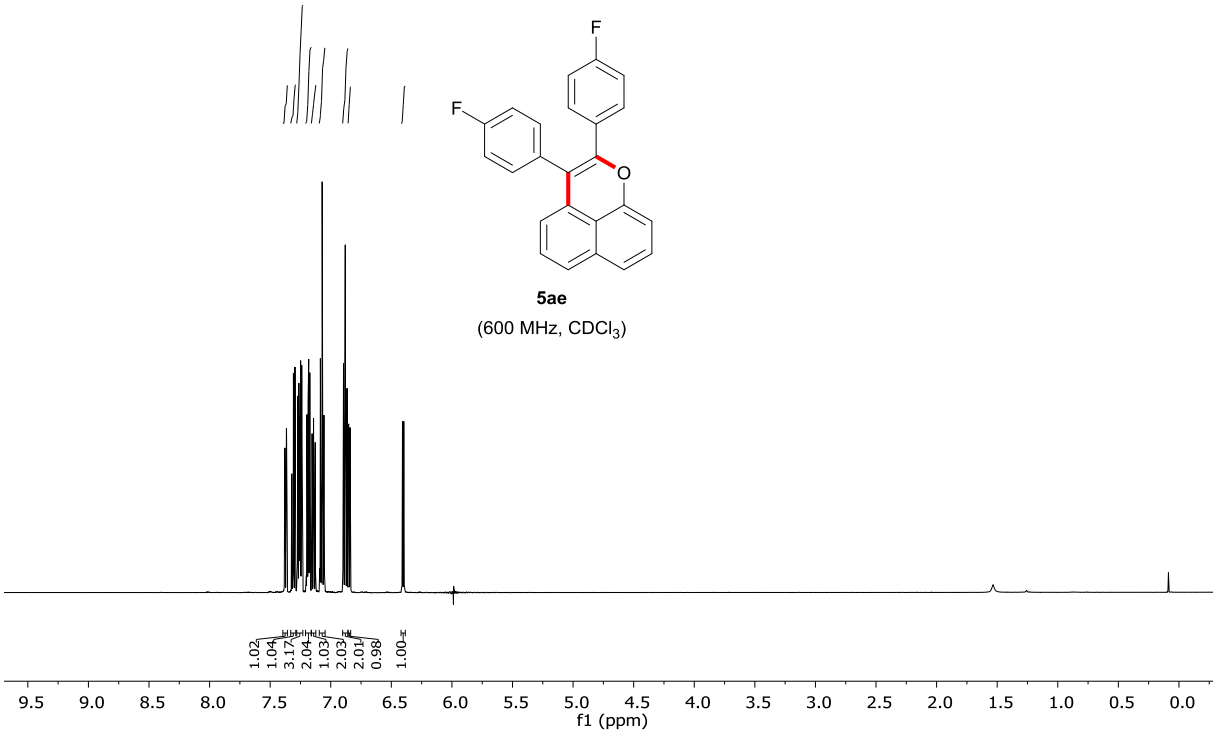
(125 MHz, $CDCl_3$)

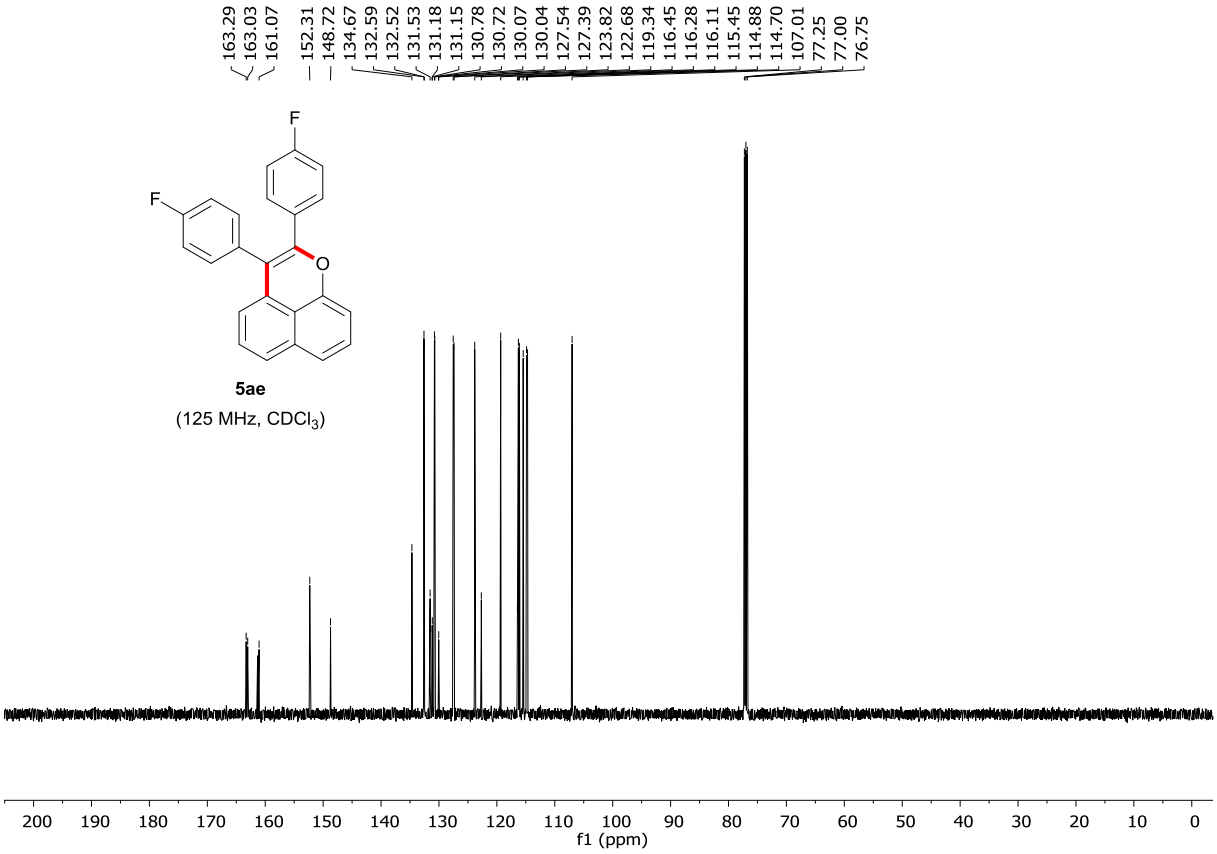


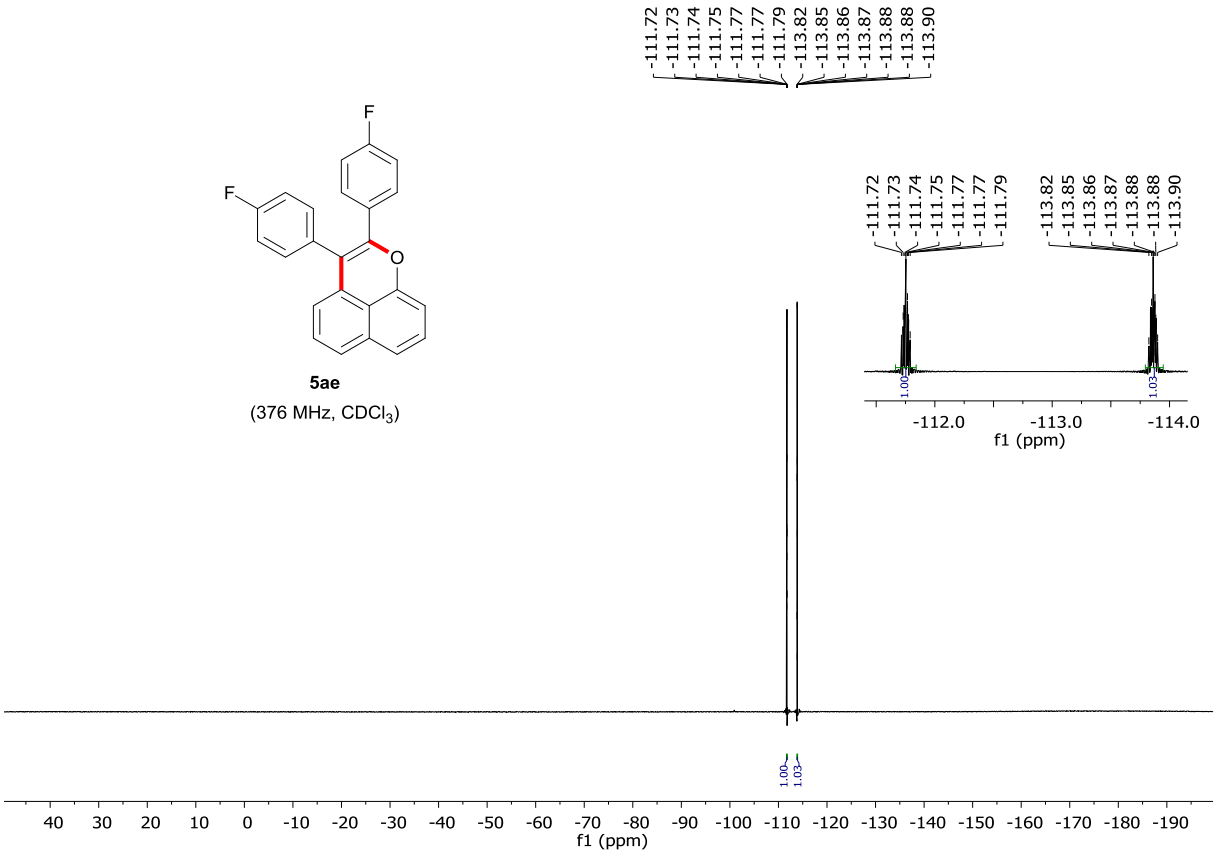
5ad

(**600 MHz, $CDCl_3$**)


152.48
150.93
148.83
148.76
147.23
146.52
134.65
132.24
128.68
127.59
127.23
126.73
123.19
123.07
122.66
121.20
118.96
116.19
116.17
115.28
114.58
114.01
112.73
106.75
77.25
77.00
76.75
71.34
71.07
56.04
55.55
22.22
22.07
Oi-Pr
OMe
OMe
i-PrO
O
5ad
(125 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
O
5ae
(600 MHz, CDCl3)
1.02
1.04
3.17
2.04
1.03
2.03
2.01
0.98
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.29
163.03
161.07
152.31
148.72
134.67
132.59
132.52
131.53
131.18
131.15
130.78
130.72
130.07
130.04
127.54
127.39
123.82
122.68
119.34
116.45
116.28
116.11
115.45
114.88
114.70
107.01
77.25
77.00
76.75
F
F
O
5ae
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.72
-111.73
-111.74
-111.75
-111.77
-111.77
-111.79
-113.82
-113.85
-113.86
-113.87
-113.88
-113.88
-113.90
F
F
O
5ae
(376 MHz, CDCl3)
1.00
1.03
-112.0
-113.0
-114.0
f1 (ppm)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)