# Supplementary information

# Electrophilic carbocyclization reactions of 2-(2-alkynylphenyl)amino-1,4-naphthoquinones

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## Contents

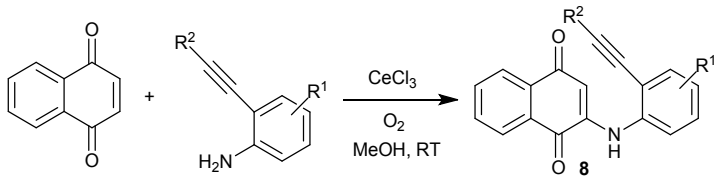
## Experimental

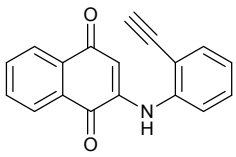
General considerations: Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the $^{13}C$ NMR signals was determined by means of DEPT 135 experiments. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102A mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh).

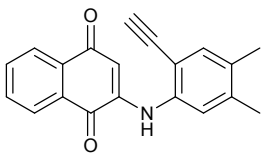
## 1) Experimental details and characterization data of the starting 2-(2-alkynylphenyl)amino-1,4-naphthoquinones 8.

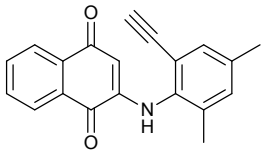
The starting 2-(2-alkynylphenyl)amino-1,4-naphthoquinones **8** were prepared by the $CeCl_3$-catalyzed conjugate addition of (2-alkynylphenyl)amines to 1,4-naphthoquinones and the results were summarized in Table S1.

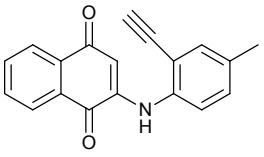
**Table S1: The preparation of starting aminonaphthoquinones 8.**

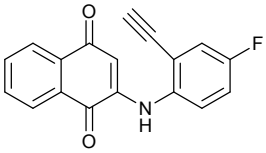




**8Aa:** 74%[a]


**8Ab:** 25%[a]


**8Ac:** 7%[b]


**8Ad:** 66%[a]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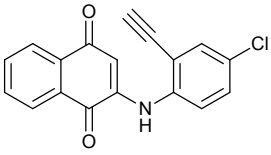
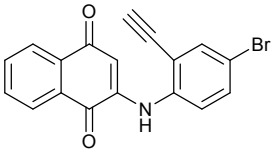
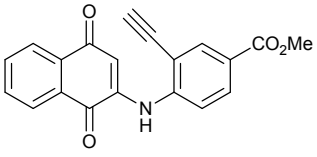
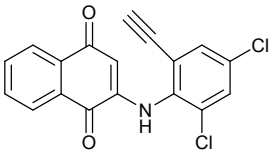

**8Af:** 75%[a]


**8Ag:** 71%[a]


**8Ah:** 61%[c]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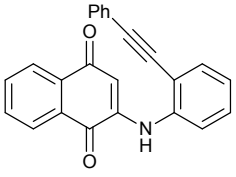
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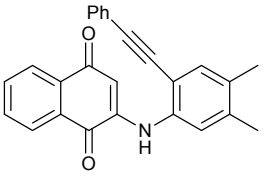
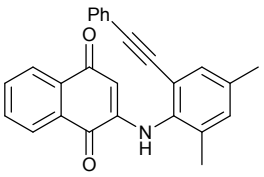
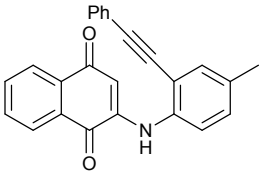

**8Bb:** 81%[a]


**8Bc:** 69%[e]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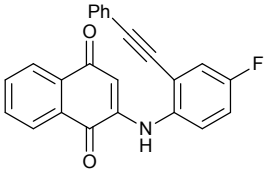
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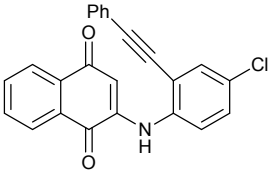
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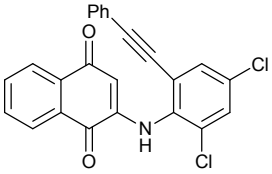
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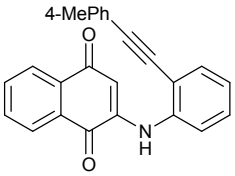
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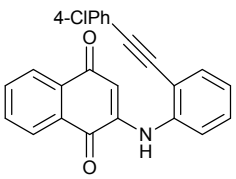
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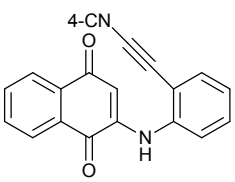
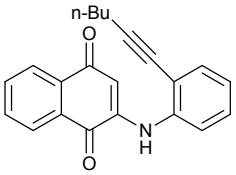

**8Bl:** 80%[g]


**8Bm:** 75%[a]

[a] reaction time: 1 d. [b] reaction time: 7 d (91% conversion). [c] reaction time: 9 d (63% conversion). [d] reaction time: 4 d (43% conversion). [e] reaction time: 7 d (82% conversion). [f] reaction time: 5 d (67% conversion). [g] reaction time: 2 d.

**Typical procedure for the preparation of 2-(2-alkynylphenylamino)-1,4-naphthoquinones 8:**

A solution of (2-ethynylphenyl)amine (1.02 g, 8.66 mmol), 1,4-naphthoquinone (1.69 g, 10.74 mmol) and $CeCl_3$ (839 mg, 2.25 mmol) in MeOH (25 mL) was stirred at RT for 24 h under $O_2$ atmosphere. The reaction mixture was then diluted with 200 mL of ethyl acetate washed with water (3 × 50 mL), dried over $Na_2SO_4$, and concentrated in

vacuo. The residue was chromatographed over 30 g of silica gel (eluted with 1:5 dichloromethane–hexanes) to give 1.79 g (74%) of **8Aa**.

**2-[(2-Ethynyl)phenyl]aminonaphthalene-1,4-dione 8Aa.** Red powders; mp 151–152 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.56 (s, 1H, CH), 6.55 (s, 1H, CH), 7.13 (td, *J* = 7.7, 1.1 Hz, 1H, ArH), 7.42 (td, *J* = 7.7, 1.4 Hz, 1H, ArH), 7.48 (d, *J* = 7.7 Hz, 1H, ArH), 7.56 (dd, *J* = 7.7, 1.4 Hz, 1H, ArH), 7.68 (td, *J* = 7.4, 1.3 Hz, 1H, ArH), 7.77 (td, *J* = 7.4, 1.4 Hz, 1H, ArH), 8.11 (d, *J* = 7.4 Hz, 1H, ArH), 8.13 (d, *J* = 7.4 Hz, 1H, ArH), 8.25 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 78.8 (s), 85.1 (d), 104.7 (d), 115.1 (s), 120.0 (d), 124.3 (d), 126.2 (d), 126.6 (d), 130.0 (d), 130.3 (s), 132.5 (d), 133.0 (s), 133.5 (d), 134.9 (d), 139.5 (s), 143.5 (s), 181.8 (s), 184.0 (s); IR (KBr): 3250, 1615, 1295, 990, 750 cm$^{-1}$; Anal. Calcd. for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.03; H, 4.03; N, 5.07.

**2-[(2-Ethynyl-4,5-dimethyl)phenyl]aminonaphthalene-1,4-dione 8Ab.** Red needles; mp 173–174 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.24 (s, 3H, $CH_3$), 2.31 (s, 3H, $CH_3$), 3.46 (s, 1H, CH), 6.50 (s, 1H, CH), 7.24 (s, 1H, ArH), 7.32 (s, 1H, ArH), 7.67 (td, *J* = 7.5, 1.3 Hz, 1H, ArH), 7.76 (td, *J* = 7.5, 1.2 Hz, 1H, ArH), 8.09–8.15 (m, 3H, NH + ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 19.1 (q), 20.3 (q), 79.1 (s), 84.0 (d), 104.1 (d), 112.6 (s), 121.6 (d), 126.1 (d), 126.6 (d), 130.4 (s), 132.4 (d), 133.2 (s), 133.3 (s), 134.2 (d), 134.8 (d), 137.1 (s), 139.3 (s), 143.8 (s), 181.9 (s), 184.1 (s); IR (KBr): 3340, 3260, 1640, 1605, 1575 cm$^{-1}$; Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.56; H, 5.01; N, 4.56.

**2-[(2-Ethynyl-4,6-dimethyl)phenyl]aminonaphthalene-1,4-dione 8Ac.** Red crystals; mp 196–197 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.20 (s, 3H, $CH_3$), 2.33 (s, 3H, $CH_3$), 3.18 (s, 1H, CH), 5.46 (s, 1H, CH), 7.11 (s, 1H, ArH), 7.26 (s, 1H, ArH), 7.29 (s, 1H, NH), 7.67 (t, *J* = 7.6 Hz, 1H, ArH), 7.75 (t, *J* = 7.6 Hz, 1H, ArH), 8.09 (d, *J* = 7.6 Hz, 1H, ArH), 8.16 (d, *J* = 7.6 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 18.1 (q), 20.8 (q), 79.9 (s), 82.3 (d), 104.2 (d), 120.2 (s), 126.2 (d), 126.3 (d), 130.6 (s), 131.9 (d), 132.2 (d), 132.7 (d), 133.4 (s), 134.3 (s), 134.7 (d), 135.4 (s), 137.6 (s), 146.3 (s), 181.8 (s), 183.6 (s); IR (KBr): 3285, 1670, 1595, 1575, 1490 cm$^{-1}$; Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.74; H, 5.06; N, 4.60.

**2-[(2-Ethynyl-4-methyl)phenyl]aminonaphthalene-1,4-dione 8Ad.** Red needles; mp 175–176 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.33 (s, 3H, $CH_3$), 3.51 (s, 1H, CH), 6.47 (s, 1H, CH), 7.21 (dd, *J* = 8.4, 1.5 Hz, 1H, ArH), 7.35 (d, *J* = 8.4 Hz, 1H, ArH), 7.36 (s, 1H, ArH), 7.67 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 7.75 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 8.10 (dd, *J* = 7.5, 1.1 Hz, 1H, ArH), 8.11 (dd, *J* = 7.5, 1.1 Hz, 1H, ArH), 8.14 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 20.6 (q), 79.0 (s), 84.6 (d), 104.1 (d), 115.1 (s), 120.3 (d), 126.1 (d), 126.5 (d), 130.3 (s), 130.7 (d), 132.4 (d), 133.1 (s), 133.8 (d), 134.3 (s), 134.8 (d), 136.9 (s) 143.7 (s), 181.8 (s), 183.9 (s); IR (KBr): 3325, 3225, 1675, 1520, 1295 cm$^{-1}$; Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.41; H, 4.58; N, 4.81.

**2-[(2-Ethynyl-4-fluoro)phenyl]aminonaphthalene-1,4-dione 8Ae.** Orange powders; mp 201–202 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.56 (s, 1H, CH), 6.40 (s, 1H, CH), 7.15 (td, *J* = 8.6, 2.7 Hz, 1H, ArH), 7.27 (dd, *J* = 8.6, 2.7 Hz, 1H, ArH), 7.43 (dd, *J* = 8.6, 4.9 Hz, 1H, ArH), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.78 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.03 (s, 1H, NH), 8.12 (td, *J* = 7.6, 1.2 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 77.9 (s), 85.8 (d), 104.2 (d), 117.27 (sd, $J_{CF}$ = 9.1 Hz), 117.30 (dd, $J_{CF}$ = 23.1 Hz), 120.1 (dd, $J_{CF}$ = 25.2 Hz), 122.5 (dd, $J_{CF}$ = 9.1 Hz), 126.2 (d), 126.6 (d), 130.3 (s), 132.6 (d), 133.0 (s), 135.0 (d), 135.7 (s), 143.9 (s), 158.7 (sd, $J_{CF}$ = 246.5 Hz), 181.7 (s), 184.0 (s); IR (KBr): 3305, 3240, 1620, 1530, 1295 cm$^{-1}$; Anal. Calcd. for $C_{18}H_{10}FNO_2$: C, 74.22; H, 3.46; N, 4.81. Found: C, 73.97; H, 3.51; N, 4.68.

**2-[(4-Chloro-2-ethynyl)phenyl]aminonaphthalene-1,4-dione 8Af.** Red needles; mp 201–202 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.60 (s, 1H, CH), 6.49 (s, 1H, CH), 7.38 (dd, *J* = 8.8, 2.2 Hz, 1H, ArH), 7.42 (d, *J* = 8.8 Hz, 1H, ArH), 7.54 (d, *J* = 2.2 Hz, 1H, ArH), 7.69 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 7.78 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 8.12 (d, *J* = 7.5 Hz, 1H, ArH), 8.13 (d, *J* = 7.5 Hz, 1H, ArH), 8.19 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 77.6 (s), 86.2 (d), 105.0 (d), 116.5 (s), 121.0 (d), 126.2 (d), 126.7 (d), 129.3 (s), 130.1 (d), 130.3 (s), 132.7 (d), 132.9 (s), 133.1 (d), 135.0 (d), 138.2 (s), 143.2 (s), 181.6 (s), 184.0 (s); IR (KBr): 3325, 3295, 1645, 1615, 1295 cm$^{-1}$; Anal. Calcd. for $C_{18}H_{10}ClNO_2$: C, 70.25; H, 3.28; N, 4.55. Found: C, 70.22; H, 3.26; N, 4.53.

**2-[(4-Bromo-2-ethynyl)phenyl]aminonaphthalene-1,4-dione 8Ag.** Red powders; mp 217–218 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.61 (s, 1H, CH), 6.51 (s, 1H, CH), 7.37 (d, *J* = 8.8 Hz, 1H, ArH), 7.53 (dd, *J* = 8.8, 2.3 Hz, 1H, ArH), 7.66–7.73 (m, 2H, ArH), 7.79 (td, *J* = 7.6, 1.1 Hz, 1H, ArH), 8.12 (dd, *J* = 7.6, 1.1 Hz, 1H, ArH), 8.14 (dd, *J* = 7.6, 1.1 Hz, 1H, ArH), 8.20 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 78.0 (s), 86.6 (d), 105.8 (d), 116.9 (s), 117.4 (s), 112.0 (d), 126.6 (d), 127.1 (d), 130.9 (s), 133.3 (d), 133.5 (s), 133.7 (d), 135.5 (d), 136.5 (d), 139.5 (s), 143.8 (s), 182.2 (s), 184.2 (s); IR (KBr): 3330, 1675, 1640, 1520, 720 cm$^{-1}$; HRMS(EI) calcd for $C_{18}H_{10}BrNO_2$: *m/z* 350.9895 [M$^+$], found *m/z* 350.9899.

**2-[(2-Ethynyl-4-methoxycarbonyl)phenyl]aminonaphthalene-1,4-dione 8Ah.** Red powders; mp 215–216 °C

(from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.66 (s, 1H, CH), 3.94 (s, 3H, $OCH_3$), 6.70 (s, 1H, CH), 7.55 (d, *J* = 8.7 Hz, 1H, ArH), 7.72 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.80 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.08 (dd, *J* = 8.7, 2.0 Hz, 1H, ArH), 8.13 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.15 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.24 (d, *J* = 2.0 Hz, 1H, ArH), 8.57 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 52.3 (q), 77.9 (s), 86.1 (d), 106.8 (d), 114.1 (s), 117.9 (d), 125.2 (s), 126.3 (d), 126.8 (d), 130.2 (s), 131.4 (d), 132.8 (s), 132.9 (d), 134.9 (d), 135.1 (d), 142.5 (s), 143.4 (s), 165.6 (s), 181.6 (s), 184.1 (s); IR (KBr): 3235, 1715, 1660, 1575, 1295 cm$^{-1}$; Anal. Calcd. for $C_{20}H_{13}NO_4$: C, 72.50; H, 3.95; N, 4.23. Found: C, 72.47; H, 3.98; N, 4.22.

**2-[(2,4-Dichloro-6-ethynyl)phenyl]aminonaphthalene-1,4-dione 8Ai.** Yellow crystals; mp 187–188 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.38 (s, 1H, CH), 5.61 (s, 1H, CH), 7.34 (s, 1H, NH), 7.51 (d, *J* = 2.3 Hz, 1H, ArH), 7.53 (d, *J* = 2.3 Hz, 1H, ArH), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.77 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.10 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.14 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 77.8 (s), 85.9 (d), 106.4 (d), 123.0 (s), 126.3 (d), 126.5 (d), 130.5 (s), 131.0 (d), 132.1 (d), 132.56 (d), 132.59 (s), 133.1 (s), 133.2 (s), 134.8 (d), 135.1 (s), 144.4 (s), 181.4 (s), 183.7 (s); IR (KBr): 3330, 3240, 1670, 1615, 1495 cm$^{-1}$; Anal. Calcd. for $C_{18}H_9Cl_2NO_2$: C, 63.18; H, 2.65; N, 4.09. Found : C, 63.11; H, 2.68; N, 4.06.

**2-[2-(Phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Ba.** Brown red needles; mp 175–176 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.61 (s, 1H, CH), 7.14 (td, *J* = 7.7, 1.2 Hz, 1H, ArH), 7.35–7.46 (m, 4H, ArH), 7.50 (d, *J* = 7.7 Hz, 1H, ArH), 7.59 (dd, *J* = 7.7, 1.2 Hz, 1H, ArH), 7.64–7.70 (m, 3H, ArH), 7.76 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.11 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.16 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.50 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 84.2 (s), 97.7 (s), 104.5 (d), 116.1 (s), 119.5 (d), 122.4 (s), 124.2 (d), 126.1 (d), 126.7 (d), 128.5 (2 × d), 128.8 (d), 129.4 (d), 130.4 (s), 131.7 (2 × d), 132.4 (d), 132.6 (d), 133.1 (s), 134.8 (d), 138.8 (s), 143.3 (s), 181.8 (s), 184.0 (s); IR (KBr): 3285, 1615, 1575, 1295, 755 cm$^{-1}$; HRMS(EI) calcd for $C_{24}H_{15}NO_2$: *m/z* 349.1103 [M$^+$], found *m/z* 349.1107.

**2-[4,5-Dimethyl-2-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Bb.** Red powders; mp 204–205 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.26 (s, 3H, $CH_3$), 2.33 (s, 3H, $CH_3$), 6.59 (s, 1H, CH), 7.29 (s, 1H, ArH), 7.32–7.43 (m, 4H, ArH), 7.59–7.65 (m, 2H, ArH), 7.68 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 7.77 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.13 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.17 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.40 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 19.2 (q), 20.3 (q), 84.5 (s), 96.7 (s), 103.9 (d), 113.6 (s), 121.1 (d), 122.7 (s), 126.1 (d), 126.7 (d), 128.5 (2 × d), 128.6 (d), 130.5 (s), 131.6 (2 × d), 132.3 (d), 133.2 (s), 133.25 (s), 133.34 (d), 134.8 (d), 136.5 (s), 138.7 (s), 143.6 (s), 182.0 (s), 184.1 (s); IR (KBr): 3300, 1605, 1575, 1530, 1305 cm$^{-1}$; Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.71; H, 5.03; N, 3.69.

**2-[2,4-Dimethyl-6-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Bc.** Red crystals; mp 218–219 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.23 (s, 3H, $CH_3$), 2.35 (s, 3H, $CH_3$), 5.52 (s, 1H, CH), 7.09 (s, 1H, ArH), 7.24–7.28 (m, 3H, ArH), 7.30 (s, 1H, ArH), 7.35–7.39 (m, 2H, ArH), 7.43 (s, 1H, NH), 7.66 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.74 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.08 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.14 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 18.2 (q), 20.8 (q), 85.7 (s), 94.9 (s), 104.3 (d), 121.2 (s), 122.7 (s), 126.2 (d), 126.3 (d), 128.3 (2 × d), 128.5 (d), 130.7 (s), 131.1 (d), 131.6 (2 × d), 132.2 (2 × d), 133.5 (s), 133.9 (s), 134.7 (d), 135.2 (s), 137.5 (s), 146.4 (s), 182.0 (s), 183.6 (s); IR (KBr): 3220, 1675, 1570, 1285, 755 cm$^{-1}$; Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.58; H, 5.04; N, 3.72.

**2-[4-Methyl-2-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Bd.** Brown red powders; mp 181–182 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.36 (s, 3H, $CH_3$), 6.56 (s, 1H, CH), 7.21 (d, *J* = 8.3 Hz, 1H, ArH), 7.36–7.44 (m, 5H, ArH), 7.62–7.67 (m, 2H, ArH), 7.68 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 7.77 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.12 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.17 (dd, *J* = 7.6, 1.0 Hz, 1H, ArH), 8.41 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 20.7 (q), 84.4 (s), 97.2 (s), 104.0 (d), 116.1 (s), 119.7 (d), 122.5 (s), 126.1 (d), 126.6 (d), 128.5 (2 × d), 128.8 (d), 130.1 (d), 130.4 (s), 131.6 (2 × d), 132.3 (d), 133.0 (d), 133.2 (s), 134.2 (s), 134.8 (d), 136.3 (s), 143.5 (s), 181.9 (s), 184.0 (s); IR (KBr): 3290, 1675, 1615, 1535, 1295 cm$^{-1}$; Anal. Calcd. for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.72; N, 3.85. Found: C, 82.64; H, 4.72; N, 3.81.

**2-[4-Fluoro-2-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Be.** Red crystals; mp 186–187 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.49 (s, 1H, CH), 7.13 (td, *J* = 8.6, 2.7 Hz, 1H, ArH), 7.31 (dd, *J* = 8.6, 2.7 Hz, 1H, ArH), 7.37–7.43 (m, 3H, ArH), 7.46 (dd, *J* = 8.6, 4.8 Hz, 1H, ArH), 7.60–7.66 (m, 2H, ArH), 7.69 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 7.78 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 8.12 (d, *J* = 7.5 Hz, 1H, ArH), 8.17 (d, *J* = 7.5 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 83.3 (s), 98.4 (s), 104.0 (d), 116.5 (dd, $J_{CF}$ = 23.1 Hz), 118.3 (sd, $J_{CF}$ = 9.1 Hz), 119.2 (dd, $J_{CF}$ = 25.2 Hz), 121.8 (dd, $J_{CF}$ = 9.1 Hz), 121.9 (s), 126.2 (d), 126.7 (d), 128.6 (2 × d), 129.2 (d), 130.4 (s), 131.8 (2 × d), 132.5 (d), 133.1 (s), 134.9 (d), 135.1 (s), 143.7 (s), 158.8 (sd, $J_{CF}$ = 245.4 Hz), 181.8 (s), 184.0 (s); IR (KBr): 3265, 1545, 1295, 720, 690 cm$^{-1}$; Anal. Calcd. for $C_{24}H_{14}FNO_2$: C, 78.46; H, 3.84; N, 3.81. Found: C, 78.12; H, 3.86; N, 3.48.

**2-[4-Chloro-2-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Bf.** Red powders; mp 219–220 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.56 (s, 1H, CH), 7.36 (dd, *J* = 8.7, 2.4 Hz, 1H, ArH), 7.39–7.43 (m, 3H, ArH), 7.45 (d, *J* = 8.7 Hz, 1H, ArH), 7.58 (d, *J* = 2.4 Hz, 1H, ArH), 7.64–7.68 (m, 2H, ArH), 7.70 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 7.78 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 8.13 (dd, *J* = 7.6, 1.3 Hz, 1H, ArH), 8.18 (dd, *J* = 7.6, 1.3 Hz, 1H, ArH), 8.46 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 83.0 (s), 98.8 (s), 104.9 (d), 117.6 (s), 120.4 (d), 121.9 (s), 126.2 (d), 126.8 (d), 128.6 (2 × d), 129.21 (s), 129.25 (d), 129.4 (d), 130.3 (s), 131.8 (2 × d), 132.2 (d), 132.6 (d), 133.0 (s), 135.0 (d), 137.4 (s), 143.1 (s), 181.7 (s), 184.0 (s); IR (KBr): 3330, 3075, 1675, 1645, 1295 cm$^{-1}$; HRMS (EI) calcd for $C_{24}H_{14}ClNO_2$: *m/z* 383.0713 [M$^+$], found *m/z* 383.0710.

**2-[2,4-Dichloro-6-(phenylethynyl)phenyl]aminonaphthalene-1,4-dione 8Bi.** Red crystals; mp 205–206 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.69 (s, 1H, CH), 7.23–7.34 (m, 3H, ArH), 7.34–7.42 (m, 2H, ArH), 7.48 (s, 1H, NH), 7.49 (d, *J* = 2.3 Hz, 1H, ArH), 7.53 (d, *J* = 2.3 Hz, 1H, ArH), 7.68 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 7.75 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 8.08 (dd, *J* = 7.6, 1.3 Hz, 1H, ArH), 8.15 (dd, *J* = 7.6, 1.3 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 83.6 (s), 98.3 (s), 106.6 (d), 121.6 (s), 124.0 (s), 126.3 (d), 126.5 (d), 128.5 (2 × d), 129.3 (d), 130.2 (d), 130.5 (s), 131.3 (d), 131.7 (2 × d), 132.3 (s), 132.5 (d), 133.1 (2 × s), 134.4 (s), 134.8 (d), 144.4 (s), 181.5 (s), 183.6 (s); IR (KBr): 3220, 3065, 1675, 1605, 1495 cm$^{-1}$; Anal. Calcd. for $C_{24}H_{13}Cl_2NO_2$: C, 68.92; H, 3.13; N, 3.35. Found: C, 68.90; H, 3.08; N, 3.33.

**2-{2-[(4-Methylphenyl)ethynyl]phenyl}aminonaphthalene-1,4-dione 8Bj.** Brown red needles; mp 176–177 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.39 (s, 3H, $CH_3$), 6.62 (s, 1H, CH), 7.13 (t, *J* = 7.8 Hz, 1H, ArH), 7.20 (d, *J* = 8.1 Hz, 2H, ArH), 7.38 (t, *J* = 7.8 Hz, 1H, ArH), 7.50 (d, *J* = 7.8 Hz, 1H, ArH), 7.55 (d, *J* = 8.1 Hz, 2H, ArH), 7.58 (d, *J* = 7.8 Hz, 1H, ArH), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.76 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.12 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.16 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.51 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 21.6 (q), 83.6 (s), 98.0 (s), 104.5 (d), 116.4 (s), 119.3 (s), 119.6 (d), 124.2 (d), 126.2 (d), 126.7 (d), 129.2 (d), 129.3 (2 × d), 130.5 (s), 131.6 (2 × d), 132.4 (d), 132.6 (d), 133.2 (s), 134.8 (d), 138.7 (s), 139.1 (s), 143.4 (s), 181.9 (s), 184.1 (s); IR (KBr): 3280, 1640, 1575, 1295, 750 cm$^{-1}$; Anal. Calcd. for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.72; N, 3.85. Found: C, 82.67; H, 4.65; N, 3.83.

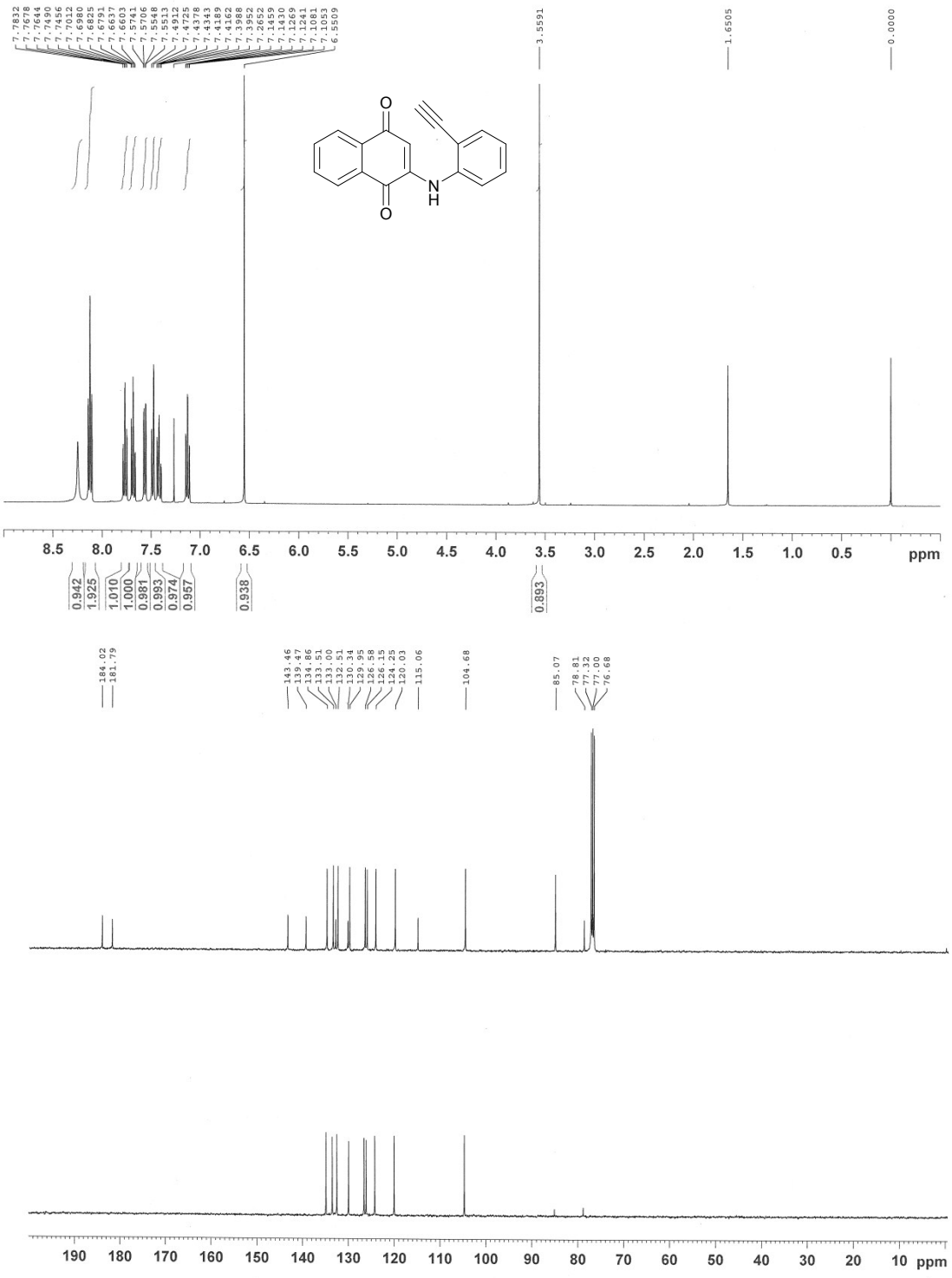
**2-{2-[(4-Chlorophenyl)ethynyl]phenyl}aminonaphthalene-1,4-dione 8Bk.** Red powders; mp 223–224 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.62 (s, 1H, CH), 7.15 (t, *J* = 7.7 Hz, 1H, ArH), 7.38 (d, *J* = 8.5 Hz, 2H, ArH), 7.42 (t, *J* = 7.7 Hz, 1H, ArH), 7.52 (d, *J* = 7.7 Hz, 1H, ArH), 7.59 (d, *J* = 7.7 Hz, 1H, ArH), 7.59 (d, *J* = 8.5 Hz, 2H, ArH), 7.70 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.78 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.13 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.17 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.48 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 85.2(s), 96.5 (s), 104.6 (d), 115.8 (s), 119.6 (d), 120.9 (s), 124.2 (d), 126.2 (d), 126.7 (d), 128.9 (2 × d), 129.6 (d), 130.4 (s), 132.5 (d), 132.6 (d), 132.9 (2 × d), 133.1 (s), 134.9 (d), 135.0 (s), 138.9 (s), 143.3 (s), 181.9 (s), 184.0 (s); IR (KBr): 3290, 1615, 1575, 1295, 750 cm$^{-1}$; HRMS (EI) calcd for $C_{24}H_{14}ClNO_2$: *m/z* 383.0713 [M$^+$], found *m/z* 383.0707.

**2-{2-[(4-Cyanophenyl)ethynyl]phenyl}aminonaphthalene-1,4-dione 8Bl.** Brown red powders; mp 243–244 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.62 (s, 1H, CH), 7.18 (t, *J* = 7.8 Hz, 1H, ArH), 7.46 (td, *J* = 7.8, 1.3 Hz, 1H, ArH), 7.54 (d, *J* = 7.6 Hz, 1H, ArH), 7.62 (dd, *J* = 7.8, 1.3 Hz, 1H, ArH), 7.70 (td, *J* = 8.5 Hz, 2H, ArH), 7.69–7.74 (m, 1H, ArH), 7.76 (d, *J* = 8.5 Hz, 2H, ArH), 7.79 (td, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.13 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 8.18 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 88.5 (s), 95.7 (s), 104.8 (d), 112.1 (s), 115.0 (s), 118.4 (s), 119.7 (d), 124.3 (d), 126.2 (d), 126.7 (d), 127.3 (s), 130.3 (s), 130.4 (d), 132.1 (2 × d), 132.2 (2 × d), 132.6 (d), 132.9 (d), 133.0 (s), 135.0 (d), 139.3 (s), 143.2 (s), 182.0 (s), 184.0 (s); IR (KBr): 3330, 2225, 2215, 1575, 1300 cm$^{-1}$; HRMS(EI) calcd for $C_{25}H_{14}N_2O_2$: *m/z* 374.1055 [M$^+$], found *m/z* 374.1062.

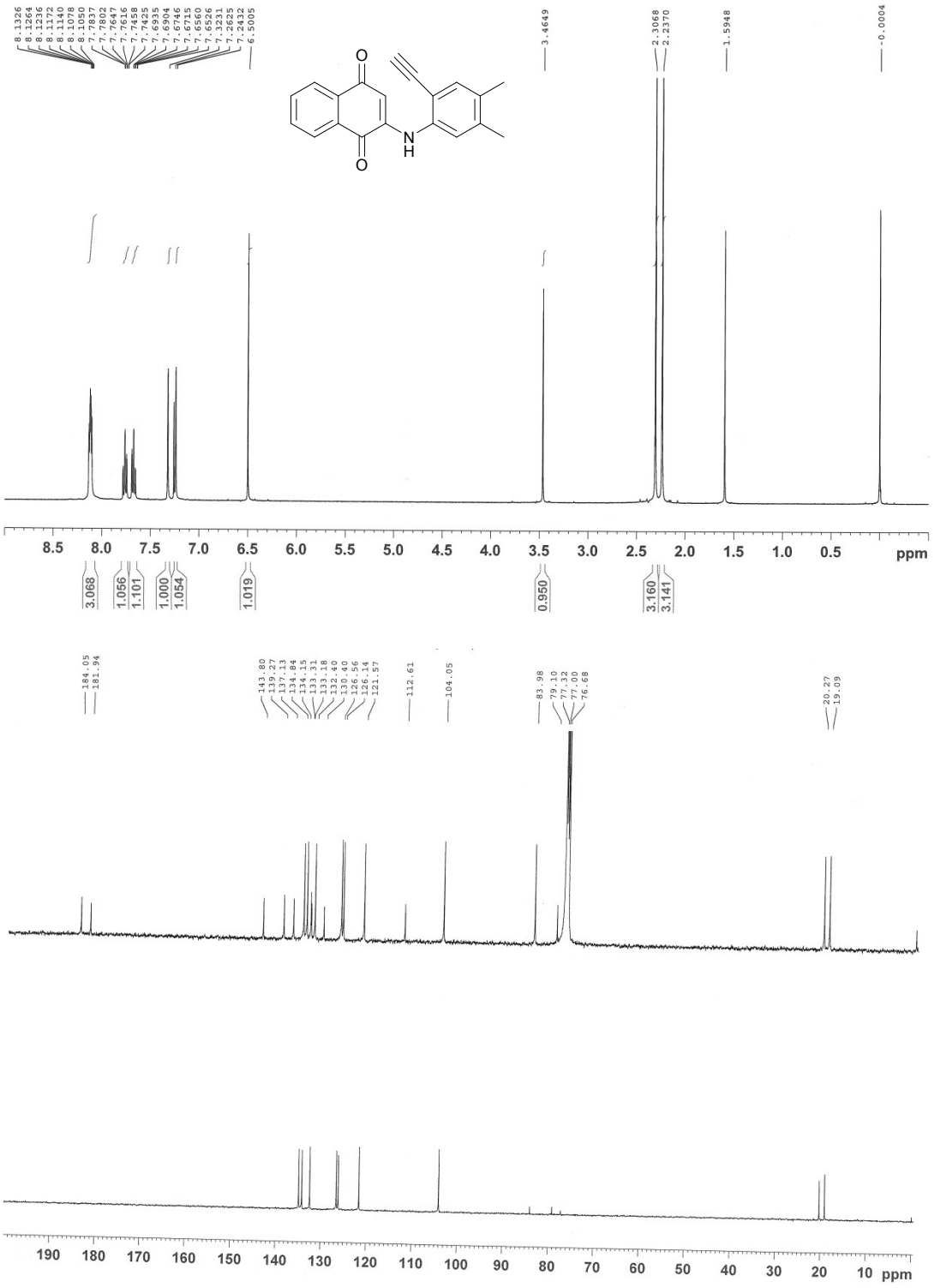
**2-[2-(Hex-1-yn-1-yl)phenyl]aminonaphthalene-1,4-dione 8Bm.** Red crystals; mp 107–108 °C (from ethyl acetate–hexanes); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.95 (t, *J* = 7.3 Hz, 3H, $CH_3$), 1.50 (sextet, *J* = 7.3 Hz, 2H, $CH_2$), 1.67 (quint, *J* = 7.3 Hz, 2H, $CH_2$), 2.53 (t, *J* = 7.3 Hz, 2H, $CH_2$), 6.56 (s, 1H, CH), 7.09 (t, *J* = 7.8 Hz, 1H, ArH), 7.33 (t, *J* = 7.8 Hz, 1H, ArH), 7.45 (d, *J* = 7.8 Hz, 1H, ArH), 7.46 (d, *J* = 7.8 Hz, 1H, ArH), 7.68 (t, *J* = 7.6 Hz, 1H, ArH), 7.76 (t, *J* = 7.6 Hz, 1H, ArH), 8.12 (d, *J* = 7.6 Hz, 1H, ArH), 8.14 (d, *J* = 7.6 Hz, 1H, ArH), 8.32 (s, 1H, NH); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 13.6 (q), 19.3 (t), 22.1 (t), 30.7 (t), 75.6 (s), 99.1 (s), 104.3 (d), 117.0 (s), 119.6 (d), 124.1 (d), 126.1 (d), 126.5 (d), 128.5 (d), 130.4 (s), 132.4 (d), 132.7 (d), 133.1 (s), 134.8 (d), 138.7 (s), 143.5 (s), 181.8 (s), 184.0 (s); IR (KBr): 3260, 2930, 2360, 1575, 1295, 755 cm$^{-1}$; Anal. Calcd. for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.20; H, 5.82; N, 4.23.

**2) Copies of $^1$H and $^{13}$C NMR spectra for the starting 2-(2-alkynylphenyl)amino-1,4-naphthoquinones 8**.

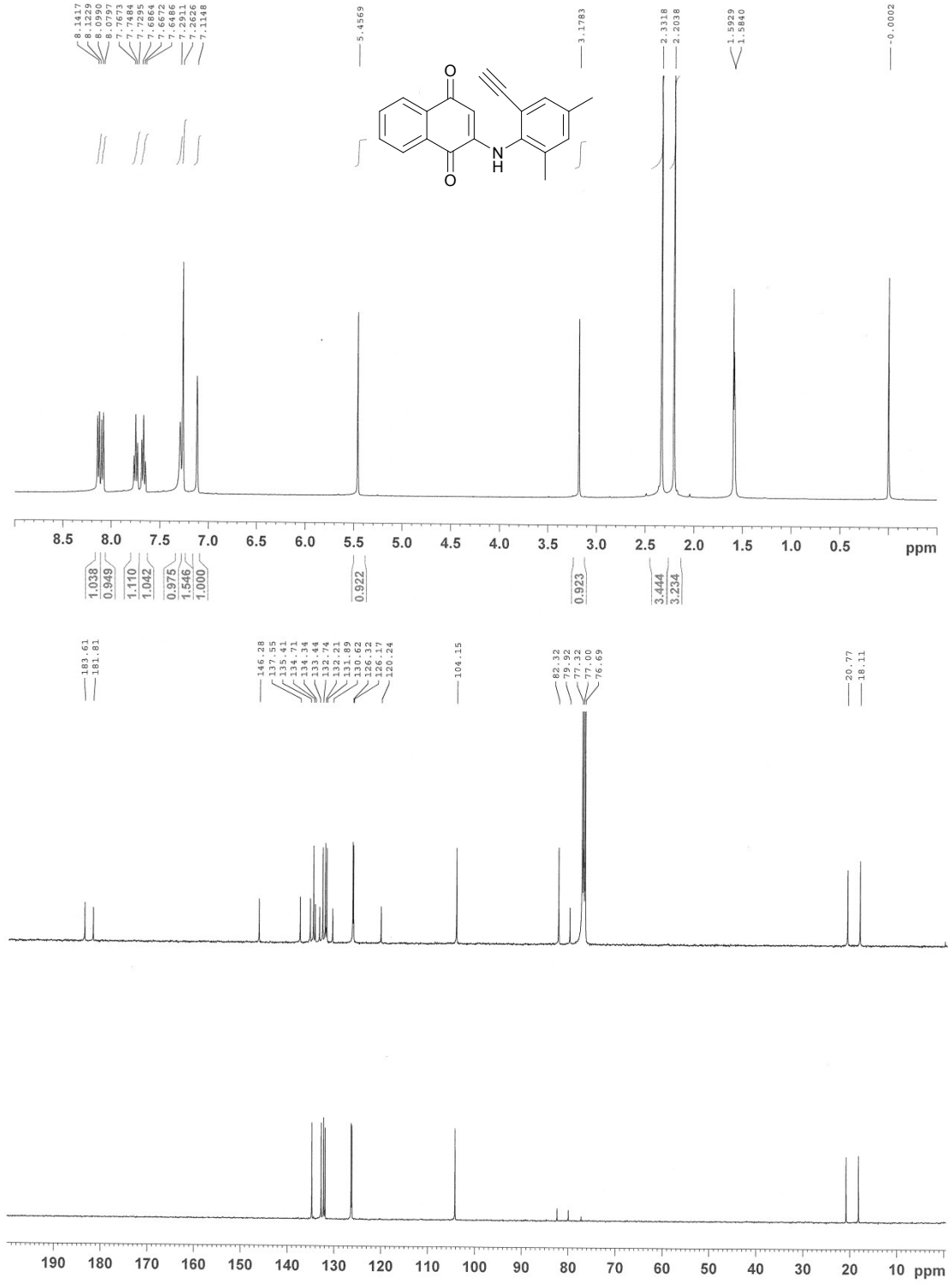
$^{1}H$ and $^{13}C$ NMR spectra of **8Aa**



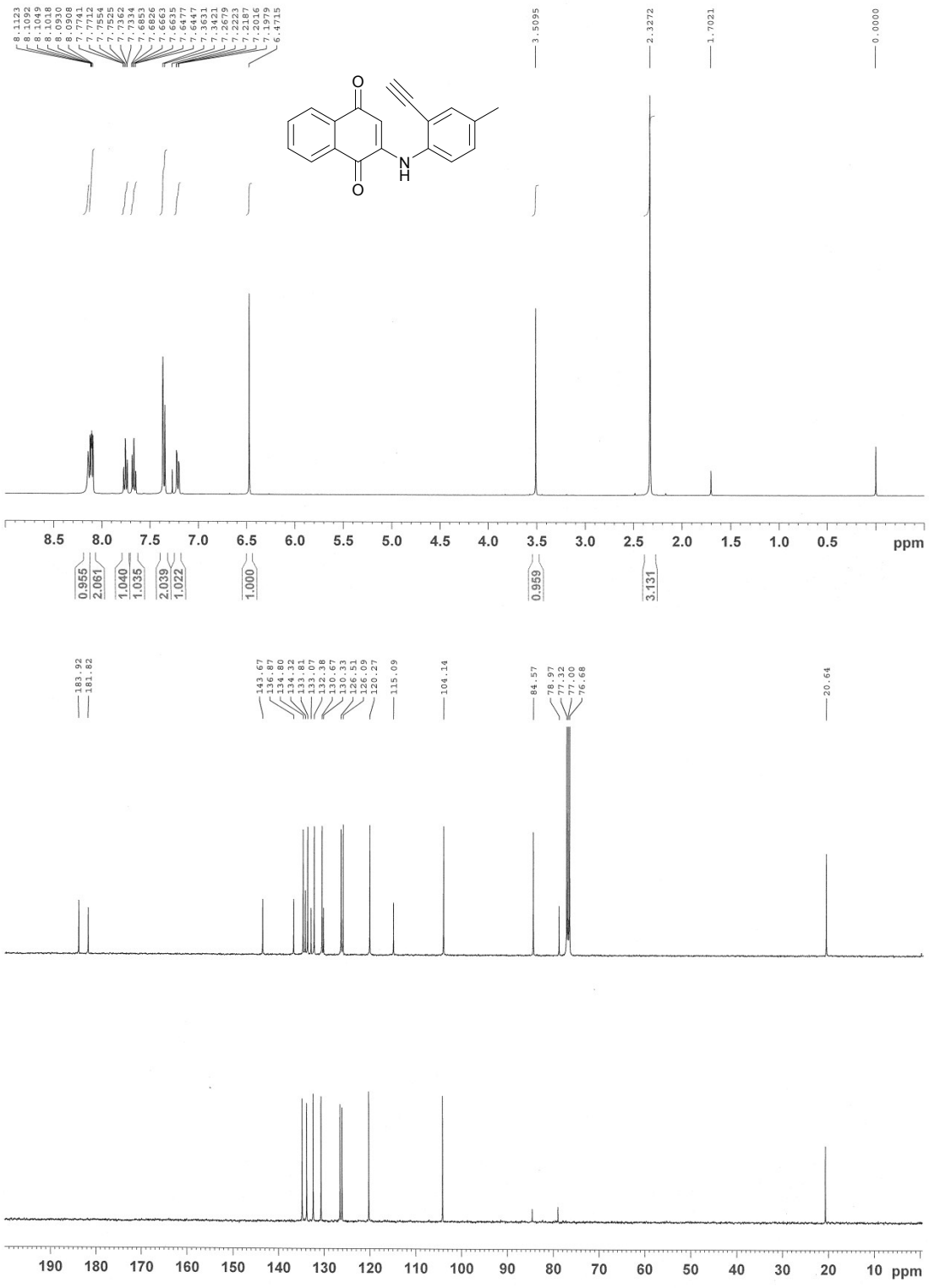
$^{1}H$ and $^{13}C$ NMR spectra of **8Ab**



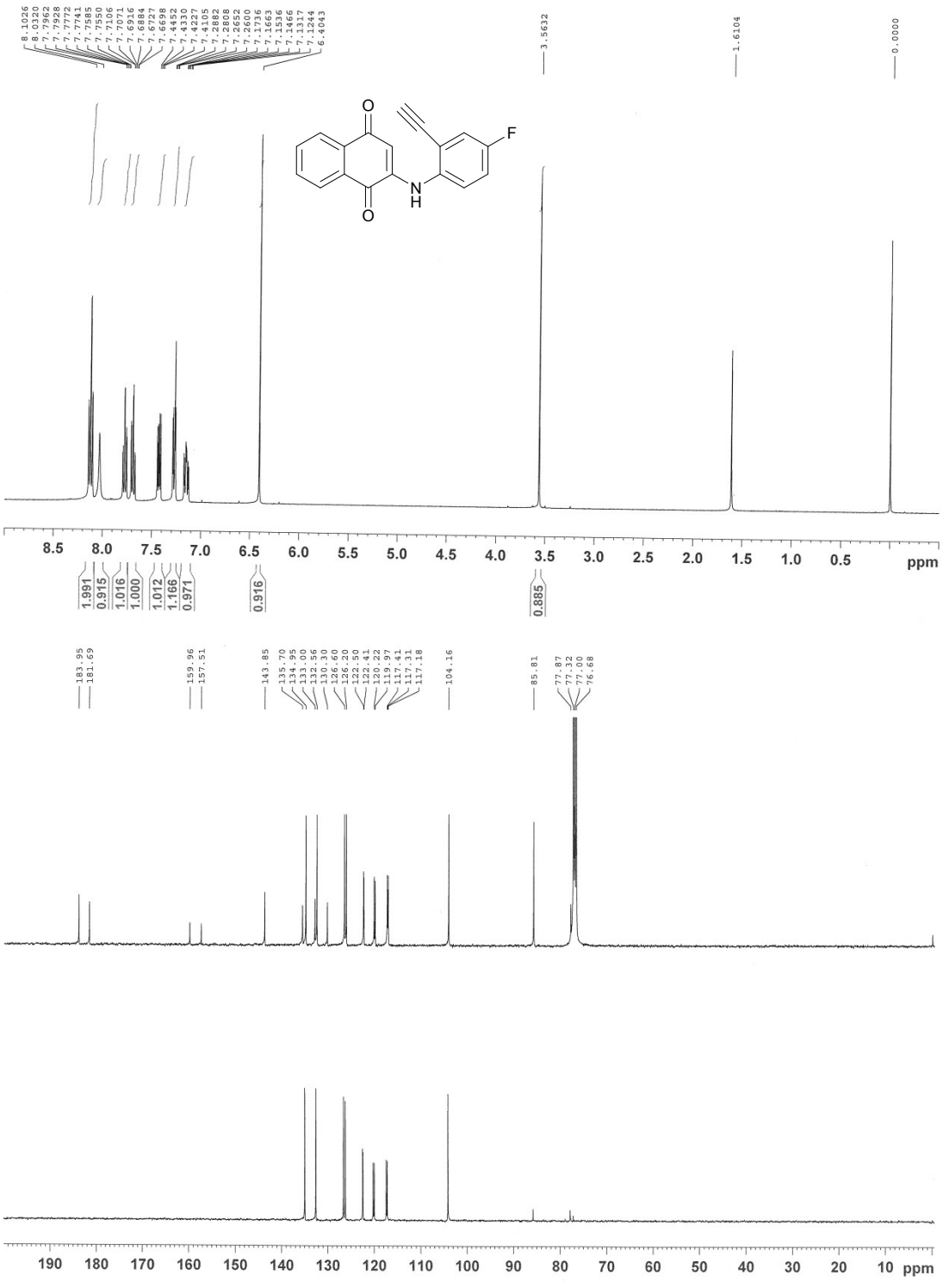
$^{1}H$ and $^{13}C$ NMR spectra of **8Ac**



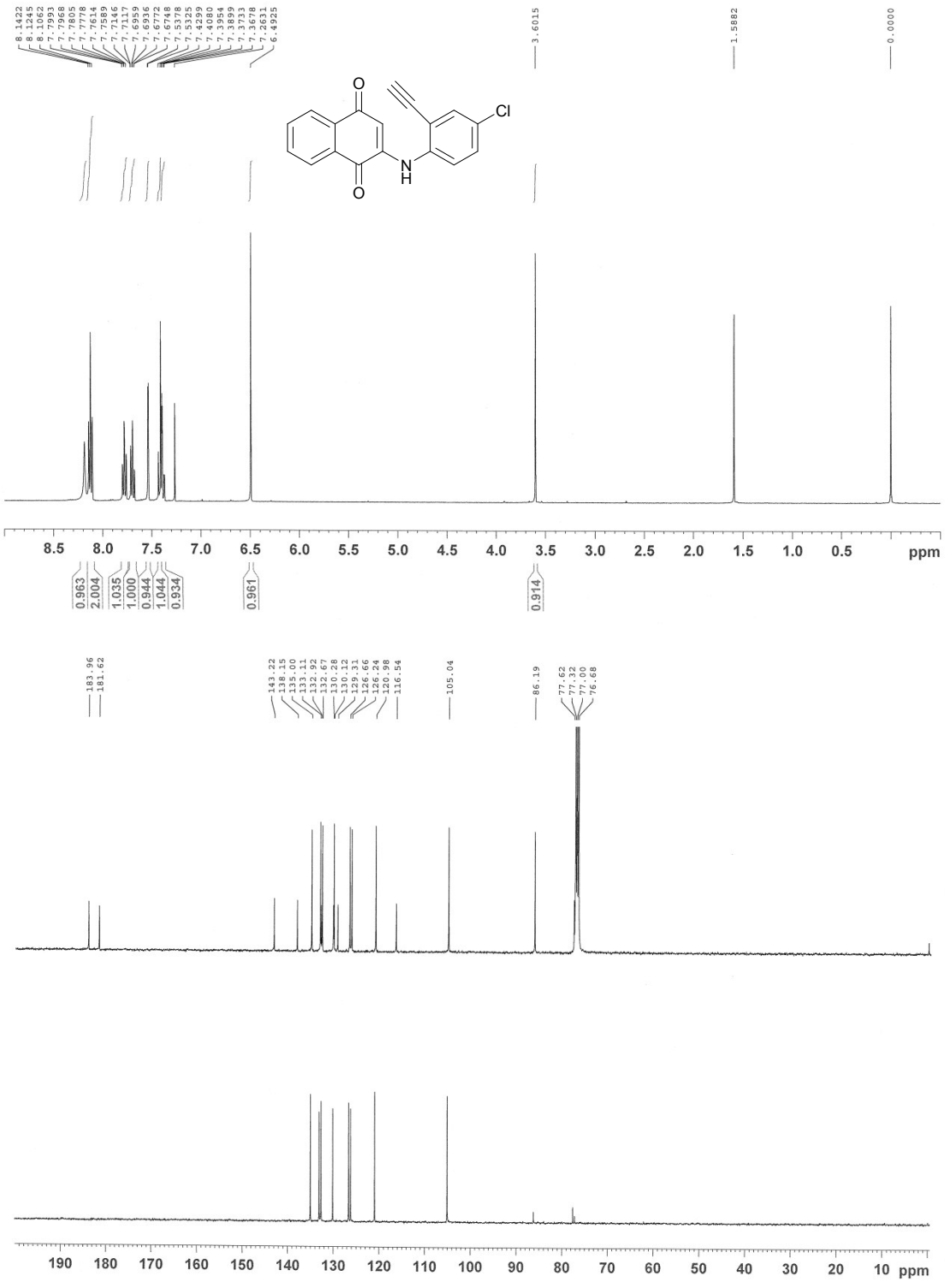
$^{1}H$ and $^{13}C$ NMR spectra of **8Ad**



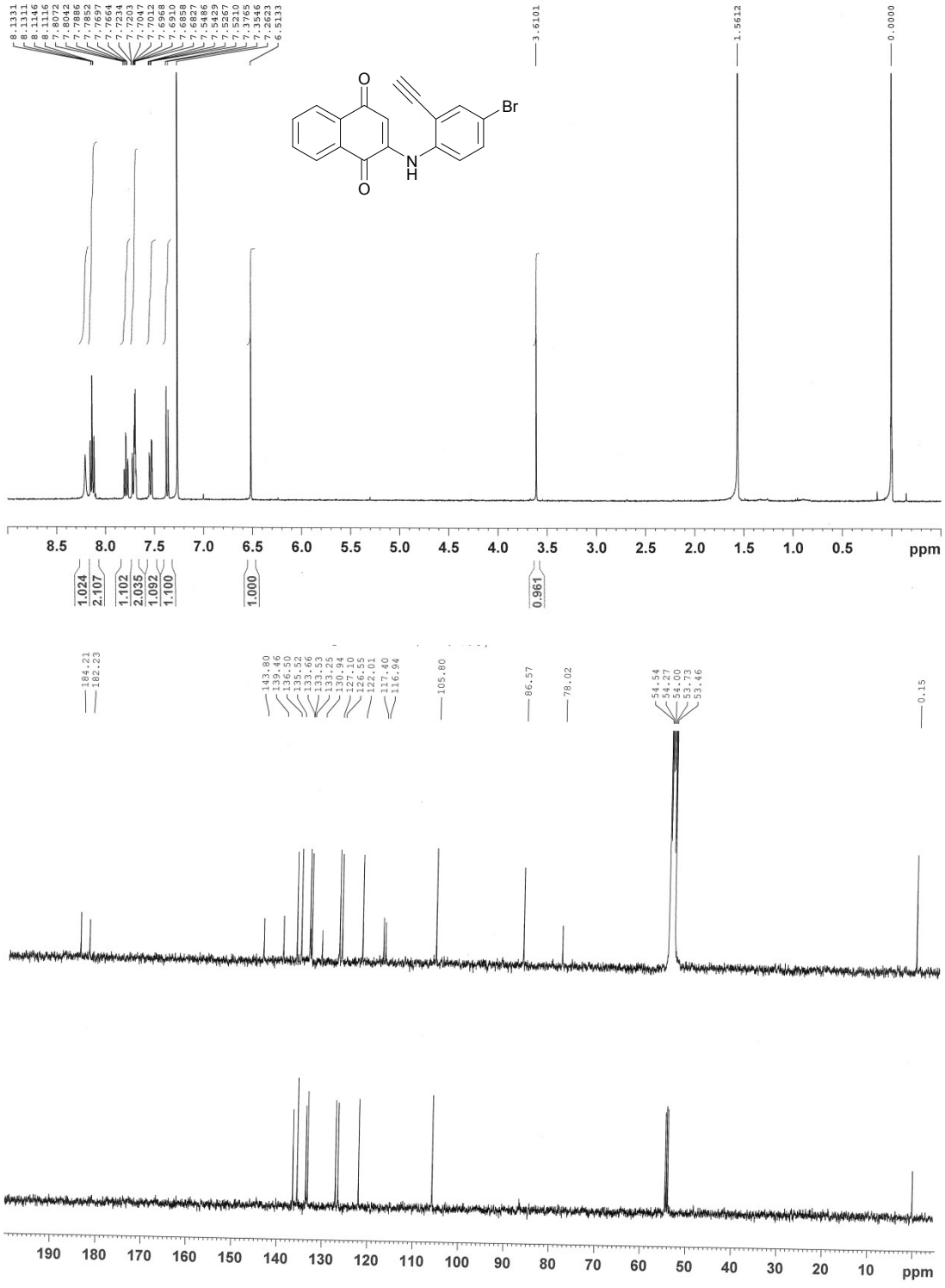
$^{1}H$ and $^{13}C$ NMR spectra of **8Ae**



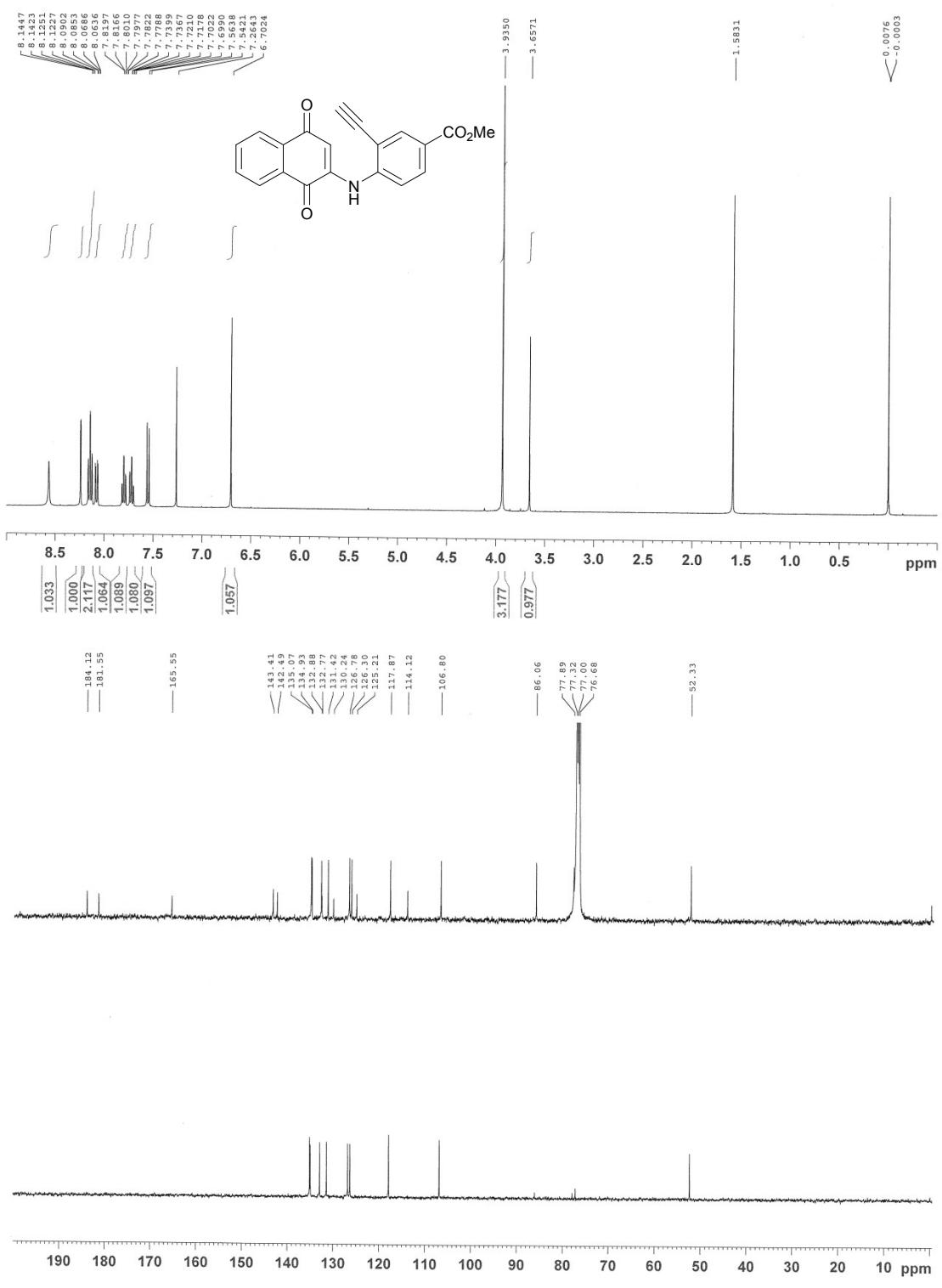
$^{1}H$ and $^{13}C$ NMR spectra of **8Af**



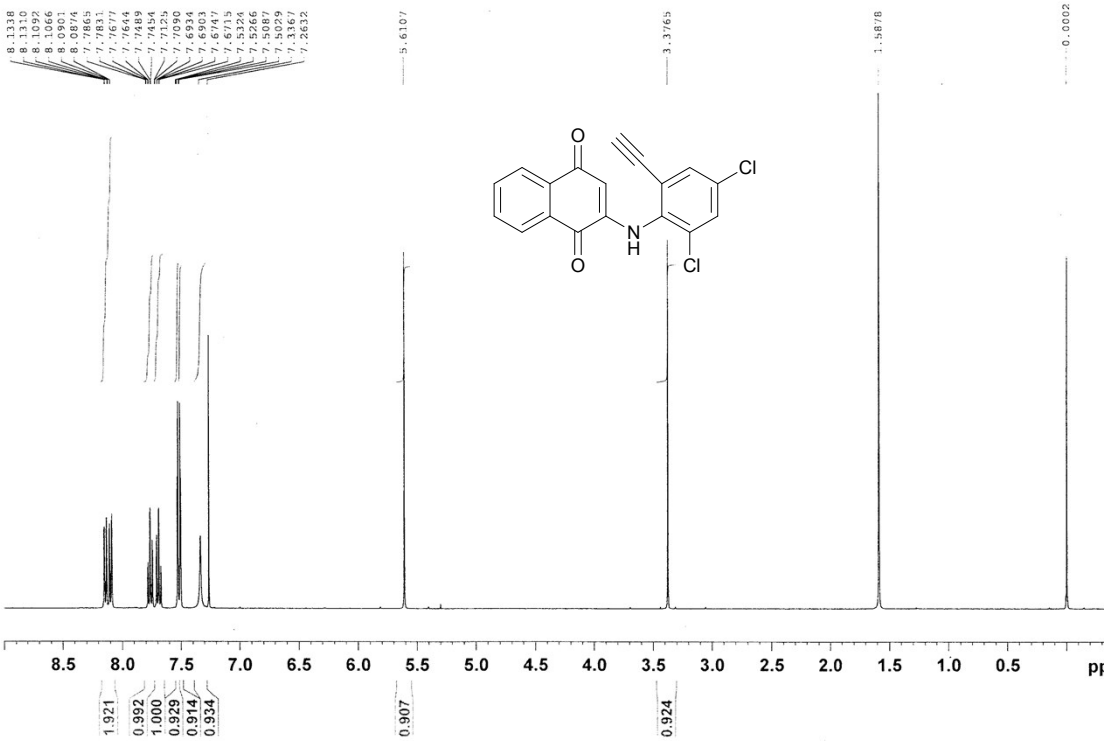
$^{1}H$ and $^{13}C$ NMR spectra of **8Ag**

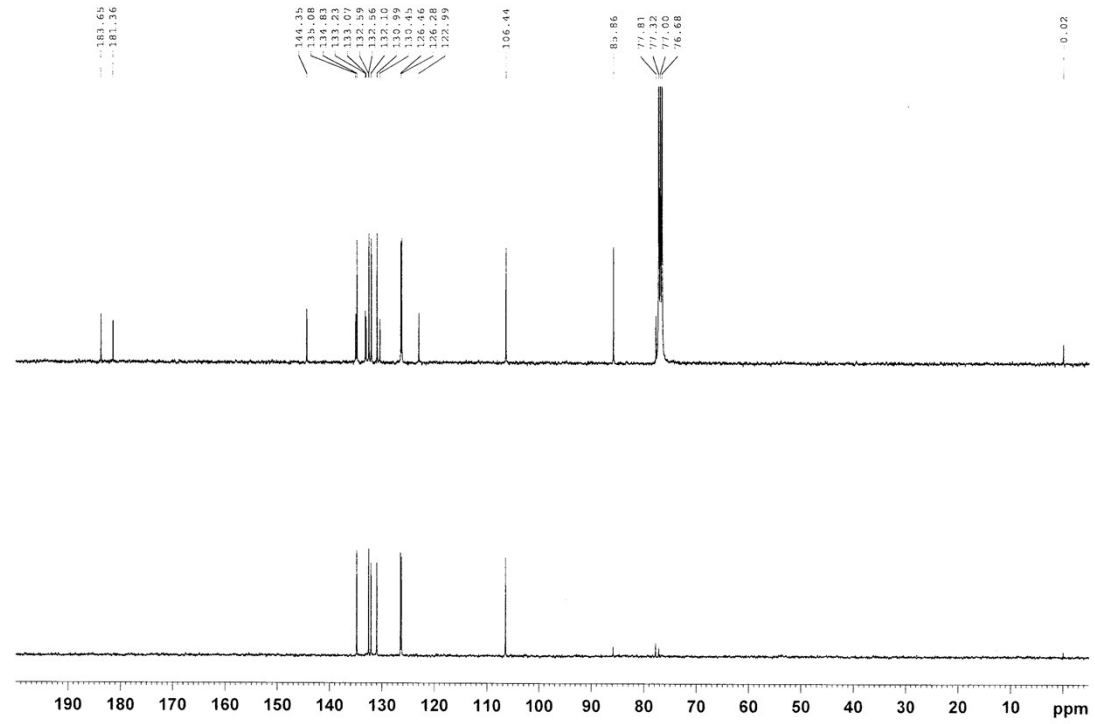


$^{1}H$ and $^{13}C$ NMR spectra of **8Ah**

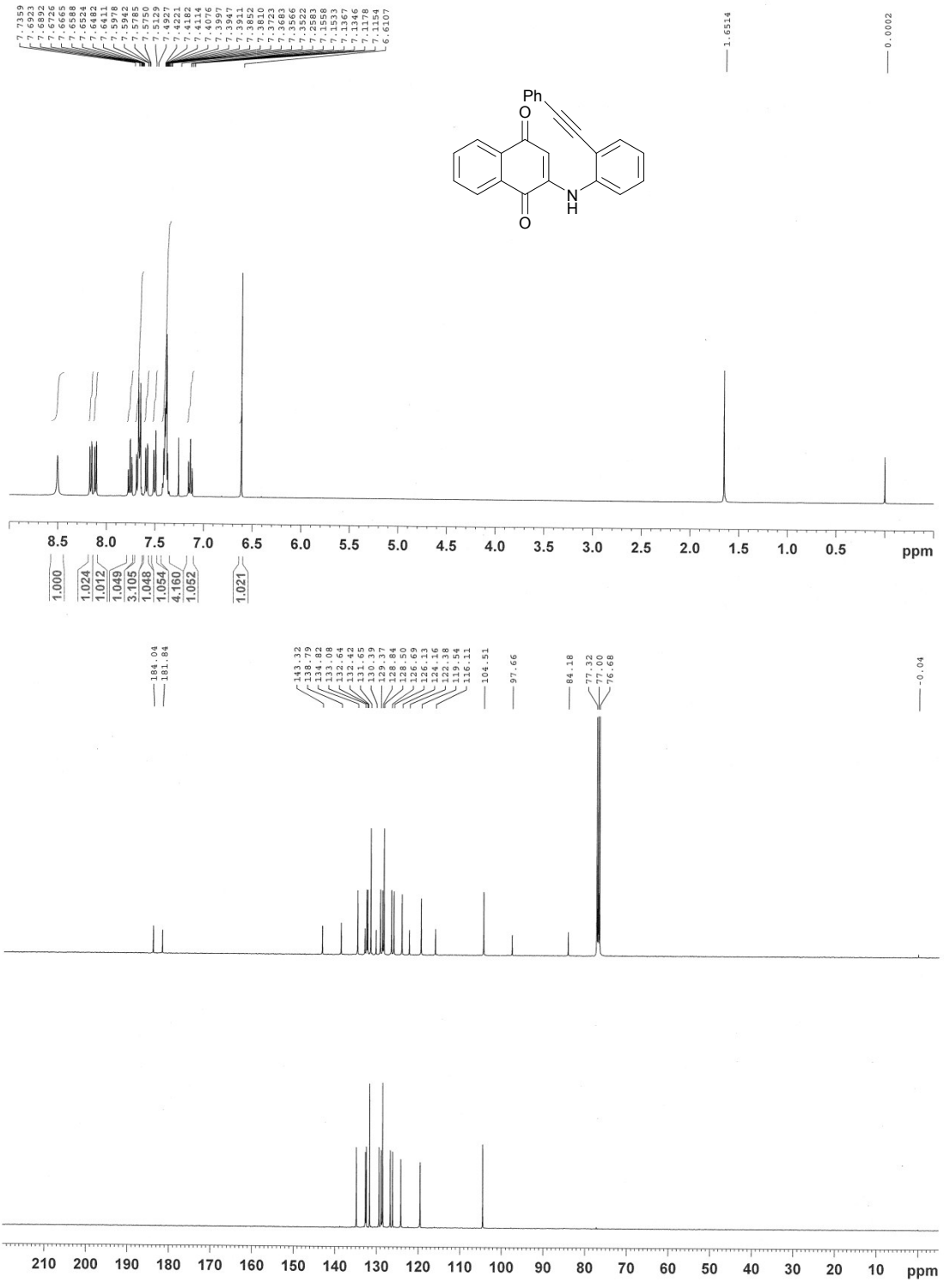


$^{1}H$ and $^{13}C$ NMR spectra of **8Ai**

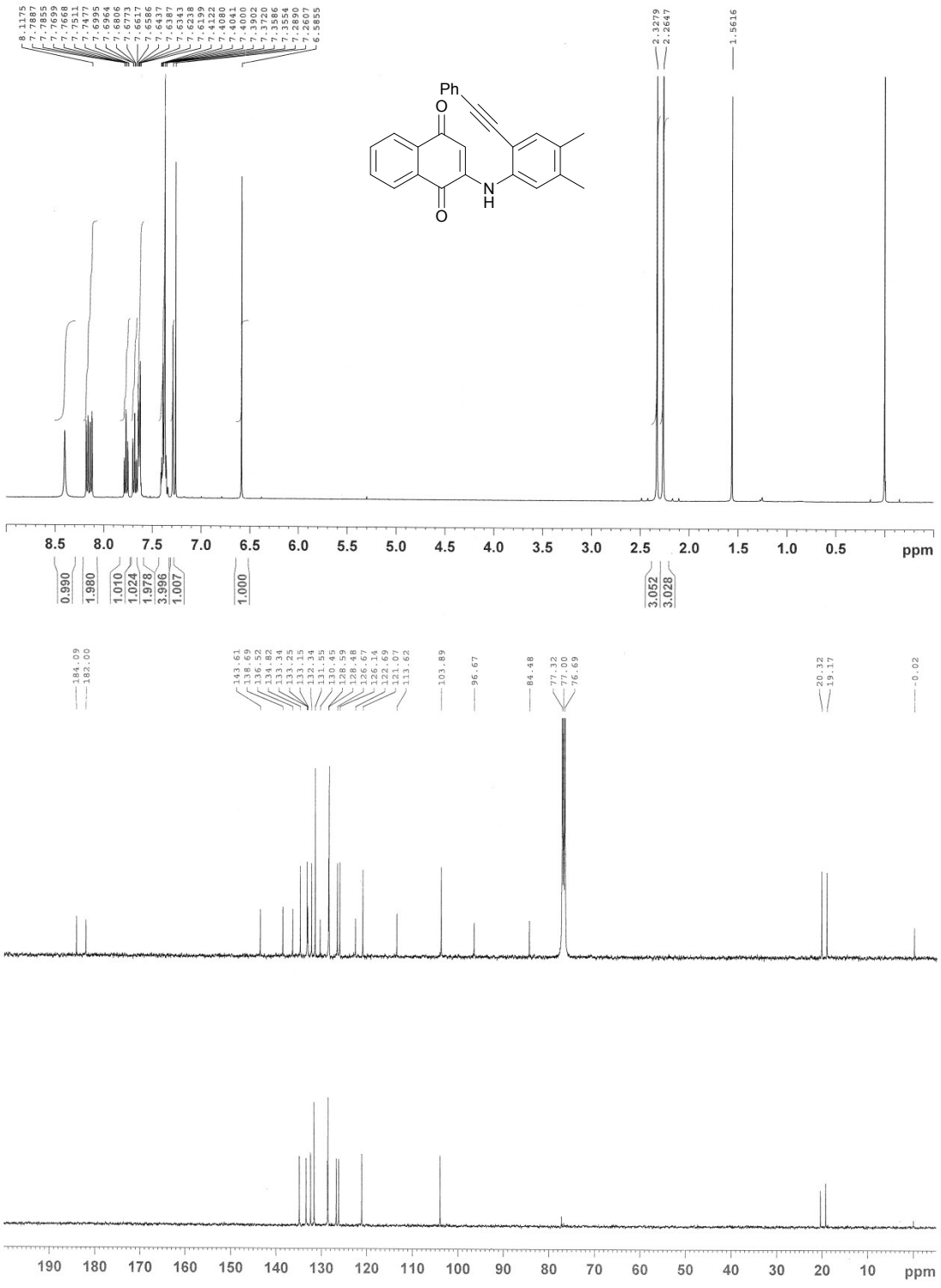


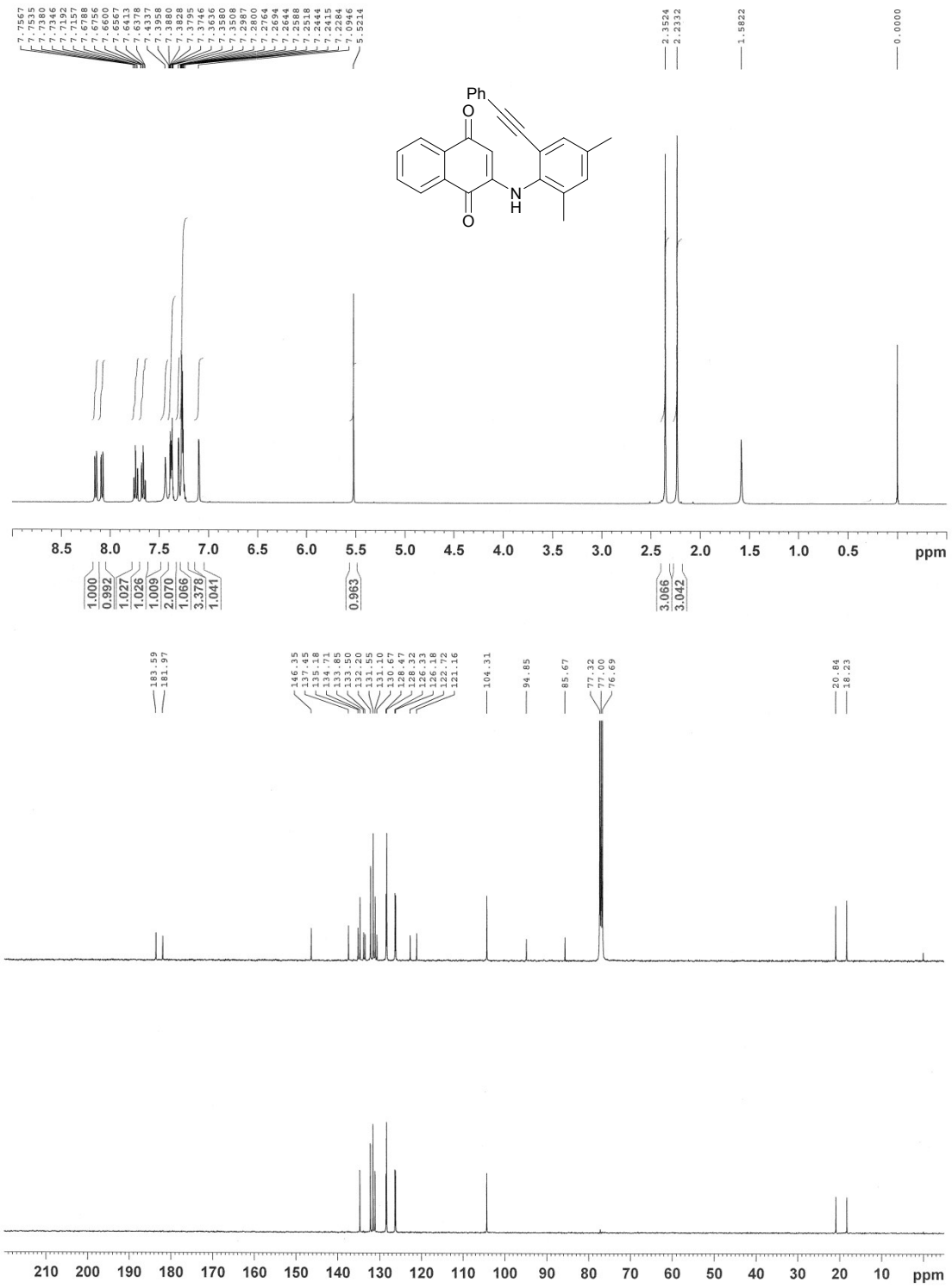
$^{1}H$ and $^{13}C$ NMR spectra of **8Ba**



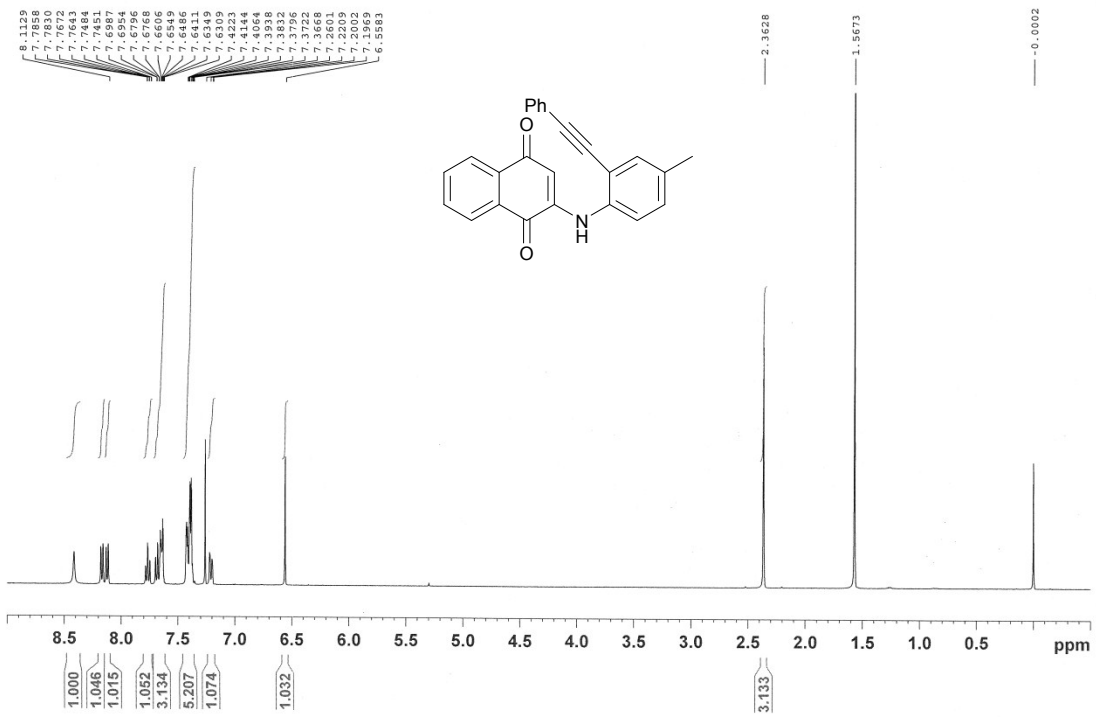
$^{1}H$ and $^{13}C$ NMR spectra of **8Bb**

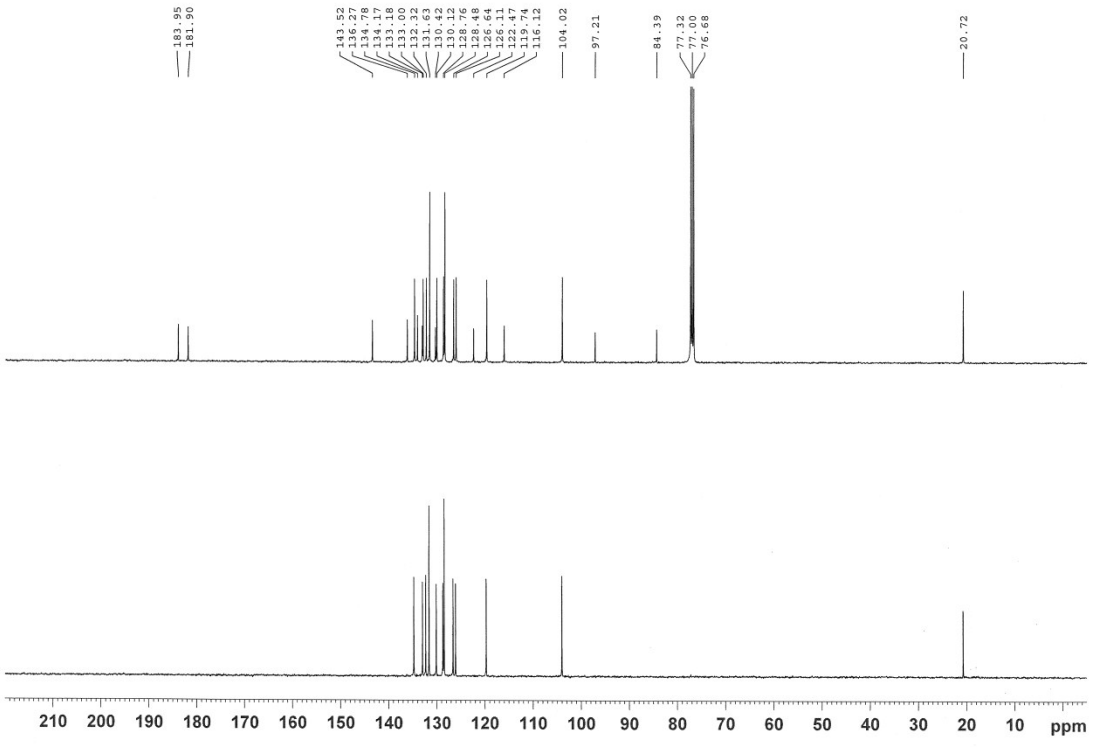


$^{1}H$ and $^{13}C$ NMR spectra of **8Bc**

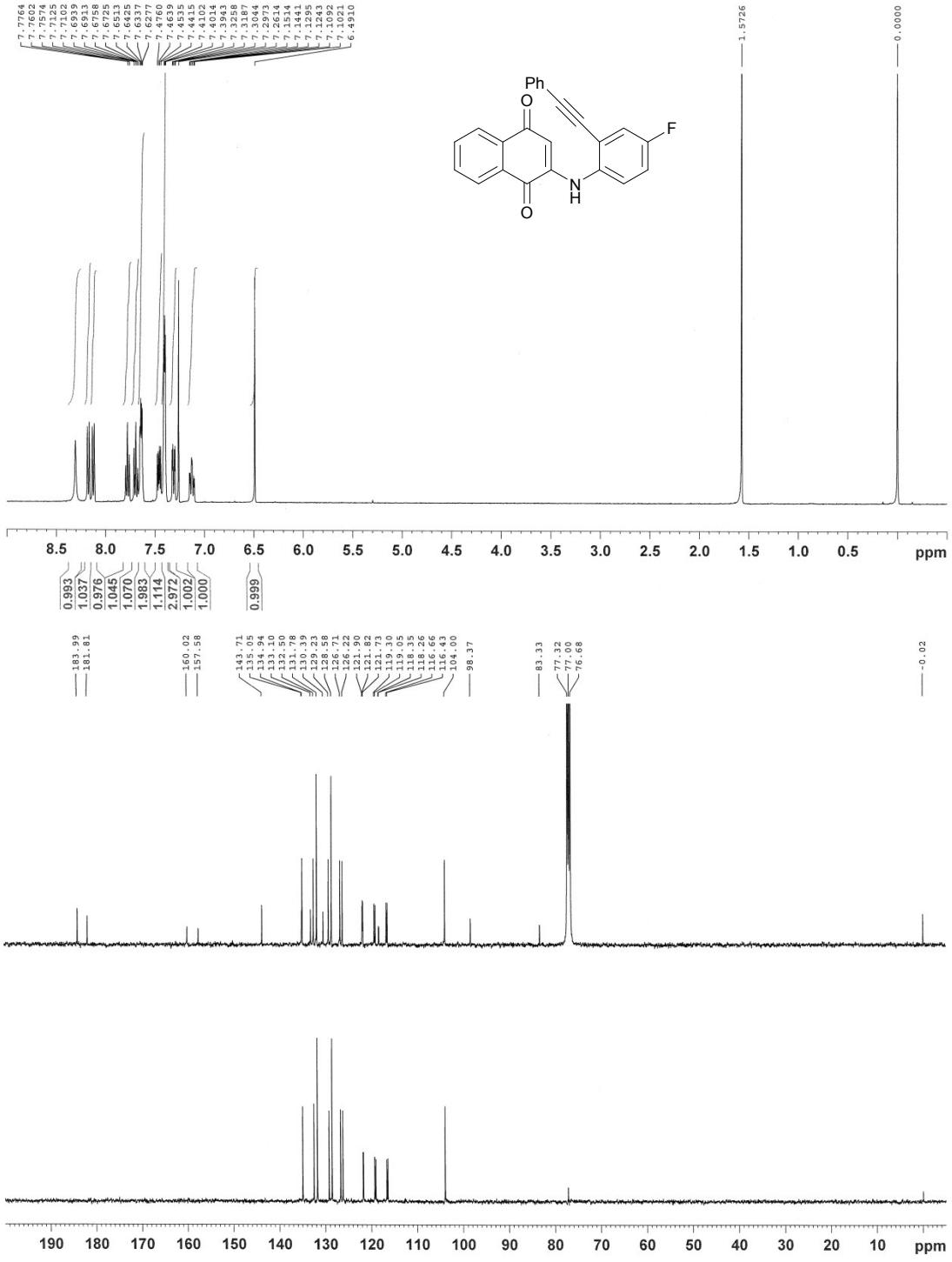


$^{1}H$ and $^{13}C$ NMR spectra of **8Bd**

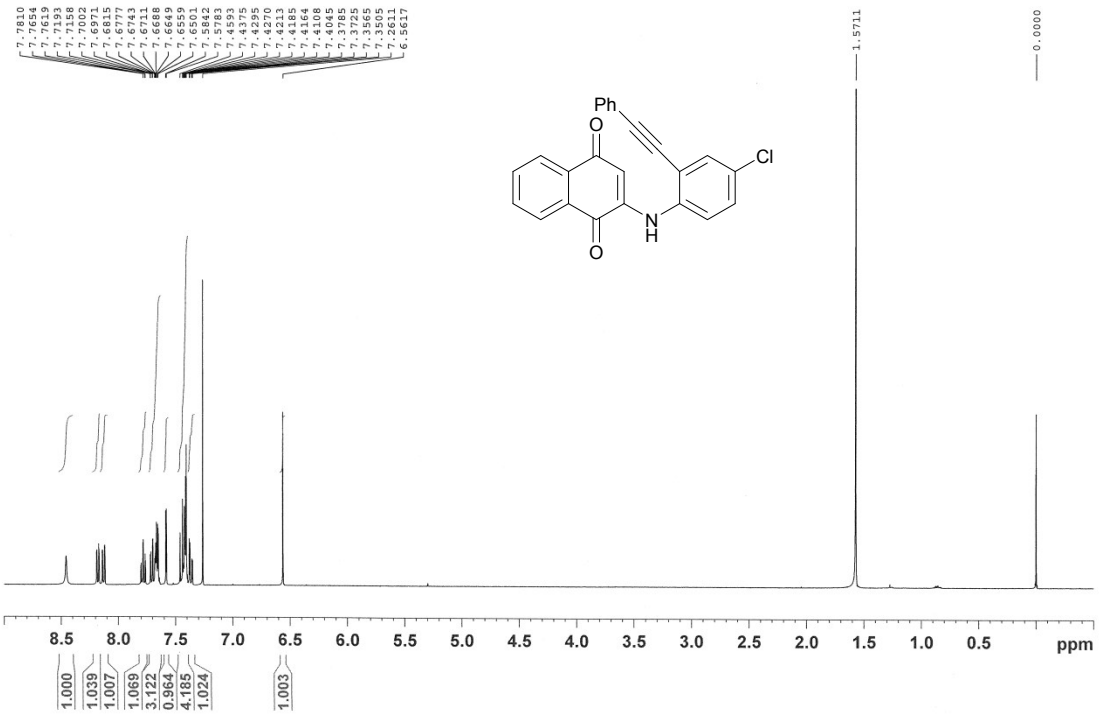


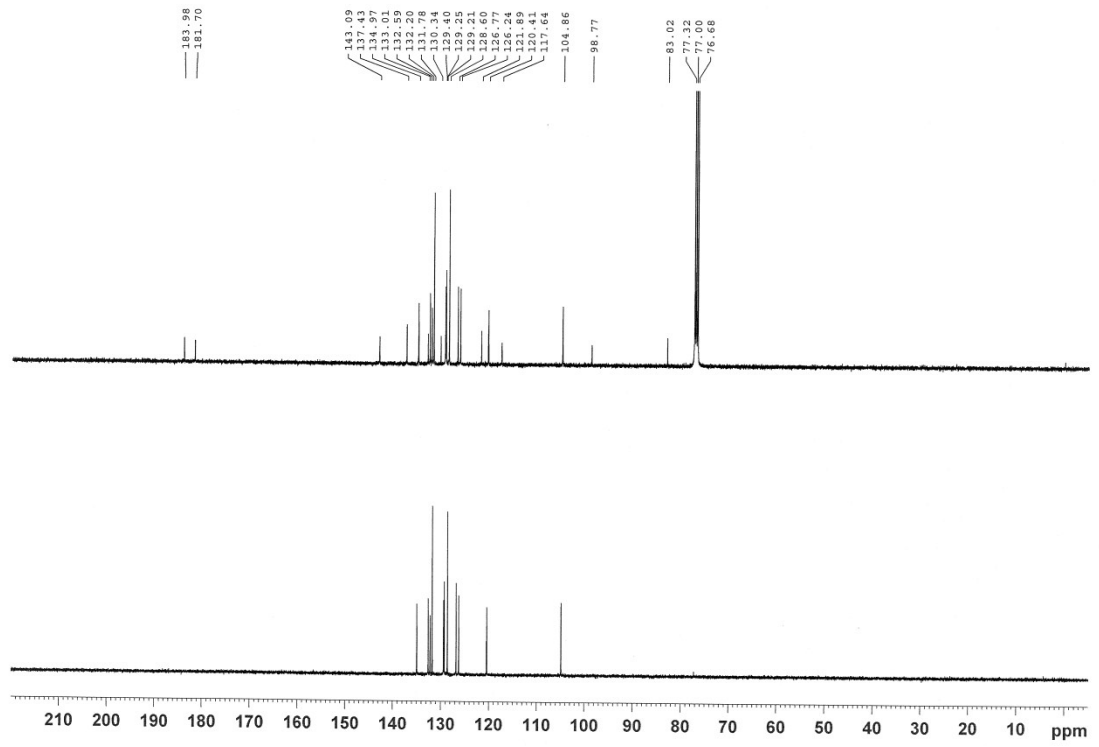



$^{1}H$ and $^{13}C$ NMR spectra of **8Be**

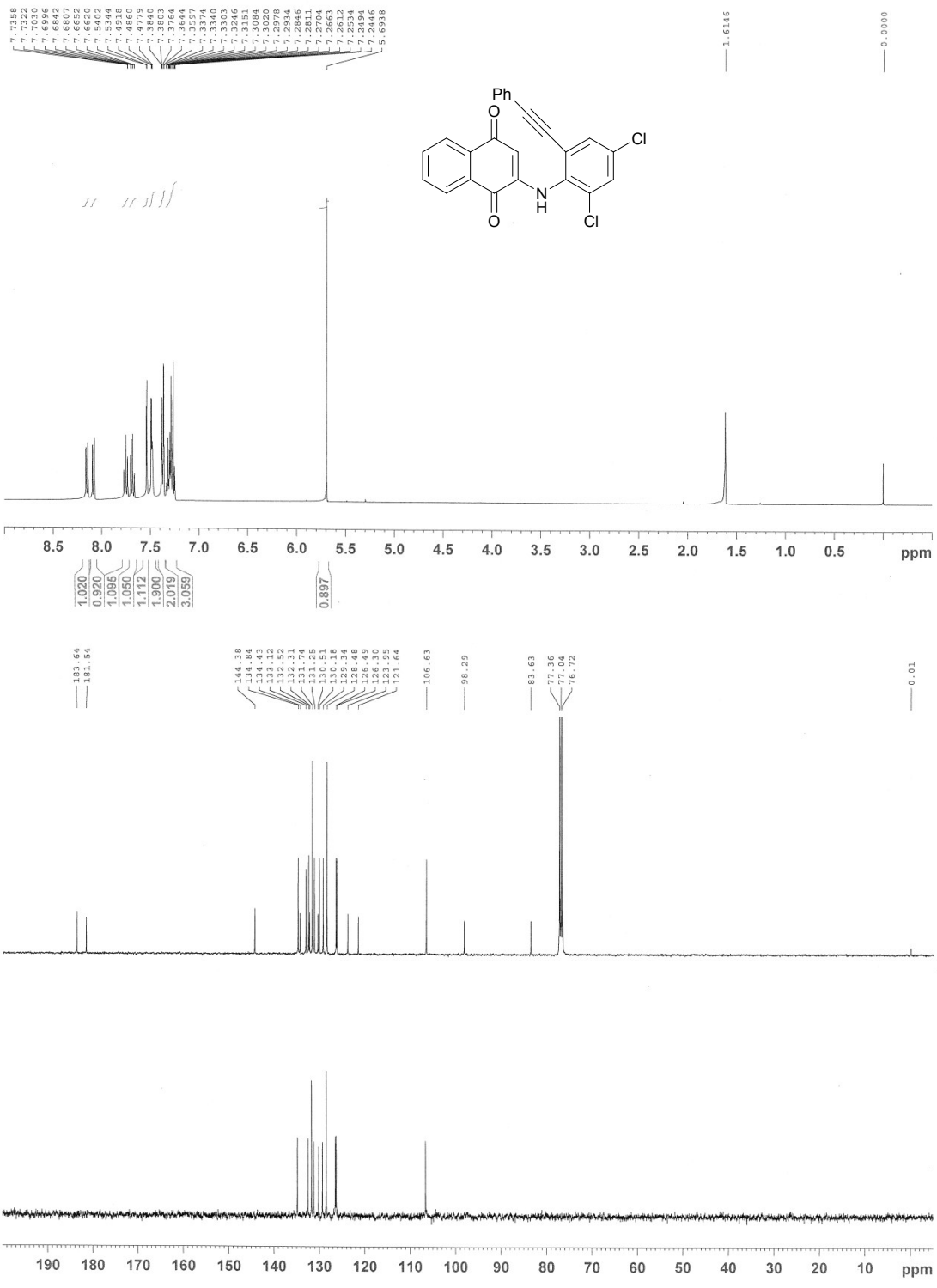


$^{1}H$ and $^{13}C$ NMR spectra of **8Bf**

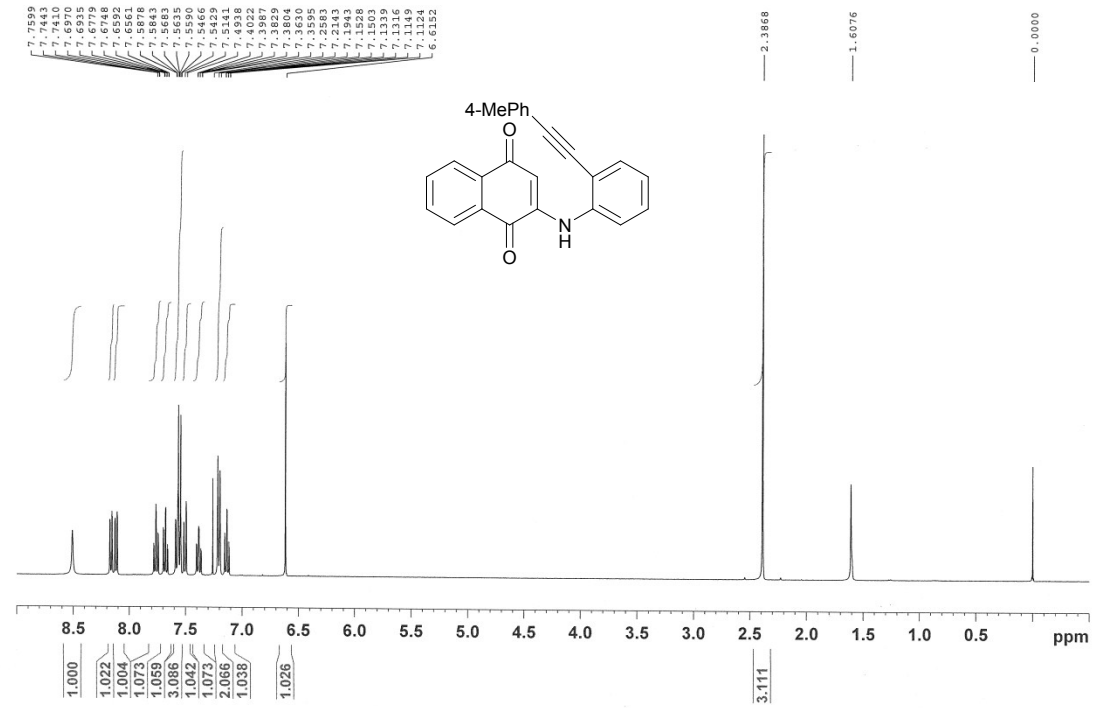


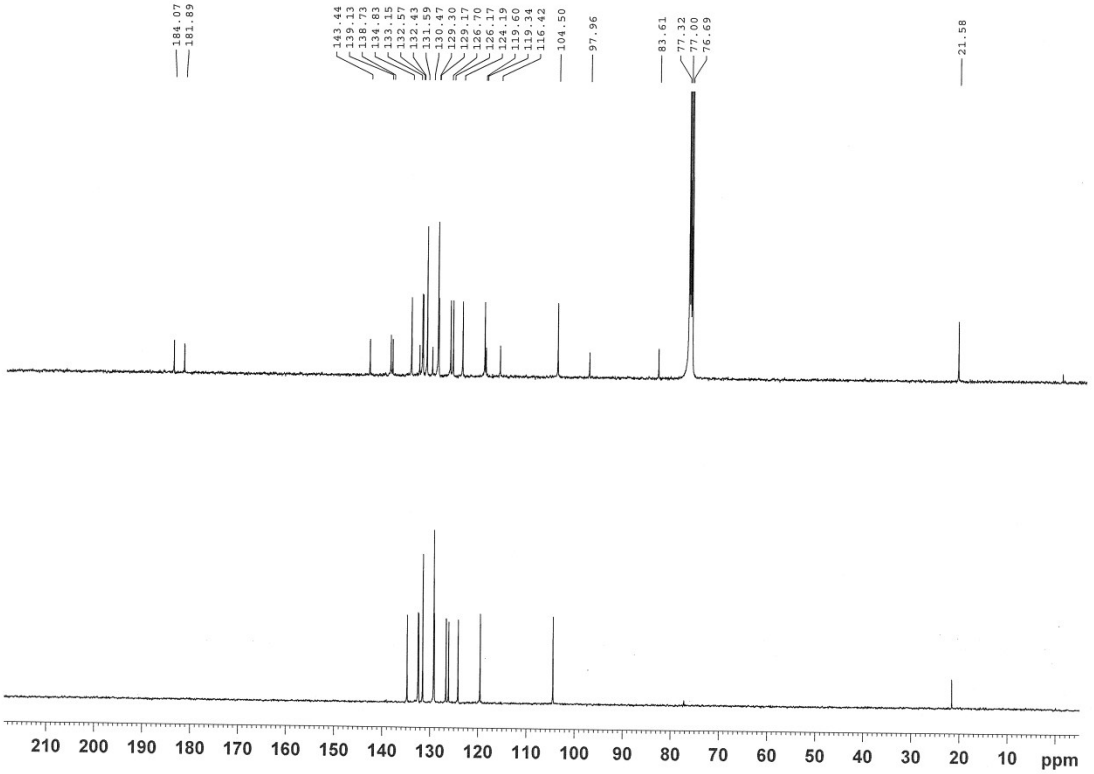



$^{1}H$ and $^{13}C$ NMR spectra of **8Bi**

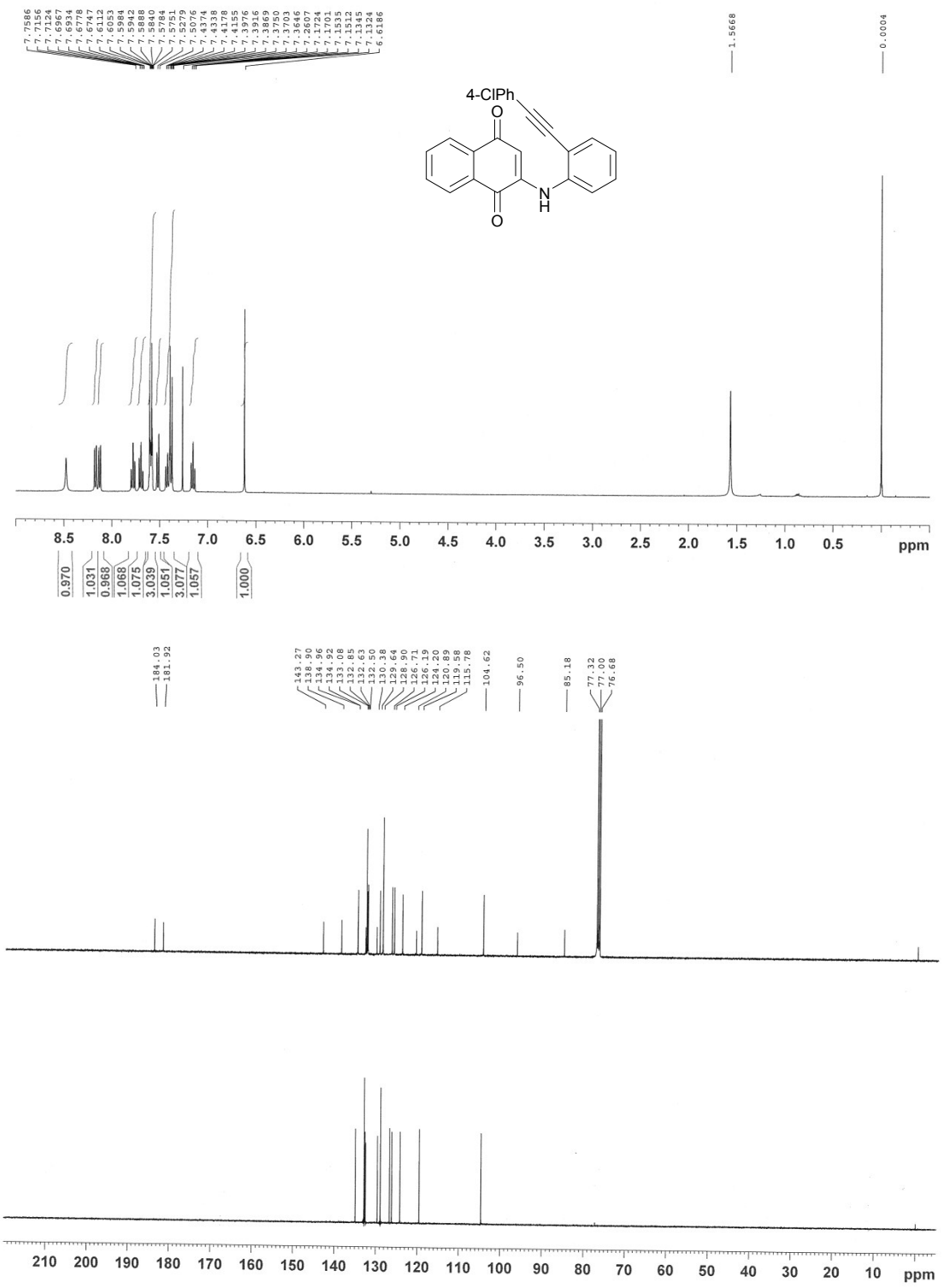


$^{1}H$ and $^{13}C$ NMR spectra of **8Bj**

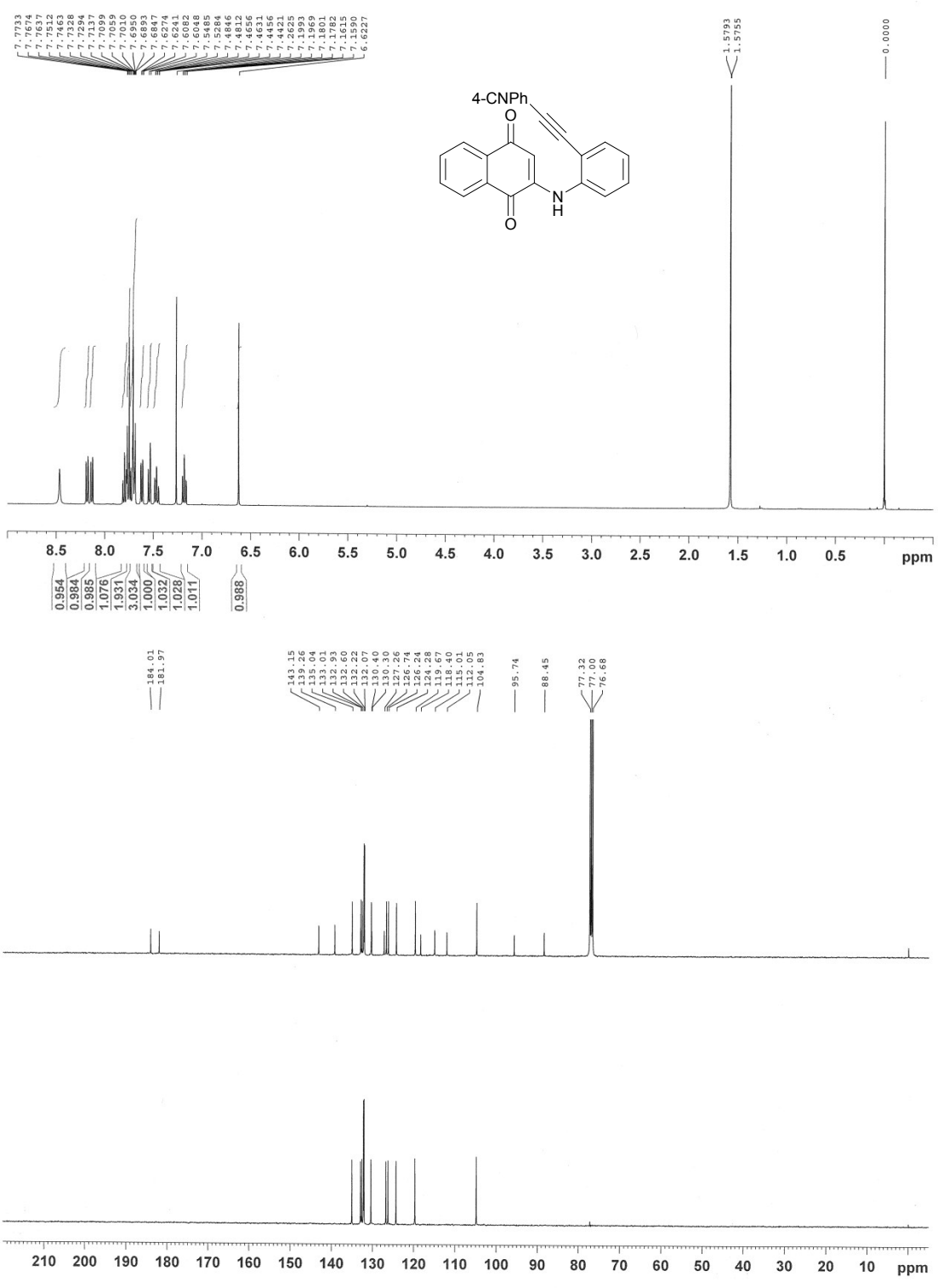


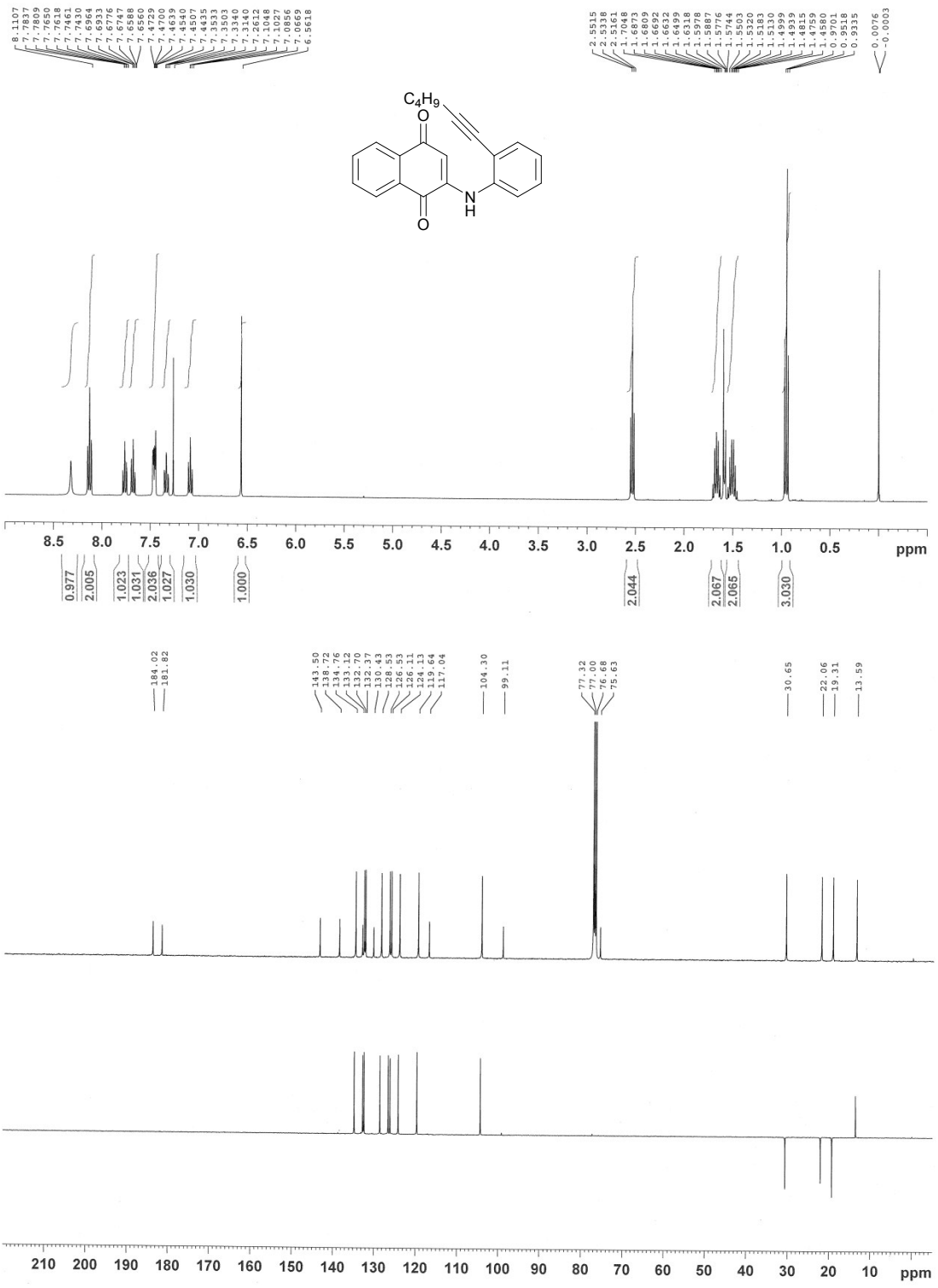
$^{1}H$ and $^{13}C$ NMR spectra of **8Bk**



$^{1}H$ and $^{13}C$ NMR spectra of **8Bl**

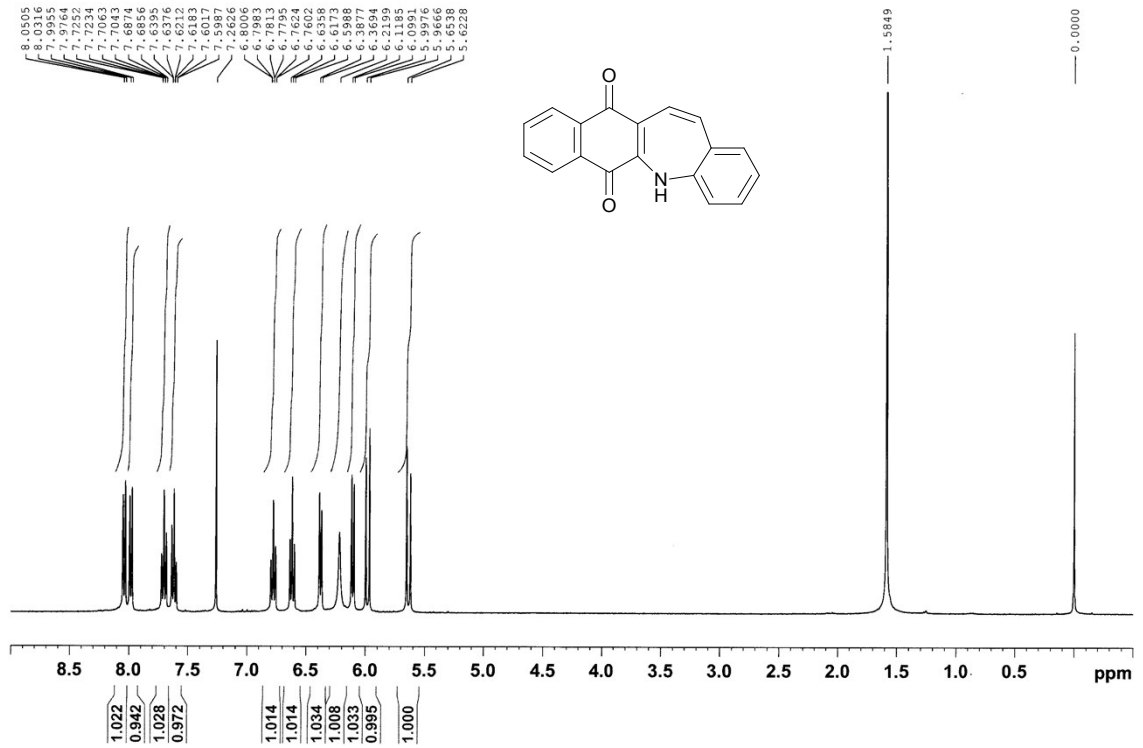


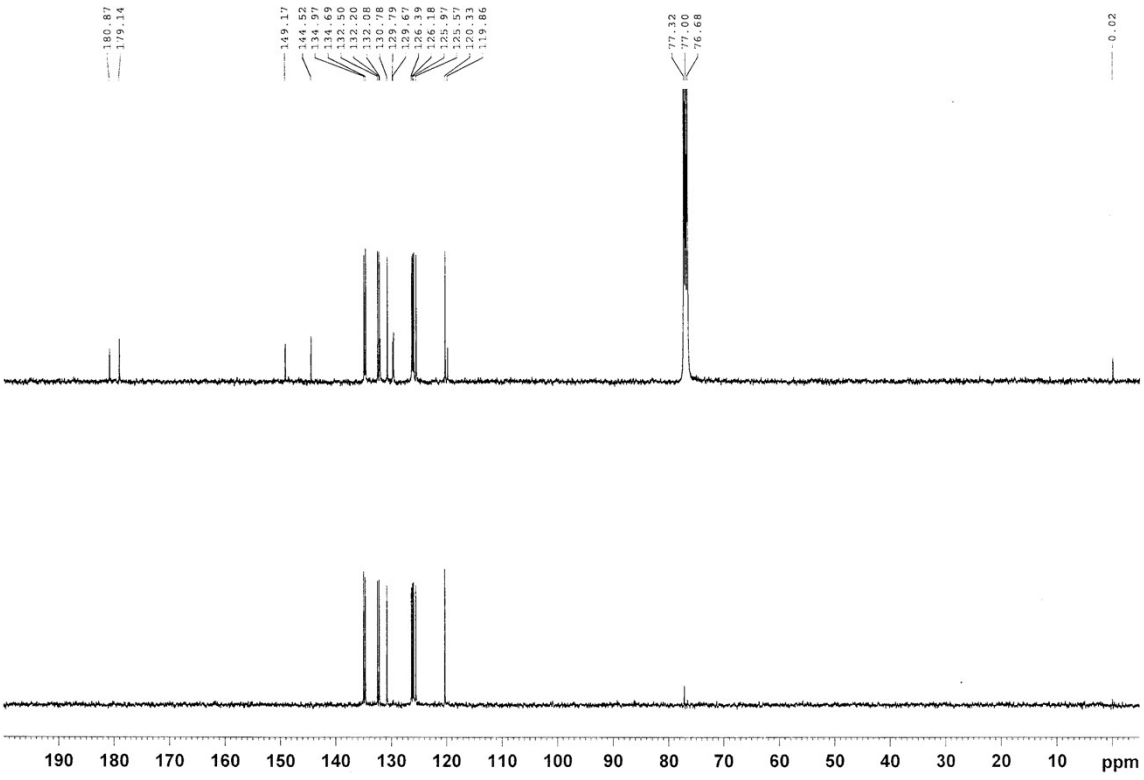
$^{1}$H and $^{13}$C NMR spectra of **8Bm**



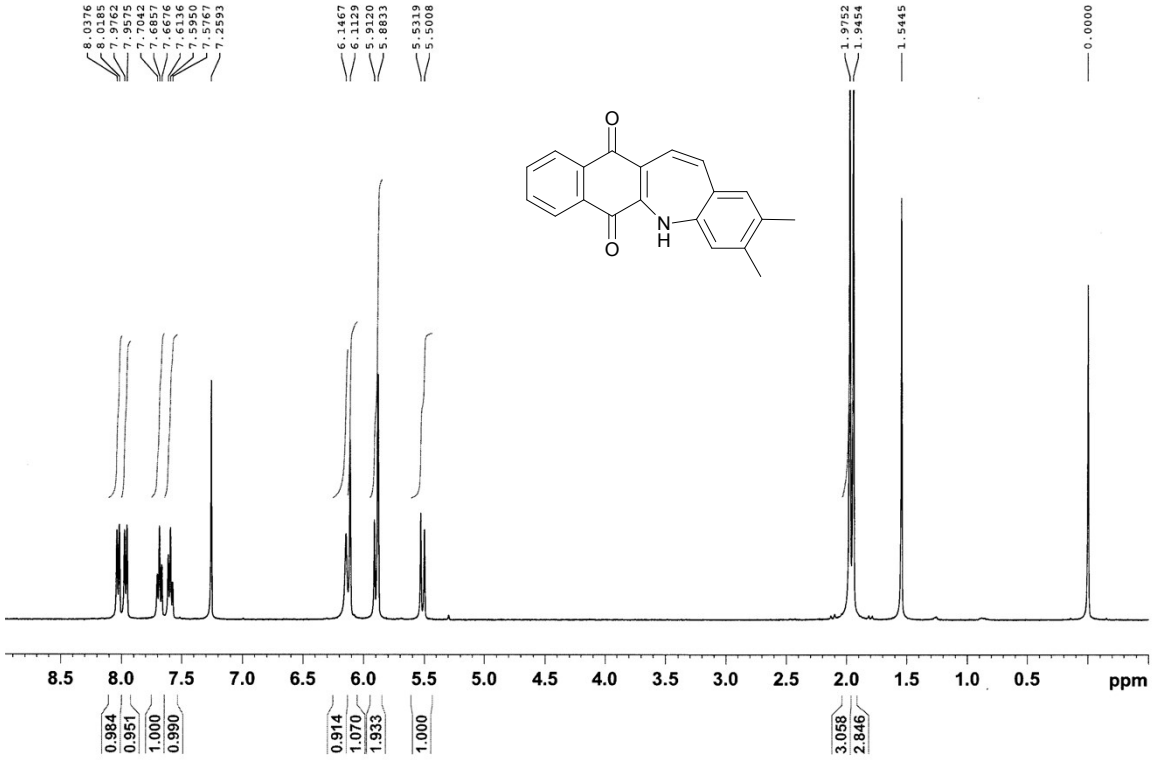

**3) Copies of $^{1}$H and $^{13}$C NMR spectra for benzazepines 11 and 13-iodo-benzazepines 13.**

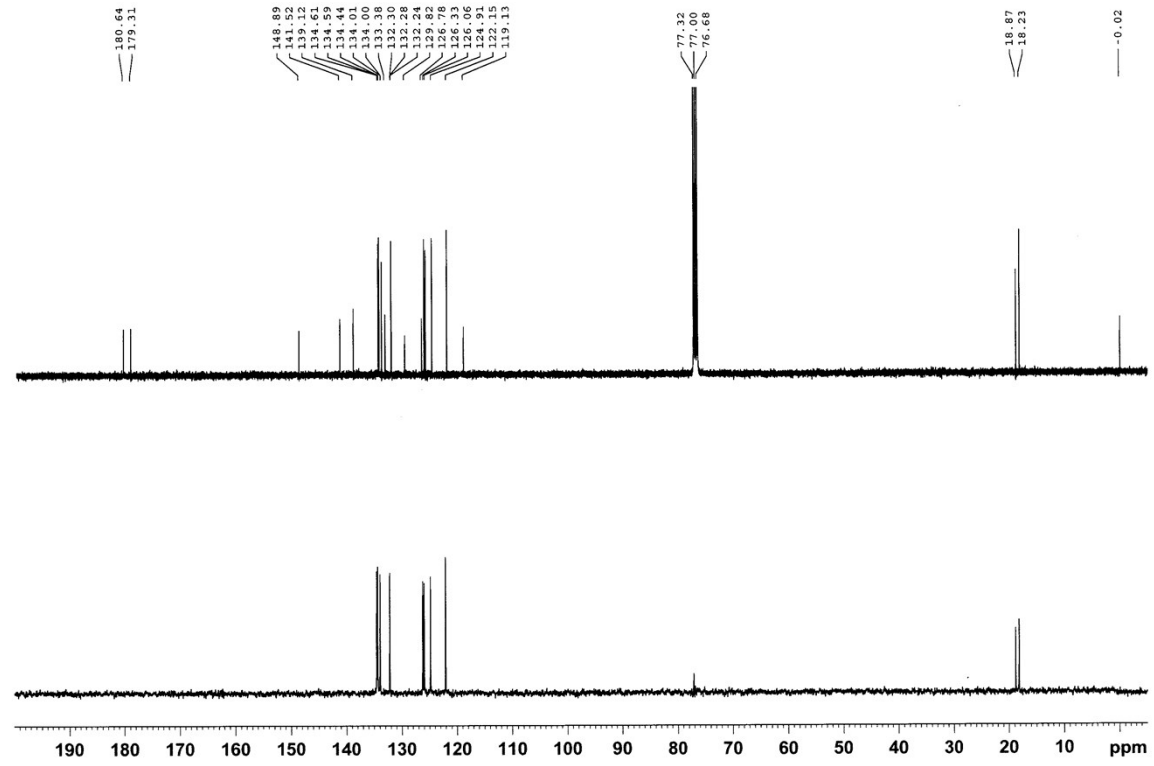
$^{1}H$ and $^{13}C$ NMR spectra of **11Aa**



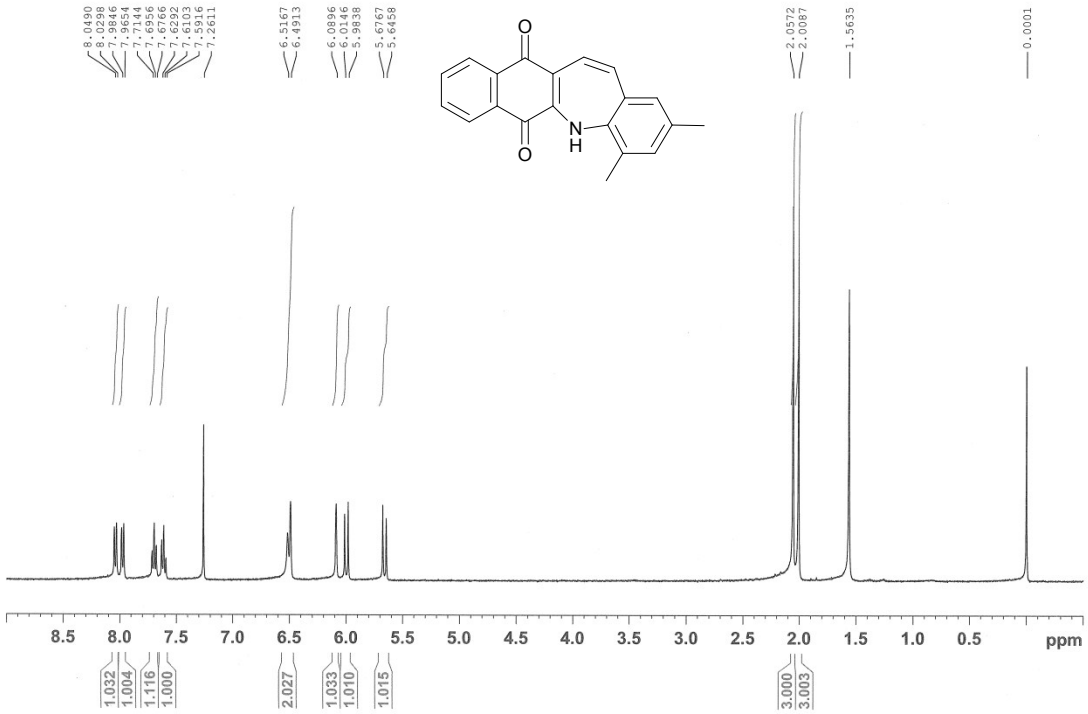



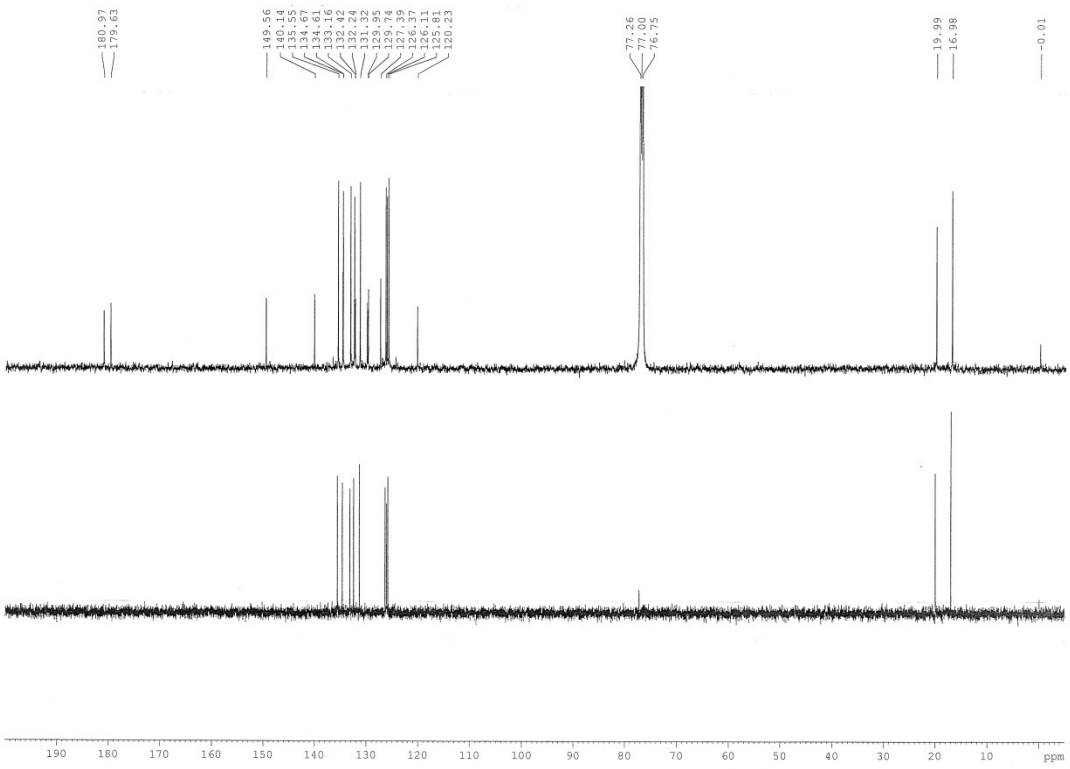
$^{1}H$ and $^{13}C$ NMR spectra of **11Ab**



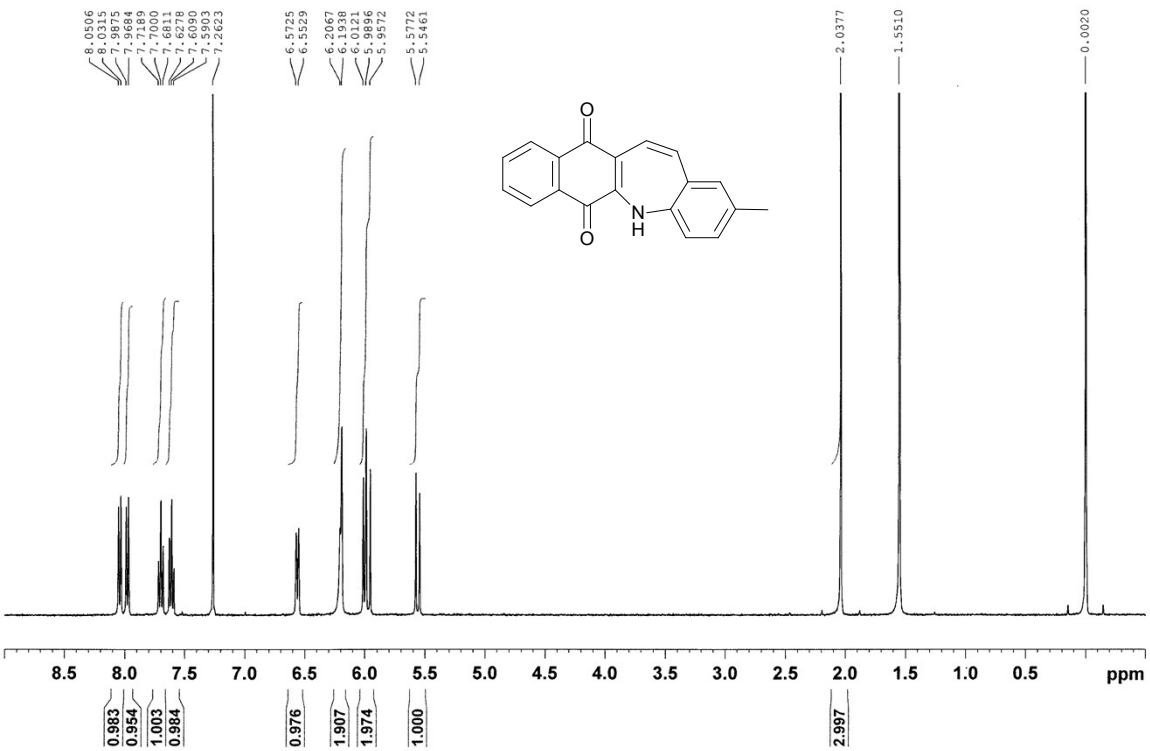



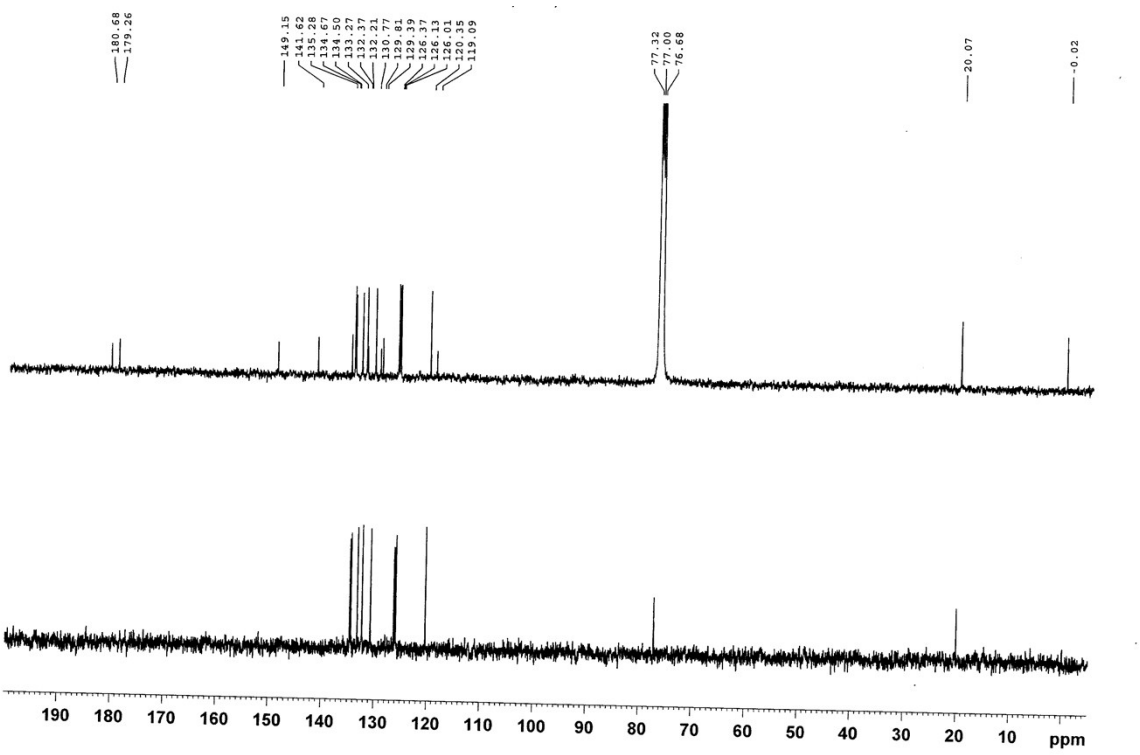
$^{1}H$ and $^{13}C$ NMR spectra of **11Ac**



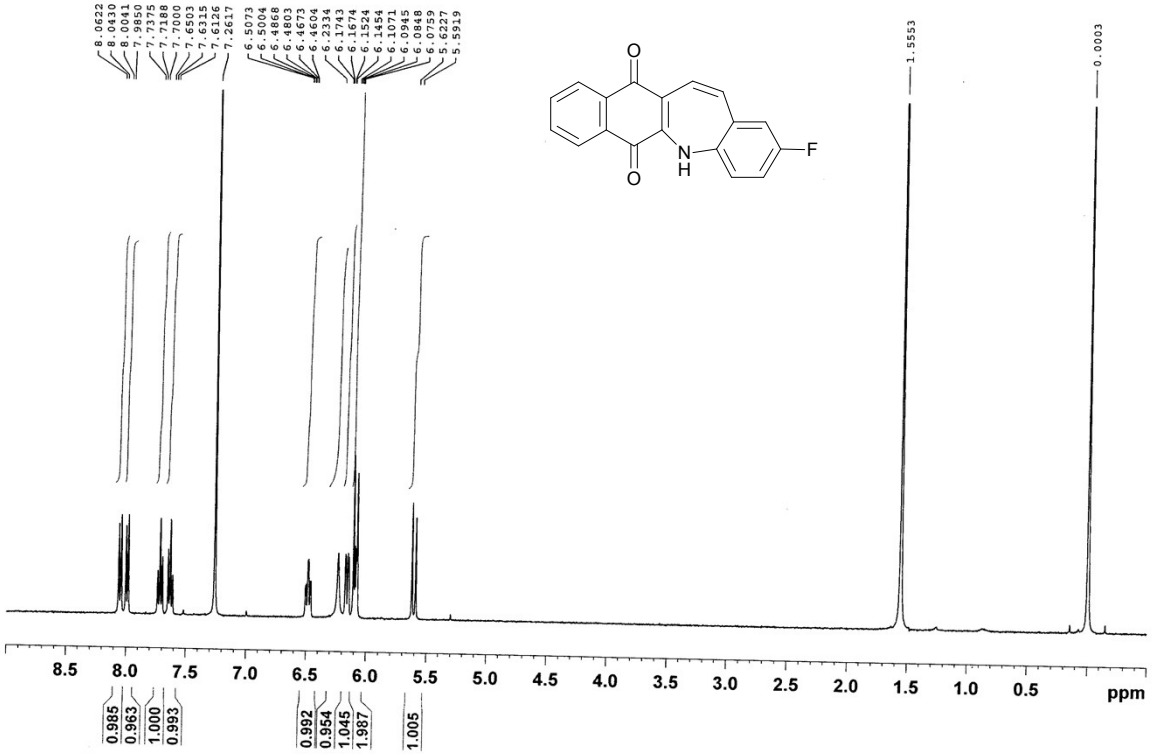



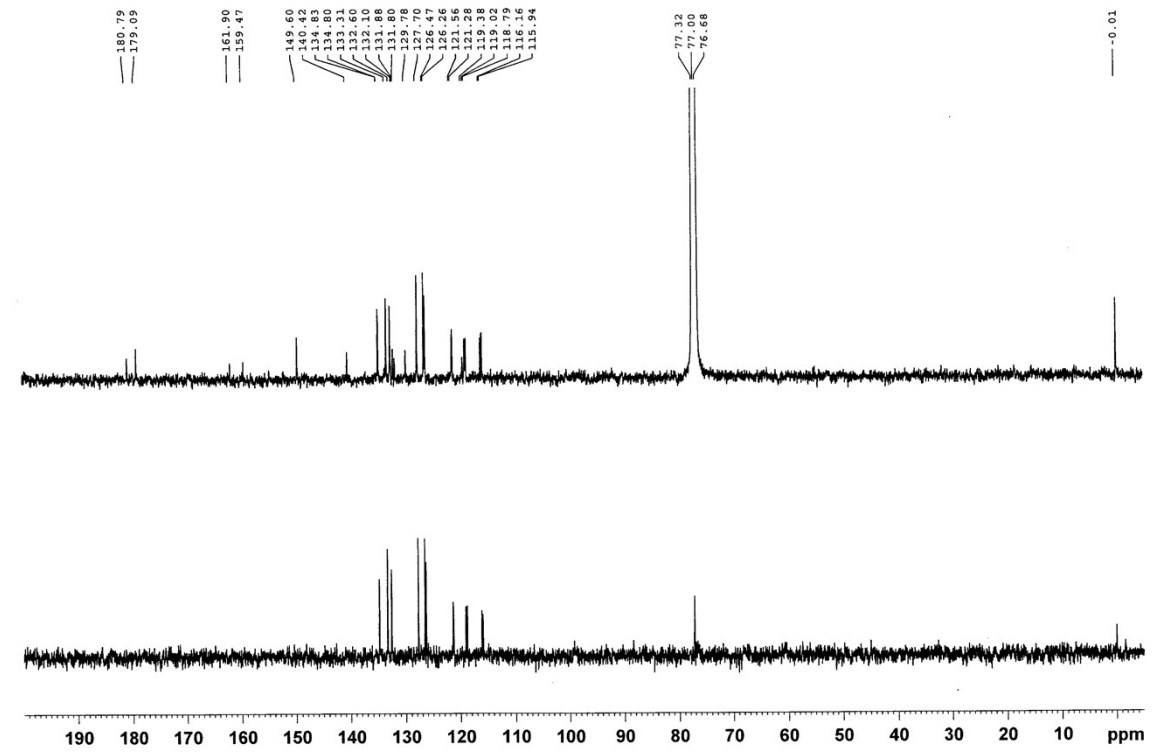
$^{1}H$ and $^{13}C$ NMR spectra of **11Ad**



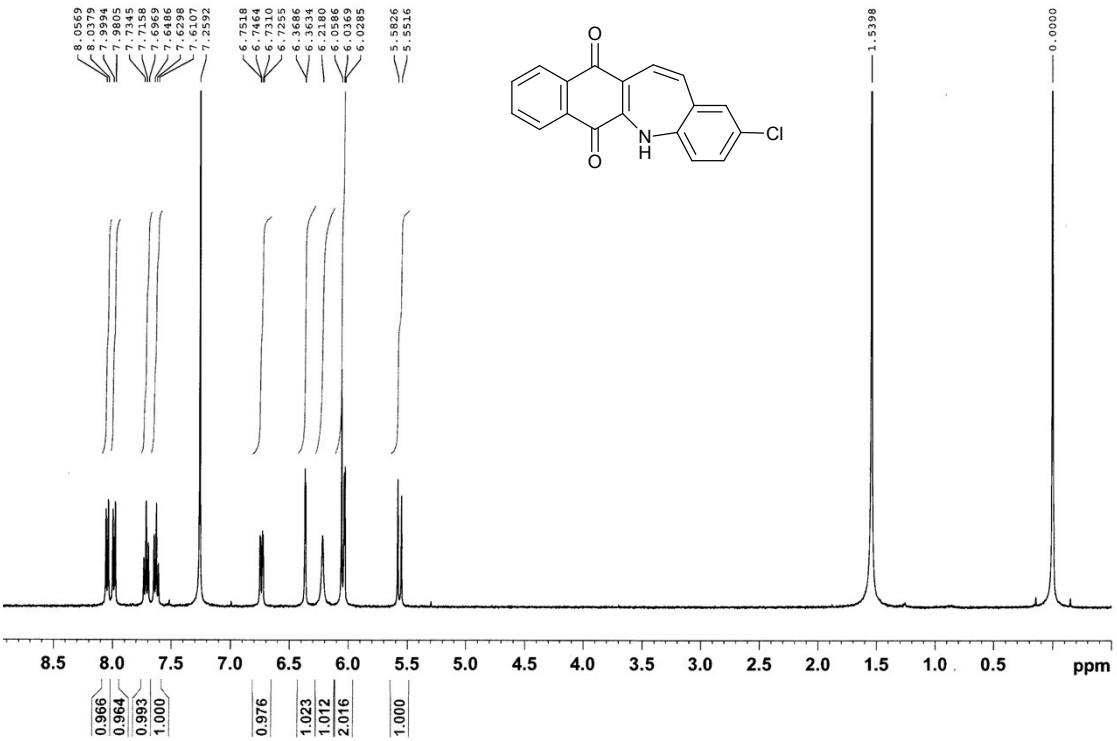



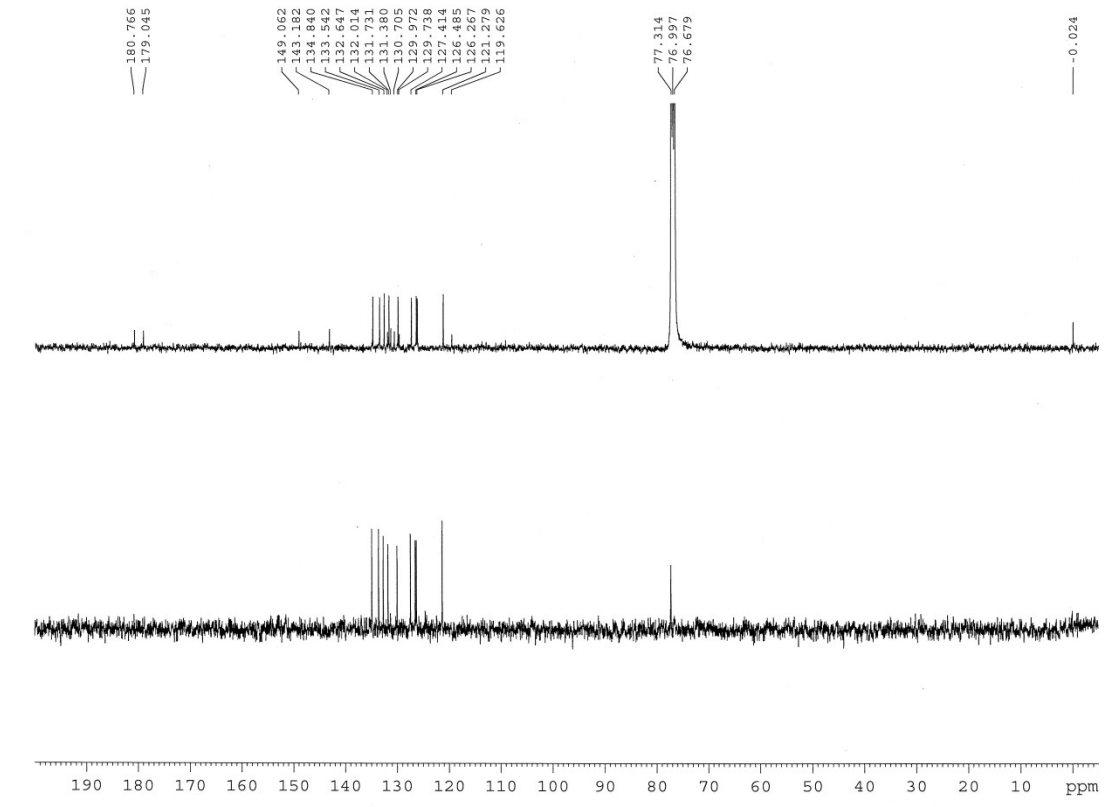
$^{1}H$ and $^{13}C$ NMR spectra of **11Ae**



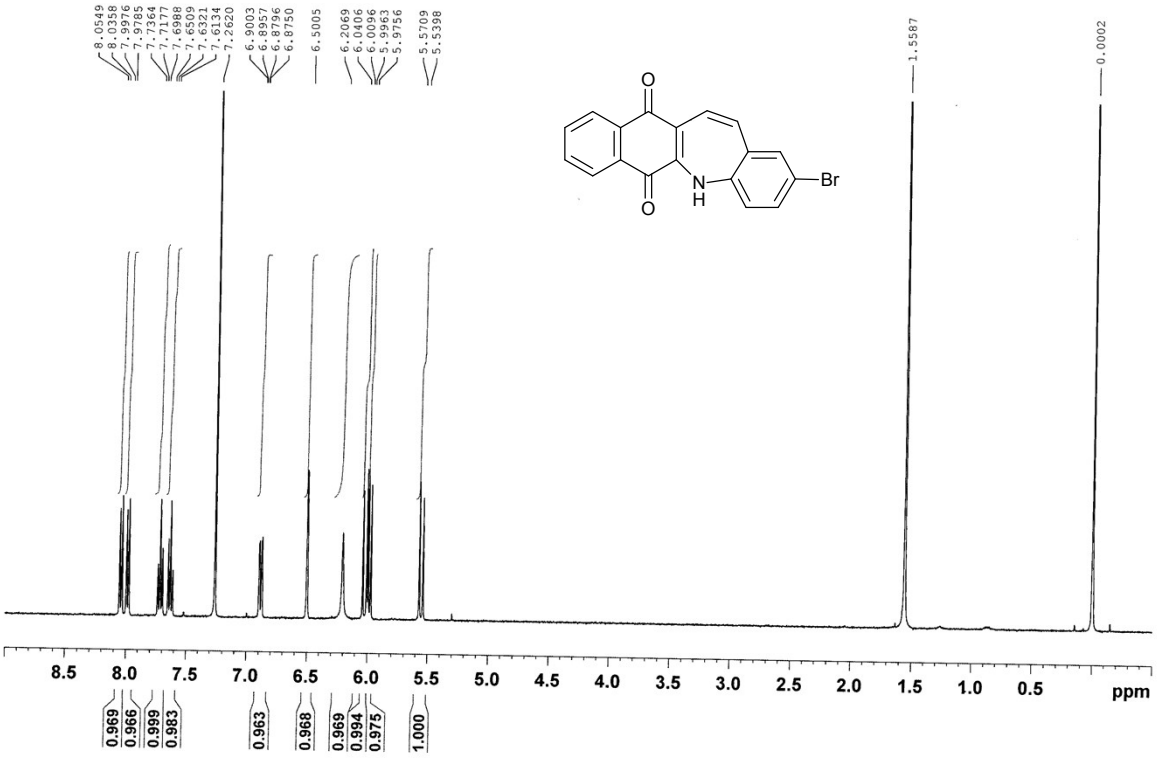



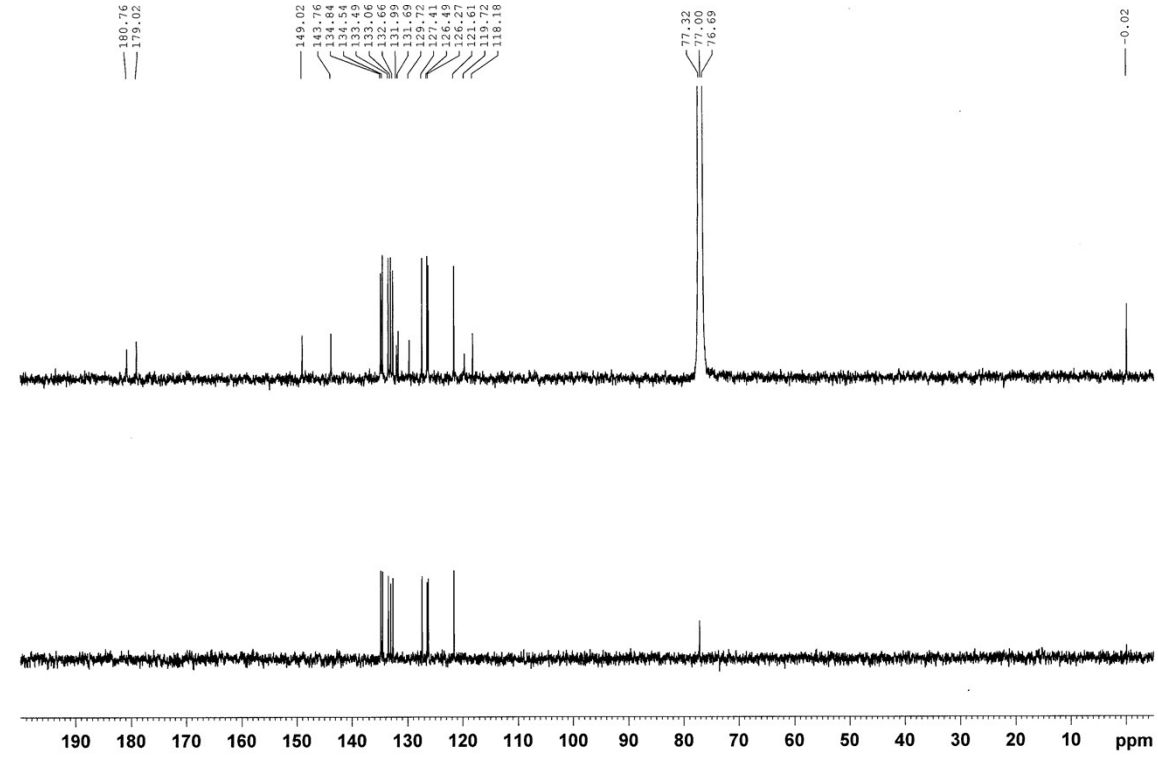
$^{1}H$ and $^{13}C$ NMR spectra of **11Af**



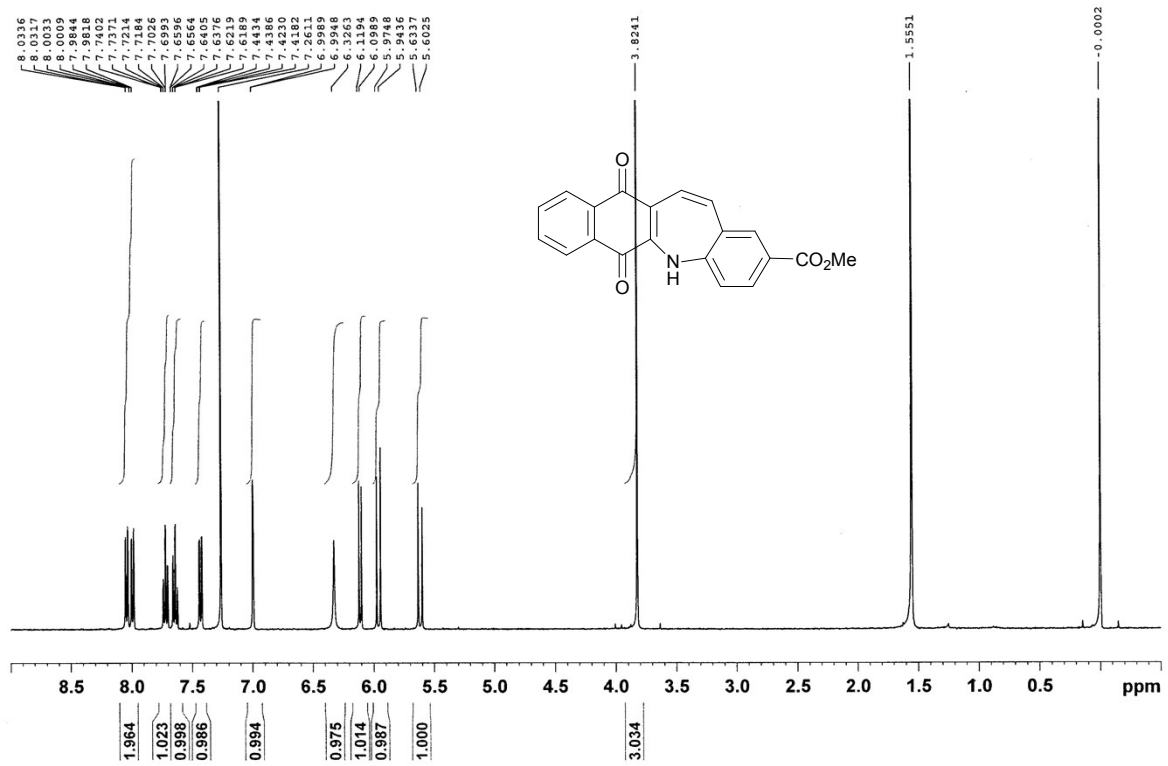



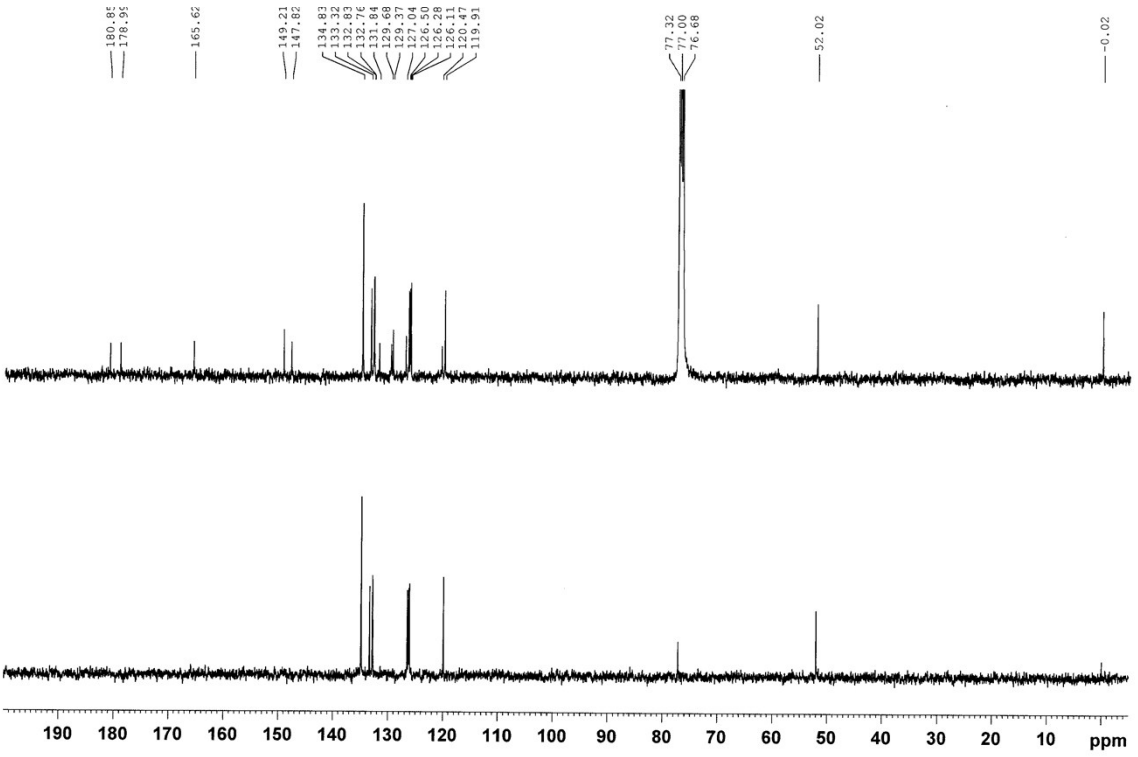
$^{1}H$ and $^{13}C$ NMR spectra of **11Ag**



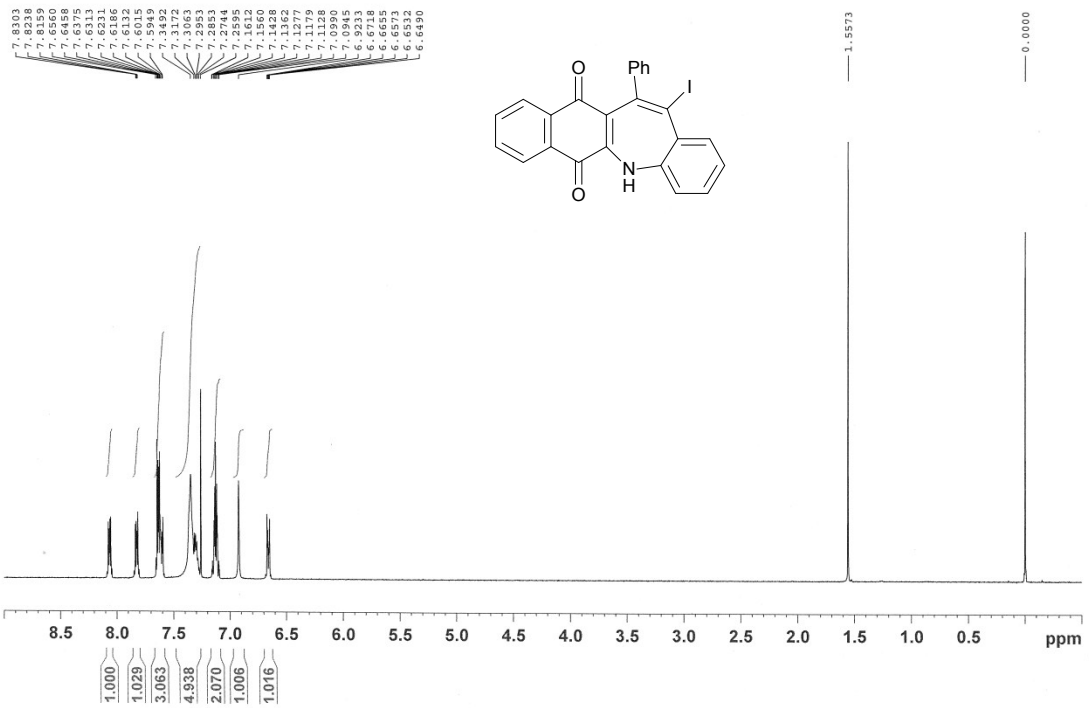



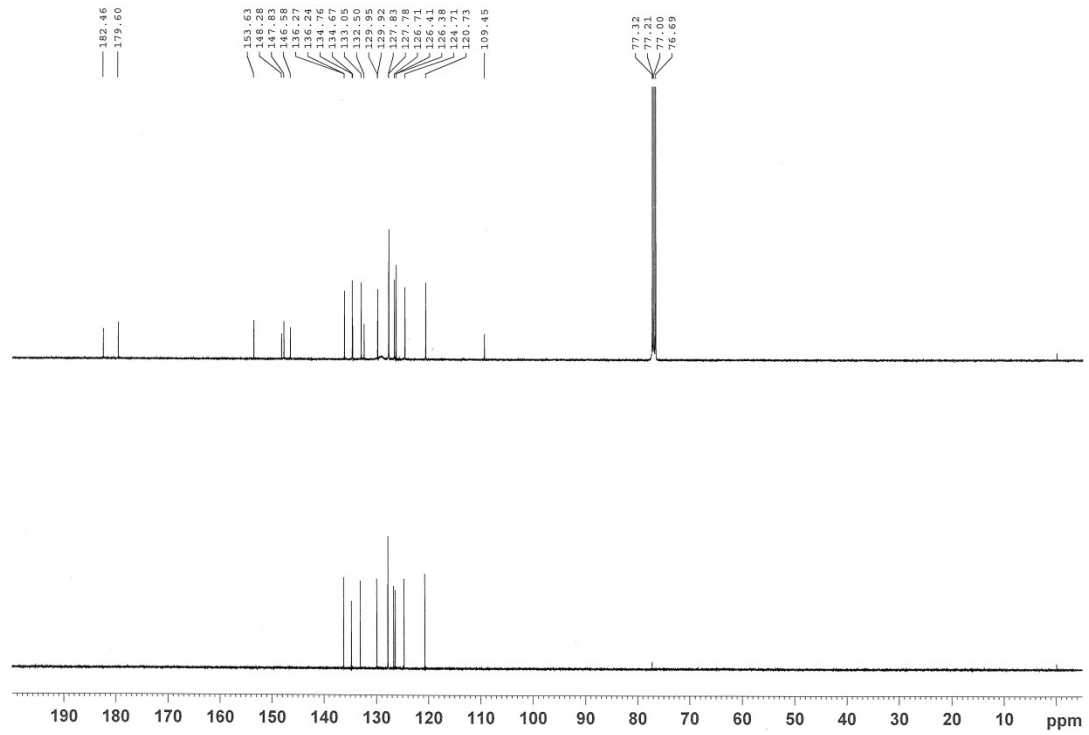
$^{1}H$ and $^{13}C$ NMR spectra of **11Ah**



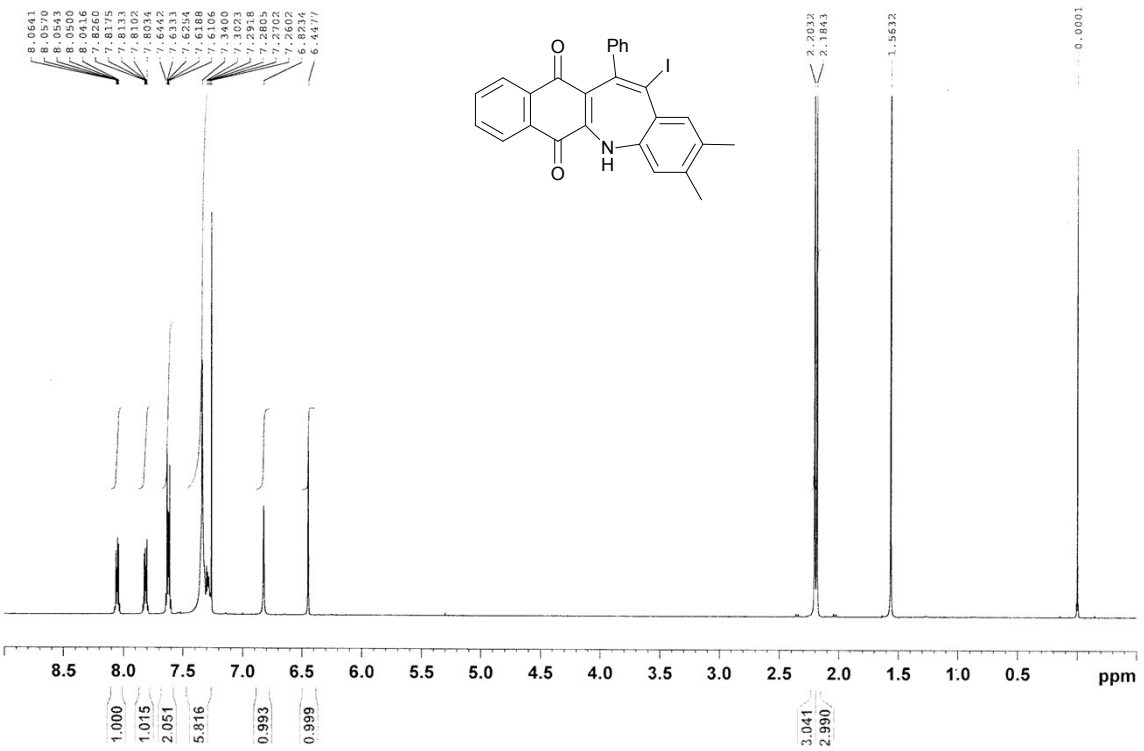



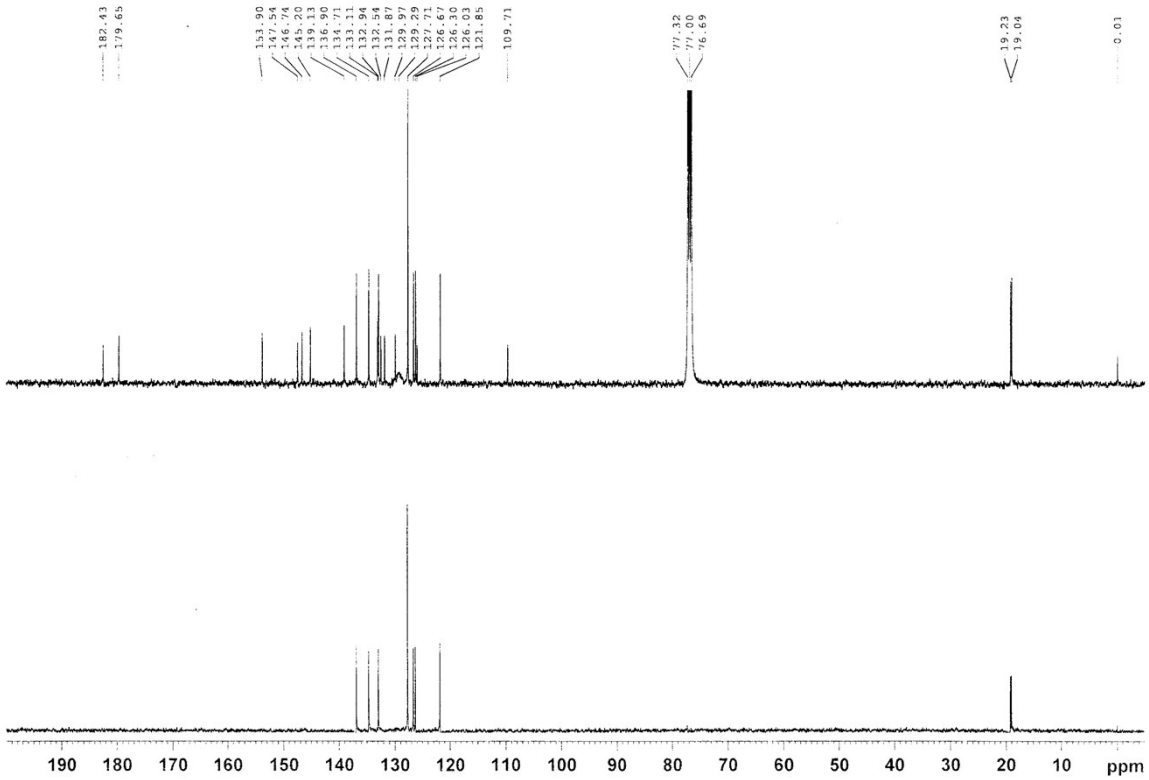
$^{1}H$ and $^{13}C$ NMR spectra of **13Ba**



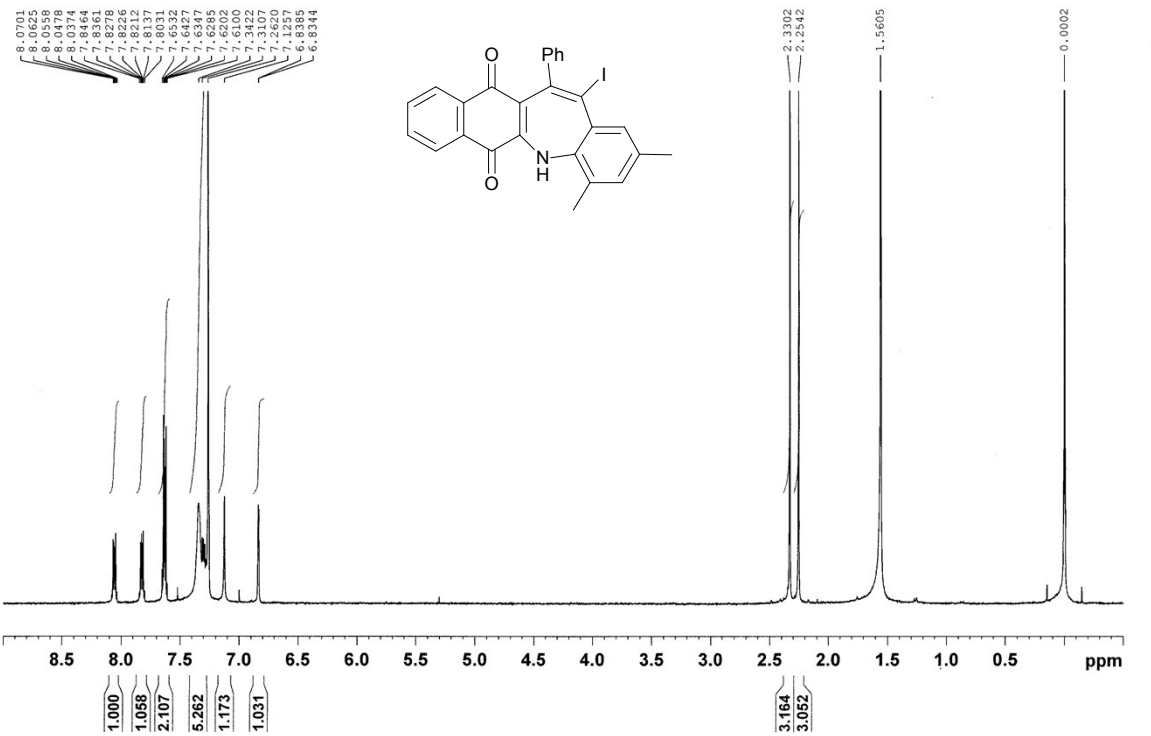



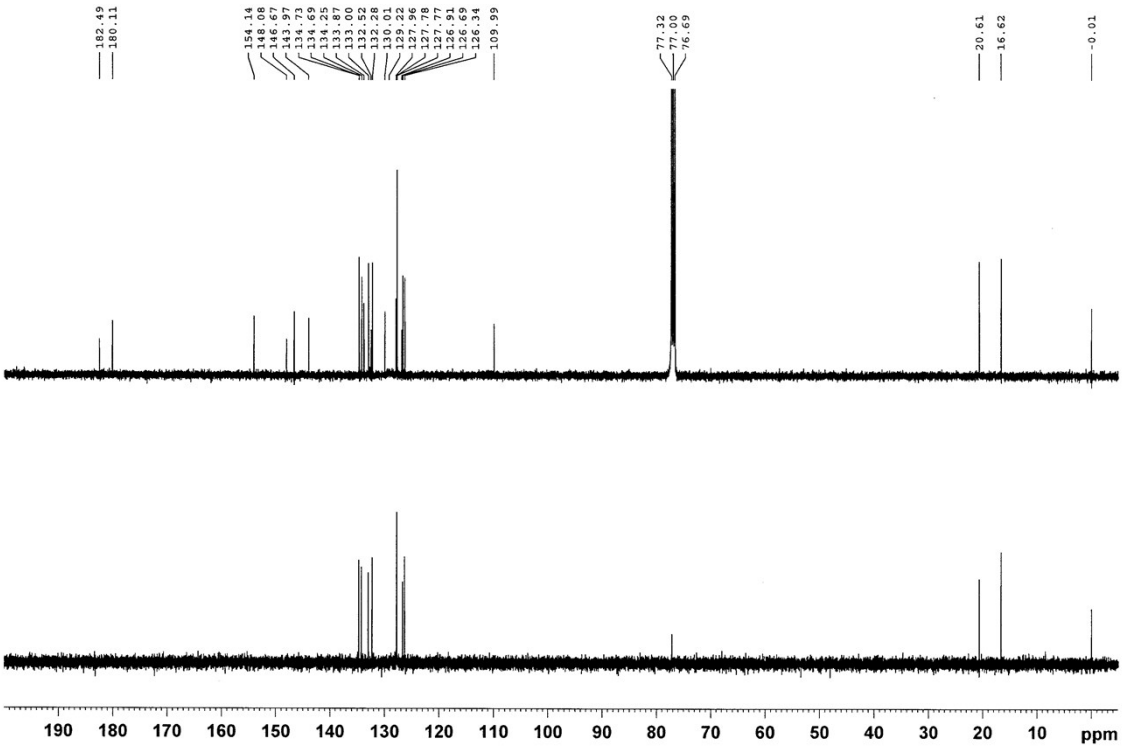
$^{1}H$ and $^{13}C$ NMR spectra of **13Bb**



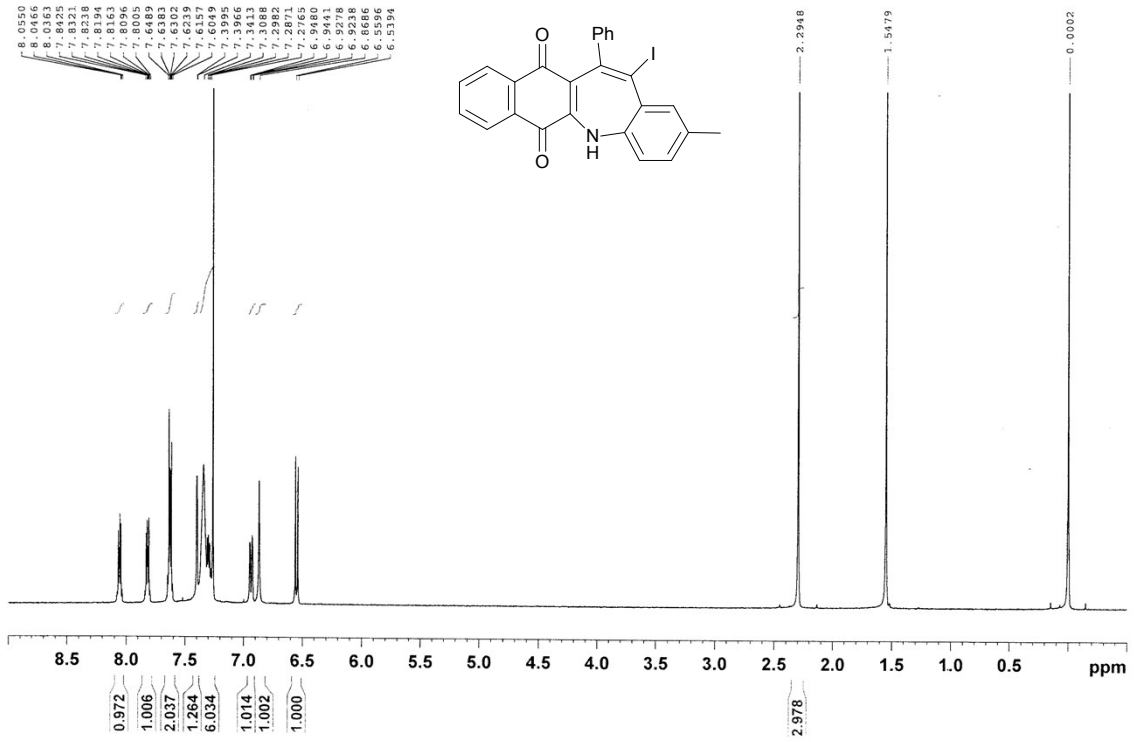



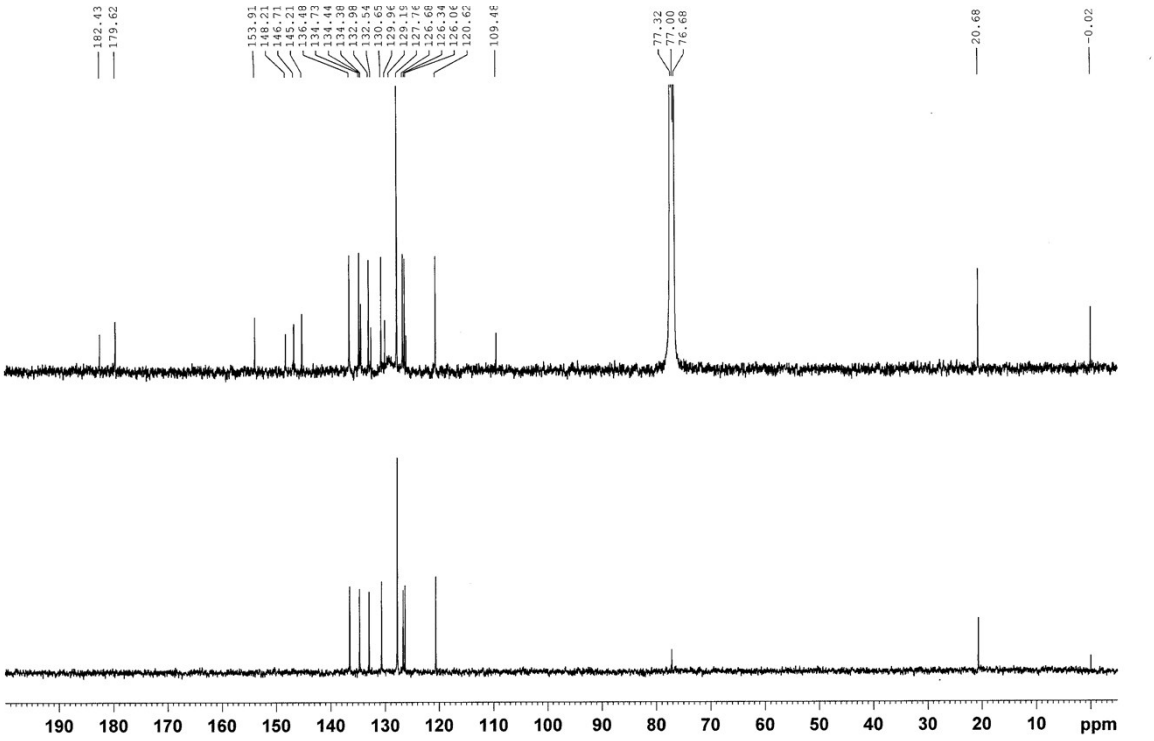
$^{1}H$ and $^{13}C$ NMR spectra of **13Bc**



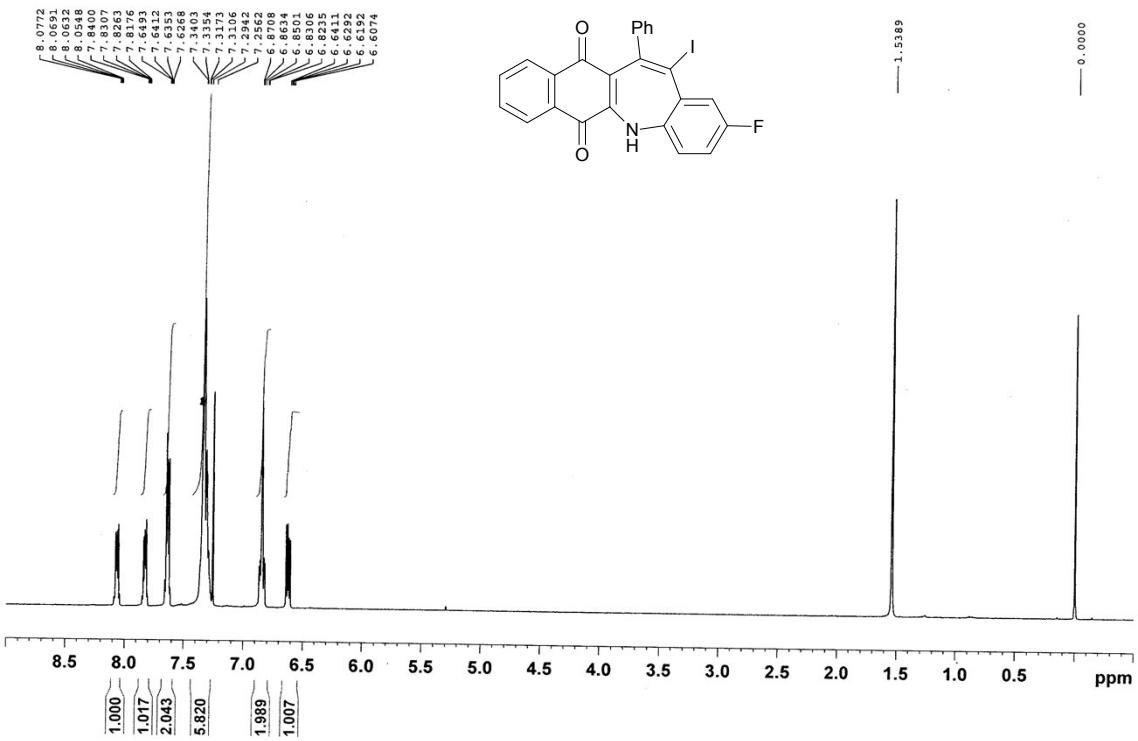



$^{1}H$ and $^{13}C$ NMR spectra of **13Bd**

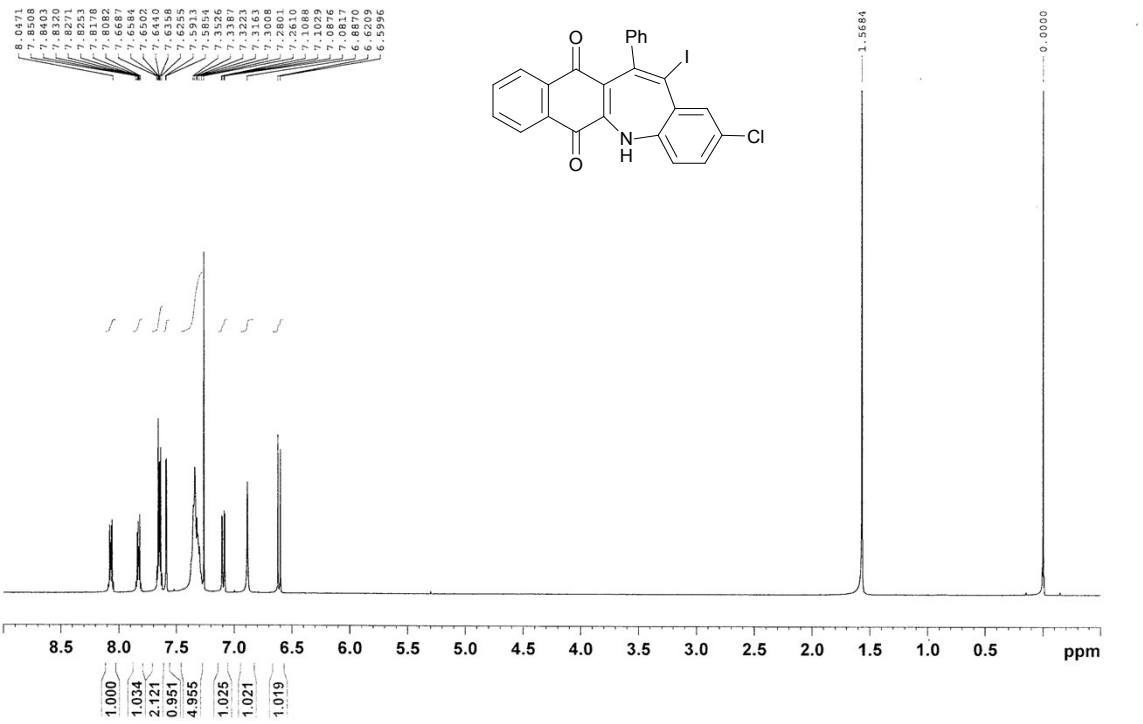


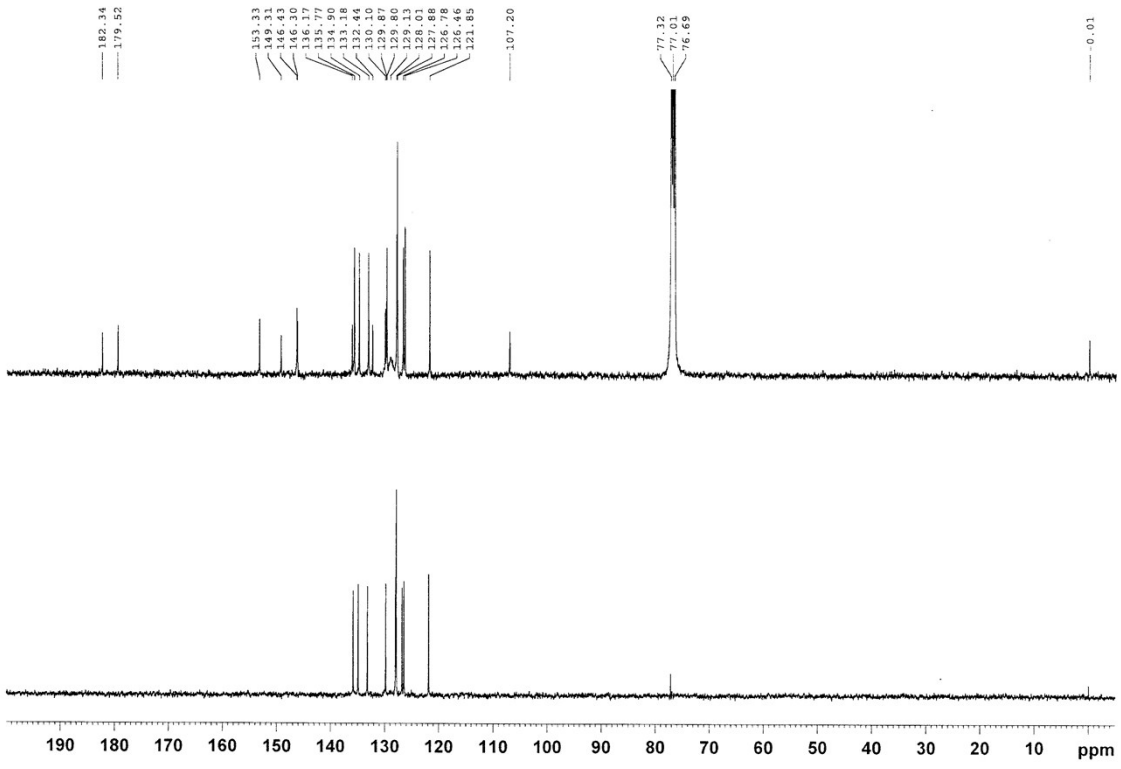



$^{1}H$ and $^{13}C$ NMR spectra of **13Be**

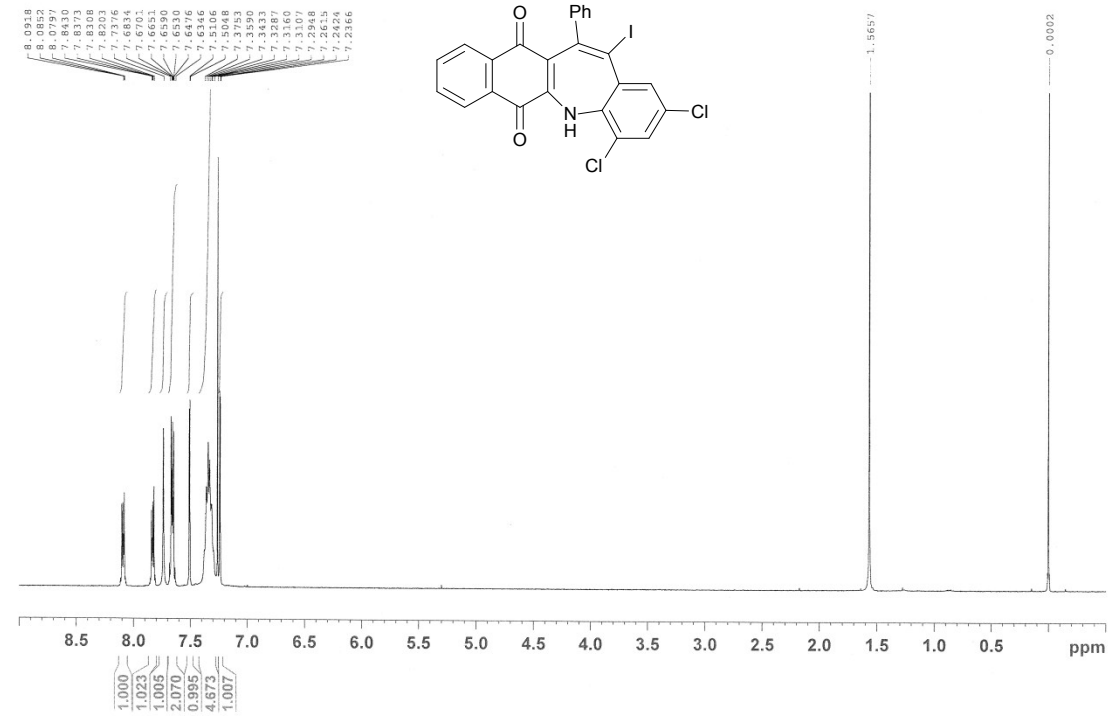


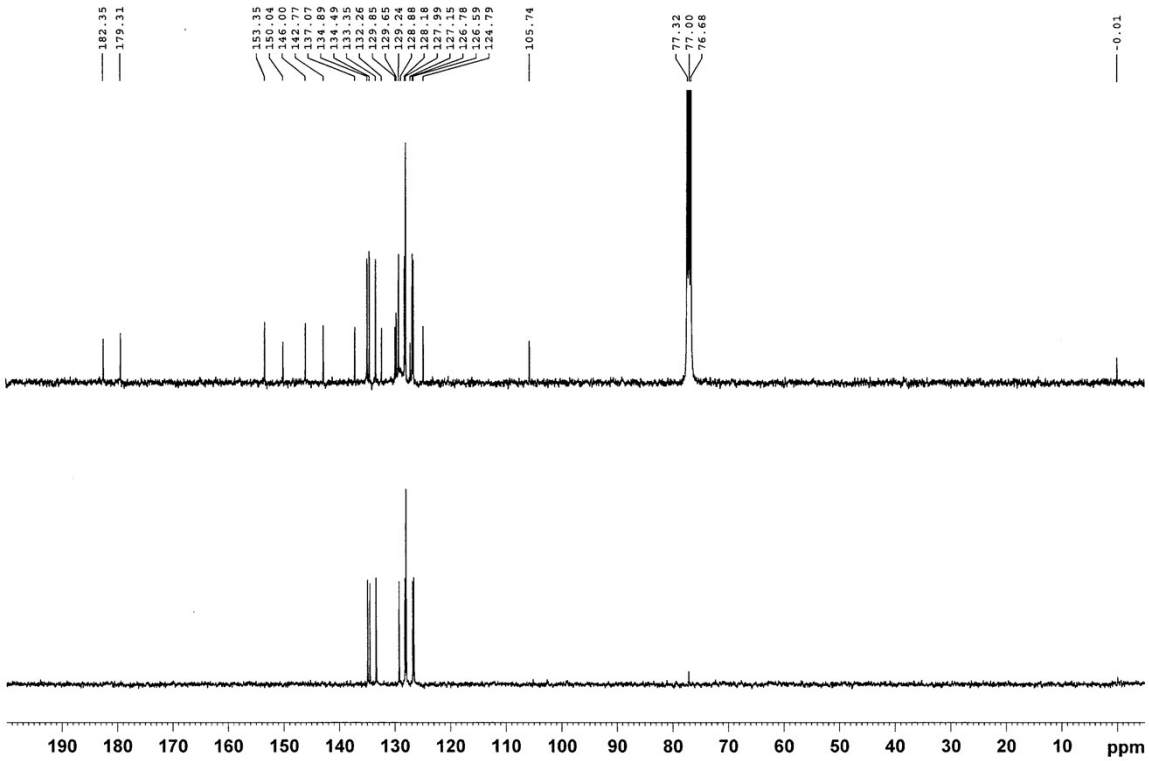
$^{1}H$ and $^{13}C$ NMR spectra of **13Bf**



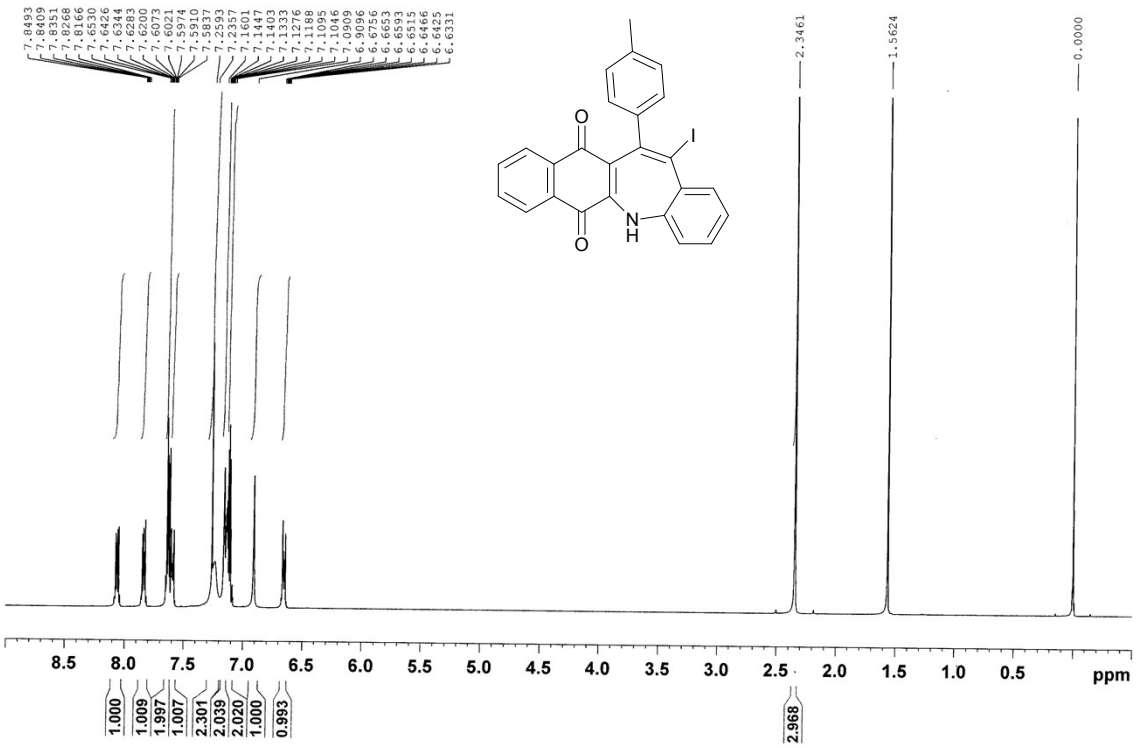



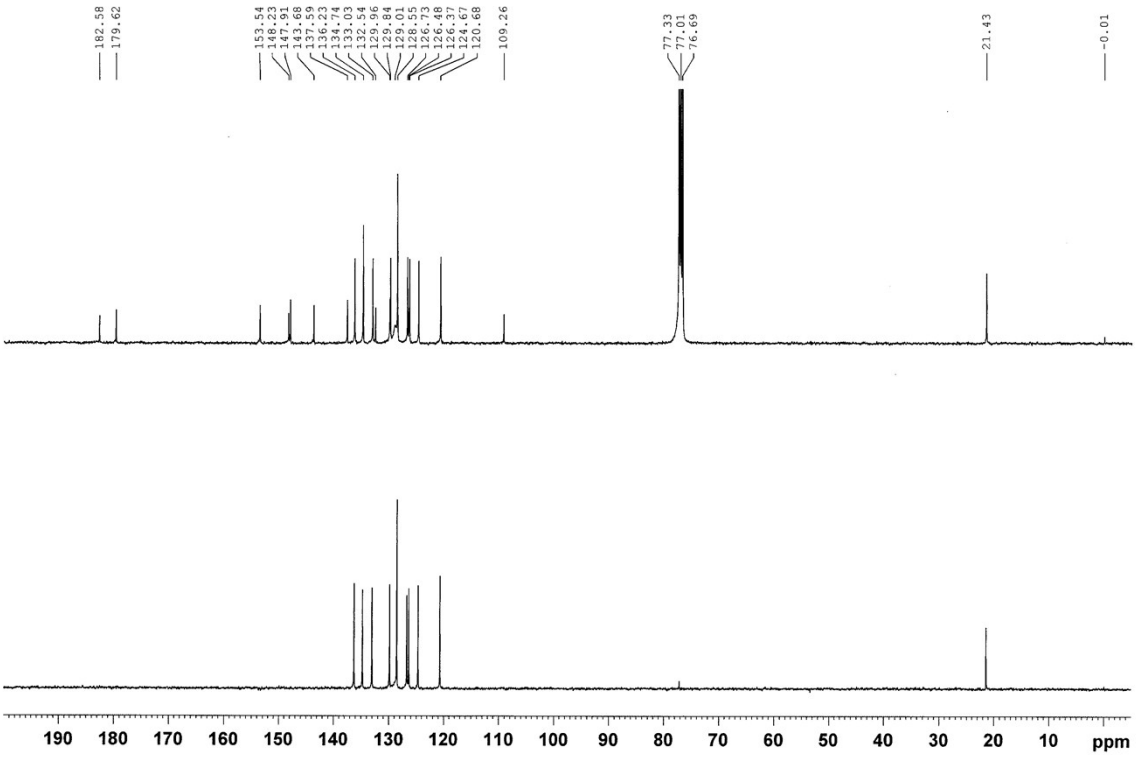
$^{1}H$ and $^{13}C$ NMR spectra of **13Bi**



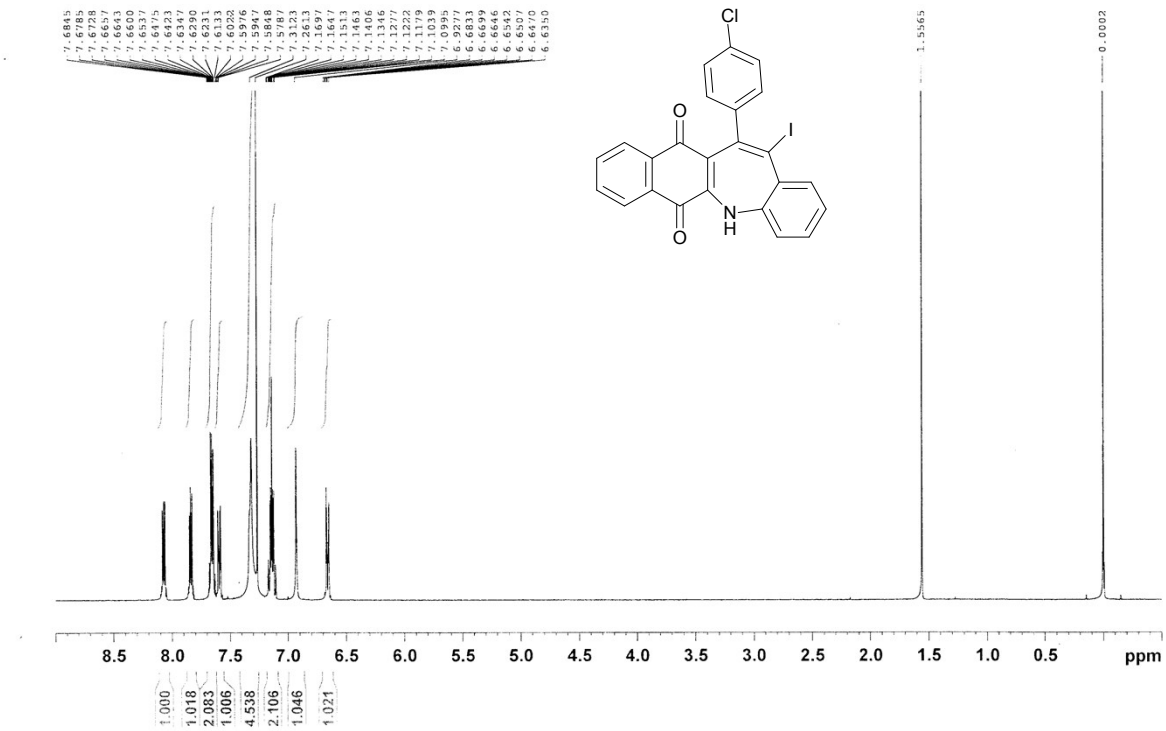



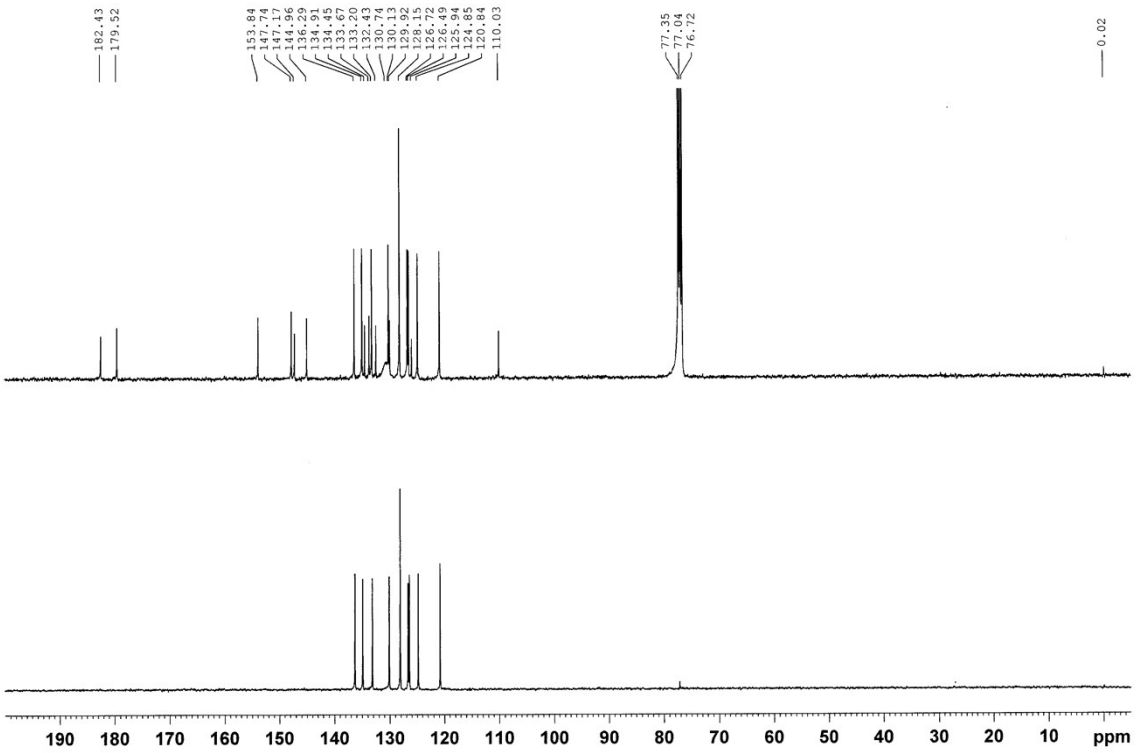
$^{1}H$ and $^{13}C$ NMR spectra of **13Bj**



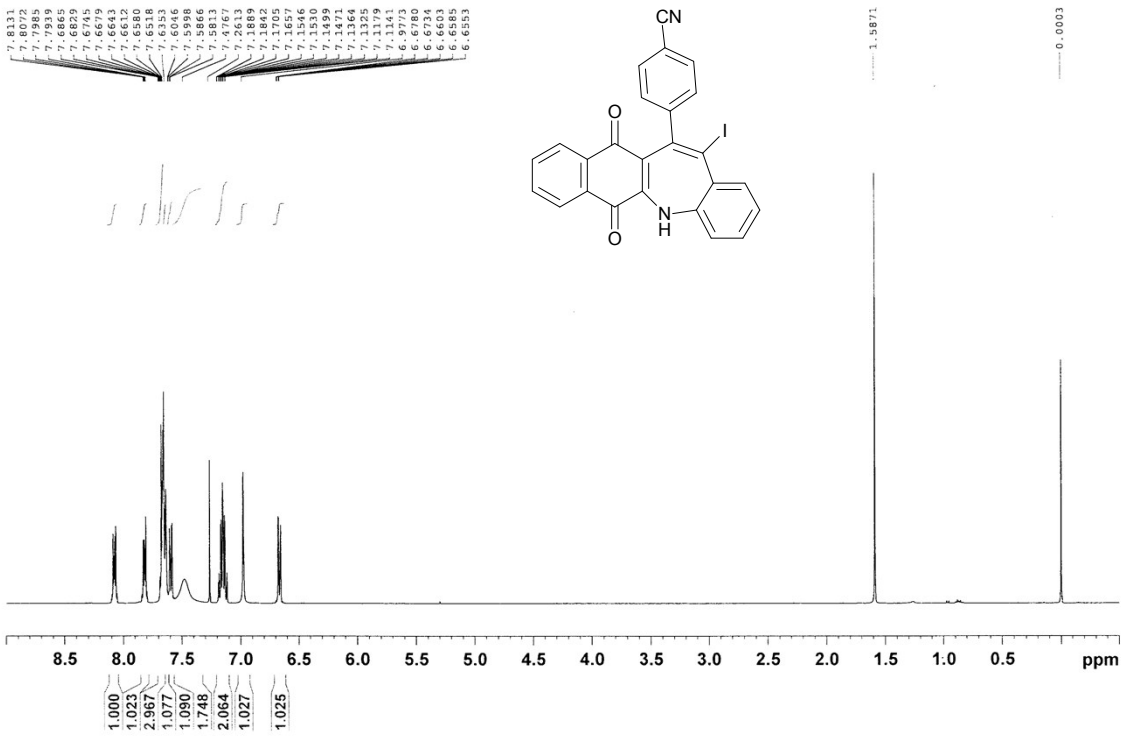



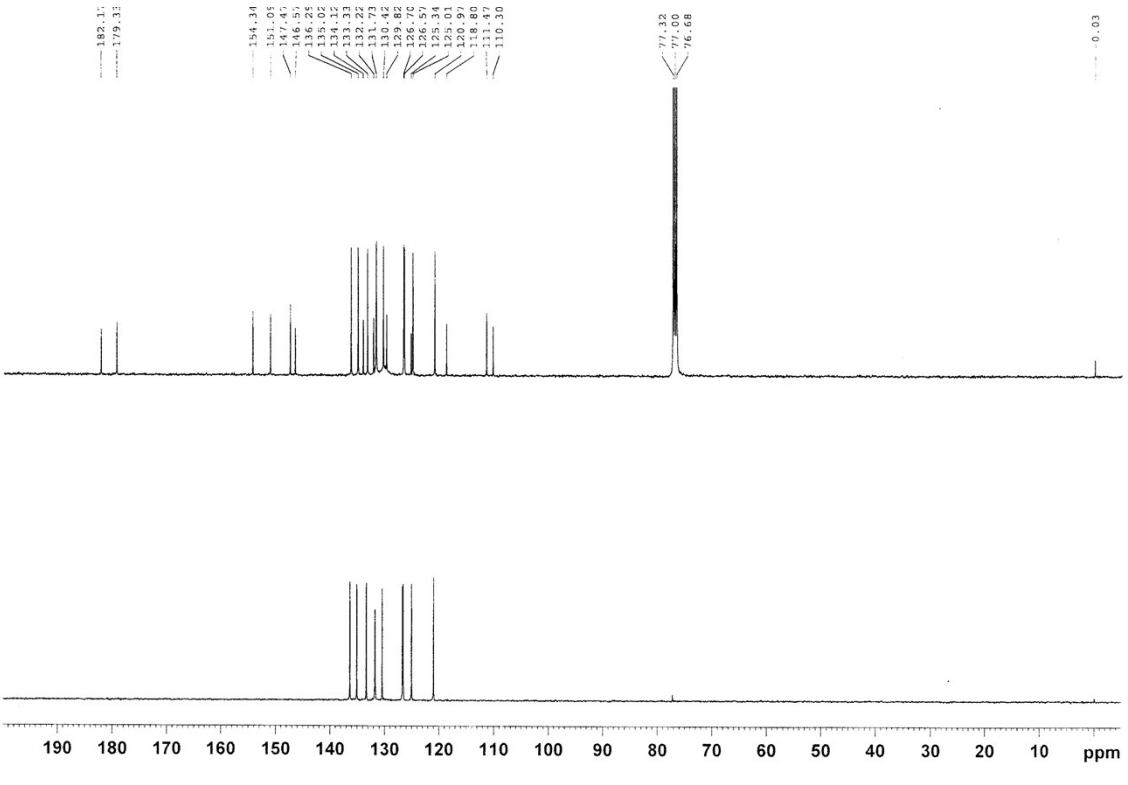
$^{1}H$ and $^{13}C$ NMR spectra of **13Bk**



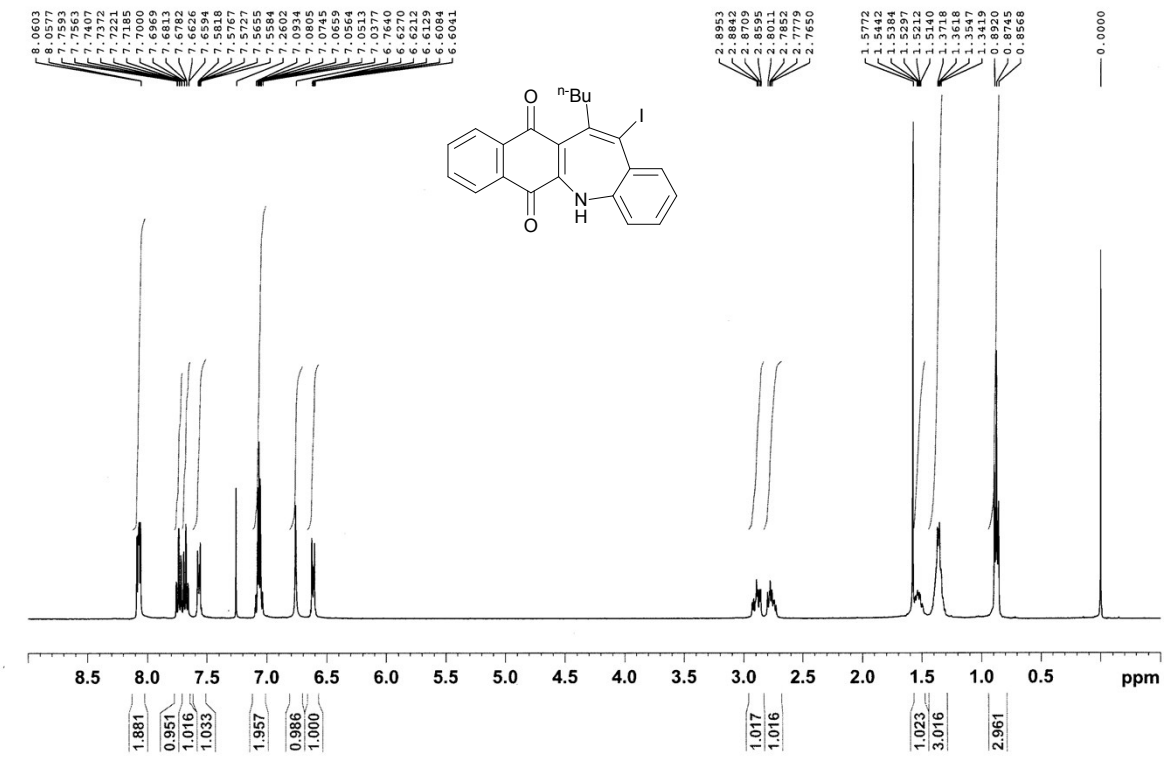



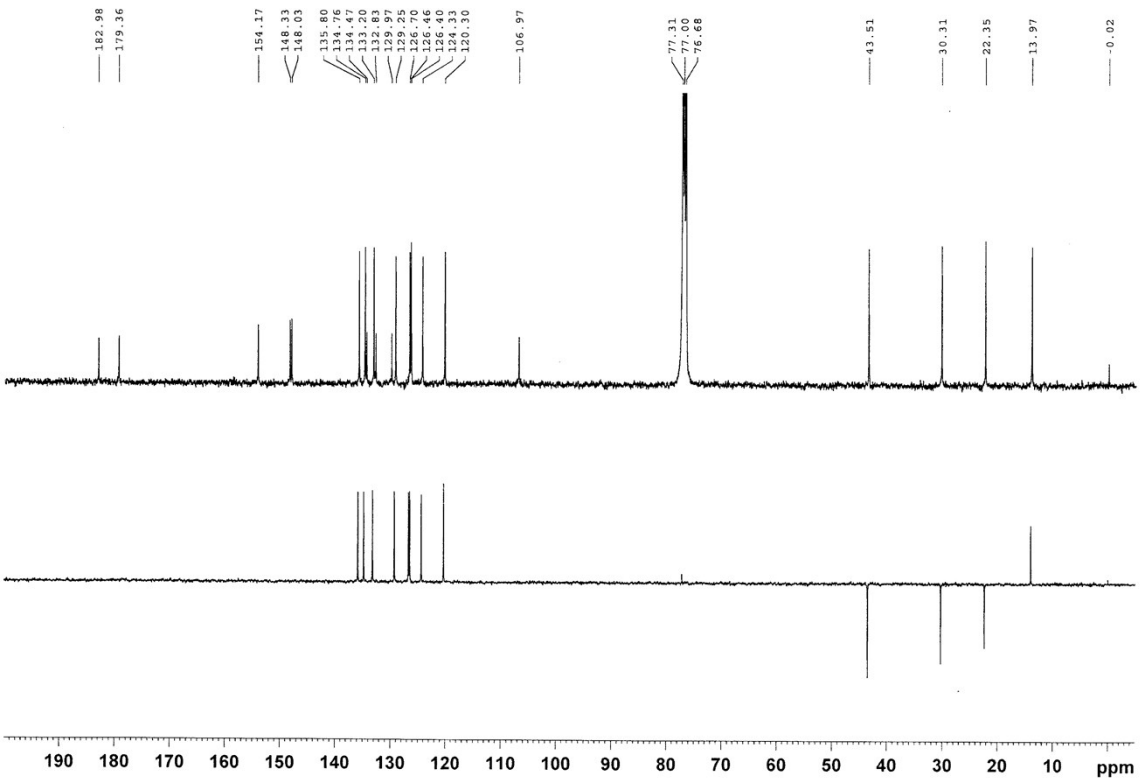
$^{1}H$ and $^{13}C$ NMR spectra of **13Bl**



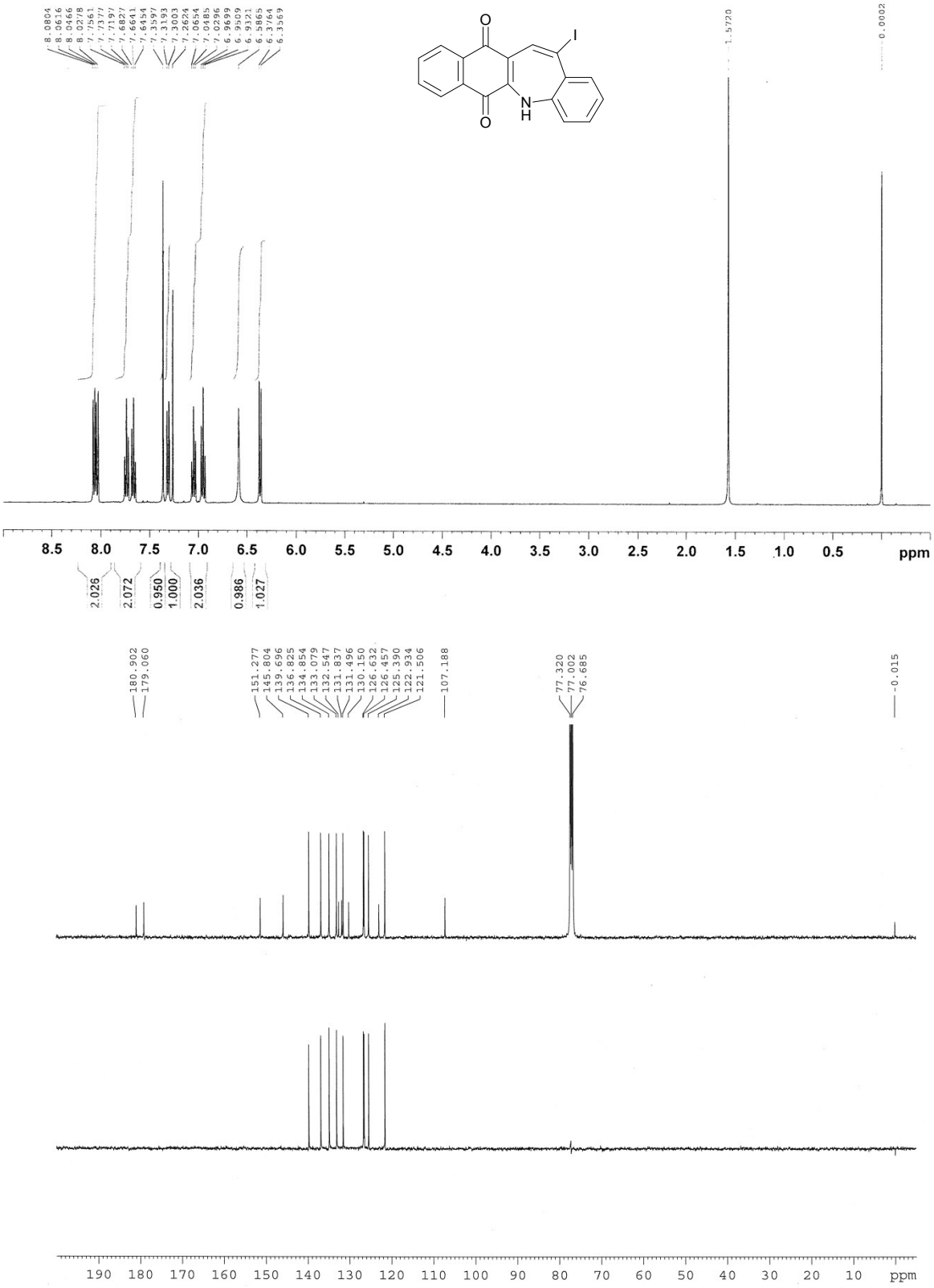



$^{1}H$ and $^{13}C$ NMR spectra of **13Bm**

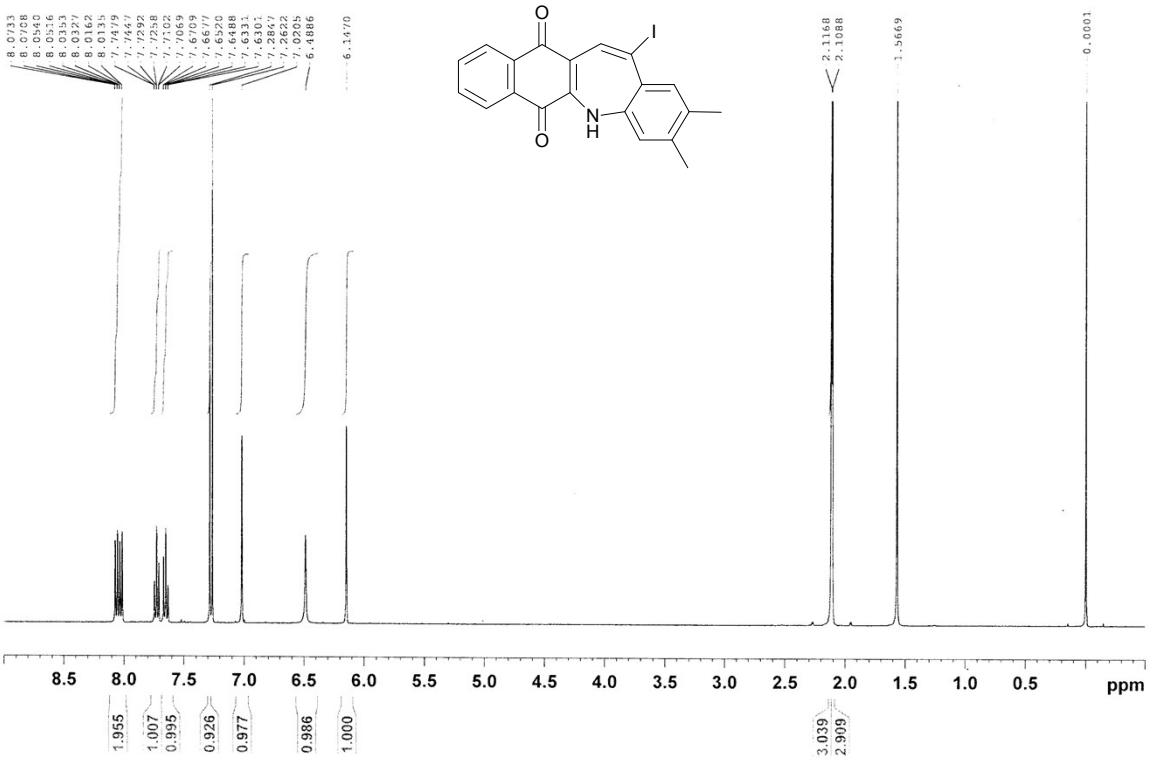


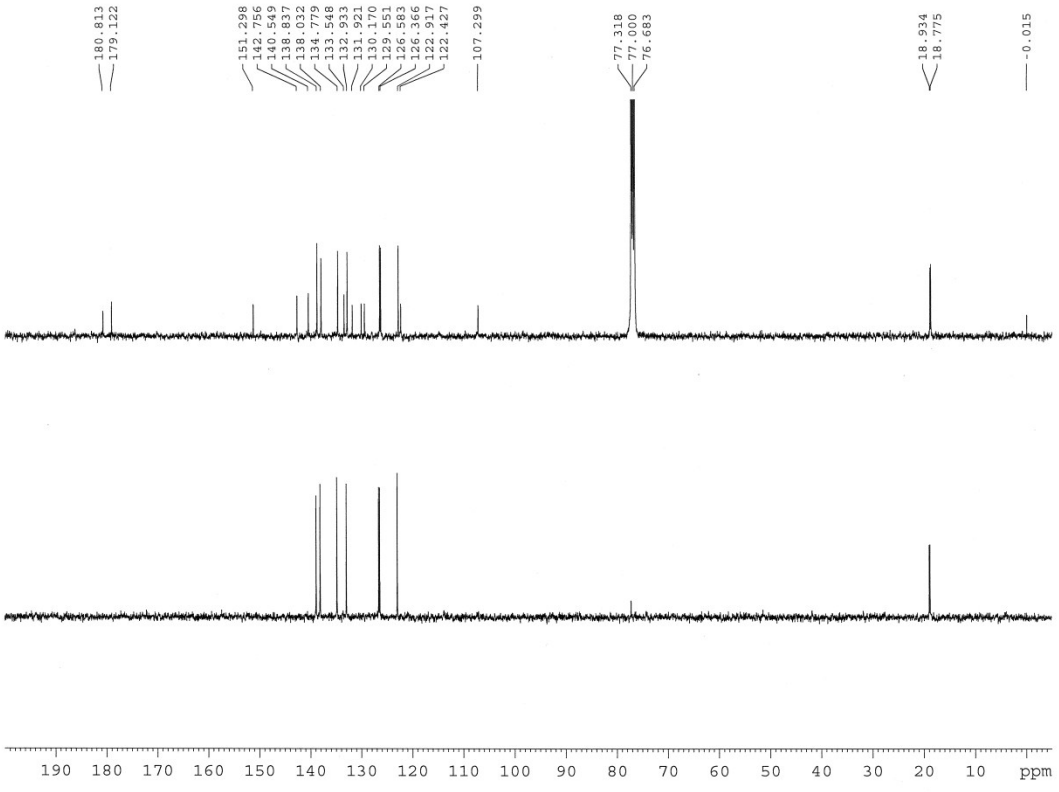



$^{1}H$ and $^{13}C$ NMR spectra of **13Aa**

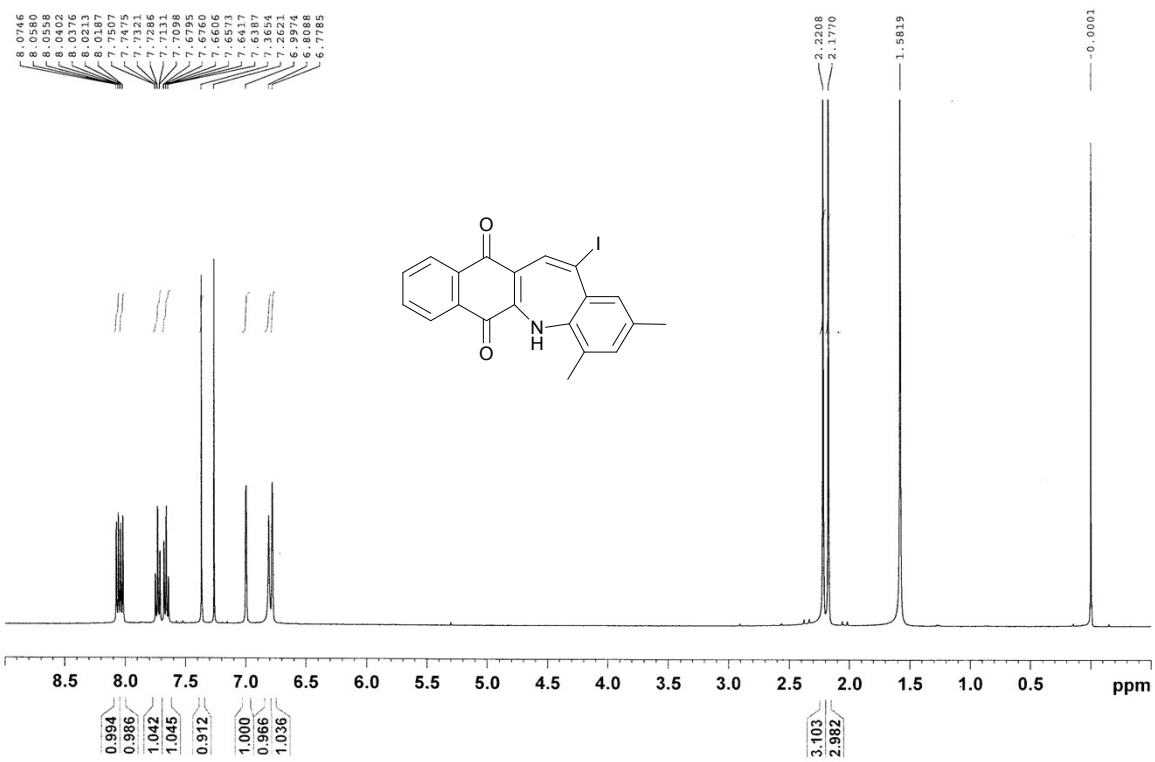


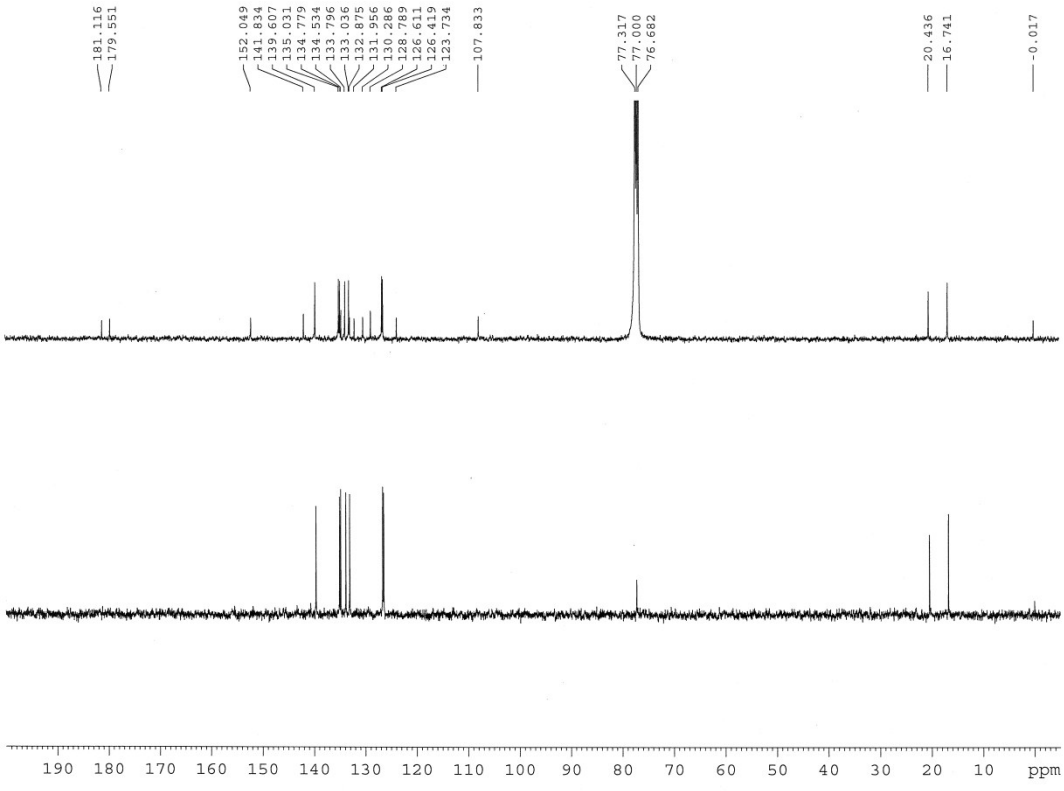
$^{1}H$ and $^{13}C$ NMR spectra of **13Ab**



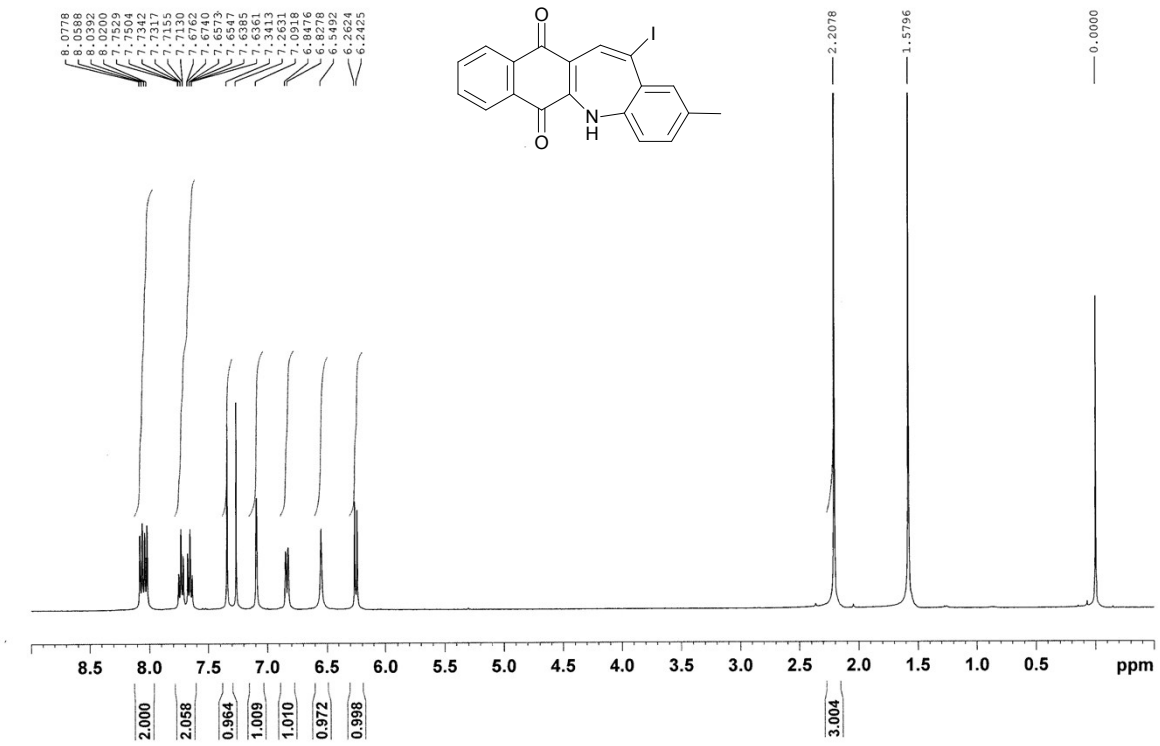



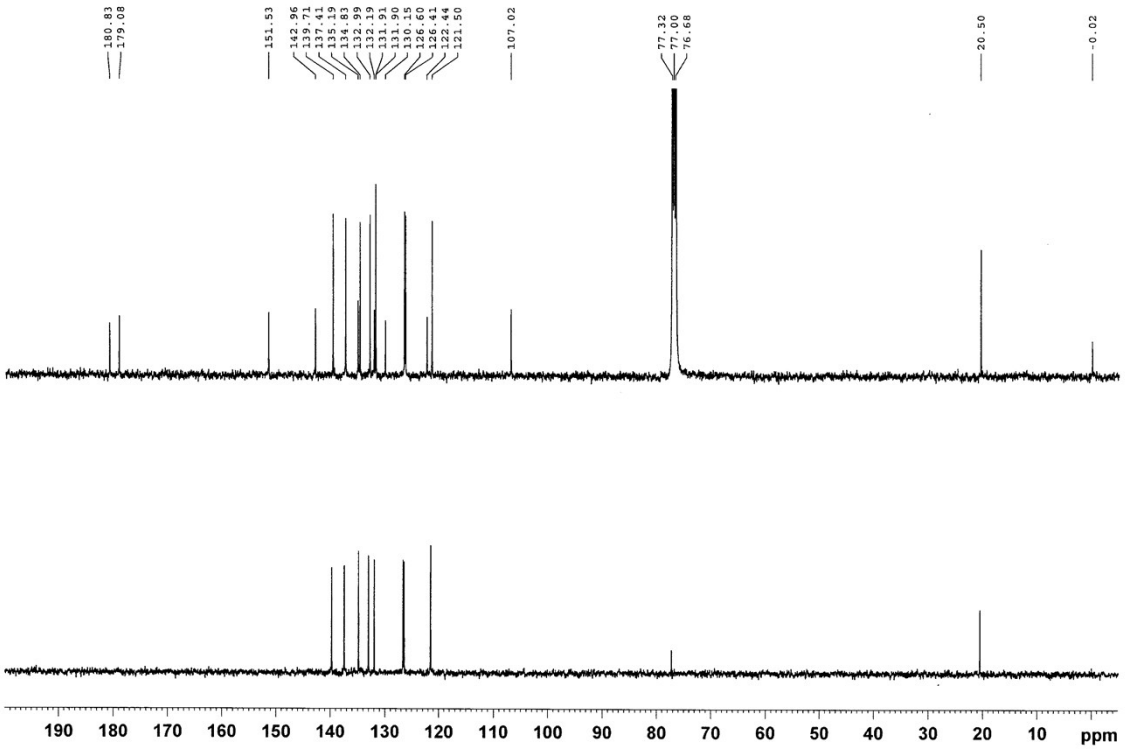
$^{1}H$ and $^{13}C$ NMR spectra of **13Ac**



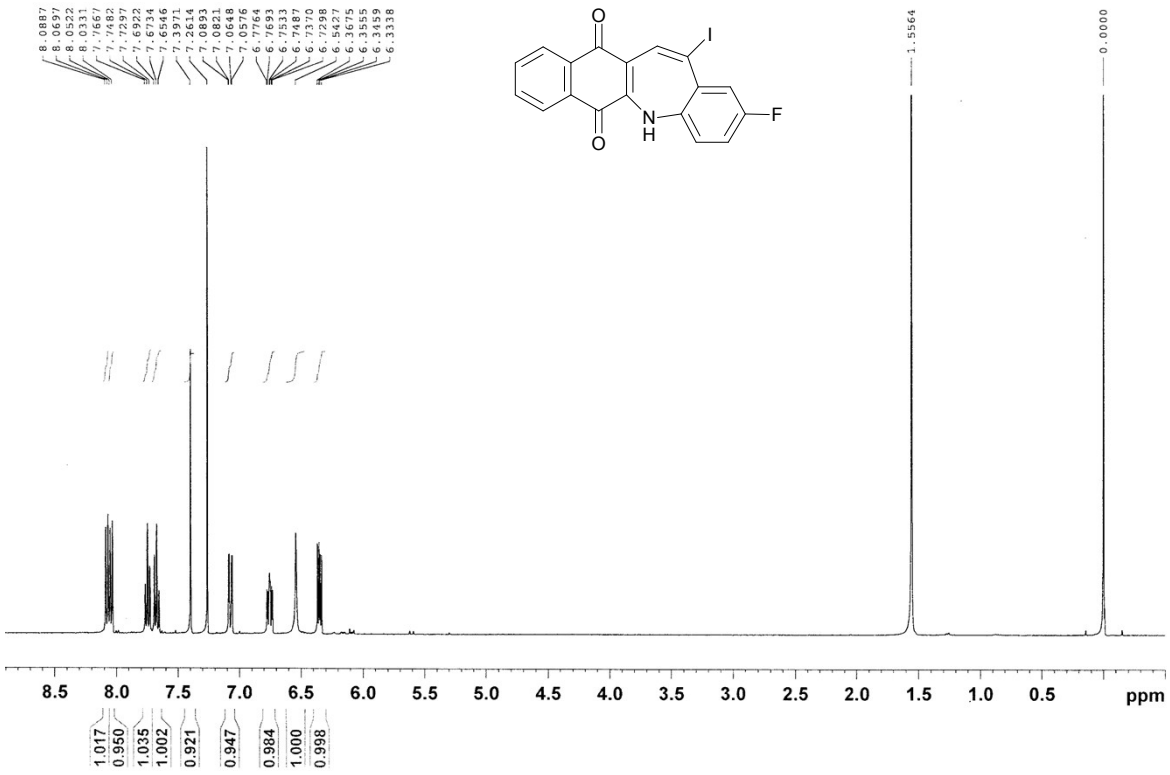



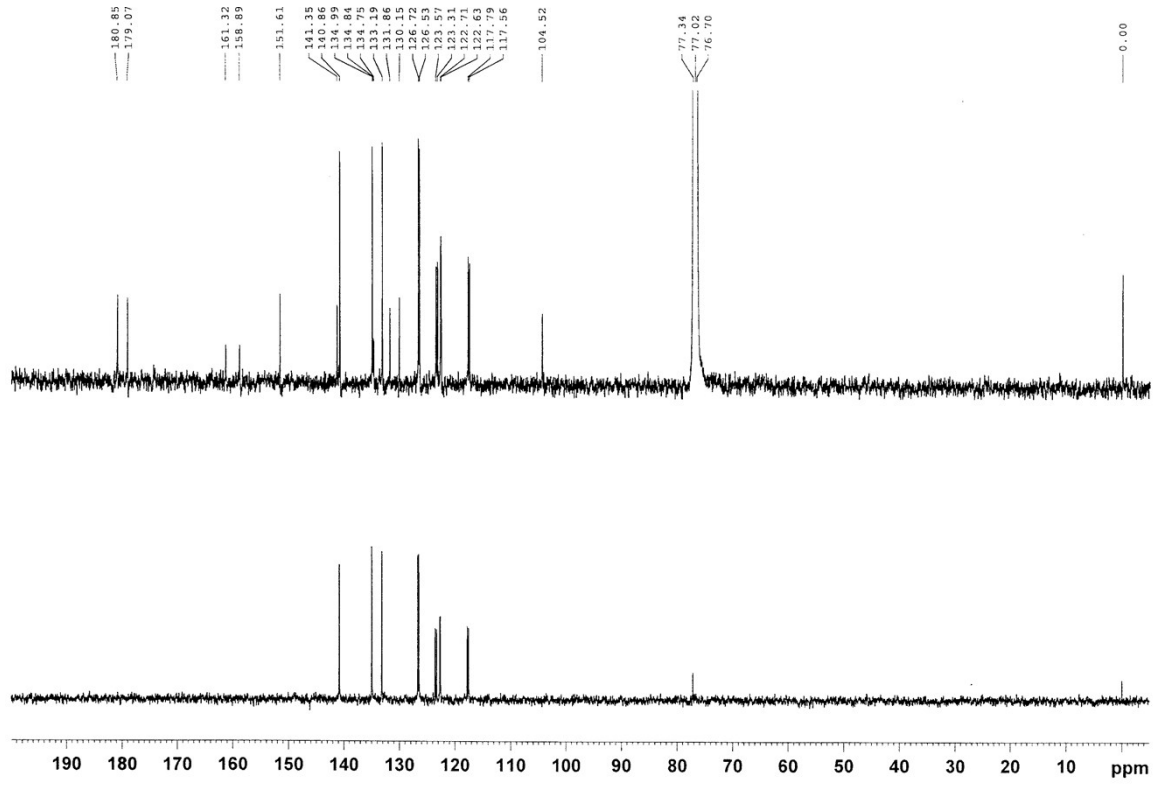
$^{1}H$ and $^{13}C$ NMR spectra of **13Ad**



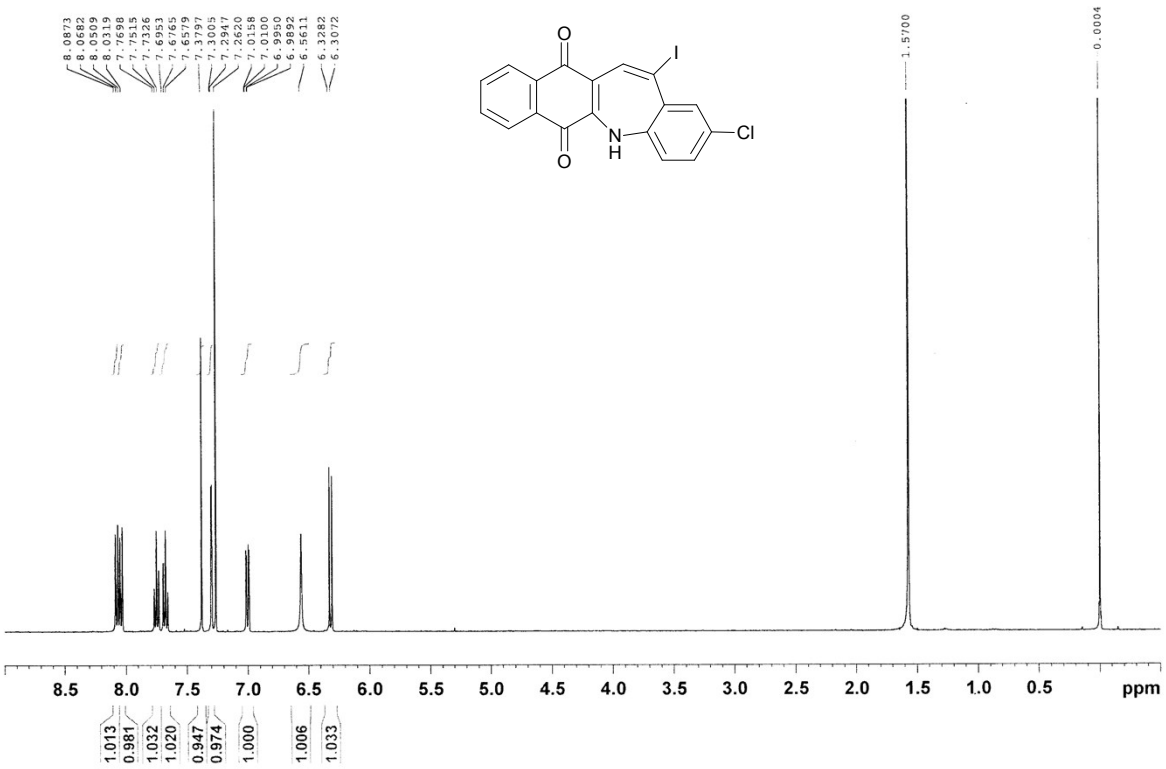



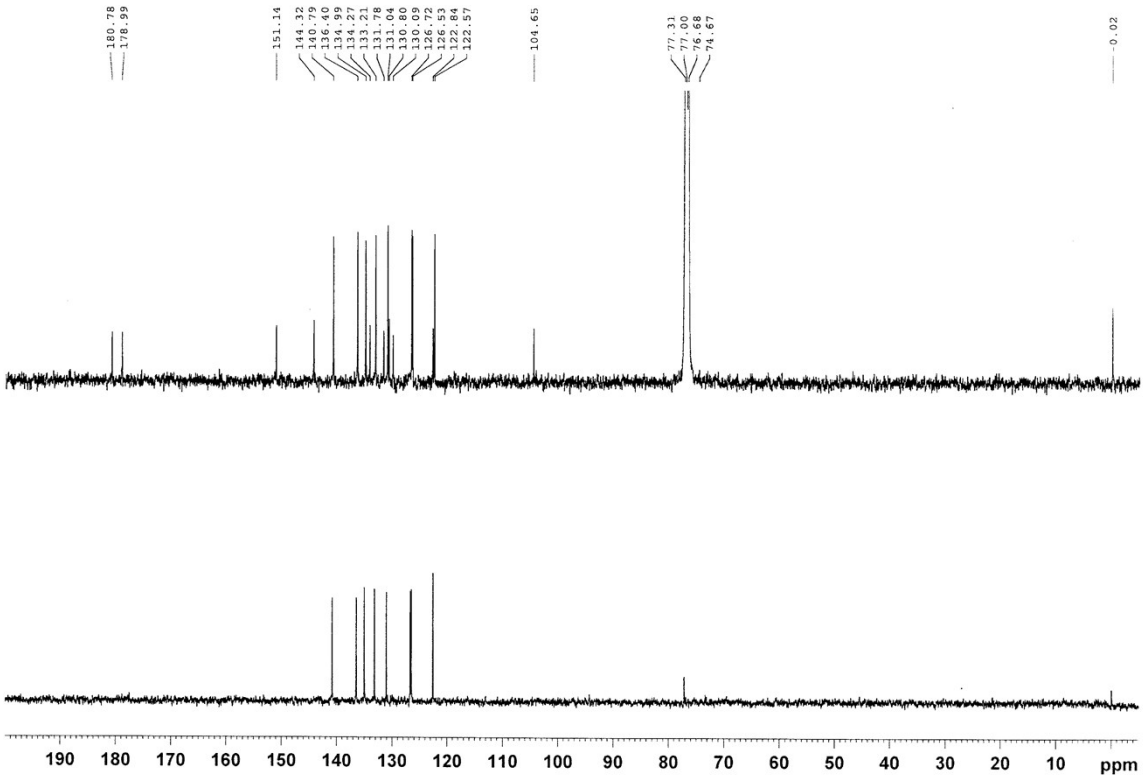
$^{1}H$ and $^{13}C$ NMR spectra of **13Ae**



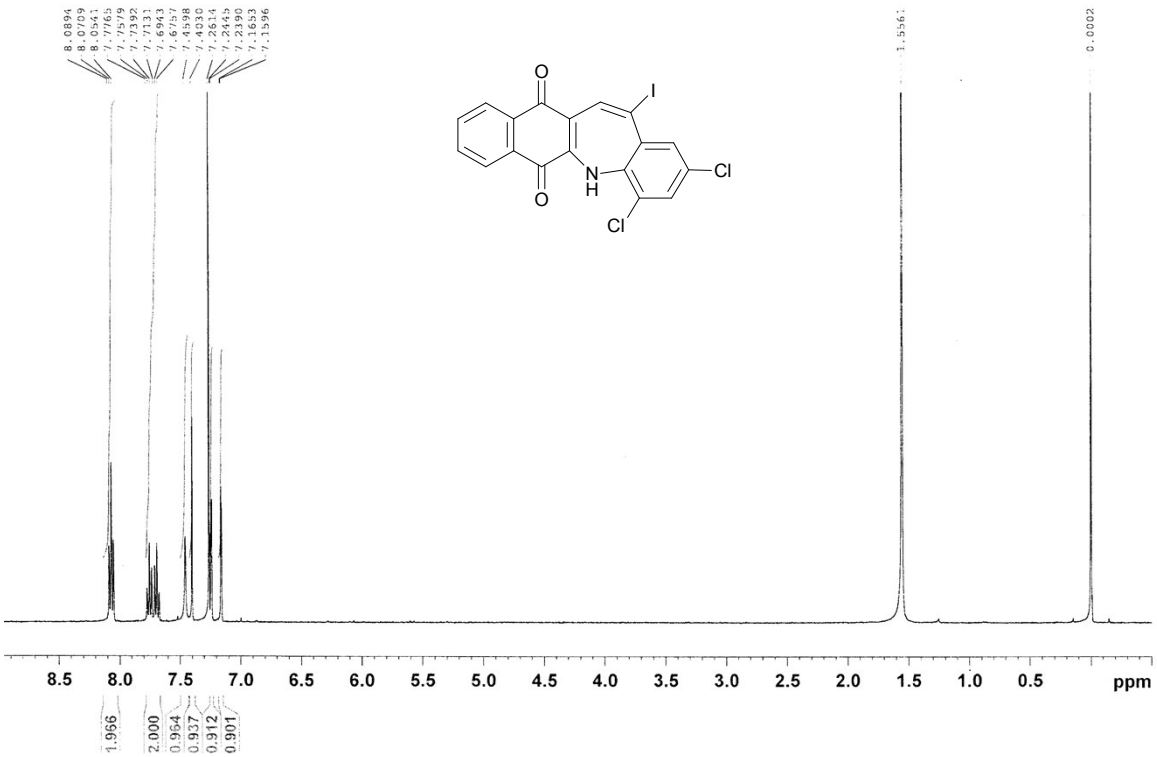



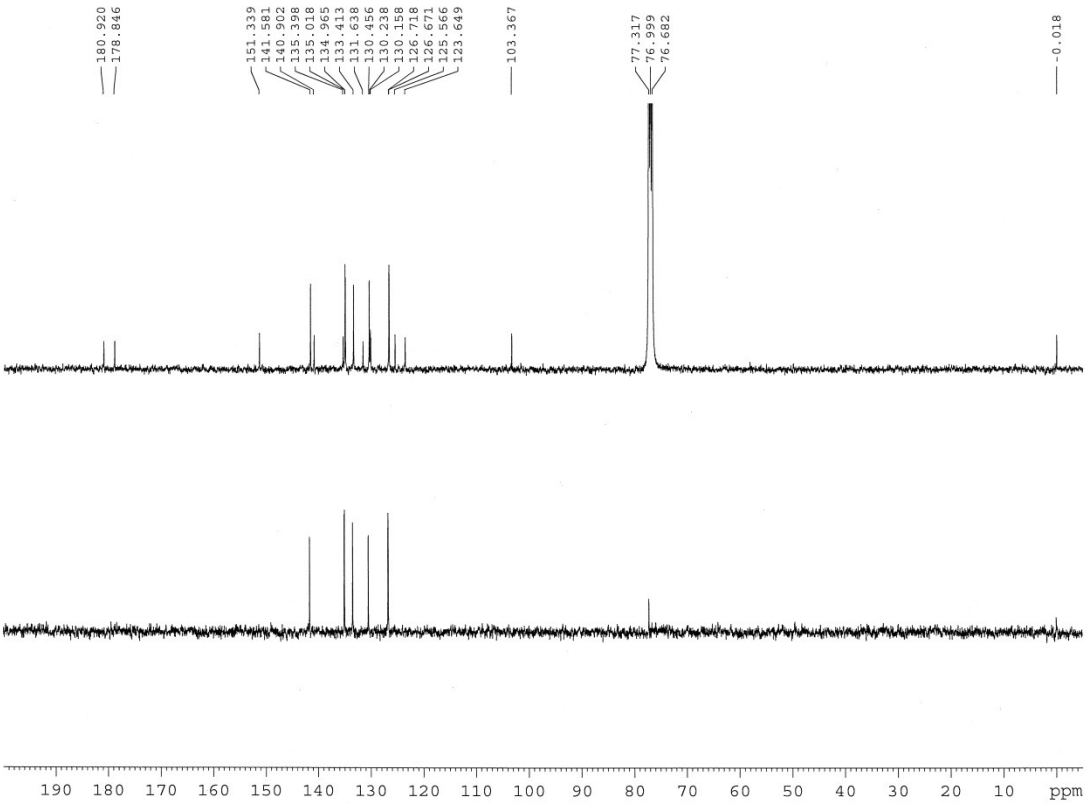
$^{1}H$ and $^{13}C$ NMR spectra of **13Af**



$^{1}H$ and $^{13}C$ NMR spectra of **13Ai**



$^{1}H$ and $^{13}C$ NMR spectra of **13Ah**