

## Supporting Information

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### Aqueous CO<sub>2</sub> Fixation: Construction of Pyridine Skeletons in Cooperation of Ammonium Cation

Shiqun Xiang,<sup>‡a,b</sup> Weibin Fan,<sup>‡a,b</sup> Wei Zhang,<sup>a</sup> Yinghua Li,<sup>a</sup> Shiwei Guo,<sup>a</sup> Deguang Huang<sup>\*a</sup>

*a. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,*

*Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

*b. University of Chinese Academy of Sciences, Beijing 100049, China.*

*‡ These authors contributed equally to this work.*

*\*To whom correspondence should be addressed. E-mail: [dhuang@fjirsm.ac.cn](mailto:dhuang@fjirsm.ac.cn)*

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## 1. General information

**Chemicals.** Unless otherwise noted, all reactions were set up using standard Schlenk techniques and carried out under carbon dioxide atmosphere. Potassium *tert*-butoxide (*t*BuOK) and monoethanolamine (MEA) were purchased from Energy Chemical. Commercially available chemicals were obtained from Energy Chemical, Innochem, Ark and SCRC (Sinopharm Chemical Reagent Co., Ltd) and used as received unless otherwise stated. Pyridines was distilled before used, acetonitrile was dried over CaH<sub>2</sub> and 1,4-dioxane was dried over sodium. All the solvent were stored in the presence of activated molecular sieve. Reactions were monitored by thin-layer chromatography (TLC) or HPLC. TLC was performed using commercially percolated silica gel plates (GF254, 100-400 mesh), and visualized by UV light 360/254 nm or iodine in silica gel. Flash column chromatography was performed on silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd

**General Physical Measurements.** The single crystal data of compounds were collected by a Cu-K $\alpha$  rotating anode source at 150 K, using a Supernova diffractometer with the  $\omega$ -scan method. ESI-MS were obtained using a Bruker Impact II quadrupole time-of-flight mass spectrometer. UV-Vis spectra are recorded with a Lambda365 (190-1100 nm) ultraviolet spectrophotometer. Fluorescence spectra are recorded with a FLS1000 Spectrometer. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on Bruker Avance III (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz) and chemical shifts are expressed in  $\delta$  ppm values with reference to tetramethylsilane (TMS) as internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Coupling constants (J) are expressed in Hz.

## 2. Crystallographic data of compounds 2g, 2k, 2m and 2v

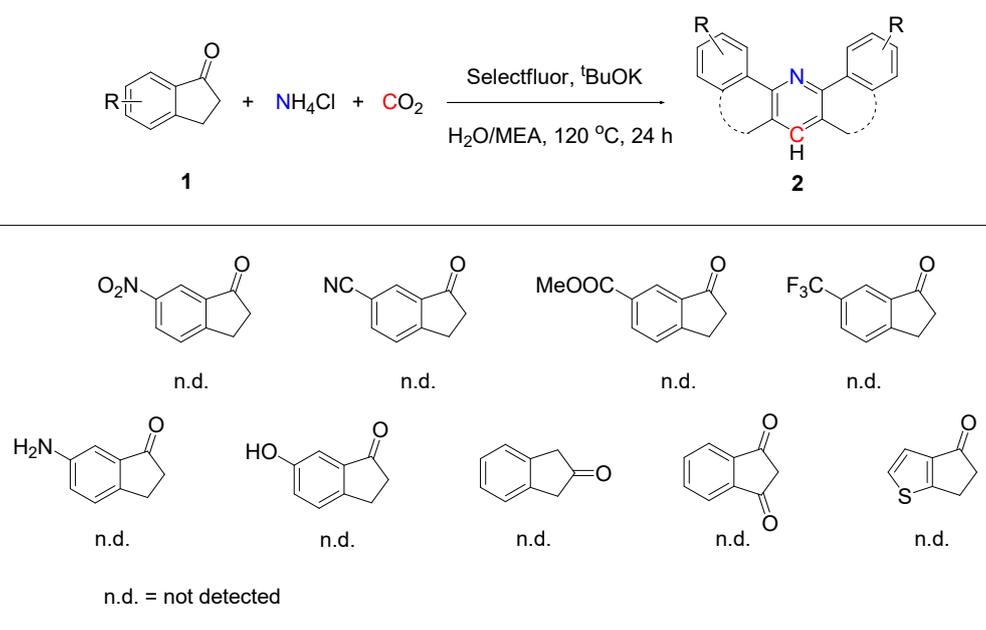
Single crystals were coated with Paratone-N oil and mounted on a Nylon loop for diffraction. The data reduction and cell refinement were processed using CrysAlisPro software.<sup>[1]</sup> Structures were solved by direct methods using the SHELXTL program packages.<sup>[2]</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added geometrically. Crystal data and refinement details were given in Tables S2.

**Table S1** Crystallographic data<sup>a</sup> for compounds **2g**, **2k**, **2m** and **2v**.

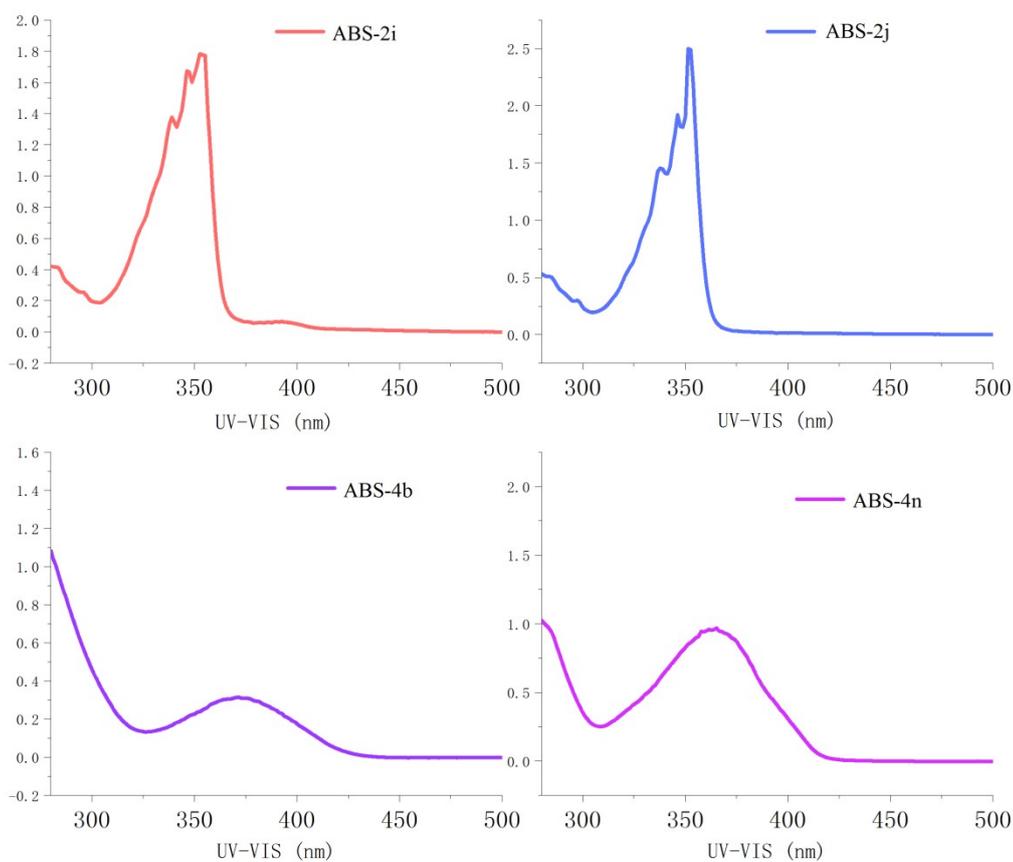
Name (CCDC)	<b>2g</b> (2057955)	<b>2k</b> (2059281)	<b>2m</b> (2088707)	<b>2v</b> (2083284)
formula	C <sub>19</sub> H <sub>11</sub> F <sub>2</sub> N	C <sub>19</sub> H <sub>11</sub> Cl <sub>2</sub> N	C <sub>21</sub> H <sub>17</sub> NO <sub>2</sub>	C <sub>23</sub> H <sub>21</sub> N
<i>M</i>	291.29	324.19	315.36	311.41
crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
space group	Cc	P-1	P 2 <sub>1</sub> /c	P bcn
<i>a</i> , Å	3.86350(10)	7.1916(3)	12.6441(2)	11.0913(14)
<i>b</i> , Å	26.7080(10)	8.2658(4)	17.5664(3)	16.1163(18)
<i>c</i> , Å	12.5375(3)	13.5299(5)	15.4560(3)	9.1839(9)
<i>α</i> , deg	90	87.021(4)	90	90
<i>β</i> , deg	90.609(3)	75.797(4)	114.037(2)	90
<i>γ</i> , deg	90	68.795(5)	90	90
<i>V</i> , Å <sup>3</sup>	1293.63(7)	726.29(6)	3135.25(10)	1641.6(3)
<i>Z</i>	4	2	8	4
<i>μ</i> , mm <sup>-1</sup>	0.892	3.957	0.684	0.549
independent data	1881	2737	5897	1351
refined parameters	200	199	437	110
<i>R</i> <sub>1</sub> <sup>b</sup> , <i>wR</i> <sub>2</sub> <sup>c</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0459, 0.1169	0.0432, 0.1269	0.0402, 0.1030	0.0498, 0.1344
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0465, 0.1172	0.0496, 0.1327	0.0466, 0.1074	0.0670, 0.1468

<sup>a</sup>T = 150(2) K, Cu Kα radiation (λ = 1.54184 Å). <sup>b</sup>R<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>c</sup>wR<sub>2</sub> = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)/(F<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>.

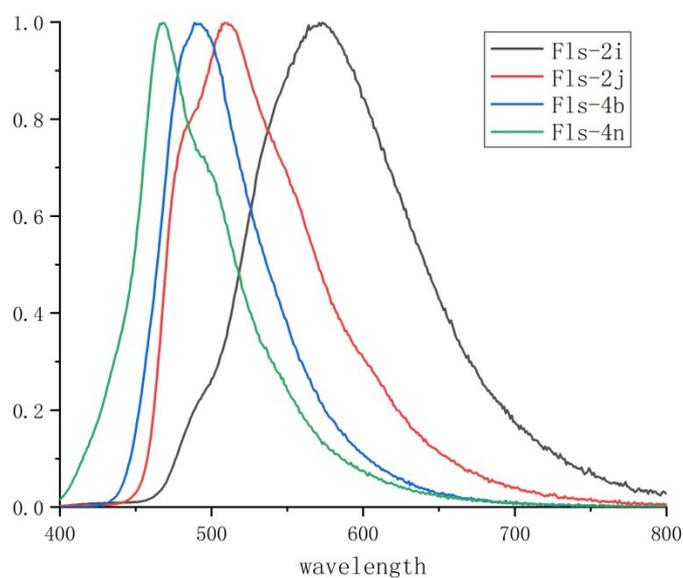
### 3. Unapplicable substrates for the synthesis of compound **2**

**Table S2** Some unsuccessful examples with respect to compound **2**.

#### 4. UV-Vis and Fls spectra of compounds **2i**, **2j**, **4b** and **4n**



**Fig. S1** UV-vis spectra (280 nm -500 nm) of **2i**, **2j**, **4b** and **4n** in CH<sub>2</sub>Cl<sub>2</sub> solution.



**Fig. S2** Fluorescence spectra of **2i**, **2j**, **4b** and **4n**. Spectral excitation/emission maxima: **2i** (353 nm/574 nm); **2j** (352 nm/509 nm); **4b** (373 nm/492 nm); **4n** (363 nm/468 nm). The Fls spectra were obtained using monochromatic light as motivation.

## 5. Photophysical data of compounds 2i, 2j and 4n

Table S3 Photophysical data of compounds 2i, 2j and 4n.

		2i	2j	4n
Powder	$\lambda_{em}$ / nm	574	509	468
	$\tau_{em}$ / ms	$< 10^{-3}$	$4.86 \times 10^{-3}$	0.27
	$\Phi_{em}$ / %	0.31	0.11	6.4

Note: The fluorescent quantum yield of **4n** (powder) is up to 6.4% with a life span of 0.276 s. It is proposed to have better quantum yield as host film on considering of the concentration quenching. It is proposed to have potential application as luminescent layer materials.

## 6. Experimental procedures and characterization data

### 6.1 General Procedure for the synthesis of compounds 2 or 4

Substrates **1** or **3** (0.2 mmol),  $\text{NH}_4\text{Cl}$  (53.5 mg, 1.0 mmol), selectfluor (70.9 mg, 0.2 mmol),  $t\text{BuOK}$  (22.4 mg, 0.2 mmol) and  $\text{MEA}/\text{H}_2\text{O}$  (1 mL/2 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charge with  $\text{CO}_2$  (1 atm.) and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and exacted with dichloromethane ( $3 \times 10$  mL). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (200–300 mesh) eluted with petroleum-ether/ethyl acetate (7:1 - 3:1 v/v) to afford the target products in yields up to 88%. Note: All the reactants must be covered by  $\text{MEA}/\text{H}_2\text{O}$ , and should not be stirred onto the wall of tube during the reaction.

### 6.2 Controlled experiments

**a)** and **b)**: Substrates **1d** (26.4 mg, 0.2 mmol),  $\text{NH}_4\text{Cl}$  (53.5 mg, 1.0 mmol), selectfluor (70.9 mg, 0.2 mmol),  $t\text{BuOK}$  (22.4 mg, 0.2 mmol), radical inhibitors (1.0 mmol, TEMPO (156.2 mg); PhSeSePh (312.13 mg)) and  $\text{MEA}/\text{H}_2\text{O}$  (1 mL/2 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charge with  $\text{CO}_2$  (1 atm.) and the mixture was stirred at 120 °C for 24 h.

After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane ( $3 \times 10$  mL). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (200–300 mesh) eluted with petroleum-ether/ethyl acetate (7:1 v/v) to afford the product **2d** in yields 80% and 79%, respectively.

**c):** Substrates **1d** (8.0 mmol),  $\text{NH}_4\text{Cl}$  (2.14 g, 40 mmol), selectfluor (2.84 g, 8 mmol),  $t\text{BuOK}$  (897.0 mg, 8 mmol) and  $\text{MEA}/\text{H}_2\text{O}$  (50 mL/5 mL) were mixed in a 250 mL Teflon screw-cap sealed tube. The tube was charge with  $\text{CO}_2$  (1 atm.) and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with water (150 mL) and extracted with dichloromethane ( $3 \times 50$  mL). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (200–300 mesh) eluted with petroleum-ether/ethyl acetate (7:1 v/v) to afford the product **2d** in 70% yield (714.8 mg).

**d):** Methyl acetoacetate (**3l**) (23.2 mg, 0.2 mmol),  $\text{NH}_4\text{Cl}$  (53.5 mg, 1.0 mmol), *o*-nitrobenzaldehyde (15.1 mg, 0.1 mmol), selectfluor (70.9 mg, 0.2 mmol),  $t\text{BuOK}$  (22.4 mg, 0.2 mmol), and  $\text{MEA}/\text{H}_2\text{O}$  (1 mL/2 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charge with  $\text{CO}_2$  (1 atm.) and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane ( $3 \times 10$  mL). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (200–300 mesh) eluted with petroleum-ether/ethyl acetate (3:1 v/v) to afford the product **5** in 32% yield (11.1 mg).

## 6.3 Characterization data

### 3,7-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (**2a**)

Yield, 88% (24.9 mg); white powder;  $R_f = 0.47$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (s, 2H), 7.89 (s, 1H), 7.45 (d,  $J = 7.6$  Hz, 2H), 7.22 (d,  $J = 7.6$  Hz, 2H), 3.85 (s, 4H), 2.51 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 141.5, 141.2, 137.1, 135.5, 129.3, 129.2, 124.9, 121.5, 34.3, 21.6; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_1$ , 284.1434; found, 284.1436.

**3,7-Dimethoxy-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2b)**

Yield, 88% (27.7 mg); white powder;  $R_f = 0.40$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (s, 1H), 7.79 (s, 2H), 7.45 (d,  $J = 8.2$  Hz, 2H), 6.99 (d,  $J = 8.2$  Hz, 2H), 3.98 (s, 6H), 3.83 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 159.5, 136.4, 136.2, 129.2, 125.9, 116.6, 104.4, 100.2, 55.8, 34.0; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_2$ , 316.1332; found, 316.1332.

**3,7-Di-tert-butyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2c)**

Yield, 88% (32.3 mg); brown powder;  $R_f = 0.70$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (s, 2H), 7.90 (s, 1H), 7.52 (d,  $J = 8.0$  Hz, 2H), 7.48 (d,  $J = 8.0$  Hz, 2H), 3.85 (s, 4H), 1.47 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9, 150.6, 141.3, 141.3, 135.5, 129.2, 125.8, 124.7, 117.9, 35.2, 34.2, 31.8; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{27}\text{H}_{30}\text{N}_1$ , 368.2373; found, 368.2376.

**10,12-Dihydrodiindeno[1,2-b:2',1'-e]pyridine (2d)**

Yield, 82% (20.9 mg); white powder;  $R_f = 0.47$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (d,  $J = 7.6$  Hz, 2H), 7.89 (s, 1H), 7.56 (d,  $J = 7.6$  Hz, 2H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.40 (t,  $J = 7.6$  Hz, 2H), 3.86 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 144.0, 141.3, 135.2, 129.2, 128.3, 127.3, 125.2, 121.1, 34.6; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{14}\text{N}_1$ , 256.1121; found, 256.1120.

**3,7-Dibromo-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2e)**

Yield, 61% (25.1 mg); white powder;  $R_f = 0.66$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.30 (s, 2H), 7.88 (s, 1H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.37 (d,  $J = 8.0$  Hz, 2H), 3.80 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 143.2, 142.6, 136.1, 131.2, 129.3, 126.7, 124.2, 121.6, 34.4; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{12}\text{N}_1\text{Br}_2$ , 410.9258; found, 410.9256.

**3,7-Dichloro-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2f)**

Yield, 60% (19.5 mg); white powder;  $R_f = 0.33$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (s, 2H), 7.90 (s, 1H), 7.45 (d,  $J$  = 8.0 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 3.84 (s, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 142.8, 142.1, 136.3, 133.7, 129.3, 128.4, 126.3, 121.3, 34.3; HRMS  $m/z$  (ESI) [ $M + H^+$ ]: calculated for C<sub>19</sub>H<sub>12</sub>N<sub>1</sub>Cl<sub>2</sub>, 326.0315; found, 326.0317.

### **3,7-Difluoro-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2g)**

Yield, 56% (16.3 mg); white powder;  $R_f$  = 0.36 in 12.5% ethyl acetate in petroleum ether; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (s, 1H), 7.89 (dd,  $J$  = 8.6, 2.2 Hz, 2H), 7.50 (dd,  $J$  = 8.2, 4.8 Hz, 2H), 7.10 (dd,  $J$  = 9.2, 2.8 Hz, 2H), 3.86 (s, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  162.9 (d,  $J$  = 242.9 Hz), 159.0, 143.3, 139.3, 136.7, 129.3, 126.24 (d,  $J$  = 8.6 Hz), 115.54 (d,  $J$  = 23.2 Hz), 107.96 (d,  $J$  = 22.7 Hz), 34.1; HRMS  $m/z$  (ESI) [ $M + H^+$ ]: calculated for C<sub>19</sub>H<sub>12</sub>F<sub>2</sub>N<sub>1</sub>, 292.0932; found, 292.0936.

### **2,8-Dimethoxy-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2h)**

Yield, 85% (26.7 mg); white powder;  $R_f$  = 0.42 in 25% ethyl acetate in petroleum ether; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.11 (d,  $J$  = 8.4 Hz, 2H), 7.75 (s, 1H), 7.06 (s, 2H), 7.02 (d,  $J$  = 8.4 Hz, 2H), 3.88 (s, 6H), 3.77 (s, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  160.4, 159.3, 146.1, 134.4, 133.5, 128.6, 121.8, 113.5, 110.5, 55.6, 34.6; HRMS  $m/z$  (ESI) [ $M + H^+$ ]: calculated for C<sub>21</sub>H<sub>18</sub>N<sub>1</sub>O<sub>2</sub>, 316.1332; found, 316.1332.

### **2,8-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2i)**

Yield, 78% (22.1 mg); white powder;  $R_f$  = 0.70 in 12.5% ethyl acetate in petroleum ether; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (d,  $J$  = 7.8 Hz, 2H), 7.84 (s, 1H), 7.36 (s, 2H), 7.29 (d,  $J$  = 7.8 Hz, 2H), 3.81 (s, 4H), 2.47 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 144.4, 138.8, 138.3, 134.6, 129.0, 128.2, 125.9, 120.8, 34.5, 21.9; HRMS  $m/z$  (ESI) [ $M + H^+$ ]: calculated for C<sub>21</sub>H<sub>18</sub>N<sub>1</sub>, 284.1434; found, 284.1436.

### **2,8-Dibromo-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2j)**

Yield, 55% (22.6 mg); white powder;  $R_f$  = 0.62 in 25% ethyl acetate in petroleum ether; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.11 (d,  $J$  = 8.2 Hz, 2H), 7.88 (s, 1H), 7.52 (s, 2H), 7.45 (d,  $J$  = 8.2 Hz, 2H),

3.85 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.8, 145.6, 139.7, 135.2, 134.3, 129.3, 127.8, 125.6, 122.0, 34.5; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{12}\text{N}_1\text{Br}_2$ , 410.9258; found, 410.9256.

#### **2,8-Dichloro-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2k)**

Yield, 52% (16.9 mg); pale yellow solid;  $R_f = 0.46$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (d,  $J = 8.2$  Hz, 2H), 7.88 (s, 1H), 7.52 (s, 2H), 7.45 (d,  $J = 8.2$  Hz, 2H), 3.85 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.9, 145.6, 139.7, 135.2, 134.3, 129.3, 127.8, 125.6, 122.0, 34.5; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{12}\text{N}_1\text{Cl}_2$ , 326.0315; found, 326.0317.

#### **2,8-Difluoro-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2l)**

Yield, 50% (14.5 mg); white powder;  $R_f = 0.38$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (dd,  $J = 7.8, 5.2$  Hz, 2H), 7.88 (s, 1H), 7.26 (dd,  $J = 9.2, 2.5$  Hz, 2H), 7.18 (td,  $J = 9.1, 2.3$  Hz, 2H), 3.87 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.5 (d,  $J = 246.6$  Hz), 158.8, 146.2 (d,  $J = 9.0$  Hz), 137.3, 134.5, 129.0, 122.2 (d,  $J = 9.0$  Hz), 114.78 (d,  $J = 23.0$  Hz), 112.49 (d,  $J = 23.0$  Hz), 34.64 (d,  $J = 2.4$  Hz); HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{12}\text{F}_2\text{N}_1$ , 292.0932; found, 292.0936.

#### **1,9-Dimethoxy-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2m)**

Yield, 80% (25.2 mg); white powder;  $R_f = 0.63$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.87 (d,  $J = 7.2$  Hz, 2H), 7.47 (t,  $J = 7.6$  Hz, 2H), 6.92 (d,  $J = 7.6$  Hz, 2H), 3.94 (s, 6H), 3.81 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.7, 156.3, 142.9, 135.4, 131.6, 128.9, 128.5, 113.8, 109.9, 55.5, 31.9; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_2$ , 316.1332; found, 316.1332.

#### **1,9-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2n)**

Yield, 85% (24.1 mg); white powder;  $R_f = 0.61$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (d,  $J = 7.2$  Hz, 2H), 7.94 (s, 1H), 7.40 (d,  $J = 7.2$  Hz, 2H), 7.23 (d,  $J = 7.2$  Hz, 2H), 3.75 (s, 4H), 2.43 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 142.9, 135.1,

134.3, 133.5, 130.8, 129.3, 127.6, 118.8, 33.6, 18.7; HRMS  $m/z$  (ESI)  $[M + H^+]$ : calculated for  $C_{21}H_{18}N_1$ , 284.1434; found, 284.1436.

**1,9-Dibromo-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2o)**

Yield, 60% (24.6 mg); white powder;  $R_f = 0.29$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.17 (d,  $J = 7.6$  Hz, 2H), 8.00 (s, 1H), 7.74 (t,  $J = 7.6$  Hz, 2H), 7.53 (d,  $J = 7.6$  Hz, 2H), 3.87 (s, 4H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  159.3, 148.5, 144.1, 136.7, 131.5, 129.3, 128.9, 122.7, 120.1, 31.6; HRMS  $m/z$  (ESI)  $[M + H^+]$ : calculated for  $C_{19}H_{12}N_1Br_2$ , 410.9258; found, 410.9256.

**1,9-Dichloro-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2p)**

Yield, 55% (17.9 mg); white powder;  $R_f = 0.45$  in 25% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.15 (d,  $J = 7.2$  Hz, 2H), 8.02 (s, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.35 (d,  $J = 7.6$  Hz, 2H), 3.93 (s, 4H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  159.1, 147.6, 147.2, 142.0, 131.3, 129.2, 128.6, 124.6, 124.1, 31.6; HRMS  $m/z$  (ESI)  $[M + H^+]$ : calculated for  $C_{19}H_{12}N_1Cl_2$ , 326.0315; found, 326.0317.

**10,10,12,12-Tetramethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2q)**

Yield, 72% (22.4 mg); white powder;  $R_f = 0.60$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.18 (d,  $J = 7.2$  Hz, 2H), 7.73 (s, 1H), 7.51 – 7.39 (m, 6H), 1.55 (s, 12H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  157.9, 154.4, 146.2, 138.9, 128.8, 127.5, 124.4, 122.5, 121.1, 45.0, 27.1; HRMS  $m/z$  (ESI)  $[M + H^+]$ : calculated for  $C_{23}H_{22}N_1$ , 312.1747; found, 312.1750.

**1,2,6,8,12,13-Hexahydrofuro[2',3':6,7]indeno[1,2-b]furo[2',3':6,7]indeno[2,1-e]pyridine (2r)**

Yield, 43% (14.5 mg); white powder;  $R_f = 0.60$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.88 (s, 1H), 7.30 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 4.74 (t,  $J = 8.7$  Hz, 4H), 3.84 (s, 4H), 3.79 (t,  $J = 8.7$  Hz, 4H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  160.4, 159.8, 138.0, 136.1, 135.9, 128.7, 124.0, 121.2, 108.8, 72.3, 34.3, 29.0; HRMS  $m/z$  (ESI)  $[M + H^+]$ : calculated for  $C_{23}H_{18}N_1O_2$ , 340.1332; found, 340.1333.

### **5,6,8,9-Tetrahydrodibenzacridine (2s)**

Yield, 78% (22.1 mg); white powder;  $R_f = 0.65$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (d,  $J = 7.6$  Hz, 2H), 7.41 (t,  $J = 7.6$  Hz, 2H), 7.32 (s, 1H), 7.31 (t,  $J = 7.6$  Hz, 2H), 7.24 (d,  $J = 7.6$  Hz, 2H), 2.95 (s, 8H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.5, 138.0, 135.4, 135.1, 130.7, 128.8, 127.8, 127.2, 125.1, 28.4, 28.0; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_1$ , 284.1434; found, 284.1435.

### **3,11-Dimethoxy-5,6,8,9-tetrahydrodibenzo[c,h]acridine (2t)**

Yield, 50% (17.2 mg); white powder;  $R_f = 0.68$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.43 (d,  $J = 8.6$  Hz, 2H), 7.25 (s, 1H), 6.92 (d,  $J = 8.6$  Hz, 2H), 6.76 (s, 2H), 3.86 (s, 6H), 2.91 (s, 8H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.2, 150.4, 139.8, 135.1, 128.8, 128.4, 126.6, 113.1, 112.6, 55.5, 28.8, 28.0; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{N}_1\text{O}_2$ , 344.1645; found, 344.1647.

### **5,9-Dimethyl-5,6,8,9-tetrahydrodibenzo[c,h]acridine (2u)**

Yield, 73% (22.7 mg); white powder;  $R_f = 0.65$  in 6.25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.55 (d,  $J = 7.6$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 2H), 7.34 (t,  $J = 7.4$  Hz, 2H), 7.32 (s, 1H), 7.27 (d,  $J = 7.6$  Hz, 1H), 3.13 (d,  $J = 8.0$  Hz, 4H), 2.74 (q,  $J = 8.2$  Hz, 2H), 1.28 (dd,  $J = 7.6, 1.6$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1, 142.9, 136.7, 134.2, 129.5, 129.1, 127.1, 126.5, 125.2, 35.6, 32.6, 20.6; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{N}_1$ , 312.1747; found, 312.1749.

### **5,6,7,9,10,11-Hexahydrobenzo[6,7]cyclohepta[1,2-b]benzo[6,7]cyclohepta[2,1-e]pyridine (2v)**

Yield, 70% (21.7 mg); white powder;  $R_f = 0.60$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (d,  $J = 7.5$  Hz, 2H), 7.41 (s, 1H), 7.40 (t,  $J = 7.4$  Hz, 2H), 7.33 (t,  $J = 7.4$  Hz, 2H), 7.25 (d,  $J = 7.5$  Hz, 2H), 2.61 (t,  $J = 7.1$  Hz, 4H), 2.55 (t,  $J = 7.1$  Hz, 4H), 2.28 (p,  $J = 7.1$  Hz, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.4, 140.6, 139.6, 137.1, 133.6, 129.1, 128.5, 126.9, 33.3, 31.4, 30.2; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{23}\text{H}_{22}\text{N}_1$ , 312.1747; found, 312.1750.

### **2, 3, 5, 6-Tetraphenyl-pyridine (2w)**

Yield, 82% (31.4 mg); white powder;  $R_f = 0.72$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (s, 1H), 7.52 – 7.48 (m, 4H), 7.34 – 7.22 (m, 17H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.5, 141.4, 140.1, 139.8, 134.5, 130.3, 129.7, 128.8, 128.5, 128.0, 127.4; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{29}\text{H}_{22}\text{N}_1$ , 384.1747; found, 384.1748.

**Diethyl 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarboxylate (4a)**<sup>[3]</sup>

Yield, 78% (29.4 mg); yellow greenish powder;  $R_f = 0.4$  in 16.7% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 – 7.28 (m, 10H), 5.48 (s, 1H), 3.95 (q,  $J = 7.1$  Hz, 4H), 3.62 (s, 2H), 0.95 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.4, 146.7, 137.0, 129.1, 128.5, 128.0, 100.3, 59.9, 26.0, 14.0.

**Diethyl 2,6-di-*m*-tolyl-1,4-dihydropyridine-3,5-dicarboxylate (4b)**

Yield, 78% (31.6 mg); pale yellow powder;  $R_f = 0.25$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 (t,  $J = 7.6$  Hz, 2H), 7.17 (d,  $J = 7.6$  Hz, 2H), 7.11 (s, 2H), 7.10 (d,  $J = 7.6$  Hz, 2H), 5.44 (s, 1H), 3.96 (q,  $J = 7.1$  Hz, 4H), 3.61 (s, 2H), 2.35 (s, 6H), 0.96 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.5, 146.9, 138.1, 137.0, 129.8, 128.5, 128.4, 125.0, 100.1, 59.8, 26.0, 21.5, 14.0; HRMS  $m/z$  (ESI)  $[\text{M} + \text{Na}^+]$ : calculated for  $\text{C}_{25}\text{H}_{27}\text{NNaO}_4$ , 428.1838; found 428.1836.

**Diethyl 2,6-bis(4-methoxyphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4c)**<sup>[4]</sup>

Yield, 60% (26.2 mg); pale yellow powder;  $R_f = 0.24$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 (d,  $J = 8.4$  Hz, 4H), 6.90 (d,  $J = 8.4$  Hz, 4H), 5.51 (s, 1H), 4.00 (q,  $J = 7.2$  Hz, 4H), 3.81 (s, 6H), 3.60 (s, 2H), 1.03 (t,  $J = 7.2$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.5, 160.3, 146.6, 129.5, 129.1, 113.8, 99.7, 59.8, 55.4, 26.0, 14.2.

**Diethyl 2,6-bis(2-fluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4d)**

Yield, 42% (17.3 mg); yellow powder;  $R_f = 0.32$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (td,  $J = 7.2, 5.2$  Hz, 2H), 7.28 (td,  $J = 7.6, 1.0$  Hz, 2H), 7.15 (td,  $J = 7.6, 1.0$  Hz, 2H), 7.08 (t,  $J = 7.6$  Hz, 2H), 5.39 (s, 1H), 3.98 (q,  $J = 7.1$  Hz, 4H), 3.64 (s, 2H), 0.98 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.7, 159.46 (d,  $J = 247.2$  Hz), 140.5,

131.0 (d,  $J = 8.3$  Hz), 129.9, 124.6 (d,  $J = 15.8$  Hz), 124.3 (d,  $J = 4.7$  Hz), 115.8 (d,  $J = 21.8$  Hz), 102.6, 60.0, 25.6, 14.0; HRMS  $m/z$  (ESI)  $[M + Na^+]$ : calculated for  $C_{23}H_{21}F_2NNaO_4$ , 436.1331; found 436.1322.

**Diethyl 2,6-bis(4-fluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4e)<sup>[4]</sup>**

Yield, 48% (19.8 mg); yellow powder;  $R_f = 0.65$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.29 (t,  $J = 8.2$  Hz, 4H), 7.06 (t,  $J = 8.2$  Hz, 4H), 5.38 (s, 1H), 3.97 (q,  $J = 7.0$  Hz, 4H), 3.60 (s, 2H), 1.00 (t,  $J = 7.1$  Hz, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  167.1, 163.2 (d,  $J = 249.1$  Hz), 145.6, 132.8 (d,  $J = 3.5$  Hz), 130.0 (d,  $J = 8.4$  Hz), 115.6 (d,  $J = 21.8$  Hz), 100.8, 60.0, 26.0, 14.0.

**Diethyl 2,6-bis(4-chlorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4f)**

Yield, 56% (25.0 mg); yellow powder;  $R_f = 0.40$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.35 (d,  $J = 8.4$  Hz, 4H), 7.24 (d,  $J = 8.4$  Hz, 4H), 5.35 (s, 1H), 3.97 (q,  $J = 7.1$  Hz, 4H), 3.59 (s, 2H), 1.01 (t,  $J = 7.1$  Hz, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  167.0, 145.4, 135.3, 135.2, 129.5, 128.8, 101.0, 60.1, 31.7, 14.1; HRMS  $m/z$  (ESI)  $[M + Na^+]$ : calculated for  $C_{23}H_{21}Cl_2NNaO_4$ , 468.0746; found 468.0743.

**Diethyl 2,6-bis(4-bromophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4g)<sup>[4]</sup>**

Yield, 58% (31.0 mg); pale yellow powder;  $R_f = 0.38$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.50 (d,  $J = 8.4$  Hz, 4H), 7.18 (d,  $J = 8.4$  Hz, 4H), 5.35 (s, 1H), 3.97 (q,  $J = 7.1$  Hz, 4H), 3.59 (s, 2H), 1.01 (t,  $J = 7.1$  Hz, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  167.0, 145.4, 135.6, 131.8, 129.7, 123.5, 101.0, 60.1, 25.9, 14.1.

**Diethyl 2,6-bis(4-trifluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4h)**

Yield, 30% (15.4 mg); yellow powder;  $R_f = 0.35$  in 12.5% ethyl acetate in petroleum ether;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.64 (d,  $J = 8.0$  Hz, 4H), 7.44 (d,  $J = 8.0$  Hz, 4H), 5.31 (s, 1H), 3.97 (q,  $J = 7.1$  Hz, 4H), 3.64 (s, 2H), 0.96 (t,  $J = 7.1$  Hz, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  166.7, 145.1, 140.4, 131.1 (q,  $J = 32.4$  Hz), 128.6, 125.6 (d,  $J = 15.1$  Hz), 121.17 (q,  $J = 273.9$  Hz), 101.7, 60.2, 25.9, 14.0; HRMS  $m/z$  (ESI)  $[M + Na^+]$ : calculated for  $C_{25}H_{21}F_6NNaO_4$ , 536.1273;

found 536.1270.

**Diethyl 2,6-bis(4-pyridyl)-1,4-dihydropyridine-3,5-dicarboxylate (4i)**

Yield, 45% (17.1 mg); yellow powder;  $R_f = 0.10$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (d,  $J = 5.6$  Hz, 4H), 7.34 (d,  $J = 5.6$  Hz, 4H), 5.38 (s, 1H), 4.10 (q,  $J = 7.1$  Hz, 4H), 3.58 (s, 2H), 1.12 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.3, 149.1, 126.2, 122.5, 115.0, 99.5, 60.0, 29.8, 14.2; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_4$ , 380.1611; found 380.1607.

**Diethyl 2,6-di(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (4j)**

Yield, 28% (10.9 mg); yellow powder;  $R_f = 0.16$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (dd,  $J = 5.1, 1.0$  Hz, 2H), 7.16 (dd,  $J = 3.5, 1.0$  Hz, 2H), 7.03 (dd,  $J = 5.1, 3.5$  Hz, 2H), 5.80 (s, 1H), 4.04 (q,  $J = 7.1$  Hz, 4H), 3.58 (s, 2H), 1.07 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.9, 139.3, 136.4, 128.4, 127.3, 127.1, 101.8, 60.2, 25.2, 14.1; HRMS  $m/z$  (ESI)  $[\text{M} + \text{H}^+]$ : calculated for  $\text{C}_{19}\text{H}_{20}\text{N}_1\text{O}_4\text{S}_2$ , 390.0834; found 390.0830.

**Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4k)<sup>[5]</sup>**

Yield, 65% 16.4 mg); yellow greenish powder;  $R_f = 0.39$  in 33% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.24 (s, 1H), 4.16 (q,  $J = 7.1$  Hz, 4H), 3.25 (s, 2H), 2.18 (s, 6H), 1.27 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.2, 145.0, 99.6, 59.8, 24.9, 19.3, 14.6.

**Dimethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4l)<sup>[5]</sup>**

Yield, 68% (15.3 mg); white powder;  $R_f = 0.30$  in 33% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.20 (s, 1H), 3.70 (s, 6H), 3.26 (s, 2H), 2.19 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.5, 145.3, 99.5, 51.2, 24.9, 19.3.

**Di-*tert*-butyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4m)<sup>[5]</sup>**

Yield, 35% (10.8 mg); white powder;  $R_f = 0.43$  in 33% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.00 (s, 1H), 3.17 (s, 2H), 2.14 (s, 6H), 1.47 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.7, 143.9, 101.1, 79.6, 28.5, 25.6, 19.4.

### Diallyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4n)<sup>[5]</sup>

Yield, 70% (19.4 mg); white powder;  $R_f = 0.70$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.94 (ddd,  $J = 22.5, 10.6, 5.4$  Hz, 2H), 5.41 (s, 1H), 5.30 (d,  $J = 17.2$  Hz, 2H), 5.20 (d,  $J = 10.4$  Hz, 2H), 4.61 (d,  $J = 5.4$  Hz, 4H), 3.32 (s, 2H), 2.23 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.7, 145.6, 133.0, 117.3, 99.4, 64.5, 24.9, 19.3.

### Di-*iso*-propyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4o)<sup>[5]</sup>

Yield, 42% (11.8 mg); white powder;  $R_f = 0.45$  in 12.5% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.09 (br, 1H), 5.06 – 5.01 (m, 2H), 3.23 (s, 2H), 2.17 (s, 6H), 1.25 (d,  $J = 6.7$  Hz, 12H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.8, 144.5, 100.0, 67.0, 25.0, 22.2, 19.4.

### Nifedipine (5)<sup>[6]</sup>

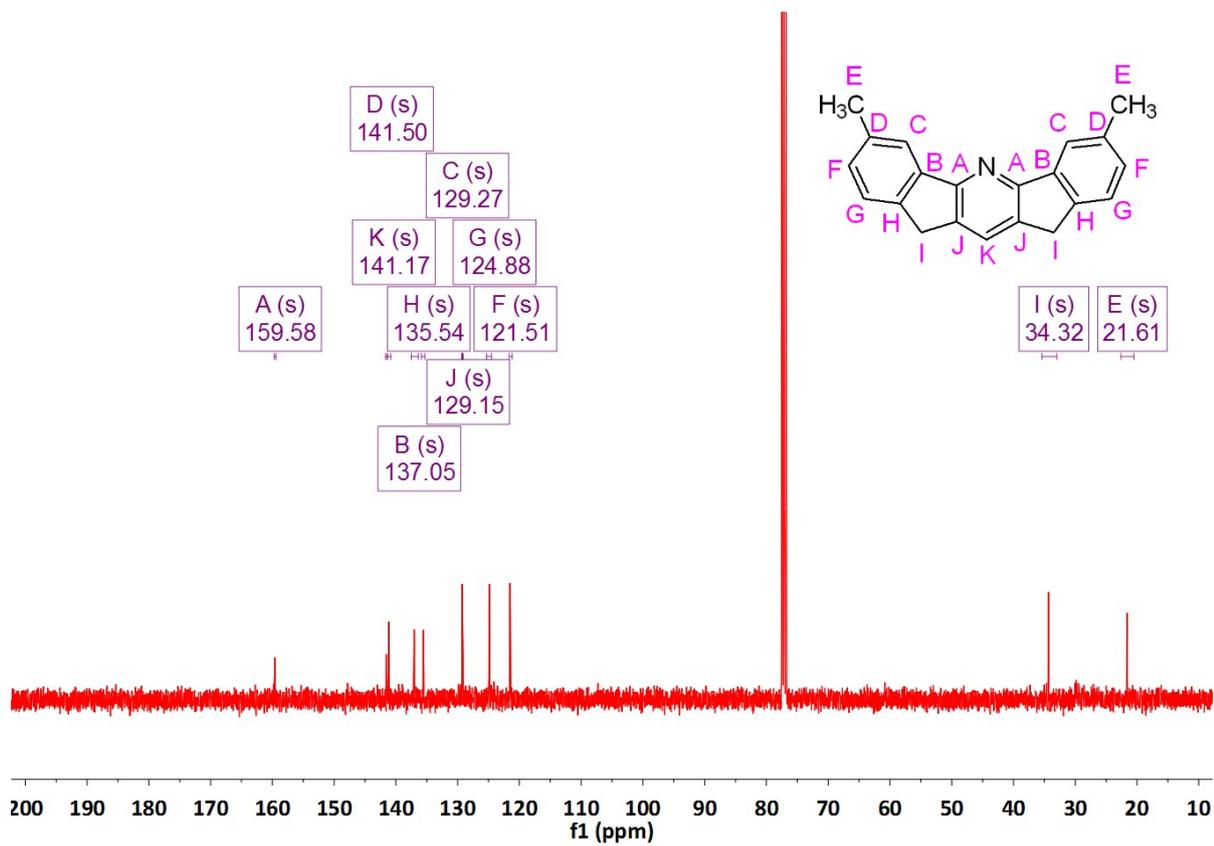
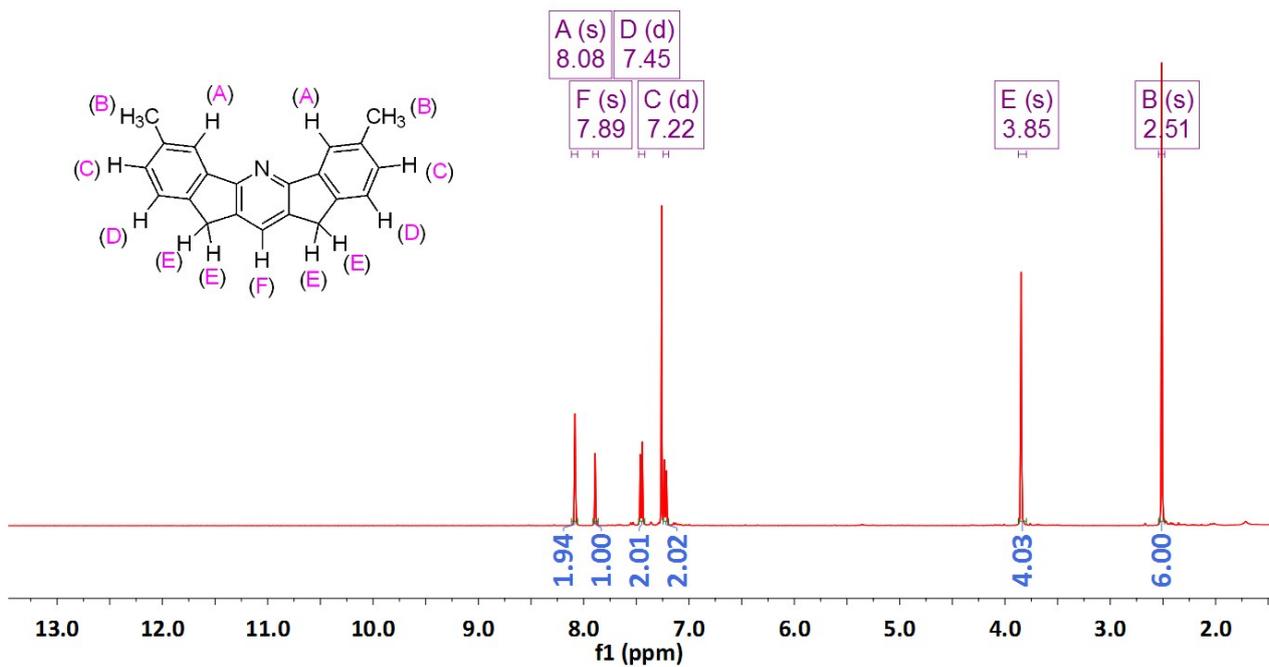
Yield, 32% (11.0 mg); colorless crystal;  $R_f = 0.18$  in 25% ethyl acetate in petroleum ether;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 7.8$  Hz, 1H), 7.49 (d,  $J = 7.8$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.20 (t,  $J = 8.0$  Hz, 1H), 6.55 (s, 1H), 5.68 (s, 1H), 3.53 (s, 6H), 2.26 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ): 167.8, 147.8, 145.5, 142.3, 132.8, 131.1, 127.1, 123.9, 103.3, 51.0, 34.5, 19.2.

## 7. References

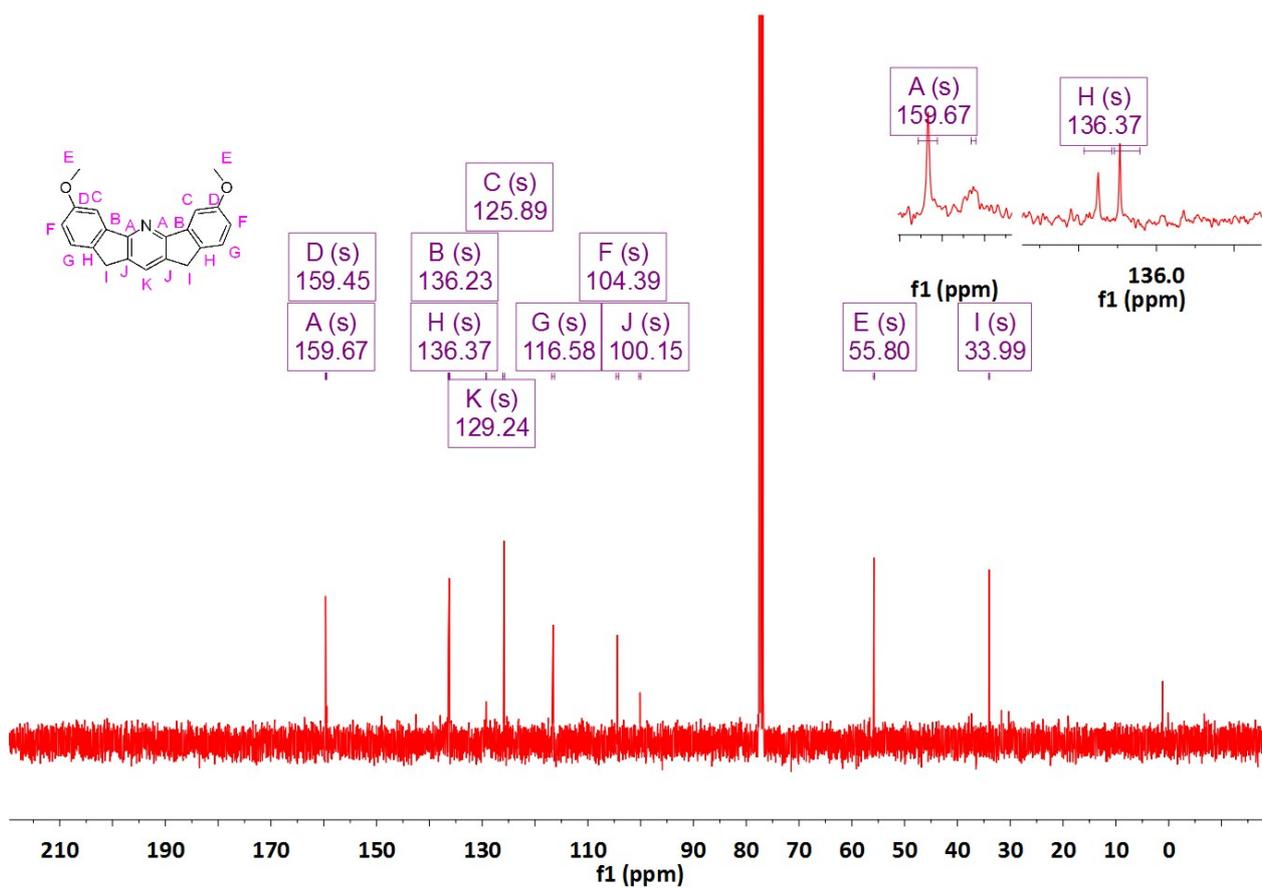
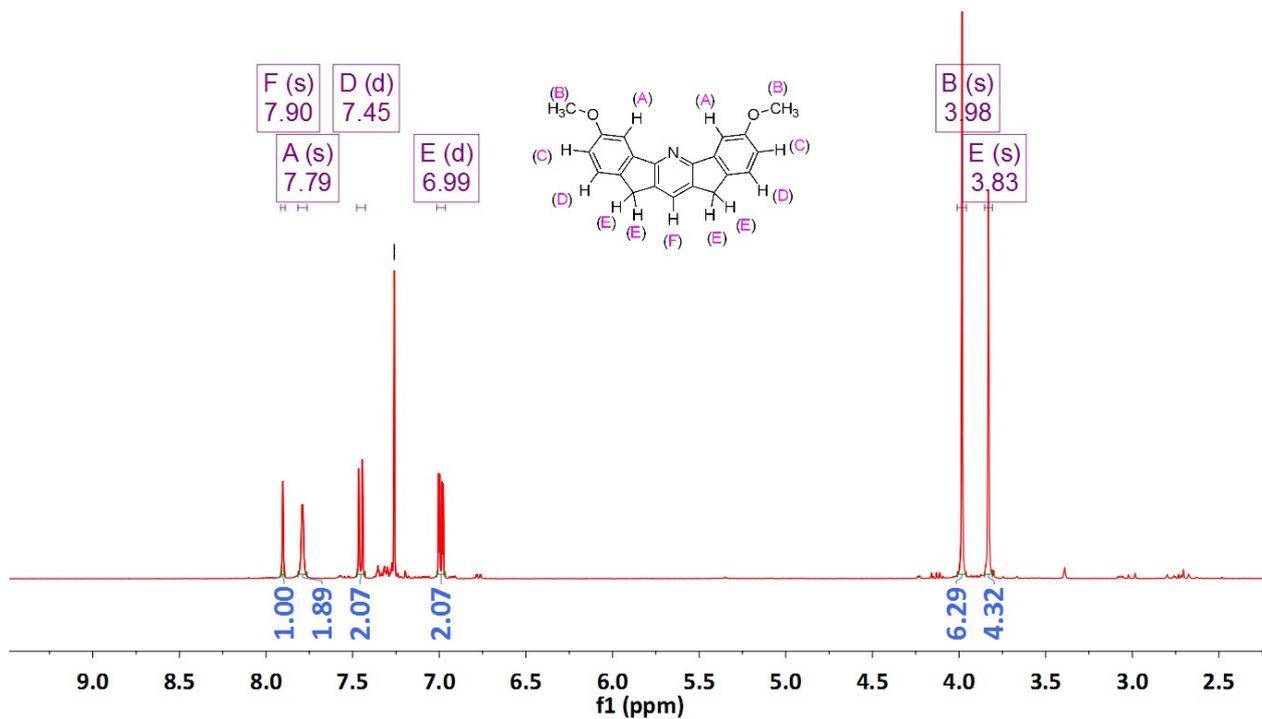
1. CrysAlisPro, Oxford Diffraction (Poland) 2010.
2. a) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure. University of Göttingen, Germany 1997. b) G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3-8.
3. H. Li, Z. He, X. Guo, W. Li, X. Zhao and Z. Li, *Org. Lett.*, 2009, **11**, 4176-4179.
4. P. Trinchera, W. Sun, J. E. Smith, D. Palomas, R. Crespo-Otero and C. R. Jones, *Org. Lett.*, 2017, **19**, 4644-4647.
5. H. T. Abdel-Mohsen, J. Conrad and U. Beifuss, *Green Chem.*, 2012, **14**, 2686-2690.
6. K. L. Bridgwood, G. E. Velch and S. V. Ley, *Org. Lett.*, 2008, **10**, 3627-3629.

## 8. NMR spectra

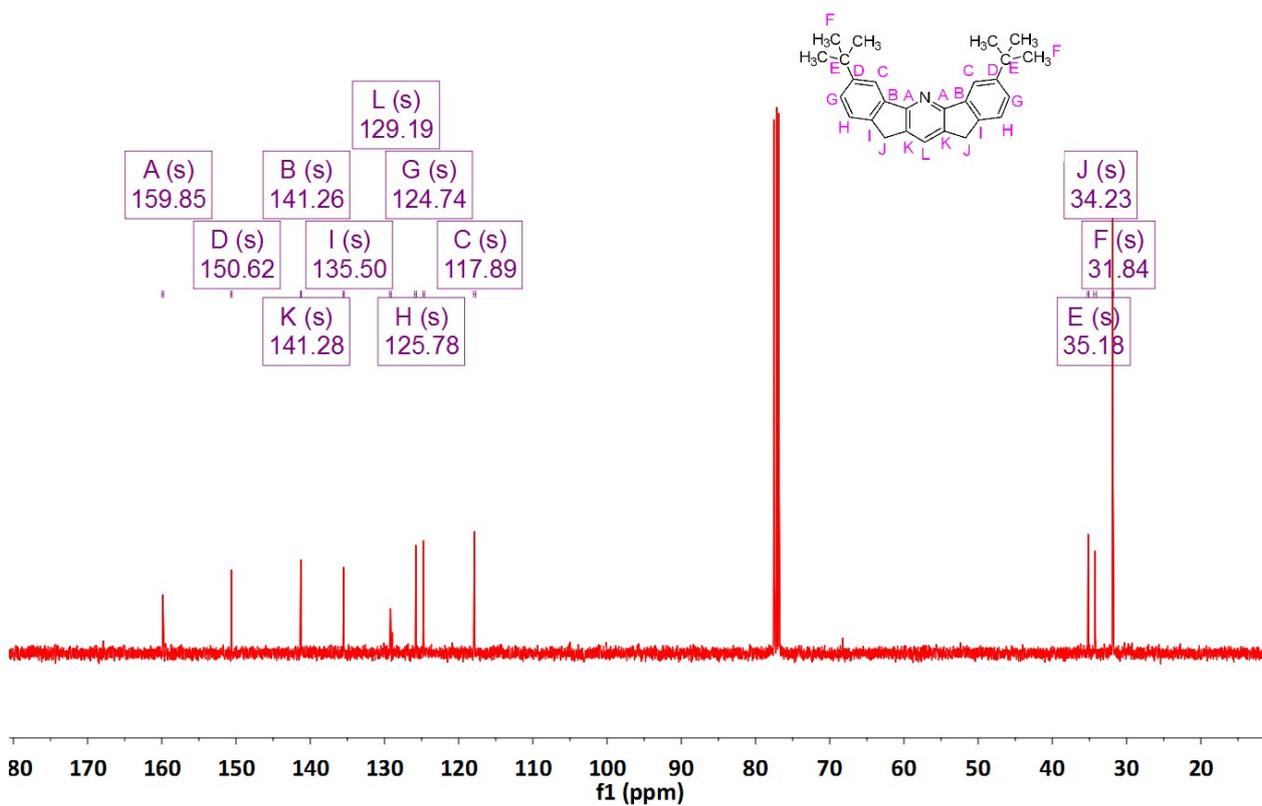
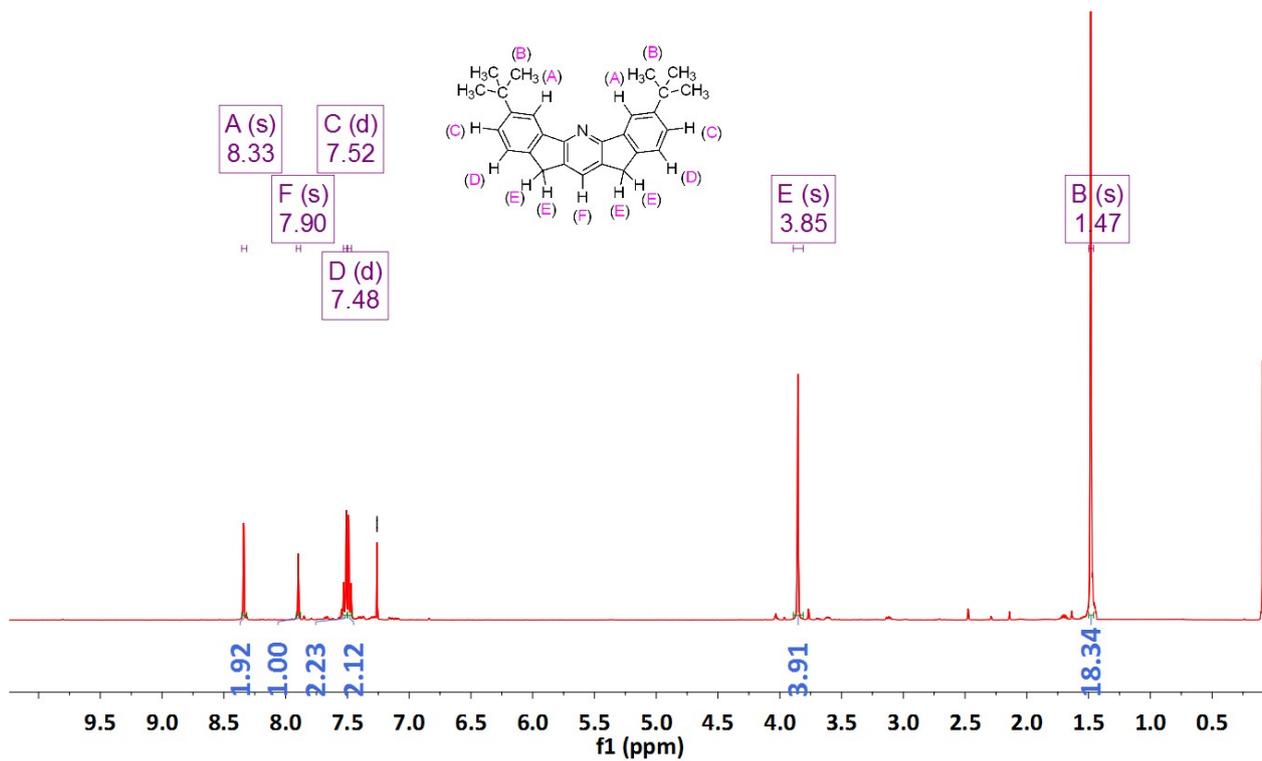
3,7-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2a)



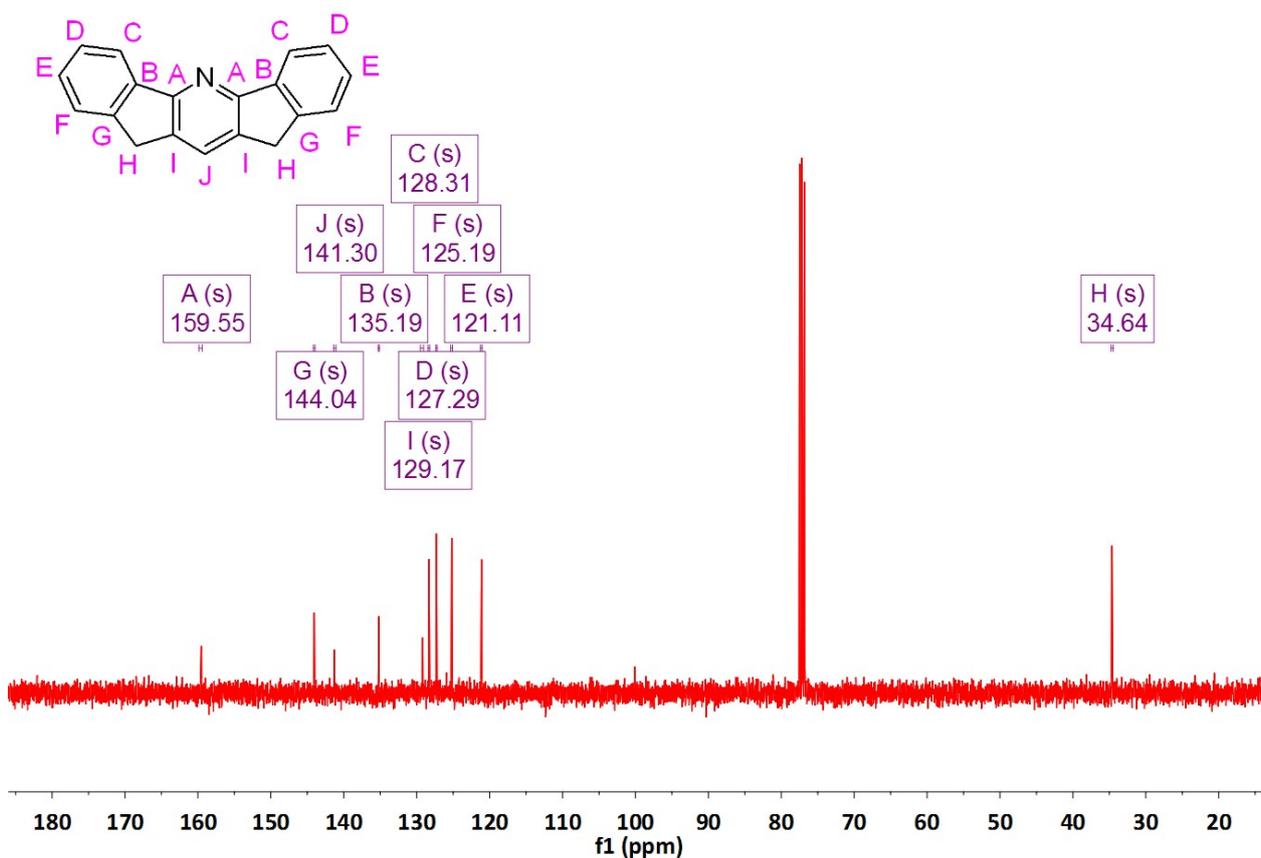
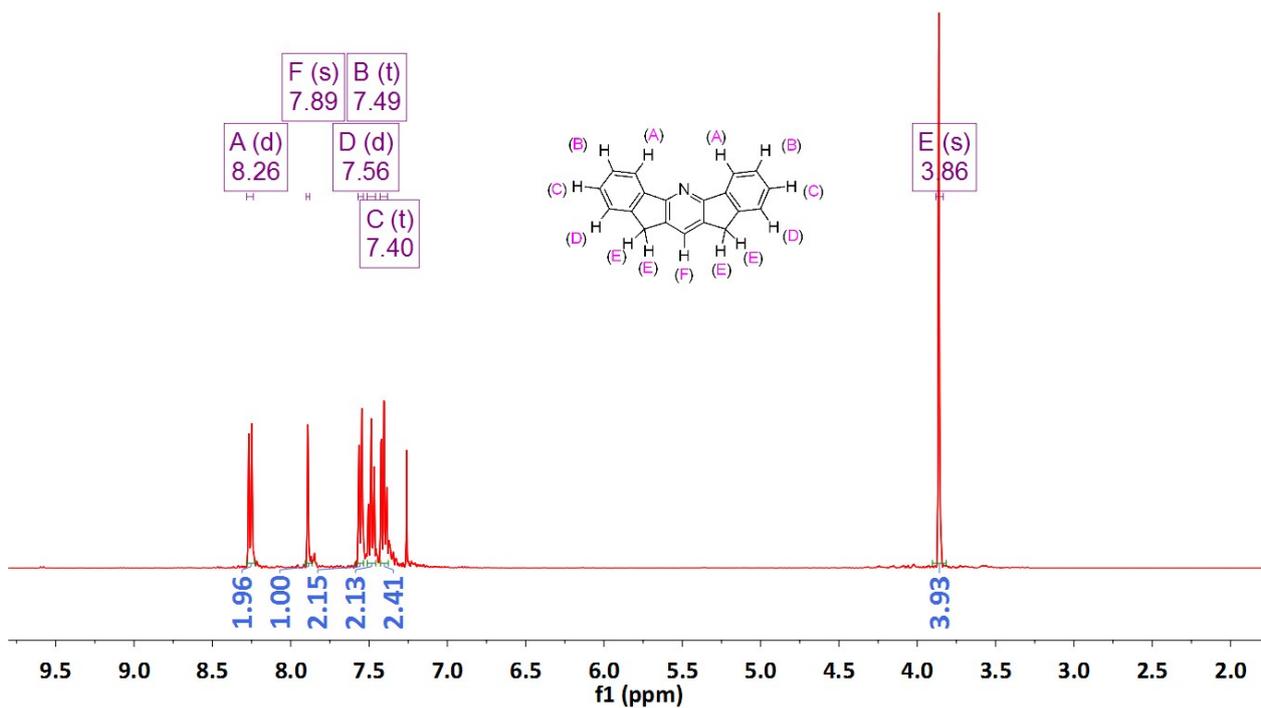
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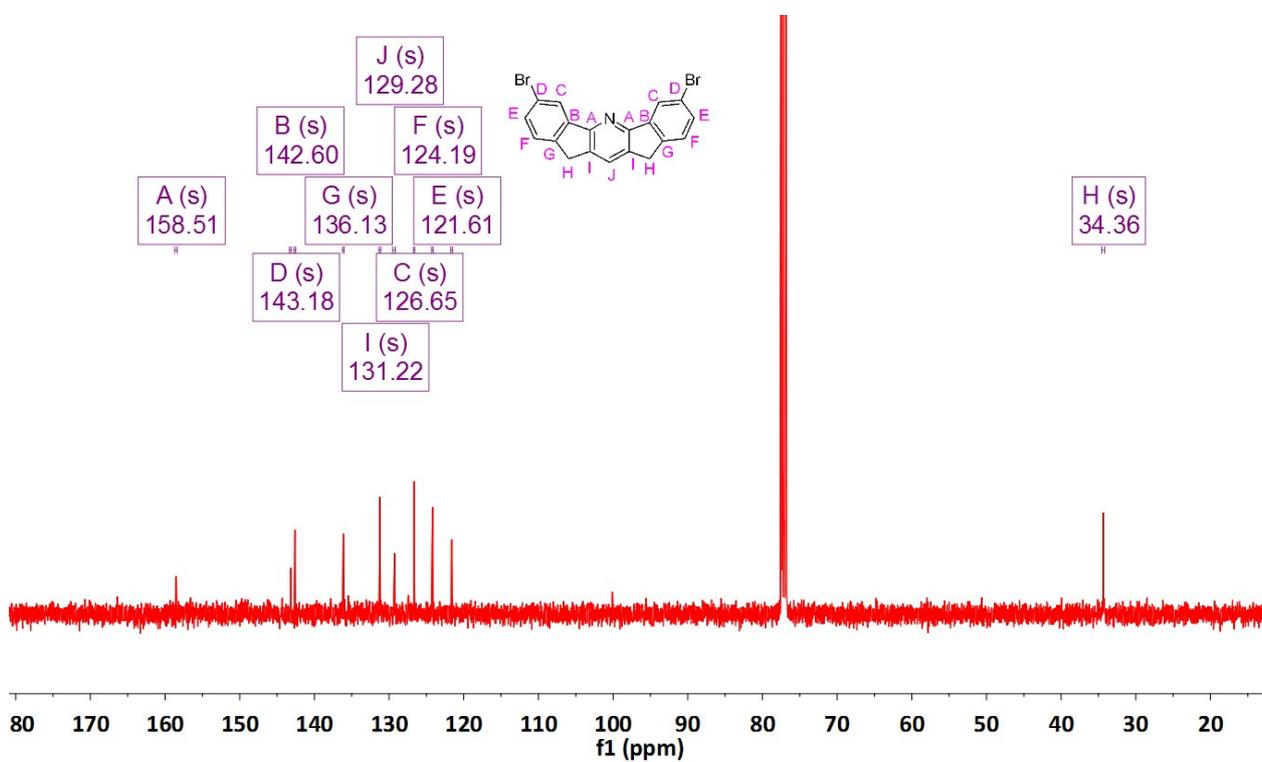
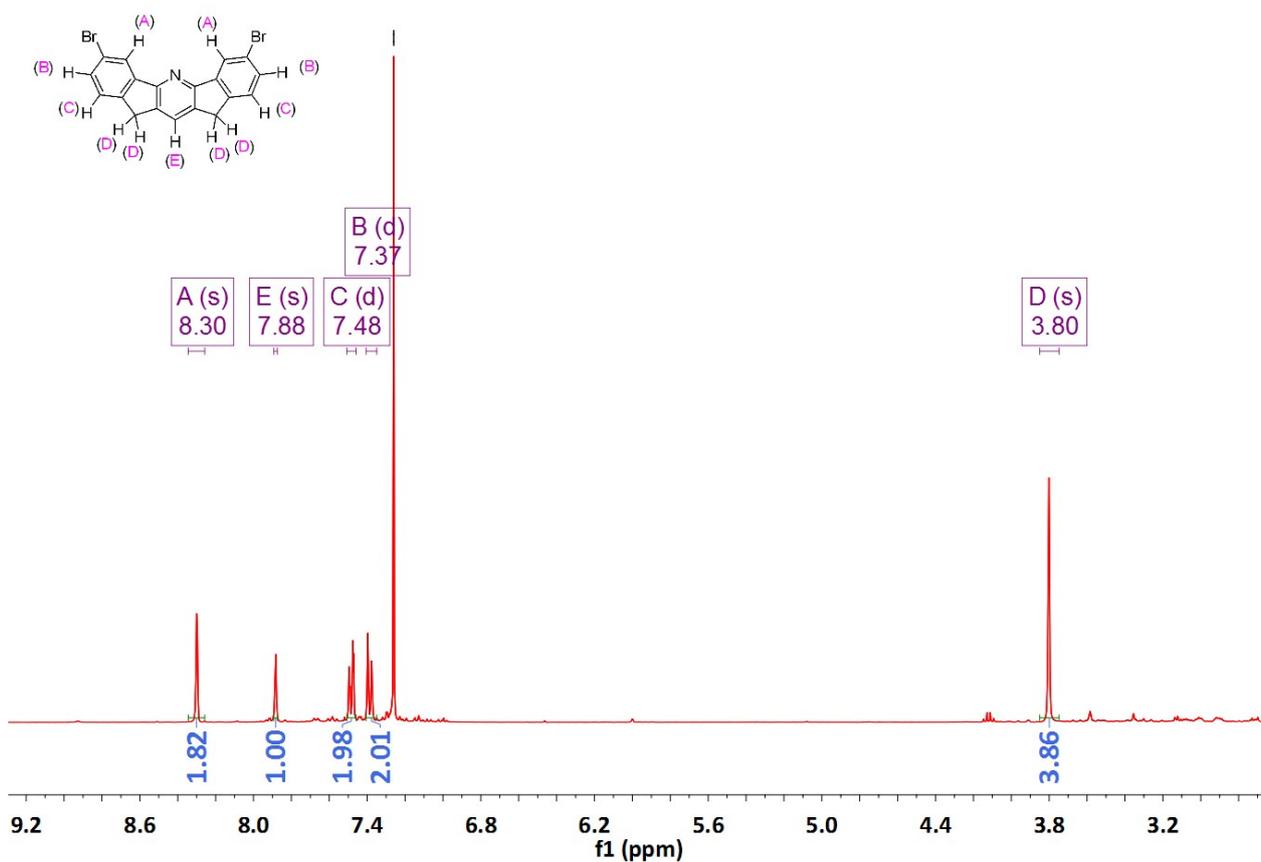
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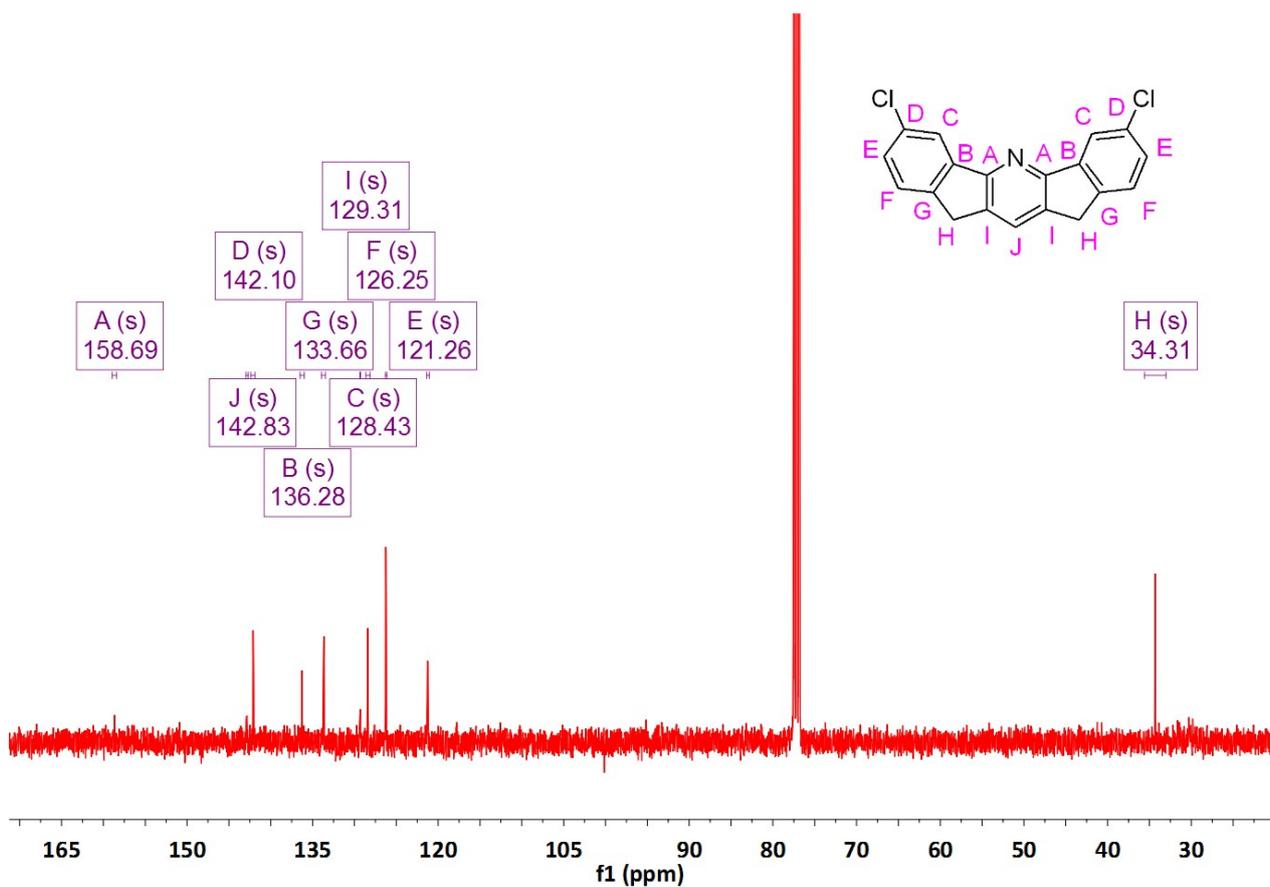
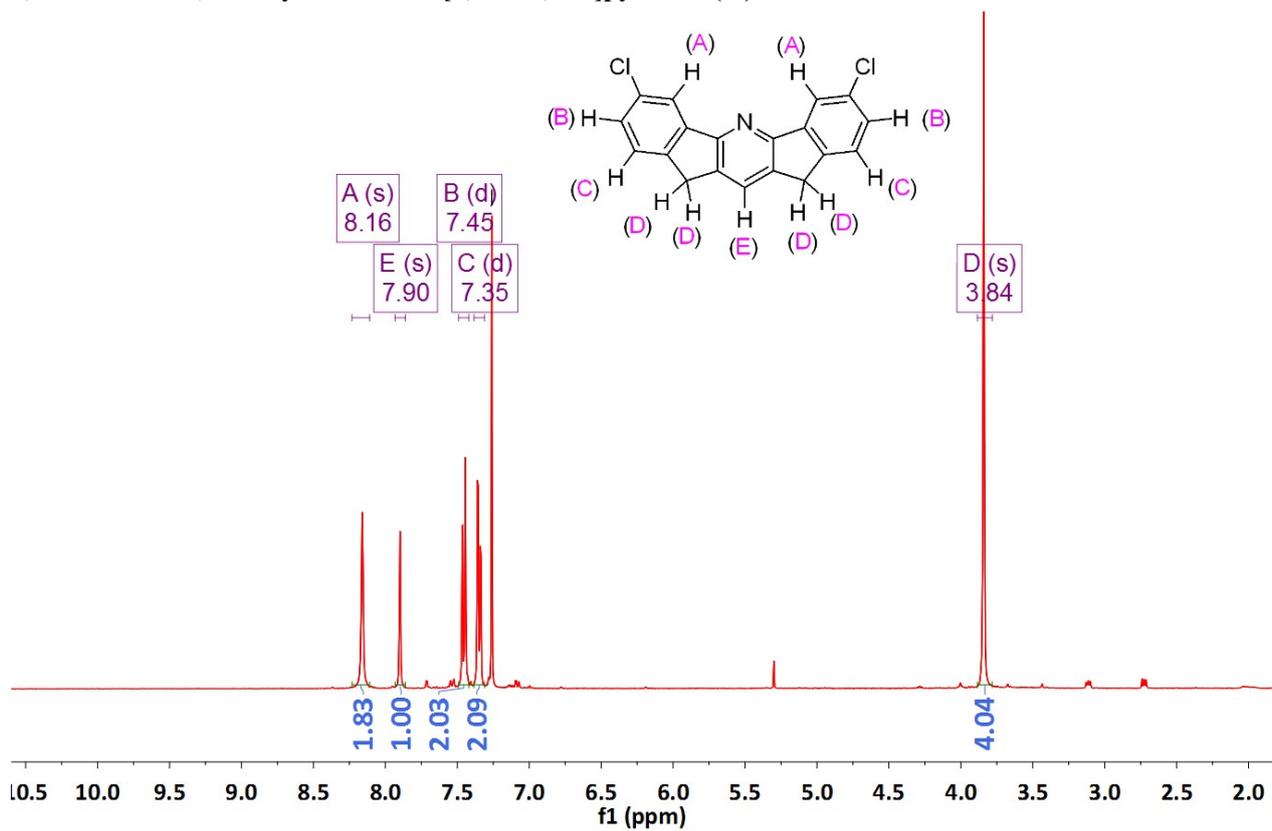
10,12-Dihydrodiindeno[1,2-b:2',1'-e]pyridine (2d)



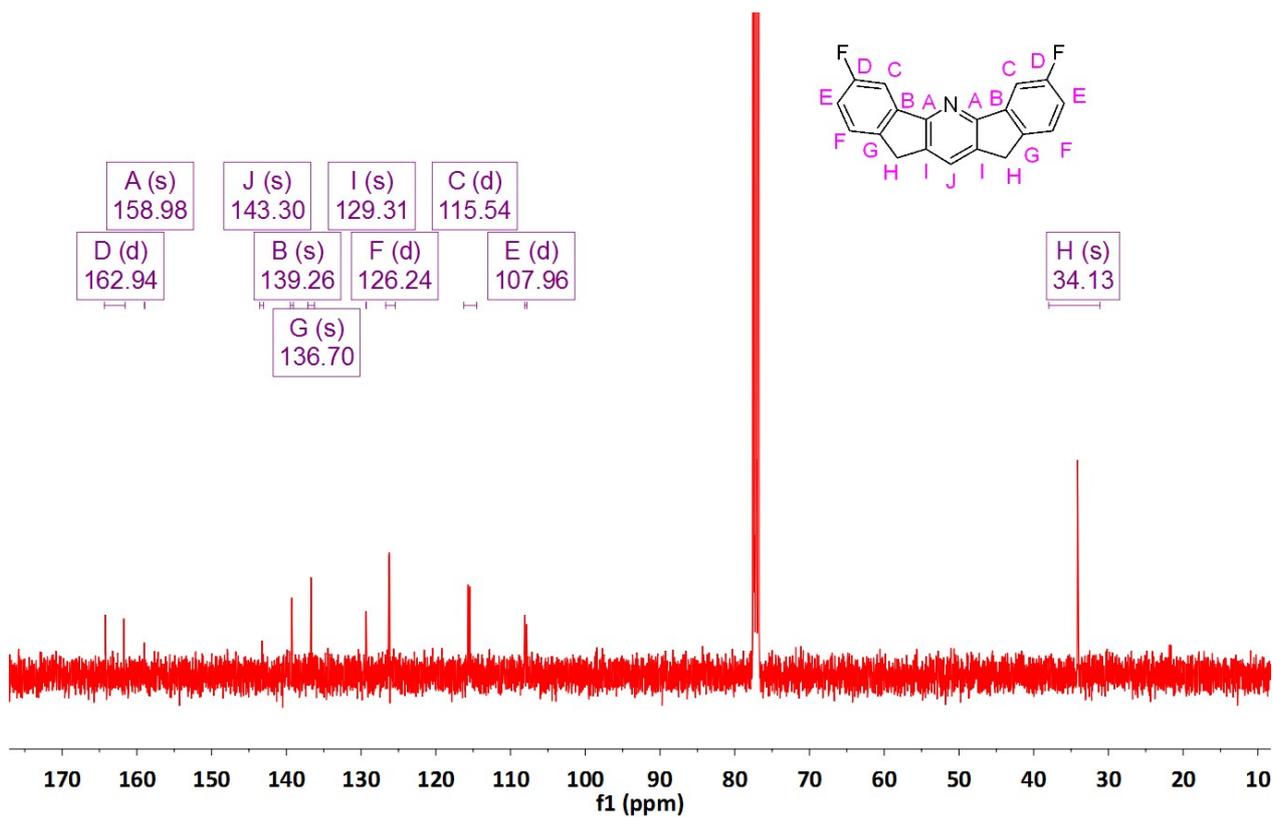
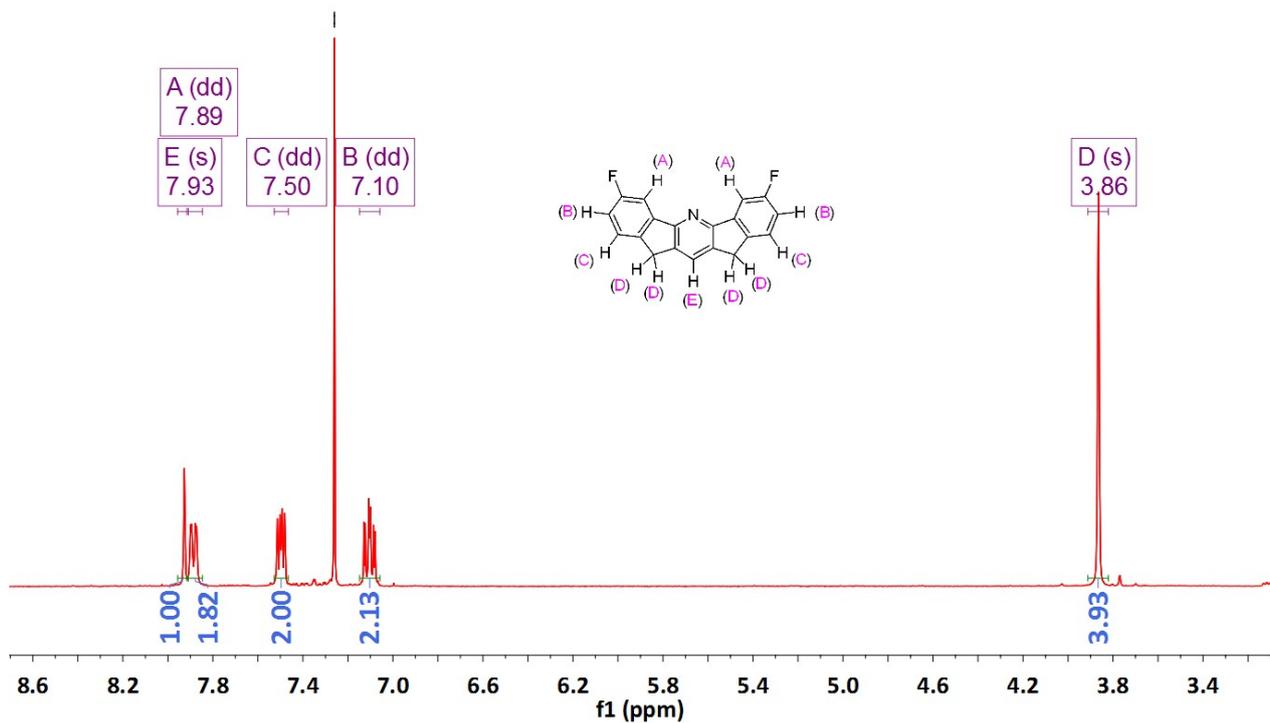
3,7-Dibromo-10,12-dihydroindiino[1,2-b:2',1'-e]pyridine (2e)



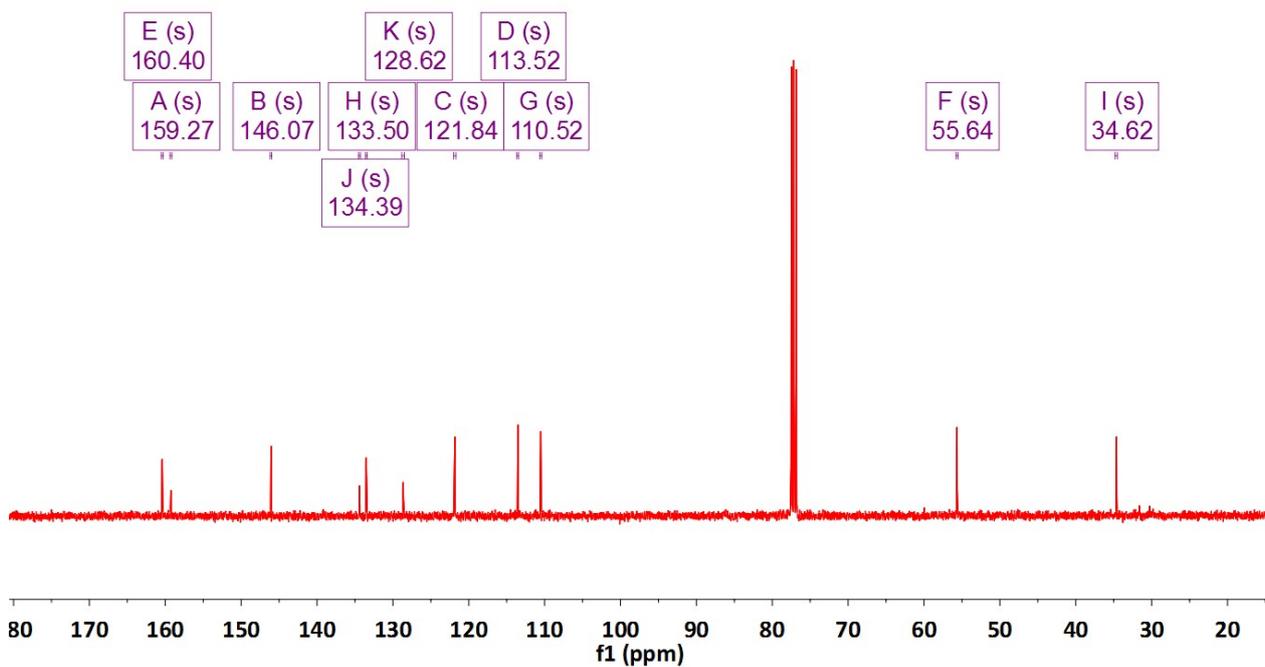
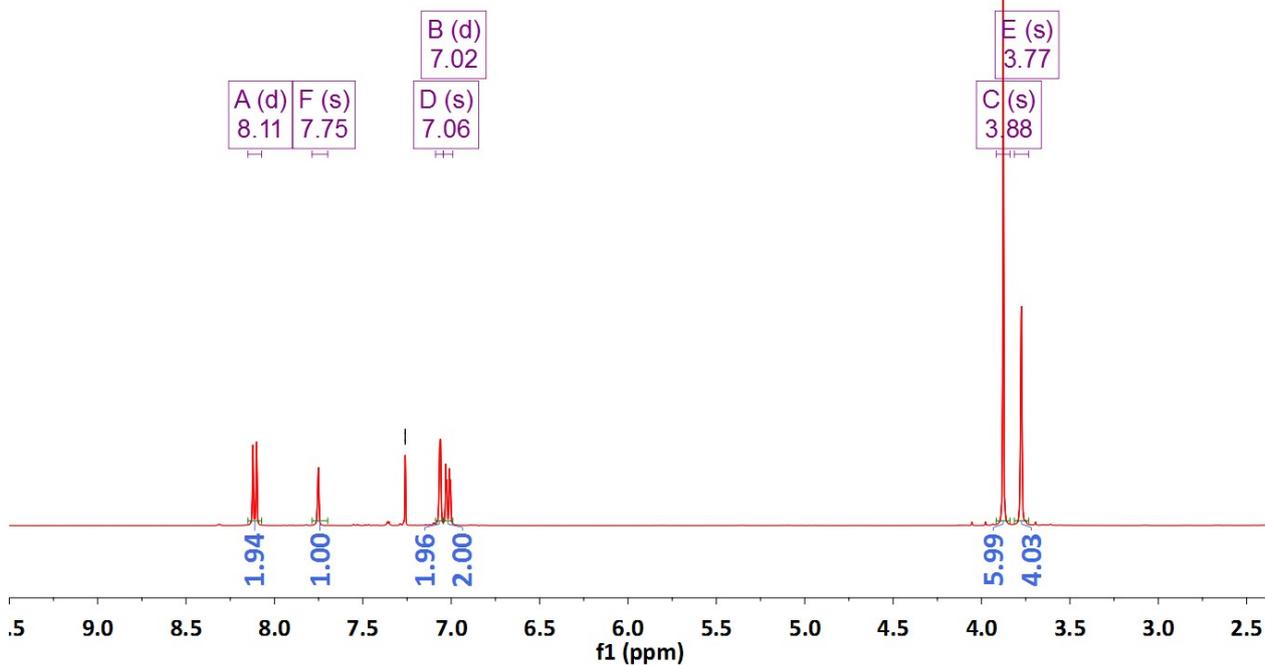
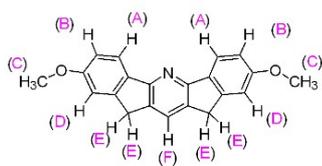
3,7-Dichloro-10,12-dihydroindeno[1,2-b:2',1'-e]pyridine (2f)



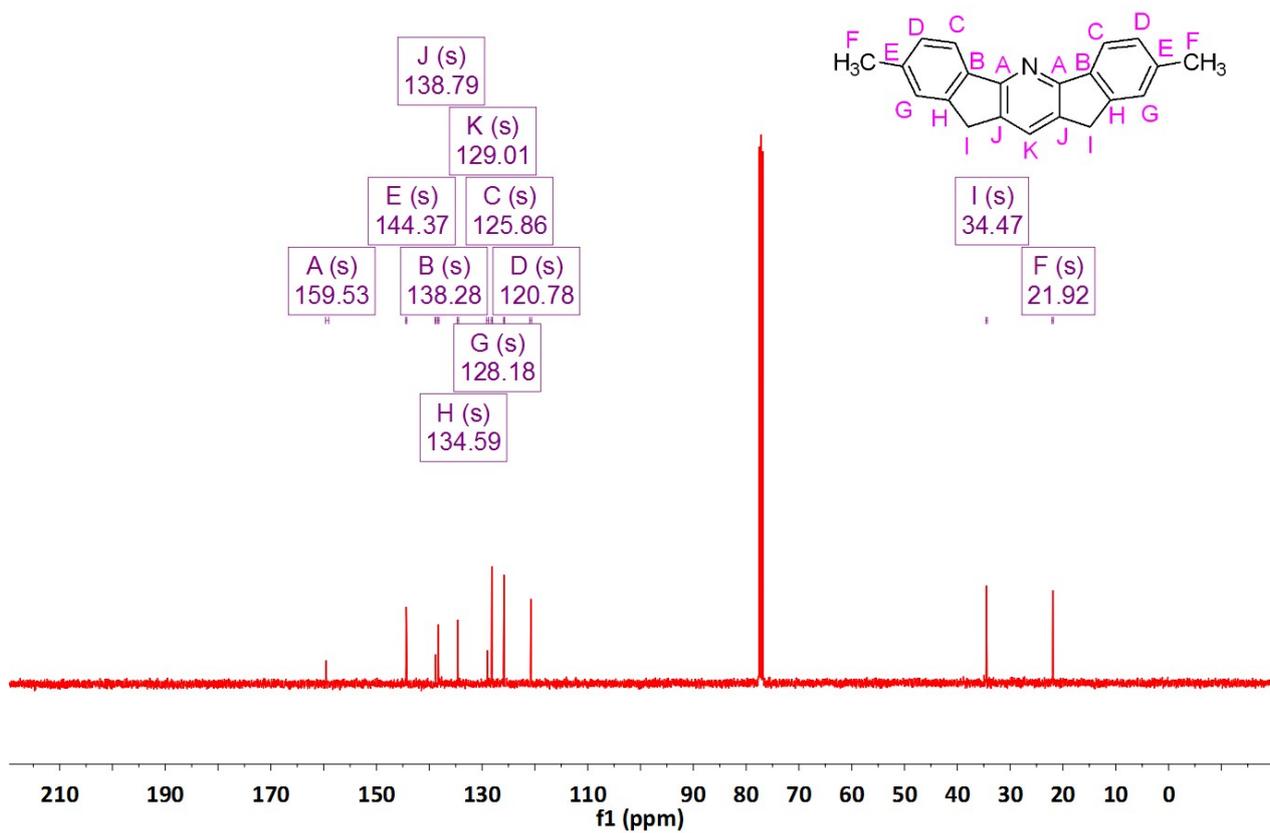
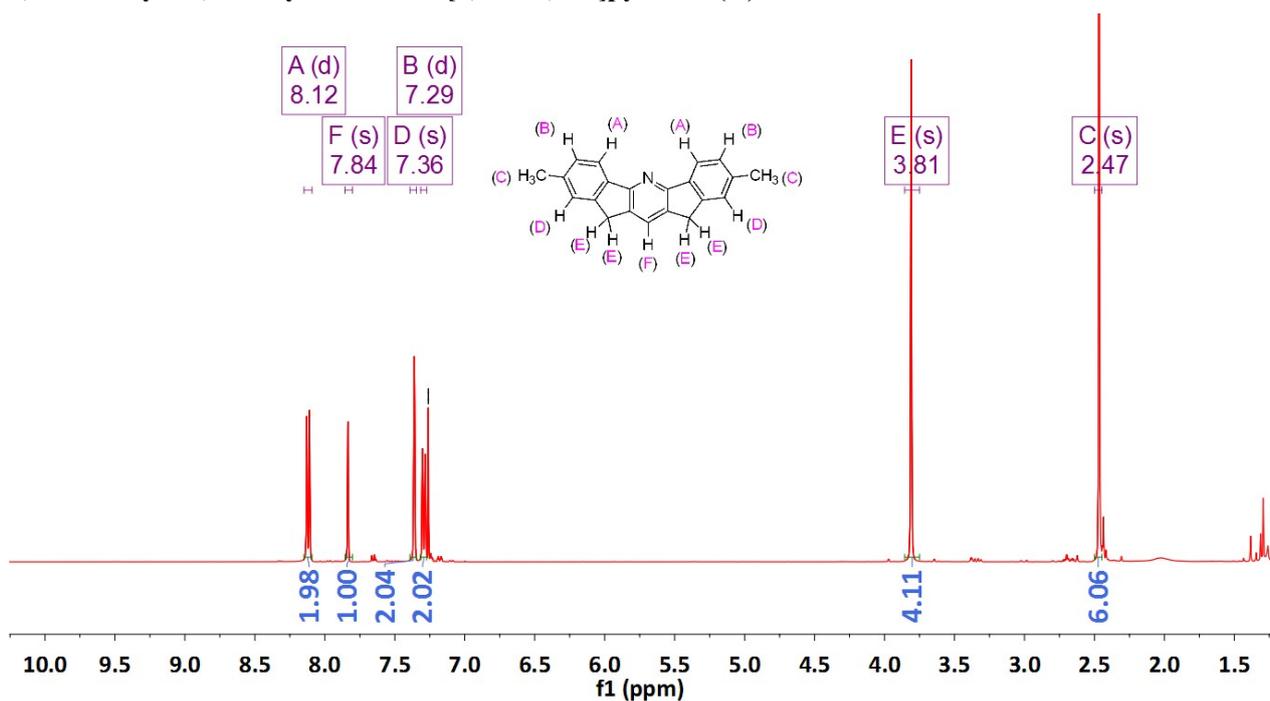
3,7-Difluoro-10,12-dihydroindiindeno[1,2-b:2',1'-e]pyridine (2g)



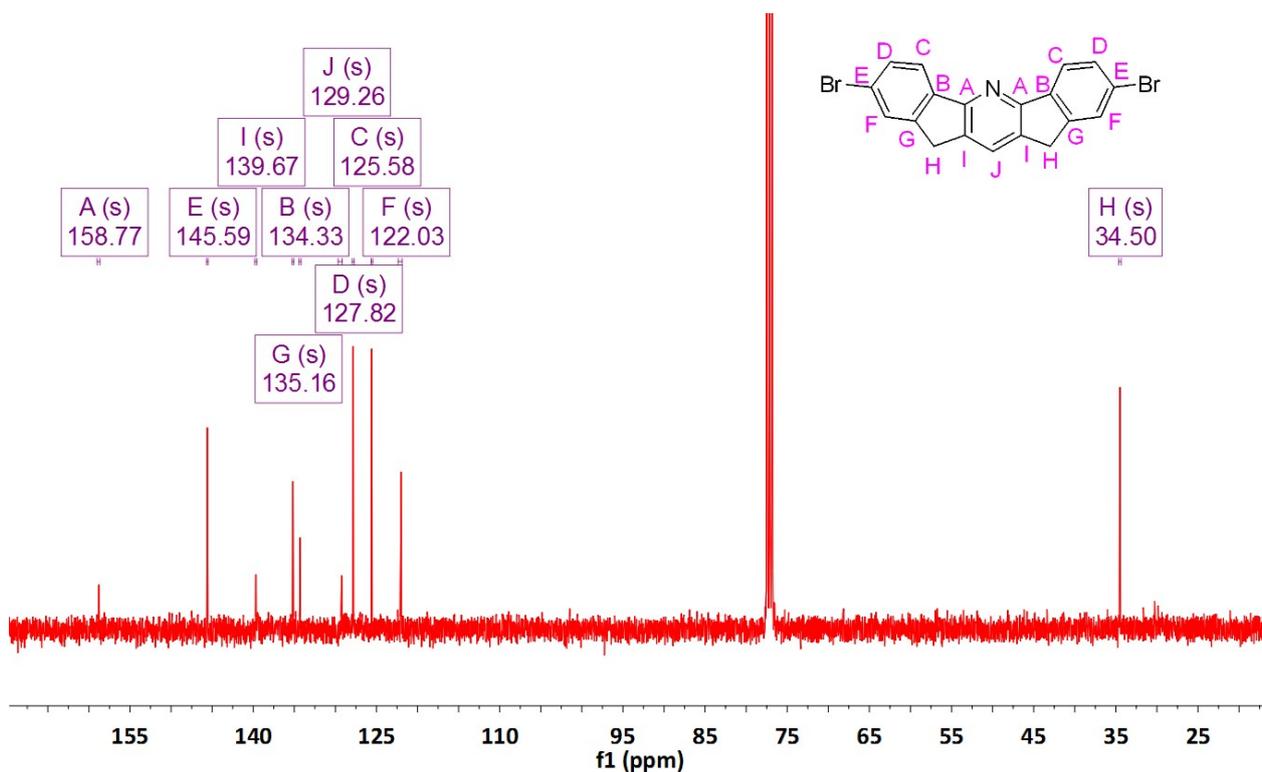
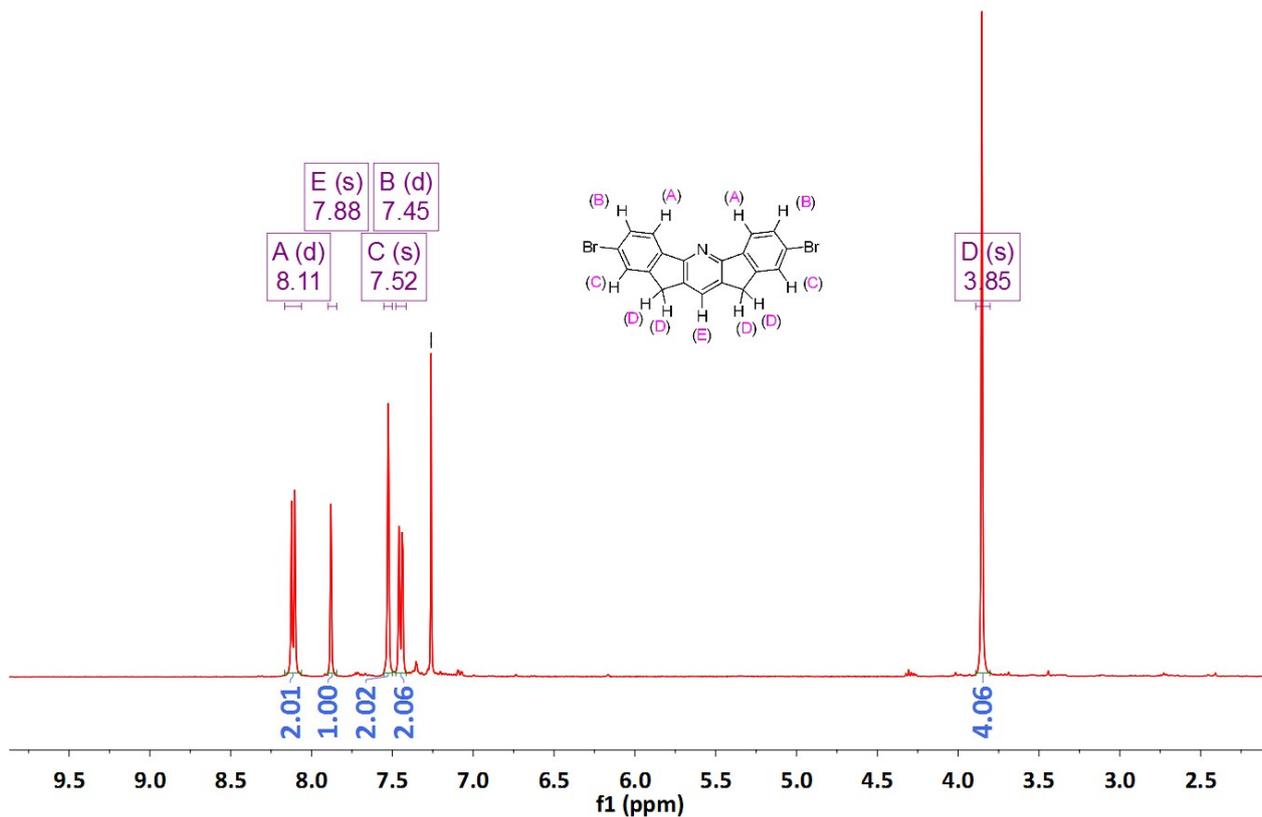
2,8-Dimethoxy-10,12-dihydroindeno[1,2-b:2',1'-e]pyridine (2h)



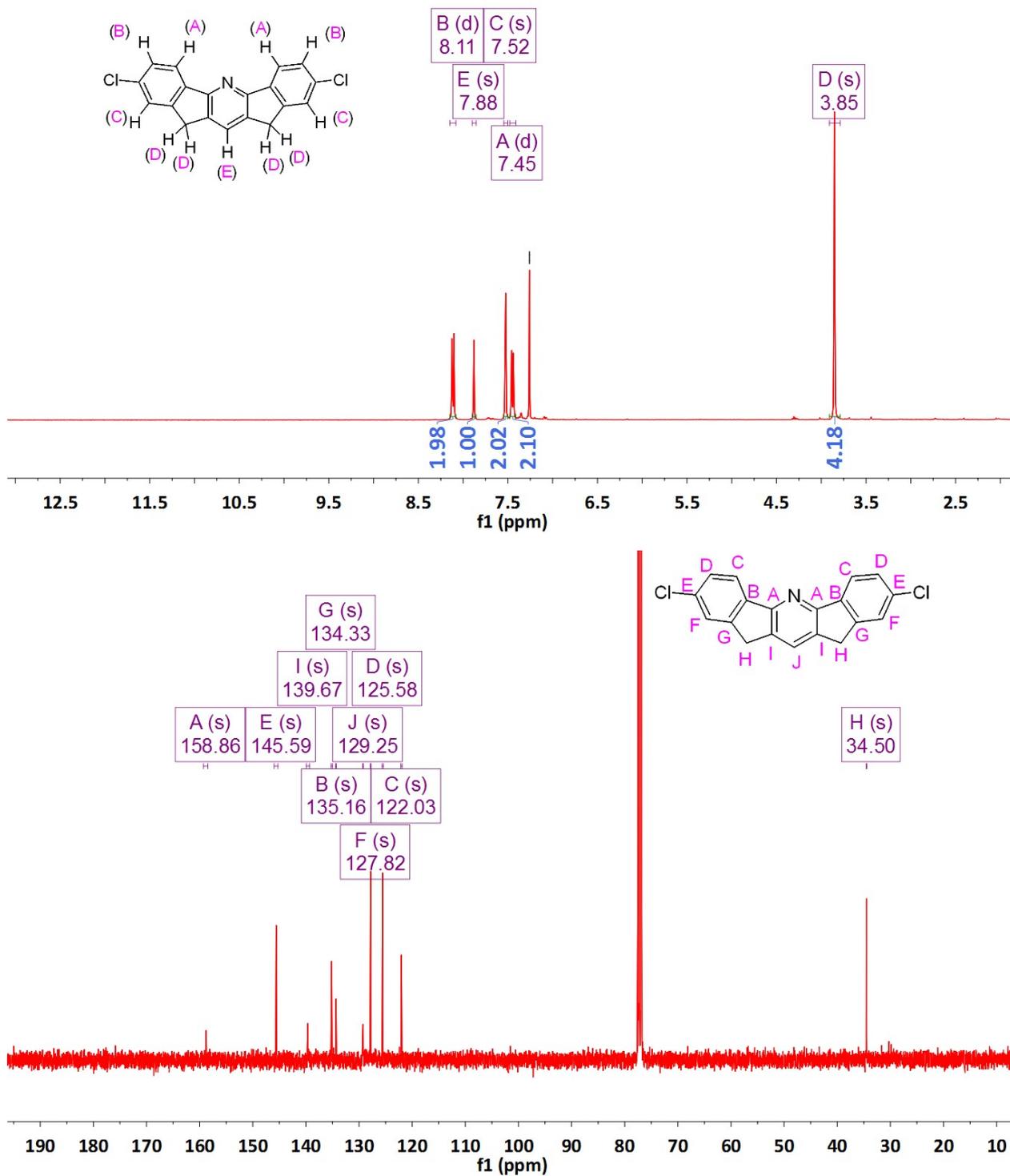
2,8-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2i)



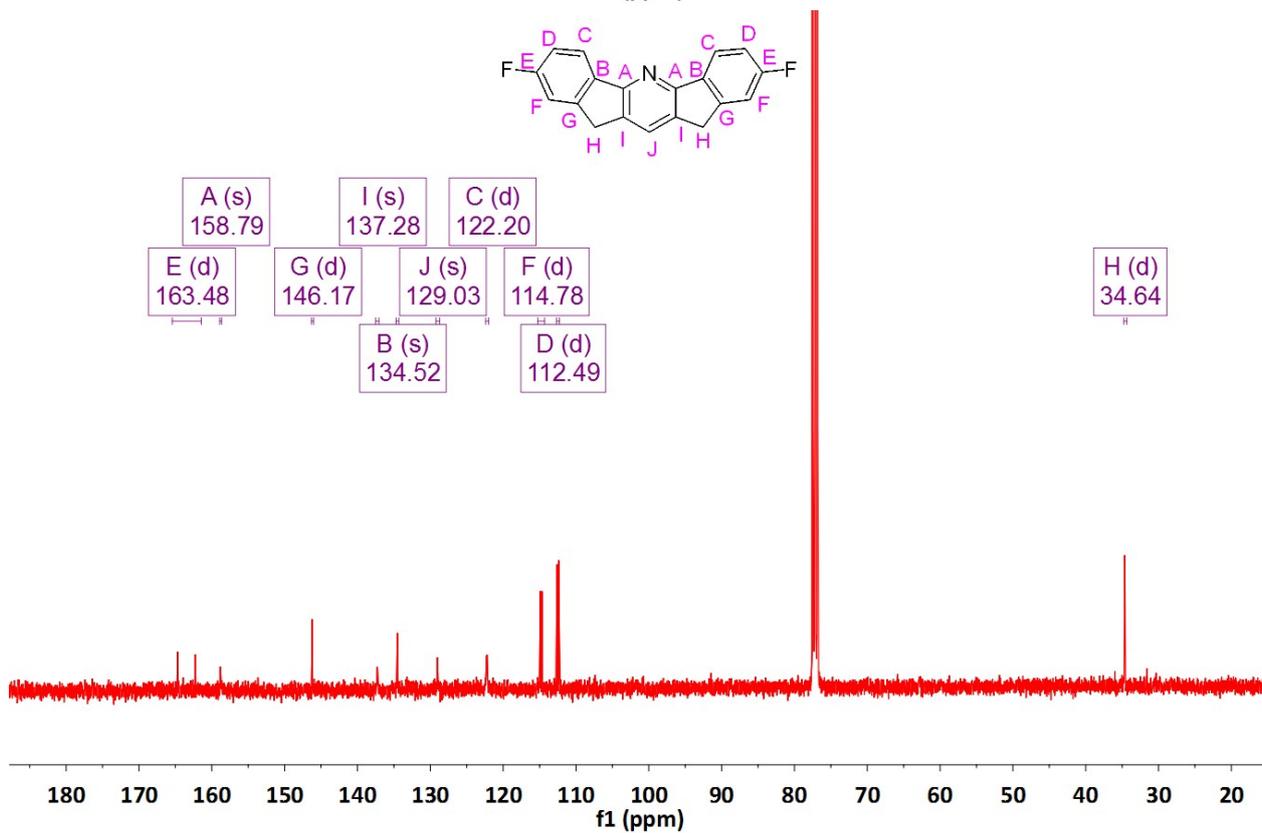
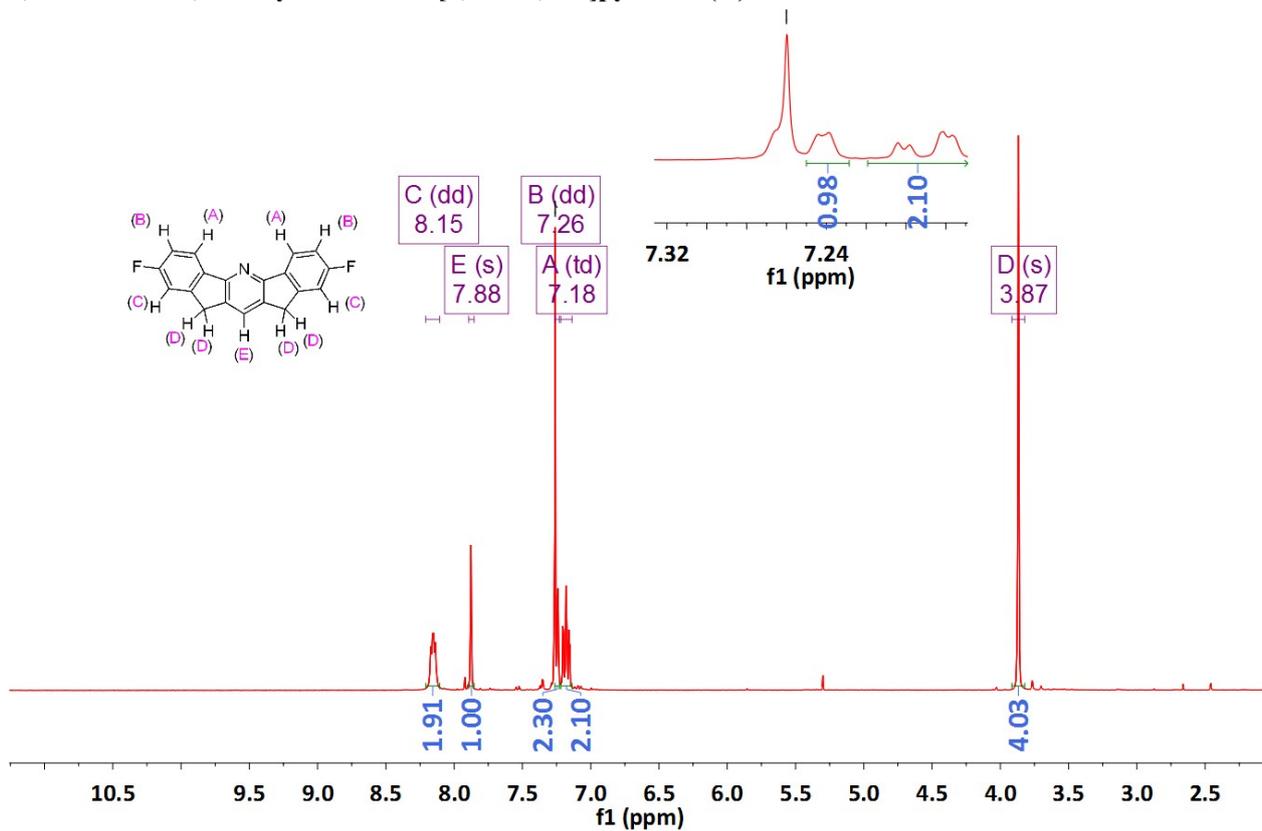
2,8-Dibromo-10,12-dihydroindeno[1,2-b:2',1'-e]pyridine (2j)



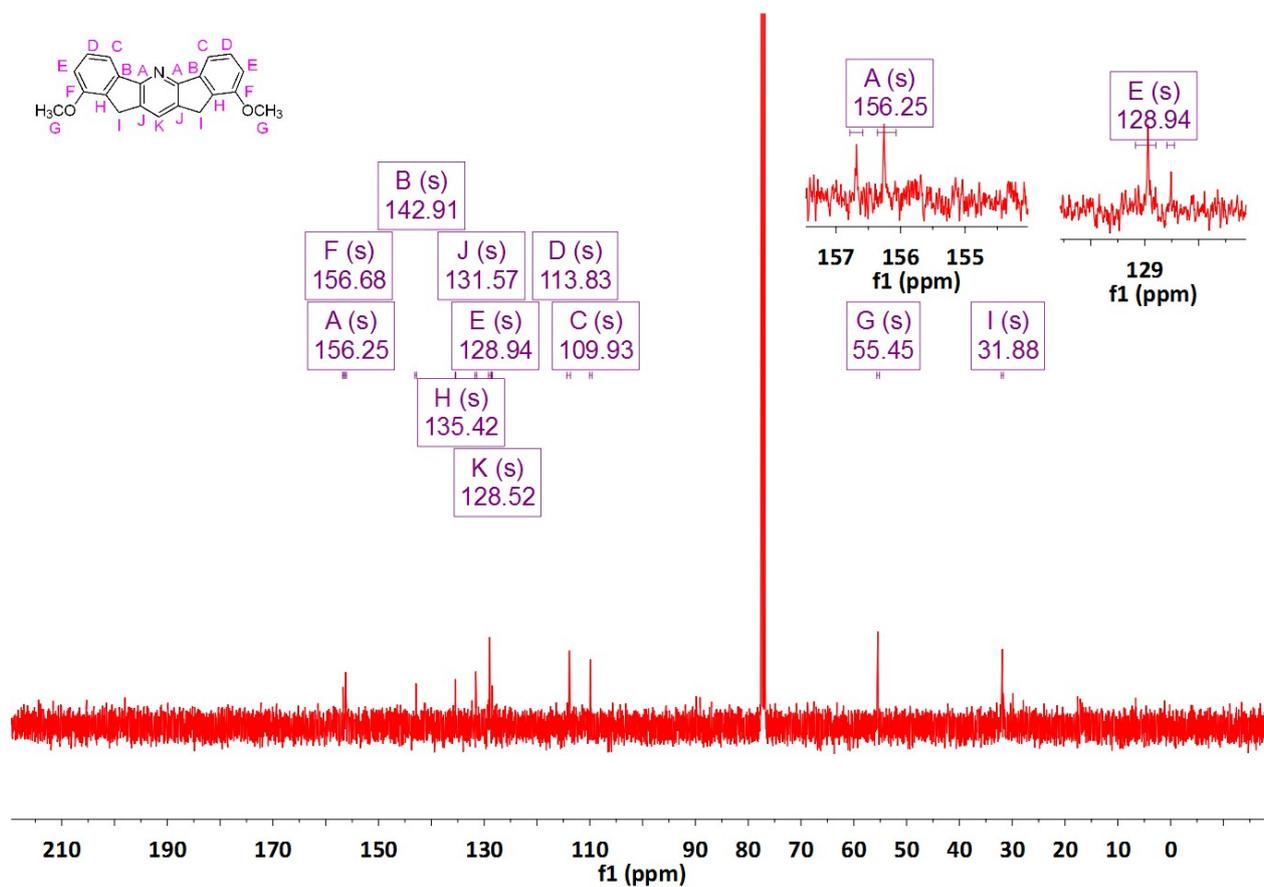
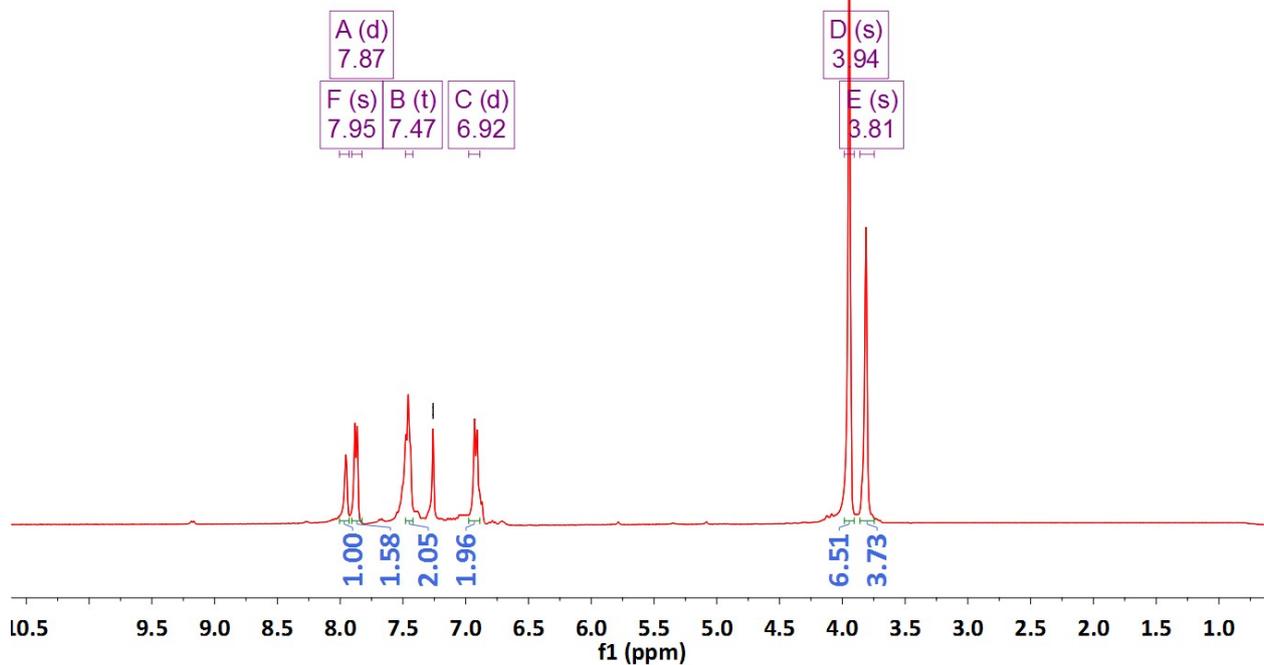
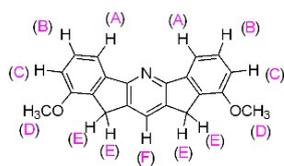
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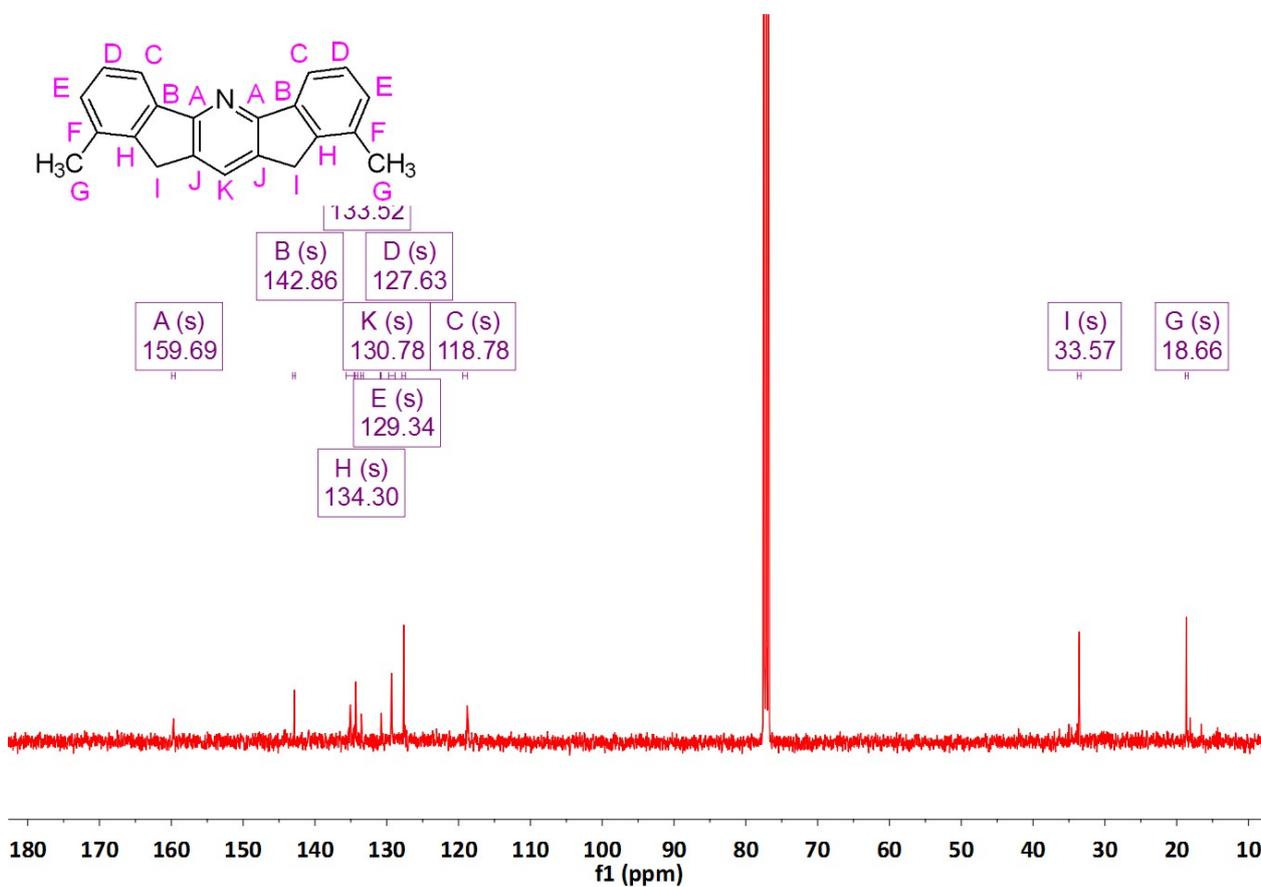
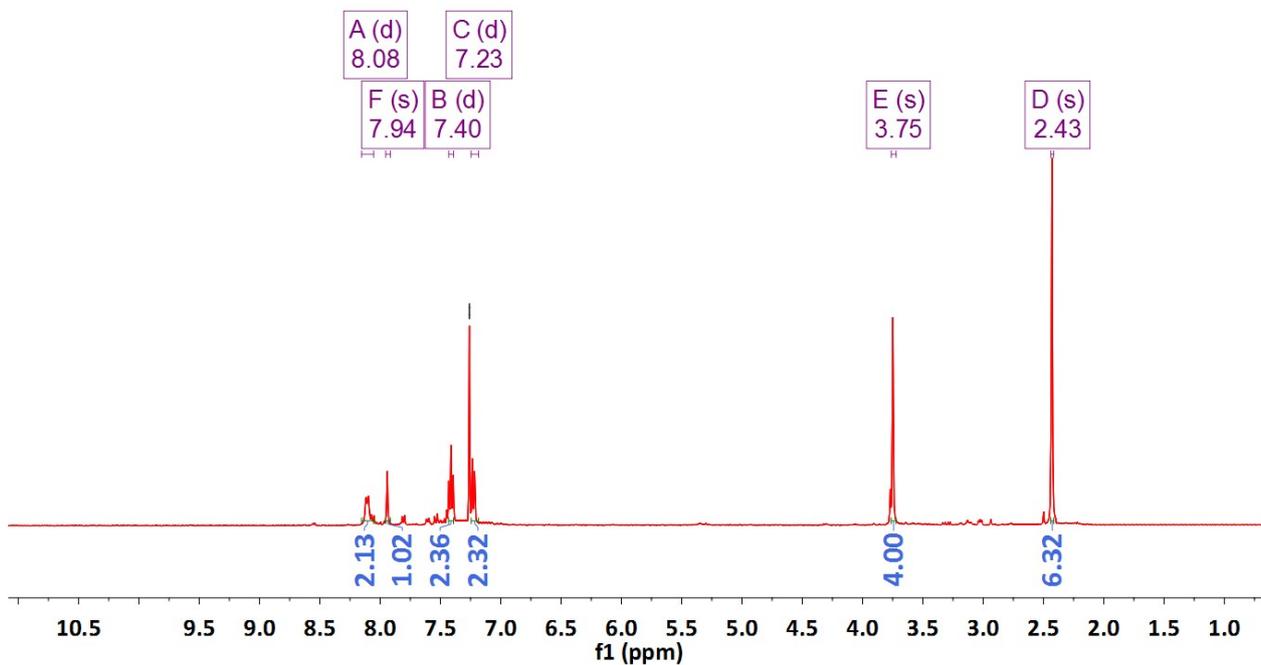
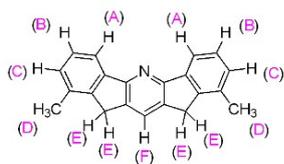
2,8-Difluoro-10,12-dihydroindiindeno[1,2-b:2',1'-e]pyridine (2l)



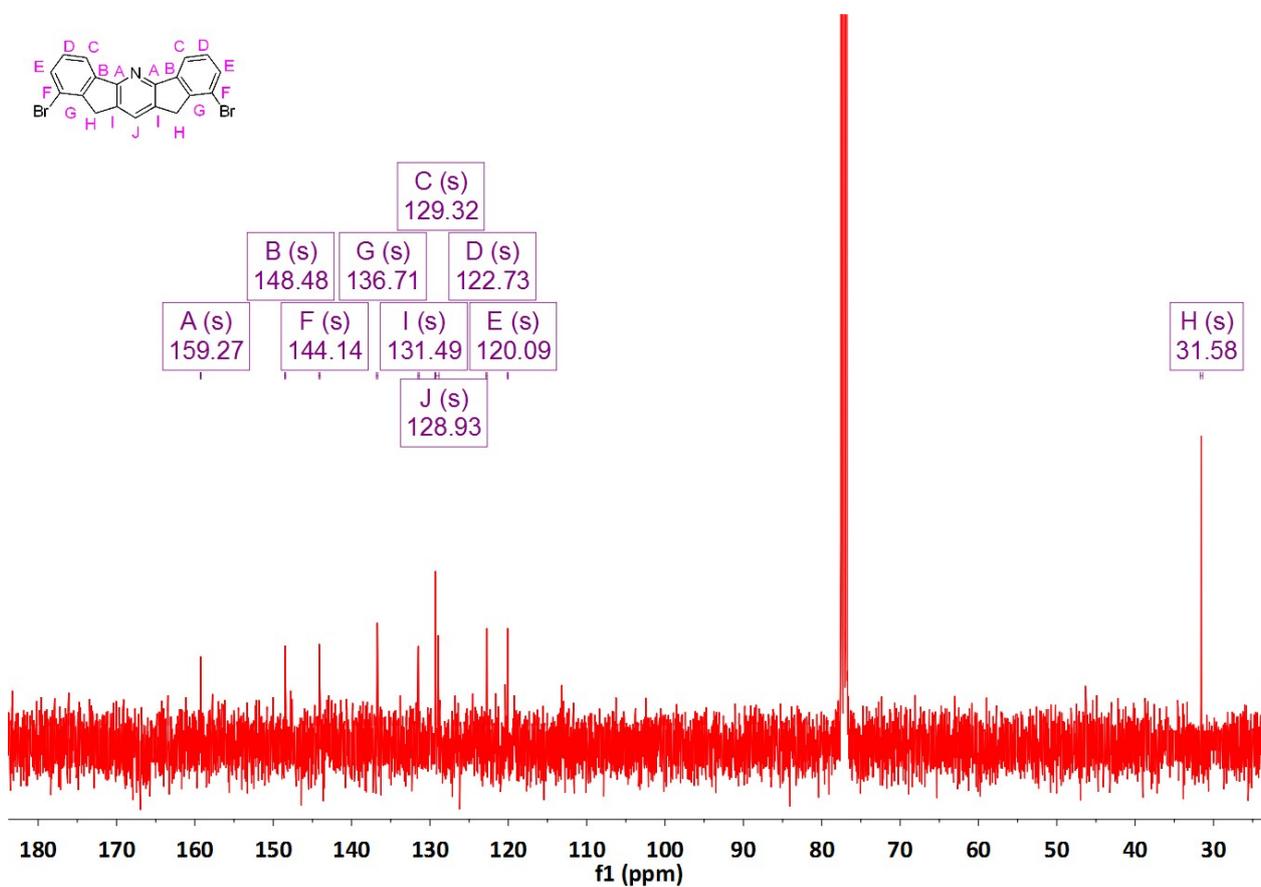
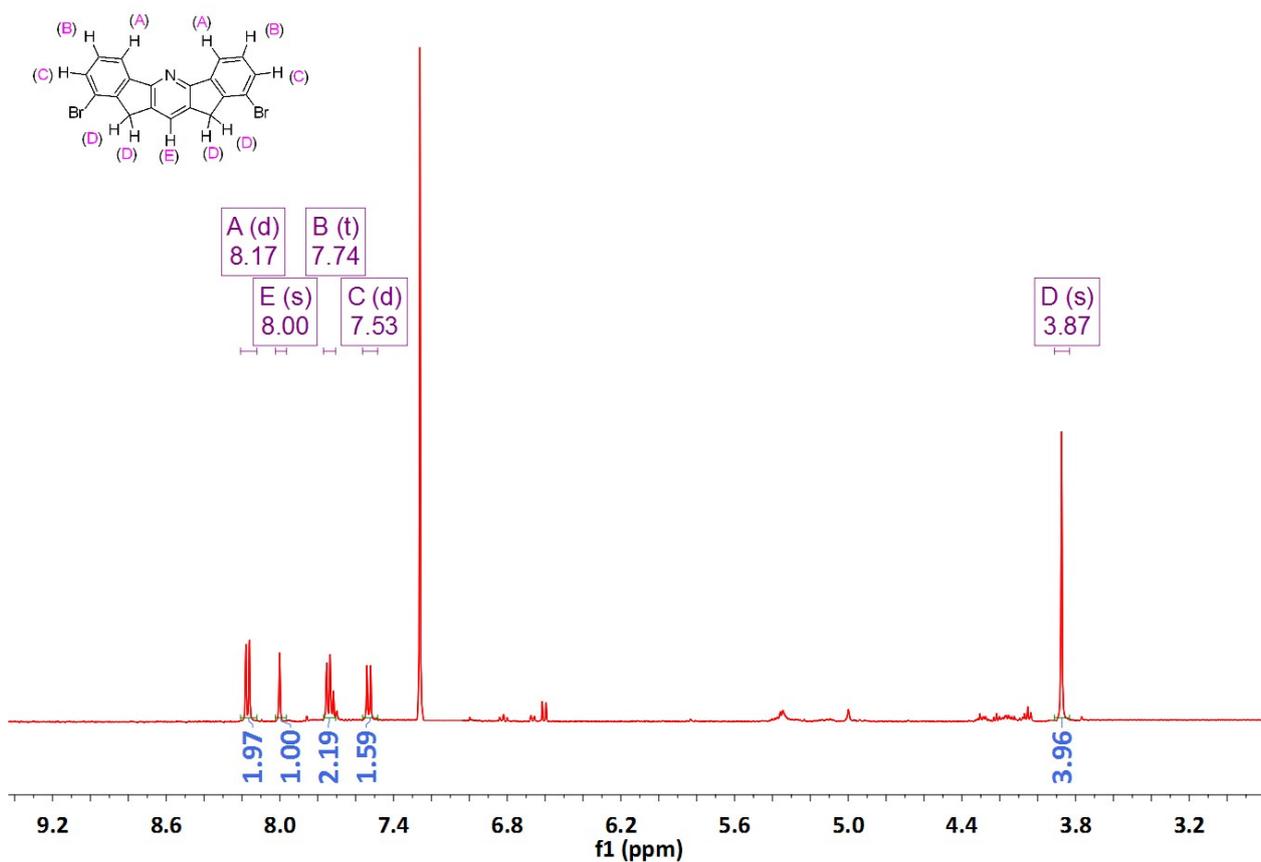
**1,9-Dimethoxy-10,12-dihydroindeno[1,2-b:2',1'-e]pyridine (2m)**



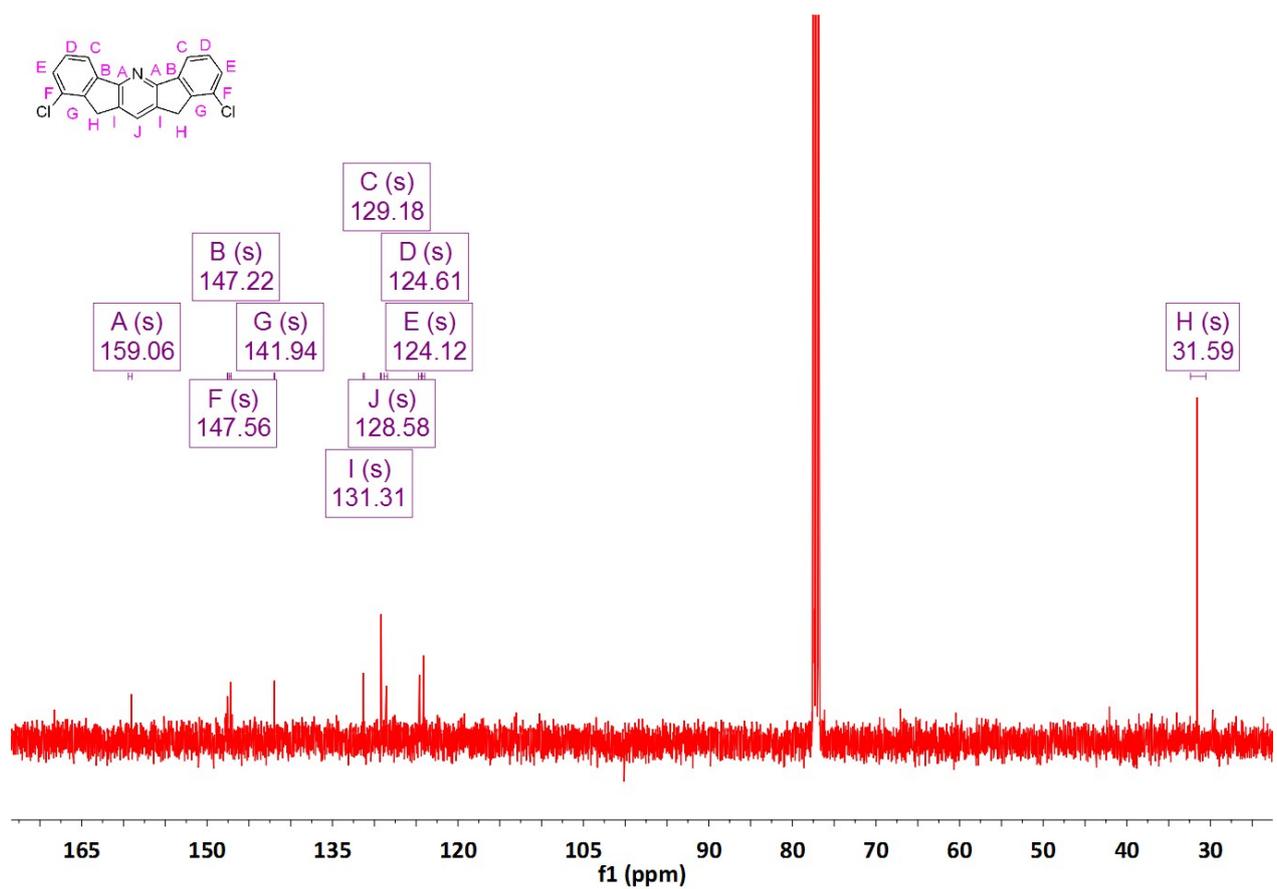
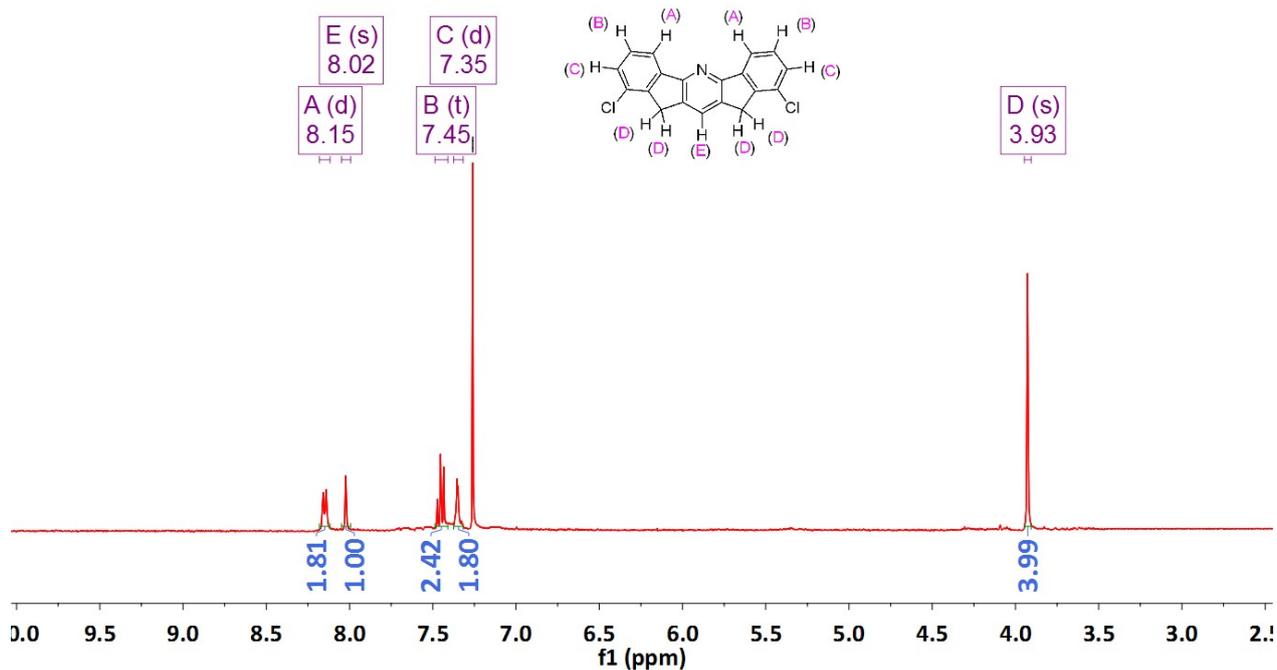
**1,9-Dimethyl-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2n)**



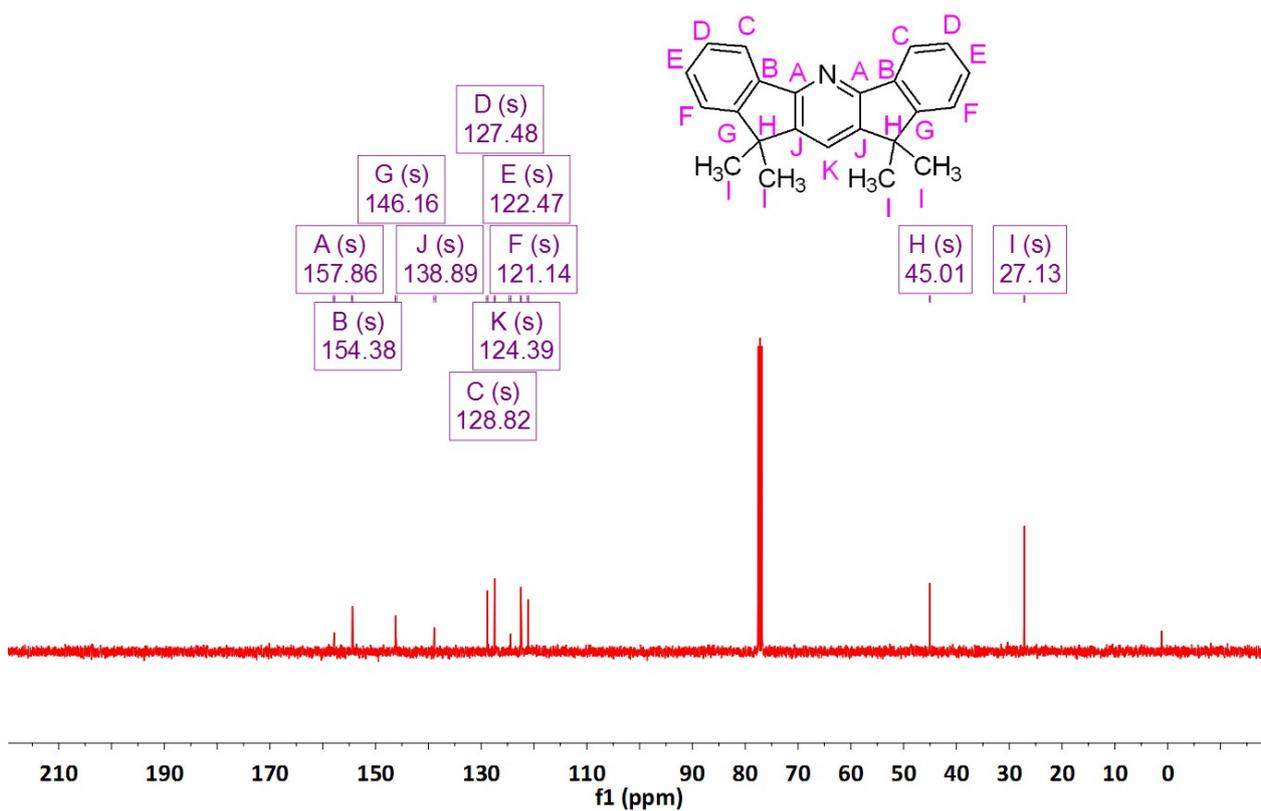
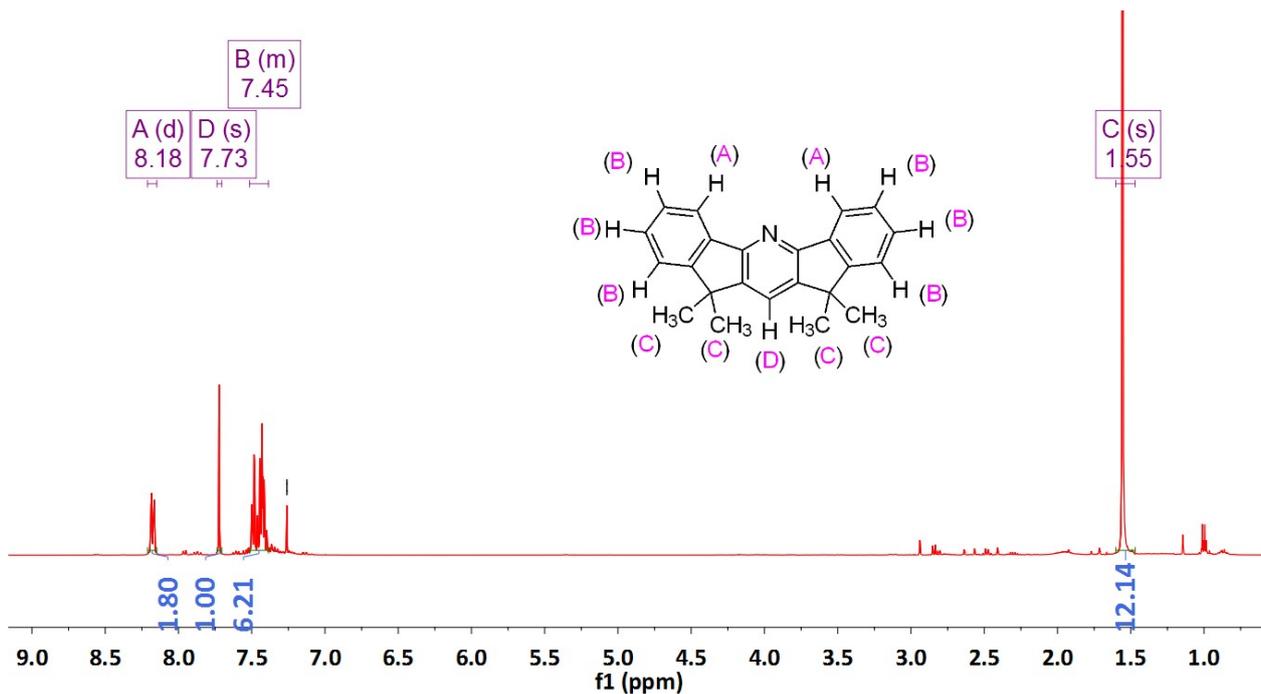
# 1,9-Dibromo-10,12-dihydrodiindeno[1,2-b:2',1'-e]pyridine (2o)



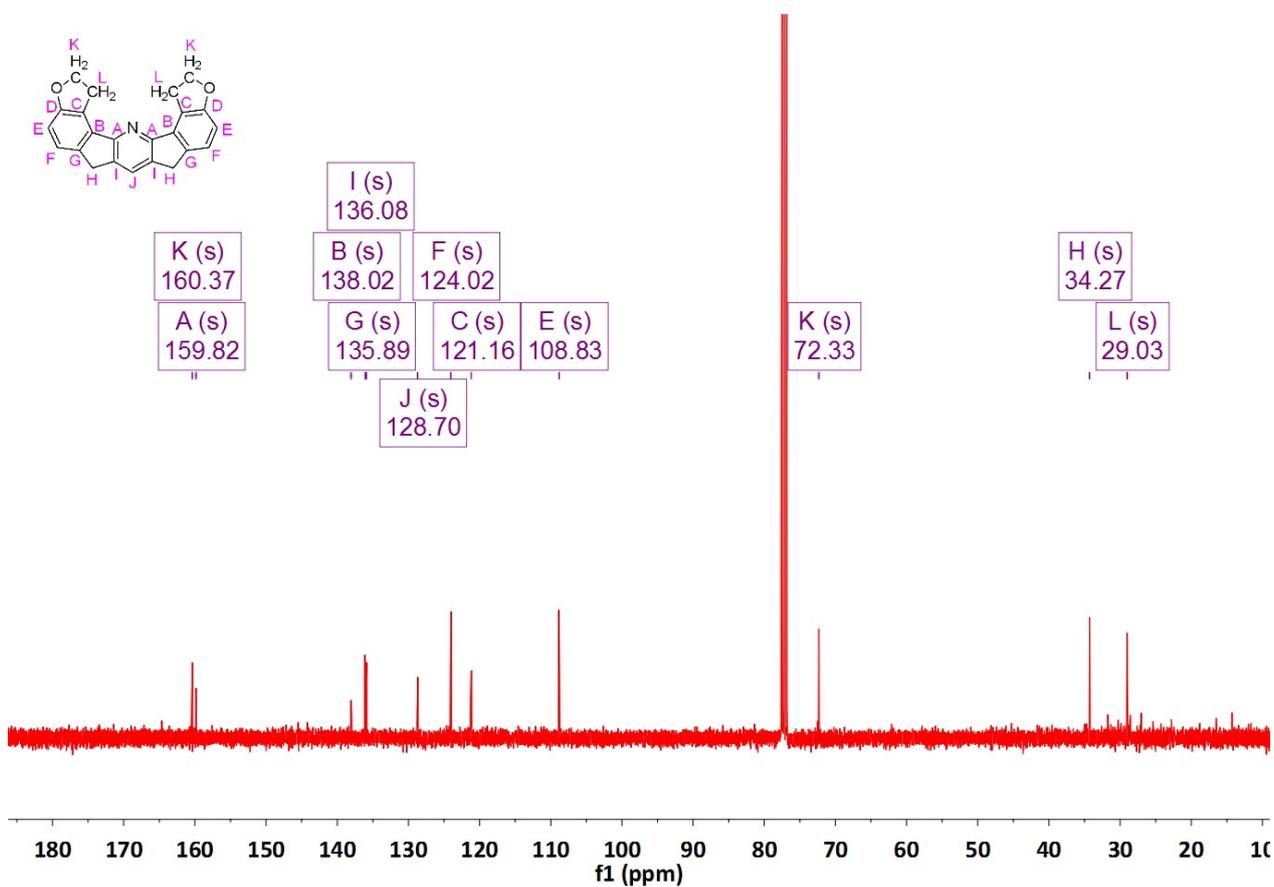
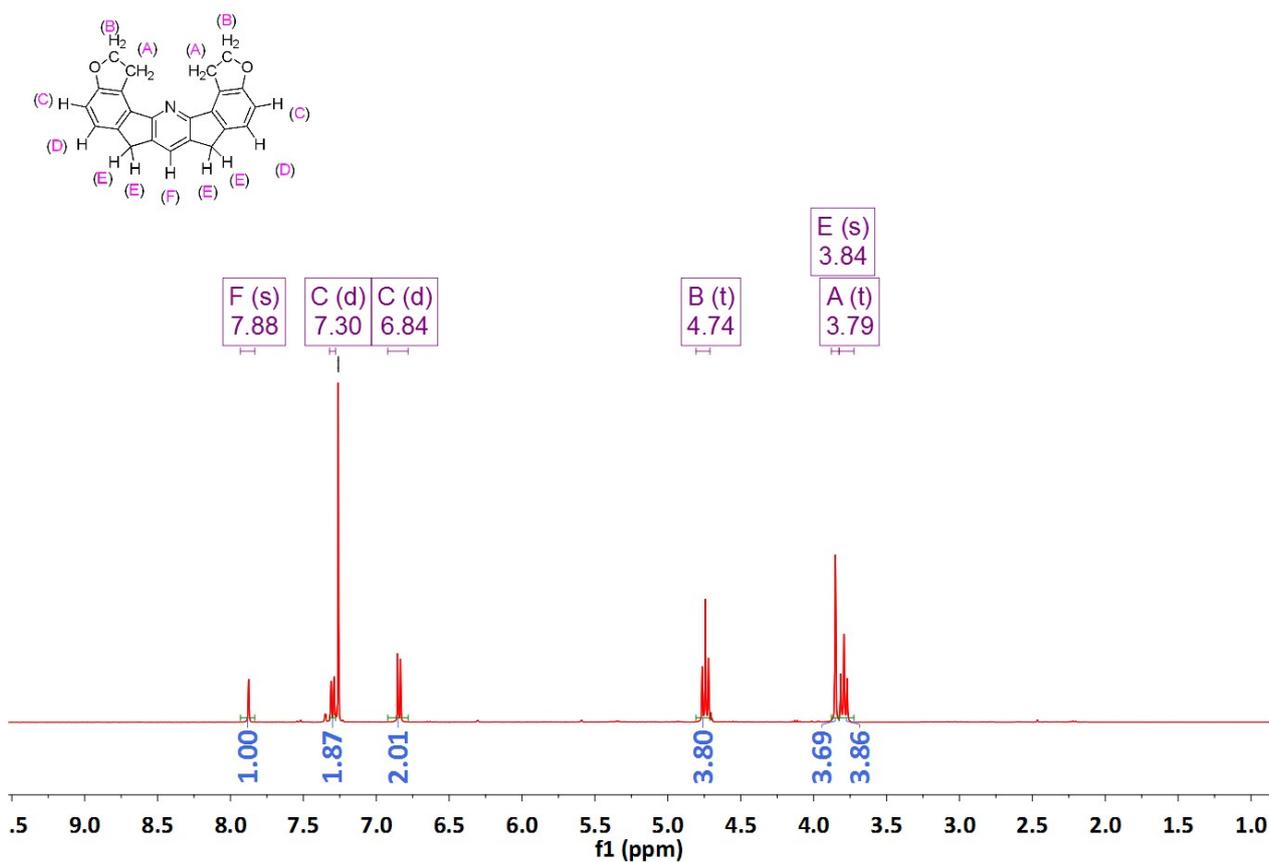
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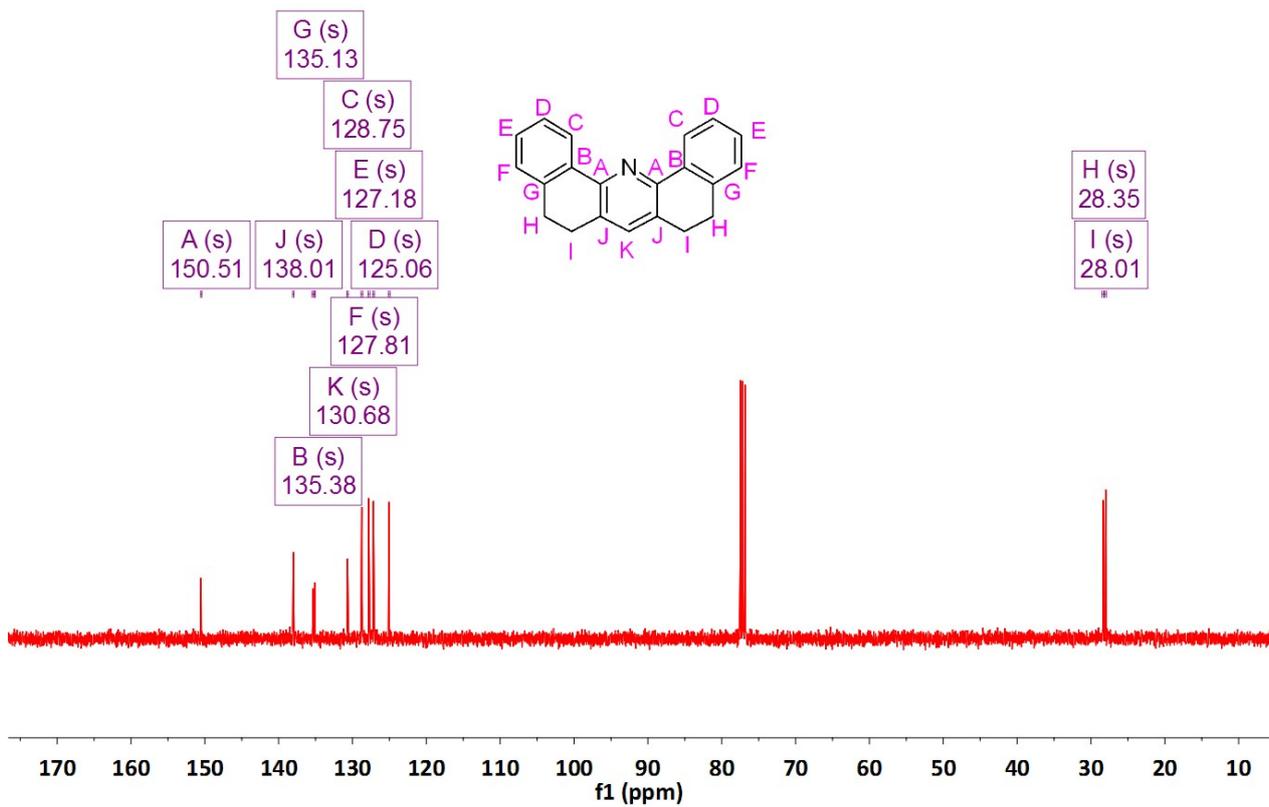
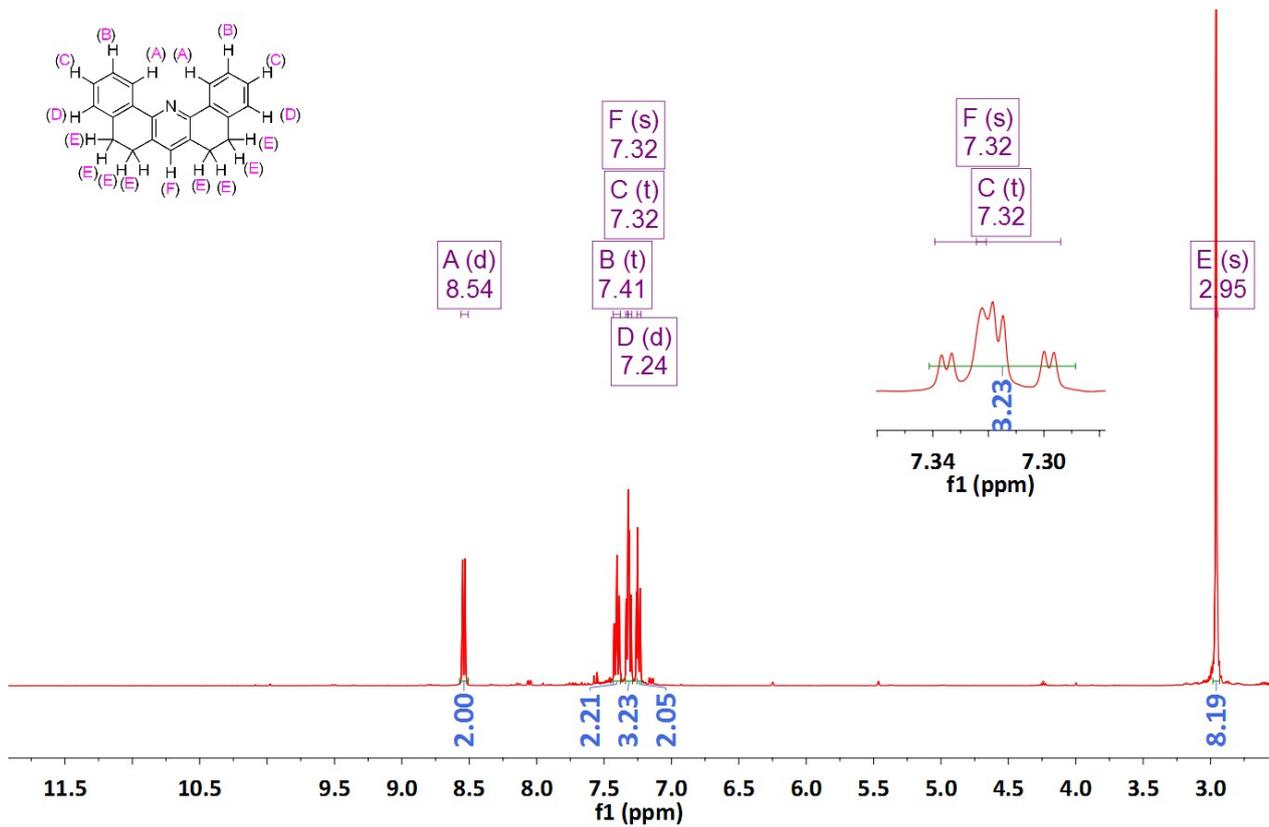
10,10,12,12-Tetramethyl-10,12-dihydroindeno[1,2-b:2',1'-e]pyridine (2q)



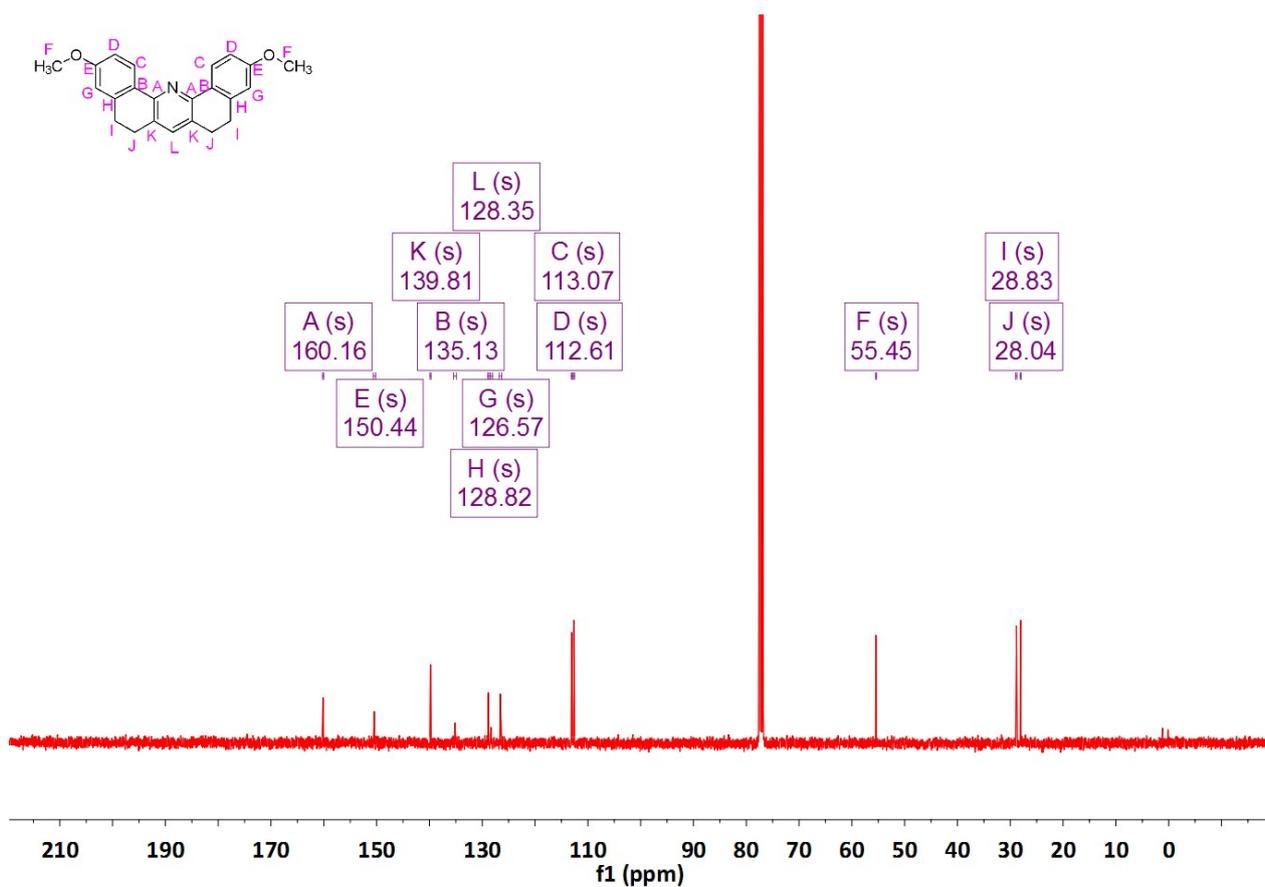
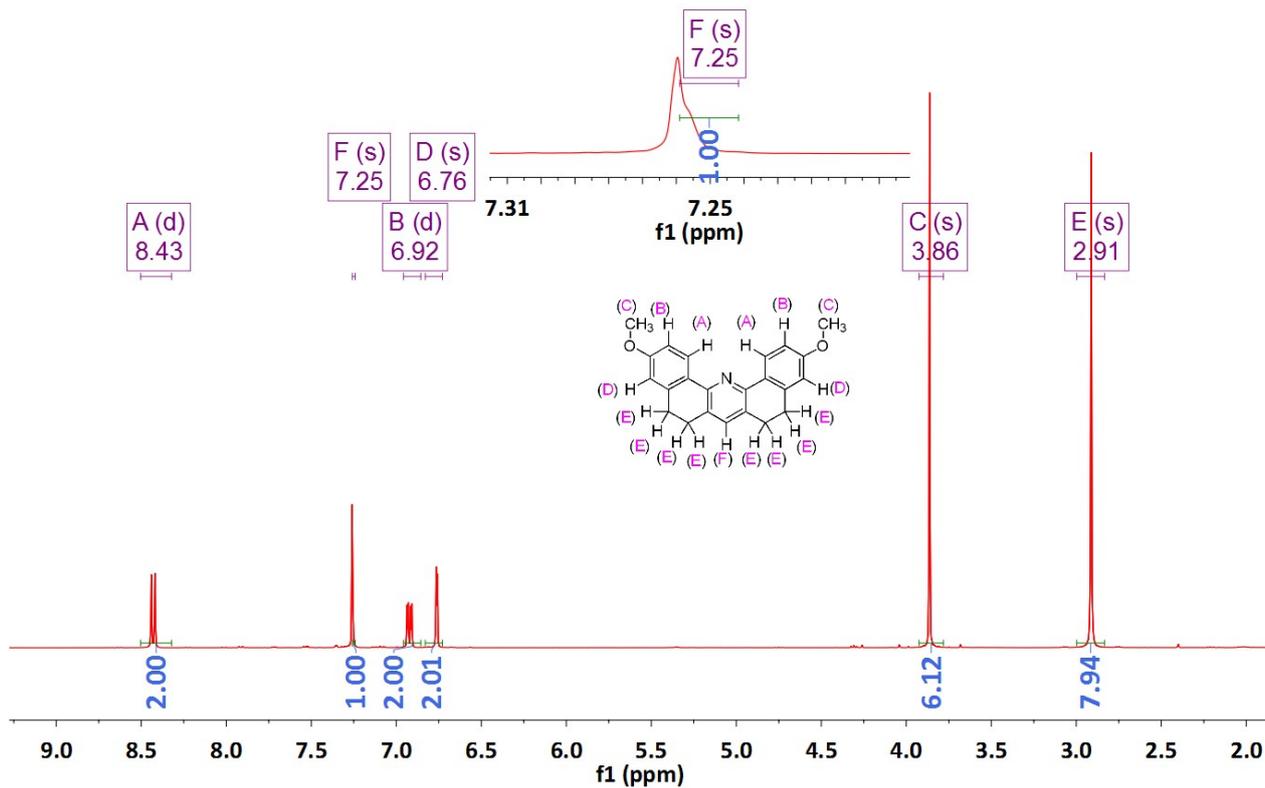
1,2,6,8,12,13-Hexahydrofuro[2',3':6,7]indeno[1,2-b]furo[2',3':6,7]indeno[2,1-e]pyridine (2r)



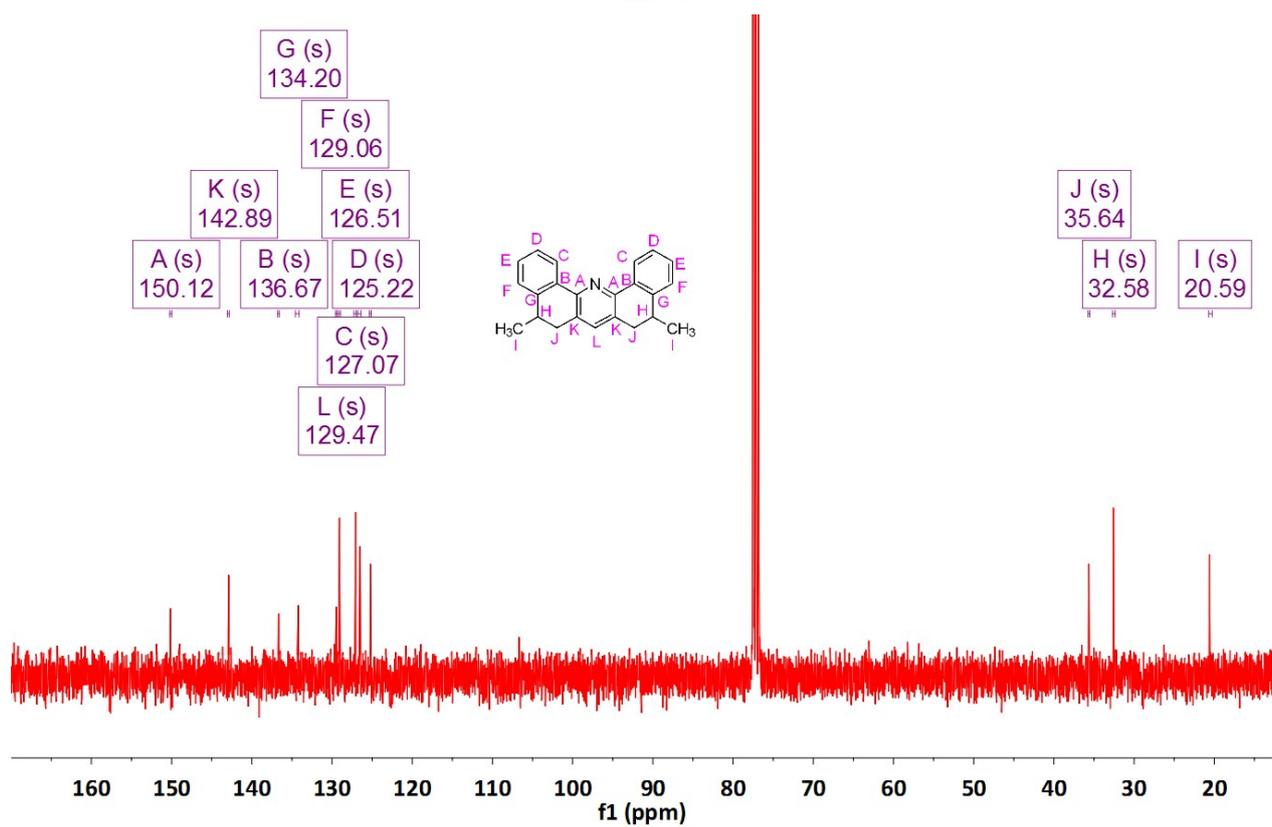
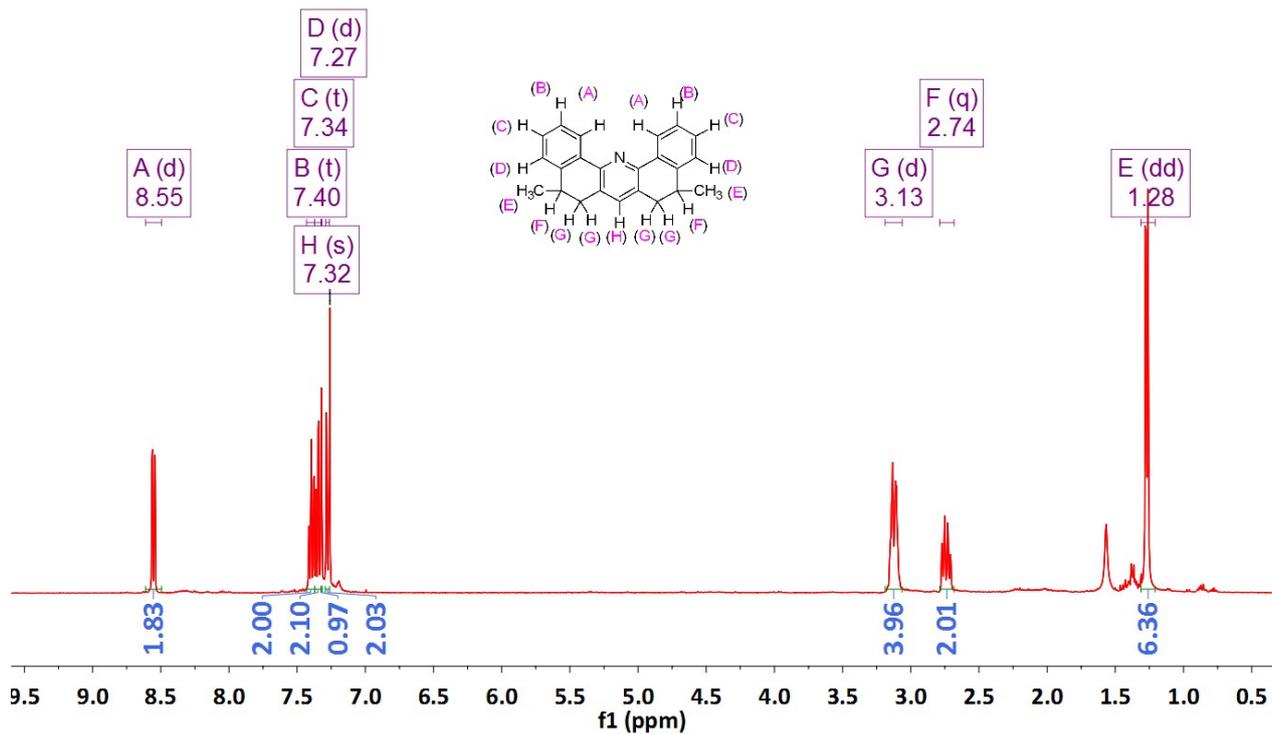
5,6,8,9-Tetrahydrodibenzacridine (2s)



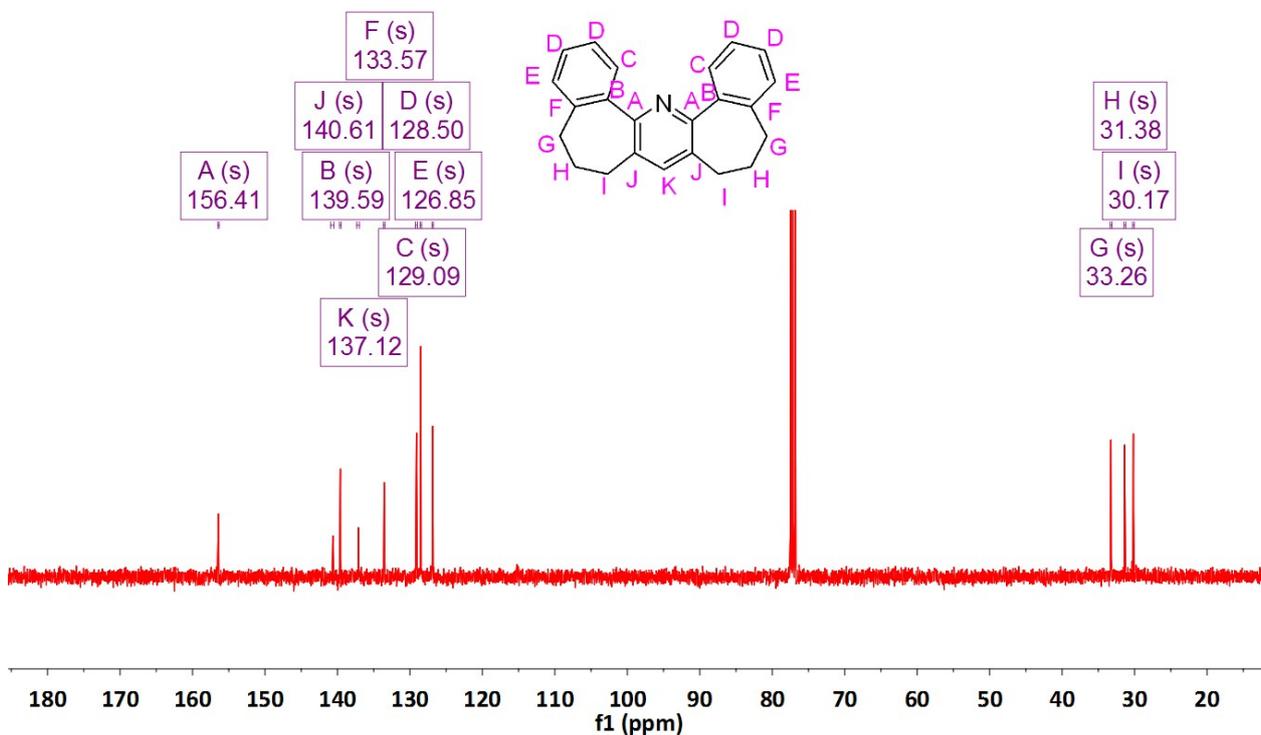
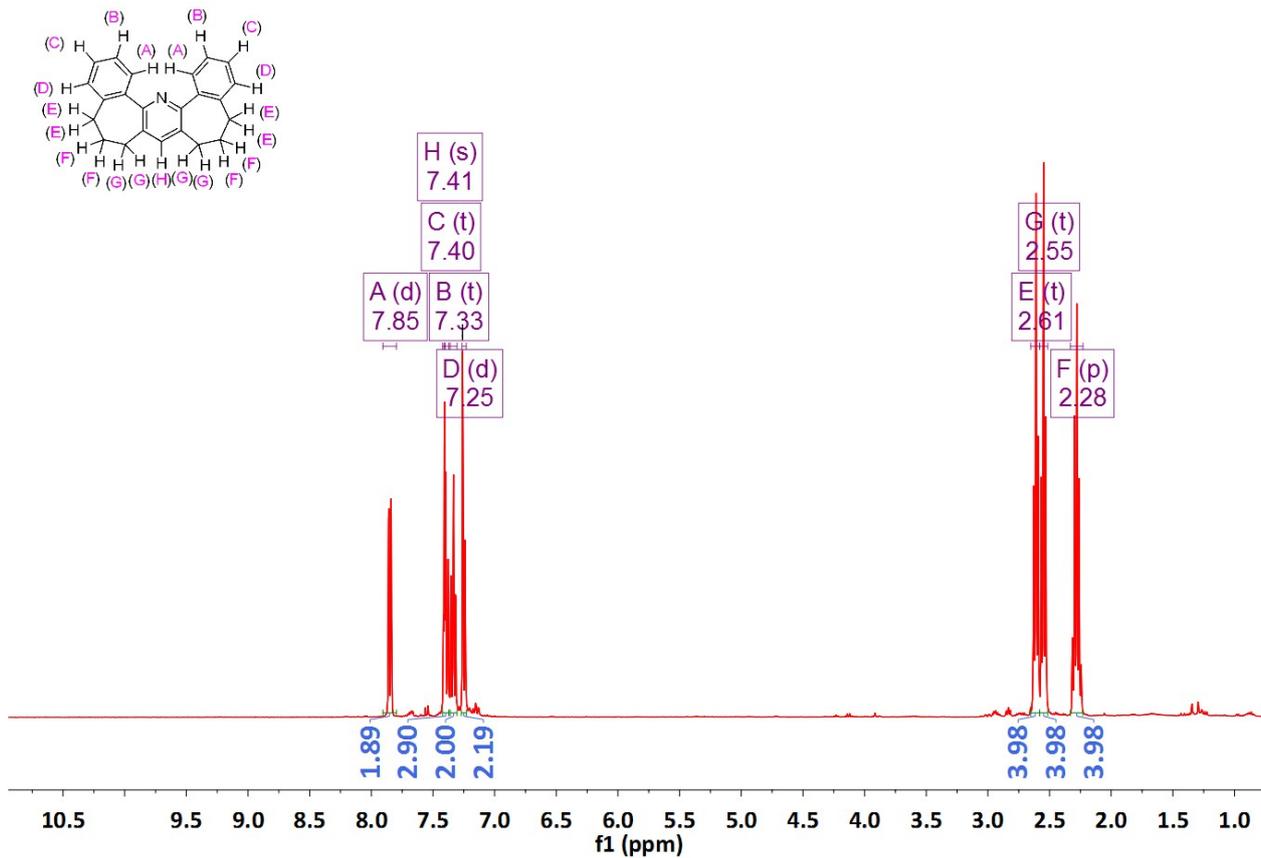
3,11-Dimethoxy-5,6,8,9-tetrahydrodibenzo[c,h]acridine (2t)



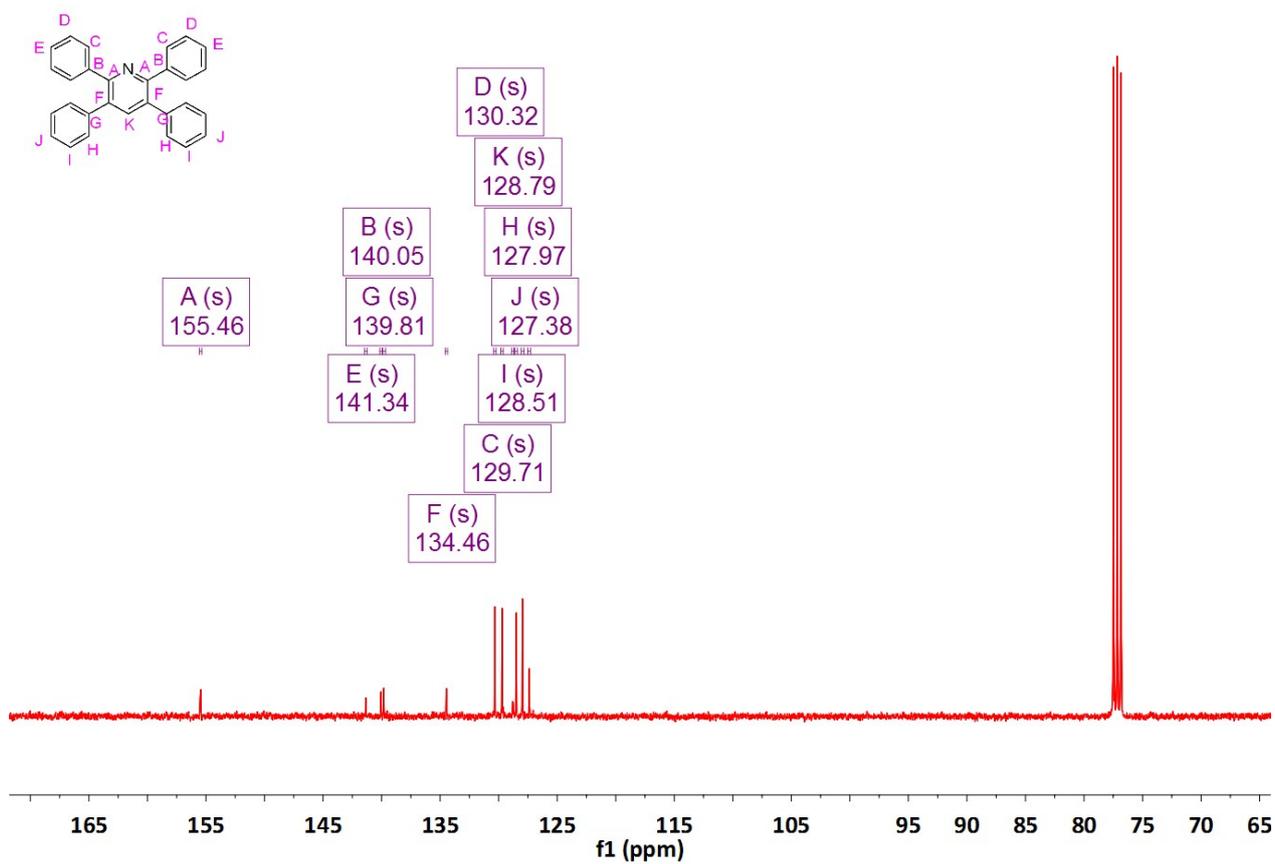
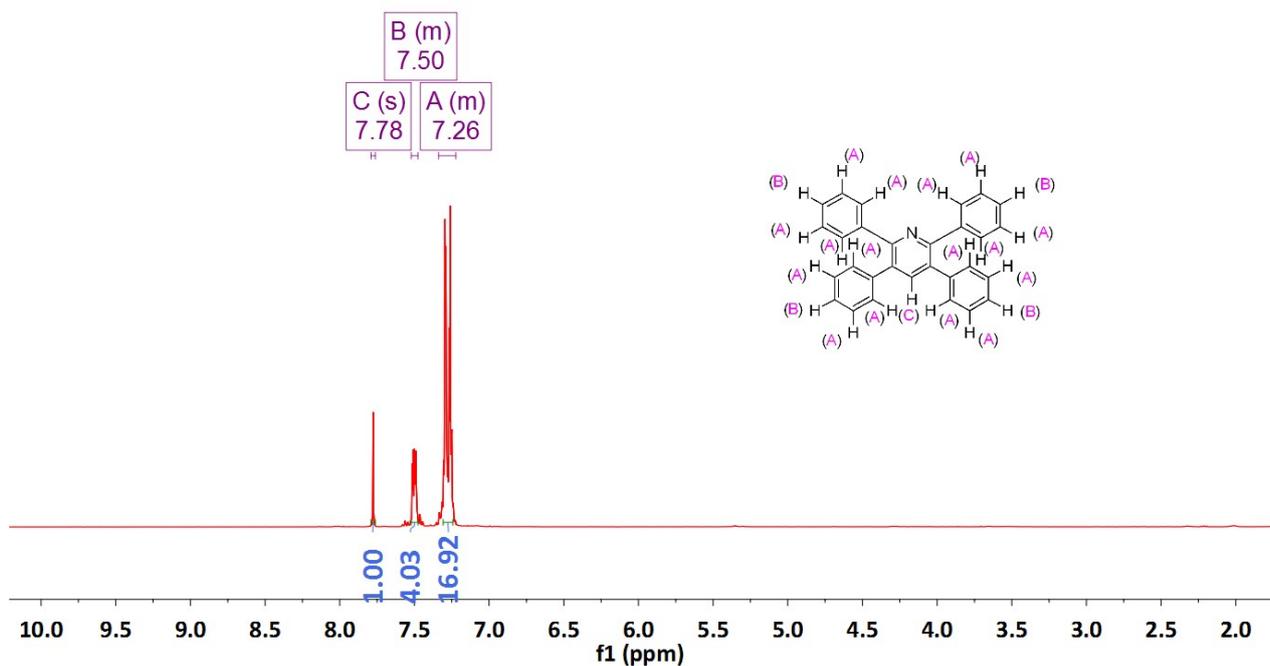
5,9-Dimethyl-5,6,8,9-tetrahydrobenzo[c,h]acridine (2u)



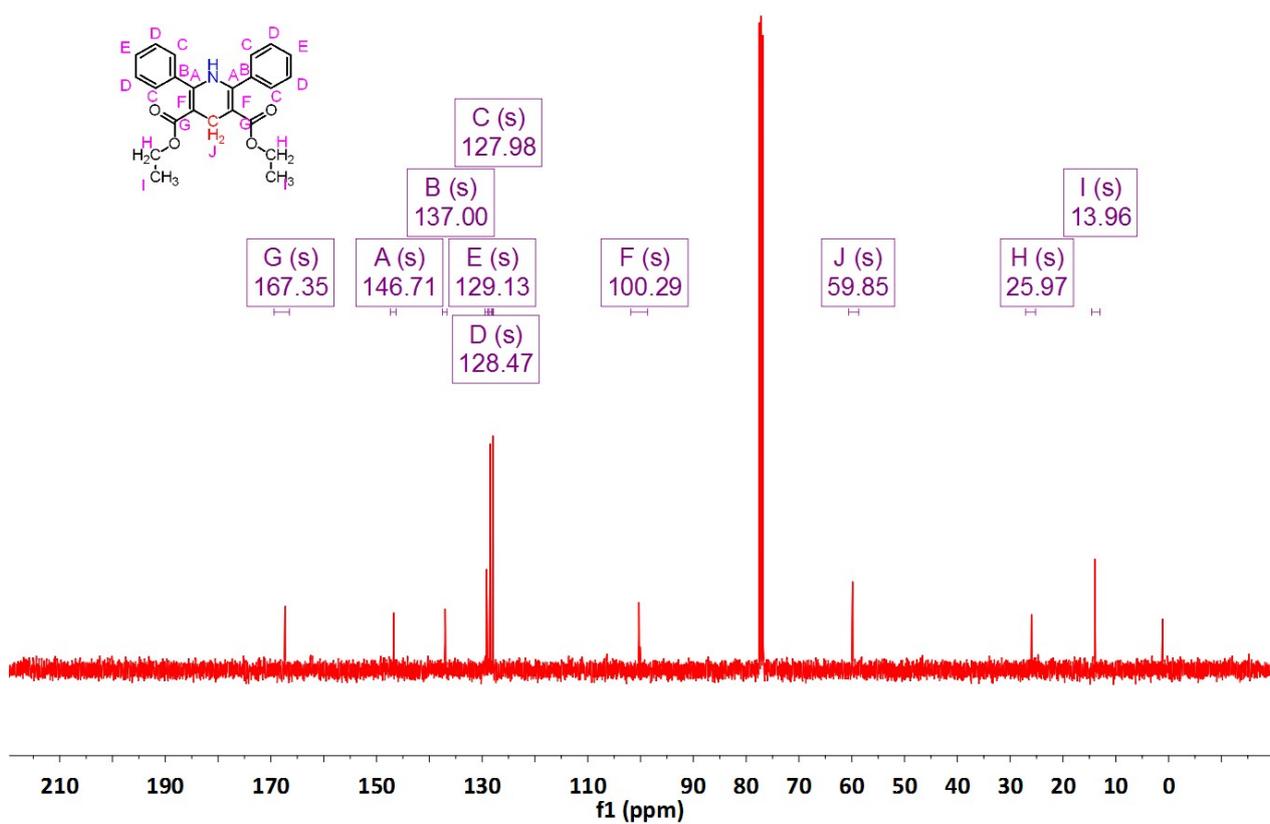
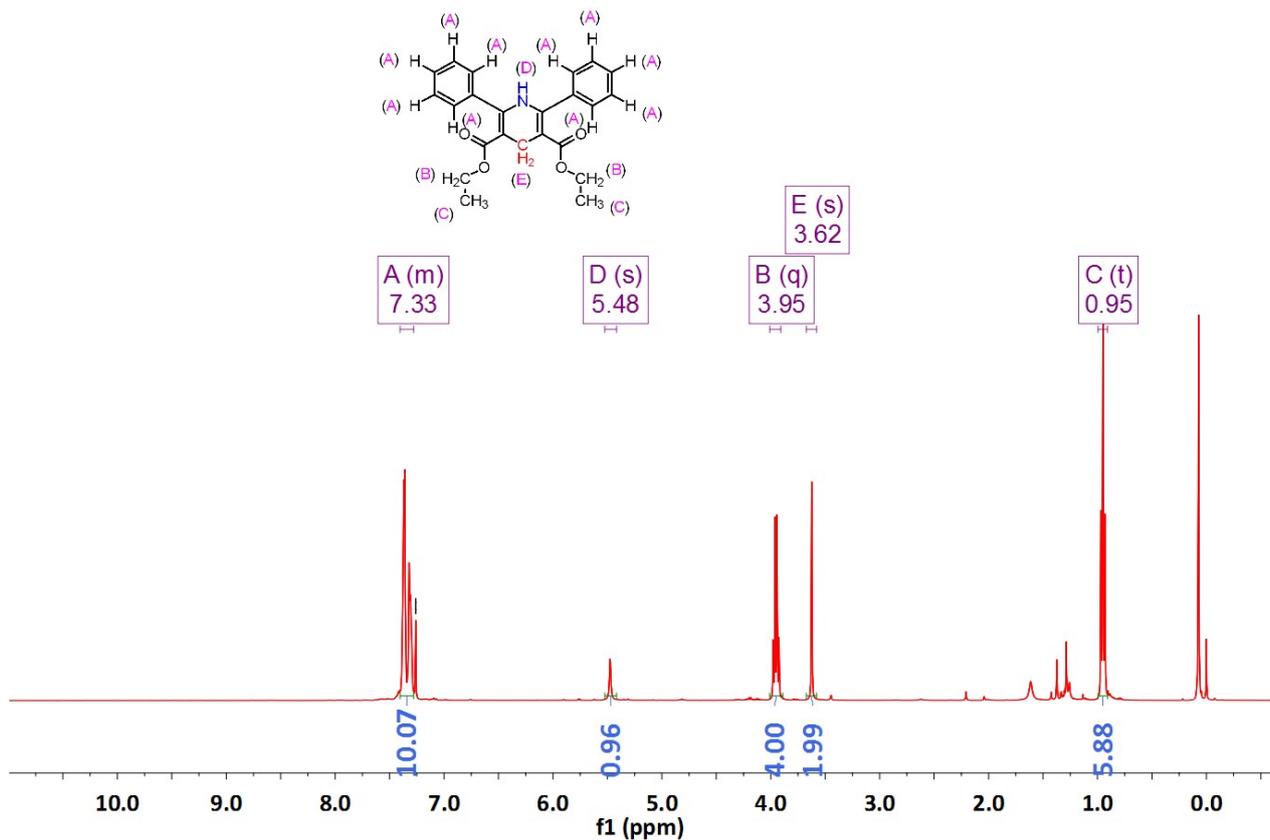
5,6,7,9,10,11-Hexahydrobenzo[6,7]cyclohepta[1,2-b]benzo[6,7]cyclohepta[2,1-e]pyridine (2v)



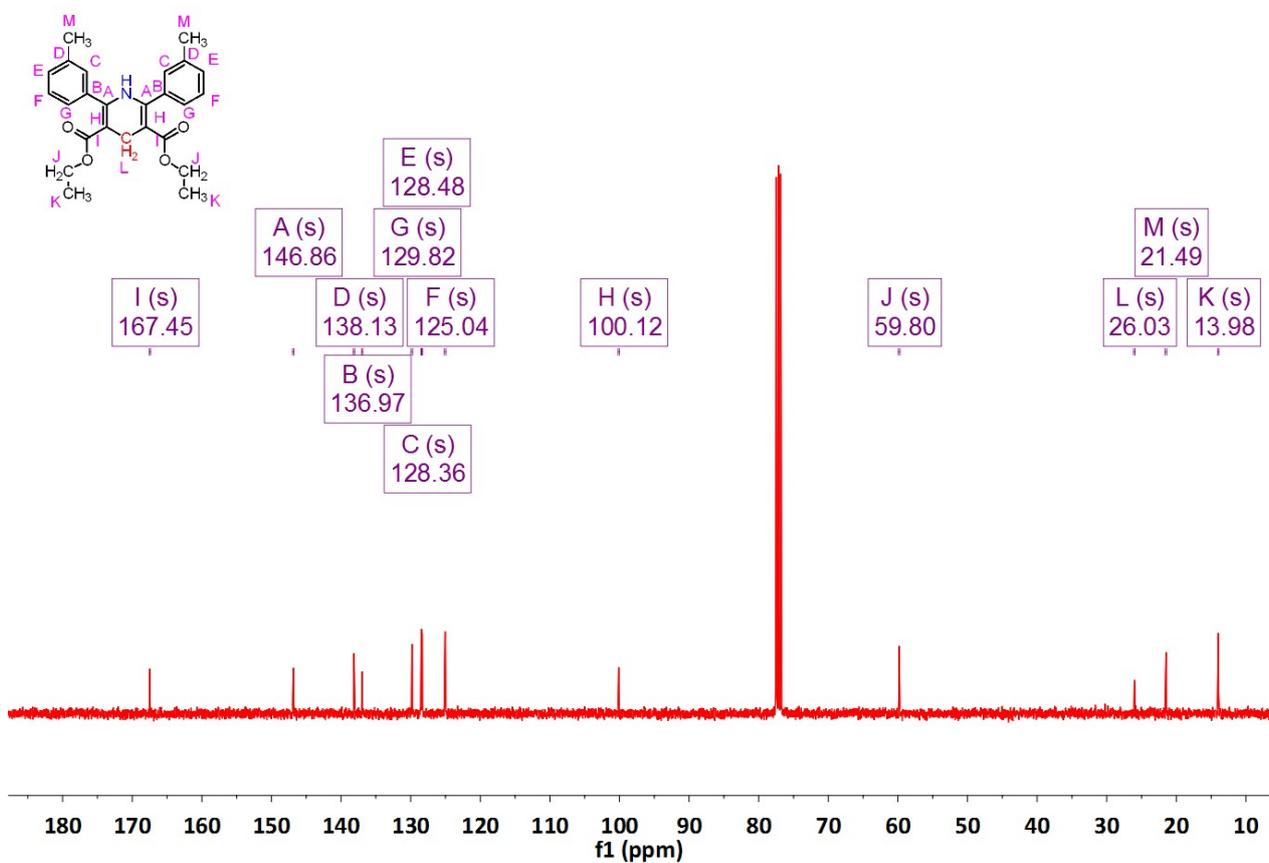
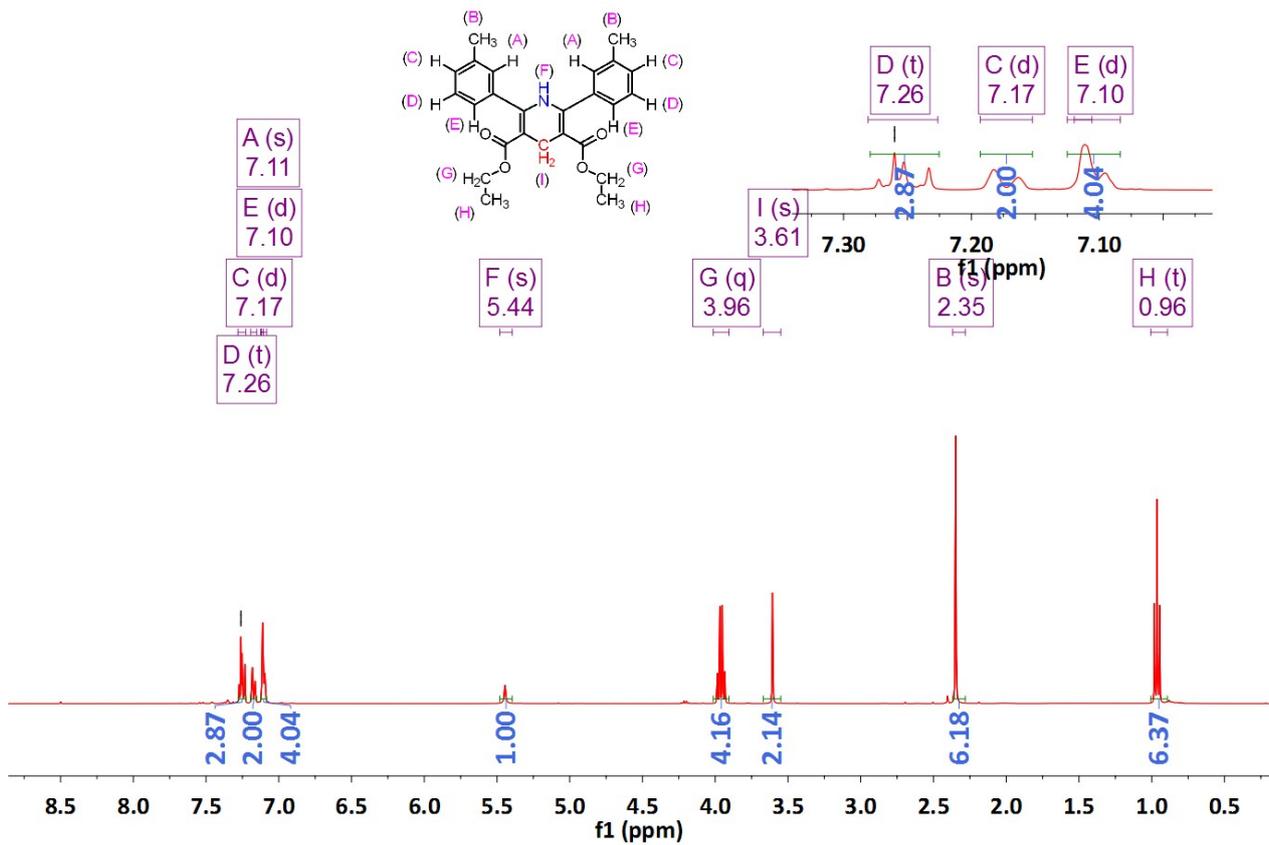
2, 3, 5, 6-Tetraphenyl-pyridine (2w)



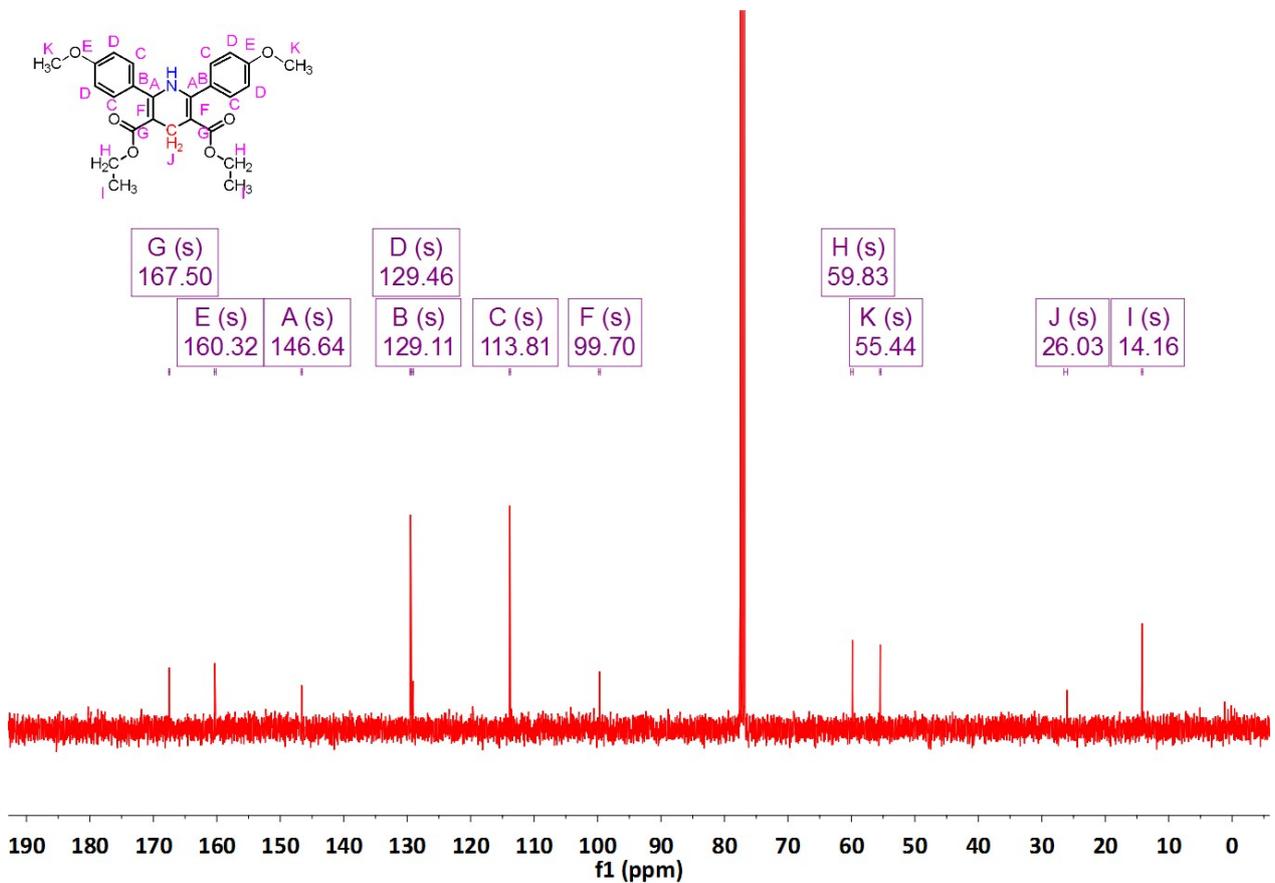
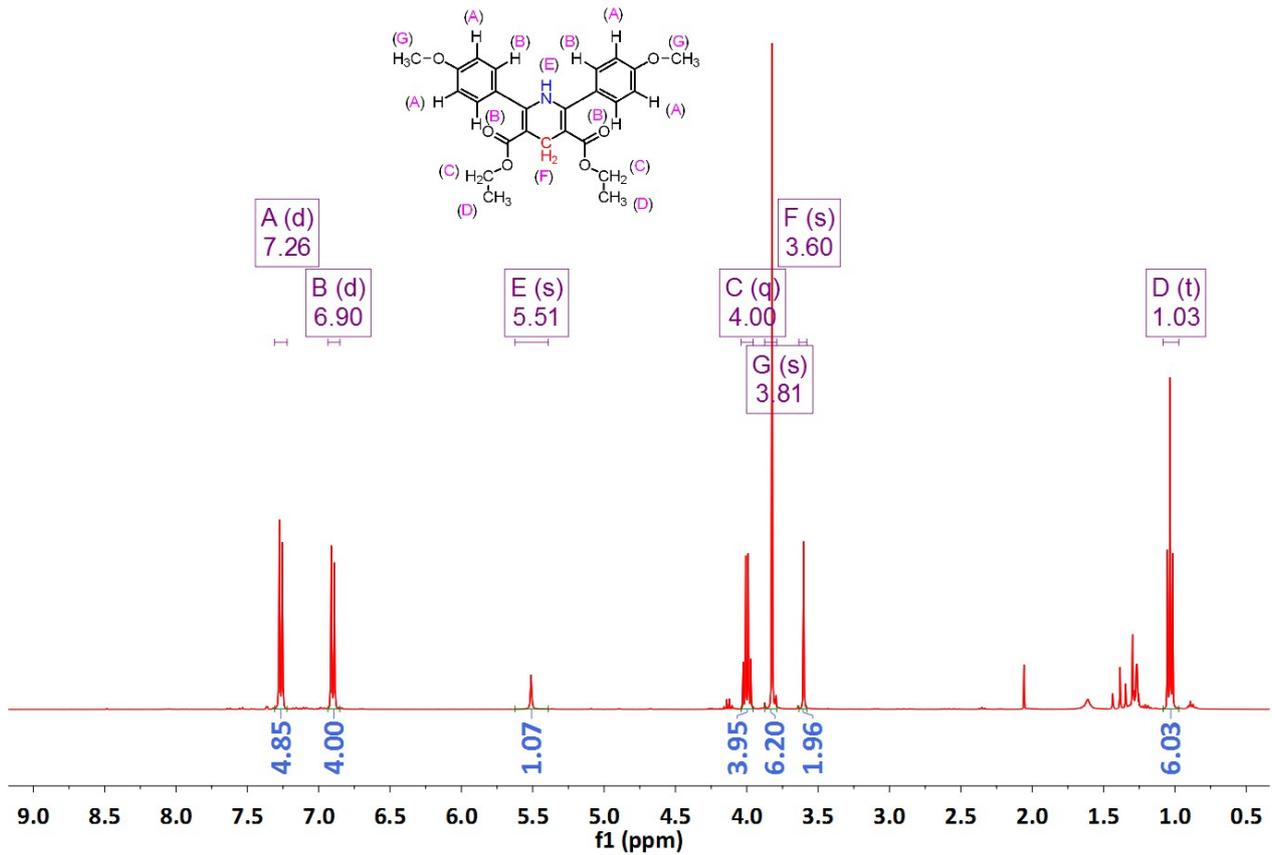
**Diethyl 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarboxylate (4a)**



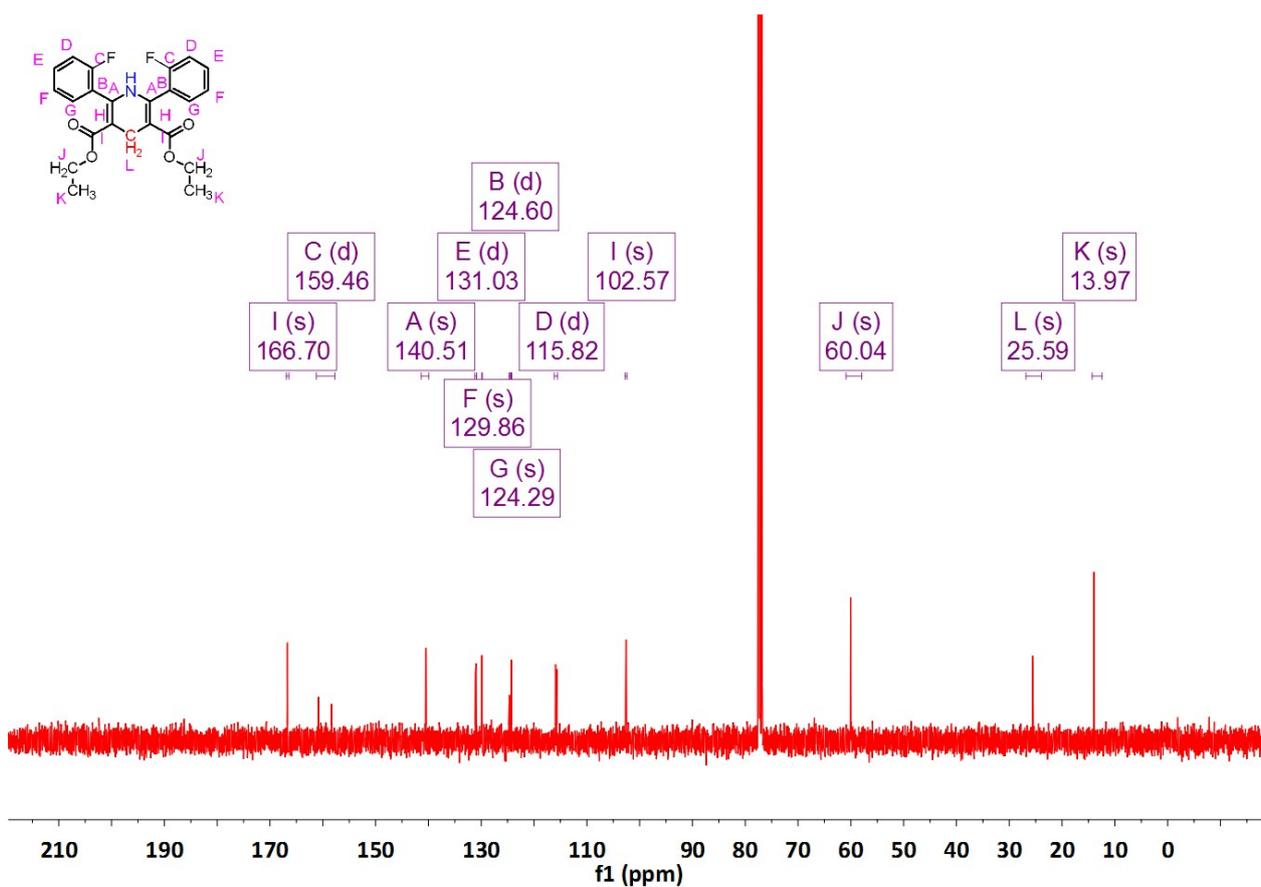
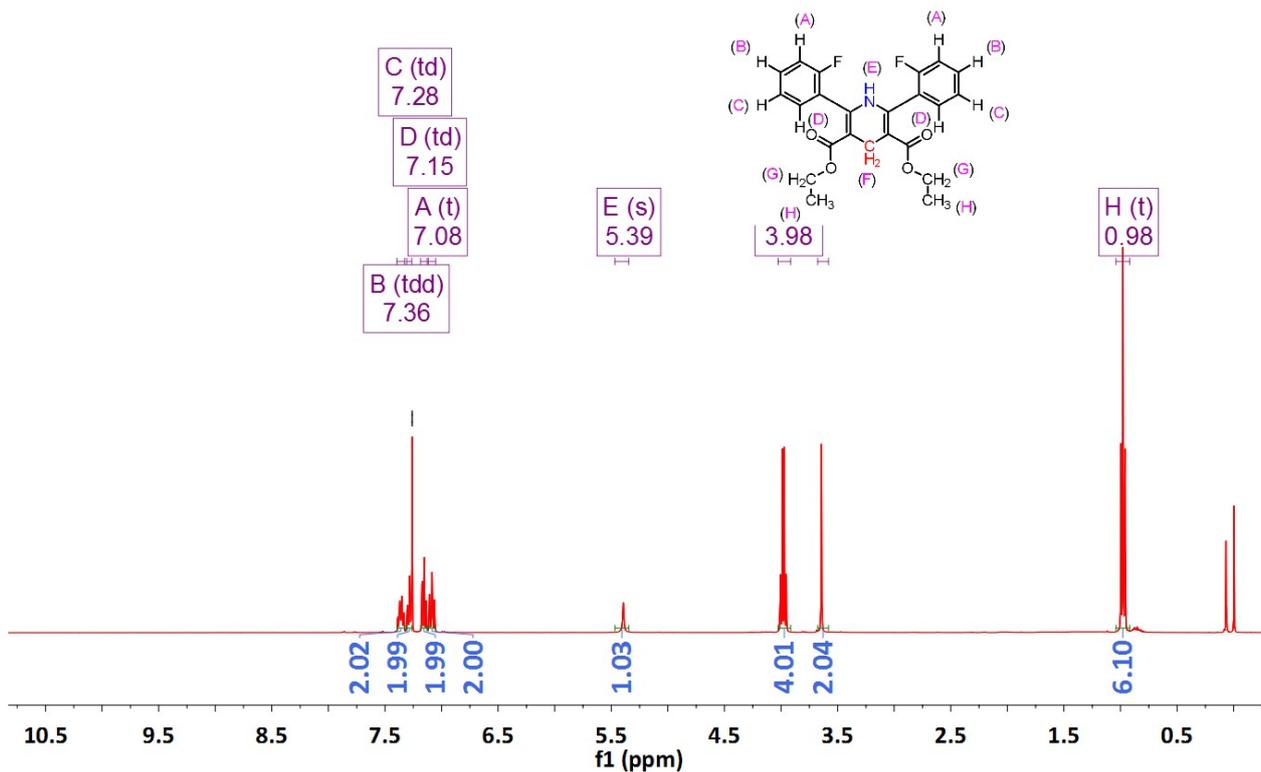
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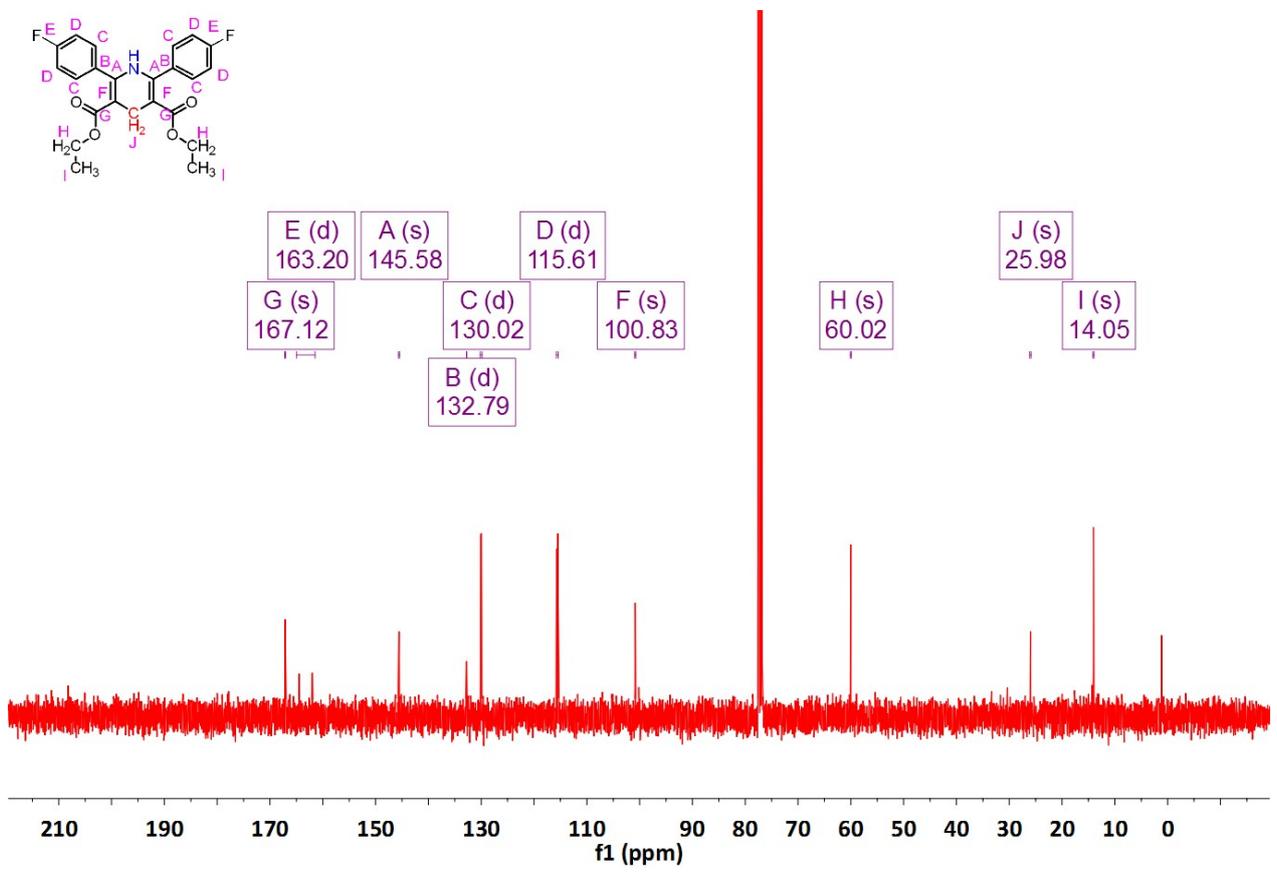
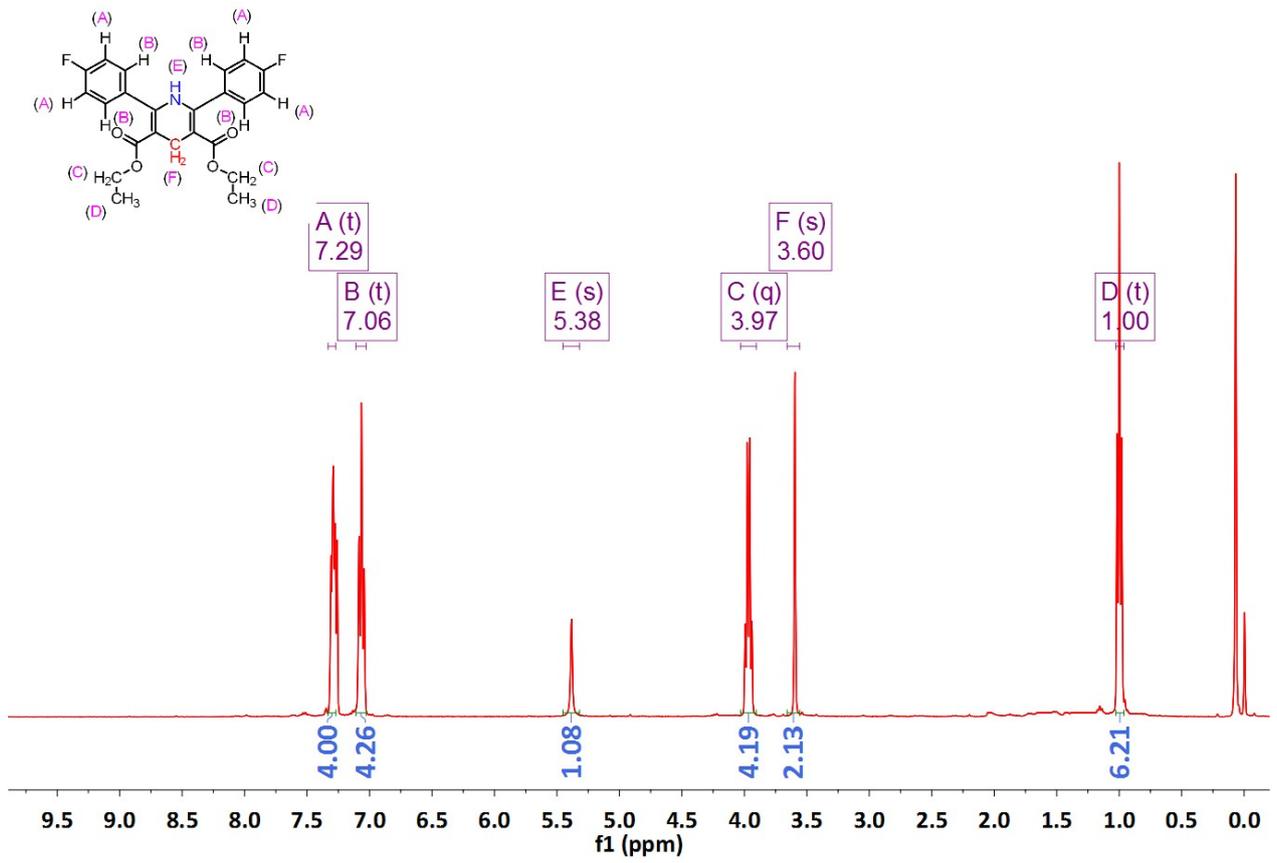
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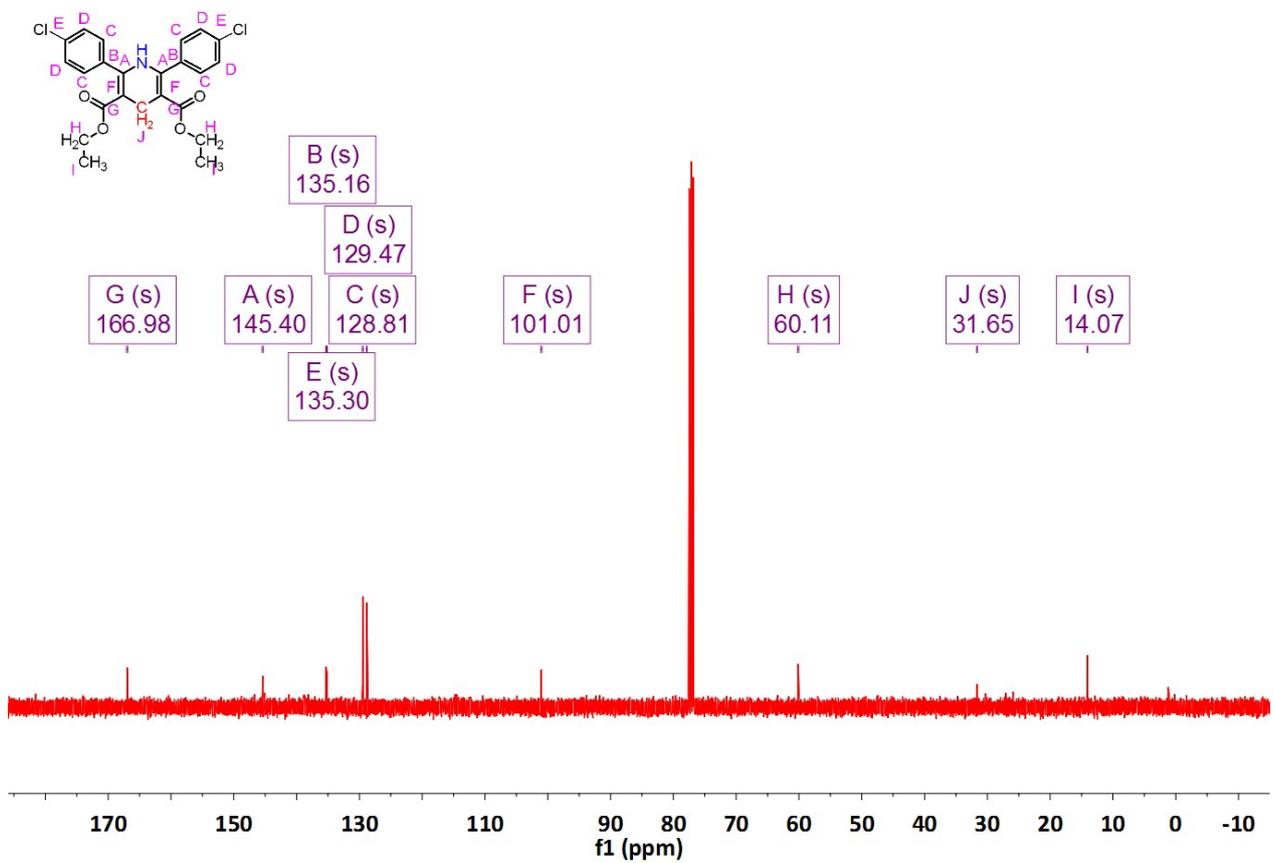
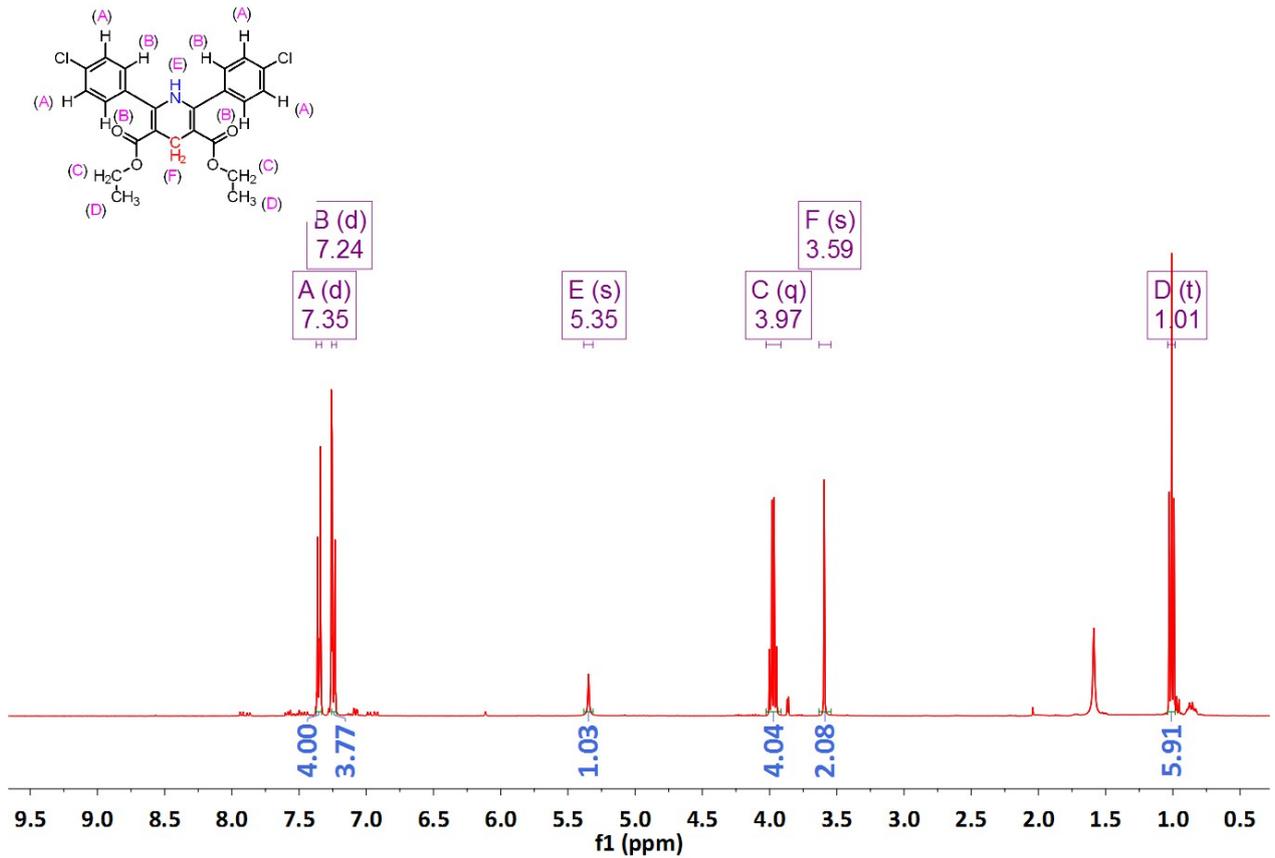
**Diethyl 2,6-bis(2-fluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4d)**



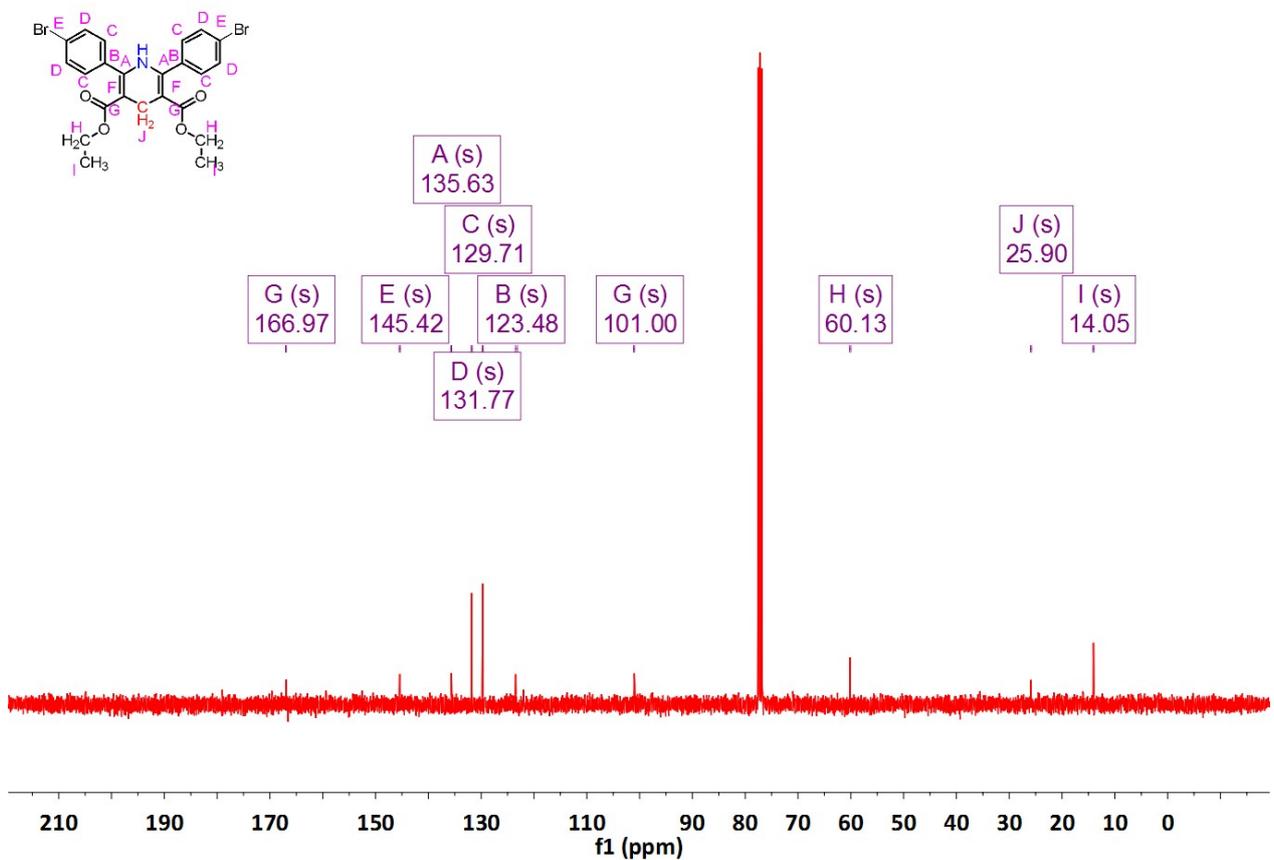
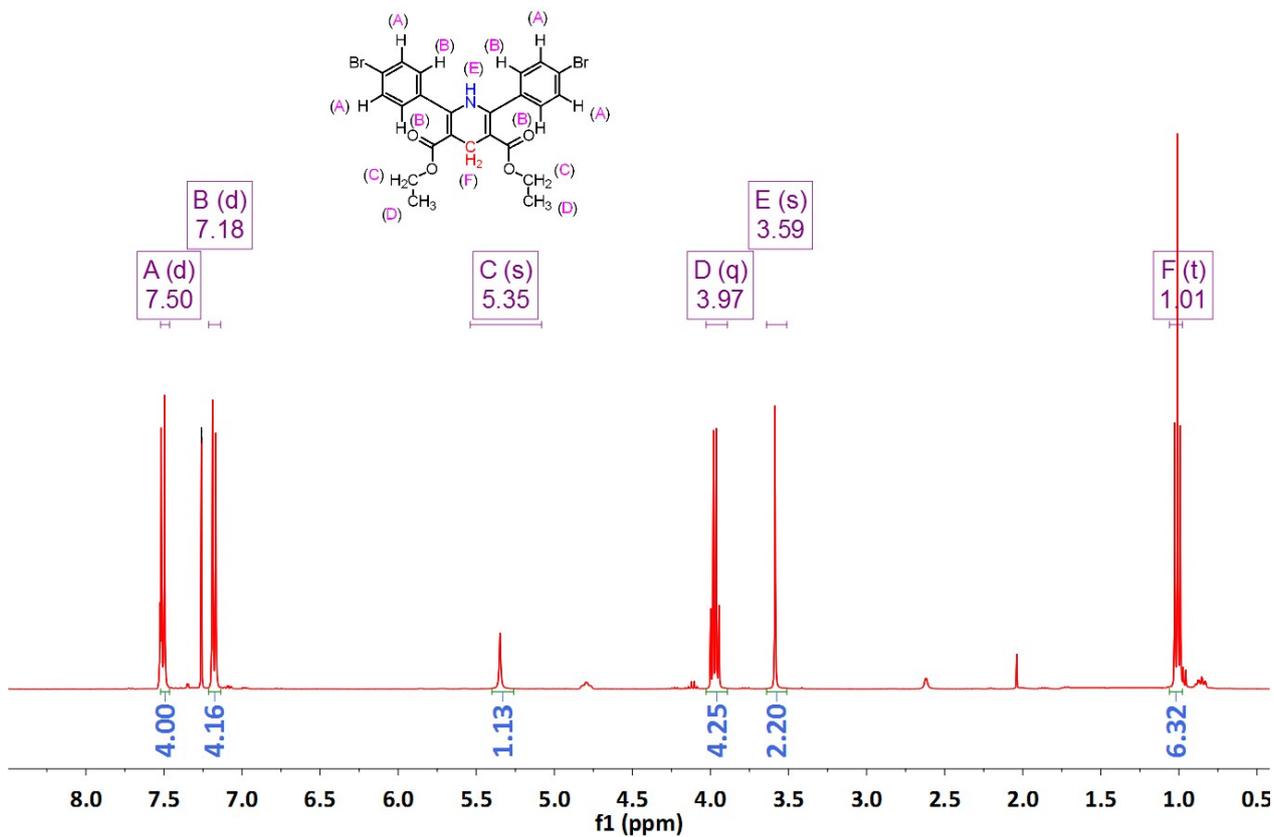
**Diethyl 2,6-bis(4-fluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4e)**



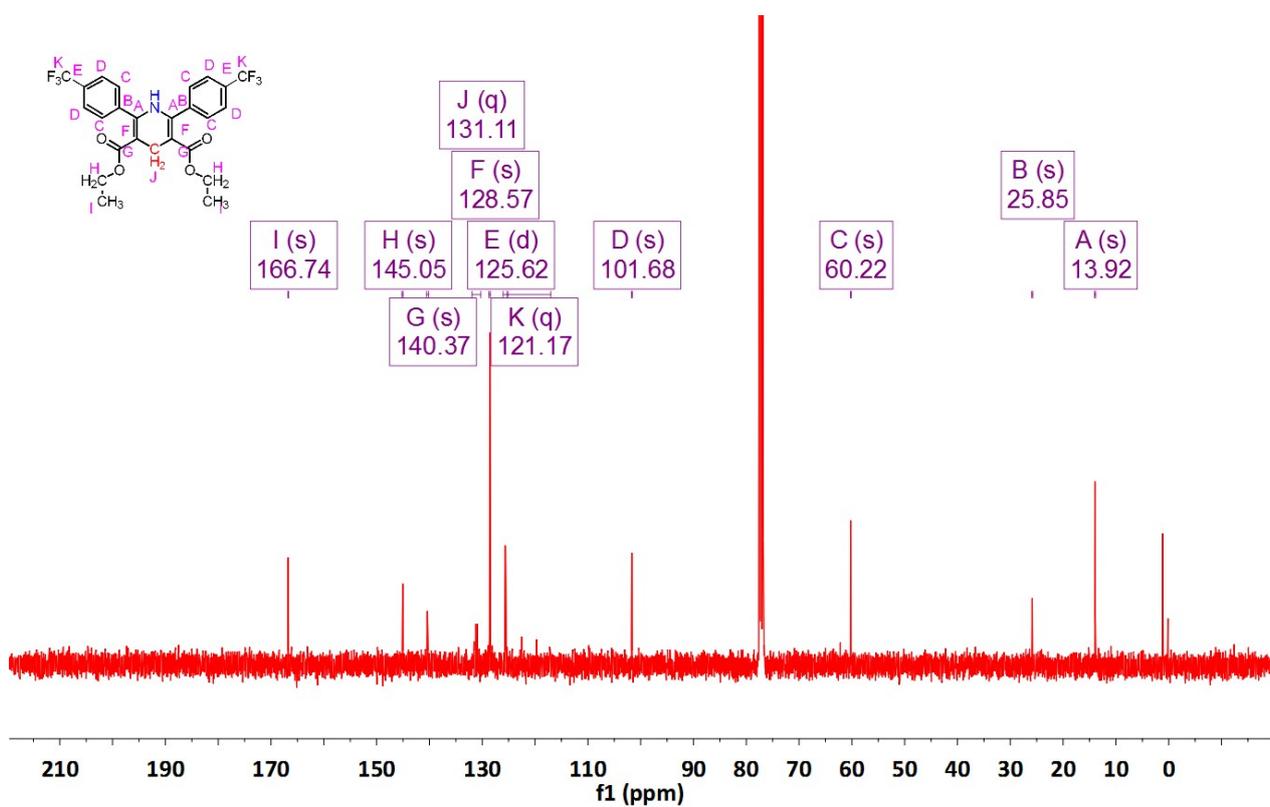
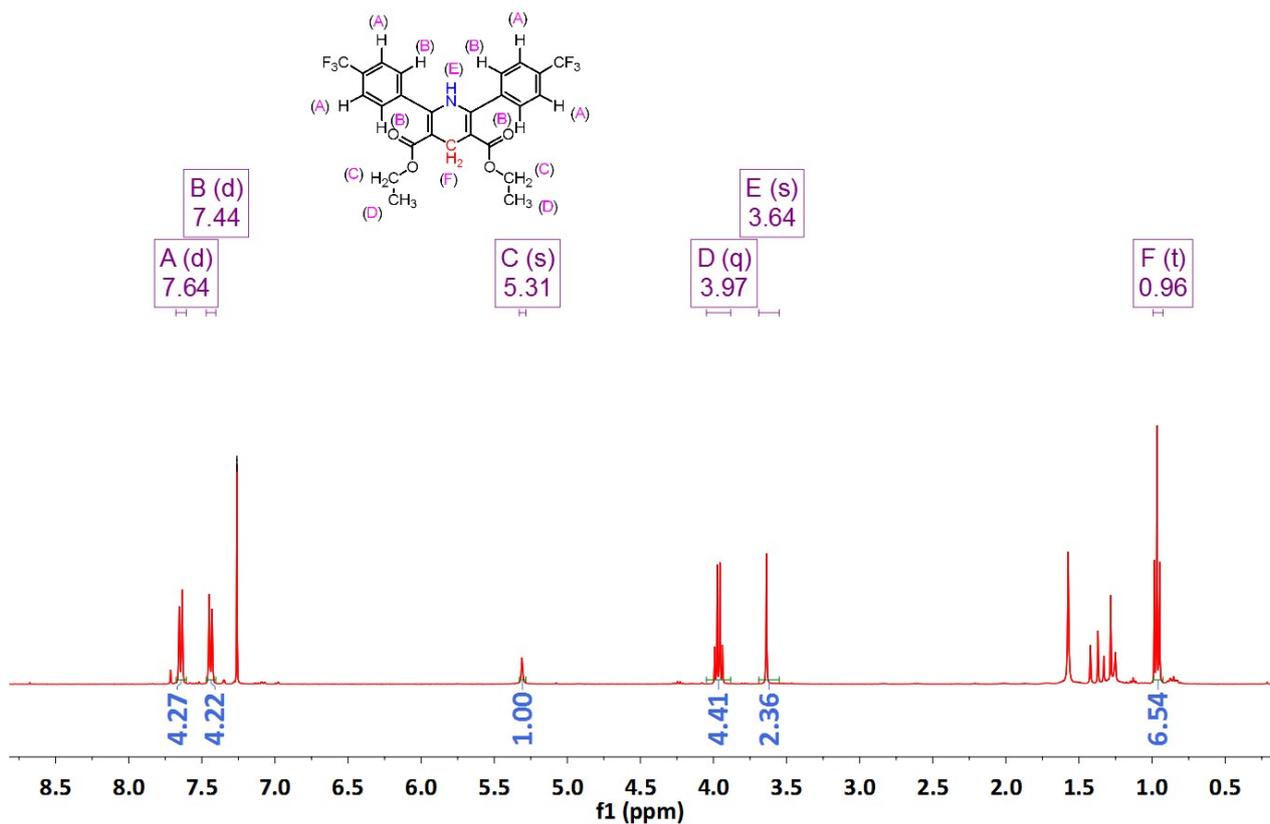
Diethyl 2,6-bis(4-chlorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4f)



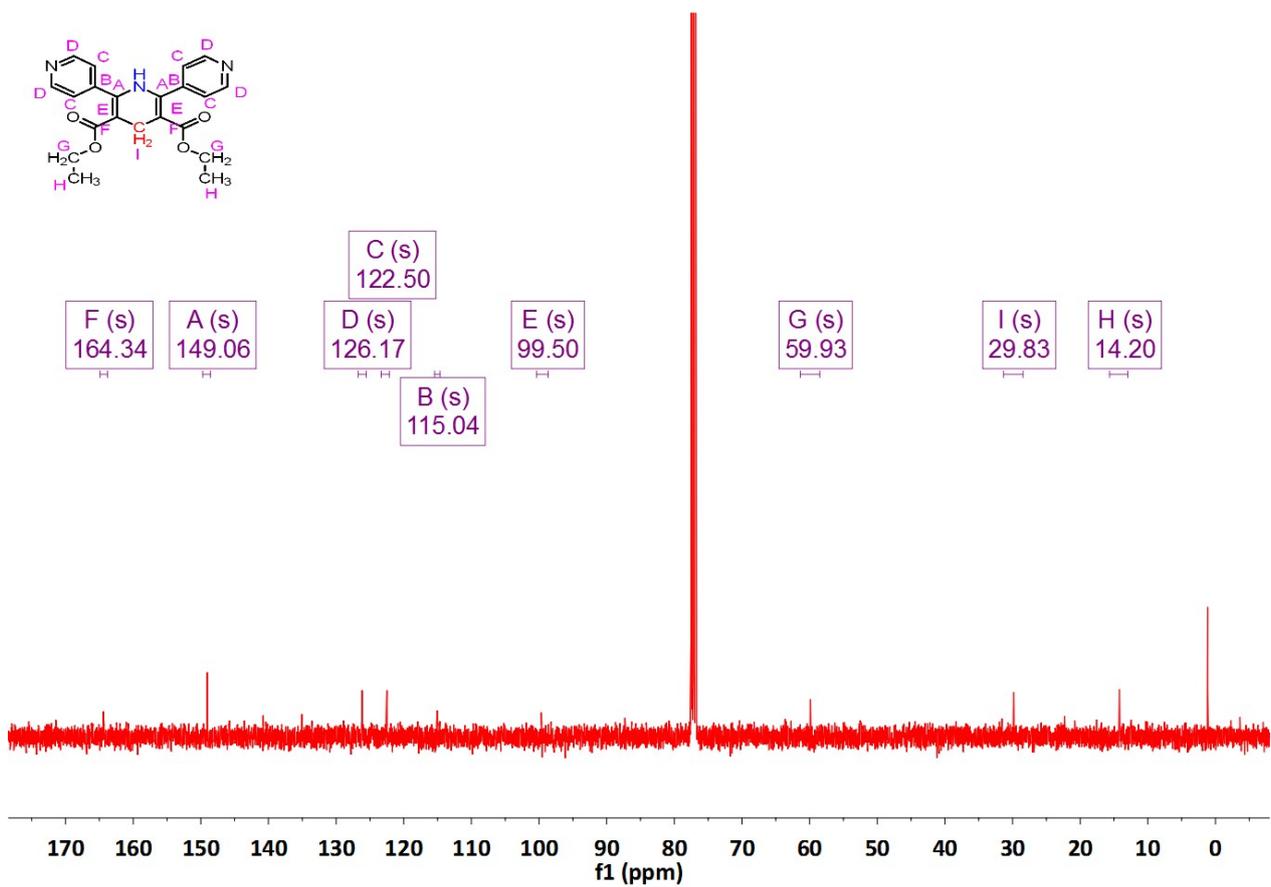
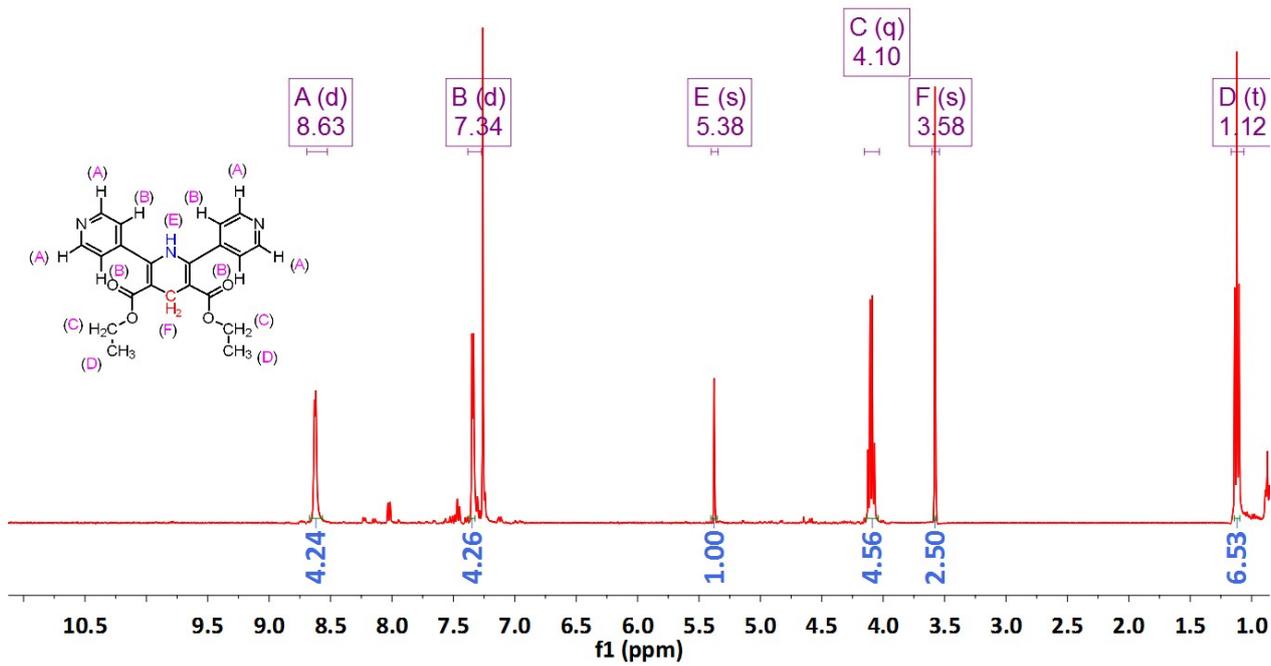
Diethyl 2,6-bis(4-bromophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4g)



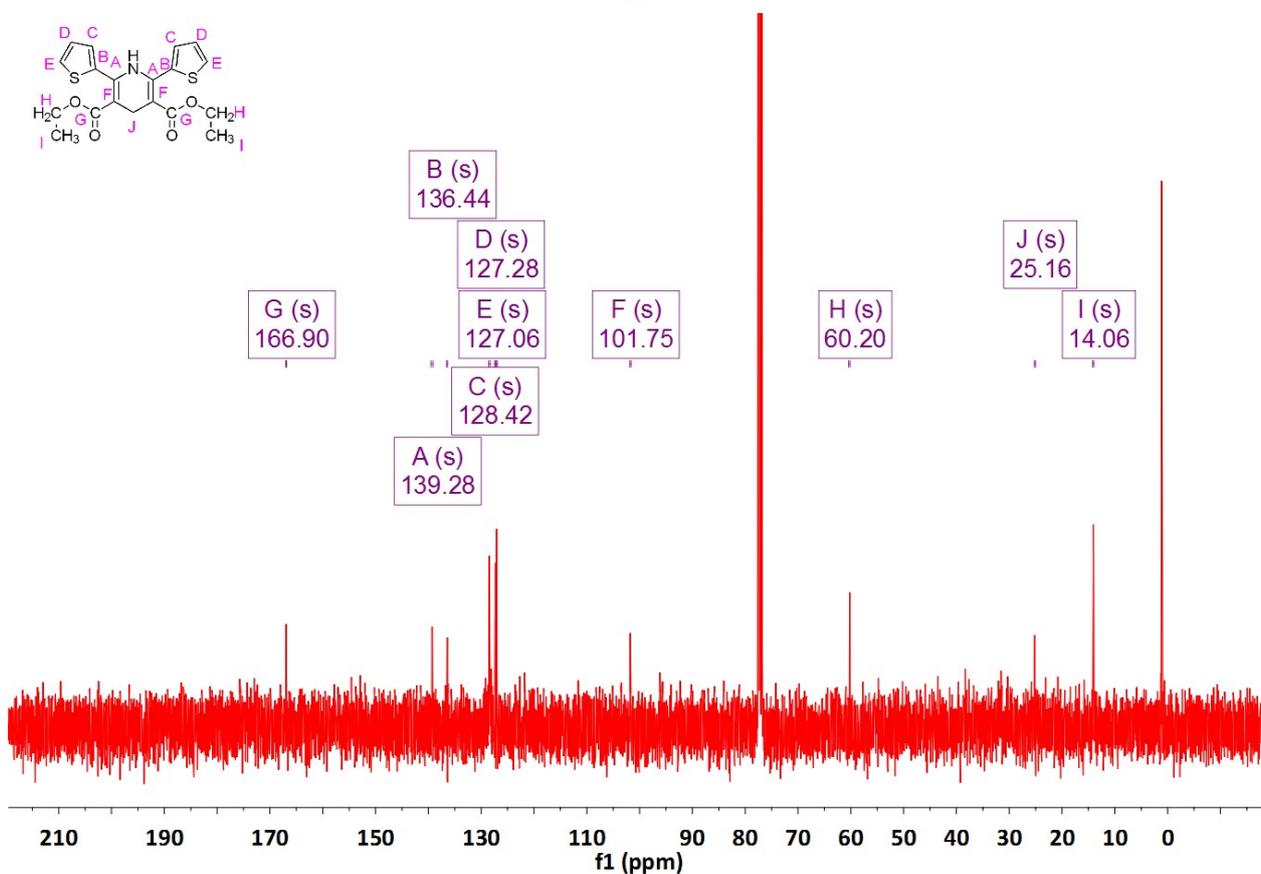
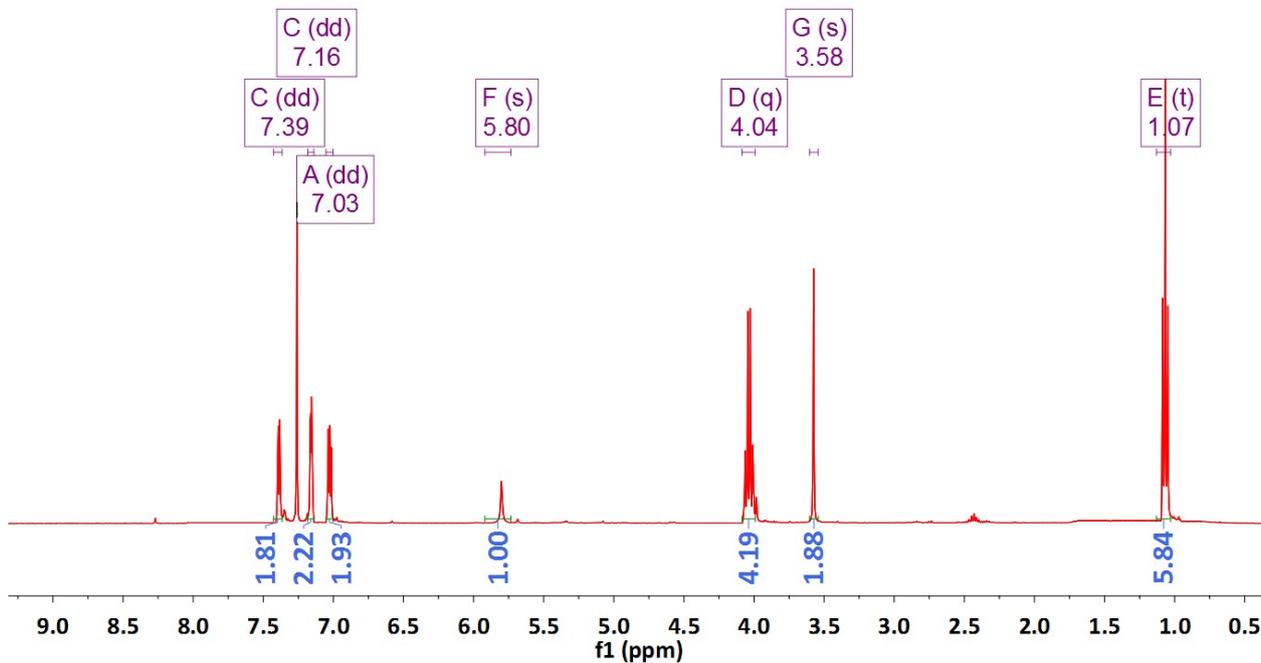
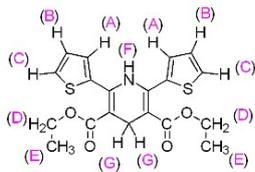
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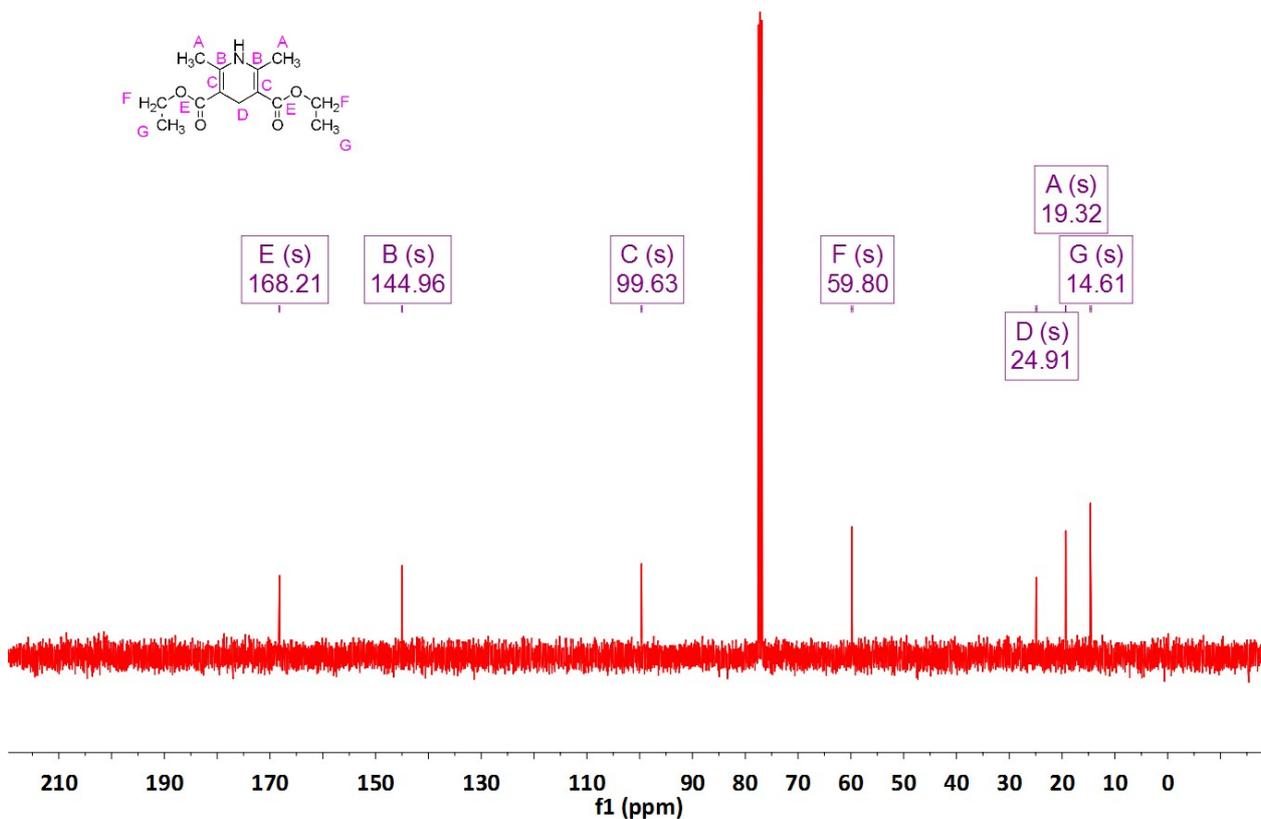
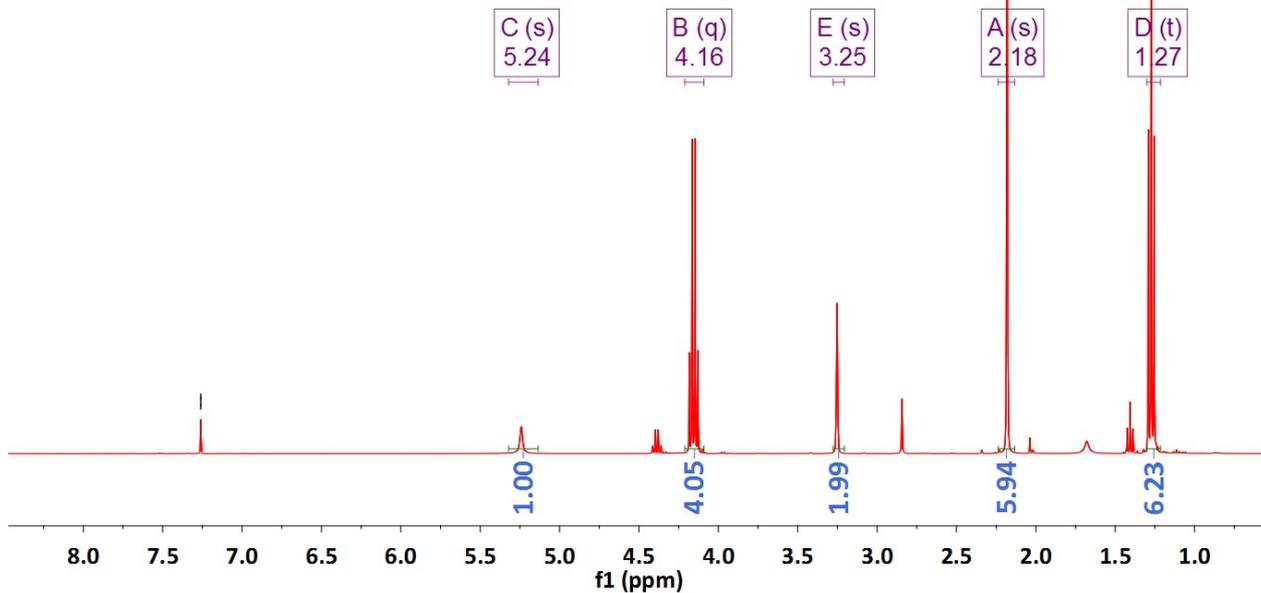
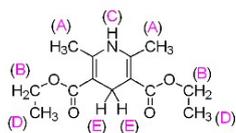
Diethyl 2,6-bis(4-pyridyl)-1,4-dihydropyridine-3,5-dicarboxylate (4i)



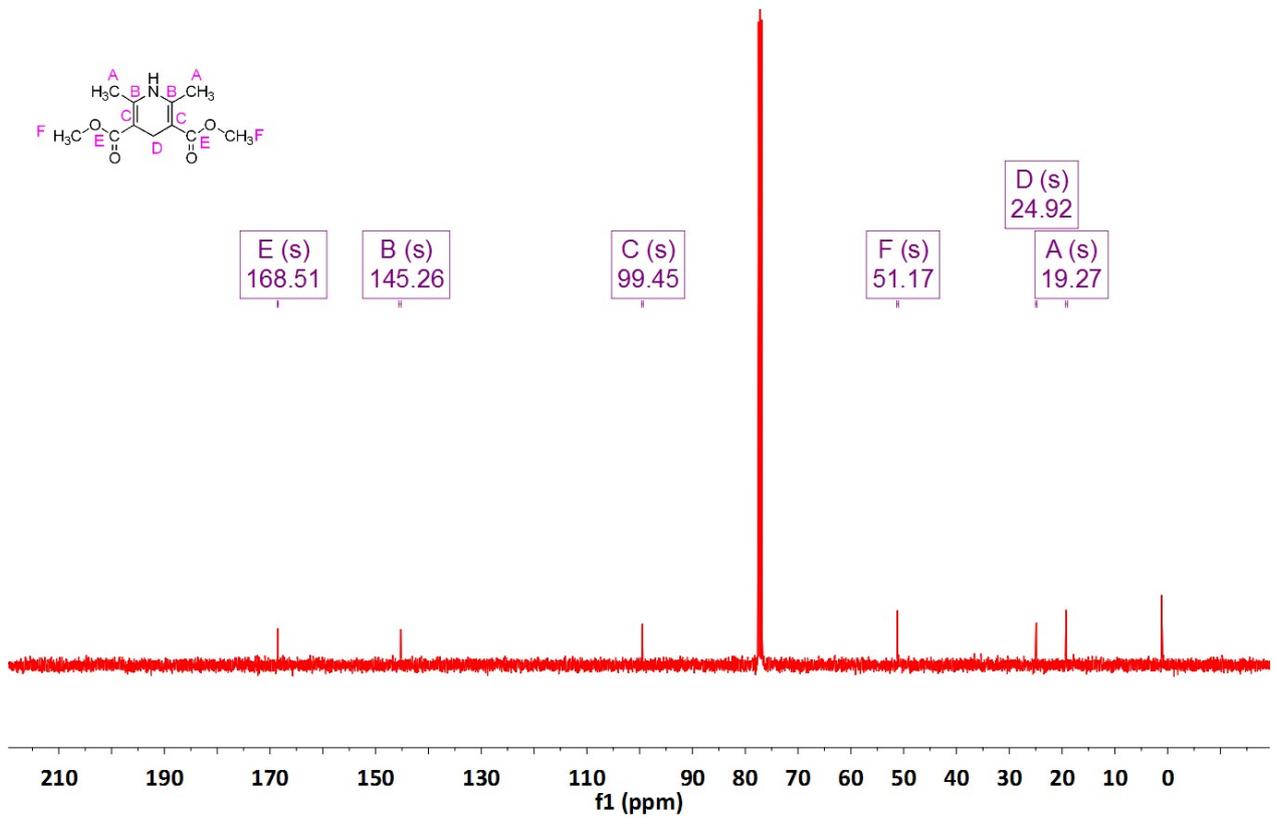
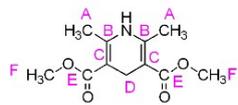
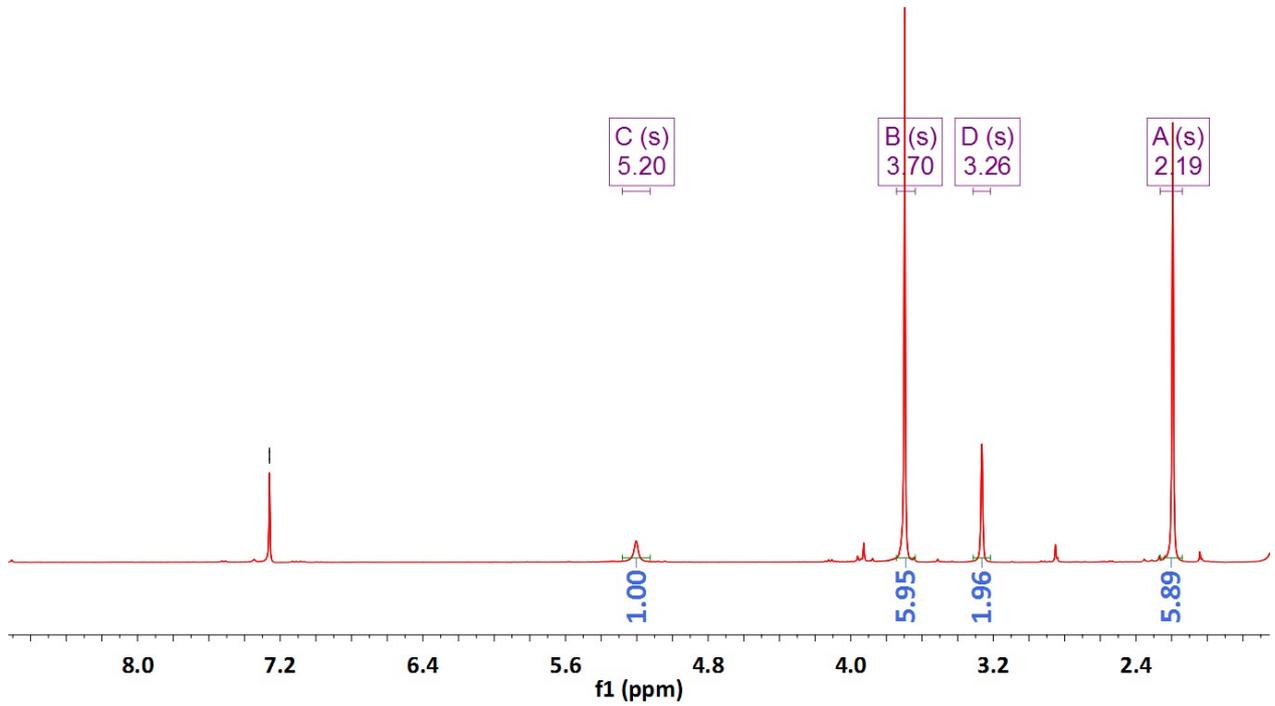
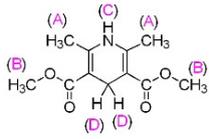
Diethyl 2,6-di(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (4j)



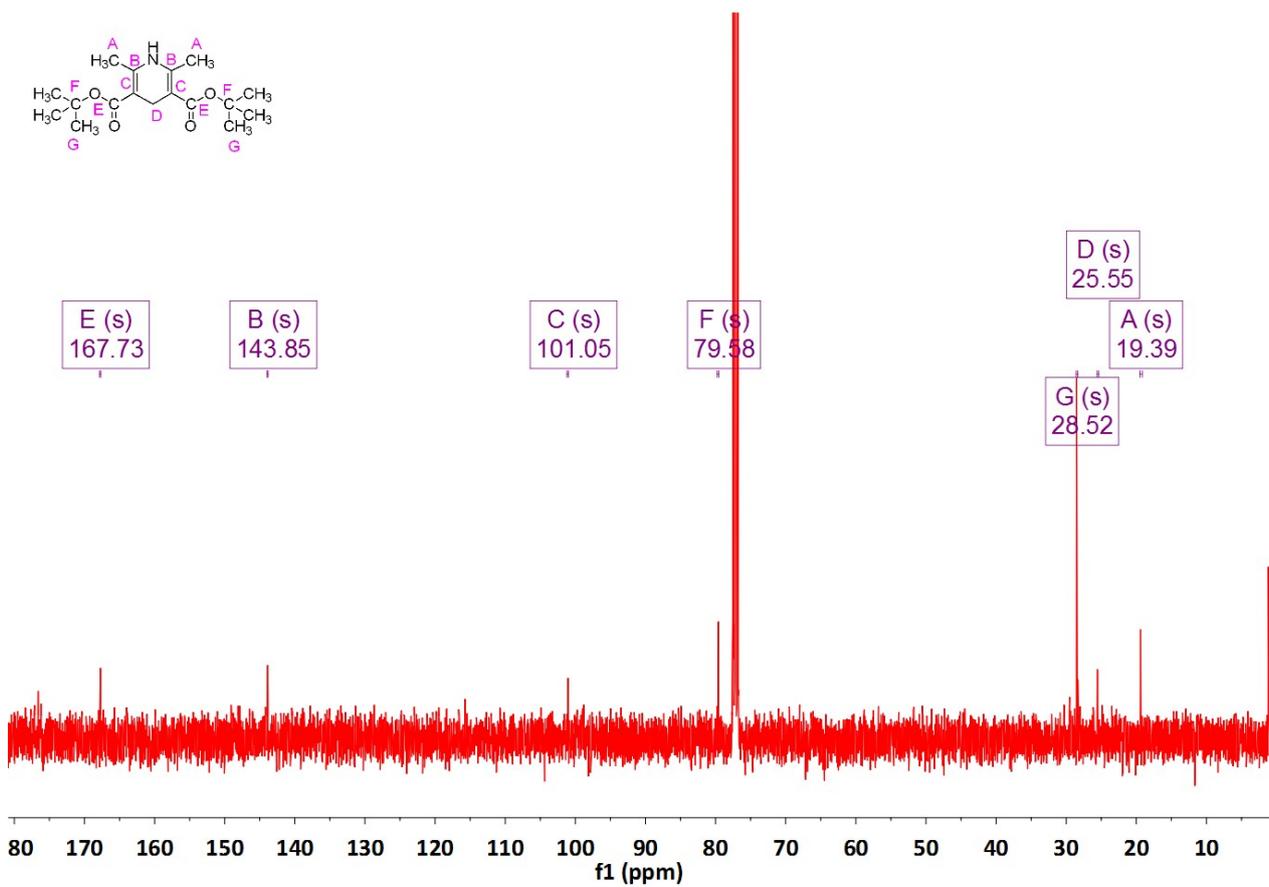
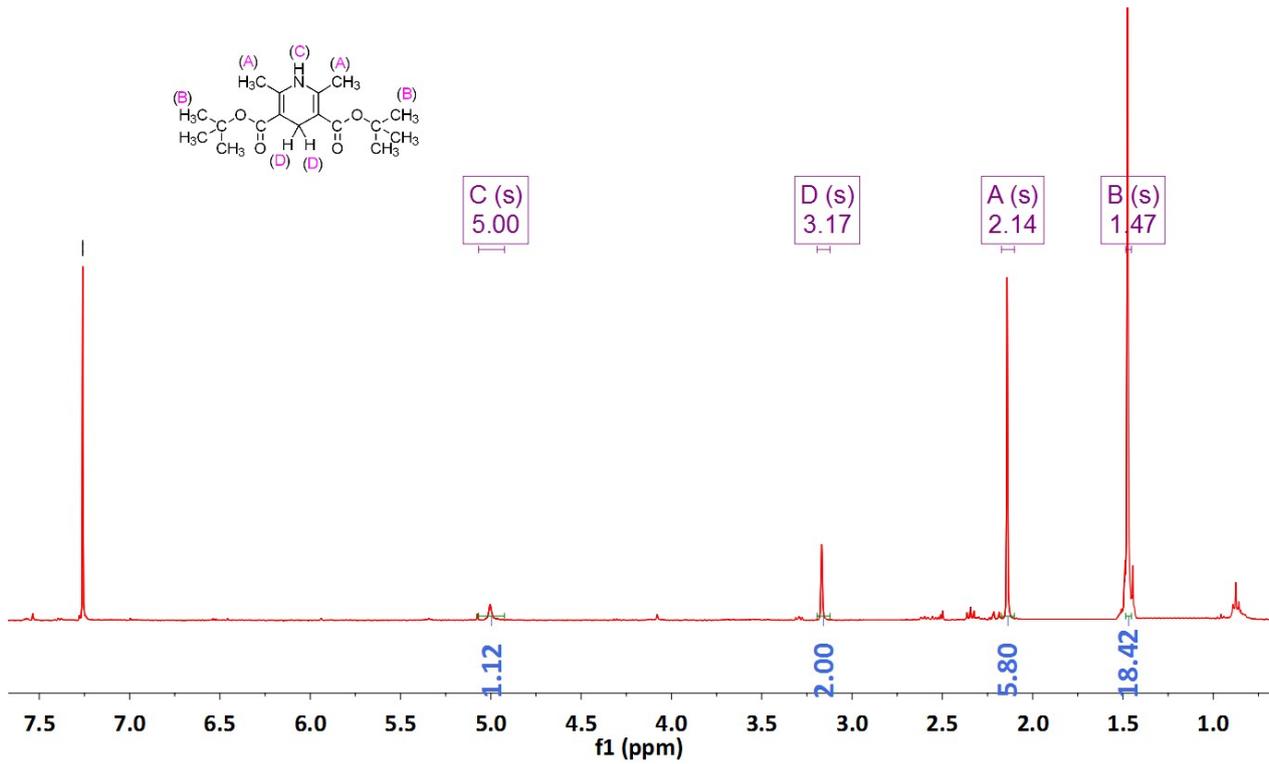
Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4k)



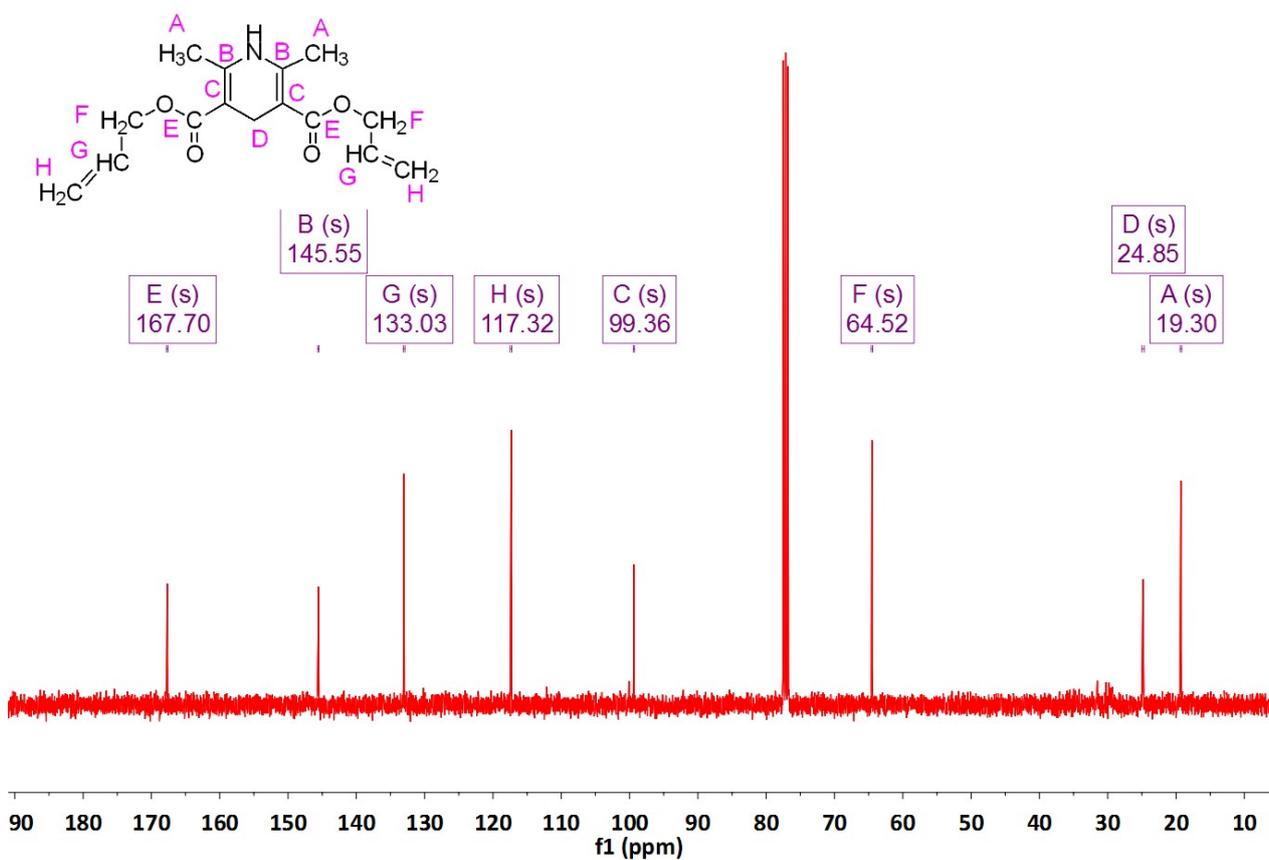
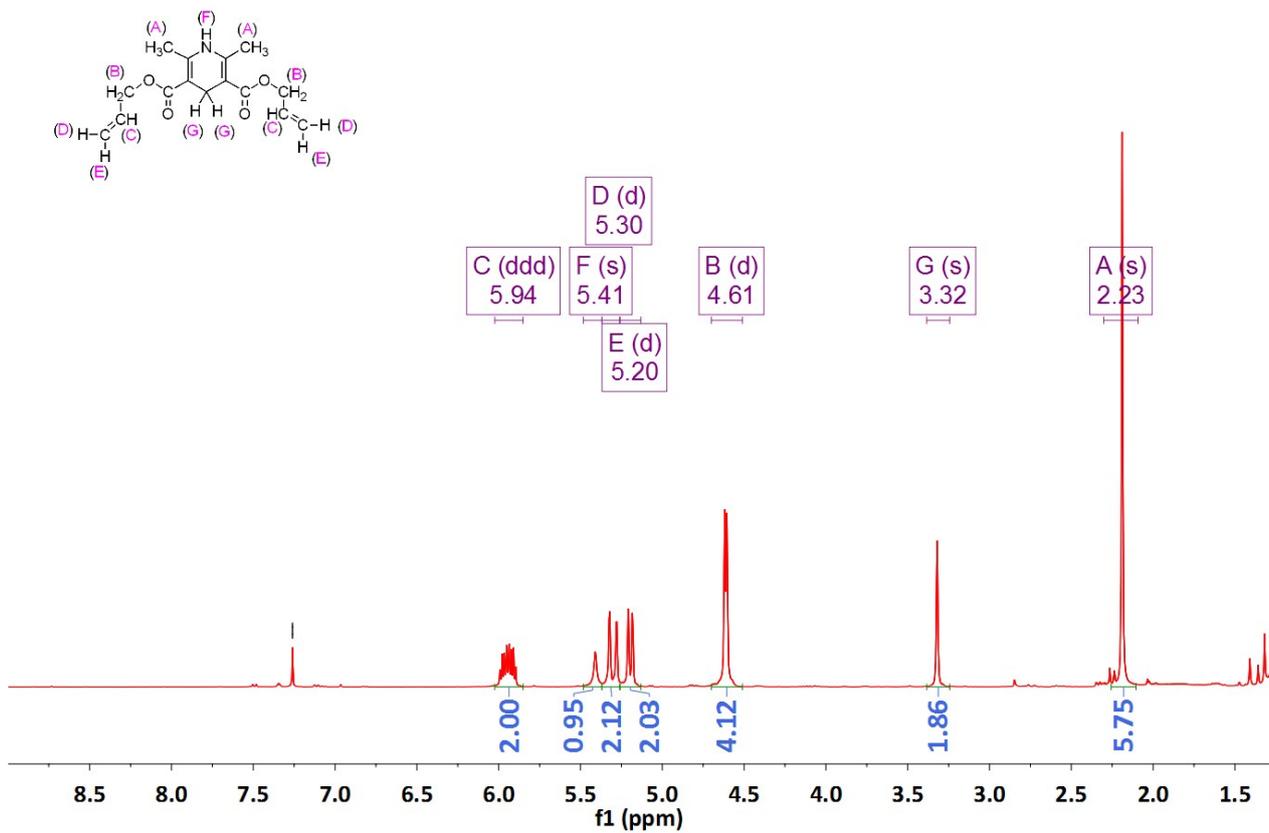
Dimethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4l)



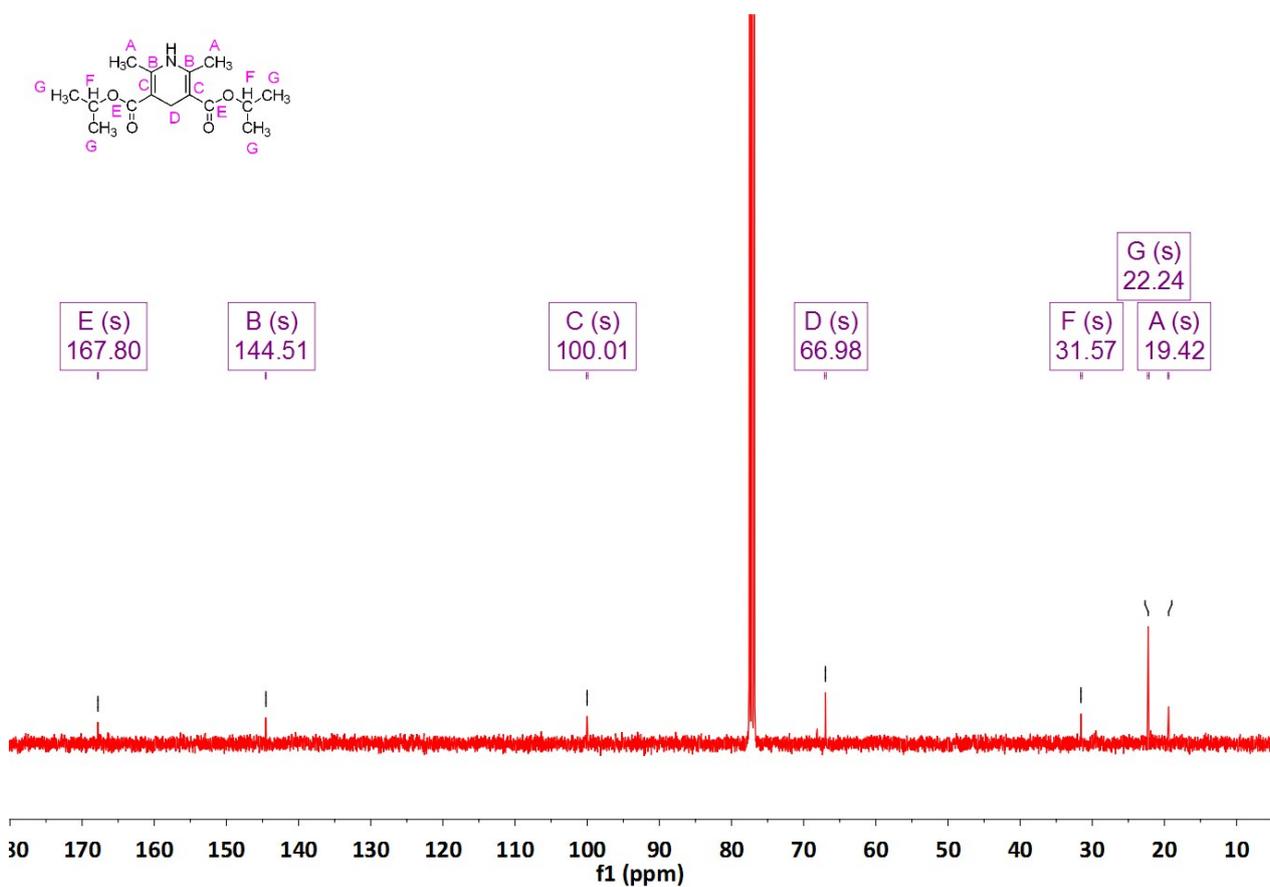
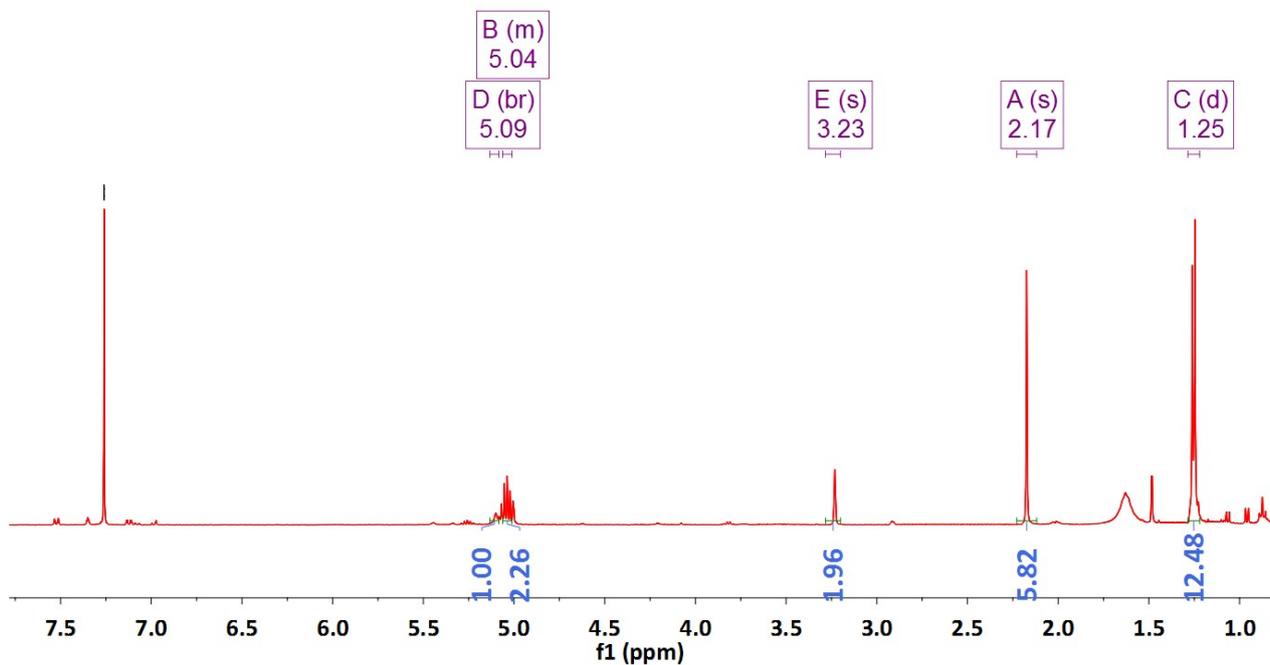
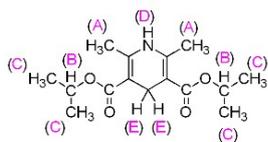
**Di-*tert*-butyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4m)**



**Di-allyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4n)**



**Di-*iso*-propyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4o)**



**Nifedipine (5)**

