

## Supporting Information

### Carbon's Three-Center-Four-Electron Tetrel Bond, Treated Experimentally

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## 1. Experimental description. General information.

**Synthesis.** Unless otherwise stated, all reagents and solvents were obtained from commercial suppliers and used without further purification. Pyridine and picoline were dried over molecular sieves (3Å). CH<sub>2</sub>Cl<sub>2</sub> was freshly distilled from CaH<sub>2</sub>. Samples were centrifuged with a Heraeus Christ Labofuge A centrifuge. Both triphenyl carbenium and its substituted analogues and 1,2-bis(pyridin-2-ylethynyl)benzene and its substituted analogues were dried for 2-3 h under vacuum prior to use. All glassware used for the preparation of [N...C...N]<sup>+</sup> tetrel bond complexes were dried under vacuum prior to use as well. For the syntheses of 2a-c previously published routes were followed.<sup>1,2</sup> Compounds **1a** and **1f** were available commercially and were used as received. Compounds **1d** and **1e** were generated according to previously published procedures with slight modifications required for **1e** (Scheme 2).<sup>3,4</sup> The [N...C...N]<sup>+</sup> complexes **3a-f** were prepared under dry conditions, with dry solvents and under an argon or nitrogen atmosphere. Compound **1** (~10 mg), or its analogues, were transferred into an NMR tube and **2** (1 eq), or its analogues, into a separate 2 ml flat bottom vial. Care must be taken in order to ensure that a 1:1 addition is made; stock solutions may be prepared for reliable additions. After drying, the contents were transferred into a glove box and approximately 300 µl dry CD<sub>2</sub>Cl<sub>2</sub> was added to both vials to dissolve all solids. Then, the CD<sub>2</sub>Cl<sub>2</sub> solution of **2** was delivered to the NMR tube containing the solution of **1** and the NMR tube was sealed with a rubber septum and tightened with Teflon tape to ensure a moisture free environment. The samples were prepared 30 min before the NMR measurements and the NMR tube was tilted from side to side to ensure proper mixing. For complexes **5b** and **5c**, CD<sub>2</sub>Cl<sub>2</sub> solutions of dried **4b** and **4c** (1 eq dissolved in ca 300 µL solution; stock solution prepared as 55 mg in 2 mL) were added into a CD<sub>2</sub>Cl<sub>2</sub> solution of **1a** (~20 mg, 200 µL).

**NMR spectroscopy.** For structural assignments <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H, <sup>13</sup>C HMBC, <sup>1</sup>H, <sup>13</sup>C HSQC, DQF-COSY and <sup>1</sup>H, <sup>15</sup>N HMBC NMR spectra were recorded on a Varian VNMR-S 500 spectrometer equipped with an HFX probe or a Varian 400-MR spectrometer equipped with a OneNMRProbe in CD<sub>2</sub>Cl<sub>2</sub> at 25° C. Variable temperature NMR spectra were obtained on a Bruker Avance Neo 500 MHz spectrometer equipped with a TXO cryogenic probe. Chemical shifts are reported on the δ scale in ppm. For the <sup>1</sup>H and <sup>13</sup>C NMR spectral data the residual solvent signal was used as internal standard (δ<sub>H</sub> 5.32 ppm and δ<sub>C</sub> 54.00 ppm). The numbering of the structures refers to those used for NMR assignment.

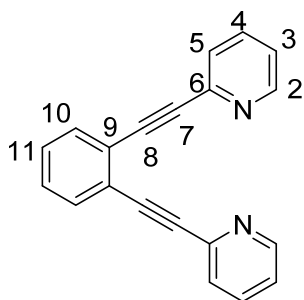
**X-ray crystallography.** Single crystals of 1-tritylpyridin-1-ium tetrafluoroborate were obtained by drying 20 mg triphenylcarbenium tetrafluoroborate (**1c**) under vacuum for 30 min, subsequently dissolving it in 500 µL dichloromethane and transferring the solution into a carefully dried NMR tube, in a glove box. Dry pyridine (2 eq, **4c**) was carefully layered on the top of the solution of **1c**, and the NMR tube was sealed with a septum and transferred into a fridge (5 ° C), without shaking. Colorless plates were formed. The X-ray data was collected at 120(2) K on an Agilent SuperNova dual wavelength diffractometer with micro-focus X-ray source and Atlas detector and using multilayer optics monochromatized Cu-K α (λ = 1.54184 Å) radiation. CrysAlisPro<sup>5</sup> software was used for data collection, integration and reduction as well as applying the analytical absorption correction. The structures were solved with direct methods (SHELXT<sup>6</sup>) and refined by full-matrix least squares on F<sup>2</sup> utilizing SHELXL-2016.<sup>7</sup> The crystal was found to be a non-merohedral 2-component twin and was refined accordingly. The data showed R<sub>int</sub> value of 0.0357 before HKLF5 refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters U<sub>eq</sub>(H) = 1.2 U<sub>eq</sub>(C). The details of the crystals data, data collection, and the refinement results are given in the Supplementary Information.

**Isothermal calorimetry.** ITC experiments were performed on a MicroCal VP-ITC device. Dichloromethane was purchased dry, stored over molecular sieves, and filtered through a micropore syringe filter prior to use. Synthesized compounds used in the measurements were dried under high

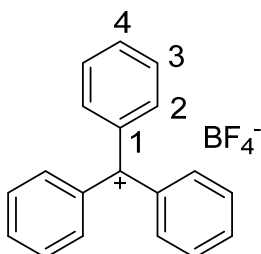
vacuum prior to use. Triphenylcarbenium tetrafluoroborate was used as purchased (*Acros Organics*) and stored under argon. For each measurement, stock solutions were freshly prepared in oven-dried glassware.

Automated baseline adjustment, peak integration, and normalization of reaction heats with respect to the molar amount of injectant were done with NITPIC.<sup>8,9</sup> Integrated heats were fitted to a binding model considering **2c/1a** stoichiometries of 1:1 and 1:2. Data were fitted by nonlinear least-squares regression in SEDPHAT<sup>9,10</sup>. 68.3% confidence intervals were determined by error-surface projection as described in detail elsewhere.<sup>11</sup> Further details along with the estimated confidence intervals (Table S1) are given in the Supplementary Information.

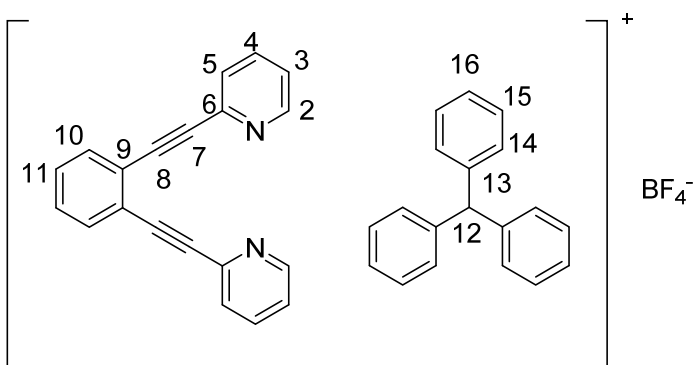
## 2. Compound characterization



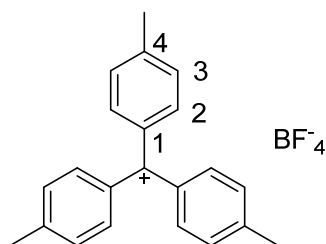
**1,2-Bis(pyridine-2-ylethynyl)benzene (2c).**<sup>2</sup> This molecule was synthesized following a previously published procedure.<sup>2</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.63 (ddd, *J* = 4.9, 1.7, 1.1 Hz, 2H, H2), 7.74 – 7.66 (m, 4H, H4 & H5), 7.66–7.68 (AA' part of AA'BB', H10), 7.41–7.42 (2H, BB' part of AA'BB, H11), 7.27 (ddd, *J* = 7.1, 4.9, 1.8 Hz, 2H, H3). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 150.7 (C2), 143.8 (C6), 136.6 (C4), 132.7 (C10), 129.4 (C11), 128.2 (C5), 125.8 (C9), 123.5 (C3), 93.6 (C7), 87.7 (C8).



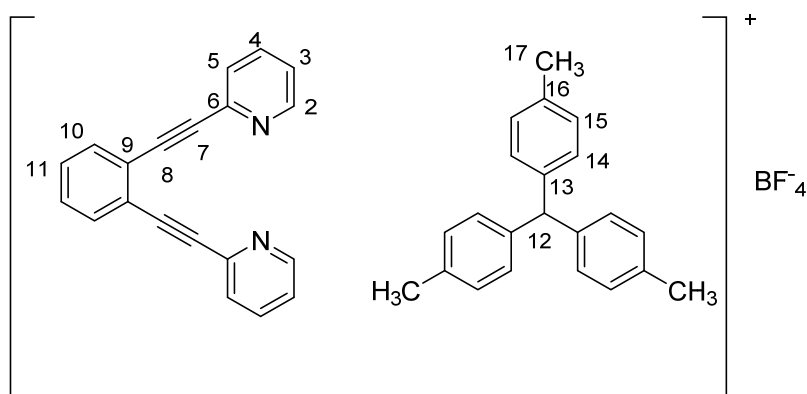
**Triphenylcarbeniumtetrafluoroborate (1a).**<sup>12</sup> This molecule is commercially available and was used as received. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.30 (dddd, *J* = 7.6, 7.6, 1.3, 1.3 Hz, 3H, H4), 7.92 (m, 6H, H3), 7.71 (m, 6H, H2). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 211.3 (C<sup>+</sup>), 143.9 (C4), 143.2 (C3), 140.4 (C1), 131.0 (C2).



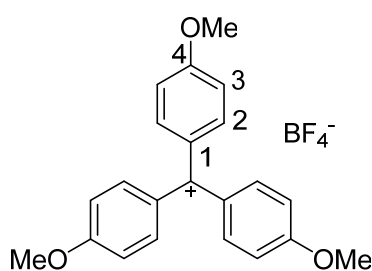
**Triphenylcarbonium1,2-bis(pyridine-2-ylethynyl)benzene tetrafluoroborate (3c).** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.84 (d, *J* = 6.3 Hz, 2H, H2), 8.24 (br dd, *J* = 7.8, 6.7 Hz 2H, H4), 8.15 (d, *J* = 7.8 Hz, 2H, H5), 7.82 (AA' part of AA'BB', 2H, H10), 7.70 (dd, *J* = 6.3, 6.7 Hz, 2H, H3), 7.54 (BB' part of AA'BB', 2H, H11), 7.40 – 7.38 (m, 9H, H15 and H16), 7.29 – 7.26 (m, 6H, H14). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 145.0 (C2), 143.3 (C4), 143.8 & 143.6 (C13), 138.5 (C6), 134.3 (C10), 132.5 (C5), 130.8 (C11), 128.68 & 128.66 (C16), 128.4 (C15), 128.27 & 128.22 (C14), 125.3 (C3), 124.1 (C9), 101.1 (C12), 98.4 (C8), 87.8 (C7).



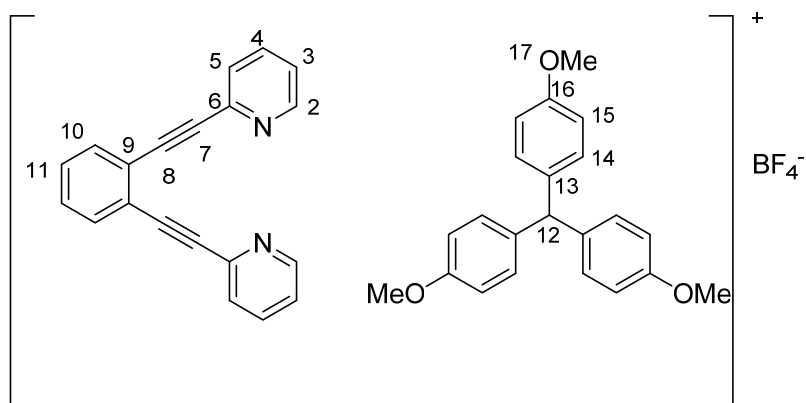
**Tri(*p*-tolyl)carbenium tetrafluoroborate (1d).**<sup>3</sup> This molecule was synthesized following a previously published procedure. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.67 (AA' part of AA'BB', 6H, H2), 7.54-7.52 (BB' part of AA'BB', 6H, H3), 2.69 (s, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 205.0 (C<sup>+</sup>) 157.3 (C4), 142.2 (C2), 137.9 (C1), 131.9 (C3), 23.4 (CH<sub>3</sub>).



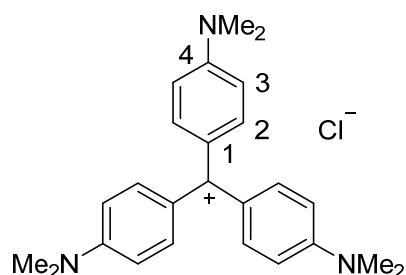
**Tri(*p*-tolyl)carbonium 1,2-bis(pyridine-2-ylethynyl)benzene tetrafluoroborate (3d).** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.95 (dd, *J* = 5.2, 1.0 Hz, 2H, H2), 8.07 (ddd, *J* = 7.8, 7.8 1.6 Hz, 2H, H4), 7.86 (ddd, *J* = 7.8, 1.1, 1.0 Hz, 2H, H5), 7.73 (AA' part of AA'BB', 2H, H10), 7.69 (ddd, *J* = 5.2, 7.8, 1.1 Hz, 2H, H3), 7.53 (BB' part of AA'BB', 2H, H11), 7.14 – 7.09 (AA'XX', 12H, H14 and H15), 2.33 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 148.1 (C2), 144.9 (C13), 141.5 (C4), 139.7 (C6), 137.3 (C16), 132.9 (C10), 130.8 (C11), 129.4 (C5), 128.2 & 129.0 (C14 and C15), 125.7 (C3), 125.1 (C9), 81.9 (C12), 90.3 (C7), 91.8 (C8), 21.2(CH<sub>3</sub>).



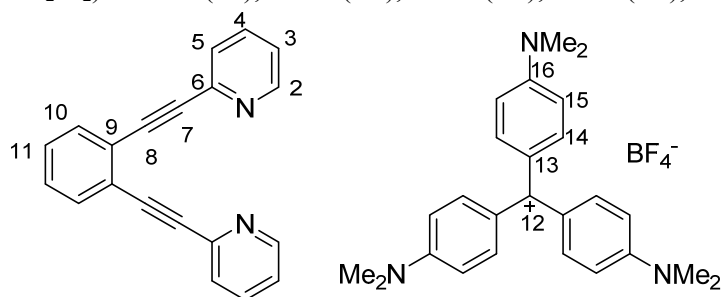
**Tris(4-methoxyphenyl)methyl cation tetrafluoroborate (1e).**<sup>3,4</sup> This molecule was synthesized by modifying a previously published procedure (Scheme S2). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.57 (AA' part of AA'XX', 6H, H2), 7.29 (XX' part of AA'XX', 6H, H3), 4.10 (s, OCH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 193.0 (C<sup>+</sup>), 171.1 (C4), 143.4 (C2), 132.6 (C1), 116.9 (C3), 57.6 (OCH<sub>3</sub>).



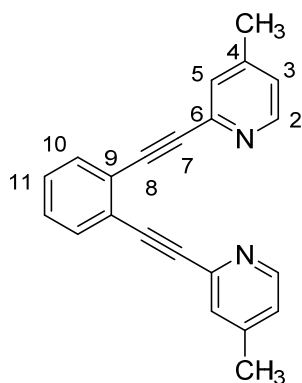
**Tris(4-methoxyphenyl)carbonium 1,2-bis(pyridine-2-ylethynyl)benzene tetrafluoroborate (3e).**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.72 (ddd,  $J = 5.1, 1.7, 0.9$  Hz, 2H, H2), 7.83 (ddd,  $J = 7.9, 7.7, 1.7$  Hz, 2H, H4), 7.77 (ddd,  $J = 7.9, 1.1, 0.9$  Hz, 2H, H5), 7.67 (AA' part of AA'BB', 2H, H10), 7.56 (AA' part of AA'XX', 6H, H14), 7.44 (BB' part of AA'BB', 2H, H11), 7.40 (ddd,  $J = 7.7, 5.2, 1.1$  Hz, 2H, H3), 7.28 (XX' part of AA'XX', 6H, H15), 4.09 (s,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  192.7 ( $\text{C}^+$ ), 171.0 (C16), 150.0 (C2), 143.3 (C14), 142.6 (C6), 138.1 (C4), 132.6 (C10), 129.8 (C11), 128.6 (C5), 125.7 (C9), 124.2 (C3), 116.9 (C15), 132.6 (C13), 92.8 (C7), 89.5 (C8), 57.6 ( $\text{OCH}_3$ ).



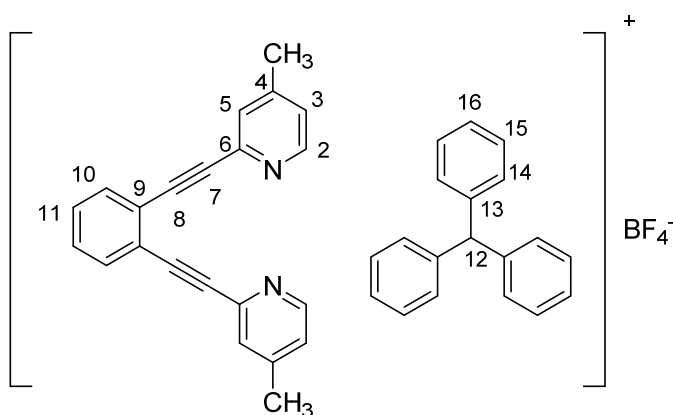
**Tris(4-(dimethylamino)phenyl)methyl cation (1f).** This molecule is commercially available and was used as received.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.32 (AA' part of AA'XX', 6H, H2), 6.85 (XX' part of AA'XX', 6H, H3), 3.23 (s, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  178.8 ( $\text{C}^+$ ), 156.1 (C1), 140.1 (C2), 127.0 (C4), 112.7 (C3), 40.8 ( $\text{CH}_3$ ).



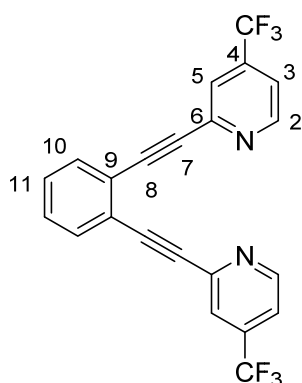
**Tris(4-(dimethylamino)phenyl)methyl cation 1,2-bis(pyridine-2-ylethynyl)benzene tetrafluoroborate (3f).**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.61 (dd,  $J = 4.7, 1.4$  Hz, 2H, H2), 7.69 – 7.72 (m, 4H, H4 and H5), 7.64 (AA' part of AA'BB', 2H, H10), 7.39 (BB' part of AA'BB', 2H, H11), 7.32 (AA' part of AA'XX', 6H, H14), 7.27 (ddd,  $J = 6.4, 4.7, 2.6$  Hz, 2H, H3), 6.85 (XX' part of AA'XX', 6H, H15), 3.22 (s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  178.8 ( $\text{C}^+$ ), 156.1 (C13), 150.5 (C2), 143.6 (C6), 140.2 (C13), 136.67 (C4), 132.70 (C10), 129.4 (C11), 128.2 (C5), 127.1 (C16), 125.8 (C9), 123.6 (C3), 112.8 (C15), 93.6 (C7), 87.7 (C8), 40.8 ( $\text{NCH}_3$ ).



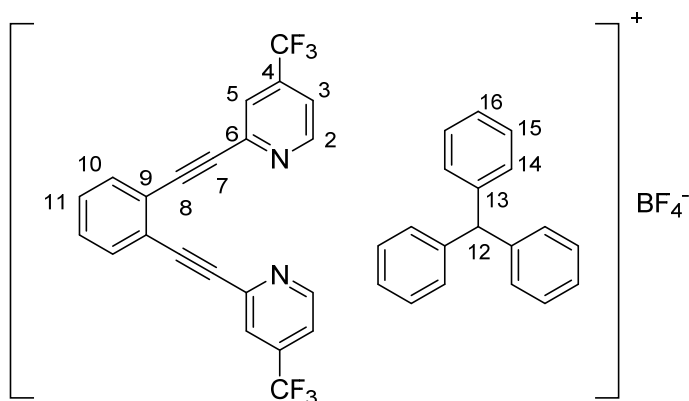
**1,2-Bis((4-methylpyridin-2-yl)ethynyl)benzene (2d).**<sup>1</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.48 (d, *J* = 5.0 Hz, 2H, H2), 7.64 (AA' part of AA'BB', 2H, H10), 7.60-7.62 (br m, 2H, H5), 7.40 (BB' part of AA'BB', 2H, H1), 7.09-7.13 (br m, 2H, H3), 2.35 (br dd, *J* = 0.7, 0.7 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 150.4 (C2), 148.0 (C4), 143.6 (C6), 132.6 (C10), 129.4 (C11), 129.3 (C5), 126.1 (C9), 124.7 (C3), 93.9 (C7), 87.4 (C8), 21.1 (CH<sub>3</sub>).



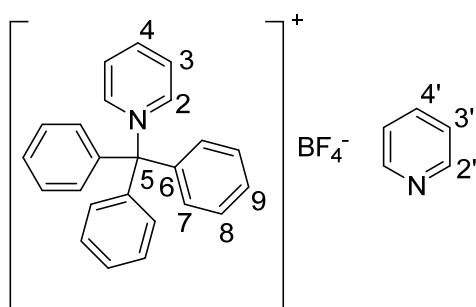
**Triphenylcarbonium 1,2-bis((4-methylpyridin-2-yl)ethynyl)benzene tetrafluoroborate (3b).** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.65 (d, *J* = 6.2 Hz, 2H, H2), 7.78 (AA' part of AA'BB', 2H, H10), 7.65-7.69 (m, 2H, H5), 7.52 (BB' part of AA'BB', 2H, H11), 7.45-7.49 (m, 2H, H3), 7.34 – 7.36 (m, 9H, H15 & H16), 7.21 – 7.23 (m, 6H, H14), 2.56 (s, 6, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 156.4 (C4), 144.3 (C2), 143.9 (C13), 138.2 (C6), 134.4 (C10), 130.3 (C11), 129.7 (C5), 128.7 (C16), 128.5 (C15), 128.3 (C14), 126.0 (C3), 124.3 (C9), 101.1 (C12), 97.8 (C8), 93.9 (C7), 21.2 (CH<sub>3</sub>).



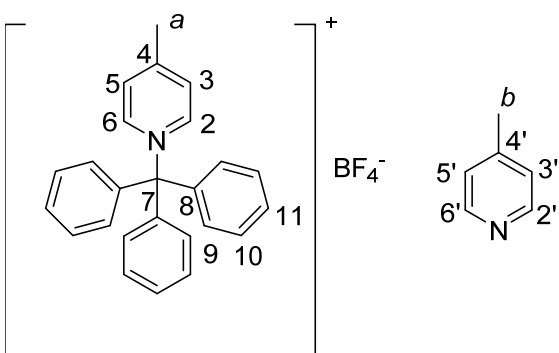
**1,2-Bis((4-(trifluoromethyl)pyridin-2-yl)ethynyl)benzene (2a).**<sup>1</sup> This compound was synthesized following a previous literature procedure.<sup>1</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.21 (dd, *J* = 5.8, 0.8 Hz, 2H, H2), 8.09-8.11 (m, 2H, H5), 7.85 (AA' part of AA'BB', 2H, H10), 7.74 (dd, *J* = 5.8, 1.9 Hz, 2H, H3), 7.67 (BB' part of AA'BB', 2H, H11). <sup>13</sup>C NMR (201 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 153.1 (C2), 144.5 (C6), 141.2 (q, <sup>2</sup>*J*<sub>CF</sub> = 35.3 Hz, C4), 133.5 (C10), 131.0 (C11), 124.4 (C5), 123.9 (C9), 123.0 (q, <sup>1</sup>*J* = 274.1 Hz, CF<sub>3</sub>), 121.1 (C3), 101.0 (C8), 90.3 (C7).



**Triphenylcarbonium 1,2-bis((4-(trifluoromethyl)pyridin-2-yl)ethynyl)benzene tetrafluoroborate (3a).**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.03 (d,  $J$  = 5.6 Hz, 2H, H2), 8.15 (br s, 1H, H5), 7.76-7.78 (AA' part of AA'XX', 2H, H10), 7.70 (d,  $J$  = 5.6 Hz, H3), 7.54-7.56 (XX' part of AA'XX', 2H, H11), 7.37-7.33 (m, 9H, H15 & H16), 7.20-7.24 (m, 6H, H14).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  150.3 (C2), 143.9 & 143.7 (C13), 143.4 (C3), 140.0 (C6), 133.1 (C10), 131.3 (C11), 129.2 (C9), 128.7 (C16), 128.7 (C14), 128.5 (C15), 125.1 (C5), 120.7 (C4), 101.1 (C12), 92.0 (C8), 90.9 (C7).

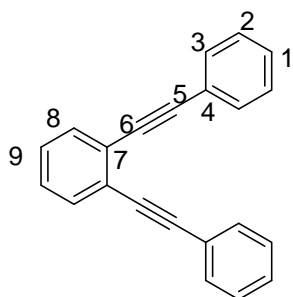


**1-(Triphenylmethyl)pyridinium pyridine tetrafluoroborate (5c).**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.77 (d,  $J$  = 5.9 Hz, 2H, H2), 8.69 (t,  $J$  = 7.7 Hz, 1H, H4), 8.59 (br d,  $J$  = 4.9 Hz, 2H, H2'), 8.13 (dd,  $J$  = 7.7, 5.9 Hz, 2H, H3), 7.76 (dd,  $J$  = 7.8, 7.8 Hz, 1H, H4'), 7.46 – 7.51 (m, 9H, H10 & H11), 7.33-7.36 (m 2H, H3'), 7.18 – 7.20 (m, 6H, H9).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  149.8 (C2'), 148.2 (C4), 145.1 (C2), 139.1 (C6), 137.1 (C4'), 130.7 (C7), 130.4 (C9), 129.8 (C8), 128.5 (C3), 124.5 (C3'), 90.4 (C5).

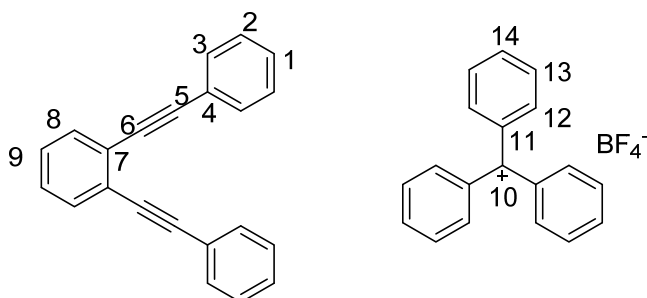


**4-Methyl-1-tritylpyridin-1-ium tetrafluoroborate 4-methylpyridin (5b).**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.56 (d,  $J$  = 7.03 Hz, 2H, H2), 8.48 (d,  $J$  = 5.4 Hz, 2H, H2'), 7.85 (d,  $J$  = 6.6 Hz, 2H, H3), 7.45 – 7.50 (m, 9H, H10 & H11), 7.34-7.36 (m, 2H, H3'), 7.20 – 7.17 (m, 6H, H9), 2.74 (s,  $\text{CH}_3$  a), 2.46 (s,  $\text{CH}_3$  b).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  162.7 (C4), 152.7 (C4'), 146.9 (C2'), 144.0 (C2), 139.2 (C8), 130.7 (C9), 130.3 (C11), 129.8 (C10), 129.1 (C3), 126.4 (C3'), 89.2 (C7), 21.9 ( $\text{CH}_3$  a), 22.7 ( $\text{CH}_3$  b).

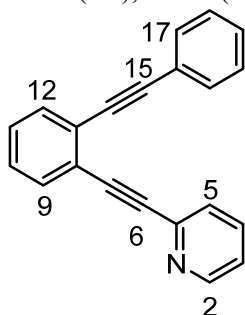




**Bis(phenylethynyl)benzene.** This molecule was synthesized following a previously published procedure.<sup>13</sup> <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.58-7.62 (m, 6H, H2, & H9), 7.37-7.40 (m, 6H, H1 & H3) 7.36 (AA' part of AA'BB', 2H, H8). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 132.4 (C9), 132.2 (C2), 129.1 (C1), 129.0 (C3), 128.8 (C8), 126.3 (C7), 123.7 (C4), 94.1 (C5), 88.7 (C6).

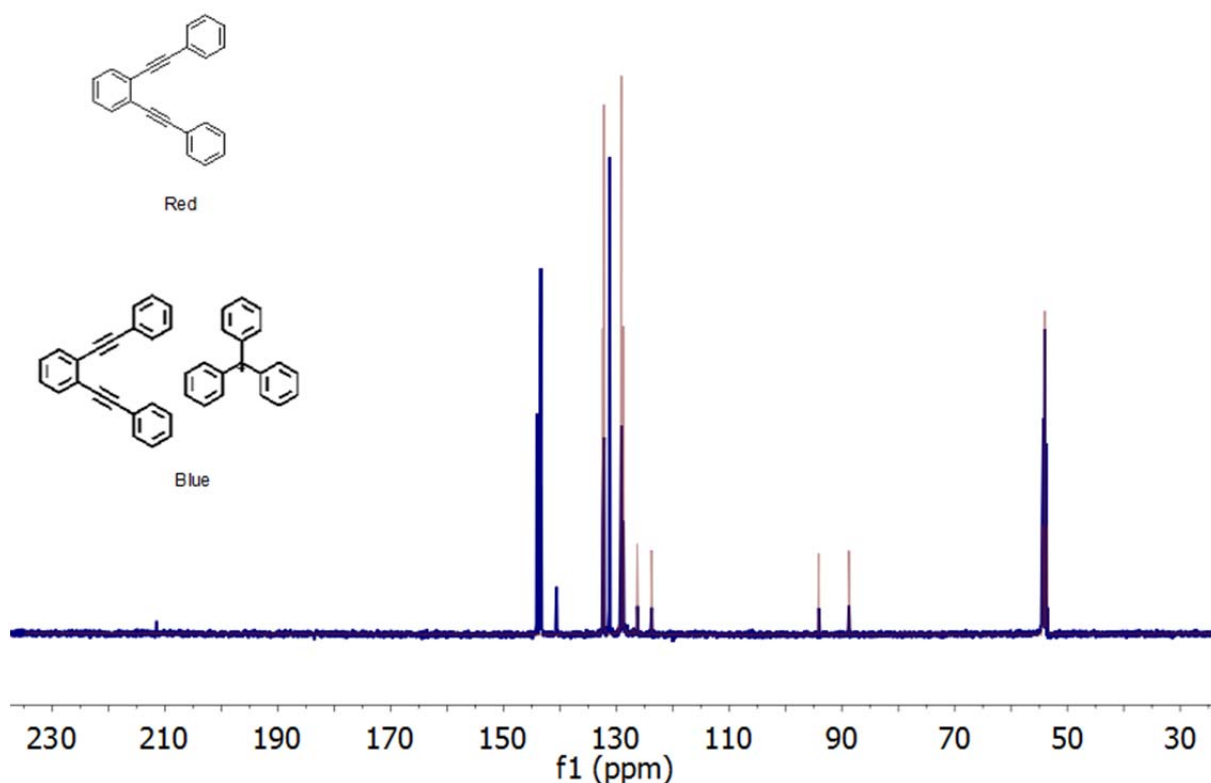


**Bis(phenylethynyl)benzene triphenylcarbenium tetrafluoroborate.** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.30 (dd,  $J = 7.4$ , Hz, 3H, H14), 7.91 (m, 6H, H13), 7.71 (m, 6H, H12), 7.58-7.62 (m, 6H, H2 & H9), 7.37-7.40 (m, 6H, H1, H3) 7.36 (AA' part of AA'BB', 2H, H8). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 211.3 (C<sup>+</sup>), 143.9 (C4), 143.2 (C3), 140.4 (C1), 132.4 (C9), 132.2 (C2), 131.0 (C2) 129.1 (C1), 129.0 (C3), 128.8 (C8), 126.3 (C7), 123.7 (C4), 94.1 (C5), 88.7 (C6).

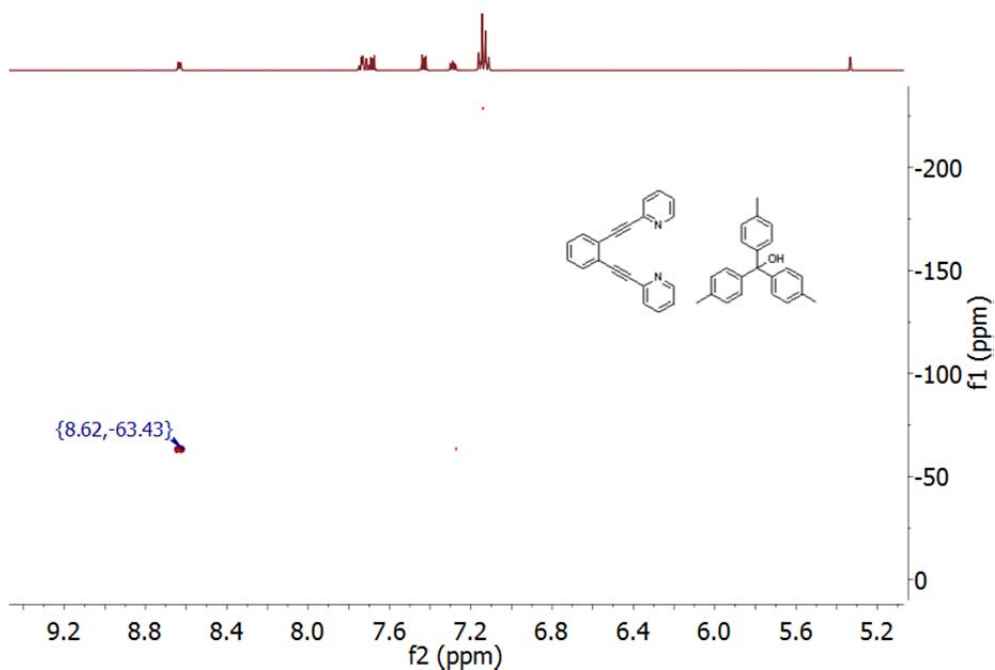


**2-((2-(phenylethynyl)phenyl)ethynyl)pyridine (7).** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.64 (ddd,  $J = 4.8, 1.8, 1.0$  Hz, 1H, H-2), 7.69 (ddd,  $J = 7.7, 7.7, 1.8$  Hz, 1H, H-4), 7.67-7.60 (m, 4H, H12, H9, 2×H17), 7.57 (ddd,  $J = 7.7, 1.1, 1.1$  Hz, 1H, H5), 7.42-7.35 (m, 5H, H10, H11, 2×H18, H19), 7.28 (ddd,  $J = 7.7, 4.8, 1.1$  Hz, 1H, H-3). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 150.8 (C2), 143.9, 136.6 (C4), 132.8, 132.33, 132.32, 129.4, 129.2, 129.0, 128.7, 127.9 (C5), 126.8, 125.3, 123.6 (C3), 123.5, 94.5 (C14), 93.3 (C6), 88.5(C7), 88.0 (C15).

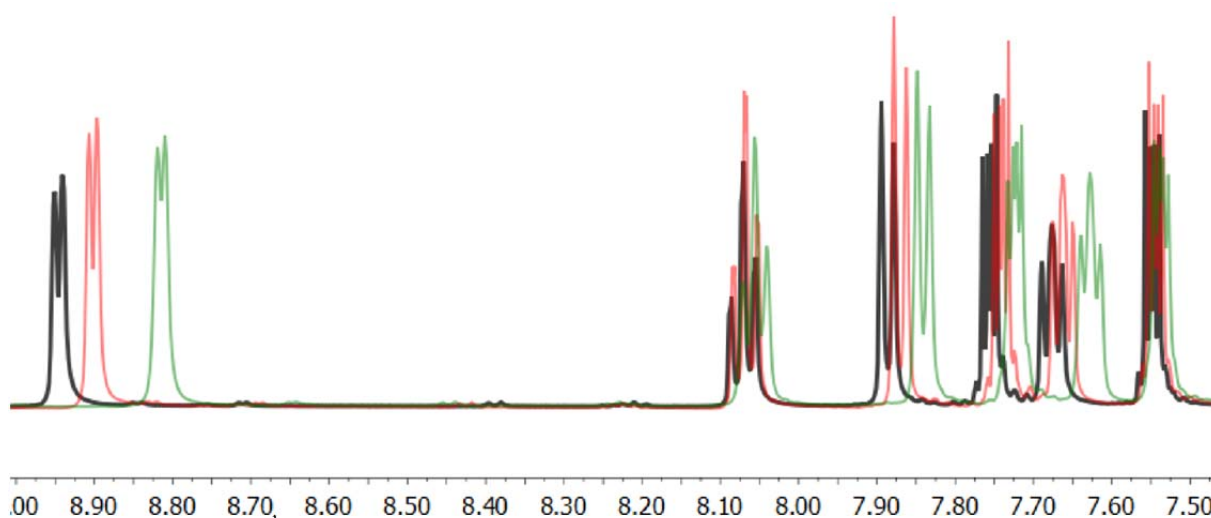
### 3. NMR spectra referred to in the main text



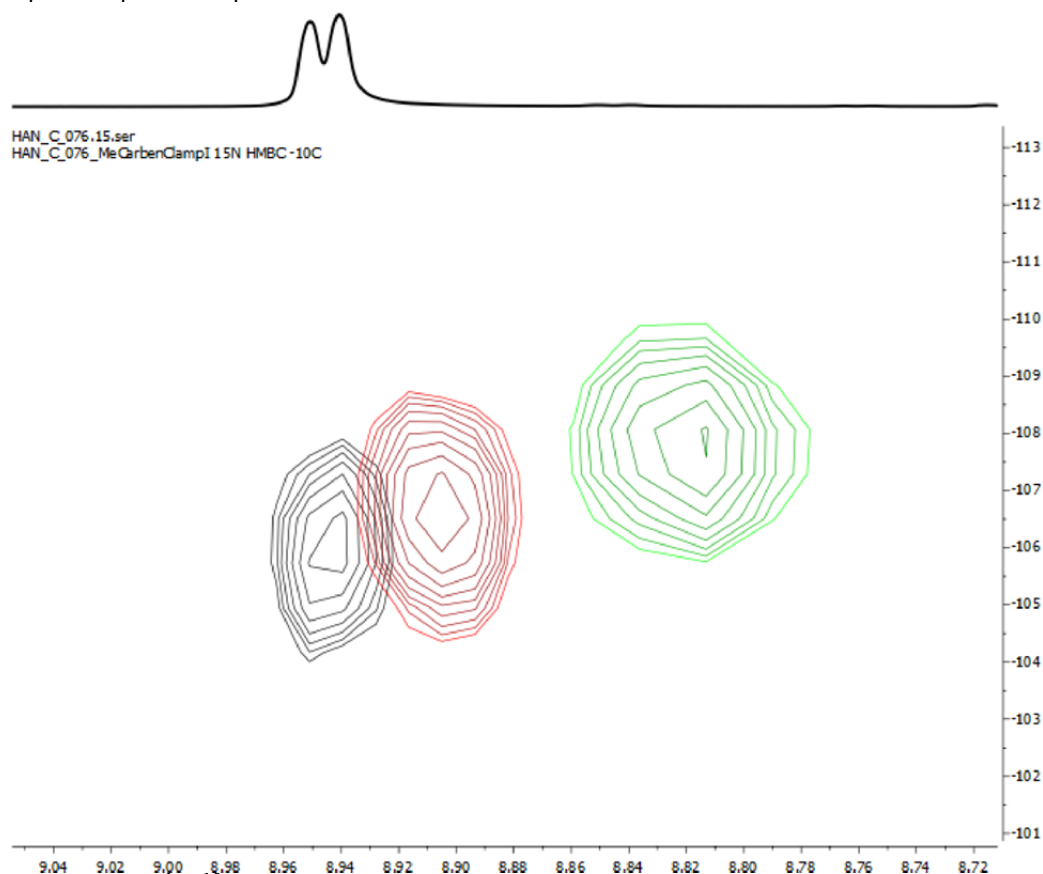
**Figure S1.** Superimposed  $^{13}\text{C}$  spectra of **1a** and bis(phenylethynyl)benzene. The unaltered chemical shifts of **1a** upon addition of bis(phenylethynyl)-benzene indicates no interaction. This confirms that the nitrogens of ligands **2** are necessary for complexation of a carbenium ion.



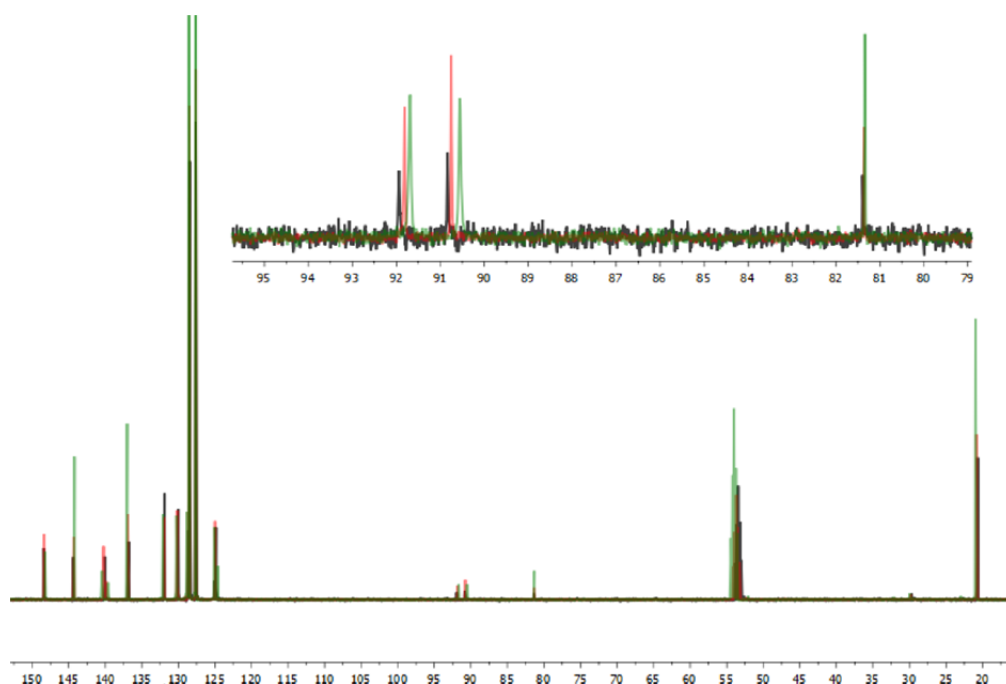
**Figure S2.**  $^1\text{H}^{15}\text{N}$  HMBC of **2c** with trityl alcohol. The lack of interaction is revealed by the unaltered  $^{15}\text{N}$  chemical shift. Thus an empty  $p_z$  orbital is necessary for interaction of **2c**, and the observed large chemical shift changes upon mixing **1a** with **2c** have to involve the carbenium carbon.



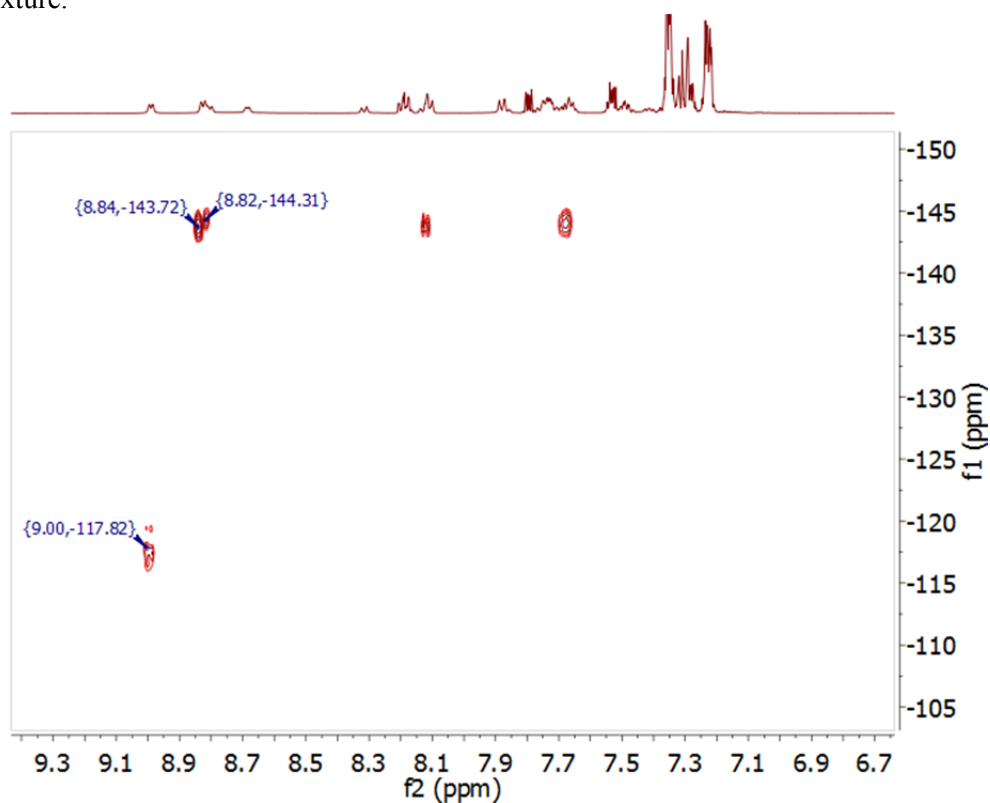
**Figure S3.** Overlaid  $^1\text{H}$  NMR spectra acquired at 25 °C (black), -10 °C (red) and -40 °C (green) showing the pyridine signals of **3d**. Observation of one set of signals at various temperatures is indicative of a static  $[\text{N}\cdots\text{C}\cdots\text{N}]^+$  geometry, whereas is incompatible with the presence of a dynamic  $[\text{N}-\text{C}\cdots\text{N}]^+ \rightleftharpoons [\text{N}\cdots\text{C}-\text{N}]^+$  mixture.



**Figure S4.** Overlaid  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC of **3d** acquired at 25 °C (black), -10 °C (red) and -40 °C (green). A single  $^{15}\text{N}$  NMR signal observed at various temperatures is indicative of a static  $[\text{N}\cdots\text{C}\cdots\text{N}]^+$  geometry, whereas is incompatible with the presence of a dynamic  $[\text{N}-\text{C}\cdots\text{N}]^+ \rightleftharpoons [\text{N}\cdots\text{C}-\text{N}]^+$  mixture.

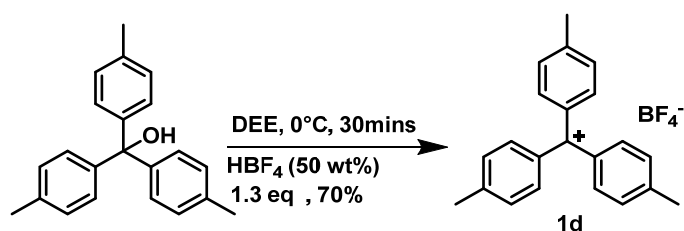


**Figure S5.** Overlaid  $^{13}\text{C}$  NMR spectra acquired at 25 °C (black), -10 °C (red) and -40 °C (green) of **3d**. The inserted expansion shows the acetylene signals at 90-92 ppm and the carbonium carbon at -80.5 ppm enlarged. A single  $^{15}\text{N}$  NMR signal observed at various temperatures is indicative of a static  $[\text{N}\cdots\text{C}\cdots\text{N}]^+$  geometry, whereas is incompatible with the presence of a dynamic  $[\text{N}-\text{C}\cdots\text{N}]^+ \rightleftharpoons [\text{N}\cdots\text{C}-\text{N}]^+$  mixture.



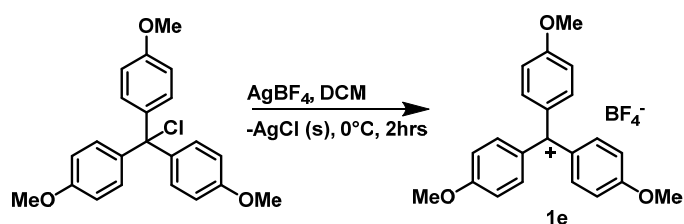
**Figure S6.**  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC of **1a:2c** (1:2). Peak splitting observed at -144 ppm upon addition of an excess of **1a** to a solution of **2c** reveals alkylation of both Lewis basic nitrogens, which was corroborated by ITC titrations.

#### 4. Compound characterization



Scheme S1. Synthesis of **1d**.

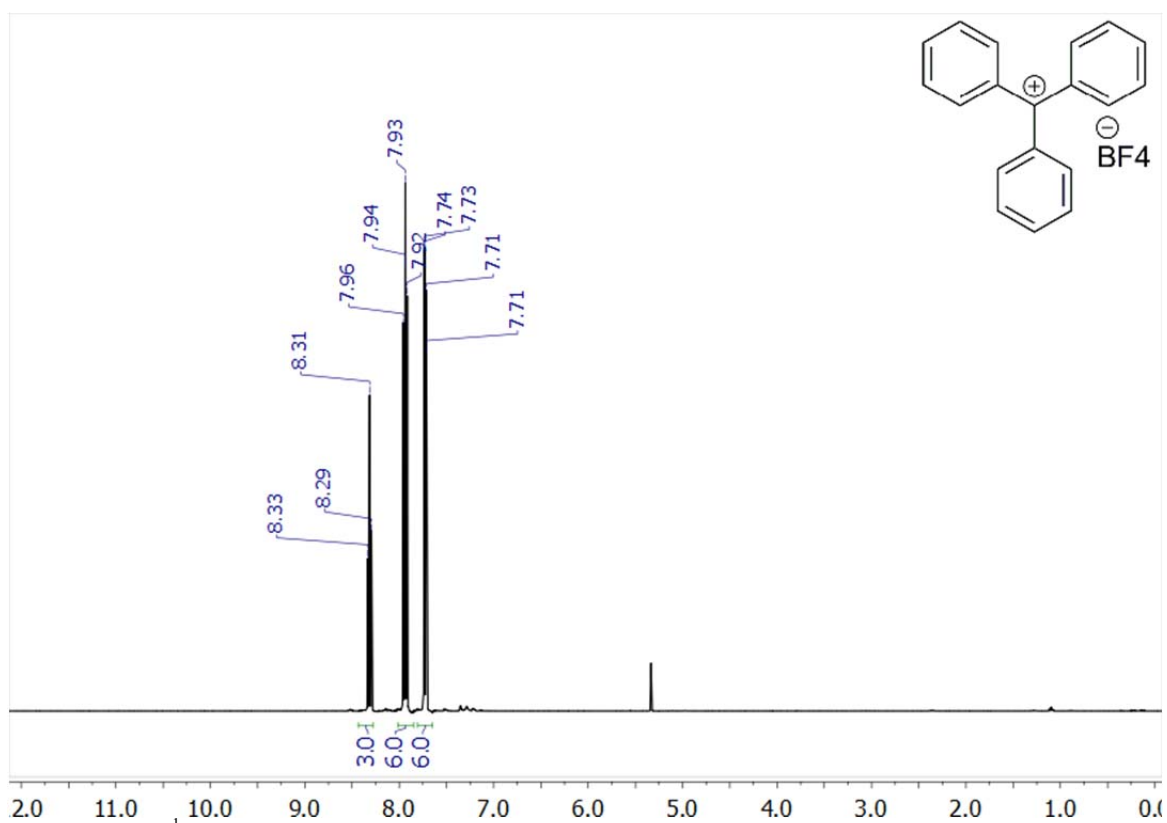
The tri-*p*-tolylmethanol was dissolved in diethyl ether and cooled to  $0^\circ\text{C}$ . Under vigorous stirring, a solution of tetrafluoroboric acid in diethyl ether (50 wt%) was added dropwise over 10 min. With each drop, a deeply colored green precipitate formed. After the solvent had been removed, the precipitate was washed with diethyl ether and dried *in vacuo* as a green solid (70%).



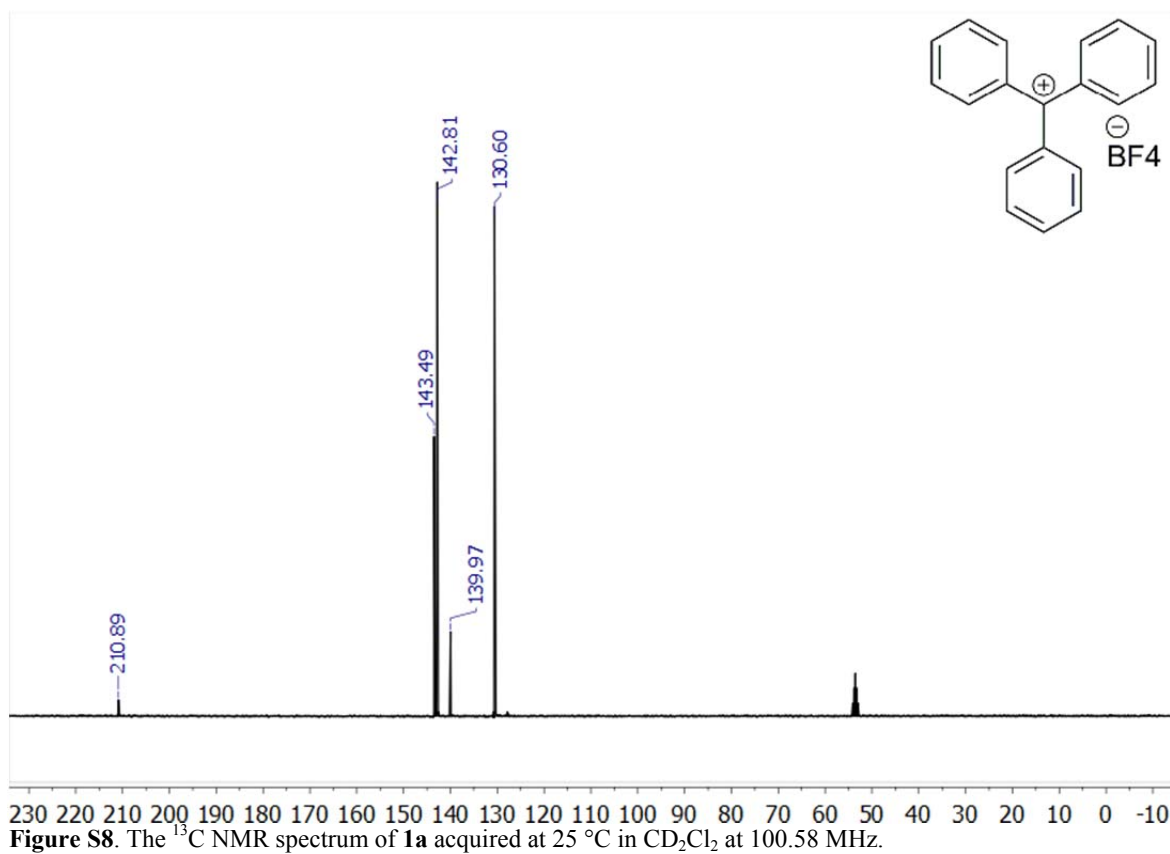
Scheme S2. Synthesis of **1e**.

Into an oven-dried vial equipped with a stir bar,  $\text{AgBF}_4$  (200 mg, 1.0274 mmol) was weighed in and an Ar balloon was inserted. 3–4 mL of dry DCM was added and the vial kept over an ice bath. Into a separate vial equipped with a stir bar, the tritylchloride (1 eq, 1.0274 mmol) was weighed in and dissolved in dry DCM. This solution was then delivered slowly to the vial containing the Ag salt. An immediate dark orange color was observed as solid  $\text{AgCl}$  precipitated out. This mixture was then vigorously stirred for 2 h over an ice bath. Then, this vial was centrifuged at 2500 rpm for 10 min, and the supernatant was transferred into a separate vial. Excess solvent was removed under a  $\text{N}_2$  flow, and **1e** was isolated as a dark red solid (65%).

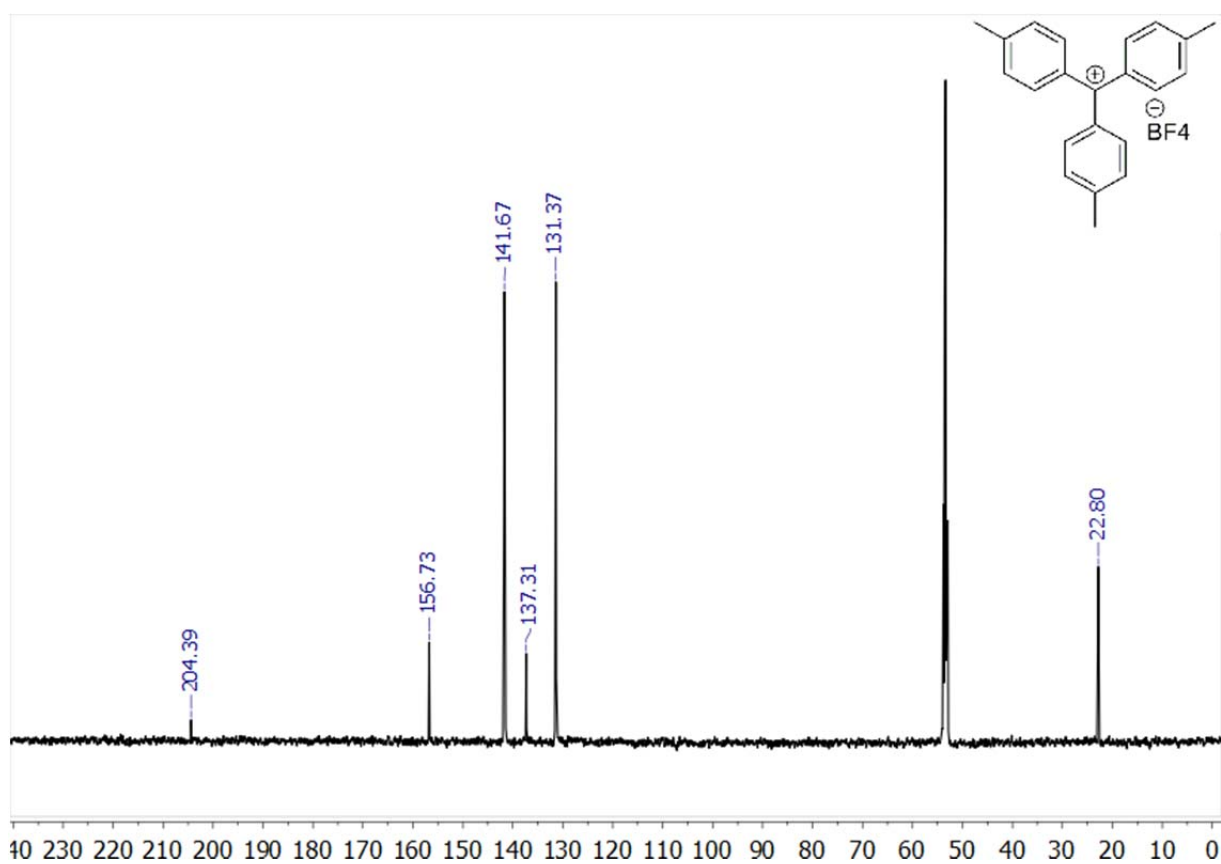
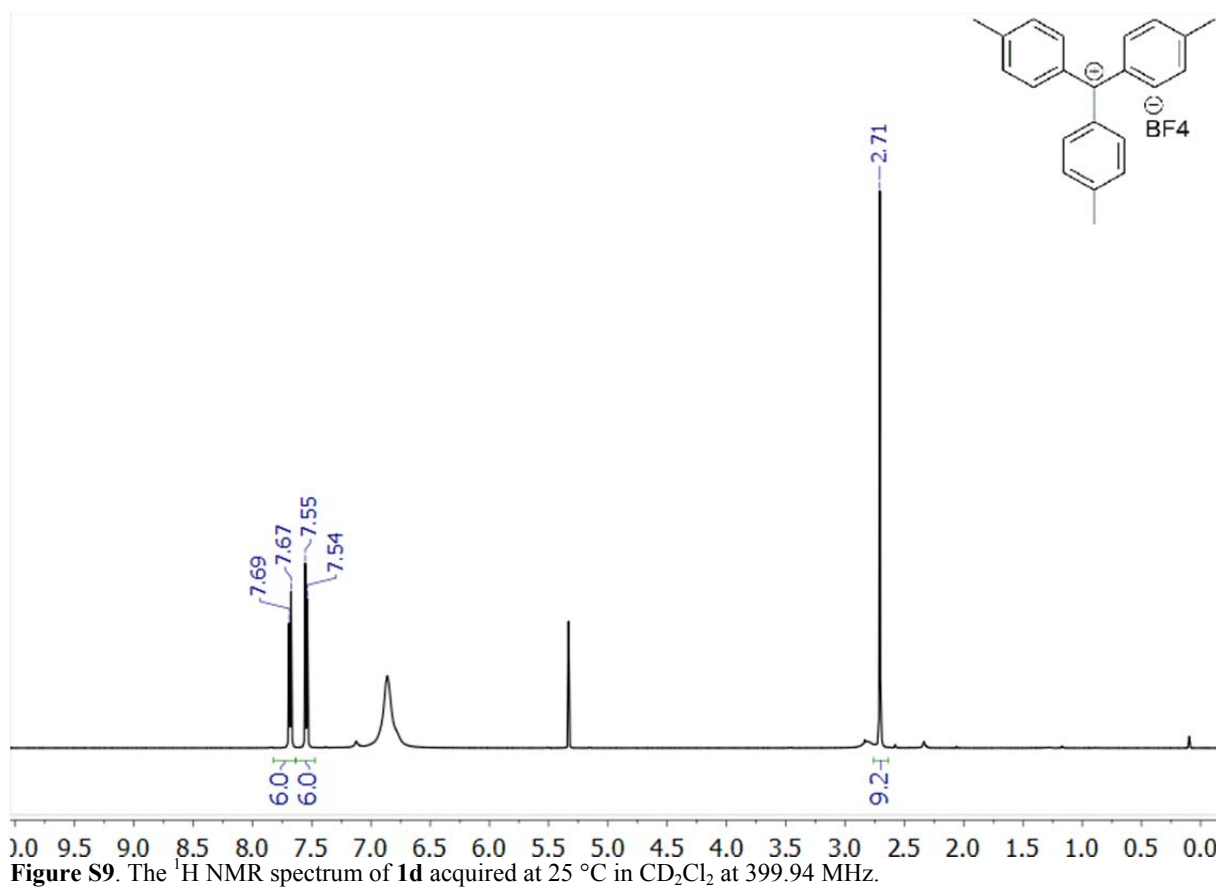
## 5. NMR spectra of the starting materials and synthesized compounds

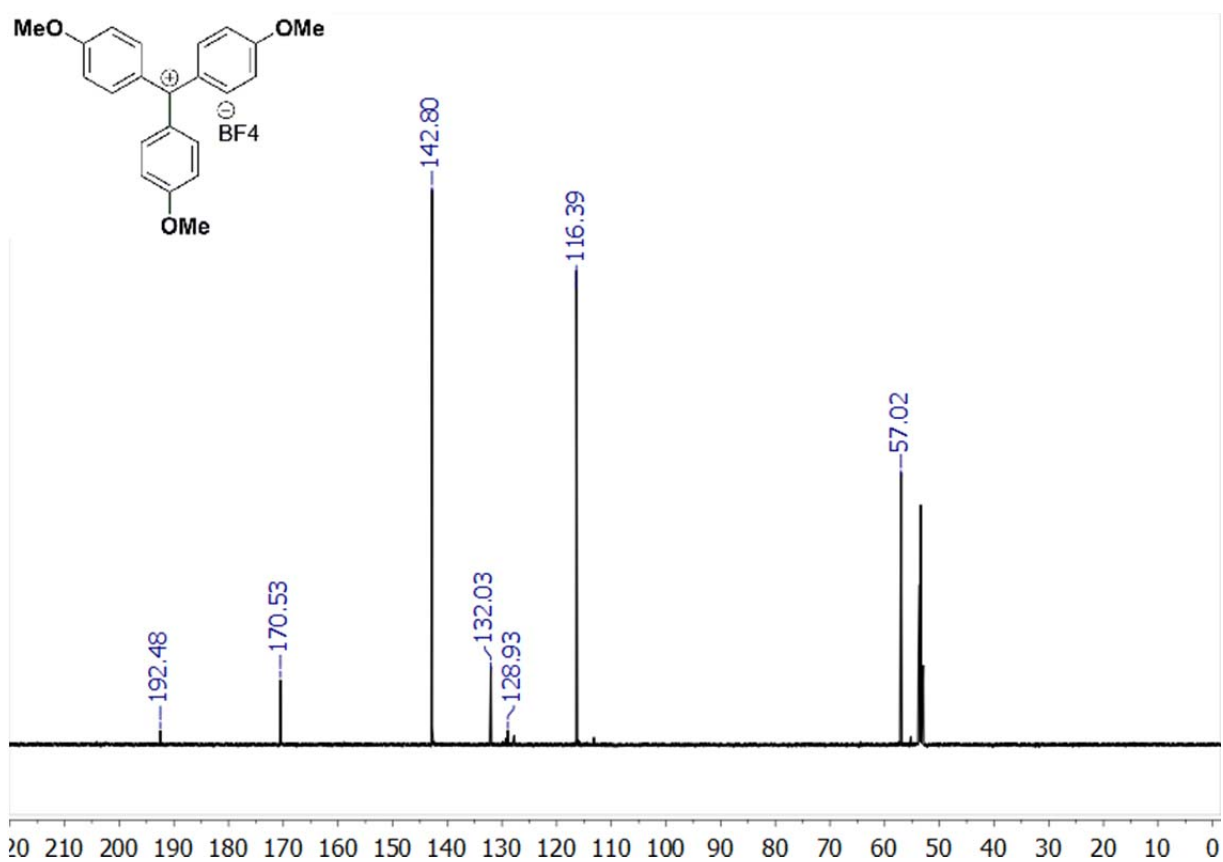
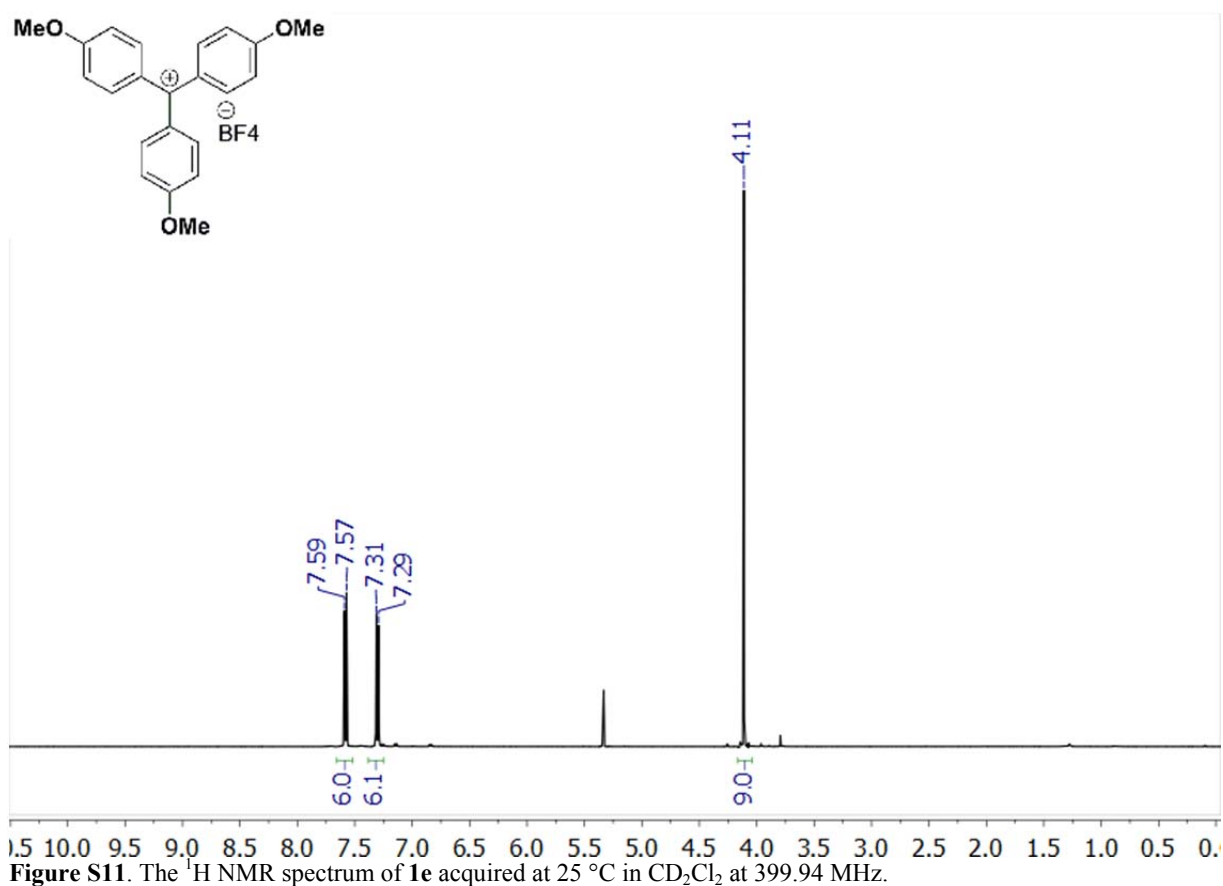


**Figure S7.** The  $^1\text{H}$  NMR spectrum of **1a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 399.94 MHz.



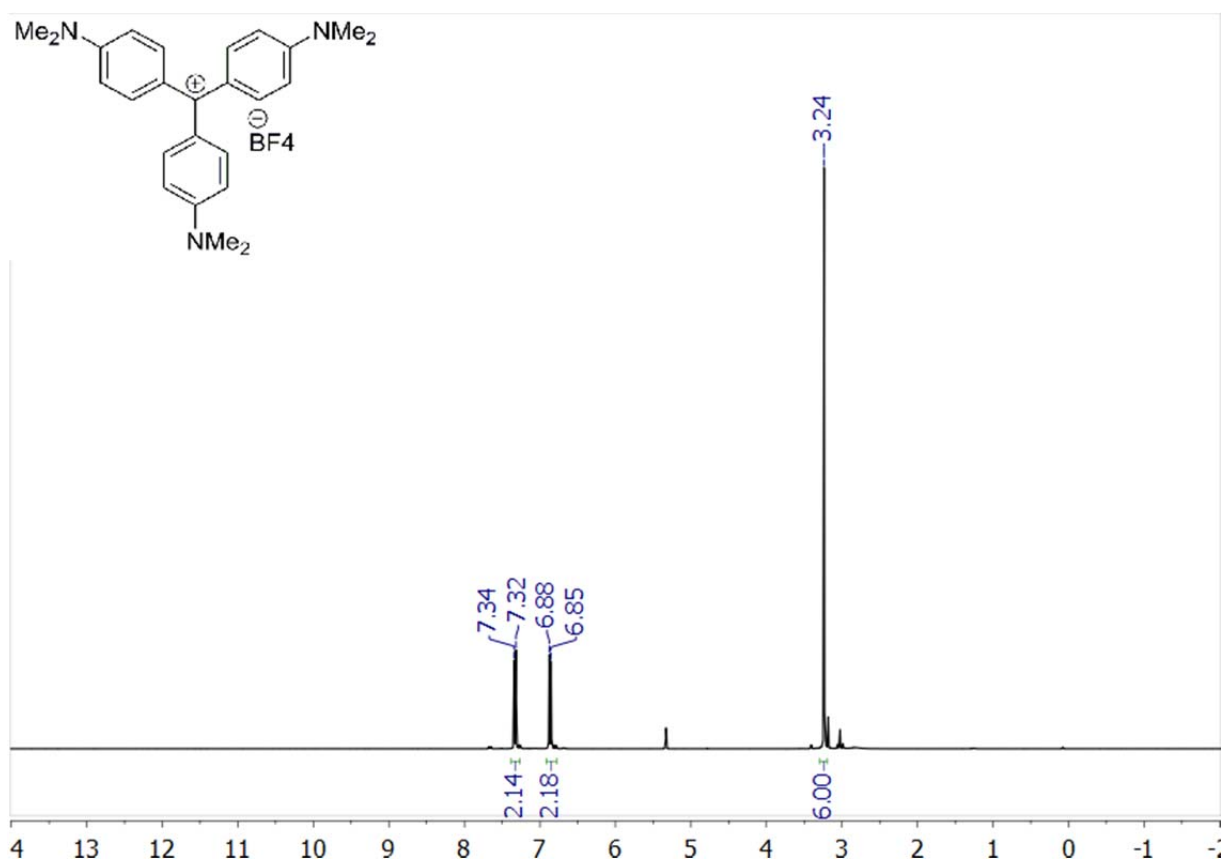
**Figure S8.** The  $^{13}\text{C}$  NMR spectrum of **1a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 100.58 MHz.



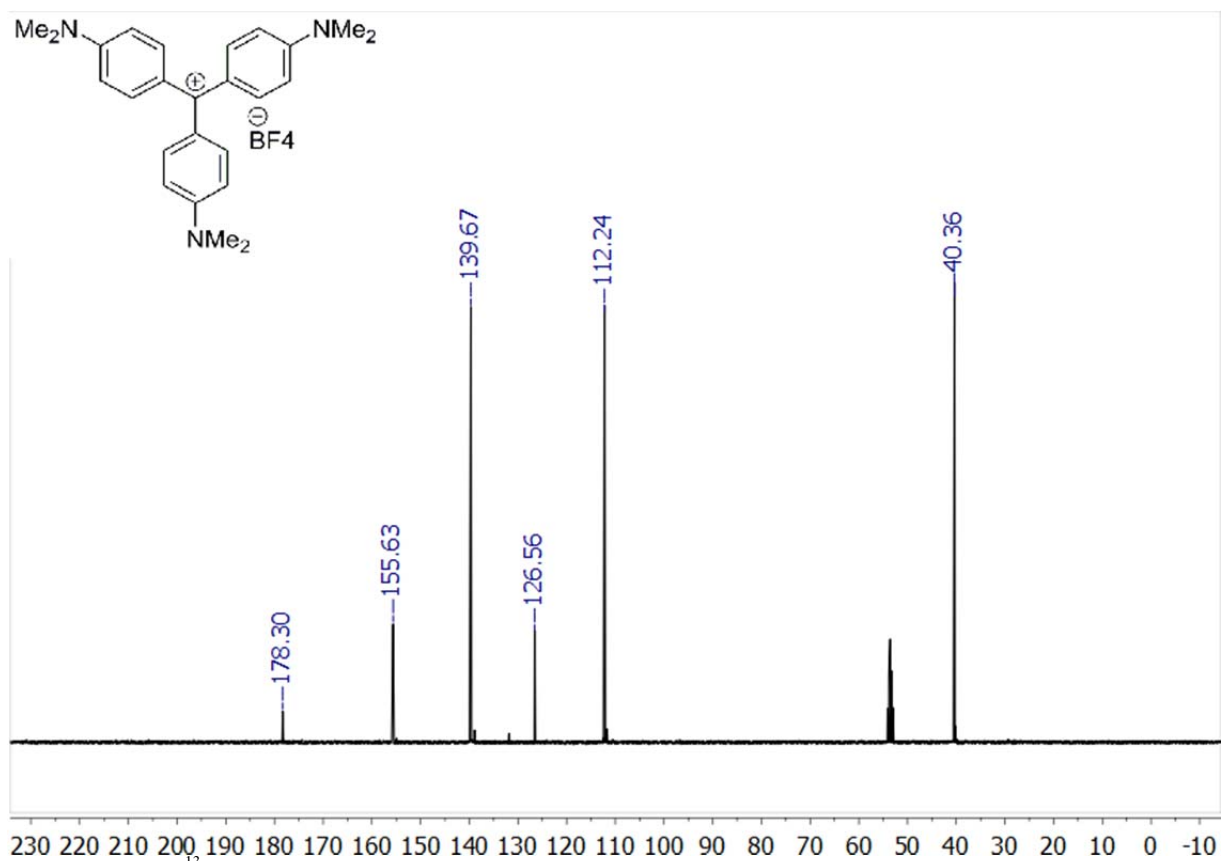


**Figure S12.** The  $^{13}\text{C}$  NMR spectrum of **1e** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 100.58 MHz.

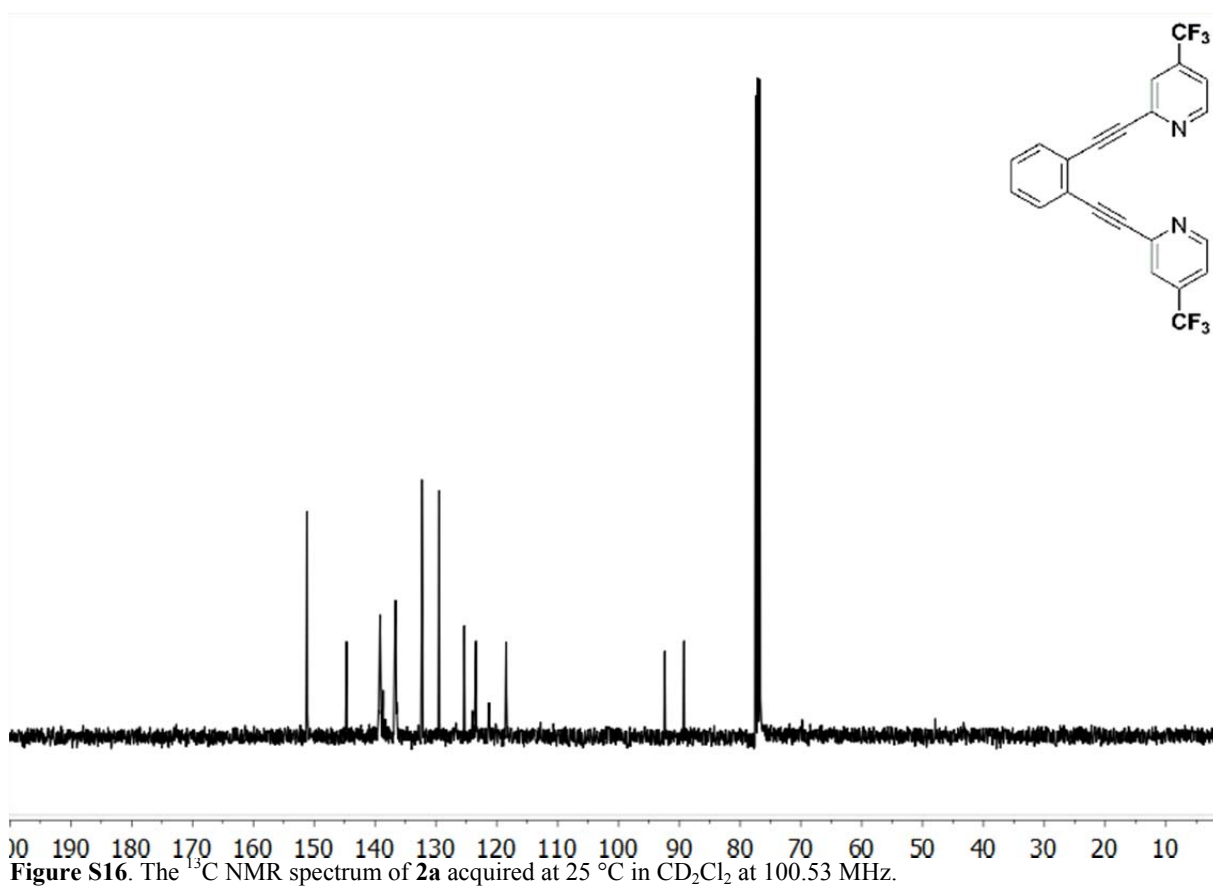
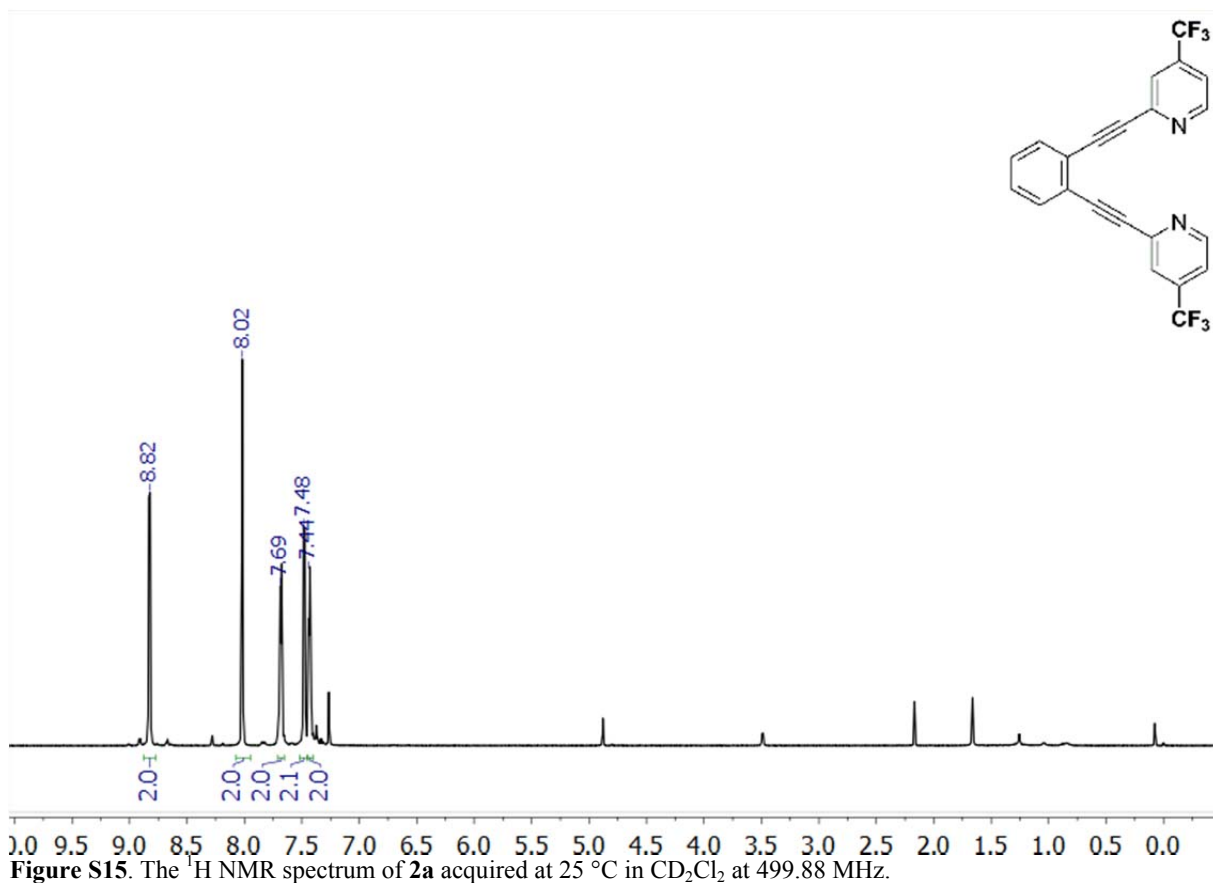


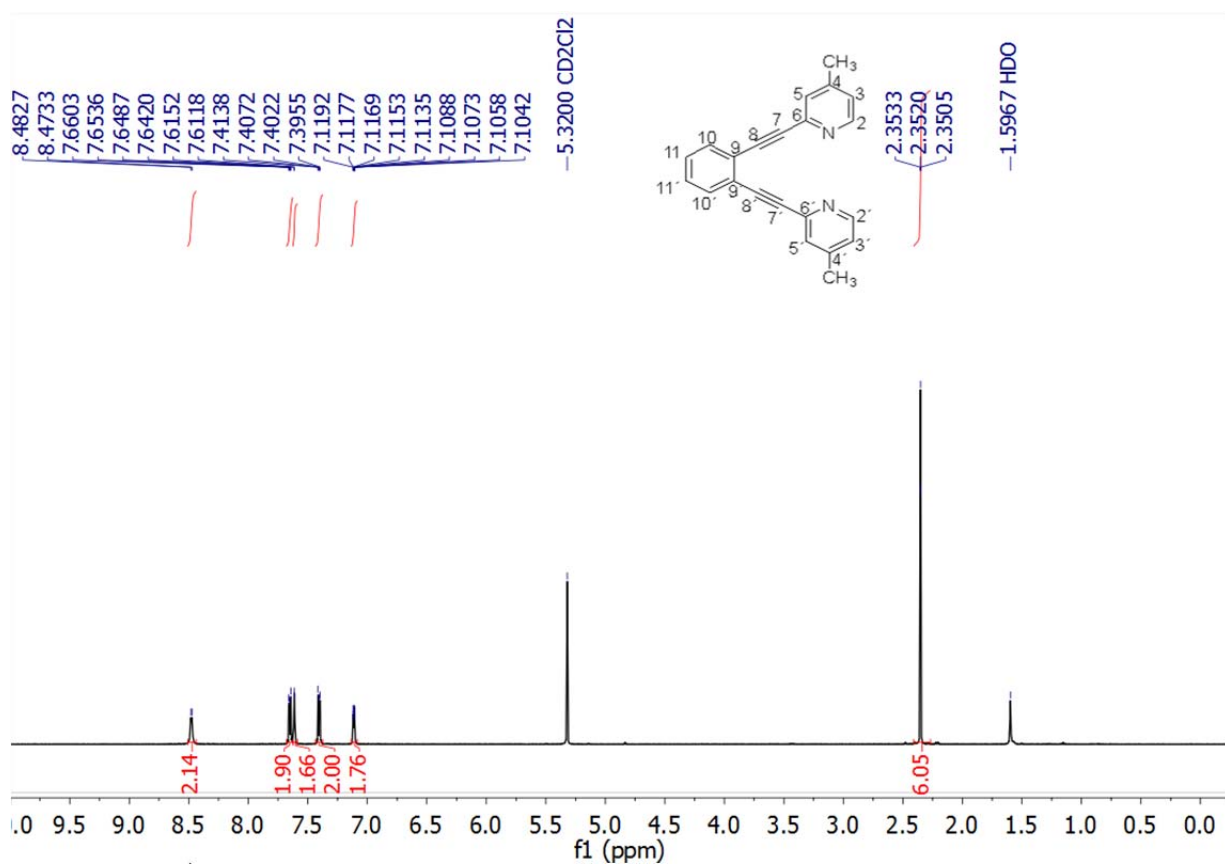
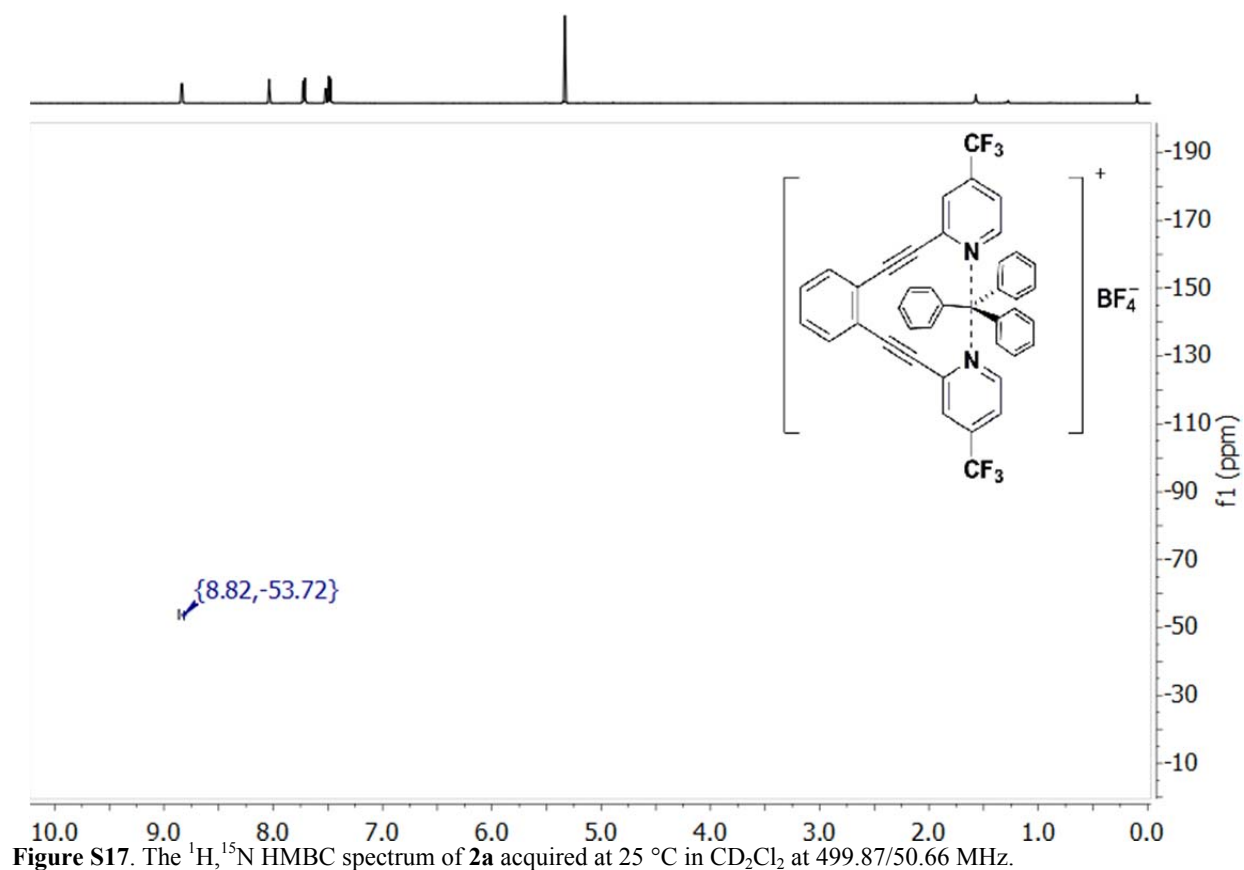


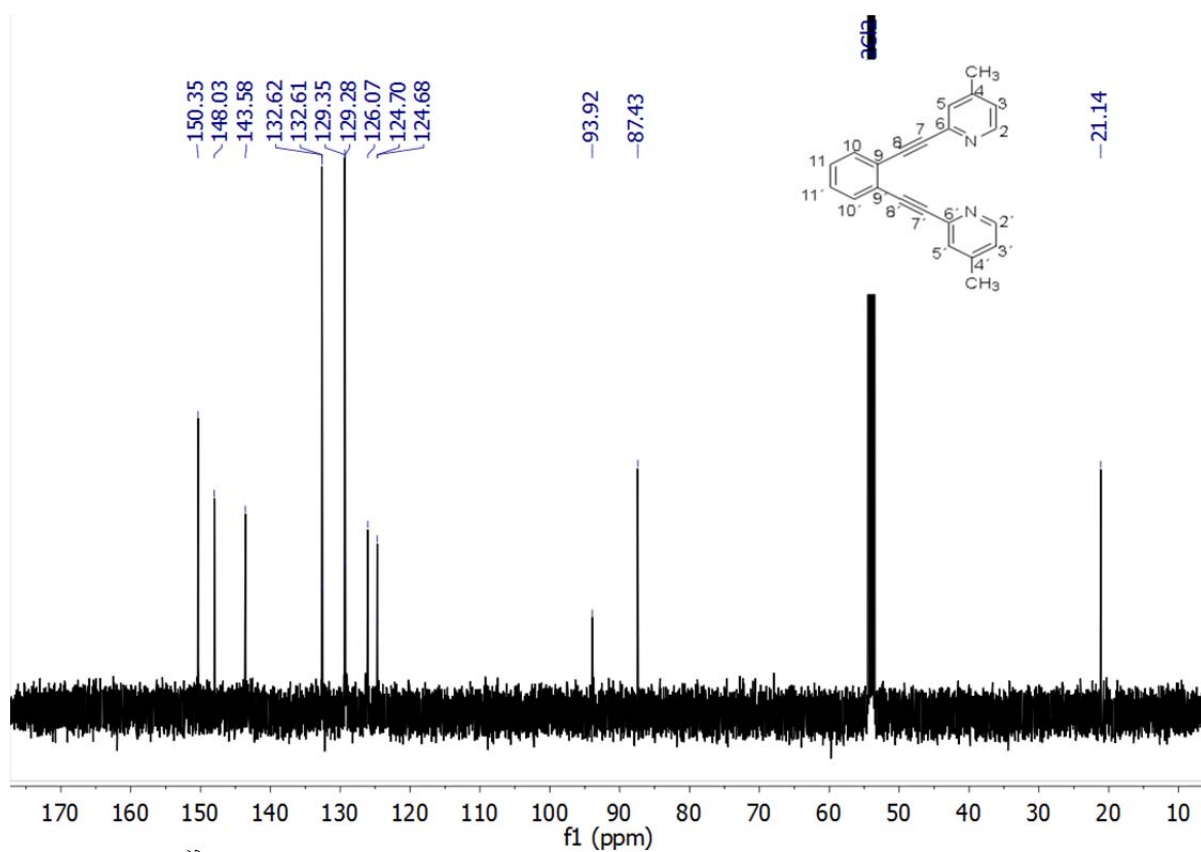
**Figure S13.** The <sup>1</sup>H NMR spectrum of **1f** acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 399.94 MHz.



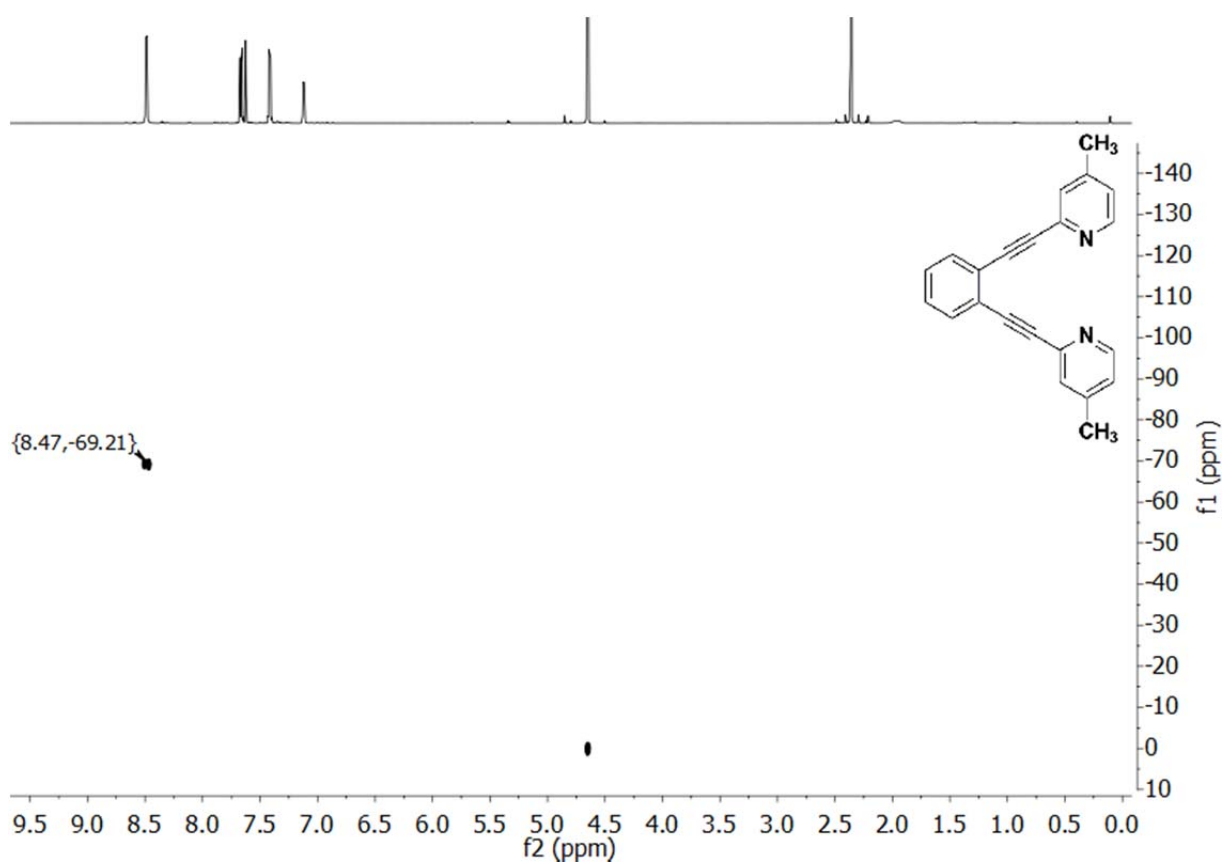
**Figure S14.** The <sup>13</sup>C NMR spectrum of **1f** acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 100.58 MHz.



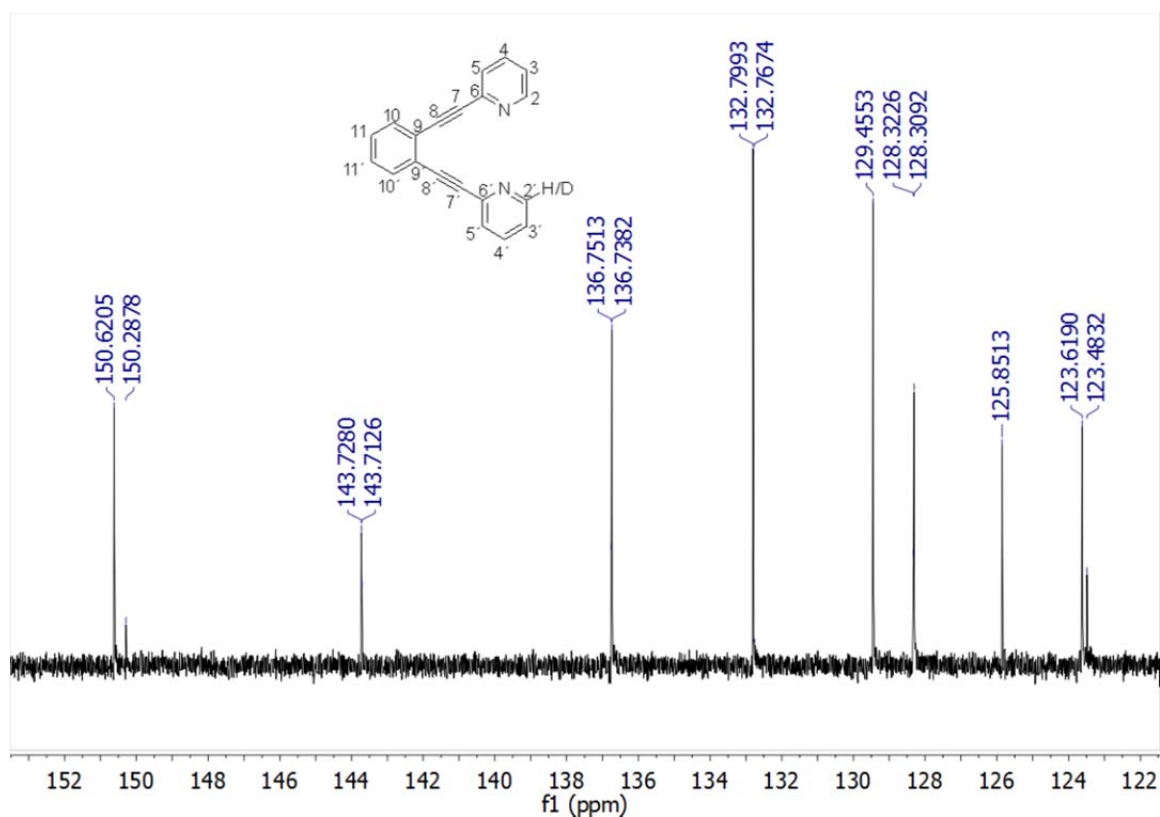
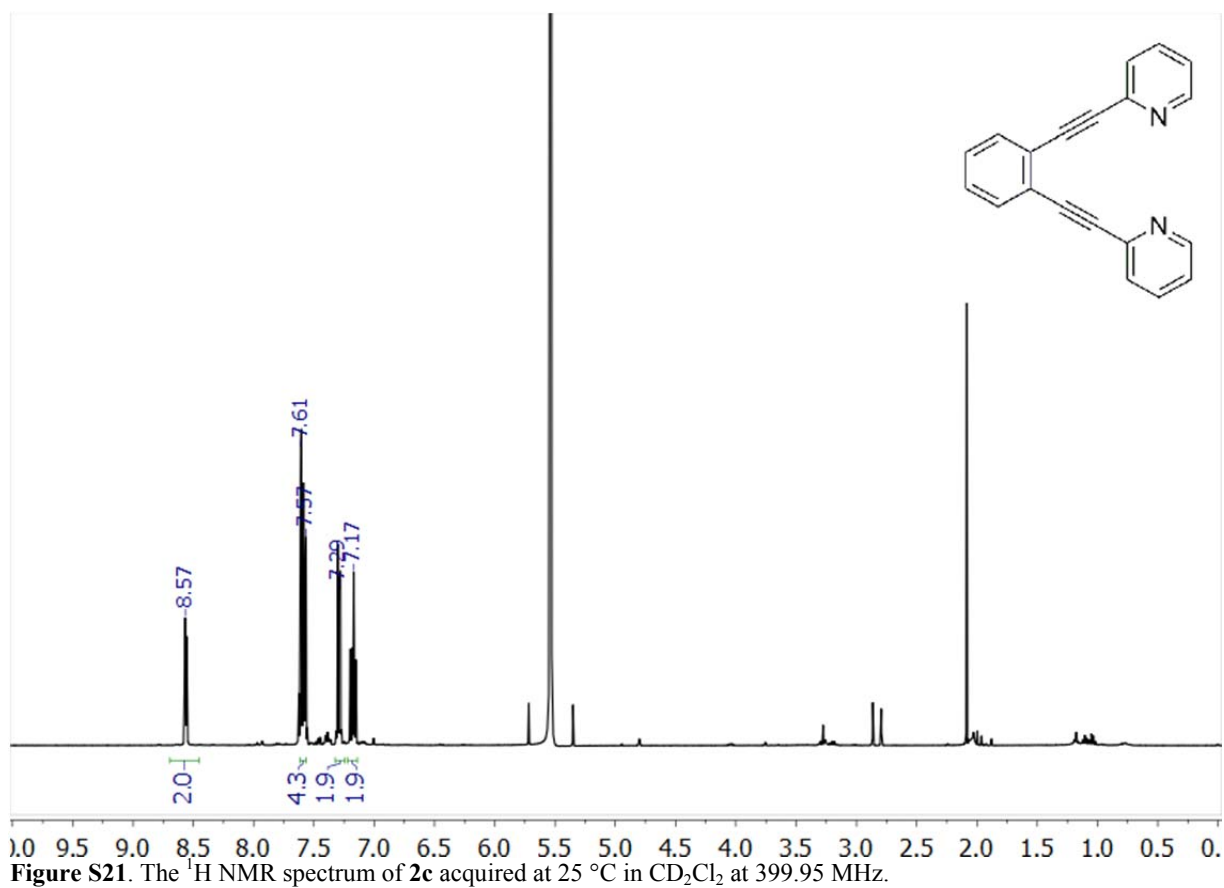


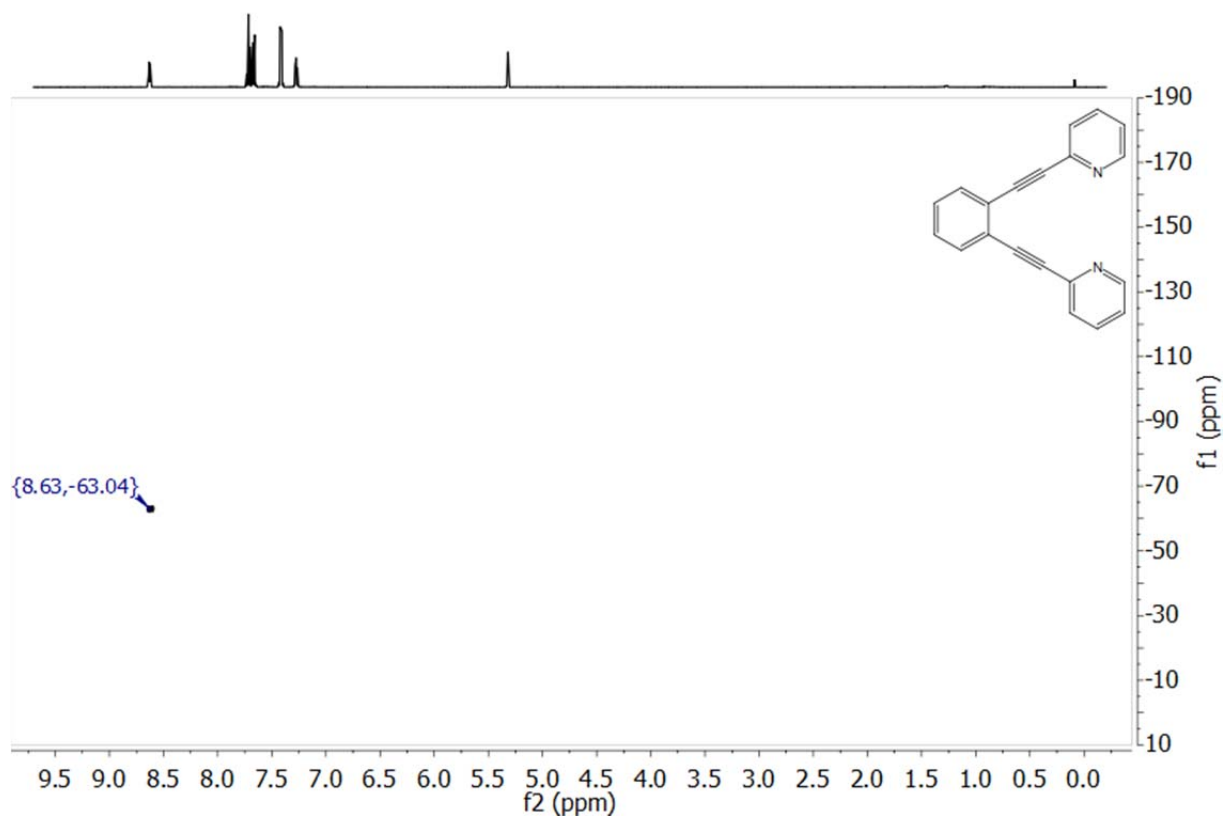


**Figure S19.** The  $^{13}\text{C}$  NMR spectrum of **2b** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 125.71 MHz.

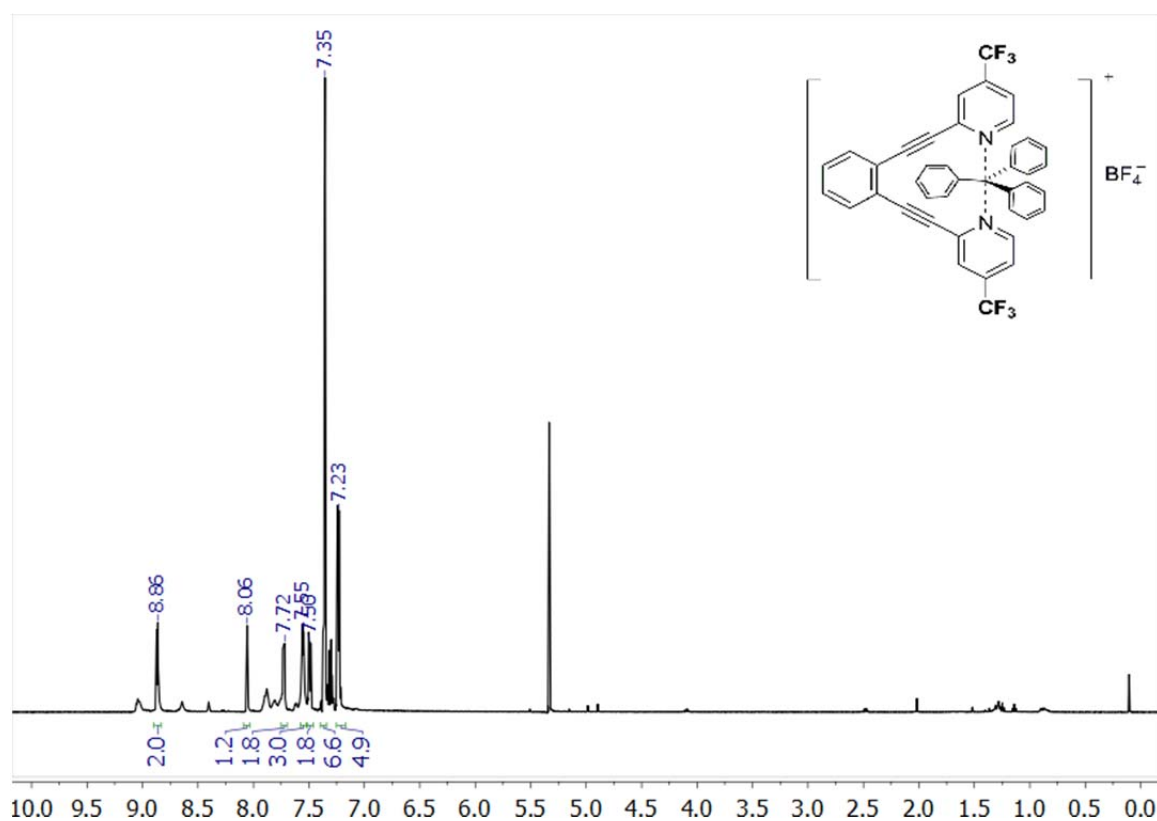


**Figure S20.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **2b** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.

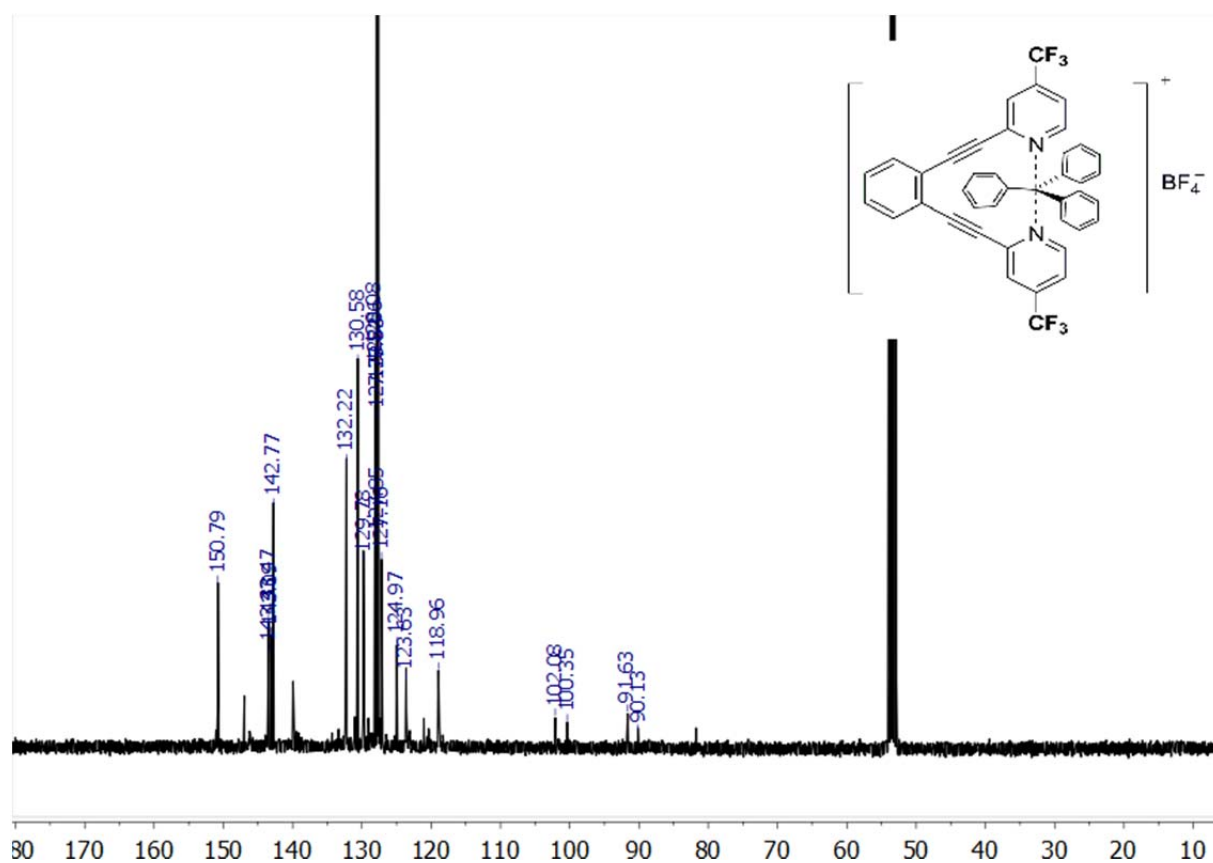




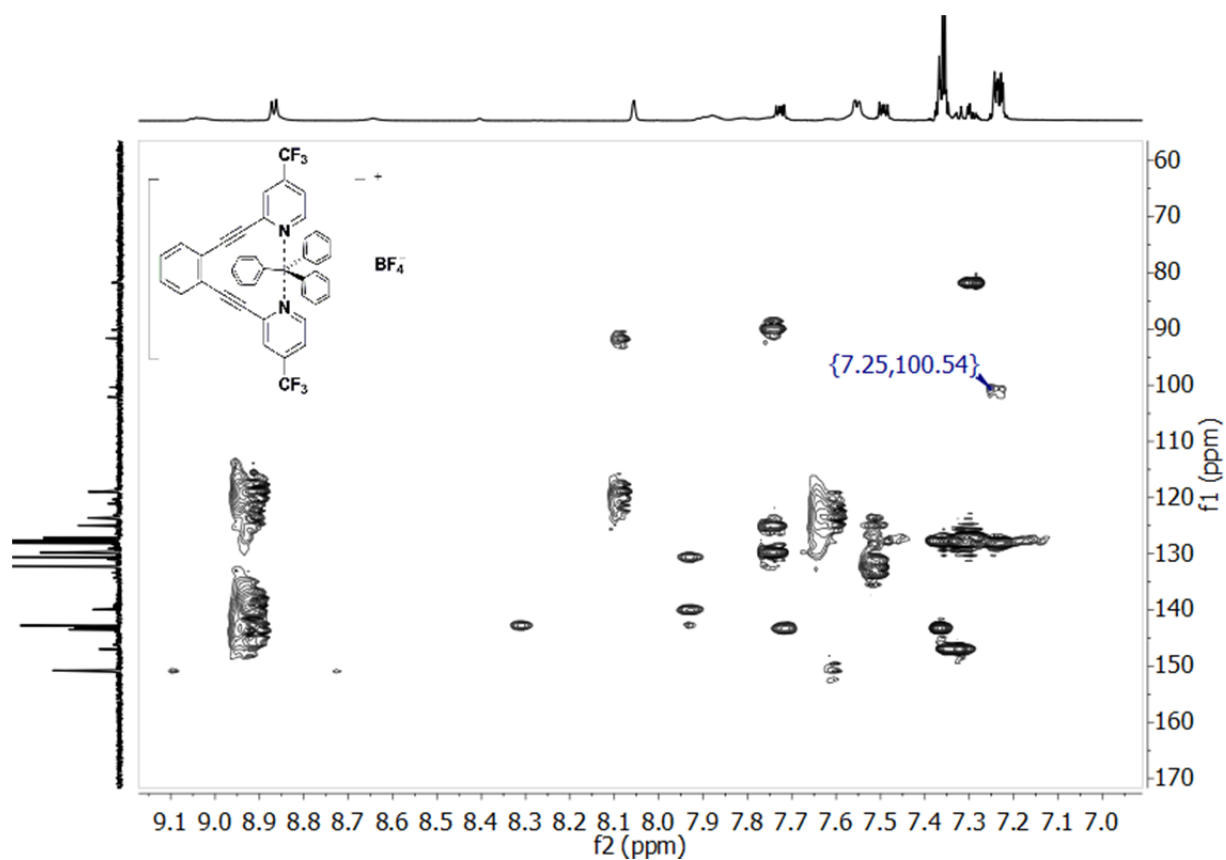
**Figure S23.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **2c** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.



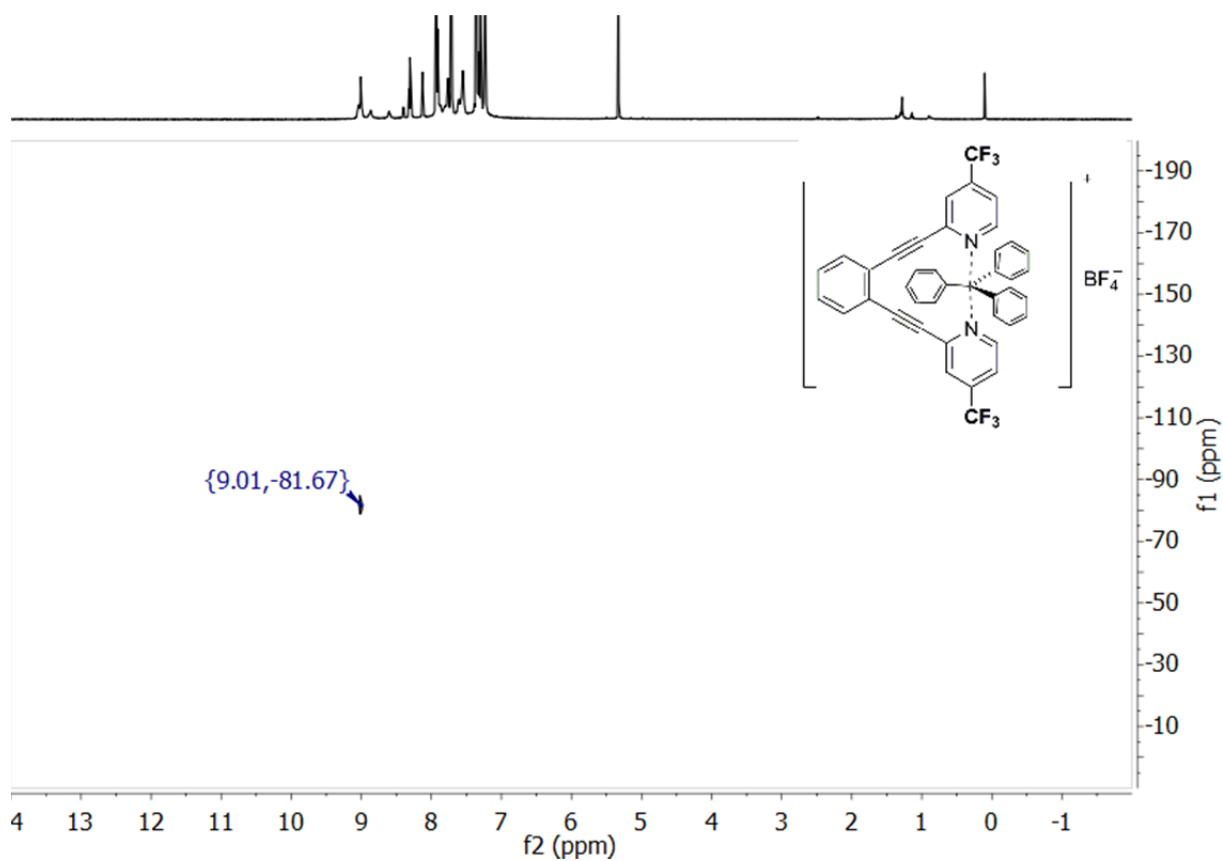
**Figure S24.** The  $^1\text{H}$  NMR spectrum of **3a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.



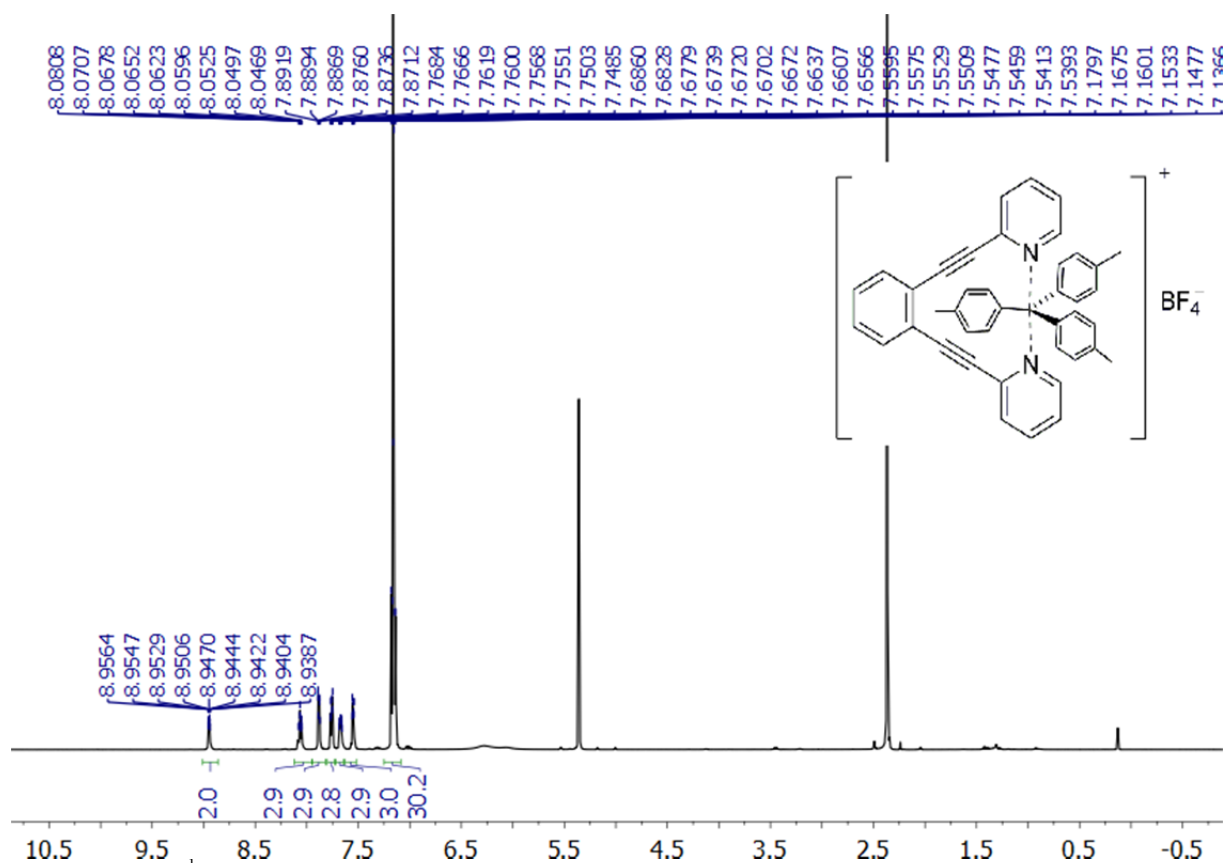
**Figure S25.** The  $^{13}\text{C}$  NMR spectrum of **3a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 125.71 MHz.



**Figure S26.** The  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of **3a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/125.71 MHz.

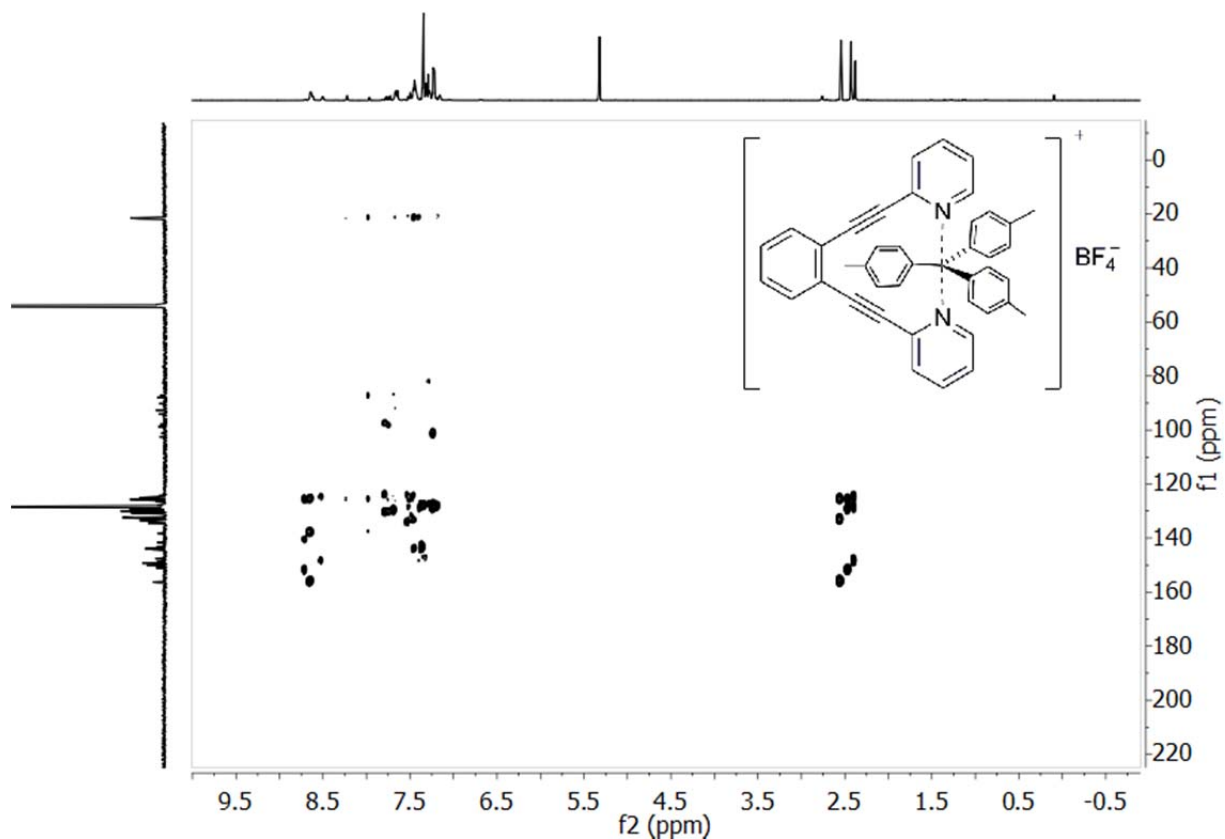
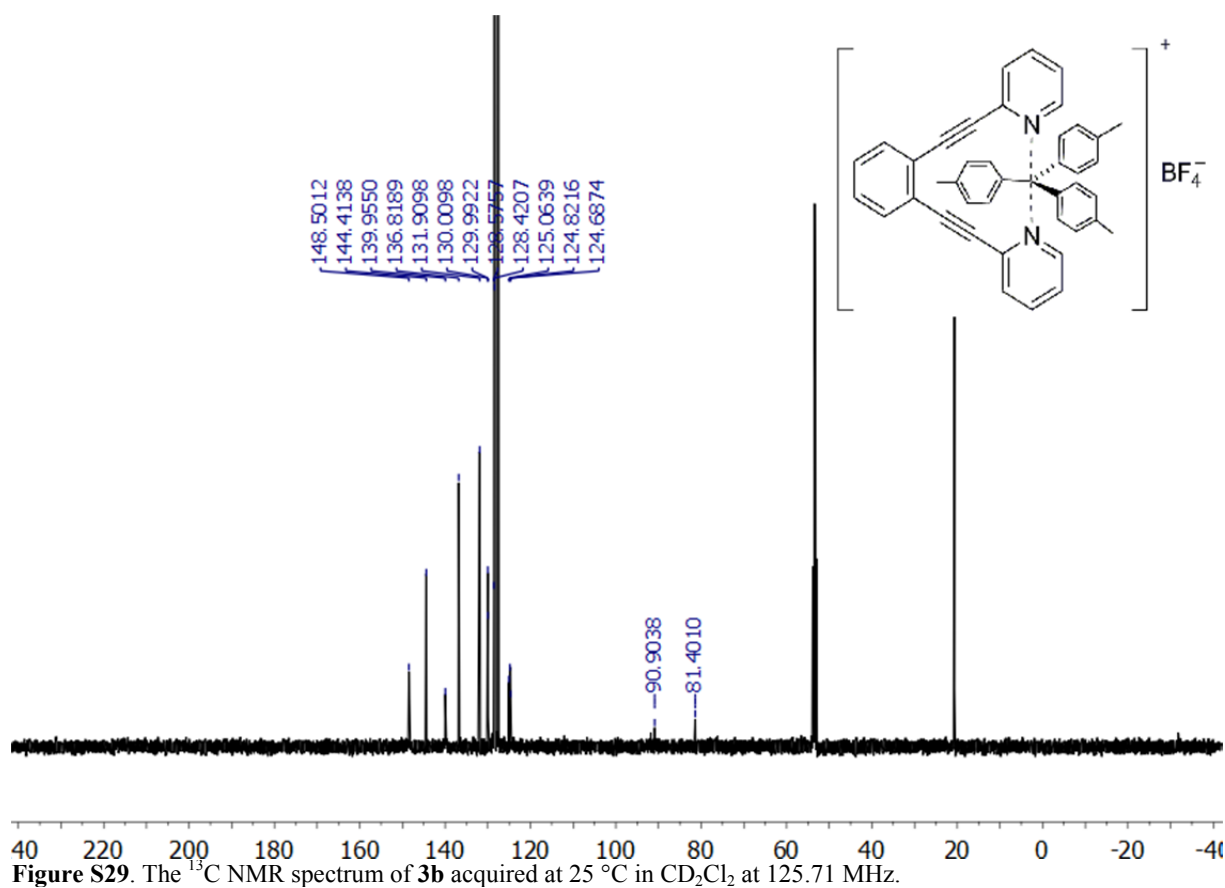


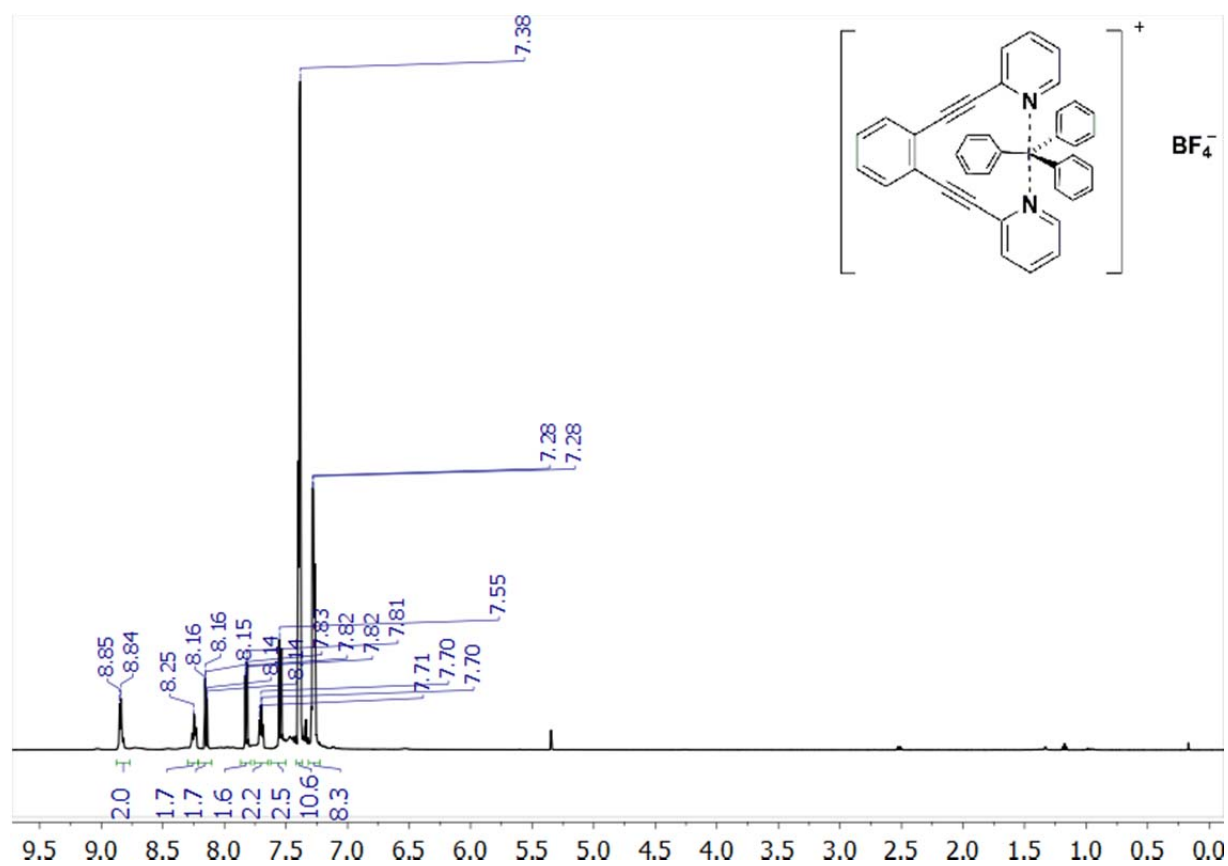
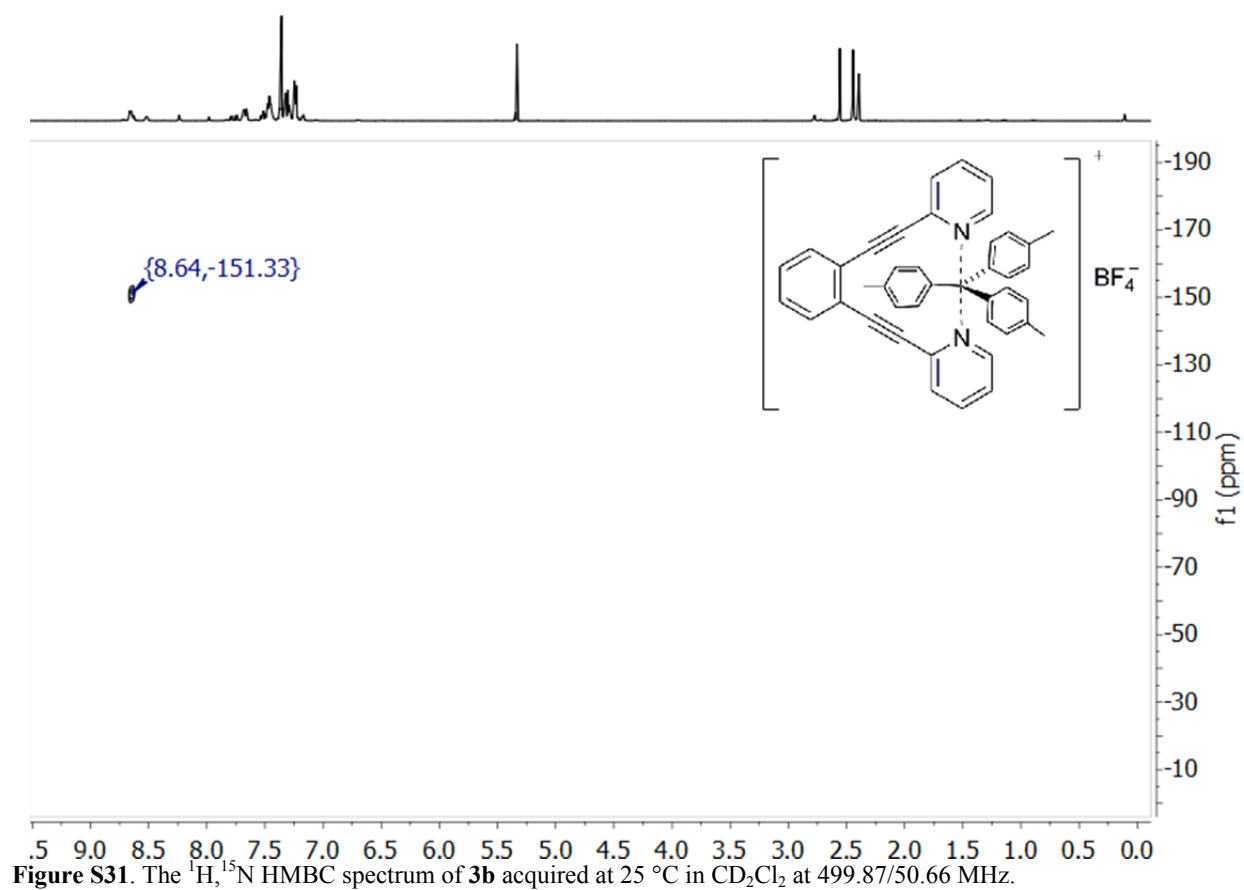
**Figure S27.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **3a** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.

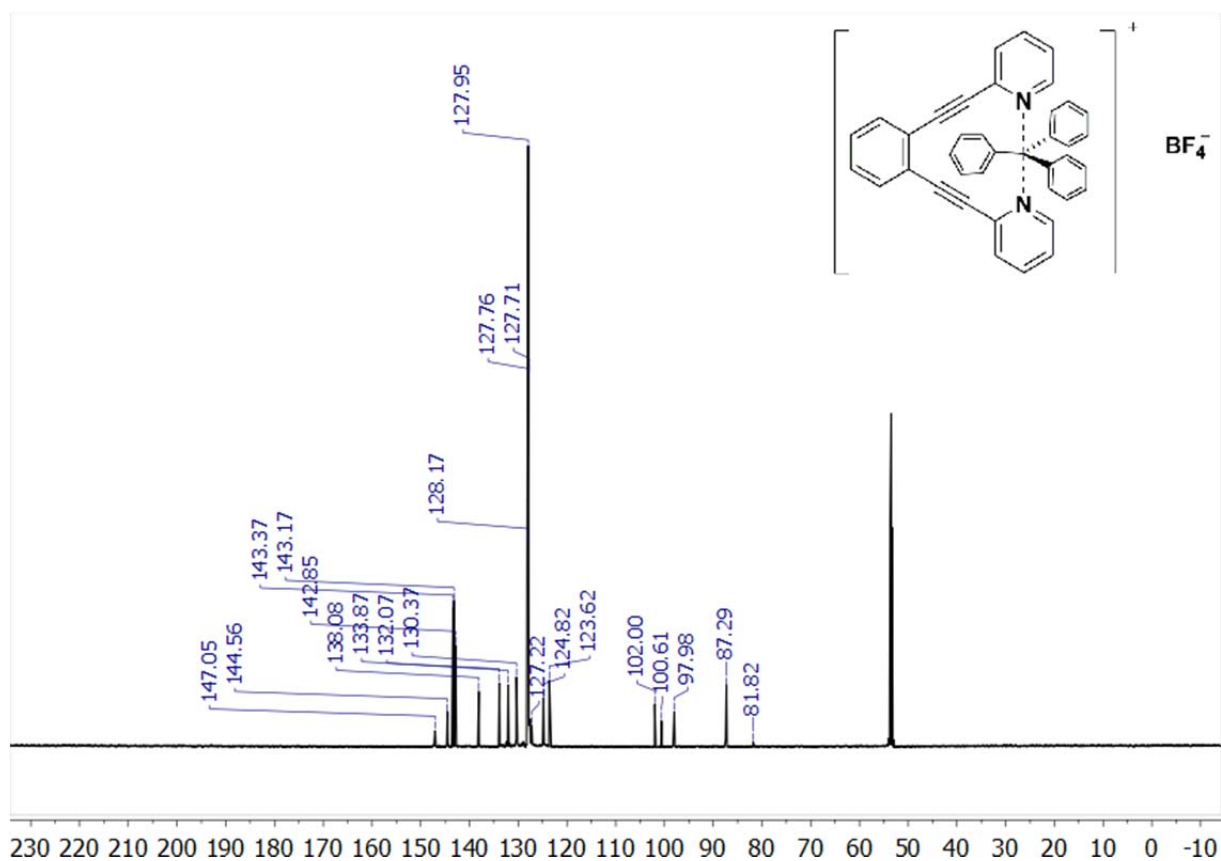


**Figure S28.** The  $^1\text{H}$  NMR spectrum of **3b** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.

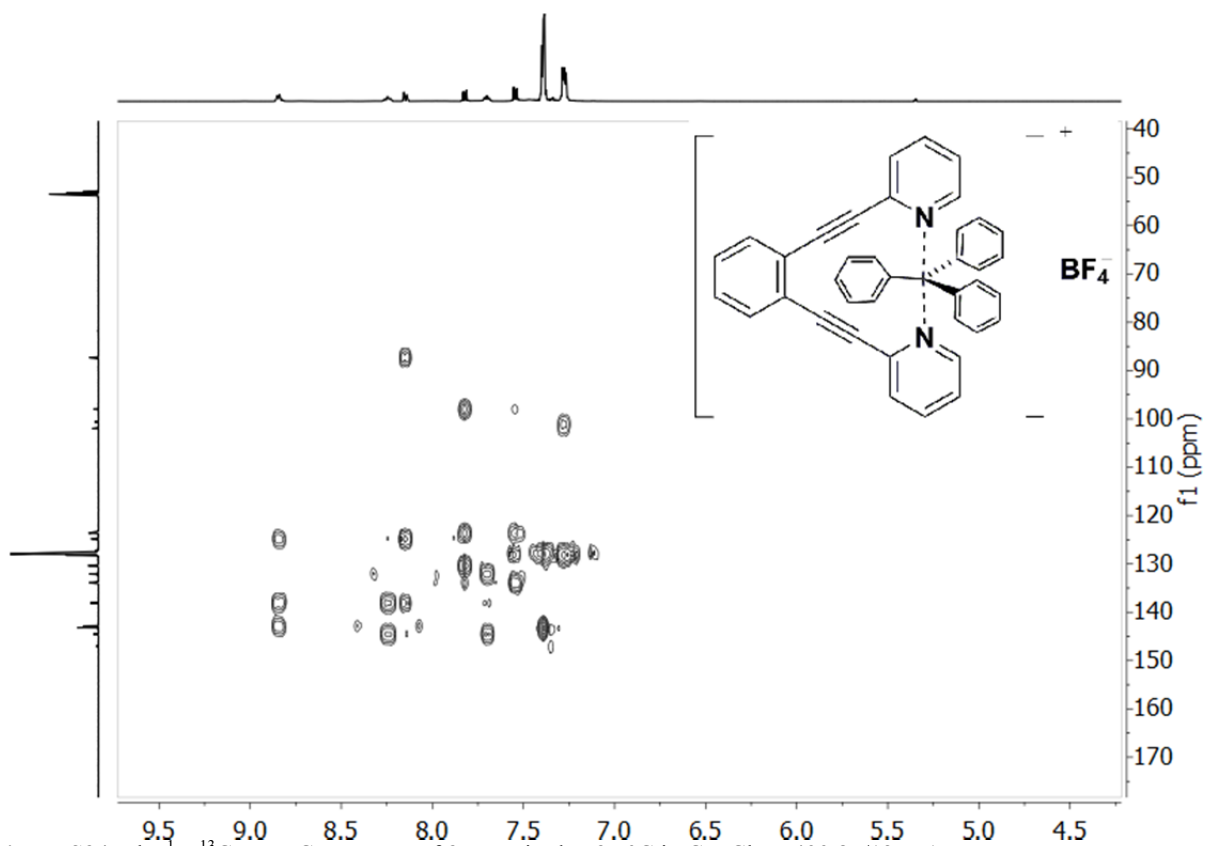




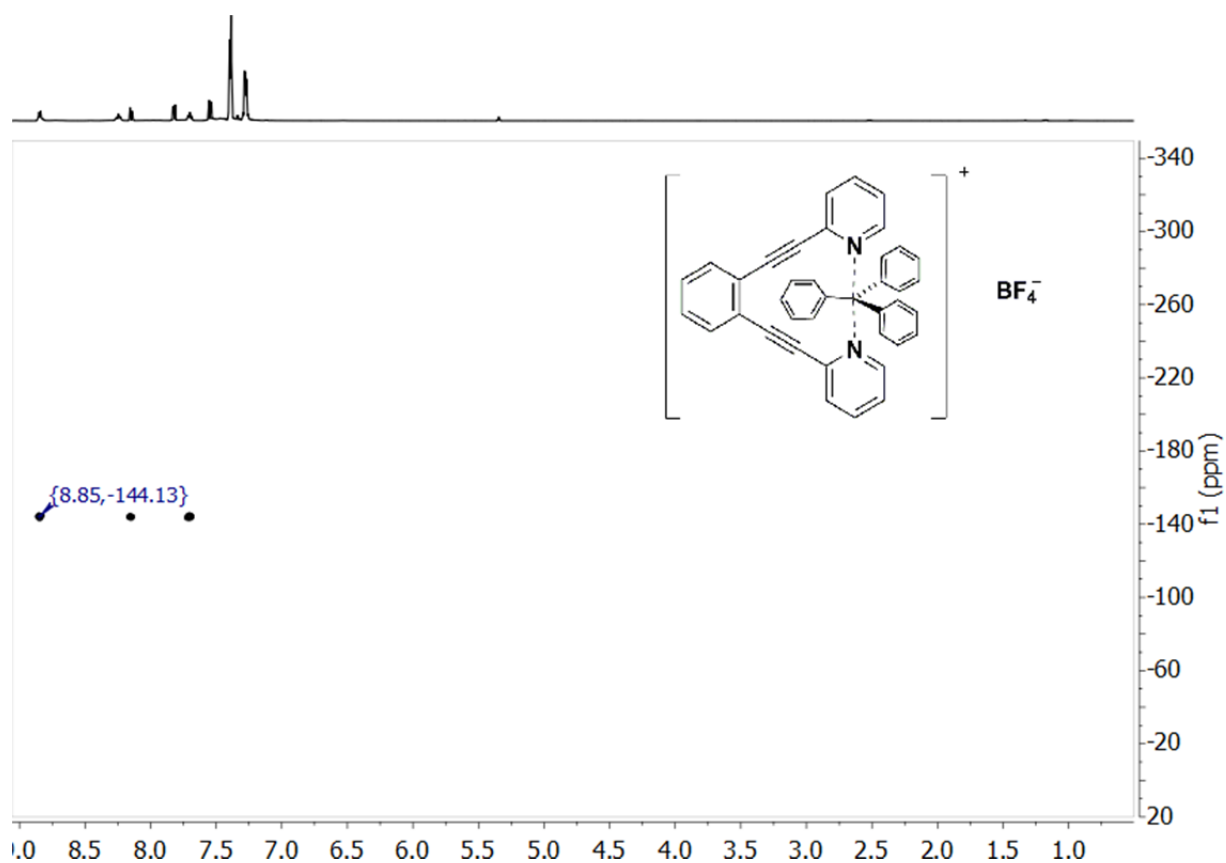




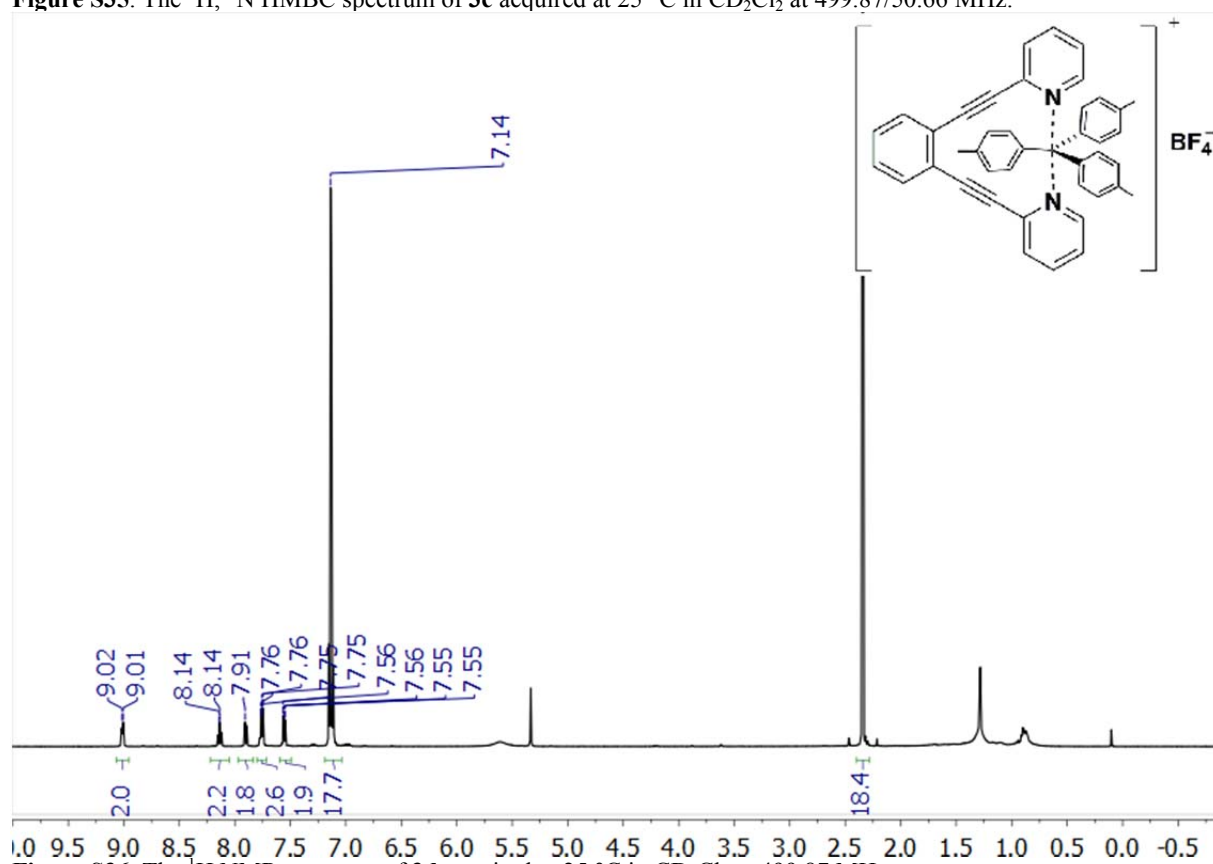
**Figure S33.** The  $^{13}\text{C}$  NMR spectrum of **3c** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 125.71 MHz.



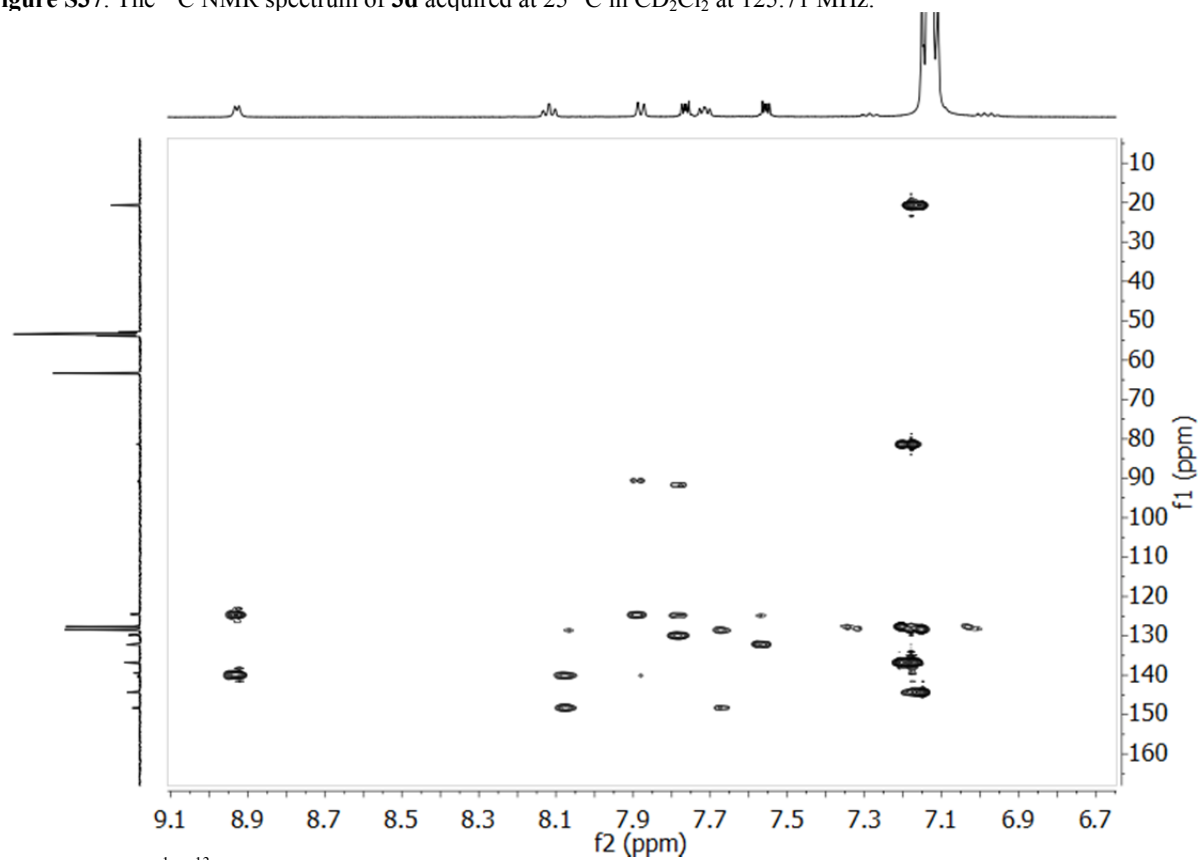
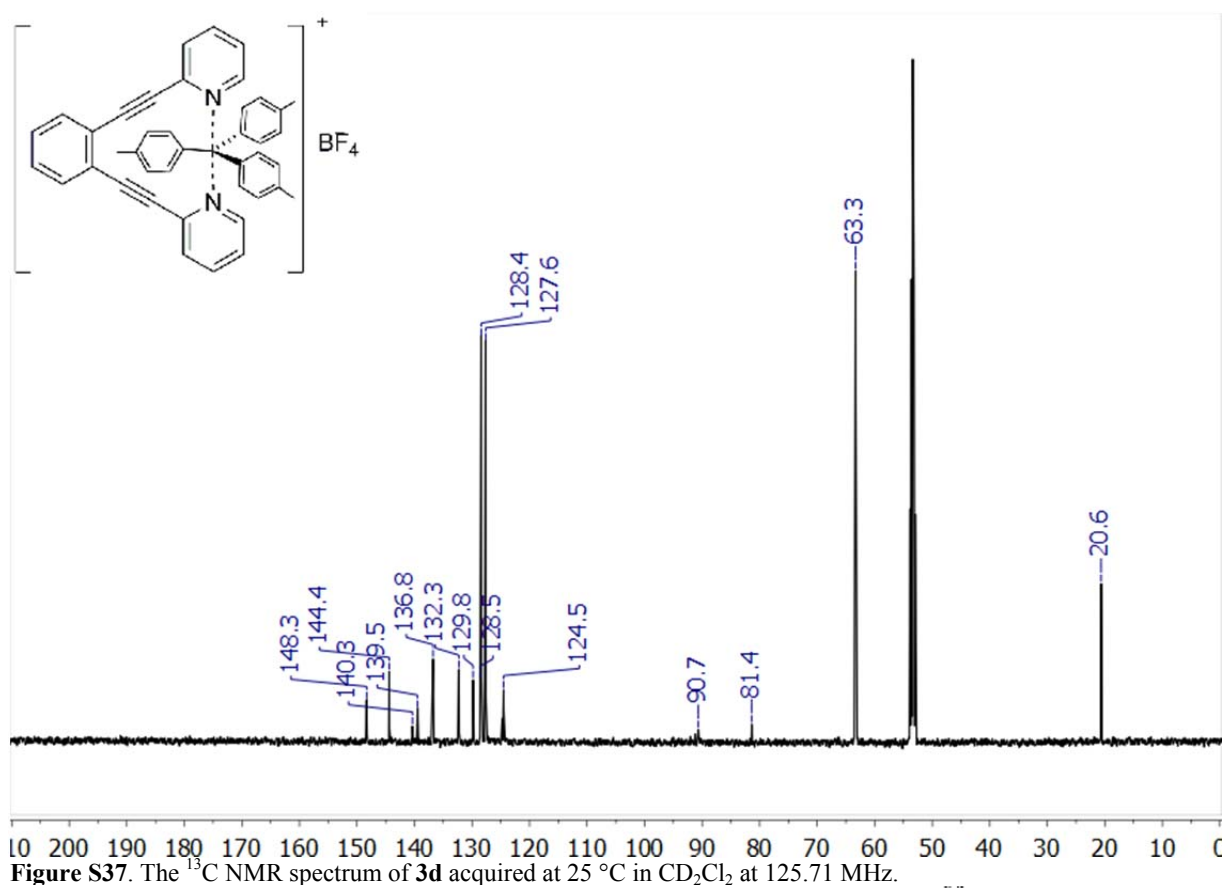
**Figure S34.** The  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of **3c** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/125.71 MHz.

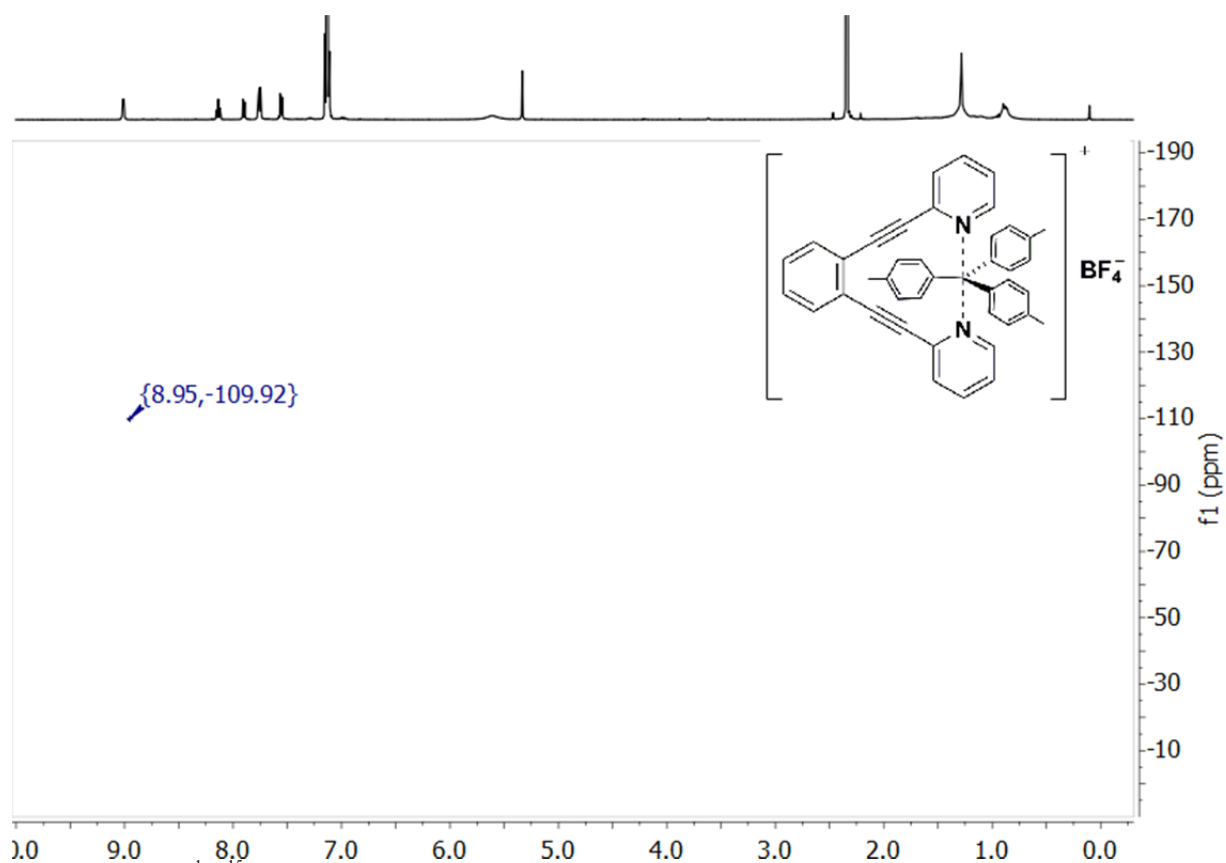


**Figure S35.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **3c** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.

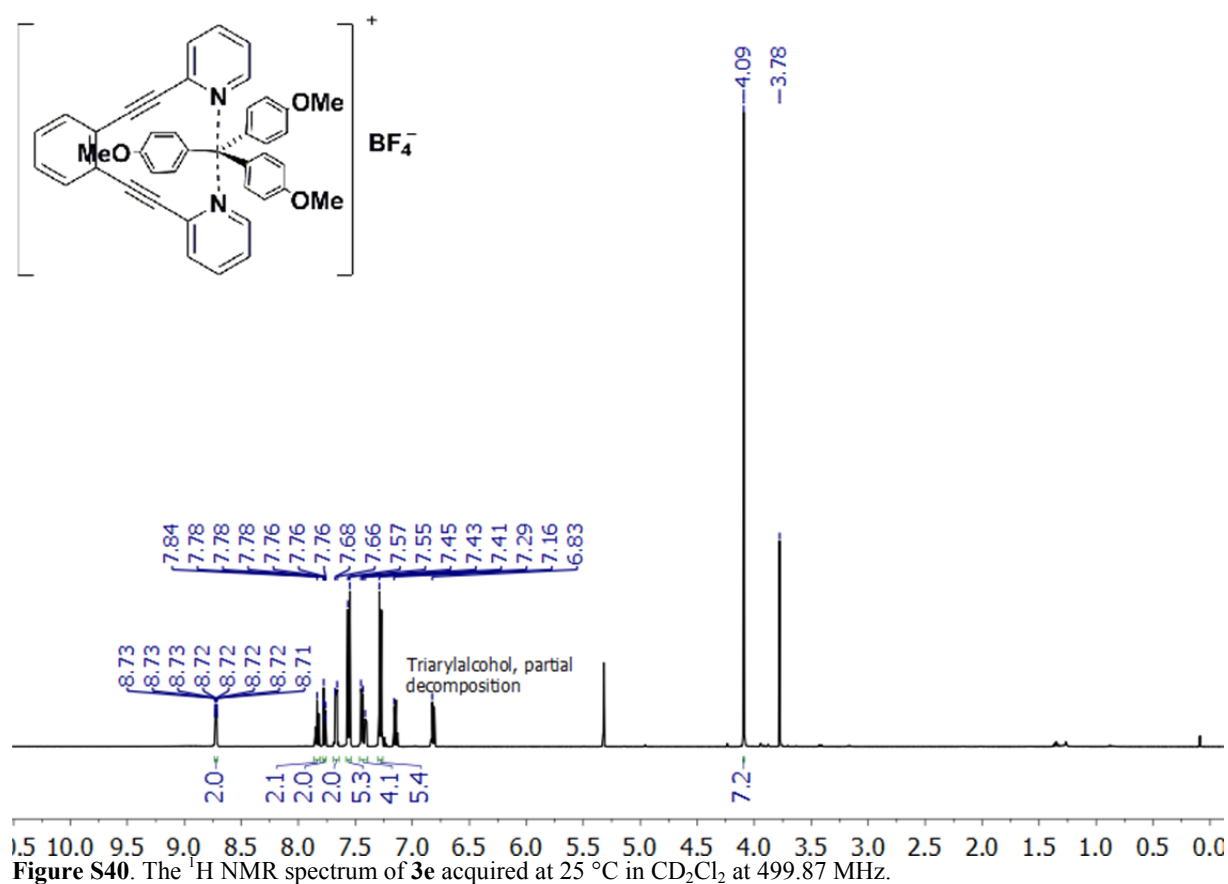


**Figure S36.** The  $^1\text{H}$  NMR spectrum of **3d** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.

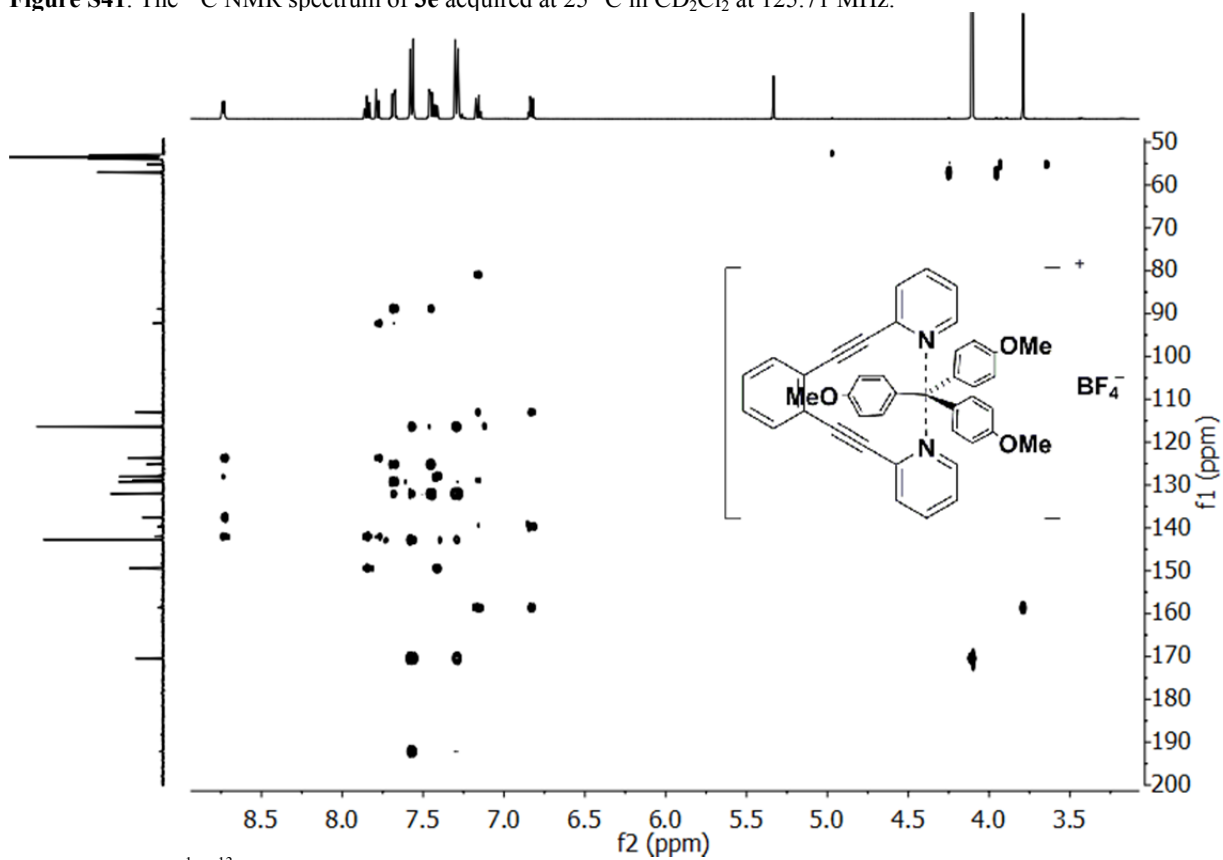
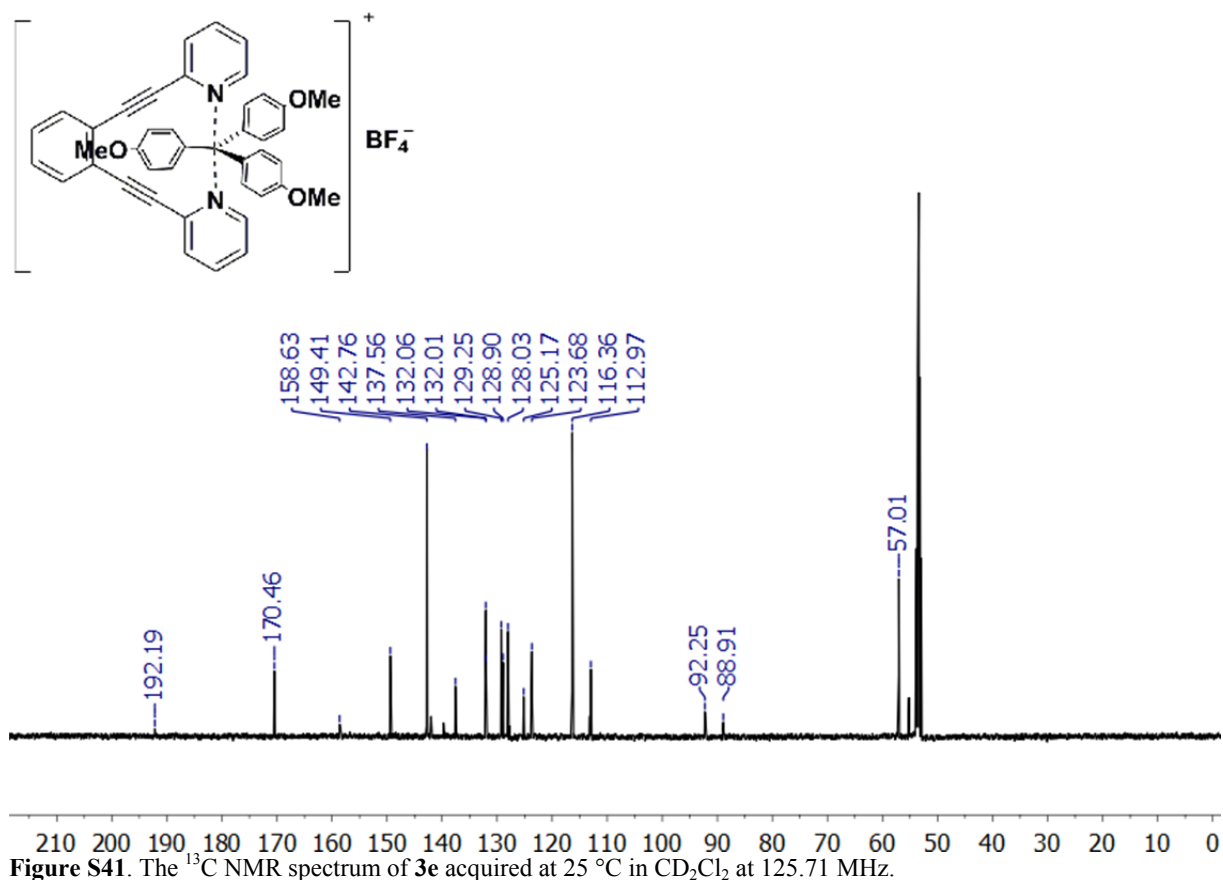


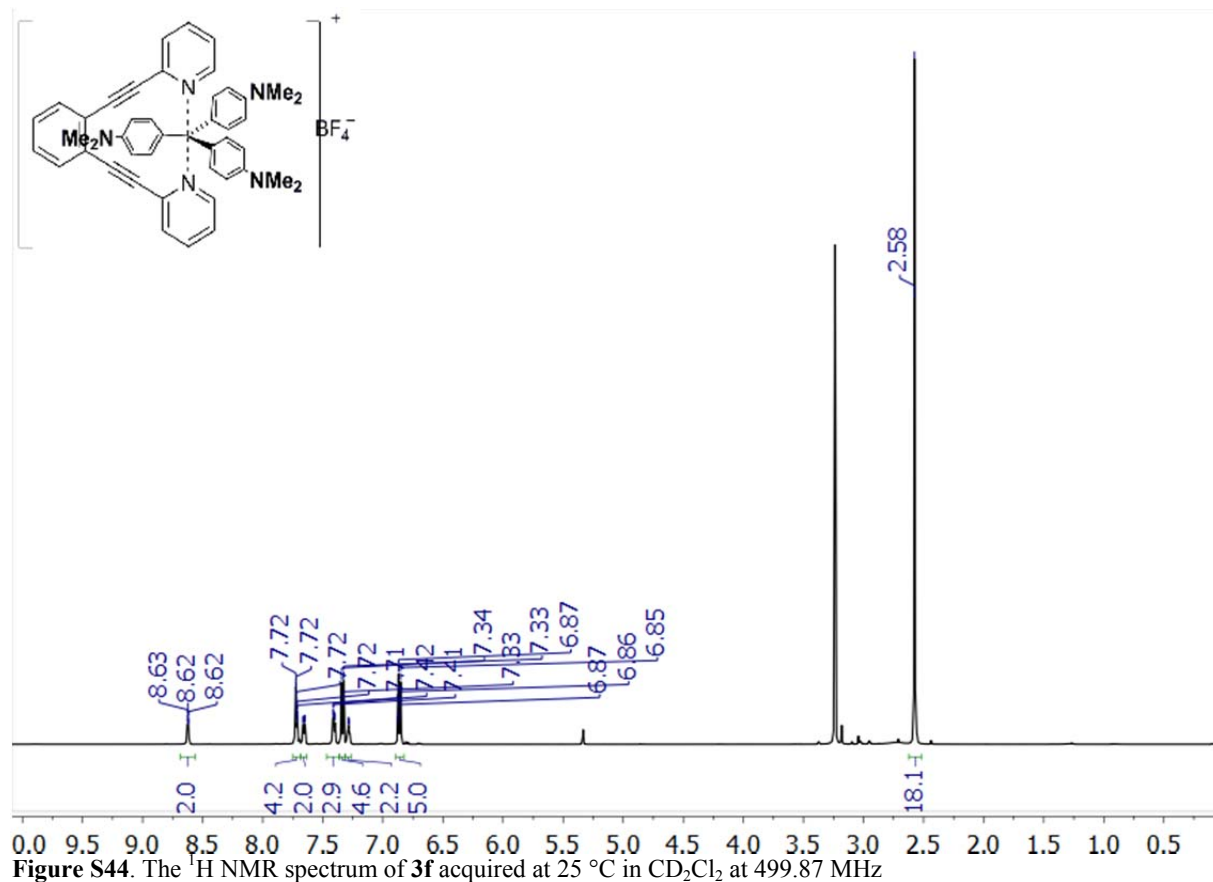
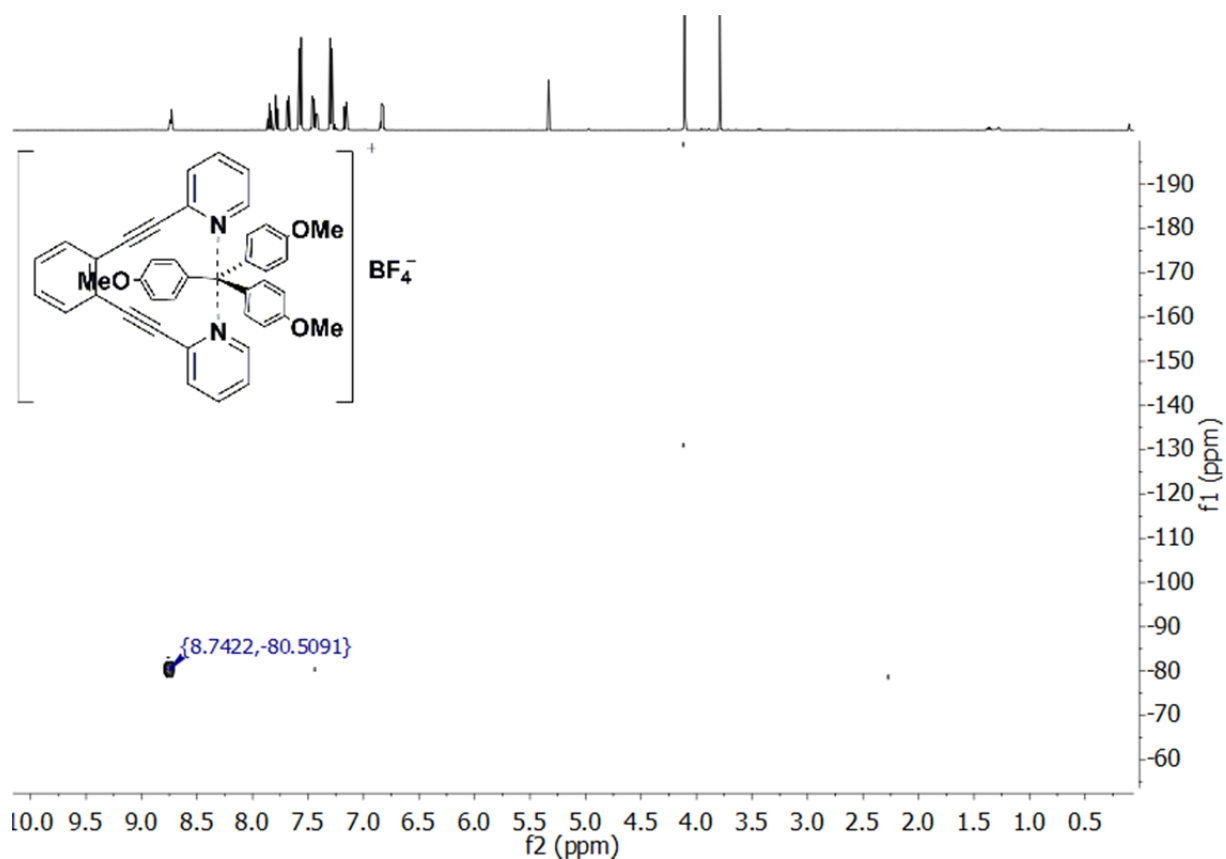


**Figure S39.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **3d** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.

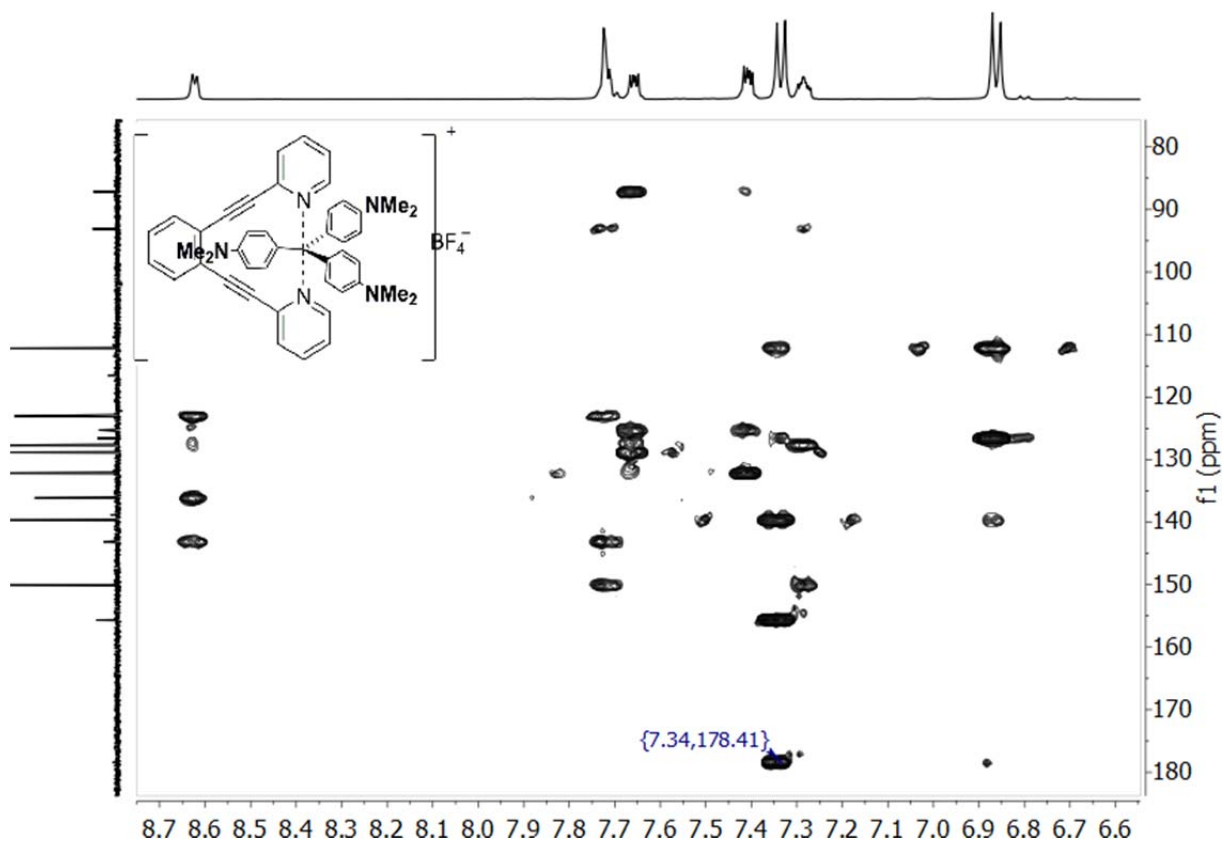
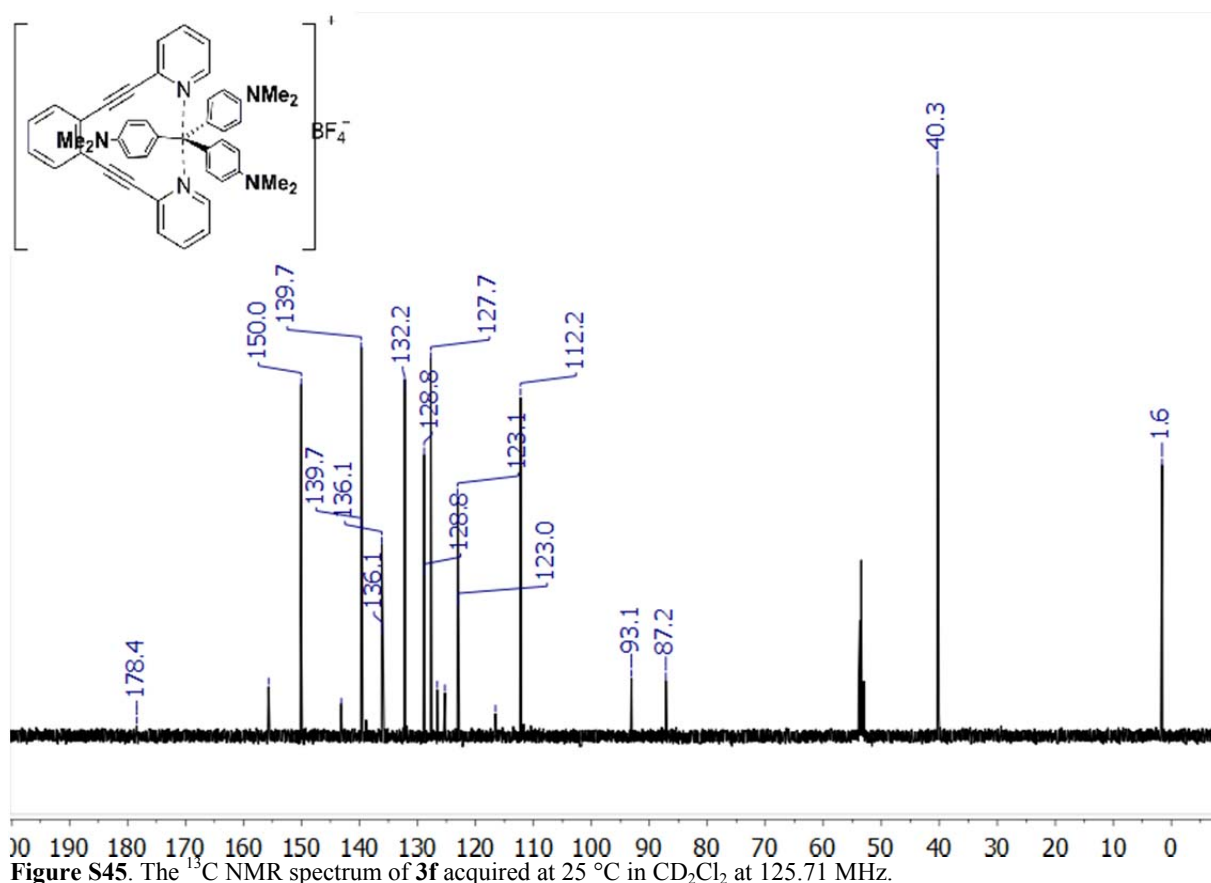


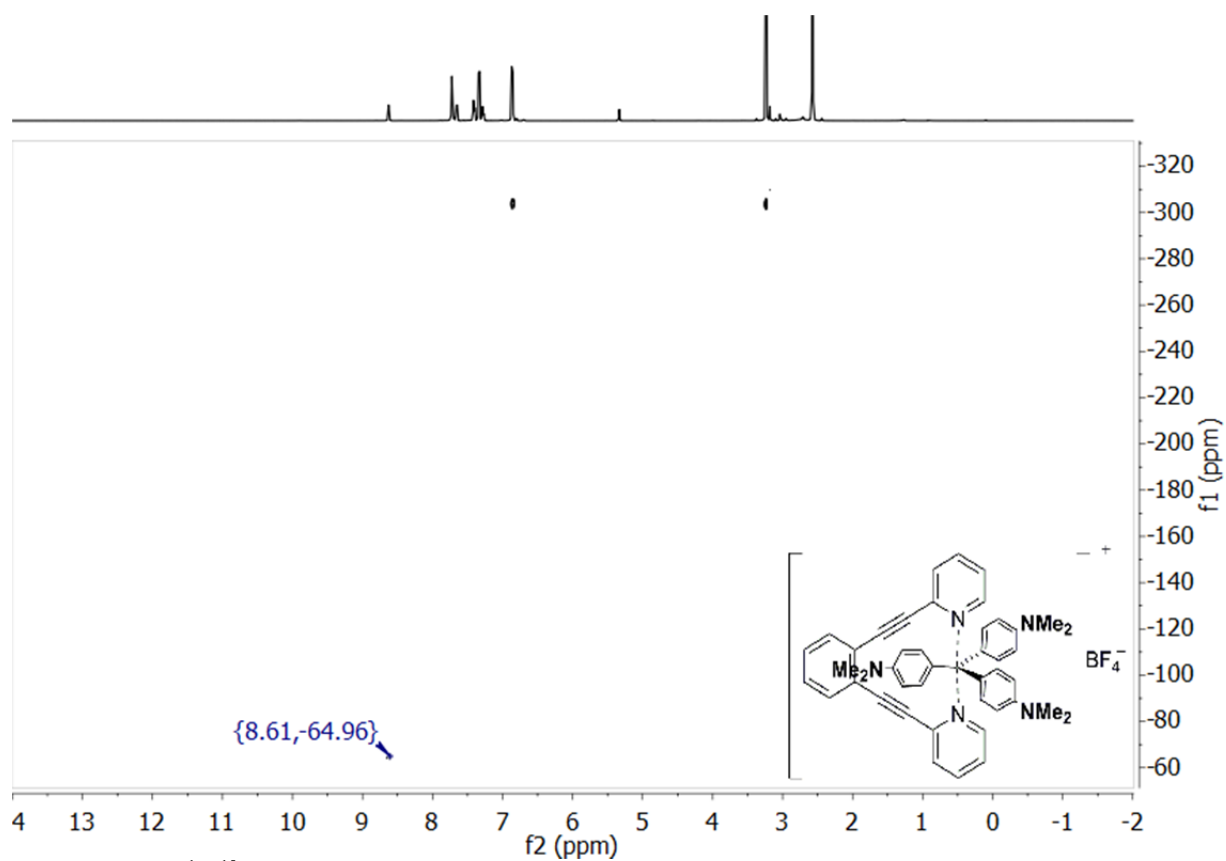
**Figure S40.** The  $^1\text{H}$  NMR spectrum of **3e** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.



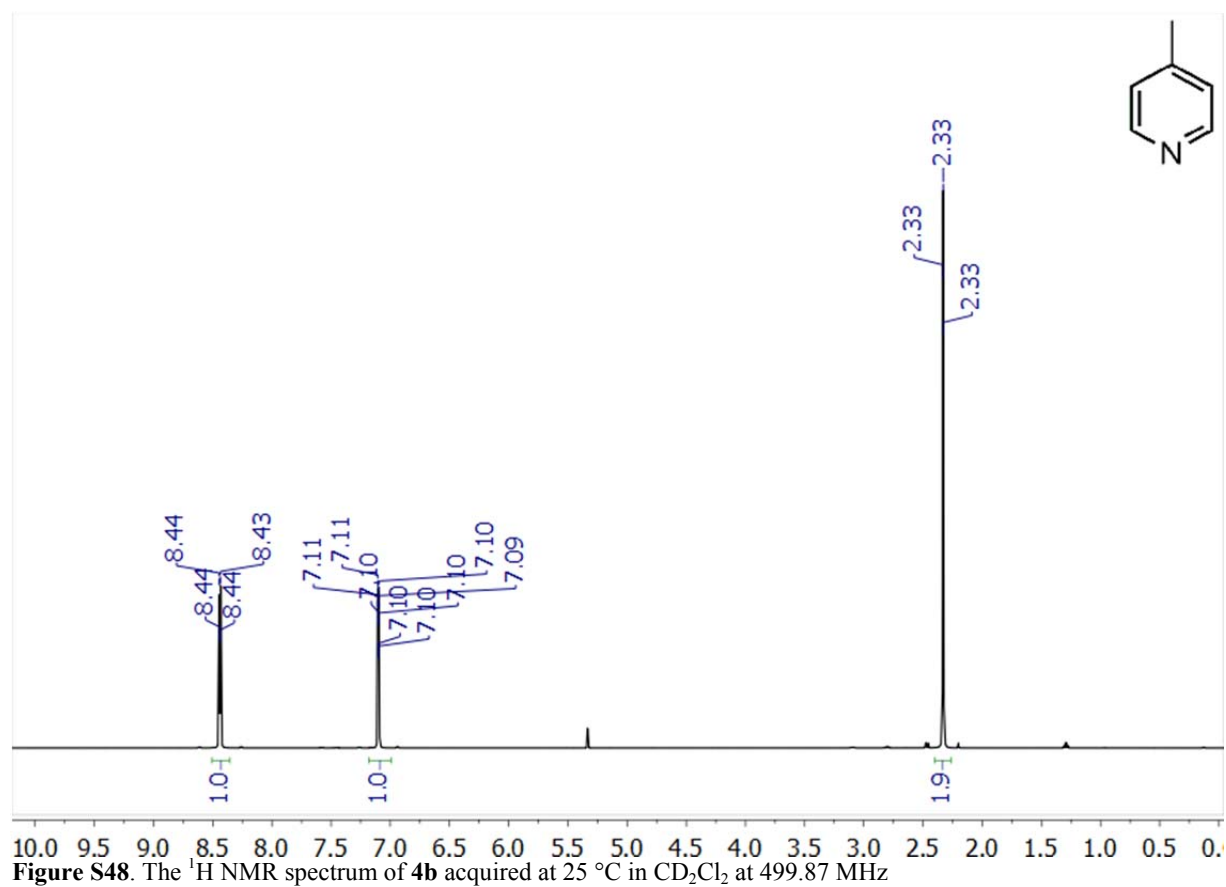




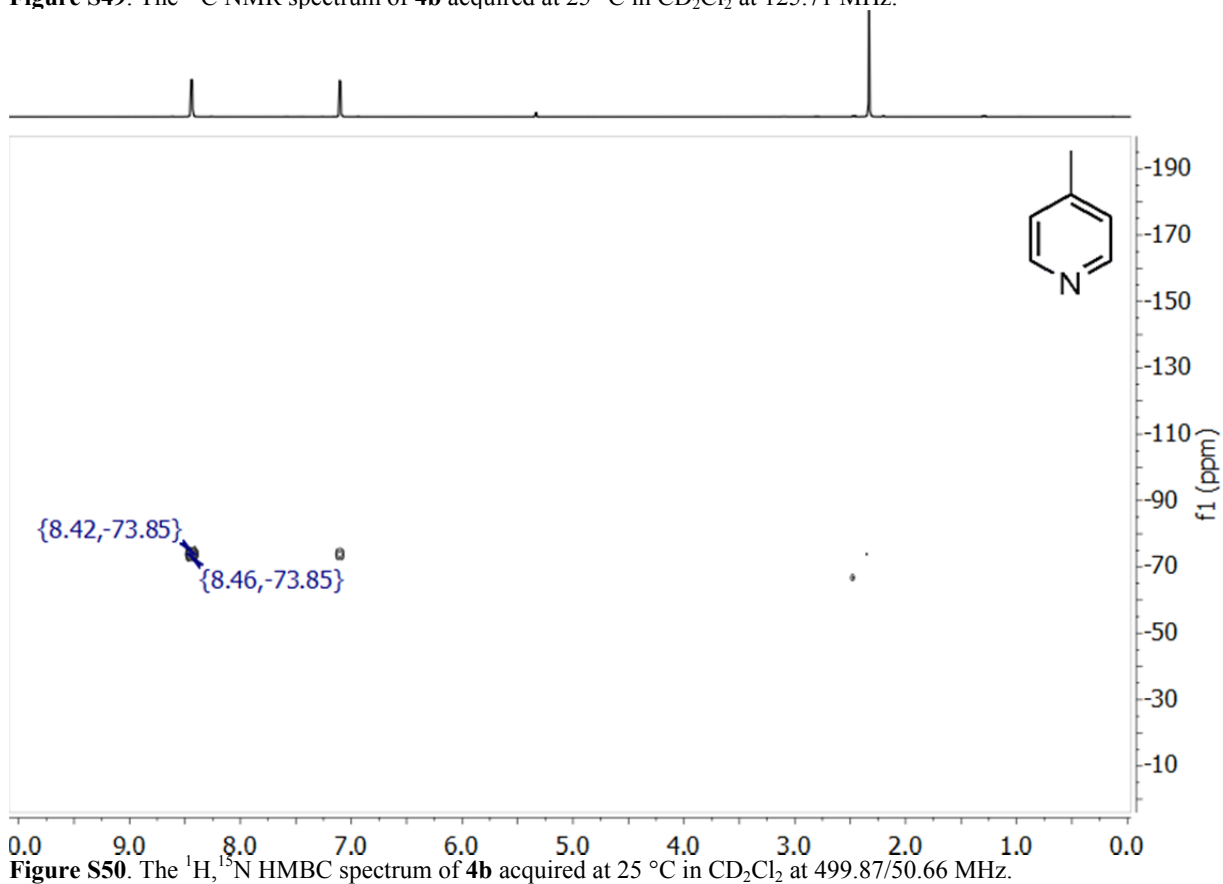
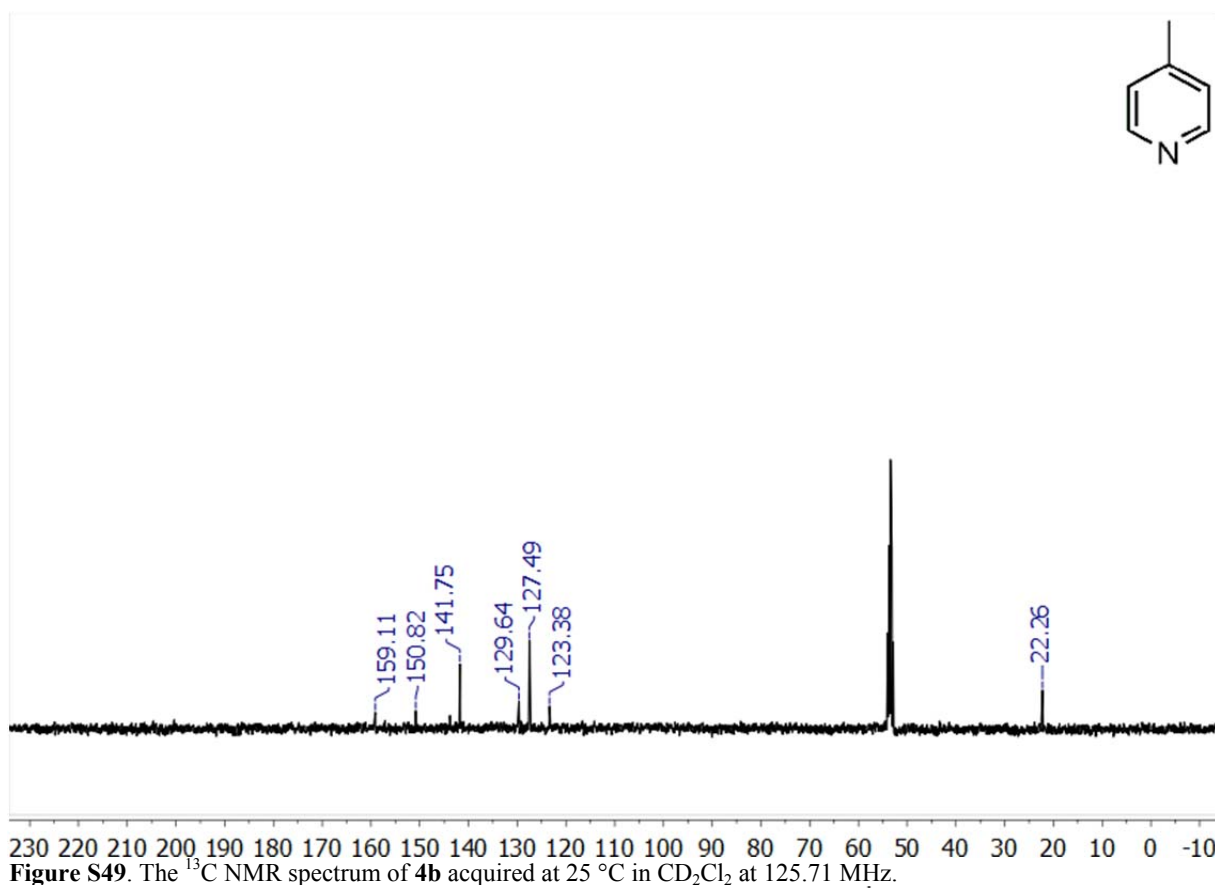


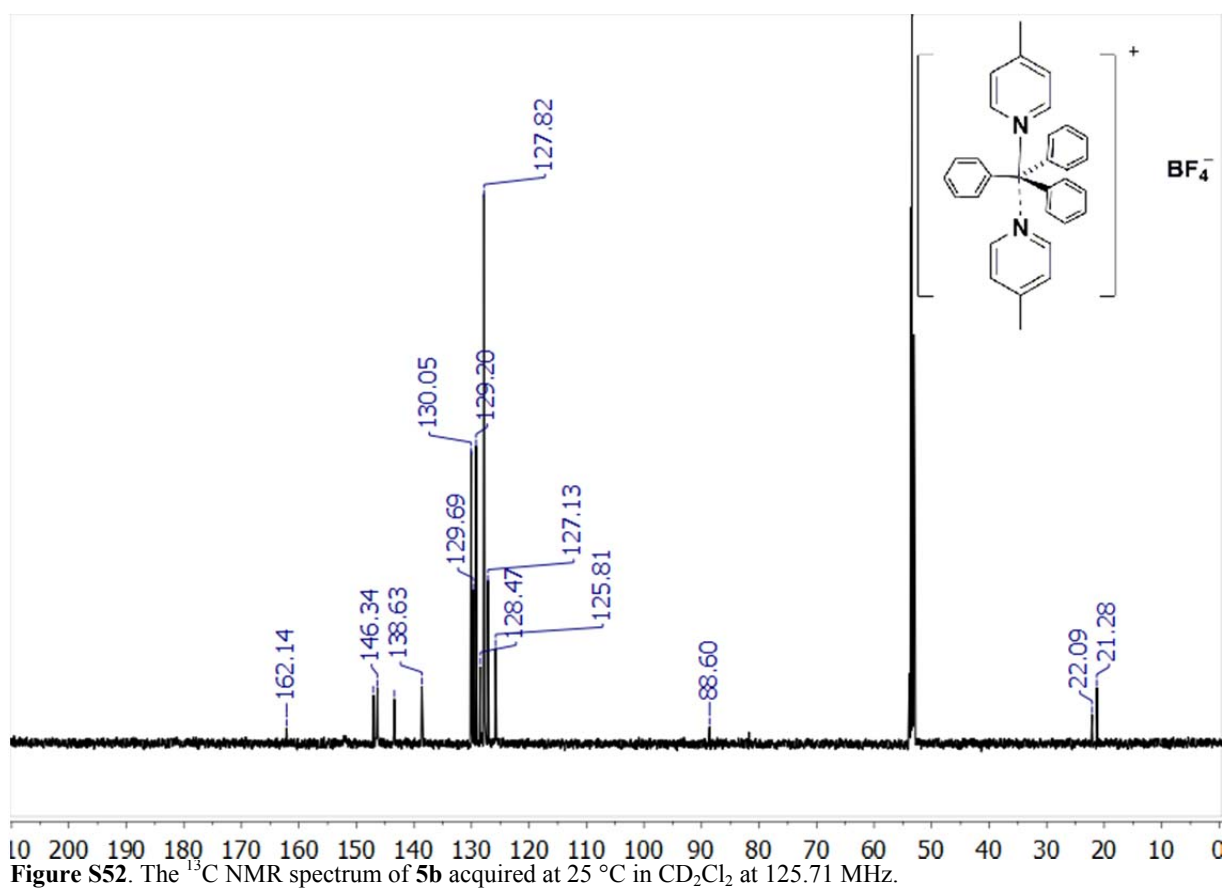
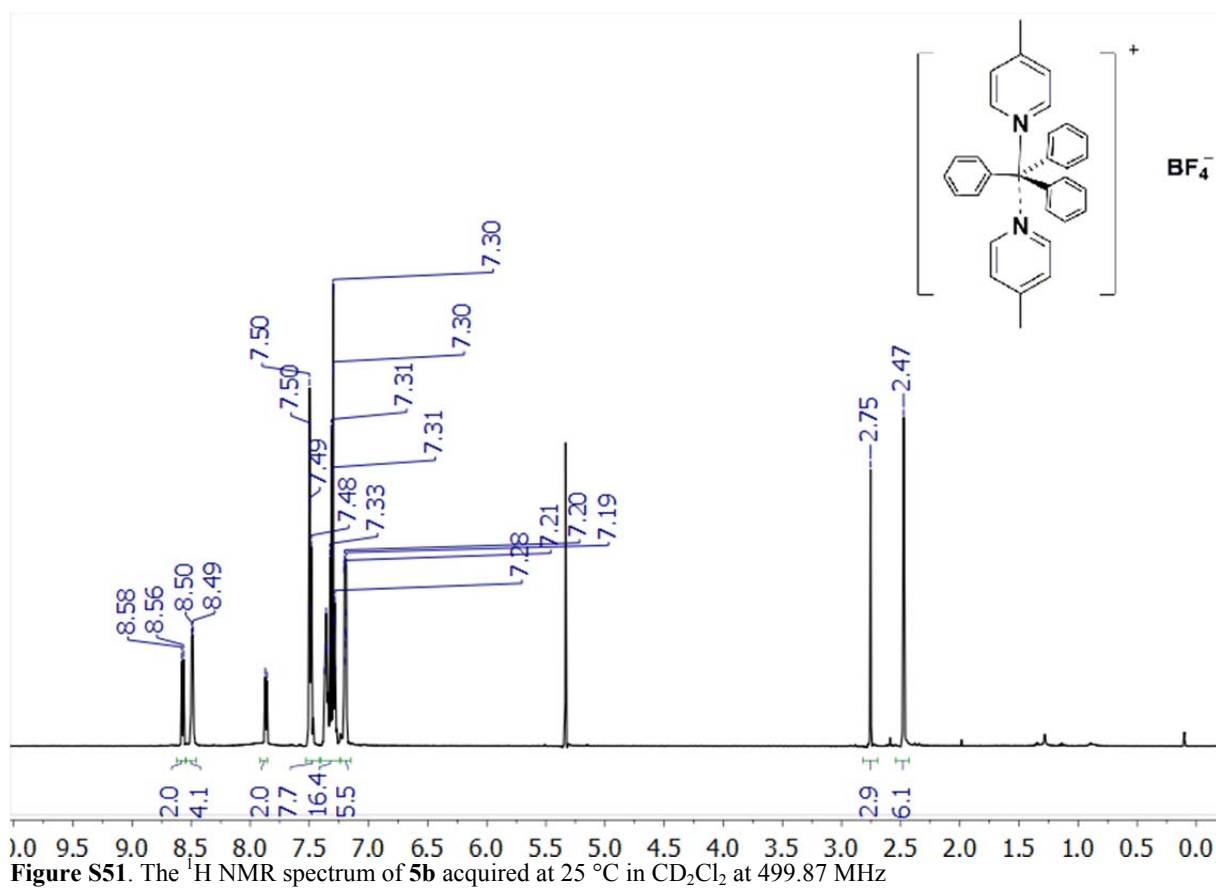


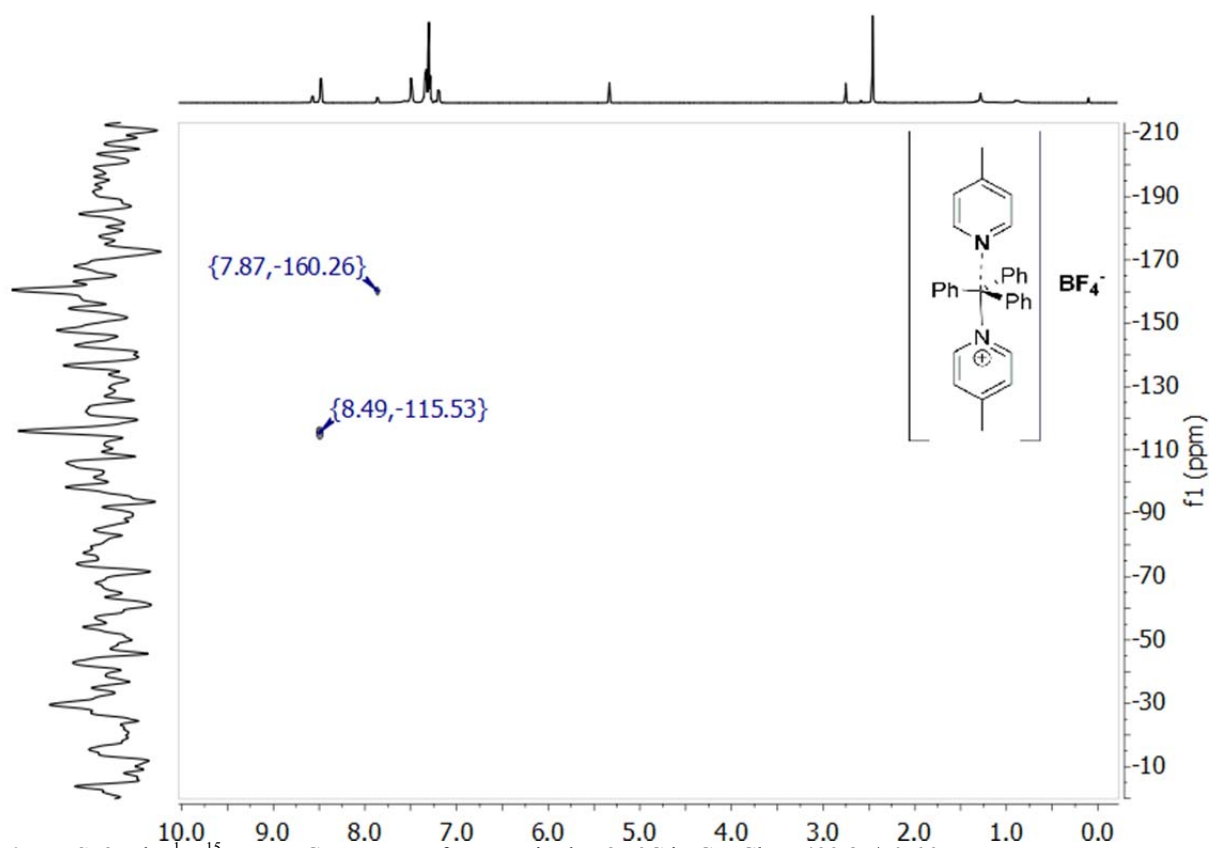
**Figure S47.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **3f** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.



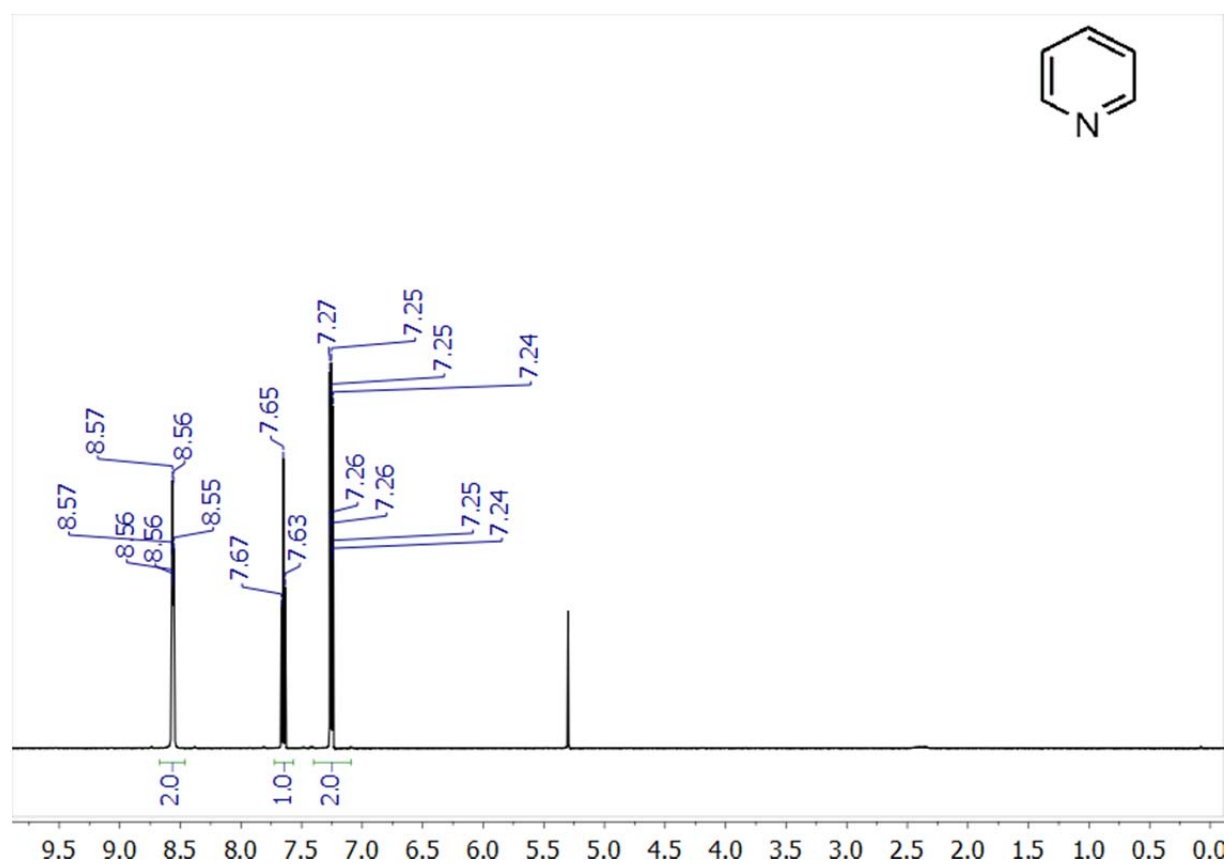
**Figure S48.** The  $^1\text{H}$  NMR spectrum of **4b** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz



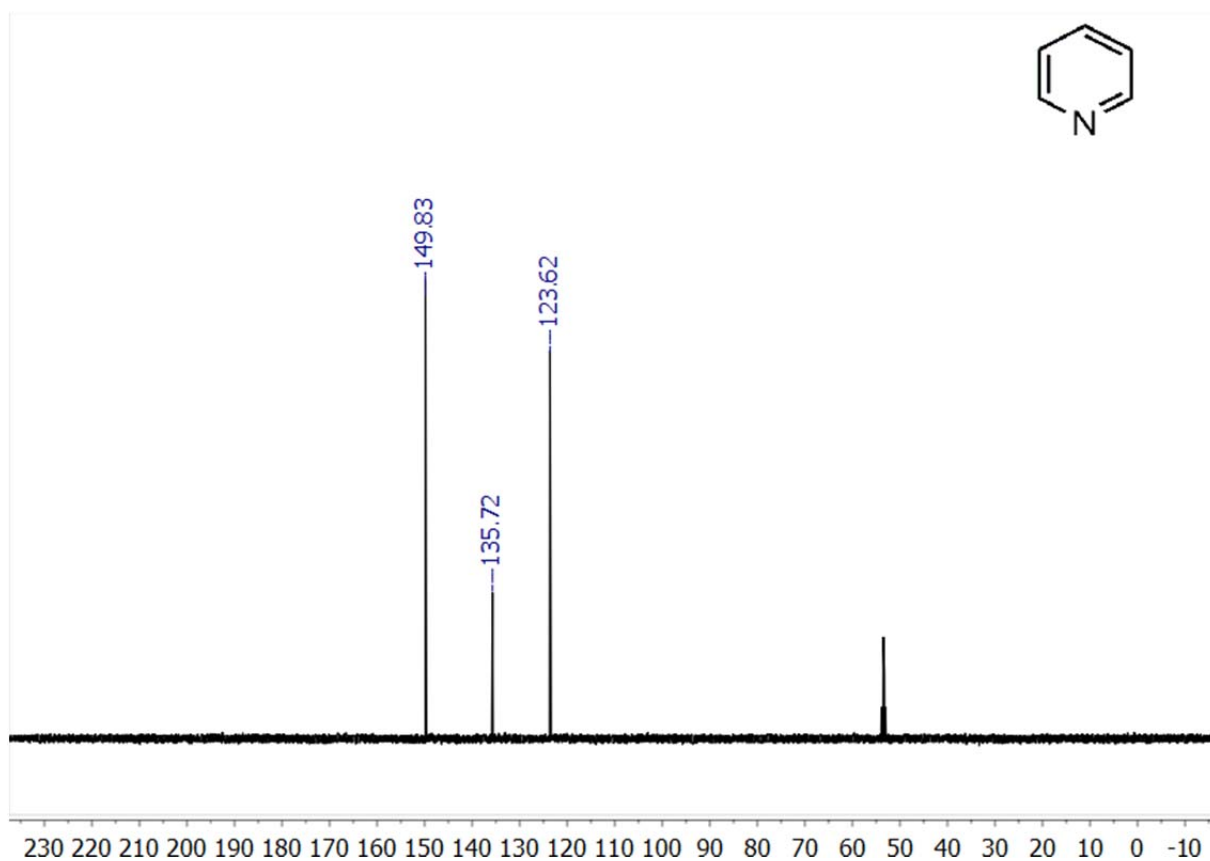




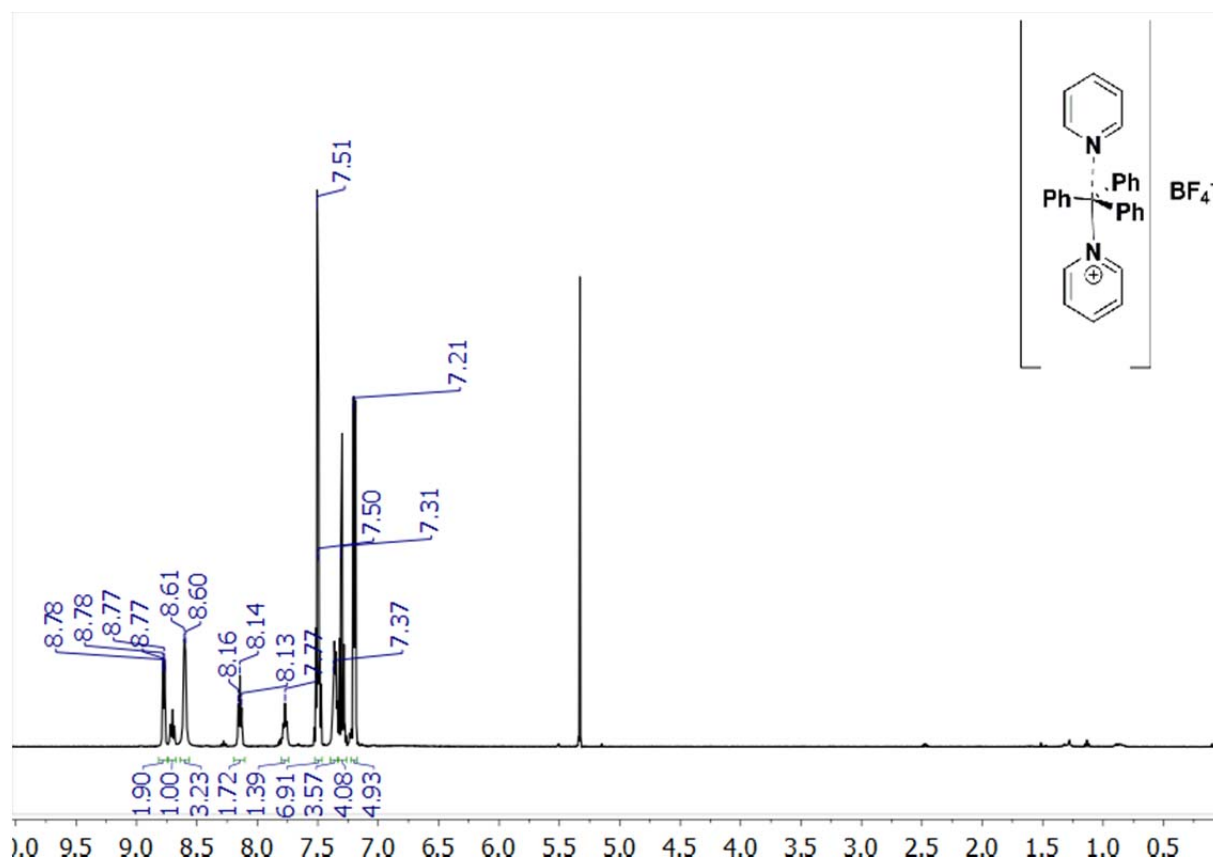
**Figure S53.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **5b** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.



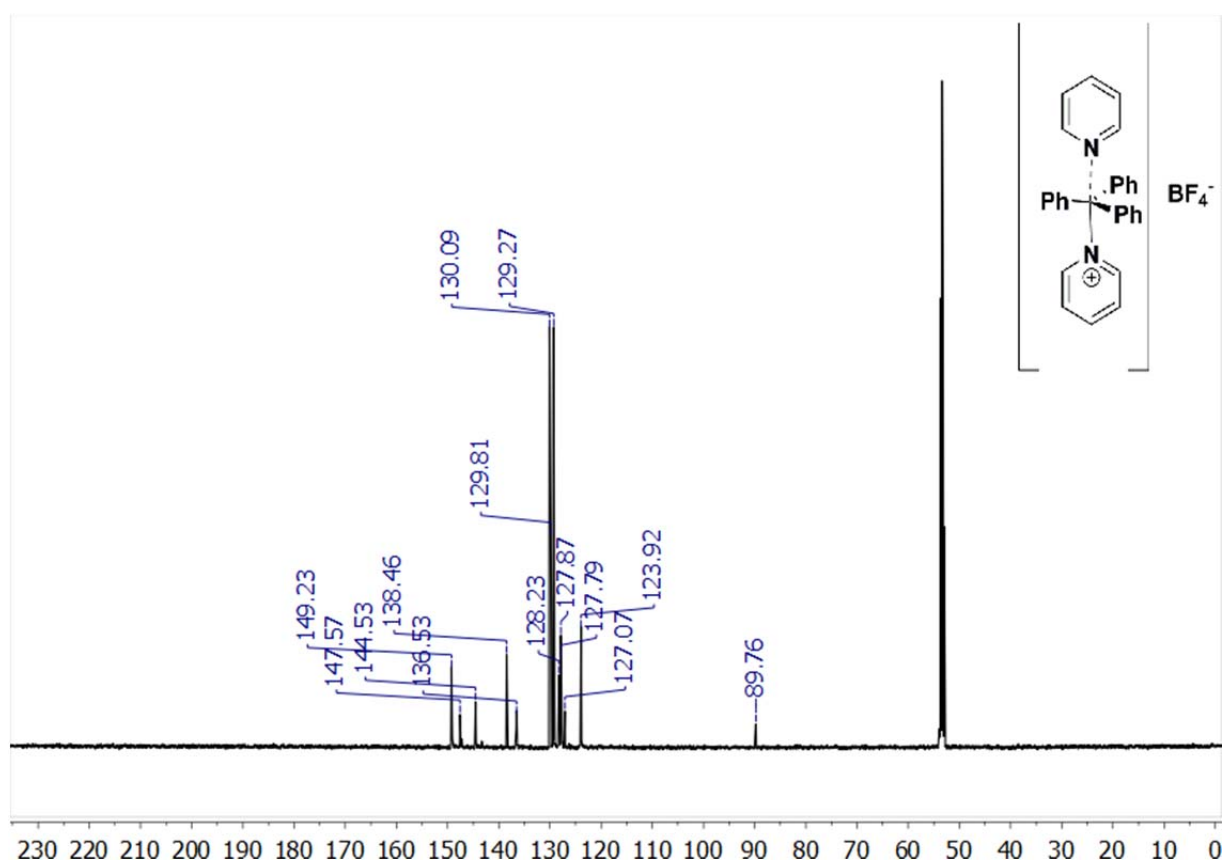
**Figure S54.** The  $^1\text{H}$  NMR spectrum of pyridine (**4c**) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.



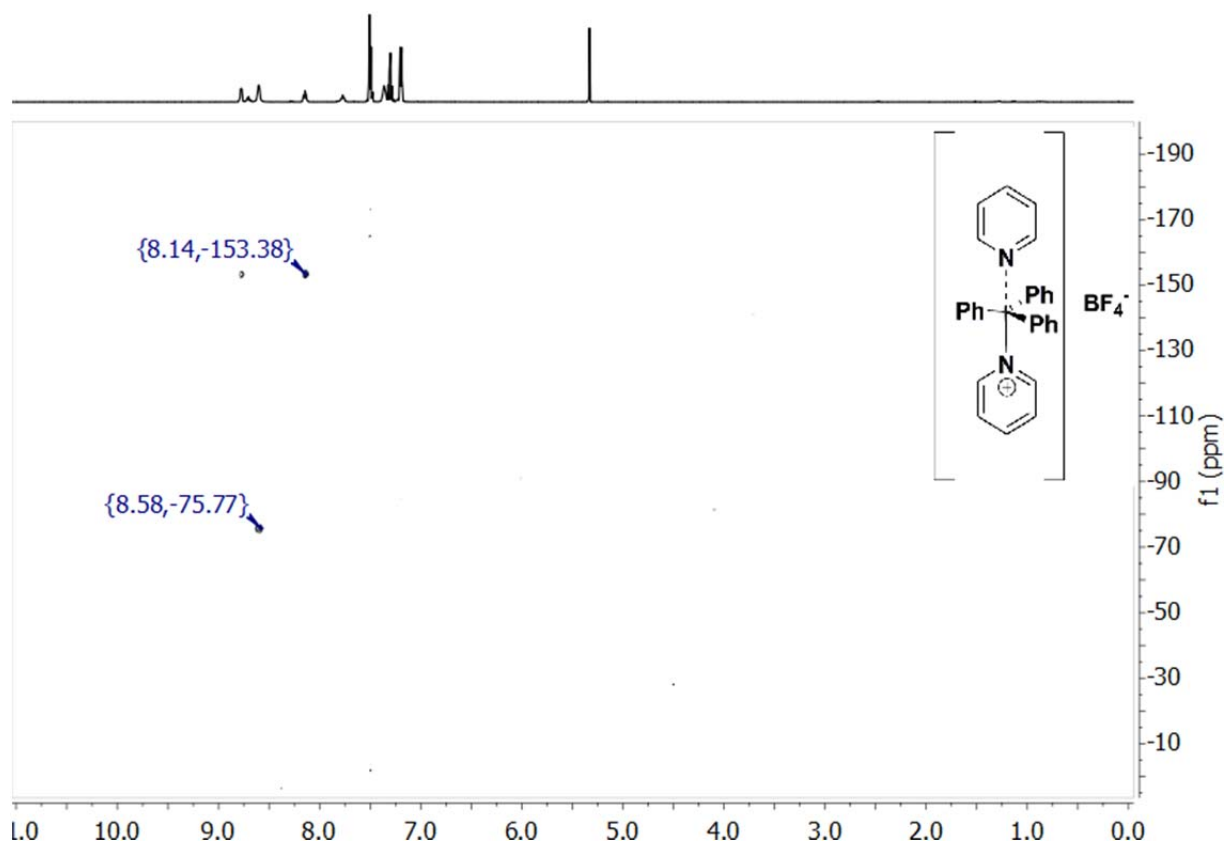
**Figure S55.** The  $^{13}\text{C}$  NMR spectrum of pyridine (**4c**) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 125.71 MHz.



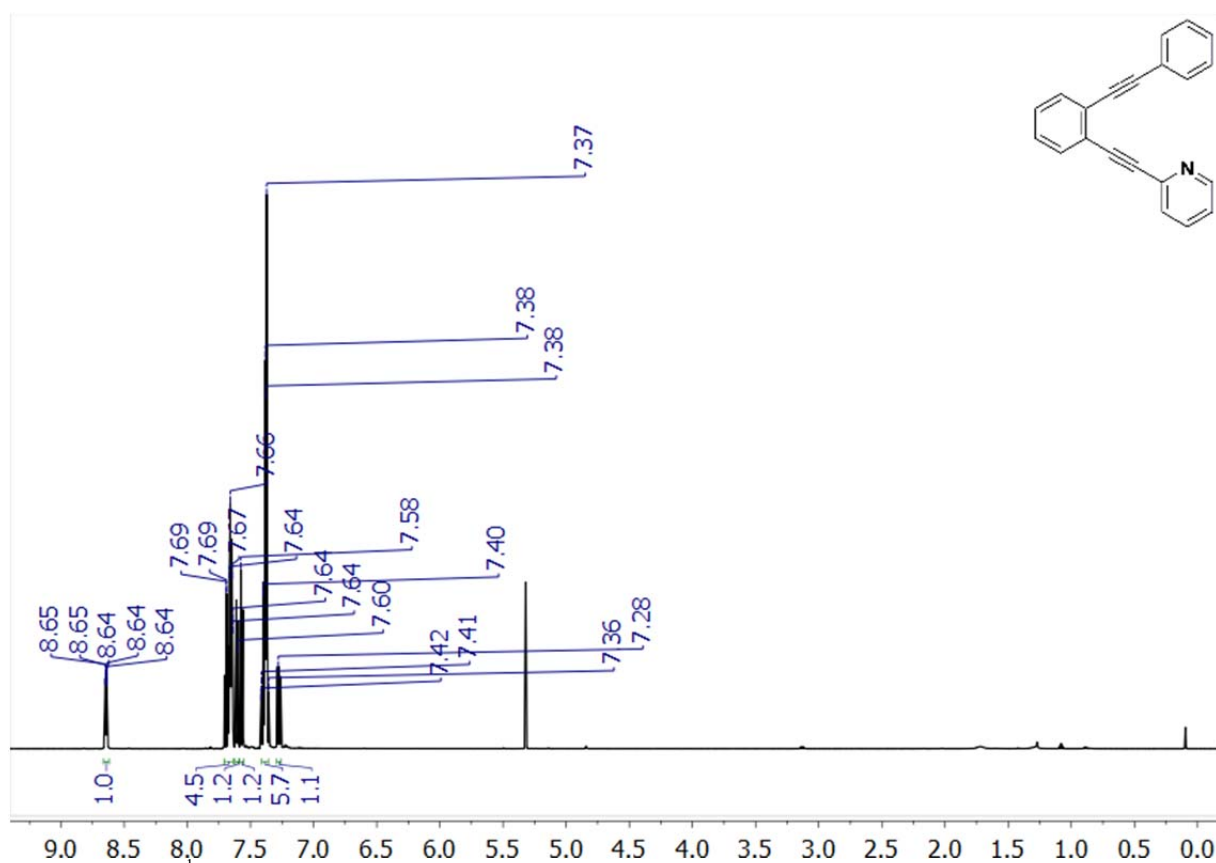
**Figure S56.** The  $^1\text{H}$  NMR spectrum of pyridine (**5c**) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.



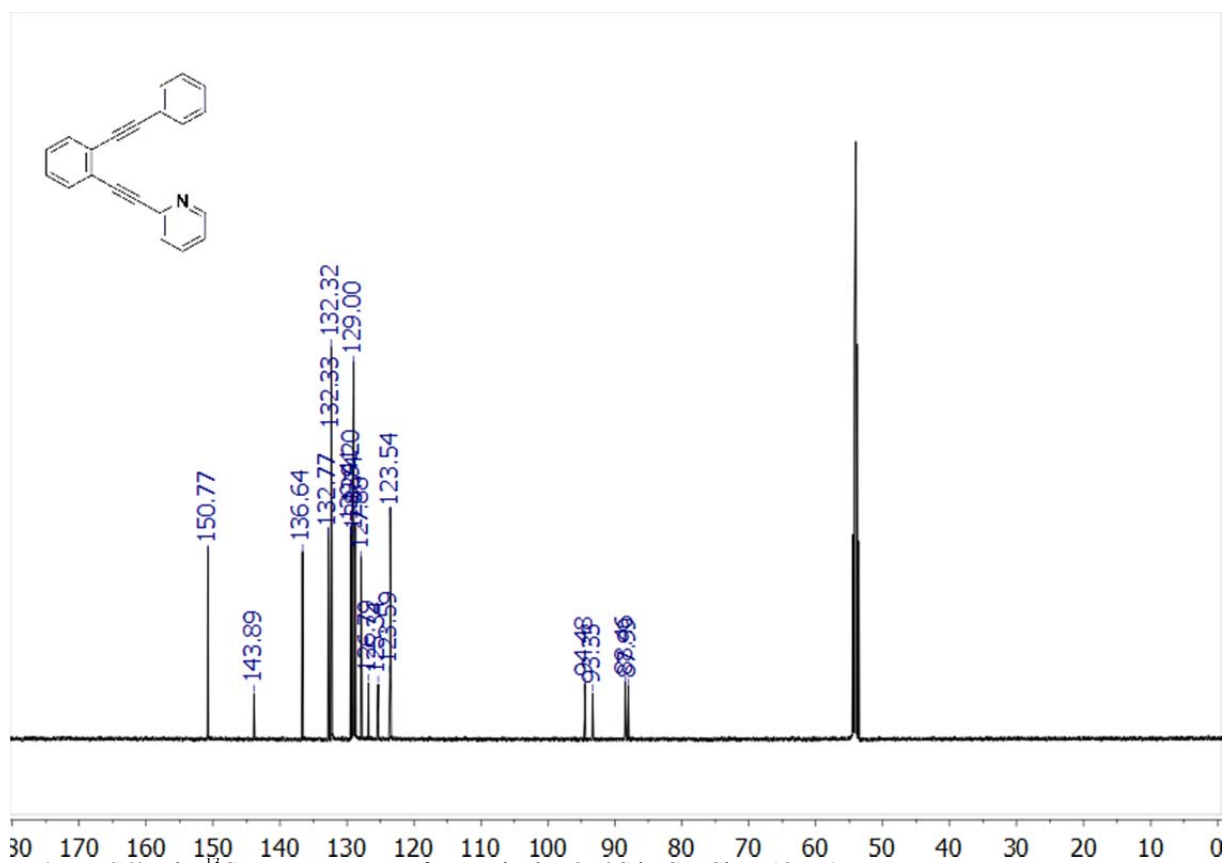
**Figure S57.** The <sup>13</sup>C NMR spectrum of pyridine (**5c**) acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 125.71 MHz.



**Figure S58.** The <sup>1</sup>H, <sup>15</sup>N HMBC spectrum of **5c** acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 499.87/50.66 MHz.

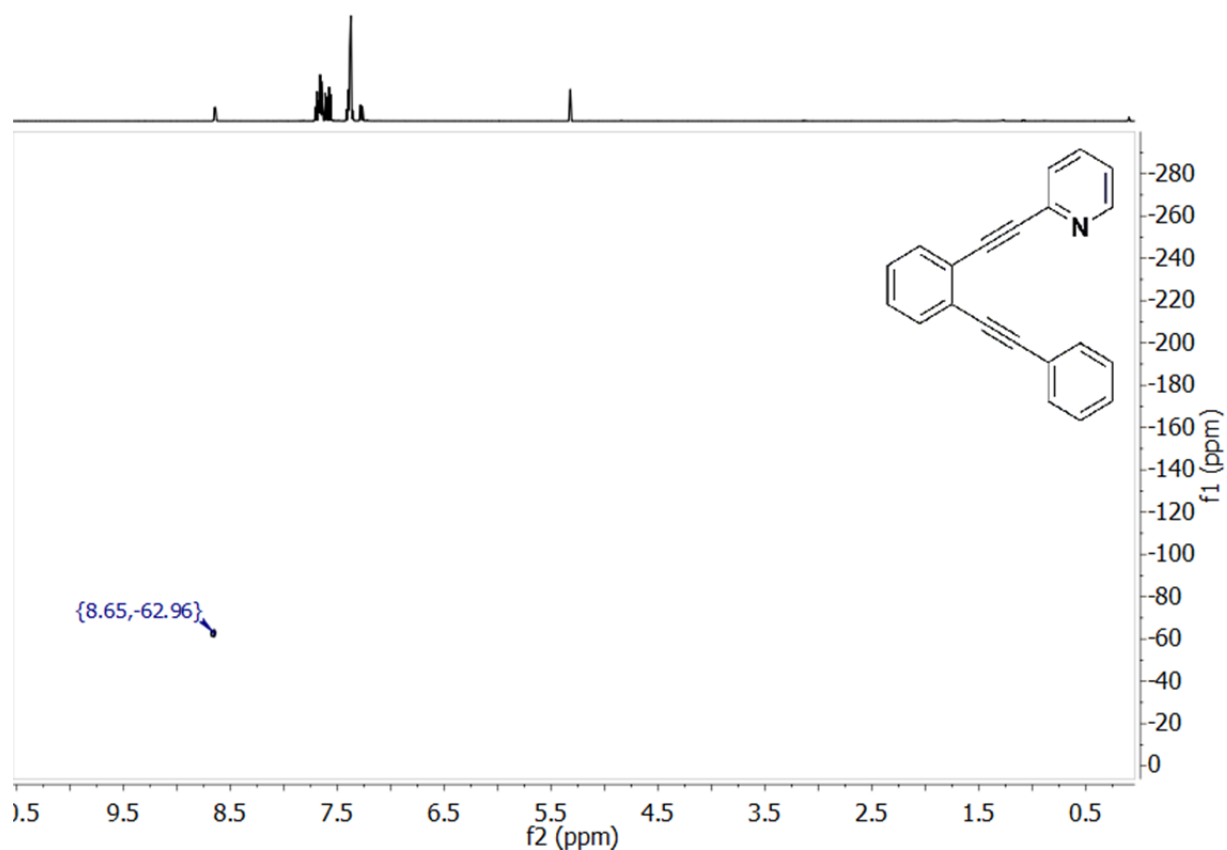


**Figure S59.** The <sup>1</sup>H NMR spectrum of **7** acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 499.87 MHz

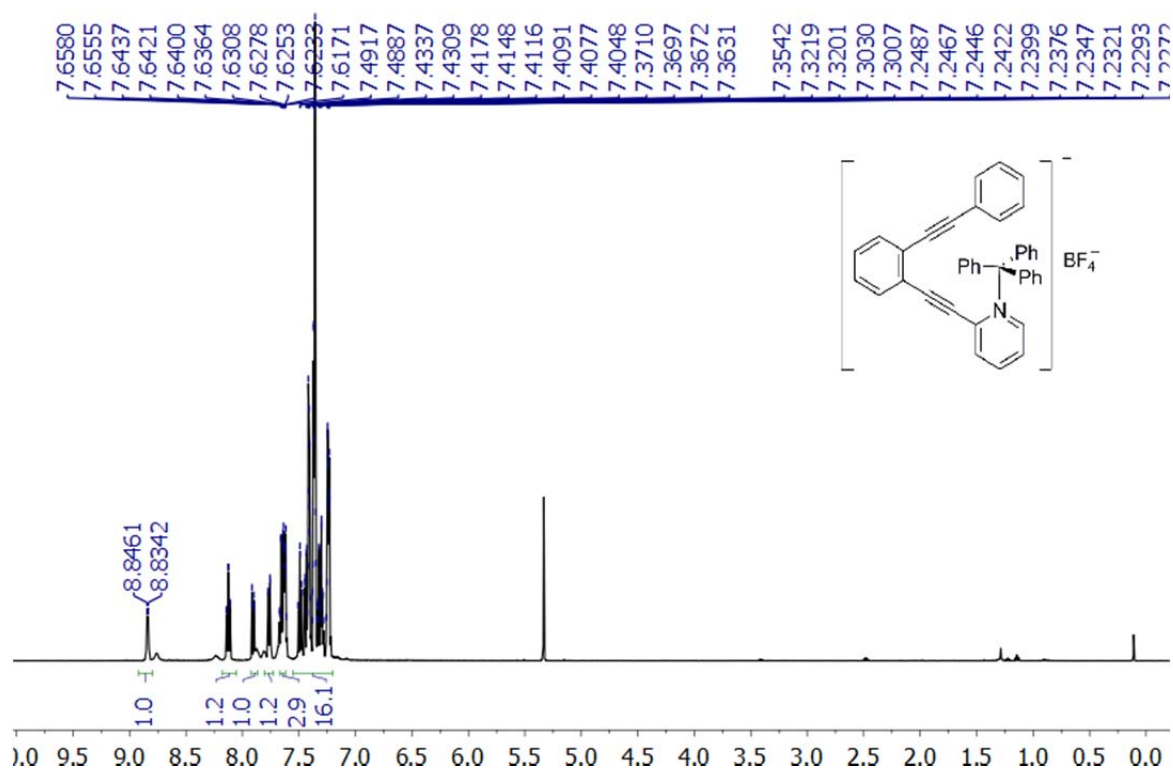


**Figure S60.** The <sup>13</sup>C NMR spectrum of **7** acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 125.71 MHz.

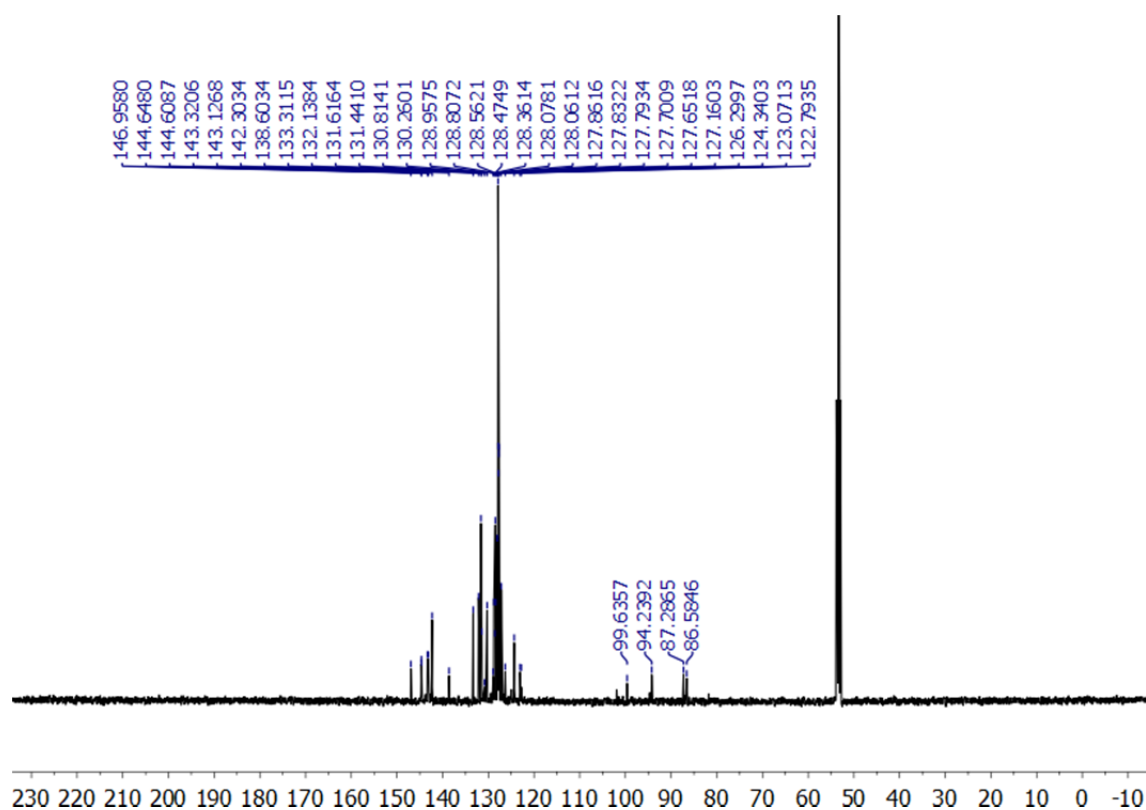




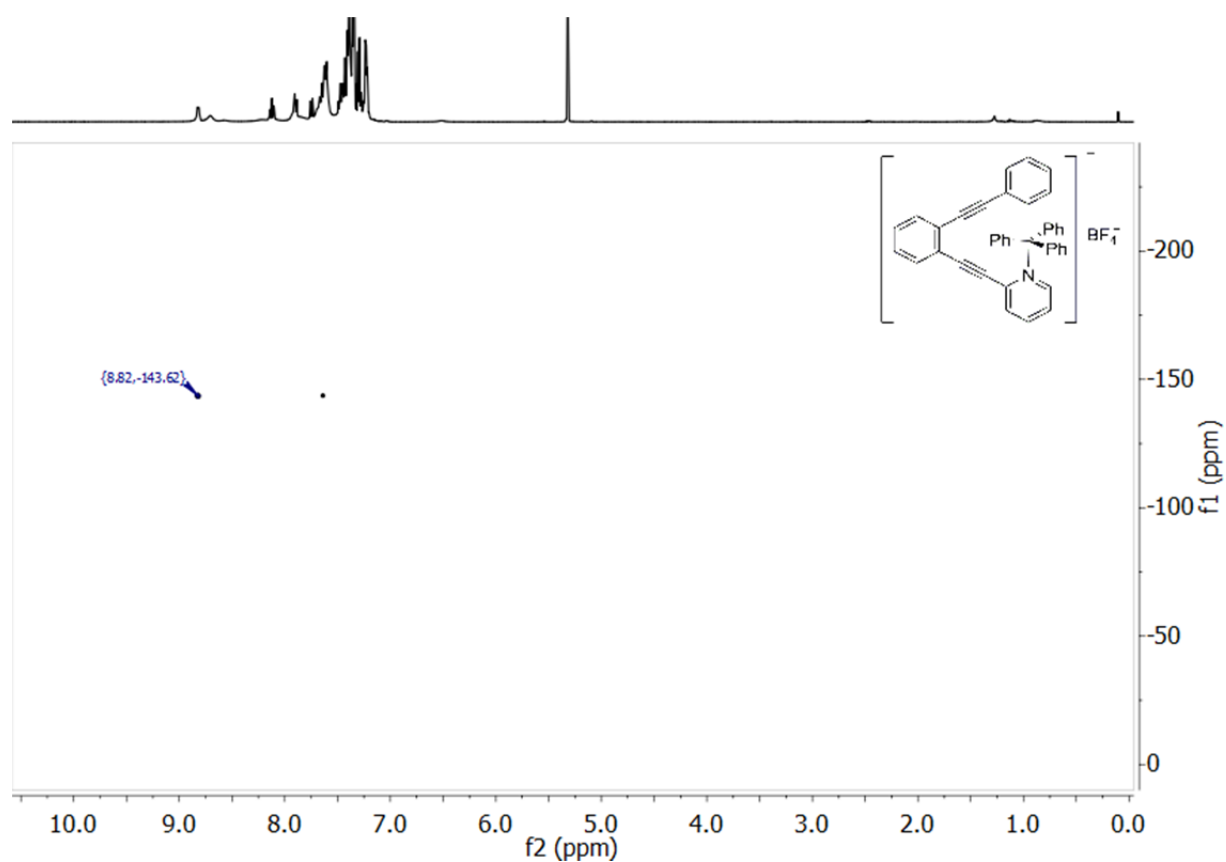
**Figure S61.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of **7** acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.



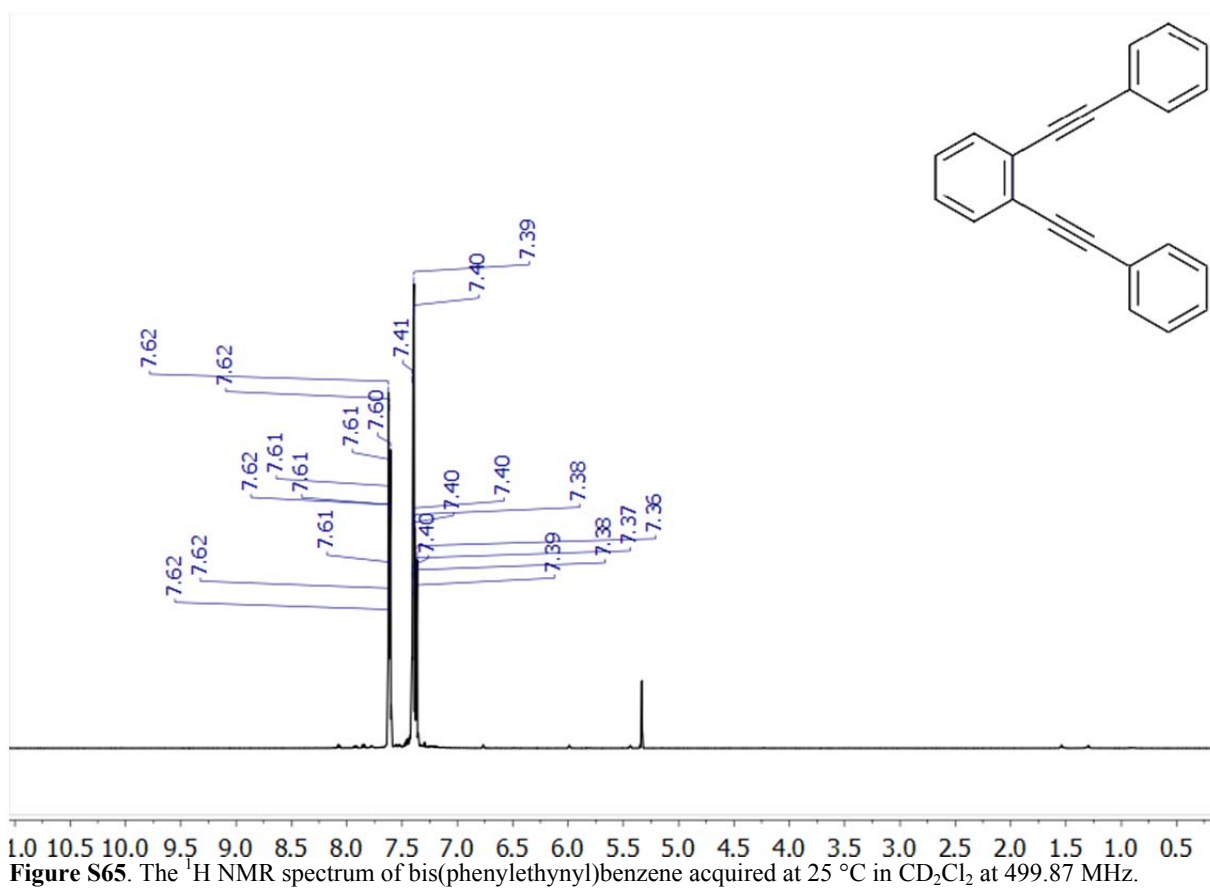
**Figure S62.** The  $^1\text{H}$  NMR spectrum of 2-((2-(phenylethynyl)phenyl)ethynyl)-1-tritylpyridin-1-ium tetrafluoroborate complex (**7**-trityl  $\text{BF}_4^-$ ) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87 MHz.



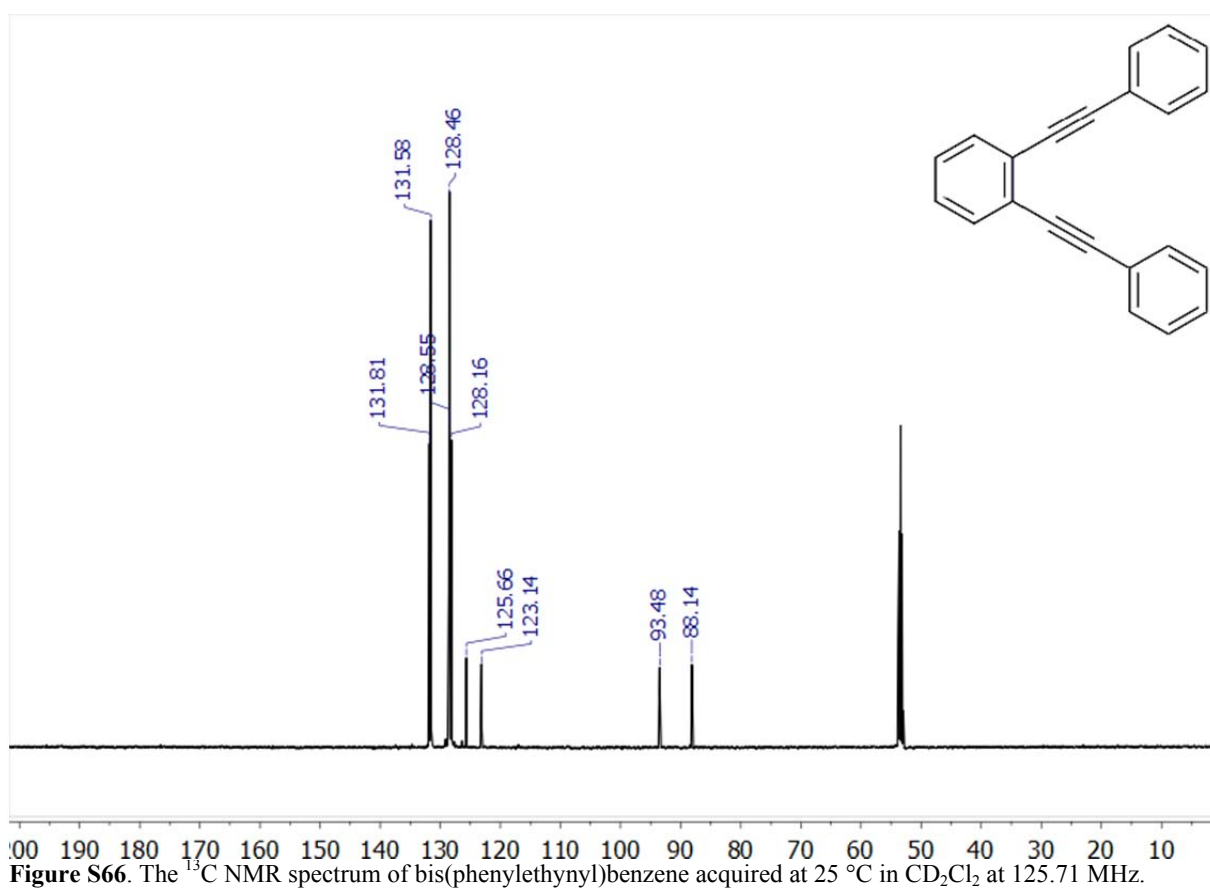
**Figure S63.** The  $^{13}\text{C}$  NMR spectrum of bis(phenylethynyl)benzene triphenylcarbenium tetrafluoroborate complex (7-trityl  $\text{BF}_4^-$ ) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 125.71 MHz.



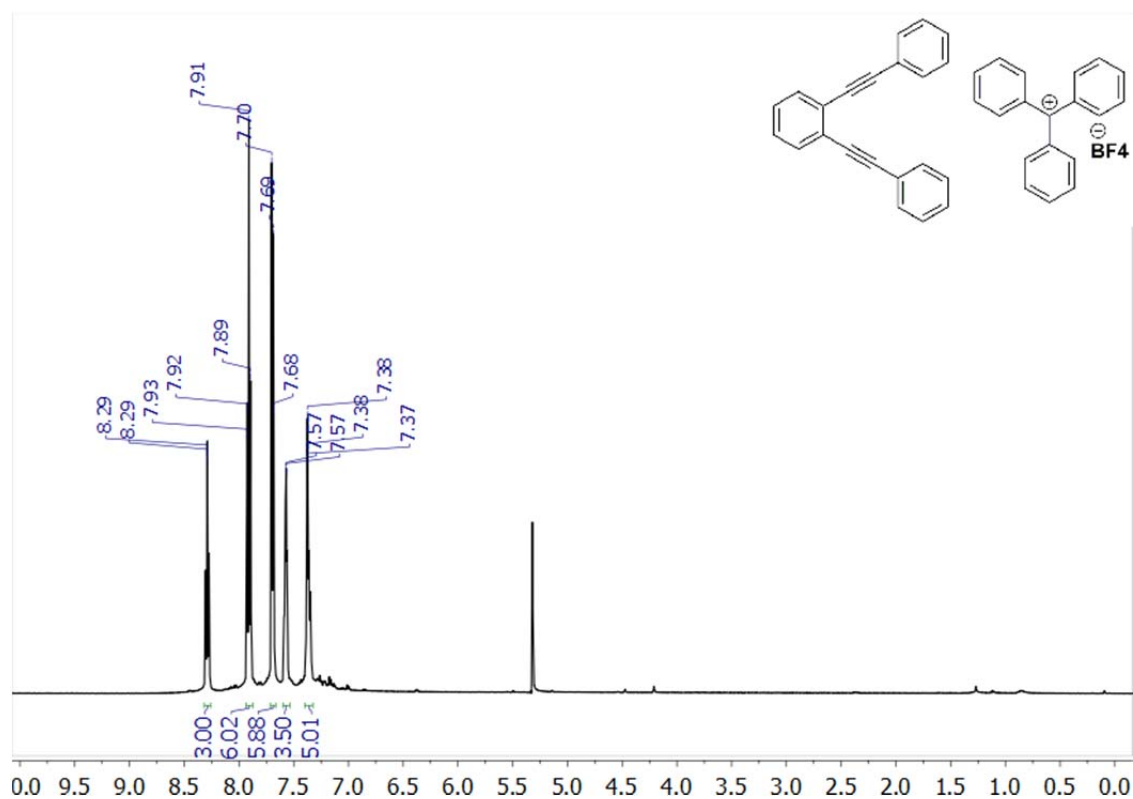
**Figure S64.** The  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC spectrum of 2-((2-(phenylethynyl)phenyl)ethynyl)-1-tritylpyridin-1-ium tetrafluoroborate (7-trityl  $\text{BF}_4^-$ ) acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/50.66 MHz.



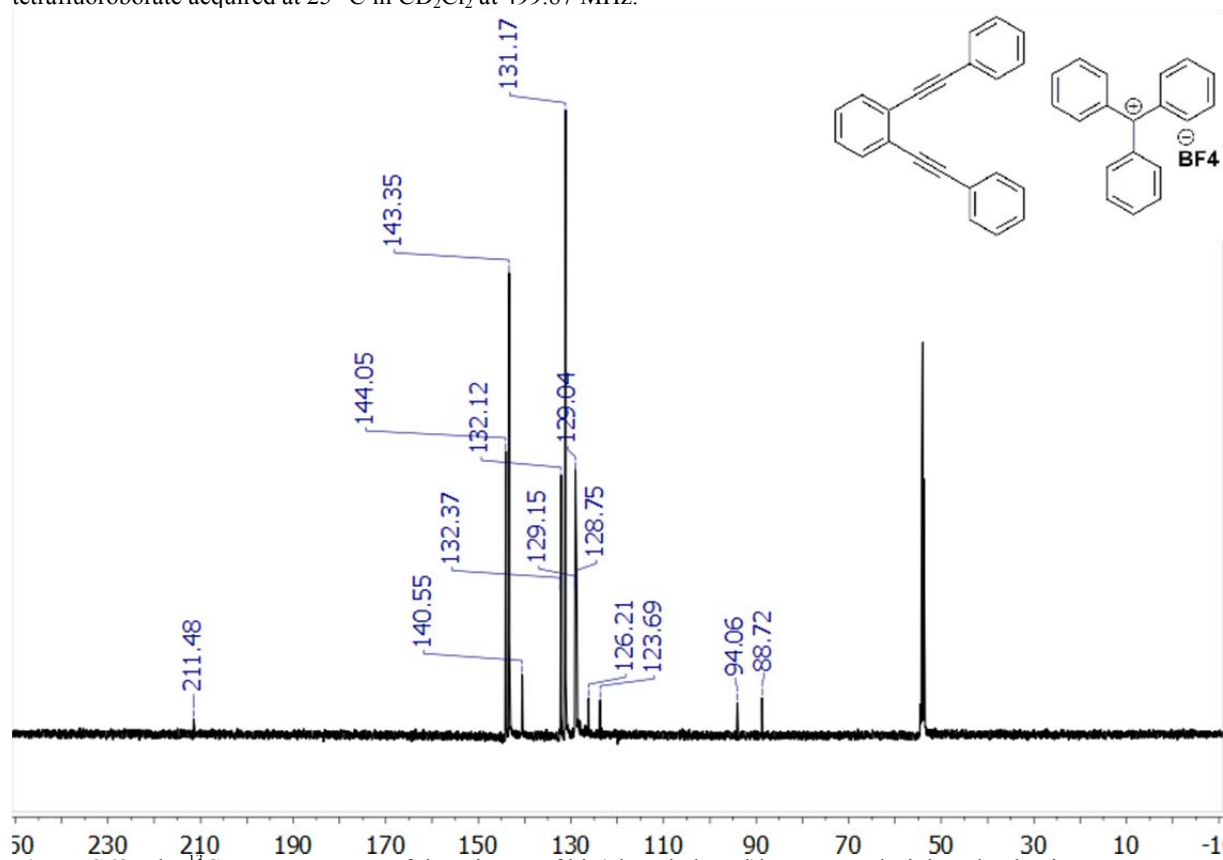
**Figure S65.** The <sup>1</sup>H NMR spectrum of bis(phenylethynyl)benzene acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 499.87 MHz.



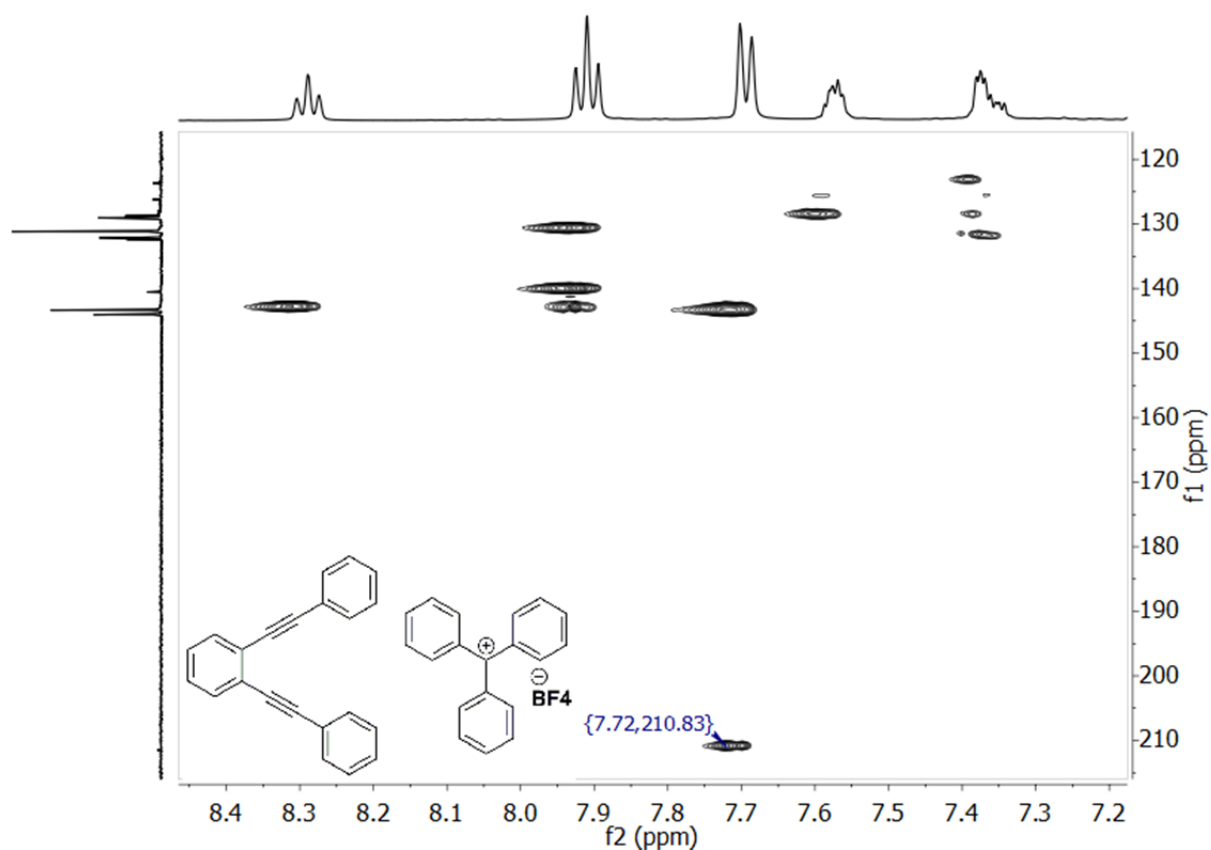
**Figure S66.** The <sup>13</sup>C NMR spectrum of bis(phenylethynyl)benzene acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 125.71 MHz.



**Figure S67.** The <sup>1</sup>H NMR spectrum of the mixture of bis(phenylethynyl)benzene and triphenylcarbenium tetrafluoroborate acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 499.87 MHz.



**Figure S68.** The <sup>13</sup>C NMR spectrum of the mixture of bis(phenylethynyl)benzene and triphenylcarbenium tetrafluoroborate acquired at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> at 125.71 MHz.



**Figure S69.** The  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of the mixture of bis(phenylethynyl)benzene and triphenylcarbenium tetrafluoroborate acquired at 25 °C in  $\text{CD}_2\text{Cl}_2$  at 499.87/125.71 MHz.

## 6. Isotopic perturbation of equilibrium (IPE) NMR

Isotopic perturbation of equilibrium (IPE) is an NMR spectroscopic technique that relies on the observation of secondary isotope effects for distinguishing a single symmetric molecule from rapidly interconverting asymmetric tautomers.<sup>14</sup> Its major advantage is that it succeeds even when the rapid exchange causes the NMR signals from the individual tautomers to coalesce into one set of signals, which in turn are virtually identical to those of a single static structure. IPE has been applied successfully for example, to symmetry determinations of carbocations,<sup>15</sup> O–H...O<sup>16,17</sup> and N–H...N<sup>18,19</sup> hydrogen bonded systems, thiapentenes,<sup>20</sup> metal chelating complexes<sup>21</sup> and halogen bond complexes.<sup>1,2,22,23</sup> The method requires substitution of a proton with deuterium (or, more generally, one isotope with another) close to the interaction site, causing changes in the vibration spectrum of the molecule, which affect the vibrationally averaged NMR parameters.<sup>24</sup> IPE relies most commonly on <sup>13</sup>C NMR spectroscopic detection. At the analysis of mixtures of a non-deuterated molecule and its deuterated analogue each NMR signal turns into two, one originating from the deuterated molecule and one from the corresponding non-deuterated one, with a small shift difference <sup>n</sup>Δ<sub>obs</sub>, between them, where *n* denotes the number of intervening bonds between the site of the <sup>1</sup>H-to-<sup>2</sup>H substitution and the investigated carbon.

$${}^n\Delta_{\text{obs}} = \delta_{\text{C(D)}} - \delta_{\text{C(H)}} \quad (1)$$

The observed shift difference consists of two independent isotope shift contributions: the intrinsic isotope shift <sup>n</sup>Δ<sub>0</sub> and the equilibrium isotope shift <sup>n</sup>Δ<sub>eq</sub> (Equation 2).

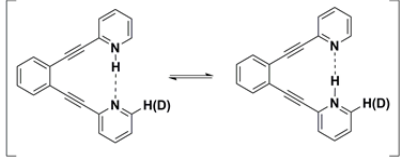
$${}^n\Delta_{\text{obs}} = {}^n\Delta_0 + {}^n\Delta_{\text{eq}} \quad (2)$$

In both static and rapidly equilibrating systems, the isotope substitution slightly changes the vibrationally averaged equilibrium geometry and induces an intrinsic shift, <sup>n</sup>Δ<sub>0</sub>, on all nearby <sup>13</sup>C nuclei. It is usually small (< 0.4 ppm) and negative as the <sup>13</sup>C NMR signal corresponding to the heavier, deuterated molecule occurs at a lower chemical shift. The magnitude of <sup>n</sup>Δ<sub>0</sub> attenuates rapidly as *n* increases. The second component, <sup>n</sup>Δ<sub>eq</sub>, is present only for systems that are involved into an equilibrium process. Isotope substitution slightly changes the vibrational zero-point energies (ZPE) of the two tautomers and, according to Boltzmann's law, the equilibrium constant *K* between the tautomers. This in turn gives a contribution <sup>n</sup>Δ<sub>eq</sub> to the isotopic shift that is significant and determined by Equation 3:

$${}^n\Delta_{\text{eq}} = D(K-1)/[2(K+1)] \quad (3)$$

where *D* equals the chemical shift difference between the signals of the tautomeric forms (halogenated N<sup>+</sup>–X and non-halogenated N, in this particular case). It is noteworthy that sizeable <sup>n</sup>Δ<sub>eq</sub> need not be restricted to small *n*. According to the van't Hoff equation,<sup>25</sup> *K* is temperature dependent, and so is therefore <sup>n</sup>Δ<sub>eq</sub>. To induce large isotope effects, selective deuterium substitution was performed as close as possible to the [N–C–N]<sup>+</sup> interaction site, at the C2 position of one of the pyridines of **2c**. Here, the monodeuterated analogue of **2c** is referred to as **2c-d**. The synthesis of **2c** and **2c-d** have followed our previously published synthetic procedure<sup>2</sup> and is therefore not given here in detail. Isotope shifts <sup>n</sup>Δ<sub>obs</sub> were obtained by acquisition of <sup>13</sup>C {<sup>1</sup>H, <sup>2</sup>H} NMR spectra of the isotopologues of **3d** dissolved in dry CD<sub>2</sub>Cl<sub>2</sub>. Similar to previous, related<sup>26</sup> measurements of intrinsic isotope shifts, a mixture of **2** and its mono-deuterated analogue **2-d**, was used as reference static structure (<sup>n</sup>Δ<sub>obs</sub> = <sup>n</sup>Δ<sub>0</sub>) most similar to the investigated XB system **3d**. As reference for a system involved into a rapid exchange process, the hydrogen bond analogue of **3d**, the analogous [N–H–N]<sup>+</sup> complex was used. Isotopic shifts for the halogen bonded complex **3d**, for the static reference system **2c** and for the most similar analogous equilibrating systems ([N–H–N]<sup>+</sup> complexes)<sup>18,19</sup> are reported in Table S1. Small equilibrium shifts are expected originating from (a) the very small difference in the Lewis basicity of the two nitrogens that is reflected by an equilibrium constant close to unity for the potential exchange process [N–C...N]<sup>+</sup> ⇌ [N...C–N]<sup>+</sup>,<sup>23</sup> and (b) from the comparably small chemical shift difference (*D*, equation 3) of the halogenated and non-halogenated, or protonated and non-protonated (ca 8 ppm at C2),<sup>26</sup> tautomeric states. Such small equilibrium isotope effects do not permit straightforward, direct differentiation between a static structure and a tautomerizing system.<sup>23</sup> Originating from their large magnitudes, the <sup>1</sup>Δ<sub>obs</sub> and <sup>2</sup>Δ<sub>obs</sub> values suffer least from measurement errors, and their comparison among the various compounds is therefore expected to provide the most accurate conclusions. Yet, the magnitude pattern of the 3-4 bond IEs may also be informative. Thus, for a static system the magnitude and the

**Table S1.** Temperature coefficients (ppm K) of the isotope shifts, observed for the CD<sub>2</sub>Cl<sub>2</sub> solutions of **2c**, its H<sup>+</sup> complex, and of **3d**. The data of **2c** and its of its H<sup>+</sup> complex are given as reference for a structurally closely related static and dynamic systems, and have previously been published.<sup>1</sup> Details of the IPE NMR technique are given in reference 1. Signal overlaps prohibited the determination of the temperature dependence of the secondary deuterium isotope effects on C4, C5 and C6 and thereby the IPE NMR study did not provide conclusive evidence, neither for a static symmetric structure nor for a dynamic mixture of asymmetric ones.

Structure	C2 <sup>1</sup> Δ <sub>obs</sub>	C3 <sup>2</sup> Δ <sub>obs</sub>	C4 <sup>3</sup> Δ <sub>obs</sub>	C5 <sup>4</sup> Δ <sub>obs</sub>	C6 <sup>3</sup> Δ <sub>obs</sub>	Σ  Δ <sub>obs</sub>
<b>2c, 2c-d</b>	-7	-7	-2	0	-3	19
 <b>2c, 2c-d + H<sup>+</sup></b>	-10	-11	-3	0	+15	39
<b>3d, 3d-d</b>	-8	-11	n.d.	n.d.	n.d.	n.d.

n.d. – not determined due to signal overlaps

temperature dependency of the IEs depends on the distance from the position of isotope substitution, whereas for systems in equilibrium it is governed by the distance from the position of the atom involved into the equilibrium process.

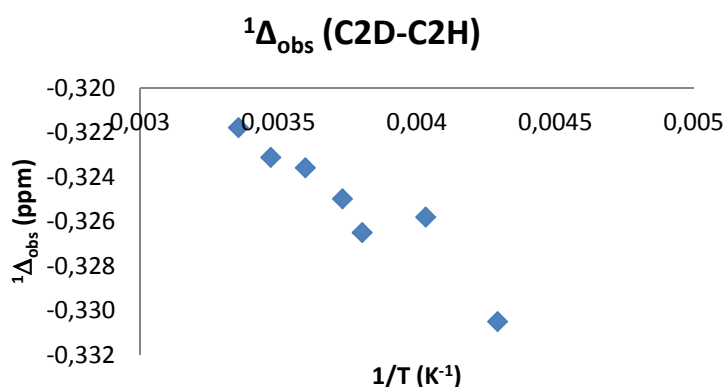
For distinguishing between a static [N-C-N]<sup>+</sup> geometry and the corresponding dynamic mixture, the temperature dependence of the isotope shifts, expressed as the slopes of <sup>n</sup>Δ<sub>obs</sub> vs. reciprocal temperature,<sup>27</sup> was studied (Table S1). As expected, the IEs of the dynamic reference [N-H-N]<sup>+</sup> complex, **2c** + H<sup>+</sup>, showed a significantly larger overall temperature dependence than those of the static reference **2c**; i.e. Σ|Δ<sub>obs</sub>| 39 vs 19 ppb/K (Table S1). In agreement with the expectations, the temperature dependence of the IEs observed on C-2 and C-3 were significantly larger than that of those observed on C4 and C6, which is in excellent agreement with the previous literature.<sup>1,2,23</sup>

The isotope effects observed on C2 and C3 for **3d/3d-d** were comparable in magnitude to those of **2c/2c-d** and of the dynamic reference **2c/2c-d+H<sup>+</sup>**. The comparison of the magnitude of the isotope dependence on these positions with those of the static and the dynamic references<sup>22,28,29</sup> did not allow reliable differentiation of the isotope effects. This might be due to the significantly larger size of **c** as compared to **2c/2c-d** and **2c/2c-d+H<sup>+</sup>**. Signal overlaps for C4, C5 and C6 with the signals of the complexed trityl cation at various temperatures prohibited reliable determination of the temperature dependency of the IEs at these positions. Overall, the magnitude and the temperature dependence of the observed IEs of **3d/3d-d** is compatible with that expected, however, this data unfortunately does not allow us to draw reliable conclusion on the static, [N<sup>+</sup>≡C≡N]<sup>+</sup>, or dynamic, [N-C≡N]<sup>+</sup> ⇌ [N≡C-N]<sup>+</sup>, nature of the complex.

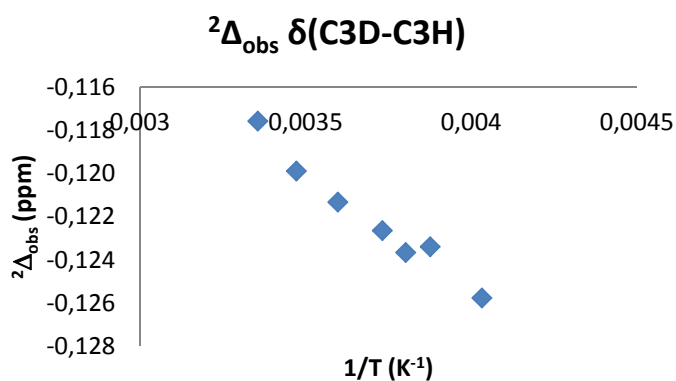
IPE NMR experiments were recorded on a Bruker Avance HD III 500 MHz spectrometer equipped with a 5 mm TCI cryogenic probe using <sup>13</sup>C detection (125 MHz) with broadband <sup>1</sup>H and inverse-gated <sup>2</sup>H decoupling. In the absence of <sup>2</sup>H decoupling, the CD <sup>13</sup>C NMR signals are split into triplets

and/or are broadened due to  $J_{CD}$  couplings, which makes the isotope shifts difficult to measure. The lack of the nuclear Overhauser enhancement additionally decreases the sensitivity of the C(D) signals if not  $^2\text{H}$ -decoupled. NMR spectra were recorded for the temperature interval 25 to  $-40\text{ }^\circ\text{C}$  (lower temperature limit of the probe), for  $\text{CD}_2\text{Cl}_2$  solutions. To obtain high quality spectra for determination of small variations in isotopic shifts ( $^n\Delta_{\text{obs}}$ )  $^{13}\text{C}$  NMR spectra have been recorded with 32768 data points and a reduced spectral window providing a ca 0.5 Hz/point original resolution. The data was then zero-filled to 262144 points providing a digital resolution of 0.07 Hz/point, using the software MestreNova V10.2. Error estimates for the IPE measurements are comparable to that of previous investigations.<sup>23</sup>

The temperature dependency of the IEs of **3d/3d-d** is shown in Figure S7-S8. The data of the common reference systems **2c/2c-d** and **2c/2c-d+H<sup>+</sup>** have been previously published and are therefore not shown here; the reader is advised to references<sup>1,22,23</sup>.



**Figure S70.** The temperature dependence of the isotope shifts of (**3/3-d**) observed on its C2 position.



**Figure S71.** The temperature dependence of the isotope shifts of (**3/3-d**) observed on its C3 position.



## 7. X-ray crystallography

The details of the crystals data, data collection, and the refinement results.

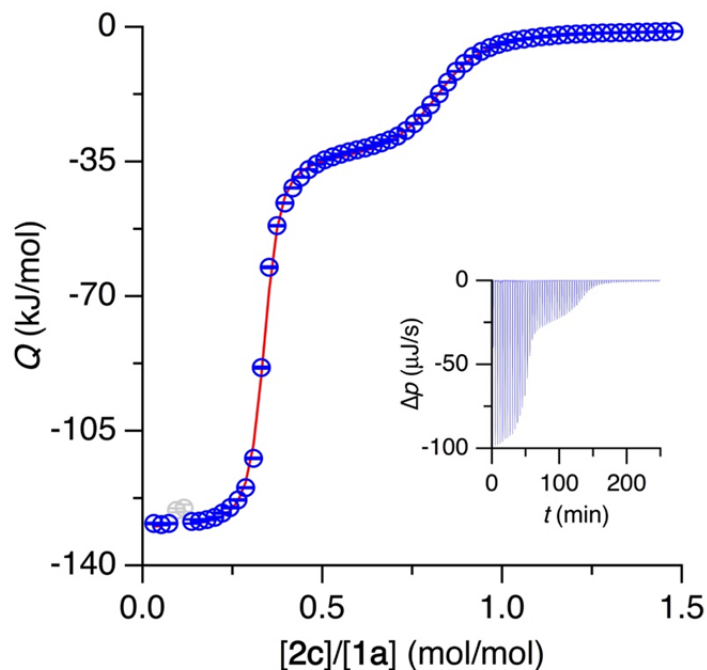
Crystal data for CCDC 1581474:  $C_{24}H_{20}BF_4N$ ,  $F_w = 409.22$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 25.7941(7)$ ,  $b = 7.4589(2)$ ,  $c = 20.1543(6)$  Å,  $\beta = 90.743(3)^\circ$ ,  $V = 3877.27(19)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calc}} = 1.402$  Mg/m<sup>3</sup>,  $\mu = 0.903$  mm<sup>-1</sup>,  $F_{000} = 1696$ , crystal size  $0.30 \times 0.14 \times 0.04$  mm<sup>3</sup>,  $\theta$  range =  $3.427\text{--}74.194^\circ$ , 11788 collected reflections (before HKLF5), 3862 independent reflections, 99.7 % data completeness, no restraints, 273 parameters, Goodness-of-fit ( $F^2$ ) = 1.140, Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R1 = 0.1142$ ,  $wR2 = 0.3662$ .  $R$  indices (all data):  $R1 = 0.1164$ ,  $wR2 = 0.3671$ . Largest residual electron densities: 0.802 and -0.676 e.Å<sup>-3</sup>.

PLAT084\_ALERT\_3\_B High wR2 Value (i.e. > 0.25) ..... 0.37 Report

Author Response: The crystal is a weak scatterer and nonmerohedric 2-component twin, resulting poor data with high  $R$  values.

## 8. Isothermal titration calorimetry

Titration of **2c** with carbenium ion **1a** revealed two well-resolved transitions (Figure 4, main text). Initially, addition of carbenium to **2c** led to formation of a 1:1 complex, as indicated by the first transition at a **1a/2c** molar ratio of 1, where the ligand became saturated with carbenium. Further addition of carbenium **1a** resulted in disruption of complex **3c** and formation of a 1:2 complex, **6c**, as borne out by the second transition occurring at a **1a/2c** molar ratio of 2. This mode of binding was quantitatively confirmed by fitting a “reverse” titration of carbenium **1a** with **2c** using the same set of best-fit parameters (Figure S9).



**Figure S72.** “Reverse” titration performed at 25°C. Titration of the carbenium ion **1a** with the bidentate ligand **2c** first yielded their strong 2:1 complex, **6c**. Upon addition of excess **2c**, the 1:1 complex of **1a/2c**, **3c** was formed. The bidentate ligand **2c** at a concentration of 3.75 mM was titrated to the triphenylcarbenium tetrafluoroborate **1a** at a concentration of 0.5 mM. The main panel shows the isotherm depicting normalized heats of reaction,  $Q$ , as a function of the **1a/2c** molar ratio in the calorimeter cell (blue circles) along with uncertainties (blue horizontal lines) resulting from baseline assignment and peak integration.<sup>8</sup> Nonlinear least-squares fits (red solid line) was based on the presumption of two interaction sites,<sup>10</sup> as reflected in the bimodal shape of the isotherm. Inset: Corresponding raw thermogram displaying differential heating power,  $\Delta p$ , versus time,  $t$ .

**Table S2.** Confidence intervals (CI) for the thermodynamic data.

	Lower 68.3% CI	Best fit	Upper 68.3% CI
$K_1$	1,0	1,9	3,6
$\Delta G^\circ_1$	-51,3	-49,8	-48,2
$\Delta H^\circ_1$	-100,5	-93,4	-88,0
$-T\Delta S^\circ_1$		43,7	
$K_2$	150	237	359
$\Delta G^\circ_2$	-39,0	-37,8	-36,8
$\Delta H^\circ_2$	-56,1	-53,1	-50,7
$-T\Delta S^\circ_2$		15,3	

## 9. Preliminary computations

**Computational model – thermochemistry and NMR properties.** All quantum-chemical calculations were performed with Density Functional Theory (DFT). For geometry optimizations and thermochemical calculations we used the M06 exchange and correlation (XC) functional<sup>30</sup> and a mixed-level basis set constructed in the following way: (i) The carbenium C atoms and the N atoms were described with Jensen's aug-pc-2<sup>31,32-34</sup> basis set., (ii) all atoms that are nearest neighbors to those mentioned in (i) were described with the pc-2<sup>31-33</sup> basis set, (iii) all other atoms, with the pc-1 basis set.<sup>31-33</sup> This basis set provides an accurate description of the interesting bonds at a reasonable overall computational cost. Solvent effects were covered with the Polarizable Continuum Model (PCM).<sup>35</sup> For all geometries, vibrational frequencies were calculated to characterize the structures and to determine thermochemical corrections. The latter were calculated for 298 K and 1 atm, corresponding to the experimental conditions. Where applicable, the basis-set interaction error (BSSE) was corrected by the counterpoise (CP) method.<sup>36</sup>

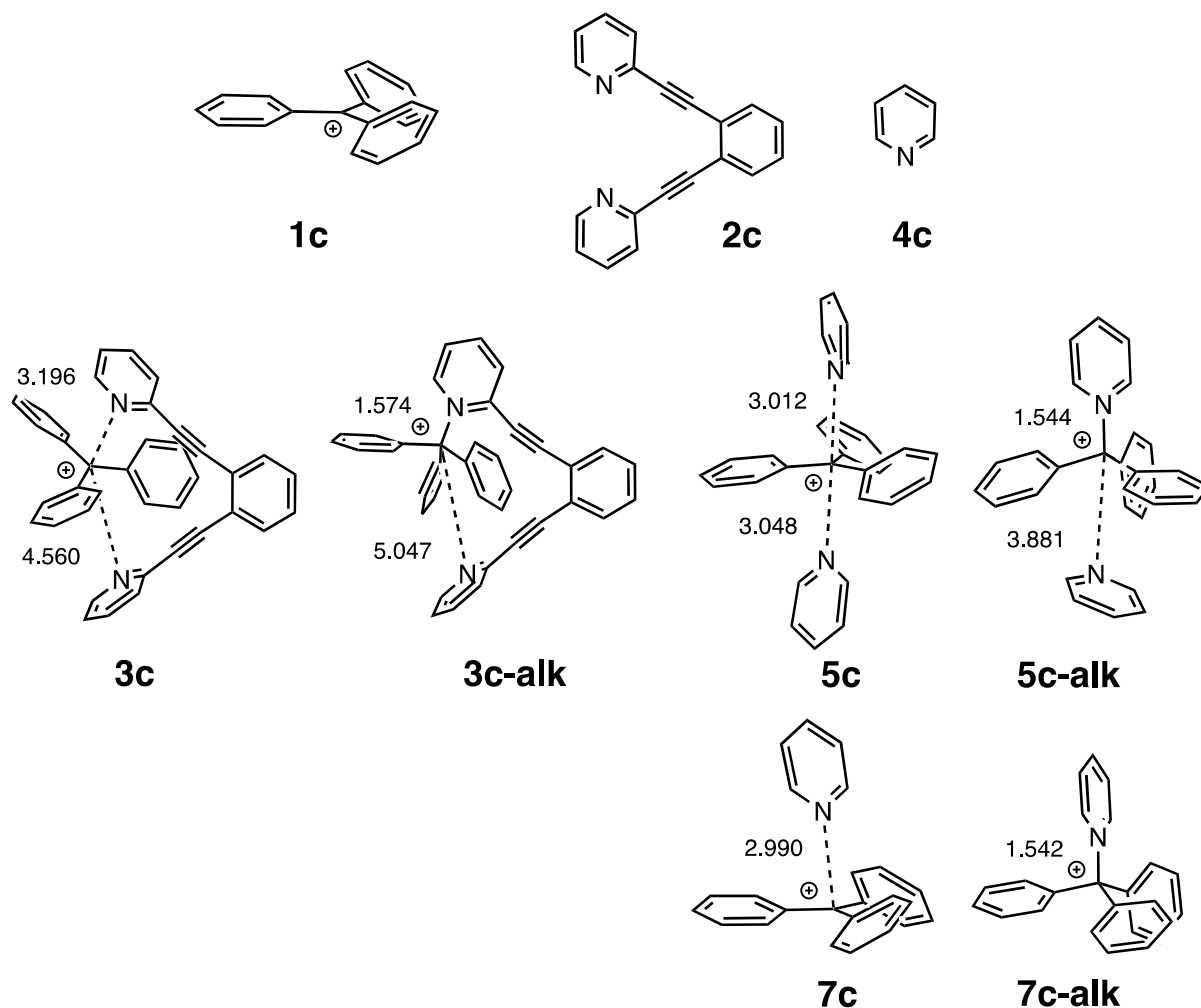
<sup>15</sup>N and <sup>13</sup>C NMR chemical shieldings were calculated at the optimized geometries obtained as above, using the gauge-independent atomic orbitals (GIAO) method.<sup>37</sup> For the NMR calculations, the modification by Wilson et al.<sup>38</sup> of the Becke 97 XC functional<sup>39</sup> (B97-2) was employed. The basis set was constructed analogously as above except that Jensen's pcS basis sets<sup>40</sup> were used. For the computation of <sup>15</sup>N NMR chemical shifts, pyridine was used as a secondary reference with an experimental shift of  $\delta_{\text{exp}}(^{15}\text{N}) = -67.0$ . For the determination of <sup>13</sup>C chemical shifts, the chemical shieldings for TMS were calculated as reference. In this latter calculation, the geometry was optimized at the M06/pc-1 level of theory. In the calculation of the shieldings, the C atoms were described with the aug-pcS-2 basis set, all other atoms, with the pcS-2 basis set. All mentioned calculations were performed with the Gaussian09 programming package.<sup>41</sup>

**Computational model – visualizations.** Calculations, providing the structures for Figure 1, were performed using release 2015-3 of the Schrödinger program package.<sup>42</sup> Geometries were optimized with density functional theory (DFT), using the M06 functional<sup>30</sup> and the LACVP\*\* basis set and effective core potentials<sup>15</sup> as implemented in Jaguar.<sup>43</sup> To obtain electron densities and electrostatic potentials, single-point calculations with the M06 functional and the (all-electron) MIDI! basis set<sup>44</sup> were performed at the optimized geometries. The molecular surfaces were generated using Gaussview 5.0. Here, 1 a.u. of electron density = electron/Å<sup>3</sup>. Atomic coordinates are given below.

**Computed geometries.** The preliminary calculations were performed for R = R' = H (Figure 2), i.e. for the compounds **1c**, **2c**, **3c**, **4c**, and **5c** (Fig S73). For reference purposes, we investigated in addition [pyridine-tris(phenyl)carbenium]<sup>+</sup> **7c**. For the species **3c**, **5c**, and **7c**, two stable geometries each were found. In one of them, the **1c** constituent has undergone *N*-alkylation with a distance between the carbenium carbon and the bonded nitrogen being 1.54-1.57 Å. The nitrogen of the second pyridine moiety (for **3c** and **5c**) is not coordinated to the carbenium carbon. Rather, it is bonded by van der Waals and electrostatic interactions, with distances to the carbenium carbon of 5.05 (**3c**) or 3.88 Å (**4c**), respectively. We denote the structures containing an *N*-alkylated **1c** moiety with the suffix **-alk**. The second stable structure found for **5c** shows two weak coordinative bonds between the N atom(s) and the carbenium carbon, with bond distances ~3 Å, i.e. a tetrel structure. For **7c**, a weakly bonded coordinative structure with a C(carbenium)-N bond length of 2.99 Å is predicted. The corresponding structure for **3c** shows one "coordinative" C(carbenium)-N bond with a bond length of 3.20 Å, whereas the second C(carbenium)-N bond length is 4.56 Å, indicating an unspecific bonding based on electrostatic and van der Waals attraction. Fig. S73 gives an overview over the obtained stable structures. The tetrel structure that is indicated by the experimental findings could not be identified.

Table S3 presents the DFT predicted thermochemical properties of the investigated compounds. According to the calculated  $\Delta G^{298}$  values, none of the experimentally investigated compounds is predicted to be thermochemically stable under ambient conditions (only the reference compound **7c** is slightly more stable than its constituents). This is in contradiction both to the outcome of the NMR investigation and to that of the calorimetric studies. For both **3c**, **5c**, and **7c**, the structure featuring an

alkylated **1c** moiety is more stable than the alternative structure. For the two structures of **5c**, the comparison with **4c** + **7c** reveals that the addition of a second pyridine to **7c** gives only a small gain in enthalpy (13 to 15 kJ mol<sup>-1</sup>) whereas results in a loss of three times as much entropy.



**Figure S73.** Overview of the structures studied in the numerical investigations.

**Table S3.** Relative energies, enthalpies and Gibbs free energies of the investigated compounds. All values are given in kJ mol<sup>-1</sup>.

Compound	Reference	$\Delta E$	$\Delta H^{298}$	$\Delta G^{298}$
<b>3c</b>	<b>1c</b> + <b>2c</b>	-46.4	-40.9	15.6
<b>3c-alk</b>	<b>1c</b> + <b>2c</b>	-77.4	-68.4	1.8
	<b>3c</b>	-31.0	-27.5	-13.8
<b>7c</b>	<b>1c</b> + <b>4c</b>	-18.8	-11.6	30.4
<b>7c-alk</b>	<b>1c</b> + <b>4c</b>	-70.4	-59.7	-2.3
	<b>7c</b>	-51.6	-48.1	-32.6
<b>5c</b>	<b>1c</b> + 2 <b>4c</b>	-36.1	-25.0	55.4
	<b>4c</b> + <b>7c</b>	-17.3	-13.4	25.1
<b>5c-alk</b>	<b>1c</b> + 2 <b>4c</b>	-91.0	-74.9	28.9
	<b>4c</b> + <b>7c-alk</b>	-20.6	-15.2	31.2
	<b>5c</b>	-54.9	-49.9	-26.5

**Table S4.** Calculated  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR Chemical Shifts and Complexation Shifts of the Investigated Compounds (All Values in ppm).

Complex	ligand	$\delta^{15}\text{N}_{\text{ligand}}$	$\delta^{15}\text{N}_{\text{complex}}$	$\Delta\delta^{15}\text{N}_{\text{coord}}$	$\delta^{13}\text{C}_{\text{ligand}}$	$\delta^{13}\text{C}_{\text{complex}}$	$\Delta\delta^{13}\text{C}_{\text{coord}}$
<b>3c</b>	<b>2c</b>	-60.94	-64.62 -65.24	-3.68 -4.30	214.25	217.95	3.70
<b>3c-alk</b>	<b>2c</b>	-60.94	-156.45 -64.26	-95.52 -3.32	214.25	96.76	-117.50
<b>5c</b>	<b>4c</b>	-67.00	-61.53 -62.15	5.47 4.85	214.25	220.08	5.82
<b>5c-alk</b>	<b>4c</b>	-67.00	-149.57 -66.34	-82.57 0.66	214.25	95.82	-118.43
<b>7c</b>	<b>4c</b>	-67.00	-62.13	4.87	214.25	217.07	2.82
<b>7c-alk</b>	<b>4c</b>	-67.00	-153.25	-86.25	214.25	95.71	-118.54

The calculated NMR properties are compiled in Table S4. For *N*-alkylation, the coordination shifts both for  $^{15}\text{N}$  and for the carbenium  $^{13}\text{C}$  are close to the experimental chemical shifts observed for **3c** ( $\delta^{15}\text{N}_{\text{coord}}$ : -79.5 ppm,  $\delta^{13}\text{C}_{\text{coord}}$ : -109.8 ppm) and **5c** ( $\delta^{15}\text{N}_{\text{coord}}$ : -86.3 ppm and -8.8,  $\delta^{13}\text{C}_{\text{coord}}$ : -121.0 ppm). However, only a single  $^{15}\text{N}$  NMR shift observed for **3c** experimentally (Table 1), which is compatible with a symmetric structure, whereas **3c-alk** is asymmetric and would be expected to show two separate peaks with different  $^{15}\text{N}$  NMR chemical shifts ( $\delta^{15}\text{N}_{\text{complex}}$  -156.45 and -64.26 ppm). The predicted chemical shifts for complex **5c** show a better agreement to the experiments (predicted  $\delta^{15}\text{N}_{\text{complex}}$  -149.57 and -66.34 ppm *versus* experimental  $\delta^{15}\text{N}_{\text{complex}}$  -153.3 and -75.8 ppm). This finding suggests that **5c** may indeed have a structure similar to **5c-alk**; however, the thermochemical stability of the complex remains unexplained. Regarding **3c**, none of the computationally predicted structures is consistent with the measured coordination shifts. For the structure **3c** (without *N*-alkylation), all calculated coordination shifts are less than 10 ppm in absolute value, and the predicted geometry is, in contrast to the experimental observation, not fully symmetric. For the structure **3c-alk**, the calculated coordination shift for one of the nitrogens and the carbenium carbon are in reasonable agreement with the experiment values. However, the calculated coordination shift of the second nitrogen atom is close to zero, which is in contradiction to the experimental findings where such a small coordination shift is not observed. Neither are the computed coordination shifts compatible with a situation where **3c** rapidly oscillates between **3c-alk** and its mirror image as in this case, the observed  $^{15}\text{N}$  coordination shift for **3c** should be considerably smaller, roughly half the value observed for **5c**.

Altogether, the computed thermochemical and NMR data for **3c** and **5c** give at hand that the calculated structures do not correctly represent the experimental ones. We ascribe this in first instance to the known difficulties of DFT to handle systems with strongly delocalized electrons arising from the self-interaction error on the one hand<sup>45</sup> and the non-dynamic correlations on the other hand.<sup>46</sup> It will thus be necessary to perform more detailed numerical investigations involving more advanced (wave-function based) computational models.

**Data for thermochemical and NMR calculations.** Coordinates are given in Ångström, energies in Hartree, and chemical shieldings in ppm. For molecules where the BSSE was calculated the fragment numbers for the atoms are given in the rightmost column of the coordinate block.

```
=====
1c
-----

Number of atoms:  34
Point group:  C1

1      1
C      0.0010624903   0.0014362931   0.0009577998
```

C	-1.9374920000	3.7490866979	-0.1892555100
C	-2.5290540796	2.6987293787	0.5088959082
C	-1.9046011793	1.4676600298	0.5587535046
C	-0.6570596058	1.2755592393	-0.0655663712
C	-0.0666321995	2.3529210631	-0.7539003413
C	-0.7110747524	3.5725607616	-0.8260468699
H	-2.4380375970	4.7158547003	-0.2379521520
H	-3.4791832104	2.8474150979	1.0190826341
H	-2.3504241626	0.6557668641	1.1318930503
H	0.8757973448	2.2053567823	-1.2795251834
H	-0.2625432901	4.3912151410	-1.3862296995
C	-2.2802054260	-3.5523675960	0.0279935283
C	-1.1009920317	-3.4827598705	0.7664616174
C	-0.3442016873	-2.3273056401	0.7478003451
C	-0.7752983465	-1.2057865632	0.0130184116
C	-1.9794120787	-1.2881953110	-0.7126798140
C	-2.7136672397	-2.4581250876	-0.7172615282
H	-2.8689662933	-4.4694443267	0.0339096619
H	-0.7777035095	-4.3344168769	1.3625696097
H	0.5604693296	-2.2618812080	1.3509273341
H	-2.3011200621	-0.4432446827	-1.3200156685
H	-3.6260990694	-2.5244573728	-1.3074239225
C	4.2165277033	-0.1994667804	0.1611767159
C	3.5508169765	0.8551088874	0.7823898811
C	2.1733777212	0.9324727787	0.7186982658
C	1.4337468652	-0.0660082153	0.0560072781
C	2.1227416585	-1.1322341642	-0.5537311341
C	3.5021239340	-1.1875709403	-0.5124607952
H	5.3040890365	-0.2518186713	0.2028208503
H	4.1136383262	1.6146820968	1.3222261523
H	1.6512238332	1.7390219156	1.2316074804
H	1.5657041228	-1.8853732863	-1.1092788712
H	4.0288754786	-1.9993551344	-1.0111991680

Electronic energy:	-732.25414602
Zero-point correction=	0.278787
Sum of electronic and zero-point Energies=	-731.975359
Sum of electronic and thermal Energies=	-731.960817
Sum of electronic and thermal Enthalpies=	-731.959872
Sum of electronic and thermal Free Energies=	-732.017466

Lowest frequency:  
A 61.3429

Electronic energy (NMR):	-732.52140100
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<sup>13</sup>C shielding for carbenium C:  
C 1 -28.9848

=====  
2c  
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Number of atoms: 34  
Point group: C2V

0	1		
C	0.0000000000	1.3901593247	-4.1318086154
C	0.0000000000	0.6962259223	-5.3311126245
C	0.0000000000	-0.6962259223	-5.3311126245
C	0.0000000000	-1.3901593247	-4.1318086154
C	0.0000000000	-0.7081924485	-2.9079770232
C	0.0000000000	0.7081924485	-2.9079770232
H	0.0000000000	2.4798419978	-4.1236005929
H	0.0000000000	1.2444952147	-6.2725397563
H	0.0000000000	-1.2444952147	-6.2725397563

H	0.0000000000	-2.4798419978	-4.1236005929
C	0.0000000000	-1.4430704777	-1.6912827892
C	0.0000000000	-2.0916938973	-0.6662058605
C	0.0000000000	1.4430704777	-1.6912827892
C	0.0000000000	2.0916938973	-0.6662058605
C	0.0000000000	2.8770806984	0.5245755575
N	0.0000000000	2.2235535037	1.6923467336
C	0.0000000000	2.9426989608	2.8037432069
C	0.0000000000	4.3298558935	2.8248553229
C	0.0000000000	5.0053805448	1.6128877932
C	0.0000000000	4.2697247357	0.4393629314
H	0.0000000000	2.3852255281	3.7370109485
H	0.0000000000	4.8674544550	3.7716320245
H	0.0000000000	6.0945607234	1.5802526921
H	0.0000000000	4.7546893673	-0.5360389526
C	0.0000000000	-2.8770806984	0.5245755575
N	0.0000000000	-2.2235535037	1.6923467336
C	0.0000000000	-2.9426989608	2.8037432069
C	0.0000000000	-4.3298558935	2.8248553229
C	0.0000000000	-5.0053805448	1.6128877932
C	0.0000000000	-4.2697247357	0.4393629314
H	0.0000000000	-2.3852255281	3.7370109485
H	0.0000000000	-4.8674544550	3.7716320245
H	0.0000000000	-6.0945607234	1.5802526921
H	0.0000000000	-4.7546893673	-0.5360389526

Electronic energy:	-878.09513347
Zero-point correction=	0.257400
Sum of electronic and zero-point Energies=	-877.837733
Sum of electronic and thermal Energies=	-877.820159
Sum of electronic and thermal Enthalpies=	-877.819214
Sum of electronic and thermal Free Energies=	-877.886122

Lowest frequency:  
B1 17.3254

Electronic energy (NMR):	-878.38011697
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15N shieldings:  
N 16 -84.9211  
N 26 -84.9211

=====  
3c  
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Number of atoms: 68  
Point group: C1

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C	4.9179719599	-0.1419458676	-2.7574904953	1	
C	3.5740848760	-0.0139320072	-2.4617501534	1	
C	3.1616224330	0.4008473673	-1.1817324297	1	
C	4.1426234997	0.6830882067	-0.2117524622	1	
C	5.4839570203	0.5319387719	-0.5056177112	1	
C	5.8732273295	0.1233233876	-1.7793082158	1	
C	1.7684420982	0.5390833253	-0.8640459349	1	
C	1.3539542605	1.5222803812	0.1027661296	1	
C	0.7890520028	-0.2749832540	-1.5177110701	1	
C	1.0740367649	-1.6080693253	-1.8750592761	1	
C	0.1213253235	-2.3749953752	-2.5133653976	1	
C	-1.1136118859	-1.8151570032	-2.8439199506	1	
C	-1.4035147420	-0.4963596902	-2.5091043782	1	
C	-0.4732188704	0.2655885741	-1.8254305958	1	
C	0.3400233126	1.2083884686	1.0208518119	1	
C	-0.0207276832	2.1187399298	1.9970403367	1	

C	0.5842800754	3.3717683008	2.0367916285	1
C	1.5698285903	3.7085798931	1.1107146919	1
C	1.9712208819	2.7838580553	0.1651916887	1
H	5.2282517274	-0.4403990004	-3.7575677311	1
H	2.8296626498	-0.1827046267	-3.2381635482	1
H	3.8366499961	0.9741049080	0.7923916318	1
H	6.2342332412	0.7268759839	0.2588729794	1
H	6.9322053808	0.0144796173	-2.0124831261	1
H	2.0256844757	-2.0476893123	-1.5799643906	1
H	0.3303247173	-3.4166767591	-2.7529698222	1
H	-1.8618582045	-2.4207214303	-3.3577091554	1
H	-2.3668445511	-0.0619913141	-2.7756022427	1
H	-0.7067841362	1.3002985654	-1.5626675764	1
H	-0.1204614742	0.2215254607	0.9912546766	1
H	-0.7802434330	1.8535883769	2.7321153507	1
H	0.2819731760	4.0959136416	2.7938952914	1
H	2.0275998797	4.6965475879	1.1329021938	1
H	2.7358927982	3.0450345020	-0.5656456045	1
C	-3.1417809883	-3.7394702348	-0.3406123362	2
C	-2.7730397992	-2.4458763649	0.0531465714	2
C	-3.6337220291	-1.3662114988	-0.2428285293	2
C	-4.8303433270	-1.6170575170	-0.9265154960	2
C	-5.1733505155	-2.9019878352	-1.3156357045	2
C	-4.3268034627	-3.9668841068	-1.0209070061	2
C	-3.3037382894	-0.0173856336	0.0778899847	2
C	-3.0829196690	1.1644476624	0.2365881772	2
C	-2.8012351304	2.5603835994	0.3739860130	2
C	-3.3583820268	3.2941243125	1.4179911767	2
C	-3.0518868380	4.6425515621	1.5154820156	2
C	-2.2081674121	5.2069703967	0.5702374720	2
C	-1.7087241681	4.3922170672	-0.4356679523	2
N	-1.9895531367	3.1025124981	-0.5420569273	2
C	-1.5231850814	-2.2799896750	0.7175889818	2
C	-0.4319766365	-2.2761413080	1.2483110201	2
C	0.8325226170	-2.3779245903	1.9106878601	2
N	1.8786735529	-1.7229890030	1.3917229695	2
C	3.0529647822	-1.8696516185	1.9888177134	2
C	3.2552467801	-2.6459789799	3.1192335526	2
C	2.1661527287	-3.3110237732	3.6628519289	2
C	0.9322056449	-3.1784980156	3.0477501019	2
H	-2.4707082666	-4.5666038303	-0.1086832710	2
H	-5.4869707902	-0.7776786715	-1.1551578979	2
H	-6.1065516842	-3.0735431299	-1.8509496963	2
H	-4.5912028593	-4.9796684228	-1.3228142256	2
H	-4.0172392091	2.8064902179	2.1352059593	2
H	-3.4705694086	5.2459777176	2.3205234816	2
H	-1.9420553858	6.2618959682	0.6084797737	2
H	-1.0442757745	4.8043146885	-1.1909665112	2
H	3.8911000055	-1.3429760055	1.5392740129	2
H	4.2465148328	-2.7264735642	3.5615100104	2
H	2.2750043123	-3.9298990764	4.5529688310	2
H	0.0484191422	-3.6868631754	3.4307438029	2

Electronic energy:	-1610.37498835
Zero-point correction=	0.537596
Sum of electronic and zero-point Energies=	-1609.837392
Sum of electronic and thermal Energies=	-1609.803656
Sum of electronic and thermal Enthalpies=	-1609.802712
Sum of electronic and thermal Free Energies=	-1609.905683

Lowest frequency:  
A 12.8823

Bond distances:  
r(C7 - N48 ) = 4.5604  
r(C7 - N52 ) = 3.1965



BSSE correction= 0.00804610

Electronic energy (NMR): -1610.89372946

15N shieldings:

N 48 -81.2422

N 52 -80.6192

13C shielding for carbenium C:

C 7 -32.6864

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3c-alk

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Number of atoms: 68

Point group: C1

1	1		
C	-1.4926155012	-2.6549334247	0.6722850378
C	-2.6940207620	-1.9090711484	0.6469467497
C	-3.8875999157	-2.5455127079	1.0096838306
C	-3.8984644529	-3.8754984548	1.3991683298
C	-2.7137199778	-4.6060486743	1.4321906824
C	-1.5238881762	-4.0012477035	1.0678714082
C	-0.2390485239	-2.1144796130	0.2888860385
C	-2.7403588773	-0.5363931127	0.2724802869
H	-4.8135505162	-1.9719892885	0.9839527278
H	-4.8402301513	-4.3459547023	1.6788758412
H	-2.7195119047	-5.6510174718	1.7384247651
H	-0.5905616273	-4.5635912101	1.0820108720
C	-2.8982373948	0.6363656790	0.0076908194
C	0.8753127414	-1.7524444413	-0.0293958863
C	-3.5385240694	4.6554927818	-0.7887107574
C	-2.6726273201	4.1985848575	0.1942320793
N	-2.4644148258	2.9153807170	0.4488391946
C	-3.1273310940	2.0169608880	-0.2857502768
C	-4.0217852639	2.3730108023	-1.2931750313
C	-4.2277009172	3.7192609446	-1.5468043529
H	-3.6710116746	5.7234227477	-0.9533143738
H	-2.1213235191	4.9070586108	0.8069264278
H	-4.5375079113	1.5999667087	-1.8615859103
H	-4.9189744095	4.0338323922	-2.3282655874
C	4.8641063250	-1.5555583078	-1.2156540753
C	4.1308935794	-0.4131702397	-1.0273405644
N	2.8400701219	-0.4310359136	-0.6478608411
C	2.2201457613	-1.6305591381	-0.4317142510
C	2.9350888026	-2.8108463642	-0.6117211705
C	4.2584457908	-2.7852321585	-1.0020096383
H	5.9040617809	-1.4699106347	-1.5178675683
H	4.5765516603	0.5593905836	-1.1649199141
H	2.4146734489	-3.7483638753	-0.4326920063
H	4.8098590574	-3.7141870002	-1.1346016956
C	2.0871991027	0.8908575170	-0.3638996116
C	4.7953723363	4.2429227413	-0.8541483465
C	4.2751222065	3.5775674733	-1.9610468789
C	3.4076923413	2.5128024780	-1.7852238086
C	3.0535774388	2.0749591629	-0.5046977849
C	3.5726164066	2.7507931778	0.5923390779
C	4.4377945407	3.8283277982	0.4189887377
H	5.4712312038	5.0871096670	-0.9885592432
H	4.5415373610	3.8963435793	-2.9682322571
H	3.0019284083	2.0094690168	-2.6641079653
H	3.2987907487	2.4587987333	1.6033826318
H	4.8264232216	4.3478748788	1.2943281310
C	-0.9501614642	1.6259871925	-3.3633364995

C	-0.6754630968	2.5521975803	-2.3628777111
C	0.2908684055	2.2825931128	-1.4080241578
C	0.9954994945	1.0779318539	-1.4180712752
C	0.7422877698	0.1774052178	-2.4438088246
C	-0.2294462583	0.4430373293	-3.4047830107
H	-1.7114009715	1.8368439349	-4.1146427481
H	-1.2090299147	3.5028258677	-2.3334405138
H	0.5118141208	3.0353939585	-0.6503608899
H	1.3040082509	-0.7493421811	-2.5416413602
H	-0.4098693021	-0.2837926069	-4.1962423015
C	0.7419117820	0.3993058095	3.7259557966
C	2.0337691525	0.0455227194	3.3504346761
C	2.4465220173	0.2190277480	2.0382782403
C	1.5822015478	0.7432815797	1.0749370909
C	0.3004648862	1.1046127512	1.4618581834
C	-0.1175685007	0.9334402547	2.7771494061
H	0.4091312846	0.2565052205	4.7538900203
H	2.7247978108	-0.3710842609	4.0826060992
H	3.4635056464	-0.0711385165	1.7685949850
H	-0.4222905399	1.4961168012	0.7503038918
H	-1.1365294860	1.2135363409	3.0472441113

Electronic energy: -1610.37876795  
 Zero-point correction= 0.540277  
 Sum of electronic and zero-point Energies= -1609.838491  
 Sum of electronic and thermal Energies= -1609.806085  
 Sum of electronic and thermal Enthalpies= -1609.805141  
 Sum of electronic and thermal Free Energies= -1609.902903

Lowest frequency:  
 A 14.2285

Bond distances:  
 r(C35 - N17 ) = 5.0474  
 r(C35 - N27 ) = 1.5475

Electronic energy (NMR): -1610.89629655

15N shieldings:  
 N 17 -83.7865  
 N 27 10.5943  
 13C shielding for carbenium C:  
 C 35 88.5113

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 4c  
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Number of atoms: 11  
 Point group: C2V

0	1		
N	0.0000000000	0.0000000000	1.4124844965
C	0.0000000000	1.1370074914	0.7242058776
C	0.0000000000	1.1929079064	-0.6603047304
C	0.0000000000	0.0000000000	-1.3691371363
C	0.0000000000	-1.1929079064	-0.6603047304
C	0.0000000000	-1.1370074914	0.7242058776
H	0.0000000000	2.0557622625	1.3056039121
H	0.0000000000	2.1542263859	-1.1726859889
H	0.0000000000	0.0000000000	-2.4593345014
H	0.0000000000	-2.1542263859	-1.1726859889
H	0.0000000000	-2.0557622625	1.3056039121

Electronic energy: -248.13185059  
 Zero-point correction= 0.088230

Sum of electronic and zero-point Energies= -248.043621  
 Sum of electronic and thermal Energies= -248.039321  
 Sum of electronic and thermal Enthalpies= -248.038377  
 Sum of electronic and thermal Free Energies= -248.070366

Lowest frequency:  
 A2 380.8710

Electronic energy (NMR): -248.21443943

15N shieldings:  
 N 1 -78.8592

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 5c  
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Number of atoms: 56  
 Point group: C1

1	1				
C	-1.7542489768	0.4072354119	1.6421621660	1	
C	-3.1363959071	0.3775509514	1.6508349686	1	
C	-3.8719859196	1.5574971318	1.8474348724	1	
C	-3.1824693955	2.7623185756	2.0575451947	1	
C	-1.7999639728	2.7832066734	2.0805272015	1	
C	-1.0848567817	1.6083188202	1.8632719714	1	
C	-5.3111065739	1.5319212230	1.8271941425	1	
C	-6.0340836811	2.6485805318	1.2805396690	1	
C	-6.0101138851	0.3939617278	2.3596472789	1	
C	-5.4667610230	-0.3312326354	3.4354398207	1	
C	-6.1561787364	-1.3967692013	3.9821684976	1	
C	-7.3885282004	-1.7725696894	3.4534557103	1	
C	-7.9310982981	-1.0799024072	2.3736400659	1	
C	-7.2535809784	-0.0015151077	1.8368867547	1	
C	-7.3013357297	3.0032544858	1.7757779535	1	
C	-7.9903710812	4.0747812139	1.2388861469	1	
C	-7.4350988085	4.8038187850	0.1906643402	1	
C	-6.1822610412	4.4656311393	-0.3146261538	1	
C	-5.4841486377	3.4042650922	0.2293202863	1	
H	-1.1918326257	-0.5071700950	1.4595224205	1	
H	-3.6645979132	-0.5543905270	1.4552937088	1	
H	-3.7462597034	3.6737961295	2.2503237069	1	
H	-1.2733387530	3.7173894580	2.2695714425	1	
H	0.0046129611	1.6284389571	1.8670485421	1	
H	-4.5257252845	-0.0106849316	3.8776658483	1	
H	-5.7397305588	-1.9331953133	4.8332423487	1	
H	-7.9290424210	-2.6156431318	3.8832399416	1	
H	-8.8832589406	-1.3906334698	1.9466594410	1	
H	-7.6584899446	0.5155537064	0.9692670454	1	
H	-7.7221808425	2.4637302510	2.6215950188	1	
H	-8.9617384731	4.3528101238	1.6448901253	1	
H	-7.9834646826	5.6436915025	-0.2358168175	1	
H	-5.7559296378	5.0275017954	-1.1440342740	1	
H	-4.5269692352	3.1101567840	-0.1968291355	1	
H	-7.0703080084	1.5292120141	-1.2093829639	2	
C	-6.4307512743	0.7725721928	-1.6635640925	2	
C	-6.7404342048	0.2640339393	-2.9133706517	2	
C	-5.8950110378	-0.6898070111	-3.4636897247	2	
C	-4.7807757332	-1.0891365072	-2.7391387973	2	
C	-4.5639251115	-0.5178638148	-1.4957221721	2	
N	-5.3682994672	0.3938124764	-0.9613111429	2	
H	-7.2056960274	1.6547994125	4.8525572760	3	
C	-6.4960763193	2.3165682449	5.3486308447	3	
N	-5.4262704363	2.6789041233	4.6487065905	3	
C	-4.5408510460	3.4748160433	5.2376169168	3	

C	-4.6820985315	3.9453916696	6.5329895901	3
C	-5.8054736553	3.5661595303	7.2538475749	3
C	-6.7342551531	2.7306812220	6.6479244313	3
H	-7.6248345338	0.6100049860	-3.4458971530	2
H	-6.1009448212	-1.1145927084	-4.4460253515	2
H	-4.0890180514	-1.8326967888	-3.1318095582	2
H	-3.6973334614	-0.8080410950	-0.9056586833	2
H	-3.6673970834	3.7503572359	4.6505207796	3
H	-3.9250264351	4.5956564379	6.9683543035	3
H	-5.9543039819	3.9147937630	8.2756511619	3
H	-7.6290502750	2.4043205836	7.1756449079	3

Electronic energy: -1228.53748978  
 Zero-point correction= 0.457402  
 Sum of electronic and zero-point Energies= -1228.080088  
 Sum of electronic and thermal Energies= -1228.053002  
 Sum of electronic and thermal Enthalpies= -1228.052058  
 Sum of electronic and thermal Free Energies= -1228.142991

Lowest frequency:  
 A 12.0080

Bond distances:  
 r(C7 - N41) = 3.0124  
 r(C7 - N44) = 3.0479

BSSE correction= 0.00590607

Electronic energy (NMR): -1228.94811370

15N shieldings:  
 N 41 -84.3275  
 N 44 -83.7074  
 13C shielding for carbenium C:  
 C 7 -34.8081

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 5c-alk  
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Number of atoms: 56  
 Point group: C1

1	1				
C	-1.2829002504	1.7582136922	4.3288509138	1	
C	-0.3954454446	0.8302508956	3.8055034515	1	
C	0.6060990795	1.2138990000	2.9091917928	1	
C	0.6822903283	2.5534105011	2.5432199816	1	
C	-0.2070042945	3.4867945072	3.0650848965	1	
C	-1.1913941523	3.0956178757	3.9601054462	1	
C	1.5770009768	0.1474650057	2.3851488631	1	
C	2.3389355732	0.5947069138	1.1318256868	1	
C	0.8020153650	-1.1598974388	2.2146999958	1	
C	-0.2781532999	-1.1544572038	1.3286688030	1	
C	-1.0726604601	-2.2793395103	1.1745033732	1	
C	-0.8186344921	-3.4284585679	1.9180994654	1	
C	0.2345715216	-3.4325473356	2.8176262272	1	
C	1.0378183003	-2.3034103129	2.9665823822	1	
C	2.1262909175	0.0402010586	-0.1230956676	1	
C	2.8412950914	0.4888019334	-1.2301889522	1	
C	3.7881734664	1.4932248581	-1.0979826833	1	
C	4.0263214063	2.0404178255	0.1582375986	1	
C	3.3127594909	1.5892061837	1.2574695119	1	
H	-2.0532504544	1.4312855524	5.0265470755	1	
H	-0.4863699519	-0.2134145236	4.1079239133	1	
H	1.4194263921	2.8933660674	1.8210141549	1	

H	-0.1305748061	4.5285632351	2.7541127947	1
H	-1.8913669587	3.8270418333	4.3636699475	1
H	-0.5024122708	-0.2520594477	0.7536046021	1
H	-1.9048049682	-2.2553383327	0.4709831085	1
H	-1.4470287430	-4.3110817782	1.8013535931	1
H	0.4382818024	-4.3155979859	3.4227823940	1
H	1.8306951117	-2.3473816643	3.7119152013	1
H	1.4029475462	-0.7580379125	-0.2639292816	1
H	2.6539666941	0.0362701713	-2.2036828207	1
H	4.3470880752	1.8426311084	-1.9658973408	1
H	4.7764236946	2.8201900691	0.2860099470	1
H	3.5334279385	2.0234108735	2.2335939992	1
H	3.6889377525	-1.2705401059	2.0628727517	1
C	3.7118467411	-0.8830157909	3.0721303965	1
C	4.7287064562	-1.1713732287	3.9433948548	1
C	4.6955023991	-0.6336379314	5.2248993482	1
C	3.6317265388	0.1778906640	5.5840984095	1
C	2.6358078835	0.4296792303	4.6685049671	1
N	2.6808163032	-0.0957640357	3.4367744204	1
H	5.5424064457	-1.8123111879	3.6155912308	1
H	5.4947459822	-0.8438946999	5.9332476122	1
H	3.5654787205	0.6272277918	6.5711541647	1
H	1.7900518083	1.0604309427	4.9002632201	1
N	-0.7658263328	1.7666725093	-0.2507716040	2
C	-0.0845990003	2.7670770639	-0.7995892707	2
C	-0.5461008551	4.0730643471	-0.8333966261	2
C	-1.7805785593	4.3524095227	-0.2625679674	2
C	-2.4967262300	3.3139067382	0.3157752604	2
C	-1.9459173631	2.0434593416	0.2929215381	2
H	0.8813995392	2.5140494498	-1.2322146581	2
H	0.0509936187	4.8562447302	-1.2984230853	2
H	-2.1787611047	5.3671852311	-0.2663553443	2
H	-3.4672105813	3.4856379428	0.7796358923	2
H	-2.4816283875	1.2091543277	0.7430021142	2

Electronic energy: -1228.55638801  
 Zero-point correction= 0.461223  
 Sum of electronic and zero-point Energies= -1228.095165  
 Sum of electronic and thermal Energies= -1228.069987  
 Sum of electronic and thermal Enthalpies= -1228.069043  
 Sum of electronic and thermal Free Energies= -1228.151082

Lowest frequency:  
 A 27.6223

Bond distances:  
 r(C7 - N41 ) = 1.5439  
 r(C7 - N46 ) = 3.8806

BSSE correction= 0.00389048

Electronic energy (NMR): -1228.95921395

15N shieldings:  
 N 41 3.7137  
 N 46 -79.5234  
 13C shielding for carbenium C:  
 C 7 89.4483

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 7c  
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Number of atoms: 45  
 Point group: C1

1	1				
C	-1.8504275583	0.2229014870	1.6500593978	1	
C	-3.2309625768	0.2415229067	1.6838635542	1	
C	-3.9256659762	1.4544007331	1.8467519075	1	
C	-3.1905380803	2.6424811234	2.0045821466	1	
C	-1.8081074711	2.6148722526	1.9969729380	1	
C	-1.1373972774	1.4094874390	1.8084474911	1	
C	-5.3625440355	1.4595419182	1.8501557530	1	
C	-6.0927473135	2.5902546820	1.3527237127	1	
C	-6.0695008093	0.3417461249	2.4200215327	1	
C	-5.5482610284	-0.3305294394	3.5395443465	1	
C	-6.2439263290	-1.3787440998	4.1141104591	1	
C	-7.4513317113	-1.7954047614	3.5615012571	1	
C	-7.9718859373	-1.1527741843	2.4401201802	1	
C	-7.2970196858	-0.0839661340	1.8830936365	1	
C	-7.3428984860	2.9288346828	1.9036744612	1	
C	-8.0549113122	4.0099843933	1.4189300114	1	
C	-7.5405302869	4.7619998504	0.3665338713	1	
C	-6.3043816868	4.4412674878	-0.1923526761	1	
C	-5.5816091769	3.3729196304	0.2991050871	1	
H	-1.3211642432	-0.7159944391	1.4956158742	1	
H	-3.7935085798	-0.6797203535	1.5369377905	1	
H	-3.7116478603	3.5806202235	2.1892708338	1	
H	-1.2464960893	3.5359307315	2.1439970874	1	
H	-0.0478131357	1.3932863557	1.7893967164	1	
H	-4.6181894287	0.0131211195	3.9898747536	1	
H	-5.8472350442	-1.8717922786	5.0001189812	1	
H	-7.9924160197	-2.6292494588	4.0083684362	1	
H	-8.9070844926	-1.4938149074	1.9992134959	1	
H	-7.6902110036	0.3983350722	0.9900838110	1	
H	-7.7286224369	2.3643420640	2.7512956102	1	
H	-9.0116015170	4.2751731083	1.8656651029	1	
H	-8.1079542831	5.6073609322	-0.0222360131	1	
H	-5.9137128181	5.0237011363	-1.0251835753	1	
H	-4.6410325052	3.0910489429	-0.1703202298	1	
H	-7.2445619005	1.3243151789	-1.1987853622	2	
C	-6.4739713794	0.7248774005	-1.6831454940	2	
C	-6.6370103641	0.3234693453	-2.9980464252	2	
C	-5.6289850241	-0.4287103588	-3.5864077959	2	
C	-4.5049606532	-0.7403322144	-2.8345351788	2	
C	-4.4426083595	-0.2907588096	-1.5256377207	2	
N	-5.4052357289	0.4236420903	-0.9538820760	2	
H	-7.5347975215	0.5954482865	-3.5505167288	2	
H	-5.7180676013	-0.7659661078	-4.6190423240	2	
H	-3.6870813728	-1.3225359482	-3.2563063188	2	
H	-3.5713398304	-0.5140401999	-0.9126227352	2	
Electronic energy:					-980.39604475
Zero-point correction=					0.368981
Sum of electronic and zero-point Energies=					-980.027064
Sum of electronic and thermal Energies=					-980.006494
Sum of electronic and thermal Enthalpies=					-980.005550
Sum of electronic and thermal Free Energies=					-980.079155
Lowest frequency:					
A		6.9220			
Bond distances:					
r(C7		- N41 ) =		2.9896	
BSSE correction=					0.00288805
Electronic energy (NMR):					-980.73471424
15N shieldings:					
N 41		-83.7291			

<sup>13</sup>C shielding for carbenium C:  
C 7 -31.8067

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7c-alk  
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Number of atoms: 45  
Point group: C1

1	1		
C	-2.8982350315	2.0125339029	1.4443127921
C	-2.0287299640	0.9831453024	1.1267360878
C	-0.9158200846	1.2078841714	0.3101578608
C	-0.7248761123	2.4779942420	-0.2175141163
C	-1.6071573057	3.5119195114	0.0866602825
C	-2.6886452840	3.2865130831	0.9231443852
C	-0.0177714476	0.0229360417	-0.0467764310
C	1.0986834224	0.3855078423	-1.0288292902
C	-0.9437946337	-1.0918348976	-0.5331850532
C	-1.7500306992	-0.8069019282	-1.6375024259
C	-2.6544126167	-1.7386493206	-2.1185202234
C	-2.7873776496	-2.9736998359	-1.4900012497
C	-2.0157138073	-3.2523379831	-0.3741142887
C	-1.1023164623	-2.3145060870	0.1036498939
C	1.2087255033	-0.1787162511	-2.2917467897
C	2.2698040011	0.1596963137	-3.1282875744
C	3.2372872127	1.0578777968	-2.7060222625
C	3.1447915622	1.6150239807	-1.4337680691
C	2.0880788271	1.2758405527	-0.6051027445
H	-3.7523469744	1.8173594347	2.0917295468
H	-2.2212373424	-0.0158473397	1.5215312388
H	0.1047404554	2.6797325456	-0.8915857348
H	-1.4440103674	4.4989390142	-0.3448364857
H	-3.3779572792	4.0962383803	1.1610559545
H	-1.6786248443	0.1671487812	-2.1233599846
H	-3.2668484857	-1.4951913978	-2.9860827496
H	-3.5007270164	-3.7073694108	-1.8644156460
H	-2.1230897910	-4.2047195369	0.1440478078
H	-0.5425363013	-2.5686064415	1.0024365406
H	0.4768340909	-0.9031675894	-2.6430028144
H	2.3379585863	-0.2951339879	-4.1160087069
H	4.0683719763	1.3196697540	-3.3603797963
H	3.9022982437	2.3153000432	-1.0833672363
H	2.0377034369	1.7152858962	0.3925972348
H	1.7235247582	-1.8467375331	-0.0044822588
C	1.6380435317	-1.4656238922	1.0039803649
C	2.3932334970	-1.9557436289	2.0359012502
C	2.2507018156	-1.4001031516	3.3022528095
C	1.3487436949	-0.3644610533	3.4817074643
C	0.6109340615	0.0821897929	2.4097338435
N	0.7487639786	-0.4705685791	1.1969824302
H	3.0953566305	-2.7623617186	1.8438342065
H	2.8460353063	-1.7664894916	4.1364794811
H	1.2131056603	0.1121143917	4.4488755370
H	-0.0928017524	0.8964272809	2.4993939190

Electronic energy:	-980.41280995
Zero-point correction=	0.371688
Sum of electronic and zero-point Energies=	-980.041122
Sum of electronic and thermal Energies=	-980.021934
Sum of electronic and thermal Enthalpies=	-980.020990
Sum of electronic and thermal Free Energies=	-980.088694

Lowest frequency:  
A 37.1979

Bond distances:  
r(C7 - N41 ) = 1.5421

Electronic energy (NMR): -980.74753824

15N shieldings:  
N 41 7.3869  
13C shielding for carbenium C:  
C 7 89.5547

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TMS  
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Number of atoms: 17  
Point group: TD

O	1			
Si		-0.0000000002	0.0000000002	0.0000000014
C		0.0000000207	-0.0000000118	1.8773946911
C		1.7700246809	-0.0000000049	-0.6257982482
C		-0.8850123433	1.5328863539	-0.6257982089
C		-0.8850123590	-1.5328863364	-0.6257982284
H		-1.0256106801	-0.0000000091	2.2753185917
H		0.5128053823	0.8882049082	2.2753185803
H		0.5128053732	-0.8882049421	2.2753185689
H		2.3161260384	-0.8882049351	-0.2749620333
H		2.3161260475	0.8882049152	-0.2749620220
H		1.8033206742	0.0000000020	-1.7253945910
H		-0.3888549849	2.4499264609	-0.2749619819
H		-1.9272710473	1.5617215437	-0.2749619705
H		-0.9016603582	1.5617215477	-1.7253945510
H		-0.9016603742	-1.5617215160	-1.7253945709
H		-1.9272710633	-1.5617215200	-0.2749619904
H		-0.3888550100	-2.4499264530	-0.2749620132

Electronic energy: -449.01016447  
Zero-point correction= 0.145638  
Sum of electronic and zero-point Energies= -448.864526  
Sum of electronic and thermal Energies= -448.855110  
Sum of electronic and thermal Enthalpies= -448.854166  
Sum of electronic and thermal Free Energies= -448.894610

Lowest frequency:  
E 169.8292

Electronic energy (NMR): -449.21587417

13C shieldings:  
C 2 185.2669  
C 3 185.2669  
C 4 185.2669  
C 5 185.2669



**Data for visualizations.** Coordinates are given in Ångström, energies in Hartree.

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**[bis(pyridine)iodine]<sup>+</sup>**

N	-5.54290	2.38590	3.83190
C	-6.52400	3.21670	4.21380
C	-6.55310	3.76290	5.48500
C	-5.53850	3.43700	6.37810
C	-4.52620	2.57480	5.97200
C	-4.55960	2.06520	4.68580
H	-7.29160	3.43730	3.47530
H	-7.36050	4.43210	5.76440
H	-5.53680	3.85150	7.38230
H	-3.71720	2.29650	6.63970
H	-3.79390	1.38700	4.31570
N	-5.55010	0.63530	-0.40910
C	-4.56900	-0.19550	-0.79100
C	-4.53990	-0.74160	-2.06220
C	-5.55450	-0.41580	-2.95530
C	-6.56680	0.44640	-2.54920
C	-6.53340	0.95600	-1.26300
H	-3.80140	-0.41610	-0.05250
H	-3.73260	-1.41090	-2.34160
H	-5.55620	-0.83030	-3.95950
H	-7.37580	0.72470	-3.21690
H	-7.29910	1.63420	-0.89290
I	-5.54650	1.51060	1.71140

E (M06/LACVP\*\*) -507.346653  
E (M06/MIDI!//M06/LACVP\*\*) -7383.267438

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**[bis(pyridine)triphenylcarbenium]<sup>+</sup>**

C	-1.79040	0.32210	1.70310
C	-3.17410	0.31210	1.72150
C	-3.89940	1.51180	1.86580
C	-3.18370	2.71800	2.00320
C	-1.79980	2.72000	2.00300
C	-1.10140	1.52420	1.84800
C	-5.34420	1.49960	1.86500
C	-6.08610	2.64150	1.37820
C	-6.05550	0.33450	2.34860
C	-5.54880	-0.42120	3.42560
C	-6.24000	-1.52380	3.89610
C	-7.43550	-1.90690	3.29120
C	-7.94600	-1.17880	2.21920
C	-7.27080	-0.06250	1.75740
C	-7.34520	2.96630	1.92300
C	-8.05140	4.06140	1.45660
C	-7.52760	4.84130	0.42780
C	-6.29060	4.52870	-0.13300
C	-5.57240	3.44460	0.33890
H	-1.24380	-0.60760	1.57110
H	-3.71310	-0.62050	1.57610
H	-3.72950	3.64490	2.15900
H	-1.25960	3.65420	2.12950
H	-0.01440	1.52920	1.84080

H	-4.64830	-0.08220	3.93000
H	-5.85410	-2.08220	4.74430
H	-7.97400	-2.77660	3.65950
H	-8.87030	-1.48870	1.73970
H	-7.65040	0.48390	0.89870
H	-7.73810	2.38080	2.74940
H	-9.01020	4.31610	1.89930
H	-8.08870	5.69590	0.05770
H	-5.89510	5.12520	-0.95030
H	-4.64080	3.15670	-0.13950
H	-7.05690	1.62320	-1.26880
C	-6.38960	0.85800	-1.67590
C	-6.67270	0.26450	-2.89940
C	-5.78970	-0.69060	-3.38860
C	-4.66360	-1.00520	-2.63890
C	-4.47450	-0.35370	-1.42590
N	-5.31680	0.55920	-0.93910
H	-7.10640	1.53790	4.94090
C	-6.41240	2.27970	5.34570
N	-5.29960	2.49290	4.63950
C	-4.42290	3.37170	5.12810
C	-4.61660	4.07450	6.31130
C	-5.78550	3.85160	7.02740
C	-6.70410	2.93110	6.53730
H	-7.56260	0.54760	-3.45430
H	-5.97490	-1.17960	-4.34160
H	-3.94260	-1.74030	-2.98440
H	-3.59490	-0.57250	-0.81650
H	-3.51080	3.51910	4.54530
H	-3.86620	4.77820	6.65980
H	-5.97630	4.38390	7.95570
H	-7.62810	2.71860	7.06730

E (M06/LACVP\*\*) -1228.470740

E (M06/MIDI!//M06/LACVP\*\*) -1221.870933

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