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Supporting Information

Azaindolo[3,2,1-*jk*]carbazoles: New Building Blocks for Functional Organic Materials

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1 General information

Column chromatography was performed on silica 60 (Merck, 40-63 μm). For preparative HPLC a Buchi Reveleris Prep Purification System with a Phenomenex Luna Prep silica (2) column (10 μm) was used. NMR spectra were recorded on a Bruker Avance DRX-400 Spectrometer. An Agilent 6230 LC TOFMS mass spectrometer equipped with an Agilent Dual AJS ESI-Source was used for high resolution mass spectrometry.

2 Experimental procedures

9*H*-Pyrido[2,3-*b*]indole,[1] 9*H*-pyrido[3,4-*b*]indole,[2] 5*H*-pyrido[4,3-*b*]indole,[3] 5*H*-pyrido[3,2-*b*]indole,[4] 2,2'-diiodo-1,1'-biphenyl[5] and allyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloropalladium(II) ((NHC)Pd(allyl)Cl)[6] were synthesized according to literature.

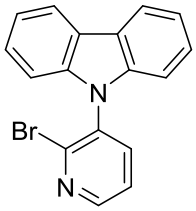
2.1 Synthesis of the precursors

General procedure for the nucleophilic aromatic substitution reactions towards carbazole precursors (GP1-A). Carbazole (1 eq.) and Cs_2CO_3 (1.1 eq.) were placed in a glass vial and flushed with argon. DMF (2 ml/mmol) and the corresponding pyridine (1 eq.) were added and the reaction was stirred at 130 °C until full conversion (16 h – 20 h). After cooling, the reaction mixture was poured into water and repeatedly extracted with CH_2Cl_2. The organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.

General procedure for the condensation reactions (GP2). 2,5-Dimethoxytetrahydrofuran (4 eq.) was added to a solution of the corresponding brominated aminopyridine (1 eq.) in acetic acid (15 ml/mmol). The reaction mixture was refluxed under argon atmosphere until full conversion according to GC-MS (18 h - 120 h). Depending on the progress of the reaction further 2,5-dimethoxytetrahydrofuran was added. After cooling, the reaction mixture was

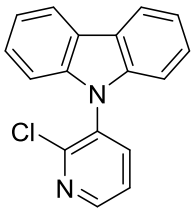
poured into cold 1N HCl and repeatedly extracted with CH_2Cl_2. The combined organic layers were washed with water and 2N NaOH, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

General procedure for the Nozaki type Buchwald Hartwig amination (GP3). NaO^tBu (6 eq.) was added to a solution of the corresponding brominated aminopyridine (1 eq.), 2,2′-diiodo-1,1′-biphenyl (1 eq.), $Pd_2(dba)_3$ (2 mol%) and 1,1′-bis(diphenylphosphino)ferrocene (4 mol%) in degassed anhydrous toluene (4 ml/mmol) under argon atmosphere in a three-necked flask. The reaction mixture was refluxed overnight. After cooling, the reaction mixture was filtered through a celite pad and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and purified by column chromatography.



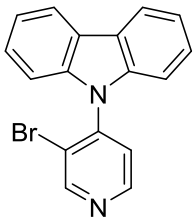
bromo-**4PCz**

*9-(2-Bromopyridin-3-yl)-9H-carbazole (bromo-**4PCz**).* Compound bromo-**4PCz** was prepared according to GP2 starting from 3-amino-2-bromopyridine (1.73 g, 10.0 mmol) and 2,5-dimethoxytetrahydrofuran (5.29 g, 40.0 mmol). The crude product was flashed over a silica pad (CH_2Cl_2). Recrystallization from EtOH gave bromo-**4PCz** (1.69 g, 5.23 mmol, 52%) as orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 4.7, 1.8 Hz, 1H), 8.17 (d, J = 7.8 Hz, 2H), 7.83 (dd, J = 7.7, 1.8 Hz, 1H), 7.53 (dd, J = 7.7, 4.7 Hz, 1H), 7.43 (t, J = 8.2 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 143.9, 140.7, 139.6, 134.8, 126.3, 123.9, 123.8, 120.7, 120.7, 109.9. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0187.



chloro-**4PCz**

*9-(2-Chloropyridin-3-yl)-9H-carbazole (chloro-**4PCz**).* Compound chloro-**4PCz** was prepared according to GP1-A starting from carbazole (502 mg, 3.00 mmol) and 2-chloro-3-fluoropyridine (399 mg, 3.03 mmol) with Cs_2CO_3 (1.08 g, 3.30 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 40% - 60%) gave chloro-**4PCz** (580 mg, 2.08 mmol, 69%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, J = 4.8, 1.8 Hz, 1H), 8.17 (d, J = 7.7 Hz, 2H), 7.89 (dd, J = 7.7, 1.8 Hz, 1H), 7.50 (dd, J = 7.7, 4.8 Hz, 1H), 7.44 (t, J = 8.3 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 149.6, 140.6, 139.7, 132.4, 126.3, 123.8, 123.6, 120.7, 120.6, 109.9. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2^+$ $[M+H]^+$ 279.0684, found 279.0697.

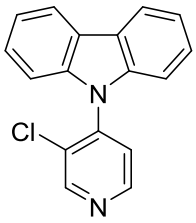


bromo-**5PCz**

*9-(3-Bromopyridin-4-yl)-9H-carbazole (bromo-**5PCz**).* Compound bromo-**5PCz** was prepared according to GP1-A starting from carbazole (502 mg, 3.00 mmol) and 3-bromo-4-chloropyridine (579 mg, 3.01 mmol) with Cs_2CO_3 (1.08 g, 3.30 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 40% - 75%) gave bromo-**5PCz** (669 mg, 2.07 mmol, 69%) as off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.75 (d, J = 5.1 Hz, 1H), 8.16 (d, J = 7.4 Hz, 2H), 7.48 (d, J = 5.1 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 149.9, 145.0, 139.8, 126.4, 125.3, 124.0, 121.0, 121.0, 120.7, 110.3. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0179.

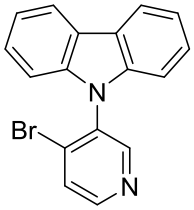
Compound bromo-**5PCz** was prepared according to GP2 starting from 4-amino-3-bromopyridine (2.60 g, 15.0 mmol) and 2,5-dimethoxytetrahydrofuran (7.93 g, 60.0 mmol). During the reaction additional 2,5-dimethoxytetrahydrofuran (11.89 g, 90.0 mmol) was added stepwise and the reaction was refluxed for 120 h. Purification by column chromatography (light petroleum/CH_2Cl_2 40% - 60%) and recrystallization from EtOH gave bromo-**5PCz** (1.53 g, 4.73 mmol, 32%) as white crystals. ^{1}H NMR according to the preparation following GP1-A.

Compound bromo-**5PCz** was prepared according to GP3 starting from 4-amino-3-bromopyridine (865 mg, 5.00 mmol) and 2,2′-dibromo-1,1′-biphenyl (2.03 g, 5.00 mmol) with NaO^tBu (2.88 g, 30.00 mmol), $Pd_2(dba)_3$ (92 mg, 0.10 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (111 mg, 0.20 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 1:1) gave bromo-**5PCz** (1.32 g, 4.08 mmol, 81%) as white solid. ^{1}H NMR according to the preparation following GP1-A.



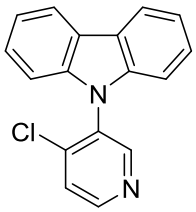
chloro-**5PCz**

*9-(3-Chloropyridin-4-yl)-9H-carbazole (chloro-**5PCz**).* Compound chloro-**5PCz** was prepared according to GP1-A starting from carbazole (502 mg, 3.00 mmol) and 3-chloro-4-fluoropyridine (395 mg, 3.00 mmol) with Cs_2CO_3 (1.08 g, 3.30 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 50% - 60%) gave chloro-**5PCz** (795 mg, 2.85 mmol, 95%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.72 (d, J = 5.1 Hz, 1H), 8.16 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 5.1 Hz, 1H), 7.44 (t, J = 8.3 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 149.4, 143.1, 139.8, 130.4, 126.4, 124.6, 124.1, 121.1, 120.7, 110.3. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2^+$ $[M+H]^+$ 279.0684, found 279.0687.



bromo-**6PCz**

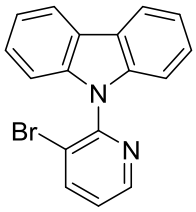
*9-(4-Bromopyridin-3-yl)-9H-carbazole (bromo-**6PCz**).* Compound bromo-**6PCz** was prepared according to GP3 starting from 3-amino-4-bromopyridine (87 mg, 0.50 mmol) and 2,2′-diiodo-1,1′-biphenyl (203 mg, 0.50 mmol) with NaO^tBu (288 mg, 3.00 mmol), $Pd_2(dba)_3$ (9 mg, 0.01 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (11 mg, 0.02 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 50%) gave bromo-**6PCz** (108 mg, 0.33 mmol, 67%) as brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.61 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 5.0 Hz, 1H), 7.43 (t, J = 8.3 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 150.3, 140.8, 134.4, 134.4, 129.1, 126.4, 123.7, 120.7, 120.7, 109.9. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0181.



chloro-**6PCz**

*9-(4-Chloropyridin-3-yl)-9H-carbazole (chloro-**6PCz**).* Compound chloro-**6PCz** was prepared according to GP1-A starting from carbazole (502 mg, 3.00 mmol) and 4-chloro-3-fluoropyridine (397 mg, 3.02 mmol) with Cs_2CO_3 (1.08 g, 3.30 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 50%) gave chloro-**6PCz** (476 mg, 1.71 mmol, 57%) as colorless oil, which crystallized after several weeks. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.70 (d, J = 5.3 Hz, 1H), 8.17 (d, J = 7.7 Hz, 2H), 7.66 (d, J = 5.3 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 152.0, 150.4, 143.7, 140.8, 132.5, 126.4, 125.8, 123.8, 120.8, 120.7, 109.8. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2^+$ $[M+H]^+$ 279.0684, found 279.0687.



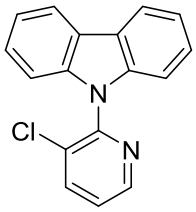
bromo-**7PCz**

*9-(3-Bromopyridin-2-yl)-9H-carbazole (bromo-**7PCz**).* Compound bromo-**7PCz** was prepared according to GP1-A starting from carbazole (836 mg, 5.00 mmol) and 3-bromo-2-chloropyridine (968 mg, 5.03 mmol) with Cs_2CO_3 (1.79 g, 5.50 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 40%) gave bromo-**7PCz** (593 mg, 1.83 mmol, 37%) as colorless oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.69 (dd, J = 4.6, 1.6 Hz, 1H), 8.24 (dd, J = 8.0, 1.6 Hz, 1H), 8.16 (d, J = 7.4 Hz, 2H), 7.43 (ddd, J = 8.3, 7.3, 1.2 Hz, 2H), 7.39 (dd, J = 8.0, 4.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.9, 149.4, 143.9, 140.5, 126.5, 125.4, 124.2, 121.1, 120.9, 119.9, 111.3. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0178.

Compound bromo-**7PCz** was prepared according to GP2 starting from 2-amino-3-bromopyridine (1.73 g, 10.0 mmol) and 2,5-dimethoxytetrahydrofuran (5.29 g, 40.0 mmol). During the reaction additional 2,5-dimethoxytetrahydrofuran (7.93 g, 60.0 mmol) was added and the reaction was stopped after refluxing for 68 h. Purification by column chromatography (light petroleum/CH_2Cl_2 40% - 60%) gave bromo-**7PCz** (1.25 g, 3.87 mmol, 39%; including minor impurities) as brown oil. ^{1}H NMR according to the preparation following GP1-A.

Compound bromo-**7PCz** was prepared according to GP3 starting from 2-amino-3-bromopyridine (554 mg, 3.20 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.30 g, 3.20 mmol) with NaO^tBu (1.83 g, 19.0 mmol), $Pd_2(dba)_3$ (59 mg, 0.06 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (71 mg, 0.12 mmol). Purification by column

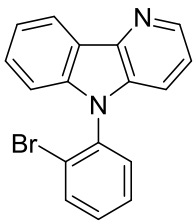
chromatography (light petroleum/CH_2Cl_2 40% - 60%) gave bromo-**7PCz** (37 mg, 0.11 mmol, 4%) as colorless oil. ^{1}H NMR according to the preparation following GP1-A.



chloro-**7PCz**

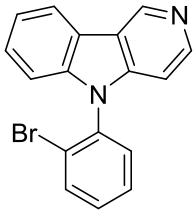
*9-(3-Chloropyridin-2-yl)-9H-carbazole (chloro-**7PCz**).* Compound chloro-**7PCz** was prepared according to GP1-A starting from carbazole (836 mg, 5.00 mmol) and 3-chloro-2-fluoropyridine (660 mg, 5.02 mmol) with Cs_2CO_3 (1.79 g, 5.50 mmol). Purification by column chromatography (light petroleum/CH_2Cl_2 40%) gave chloro-**7PCz** (1.31 g, 4.70 mmol, 94%) as colorless oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (dd, J = 4.6, 1.5 Hz, 1H), 8.17 (d, J = 7.7 Hz, 2H), 8.06 (dd, J = 8.1, 1.5 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.7, 148.6, 140.6, 140.5, 130.0, 126.5, 125.1, 124.3, 121.2, 120.8, 111.4. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2^+$ $[M+H]^+$ 279.0684, found 279.0686.

General procedure for the nucleophilic aromatic substitution reactions towards carboline precursors (GP1-B). The corresponding carboline (1 eq.) and Cs_2CO_3 (2 eq.) were placed in a glass vial and flushed with argon. DMF (2 ml/mmol) and 1-bromo-2-fluorobenzene (2 eq.) were added and the reaction was stirred at 130 °C for 16 h. After cooling, the reaction mixture was poured into water and repeatedly extracted with CH_2Cl_2. The organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.



4PCb

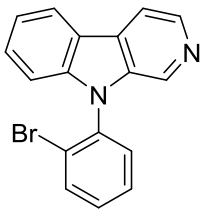
*5-(2-Bromophenyl)-5H-pyrido[3,2-b]indole (**4PCb**).* Compound **4PCb** was prepared according to GP1-B starting from 5*H*-pyrido[3,2-*b*]indole (841 mg, 5.00 mmol) and 1-bromo-2-fluorobenzene (1.75 g, 10.0 mmol) with Cs_2CO_3 (3.26 g, 10.0 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 0% - 1%) gave **4PCb** (1.39 g, 4.30 mmol, 86%) as light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.6 Hz, 1H), 8.47 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.58 – 7.35 (m, 6H), 7.32 (dd, J = 8.2, 4.7 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.2, 141.8, 136.0, 134.5, 134.5, 131.0, 130.7, 129.1, 128.2, 123.7, 122.4, 121.1, 121.1, 120.3, 117.4, 110.4. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0179.



5PCb

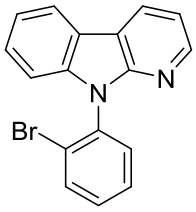
*5-(2-Bromophenyl)-5H-pyrido[4,3-b]indole (**5PCb**).* Compound **5PCb** was prepared according to GP1-B starting from 5*H*-pyrido[4,3-*b*]indole (842 mg, 5.01 mmol) and 1-bromo-2-fluorobenzene (1.75 g, 10.0 mmol) with Cs_2CO_3 (3.26 g, 10.0 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 3%) gave **5PCb** (1.33 g, 4.11 mmol, 82%) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.51 (d, J = 5.8 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 8.4, 1.4 Hz, 1H), 7.56 (ddd, J = 8.0, 7.1, 1.5 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.39 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.00 (dd, J = 5.8, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 145.1, 142.7, 141.0, 135.5, 134.5, 131.0, 130.8, 129.1,

127.3, 123.5, 121.7, 121.6, 120.9, 120.2, 110.6, 105.6. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0179.



6PCb

*9-(2-Bromophenyl)-9H-pyrido[3,4-b]indole (**6PCb**).* Compound **6PCb** was prepared according to GP1-B starting from 9*H*-pyrido[3,4-*b*]indole (505 mg, 3.00 mmol) and 1-bromo-2-fluorobenzene (1.05 g, 6.00 mmol) with Cs_2CO_3 (1.96 g, 6.00 mmol). Purification by column chromatography (CH_2Cl_2/Et_2O 1% - 3%) gave **6PCb** (894 mg, 2.77 mmol, 92%) as orange oil which crystallized after several days. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.52 (m, 2H), 8.21 (d, J = 7.9 Hz, 1H), 8.03 (dd, J = 5.3, 1.0 Hz, 1H), 7.88 (dd, J = 8.0, 1.3 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.46 (ddd, J = 8.0, 7.2, 1.9 Hz, 1H), 7.36 (ddd, J = 8.0, 7.2, 0.9 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.2, 137.0, 135.9, 134.6, 133.5, 130.9, 130.8, 129.1, 129.0, 128.8, 123.6, 122.0, 121.6, 120.8, 114.7, 110.9. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0182.

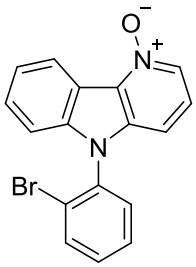


7PCb

*9-(2-Bromophenyl)-9H-pyrido[2,3-b]indole (**7PCb**).* Compound **7PCb** was prepared according to GP1-B starting from 9*H*-pyrido[2,3-*b*]indole (506 mg, 3.01 mmol) and 1-bromo-2-fluorobenzene (1.05 g, 6.00 mmol) with Cs_2CO_3 (1.96 g, 6.00 mmol). After 16 h additional 1-bromo-2-fluorobenzene (1.05 g, 6.00 mmol) was added and the reaction was stopped after 48 h. Purification by column chromatography (light petroleum/CH_2Cl_2 80% - 100%) gave **7PCb** (331 mg, 1.02 mmol, 34%) as colorless oil which crystallized after several days. ^{1}H

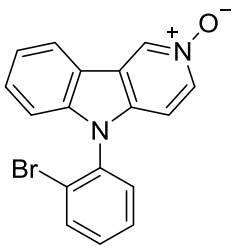
NMR (400 MHz, CD_2Cl_2) δ 8.46 – 8.41 (m, 2H), 8.17 (d, J = 8.1 Hz, 1H), 7.88 (dd, J = 8.1, 1.1 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.51 – 7.44 (m, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.26 (dd, J = 7.3, 5.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 152.7, 147.1, 140.6, 136.3, 134.5, 132.1, 131.0, 129.3, 128.9, 127.5, 124.5, 121.6, 121.3, 121.3, 116.7, 116.7, 111.0. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2^+$ $[M+H]^+$ 323.0178, found 323.0178.

General procedure for the N-oxide preparation (GP4). The corresponding PCb (1 eq.) was dissolved in CH_2Cl_2 (2 ml/mmol) and cooled to 0 °C. mCPBA (4 eq.) was added portionwise and the reaction was slowly warmed to room temperature and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with 2N NaOH. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.



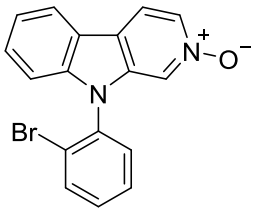
4PCb-Ox

*5-(2-Bromophenyl)-5H-pyrido[3,2-b]indole 1-oxide (**4PCb-Ox**).* Compound **4PCb-Ox** was prepared according to GP4 starting from **4PCb** (729 mg, 2.26 mmol) with mCPBA (1.55 g, 8.98 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 2%) gave **4PCb-Ox** (663 mg, 1.95 mmol, 87%) as light brown solid. ^1H NMR (400 MHz, CD_2Cl_2) δ 8.88 (d, J = 7.9 Hz, 1H), 8.19 (d, J = 6.3 Hz, 1H), 7.90 (dd, J = 8.0, 1.1 Hz, 1H), 7.63 – 7.48 (m, 4H), 7.41 (t, J = 8.0 Hz, 1H), 7.24 (dd, J = 8.3, 6.4 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 140.9, 138.2, 135.5, 135.0, 132.6, 131.8, 131.7, 131.5, 129.8, 129.1, 124.0, 123.9, 122.0, 121.8, 118.1, 110.3, 108.0. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2O^+$ $[M+H]^+$ 339.0128, found 339.0129.



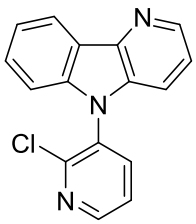
5PCb-Ox

*5-(2-Bromophenyl)-5H-pyrido[4,3-b]indole 2-oxide (**5PCb-Ox**).* Compound **5PCb-Ox** was prepared according to GP4 starting from **5PCb** (802 mg, 2.48 mmol) with mCPBA (1.71 g, 9.91 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 4%) gave **5PCb-Ox** (512 mg, 1.51 mmol, 61%) as light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.23 (dd, J = 7.0, 1.3 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 6.94 (d, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.7, 136.9, 134.8, 134.7, 132.1, 131.4, 130.7, 129.3, 128.7, 123.2, 122.1, 121.4, 121.3, 119.9, 111.1, 107.3. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2O^+$ $[M+H]^+$ 339.0128, found 339.0132.



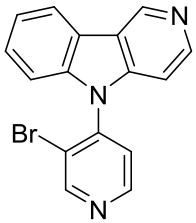
6PCb-Ox

*9-(2-Bromophenyl)-9H-pyrido[3,4-b]indole 2-oxide (**6PCb-Ox**).* Compound **6PCb-Ox** was prepared according to GP4 starting from **6PCb** (488 mg, 1.51 mmol) with mCPBA (1.04 g, 6.03 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 3%) gave **6PCb-Ox** (463 mg, 1.37 mmol, 90%) as light brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 6.7, 1.5 Hz, 1H), 8.14 (d, J = 0.9 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 6.7 Hz, 1H), 7.86 (dd, J = 7.5, 2.3 Hz, 1H), 7.56 (ddd, J = 8.1, 7.1, 1.7 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.36 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.2, 134.7, 134.7, 132.5, 131.5, 130.7, 129.3, 128.4, 123.7, 123.3, 121.9, 121.5, 121.3, 121.2, 116.5, 111.0. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2O^+$ $[M+H]^+$ 339.0128, found 339.0130.



4,12PyCb

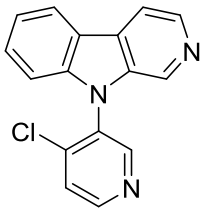
*5-(2-Chloropyridin-3-yl)-5H-pyrido[3,2-b]indole (**4,12PyCb**).* Sodium hydride (144 mg, 6.00 mmol, 2 eq.) was added in portions to a stirred solution of 5*H*-pyrido[3,2-*b*]indole (505 mg, 3.00 mmol, 1 eq.) in 6 ml DMF under argon atmosphere. The solution was heated to 40 °C and stirred for 1 h. 2-Chloro-3-fluoropyridine (592 mg, 4.50 mmol, 1.5 eq.) was added and the reaction was stirred at 50 °C for 16 h. After cooling, the reaction mixture was quenched with water and repeatedly extracted with CH_2Cl_2. The organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography (CH_2Cl_2/MeOH 1%) gave **4,12PyCb** (749 mg, 2.68 mmol, 89%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.60 (m, 2H), 8.46 (d, J = 7.7 Hz, 1H), 7.90 (dd, J = 7.8, 1.8 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.45 – 7.37 (m, 2H), 7.34 (dd, J = 8.3, 4.6 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 150.0, 143.2, 142.7, 141.4, 139.5, 134.1, 131.5, 128.4, 123.7, 122.9, 121.7, 121.2, 120.5, 117.1, 110.1. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClN_3^+$ $[M+H]^+$ 280.0636, found 280.0637.



5,11PyCb

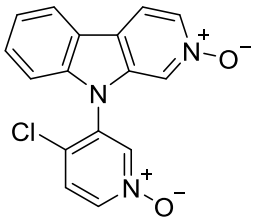
*5-(3-Bromopyridin-4-yl)-5H-pyrido[4,3-b]indole (**5,11PyCb**).* Compound **5,11PyCb** was prepared according to GP1-A starting from 5*H*-pyrido[4,3-*b*]indole (336 mg, 2.00 mmol) and 3-bromo-4-chloropyridine (385 mg, 2.00 mmol) with Cs_2CO_3 (717 mg, 2.20 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 3%) gave **5,11PyCb** (246 mg, 0.76 mmol, 38%) as red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 9.08 (s, 1H), 8.79

(d, J = 5.1 Hz, 1H), 8.55 (d, J = 5.7 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.03 (dd, J = 5.7, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.3, 145.8, 144.1, 143.6, 143.3, 139.8, 127.5, 124.9, 122.4, 122.1, 121.1, 120.7, 120.6, 110.6, 105.6. HRMS (ESI): m/z calcd for $C_{16}H_{11}BrN_3^+$ $[M+H]^+$ 324.0131, found 324.0132.



6,10PyCb

*9-(4-Chloropyridin-3-yl)-9H-pyrido[3,4-b]indole (**6,10PyCb**).* Compound **6,10PyCb** was prepared according to GP1-A starting from 9*H*-pyrido[3,4-*b*]indole (288 mg, 1.71 mmol) and 4-chloro-3-fluoropyridine hydrochloride (287 mg, 1.71 mmol) with Cs_2CO_3 (1.11 g, 3.42 mmol). Purification by column chromatography (CH_2Cl_2/MeOH 1% - 2%) gave **6,10PyCb** (231 mg, 0.83 mmol, 49%) as light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.73 (d, J = 5.3 Hz, 1H), 8.57 (d, J = 5.3 Hz, 1H), 8.54 (d, J = 0.8 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.03 (dd, J = 5.3, 1.0 Hz, 1H), 7.68 (d, J = 5.3 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 151.0, 143.4, 141.6, 140.8, 136.9, 133.0, 131.6, 129.6, 129.1, 125.9, 122.1, 122.0, 121.5, 114.9, 110.5. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClN_3^+$ $[M+H]^+$ 280.0636, found 280.0638.



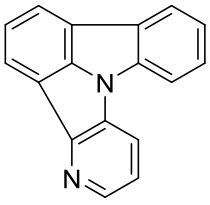
6,10PyCb-Ox

*9-(4-Chloro-1-oxidopyridin-3-yl)-9H-pyrido[3,4-b]indole 2-oxide (**6,10PyCb-Ox**).* Compound **6,10PyCb-Ox** was prepared according to GP4 with double amount of oxidant starting from **6,10PyCb** (356 mg, 1.27 mmol) with mCPBA (1.73 g, 10.02 mmol). After 20 h

additional mCPBA (431 mg, 2.50 mmol) was added and the reaction was stirred overnight again. After standard work up purification by column chromatography (CH_2Cl_2/MeOH 5% - 10%) gave **6,10PyCb-Ox** (202 mg, 0.65 mmol, 51%) as light brown solid. ^{1}H NMR (400 MHz, DMSO) δ 8.84 (d, J = 2.0 Hz, 1H), 8.66 (d, J = 0.9 Hz, 1H), 8.47 (dd, J = 7.1, 2.1 Hz, 1H), 8.26 (dd, J = 9.2, 7.4 Hz, 2H), 8.17 (dd, J = 6.7, 1.5 Hz, 1H), 7.89 (d, J = 7.1 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 141.7, 141.3, 141.1, 138.0, 132.8, 132.2, 129.4, 128.1, 127.8, 123.4, 122.0, 121.5, 121.3, 119.9, 117.2, 110.7. HRMS (ESI): m/z calcd for $C_{16}H_{11}ClN_3O_2^+$ $[M+H]^+$ 312.0534, found 312.0538.

2.2 Synthesis of mono substituted NICzs

General procedure for the ring closing C-H activation reactions (GP5). A glass vial was charged with the corresponding halogenated precursor (1 eq.), K_2CO_3 (2 eq.) and (NHC)Pd(allyl)Cl (5 mol%) and flushed with argon. After addition of 10 ml/mmol degassed DMA, the reaction was stirred under argon atmosphere until full conversion at 130 °C (4 h – 8 h). After cooling, the reaction mixture was poured into water and repeatedly extracted with CH_2Cl_2. The organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.

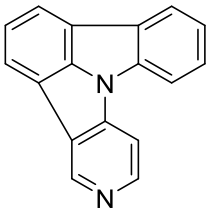


4NICz

*Pyrido[2',3':4,5]pyrrolo[3,2,1-jk]carbazole (**4NICz**).* Compound **4NICz** was prepared according to GP5 starting from bromo-**4PCz** (323 mg, 1.00 mmol) with K_2CO_3 (278 mg, 2.01 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 0% - 2%) gave **4NICz** (224 mg, 0.93 mmol, 93%) as off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 4.9, 1.2 Hz, 1H), 8.28 (d, J = 7.5 Hz,

1H), 8.14 – 8.06 (m, 3H), 7.80 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 8.2 Hz, 1H), 7.41 (dd, J = 8.3, 4.9 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 144.0, 143.1, 138.8, 133.1, 129.7, 127.2, 123.8, 123.4, 122.5, 121.3, 120.5, 120.4, 119.2, 118.7, 117.6, 112.3. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0921.

Compound **4NICz** was prepared according to GP5 starting from chloro-**4PCz** (279 mg, 1.00 mmol) with K_2CO_3 (279 mg, 2.02 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 0% - 2%) gave **4NICz** (238 mg, 0.98 mmol, 98%) as off-white solid. ^{1}H NMR according to the preparation starting from bromo-**4PCz**.

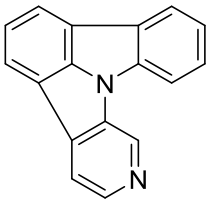


5NICz

Pyrido[3',4':4,5]pyrrolo[3,2,1-jk]carbazole ***(5NICz)***. Compound **5NICz** was prepared according to GP5 starting from bromo-**5PCz** (324 mg, 1.00 mmol) with K_2CO_3 (277 mg, 2.00 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 1%) gave **5NICz** (233 mg, 0.96 mmol, 96%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.65 (d, J = 5.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.95 (t, J = 7.9 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 5.6 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.36 (t, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 144.7, 143.6, 142.4, 138.2, 130.7, 127.2, 126.1, 124.1, 123.4, 123.0, 120.3, 120.0, 118.8, 116.2, 112.8, 107.5. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0922.

Compound **5NICz** was prepared according to GP5 starting from chloro-**5PCz** (280 mg, 1.00 mmol) with K_2CO_3 (282 mg, 2.04 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml

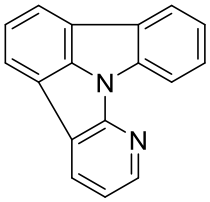
DMA. Purification by column chromatography (CH_2Cl_2/MeOH 1%) gave **5NICz** (235 mg, 0.97 mmol, 97%) as white solid. ^{1}H NMR according to the preparation starting from bromo-**5PCz**.



6NICz

*Pyrido[4',3':4,5]pyrrolo[3,2,1-jk]carbazole (**6NICz**).* Compound **6NICz** was prepared according to GP5 starting from bromo-**6PCz** (129 mg, 0.40 mmol) with K_2CO_3 (2 eq., 112 mg, 0.81 mmol) and (NHC)Pd(allyl)Cl (5 mol%, 11 mg, 0.02 mmol) in 4 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 1%) gave **6NICz** (77 mg, 0.32 mmol, 80%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, J = 0.9 Hz, 1H), 8.57 (d, J = 5.2 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.99 (d, J = 7.5 Hz, 1H), 7.93 (dd, J = 5.2, 1.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.35 (td, J = 7.7, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.3, 138.4, 135.9, 134.8, 134.3, 129.9, 127.4, 123.5, 123.4, 122.5, 121.8, 120.8, 119.4, 117.6, 116.3, 112.6. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0920.

Compound **6NICz** was prepared according to GP5 starting from chloro-**6PCz** (281 mg, 1.01 mmol) with K_2CO_3 (281 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 1%) gave **6NICz** (225 mg, 0.93 mmol, 92%) as yellow solid. ^{1}H NMR according to the preparation starting from bromo-**6PCz**.

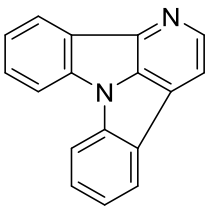


7NICz

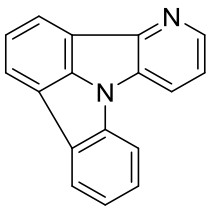
Pyrido[3',2':4,5]pyrrolo[3,2,1-jk]carbazole (7NICz). Compound **7NICz** was prepared according to GP5 starting from bromo-**7PCz** (326 mg, 1.01 mmol) with K_2CO_3 (282 mg, 2.04 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (light petroleum/CH_2Cl_2 60%) gave **7NICz** (205 mg, 0.85 mmol, 84%) as white solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.52 (dd, J = 5.0, 1.6 Hz, 1H), 8.37 (dd, J = 7.7, 1.6 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.4 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.41 (td, J = 7.7, 1.0 Hz, 1H), 7.28 (dd, J = 7.7, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.4, 146.5, 143.3, 138.6, 131.2, 130.6, 127.7, 124.0, 123.9, 123.5, 123.2, 120.8, 120.5, 119.5, 117.7, 116.5, 114.3. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0921.

Compound **7NICz** was prepared according to GP5 starting from chloro-**7PCz** (281 mg, 1.01 mmol) with K_2CO_3 (280 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (light petroleum/CH_2Cl_2 60%) gave **7NICz** (235 mg, 0.97 mmol, 96%) as white solid. ^{1}H NMR according to the preparation starting from bromo-**7PCz**.

General procedure for the reduction of the N-oxides (GP6). The mixture of the N-oxide isomers (1 eq.) and iron powder (2 eq.) were dissolved in AcOH (22 ml/mmol) and stirred at 60°C under argon atmosphere for 2 hours. After cooling, the reaction mixture was poured into cold 2N NaOH and repeatedly extracted with CH_2Cl_2. The organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography.



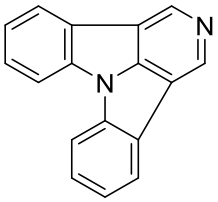
1NICz



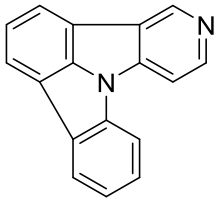
4NICz

Dibenzo[b,e]pyrido[2,3,4-gh]pyrrolizine ***(1NICz)*** and *pyrido[2',3':4,5]pyrrolo[3,2,1-jk]carbazole* ***(4NICz)***. Compounds **1NICz** and **4NICz** were prepared according to GP5 starting from **4PCb** (323 mg, 1.00 mmol) with K_2CO_3 (280 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by repeated column chromatography (CH_2Cl_2/Et_2O 1%) gave pure **1NICz** (108 mg, 0.45 mmol, 45%) and **4NICz** (37 mg, 0.15 mmol, 15%) as off-white solids. Additional mixed fractions included dehalogenated side product which could not be separated. **1NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 5.1 Hz, 1H), 8.32 (d, J = 7.5 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.80 – 7.76 (m, 3H), 7.61 – 7.55 (m, 2H), 7.38 (t, J = 8.1 Hz, 1H), 7.32 (t, J = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.4, 140.2, 140.2, 138.4, 129.6, 129.3, 129.2, 128.7, 124.9, 124.6, 123.0, 122.8, 122.4, 113.9, 112.9, 112.7. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0919. ^{1}H NMR of **4NICz** according to the preparation starting from bromo-**4PCz**.

Compounds **1NICz** and **4NICz** were prepared according to GP5 starting from **4PCb-Ox** (339 mg, 1.00 mmol) with K_2CO_3 (281 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. The crude product was flashed over silica to give a mixture of the formed N-oxide isomers (238 mg, 0.92 mmol, 92%). The N-oxides were then reduced according to GP6 with iron-powder (101 mg, 1.81 mmol) in 20 ml AcOH. Purification by repeated column chromatography (CH_2Cl_2/Et_2O 1%) gave pure **1NICz** (141 mg, 0.58 mmol, 58%) and **4NICz** (8 mg, 0.03 mmol, 3%) as off-white solids. According to ^{1}H-NMR the formed isomeric NICz mixture (167 mg, 0.69 mmol) contained **1NICz** (0.61 mmol) and **4NICz** (0.07 mmol). ^{1}H NMR according to the preparation starting from **4PCb** and bromo-**4PCz**, respectively.



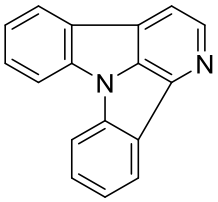
2NICz



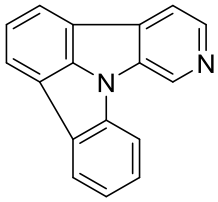
5NICz

*Dibenzo[b,e]pyrido[3,4,5-gh]pyrrolizine (**2NICz**)* and *pyrido[3',4':4,5]pyrrolo[3,2,1-jk]carbazole (**5NICz**).* Compounds **2NICz** and **5NICz** were prepared according to GP5 starting from **5PCb** (322 mg, 1.00 mmol) with K_2CO_3 (279 mg, 2.02 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by repeated column chromatography (CH_2Cl_2/MeOH 1% - 2%) gave pure **2NICz** (111 mg, 0.46 mmol, 46%) as off-white solid. According to ^{1}H-NMR the formed isomeric NICz mixture (211 mg, 0.87 mmol) contained **2NICz** (0.76 mmol) and **5NICz** (0.11 mmol). **2NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 2H), 8.09 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 139.0, 138.8, 128.2, 127.8, 124.0, 122.9, 115.9, 112.6. HRMS (ESI): m/z calcd for $C_{17}H_{11}N_2^+$ $[M+H]^+$ 243.0917, found 243.0920.

Compounds **2NICz** and **5NICz** were prepared according to GP5 starting from **5PCb-Ox** (339 mg, 1.00 mmol) with K_2CO_3 (277 mg, 2.00 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. The crude product was flashed over silica to give a mixture of the formed N-oxide isomers (231 mg, 0.89 mmol, 89%). The N-oxides were then reduced according to GP6 with iron-powder (98 mg, 1.76 mmol) in 20 ml AcOH. Purification by repeated column chromatography (CH_2Cl_2/MeOH 1% - 2%) gave pure **2NICz** (106 mg, 0.44 mmol, 44%) and **5NICz** (10 mg, 0.04 mmol, 4%) as off-white and white solid, respectively. According to ^{1}H-NMR the formed isomeric NICz mixture (184 mg, 0.76 mmol) contained **2NICz** (0.62 mmol) and **5NICz** (0.14 mmol). ^{1}H NMR according to the preparation starting from **5PCb** and bromo-**5PCz**, respectively.



1NICz

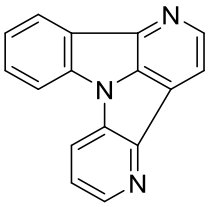


6NICz

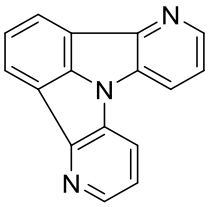
Dibenzo[b,e]pyrido[2,3,4-gh]pyrrolizine ***(1NICz)*** and *pyrido[4',3':4,5]pyrrolo[3,2,1-jk]carbazole* ***(6NICz)***. Compounds **1NICz** and **6NICz** were prepared according to GP5 starting from **6PCb** (324 mg, 1.00 mmol) with K_2CO_3 (281 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by repeated column chromatography (CH_2Cl_2/Et_2O 1% - 5%) gave pure **1NICz** (38 mg, 0.16 mmol, 16%) and **6NICz** (148 mg, 0.61 mmol, 61%) as off-white and yellow solid, respectively. According to ^{1}H-NMR the formed isomeric NICz mixture (225 mg, 0.93 mmol) contained **1NICz** (0.19 mmol) and **6NICz** (0.74 mmol). ^{1}H NMR according to the preparation starting from **4PCb** and bromo-**6PCz**, respectively.

Compounds **1NICz** and **6NICz** were prepared according to GP5 starting from **6PCb-Ox** (339 mg, 1.00 mmol) with K_2CO_3 (281 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. The crude product was flashed over silica to give a mixture of the formed N-oxide isomers (232 mg, 0.90 mmol, 90%). The N-oxides were then reduced according to GP6 with iron-powder (98 mg, 1.76 mmol) in 20 ml AcOH. Purification by repeated column chromatography (CH_2Cl_2/Et_2O 1% - 5%) gave pure **1NICz** (138 mg, 0.57 mmol, 57%) and **6NICz** (28 mg, 0.12 mmol, 12%) as off-white and white solids, respectively. According to ^{1}H-NMR the formed isomeric NICz mixture (210 mg, 0.87 mmol) contained **1NICz** (0.71 mmol) and **6NICz** (0.16 mmol). ^{1}H NMR according to the preparation starting from **4PCb** and bromo-**6PCz**, respectively.

2.3 Synthesis of twofold substituted NICzs

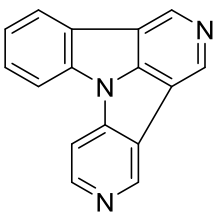


1,4NICz

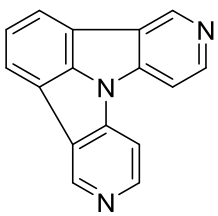


4,12NICz

Benzo[b]dipyrido[3,2-e:4',3',2'-gh]pyrrolizine ***(1,4NICz)*** and *pyrido[3,2-b]pyrido[2',3':4,5]pyrrolo[3,2,1-hi]indole* ***(4,12NICz).*** Compounds **1,4NICz** and **4,12NICz** were prepared according GP5 starting from **4,12PyCb** (280 mg, 1.00 mmol) with K_2CO_3 (280 mg, 2.03 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography and preparative HPLC (CH_2Cl_2/MeOH 1% - 3%) gave **1,4NICz** (98 mg, 0.40 mmol, 40%) and **4,12NICz** (50 mg, 0.21 mmol, 21%) as white solids. According to ^{1}H-NMR the formed isomeric NICz mixture (228 mg, 0.94 mmol) contained **1,4NICz** (0.65 mmol) and **4,12NICz** (0.28 mmol). **1,4NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 5.2 Hz, 1H), 8.58 (dd, J = 4.8, 1.3 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.03 – 7.95 (m, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 8.3 Hz, 1H), 7.44 (dd, J = 8.3, 4.8 Hz, 1H), 7.36 (t, J = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 145.6, 144.0, 141.6, 140.3, 138.1, 134.9, 129.2, 129.2, 123.5, 123.5, 123.2, 122.7, 119.7, 114.2, 112.7. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0871. **4,12NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 4.9, 1.3 Hz, 2H), 8.30 (d, J = 7.5 Hz, 2H), 7.96 (dd, J = 8.2, 1.3 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.38 (dd, J = 8.2, 4.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 144.0, 143.8, 133.1, 124.6, 122.2, 120.8, 118.7, 118.1. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0870.

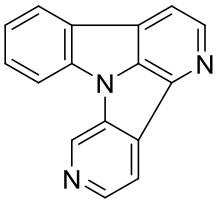


2,5NICz

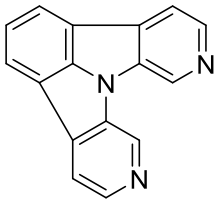


5,11NICz

Benzo[b]dipyrido[4,3-e:3',4',5'-gh]pyrrolizine ***(2,5NICz)*** *and pyrido[4,3-b]pyrido[3',4':4,5]pyrrolo[3,2,1-hi]indole* ***(5,11NICz).*** Compounds **2,5NICz** and **5,11NICz** were prepared according GP5 starting from **5,11PyCb** (324 mg, 1.00 mmol) with K_2CO_3 (278 mg, 2.01 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography and preparative HPLC (CH_2Cl_2/MeOH 2% - 4%) gave **2,5NICz** (130 mg, 0.53 mmol, 53%) and **5,11NICz** (37 mg, 0.15 mmol, 15%) as white solids. According to ^{1}H-NMR the formed isomeric NICz mixture (222 mg, 0.91 mmol) contained **2,5NICz** (0.72 mmol) and **5,11NICz** (0.19 mmol). **2,5NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 9.24 (s, 1H), 9.20 (s, 1H), 8.76 (d, J = 5.6 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 5.6 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 148.0, 145.6, 142.9, 139.9, 139.9, 138.4, 128.9, 128.4, 124.5, 124.4, 124.2, 116.2, 113.8, 113.2, 107.9. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0871. **5,11NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 2H), 8.74 (d, J = 5.5 Hz, 2H), 8.05 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 5.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 145.1, 143.5, 142.4, 126.7, 125.3, 121.1, 116.6, 108.1. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0873.



1,10NICz



6,10NICz

Benzo[b]dipyrido[3,4-e:2',3',4'-gh]pyrrolizine ***(1,10NICz)*** and *pyrido[3,4-b]pyrido[4',3':4,5]pyrrolo[3,2,1-hi]indole* ***(6,10NICz).*** Compounds **1,10NICz** and **6,10NICz** were prepared according GP5 starting from **6,10PyCb** (280 mg, 1.00 mmol) with K_2CO_3 (279 mg, 2.02 mmol) and (NHC)Pd(allyl)Cl (29 mg, 0.05 mmol) in 10 ml DMA. Purification by column chromatography (CH_2Cl_2/MeOH 1% - 4%) gave **1,10NICz** (11 mg, 0.5 mmol, 5%) and **6,10NICz** (186 mg, 0.76 mmol, 76%) as yellow and light brown solid, respectively.

1,10NICz: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.88 (d, J = 5.0 Hz, 1H), 8.63 (d, J = 5.1 Hz, 1H), 8.15 (d, J = 5.1 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 5.0 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.4, 140.0, 139.2, 138.1, 135.9, 135.7, 134.9, 130.2, 129.1, 125.9, 125.3, 123.2, 117.2, 115.9, 113.4. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0872. **6,10NICz**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 2H), 8.60 (d, J = 5.2 Hz, 2H), 8.09 (d, J = 7.5 Hz, 2H), 7.91 (dd, J = 5.2, 0.9 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 143.1, 135.8, 134.6, 134.5, 124.2, 123.4, 117.7, 117.2. HRMS (ESI): m/z calcd for $C_{16}H_{10}N_3^+$ $[M+H]^+$ 244.0869, found 244.0871.

Compounds **1,10NICz** and **6,10NICz** were prepared according GP5 starting from **6,10PyCb-Ox** (188 mg, 0.60 mmol) with K_2CO_3 (2 eq., 168 mg, 1.22 mmol) and (NHC)Pd(allyl)Cl (5 mol%, 17 mg, 0.03 mmol) in 10 ml DMA. The crude product was flashed over silica to give a mixture of the formed N-oxide isomers (96 mg, 0.35 mmol, 58%). The N-oxides were then reduced according to GP6 with iron-powder (4 eq., 78 mg, 1.4 mmol) in 8 ml AcOH. Purification with preparative HPLC (CH_2Cl_2/MeOH 2% - 4%) gave **1,10NICz** (57 mg, 0.23 mmol, 38%) and **6,10NICz** (4 mg, 0.02 mmol, 3%) as yellow and light brown solid, respectively. ^{1}H NMR according to the preparation starting from **6,10PyCb**.

3 NMR Spectra

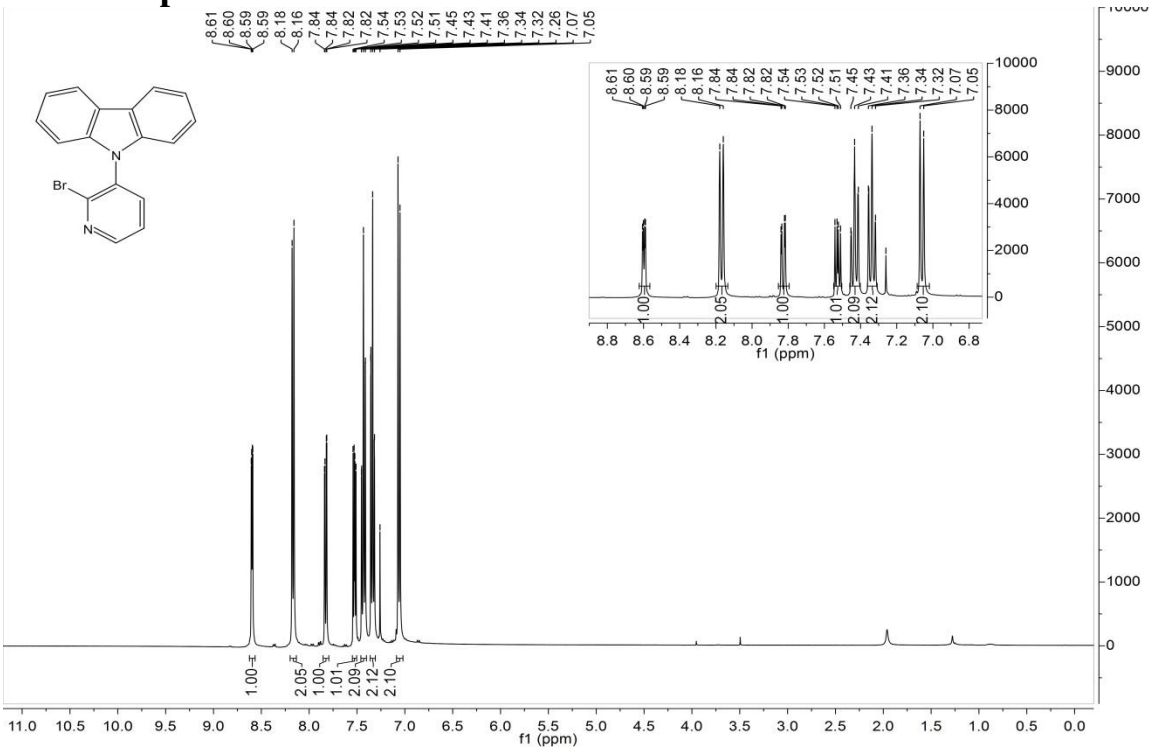


Figure S1. ^{1}H NMR spectrum of bromo-**4PCz** in $CDCl_3$.

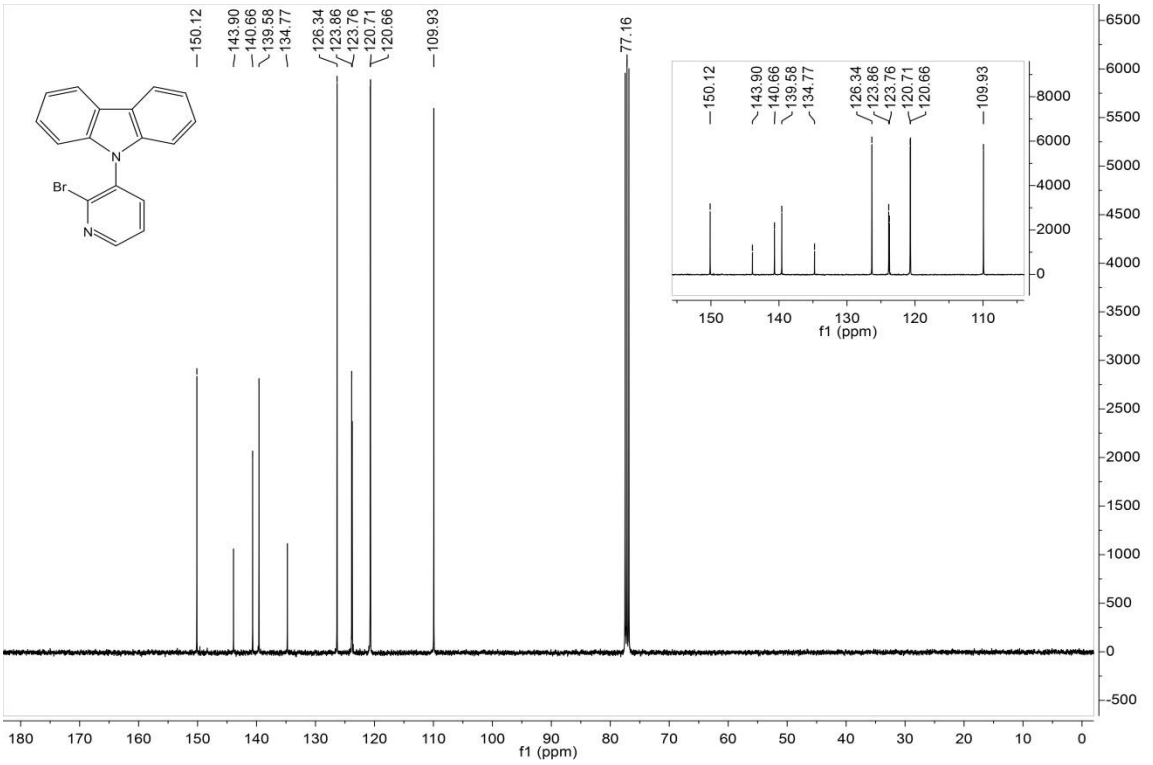


Figure S2. ^{13}C NMR spectrum of bromo-**4PCz** in $CDCl_3$.

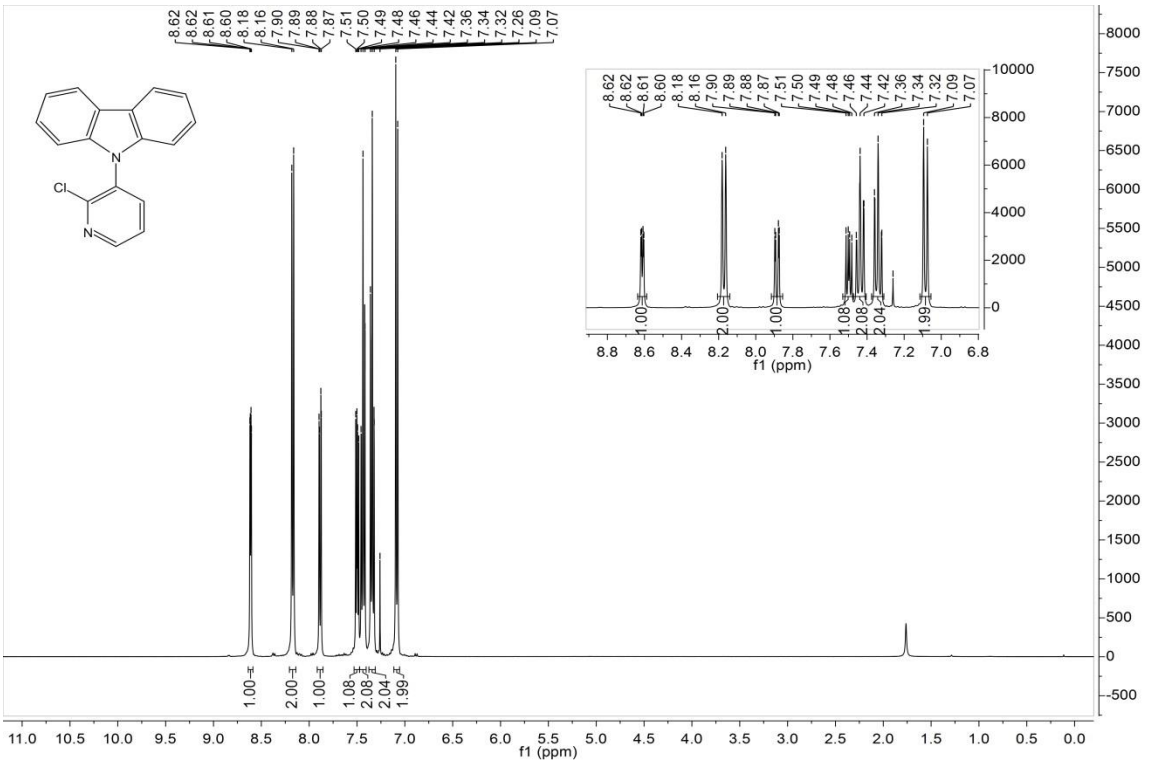


Figure S3. ^{1}H NMR spectrum of chloro-**4PCz** in $CDCl_3$.

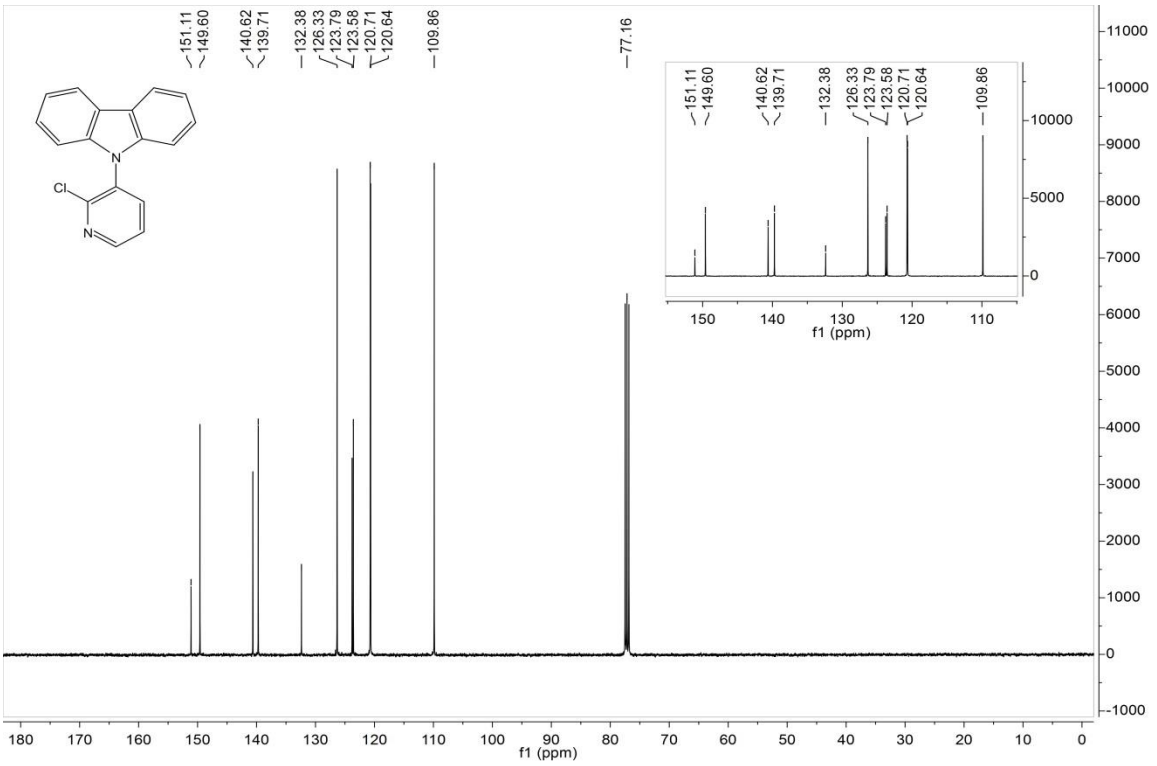


Figure S4. ^{13}C NMR spectrum of chloro-**4PCz** in $CDCl_3$.

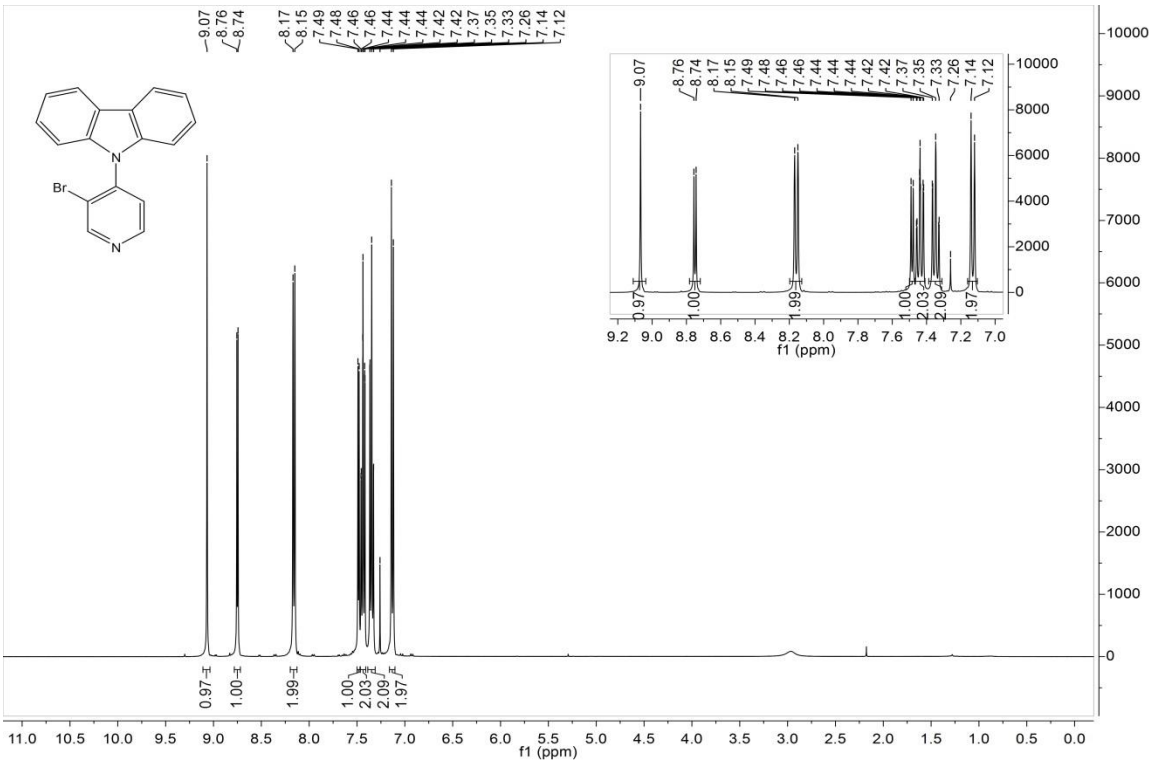


Figure S5. ^{1}H NMR spectrum of bromo-**5PCz** in $CDCl_3$.

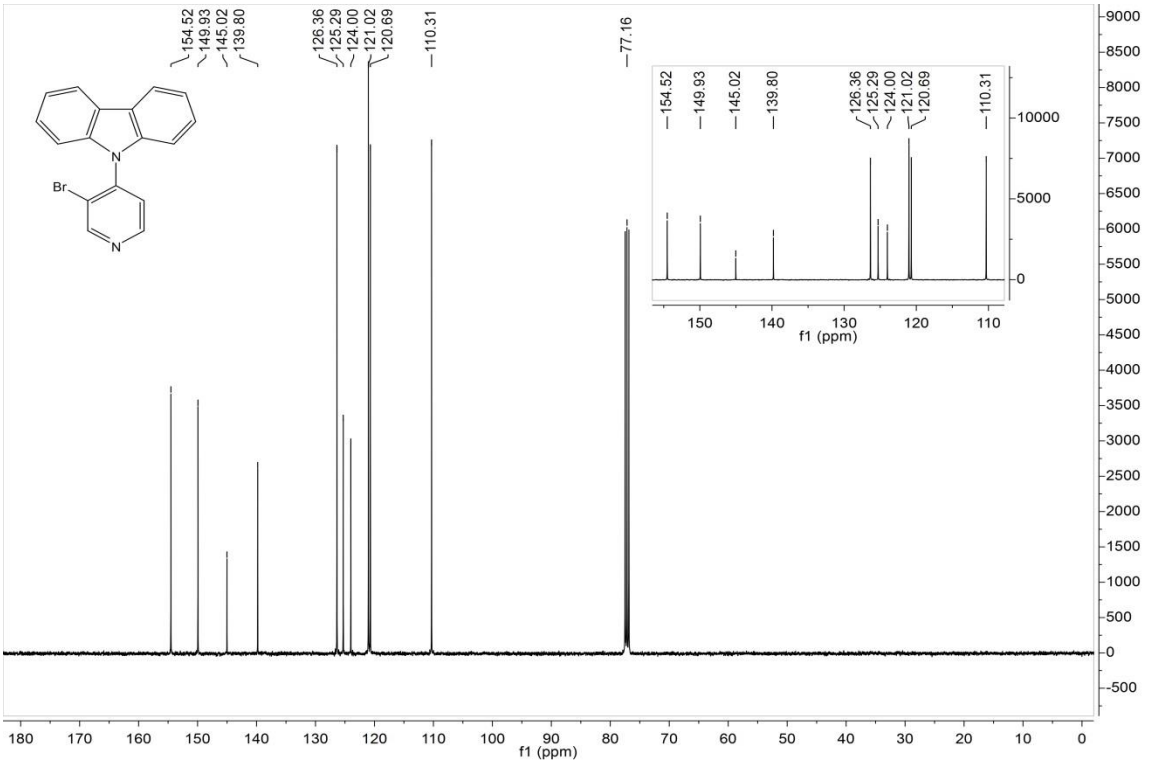


Figure S6. ^{13}C NMR spectrum of bromo-**5PCz** in $CDCl_3$.

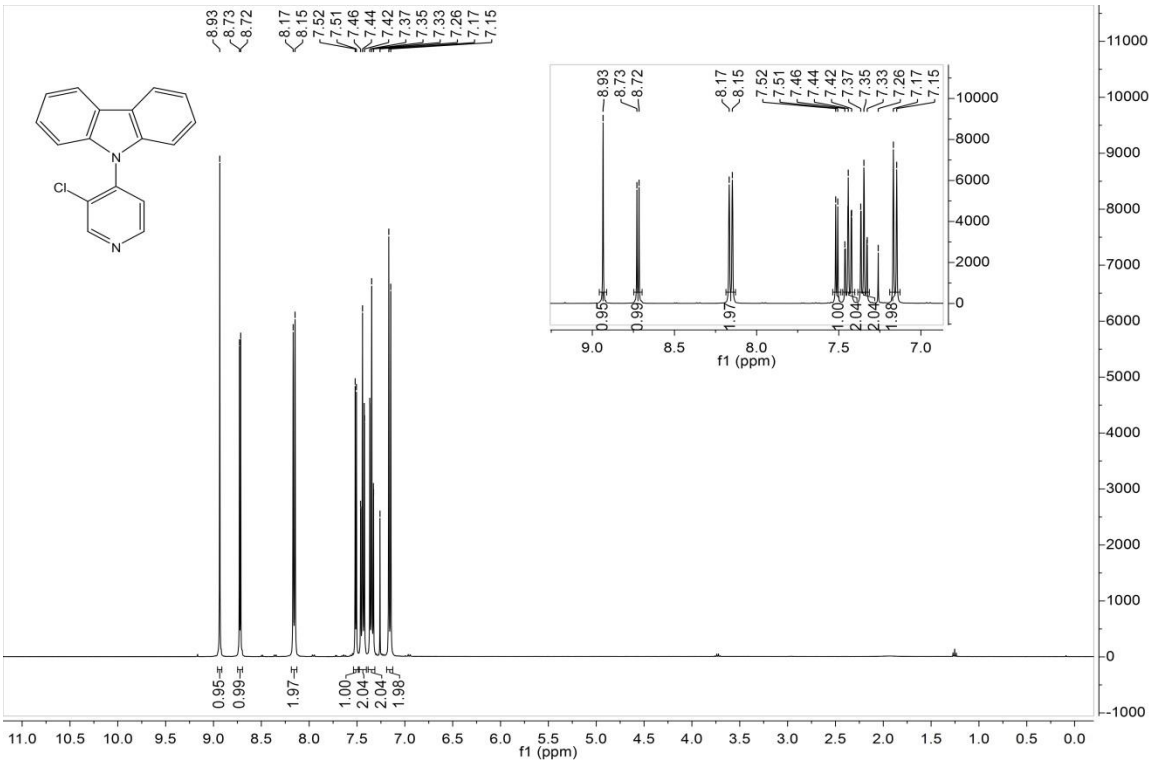


Figure S7. ^{1}H NMR spectrum of chloro-**5PCz** in $CDCl_3$.

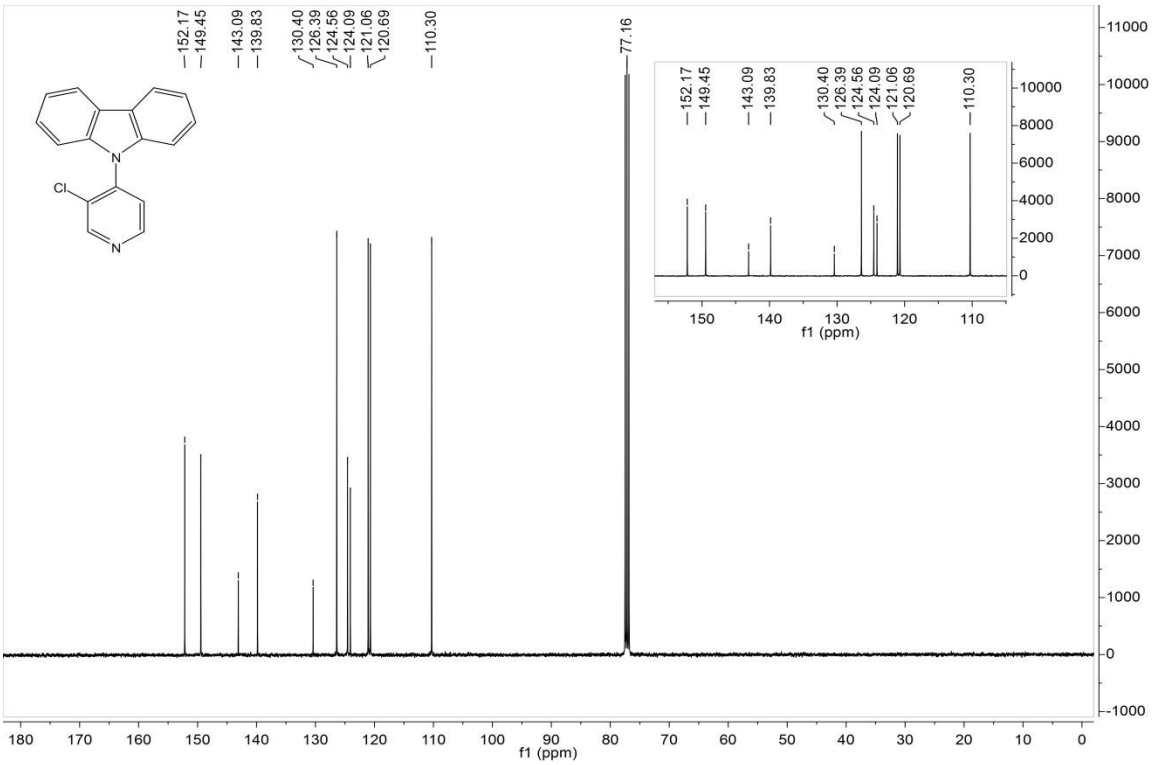


Figure S8. ^{13}C NMR spectrum of chloro-**5PCz** in $CDCl_3$.

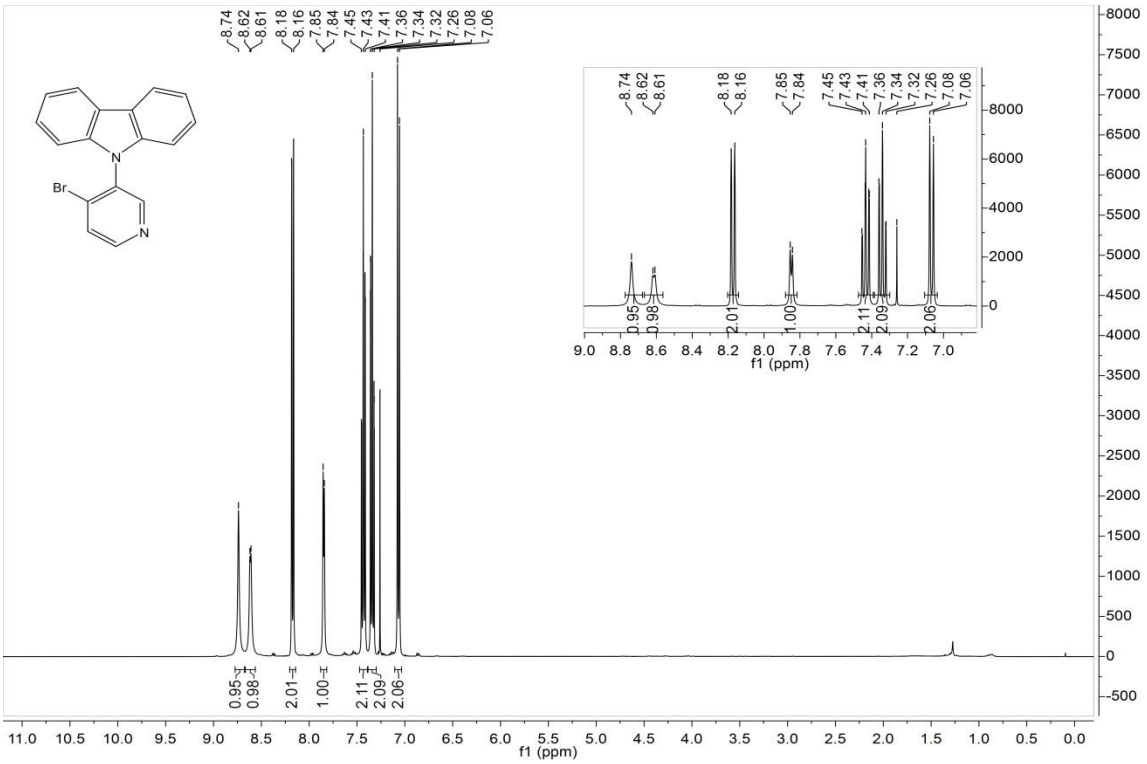


Figure S9. ^{1}H NMR spectrum of bromo-**6PCz** in $CDCl_3$.

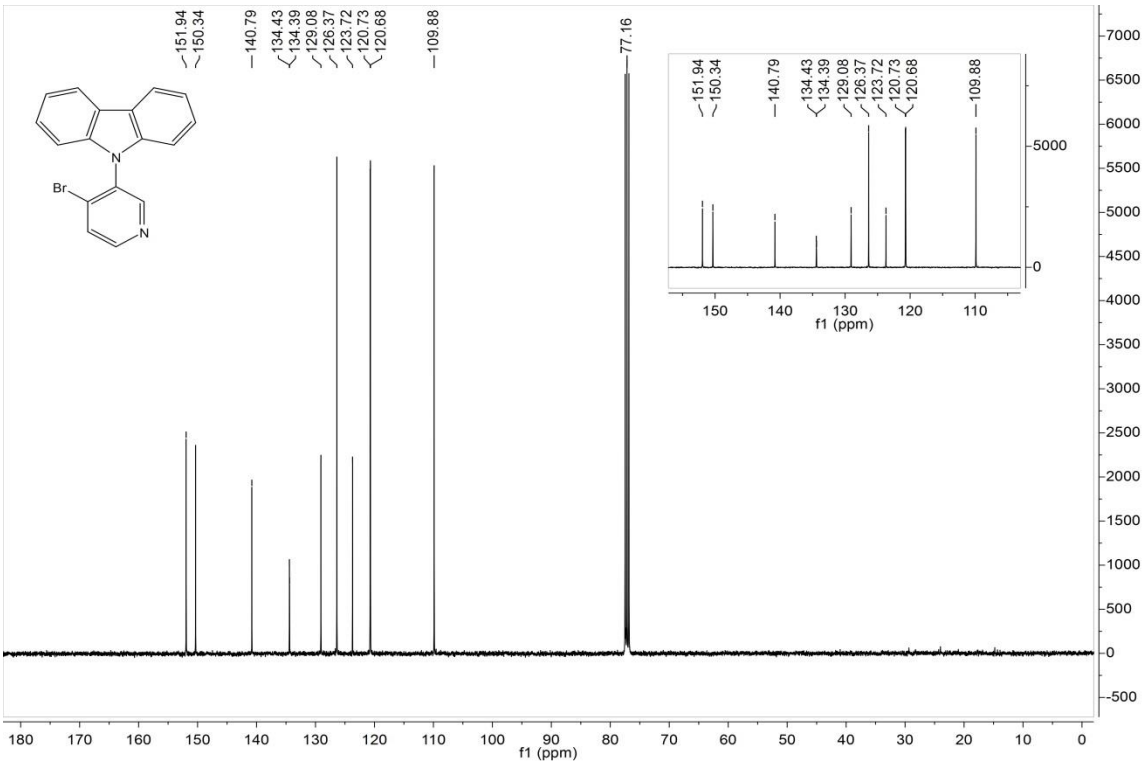


Figure S10. ^{13}C NMR spectrum of bromo-**6PCz** in $CDCl_3$.

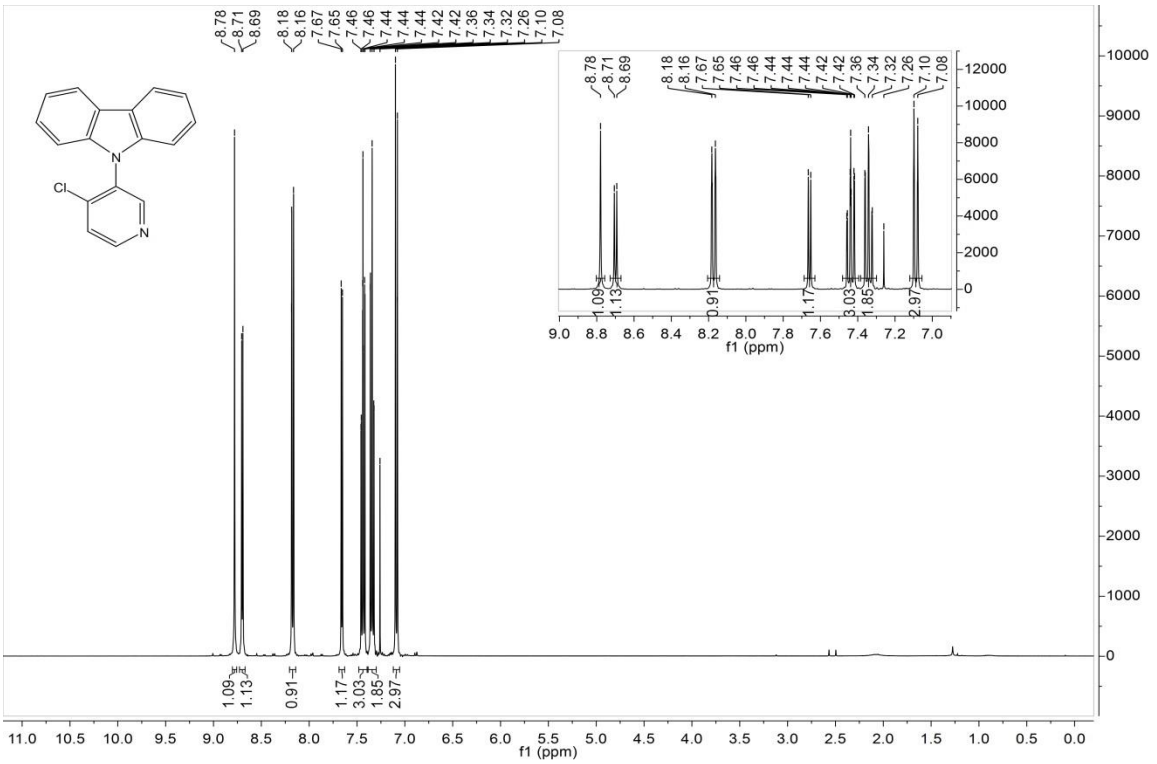


Figure S11. ^{1}H NMR spectrum of chloro-**6PCz** in $CDCl_3$.

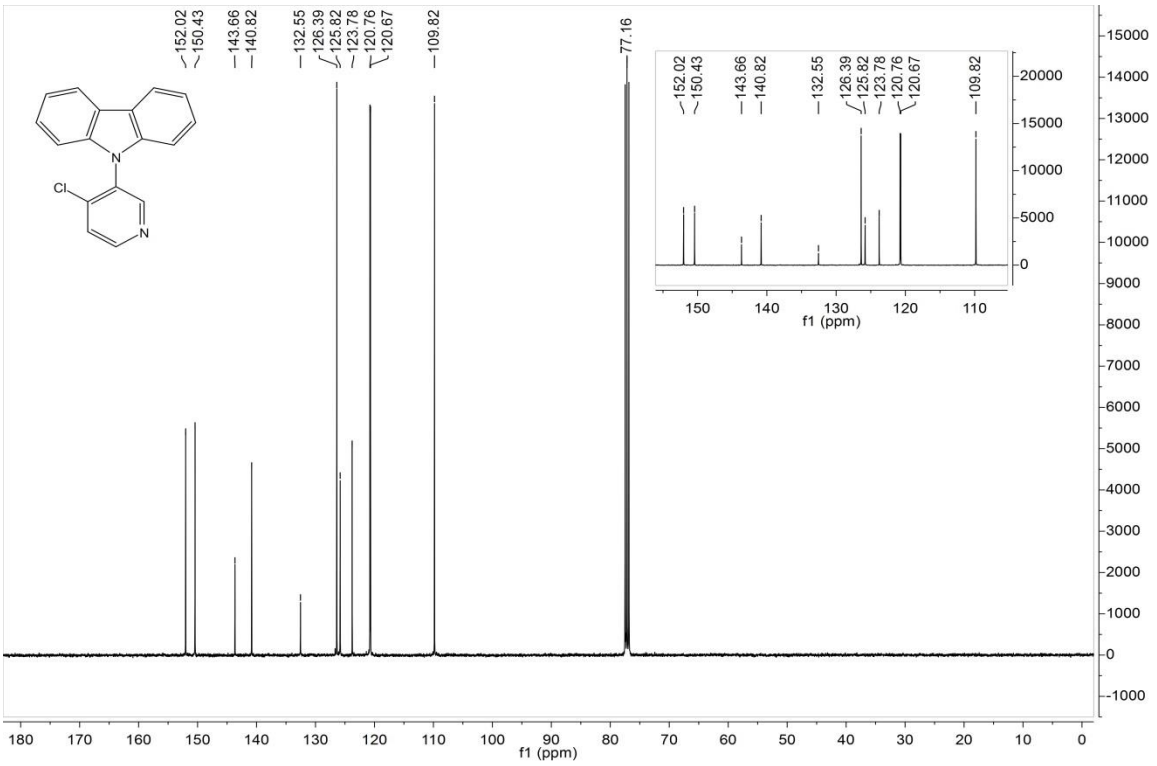


Figure S12. ^{13}C NMR spectrum of chloro-**6PCz** in $CDCl_3$.

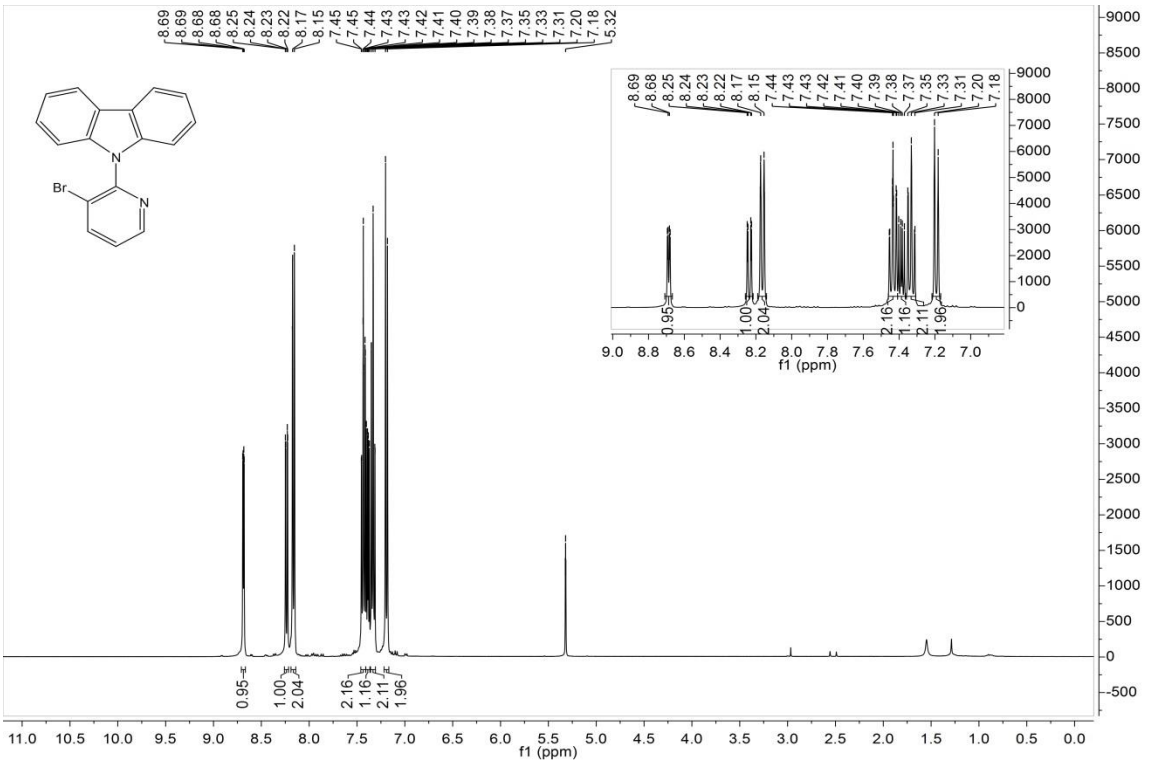


Figure S13. ^{1}H NMR spectrum of bromo-**7PCz** in CD_2Cl_2.

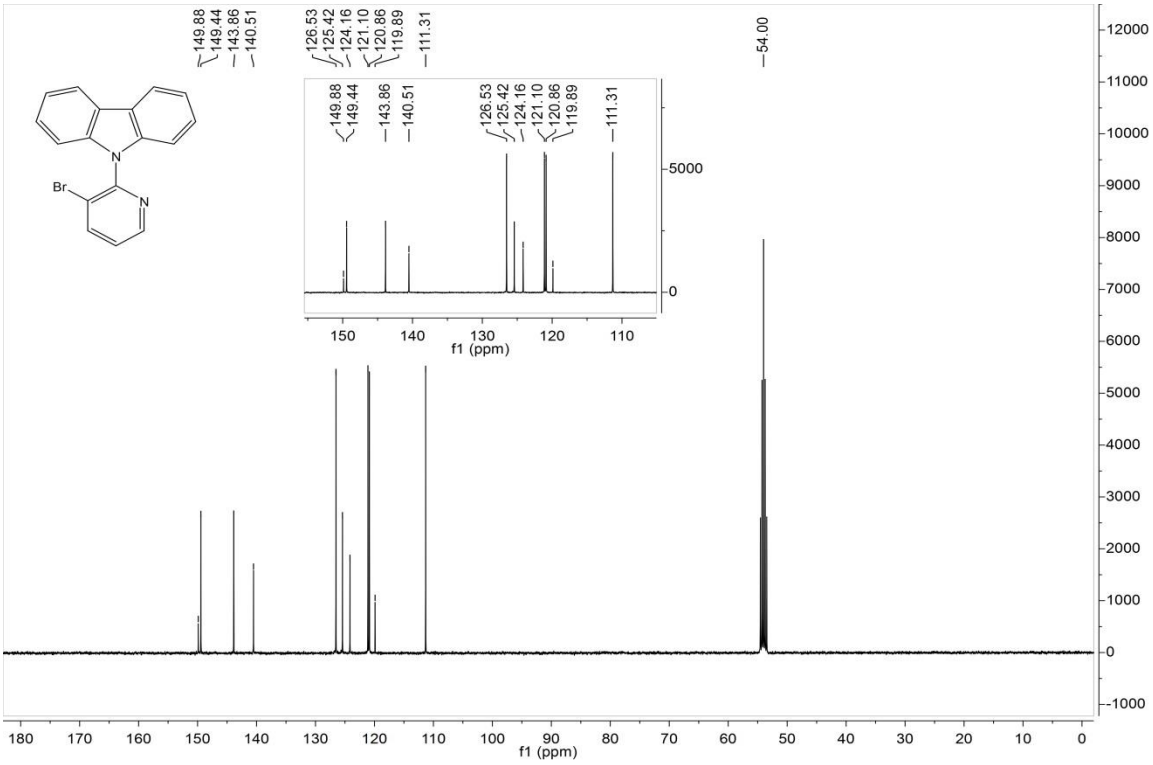


Figure S14. ^{13}C NMR spectrum of bromo-**7PCz** in CD_2Cl_2.

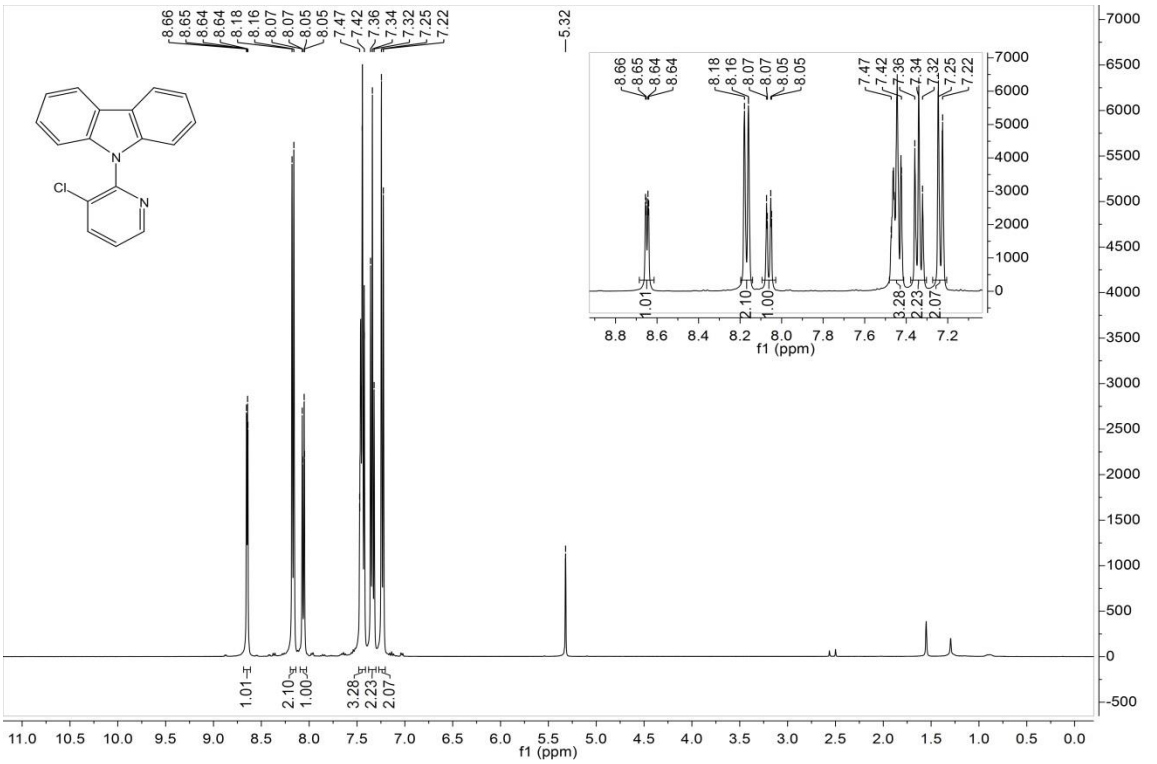


Figure S15. ^{1}H NMR spectrum of chloro-**7PCz** in CD_2Cl_2.

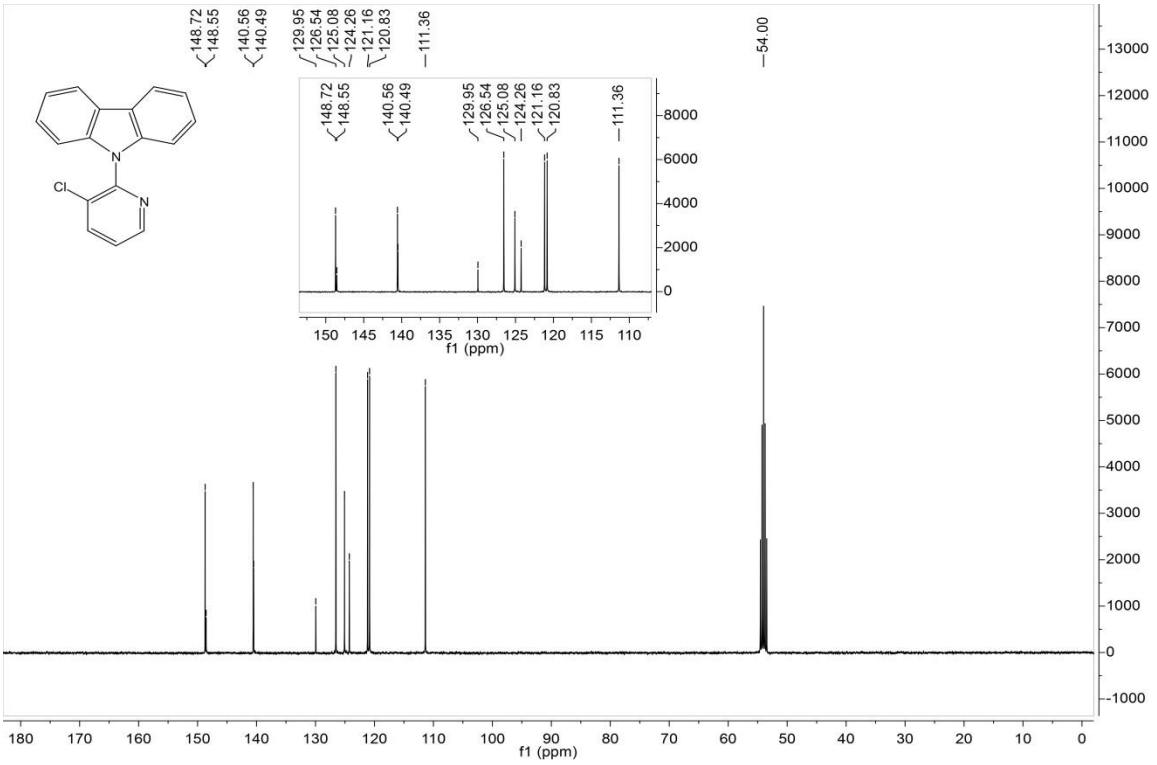


Figure S16. ^{13}C NMR spectrum of chloro-**7PCz** in CD_2Cl_2.

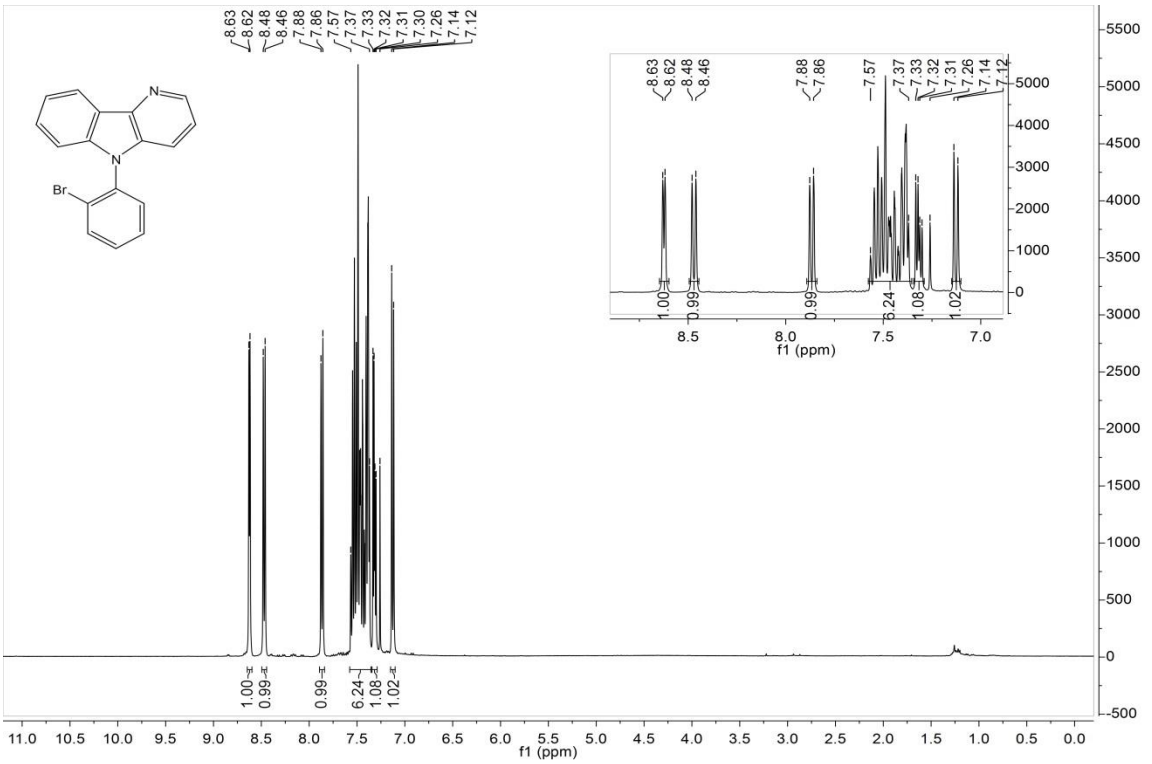


Figure S17. ^{1}H NMR spectrum of **4PCb** in $CDCl_3$.

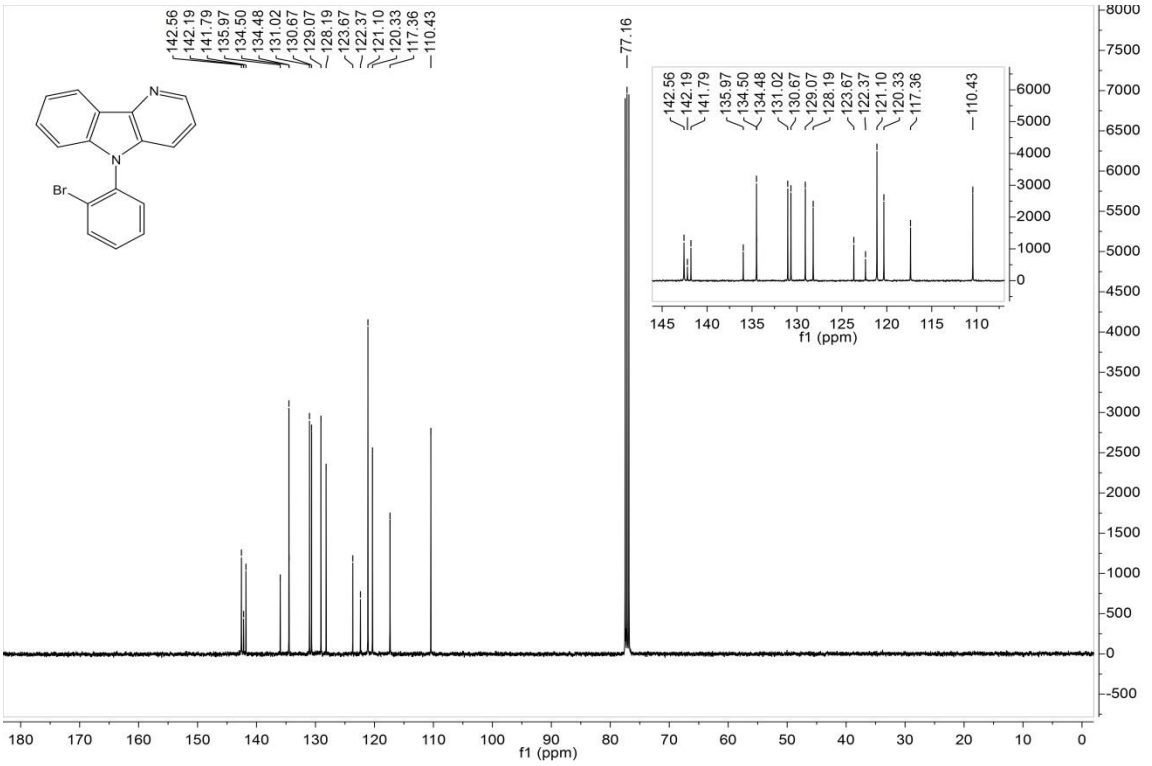


Figure S18. ^{13}C NMR spectrum of **4PCb** in $CDCl_3$.

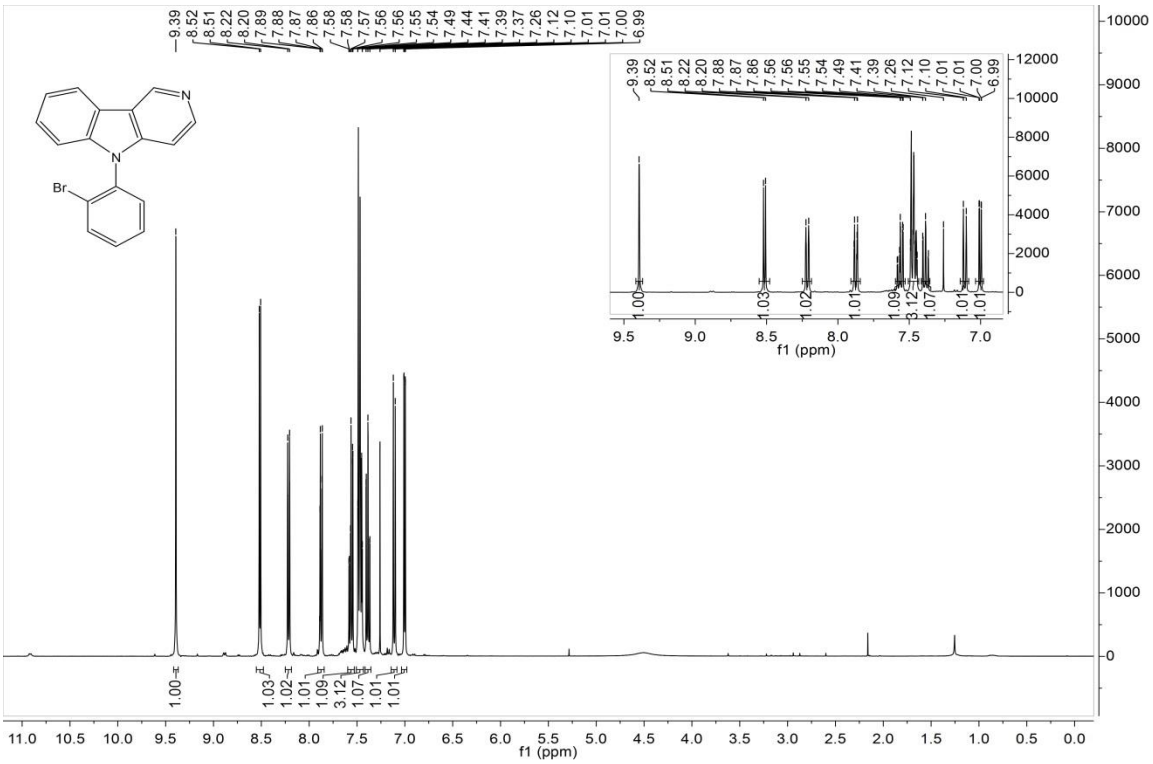


Figure S19. ^{1}H NMR spectrum of **5PCb** in $CDCl_3$.

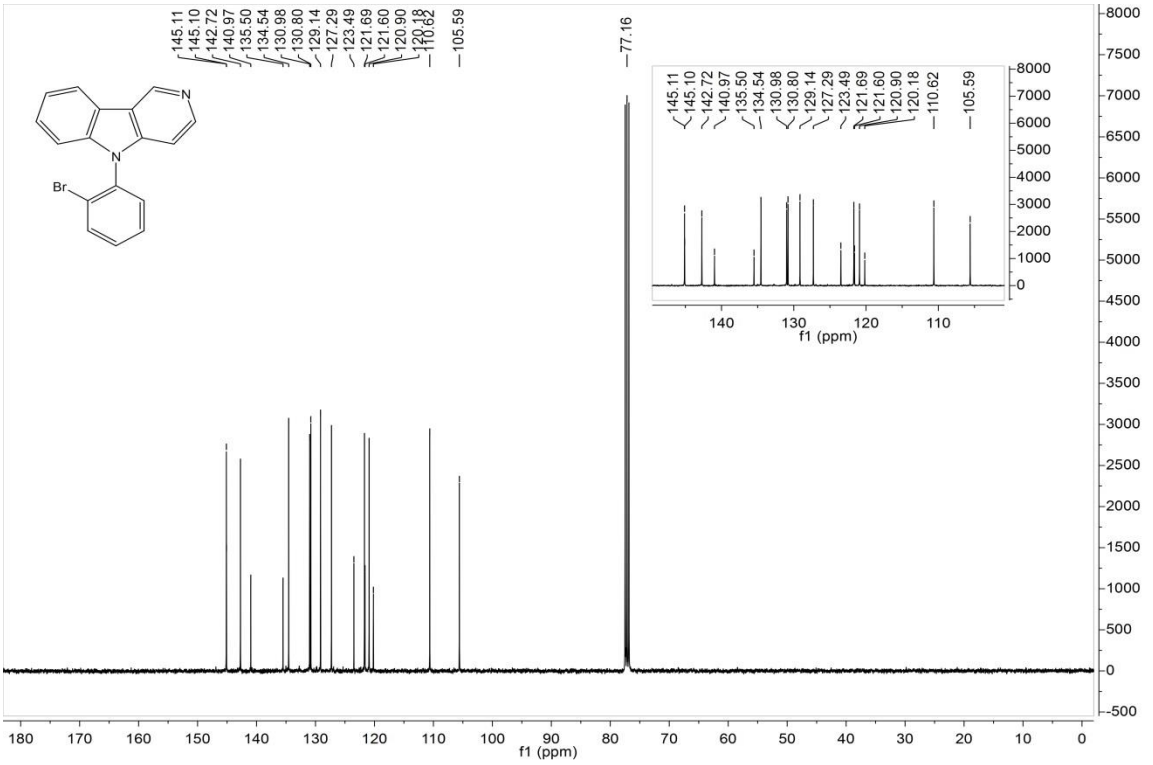


Figure S20. ^{13}C NMR spectrum of **5PCb** in $CDCl_3$.

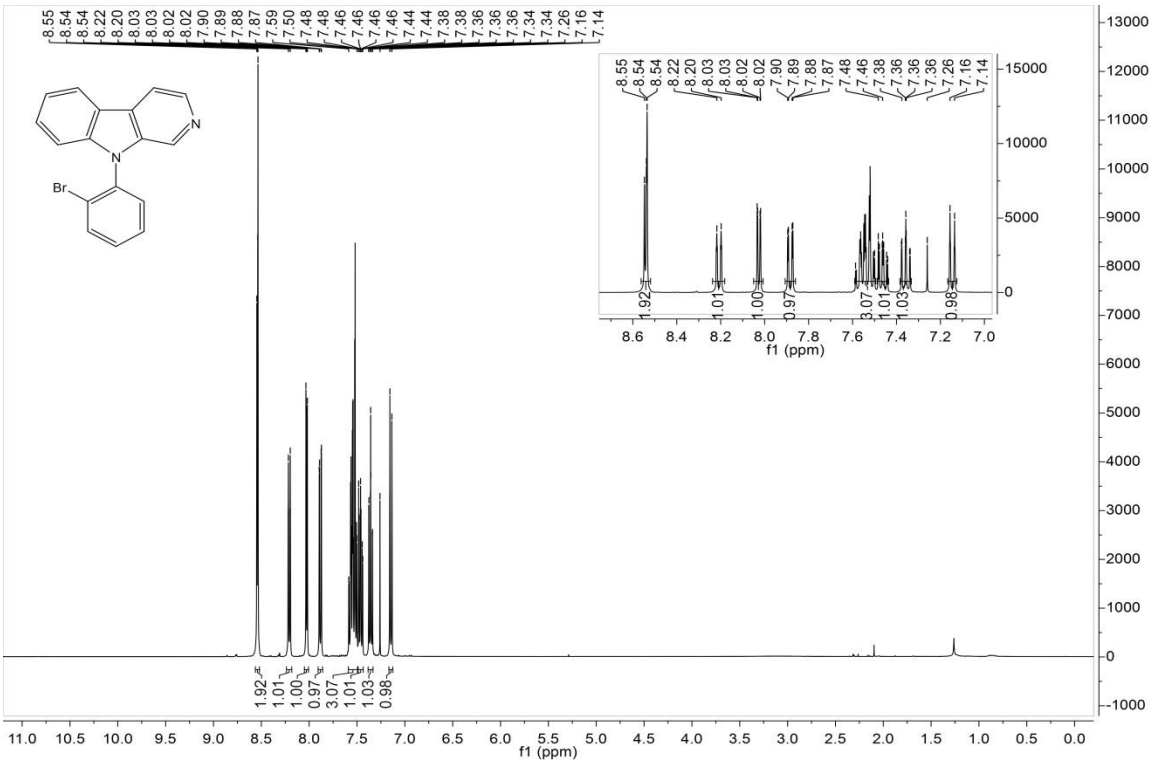


Figure S21. ^{1}H NMR spectrum of **6PCb** in $CDCl_3$.

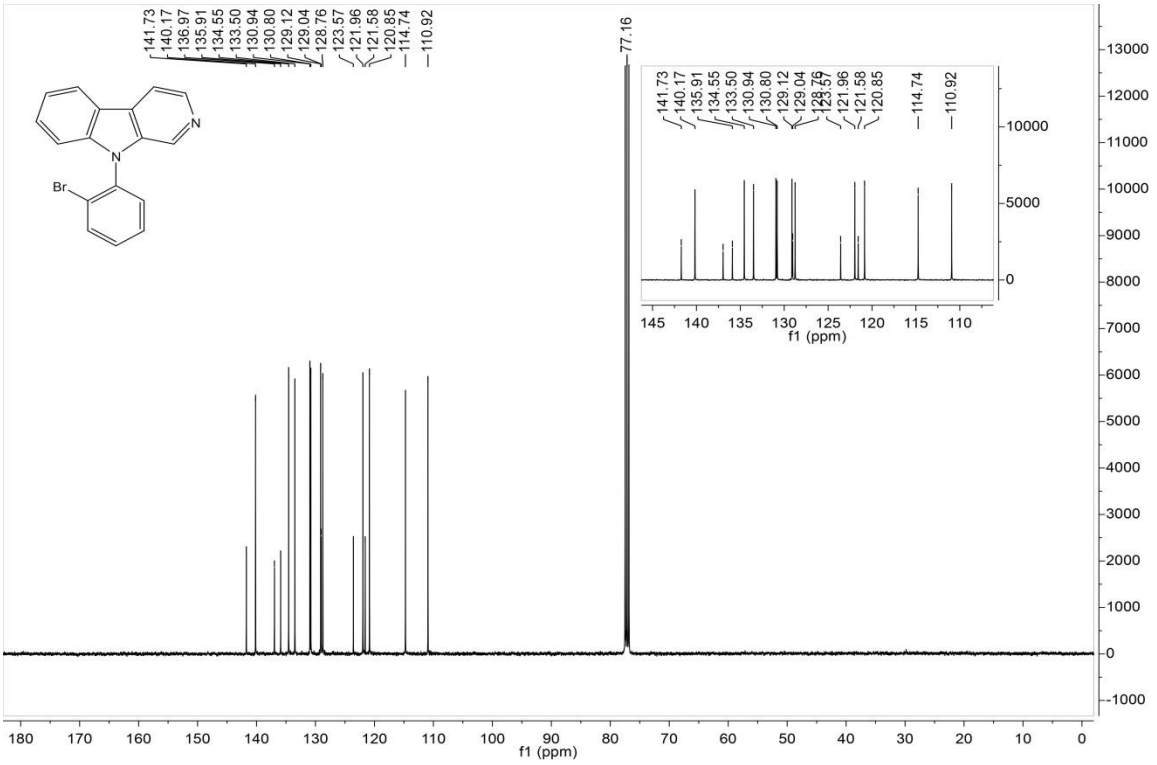


Figure S22. ^{13}C NMR spectrum of **6PCb** in $CDCl_3$.

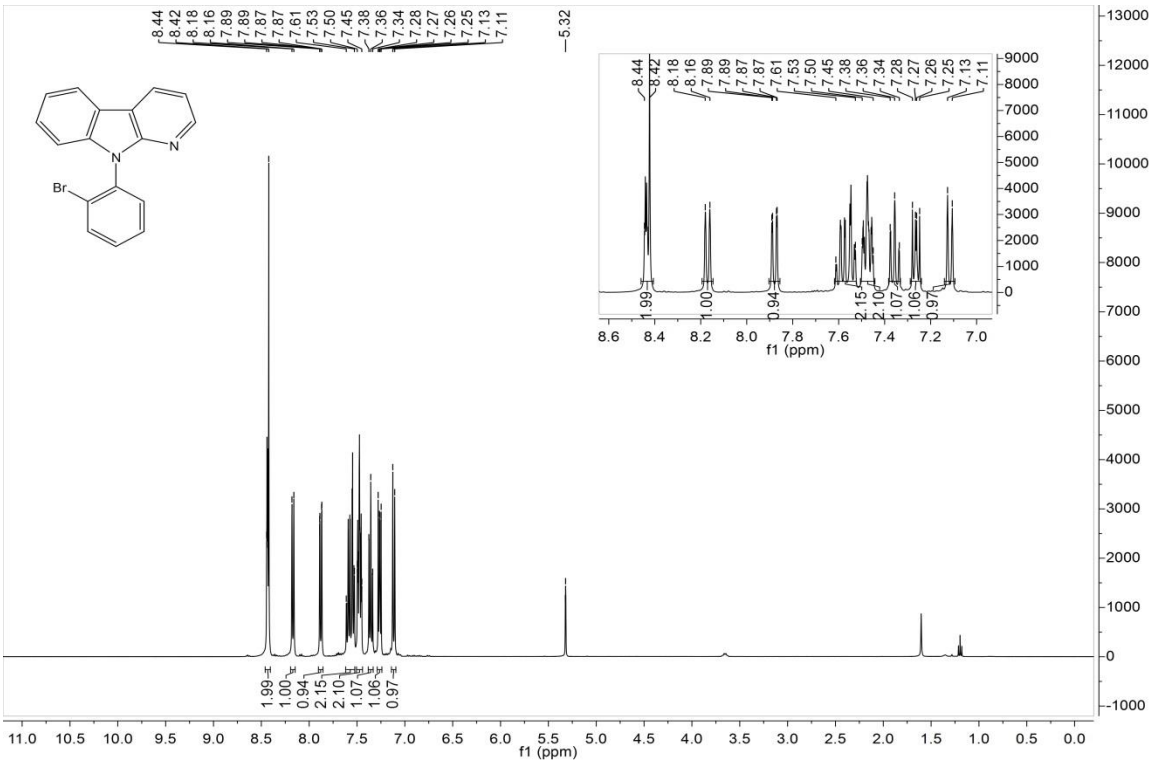


Figure S23. ^{1}H NMR spectrum of **7PCb** in CD_2Cl_2.

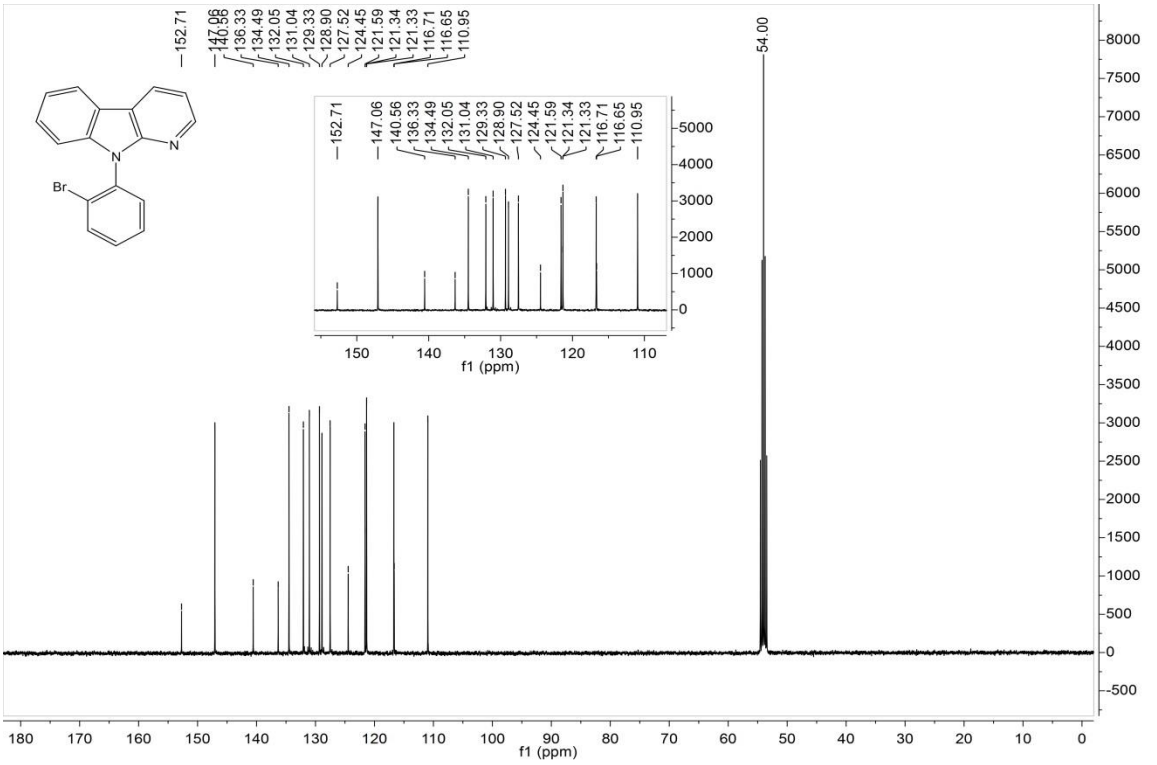


Figure S24. ^{13}C NMR spectrum of **7PCb** in CD_2Cl_2.

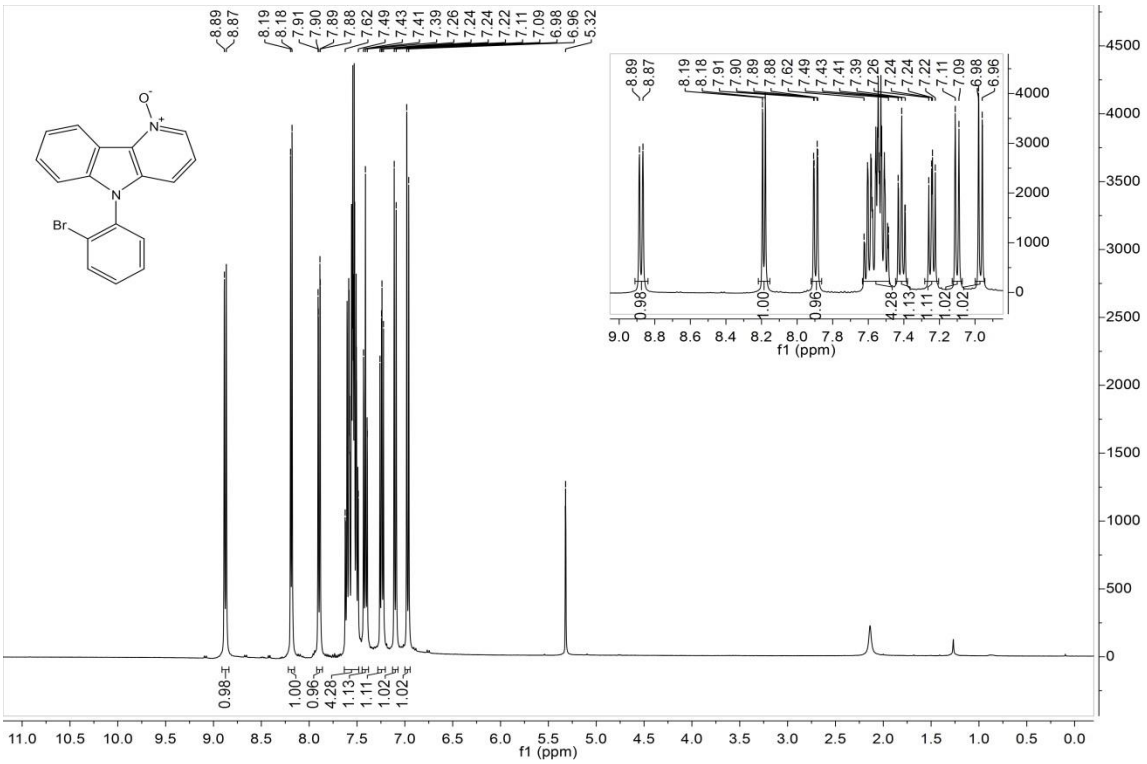


Figure S25. ^{1}H NMR spectrum of **4PCb-Ox** in CD_2Cl_2.

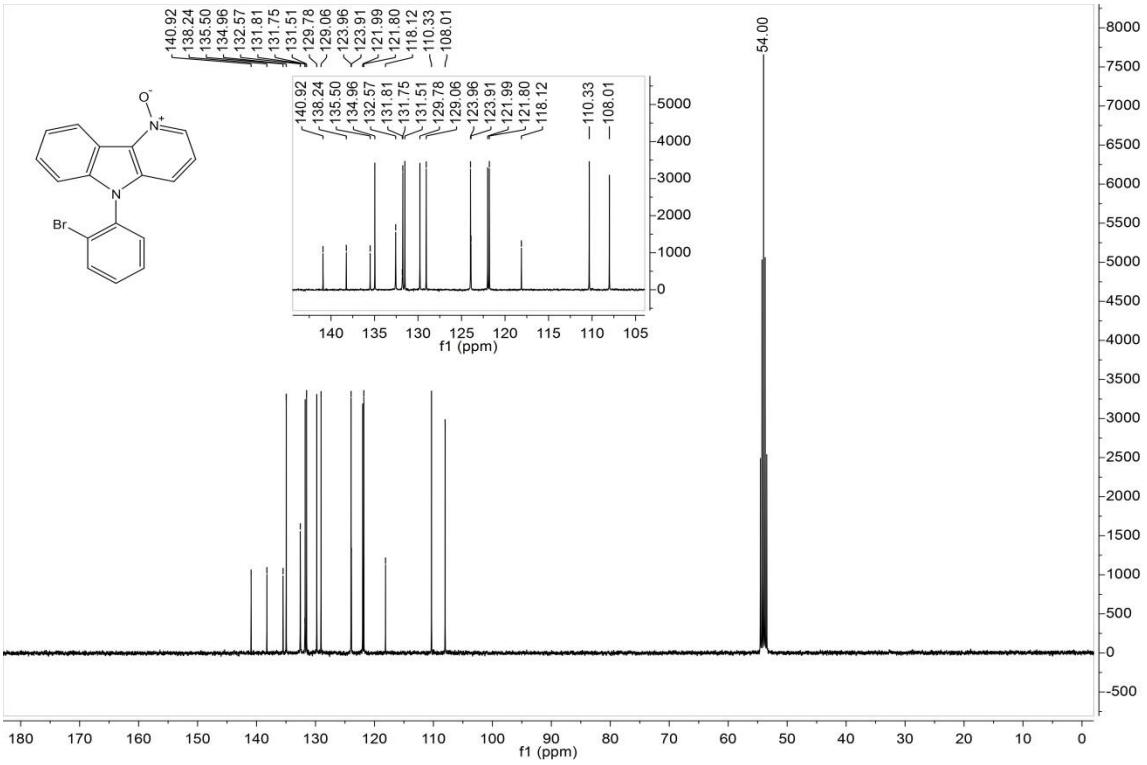


Figure S26. ^{13}C NMR spectrum of **4PCb-Ox** in CD_2Cl_2.

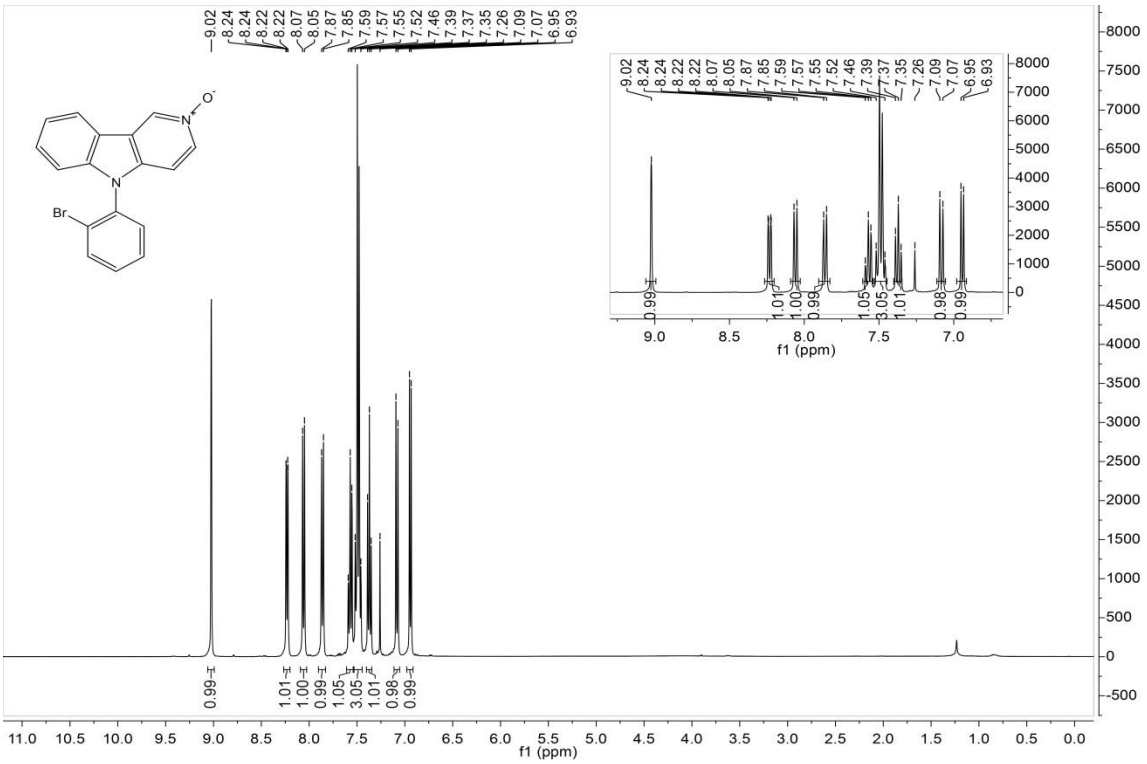


Figure S27. ^{1}H NMR spectrum of **5PCb-Ox** in $CDCl_3$.

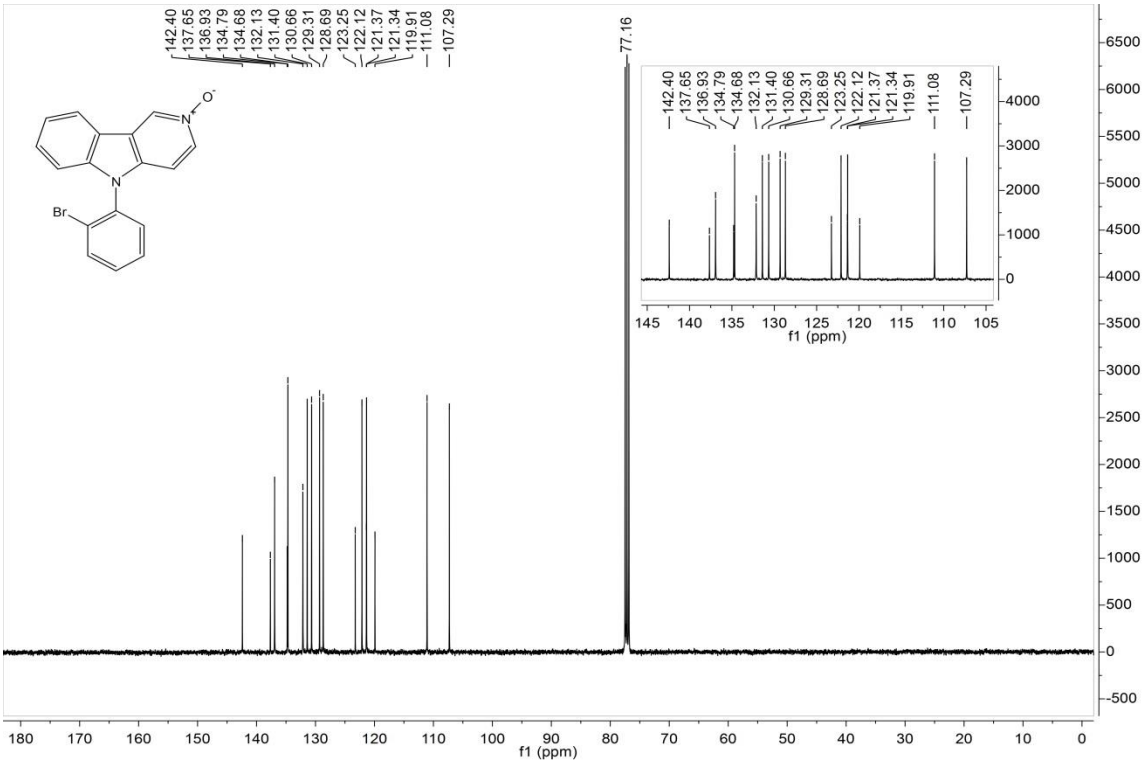


Figure S28. ^{13}C NMR spectrum of **5PCb-Ox** in $CDCl_3$.

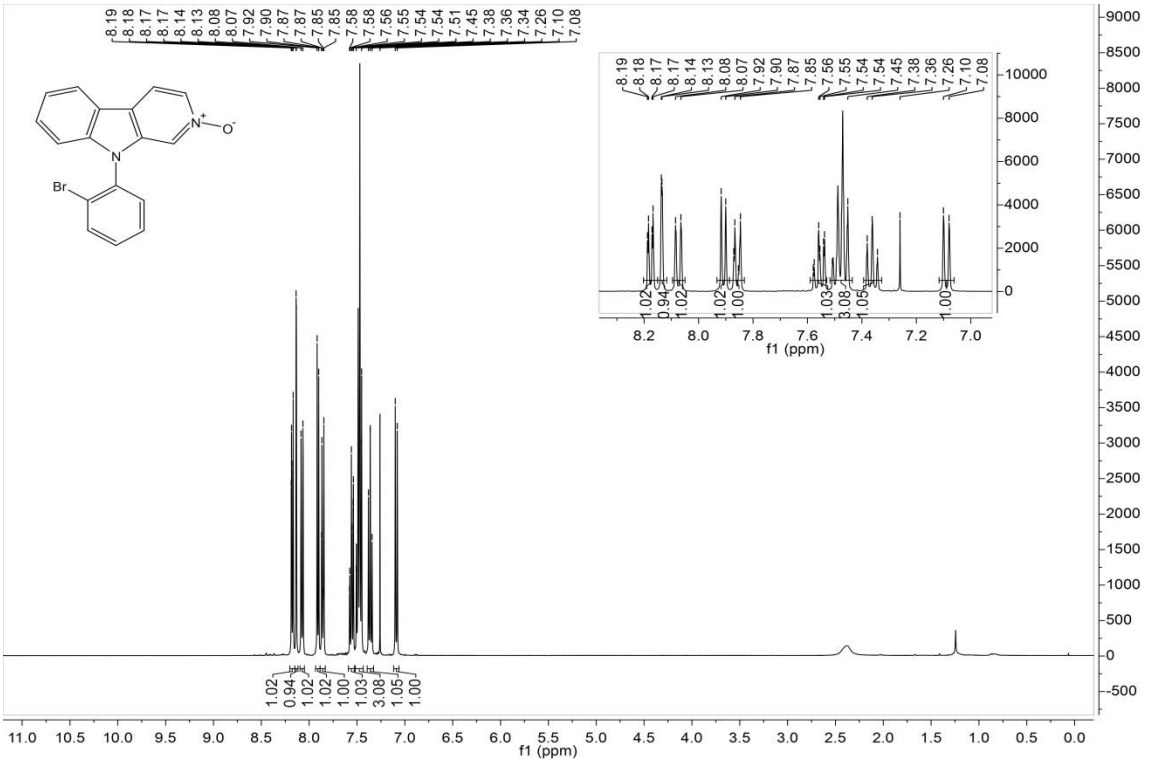


Figure S29. ^{1}H NMR spectrum of **6PCb-Ox** in $CDCl_3$.

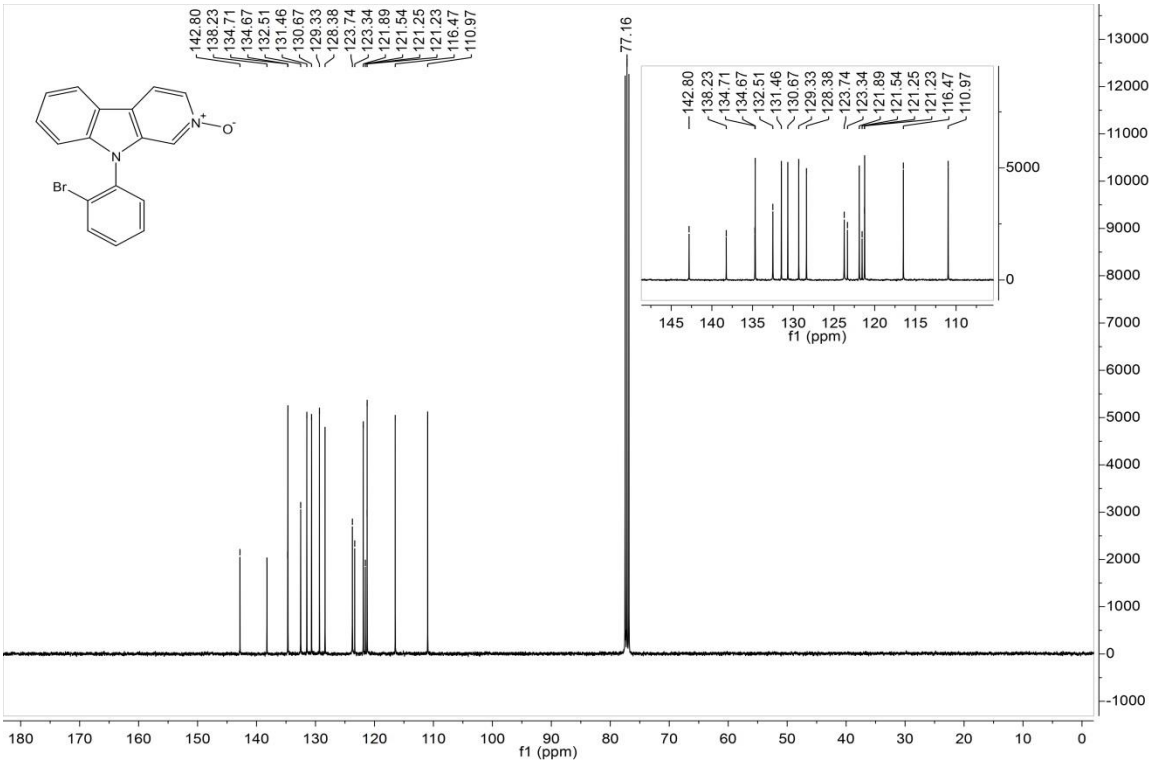


Figure S30. ^{13}C NMR spectrum of **6PCb-Ox** in $CDCl_3$.

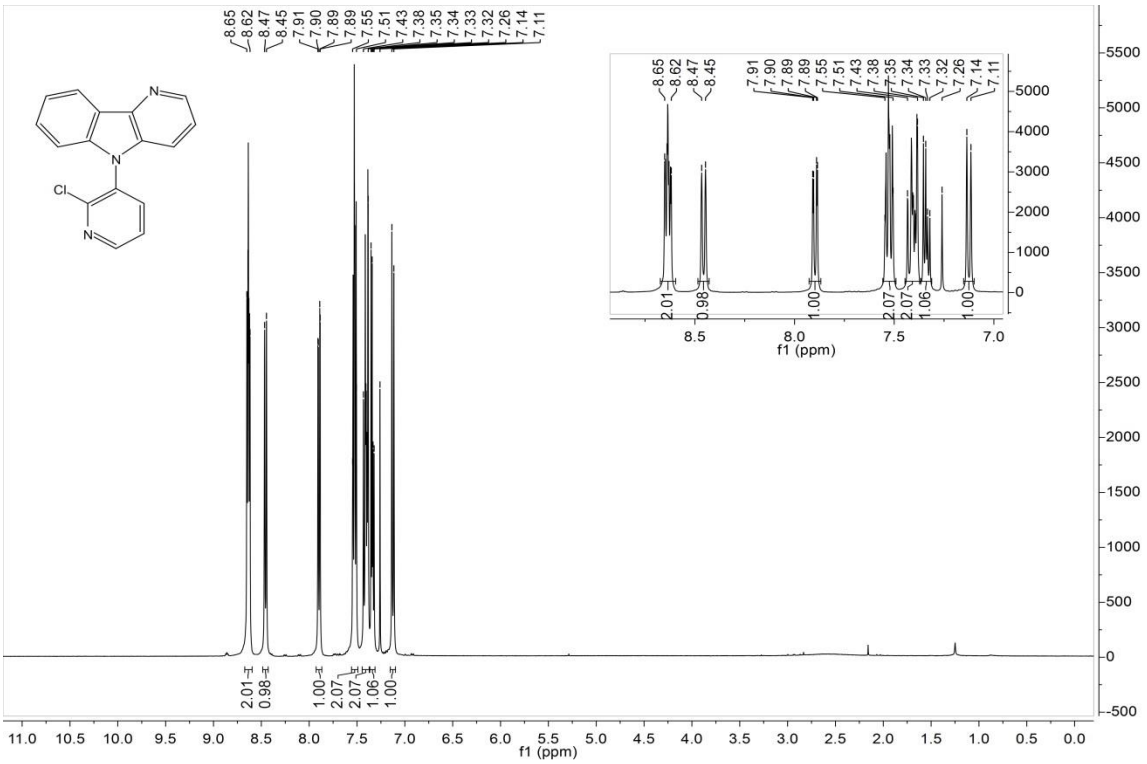


Figure S31. ^{1}H NMR spectrum of **4,12PyCb** in $CDCl_3$.

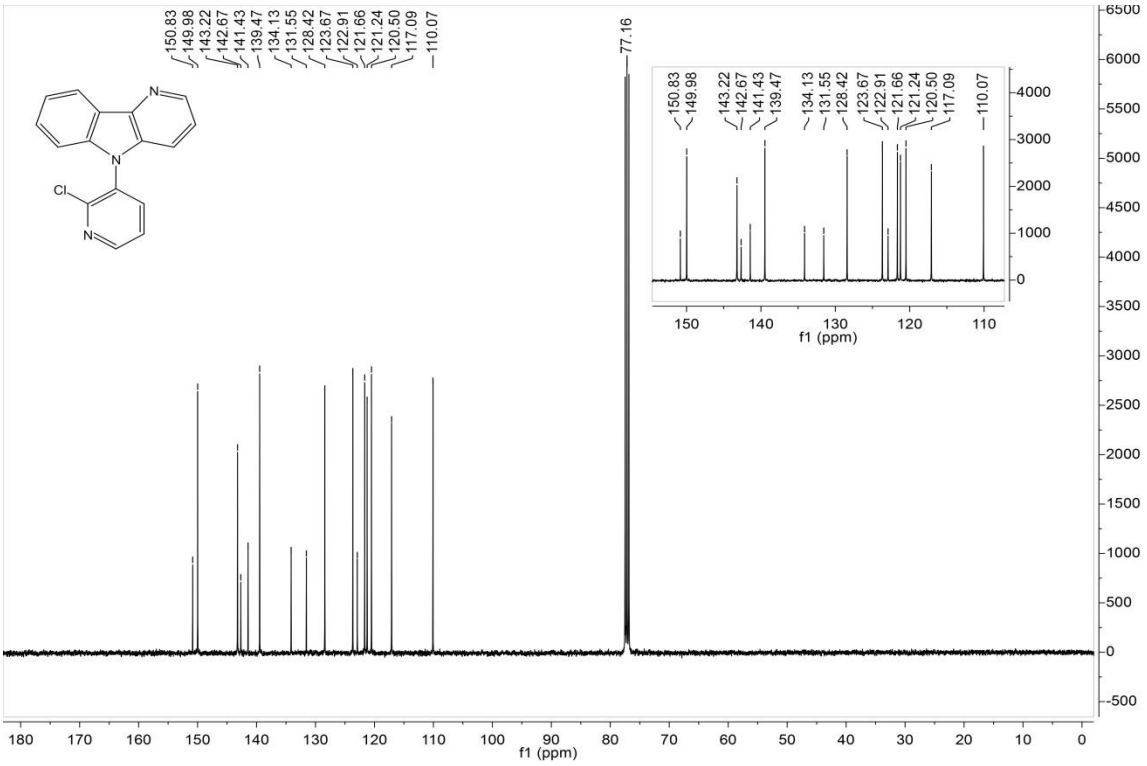


Figure S32. ^{13}C NMR spectrum of **4,12PyCb** in $CDCl_3$.

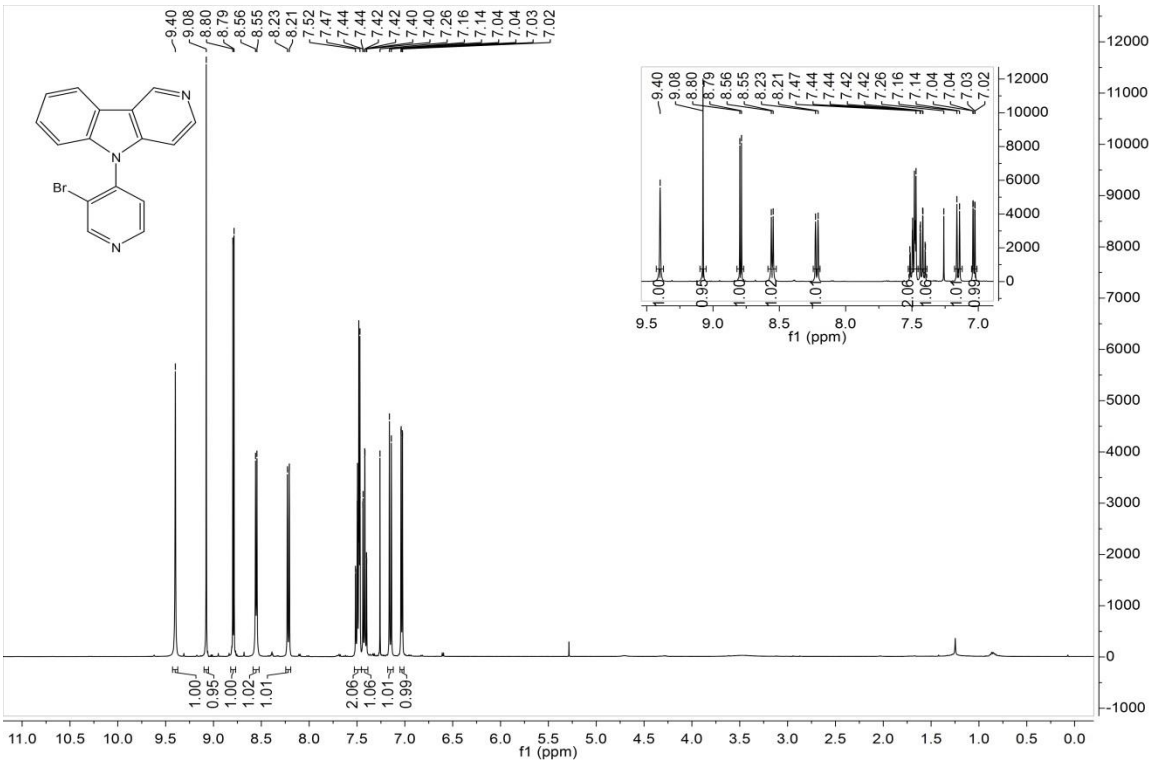


Figure S33. ^{1}H NMR spectrum of **5,11PyCb** in $CDCl_3$.

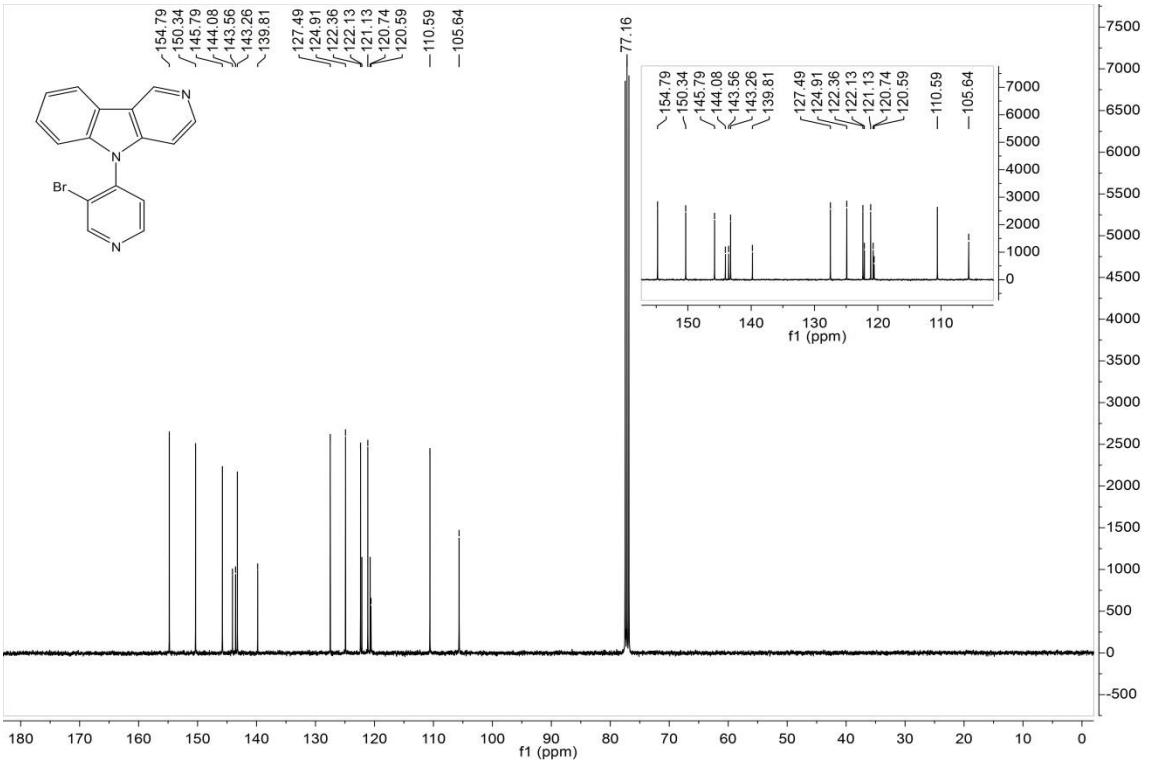


Figure S34. ^{13}C NMR spectrum of **5,11PyCb** in $CDCl_3$.

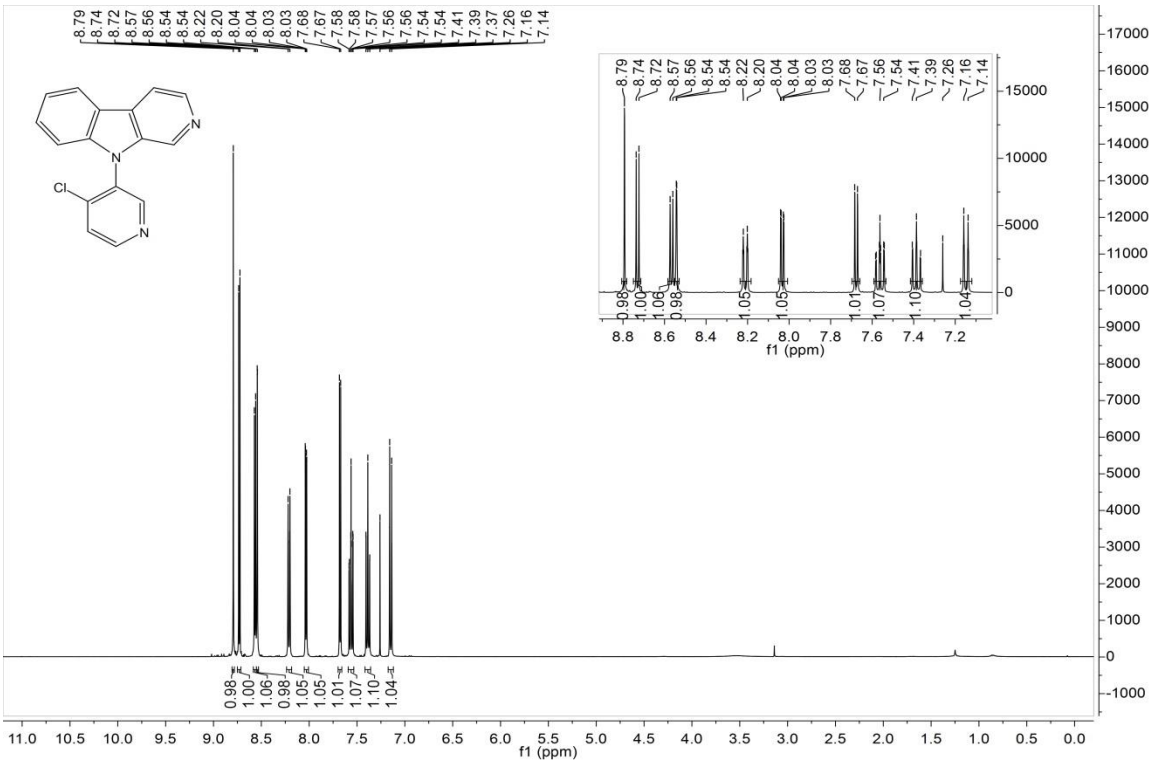


Figure S35. ^{1}H NMR spectrum of **6,10PyCb** in $CDCl_3$.

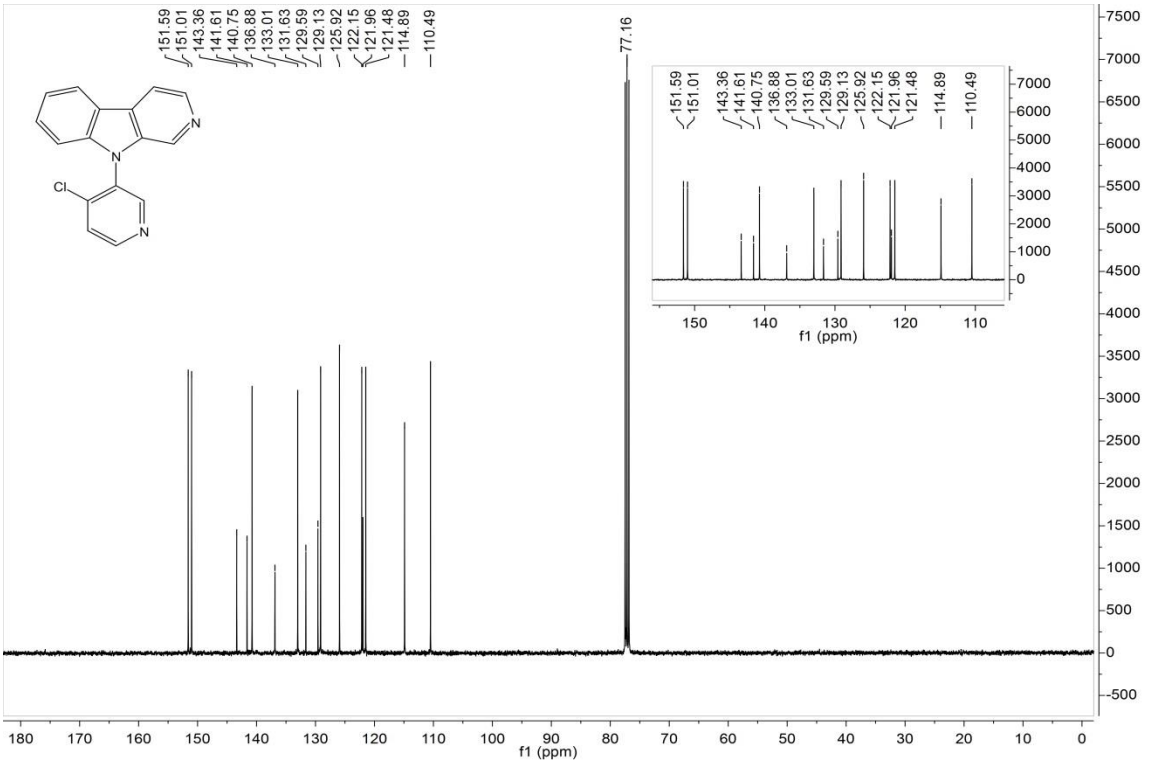


Figure S36. ^{13}C NMR spectrum of **6,10PyCb** in $CDCl_3$.

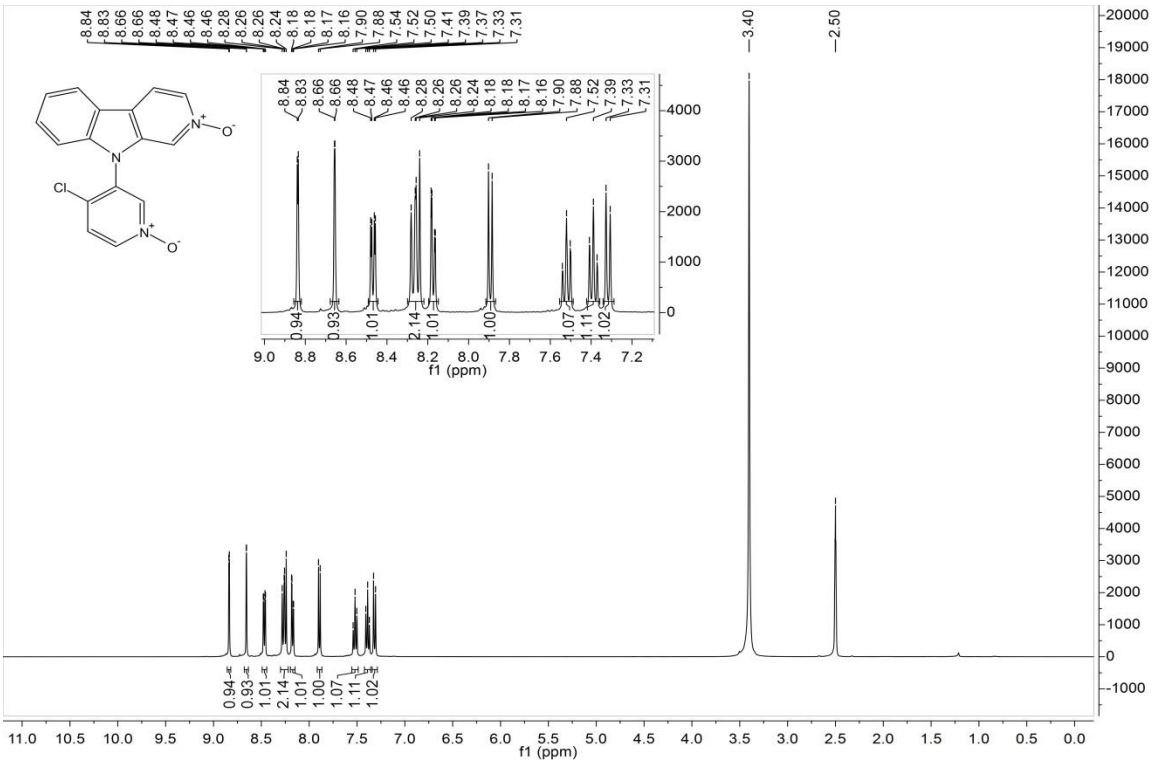


Figure S37. ^{1}H NMR spectrum of **6,10PyCb-Ox** in DMSO.

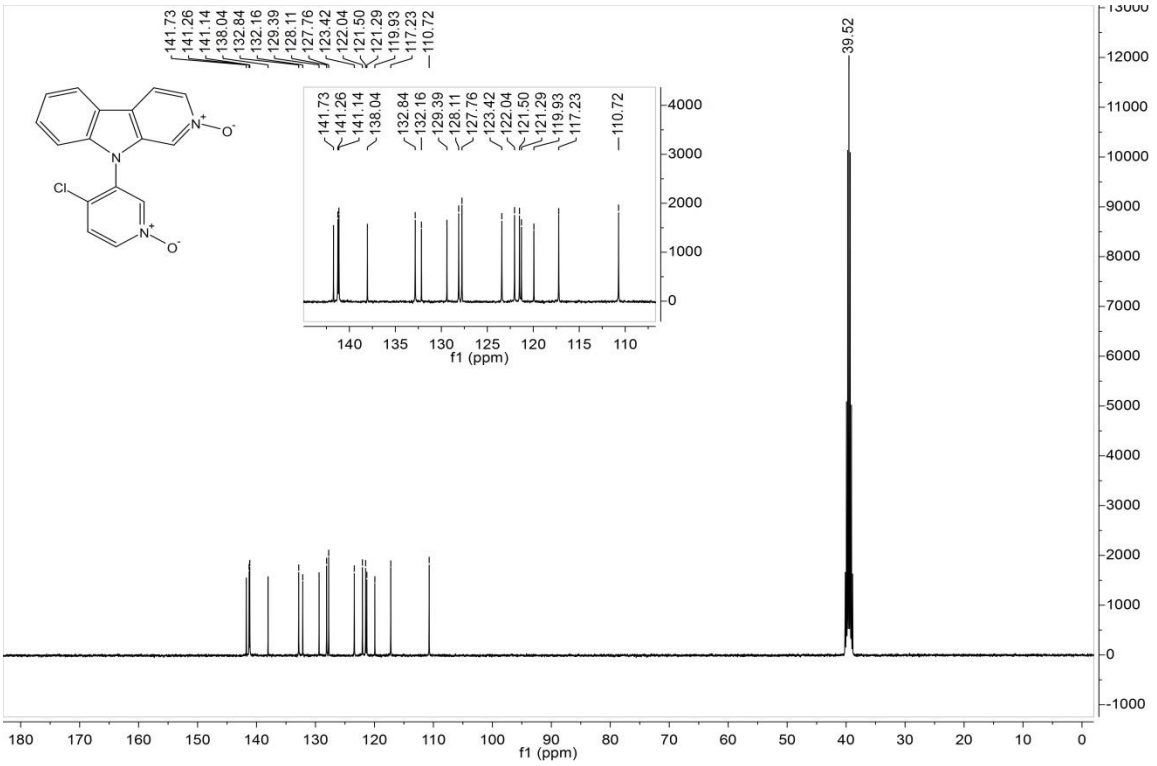


Figure S38. ^{13}C NMR spectrum of **6,10PyCb-Ox** in DMSO.

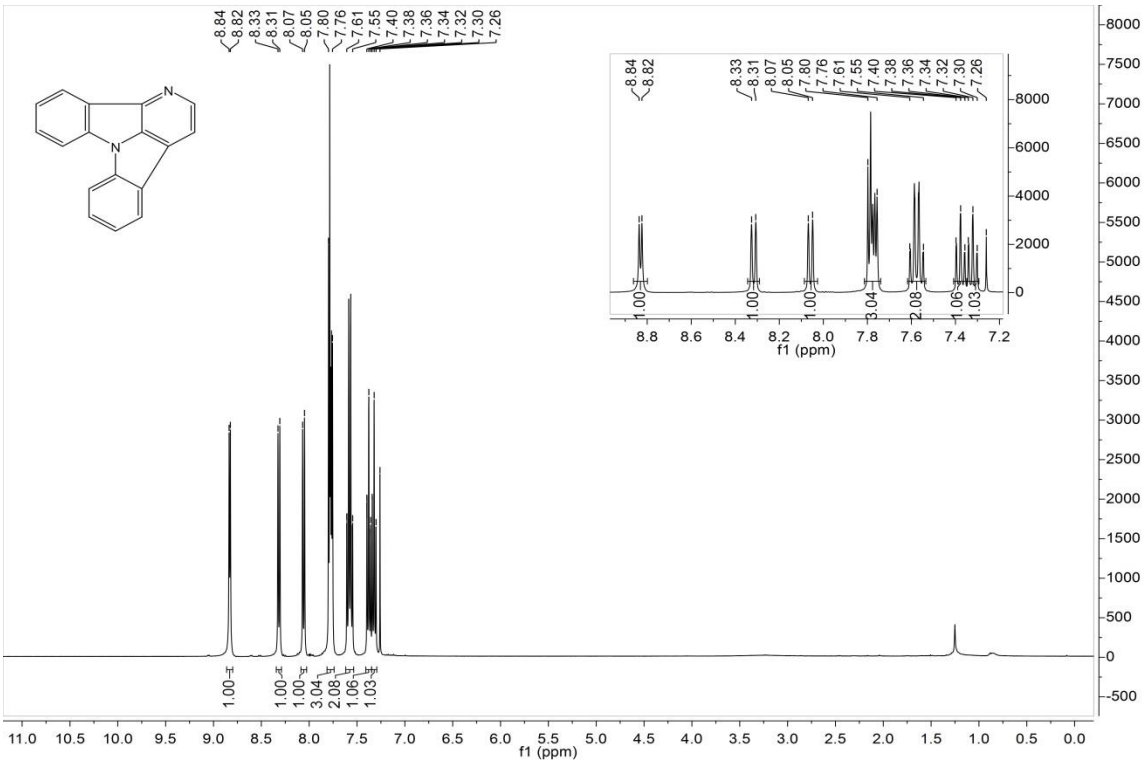


Figure S39. ^{1}H NMR spectrum of **1NICz** in $CDCl_3$.

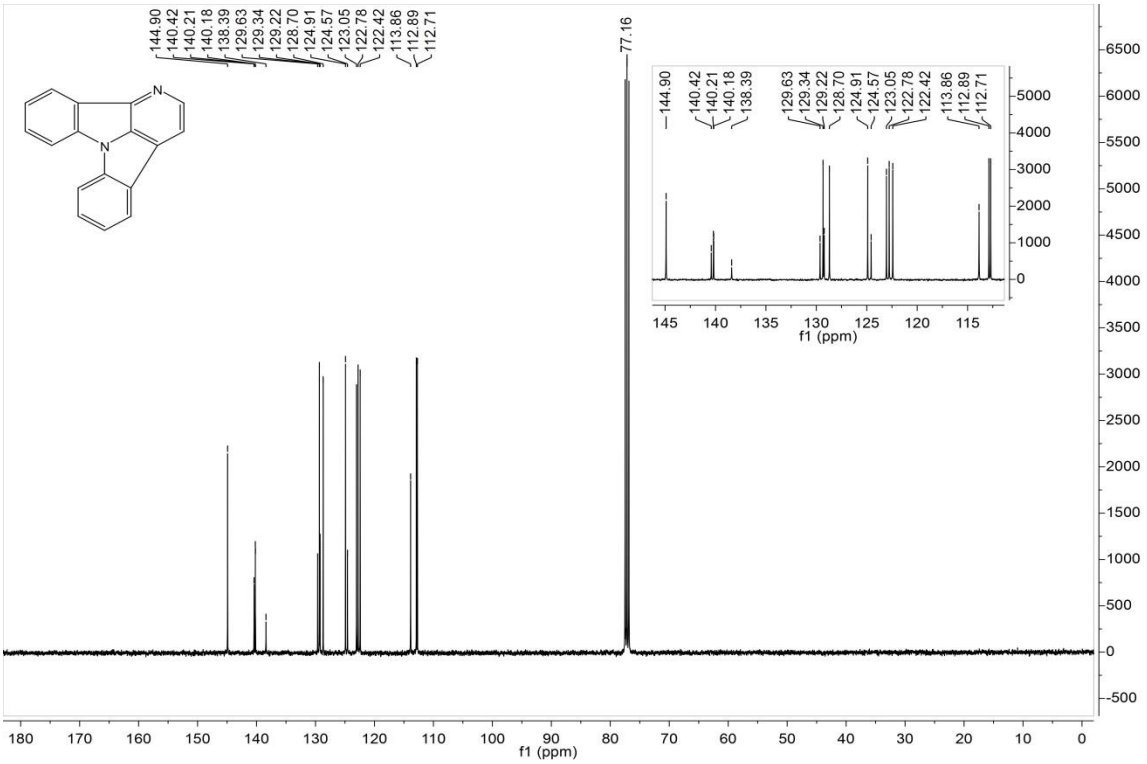


Figure S40. ^{13}C NMR spectrum of **1NICz** in $CDCl_3$.

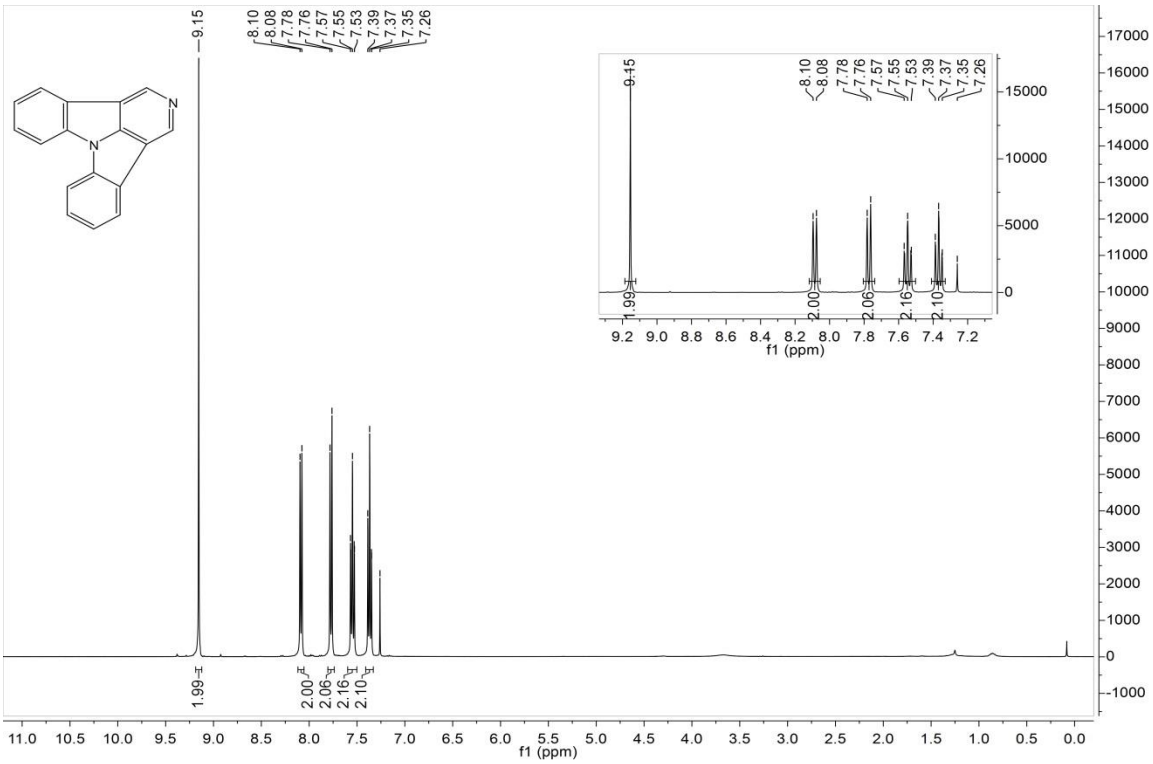


Figure S41. ^{1}H NMR spectrum of **2NICz** in $CDCl_3$.

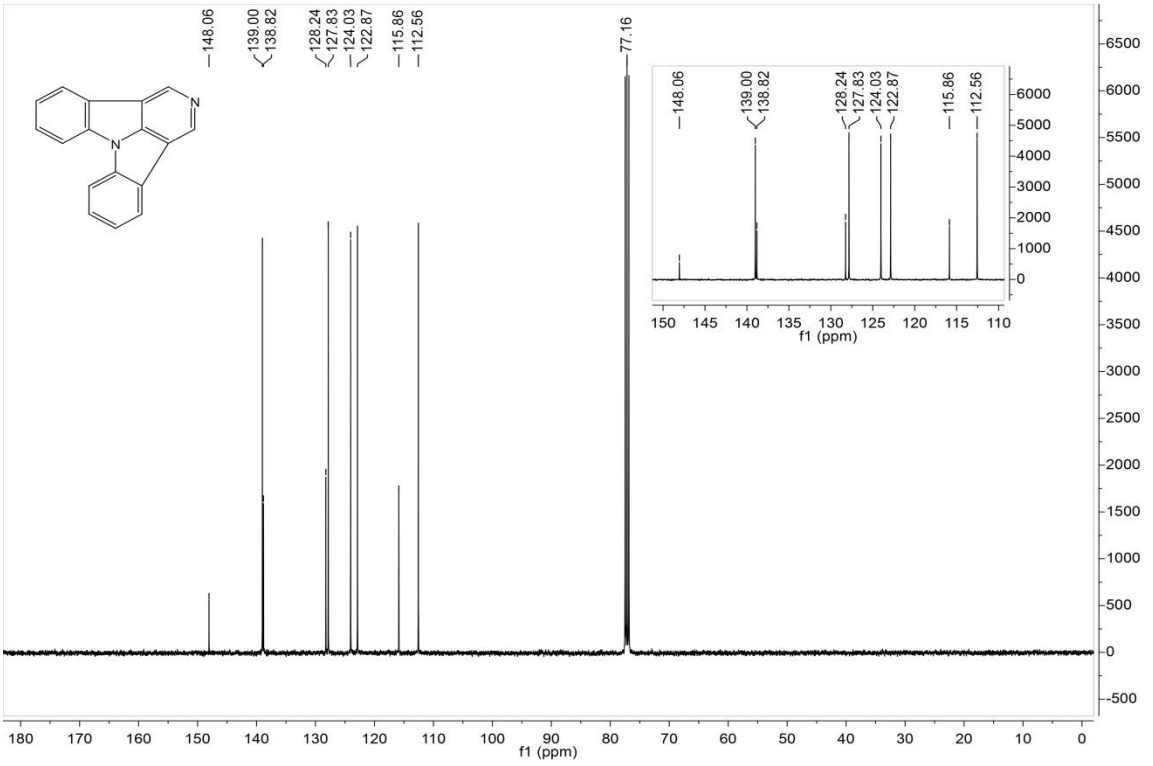


Figure S42. ^{13}C NMR spectrum of **2NICz** in $CDCl_3$.

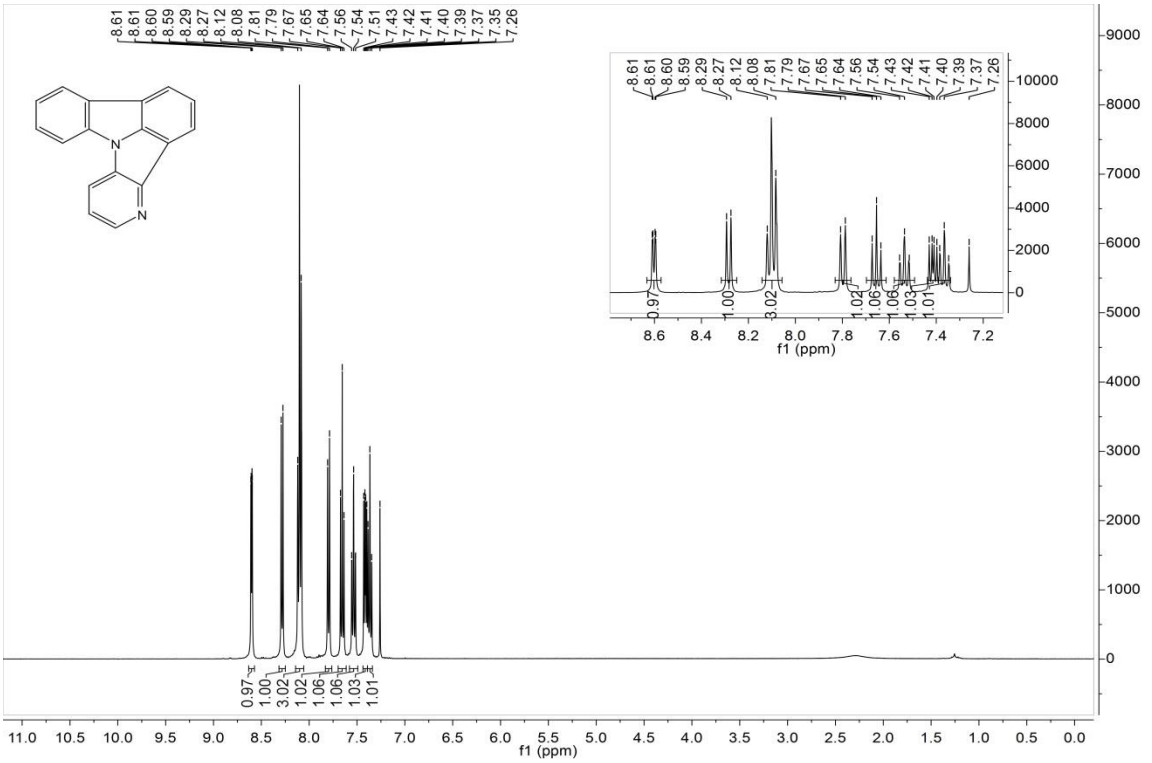


Figure S43. ^{1}H NMR spectrum of **4NICz** in $CDCl_3$.

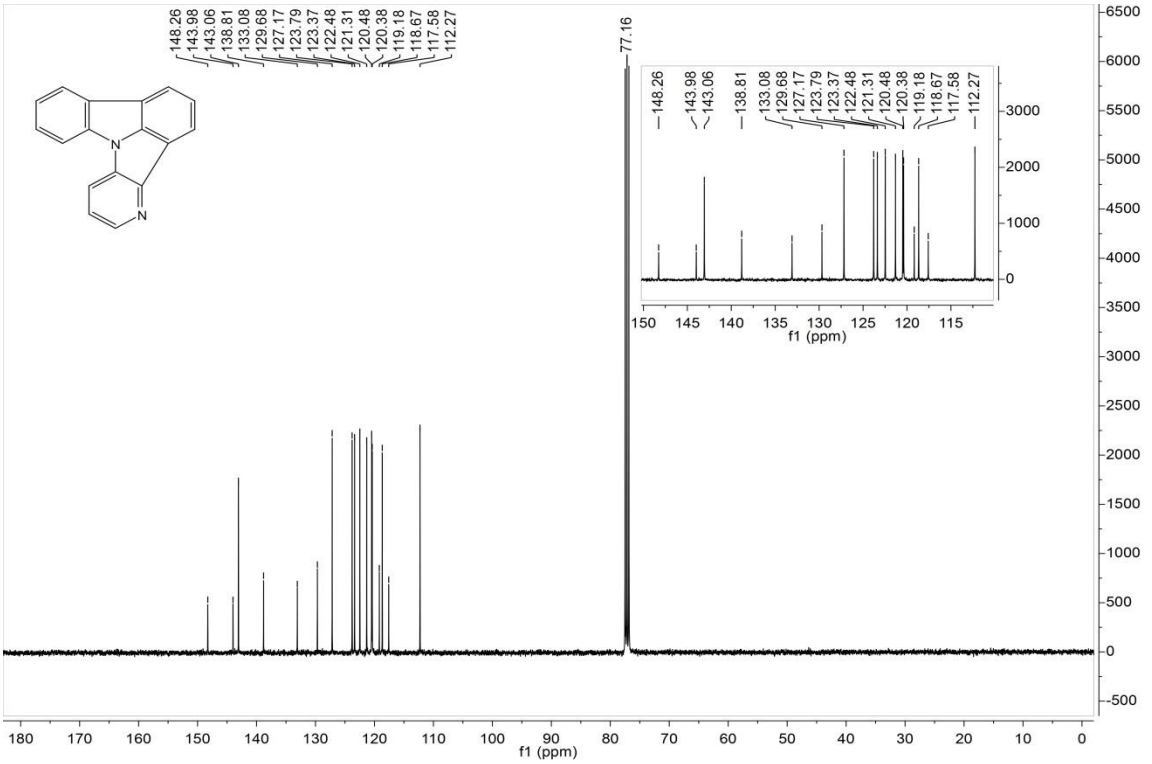


Figure S44. ^{13}C NMR spectrum of **4NICz** in $CDCl_3$.

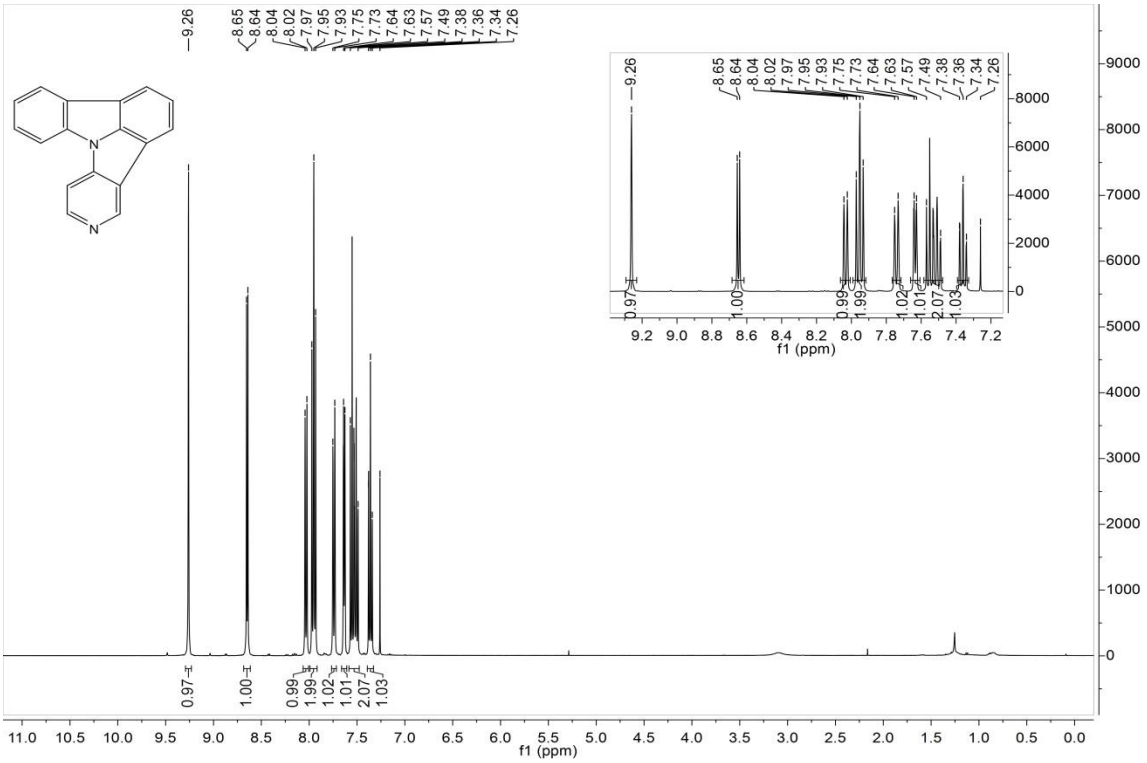


Figure S45. ^{1}H NMR spectrum of **5NICz** in $CDCl_3$.

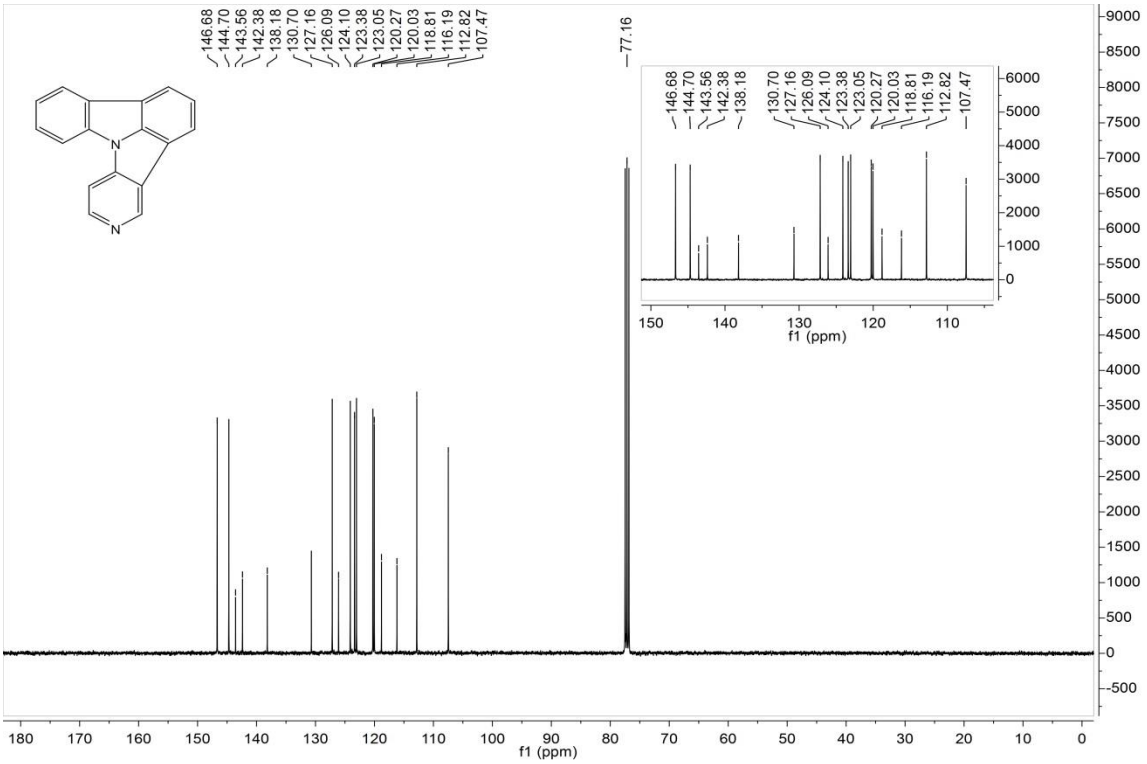


Figure S46. ^{13}C NMR spectrum of **5NICz** in $CDCl_3$.

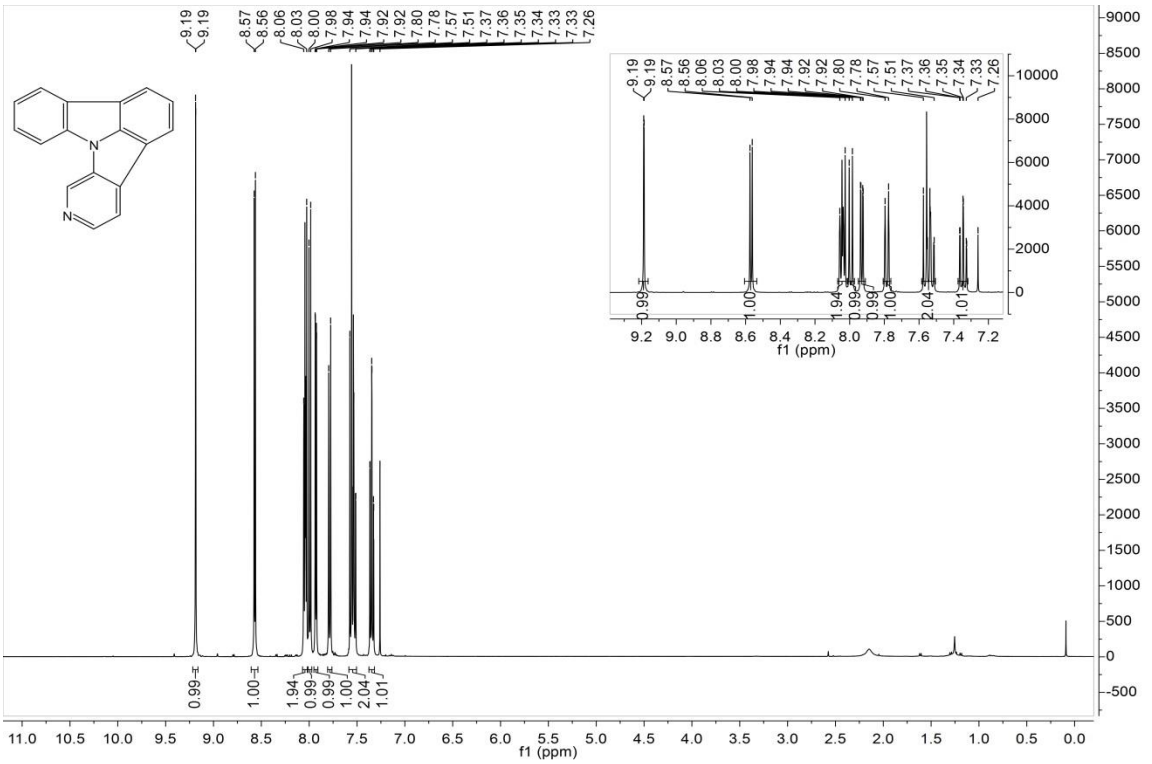


Figure S47. ^{1}H NMR spectrum of **6NICz** in $CDCl_3$.

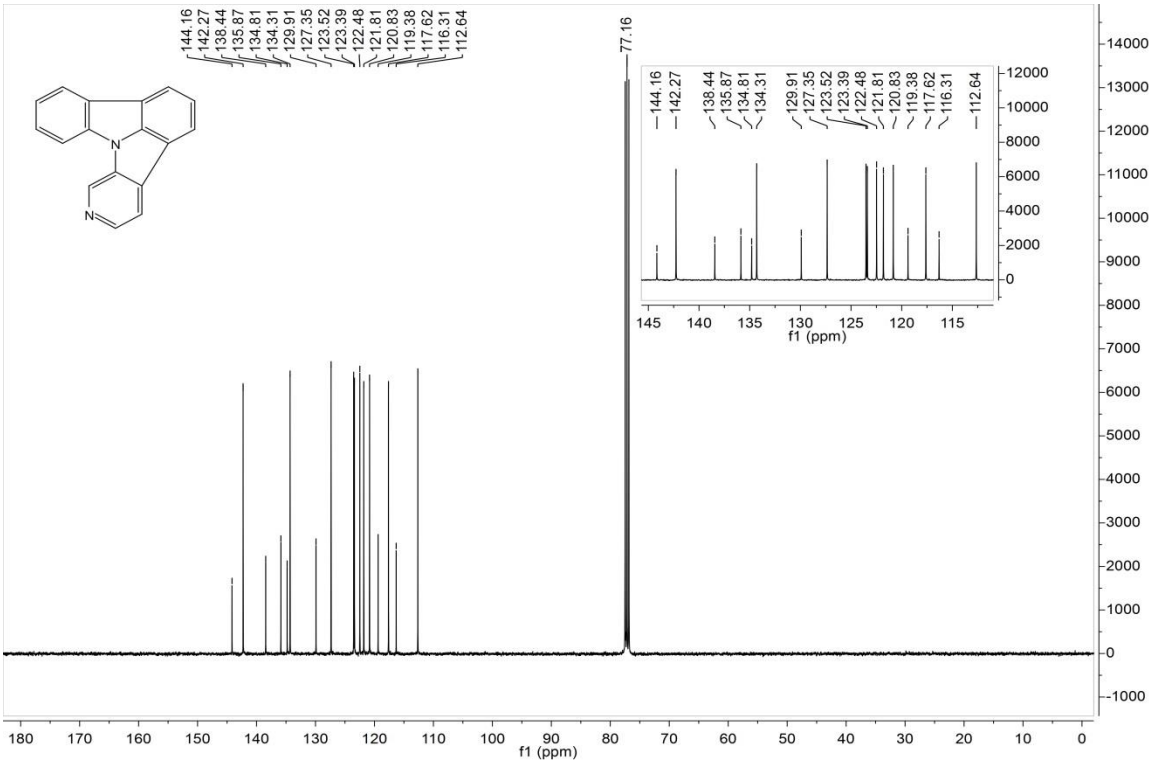


Figure S48. ^{13}C NMR spectrum of **6NICz** in $CDCl_3$.

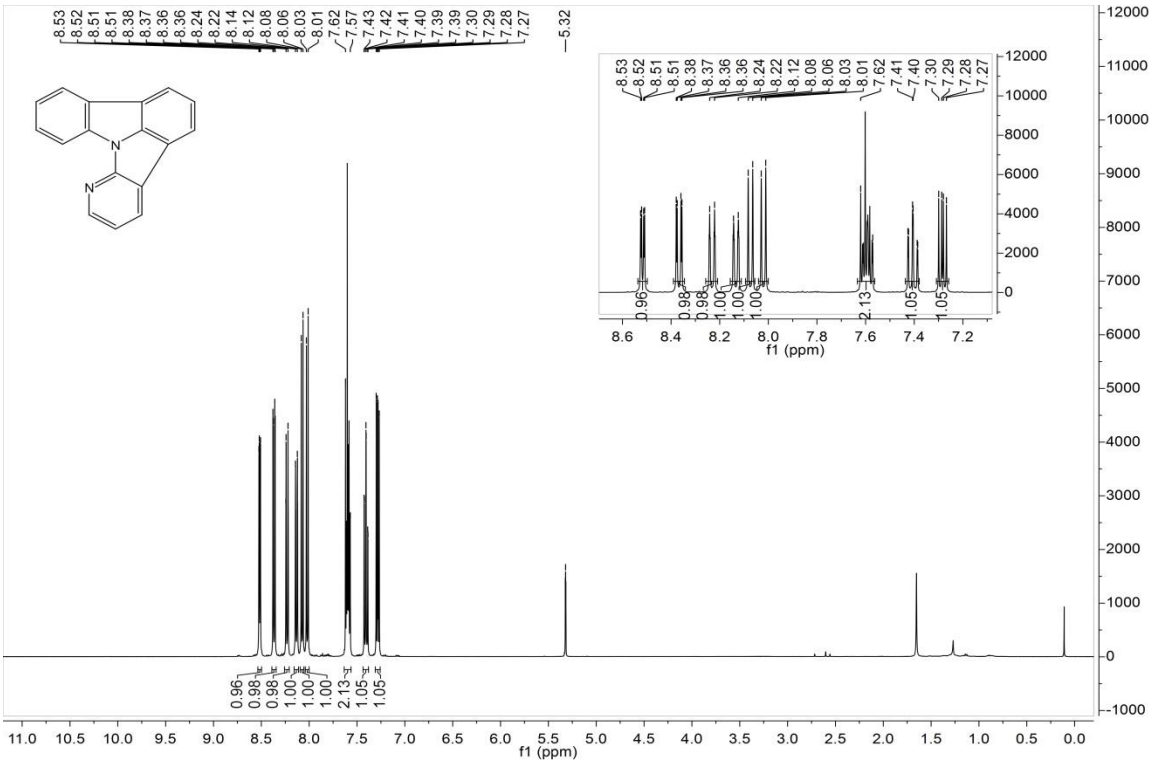


Figure S49. ^{1}H NMR spectrum of **7NICz** in CD_2Cl_2.

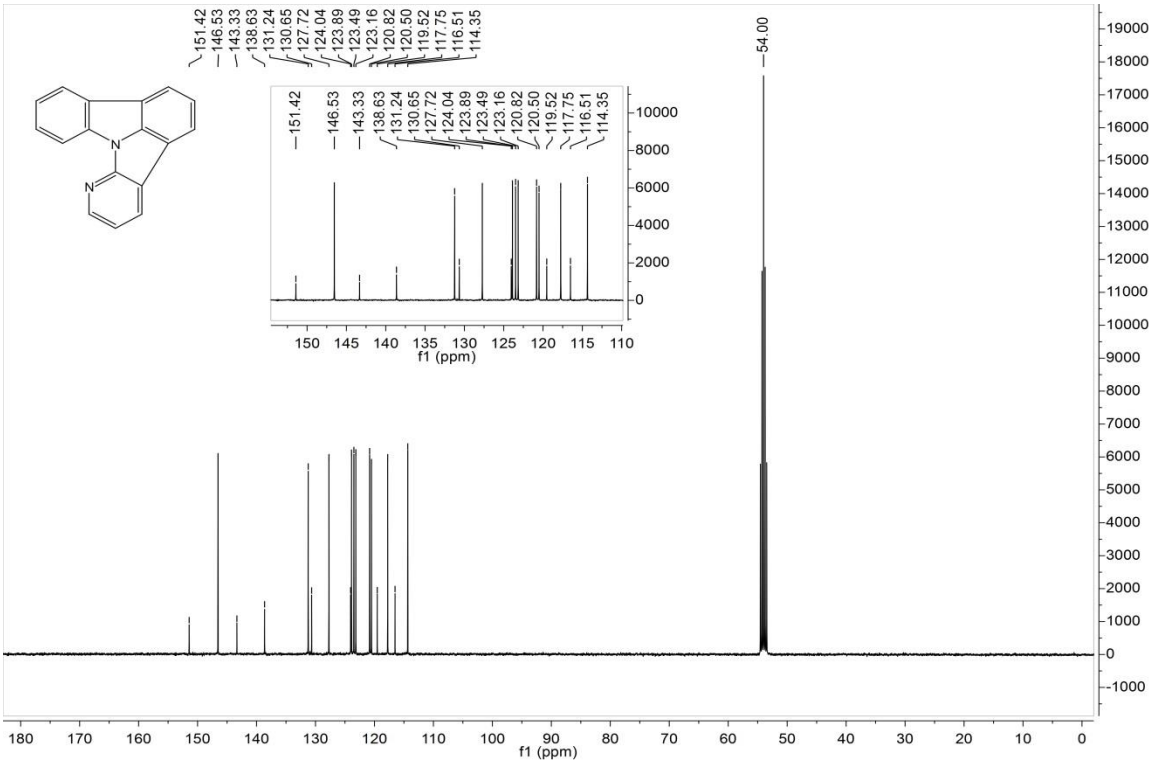


Figure S50. ^{13}C NMR spectrum of **7NICz** in CD_2Cl_2.

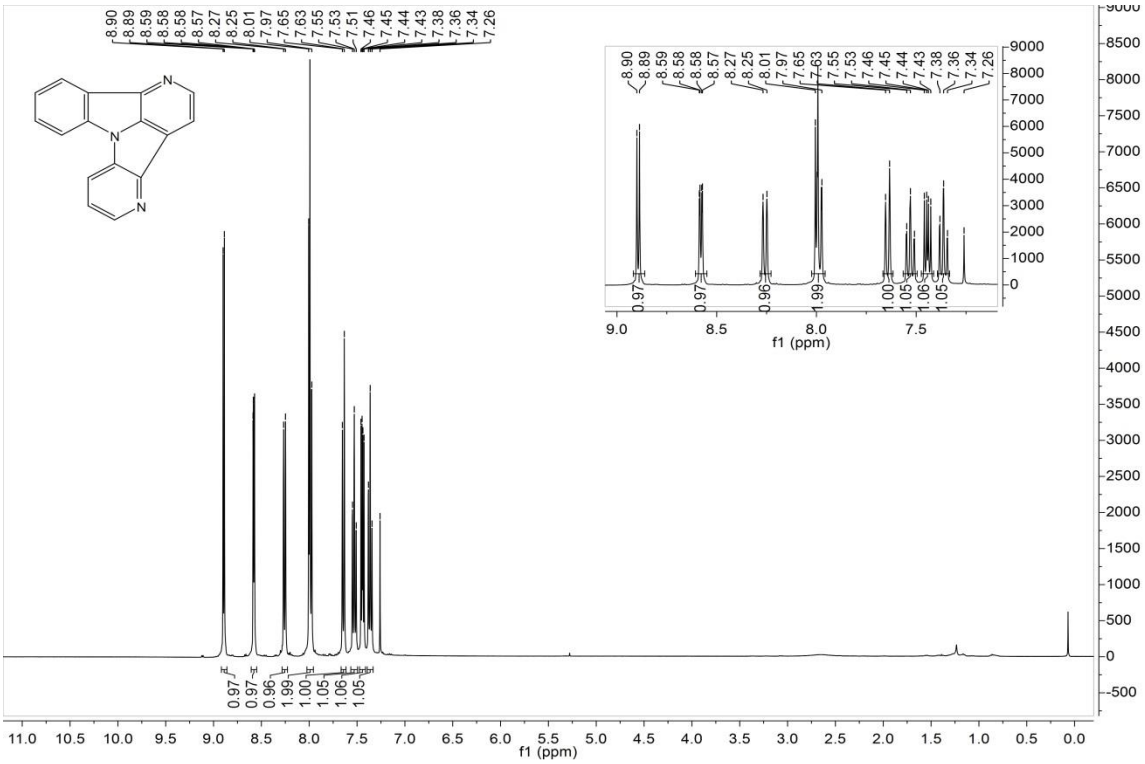


Figure S51. ^{1}H NMR spectrum of **1,4NICz** in $CDCl_3$.

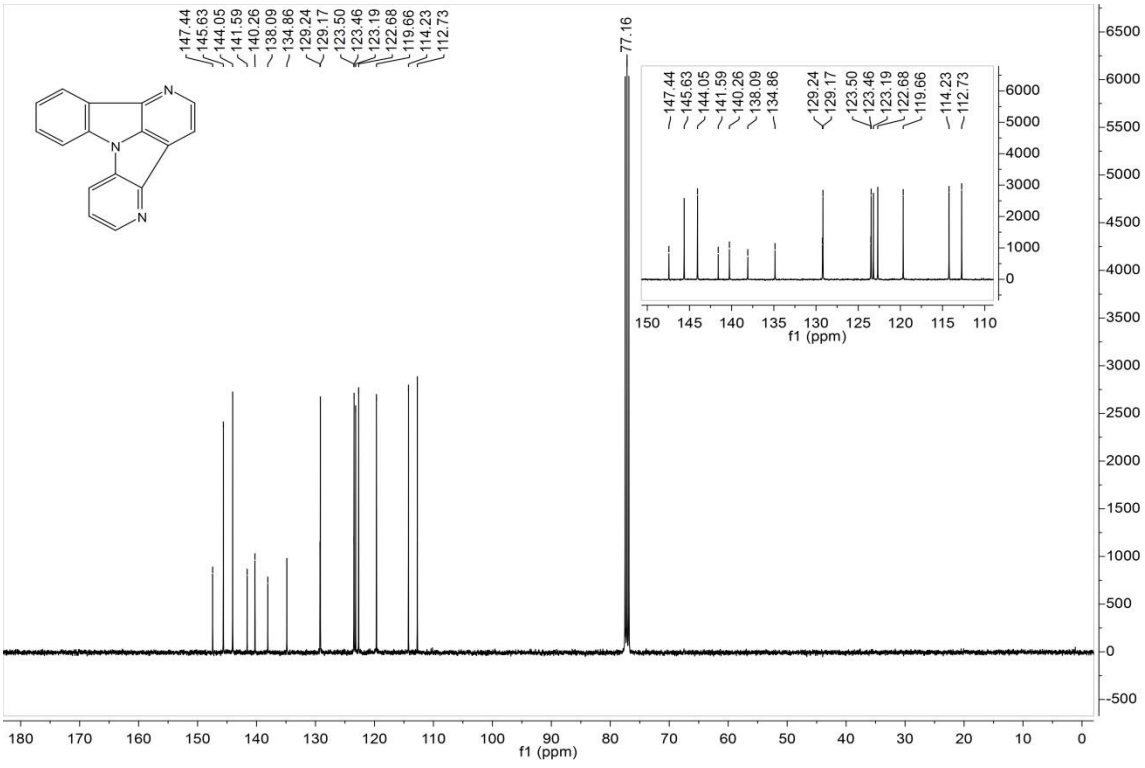


Figure S52. ^{13}C NMR spectrum of **1,4NICz** in $CDCl_3$.

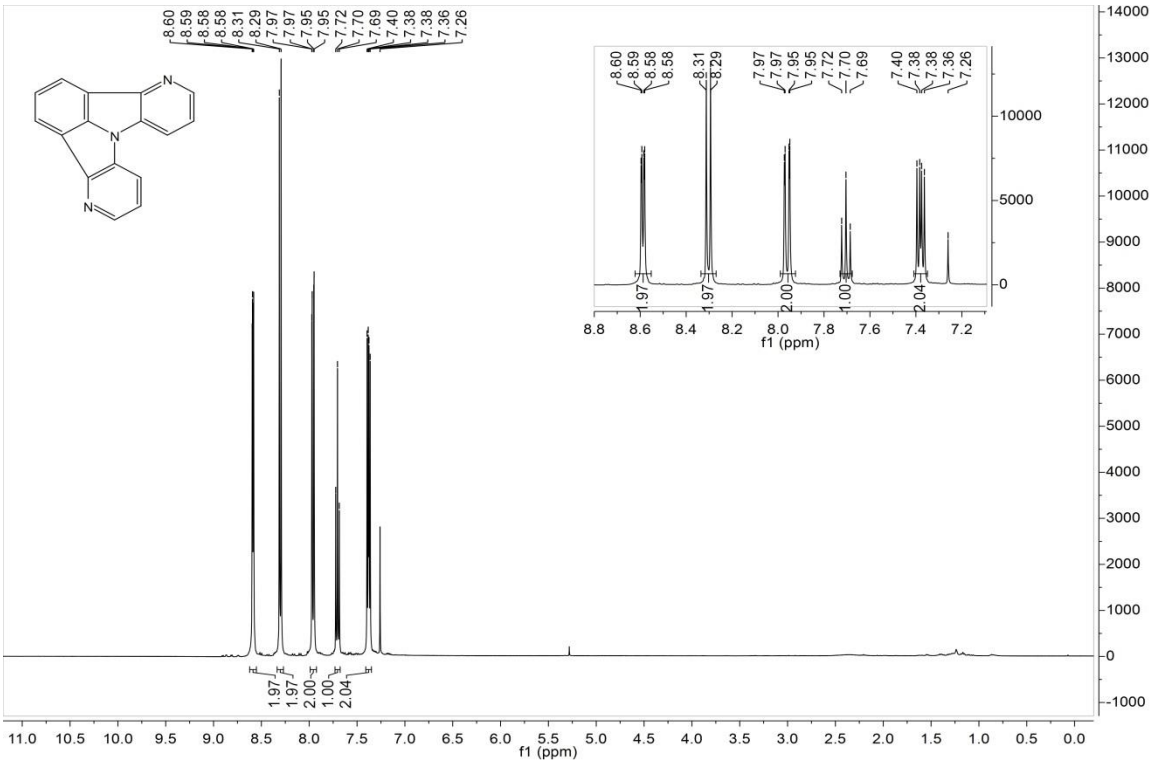


Figure S53. ^{1}H NMR spectrum of **4,12NICz** in $CDCl_3$.

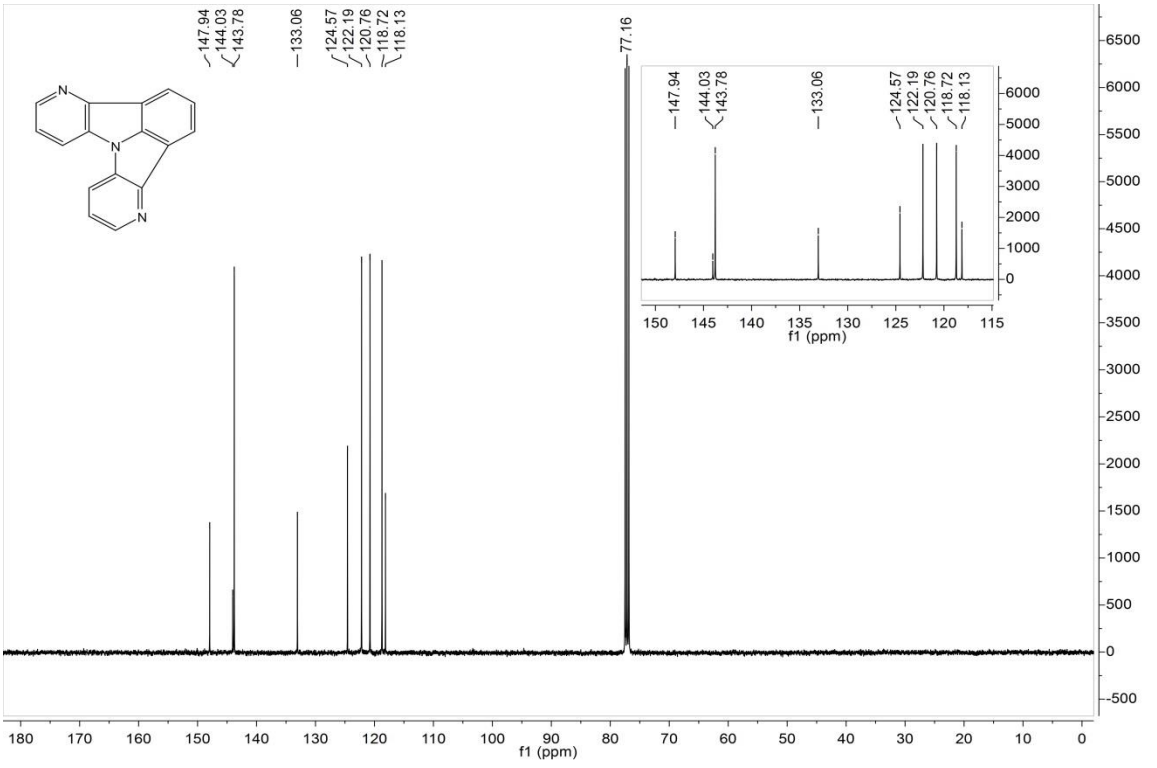


Figure S54. ^{13}C NMR spectrum of **4,12NICz** in $CDCl_3$.

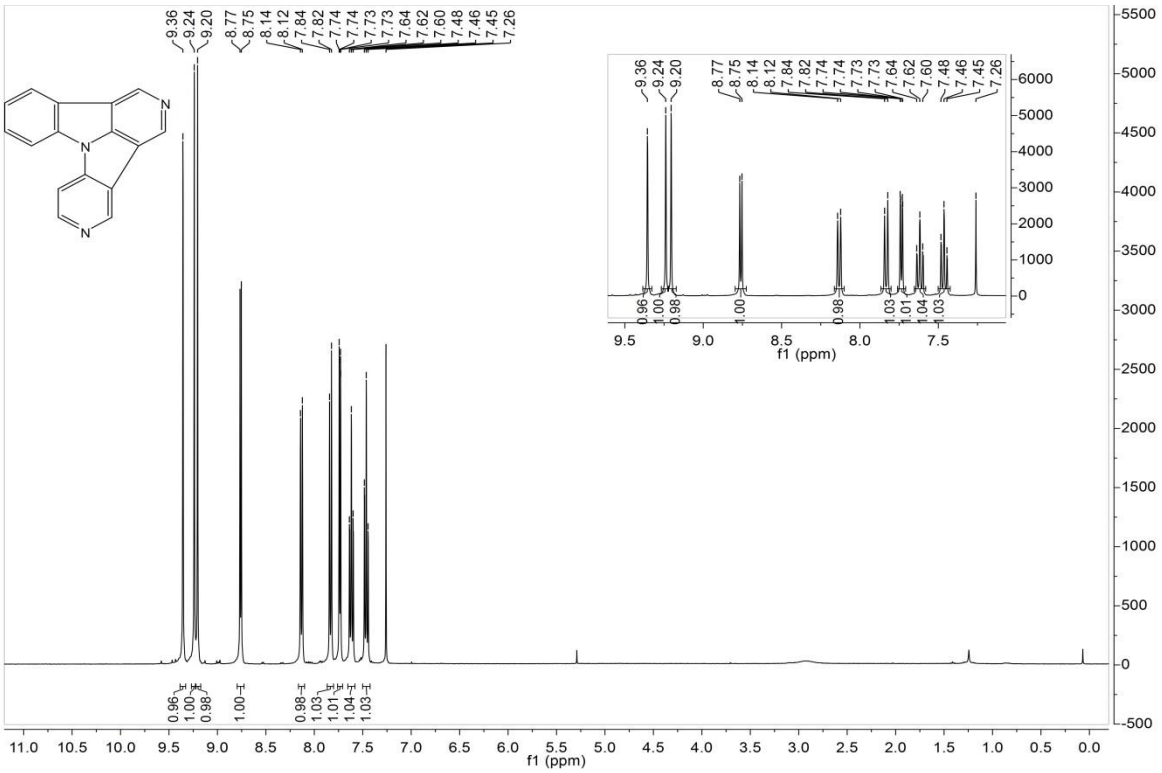


Figure S55. ^{1}H NMR spectrum of **2,5NICz** in $CDCl_3$.

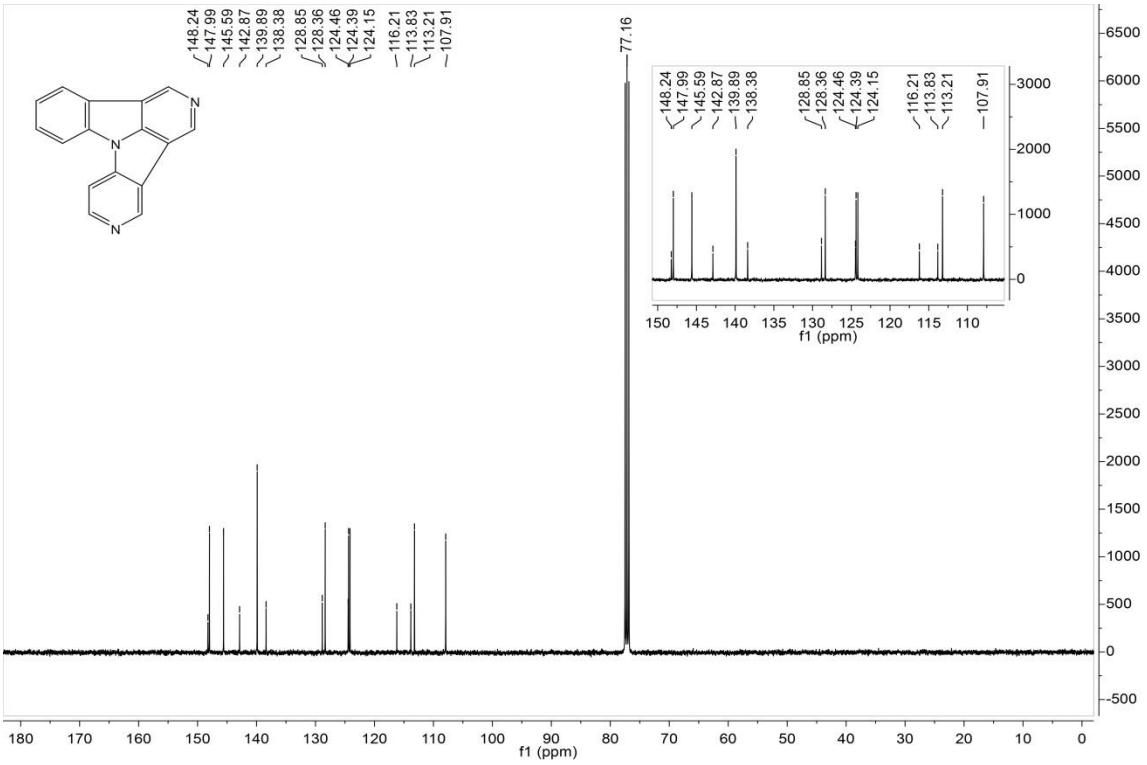


Figure S56. ^{13}C NMR spectrum of **2,5NICz** in $CDCl_3$.

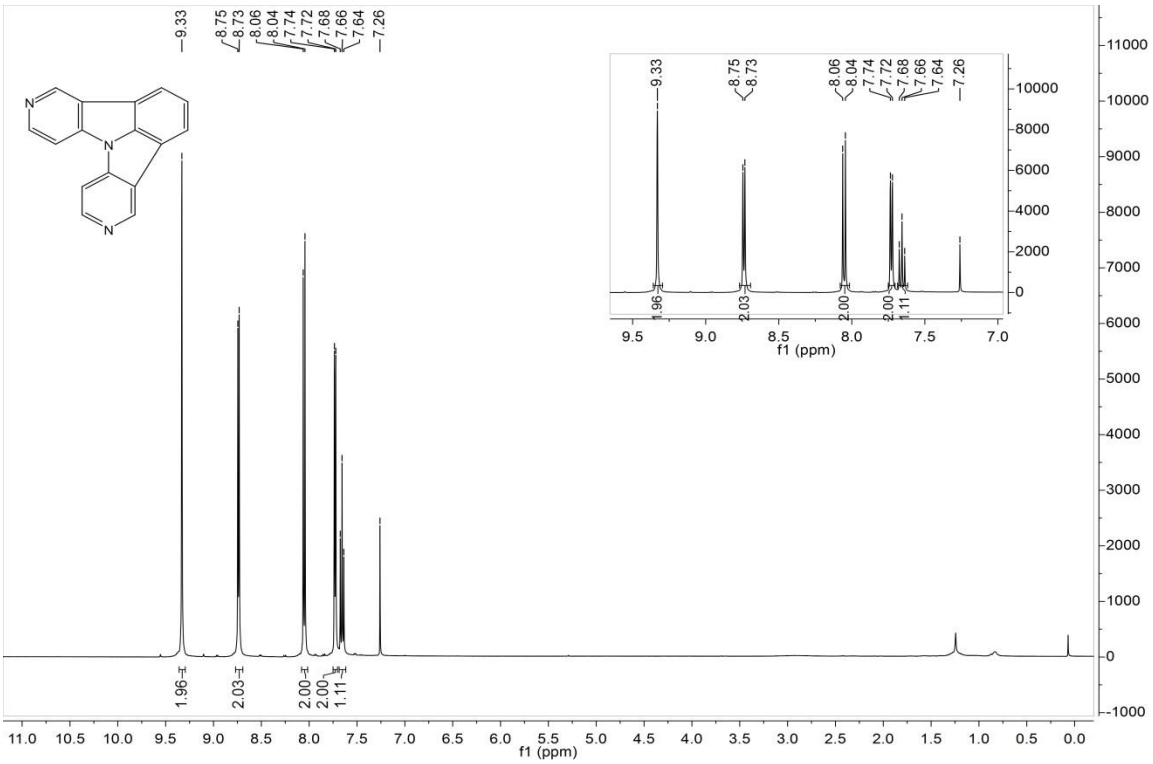


Figure S57. ^{1}H NMR spectrum of **5,11NICz** in $CDCl_3$.

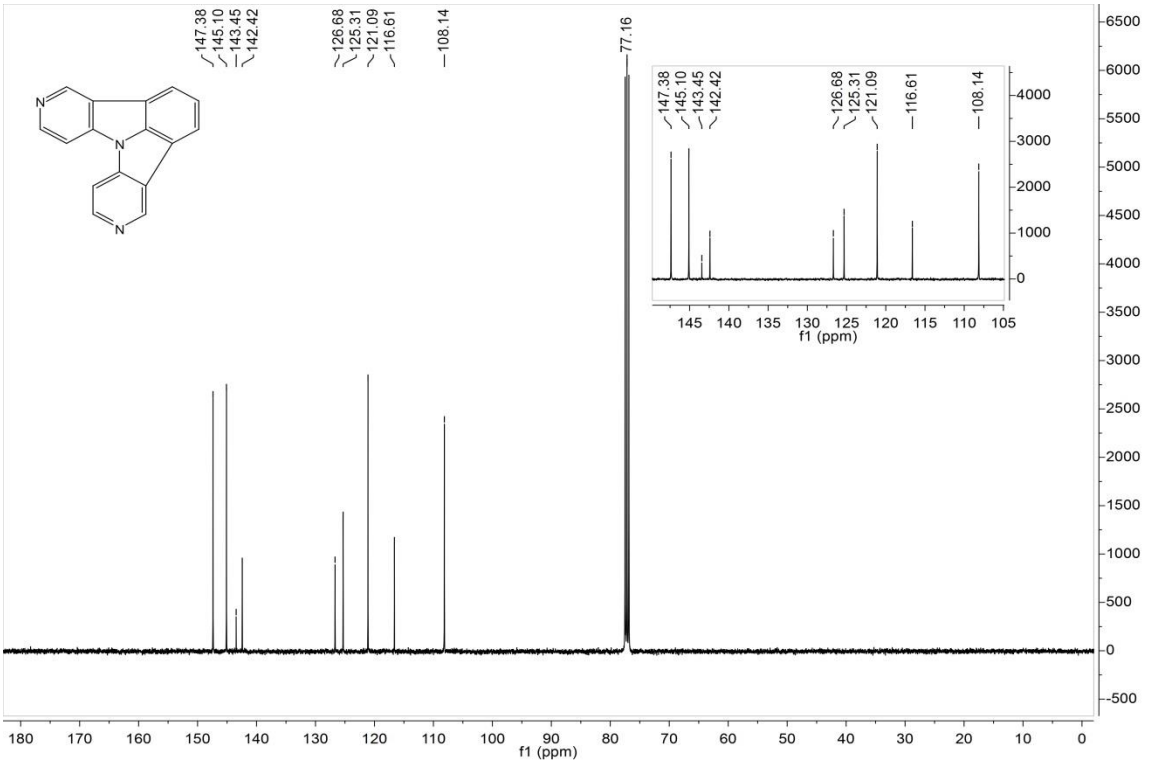


Figure S58. ^{13}C NMR spectrum of **5,11NICz** in $CDCl_3$.

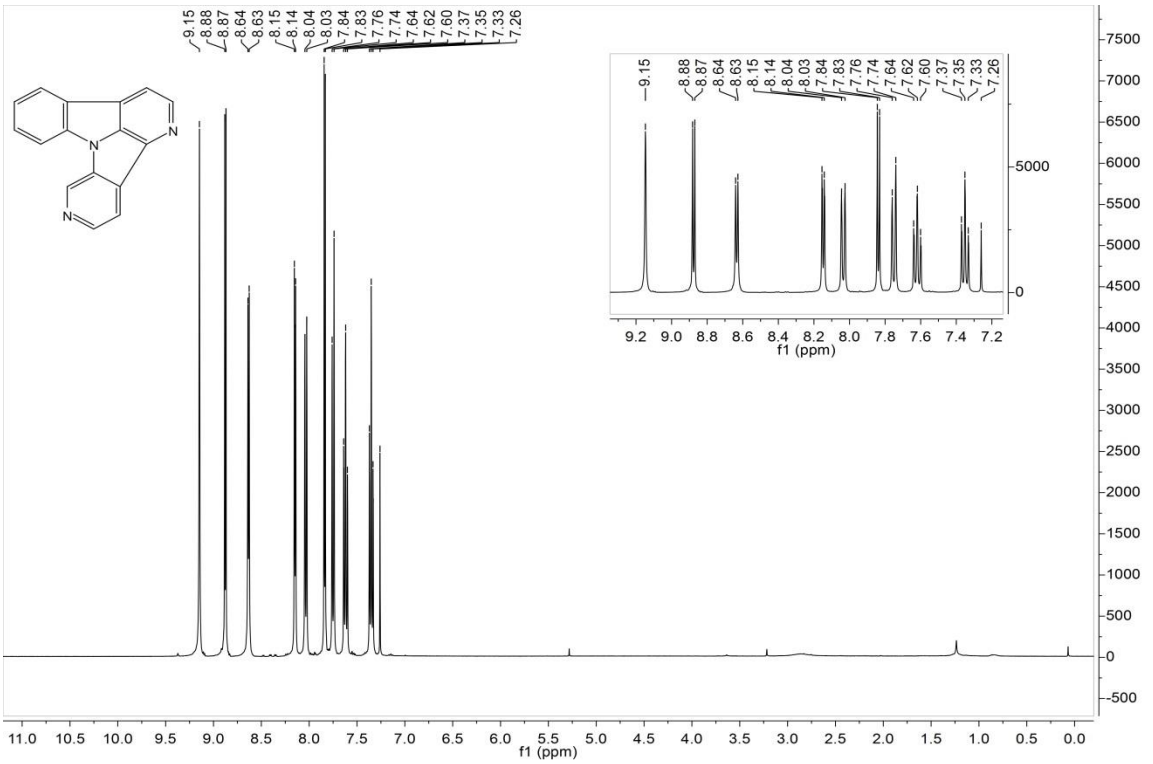


Figure S59. ^{1}H NMR spectrum of **1,10NICz** in $CDCl_3$.

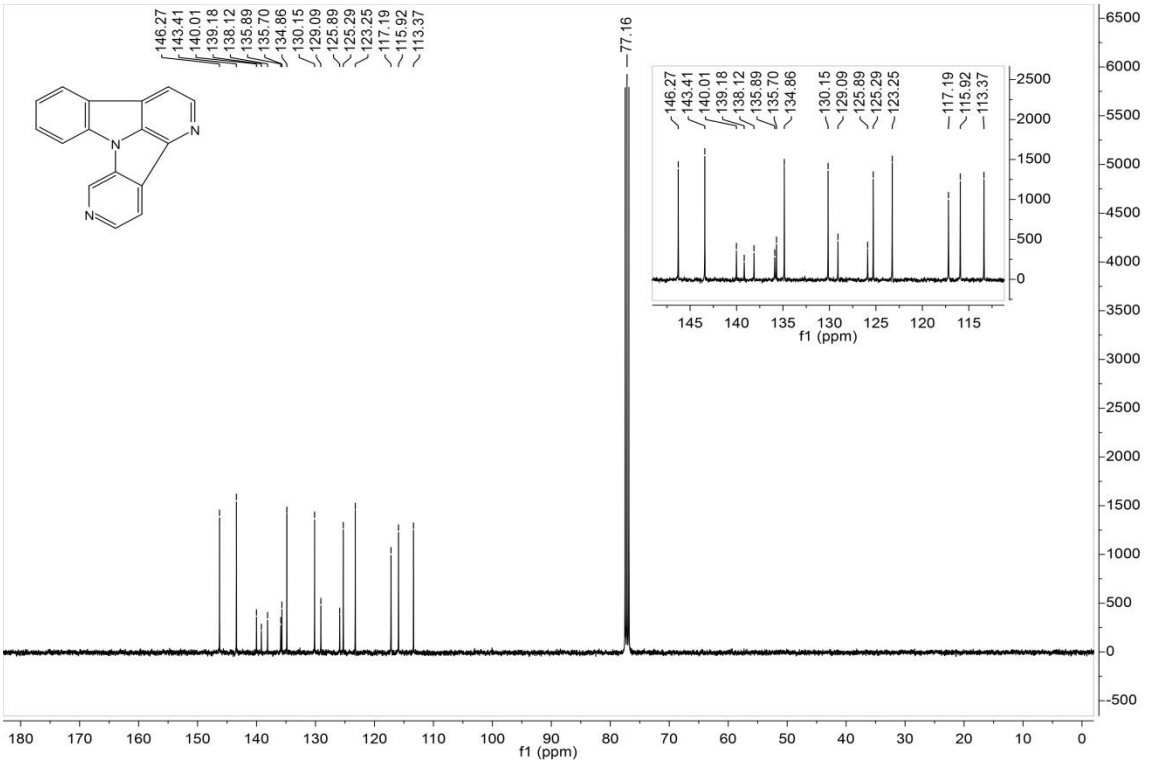


Figure S60. ^{13}C NMR spectrum of **1,10NICz** in $CDCl_3$.

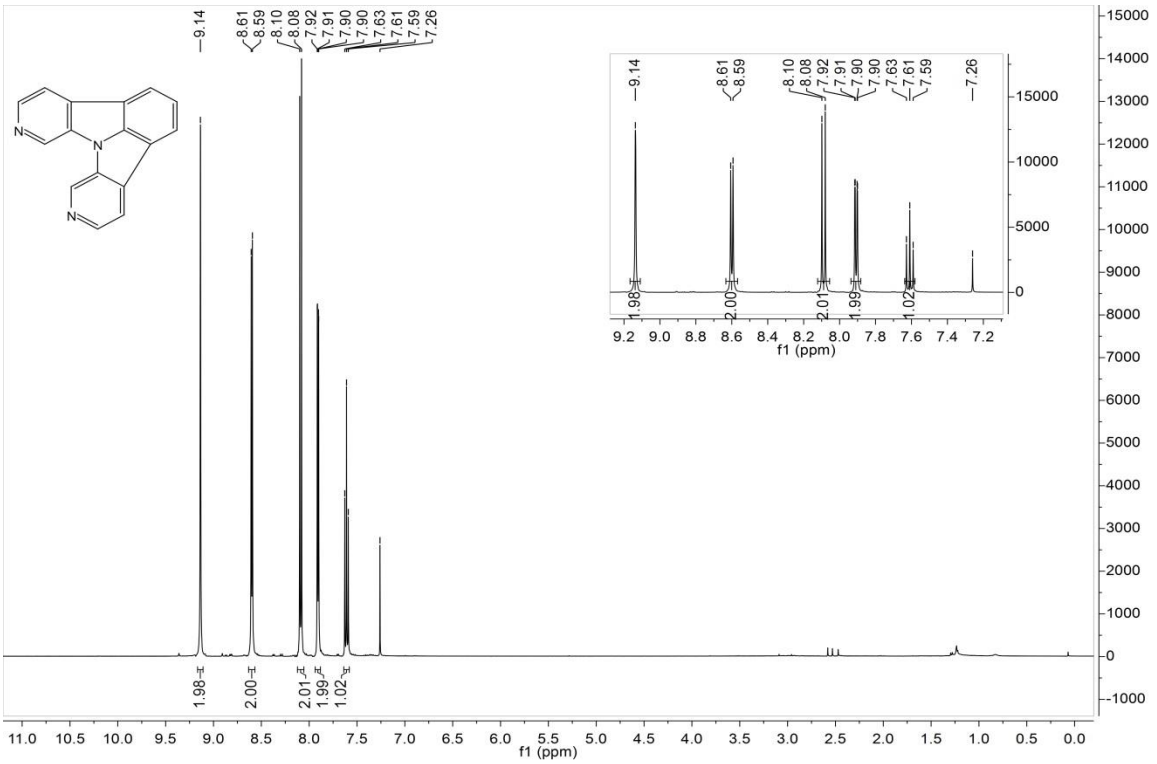


Figure S61. ^{1}H NMR spectrum of **6,10NICz** in $CDCl_3$.

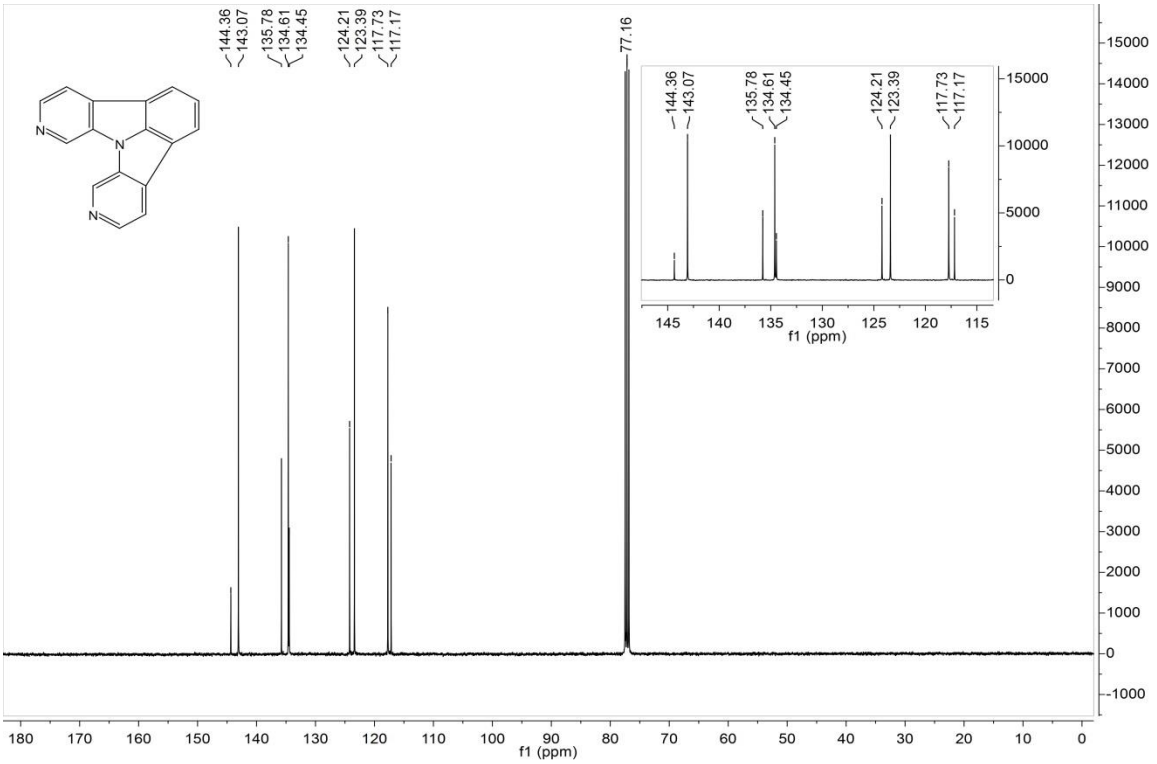


Figure S62. ^{13}C NMR spectrum of **6,10NICz** in $CDCl_3$.

4 Additional Screening results

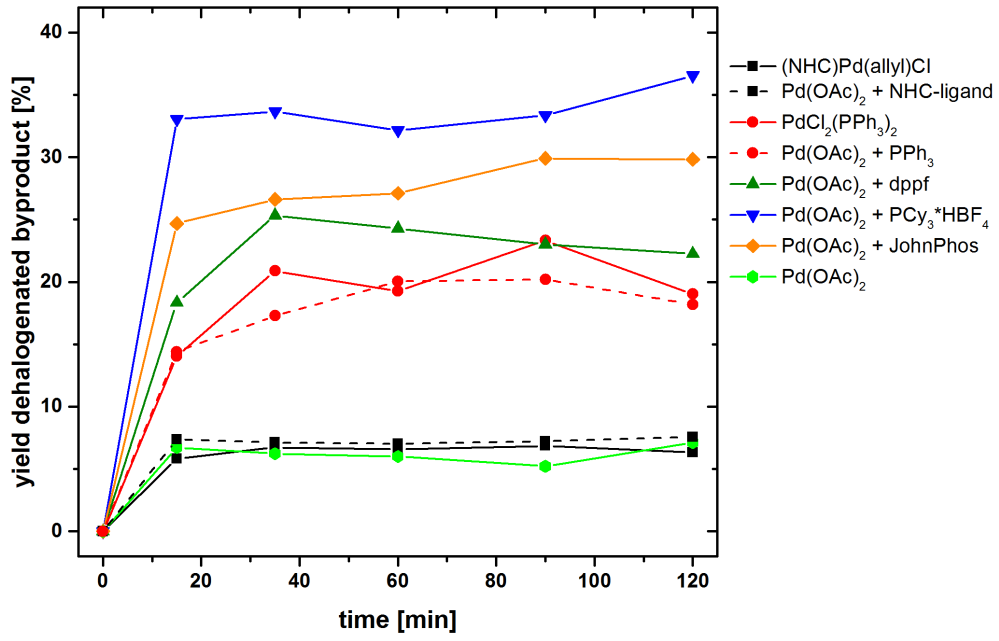


Figure S63. Formation of dehalogenated byproduct during C-H activation of bromo-**4PCz** towards **4NICz** applying different catalysts. Reaction conditions: bromo-**4PCz** (0.025 mmol), K_2CO_3 (2 eq.), catalyst (10 mol%) and ligand (12 mol%: NHC, dppf; 22 mol%: PPh_3, PCy_3*HBF_4, JohnPhos), DMA, 130 °C.

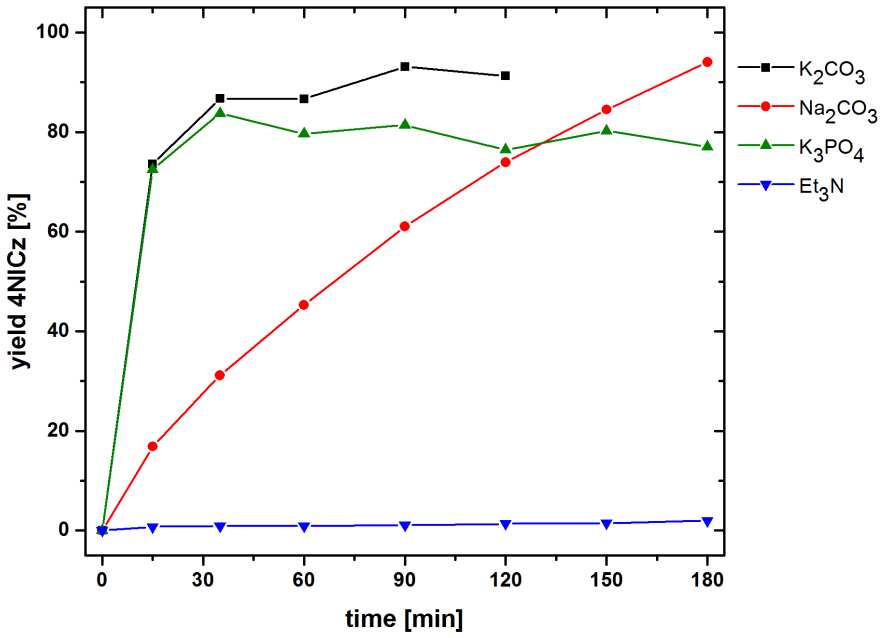


Figure S64. C-H activation of bromo-**4PCz** towards **4NICz** applying different bases. Reaction conditions: bromo-**4PCz** (0.025 mmol), base (2 eq.), (NHC)Pd(allyl)Cl (10 mol%), DMA, 130 °C.

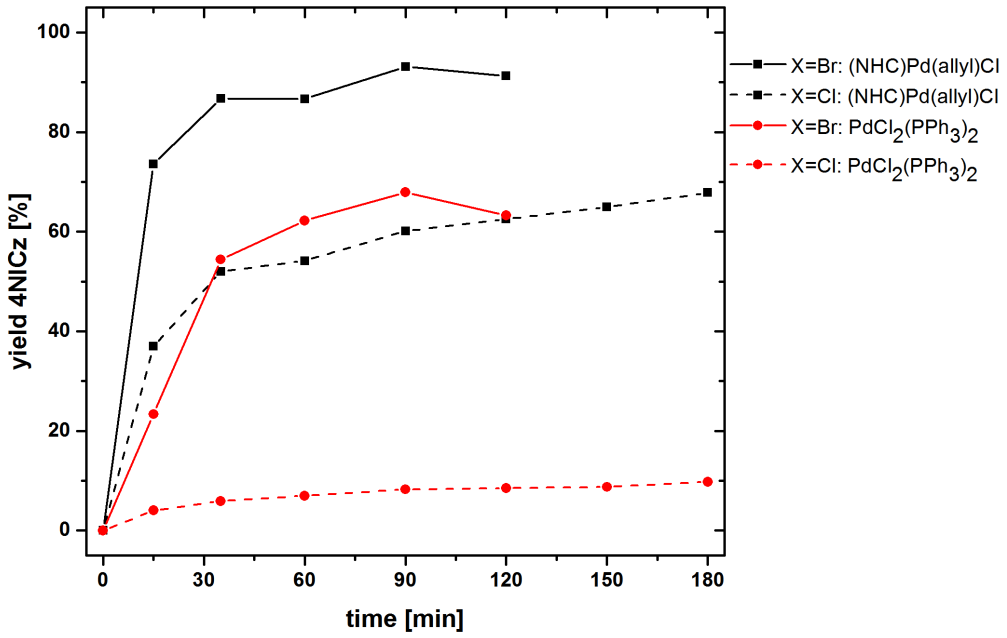


Figure S65. C-H activation towards **4NICz** applying bromine and chlorine precursor. Reaction conditions: **4PCz** (0.025 mmol), K_2CO_3 (2 eq.), (NHC)Pd(allyl)Cl (10 mol%), DMA, 130 °C.

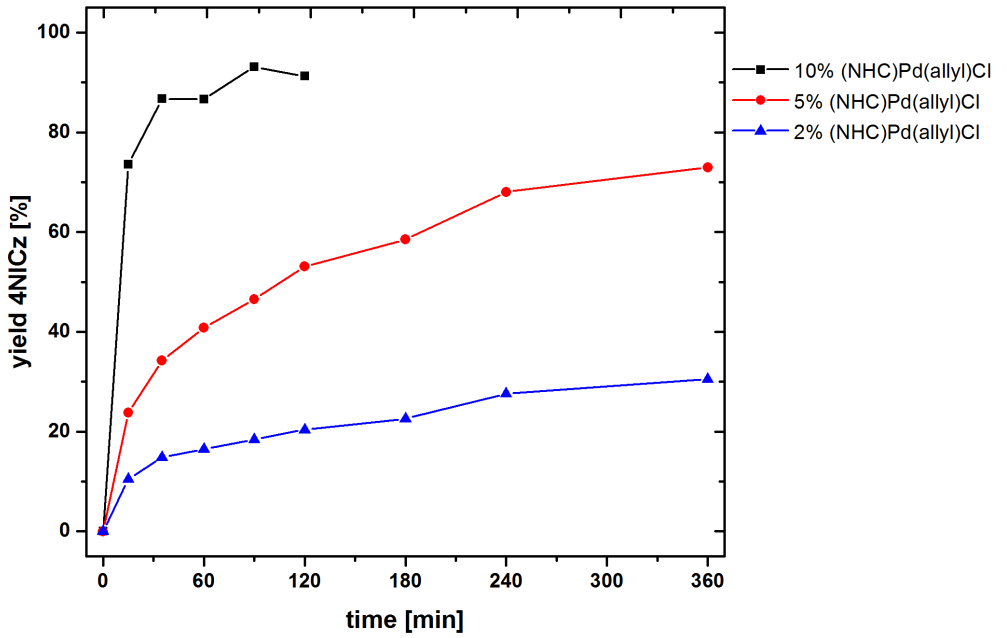


Figure S66. C-H activation of bromo-**4PCz** towards **4NICz** applying different catalyst amounts. Reaction conditions: bromo-**4PCz** (0.025 mmol), K_2CO_3 (2 eq.), (NHC)Pd(allyl)Cl (2 – 10 mol%), DMA, 130 °C.

5 Molar attenuation coefficient

Table S1. Molar attenuation coefficients of peak maxima and lowest energy peaks of ICz and the synthesized NICz derivatives.

	maximum[a]		lowest energy peak	
	λ [nm]	ε [L*mol^{-1}*cm^{-1}]	λ [nm]	ε [L*mol^{-1}*cm^{-1}]
ICz	285	38100	363	11120
1NICz	280	16100	372	5660
2NICz	279	16400	344	2840
4NICz	297	22100	362	4820
5NICz	283	24860	351	19300
6NICz	284	25500	373	11640
7NICz	287	24220	357	7380
1,4NICz	294	23620	372	4780
2,5NICz	-[b]	-	341	4040
1,10NICz	283	16300	385	6820
4,12NICz	297	28140	351	4180
5,11NICz	285	12780	343	25160
6,10NICz	280	21060	379	14640

[a] Only peaks >270 nm considered due to possible influence of the solvent. [b] No distinct peak maximum above 270 nm observable.

6 Cyclic Voltammetry

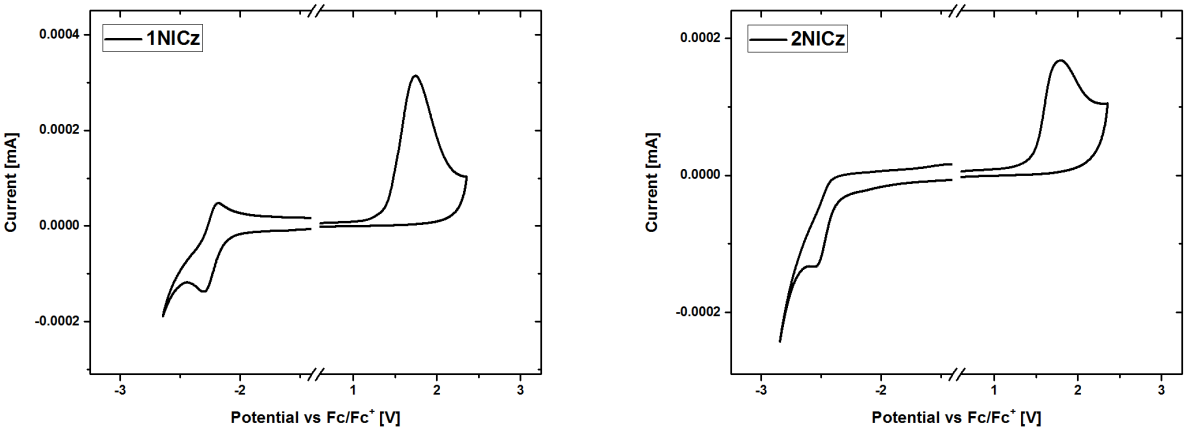


Figure S67. Cyclic voltammograms of **1NICz** (left) and **2NICz** (right).

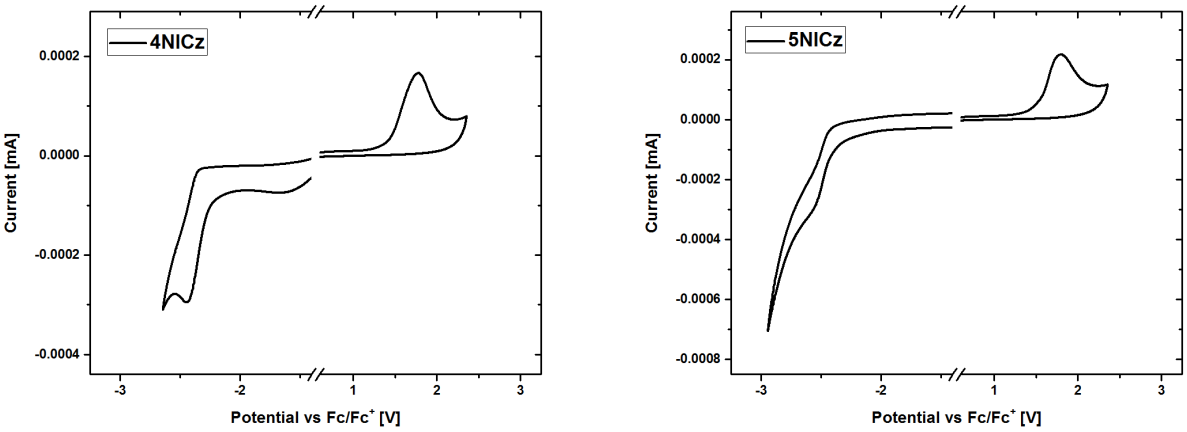


Figure S68. Cyclic voltammograms of **4NICz** (left) and **5NICz** (right).

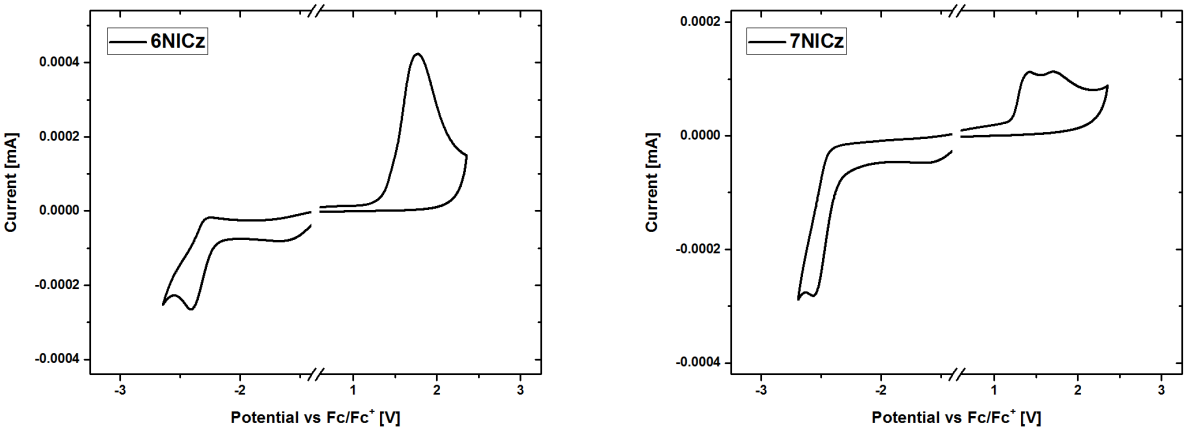


Figure S69. Cyclic voltammograms of **6NICz** (left) and **7NICz** (right).

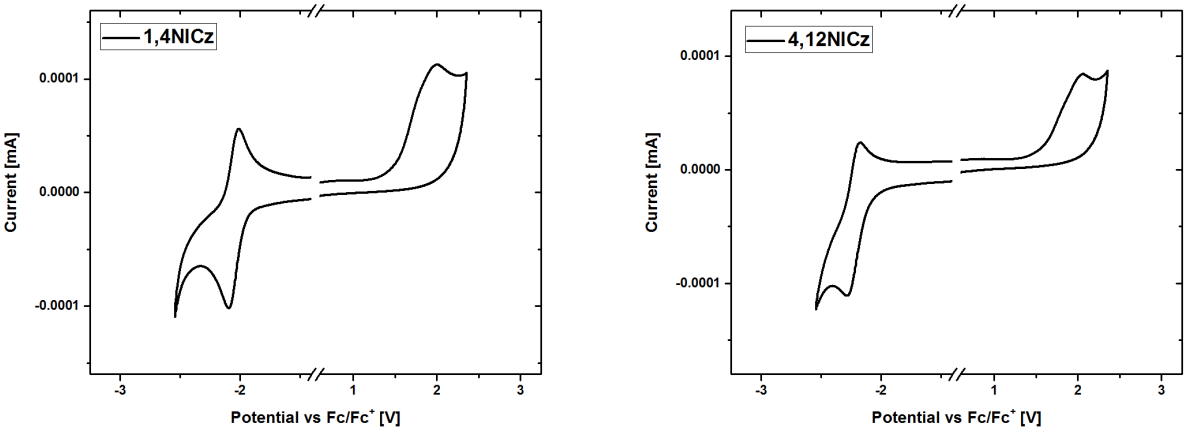


Figure S70. Cyclic voltammograms of **1,4NICz** (left) and **4,12NICz** (right).

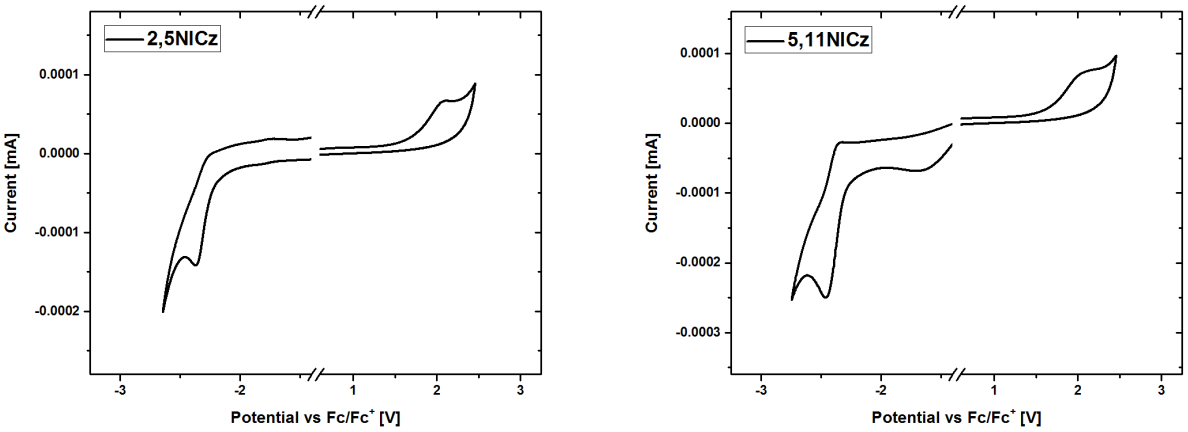


Figure S71. Cyclic voltammograms of **2,5NICz** (left) and **5,11NICz** (right).

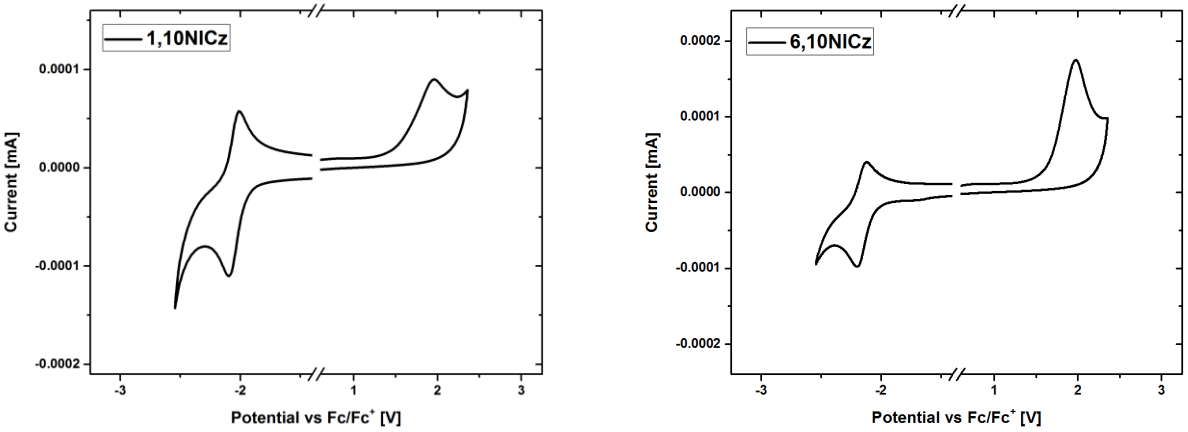


Figure S72. Cyclic voltammograms of **1,10NICz** (left) and **6,10NICz** (right).

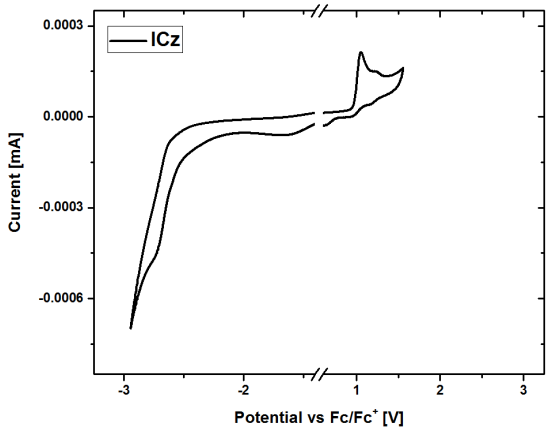


Figure S73. Cyclic voltammogram of **ICz**.

7 HOMO / LUMO energy levels

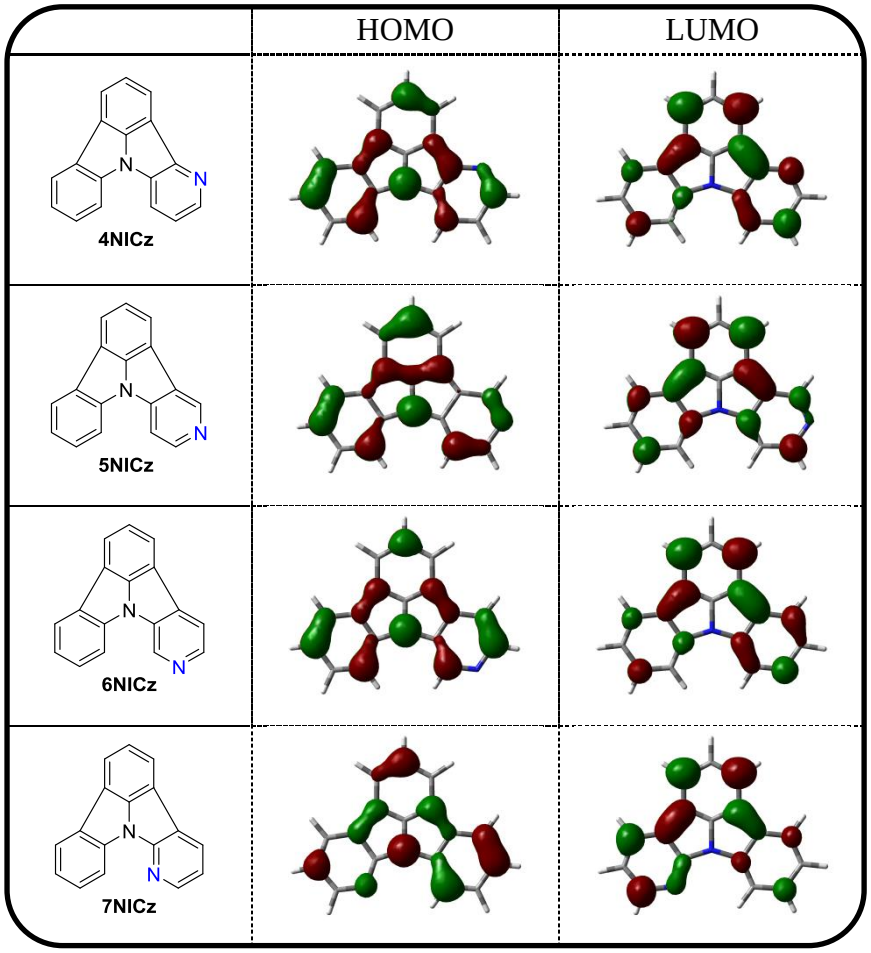


Figure S74. Spatial distribution of the HOMO and LUMO levels of mono substituted isomers **4NICz**, **5NICz**, **6NICz** and **7NICz**.

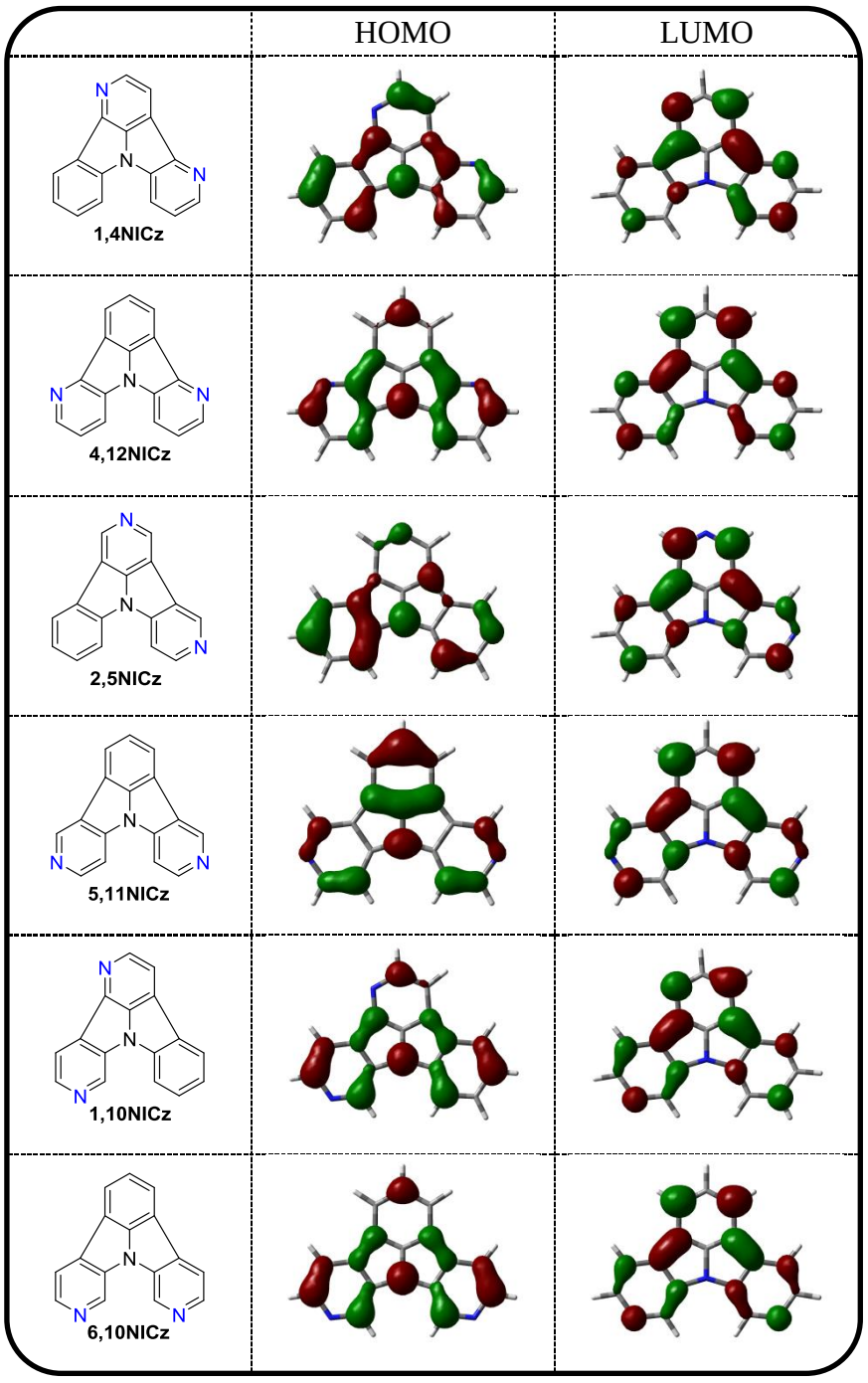


Figure S75. Spatial distribution of the HOMO and LUMO levels of twofold substituted NICzs.

8 Crystal packing

Table S2. Geometries of the C—H···N contacts described in the text. **A**ll C--H distances are exactly 0.96 Å since the H atoms were refined asriding on the parent C atoms.

	H···N [Å]	C···N [Å]	C—H···N [°]
2NICz			
C7—H7···N2	2.64	3.595(10)	174.52
C9—H9···N2	2.58	3.539(10)	174.62
5NICz			
C7—H7···N5	2.49	3.438(9)	168.98
C9—H9···N5	2.80	3.756(8)	172.63
C7'—H7'···N5'	2.48	3.411(6)	162.73
C9'—H9'···N5'	2.85	3.806(7)	172.47
2,5NICz			
C7—H7···N2 (2×)	2.59	3.525(3)	165.32
1,10NICz			
C2—H2···N10'	2.85	3.715(6)	150.62
C9—H9···N1'	2.68	3.565(6)	153.38
C2'—H2'···N10	2.82	3.695(6)	152.58
C9'—H9'···N1	2.69	3.572(6)	153.54
6NICz			
C7—H7···N6	2.58	3.532(3)	173.39
C9—H9···N6	2.54	3.498(3)	175.10
C2'—H2'···N6'	2.74	3.489(3)	135.06
6,10NICz			
C7—H7···N6	2.51	3.351(2)	146.19
C9—H9···N6	2.70	3.575(2)	151.42

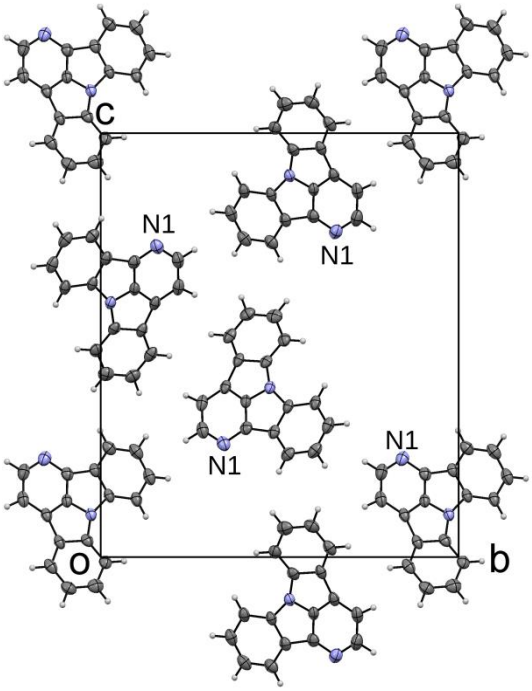


Figure S76. Packing of **1NICz**. Color codes as in Figure 6. Disordered solvent molecules have been omitted.

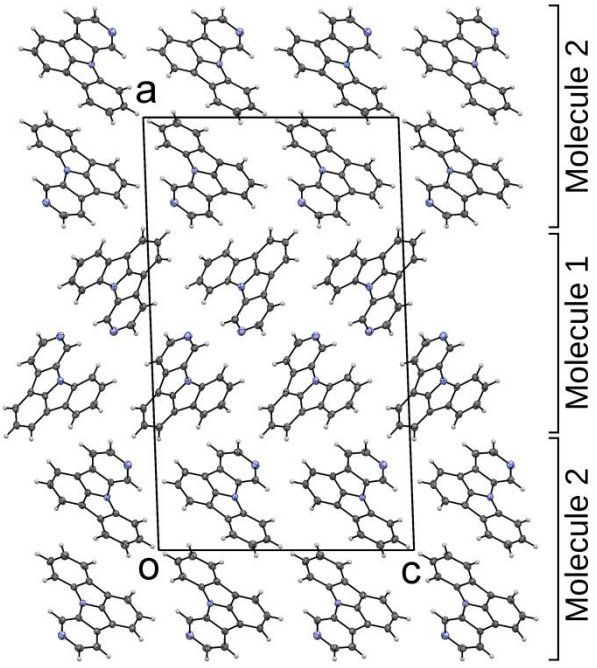


Figure S77. Packing of the **6NICz** molecules. Color codes as in Figure 6.

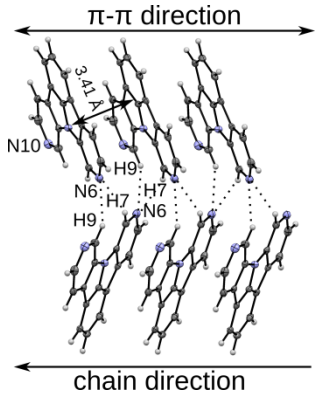


Figure S78. Chains of **6,10NICz** connected by hydrogen bonding. Color codes as in Figure 6.

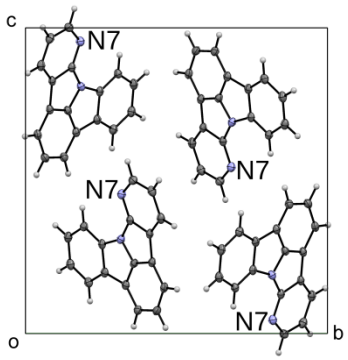


Figure S79. Packing of **7NICz**. Color codes as in Figure 6.

9 References

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