Electronic Supplementary Information for

Blue fluorescence from *N,O*-coordinated BF_2 complexes having aromatic chromophores in solution and solid state

Minoru Yamaji,[1,*] Kazuhiro Tomonari,[2] Keisuke Ikuma,[2] Kenta Goto,[3] Fumito Tani[3] and Hideki Okamoto[4]

[1] Division of Molecular Science, Graduate School of Science and Technology, Gunma University, Ota, Gunma 373-0057, Japan
[2] Education Program of Materials and Bioscience, Graduate School of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan
[3] Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan
[4] Division of Earth, Life, and Molecular Sciences, Graduate School of Natural Sciences and Technology, Okayama University, Okayama 700-8530, Japan

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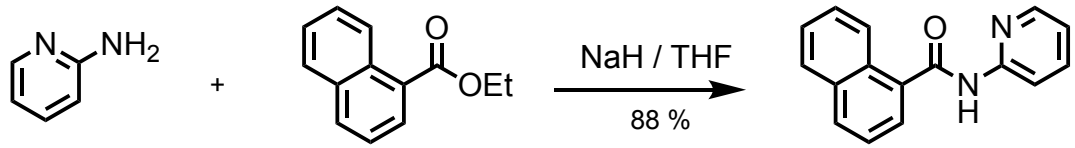
1. Synthesis of the ligands and BF_2 complexes.

1-1. Synthesis of 1-Np@Py

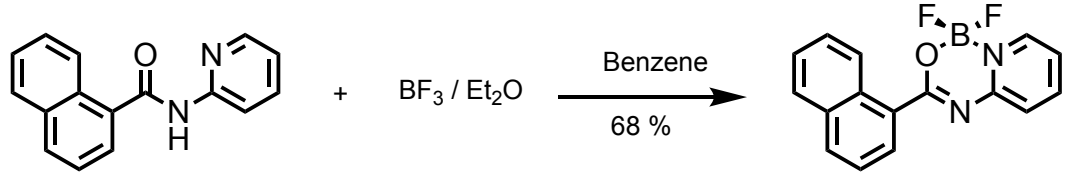
1-1-1. Preparation of 1-Np^Py



1-Np^Py

To dry THF (30 ml), 2-aminopyridine (288 mg, 3.0 mmol) and NaH (620 mg, 26 mmol) were added. After the solution was refluxed for 30 min, ethyl 1-naphthoate (0.54 ml, 3.0 mmol) was added, and the solution was refluxed for 1 h. Hydrochloric acid (2 M, 50 ml) was added to the solution, and the precipitated product was extracted with benzene (50 ml × 2), and the extract was washed with aqueous $NaHCO_3$ and brine. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (3:1, v/v) as the eluent to obtain **1-Np^Py** (660 mg, 88 %). Mp 153–154 °C. ^{1}H NMR (600 MHz, CD_3OD) δ_H = 8.78–8.30 (1H, two signals overlap), 8.28 (d, 1H, J = 8.1 Hz), 8.05 (d, 1H, J = 8.4 Hz), 7.97 (dd, 1H, J = 7.3, 1.7 Hz), 7.88 (td, 1H, J = 7.2, 1.0 Hz), 7.80 (dd, 1H, J = 7.2, 1.0 Hz), 7.61–7.55 (m, 2H), 7.19 (dd, J = 7.3, 5.2 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 168.0, 151.8, 148.0, 138.6, 133.9, 131.6, 130.2, 128.6, 127.6, 126.8, 125.6, 125.4, 124.8, 120.1, 114.3. HRMS (FAB) m/z calcd. for $C_{16}H_{12}N_2O$ 249.1028, found 249.1058.

1-1-2. Synthesis of 1-Np@Py

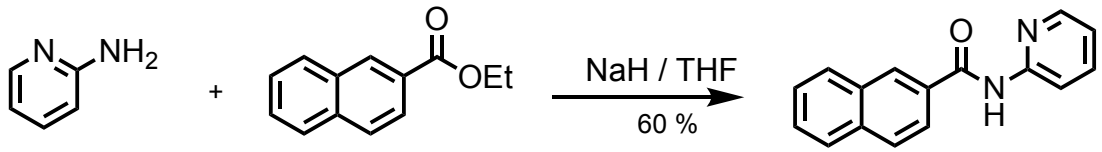


1-Np^Py **1-Np@Py**

1-Np^Py (300 mg, 1.2 mmol) and boron trifluoride diethyl etherate (46 %, 0.63 ml, 2.4 mmol) were added to 10 ml benzene, then the solution was refluxed for 2.5 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a benzene/ethyl acetate mixture (3:1, v/v) as the eluent to obtain **1-Np@Py** (240 mg, 68 %). Mp 134–135 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 9.12 (d, 1H, J = 8.6 Hz), 8.44 (brd, 1H, J = 5.8 Hz), 8.42 (dd, 1H, J = 7.3, 1.1 Hz), 8.14 (m, 1H), 8.06 (d, 1H, J = 8.2 Hz), 7.92 (d, 1H, J = 8.2 Hz), 7.66-7.61 (2H, two signals overlap), 7.59-7.54 (2H, two signals overlap), 7.45 (m, 1H). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 167.8, 154.5, 144.0, 138.8, 134.2, 133.8, 131.4, 131.2, 129.6, 128.9, 127.8, 126.3, 126.3, 124.9, 123.8, 121.0. HRMS (FAB) m/z calcd. for $C_{16}H_{11}BF_2N_2O$ 297.1014, found 297.1018.

1-2. Synthesis of 2-Np@Py

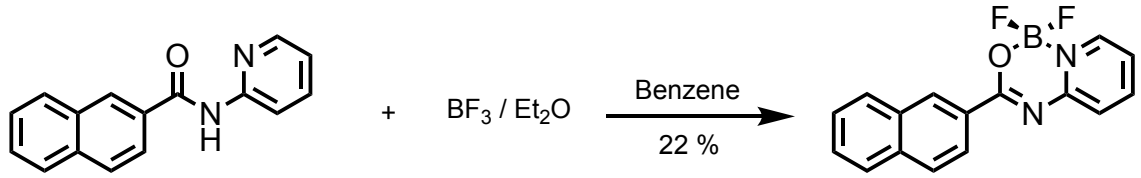
1-2-1. Preparation of 2-Np^Py



2-Np^Py

To dry THF (15 ml), 2-aminopyridine (192 mg, 2.0 mmol) and NaH (414 mg, 17 mmol) were added. After the solution was refluxed for 30 min, ethyl 2-naphthoate (0.35 ml, 2.0 mmol) was added, and the solution was refluxed for 1 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (3:1, v/v) as the eluent to obtain **2-Np^Py** (300 mg, 60 %). Mp 88–89 °C. ^{1}H NMR (600 MHz, CD_3OD) δ_H = 8.56, (s, 1H), 8.38 (brd, 1H, J = 4.4 Hz), 8.28 (d, 1H J = 8.2 Hz), 8.06–7.99 (m, 3H), 7.96 (d, 1H, J = 8.0 Hz), 7.86 (ddd, 1H, J = 8.0, 7.2, 1.7 Hz), 7.63 (ddd, 1H, J = 8.2, 7.2, 1.7 Hz), 7.60 (ddd, 1H, J = 8.2, 7.2, 1.4 Hz), 7.18 (ddd, 1H, J = 7.2, 4.9, 1.0 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 166.0, 151.8, 148.1, 138.7, 135.2, 132.7, 131.6, 129.2, 129.0, 128.3, 129.1, 127.95, 127.14, 123.7, 120.1, 114.4. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{12}N_2O$ 249.1028, found 249.1027.

1-2-2. Synthesis of 2-Np@Py

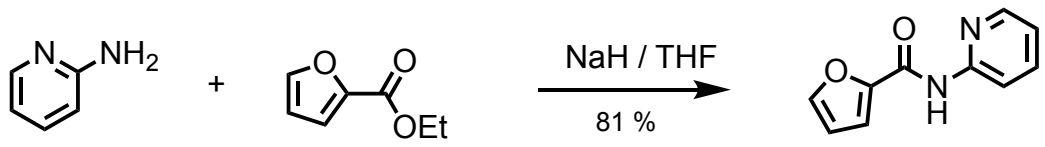


2-Np^Py **2-Np@Py**

2-Np^Py (580 mg, 2.3 mmol) and boron trifluoride diethyl etherate (46 %, 0.58 ml, 4.6 mmol) were added to 20 ml benzene, then the solution was refluxed for 1 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a benzene/ethyl acetate mixture (3:1, v/v) as the eluent to obtain **2-Np@Py** (150 mg, 22 %). Mp 223–224 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.94 (s, 1H), 8.43-8.37 (2H, two signal overlap), 8.12 (m, 1H), 8.01 (d, 1H, J = 8.0 Hz), 7.92 (d, 1H, J = 7.9 Hz), 7.90 (d, 1H, J = 8.0 Hz), 7.63-7.54 (3H, three signals overlap), 7.40 (t, 1H, J = 6.5 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 165.8, 154.8, 143.8, 138.8, 136.0, 132.8, 131.5, 129.8, 129.6, 128.6, 128.3, 127.9, 126.8, 125.3, 123.7, 120.6. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{11}BF_2N_2O$ 297.1014, found 297.1039.

1-3. Synthesis of 2-F@Py

1-3-1. Preparation of 2-F^Py

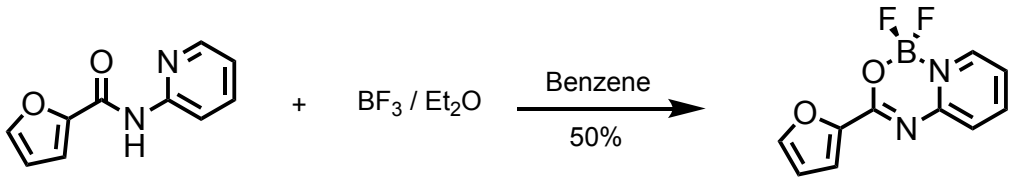


2-F^Py

To dry THF (20 ml), 2-aminopyridine (510 mg, 5.0 mmol) and NaH (1035 mg, 40 mmol) were added. After the solution was refluxed for 3 h, ethyl 2-furancarboxylate (0.35 ml, 2.0 mmol) was added, and the solution

was refluxed for 3 h. After removal of the solvent, the product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **2-F^Py** (770 mg, 81 %). Mp 85–86 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.75 (br, 1H), 8.32 (m, 2H), 7.73 (m, 1H), 7.53 (m, 1H), 7.28 (m, 1H), 7.07 (m, 1H), 6.57 (m, 1H). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 156.3, 151.1, 148.2, 147.5, 144.9, 138.5, 120.1, 116.0, 114.3, 112.8. HRMS (FAB) *m*/*z* calcd. for $C_{10}H_8N_2O_2$ 189.0664, found 189.0659.

1-3-2. Synthesis of 2-F@Py

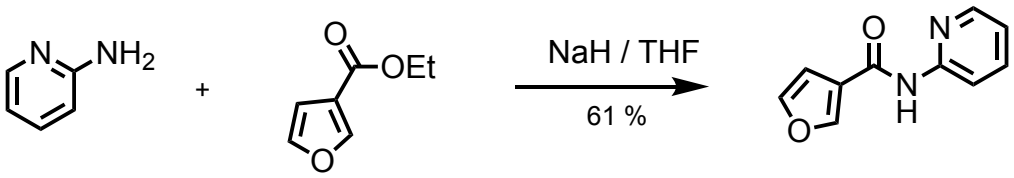


2-F^Py **2-F@Py**

2-F^Py (580 mg, 2.3 mmol) and boron trifluoride diethyl etherate (46 %, 0.76 ml, 6.0 mmol) were added to 20 ml benzene, then the solution was refluxed for 1 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a benzene/ethyl acetate mixture (3:1, v/v) as the eluent to obtain **2-F@Py** (360 mg, 50 %). Mp 165–166 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.35 (brd, 1H, *J* = 5.9 Hz), 8.09 (ddd, 1H, *J* = 8.1, 7.4, 1.7 Hz), 7.69 (m, 1H), 7.56 (d, 1H, *J* = 8.5 Hz), 7.45 (dd, 1H, *J* = 3.6, 0.6 Hz), 7.39 (ddd, 1H, *J* = 7.3, 6.2, 1.2 Hz), 6.61 (dd, 1H, *J* = 3.6, 1.7 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 157.5, 154.5, 147.6, 147.1, 144.0, 139.0, 123.6, 120.7, 119.6, 112.9. HRMS (FAB) *m*/*z* calcd. for $C_{10}H_7BF_2N_2O_2$ 237.0649, found 237.0636.

1-4. Synthesis of 3-F@Py

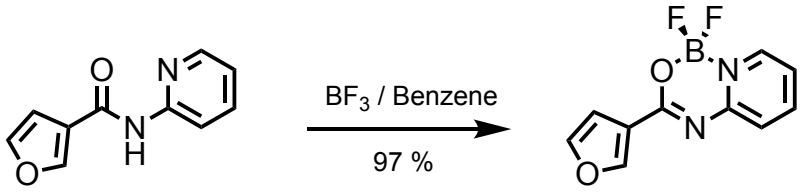
1-4-1. Preparation of 3-F^Py



3-F^Py

To dry THF (20 ml), 2-aminopyridine (291 mg, 3.0 mmol) and NaH (277 mg, 24 mmol) were added. After the solution was refluxed for 20 min, ethyl 3-furancarboxylate (0.38 ml, 3.0 mmol) was added, and the solution was refluxed for 2 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **3-F^Py** (347 mg, 61 %). Mp 112–113 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.312 (d, 1H, *J* = 8.5 Hz), 8.29 (m, 1H), 8.22 (br, 1H), 8.08 (brs, 1H), 7.74 (t, 1H, *J* = 7.7 Hz), 7.50 (m, 1H), 7.07 (m, 1H), 6.77 (m, 1H). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 160.8, 151.4, 148.0, 145.7, 144.4, 138.7, 123.0, 120.1, 114.4, 108.5. HRMS (FAB) *m*/*z* calcd. for $C_{10}H_8N_2O_2$ 189.0664, found 189.06732.

1-4-2. Synthesis of 3-F@Py

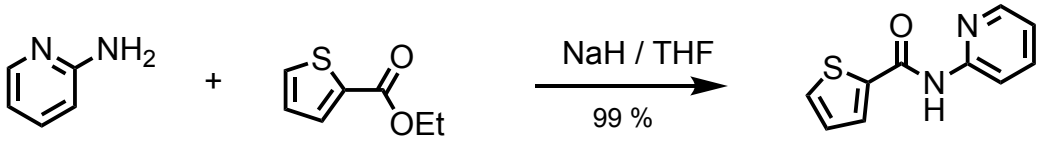


3-F^Py **3-F@Py**

3-F^Py (277 mg, 2.0 mmol) and boron trifluoride diethyl etherate (46 %, 0.50 ml, 4.0 mmol) were added to 20 ml benzene, then the solution was refluxed for 3 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a benzene/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **3-F@Py** (460 mg, 97 %). Mp 144–145 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.34 (brd, 1H, J = 5.2 Hz), 8.25 (m, 1H), 8.06 (ddd, 1H, J = 8.9, 7.7, 1.8 Hz), 7.48 (t, 1H, J = 1.6 Hz), 7.44 (d, 1H, J = 8.6 Hz), 7.36 (ddd, 1H, J = 7.3, 6.3, 1.2 Hz), 6.94 (m, 1H). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 162.6, 154.7, 148.7, 144.2, 143.8, 138.8, 123.3, 122.4, 120.4, 109.8. HRMS (FAB) *m*/*z* calcd. for $C_{10}H_7BF_2N_2O_2$ 237.0649, found 237.0663.

1-5. Synthesis of 2-T@Py

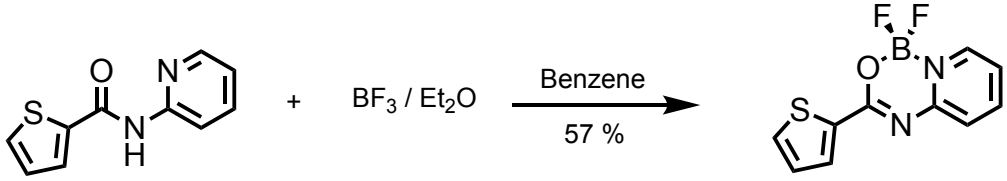
1-5-1. Preparation of 2-T^Py



2-T^Py

To dry THF (30 ml), 2-aminopyridine (950 mg, 10.0 mmol) and NaH (1.97 g, 82 mmol) were added. After the solution was refluxed for 3 h, ethyl 2-thiophenecarboxylate (1.34 ml, 10.0 mmol) was added, and the solution was refluxed for 1 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **2-T^Py** (2.0 g, 99 %). Mp 93–94 °C. ^{1}H NMR (600 MHz, methanol-d_4) δ_H = 8.33 (m, 1H), 8.14 (d, 1H, J = 8.5 Hz), 7.93 (dd, 1H, J = 3.8, 1.2 Hz), 7.80 (ddd, 1H, J = 8.4, 7.5, 1.9 Hz), 7.76 (dd, 1H,J = 5.0, 1.0 Hz), 7.18 dd, 1H, J = 5.0, 3.8 Hz), 7.14 (ddd, J = 7.4, 5.0, 1.0 Hz). ^{13}C NMR (151 MHz, methanol-d_4) δ_C = 162.5, 153.0, 149.1, 140.2, 139.6, 133.3, 130.8, 129.1, 121.2, 116.2. HRMS (FAB) *m*/*z* calcd. for $C_{10}H_8N_2OS$ 205.0436, found 205.0439.

1-5-2. Synthesis of 2-T@Py



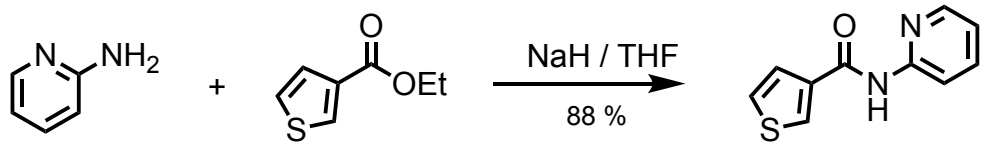
2-T^Py **2-T@Py**

2-T^Py (1.59 g, 7.8 mmol) and boron trifluoride diethyl etherate (46 %, 1.97 ml, 15.6 mmol) were added to 40 ml benzene, then the solution was refluxed for 2 h. After removal of the solvent, the crude product

was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **2-T@Py** (1.12 g, 57 %). Mp 151–152 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ_H = 8.48 (br, 1H), 8.38 (m, 1H,), 8.02 (dd, 1H, J = 3.7, 1.2 Hz), 7.92 (brd, 1H, J = 4.8 Hz), 7.66 (t, 1H, J = 6.8 Hz), 7.54 (d, 1H, J = 8.4 Hz), 7.28 (dd, 1H, J = 5.0, 4.0 Hz). ^{13}C NMR (151 MHz, acetone-d_6) δ_C = 162.0, 154.8, 146.0, 139.8, 137.9, 135.1, 134.2, 129.4, 123.9, 122.3. HRMS (FAB) m/z calcd. for $C_{10}H_7BF_2N_2OS$ 253.0420, found 253.0370.

1-6. Synthesis of 3-T@Py

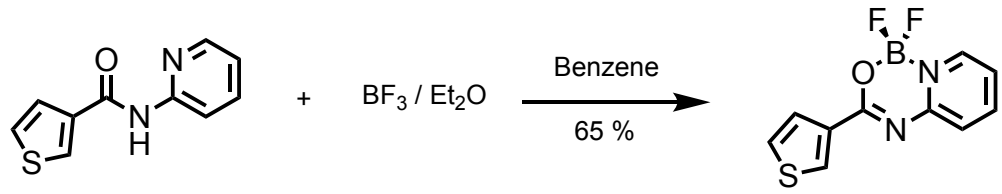
1-6-1. Preparation of 3-T^Py



3-T^Py

To dry THF (20 ml), 2-aminopyridine (474 mg, 5.0 mmol) and NaH (1.08 g, 45 mmol) were added. After the solution was refluxed for 3 h, ethyl 3-thiophenecarboxylate (0.66 ml, 5.0 mmol) was added, and the solution was refluxed for 2 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **3-T^Py** (960 mg, 88 %). Mp 106–107 °C. ^{1}H NMR (600 MHz, methanol-d_4) δ_H = 8.33, (m, 1H), 8.29 (dd, 1H, J = 3.0, 1.5 Hz), 8.18 (d, 1H, J = 8.3 Hz), 7.81 (ddd, 1H, J = 8.4, 7.4, 1.9 Hz), 7.64 (dd, 1H, J = 5.1, 3.1 Hz), 7.53 (dd, 1H, J = 5.0, 3.0 Hz), 7.14 (ddd, 1H, J = 7.3, 4.8, 0.9 Hz). ^{13}C NMR (151 MHz, methanol-d_4) δ_C = 163.6, 153.1, 149.1, 139.6, 138.3, 131.2, 127.9, 127.8, 121.2, 116.3. HRMS (FAB) m/z calcd. for $C_{10}H_8N_2OS$ 205.0436, found 205.0440.

1-6-2. Synthesis of 3-T@Py

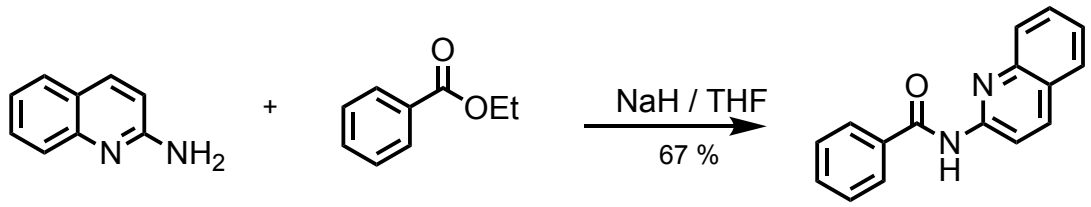


3-T^Py **3-T@Py**

3-T^Py (580 mg, 2.8 mmol) and boron trifluoride diethyl etherate (46 %, 0.71 ml, 5.6 mmol) were added to 20 ml benzene, then the solution was refluxed for 1.5 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **3-T@Py** (465 mg, 65 %). Mp 136–137 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ_H = 8.80-8.46 (two signals overlap, 2H), 8.38 (ddd, 1H, J = 8.3, 7.3, 1.8 Hz), 7.76 (dd, 1H, J = 5.0, 1.3 Hz), 7.67 (ddd, 1H, J = 7.3, 6.2, 1.0 Hz), 7.62 (dd, 1H, J = 5.1, 3.1 Hz), 7.59 (d, 1H, J = 8.5 Hz). ^{13}C NMR (151 MHz, acetone-d_6) δ_C = 162.3, 155.2, 145.9, 139.8, 137.2, 133.9, 128.4, 127.9, 124.1, 122.4. HRMS (FAB) m/z calcd. for $C_{10}H_7BF_2N_2OS$ 253.0420, found 253.0423.

1-7. Synthesis of Ph@Q

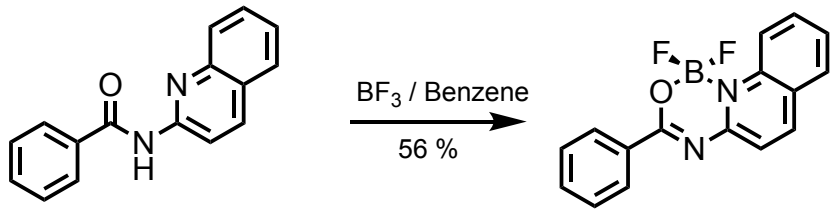
1-7-1. Preparation of Ph^Q



Ph^Q

A THF solution (15 ml) of 2-aminoquinoline (210 mg, 1.38 mmol) and NaH (308 mg, 11 mmol) was stirred for 20 min at 50 ℃. To the solution, ethyl benzoate (0.20 ml, 1.38 mmol) was added, and the solution was refluxed for 1 h. The solvent was removed, and the crude product was extracted with benzene (50 ml × 3), and purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **Ph^Q** (230 mg, 67 %). Mp 125-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.84 (br, 1H), 9.60 (d, 1H, J = 9.0 Hz), 8.23 (d, 1H, J = 9.0 Hz), 7.99 (d, 2H, J = 7.8 Hz), 7.84 (d, 1H, J = 8.3 Hz), 7.81 (d, 1H, J = 8.1 Hz), 7.68 (t, 1H, J = 7.8 Hz), 7.59 (t, 1H, J = 7.7 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.47 (t, 1H, J = 7.5 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 166.1, 151.2, 146.8, 138.8, 134.3, 132.6, 130.2, 129.0, 127.8, 127.50, 127.47, 126.6, 125.4, 114.5. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{12}N_2O_2$ 249.1028, found 249.1029.

1-7-2. Synthesis of Ph@Q

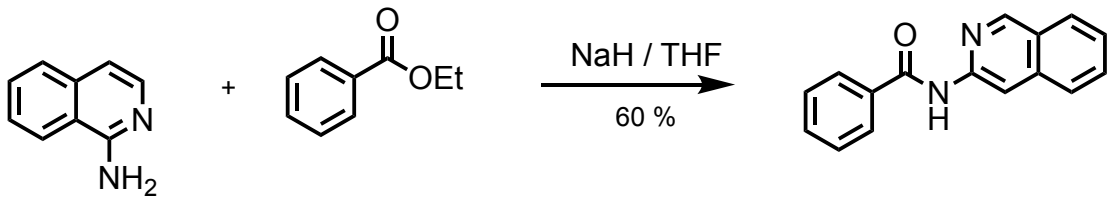


Ph^Q **Ph@Q**

Ph^Q (153 mg, 0,60 mmol) and boron trifluoride diethyl etherate (46 %, 0.15 ml, 1.2 mmol) were added to 00 ml benzene, then the solution was refluxed for 3 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **Ph@Q** (100 mg, 56 %). Mp 196–197 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.65 (m, 1H), 8.44 (m, 2H), 8.39 (d, 1H, J = 8.8 Hz), 7.88-7.84 (2H, two signals overlap), 7.63 (m, 2H), 7.54-7.50 (3H, two signals overlap). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 166.9, 156.6, 144.0, 133.8, 132.7, 130.1, 128.64, 128.60, 127.2, 126.6, 123.22, 123.16, 123.12, 122.3. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{11}BF_2N_2O$ 297.1014, found 297.1010.

1-8. Synthesis of Ph@IQ

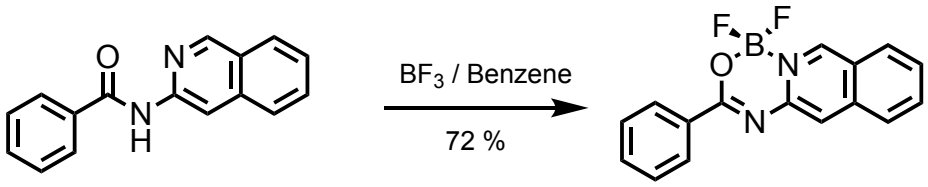
1-8-1. Preparation of Ph^IQ



Ph^IQ

A THF solution (20 ml) of 2-aminoisoquinoline (500 mg, 3.5 mmol) and NaH (580 mg, 24 mmol) was stirred for 20 min at 50 °C. To the solution, ethyl benzoate (0.49 ml, 3.5 mmol) was added, and the solution was refluxed for 1 h. The solvent was removed, and the crude product was extracted with benzene (50 ml × 3), and purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **Ph^IQ** (520 mg, 60 %). Mp 104-105 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.84 (br, 1H), 9.60 (d, 1H, J = 9.0 Hz), 8.23 (d, 1H, J = 9.0 Hz), 7.99 (d, 2H, J = 7.8 Hz), 7.84 (d, 1H, J = 8.3 Hz), 7.81 (d, 1H, J = 8.1 Hz), 7.68 (t, 1H, J = 7.8 Hz), 7.59 (t, 1H, J = 7.7 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.47 (t, 1H, J = 7.5 Hz). ^{13}C NMR (151 MHZ, $CDCl_3$) δ_C = 166.1, 151.2, 146.8, 138.8, 134.3, 132.6, 130.2, 129.0, 127.8, 127.50, 127.47, 126.6, 125.4, 114.5. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{12}N_2O_2$ 249.1028, found 249.1050.

1-8-2. Synthesis of Ph@IQ

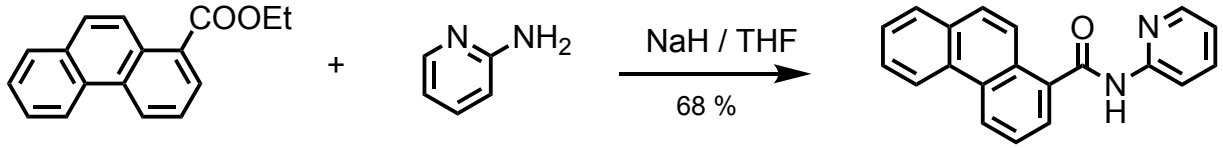


Ph^IQ **Ph@IQ**

Ph^IQ (420 mg, 1.7 mmol) and boron trifluoride diethyl etherate (46 %, 0.42 ml, 3.4 mmol) were added to 15 ml benzene, then the solution was refluxed for 3 h. After removal of the solvent, the product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (2:1, v/v) as the eluent to obtain **Ph@IQ** (360 mg, 72 %). Mp 196–197 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 9.04 (br 1H), 8.47 (br 2H), 7.79 (br, t, J = 6.6 Hz), 7.74–7.63, (2H, two signals overlap), 7.57–7.32 (m, 4H), 7.04 (br, 1H). ^{13}C NMR (151 MHZ, CD_3OD) δ_C = 151.5, 141.6, 139.6, 135.2, 134.6, 133.5, 132.7, 132.3, 130.4, 129.8, 129.1, 128.2, 126.6, 126.1, 122.1. HRMS (FAB) *m*/*z* calcd. for $C_{16}H_{11}BF_2N_2O$ 297.1014, found 297.1011.

1-9. Synthesis of 1-Phen@Py

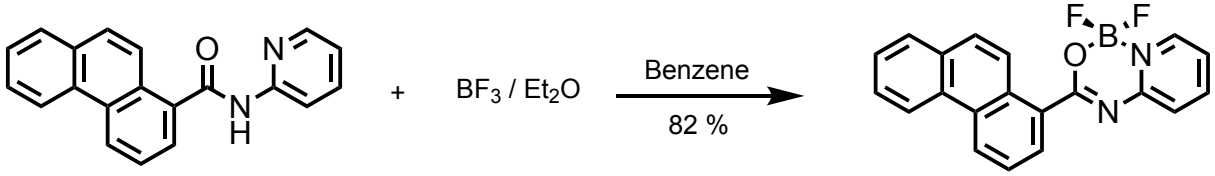
1-9-1. Preparation of 1-Phen^Py



1-Phen^Py

A THF solution (30 ml) of 2-aminopyridine (223 mg, 2.4 mmol) and NaH (380 mg, 16 mmol) was stirred for 20 min at 50 ℃. To the solution, 1-phenanthrenecarboxylic acid ethyl ester (496 mg, 2.0 mmol) was added, and the solution was refluxed for 1 h. The solvent was removed, and crude product was extracted with benzene (50 ml × 3), and purified by silica gel chromatography with a chloroform/ethyl acetate mixture (1:1, v/v) as the eluent to obtain **1-Phen^Py** (396 mg, 68 %). Mp 206-207 °C. ^{1}H NMR (acetone-d_6, 600 MHz) δ_H 10.01 (br, 1H), 9.00 (d, 1H, J = 8.4 Hz), 8.88 (d, 1H, J = 8.2 Hz), 8.49 (d, 1H, J = 8.2 Hz), 8.28–8.23 (2H, two signals overlap), 8.02 (m, 1H), 7.95 (dd, 1H, J = 7.2, 1.0 Hz), 7.93 (d, 1H, J = 9.2 Hz), 7.88 (ddd, J = 8.7, 7.7, 1.8 Hz), 7.77 (dd, 1H, J = 8.5, 7.7 Hz) 7.74 (ddd, 1H, J = 8.4, 7.1, 1.4 Hz), 7.69 (ddd, 1H, J = 7.8, 7.1, 1.1 Hz), 7.15 (m, 1H). ^{13}C NMR (acetone-d_6, 151 MHz) δ_C 169.0, 153.4, 149.0, 138.9, 136.2, 132.7, 131.6, 131.0, 129.9, 129.4, 128.8, 128.1, 128.0, 127.0, 126.7, 125.9, 124.5, 123.8, 120.7, 114.9. HRMS (FAB) *m*/*z* calcd. for $C_{20}H_{15}N_2O$ 299.1184, found 299.1184.

1-9-2. Synthesis of 1-Phen@Py

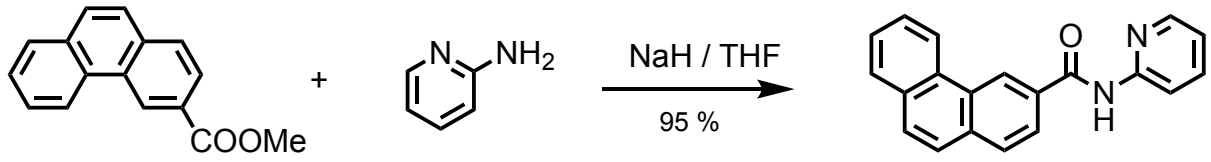


1-Phen^Py **1-Phen@Py**

1-Phen^Py (360 mg, 1.2 mmol) and boron trifluoride diethyl etherate (46 %, 0.30 ml, 2.4 mmol) were added to 10 ml benzene, then the solution was refluxed for 2 h. After removal of the solvent, the crude product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (2:1, v/v) as the eluent to obtain **Ph@IQ** (340 mg, 82 %). Mp 174–175 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.95 (d, 1H, J = 8.1 Hz), 8.92 (d, 1H, J = 8.3 Hz), 8.45 (brd, 1H, J = 5.6 Hz), 8.41 (dd, 1H, J = 7.4, 1.2 Hz), 8.15 (ddd, J = 8.4, 7.4, 1.8 Hz), 7.93 (d, 1H, J = 9.3 Hz), 7.74 (dd, 1H, J = 8.3, 7.5 Hz), 7.71 (ddd, 1H, J = 8.2, 7.0, 1.4 Hz), 7.67–7.62 (2H, ddd and d signals overlap), 7.46 (ddd, 1H, J = 7.3, 6.1, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 154.4, 144.1, 138.8, 131.7, 131.2, 130.8, 130.6, 130.2, 128.7, 128.6, 127.4, 127.2, 127.0, 125.6, 124.2, 123.8, 123.0, 122.1, 121.2. HRMS (FAB) *m*/*z* calcd. for $C_{20}H_{14}BF_2N_2O$ 347.1171, found 347.1191.

1-10. Synthesis of 3-Phen@Py

1-10-1. Preparation of 3-Phen^Py

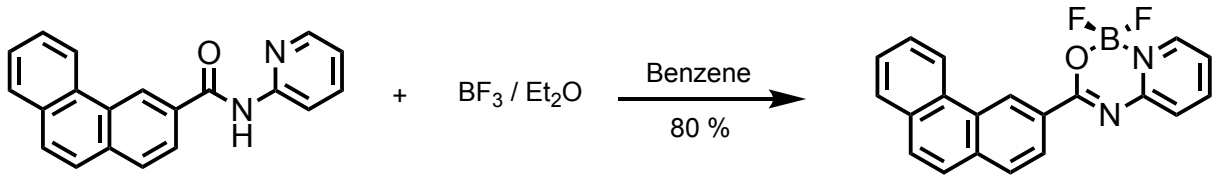


3-Phen^Py

A THF solution (20 ml) of 2-aminopyridine (197 mg, 2.1 mmol) and NaH (384 mg, 16 mmol) was stirred for 20 min at 50 ℃. To the solution, 3-phenanthrenecarboxylic acid methyl ester (500 mg, 2.1 mmol) was added, and the solution was refluxed for 1 h. The crude product was extracted with benzene (50 ml × 3), and purified by silica gel chromatography with a chloroform/ethyl acetate mixture (9:1, v/v) as the eluent to obtain **3-Phen^Py** (600 mg, 95 %). Mp 187-188 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ_H = 10.08 (bs, 1H), 9.62 (s, 1H), 9.05 (d, 1H, J = 8.2 Hz), 8.47 (dt, 1H, J = 8.3, 1.0 Hz), 8.38 (ddd, 1H, J = 4.8, 1.9, 1.0 Hz), 8.32 (dd, 1H, J = 8.2, 1.6 Hz), 8.13 (d, 1H, J = 8.2 Hz), 8.03 (brd, 1H, J = 7.7 Hz), 7.98 (d, 1H, J = 8.9 Hz), 7.93 (d, 1H, J = 8.9 Hz), 7.87 (ddd, 1H, J = 8.5, 7.4, 1.9 Hz), 7.77 (ddd, 1H, J = 8.3, 7.0, 1.2 Hz), 7.70 (ddd, 1H, J = 8.0, 7.0, 1.2 Hz), 7.16 (ddd, 1H, J = 7.3, 4.8, 1.0 Hz). ^{13}C NMR (151 MHz, acetone-d_6)

δ_C = 166.7, 153.5, 149.0, 138.9, 135.2 133.3, 133.2, 131.5, 130.7, 130.0, 129.8, 129.6, 128.1, 127.2, 126.5, 124.1, 123.6, 120.6, 115.1. HRMS (FAB) *m/z* calcd. for $C_{20}H_{15}N_2O$ 299.1184, found 299.1192.

1-10-2. Synthesis of 3-Phen@Py



3-Phen^Py **3-Phen@Py**

3-Phen^Py (450 mg, 1.5 mmol) and boron trifluoride diethyl etherate (46 %, 0.38 ml, 3.0 mmol) were added to 15 ml benzene, then the solution was refluxed for 2 h. After removal of the solvent, the product was purified by silica gel chromatography with a chloroform/ethyl acetate mixture (9:1, v/v) as the eluent to obtain **Ph@IQ** (415 mg, 80 %). Mp 239–240 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ_H = 9.78 (s, 1H), 8.95 (d, 1H, *J* = 8.4 Hz), 8.57 (brd, 1H, *J* = 5.4 Hz), 8.54 (dd, 1H, *J* = 8.3, 1.6 Hz), 8.45 (ddd, 1H, *J* = 8.7, 7.4, 1.7 Hz), 8.14 (d, 1H, *J* = 8.4 Hz), 8.04 (d, 1H, *J* = 7.9 Hz), 8.01 (d, 1H, *J* = 8.9 Hz), 7.94, d, 1H, *J* = 8.9 Hz), 7.82 (ddd, 1H, *J* = 8.2, 7.0, 1.2 Hz), 7.77 (d, 1H, *J* = 8.3 Hz), 7.75-7.71 (m, 2H). ^{13}C NMR (151 MHz, acetone-d_6) δ_C = 165.7, 154.9, 146.1, 139.9, 136.1, 133.2, 131.3, 131.2, 130.65, 130.62, 129.8, 129.8, 128.5, 128.3, 127.3, 127.2, 125.4, 124.5, 123.7, 122.8. HRMS (FAB) *m/z* calcd. for $C_{20}H_{14}BF_2N_2O$ 347.1171, found 347.1172.

2. ^{1}H and ^{13}C NMR spectra

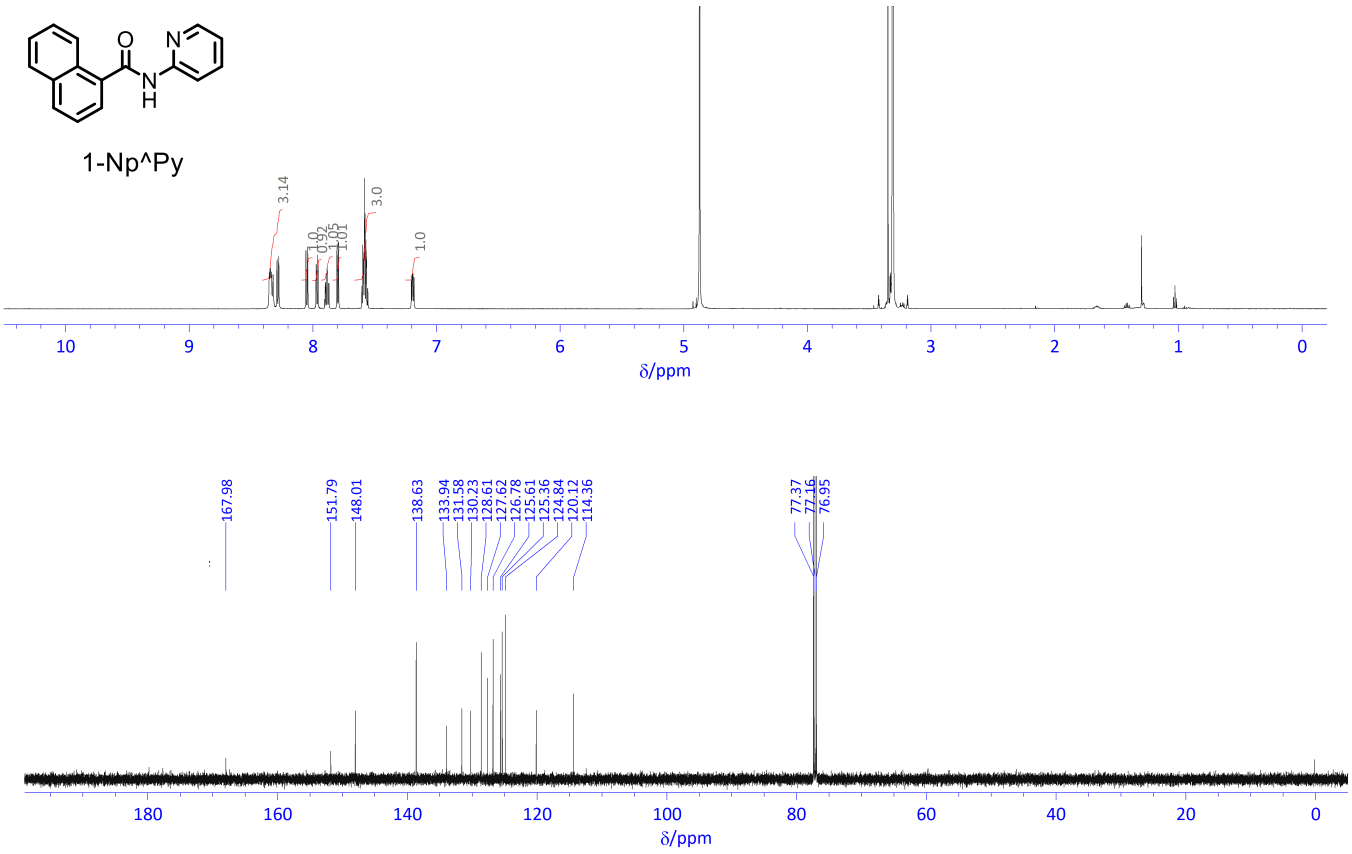


Figure S1. ^{1}H (600 MHz, CD_3OD, upper) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **1-Np^Py**.

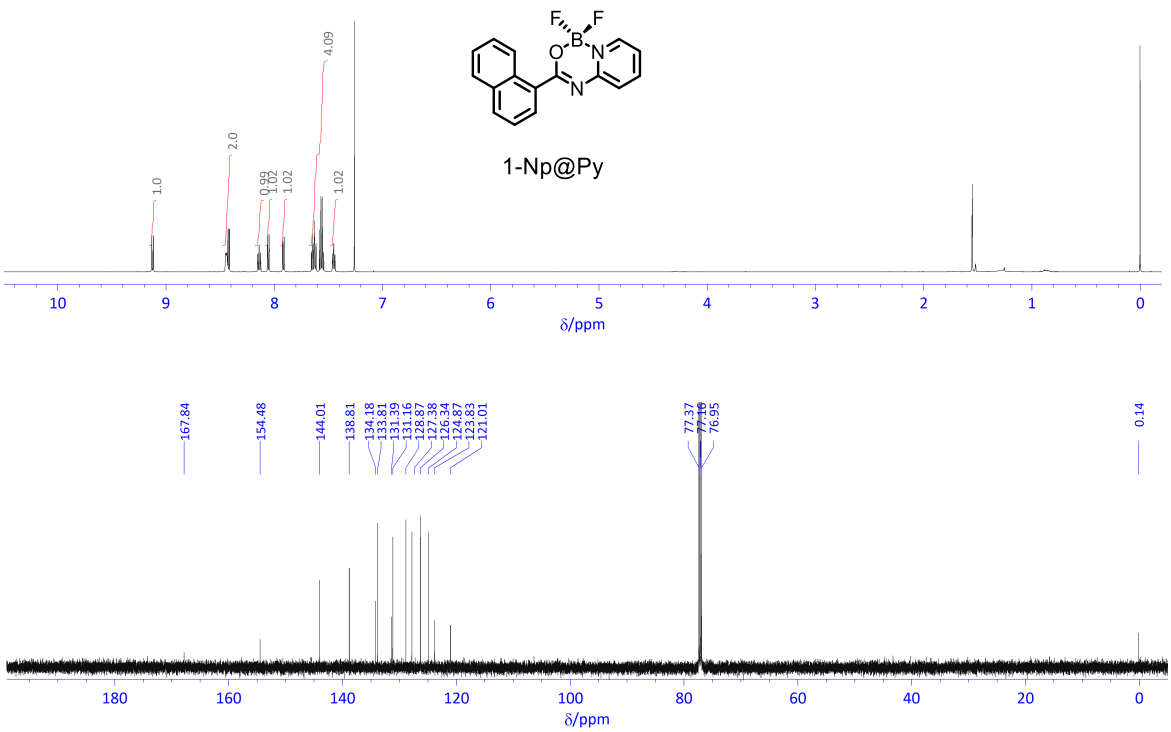


Figure S2. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **1-Np@Py**.

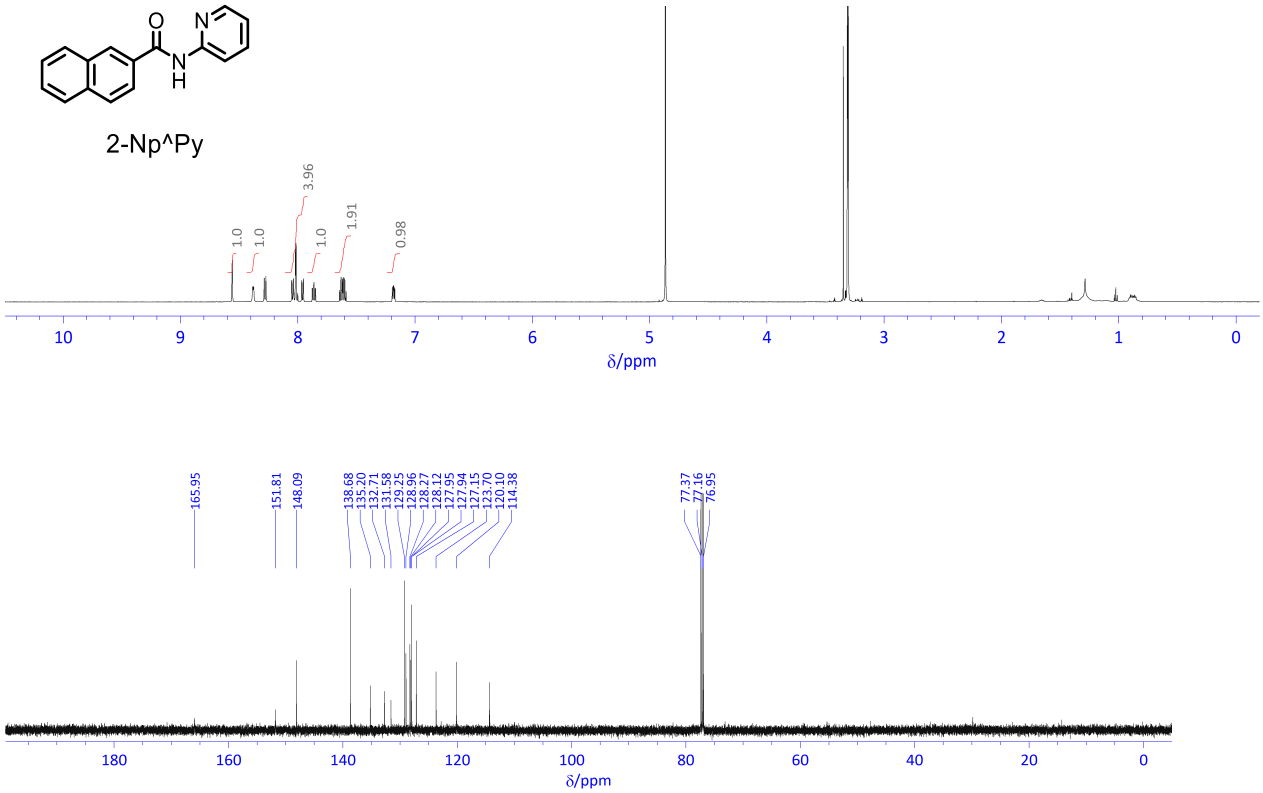


Figure S3. ^{1}H (600 MHz, CD_3OD, upper) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **2-Np^Py**.

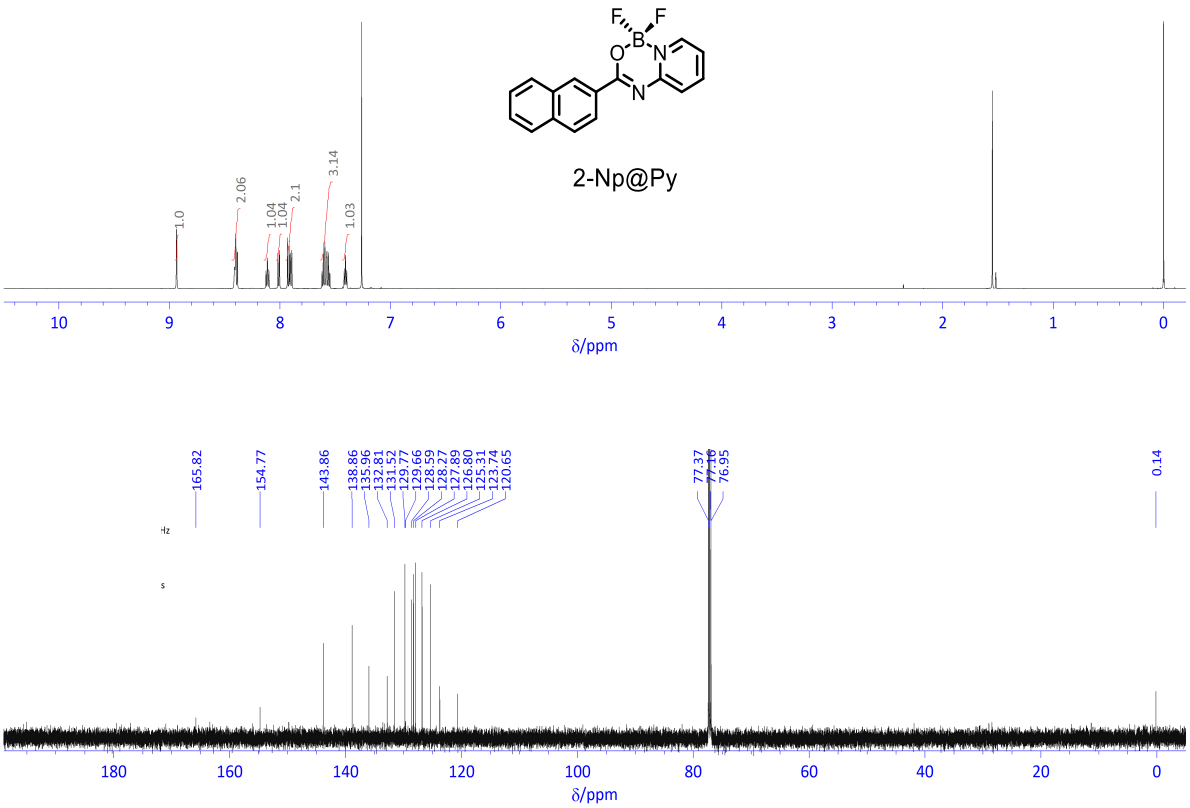


Figure S4. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **2-Np@Py**.

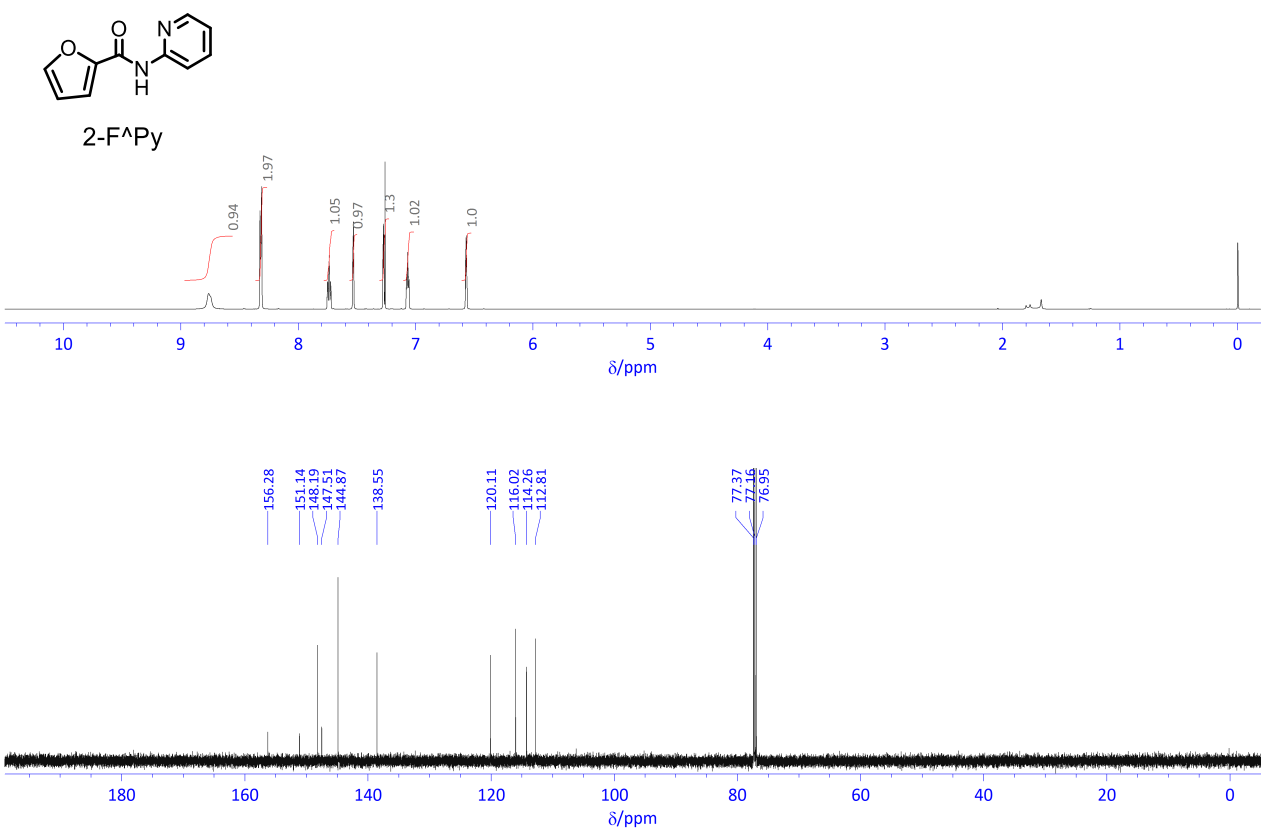


Figure S5. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **2-F^Py**.

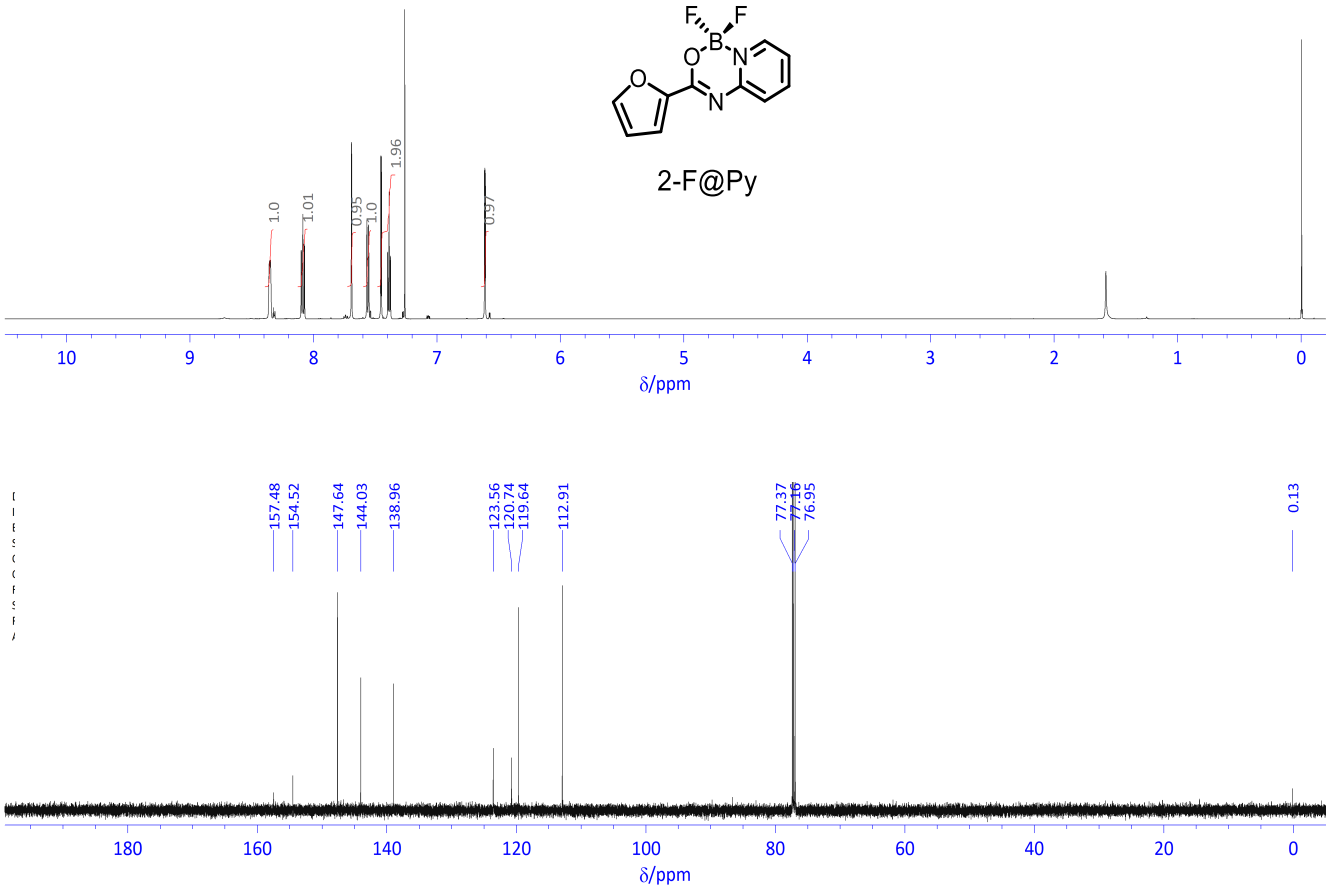


Figure S6. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **2-F@Py**.

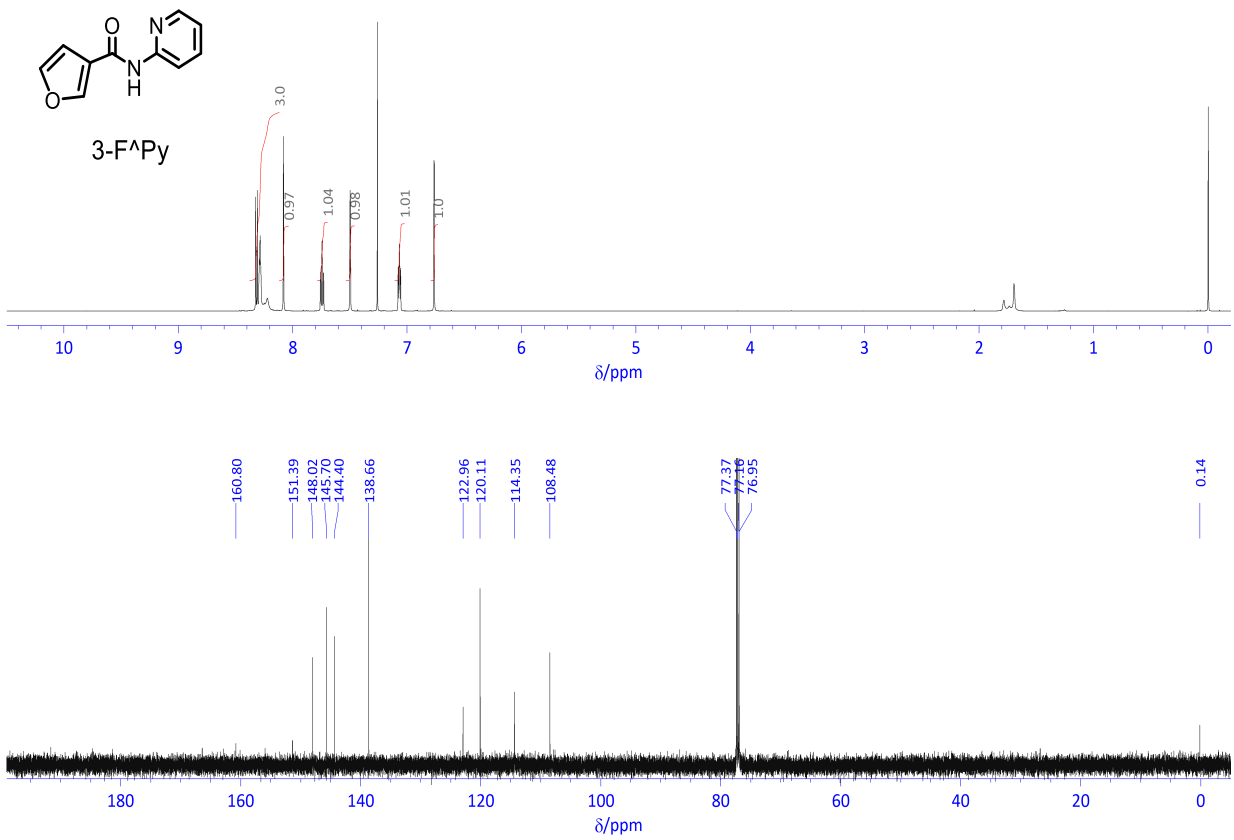


Figure S7. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **3-F^Py**.

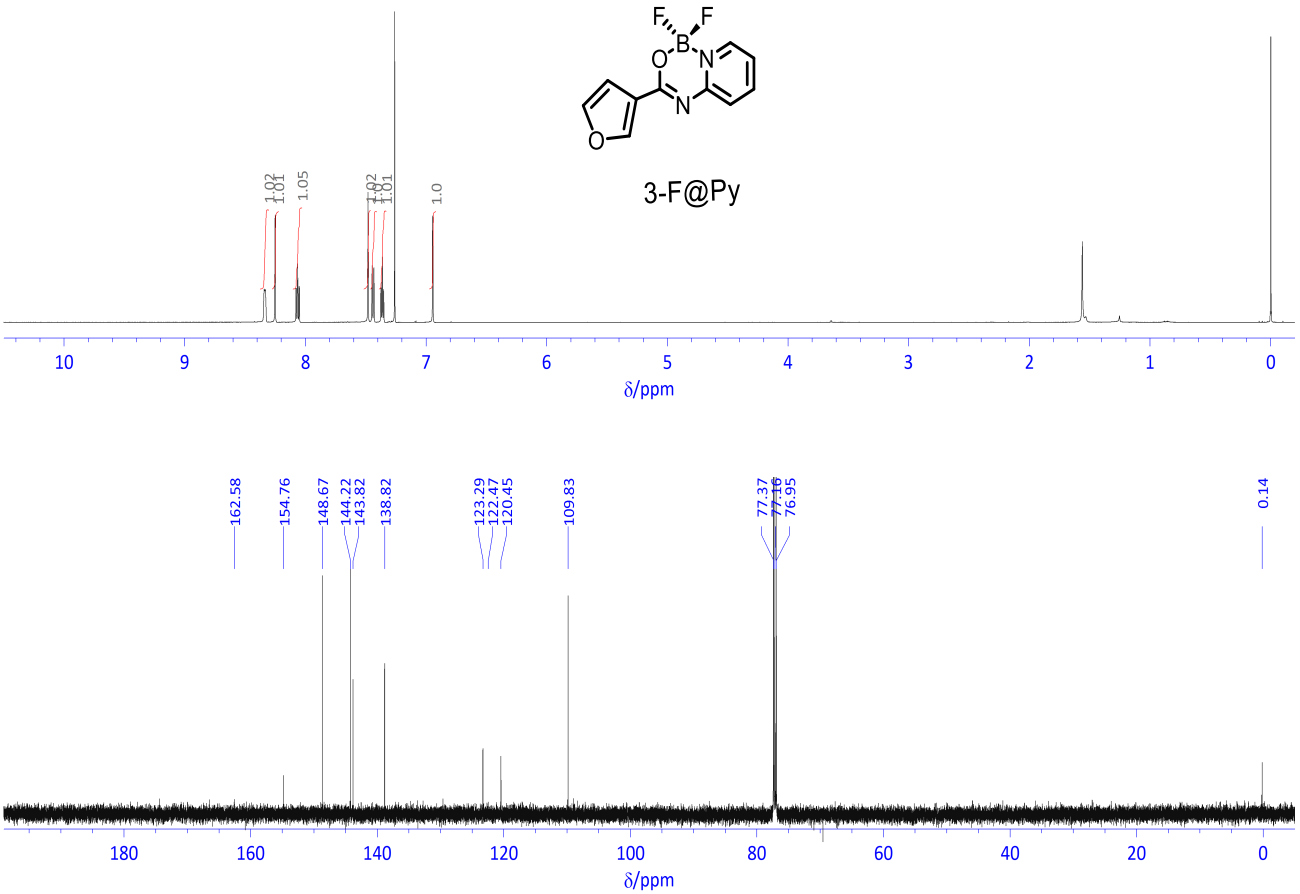


Figure S8. ^{1}H (600 MHz, $CDCl_3$, upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **3-F@Py**.

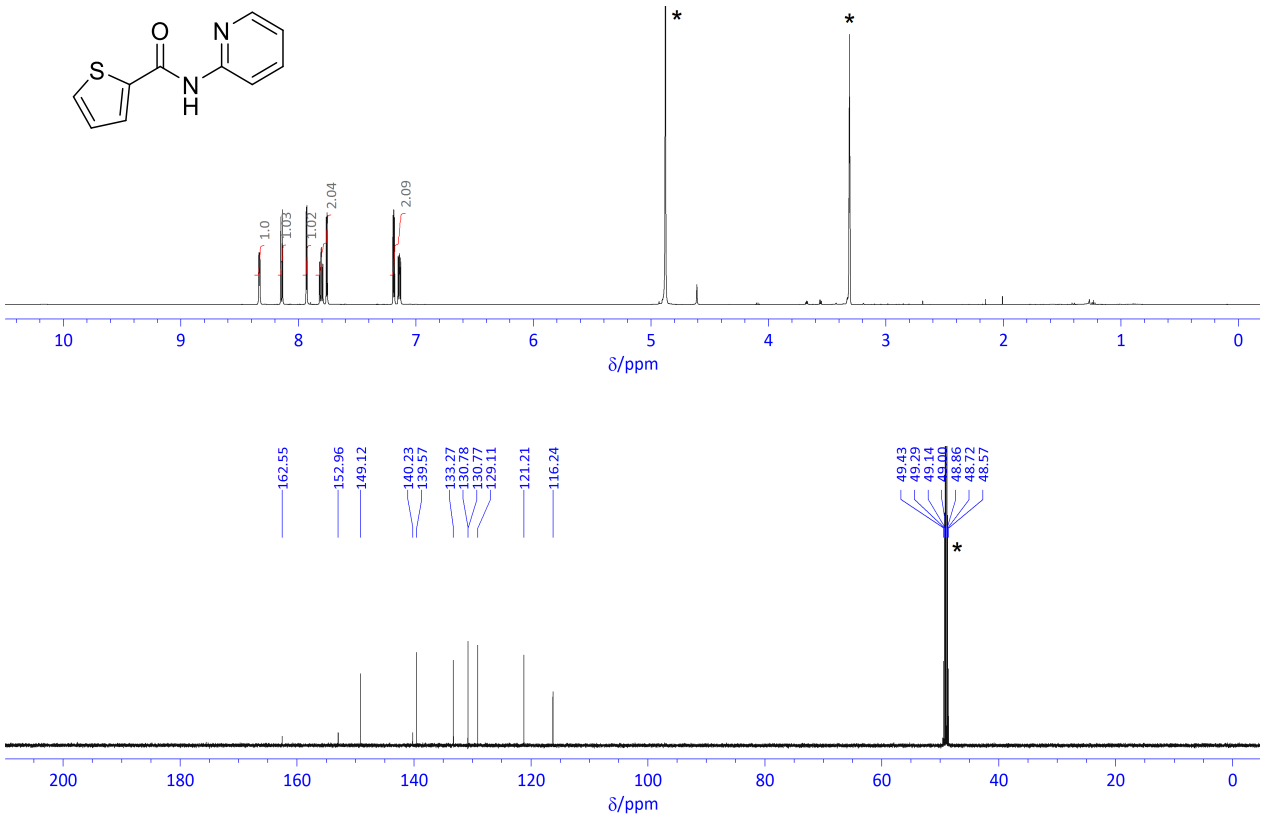


Figure S9. ^{1}H (600 MHz, CD_3OD upper)) and ^{13}C (151 MHz, CD_3OD, lower) NMR spectra of **2-T^Py**.

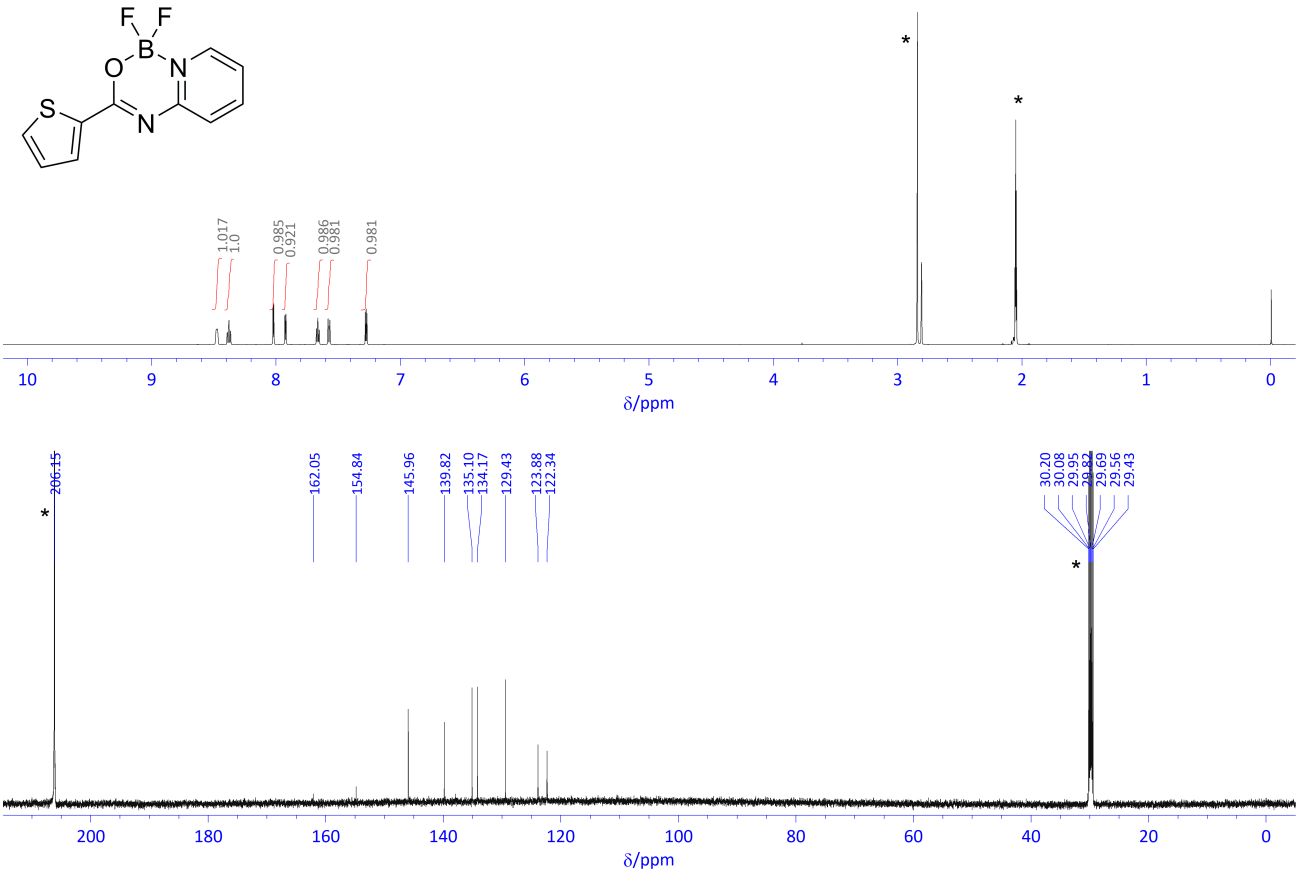


Figure S10. ^{1}H (600 MHz, acetone-d_6 upper)) and ^{13}C (151 MHz, acetone-d_6, lower) NMR spectra of **2-T@Py**.

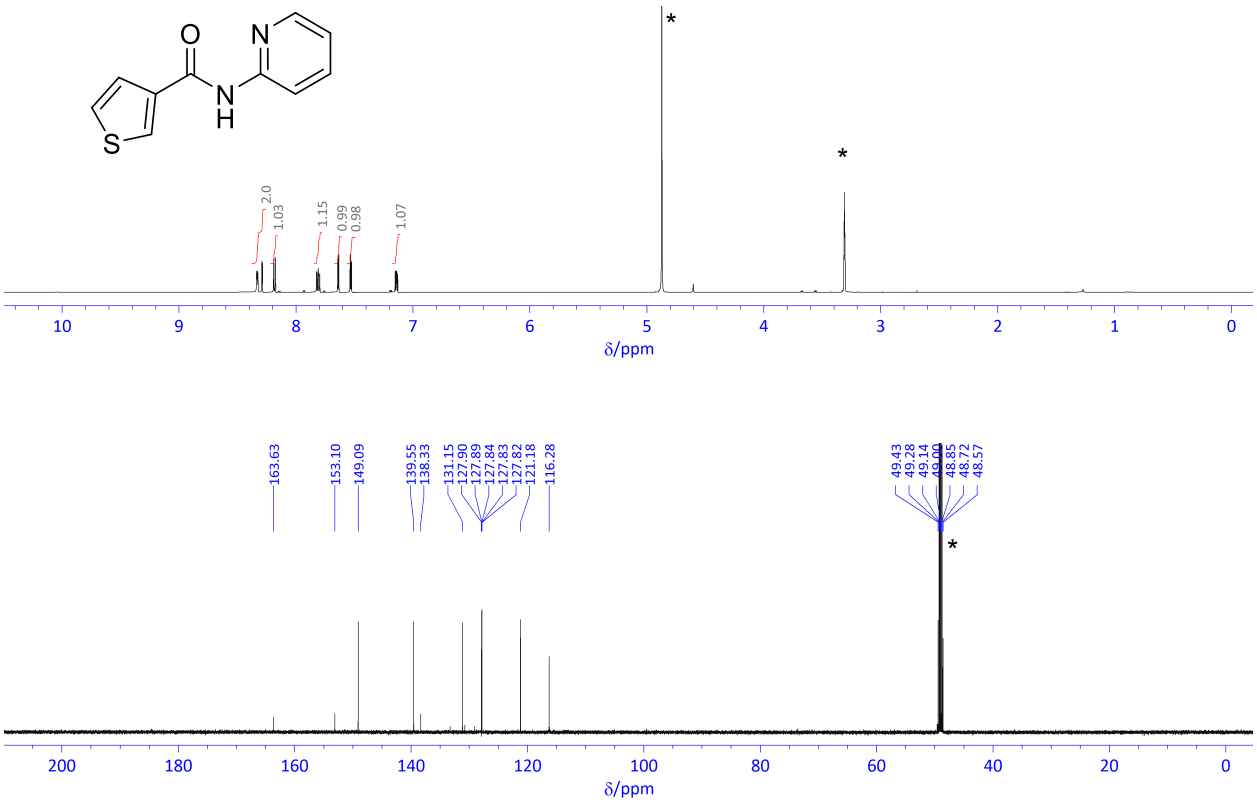


Figure S11. ^{1}H (600 MHz, CD_3OD upper)) and ^{13}C (151 MHz, CD_3OD, lower) NMR spectra of **3-T^Py**.

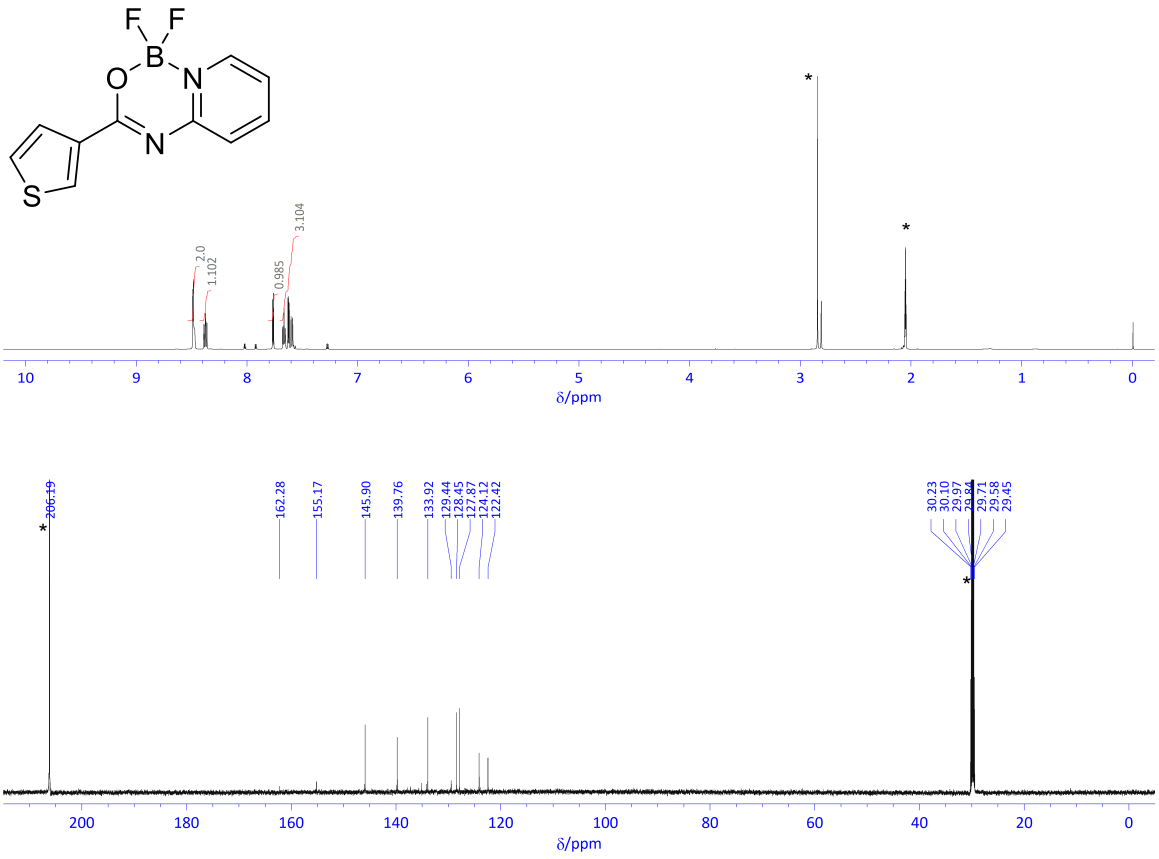


Figure S12. ^{1}H (600 MHz, acetone-d_6 upper)) and ^{13}C (151 MHz, acetone-d_6, lower) NMR spectra of **3-T@Py**.

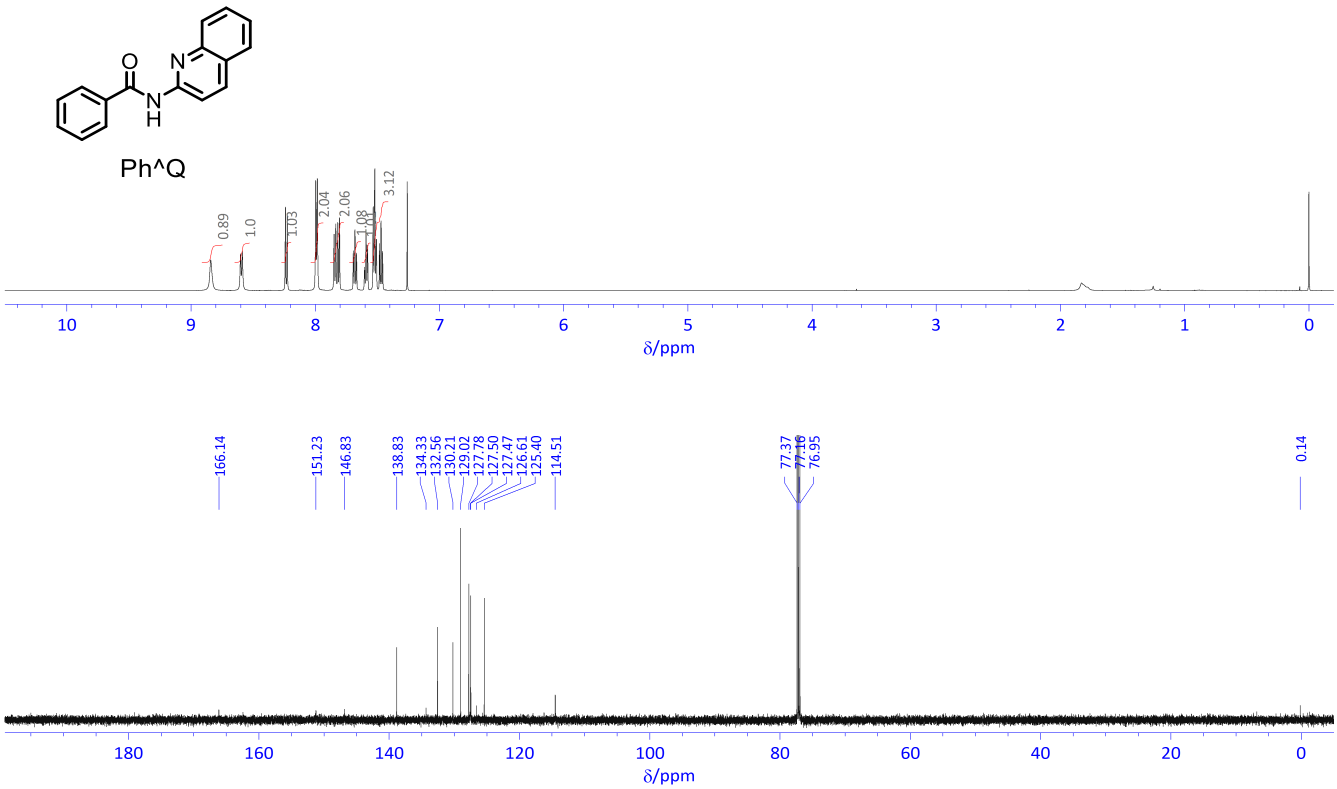


Figure S13. ^{1}H (600 MHz, $CDCl_3$ upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **Ph^Q**.

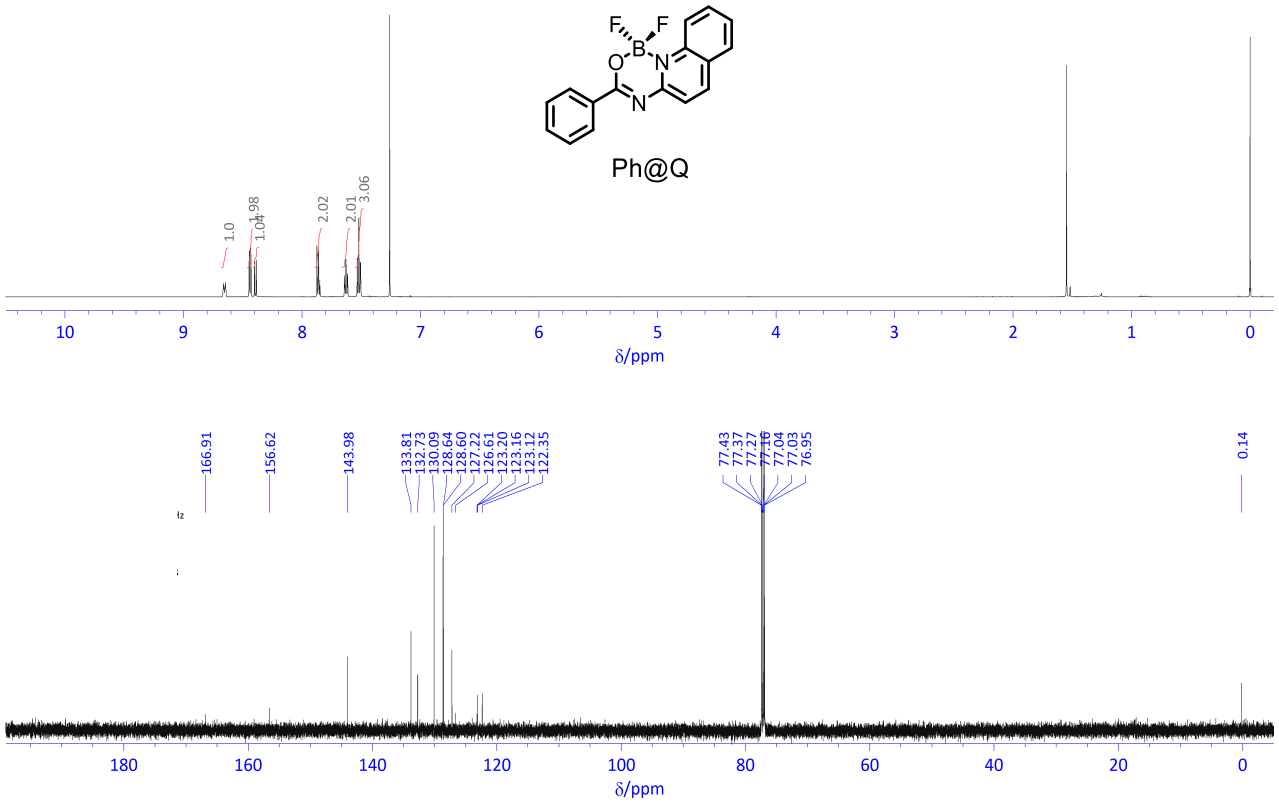


Figure S14. ^{1}H (600 MHz, $CDCl_3$ upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **Ph@Q**.

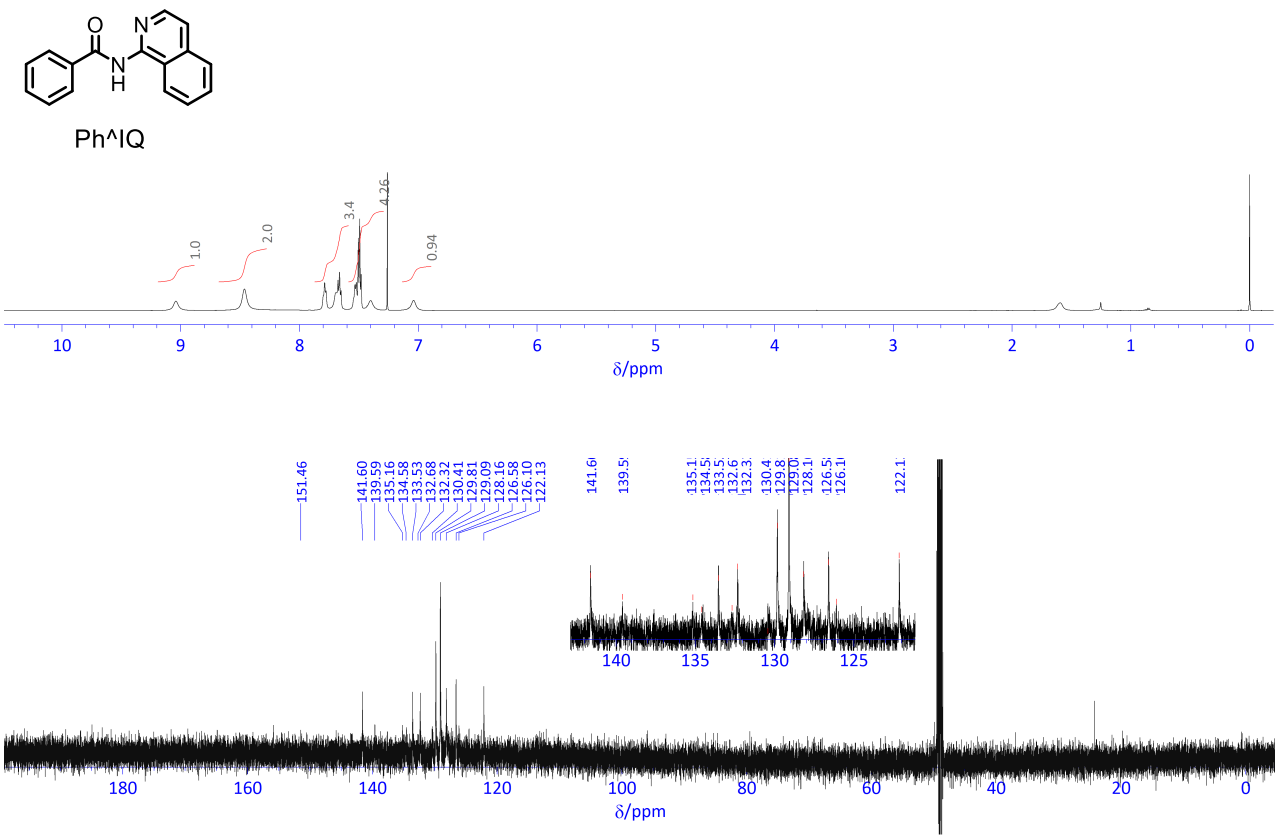


Figure S15. ^{1}H (600 MHz, $CDCl_3$ upper)) and ^{13}C (151 MHz, CD_3OD, lower) NMR spectra of **Ph^IQ**.

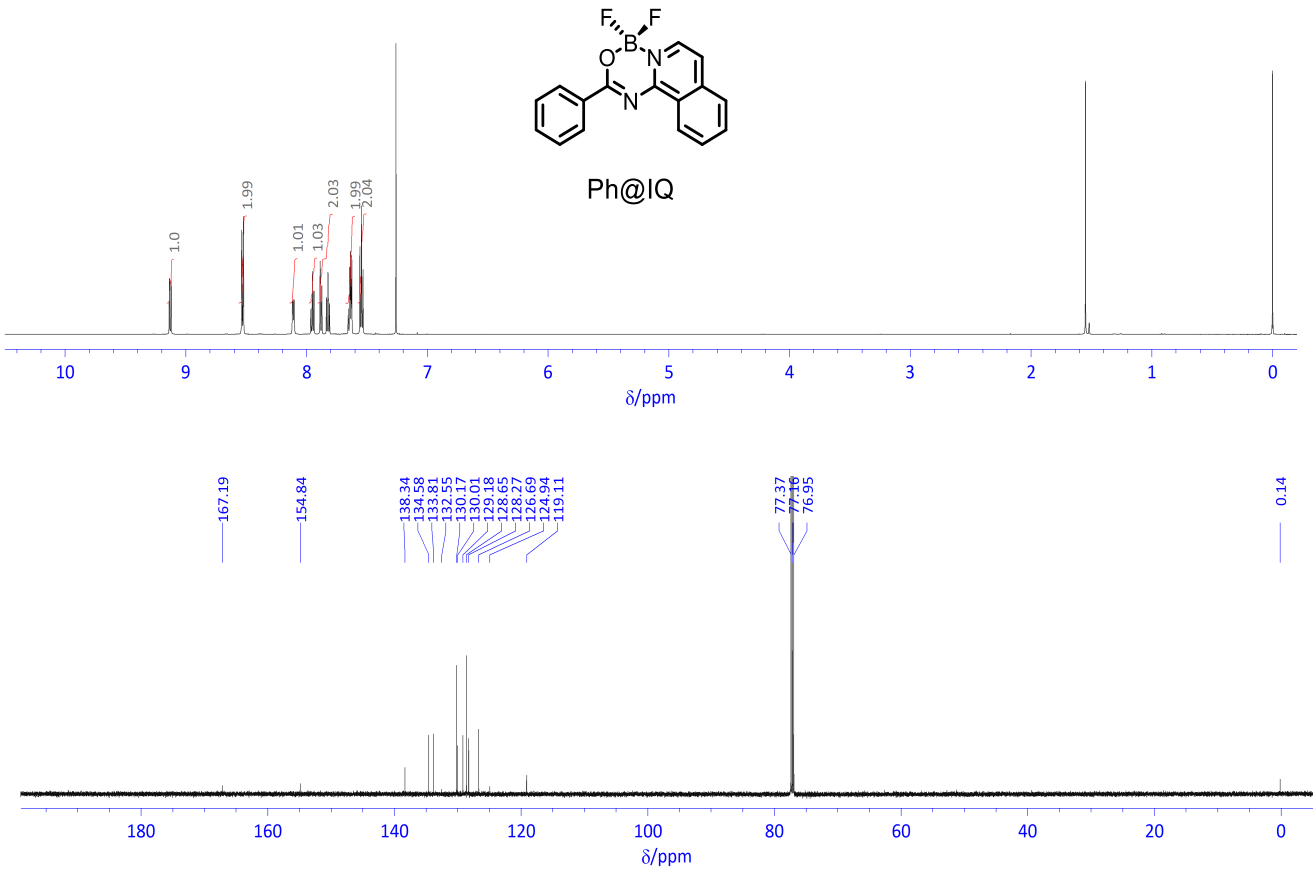


Figure S16. ^{1}H (600 MHz, $CDCl_3$ upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of **Ph@IQ**.

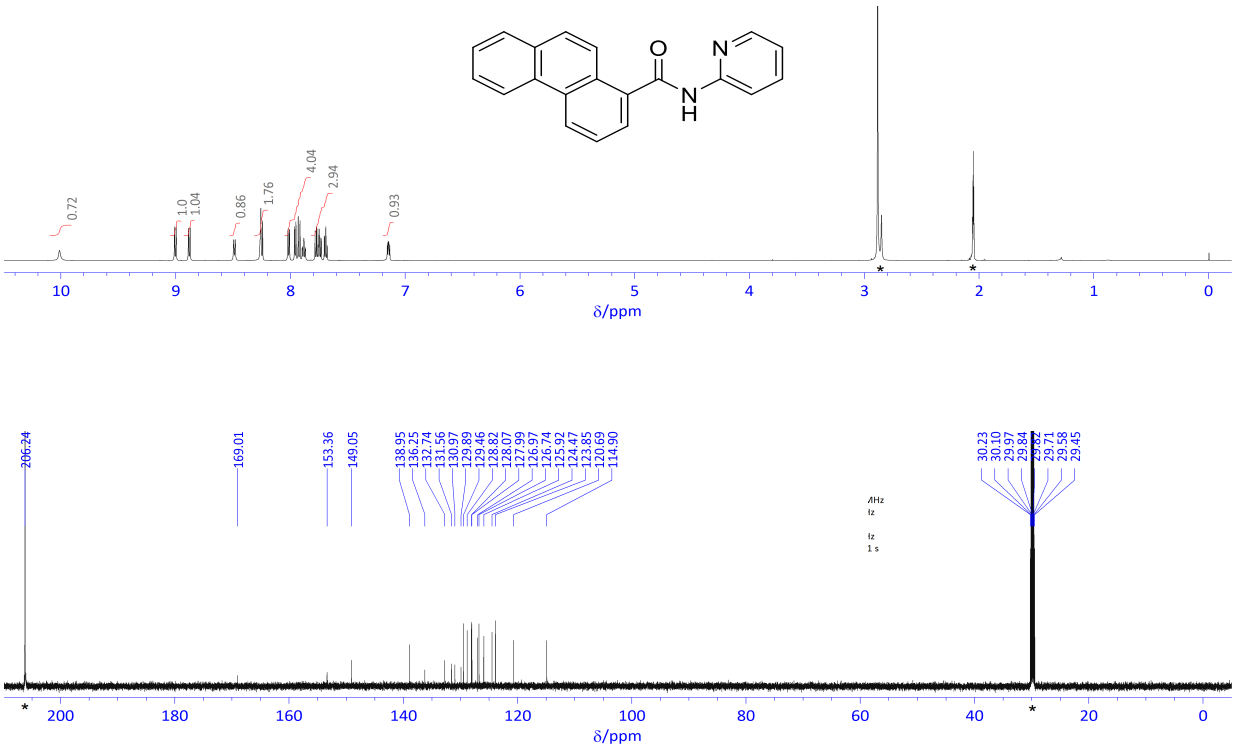


Figure S17. ^{1}H (600 MHz, acetone-d_6 upper)) and ^{13}C (151 MHz, acetone-d_6, lower) NMR spectra of **1-Phen^Py**.

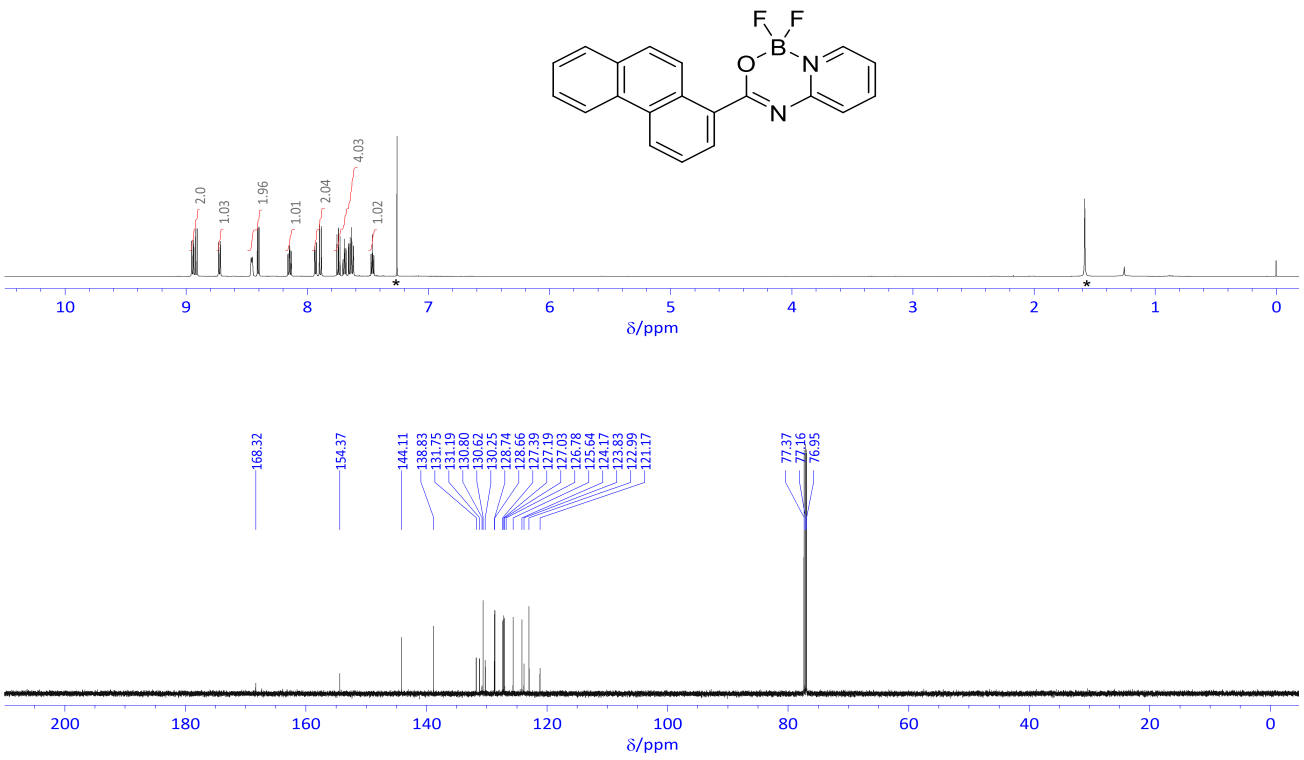


Figure S18. ^{1}H (600 MHz, $CDCl_3$ upper)) and ^{13}C (151 MHz, $CDCl_3$, lower) NMR spectra of 1-**Phen@Py**.

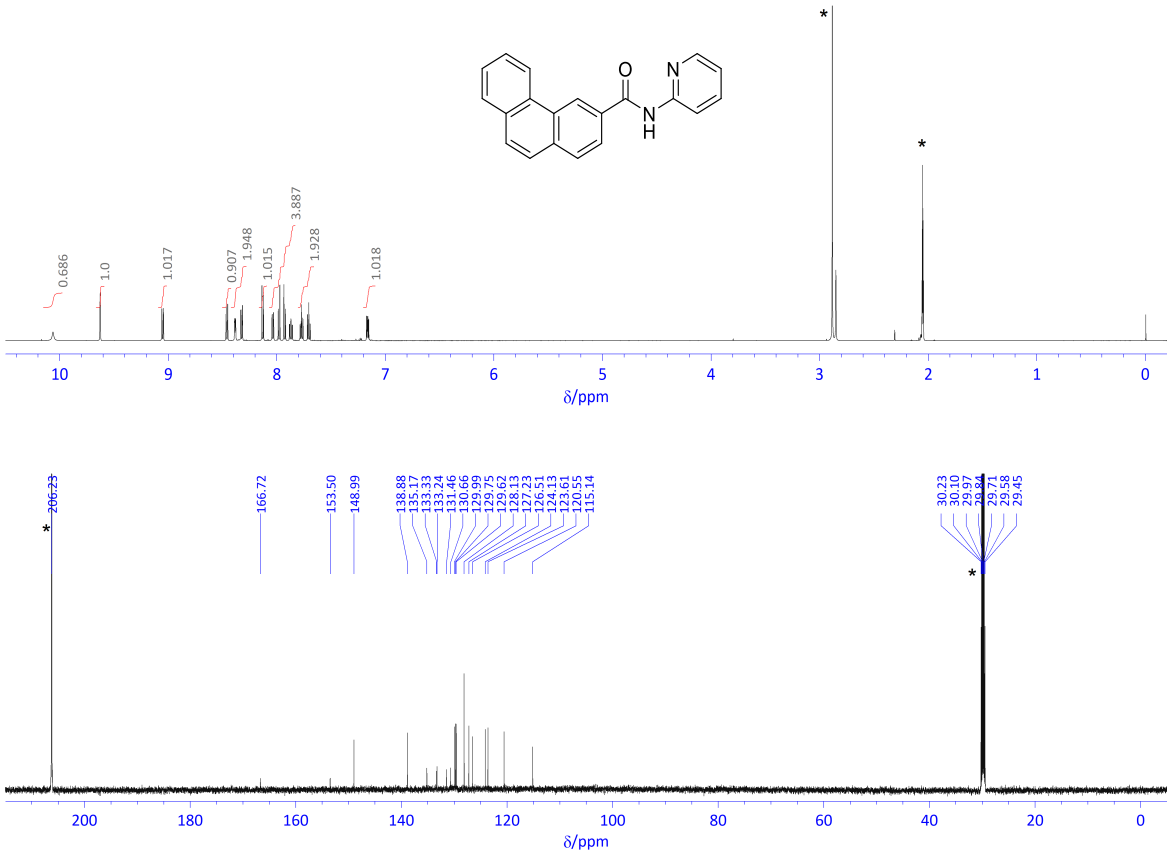


Figure S19. ^{1}H (600 MHz, acetone-d$_6$ upper)) and ^{13}C (151 MHz, acetone-d$_6$, lower) NMR spectra of **3-Phen^Py**.

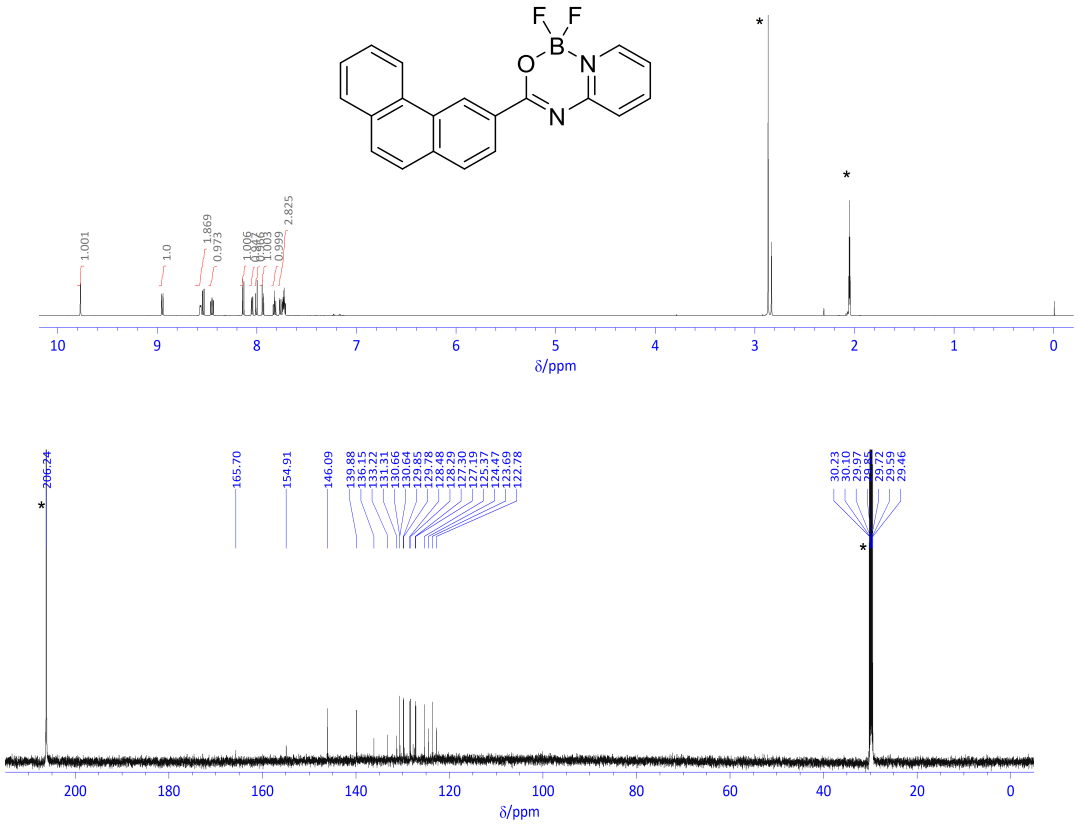


Figure S20. ^{1}H (600 MHz, acetone-d$_6$ upper)) and ^{13}C (151 MHz, acetone-d$_6$, lower) NMR spectra of **3-Phen@Py**.

3. Decay profiles of fluorescence in $CHCl_3$.

Figure S21 shows decay profiles of fluorescence for Ar@HC in $CHCl_3$.

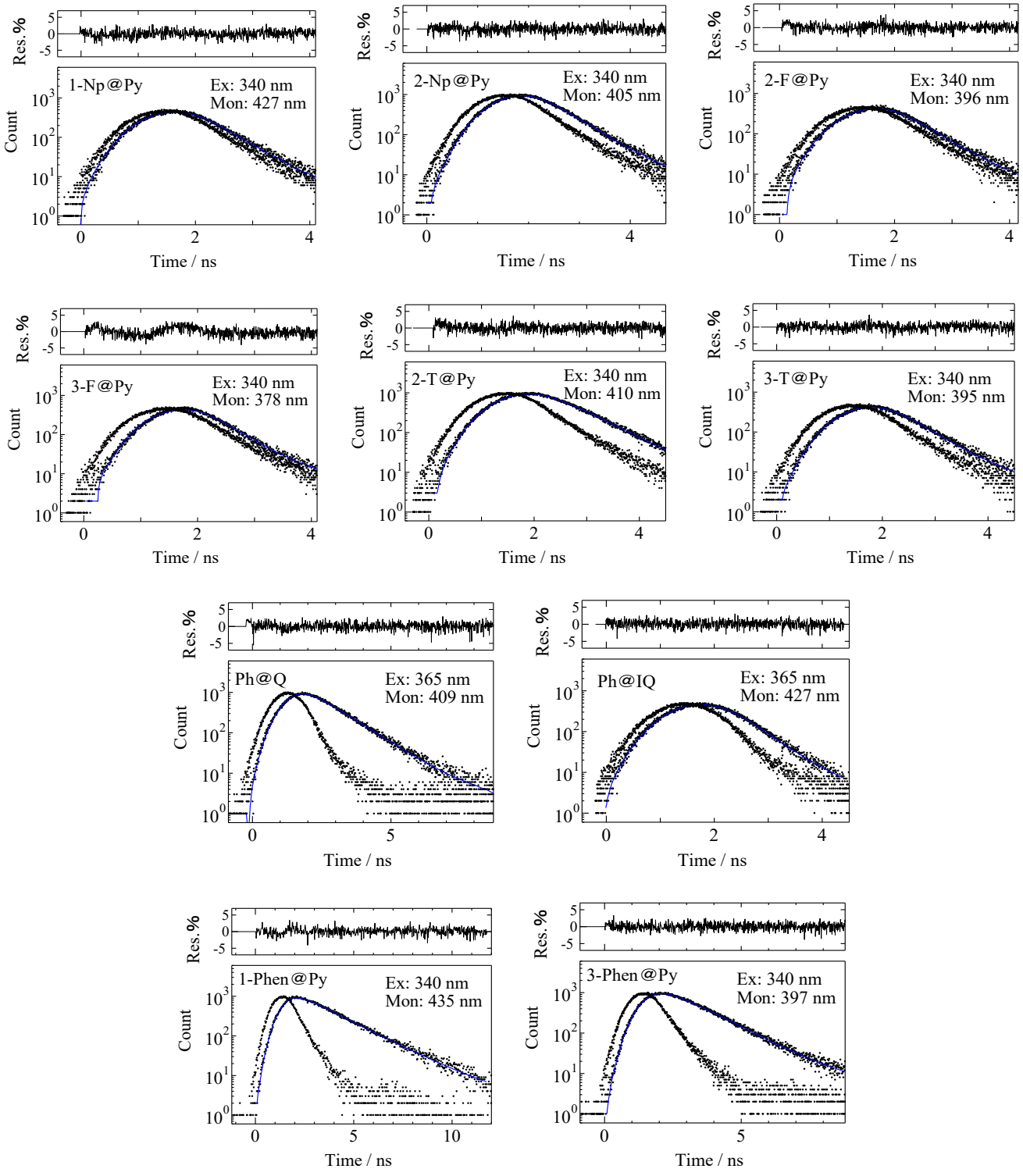


Figure S21. Decay profiles of fluorescence of Ar@HC in $CHCl_3$ at 295 K. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.

Figure S22 shows decay profiles of fluorescence for Ar@HC in the solid state.

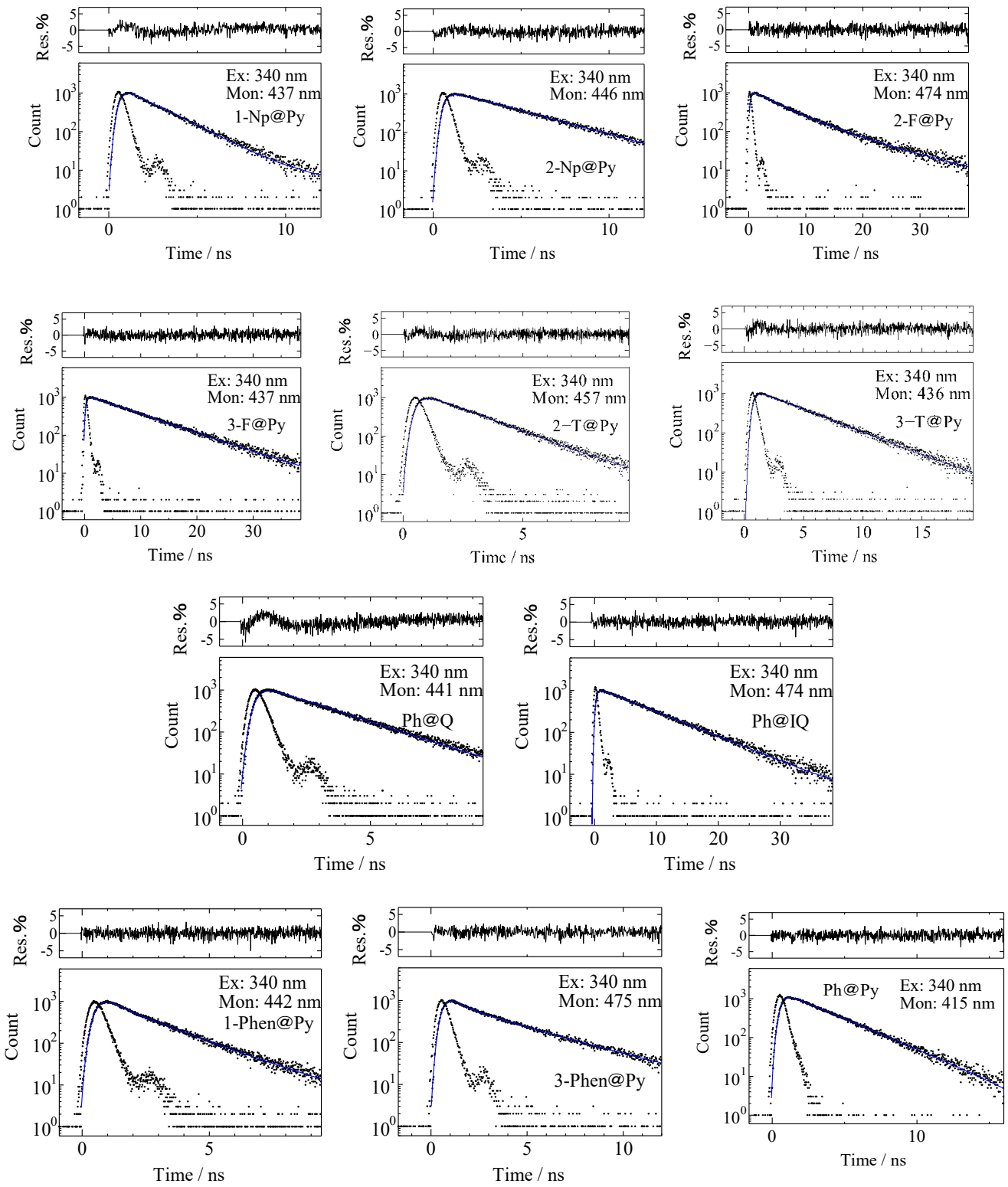


Figure S22. Decay profiles of fluorescence of Ar@HC in the solid state at 295 K. Ex and Mon in the figure indicate the excitation and monitoring wavelengths, respectively.

4. Results of DFT and TD-DFT calculations (atom coordinates and sum of electronic and zero-point energies)

The calculation was carried out at the DFT level, using the Gaussian 09 software package.[1] The geometries of Ar@HC were fully optimized by using the 6-31+G(d) base set at the B3LYP method. Atom coordinates for the optimized geometries of Ar@HC in vacuum and $CHCl_3$ are as follows.

Table S1. Atom coordinates for the optimized geometry of **1-Np@Py** in vacuum.

Atom	X	Y	Z
C	-3.710544	0.557580	0.045773
C	-3.866180	1.949934	0.277513
C	-2.770042	2.775367	0.395118
C	-1.473797	2.232543	0.299654
C	-1.263745	0.872364	0.104991
C	-2.392540	-0.014463	-0.045222
C	0.147975	0.420471	0.077312
O	0.385364	-0.804273	0.491385
N	1.077002	1.269619	-0.301195
C	2.388647	0.907130	-0.241995
C	3.384918	1.872477	-0.516969
C	4.720901	1.529334	-0.447027
C	5.089110	0.214656	-0.101563
C	4.088669	-0.699060	0.151135
N	2.777725	-0.362491	0.079227
B	1.678527	-1.490574	0.300845
F	1.636447	-2.280282	-0.842153
F	2.006039	-2.217974	1.428234
C	-2.297119	-1.407965	-0.326904
C	-3.428054	-2.182591	-0.485596
C	-4.720737	-1.619899	-0.370406
C	-4.853387	-0.274683	-0.112035
H	-4.872784	2.355670	0.353005
H	-2.895724	3.840820	0.566628
H	-0.608667	2.879159	0.393613
H	3.054699	2.871986	-0.775419
H	5.485114	2.272796	-0.656915
H	6.128403	-0.087305	-0.036503

H	4.286810	-1.730509	0.419889
H	-1.324333	-1.870558	-0.415713
H	-3.319660	-3.242194	-0.702192
H	-5.600372	-2.246379	-0.492721
H	-5.838961	0.178801	-0.032609

Sum of electronic and zero-point energies = -1025.608363 Hartree

Table S2. Atom coordinates for the optimized geometry of 2-**Np@Py** in vacuum.

Atom	X	Y	Z
C	-3.287992	-0.422942	-0.053318
C	-3.782524	0.921276	0.020053
C	-2.844601	1.991542	0.083994
C	-1.492051	1.752992	0.075737
C	-0.997332	0.417779	0.002466
C	-1.887549	-0.642887	-0.059757
C	0.456290	0.166226	-0.004385
O	0.814665	-1.092521	-0.133798
N	1.286602	1.178933	0.090317
C	2.629451	0.956552	0.017940
C	3.511742	2.060642	-0.010573
C	4.874459	1.856283	-0.109116
C	5.381719	0.544970	-0.180872
C	4.488637	-0.504675	-0.141696
N	3.152494	-0.303740	-0.042017
B	2.190837	-1.570184	0.090069
F	2.541389	-2.494301	-0.876003
F	2.329767	-2.073019	1.375901
C	-4.217296	-1.499060	-0.116021
C	-5.574310	-1.258230	-0.107659
C	-6.062315	0.071349	-0.035853
C	-5.186370	1.135543	0.026530
H	-3.217729	3.011756	0.139746
H	-0.779778	2.568741	0.124524
H	-1.508101	-1.658458	-0.112826
H	3.075205	3.051418	0.040949
H	5.551663	2.705749	-0.133182

H	6.445158	0.349134	-0.260315
H	4.797978	-1.542834	-0.186889
H	-3.837044	-2.516540	-0.170502
H	-6.275943	-2.086748	-0.155736
H	-7.134615	0.249412	-0.029754
H	-5.562117	2.154837	0.082025

Sum of electronic and zero-point energies = -1025.616741 Hartree

Table S3. Atom coordinates for the optimized geometry of **2-F@Py** in vacuum.

Atom	X	Y	Z
C	2.340994	-0.333207	-0.024757
C	0.906436	-0.113490	-0.016521
O	0.515917	1.128159	-0.164709
N	0.127610	-1.165052	0.110998
C	-1.221469	-0.997138	0.045107
C	-2.062687	-2.134116	0.051135
C	-3.432039	-1.982829	-0.043693
C	-3.988675	-0.693204	-0.145973
C	-3.135371	0.389384	-0.138852
N	-1.791731	0.242103	-0.042119
B	-0.882057	1.551364	0.061272
F	-1.277269	2.441008	-0.917622
F	-1.031467	2.065840	1.340047
O	3.163073	0.756175	-0.131725
C	4.434922	0.295178	-0.111092
C	4.457401	-1.069448	0.007406
C	3.095376	-1.479675	0.062824
H	-1.589409	-3.106473	0.124420
H	-4.077144	-2.857281	-0.041778
H	-5.059077	-0.539289	-0.223847
H	-3.483923	1.413669	-0.208035
H	5.206207	1.047261	-0.188080
H	5.336892	-1.697146	0.049253
H	2.702964	-2.481957	0.155694

Sum of electronic and zero-point energies = -869.818514 Hartree

Table S4. Atom coordinates for the optimized geometry of **3-F@Py** in vacuum.

Atom	X	Y	Z
C	2.350221	-0.209519	-0.028402
C	0.900868	-0.061195	-0.016844
O	0.472054	1.173611	-0.146028
N	0.143724	-1.128742	0.095776
C	-1.210777	-0.993137	0.039503
C	-2.022546	-2.150916	0.047023
C	-3.396231	-2.034620	-0.034799
C	-3.986486	-0.759291	-0.125737
C	-3.161139	0.344503	-0.121967
N	-1.812943	0.230894	-0.038144
B	-0.939366	1.563067	0.050949
F	-1.342333	2.423941	-0.951949
F	-1.119299	2.103596	1.315311
C	3.337894	0.836214	-0.114896
C	4.543927	0.214173	-0.086055
O	4.377482	-1.147383	0.012385
C	3.048586	-1.388222	0.045782
H	-1.523921	-3.111100	0.112301
H	-4.018648	-2.925339	-0.031047
H	-5.061141	-0.632435	-0.193177
H	-3.536463	1.359745	-0.184179
H	3.146265	1.897036	-0.186087
H	5.566920	0.555285	-0.122258
H	2.740850	-2.419174	0.123537

Sum of electronic and zero-point energies = -869.818944 Hartree

Table S5. Atom coordinates for the optimized geometry of **2-T@Py** in vacuum.

Atom	X	Y	Z
C	2.093073	-0.413324	-0.011819
C	0.657020	-0.185426	-0.008920
O	0.289192	1.069182	-0.158241
N	-0.153307	-1.212313	0.111180
C	-1.497798	-1.008354	0.040331
C	-2.367133	-2.123807	0.034714

C	-3.732120	-1.937952	-0.063095
C	-4.256327	-0.634282	-0.156739
C	-3.376454	0.426660	-0.138537
N	-2.037150	0.245031	-0.039222
B	-1.095558	1.528776	0.075331
F	-1.467234	2.439110	-0.894038
F	-1.228443	2.036161	1.359039
S	3.215715	0.919294	-0.126546
C	4.556536	-0.163876	-0.062389
C	4.165861	-1.480266	0.043142
C	2.755607	-1.623477	0.071417
H	-1.918360	-3.108131	0.102077
H	-4.398659	-2.796147	-0.070004
H	-5.322330	-0.453194	-0.236479
H	-3.699162	1.459842	-0.200635
H	5.566207	0.225173	-0.105443
H	4.862992	-2.309428	0.097266
H	2.226844	-2.566012	0.149867

Sum of electronic and zero-point energies = -1192.801899 Hartree

Table S6. Atom coordinates for the optimized geometry of **3-T@Py** in vacuum.

Atom	X	Y	Z
C	2.055428	-0.037293	-0.029724
C	0.592276	0.034299	-0.017722
O	0.097197	1.244812	-0.147963
N	-0.111193	-1.068964	0.094499
C	-1.470581	-1.002608	0.036567
C	-2.221926	-2.200619	0.037703
C	-3.599694	-2.154995	-0.046028
C	-4.254760	-0.911432	-0.132633
C	-3.487235	0.233339	-0.122939
N	-2.135254	0.188857	-0.037165
B	-1.329887	1.562168	0.059484
F	-1.780822	2.410753	-0.933633
F	-1.530305	2.082205	1.329632

C	2.916594	1.107872	-0.130282
C	4.238760	0.768724	-0.117864
S	4.458061	-0.953416	0.018216
C	2.759687	-1.220122	0.056906
H	-1.674738	-3.134205	0.099637
H	-4.175362	-3.076628	-0.047290
H	-5.334416	-0.839728	-0.201475
H	-3.914092	1.228202	-0.182207
H	2.547598	2.123441	-0.205763
H	5.099521	1.421675	-0.178371
H	2.348363	-2.216304	0.141075

Sum of electronic and zero-point energies = -1192.802186 Hartree

Table S7. Atom coordinates for the optimized geometry of **Ph@Q** in vacuum.

Atom	X	Y	Z
C	5.239833	-1.009061	0.000370
C	5.890181	0.229022	0.000208
C	5.142553	1.412178	-0.000030
C	3.750250	1.359686	-0.000087
C	3.092303	0.117635	0.000085
C	3.846692	-1.067845	0.000314
C	1.616146	0.057227	0.000042
O	1.099057	-1.143085	0.000519
N	0.919536	1.170259	-0.000392
C	-0.441039	1.115311	-0.000167
C	-1.126071	2.369237	-0.000149
C	-2.488503	2.409049	0.000050
C	-3.242695	1.200560	0.000193
C	-2.536546	-0.037170	0.000129
N	-1.141579	-0.044066	0.000046
B	-0.350113	-1.433503	-0.000228
F	-0.670492	-2.137745	1.150890
F	-0.669753	-2.136596	-1.152264
C	-4.658682	1.200067	0.000308
C	-5.361307	0.012601	0.000281

C	-4.656447	-1.209980	0.000138
C	-3.273592	-1.244667	0.000066
H	5.818188	-1.929043	0.000521
H	6.976438	0.272523	0.000268
H	5.646574	2.375046	-0.000188
H	3.157832	2.268086	-0.000279
H	3.334575	-2.023852	0.000418
H	-0.512248	3.262110	-0.000315
H	-3.015017	3.360629	0.000076
H	-5.178913	2.154927	0.000379
H	-6.447516	0.015776	0.000346
H	-5.206279	-2.147114	0.000075
H	-2.757474	-2.194280	-0.000020

Sum of electronic and zero-point energies = -1025.617054 Hartree

Table S8. Atom coordinates for the optimized geometry of **Ph@IQ** in vacuum.

Atom	X	Y	Z
C	-5.107541	-0.228820	-0.069699
C	-5.221037	-1.622097	-0.033274
C	-4.069668	-2.416501	0.010716
C	-2.809869	-1.821569	0.017342
C	-2.690032	-0.421790	-0.019033
C	-3.849082	0.371801	-0.062229
C	-1.356130	0.215171	-0.011410
O	-1.358655	1.522036	-0.084423
N	-0.278204	-0.535654	0.051069
C	0.950674	0.044405	0.013645
C	2.117956	-0.805208	0.007677
C	3.409778	-0.205620	-0.047238
C	3.495887	1.218533	-0.094029
C	2.354980	1.961503	-0.080656
N	1.108365	1.385039	-0.026351
B	-0.144178	2.356752	0.047685
F	-0.133022	2.989136	1.281993
F	-0.074074	3.257288	-1.000357

C	2.000106	-2.214657	0.054716
C	3.132282	-3.006525	0.048441
C	4.415443	-2.415686	-0.006686
C	4.553258	-1.041769	-0.054022
H	-5.999820	0.390496	-0.102983
H	-6.203150	-2.088131	-0.038881
H	-4.155679	-3.499524	0.039033
H	-1.910290	-2.425889	0.050618
H	-3.753089	1.451680	-0.088564
H	4.462730	1.709521	-0.137745
H	2.354735	3.044334	-0.112491
H	1.008767	-2.650088	0.096787
H	3.038275	-4.088238	0.085845
H	5.299033	-3.048615	-0.011636
H	5.539313	-0.586122	-0.096343

Sum of electronic and zero-point energies = -1025.619681 Hartree

Table S9. Atom coordinates for the optimized geometry of **1-Phen@Py** in vacuum.

Atom	X	Y	Z
C	-2.648234	1.005050	0.116643
C	-2.657342	2.403117	0.326707
C	-1.484922	3.132294	0.412381
C	-0.249826	2.482750	0.306786
C	-0.182173	1.101928	0.132048
C	-1.387354	0.330174	0.011430
C	1.179633	0.513774	0.096153
O	1.318324	-0.692986	0.599369
N	2.168122	1.242298	-0.370570
C	3.442986	0.762630	-0.319235
C	4.514589	1.609723	-0.684060
C	5.814896	1.147192	-0.625009
C	6.070308	-0.171081	-0.201201
C	4.998111	-0.967947	0.138460
N	3.722546	-0.514133	0.077637
B	2.529418	-1.514389	0.405172

F	2.363943	-2.357559	-0.687742
F	2.831161	-2.206365	1.560904
C	-1.385619	-1.080865	-0.270538
C	-2.548481	-1.777345	-0.406872
C	-3.828490	-1.151099	-0.269547
C	-3.891684	0.248140	-0.007477
C	-5.022779	-1.901004	-0.398355
C	-6.259204	-1.297318	-0.271708
C	-6.330626	0.085685	-0.010806
C	-5.174402	0.837330	0.116202
H	-3.600633	2.930195	0.414446
H	-1.521162	4.207161	0.566808
H	0.674629	3.044823	0.375136
H	4.270198	2.617007	-1.001117
H	6.637666	1.799894	-0.903931
H	7.078665	-0.565238	-0.142638
H	5.108709	-1.993786	0.471404
H	-0.443790	-1.599772	-0.376747
H	-2.514756	-2.842212	-0.626035
H	-4.948570	-2.967414	-0.599666
H	-7.169805	-1.882145	-0.371321
H	-7.298815	0.568759	0.093022
H	-5.272958	1.897941	0.319908

Sum of electronic and zero-point energies = -1179.210135 Hartree

Table S10. Atom coordinates for the optimized geometry of **3-Phen@Py** in vacuum.

Atom	X	Y	Z
C	2.447405	-0.497816	-0.009990
C	2.682408	-1.906066	0.026959
C	1.578812	-2.796272	0.052629
C	0.282094	-2.332316	0.042157
C	0.038826	-0.937282	0.004684
C	1.110415	-0.048324	-0.019962
C	-1.343627	-0.423259	-0.003901
O	-1.464440	0.882691	-0.108026

N	-2.346883	-1.267532	0.066148
C	-3.625098	-0.800695	-0.003878
C	-4.695562	-1.722786	-0.056622
C	-5.996951	-1.269419	-0.151303
C	-6.254502	0.114097	-0.194999
C	-5.183927	0.980498	-0.133396
N	-3.907785	0.535407	-0.037507
B	-2.731368	1.600615	0.120170
F	-2.900120	2.590501	-0.830003
F	-2.782791	2.099230	1.414300
C	3.585533	0.415706	-0.034294
C	4.906193	-0.126318	-0.021152
C	5.090129	-1.549757	0.015125
C	4.027255	-2.402574	0.038147
C	3.445573	1.823573	-0.070285
C	4.551931	2.656712	-0.091842
C	5.853335	2.116860	-0.078580
C	6.021817	0.745183	-0.043908
H	1.773471	-3.866002	0.080739
H	-0.560065	-3.014645	0.062132
H	0.886413	1.010233	-0.045373
H	-4.449195	-2.777864	-0.025900
H	-6.818542	-1.979323	-0.193816
H	-7.263501	0.503647	-0.270772
H	-5.296910	2.058523	-0.157680
H	6.106228	-1.938037	0.024101
H	4.182827	-3.478549	0.065836
H	2.457974	2.271891	-0.081025
H	4.411975	3.734159	-0.118757
H	6.717455	2.775723	-0.095444
H	7.020761	0.314464	-0.033395

Sum of electronic and zero-point energies = -1179.219964 Hartree

5. X-ray crystallographic analysis data of BF_2 complexes.

Crystallographic data of the studied Ar@HCs are listed in Tables S 11-14. We were unable to prepare single crystals of **Ph@Q** and **3-Phen@Py** for X-ray analysis. The X-ray crystal structure was solved by direct methods (Sir2011)[2] and refined by full-matrix least-squares analysis (SHELXL-2013),[3] using an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically, whereby hydrogen positions are based on stereochemical considerations.

Table S11. Crystallographic data of compounds **1-Np@Py** and **2-Np@Py**

Compound	**1-Np@Py (CCDC-1881146)**	**2-Np@Py (CCDC-1881147)**
Empirical formula (FW)	$C_{16}H_{11}BF_2N_2O$ (296.08)	$C_{16}H_{11}BF_2N_2O$ (296.08)
Crystal dimensions	0.300 ×0.240 × 0.030 mm (colorless platelete)	0.190 ×0.140 × 0.050 mm (colorless prism)
Crystal system	triclinic	triclinic
a	7.5092(4) Å	7.0633(4) Å
b	7.9819(4) Å	8.1684(4) Å
c	11.4185(5) Å	11.4242(6) Å
α	100.717(7) °	85.790(6) °
β	98.301(7) °	83.433(6) °
γ	97.041(7) °	88.598(6) °
V	657.51(6) $Å^3$	652.96(6) $Å^3$
Space group	P-1 (No. 2)	P-1 (No. 2)
Z	2	2
ρ_{calcd}	1.495 g/cm^3	1.506 g/cm^3
F(000)	304.00	304.00
μ(CuKα)	9.540 cm^{-1}	9.606 cm^{-1}
$2\theta_{max}$	136.5 °	136.5°
Obs. Temp.	−150 °C	−150 °C
Total reflections measured	Total: 7844 Unique: 2364 (R_{int} = 0.0556)	Total: 7851 Unique: 2338 (R_{int} = 0.0375)
Number of parameters	199	243
Data/parameter ratio	12.79	9.62
R1 (I>2.00σ(I))	0.0540	0.0548
*wR*2 (All reflections)	0.1582	0.1853
GOF	1.06	1.07
Max/min residual density	0.37/−0.31 e^- $Å^3$	0.45/−0.30 e^- $Å^3$

Table S12. Crystallographic data of compounds **2-F@Py** and **3-F@Py**

Compound	**2-F@Py (CCDC-1881148)**	**3-F@Py (CCDC-1881149)**
Empirical formula (FW)	$C_{10}H_7BF_2N_2O_2$ (235.98)	$C_{10}H_7BF_2N_2O_2$ (235.98)
Crystal dimensions	0.520 ×0.240 × 0.100 mm (colorless prism)	0.200 ×0.080 × 0.040 mm (colorless prism)
Crystal system	triclinic	monoclinic
a	7.1941(3) Å	11.1853(4) Å
b	8.5967(4) Å	26.0241(9) Å
c	9.1402(4) Å	7.1318(3) Å
α	88.519(6) °	
β	70.424(5) °	105.872(8)°
γ	67.994(5) °	
V	490.57(4) $Å^3$	1996.83(15) $Å^3$
Space group	P-1 (No. 2)	$P2_{1/c}$ (No. 14)
Z	2	8
ρ_{calcd}	1.597 g/cm^3	1.570 g/cm^3
F(000)	240.00	960.00
μ(CuKα)	11.820 cm^{-1}	11.616 cm^{-1}
$2\theta_{max}$	136.4 °	136.4 °
Obs. Temp.	−150.0 °C	−150.0 °C
Total reflections measured	Total: 5873 Unique: 1767 (R_{int} = 0.0458)	Total: 13554 Unique: 3577 (R_{int} = 0.0870)
Number of parameters	154	307
Data/parameter ratio	11.47	11.65
R1 (I>2.00σ(I))	0.0665	0.0964
*wR*2 (All reflections)	0.2008	0.2904
GOF	1.015	1.022
Max/min residual density	0.68/−0.64 e^- $Å^3$	0.52/−0.43 e^- $Å^3$

Table S13. Crystallographic data of compounds **2-T@Py** and **3-T@Py**

Compound	**2-T@Py (CCDC-1881152)**	**3-T@Py (CCDC-1881150)**
Empirical formula (FW)	$C_{10}H_7BF_2N_2OS$ (252.04)	$C_{10}H_7BF_2N_2OS$ (252.04)
Crystal dimensions	0.300 ×0.030 × 0.010 mm (colorless prism)	0.300 ×0.200 × 0.100 mm (colorless platelet)
Crystal system	orthorthombic	triclinic
a	15.855(5) Å	7.3383(3) Å
b	13.112(4) Å	11.6331(5) Å
c	4.9675(14)Å	12.4095(5) Å
α		83.136(6)°
β		79.631(6)°
γ		83.755(6)°
V	1032.7(5) $Å^3$	1030.46(8) $Å^3$
Space group	$P_{na}2_1$ (No. 33)	P-1 (No. 2)
Z	4	4
ρ_{calcd}	1.621/cm^3	1.625 g/cm^3
F(000)	512.00	512.00
μ(MoKα)	3.223 cm^{-1}	
μ(CuKα)		29.348 cm^{-1}
$2\theta_{max}$	55.0 °	136.4 °
Obs. Temp.	−149.8 °C	−150.0 °C
Total reflections measured	Total: 5597 Unique: 2246 (R_{int} = 0.0311)	Total: 12208 Unique: 3703 (R_{int} = 0.0548)
Number of parameters	200	307
Data/parameter ratio	11.23	12..06
R1 (I>2.00σ(I))	0.0390	0.0515
*wR*2 (All reflections)	0.0758	0.1465
GOF	1.115	1.084
Max/min residual density	0.23/−0.19 e^- $Å^3$	0.55/−0.42 e^- $Å^3$

Table S14. Crystallographic data of compounds **Ph@IQ** and **1-Phen@Py**

Compound	**Ph@IQ (CCDC-1881151)**	**1-Phen@Py (CCDC-1880203)**
Empirical formula (FW)	$C_{16}H_{11}BF_2N_2O$ (296.08)	$C_{20}H_{13}BF_2N_2O$ (346.13)
Crystal dimensions	0.200 ×0.100 × 0.105 mm (yellow prism)	0.250 ×0.100 × 0.050 mm (colorless platelet)
Crystal system	monoclinic	monoclinic
a	7.2084(2) Å	7.2247(7) Å
b	10.4274(4) Å	8.2901(6) Å
c	17.7519(6) Å	12.9787(14) Å
α		94.973(7)°
β	94.312(7) °	93.331(8)°
γ		98.458(7)°
V	1330.54(8)Å^3	764.01(12) Å^3
Space group	Pn (No. 7)	P-1 (No. 2)
Z	4	2
ρ_{calcd}	1.478 g/cm^3	1.505 g/cm^3
F(000)	608.00	356.00
μ(CuKα)	9.248 cm^{-1}	
μ(MoKα)		11.00 cm^{-1}
$2\theta_{max}$	136.4 °	50.7 °
Obs. Temp.	−150.0 °C	−150.0 °C
Total reflections measured	Total: 15104 Unique: 4483 (R_{int} = 0.0357)	Total: 7323 Unique: 2772 (R_{int} = 0.0270)
Number of parameters	397	235
Data/parameter ratio	11.29	11.80
R1 (I>2.00σ(I))	0.0451	0.0414
*wR*2 (All reflections)	0.1035	0.1198
GOF	1.046	1.022
Max/min residual density	0.29/−0.26 e$^-$ Å^3	0.23/−0.21 e$^-$ Å^3

We were unable to prepare single crystals of **Ph@Q** and **3-Phen@Py** for X-ray analysis.

X-ray structures and crystal packing of studied compounds except for **1-Np@Py**, **3-T@Py**, **Ph@Q, 1-Phen@Py** and **3-Phen@Py** are shown below in Figures S23-27.

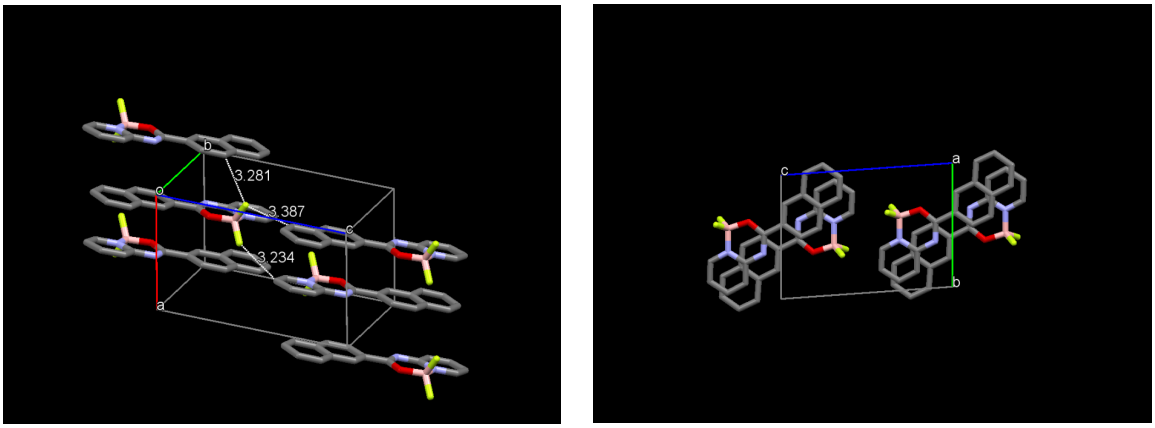


Figure S23. In the crystal of **2-Np@Py**, the molecule is stacked to form a dimeric head-to tail structure in an anti-fashion along with the a-axis. The face-to-face distance the molecules in the column was 3.49 Å. No full-overlap between the naphthyl and BF_2 moieties was observed. The fluorine atoms at BF_2 unit were interacted with the hydrogen atoms of furan, pyridine and naphthyl rings.

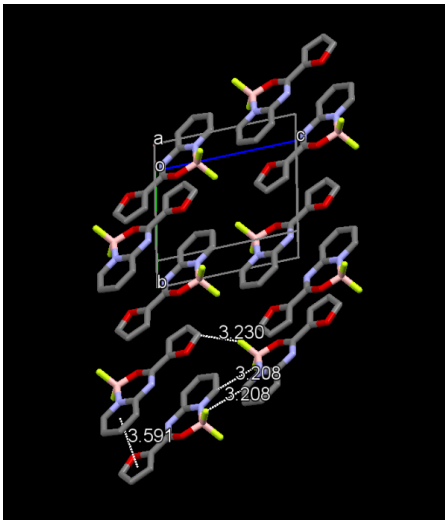


Figure S24. In the crystal of **2-F@Py**, the molecule is stacked along the a-axis to form dimeric head-to-tail structure. The center-to-center distance between the furan and pyridine rings was 3.52 Å. The fluorine atoms at BF_2 unit were interacted with the hydrogen atoms of furan and pyridine rings at the neighboring column in the distances of 3.21-3.23 Å.

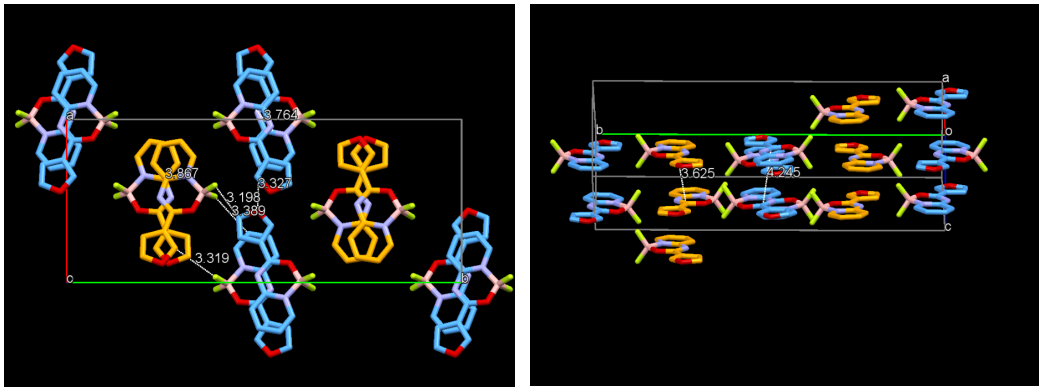


Figure S25. Two-type coordinates were seen in the single crystal of **3-F@Py** depending on the dihedral angles between the furan and BF_2 rings, which were 4.33° shown in blue color and 1.33° in yellow color. In the single crystalline of 3-F@Py, the molecule is stacked to form two-type columns along the c-axis in anti, head-to-tail (blue) and anti, head-to-head forms (yellow). The centroid distances between the molecules were 4.25 Å for the blue column (anti, head-to-tail type) and 3.63 Å for the yellow one (anti, head-to-head).

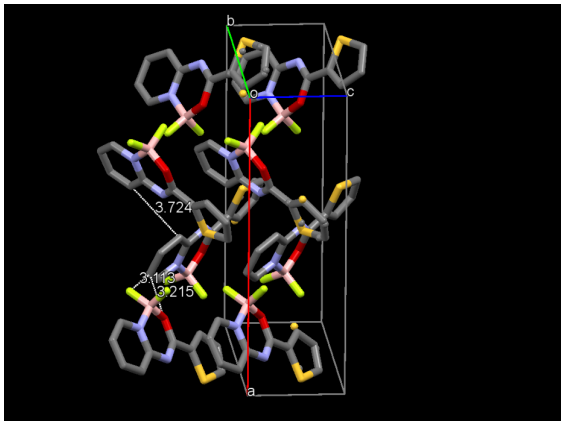


Figure S26. The molecule **2-T@Py** adopted *syn*- and *anti*- configurations due to the orientation of the thiophen ring. In the crystal, a disorder was observed in a ratio of 15: 85 (*syn* to *anti*). A slipped-stack column was seen along the c-axis. The face-to-face distance between the BF_2 moieties was 3.47 Å. The neighbored columns are interacted between F and H atoms of the corresponding BF_2 unit and the pyridine ring, respectively.

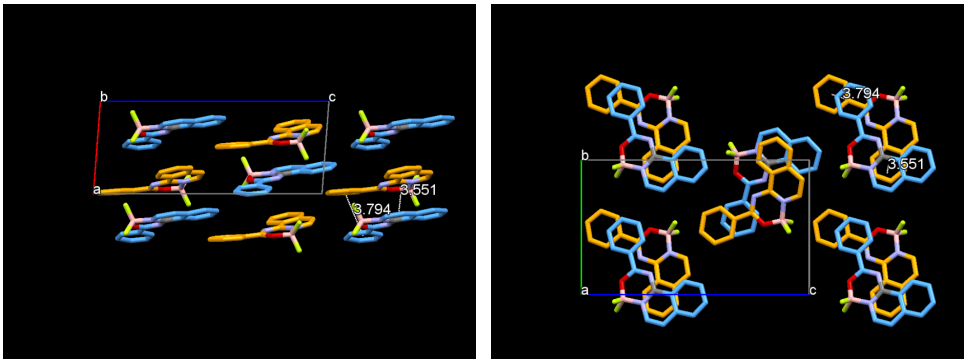


Figure S27. Two-type coordinates were seen in the single crystal of **Ph@IQ** depending on the dihedral angles between the neighbored **Ph@IQ** molecules, which were 4.68° shown in blue color and 6.37° in yellow color. The blue- and yellow-colored molecules are mutually stacked in anti, head-to-head form along the a-axis. The distances between the isoquinolines moieties was 3.79 Å whereas that between the phenyl rings was 3.55 Å.

6. References

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