Supporting Information

Synthesis of phenanthridine derivatives via cascade annulation of diaryliodonium salts and nitriles

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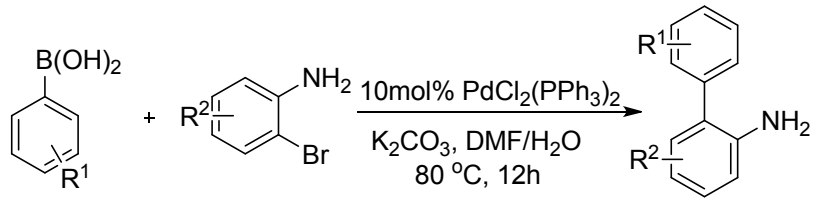
General Remarks.

All reactions were carried out under an air atmosphere condition. Various reagents were purchased from Aldrich, Acros or Alfa. Flash column chromatography was performed using silica gel (200–300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on Bruker NMR-300 (300MHz), NMR-400 (400MHz) and NMR-500 (500MHz) with TMS as an internal reference. The model of HRMS is Bruker maXis UHR-TOF and HPLC is Agilent 1260.

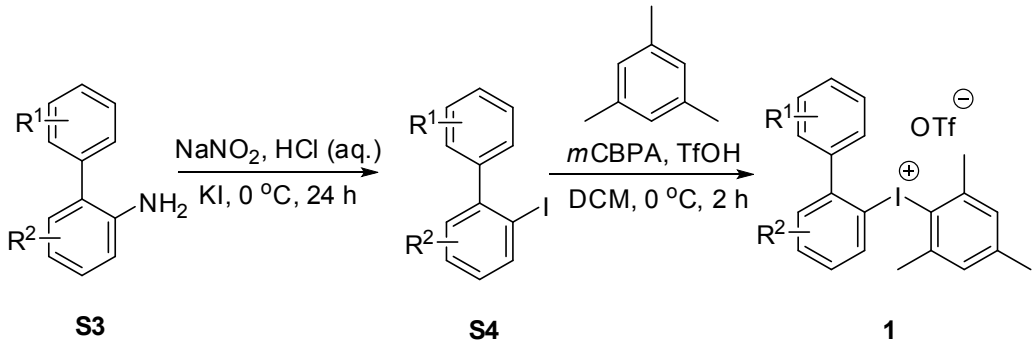
1. Experimental Procedure for the Synthesis of 2-Aminobiaryl Compounds S3.[1,2]



S1 **S2** **S3**

$PdCl_2(PPh_3)_2$ (10 mol%), aryl boronic acid **S1**(15 mmol), 2-bromoaniline **S2**(10 mmol), $K_3PO_4 \cdot 7H_2O$ (3 equiv) and DMF/H_2O (5mL/5mL) were added subsequently in a 100 mL two-neck flask under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12h. Upon completion of the reaction, the resulting mixture was cooled to room temperature and filtered through a short path of silica gel, eluting with 20mL of CH_2Cl_2. The organic layer was washed with H_2O and dried over anhydrous Na_2SO_4. The volatile compounds were removed in vacuo and the residue was purified by column chromatography on silica gel to afford 2-Aminobiaryl Compounds **S3**.

2. Experimental Procedure for the Synthesis of Diaryliodonium Salts 1.[3-6]

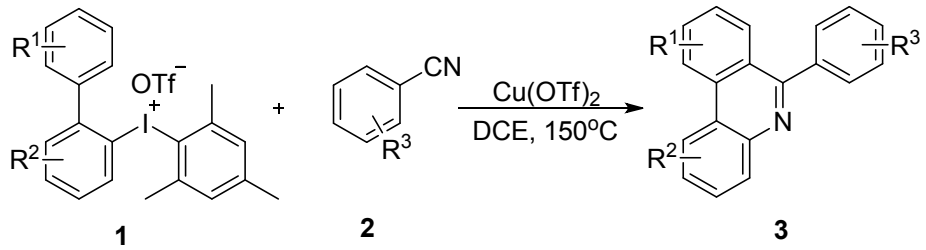


S3 **S4** **1**

An aqueous sodium nitrite solution (2 M, 10.0 mL) was added dropwise into a reaction mixture of **S3** (13 mmol) and 35% hydrochloric acid (7.0 mL), and the resulting mixture was stirred at 0 °C for 15 min. The above mixture was poured into a solution containing potassium iodide (50 mmol) and water (30 mL) and the combined reaction solution was stirred at room temperature overnight. The mixture was extracted with ethyl acetate (3 * 30 mL). The combined organic layers were washed with H_2O (3 * 30 mL) and dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure and the resultant was purified by column chromatography to give compound **S4**.

*m*CPBA10 (85%, 2.5 mmol), **S4** (2.0 mmol), and Mesitylene (3.0 mmol) were dissolved in CH_2Cl_2 (5 mL). Then, TfOH (5.0 mmol) was added to the solution dropwise at 0 °C and the mixture was stirred at r.t. for 2 h and the solution was concentrated in vacuo. Et_2O (1 mL) was added and the mixture was stirred at r.t. for 10 min to precipitate out an off-white solid. The precipitate was filtered off, washed with Et_2O, and dried under vacuum to give salt **1**.

3. General Procedure for Cascade Annulation of Diaryliodonium Salts and Nitriles



A solution of diaryliodonium salts **1** (1 mmol), nitriles **2** (2.0 mmol) and $Cu(OTf)_2$ (36 mg, 0.1 mmol) in DCE (2 mL) was stirred at 150 ºC for 20 h. After completion of the reaction (observed on TLC), the solvent was evaporated under reduced pressure to obtain the crude mixture. The residues was purified by silica-gel column chromatography (Ethyl acetate / Petroleum ether = 1/10 - 1/4) to afford the pure product **3**. The obtained product was analyzed by ^{1}H NMR, ^{13}C NMR and HRMS.

Refferences:

[1] V. Rajeshkumar, F.-W. Chan and S.-C. Chuang, *Adv. Synth. Catal.* 2012, **354**, 2473.

[2] S. W. Youn and J. H. Bihn, *Tetrahedron Lett.* 2009, **50**, 4598.

[3] M. R. Stillings, A. Welbourn and D. S. J. Walter, *J. Med. Chem.*, 1986, **29**, 2280.

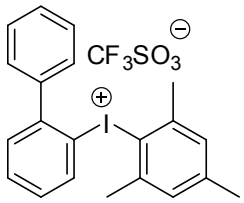
[4] I. Bonnaventure and A. B. Charette, *J. Org. Chem.*, 2008, **73**, 6330.

[5] M. Bielawski, M. Zhu, and B. Olofsson, *Adv. Synth. Catal.* 2007, **349**, 2610.

[6] M. Zhu, N. Jalalian and B. Olofsson, *Synlett* 2008, **4**, 592.

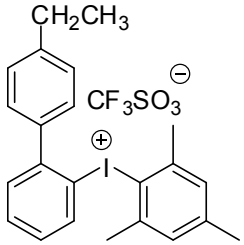
Characterization of compounds 1 and 3

Biphenyl-2-yl(mesityl)iodonium **(1a)**.



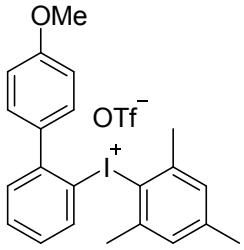
Withe solid (0.94g, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H), 7.54-7.52 (m, 1H), 7.38-7.33 (m, 3H), 7.29-7.28 (m, 1H), 7.08 (s, 2H), 2.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.2, 144.7, 142.7, 140.1, 134.6, 133.7, 132.1, 132.0, 131.2, 130.5, 130.2, 129.9, 129.8, 128.4, 128.3, 120.5, 114.5, 26.8, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{20}I$ ([M^+]): 399.0604 found 399.0610. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9520.

(4'-Ethylbiphenyl-2-yl)(mesityl)iodonium **(1b).**



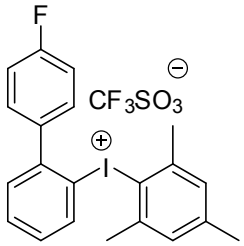
Withe solid (0.95g, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 1H), 7.53-7.51 (m, 1H), 7.42-7.40 (m, 2H), 7.32 (t, J = 8.2 Hz, 1H), 7.26-7.24 (m, 2H), 7.18-7.16 (m, 1H), 7.09 (s, 2H), 2.77 (q, J = 7.6 Hz, 2H), 2.43 (s, 6H), 2.37 (s, 3H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.7, 144.8, 144.2, 142.7, 136.0, 132.3, 132.2, 131.3, 130.5, 130.4, 120.5, 117.1, 116.9, 114.6, 26.8, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{23}H_{24}I$ ([M^+]): 427.0917 found 427.0922. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9520.

(4'-Methoxybiphenyl-2-yl)(mesityl)iodonium **(1c).**



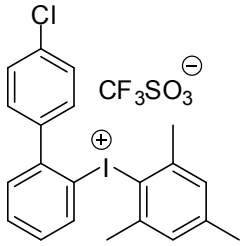
Withe solid (0.75g, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 3H), 7.52-7.50 (m, 1H), 7.33-7.26 (m, 3H), 7.18 (d, J = 8.0 Hz, 1H), 7.09-7.07 (m, 4H), 3.90 (s, 3H), 2.43 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 144.8, 144.7, 142.8, 132.1, 131.8, 130.9, 130.8, 130.5, 129.6, 120.5, 115.4, 55.6, 26.9, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{22}H_{22}IO$ ([M^+]): 429.0710 found 429.0701. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9517.

(4'-Fluorobiphenyl-2-yl)(mesityl)iodonium **(1d).**



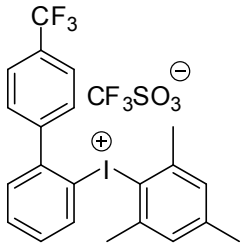
Withe solid (0.80g, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 3H), 7.40 (dd, J = 5.0, 8.7 Hz, 1H), 7.33-7.31 (m, 2H), 7.25-7.24 (m, 1H), 7.12-7.07 (m, 1H), 7.06 (s, 2H), 2.36-2.35 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.1, 142.7, 138.2, 136.7, 132.7, 132.2, 131.4, 130.6, 130.1, 129.8, 120.6, 114.5, 26.8, 21.2. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}FI$ ([M^+]): 417.0510 found 417.0509. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9528.

(4'-Chlorobiphenyl-2-yl)(mesityl)iodonium **(1e).**



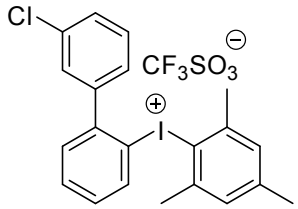
Withe solid (0.72g, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1H), 7.54-7.52 (m, 2H), 7.50-7.45 (m, 2H), 7.39-7.35 (m, 1H), 7.29-7.27 (m, 2H), 7.06 (s, 2H), 2.37-2.36 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.8, 142.6, 141.4, 135.7, 133.2, 132.2, 131.5, 131.1, 130.6, 130.2, 128.5, 126.6, 120.4, 114.1, 26.7, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}ClI$ ([M^+]): 433.0214 found 433.0220. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9521.

Mesityl(4'-(trifluoromethyl)biphenyl-2-yl)iodonium **(1f).**



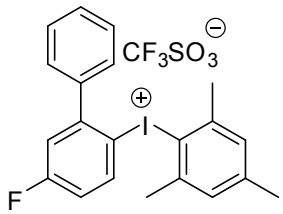
Withe solid (0.53g, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.66-7.64 (m, 2H), 7.51-7.44 (m, 4H), 7.02 (s, 2H), 2.35-2.31 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.8, 142.6, 134.1, 132.4, 132.2, 131.6, 130.5, 129.1, 126.6, 120.3, 114.1, 26.6, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{22}H_{19}F_3I$ ([M^+]): 467.0478 found 467.0483. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9522.

(3'-Chlorobiphenyl-2-yl)(mesityl)iodonium **(1g).**



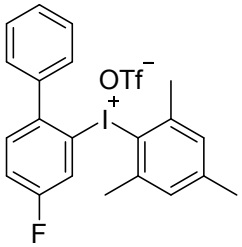
Withe solid (0.78g, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 7.5 Hz, 1H), 7.53-7.48 (m, 4H), 7.40 (t, J = 7.5 Hz, 1H), 7.27 (s, 1H), 7.15 (s, 1H), 7.06 (s, 2H), 2.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.7, 142.7, 140.8, 137.2, 131.9, 131.7, 130.9, 130.7, 130.6, 130.4, 129.9, 128.3, 128.0, 120.7, 114.7, 26.9, 21.4, 21.1. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}ClI$ ([M^+]): 433.0214 found 433.0211. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9520.

(5-Fluorobiphenyl-2-yl)(mesityl)iodonium **(1h).**



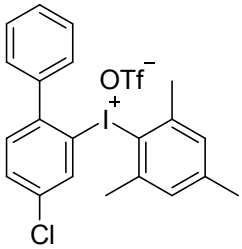
Withe solid (0.81g, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 3H), 7.38(dd, J = 5.0, 8.9 Hz, 1H), 7.33-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.12-7.07 (m, 1H), 7.06 (s, 2H), 2.37-2.36 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 163.2, 147.9, 144.8, 142.6, 139.1, 134.6, 130.6, 130.0, 128.2, 121.2, 119.6, 119.4, 118.6, 118.4, 108.0, 26.7, 21.7. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}FI$ ([M^+]): 417.0510 found 417.0512. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9523.

***(4-Fluorobiphenyl-2-yl)(mesityl)iodonium* (1i).**



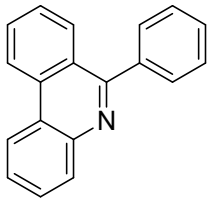
Withe solid (0.79g, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 4H), 7.48-7.45 (m, 1H), 7.34-7.31 (m, 2H), 7.14-7.11 (m, 3H), 2.43 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.5, 142.6, 138.9, 136.7, 132.5, 132.1, 130.7, 130.6, 130.1, 128.2, 121.0, 114.5, 26.9, 21.2. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}FI$ ([M^+]): 417.0510 found 417.0511. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9522.

***(4-Chlorobiphenyl-2-yl)(mesityl)iodonium* (1j).**



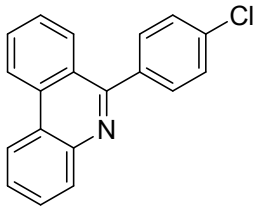
Withe solid (0.99g, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 3H), 7.54-7.50 (m, 1H), 7.35-7.29 (m, 3H), 7.13 (s, 2H), 6.85-6.82 (m, 1H), 2.46 (s, 6H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 162.1, 145.2, 142.7, 141.2, 138.9, 132.8, 130.7, 130.6, 130.2, 128.3, 121.2, 119.2, 119.0, 118.0, 117.8, 114.1, 26.9, 21.2. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{19}ClI$ ([M^+]): 433.0214 found 433.0201. HRMS (ESI) calcd for CF_3O_3S ([M^-]): 148.9526 found 148.9523.

***6-Phenylphenanthridine*(3a).**



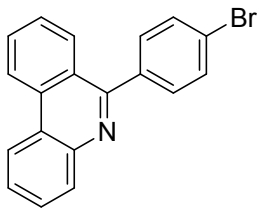
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.1 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.79-7.70 (m, 4H), 7.64-7.61 (m, 1H), 7.57-7.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 143.8, 139.8, 133.5, 130.6, 130.4, 129.7, 128.8, 128.7, 128.5, 127.1, 126.8, 125.3, 123.7, 122.2, 121.9. EI-MS *m/z* Calcd for $C_{19}H_{13}N$ [M]$^{+}$: 255, found 255.

***6-(4-Chlorophenyl)phenanthridine*(3b).**



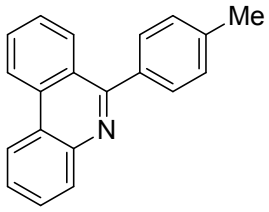
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.72-7.69 (m, 3H), 7.64 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 143.7, 138.5, 134.7, 133.5, 131.2, 129.5, 128.7, 128.5, 127.2, 127.1, 125.1, 123.6, 122.4, 122.0. EI-MS *m/z* Calcd for $C_{19}H_{12}ClN$ [M]$^{+}$: 289, found 289.

***6-(4-Bromophenyl)phenanthridine*(3c).**



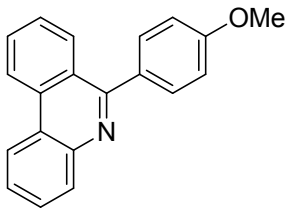
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.2 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.73-7.70 (m, 3H), 7.65-7.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 143.7, 138.7, 133.5, 131.6, 131.4, 130.7, 130.4, 128.9, 128.5, 127.3, 127.1, 124.9, 123.7, 122.4, 122.0. EI-MS *m/z* Calcd for $C_{19}H_{12}BrN$ [M]$^{+}$: 333, found 333.

6-p-Tolylphenanthridine **(3d).**



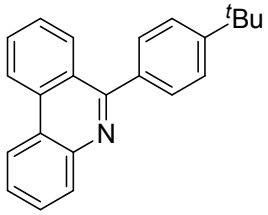
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.2 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.70-7.60 (m, 4H), 7.37 (d, J = 7.8 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 143.9, 138.6, 136.9, 133.4, 130.5, 130.3, 129.7, 129.1, 128.9, 128.7, 127.1, 126.8, 125.3, 123.7, 122.2, 121.9, 21.4. EI-MS *m/z* Calcd for $C_{20}H_{15}N$ [M]$^{+}$: 269, found 269.

***6-(4-methoxyphenyl)phenanthridine* (3e).**



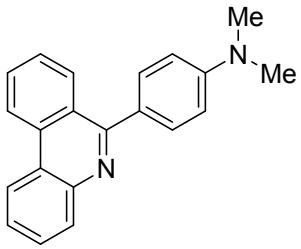
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.3, 19.4 Hz, 2H), 8.26 (d, J = 8.0 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 9.1 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.09-7.07 (m, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 157.3, 144.0, 132.8, 130.9, 130.4, 130.3, 129.0, 128.9, 128.6, 127.0, 126.8, 126.1, 124.1, 122.0, 121.9, 121.0, 111.1, 55.5. MS (*m/z*): HRMS (ESI) Calcd for $C_{20}H_{15}NO[M + H]^+$: 286.1233, found 286.1228.

***6-(4-(tert-butyl)phenyl)phenanthridine* (3f).**



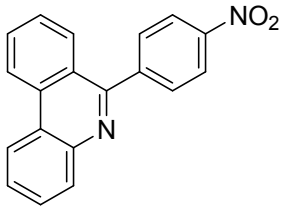
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.3 Hz, 1H), 8.62 (d, J = 8.1 Hz, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.85 (t, J = 7.8 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.71-7.66 (m, 3H), 7.62-7.58 (m, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 151.7, 143.9, 136.9, 133.5, 130.5, 130.4, 129, 129.1, 128.8, 127.1, 126.8, 125.4, 122.2, 121.9, 31.4. MS (*m/z*): HRMS (ESI) Calcd for $C_{23}H_{21}N$ $[M + H]^+$: 312.1753, found 312.1759.

***N,N-dimethyl-4-(phenanthridin-6-yl)aniline*(3g).**



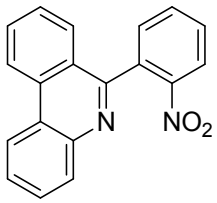
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67-8.65 (m, 1H), 8.58-8.55 (m, 1H), 8.28-8.20 (m, 2H), 7.84-7.79 (m, 1H), 7.74-7.67 (m, 3H), 7.62-7.57 (m, 2H), 6.90-6.87 (m, 2H), 3.04 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 161.3, 150.9, 144.1, 133.6, 130.9, 130.2, 130.1, 129.2, 128.6, 127.7, 126.8, 126.3, 125.5, 123.4, 122.1, 121.8, 112.1, 40.5. MS (*m/z*): HRMS (ESI) Calcd for $C_{21}H_{18}N_2$[M + H]$^{+}$: 299.1548, found 299.1540.

***6-(4-nitrophenyl)phenanthridine* (3h).**



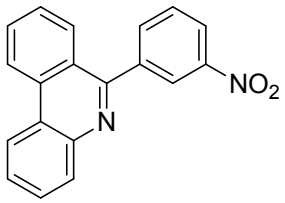
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.01-7.98 (d, J = 8.3 Hz, 1H), 7.95-7.90 (m, 3H), 7.82-7.73 (m, 2H), 7.67 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.0, 146.1, 143.6, 133.6, 131.0, 130.9, 130.5, 129.2, 127.9, 127.7, 127.6, 124.6, 123.9, 123.7, 122.6, 122.1. MS (*m/z*): HRMS (ESI) Calcd for $C_{19}H_{12}N_2O_2$ [M + H] $^{+}$: 301.0978, found 301.0963.

***6-(2-nitrophenyl)phenanthridine* (3i).**



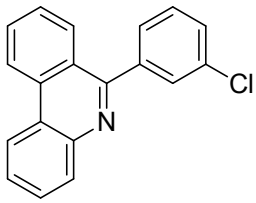
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.3 Hz, 1H), 8.64 (d, J = 7.9 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.86-7.71 (m, 5H), 7.67-7.63 (m, 2H), 7.60-7.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.6, 143.6, 135.2, 133.6, 133.0, 132.1, 130.9, 130.2, 129.7, 127.6, 127.4, 127.1, 125.3, 124.8, 124.0, 122.5, 122.2. MS (*m/z*): HRMS (ESI) Calcd for $C_{19}H_{12}N_2O_2$ $[M + H]^+$: 301.0978, found 301.0983.

***6-(3-nitrophenyl)phenanthridine* (3j).**



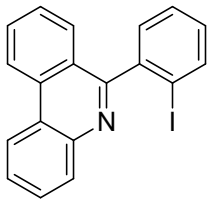
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.3 Hz, 1H), 8.66-8.64 (m, 2H), 8.41 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.92 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 148.3, 143.6, 141.4, 135.9, 133.6, 131.1, 130.4, 129.5, 129.2. 127.9, 127.6, 124.9, 124.6, 123.9, 123.6, 122.6, 122.1. MS (*m/z*): HRMS (ESI) Calcd for $C_{19}H_{12}N_2O_2$ $[M + H]^+$: 301.0978, found 301.0981.

***6-(3-chlorophenyl)phenanthridine*(3k).**



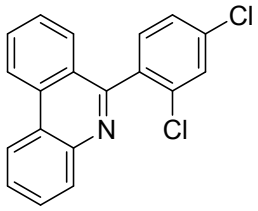
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74-8.71 (m, 1H), 8.65-8.62 (m, 1H), 8.25-8.22 (m, 1H), 8.07-8.05 (m, 1H), 7.91-7.86 (m, 1H), 7.81-7.71 (m, 3H), 7.67-7.61 (m, 2H), 7.51-7.49 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.7, 141.6, 134.6, 133.6, 130.9, 130.5, 129.9, 129.8, 129.1, 128.9, 128.6, 128.0, 127.4, 127.3, 125.1, 123.9, 122.4, 122.1. EI-MS *m/z* Calcd for $C_{19}H_{12}ClN$ [M]$^{+}$: 289, found 289.

***6-(2-iodophenyl)phenanthridine* (3l).**



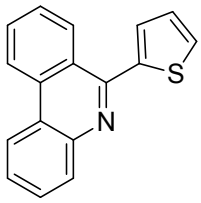
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.1 Hz, 1H), 8.29-8.26 (m, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.89-7.85 (m, 1H), 7.81-7.72 (m, 2H), 7.67-7.65 (m, 1H), 7.62-7.49 (m, 3H), 7.23 (td, J = 8.0, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 144.3, 143.6, 139.3, 133.1, 130.8, 130.4, 130.2, 130.0, 128.9, 128.5, 128.2, 124.9, 124.1, 122.2, 122.0, 97.6. MS (*m/z*): HRMS (ESI) Calcd for $C_{19}H_{12}IN$ [M + H] $^{+}$: 382.0093, found 382.0081.

***6-(2,4-dichlorophenyl)phenanthridine* (3m).**



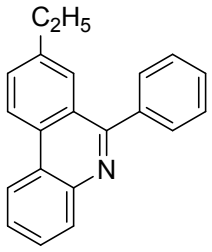
White solid;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.2 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.89-7.85 (m, 1H), 7.81-7.71 (m, 2H), 7.69-7.67 (m, 1H), 7.64-7.60 (m, 2H), 7.50-7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 137.2, 135.3, 134.3, 133.0, 131.9, 130.9, 130.4, 129.6, 129.0, 128.1, 127.5, 127.4, 125.2, 124.1, 122.3, 122.1. MS (*m/z*): HRMS (ESI) Calcd for $C_{19}H_{11}Cl_2N$ [M + H] $^{+}$: 324.0347, found 324.0342.

6-(Thiophen-2-yl)phenanthridine **(3n).**



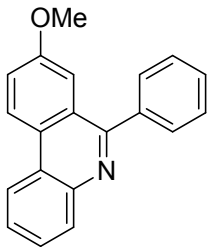
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.3 Hz, 1H), 8.58 (dd, J = 8.0, 3.6 Hz, 2H), 8.21 (d, J = 8.1 Hz, 1H), 7.90-7.86 (m, 1H), 7.79-7.73 (m, 1H), 7.70-7.64 (m, 3H), 7.56 (d, J = 5.0 Hz, 1H), 7.25-7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.8, 142.6, 133.7, 130.7, 130.3, 129.3, 128.9, 128.1, 127.9, 127.5, 127.4, 127.1, 124.8, 123.6, 122.4, 121.9. EI-MS *m/z* Calcd for $C_{17}H_{11}NS$ [M]$^{+}$: 261, found 261.

8-Ethyl-6-phenylphenanthridine **(3o).**



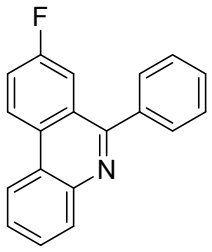
White solid;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J = 8.4, 15.3 Hz, 2H), 8.23 (d, J = 8.1 Hz, 1H), 7.89 (s, 1H), 7.74-7.63 (m, 5H), 7.59-7.55 (m, 3H), 2.81 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 143.5, 143.4, 140.0, 131.5, 131.1, 130.3, 129.7, 128.6, 128.4, 127.1, 126.8, 125.4, 123.8, 122.3, 121.8, 29.0, 15.6. MS (*m/z*): HRMS (ESI) calcd for $C_{21}H_{17}N$ $[M + H]^+$: 284.1439 found 284.1434.

8-Methoxy-6-phenylphenanthridine **(3p).**



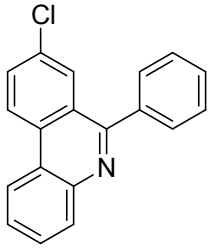
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.6 Hz, 1H), 8.52 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.76-7.75 (m, 2H), 7.70-7.65 (m, 2H), 7.59-7.52 (m, 3H), 7.50-7.47 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 158.4, 143.0, 139.9, 130.3, 129.5, 128.7, 128.5, 127.8, 126.9, 126.5, 123.9, 121.5, 120.9, 108.9, 55.4. MS (*m/z*): HRMS (ESI) Calcd for $C_{20}H_{15}NO[M + H]^+$: 286.1233, found 286.1228.

8-Fluoro-6-phenylphenanthridine **(3q).**



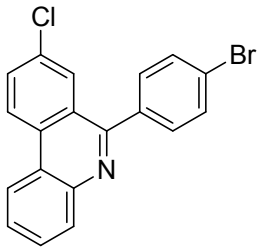
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 5.3, 9.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.78-7.70 (m, 5H), 7.64-7.54 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.4, 160.0, 143.5, 139.3, 130.5, 130.2, 129.0, 128.7, 128.6, 127.4, 124.8, 121.8, 119.9, 119.7, 113.4, 113.1. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}FN$ $[M + H]^+$: 274.1032 found 274.1027.

8-Chloro-6-phenylphenanthridine **(3r).**



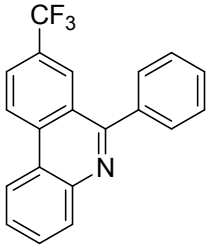
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.8 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.08-8.07 (m, 1H), 7.82-7.76 (m, 2H), 7.73-7.68 (m, 3H), 7.60-7.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 143.7, 139.2, 133.2, 131.8, 131.2, 130.5, 129.6, 129.2, 129.0, 128.7, 127.9, 126.2, 124.0, 123.2, 121.8. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}ClN$ $[M + H]^+$: 290.0737 found 290.0734.

6-(4-Bromophenyl)-8-chlorophenanthridine **(3s).**



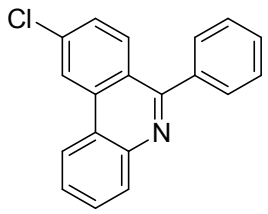
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 8.7 Hz, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.22 (d, J = 8.1 Hz, 1H), 8.02 (s, 1H), 7.83-7.79 (m, 2H), 7.74-7.73 (m, 2H), 7.64-7.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.6, 138.0, 133.3, 131.9, 131.8, 131.3, 130.5, 129.4, 128.4, 127.6, 127.5, 125.9, 124.2, 123.5, 123.1, 121.9. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{11}BrClN$ $[M + H]^+$: 367.9842 found 367.9839.

6-Phenyl-8-(trifluoromethyl)phenanthridine **(3t).**



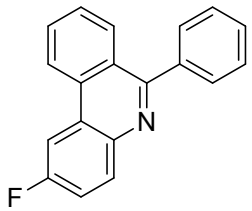
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 8.6 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.07-8.05 (m, 1H), 7.86 (t, J = 1.0 Hz, 1H), 7.76-7.75 (m, 3H), 7.62-7.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 144.5, 138.8, 125.8, 130.6, 130.1, 129.7, 129.2, 128.7, 127.5, 126.4, 126.2, 124.5, 123.4, 122.8, 122.4. MS (*m/z*): HRMS (ESI) calcd for $C_{20}H_{12}F_3N$ $[M + H]^+$: 324.1000 found 324.0995.

9-Chloro-6-phenylphenanthridine **(3u).**



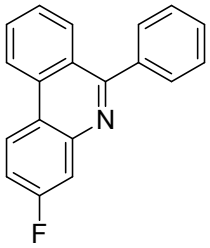
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.53 (d, J = 8.2 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.79 (t, J = 7.2 Hz, 1H), 7.72-7.71 (m, 3H), 7.57-7.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 144.2, 139.4, 137.1, 134.8, 130.6, 130.4, 129.7, 129.5, 128.9, 128.5, 127.7, 127.2, 123.5, 122.7, 122.0, 121.9. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}ClN$ $[M + H]^+$: 290.0737 found 290.0731.

2-Fluoro-6-phenylphenanthridine **(3v).**



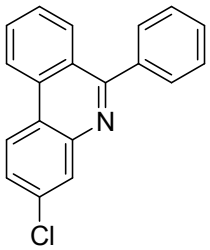
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.3 Hz, 1H), 8.25-8.21 (m, 2H), 8.12 (d, J = 8.3 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H), 7.57-7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.6, 160.4, 140.6, 139.5, 132.6, 132.5, 130.6, 129.7, 128.9, 128.8, 128.5, 127.8, 125.3, 122.4, 117.8, 117.6, 107.0, 106.8. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}FN$ $[M + H]^+$: 274.1032 found 274.1029.

3-Fluoro-6-phenylphenanthridine **(3w).**



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63-8.57 (m, 2H), 8.11 (d, J = 8.2 Hz, 1H), 7.91-7.84 (m, 2H), 7.74-7.72 (m, 2H), 7.63-7.54 (m, 4H), 7.44 (td, J = 8.2, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 162.6, 161.8, 145.1, 139.5, 133.3, 130.9, 129.7, 129.1, 128.9, 128.5, 126.9, 124.8, 123.8, 121.9, 120.4, 116.1, 115.9, 114.8, 114.7. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}FN$ $[M + H]^+$: 274.1032 found 274.1024.

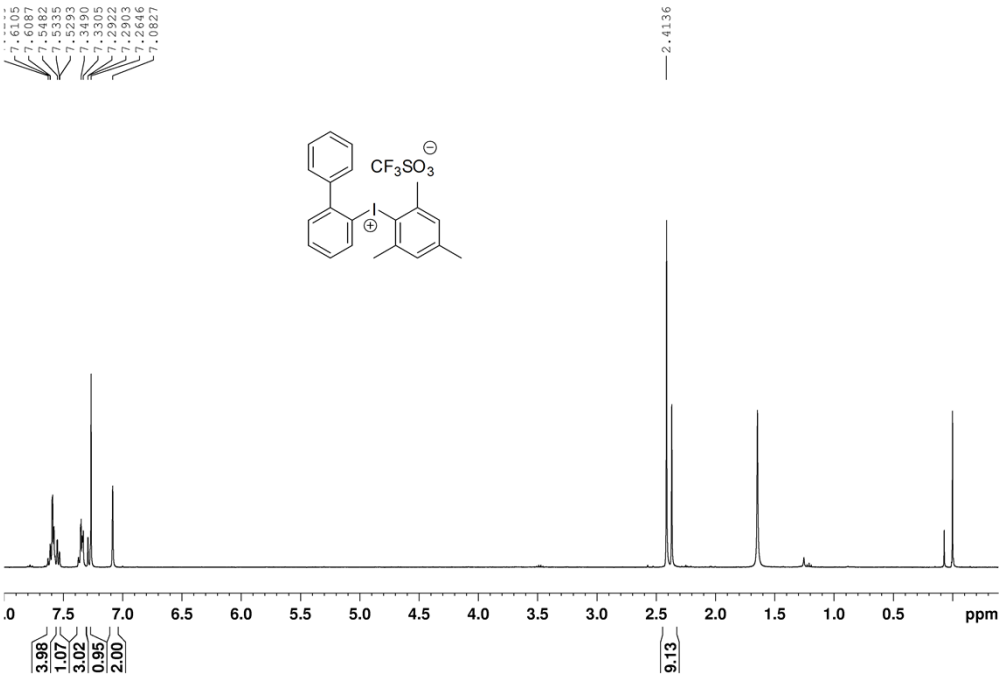
3-Chloro-6-phenylphenanthridine **(3x).**

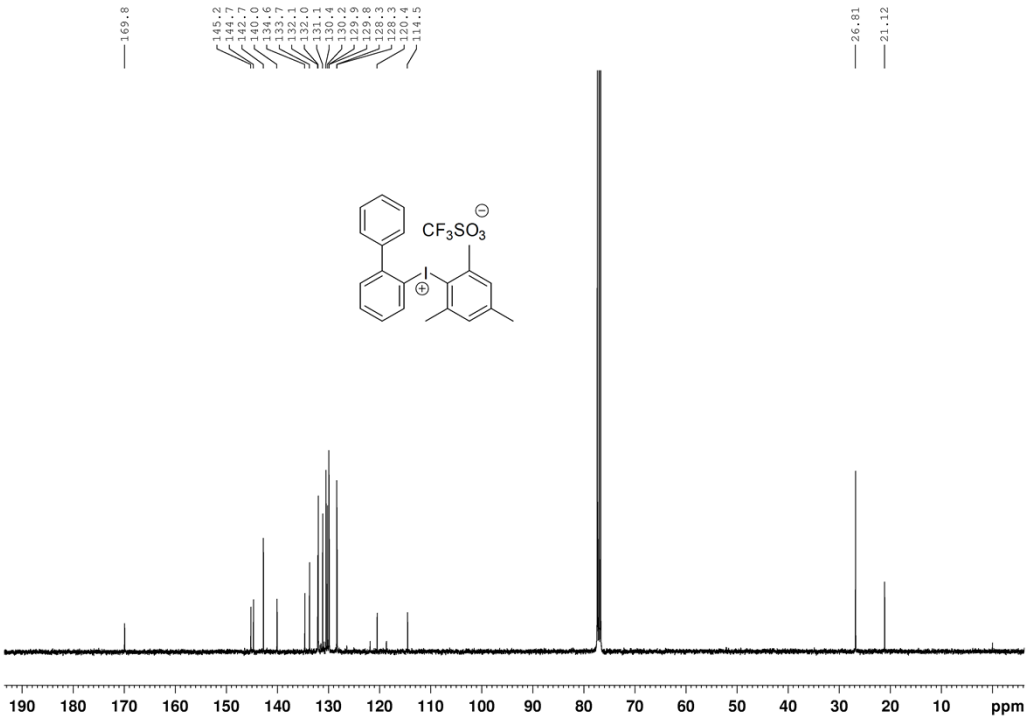


White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 8.3 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 1.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.90-7.86 (m, 1H), 7.74-7.72 (m, 2H), 7.66-7.63 (m, 2H), 7.57-7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 144.5, 139.4, 134.5, 133.1, 130.9, 129.7, 129.5, 129.1, 128.9, 128.5, 127.5, 127.4, 125.2, 123.4, 122.2, 122.1. MS (*m/z*): HRMS (ESI) calcd for $C_{19}H_{12}ClN$ $[M + H]^+$: 290.0737 found 290.0729.

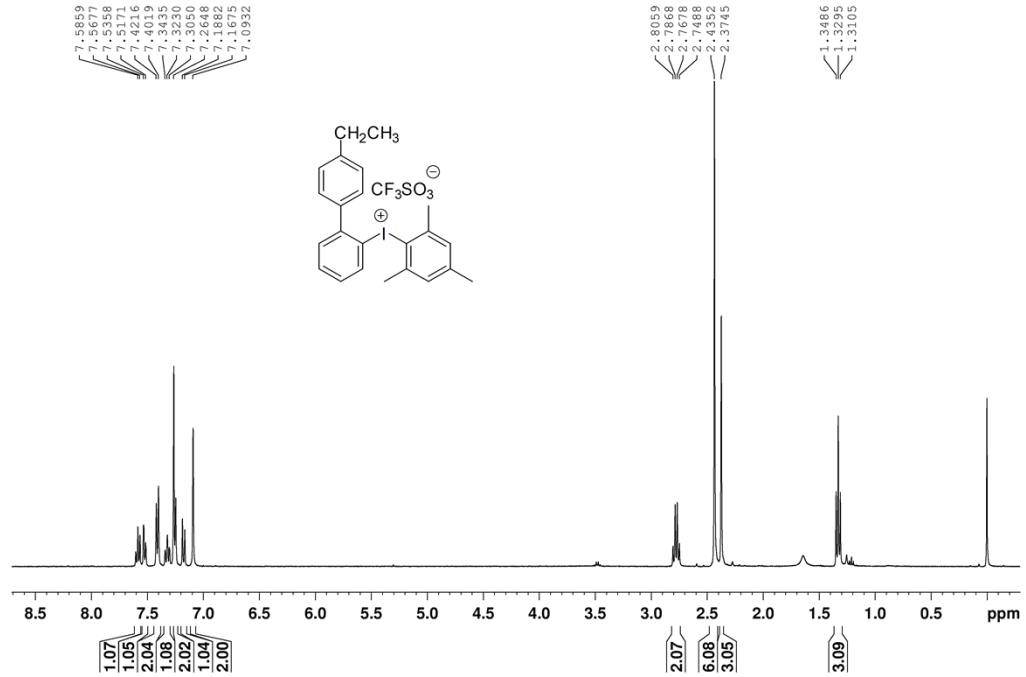
NMR spectra of all compounds 1 and 3

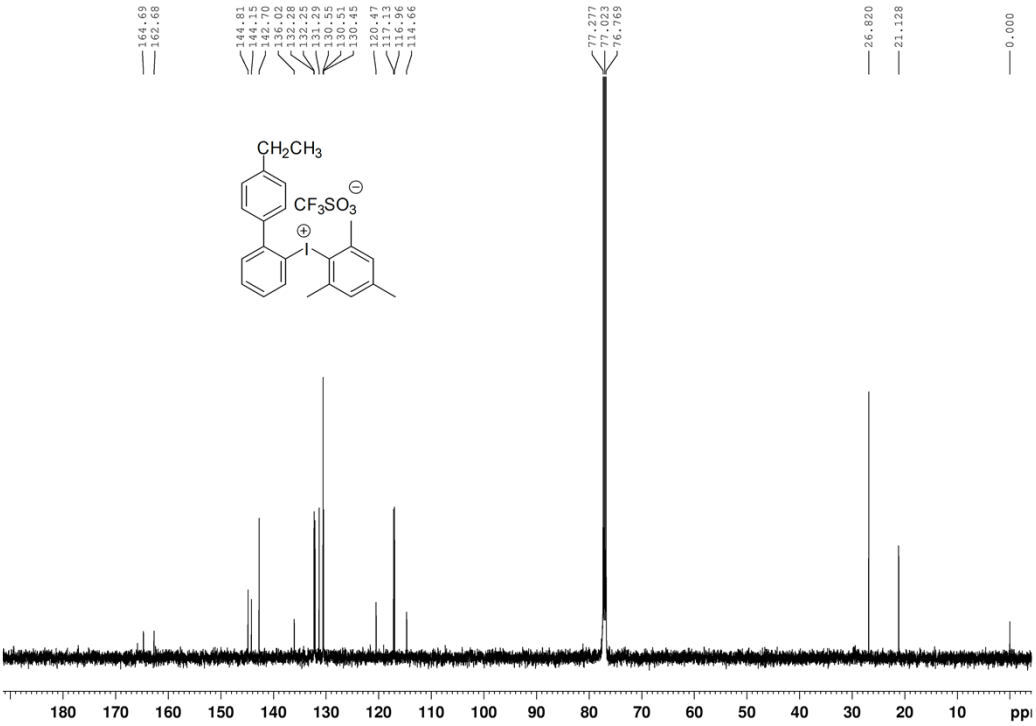
NMR spectra of 1a



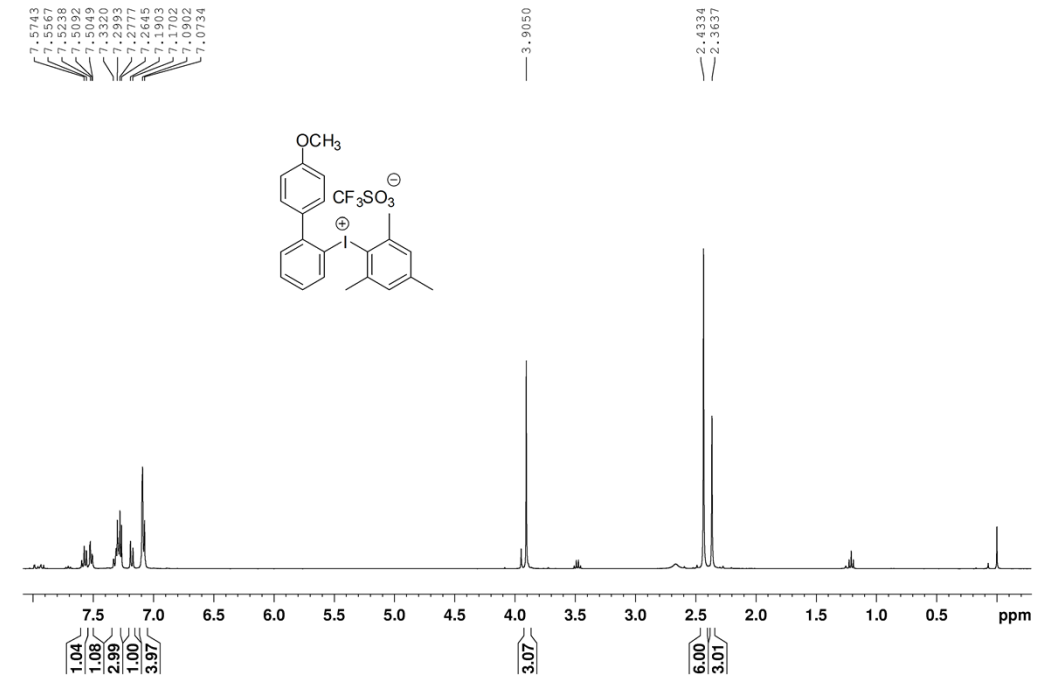


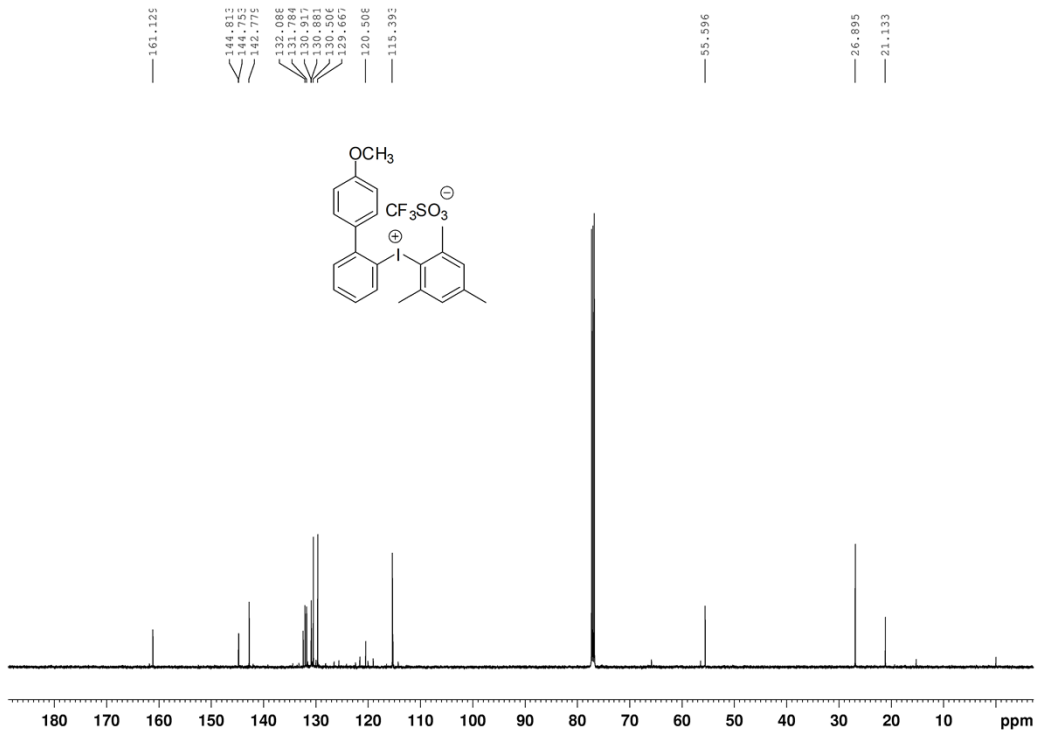
NMR spectra of 1b



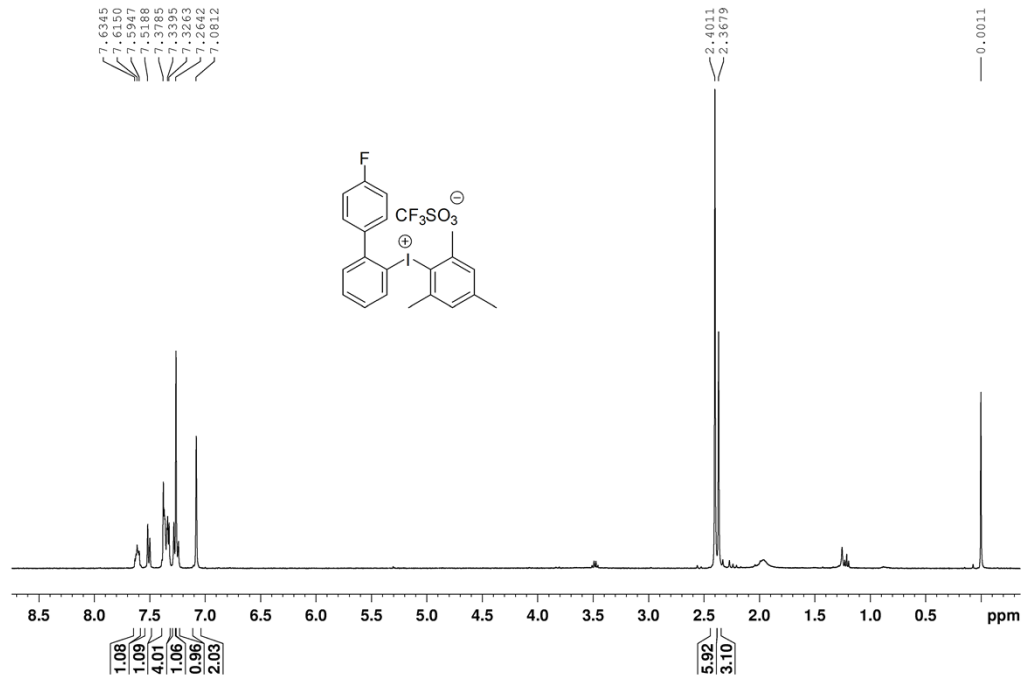


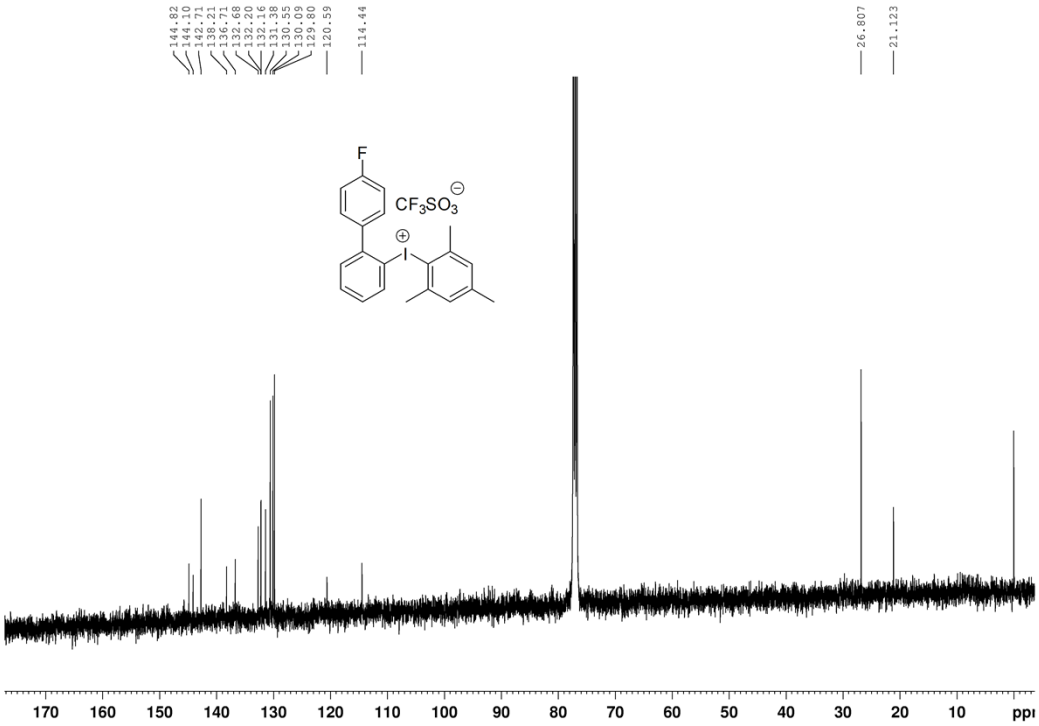
NMR spectra of 1c



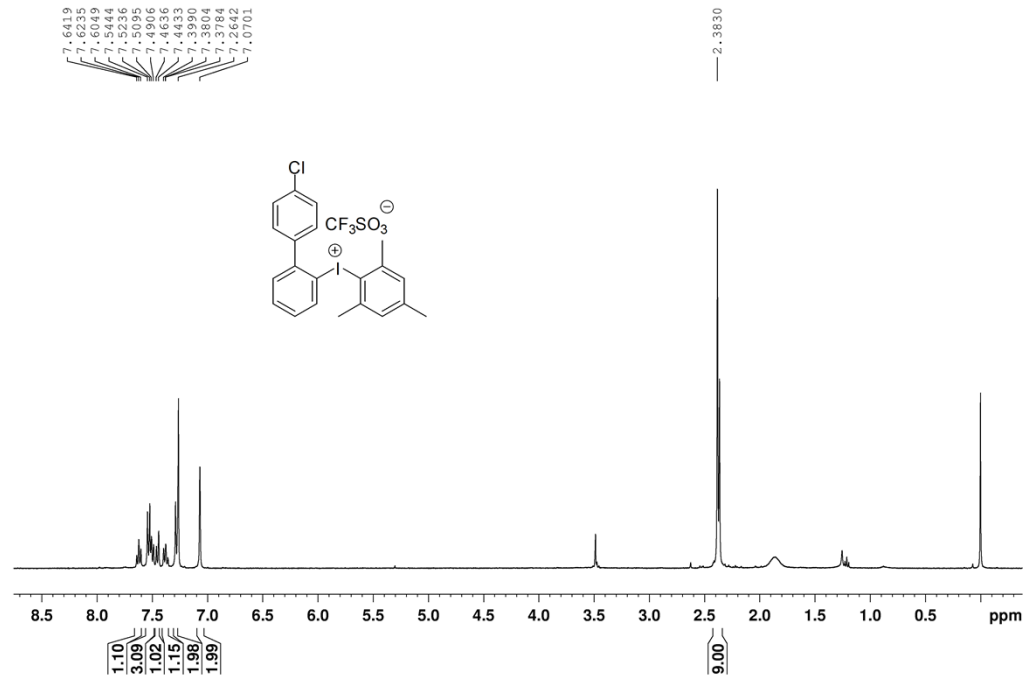


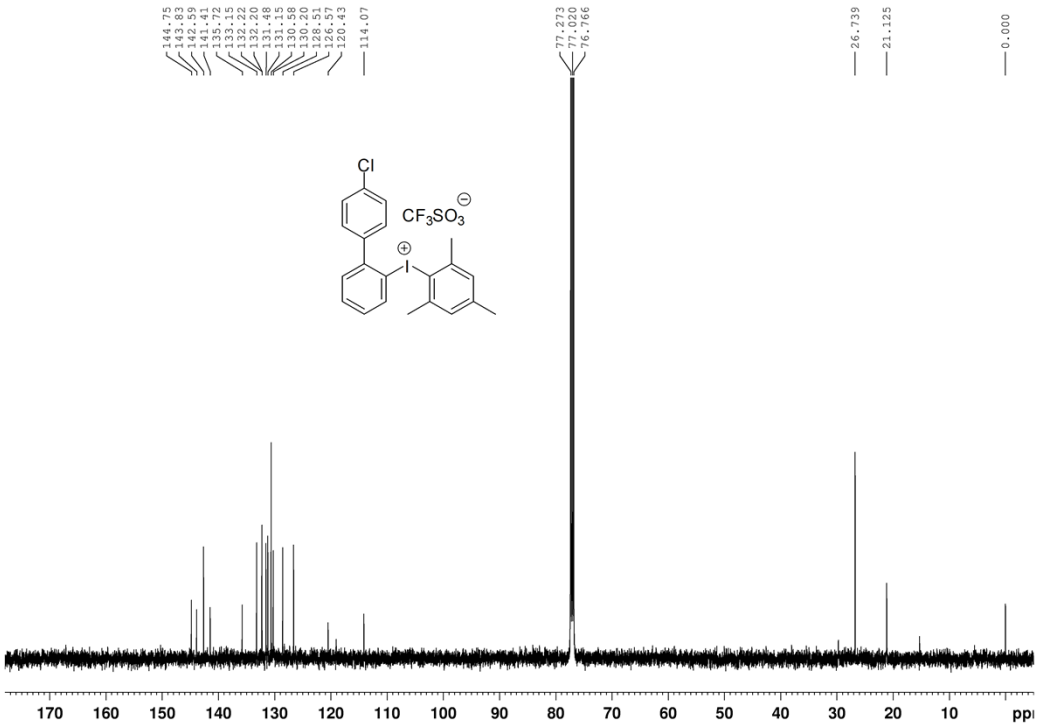
NMR spectra of 1d



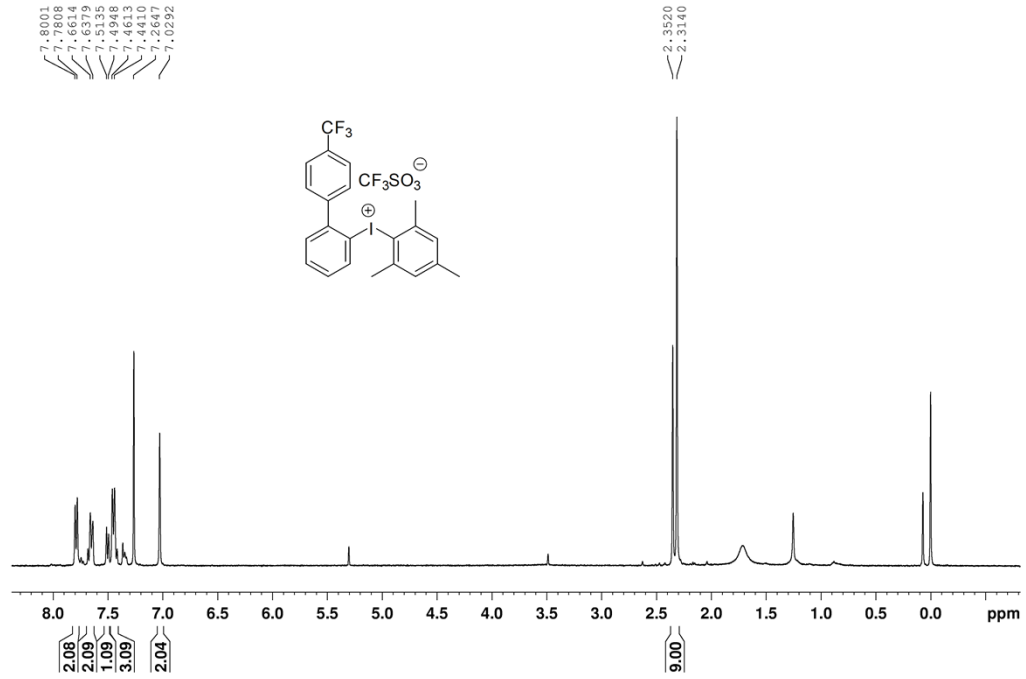


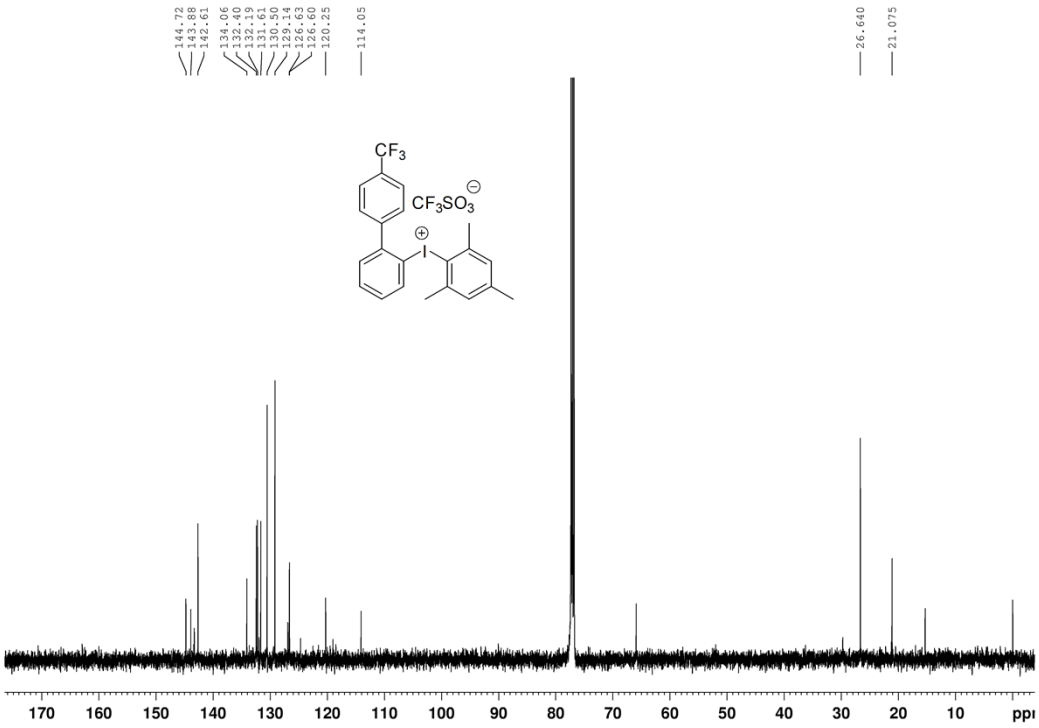
NMR spectra of 1e



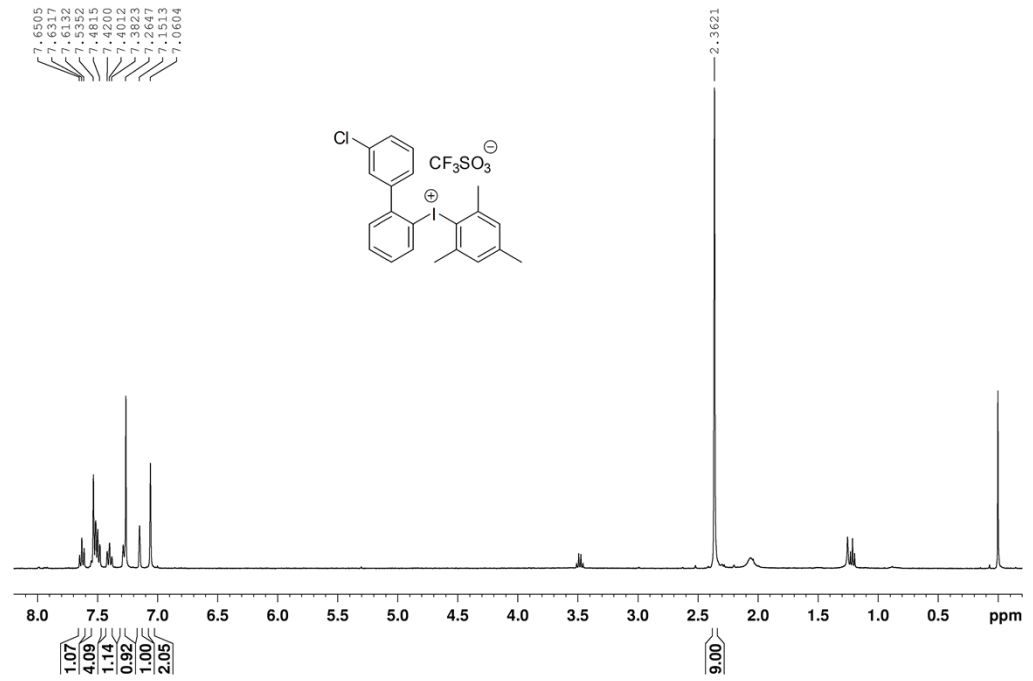


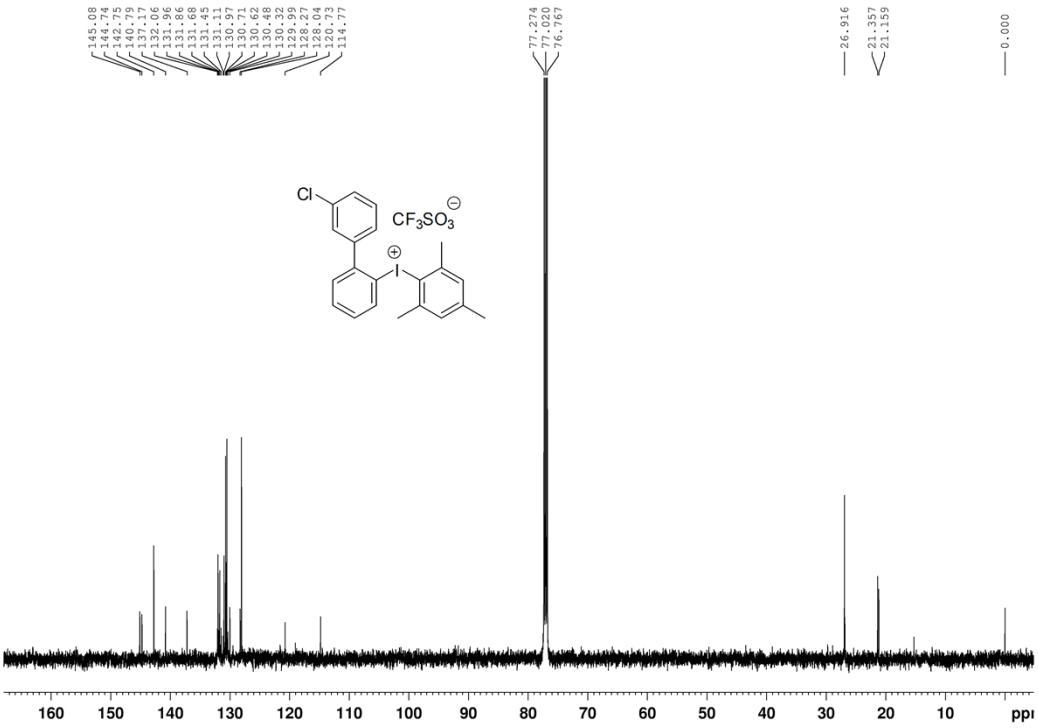
NMR spectra of 1f



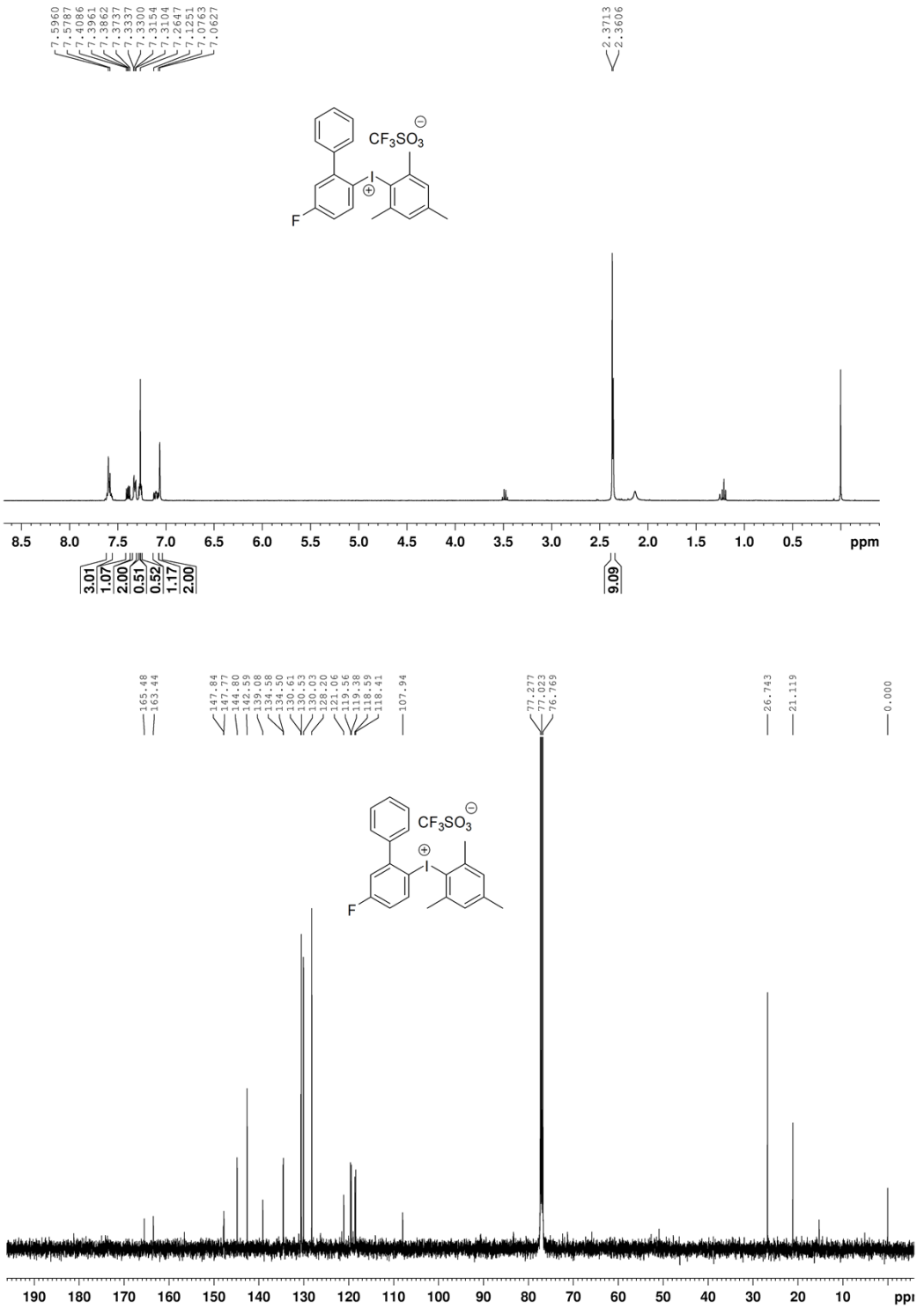


NMR spectra of 1g

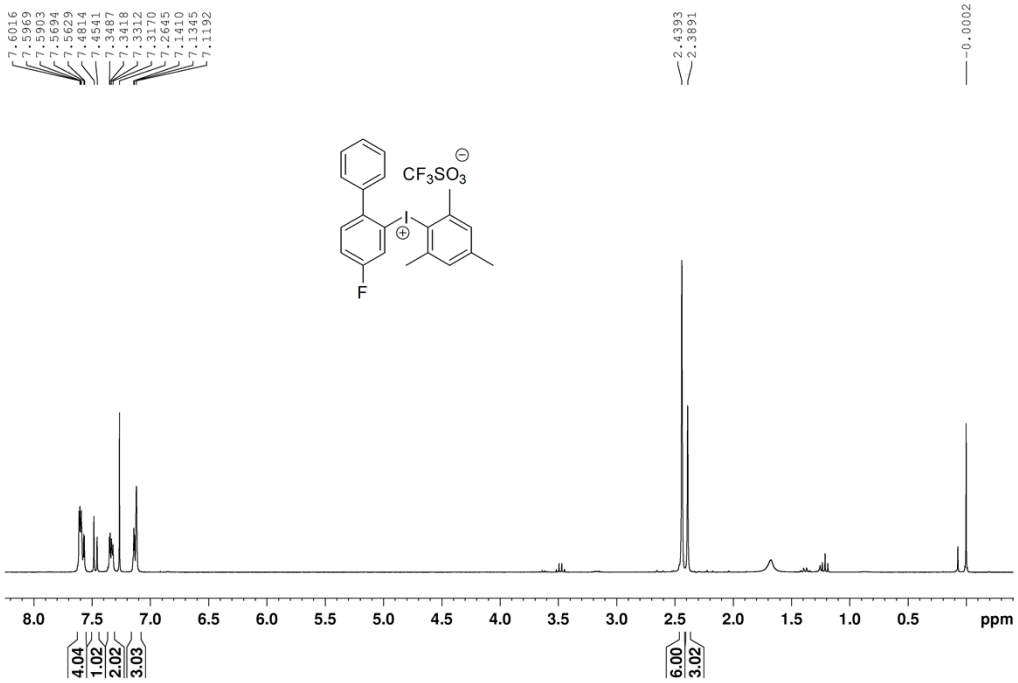


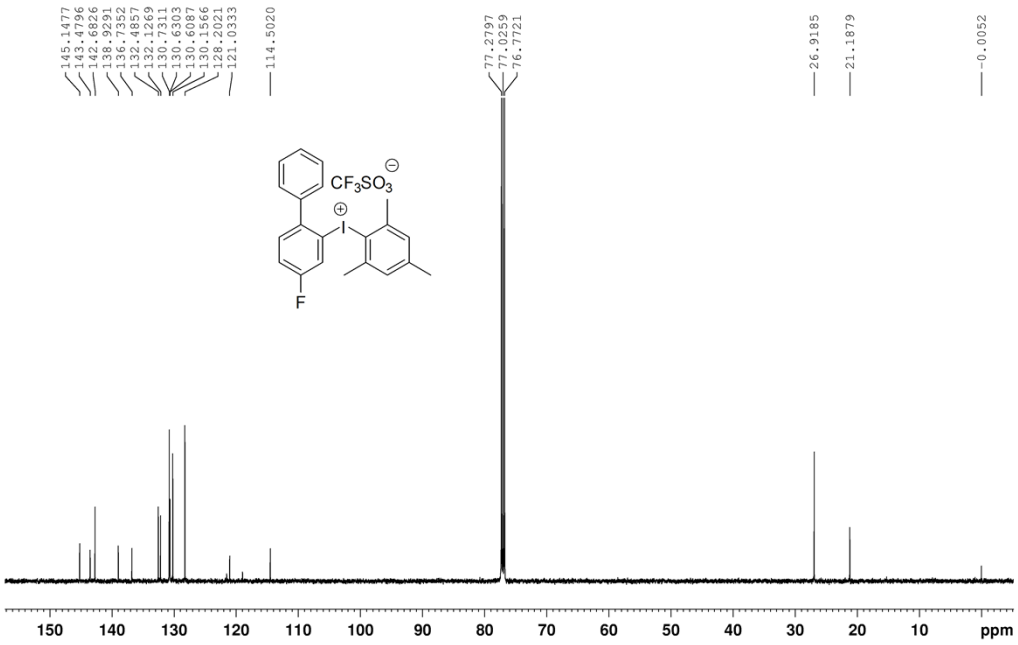


NMR spectra of 1h

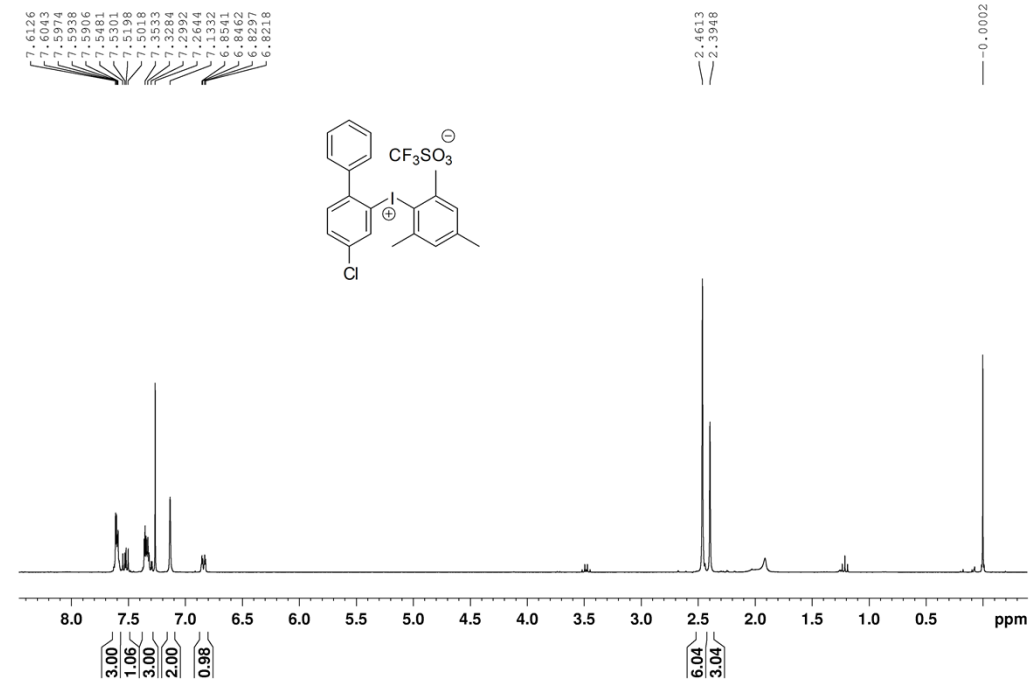


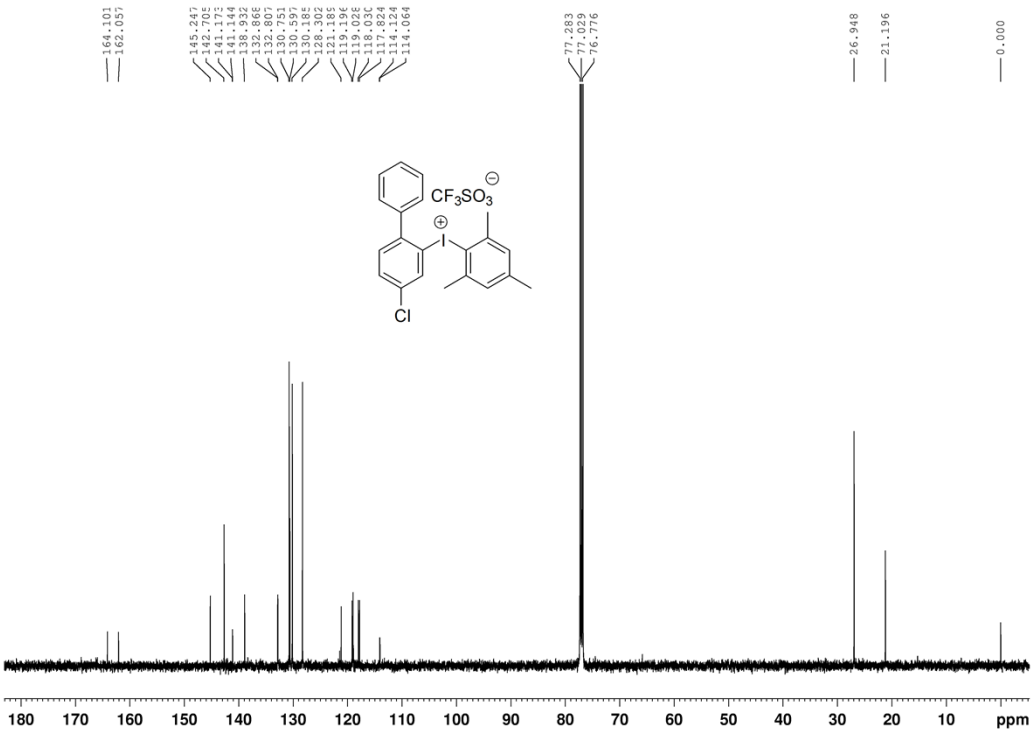
NMR spectra of 1i



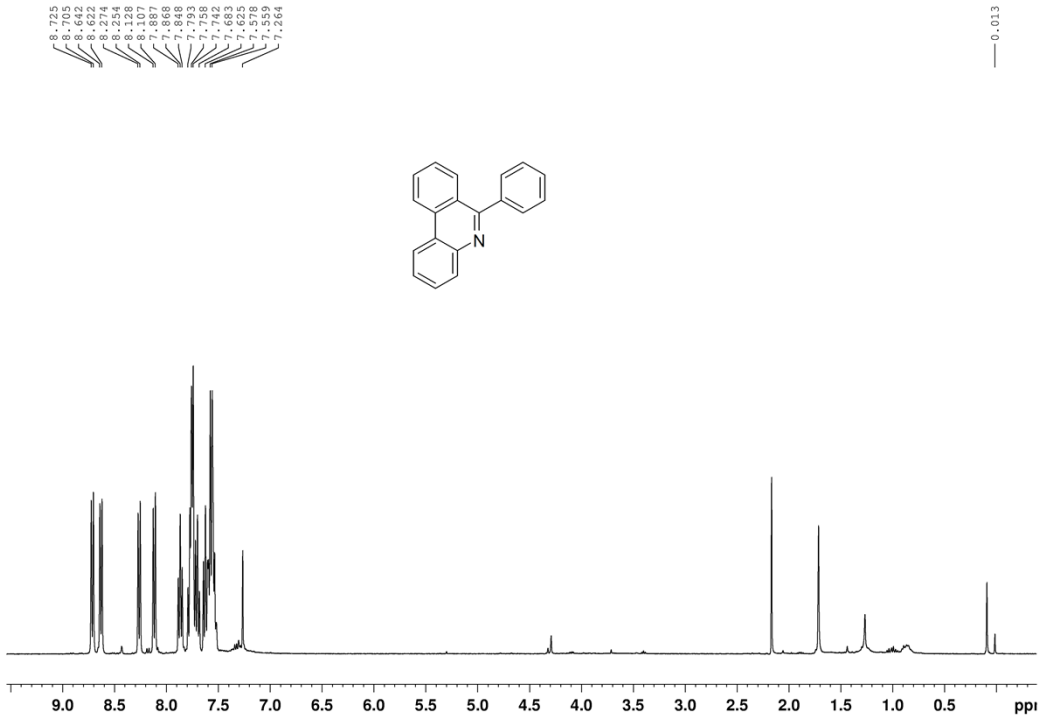


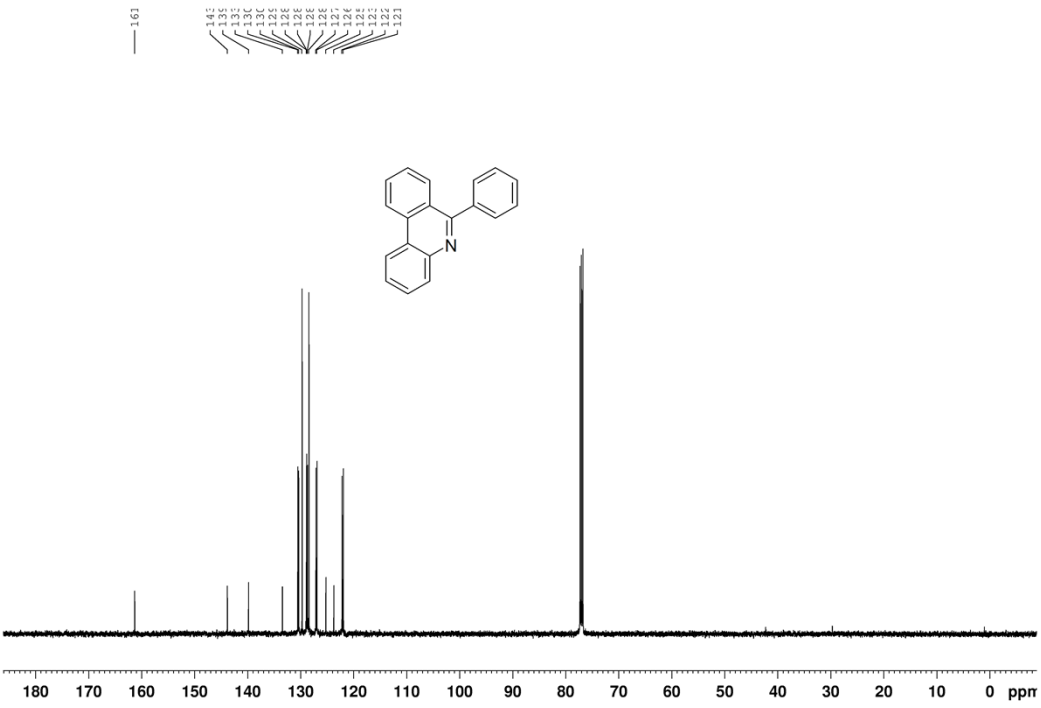
NMR spectra of 1j



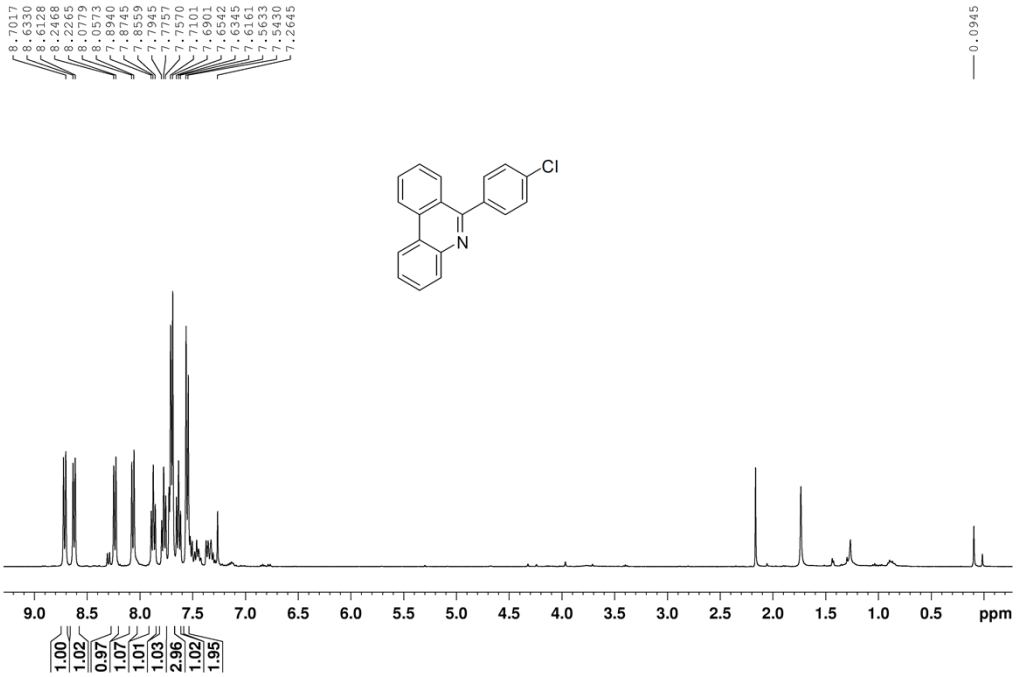


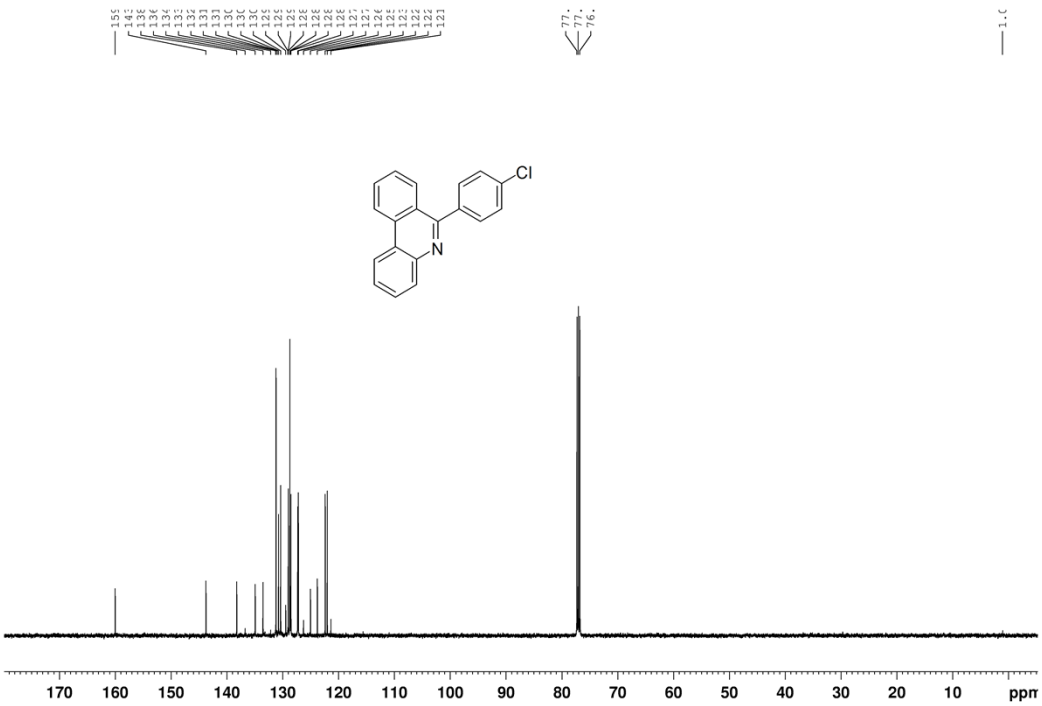
NMR spectra of 3a



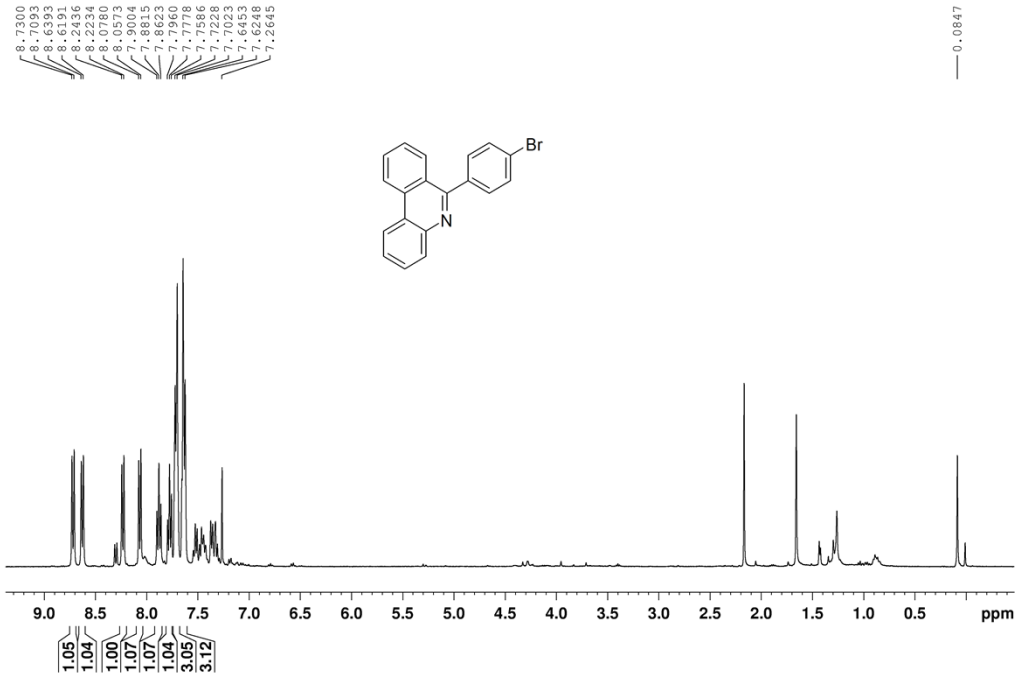


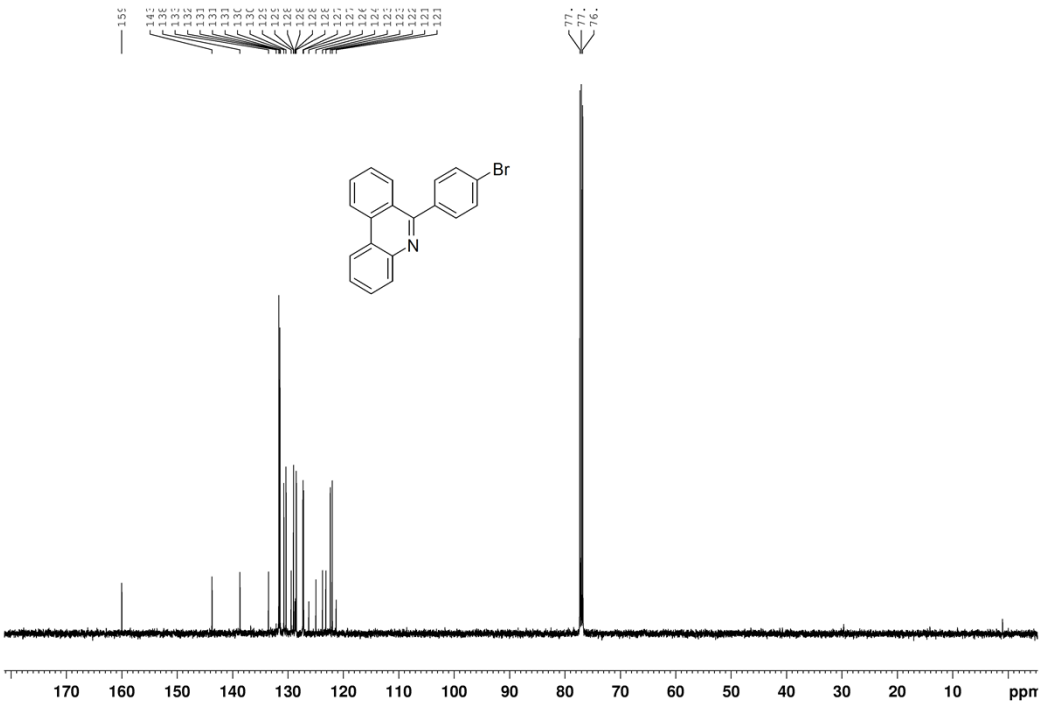
NMR spectra of 3b



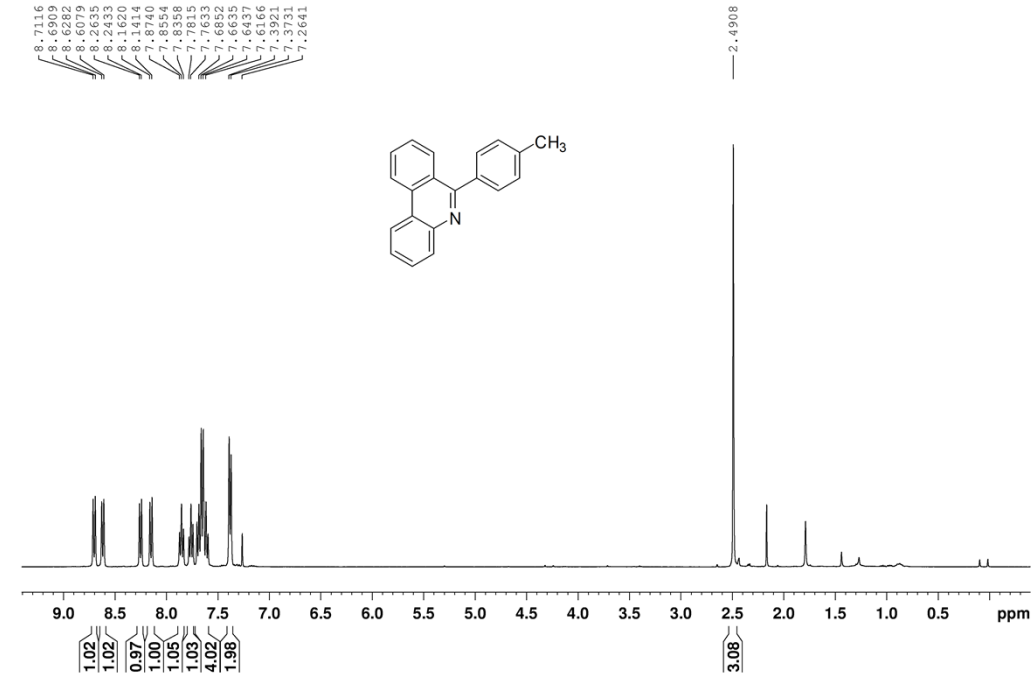


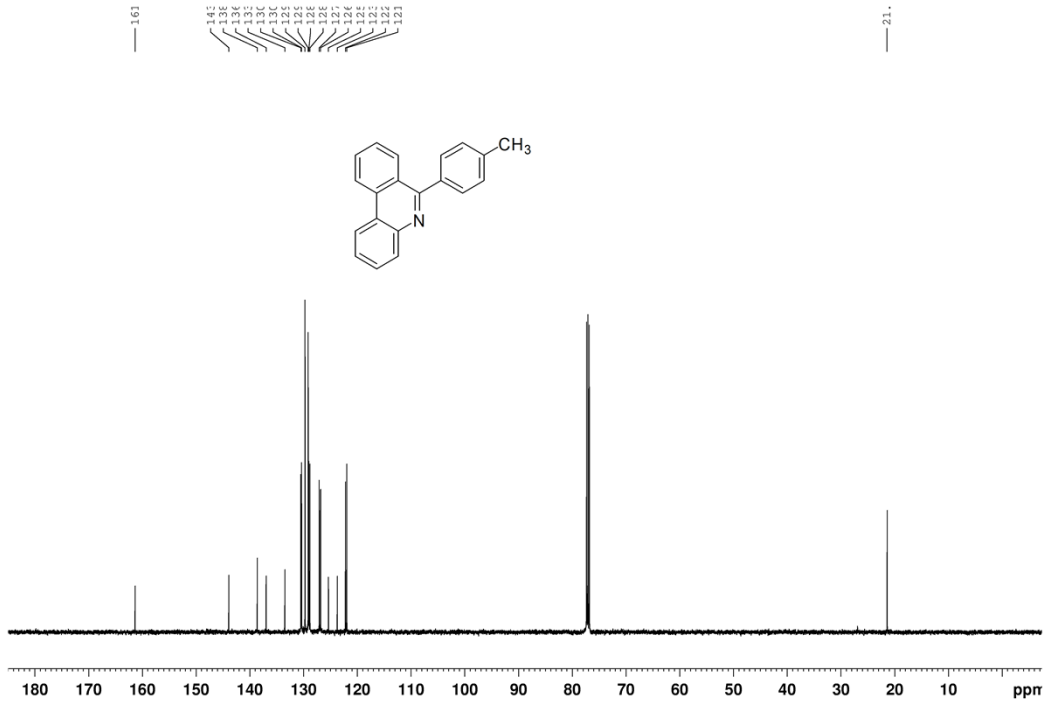
NMR spectra of 3c



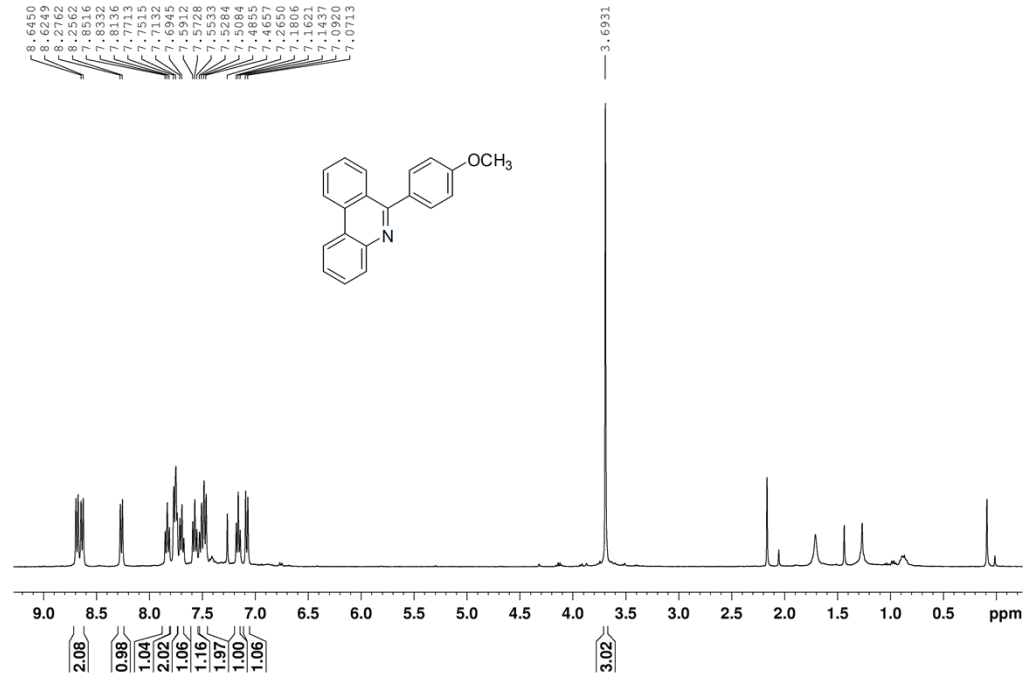


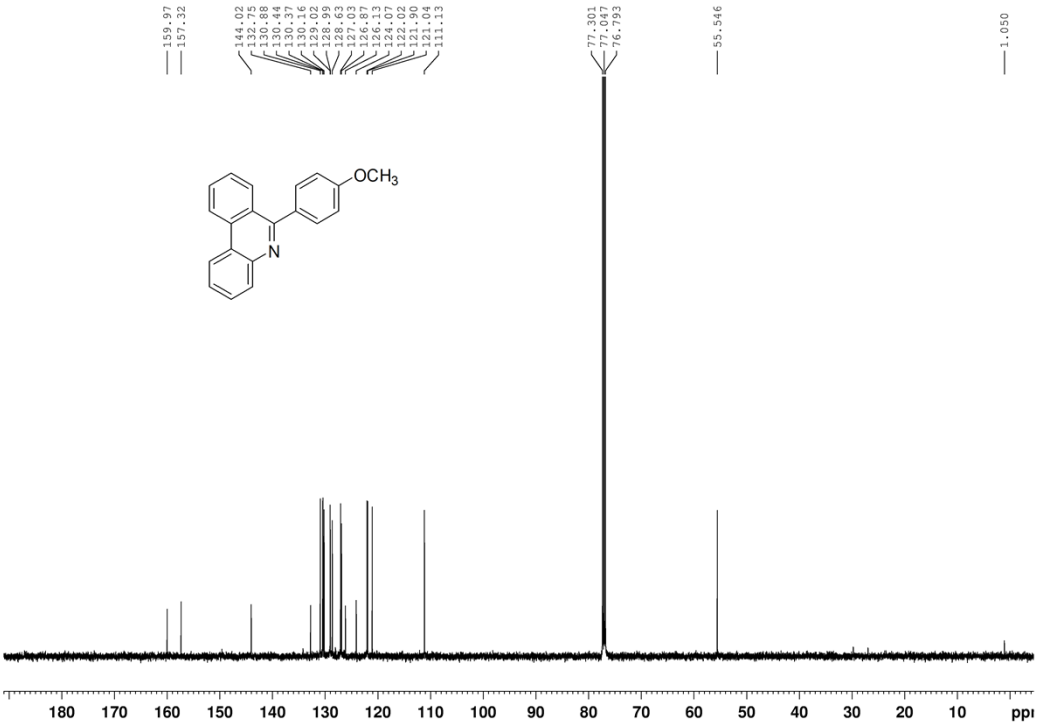
NMR spectra of 3d



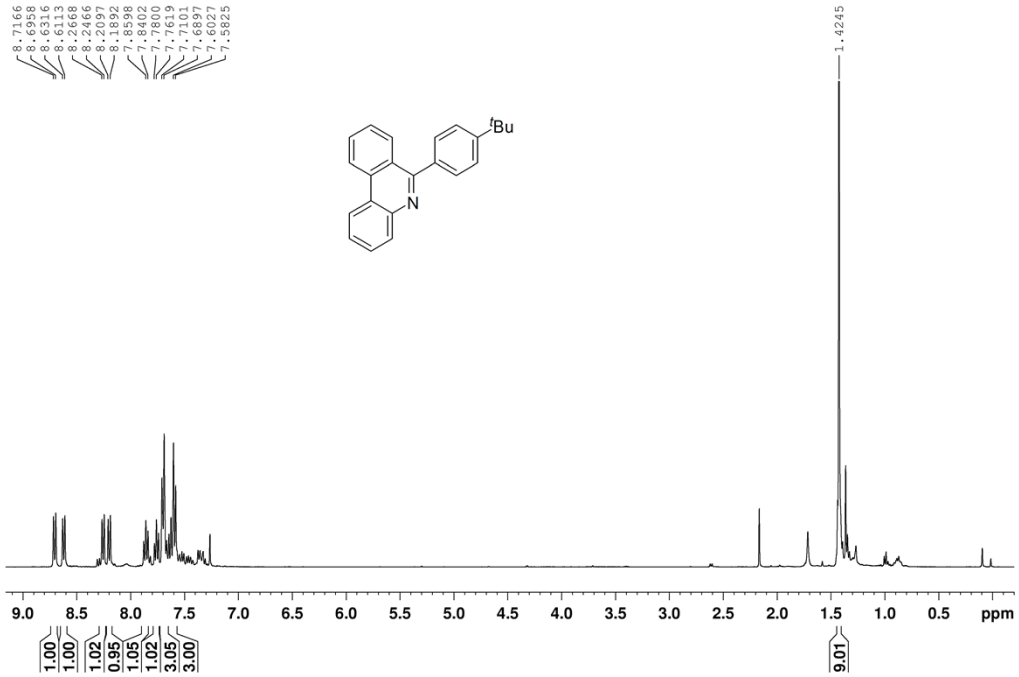


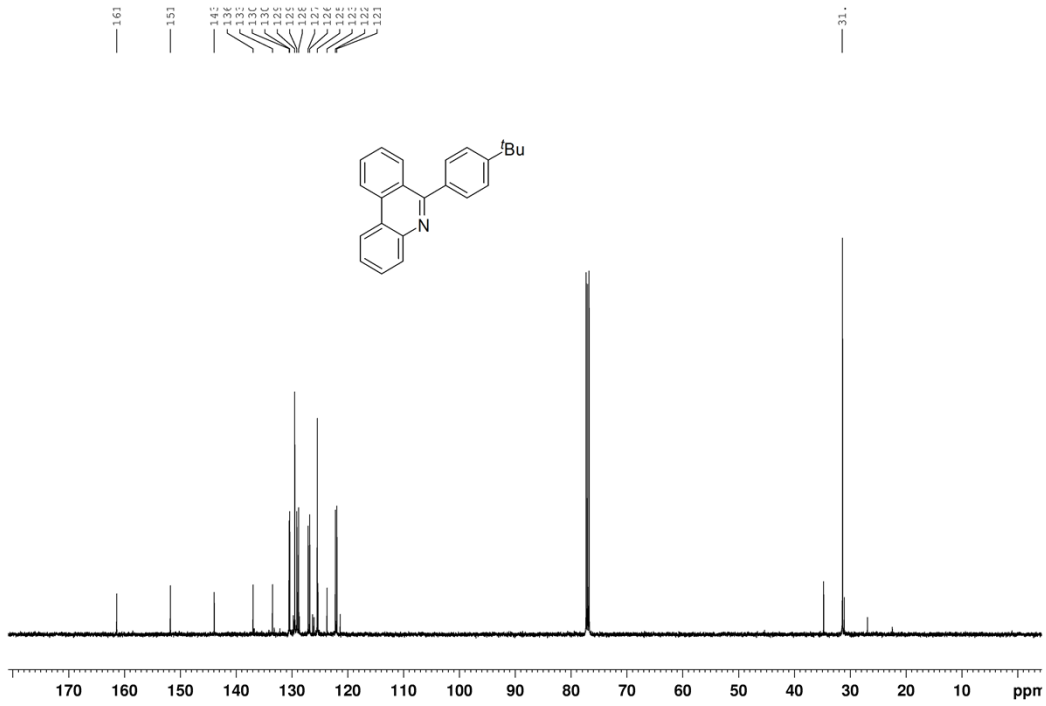
NMR spectra of 3e



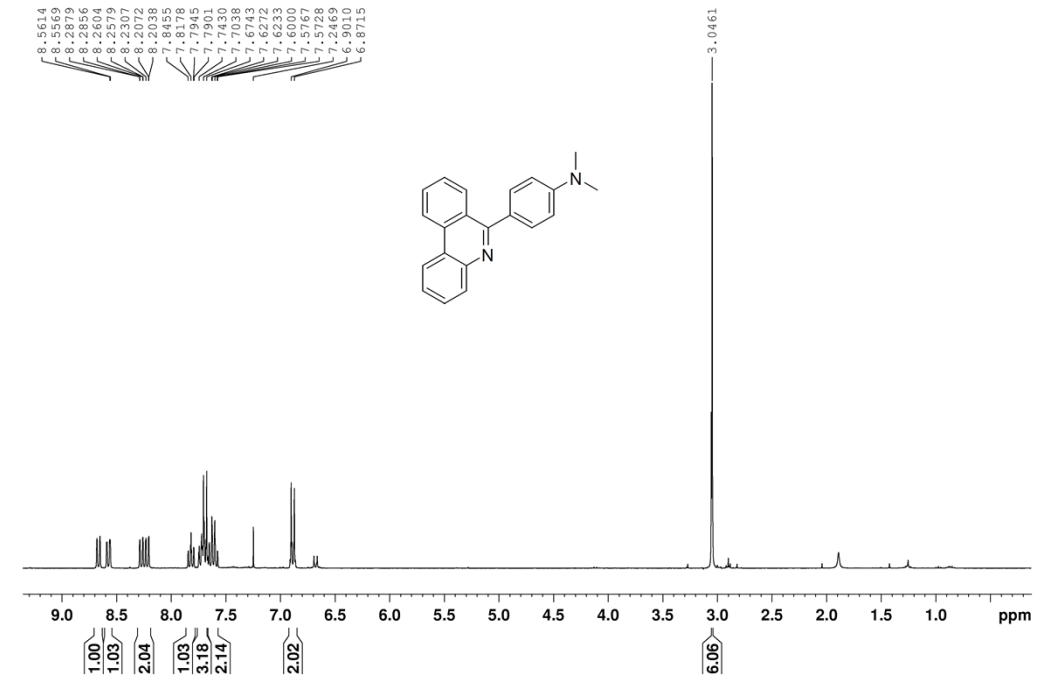


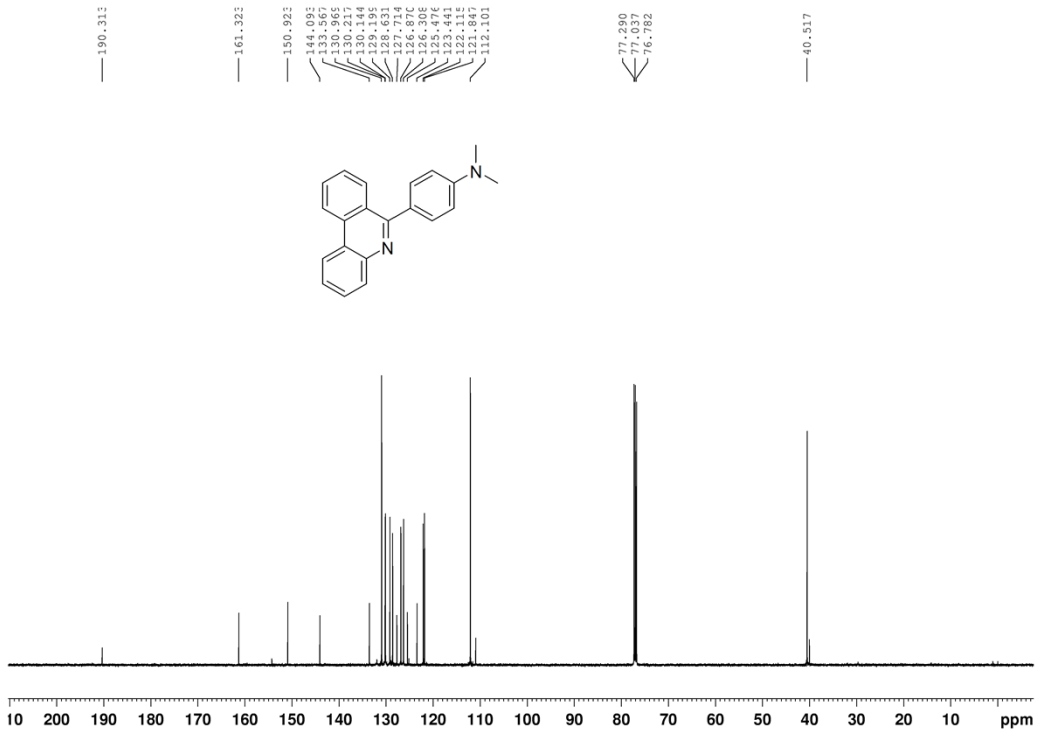
NMR spectra of 3f



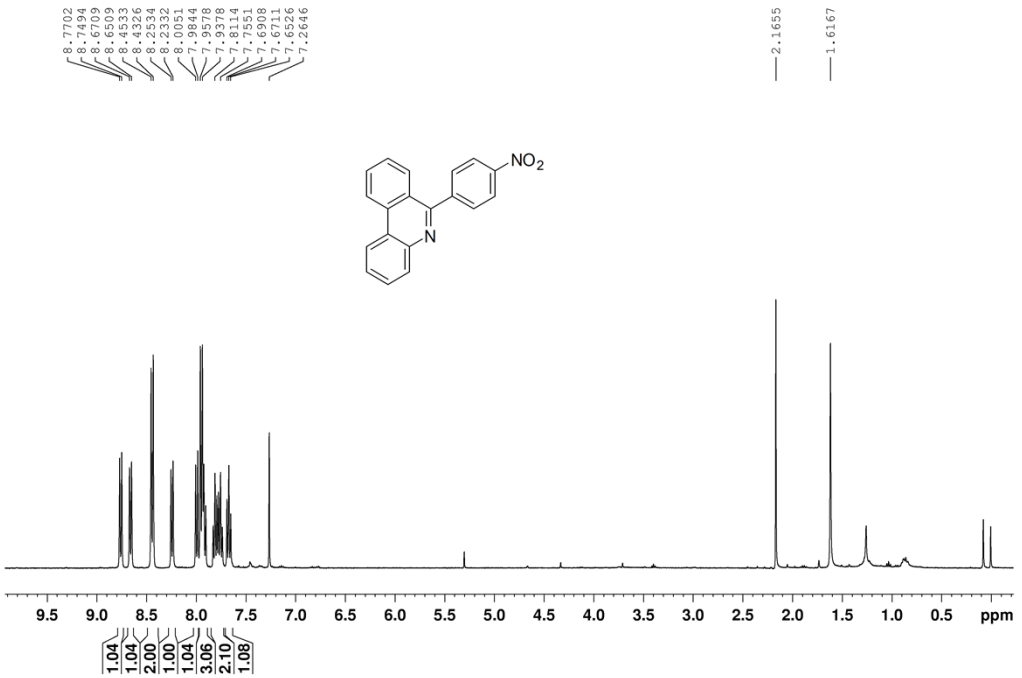


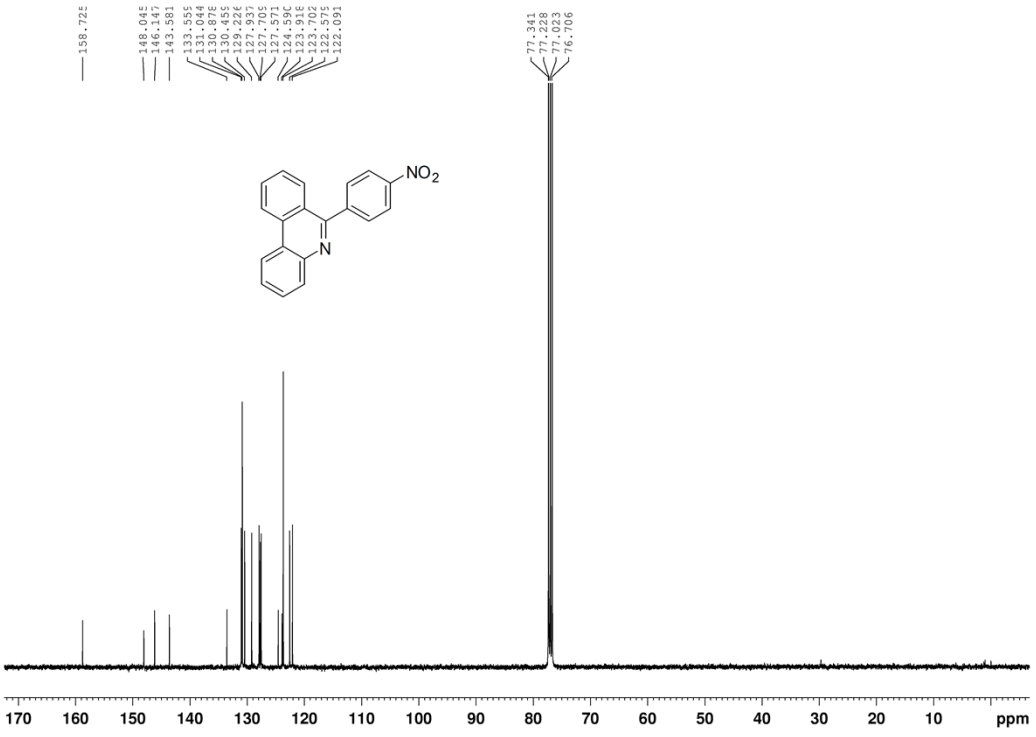
NMR spectra of 3g



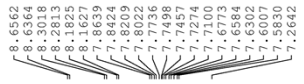


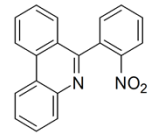
NMR spectra of 3h

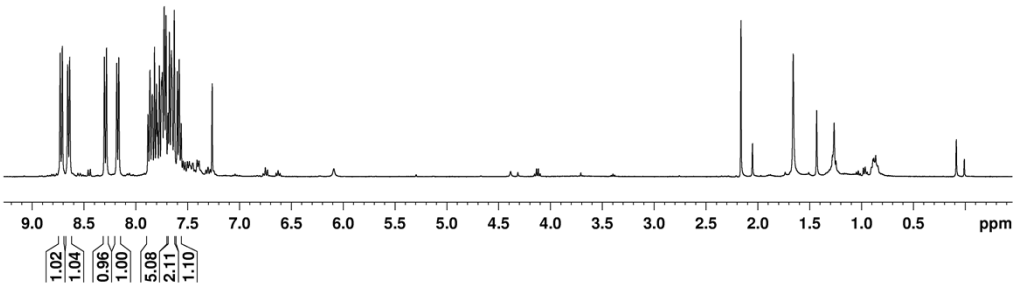


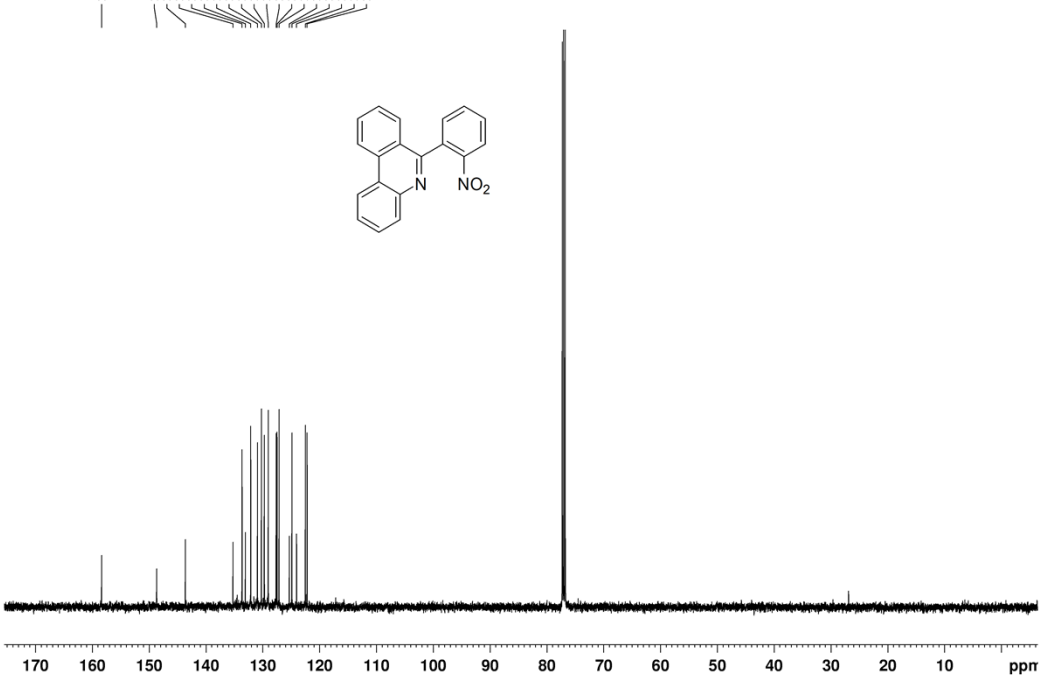


NMR spectra of 3i

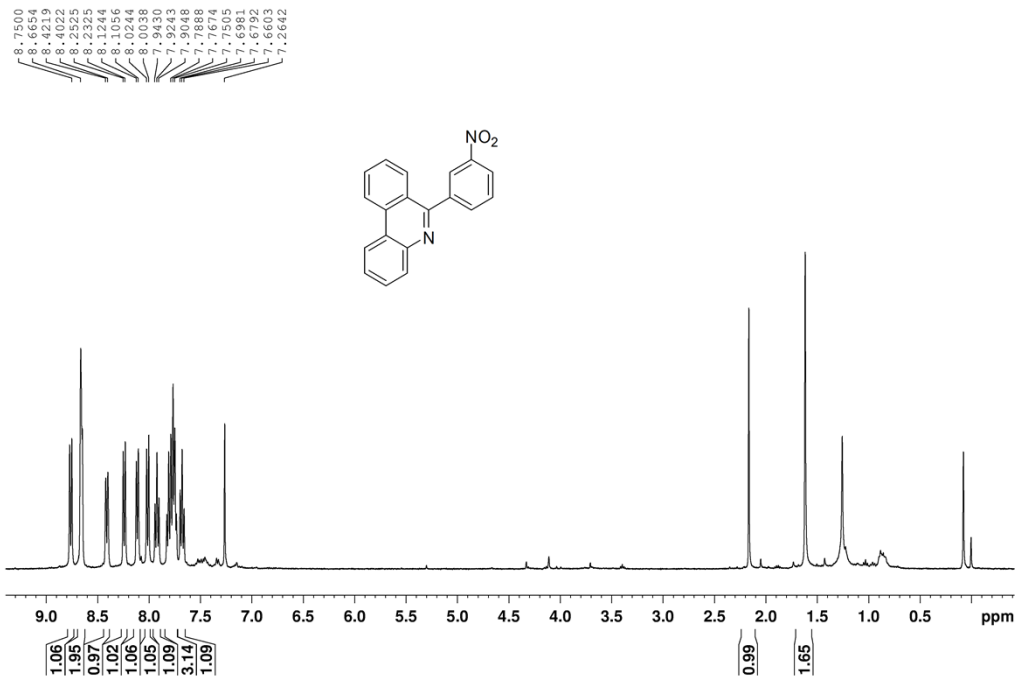


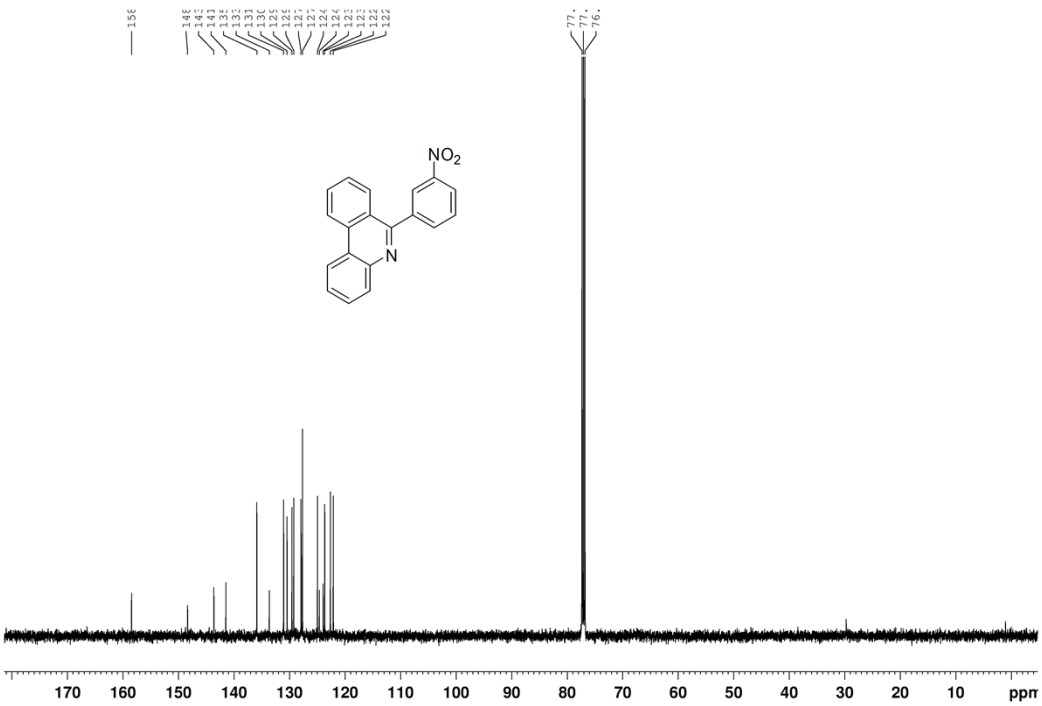




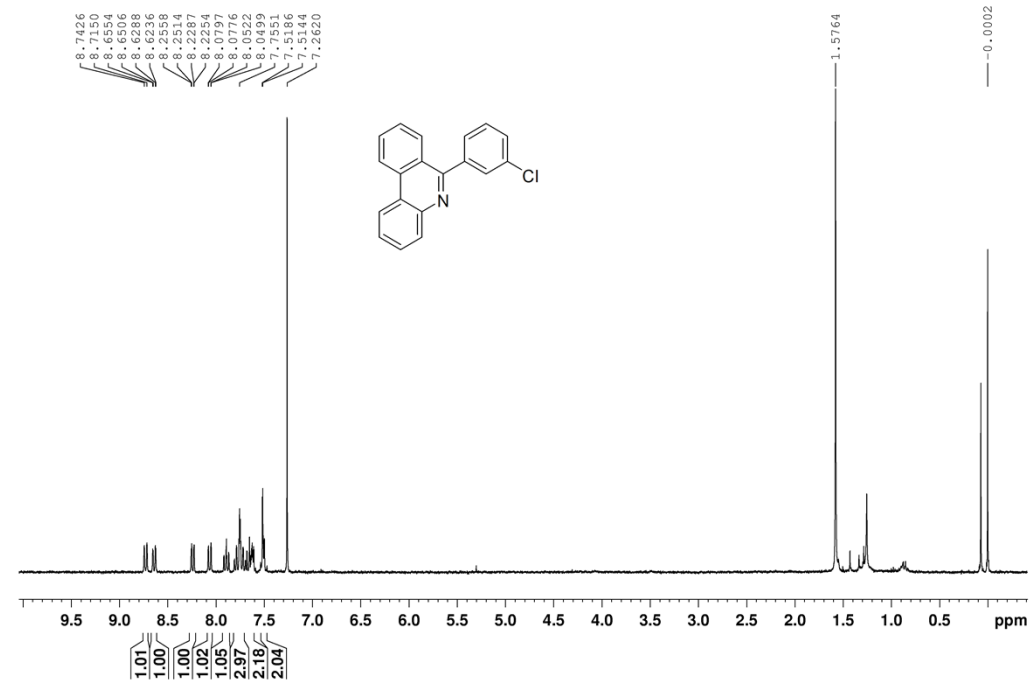


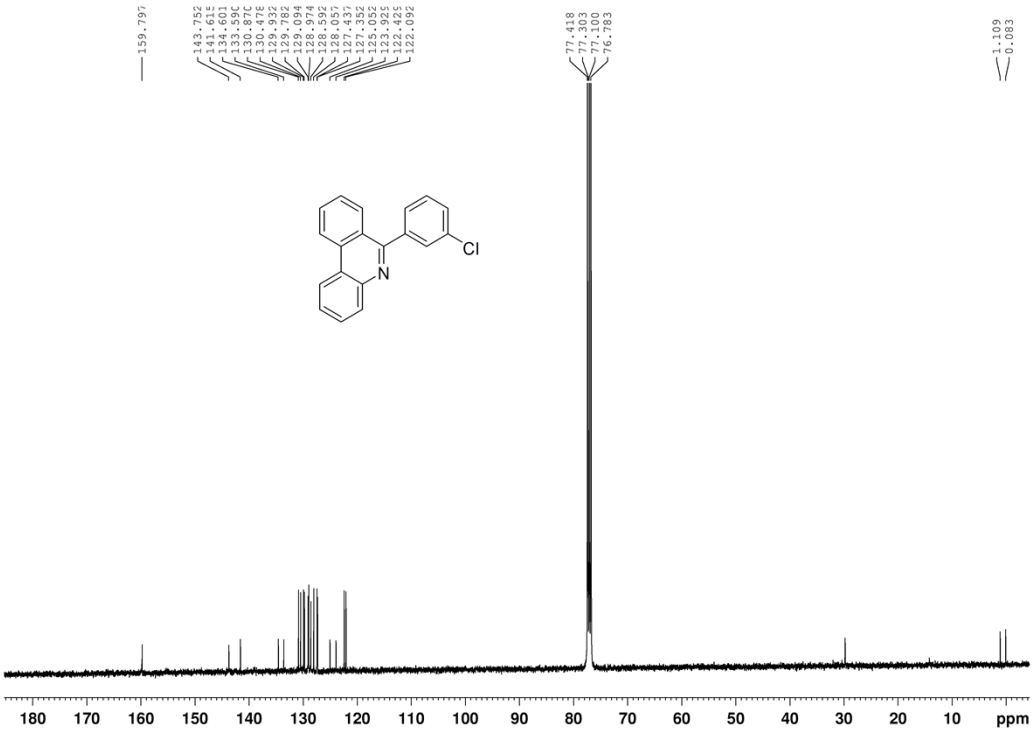
NMR spectra of 3j



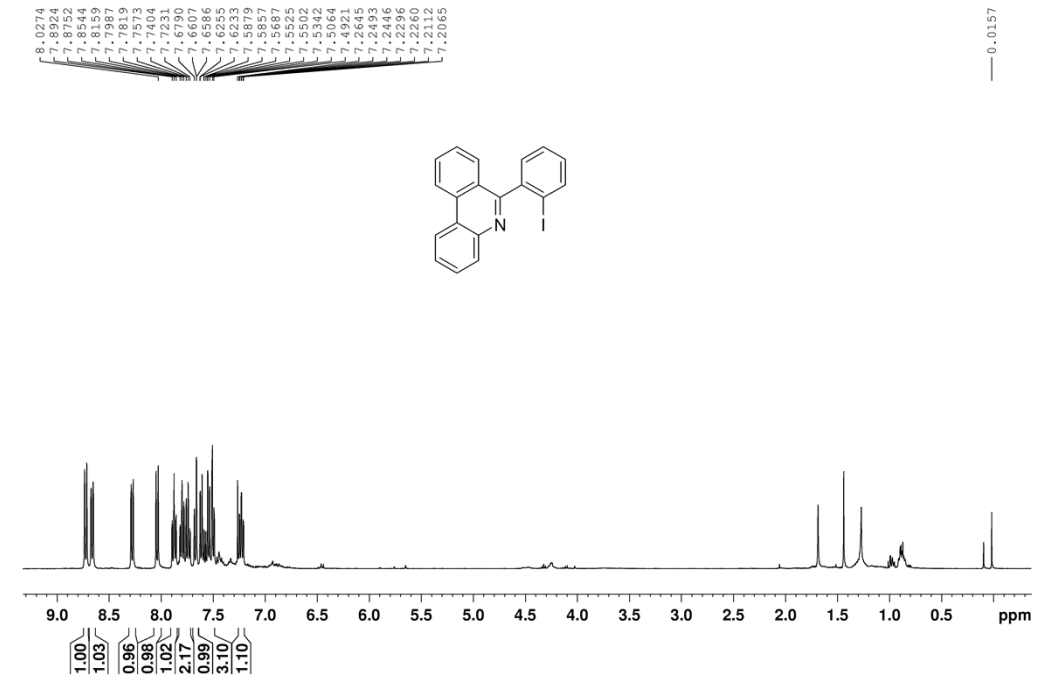


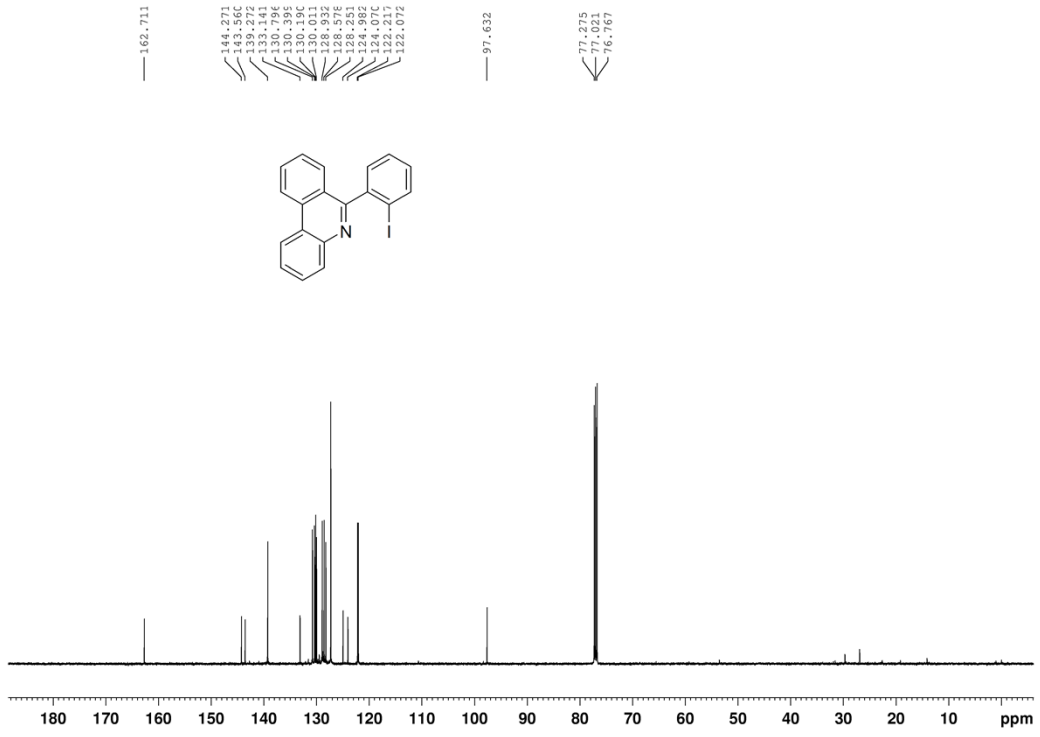
NMR spectra of 3k



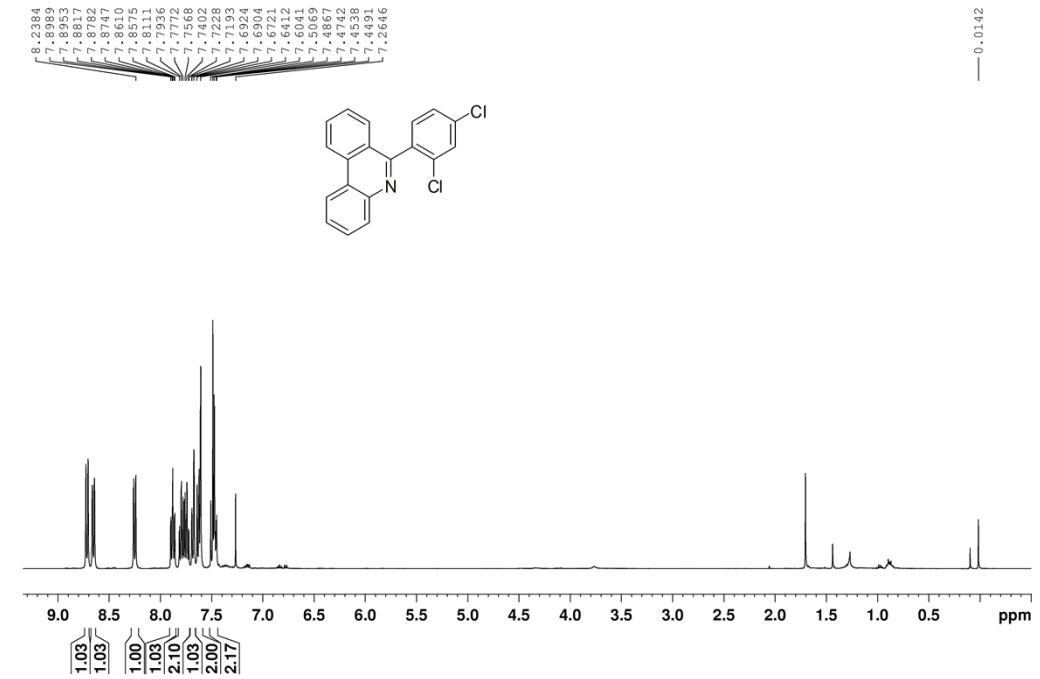


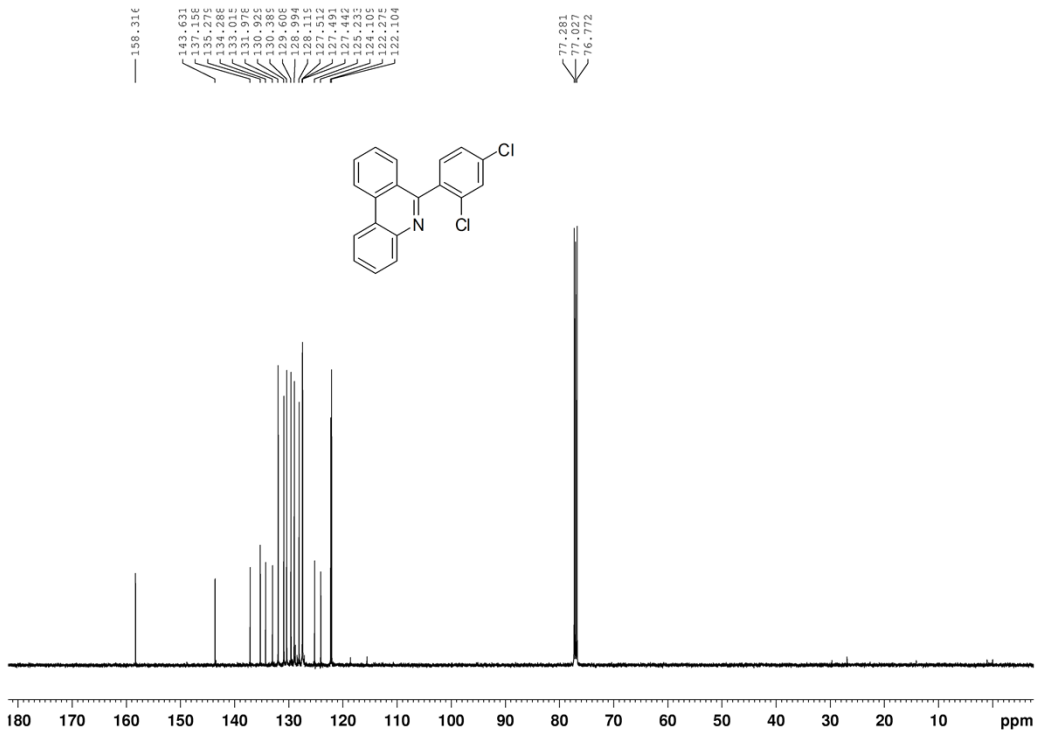
NMR spectra of 3l



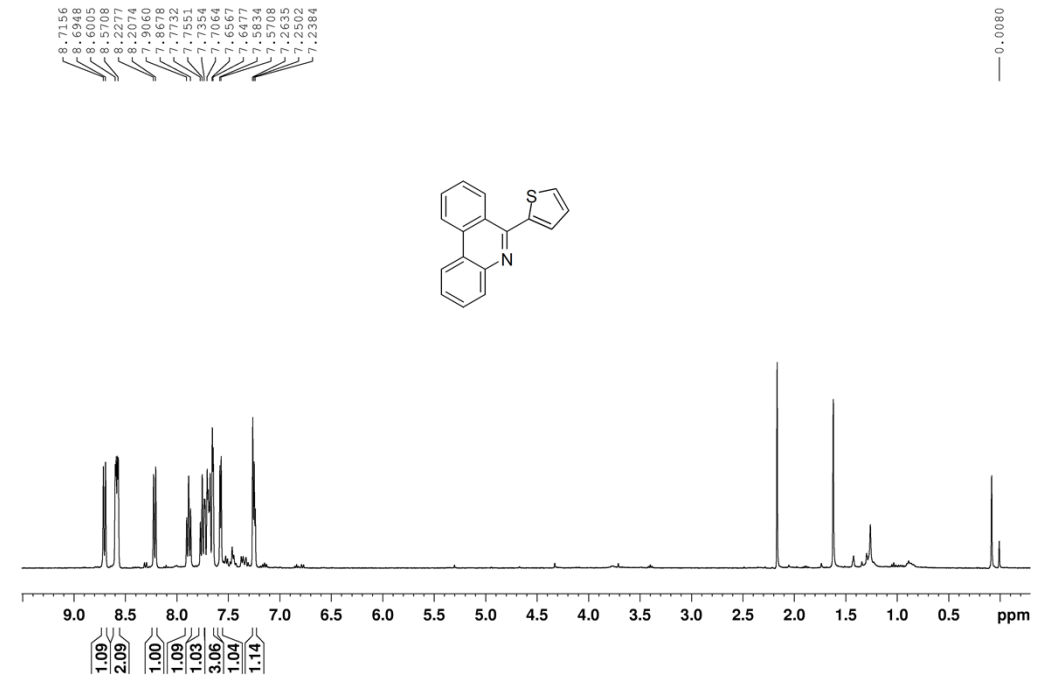


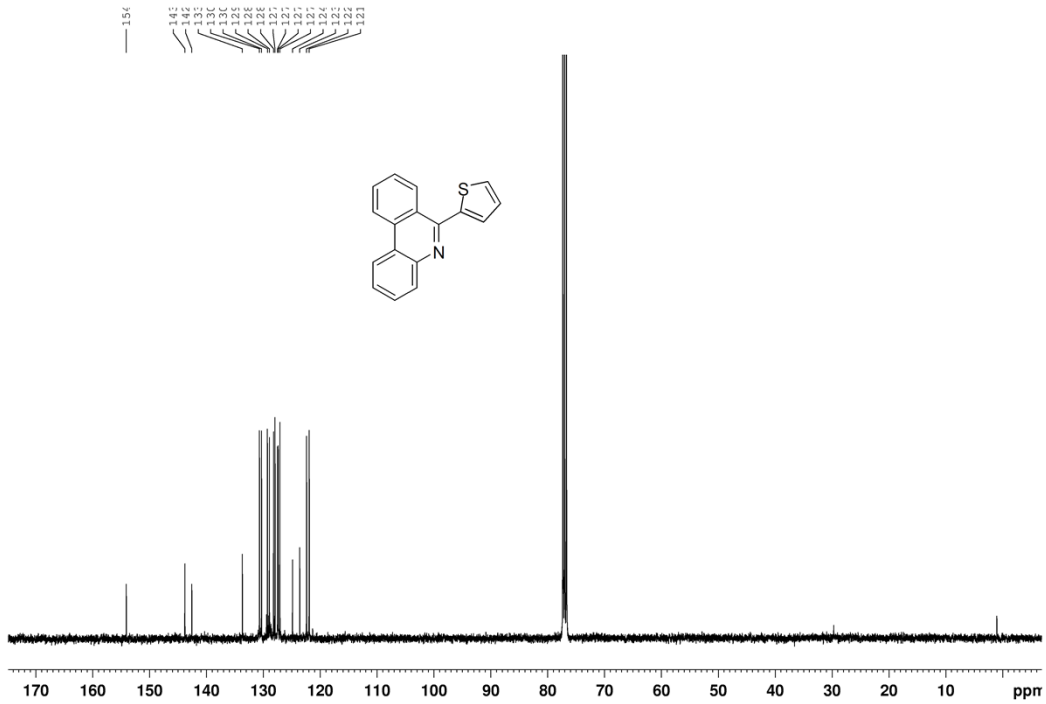
NMR spectra of 3m



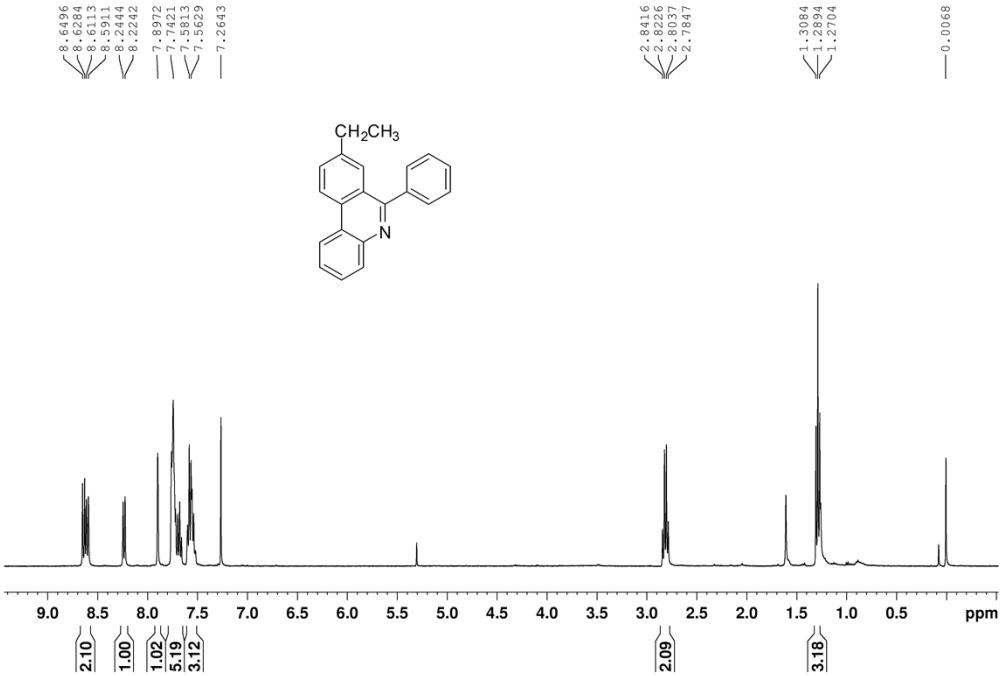


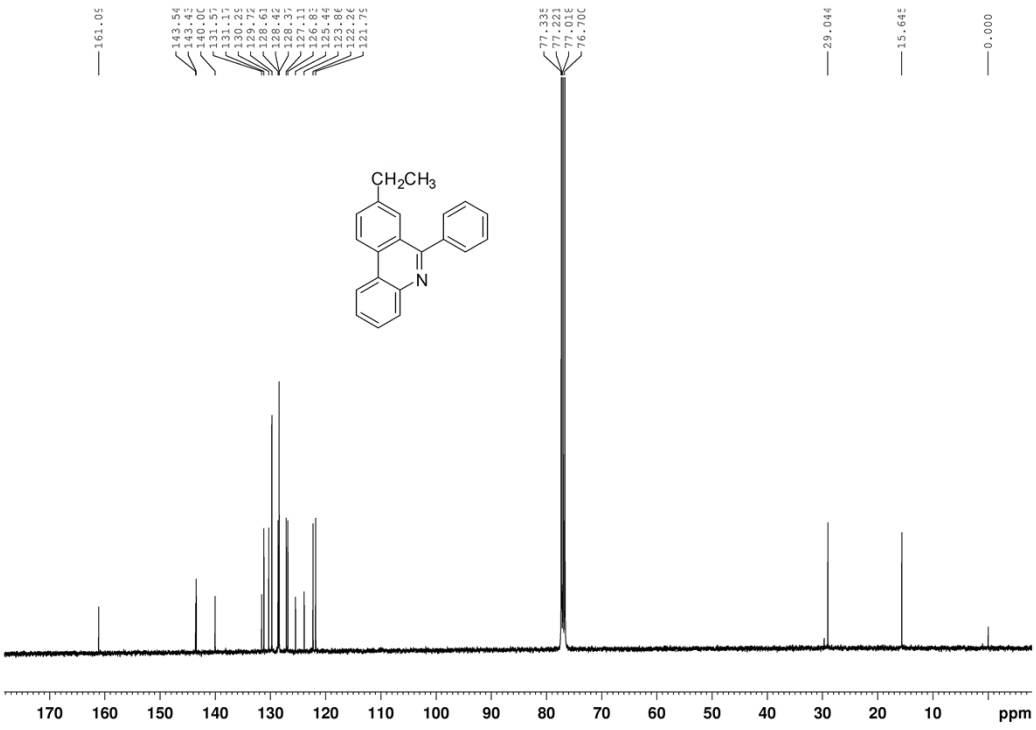
NMR spectra of 3n



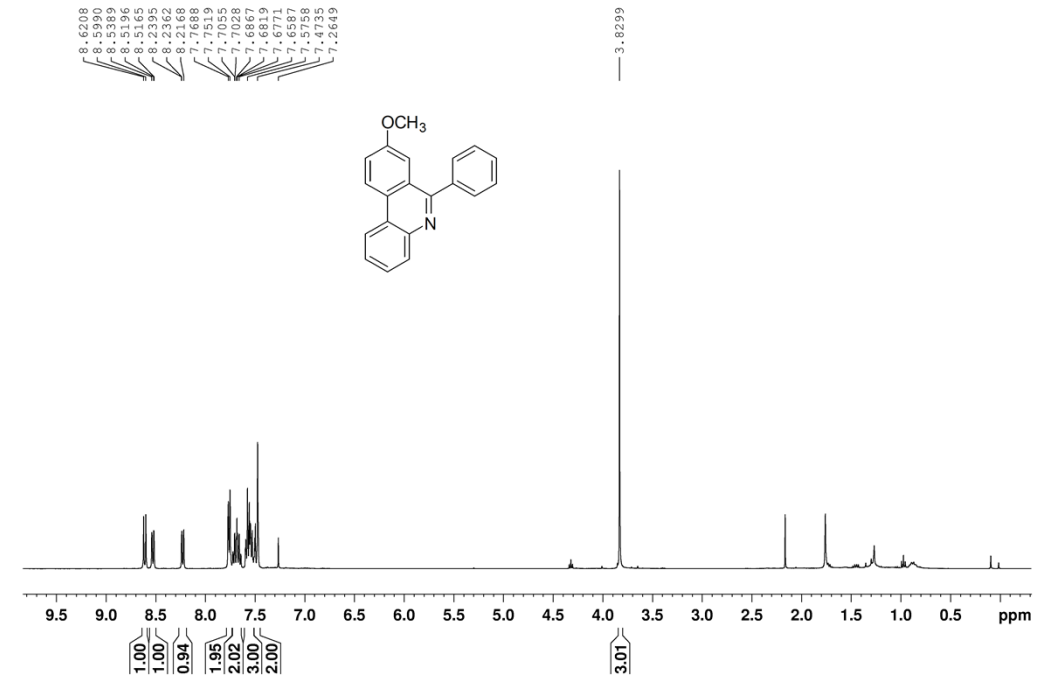


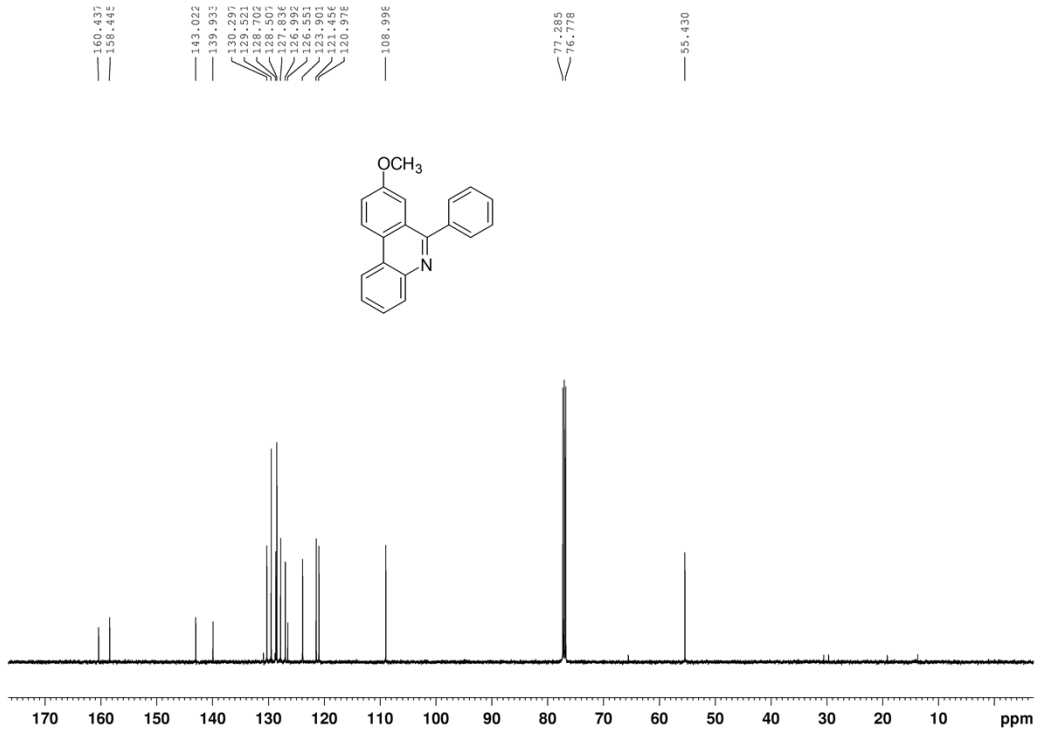
NMR spectra of 3o



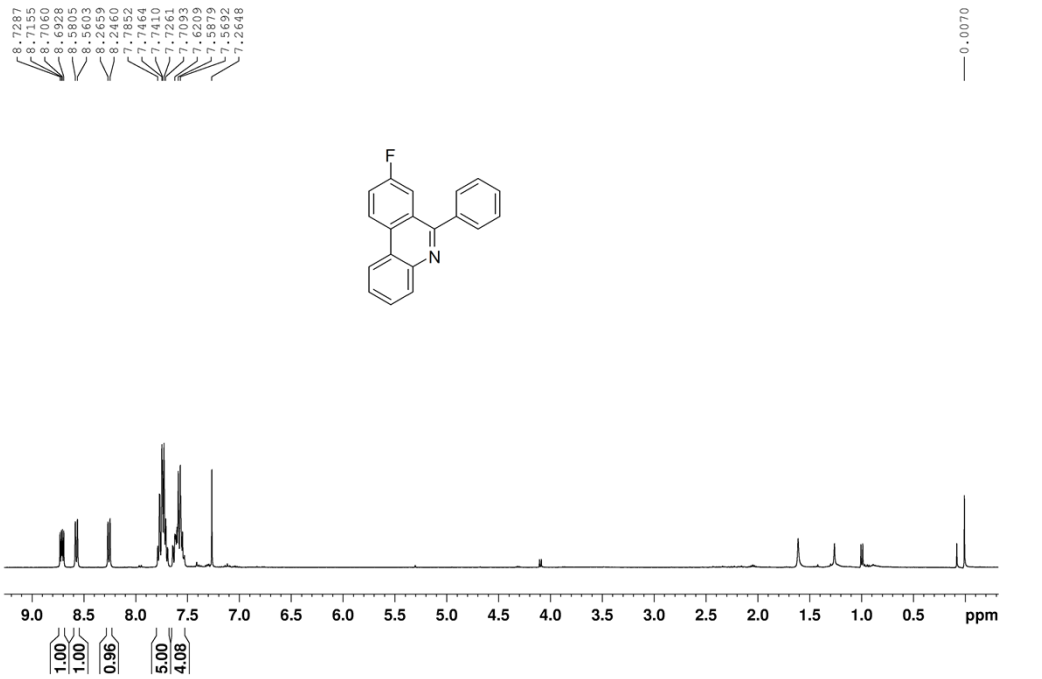


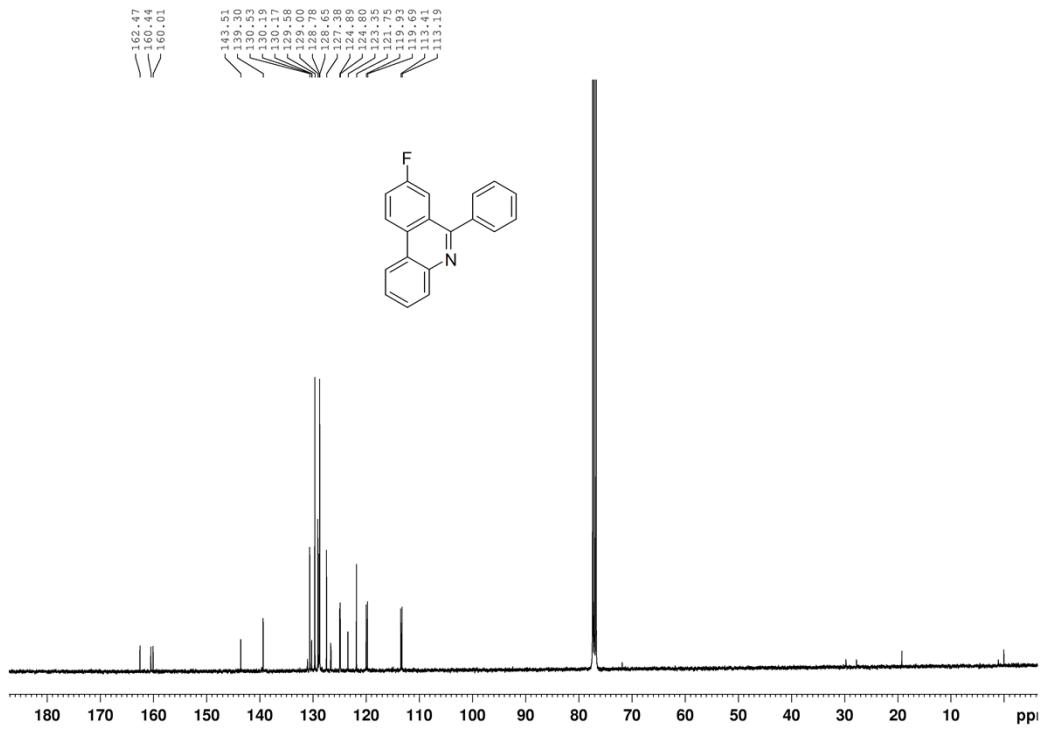
NMR spectra of 3p



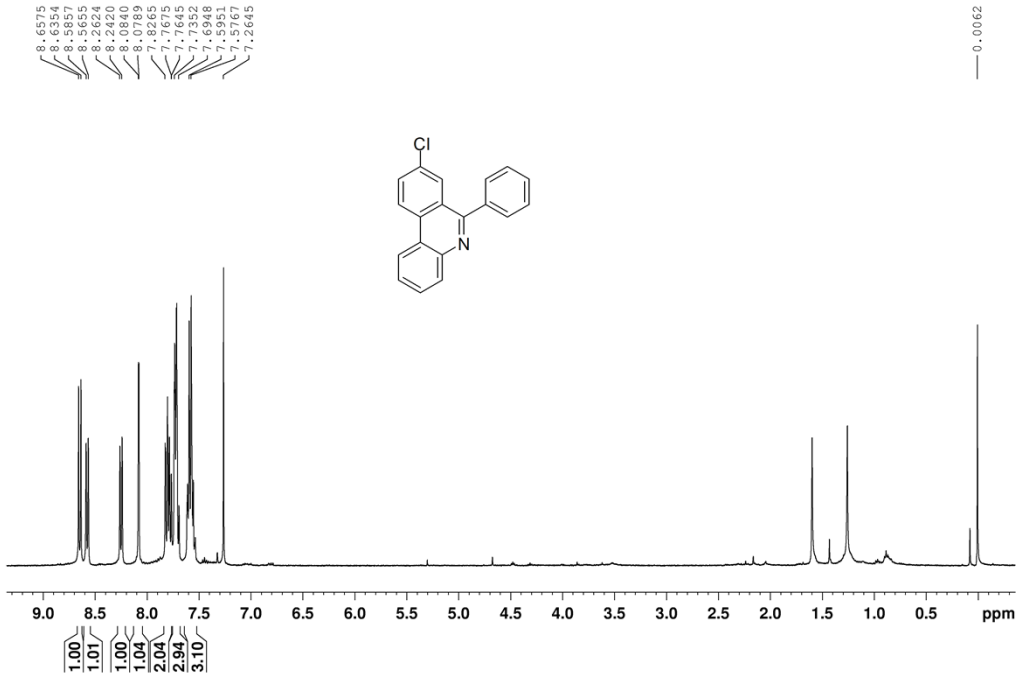


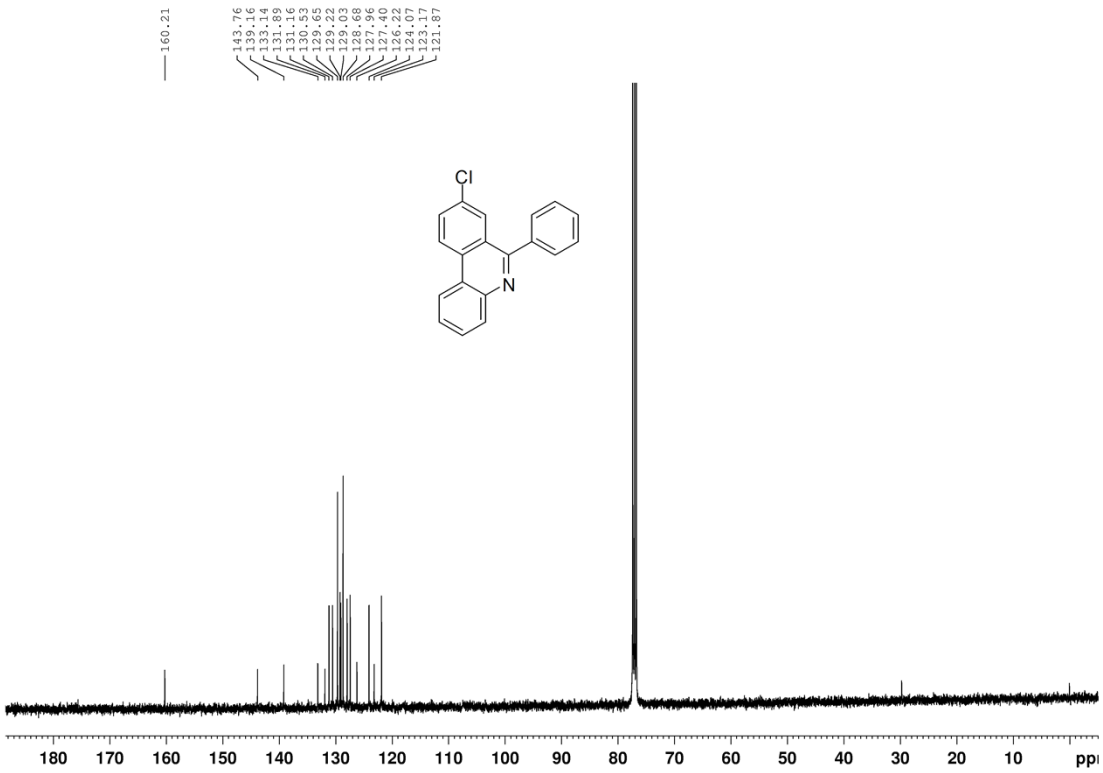
NMR spectra of 3q



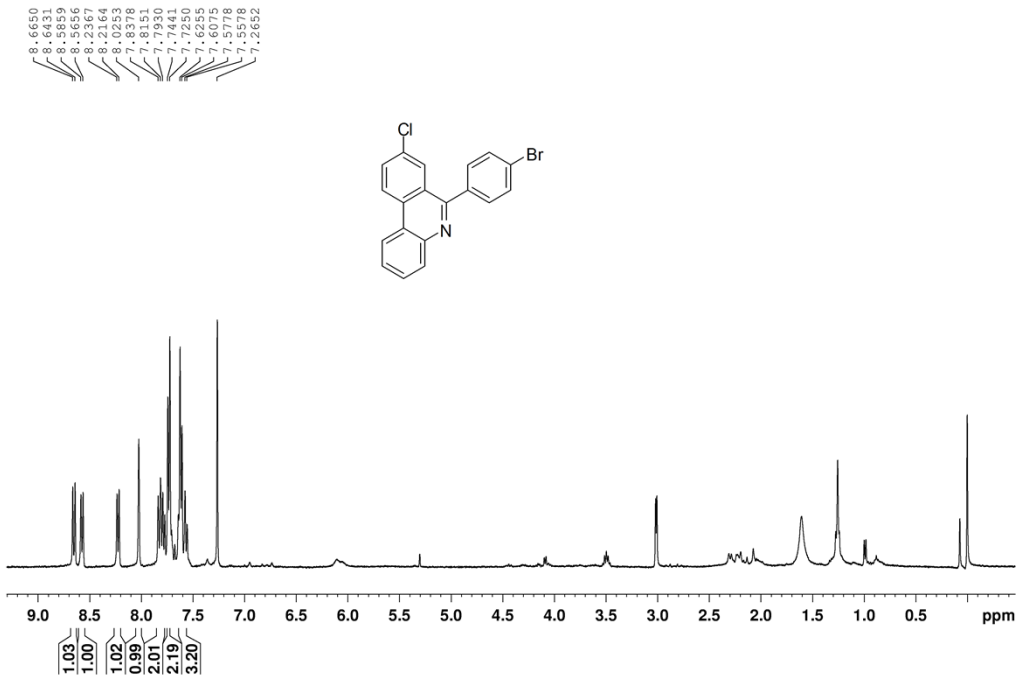


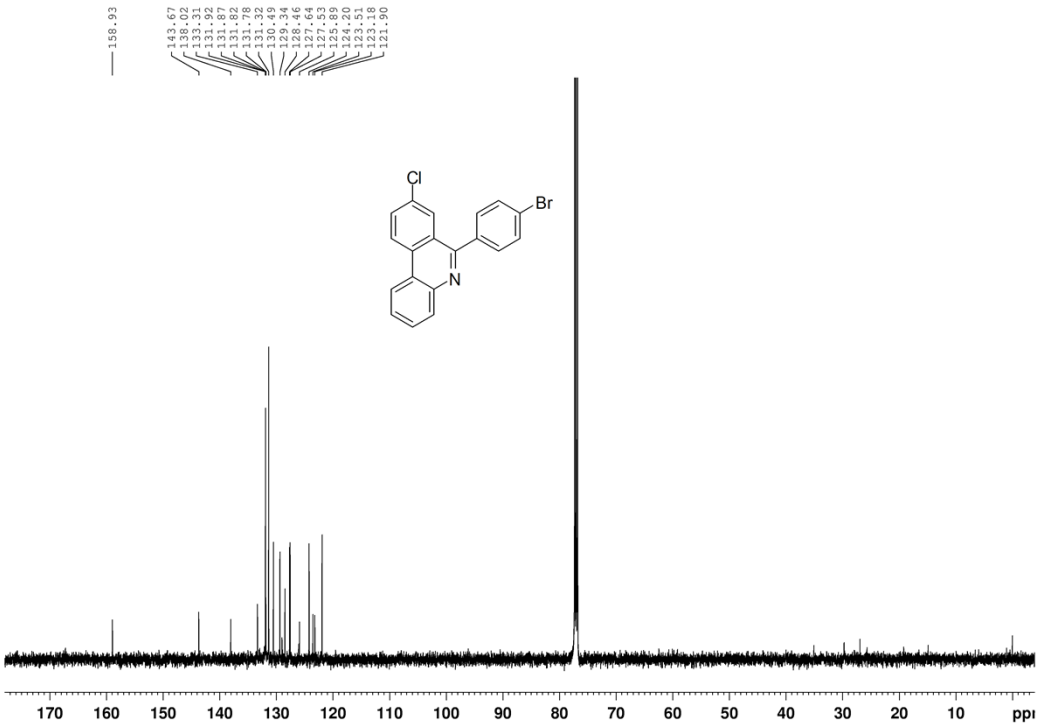
NMR spectra of 3r



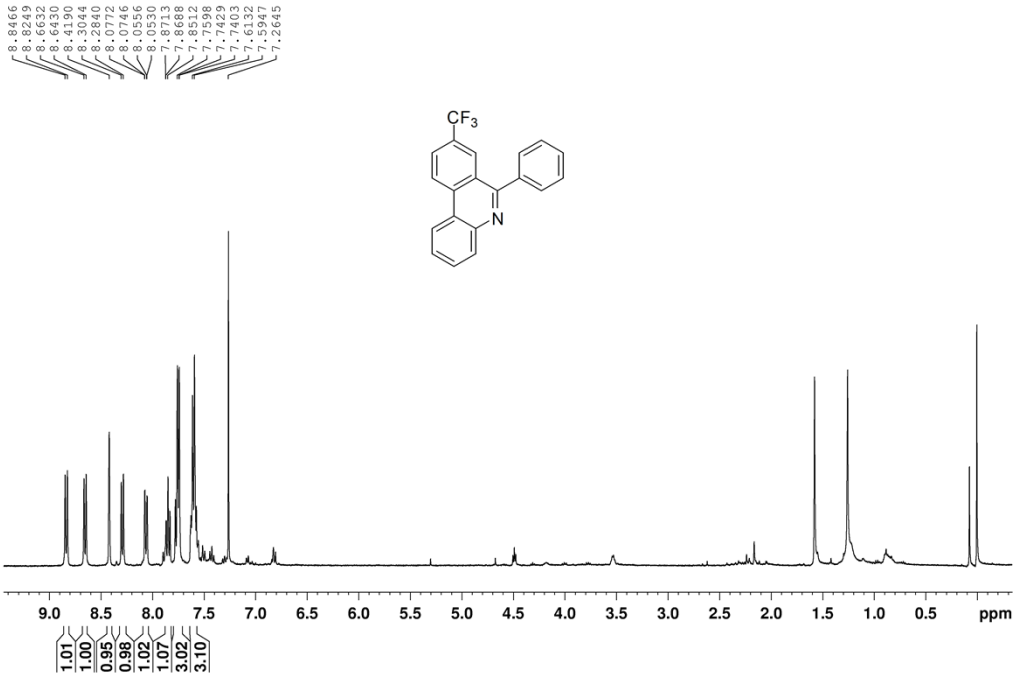


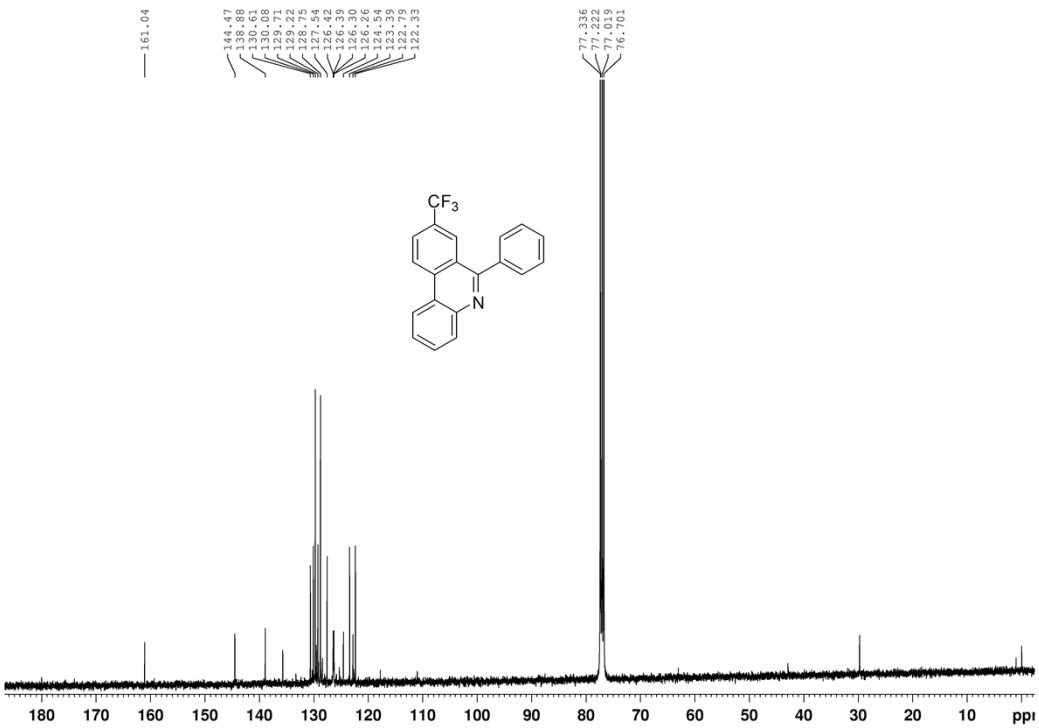
NMR spectra of 3s



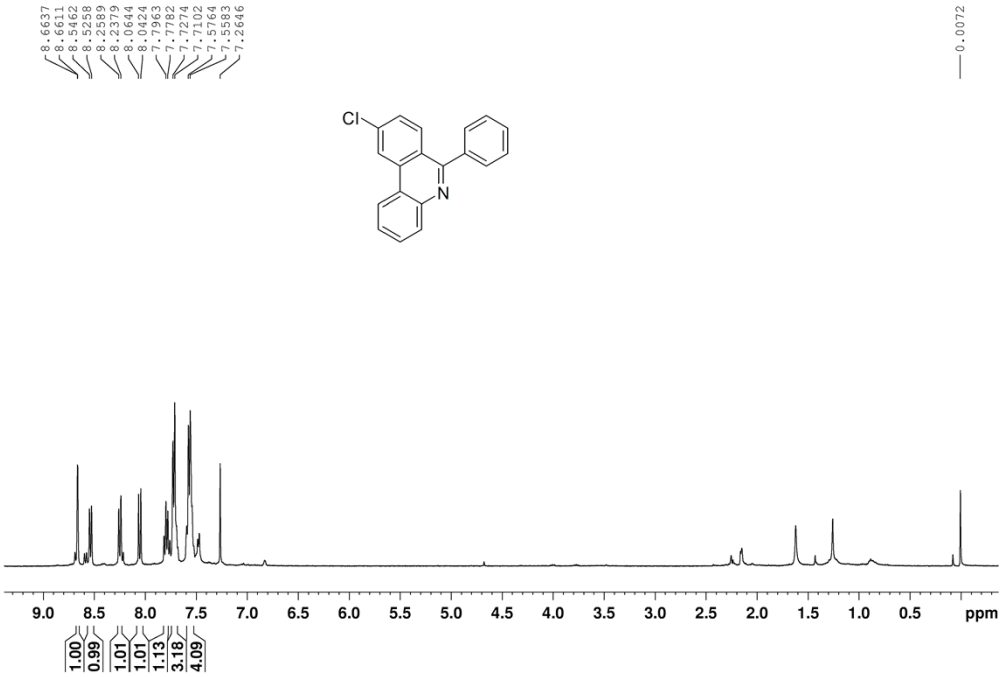


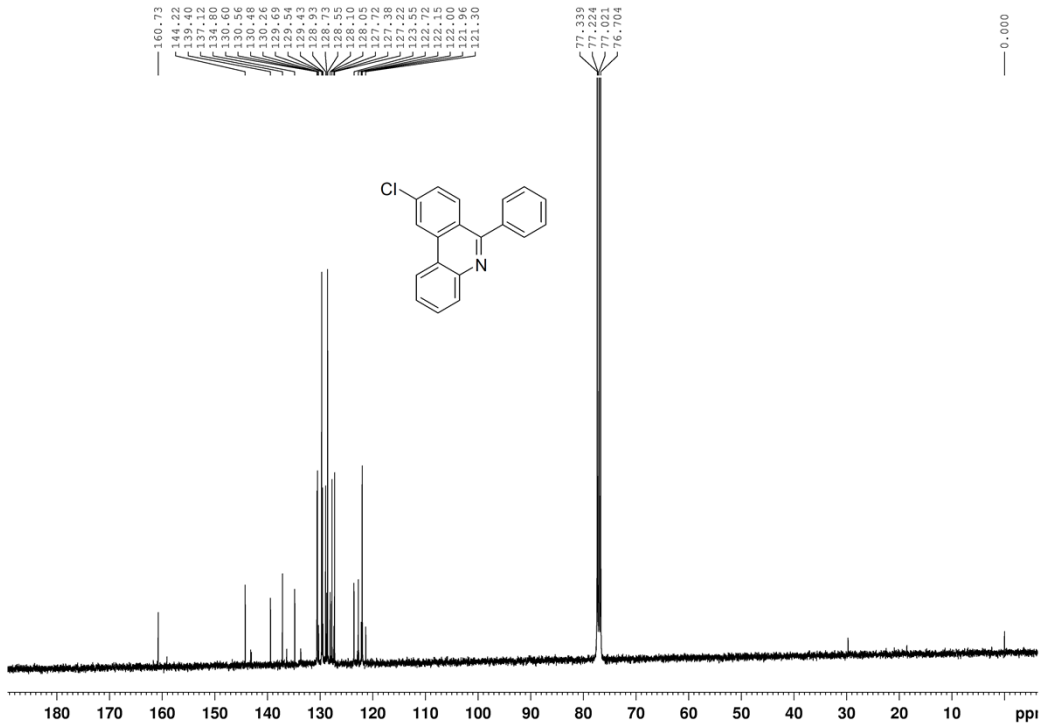
NMR spectra of 3t



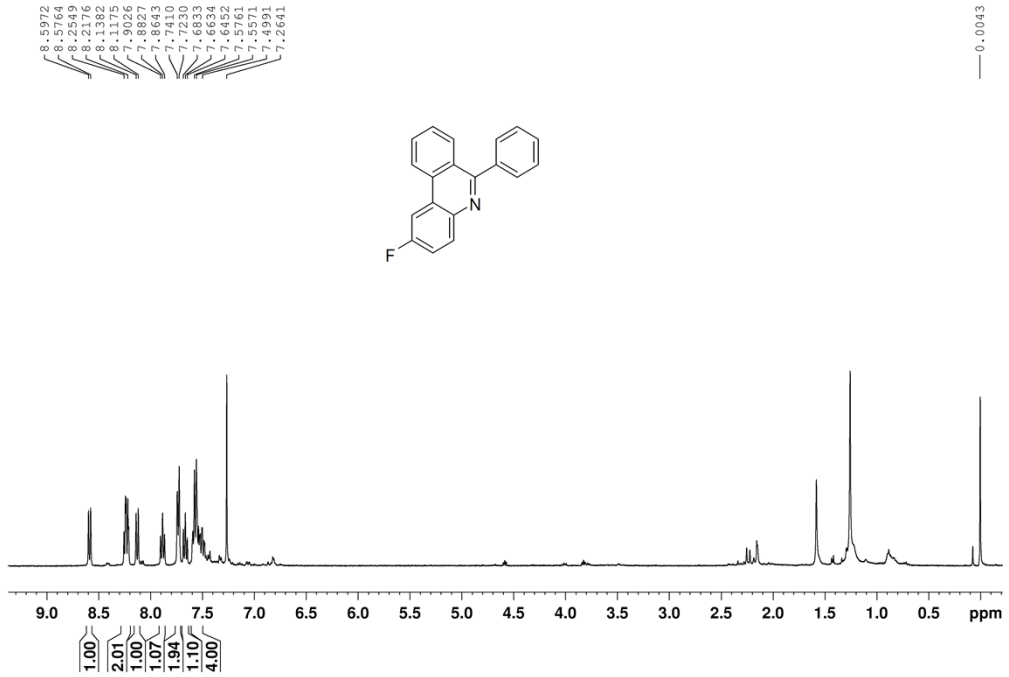


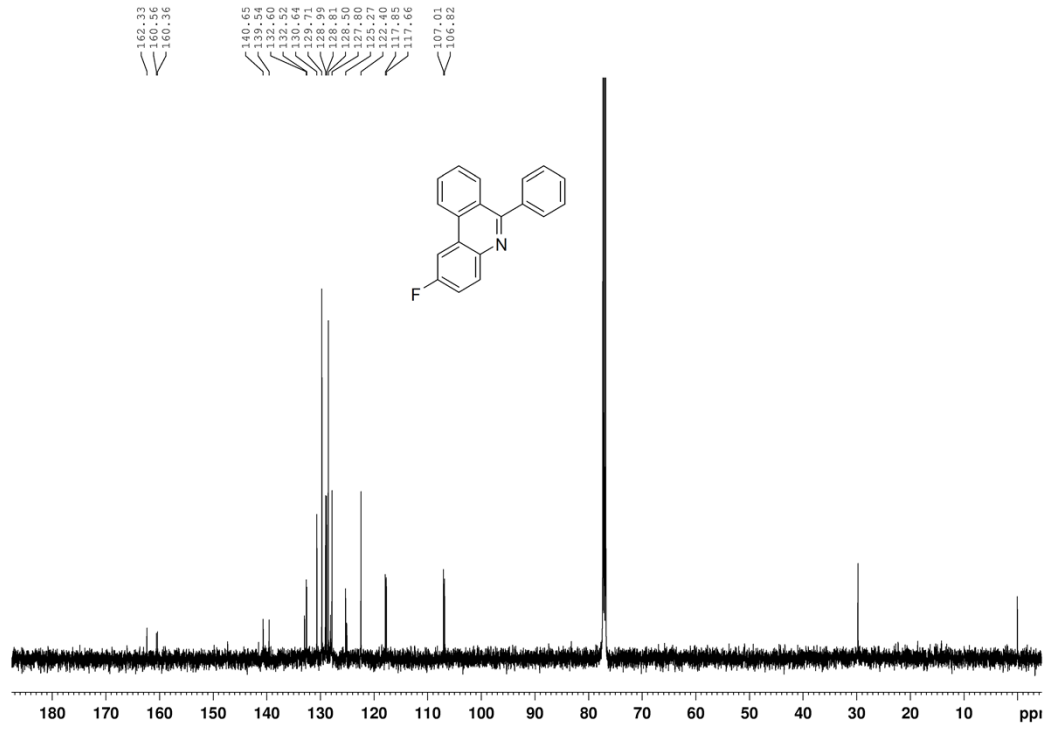
NMR spectra of 3u



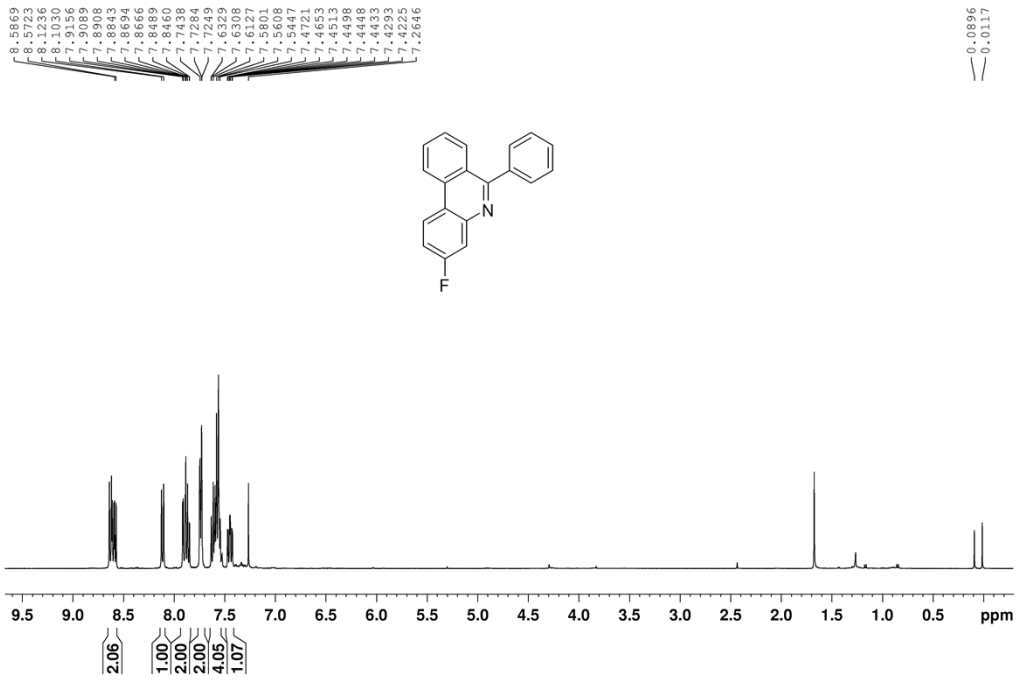


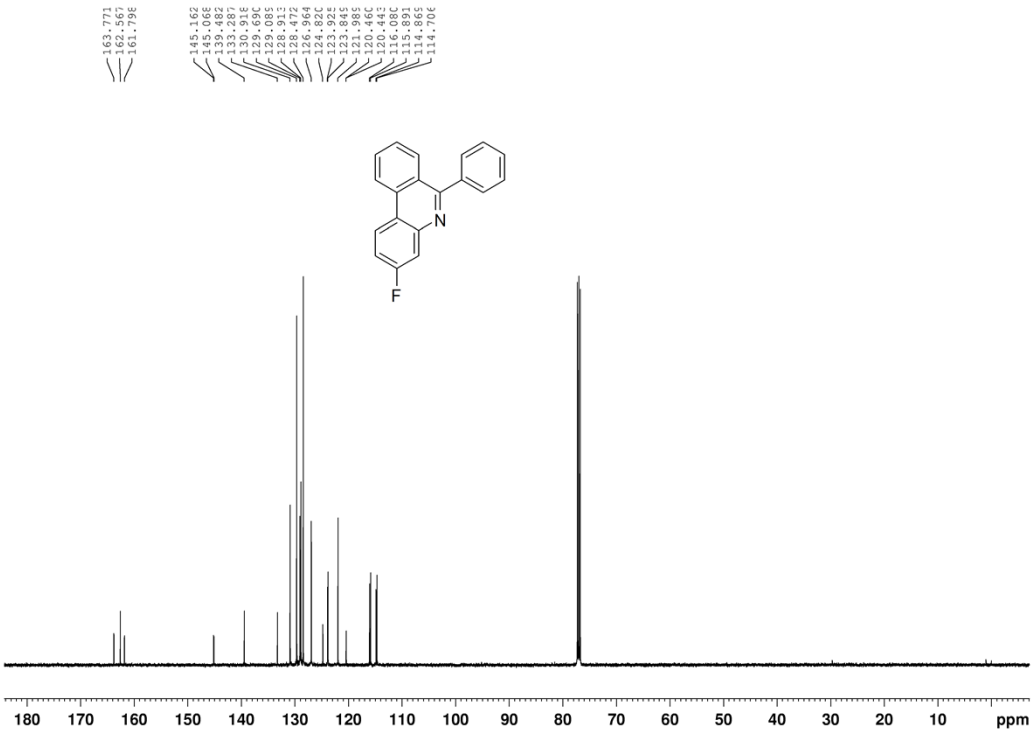
NMR spectra of 3v





NMR spectra of 3w





NMR spectra of 3x