Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Electrochemical oxidative homo-coupling reaction of imidazopyridine heterocycles to biheteroaryls

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Table of Contends

1. General information

All commercial reagents were used without additional purification unless otherwise specified. Solvents were purified and dried according to standard methods prior to use. All reactions were run in a sealed tube with a Teflon lined cap under argon, unless otherwise noted. All experiments were monitored by thin layer chromatography (TLC) using UV light as visualizing agent. TLC was performed on pre-coated silica gel plated. Column chromatography was performed using silica gel 60 (300-400 mesh). ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) were measured on a Bruker AVANCE III-400 spectrometer. Chemical shifts are reported in ppm (δ) relative to internaltetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constants [Hz], integration). Melting points are uncorrected. Infrared spectra were obtained on a Agilent Cary 630 instrument on a diamond plate by way of technology Attenuated Total Reflection (ATR). HRMS were conducted on an Agilent 6540Q-TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive ion mode.

2. General experimental procedure for the homo-coupling reaction of 2-arylimidazo[1,2-*a*]pyridines

An undivided cell was equipped with a carbon anode (1×1 cm^2) and a Platinum cathode (1×1 cm^2) and connected to a DC regulated power supply. To the cell was added 2-phenylimidazo[1,2-*a*]pyridine **1a** (58.2 mg, 0.3 mmol), *n*Bu_4NPF_6 (232.5 mg, 0.6 mmol) and 6 mL of CH_3CN/CF_3CH_2OH. The mixture was electrolyzed using constant current conditions (2 mA/cm^2) at room temperature under argon atmosphere, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with DCM or ethyl acetate (15 mL × 3). The

combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300−400 mesh) column chromatography using hexane/EtOAc (3:1, v/v) or hexane/acetone (5:1, v/v) as eluent to afford the desired product **2a**.

2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyridine (**2a**). White solid (46.9 mg, 81% yield); mp 255−256 °C (lit.[1] 245−246 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.78 (d, J = 9.0 Hz, 2H), 7.76 – 7.60 (m, 4H), 7.47 (d, J = 6.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 4.3 Hz, 6H), 6.65 (t, J = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.6, 145.8, 133.3, 128.9, 128.4, 126.6, 126.2, 123.9, 117.7, 112.9, 108.3.

2,2'-di-p-tolyl-3,3'-biimidazo[1,2-a]pyridine (**2b**). White solid (51.6 mg, 83% yield); mp 289−290 °C (lit.[1] 277−278 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 8.2 Hz, 4H), 7.45 (d, J = 6.8 Hz, 2H), 7.26 (m, 2H), 7.05 (d, J = 8.0 Hz, 4H), 6.64 (td, J = 6.8, 0.8 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.5, 145.9, 138.3, 130.5, 129.6, 126.5, 126.0, 123.9, 117.6, 112.8, 108.0, 21.25.

2,2'-bis(4-(tert-butyl)phenyl)-3,3'-biimidazo[1,2-a]pyridine (**2c**). White solid (56.8 mg, 76% yield); mp 290−291 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.78 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 8.5 Hz, 4H), 7.47 (d, J = 6.8 Hz, 2H), 7.32 – 7.19 (m, 6H), 6.66 (t, J = 6.8 Hz, 2H), 1.24 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.4, 146.5, 146.0, 130.4, 126.3, 126.0, 125.8, 123.9, 117.6, 112.8, 107.9, 31.2; HRMS-ESI (m/z): calcd for $C_{34}H_{35}N_4^+$ $[M + H]^+$ 499.2862, found 499.2858.

2,2'-bis(3-methoxyphenyl)-3,3'-biimidazo[1,2-a]pyridine (**2d**). White solid (58.9 mg, 88% yield); mp 291−292 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.77 (d, J = 9.1 Hz, 2H), 7.49 (d, J = 6.8 Hz, 2H), 7.33 – 7.22 (m, 6H), 7.12 (t, J = 8.0 Hz, 2H), 6.84 – 6.75 (m, 2H), 6.67 (td, J = 6.8, 1.0 Hz, 2H), 3.58 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.9, 146.5, 145.7, 134.6, 129.9, 126.2, 124.0, 119.0, 117.7, 115.3, 113.0, 110.8, 108.4, 55.0; HRMS-ESI (m/z): calcd for $C_{28}H_{23}N_4O_2^+$ $[M + H]^+$ 447.1819, found 447.1821.

2,2'-di-o-tolyl-3,3'-biimidazo[1,2-a]pyridine (**2e**). White solid (48.5 mg, 78% yield); mp 245−246 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.74 (d, J = 9.1 Hz, 2H), 7.57 (d, J = 6.8 Hz, 2H), 7.30 (ddd, J = 9.0, 6.8, 1.2 Hz, 2H), 7.10 (m, 4H), 6.92 – 6.84 (m, 2H), 6.81 (td, J = 6.8, 1.0 Hz, 2H), 6.74 (d, J = 7.1 Hz, 2H), 1.97 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 148.4, 145.8, 137.1,

133.0, 130.2, 129.7, 128.1, 125.3, 125.3, 123.7, 118.2, 113.0, 110.3, 19.8; HRMS-ESI (m/z): calcd for $C_{28}H_{23}N_4^+$ $[M + H]^+$ 415.1923, found 415.1917.

2,2'-bis(3,4-dimethylphenyl)-3,3'-biimidazo[1,2-a]pyridine (**2f**). Yellow solid (47.8 mg, 72% yield); mp 273−274 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76 (d, J = 9.0 Hz, 2H), 7.69 (s, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.32 – 7.18 (m, 4H), 6.92 (d, J = 7.9 Hz, 2H), 6.63 (td, J = 6.8, 1.0 Hz, 2H), 2.18 (s, 6H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.5, 146.0, 137.0, 130.8, 130.1, 127.9, 125.9, 124.0, 123.8, 117.5, 112.7, 108.0, 19.7, 19.6; HRMS-ESI (m/z): calcd for $C_{30}H_{27}N_4^+$ $[M + H]^+$ 443.2236, found 443.2232.

2,2'-bis(2,4-dichlorophenyl)-3,3'-biimidazo[1,2-a]pyridine (**2g**). White solid (43.1 mg, 55% yield); mp 253−254 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.80 (d, J = 9.1 Hz, 2H), 7.67 (d, J = 6.8 Hz, 2H), 7.39 (ddd, J = 9.0, 6.8, 1.1 Hz, 2H), 7.19 (d, J = 2.0 Hz, 2H), 7.00 (dd, J = 8.3, 2.0 Hz, 2H), 6.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.2, 143.9, 134.4, 133.5, 132.6, 131.2, 129.2, 126.8, 125.9, 124.1, 118.6, 113.7, 111.4; HRMS-ESI (m/z): calcd for $C_{26}H_{15}C_{l4}N_4^+$ $[M + H]^+$ 523.0051, found 523.0052.

2,2'-bis(4-chlorophenyl)-3,3'-biimidazo[1,2-a]pyridine (**2h**). White solid (42.9 mg, 63% yield); mp 317−318 °C; ^{1}H NMR (DMSO-d_6 with a drop of conc. HCl, 400 MHz): δ (ppm) 8.58 (d, J = 6.6 Hz, 2H), 8.24 (d, J = 8.9 Hz, 2H), 8.15 – 8.05 (m, 2H), 7.69 (d, J = 8.6 Hz, 4H), 7.46 (dd, J = 15.8, 7.8 Hz, 6H); ^{13}C NMR (DMSO-d_6 with a drop of conc. HCl, 100 MHz): δ (ppm) 142.2, 137.7, 136.3, 135.4, 130.1, 129.7, 127.6, 124.9, 118.7, 113.8, 106.6; HRMS-ESI (m/z): calcd for $C_{26}H_{17}Cl_2N_4^+$ $[M + H]^+$ 455.0830, found 455.0831.

2,2'-bis(3-chlorophenyl)-3,3'-biimidazo[1,2-a]pyridine (**2i**). White solid (51.7 mg, 76% yield); mp 257−258 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.93 (t, J = 1.7 Hz, 2H), 7.79 (d, J = 9.1 Hz, 2H), 7.47 (d, J = 6.8 Hz, 2H), 7.33 (m, 4H), 7.24 – 7.17 (m, 2H), 7.09 (t, J = 7.9 Hz, 2H), 6.73 (td, J = 6.8, 0.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.7, 144.6, 135.0, 135.0, 130.1, 128.6, 127.0, 126.7, 124.2, 123.8, 118.0, 113.4, 108.3; HRMS-ESI (m/z): calcd for $C_{26}H_{17}Cl_2N_4^+$ $[M + H]^+$ 455.0830, found 455.0828.

2,2'-bis(3-bromophenyl)-3,3'-biimidazo[1,2-a]pyridine (**2j**). Yellow solid (67.5 mg, 83% yield); mp 267−268 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.11 (t, J = 1.7 Hz, 2H), 7.79 (d, J = 9.1 Hz, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.41 – 7.28 (m, 6H), 7.02 (t, J = 7.9 Hz, 2H), 6.73 (td, J = 6.8,

0.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.7, 144.4, 135.2, 131.5, 130.4, 123.0, 126.7, 124.6, 123.8, 123.2, 118.0, 113.5, 108.3; HRMS-ESI (m/z): calcd for $C_{26}H_{17}Br_2N_4^+$ [M + H]$^+$ 542.9820, found 542.9821.

3,3'-([3,3'-biimidazo[1,2-a]pyridine]-2,2'-diyl)dibenzonitrile (**2k**). White solid (55.6 mg, 85% yield); mp 308−309 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.19 (s, 2H), 7.83 (d, J = 9.1 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 6.8 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.28 (dd, J = 10.7, 4.9 Hz, 2H), 6.80 (t, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.9, 143.9, 134.5, 131.9, 130.5, 130.2, 129.7, 127.1, 123.7, 118.3, 114.0, 113.3, 108.1; HRMS-ESI (m/z): calcd for $C_{28}H_{17}N_6^+$ [M + H]$^+$ 437.1515, found 437.1517.

6,6'-dimethyl-2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyridine (**2l**). White solid (44.1 mg, 71% yield); mp 330−331 °C (lit.[2]); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.79 – 7.64 (m, 6H), 7.26 – 7.19 (m, 8H), 7.14 (dd, J = 9.2, 1.5 Hz, 2H), 2.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 145.7, 145.6, 133.5, 129.4, 128.8, 128.2, 126.5, 122.8, 121.5, 117.0, 108.1, 18.2.

6,6'-dichloro-2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyridine (**2m**). White solid (43.6 mg, 64% yield); mp 333−334 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.73 (d, J = 9.5 Hz, 2H), 7.69 (dd, J = 6.7, 3.0 Hz, 4H), 7.46 (d, J = 1.2 Hz, 2H), 7.28 (m, 6H), 7.27 – 7.23 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.1, 145.1, 132.6, 129.1, 129.0, 127.8, 126.6, 121.7, 121.6, 118.2, 108.1; HRMS-ESI (m/z): calcd for $C_{26}H_{17}Cl_2N_4^+$ [M + H]$^+$ 455.0830, found 455.0826.

8,8'-dimethyl-2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyridine (**2n**). White solid (52.8 mg, 85% yield); mp 243−244 °C (lit.[2]); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.75 (dd, J = 7.5, 1.8 Hz, 4H), 7.31 (d, J = 6.8 Hz, 2H), 7.27 – 7.15 (m, 6H), 7.03 (d, J = 6.8 Hz, 2H), 6.52 (t, J = 6.8 Hz, 2H), 2.76 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.0, 145.3, 133.7, 128.8, 128.1, 127.7, 126.7, 124.8, 121.7, 112.8, 109.0, 17.0.

7,7'-dimethyl-2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyridine (**2o**). White solid (54.1 mg, 87% yield); mp 286−287 °C (lit.[1] 263−265 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.79 – 7.65 (m, 4H), 7.51 (s, 2H), 7.33 (d, J = 6.9 Hz, 2H), 7.27 – 7.15 (m, 6H), 6.46 (d, J = 6.9 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.0, 145.5, 137.2, 133.5, 128.8, 128.2, 126.5, 123.1, 116.1, 115.5, 107.9, 21.4.

6,6'-dimethyl-2,2'-di-p-tolyl-3,3'-biimidazo[1,2-a]pyridine (**2p**). White solid (42.5 mg, 64% yield);

mp 288−289 °C (lit.[1] 268−269 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.67 (d, J = 9.1 Hz, 2H), 7.60 (d, J = 8.2 Hz, 4H), 7.21 (s, 2H), 7.12 (dd, J = 9.2, 1.3 Hz, 2H), 7.03 (d, J = 8.1 Hz, 4H), 2.27 (s, 6H), 2.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 145.9, 145.5, 138.1, 130.7, 129.5, 129.2, 126.4, 122.6, 121.5, 116.9, 107.8, 21.2, 18.2.

6,6'-dimethyl-2,2'-bis(4-(trifluoromethyl)phenyl)-3,3'-biimidazo[1,2-a]pyridine (**2q**). White solid (58.6 mg, 71% yield); mp 312−313 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.78 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 9.2 Hz, 2H), 7.49 (d, J = 8.3 Hz, 4H), 7.25 (d, J = 0.7 Hz, 2H), 7.21 (dd, J = 9.2, 1.5 Hz, 2H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 145.9, 144.4, 136.8, 130.1, 130.0 (q, J = 32.1 Hz), 126.6, 125.8, 125.7, 124.0 (q, J = 270.4 Hz), 123.8, 121.2, 117.4, 108.4, 18.2; HRMS-ESI (m/z): calcd for $C_{30}H_{21}F_6N_4^+$ $[M + H]^+$ 551.1670, found 551.1666.

2,2'-di(thiophen-2-yl)-3,3'-biimidazo[1,2-a]pyridine (**2r**). White solid (49.0 mg, 82% yield); mp 268−269 °C (lit.[1] 253−254 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.79 (d, J = 9.1 Hz, 2H), 7.55 (d, J = 6.8 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.22 (d, J = 4.9 Hz, 2H), 6.98 (d, J = 3.5 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.76 (t, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.8, 142.4, 136.0, 128.0, 126.5, 126.5, 125.1, 124.1, 117.7, 113.2, 106.1.

2,2'-di(naphthalen-2-yl)-3,3'-biimidazo[1,2-a]pyridine (**2s**). Yellow solid (56.9 mg, 78% yield); mp 247−248 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 8.23 (s, 2H), 7.88 (d, J = 9.0 Hz, 2H), 7.83 – 7.73 (m, 6H), 7.70 (dd, J = 5.9, 3.5 Hz, 2H), 7.61 (dd, J = 8.6, 1.5 Hz, 2H), 7.49 – 7.39 (m, 6H), 6.84 (t, J = 6.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 146.1, 144.7, 132.8, 132.5, 130.9, 128.3, 128.1, 127.5, 126.8, 126.5, 126.4, 125.4, 124.6, 123.6, 117.3, 113.5, 108.3; HRMS-ESI (m/z): calcd for $C_{34}H_{23}N_4^+$ $[M + H]^+$ 487.1923, found 487.1918.

2,2'-di([1,1'-biphenyl]-4-yl)-3,3'-biimidazo[1,2-a]pyridine (**2t**). Yellow solid (61.4 mg, 76% yield); mp 323−324 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.84 (dd, J = 8.6, 2.0 Hz, 6H), 7.61 – 7.50 (m, 10H), 7.42 (t, J = 7.5 Hz, 4H), 7.33 (dd, J = 11.4, 4.3 Hz, 4H), 6.72 (t, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.7, 145.5, 141.0, 140.3, 132.2, 128.8, 127.5, 127.4, 127.0, 126.9, 126.3, 124.0, 117.7, 113.1, 108.3; HRMS-ESI (m/z): calcd for $C_{38}H_{27}N_4^+$ $[M + H]^+$ 539.2236, found 539.2234.

3,3'-biimidazo[1,2-a]pyridine (**2u**). White solid (6.3 mg, 18% yield); mp 160−161°C (lit.[2]); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90 (t, J = 3.2 Hz, 4H), 7.78 (d, J = 9.1 Hz, 2H), 7.38 – 7.28

(m, 2H), 6.88 (t, J = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.7, 135.2, 125.6, 123.8, 118.4, 113.3, 112.7.

2,2'-dimethyl-3,3'-biimidazo[1,2-a]pyridine (**2v**). White solid (9.0 mg, 23% yield); mp 160−161°C (lit.[2]); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.68 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 6.8 Hz, 2H), 7.28 (ddd, J = 8.9, 6.7, 1.5 Hz, 2H), 6.79 (td, J = 6.8, 0.9 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.1, 145.4, 125.3, 123.7, 117.4, 112.6, 109.1, 14.0.

3-(2,2-diphenylvinyl)-2-phenylimidazo[1,2-a]pyridine (**2a'**). White solid (31.3 mg, 28% yield); mp 121−122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.99 – 7.91 (m, 2H), 7.55 (dd, J = 15.6, 8.0 Hz, 2H), 7.45 (dd, J = 6.7, 3.1 Hz, 2H), 7.42 – 7.36 (m, 5H), 7.34 – 7.29 (m, 1H), 7.12 – 7.00 (m, 7H), 6.46 (td, J = 6.8, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.3, 144.8, 142.4, 139.7, 134.6, 129.8, 129.5, 129.1, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 124.4, 124.2, 118.8, 117.1, 115.1, 111.4; HRMS-ESI (m/z): calcd for $C_{27}H_{21}N_2^+$ $[M + H]^+$ 373.1705, found 373.1706.

2,2'-diphenyl-3,3'-biimidazo[1,2-a]pyrimidine (**4a**). Yellow solid (27.9 mg, 48% yield); mp 339−340 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.63 (s, 2H), 7.78 (t, J = 7.1 Hz, 6H), 7.29 (d, J = 14.2 Hz, 6H), 6.74 (d, J = 4.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.6, 149.8, 147.2, 132.5, 131.7, 129.3, 129.2, 126.9, 109.3, 105.9; HRMS-ESI (m/z): calcd for $C_{24}H_{17}N_6^+$ $[M + H]^+$ 389.1515, found 389.1512.

2,2'-diphenyl-3,3'-bibenzo[d]imidazo[2,1-b]thiazole (**6a**). White solid (60.5 mg, 81% yield); mp 313−314 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76 (d, J = 7.4 Hz, 4H), 7.65 (d, J = 7.9 Hz, 2H), 7.29 – 7.15 (m, 8H), 7.08 (t, J = 7.8 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 149.8, 148.0, 133.1, 132.5, 130.3, 128.8, 128.1, 126.8, 126.3, 125.1, 124.4, 112.7, 110.9; HRMS-ESI (m/z): calcd for $C_{30}H_{19}N_4S_2^+$ $[M + H]^+$ 499.1051, found 499.1048.

2,2'-di-p-tolyl-3,3'-bibenzo[d]imidazo[2,1-b]thiazole (**6b**). White solid (53.7 mg, 68% yield); mp 288−289 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.64 (dd, J = 11.1, 4.3 Hz, 6H), 7.22 – 7.14 (m, 2H), 7.11 – 6.98 (m, 6H), 6.74 (dd, J = 8.2, 0.5 Hz, 2H), 2.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 149.6, 148.1, 137.9, 132.5, 130.4, 130.2, 129.5, 126.7, 126.2, 124.9, 124.2, 112.6, 110.5, 21.2; HRMS-ESI (m/z): calcd for $C_{32}H_{23}N_4S_2^+$ $[M + H]^+$ 527.1364, found 527.1362.

2,2'-bis(3-methoxyphenyl)-3,3'-bibenzo[d]imidazo[2,1-b]thiazole (**6c**). White solid (60.3 mg, 72%

yield); mp 271−272 °C (lit.[1] 260−262 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66 (d, J = 7.6 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.24 – 7.17 (m, 2H), 7.10 (m, 4H), 6.81 – 6.68 (m, 4H), 3.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.8, 149.7, 147.9, 134.4, 132.4, 130.2, 129.8, 126.8, 125.2, 124.3, 118.7, 115.0, 112.7, 111.1, 110.6, 55.0.

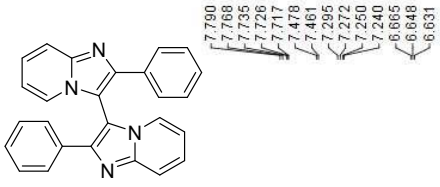
6,6'-diphenyl-5,5'-biimidazo[2,1-b]thiazole (**6d**). White solid (38.2 mg, 64% yield); mp 279−280 °C (lit.[1] 268−270 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.73 – 7.63 (m, 4H), 7.34 – 7.24 (m, 6H), 6.76 (d, J = 4.5 Hz, 2H), 6.67 (d, J = 4.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 150.8, 146.0, 133.6, 128.9, 127.9, 126.3, 118.1, 112.7, 110.9.

Reference

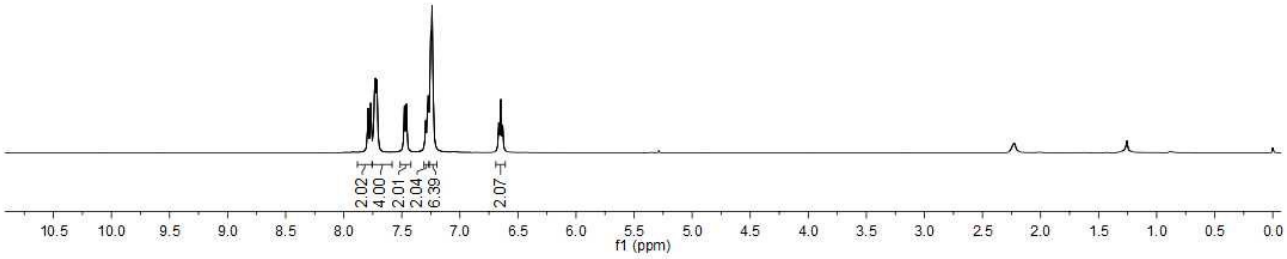
1. S. M. A. Shakoor, S. K. Mandal and R. Sakhuja, *Eur. J. Org. Chem.*, 2017, 2596–2602.

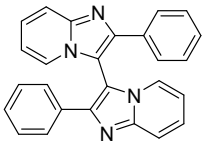
2. S. Lei, H. Cao, L. Chen, J. Liu, H. Cai and J. Tan, *Adv. Synth. Catal.* 2015, **357**, 3109 –3114.

3. NMR spectra for compounds 2, 4 and 6

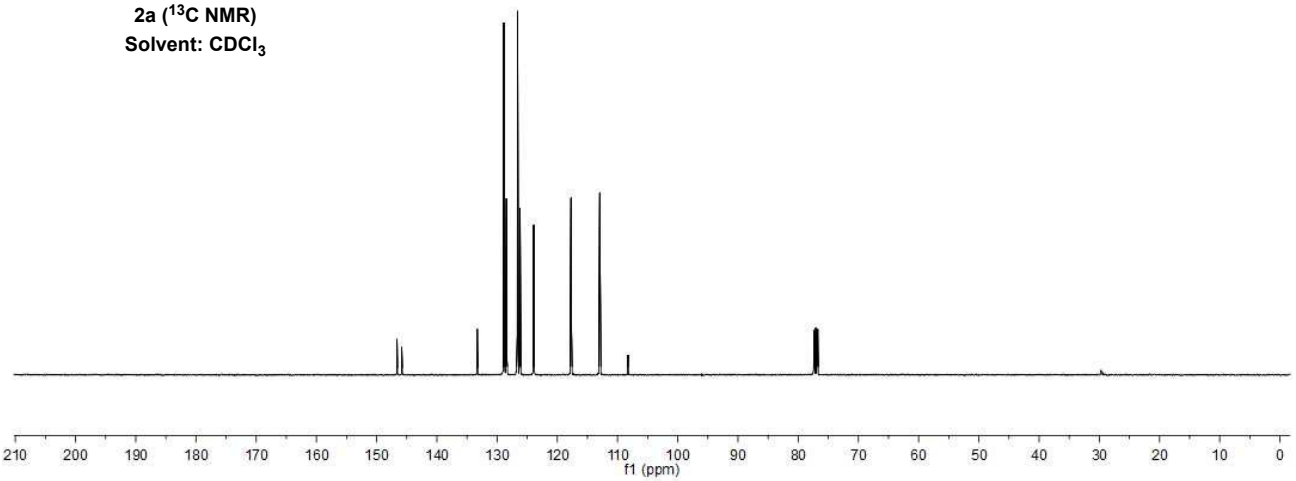


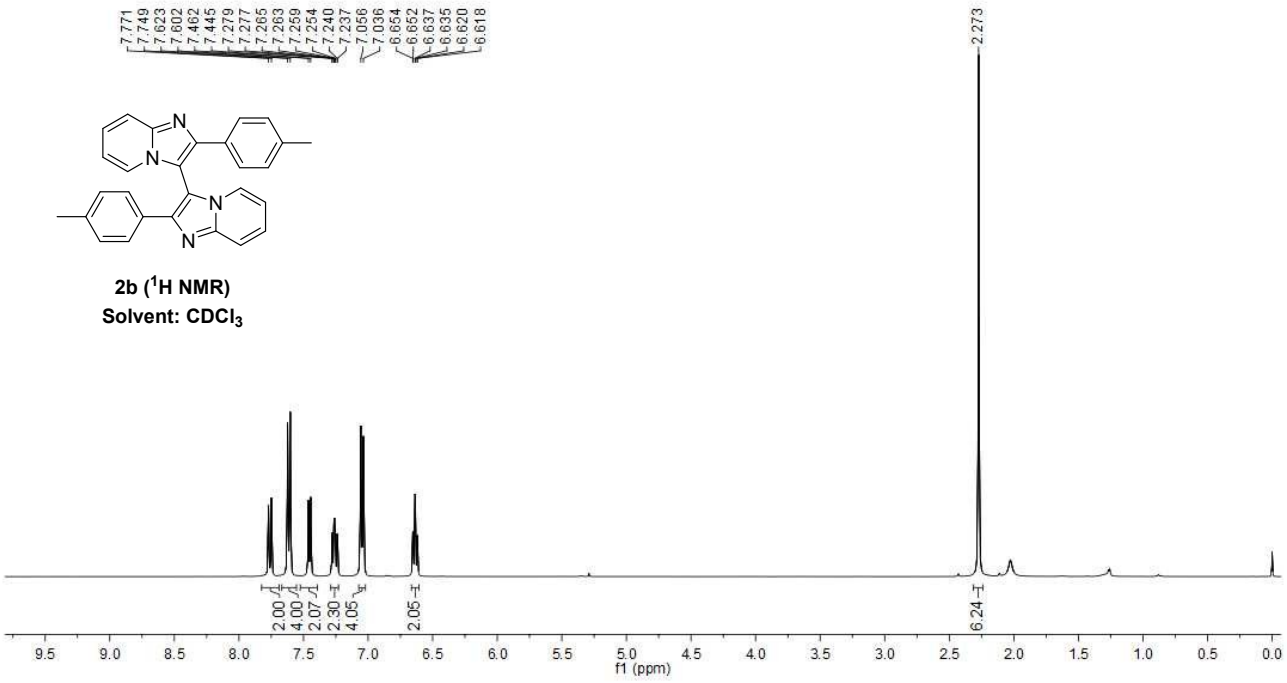
2a (^{1}H NMR)
Solvent: $CDCl_3$



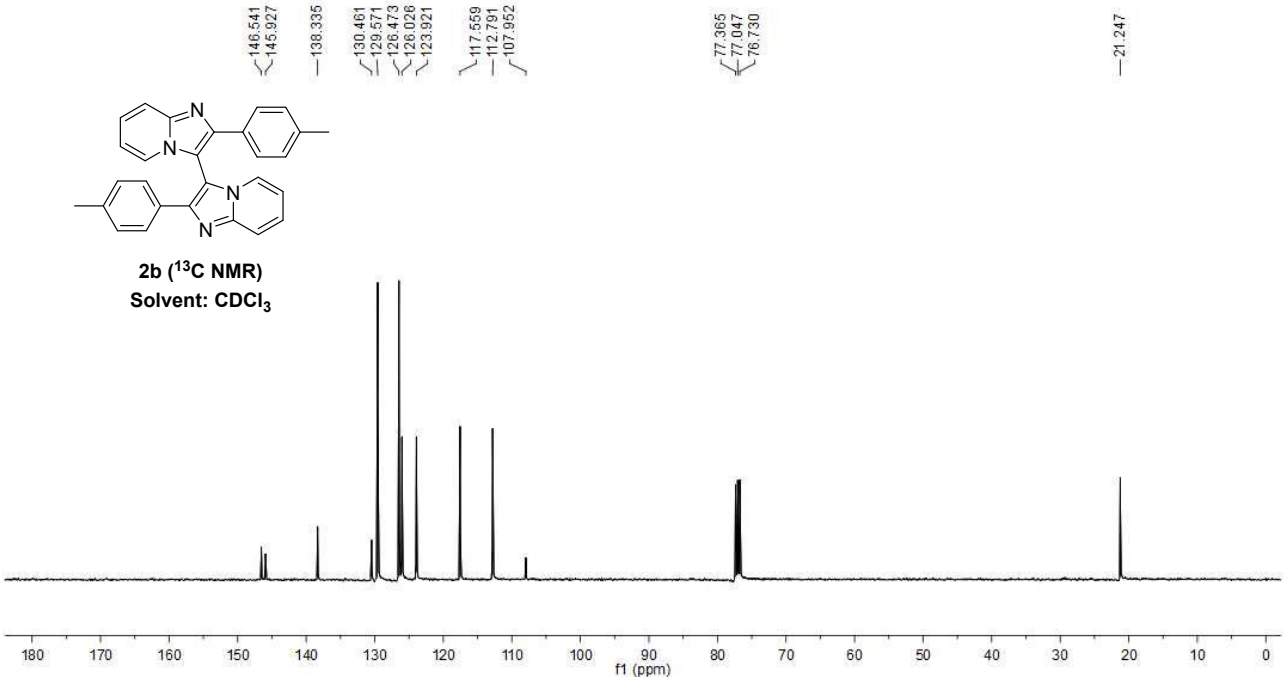


2a (^{13}C NMR)
Solvent: $CDCl_3$

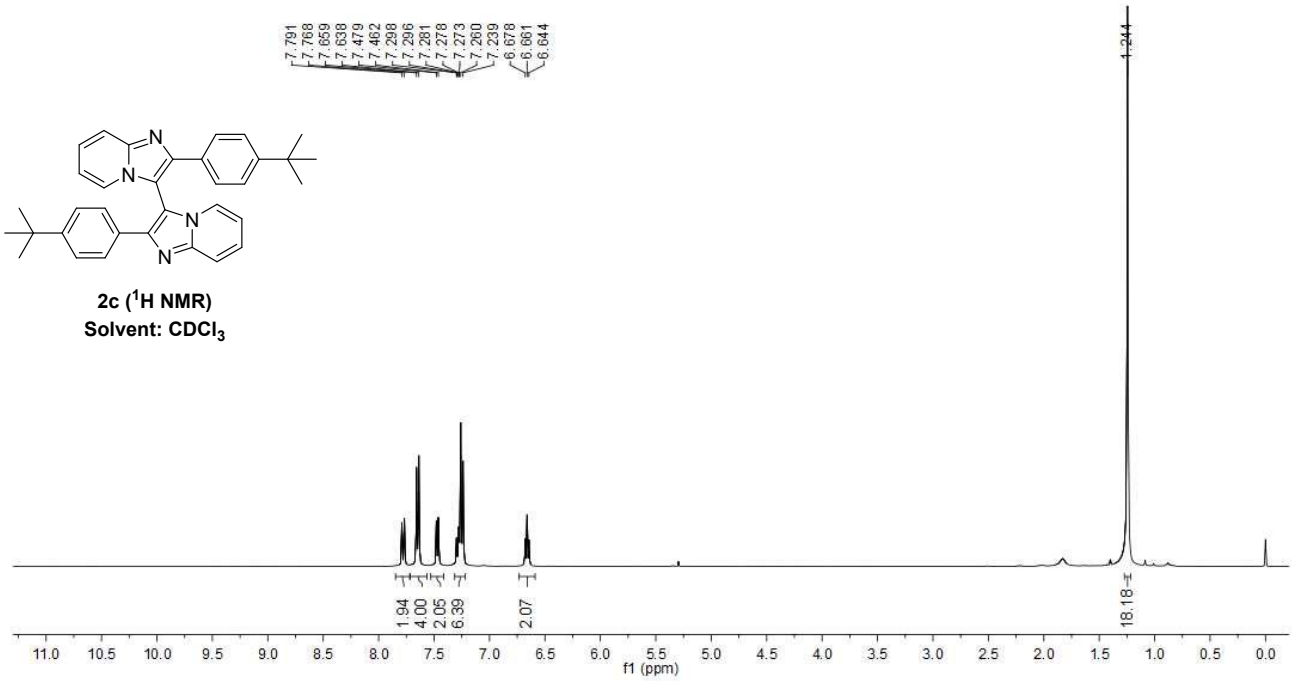




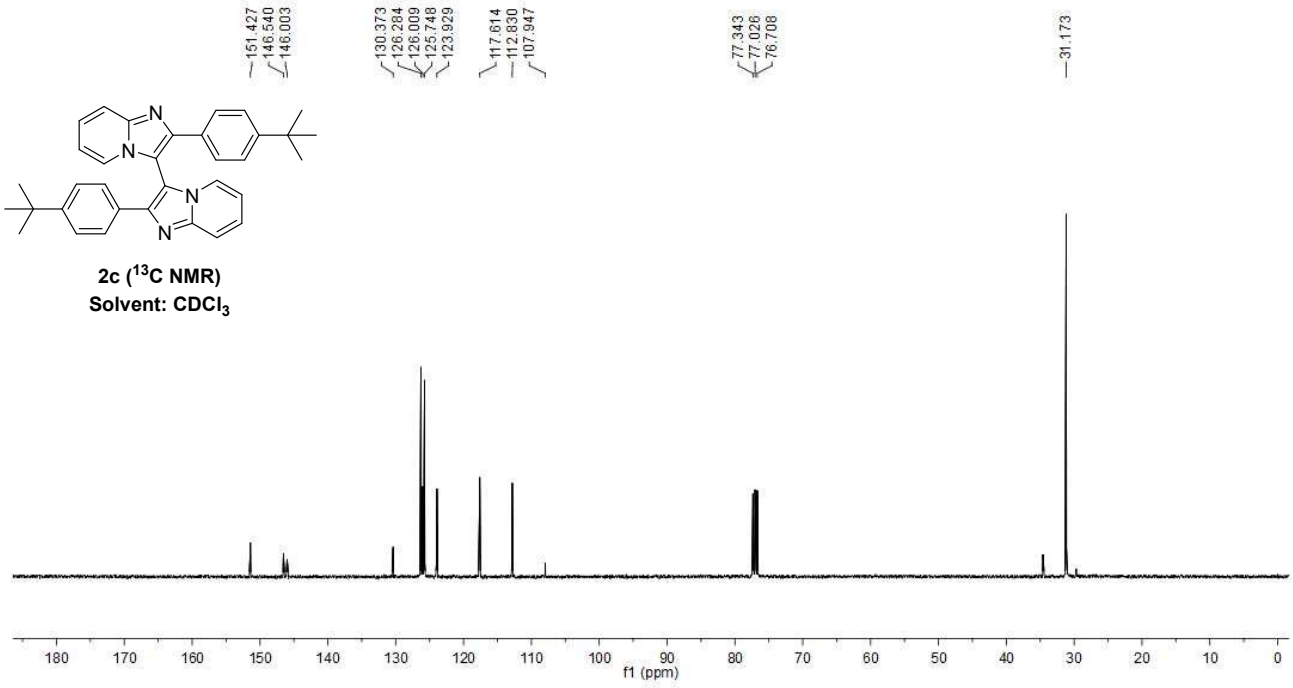
2b (^{1}H NMR)
Solvent: $CDCl_3$



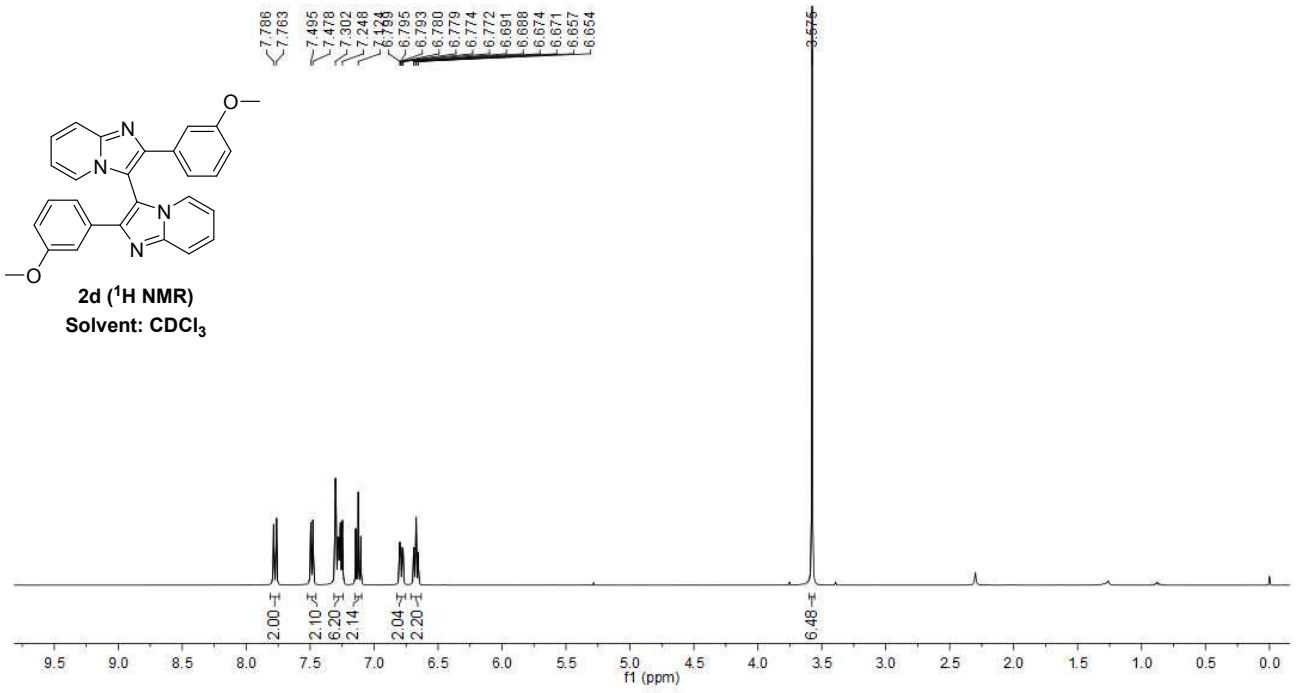
2b (^{13}C NMR)
Solvent: $CDCl_3$



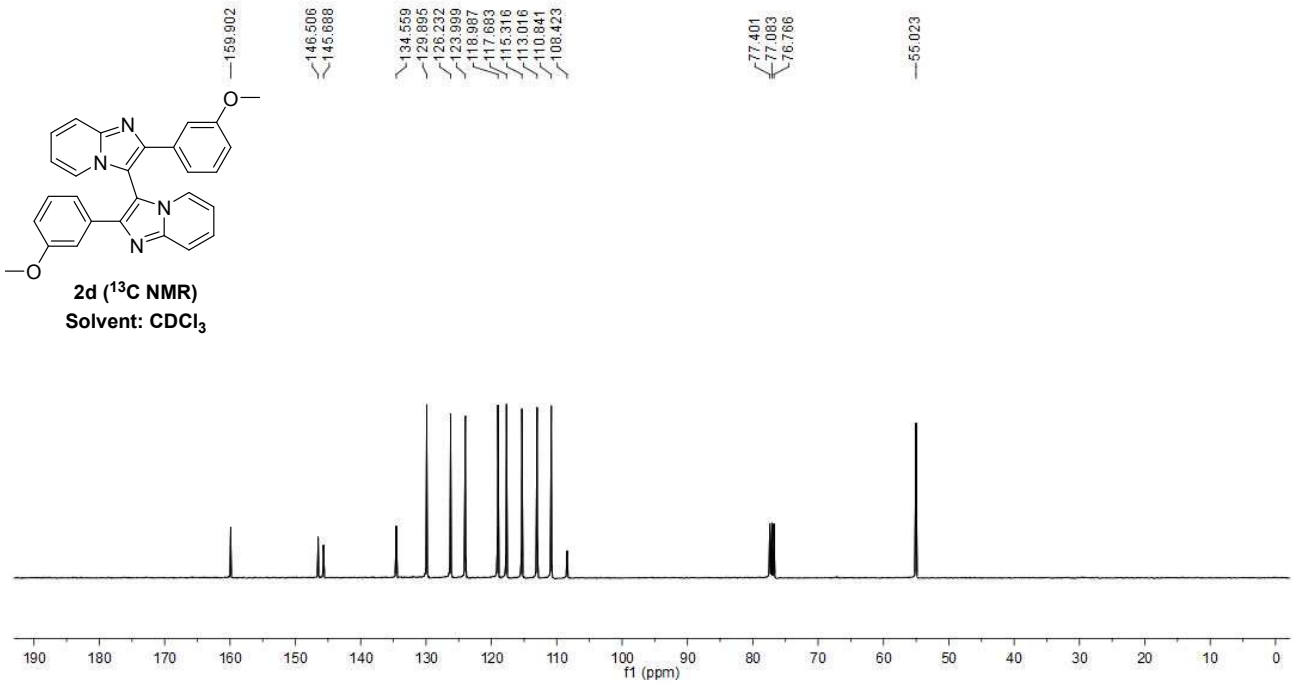
2c (^{1}H NMR)
Solvent: $CDCl_3$



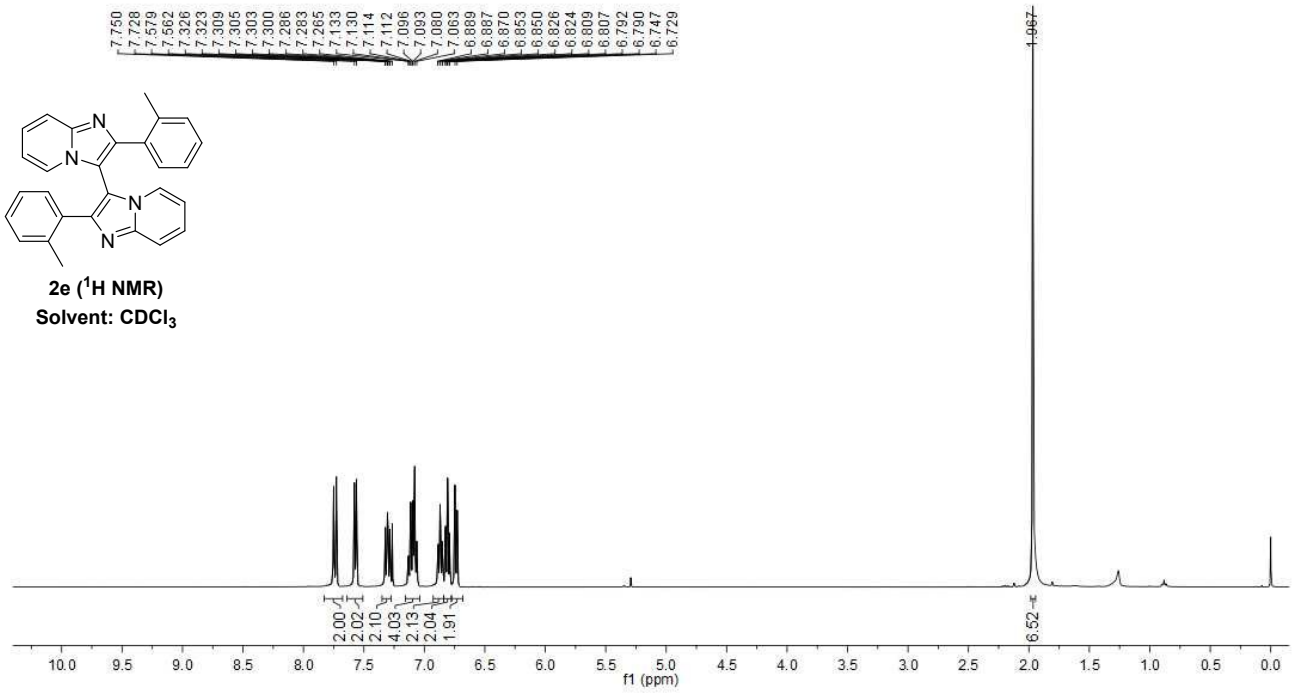
2c (^{13}C NMR)
Solvent: $CDCl_3$



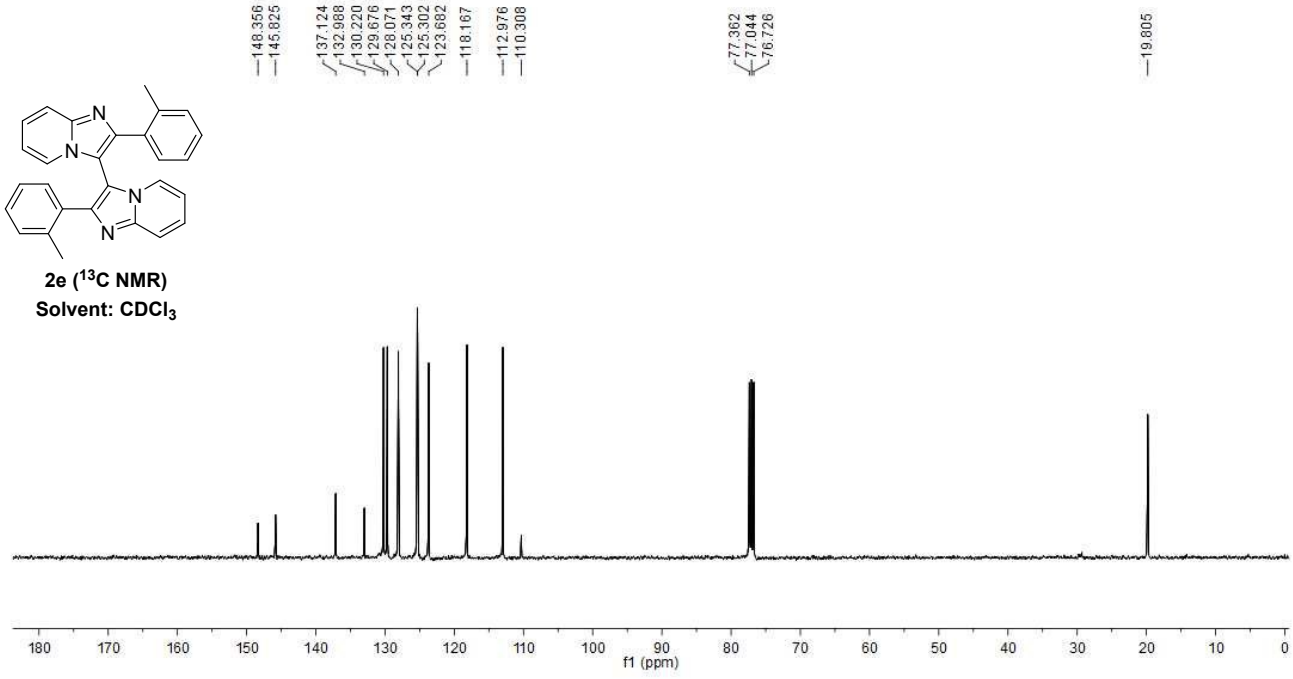
2d (^{1}H NMR)
Solvent: $CDCl_3$



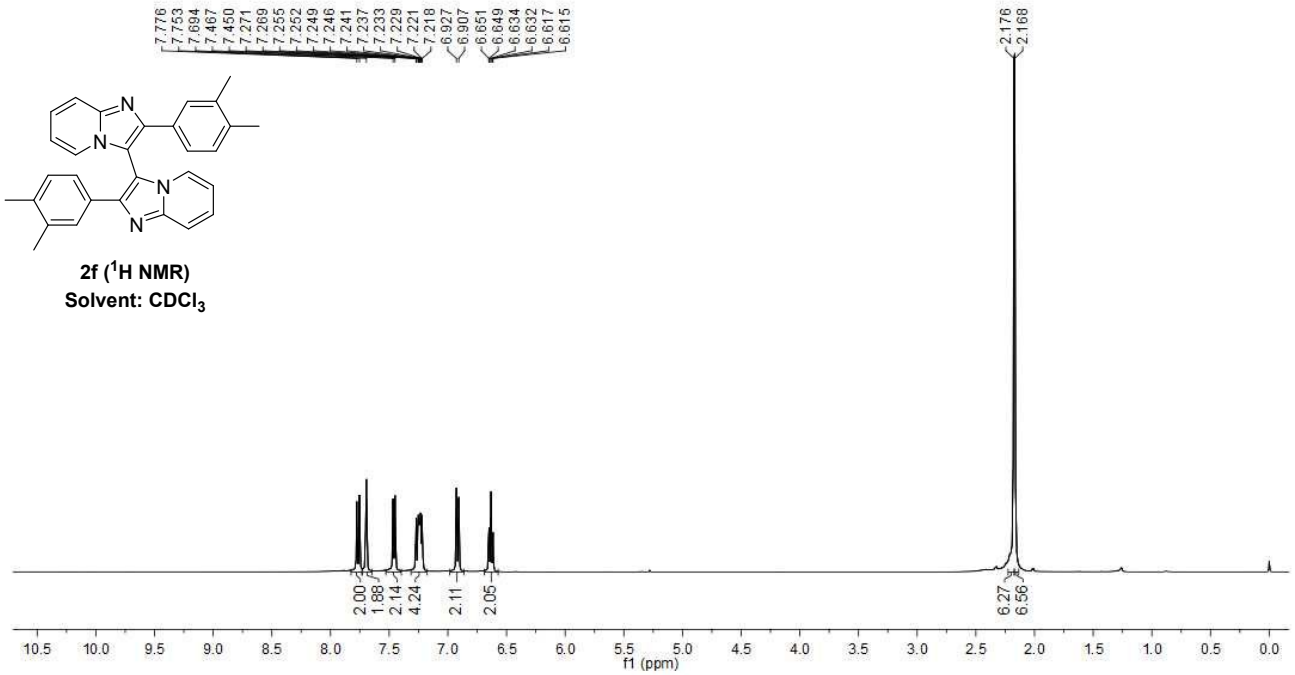
2d (^{13}C NMR)
Solvent: $CDCl_3$



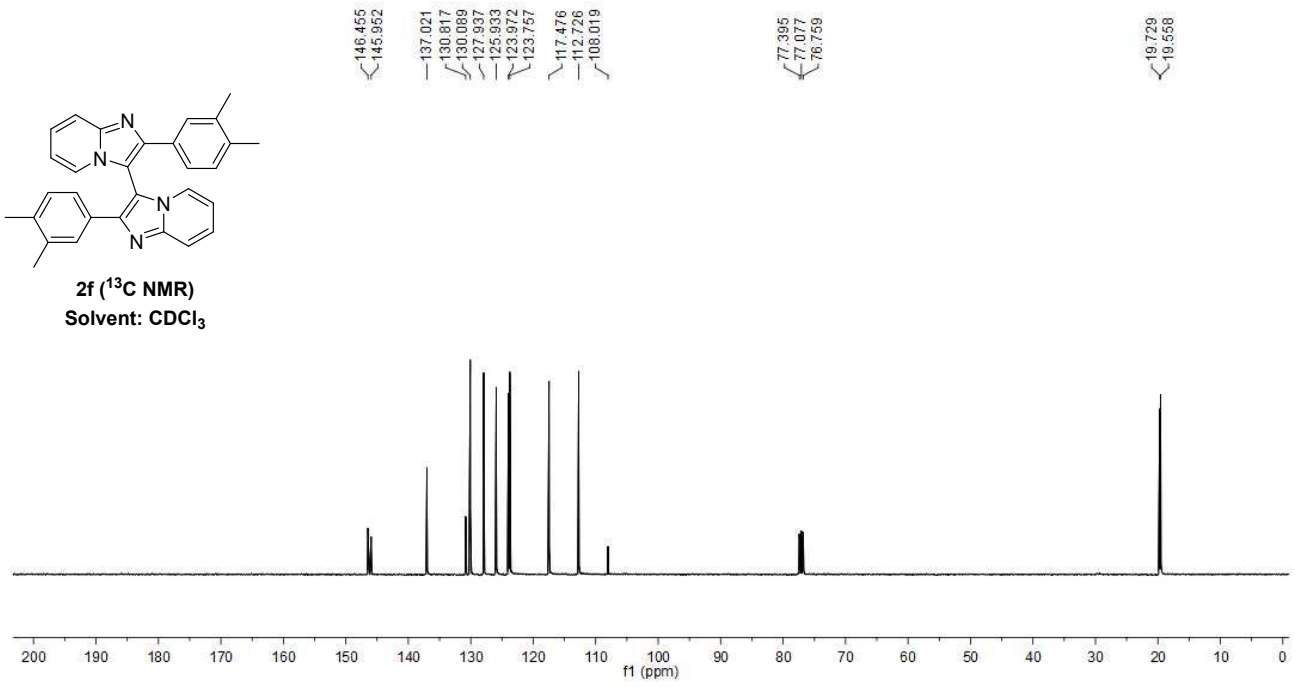
2e (^{1}H NMR)
Solvent: $CDCl_3$



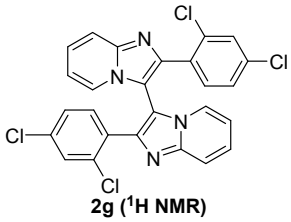
2e (^{13}C NMR)
Solvent: $CDCl_3$



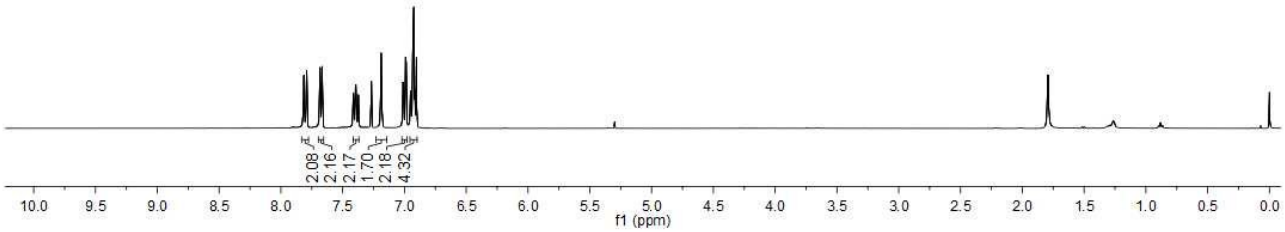
2f (^{1}H NMR)
Solvent: $CDCl_3$

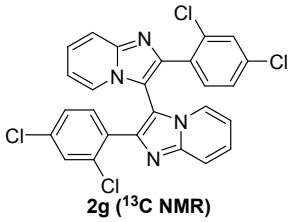


2f (^{13}C NMR)
Solvent: $CDCl_3$

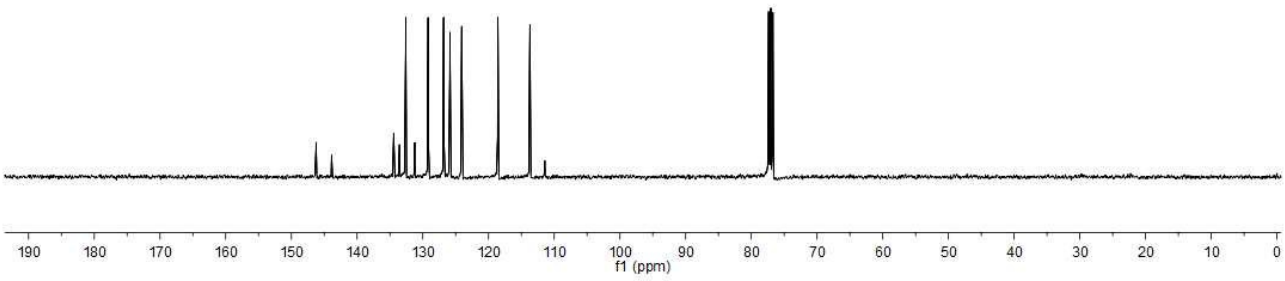


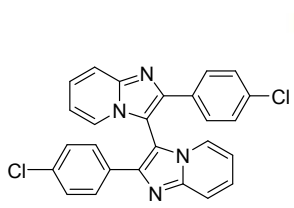
2g (^{1}H NMR)
Solvent: $CDCl_3$

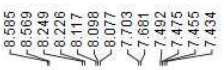




2g (^{13}C NMR)
Solvent: $CDCl_3$

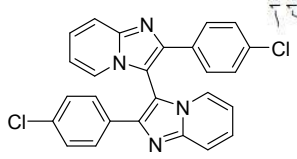


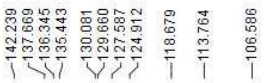




2h (^{1}H NMR)

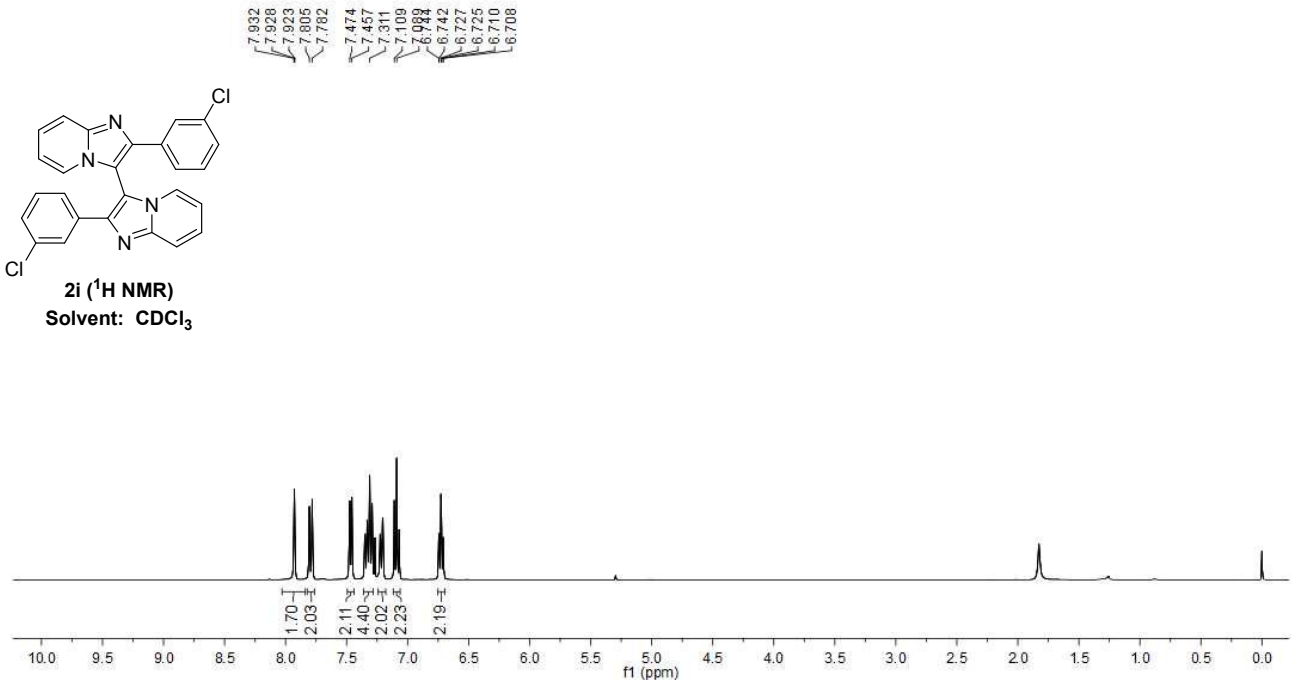
Solvent: DMSO-d_6 with a drop of *conc*. HCl



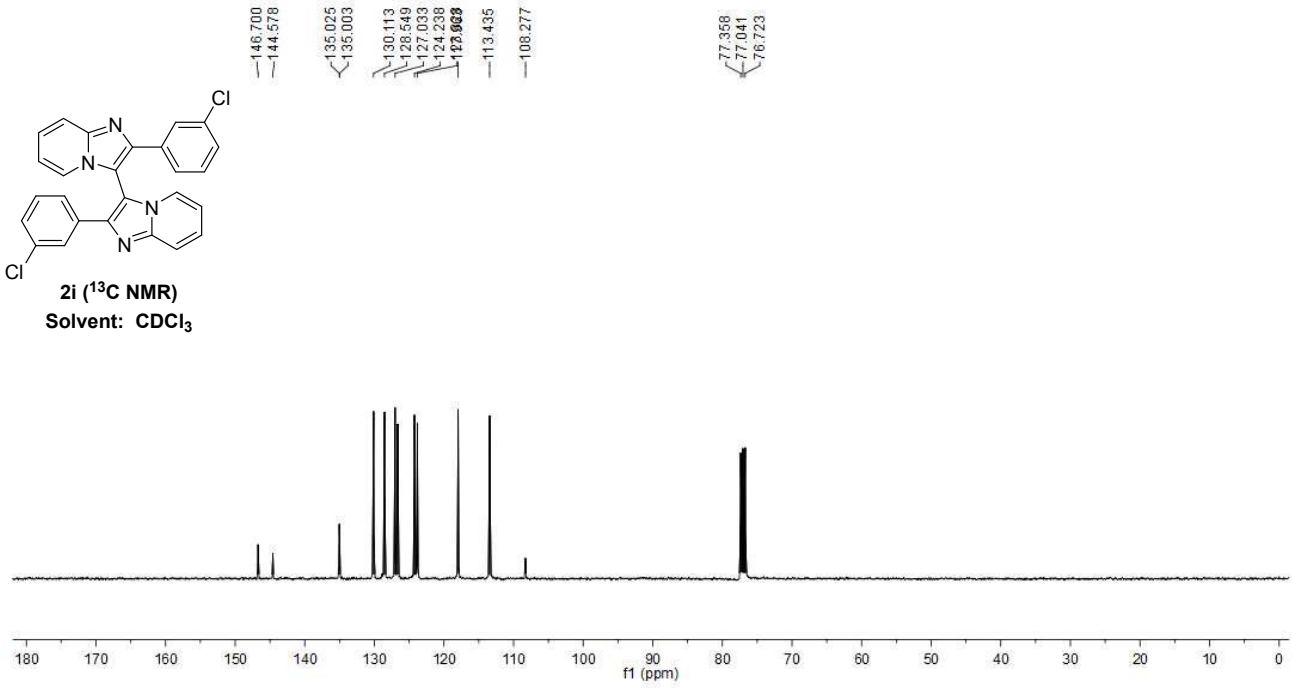


2h (^{13}C NMR)

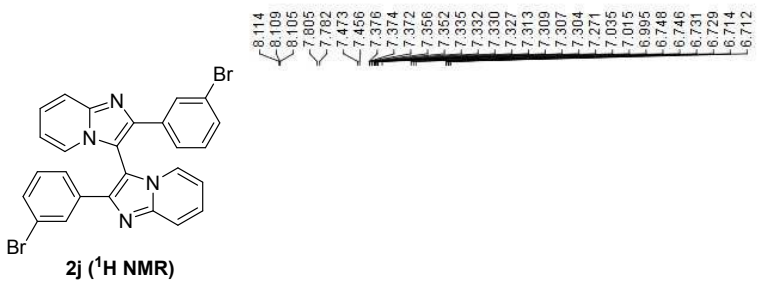
Solvent: DMSO-d_6 with a drop of *conc*. HCl



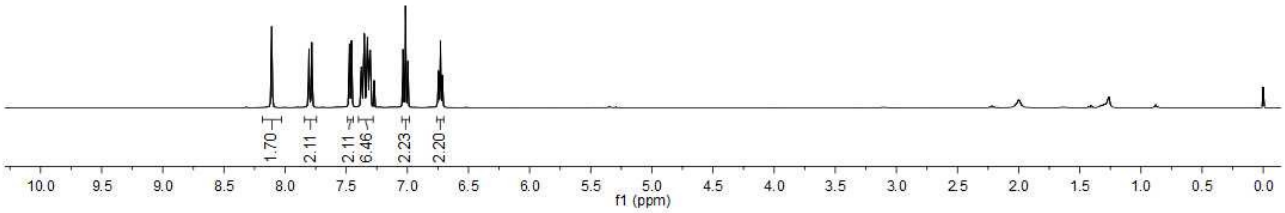
2i (^{1}H NMR)
Solvent: $CDCl_3$

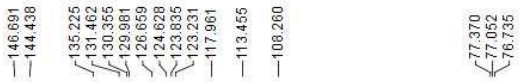


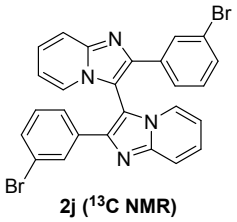
2i (^{13}C NMR)
Solvent: $CDCl_3$



2j (^{1}H NMR)
Solvent: $CDCl_3$







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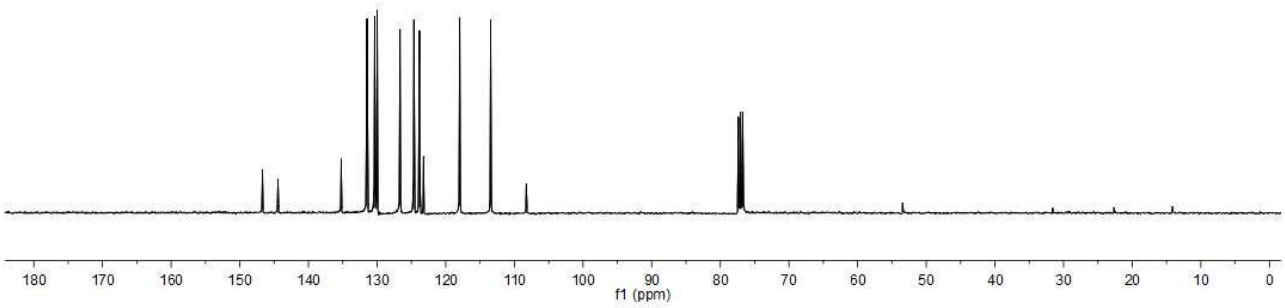
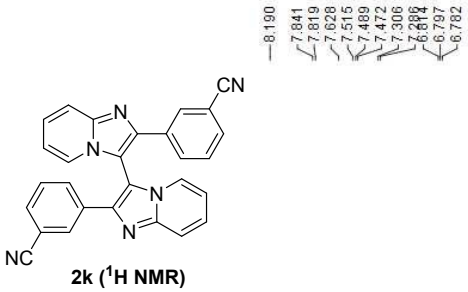
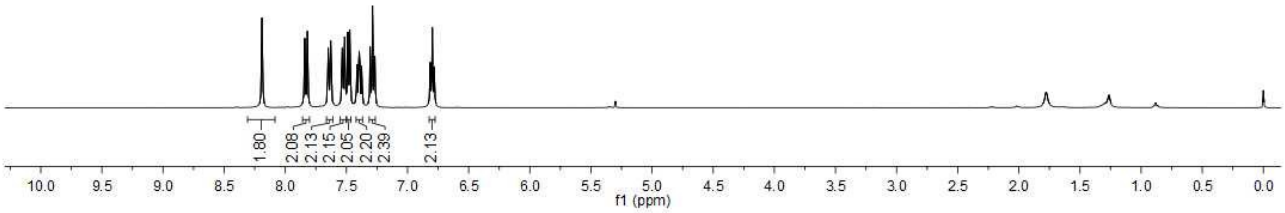
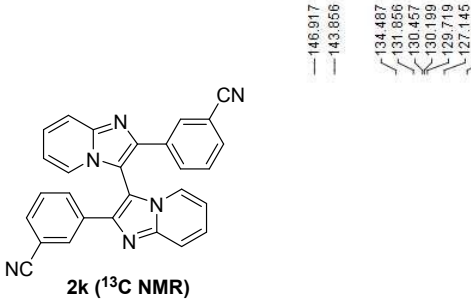
Solvent: $CDCl_3$



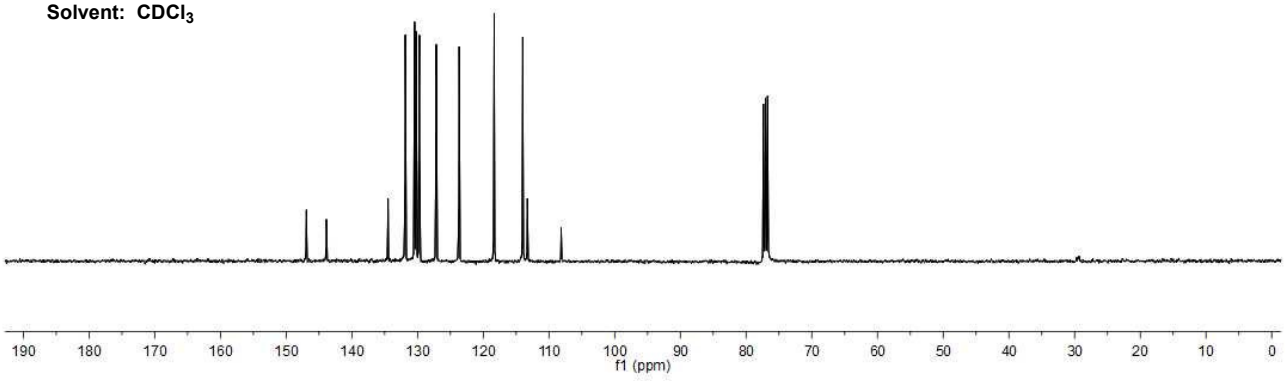


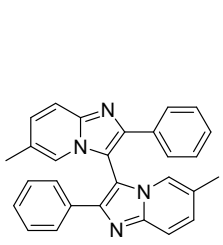
2k (^{1}H NMR)
Solvent: $CDCl_3$





2k (^{13}C NMR)
Solvent: $CDCl_3$





2l (^{1}H NMR)
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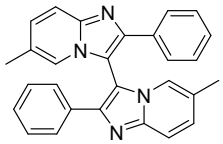

2l (^{13}C NMR)
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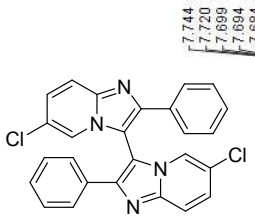

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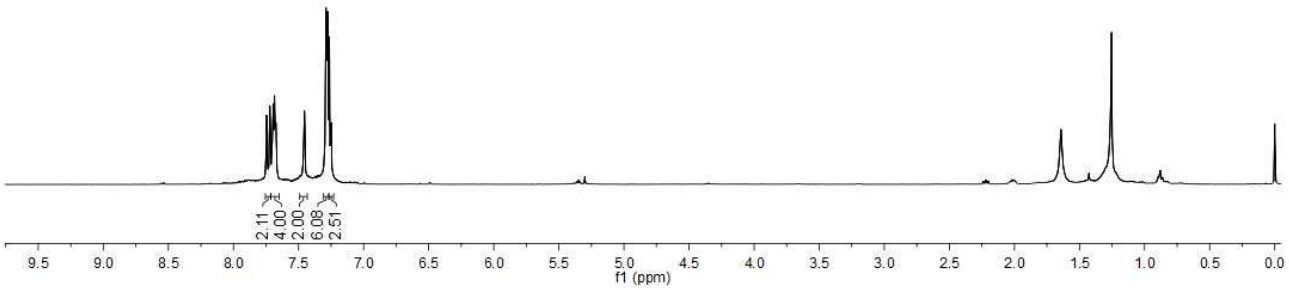

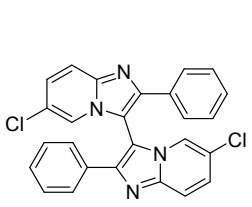

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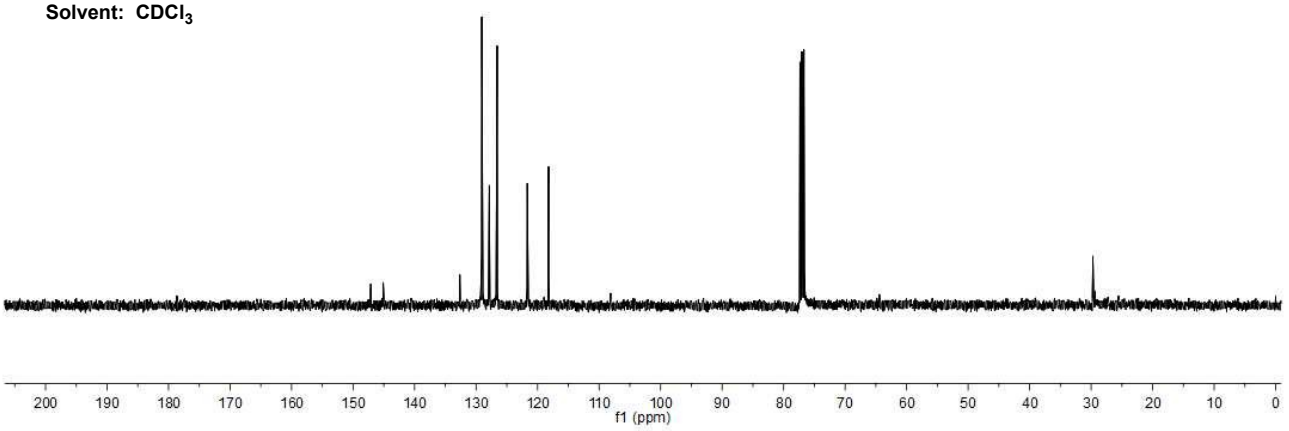
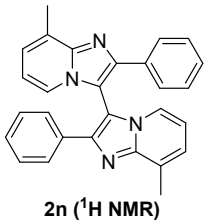
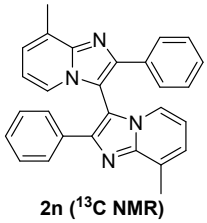
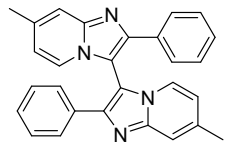




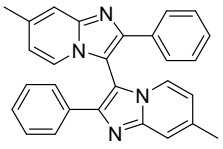
2n (^{1}H NMR)
Solvent: $CDCl_3$



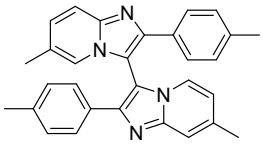
2n (^{13}C NMR)
Solvent: $CDCl_3$



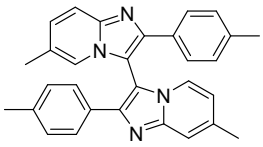
2o (^{1}H NMR)
Solvent: $CDCl_3$



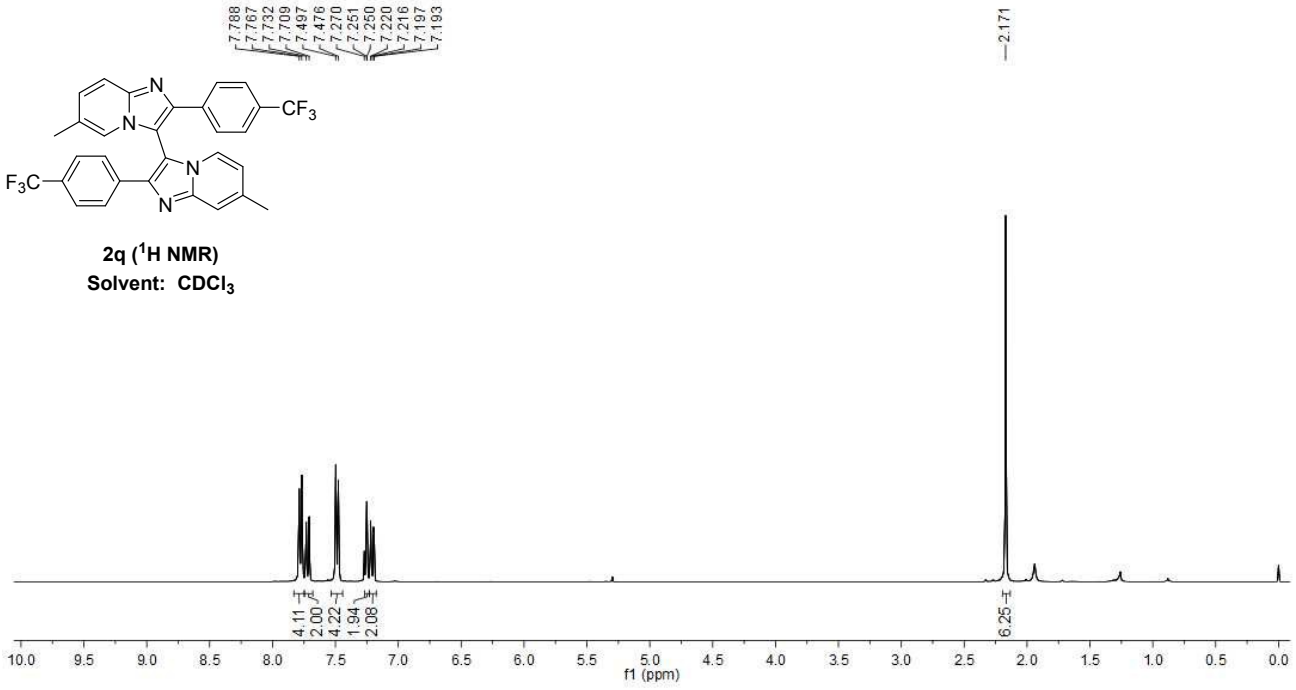
2o (^{13}C NMR)
Solvent: $CDCl_3$



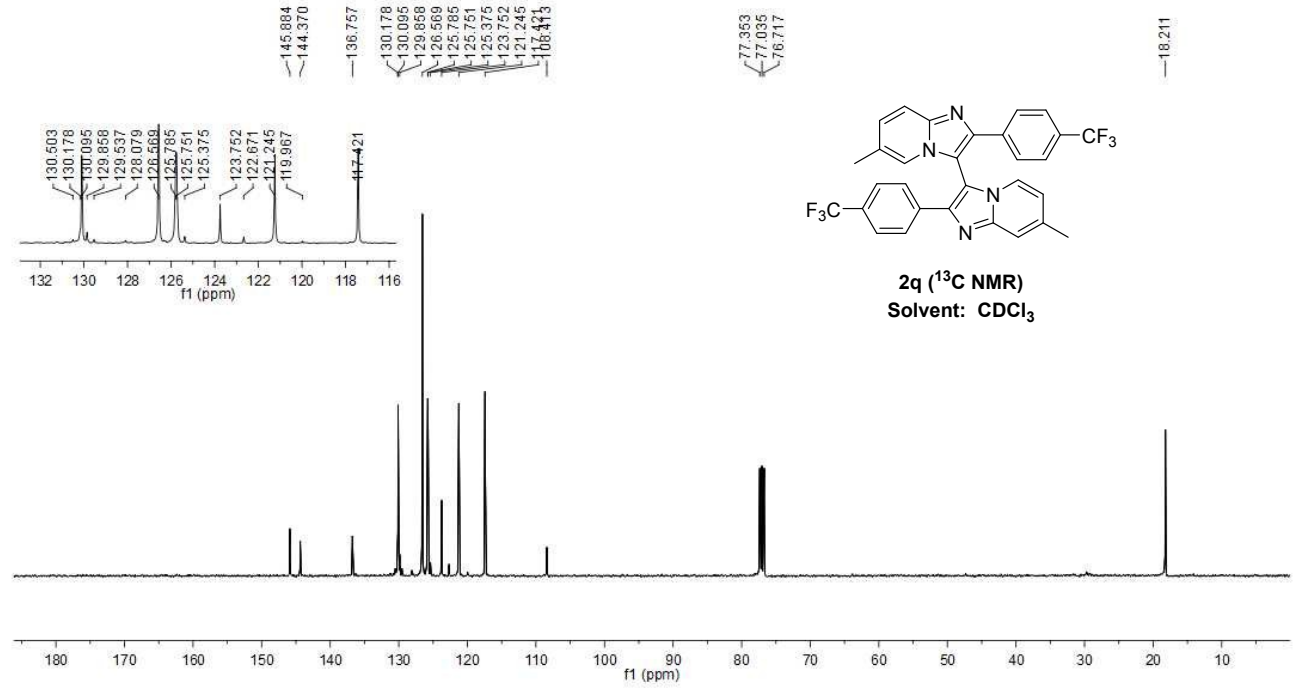
2p (^{1}H NMR)
Solvent: $CDCl_3$



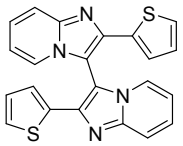
2p (^{13}C NMR)
Solvent: $CDCl_3$



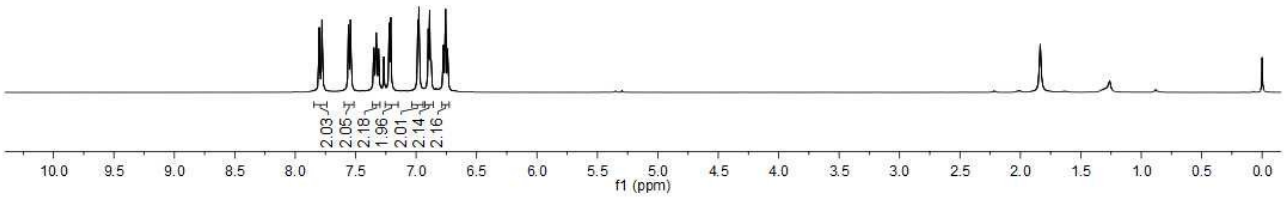
2q (^{1}H NMR)
Solvent: $CDCl_3$

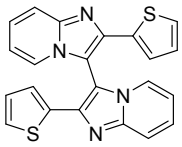


2q (^{13}C NMR)
Solvent: $CDCl_3$

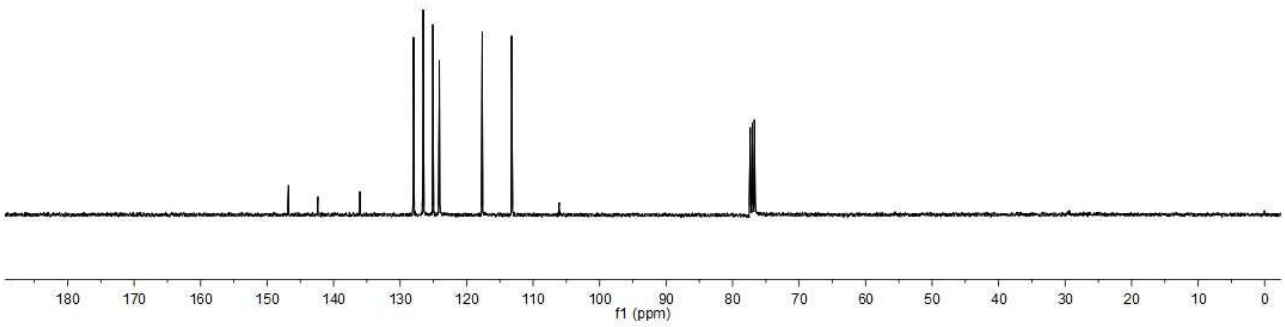


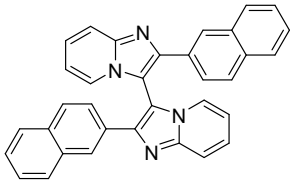
2r (^{1}H NMR)
Solvent: $CDCl_3$



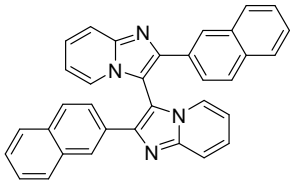


2r (^{13}C NMR)
Solvent: $CDCl_3$

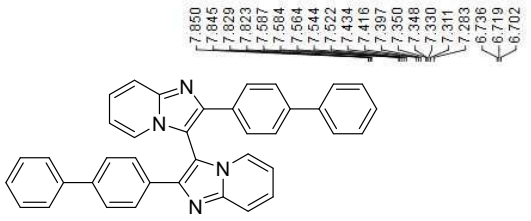




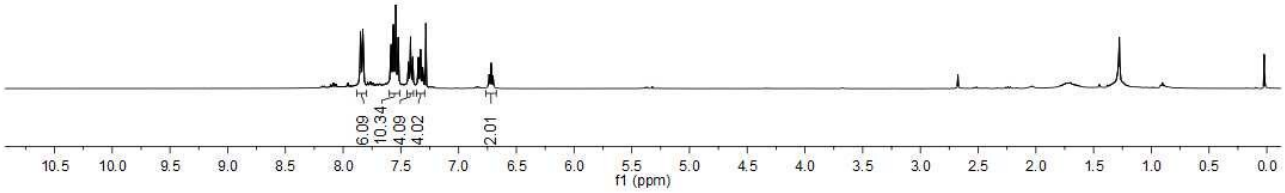
2s (^{1}H NMR)
Solvent: DMSO-d_6

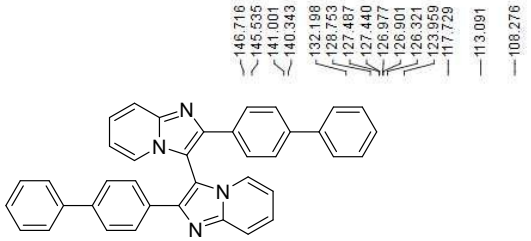


2s (^{13}C NMR)
Solvent: DMSO-d_6

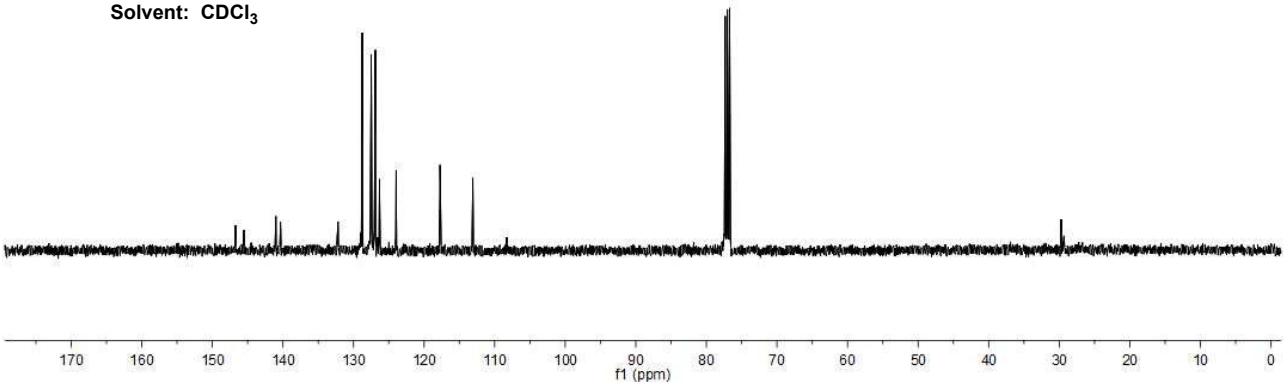


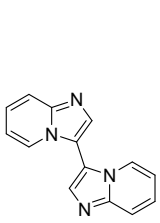
2t (^{1}H NMR)
Solvent: $CDCl_3$



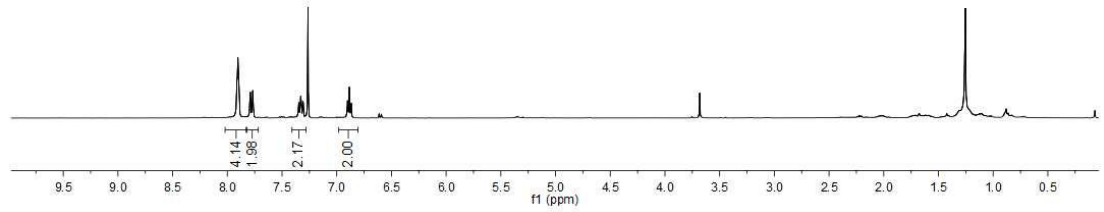


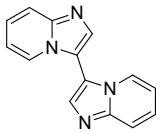
2t (^{13}C NMR)
Solvent: $CDCl_3$



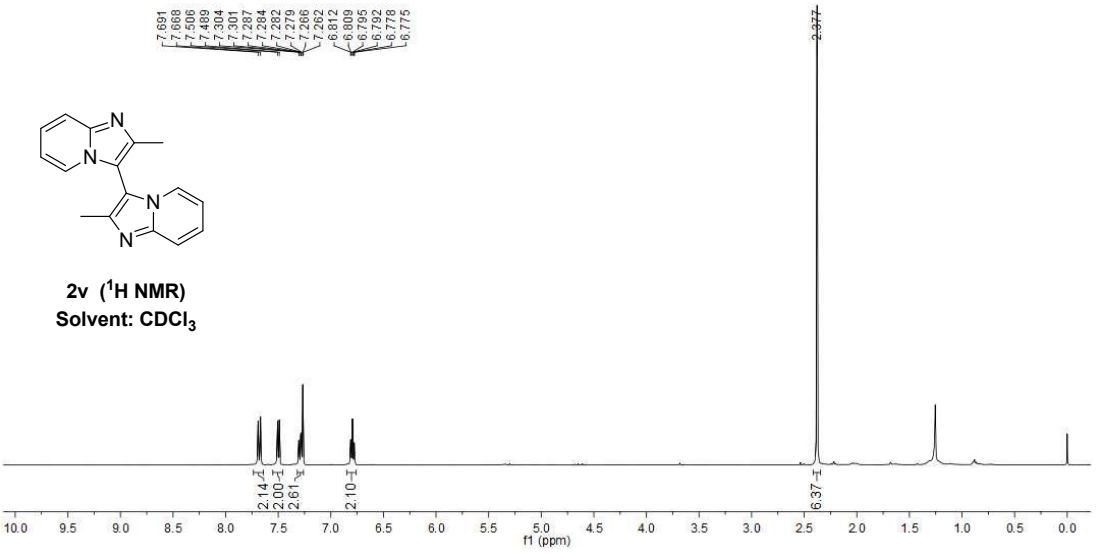


2u (^{1}H NMR)
Solvent: $CDCl_3$

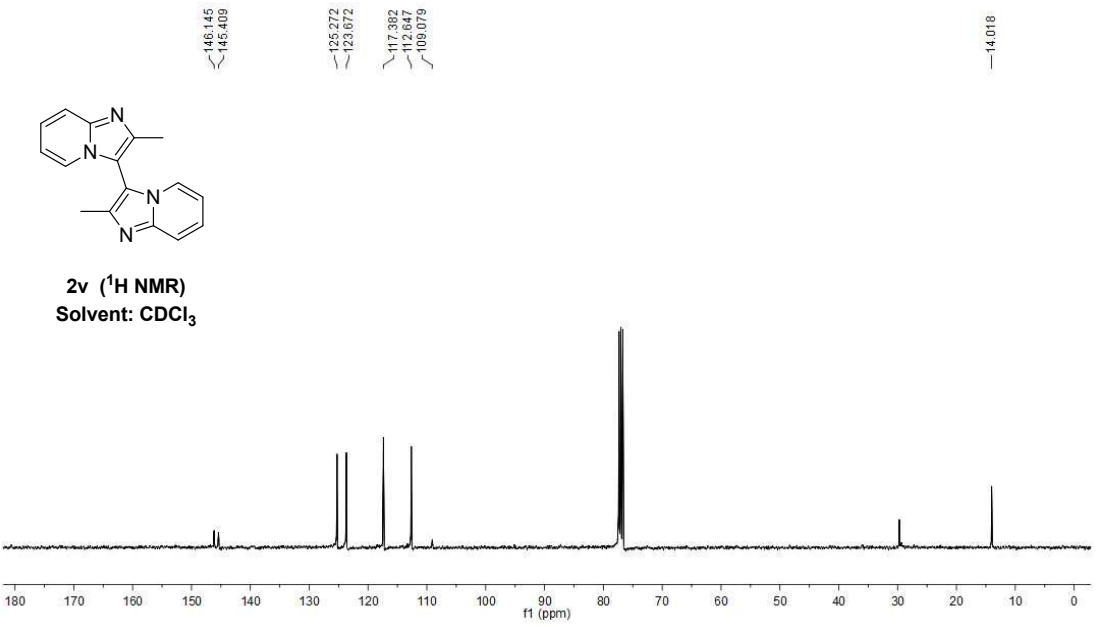




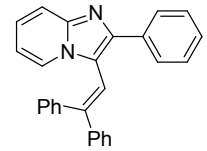
2u (^{1}H NMR)
Solvent: $CDCl_3$



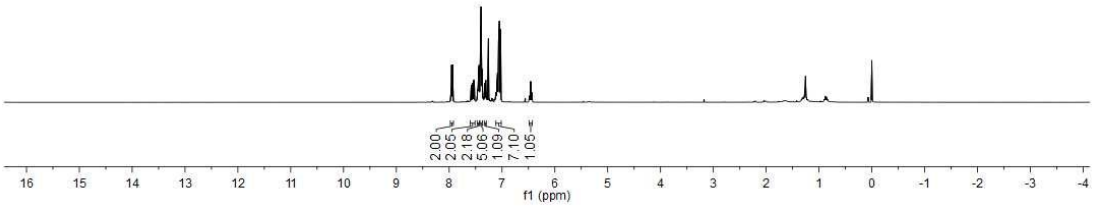
2v (^{1}H NMR)
Solvent: $CDCl_3$

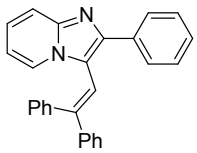


2v (^{1}H NMR)
Solvent: $CDCl_3$

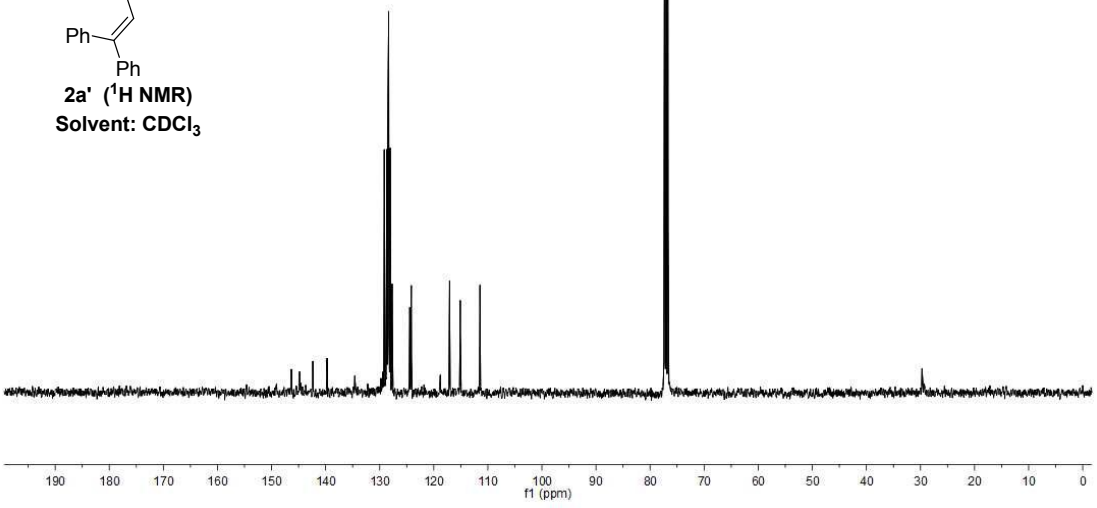


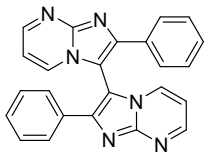
2a' (^{1}H NMR)
Solvent: $CDCl_3$



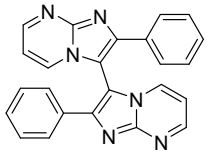


2a' (^{1}H NMR)
Solvent: $CDCl_3$

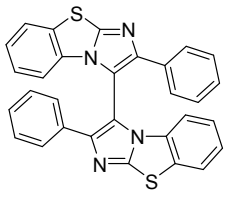




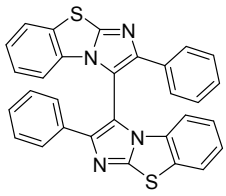
4a (^{1}H NMR)
Solvent: $CDCl_3$



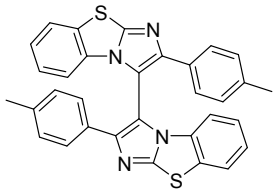
4a (^{13}C NMR)
Solvent: $CDCl_3$



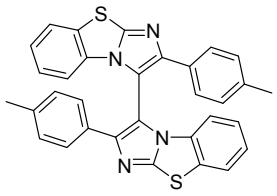
6a (^{1}H NMR)
Solvent: $CDCl_3$



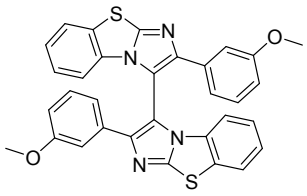
6a (^{13}C NMR)
Solvent: $CDCl_3$



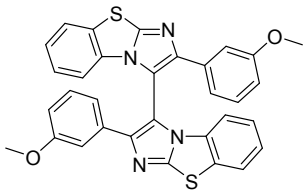
6b (^{1}H NMR)
Solvent: $CDCl_3$



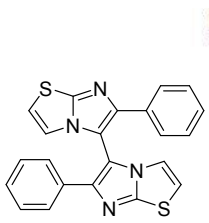
6b (^{13}C NMR)
Solvent: $CDCl_3$



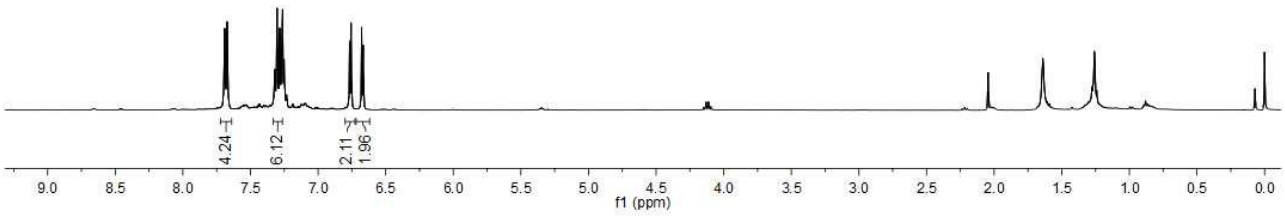
6c (^{1}H NMR)
Solvent: $CDCl_3$

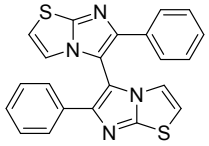


6c (^{13}C NMR)
Solvent: $CDCl_3$



6d (^{1}H NMR)
Solvent: $CDCl_3$





6d (^{13}C NMR)
Solvent: $CDCl_3$