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Annulation of Imidazo[1,2-a]pyridines Under Metal-free Conditions

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Experimental Section:

General: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C {H} NMR spectra were recorded at 600, 500, 150, and 125 MHz, respectively. The spectra were recorded in $CDCl_3$ as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^{1}H NMR (7.26), and ^{13}C {H} NMR (77.0) are deuterated solvent chloroform, [δ value around (1.5) in ^{1}H NMR is of water]. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent, unless otherwise indicated.

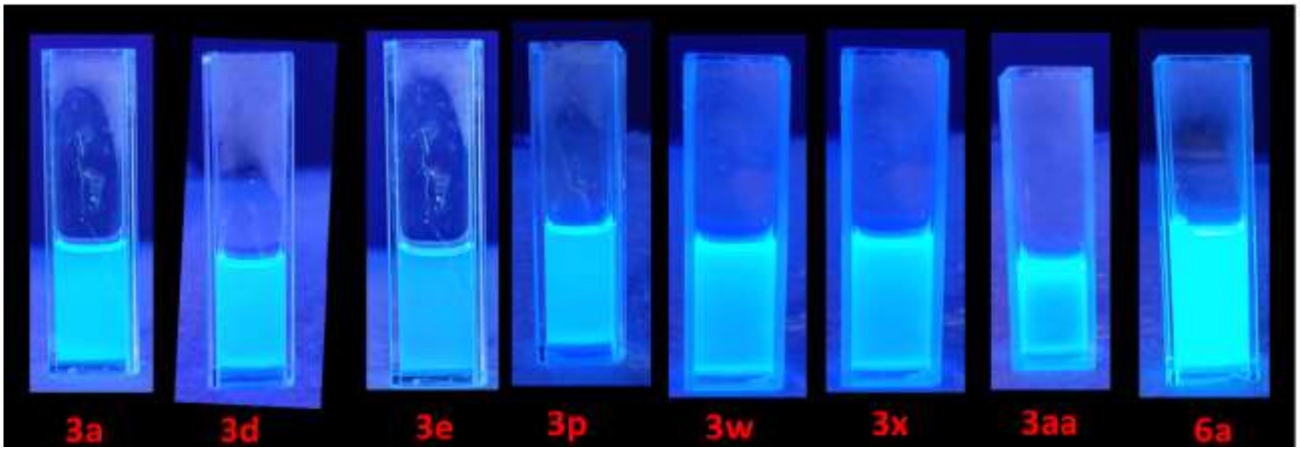
General procedure for the synthesis of 2-phenylimidazo[1,2-a]pyridine (1a)[1]:

470 mg (5.0 mmol) of 2-aminopyridine, 1200 mg (10 mmol) of acetophenone, CuI 5 mol% (47 mg; 0.25 mmol), $BF_3{\cdot}Et_2O$ (45–50% purity); 10 mol%, (0.5 mmol) and DMF (2 mL) were placed in a 25-mL double-necked round-bottomed flask. The mixture was heated in oil bath at 60 °C for 24 h under an oxygen atmosphere (balloon). After completion of the reaction, it was allowed to attain to room temperature and then the mixture was poured into 20 mL of sodium carbonate solution. The product was extracted with DCM (50 mL X 3) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and the left residue that was purified through column chromatography using silica gel (30% EtOAc/hexane) to afford **1a**; yield: 0.799 g (82%) experimental data also matched with reported literature the same method was applied for all the reported starting substrates (1,6 and their derivatives).[1]

General procedure for the synthesis of 1-phenylbenzo[a]imidazo[5,1,2-cd]indolizine (3a): To a reaction tube equipped with a magnetic stir bar, added 2-phenylimidazo[1,2-a]pyridine (**1a**) (39 mg, 0.20 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (119 mg, 0.40 mmol), potassium carbonate (55 mg, 0.40 mmol) and 18-Crown-6 (105 mg, 0.40 mmol) in 2.0 mL of acetone. The mixture was heated in an oil bath at 45 °C in a closed tube. Reaction was monitored by TLC, after completion of the reaction; it was allowed to attain room temperature. Acetone solvent of the reaction mixture is removed under vacuumed in rotatory evaporator. Then the mixture was poured into 20 mL of water and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under vacuum. The crude residue was purified by silica gel column chromatography using 20 % EtOAc/hexane to afford **3a** (50.92 mg; 95 % yield).

General procedure for the synthesis of 1-phenyl-2,2a1,3-triazacyclopenta[jk]fluorene (6a): To a reaction tube equipped with a magnetic stir bar, added 2-phenylimidazo[1,2-a]pyrimidine (**1a**) (39 mg, 0.20 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (119 mg, 0.40 mmol), potassium carbonate (55 mg, 0.40 mmol) and 18-Crown-6 (105 mg, 0.40 mmol) in 2.0 mL of acetone. The mixture was heated in an oil bath at 45 ^{o} C in a closed tube. Reaction was monitored by TLC, after completion of the reaction; it was allowed to attain room temperature. Acetone solvent of the reaction mixture is removed under vacuum in rotatory evaporator at low temperature. Then the mixture was poured into 20 mL of water and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under vacuum. The crude residue was purified by silica gel column chromatography using 40 % EtOAc/hexane to afford **6a** (37.6 mg; 70 % yield).

General procedure for the synthesis of 7H-benzo[kl]acridine (7): To a reaction tube equipped with a magnetic stir bar, added naphthalen-1-amine (**1a**) (28.6 mg, 0.20 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) (119 mg, 0.40 mmol), potassium carbonate (55 mg, 0.40 mmol) and 18-Crown-6 (105 mg, 0.40 mmol) in 2.0 mL of acetone. The mixture was heated in an oil bath at 45 ^{o} C in a closed tube. Reaction was monitored by TLC, after completion of the reaction; it was allowed to attain room temperature. Acetone solvent of the reaction mixture is removed under vacuum in rotatory evaporator at low temperature. Then the mixture was poured into 20 mL of water and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under vacuum at low temperature. The crude residue was purified by silica gel column chromatography using 5 % EtOAc/hexane to afford **7** (26.0 mg; 60 % yield).



Digital photograph of the fluorescent imidazopyridines in DCM under UV light

Table xx. Spectral properties of selected imidazopyridines in Ethanol at RT (10 μM solution):

Comp	$\lambda_{abs(max)}$ nm	$\lambda_{ex(max)}$ nm	$\lambda_{em(max)}$ nm	Δ_{stokes} nm	ϕ_f
3a	397	390	453	56	0.60
3d	396	390	450	54	0.68
3e	407	405	466	59	0.33
3p	403	400	461	58	0.41
3w	401	400	458	57	0.34
3x	395	390	453	58	0.53
3aa	399	390	455	56	0.67
6a	421	420	456	35	0.48

Quantum yield calculations:

For the calculation of fluorescence quantum yield an optically identical solution of Anthracene (Φ_f = 0.27 in ethanol) was used as standard at an excitation wavelength of 390 nm and the quantum yield was calculated using the following equation.

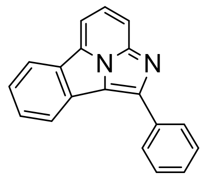
$$\Phi_{unk} = \Phi_{std} \times \frac{(F_{unk}/A_{unk})}{(F_{std}/A_{std})}\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$

Where Φ_{unk} and Φ_{std} are the radiative quantum yields of the sample and standard, respectively. A_{unk} and A_{std} are the absorbances of the sample and standard at the excitation wavelength, respectively and η_{unk} and η_{std} are the indices of refraction of the sample and standard solutions, respectively.

F_{unk} and F_{std} are the integrated emission intensities of the corrected spectra for the sample and standard, respectively.

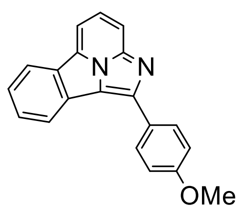
Characterization data :

1-phenylbenzo[a]imidazo[5,1,2-cd]indolizine (3a):[2]



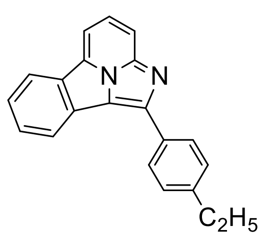
(Eluent: 20% EtOAc/hexane); 95% yield (50.9 mg); brown solid, Mp: 114-116 ^{0}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, J = 11.9, 4.7 Hz, 3H), 8.29 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H), 7.88 (dd, J = 8.2, 7.4 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.63 (dd, J = 10.8, 4.7 Hz, 2H), 7.57 – 7.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 139.5, 134.5, 131.2, 130.3, 129.0, 128.9, 128.3, 126.3, 124.7, 123.0, 120.7, 113.1, 108.6. ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 139.5, 134.5, 131.2, 130.3, 129.0, 128.3, 126.3, 124.7, 123.0, 120.7, 113.1, 108.6.

1-(4-methoxyphenyl)benzo[a]imidazo[5,1,2-cd]indolizine(3b): [3]



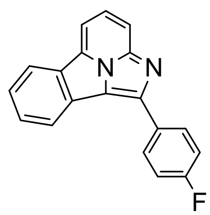
(Eluent: 20% EtOAc/hexane); 72% yield (42.9 mg); yellow solid, Mp:164-166 ^{0}C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.1 Hz, 1H), 8.36 – 8.30 (m, 3H), 7.99 (dd, J = 20.1, 7.8 Hz, 2H), 7.89 (t, J = 7.8 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.7 Hz, 2H), 3.93 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 146.5, 139.5, 131.0, 130.0, 129.6, 128.8, 127.2, 126.1, 124.4, 123.0, 120.5, 120.1, 114.4, 112.6, 108.3, 55.4.

1-(4-ethylphenyl)benzo[a]imidazo[5,1,2-cd]indolizine (3c):



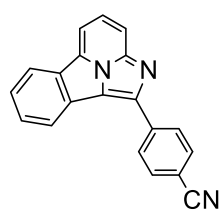
(Eluent: 15% EtOAc/hexane); 81% yield (47.9 mg); gummy liquid,; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H), 8.32 (d, J = 7.7 Hz, 2H), 8.06 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.92 (t, J = 7.9 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.6 Hz, 2H), 2.79 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 145.4, 139.5, 131.9, 131.2, 130.2, 129.0, 128.6, 128.3, 126.3, 124.6, 123.0, 120.8, 112.9, 108.5, 28.8, 15.4. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{21}H_{16}N_2Na$: 319.1211; Found: 319.1220.

1-(4-fluorophenyl)benzo[a]imidazo[5,1,2-cd]indolizine (3d): [2]



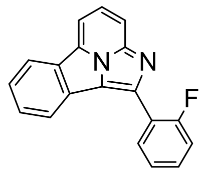
(Eluent: 15% EtOAc/hexane); 69% yield (39.4 mg); yellow solid, Mp: 130-132 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.21 (m, 4H), 7.98 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 14.9, 6.3 Hz, 2H). ^{13}C NMR (125 M Hz, $CDCl_3$) δ 163.2 (d, J_{C-F}= 249.4 Hz), 145.2, 139.3, 131.1, 130.7, 130.2, 129.9(d, J_{C-F}= 8.0 Hz), 129.0, 128.6, 126.4, 124.7, 123.0, 120.4, 116.0 (d, J_{C-F}= 21.6 Hz), 112.9, 108.5.

4-(benzo[a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3e):



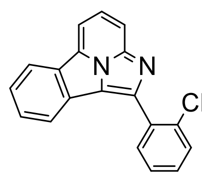
Eluent: 40% EtOAc/hexane); 82% yield (48.0 mg); yellow solid, Mp:228-230 ^{0}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J = 8.1 Hz, 2H), 8.37 (d, J = 7.9 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 12.0, 7.8 Hz, 2H), 7.99 – 7.92 (m, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 139.5, 138.9, 132.7, 131.6, 130.7, 129.4, 128.4, 127.2, 125.4, 123.3, 121.6, 120.8, 118.8, 113.8, 111.9, 109.2. HRMS-ESI (m/z) $[M+H]^+$ calcd. For $C_{20}H_{12}N_3$: 294.1031; Found: 294.1058.

1-(2-fluorophenyl)benzo[a]imidazo[5,1,2-cd]indolizine (3f):



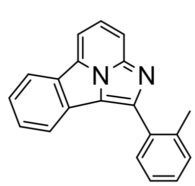
(Eluent: 10% EtOAc/hexane); 70% yield (40.0 mg); yellow solid, Mp:150-152 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 7.9 Hz, 1H), 8.31 (ddd, J = 10.5, 6.1, 2.2 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.95 (dd, J = 8.3, 7.3 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.63 – 7.57 (m, 1H), 7.53 – 7.46 (m, 1H), 7.37 (dddd, J = 11.7, 9.3, 7.9, 1.1 Hz,1 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0 (d, J_{C-F}= 248.5 Hz), 139.2(d, J= 41.7 Hz), 131.5, 130.7, 130.5(d, J=8.0Hz), 129.5, 129.1, 126.5, 124.8, 122.8, 122.7, 122.5, 122.4, 116.0 (J= 21.6 Hz), 113.3, 108.6. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{19}H_{11}FN_2Na$: 309.0804; Found: 309.0778.

1-(2-chlorophenyl)benzo[a]imidazo[5,1,2-cd]indolizine (3g) :



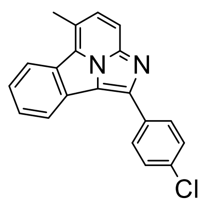
(Eluent: 15% EtOAc/hexane); 66% yield (39.8 mg); yellow solid, Mp:170-172 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.1 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.97 (t, J = 7.7 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.53 – 7.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 139.1, 133.9, 132.8, 131.5, 130.7, 130.0, 129.9, 129.2, 128.9, 127.0, 126.4, 124.8, 122.7, 113.7, 108.9. HRMS-ESI (m/z) $[M+K]^+$calcd. For $C_{19}H_{11}ClKN_2$: 341.0248; Found: 341.0232.

1-(o-tolyl)benzo[a]imidazo[5,1,2-cd]indolizine (3h) :[3]



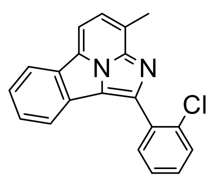
(Eluent: 10% EtOAc/hexane); 71% yield (40.0 mg); yellow solid, Mp:108-109 ^{0}C ; ^{1}H NMR (500 MHz, CDCl3) δ 8.45 – 8.36 (m, 3H), 8.33 (dd, J = 7.9, 0.7 Hz, 1H), 7.90 (d, J = 7.4 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.63 (dd, J = 10.7, 4.7 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.49 (dd, J = 10.6, 4.3 Hz, 1H), 3.01 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 139.5, 134.83, 131.4, 129.0, 128.8, 128.7, 128.5, 128.3, 126.5, 124.6, 122.7, 120.8, 108.8, 16.4.

1-(4-chlorophenyl)-5-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3i)



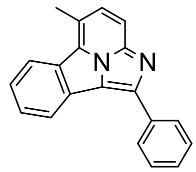
(Eluent: 15% EtOAc/hexane); 83% yield (52.4 mg); yellow solid, Mp:198-200 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.18 (m, 4H), 7.86 (d, J = 8.5 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.57 – 7.50 (m, 3H), 2.94 (s, 3H).13C NMR (125 MHz, $CDCl_3$) δ 144.3, 138.2, 134.5, 133.2, 131.4, 129.7, 129.1, 128.2, 127.7, 124.7, 123.9, 122.0, 120.5, 112.8, 17.4. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{20}H_{13}ClN_2Na$: 339.0657; Found: 339.0665.

41-(2-chlorophenyl)-3-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3j)



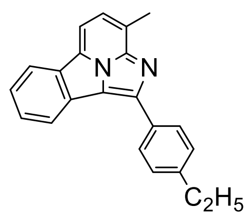
(Eluent:10% EtOAc/hexane); 63% yield (39.8 mg); yellow solid, Mp: 160-162 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.01 (dd, J = 7.4, 1.9 Hz, 1H), 7.95 (d, J = 7.4 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.64 (dd, J = 7.7, 1.4 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.46 (dqd, J = 15.0, 7.4, 1.6 Hz, 2H), 3.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.0, 134.1, 132.9, 131.6, 130.0, 129.8, 129.1, 128.8, 128.3, 127.0, 126.5, 125.1, 124.7, 122.6, 122.4, 109.1, 16.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{20}H_{14}ClN_2$: 317.0846; Found: 317.0852.

5-methyl-1-phenylbenzo[a]imidazo[5,1,2-cd]indolizine (3k)



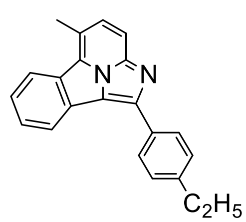
(Eluent: 10% EtOAc/hexane); 71% yield (40.0 mg); yellow solid, Mp: 200-202 ^{0}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.32 (m, 3H), 8.26 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 10.5 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H), 7.50 (dt, J = 14.8, 7.6 Hz, 2H), 2.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 139.5, 137.8, 134.7, 130.9, 129.6, 129.2, 128.9, 128.7, 128.1, 124.4, 122.9, 120.7, 120.3, 112.8, 110.3, 22.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{20}H_{14}N_2Na$: 305.1055; Found: 305.1045.

1-(4-ethylphenyl)-3-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3l) :



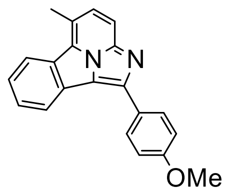
(Eluent: 10% EtOAc/hexane); 65% yield (40.3mg); brown semi solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.1 Hz, 1H), 8.36 – 8.28 (m, 3H), 7.91 (d, J = 7.4 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.69 (dd, J = 7.4, 0.9 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.46 (d, J = 8.2 Hz, 2H), 3.01 (s, 3H), 2.79 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 145.1, 139.5, 132.2, 131.3, 128.9, 128.6, 126.4, 126.1, 124.4, 122.7, 120.8, 108.7, 28.8, 16.4, 15.5. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{18}N_2Na$: 333.1368; Found: 333.1368.

1-(4-ethylphenyl)-5-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3m) :



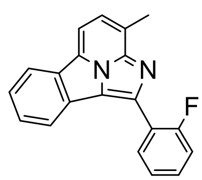
(Eluent: 10% EtOAc/hexane); 60% yield (37.2 mg);brown semi solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.1 Hz, 1H), 8.29 (t, J = 7.9 Hz, 3H), 7.89 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.9 Hz, 2H), 2.95 (s, 3H), 2.79 (d, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 145.1, 138.3, 132.1, 131.3, 129.3, 128.49, 128.42, 128.20, 128.1, 127.6, 124.3, 123.8, 121.6, 120.5, 112.5, 28.8, 17.4, 15.4. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{19}N_2$: 311.1548; Found: 311.1557.

1-(4-methoxyphenyl)-5-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3n) :



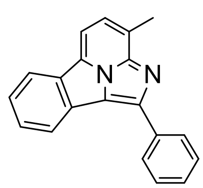
(Eluent: 20% EtOAc/hexane); 72% yield (44.9 mg); brown solid, Mp: 118-120 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, J = 14.0, 8.1 Hz, 2H), 8.32 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 3.93 (s, 3H), 3.02 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 145.9, 138.4, 131.4, 129.5, 129.3, 128.4, 128.2, 127.7, 127.3, 124.4, 124.0, 121.6, 120.5, 114.4, 112.3, 55.4, 17.5. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{21}H_{17}N_2O$: 313.1341. Found: 313.1362.

1-(2-fluorophenyl)-3-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3o) :



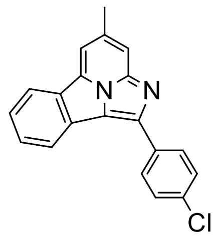
(Eluent: 15% EtOAc/hexane); 60% yield (36.0 mg); brown semi solid, ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.25 (m, 3H), 7.93 (d, J = 7.3 Hz, 1H), 7.71 (ddd, J = 6.9, 3.9, 1.0 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.45 (m, 1H), 7.36 (dddd, J = 11.5, 9.2, 7.9, 1.0 Hz, 2H), 3.02 (s, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0(d, J= 208 Hz), 139.3, 138.0, 131.7, 130.3 (d, J= 6.6 Hz), 128.8, 128.5, 126.5, 124.8, 124.79, 124.71, 122.49, 122.42 116.0(d, J=18.1 Hz), 108.9, 16.5. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{20}H_{14}FN_2$: 301.1141. Found: 301.1152.

3-methyl-1-phenylbenzo[a]imidazo[5,1,2-cd]indolizine (3p) :



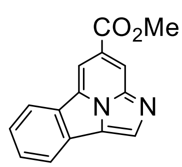
(Eluent: 10% EtOAc/hexane); 75% yield (42.3 mg); yellow solid, Mp: 198-200 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 – 8.33 (m, 3H), 8.28 (dd, J = 7.9, 0.7 Hz, 1H), 7.80 (d, J = 5.6 Hz, 2H), 7.72 (dd, J = 7.9, 7.4 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 2.80 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 139.5, 137.9, 134.7, 130.9, 129.7, 129.2, 128.9, 128.1, 128.2, 124.5, 123.0, 120.7, 112.8, 110.3, 22.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{20}H_{15}N_2$: 283.1235; Found: 283.1245.

1-(4-chlorophenyl)-4-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3q) :



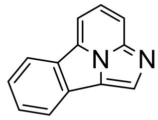
(Eluent: 15% EtOAc/hexane); 35% yield (22.1 mg); yellow solid; Mp: 198-200 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 14.8 Hz, 2H), 7.80 – 7.72 (m, 1H), 7.58 (d, J = 8.5 Hz, 3H), 2.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 139.8, 134.9, 133.5, 131.3, 129.8, 129.4, 125.0, 123.4, 120.9, 113.2, 110.8, 23.1. HRMS-ESI (m/z) $[M+H]^+$ calcd. For $C_{20}H_{14}ClN_2$: 317.0846; Found: 317.0831.

methyl benzo[a]imidazo[5,1,2-cd]indolizine-4-carboxylate (3r) :



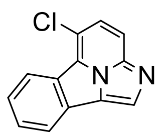
(Eluent: 50% EtOAc/hexane); 50% yield (25.0 mg); gummy liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.77 (s, 1H), 8.62 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.4 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 4.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 138.5, 134.8, 131.9, 129.7, 129.6, 129.5, 128.0, 125.5, 123.2, 121.3, 116.0, 109.6, 52.9. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{15}H_{11}N_2O_2$: 251.0821; Found: 251.0831.

benzo[a]imidazo[5,1,2-cd]indolizine (3s) :



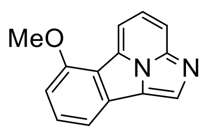
(Eluent: 30% EtOAc/hexane); 78% yield (29.9 mg); brown semi solid, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 7.0 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 132.2, 131.3, 129.1, 126.2, 124.9, 124.3, 123.0, 121.0, 114.0, 109.0. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{13}H_9N_2$: 193.0766; Found: 193.0756.

. 5-chlorobenzo[a]imidazo[5,1,2-cd]indolizine (3t) :



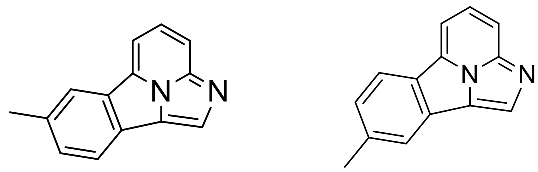
(Eluent: 30% EtOAc/hexane); 45% yield (20.3 mg); brown solid, Mp: 164-166 ^{0}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 15.2 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.2, 130.5, 129.5, 128.8, 127.6, 127.2, 125.3, 124.5, 120.9, 118.6, 114.3. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{13}H_{18}ClN_2$: 227.0376; Found: 227.0384.

6-methoxybenzo[a]imidazo[5,1,2-cd]indolizine (3u)



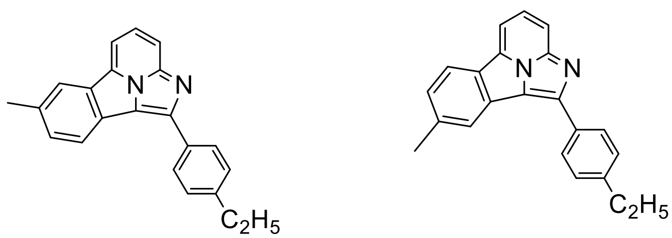
(Eluent: 35% EtOAc/hexane); 70% yield (31.0 mg); brown solid, Mp:178-180 ^{0}C ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.16 (d, *J* = 7.3 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.99 – 7.91 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.8, 139.3, 132.4, 130.5, 130.2, 129.6, 126.6, 124.4, 120.5, 113.3, 111.7, 105.7, 55.7. HRMS-ESI (m/z) [M+H]+calcd. For C14H11N2O: 223.0871; Found: 223.0888.

Isomer of 7-methylbenzo[a]imidazo[5,1,2-cd]indolizine and 8-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3v):



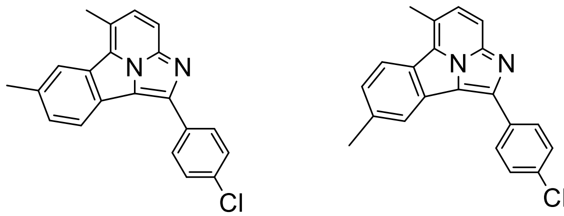
(Eluent: 30% EtOAc/hexane); 65% yield (26.7 mg); brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.7 Hz, 1H), 8.25 – 8.13 (m, 1H), 8.08 (dd, *J* = 18.9, 9.4 Hz, 2H), 8.03 – 7.98 (m, 1H), 7.93 (t, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 91.2, 8.1 Hz, 1H), 2.64 (d, *J* = 8.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 131.9, 131.6, 130.6, 126.4, 126.2, 126.0, 122.9, 122.6, 121.1, 120.6, 113.8, 113.5, 108.8, 108.4, 22.8, 21.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{14}H_{11}N_2$: 207.0922; Found: 207.0918.

Isomer of 1-(4-ethylphenyl)-7-methylbenzo[a]imidazo[5,1,2-cd]indolizine and 1-(4-ethylphenyl)-8-methylbenzo[a]imidazo[5,1,2-cd]indolizine (3w):



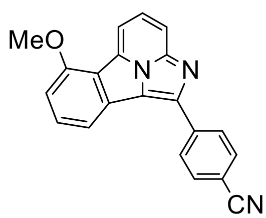
(Eluent: 15% EtOAc/hexane); 72% yield (44.6 mg); brown semi liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.19 (m, 3H), 8.15 (d, J = 25.4 Hz, 1H), 8.04 – 7.97 (m, 1H), 7.95 – 7.85 (m, 2H), 7.58 – 7.37 (m, 3H), 2.79 (qd, J = 7.6, 4.4 Hz, 2H), 2.63 (d, J = 20.6 Hz, 3H), 1.35 (td, J = 7.6, 4.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 146.0, 145.3, 139.5, 134.6, 131.8, 130.5, 130.2, 129.3, 128.9, 128.5, 128.3, 128.2, 126.8, 126.25, 126.21, 126.0, 122.9, 122.6, 120.8, 120.4, 112.7, 112.4, 108.2, 107.9, 28.8, 22.4, 21.7, 15.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{19}N_2$: 311.1548; Found: 311.1554.

1-(4-chlorophenyl)-5,7-dimethylbenzo[a]imidazo[5,1,2-cd]indolizine and 1-(4-chlorophenyl)-5,8-dimethylbenzo[a]imidazo[5,1,2-cd]indolizine (3x)



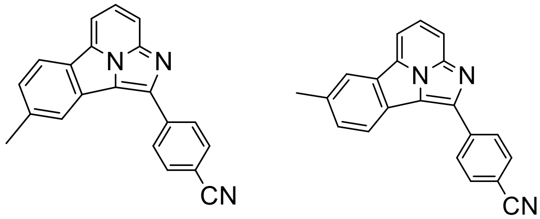
(Eluent: 15% EtOAc/hexane); 69% yield (45.5 mg); brown solid, Mp: 145-147 ^{0}C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 2H), 8.20 (dd, J = 11.7, 8.2 Hz, 1H), 8.10 (d, J = 16.5 Hz, 1H), 7.88 (dd, J = 8.4, 5.1 Hz, 1H), 7.65 (dd, J = 8.5, 4.5 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.42 – 7.38 (m, 1H), 2.98 (d, J = 7.0 Hz, 3H), 2.64 (d, J = 11.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 138.8, 138.3, 134.8, 134.5, 134.4, 133.4, 129.8, 129.4, 126.4, 124.0, 123.7, 121.3, 120.6, 120.3, 112.7, 112.6, 22.3, 21.9, 17.4. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{21}H_{16}ClN_2$: 331.1002; Found: 331.1008.

4-(6-methoxybenzo[a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3y) :



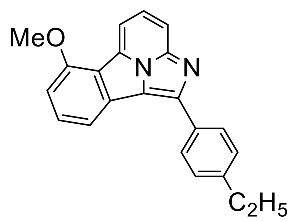
(Eluent: 30% EtOAc/hexane); 80 % yield (51.6 mg); yellow solid, Mp: 275-277 ^{0}C ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 8.1 Hz, 2H), 8.14 (d, J = 7.1 Hz, 1H), 8.02 (t, J = 7.0 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.72 (t, J = 8.1 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 4.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.0, 143.6, 139.3, 139.0, 132.7, 130.8, 128.5, 127.7, 121.8, 120.7, 118.9, 113.1, 112.0, 111.8, 106.4, 55.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For C_{21} $H_{14}N_3O$: 323.1059; Found: 324.1147.

4-(7-methylbenzo[a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile and 4-(8 methylbenzo[a]imidazo[5,1,2-cd]indolizin-1-yl)benzonitrile (3z) :



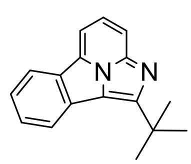
(Eluent: 30% EtOAc/hexane); 75 % yield (46.05 mg); yellow solid, Mp: 270-272 ^{0}C ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 – 8.37 (m, 2H), 8.26 – 8.13 (m, 2H), 8.03 (dd, J = 22.6, 14.6 Hz, 1H), 7.93 (ddd, J = 16.1, 13.2, 4.7 Hz, 2H), 7.86 (dd, J = 15.6, 8.2 Hz, 2H), 7.51 (dd, J = 81.9, 8.0 Hz, 1H), 2.65 (d, J = 21.1 Hz, 3H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 142.8, 140.0, 139.5, 139.0, 135.7, 132.72, 132.0, 130.9, 130.7, 129.4, 128.9, 128.4, 127.2, 127.0, 126.4, 123.2, 122.9, 121.7, 120.8, 120.5, 118.9, 113.7, 113.3, 111.8, 109.0, 108.7, 22.4, 21.8. HRMS-ESI (m/z) $[M+H]^+$calcd. For C_{21} $H_{14}N_3$: 308.1188; Found: 308.1177.

1-(4-ethylphenyl)-6-methoxybenzo[a]imidazo[5,1,2-cd]indolizine (3aa) :



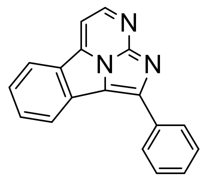
(Eluent: 20% EtOAc/hexane); 76% yield (49.5 mg);yellow solid, Mp: 140-142 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 7.2 Hz, 1H), 7.98 (dd, J = 16.0, 8.1 Hz, 2H), 7.90 (dd, J = 8.4, 7.3 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 4.12 (s, 3H), 2.79 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 146.7, 145.3, 139.3, 132.0, 130.2, 130.1, 129.1, 128.5, 128.3, 126.6, 120.7, 120.2, 113.2, 112.1, 111.2, 105.3, 55.6, 28.8, 15.4. HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{18}N_2NaO$: 349.1317; Found: 349.1320.

1-(tert-butyl)benzo[a]imidazo[5,1,2-cd]indolizine (3ab)



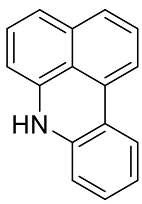
(Eluent: 10% EtOAc/hexane); 62% yield (30.7 mg); brown semi liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.91 (dd, J = 8.5, 7.2 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.62 – 7.54 (m, 1H), 1.77 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 130.8, 128.7, 125.3, 124.0, 122.9, 121.5, 112.5, 108.1, 30.9. HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{17}H_{16}N_2Na$:271.1211; Found: 271.1207.

1-phenyl-2,2a1,3-triazacyclopenta[jk]fluorine (6a) :[2]



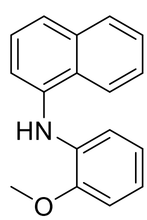
(Eluent: 20% EtOAc/hexane); 70% yield (37.6 mg); brown gummy solid, ^{1}H NMR (600 MHz,) δ 9.18 (d, *J* = 4.7 Hz, 1H), 8.47 (dd, *J* = 12.8, 5.5 Hz, 4H), 7.99 (d, *J* = 5.1 Hz, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.71 – 7.63 (m, 3H), 7.55 (t, *J* = 7.3 Hz, 1H) ^{13}C NMR (150 MHz,) δ 150.4, 148.8, 135.1, 133.8, 131.7, 130.7, 129.9, 129.1, 128.7, 125.5, 124.9, 121.4, 104.5.

7H-benzo[kl]acridine (7) :[4]



(Eluent: 5% EtOAc/hexane); 60% yield (26.0 mg); brown liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.47 – 6.36 (m, 3H), 6.32 (d, J = 4.8 Hz, 2H), 6.22 (t, J = 7.6 Hz, 2H), 6.12 – 6.06 (m, 1H), 5.80 (t, J = 7.5 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 139.4, 134.7, 133.6, 128.3, 128.0, 127.1, 126.0, 125.9, 125.8, 125.3, 121.8, 121.4, 119.6, 118.6, 113.4, 74.5.

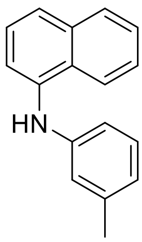
N-(2-methoxyphenyl)naphthalen-1-amine (8) :



(Eluent: 5% (EtOAc/hexane); 63% yield (31.3 mg) brown liquid,; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 0.9 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.62 (t, J = 4.6 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.45 – 7.42 (m, 2H), 7.19 (t, J = 8.1 Hz, 1H), 6.63 – 6.56 (m, 2H), 6.54 – 6.48 (m, 1H), 5.95 (s, 1H), 3.78 (s, 3H).;

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 146.3, 138.3, 134.6, 130.0, 128.4, 127.9, 126.0, 125.6, 123.2, 121.8, 116.7, 109.7, 105.5, 102.8, 55.1.

N-(m-tolyl)naphthalen-1-amine (9) :[5]



(Eluent: 3% (EtOAc/hexane); 60% yield (27.9 mg); brown liquid, ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 1H), 7.90 – 7.86 (m, 1H), 7.60 (t, J = 4.6 Hz, 1H), 7.50 (pd, J = 6.8, 1.4 Hz, 2H), 7.42 (d, J = 4.6 Hz, 2H), 7.17 (t, J = 8.1 Hz, 1H), 6.62 – 6.57 (m, 1H), 6.56 (t, J = 2.2 Hz, 1H), 6.48 (dd, J = 8.2, 2.3 Hz, 1H), 5.94 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 146.3, 138.3, 134.6, 130.0, 128.4, 127.9, 126.1, 125.8, 123.2, 121.8, 116.7, 109.7, 105.5, 102.9, 55.1.

References:

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2. M. Aginagalde, Y. Vara, A. Arrieta, R. Zangi, V. L. Cebolla, A. D. Camón, and F. P. Cossío. Tandem [8+2] Cycloaddition – [2+6+2] Deh ydrogenation Reactions Involving Imidazo[1,2-a]pyridines and Imidazo[1,2-a]pyrimidines, *J. Org. Chem*. 2010, **75**, 2776–2784.
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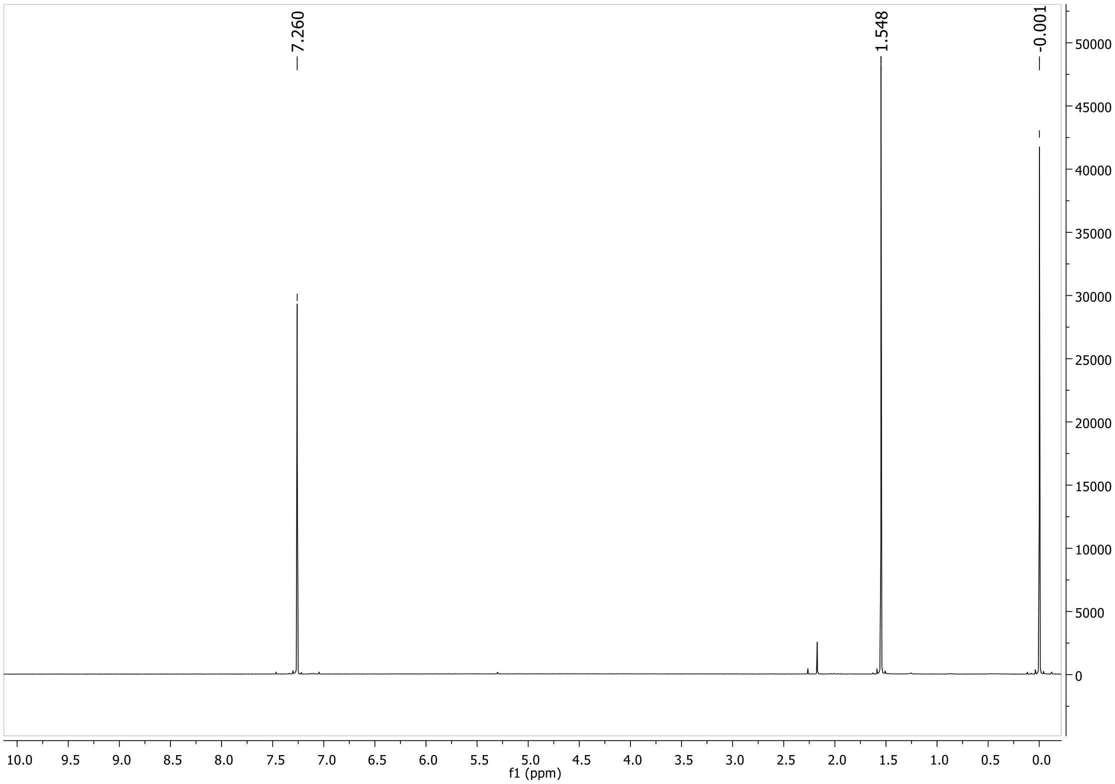
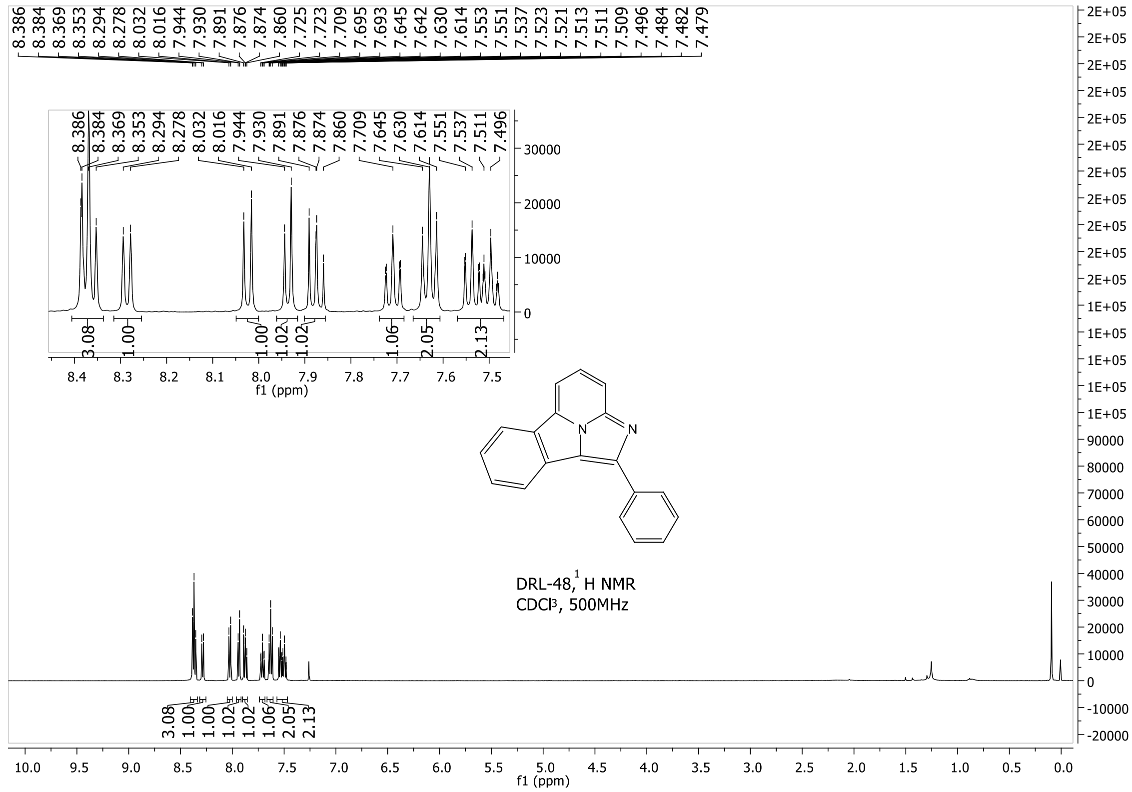
4. Baek, Yeong Mi et al From Repub. Korean Kongkae Taeho Kongbo, 2015086071, 27 Jul 2015.
5. From Ger., 102012005215, 11 Apr 2013.

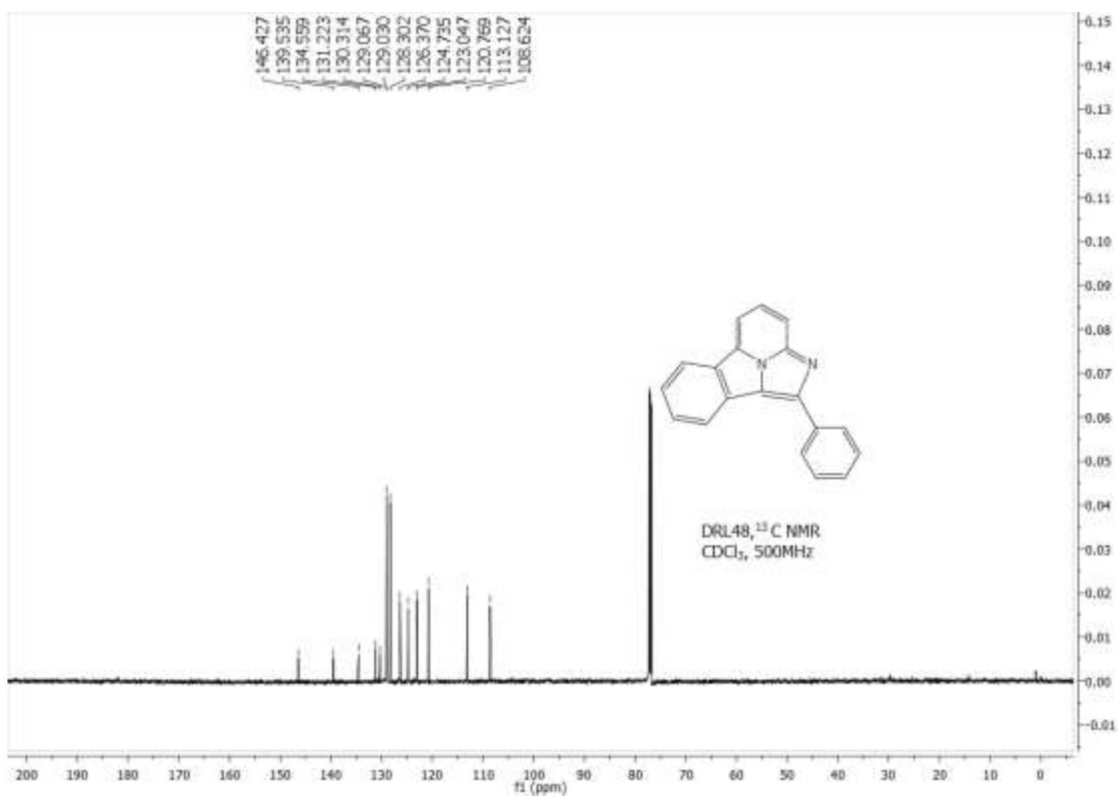
^1H NMR and ^{13}C NMR Spectra



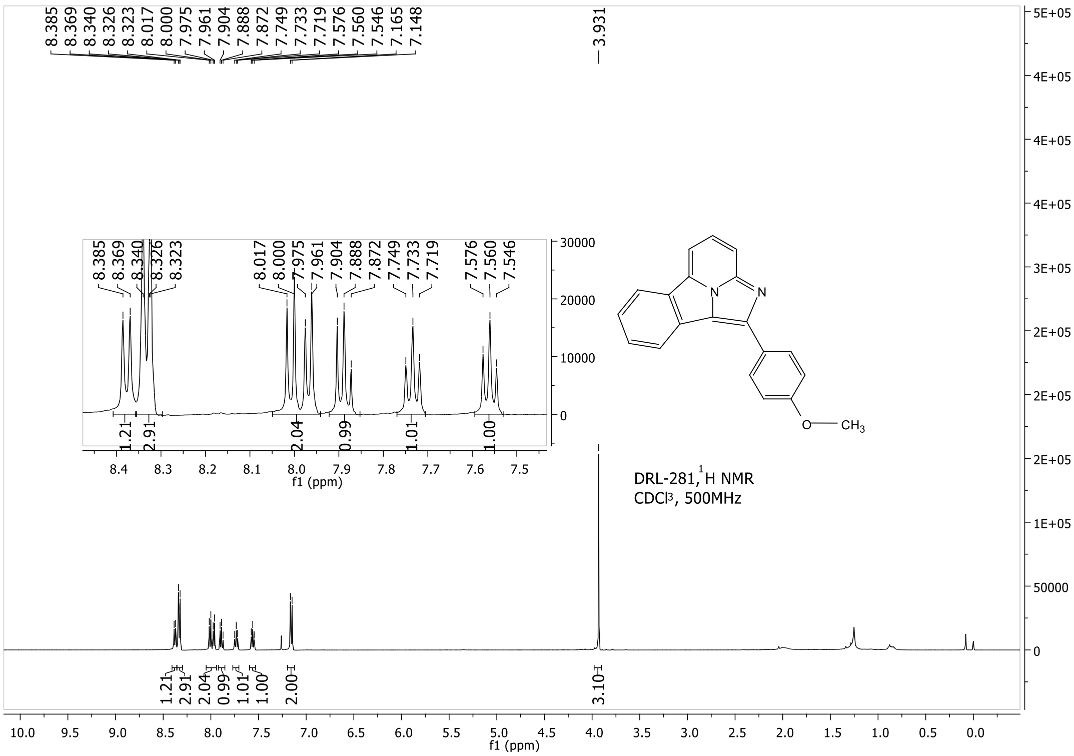
^{1}H NMR of $CDCl_3$



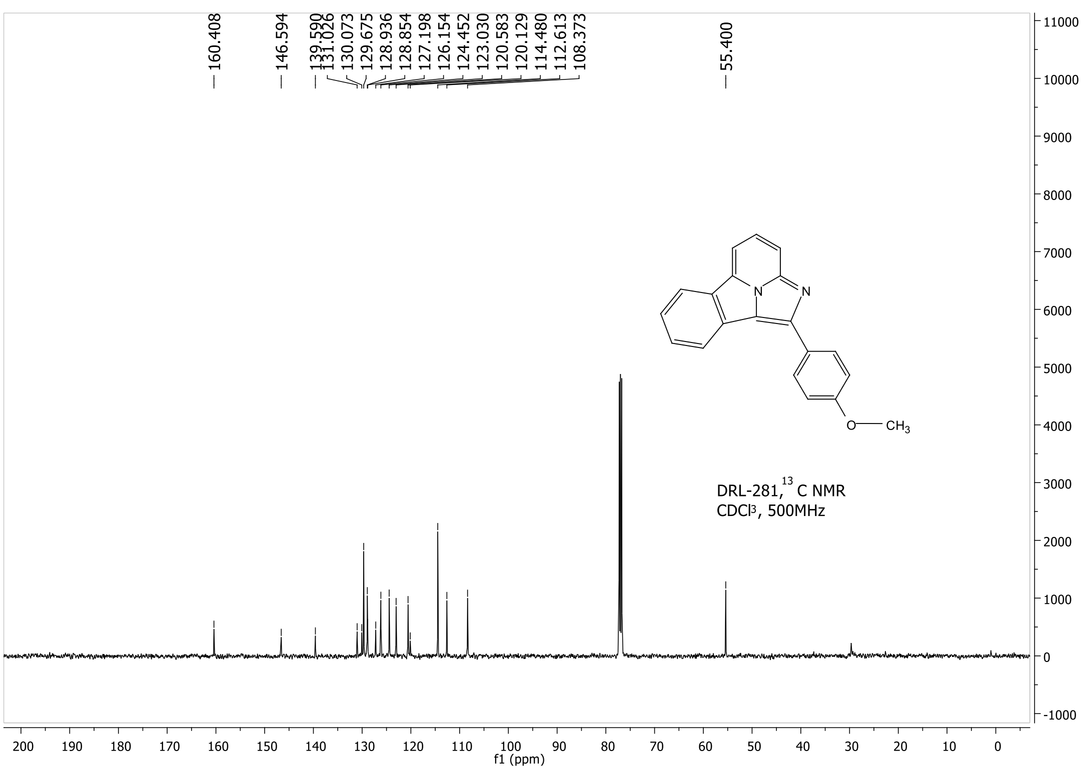
[1]H NMR of 3a



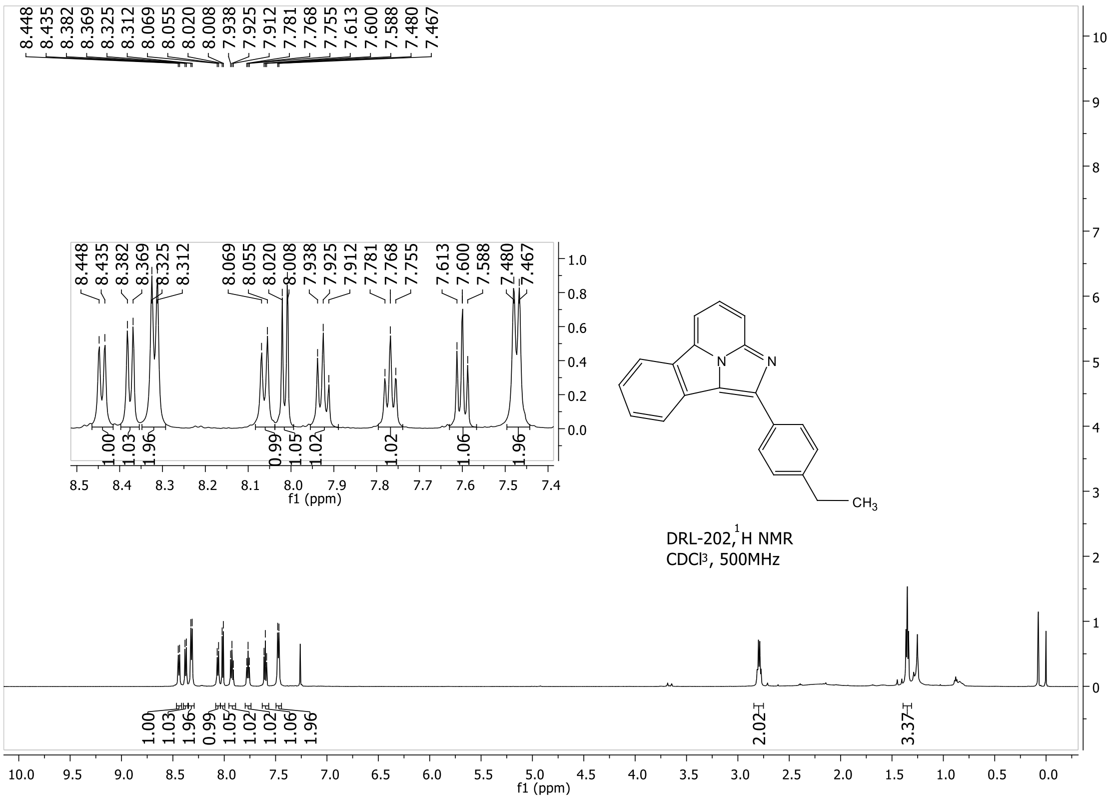
[13]C NMR of 3a



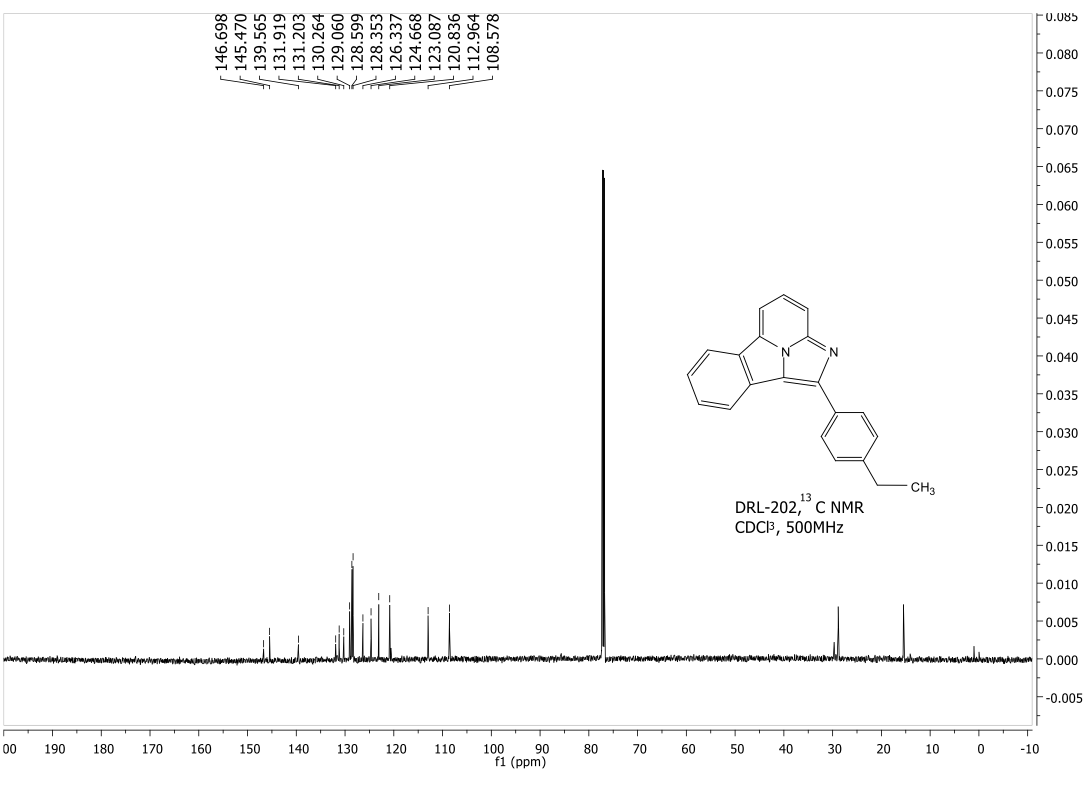
^{1}H NMR of 3b



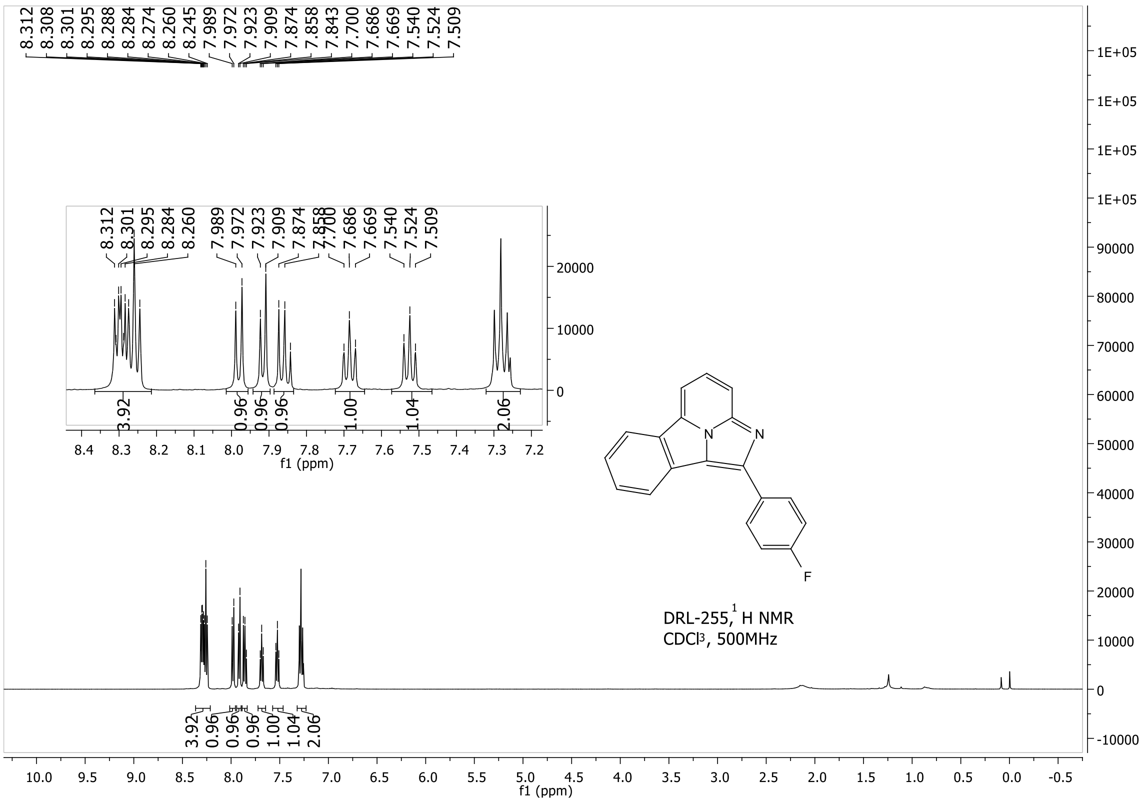
^{13}C NMR of 3b



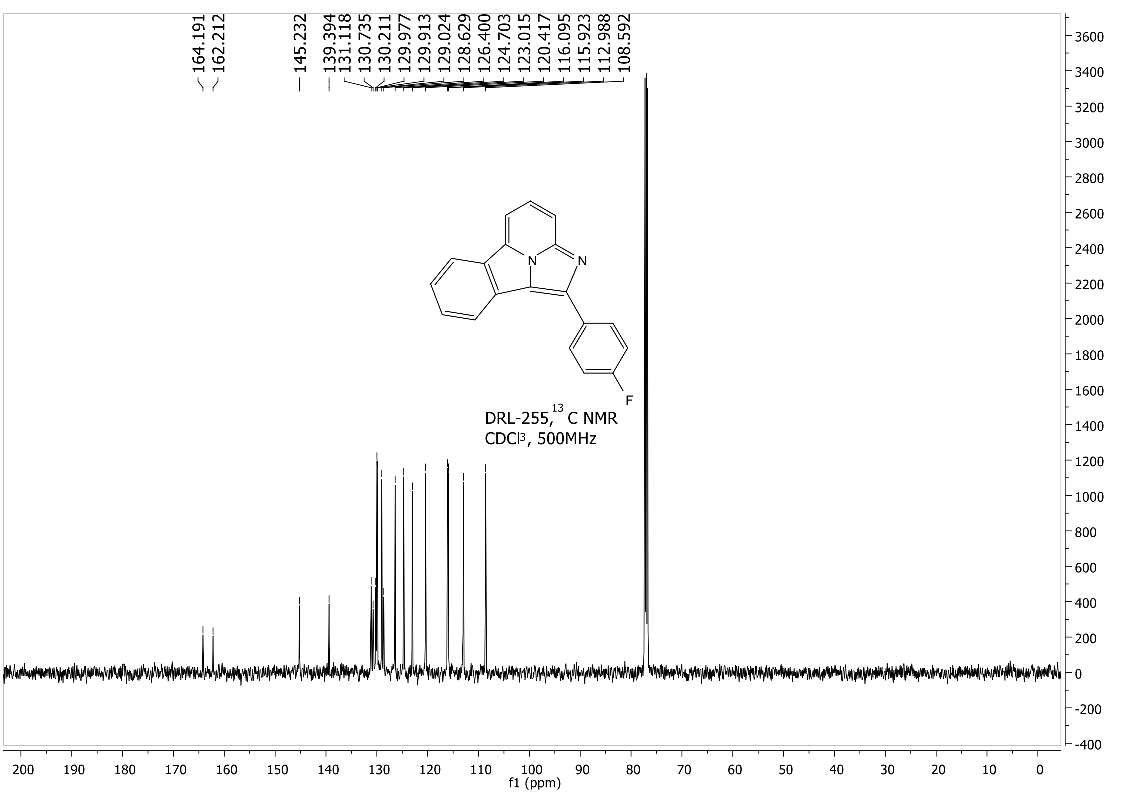
[1]H NMR of 3c



[13]C NMR of 3c



[1]H NMR of 3d



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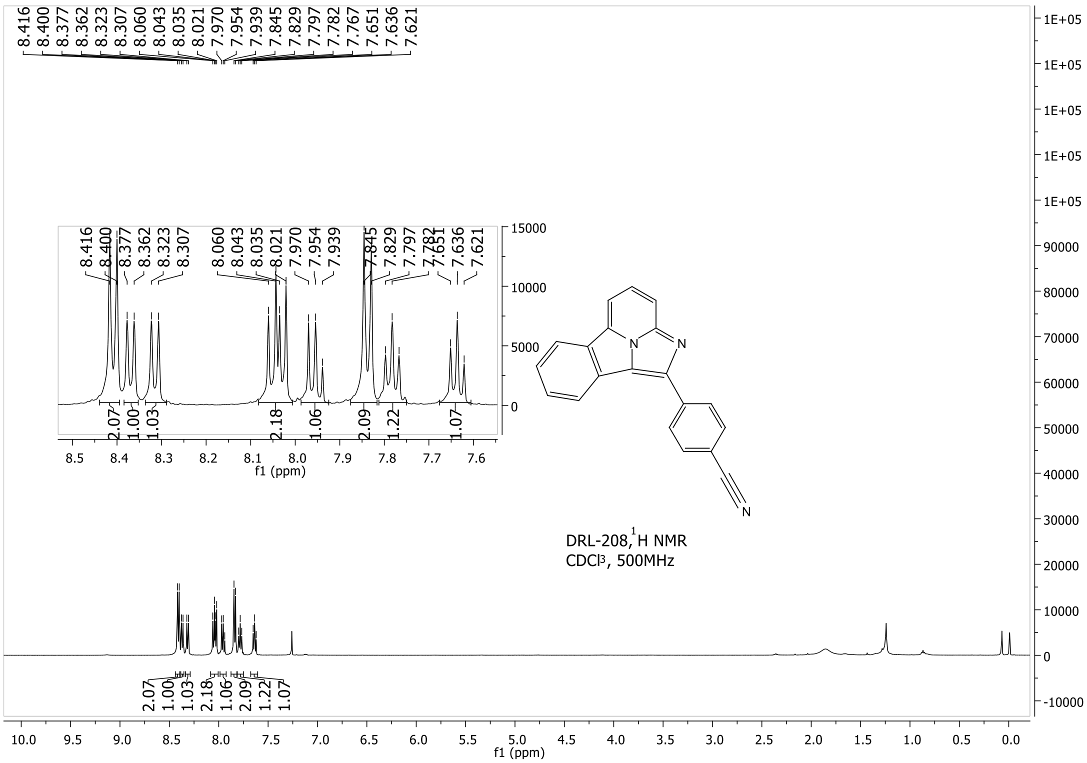
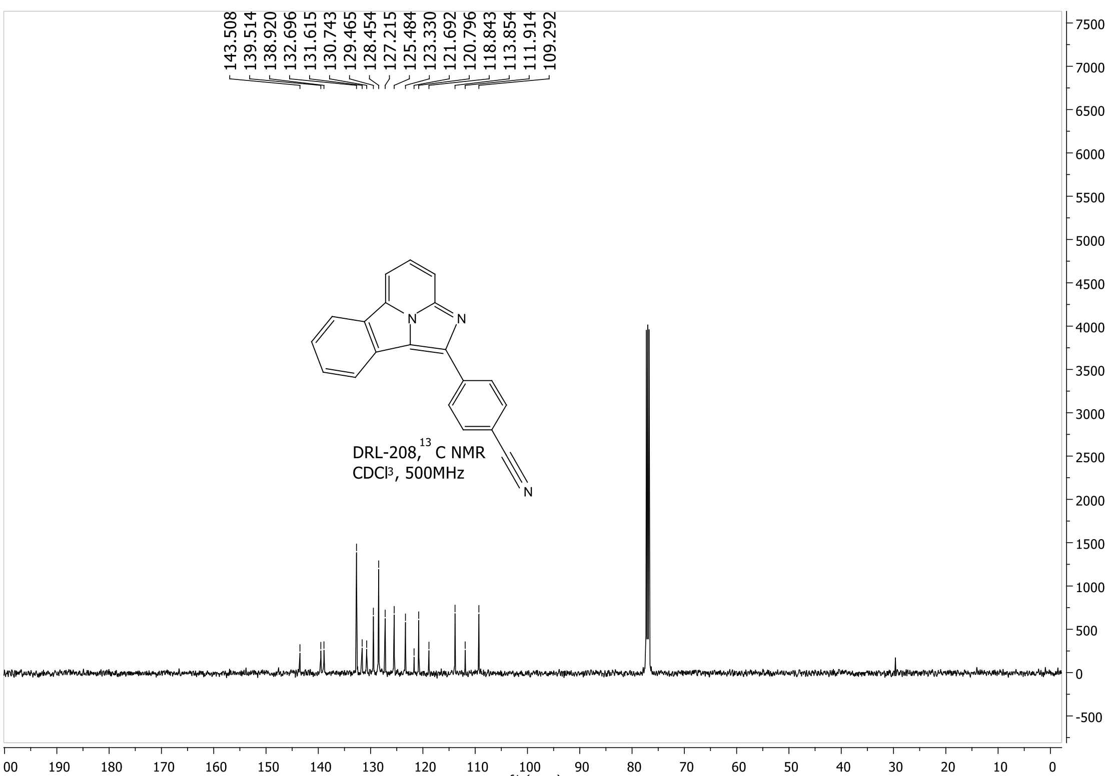
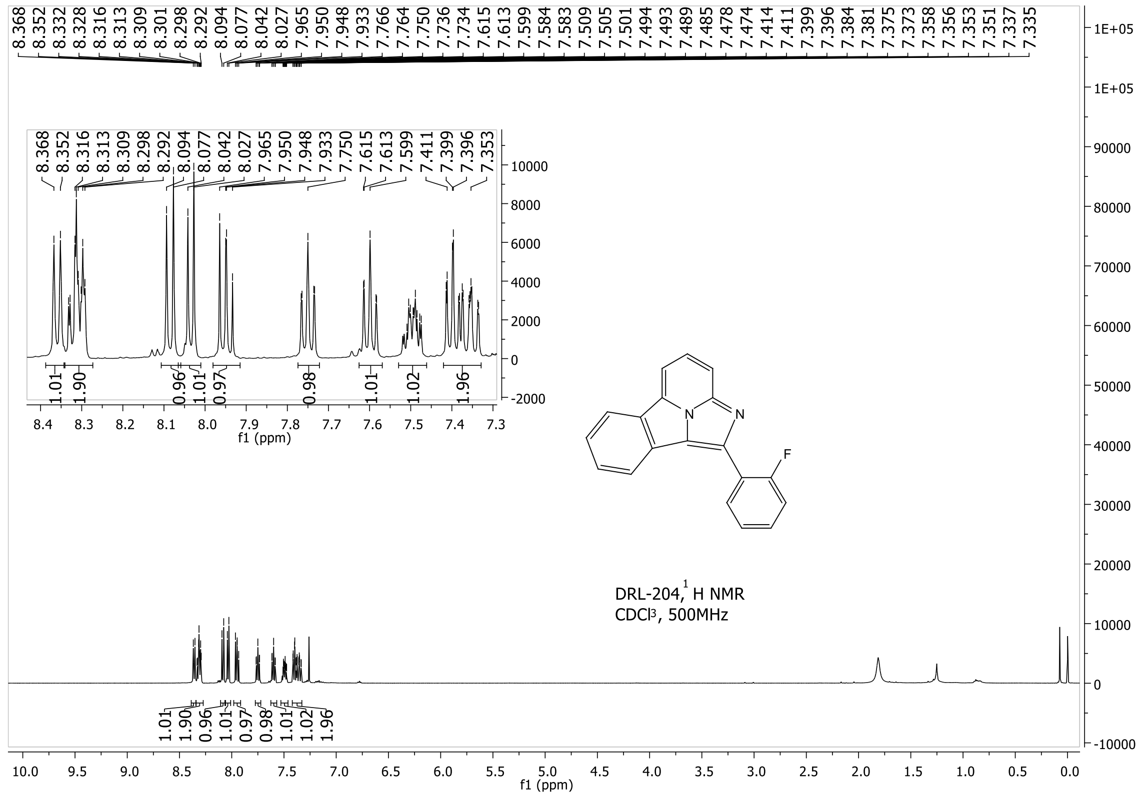


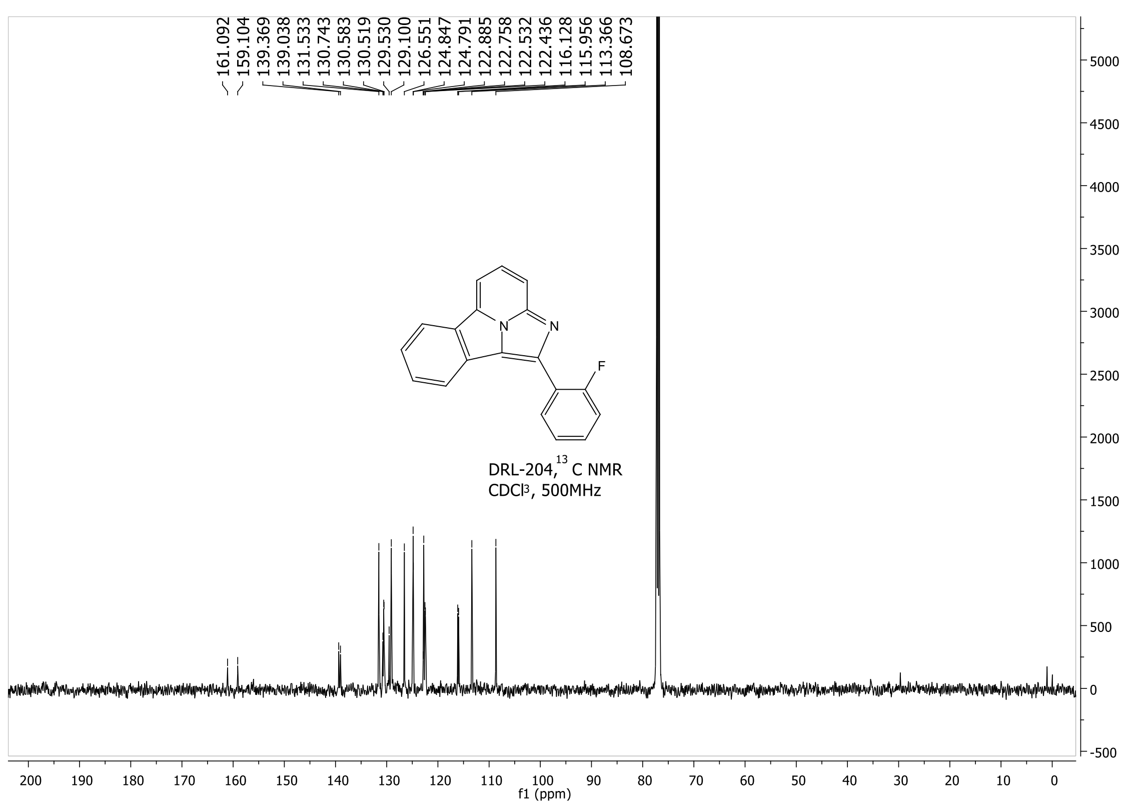
^{1}H NMR of 3e



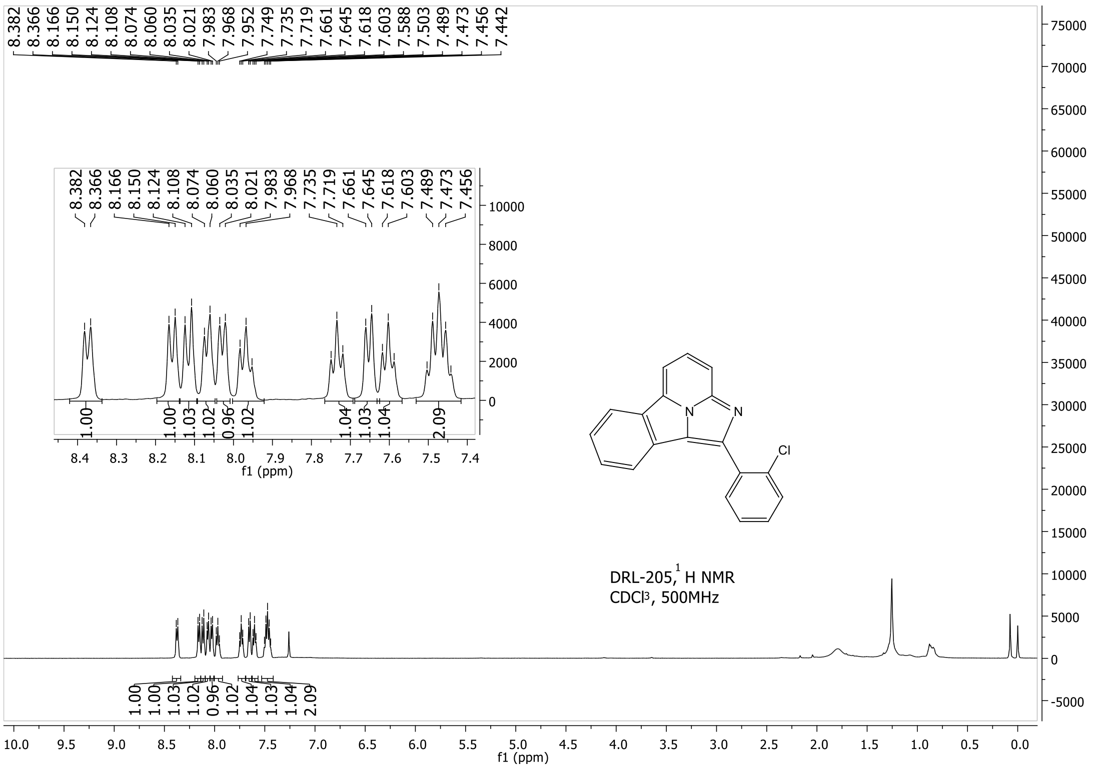
^{13}C NMR of 3e



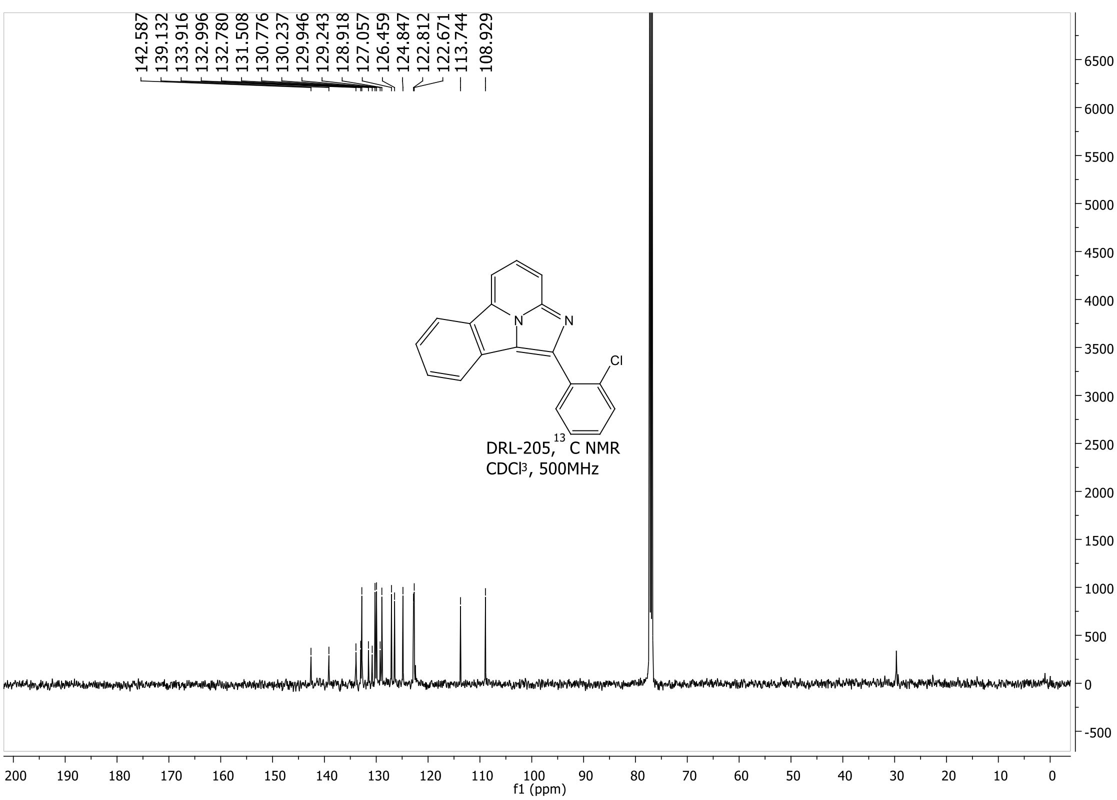
^{1}H NMR of 3f



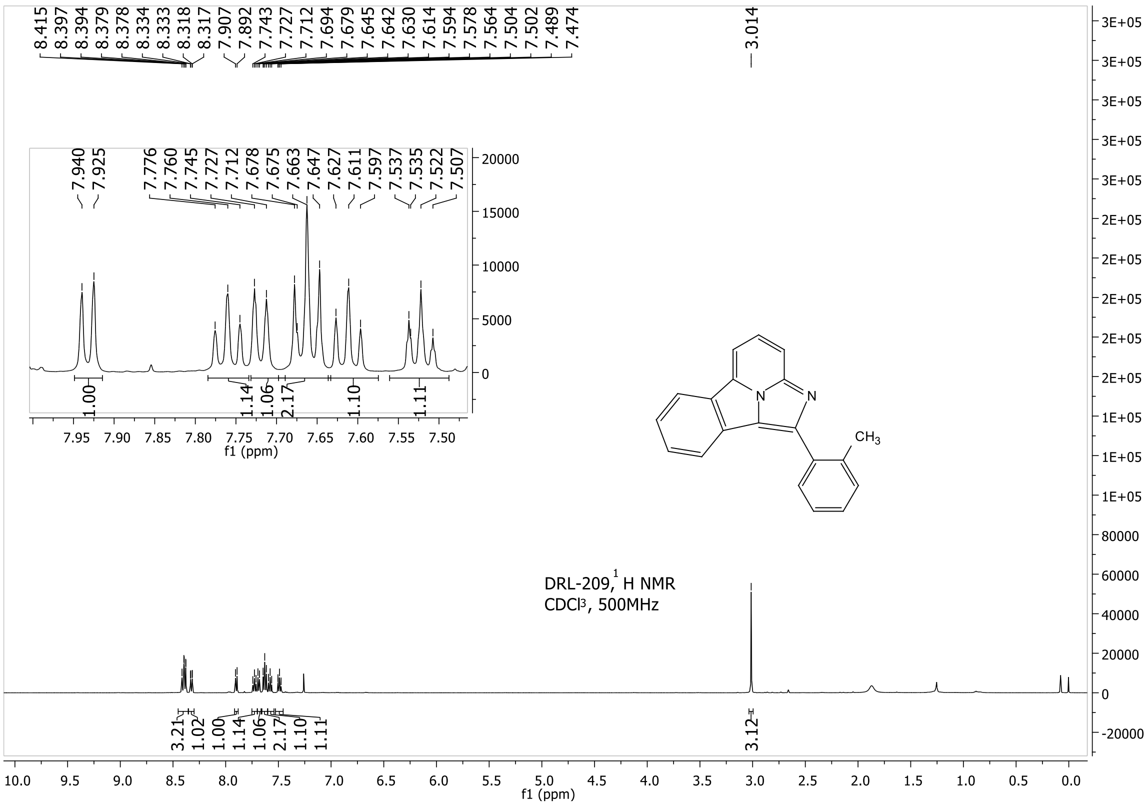
^{13}C NMR of 3f



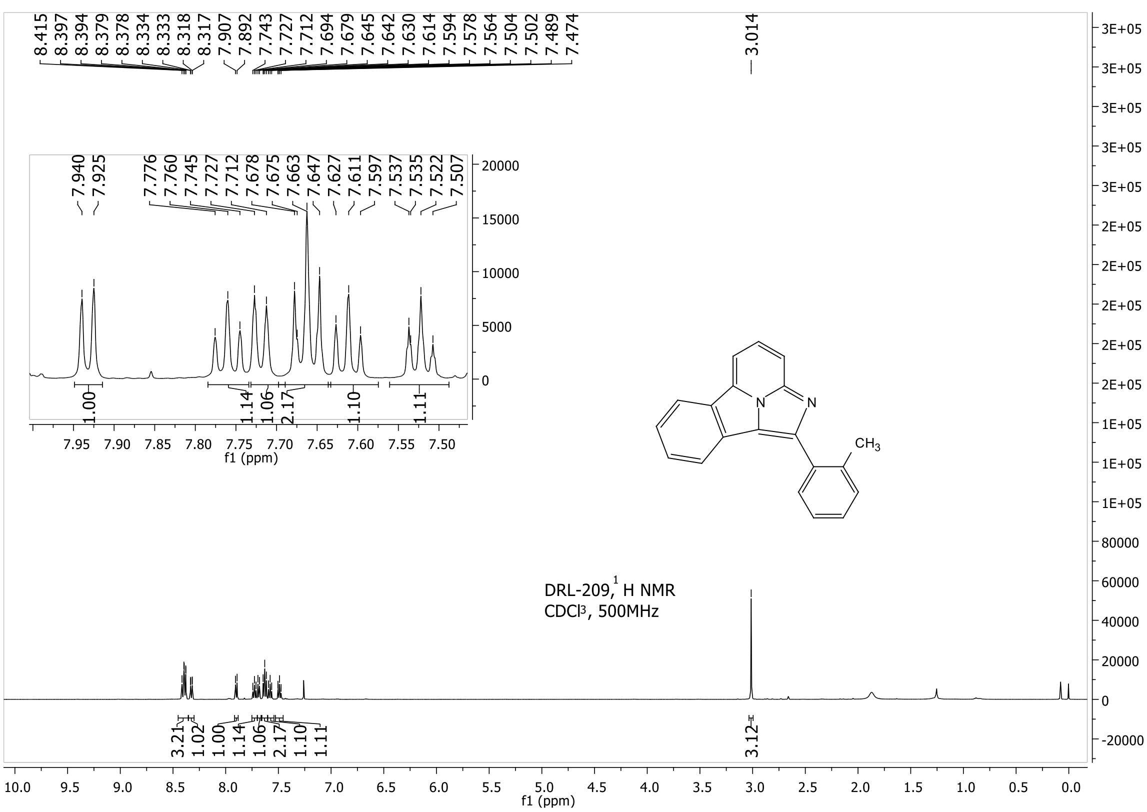
^{1}H NMR of 3g



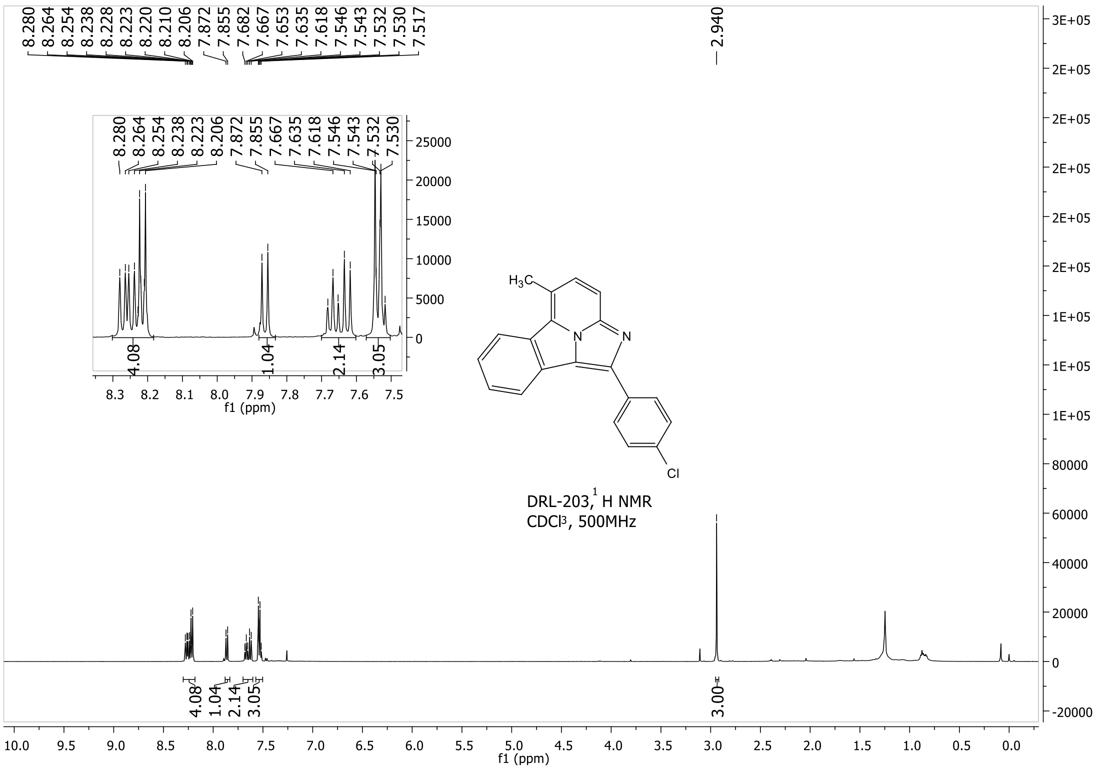
^{13}C NMR of 3g



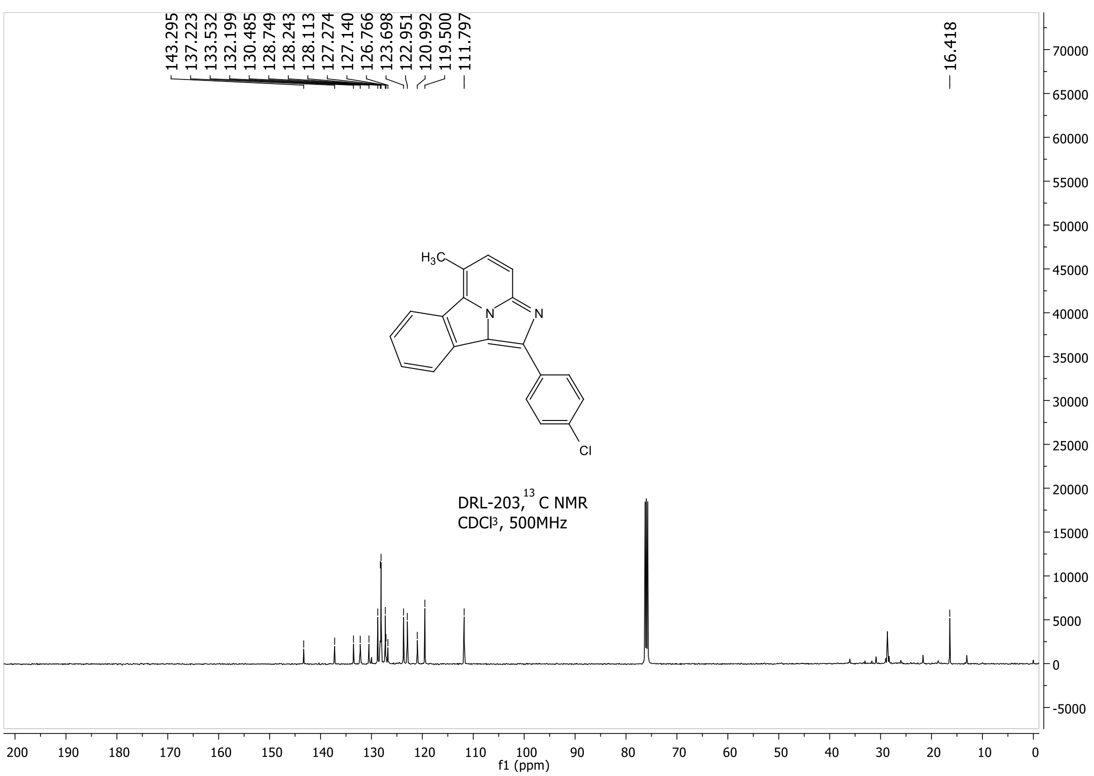
^{1}H NMR of 3h



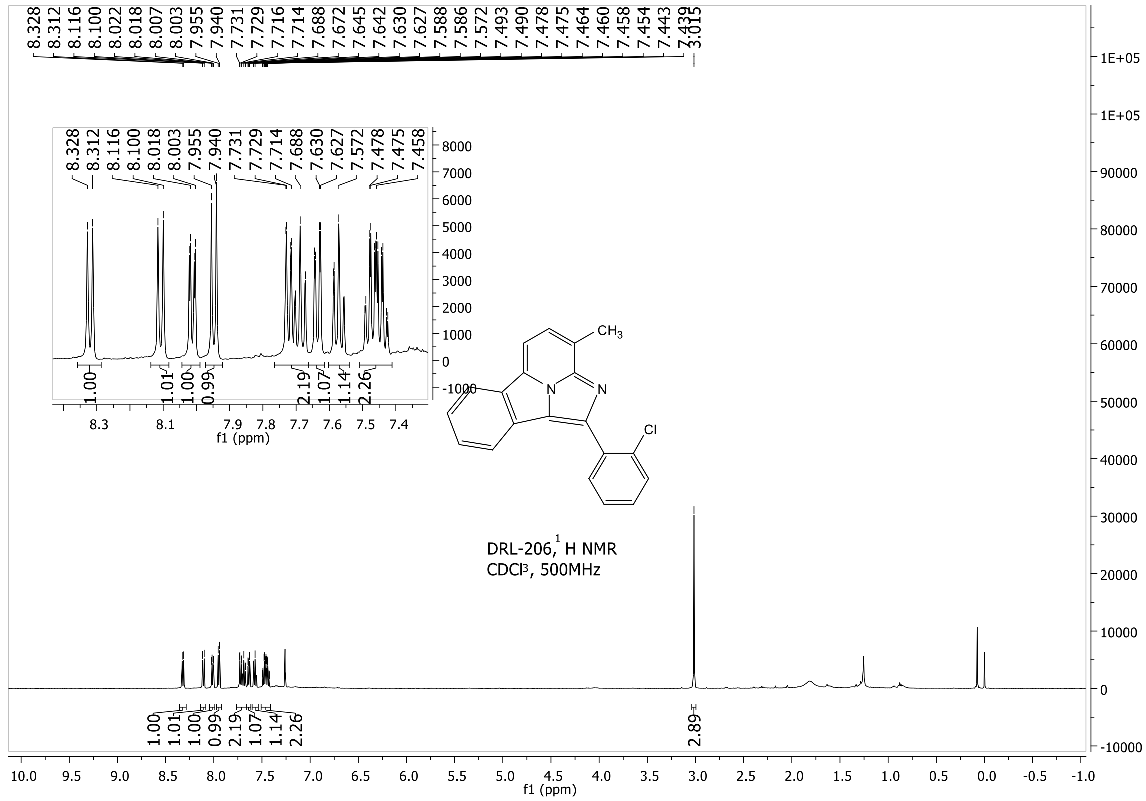
^{13}C NMR of 3h



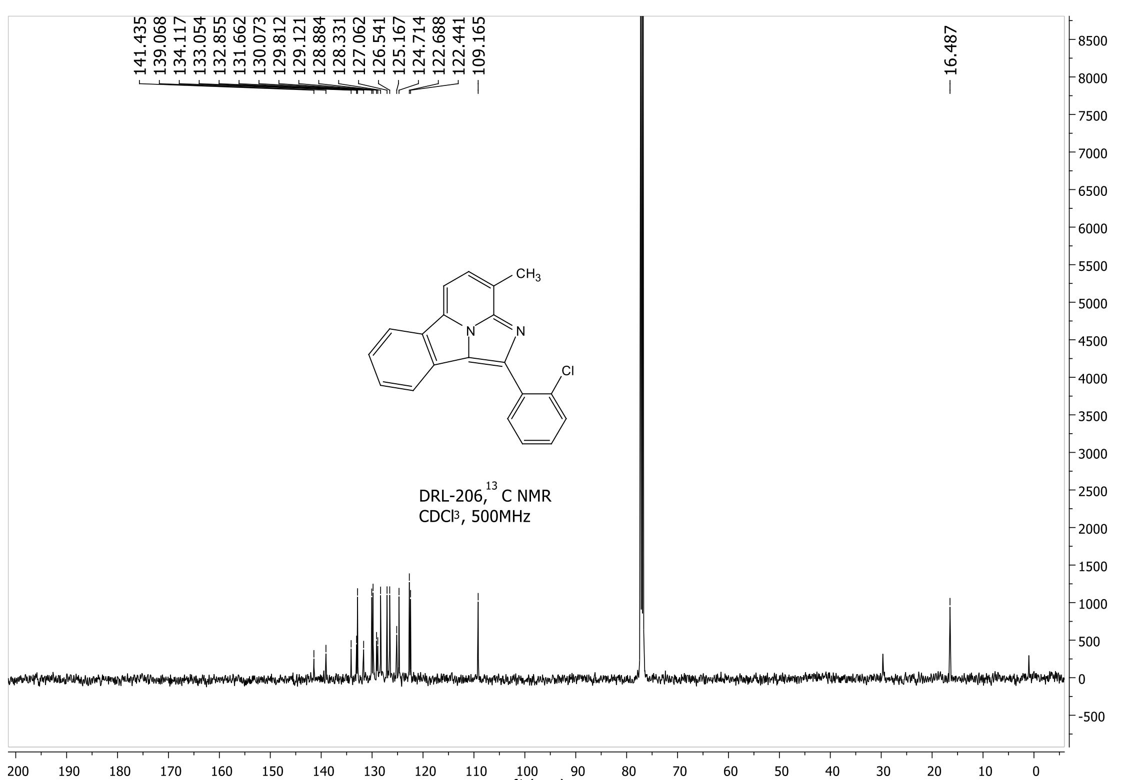
^{1}H NMR of 3i



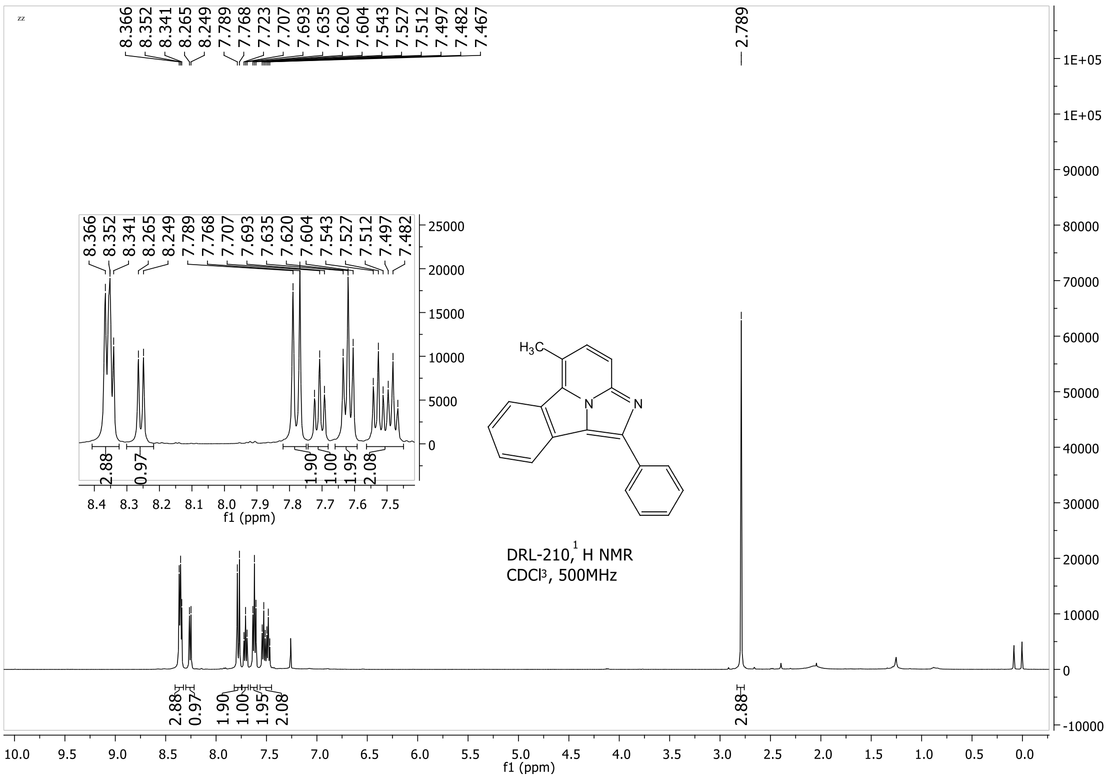
^{13}C NMR of 3i



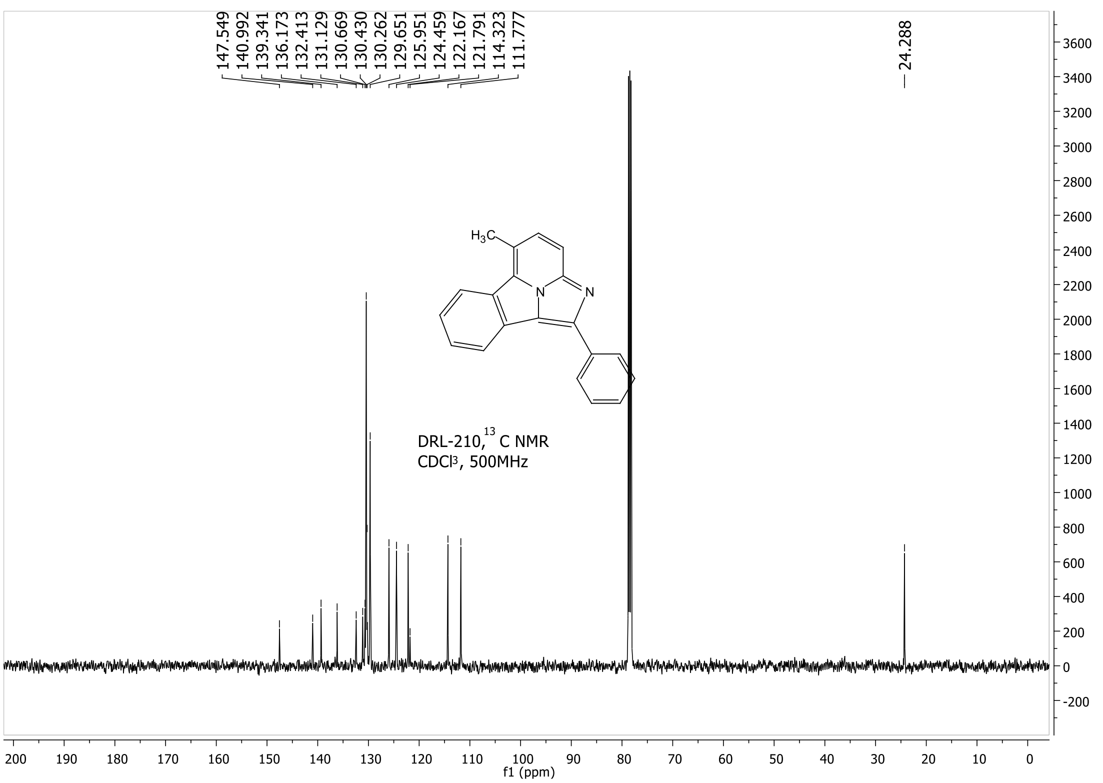
^{1}H NMR of 3j



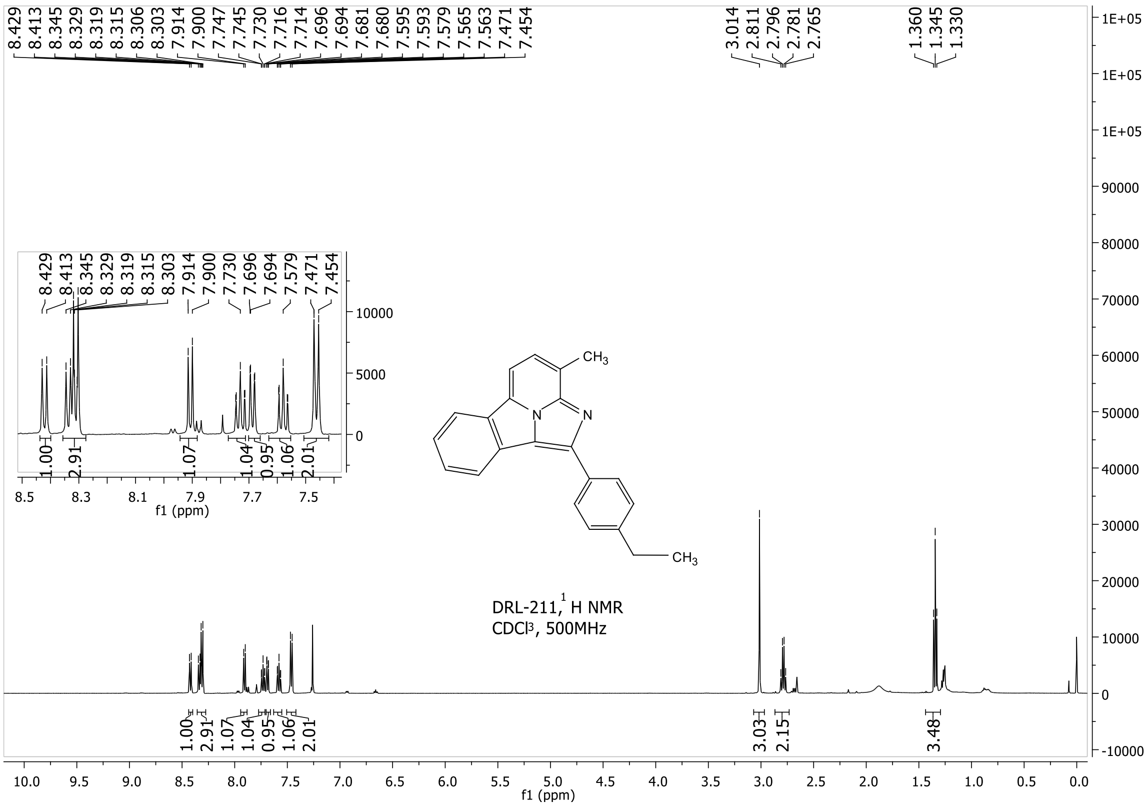
^{13}C NMR of 3j



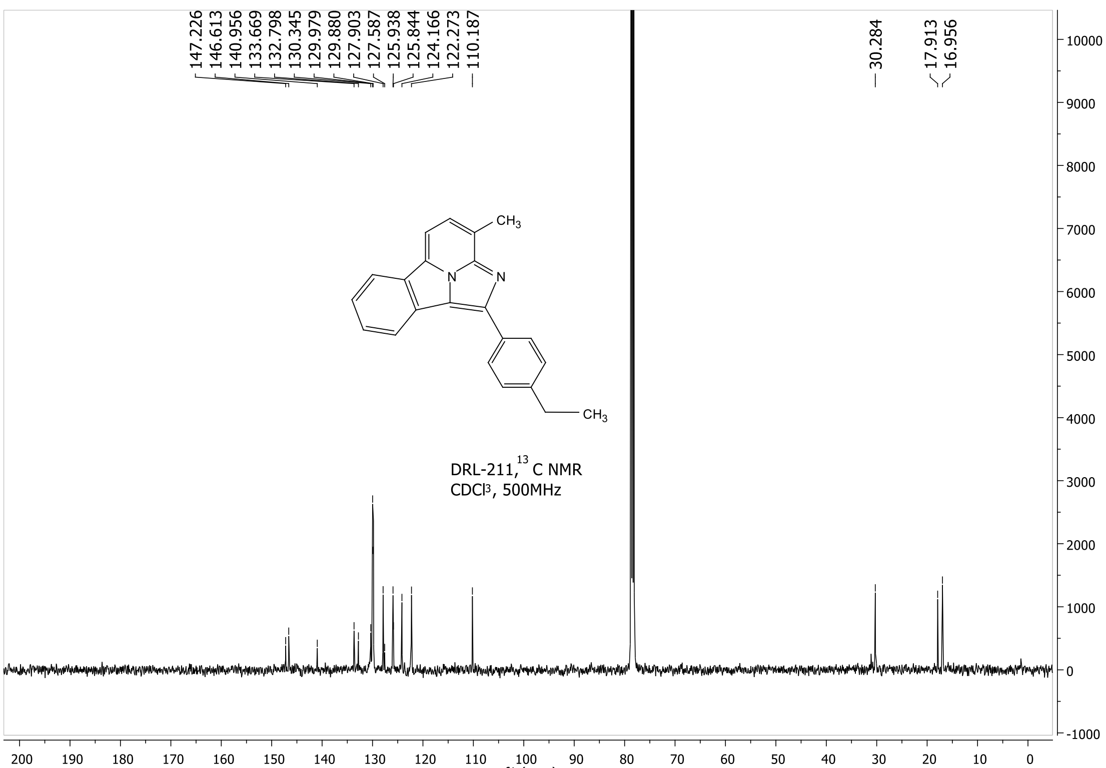
^{1}H NMR of 3k



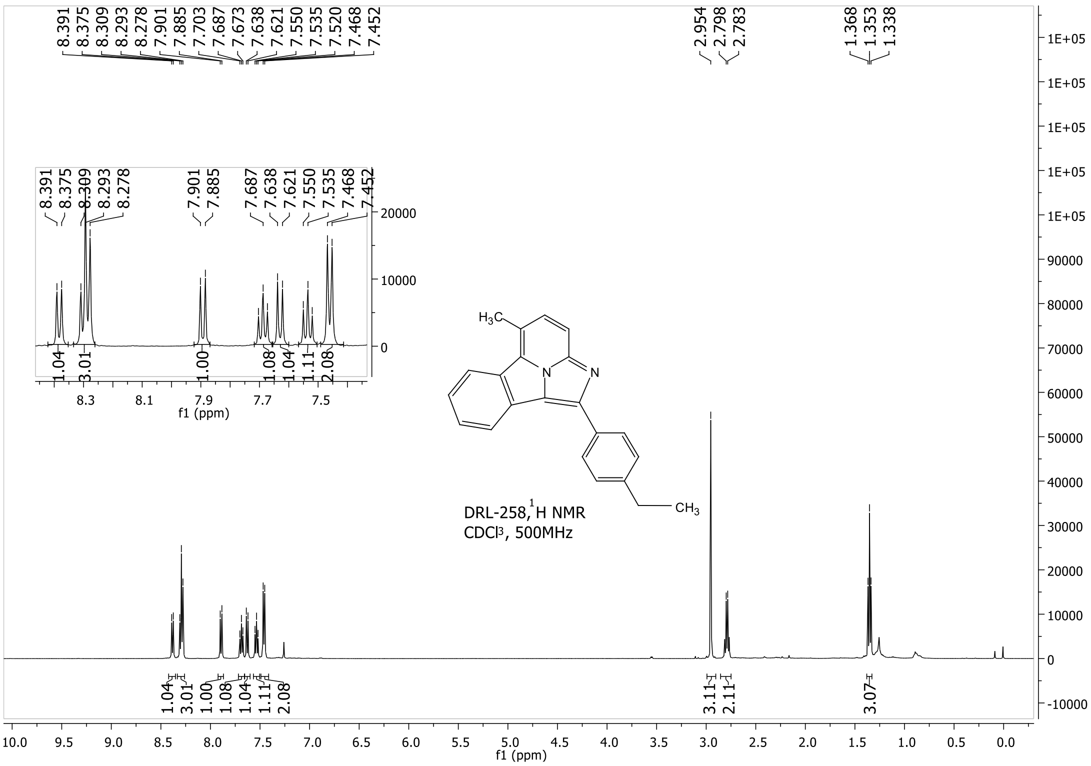
^{13}C NMR of 3k



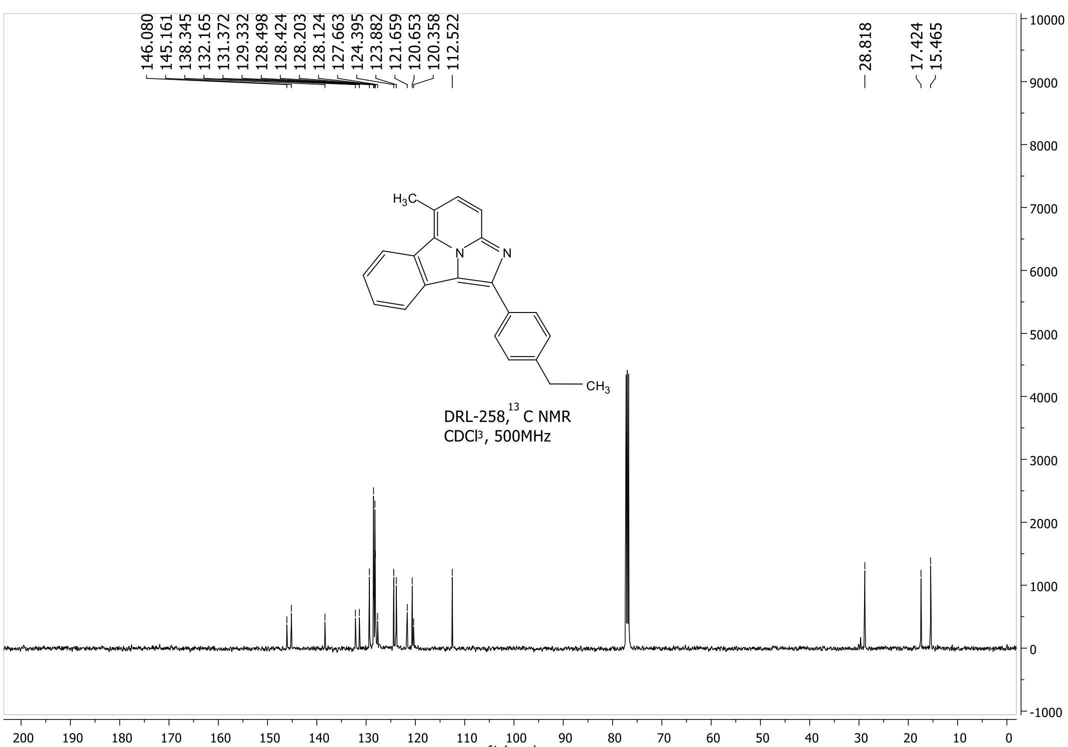
^{1}H NMR of 3l



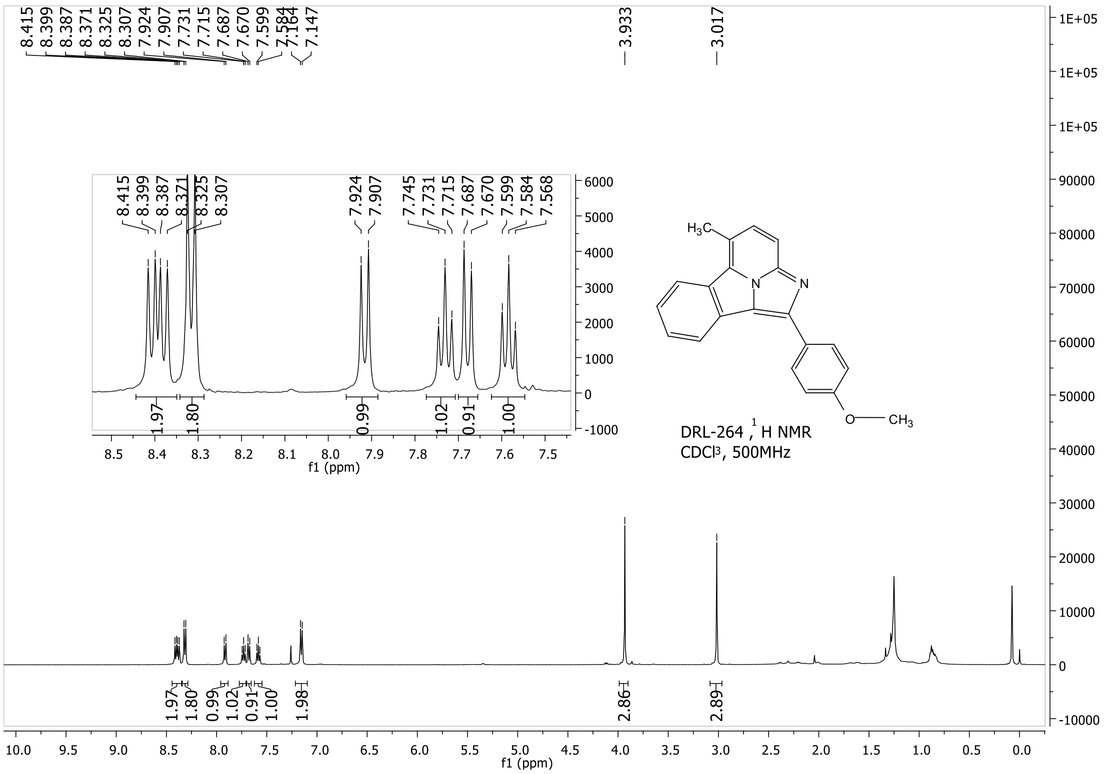
^{13}C NMR of 3l



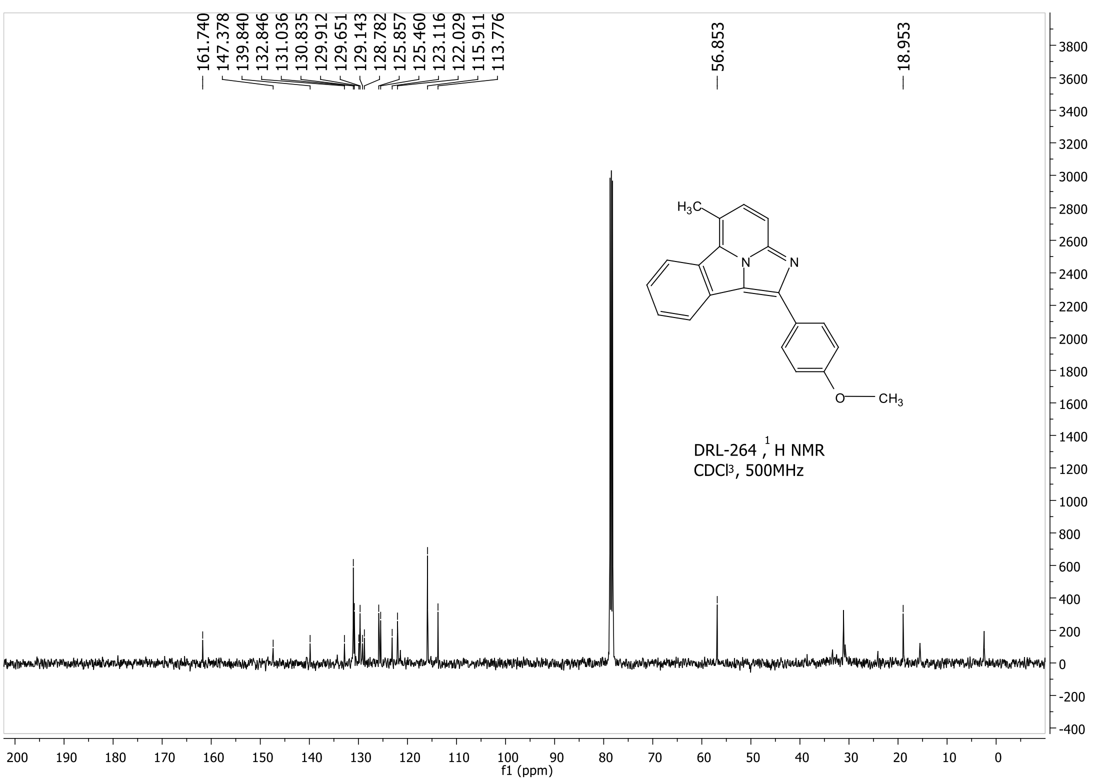
^{1}H NMR of 3m



^{13}C NMR of 3m



[1]H NMR of 3n



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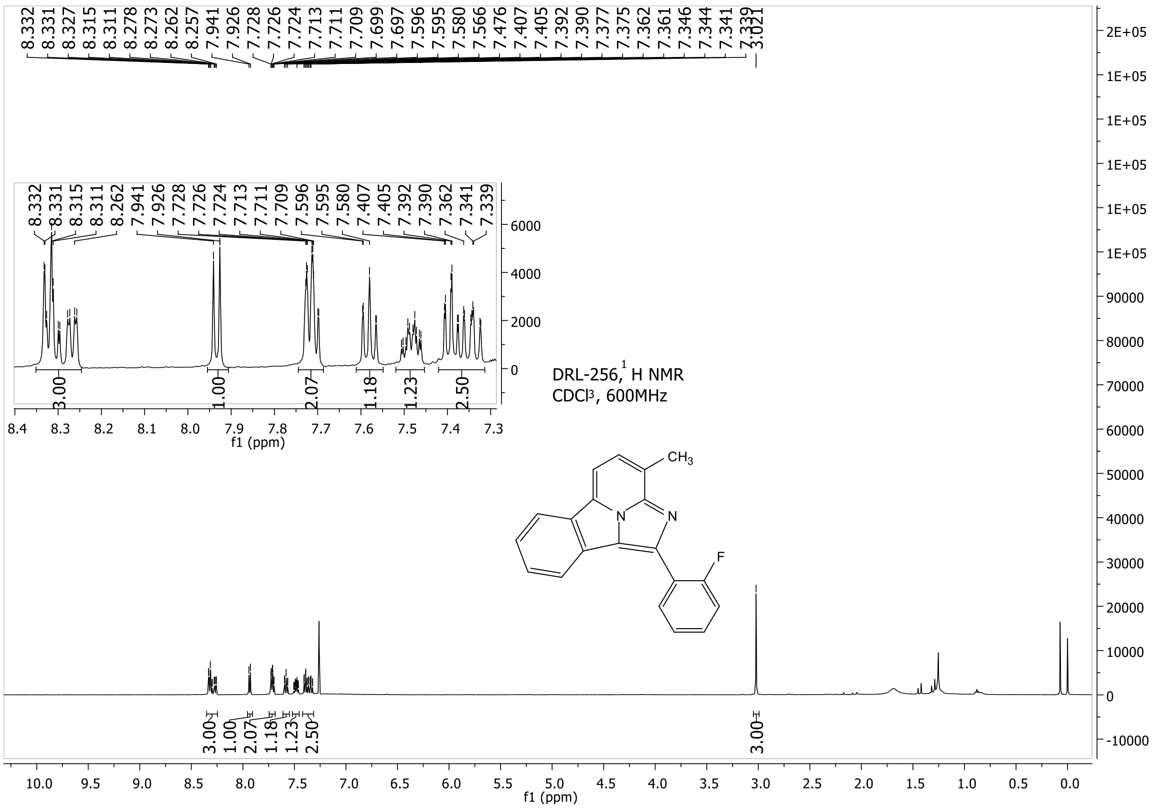
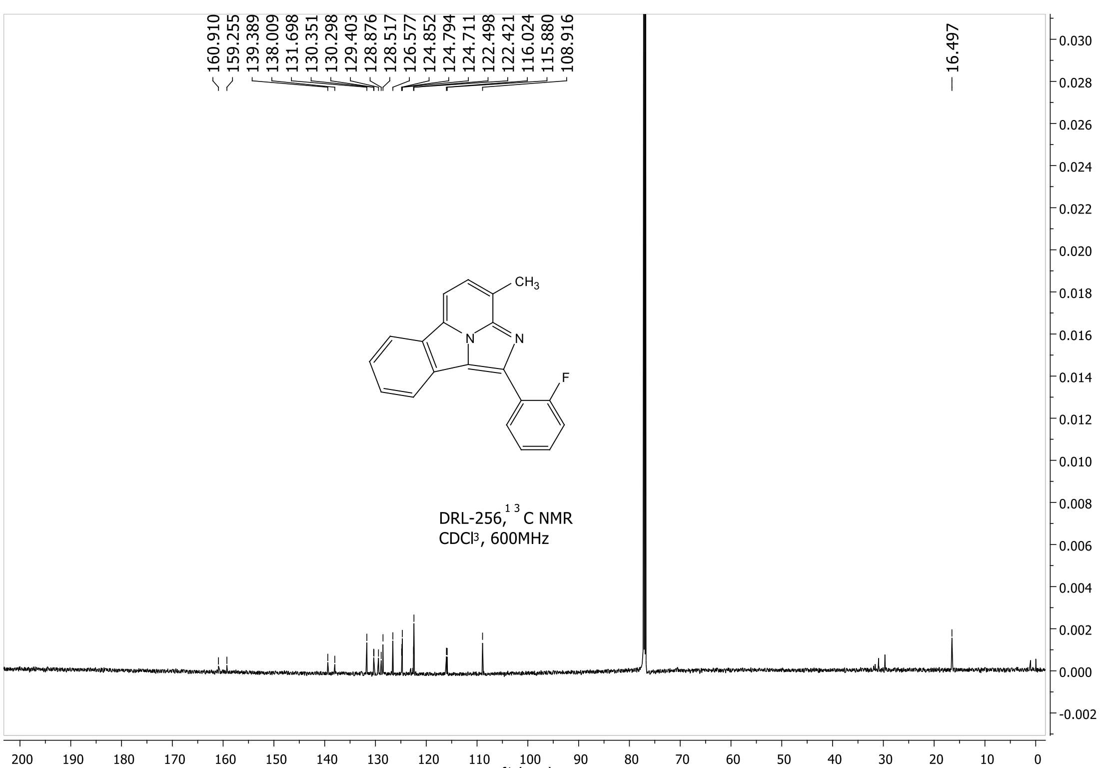
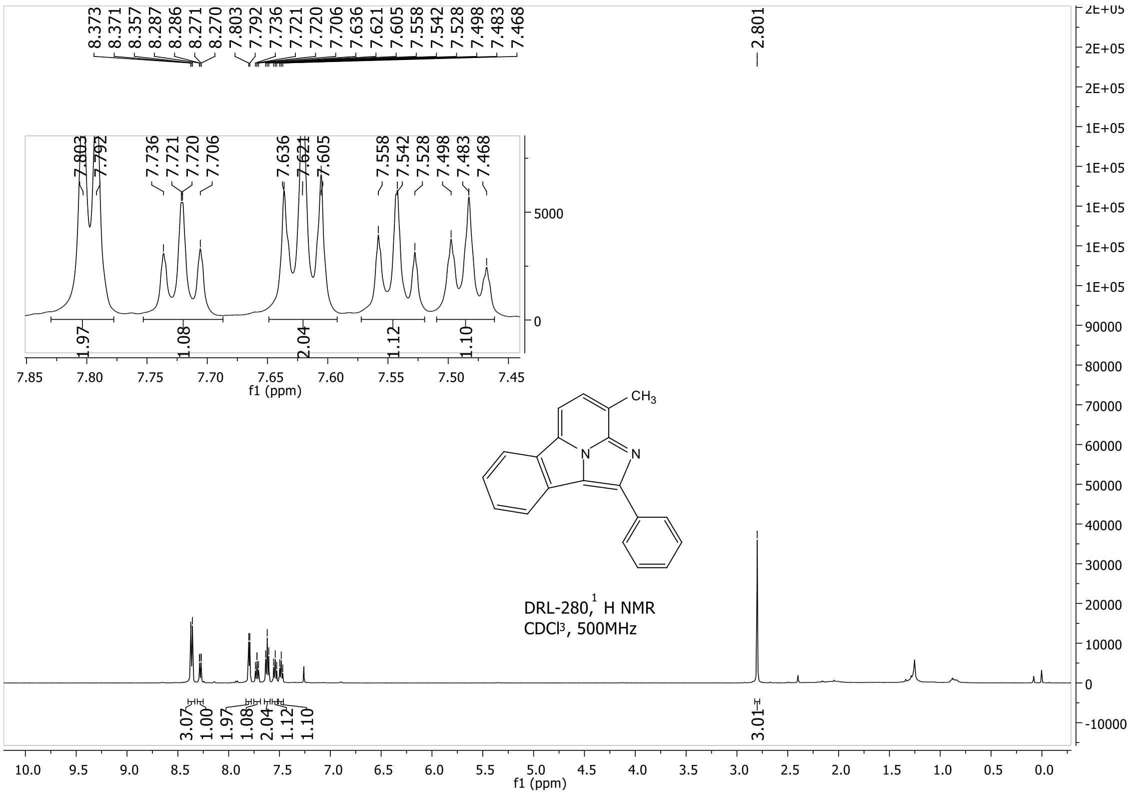


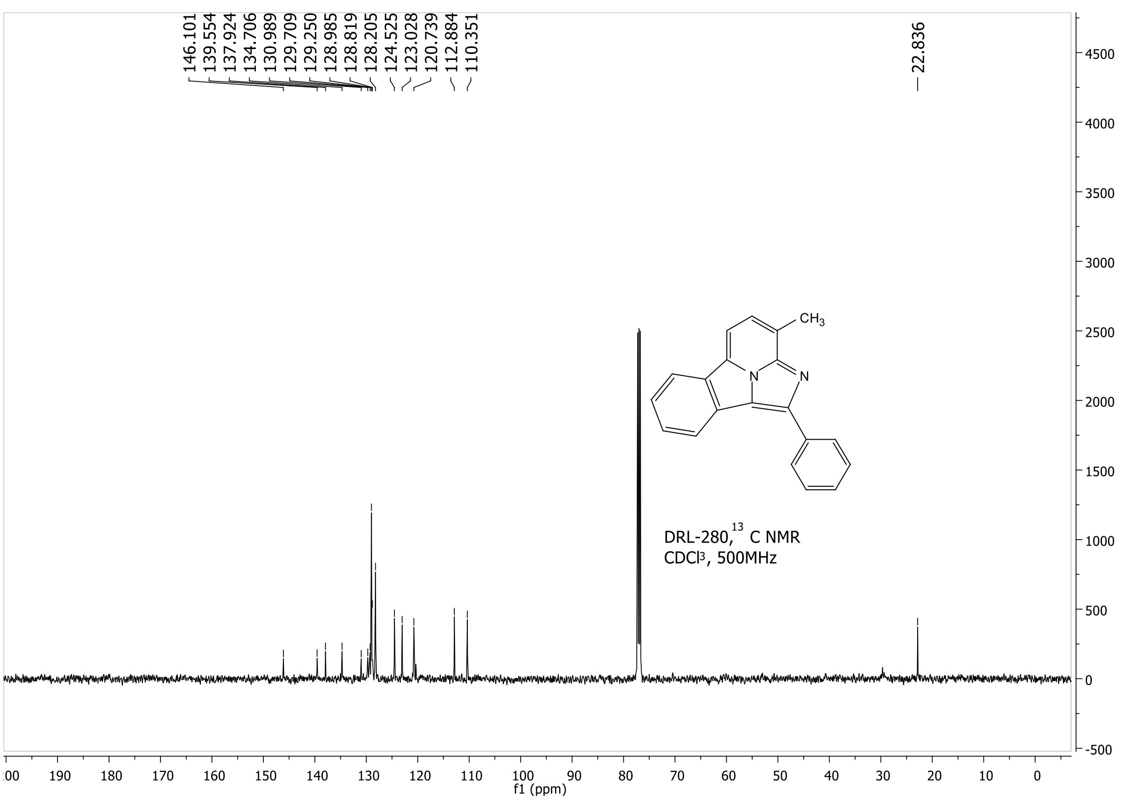
^{1}H NMR of 3o



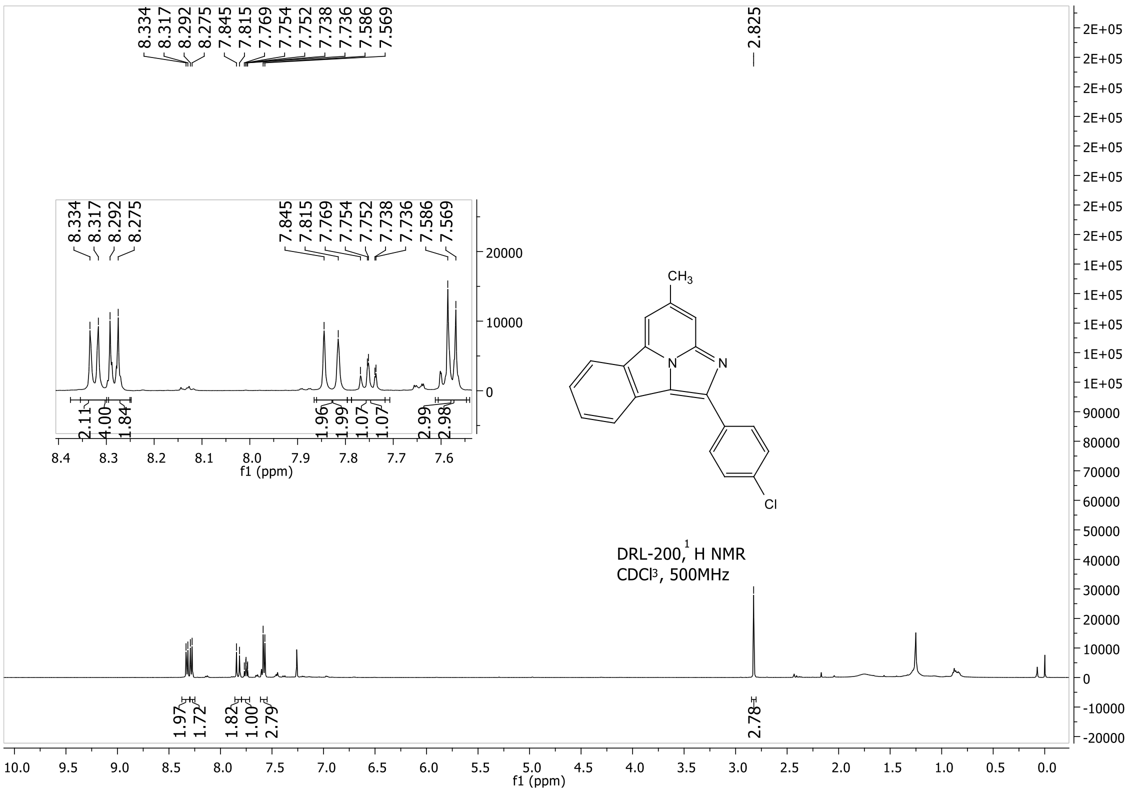
^{13}C NMR of 3o



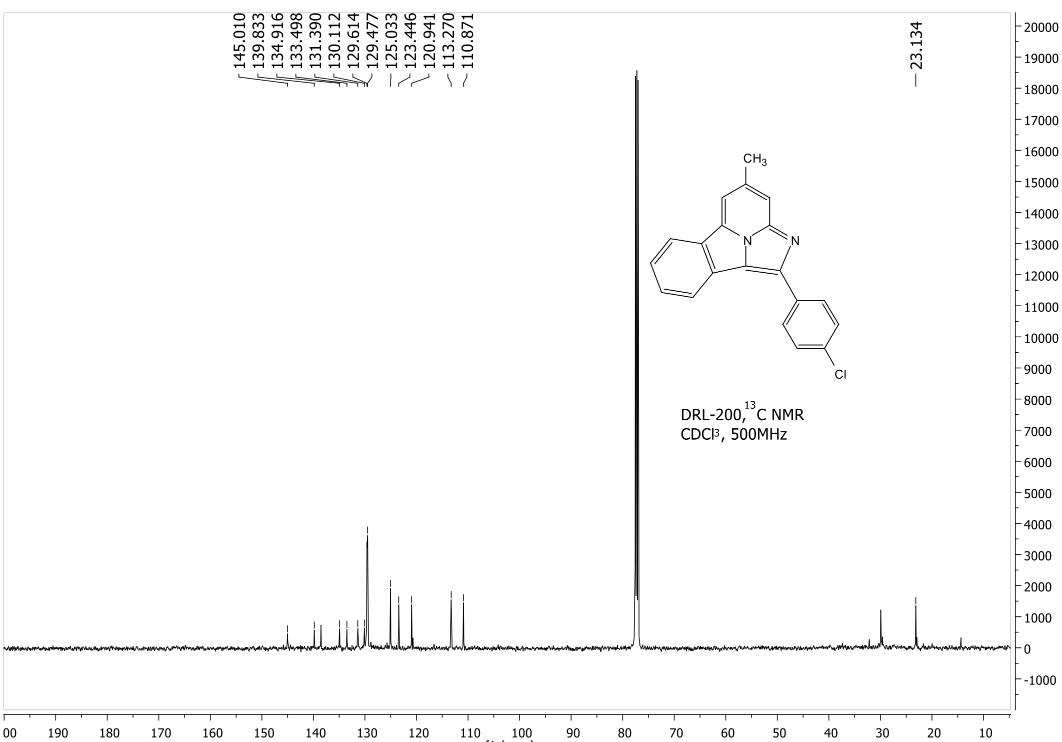
^{1}H NMR of 3p



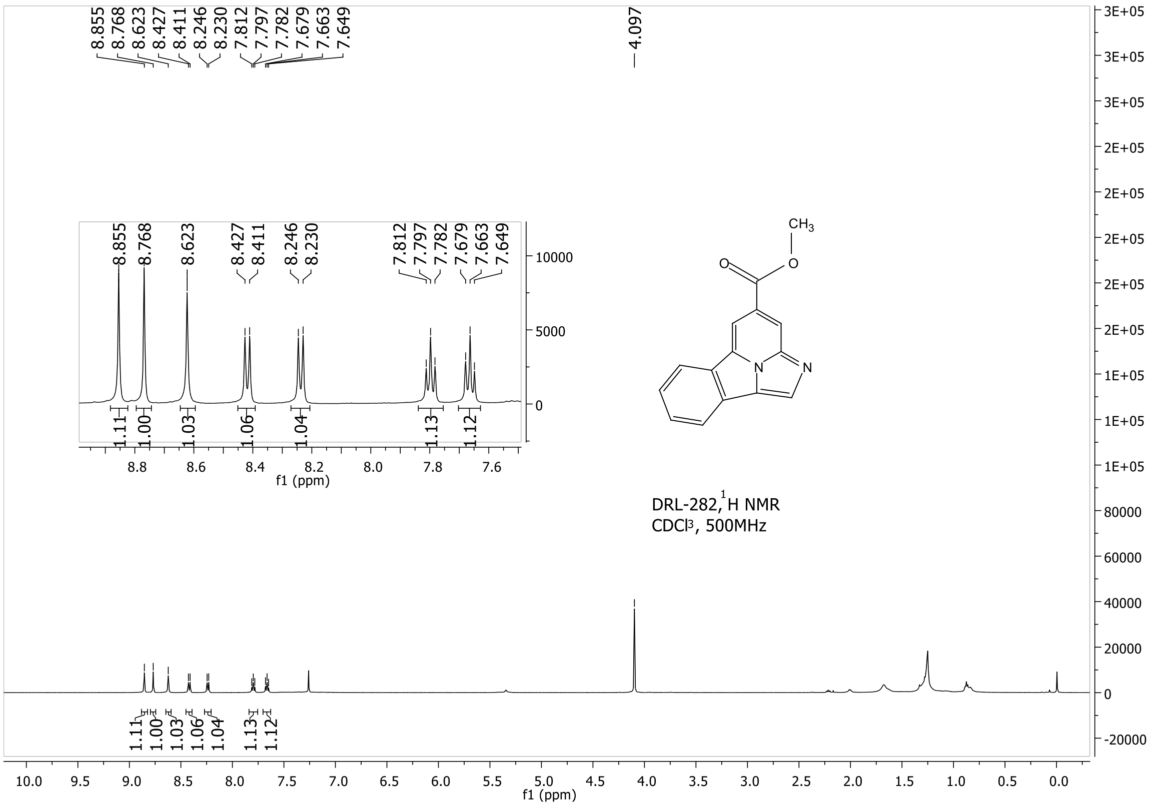
^{13}C NMR of 3p



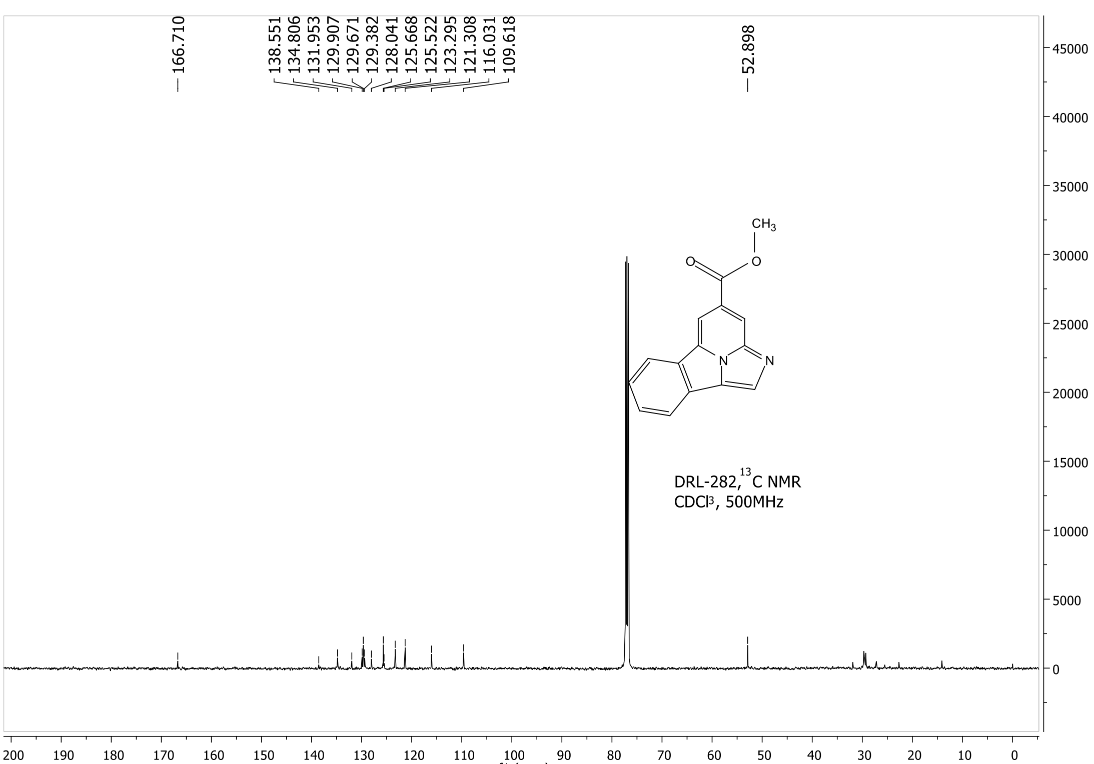
^{1}H NMR of 3q



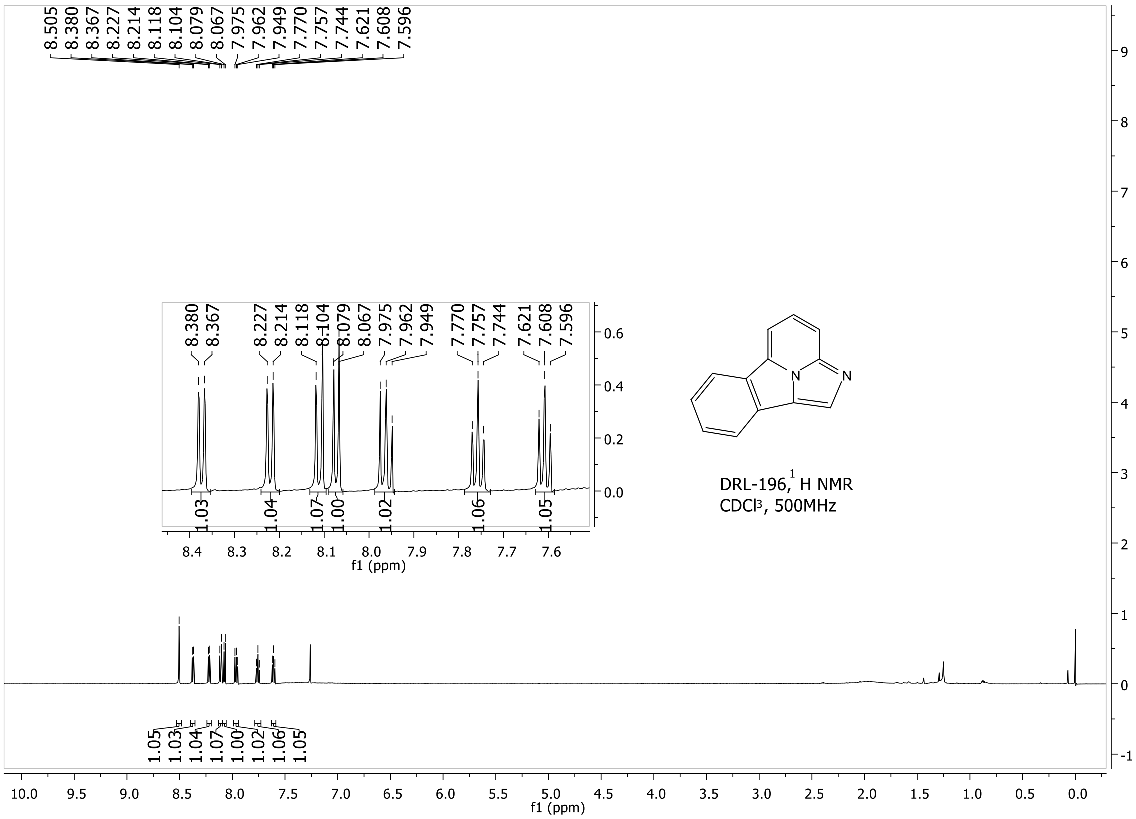
^{13}C NMR of 3q



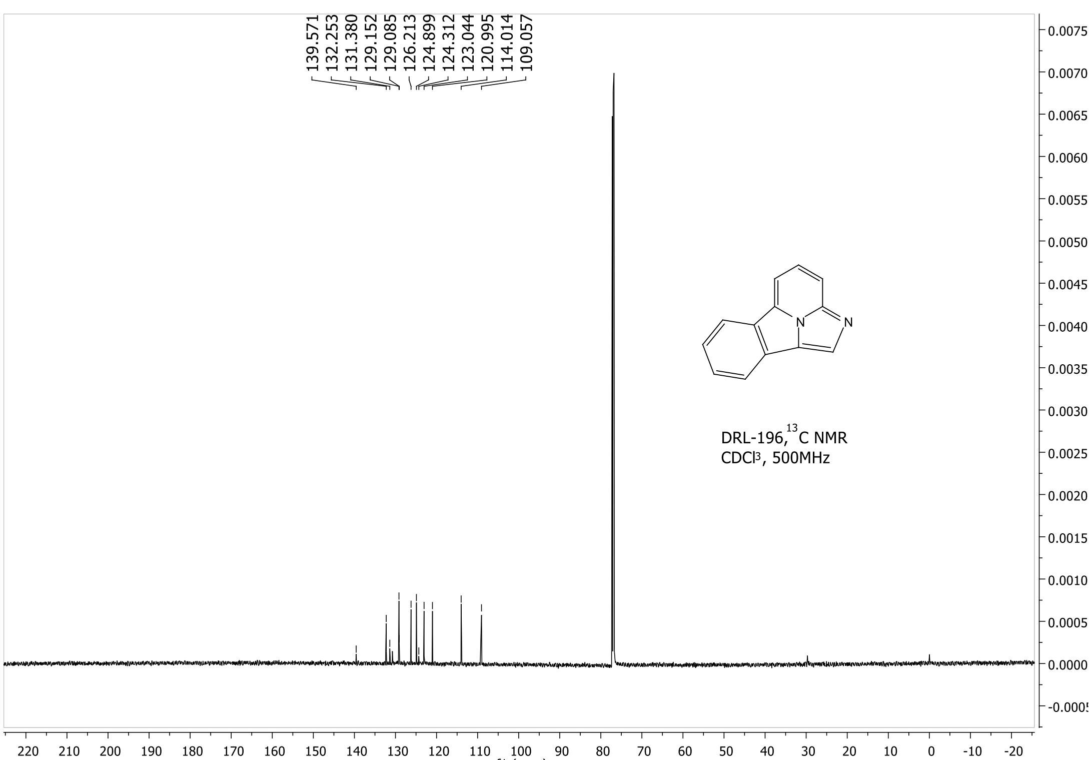
^{1}H NMR of 3r



^{13}C NMR of 3r



^{1}H NMR of 3s



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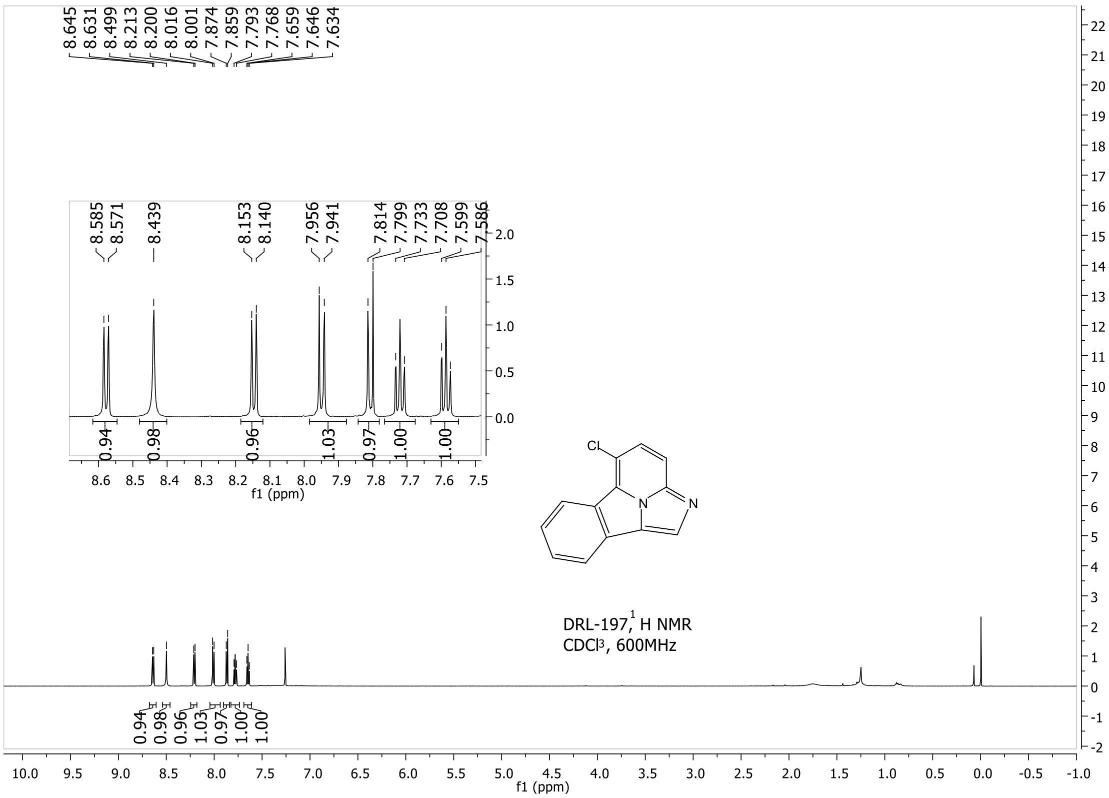
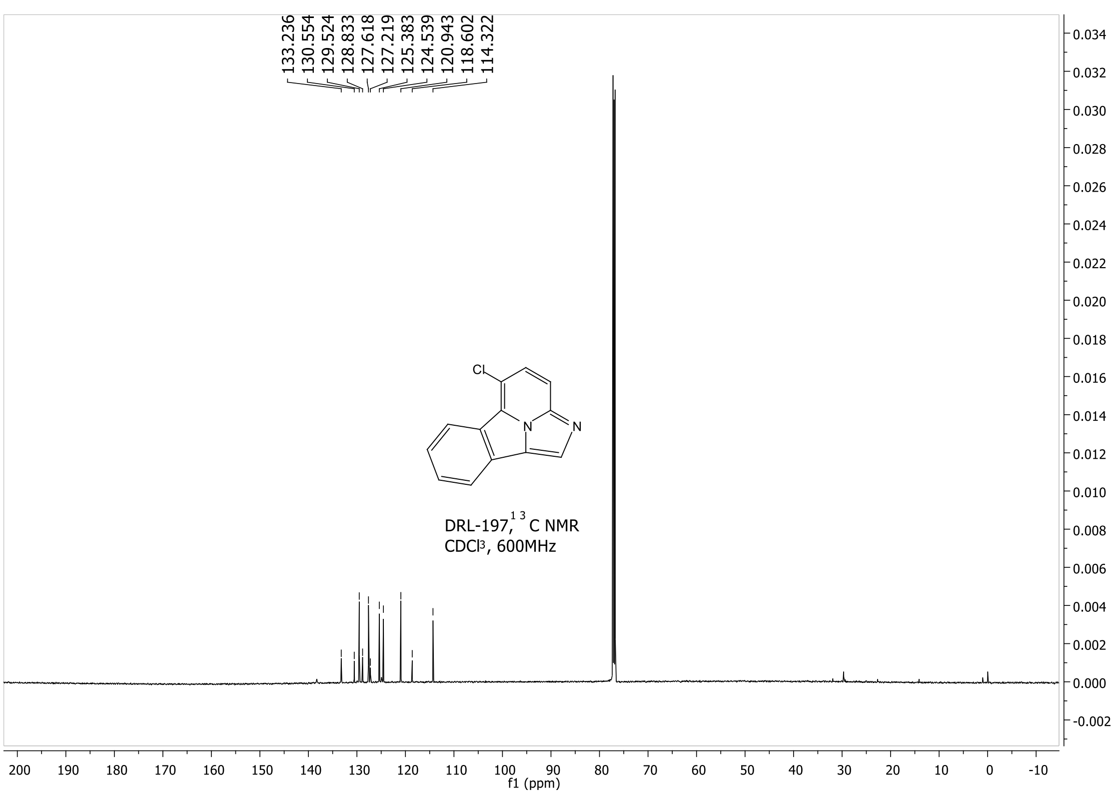


^{1}H NMR of 3t



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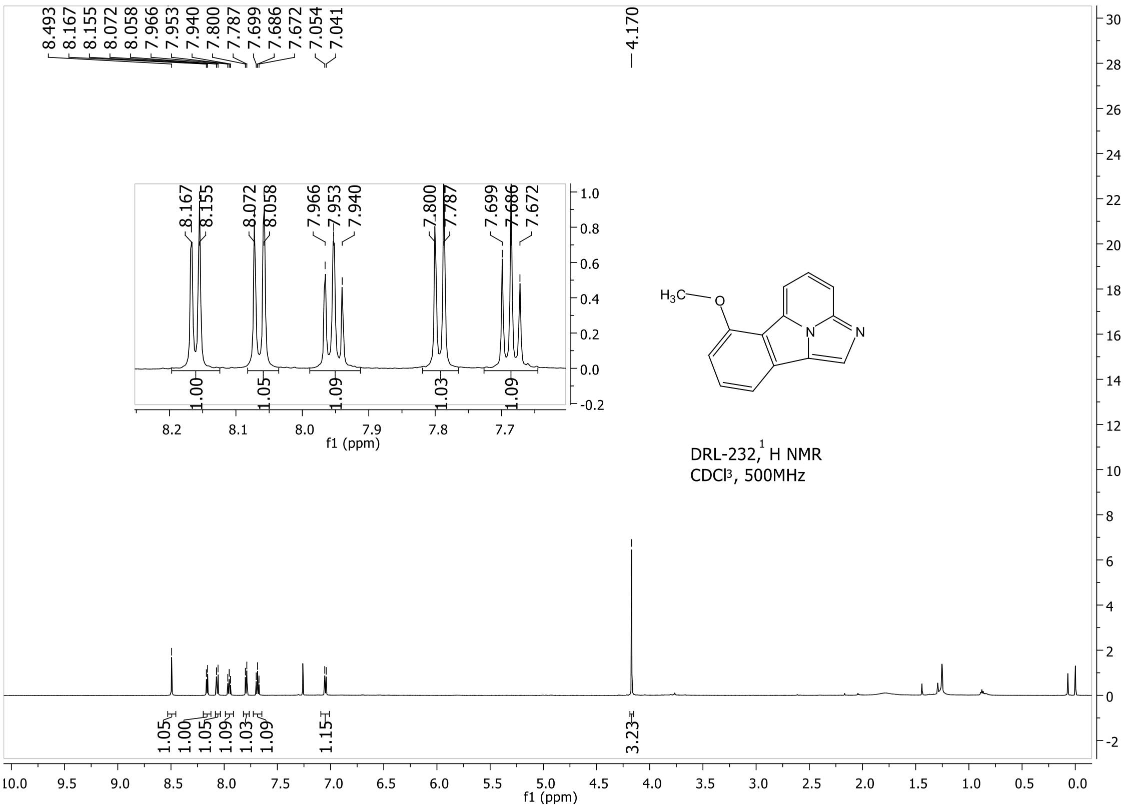

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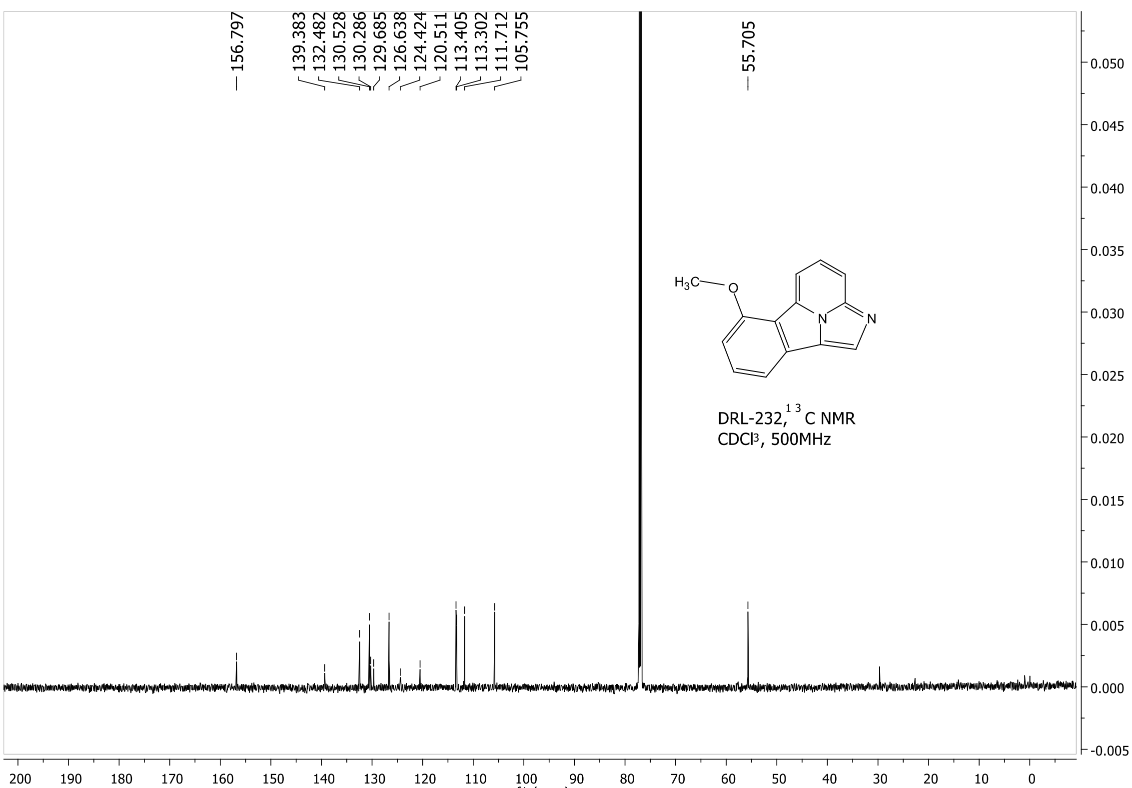
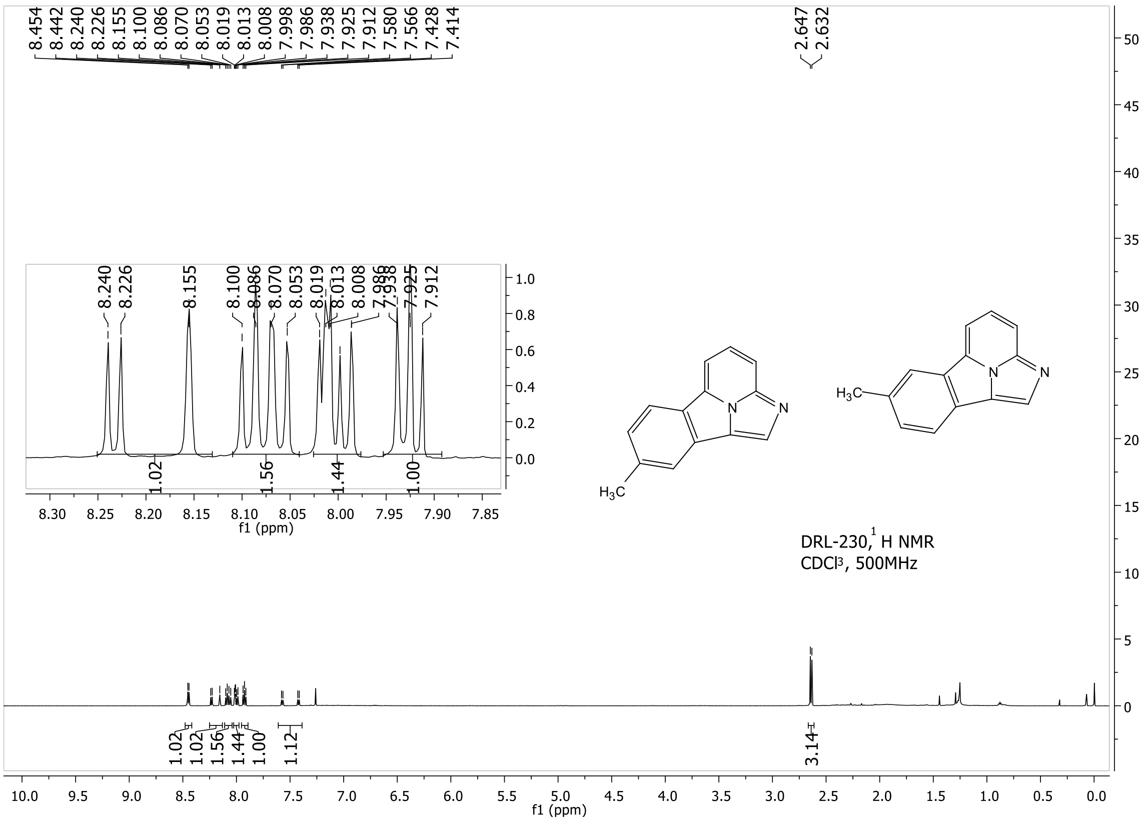


[13]C NMR of 3u



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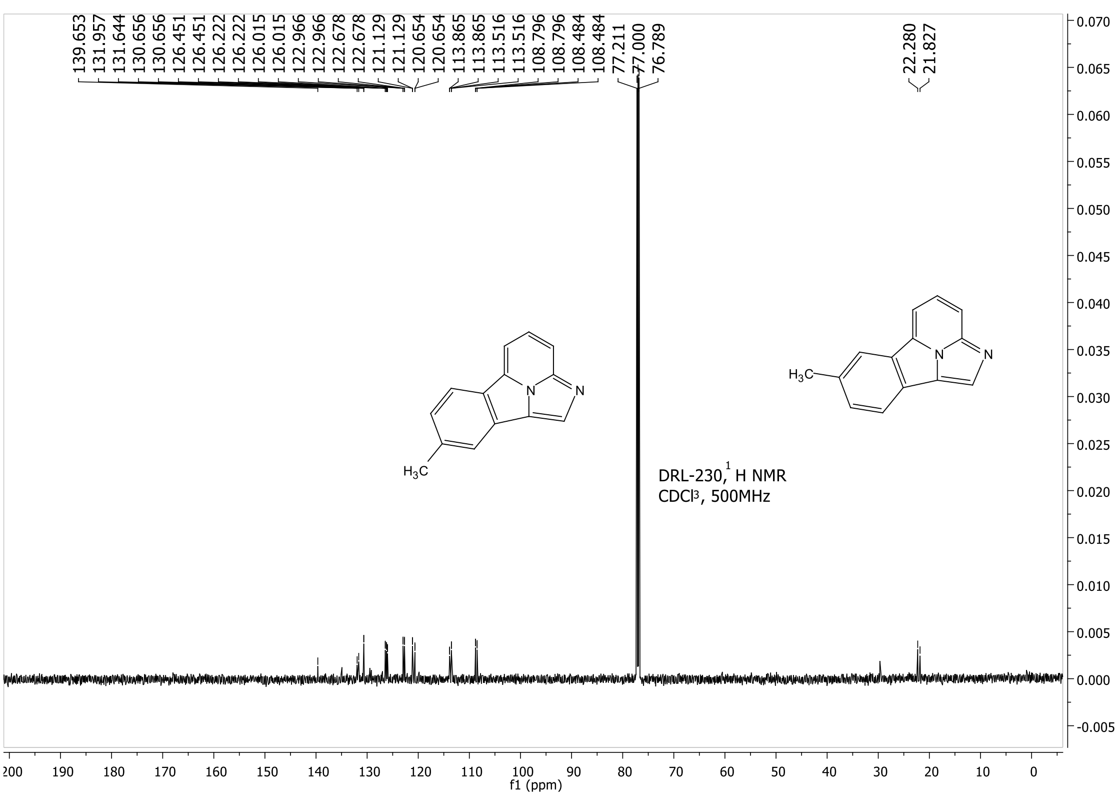
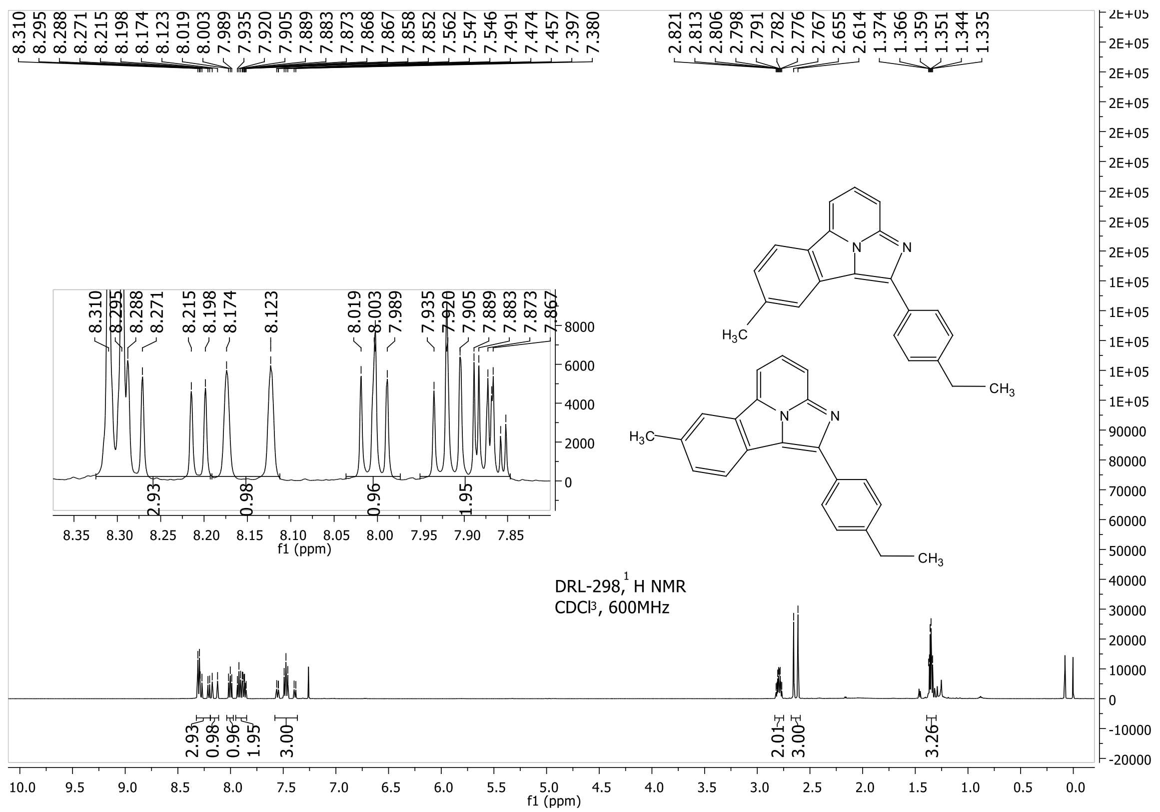
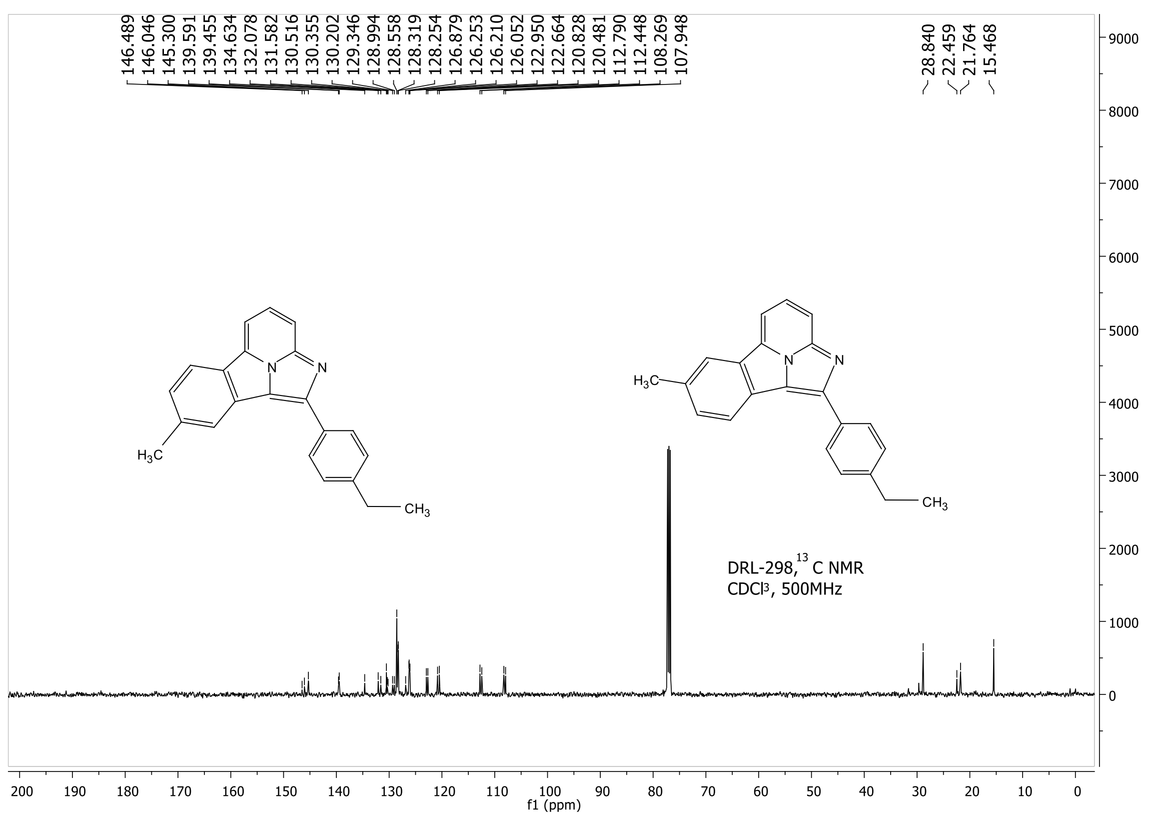


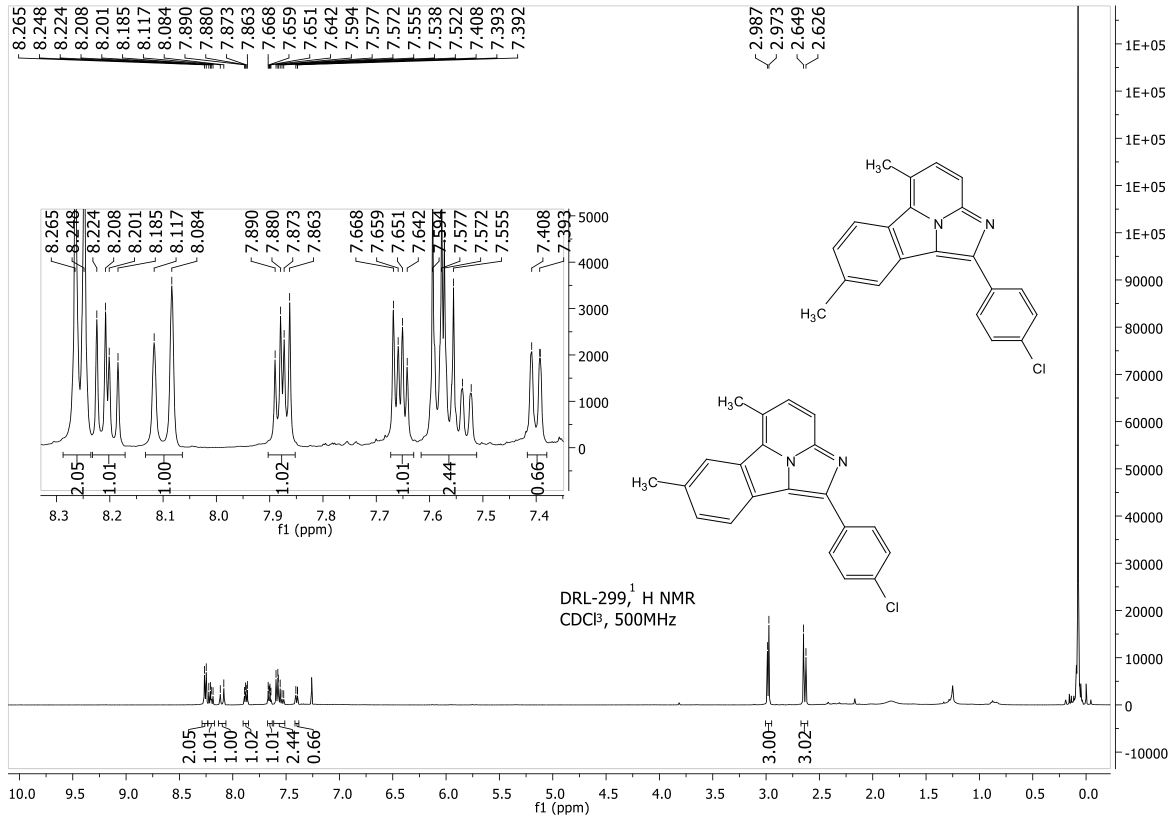
^{13}C NMR of 3v



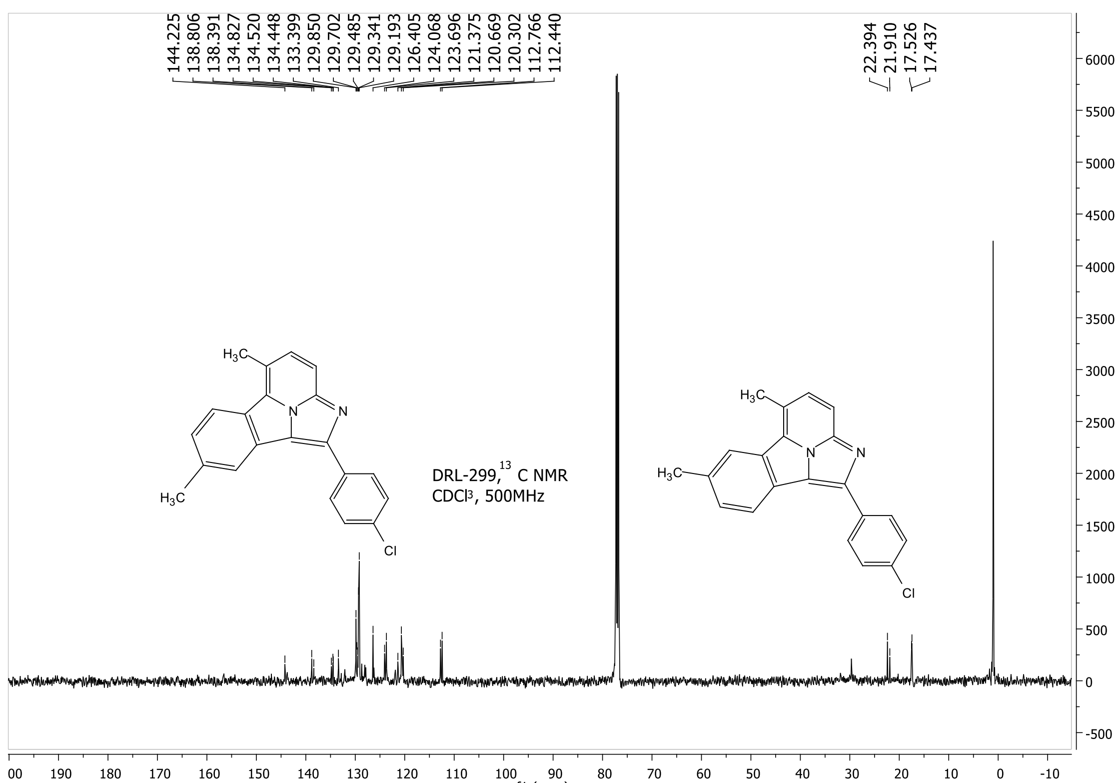
^{1}H NMR of 3w



^{13}C NMR of 3w



^{1}H NMR of 3x



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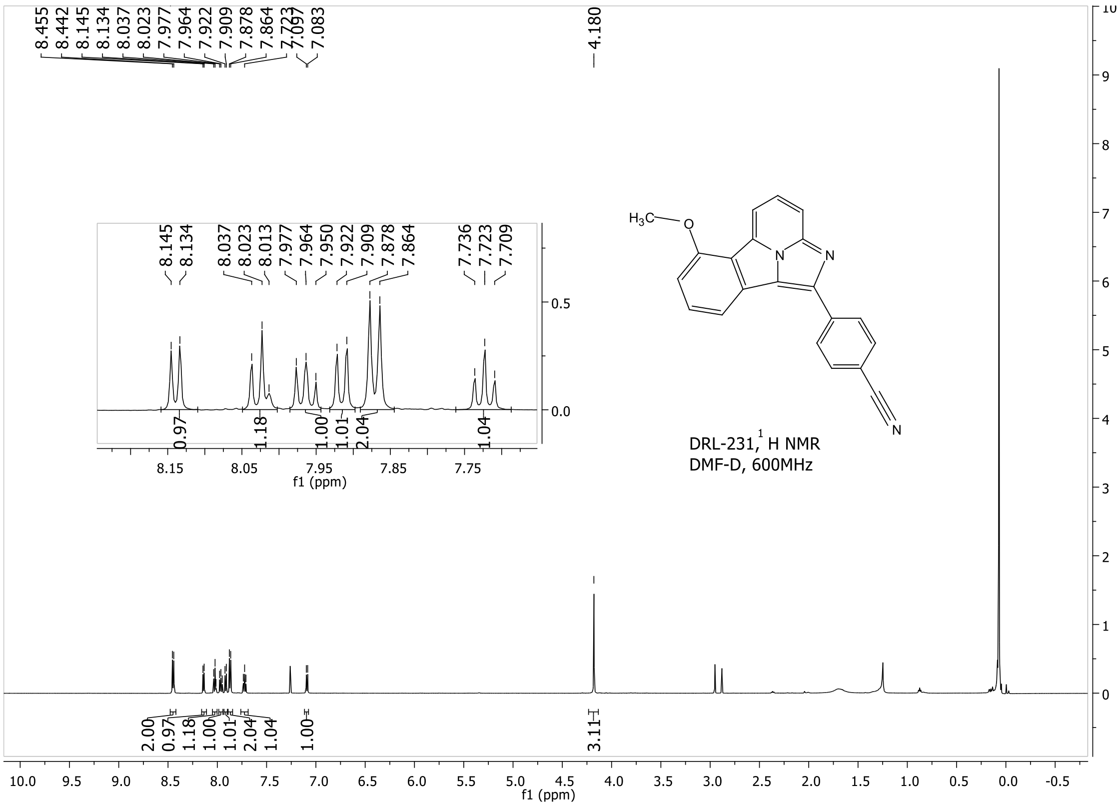

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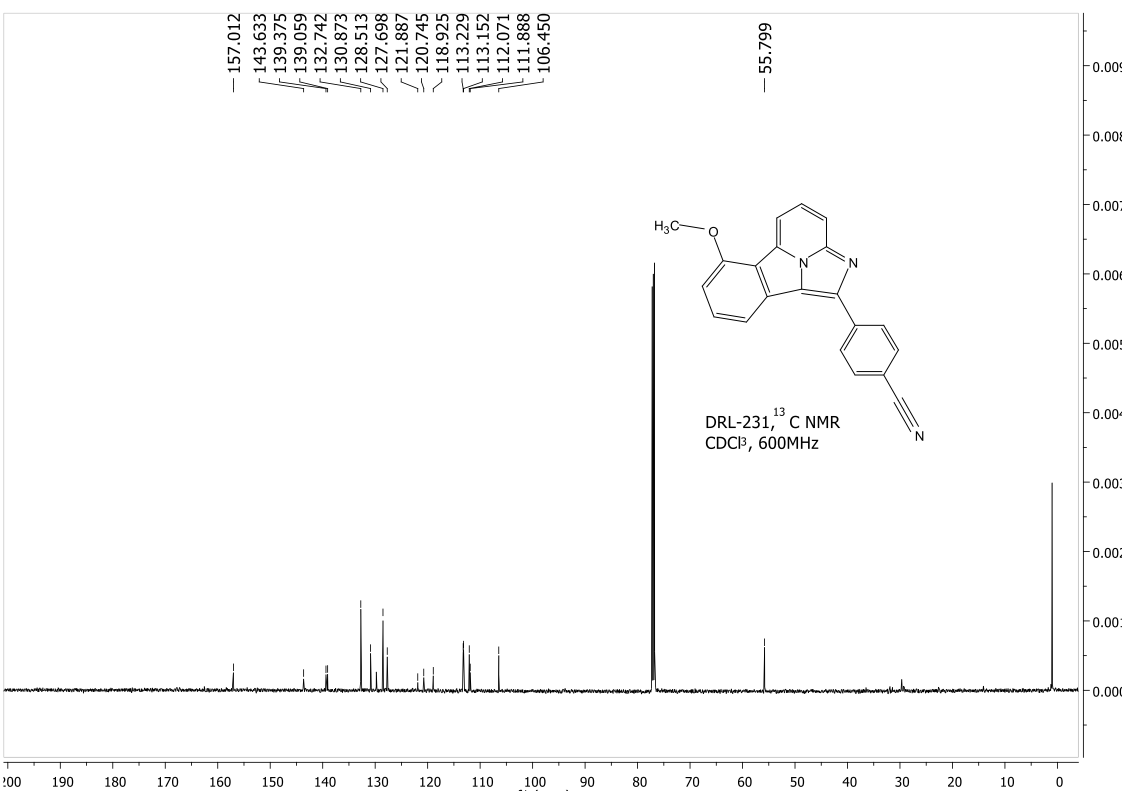

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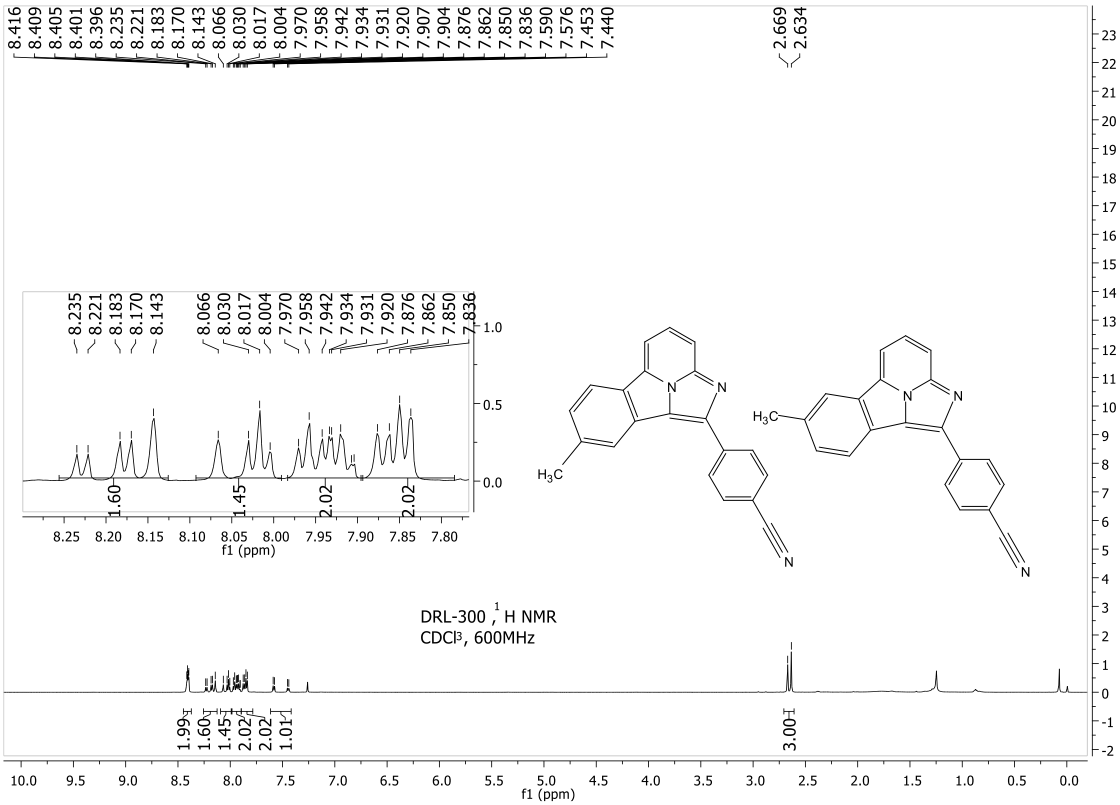
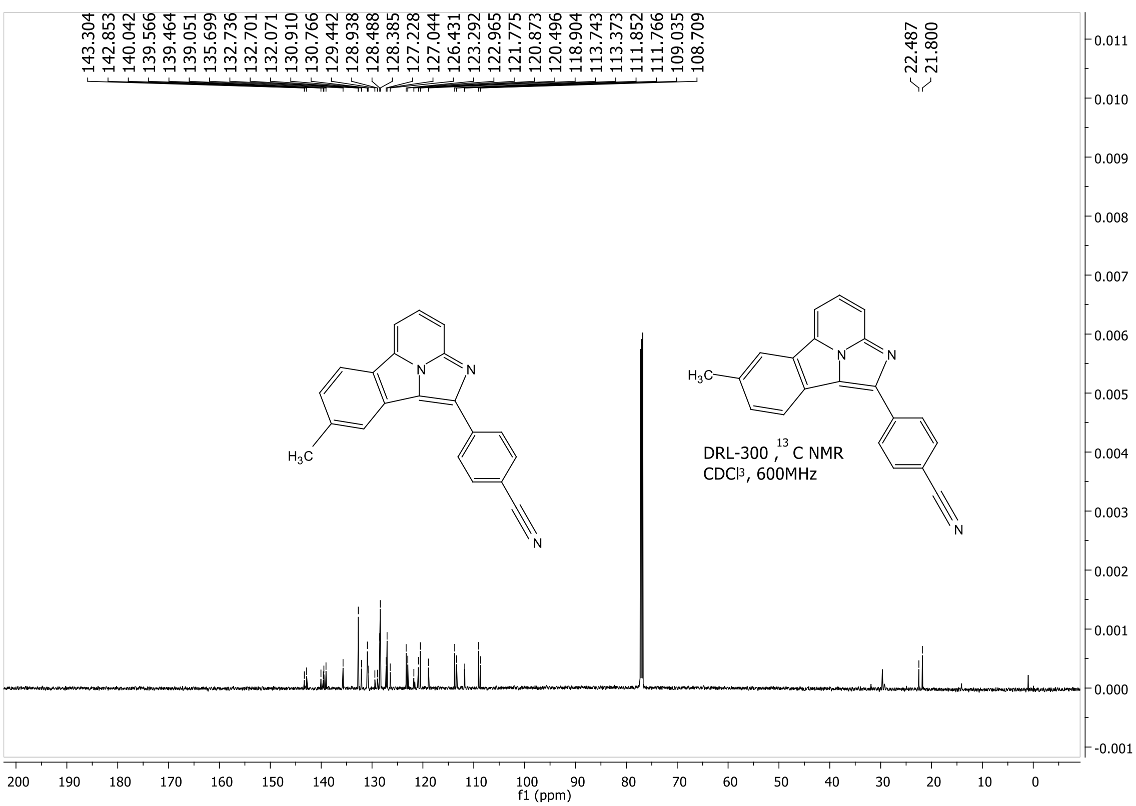


^{1}H NMR of 3z



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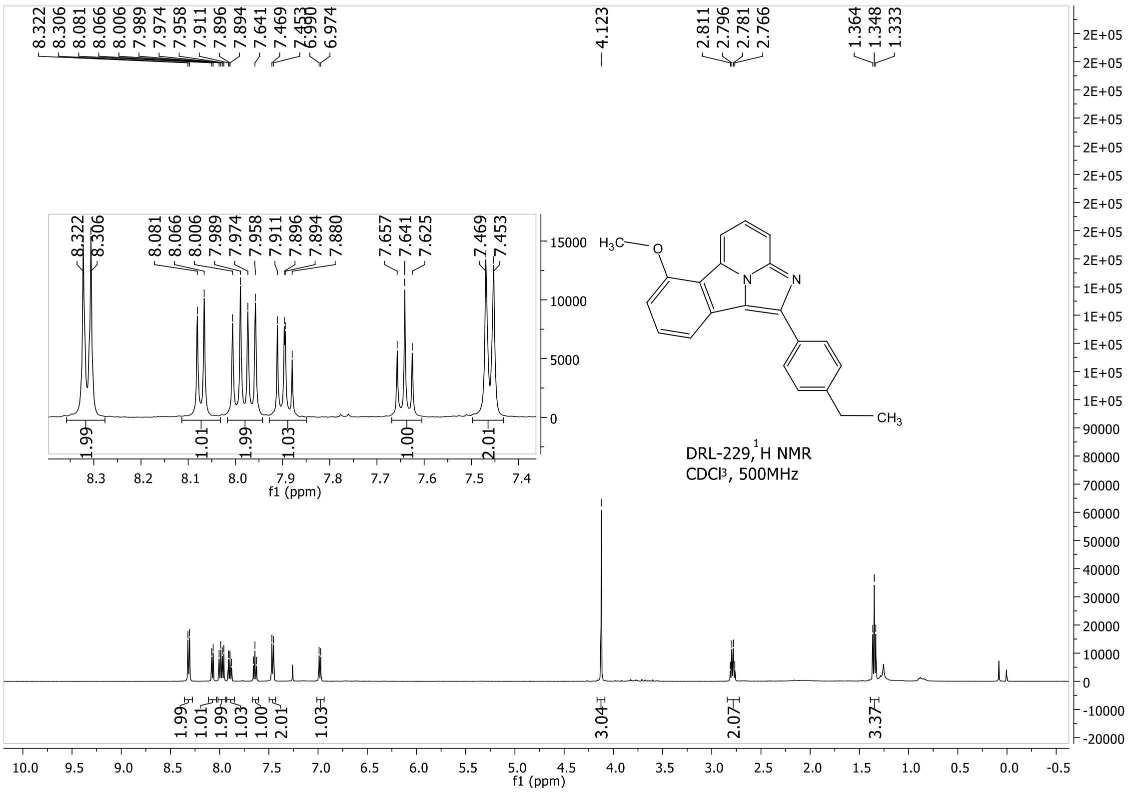
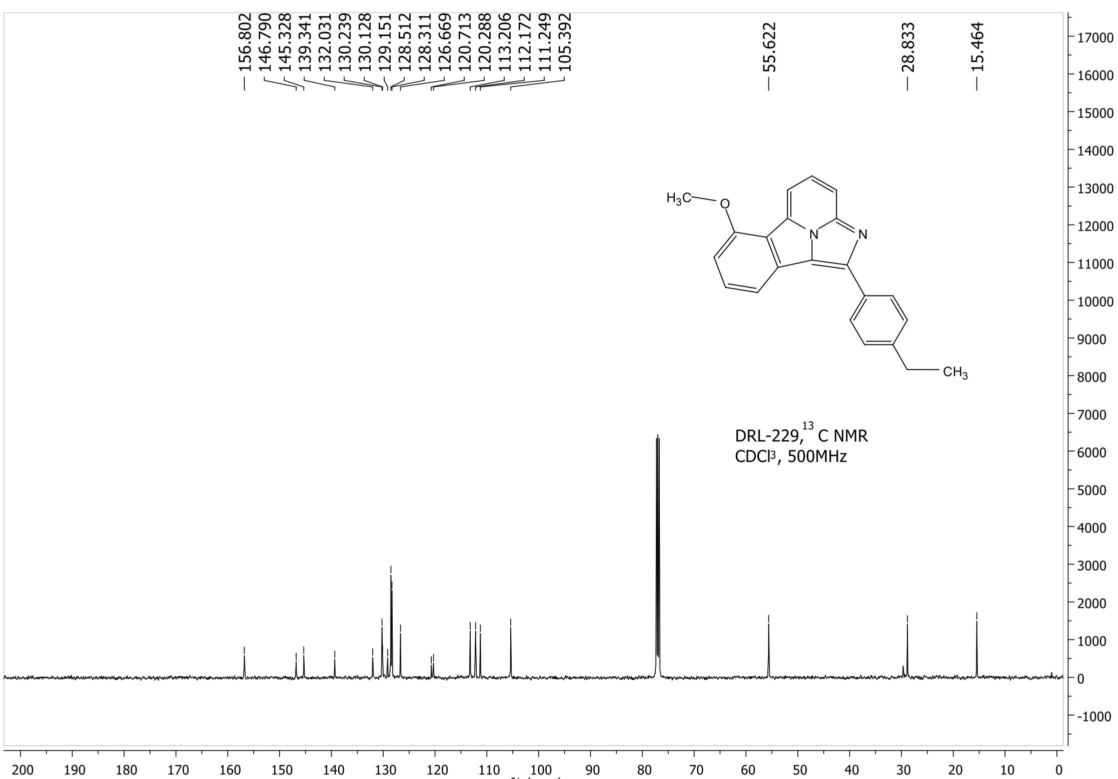
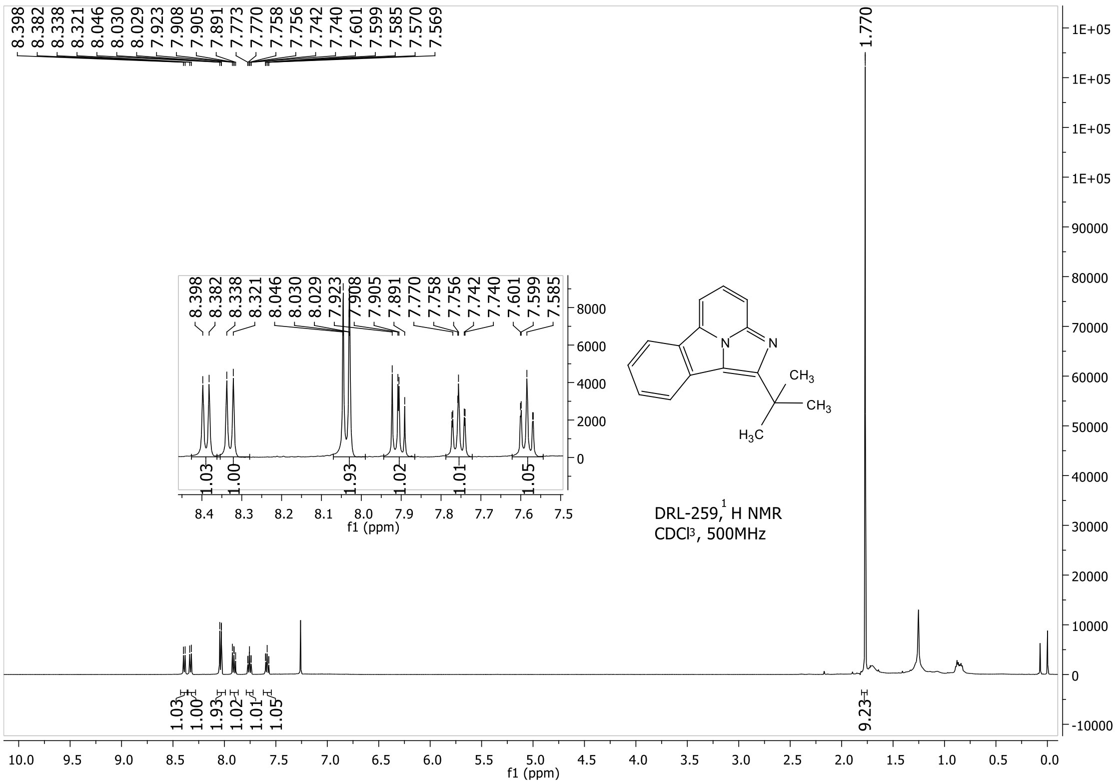


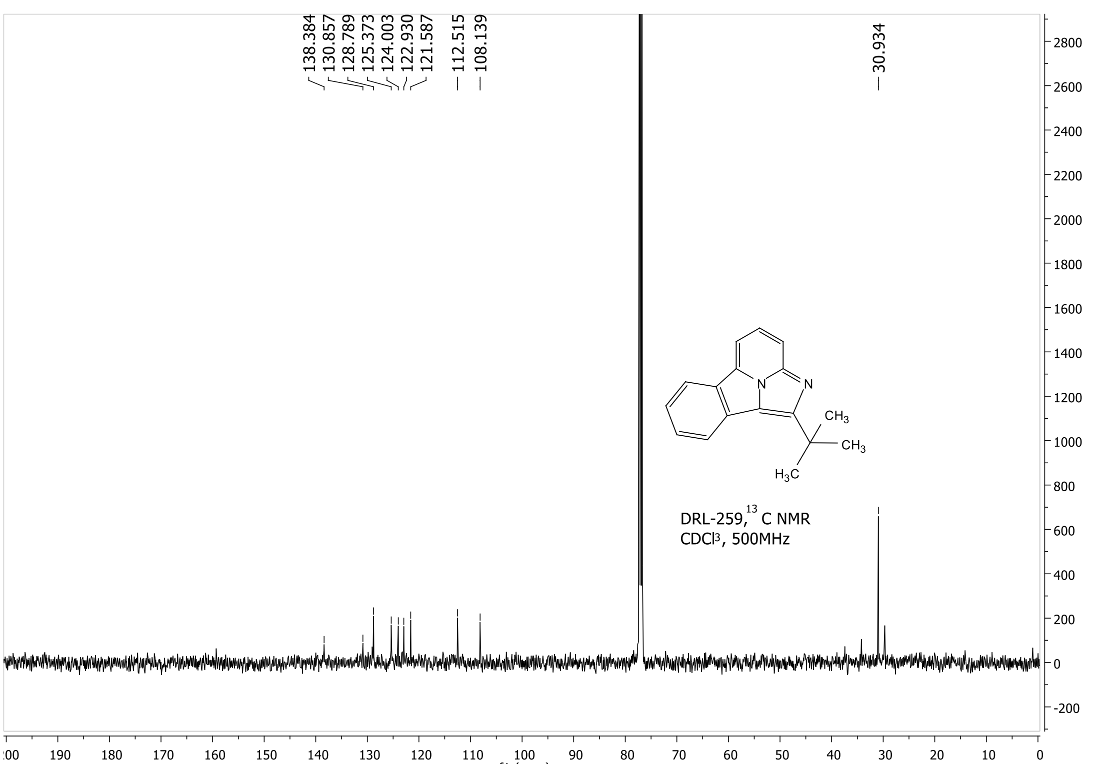
^{1}H NMR of 3aa



^{13}C NMR of 3aa



[1]H NMR of 3ab



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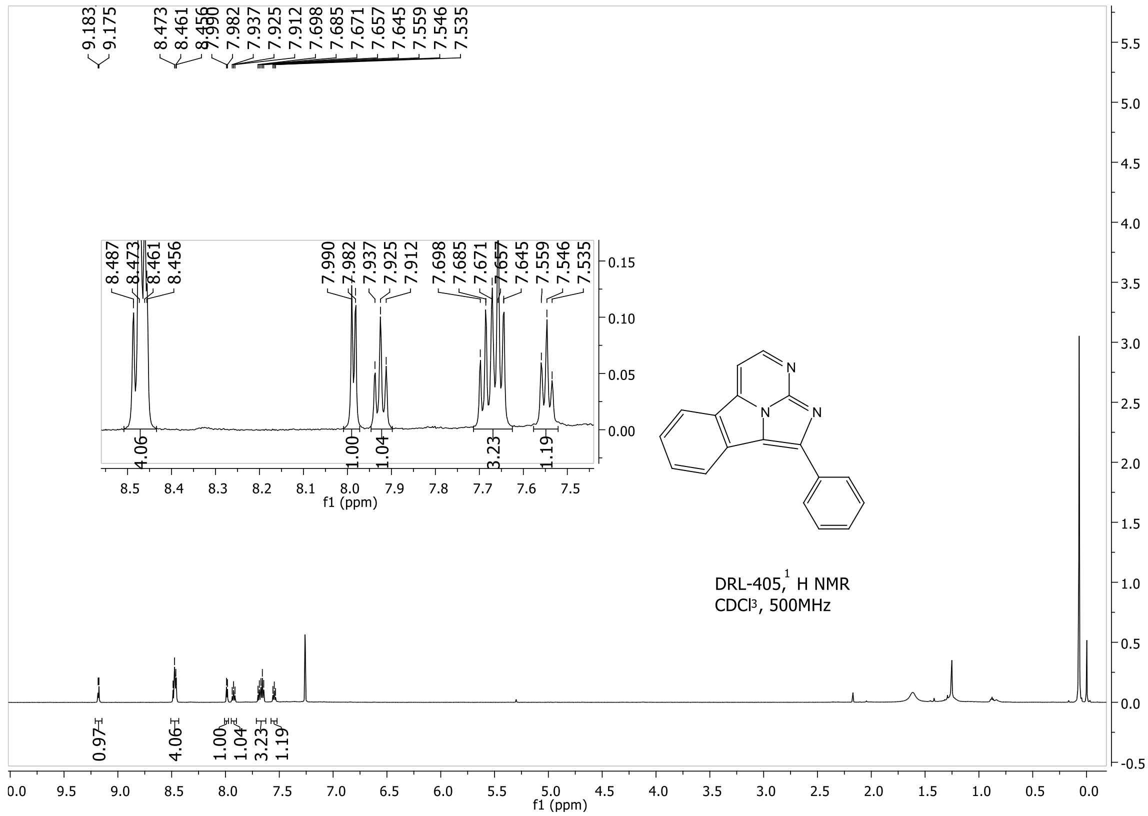

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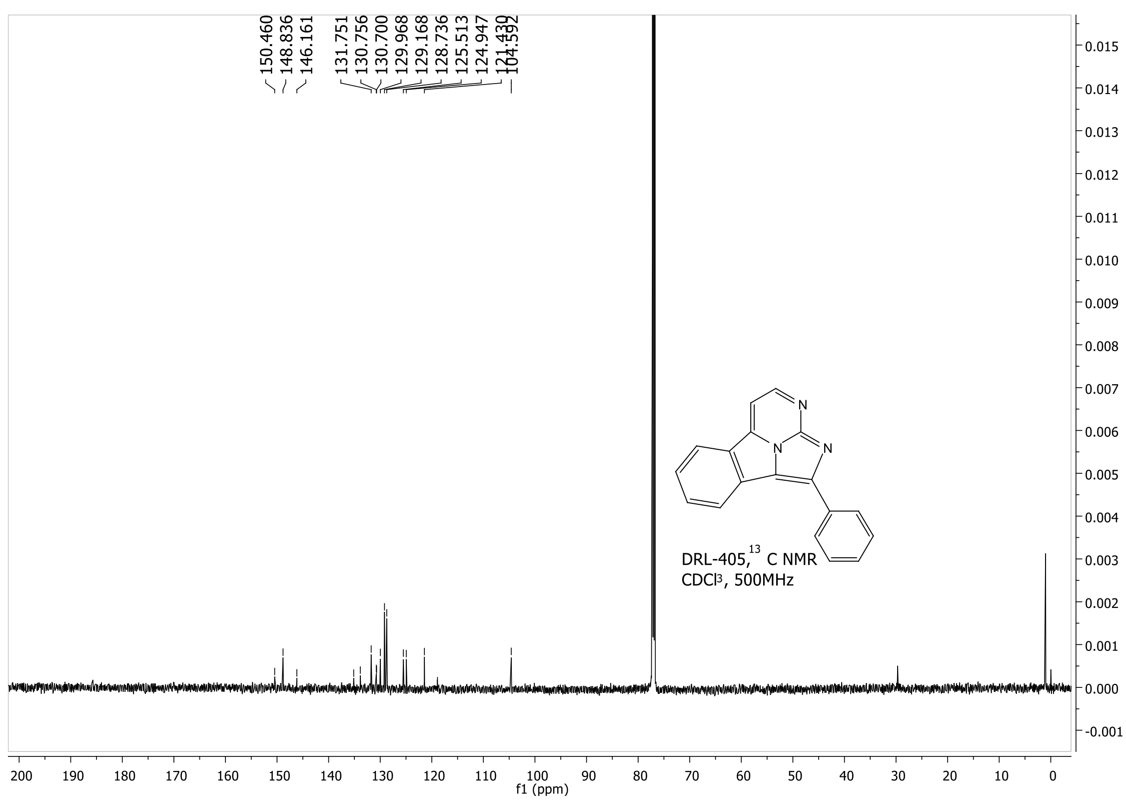

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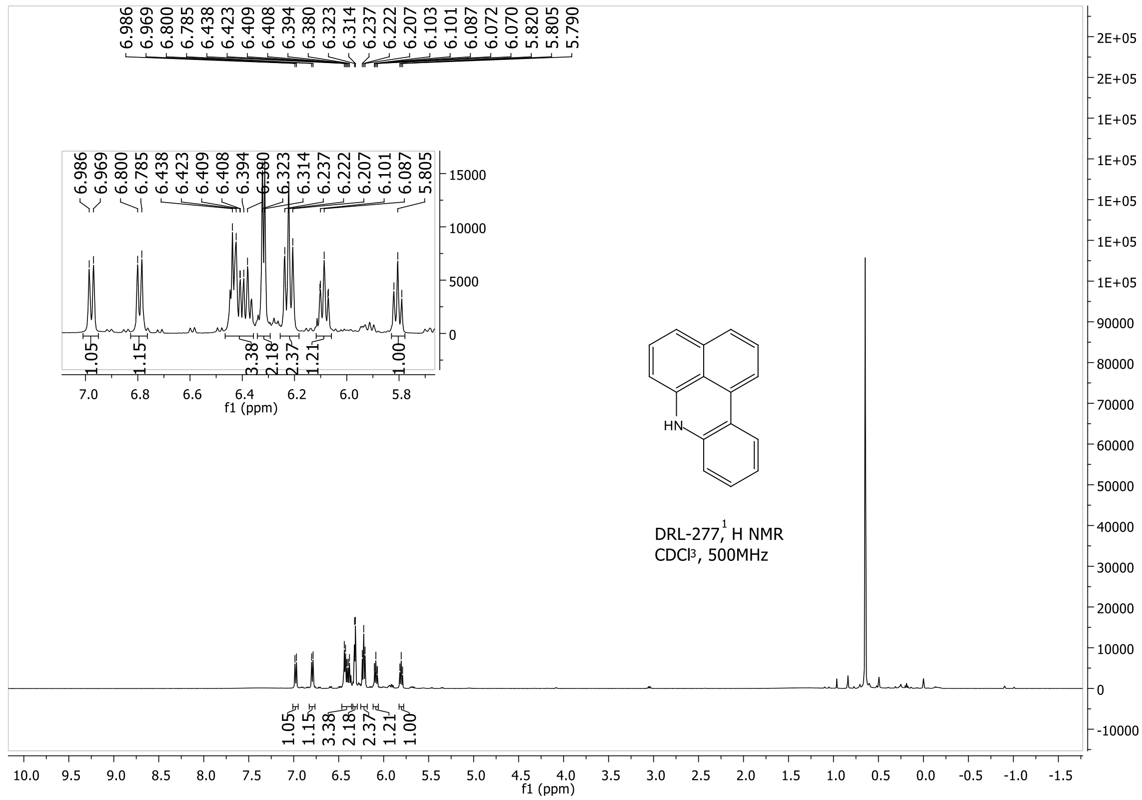

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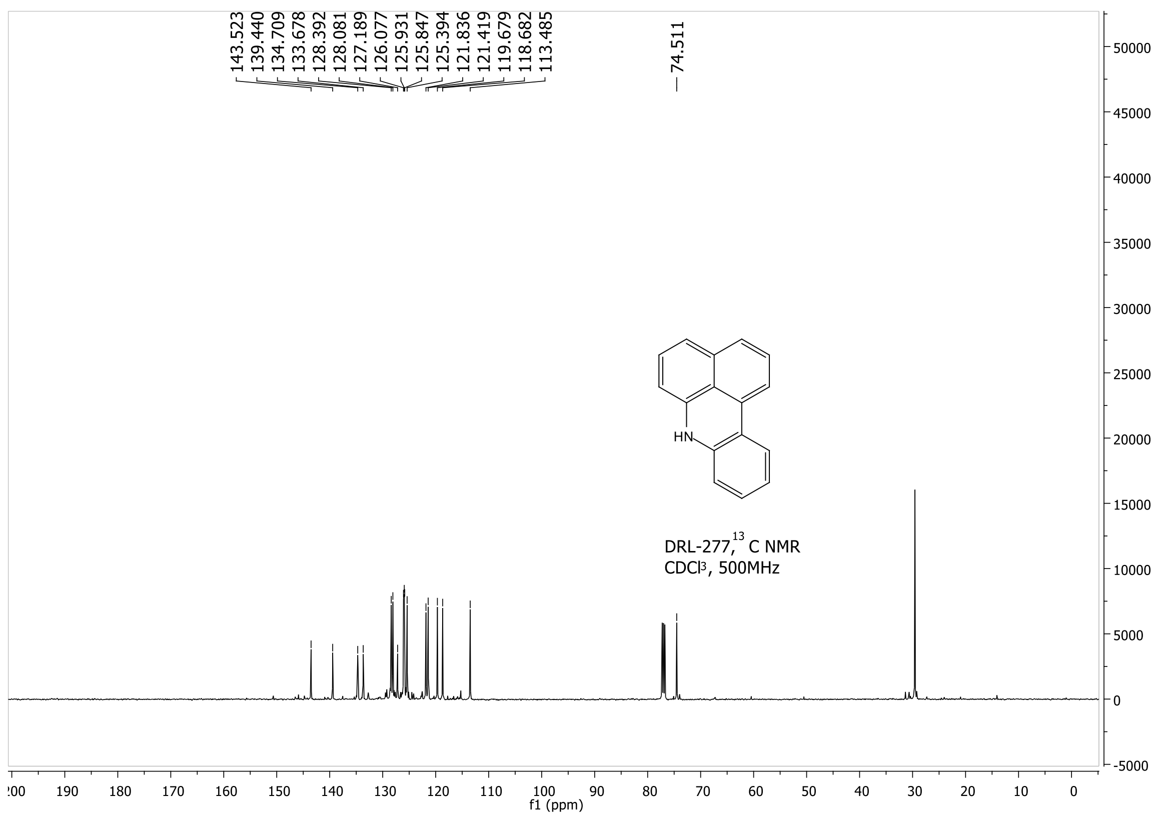

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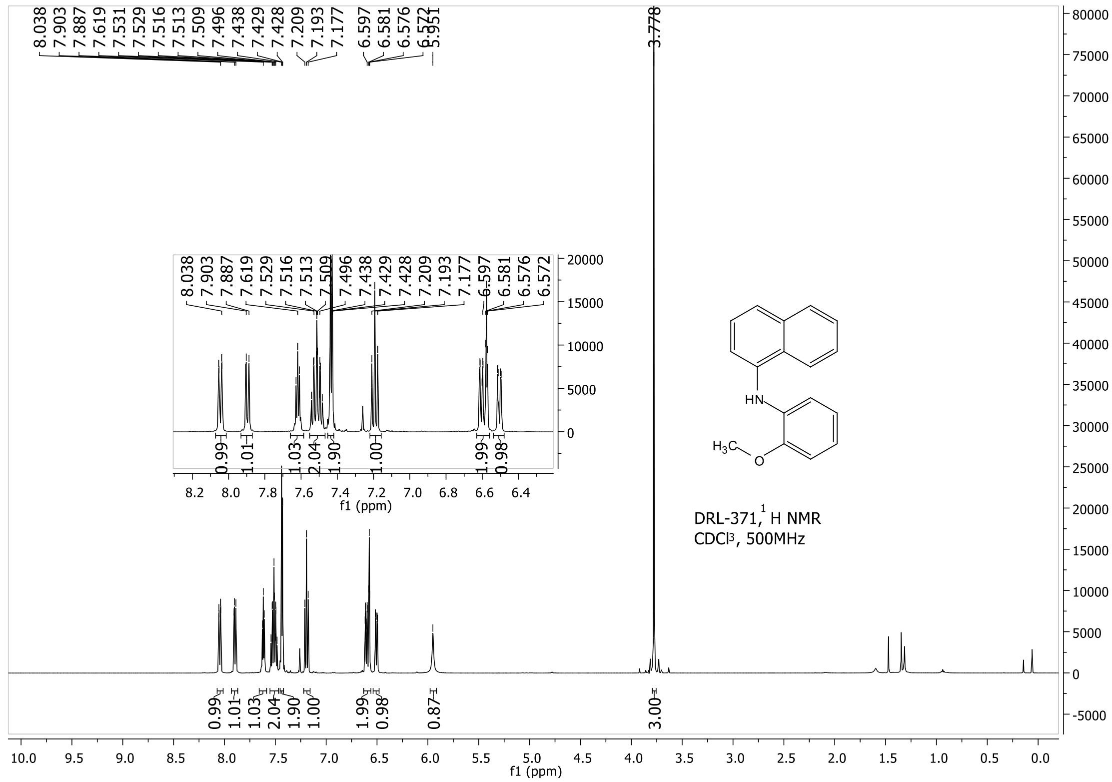

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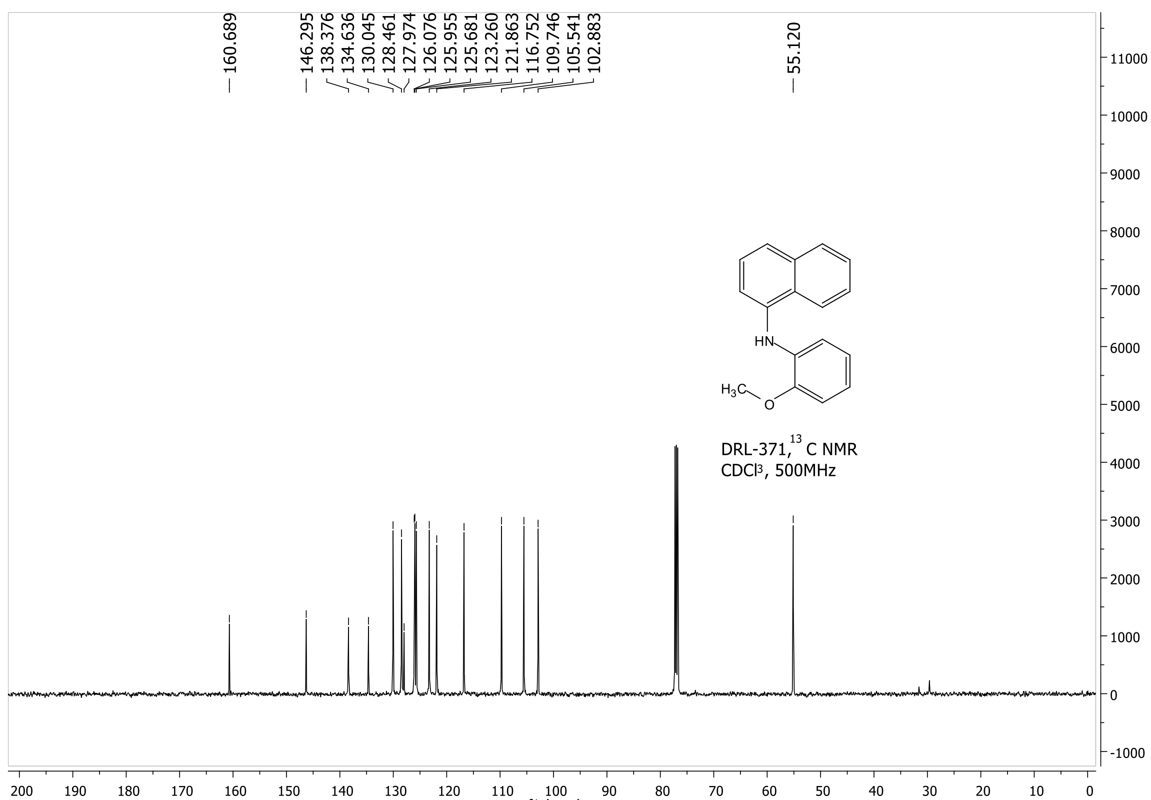
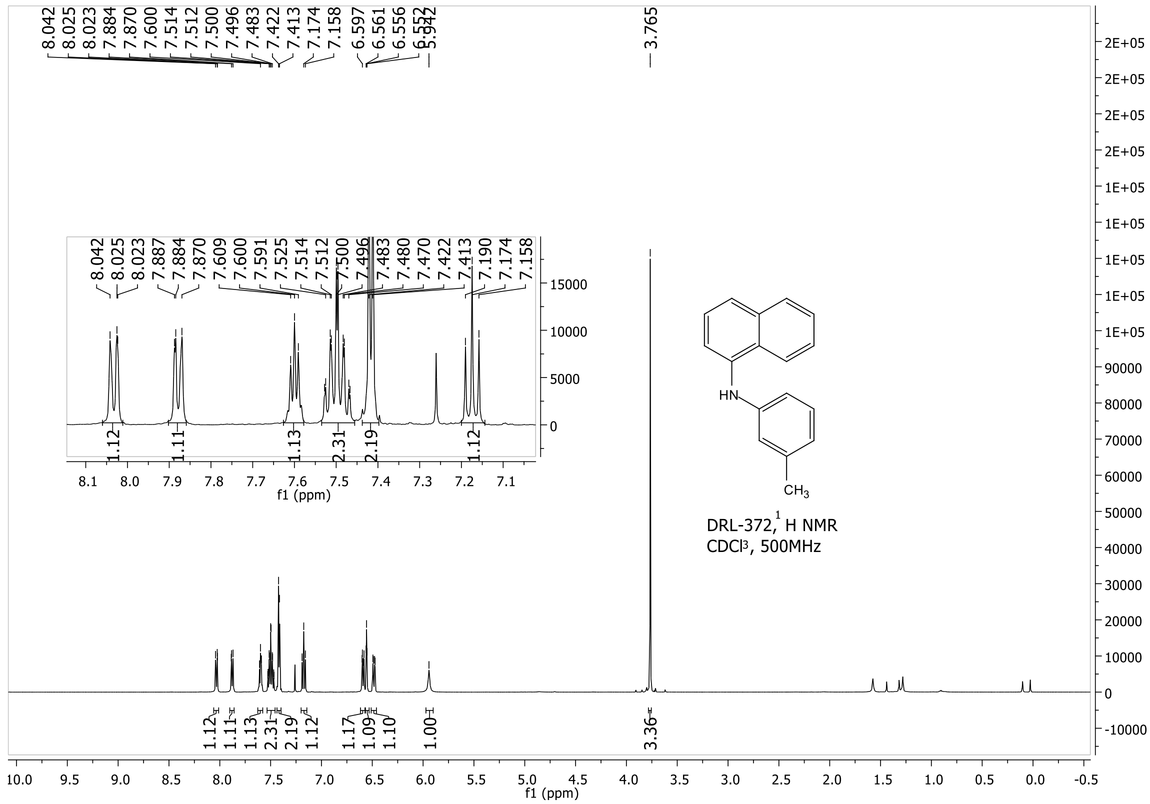
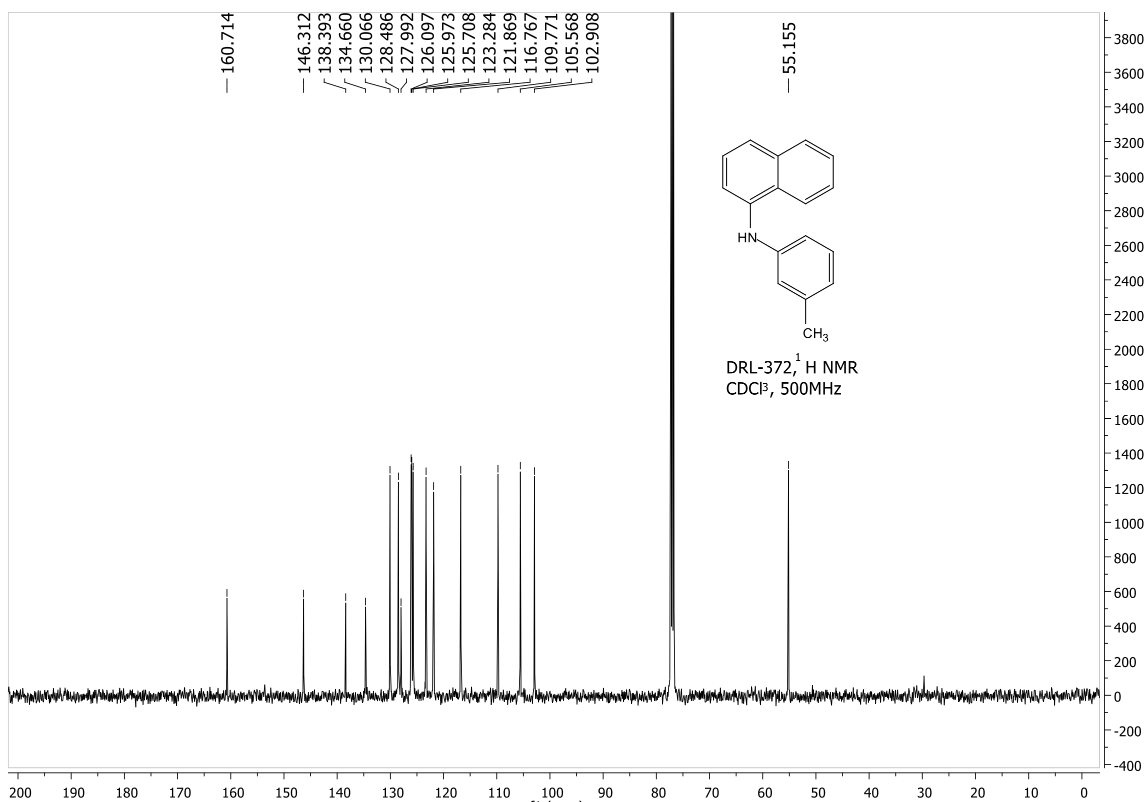


[13]C NMR of 8



^{1}H NMR of 9



^{13}C NMR of 9