Supporting Information

For

Gold catalysed redox synthesis of imidazo[1,2-*a*]pyridines using pyridine *N*-oxide and alkynes

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1. General details

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on either a Bruker 500 MHz AVANCE III equipped with 5mm BBFO SmartProbe or a 400 MHz AVANCE I equipped with a 1H/13C inverse dual probe. Chemical shifts are reported in ppm (δ) relative to the internal deuterium resonance of the solvent ($CDCl_3$ at 7.26 ppm and d_6-DMSO at 2.50 ppm). Carbon chemical shifts are reported in ppm with respect to solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm and d_6-DMSO at 39.52 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), broad (br)], coupling constants [Hz], integration). All the NMR spectra were acquired at ambient temperature and the coupling constants are rounded to the nearest 0.5 Hz. Analytical thinlayer chromatography (TLC) was performed using Merck Silica Gel 60 Å F254 pre-coated plates (0.25 mm thickness). High resolution mass spectrometry for accurate mass elcuidation was performed on a Thermo LTQ Orbitrap XL or Bruker microTOF-Q III utilising electrospray ionisation. Infrared spectra were recorded from a solid sample on an AVATAR 360 FT-IR, utilising the Golden Gate ATR Platform method. Prepative HPLC was performed on a Agilent 1200 series instrument using a XSelect CSH Prep C18, 30 x 100 mm, 5 micron column at 20°C column. Eluents were A=0.1% formic acid in Water, B=0.1% formic acid in MeCN utilising the following gradient: 0.0-0.5 min 30% B 30 mL/min; 0.5-1.0 min 30% B 30-50 mL/min; 1.0-7.25 min 30-70% B, 7.25 - 7.3 min 70-98% B, 7.3-9.3 min 98% B, 9.3-9.5min 98-30% B 50 mL/min. The products were collected by UV (220 and 254 nm) and mass directed ($[M+H]^+$) trigger.

2. Procedure A: Synthesis of 2-aminopyridine *N*-oxides

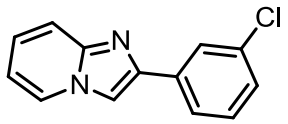
m-CPBA (1.1 eq.) was added to a solution of amino pyridine (1 eq) at 0°C in acetone (0.1 M) and the reaction mixture was stirred 30 min at this temperature. The reaction was then warmed up at room temperature and the reaction mixture was stirred for 15 h at this temperature. The reaction was then concentrated under reduced pressure and purified by column chromatography (0% → 10% MeOH in CH_2Cl_2).

3. Procedure B: Synthesis of imidazo[1,2-*a*]pyridines

Acid (TFA, 1 eq.) was added to a solution of 2-aminopyridine *N*-oxide (1.0 eq.) in CH_2Cl_2 (0.2 M). The reaction mixture was stirred for 10 min, then alkyne (1eq.) and $PicAuCl_2$ (10 mol %) were added. After stirring overnight at 40°C, Et_3N (0.10 ml per 1.0 mmol) was added and the reaction mixture was concentrated under reduced pressure and purified by prep HPLC or column chromatography to give pure imidazo[1,2-*a*]pyridine.

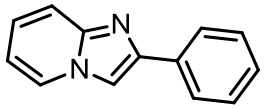
4. Characterization data for imidazo[1,2-*a*]pyridines

2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (2)



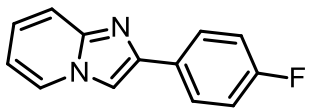
- **IR** (neat): 2355, 1674, 1201, 1131, 784, 756.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.13 (d, J=6.8 Hz, 1H), 7.97 (s, 1H), 7.90 - 7.80 (m, 2H), 7.65 (d, J=9.0 Hz, 1H), 7.37 (t, J=7.8 Hz, 1H), 7.30 (d, J=8.3 Hz, 1H), 7.20 (t, J=7.5 Hz, 1H), 6.81 (t, J=6.5 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 145.7, 144.4, 135.6, 134.8, 130.0, 127.9, 126.1, 125.7, 125.1, 124.1, 117.7, 112.7, 108.5.
- **LRMS** (ESI): 229.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 229.0528; $C_{13}H_{10}N_2Cl$ requires 229.0527.

2-phenylimidazo[1,2-*a*]pyridine (3)



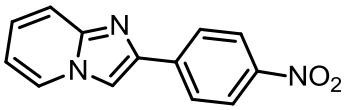
- **IR** (neat): 3133, 3068, 2935, 1633, 1475, 1371, 1270, 740.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.11 (d, J=6.8 Hz, 1H), 8.02 - 7.93 (m, 2H), 7.85 (s, 1H), 7.66 (d, J=9.3 Hz, 1H), 7.50 - 7.40 (m, 2H), 7.39 - 7.30 (m, 1H), 7.22 - 7.13 (m, 1H), 6.78 (t, J=6.8 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 145.7, 145.6, 133.6, 128.7, 128.0, 126.1, 125.6, 124.8, 117.5, 112.5, 108.1.
- **LRMS** (ESI): 195.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 195.0914; $C_{13}H_{11}N_2$ requires 195.0917.

2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (4)



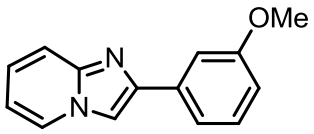
- **IR** (neat): 1769, 1705, 1503, 1485, 1394, 1367, 1224, 714
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.13 (dt, J=6.8, 1.2 Hz, 1H), 7.98 - 7.90 (m, 2H), 7.82 (s, 1H), 7.65 (d, J=9.2, 1.2 Hz, 1H), 7.21 (m, 1H), 7.14 (m, 2H), 6.81 (td, J=6.8, 1.2 Hz, 1H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 162.8 (d, J=246 Hz), 145.6, 144.8, 129.8 (d, J=3 Hz), 127.8 (d, J=8 Hz), 125.6, 125.0, 117.5, 115.7 (d, J=22 Hz), 112.6, 107.8.
- **LRMS** (ESI): 213.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 213.0822; $C_{17}H_{10}N_2F$ requires 213.0823.

2-(4-nitrophenyl)imidazo[1,2-*a*]pyridine (5)



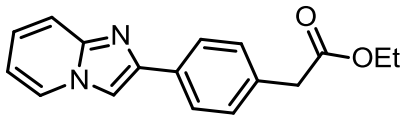
- **IR** (neat): 2362, 1682, 1599, 1511, 1339, 1204, 1109, 855, 719.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.36 - 8.29 (m, J=8.8 Hz, 2H), 8.25 (d, J=6.8 Hz, 1H), 8.16 - 8.10 (m, J=8.8 Hz, 2H), 8.04 (s, 1H), 7.99 (d, J=9.1 Hz, 1H), 7.51 - 7.41 (m, 1H), 7.05 (t, J=6.7 Hz, 1H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 147.8, 144.5, 140.7, 137.1, 128.4, 126.9, 126.1, 124.4, 116.8, 114.9, 110.2.
- **LRMS** (ESI): 240.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 240.0768; $C_{13}H_{10}N_3O_2$ requires 240.0768.

2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (formic acid salt) (6)



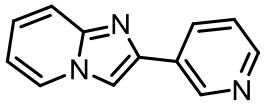
- **IR** (neat): 3130, 3084, 2939, 2836, 1605, 1504, 1372, 1234, 1043, 753.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.35 (s, 1H, *H*CO_2H), 8.16 (d, *J*=6.6 Hz, 1H), 7.86 (s, 1H), 7.82 (d, *J*=9.0 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J*=7.6 Hz, 1H), 7.37 (t, *J*=7.9 Hz, 1H), 7.31 - 7.23 (m, 1H), 6.97 - 6.81 (m, 2H), 3.92 (s, 3H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 164.4, 160.1, 145.0, 144.6, 133.8, 129.8, 126.0, 118.7, 117.0, 114.7, 113.3, 111.3, 108.5, 55.4.
- **LRMS** (ESI): 225.1 (100, M+H^+); **HRMS** (ESI): M+H^+ found 225.1022; $C_{14}H_{13}N_2O$ requires 225.1022.

ethyl 2-(4-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)acetate (7)



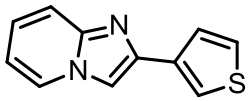
- **IR** (neat): 2982, 1731, 1634, 1487, 1371, 1249, 1157, 1030, 755.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.10 (d, J=6.8 Hz, 1H), 7.93 - 7.88 (m, J=8.3 Hz, 2H), 7.83 (s, 1H), 7.64 (d, J=9.1 Hz, 1H), 7.39 - 7.33 (m, J=8.3 Hz, 2H), 7.20 - 7.14 (m, 1H), 6.80 - 6.74 (m, 1H), 4.17 (q, J=7.2 Hz, 2H), 3.65 (s, 2H), 1.26 (t, J=7.1 Hz, 3H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 171.5, 164.7, 145.6, 145.3, 133.9, 132.4, 129.8, 129.7, 126.3, 125.6, 124.8, 117.4, 112.5, 108.1, 60.9, 41.3, 14.1
- **LRMS** (ESI): 281.1 (100, M+H^+); **HRMS** (ESI): M+H^+ found 281.1285; $C_{17}H_{17}N_2O_2$ requires 281.1285.

2-(pyridin-3-yl)imidazo[1,2-*a*]pyridine (8)



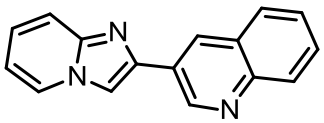
- **IR** (neat): 3363 (br), 1636, 1499, 1465, 1412, 1374, 753
- **^{1}H NMR** (400 MHz, $CDCl_3$): 9.16 (s, 1H), 8.60 (d, J=4.3 Hz, 1H), 8.41 (d, J=7.8 Hz, 1H), 8.20 (d, J=6.8 Hz, 1H), 7.99 (s, 1H), 7.76 (d, J=9.3 Hz, 1H), 7.45 (dd, J=4.8, 7.8 Hz, 1H), 7.34 - 7.27 (m, 1H), 6.90 (t, J=6.8 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 148.5, 146.9, 145.4, 141.7, 134.1, 129.3, 126.1, 125.9, 124.0, 117.4, 113.5, 108.7.
- **LRMS** (ESI): 196.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 196.0871; $C_{12}H_{10}N_3$ requires 196.0869.

2-(thiophen-3-yl)imidazo[1,2-*a*]pyridine (formic acid salt) (9)



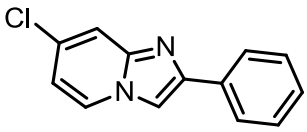
- **IR** (neat): 3099, 1657, 1586, 1479, 1342, 1278, 1249, 752
- **^{1}H NMR** (400 MHz, $CDCl_3$): 9.75 (br. s., 1H, HCO_2H), 8.42 (s, 1H, HCO_2H), 8.15 (d, *J*=6.8 Hz, 1H), 7.93 - 7.85 (m, 1H), 7.82 (d, *J*=9.0 Hz, 1H), 7.75 (s, 1H), 7.49 - 7.43 (m, 1H), 7.38 (dd, *J*=2.9, 4.9 Hz, 1H), 7.34 - 7.23 (m, 1H), 6.89 (t, *J*=6.7 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 165.3, 144.1, 139.3, 132.7, 127.0, 126.6, 126.0, 123.0, 116.0, 113.9, 108.4
- **LRMS** (ESI): 201.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 201.0482; $C_{11}H_9N_2S$ requires 201.0842.

3-(imidazo[1,2-*a*]pyridin-2-yl)quinoline (10)



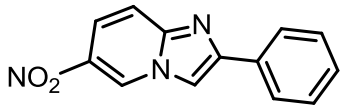
- **IR** (neat): 3313 (br), 2927, 2361, 1683, 1505, 1378, 1353, 1327, 1284, 1200, 1129, 753.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 9.46 - 9.40 (m, 1H), 8.84 (s, 1H), 8.20 (d, *J*=6.6 Hz, 1H), 8.15 (d, *J*=8.3 Hz, 1H), 8.09 (s, 1H), 7.93 (d, *J*=7.8 Hz, 1H), 7.76 - 7.69 (m, 2H), 7.62 - 7.55 (m, 1H), 7.30-7.23 (m, 1H), 6.86 (t, *J*=6.8 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 148.7, 147.5, 146.0, 142.7, 132.5, 129.5, 129.1, 128.3, 128.3, 127.1, 126.9, 125.8, 125.6, 117.6, 113.0, 108.9.
- **LRMS** (ESI): 246.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 246.1026; $C_{16}H_{12}N_3$ requires 246.1026.

7-chloro-2-phenylimidazo[1,2-*a*]pyridine (11)



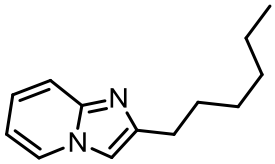
- **IR** (neat): 1633, 1526, 1434, 1351, 1332.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.22 (d, J=7.1 Hz, 1H), 8.11 (s, 1H), 7.95 (s, 1H), 7.80 (dd, J=1.6, 7.7 Hz, 2H), 7.48 - 7.38 (m, 3H), 7.05 (dd, J=2.0, 7.1 Hz, 1H
- **^{13}C NMR** (100 MHz, $CDCl_3$): 141.8, 140.1, 137.8, 130.4, 129.4, 127.0, 126.8, 126.3, 118.0, 113.7, 109.2.
- **HRMS** (ESI): $M+H^+$ found 229.0523; $C_{13}H_{10}ClN_2$ requires 229.0527.

6-nitro-2-phenylimidazo[1,2-*a*]pyridine (12)



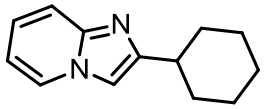
- **IR** (neat): 1642, 1541, 1522, 1506, 1478, 1441, 1350, 1330.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 9.29 (dd, *J* = 2.2, 0.8 Hz, 1H), 8.06 (s, 1H), 8.04 – 7.95 (m, 3H), 7.76 (d, *J* = 9.9 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.43 (d, *J* = 7.3 Hz, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 149.2, 145.4, 137.4, 131.9, 129.3, 129.0, 126.4, 125.6, 119.2, 116.8, 110.1.
- **HRMS** (ESI): $M+H^+$ found 240.0762; $C_{13}H_{10}N_3O_2$ requires 240.0767.

2-hexylimidazo[1,2-*a*]pyridine (13)



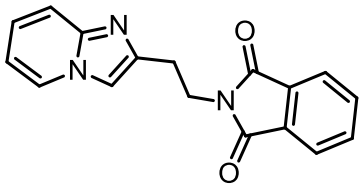
- **IR** (neat): 2929, 2854, 1684, 1504, 1200
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.05 (d, J=6.8 Hz, 1H), 7.55 (d, J=9.1 Hz, 1H), 7.34 (s, 1H), 7.13 (dd, J=7.3, 8.6 Hz, 1H), 6.73 (t, J=6.8 Hz, 1H), 2.83 - 2.76 (m, 2H), 1.77 (td, J=7.6, 15.2 Hz, 2H), 1.44 - 1.38 (m, 2H), 1.36 - 1.30 (m, 4H), 0.93 - 0.86 (m, 3H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 148.1, 144.9, 125.3, 124.0, 116.9, 111.8, 108.9, 31.7, 29.3, 29.2, 28.9, 22.6, 14.1
- **LRMS** (ESI): 203.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 203.1542; $C_{13}H_{19}N_2$ requires 203.1543.

2-cyclohexylimidazo[1,2-*a*]pyridine (14)



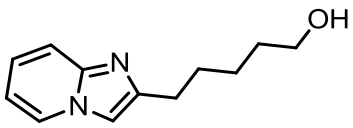
- **IR** (neat): 2925, 2851, 1634, 1504, 1449, 1358, 1284, 757, 740.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.04 (d, J=6.8 Hz, 1H), 7.54 (d, J=9.1 Hz, 1H), 7.31 (s, 1H), 7.14 - 7.05 (m, 1H), 6.75 - 6.67 (m, 1H), 2.78 (tt, J=3.4, 11.1 Hz, 1H), 2.23 - 2.07 (m, 2H), 1.84 (dd, J=2.8, 12.4 Hz, 2H), 1.79 - 1.70 (m, 1H), 1.57 - 1.36 (m, 4H), 1.36 - 1.23 (m, 1H).
- **^{13}C NMR** (100 MHz, $CDCl_3$): 153.2, 144.8, 125.4, 123.9, 120.3, 117.1, 111.7, 107.5, 38.1, 33.0, 26.4, 26.2, 25.8
- **LRMS** (ESI): 201.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 201.1386; $C_{13}H_{17}N_2$ requires 201.1386.

2-(2-(imidazo[1,2-*a*]pyridin-2-yl)ethyl)isoindoline-1,3-dione (15)



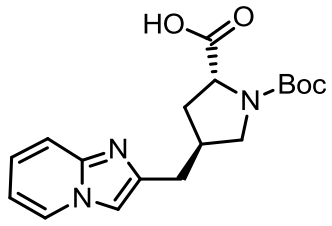
- **IR** (neat): 1698, 1504, 1394, 1370, 1325, 997, 715.
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.03 (d, *J*=6.6 Hz, 1H), 7.89 - 7.76 (m, 2H), 7.75 - 7.63 (m, 2H), 7.53 (d, *J*=9.1 Hz, 1H), 7.44 (s, 1H), 7.18 - 7.07 (m, 1H), 6.73 (t, *J*=6.7 Hz, 1H), 4.11 (t, *J*=7.3 Hz, 2H), 3.21 (t, *J*=7.3 Hz, 2H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 168.2, 145.1, 143.8, 133.8, 132.2, 125.5, 124.3, 123.2, 117.1, 112.0, 109.7, 37.6, 27.9
- **LRMS** (ESI): 292.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 292.1082; $C_{17}H_{13}N_3O_2$ requires 292.1081.

5-(imidazo[1,2-*a*]pyridin-2-yl)pentan-1-ol (16)



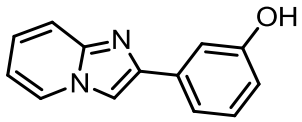
- **IR** (neat): 3370.6 (br), 2933, 2859, 2357, 2334, 1504, 758
- **^{1}H NMR** (400 MHz, $CDCl_3$): 8.03 (d, *J*=6.6 Hz, 1H), 7.53 (d, *J*=9.1 Hz, 1H), 7.33 (s, 1H), 7.15 - 7.07 (m, 1H), 6.76 - 6.69 (m, 1H), 3.66 (t, *J*=6.4 Hz, 2H), 2.80 (t, *J*=7.6 Hz, 2H), 1.80 (quin, *J*=7.6 Hz, 2H), 1.68 - 1.59 (m, 2H), 1.53 - 1.43 (m, 2H)
- **^{13}C NMR** (100 MHz, $CDCl_3$): 147.7, 145.0, 125.3, 124.1, 116.9, 111.9, 109.0, 62.7, 53.4, 32.5, 28.9, 25.4
- **LRMS** (ESI): 205.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 205.1334; $C_{12}H_{17}N_2O$ requires 205.1335.

(2R,4R)-1-(tert-butoxycarbonyl)-4-(imidazo[1,2-*a*]pyridin-2-ylmethyl)pyrrolidine-2-carboxylic acid (formic acid salt) (17)



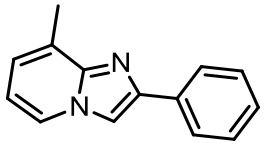
- **IR** (neat): 1678, 1654, 1532, 1402, 1366, 1166, 1129.
- **^{1}H NMR** (400 MHz, d_6-DMSO): (d, *J* = 6.7 Hz, 1H), 8.29 (s, 1H), 7.95 – 7.77 (m, 3H), 7.40 (t, *J* = 7.0 Hz, 1H), 4.25 (dd, *J* = 7.7, 5.5 Hz, 1H), 3.67 (td, *J* = 10.8, 8.7, 5.2 Hz, 1H), 3.21 (dd, *J* = 10.8, 7.1 Hz, 1H), 3.04 – 2.96 (m, 2H), 2.82 – 2.70 (m, 1H), 2.15 (t, *J* = 7.8 Hz, 2H), 1.40 (d, *J* = 21.2 Hz, 10H).
- **^{13}C NMR** (100 MHz, d_6-DMSO): 181.5, 169.8, 158.3, 142.2, 137.6, 135.9, 130.9, 119.6, 114.9, 114.0, 84.4, 84.3, 62.7, 53.2, 38.3, 38.0, 30.0. other signals due to rotamer.
- **HRMS** (ESI): $M-H^+$ found 344.1608; $C_{18}H_{22}N_3O_4$ requires 344.1616.

3-(imidazo[1,2-*a*]pyridin-2-yl)phenol (18)



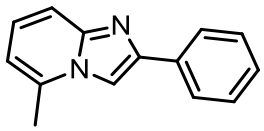
- **IR** (neat): 2361, 2342.
- **^{1}H NMR** (500 MHz, d_4-MeOH): 8.42 (d, J=6.7 Hz, 1H), 8.14 (s, 1H), 7.56 (d, J=9.1 Hz, 1H), 7.39 (m, 2H), 7.32 (t, J=7.9 Hz, 1H), 7.26 (t, J=7.8 Hz, 1H), 6.92 (t, J=6.7 Hz, 1H), 6.79 (d, J=8.0 Hz, 1H).
- **^{13}C NMR** (126 MHz, d_4-MeOH): 159.0, 146.9, 146.4, 136.0, 130.9, 127.8, 127.0, 118.5, 117.1, 116.2, 114.0, 113.9, 110.4.
- **LRMS** (ESI): 211.1 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 211.0861; $C_{13}H_{11}N_2O$ requires 211.0866.

8-methyl-2-phenylimidazo[1,2-*a*]pyridine (19)



- **IR** (neat): 2359, 2342.
- **^{1}H NMR** (500 MHz, d_4-MeOH): 8.28 (d, J=6.7 Hz, 1H), 8.16 (s, 1H), 7.95 (d, J=7.5 Hz, 2H), 7.45 (t, J=7.5 Hz, 2H), 7.36 (t, J=7.4 Hz, 1H), 7.11 (d, J=6.8 Hz, 1H), 6.83 (t, J=6.8 Hz, 1H), 2.62 (s, 3H).
- **^{13}C NMR** (126 MHz, d_4-MeOH): 147.4, 146.2, 135.0, 129.7, 129.0, 127.7, 127.4, 125.8, 125.6, 114.0, 110.9, 17.2.
- **LRMS** (ESI): 209.2 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 209.1067; $C_{14}H_{13}N_2$ requires 209.1073.

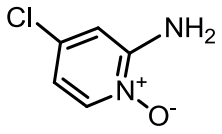
5-methyl-2-phenylimidazo[1,2-*a*]pyridine (20)



- **IR** (neat): 2359, 2341.
- **^{1}H NMR** (500 MHz, d_4-MeOH): 8.14 (s, 1H), 7.99 (d, J=7.3 Hz, 2H), 7.47 (m, 3H), 7.36 (t, J=7.4 Hz, 1H), 7.31 (dd, J=8.8, 7.0 Hz, 1H), 6.80 (d, J=6.9 Hz, 1H), 2.70 (s, 3H).
- **^{13}C NMR** (126 MHz, d_4-MeOH): 147.4, 146.3, 136.9, 134.8, 129.8, 129.2, 127.3, 127.2, 114.5, 113.1, 107.65, 18.6.
- **LRMS** (ESI): 209.2 (100, $M+H^+$); **HRMS** (ESI): $M+H^+$ found 209.1071; $C_{14}H_{13}N_2$ requires 209.1073.

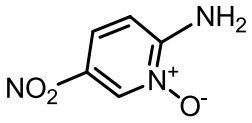
5. Characterization data for pyridine *N*-oxides

2-amino-4-chloropyridine 1-oxide



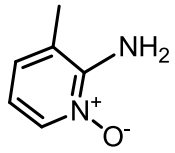
- **IR** (neat): 3291, 3100, 1647, 1562, 1495, 1441, 1194, 1100.
- **^{1}H NMR** (400 MHz, d_6-DMSO): 8.03 (d, J=7.1 Hz, 1H), 7.03 (br. s., 2H), 6.83 (d, J=2.8 Hz, 1H), 6.65 (dd, J=2.9, 6.9 Hz, 1H)
- **^{13}C NMR** (100 MHz, d_6-DMSO): 151.2, 137.8, 130.7, 111.9, 107.7
- **HRMS** (ESI): $M+H^+$ found 145.0161 $C_5H_6ClN_3O$ requires 145.013.

2-amino-5-nitropyridine 1-oxide



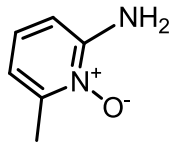
- **IR** (neat): 1632, 1581, 1500, 1334, 1267, 1197, 1092.
- **^{1}H NMR** (400 MHz, d_6-DMSO): 8.92 (d, J=2.4 Hz, 1H), 7.97 (dd, J=9.3, 2.5 Hz, 1H), 6.86 (d, *J* = 9.3 Hz, 1H).
- **^{13}C NMR** (100 MHz, d_6-DMSO): 155.1, 133.9, 133.9, 123.2, 106.4
- **HRMS** (ESI): $M+H^+$ found 156.0408 $C_5H_6N_3O_3$ requires 156.0403.

2-amino-3-methylpyridine 1-oxide



- **IR** (neat): 3396, 3265, 3122, 1644, 1620, 1583, 1506, 1452, 1438, 1231, 1154, 769.
- **^{1}H NMR** (400 MHz, d_6-DMSO): 7.95 (d, J=6.3 Hz, 1H), 7.00 (d, J=7.5 Hz, 1H), 6.70 (br s, 2H), 6.53 (dd, J=7.5, 6.3 Hz, 1H), 2.15 (s, 3H).
- **^{13}C NMR** (100 MHz, d_6-DMSO): 150.1, 135.0, 127.8, 118.6, 111.8, 17.2.
- **HRMS** (ESI): $M+H^+$ found 125.0715 $C_6H_9N_2O$ requires 125.0709.

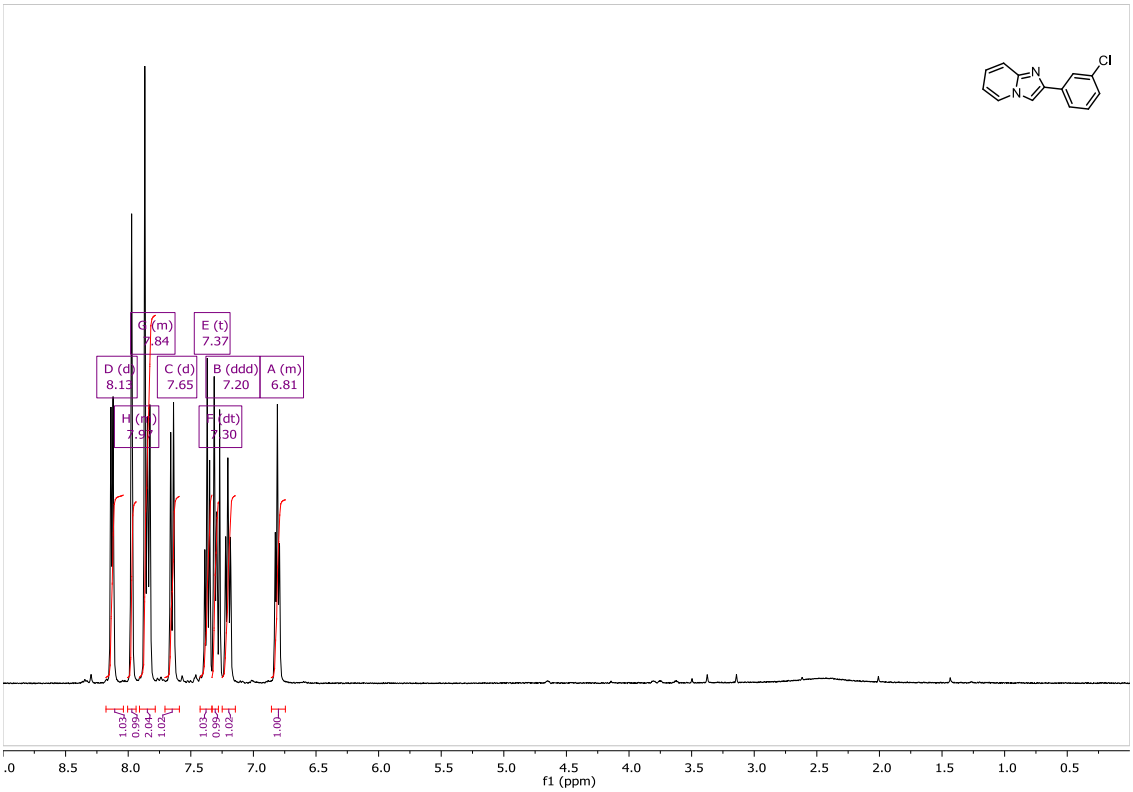
2-amino-6-methylpyridine 1-oxide

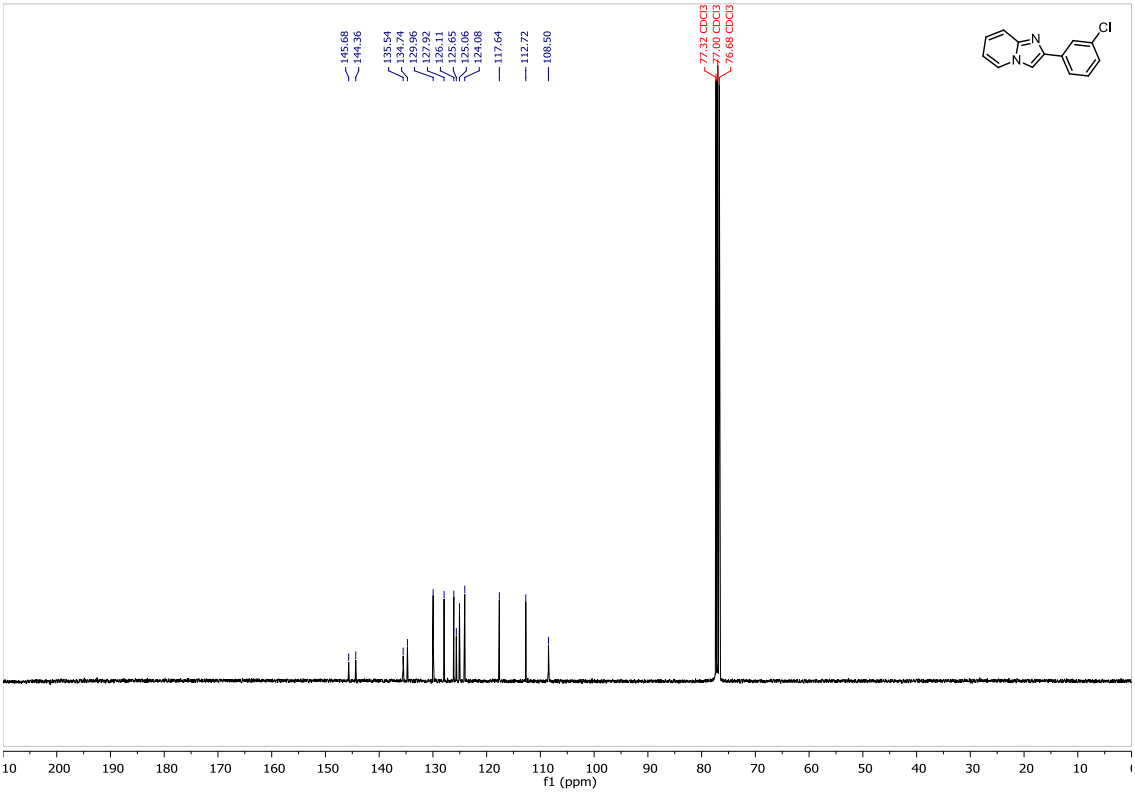


- **IR** (neat): 3386, 3325, 3236, 3077, 1645, 1629, 1575, 1504, 1449, 1413, 1200, 1188, 1164.
- **^{1}H NMR** (400 MHz, d_6-DMSO): 6.99 (app t, J=7.9 Hz, 1H), 6.74 (br s, 2H), 6.68 (dd, J=7.3, 1.3 Hz, 1H), 6.60 (dd, J=7.5, 1.3 Hz, 1H), 2.38 (s, 3H).
- **^{13}C NMR** (100 MHz, d_6-DMSO): 151.1, 146.5, 126.1, 112.7, 106.6, 18.2.
- **HRMS** (ESI): $M+H^+$ found 125.0708 $C_6H_9N_2O$ requires 125.0709.

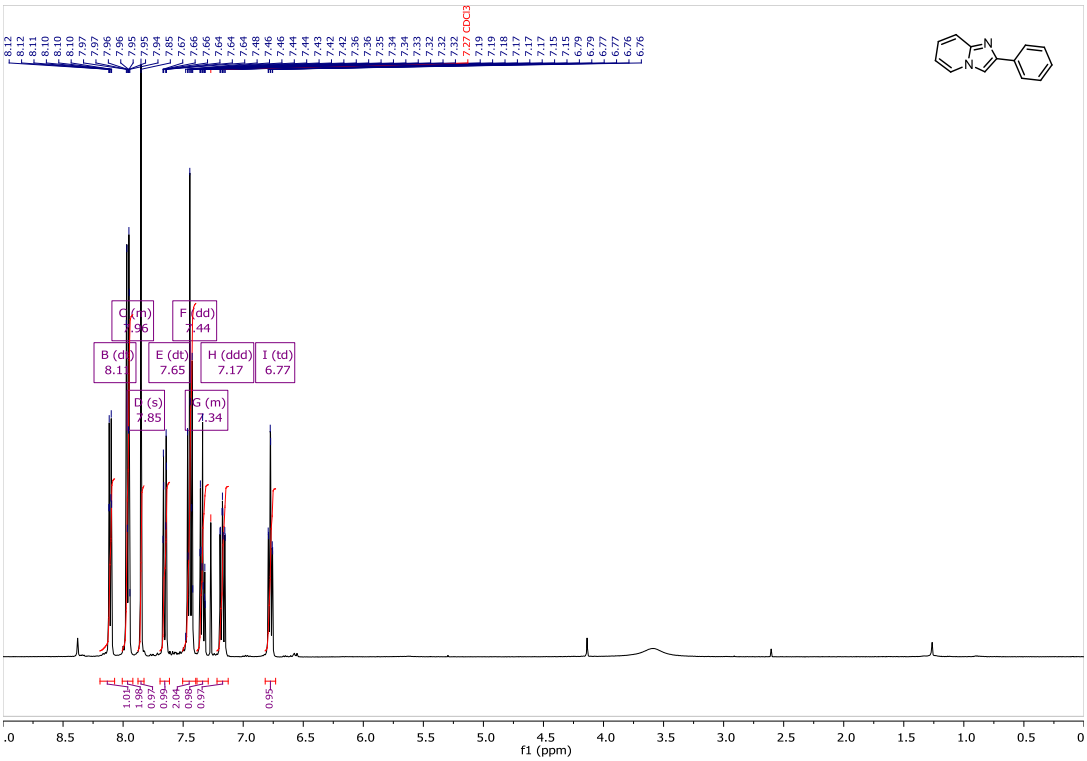
6. ^{1}H and ^{13}C spectra

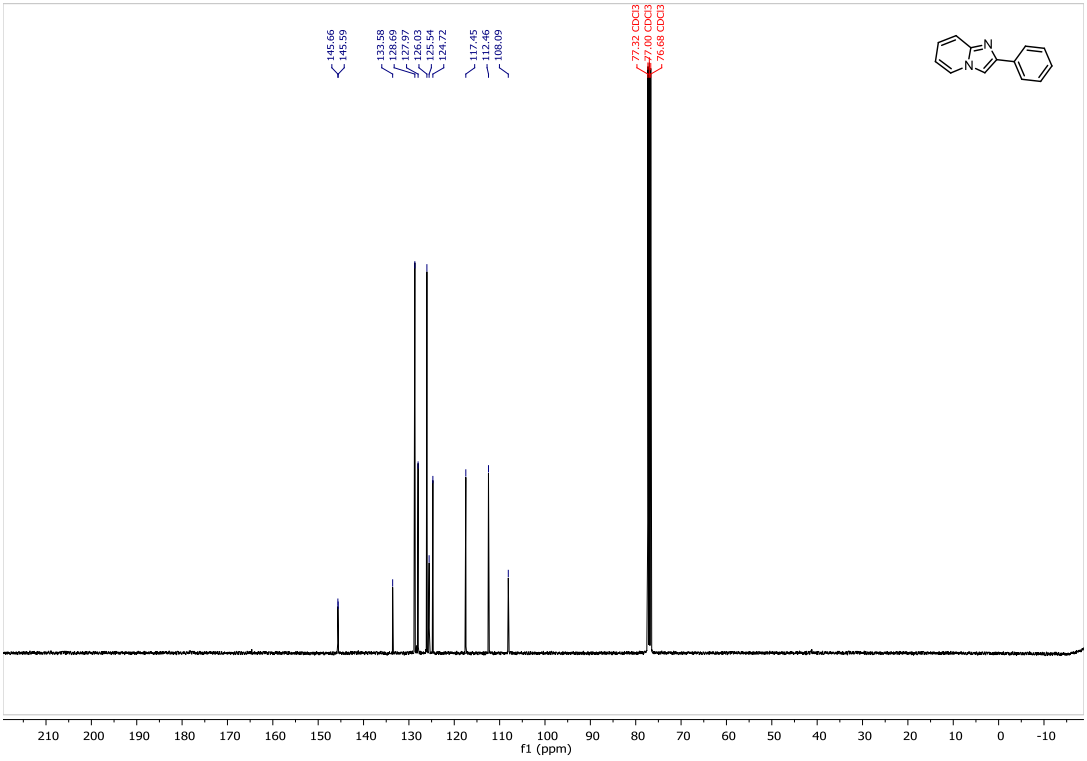
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **2**



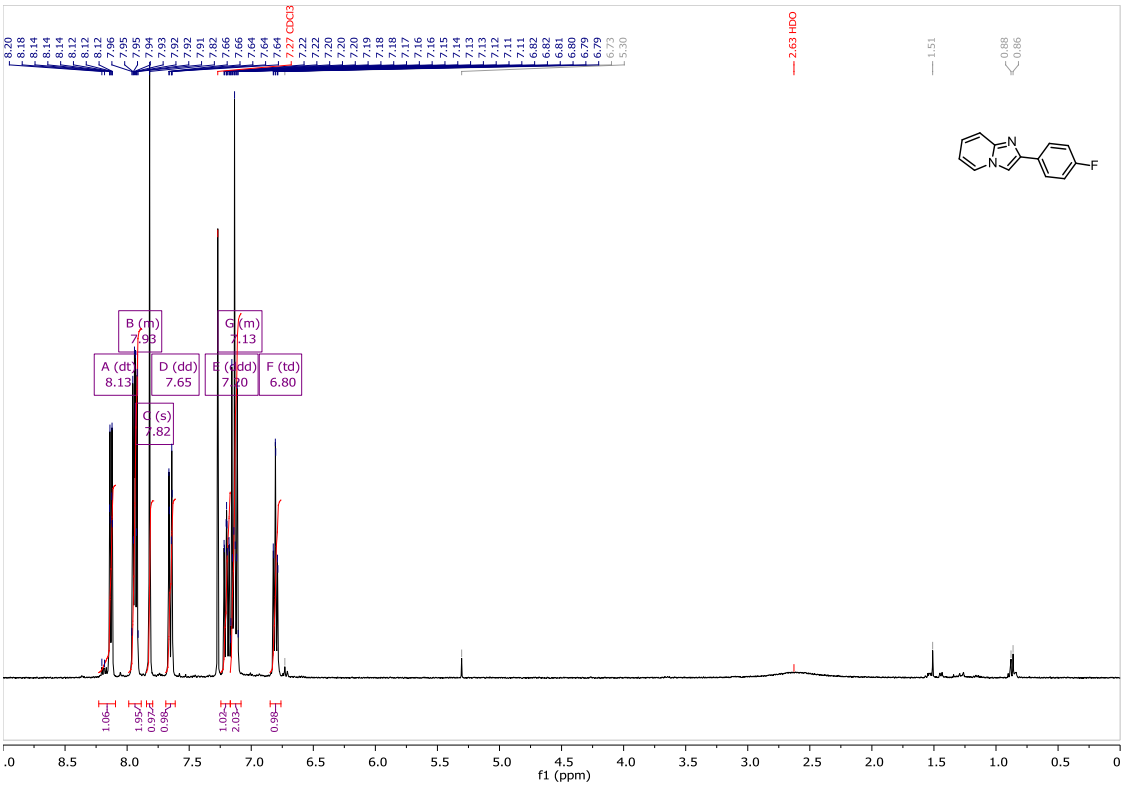


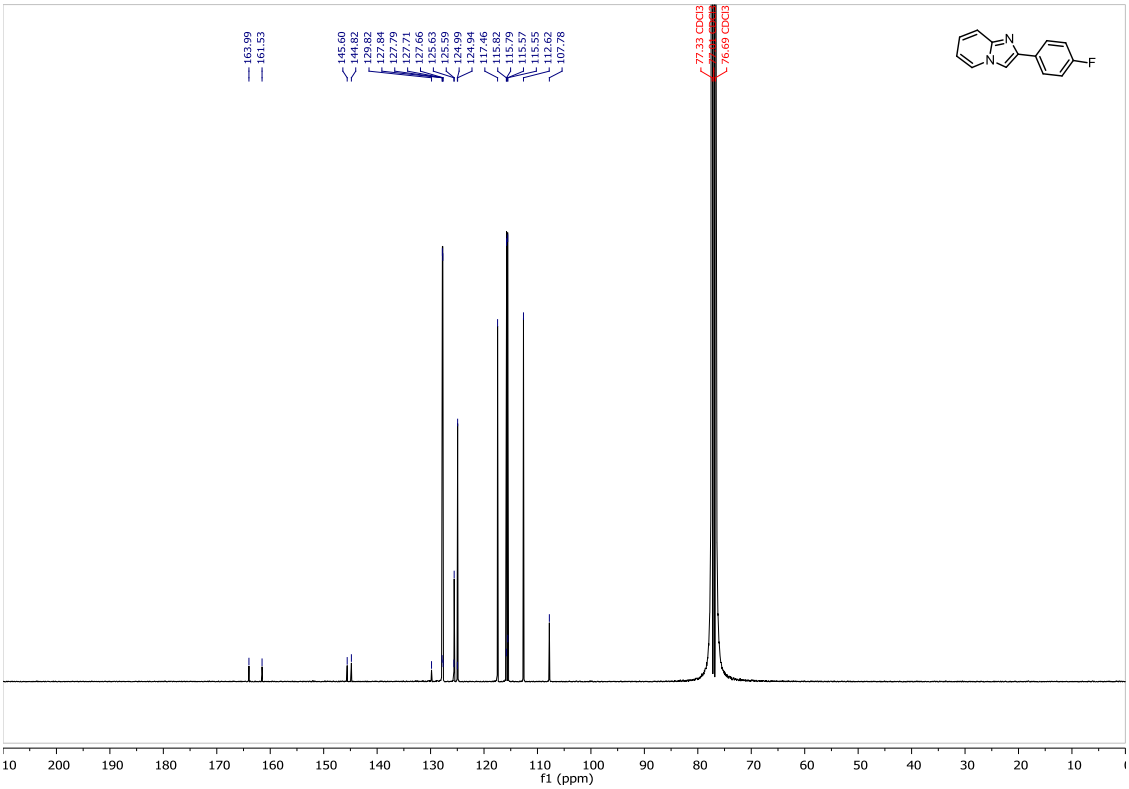
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **3**



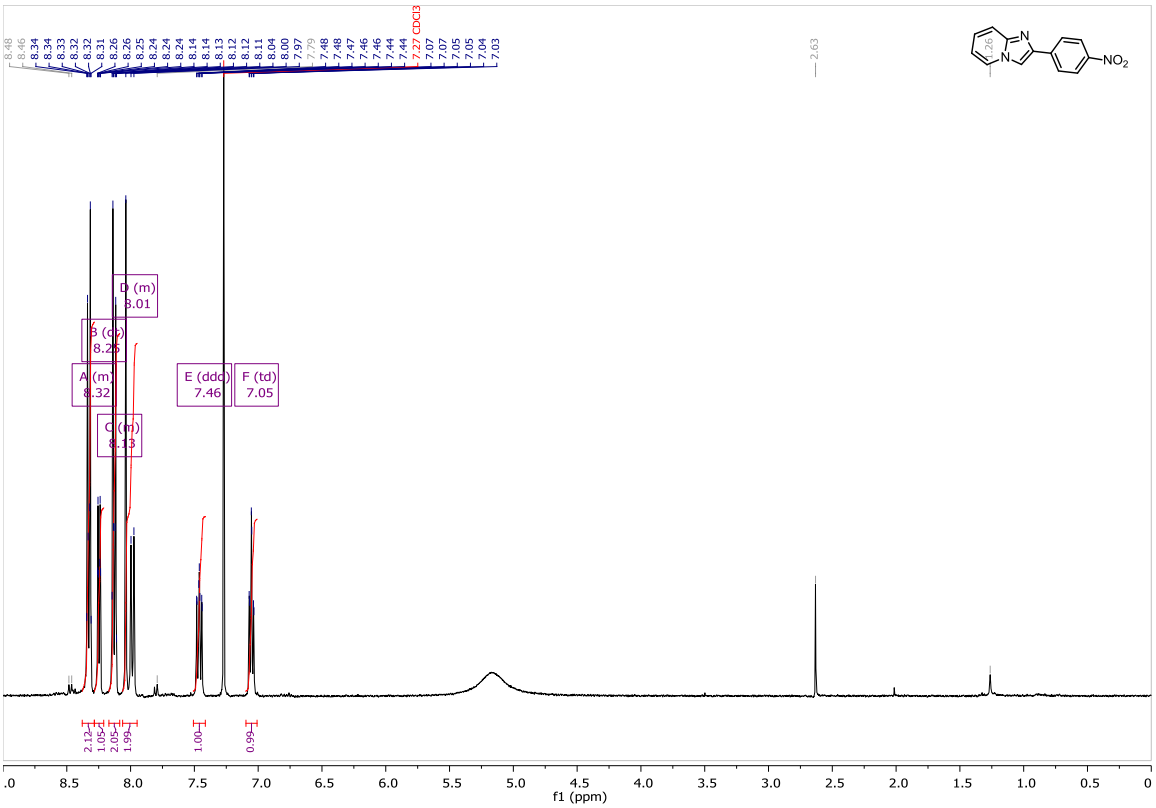


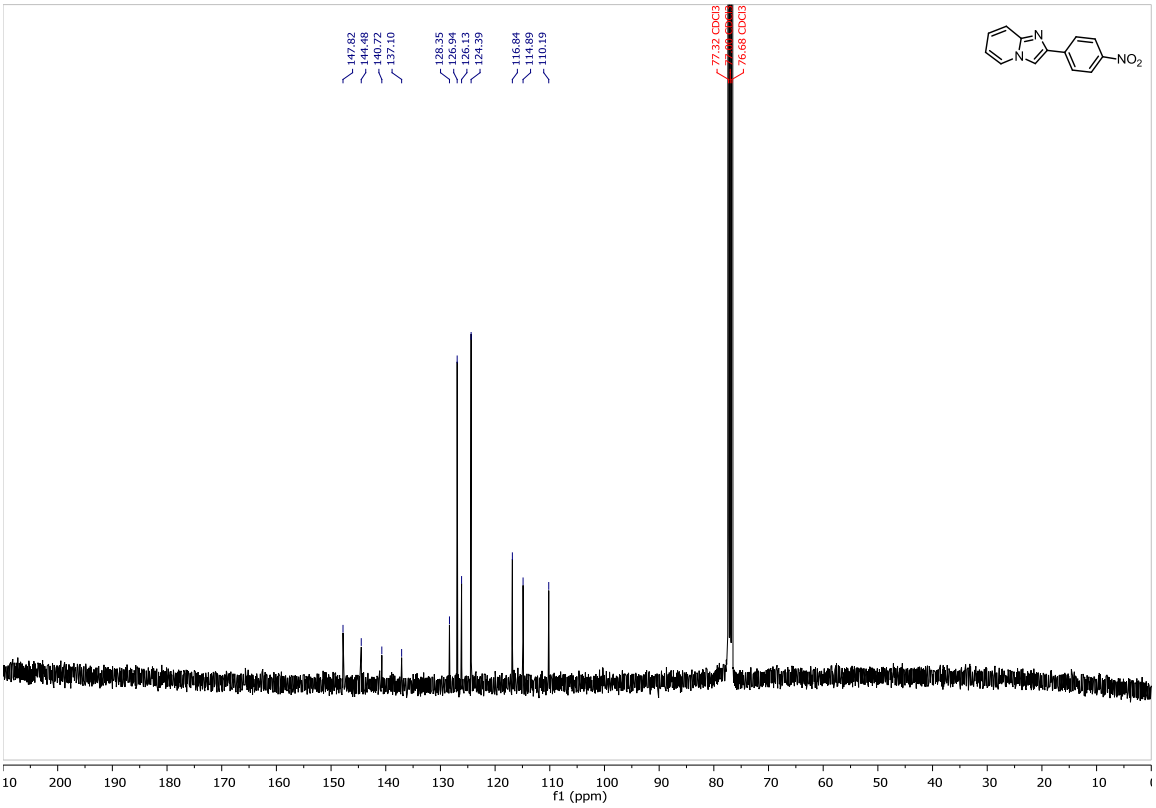
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **4**



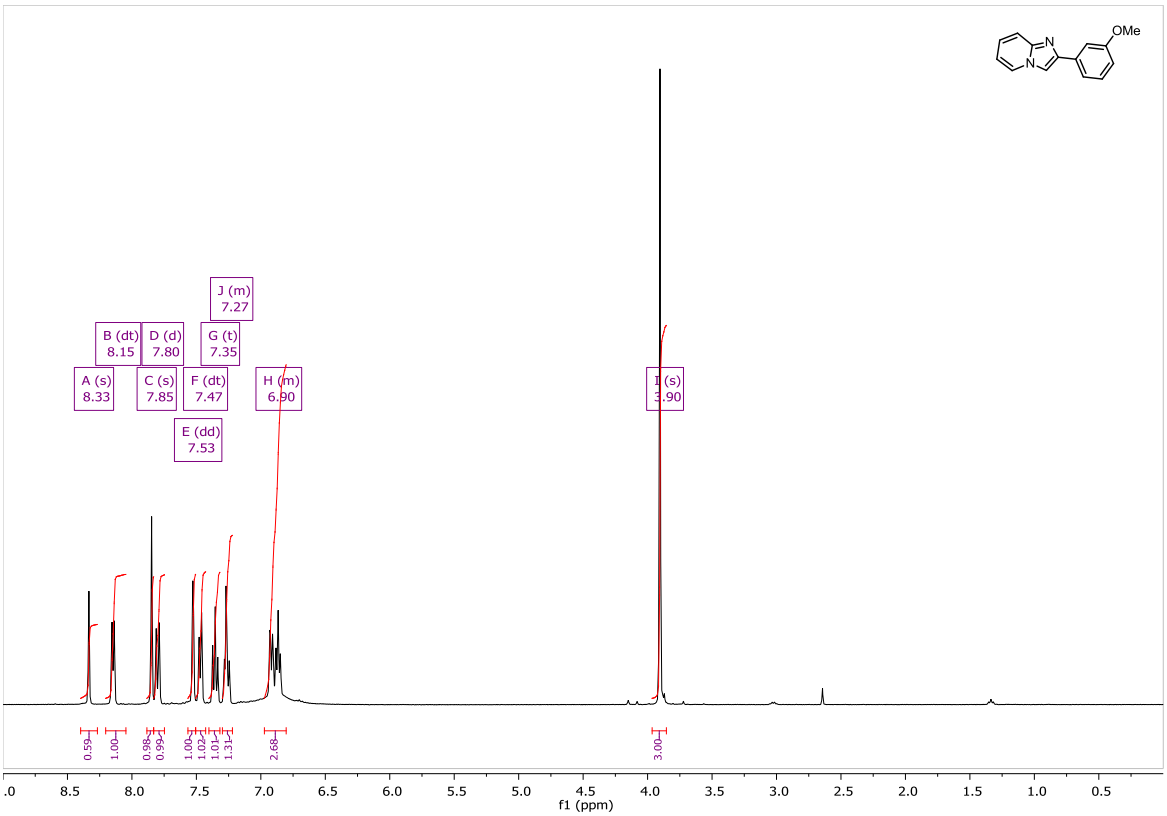


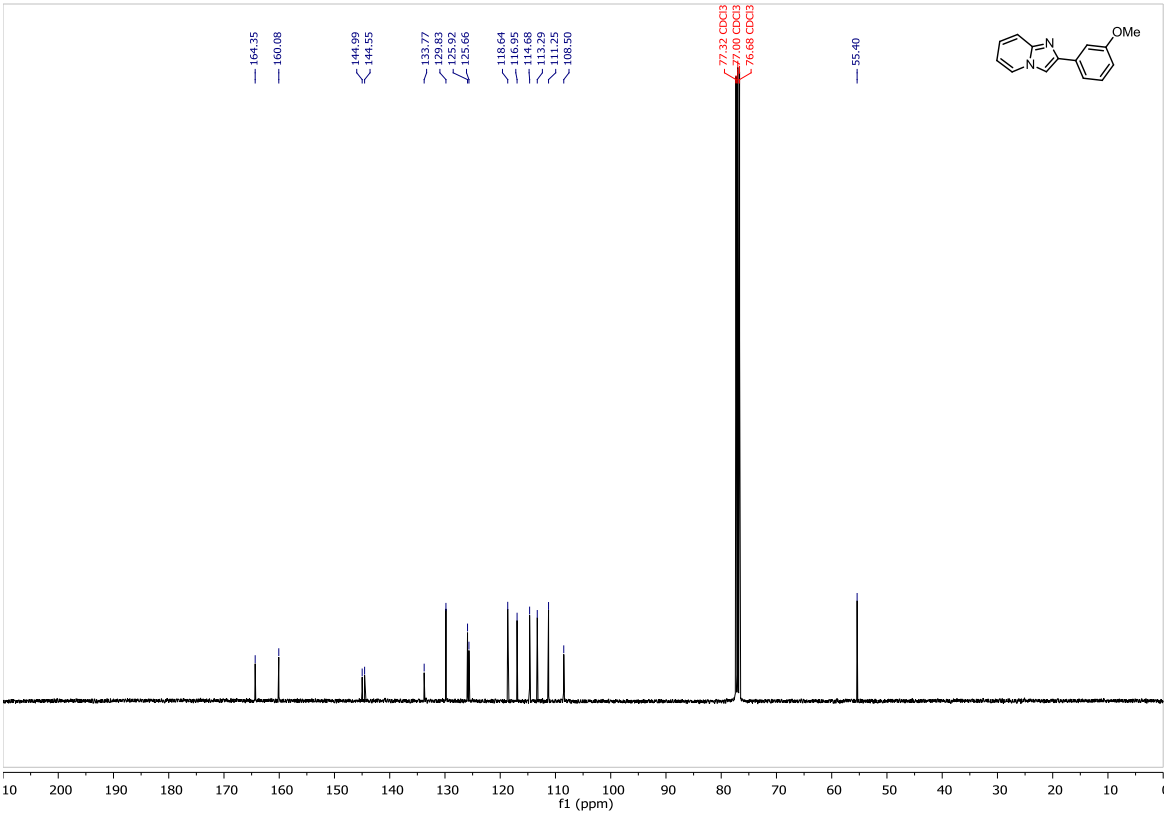
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5**



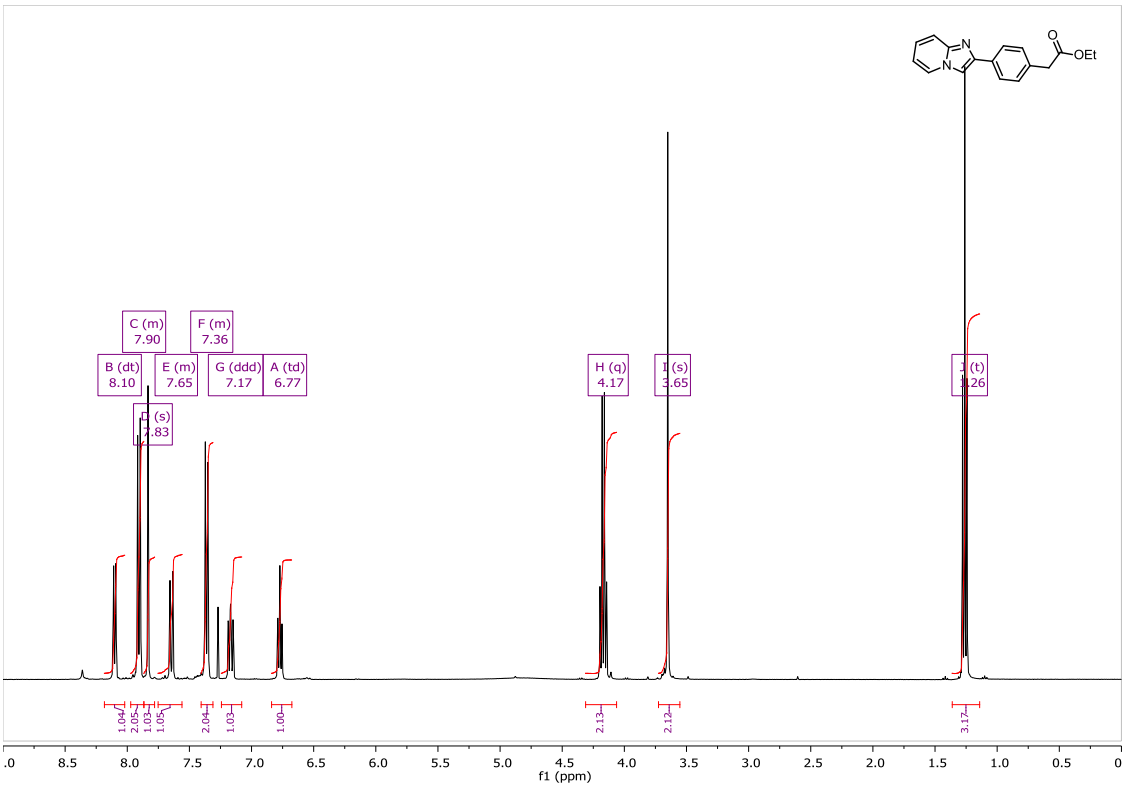


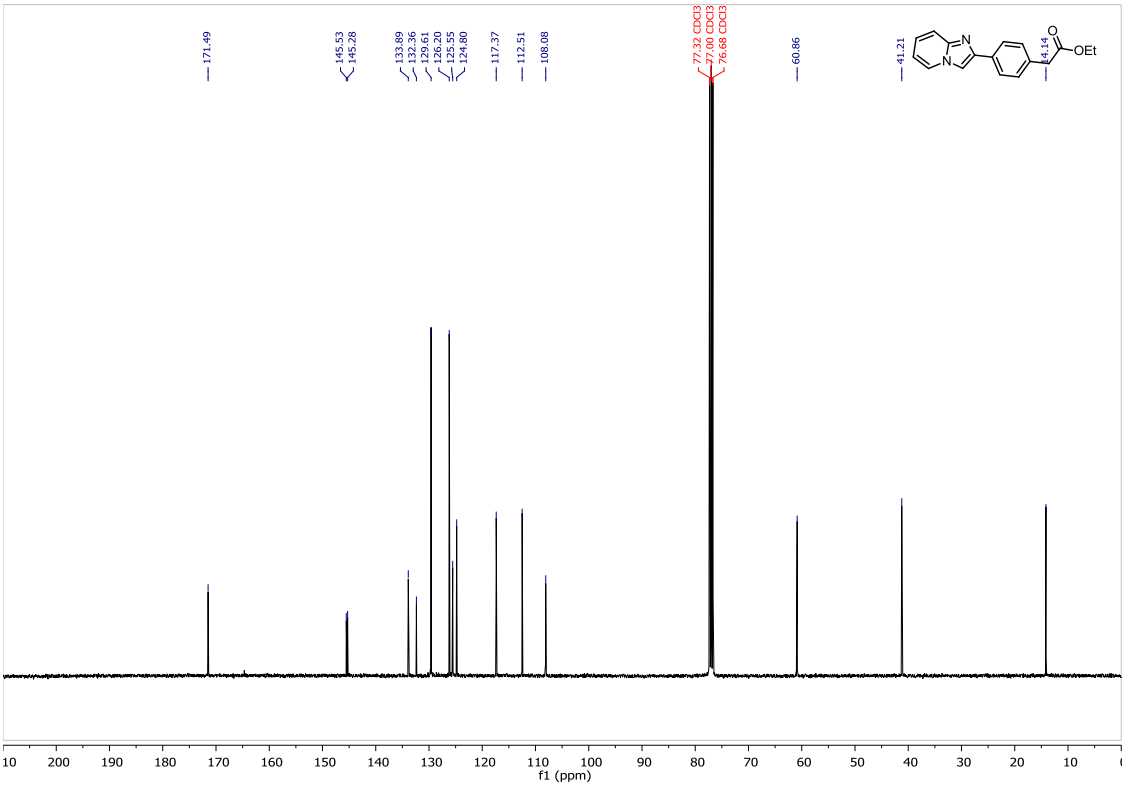
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **6**



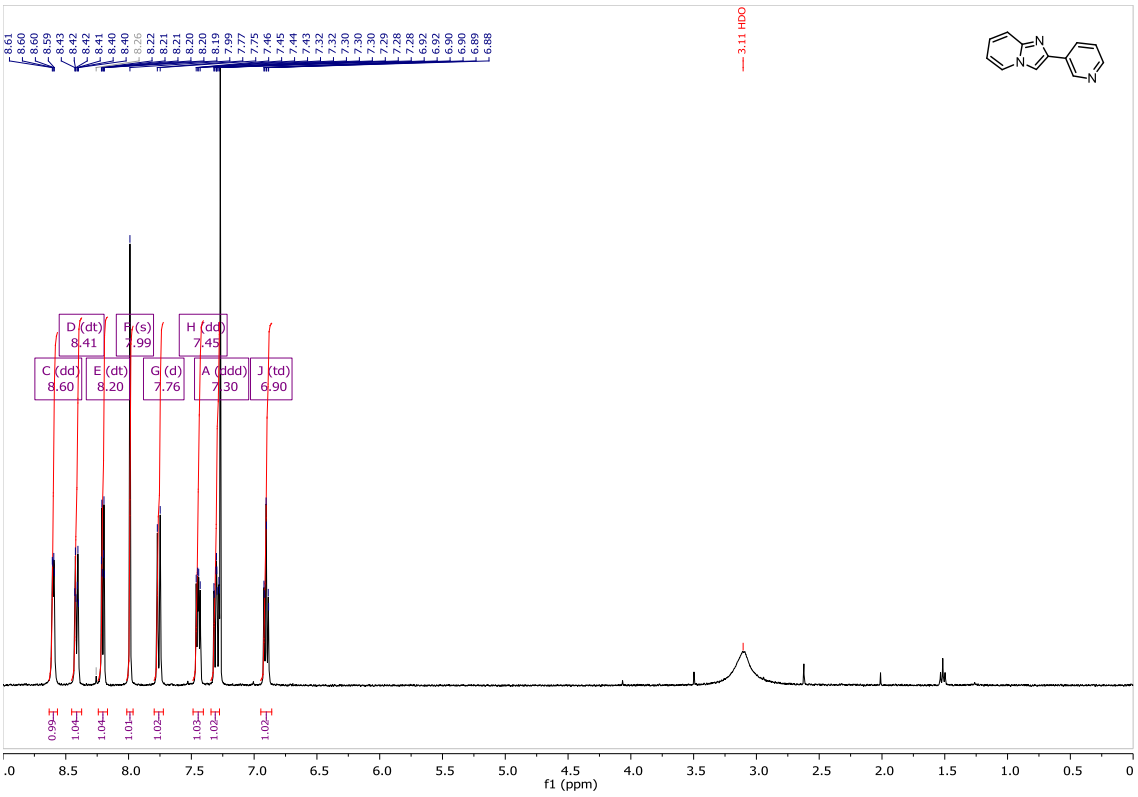


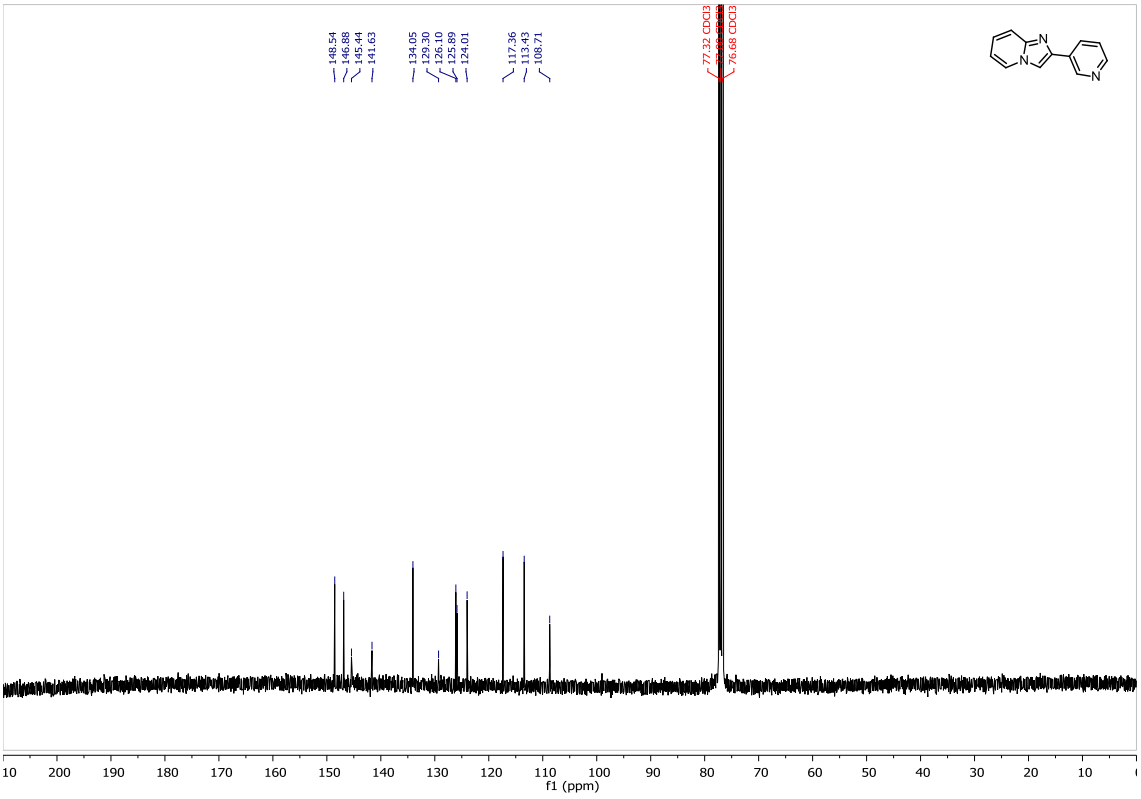
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **7**



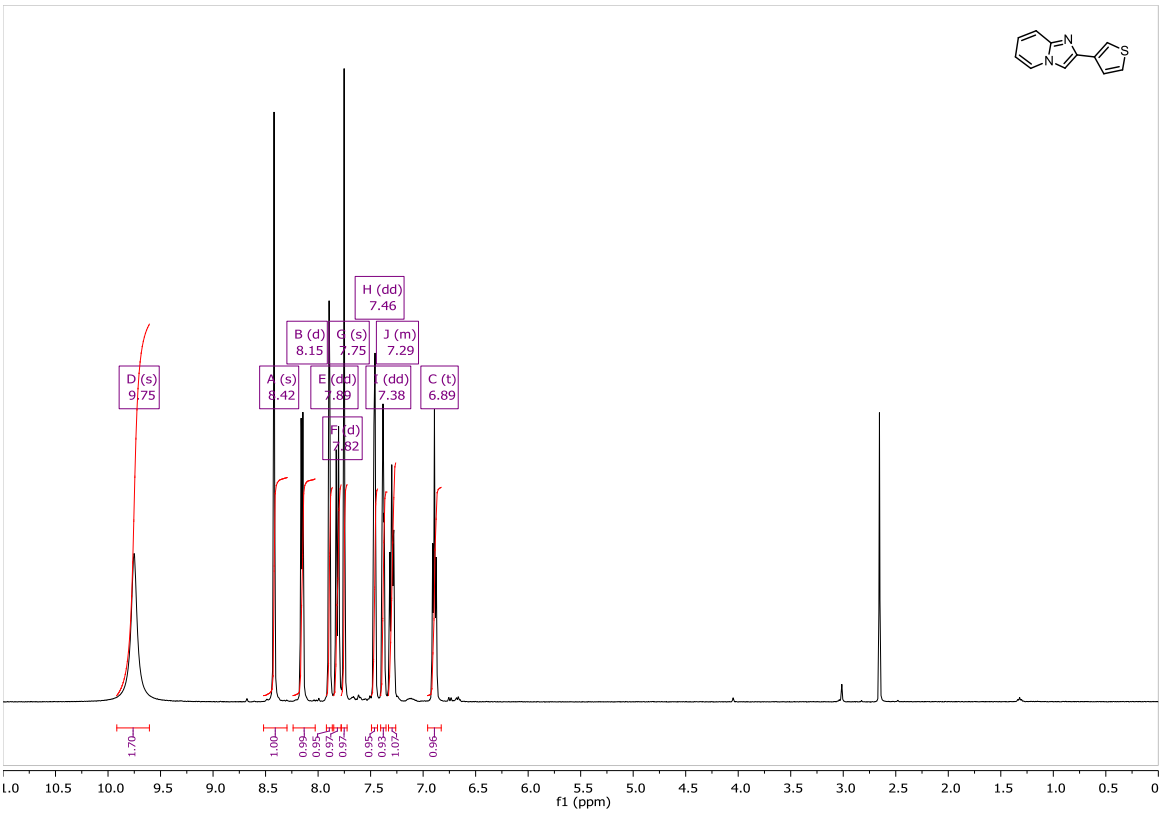


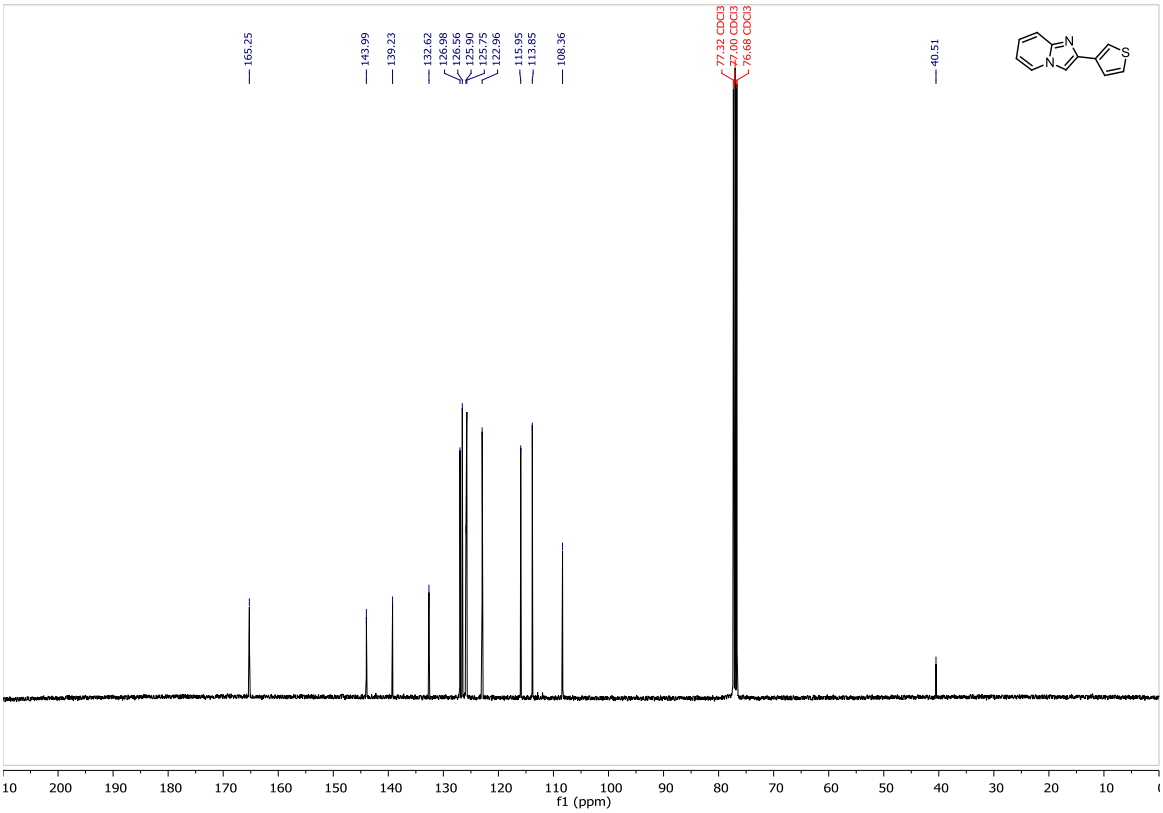
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **8**



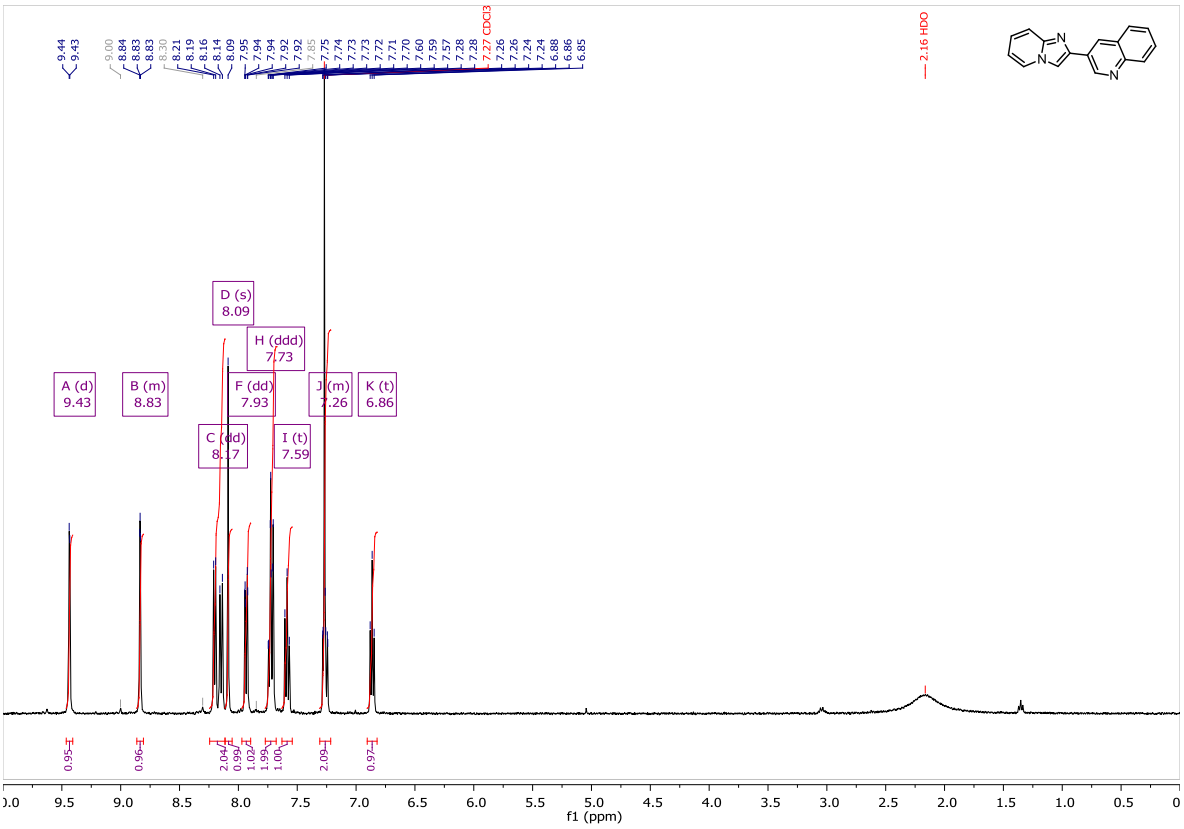


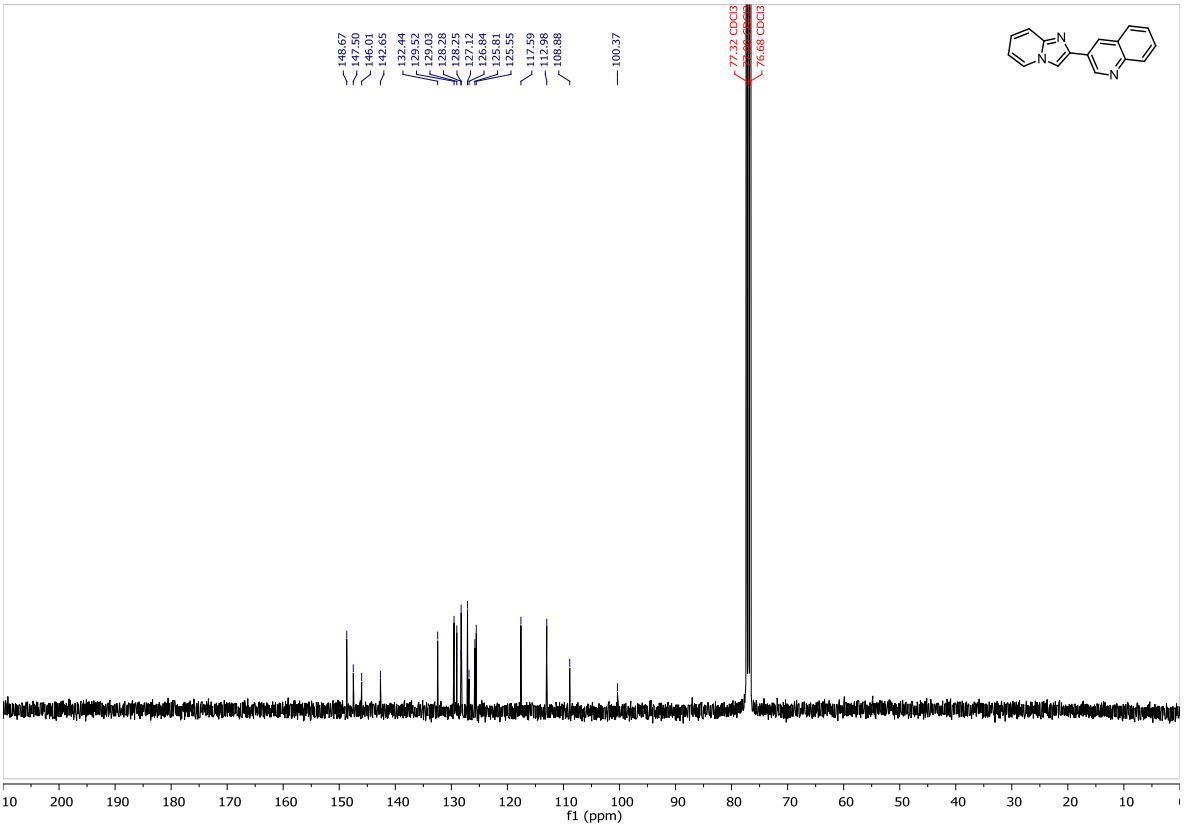
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **9**



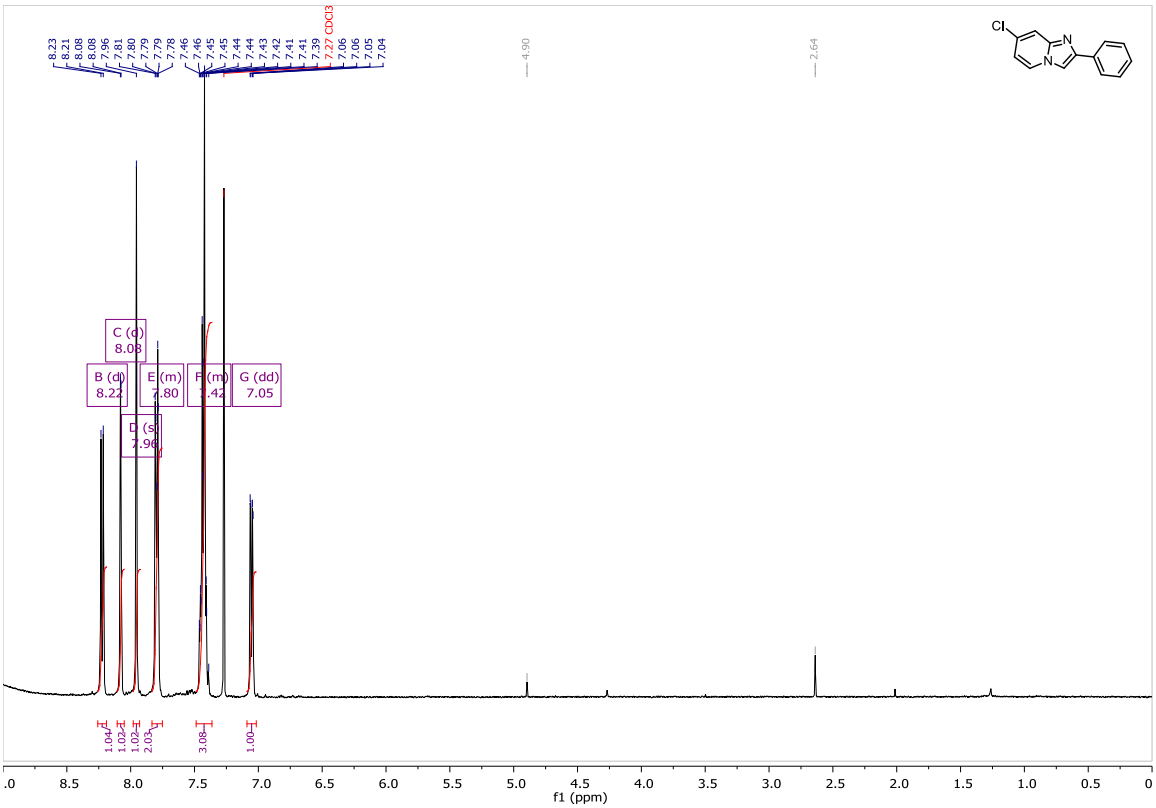


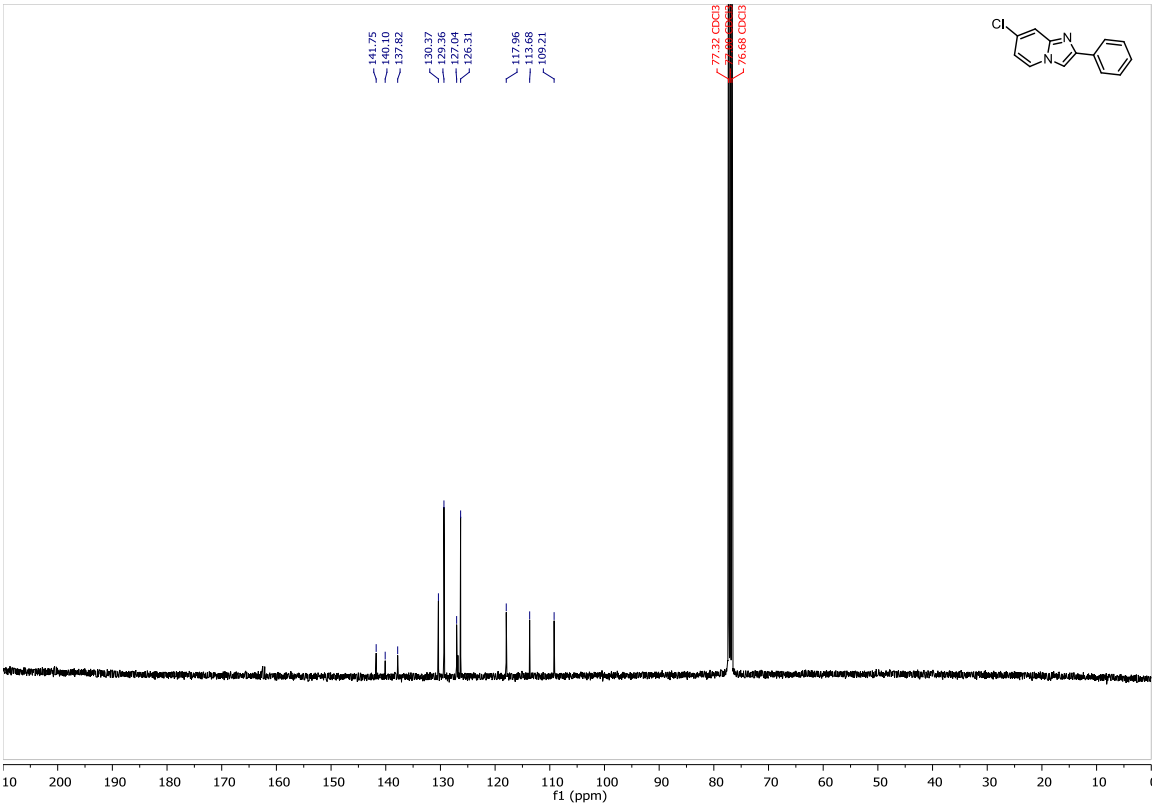
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **10**



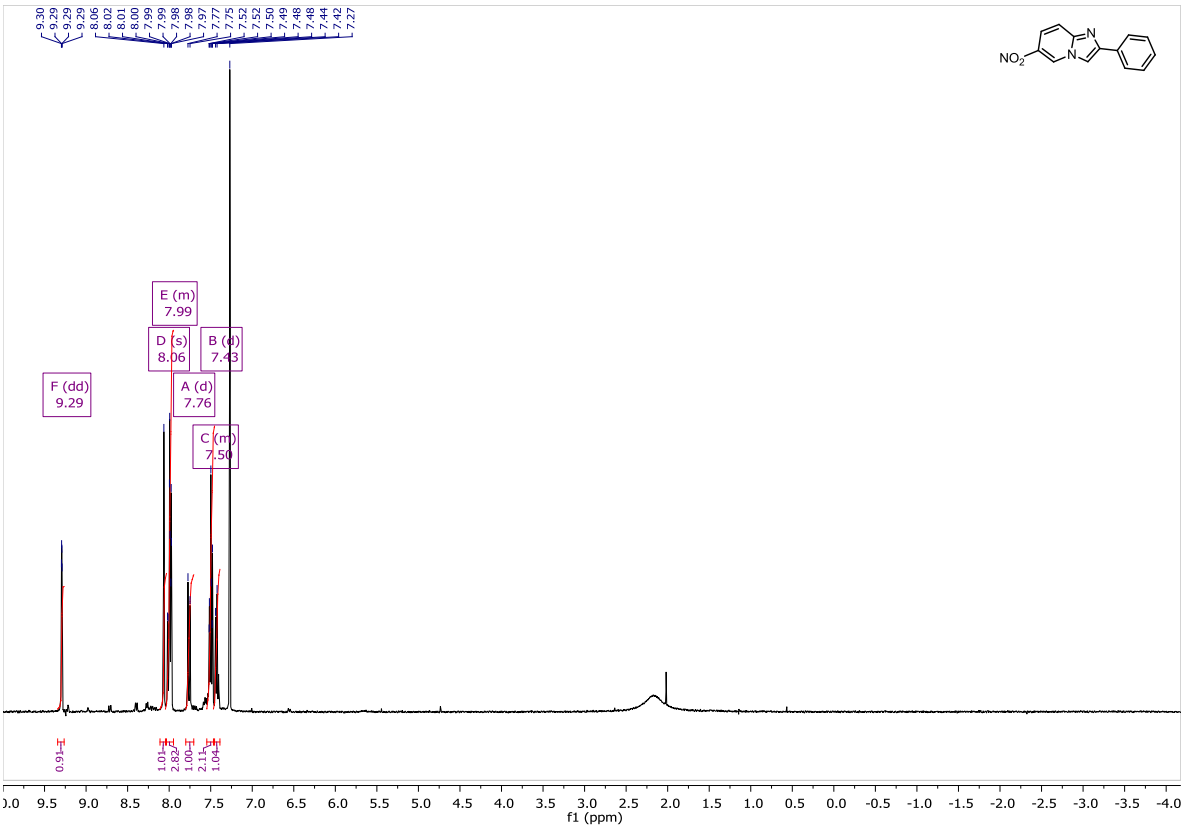


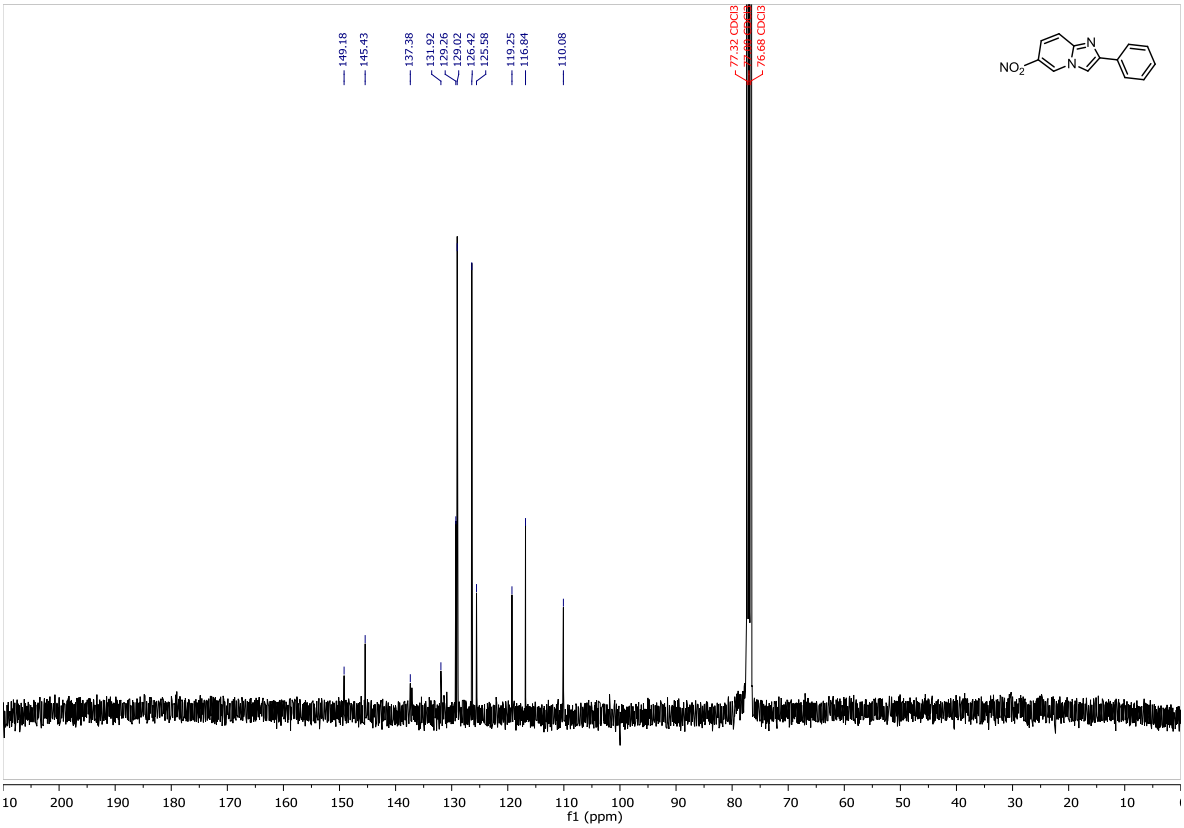
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **11**



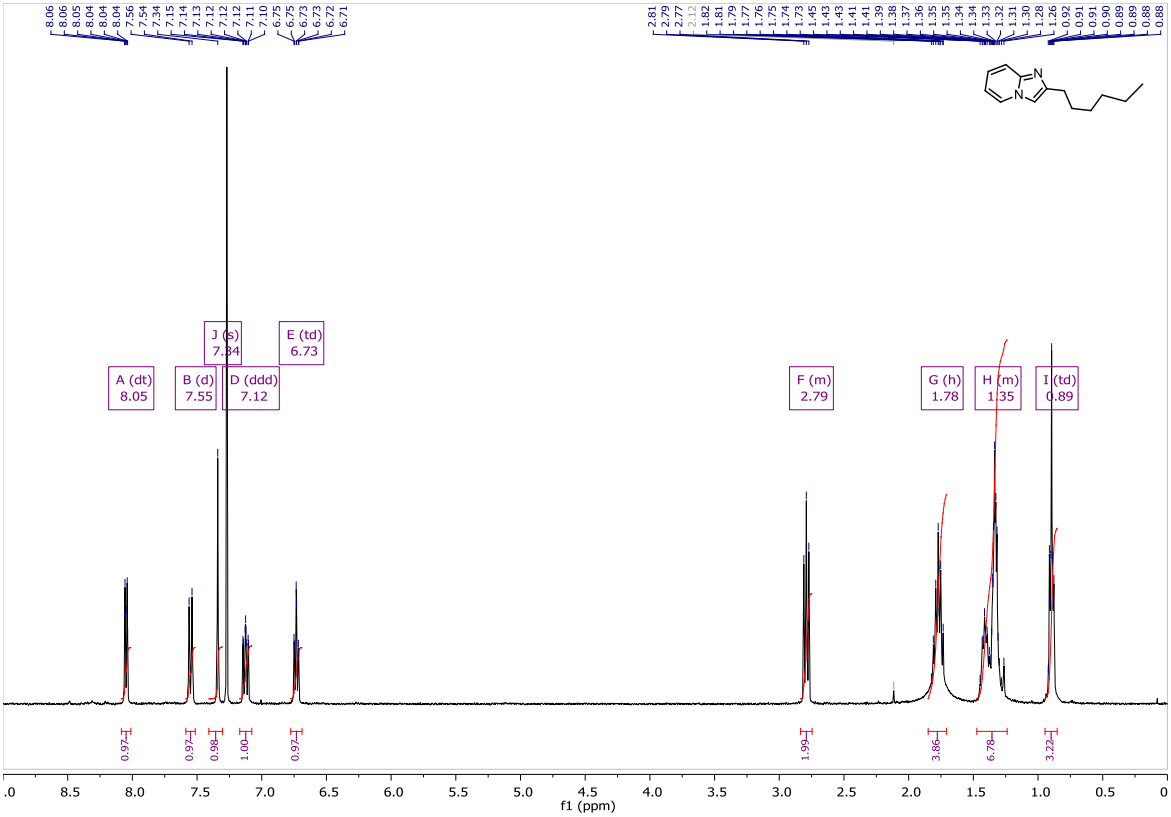


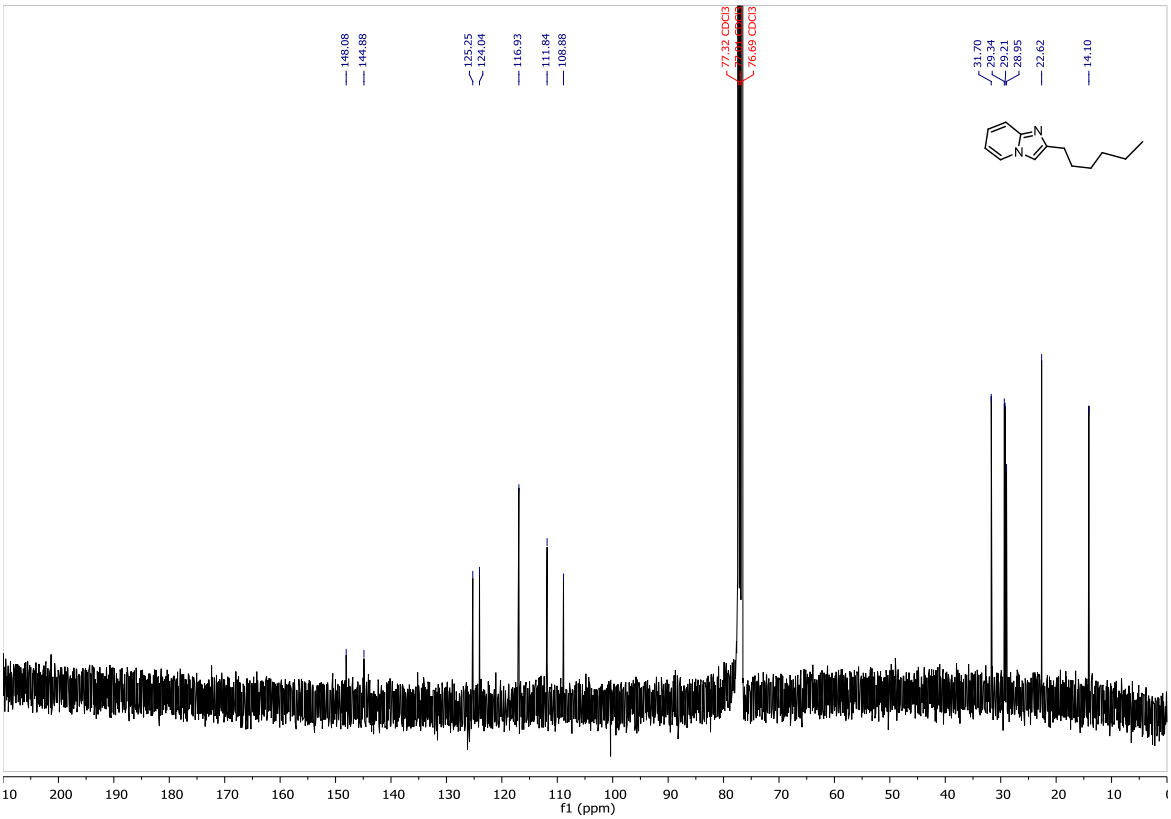
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12**



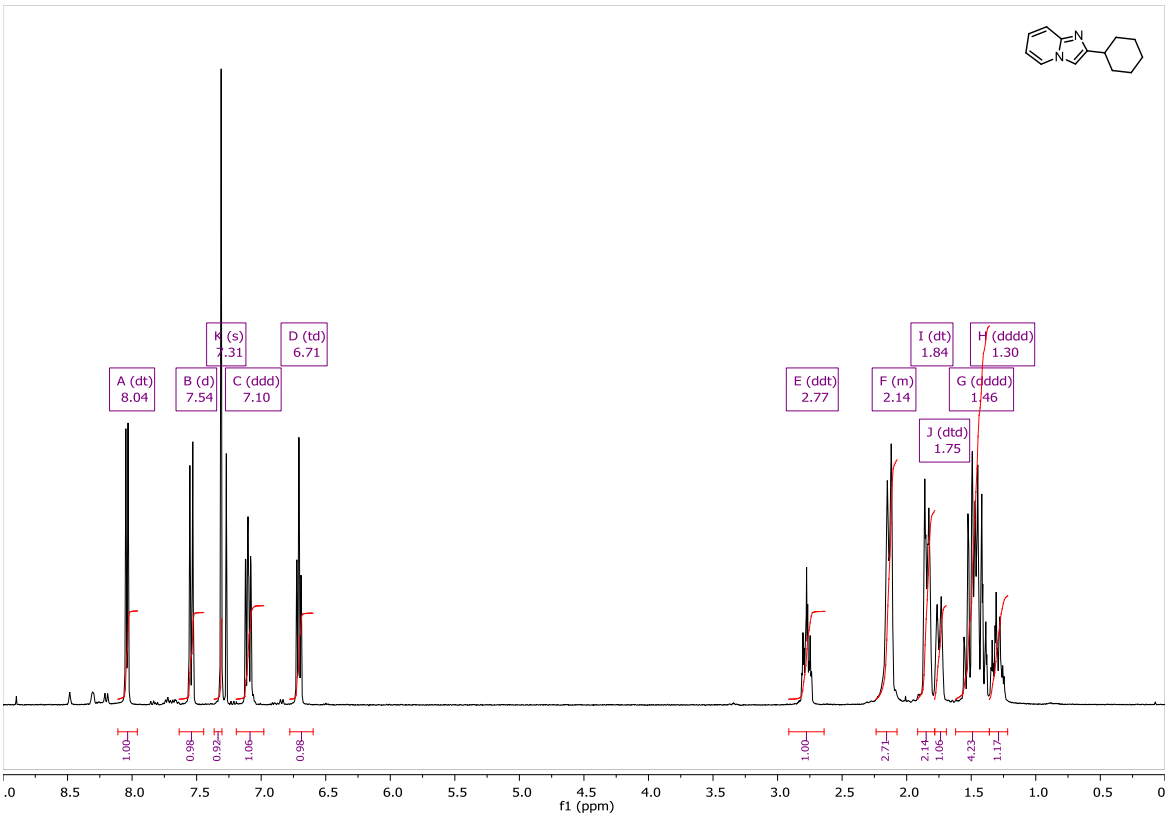


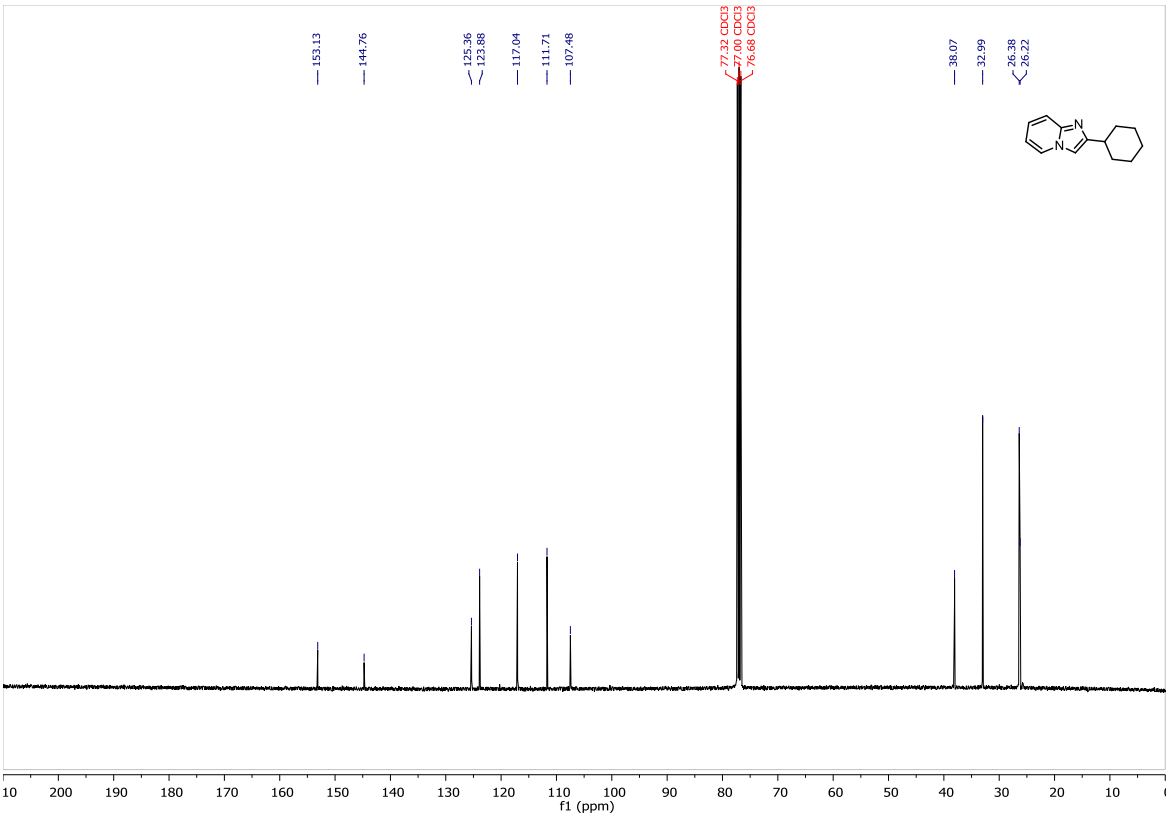
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **13**



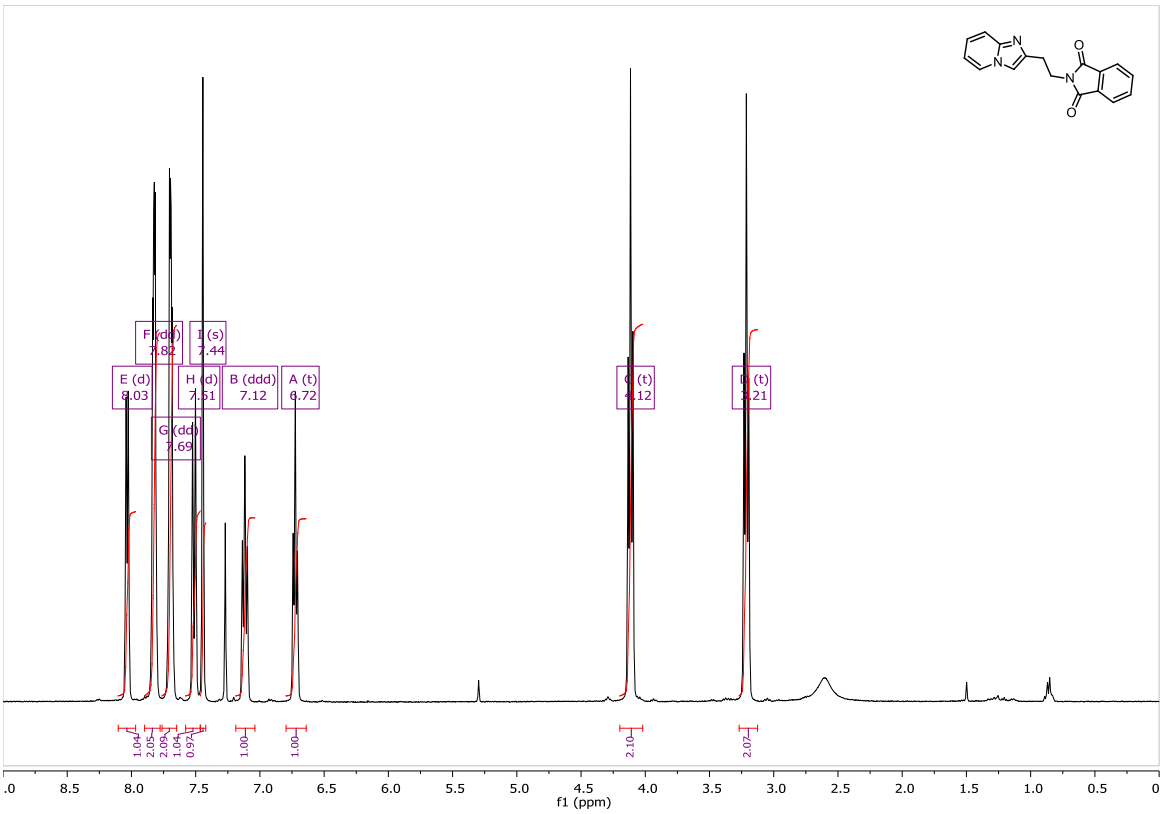


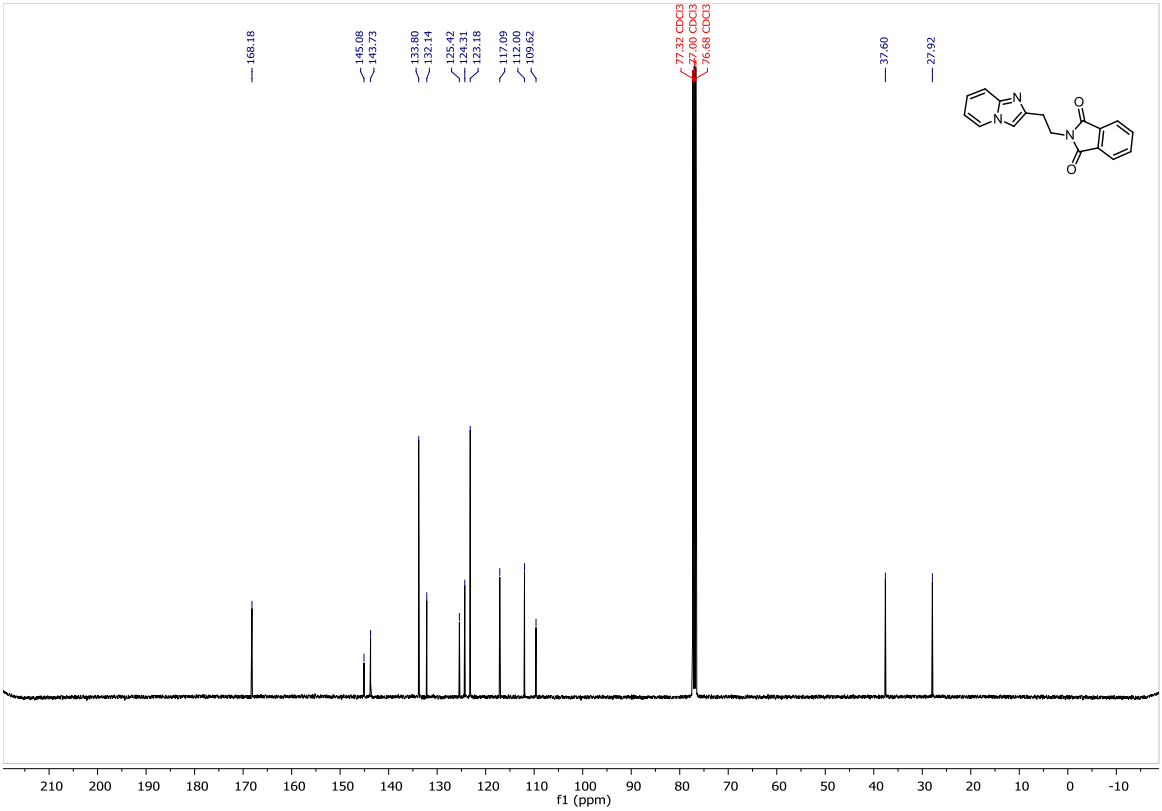
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **14**



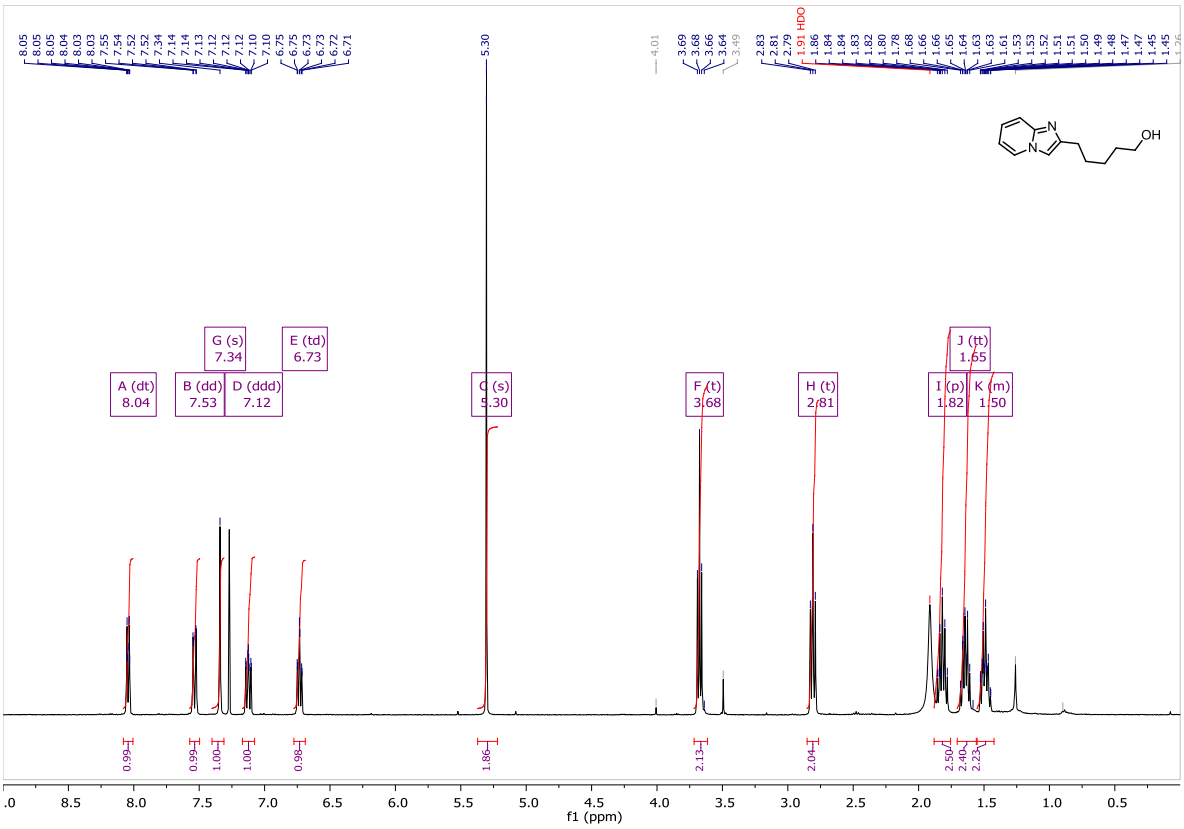


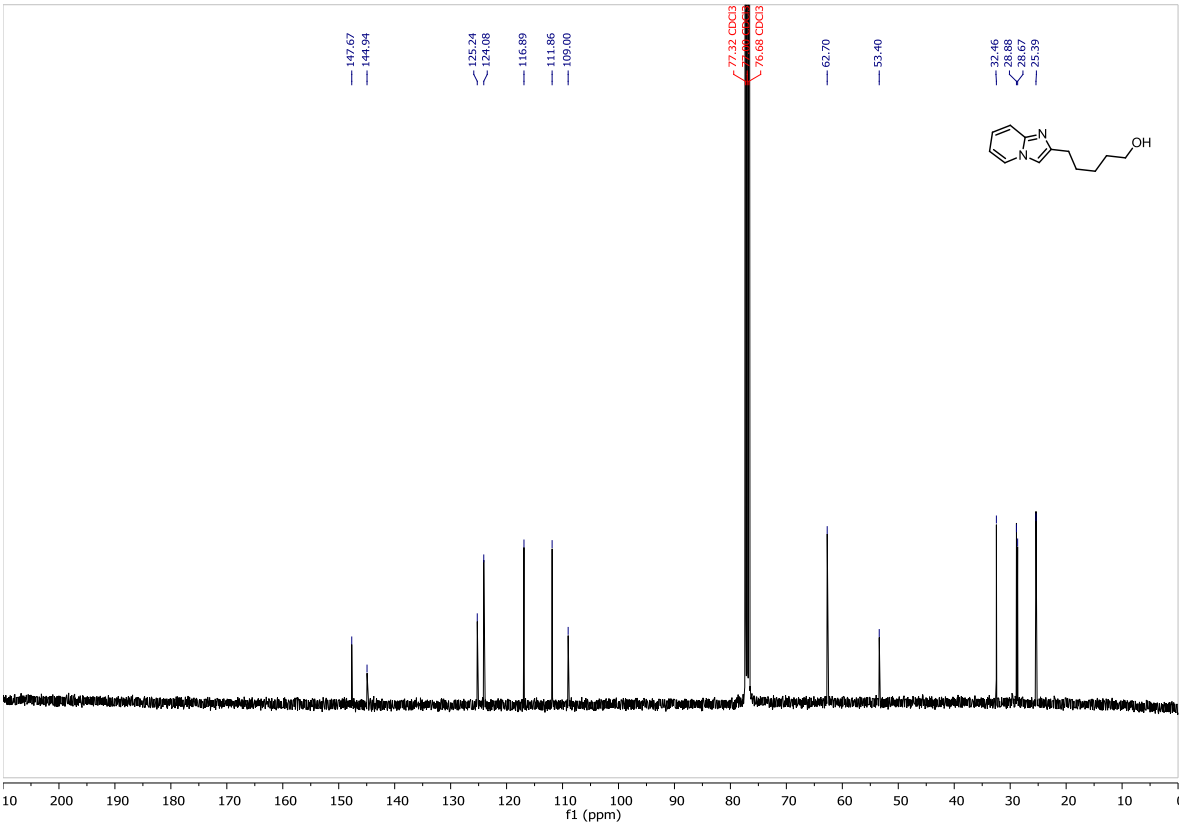
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **15**



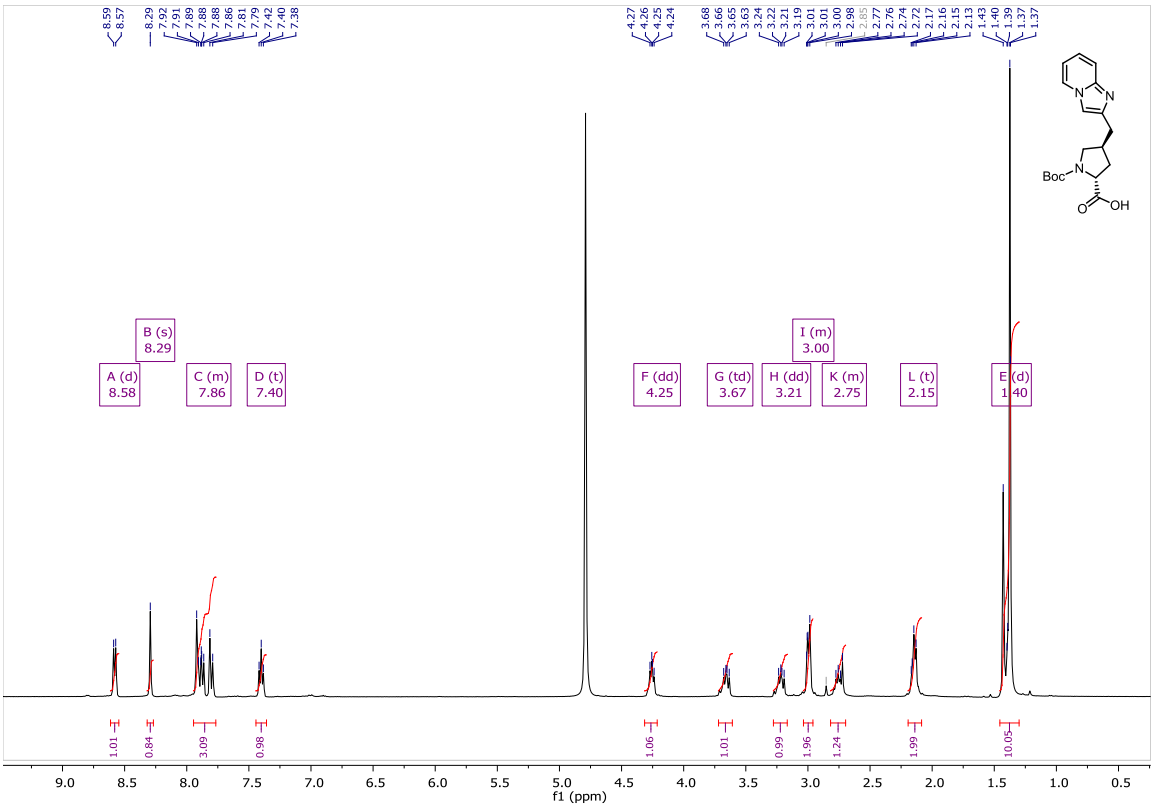


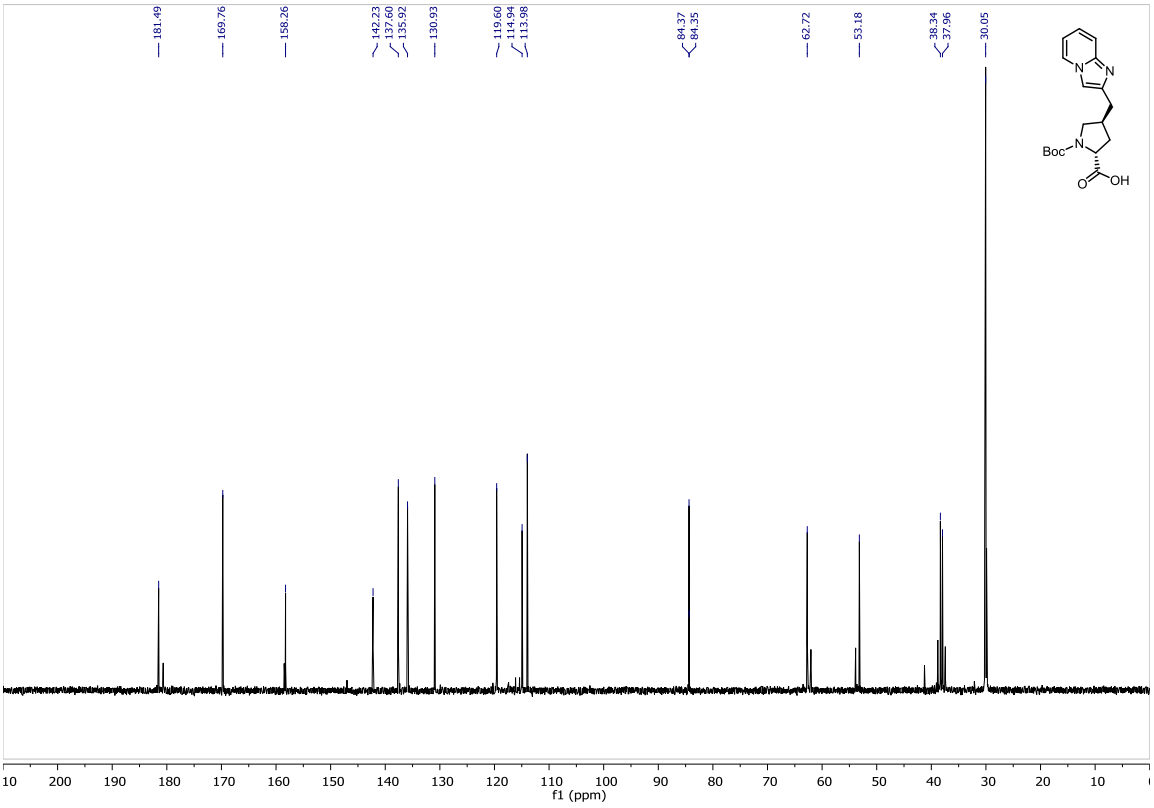
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **16**



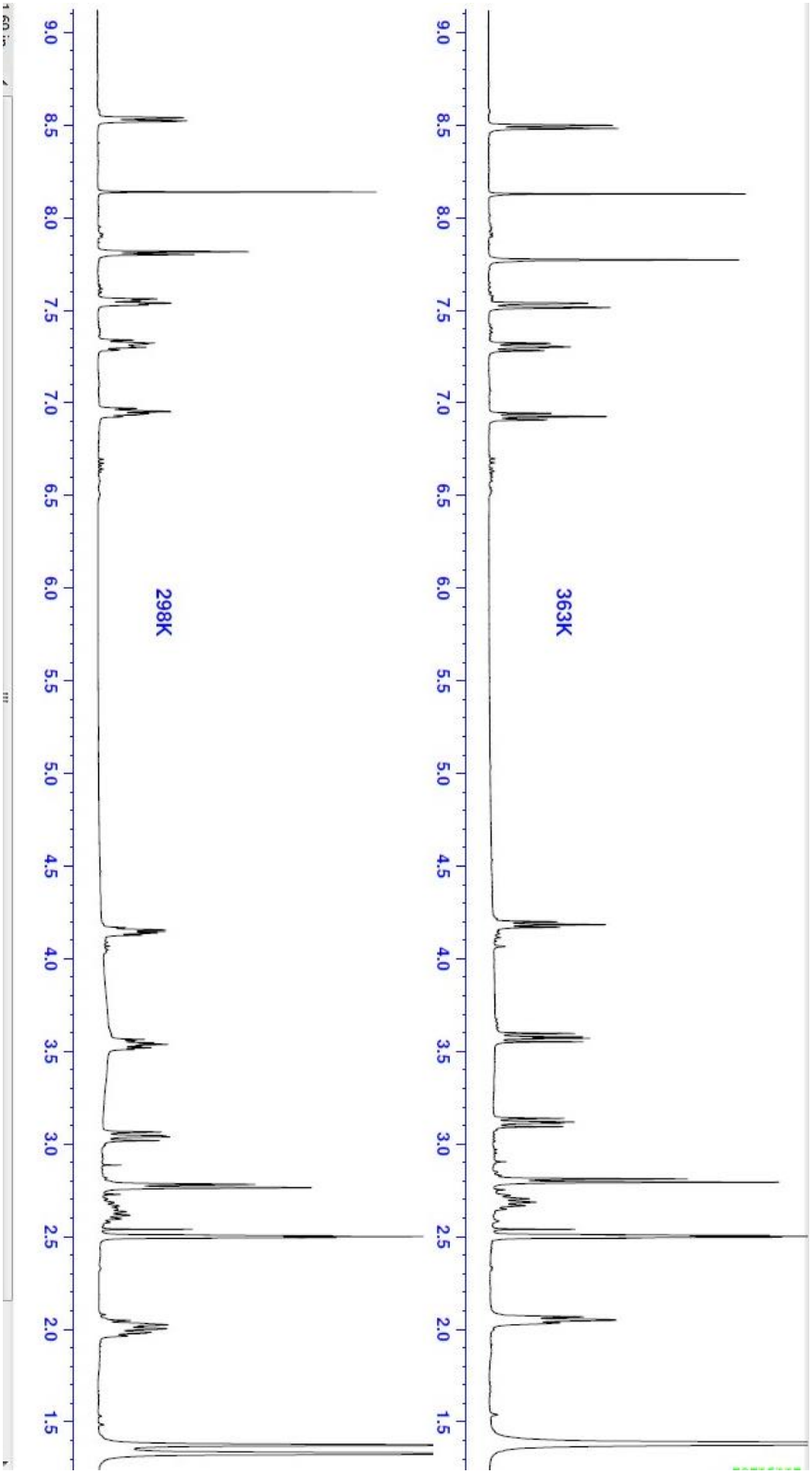


^{1}H NMR (400 MHz, d_6-DMSO) and ^{13}C NMR (100 MHz, d_6-DMSO) of **17**

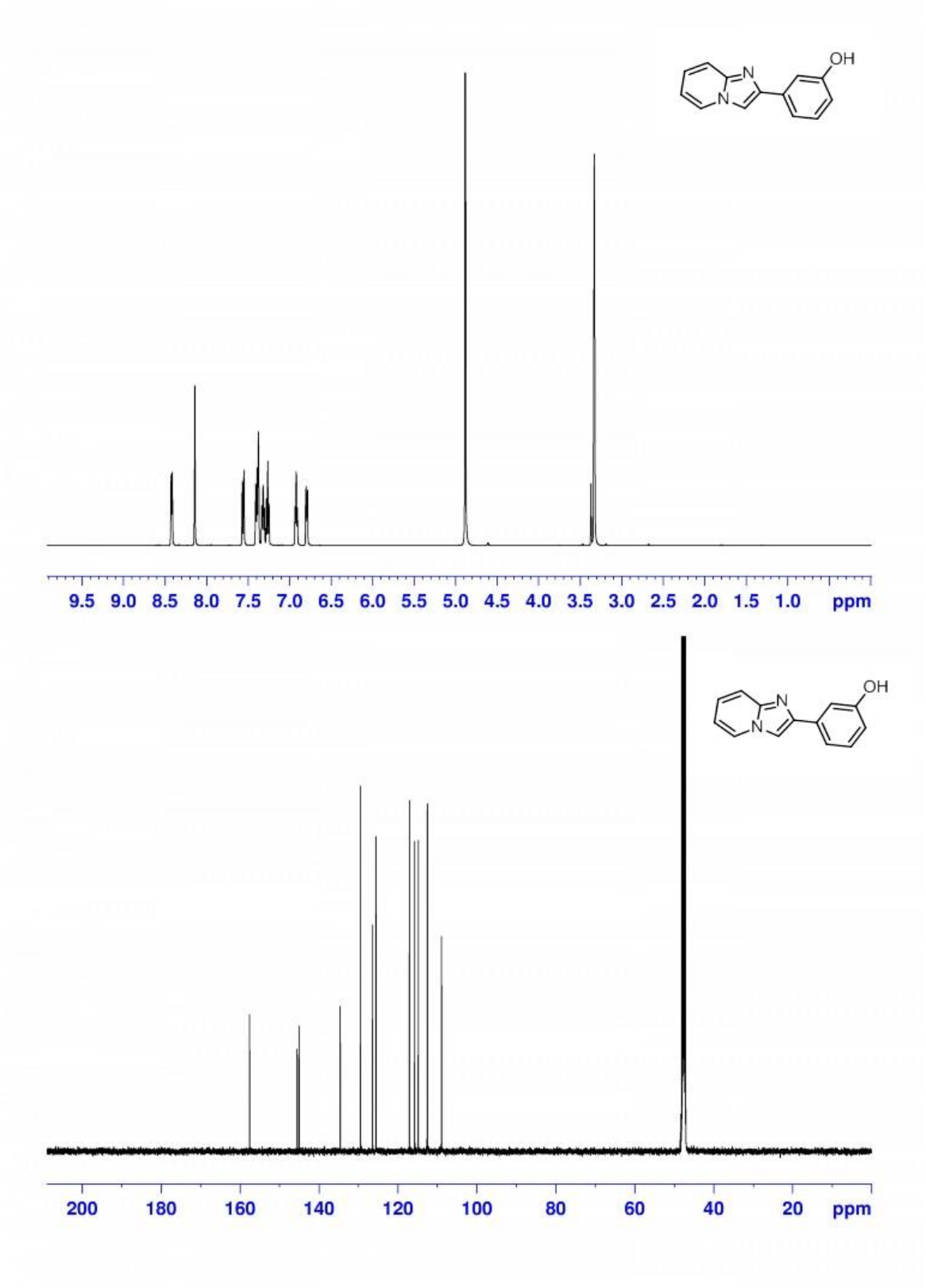




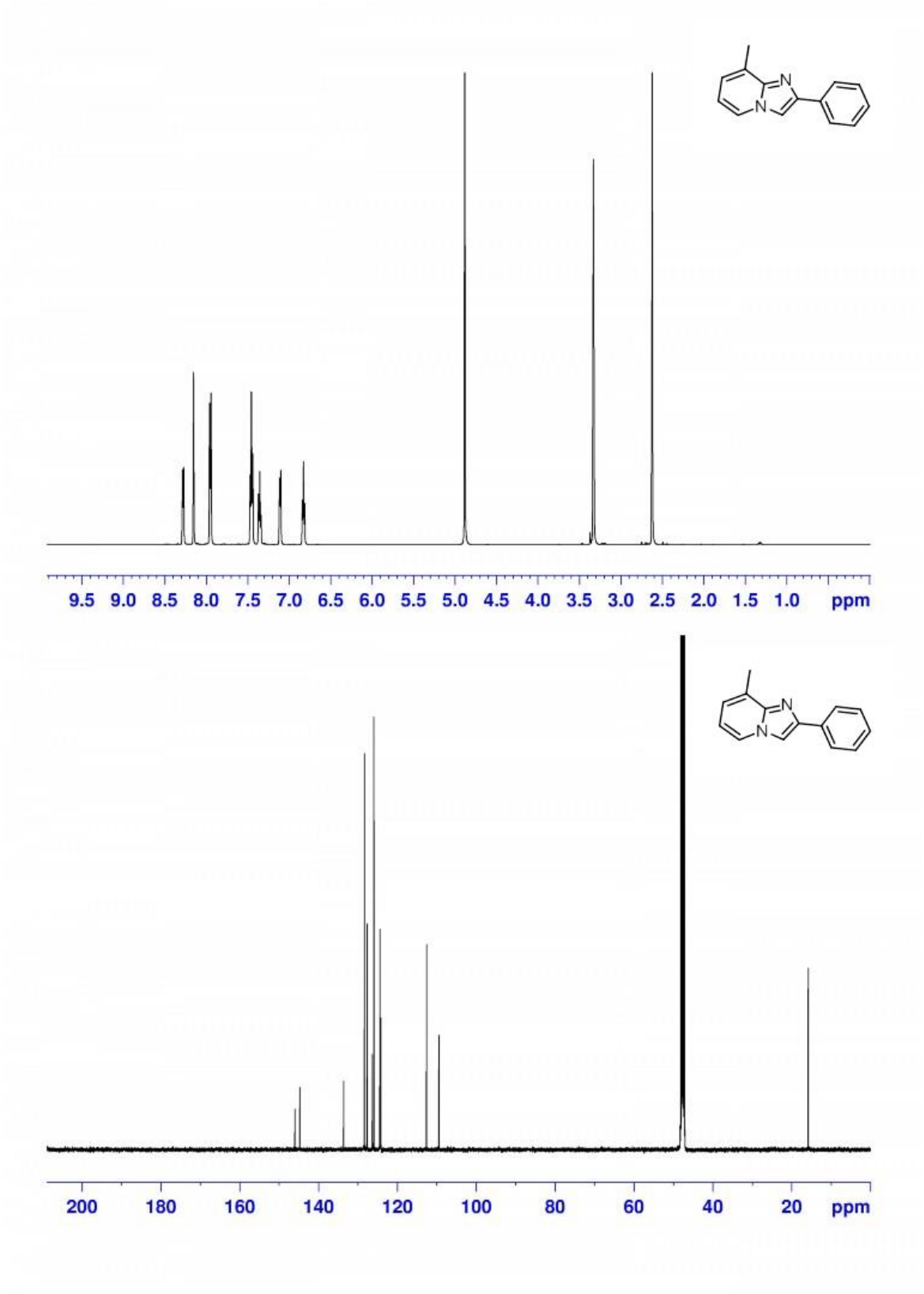
^{1}H NMR (400 MHz, d_6-DMSO) variable temperature of **17**



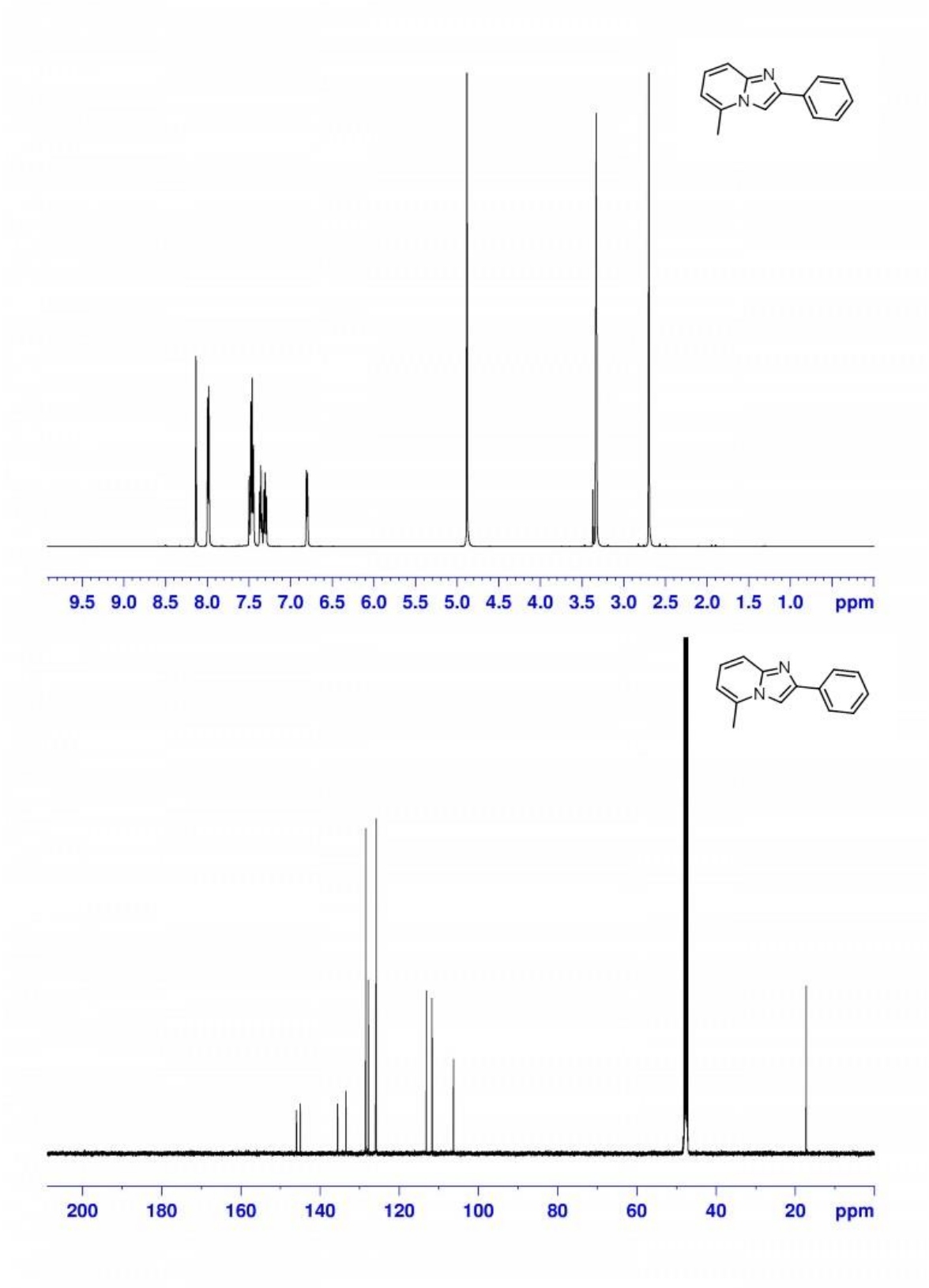
^{1}H NMR (500 MHz, d_4-MeOH) and ^{13}C NMR (126 MHz, d_4-MeOH) of **18**



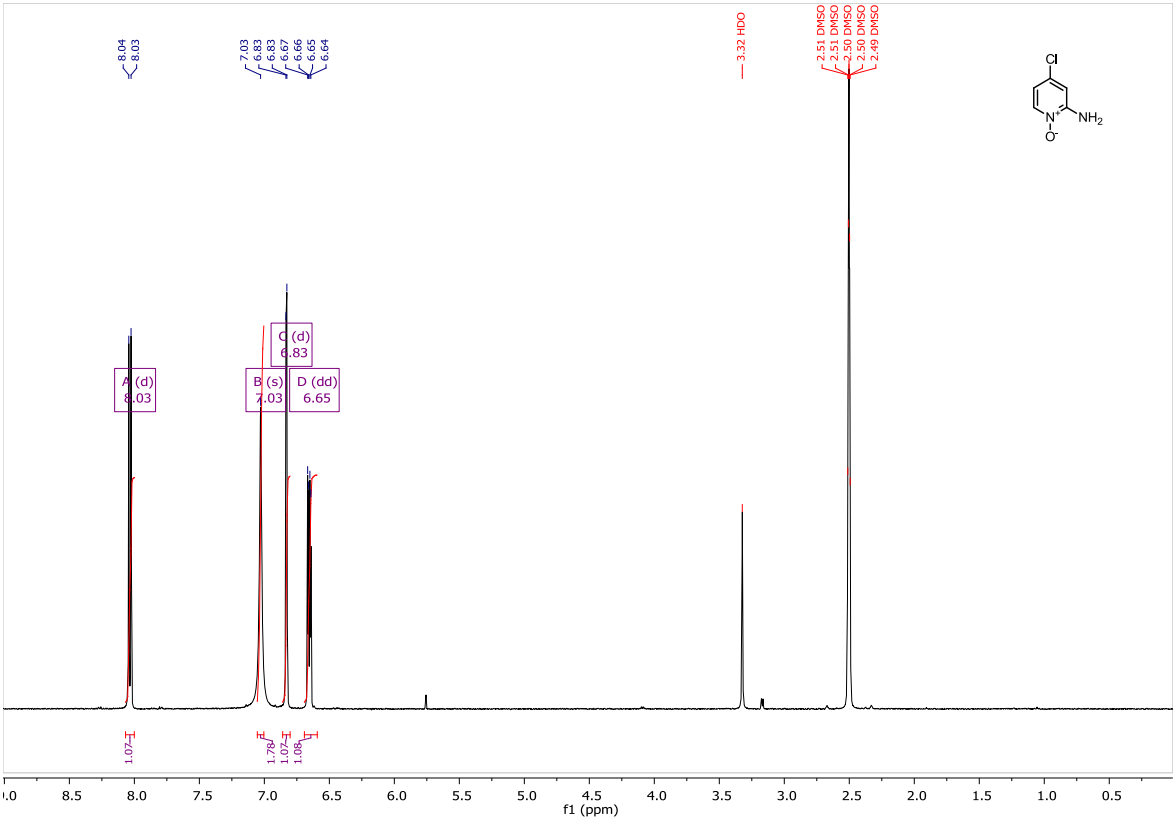
^{1}H NMR (500 MHz, d_4-MeOH) and ^{13}C NMR (126 MHz, d_4-MeOH) of **19**

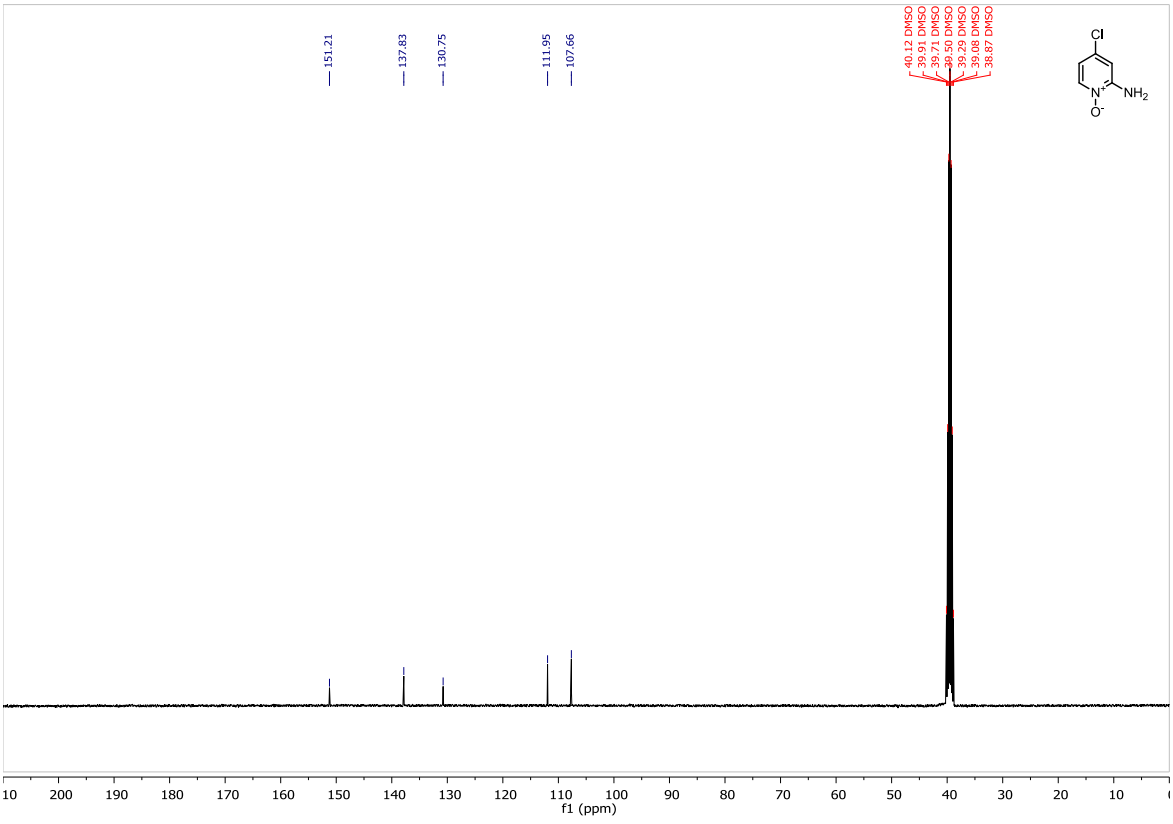


^{1}H NMR (500 MHz, d_4-MeOH) and ^{13}C NMR (126 MHz, d_4-MeOH) of **20**

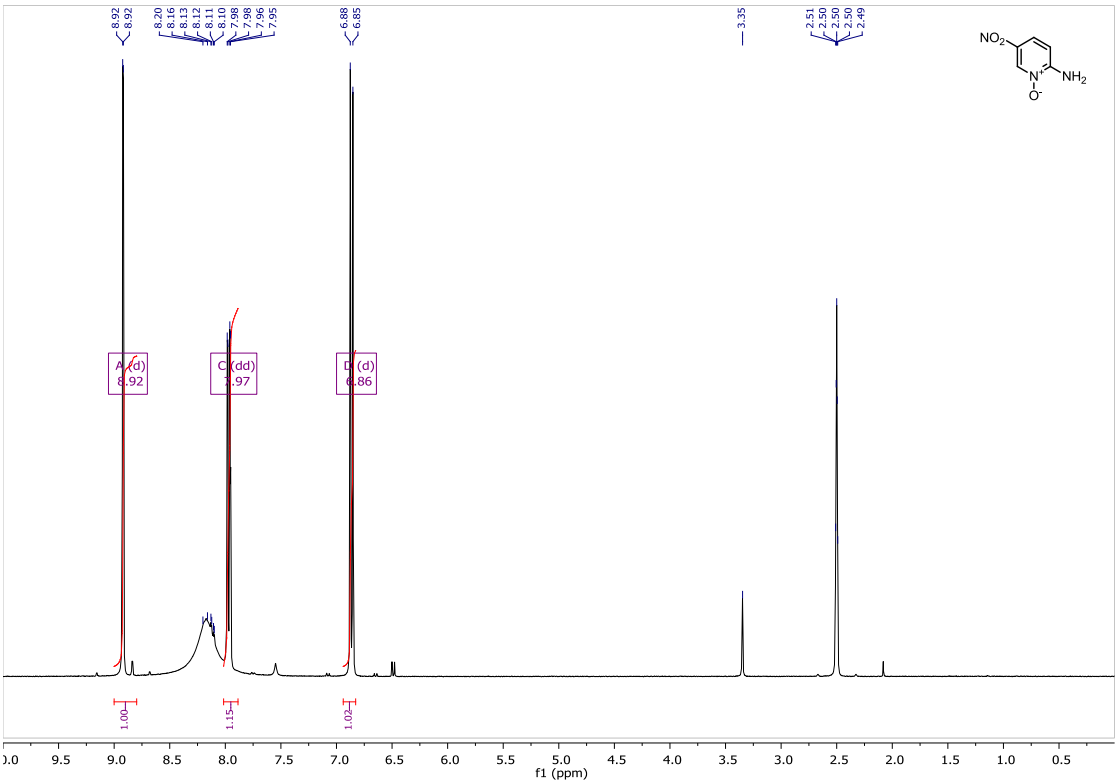


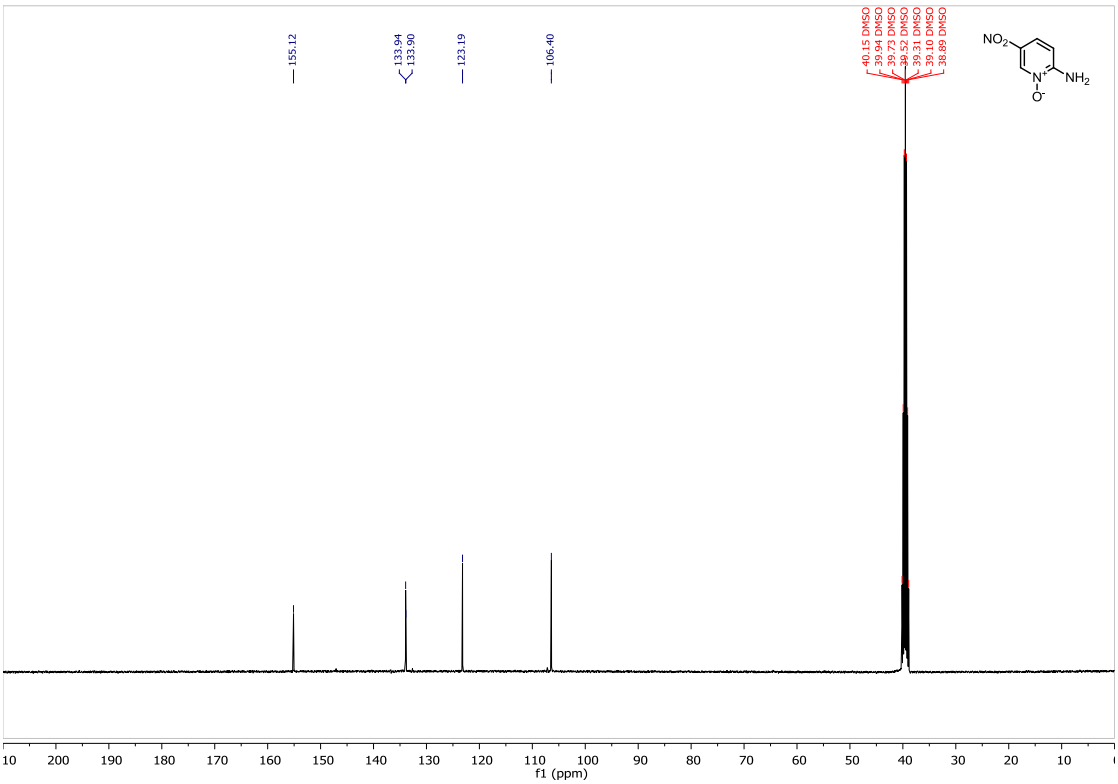
^{1}H NMR (400 MHz, d_6-DMSO) and ^{13}C NMR (100 MHz, d_6-DMSO).



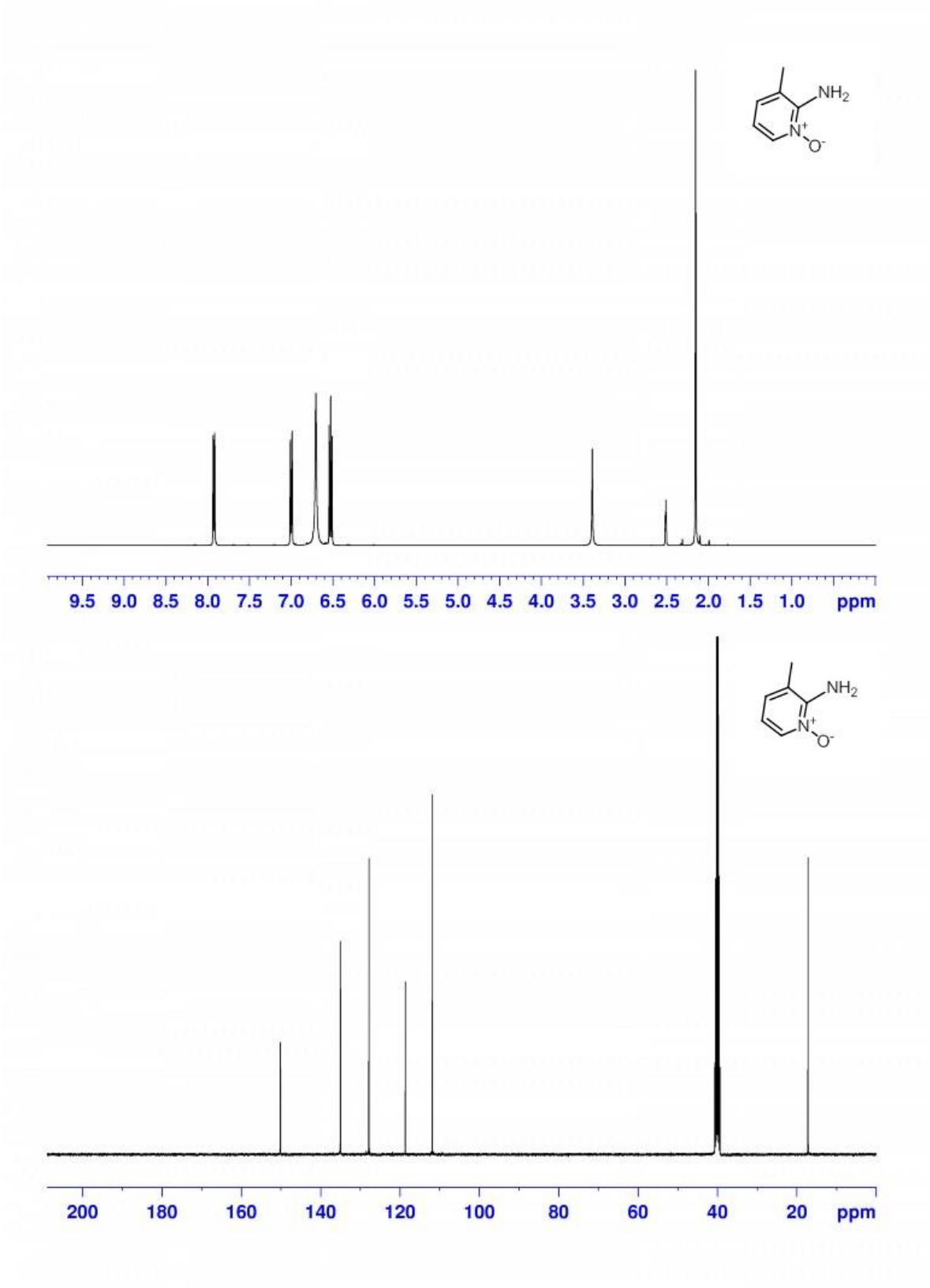


^{1}H NMR (400 MHz, d_6-DMSO) and ^{13}C NMR (100 MHz, d_6-DMSO).





^{1}H NMR (400 MHz, d_6-DMSO) and ^{13}C NMR (100 MHz, d_6-DMSO).



^{1}H NMR (400 MHz, d_6-DMSO) and ^{13}C NMR (100 MHz, d_6-DMSO).