Synthesis of Indolo- and Pyrrolo[1,2-a]quinoxalinones through Palladium-Catalyzed Oxidative Carbonylation of C_2 Position of Indole

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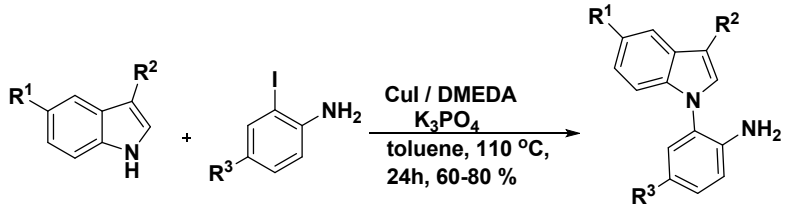
Supporting information:

General procedure for Synthesis of 2-(1*H*-indol-1-yl)anilines (1-5): [A1]



To a 20 mL oven dried reaction tube were added Indole (1equiv.), *N,N'*-Dimethylethylenediamine (DMEDA) (0.2 equiv.), aryl halide (1.1 equiv.) and CuI (0.1 equiv). Then toluene was added to the reaction mixture followed by K_3PO_4 (2.5equiv.). The reaction mixture was stirred under N_2 atmosphere at 110 ^oC for 24h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), filtered through a Celite pad and washed with additional ethyl acetate (10-20 mL). The filtrate was concentrated and the resulting residue was purified by column chromatography.

Spectral data

2-(1*H*-indol-1-yl)aniline (1): [A2]

Pale yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 1H), 7.19-7.06 (m, 6H), 6.81-6.75 (m, 2H), 6.61 (d, *J* = 2.8 Hz, 1H), 3.16 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 136.5, 129.3, 128.76, 128.73, 128.6, 125.0, 122.3, 121.0, 120.2, 118.8, 116.4, 110.8, 103.3.

2-(1*H*-indol-1-yl)-4-methylaniline (2): [A2]

Light brown liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 1H), 7.12-7.05 (m, 4H), 6.99-6.97 (m, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 0.4 Hz 3.2 Hz, 1H), 3.00 (br, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 136.5, 129.8, 129.0, 128.7, 128.6, 128.3, 125.0, 122.2, 121.0, 120.2, 116.5, 110.8, 103.2, 20.4.

4-*tert*-butyl-2-(1*H*-indol-1-yl)aniline (3):

Brownish yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.60 (m, 1H), 7.20 (dd, *J* = 2.4 Hz 8.4 Hz, 1H), 7.168-7.161 (m, 1H), 7.13-7.06 (m, 4H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 3.04 (br, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 140.3, 136.5, 128.8, 128.6, 126.1, 125.5, 124.7, 122.3, 121.0, 120.2, 116.2, 110.9, 103.1, 34.2, 31.6.

2-(5-chloro-1*H*-indol-1-yl)aniline (4): [A2]

Pale yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.19-7.14 (m, 2H), 7.09-7.04 (m, 2H), 6.98-6.96 (m, 1H), 6.80-6.75 (m, 2H), 6.54 (d, *J* = 2.4 Hz, 1H), 3.14 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 134.9, 130.0, 129.7, 129.6, 128.6, 126.0, 124.5, 122.6, 120.4, 118.8, 116.5, 111.9, 102.9.

2-(3-methyl-1*H*-indol-1-yl)aniline (5): [A2]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 6.8 Hz, 1H), 7.151-7.01 (m, 5H), 6.90 (s, 1H), 6.78-6.72 (m, 2H), 3.13 (br, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 136.8, 129.1, 128.9, 128.7, 126.2, 125.3, 122.3, 119.6, 119.1, 118.7, 116.3, 112.5, 110.7, 9.76.

***N*-(2-(1*H*-indol-1-yl)phenyl)acetamide (6):** [A2]

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.65-7.63 (m, 1H), 7.38(t, *J* = 7.2Hz, 1H), 7.18-7.10 (m, 4H), 7.0 (d, *J* = 4.8Hz, 1H) , 6.76 (s,1H), 6.68(d, *J* = 2Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 136.8, 134.5, 129.2, 128.8, 128.6, 128.1, 124.7, 123.0, 122.3, 121.4, 120.9, 110.4, 104.5, 24.7.

N-(2-(1H-indol-1-yl)phenyl)tosylamide (7): [A3]

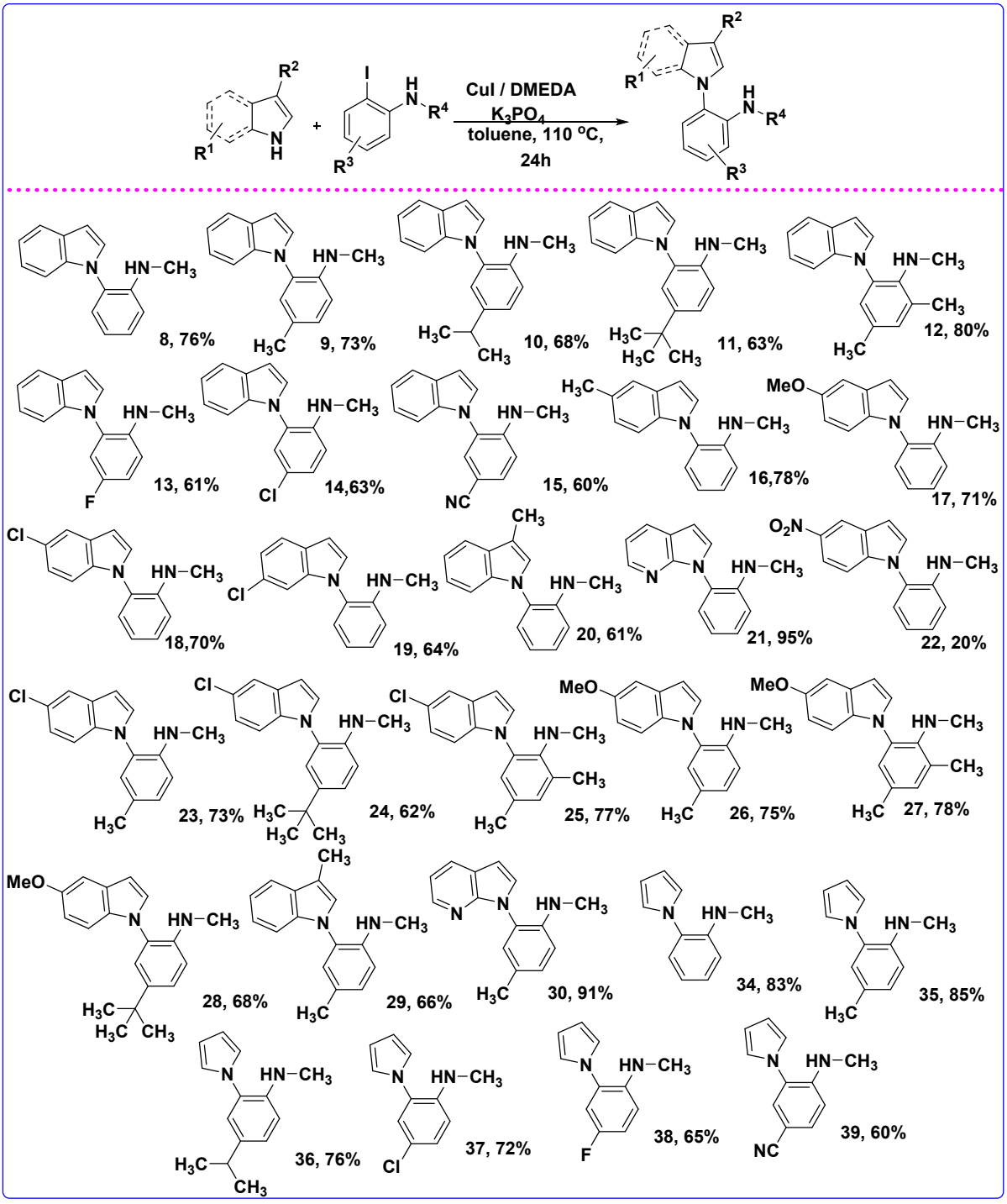
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 0.8 Hz, 8.3Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.46-7.40 (m, 3H), 7.23-7.07 (m, 6H), 6.67-6.62 (m, 3H), 6.34 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 136.8, 135.7, 133.9, 129.7, 129.6, 128.9, 128.6, 128.0, 127.2, 125.5, 123.0, 121.8, 121.3, 120.9, 109.8, 104.6, 21.7.

Methylation of iodoanilines: Reported procedure is followed.[B]

General procedure for Synthesis of 2-(1*H*-indol-1-yl)-*N*-methylanilines and *N*-methyl-2-(1*H*-pyrrol-1-yl)anilines :

To a 20 mL oven dried reaction tube were added Indole or pyrrole (1 equiv.), *N,N*′-dimethylethylenediamine (DMEDA) (0.2 equiv.), 2-iodo-*N*-methylaniline (1.2 equiv.) and CuI (0.1 equiv). Then toluene was added to the reaction mixture followed by K_3PO_4 (2.5equiv.). The reaction mixture was stirred under N_2 atmosphere at 110 ^{o}C for 24h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (5mL), filtered through a celite pad and

washed with additional ethyl acetate (10-20 mL). The filtrate was concentrated and the resulting residue was purified by column chromatography.



(**3-iodo-4-(methylamino)benzonitrile**: 4-aminonitrile is converted into 4-(methylamino)benzonitrile[B] followed by iodination).[C]

Spectral data

2-(1*H*-indol-1-yl)-*N*-methylaniline (8):

Color less oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 1H), 7.29-7.24 (m, 1H), 7.10-7.07 (m, 4H), 7.03-7.00 (m, 1H), 6.71-6.67 (m, 2H), 6.61 (d, *J* = 2.8 Hz, 1H), 3.50 (br, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 136.6, 129.6, 128.9, 128.6, 128.4, 124.5, 122.3, 121.0, 120.2, 116.6, 110.89, 110.86, 103.2, 30.3; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_2Na$ 245.1049 (M+Na), found 245.1058.

2-(1*H*-indol-1-yl)-*N*,4-dimethylaniline (9):

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 6.8 Hz, 1H), 7.10-7.01 (m, 5H), 6.92 (s, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 3.35 (br, 1H), 2.65 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 136.6, 130.0, 129.0, 128.9, 128.6, 126.0, 124.5, 122.2, 121.0, 120.2, 111.0, 110.8, 103.1, 30.6, 20.3; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}N_2$ 237.1386 (M+H), found 237.1386.

2-(1*H*-indol-1-yl)-4-isopropyl-*N*-methylaniline (10):

Pale orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.2 Hz, 1H), 7.16-7.04 (m, 5H), 6.97 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 3.37 (br, 1H), 2.78 (m, 1H), 2.66 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.5, 136.7, 129.0, 128.6, 127.4, 126.3, 124.5, 122.2, 121.0, 120.2, 111.0, 110.9, 103.1, 33.1, 30.6, 24.36, 24.30; HRMS (ESI, m/z) Calcd for $C_{18}H_{21}N_2$ 265.1705 (M+H), found 265.1697.

4-*tert*-butyl-2-(1*H*-indol-1-yl)-*N*-methylaniline (11):

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 6.8 Hz, 1H), 7.30 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.17-7.03 (m, 5H), 6.68 (d, *J* = 8.8 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 3.39 (br, 1H), 2.67 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 139.8, 136.7, 129.0, 128.6, 126.2, 125.5, 124.2, 122.2, 121.0, 120.2, 110.9, 110.6, 103.1, 34.0, 31.6, 30.5; HRMS (ESI, m/z) Calcd for $C_{19}H_{23}N_2$ 280.1888 (M+H), found 280.1887.

2-(1*H*-indol-1-yl)-*N*,4,6-trimethylaniline (12):

Pale red oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.12-7.04 (m, 4H), 6.94 (s, 1H), 6.82 (s, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), (br, 1H), 2.25-2.24 (m, 6H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.4, 131.9, 129.9, 129.2, 128.8, 128.6, 128.4, 127.3, 122.2, 120.8, 120.1, 110.8, 102.9, 34.7, 20.4, 18.8; HRMS (ESI, m/z) Calcd for $C_{17}H_{19}N_2$ 251.1548 (M+H), found 251.1563.

4-fluoro-2-(1*H*-indol-1-yl)-*N*-methylaniline (13):

Pale yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.13-7.08 (m, 3H), 7.03-6.98 (m, 2H), 6.88 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 6.64-6.61 (m, 2H), 3.36 (br, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 153.3, 142.4, 136.4, 128.7, 128.6, 124.7, 124.6, 122.6, 121.1, 120.5, 116.0, 115.8, 115.6, 115.4, 111.3, 111.2, 110.7, 103.8, 30.8; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_2F$ 241.1141 (M+H), found 241.1145.

4-chloro-2-(1*H*-indol-1-yl)-*N*-methylaniline (14):

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 1H), 7.23 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.14-7.06 (m, 4H), 7.02-7.00 (m, 1H), 6.63-6.61 (m, 2H), 3.51 (d, *J* = 3.6 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 136.4, 129.4, 128.7, 128.5, 128.3, 125.1, 122.6, 121.1, 120.7, 120.5, 111.7, 110.7, 103.9, 30.4; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_2Cl$ 257.0846 (M+H), found 257.0873.

3-(1H-indol-1-yl)-4-(methylamino)benzonitrile (15):

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.719-7.69 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.21-7.19 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 3.2 Hz, 1H), 4.18 (d, *J* = 3.6 Hz, 1H), 2.82 (d, *J* = 5.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 136.3, 134.1, 132.2, 128.8, 128.2, 124.3, 122.9, 121.3, 120.8, 119.5, 110.6, 110.4, 104.5, 98.4, 29.8; HRMS (ESI, m/z) Calcd for $C_{16}H_{13}N_3Na$ 270.1002 (M+Na), found 270.1009.

***N*-methyl-2-(5-methyl-1*H*-indol-1-yl)aniline (16):**

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.28-7.24 (m, 1H), 7.09-7.05 (m, 2H), 6.92 (s, 2H), 6.71-6.67 (m, 2H), 6.52 (d, *J* = 2.8 Hz, 1H), 3.53 (br, 1H), 2.67 (s, 3H), 2.38 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 135.0, 129.5, 129.0, 128.4, 128.2, 127.8, 124.7, 123.9, 120.6, 116.6, 110.8, 110.5, 102.7, 30.3, 21.5; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}N_2$ 237.1386 (M+H), found 237.1396.

2-(5-methoxy-1*H*-indol-1-yl)-N**-methylaniline (17):**

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.22 (m, 1H), 7.07-7.05 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.75-6.67 (m, 3H), 6.51 (d, *J* = 2.8 Hz, 1H), 3.76 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 145.5, 131.8, 129.5, 129.4, 129.0, 128.4, 124.8, 116.8, 112.5, 111.6, 111.1, 102.9, 102.6, 55.9, 30.4; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}N_2O$ 253.1337 (M+H), found 237.1343.

2-(5-chloro-1*H*-indol-1-yl)-*N*-methylaniline (18):

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.0 Hz, 1H), 7.30-7.26 (m, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.07-7.02 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.73-6.69 (m, 2H), 6.54 (d, *J* = 3.2 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 135.0, 130.2, 129.9, 129.6, 128.4, 126.0, 124.1, 122.6, 120.4, 116.8, 111.9, 111.2, 102.9, 30.4; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_2Cl$ 257.0841 (M+H), found 257.0839.

2-(6-chloro-1*H*-indol-1-yl)-*N*-methylaniline (19):

Light brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.32-7.27 (m, 1H), 7.10-7.01 (m, 4H), 6.77-6.71 (m, 2H), 6.58 (d, *J* = 3.2 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 137.1, 130.0, 129.6, 128.5, 128.4, 127.1, 124.1, 121.8, 121.0, 117.1, 111.4, 110.8, 103.4, 30.5; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_2Cl$ 257.0840 (M+H), found 257.0842.

***N*-methyl-2-(3-methyl-1*H*-indol-1-yl)aniline (20):**

Pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 1H), 7.27-7.23 (m, 1H), 7.10-7.06 (m, 3H), 6.99-6.97 (m, 1H), 6.88 (s, 1H), 6.73-6.68 (m, 2H), 2.67 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 136.9, 129.3, 129.0, 128.4, 126.4, 124.9, 122.2, 119.6, 116.1, 116.8, 112.5, 111.0, 110.7, 30.4, 9.7; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}N_2$ 237.1386 (M+H), found 237.1387.

***N*-methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)aniline (21):**

White solid, Mp: 75-80 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.38-7.31 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14-7.11 (m, 1H), 6.87-6.81 (m, 2H), 6.66-6.65 (d, *J* = 3.6 Hz, 1H), 3.98 (br, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 145.5, 143.9, 129.8, 129.7, 129.3, 128.4, 124.3, 120.9, 117.2, 116.5, 111.7, 101.6, 30.5; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_3Na$ 246.1002 (M+H), found 246.1009.

_N_-methyl-2-(5-nitro-1_H_-indol-1-yl)aniline (22):

Yellow solid, Mp: 136-138 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.34-7.32 (m, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 9.2 Hz, 1H), 6.78-6.72 (m, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 142.3, 139.5, 132.2, 130.4, 128.2, 127.8, 123.2, 118.2, 117.9, 116.9, 111.3, 110.9, 105.6, 30.3; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_3O_2$ 268.1081 (M+H), found 268.1084.

2-(5-chloro-1_H_-indol-1-yl)-_N_,4-dimethylaniline (23):

Pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.13-7.03 (m, 3H), 6.94-6.90 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 3.2 Hz, 1H), 2.65 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 135.0, 130.35, 130.32, 129.6, 128.9, 126.8, 126.0, 124.3, 122.6, 120.3, 111.9, 111.7, 102.8, 30.8, 20.3; HRMS (ESI, m/z) Calcd for $C_{16}H_{15}N_2Cl$ 271.0997 (M+H), found 271.0996.

4-_tert_-butyl-2-(5-chloro-1_H_-indol-1-yl)-_N_-methylaniline (24):

Light orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.30 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.14-7.13 (m, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 2.8 Hz, 1H), 3.51 (br, 1H), 2.64 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 140.2, 135.1, 130.3, 129.6, 126.5, 125.9, 125.3, 123.9, 122.6, 120.3, 112.0, 111.1, 102.7, 34.0, 31.6, 30.6; HRMS (ESI, m/z) Calcd for $C_{19}H_{22}N_2Cl$ 313.1486 (M+H), found 313.1479.

2-(5-chloro-1_H_-indol-1-yl)-_N_,4,6-trimethylaniline (25):

Orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 7.057-7.031 (m, 1H), 6.98-6.95 (m, 2H), 6.80 (s, 1H), 6.52 (d, *J* = 2.8 Hz, 1H), 2.25 (s, 3H), 2.19 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 135.8, 132.1, 130.5, 130.4, 129.4, 128.9, 128.1, 127.7, 127.3, 125.8, 122.5, 120.2, 111.9, 102.6, 34.5, 20.4, 18.7; HRMS (ESI, m/z) Calcd for $C_{17}H_{18}N_2Cl$ 285.1153 (M+H), found 285.1155.

2-(5-methoxy-1*H*-indol-1-yl)-*N*,4-dimethylaniline (26):

Colorless oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.085-7.064 (m, 3H), 6.92-6.90 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 8 Hz, 1H), 6.51 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 3.38 (br, 1H), 2.66 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 143.4, 131.9, 129.9, 129.5, 129.0, 128.8, 126.0, 124.6, 112.4, 111.6, 111.0, 102.8, 102.6, 56.0, 30.6, 20.2; HRMS (ESI, m/z) Calcd for $C_{17}H_{19}N_2O$ 267.1492 (M+H), found 267.1497.

2-(5-methoxy-1*H*-indol-1-yl)-*N*,4,6-trimethylaniline (27):

Colorless oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 2.8 Hz, 1H), 7.05 (s, 1H), 6.97-6.93 (m, 2H), 6.81 (s, 1H), 6.75 (s, 1H), 6.50 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 2.71 (br, 1H), 2.25 (d, *J* = 2.0 Hz, 6H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 143.1, 132.7, 131.8, 130.1, 129.6, 128.8, 128.7, 127.7, 127.3, 112.4, 111.5, 102.6, 102.4, 55.9, 34.7, 20.4, 18.8; HRMS (ESI, m/z) Calcd for $C_{18}H_{21}N_2O$ 281.1648 (M+H), found 281.1663.

4-*tert*-butyl-2-(5-methoxy-1*H*-indol-1-yl)-*N*-methylaniline (28):

Light brown oil, ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 1.6 Hz, 8.4 Hz 1H), 7.19-7.16 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.86-6.84 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.50 (br, 1H), 2.76 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 143.2, 139.8, 131.9, 129.5, 129.0, 126.1, 125.4, 124.3, 112.5, 111.7, 110.6, 102.7, 102.6, 56.0, 34.0, 31.6, 30.6; HRMS (ESI, m/z) Calcd for $C_{20}H_{25}N_2O$ 309.1961 (M+H), found 309.1964.

***N*,4-dimethyl-2-(3-methyl-1*H*-indol-1-yl)aniline (29):**

White solid, Mp: 55-57 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.09-7.05 (m, 3H), 6.99-6.97 (m, 1H), 6.89 (s, 1H), 6.86 (s, 1H), 6.62 (d, *J* = 8 Hz, 1H), 3.40 (br, 1H), 2.65 (s, 3H), 2.30 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 136.9, 129.7, 129.0, 128.9, 126.4, 126.0, 124.8, 122.2, 119.5, 119.0, 112.3, 111.0, 110.7, 30.6, 20.3, 9.7; HRMS (ESI, m/z) Calcd for $C_{17}H_{19}N_2$ 251.1543 (M+H), found 251.1543.

***N*,4-dimethyl-2-(1*H*-pyrrolo[2,3-b]pyridin-1-yl)aniline (30):**

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.4 Hz, 1H), 7.98 (d, *J* = 8 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.17 (d, *J* = 8 Hz, 1H), 7.13-7.10 (m, 1H), 7.01 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 3.74 (br, 1H), 2.77 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 143.9, 143.4, 130.2, 129.8, 129.2, 129.0, 126.6, 124.2, 120.9, 116.4, 111.8, 101.4, 30.8, 20.3; HRMS (ESI, m/z) Calcd for $C_{15}H_{16}N_3$ 238.1349 (M+H), found 251.1339.

***N*-methyl-2-(1*H*-pyrrol-1-yl)aniline (34):**

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1H), 7.14 (d, *J* = 8 Hz, 1H), 6.80 (s, 2H), 6.75-6.71 (m, 2H), 6.34 (s, 2H), 3.84 (br, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 129.1, 127.2, 127.0, 122.0, 116.3, 110.6, 109.4, 30.4; HRMS (ESI, m/z) Calcd for $C_{11}H_{13}N_2$ 173.1073 (M+H), found 173.1077.

***N*,4-dimethyl-2-(1*H*-pyrrol-1-yl)aniline (35):**

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, *J* = 8 Hz, 1H), 6.88 (s, 1H), 6.70 (d, *J* = 1.2 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.25 (s, 2H), 3.60 (br, 1H), 2.69 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 129.4, 127.6, 127.2, 125.9, 122.0, 110.8, 109.3, 30.7, 20.2; HRMS (ESI, m/z) Calcd for $C_{12}H_{15}N_2$ 187.1232 (M+H), found 187.1230.

4-isopropyl-*N*-methyl-2-(1*H*-pyrrol-1-yl)aniline (36):

Pale orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 2.4 Hz, 8.8 Hz, 1H), 7.02 (d, *J* = 2 Hz, 1H), 6.81 (t, *J* = 2 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.34 (t, *J* = 2 Hz, 2H), 3.71 (br, 1H), 2.86 (m, 1H), 2.81 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 137.3, 128.2, 126.8, 125.0, 122.0, 110.7, 109.3, 33.1, 30.6, 24.3; HRMS (ESI, m/z) Calcd for $C_{14}H_{19}N_2$ 215.1543 (M+H), found 215.1553.

4-chloro-*N*-methyl-2-(1*H*-pyrrol-1-yl)aniline (37):

Pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 2.4 Hz, 8.8 Hz, 1H), 7.12 (d, *J* = 2 Hz, 1H), 6.77 (t, *J* = 2 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.34 (t, *J* = 2 Hz, 2H), 3.85 (br, 1H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 128.8, 127.8, 126.9, 121.8, 120.7, 111.4, 109.9, 30.4; HRMS (ESI, m/z) Calcd for $C_{11}H_{12}N_2Cl$ 207.0684 (M+H), found 207.0687.

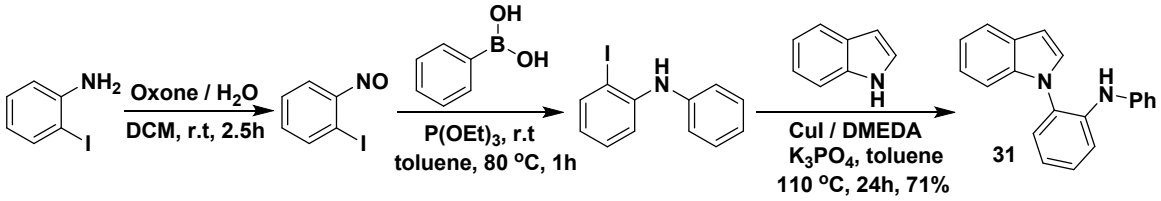
4-fluoro-*N*-methyl-2-(1*H*-pyrrol-1-yl)aniline (38):

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03-6.98 (m, 1H), 6.91 (dd, *J* = 2.8 Hz, 8.8 Hz, 1H), 6.79 (t, *J* = 2 Hz, 2H), 6.64-6.60 (m, 1H), 6.34 (t, *J* = 2 Hz, 2H), 3.70 (br, 1H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 153.3, 141.4, 127.3, 127.2, 121.8, 115.3, 115.1, 114.4, 114.1, 111.1, 111.0, 109.8, 30.9; HRMS (ESI, m/z) Calcd for $C_{11}H_{12}N_2F$ 191.0979 (M+H), found 191.0979.

4-(methylamino)-3-(1*H*-pyrrol-1-yl)benzonitrile (39):

Light orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 2.0 Hz, 8.8 Hz, 1H), 7.37 (d, *J* = 2 Hz, 1H), 6.73 (t, *J* = 2 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.36 (t, *J* = 2 Hz, 2H), 4.42 (br, 1H), 2.84 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 133.6, 130.6, 126.8, 121.7, 119.6, 110.5, 110.3, 98.1, 29.9; HRMS (ESI, m/z) Calcd for $C_{12}H_{11}N_3Na$ 220.0851 (M+H), found 207.0862.

Synthesis of 2-(1*H*-indol-1-yl)-*N*-phenylaniline (31):

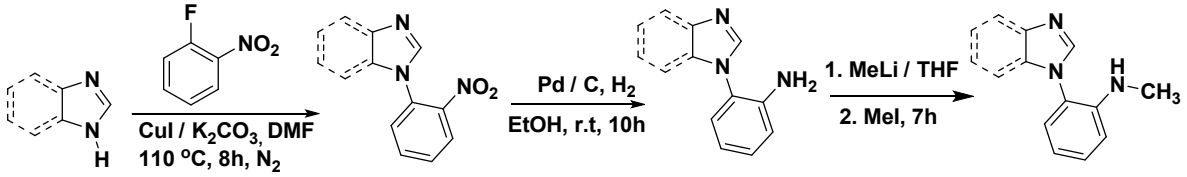


First 2-iodoaniline converted into 1-iodo-2-nitrosobenzene.[D] 1-iodo-2-nitrosobenzene treated with phenylboronic acid to get 2-iodo-*N*-phenylaniline.[E] 2-(1*H*-indol-1-yl)-*N*-phenylaniline was synthesized from 2-iodo-*N*-phenylaniline using general procedure IV.[A]

Spectral data of 31:

Light orange oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 6.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.23-7.07 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.89-6.85 (m, 2H), 6.61 (d, *J* = 2.4 Hz, 1H), 5.33 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 140.5, 136.7, 129.4, 128.9, 128.8, 127.1, 122.6, 122.5, 121.1, 120.5, 120.2, 120.0, 116.1, 110.7, 103.8; HRMS (ESI, m/z) Calcd for $C_{15}H_{16}N_3$ 285.1392 (M+H), found 285.1397.

Synthesis of 2-(1*H*-imidazol-1-yl)-*N*-methylaniline (32) & 2-(1*H*-benzo[d]imidazol-1-yl)-*N*-methylaniline (**33**):



Compound **32** and **33** are synthesized by methylation[B] of corresponding anilines. 2-(1H-imidazol-1-yl)aniline and 2-(1H-benzo[d]imidazol-1-yl)aniline were prepared using reported procedure.[F]

Spectral data

2-(1*H*-imidazol-1-yl)-*N*-methylaniline (32):

White solid, Mp: 78-80 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.35-7.31 (m, 1H), 7.26-7.23 (m, 1H), 7.09-7.08 (m, 2H), 6.76-6.73 (m, 2H), 3.65 (br, 1H), 2.79 (d, J = 3.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 130.3, 130.1, 127.1, 127.0, 123.0, 120.5, 116.6, 111.0, 30.3; HRMS (ESI, m/z) Calcd for $C_{10}H_{12}N_3$ 174.1031 (M+H), found 174.1053.

2-(1*H*-benzo[d]imidazol-1-yl)-*N*-methylaniline (**33**):

White crystalline solid, Mp: 157-159 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.43-7.39 (m, 1H), 7.35-7.28 (m, 2H), 7.20-7.15 (m, 2H), 6.84-6.79 (m, 2H), 3.54 (br, 1H), 2.78 (d, J = 4.8 Hz, 3H); 145.2, 143.68, 143.62, 134.2, 130.7, 128.1, 123.7, 122.8, 120.9, 120.6, 116.8, 111.2, 110.9, 30.2; HRMS (ESI, m/z) Calcd for $C_{14}H_{14}N_3$ 224.1188 (M+H), found 224.1187.

References:

A. 1) Antilla, J. C.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 11684. 2) Wang, X.; Li, N.; Li, Z.; Rao, H. *J. Org. Chem.* **2017**, *82*, 10158. 3) Wang, L.; Guo, W.; Zhang, X. X; Xia, X.-D.; Xiao, W. –J. *Org. Lett*. **2012**, 14, 740.

B. Nakamura, I.; Sato, Y.; Konta, S.; Terada, M. *Tetrahedron Letters*. **2009**, *50*, 2075.

C. Baumann, M.; Baxendale, I. R. *J. Org. Chem*. **2015**, *80*, 10806.

D. Purkait, A.; Roy, S. K.; Srivastava, H. K.; Jana, C. K. *Org. Lett.* **2017**, *19*, 2540.

E. Roscales, S.; Csaky, A. G.; *Org, Lett*. **2018**, *20*, 1667.

F. Wang, X.; Jin, Y.; Zhao, Y.; Zhu, L.; Fu, H. *Org, Lett*. **2012**, *14*, 452.

X. NMR Spectra of the reaction products

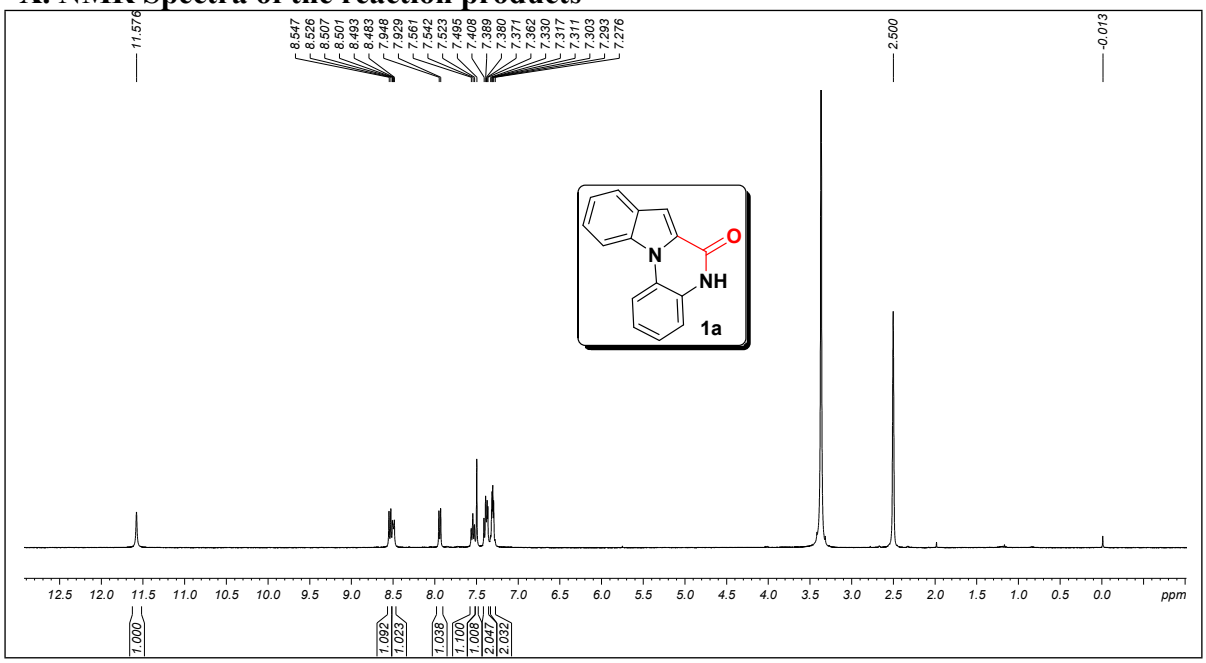


Figure S1. 400 MHz ^{1}H NMR spectrum of **1a** in DMSO-d_6

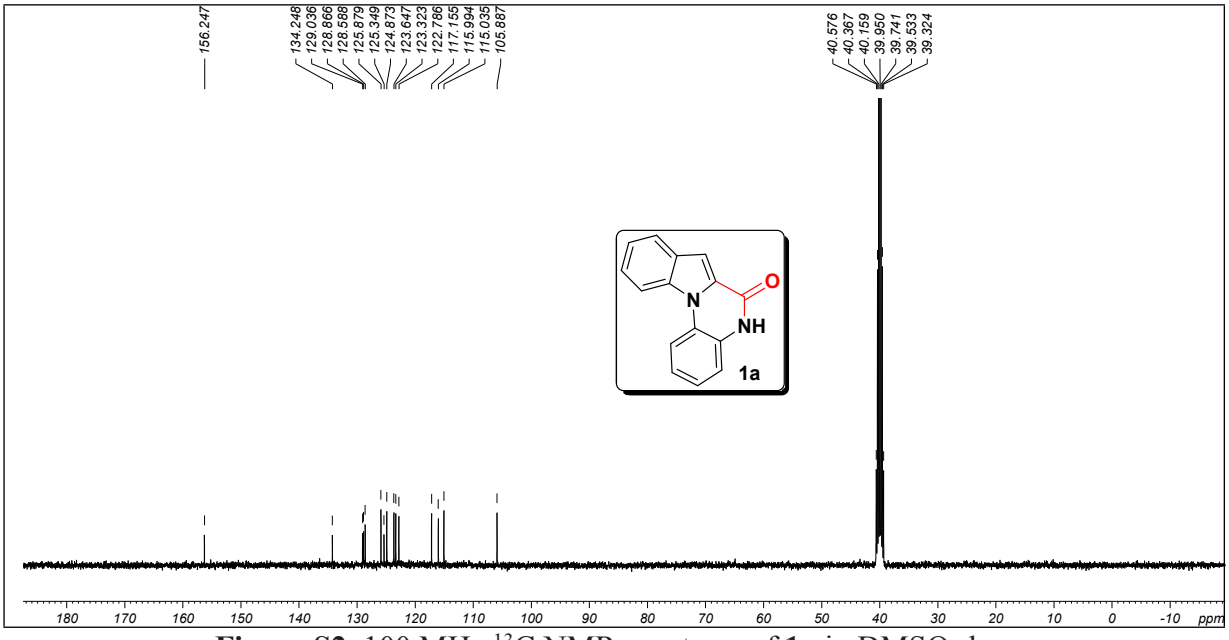


Figure S2. 100 MHz ^{13}C NMR spectrum of **1a** in DMSO-d_6

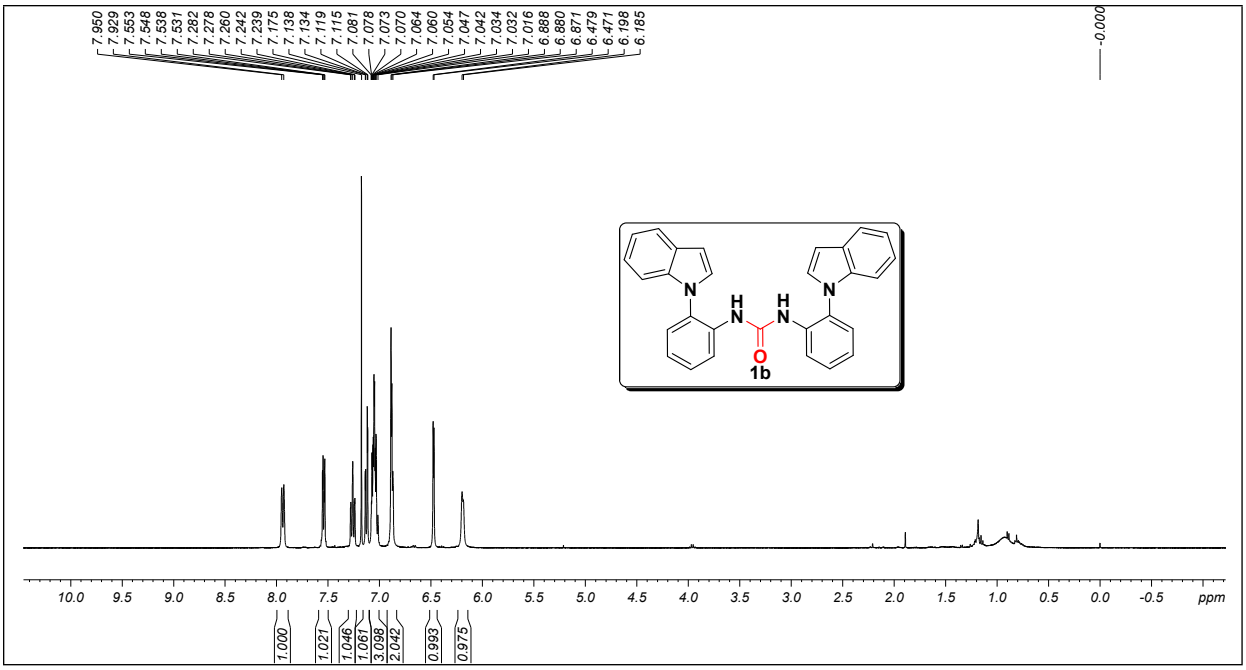


Figure S3. 400 MHz ^{1}H NMR spectrum of **1b** in $CDCl_3$

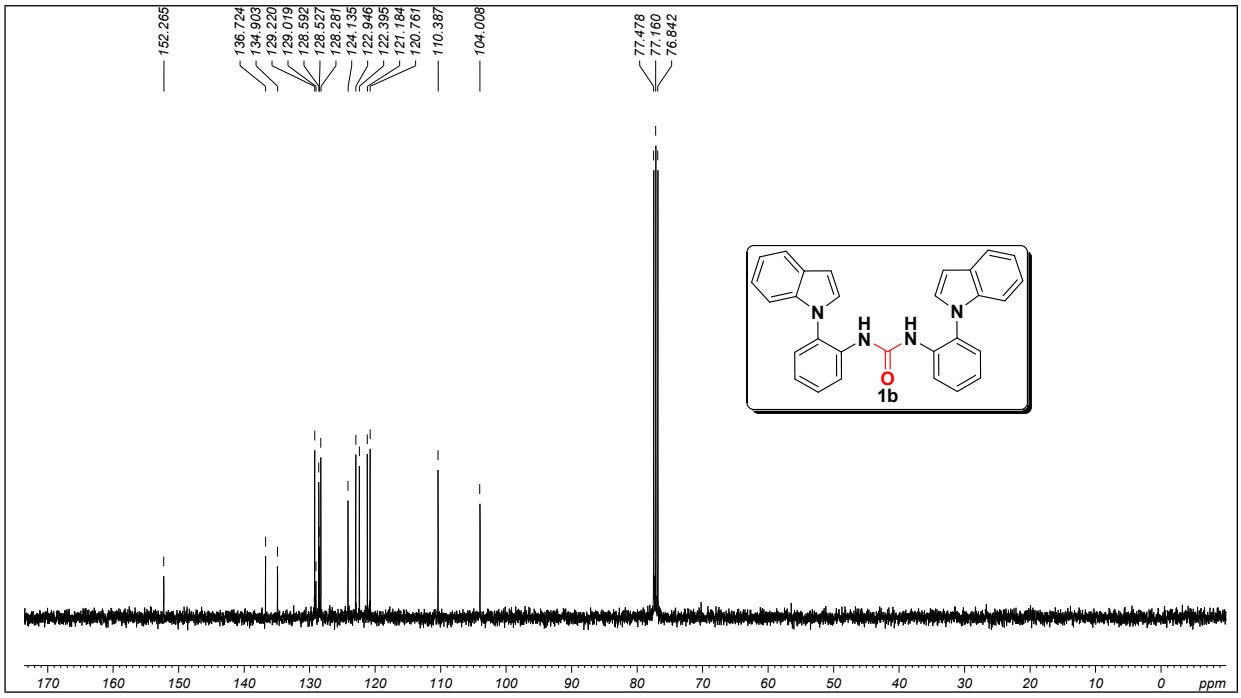


Figure S4. 100 MHz ^{13}C NMR spectrum of **1b** in $CDCl_3$

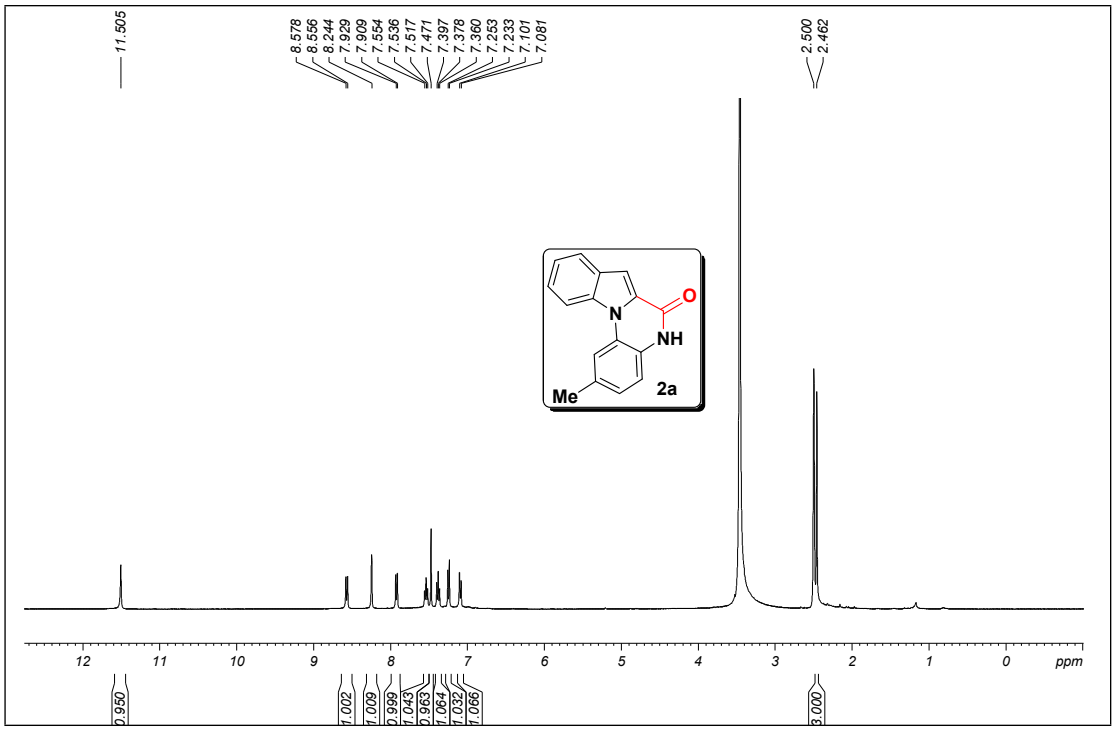


Figure S5. 400 MHz ^{1}H NMR spectrum of **2a** in DMSO-d_6

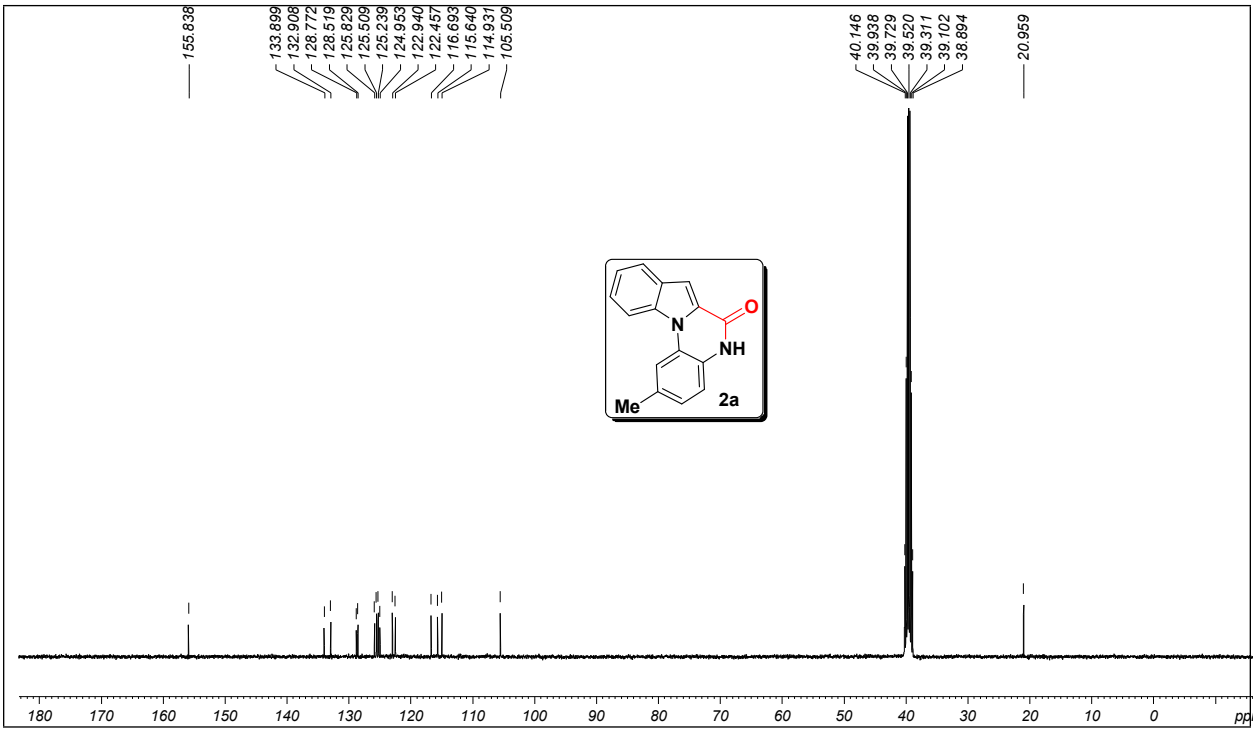


Figure S6. 100 MHz ^{13}C NMR spectrum of **2a** in DMSO-d_6

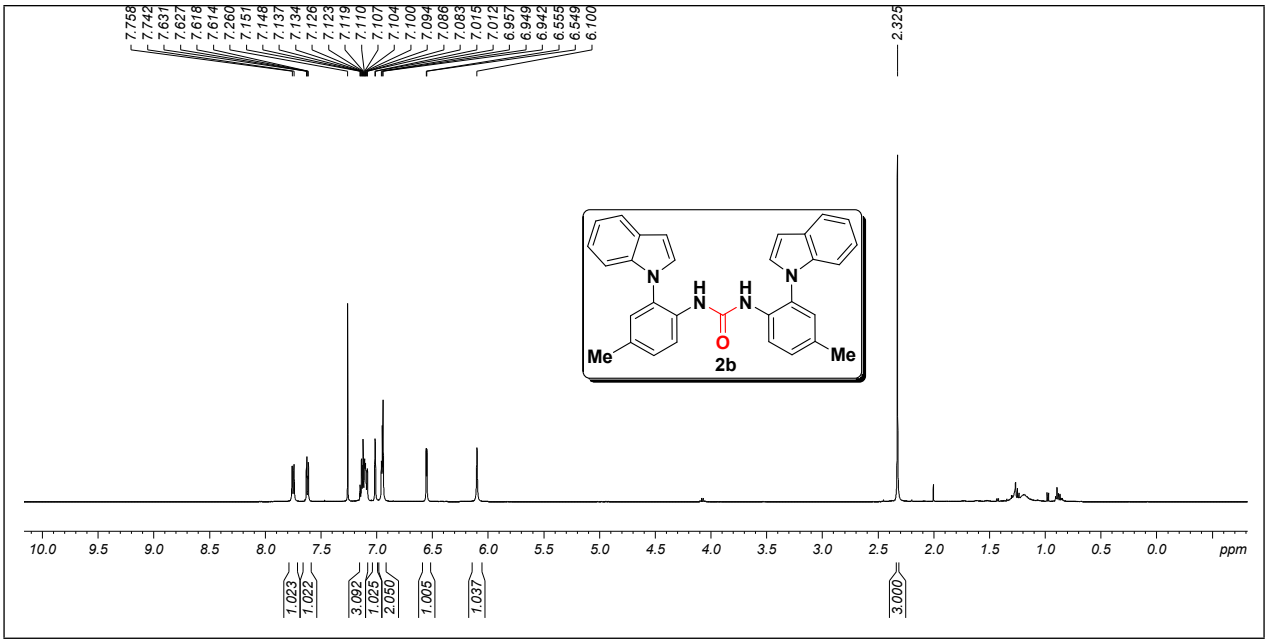


Figure S7. 500 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$

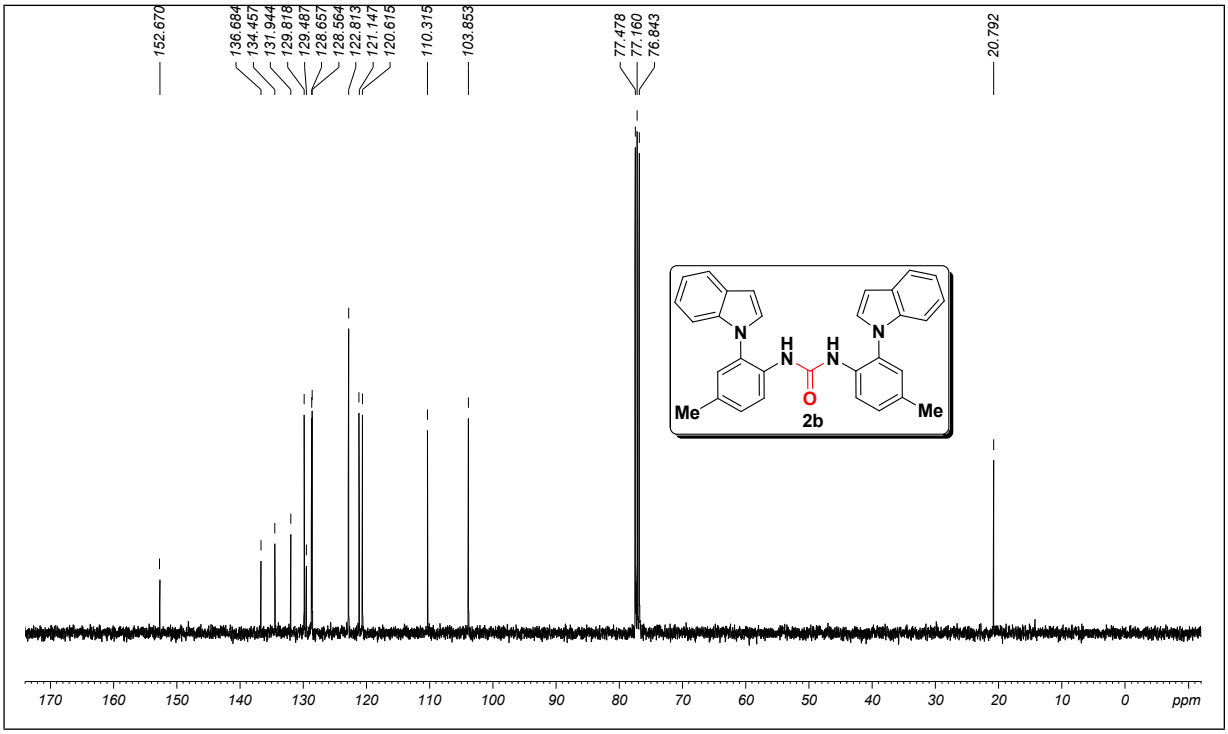


Figure S8. 100 MHz ^{13}C NMR spectrum of **2b** in $CDCl_3$

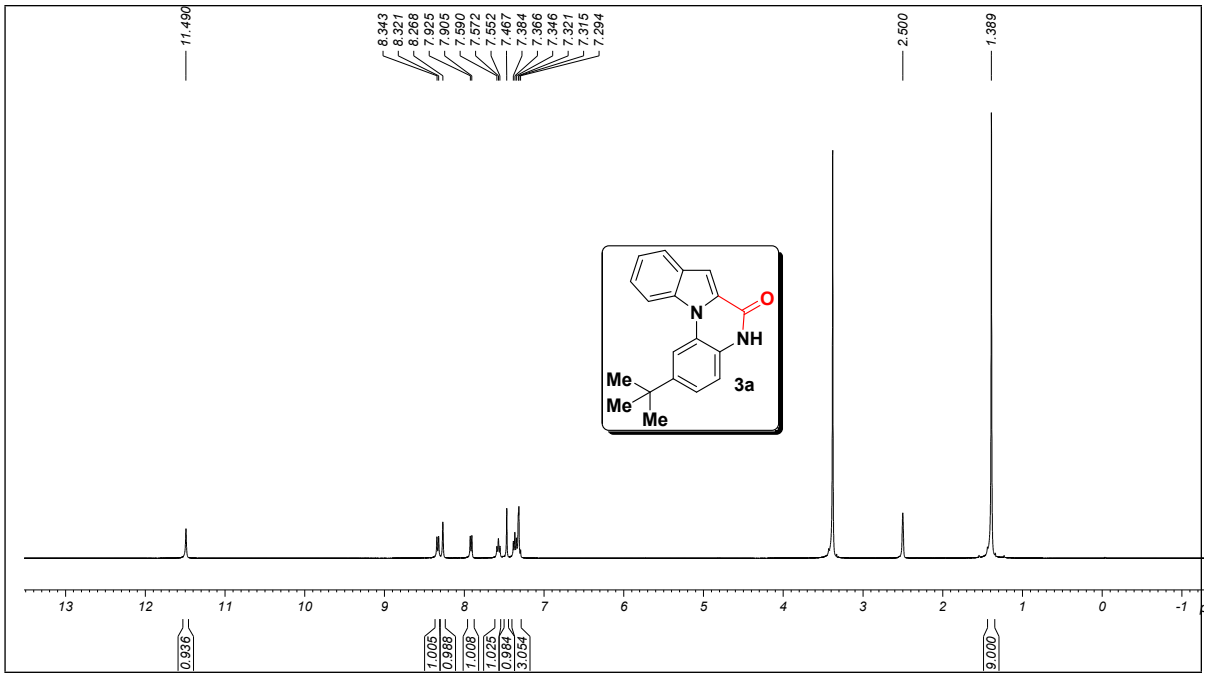


Figure S9. 400 MHz ^{1}H NMR spectrum of **3a** in DMSO-d_6

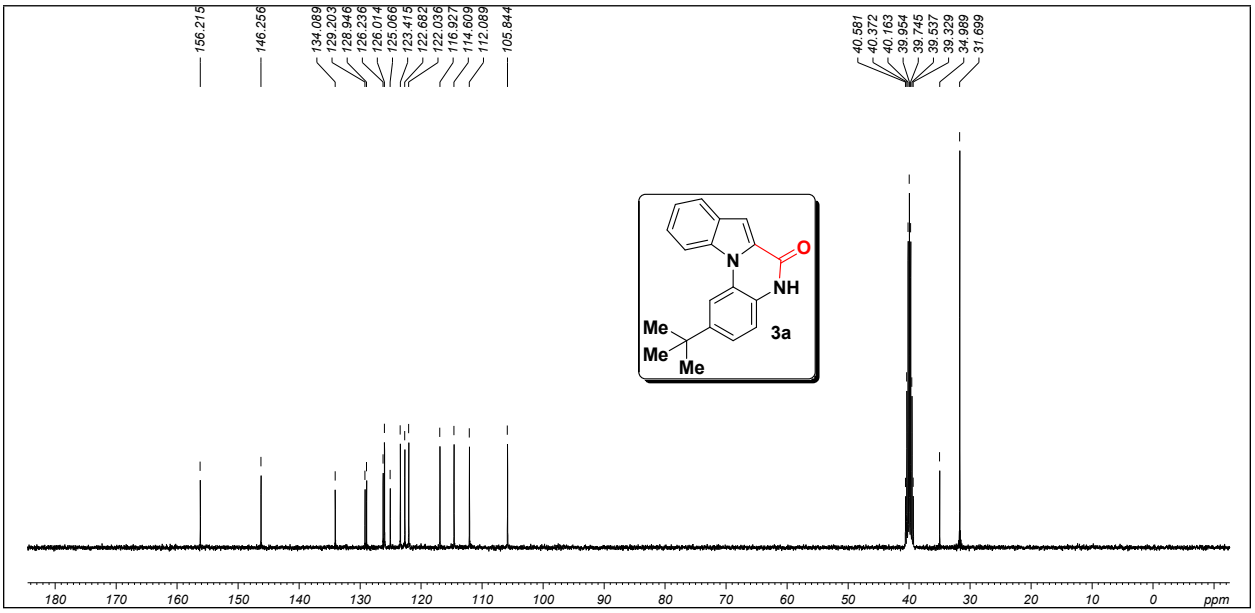


Figure S10. 100 MHz ^{13}C NMR spectrum of **3a** in DMSO-d_6

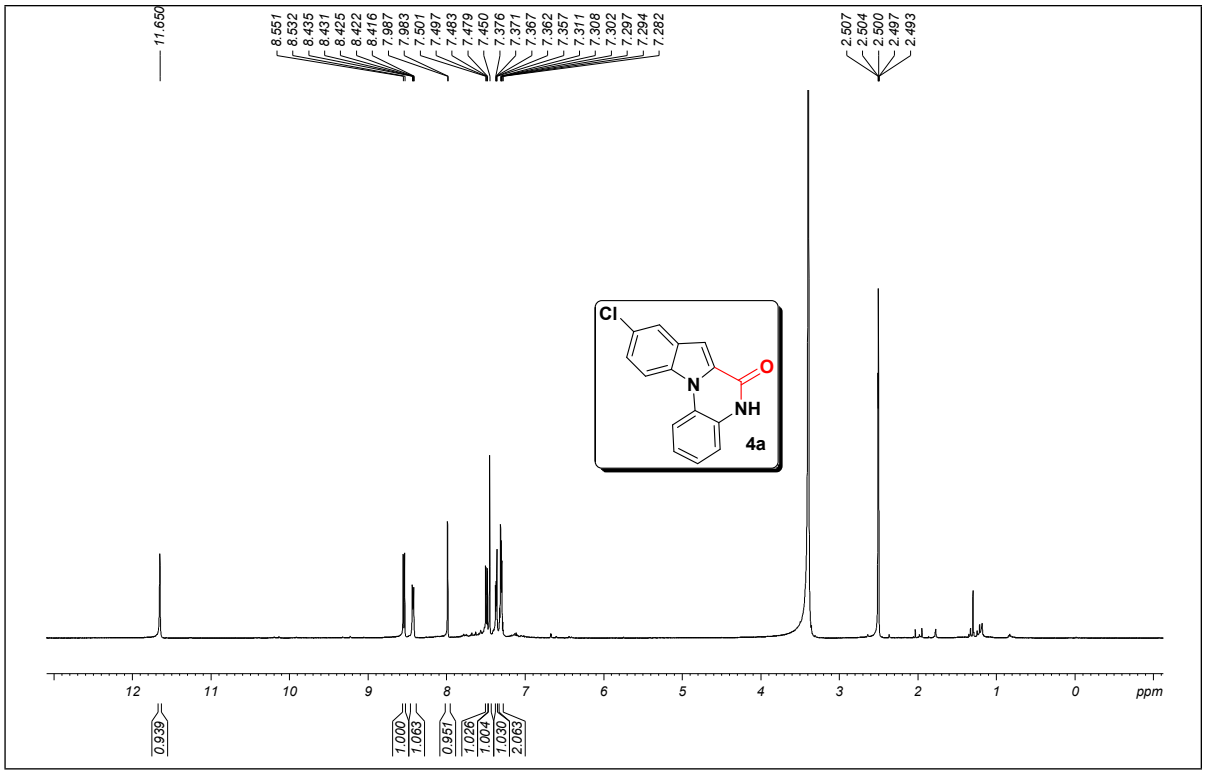


Figure S11. 500 MHz ^{1}H NMR spectrum of **4a** in DMSO-d_6

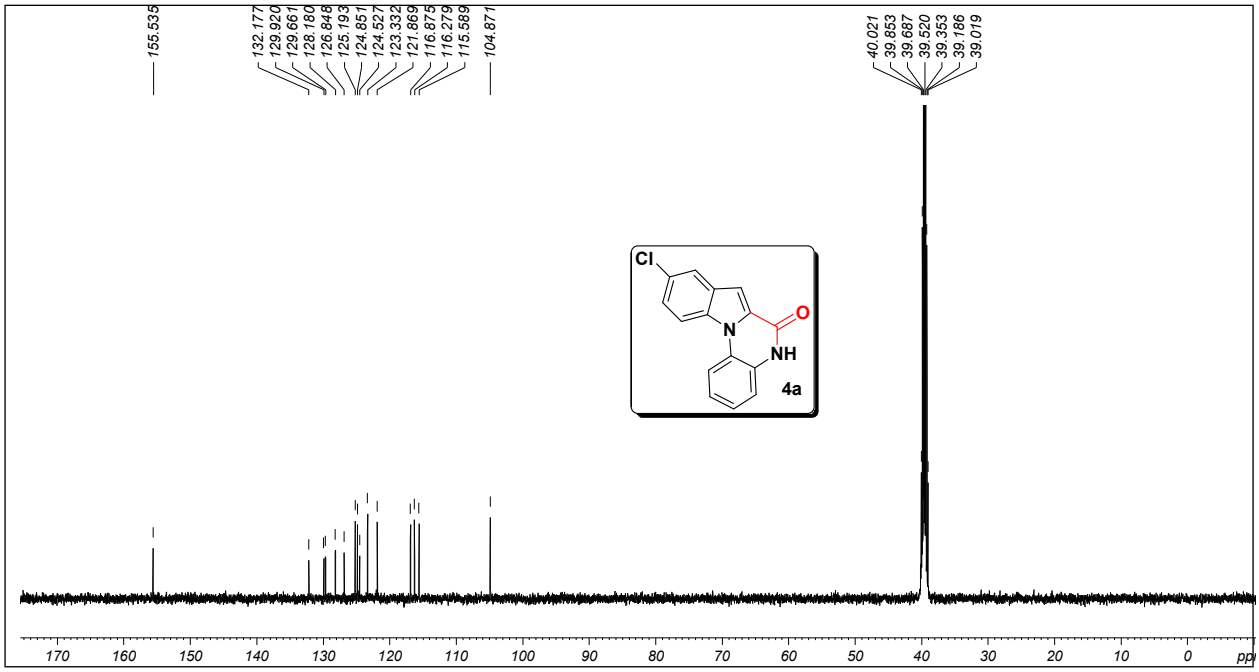


Figure S12. 125 MHz ^{13}C NMR spectrum of **4a** in DMSO-d_6

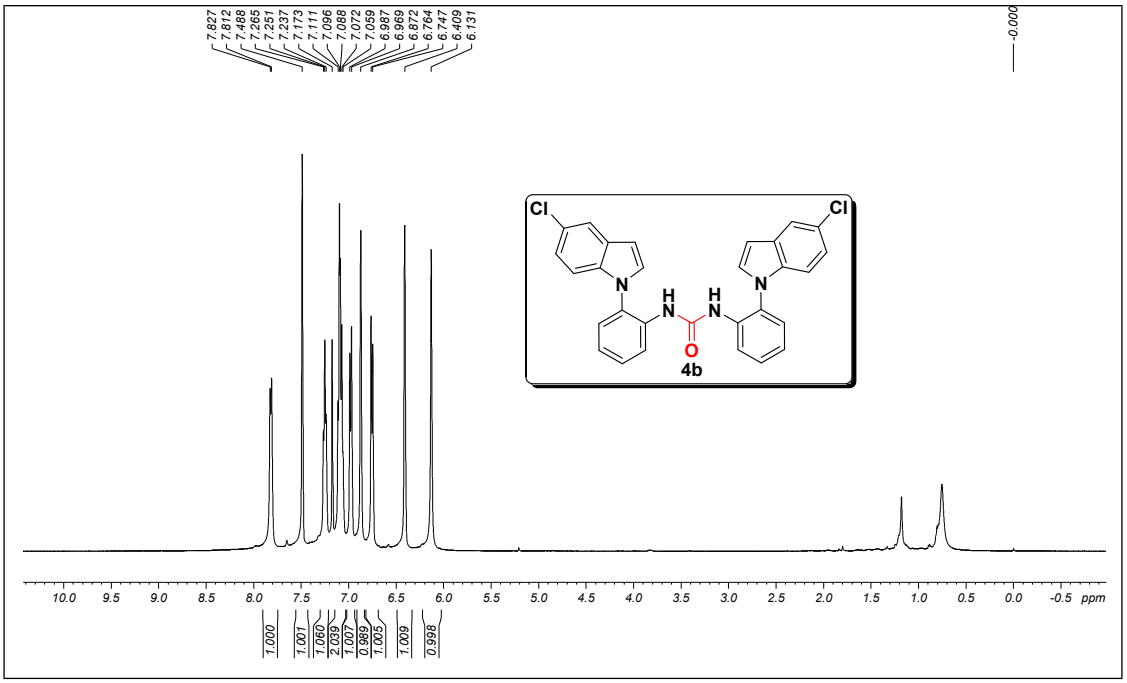


Figure S13. 500 MHz ^{1}H NMR spectrum of **4b** in $CDCl_3$

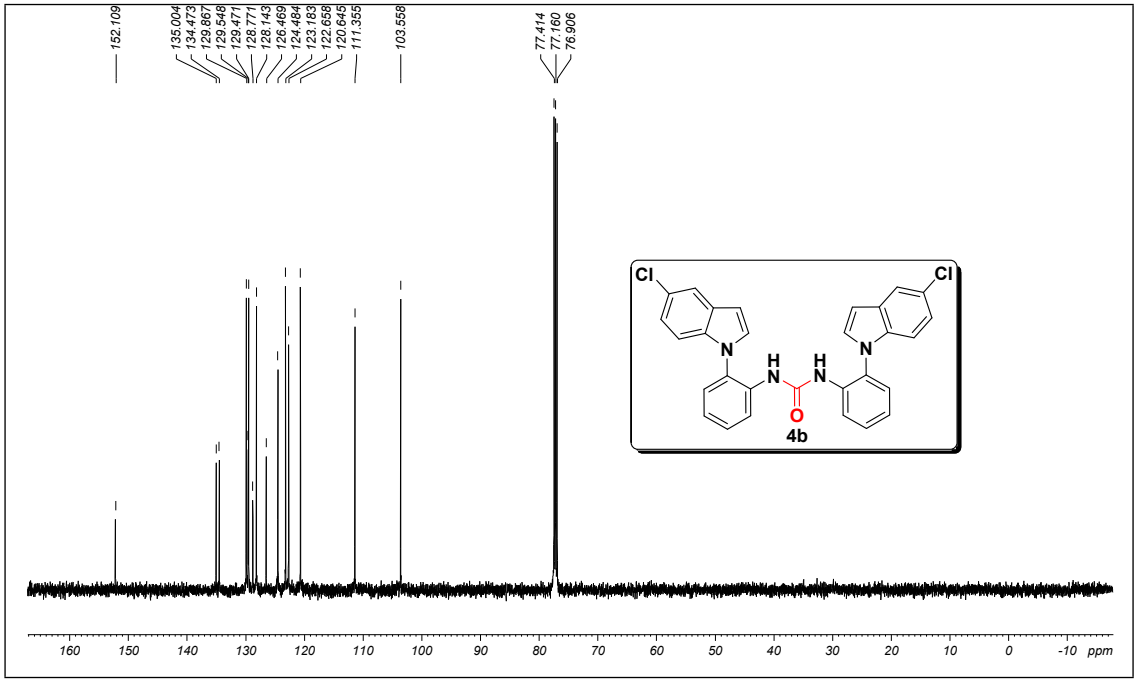


Figure S14. 125 MHz ^{13}C NMR spectrum of **4b** in $CDCl_3$

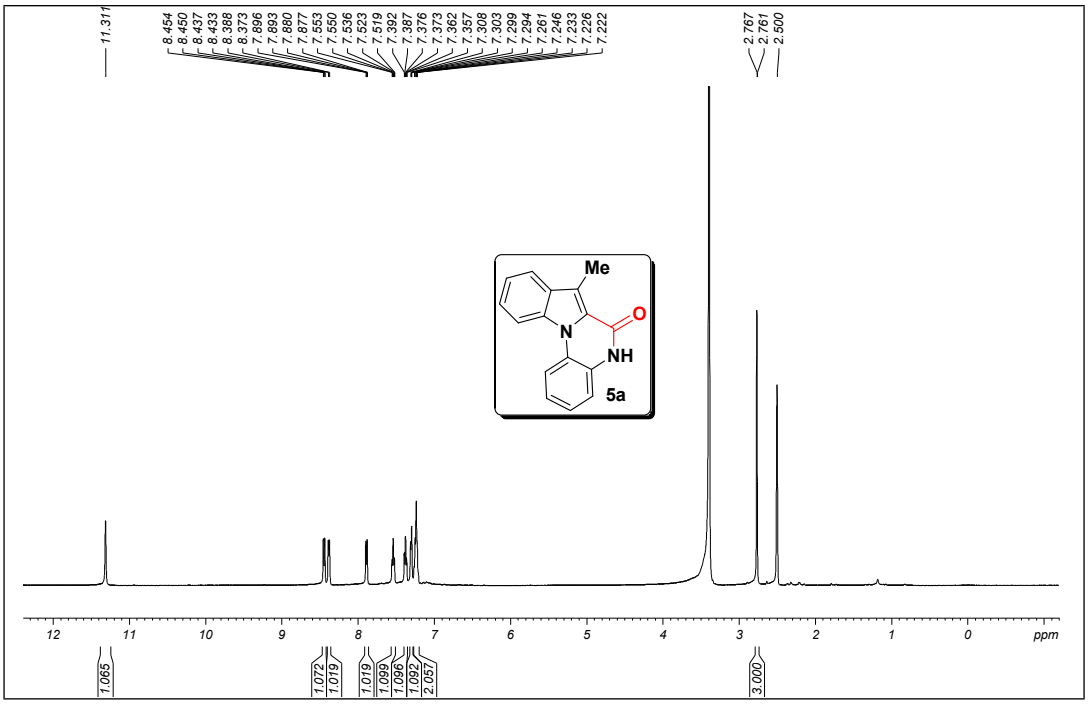


Figure S15. 500 MHz ^{1}H NMR spectrum of **5a** in DMSO-d_6

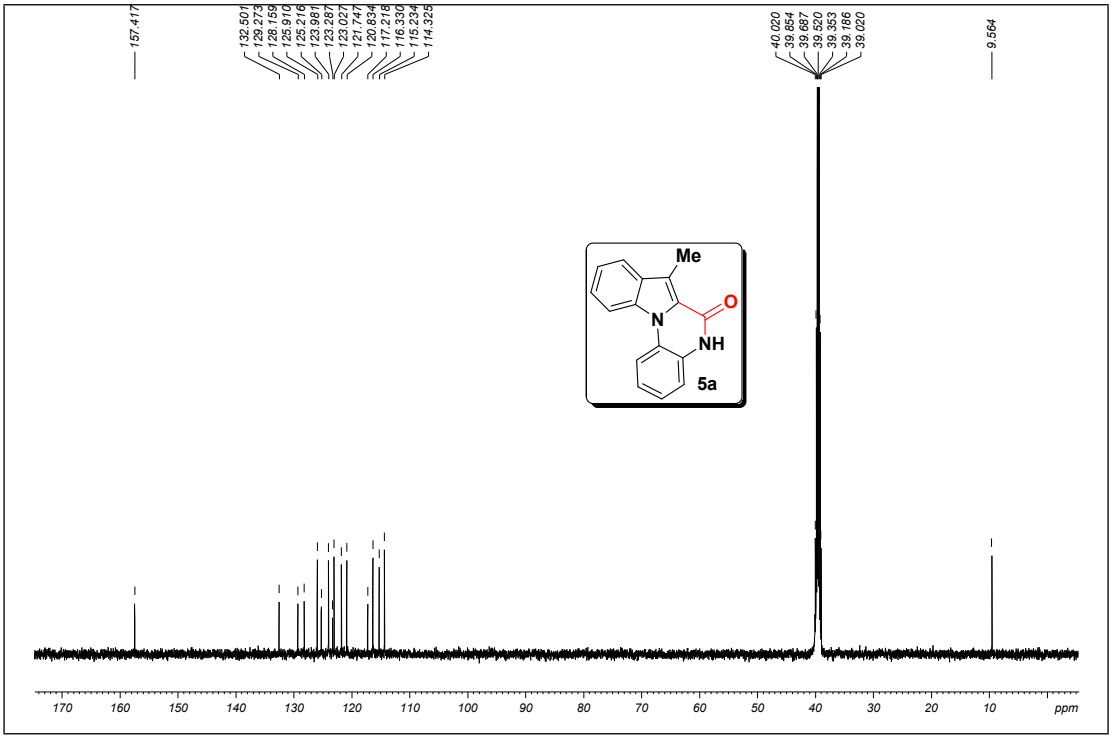


Figure S16. 125 MHz ^{13}C NMR spectrum of **5a** in DMSO-d_6

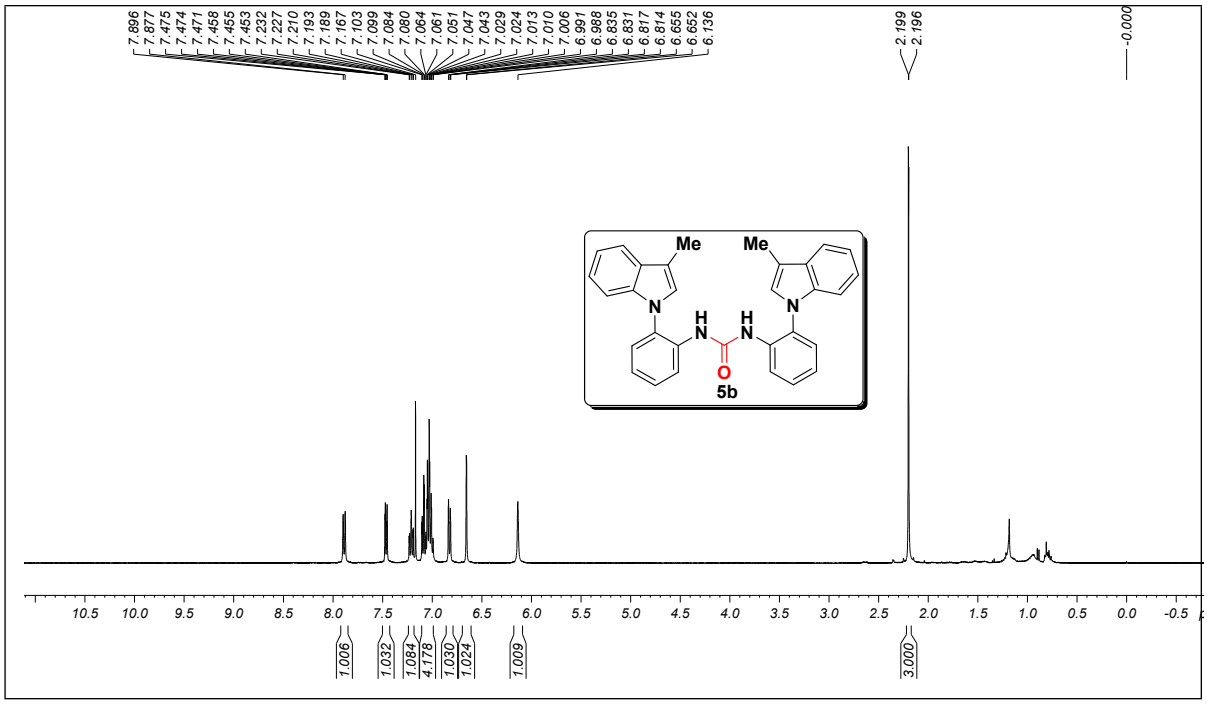


Figure S17. 400 MHz ^{1}H NMR spectrum of **5b** in $CDCl_3$

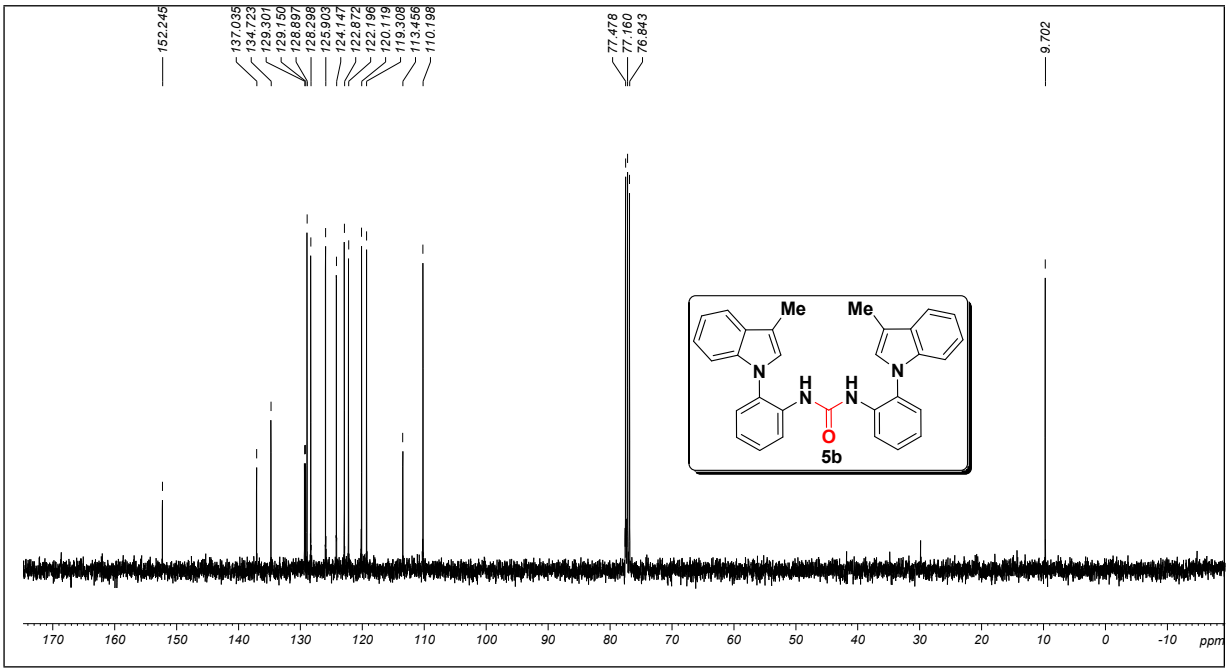


Figure S18. 100 MHz ^{13}C NMR spectrum of **5b** in $CDCl_3$

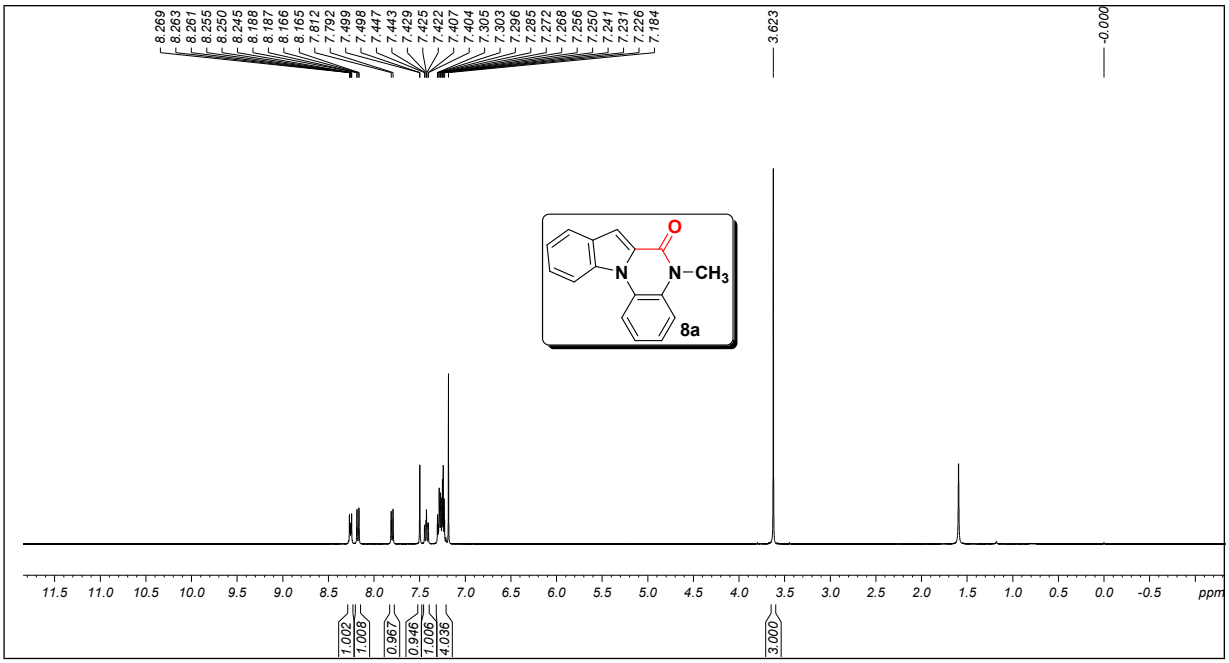


Figure S19. 400 MHz ^{1}H NMR spectrum of **8a** in $CDCl_3$

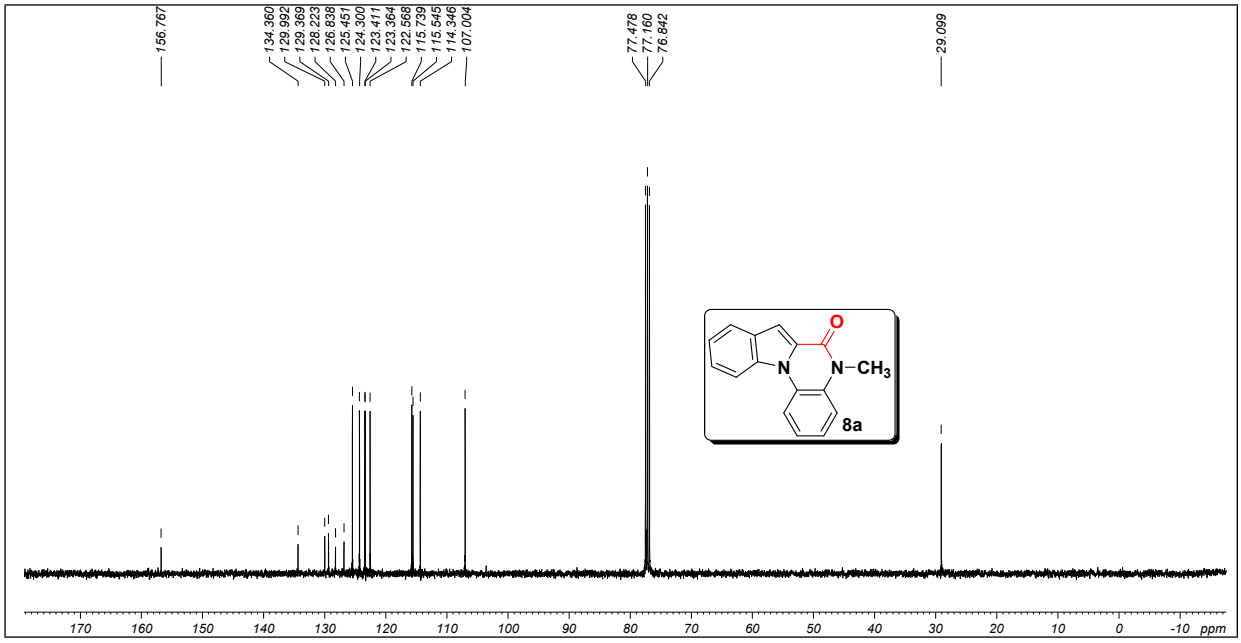


Figure S20. 100 MHz ^{13}C NMR spectrum of **8a** in $CDCl_3$

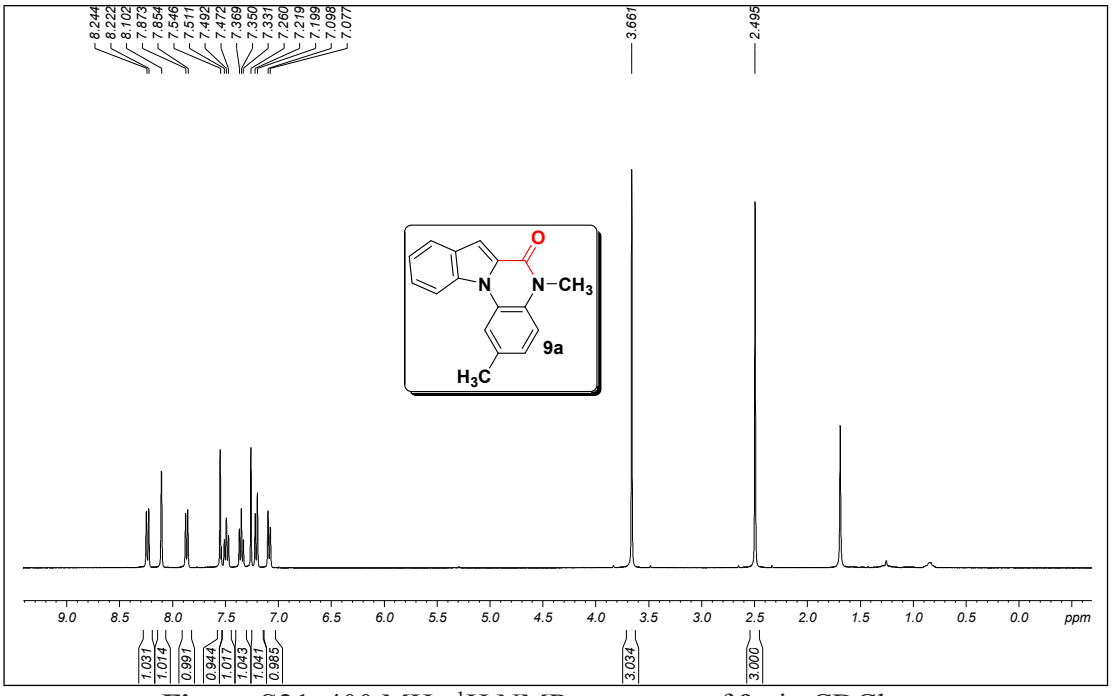


Figure S21. 400 MHz ^{1}H NMR spectrum of **9a** in $CDCl_3$

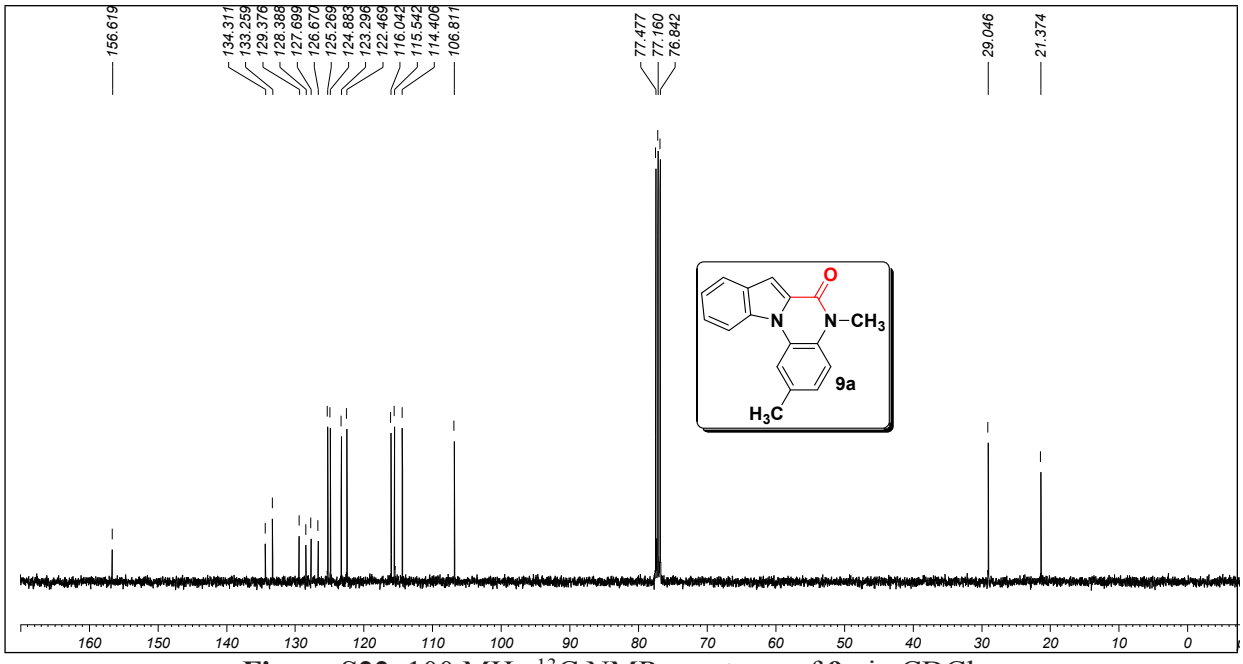


Figure S22. 100 MHz ^{13}C NMR spectrum of **9a** in $CDCl_3$

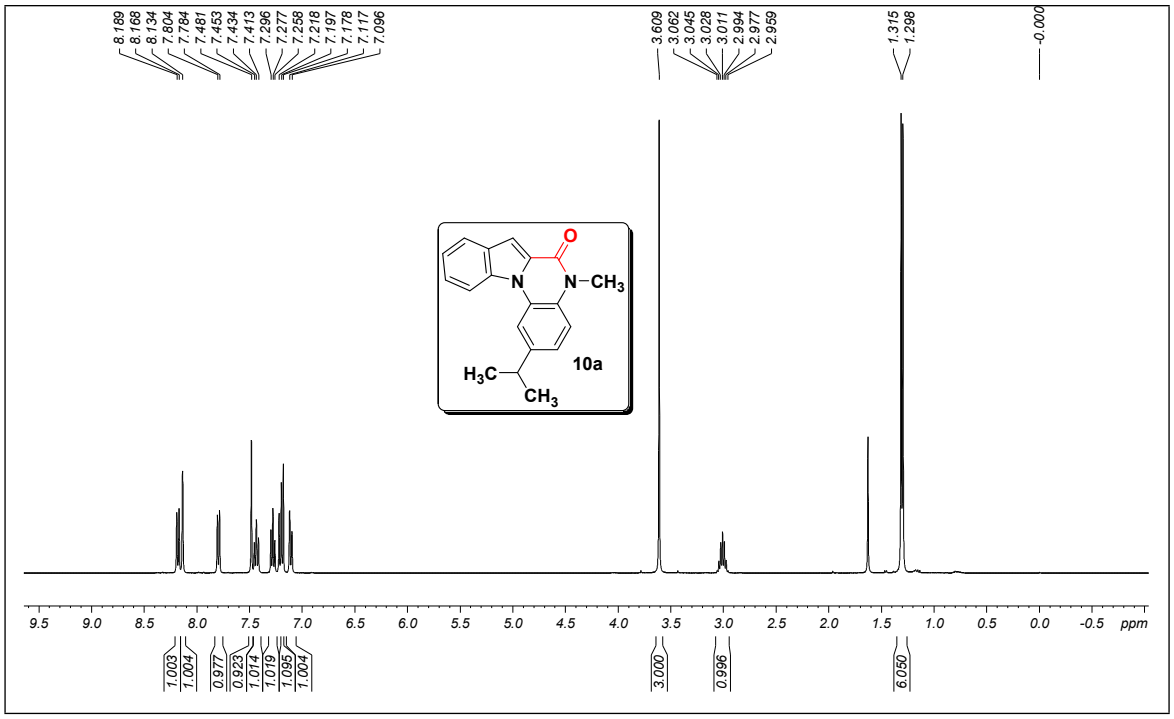


Figure S23. 400 MHz ^{1}H NMR spectrum of **10a** in $CDCl_3$

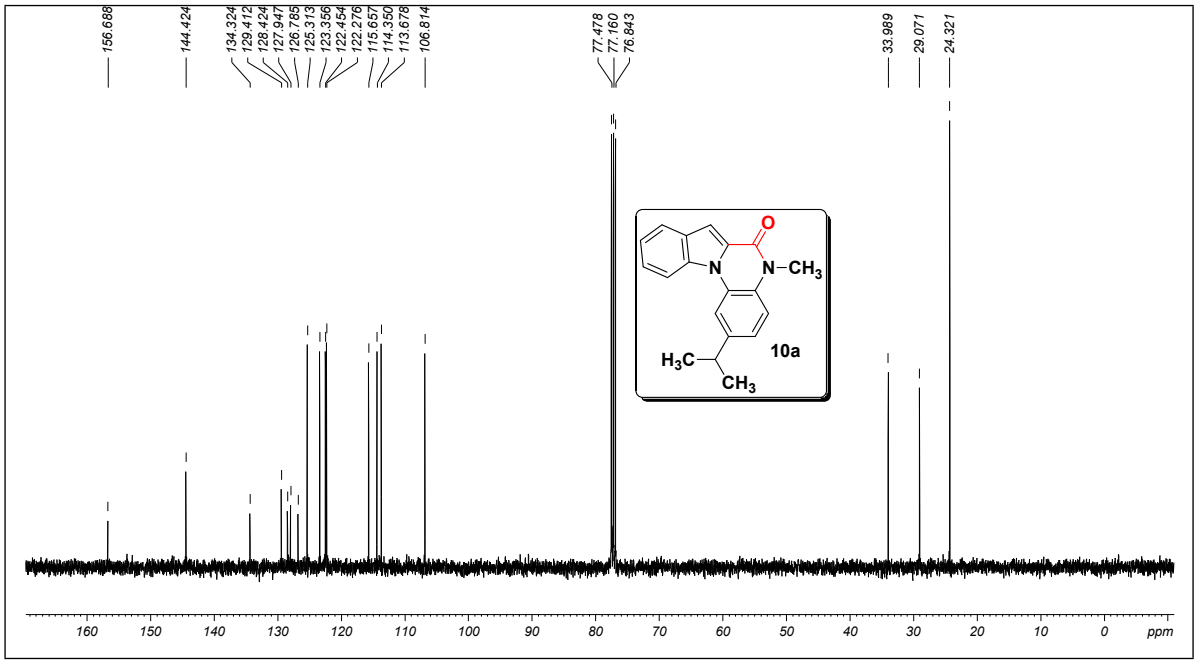


Figure S24. 100 MHz ^{13}C NMR spectrum of **10a** in $CDCl_3$

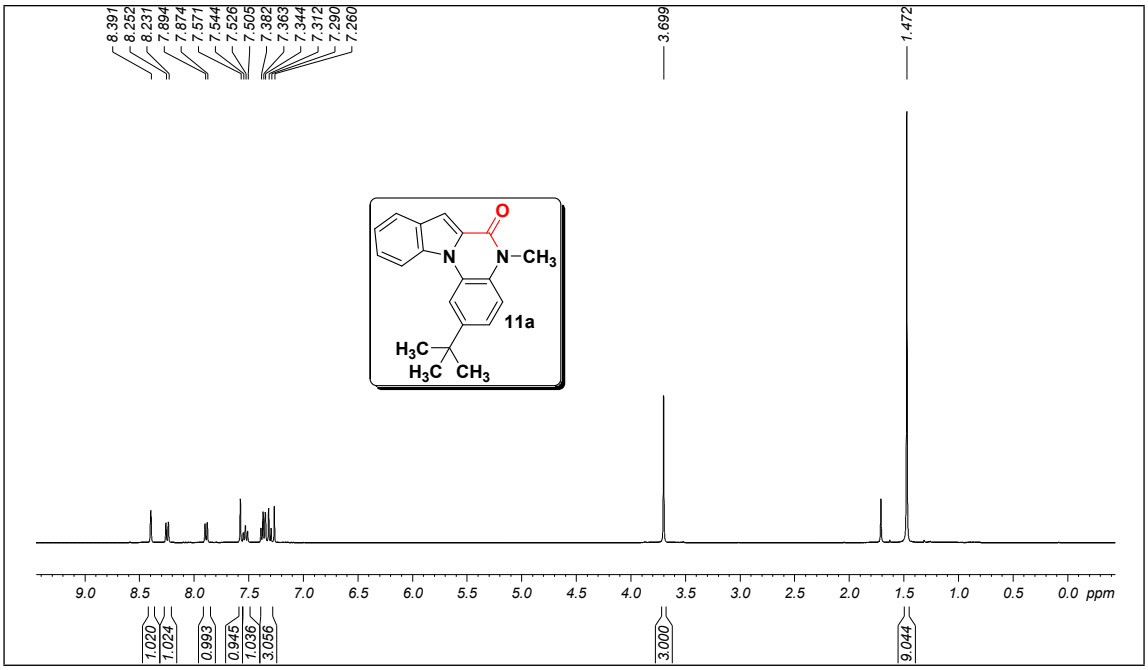


Figure S25. 400 MHz ^{1}H NMR spectrum of **11a** in $CDCl_3$

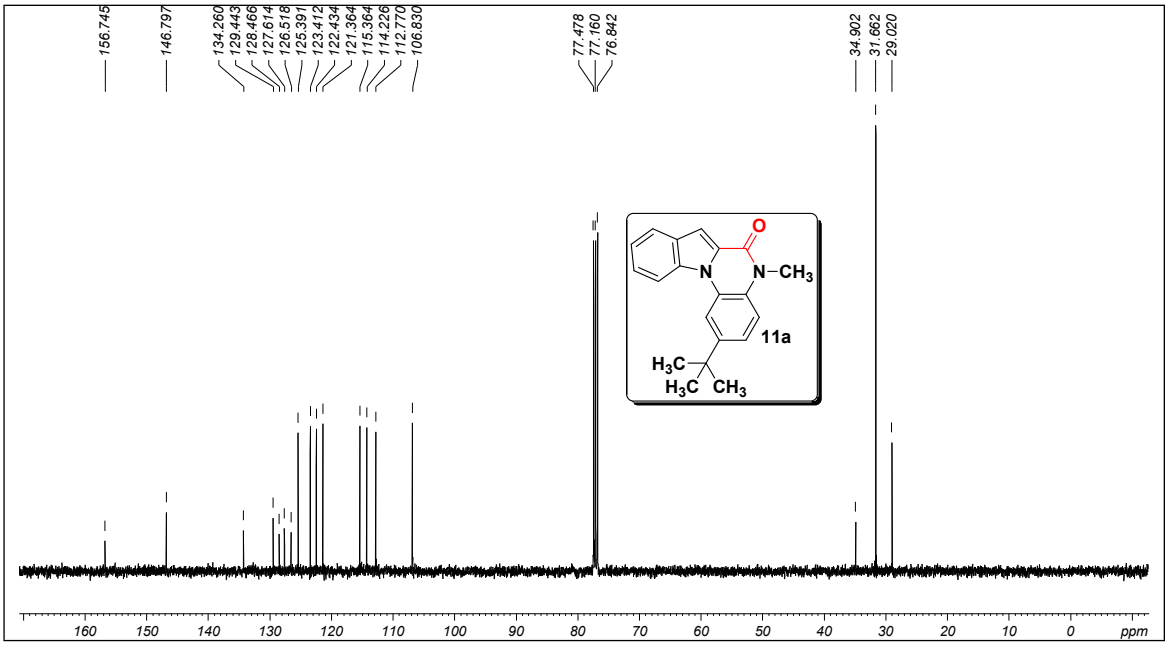


Figure S26. 100 MHz ^{13}C NMR spectrum of **11a** in $CDCl_3$

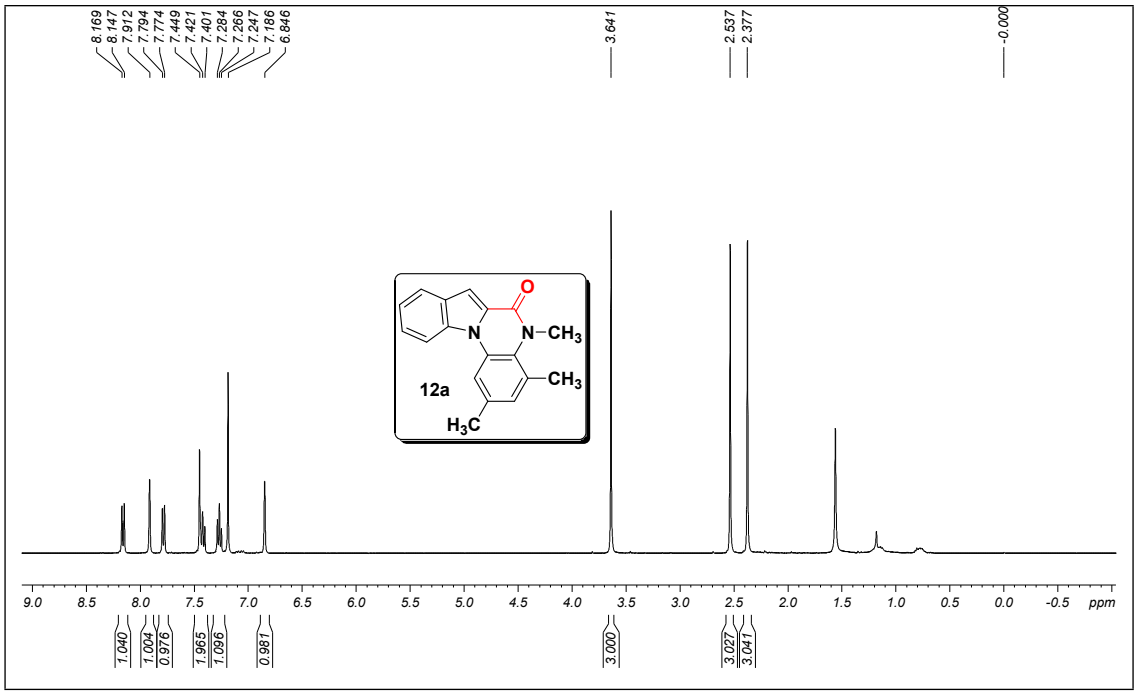


Figure S27. 400 MHz ^{1}H NMR spectrum of **12a** in $CDCl_3$

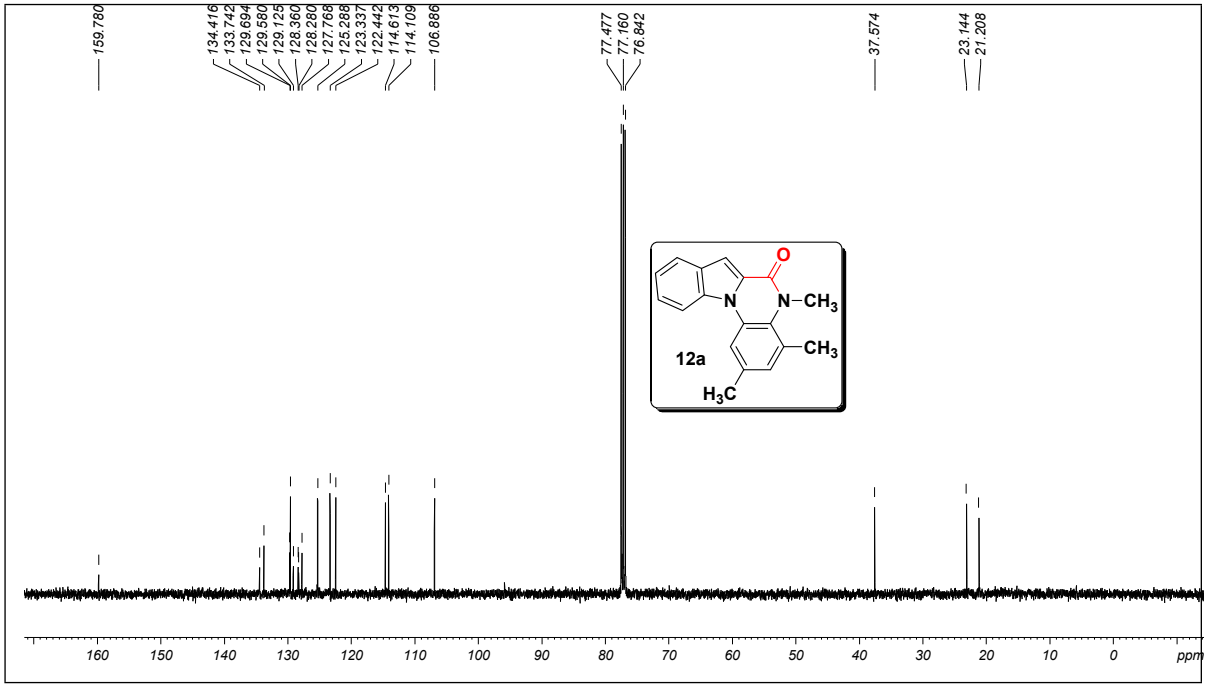


Figure S28. 100 MHz ^{13}C NMR spectrum of **12a** in $CDCl_3$

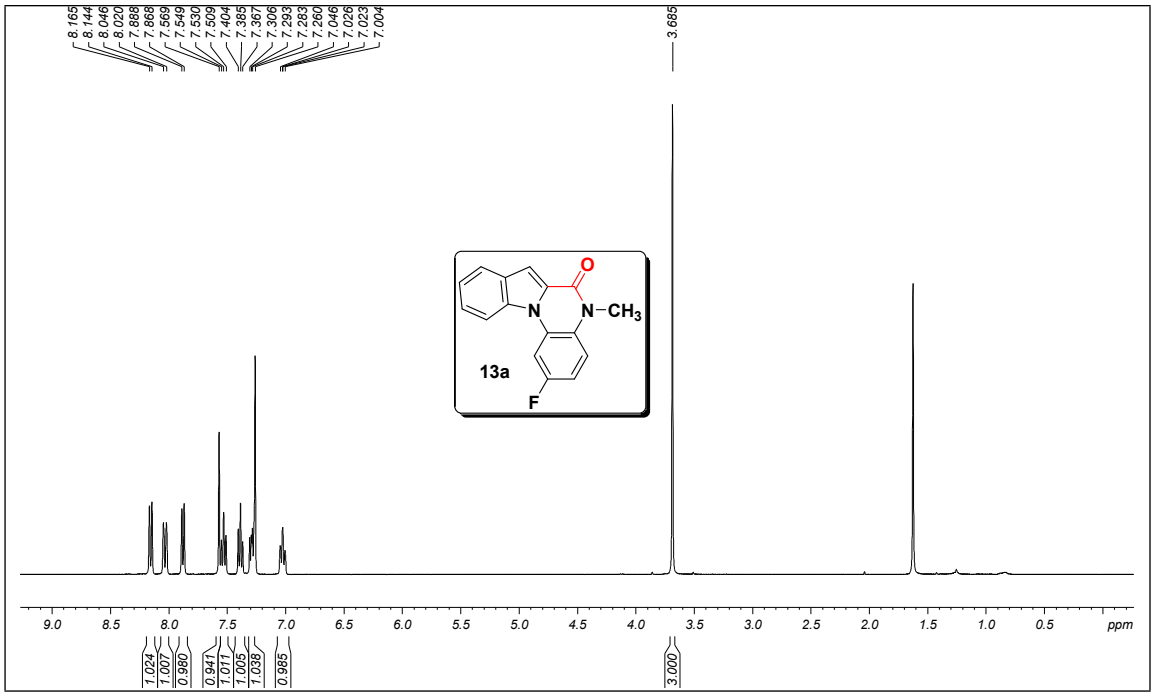


Figure S29. 400 MHz ^{1}H NMR spectrum of **13a** in $CDCl_3$

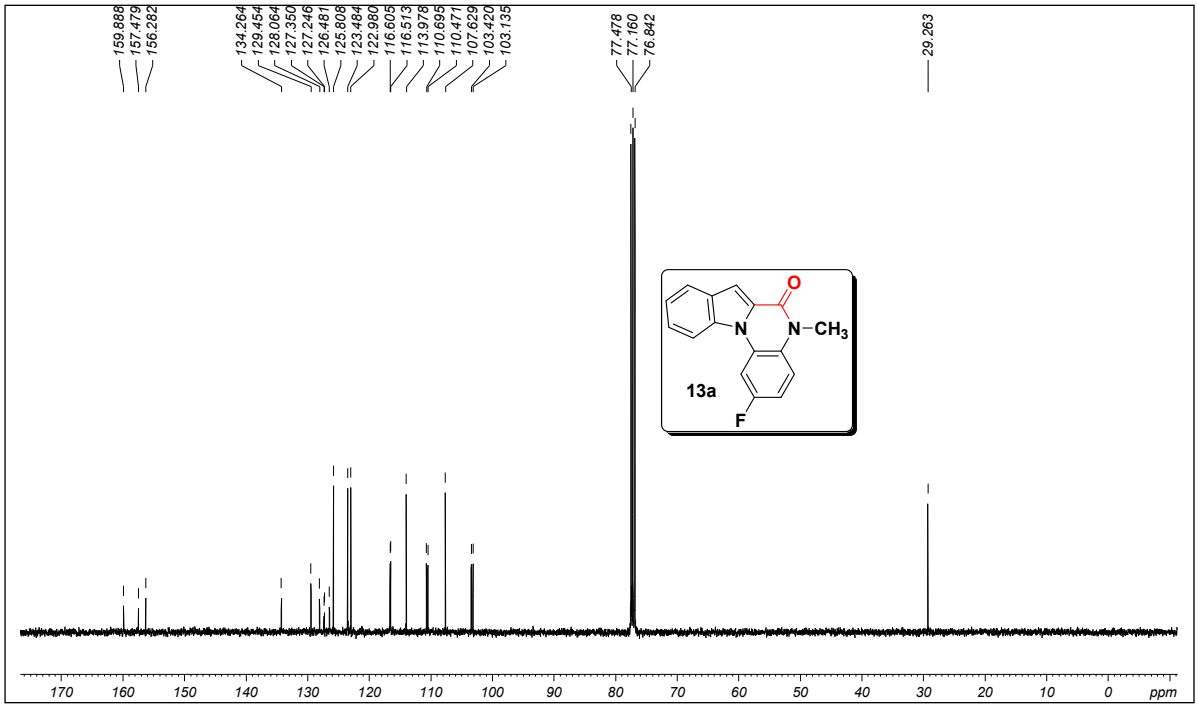


Figure S30. 100 MHz ^{13}C NMR spectrum of **13a** in $CDCl_3$

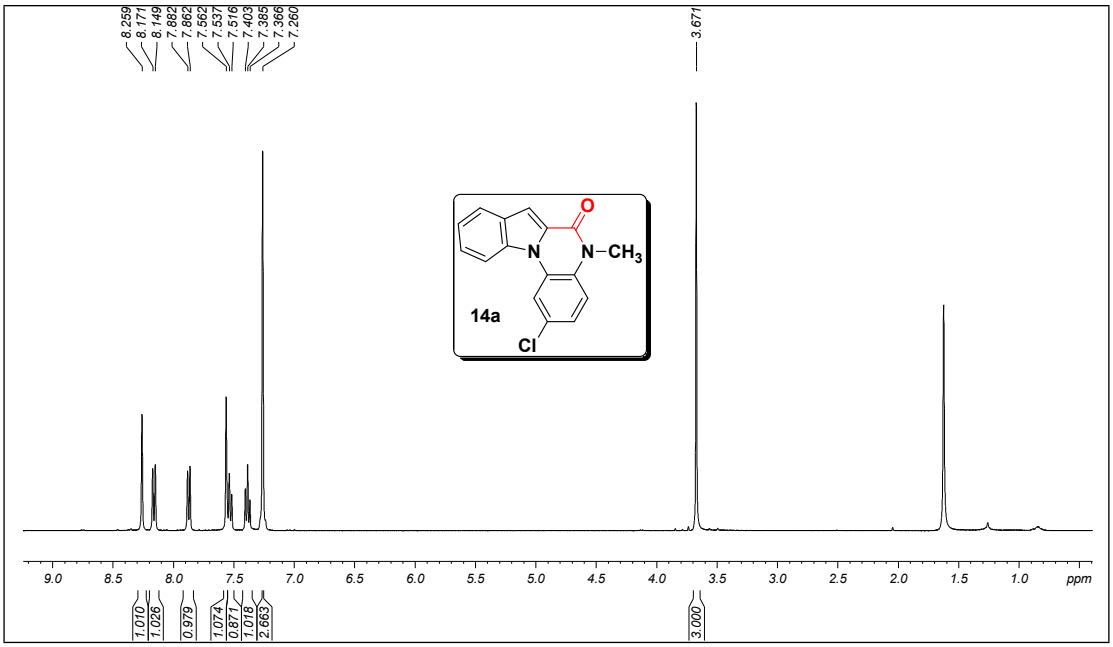


Figure S31. 400 MHz ^{1}H NMR spectrum of **14a** in $CDCl_3$

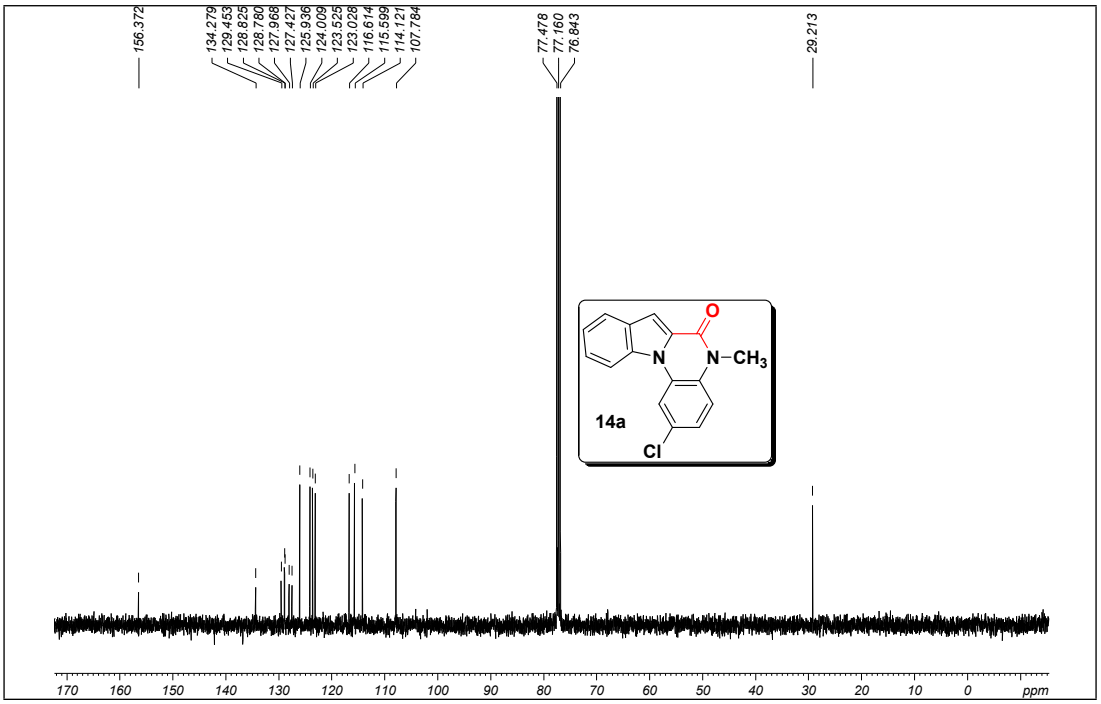


Figure S32. 100 MHz ^{13}C NMR spectrum of **14a** in $CDCl_3$

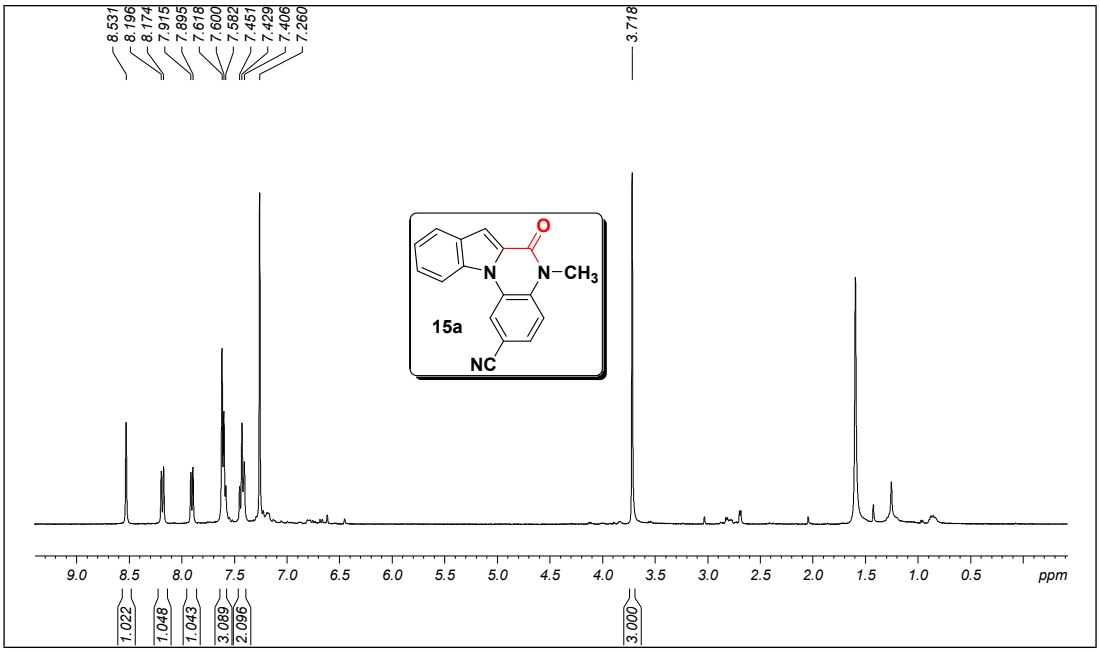


Figure S33. 400 MHz ^{1}H NMR spectrum of **15a** in $CDCl_3$

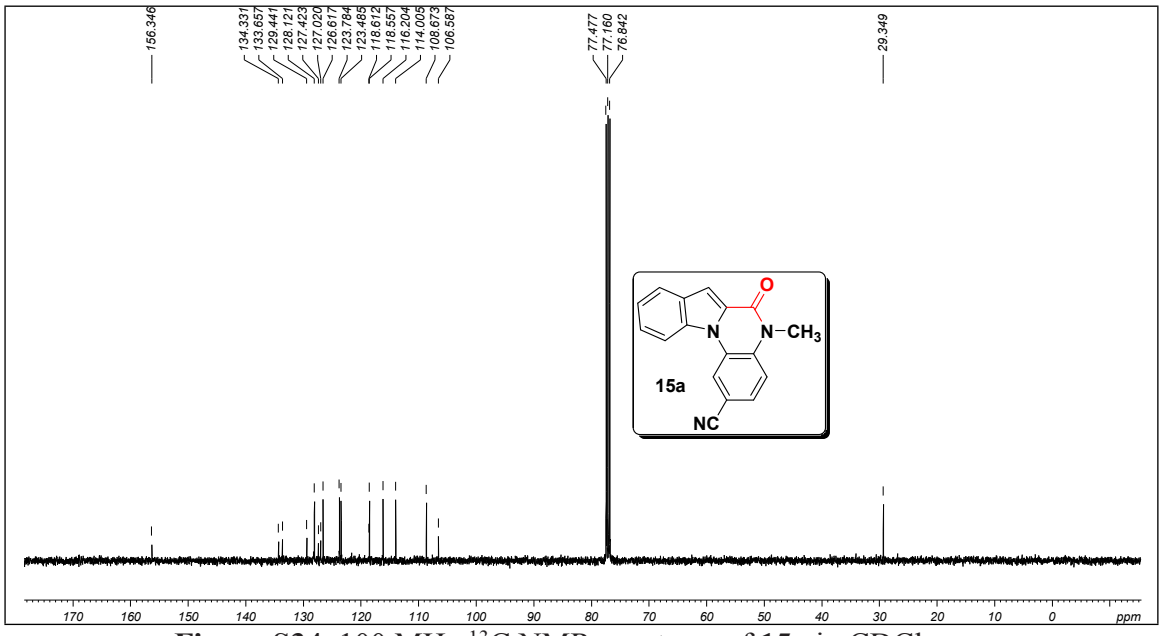


Figure S34. 100 MHz ^{13}C NMR spectrum of **15a** in $CDCl_3$

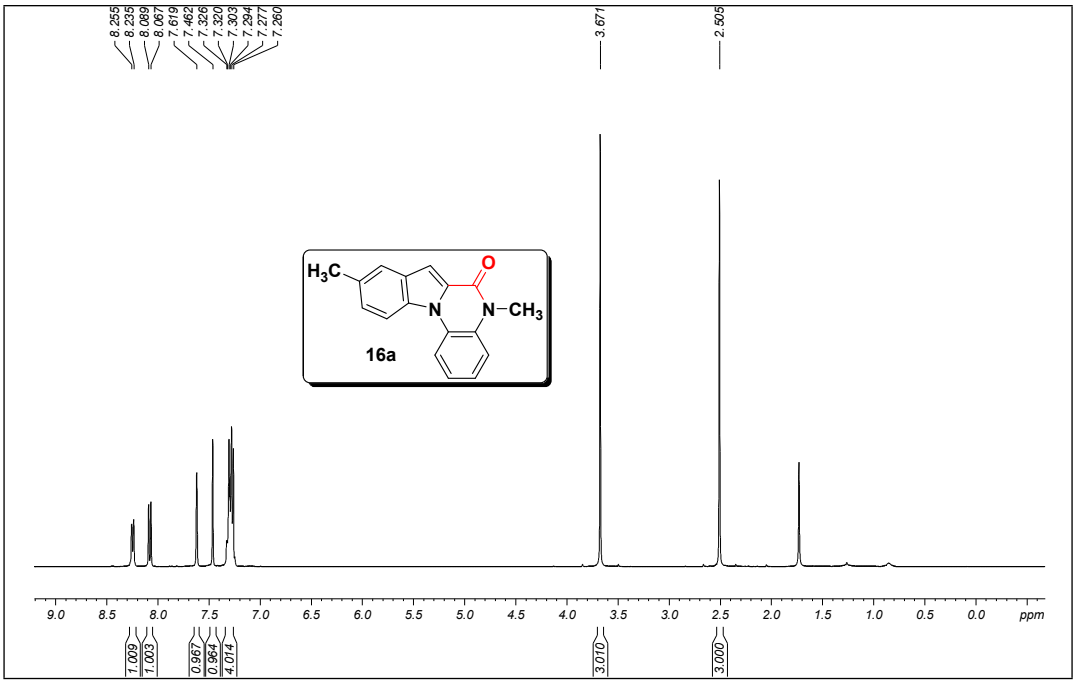


Figure S35. 400 MHz ^{1}H NMR spectrum of **16a** in $CDCl_3$

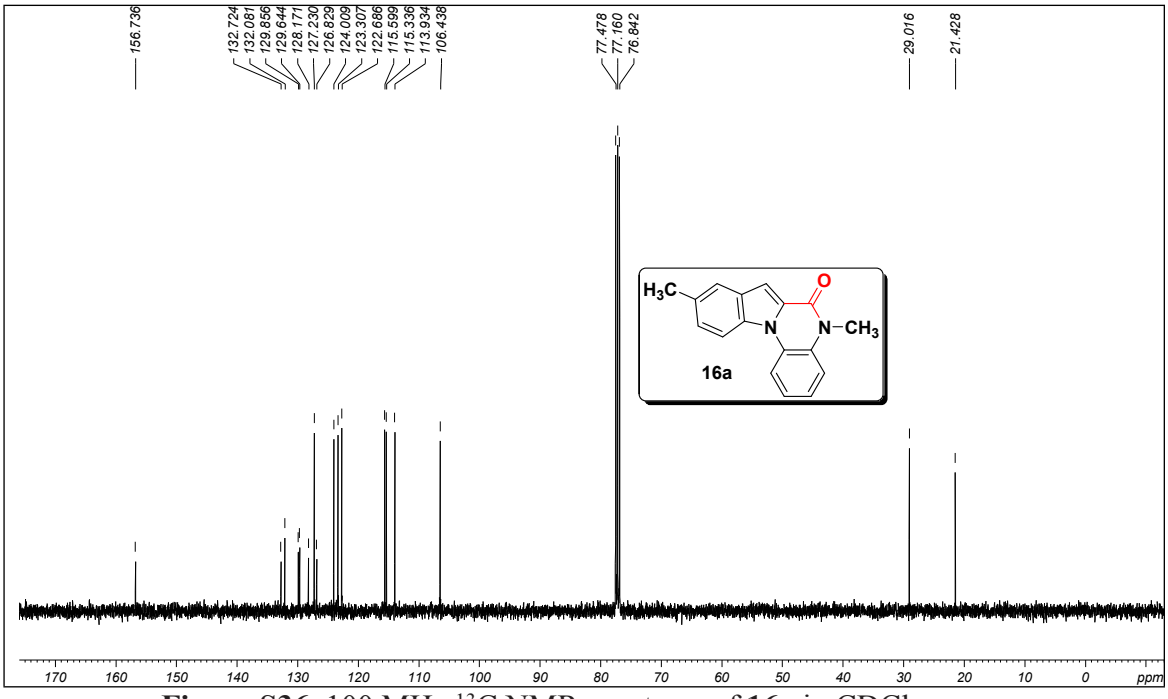


Figure S36. 100 MHz ^{13}C NMR spectrum of **16a** in $CDCl_3$

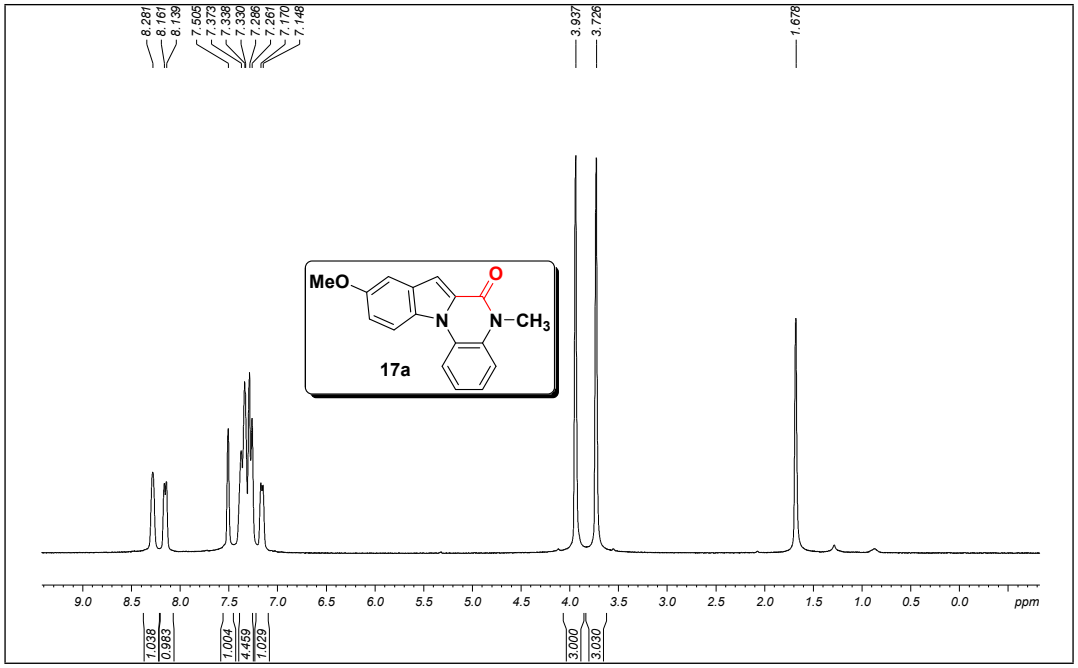


Figure S37. 400 MHz ^{1}H NMR spectrum of **17a** in $CDCl_3$

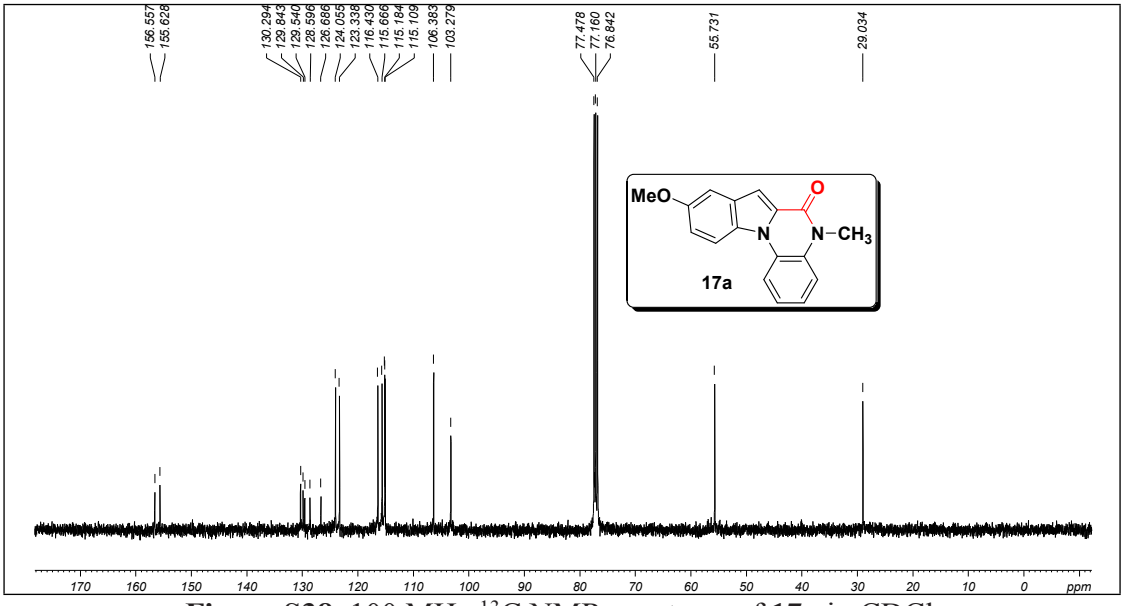


Figure S38. 100 MHz ^{13}C NMR spectrum of **17a** in $CDCl_3$

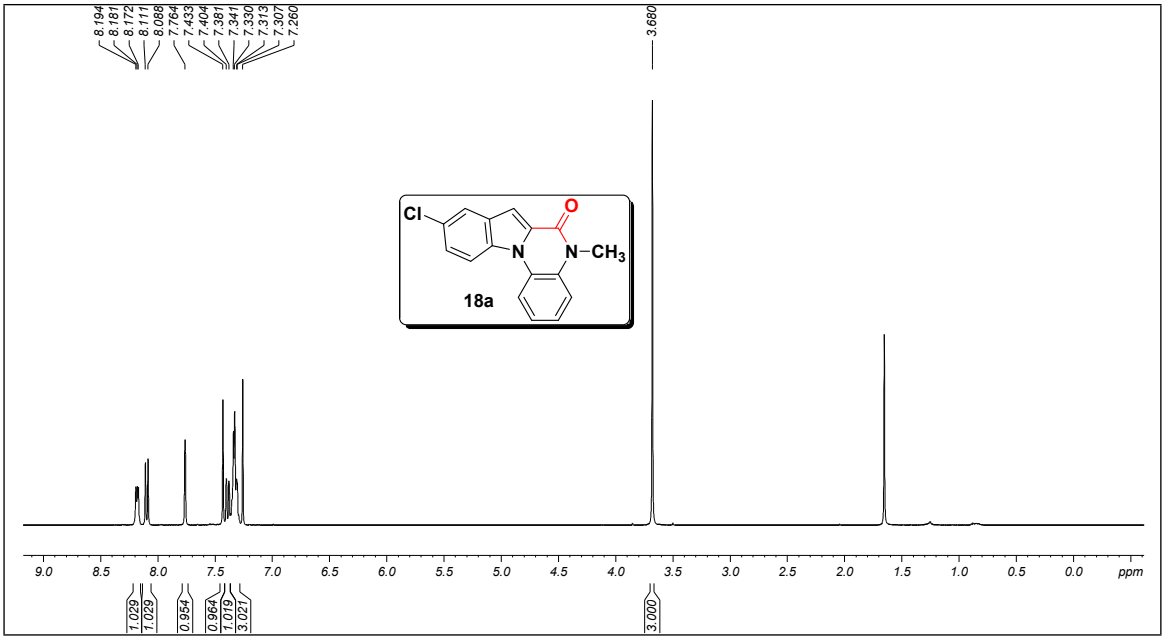


Figure S39. 400 MHz ^{1}H NMR spectrum of **18a** in $CDCl_3$

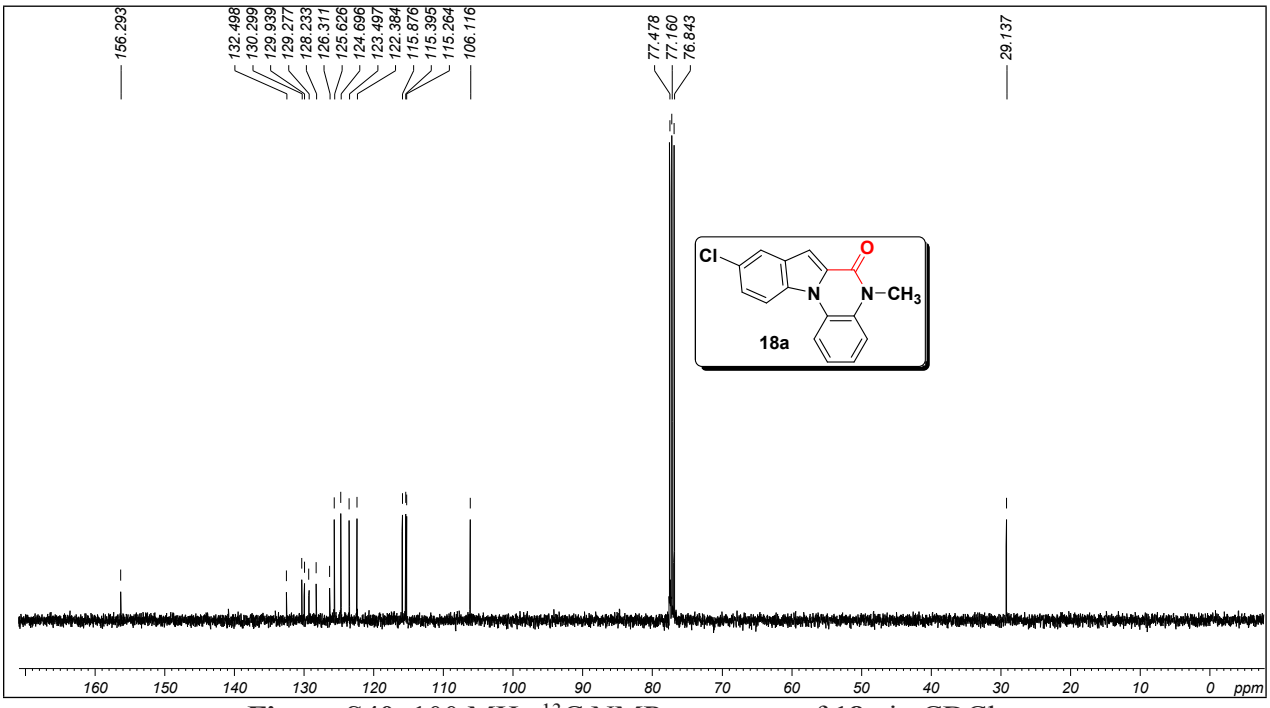


Figure S40. 100 MHz ^{13}C NMR spectrum of **18a** in $CDCl_3$

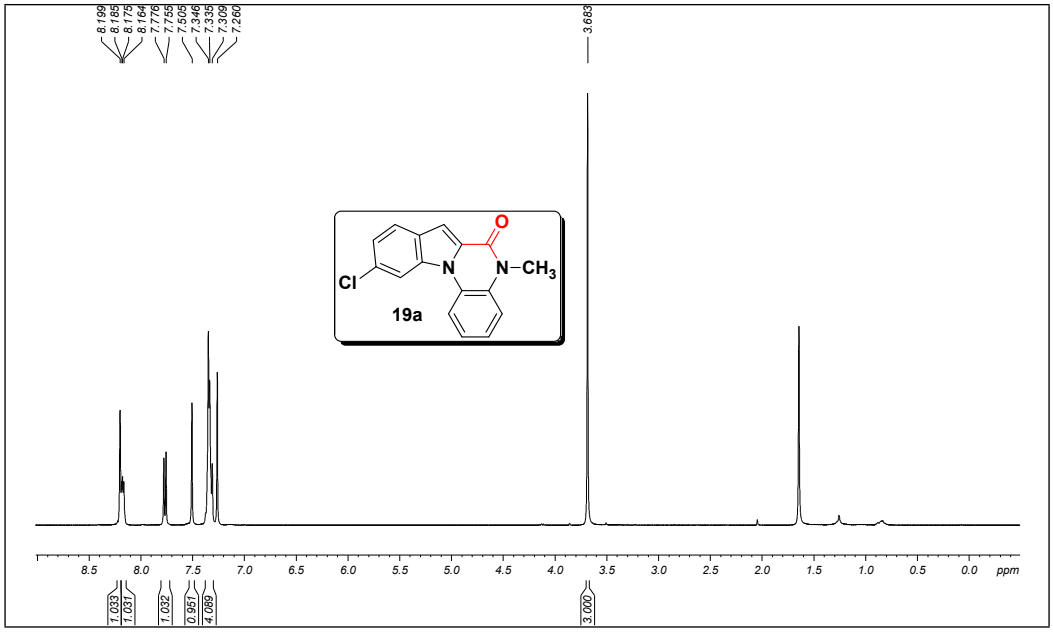


Figure S41. 400 MHz ^{1}H NMR spectrum of **19a** in $CDCl_3$

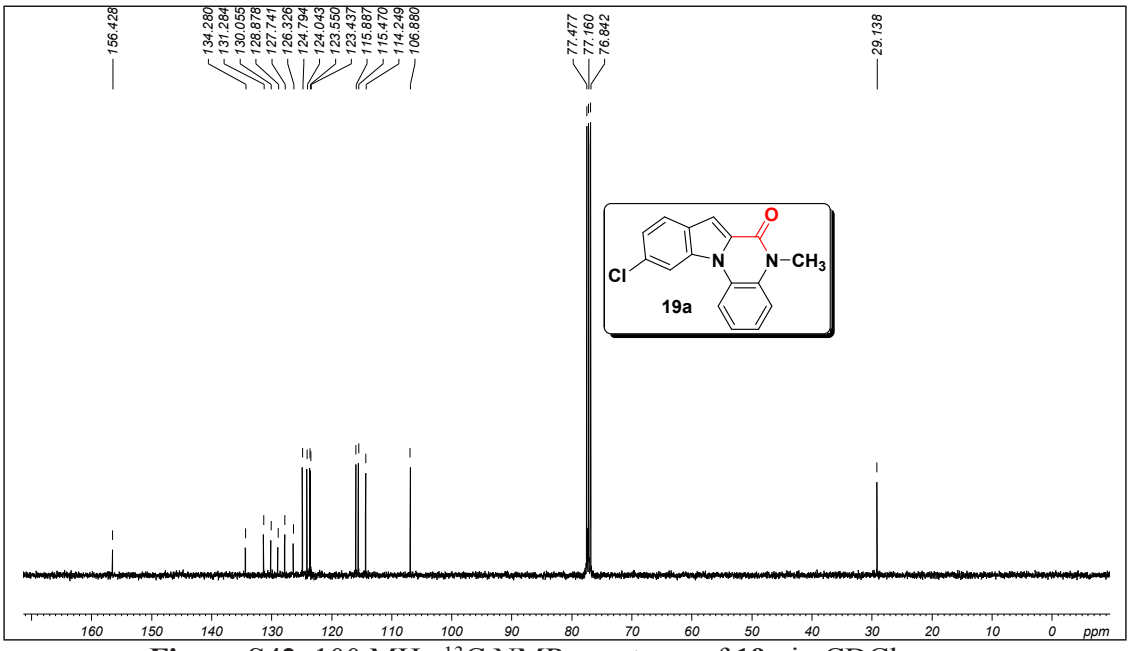


Figure S42. 100 MHz ^{13}C NMR spectrum of **19a** in $CDCl_3$

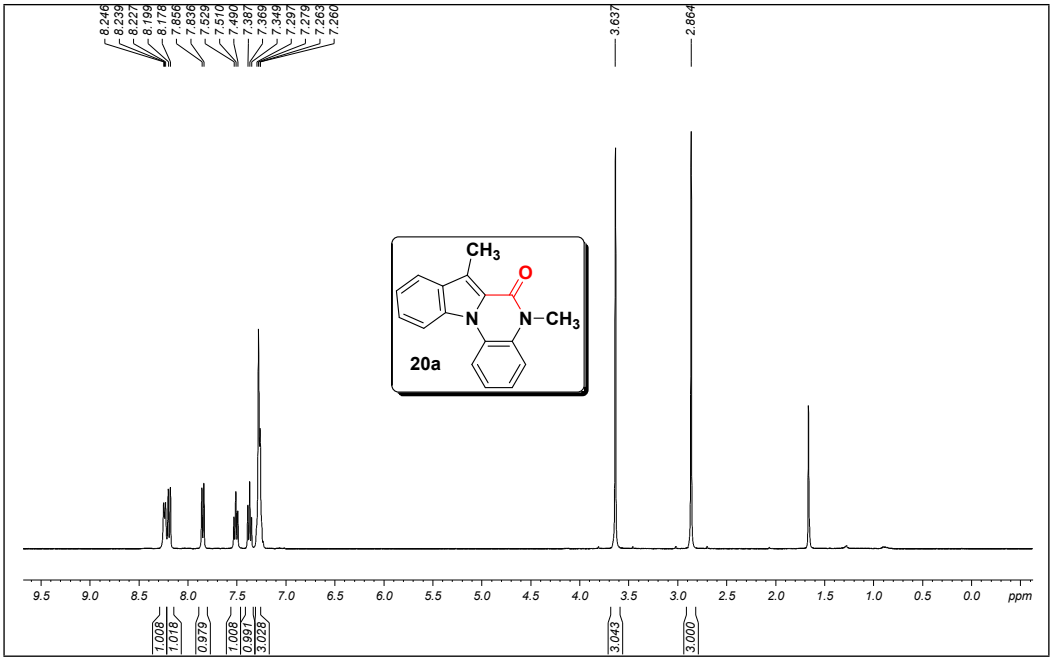


Figure S43. 400 MHz ^{1}H NMR spectrum of **20a** in $CDCl_3$

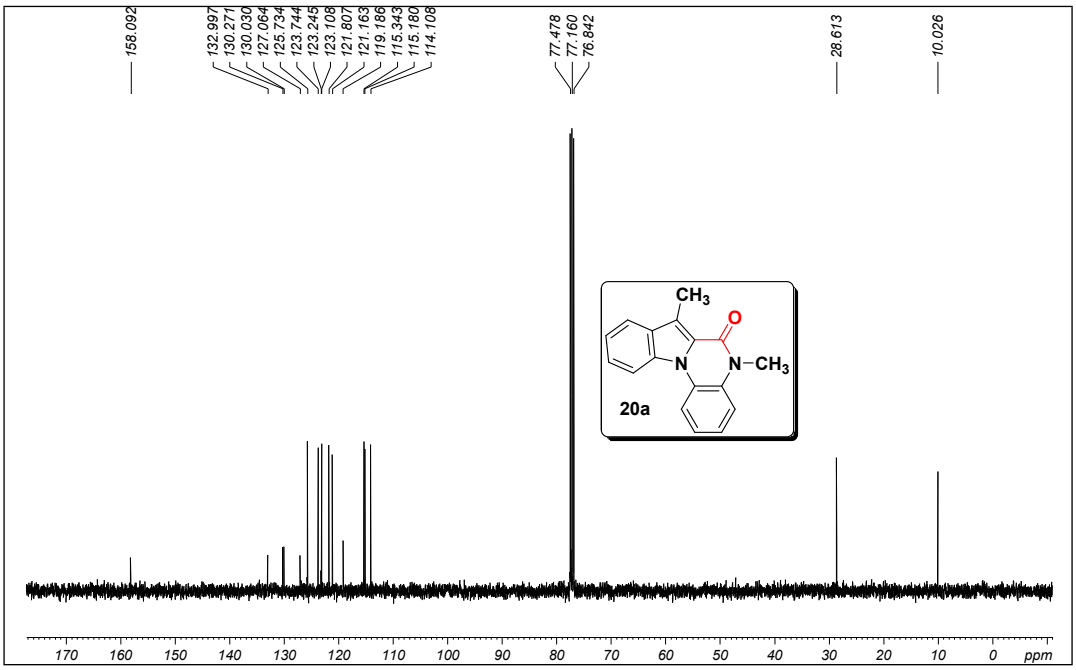


Figure S44. 100 MHz ^{13}C NMR spectrum of **20a** in $CDCl_3$

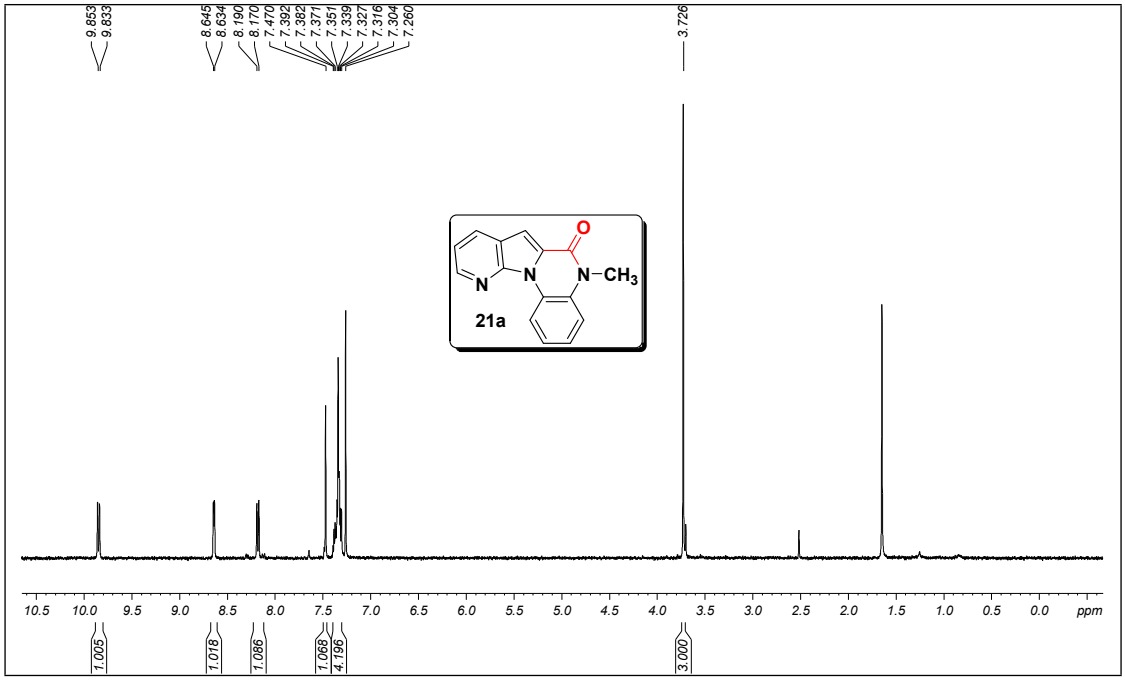


Figure S45. 400 MHz ^{1}H NMR spectrum of **21a** in $CDCl_3$

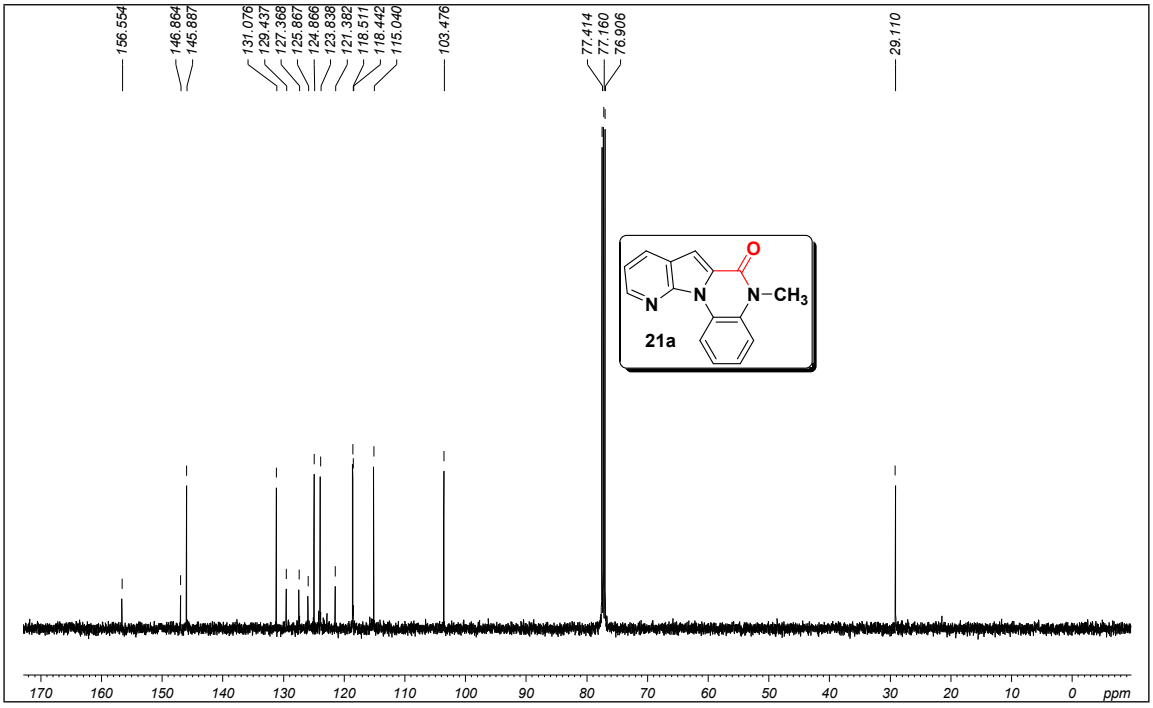


Figure S46. 125 MHz ^{13}C NMR spectrum of **21a** in $CDCl_3$

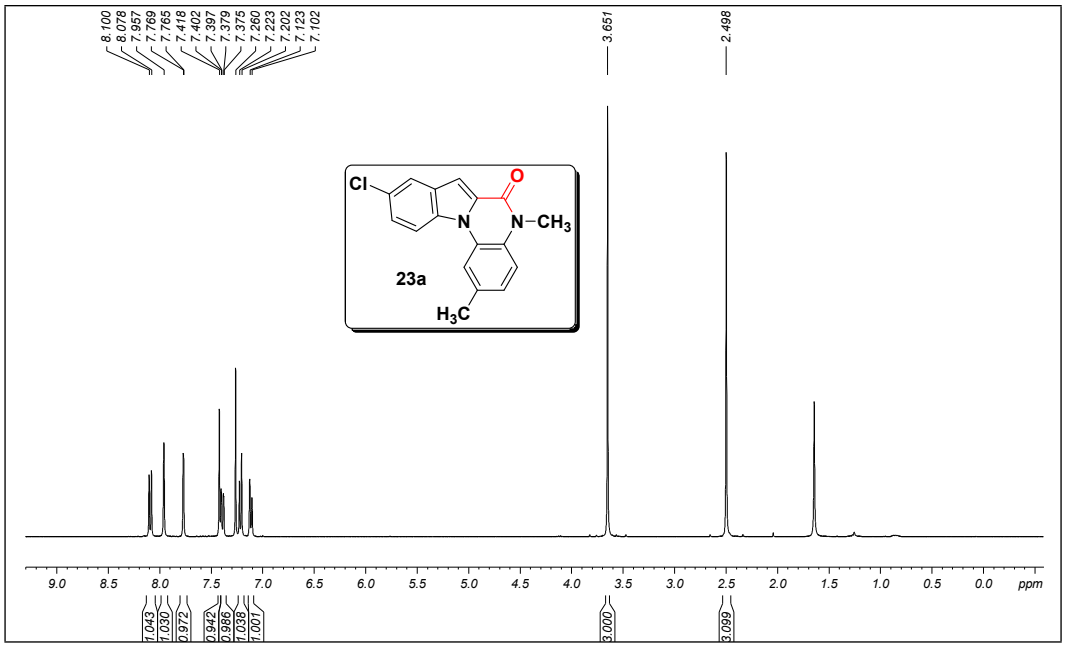


Figure S47. 400 MHz ^{1}H NMR spectrum of **23a** in $CDCl_3$

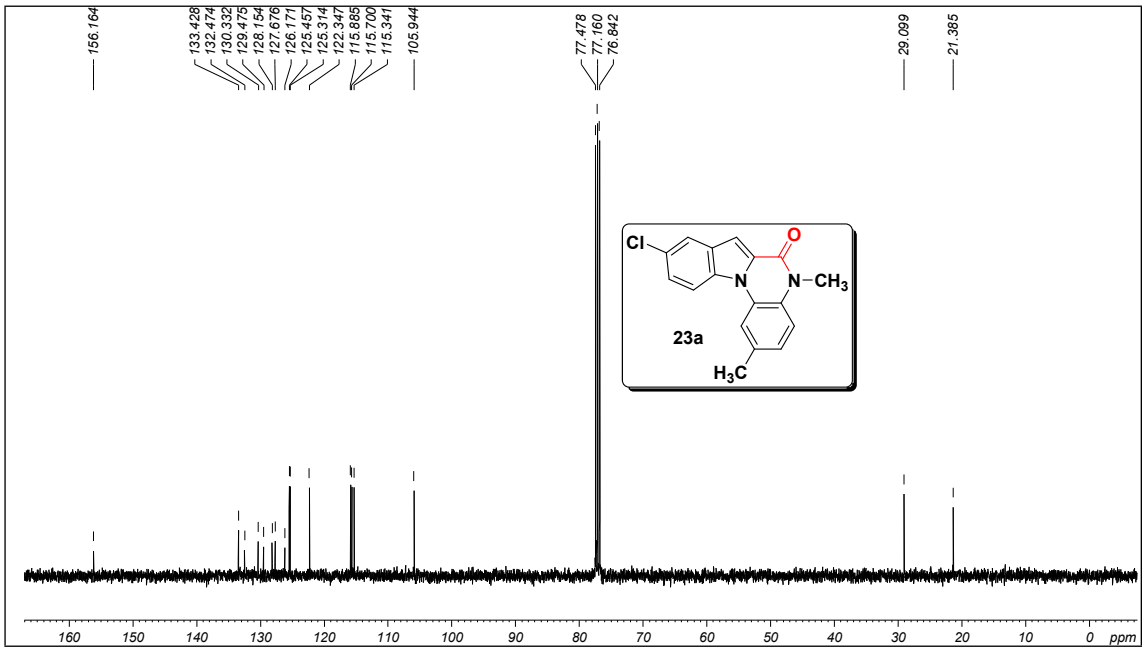


Figure S48. 100 MHz ^{13}C NMR spectrum of **23a** in $CDCl_3$

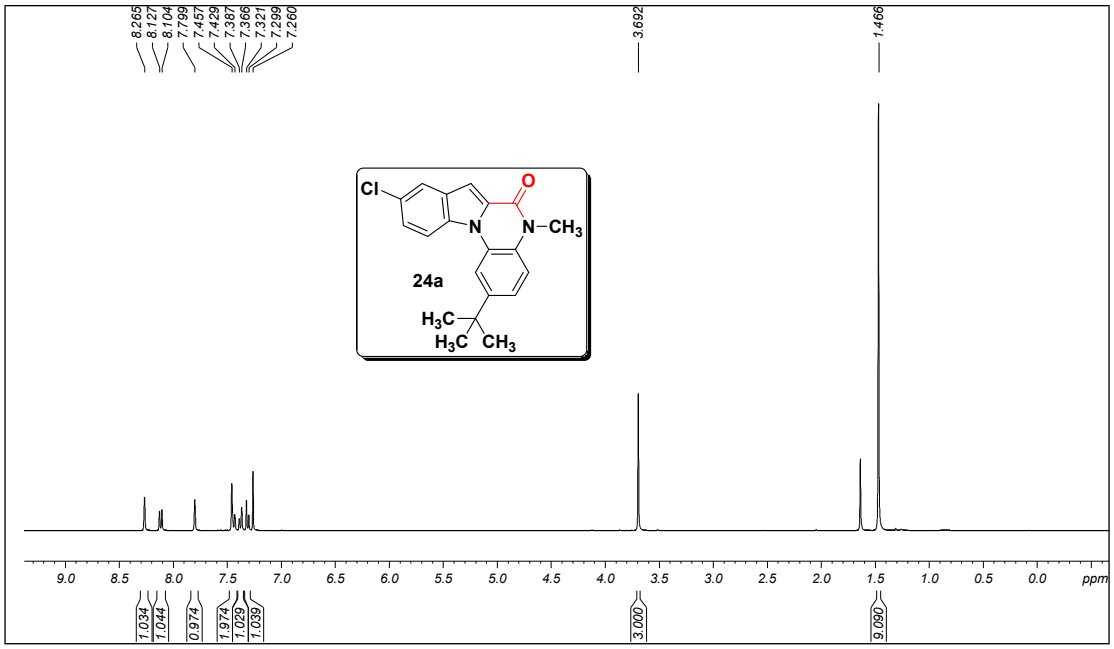


Figure S49. 400 MHz ^{1}H NMR spectrum of **24a** in $CDCl_3$

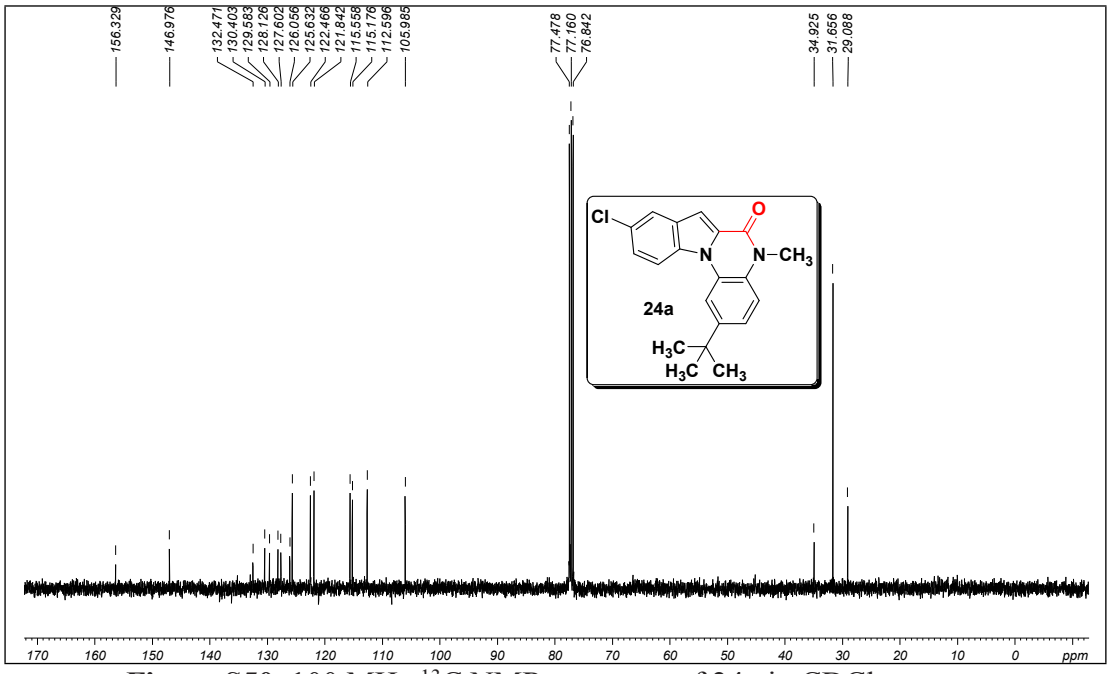


Figure S50. 100 MHz ^{13}C NMR spectrum of **24a** in $CDCl_3$

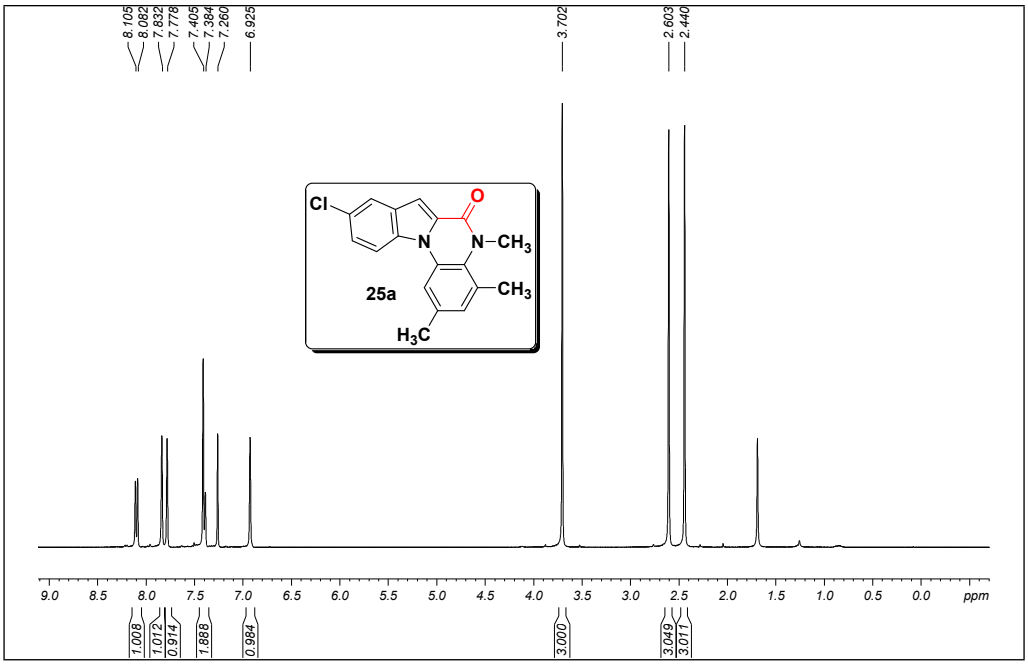


Figure S51. 400 MHz ^{1}H NMR spectrum of **25a** in $CDCl_3$

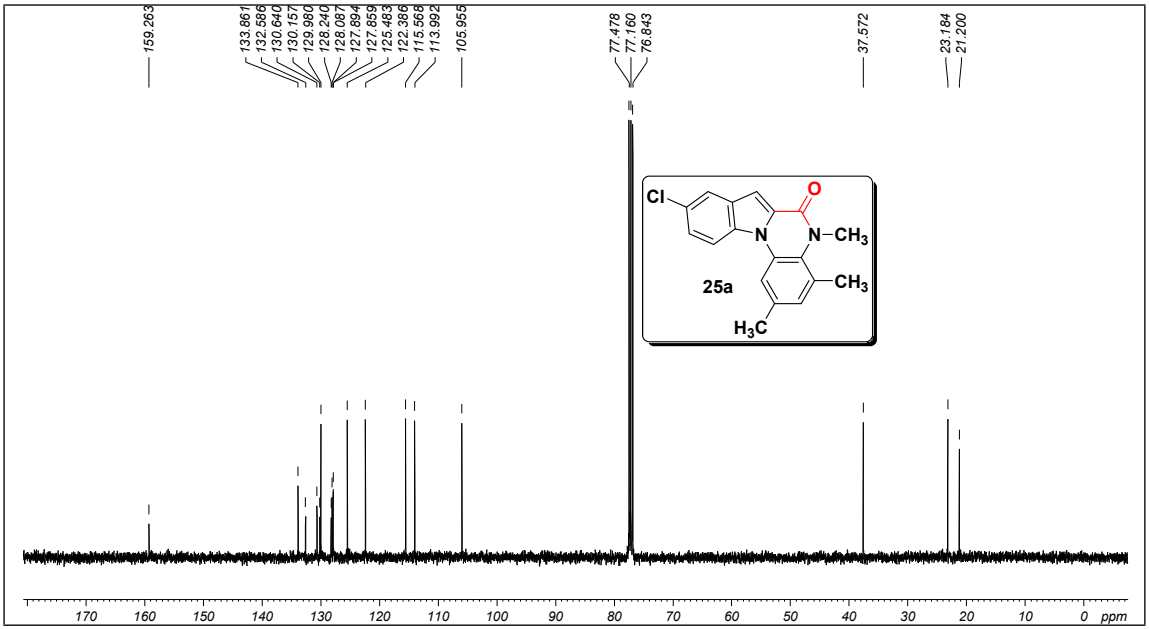


Figure S52. 100 MHz ^{13}C NMR spectrum of **25a** in $CDCl_3$

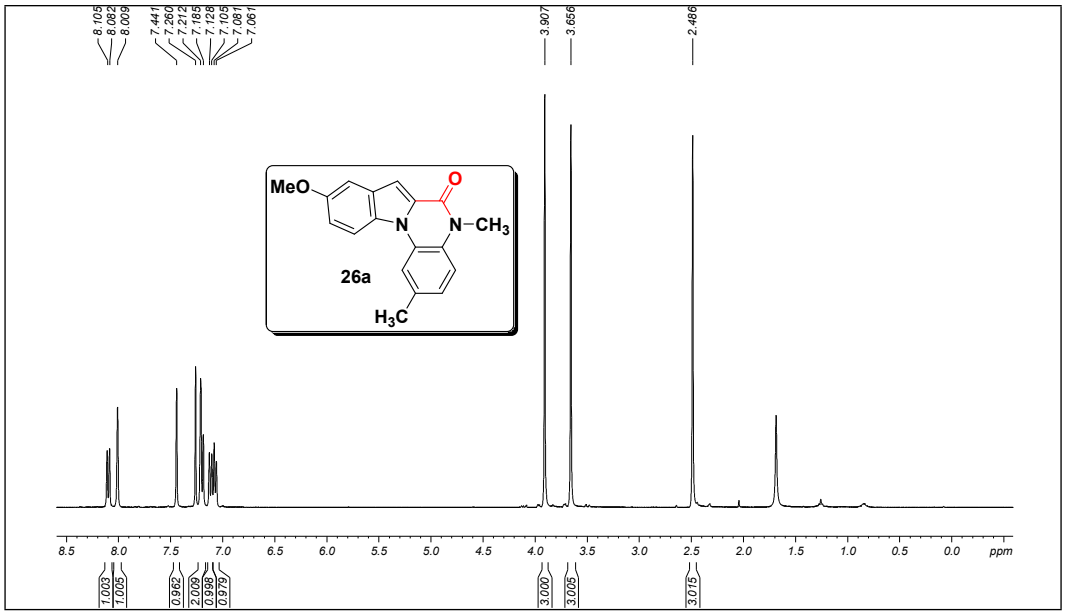


Figure S53. 400 MHz ^{1}H NMR spectrum of **26a** in $CDCl_3$

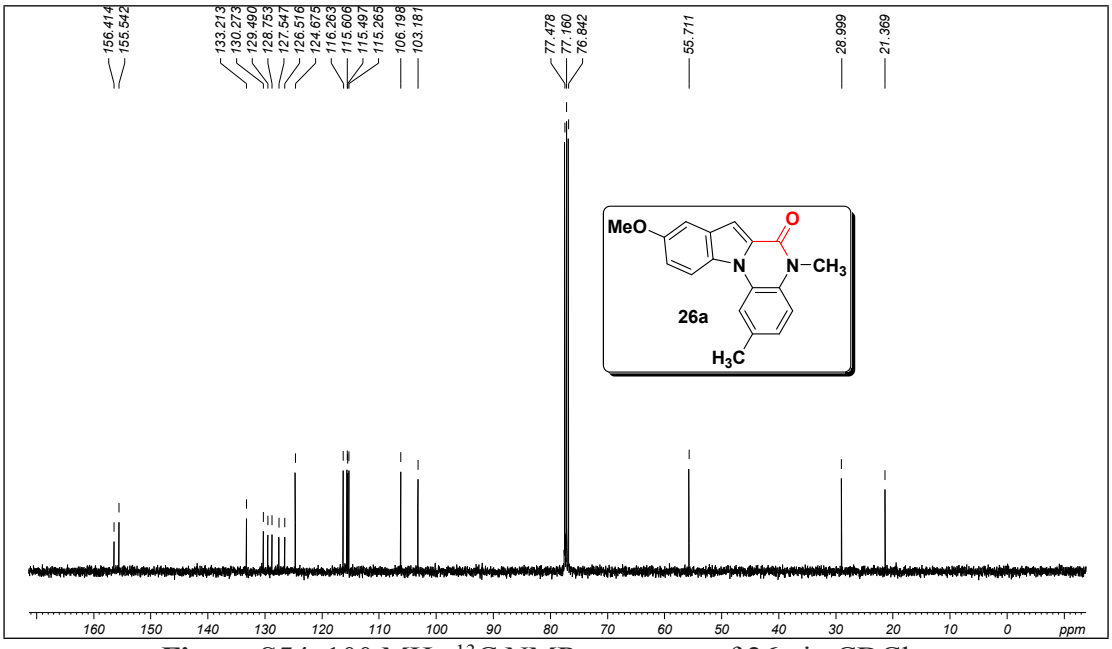


Figure S54. 100 MHz ^{13}C NMR spectrum of **26a** in $CDCl_3$

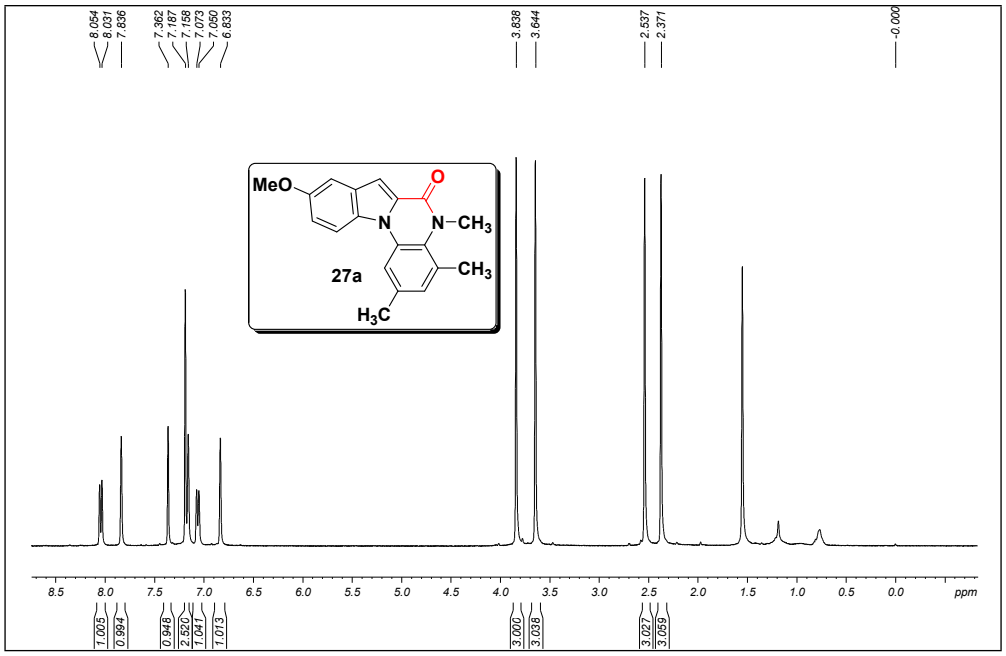


Figure S55. 400 MHz ^{1}H NMR spectrum of **27a** in $CDCl_3$

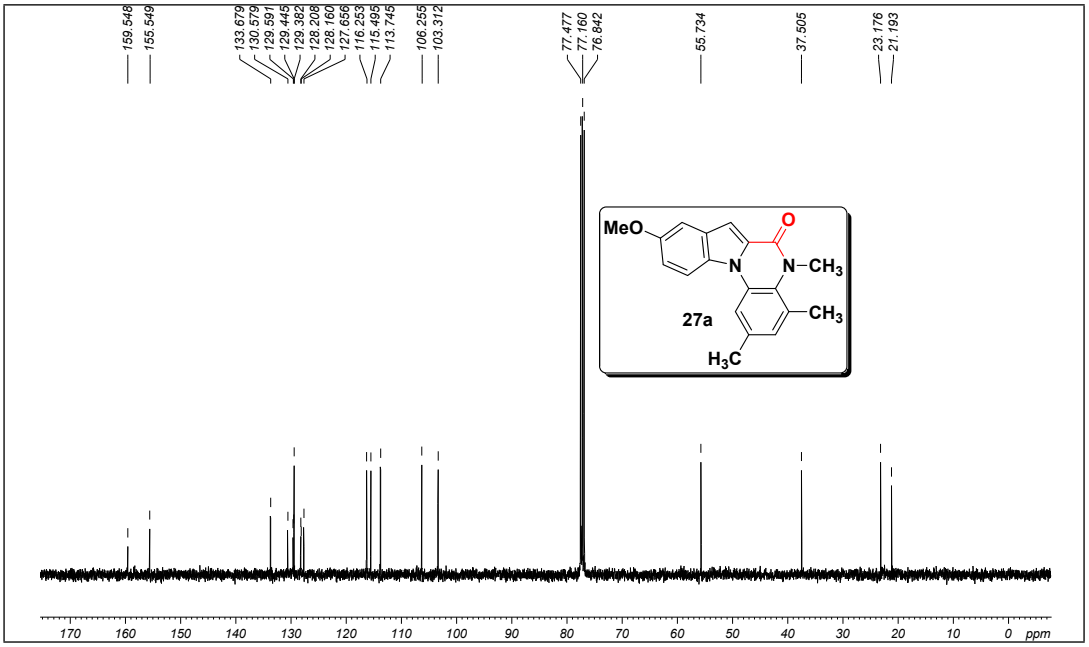


Figure S56. 100 MHz ^{13}C NMR spectrum of **27a** in $CDCl_3$

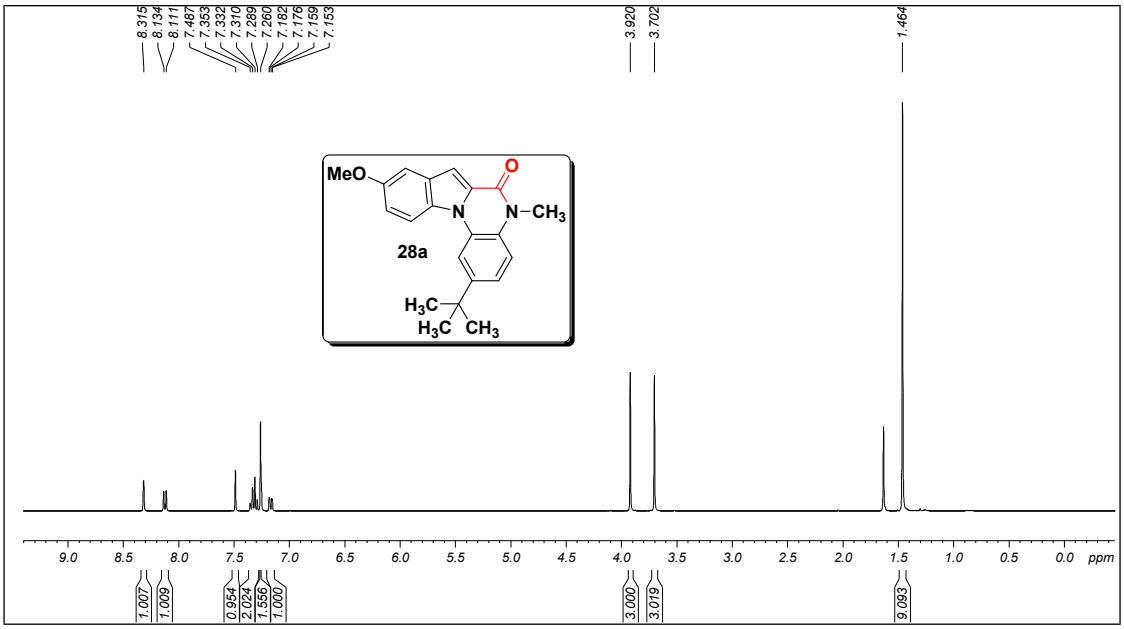


Figure S57. 400 MHz ^{1}H NMR spectrum of **28a** in $CDCl_3$

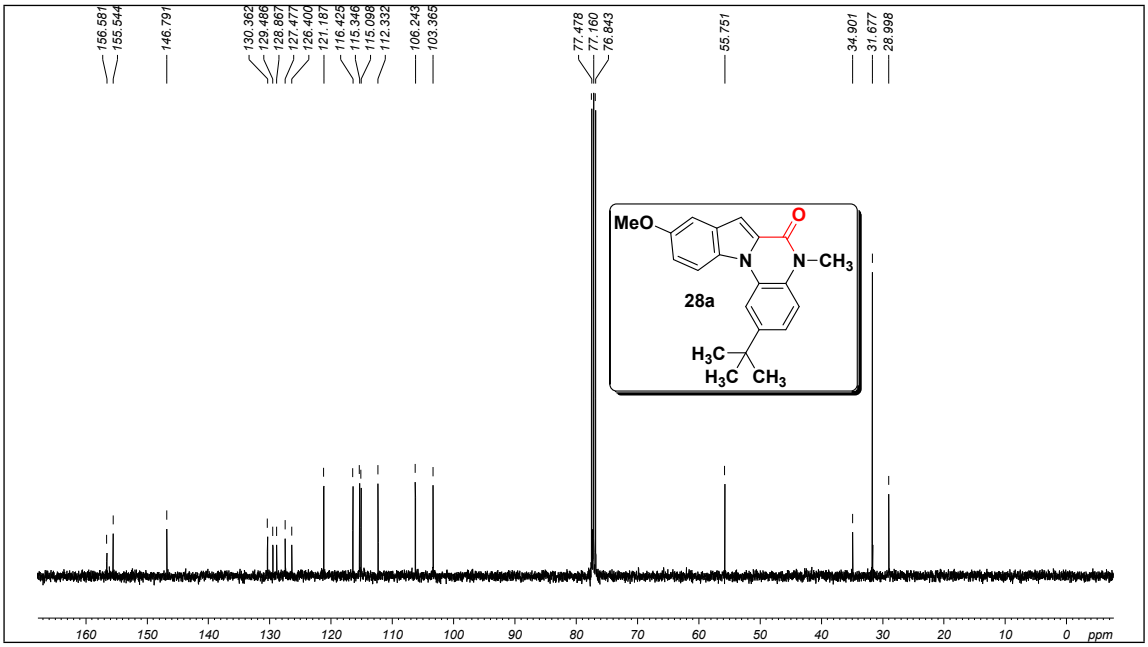


Figure S58. 100 MHz ^{13}C NMR spectrum of **28a** in $CDCl_3$

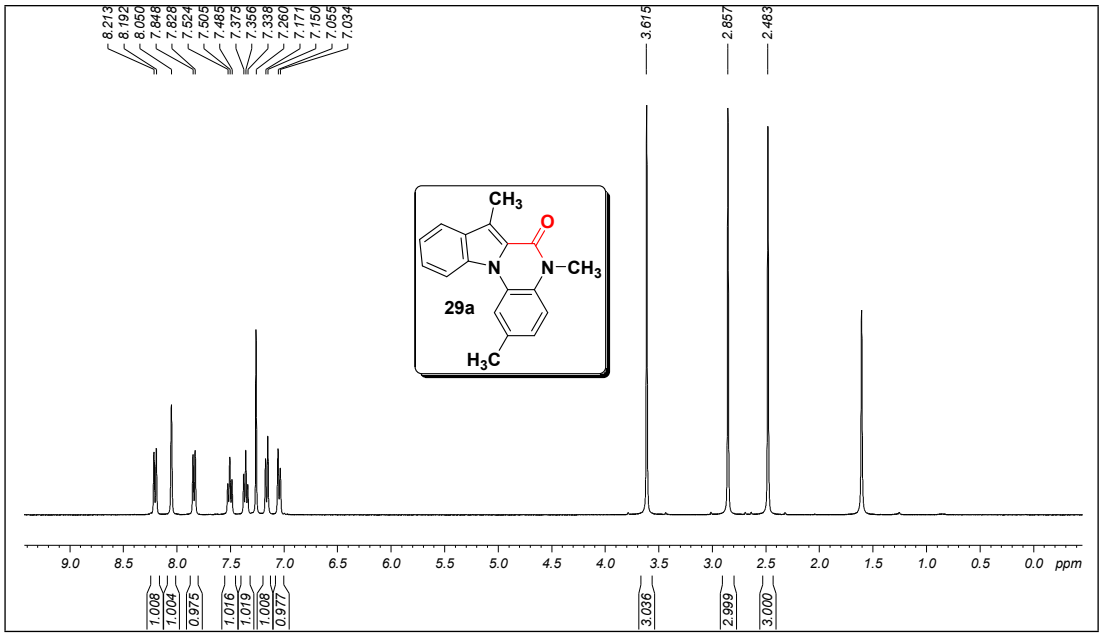


Figure S59. 400 MHz ^{1}H NMR spectrum of **29a** in $CDCl_3$

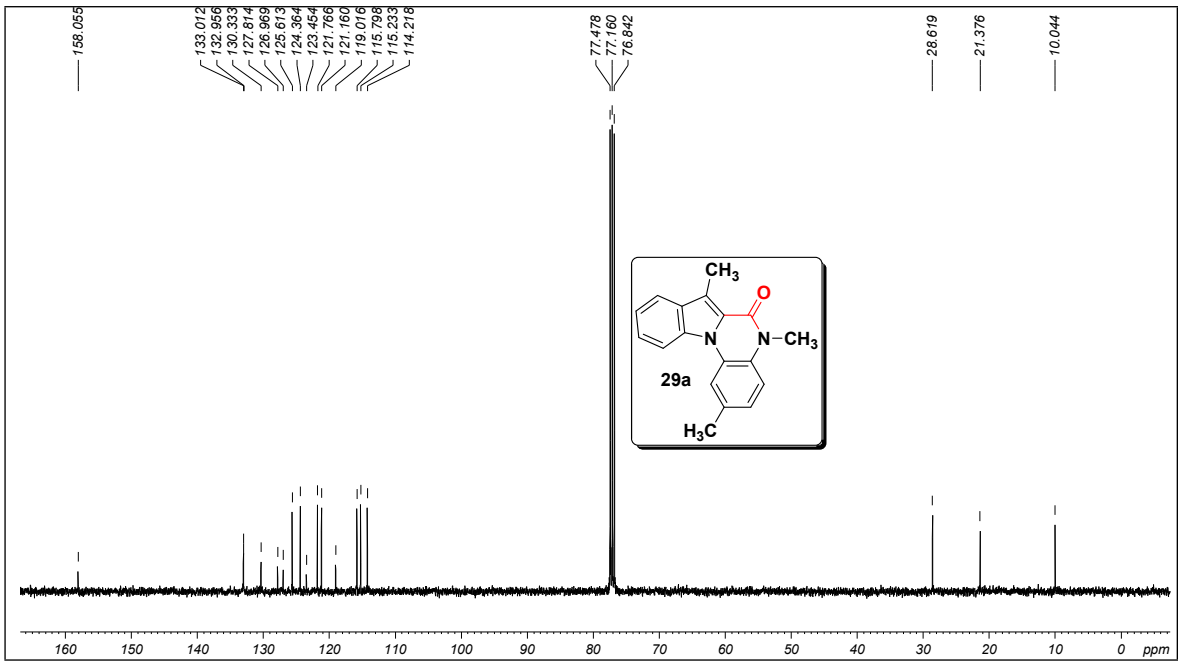


Figure S60. 100 MHz ^{13}C NMR spectrum of **29a** in $CDCl_3$

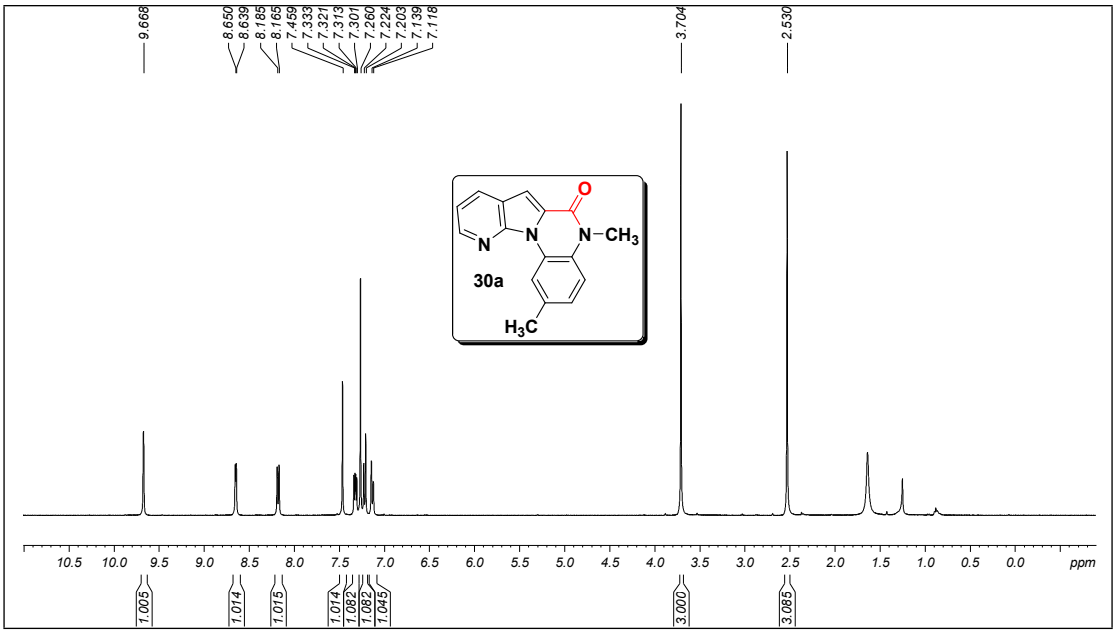


Figure S61. 400 MHz ^{1}H NMR spectrum of **30a** in $CDCl_3$

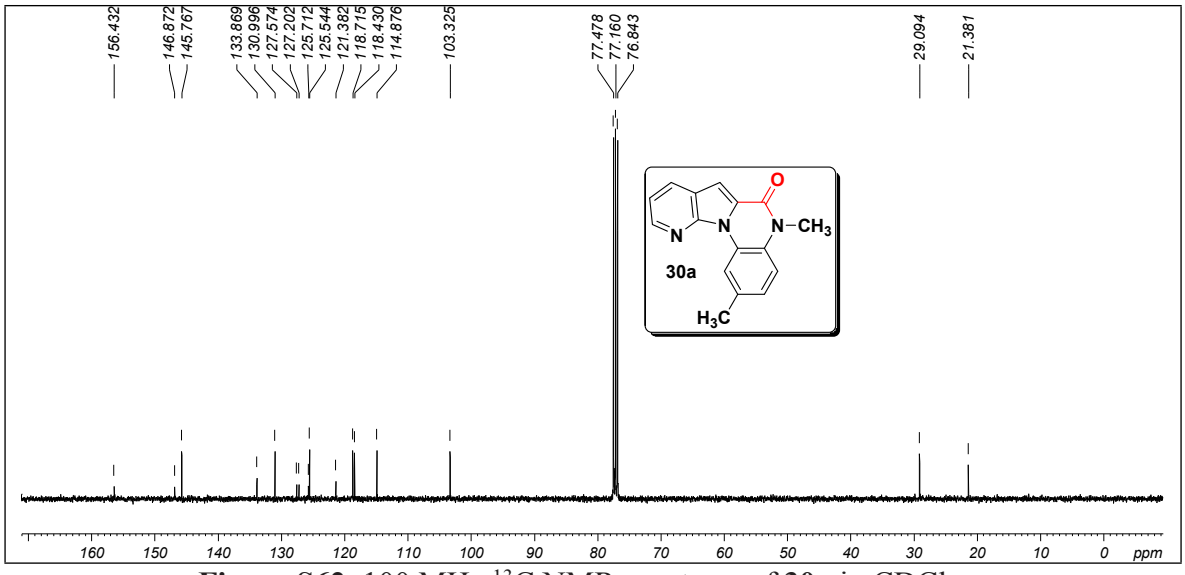


Figure S62. 100 MHz ^{13}C NMR spectrum of **30a** in $CDCl_3$

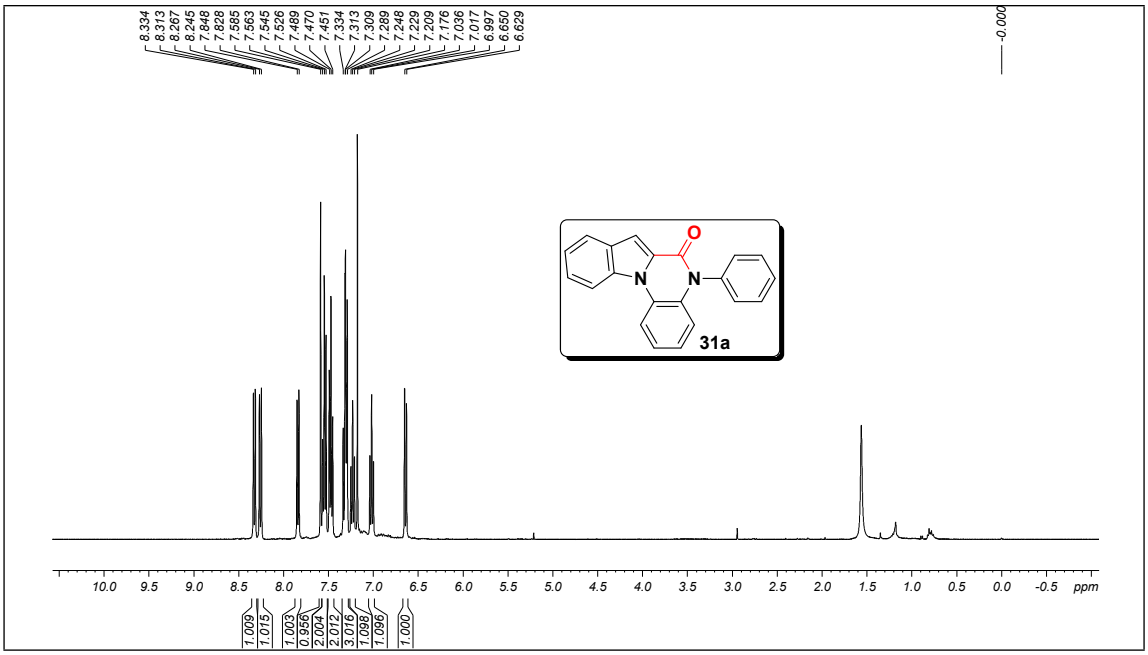


Figure S63. 400 MHz ^{1}H NMR spectrum of **31a** in $CDCl_3$

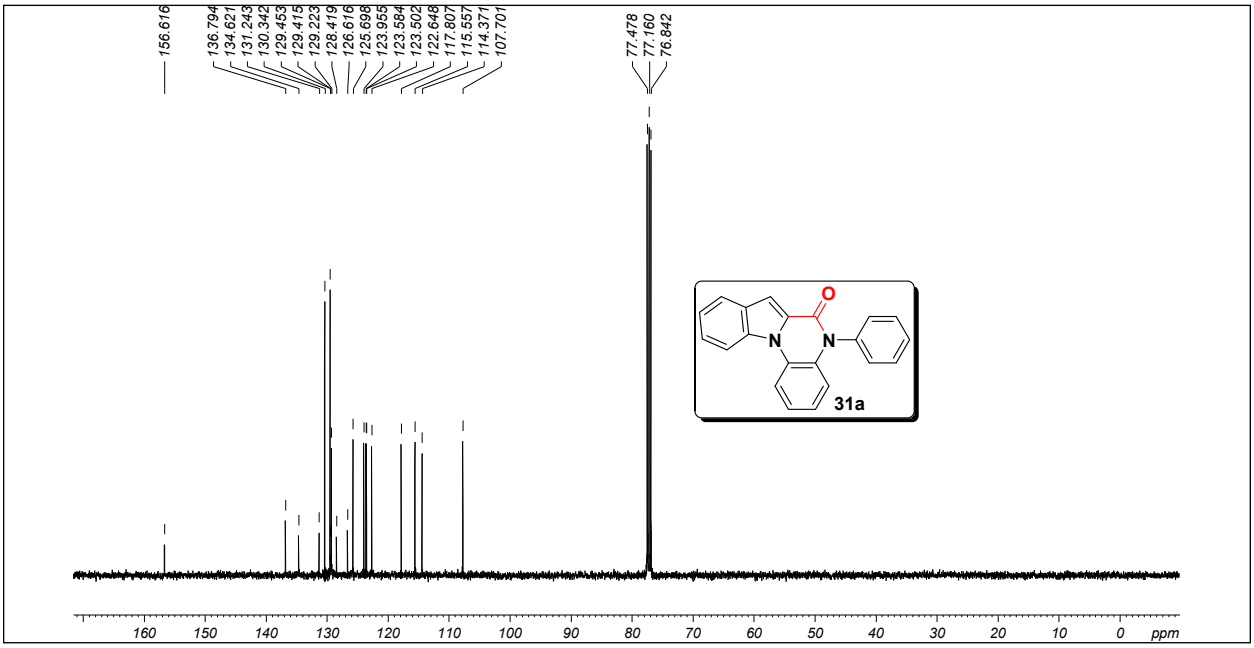


Figure S64. 100 MHz ^{13}C NMR spectrum of **31a** in $CDCl_3$

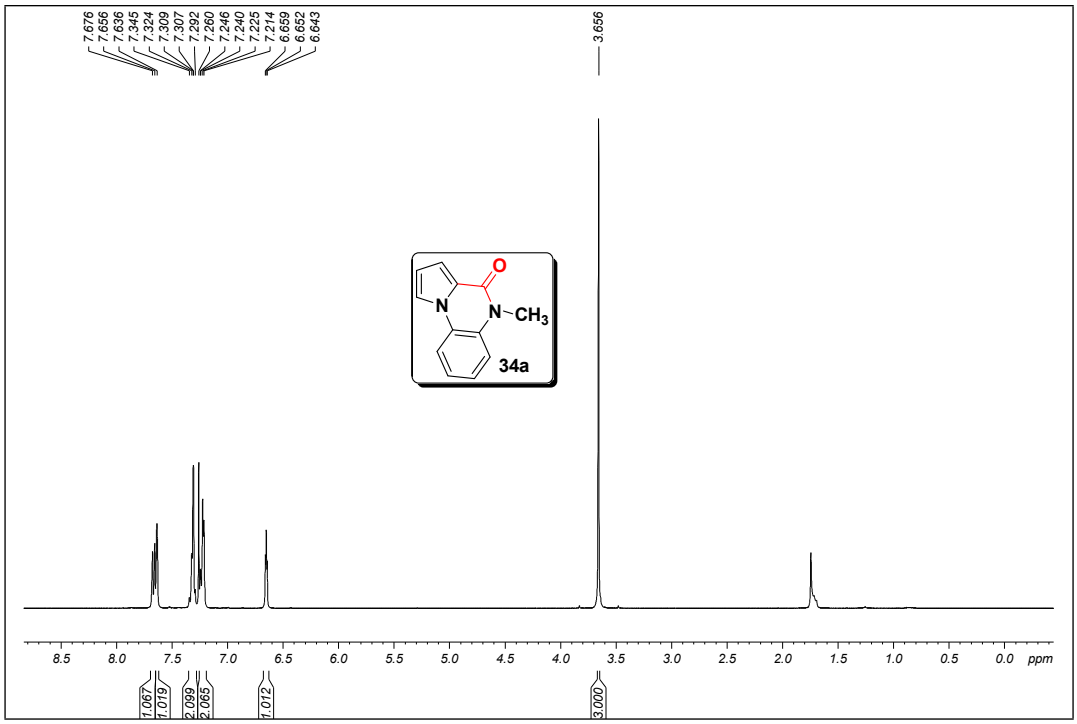


Figure S65. 400 MHz ^{1}H NMR spectrum of **34a** in $CDCl_3$

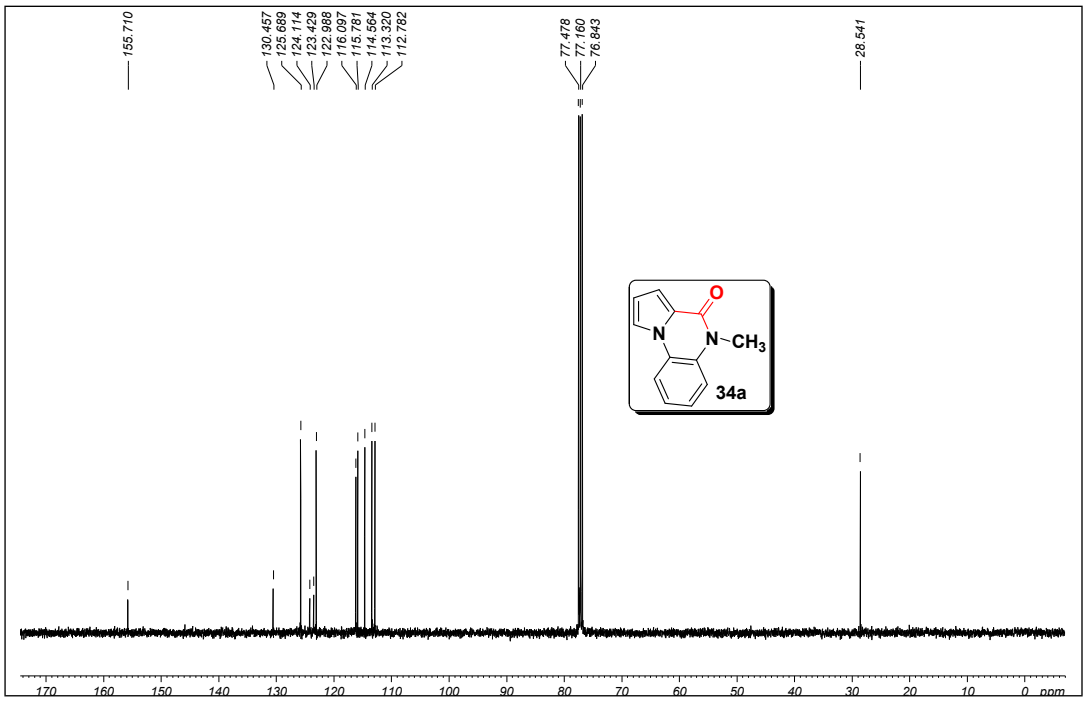


Figure S66. 100 MHz ^{13}C NMR spectrum of **34a** in $CDCl_3$

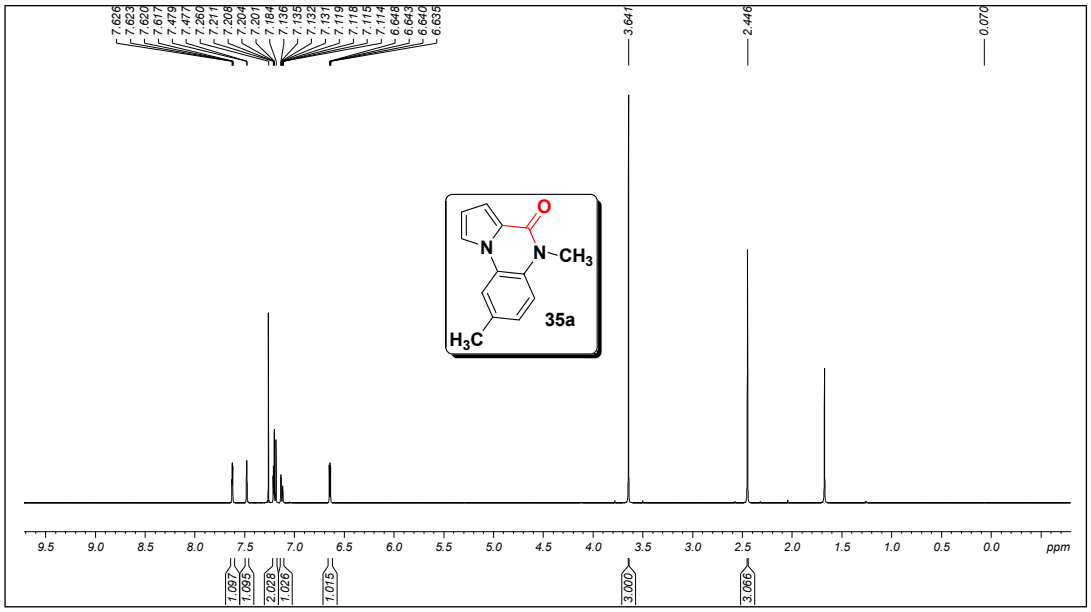


Figure S67. 500 MHz ^{1}H NMR spectrum of **35a** in $CDCl_3$

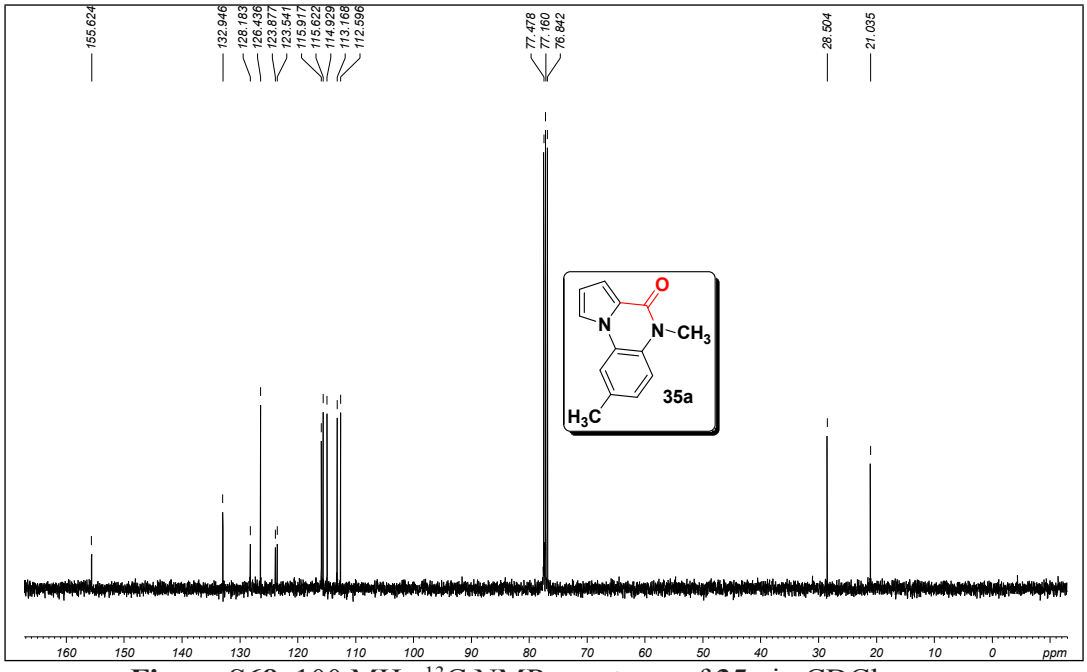


Figure S68. 100 MHz ^{13}C NMR spectrum of **35a** in $CDCl_3$

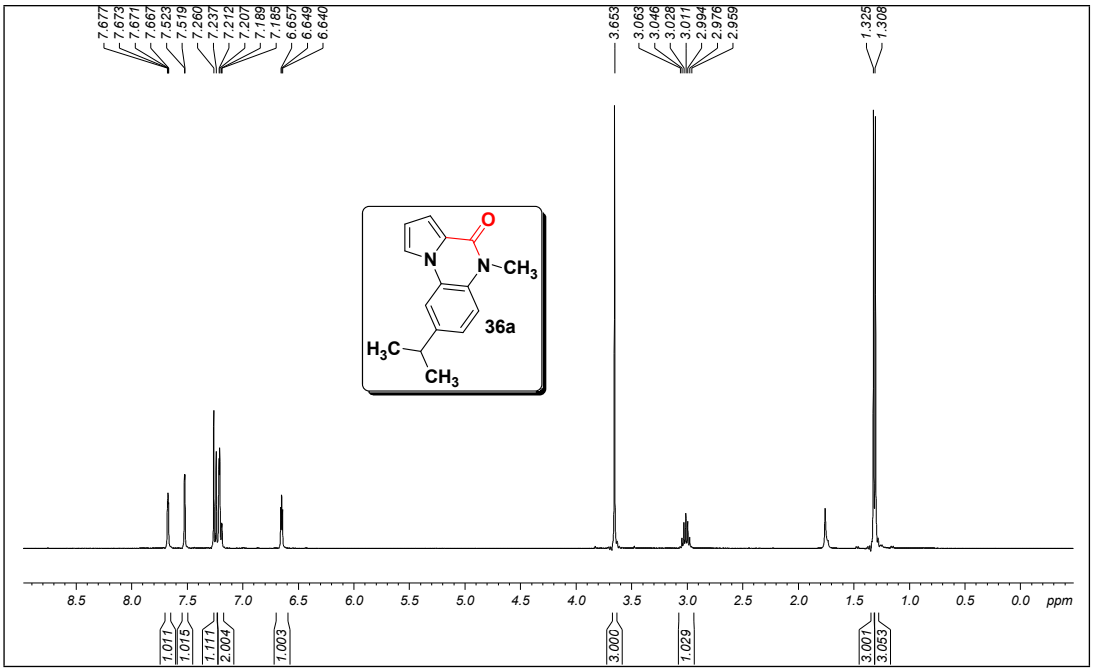


Figure S69. 400 MHz ^{1}H NMR spectrum of **36a** in $CDCl_3$

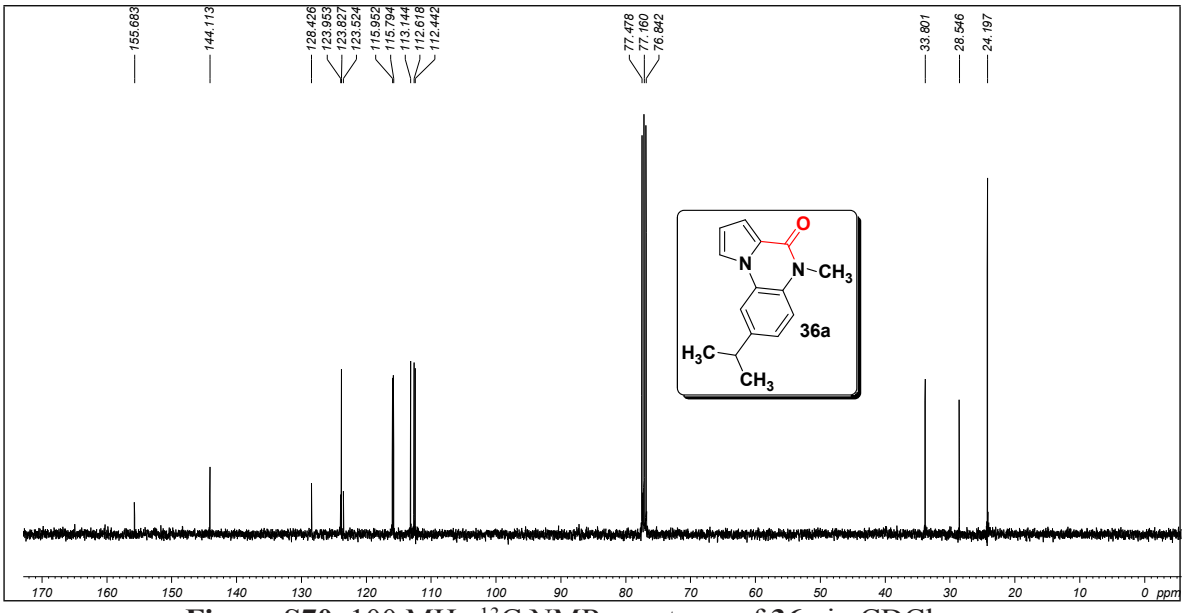


Figure S70. 100 MHz ^{13}C NMR spectrum of **36a** in $CDCl_3$

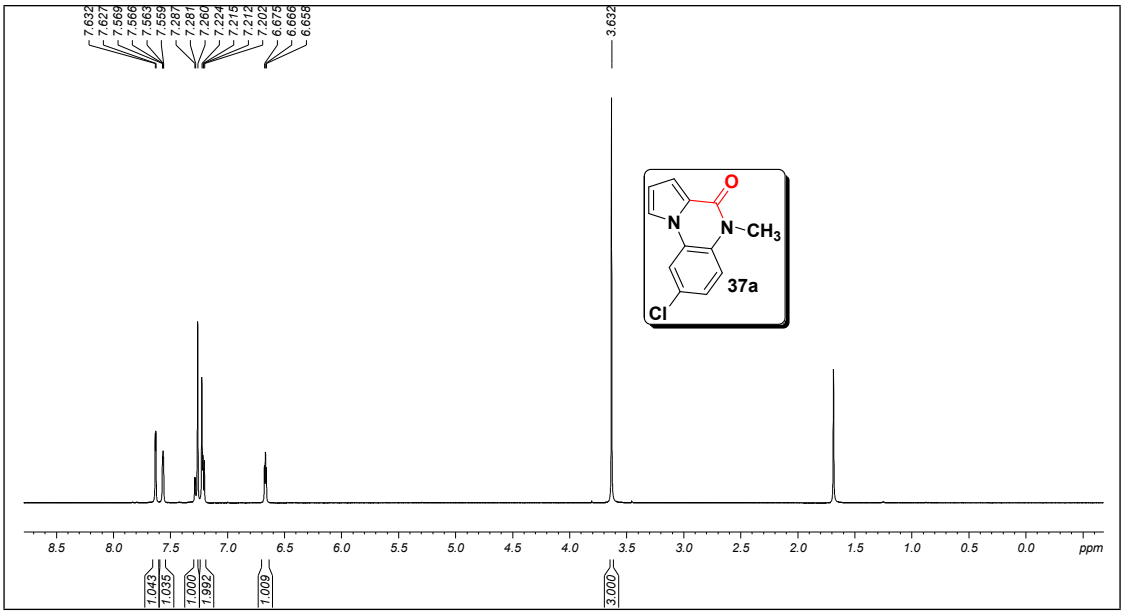


Figure S71. 400 MHz ^{1}H NMR spectrum of **37a** in $CDCl_3$

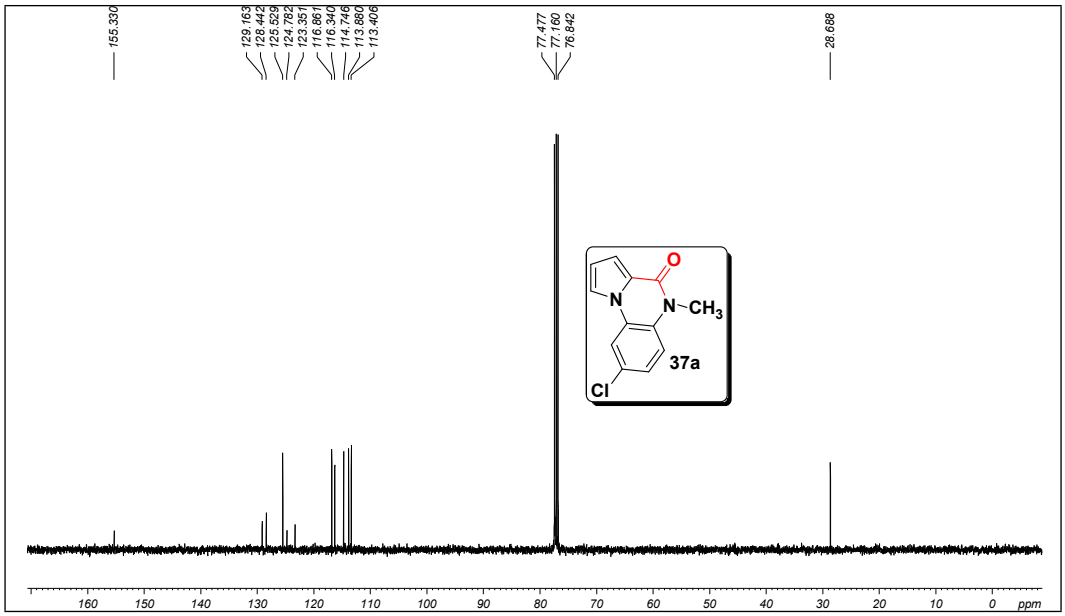


Figure S72. 100 MHz ^{13}C NMR spectrum of **37a** in $CDCl_3$

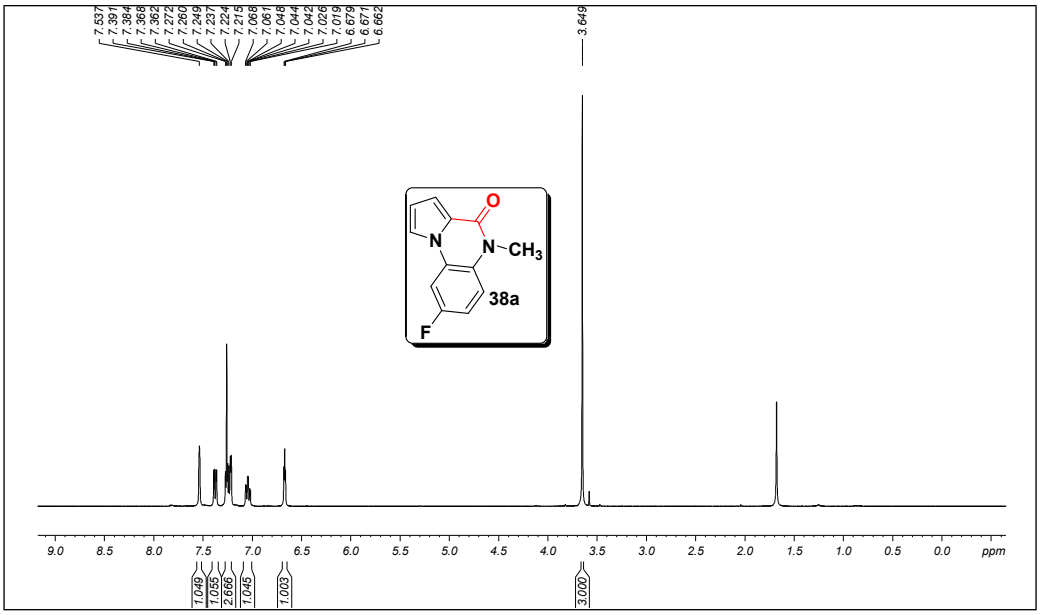


Figure S73. 400 MHz ^{1}H NMR spectrum of **38a** in $CDCl_3$

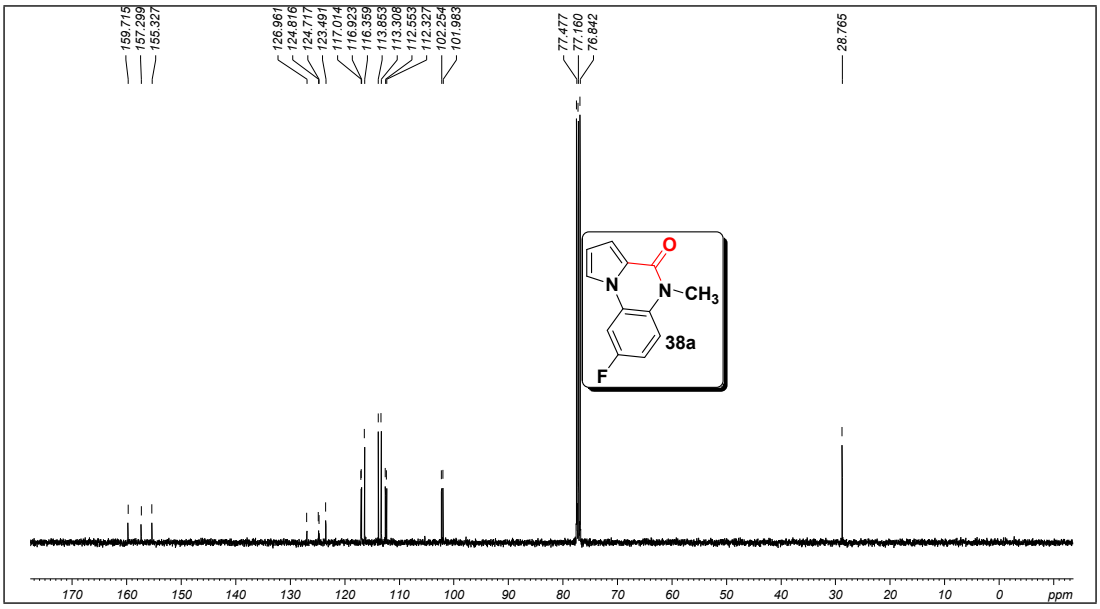


Figure S74. 100 MHz ^{13}C NMR spectrum of **38a** in $CDCl_3$

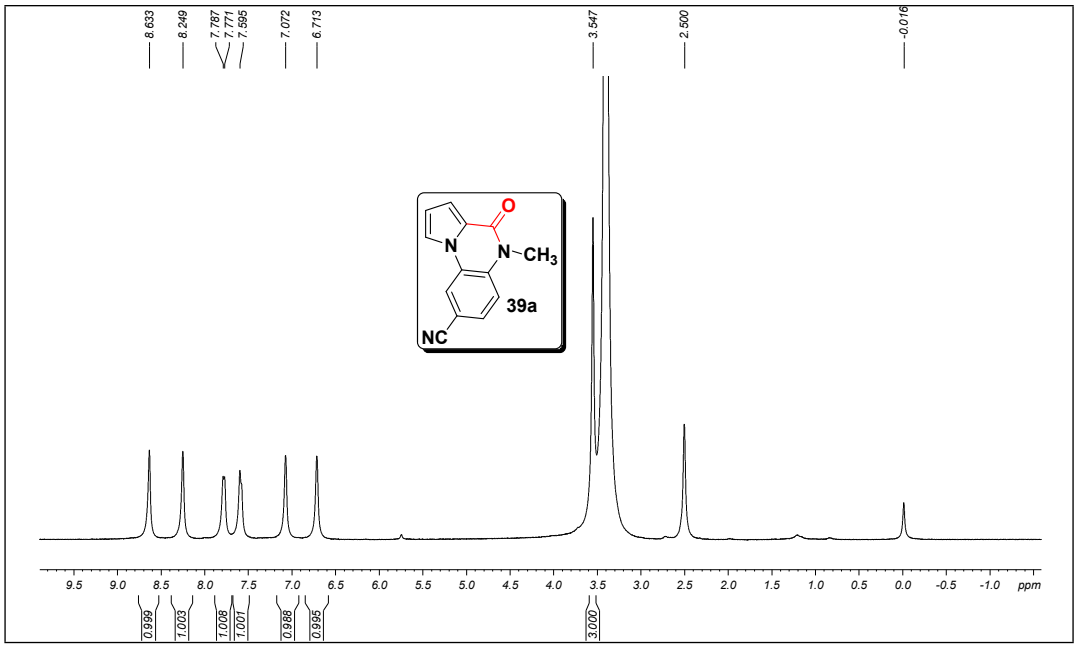


Figure S75. 400 MHz ^{1}H NMR spectrum of **39a** in DMSO-d6

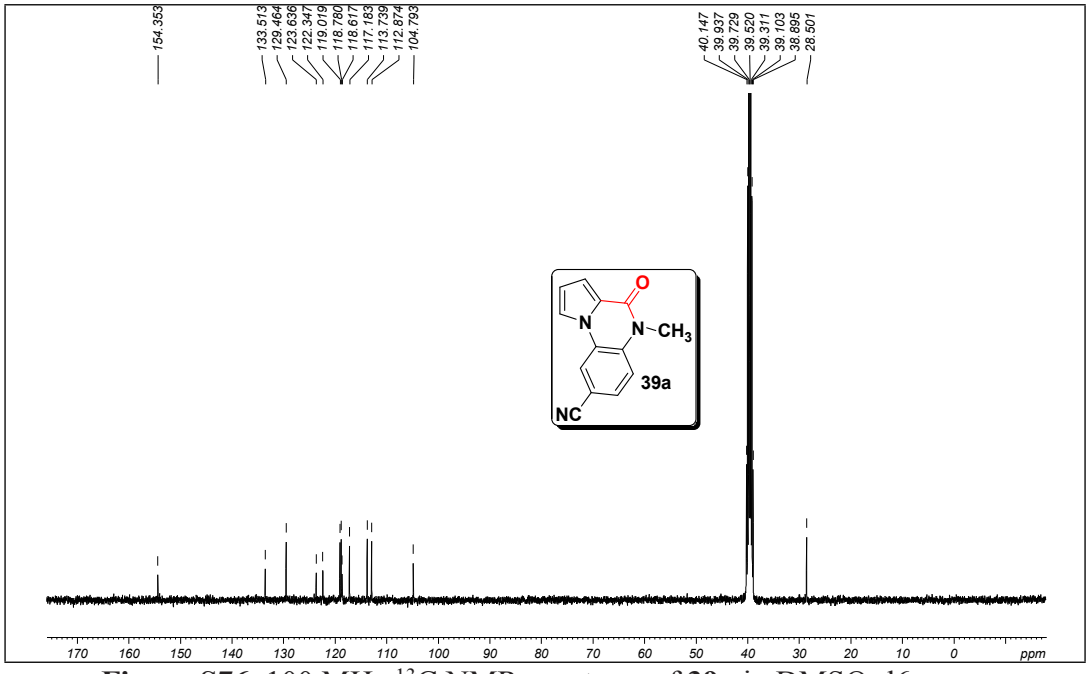


Figure S76. 100 MHz ^{13}C NMR spectrum of **39a** in DMSO-d6

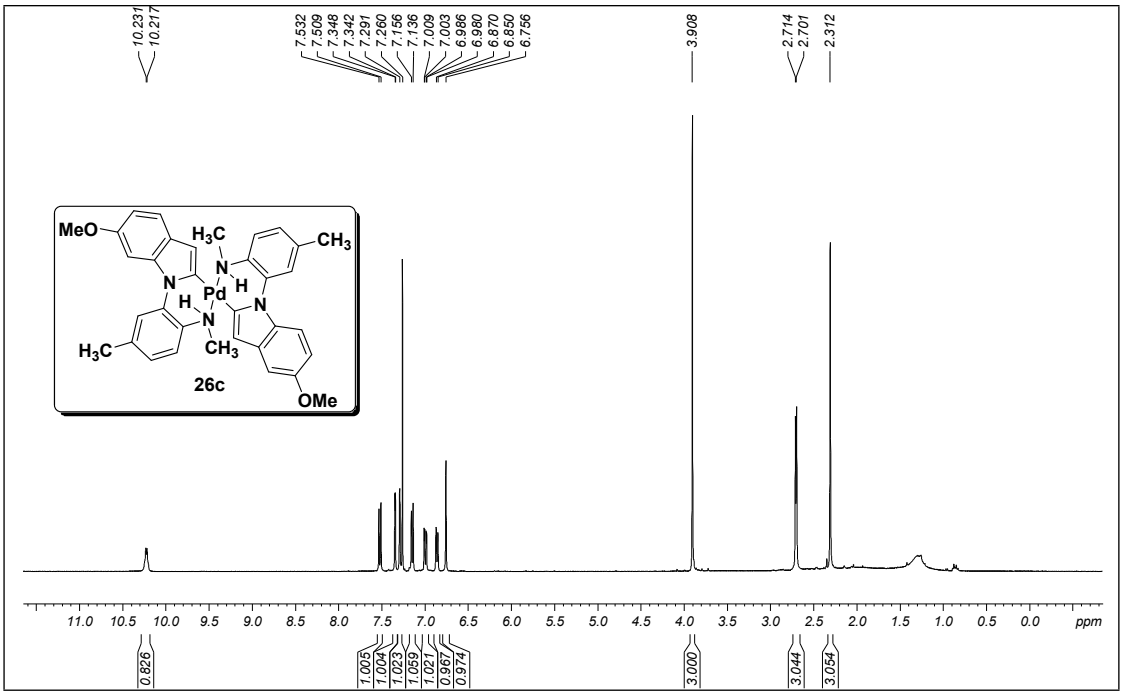


Figure S77. 400 MHz ^{1}H NMR spectrum of **26c** in $CDCl_3$

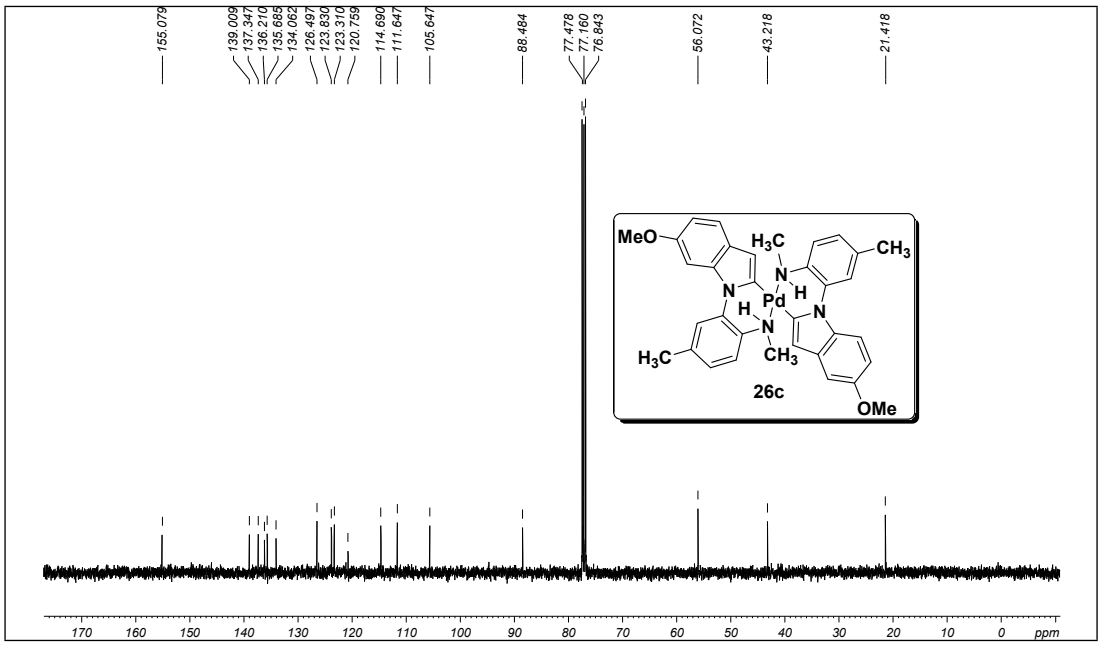


Figure S78. 100 MHz ^{13}C NMR spectrum of **26c** in $CDCl_3$

XI. NMR Spectra of the substrates

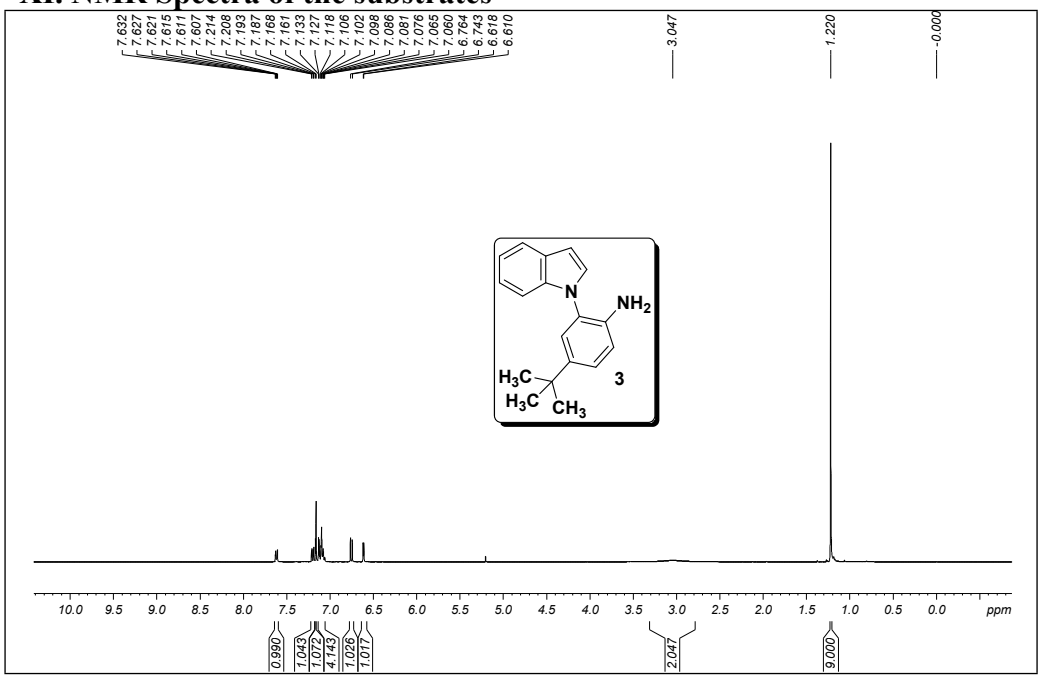


Figure S79. 400 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$

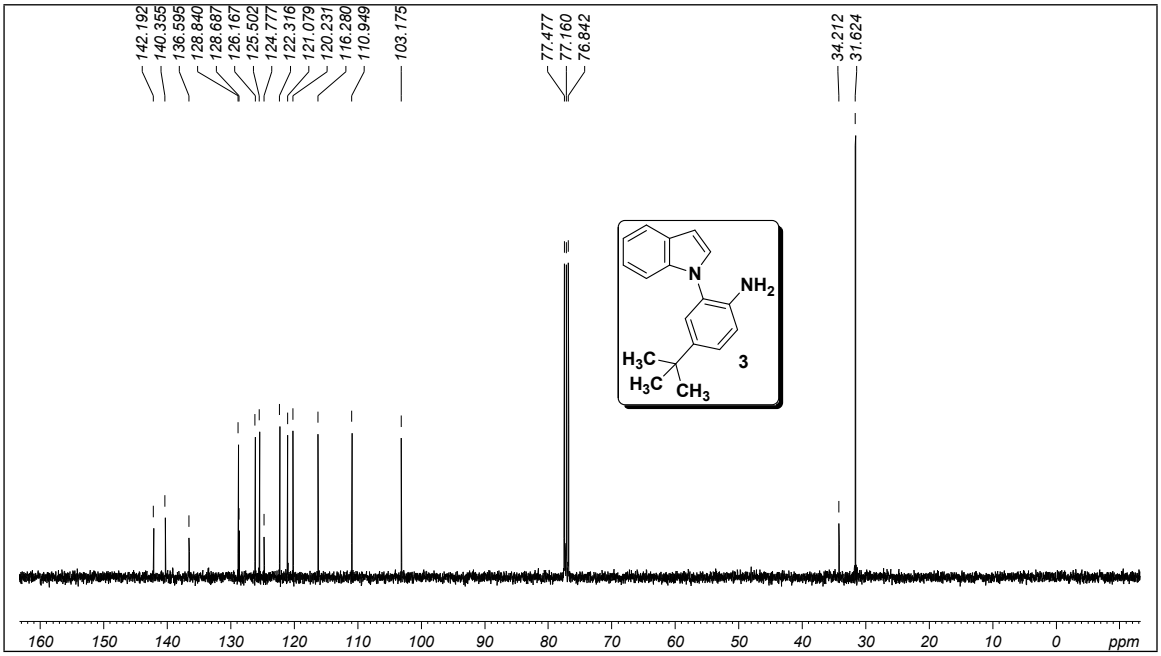


Figure S80. 100 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$

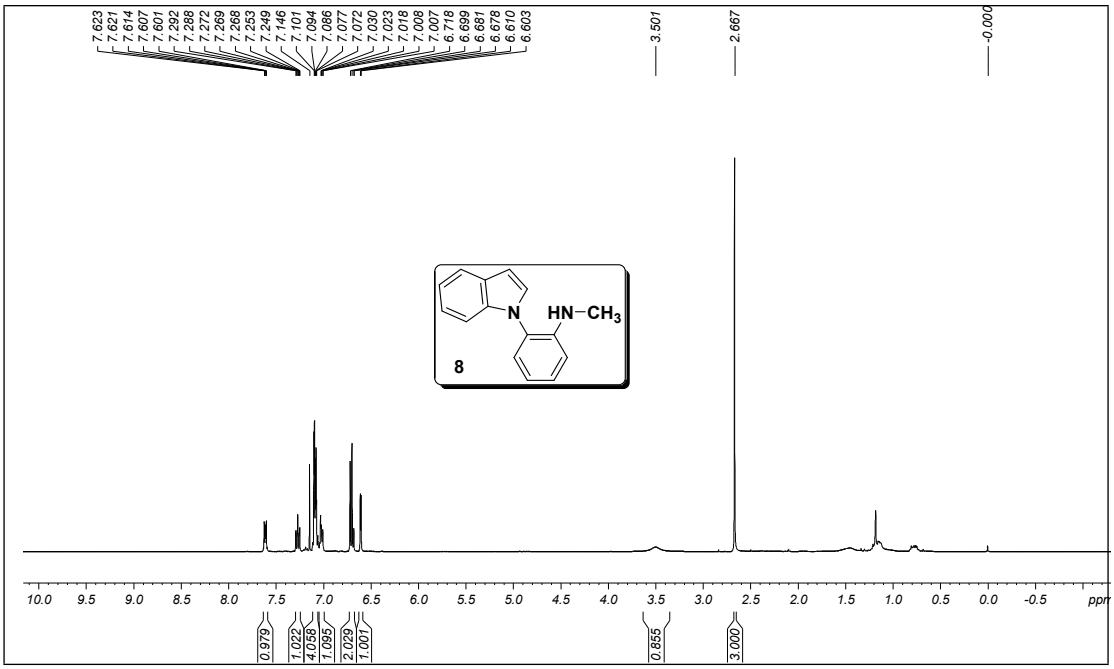


Figure S81. 400 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$

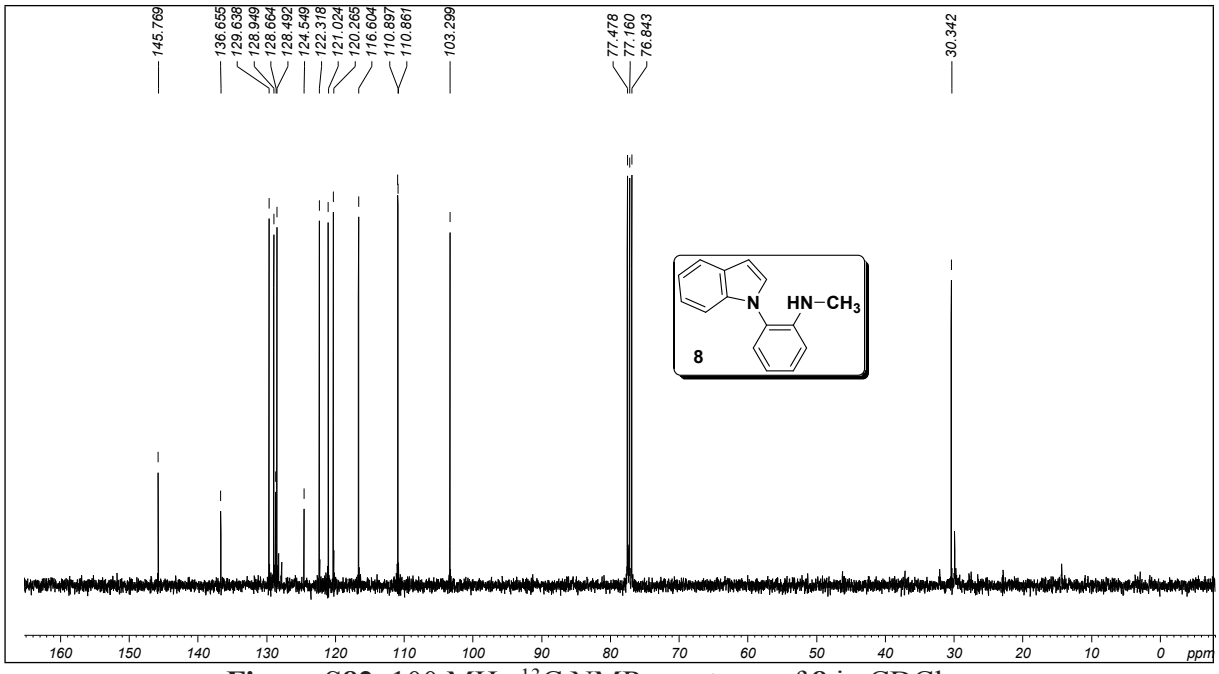


Figure S82. 100 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$

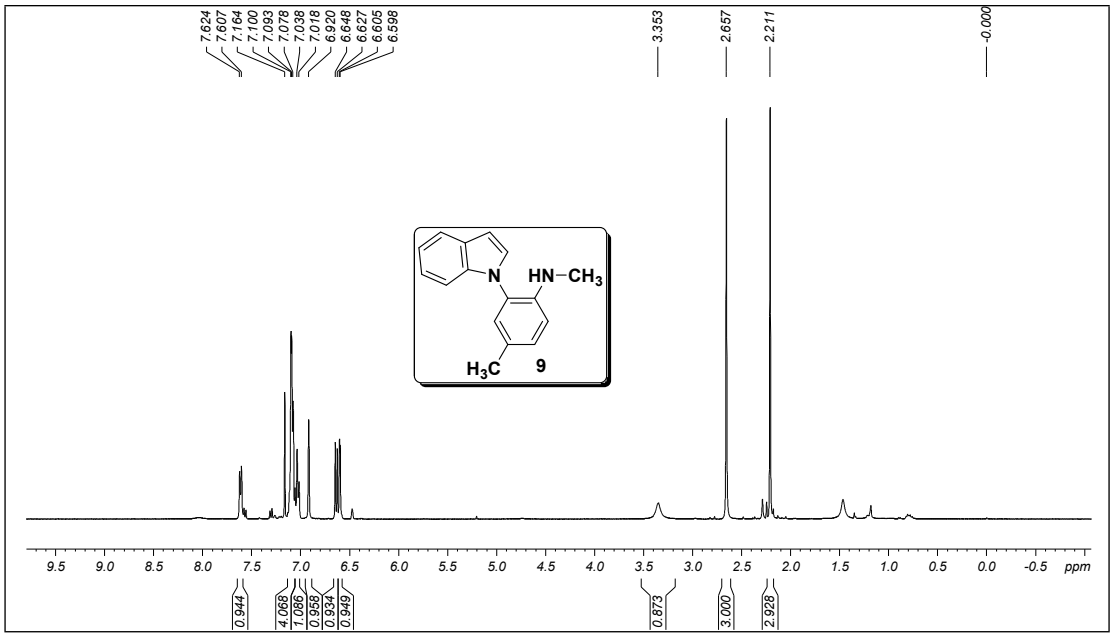


Figure S83. 400 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$

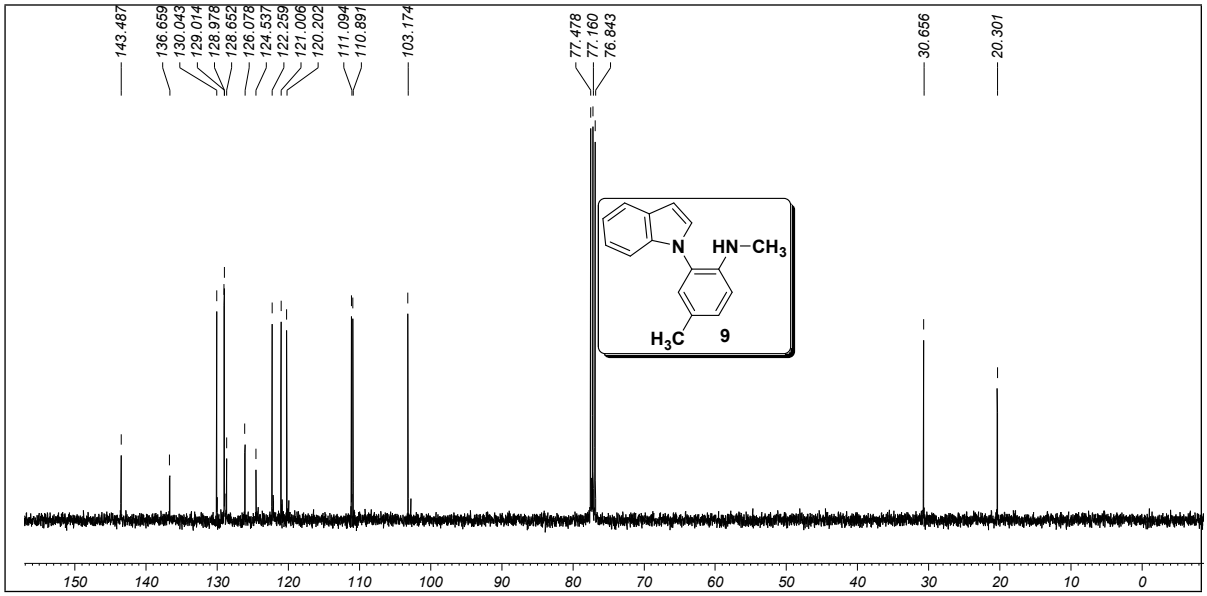


Figure S84. 100 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$

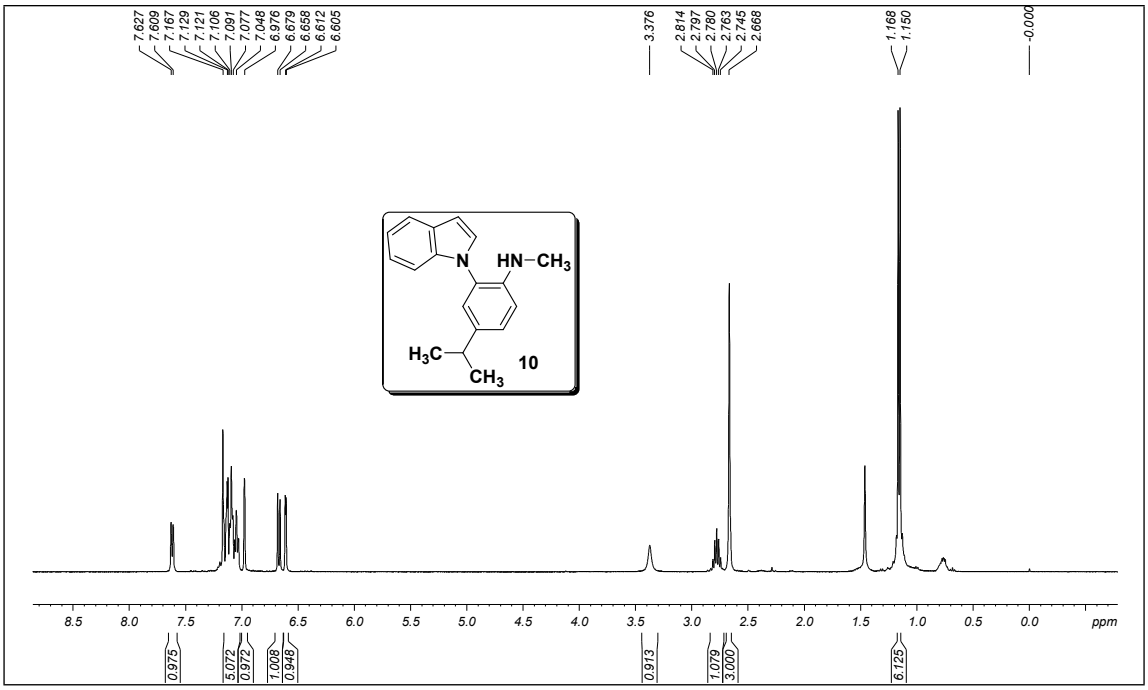


Figure S85. 400 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$

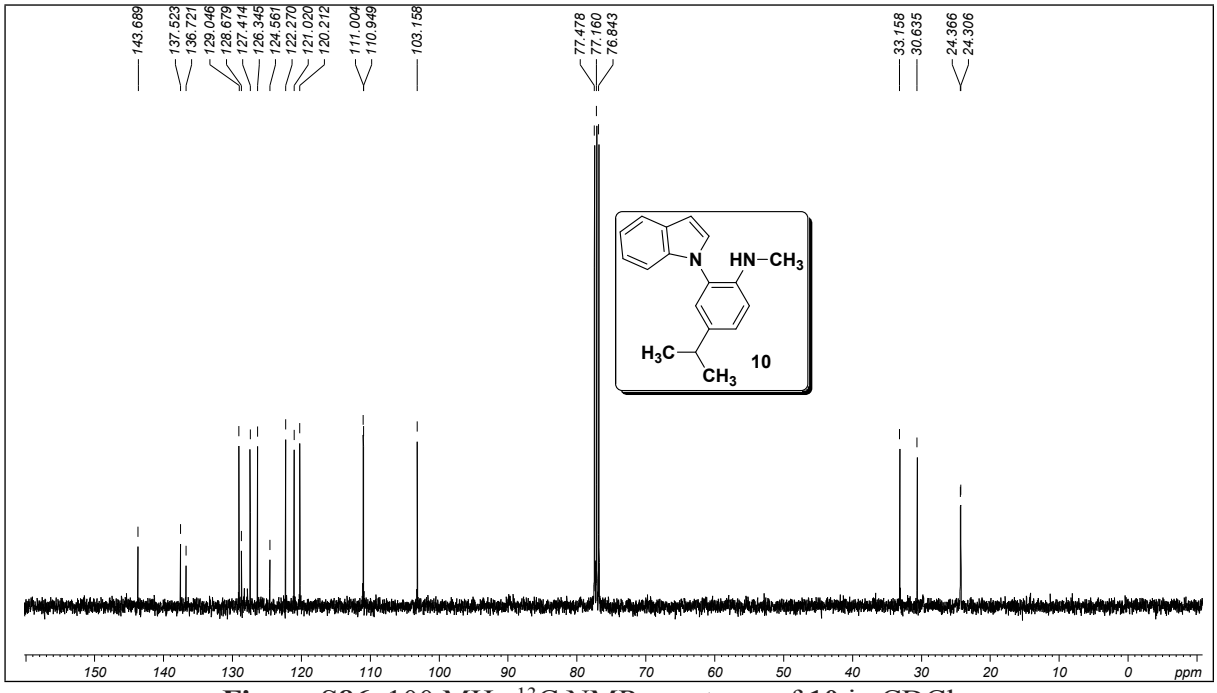


Figure S86. 100 MHz ^{13}C NMR spectrum of **10** in $CDCl_3$

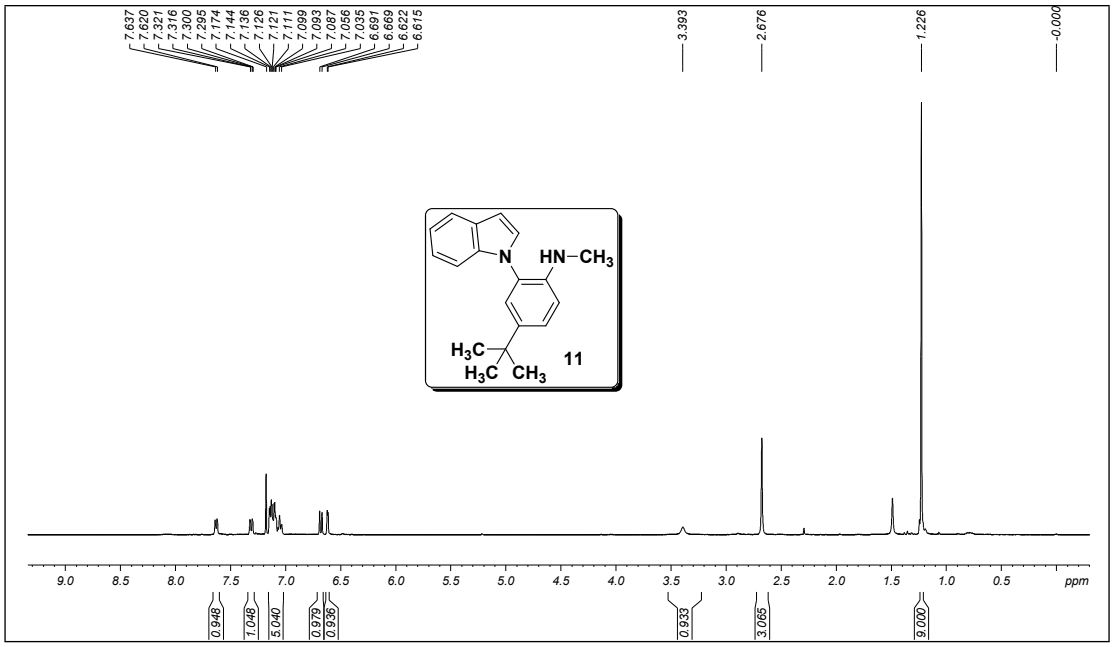


Figure S87. 400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$

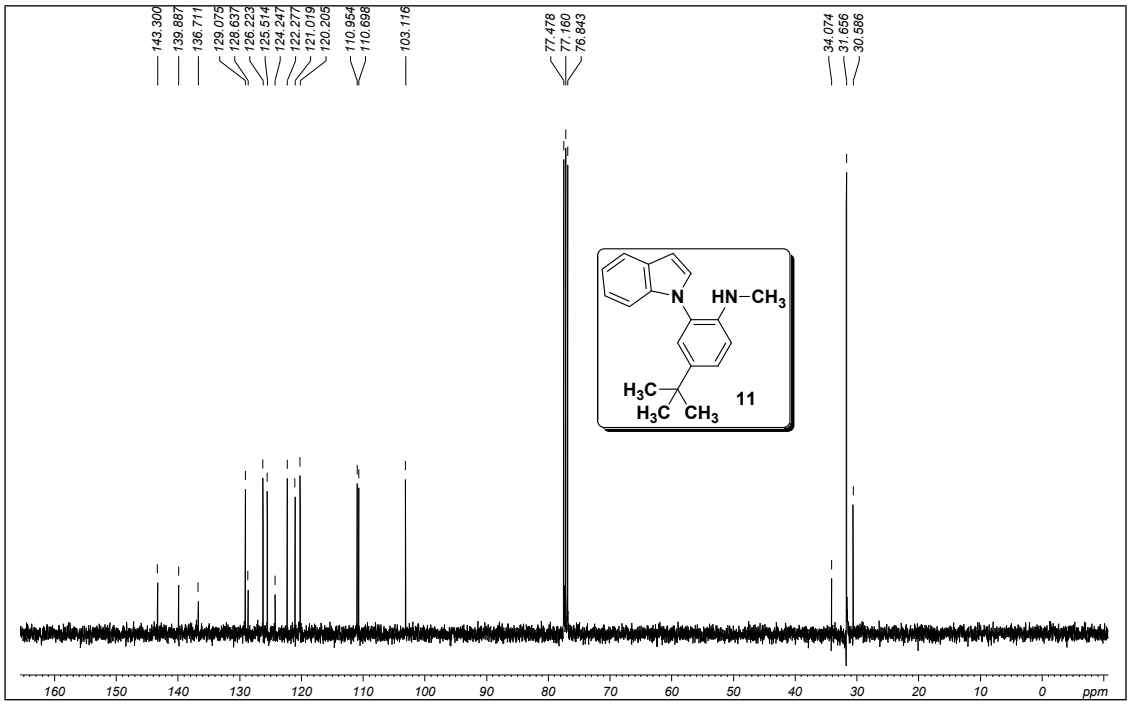


Figure S88. 100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$

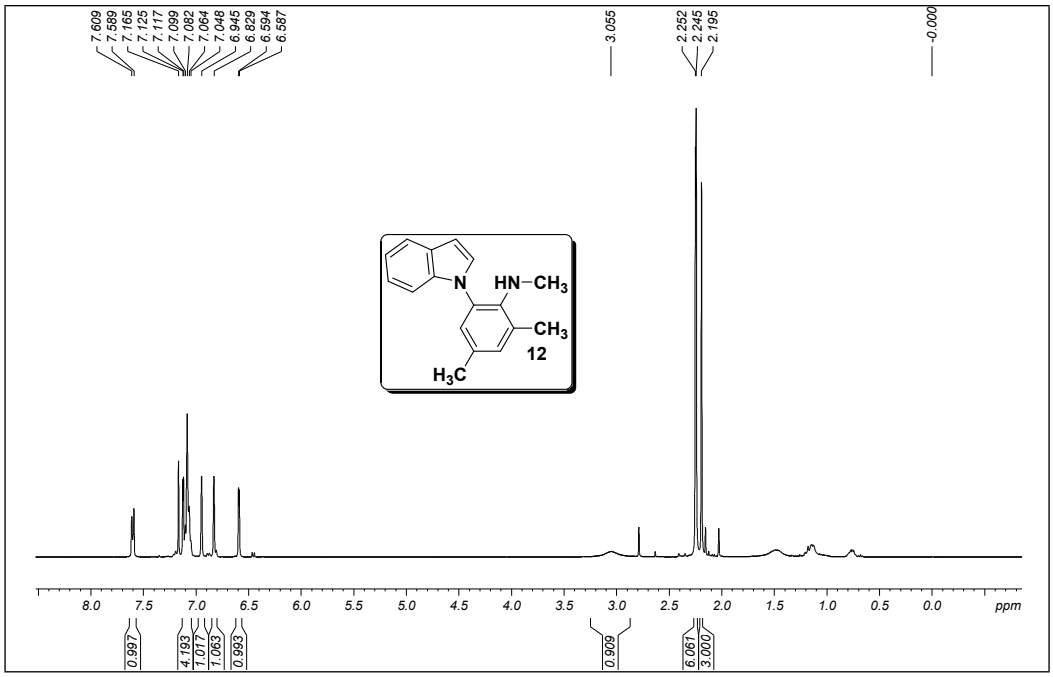


Figure S89. 400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$

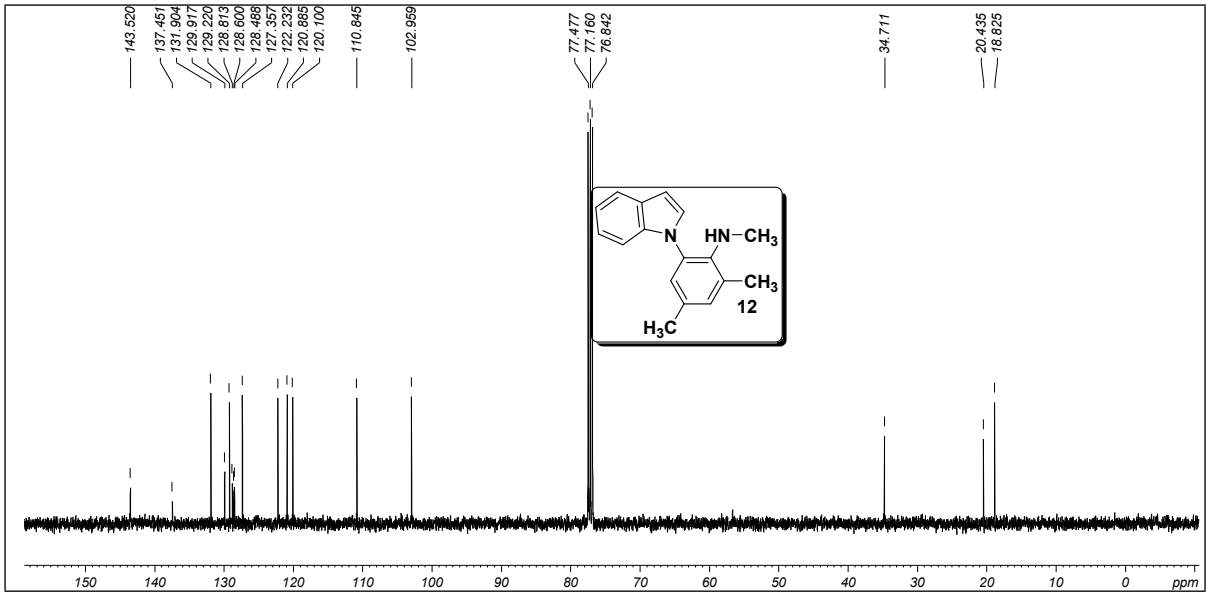


Figure S90. 100 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$

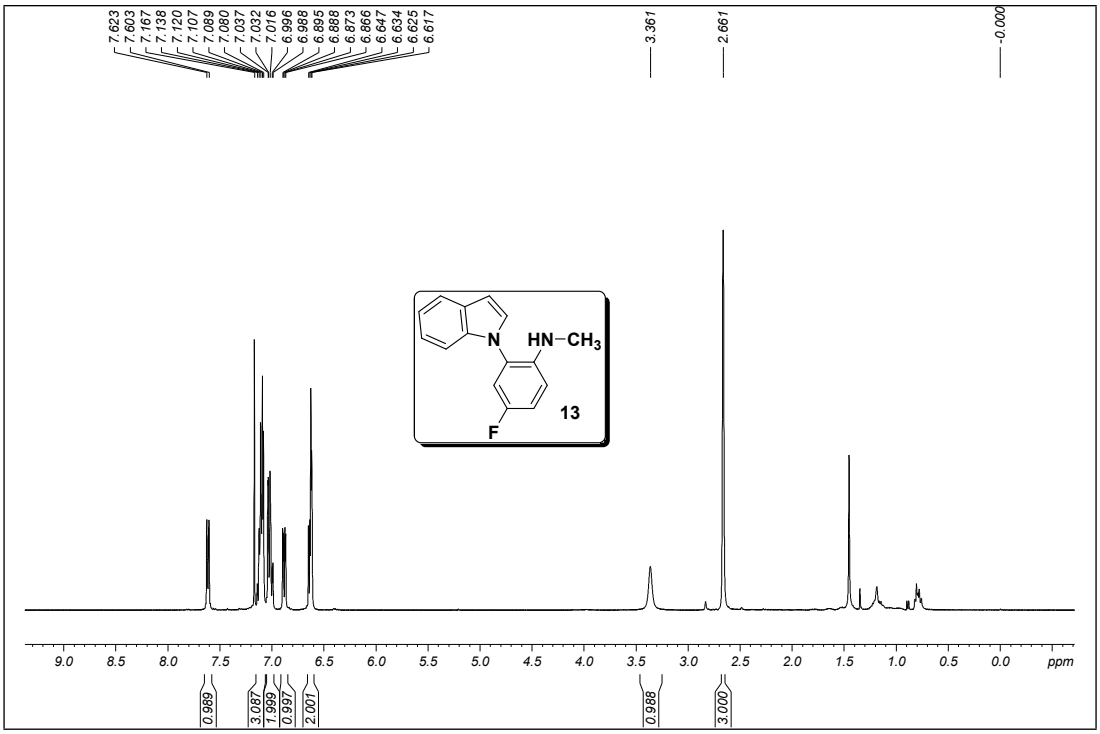


Figure S91. 400 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$

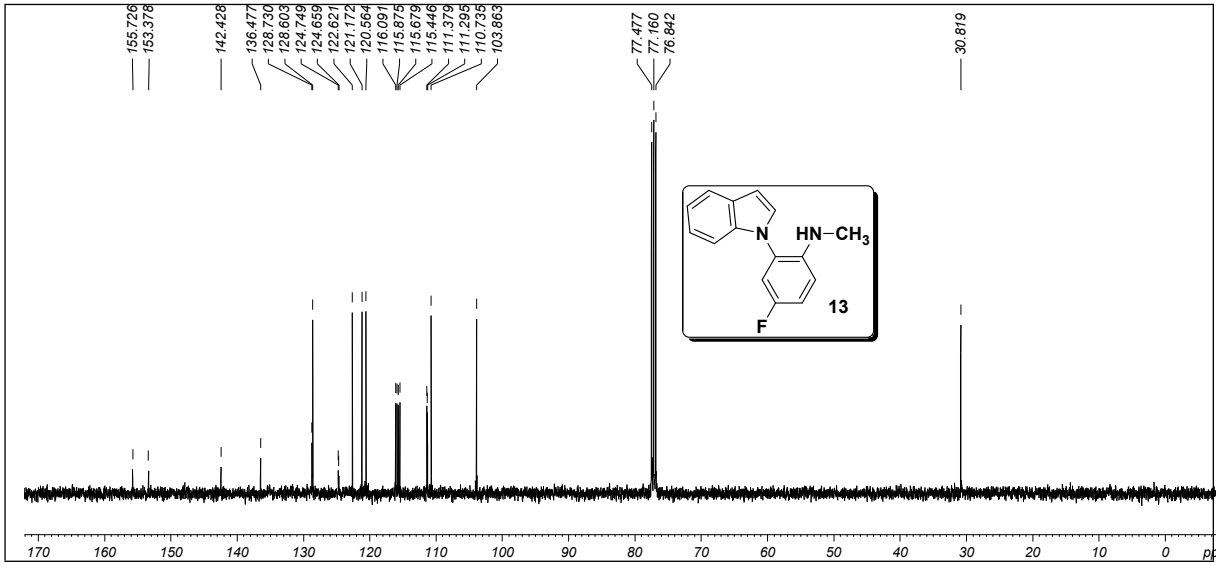


Figure S92. 100 MHz ^{13}C NMR spectrum of **13** in $CDCl_3$

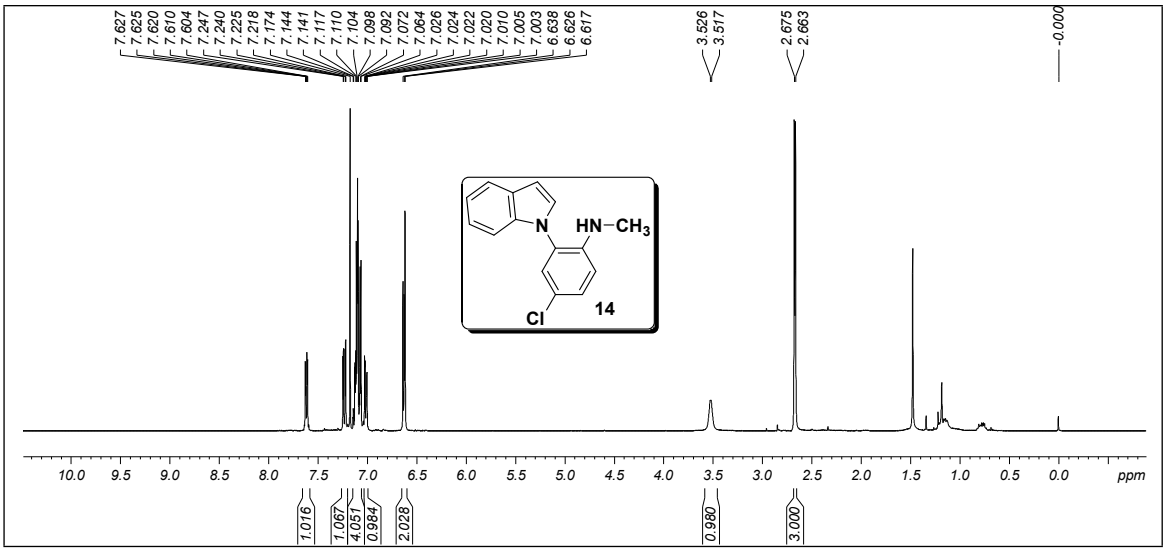


Figure S93. 400 MHz ^{1}H NMR spectrum of **14** in $CDCl_3$

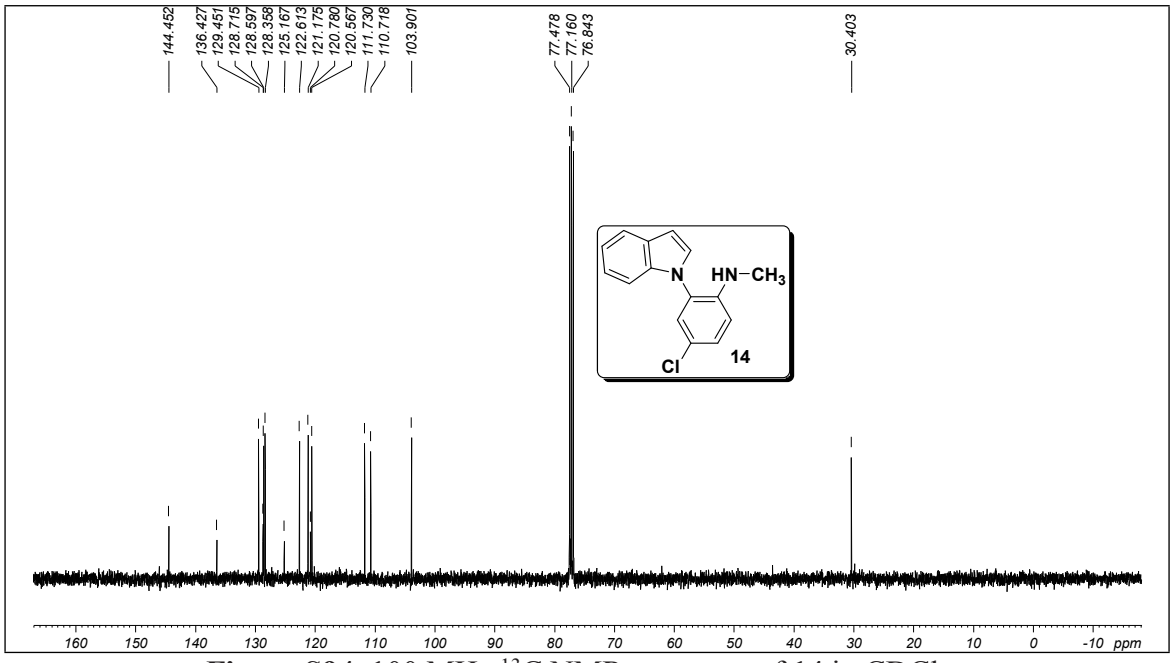


Figure S94. 100 MHz ^{13}C NMR spectrum of **14** in $CDCl_3$

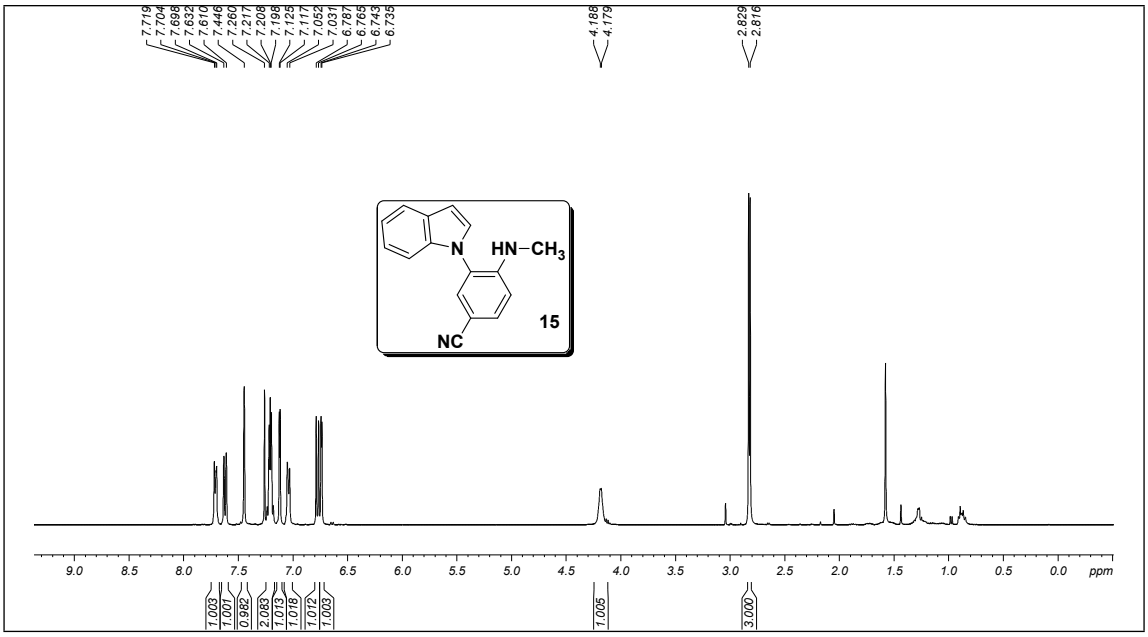


Figure S95. 400 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$

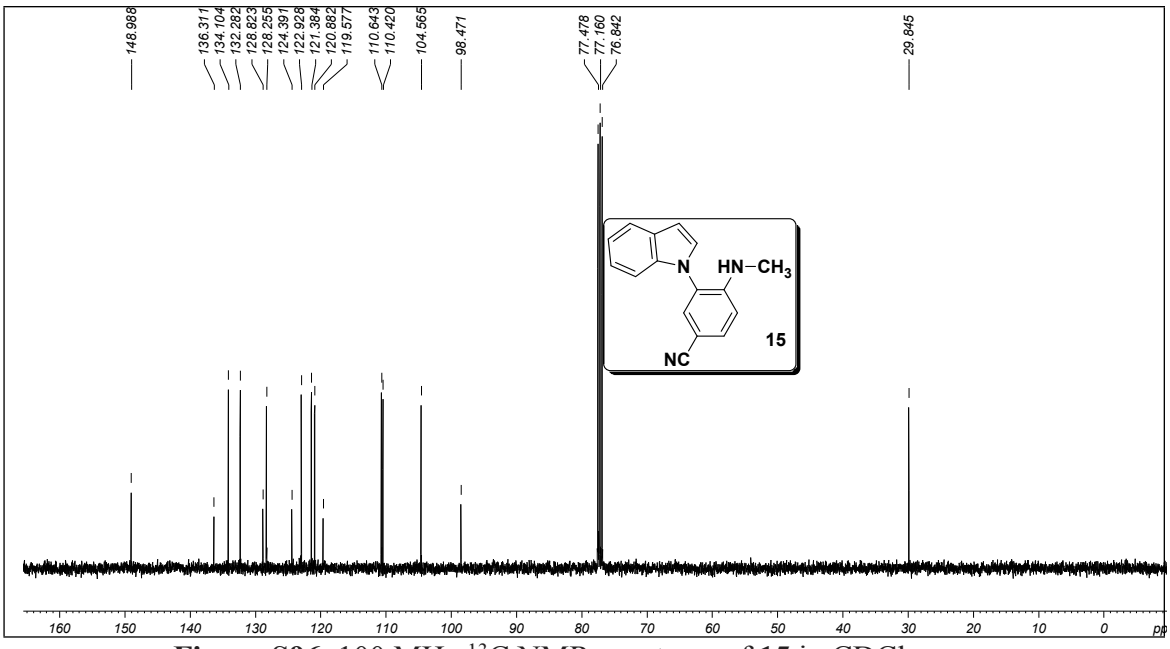


Figure S96. 100 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$

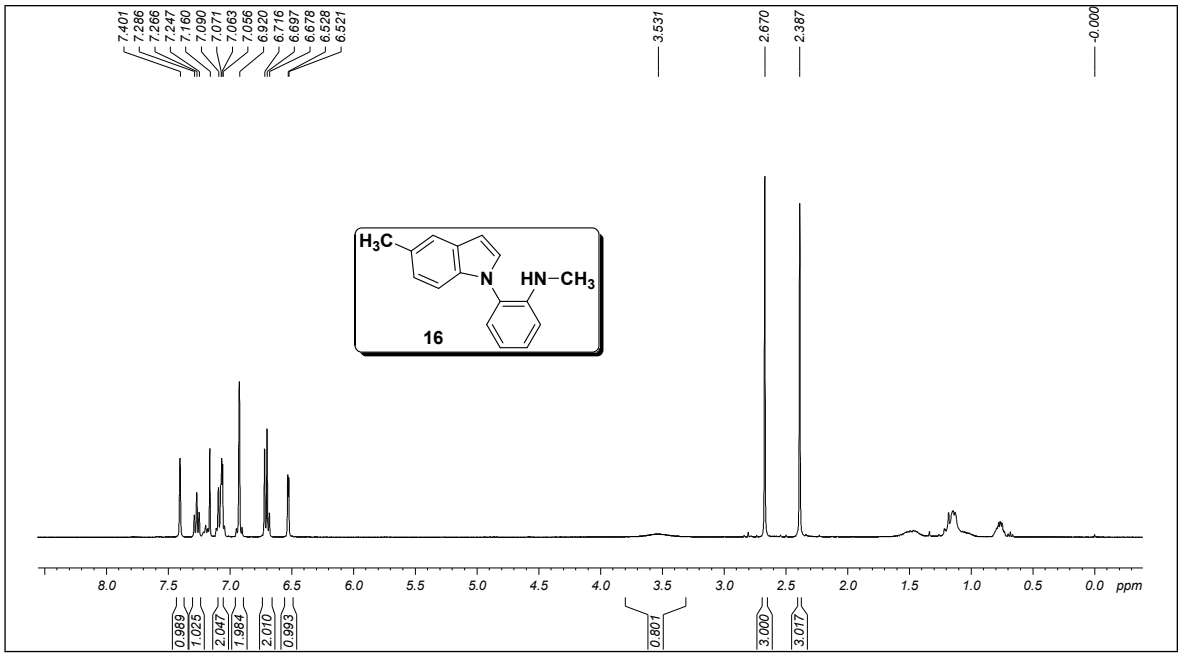


Figure S97. 400 MHz ^{1}H NMR spectrum of **16** in $CDCl_3$

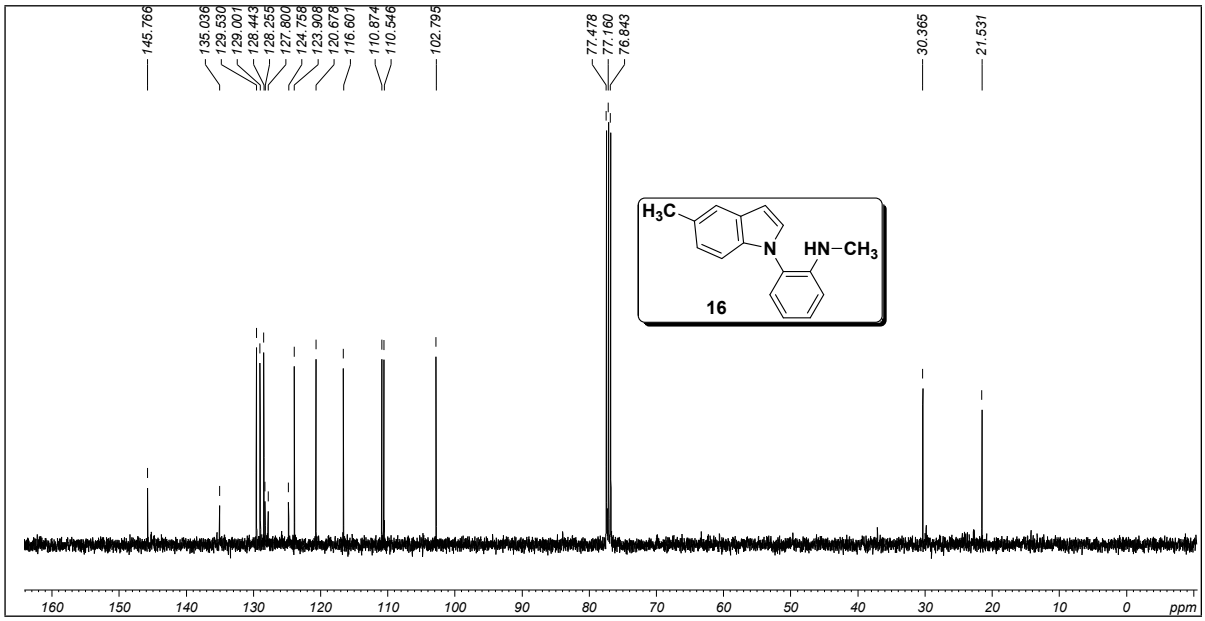


Figure S98. 100 MHz ^{13}C NMR spectrum of **16** in $CDCl_3$

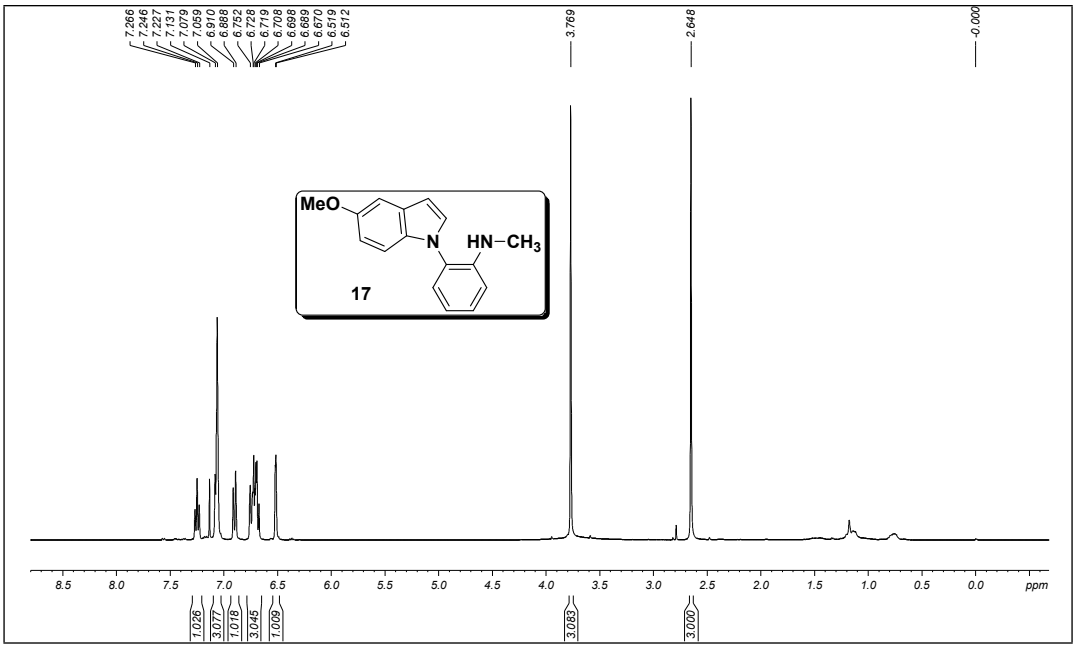


Figure S99. 400 MHz ^{1}H NMR spectrum of **17** in $CDCl_3$

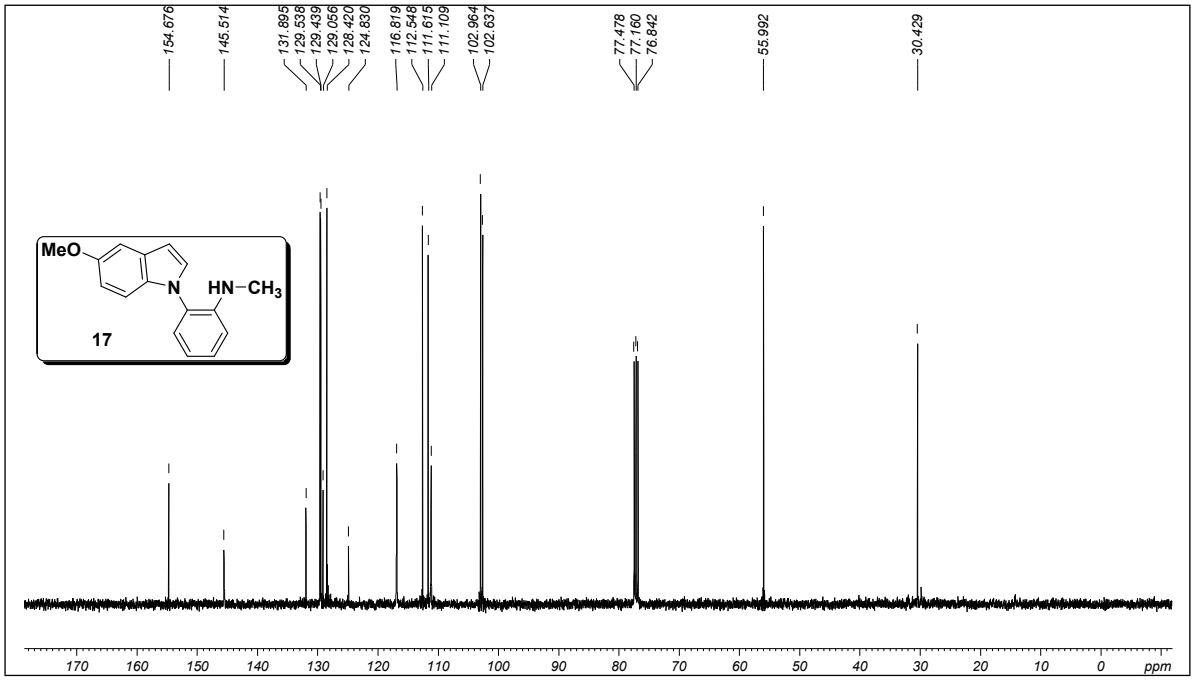


Figure S100. 100 MHz ^{13}C NMR spectrum of **17** in $CDCl_3$

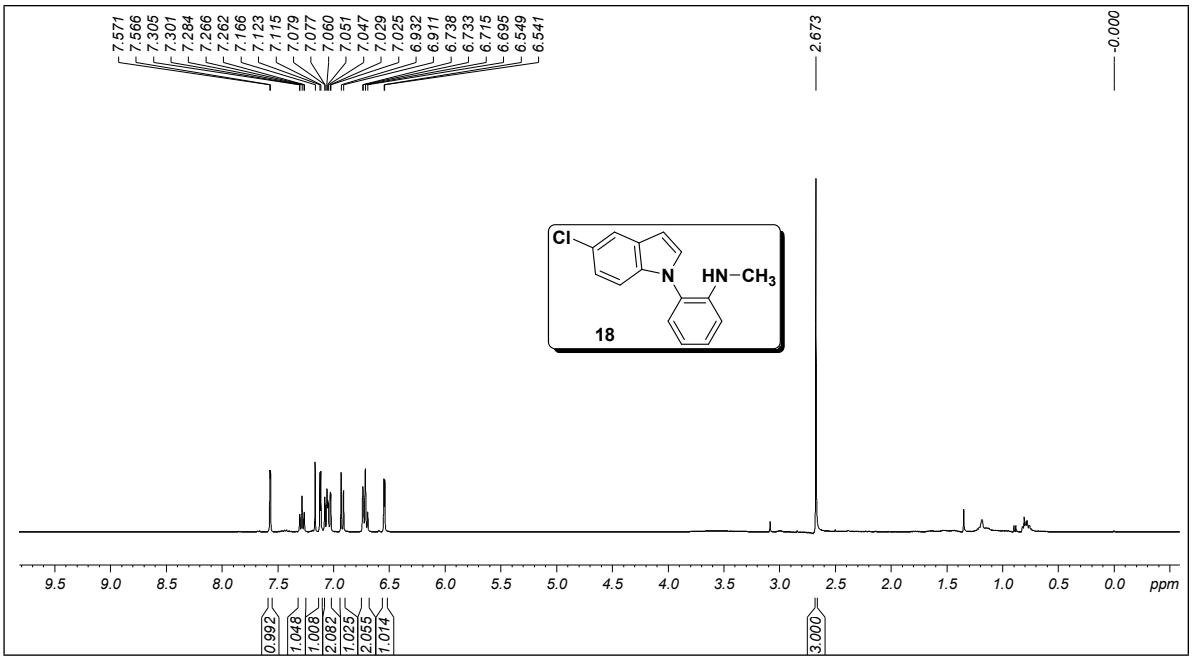


Figure S101. 400 MHz ^{1}H NMR spectrum of **18** in $CDCl_3$

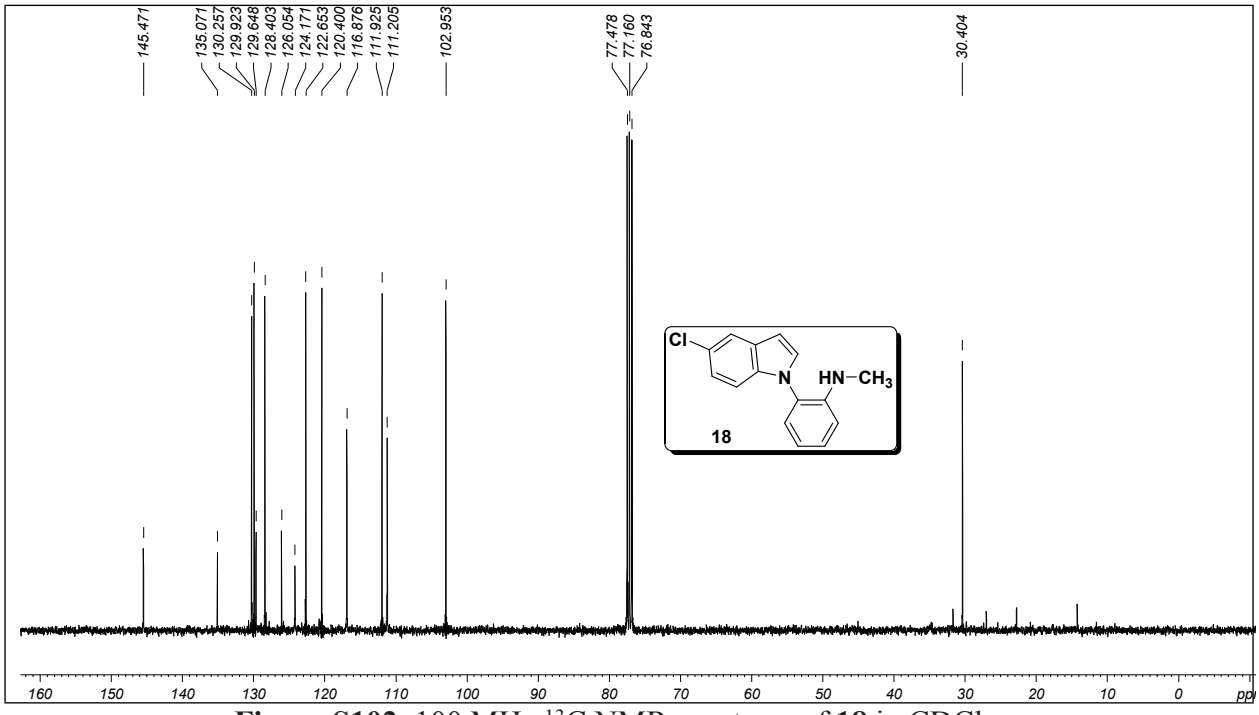


Figure S102. 100 MHz ^{13}C NMR spectrum of **18** in $CDCl_3$

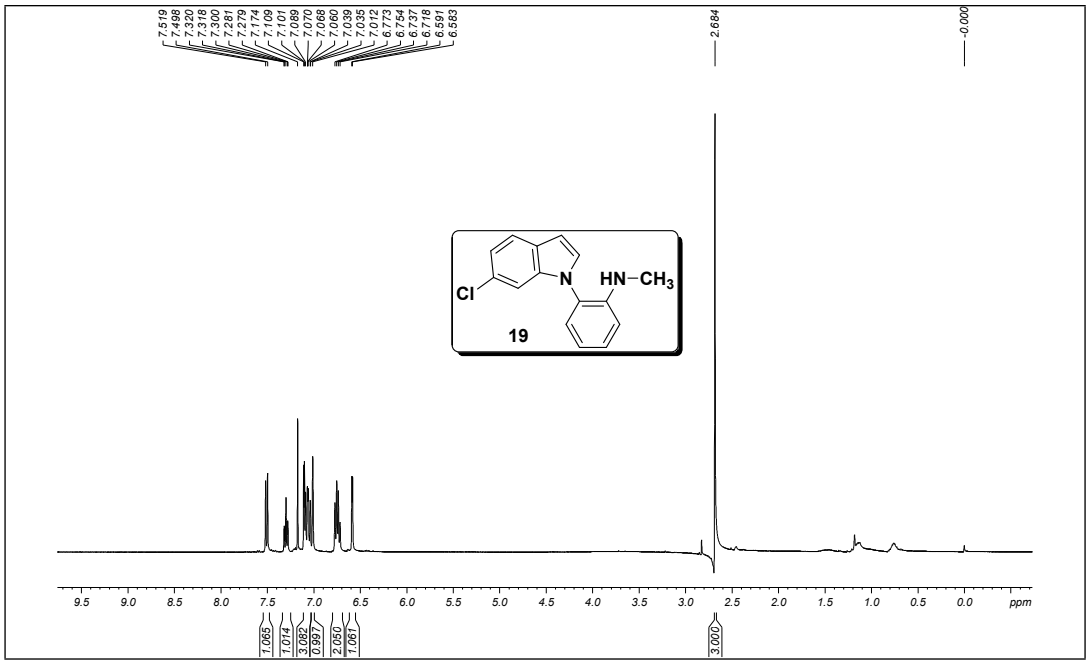


Figure S103. 400 MHz ^{1}H NMR spectrum of **19** in $CDCl_3$

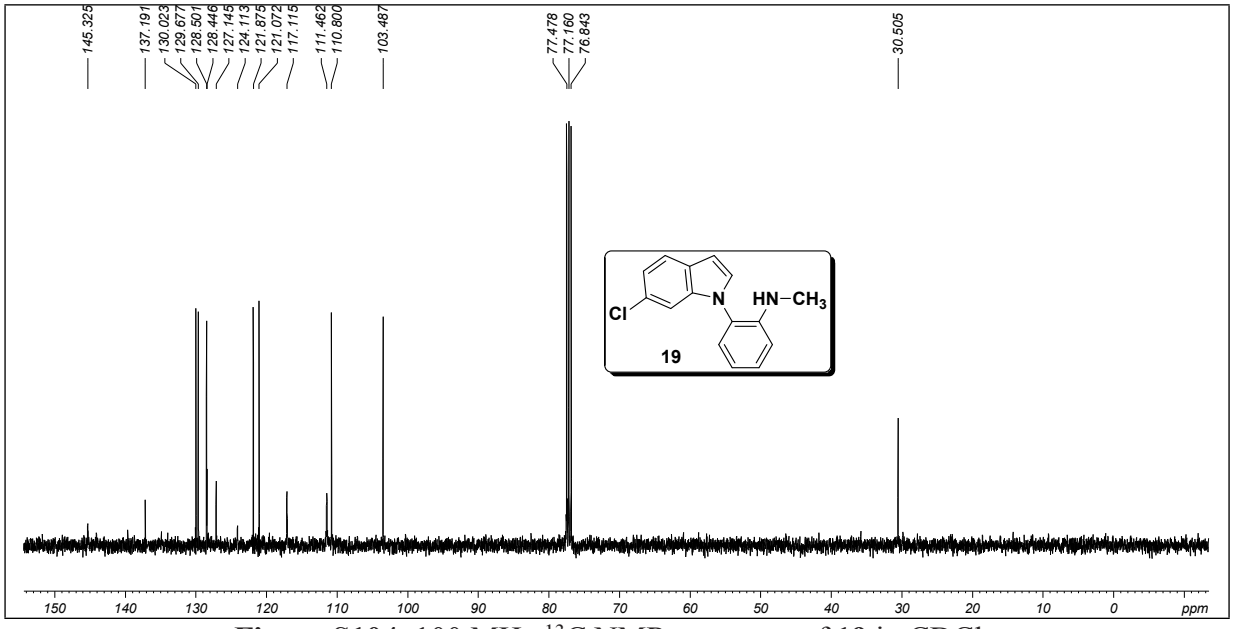


Figure S104. 100 MHz ^{13}C NMR spectrum of **19** in $CDCl_3$

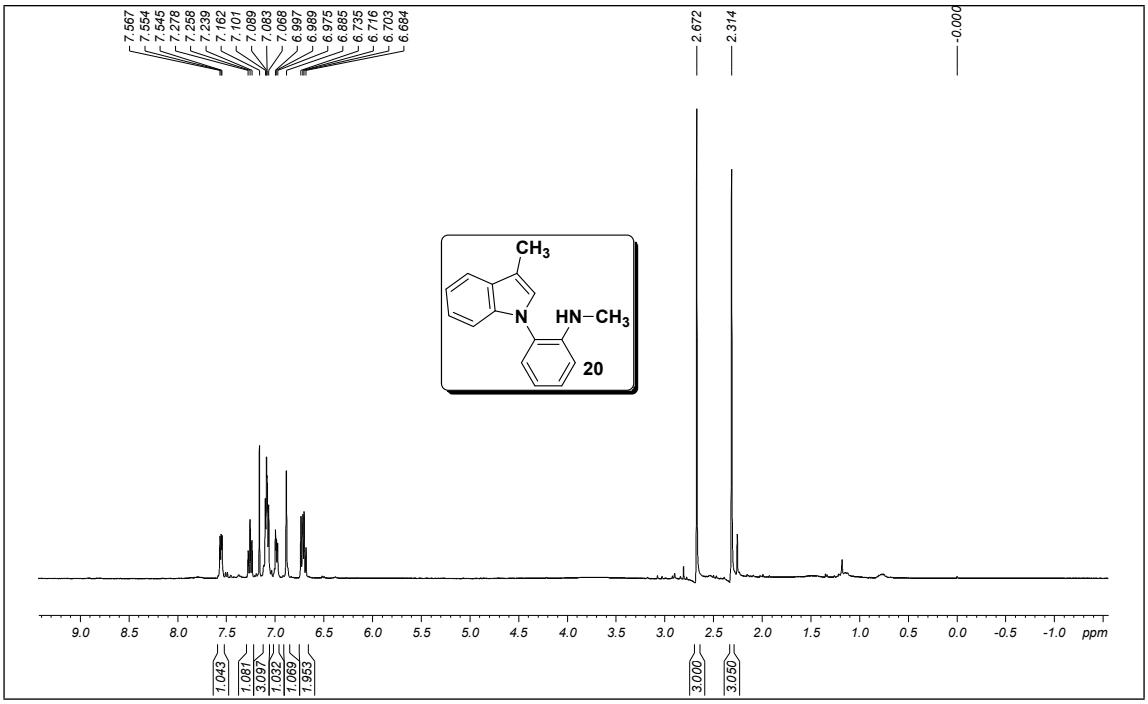


Figure S105. 400 MHz ^{1}H NMR spectrum of **20** in $CDCl_3$

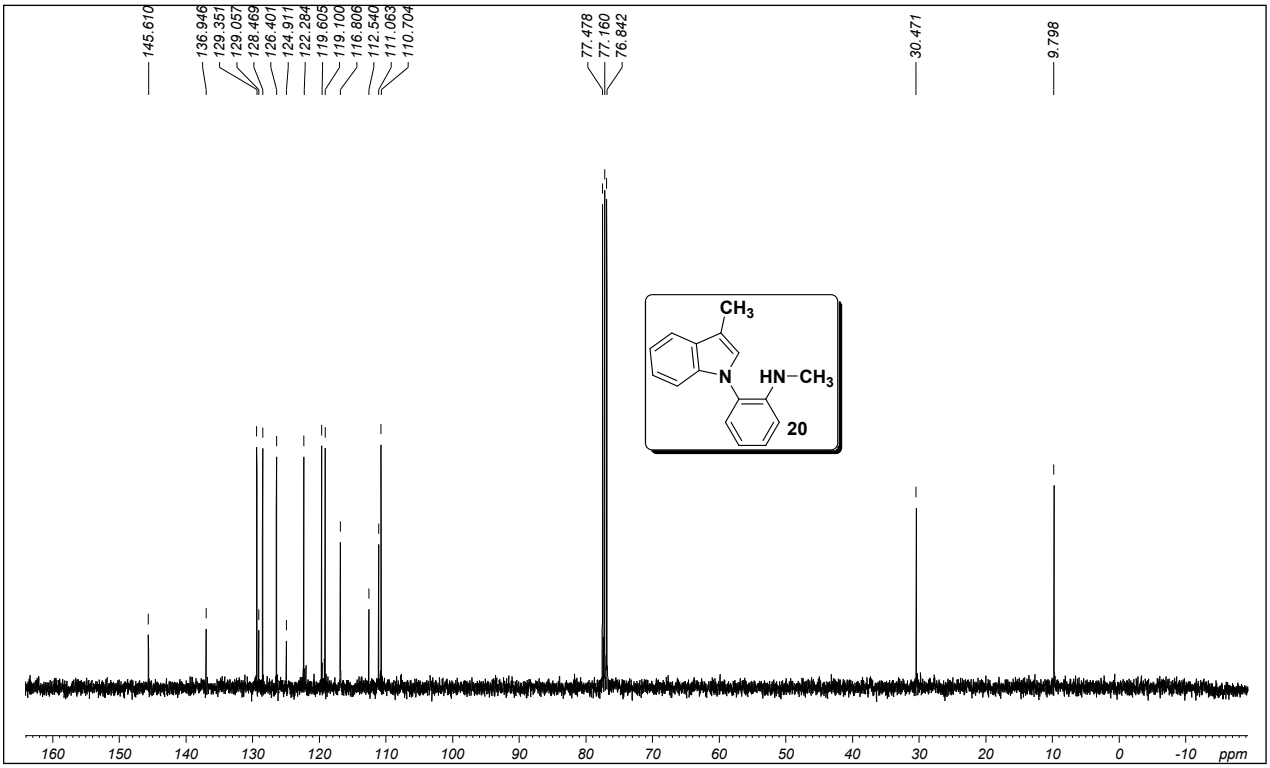


Figure S106. 100 MHz ^{13}C NMR spectrum of **20** in $CDCl_3$

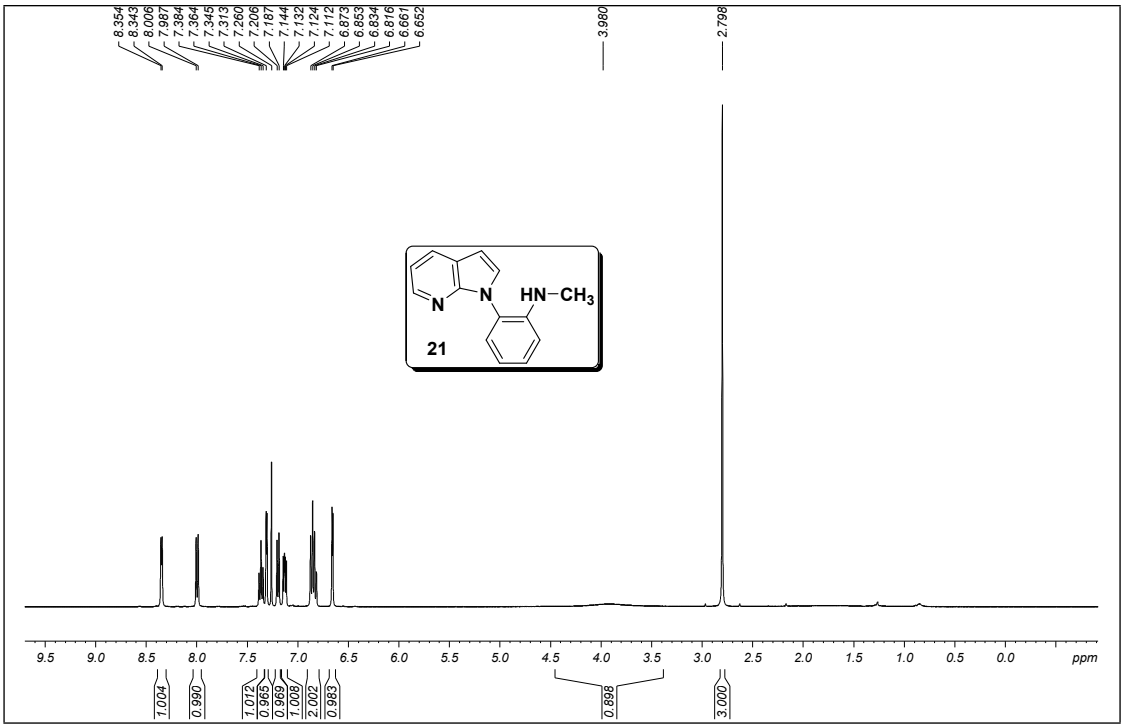


Figure S107. 400 MHz ^{1}H NMR spectrum of **21** in $CDCl_3$

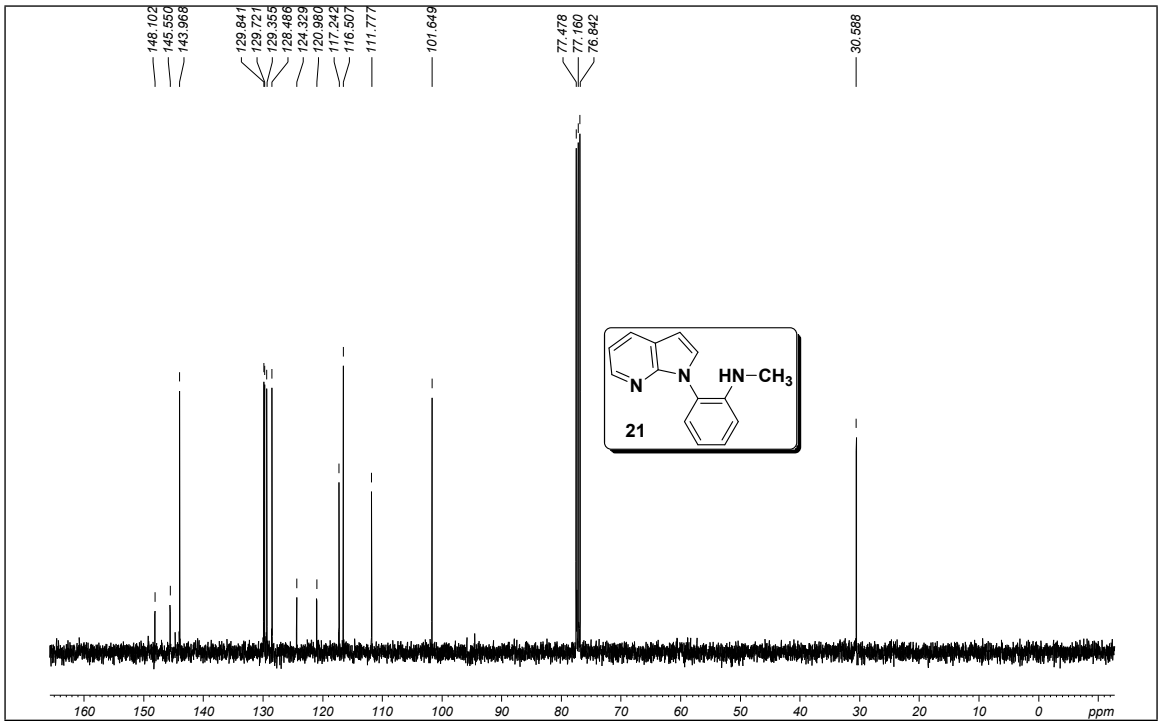


Figure S108. 100 MHz ^{13}C NMR spectrum of **21** in $CDCl_3$

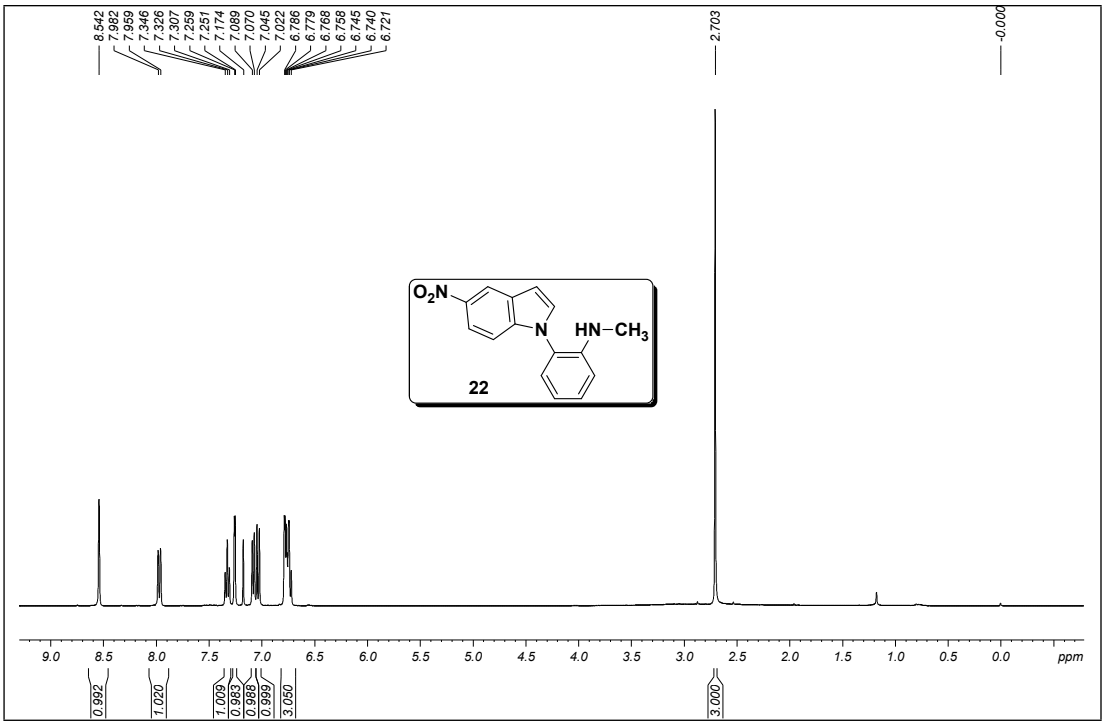


Figure S109. 400 MHz ^{1}H NMR spectrum of **22** in $CDCl_3$

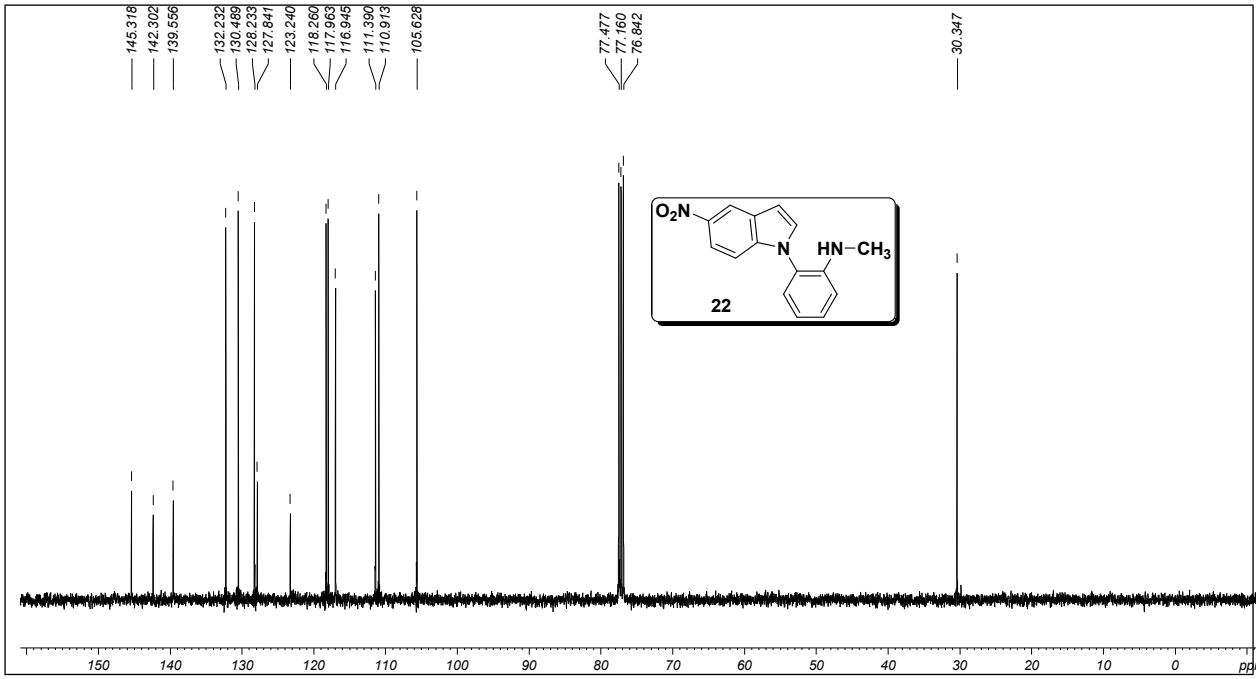


Figure S110. 100 MHz ^{13}C NMR spectrum of **22** in $CDCl_3$

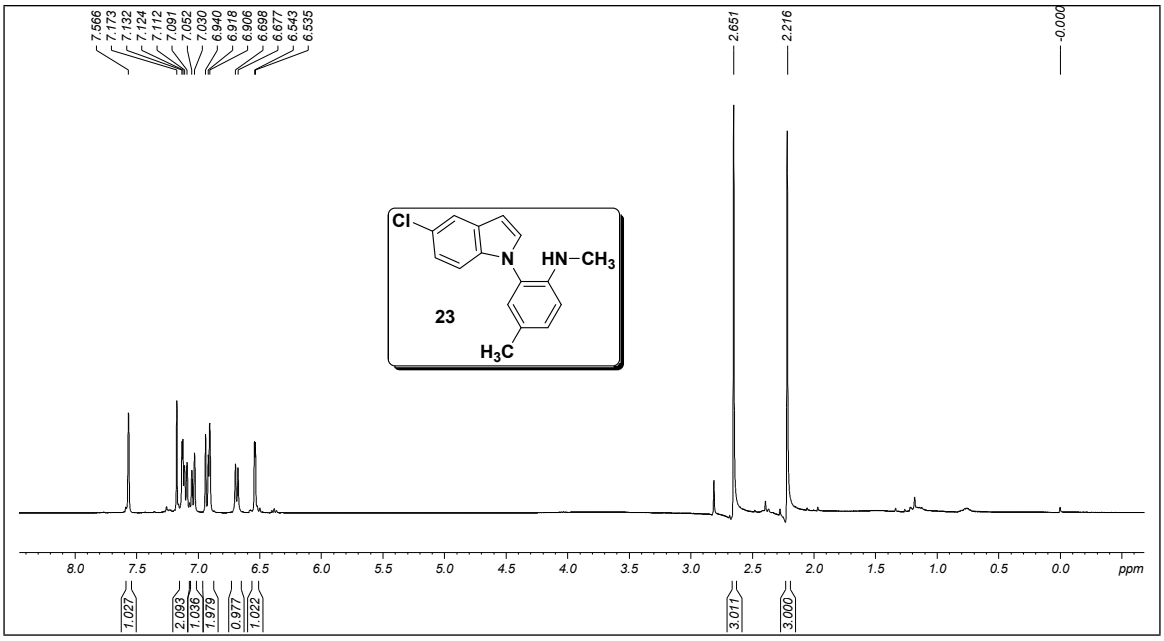


Figure S111. 400 MHz ^{1}H NMR spectrum of **23** in $CDCl_3$

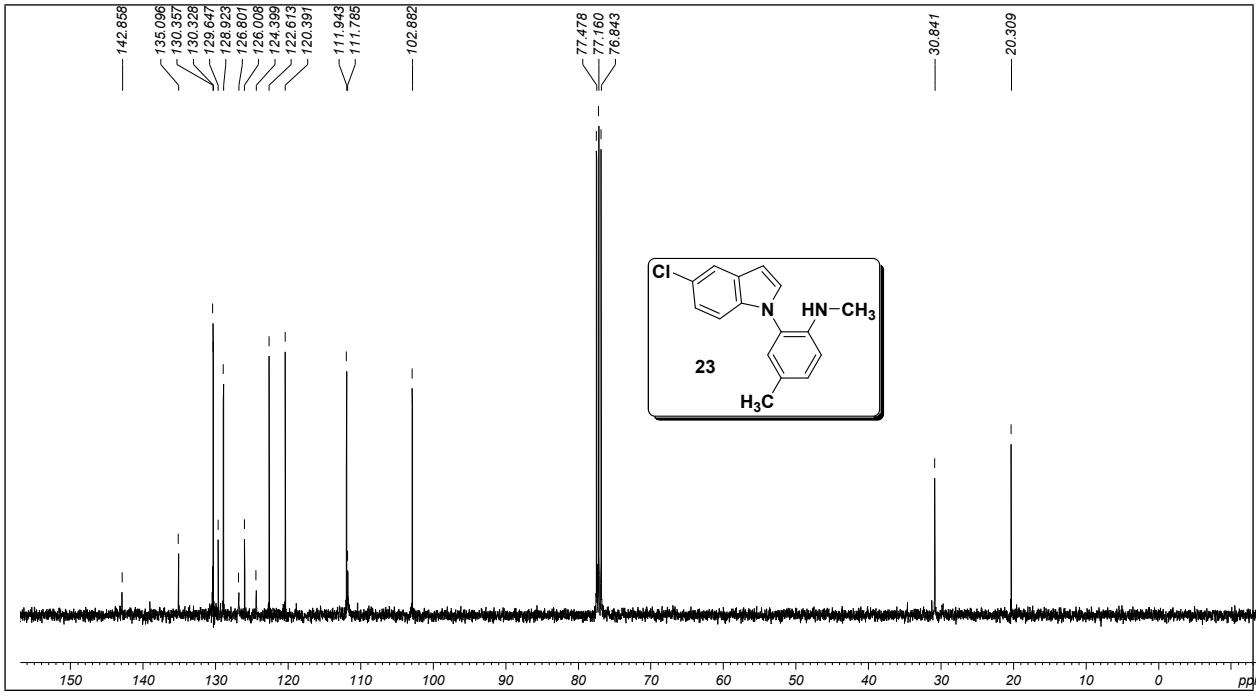


Figure S112. 100 MHz ^{13}C NMR spectrum of **23** in $CDCl_3$

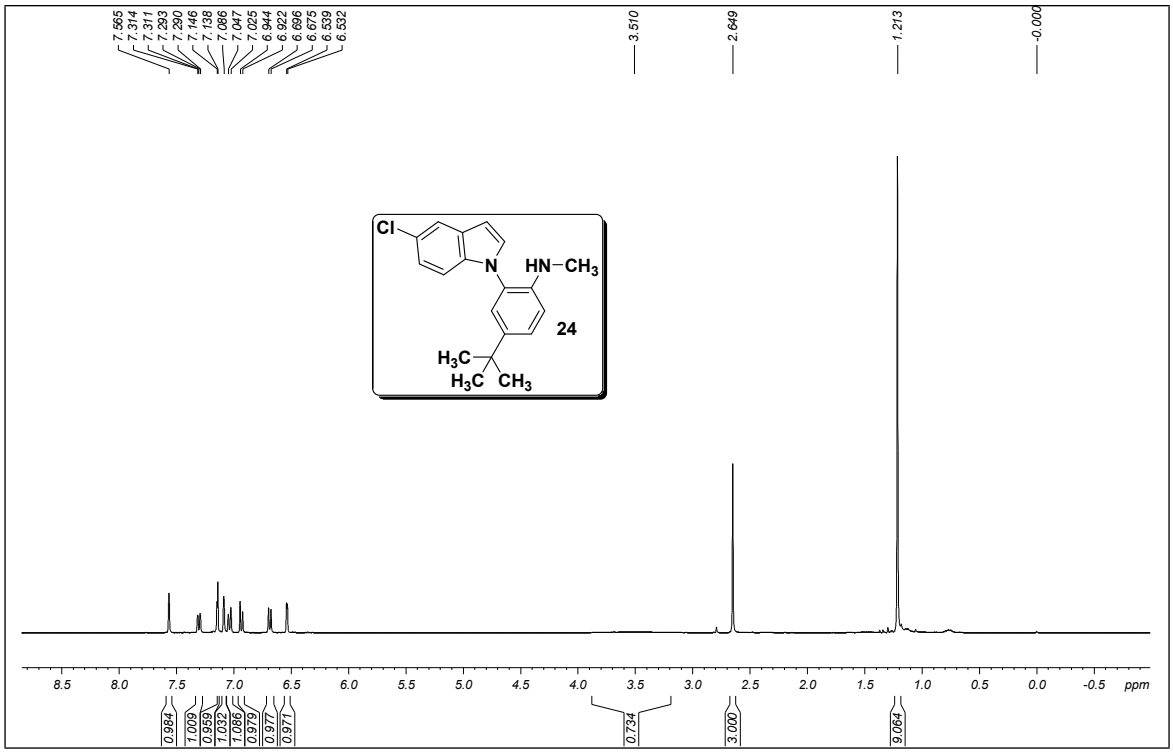


Figure S113. 400 MHz ^{1}H NMR spectrum of **24** in $CDCl_3$

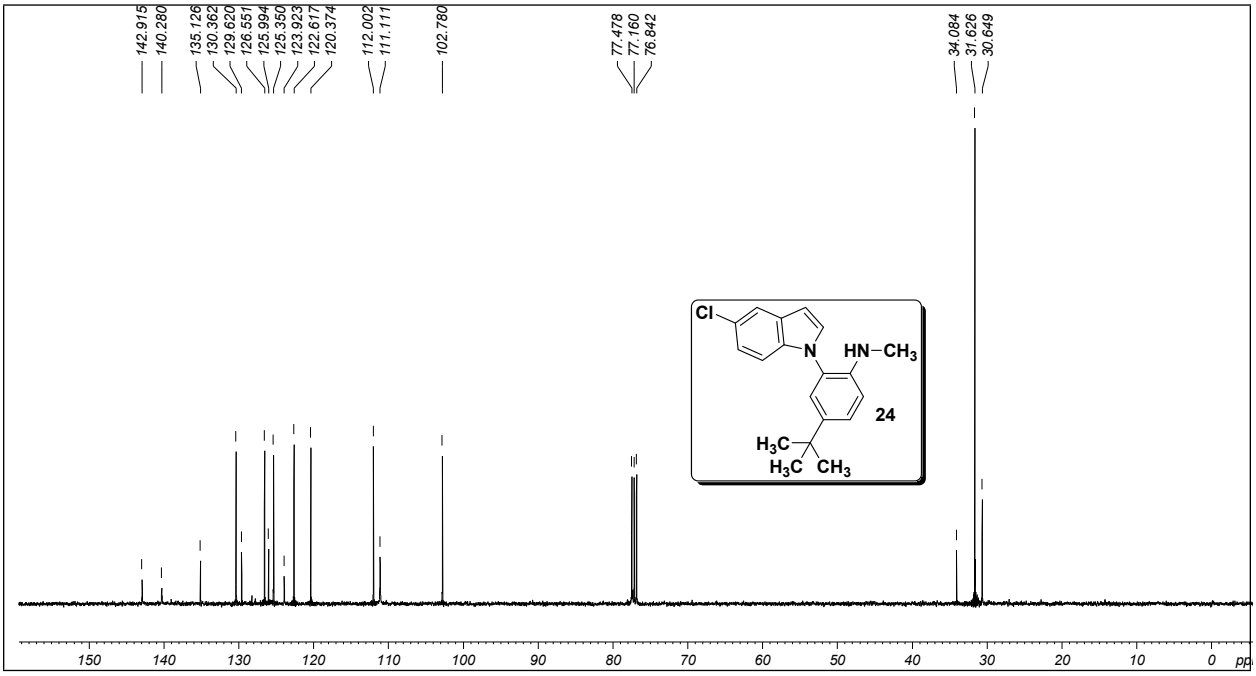


Figure S114. 100 MHz ^{13}C NMR spectrum of **24** in $CDCl_3$

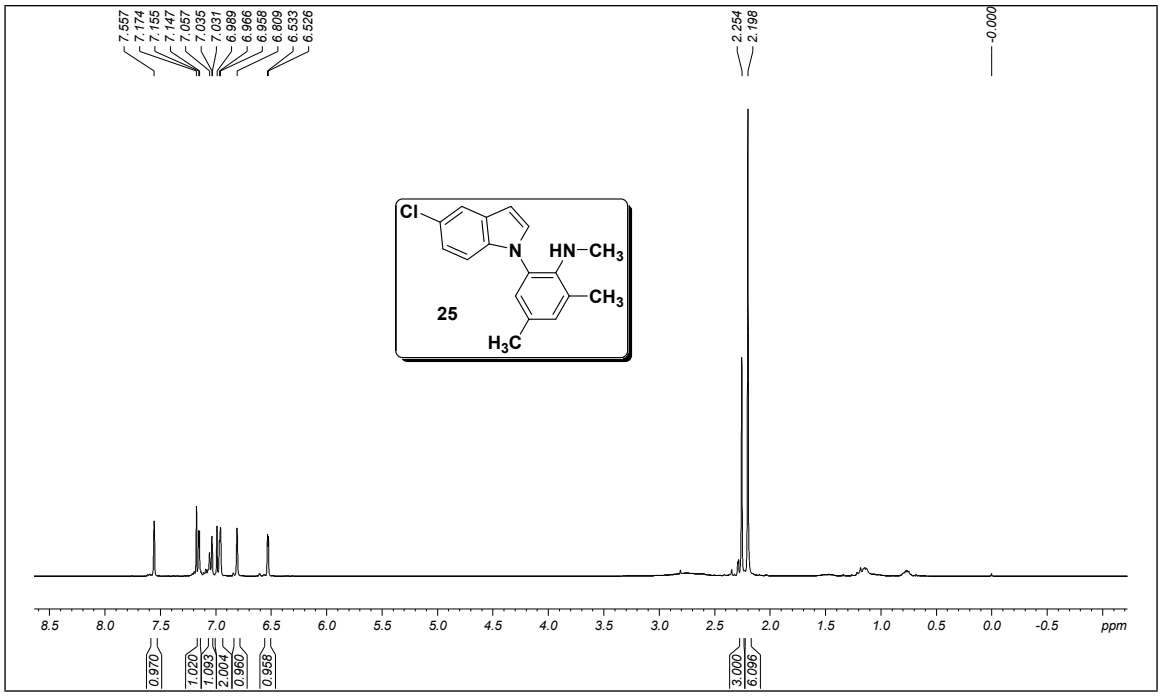


Figure S115. 400 MHz ^{1}H NMR spectrum of **25** in $CDCl_3$

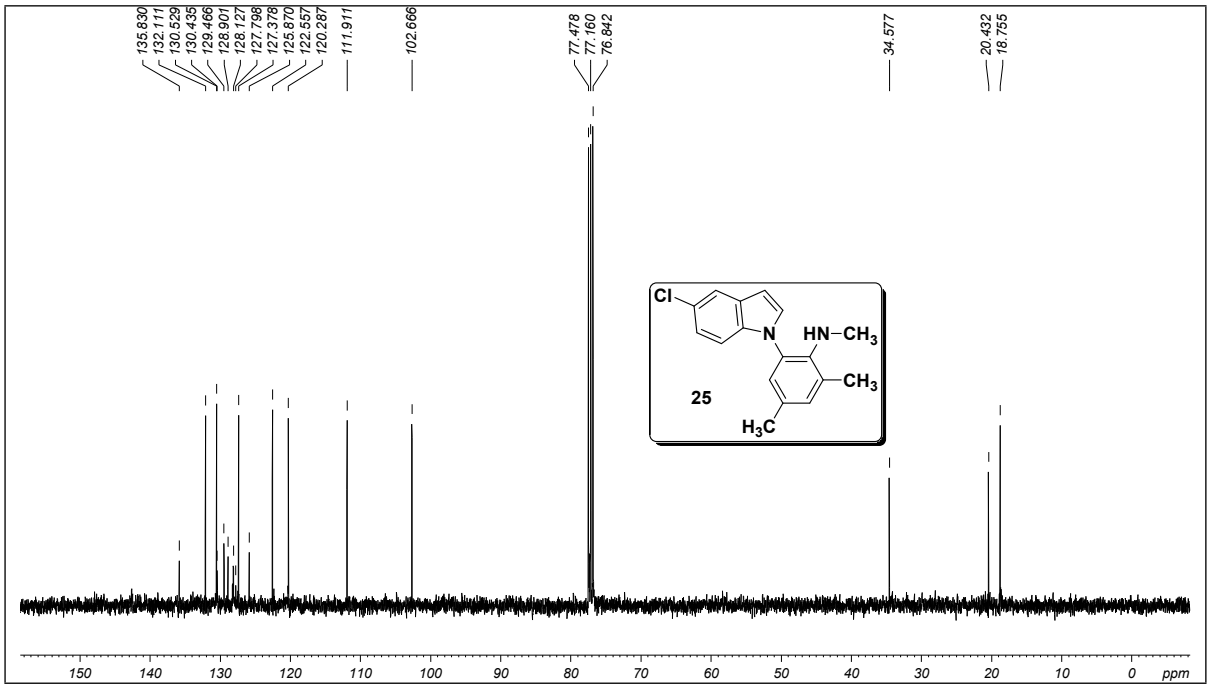


Figure S116. 100 MHz ^{13}C NMR spectrum of **25** in $CDCl_3$

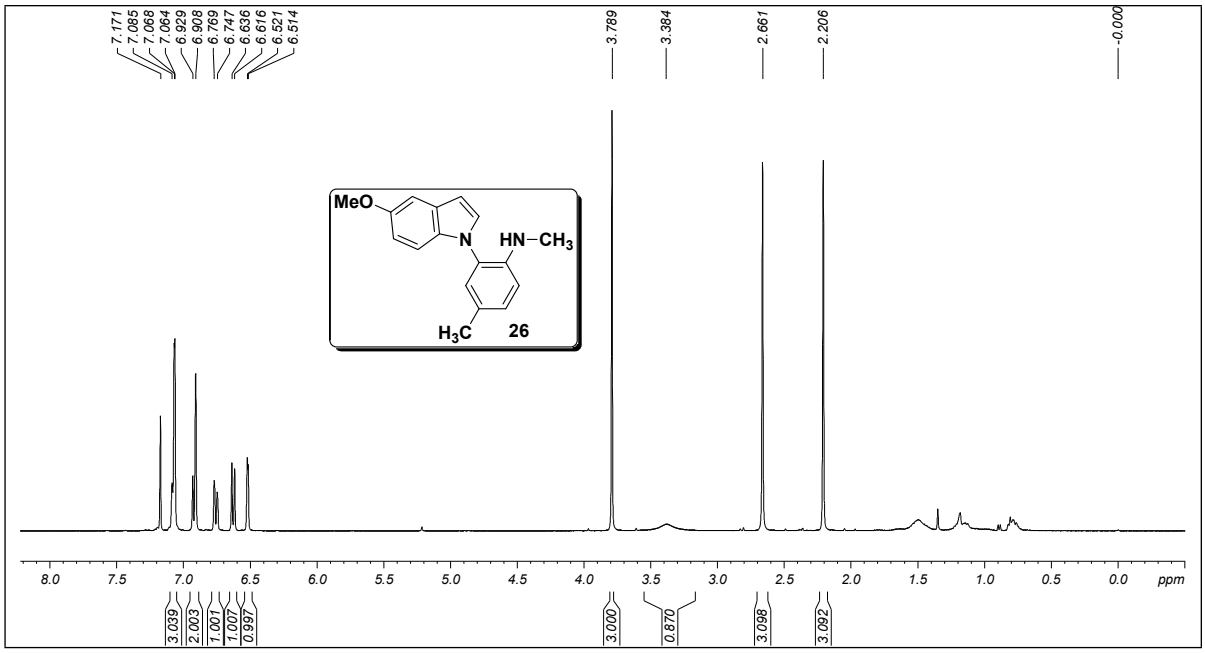


Figure S117. 400 MHz ^{1}H NMR spectrum of **26** in $CDCl_3$

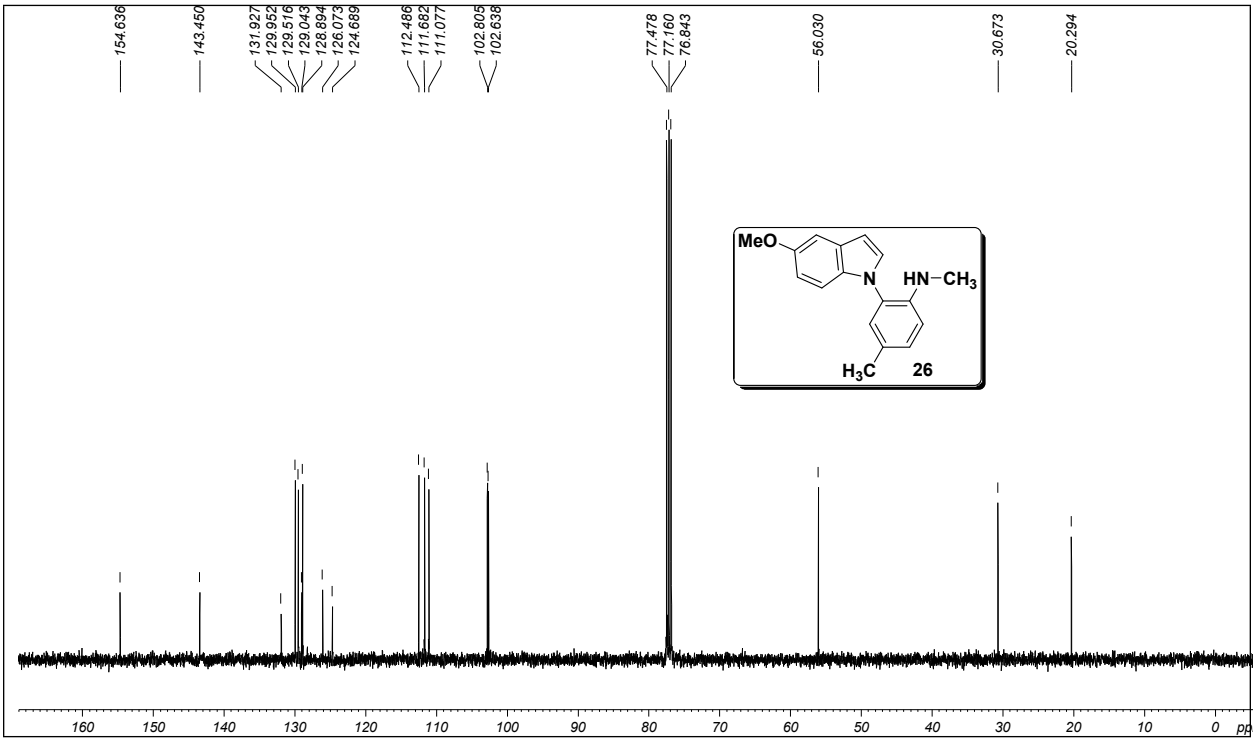


Figure S118. 100 MHz ^{13}C NMR spectrum of **26** in $CDCl_3$

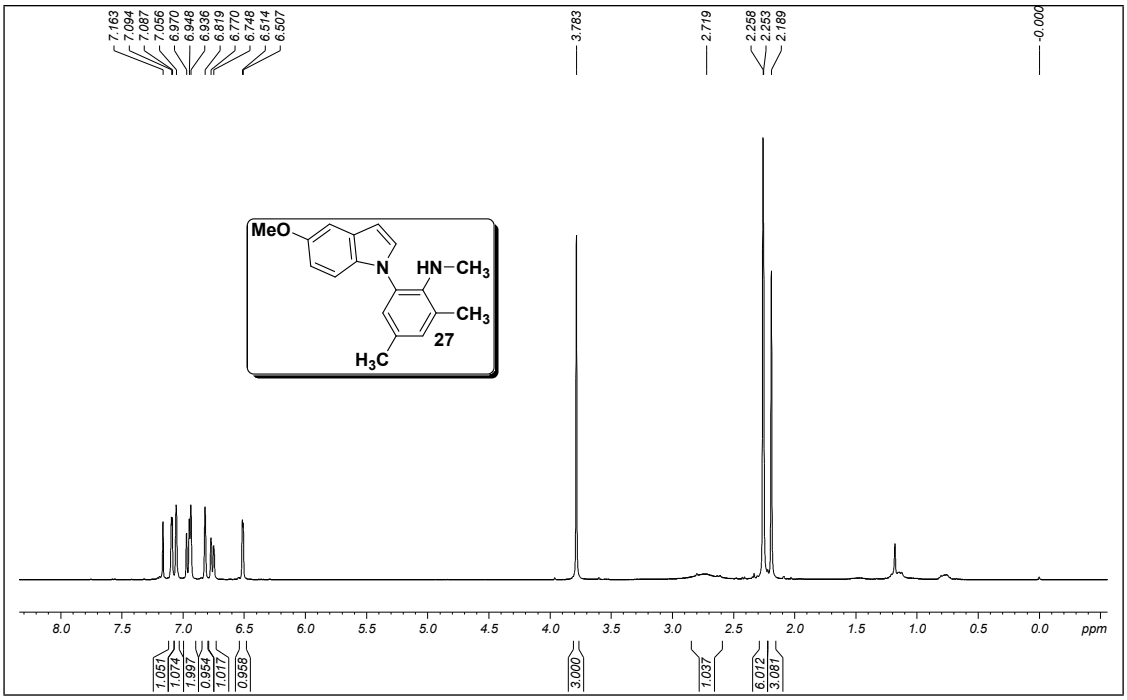


Figure S119. 400 MHz ^{1}H NMR spectrum of **27** in $CDCl_3$

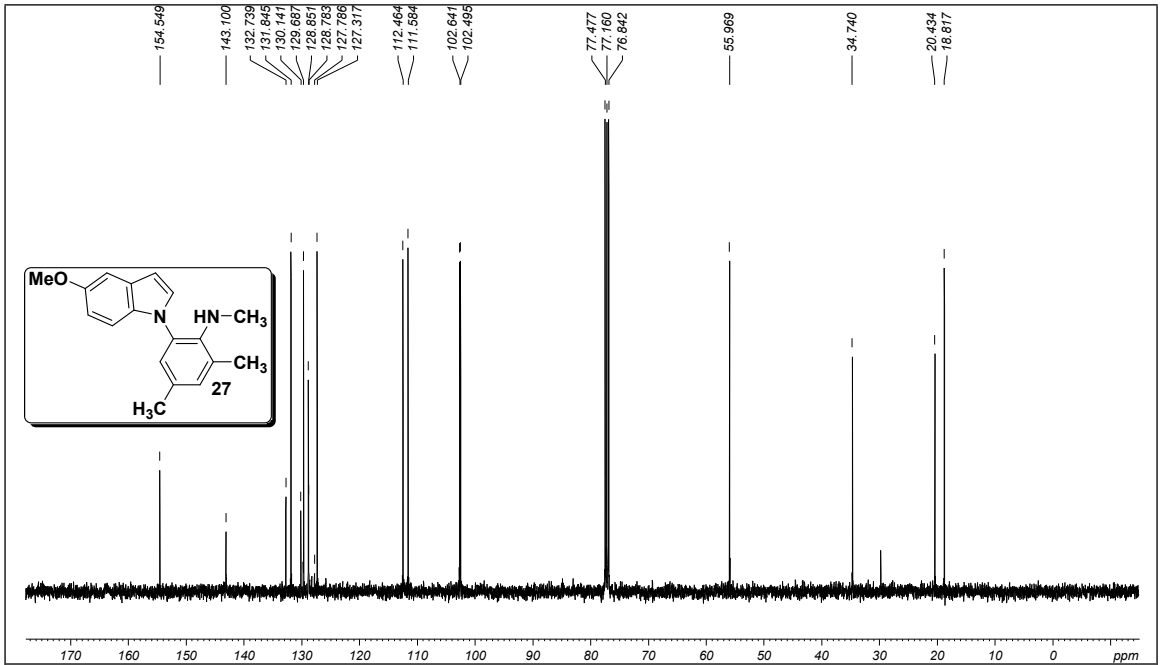


Figure S120. 100 MHz ^{13}C NMR spectrum of **27** in $CDCl_3$

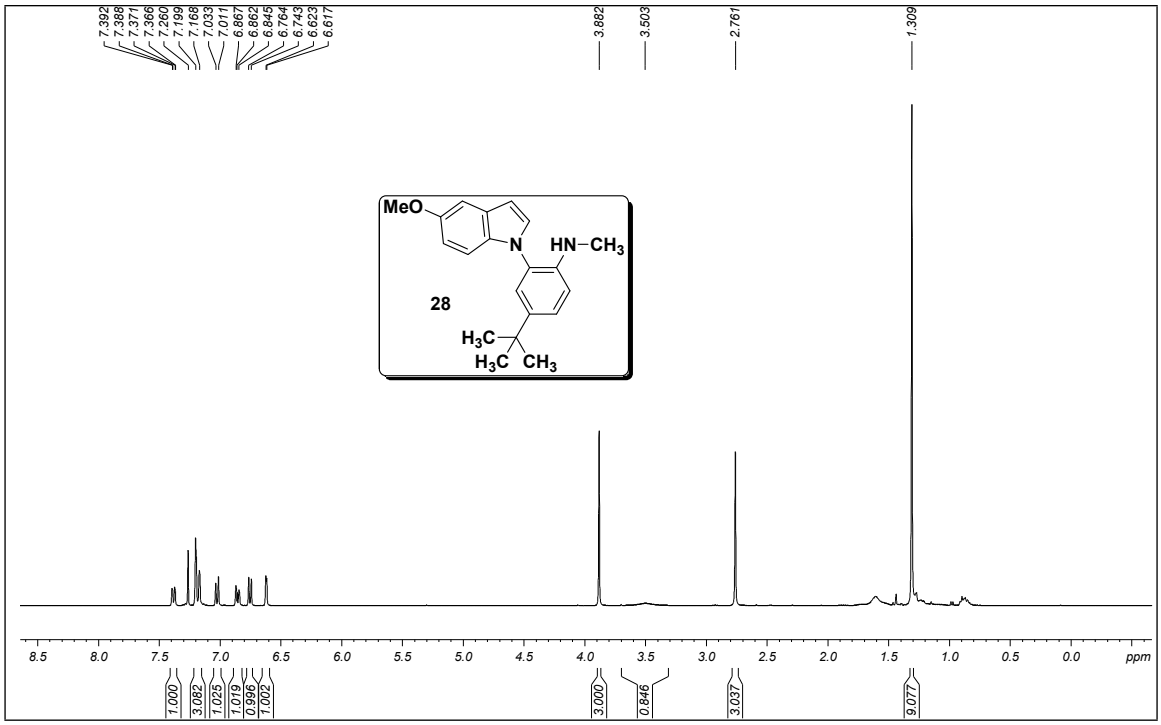


Figure S121. 400 MHz ^{1}H NMR spectrum of **28** in $CDCl_3$

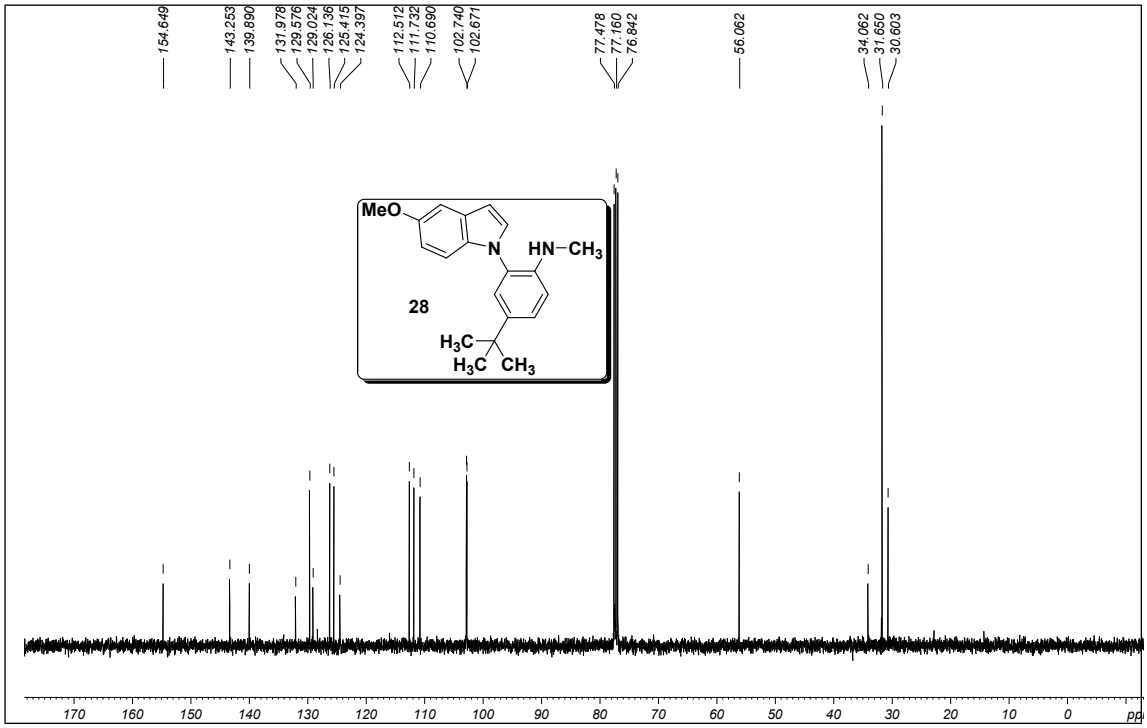


Figure S122. 100 MHz ^{13}C NMR spectrum of **28** in $CDCl_3$

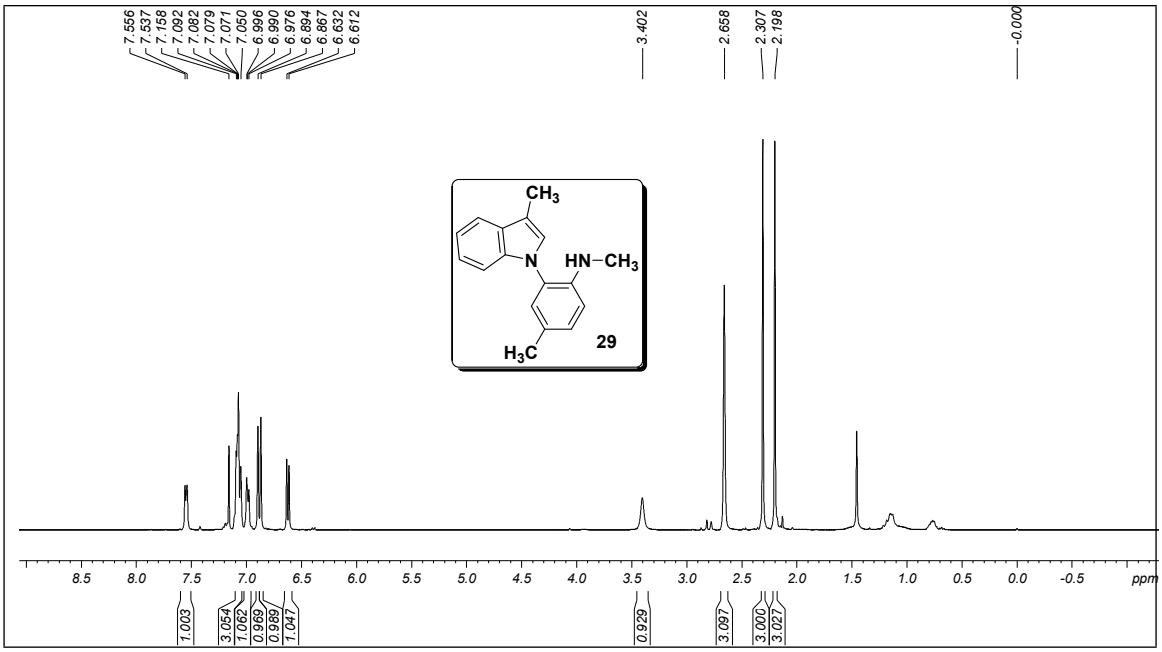


Figure S123. 400 MHz ^{1}H NMR spectrum of **29** in $CDCl_3$

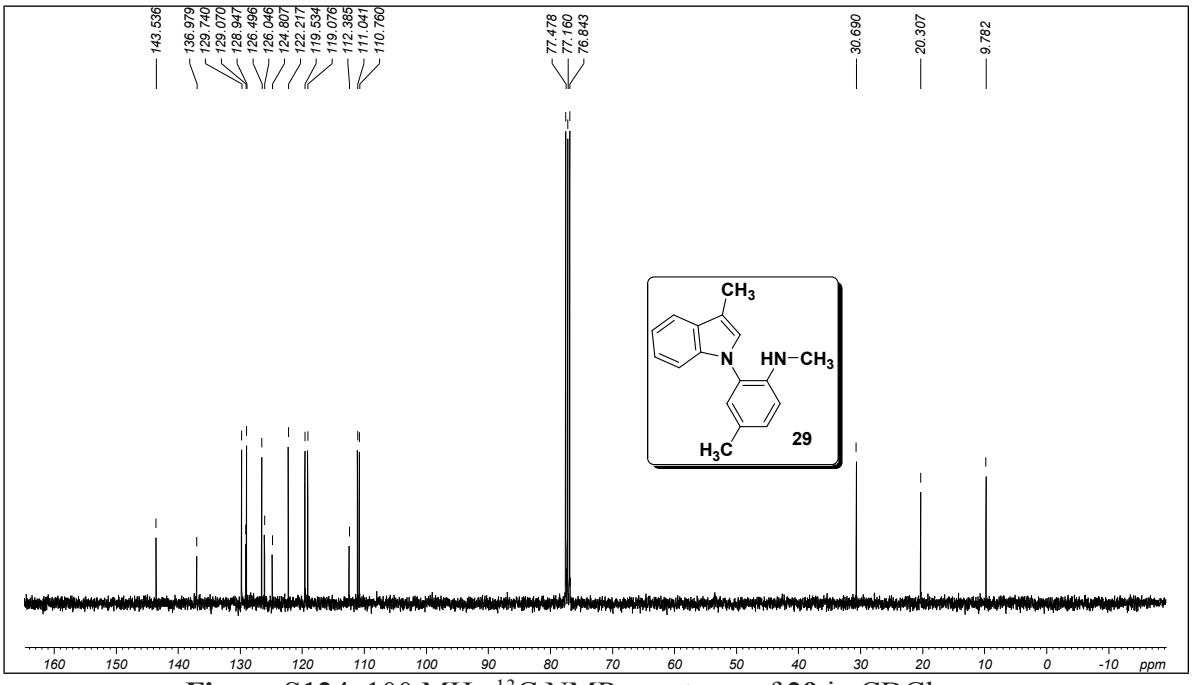


Figure S124. 100 MHz ^{13}C NMR spectrum of **29** in $CDCl_3$

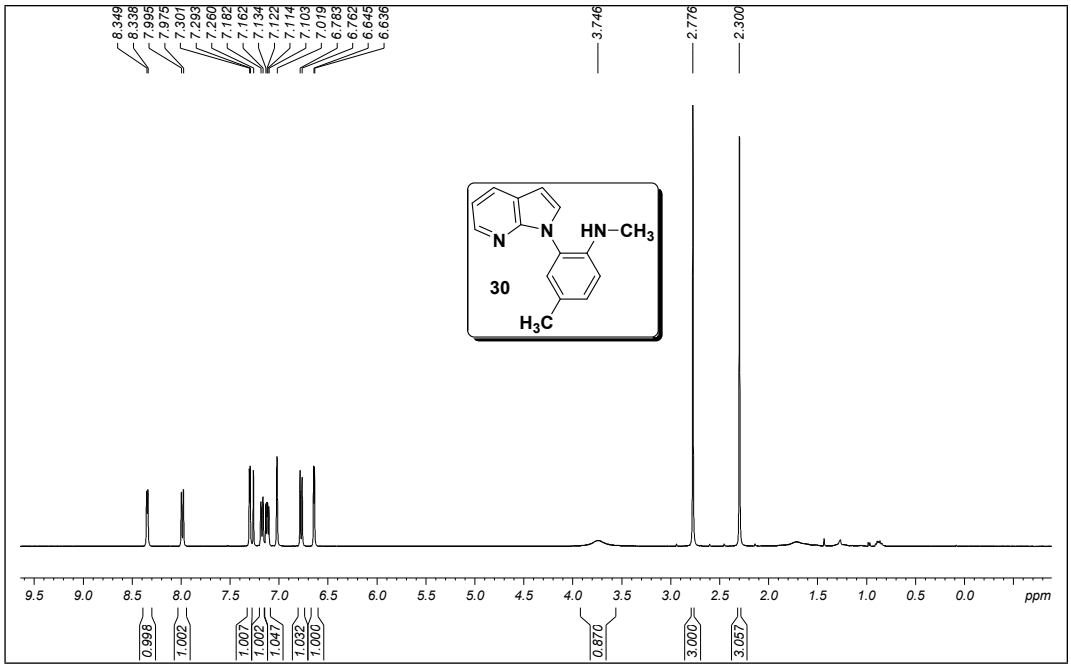


Figure S125. 400 MHz ^{1}H NMR spectrum of **30** in $CDCl_3$

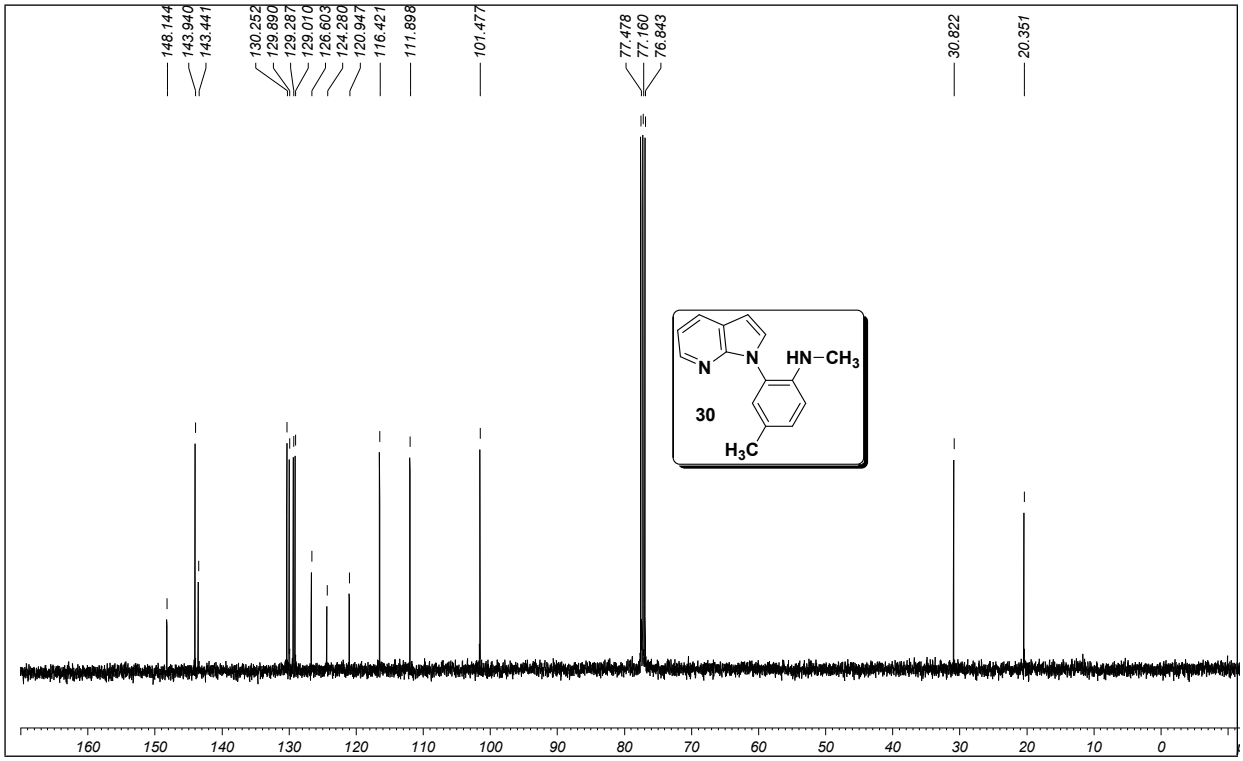


Figure S126. 100 MHz ^{13}C NMR spectrum of **30** in $CDCl_3$

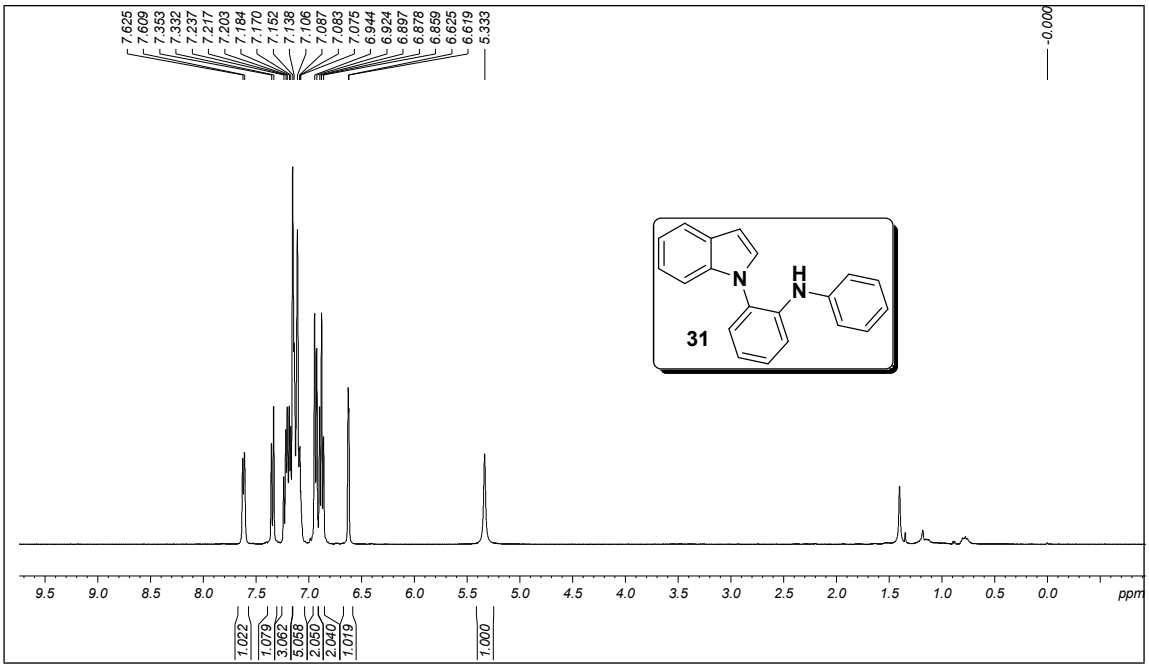


Figure S127. 400 MHz ^{1}H NMR spectrum of **31** in $CDCl_3$

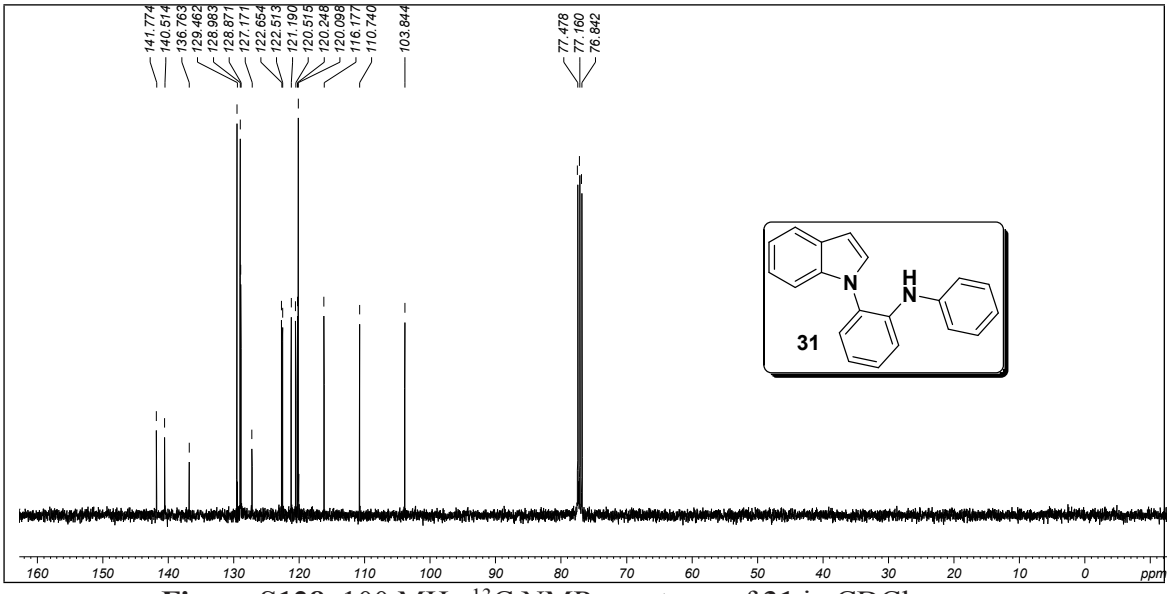


Figure S128. 100 MHz ^{13}C NMR spectrum of **31** in $CDCl_3$

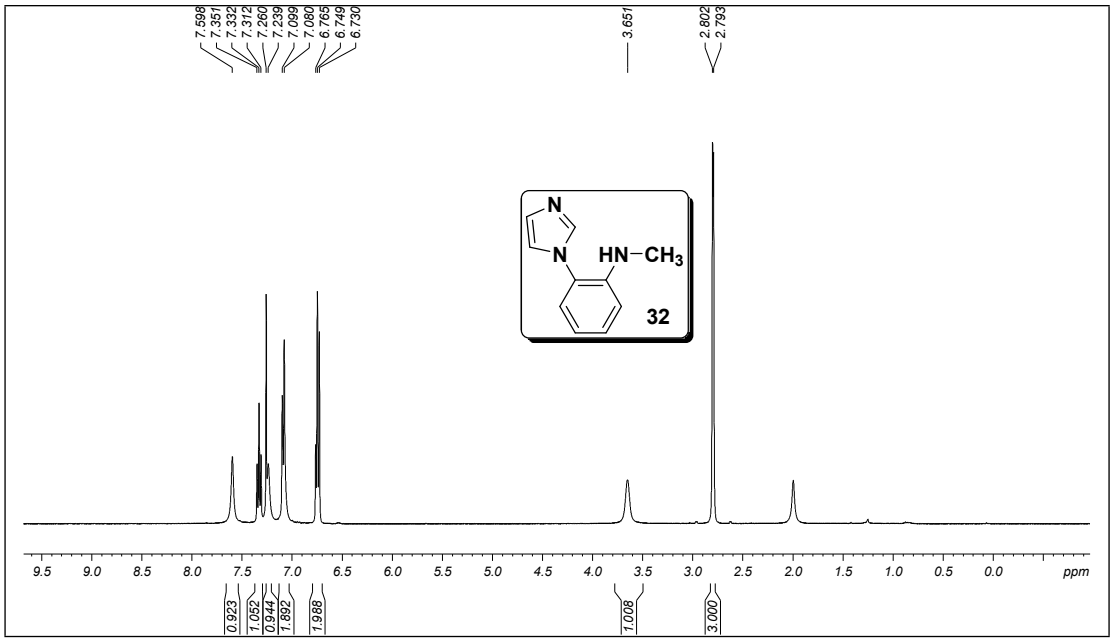


Figure S129. 400 MHz ^{1}H NMR spectrum of **32** in $CDCl_3$

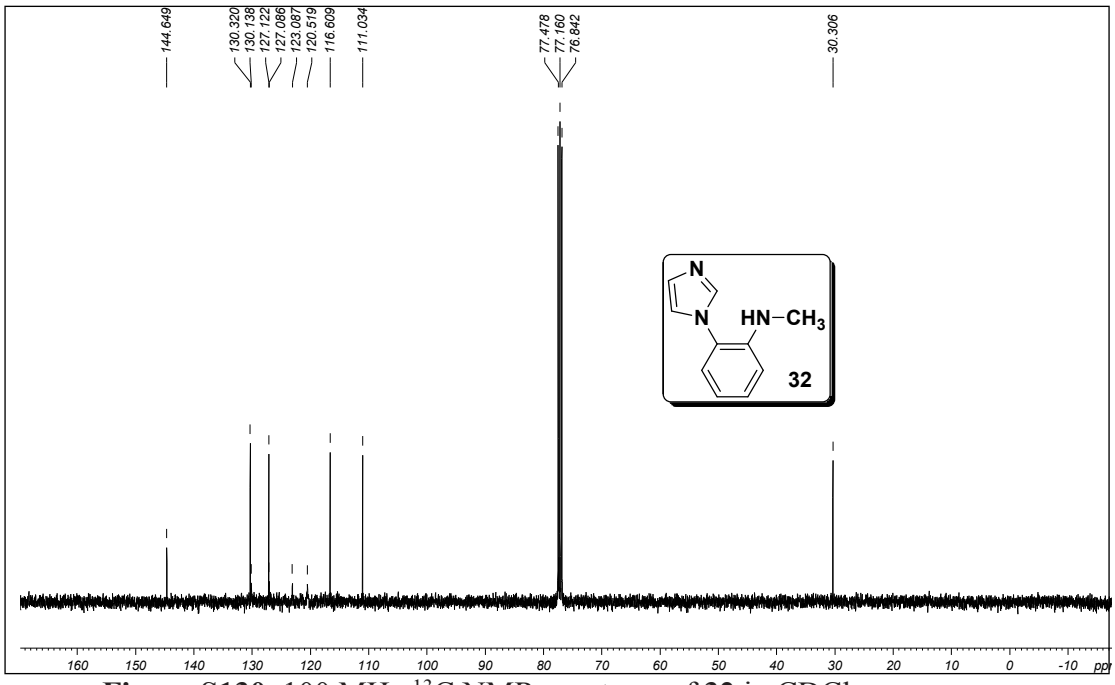


Figure S130. 100 MHz ^{13}C NMR spectrum of **32** in $CDCl_3$

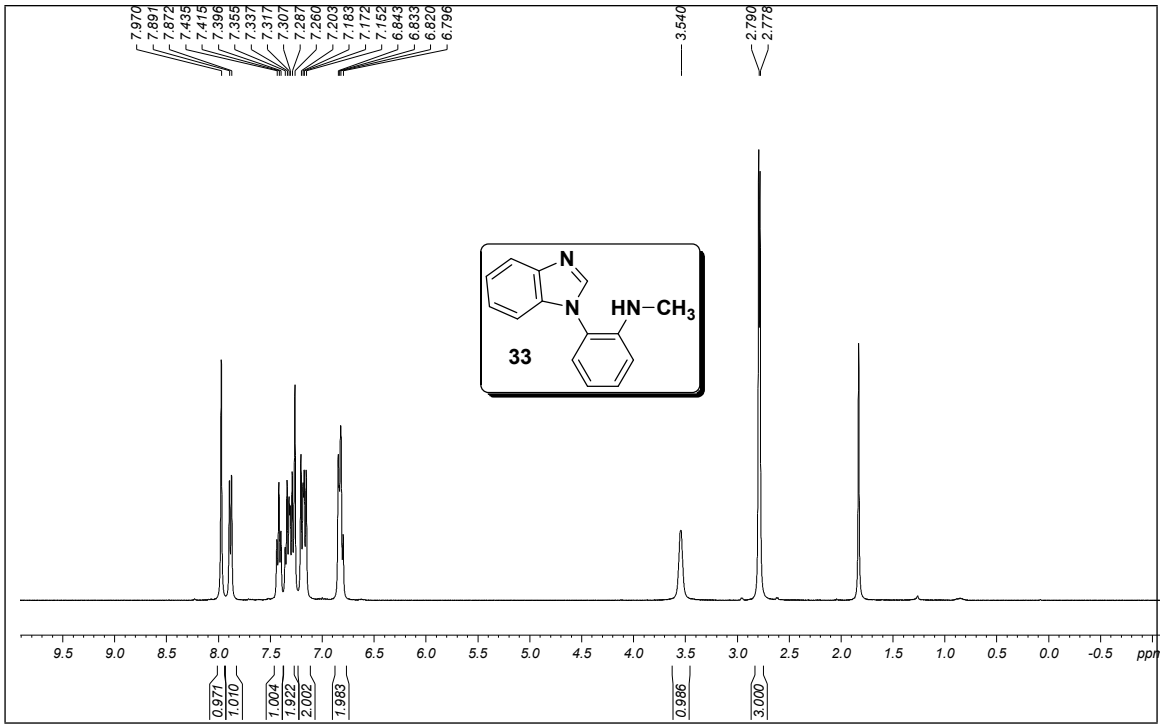


Figure S131. 400 MHz ^{1}H NMR spectrum of **33** in $CDCl_3$

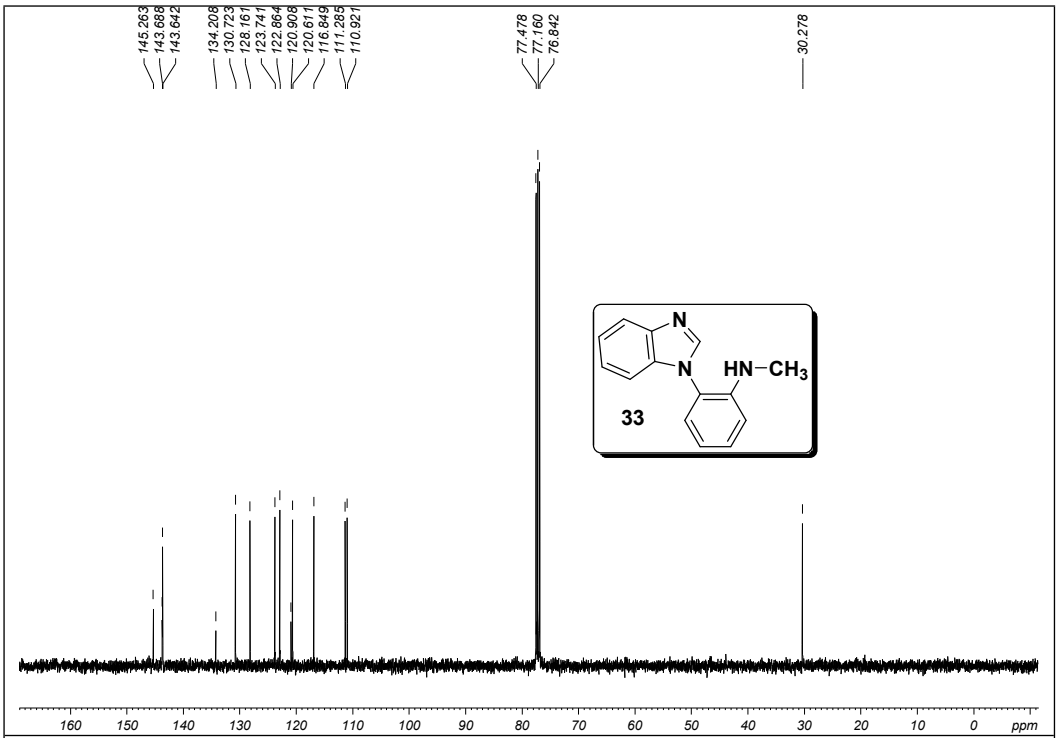


Figure S132. 100 MHz ^{13}C NMR spectrum of **33** in $CDCl_3$

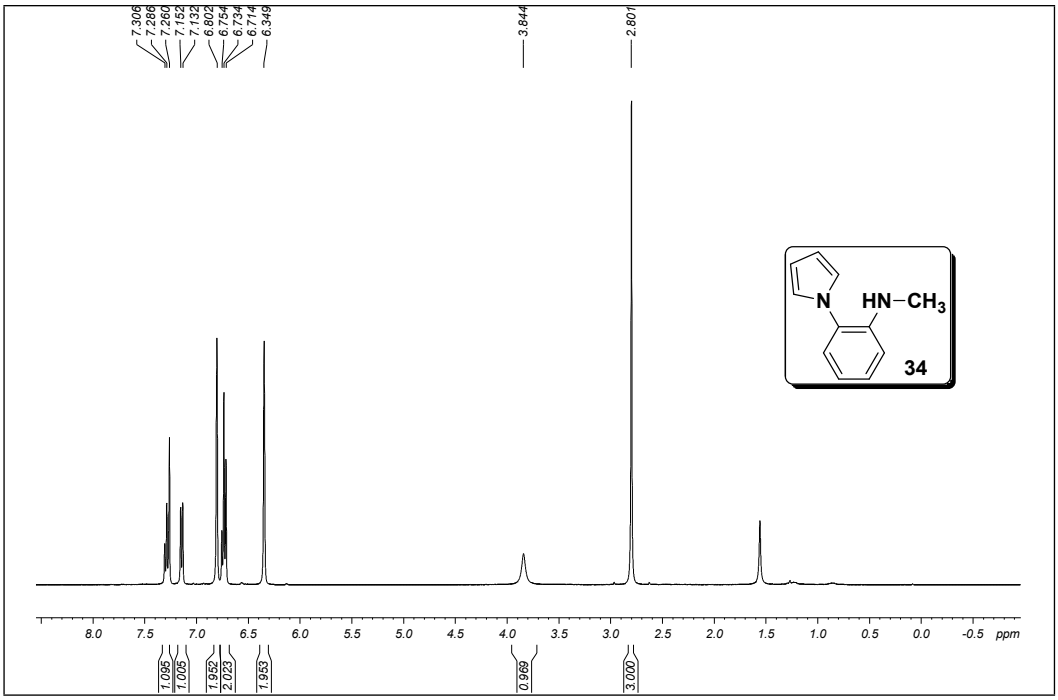


Figure S133. 400 MHz ^{1}H NMR spectrum of **34** in $CDCl_3$

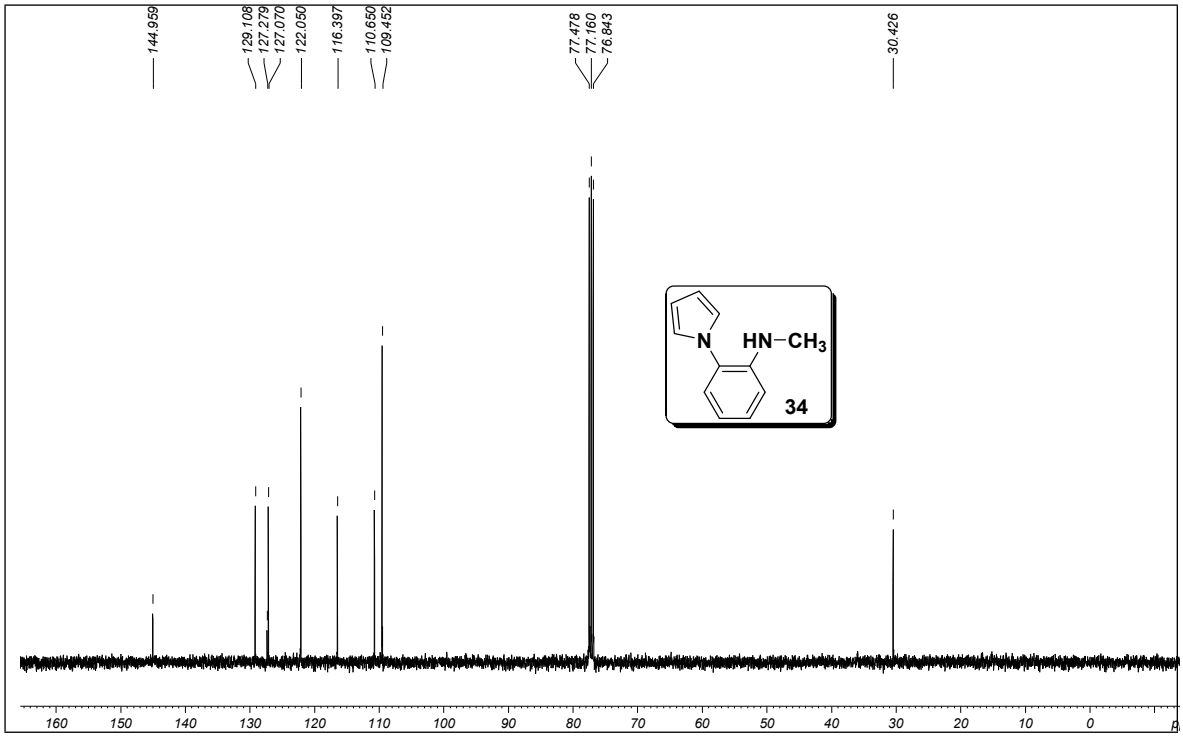


Figure S134. 100 MHz ^{13}C NMR spectrum of **34** in $CDCl_3$

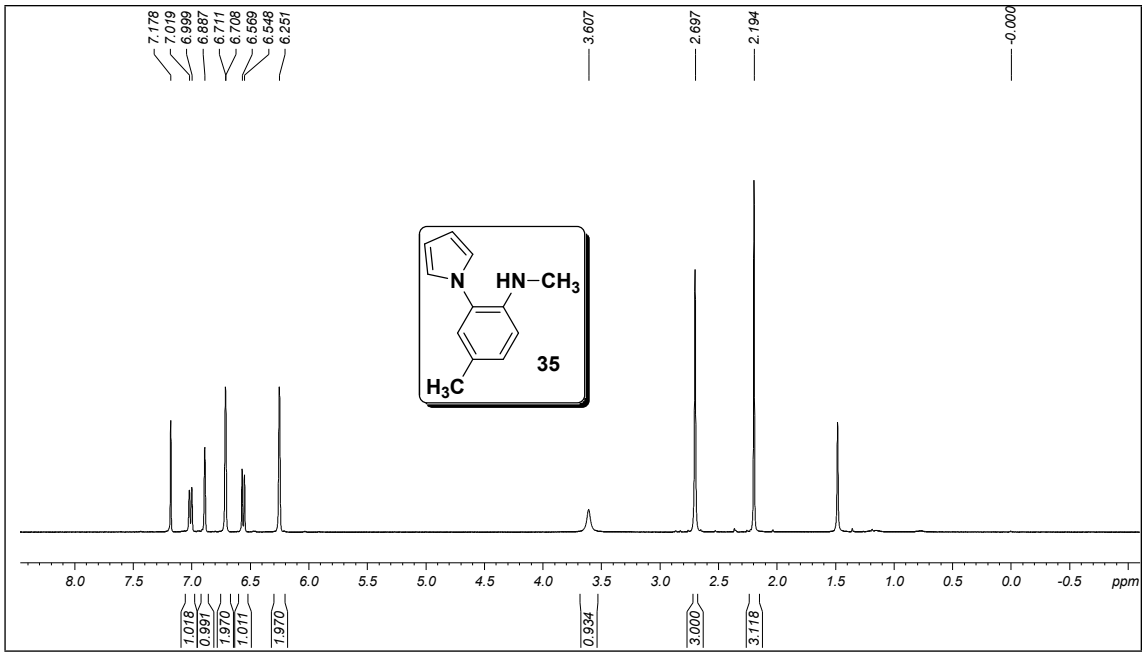


Figure S135. 400 MHz ^{1}H NMR spectrum of **35** in $CDCl_3$

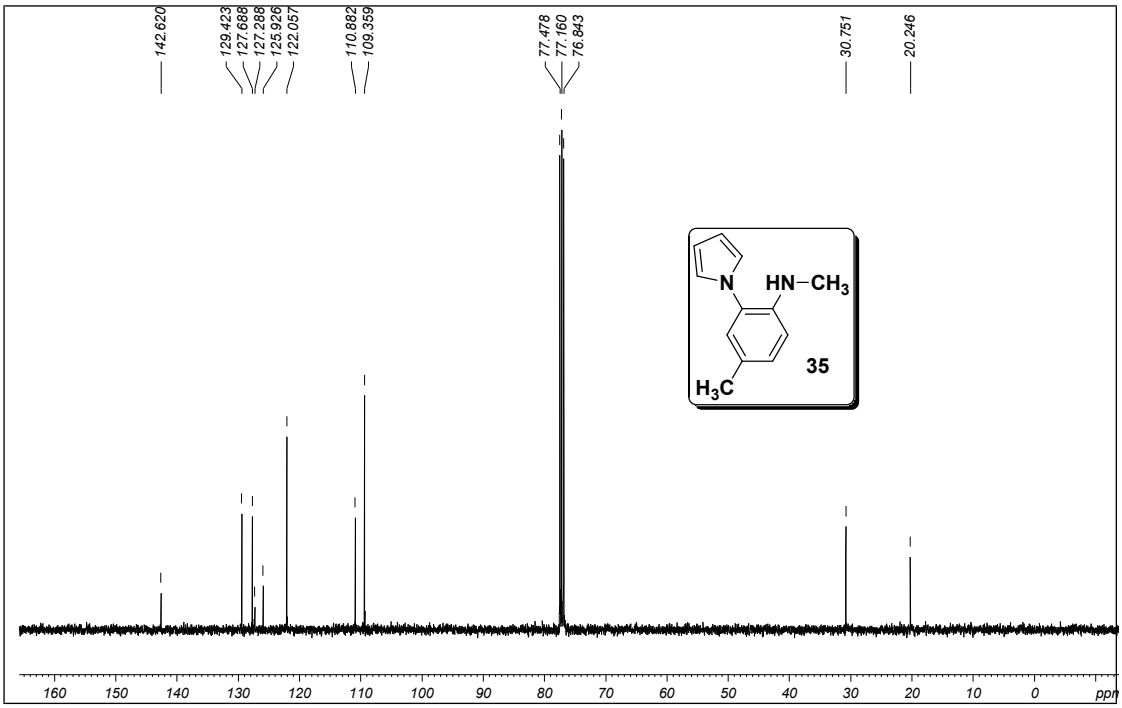


Figure S136. 100 MHz ^{13}C NMR spectrum of **35** in $CDCl_3$

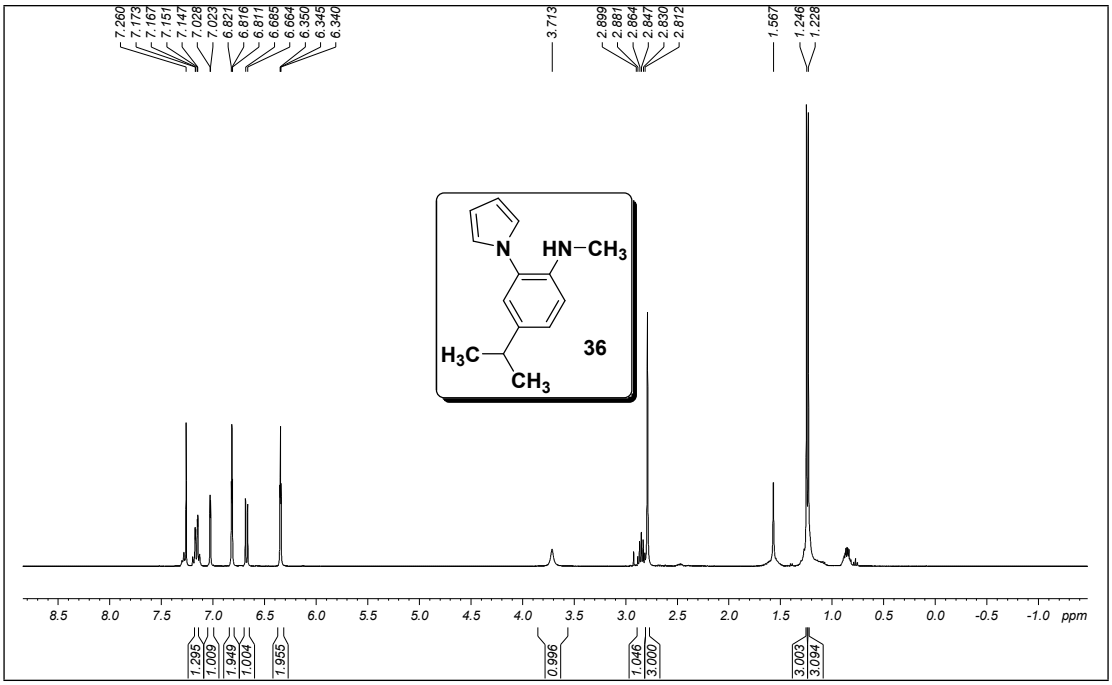


Figure S137. 400 MHz ^{1}H NMR spectrum of **36** in $CDCl_3$

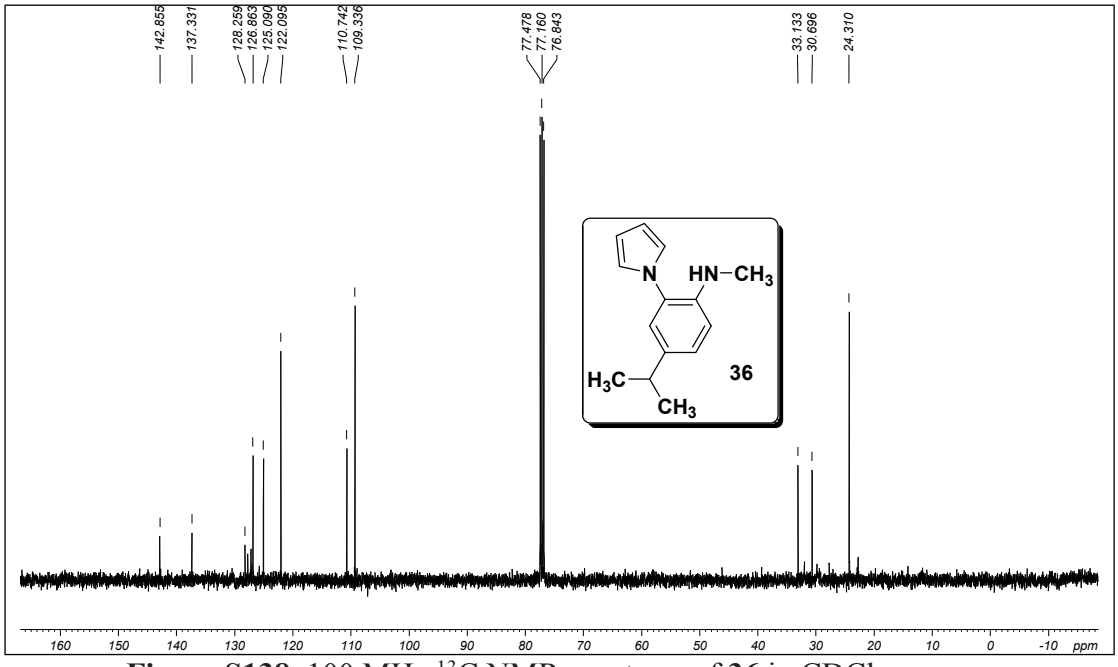


Figure S138. 100 MHz ^{13}C NMR spectrum of **36** in $CDCl_3$

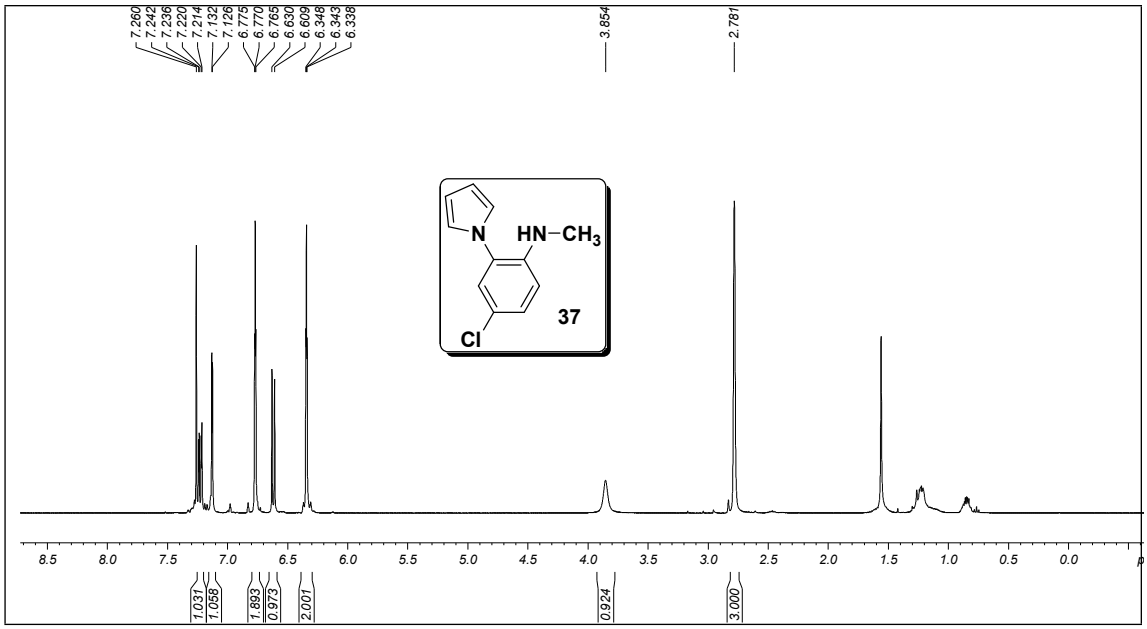


Figure S139. 400 MHz ^{1}H NMR spectrum of **37** in $CDCl_3$

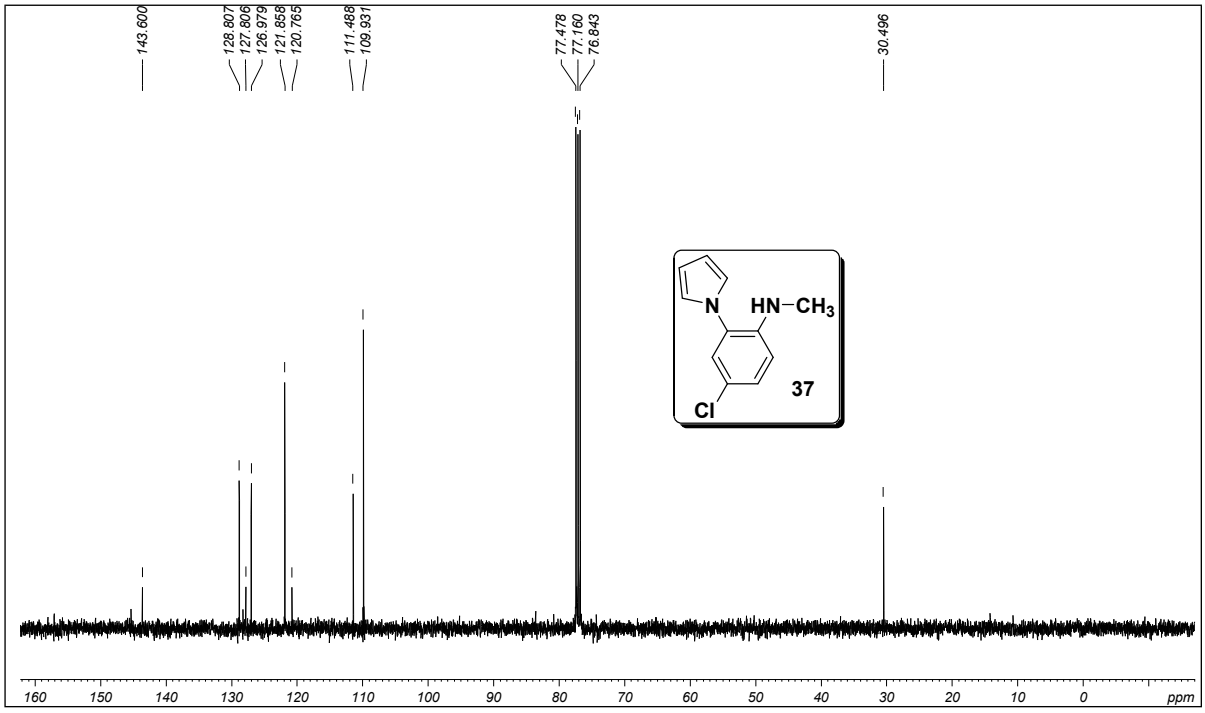


Figure S140. 100 MHz ^{13}C NMR spectrum of **37** in $CDCl_3$

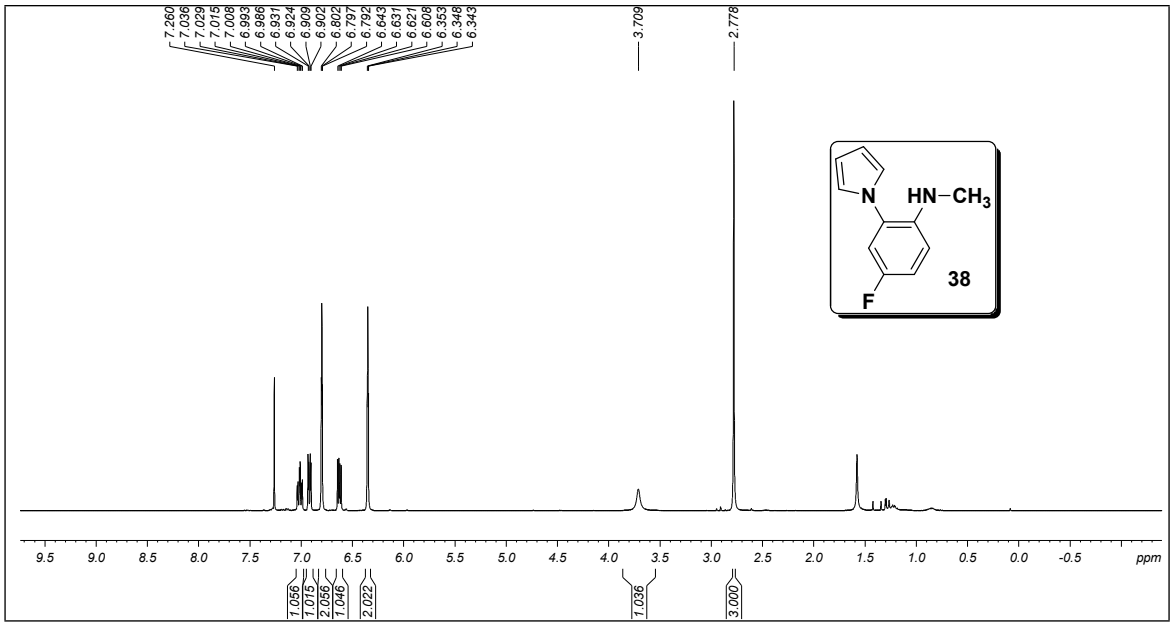


Figure S141. 400 MHz ^{1}H NMR spectrum of **38** in $CDCl_3$

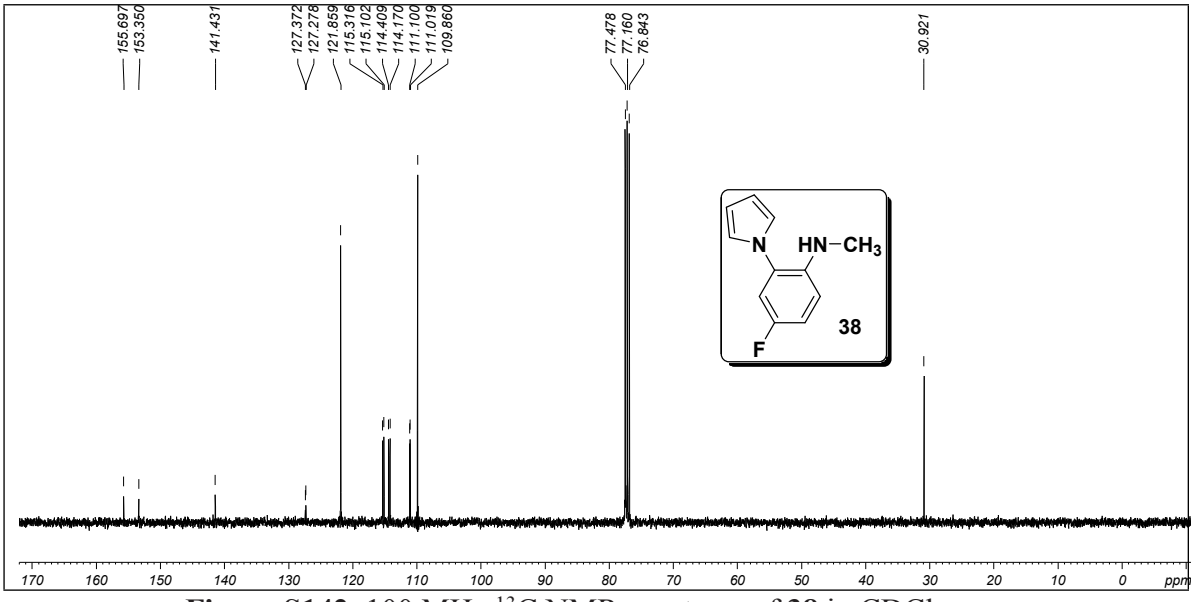


Figure S142. 100 MHz ^{13}C NMR spectrum of **38** in $CDCl_3$

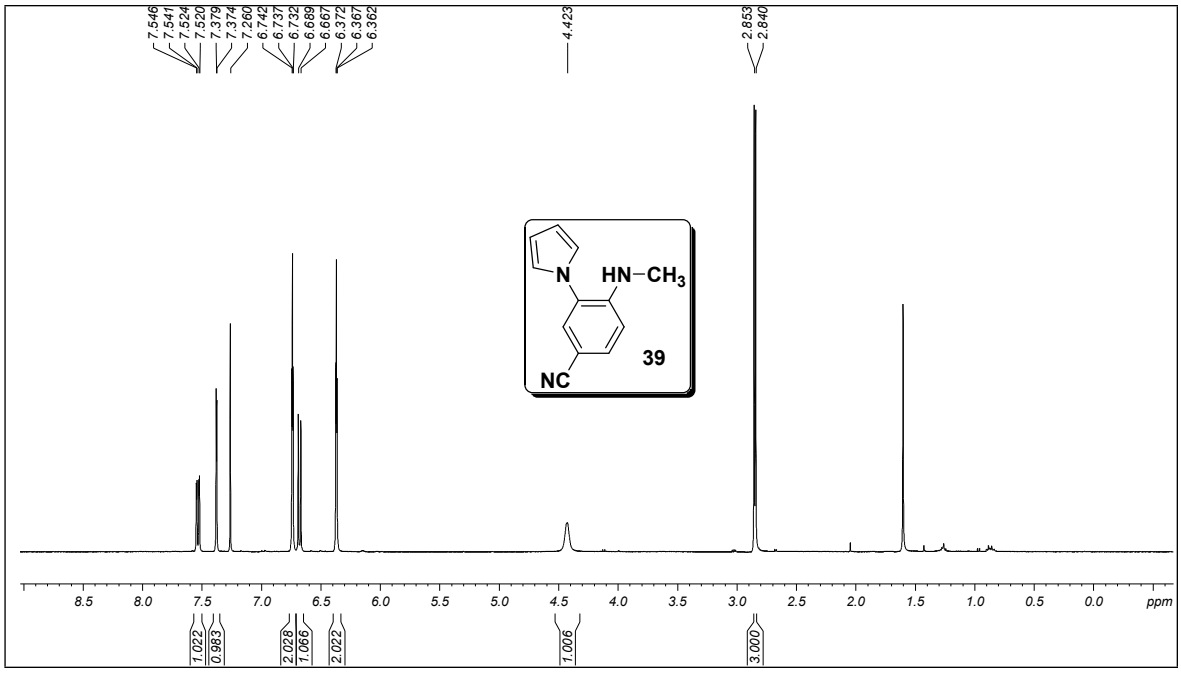


Figure S143. 400 MHz ^{1}H NMR spectrum of **39** in $CDCl_3$

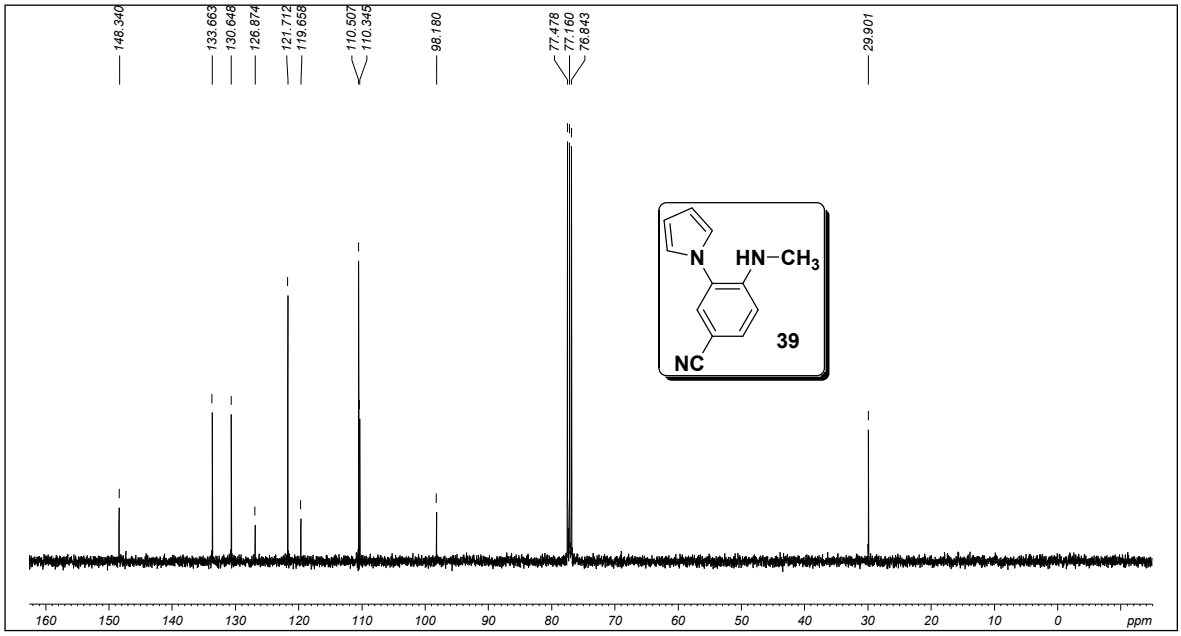
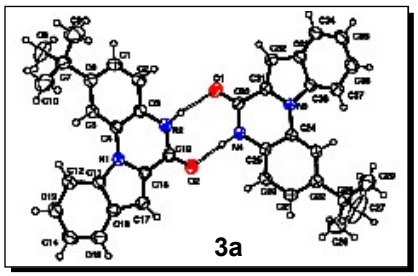


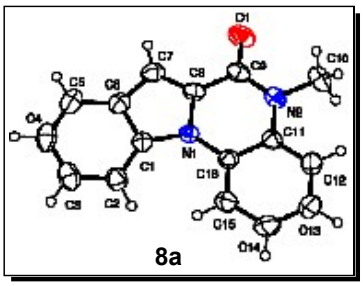
Figure S144. 100 MHz ^{13}C NMR spectrum of **39** in $CDCl_3$

XII. Table 1. Crystal data and structure refinement for '**3a'**



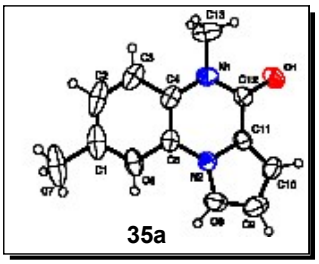
Identification code	ACS1313	
Empirical formula	C19 H18 N2 O	
Formula weight	290.35	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6986(5) Å	α= 81.323(3)°.
	b = 11.3012(5) Å	β= 89.730(3)°.
	c = 14.4283(6) Å	γ = 61.927(2)°.
Volume	1517.23(12) $Å^3$	
Z	4	
Density (calculated)	1.271 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	616	
Crystal size	0.300 x 0.250 x 0.200 mm^3	
Theta range for data collection	2.072 to 25.000°	
Index ranges	-12<=h<=12, -13<=k<=13, -17<=l<=17	
Reflections collected	35239	
Independent reflections	5347 [R(int) = 0.0414]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7027	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5347 / 0 / 407	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1081	
R indices (all data)	R1 = 0.0708, wR2 = 0.1287	
Extinction coefficient	0.0068(11)	
Largest diff. peak and hole	0.181 and -0.170 $e.Å^{-3}$	

XIII. Table 2. Crystal data and structure refinement for '**8a'**



Identification code	1328B	
Empirical formula	C16 H12 N2 O	
Formula weight	248.28	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.480(6) Å	α= 90°.
	b = 10.122(7) Å	β= 96.16(3)°.
	c = 15.888(11) Å	γ = 90°.
Volume	1196.0(15) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	520	
Crystal size	0.150 x 0.150 x 0.100 mm^3	
Theta range for data collection	3.150 to 24.999°	
Index ranges	-8<=h<=8, -12<=k<=12, -18<=l<=18	
Reflections collected	18307	
Independent reflections	2094 [R(int) = 0.0334]	
Completeness to theta = 24.999°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.6786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2094 / 0 / 173	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1050	
R indices (all data)	R1 = 0.0555, wR2 = 0.1197	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.159 and -0.145 $e.Å^{-3}$	

XIV. Table 3. Crystal data and structure refinement for '**35a'**



Identification code	ACS1461	
Empirical formula	C13 H12 N2 O	
Formula weight	212.25	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 6.9280(2) Å	α= 90°.
	b = 10.4940(3) Å	β= 102.9760(10)°.
	c = 15.3990(4) Å	γ = 90°.
Volume	1090.96(5) $Å^3$	
Z	4	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	448	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	3.017 to 24.995°	
Index ranges	-8<=h<=8, -12<=k<=12, -18<=l<=18	
Reflections collected	27684	
Independent reflections	1967 [R(int) = 0.2297]	
Completeness to theta = 24.995°	99.7 %	
Absorption correction	Mnulti-scan	
Max. and min. transmission	0.7456 and 0.5782	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1967 / 1 / 149	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0622, wR2 = 0.1624	
R indices (all data)	R1 = 0.0738, wR2 = 0.1800	
Extinction coefficient	0.27(3)	
Largest diff. peak and hole	0.246 and -0.248 $e.Å^{-3}$	