Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for

Friedel-Crafts alkylation of indoles with β-nitroalkenes using ammonium niobium oxalate as a recyclable catalyst

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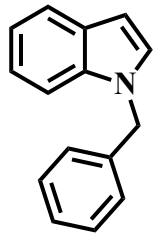
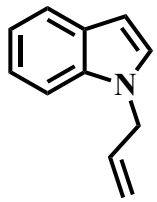
1. ^{1}H NMR spectral data of *N*-alkylated indoles (1i-1k) and nitroalkenes (2b-2m)

1-benzyl-1*H*-indole (1j)[1]



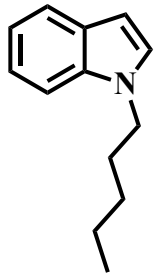
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.31 (dd, *J* = 16.7, 6.6 Hz, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.19-7.13 (m, 4H), 6.61 (d, *J* = 2.8 Hz, 1H), 5.37 (s, 2H).

1-allyl-1*H*-indole (1k)[1]



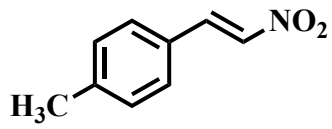
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.26 (dd, *J* = 12.7, 5.2 Hz, 1H), 7.16 (dd, *J* = 11.2, 4.8 Hz, 2H), 6.57 (d, *J* = 2.5 Hz, 1H), 6.05 (ddd, *J* = 22.3, 10.5, 5.4 Hz, 1H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.78 (d, *J* = 5.3 Hz, 2H).

1-pentyl-1*H*-indole (1l)[2]



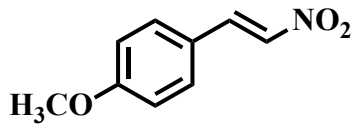
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 8.3, 5.3 Hz, 2H), 6.56 (d, *J* = 2.1 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 1.94-1.86 (m, 2H), 1.45-1.35 (m, 4H), 0.96 (t, *J* = 6.9 Hz, 3H).

(*E*)-1-methyl-4-(2-nitrovinyl)benzene (2b)[3]



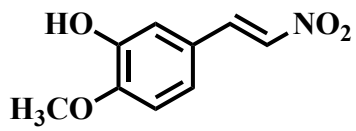
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.56 (d, *J* = 13.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.25 (d, 2H), 2.41 (s, 3H).

(*E*)-1-methoxy-4-(2-nitrovinyl)benzene (2c)[3]



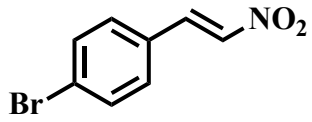
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.51 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H).

(*E*)-2-methoxy-5-(2-nitrovinyl)phenol (2d)[4]



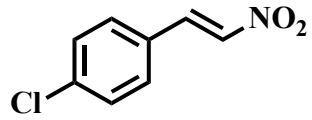
^{1}H NMR (500 MHz, DMSO-d_6): δ 10.00 (s, 1H), 8.13 (d, J = 13.4 Hz, 1H), 8.01 (d, J = 13.4 Hz, 1H), 7.46 (s, 1H), 7.28 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 3.81 (d, J = 5.4 Hz, 3H)

(*E*)-1-bromo-4-(2-nitrovinyl)benzene (2e)[3]



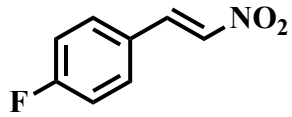
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 13.7 Hz, 1H), 7.63-7.59 (m, 2H), 7.57 (d, J = 13.7 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H)

(*E*)-1-chloro-4-(2-nitrovinyl)benzene (2f)[3]



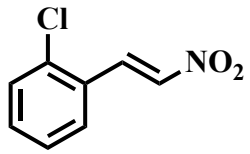
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 13.7 Hz, 1H), 7.56 (d, J = 13.7 Hz, 1H), 7.51-7.47 (m, 2H), 7.46-7.41 (m, 2H).

(*E*)-1-fluoro-4-(2-nitrovinyl)benzene (2g)[3]



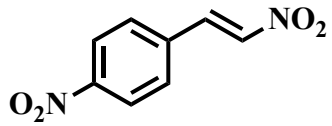
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 13.7 Hz, 1H), 7.51-7.44 (m, 3H), 7.11-7.04 (m, 2H).

(*E*)-1-chloro-2-(2-nitrovinyl)benzene (2h)[3]



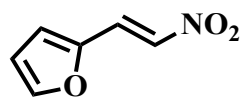
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 13.7 Hz, 1H), 7.62-7.56 (m, 2H), 7.50 (dd, J = 8.1, 1.2 Hz, 1H), 7.43 (td, J = 7.7, 1.6 Hz, 1H), 7.37-7.30 (m, 1H).

(*E*)-1-nitro-4-(2-nitrovinyl)benzene (2i)[5]



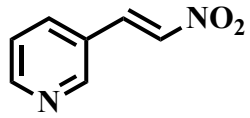
^{1}H NMR (500 MHz, DMSO-d_6): δ 8.37 (d, J = 13.7 Hz, 1H), 8.34-8.28 (m, 2H), 8.25 (d, J = 13.7 Hz, 1H), 8.15-8.10 (m, 2H).

(*E*)-2-(2-nitrovinyl)furan (2j)[3]



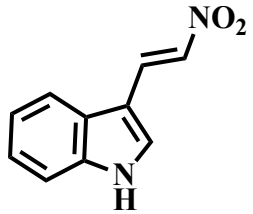
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 13.2 Hz, 1H), 7.56 (d, J = 1.4 Hz, 1H), 7.50 (d, J = 13.2 Hz, 1H), 6.86 (d, J = 3.5 Hz, 1H), 6.55 (dd, J = 3.5, 1.8 Hz, 1H).

(*E*)-3-(2-nitrovinyl)pyridine (2k)[6]



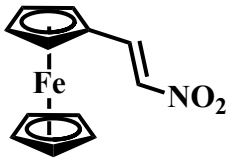
^{1}H NMR (500 MHz, DMSO-d_6): δ 8.99 (d, J = 2.0 Hz, 1H), 8.67 (dd, J = 4.8, 1.6 Hz, 1H), 8.32 (d, J = 13.7 Hz, 1H), 8.28 (dt, J = 8.0, 1.8 Hz, 1H), 8.17 (d, J = 13.7 Hz, 1H), 7.51 (dd, J = 8.0, 4.8 Hz, 1H).

(*E*)-3-(2-nitrovinyl)-1*H*-indole (2l)[7]



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.23 (d, J = 13.5 Hz, 1H), 7.77-7.71 (m, 2H), 7.61 (d, J = 2.9 Hz, 1H), 7.44-7.39 (m, 1H), 7.31-7.25 (m, 2H).

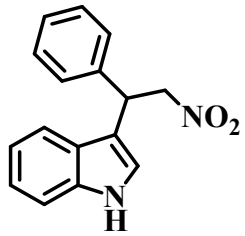
(*E*)-(2-nitrovinyl)ferrocene (2m)[8]



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 13.3 Hz, 1H), 7.26 (d, J = 13.3 Hz, 1H), 4.63-4.53 (m, 4H), 4.26 (d, J = 21.1 Hz, 5H).

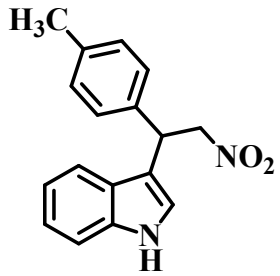
2. Spectral data of alkylated products 3a-3x, 4a and 6a

3-(2-nitro-1-phenylethyl)-1*H*-indole (3a)[3]



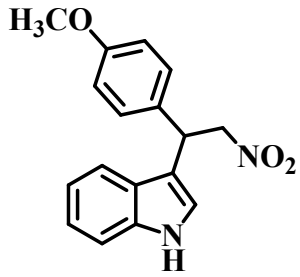
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36-7.28 (m, 5H), 7.24 (dt, J = 6.3, 2.2 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 5.18 (t, J = 8.0 Hz, 1H), 5.05 (dd, J = 12.5, 7.7 Hz, 1H), 4.92 (dd, J = 12.5, 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.22, 136.51, 128.95, 127.79, 127.59, 126.12, 122.72, 121.64, 119.98, 118.95, 114.42, 111.43, 79.56, 41.57.

3-(2-nitro-1-(*p*-tolyl)ethyl)-1*H*-indole (3b)[3]



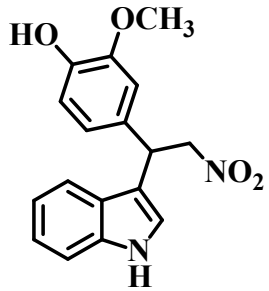
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.12 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.30-7.19 (m, 3H), 7.19-7.08 (m, 3H), 7.03 (s, 1H), 5.19 (t, *J* = 8.0 Hz, 1H), 5.08 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.95 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.23, 136.52, 136.18, 129.62, 127.64, 126.15, 122.66, 121.59, 119.93, 118.97, 114.61, 111.40, 79.67, 41.23, 21.06.

3-(1-(4-methoxyphenyl)-2-nitroethyl)-1*H*-indole (3c)[3]



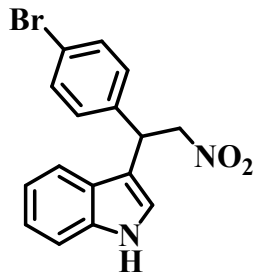
^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.03 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.21-7.17 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.07 (t, *J* = 8.0 Hz, 1H), 4.98 (dd, *J* = 12.3, 7.5 Hz, 1H), 4.83 (dd, *J* = 12.3, 8.5 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 158.91, 136.53, 131.19, 128.84, 126.11, 122.69, 121.47, 119.94, 119.01, 114.79, 114.29, 111.38, 79.77, 55.27, 40.87.

4-(1-(1*H*-indol-3-yl)-2-nitroethyl)-2-methoxyphenol (3d)[9]



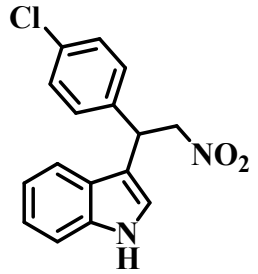
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 1.8 Hz, 1H), 6.78-6.67 (m, 3H), 5.59 (s, 1H), 5.01 (t, *J* = 7.9 Hz, 1H), 4.92 (dd, *J* = 12.3, 7.4 Hz, 1H), 4.78 (dd, *J* = 12.2, 8.5 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 146.82, 144.97, 136.56, 131.18, 126.11, 122.65, 121.65, 120.32, 119.90, 118.93, 114.70, 114.56, 111.48, 110.65, 79.81, 55.94, 41.38.

3-(1-(4-bromophenyl)-2-nitroethyl)-1*H*-indole (3e)[3]



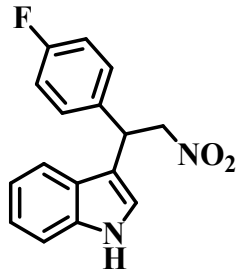
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 8.4 Hz, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 0.7 Hz, 1H), 5.07 (t, *J* = 7.9 Hz, 1H), 4.96 (dd, *J* = 12.6, 7.4 Hz, 1H), 4.82 (dd, *J* = 12.6, 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.29, 136.52, 132.09, 129.53, 125.90, 122.90, 121.58, 121.55, 120.13, 118.81, 113.85, 111.53, 79.23, 41.04.

3-(1-(4-chlorophenyl)-2-nitroethyl)-1*H*-indole (3f)[3]



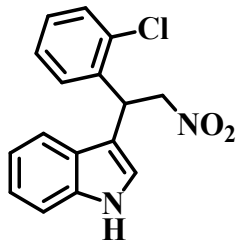
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.21-7.14 (m, 4H), 7.14-7.09 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 1.8 Hz, 1H), 5.06 (t, J = 8.0 Hz, 1H), 4.94 (dd, *J* = 12.5, 7.4 Hz, 1H), 4.79 (dd, *J* = 12.5, 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.78, 136.53, 133.43, 129.18, 129.13, 125.92, 122.89, 121.57, 120.12, 118.82, 113.92, 111.54, 79.32, 40.98.

3-(1-(4-fluorophenyl)-2-nitroethyl)-1*H*-indole (3g)[3]



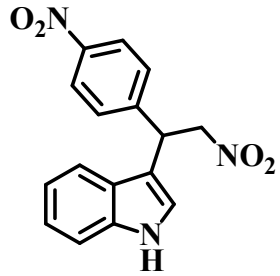
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.25-7.20 (m, 2H), 7.16-7.11 (m, 1H), 7.04-6.99 (m, 1H), 6.96-6.90 (m, 3H), 5.10 (t, *J* = 8.0 Hz, 1H), 4.97 (dd, *J* = 12.5, 7.4 Hz, 1H), 4.83 (dd, *J* = 12.5, 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.18 (s), 161.22 (s), 136.65 (s), 135.09 (d, *J* = 3.3 Hz), 129.48 (d, *J* = 8.2 Hz), 126.07 (s), 122.92 (s), 121.58 (s), 120.15 (s), 118.95 (s), 116.01 (s), 115.83 (s), 114.35 (s), 111.58 (s), 79.66 (s), 40.99 (s).

3-(1-(2-chlorophenyl)-2-nitroethyl)-1*H*-indole (3h)[3]



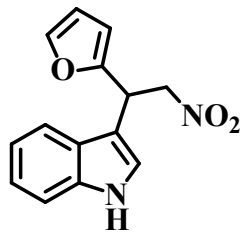
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.46-7.36 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.20-7.11 (m, 4H), 7.08-7.02 (m, 2H), 5.77-5.65 (m, 1H), 4.9-4.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.52, 133.89, 130.17, 128.99, 128.85, 127.29, 126.22, 122.81, 121.97, 120.06, 118.95, 113.33, 111.39, 77.74, 38.00.

3-(2-nitro-1-(4-nitrophenyl)ethyl)-1*H*-indole (3i)[10]



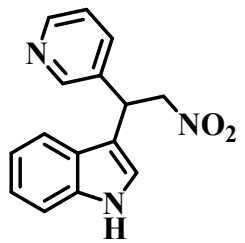
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.22-8.19 (m, 2H), 7.57-7.53 (m, 2H), 7.43-7.39 (m, 2H), 7.25 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.12 (ddd, *J* = 8.0, 5.6, 1.0 Hz, 1H), 7.09-7.07 (m, 1H), 5.35-5.29 (m, 1H), 5.14 (dd, *J* = 12.8, 7.0 Hz, 1H), 5.02 (dd, *J* = 12.8, 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.37, 146.73, 136.52, 128.79, 128.67, 125.66, 124.75, 124.20, 123.15, 121.63, 120.37, 118.52, 112.98, 111.67, 78.74, 41.26.

3-(1-(furan-2-yl)-2-nitroethyl)-1*H*-indole (3j)[3]



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.31-7.23 (m, 2H), 7.15-7.10 (m, 1H), 7.04 (ddd, *J* = 8.0, 7.2, 0.9 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.22 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 5.16 (t, *J* = 7.8 Hz, 1H), 4.96 (dd, *J* = 12.6, 8.1 Hz, 1H), 4.82 (dd, *J* = 12.6, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.25, 142.27, 136.37, 125.73, 122.74, 122.67, 120.09, 118.72, 111.65, 111.57, 110.50, 107.40, 77.92, 35.75.

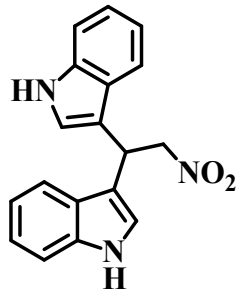
3-(2-nitro-1-(pyridin-3-yl)ethyl)-1*H*-indole (3k)[11]



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 1.3 Hz, 1H), 8.49-8.41 (m, 1H), 8.34 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 15.4, 8.1 Hz, 2H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.14 (dd, *J* = 11.3, 3.8 Hz, 1H), 7.02 (dd, *J* = 11.2, 3.9 Hz, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 5.15 (t, *J* = 8.0 Hz, 1H), 5.03 (dd, *J* = 12.7, 7.2 Hz, 1H), 4.89 (dd, *J* = 12.7, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.11, 148.72,

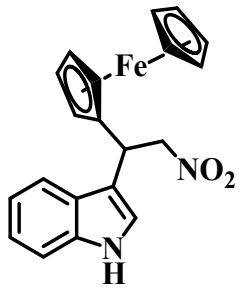
136.55, 135.59, 135.15, 125.71, 123.86, 123.00, 121.71, 120.24, 118.60, 113.14, 111.61, 78.86, 39.18.

3,3'-(2-nitroethane-1,1-diyl)bis(1*H*-indole) (3l)[12]



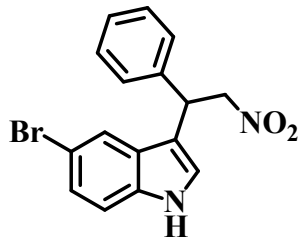
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.49 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 2.4 Hz, 2H), 5.38 (t, J = 7.8 Hz, 1H), 4.97 (d, J = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.60, 126.16, 122.48, 122.42, 119.82, 118.97, 114.25, 111.50, 79.18, 33.80.

3-(1-ferrocenyl)-2-nitroethyl-1*H*-indole (3m)[13]



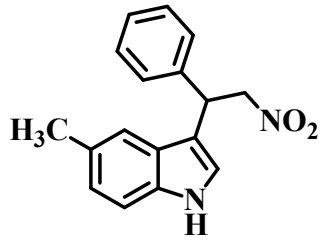
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.38 (d, J = 6.6 Hz, 1H), 7.23 (s, 1H), 7.14 (t, J = 6.8 Hz, 1H), 7.03 (s, 1H), 5.01 (dd, J = 20.5, 8.1 Hz, 2H), 4.91 (d, J = 8.6 Hz, 1H), 4.26 (d, J = 23.8 Hz, 4H), 4.16 (s, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.26, 125.86, 122.44, 122.37, 119.87, 119.00, 115.33, 111.54, 88.70, 80.53, 69.28, 68.43, 68.35, 67.83, 66.94, 36.60.

5-bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3n)[3]



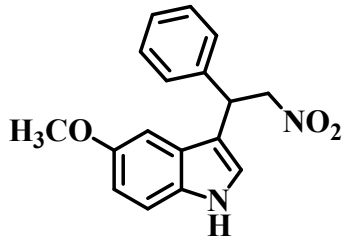
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.27-7.24 (m, 1H), 7.23-7.22 (m, 2H), 7.22-7.18 (m, 2H), 7.17 (d, J = 1.9 Hz, 1H), 7.12 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 2.2 Hz, 1H), 5.04 (t, J = 8.0 Hz, 1H), 4.93 (dd, J = 12.5, 8.0 Hz, 1H), 4.83 (dd, J = 12.5, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.77, 135.15, 129.05, 127.91, 127.76, 127.66, 125.69, 122.77, 121.50, 114.13, 113.29, 112.85, 79.43, 41.33.

5-methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3o)[14]



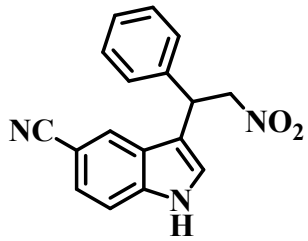
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.41-7.33 (m, 4H), 7.33-7.25 (m, 3H), 7.06 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 1.5 Hz, 1H), 5.20 (t, J = 8.0 Hz, 1H), 5.08 (dd, J = 12.5, 7.4 Hz, 1H), 4.96 (dd, J = 12.5, 8.6 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.26, 134.82, 129.31, 128.93, 127.78, 127.55, 126.35, 124.37, 121.84, 118.44, 113.87, 111.10, 79.55, 41.53, 21.54.

5-methoxy-3-(2-nitro-1-phenylethyl)-1*H*-indole (3p)[3]



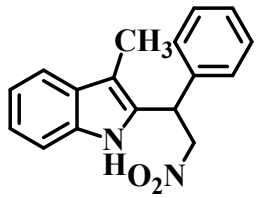
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.94 (s, 1H), 7.24 (dd, *J* = 7.7, 5.7 Hz, 4H), 7.20-7.13 (m, 2H), 6.91 (s, 1H), 6.83-6.71 (m, 2H), 5.05 (t, *J* = 7.9 Hz, 1H), 4.96 (dd, *J* = 12.4, 7.5 Hz, 1H), 4.85 (dd, *J* = 12.4, 8.4 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.20, 139.17, 131.61, 128.94, 127.78, 127.59, 126.58, 122.30, 114.09, 112.75, 112.12, 100.87, 79.51, 55.86, 41.54.

3-(2-nitro-1-phenylethyl)-1*H*-indole-5-carbonitrile (3q)[11]



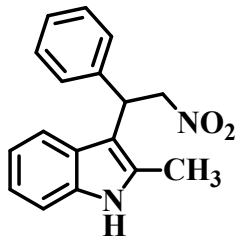
^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.63 (s, 1H), 7.64 (s, 1H), 7.34-7.30 (m, 2H), 7.28-7.24 (m, 2H), 7.22-7.19 (m, 3H), 7.17 (dd, *J* = 2.4, 0.7 Hz, 1H), 5.09 (t, *J* = 8.0 Hz, 1H), 4.96 (dd, *J* = 12.6, 8.6 Hz, 1H), 4.86 (dd, *J* = 12.6, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.44, 138.25, 129.21, 128.02, 127.64, 126.09, 125.59, 124.72, 123.65, 120.45, 115.32, 112.43, 103.07, 79.41, 41.25.

3-methyl-2-(2-nitro-1-phenylethyl)-1*H*-indole (3t)[15]



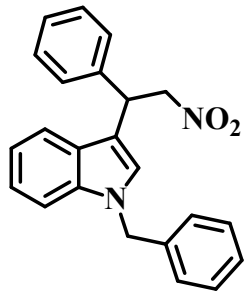
1H NMR (500 MHz, CDCl3): *δ* 7.56 (s, 1H), 7.48-7.41 (m, 1H), 7.34-7.28 (m, 2H), 7.25 (dt, *J* = 4.4, 1.8 Hz, 1H), 7.23-7.20 (m, 2H), 7.16-7.13 (m, 1H), 7.05 (dddd, *J* = 8.8, 8.1, 7.0, 1.2 Hz, 2H), 5.17 (t, *J* = 7.9 Hz, 1H), 5.00 (dd, *J* = 12.9, 8.3 Hz, 1H), 4.87 (dd, *J* = 12.9, 7.7 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 137.09, 135.80, 130.61, 129.41, 129.13, 128.07, 127.31, 122.32, 119.65, 118.76, 110.82, 109.46, 77.65, 41.13, 8.63.

2-methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3u)[10]



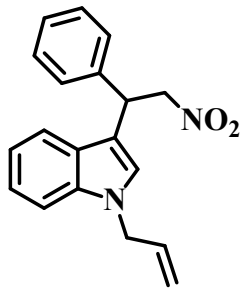
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.79 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.26-7.12 (m, 6H), 7.02 (dd, *J* = 11.2, 3.9 Hz, 1H), 6.94 (dd, *J* = 11.1, 3.9 Hz, 1H), 5.18-5.08 (m, 2H), 5.08-4.98 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.52, 135.42, 132.87, 128.80, 127.33, 127.09, 126.87, 121.36, 119.77, 118.62, 110.72, 108.88, 78.64, 40.45, 12.02.

1-benzyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3v)[16]



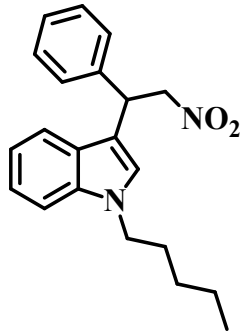
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.9 Hz, 1H), 7.29 (q, *J* = 6.2 Hz, 5H), 7.25-7.18 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 3H), 6.93 (s, 1H), 5.24 (s, 2H), 5.16 (t, *J* = 7.9 Hz, 1H), 5.01 (dd, *J* = 12.4, 7.5 Hz, 1H), 4.90 (dd, *J* = 12.4, 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.28, 137.20, 136.98, 128.94, 128.85, 127.78, 127.74, 127.56, 126.84, 126.66, 125.73, 122.47, 119.74, 119.16, 113.51, 110.05, 79.64, 50.13, 41.59.

1-allyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3w)[16]



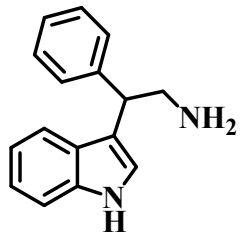
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.41-7.27 (m, 6H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.00 (ddt, *J* = 16.1, 10.5, 5.3 Hz, 1H), 5.23 (t, *J* = 10.2 Hz, 2H), 5.10 (dd, *J* = 18.8, 6.4 Hz, 2H), 4.97 (dd, *J* = 12.4, 8.5 Hz, 1H), 4.72 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.34, 136.75, 133.21, 128.93, 127.78, 127.54, 126.78, 125.30, 122.29, 119.63, 119.12, 117.53, 113.23, 109.92, 79.62, 48.86, 41.58.

3-(2-nitro-1-phenylethyl)-1-pentyl-1*H*-indole (3x)



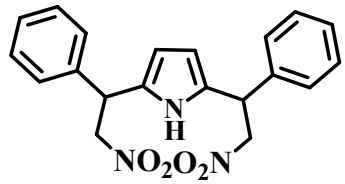
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.29-7.21 (m, 5H), 7.20-7.17 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 11.1, 3.9 Hz, 1H), 6.83 (s, 1H), 5.10 (t, *J* = 8.0 Hz, 1H), 4.98 (dd, *J* = 12.4, 7.5 Hz, 1H), 4.86 (dd, *J* = 12.4, 8.5 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 2H), 1.79-1.67 (m, 2H), 1.30-1.17 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.43, 136.59, 128.90, 127.77, 127.49, 126.65, 125.33, 122.05, 119.34, 119.07, 112.64, 109.71, 79.64, 46.47, 41.57, 29.88, 29.11, 22.29, 13.97. HR-MS: *m/z* 337.1917 $[M+H]^+$.

2-(1*H*-indol-3-yl)-2-phenylethanamine (4a)[17]



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.17-7.13 (m, 4H), 7.07 (ddd, J = 11.1, 5.6, 3.2 Hz, 1H), 7.05-7.01 (m, 1H), 6.91 (dd, J = 11.5, 4.4 Hz, 2H), 4.14 (t, J = 7.4 Hz, 1H), 3.26 (dd, J = 12.3, 7.4 Hz, 1H), 3.12 (dd, J = 12.2, 7.7 Hz, 1H), 2.55 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.56, 136.68, 128.68, 128.22, 127.05, 126.67, 122.24, 121.71, 119.48, 119.45, 116.61, 111.43, 46.50, 45.63.

2,5-bis(2-nitro-1-phenylethyl)-1*H*-pyrrole (6a)[13]



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.35-7.27 (m, 6H), 7.19-7.12 (m, 4H), 6.00 (dd, J = 9.7, 2.8 Hz, 2H), 4.93-4.87 (m, 2H), 4.81-4.70 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.85, 129.66, 129.29, 128.28, 127.91, 106.65, 106.29, 79.30, 42.92.

3. Powder XRD pattern of ANO

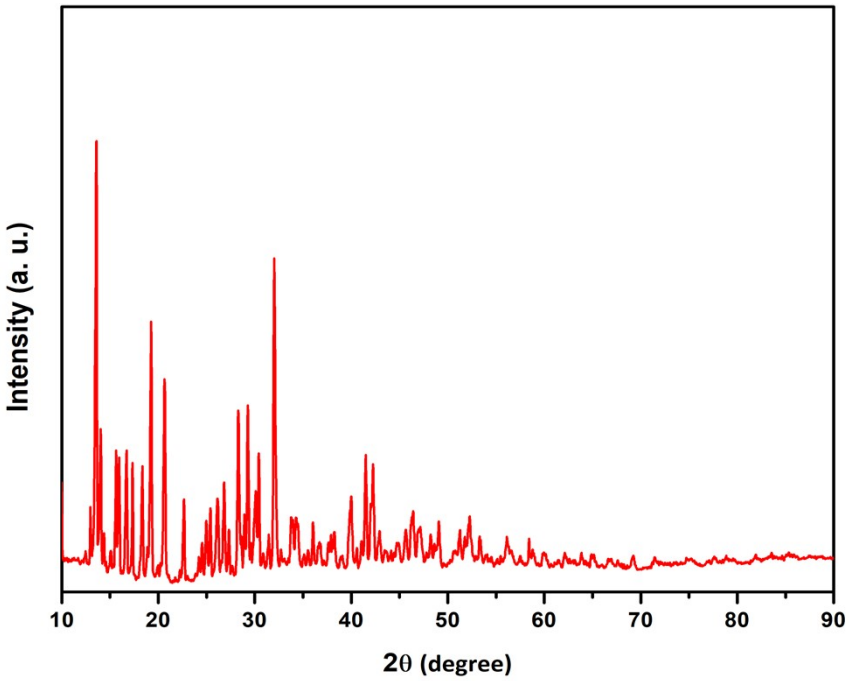


Fig. S1. Powder XRD pattern of ANO[18,19]

4. ^{1}H NMR spectra of *N*-alkylated indoles (1j-1l) and nitroalkenes (2b-2m)

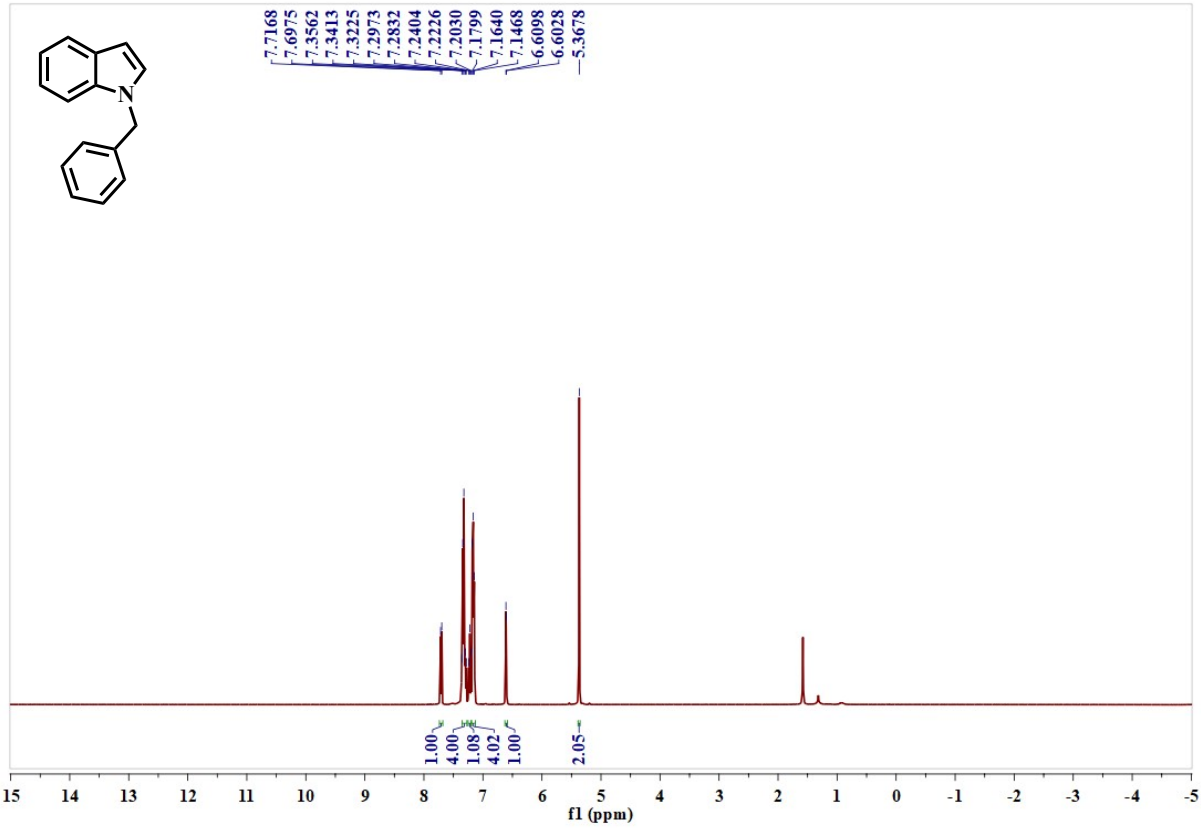


Fig. S2. ^{1}H NMR spectrum of **1j**.

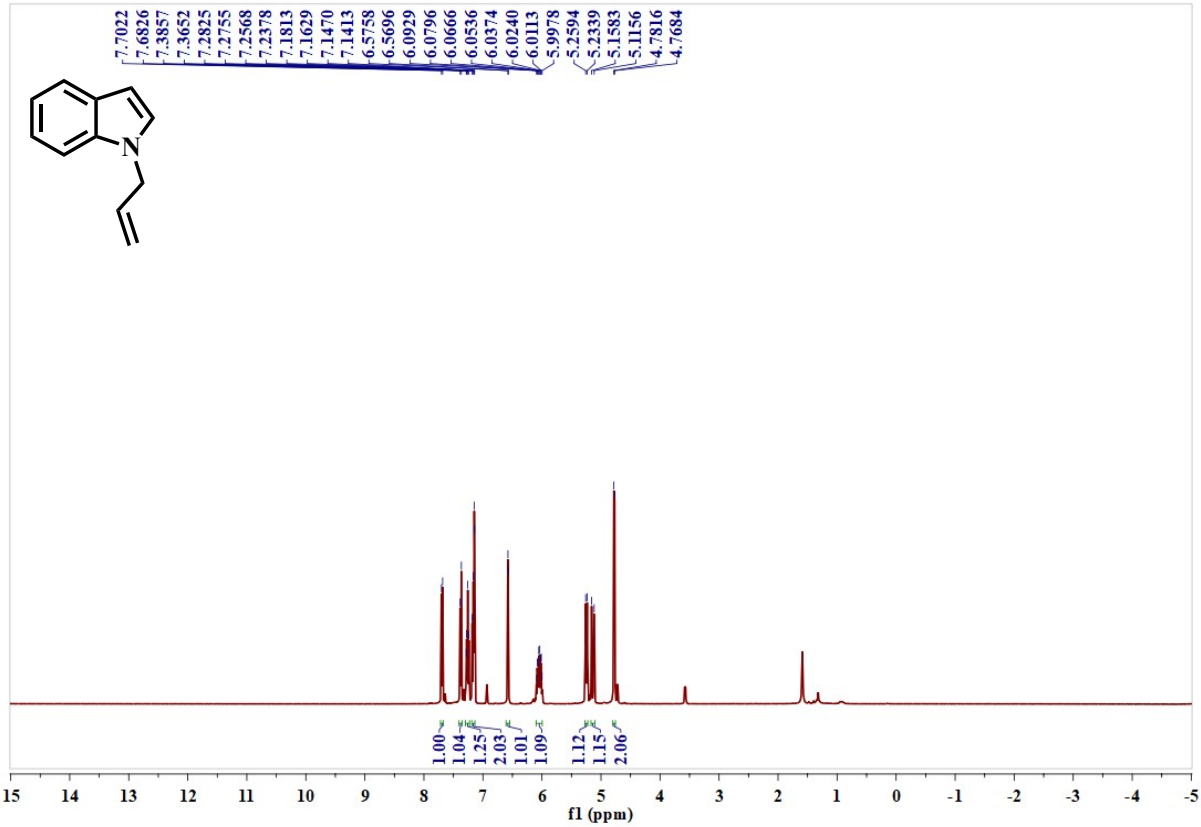


Fig. S3. ^{1}H NMR spectrum of **1k**.

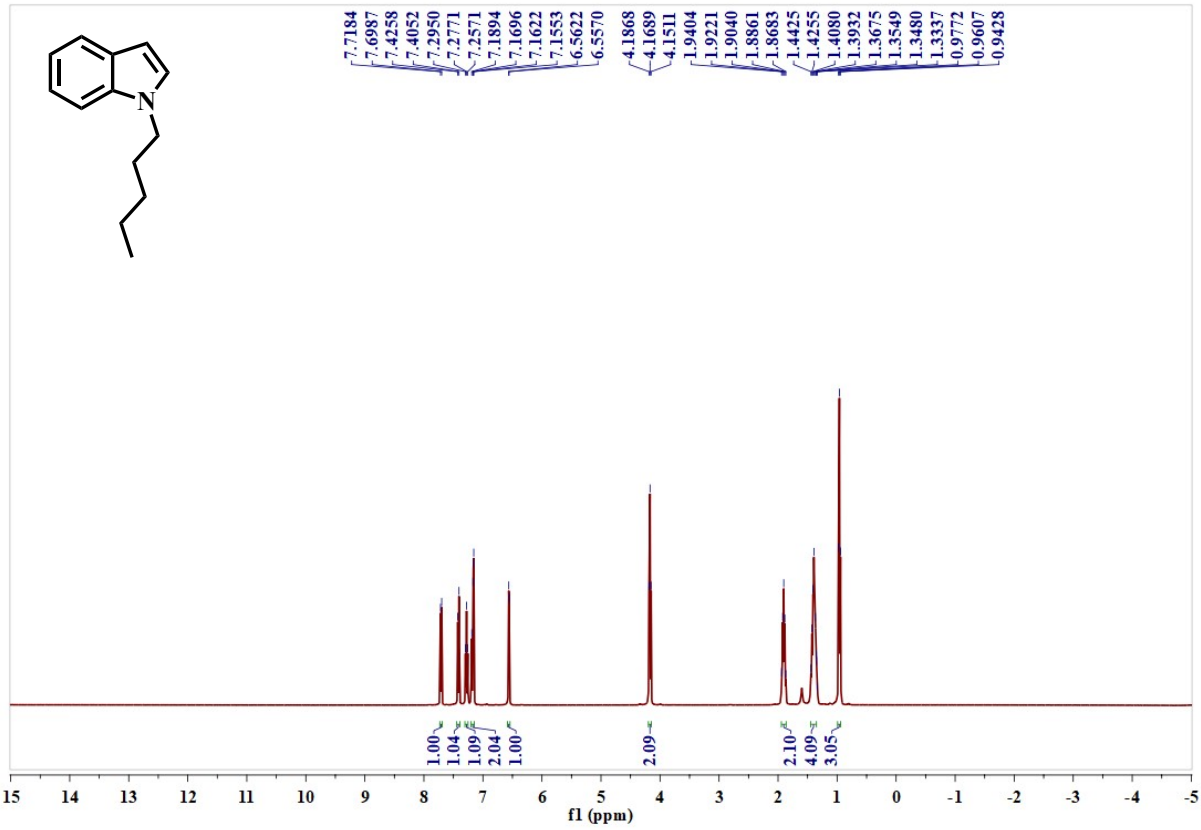


Fig. S4. ^{1}H NMR spectrum of **1l**.

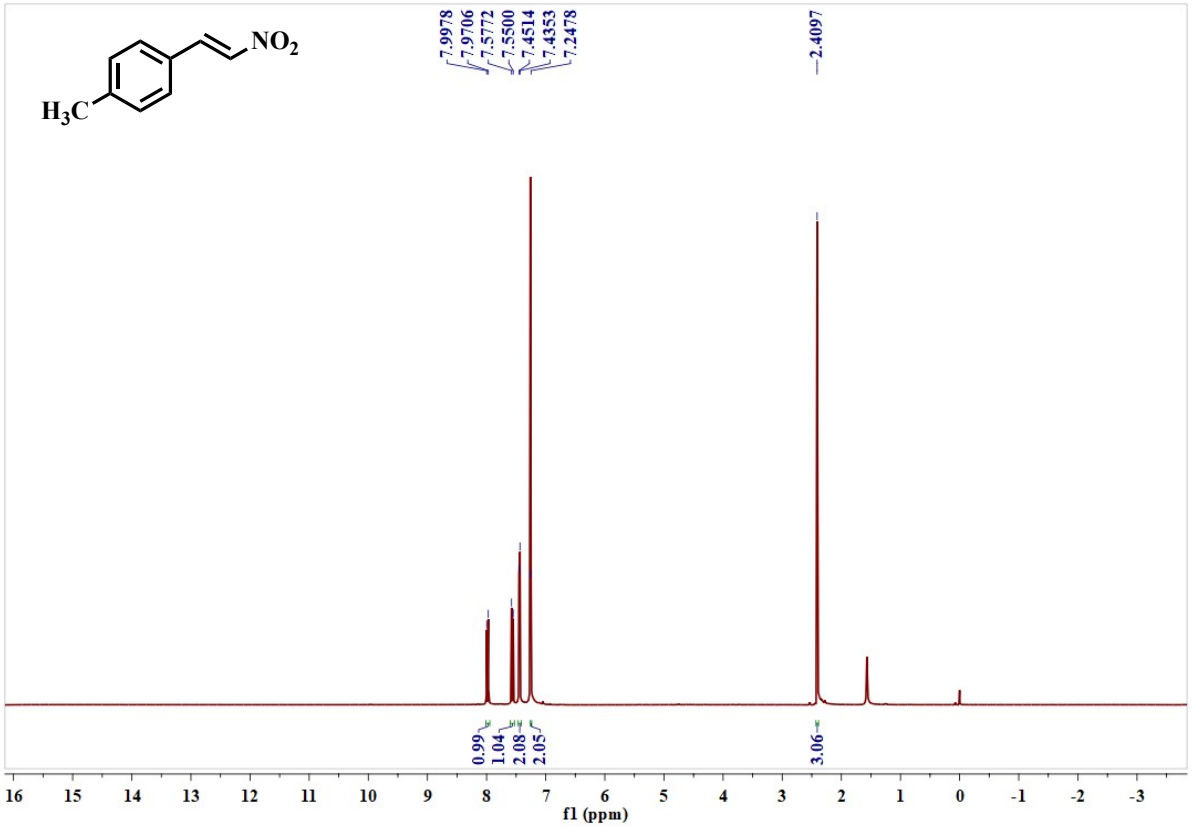


Fig. S5. ^{1}H NMR spectrum of **2b**.

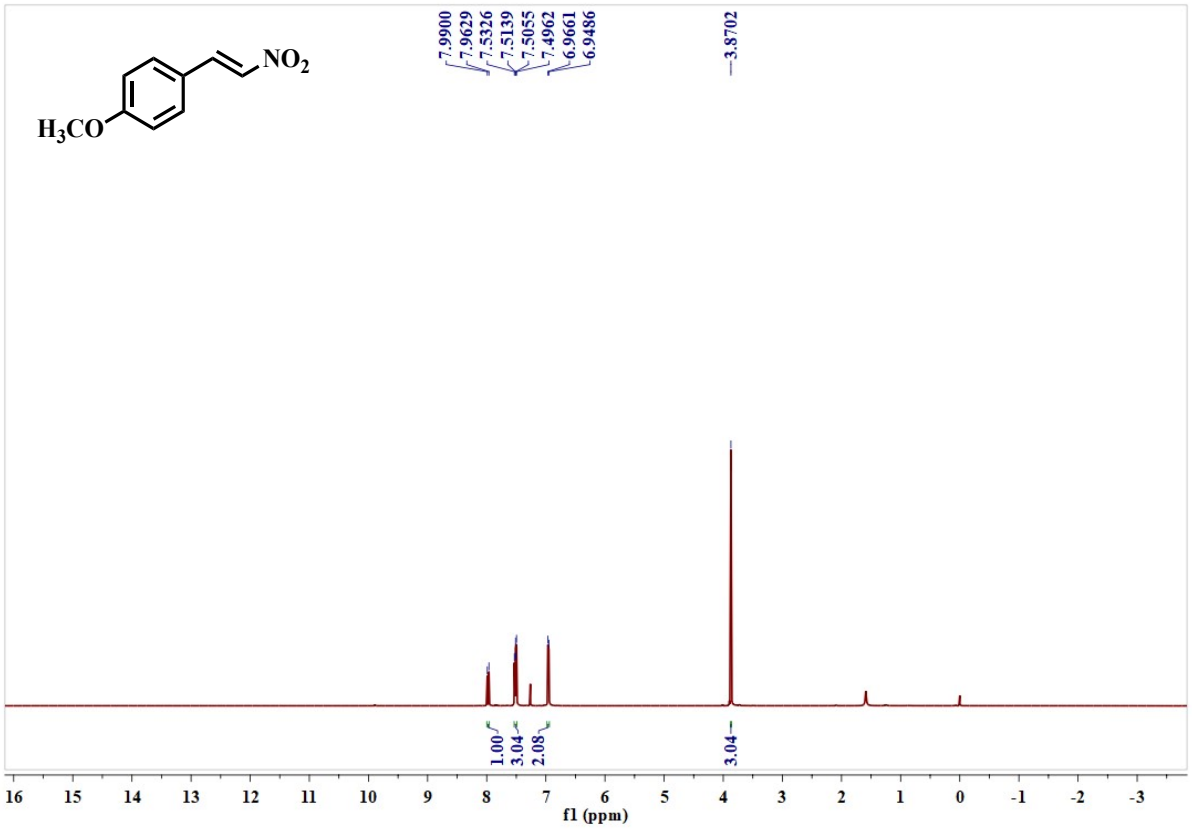


Fig. S6. ^{1}H NMR spectrum of **2c**.

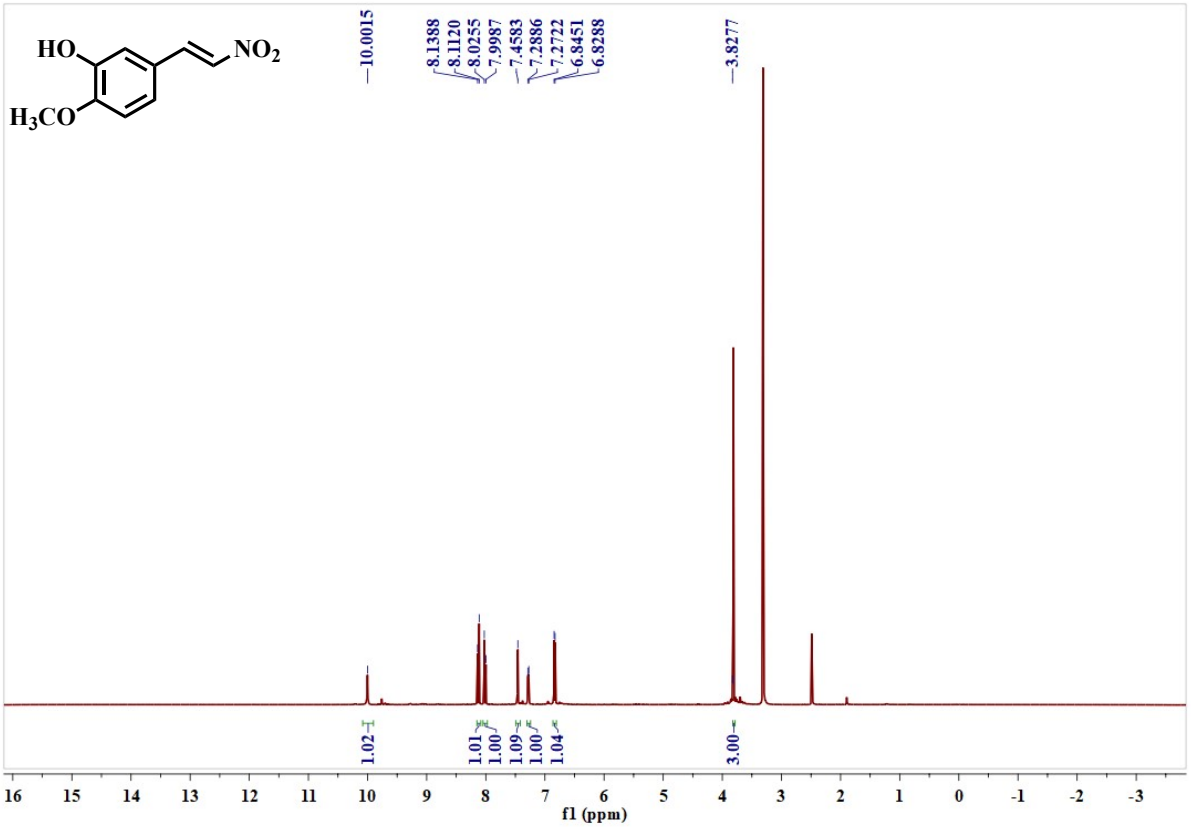


Fig. S7. ^{1}H NMR spectrum of **2d**.

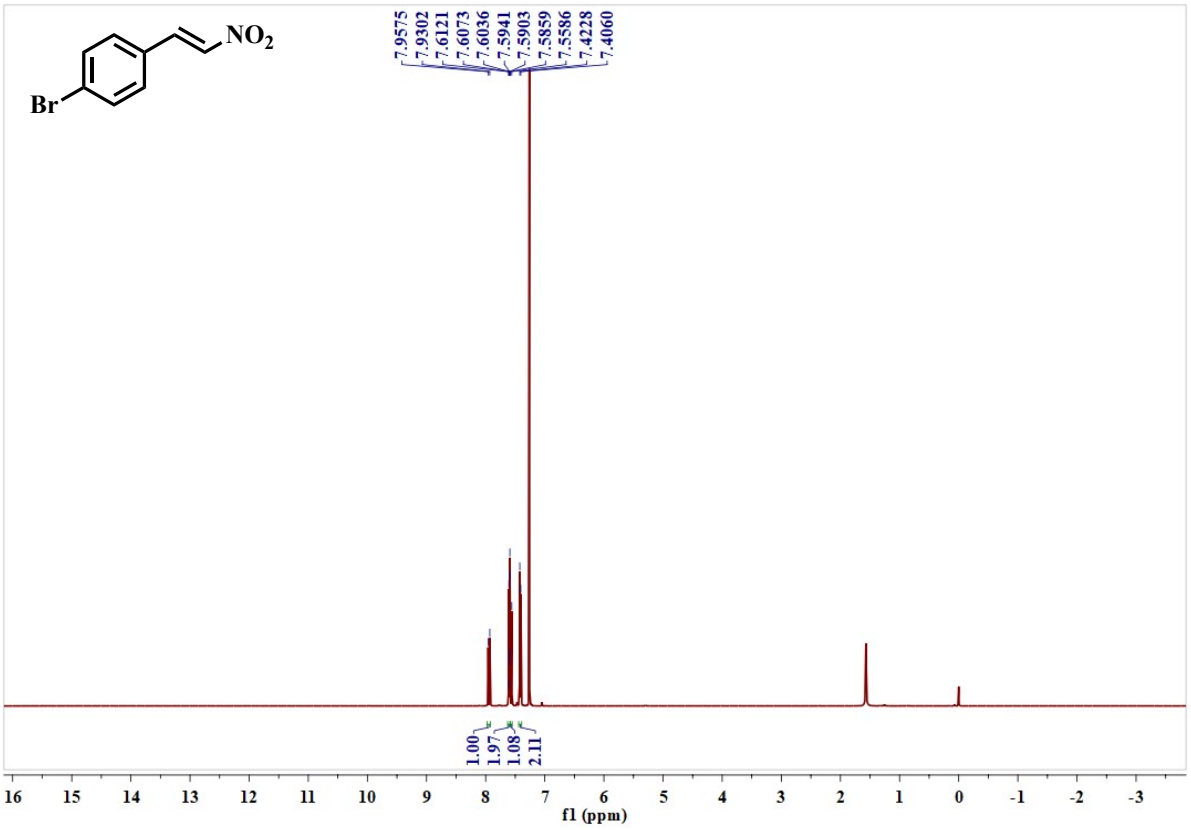


Fig. S8. ^{1}H NMR spectrum of **2e**.

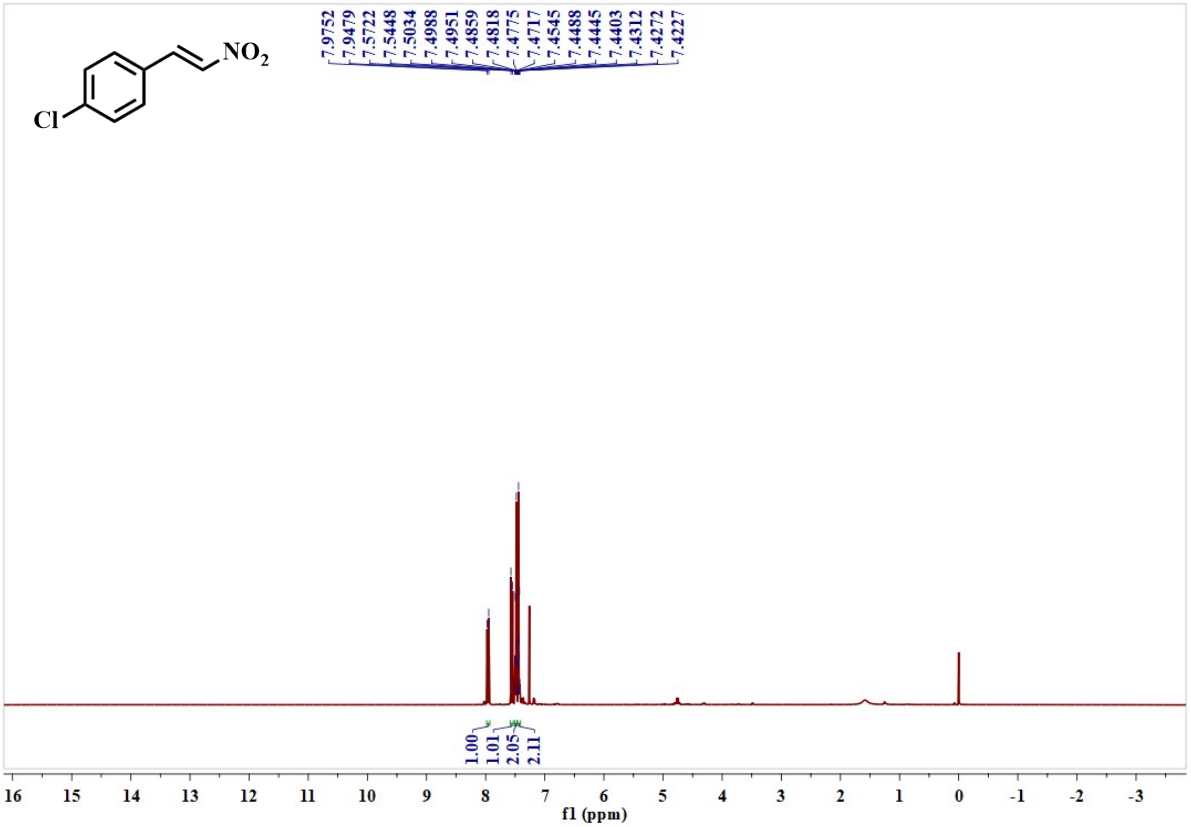


Fig. S9. ^{1}H NMR spectrum of **2f**.

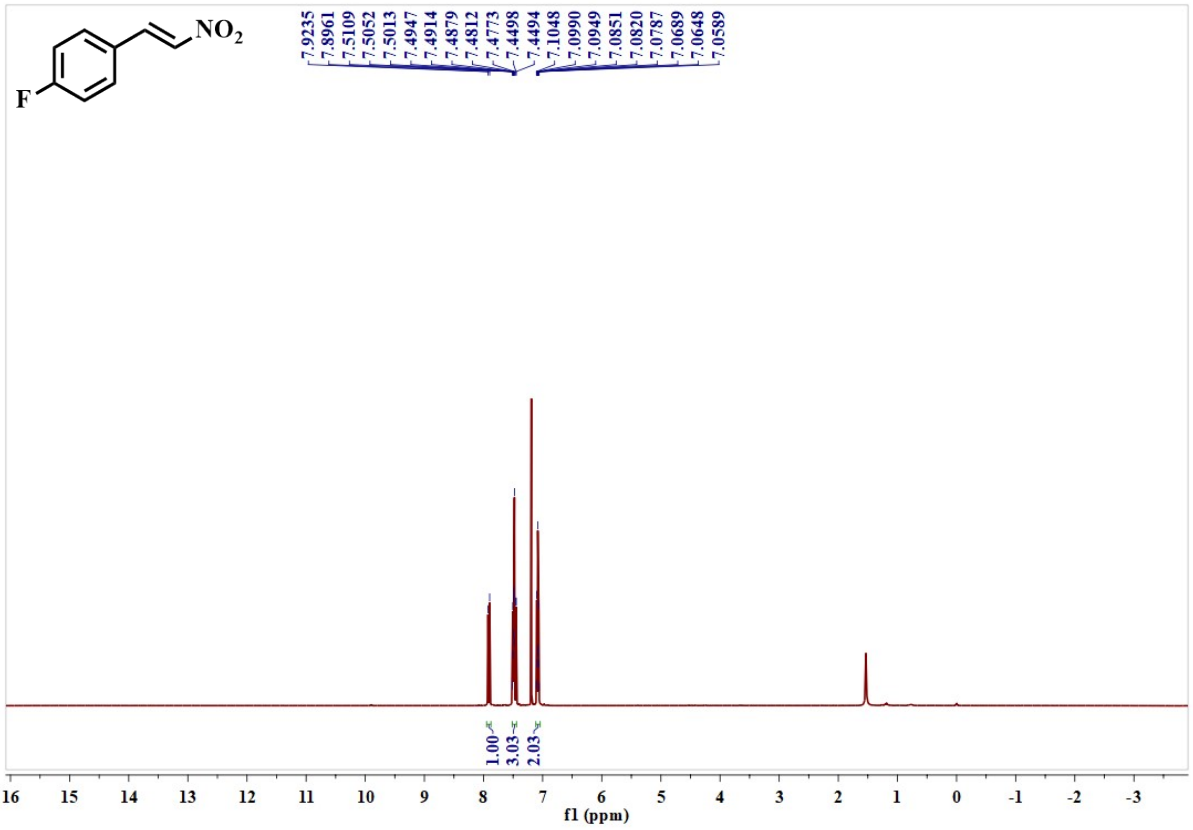


Fig. S10. ^{1}H NMR spectrum of **2g**.

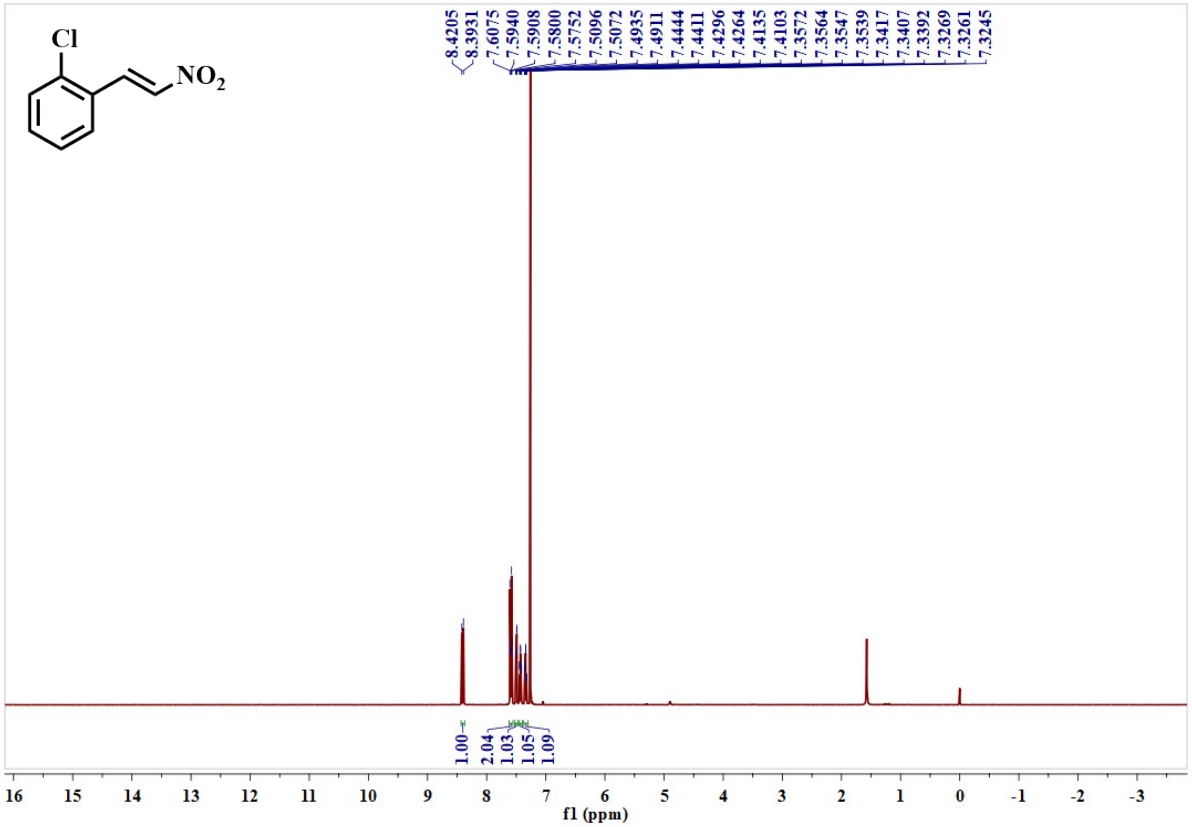


Fig. S11. ^{1}H NMR spectrum of **2h**.

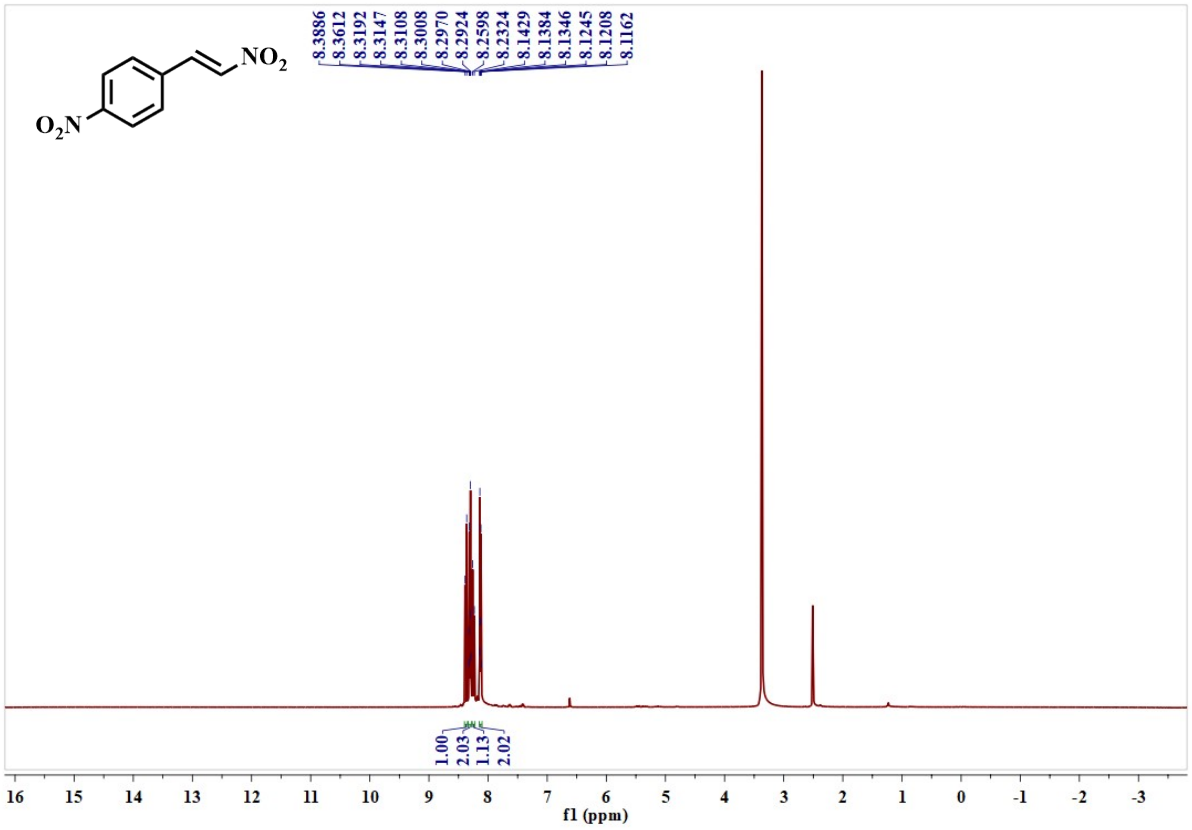


Fig. S12. ^{1}H NMR spectrum of **2i**.

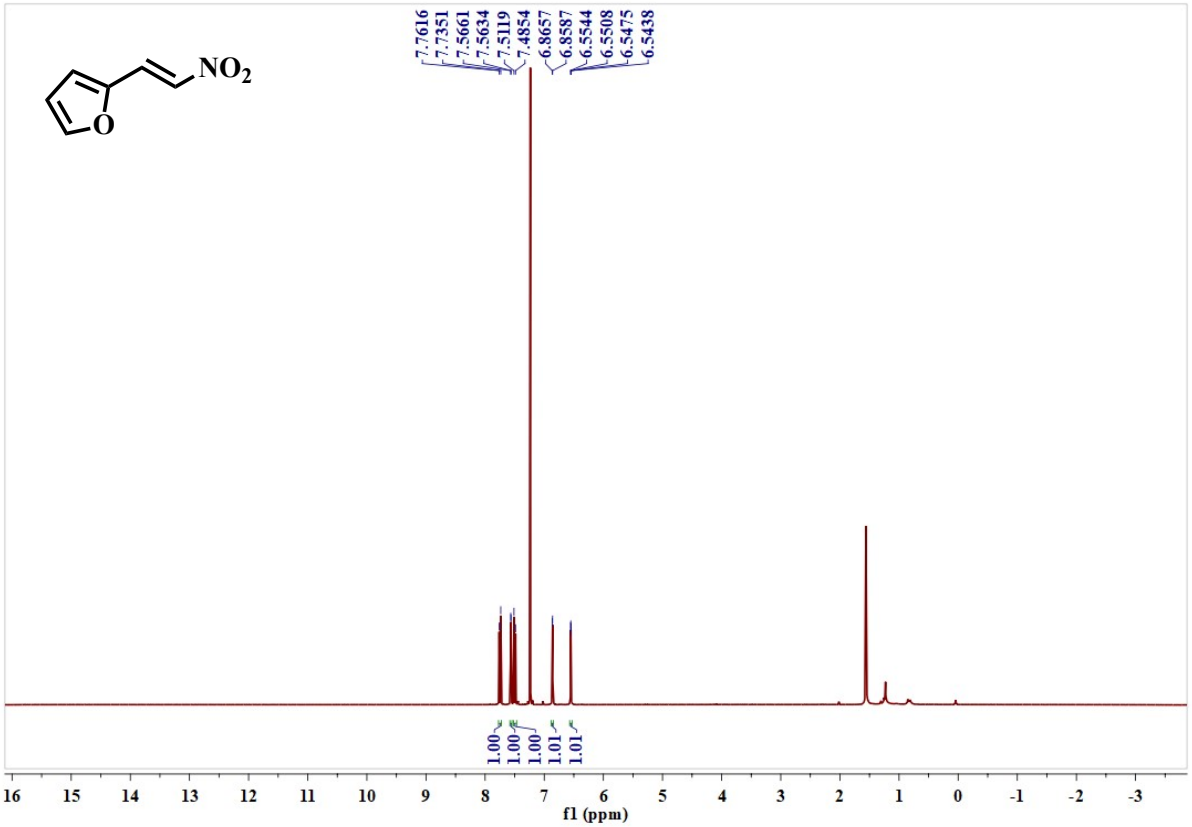


Fig. S13. ^{1}H NMR spectrum of **2j**.

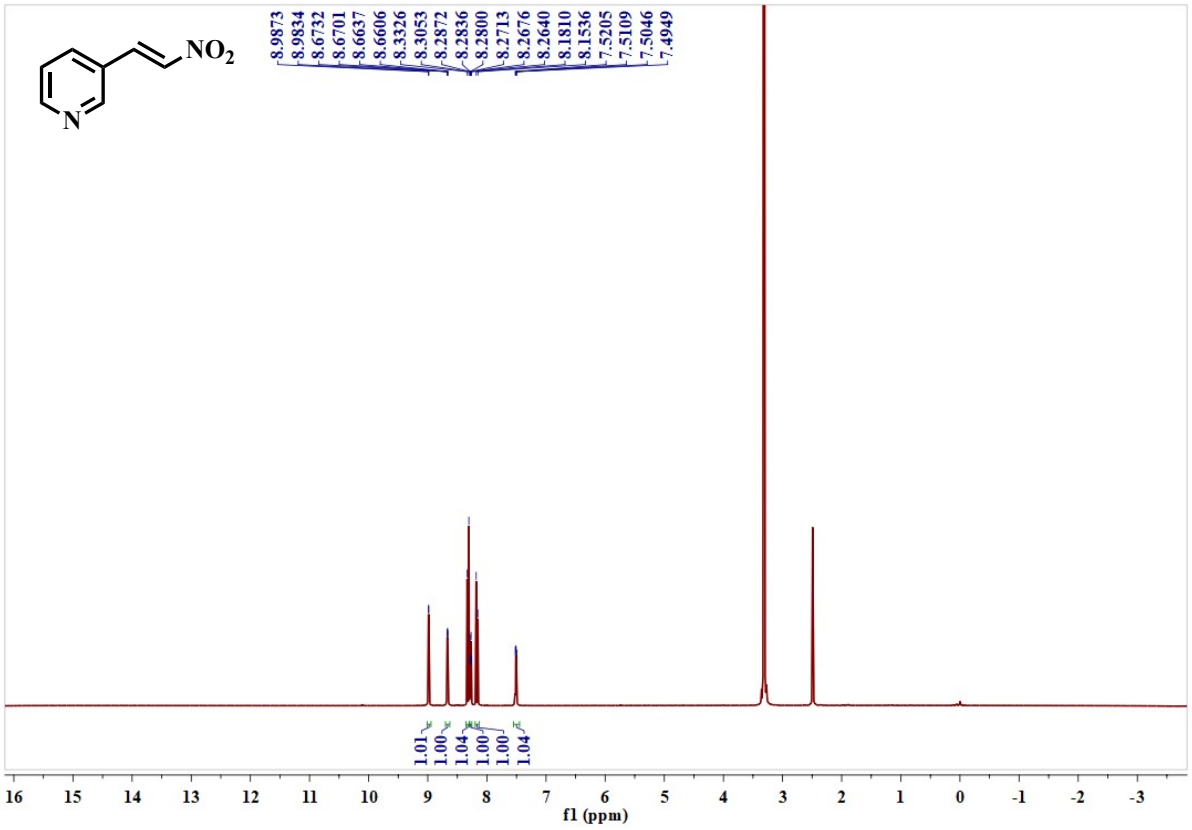


Fig. S14. ^{1}H NMR spectrum of **2k**.

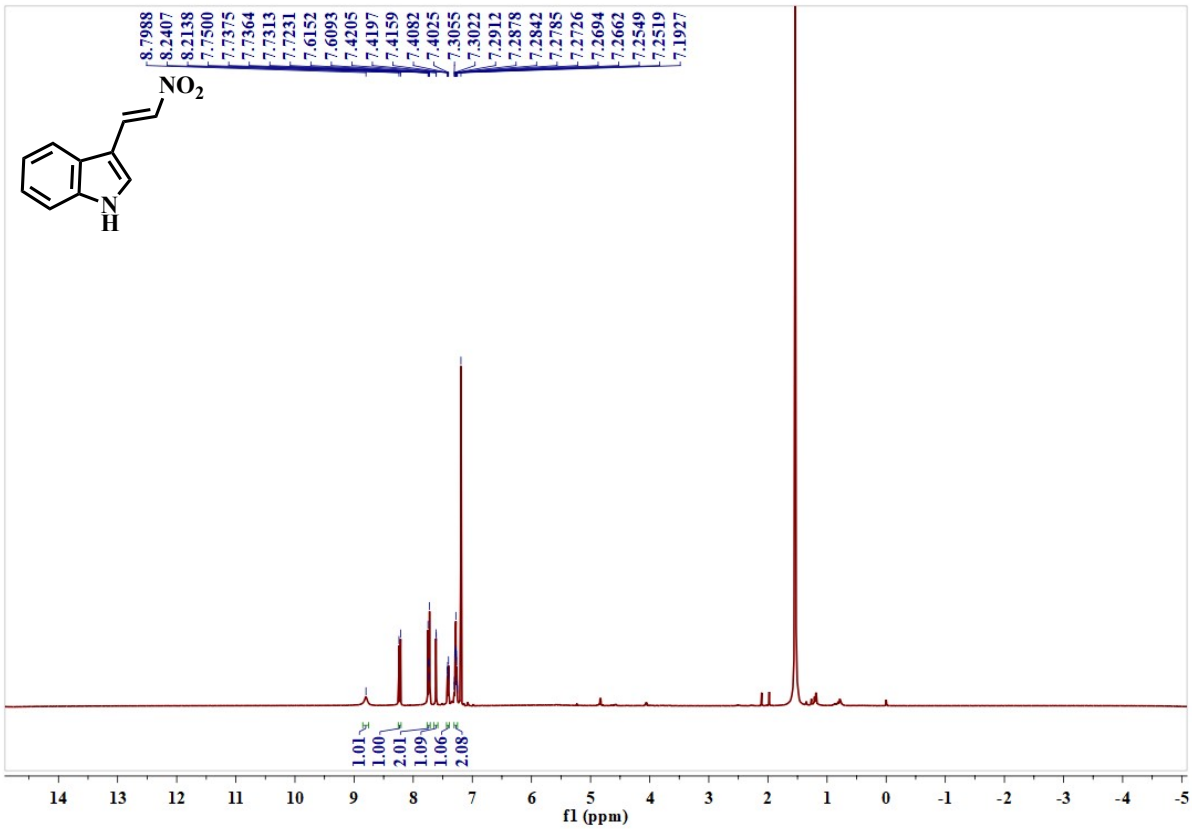


Fig. S15. ^{1}H NMR spectrum of **2l**.

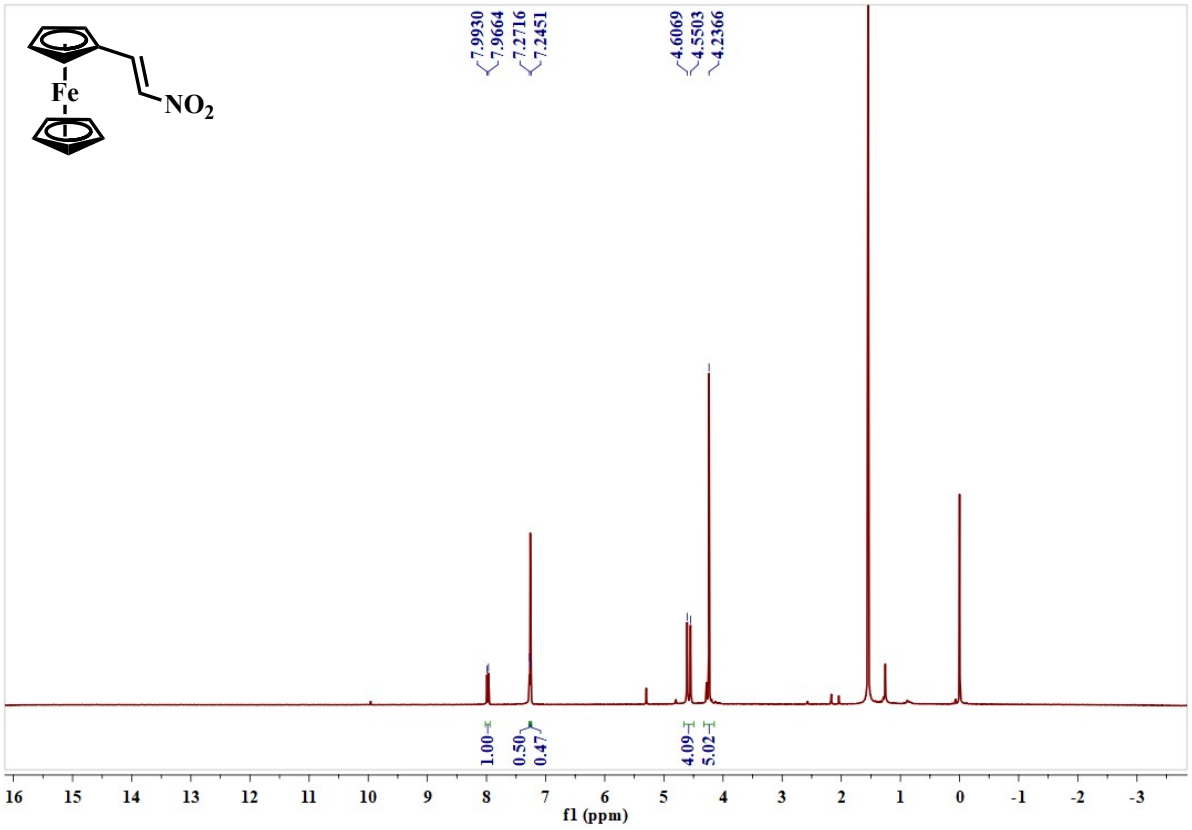


Fig. S16. ^{1}H NMR spectrum of **2m**.

5. ^{1}H and ^{13}C NMR spectra of alkylated products 3a-3x, 4a and 6a

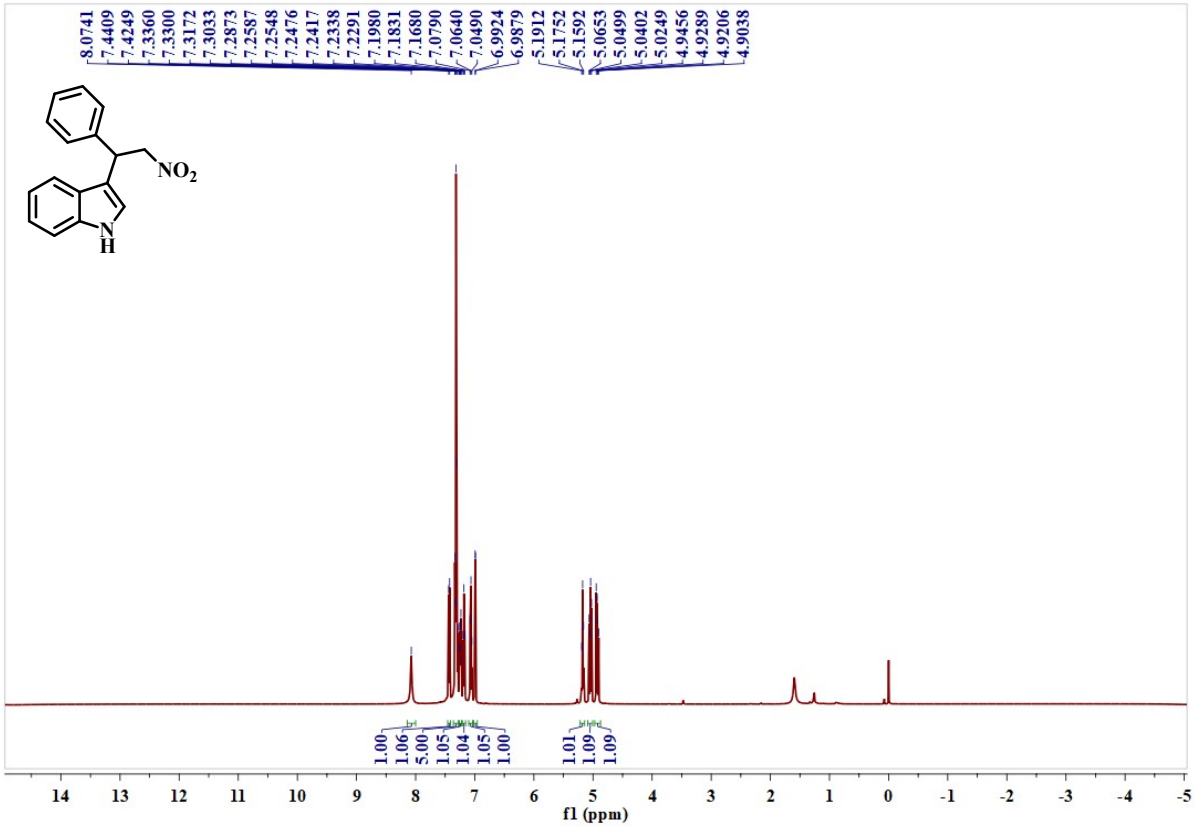


Fig. S17. ^{1}H NMR spectrum of **3a**.

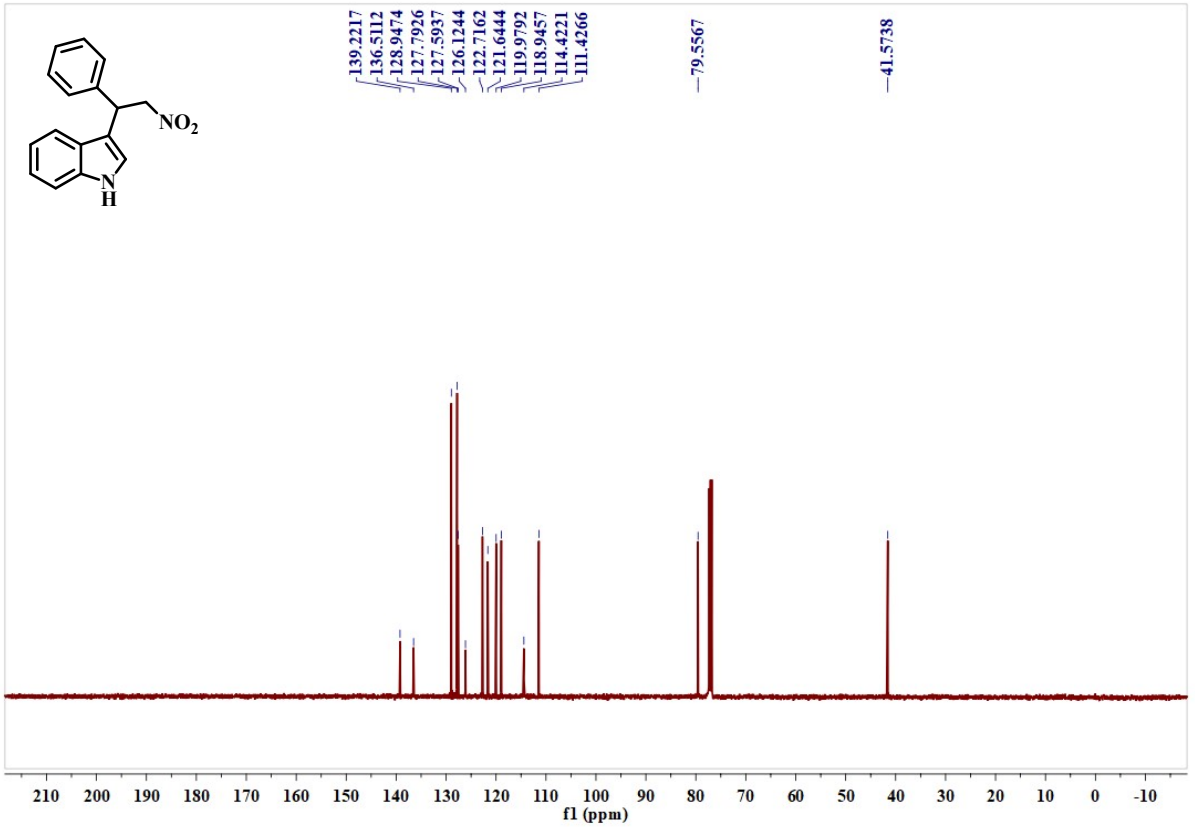


Fig. S18. ^{13}C NMR spectrum of **3a**.

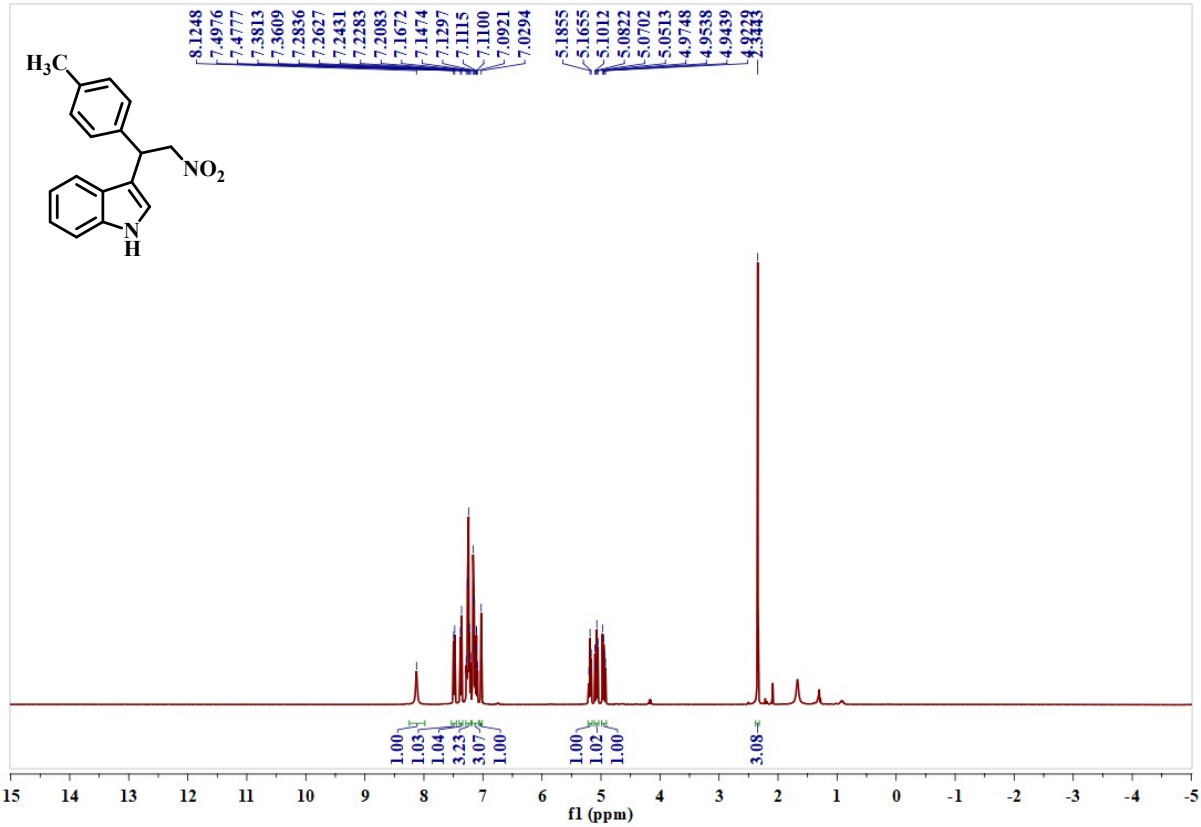


Fig. S19. ^{1}H NMR spectrum of **3b**.

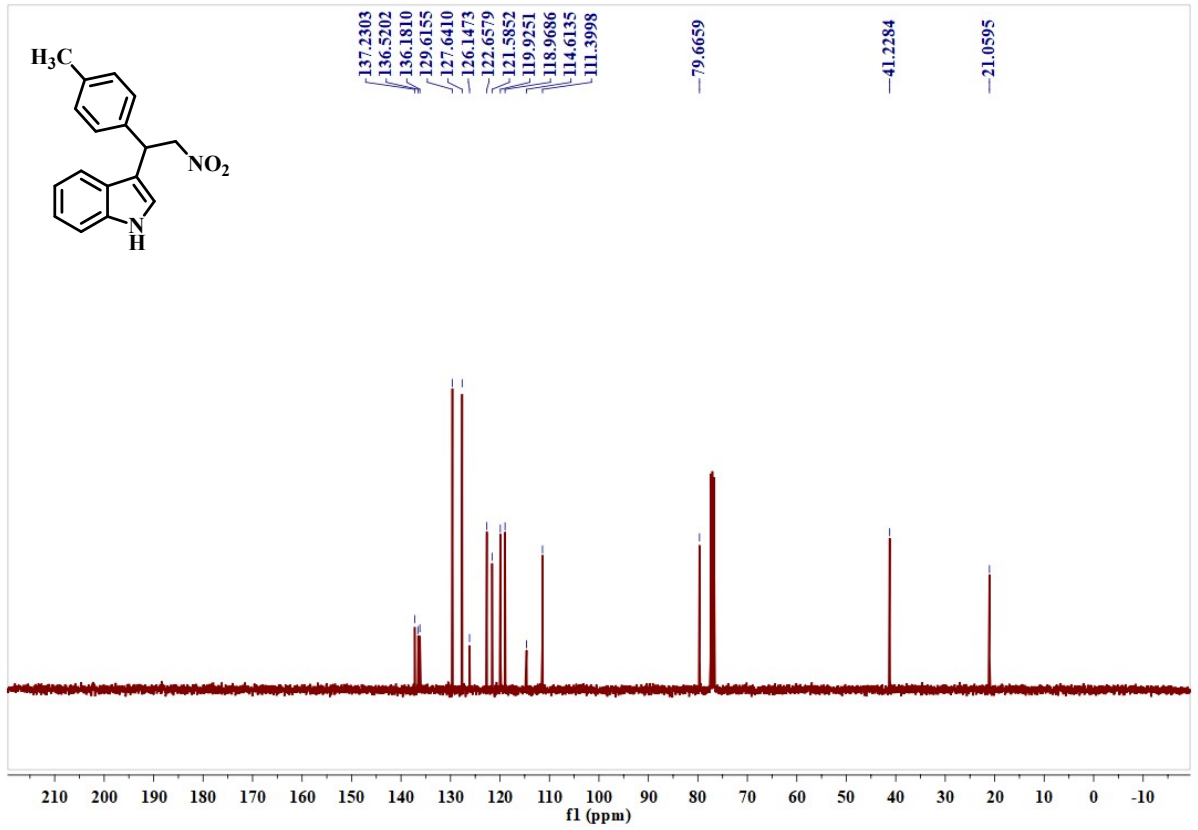


Fig. S20. ^{13}C NMR spectrum of **3b**.

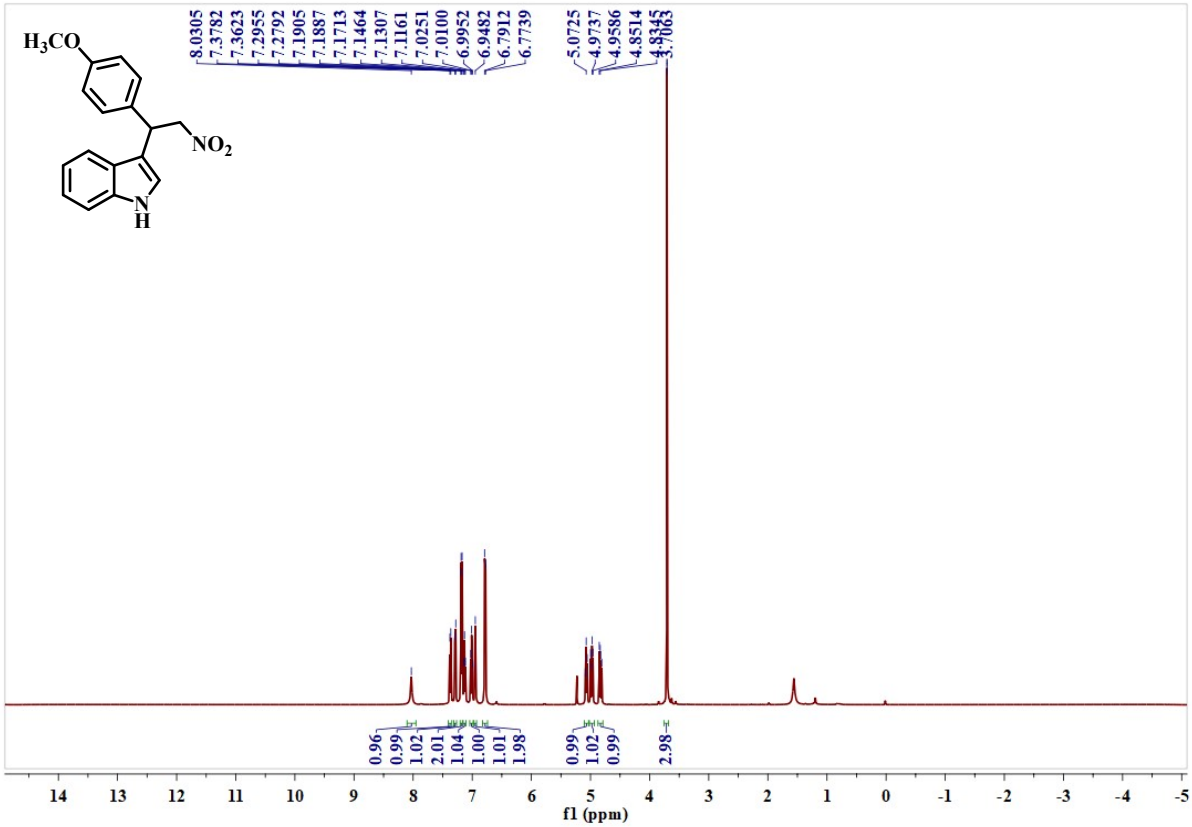


Fig. S21. ^{1}H NMR spectrum of **3c**.

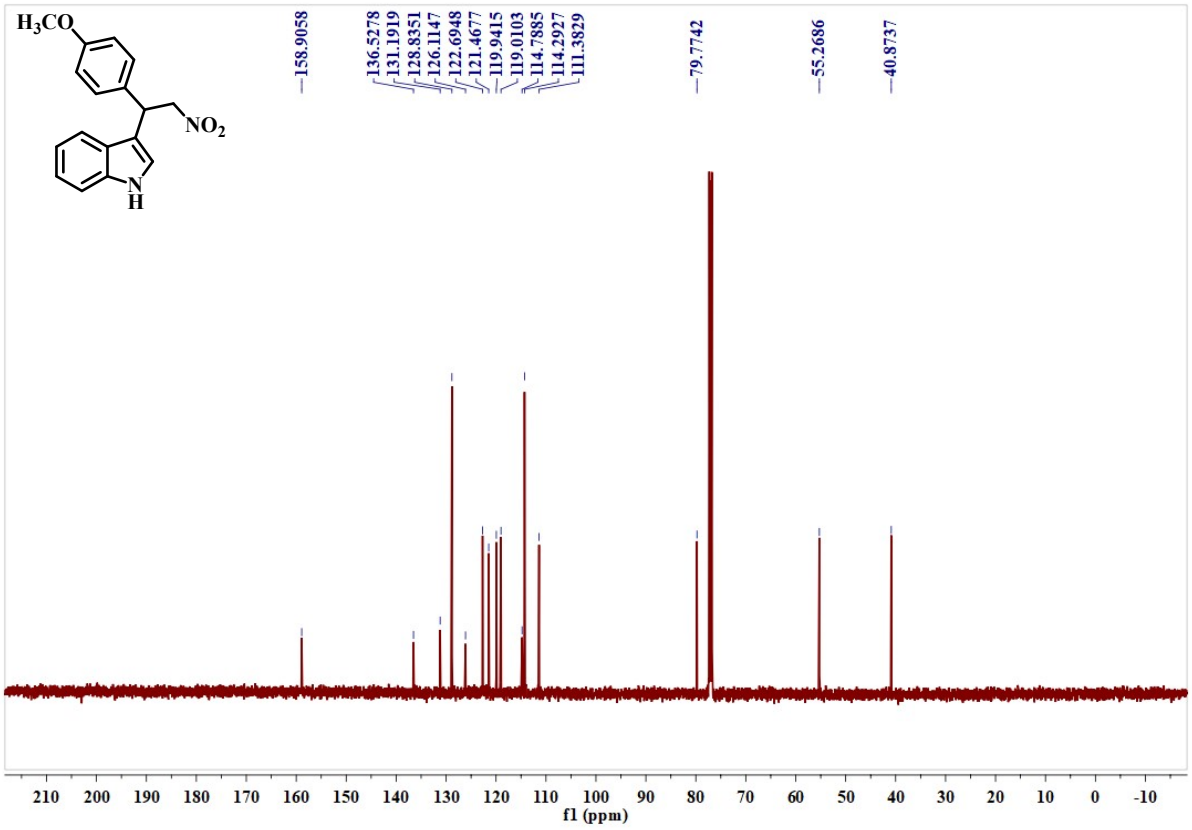


Fig. S22. ^{13}C NMR spectrum of **3c**.

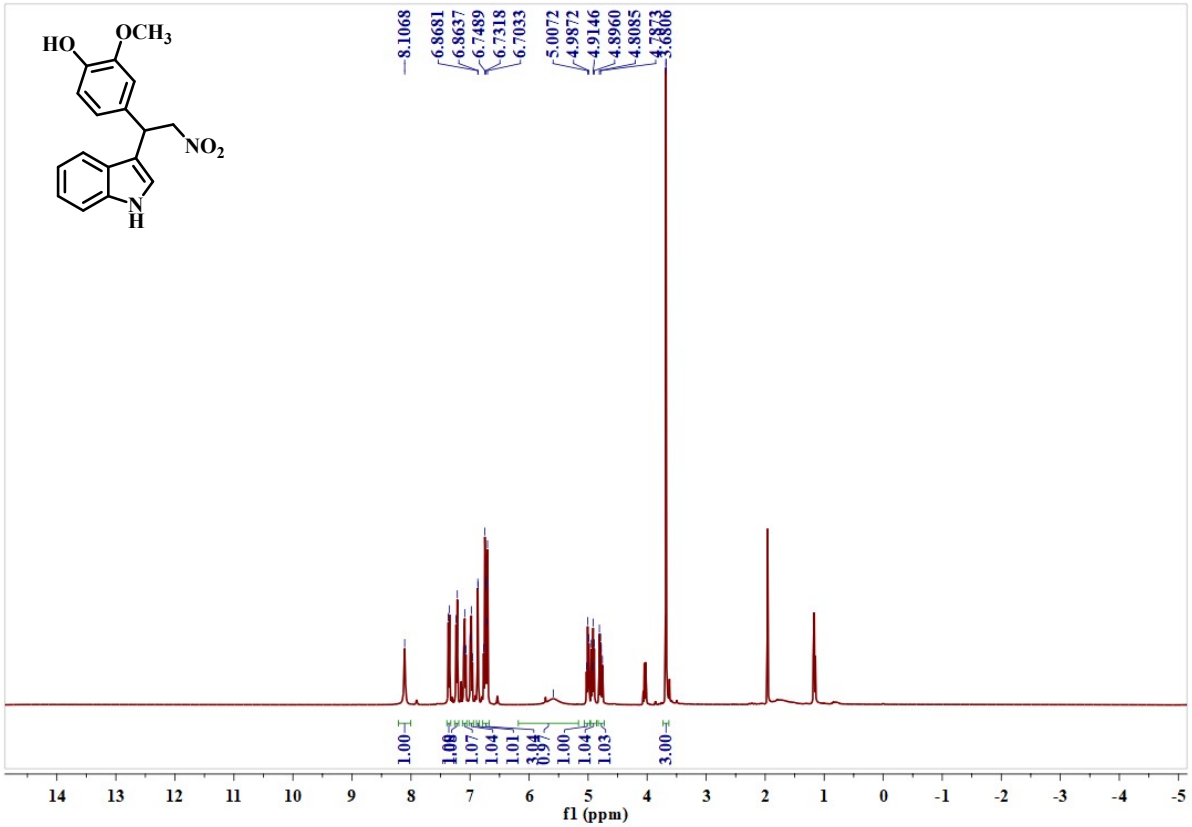


Fig. S23. ^{1}H NMR spectrum of **3d**.

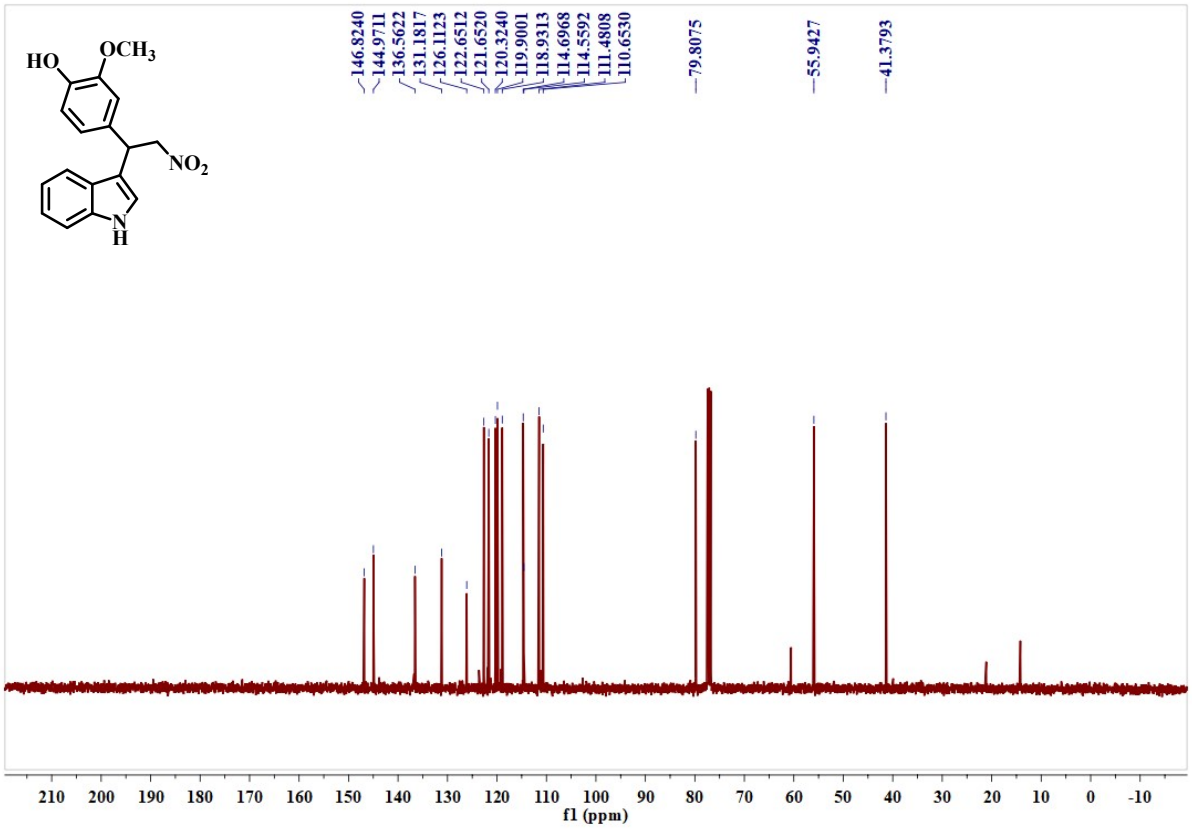


Fig. S24. ^{13}C NMR spectrum of **3d**.

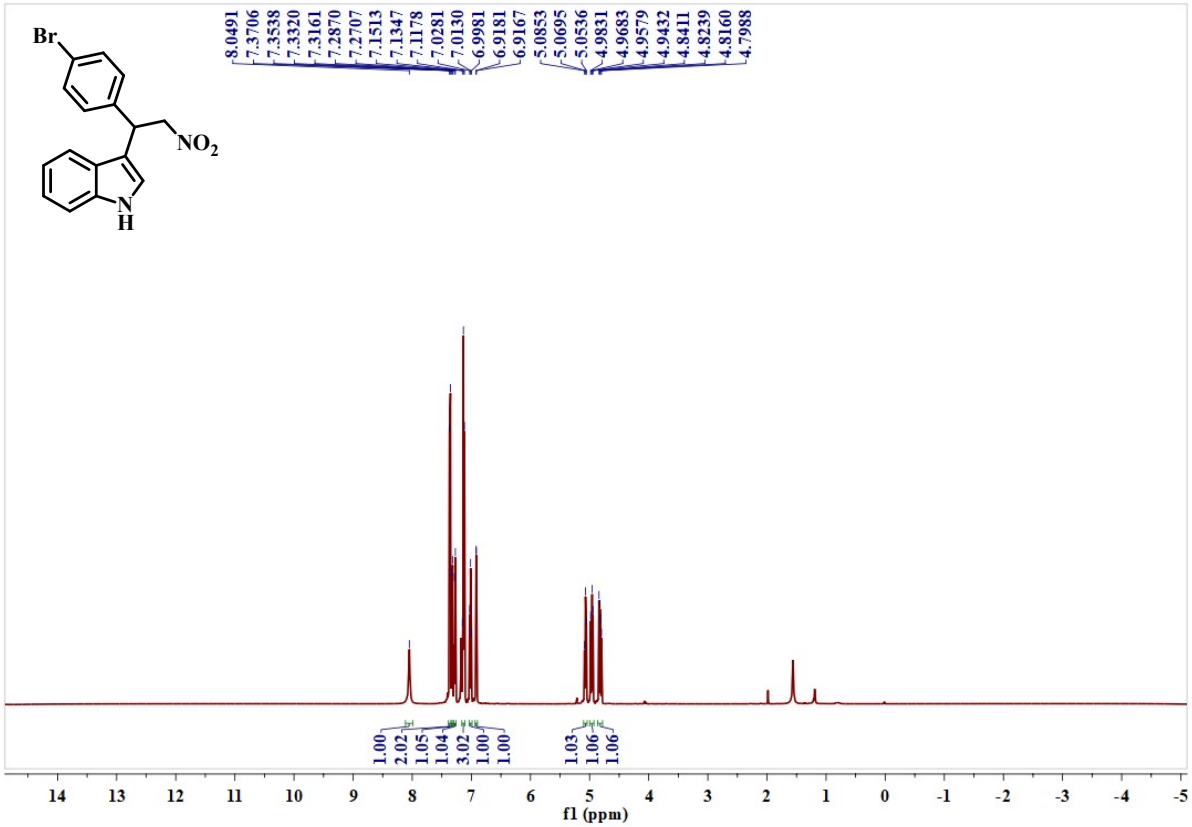


Fig. S25. ^{1}H NMR spectrum of **3e**.

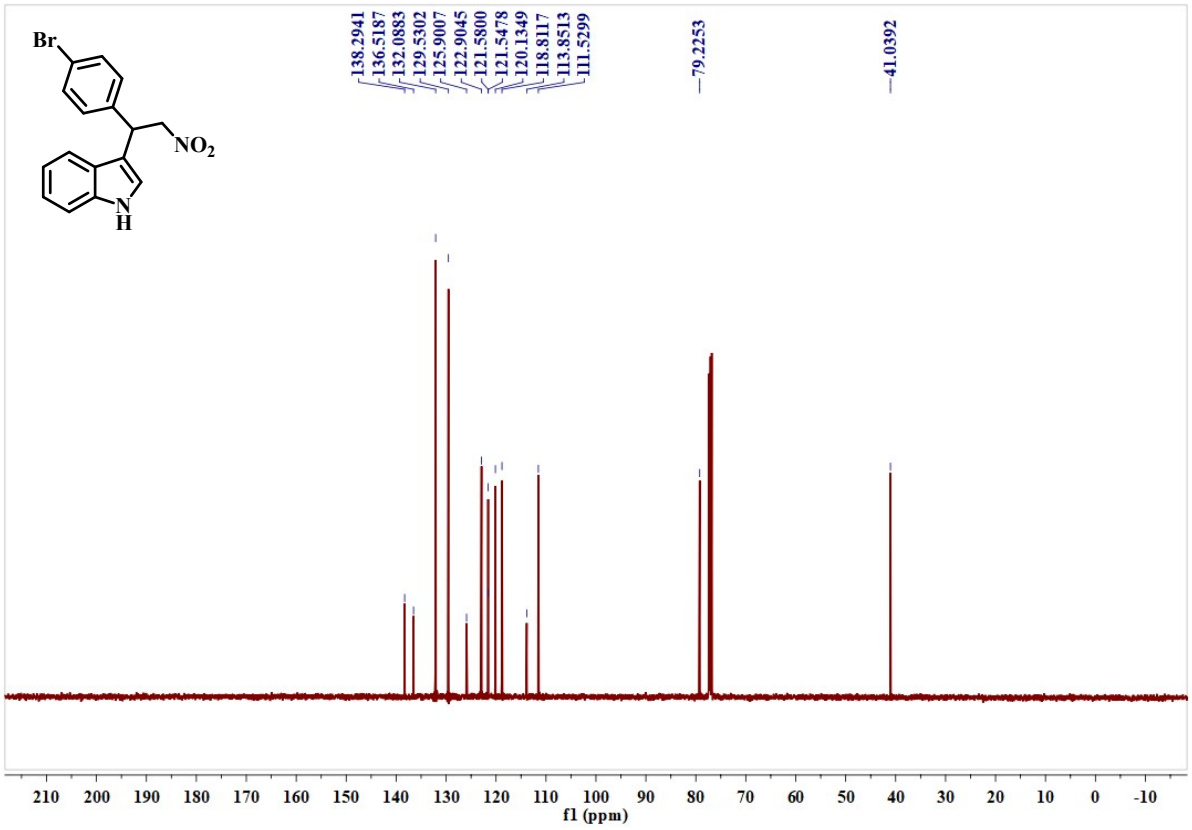


Fig. S26. ^{13}C NMR spectrum of **3e**.

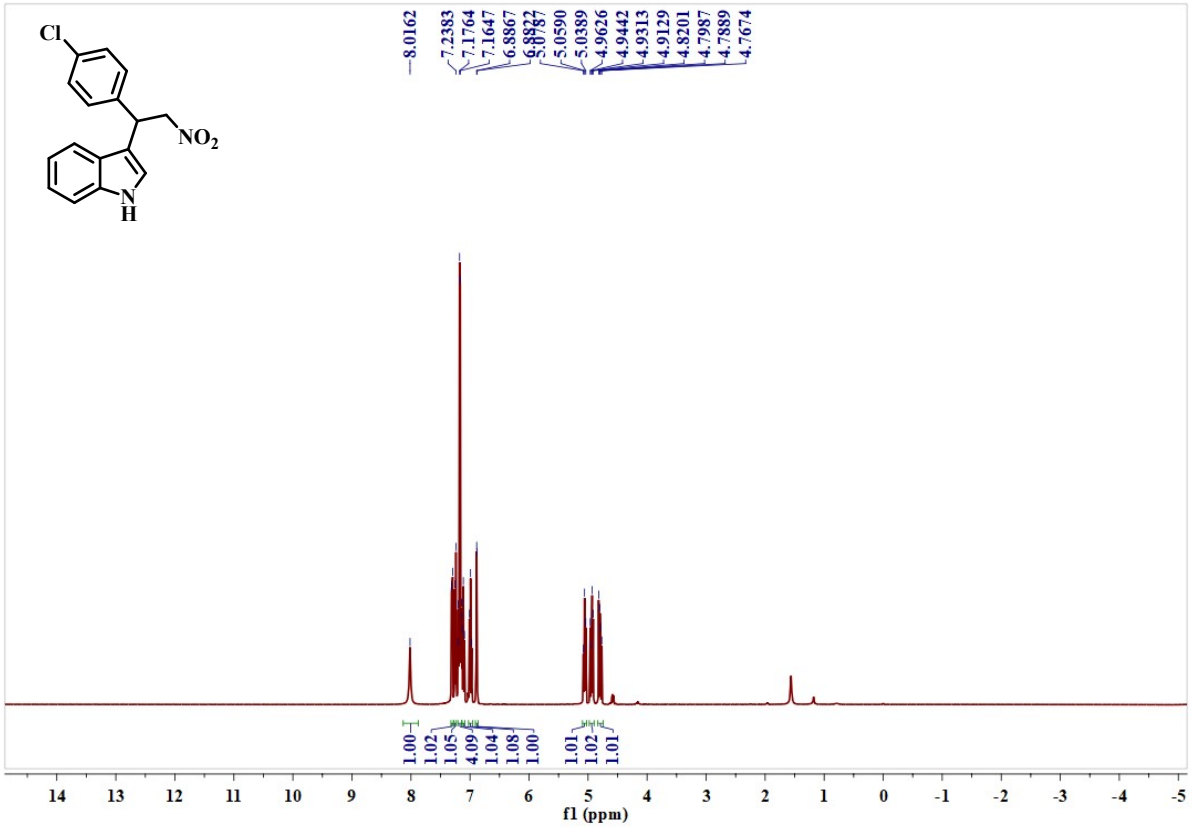


Fig. S27. ^{1}H NMR spectrum of **3f**.

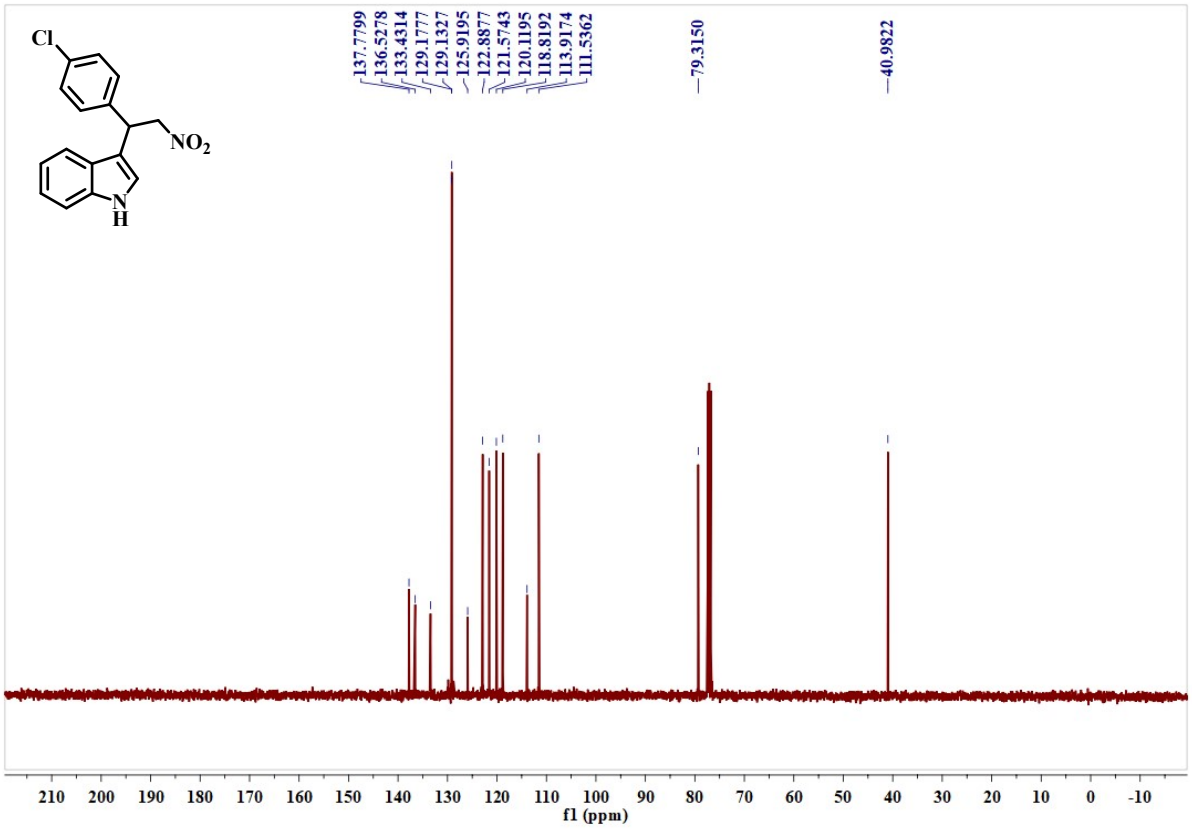


Fig. S28. ^{13}C NMR spectrum of **3f**.

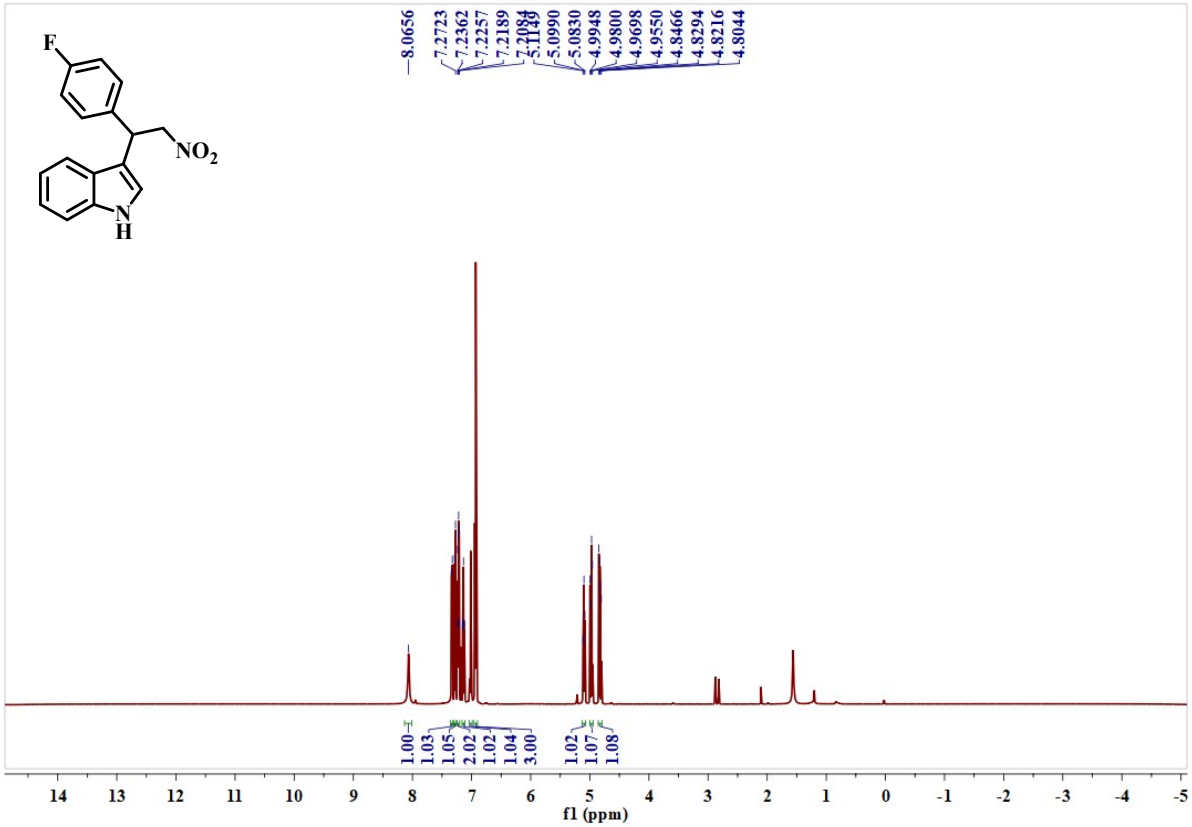


Fig. S29. ^{1}H NMR spectrum of **3g**.

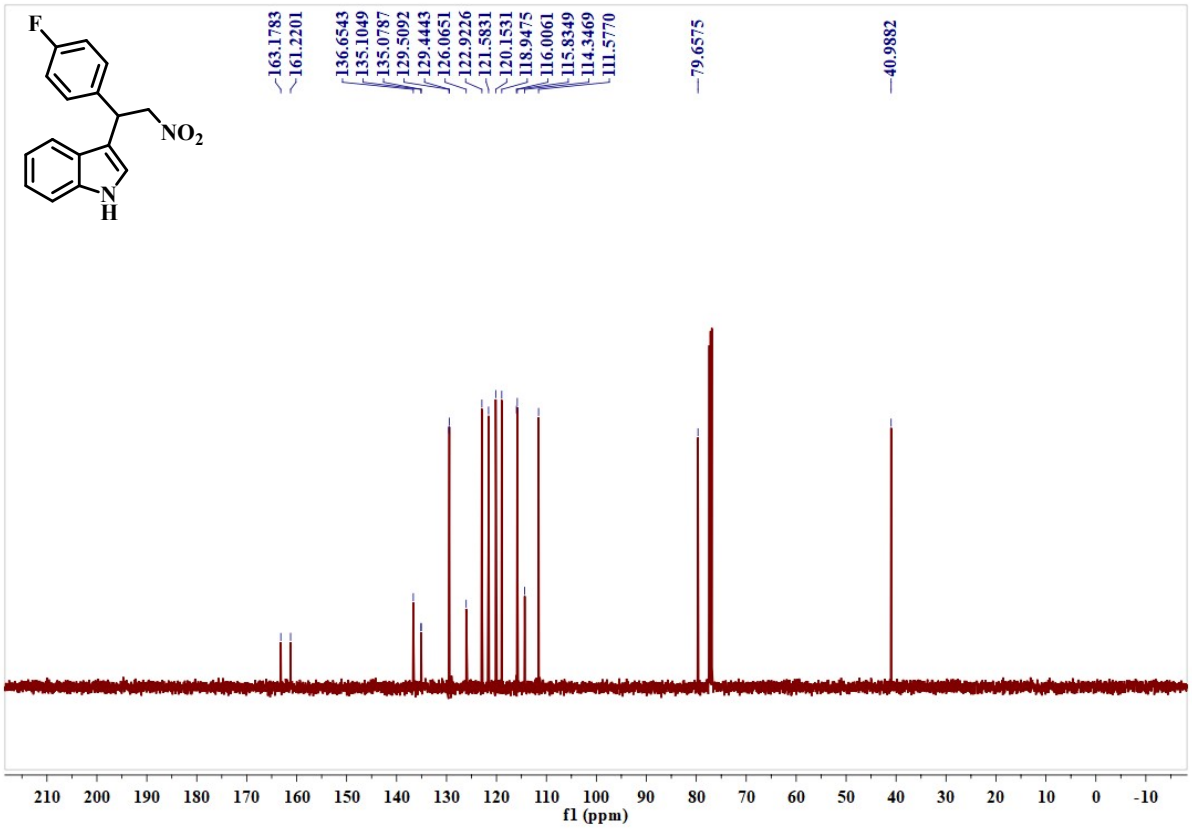


Fig. S30. ^{13}C NMR spectrum of **3g**.

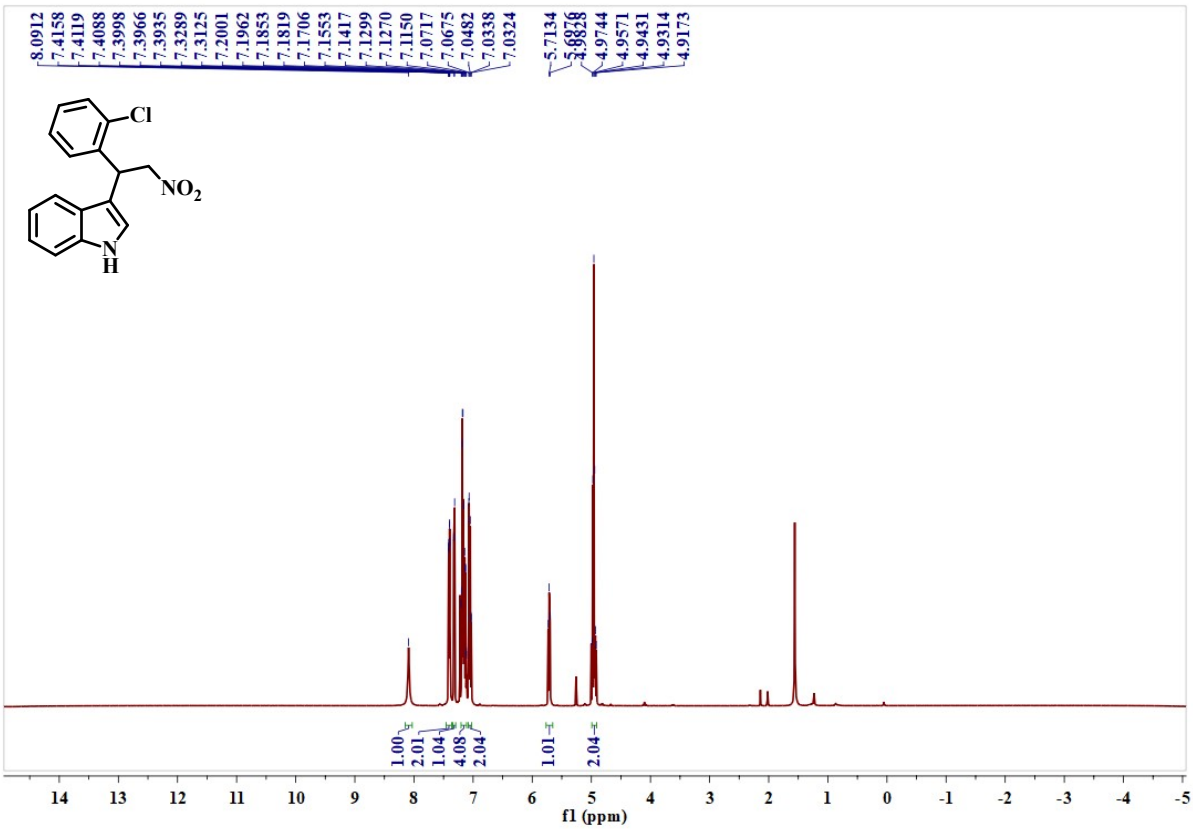


Fig. S31. ^{1}H NMR spectrum of **3h**.

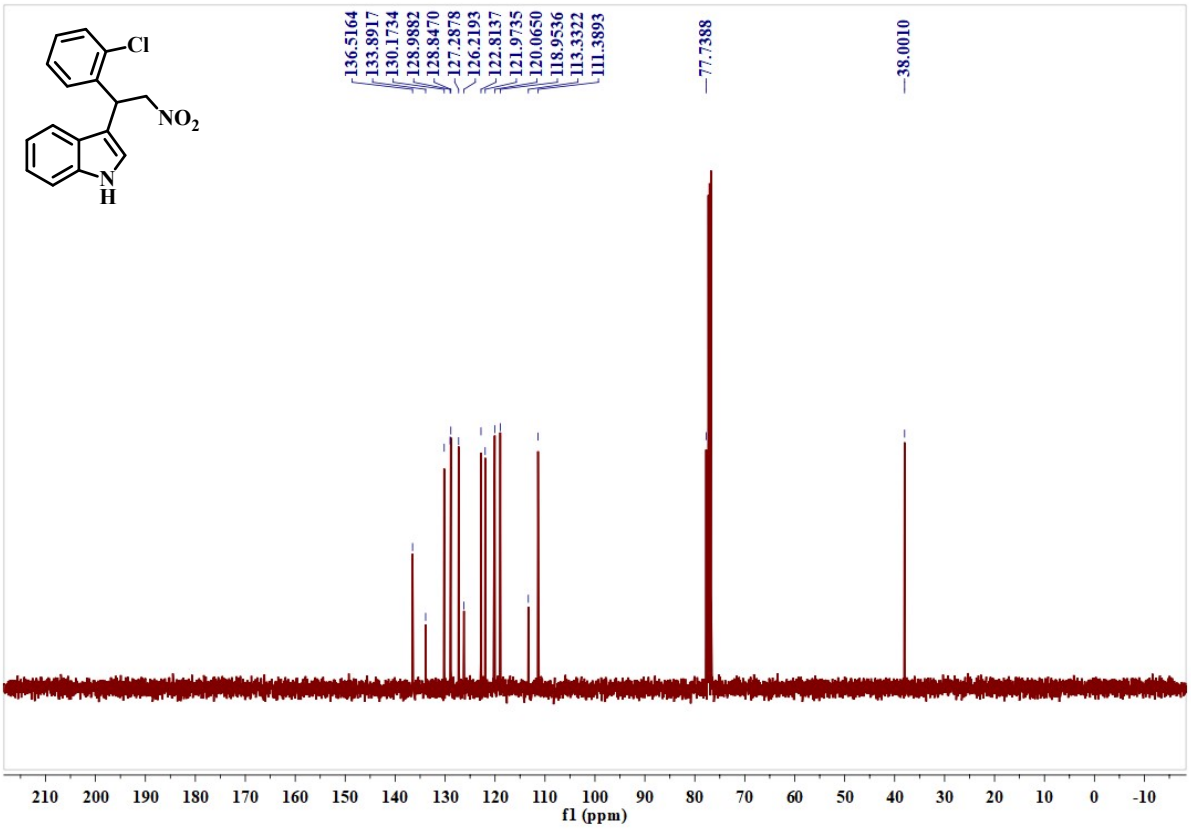


Fig. S32. ^{13}C NMR spectrum of **3h**.

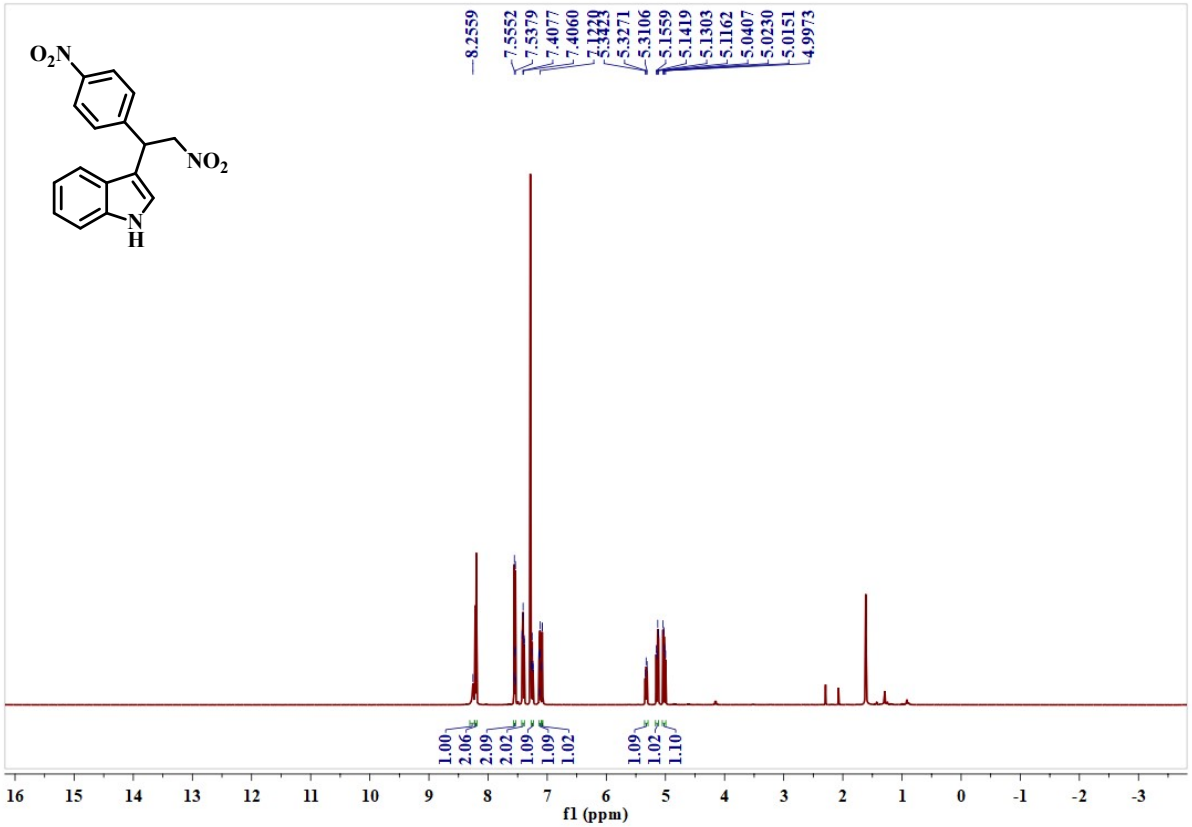


Fig. S33. ^{1}H NMR spectrum of **3i**.

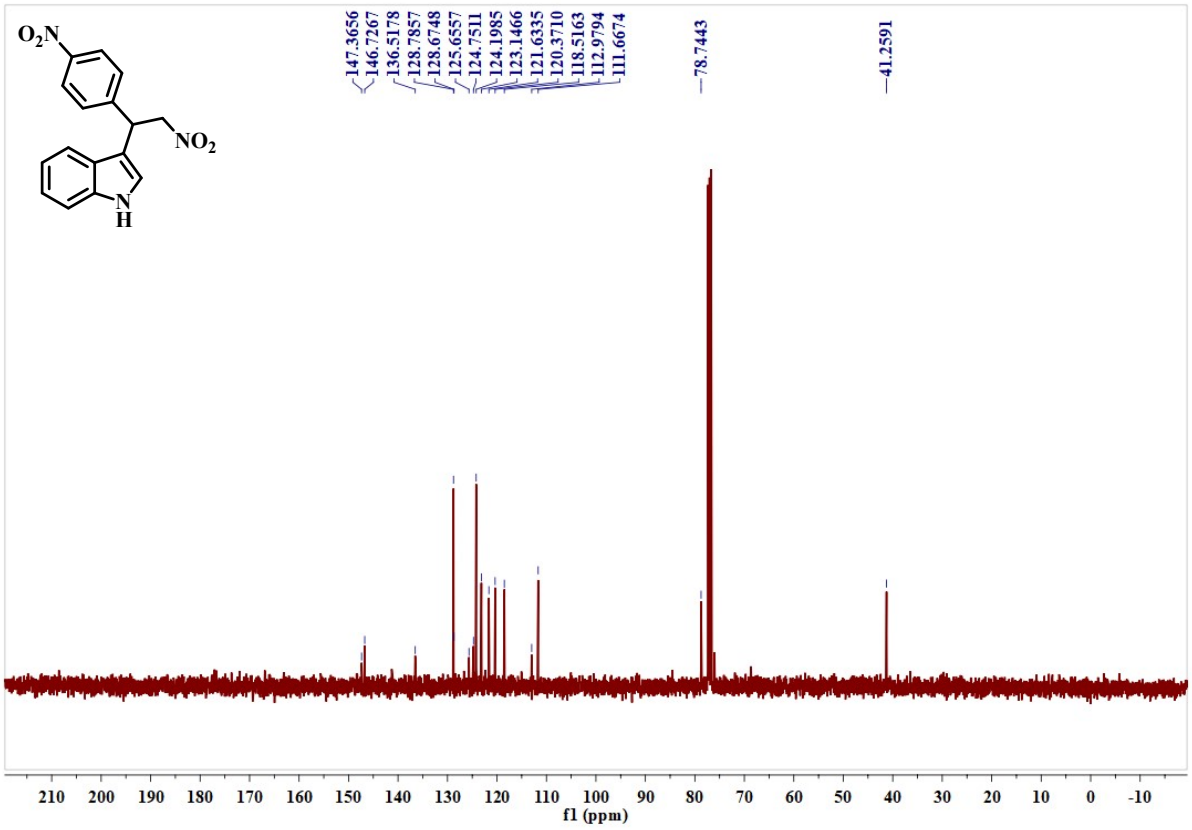


Fig. S34. ^{13}C NMR spectrum of **3i**.

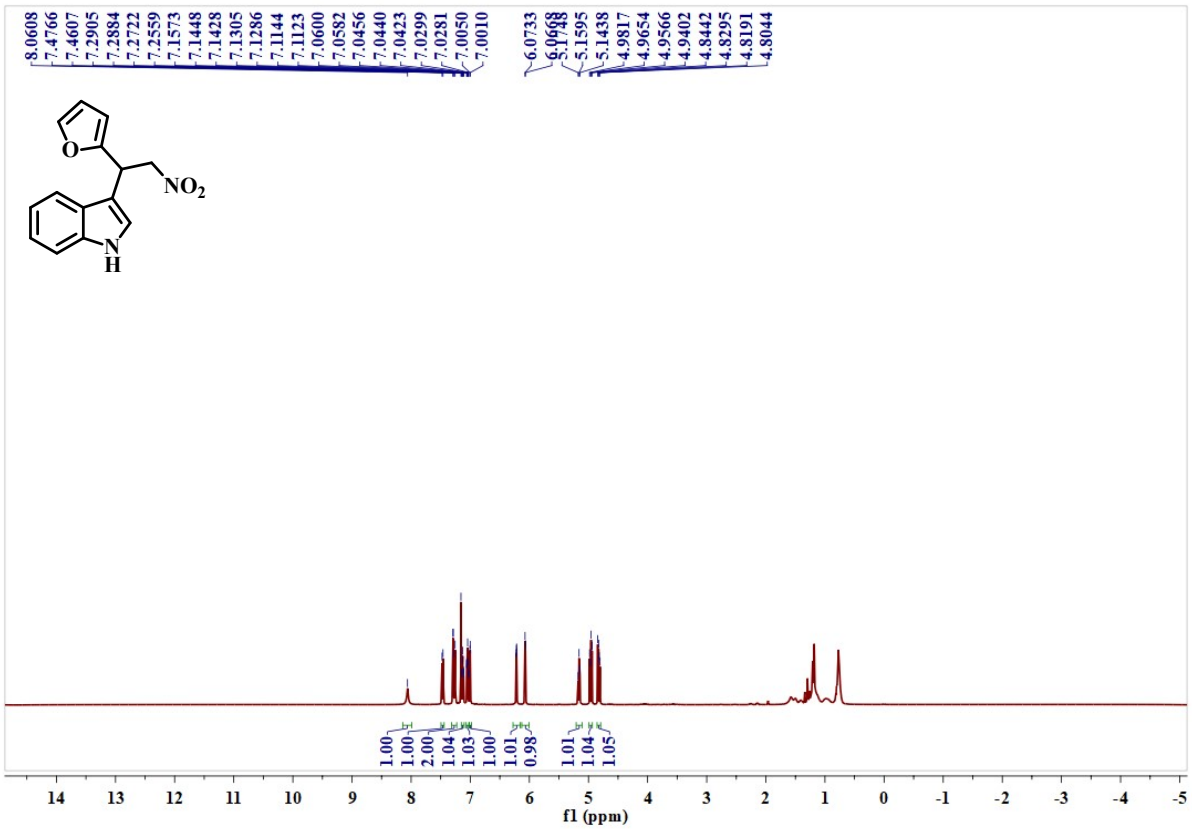


Fig. S35. ^{1}H NMR spectrum of **3j**.

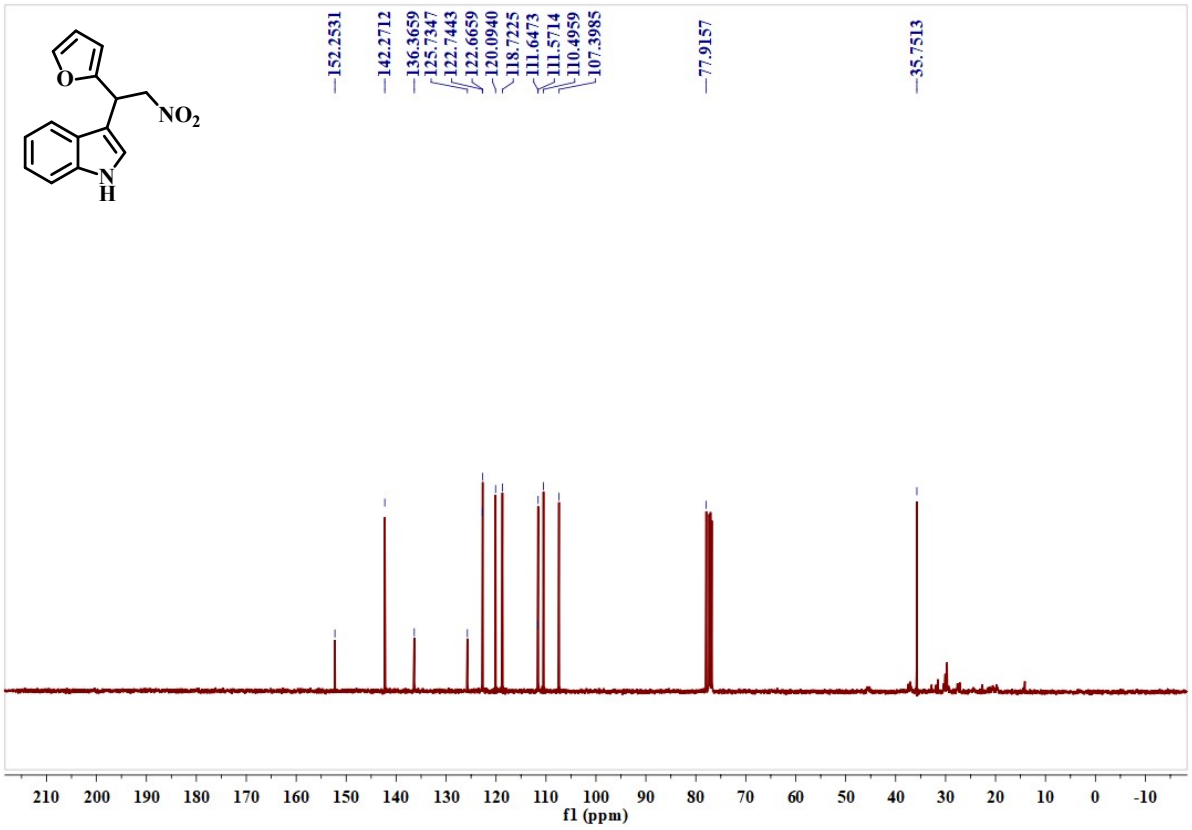


Fig. S36. ^{13}C NMR spectrum of **3j**.

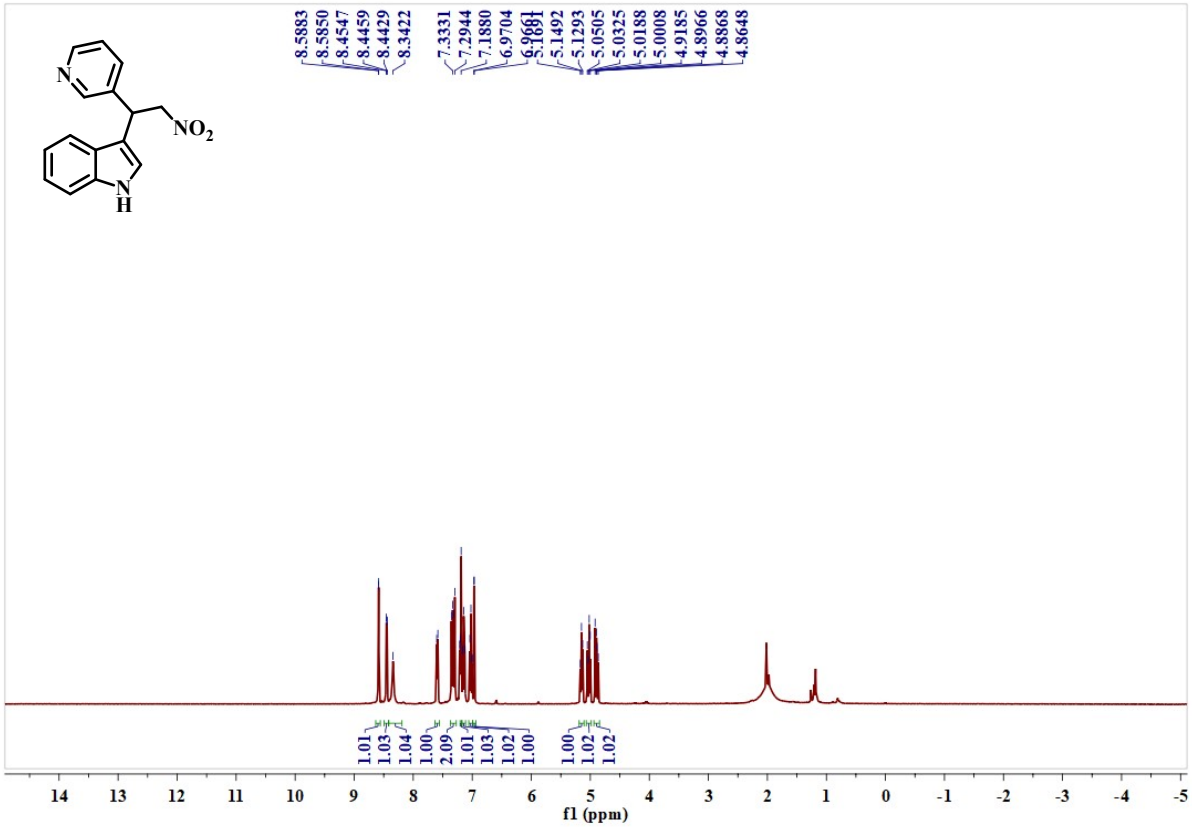


Fig. S37. ^{1}H NMR spectrum of **3k**.

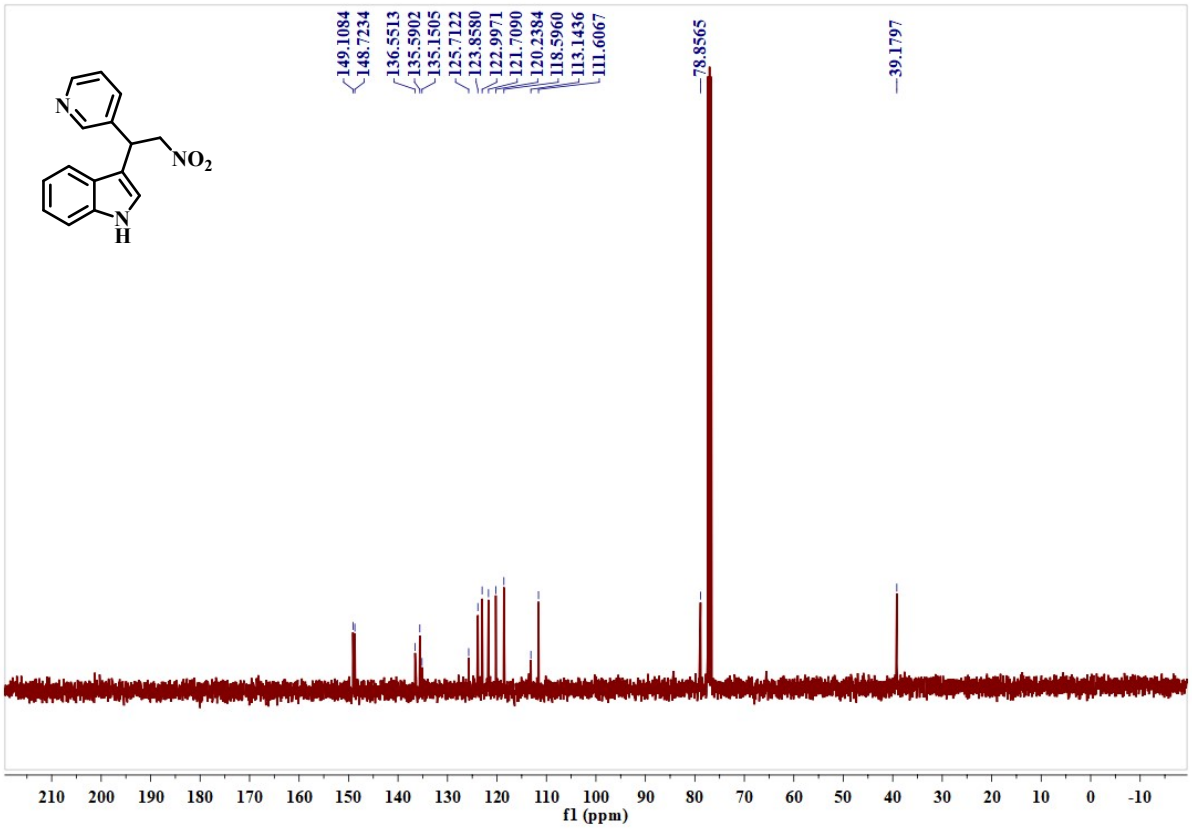


Fig. S38. ^{13}C NMR spectrum of **3k**.

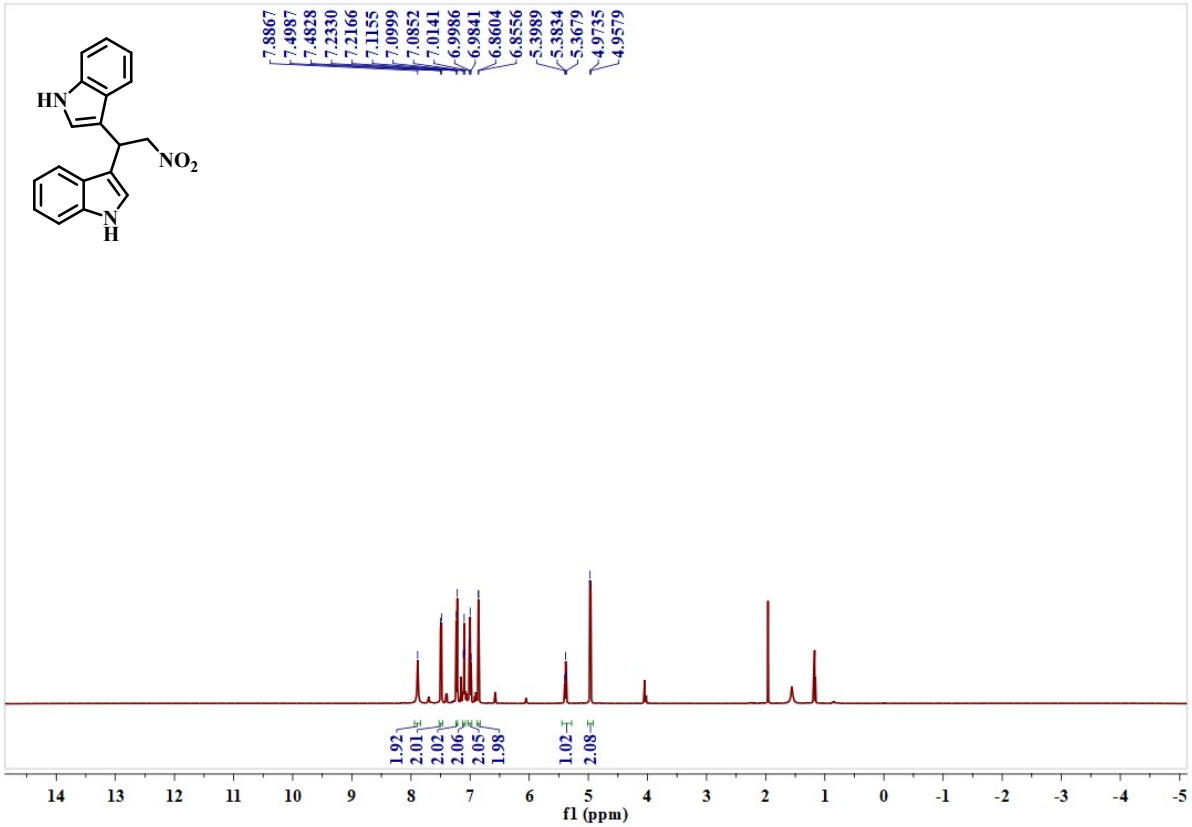


Fig. S39. ^{1}H NMR spectrum of **3l**.

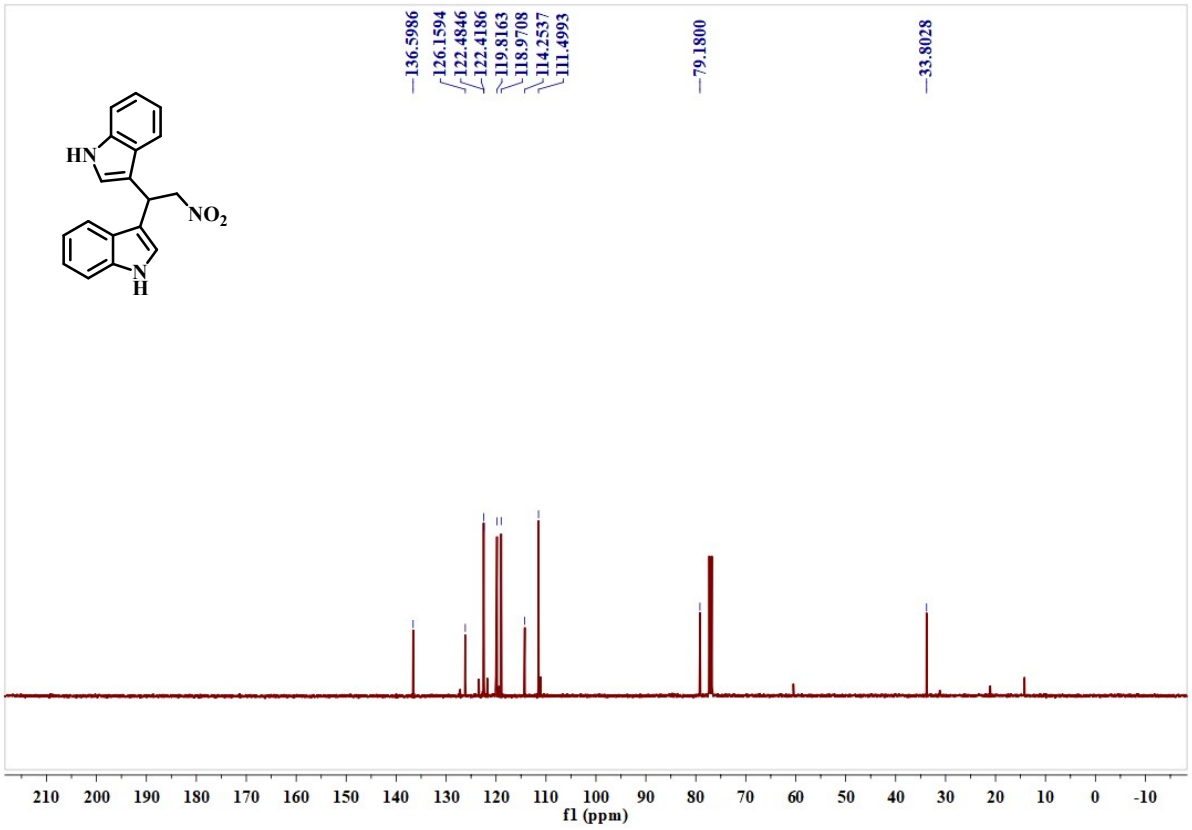


Fig. S40. ^{13}C NMR spectrum of **3l**.

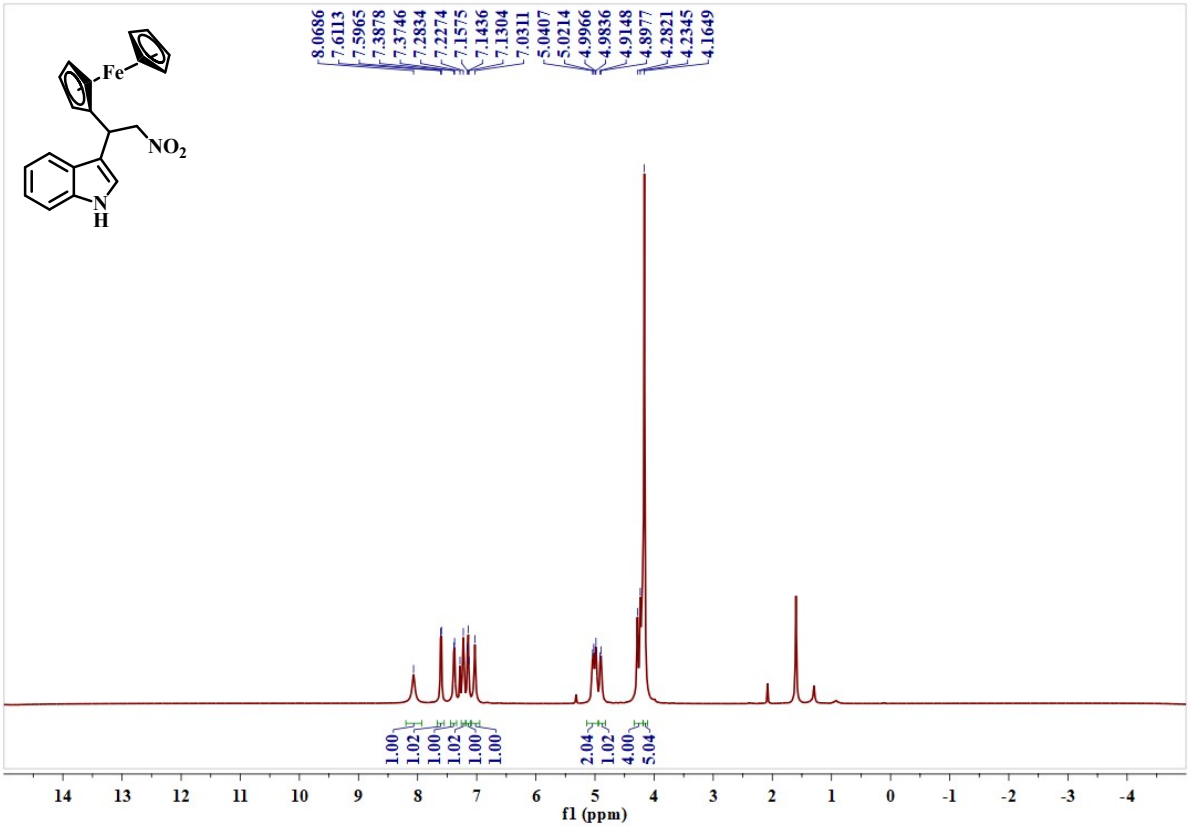


Fig. S41. ^{1}H NMR spectrum of **3m**.

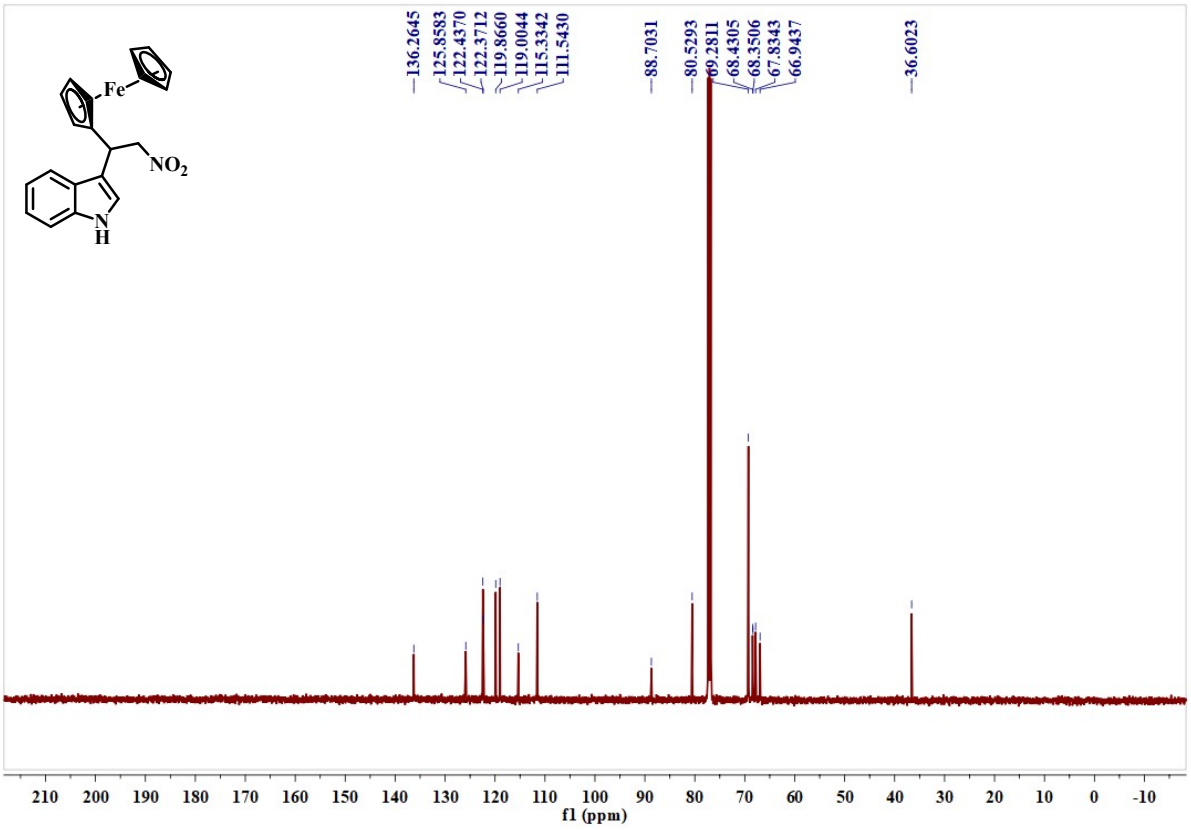


Fig. S42. ^{13}C NMR spectrum of **3m**.

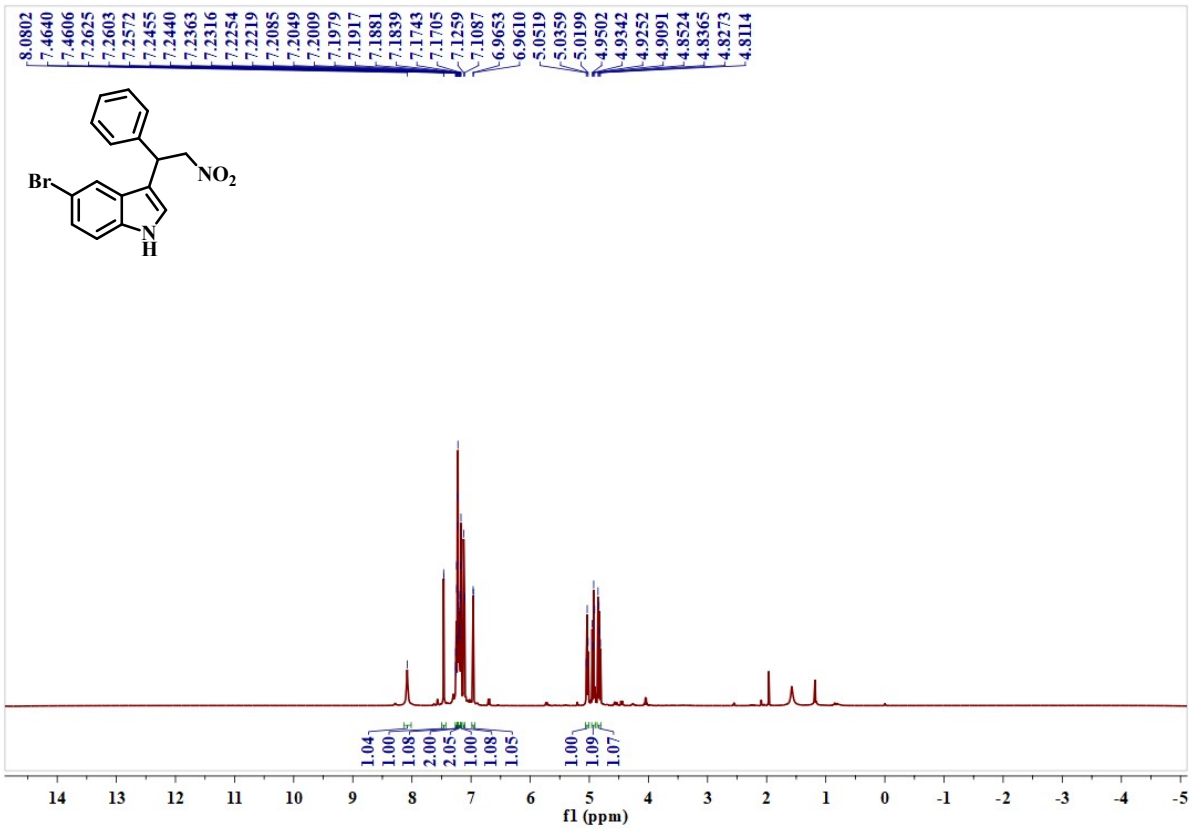


Fig. S43. ^{1}H NMR spectrum of **3n**.

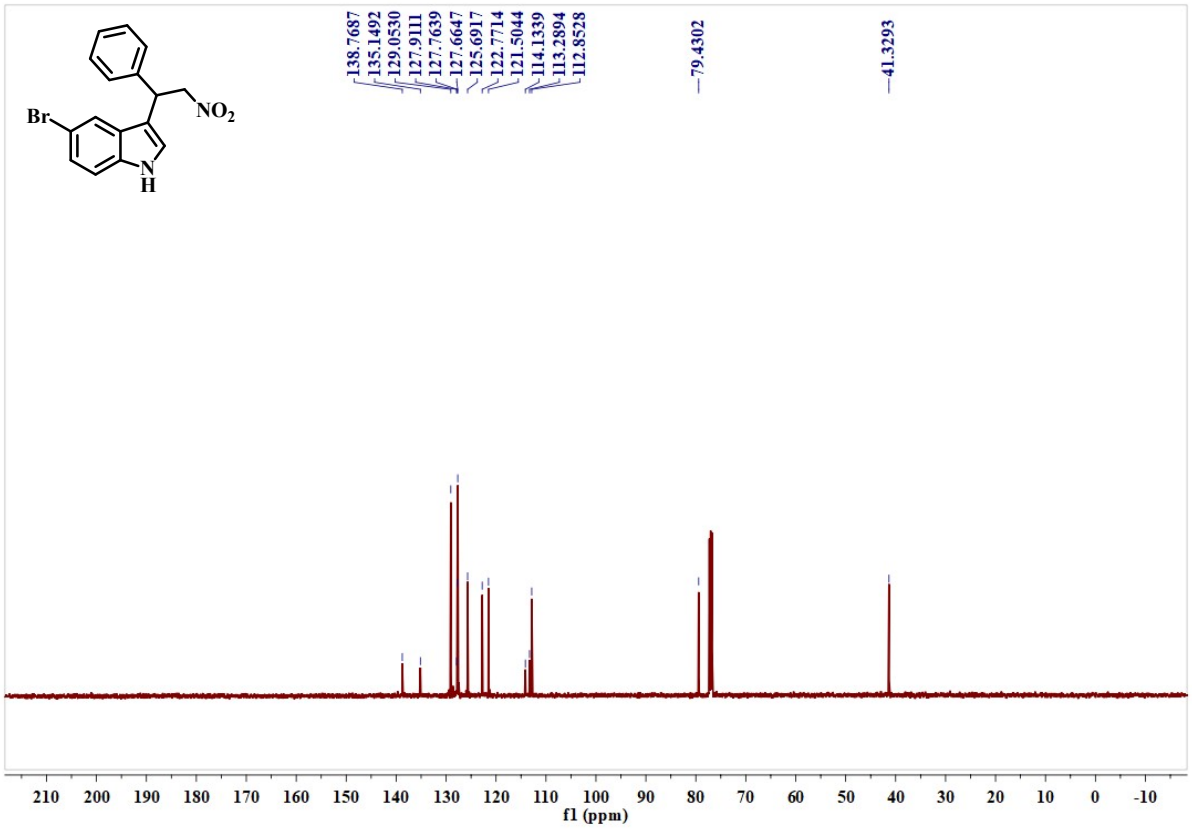


Fig. S44. ^{13}C NMR spectrum of **3n**.

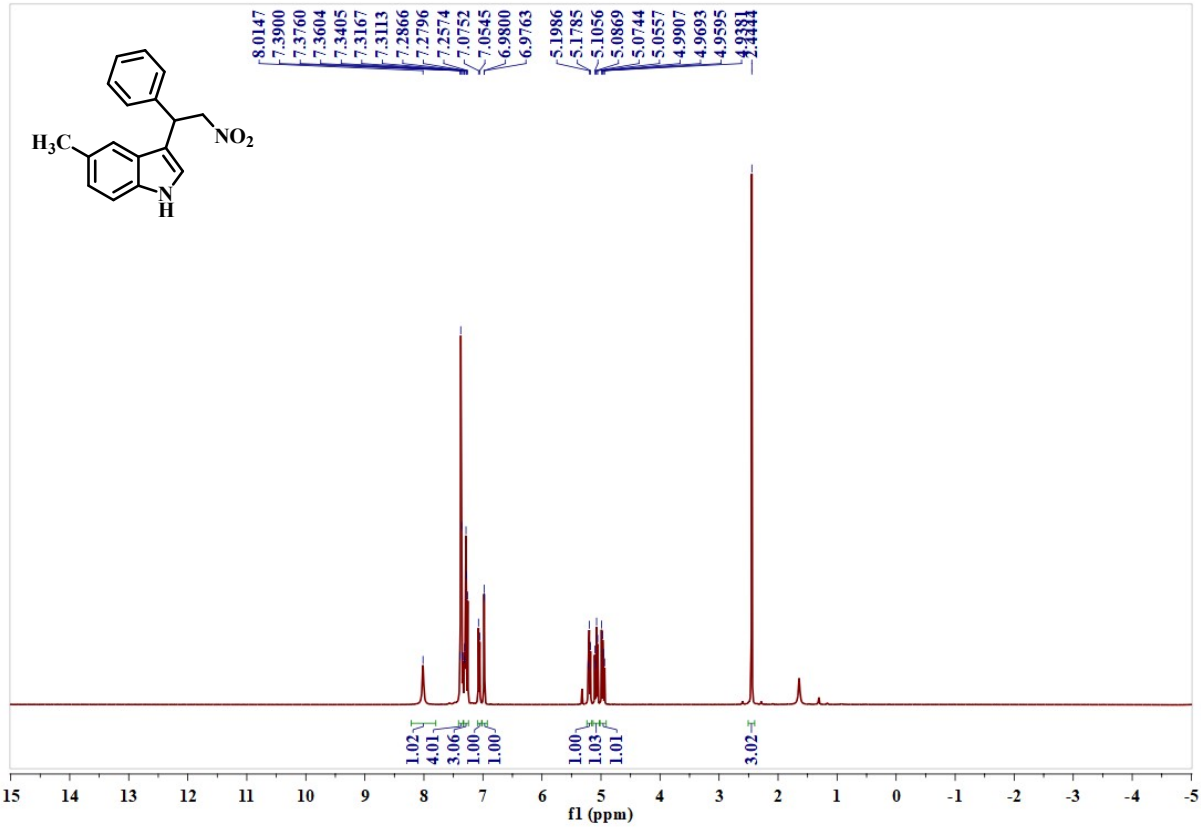


Fig. S45. ^{1}H NMR spectrum of **3o**.

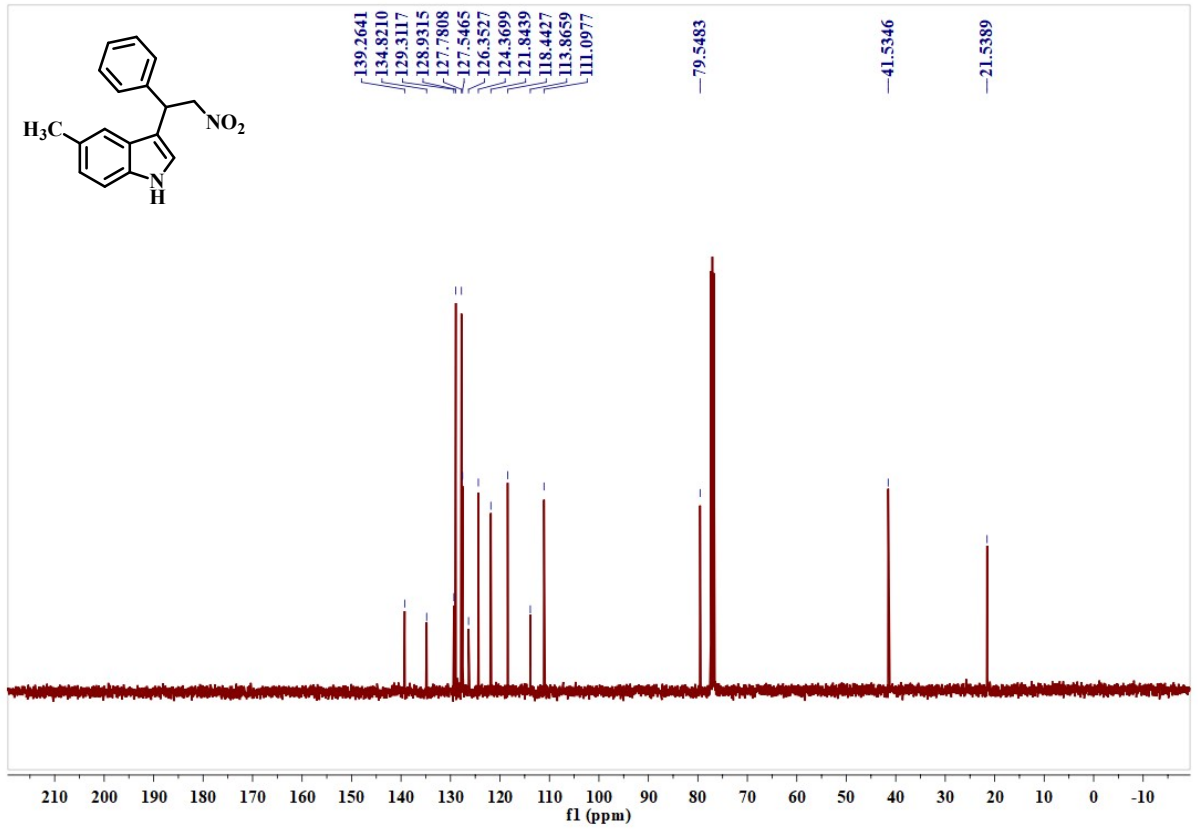


Fig. S46. ^{13}C NMR spectrum of **3o**.

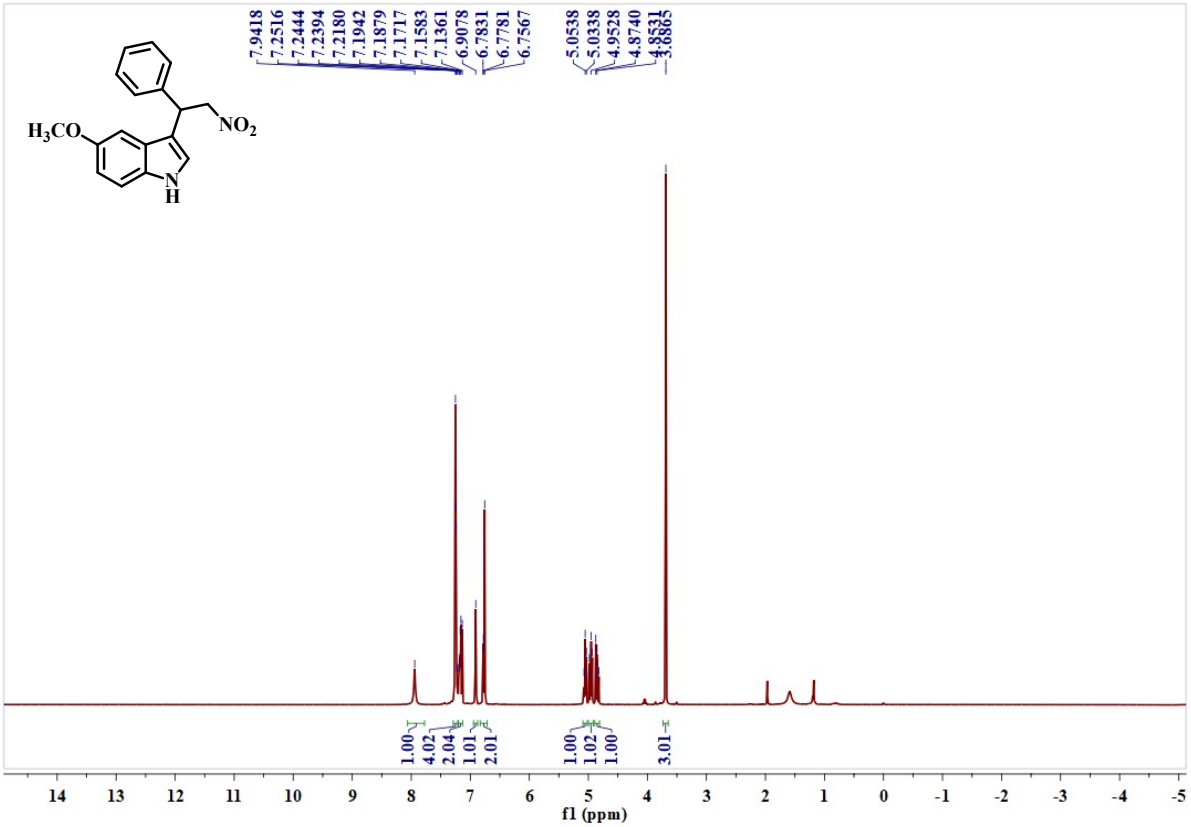


Fig. S47. ^{1}H NMR spectrum of **3p**.

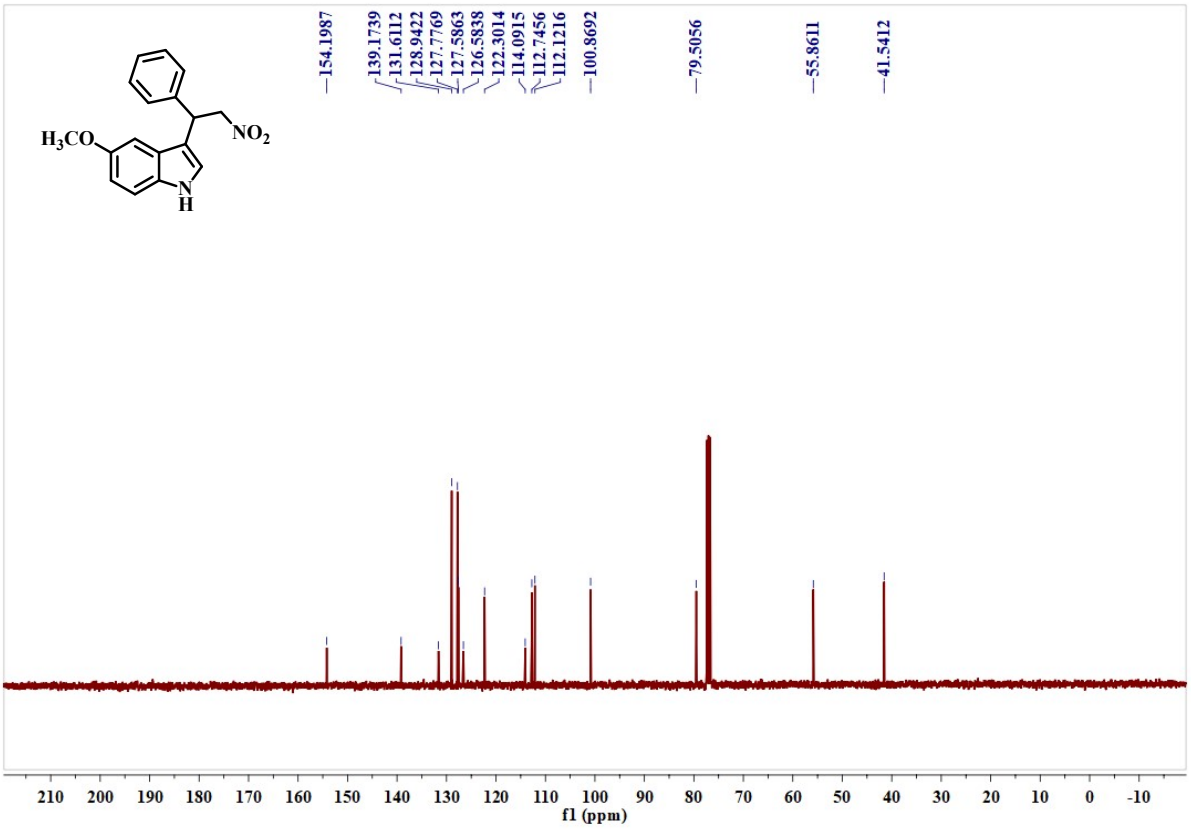


Fig. S48. ^{13}C NMR spectrum of **3p**.

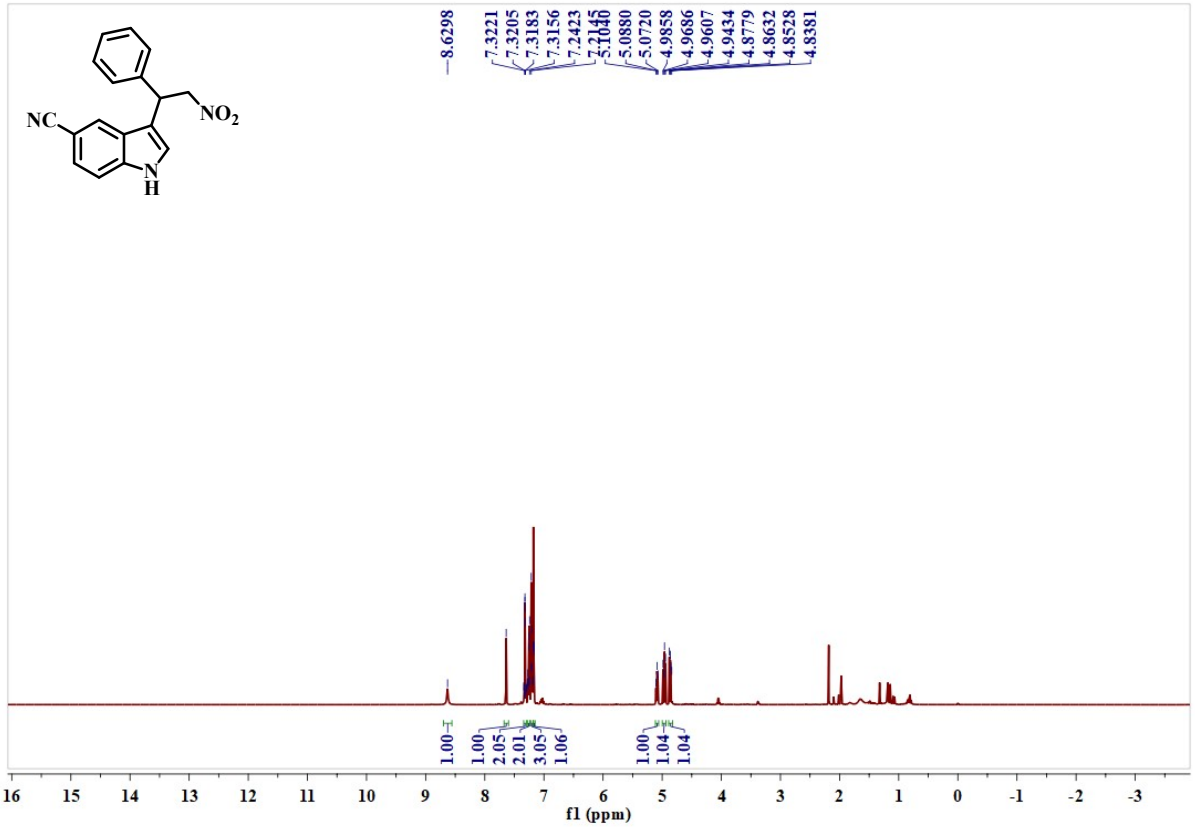


Fig. S49. ^{1}H NMR spectrum of **3q**.

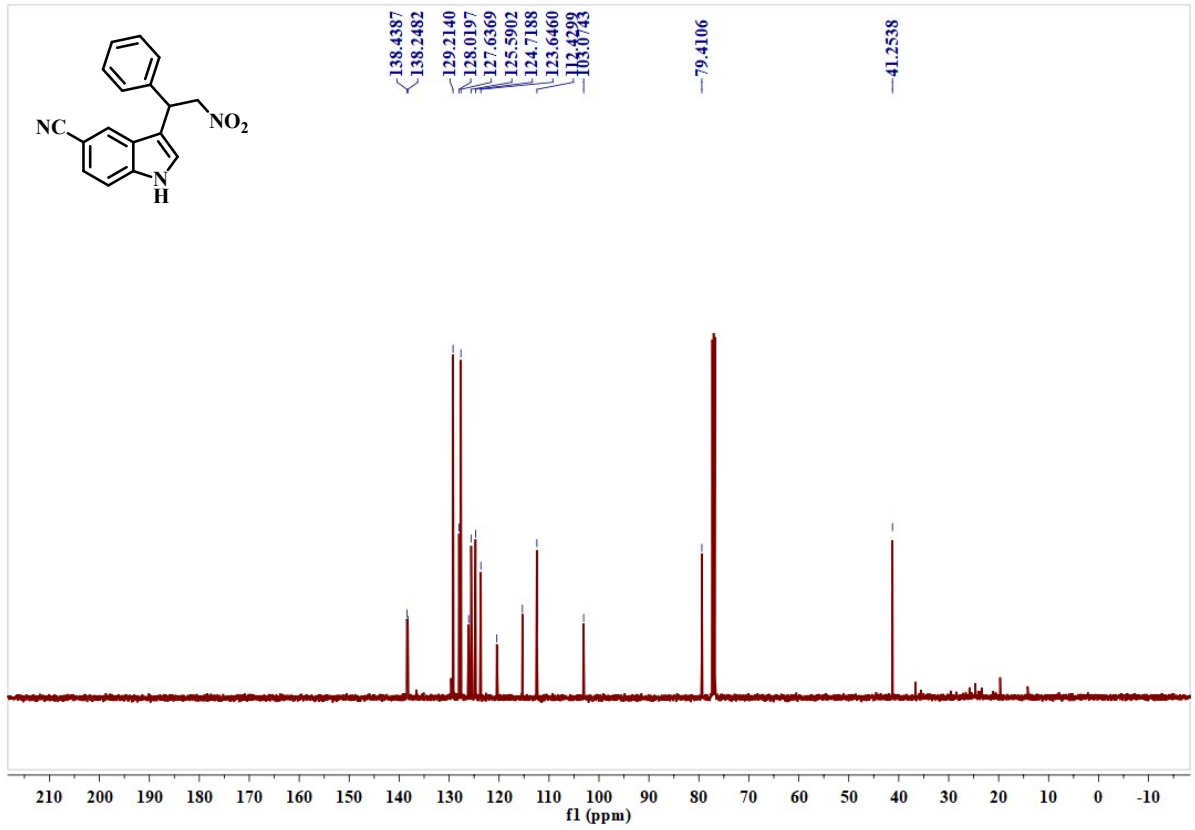


Fig. S50. ^{13}C NMR spectrum of **3q**.

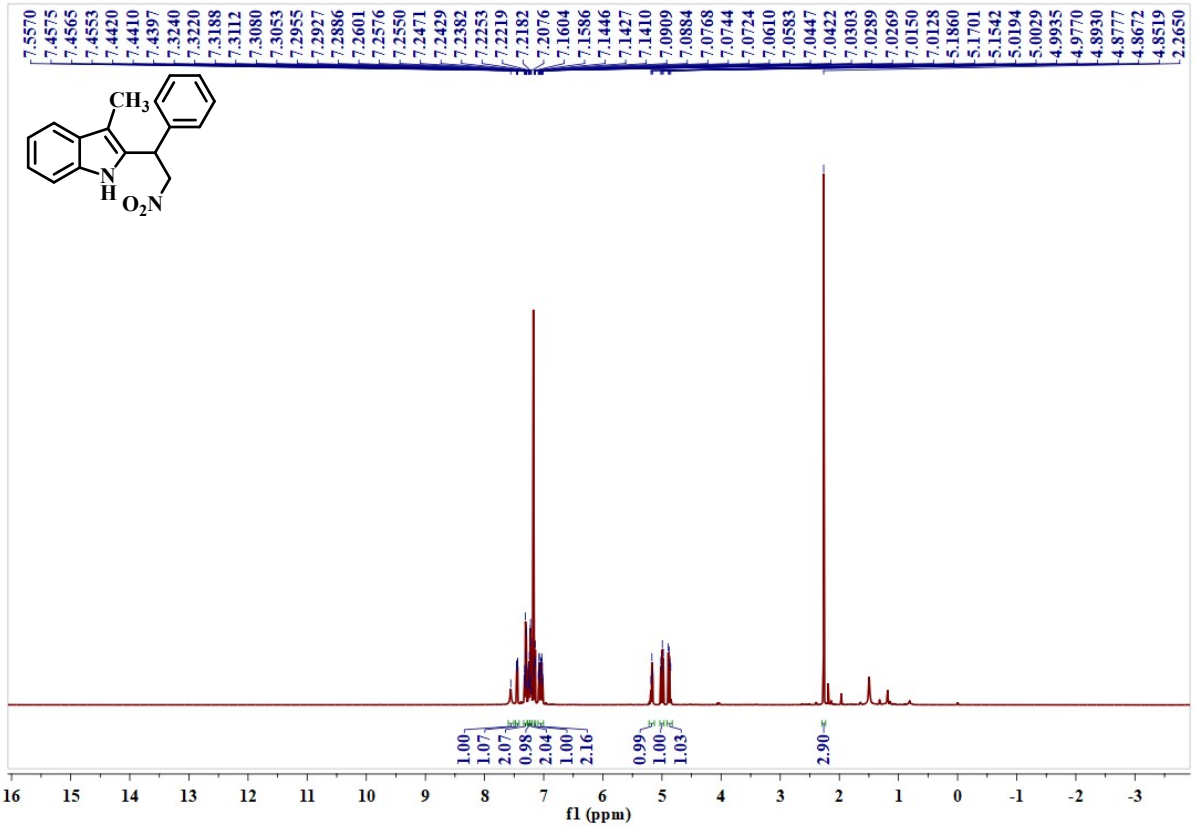


Fig. S51. ^{1}H NMR spectrum of **3t**.

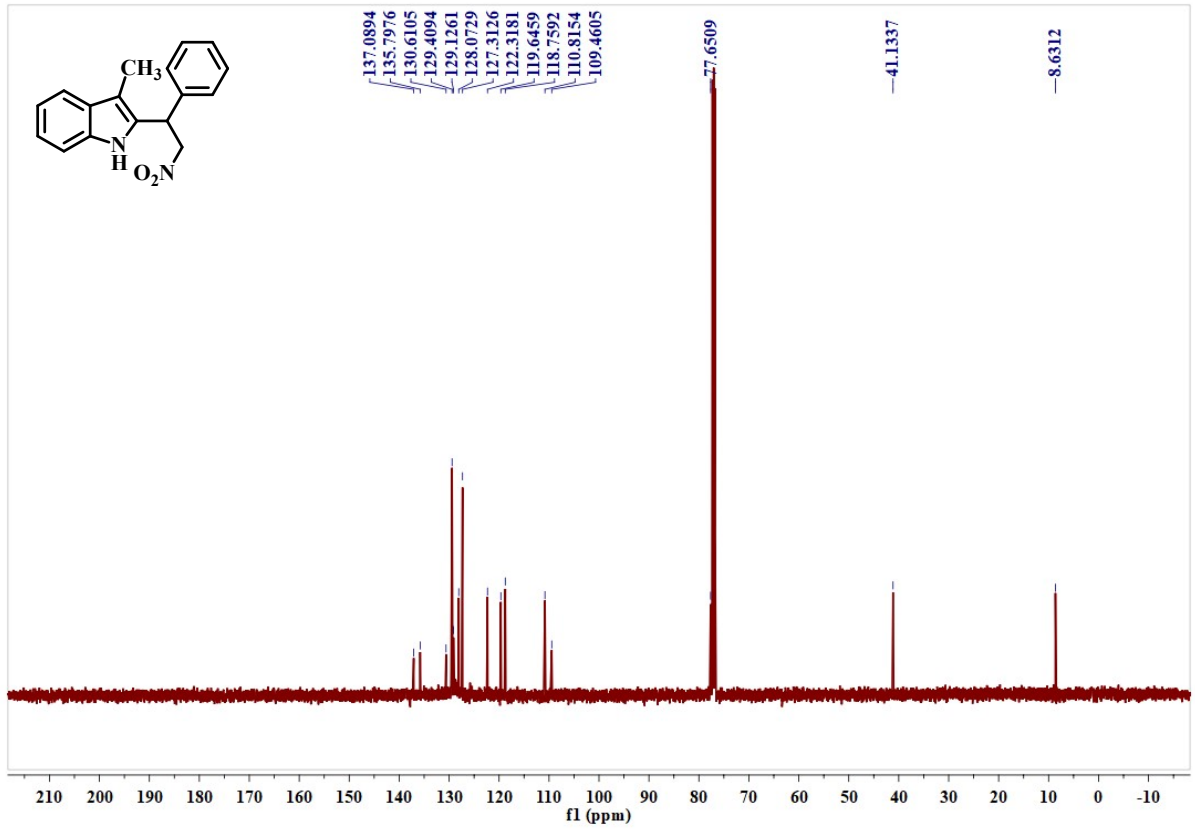


Fig. S52. ^{13}C NMR spectrum of **3t**.

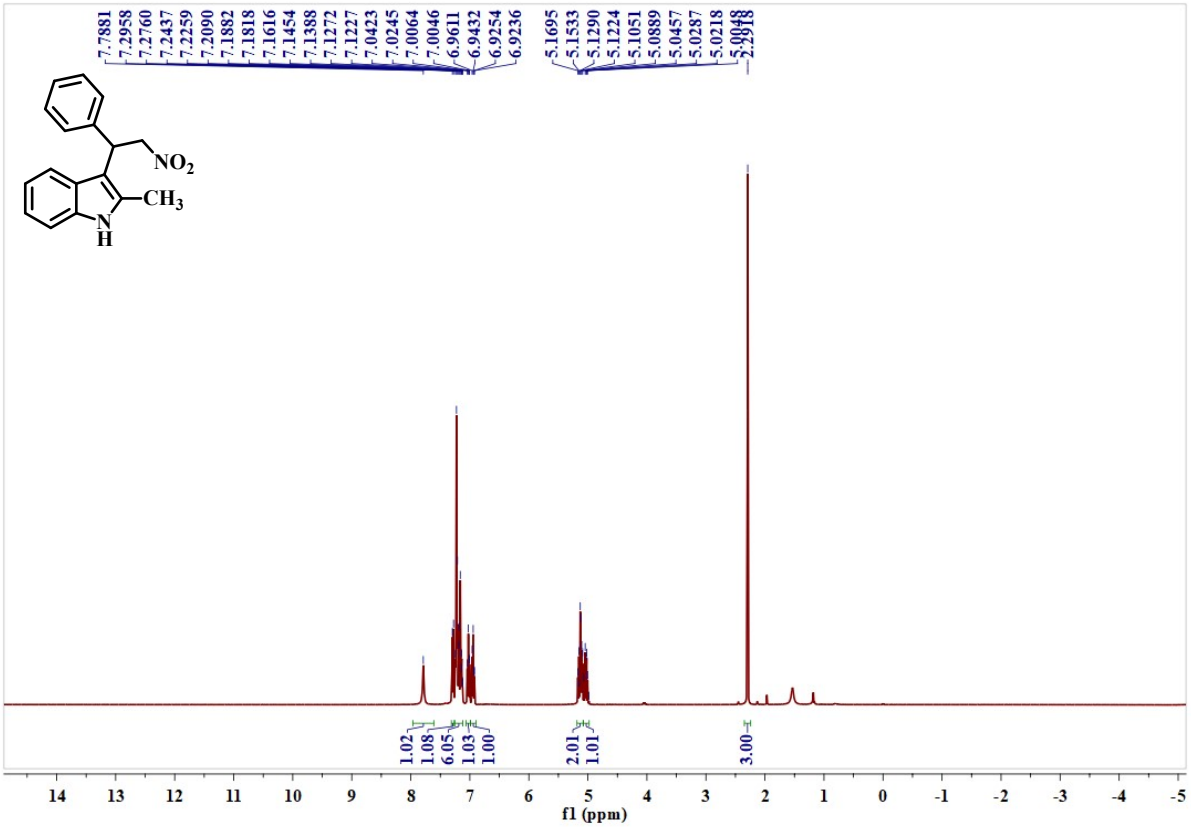


Fig. S53. ^{1}H NMR spectrum of **3u**.

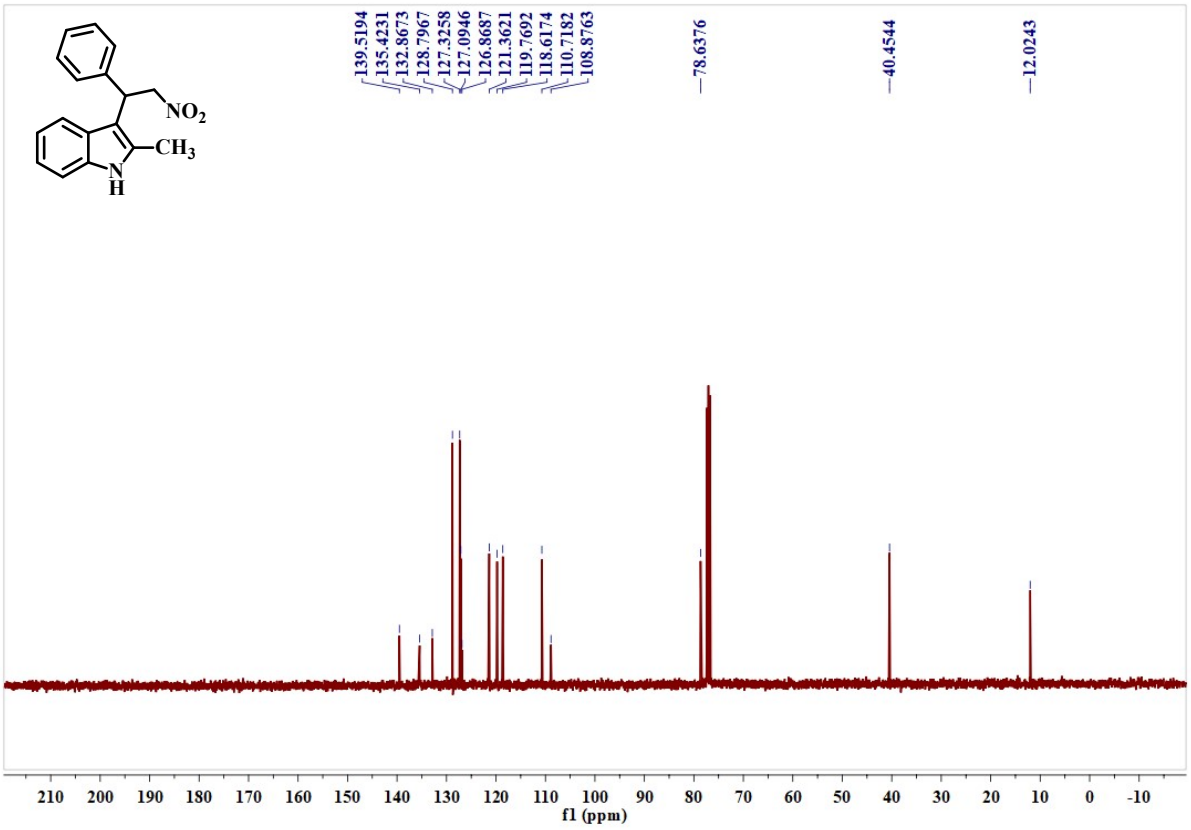


Fig. S54. ^{13}C NMR spectrum of **3u**.

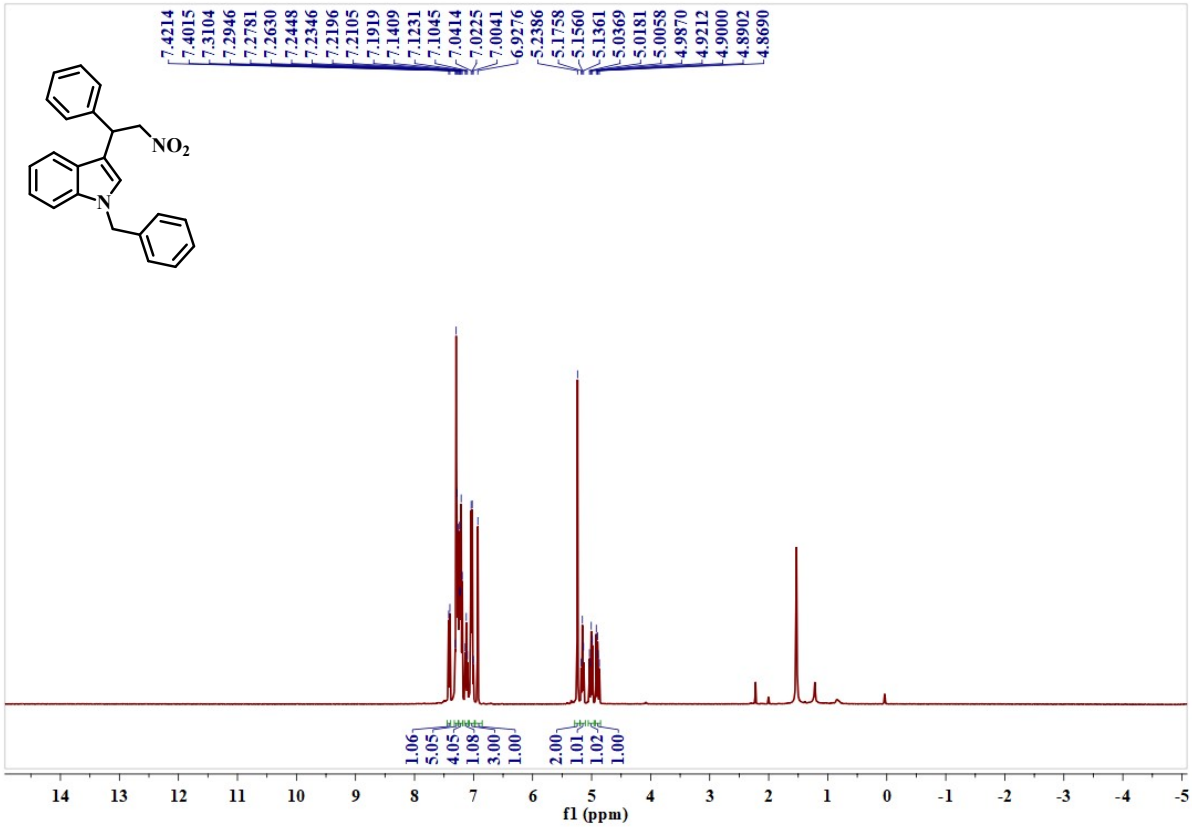


Fig. S55. ^{1}H NMR spectrum of **3v**.

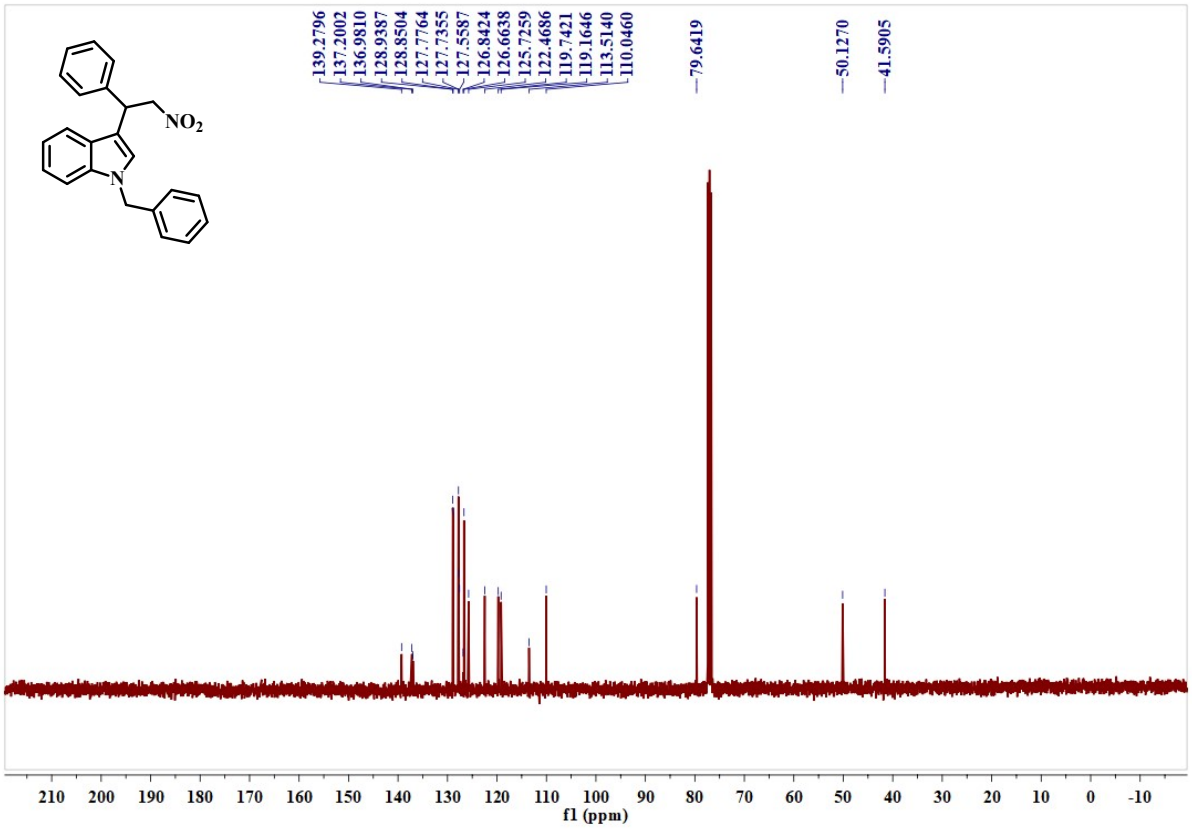


Fig. S56. ^{13}C NMR spectrum of **3v**.

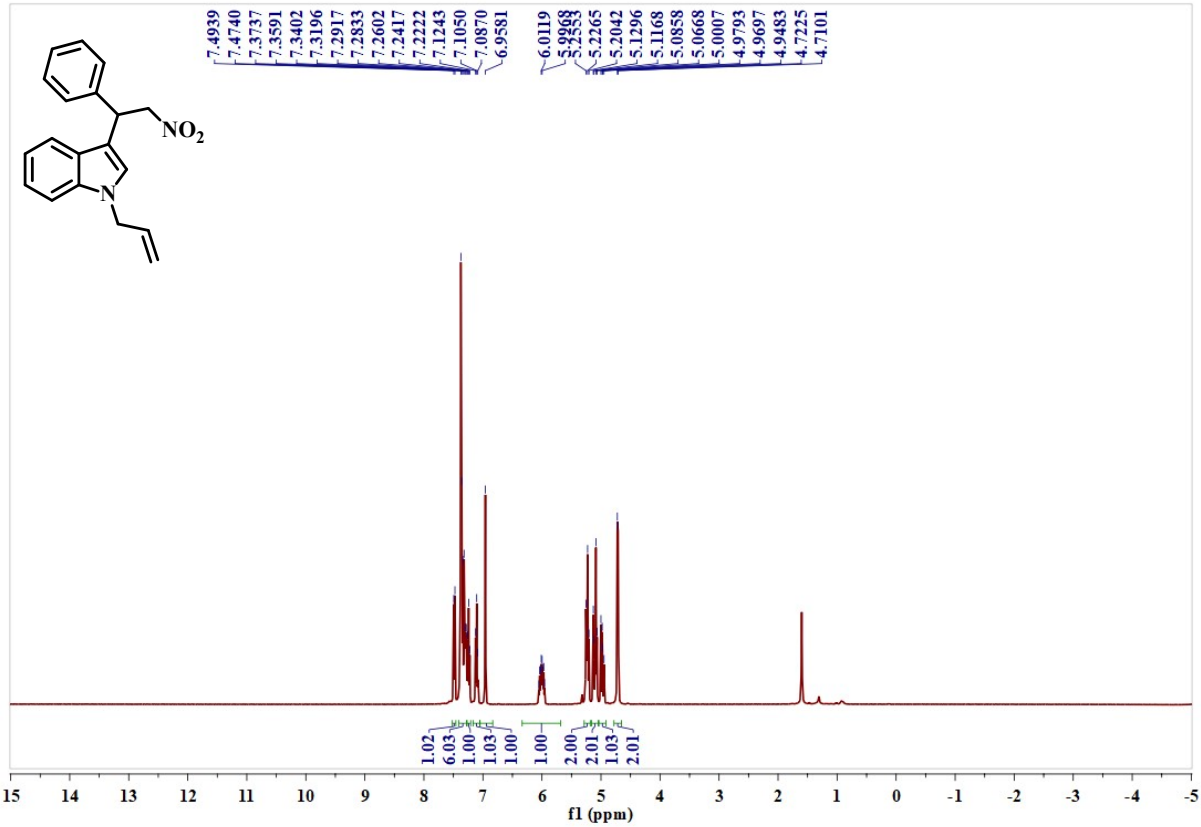


Fig. S57. ^{1}H NMR spectrum of **3w**.

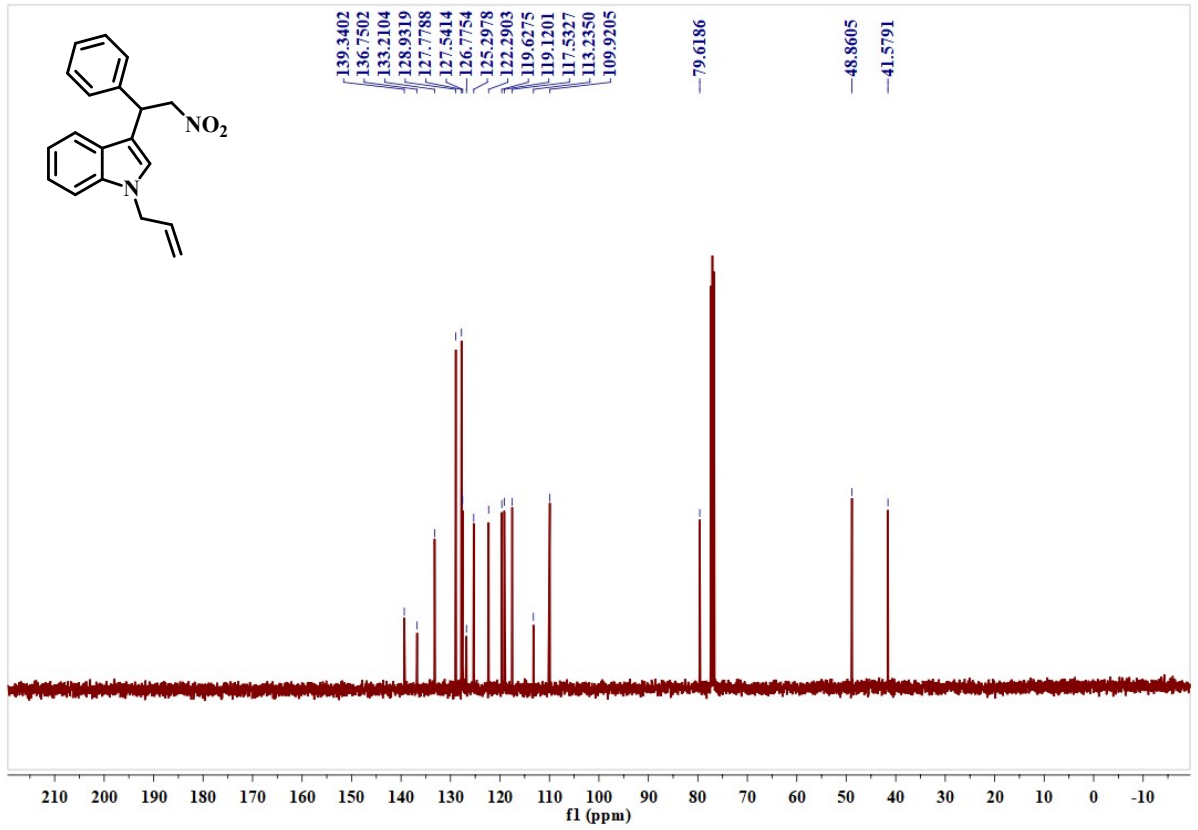


Fig. S58. ^{13}C NMR spectrum of **3w**.

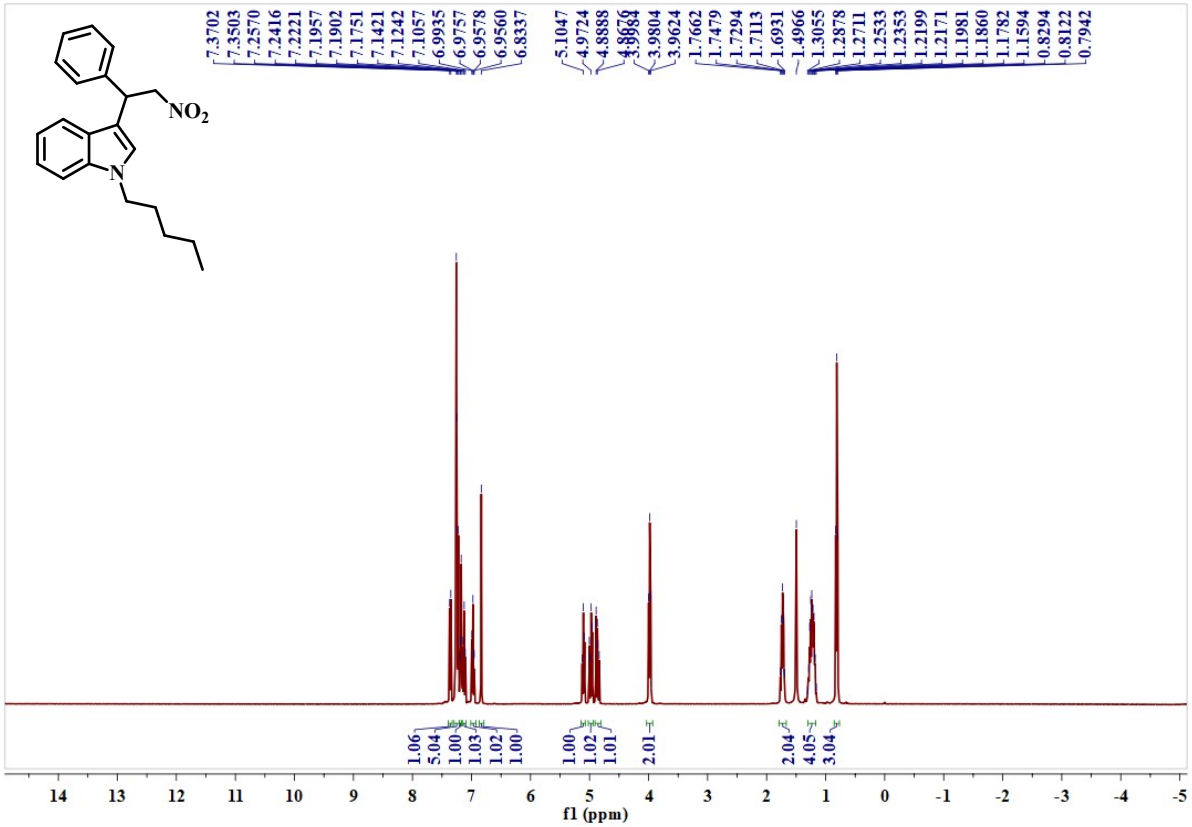


Fig. S59. ^{1}H NMR spectrum of **3x**.

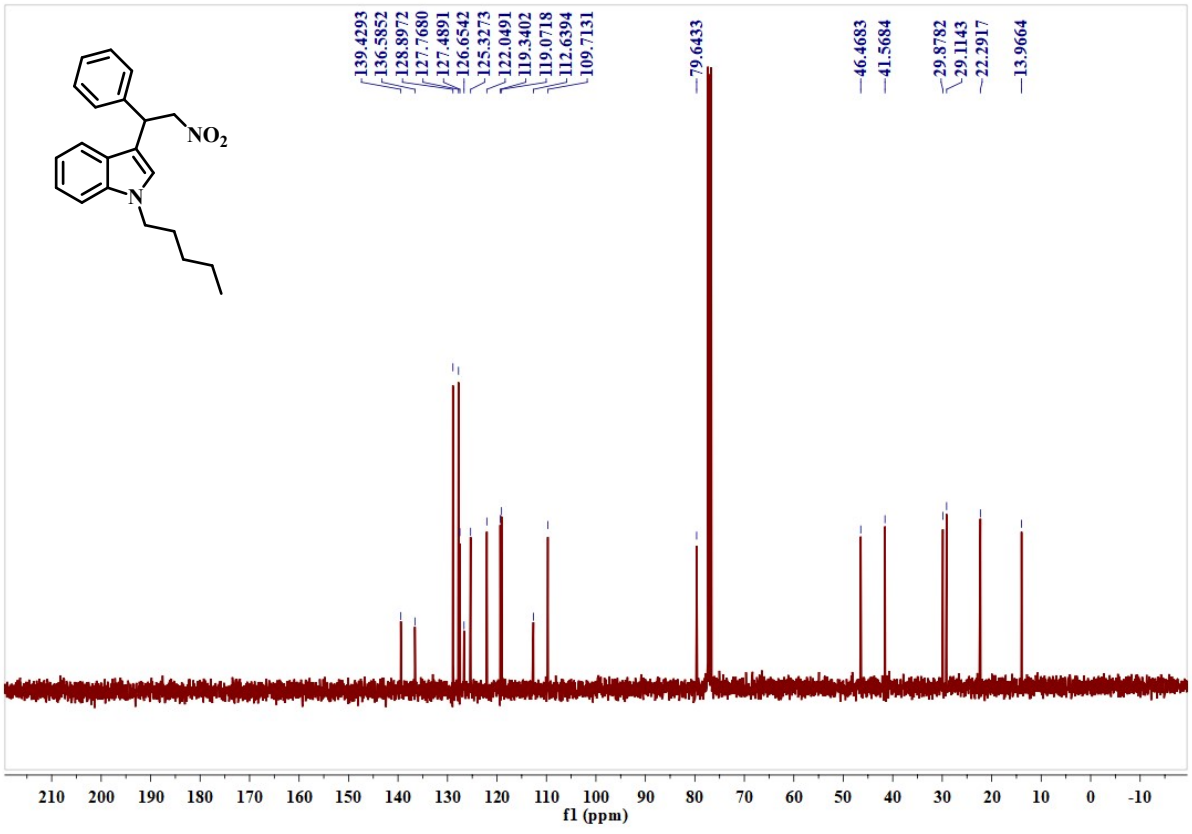


Fig. S60. ^{13}C NMR spectrum of **3x**.

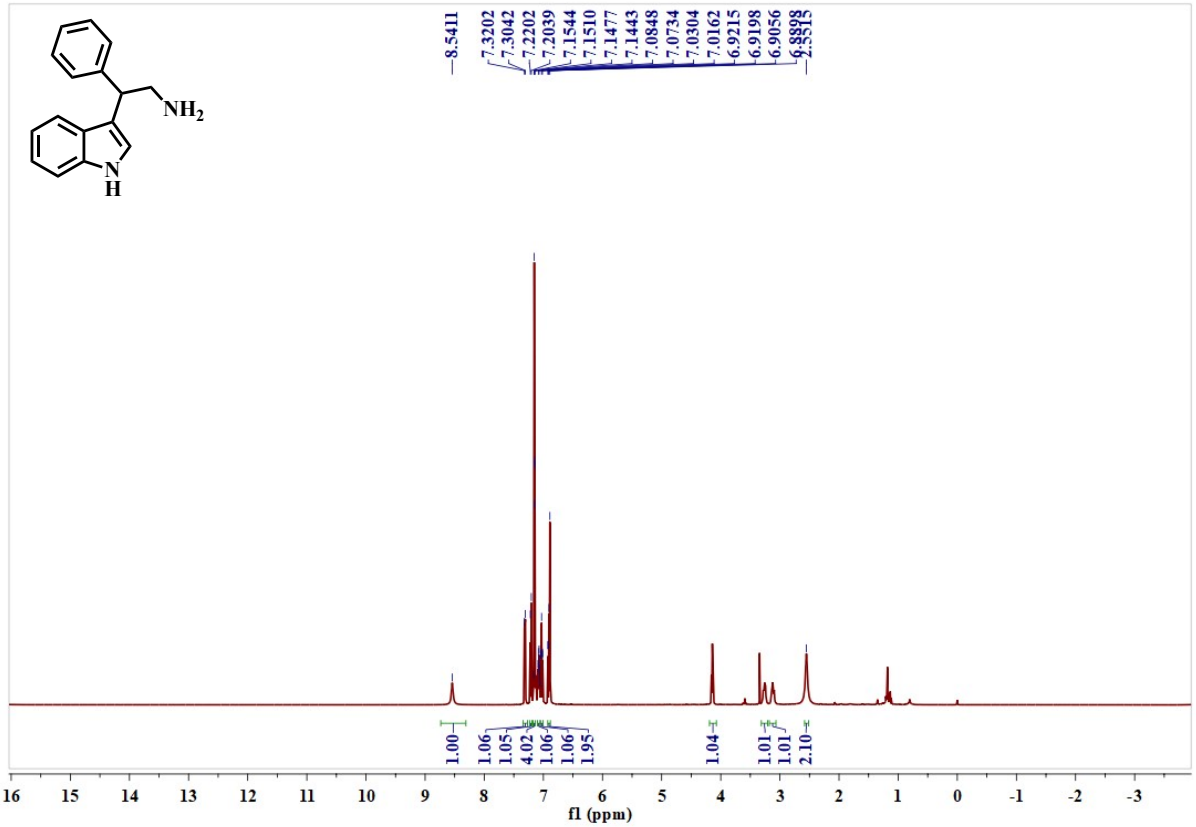


Fig. S61. ^{1}H NMR spectrum of **4a**.

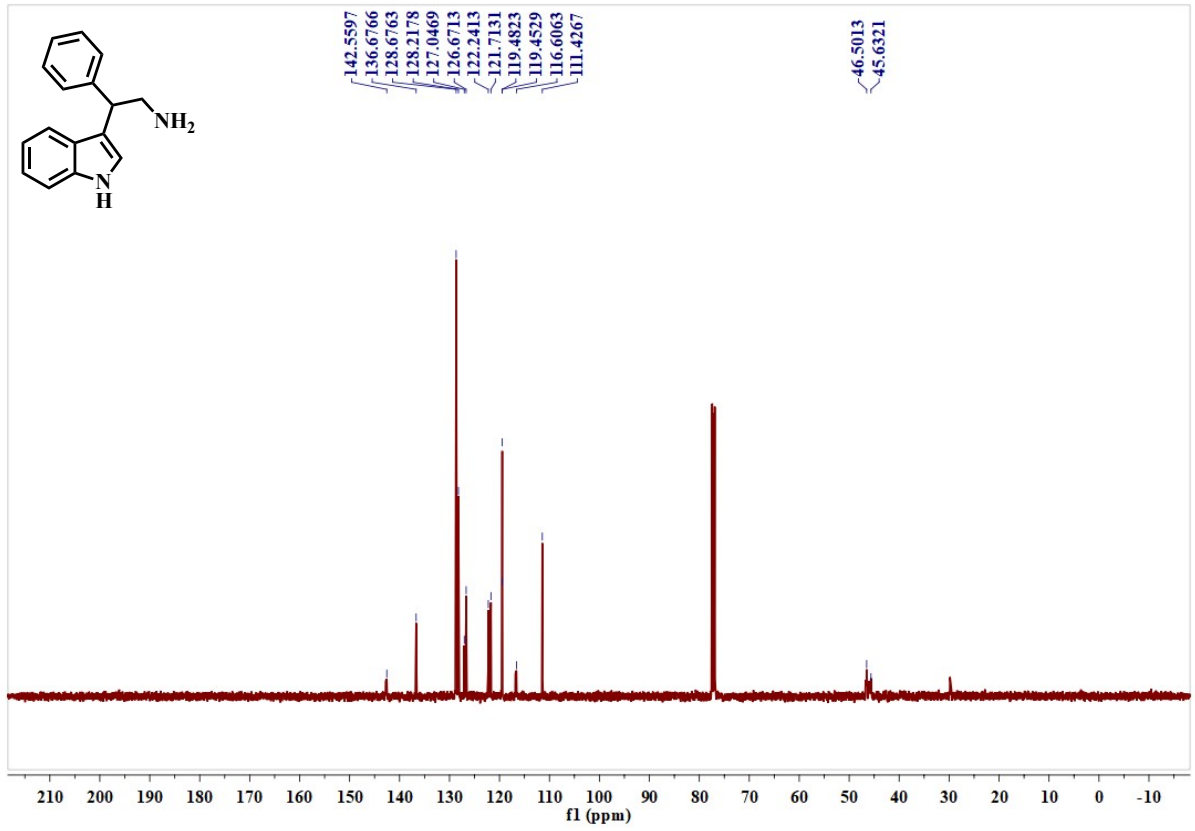


Fig. S62. ^{13}C NMR spectrum of **4a**.

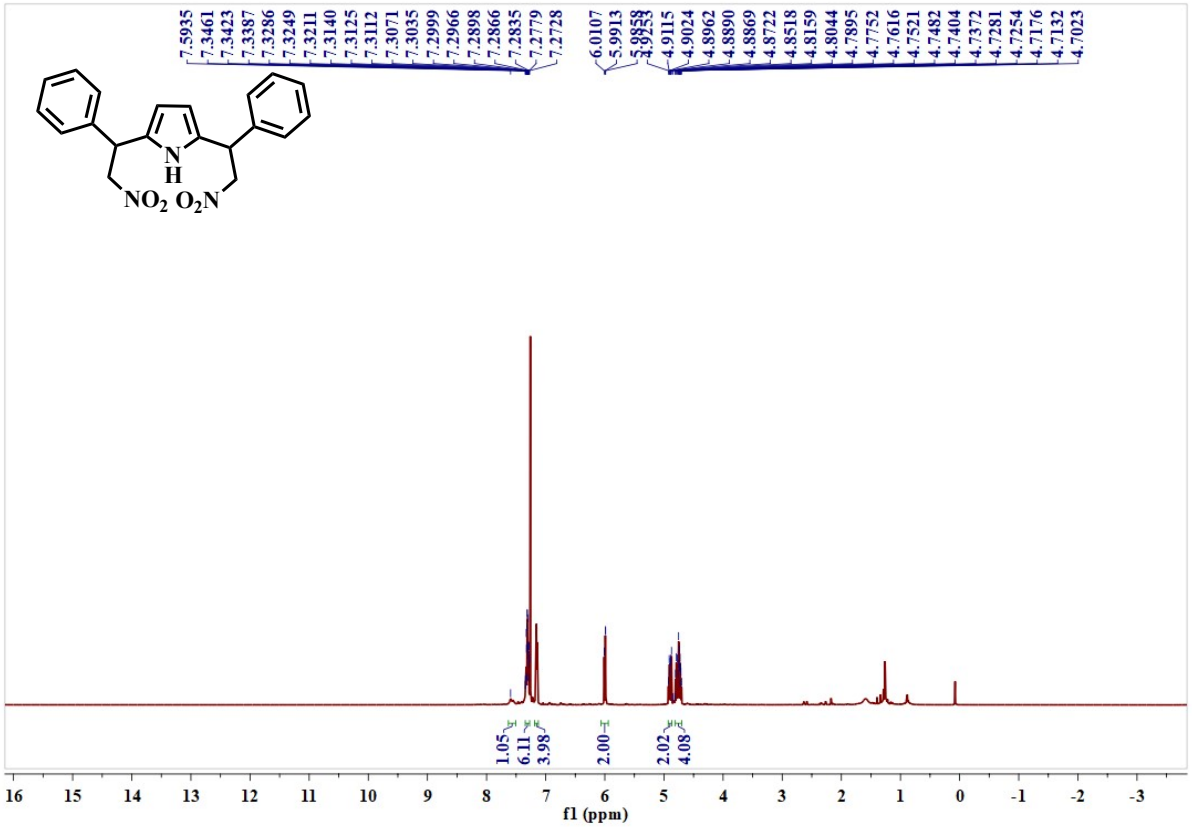


Fig. S63. ^{1}H NMR spectrum of **6a**.

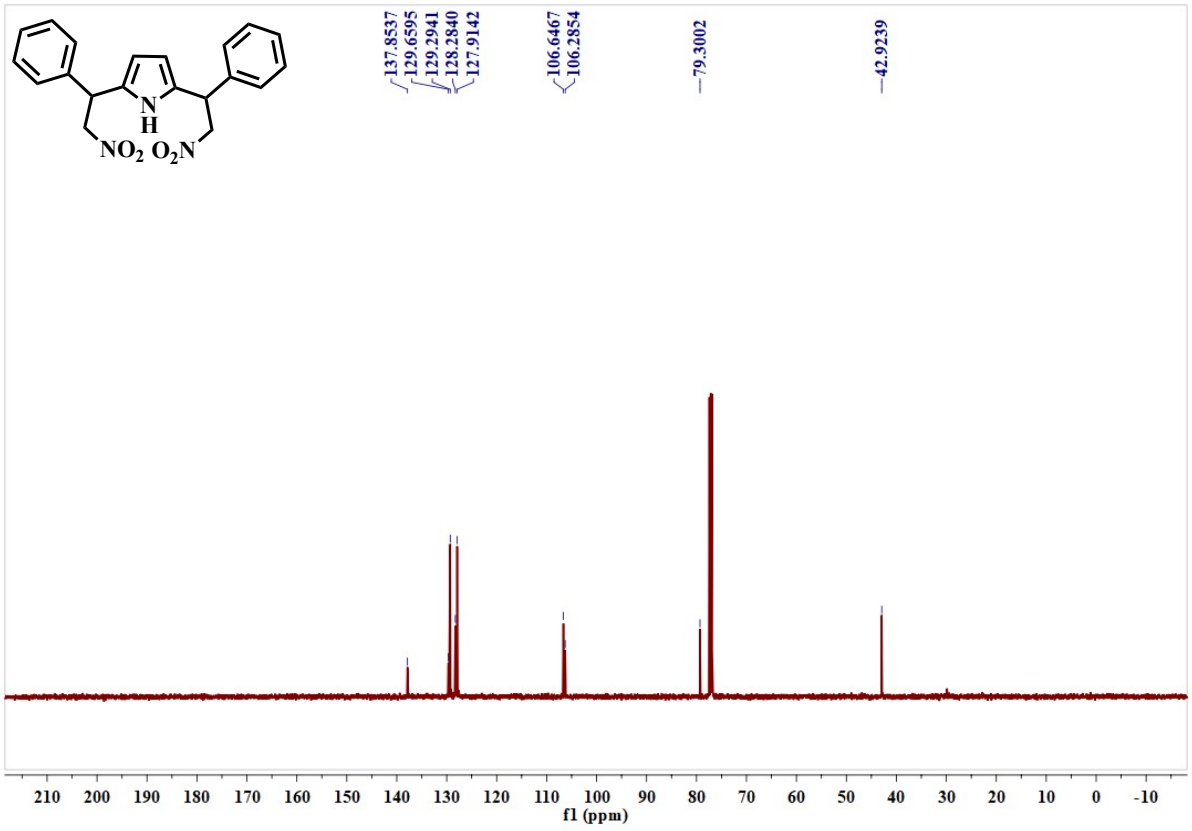


Fig. S64. ^{13}C NMR spectrum of **6a**.

5. HR-MS spectrum of 3x

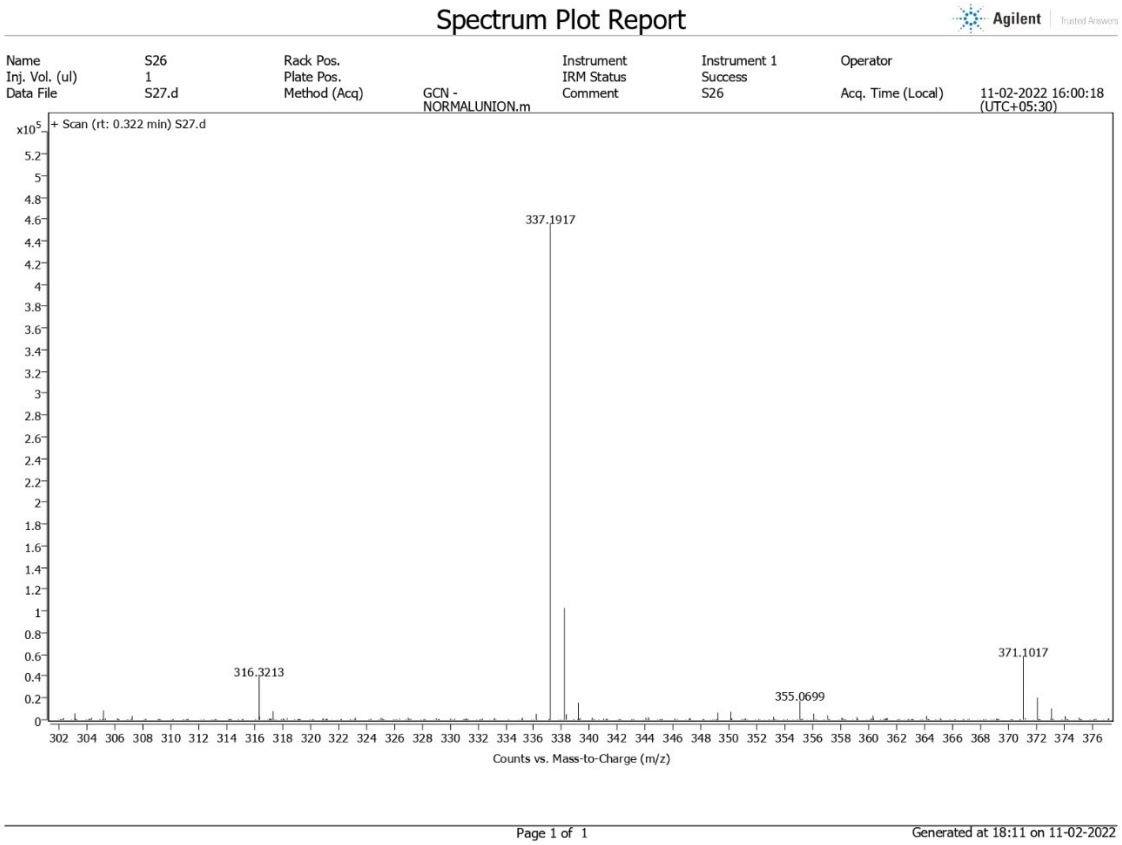


Fig. S65. HR-MS spectrum of **3x**.

6. FT-IR spectra of the fresh and recovered catalysts

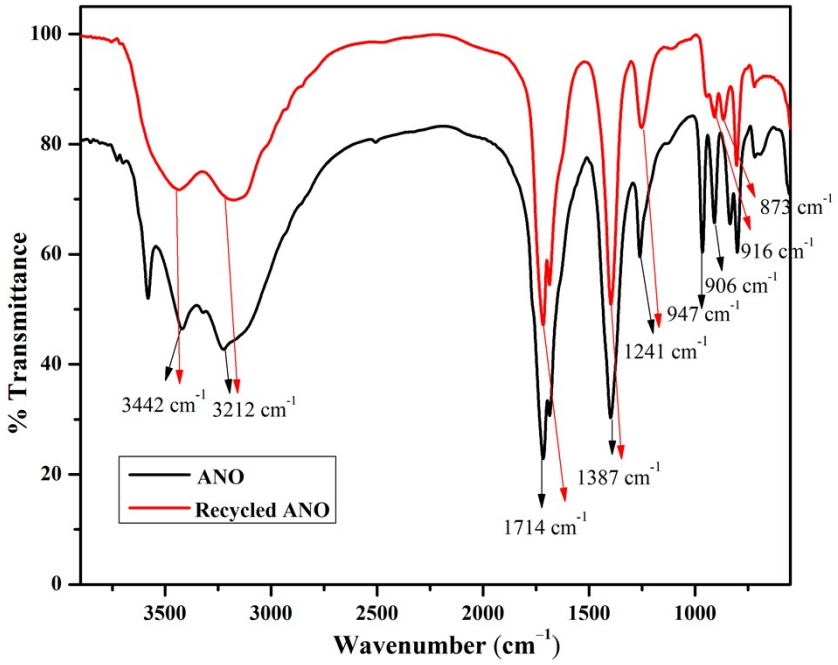


Fig. S66. FI-IR spectra of fresh ANO and recovered ANO.

7. Structure of the acylthiourea (L1)[20]

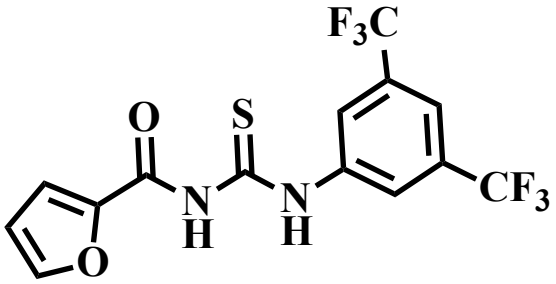


Fig. S67. Structure of the acylthiourea (L1).

8. Solvent optimization

S. No.	Solvent	Yield (%)
1	Neat	86
2	H_2O	73
3	EtOH	61
4	H_2O-EtOH (1:1)	88
5	H_2O-EtOH (3:1)	93
6	THF	17
7	DMSO	10
8	Toluene	8
9	PEG-200	42

Table S1: Solvent optimization

(Reaction conditions: 0.25 mmol of indole, 0.25 mmol of nitroalkenes, 1 mol% of ANO, 80 °C, 12 h.)

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