

Supplementary Materials: Highly Efficient Tetranuclear $\text{Zn}^{\text{II}}_2\text{Ln}^{\text{III}}_2$ Catalysts for the Friedel–Crafts Alkylation of Indoles and Nitrostyrenes

Prashant Kumar, Smaragda Lymperopoulou, Kieran Griffiths, Stavroula I. Sampani and George E. Kostakis

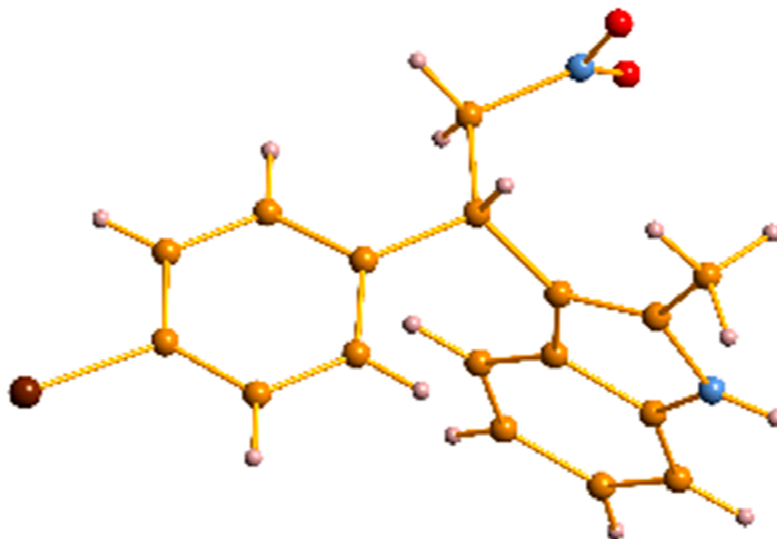
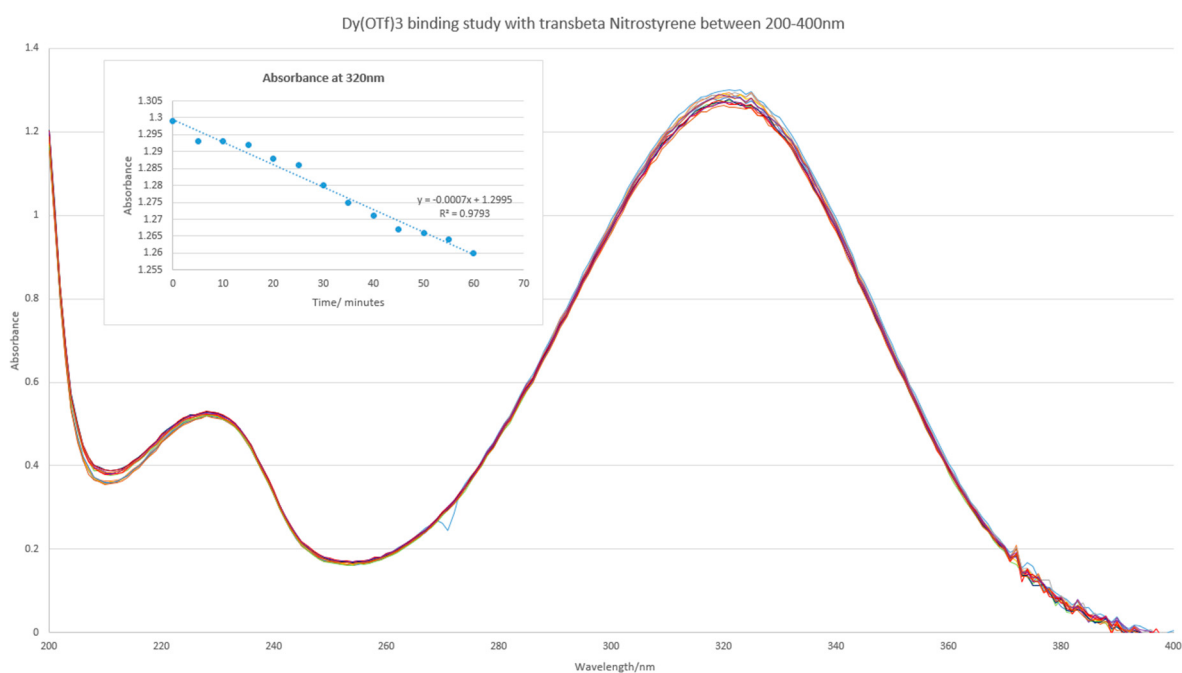
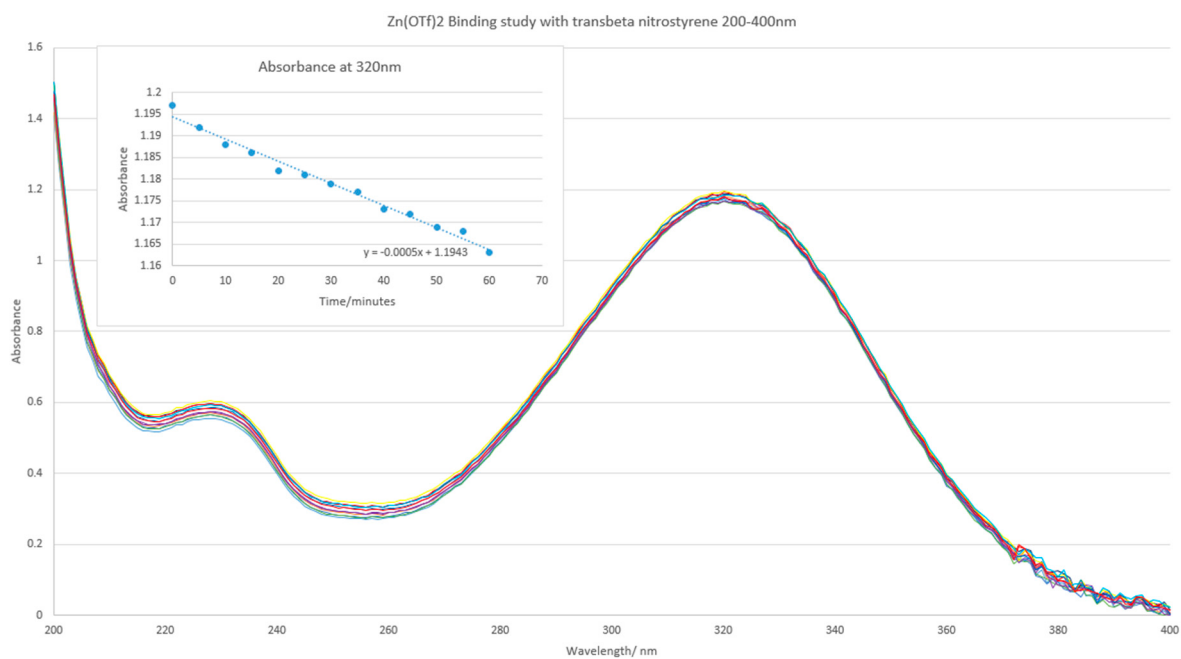


Figure S1. The crystal structure of compound **6h**.

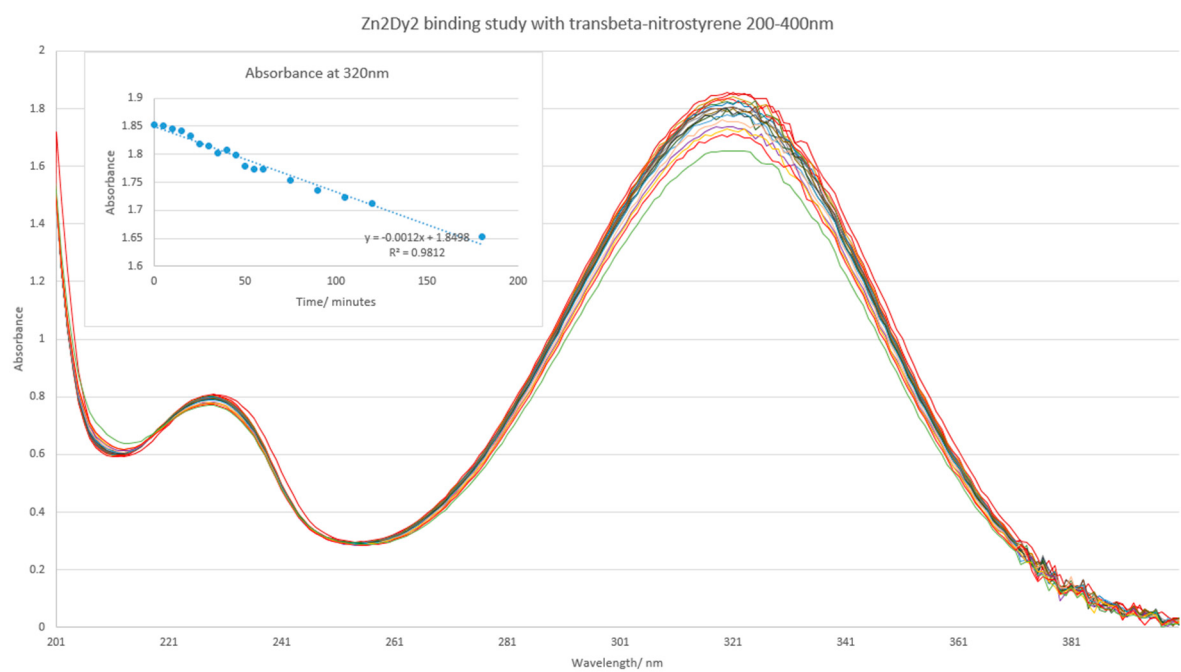


(a)

Figure S2. *Cont.*

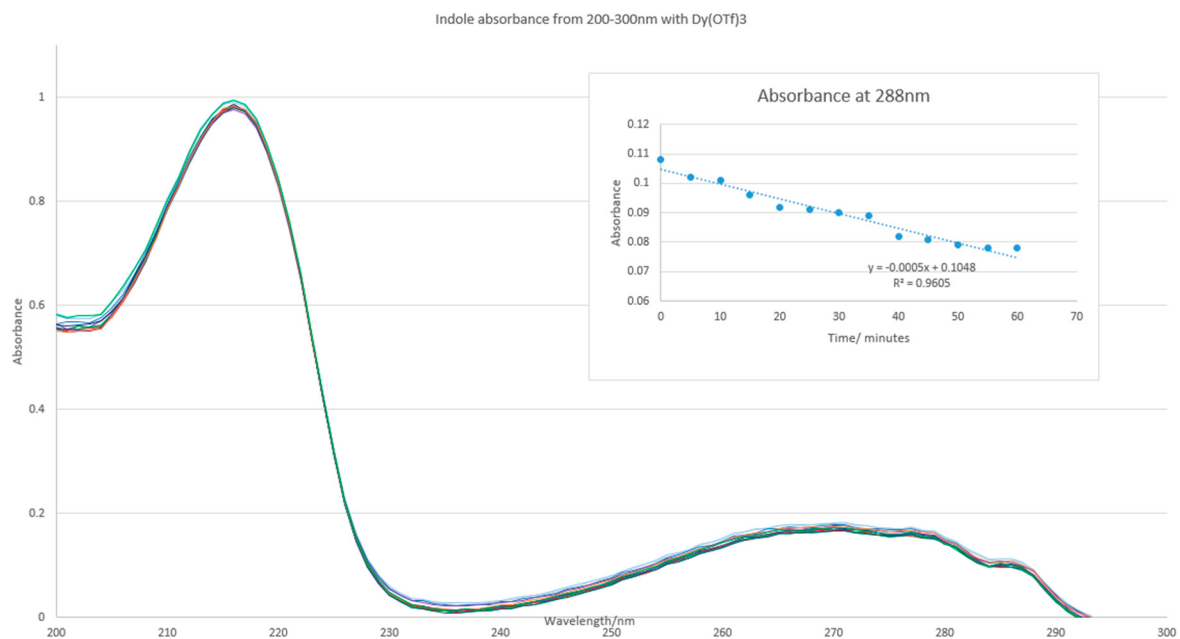


(b)

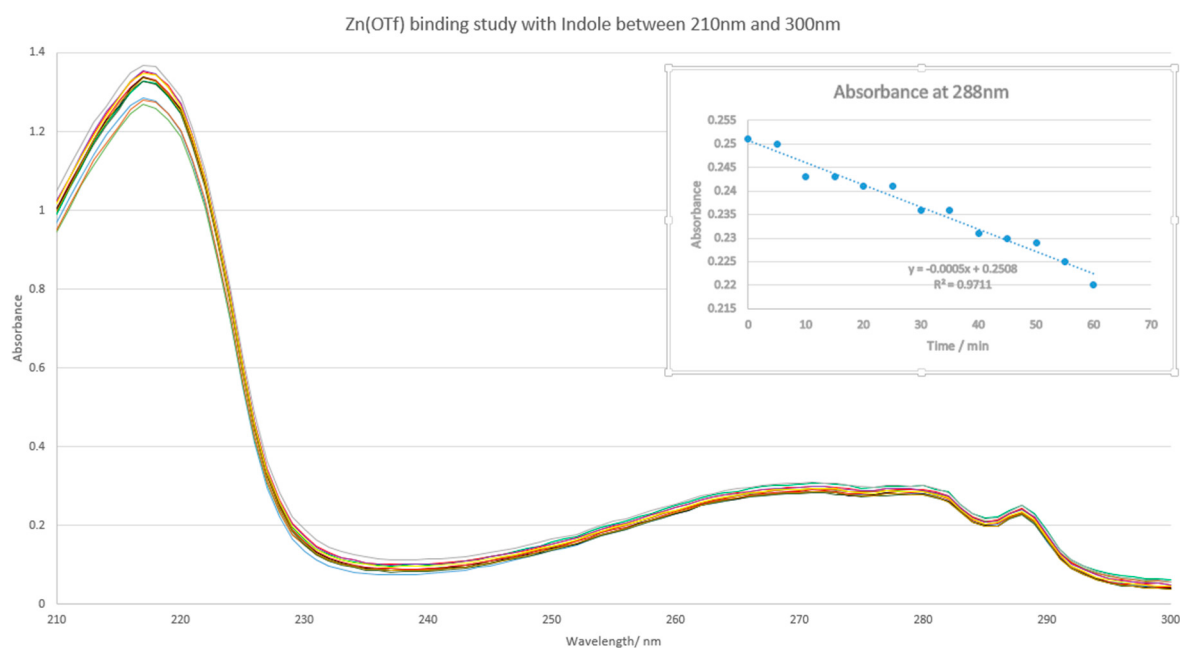


(c)

Figure S2. UV-Vis binding studies of Dy(OTf)₃ (a), Zn(OTf)₂ (b) and 1Dy (c) with trans- β -nitro-styrene recorded over 3 h with 5 min intervals between measurements.



(a)



(b)

Figure S3. Cont.

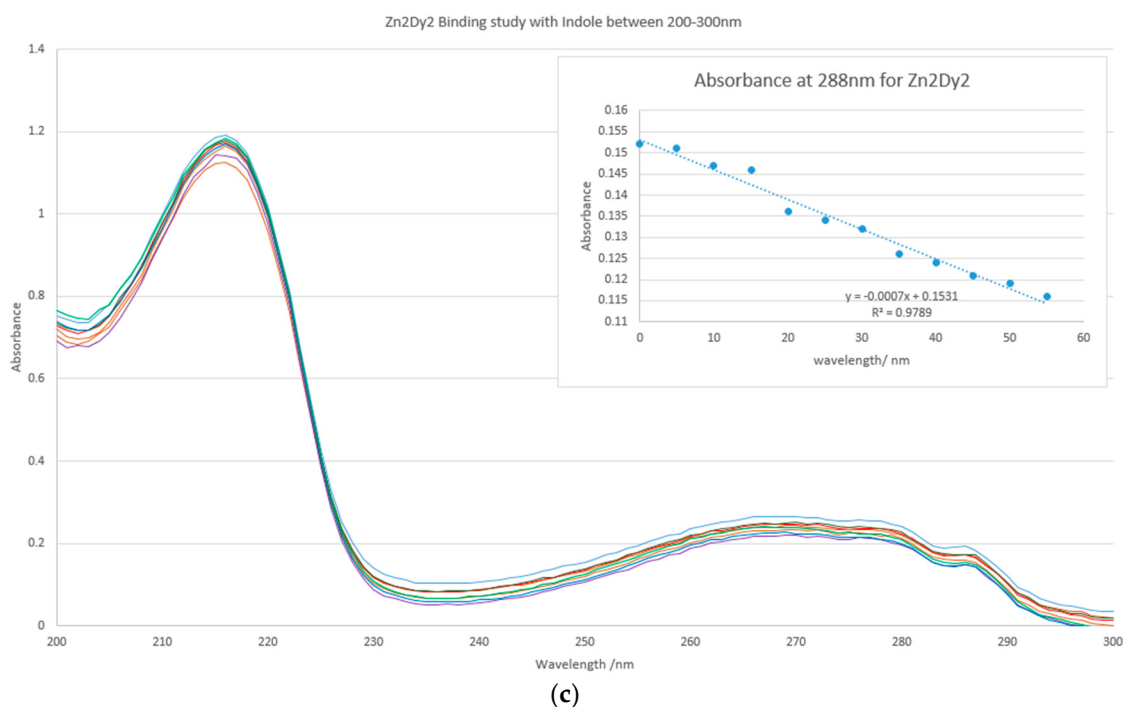


Figure S3. UV-Vis binding studies of Dy(OTf)₃ (a), Zn(OTf)₂ (b) and **1Dy** (c) with indole recorded over 3 h with 5 min intervals between measurements

General Methods

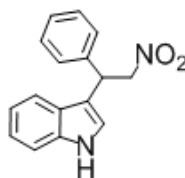
All chemicals and solvents were purchased from Sigma Aldrich, S.D. Fine Chemicals, and commercial suppliers. The progress of the reaction was monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 plates. Products were purified by column chromatography on silica gel (60–120 mesh). NMR spectra were collected using a Bruker Advance III HD 500 MHz Spectrometer. The ¹H and ¹³C NMR spectroscopic data were analysed with a 500 MHz spectrometer in either CDCl₃. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as the internal standard. The coupling constants (*J*) are reported in Hz, and the splitting patterns of the proton signals are described as s (singlet), d (doublet), t (triplet), and m (multiplet).

Synthesis of Complexes

H₂L1 (48 mg, 0.2 mmol) and Et₃N (61 μL, 0.4 mmol) were added to EtOH (20 mL) and the resultant solution was stirred for 5 m under reflux. Upon completion, Zn(NO₃)₂·6H₂O (56 mg, 0.2 mmol) and Ln(NO₃)₃·xH₂O (0.2 mmol) where Ln is Dy (**1Dy**), Y (**1Y**), Eu (**1Eu**) Gd (**1Gd**), Nb (**1Nb**), and Tb (**1Tb**) were added and the solution was refluxed for a further 2 h. After cooling, the yellow precipitate was filtered, washed with Et₂O and dissolved in DMF (10 mL). The resultant solution underwent vapor diffusion and after a week long yellow crystals with the formula Zn^{II}₂Ln^{III}₂L₄(NO₃)₂(DMF)₂] were afforded in a good yield.

Products

Synthesis of 3-(2-nitro-1-phenylethyl)-1H-indole (**4a**):



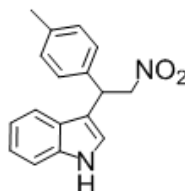
Chemical Formula: $C_{16}H_{14}N_2O_2$
Molecular Weight: 266.1

Indole (58 mg, 0.5 mmol), *trans*- β -nitrostyrene (74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4a** (263 mg, 0.99 mmol, 99%).

1H NMR ($CDCl_3$, 500 MHz): δ = 8.10 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.35–7.26 (m, 5H), 7.21–7.18 (m, 1H), 7.08–7.02 (m, 2H), 5.21 (t, J = 8.0 Hz, 1H), 5.08 (dd, J = 7.5 Hz, 2.5 Hz, 1H), 4.96 (dd, J = 8.5 Hz, 8.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.46, 136.41, 128.88, 127.73, 127.52, 125.90, 122.71, 121.56, 119.98, 118.93, 114.66, 111.32, 79.52, 41.56.

Synthesis of 3-(2-nitro-1-(*p*-tolyl)ethyl)-1H-indole (**4b**):



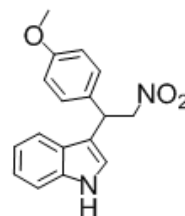
Chemical Formula: $C_{17}H_{16}N_2O_2$
Molecular Weight: 280.1

Indole (58 mg, 0.5 mmol), *trans*-4-methyl- β -nitrostyrene (81 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4b** (274 mg, 0.98 mmol, 98%).

1H NMR ($CDCl_3$, 500 MHz): δ = 8.08 (s, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 8.0, 1H), 7.21–7.16 (m, 3H), 7.15–7.10 (m, 2H), 7.09 (d, J = 2.5 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 5.17 (t, J = 7.8 Hz, 1H), 5.06 (dd, J = 7.0 Hz, 2.5 Hz, 1H), 4.95 (dd, J = 8.2 Hz, 8.1 Hz, 1H), 2.32 (s, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.60, 137.17, 134.62, 129.56, 127.59, 126.15, 124.76, 122.66, 121.49, 119.93, 118.96, 114.68, 111.29, 79.63, 41.21, 20.99.

Synthesis of 3-(1-(4-methoxyphenyl)-2-nitroethyl)-1H-indole (**4c**):



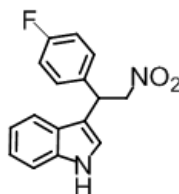
Chemical Formula: $C_{17}H_{16}N_2O_3$
Molecular Weight: 296.1

Indole (58 mg, 0.5 mmol), *trans*-4-methoxy- β -nitrostyrene (89 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4c** (284 mg, 0.96 mmol, 96%).

1H NMR ($CDCl_3$, 500 MHz): δ = 8.09 (s, 1H), 7.45 (d, J = 6.9 Hz, 1H), 7.37 (d, J = 8.2, 1H), 7.26–7.19 (m, 3H), 7.09 (d, J = 3.0 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.86–6.78 (m, 2H), 5.15 (t, J = 7.2 Hz, 1H), 5.06 (dd, J = 7.0 Hz, 2.5 Hz, 1H), 4.91 (dd, J = 7.8 Hz, 7.6 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 158.93, 131.30, 128.78, 122.68, 121.42, 119.93, 118.99, 114.30, 111.31, 109.99, 107.75, 103.39, 79.75, 55.23, 40.87.

Synthesis of 3-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole (**4d**):



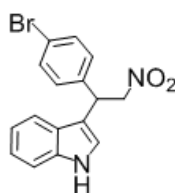
Chemical Formula: $\text{C}_{16}\text{H}_{13}\text{FN}_2\text{O}_2$
Molecular Weight: 284.1

Indole (58 mg, 0.5 mmol), *trans*-4-fluoro- β -nitrostyrene (83 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4d** (261 mg, 0.92 mmol, 92%).

^1H NMR (CDCl_3 , 500 MHz): δ = 8.11 (s, 1H), 7.40–7.34 (m, 2H), 7.31–7.26 (m, 2H), 7.22 (dd, J = 6.8 Hz, 2.4 Hz, 1H), 7.10 (dd, J = 7.1 Hz, 3.0 Hz, 1H), 7.02–6.94 (m, 3H), 5.19 (t, J = 6.6 Hz, 1H), 5.07 (dd, J = 7.2 Hz, 2.4 Hz, 1H), 4.92 (dd, J = 7.6 Hz, 7.3 Hz, 1H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 161.1, 136.5, 131.3, 129.4, 128.3, 125.9, 122.8, 121.4, 120.0, 118.8, 115.8 (2C), 115.7, 114.3, 79.5, 40.8.

Synthesis of 3-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole (**4e**):



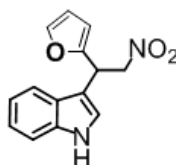
Chemical Formula: $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2$
Molecular Weight: 344.2

Indole (58 mg, 0.5 mmol), *trans*-4-bromo- β -nitrostyrene (114 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4e** (323 mg, 0.94 mmol, 94%).

^1H NMR (CDCl_3 , 500 MHz): δ = 8.15 (s, 1H), 7.46–7.38 (m, 2H), 7.37–7.30 (m, 2H), 7.22–7.14 (m, 3H), 7.10 (dd, J = 6.8 Hz, J = 2.6 Hz, 1H), 7.03 (d, J = 3.0 Hz, 1H), 5.16 (t, J = 7.4 Hz, 1H), 5.06 (dd, J = 6.9 Hz, 2.8 Hz, 1H), 4.92 (dd, J = 8.0 Hz, 7.7 Hz, 1H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 138.2, 136.8, 132.0, 131.3, 129.4, 122.8, 121.5 (2C), 120.1, 118.7, 115.1, 111.5, 79.1, 41.0.

Synthesis of 3-(1-(2-furanyl)-2-nitroethyl)-1H-indole (**4f**):



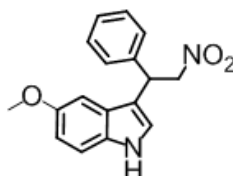
Chemical Formula: $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$
Molecular Weight: 256.2

Indole (58 mg, 0.5 mmol), *trans*-2-furanyl- β -nitrostyrene (69 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4f** (253 mg, 0.99 mmol, 99%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 8.12 (s, 1H), 7.58 (d, J = 5.8 Hz, 1H), 7.39–7.33 (m, 2H), 7.25–7.18 (m, 1H), 7.16–7.10 (m, 2H), 6.33 (d, J = 4.2 Hz, 1H), 6.18 (d, J = 4.0 Hz, 1H), 5.27 (t, J = 8.2 Hz, 1H), 5.07 (dd, J = 6.8 Hz, 2.8 Hz, 1H), 4.92 (dd, J = 7.2 Hz, 7.0 Hz, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 152.2, 142.2, 136.3, 125.7, 122.6 (2C), 120.3, 120.1, 118.7, 111.8, 111.4, 110.4, 107.3, 77.8, 35.7.

Synthesis of 5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole (**4g**):



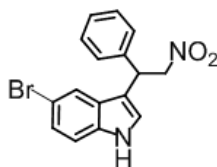
Chemical Formula: $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$
Molecular Weight: 296.3

5-methoxyindole (73 mg, 0.5 mmol), *trans*- β -nitrostyrene (74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4g** (287 mg, 0.97 mmol, 97%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 8.00 (s, 1H), 7.34 (d, J = 8.0 Hz, 4H), 7.26–7.18 (m, 2H), 7.21–7.18 (m, 1H), 7.02–6.92 (m, 2H), 5.15 (t, J = 7.2 Hz, 1H), 5.06 (dd, J = 8.0 Hz, 2.8 Hz, 1H), 4.95 (dd, J = 7.6 Hz, 6.8 Hz, 1H), 3.78 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 154.39, 139.06, 131.46, 128.75, 127.30, 127.05, 126.22, 123.77, 112.81, 112.19, 111.45, 110.45, 100.68, 77.83, 55.91, 40.85.

Synthesis of 5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole (**4h**):



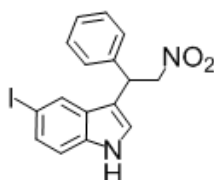
Chemical Formula: $\text{C}_{16}\text{H}_{13}\text{BrN}_2\text{O}_2$
Molecular Weight: 345.2

5-bromoindole (98 mg, 0.5 mmol), *trans*- β -nitrostyrene ((74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4h** (328 mg, 0.95 mmol, 95%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 8.22 (s, 1H), 7.6 (d, J = 1 Hz, 1H), 7.33–7.18 (m, 7H), 7.03 (d, J = 2.5 Hz, 1H), 5.12 (t, J = 8.0 Hz, 1H), 5.01 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 4.91 (dd, J = 8.0 Hz, 8.0 Hz, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 138.29, 136.54, 132.05, 129.46, 127.86, 126.95, 125.90, 122.88, 121.51, 120.12, 118.78, 113.96, 111.43, 79.19, 41.04.

Synthesis of 5-iodo-3-(2-nitro-1-phenylethyl)-1H-indole (**4i**):



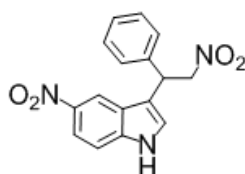
Chemical Formula: $C_{16}H_{13}IN_2O_2$
Molecular Weight: 392.2

5-iodoindole (121 mg, 0.5 mmol), *trans*- β -nitrostyrene ((74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4i** (368 mg, 0.94 mmol, 94%).

1H NMR ($CDCl_3$, 500 MHz): δ = 8.15 (s, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 2.8 Hz, 1H), 7.33–7.24 (m, 5H), 7.15 (d, J = 2.8 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 5.14 (t, J = 7.6 Hz, 1H), 5.03 (dd, J = 8.2 Hz, 8.0 Hz, 1H), 4.93 (dd, J = 8.1 Hz, 7.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.63, 135.5, 131.18, 129.02, 128.6, 127.7 (2C), 127.63, 127.63, 126.13, 122.33, 120.88, 114.47, 113.9, 113.26, 79.39, 41.26.

Synthesis of 5-nitro-3-(2-nitro-1-phenylethyl)-1H-indole (**4j**):



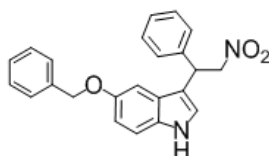
Chemical Formula: $C_{16}H_{13}N_3O_4$
Molecular Weight: 311.3

5-nitroindole (81 mg, 0.5 mmol), *trans*- β -nitrostyrene ((74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4j** (236 mg, 0.76 mmol, 76%).

1H NMR ($CDCl_3$, 500 MHz): δ = 8.47 (s, 1H), 8.38 (d, J = 2.5 Hz, 1H), 8.13 (dd, J = 3.5 Hz, 3.0 Hz, 1H), 7.35–7.22 (m, 7H), 5.25 (t, J = 7.2 Hz, 1H), 5.08 (dd, J = 7.8 Hz, 7.6 Hz, 1H), 4.97 (dd, J = 8.0 Hz, 7.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 142.6, 139.0, 132.30, 128.7, 126.5, 126.23, 124.10, 122.18, 117.3, 114.2, 113.2, 111.58, 79.78, 40.85.

Synthesis of 5-benzyoxy-3-(2-nitro-1-phenylethyl)-1H-indole (**4k**):



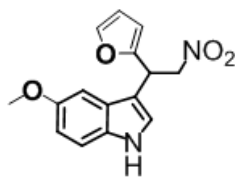
Chemical Formula: $C_{23}H_{20}N_2O_3$
Molecular Weight: 372.4

5-benzyoxyindole (111 mg, 0.5 mmol), *trans*- β -nitrostyrene ((74 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4k** (357 mg, 0.96 mmol, 96%).

1H NMR ($CDCl_3$, 500 MHz): δ = 7.98 (s, 1H), 7.48–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.33–7.26 (m, 4H), 7.25 (d, J = 2.5 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 3.0 Hz, 2H), 5.12 (t, J = 6.5 Hz, 1H), 5.02–4.98 (m, 3H), 4.93 (dd, J = 8.0 Hz, 7.8 Hz, 1H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 153.4, 152.1, 142.2, 137.4, 131.6, 128.5, 127.8, 127.5, 126.1, 123.3, 122.18, 113.5, 112.1, 111.5, 110.4, 107.3, 102.4, 77.7, 71.03, 35.7.

Synthesis of 5-methoxy-3-(1-(2-furanyl)-2-nitroethyl)-1H-indole (**4l**):



Chemical Formula: $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$

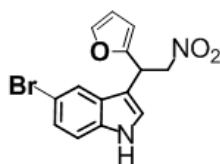
Molecular Weight: 286.2

5-methoxyindole (73 mg, 0.5 mmol), *trans*-2-furanyl- β -nitrostyrene (69 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4l** (280 mg, 0.98 mmol, 98%).

^1H NMR (CDCl_3 , 500 MHz): δ = 8.08 (s, 1H), 7.40 (d, J = 4.2 Hz, 1H), 7.27–7.21 (m, 1H), 7.10 (d, J = 2.8 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.89 (d, J = 3.0 Hz, 1H), 6.33 (d, J = 3.0 Hz, 1H), 6.19 (d, J = 3.8 Hz, 1H), 5.22 (t, J = 7.6 Hz, 1H), 5.05 (dd, J = 7.4 Hz, 7.3 Hz, 1H), 4.91 (dd, J = 7.6 Hz, 7.4 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 154.39, 152.25, 142.20, 131.46, 126.22, 123.27, 112.81, 112.19, 111.45, 110.45, 107.33, 100.68, 77.83, 55.91, 35.69.

Synthesis of 5-bromo-3-(1-(2-furanyl)-2-nitroethyl)-1H-indole (**4m**):



Chemical Formula: $\text{C}_{14}\text{H}_{11}\text{BrN}_2\text{O}_3$

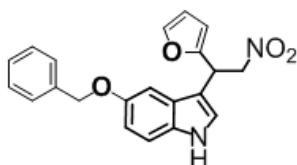
Molecular Weight: 335.1

5-bromoindole (98 mg, 0.5 mmol), *trans*-2-furanyl- β -nitrostyrene (69 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4m** (318 mg, 0.95 mmol, 95%).

^1H NMR (CDCl_3 , 500 MHz): δ = 8.20 (s, 1H), 7.56 (d, J = 5.8 Hz, 1H), 7.44 (d, J = 4.2 Hz, 1H), 7.38–7.34 (m, 1H), 7.25–7.18 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.28 (d, J = 3.8 Hz, 1H), 6.18 (d, J = 4.0 Hz, 1H), 5.16 (t, J = 7.4 Hz, 1H), 5.06 (dd, J = 8.2 Hz, 8.0 Hz, 1H), 4.94 (dd, J = 8.1 Hz, 8.0 Hz, 1H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 155.37, 142.22, 136.34, 129.40, 122.6 (2C), 120.11, 118.71, 115.81, 111.47, 110.44, 107.36, 77.87, 35.72.

Synthesis of 5-benzyloxy-3-(1-(2-furanyl)-2-nitroethyl)-1H-indole (**4n**):



Chemical Formula: $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4$

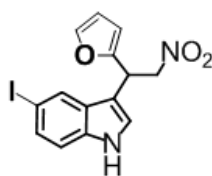
Molecular Weight: 362.3

5-benzyloxyindole (111 mg, 0.5 mmol), *trans*-2-furanyl- β -nitrostyrene (69 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4n** (348 mg, 0.96 mmol, 96%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 8.04 (s, 1H), 7.48–7.41 (m, 2H), 7.39–7.34 (m, 3H), 7.33–7.28 (m, 1H), 7.27–7.22 (m, 1H), 7.10 (t, J = 4.2 Hz, 1H), 7.06 (t, J = 3.6 Hz, 1H), 6.97 (d, J = 2.8 Hz, 2H), 6.31 (d, J = 4.0 Hz, 1H), 6.15 (d, J = 3.8 Hz, 1H), 5.20 (t, J = 7.0 Hz, 1H), 5.10–5.03 (m, 3H), 4.87 (dd, J = 7.6 Hz, 7.4 Hz, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 153.4, 152.1, 142.2, 137.4, 131.6, 128.5, 127.8, 127.5, 126.1, 123.3, 122.18, 113.5, 112.1, 111.5, 110.4, 107.3, 102.4, 77.7, 71.03, 35.7.

Synthesis of 5-iodo-3-(1-(2-furanyl)-2-nitroethyl)-1H-indole (**4o**):



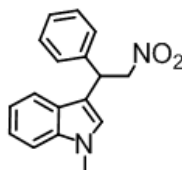
Chemical Formula: $\text{C}_{14}\text{H}_{11}\text{IN}_2\text{O}_3$
Molecular Weight: 362.3

5-iodoindole (137 mg, 0.5 mmol), *trans*-2-furanyl- β -nitrostyrene (69 mg, 0.5 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **4o** (344 mg, 0.95 mmol, 95%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 8.22 (s, 1H), 7.89 (d, J = 4.0 Hz, 1H), 7.48 (dd, J = 6.2 Hz, 4.0 Hz, 1H), 7.40–7.35 (m, 1H), 7.15–7.08 (m, 2H), 6.33 (d, J = 4.0 Hz, 1H), 6.16–6.10 (m, 1H), 5.19 (t, J = 8.0 Hz, 1H), 5.04–4.98 (m, 1H), 4.90 (dd, J = 8.2 Hz, 8.0 Hz, 1H)

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 156.58, 142.37, 131.14, 127.61, 126.15, 123.43, 119.91, 113.38, 110.51, 107.51, 88.11, 35.47.

Synthesis of 3-(2-nitro-1-phenylethyl)-1-methyl-indole (**6a**):



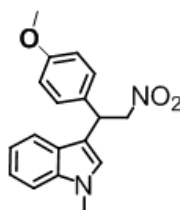
Chemical Formula: $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$
Molecular Weight: 280.3

N-methylindole (39 mg, 0.3 mmol), *trans*- β -nitrostyrene (44 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6a** (277 mg, 0.99 mmol, 99%).

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ = 7.45 (d, J = 7.6 Hz, 1H), 7.33–7.26 (m, 5H), 7.24–7.18 (m, 1H), 7.08–7.02 (m, 2H), 6.87 (s, 1H), 5.19 (t, J = 7.8 Hz, 1H), 5.06 (dd, J = 7.2 Hz, 2.8 Hz, 1H), 4.95 (dd, J = 8.0 Hz, 7.8 Hz, 1H), 3.76 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 126 MHz): δ = 139.46, 136.41, 128.88, 127.73, 127.52, 125.90, 122.71, 121.56, 119.98, 118.93, 114.66, 111.32, 79.52, 41.56.

Synthesis of 3-(1-(4-methoxyphenyl)-2-nitroethyl)-1-methyl-indole (**6b**):



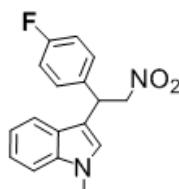
Chemical Formula: $C_{18}H_{18}N_2O_3$
Molecular Weight: 310.3

N-methylindole (39 mg, 0.3 mmol), *trans*-4-methoxy- β -nitrostyrene (54 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6b** (307 mg, 0.99 mmol, 99%).

1H NMR ($CDCl_3$, 500 MHz): δ = 7.48 (d, J = 7.0 Hz, 1H), 7.35–7.28 (m, 4H), 7.25–7.18 (m, 1H), 6.89 (d, J = 3.0 Hz, 3H), 5.18 (t, J = 7.0 Hz, 1H), 5.06 (dd, J = 7.2 Hz, 2.8 Hz, 1H), 4.86 (dd, J = 8.2 Hz, 7.8 Hz, 1H), 3.67 (s, 3H), 3.62 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 158.90, 137.35, 131.41, 128.75, 126.56, 126.23, 124.10, 122.18, 119.40, 119.03, 117.73, 114.28, 113.22, 109.45, 79.78, 55.23, 40.85, 32.76.

Synthesis of 3-(1-(4-fluorophenyl)-2-nitroethyl)-1-methyl-indole (**6c**):



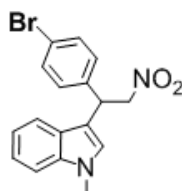
Chemical Formula: $C_{17}H_{15}FN_2O_2$
Molecular Weight: 298.3

N-methylindole (39 mg, 0.3 mmol), *trans*-4-fluoro- β -nitrostyrene (50 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6c** (277 mg, 0.93 mmol, 93%).

1H NMR ($CDCl_3$, 500 MHz): δ = 7.42–7.37 (m, 1H), 7.32–7.24 (m, 3H), 7.24 (dd, J = 7.0 Hz, 2.6 Hz, 1H), 7.09 (dd, J = 7.4 Hz, 2.8 Hz, 1H), 7.02–6.96 (m, 2H), 6.86 (s, 1H), 5.18 (t, J = 7.2 Hz, 1H), 5.05 (dd, J = 8.0 Hz, 2.5 Hz, 1H), 4.91 (dd, J = 8.0 Hz, 8.1 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 161.09, 137.37, 135.20, 135.17, 129.35, 129.29, 126.42, 126.19, 122.35, 119.55, 118.90, 115.86, 115.69, 109.56, 79.57, 40.87, 32.80.

Synthesis of 3-(1-(4-bromophenyl)-2-nitroethyl)-1-methyl-indole (**6d**):



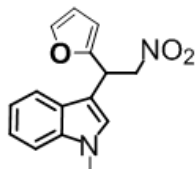
Chemical Formula: $C_{17}H_{15}BrN_2O_2$
Molecular Weight: 359.2

N-methylindole (39 mg, 0.3 mmol), *trans*-4-bromo- β -nitrostyrene (68 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6d** (341 mg, 0.95 mmol, 95%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.46–7.42 (m, 2H), 7.41–7.34 (m, 1H), 7.31 (dd, J = 2.8 Hz, 1H), 7.24–7.16 (m, 3H), 7.09 (dd, J = 7.0 Hz, J = 2.8 Hz, 1H), 6.85 (s, 1H), 5.15 (t, J = 7.6 Hz, 1H), 5.04 (dd, J = 7.2 Hz, 2.5 Hz, 1H), 4.91 (dd, J = 8.0 Hz, 7.8 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 139.46, 136.26, 134.43, 132.03, 129.26, 126.26, 125.27, 122.39, 119.60, 118.82, 109.99, 109.57, 79.21, 41.01, 32.82.

Synthesis of 3-(1-(2-furanyl)-2-nitroethyl)-1-methyl-indole (**6e**):



Chemical Formula: $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$

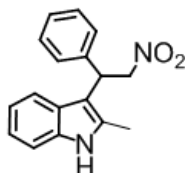
Molecular Weight: 270.2

N-methylindole (39 mg, 0.3 mmol), *trans*-2-furanyl- β -nitrostyrene (42 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6e** (267 mg, 0.99 mmol, 99%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.56–7.48 (m, 1H), 7.40 (dd, J = 4.3 Hz, 1H), 7.32–7.29 (m, 1H), 7.27–7.21 (m, 1H), 7.14 (dd, J = 7.1 Hz, J = 2.8 Hz, 1H), 6.99 (s, 1H), 6.33 (d, J = 4.0 Hz, 1H), 6.18 (d, J = 4.2 Hz, 1H), 5.25 (t, J = 8.0 Hz, 1H), 5.05 (dd, J = 7.0 Hz, 3.0 Hz, 1H), 4.92 (dd, J = 7.2 Hz, 7.0 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 152.38, 142.16, 137.16, 127.25, 126.19, 122.17, 119.58, 118.76, 110.42, 110.05, 109.60, 107.23, 77.99, 35.68, 32.80.

Synthesis of 3-(2-nitro-1-phenylethyl)-2-methyl-1H-indole (**6f**):



Chemical Formula: $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$

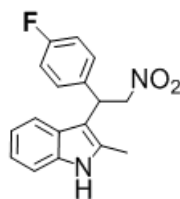
Molecular Weight: 280.3

2-methylindole (39 mg, 0.3 mmol), *trans*- β -nitrostyrene (44 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6f** (277 mg, 0.99 mmol, 99%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.86 (s, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.30–7.21 (m, 6H), 7.13–7.08 (m, 1H), 7.05 (dd, J = 6.0 Hz, 1H), 5.23–5.16 (m, 2H), 5.13 (dd, J = 8.0 Hz, 2.6 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 139.54, 135.44, 132.77, 128.75, 127.30, 127.73, 127.05, 126.91, 122.71, 121.36, 119.77, 110.67, 109.99, 108.98, 78.63, 41.47, 11.99.

3-(1-(4-fluorophenyl)-2-nitroethyl)-2-methyl-1H-indole (**6g**):



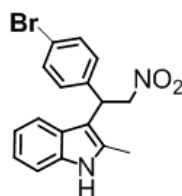
Chemical Formula: $C_{17}H_{15}FN_2O_2$
Molecular Weight: 298.1

2-methylindole (39 mg, 0.3 mmol), *trans*-4-fluoro- β -nitrostyrene (50 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6g** (280 mg, 0.94 mmol, 94%).

1H NMR ($CDCl_3$, 500 MHz): δ = 7.89 (s, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.29–7.20 (m, 3H), 7.14–7.08 (m, 1H), 7.05 (dd, J = 6.2 Hz, 1H), 6.99–6.92 (m, 2H), 5.20–5.12 (m, 2H), 5.09 (dd, J = 8.2 Hz, 3.0 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 162.74, 135.42, 132.69, 128.90, 128.84, 126.72, 121.50, 119.89, 118.44, 115.69, 115.52, 115.69, 110.72, 109.99, 108.83, 78.66, 40.87, 39.85, 12.03.

3-(1-(4-bromophenyl)-2-nitroethyl)-2-methyl-1H-indole (**6h**):



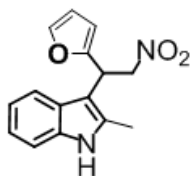
Chemical Formula: $C_{17}H_{15}BrN_2O_2$
Molecular Weight: 359.2

2-methylindole (39 mg, 0.3 mmol), *trans*-4-bromo- β -nitrostyrene (68 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6h** (344 mg, 0.96 mmol, 96%).

1H NMR ($CDCl_3$, 500 MHz): δ = 7.91 (s, 1H), 7.43–7.38 (m, 2H), 7.30–7.24 (m, 2H), 7.20–7.15 (m, 2H), 7.14–7.09 (m, 1H), 7.05–6.99 (m, 1H), 5.21 (d, J = 8.0 Hz, 7.8 Hz, 1H), 5.15–5.10 (m, 1H), 5.08 (dd, J = 7.6 Hz, 3.2 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.59, 135.43, 132.79, 131.85, 130.50, 129.02, 126.65, 124.79, 121.04, 119.94, 118.38, 110.75, 108.46, 78.32, 41.01, 39.97, 12.02.

Synthesis of 3-(1-(2-furanyl)-2-nitroethyl)-2-methyl-1H-indole (**6i**):



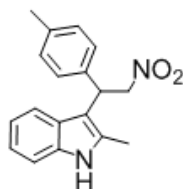
Chemical Formula: $C_{15}H_{14}N_2O_3$
Molecular Weight: 270.2

2-methylindole (39 mg, 0.3 mmol), *trans*-2-furanyl- β -nitrostyrene (42 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6i** (267 mg, 0.99 mmol, 99%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.90 (s, 1H), 7.39–7.32 (m, 2H), 7.28–7.22 (m, 1H), 7.14–7.08 (m, 1H), 7.06–6.99 (m, 1H), 6.31 (d, J = 3.8 Hz, 1H), 6.10 (d, J = 4.0 Hz, 1H), 5.20–5.12 (m, 2H), 4.95–4.88 (m, 1H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 152.31, 141.94, 135.40, 133.07, 126.63, 121.47, 119.75, 118.53, 110.63, 110.43, 109.99, 107.21, 78.71, 35.68, 35.29, 11.77.

Synthesis of 3-(2-nitro-1-(p-tolyl)ethyl)-2-methyl-1H-indole (**6j**):

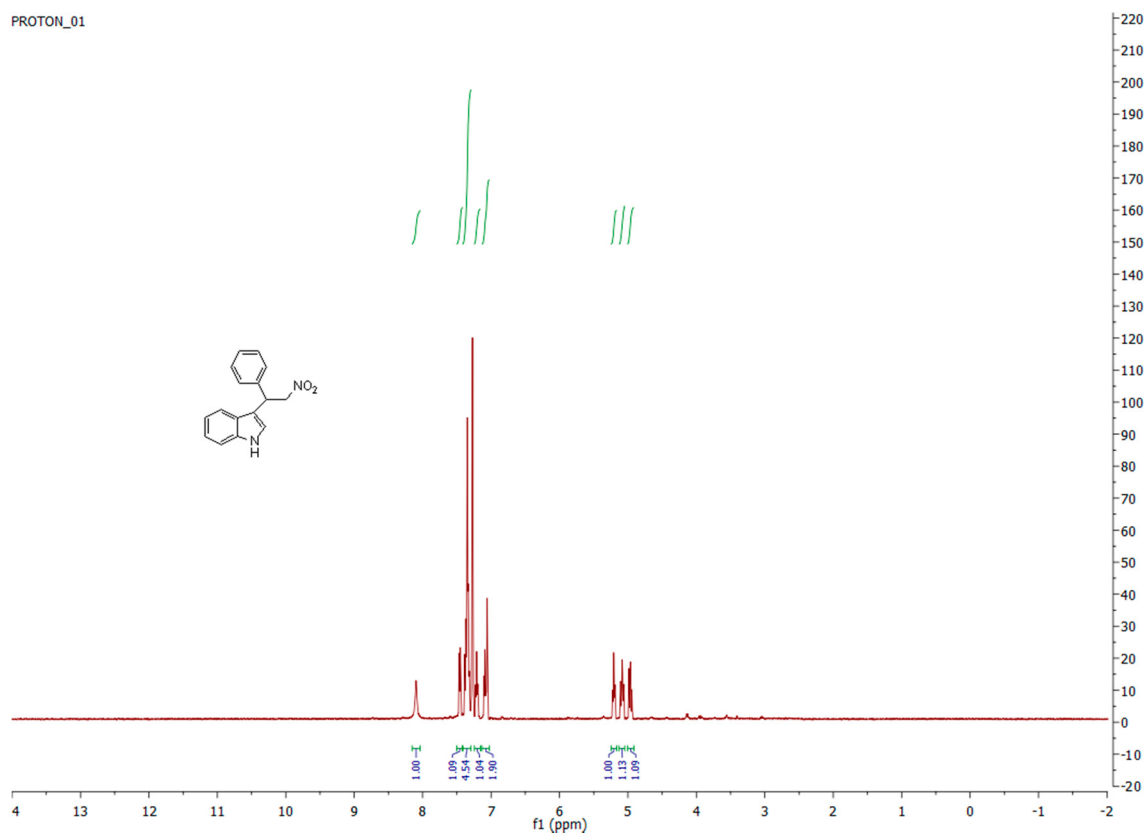


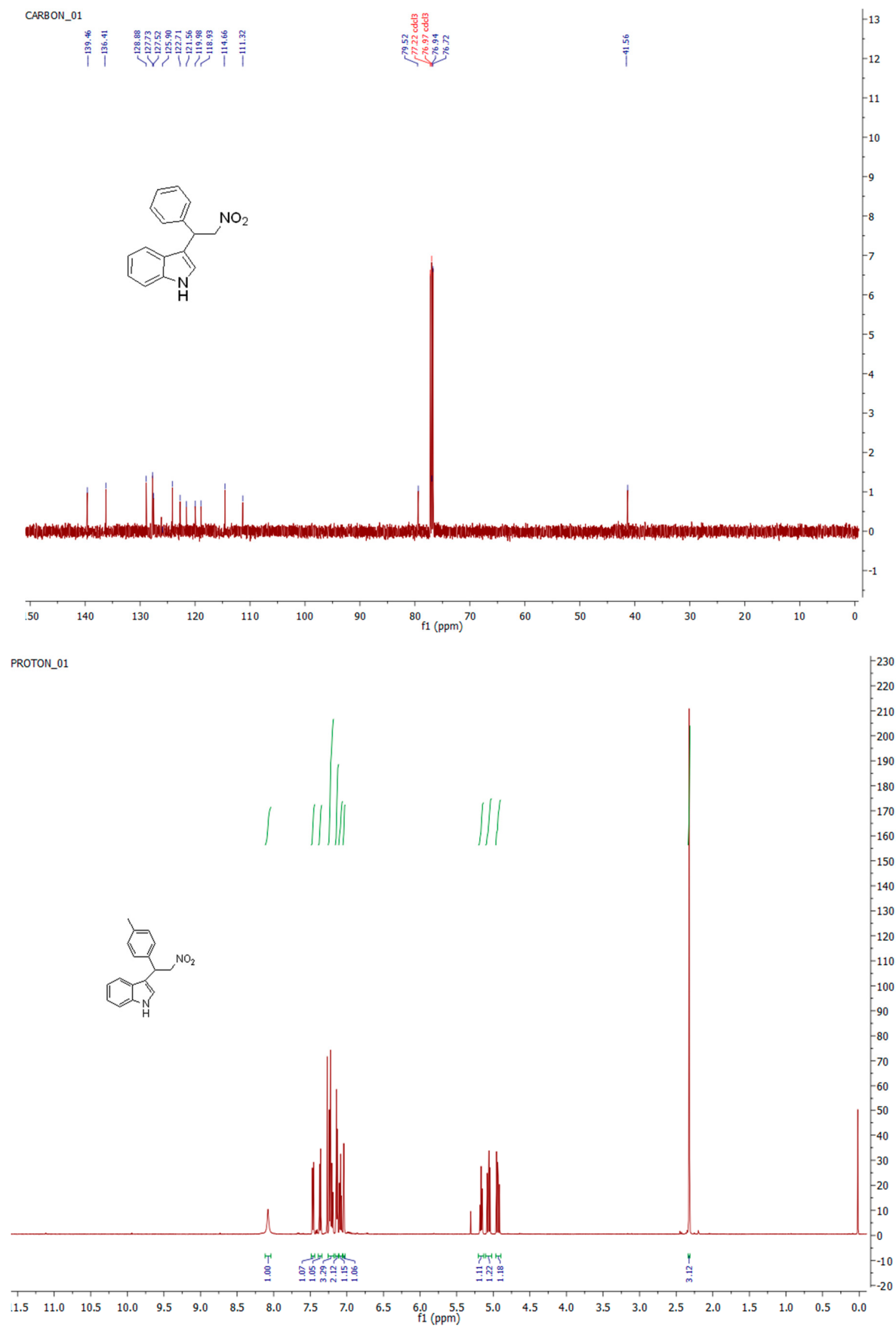
Chemical Formula: $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$
Molecular Weight: 294.3

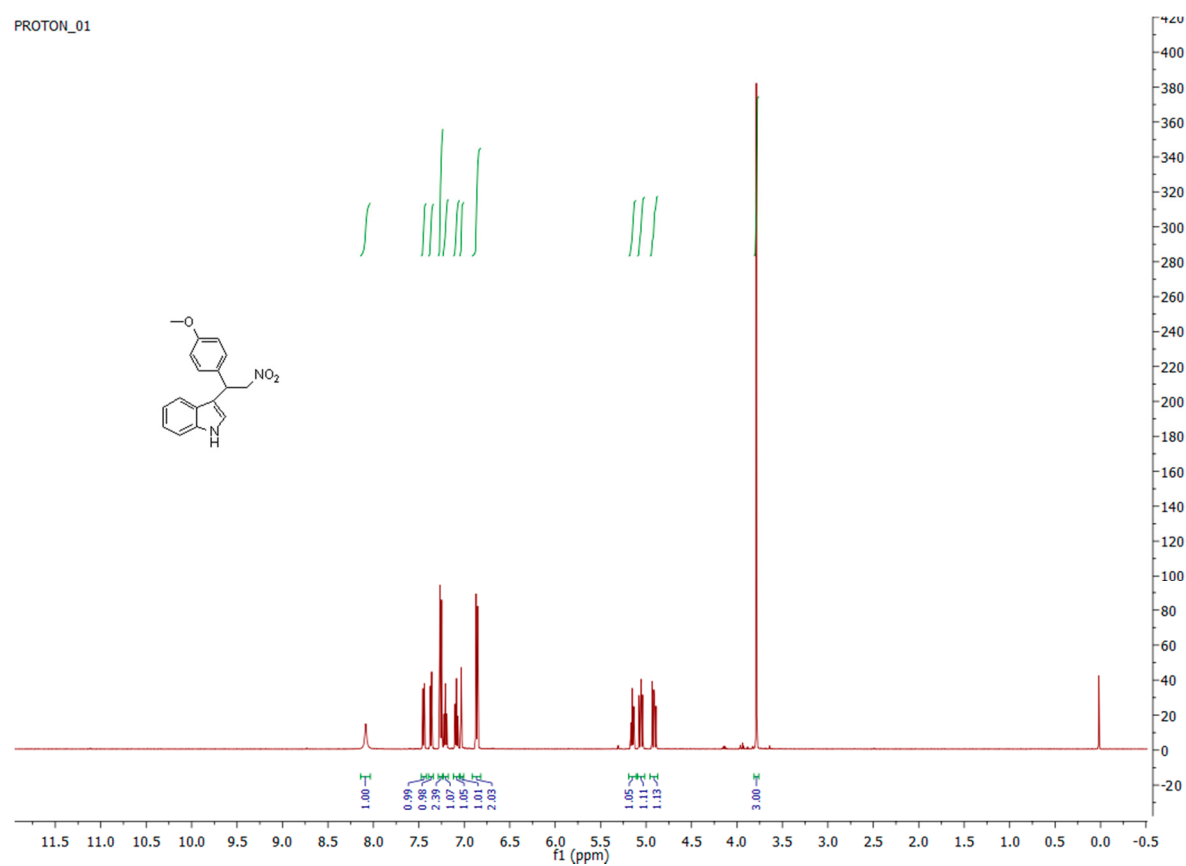
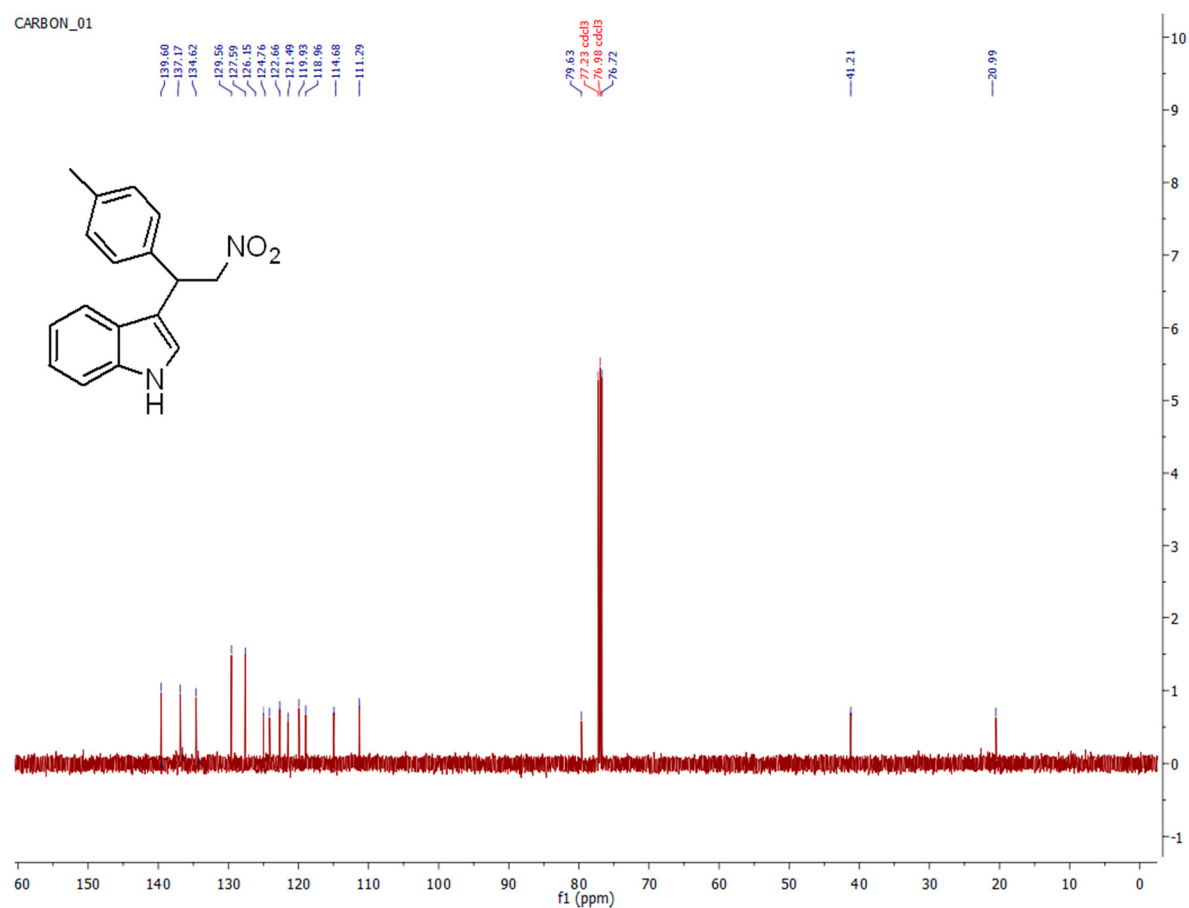
2-methylindole (39 mg, 0.3 mmol), *trans*-4-methyl- β -nitrostyrene (49 mg, 0.3 mmol), 1.0 mol % pre-catalyst **Dy** (**1Dy**), 3 mL EtOH, rt, 24 h. The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **6j** (288 mg, 0.98 mmol, 98%).

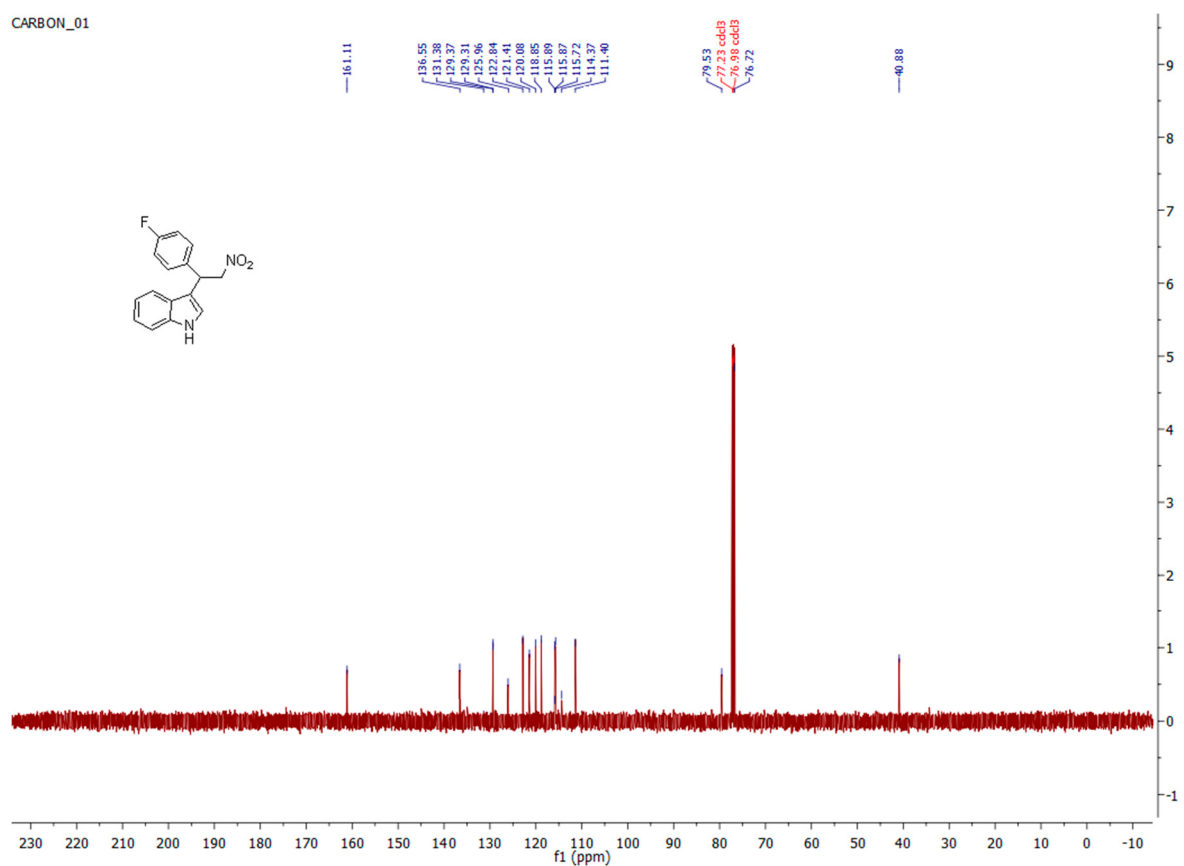
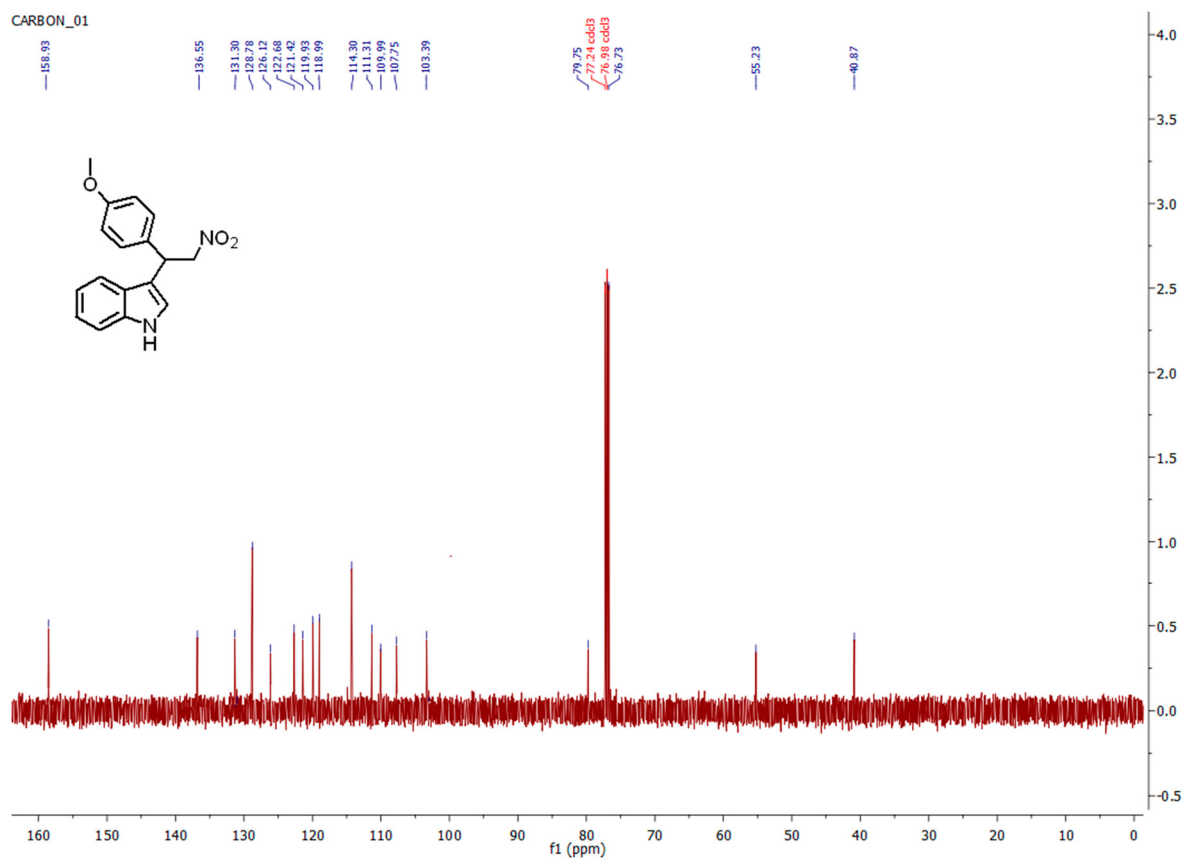
^1H NMR (CDCl_3 , 500 MHz): δ = 7.85 (s, 1H), 7.38 (d, J = 4.2 Hz, 1H), 7.32–7.25 (m, 3H), 7.20–7.12 (m, 3H), 7.08–7.01 (m, 1H), 5.20–5.08 (m, 3H), 2.46 (s, 1H), 2.42 (s, 3H).

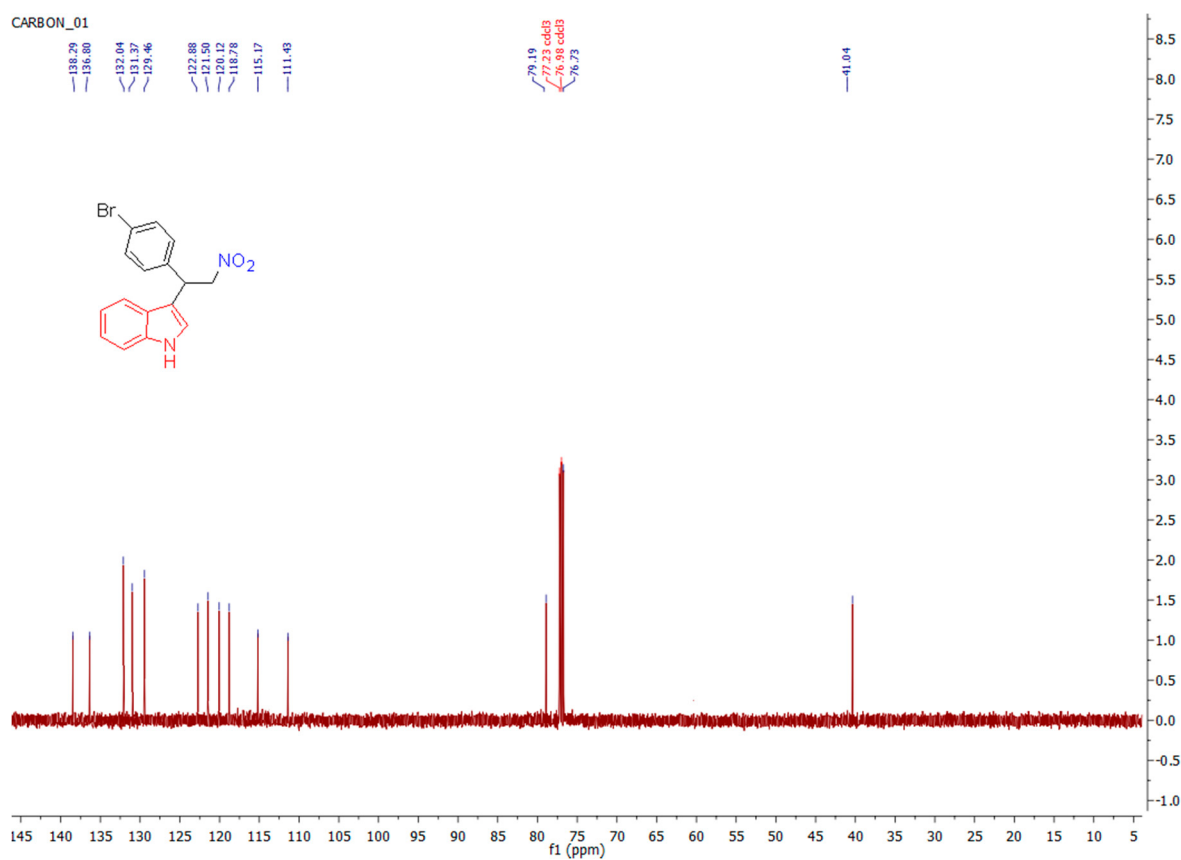
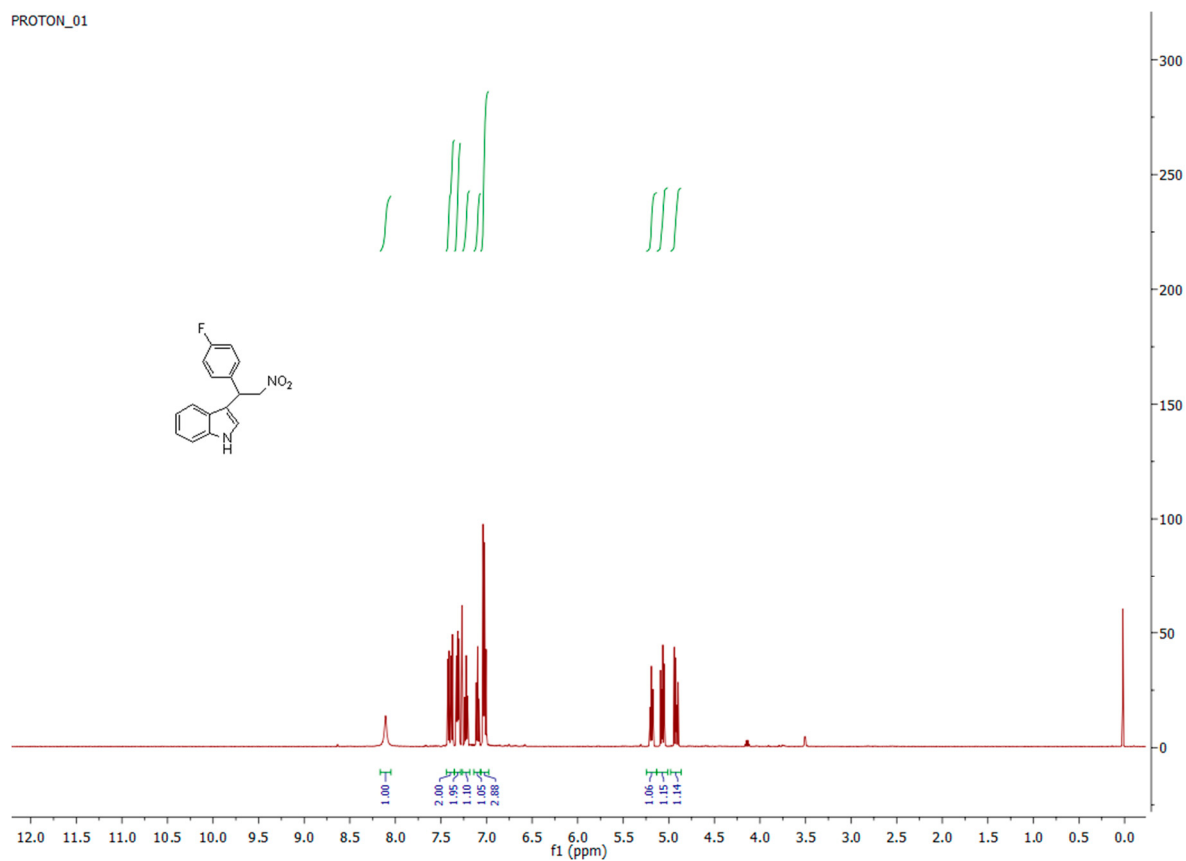
^{13}C NMR (CDCl_3 , 126 MHz): δ = 136.66, 136.45, 135.42, 132.64, 129.41, 127.16, 126.93, 121.31, 119.72, 118.65, 110.60, 109.60, 78.73, 41.01, 40.14, 20.91, 12.02.

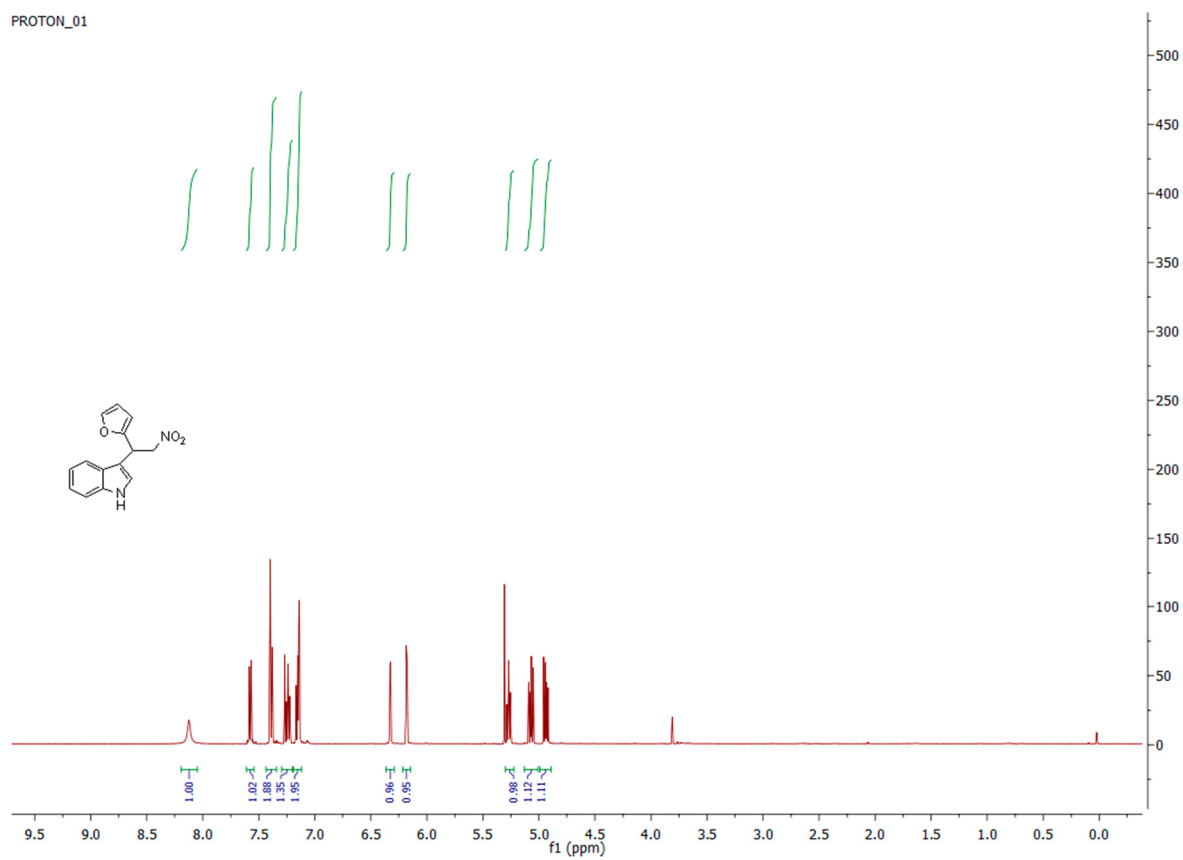
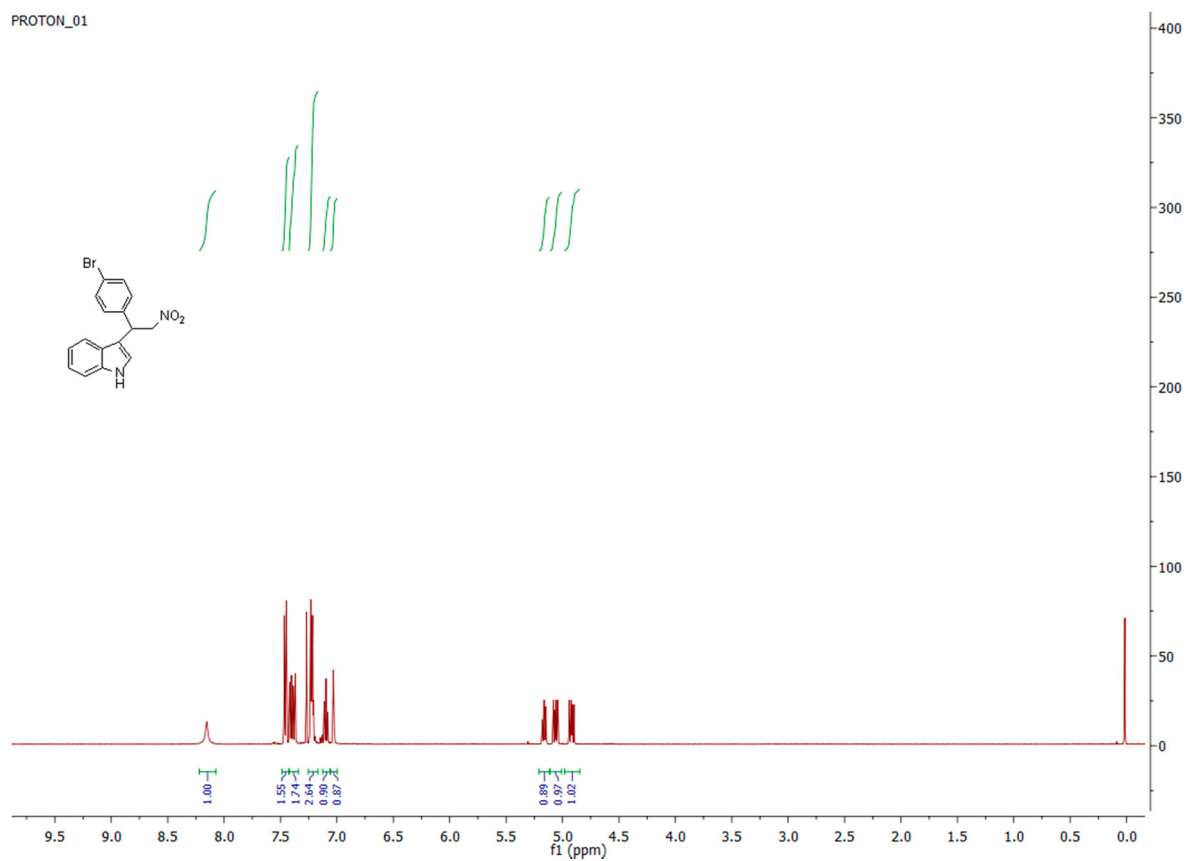


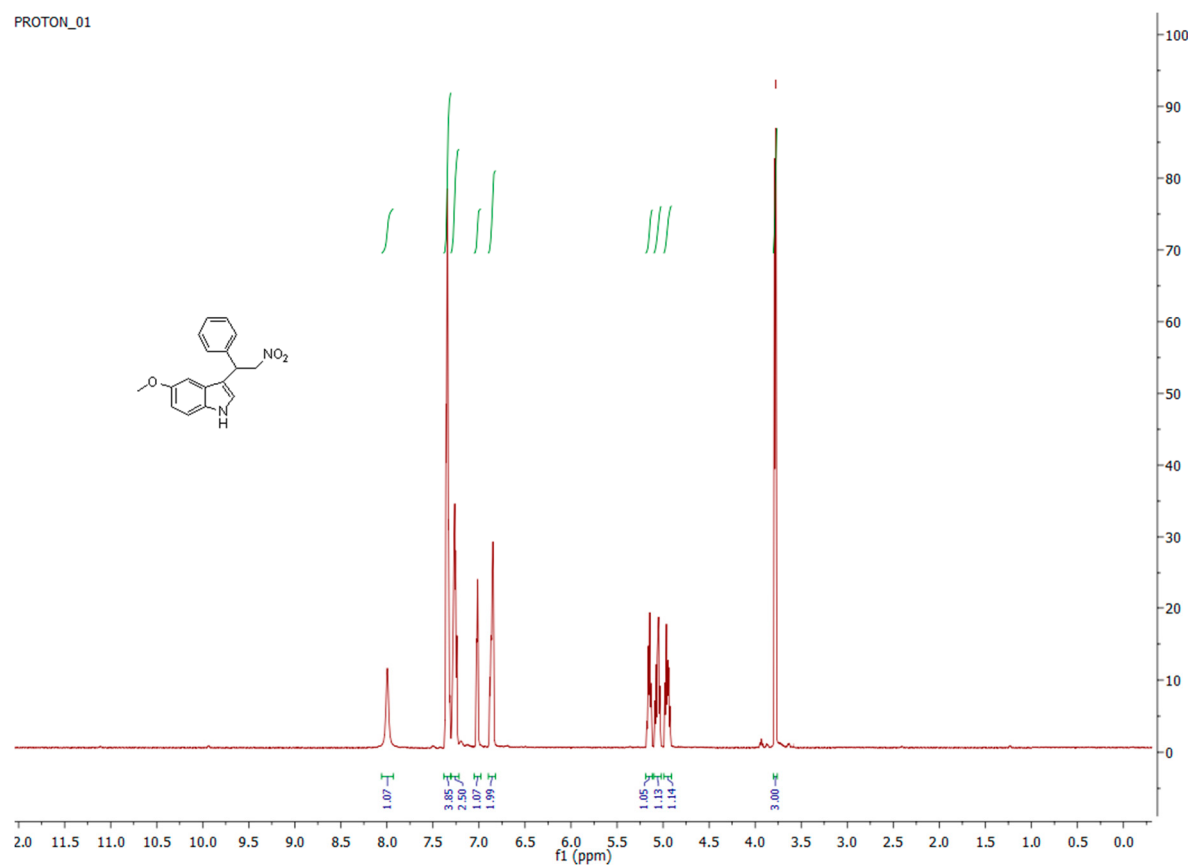
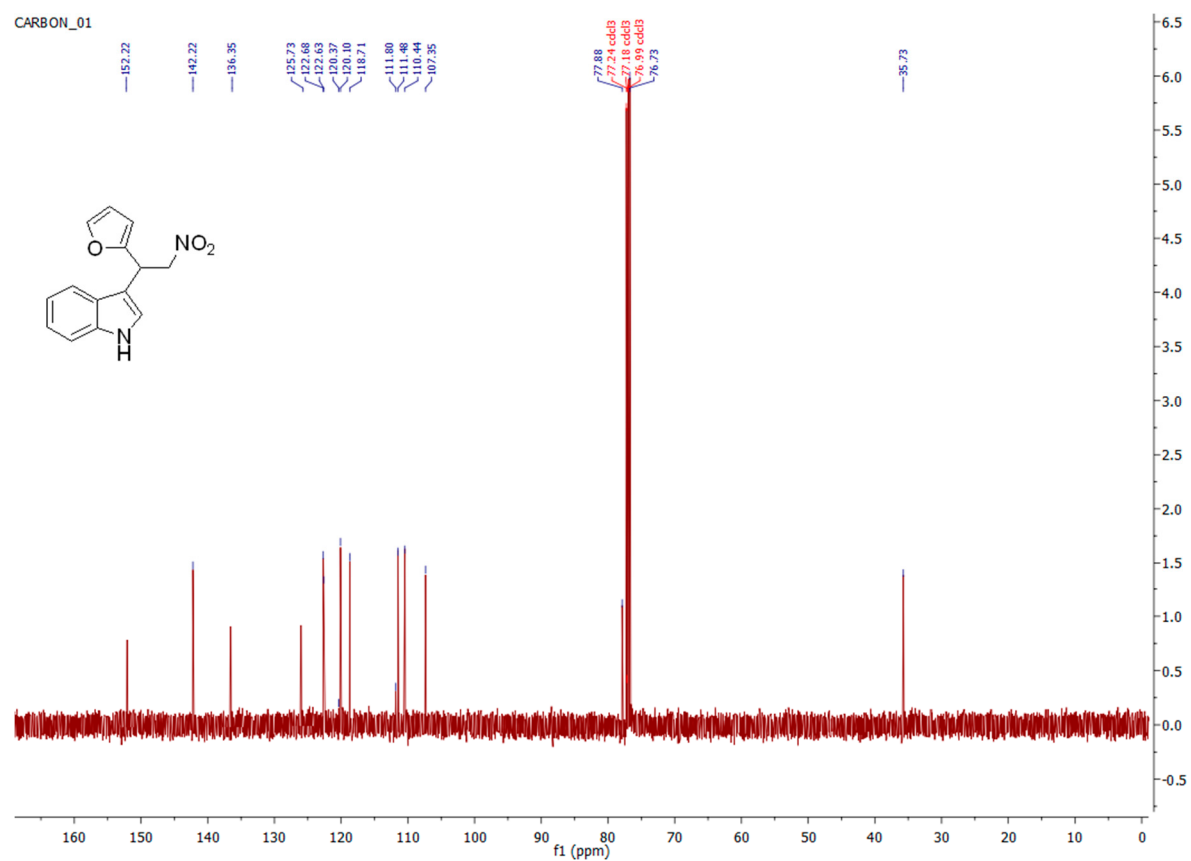


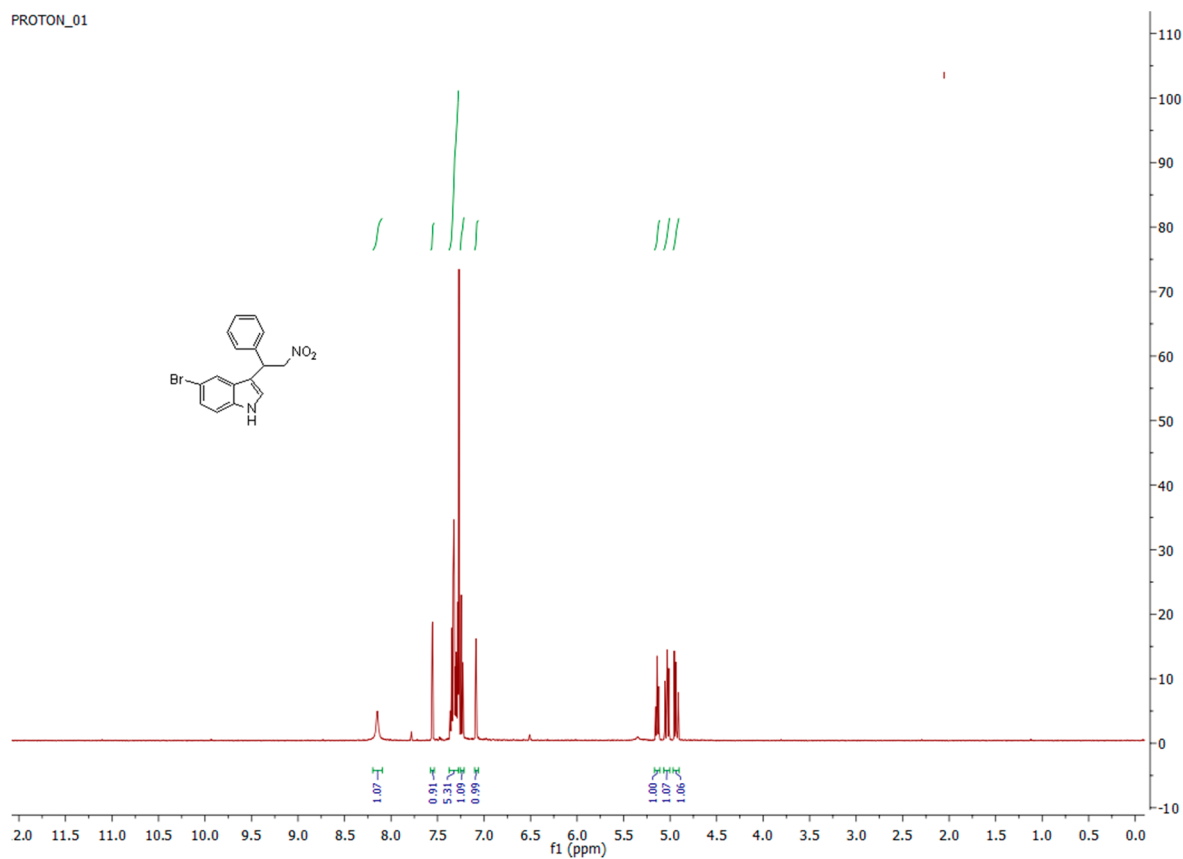
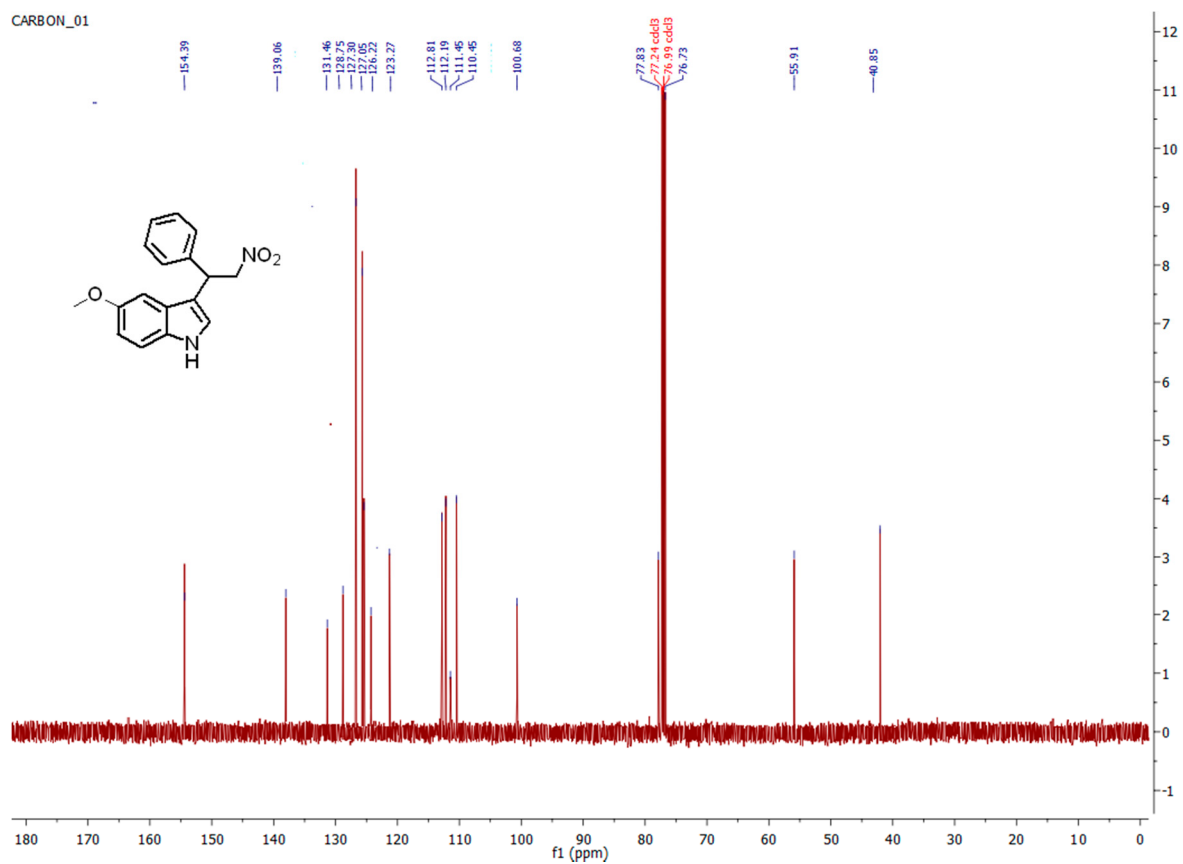


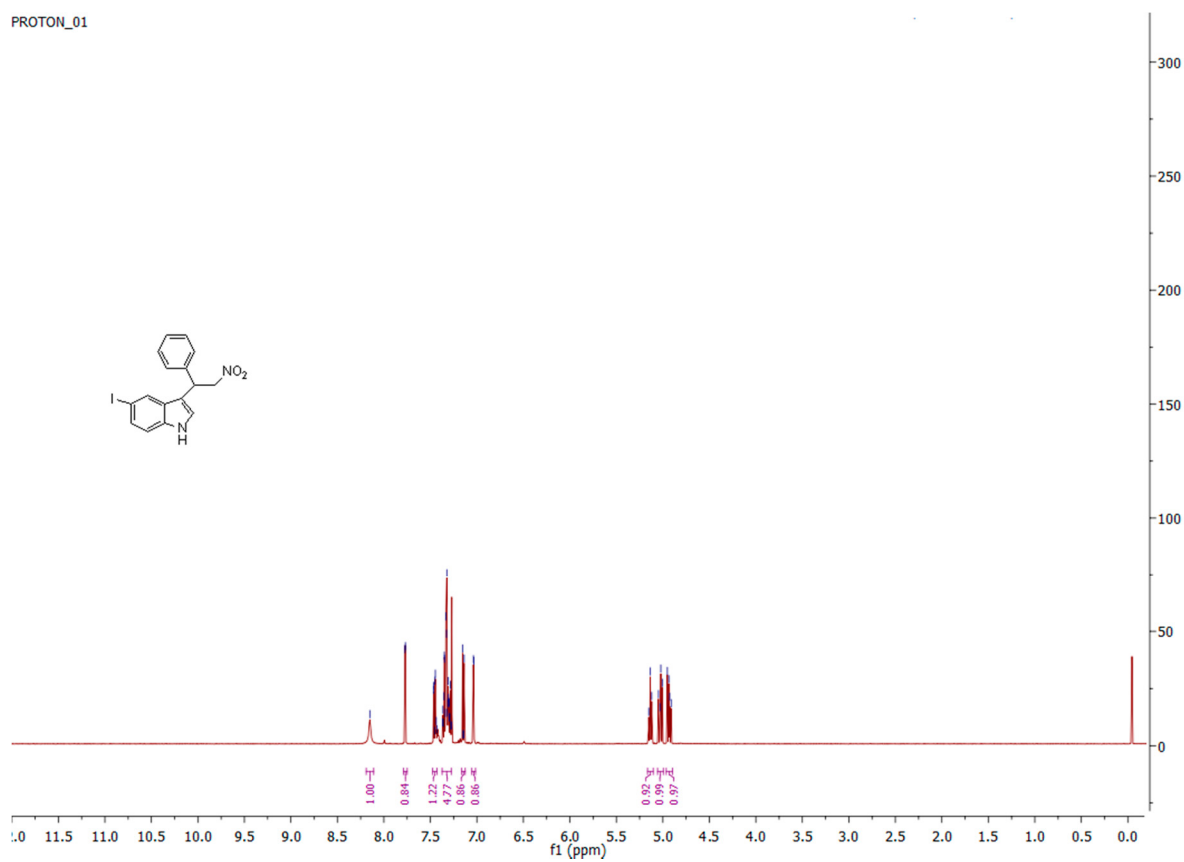
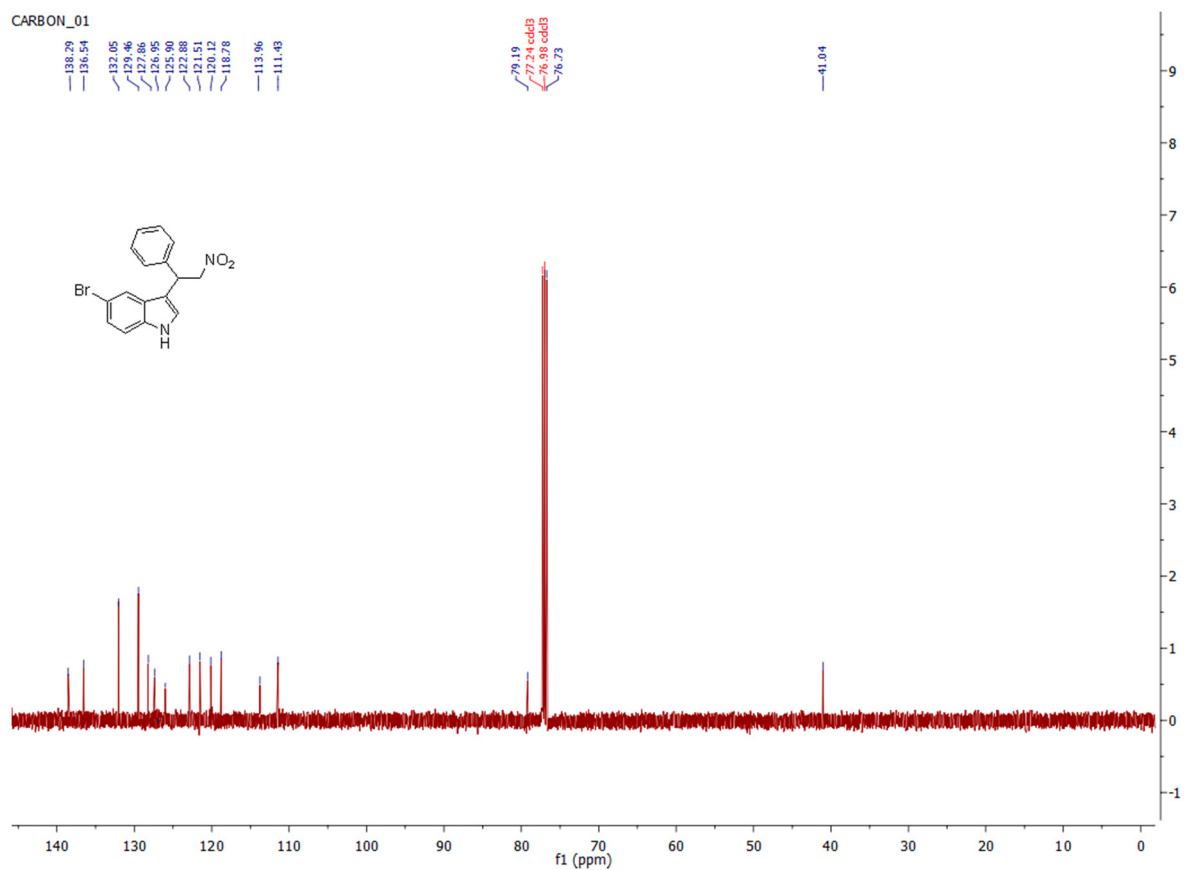


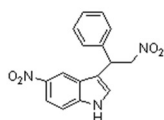
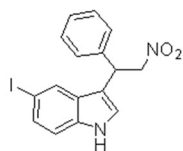


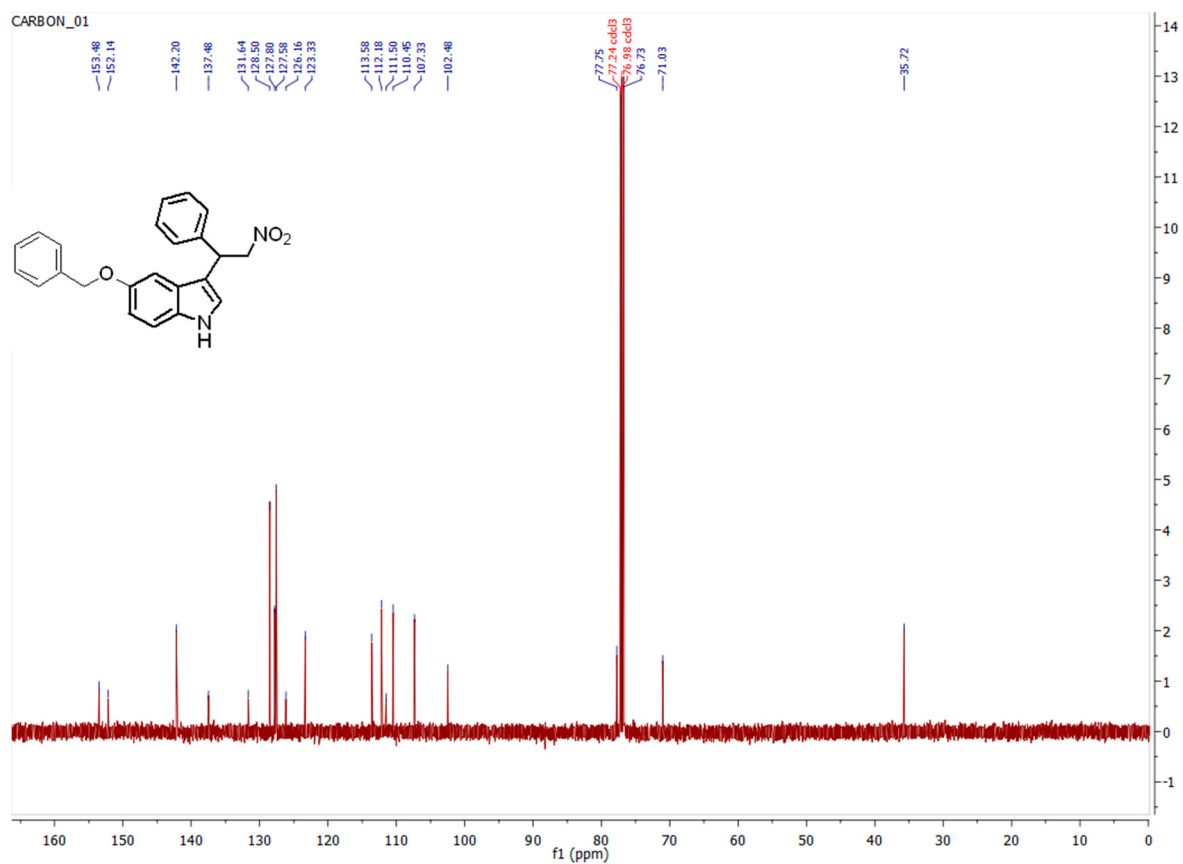
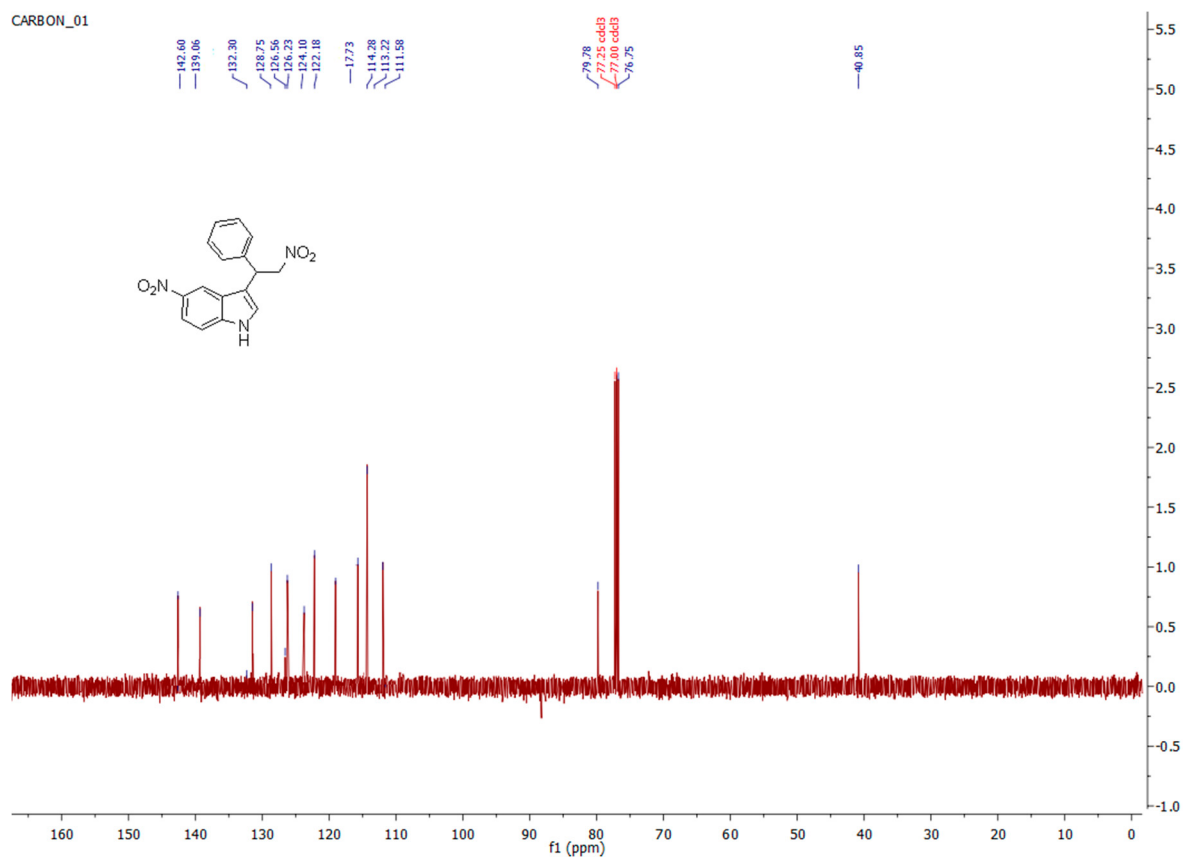


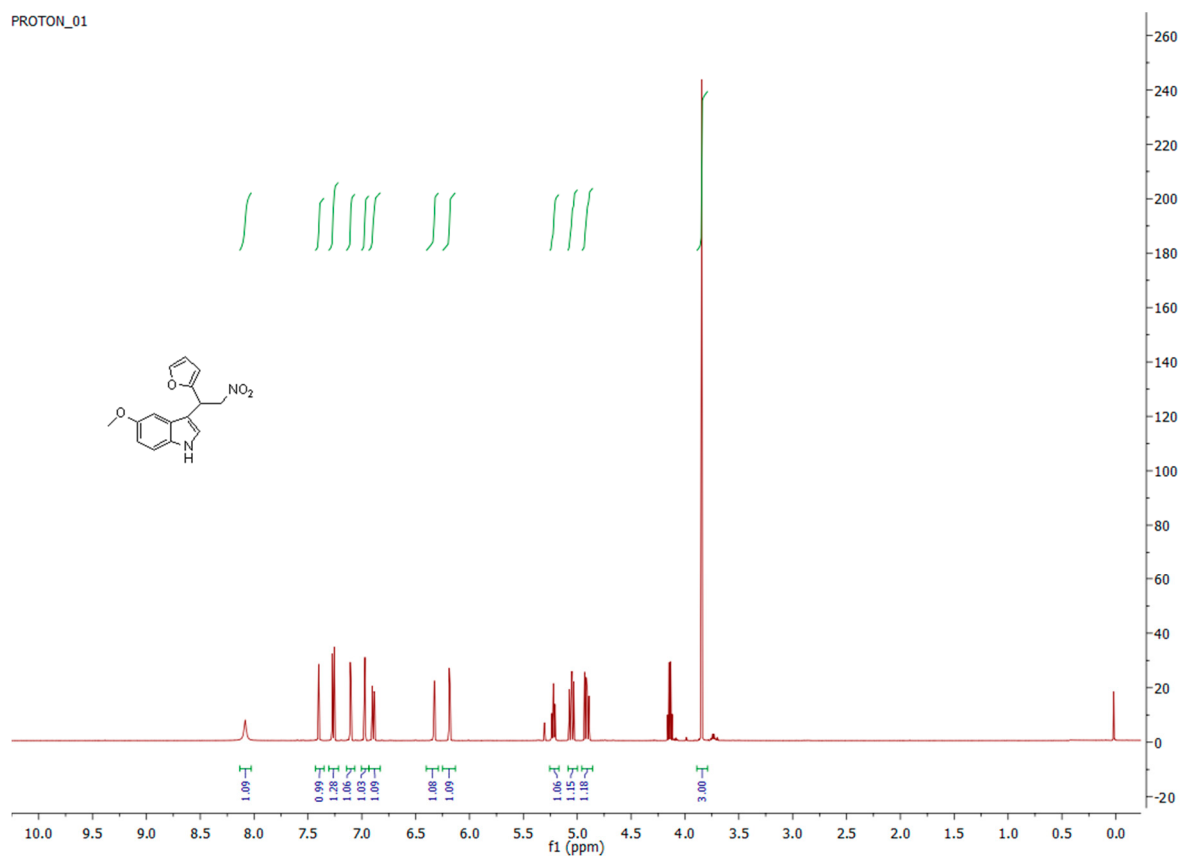
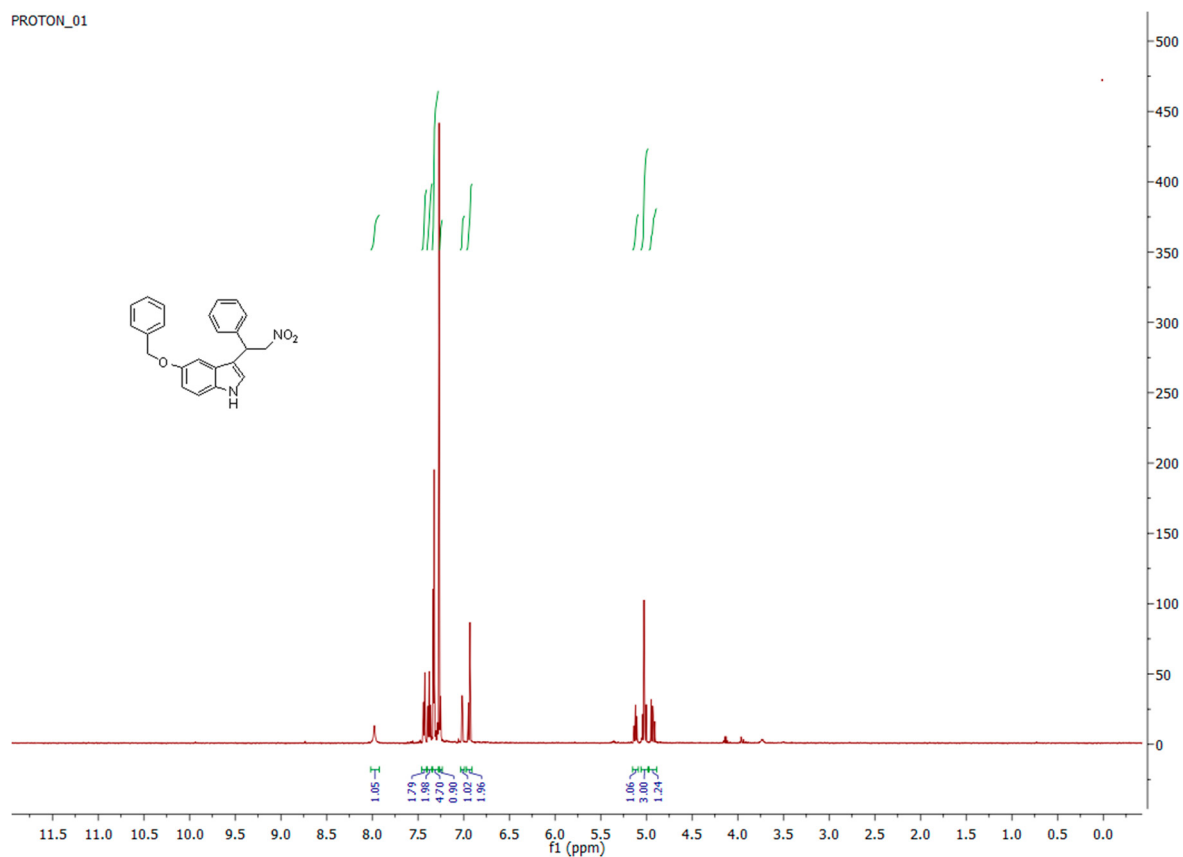


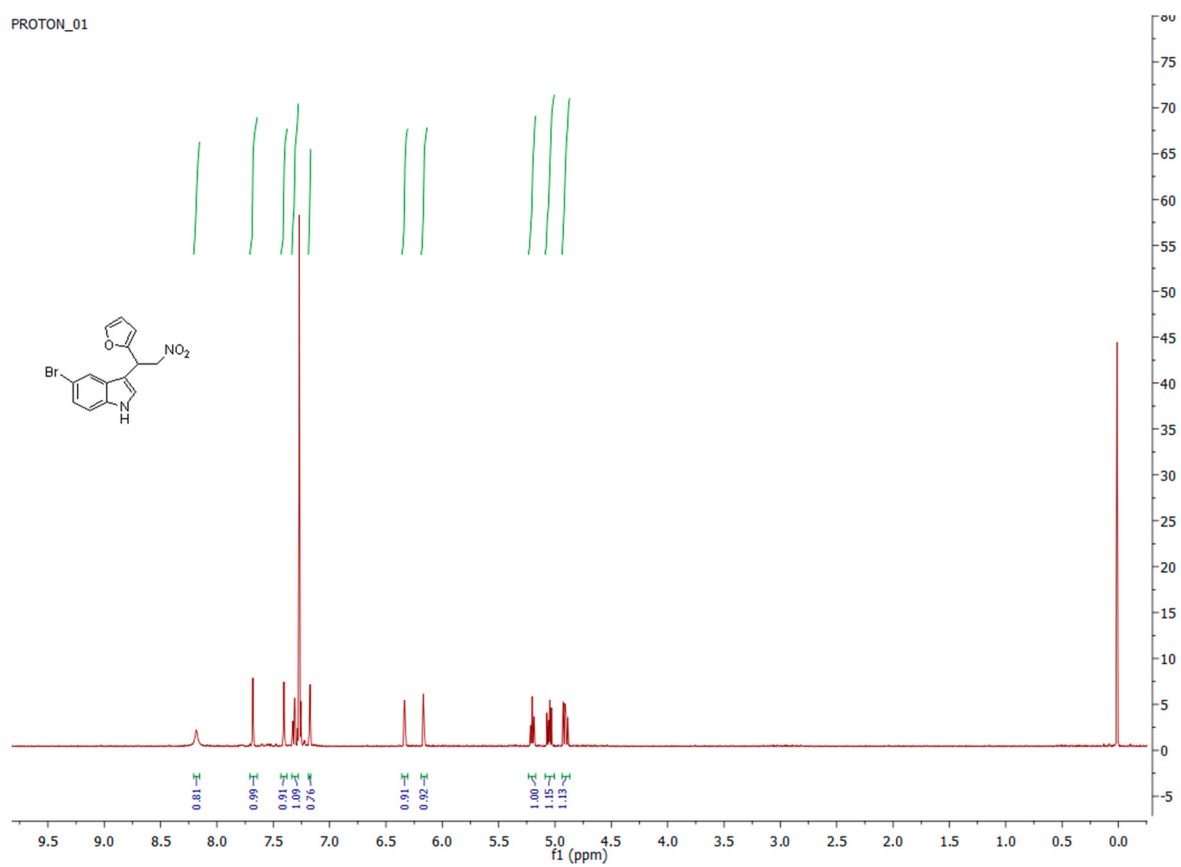
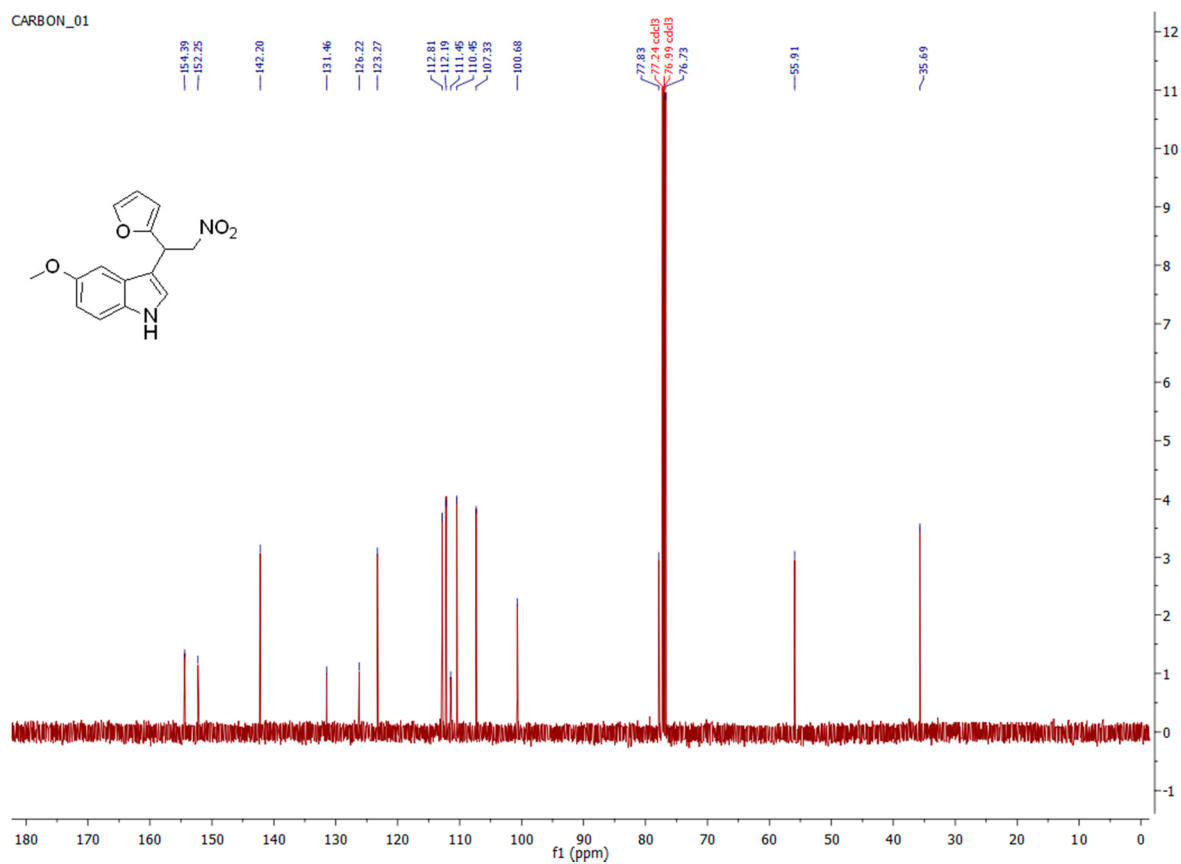


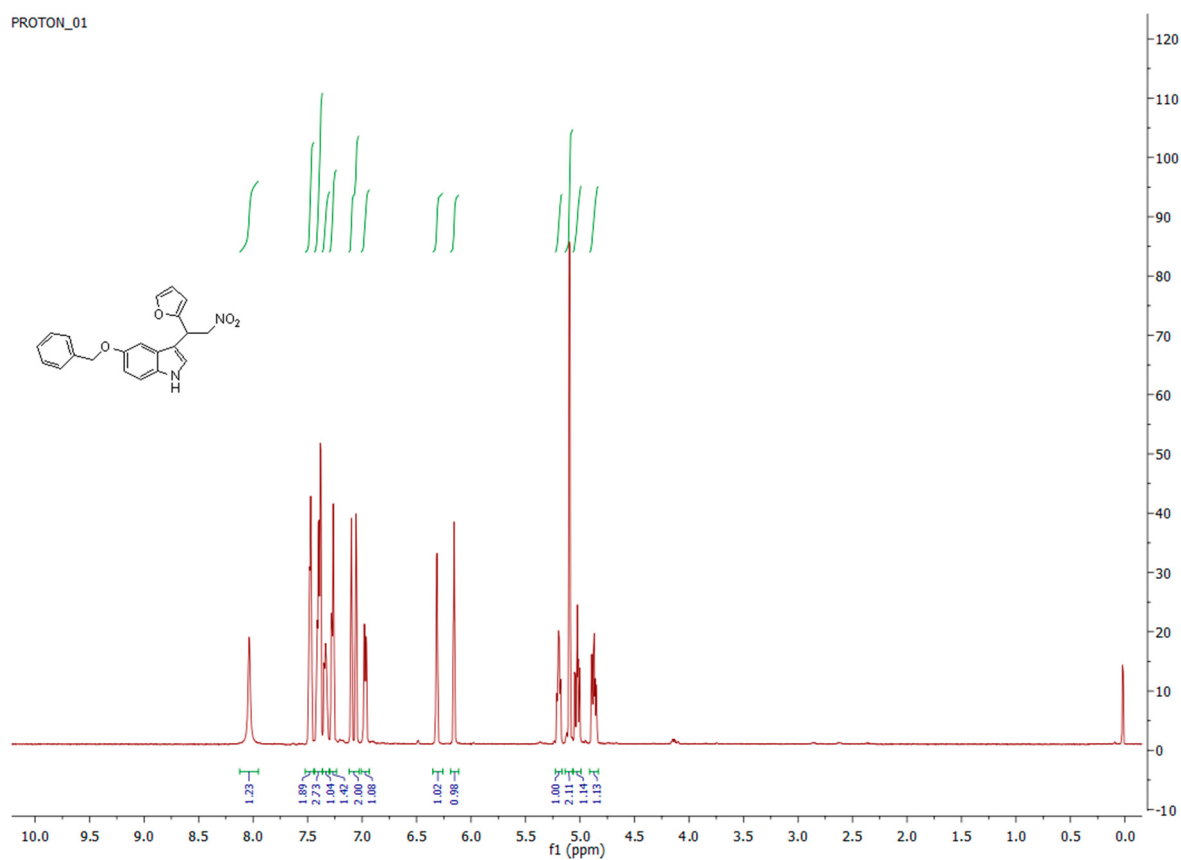
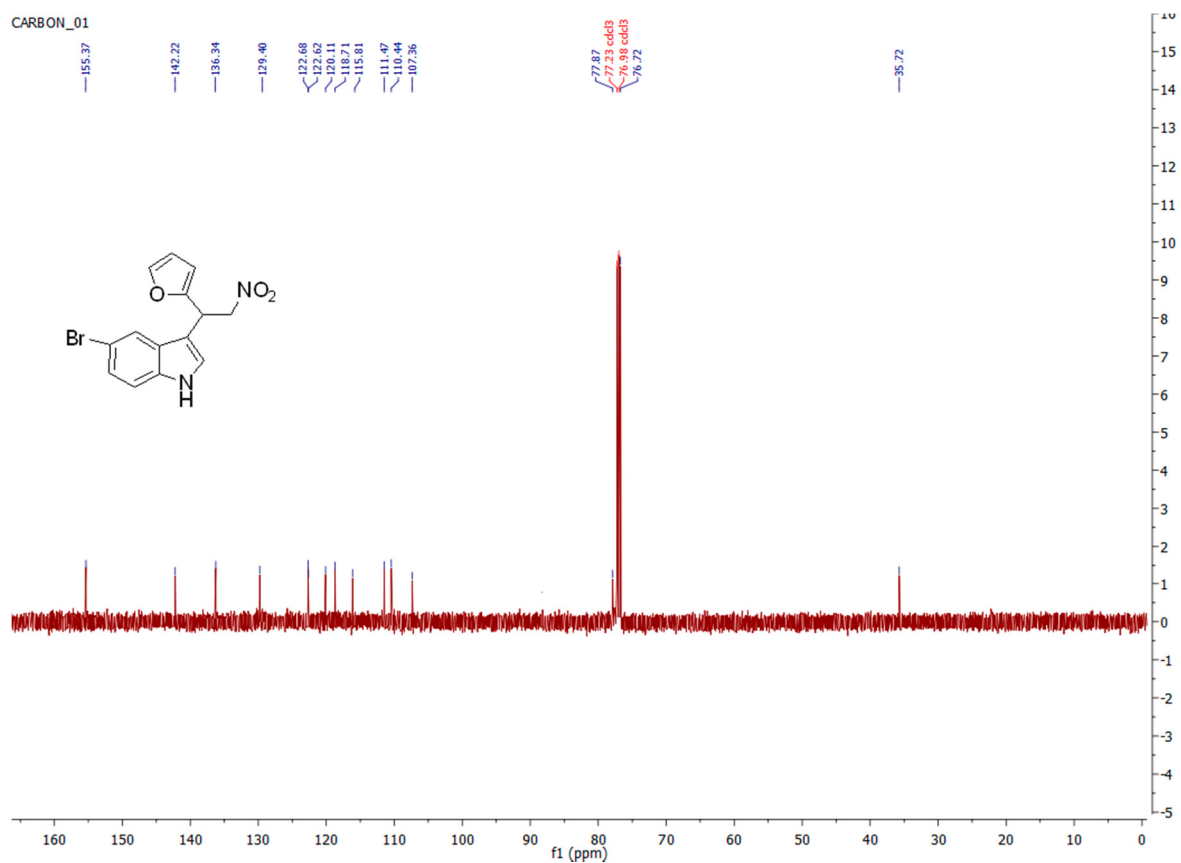


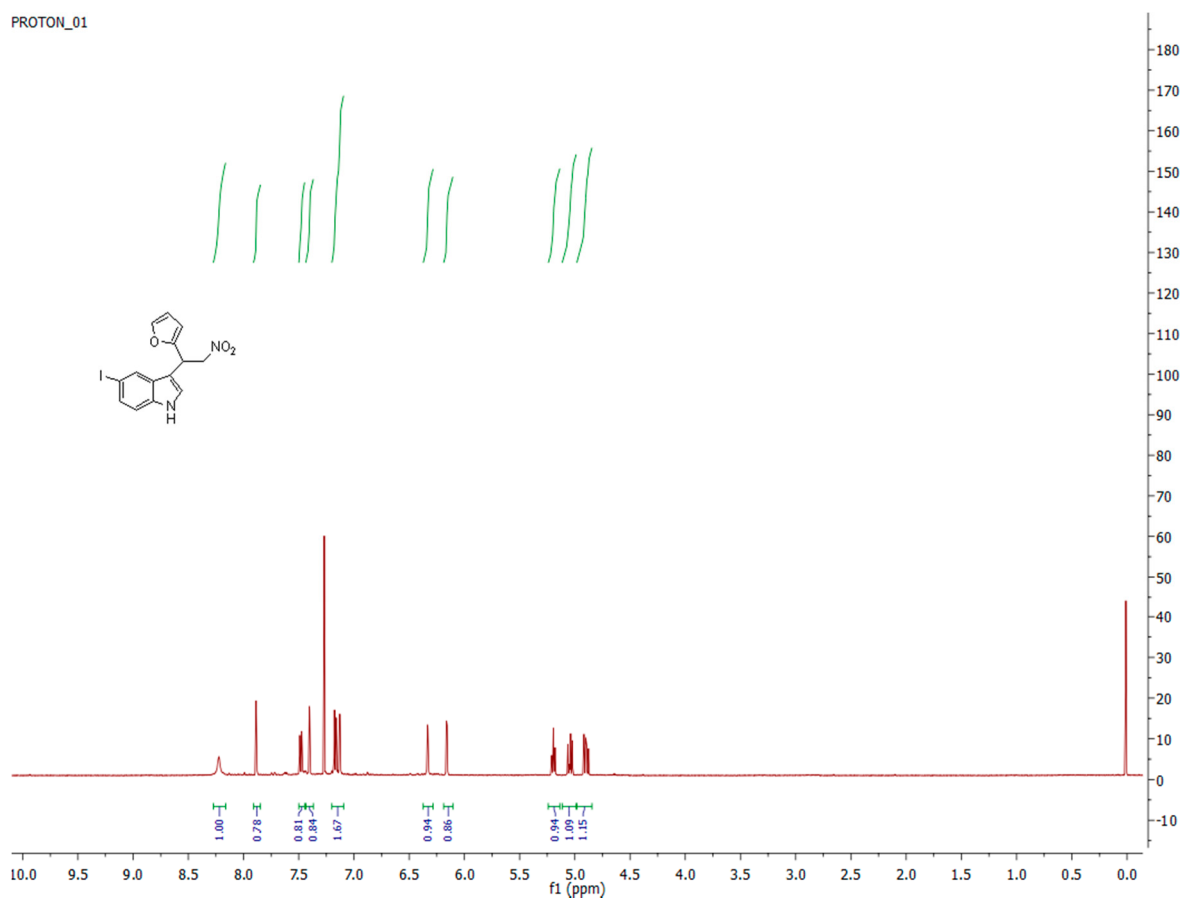
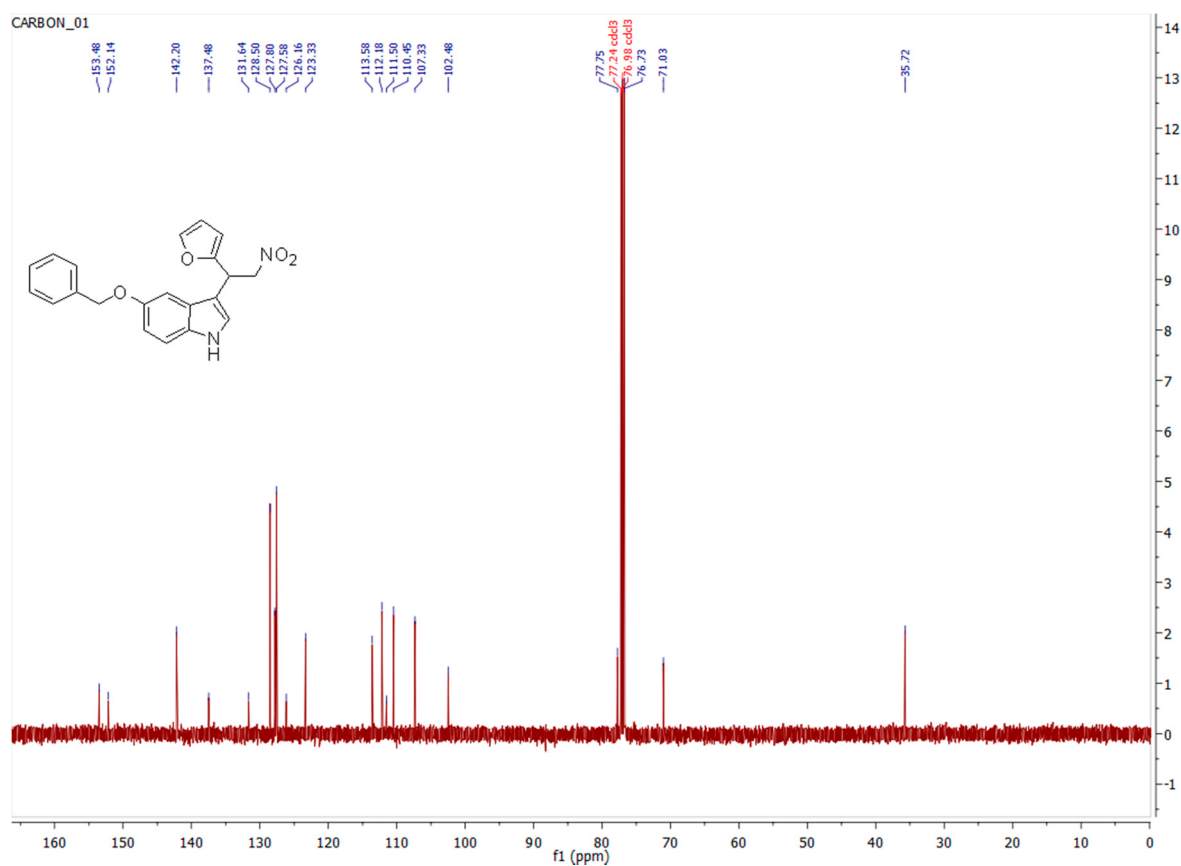


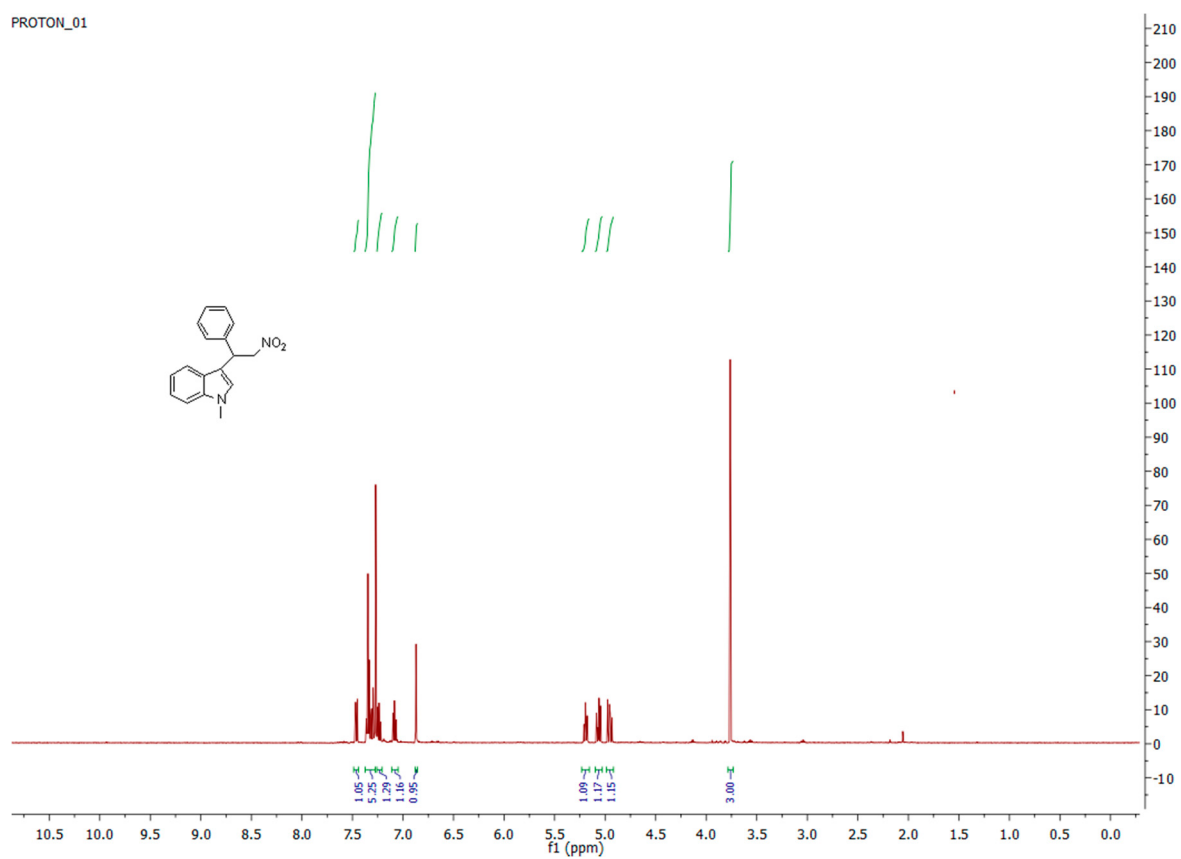
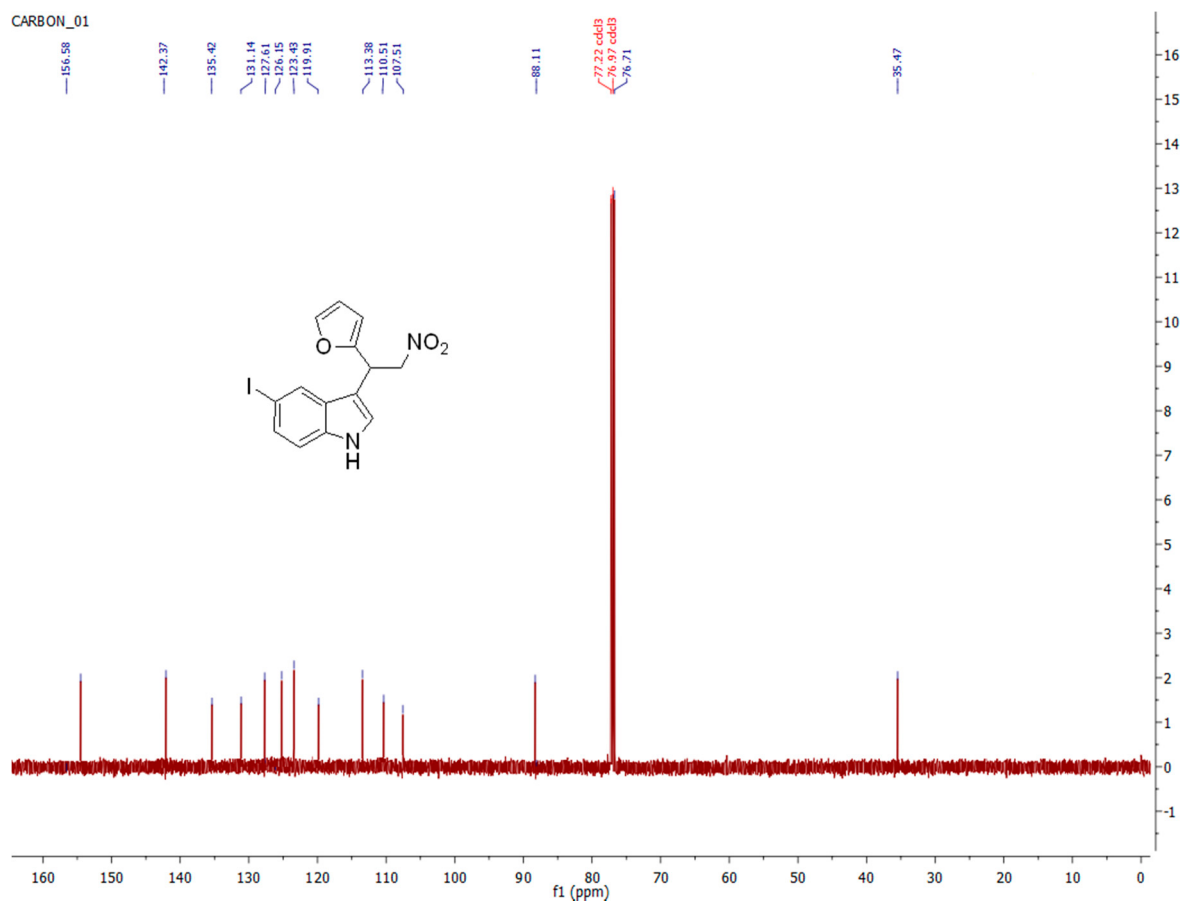


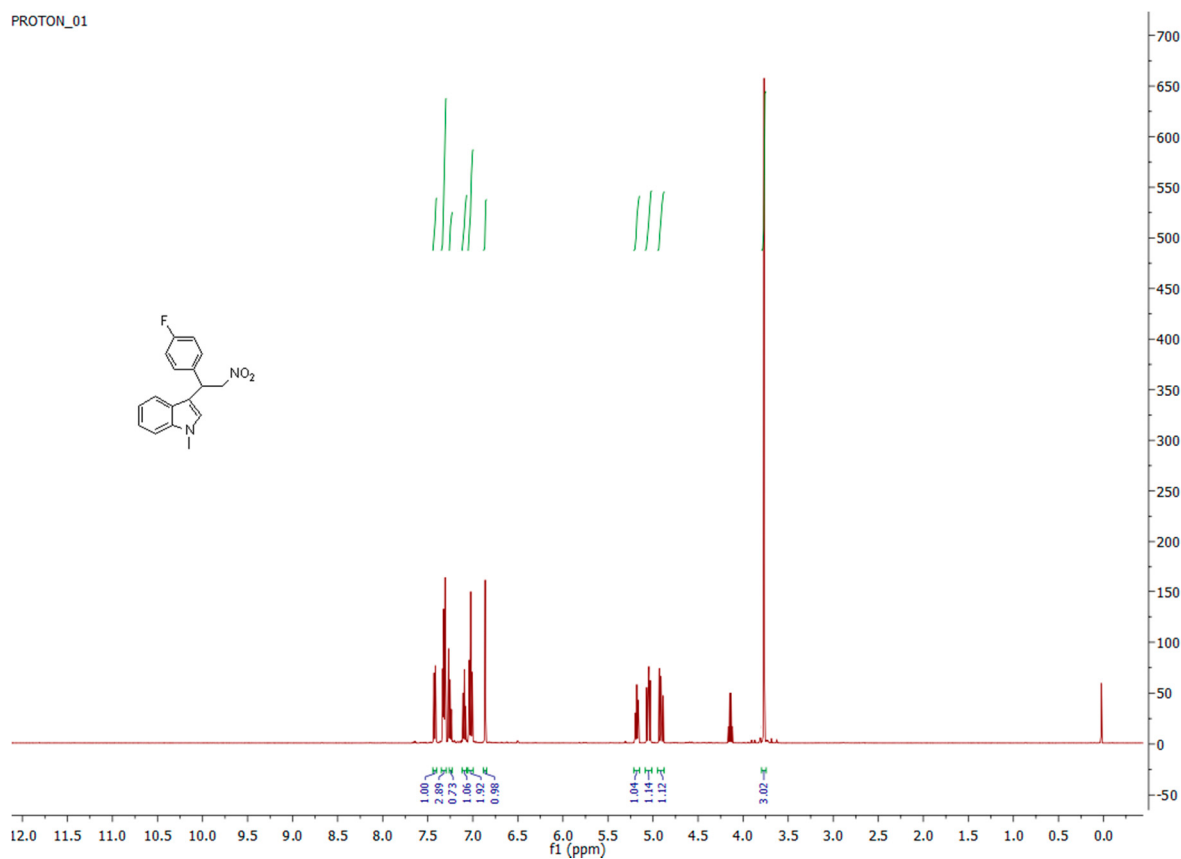
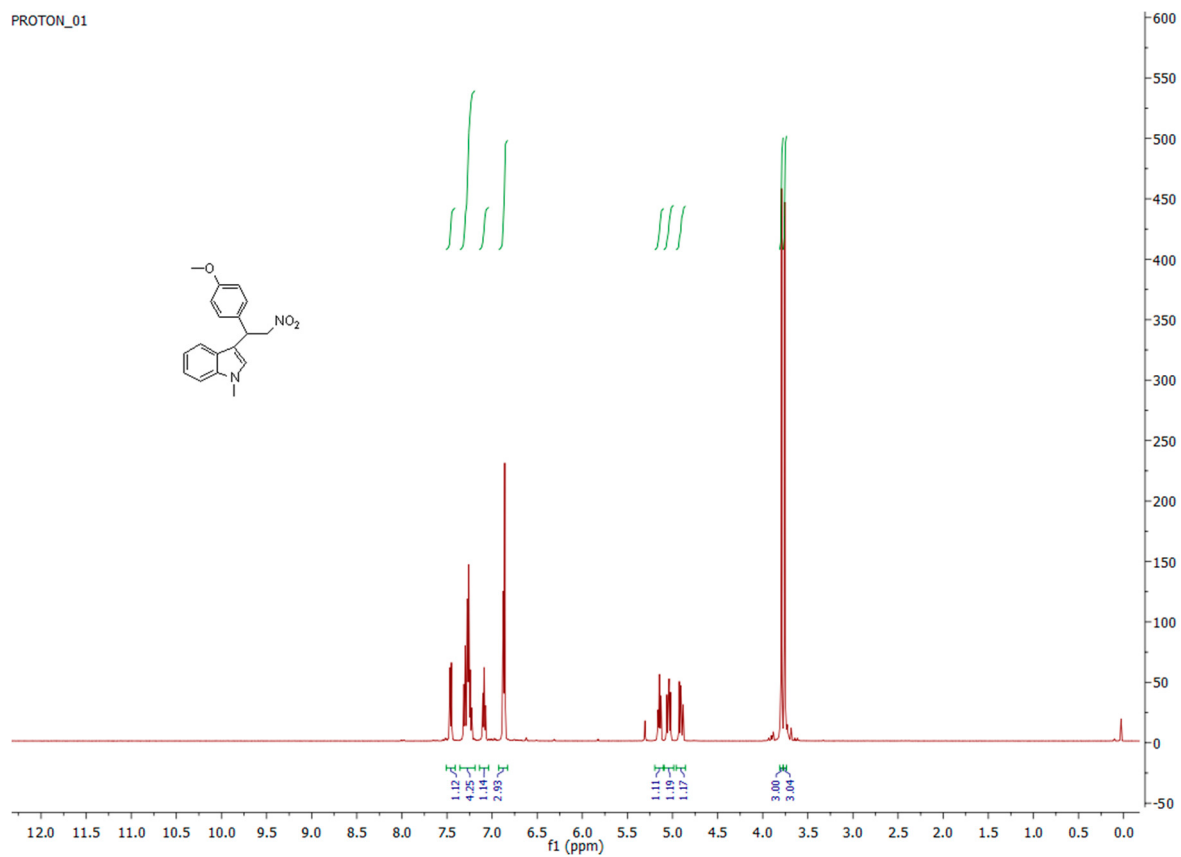


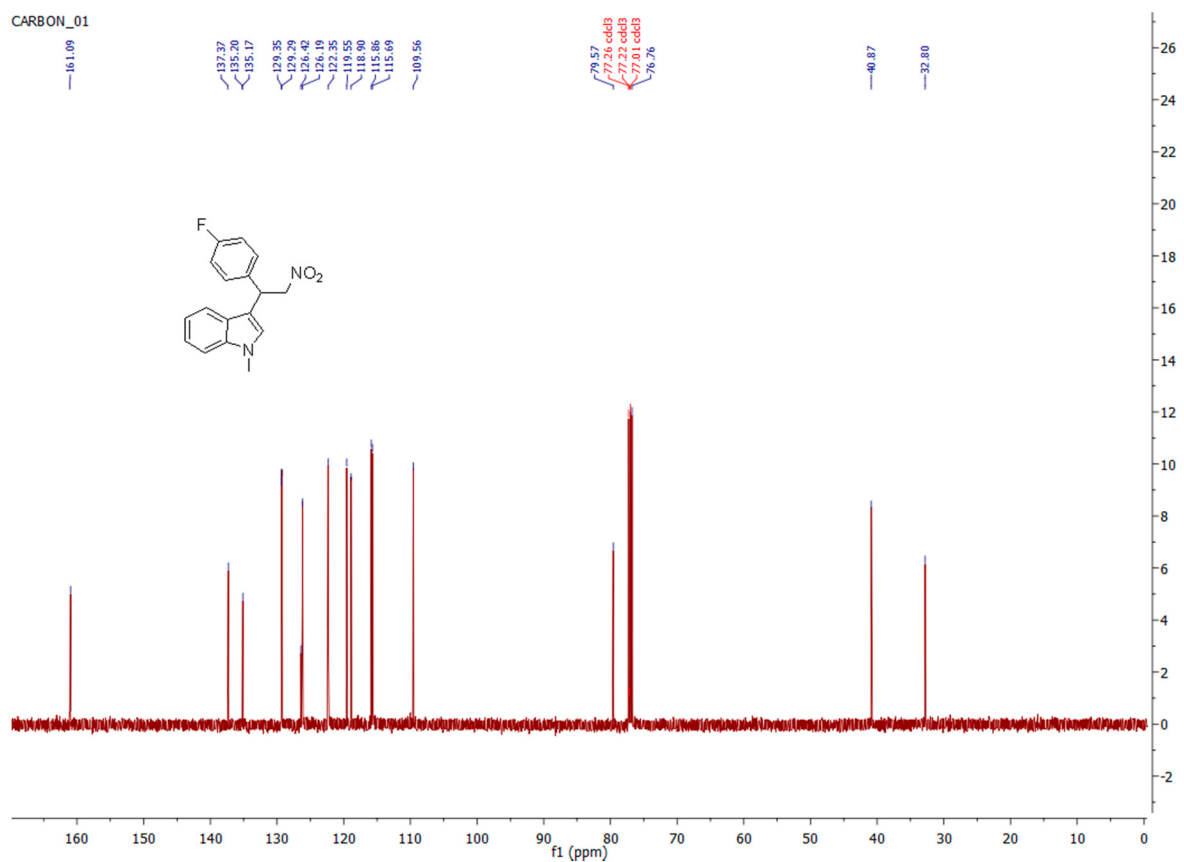
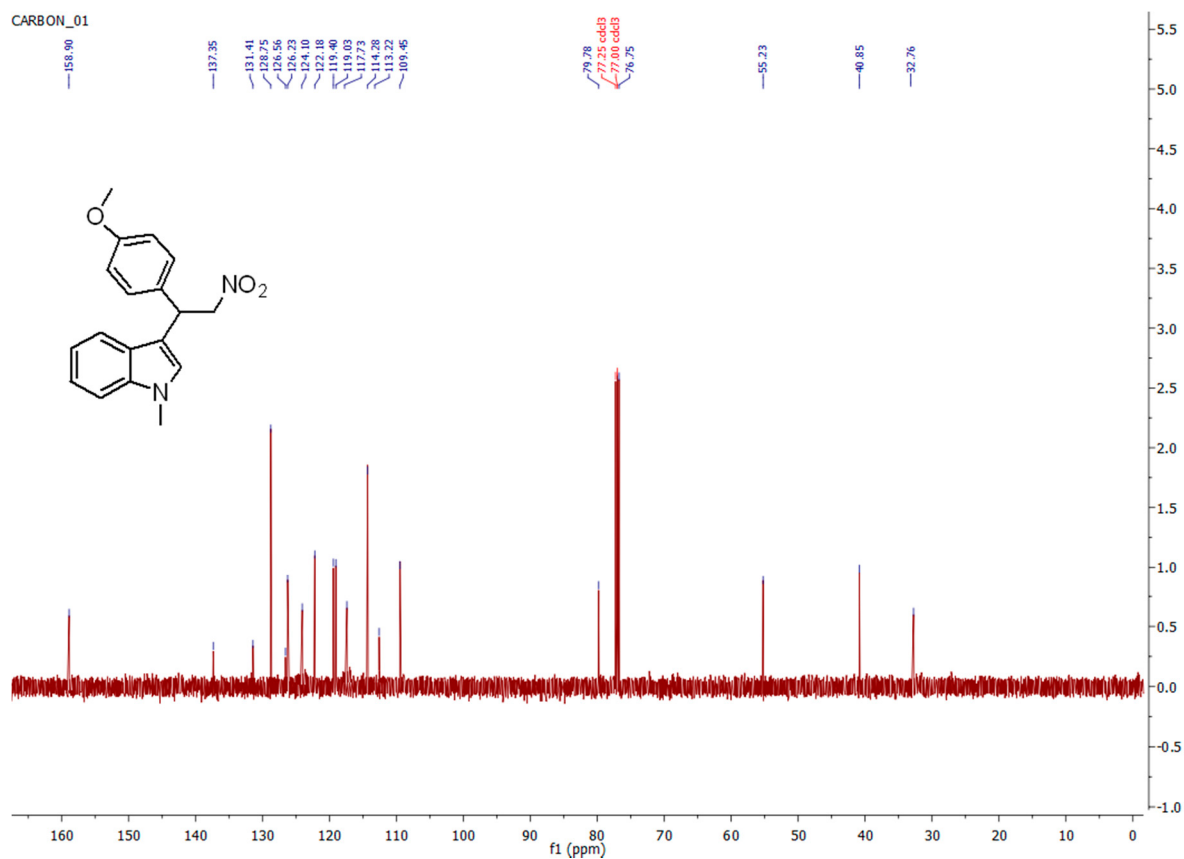


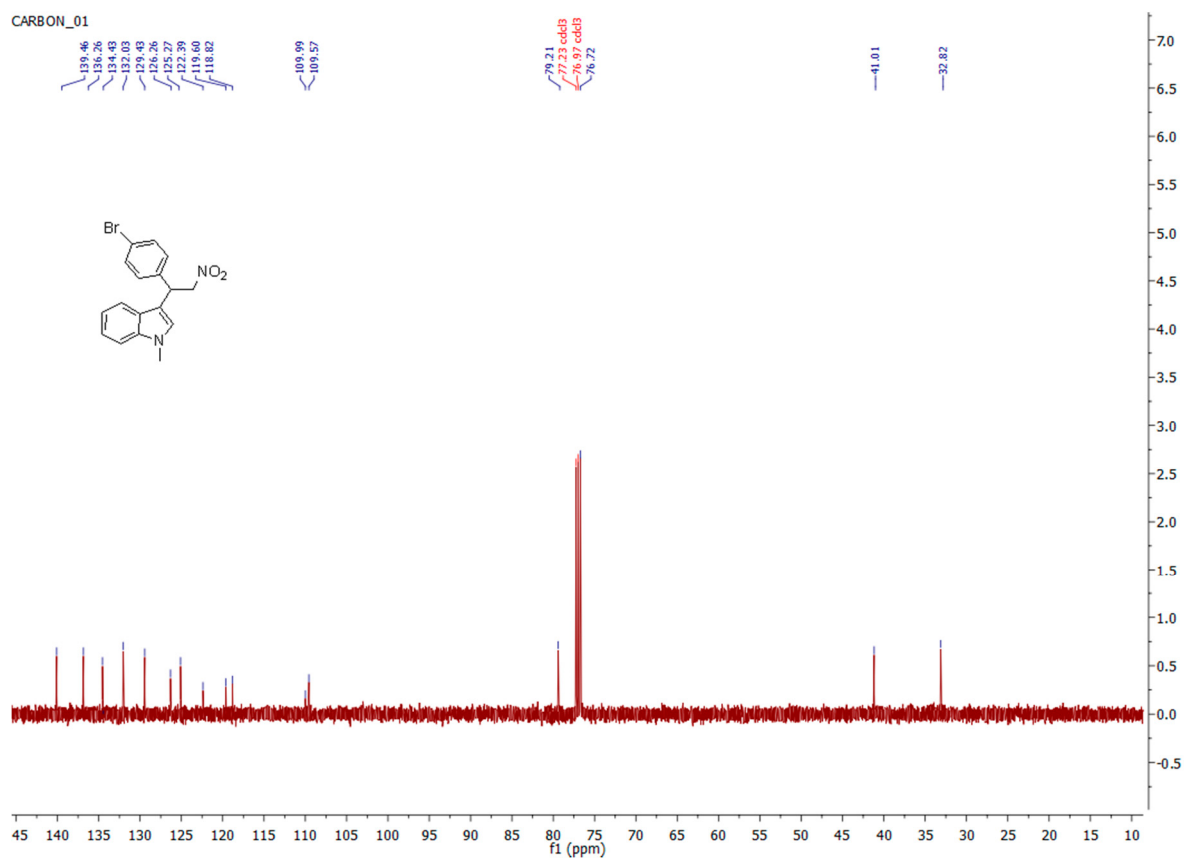
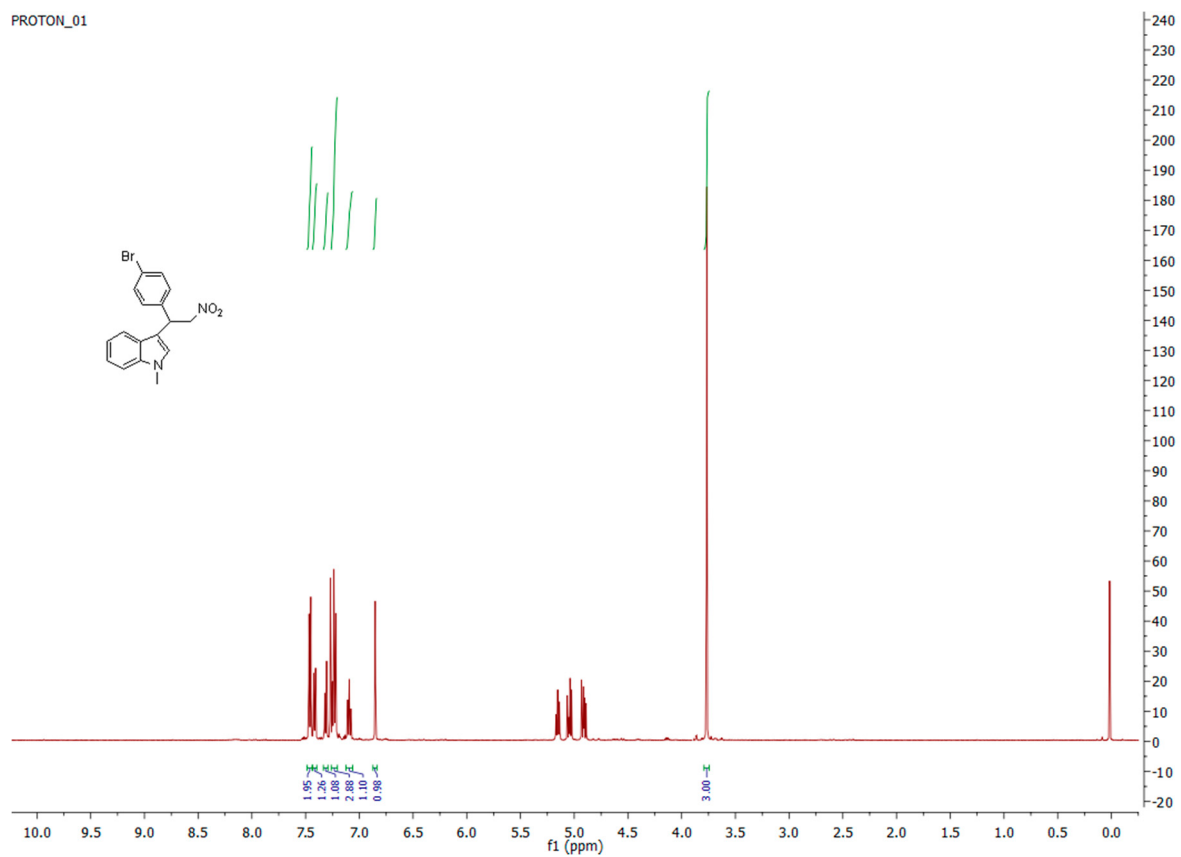




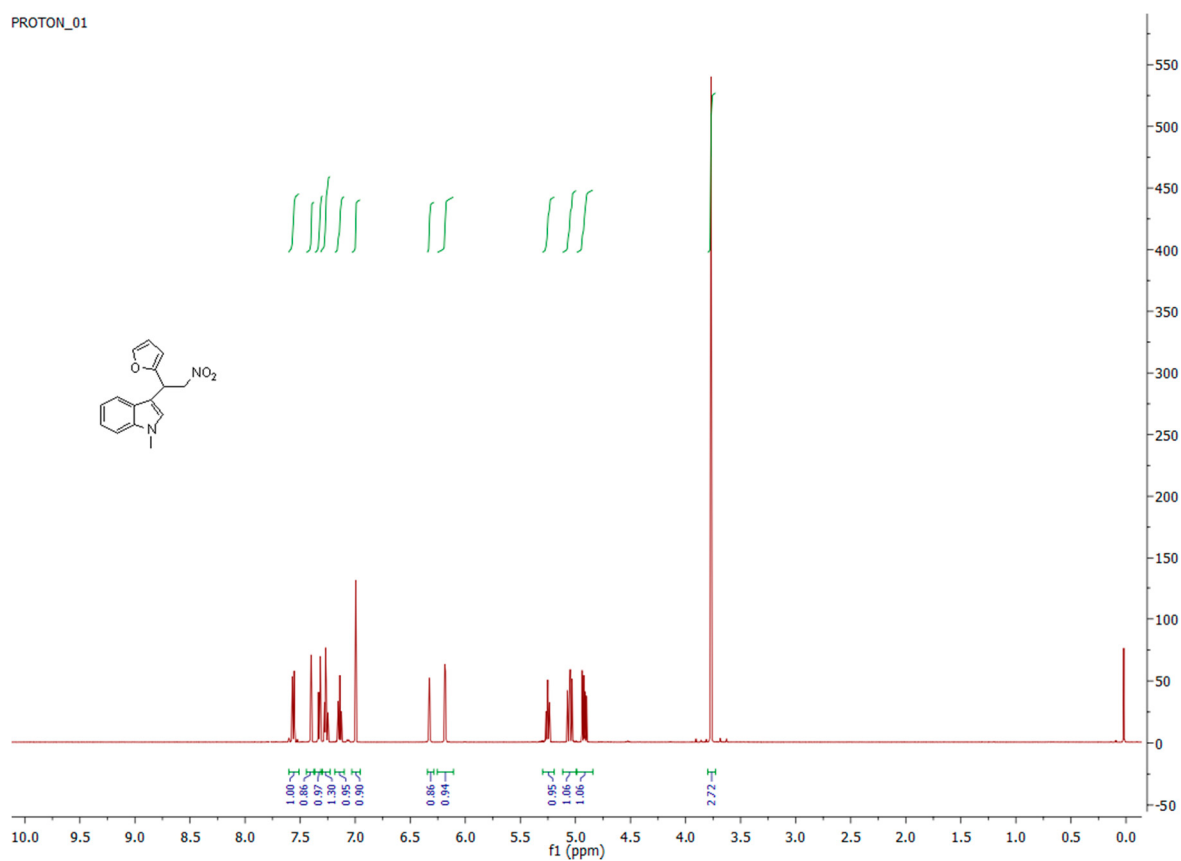




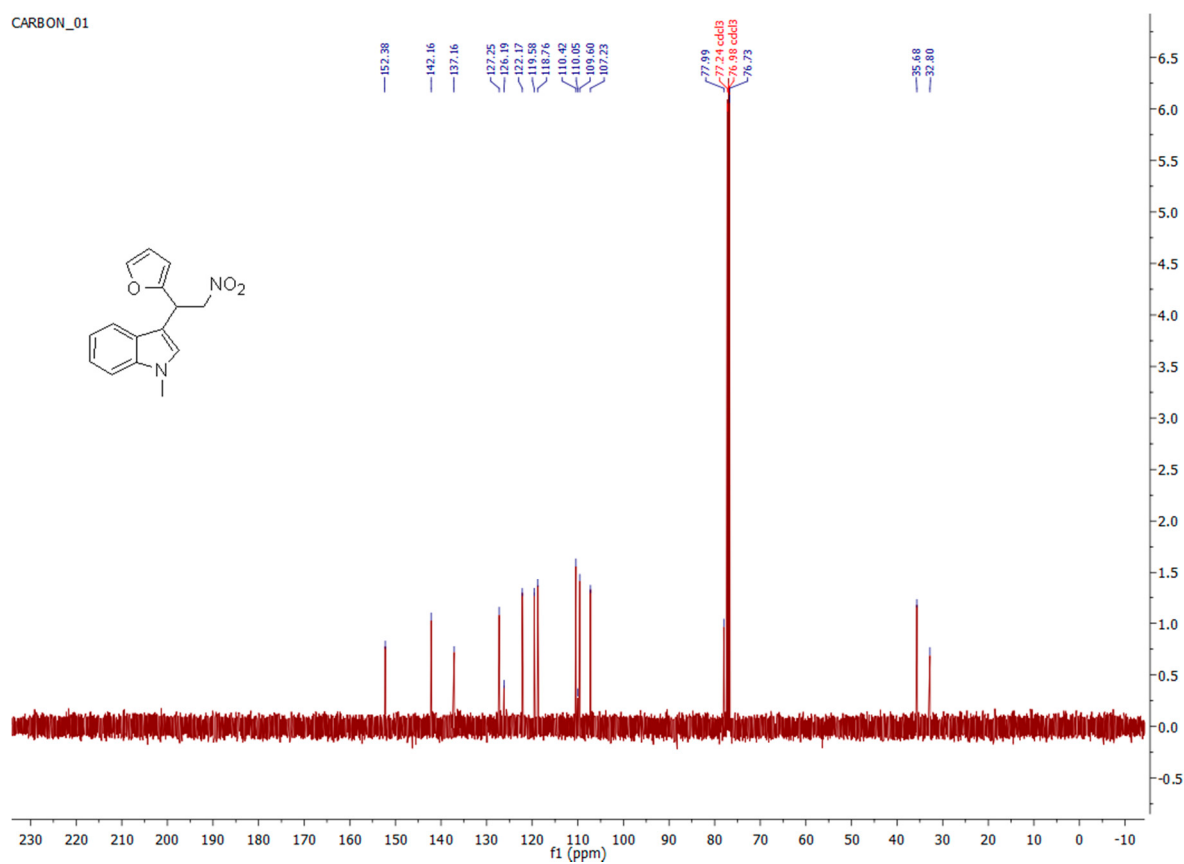




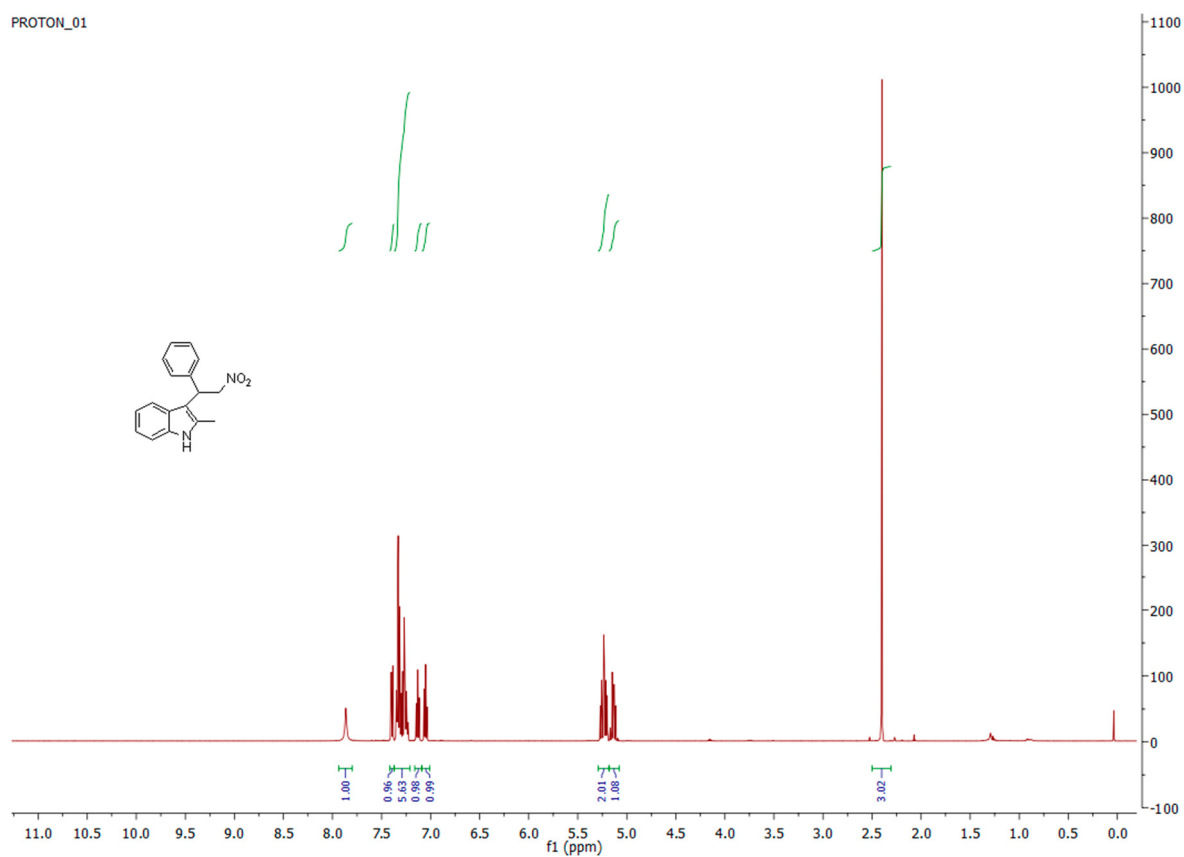
PROTON_01



CARBON_01



PROTON_01



CARBON_01

