Electronic supplementary materials

Sustainable Ruthenium-Catalyzed C–H Alkylation of 2-(Hetero)aryl Benzimidazoles with Maleimides

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Supplementary Data

Table of contents

S1. General information and additional experimental data

General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Fourier300 (300 and 75 MHz, respectively) spectrometer. Chemical shifts are given relative to the residual signals of protons of chloroform-*d* (7.26 for ^{1}H NMR) or carbon signals in chloroform-*d* (77.16 ppm for ^{13}C NMR).

High-resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was applied for the analysed solutions at a flow rate 3 μL min^{-1}. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was established at 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software package.

Materials

1-methyl-2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole (**1a**)[S1], 2-(furan-2-yl)-1-methyl-1*H*-benzo[*d*]imidazole (**1b)**[S2], 1-methyl-2-(5-methylfuran-2-yl)-1*H*-benzo[d]imidazole (**1c**)[S3], 1-methyl-2-(p-tolyl)-1*H*-benzo[*d*]imidazole (**1d**)[S4], 2-(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**1e**)[S5], 2-(3,4-dimethoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**1f**)[S6].

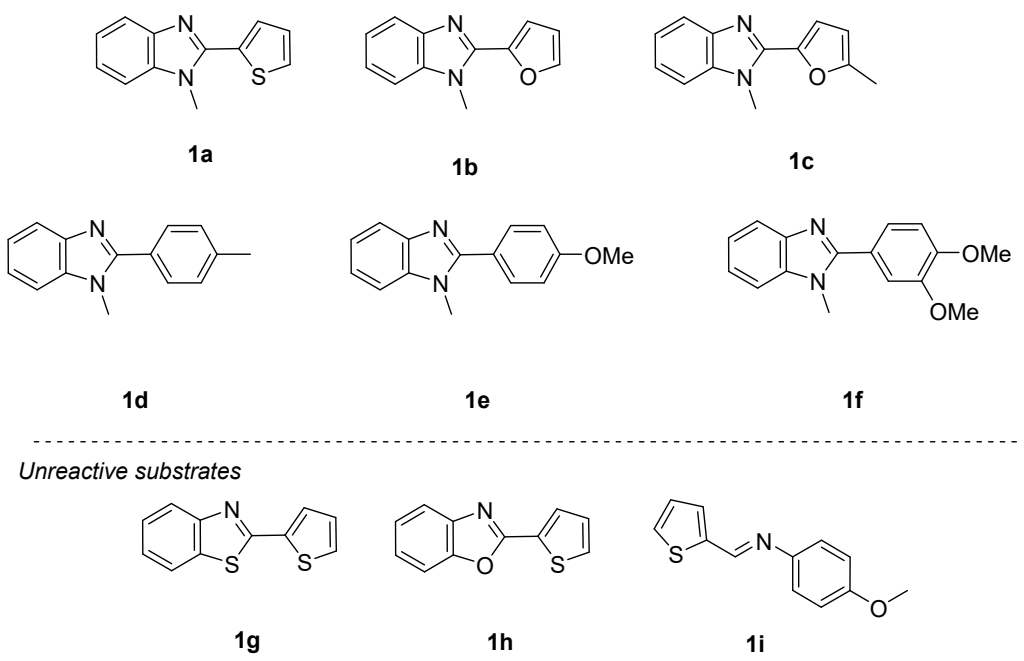


Figure S1. Substrates used in the study

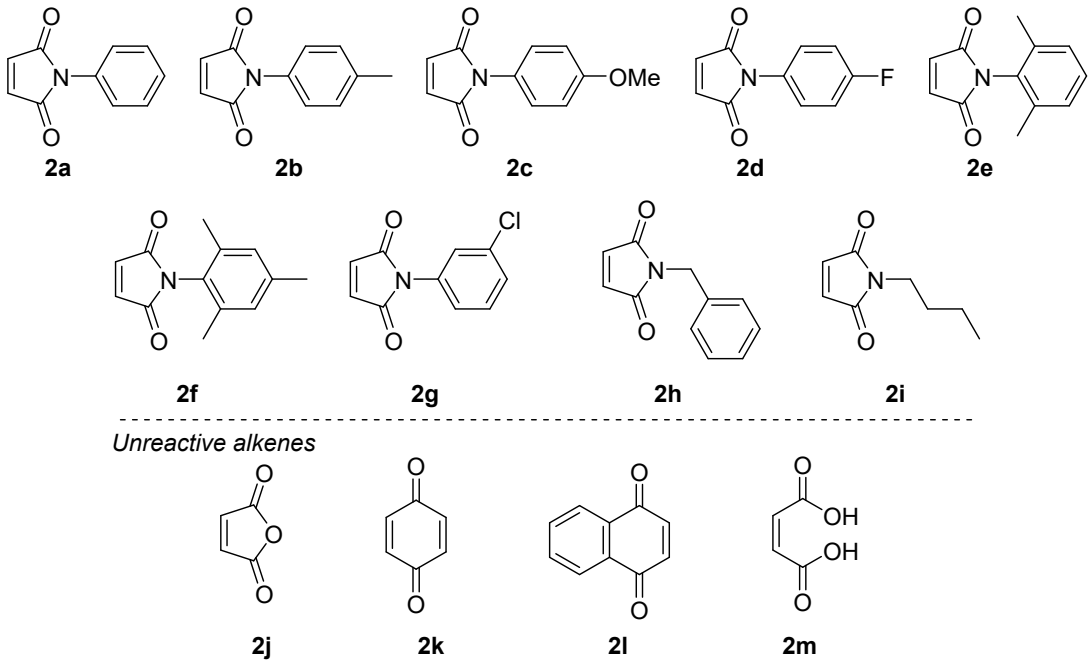
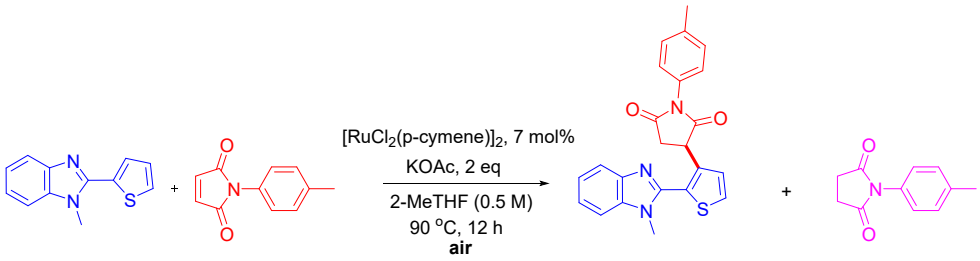


Figure S2. Maleimides used in the study.

S2. Extended experimental data

Table S1. Formation of side product **5** during reaction



1a + **2b** (1.0 - 2.0 eq) → **3b** + **5**

Entry	Amount of maleimide	Yield **3b**,[b]%	Yield of **5**,[b] %
1	**2b**, 2.0 eq	80	20
2	**2b**, 1.6 eq	80	19
3	**2b**, 1.0 eq	59	5
4	**2b**, 1.4 eq	79	9

[a] Reaction conditions: **1a** (0.25 mmol), **2b** (0.5 mmol), KOAc (0.5 mmol), MeTHF (0.5 mL), [Ru] (7 mol%) [b] The yields determined by GC-MS

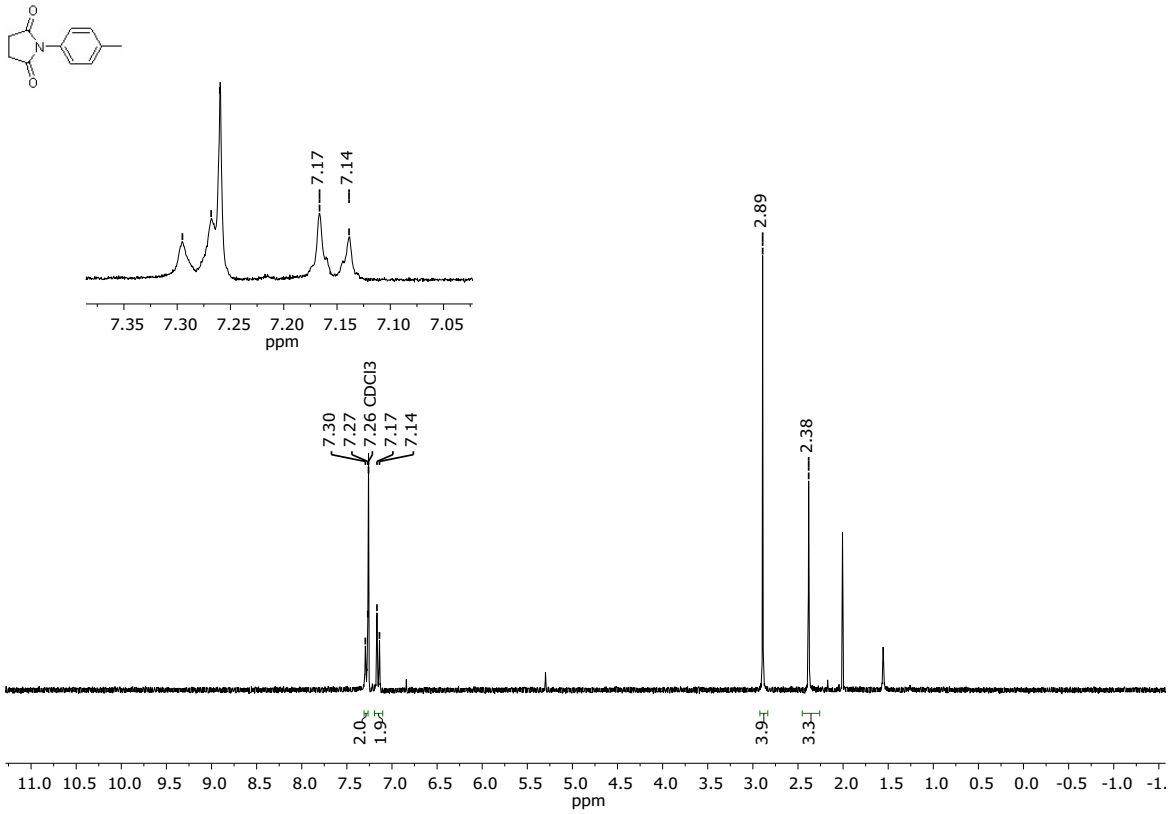
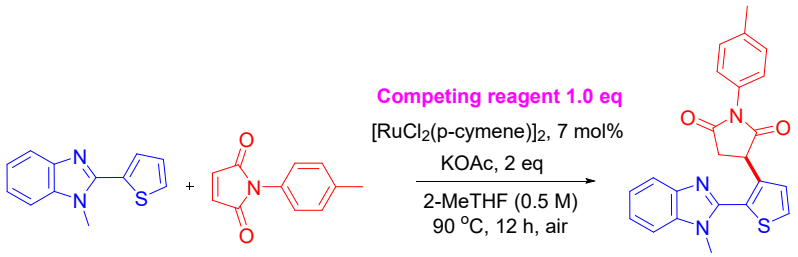
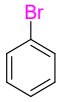
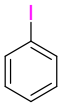
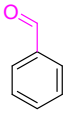
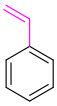
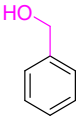
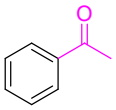
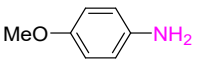
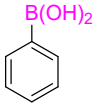


Table S2. Robustness screening



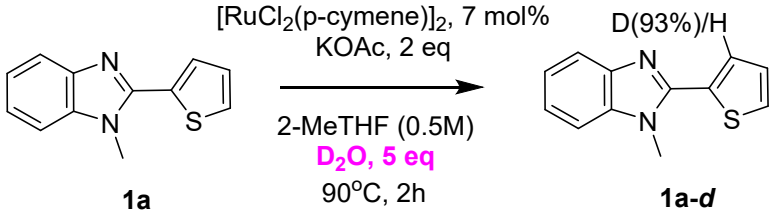
1a **2b** **3b**

Entry	Competing reagent	Yield **3b**,[b]%	Entry	Competing reagent	Yield **3b**,[b]%
1		**75**	6		**29**
2		**77**	7		**trace**
3		**65**	8		**81**
4		**79**	9		**trace**
5		**14**	10		**51**

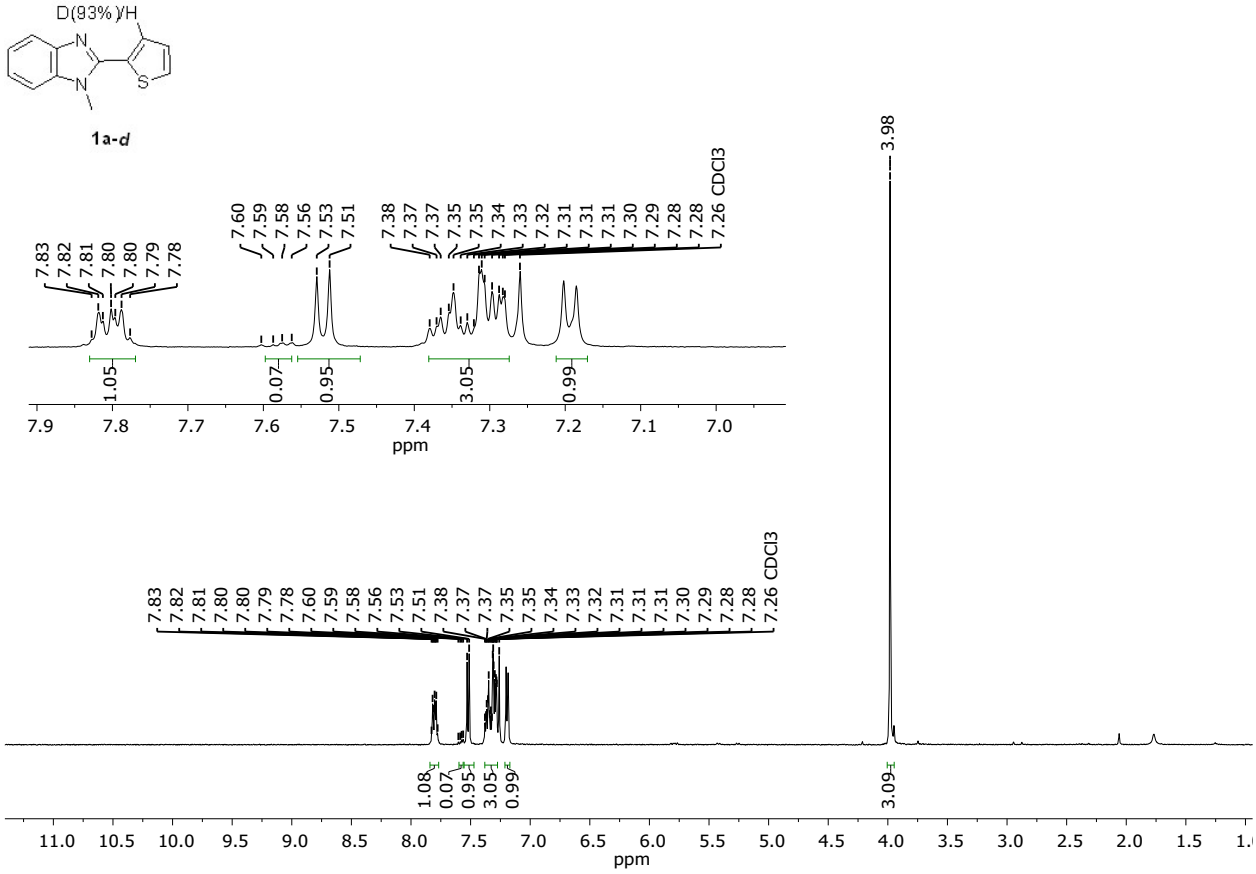
[a] Reaction conditions: **1a** (0.25 mmol), **2b** (0.5 mmol), KOAc (0.5 mmol), MeTHF (0.5 mL), [Ru] (7 mol%), additive (0.25) [b] The yields determined by GC-MS

S2. Mechanistic study

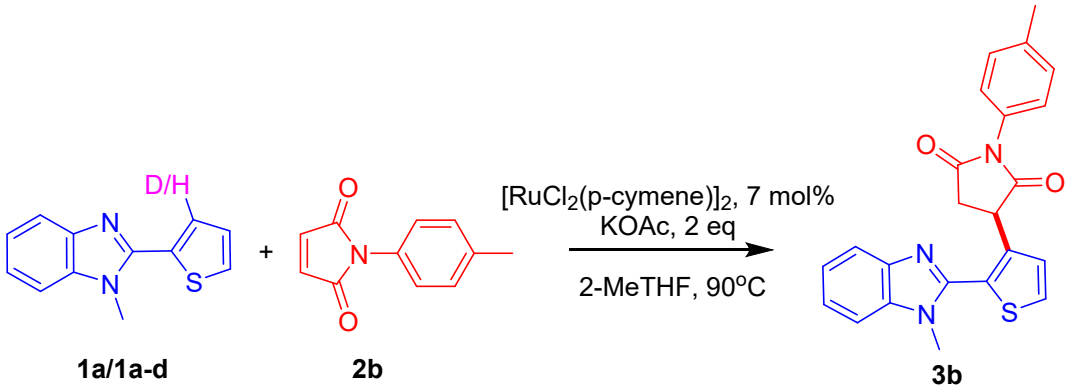
2.1 Deuteroexhange



A mixture of compound **1a** (53 mg, 0.25 mmol), KOAc (0. g, 0.5 mmol), [RuCl2(p-cymene)]2 (0.008 g, 0.00175 mmol, 7 mol%), 2-MeTHF (0.5 mL) and D_2O (0.06 mL) was stirred under an argon atmosphere at 90 °C for 2 h. Then, the mixture was cooled to room temperature, diluted with 2 ml of DCM and filtered through a short pad of Celite. The filtrate obtained was evaporated in vacuo and purified by column chromatography on silica gel (DCM-EtOAc (10:1) mixture as the eluent).



2.2. Determination of KIE effect



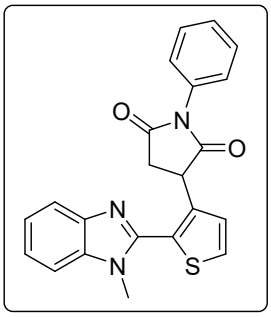
In a screw-capped with a Teflon seal 4 mL high-pressure glass tube equipped with a magnetic stir bar a mixture of compound **1a** or **1a-*d*** (0.054 g., 0.25 mmol), the maleimide **2b** (0.094 g., 0.5 mmol), KOAc (0.049 g, 0.5 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (0.011 g, 0.0175 mmol, 7 mol %) in 2-methyltetrahydrofuran (0.5 mL) was heated at 90 °C for 1, 2, 4 and 8 h while stirring. After being cooled to room temperature, the mixture was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure, and the crude mixture was analyzed by NMR using mesitylene as an internal standard.

Table S3 Determination of the reaction kinetic isotope effect (KIE)

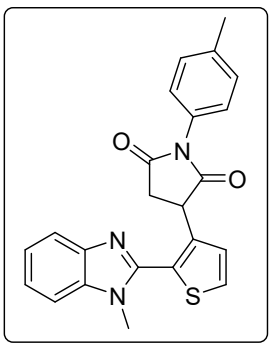
T, h	**Yield of 3b with 1a, %**	**Yield of 3b with 1a-*d*, %**	**KIE**
1	5	5	**1.00**
2	8	8	**1.00**
4	21	20	**1.05**
8	58	56	**1.04**
Average KIE	**1.02**		

S2. Synthetic procedures and characterization of isolated compounds

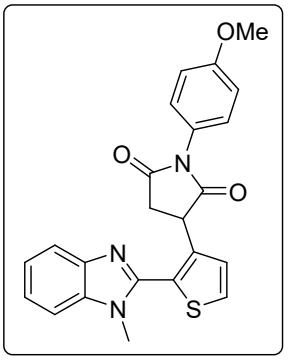
General procedure for the synthesis of compounds 3a-s. The reaction was performed under air atmosphere in a screw-capped with a Teflon seal 4 mL high-pressure glass tube equipped with a magnetic stir bar. A mixture of compound **1a-e** (0.25 mmol), the corresponding maleimide **2a-i** (0.5 mmol), KOAc (0.049 g, 0.5 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (0.011 g, 0.0175 mmol, 7 mol %) in 2-methyltetrahydrofuran (0.5 mL) was heated at 90 °C for 12 h while stirring. After being cooled to room temperature, the mixture was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel using a hexane/EtOAc (1:1) mixture as the eluent.



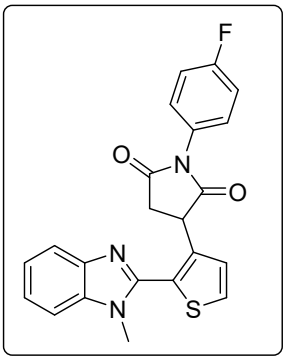
3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)-1-phenyl-pyrrolidine-2,5-dione (3a). Yield 0.074 g (76%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.26 – 3.46 (m, 2H), 3.89 (s, 2H), 4.61 (dd, J = 9.0, 6.8 Hz, 1H), 6.93 – 7.01 (m, 2H), 7.15 (d, J = 5.2 Hz, 1H), 7.22 – 7.41 (m, 6H), 7.57 (d, J = 5.1 Hz, 1H), 7.63 – 7.73 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.6, 37.6, 41.6, 109.9, 120.2, 122.8, 123.5, 126.5, 127.5, 128.1, 128.5, 128.9, 129.1, 132.0, 136.2, 139.3, 142.9, 146.7, 175.3, 176.5. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{22}H_{18}N_3O_2S]^+$ *m/z*: 388.1114 , found 388.1115.



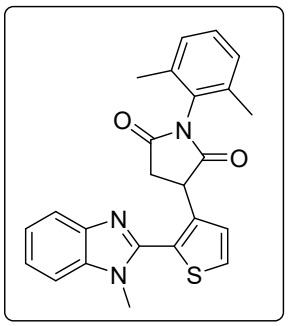
3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)-1-(p-tolyl)pyrrolidine-2,5-dione (3b). Yield 0.074 g (74%), white powder.^{1}H NMR ($CDCl_3$, 300 MHz): 2.32 (s, 3H), 3.19 – 3.47 (m, 2H), 3.89 (s, 3H), 4.60 (dd, J = 9.1, 6.8 Hz, 1H), 6.84 (dd, J = 8.4, 1.8 Hz, 2H), 7.06 – 7.20 (m, 3H), 7.24 – 7.41 (m, 3H), 7.57 (d, J = 5.2 Hz, 1H), 7.68 – 7.73 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 31.6, 37.7, 41.6, 109.9, 120.3, 122.9, 123.5, 126.4, 127.6, 128.1, 128.8, 129.3, 129.8, 136.3, 138.7, 139.4, 142.9, 146.7, 175.4, 176.7. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{23}H_{22}N_3O_2S]^+$ *m/z*: 402.1271, found 402.1277.



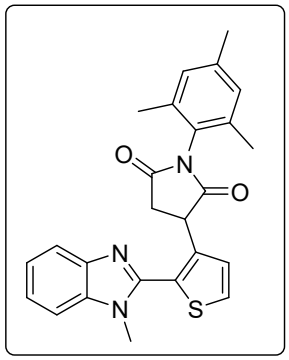
1-(4-methoxyphenyl)-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3c). Yield 0.078 g (75%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.35 (dd, J = 7.9, 5.3 Hz, 2H), 3.77 (s, 3H), 3.89 (s, 2H), 4.59 (dd, J = 9.0, 6.8 Hz, 1H), 6.76 – 6.93 (m, 4H), 7.14 (d, J = 5.1 Hz, 1H), 7.27 – 7.42 (m, 3H), 7.57 (d, J = 5.1 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ, 31.7, 37.6, 41.6, 55.6, 109.9, 114.4, 120.3, 122.8, 123.5, 124.6, 125.6, 127.5, 127.8, 128.1, 128.8, 136.2, 139.4, 142.9, 175.5, 176.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{23}H_{20}N_3O_3S]^+$ *m/z*: 418.1220, found 418.1225.



1-(4-fluorophenyl)-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3d). Yield 0.050 g (49%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.38 (d, J = 7.9 Hz, 2H), 3.91 (s, 3H), 4.60 (t, J = 7.9 Hz, 1H), 6.87 – 7.05 (m, 4H), 7.15 (d, J = 5.2 Hz, 1H), 7.23 – 7.43 (m, 3H), 7.58 (d, J = 5.1 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ, 31.7, 37.6, 41.7, 109.9, 115.9, 116.2, 120.2, 122.9, 123.6, 128.0, 128.3, 128.4, 129.4, 139.2, 142.8, 168.5, 171.9, 175.2, 176.5. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{22}H_{17}FN_3O_3S]^+$ *m/z*: 406.1020, found 406.1026.

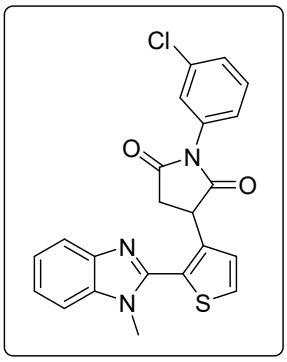


1-(2,6-dimethylphenyl)-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3e). Yield 0.067 g (65%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.10 (s, 3H), 2.12 (s, 3H), 3.19 (ddd, J = 18.8, 5.8, 1.6 Hz, 1H), 3.59 (ddd, J = 18.8, 9.8, 1.6 Hz, 1H), 3.93 (s, 3H), 4.81 (dd, J = 9.7, 5.8 Hz, 1H), 7.09 – 7.26 (m, 4H), 7.34 – 7.50 (m, 3H), 7.65 (d, J = 5.2 Hz, 1H), 7.85 (dd, J = 7.3, 1.8 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.0, 31.6, 37.8, 41.3, 110.0, 120.2, 122.9, 123.6, 126.2, 126.2, 128.7, 128.8, 129.0, 129.7, 135.7, 136.3, 139.3, 143.0, 146.6, 175.0, 176.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{24}H_{22}N_3O_2S]^+$ *m/z*: 416.1427, found 416.1433.

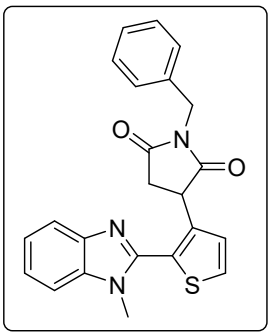


1-mesityl-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3f). Yield 0.063 g (59%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.91 – 2.09 (m, 6H), 2.28 (s, 3H), 3.15 (dd, J =

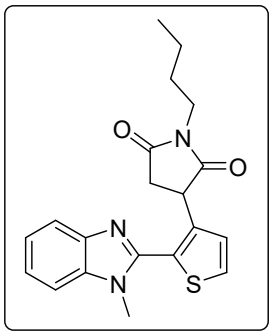
18.7, 5.7 Hz, 1H), 3.55 (dd, *J* = 18.7, 9.7 Hz, 1H), 3.89 (s, 3H), 4.75 (dd, *J* = 9.7, 5.6 Hz, 1H), 6.94 (s, 2H), 7.12 (d, *J* = 5.2 Hz, 1H), 7.29 – 7.47 (m, 3H), 7.61 (d, *J* = 5.2 Hz, 1H), 7.82 (dd, *J* = 6.2, 2.9 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.90, 17.95, 21.2, 31.6, 37.7, 41.2, 110.0, 120.2, 122.9, 123.6, 126.2, 127.6, 128.5, 129.0, 129.5, 129.6, 135.3, 136.2, 139.4, 139.6, 143.0, 146.6, 175.2, 176.3.ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{25}H_{24}N_3O_2S]^+$ *m/z*: 430.1584, found 430.1589.



1-(3-chlorophenyl)-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3g). Yield 0.073 g (69%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.38 (dd, *J* = 8.0, 1.9 Hz, 2H), 3.90 (s, 3H), 4.59 (dd, *J* = 8.8, 7.2 Hz, 1H), 6.87 (d, *J* = 5.9 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 7.15 (d, *J* = 5.1 Hz, 1H), 7.20 – 7.41 (m, 4H), 7.57 (d, *J* = 5.1 Hz, 1H), 7.60 – 7.68 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.7, 37.6, 41.8, 109.9, 120.2, 123.0, 123.7, 124.7, 126.8, 127.4, 128.0, 128.7, 129.4, 129.9, 133.1, 134.6, 136.2, 139.0, 142.8, 146.7, 174.9, 176.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{22}H_{17}ClN_3O_2S]^+$ *m/z*: 422.0725, found 422.0729.

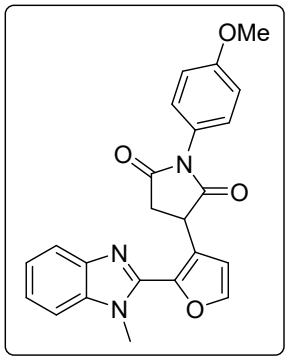


1-benzyl-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3h). Yield 0.075 g (75%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.98 (dd, J = 18.3, 5.5 Hz, 1H), 3.27 (dd, *J* = 18.9, 9.5 Hz, 1H), 3.90 (d, *J* = 1.5 Hz, 3H), 4.40 (d, *J* = 14.3 Hz, 1H), 4.44 – 4.54 (m, 1H), 4.59 (d, *J* = 14.1 Hz, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 7.25 – 7.43 (m, 8H), 7.52 (d, *J* = 5.2 Hz, 1H), 7.63 – 7.84 (m, 1H). .^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.6, 37.6, 41.1, 42.7, 109.9, 120.1, 122.8, 123.5, 127.6, 128.0, 128.4, 128.7, 128.8, 135.9, 136.2, 139.7, 142.8, 146.6, 175.9, 177.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{23}H_{20}N_3O_2S]^+$ *m/z*: 402.1271, found 402.1285.

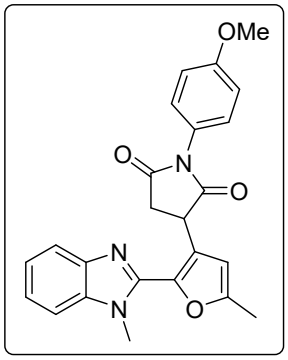


1-butyl-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)pyrrolidine-2,5-dione (3i). Yield 0.072 g (79%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.84 (t, *J* = 7.2 Hz, 3H), 1.12 – 1.43 (m, 4H), 3.02 (dd, *J* = 18.2, 5.6 Hz, 1H), 3.16 – 3.47 (m, 3H), 3.89 (s, 3H), 4.43 (dd, *J* = 9.5, 5.6 Hz, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 7.22 – 7.41 (m, 3H), 7.54 (d, *J* = 5.1 Hz, 1H), 7.67 – 7.76 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.7, 20.1, 29.7, 31.5, 37.6, 38.9, 41.0, 109.8, 120.1, 122.8, 123.5, 127.7, 128.3, 136.2,

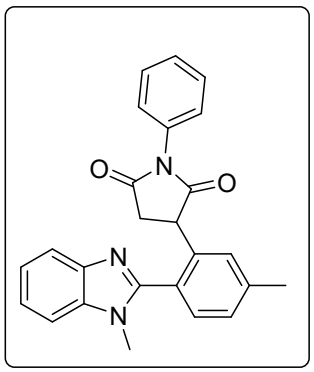
139.7, 142.8, 146.6, 158.3, 176.3, 177.6.ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{20}H_{22}N_3O_2S]^+$ *m/z*: 368.1427, found 368.1420.



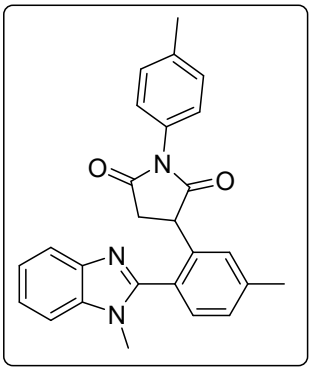
1-(4-methoxyphenyl)-3-(2-(1-methyl-1H-benzo[d]imidazol-2-yl)furan-3-yl)pyrrolidine-2,5-dione (3j). Yield 0.049 g (49%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.26 (dd, *J* = 17.9, 6.4 Hz, 1H), 3.45 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.87 (s, 3H), 4.15 (s, 3H), 4.72 (dd, *J* = 9.6, 6.3 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.47 (m, 5H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.8, 36.6, 38.9, 55.6, 109.5, 114.4, 114.5, 120.1, 122.7, 123.2, 123.8, 125.2, 128.0, 136.0, 142.9, 143.1, 143.7, 159.5, 176.1, 176.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{23}H_{20}N_3O_4]^+$ *m/z*: 402.1448, found 402.1455.



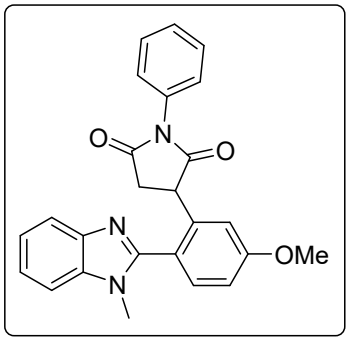
1-(4-methoxyphenyl)-3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)furan-3-yl)pyrrolidine-2,5-dione (3k). Yield 0.058 g (56%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.45 (d, *J* = 1.0 Hz, 3H), 3.18 (dd, *J* = 17.9, 6.3 Hz, 1H), 3.38 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.83 (s, 3H), 4.09 (s, 3H), 4.64 (dd, *J* = 9.6, 6.3 Hz, 1H), 6.24 (d, *J* = 1.1 Hz, 1H), 6.90 – 7.02 (m, 2H), 7.22 (d, *J* = 1.3 Hz, 1H), 7.22 – 7.34 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.8, 36.6, 38.9, 55.6, 109.5, 114.4, 114.5, 120.1, 122.7, 123.2, 123.8, 125.2, 128.0, 136.0, 142.9, 143.1, 143.7, 159.5, 176.1, 176.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{24}H_{22}N_3O_4]^+$ *m/z*: 416.1605, found 416.1600.



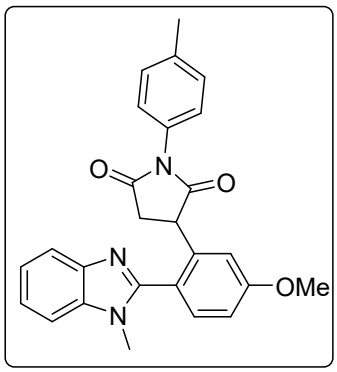
3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3l). Yield 0.085 g (86%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.35 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.57 – 3.71 (m, 4H), 4.34 (dd, *J* = 9.8, 6.3 Hz, 1H), 6.52 – 6.69 (m, 2H), 7.18 – 7.42 (m, 9H), 7.66 – 7.83 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 31.1, 38.6, 45.9, 110.0, 120.2, 122.7, 123.1, 126.4, 127.2, 128.4, 128.7, 128.9, 131.1, 131.2, 131.8, 136.0, 137.7, 140.7, 142.8, 152.6, 175.3, 177.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{25}H_{22}N_3O_2]^+$ *m/z*: 396.1707, found 396.1700.



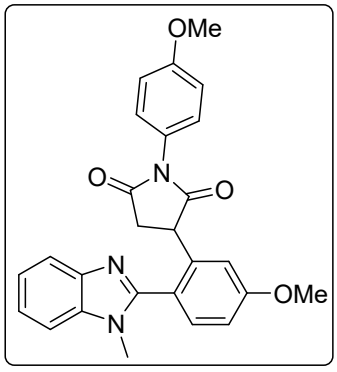
3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-(p-tolyl)pyrrolidine-2,5-dione (3m). Yield 0.082 g (80%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.28 (d, *J* = 2.5 Hz, 3H), 2.46 (d, *J* = 2.6 Hz, 3H), 3.32 (dd, *J* = 18.1, 9.8 Hz, 1H), 3.51 – 3.72 (m, 4H), 4.31 (dd, *J* = 9.7, 6.2 Hz, 1H), 6.38 – 6.52 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.42 (m, 6H), 7.61 – 7.84 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2, 31.1, 38.5, 46.0, 55.6, 110.0, 112.8, 116.5, 120.1, 122.4, 122.6, 123.1, 126.3, 129.1, 129.7, 132.6, 136.0, 138.5, 139.5, 142.8, 152.5, 161.0, 175.4, 176.9.ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{26}H_{24}N_3O_2]^+$ *m/z*: 410.1863 , found 410.1869.



3-(5-methoxy-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3n). Yield 0.083 g (81%), white solid. NMR ($CDCl_3$, 300 MHz): 3.33 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.58 – 3.71 (m, 4H), 3.91 (s, 3H), 4.33 (dd, *J* = 9.8, 6.3 Hz, 1H), 6.52 – 6.65 (m, 1H), 6.92 – 7.06 (m, 2H), 7.22 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.27 – 7.41 (m, 4H), 7.69 – 7.77 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 38.5, 46.0, 55.6, 109.9, 112.8, 116.6, 120.1, 122.3, 122.6, 123.1, 126.4, 128.4, 129.0, 131.7, 132.6, 136.0, 139.4, 142.8, 152.5, 161.0, 175.2, 176.7. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{25}H_{22}N_3O_3]^+$ *m/z*: 412.1656 , found 412.1666.

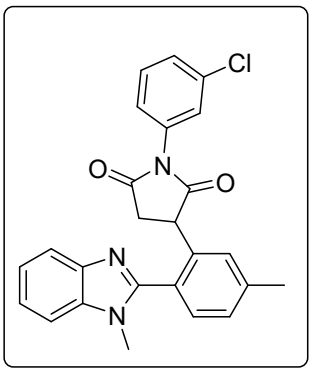


3-(5-methoxy-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-(p-tolyl)pyrrolidine-2,5-dione (3o). Yield 0.076 g (72%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.28 (s, 3H), 3.32 (dd, *J* = 18.1, 9.8 Hz, 1H), 3.50 – 3.73 (m, 3H), 3.90 (s, 2H), 4.31 (dd, *J* = 9.8, 6.2 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 2H), 6.87 – 7.11 (m, 4H), 7.24 – 7.42 (m, 4H), 7.73 (dd, *J* = 7.8, 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2, 21.6, 31.1, 38.6, 45.8, 110.0, 120.2, 122.6, 123.1, 126.3, 127.3, 128.7, 129.1, 129.7, 131.1, 136.0, 137.7, 138.5, 140.7, 142.8, 175.5, 177.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{26}H_{24}N_3O_3]^+$ *m/z*: 426.1812, found 426.1822.

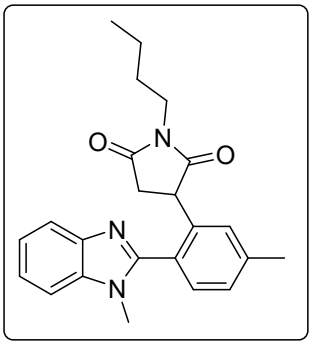


3-(5-methoxy-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3p). Yield 0.072 g

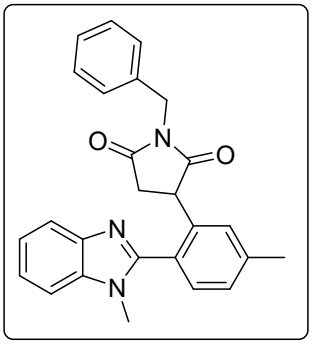
(65%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.30 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.66 (s, 4H), 3.74 (s, 3H), 3.90 (s, 3H), 4.30 (dd, *J* = 9.8, 6.3 Hz, 1H), 6.36 – 6.55 (m, 2H), 6.62 – 6.78 (m, 2H), 6.90 – 7.09 (m, 2H), 7.26 – 7.42 (m, 4H), 7.73 (dd, *J* = 7.0, 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 38.5, 46.0, 55.5, 55.6, 110.0, 112.8, 114.3, 116.6, 120.1, 122.3, 122.6, 123.1, 124.4, 127.6, 132.6, 136.0, 139.4, 142.8, 152.5, 159.3, 161.0, 175.5, 177.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{26}H_{24}N_3O_4]^+$ *m/z*: 442.1761, found 442.1770.



1-(3-chlorophenyl)-3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)pyrolidine-2,5-dione (3q). Yield 0.083 g (77%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.48 (s, 3H), 3.31 (ddd, *J* = 18.2, 9.9, 1.4 Hz, 1H), 3.66 (s, 3H), 3.68 – 3.81 (m, 1H), 4.19 – 4.42 (m, 1H), 6.42 – 6.55 (m, 2H), 7.04 – 7.24 (m, 3H), 7.24 – 7.42 (m, 5H), 7.71 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 31.1, 38.7, 46.3, 109.9, 120.1, 122.8, 123.5, 124.6, 126.6, 127.0, 128.6, 128.8, 129.8, 131.2, 131.9, 132.8, 134.4, 135.9, 137.4, 140.7, 142.6, 152.6, 174.9, 176.6. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{25}H_{21}ClN_3O_2]^+$ *m/z*: 430.1317 , found 430.1323.

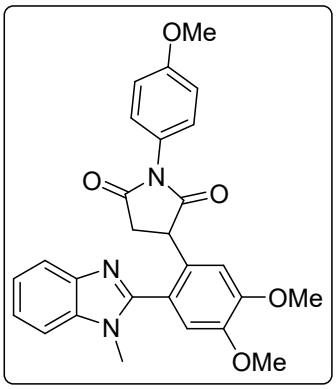


1-butyl-3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)pyrrolidine-2,5-dione (3r). Yield 0.080 g (85%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80 (d, *J* = 6.6 Hz, 3H), 1.05 – 1.27 (m, 4H), 2.43 (s, 3H), 2.91 – 3.31 (m, 3H), 3.68 (s, 3H), 4.11 (dd, *J* = 9.2, 6.0 Hz, 1H), 7.10 (d, *J* = 1.6 Hz, 1H), 7.21 – 7.43 (m, 5H), 7.72 (dd, *J* = 6.7, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.6, 37.6, 41.1, 42.7, 109.9, 120.1, 122.8, 123.5, 127.6, 128.0, 128.4, 128.7, 128.8, 135.9, 136.2, 139.7, 142.8, 146.6, 175.9, 177.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{23}H_{26}N_3O_2]^+$ *m/z*: 376.2020, found 376.2025.



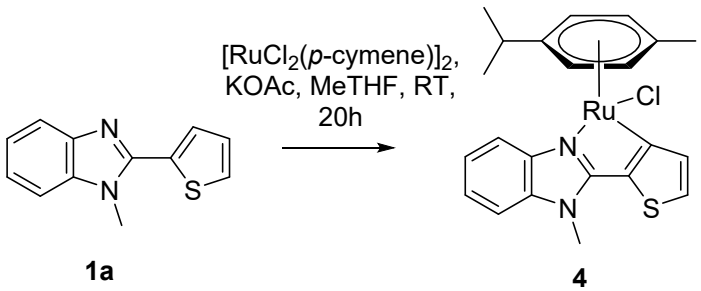
1-benzyl-3-(5-methyl-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)pyrrolidine-2,5-dione (3s). Yield 0.089 g (87%), yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.11 – 3.23 (m, 2H), 3.70 (s, 3H), 4.04 (d, *J* = 14.1 Hz, 1H), 4.12 (dd, *J* = 8.1, 6.8 Hz, 1H), 4.26 (d, *J* = 14.1 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 7.24 (s, 5H), 7.26 – 7.46 (m, 5H), 7.66 – 7.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 31.2, 38.6,

42.3, 44.8, 109.8, 120.0, 122.6, 123.1, 127.2, 127.9, 128.6, 128.7, 128.8, 130.0, 130.8, 135.9, 135.9, 138.4, 140.8, 142.6, 152.5, 176.1, 177.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{26}H_{24}N_3O_2]^+$ *m/z*: 410.1863 , found 410.1850.



3-(4,5-dimethoxy-2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3t). Yield 0.077 g (65%), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.29 (dd, *J* = 18.1, 9.8 Hz, 1H), 3.49 – 3.85 (m, 7H), 3.89 (s, 3H), 3.98 (s, 3H), 4.20 (dd, *J* = 9.7, 6.2 Hz, 1H), 6.38 – 6.52 (m, 2H), 6.66 – 6.75 (m, 2H), 6.89 (d, *J* = 13.0 Hz, 2H), 7.28 – 7.42 (m, 3H), 7.74 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 38.7, 45.7, 55.5, 56.2, 56.4, 110.0, 113.0, 113.8, 114.3, 120.2, 122.3, 122.7, 123.2, 127.6, 130.7, 135.9, 142.7, 148.4, 150.5, 152.5, 154.6, 159.4, 175.5, 177.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{27}H_{26}N_3O_5]^+$ *m/z*: 472.1867, found 472.1877.

Synthesis of complex 4



1a **4**

Synthes of complex 4 was preformed according previous reported method[7] with little modifications. A mixture of $[RuCl_2(p\text{-cymene})]_2$ (0.061 g, 0.1 mmol), compound **1a** (0.043 g, 0.2 mmol) and dry KOAc (0.02 g, 0.2 mmol) in 10 ml of 2-MeTHF was stirred under an argon atmosphere at 25 °C for 20 h. Then, the reaction mixture was filtered and evaporated in vacuo. The crude product was purified by column chromatography on SiO_2 using a mixture of DCM-EtOAc (1:1) as the eluent. The obtained product was washed with Et_2O and dried in vacuo. Yield 0.041 g (40%), orange powder, mp = 201–202 °C (decomposition). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.86 (d, *J* = 6.9 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 2.07 (s, 3H), 2.40 (p, *J* = 6.9 Hz, 1H), 3.95 (s, 3H), 5.26 (dd, *J* = 5.8, 1.2 Hz, 1H), 5.34 – 5.48 (m, 1H), 5.78 (d, *J* = 5.7 Hz, 1H), 5.81 (d, *J* = 5.8 Hz, 1H), 7.26 – 7.40 (m, 3H), 7.60 (d, *J* = 4.7 Hz, 1H), 7.73 – 7.84 (m, 2H). 13C NMR (CDCl3, 75 MHz): δ = 19.1, 21.9, 22.9, 31.2, 31.3, 81.0, 81.2, 87.3, 87.4, 100.3, 100.4, 109.8, 115.7, 122.3,

122.6, 123.2, 128.7, 135.6, 137.1, 142.1, 157.2, 186.0. HRMS (ESI) m/z: [M-Cl]+ calcd for $[C_{23}H_{17}N_2OS]$+ m/z: 369.1056, found m/z 369.1062.

Gram-scale experiment

The reaction was performed under air atmosphere in a round bottom flask equipped with a magnetic stir bar. A mixture of compound **1e** (1.19 g, 5 mmol), the maleimide **2ab** (1.31 g, 7 mmol), KOAc (0.98 g, 10 mmol), and $[RuCl_2(p\text{-cymene})]_2$ in 2-methyltetrahydrofuran (20 mL) was refluxed appropriate time (see table S4) while stirring. After being cooled to room temperature, the mixture was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel using a hexane/EtOAc (1:1) mixture as the eluent to obtain compound **3m**.

Table S4 Influence catalyst loading on yield of **3m**

Catalyst Loading	Time (h)	Yield of **3m**	TON
7.0 mol%	12	68%	9.71
2.5 mol%	12	28%	11.20
2.5 mol%	24	35%	14.00

S3. X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a four-circle Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE area detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[S7] The structure was solved by direct methods using SHELXT-2014/5[S8] and refined on F^2 using SHELXL-2018/3[S9] in the OLEX2 program.[S10] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters; bond distances to H-atoms were refined. A rotating group model was applied for methyl groups.

Table S5. Crystal data, data collection and structure refinement details for **3a** and **3m**

Identification code	**3a**	**3m**
Moiety formula	$C_{22}H_{17}N_3O_2S$	$C_{26}H_{23}N_3O_3$
Formula weight	387.44	425.47
Temperature, K	100.0(3)	100.0(2)
Wavelength, Å	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1$
Unit cell dimensions		
a, Å	12.77135(6)	9.40197(15)
b, Å	14.83370(7)	9.52044(13)
c, Å	9.99137(5)	12.31548(18)
α, °	90	90.0
β, °	103.1472(4)	110.1561(17)
γ, °	90	90.0
Volume, Å^3	1843.215(16)	1034.86(3)
Z	4	2
Calculated density, g·cm^{-3}	1.396	1.365
Absorption coefficient (μ), mm^{-1}	1.755	0.731
F(000)	808	448
Crystal size, mm	0.616×0.254×0.166	0.243×0.241×0.153
θ range for data collection, °	4.640 – 79.848	3.823 - 79.901
Index ranges	-16 ≤ h ≤ 16,	-11 ≤ h ≤ 11,

	-18 ≤ k ≤ 18, -12 ≤ l ≤ 11	-12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections		
Collected	30432	43379
Independent [R_{int}]	3862 [0.0322]	8582 [0.0509]
Observed with I>2σ(I)	3855	8517
Completeness to $\theta_{full}/\theta_{max}$	100%	100%
Transmission max/min	1.000/0.386	0.919/0.861
Data/restraints/parameters	3862/2/269	8582/1/309
Goodness-of-fit on F^2	1.037	1.064
$R_1/\omega R_2$ for I>2σ(I)	0.0233/0.0606	0.0362/0.1028
$R_1/\omega R_2$ for all data	0.0234/0.0606	0.0364/0.1032
Extinction coefficient	0.00233(19)	-
$\Delta\rho_{max}/\Delta\rho_{min}$, ē·Å^{-3}	0.207/-0.147	0.276 /-0.204
CCDC deposition number	2494737	2494738

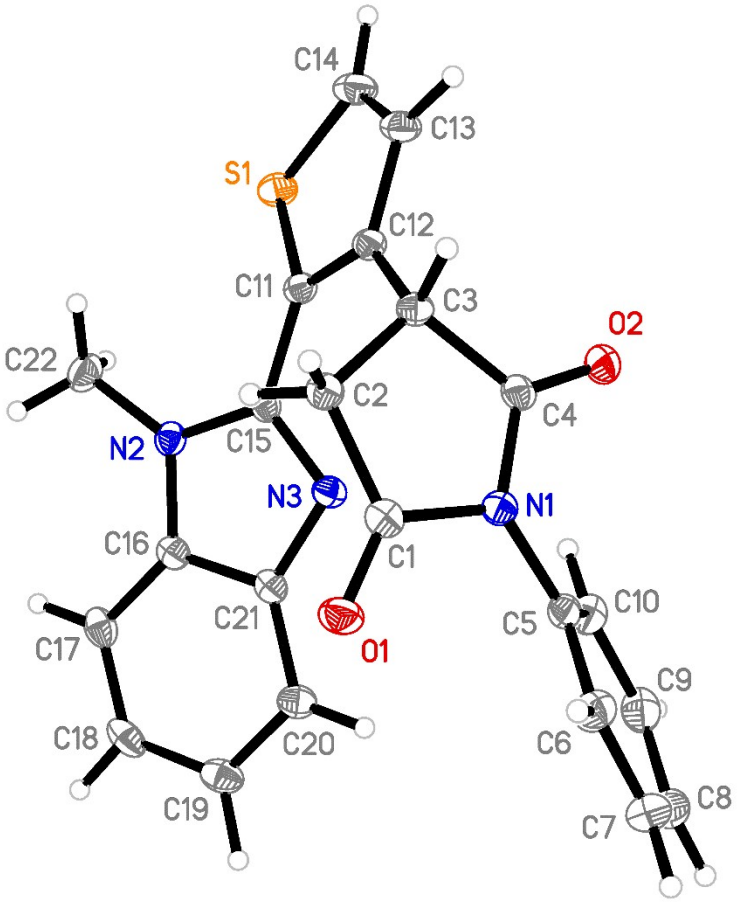


Figure S3. The crystal structure of **3a**. Displacement ellipsoids of nonhydrogen atoms are set to a 50% probability level.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	8269(1)	4922(1)	5084(1)	20(1)
N(1)	4057(1)	5749(1)	5892(2)	15(1)
C(1)	4602(1)	6377(1)	6855(2)	17(1)
C(2)	5670(1)	5981(1)	7581(2)	17(1)
C(3)	5735(1)	5063(1)	6902(2)	16(1)
C(4)	4689(2)	4994(1)	5804(2)	16(1)
O(1)	4249(1)	7110(1)	7048(1)	22(1)
O(2)	4429(1)	4374(1)	5014(2)	21(1)
C(5)	3140(1)	5992(1)	4830(2)	16(1)
C(6)	2259(2)	6405(1)	5163(2)	23(1)
C(7)	1415(2)	6695(1)	4106(2)	28(1)
C(8)	1443(2)	6565(1)	2744(2)	27(1)
C(9)	2324(2)	6139(1)	2422(2)	25(1)
C(10)	3178(1)	5860(1)	3463(2)	20(1)
C(11)	7186(1)	5441(1)	5540(2)	15(1)
C(12)	6705(1)	4868(1)	6316(2)	16(1)
C(13)	7230(2)	4018(1)	6520(2)	20(1)
C(14)	8082(2)	3948(1)	5920(2)	23(1)
C(15)	6788(1)	6316(1)	4978(2)	15(1)
N(2)	7406(1)	7030(1)	4720(2)	16(1)
N(3)	5746(1)	6492(1)	4648(2)	16(1)
C(16)	6697(1)	7708(1)	4178(2)	16(1)
C(17)	6869(2)	8584(1)	3750(2)	20(1)
C(18)	5960(2)	9108(1)	3306(2)	22(1)
C(19)	4921(2)	8780(1)	3284(2)	21(1)
C(20)	4757(1)	7911(1)	3704(2)	18(1)
C(21)	5668(1)	7370(1)	4157(2)	15(1)
C(22)	8573(1)	7099(1)	4919(2)	23(1)

Table S7. Bond lengths [Å] and angles [°] for **3a**.

S(1)-C(11)	1.7321(17)
S(1)-C(14)	1.712(2)
N(1)-C(1)	1.405(2)
N(1)-C(4)	1.394(2)
N(1)-C(5)	1.437(2)
C(1)-C(2)	1.510(2)
C(1)-O(1)	1.208(2)
C(2)-H(2A)	0.936(18)
C(2)-H(2B)	0.936(19)
C(2)-C(3)	1.532(2)
C(3)-H(3)	0.95(3)
C(3)-C(4)	1.527(2)
C(3)-C(12)	1.513(2)
C(4)-O(2)	1.208(2)
C(5)-C(6)	1.386(3)
C(5)-C(10)	1.392(3)
C(6)-H(6)	0.95(3)
C(6)-C(7)	1.395(3)
C(7)-H(7)	0.95(3)
C(7)-C(8)	1.383(3)
C(8)-H(8)	0.97(3)
C(8)-C(9)	1.390(3)
C(9)-H(9)	0.99(3)
C(9)-C(10)	1.388(3)
C(10)-H(10)	0.99(3)
C(11)-C(12)	1.384(3)
C(11)-C(15)	1.459(2)
C(12)-C(13)	1.421(2)
C(13)-H(13)	0.99(3)
C(13)-C(14)	1.360(3)
C(14)-H(14)	0.96(3)
C(15)-N(2)	1.380(2)
C(15)-N(3)	1.322(2)
N(2)-C(16)	1.380(2)
N(2)-C(22)	1.463(2)
N(3)-C(21)	1.387(2)
C(16)-C(17)	1.400(2)
C(16)-C(21)	1.402(2)

C(17)-H(17)	0.96(3)
C(17)-C(18)	1.384(3)
C(18)-H(18)	0.96(3)
C(18)-C(19)	1.408(3)
C(19)-H(19)	1.01(3)
C(19)-C(20)	1.386(3)
C(20)-H(20)	0.94(3)
C(20)-C(21)	1.400(2)
C(22)-H(22A)	0.953(17)
C(22)-H(22B)	0.953(16)
C(22)-H(22C)	0.953(16)

C(14)-S(1)-C(11)	92.17(9)
C(1)-N(1)-C(5)	122.18(14)
C(4)-N(1)-C(1)	111.85(14)
C(4)-N(1)-C(5)	122.78(15)
N(1)-C(1)-C(2)	108.87(14)
O(1)-C(1)-N(1)	124.11(17)
O(1)-C(1)-C(2)	127.03(17)
C(1)-C(2)-H(2A)	110.6
C(1)-C(2)-H(2B)	110.6
C(1)-C(2)-C(3)	105.49(14)
H(2A)-C(2)-H(2B)	108.8
C(3)-C(2)-H(2A)	110.6
C(3)-C(2)-H(2B)	110.6
C(2)-C(3)-H(3)	107.3
C(4)-C(3)-C(2)	104.55(13)
C(4)-C(3)-H(3)	107.3
C(12)-C(3)-C(2)	118.22(14)
C(12)-C(3)-H(3)	107.3
C(12)-C(3)-C(4)	111.62(15)
N(1)-C(4)-C(3)	108.96(15)
O(2)-C(4)-N(1)	125.12(17)
O(2)-C(4)-C(3)	125.88(16)
C(6)-C(5)-N(1)	120.22(17)
C(6)-C(5)-C(10)	120.65(17)
C(10)-C(5)-N(1)	119.00(16)
C(5)-C(6)-H(6)	120.5
C(5)-C(6)-C(7)	119.0(2)
C(7)-C(6)-H(6)	120.5

C(6)-C(7)-H(7)	119.6
C(8)-C(7)-C(6)	120.89(19)
C(8)-C(7)-H(7)	119.6
C(7)-C(8)-H(8)	120.2
C(7)-C(8)-C(9)	119.63(19)
C(9)-C(8)-H(8)	120.2
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-C(8)	120.1(2)
C(10)-C(9)-H(9)	119.9
C(5)-C(10)-H(10)	120.1
C(9)-C(10)-C(5)	119.72(18)
C(9)-C(10)-H(10)	120.1
C(12)-C(11)-S(1)	110.97(13)
C(12)-C(11)-C(15)	126.92(16)
C(15)-C(11)-S(1)	121.55(13)
C(11)-C(12)-C(3)	127.32(16)
C(11)-C(12)-C(13)	111.66(16)
C(13)-C(12)-C(3)	121.02(16)
C(12)-C(13)-H(13)	123.1
C(14)-C(13)-C(12)	113.81(17)
C(14)-C(13)-H(13)	123.1
S(1)-C(14)-H(14)	124.3
C(13)-C(14)-S(1)	111.39(13)
C(13)-C(14)-H(14)	124.3
N(2)-C(15)-C(11)	126.20(15)
N(3)-C(15)-C(11)	120.99(15)
N(3)-C(15)-N(2)	112.81(15)
C(15)-N(2)-C(16)	106.32(14)
C(15)-N(2)-C(22)	129.63(15)
C(16)-N(2)-C(22)	124.03(15)
C(15)-N(3)-C(21)	105.16(14)
N(2)-C(16)-C(17)	131.42(16)
N(2)-C(16)-C(21)	105.91(15)
C(17)-C(16)-C(21)	122.63(16)
C(16)-C(17)-H(17)	121.9
C(18)-C(17)-C(16)	116.10(17)
C(18)-C(17)-H(17)	121.9
C(17)-C(18)-H(18)	119.0
C(17)-C(18)-C(19)	121.96(17)
C(19)-C(18)-H(18)	119.0

C(18)-C(19)-H(19)	119.2
C(20)-C(19)-C(18)	121.56(17)
C(20)-C(19)-H(19)	119.2
C(19)-C(20)-H(20)	121.3
C(19)-C(20)-C(21)	117.32(17)
C(21)-C(20)-H(20)	121.3
N(3)-C(21)-C(16)	109.78(15)
N(3)-C(21)-C(20)	129.79(16)
C(20)-C(21)-C(16)	120.42(16)
N(2)-C(22)-H(22A)	109.5
N(2)-C(22)-H(22B)	109.5
N(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	21(1)	23(1)	-1(1)	6(1)	5(1)
N(1)	16(1)	15(1)	14(1)	1(1)	3(1)	0(1)
C(1)	19(1)	17(1)	14(1)	1(1)	6(1)	0(1)
C(2)	19(1)	17(1)	14(1)	0(1)	3(1)	1(1)
C(3)	18(1)	16(1)	14(1)	3(1)	2(1)	1(1)
C(4)	17(1)	15(1)	17(1)	3(1)	6(1)	-1(1)
O(1)	24(1)	18(1)	23(1)	-3(1)	3(1)	5(1)
O(2)	20(1)	17(1)	26(1)	-5(1)	3(1)	-1(1)
C(5)	16(1)	15(1)	17(1)	3(1)	2(1)	-2(1)
C(6)	20(1)	24(1)	24(1)	1(1)	6(1)	1(1)
C(7)	20(1)	24(1)	38(1)	2(1)	3(1)	4(1)
C(8)	23(1)	22(1)	32(1)	7(1)	-5(1)	-1(1)
C(9)	28(1)	25(1)	19(1)	4(1)	1(1)	-5(1)
C(10)	20(1)	23(1)	18(1)	2(1)	4(1)	-2(1)
C(11)	15(1)	16(1)	15(1)	-1(1)	2(1)	2(1)
C(12)	16(1)	14(1)	14(1)	-1(1)	0(1)	1(1)
C(13)	24(1)	16(1)	17(1)	2(1)	1(1)	5(1)
C(14)	26(1)	19(1)	22(1)	0(1)	3(1)	8(1)
C(15)	16(1)	14(1)	13(1)	-2(1)	3(1)	-1(1)
N(2)	16(1)	17(1)	14(1)	0(1)	3(1)	-2(1)
N(3)	16(1)	14(1)	17(1)	1(1)	4(1)	1(1)
C(16)	21(1)	15(1)	12(1)	-1(1)	3(1)	0(1)
C(17)	26(1)	17(1)	16(1)	0(1)	6(1)	-5(1)
C(18)	35(1)	12(1)	18(1)	1(1)	7(1)	-1(1)
C(19)	29(1)	18(1)	16(1)	1(1)	6(1)	6(1)
C(20)	20(1)	18(1)	18(1)	1(1)	6(1)	3(1)
C(21)	20(1)	14(1)	12(1)	0(1)	4(1)	0(1)
C(22)	16(1)	26(1)	26(1)	5(1)	2(1)	-4(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

	x	y	z	U(eq)
H(2A)	5701(2)	5912(2)	8520(19)	20
H(2B)	6236(11)	6354(7)	7474(3)	20
H(3)	5712(2)	4613(13)	7575(19)	19
H(6)	2231(2)	6489(3)	6090(30)	27
H(7)	810(20)	6986(10)	4325(8)	34
H(8)	851(18)	6772(6)	2020(20)	33
H(9)	2341(2)	6034(4)	1450(30)	30
H(10)	3812(17)	5568(8)	3234(6)	24
H(13)	6997(7)	3522(14)	7050(15)	23
H(14)	8521(13)	3421(16)	5960(2)	27
H(17)	7578(19)	8808(6)	3764(2)	24
H(18)	6039(3)	9710(19)	3006(9)	26
H(19)	4278(17)	9189(11)	2952(9)	25
H(20)	4070(20)	7694(6)	3685(2)	22
H(22A)	8790(4)	7707(11)	5127(18)	34
H(22B)	8777(4)	6918(12)	4100(16)	34
H(22C)	8913(6)	6718(11)	5658(18)	34

Table S10. Torsion angles [°] for **3a**.

S(1)-C(11)-C(12)-C(3)	-179.49(15)
S(1)-C(11)-C(12)-C(13)	-0.1(2)
S(1)-C(11)-C(15)-N(2)	-37.9(2)
S(1)-C(11)-C(15)-N(3)	141.44(15)
N(1)-C(1)-C(2)-C(3)	2.73(19)
N(1)-C(5)-C(6)-C(7)	175.27(17)
N(1)-C(5)-C(10)-C(9)	-176.35(16)
C(1)-N(1)-C(4)-C(3)	5.7(2)
C(1)-N(1)-C(4)-O(2)	-176.65(17)
C(1)-N(1)-C(5)-C(6)	-54.7(2)
C(1)-N(1)-C(5)-C(10)	121.34(18)
C(1)-C(2)-C(3)-C(4)	0.52(18)
C(1)-C(2)-C(3)-C(12)	125.34(16)
C(2)-C(3)-C(4)-N(1)	-3.63(19)
C(2)-C(3)-C(4)-O(2)	178.71(18)
C(2)-C(3)-C(12)-C(11)	-43.6(3)
C(2)-C(3)-C(12)-C(13)	137.09(17)
C(3)-C(12)-C(13)-C(14)	179.52(17)
C(4)-N(1)-C(1)-C(2)	-5.3(2)
C(4)-N(1)-C(1)-O(1)	174.88(18)
C(4)-N(1)-C(5)-C(6)	147.12(17)
C(4)-N(1)-C(5)-C(10)	-36.9(2)
C(4)-C(3)-C(12)-C(11)	77.7(2)
C(4)-C(3)-C(12)-C(13)	-101.64(19)
O(1)-C(1)-C(2)-C(3)	-177.48(18)
C(5)-N(1)-C(1)-C(2)	-165.65(15)
C(5)-N(1)-C(1)-O(1)	14.5(3)
C(5)-N(1)-C(4)-C(3)	165.86(15)
C(5)-N(1)-C(4)-O(2)	-16.5(3)
C(5)-C(6)-C(7)-C(8)	0.8(3)
C(6)-C(5)-C(10)-C(9)	-0.3(3)
C(6)-C(7)-C(8)-C(9)	0.2(3)
C(7)-C(8)-C(9)-C(10)	-1.2(3)
C(8)-C(9)-C(10)-C(5)	1.3(3)
C(10)-C(5)-C(6)-C(7)	-0.7(3)
C(11)-S(1)-C(14)-C(13)	-0.01(16)
C(11)-C(12)-C(13)-C(14)	0.1(2)
C(11)-C(15)-N(2)-C(16)	179.15(17)

C(11)-C(15)-N(2)-C(22)	0.6(3)
C(11)-C(15)-N(3)-C(21)	179.95(15)
C(12)-C(3)-C(4)-N(1)	-132.55(15)
C(12)-C(3)-C(4)-O(2)	49.8(2)
C(12)-C(11)-C(15)-N(2)	151.39(18)
C(12)-C(11)-C(15)-N(3)	-29.2(3)
C(12)-C(13)-C(14)-S(1)	0.0(2)
C(14)-S(1)-C(11)-C(12)	0.06(14)
C(14)-S(1)-C(11)-C(15)	-171.98(15)
C(15)-C(11)-C(12)-C(3)	-8.0(3)
C(15)-C(11)-C(12)-C(13)	171.42(17)
C(15)-N(2)-C(16)-C(17)	178.89(19)
C(15)-N(2)-C(16)-C(21)	0.99(18)
C(15)-N(3)-C(21)-C(16)	1.23(19)
C(15)-N(3)-C(21)-C(20)	-177.84(19)
N(2)-C(15)-N(3)-C(21)	-0.6(2)
N(2)-C(16)-C(17)-C(18)	-177.21(19)
N(2)-C(16)-C(21)-N(3)	-1.40(19)
N(2)-C(16)-C(21)-C(20)	177.77(17)
N(3)-C(15)-N(2)-C(16)	-0.3(2)
N(3)-C(15)-N(2)-C(22)	-178.86(17)
C(16)-C(17)-C(18)-C(19)	-0.1(3)
C(17)-C(16)-C(21)-N(3)	-179.52(16)
C(17)-C(16)-C(21)-C(20)	-0.4(3)
C(17)-C(18)-C(19)-C(20)	-0.2(3)
C(18)-C(19)-C(20)-C(21)	0.2(3)
C(19)-C(20)-C(21)-N(3)	179.03(17)
C(19)-C(20)-C(21)-C(16)	0.0(3)
C(21)-C(16)-C(17)-C(18)	0.4(3)
C(22)-N(2)-C(16)-C(17)	-2.4(3)
C(22)-N(2)-C(16)-C(21)	179.69(16)

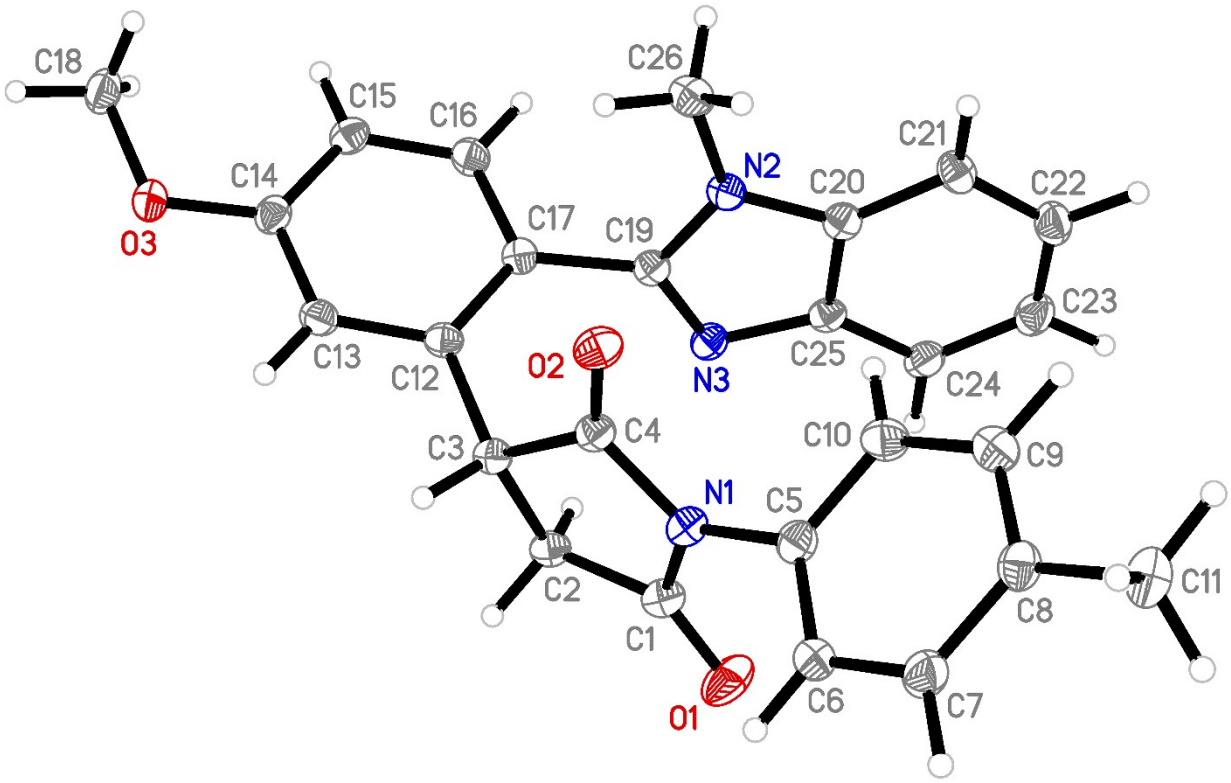


Figure S4. The crystal structure of **3n**. Displacement ellipsoids of nonhydrogen atoms are set to a 50% probability level.

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3n**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4577(2)	3927(2)	6331(1)	18(1)
C(1)	5712(2)	4794(2)	6199(2)	21(1)
C(2)	5271(2)	5158(2)	4933(2)	19(1)
C(3)	3905(2)	4216(2)	4309(2)	16(1)
C(4)	3422(2)	3638(2)	5286(2)	17(1)
O(1)	6817(2)	5174(2)	6988(1)	32(1)
O(2)	2284(2)	2996(2)	5191(1)	22(1)
C(5)	4546(2)	3377(2)	7409(2)	19(1)
C(6)	5661(2)	2452(3)	8037(2)	22(1)
C(7)	5562(3)	1840(3)	9039(2)	24(1)
C(8)	4356(3)	2158(2)	9421(2)	21(1)
C(9)	3279(3)	3129(3)	8788(2)	23(1)

C(10)	3359(3)	3735(3)	7784(2)	22(1)
C(11)	4220(3)	1462(3)	10483(2)	25(1)
C(12)	2610(2)	4865(2)	3340(2)	17(1)
C(13)	2293(2)	4374(2)	2218(2)	18(1)
C(14)	1103(2)	4934(2)	1295(2)	19(1)
C(15)	212(2)	6007(2)	1485(2)	20(1)
C(16)	513(2)	6483(2)	2610(2)	20(1)
C(17)	1694(2)	5935(2)	3540(2)	16(1)
O(3)	879(2)	4332(2)	240(1)	24(1)
C(18)	-447(3)	4757(3)	-700(2)	25(1)
C(19)	1881(2)	6462(2)	4716(2)	16(1)
N(2)	842(2)	6136(2)	5229(2)	17(1)
N(3)	2958(2)	7321(2)	5340(1)	18(1)
C(20)	1279(2)	6844(2)	6267(2)	18(1)
C(21)	634(3)	6913(2)	7133(2)	20(1)
C(22)	1365(3)	7768(2)	8067(2)	23(1)
C(23)	2666(3)	8543(3)	8130(2)	25(1)
C(24)	3302(2)	8464(2)	7272(2)	22(1)
C(25)	2602(2)	7578(2)	6328(2)	17(1)
C(26)	-440(3)	5179(3)	4800(2)	22(1)

Table S12. Bond lengths [Å] and angles [°] for **3n**.

N(1)-C(1)	1.403(3)
N(1)-C(4)	1.396(3)
N(1)-C(5)	1.436(2)
C(1)-C(2)	1.509(3)
C(1)-O(1)	1.208(3)
C(2)-H(2A)	1.01(2)
C(2)-H(2B)	1.01(2)
C(2)-C(3)	1.538(3)
C(3)-H(3)	0.97(3)
C(3)-C(4)	1.527(3)
C(3)-C(12)	1.512(3)
C(4)-O(2)	1.203(3)
C(5)-C(6)	1.384(3)
C(5)-C(10)	1.390(3)
C(6)-H(6)	0.94(4)
C(6)-C(7)	1.397(3)
C(7)-H(7)	1.00(4)
C(7)-C(8)	1.401(3)
C(8)-C(9)	1.394(3)
C(8)-C(11)	1.511(3)
C(9)-H(9)	0.98(3)
C(9)-C(10)	1.390(3)
C(10)-H(10)	0.89(4)
C(11)-H(11A)	1.01(2)
C(11)-H(11B)	1.01(2)
C(11)-H(11C)	1.01(2)
C(12)-C(13)	1.391(3)
C(12)-C(17)	1.409(3)
C(13)-H(13)	0.94(3)
C(13)-C(14)	1.397(3)
C(14)-C(15)	1.391(3)
C(14)-O(3)	1.368(2)
C(15)-H(15)	0.92(3)
C(15)-C(16)	1.392(3)
C(16)-H(16)	0.97(3)
C(16)-C(17)	1.393(3)
C(17)-C(19)	1.486(3)
O(3)-C(18)	1.436(3)

C(18)-H(18A)	0.97(2)
C(18)-H(18B)	0.97(2)
C(18)-H(18C)	0.97(2)
C(19)-N(2)	1.369(3)
C(19)-N(3)	1.322(3)
N(2)-C(20)	1.377(3)
N(2)-C(26)	1.457(3)
N(3)-C(25)	1.390(3)
C(20)-C(21)	1.398(3)
C(20)-C(25)	1.406(3)
C(21)-H(21)	0.93(3)
C(21)-C(22)	1.383(3)
C(22)-H(22)	0.99(3)
C(22)-C(23)	1.407(4)
C(23)-H(23)	1.02(4)
C(23)-C(24)	1.383(3)
C(24)-H(24)	1.04(3)
C(24)-C(25)	1.403(3)
C(26)-H(26A)	0.95(2)
C(26)-H(26B)	0.95(2)
C(26)-H(26C)	0.95(2)

C(1)-N(1)-C(5)	125.48(17)
C(4)-N(1)-C(1)	112.94(16)
C(4)-N(1)-C(5)	121.57(17)
N(1)-C(1)-C(2)	107.80(17)
O(1)-C(1)-N(1)	124.10(19)
O(1)-C(1)-C(2)	128.1(2)
C(1)-C(2)-H(2A)	110.6
C(1)-C(2)-H(2B)	110.6
C(1)-C(2)-C(3)	105.53(16)
H(2A)-C(2)-H(2B)	108.8
C(3)-C(2)-H(2A)	110.6
C(3)-C(2)-H(2B)	110.6
C(2)-C(3)-H(3)	107.3
C(4)-C(3)-C(2)	103.88(16)
C(4)-C(3)-H(3)	107.3
C(12)-C(3)-C(2)	117.57(18)
C(12)-C(3)-H(3)	107.3
C(12)-C(3)-C(4)	113.04(16)

N(1)-C(4)-C(3)	107.94(17)
O(2)-C(4)-N(1)	124.95(18)
O(2)-C(4)-C(3)	127.05(18)
C(6)-C(5)-N(1)	119.76(19)
C(6)-C(5)-C(10)	120.7(2)
C(10)-C(5)-N(1)	119.45(19)
C(5)-C(6)-H(6)	120.3
C(5)-C(6)-C(7)	119.4(2)
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-H(7)	119.5
C(6)-C(7)-C(8)	120.9(2)
C(8)-C(7)-H(7)	119.5
C(7)-C(8)-C(11)	121.0(2)
C(9)-C(8)-C(7)	118.2(2)
C(9)-C(8)-C(11)	120.8(2)
C(8)-C(9)-H(9)	119.3
C(10)-C(9)-C(8)	121.4(2)
C(10)-C(9)-H(9)	119.3
C(5)-C(10)-C(9)	119.3(2)
C(5)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(12)-C(3)	119.00(18)
C(13)-C(12)-C(17)	118.81(18)
C(17)-C(12)-C(3)	122.18(17)
C(12)-C(13)-H(13)	119.4
C(12)-C(13)-C(14)	121.1(2)
C(14)-C(13)-H(13)	119.4
C(15)-C(14)-C(13)	120.26(19)
O(3)-C(14)-C(13)	115.51(19)
O(3)-C(14)-C(15)	124.21(19)
C(14)-C(15)-H(15)	120.7
C(14)-C(15)-C(16)	118.61(19)
C(16)-C(15)-H(15)	120.7
C(15)-C(16)-H(16)	119.1

C(15)-C(16)-C(17)	121.82(19)
C(17)-C(16)-H(16)	119.1
C(12)-C(17)-C(19)	122.69(18)
C(16)-C(17)-C(12)	119.34(17)
C(16)-C(17)-C(19)	117.89(18)
C(14)-O(3)-C(18)	117.00(17)
O(3)-C(18)-H(18A)	109.5
O(3)-C(18)-H(18B)	109.5
O(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(2)-C(19)-C(17)	120.68(18)
N(3)-C(19)-C(17)	125.80(18)
N(3)-C(19)-N(2)	113.42(17)
C(19)-N(2)-C(20)	106.59(17)
C(19)-N(2)-C(26)	127.34(17)
C(20)-N(2)-C(26)	126.01(17)
C(19)-N(3)-C(25)	104.47(17)
N(2)-C(20)-C(21)	131.5(2)
N(2)-C(20)-C(25)	105.53(17)
C(21)-C(20)-C(25)	123.0(2)
C(20)-C(21)-H(21)	122.0
C(22)-C(21)-C(20)	116.1(2)
C(22)-C(21)-H(21)	122.0
C(21)-C(22)-H(22)	119.1
C(21)-C(22)-C(23)	121.8(2)
C(23)-C(22)-H(22)	119.1
C(22)-C(23)-H(23)	119.1
C(24)-C(23)-C(22)	121.7(2)
C(24)-C(23)-H(23)	119.1
C(23)-C(24)-H(24)	121.2
C(23)-C(24)-C(25)	117.6(2)
C(25)-C(24)-H(24)	121.2
N(3)-C(25)-C(20)	109.98(18)
N(3)-C(25)-C(24)	130.2(2)
C(24)-C(25)-C(20)	119.74(19)
N(2)-C(26)-H(26A)	109.5
N(2)-C(26)-H(26B)	109.5
N(2)-C(26)-H(26C)	109.5

H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3n**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	18(1)	18(1)	17(1)	0(1)	4(1)	-1(1)
C(1)	18(1)	21(1)	22(1)	0(1)	5(1)	0(1)
C(2)	16(1)	18(1)	20(1)	0(1)	5(1)	-1(1)
C(3)	16(1)	14(1)	19(1)	-1(1)	6(1)	0(1)
C(4)	17(1)	14(1)	18(1)	0(1)	4(1)	2(1)
O(1)	25(1)	41(1)	24(1)	1(1)	0(1)	-14(1)
O(2)	19(1)	20(1)	24(1)	1(1)	5(1)	-4(1)
C(5)	20(1)	18(1)	18(1)	-1(1)	5(1)	-1(1)
C(6)	21(1)	26(1)	19(1)	-1(1)	7(1)	4(1)
C(7)	26(1)	24(1)	19(1)	2(1)	6(1)	6(1)
C(8)	24(1)	20(1)	19(1)	-3(1)	7(1)	-3(1)
C(9)	22(1)	22(1)	26(1)	-2(1)	10(1)	0(1)
C(10)	21(1)	20(1)	25(1)	2(1)	7(1)	3(1)
C(11)	32(1)	24(1)	20(1)	-1(1)	9(1)	-4(1)
C(12)	14(1)	16(1)	19(1)	0(1)	6(1)	-1(1)
C(13)	16(1)	18(1)	21(1)	-2(1)	7(1)	0(1)
C(14)	18(1)	21(1)	17(1)	-2(1)	6(1)	-4(1)
C(15)	18(1)	20(1)	18(1)	2(1)	3(1)	2(1)
C(16)	20(1)	17(1)	20(1)	0(1)	7(1)	4(1)
C(17)	17(1)	14(1)	17(1)	0(1)	6(1)	-1(1)
O(3)	23(1)	30(1)	16(1)	-4(1)	5(1)	4(1)
C(18)	27(1)	28(1)	16(1)	-2(1)	4(1)	3(1)
C(19)	17(1)	12(1)	18(1)	0(1)	5(1)	2(1)
N(2)	17(1)	15(1)	20(1)	-2(1)	6(1)	-1(1)
N(3)	18(1)	17(1)	17(1)	-1(1)	5(1)	-1(1)
C(20)	19(1)	14(1)	19(1)	1(1)	5(1)	3(1)
C(21)	23(1)	18(1)	22(1)	1(1)	11(1)	3(1)
C(22)	27(1)	24(1)	20(1)	0(1)	9(1)	7(1)
C(23)	26(1)	24(1)	21(1)	-5(1)	4(1)	4(1)
C(24)	19(1)	21(1)	21(1)	-2(1)	2(1)	1(1)
C(25)	16(1)	14(1)	19(1)	1(1)	4(1)	2(1)
C(26)	20(1)	18(1)	29(1)	-5(1)	10(1)	-4(1)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3n**.

	x	y	z	U(eq)
H(2A)	6130(20)	4964(5)	4646(7)	22
H(2B)	4986(7)	6180(20)	4800(4)	22
H(3)	4278(13)	3430(30)	3984(11)	20
H(6)	6470(30)	2238(8)	7793(9)	27
H(7)	6360(30)	1170(20)	9490(16)	28
H(9)	2450(30)	3389(9)	9056(9)	27
H(10)	2650(30)	4350(30)	7384(17)	27
H(11A)	3390(30)	1929(19)	10692(12)	38
H(11B)	5210(20)	1560(20)	11147(16)	38
H(11C)	3970(30)	430(20)	10318(7)	38
H(13)	2890(20)	3650(30)	2079(5)	22
H(15)	-560(30)	6395(14)	880(20)	24
H(16)	-120(20)	7210(30)	2751(5)	23
H(18A)	-477(13)	4270(20)	-1396(16)	37
H(18B)	-414(12)	5760(20)	-814(12)	37
H(18C)	-1340(20)	4520(20)	-520(9)	37
H(21)	-240(30)	6412(19)	7084(3)	24
H(22)	961(13)	7837(3)	8710(20)	28
H(23)	3154(17)	9180(20)	8830(20)	30
H(24)	4260(30)	9039(19)	7326(2)	26
H(26A)	-426(14)	4540(20)	5393(14)	33
H(26B)	-371(13)	4676(19)	4155(18)	33
H(26C)	-1356(19)	5700(11)	4573(17)	33

Table S15. Torsion angles [°] for **3n**.

N(1)-C(1)-C(2)-C(3)	-9.4(2)
N(1)-C(5)-C(6)-C(7)	-175.3(2)
N(1)-C(5)-C(10)-C(9)	175.8(2)
C(1)-N(1)-C(4)-C(3)	7.7(2)
C(1)-N(1)-C(4)-O(2)	-174.9(2)
C(1)-N(1)-C(5)-C(6)	-64.1(3)
C(1)-N(1)-C(5)-C(10)	118.6(2)
C(1)-C(2)-C(3)-C(4)	13.3(2)
C(1)-C(2)-C(3)-C(12)	139.03(18)
C(2)-C(3)-C(4)-N(1)	-13.0(2)
C(2)-C(3)-C(4)-O(2)	169.7(2)
C(2)-C(3)-C(12)-C(13)	114.7(2)
C(2)-C(3)-C(12)-C(17)	-66.4(2)
C(3)-C(12)-C(13)-C(14)	179.64(18)
C(3)-C(12)-C(17)-C(16)	-179.61(19)
C(3)-C(12)-C(17)-C(19)	-2.9(3)
C(4)-N(1)-C(1)-C(2)	1.2(2)
C(4)-N(1)-C(1)-O(1)	-179.9(2)
C(4)-N(1)-C(5)-C(6)	116.4(2)
C(4)-N(1)-C(5)-C(10)	-60.9(3)
C(4)-C(3)-C(12)-C(13)	-124.2(2)
C(4)-C(3)-C(12)-C(17)	54.7(3)
O(1)-C(1)-C(2)-C(3)	171.7(2)
C(5)-N(1)-C(1)-C(2)	-178.34(19)
C(5)-N(1)-C(1)-O(1)	0.6(4)
C(5)-N(1)-C(4)-C(3)	-172.74(17)
C(5)-N(1)-C(4)-O(2)	4.6(3)
C(5)-C(6)-C(7)-C(8)	-0.5(3)
C(6)-C(5)-C(10)-C(9)	-1.5(3)
C(6)-C(7)-C(8)-C(9)	-1.6(3)
C(6)-C(7)-C(8)-C(11)	178.0(2)
C(7)-C(8)-C(9)-C(10)	2.1(3)
C(8)-C(9)-C(10)-C(5)	-0.6(3)
C(10)-C(5)-C(6)-C(7)	2.0(3)
C(11)-C(8)-C(9)-C(10)	-177.4(2)
C(12)-C(3)-C(4)-N(1)	-141.53(18)
C(12)-C(3)-C(4)-O(2)	41.2(3)
C(12)-C(13)-C(14)-C(15)	0.3(3)

C(12)-C(13)-C(14)-O(3)	-178.03(19)
C(12)-C(17)-C(19)-N(2)	-107.4(2)
C(12)-C(17)-C(19)-N(3)	76.5(3)
C(13)-C(12)-C(17)-C(16)	-0.7(3)
C(13)-C(12)-C(17)-C(19)	175.95(19)
C(13)-C(14)-C(15)-C(16)	-1.4(3)
C(13)-C(14)-O(3)-C(18)	172.38(19)
C(14)-C(15)-C(16)-C(17)	1.4(3)
C(15)-C(14)-O(3)-C(18)	-5.9(3)
C(15)-C(16)-C(17)-C(12)	-0.3(3)
C(15)-C(16)-C(17)-C(19)	-177.1(2)
C(16)-C(17)-C(19)-N(2)	69.3(3)
C(16)-C(17)-C(19)-N(3)	-106.8(2)
C(17)-C(12)-C(13)-C(14)	0.7(3)
C(17)-C(19)-N(2)-C(20)	-176.34(18)
C(17)-C(19)-N(2)-C(26)	6.3(3)
C(17)-C(19)-N(3)-C(25)	176.22(19)
O(3)-C(14)-C(15)-C(16)	176.9(2)
C(19)-N(2)-C(20)-C(21)	179.1(2)
C(19)-N(2)-C(20)-C(25)	-0.2(2)
C(19)-N(3)-C(25)-C(20)	0.0(2)
C(19)-N(3)-C(25)-C(24)	-176.7(2)
N(2)-C(19)-N(3)-C(25)	-0.1(2)
N(2)-C(20)-C(21)-C(22)	-178.5(2)
N(2)-C(20)-C(25)-N(3)	0.1(2)
N(2)-C(20)-C(25)-C(24)	177.21(19)
N(3)-C(19)-N(2)-C(20)	0.2(2)
N(3)-C(19)-N(2)-C(26)	-177.1(2)
C(20)-C(21)-C(22)-C(23)	1.1(3)
C(21)-C(20)-C(25)-N(3)	-179.26(19)
C(21)-C(20)-C(25)-C(24)	-2.2(3)
C(21)-C(22)-C(23)-C(24)	-1.5(4)
C(22)-C(23)-C(24)-C(25)	0.1(3)
C(23)-C(24)-C(25)-N(3)	178.1(2)
C(23)-C(24)-C(25)-C(20)	1.7(3)
C(25)-C(20)-C(21)-C(22)	0.7(3)
C(26)-N(2)-C(20)-C(21)	-3.5(4)
C(26)-N(2)-C(20)-C(25)	177.20(19)

S4. ^{1}H and ^{13}C NMR spectra

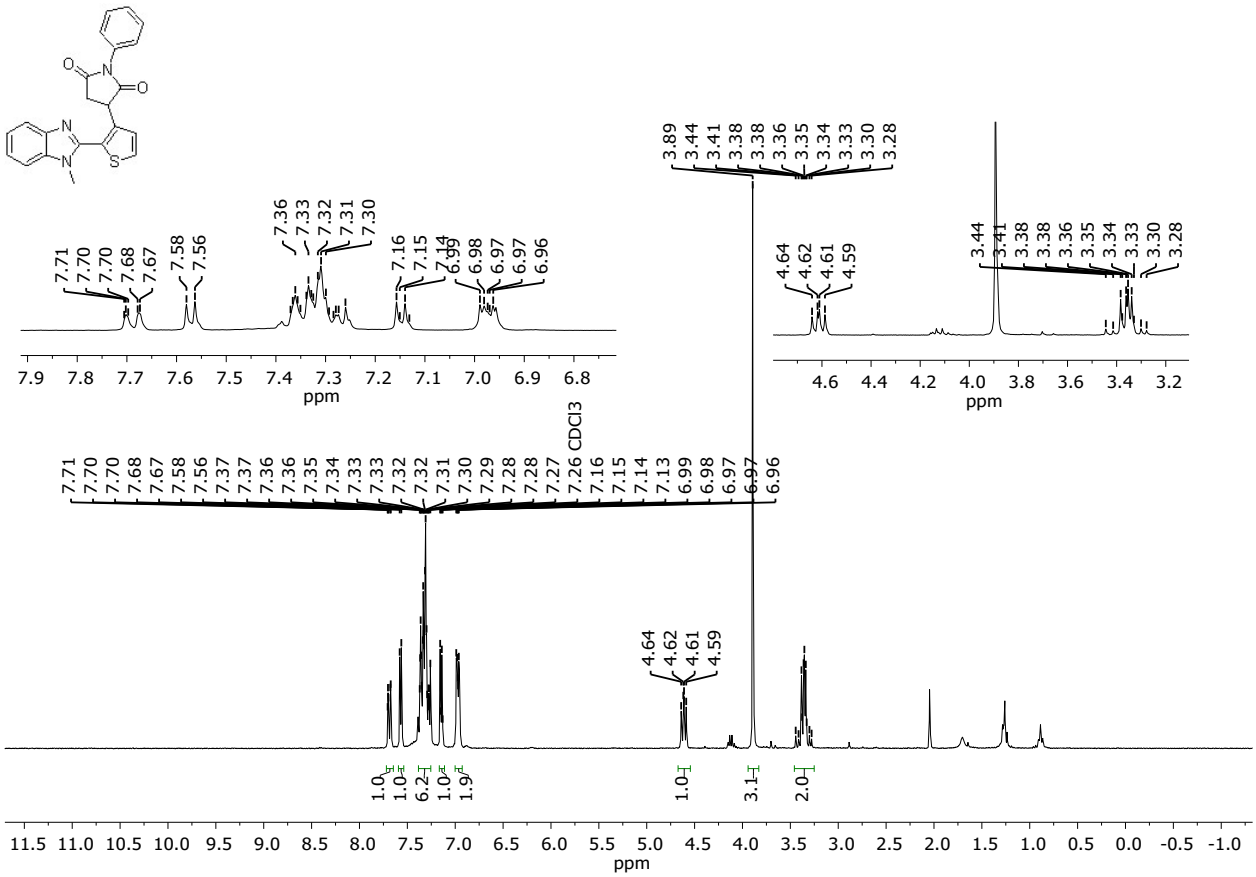


Figure S5. ^{1}H NMR spectrum of compound **3a** (300 MHz, $CDCl_3$).

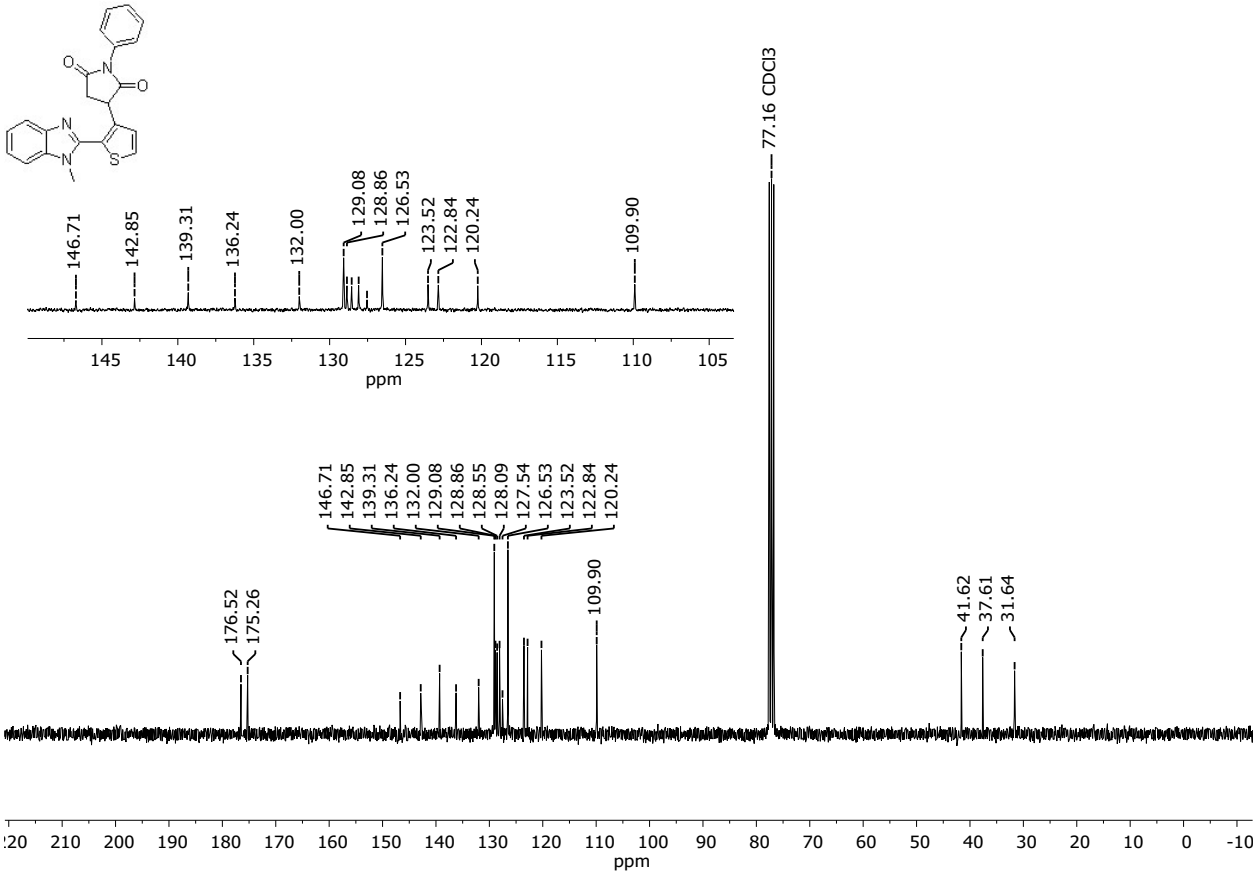


Figure S6. ^{13}C NMR spectrum of compound **3a** (75 MHz, $CDCl_3$).

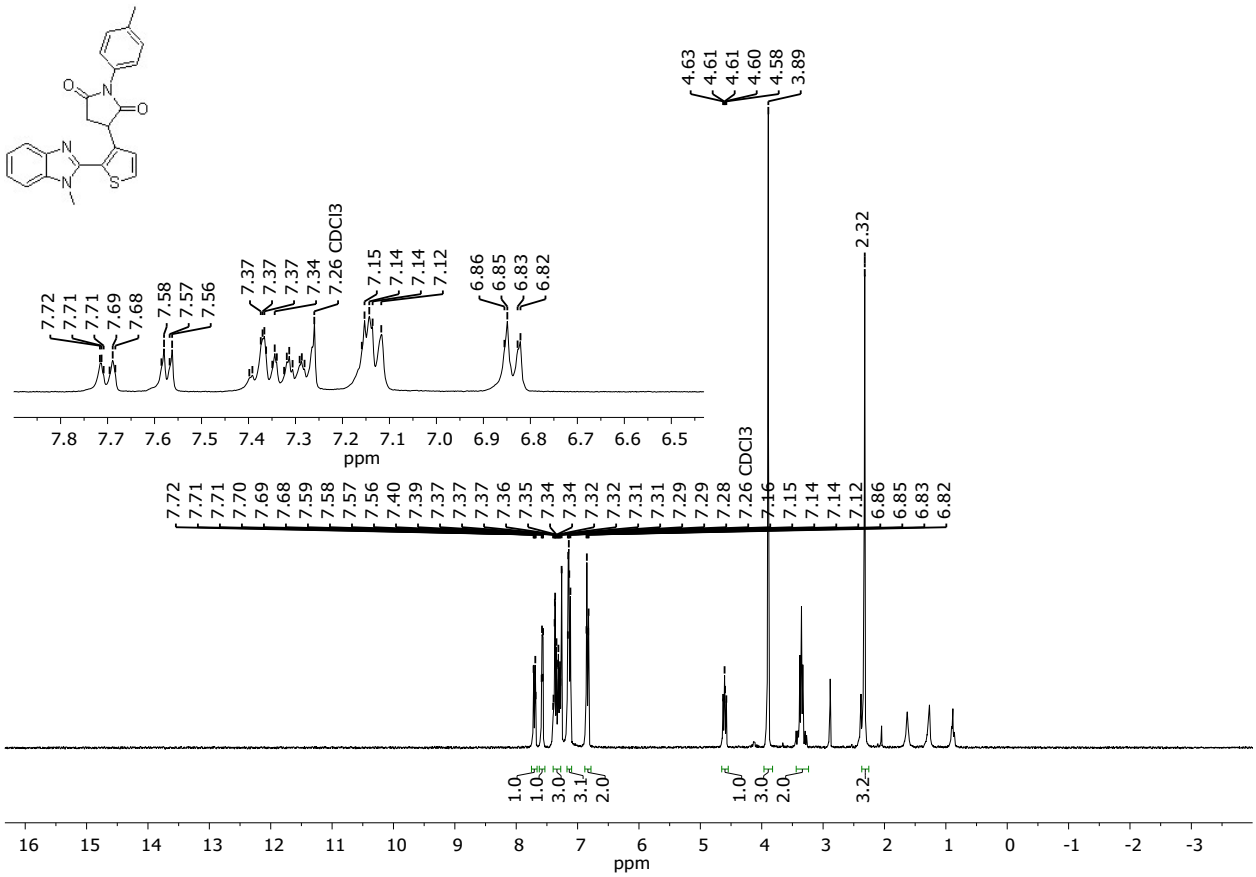


Figure S7. ^{1}H NMR spectrum of compound **3b** (300 MHz, $CDCl_3$).

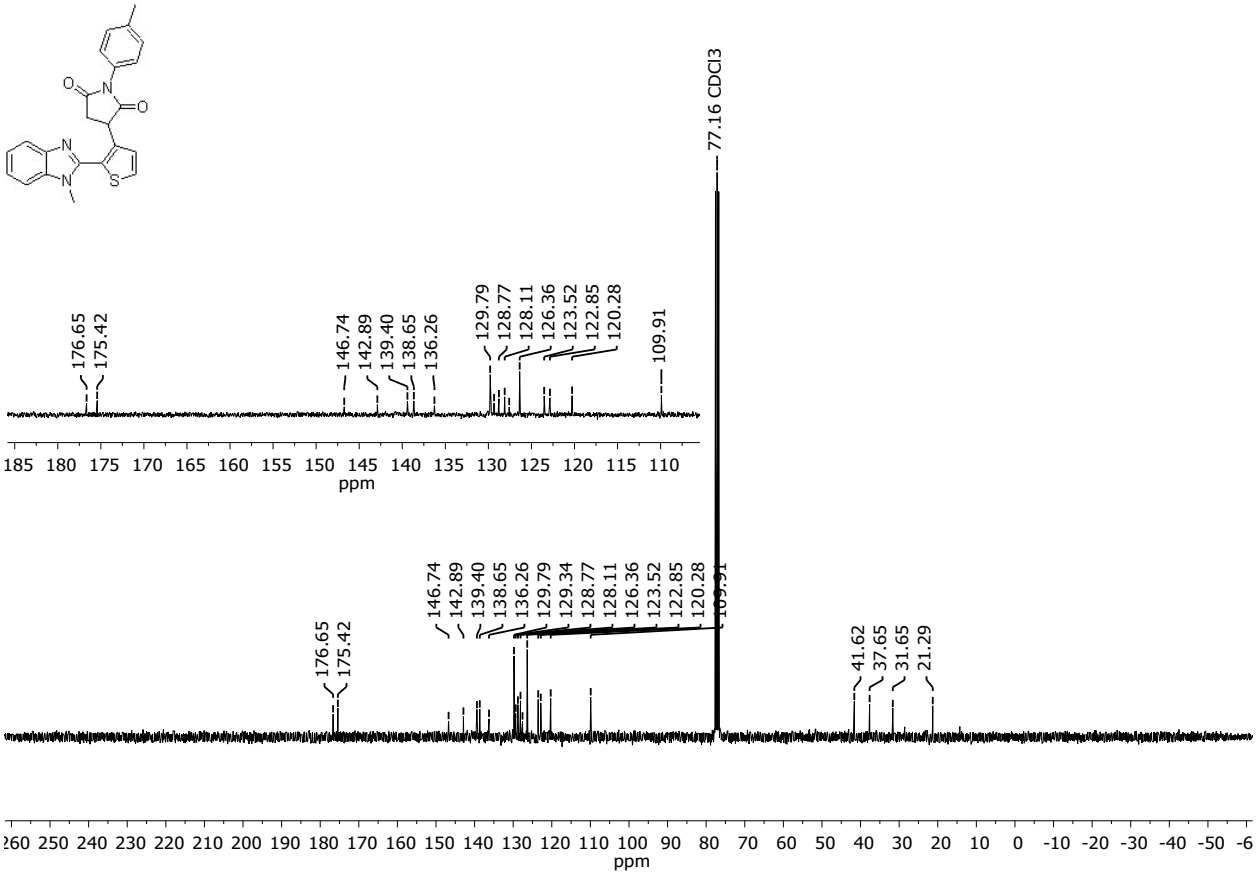


Figure S8. ^{13}C NMR spectrum of compound **3b** (75 MHz, $CDCl_3$).

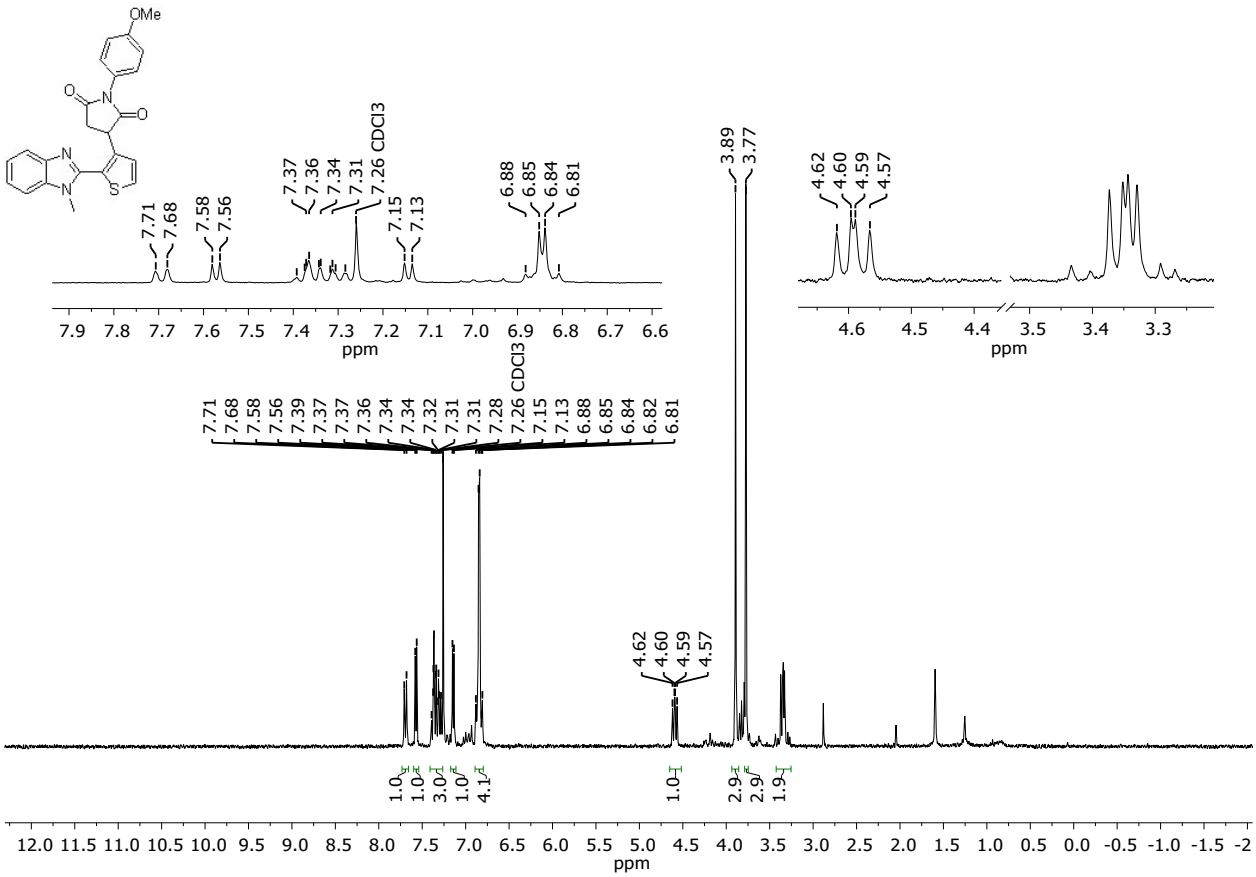


Figure S9. ^{1}H NMR spectrum of compound **3c** (300 MHz, $CDCl_3$).

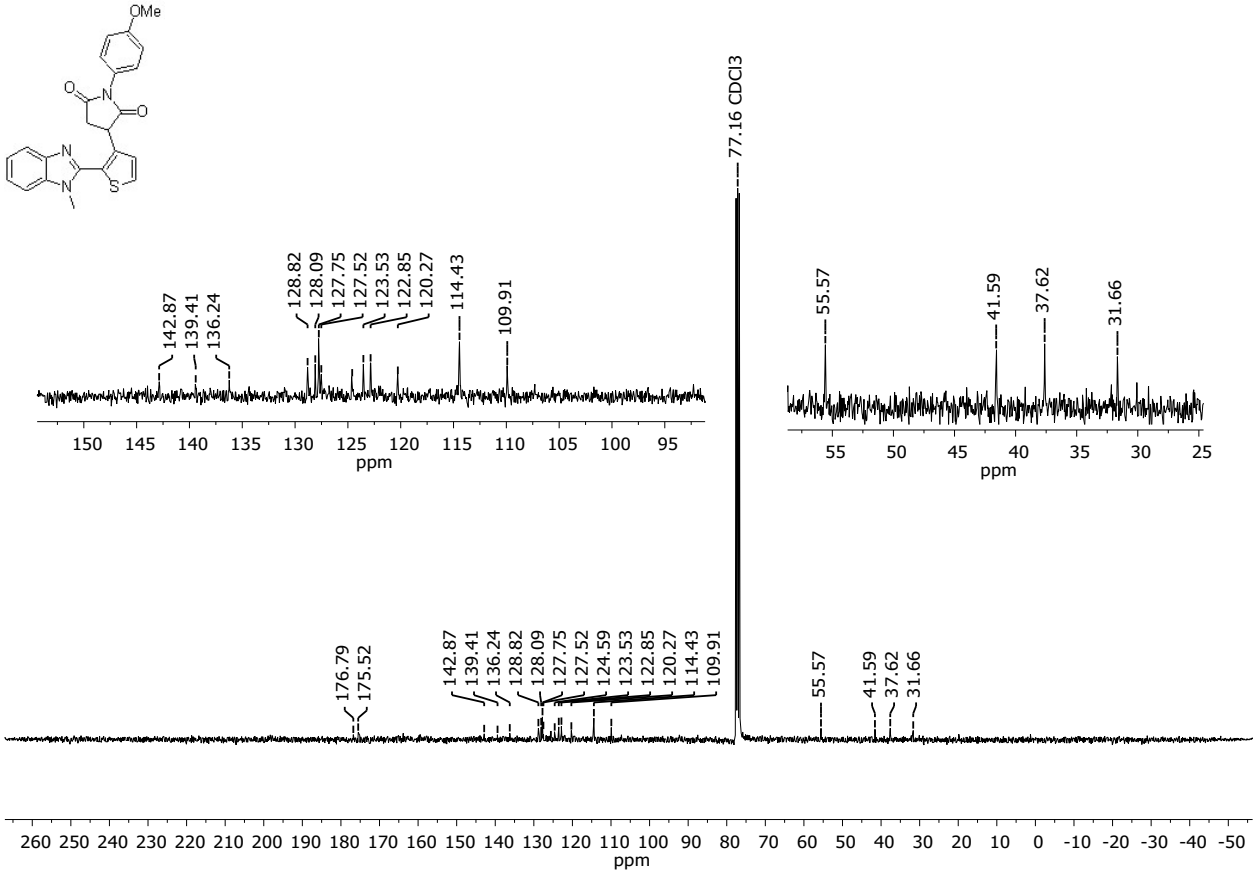


Figure S10. ^{13}C NMR spectrum of compound **3c** (75 MHz, $CDCl_3$).

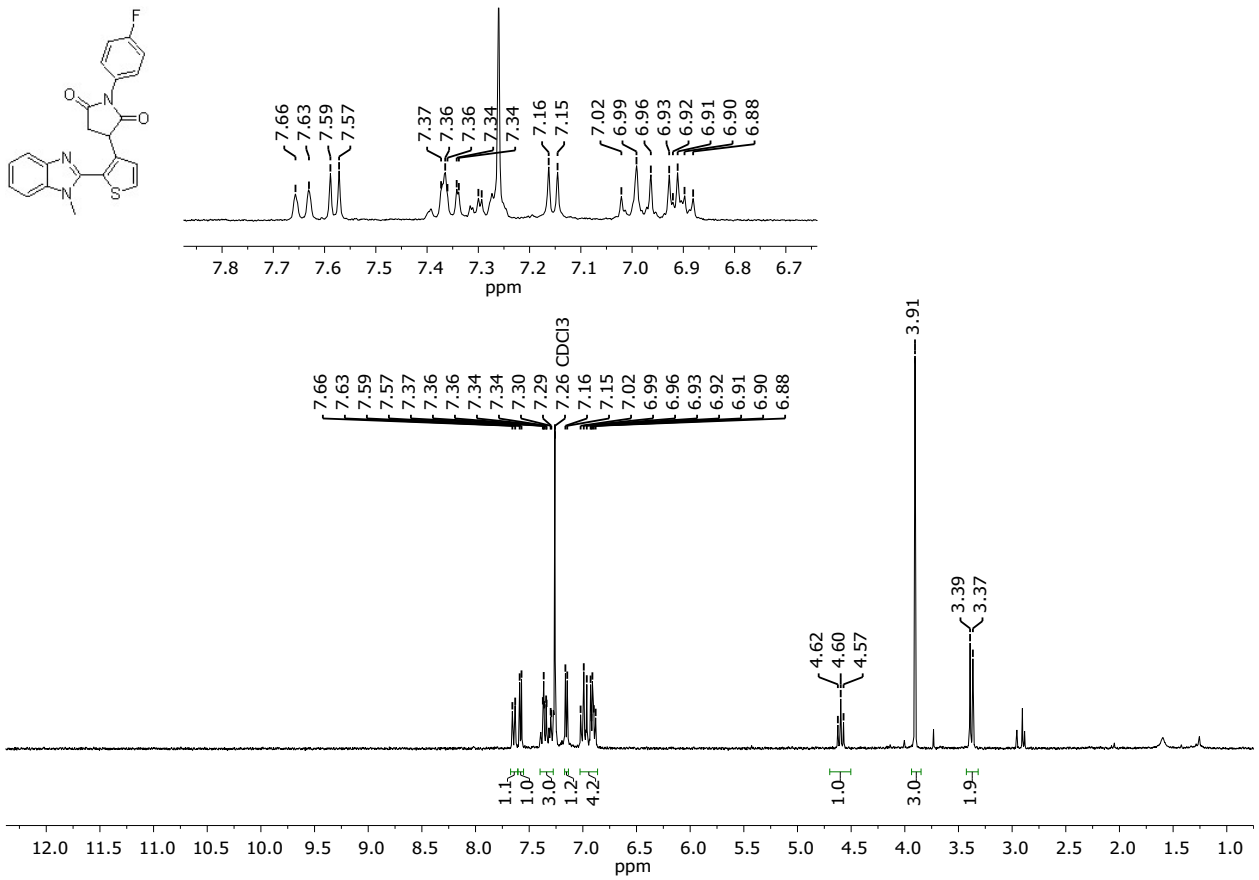


Figure S11. ^{1}H NMR spectrum of compound **3d** (300 MHz, $CDCl_3$).

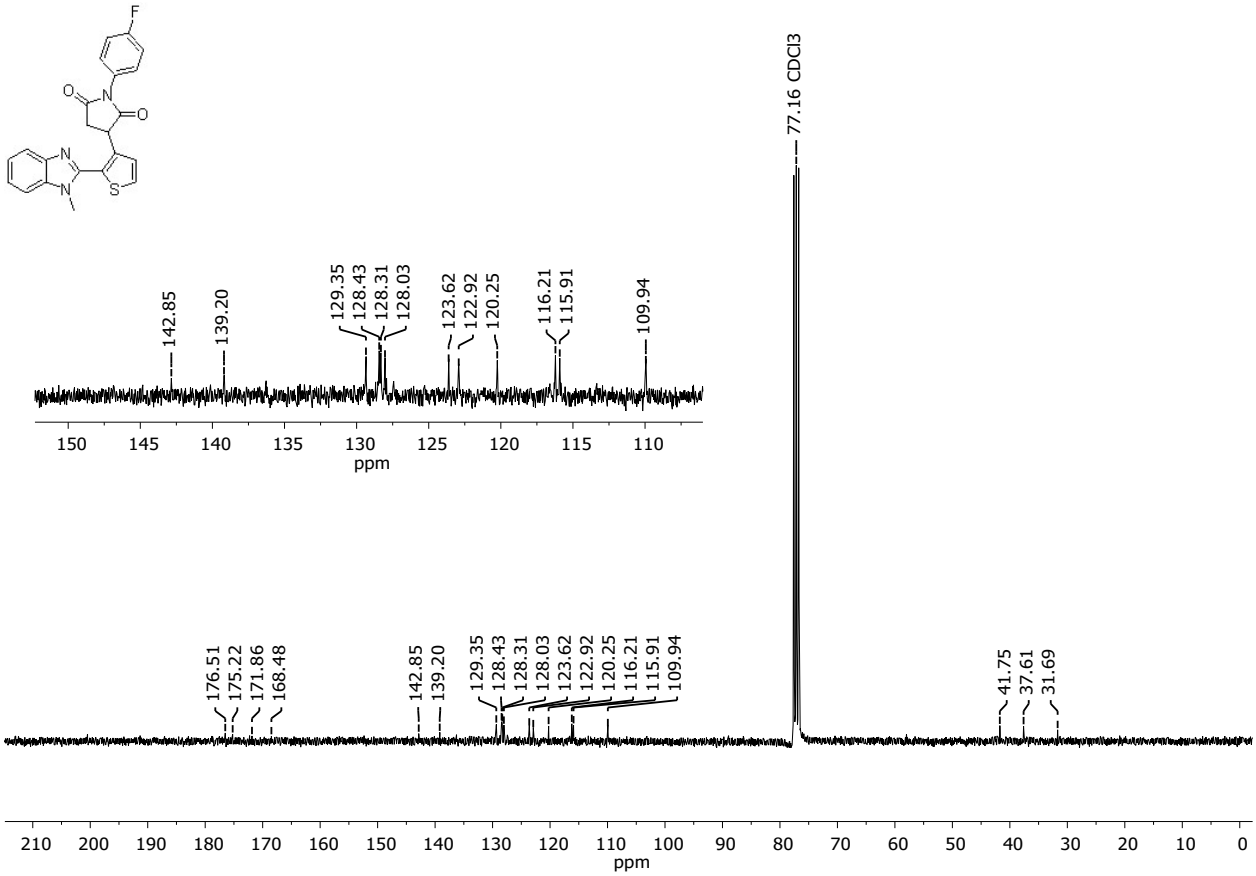


Figure S12. ^{13}C NMR spectrum of compound **3d** (75 MHz, $CDCl_3$).

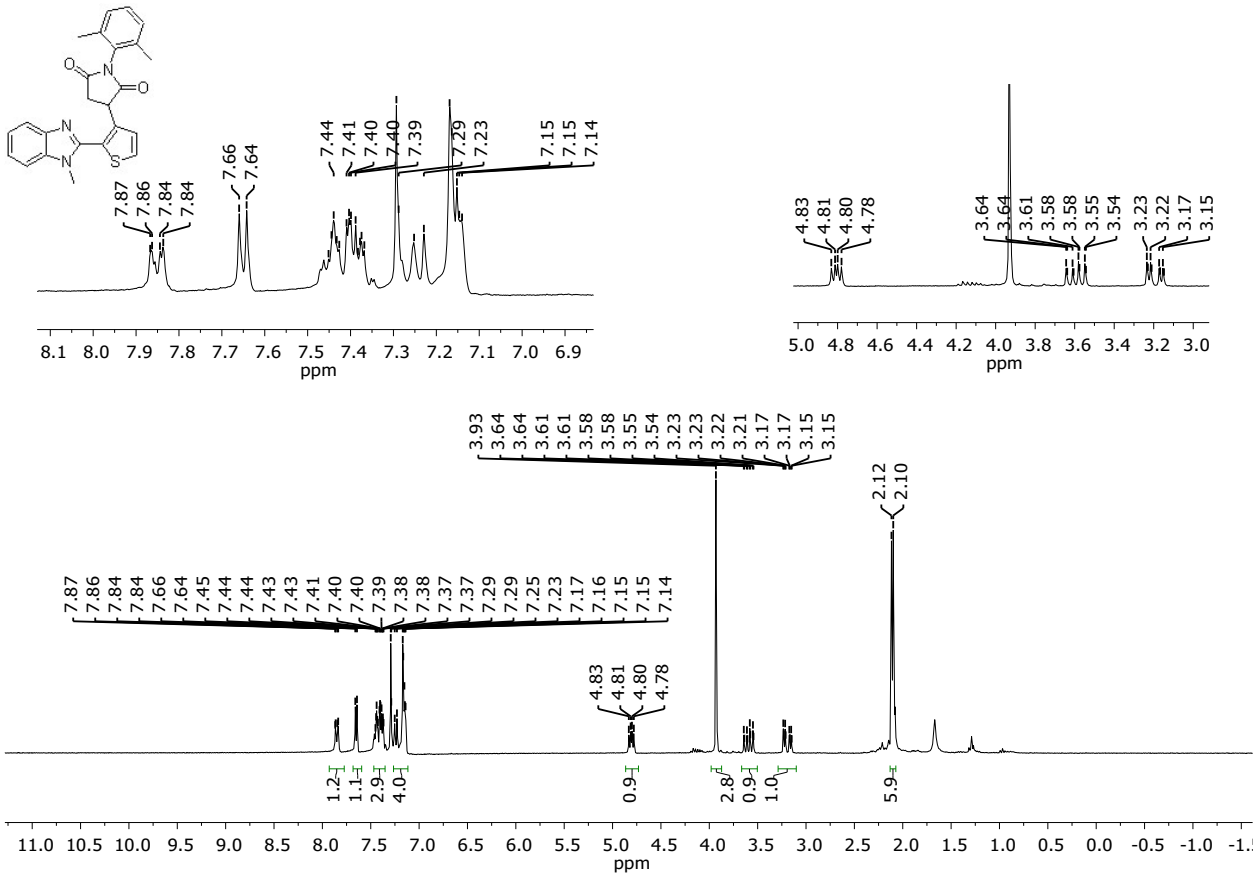


Figure S13. ^{1}H NMR spectrum of compound 3**e** (300 MHz, $CDCl_3$).

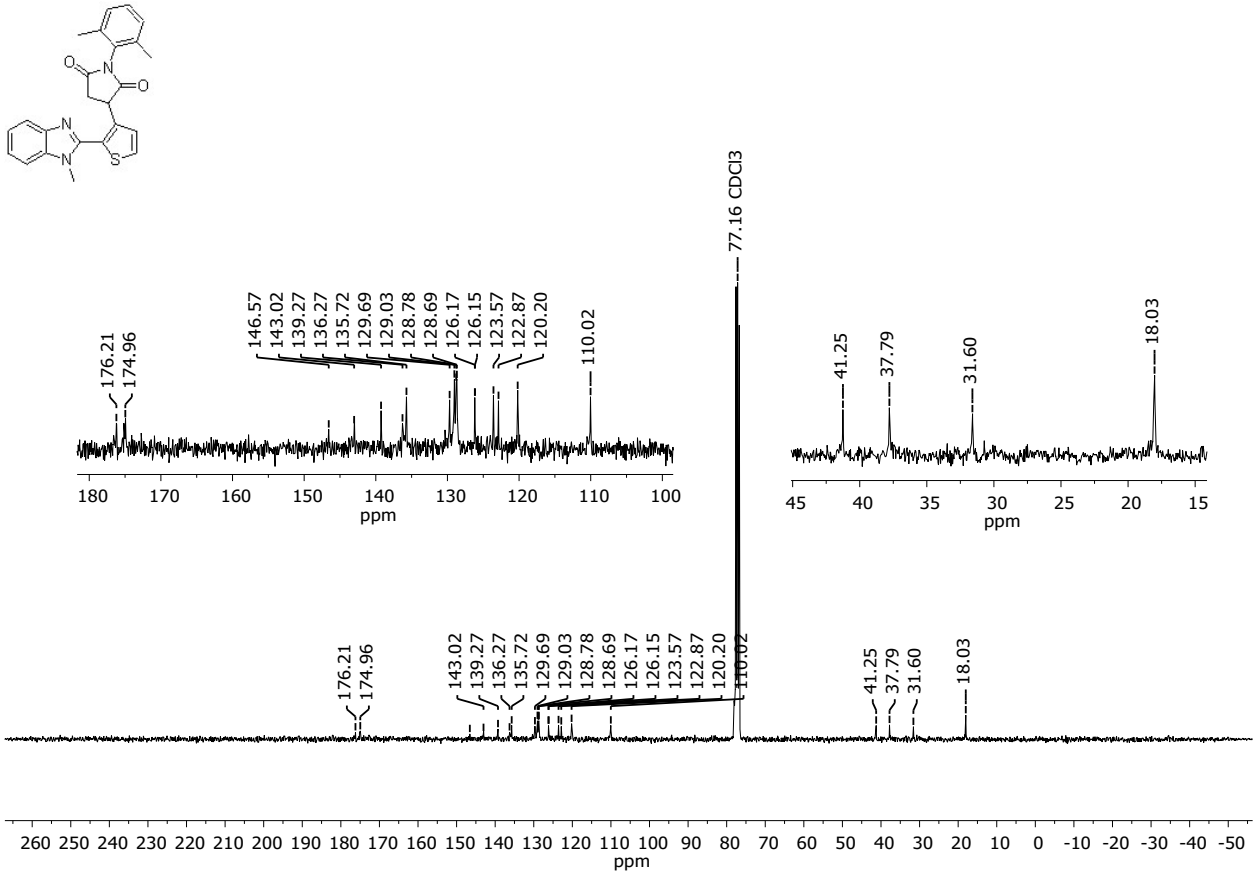


Figure S14. ^{13}C NMR spectrum of compound **3e** (75 MHz, $CDCl_3$).

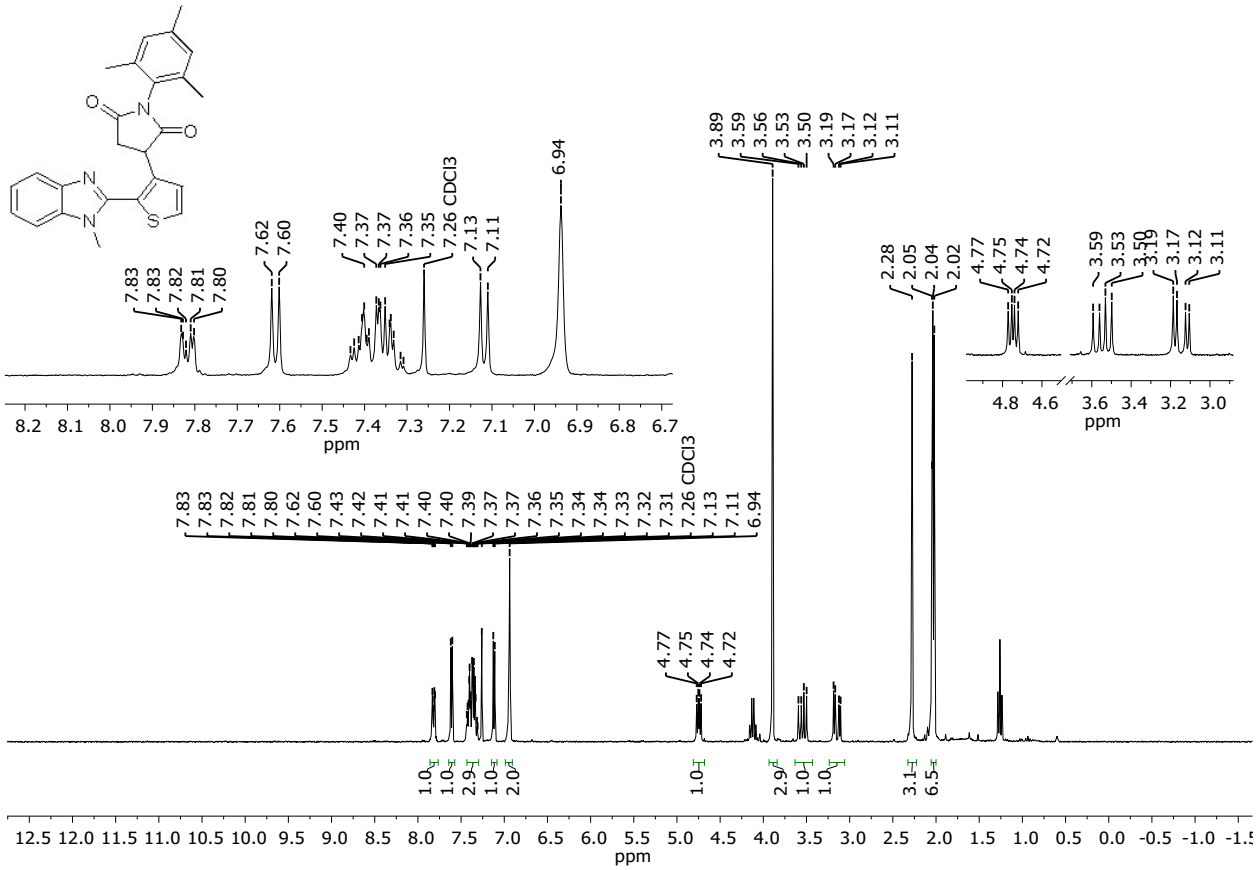


Figure S15. ^{1}H NMR spectrum of compound **3f** (300 MHz, $CDCl_3$).

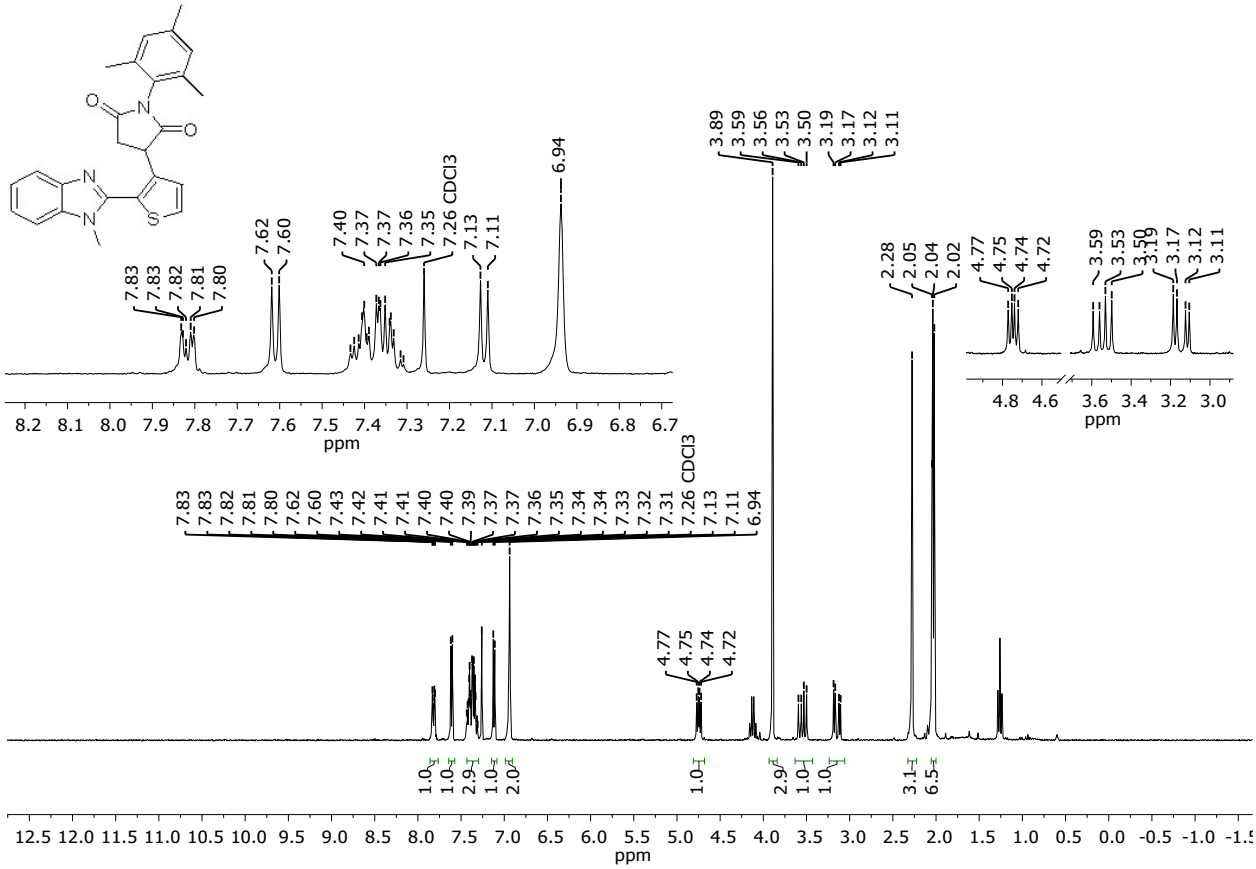


Figure S16. ^{13}C NMR spectrum of compound **3f** (75 MHz, $CDCl_3$).

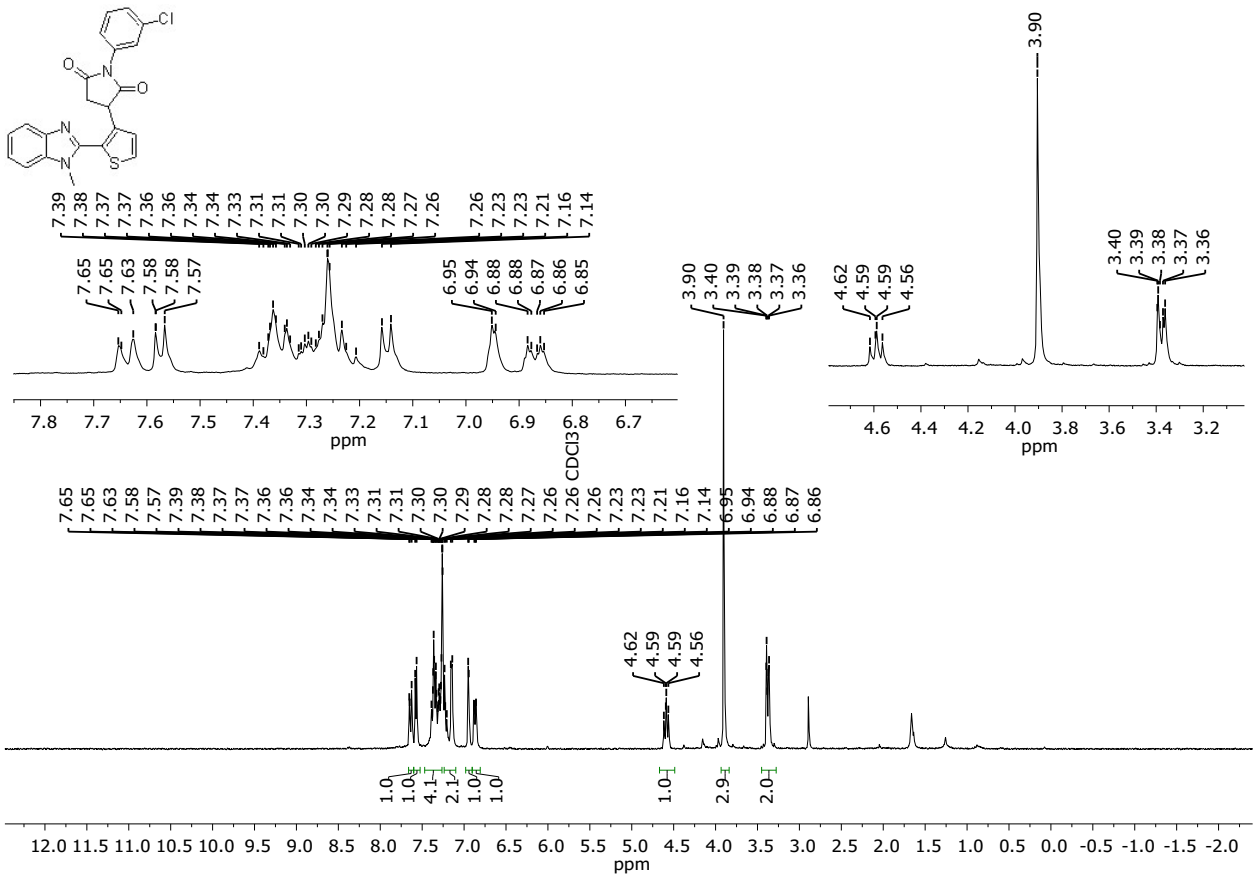


Figure S17. ^{1}H NMR spectrum of compound **3g** (300 MHz, $CDCl_3$).

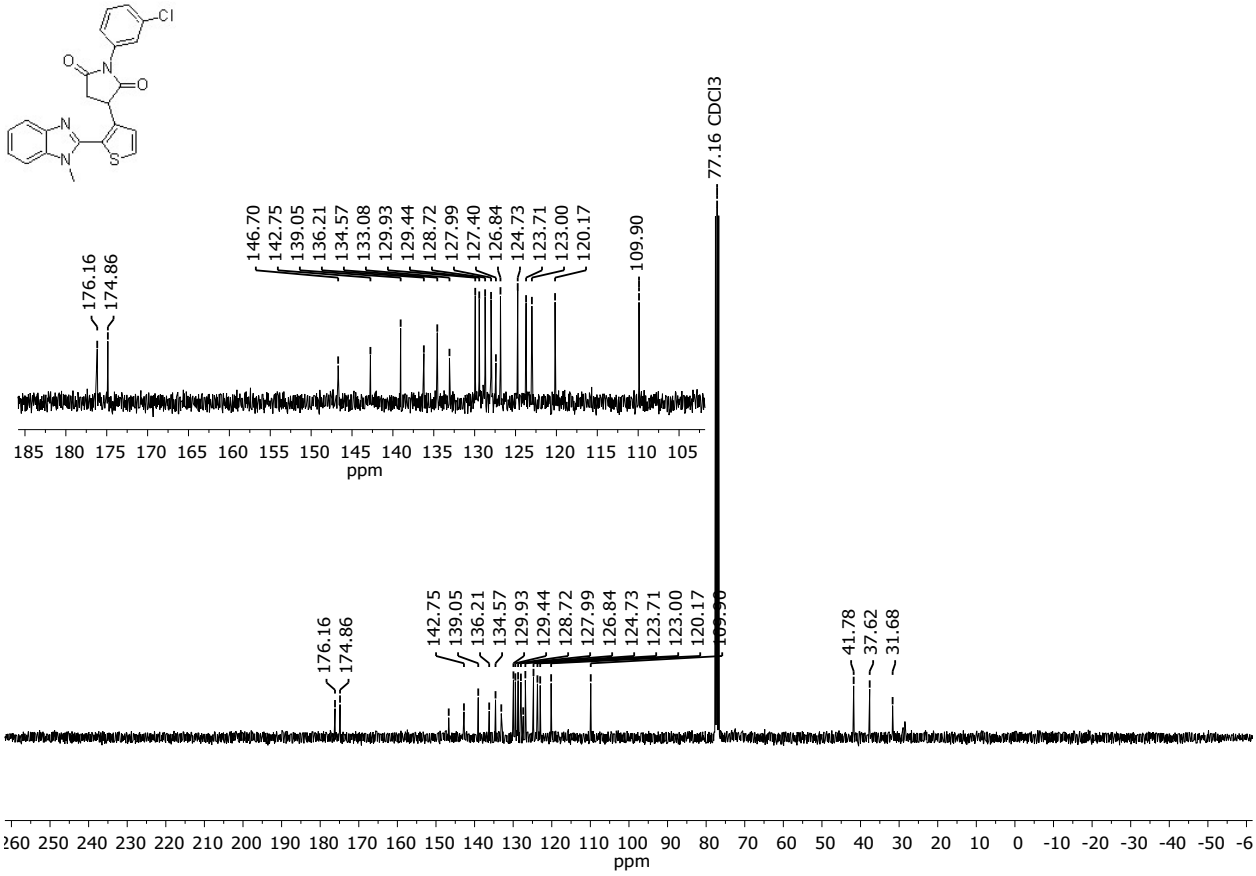


Figure S18. ^{13}C NMR spectrum of compound **3g** (75 MHz, $CDCl_3$).

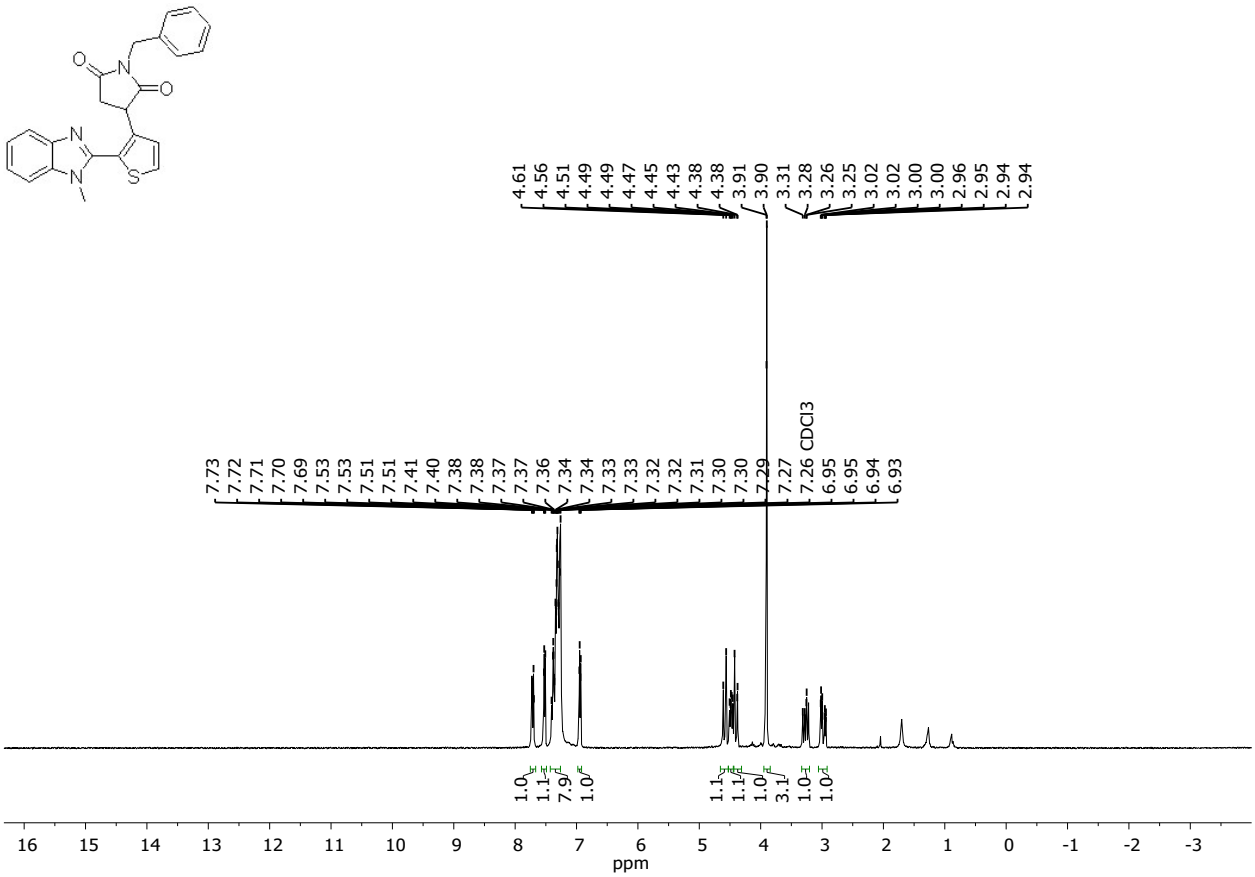


Figure S19. ^{1}H NMR spectrum of compound **3h** (300 MHz, $CDCl_3$).

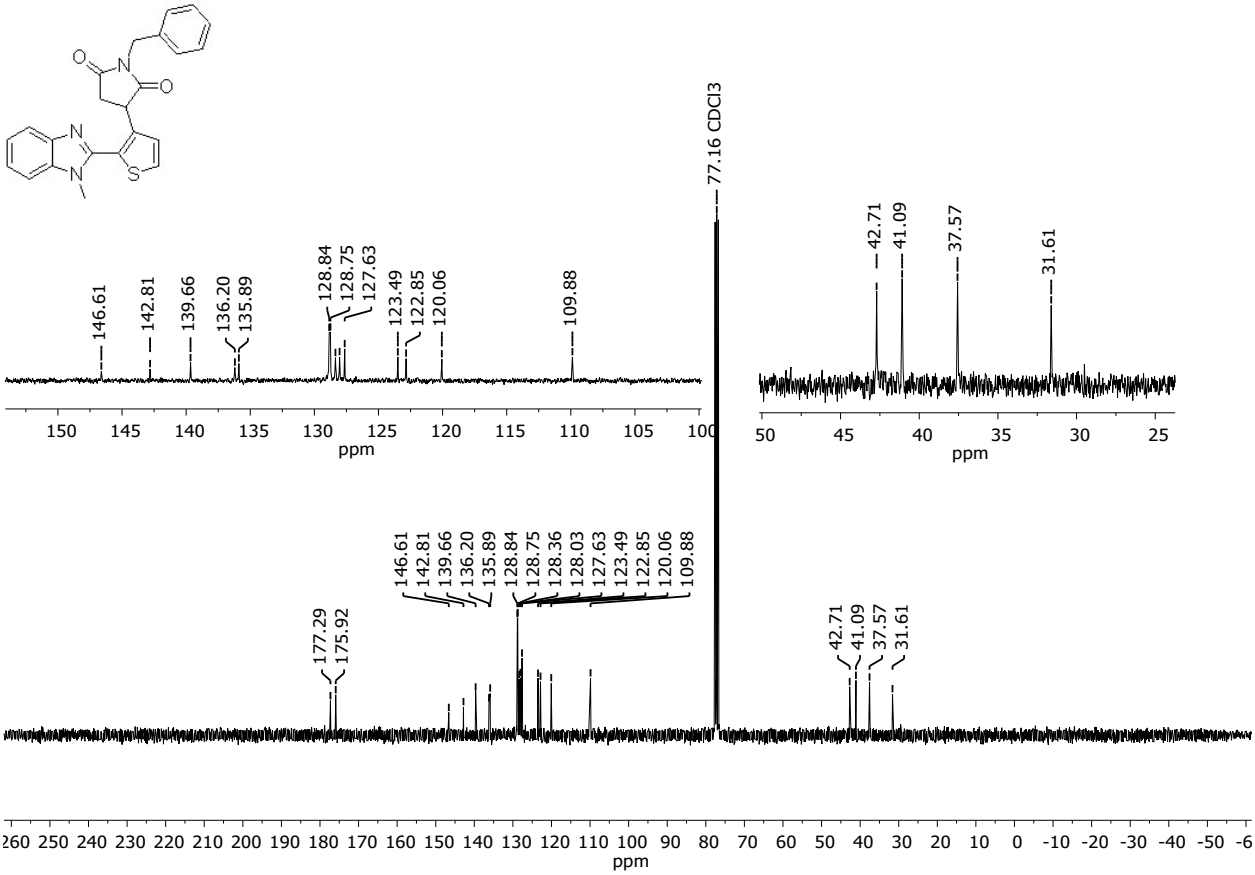


Figure S20. ^{13}C NMR spectrum of compound **3h** (75 MHz, $CDCl_3$).

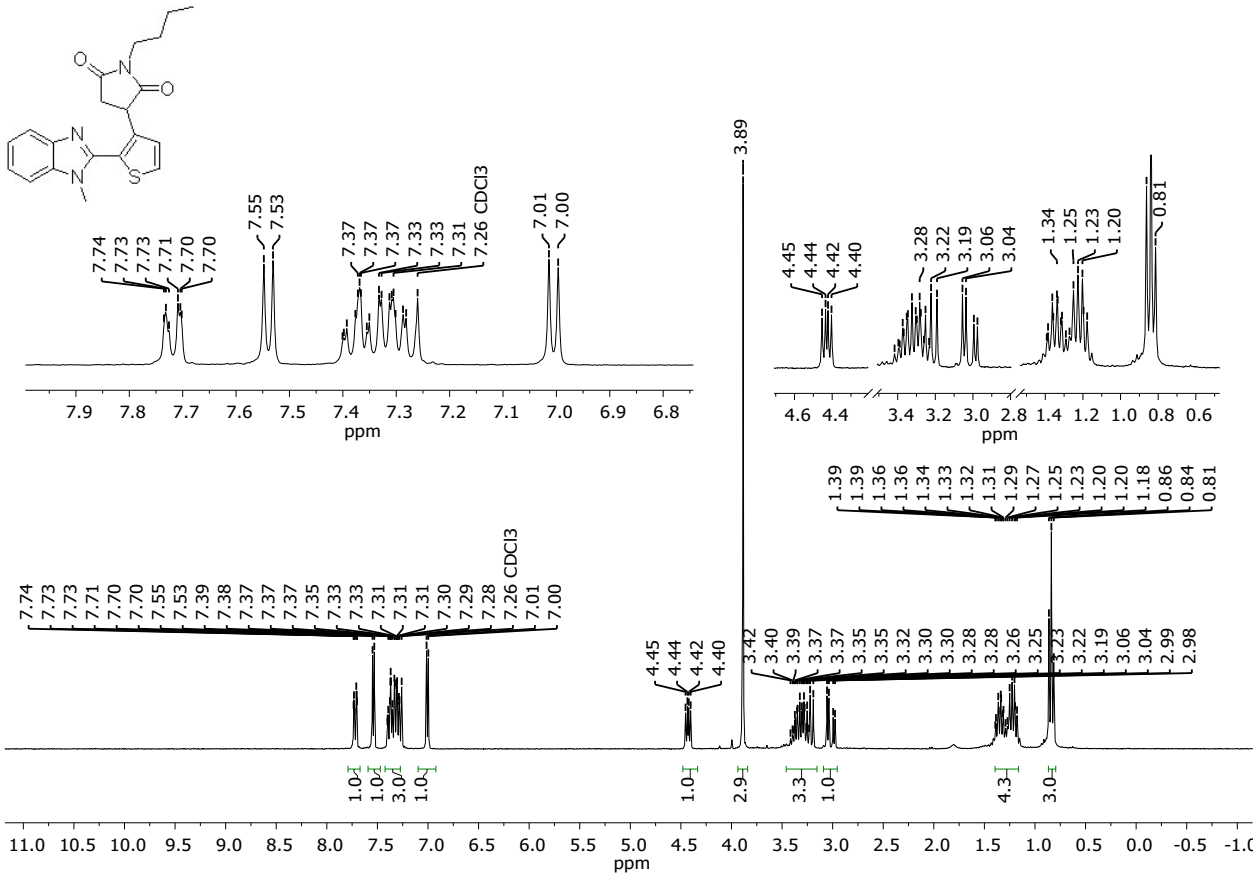


Figure S21. ^{1}H NMR spectrum of compound **3i** (300 MHz, $CDCl_3$).

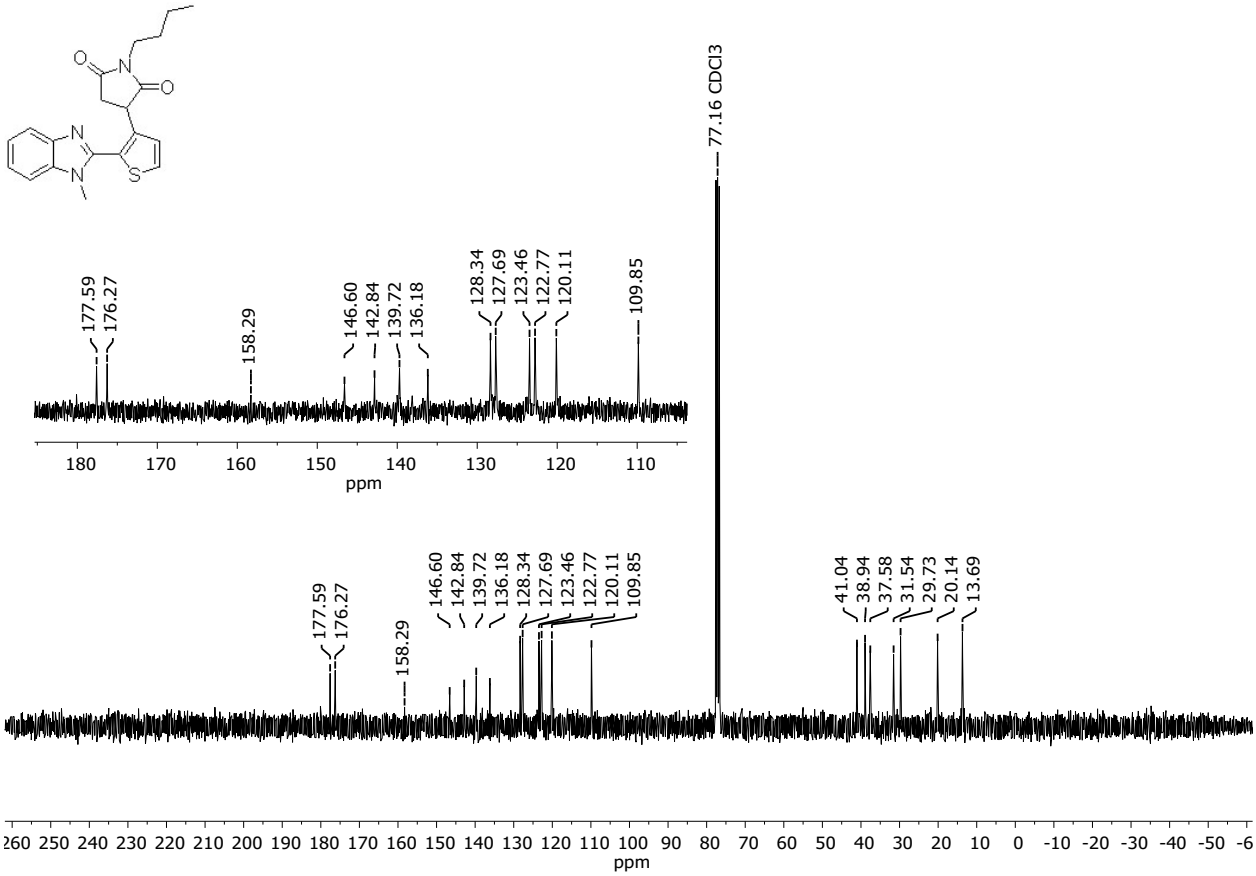


Figure S22. ^{13}C NMR spectrum of compound **3i** (75 MHz, $CDCl_3$).

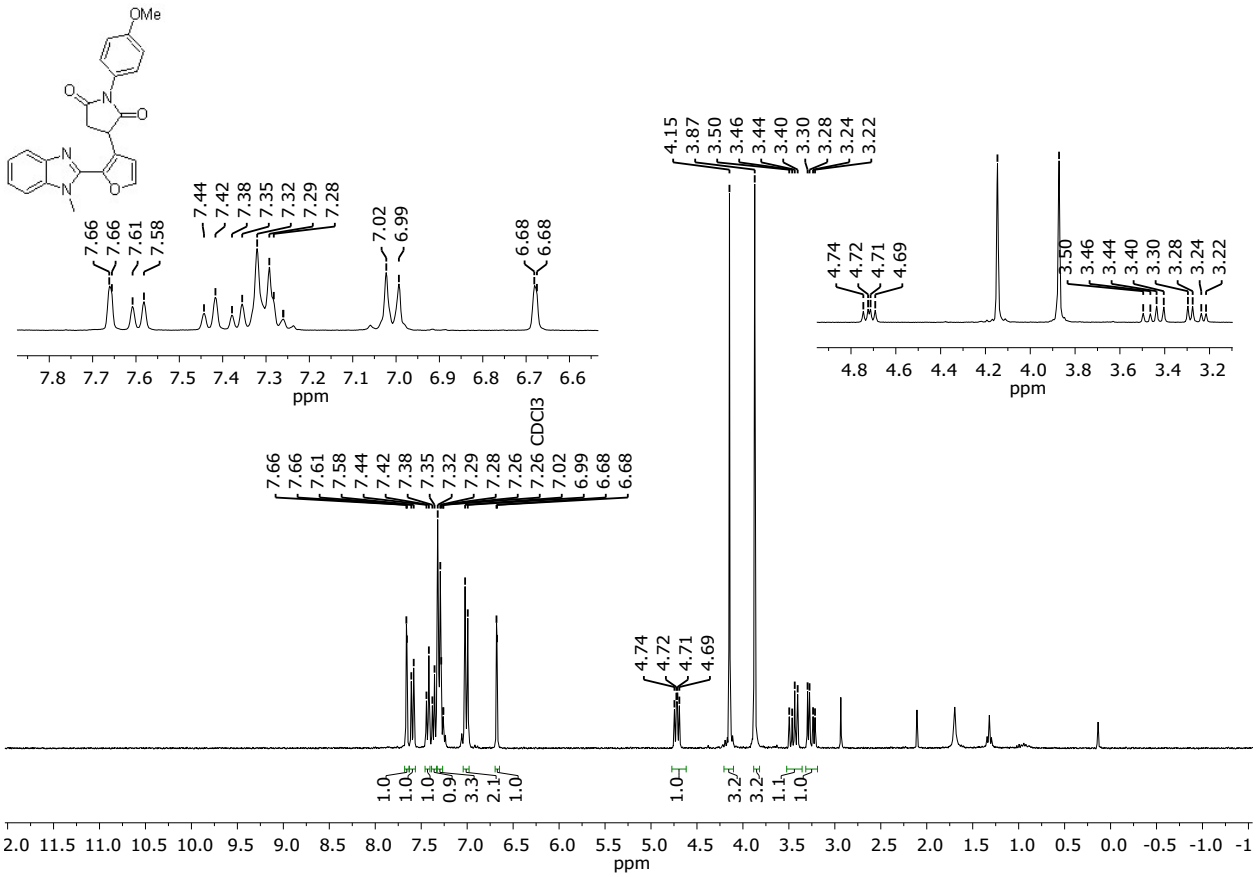


Figure S23. ^{1}H NMR spectrum of compound **3j** (300 MHz, $CDCl_3$).

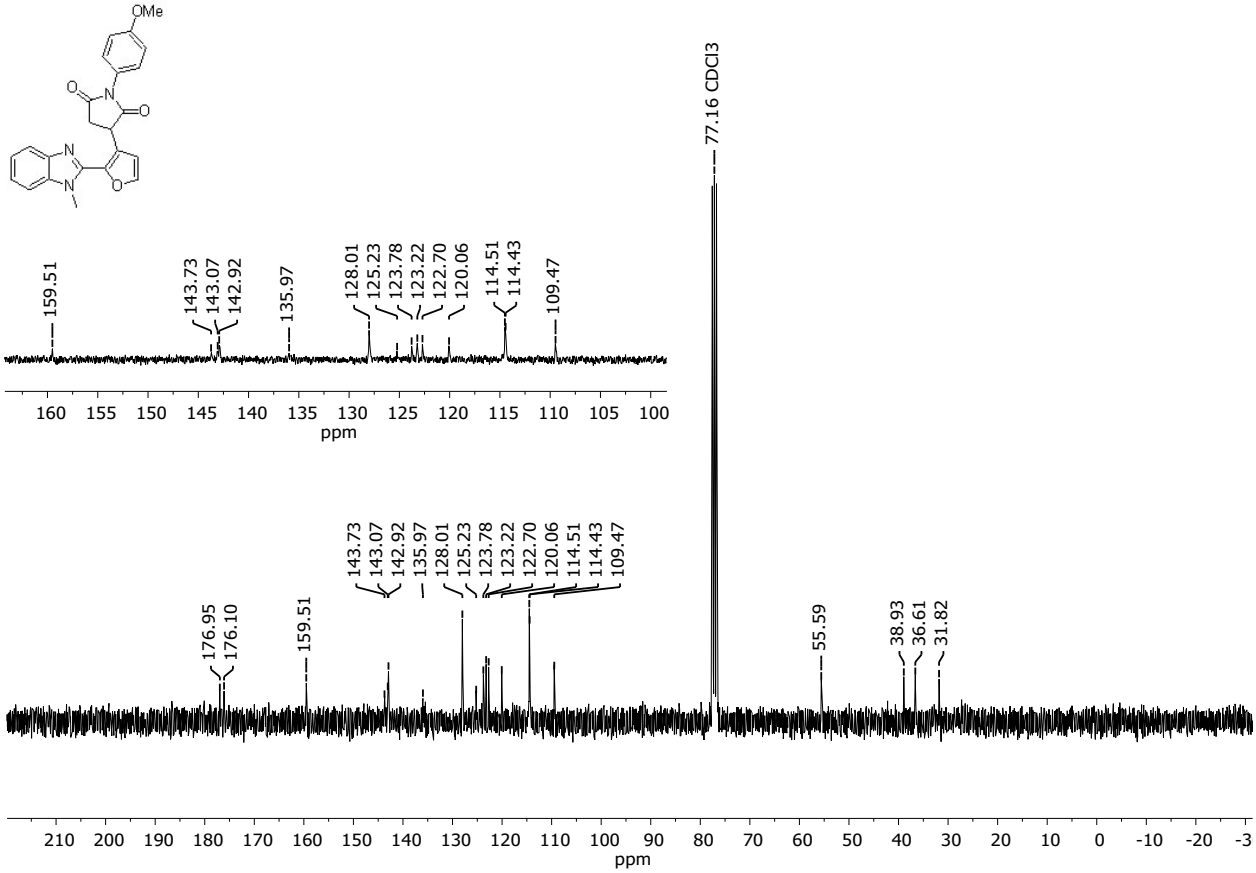


Figure S24. ^{13}C NMR spectrum of compound **3j** (75 MHz, $CDCl_3$).

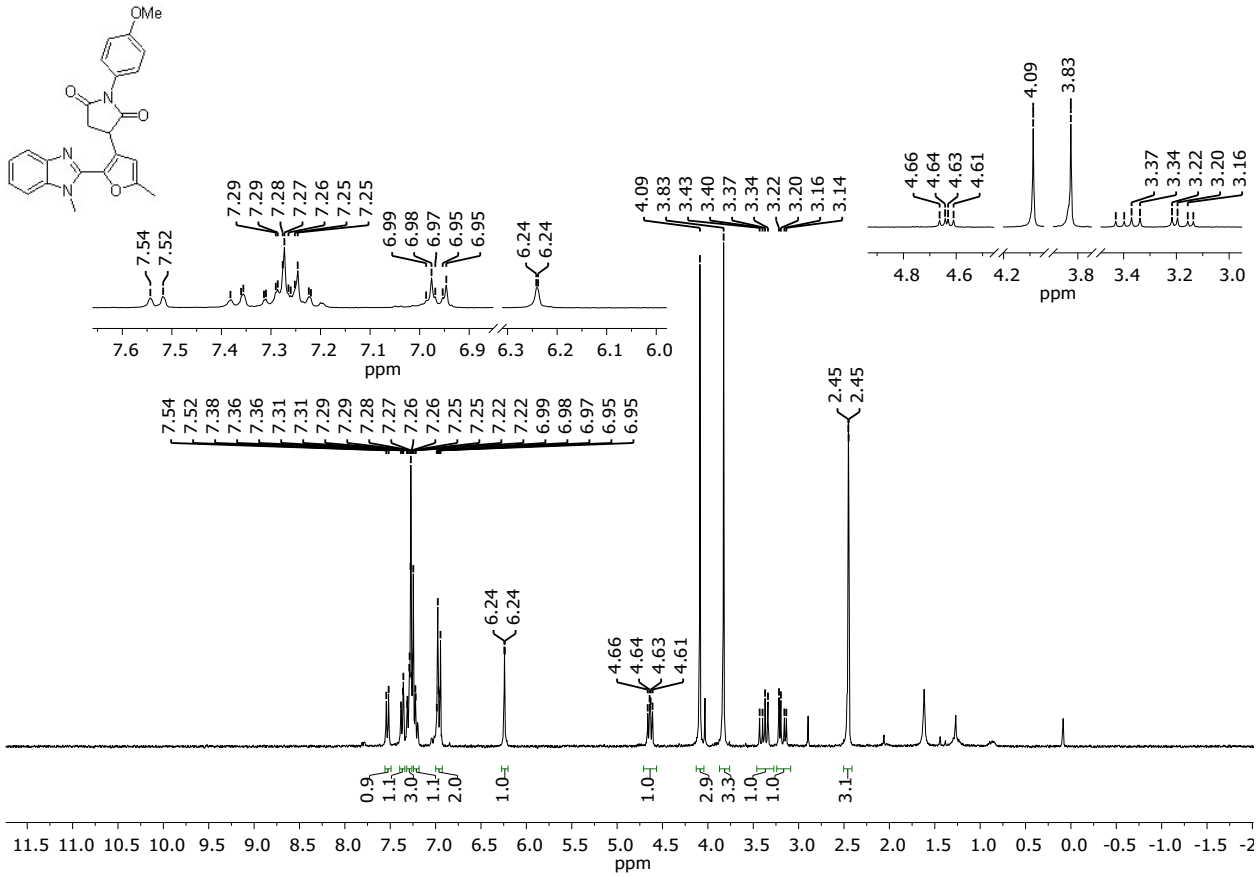


Figure S25. ^{1}H NMR spectrum of compound **3k** (300 MHz, $CDCl_3$).

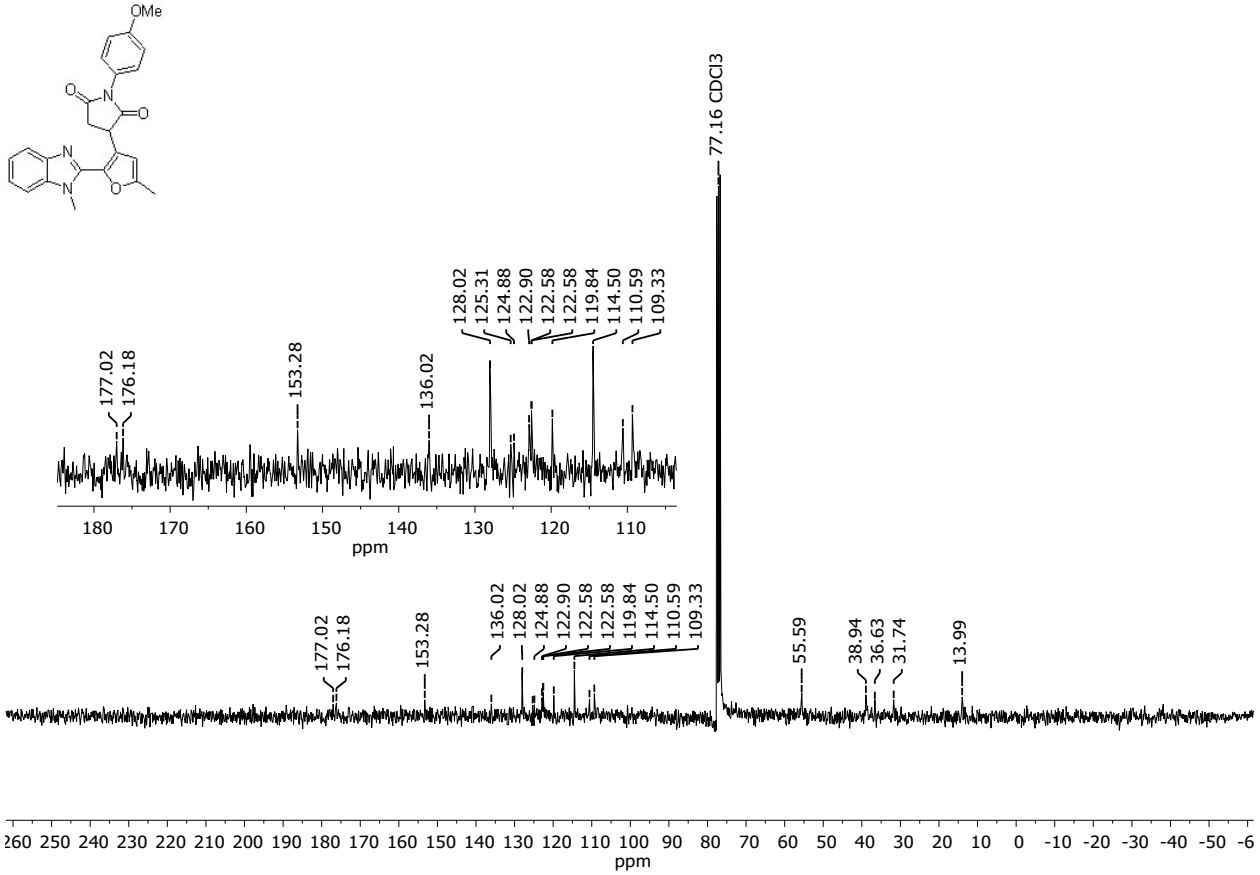


Figure S26. ^{13}C NMR spectrum of compound **3k** (75 MHz, $CDCl_3$).

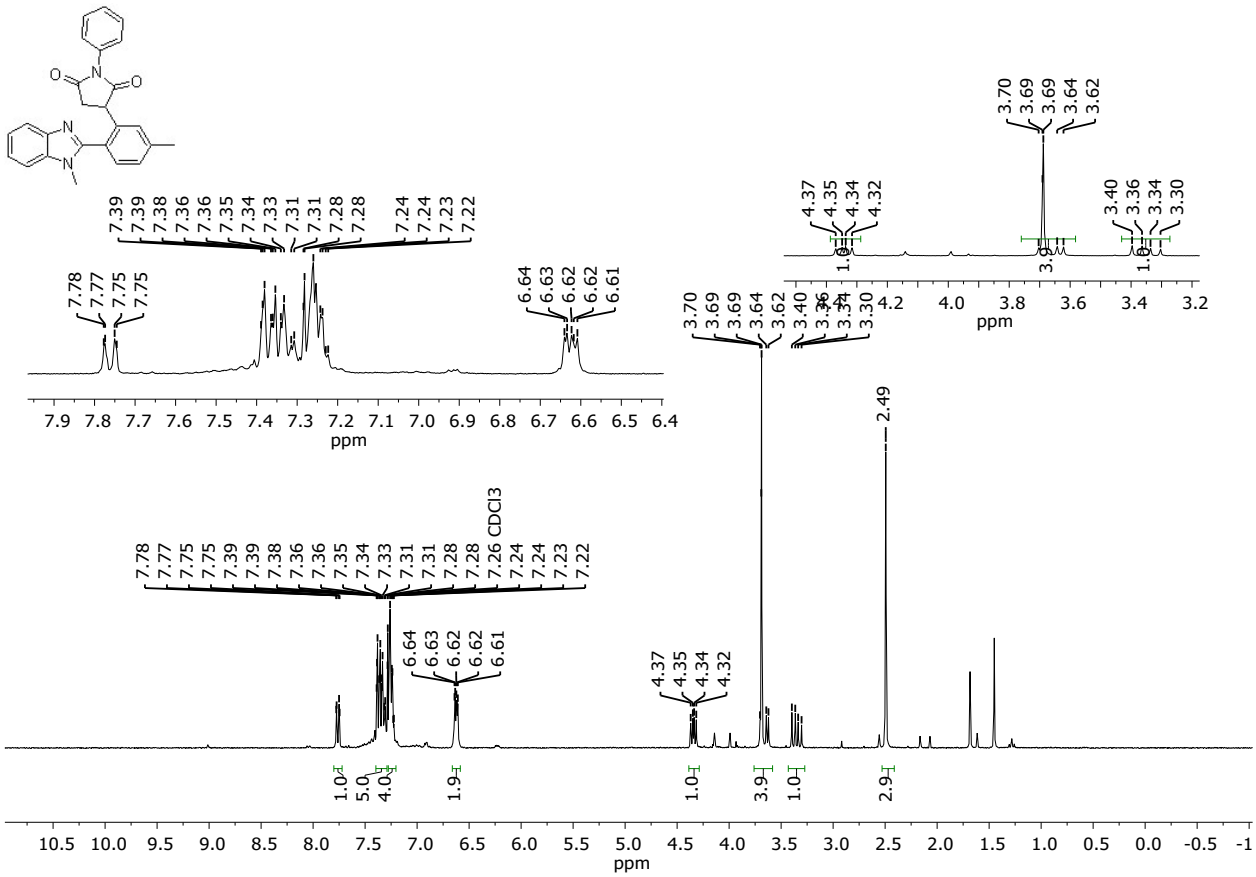


Figure S27. ^{1}H NMR spectrum of compound **3l** (300 MHz, $CDCl_3$).

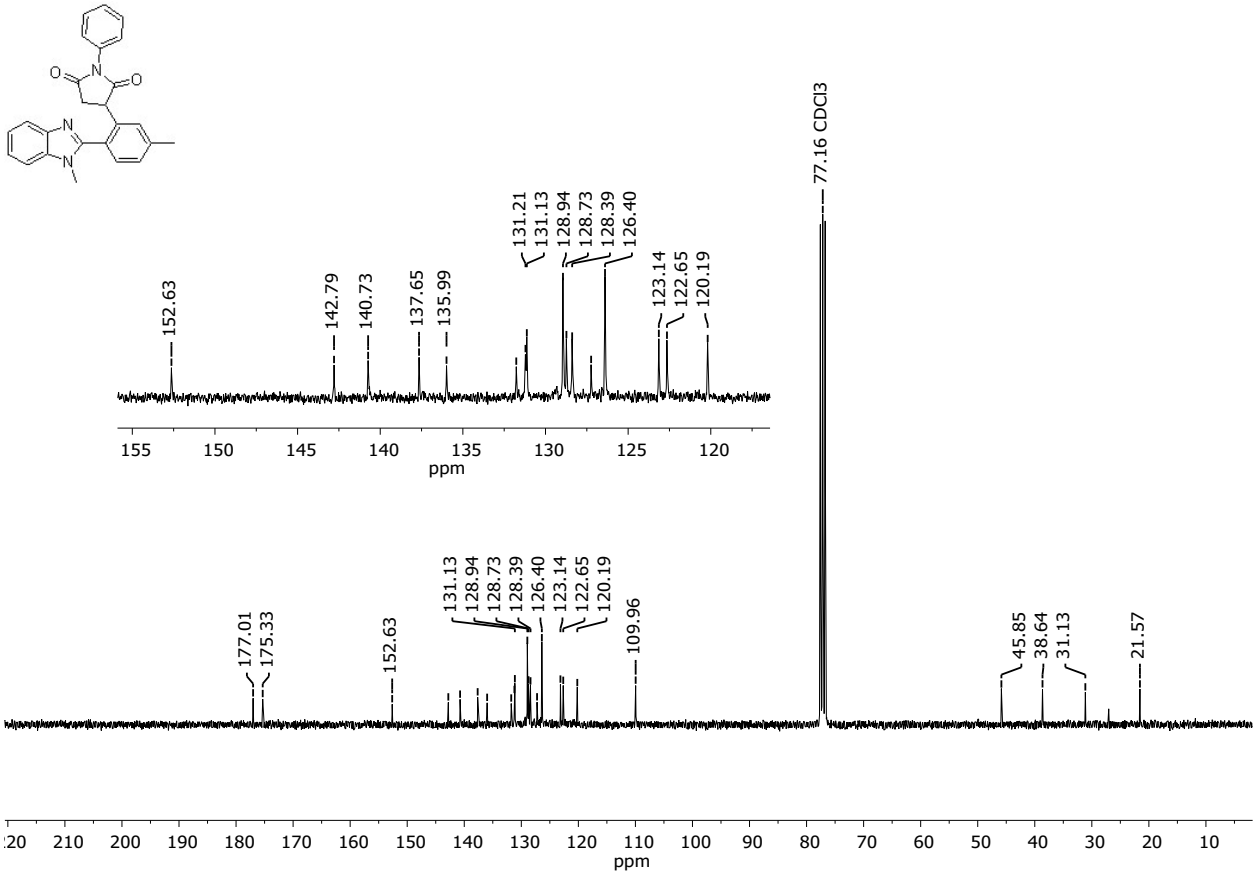


Figure S28. ^{13}C NMR spectrum of compound **3l** (75 MHz, $CDCl_3$).

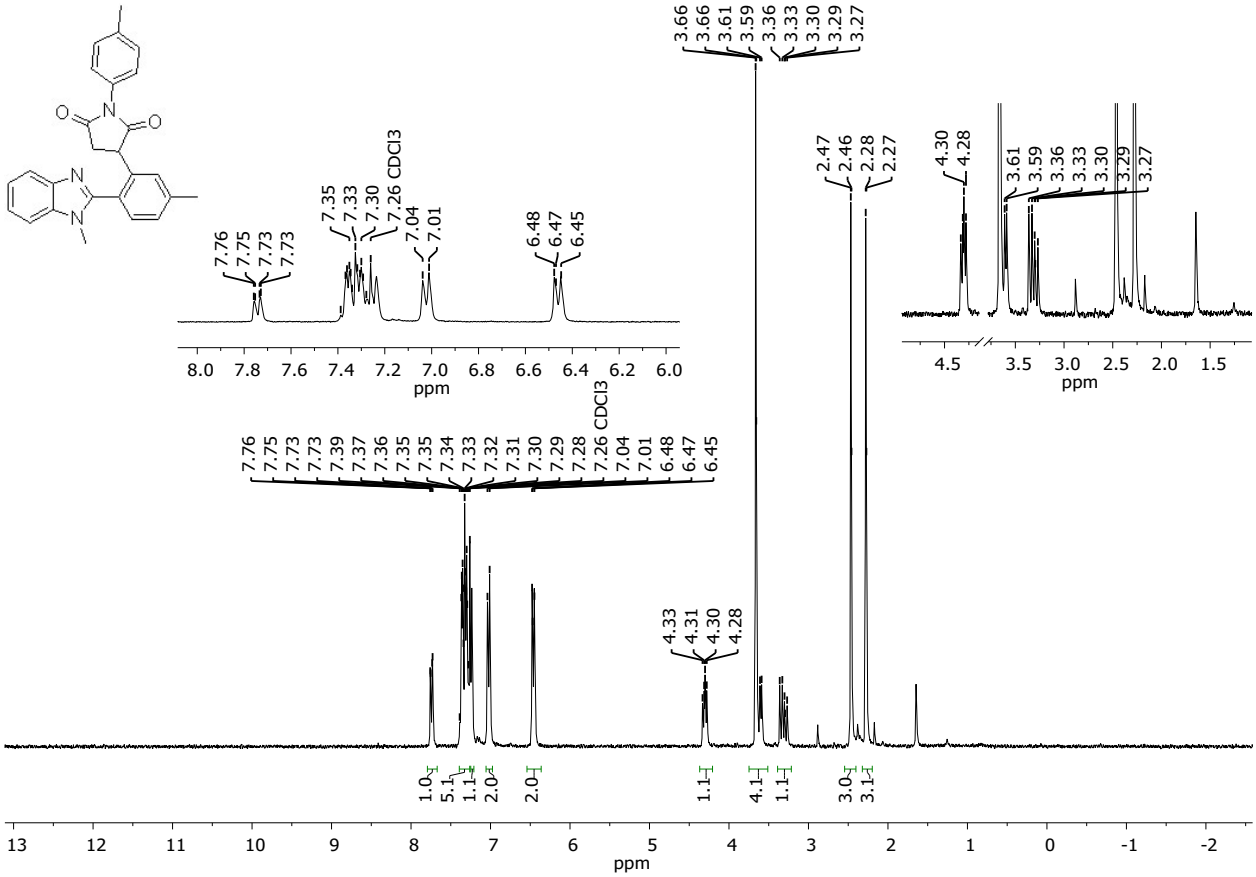


Figure S29. ^{1}H NMR spectrum of compound **3m** (300 MHz, $CDCl_3$).

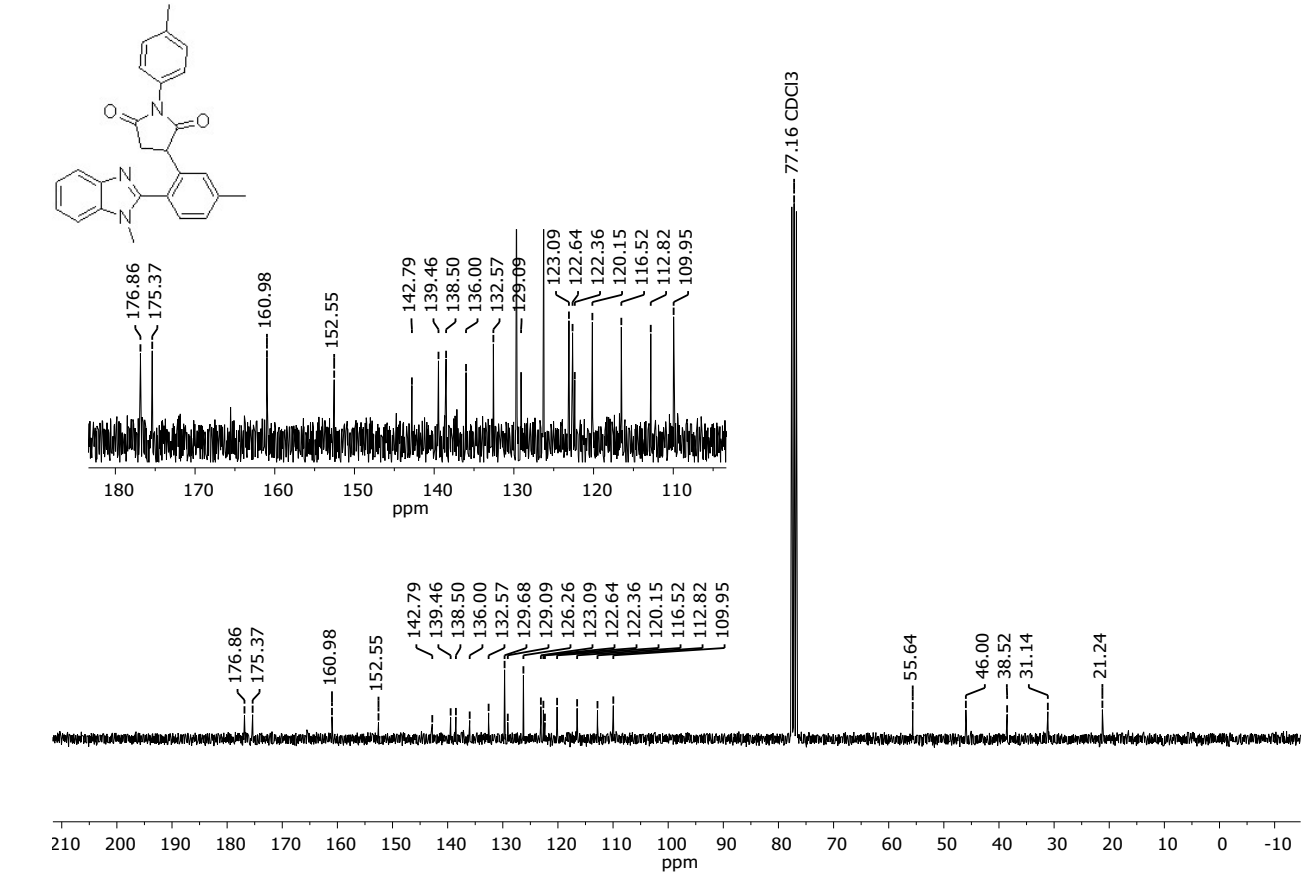


Figure S30. ^{13}C NMR spectrum of compound **3m** (75 MHz, $CDCl_3$).

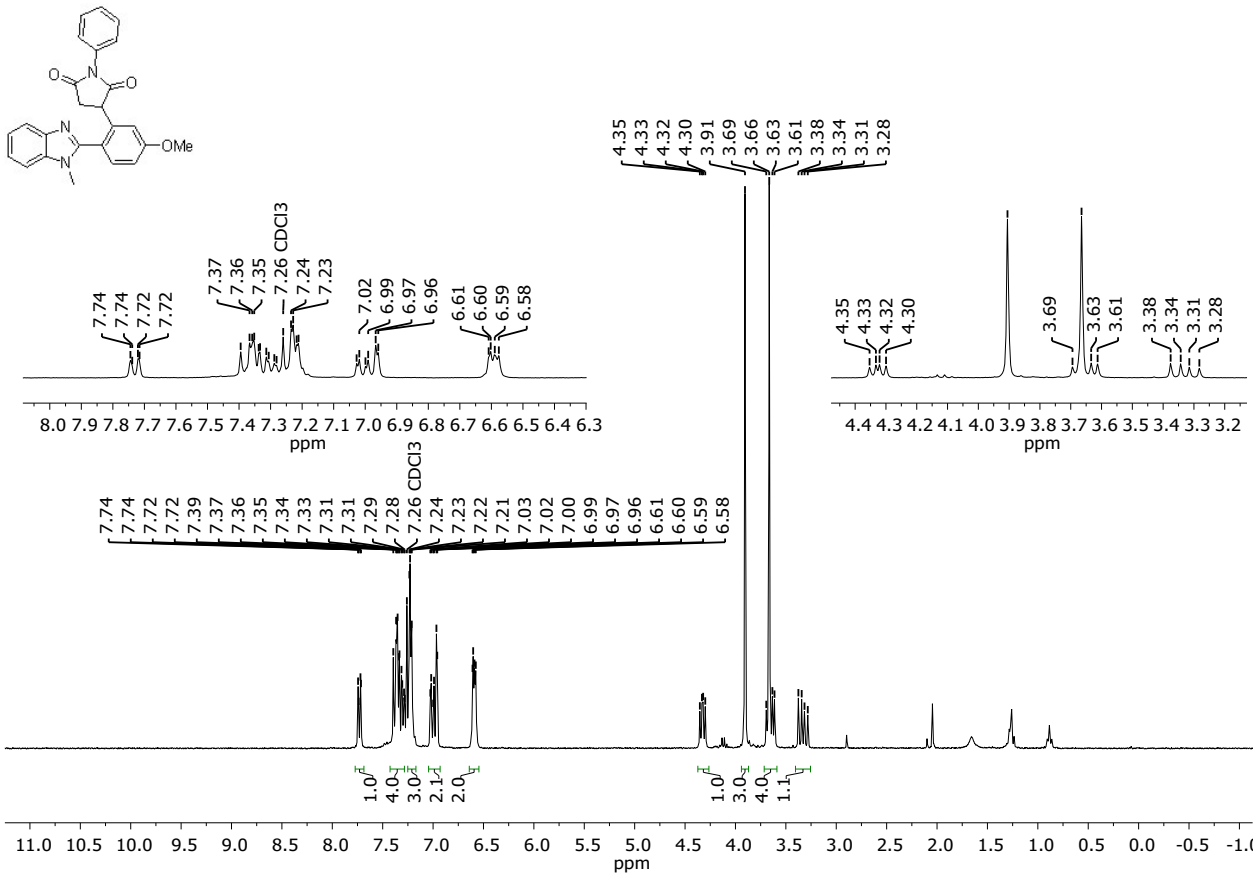


Figure S31. ^{1}H NMR spectrum of compound **3n** (300 MHz, $CDCl_3$).

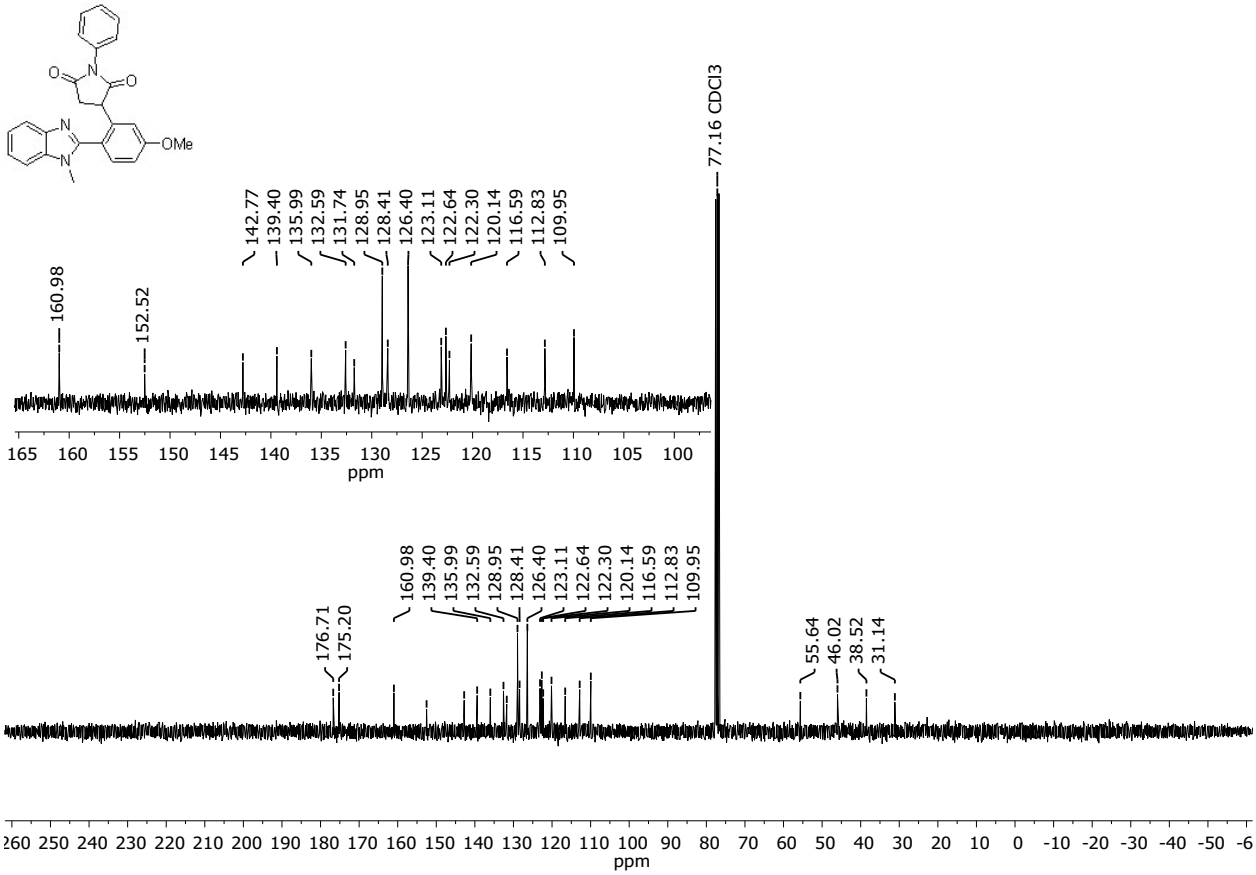


Figure S32. ^{13}C NMR spectrum of compound **3n** (75 MHz, $CDCl_3$).

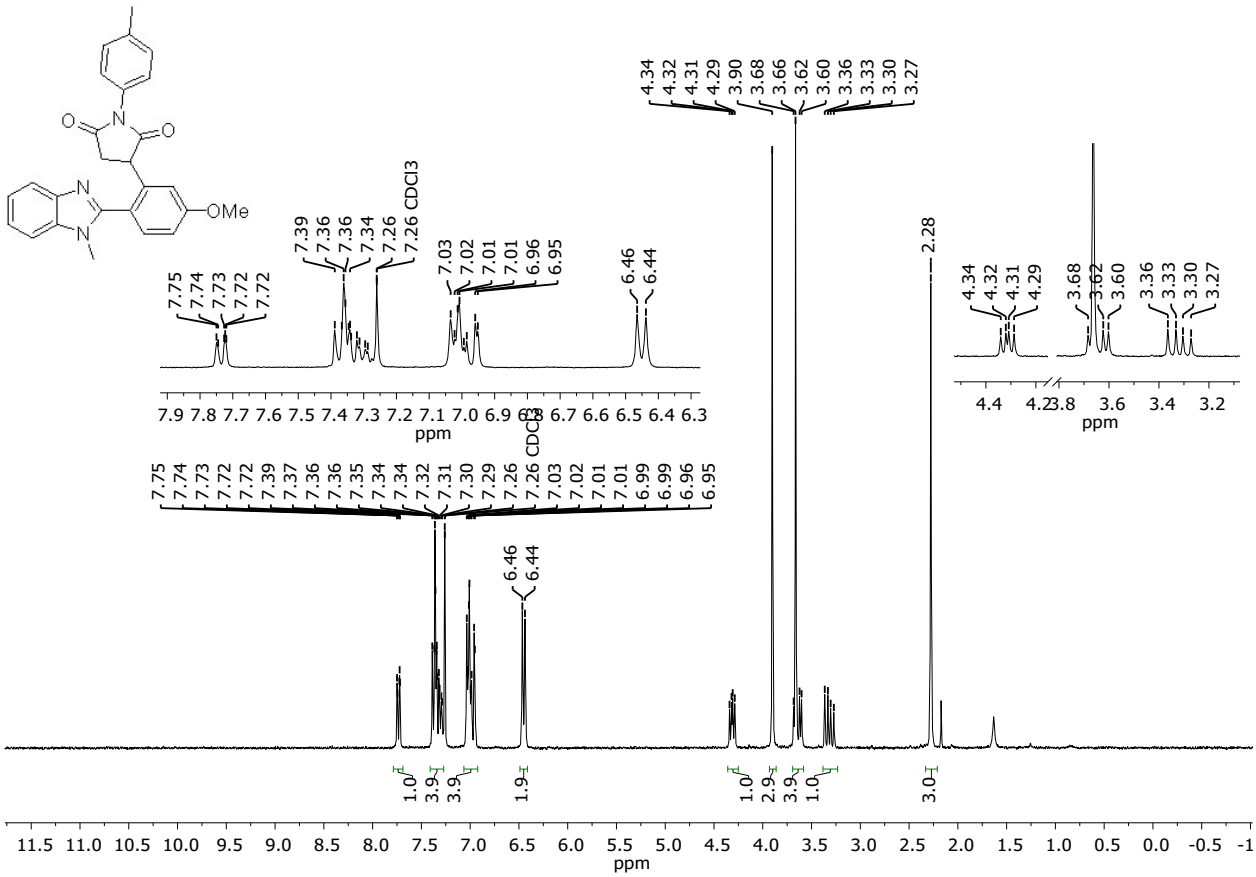


Figure S33. ^{1}H NMR spectrum of compound **3o** (300 MHz, $CDCl_3$).

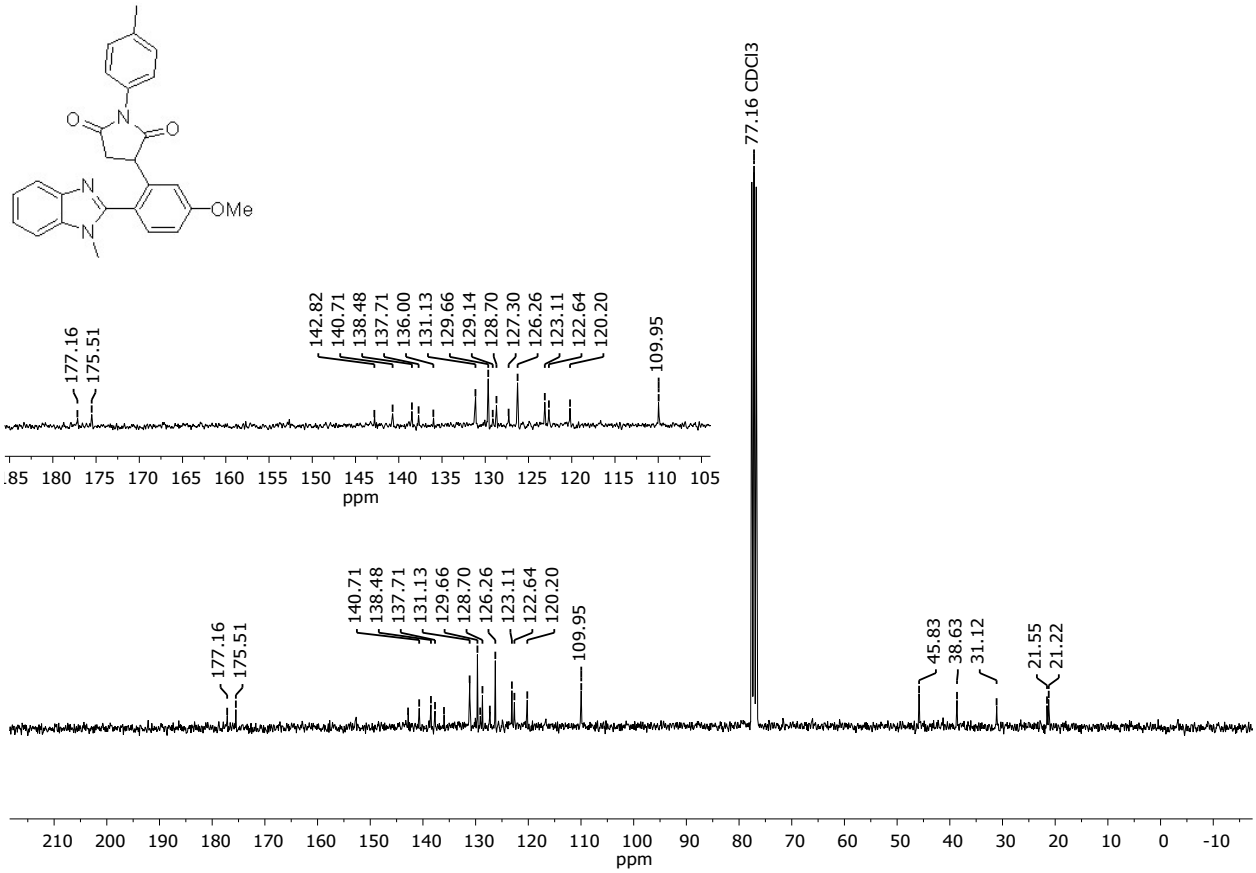


Figure S34. ^{13}C NMR spectrum of compound **3o** (75 MHz, $CDCl_3$).

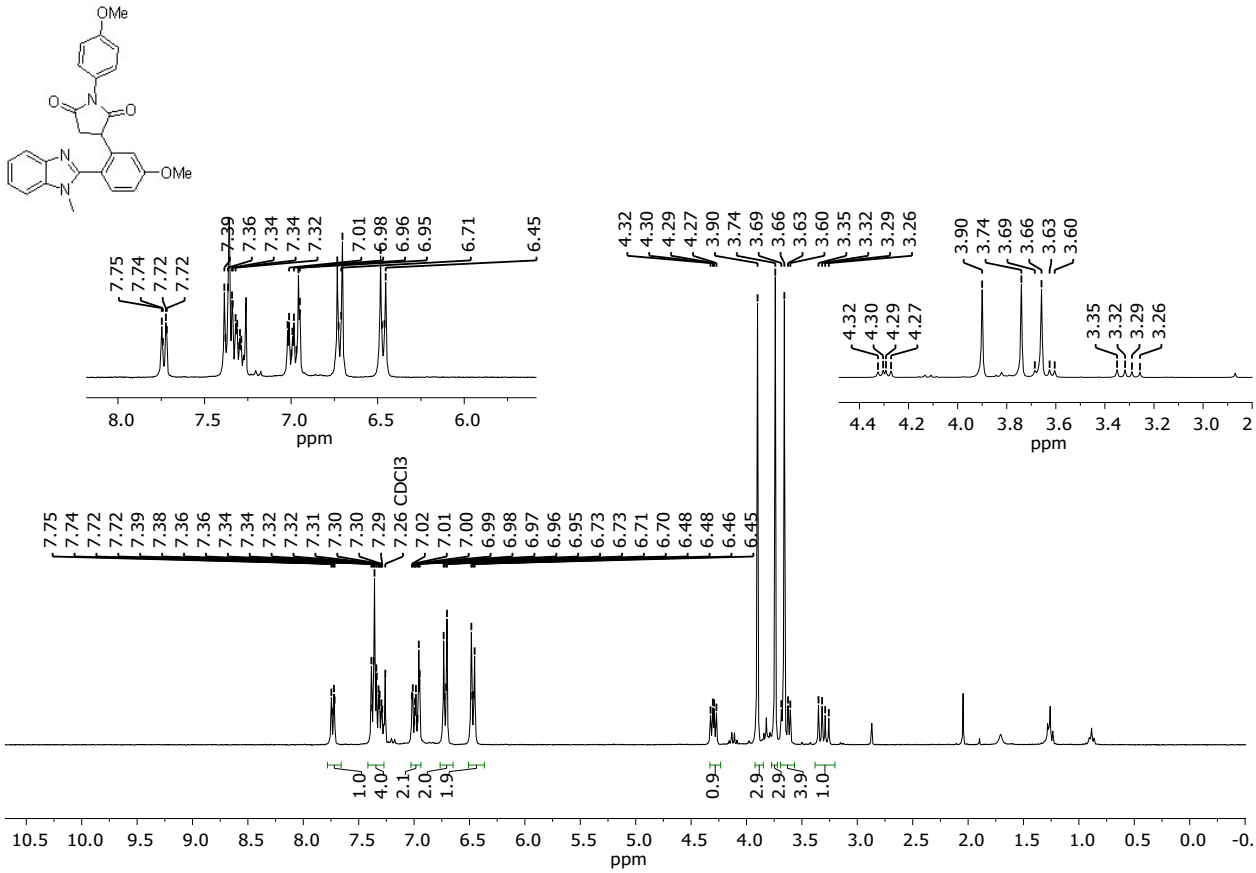


Figure S35. ^{1}H NMR spectrum of compound **3p** (300 MHz, $CDCl_3$).

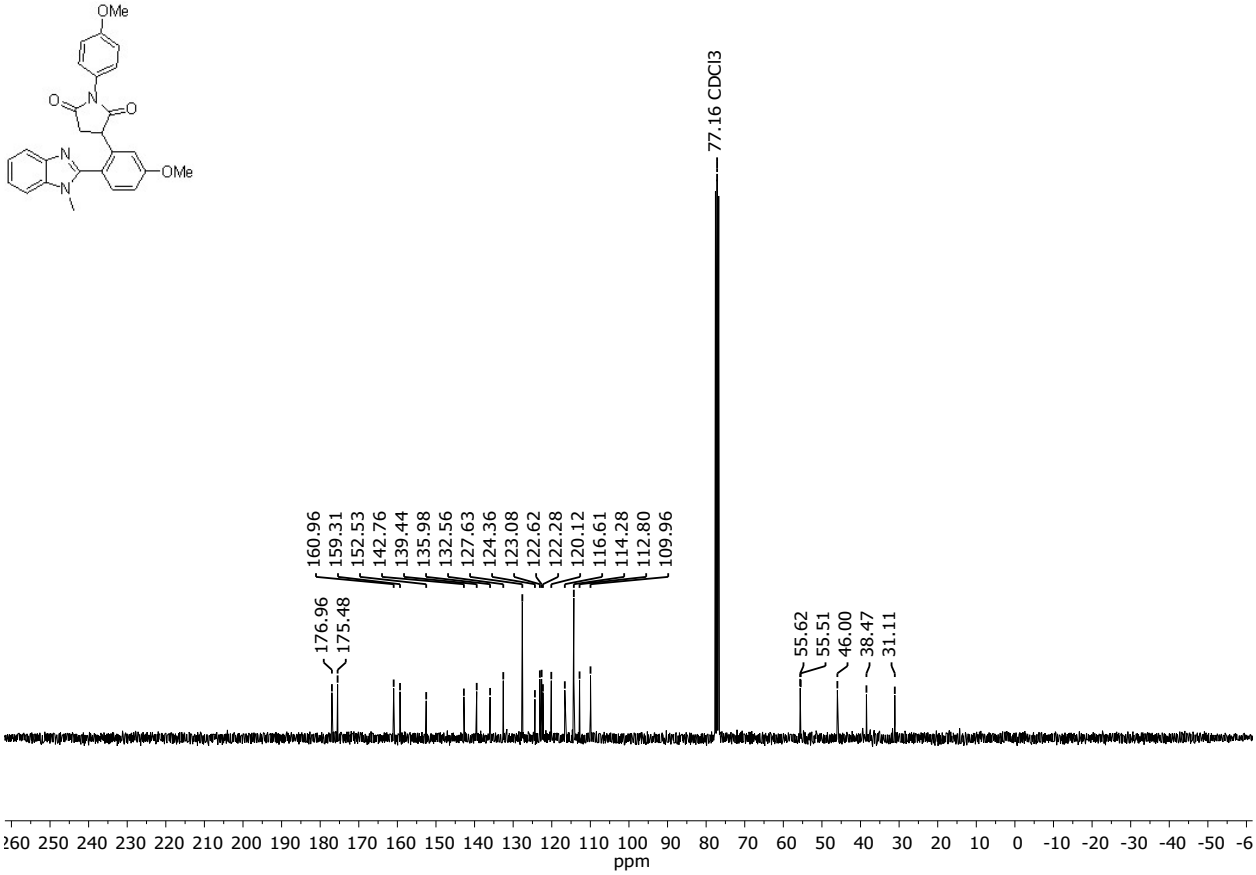


Figure S36. ^{13}C NMR spectrum of compound **3p** (75 MHz, $CDCl_3$).

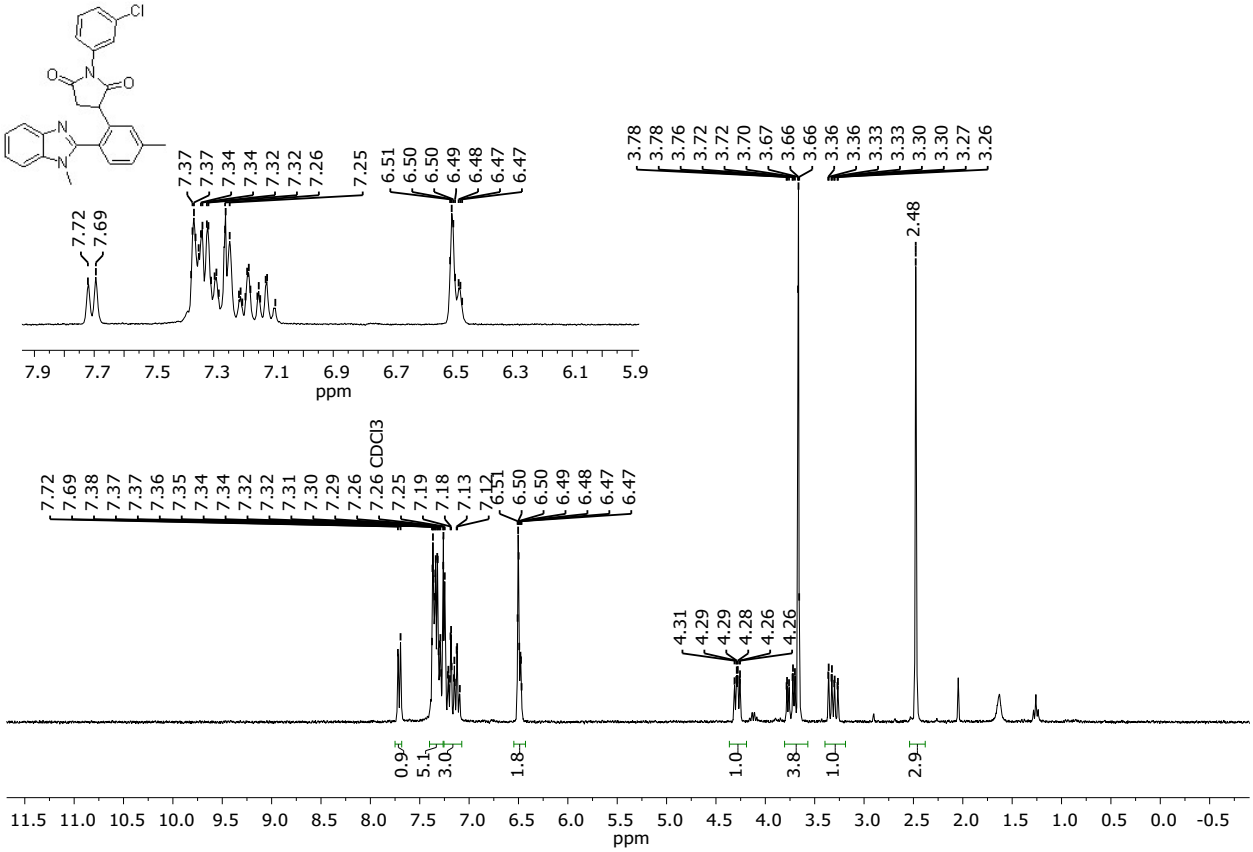


Figure S37. ^{1}H NMR spectrum of compound **3q** (300 MHz, $CDCl_3$).

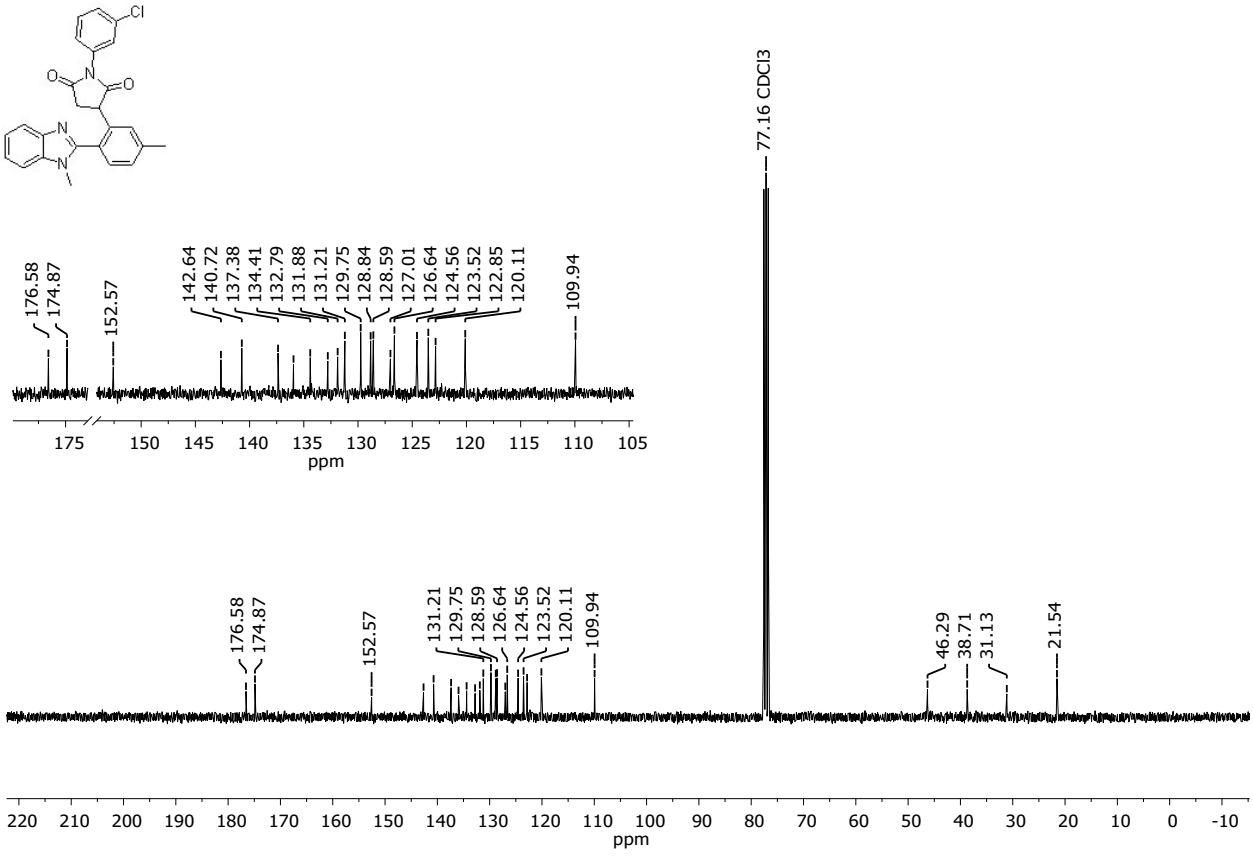


Figure S38. ^{13}C NMR spectrum of compound **3q** (75 MHz, $CDCl_3$).

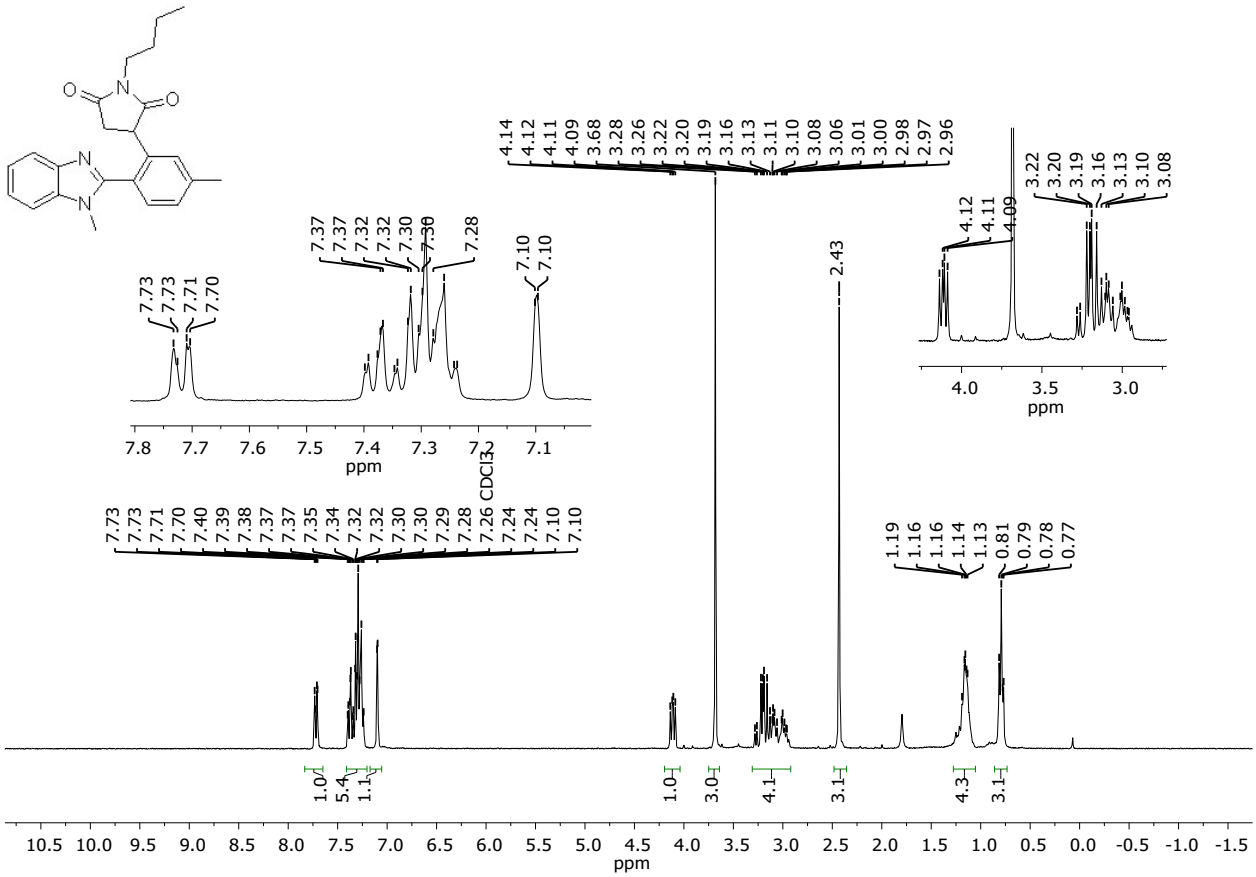


Figure S39. ^{1}H NMR spectrum of compound **3r** (300 MHz, $CDCl_3$).

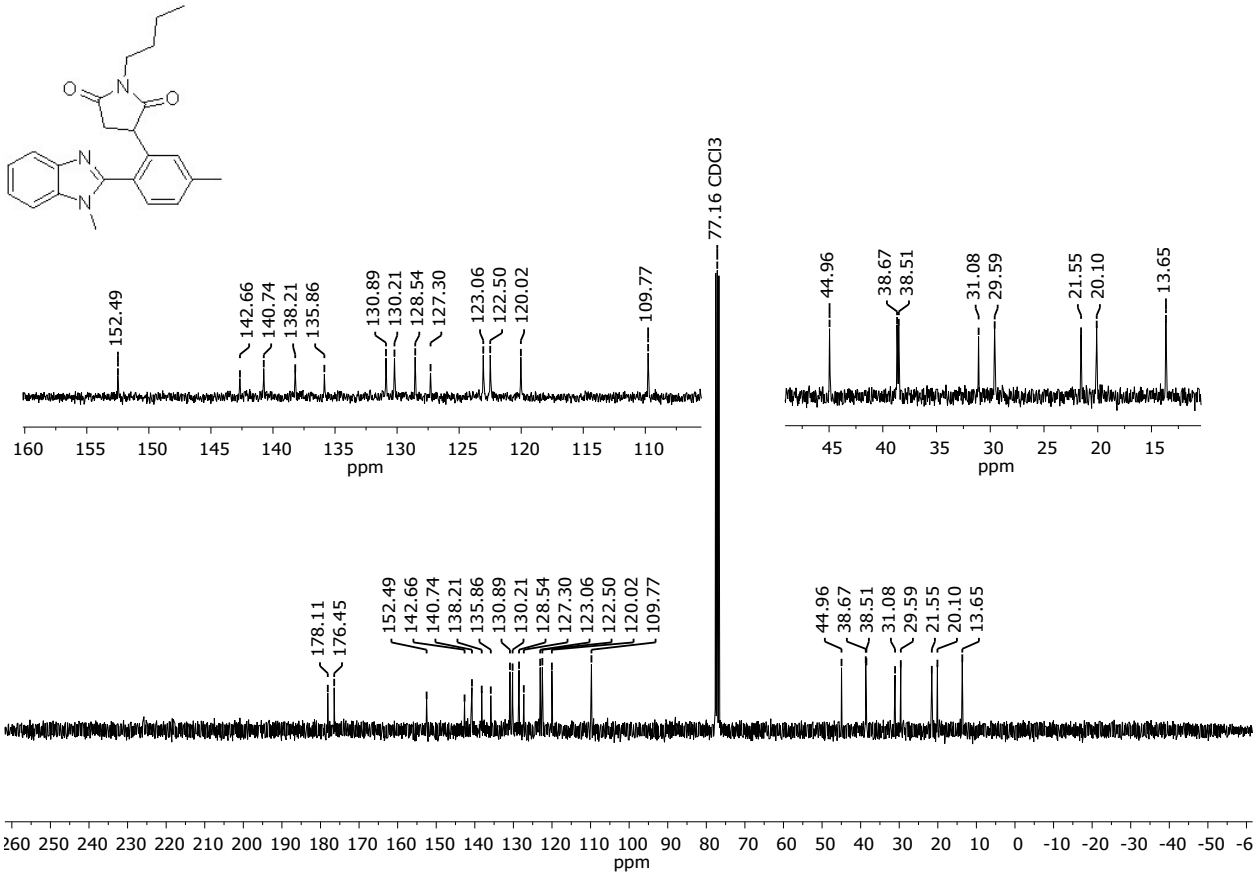


Figure S40. ^{13}C NMR spectrum of compound **3r** (75 MHz, $CDCl_3$).

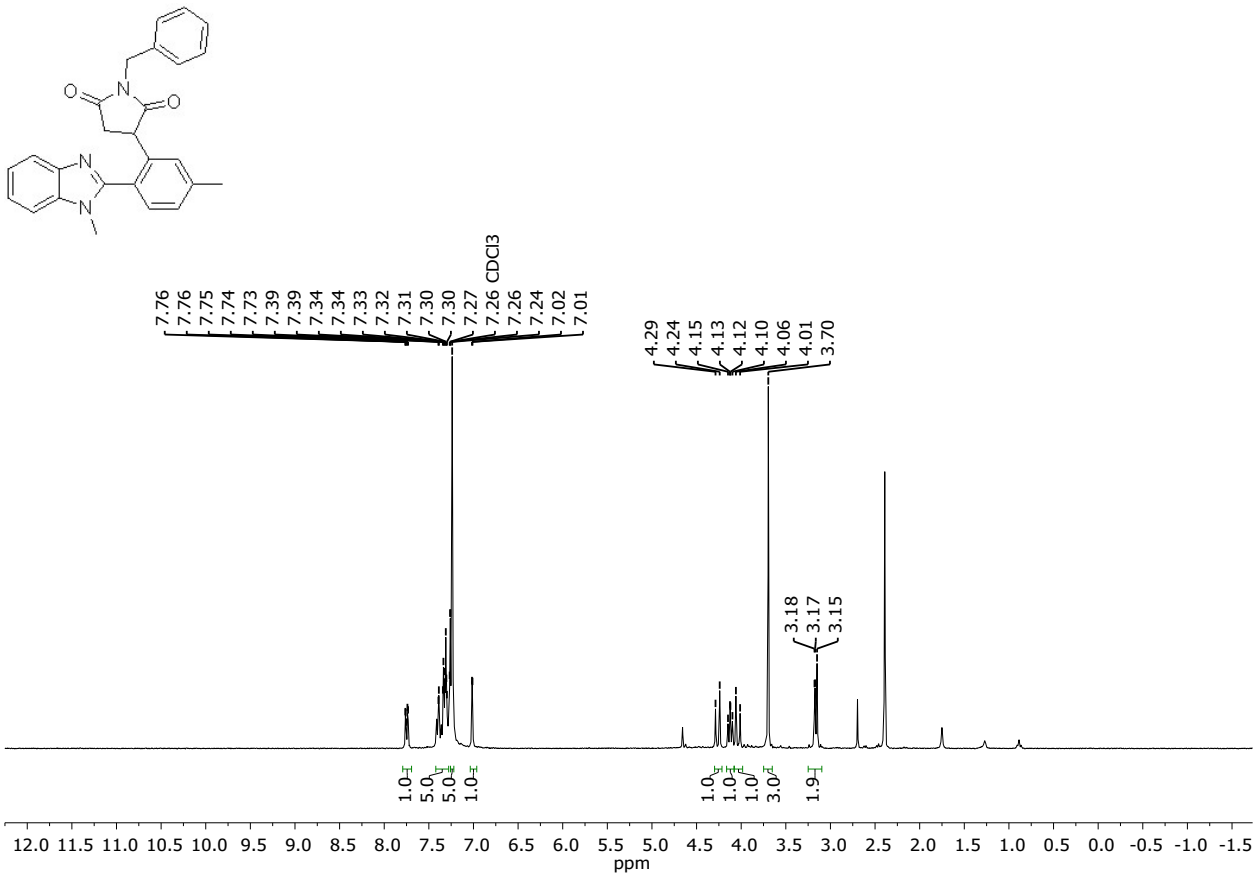


Figure S41. ^{1}H NMR spectrum of compound **3s** (300 MHz, $CDCl_3$).

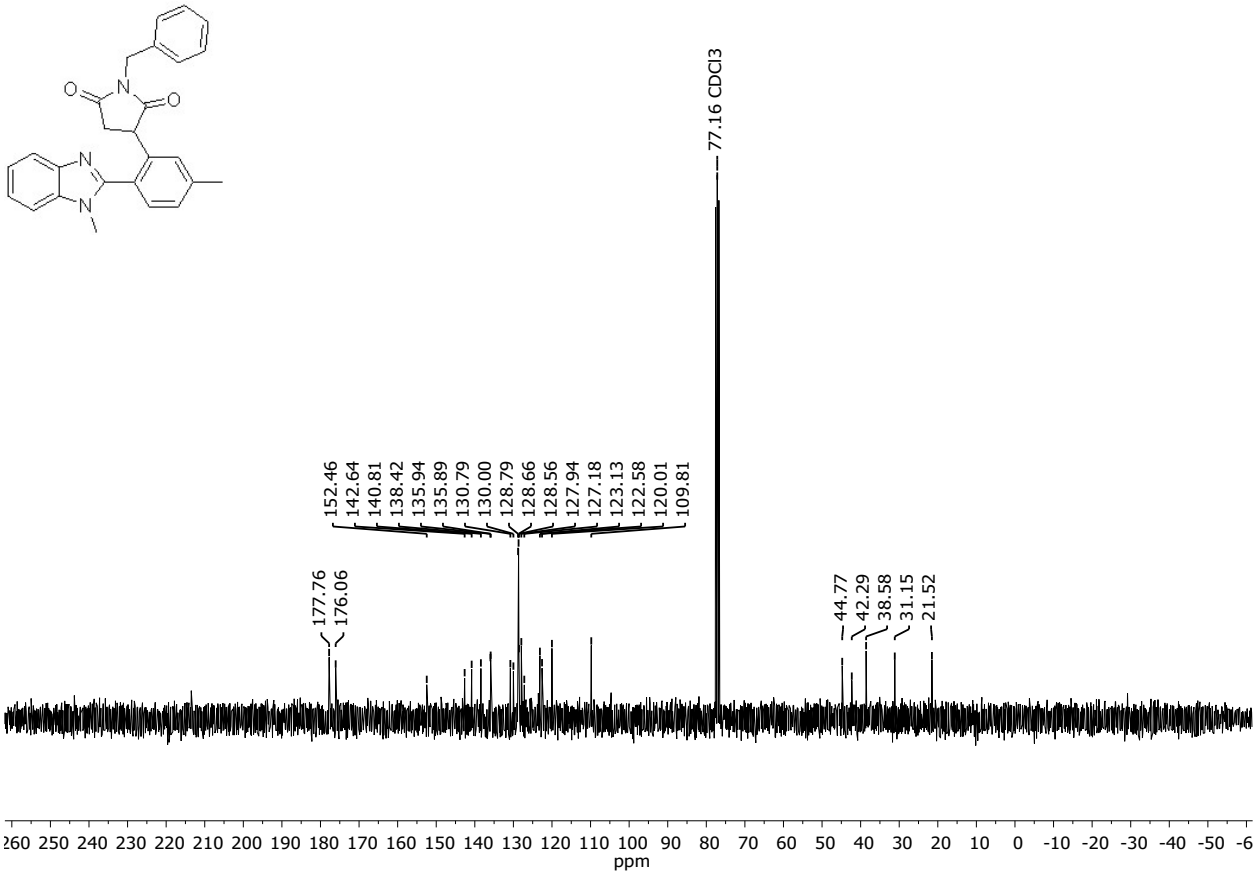


Figure S42. ^{13}C NMR spectrum of compound **3s** (75 MHz, $CDCl_3$).

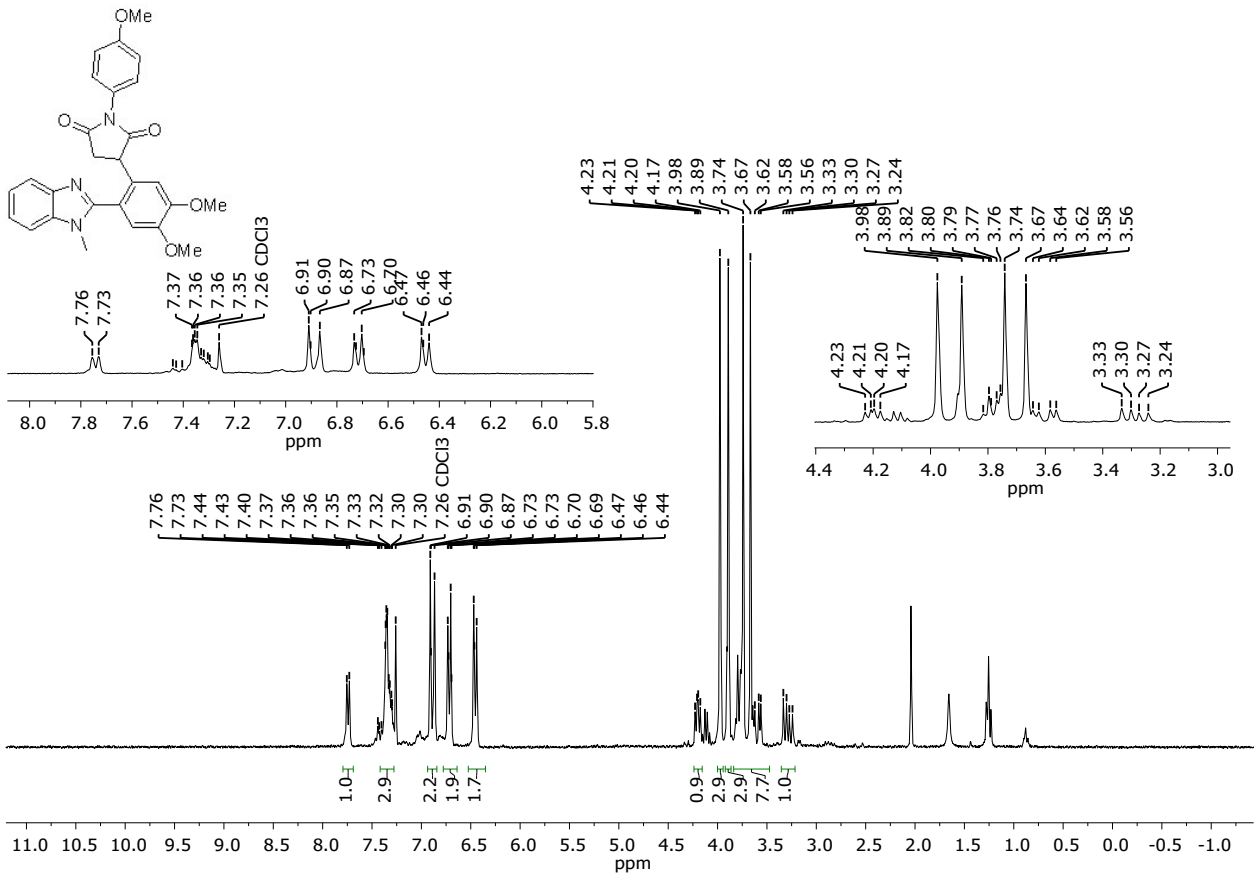


Figure S43. ^{1}H NMR spectrum of compound **3t** (300 MHz, $CDCl_3$).

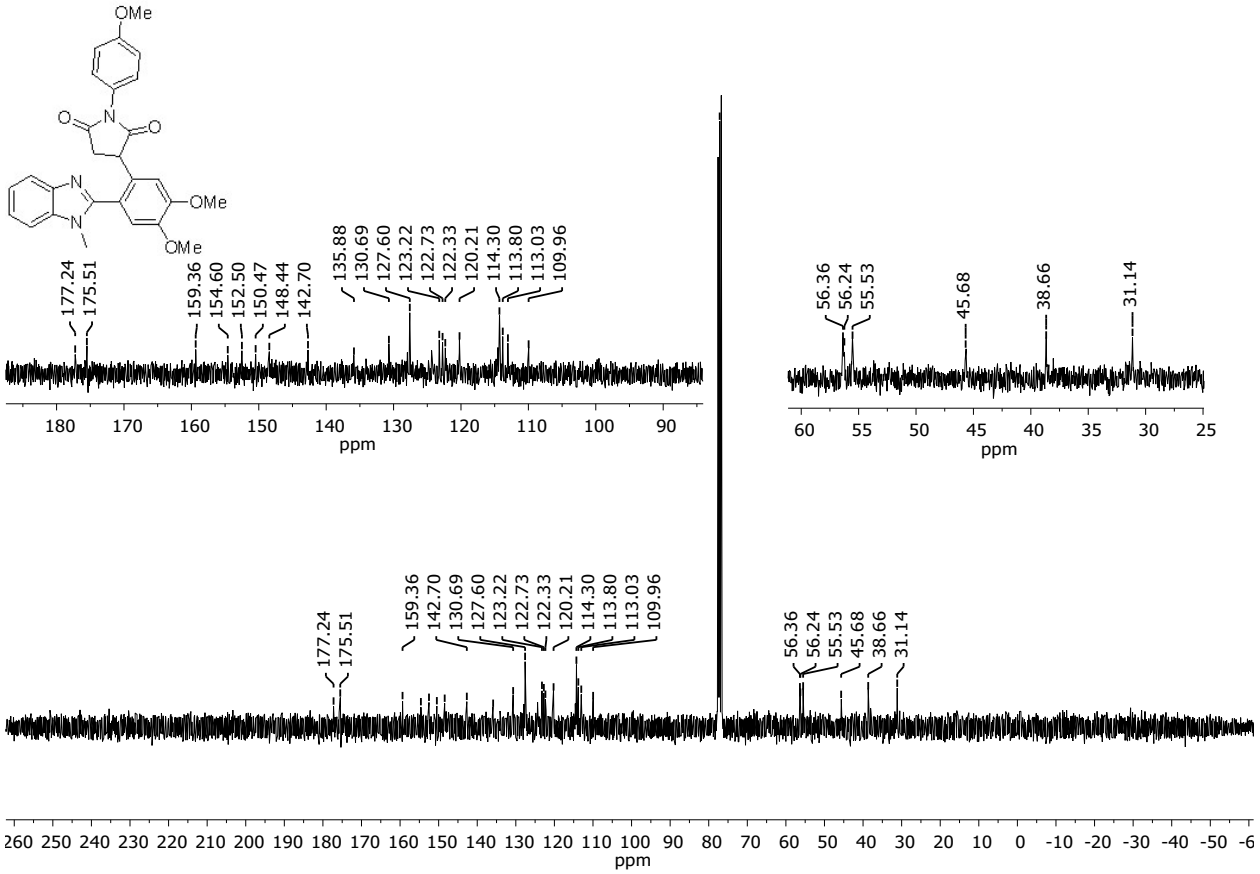


Figure S44. ^{13}C NMR spectrum of compound **3t** (75 MHz, $CDCl_3$).

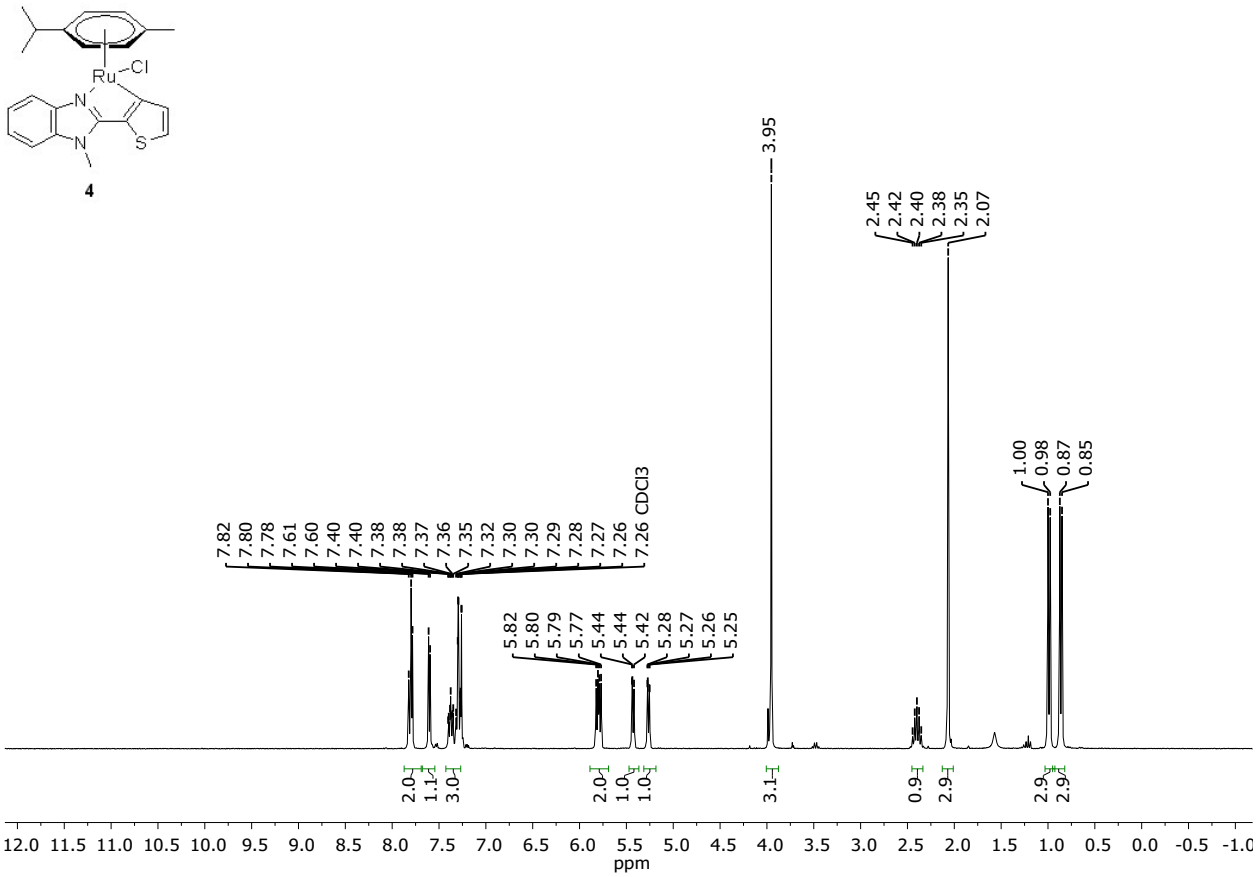


Figure S45. ^{1}H NMR spectrum of compound **4** (300 MHz, $CDCl_3$).

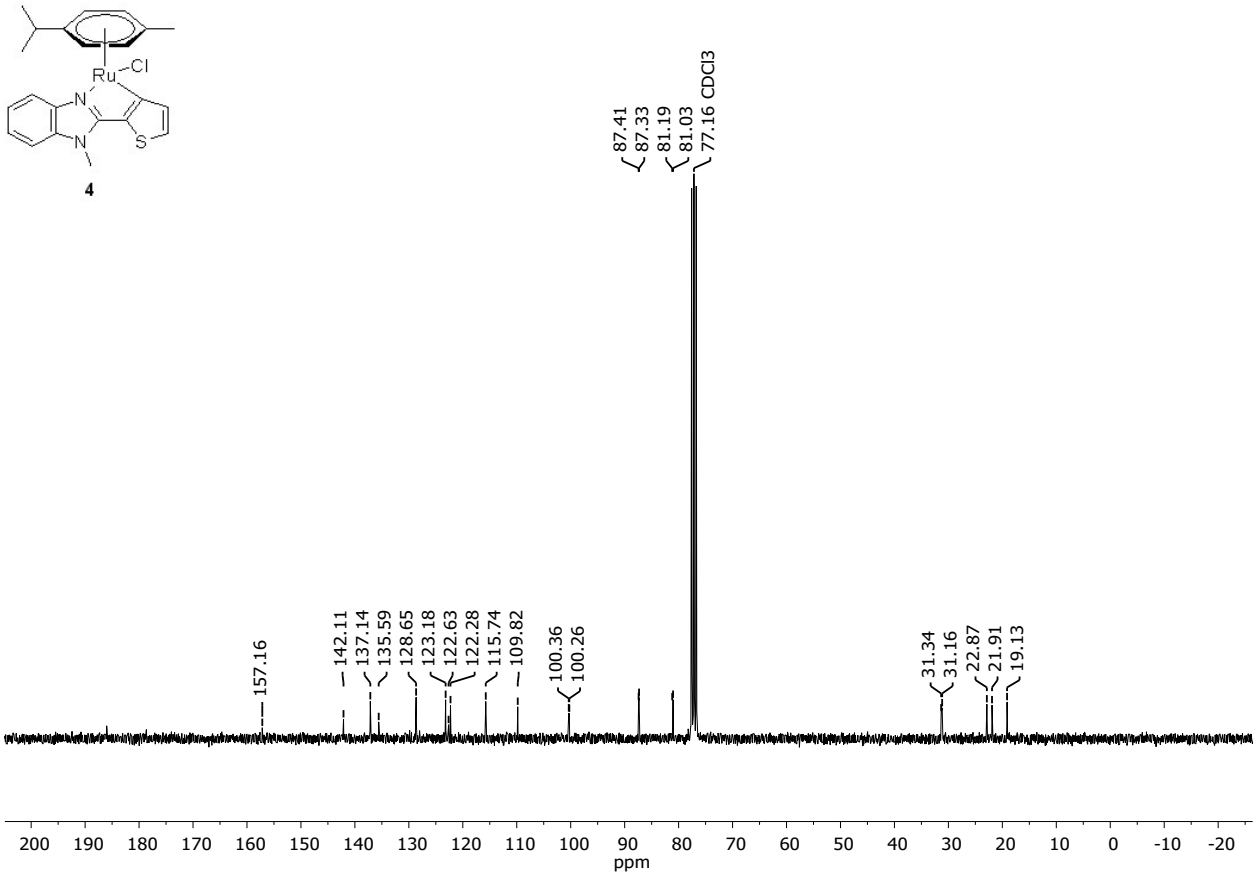


Figure S46. ^{13}C NMR spectrum of compound **4** (75 MHz, $CDCl_3$).

Supplementary references

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