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Ruthenium(II)-catalyzed C(3)–H arylation of furan moiety in fuberidazole derivatives

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Synthetic procedures and characterization of isolated compounds

General Information

^{1}H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker Avance Neo 300 spectrometer. Chemical shifts (δ, ppm) are given relative to the residual signals of chloroform-*d* protons (7.26 ppm 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 dm^3 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.

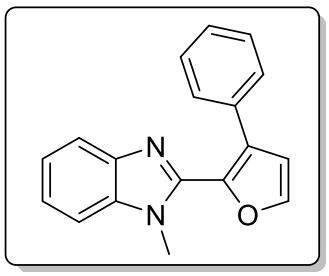
Melting points were determined in open capillary tubes using a Thiele apparatus and are uncorrected.

Materials

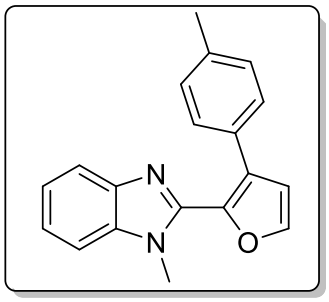
2-(Furan-2-yl)-1-methyl-1*H*-benz[*d*]imidazole **(1a)**,[S1] 1-benzyl-2-(5-methylfuran-2-yl)-1*H*-benz[*d*]imidazole**(1b)**,[S2] (5-(1-methyl-1*H*-benz[*d*]imidazol-2-yl)furan-2-yl)(phenyl)methanone **(1c)**,[S3] 2-(furan-2-yl)-1-(furan-2-ylmethyl)-1*H*-benz[*d*]imidazole**(1d)**,[S4] were synthesized according to previously described procedures. All other reagents are commercially available.

General procedure for the synthesis of compounds 2a-n

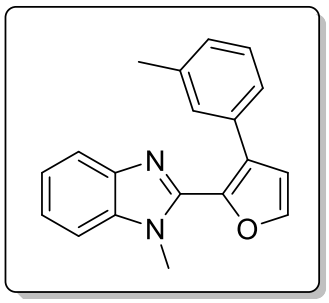
A mixture of an appropriate compound **1a-d** (0.25 mmol), the corresponding aryl bromide (0.5 mmol), K_2CO_3 (0.069 g, 0.5 mmol), $[RuCl_2(cymene)]_2$ (0.008 g, 0.0125 mmol, 5 mol %), pivalic acid (0.075 mmol) and 1,4-dioxane (2 ml) was stirred under argon atmosphere at 100 °C within 24 h. Then the mixture was cooled to room temperature and filtered through a short pad of Celite. The filtrate obtained was evaporated *in vacuo* to leave the crude product which was purified by column chromatography on silica-gel (hexane - EtOAc 3:1 as eluent).



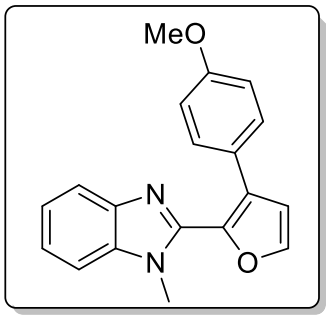
1-Methyl-2-(3-phenylfuran-2-yl)-1*H*-benz[*d*]imidazole (2a). Yield 0.064 g (94%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.64 (s, 3H), 6.79 (d, J = 1.9 Hz, 1H), 7.10 – 7.24 (m, 3H), 7.27 – 7.45 (m, 5H), 7.66 – 7.70 (m, 1H), 7.73 (d, J = 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 109.8, 112.4, 120.5, 122.7, 123.4, 127.9, 128.0, 128.3, 128.9, 132.3, 135.8, 139.0, 143.3, 144.4, 145.1. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O^+$ *m/z* 275.1179, found *m/z* 275.1187.



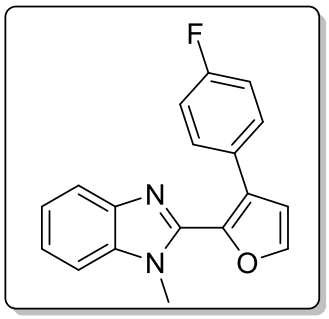
1-Methyl-2-(3-(*p*-tolyl)furan-2-yl)-1*H*-benz[*d*]imidazole (2b). Yield 0.056 g (78%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H), 3.46 (s, 3H), 6.77 (d, *J* = 1.9 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H), 7.29 – 7.36 (m, 6H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.80 – 7.89 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 31.2, 109.8, 112.5, 120.5, 122.7, 123.3, 127.9, 128.3, 129.4, 129.7, 135.9, 137.8, 138.8, 143.4, 144.4, 145.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O^+$ *m/z* 289.1335, found *m/z* 289.1333.



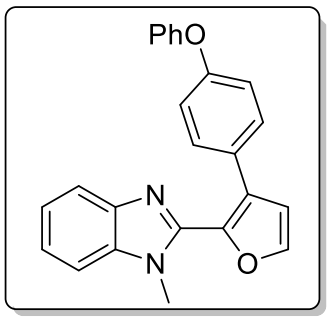
1-Methyl-2-(3-(*m*-tolyl)furan-2-yl)-1*H*-benz[*d*]imidazole (2c). Yield 0.061 g (84%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H), 3.46 (s, 3H), 6.78 (d, J = 1.9 Hz, 1H), 7.08 – 7.20 (m, 3H), 7.28 – 7.34 (m, 4H), 7.67 (d, J = 1.9 Hz, 1H), 7.81 – 7.89 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 31.2, 109.8, 112.6, 120.5, 122.7, 123.3, 125.1, 128.4, 128.66, 128.71, 128.8, 132.3, 135.8, 138.6, 139.1, 143.4, 144.4, 145.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O^+$ *m/z* 289.1335, found *m/z* 289.1325.



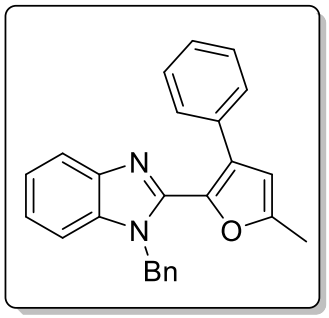
2-(3-(4-Methoxyphenyl)furan-2-yl)-1-methyl-1*H*-benz[*d*]imidazole (2d). Yield 0.053 g (70%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.50 (s, 3H), 3.80 (s, 3H), 6.76 (d, *J* = 1.8 Hz, 1H), 6.82 – 6.92 (m, 2H), 7.32 – 7.38 (m, 5H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.83 – 7.93 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4, 67.2, 109.9, 112.5, 114.5, 120.3, 123.0, 123.6, 124.6, 128.5, 129.2, 135.7, 138.0, 142.7, 144.6, 145.2, 159.5. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O_2^+$ *m/z* 305.1285, found *m/z* 305.1280.



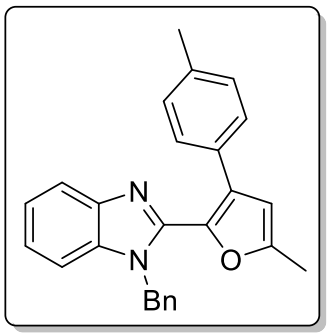
2-(3-(4-Fluorophenyl)furan-2-yl)-1-methyl-1*H*-benz[*d*]imidazole (2e). Yield 0.060 g (82%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.58 (s, 3H), 6.76 (d, *J* = 1.9 Hz, 1H), 6.99-7.05 (m, 2H), 7.31-7.36 (m, 3H), 7.43 – 7.52 (m, 2H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.80 – 7.86 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.3, 109.8, 112.5, 115.9 (d, *J* = 21.6 Hz), 120.5, 122.8, 123.6, 127.5, 128.4 (d, *J* = 3.2 Hz), 129.9 (d, *J* = 7.9 Hz), 135.8, 139.1, 143.2, 144.4, 144.8, 162.6 (d, *J* = 247.9 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}FN_2O^+$ *m/z* 293.1085, found *m/z* 293.1075.



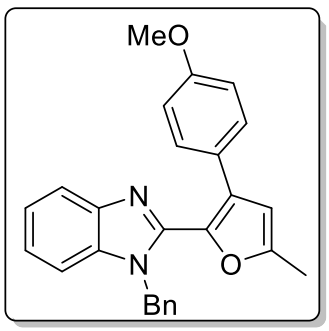
1-Methyl-2-(3-(4-phenoxyphenyl)furan-2-yl)-1*H*-benz[*d*]imidazole (2f). Yield 0.065 g (71%), white solid, mp = 102-103°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.57 (s, 3H), 6.78 (d, *J* = 1.9 Hz, 1H), 6.93 – 6.98 (m, 2H), 6.99 – 7.05 (m, 2H), 7.08 – 7.15 (m, 1H), 7.28 – 7.40 (m, 5H), 7.41 – 7.49 (m, 2H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.79 – 7.87 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.3, 109.8, 112.5, 118.9, 119.4, 120.5, 122.7, 123.4, 123.7, 127.1, 127.8, 129.5, 130.0, 135.9, 138.9, 143.3, 144.4, 145.1, 156.9, 157.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}N_2O_2^+$ *m/z* 367.1441, found *m/z* 367.1430.



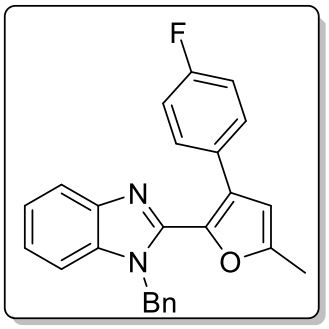
1-Benzyl-2-(5-methyl-3-phenylfuran-2-yl)-1*H*-benz[*d*]imidazole (2g). Yield 0.085 g (93%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38 (s, 3H), 5.13 (s, 2H), 6.37 (s, 1H), 6.88 – 6.99 (m, 2H), 7.15 – 7.22 (m, 5H), 7.26 – 7.33 (m, 4H), 7.35 – 7.46 (m, 1H), 7.84 (d, J = 7.4 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8, 48.4, 108.6, 110.7, 120.6, 122.7, 123.4, 126.8, 127.8, 127.9, 128.8, 128.8, 129.3, 132.5, 135.2, 136.3, 137.2, 143.6, 145.5, 154.4 two signals are overlapped. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}N_2O^+$ *m/z* 365.1648, found *m/z* 365.1641.



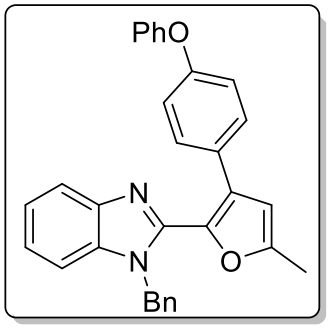
1-Benzyl-2-(5-methyl-3-(*p*-tolyl)furan-2-yl)-1*H*-benz[*d*]imidazole (2h). Yield 0.076 g (80%), white solid, mp = 103-105 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38 (s, 3H), 5.13 (s, 2H), 6.37 (s, 1H), 6.88 – 6.99 (m, 2H), 7.15 – 7.33 (m, 10H), 7.35 – 7.46 (m, 1H), 7.84 (d, J = 7.4 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8, 48.4, 108.6, 110.7, 120.6, 122.7, 123.4, 126.8, 127.8, 127.9, 128.8, 128.8, 129.3, 132.5, 135.2, 136.3, 137.2, 143.6, 145.5, 154.4. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{23}N_2O^+$ *m/z* 379.1805, found *m/z* 379.1810.



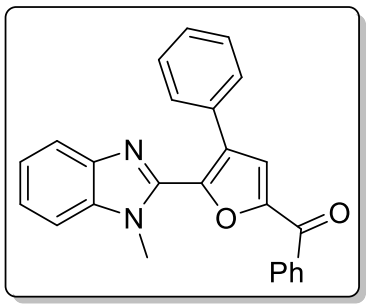
1-Benzyl-2-(3-(4-methoxyphenyl)-5-methylfuran-2-yl)-1*H*-benz[*d*]imidazole (2i). Yield 0.066 g (67%), white solid, mp = 112-113˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.36 (d, *J* = 1.0 Hz, 3H), 3.79 (s, 3H), 5.15 (s, 2H), 6.32 (d, *J* = 1.0 Hz, 1H), 6.78 – 6.85 (m, 2H), 6.93 – 6.96 (m, 2H), 7.16 – 7.23 (m, 5H), 7.22 – 7.32 (m, 1H), 7.32 – 7.37 (m, 2H), 7.75 – 7.93 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 48.4, 55.4, 108.6, 110.7, 114.3, 120.5, 122.6, 123.3, 124.9, 126.8, 127.7, 128.7, 129.07, 129.13, 135.2, 136.4, 136.5, 145.7, 154.3, 159.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{23}N_2O_2^+$ *m/z* 395.1754, found *m/z* 395.1759.



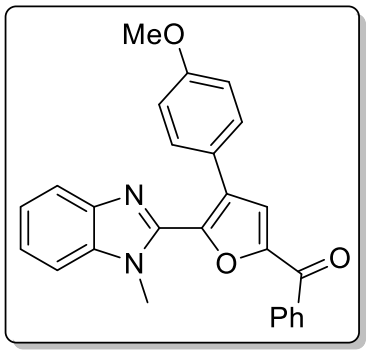
1-Benzyl-2-(3-(4-fluorophenyl)-5-methylfuran-2-yl)-1*H*-benzo[*d*]imidazole (2j). Yield 0.070 g (73%), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38 (d, *J* = 1.0 Hz, 3H), 5.25 (s, 2H), 6.34 (d, *J* = 1.1 Hz, 1H), 6.95 – 7.03 (m, 4H), 7.26 (m, 6H), 7.40 – 7.47 (m, 2H), 7.80 – 7.88 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8, 48.5, 108.7, 110.6, 115.7 (d, *J* = 21.4 Hz), 120.5, 122.8, 123.6, 126.8, 127.8, 128.5 (d, *J* = 3.5 Hz), 128.6, 128.8, 129.72 (d, *J* = 8.0 Hz), 135.2, 136.3, 143.3, 145.1, 154.4, 162.4 (d, *J* = 247.3 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}FN_2O^+$ *m/z* 383.1554, found *m/z* 383.1559.



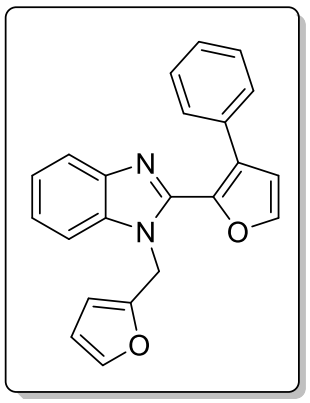
1-Benzyl-2-(3-(4-phenoxyphenyl)-5-methylfuran-2-yl)-1*H*-benz[*d*]imidazole (2k). Yield 0.086 g (75%), colorless viscous oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ δ 2.37 (d, *J* = 1.0 Hz, 3H), 5.23 (s, 2H), 6.34 (d, *J* = 1.1 Hz, 1H), 6.89 – 6.95 (m, 2H), 6.97 – 7.05 (m, 4H), 7.08 – 7.14 (m, 1H), 7.18 – 7.25 (m, 5H), 7.27 – 7.44 (m, 5H), 7.80 – 7.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8, 48.5, 108.6, 110.6, 118.8, 119.3, 120.6, 122.7, 123.4, 123.6, 126.9, 127.3, 127.8, 128.8, 128.8, 129.4, 129.9, 135.3, 136.4, 137.0, 143.6, 145.4, 154.3, 156.9, 157.1. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{25}N_2O_2^+$ *m/z* 457.1911, found *m/z* 457.1903



(5-(1-Methyl-1*H*-benz[*d*]imidazol-2-yl)-4-phenylfuran-2-yl)(phenyl)-methanone (2l). Yield 0.067 g (71%), yellow crystals, mp = 99-100˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.70 (s, 3H), 7.34 – 7.40 (m, 6H), 7.51 – 7.58 (m, 4H), 7.59 (s, 1H), 7.60 – 7.66 (m, 1H), 7.84 – 7.87 (m, 1H), 8.05 – 8.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.5, 110.0, 120.9, 121.6, 123.1, 124.1, 128.3, 128.6, 128.8, 129.0, 129.6, 130.2, 131.0, 133.1, 136.0, 137.0, 143.0, 143.3, 143.5, 152.6, 182.4. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O_2^+$ *m/z* 379.1441, found *m/z* 379.1447.



(4-(4-Methoxyphenyl)-5-(1-methyl-1*H*-benz[*d*]imidazol-2-yl)furan-2-yl)(phenyl)methanone (2m). Yield 0.061 g (60%), yellow solid, mp = 100-101˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.72 (s, 3H), 3.81 (s, 3H), 6.84 – 6.94 (m, 2H), 7.28-7.43 (m, 3H), 7.49 – 7.63 (m, 5H), 7.58 – 7.69 (m, 1H), 7.84 – 7.88 (m, 1H), 8.04 – 8.14 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.5, 55.5, 109.9, 114.4, 120.9, 121.6, 123.0, 123.3, 124.0, 128.7, 129.6, 129.6, 129.9, 133.1, 136.0, 137.0, 142.4, 143.3, 143.7, 152.5, 159.9, 182.4. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{21}N_2O_3^+$ *m/z* 409.1547, found *m/z* 409.1550.



1-(Furan-2-yl-methyl)-2-(3-phenylfuran-2-yl)-1*H*-benz[*d*]imidazole (2n). Yield 0.056 g (66%), yellow oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.18 (s, 2H), 6.01 (d, *J* = 3.2 Hz, 1H), 6.15 – 6.23 (m, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.27 – 7.35 (m, 5H), 7.42 – 7.49 (m, 3H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.80 – 7.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 41.5, 108.5, 110.5, 110.6, 112.5, 120.7, 122.8, 123.7, 127.9, 128.1, 128.6, 128.8, 132.0, 135.1, 139.0, 142.7, 143.4, 144.2, 144.5, 149.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_2^+$ *m/z* 341.1285, found *m/z* 341.1295.

X-Ray structure determination

X-ray crystallographic data and refinement details for 2f and 2i

X-ray diffraction data were collected at 100 K on a four-circle Rigaku Synergy-S diffractometer equipped with a HyPix-600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and analytically corrected for absorption and decay by the CrysAlisPro program.[S5] The structures were solved by direct methods using SHELXT [S6] and refined by full-matrix least-squares on F^2 using SHELXL-2018 [S7] in the OLEX2 program. [S8] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.950 Å for aromatic, 0.980 Å for methyl hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters (taken as U_{iso}(H)=1.5U_{eq}(C) for methyl groups and U_{iso}(H)=1.2U_{eq}(C) for aromatic hydrogen atoms). A rotating group model was applied for methyl groups.

Crystal data, data collection and structure refinement details for **3f** and **3i** are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2150291 and 2150292; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/data_request/cif

Table S1 Crystal data, data collection and structure refinement details for **2i** and **2f**

Identification code	**2f**	**2i**
Empirical formula	$C_{24}H_{18}N_2O_2$	$C_{26}H_{22}N_2O_2$
Formula weight	366.40	394.45
Temperature, K	100.0(1)	100.0(1)
Wavelength, Å	1.54184	1.54184
Crystal system	Triclinic	Triclinic
Space group	P1	$P\bar{1}$
Unit cell dimensions		
a, Å	7.95355(7)	8.37238(8)
b, Å	9.21984(6)	11.18203(13)
c, Å	24.96305(11)	12.01925(12)
α, °	84.7922(4)	66.9764(10)
β, °	88.1032(6)	78.2678(8)
γ, °	88.5825(6)	84.5945(9)
Volume, $Å^3$	1821.56(2)	1013.84(2)
Z	4	2
Calculated density, g/cm^3	1.336	1.292
Absorption coefficient, mm^{-1}	0.686	0.652
F(000)	768	416
Crystal size, mm	0.58×0.38×0.07	0.55×0.45×0.32
θ range for data collection, °	3.558 to 79.601	4.064 to 79.561
Index ranges	-10<=h<=10,	-10<=h<=10,
	-11<=k<=11,	-14<=k<=14,
	-29<=l<=31	-14<=l<=15
Reflections		
Collected	82483	22636
Independent [R_{int}]	14980 [0.0784]	4380 [0.0281]
Observed (with I>2σ(I))	14725	4279
Completeness to θ_{full} / θ_{max},°	0.999 / 0.990	0.998 / 0.990
Transmission max. / min.	0.951 / 0.763	0.855 / 0.778
Data / restraints / parameters	14980 / 3 / 1014	4380 / 12 / 290
Goodness-of-fit on F^2	1.074	1.038
Final R1 / wR2 indices with I>2σ(I)	0.0495 / 0.1382	0.0389 / 0.0977
Final R1 / wR2 indices (all data)	0.0499 / 0.1390	0.0395 / 0.0981
Absolute structure parameter	0.12(13)	-
Extinction coefficient	0.0023(5)	0.0135(8)
Largest diff. peak / hole, $ē·Å^3$	0.326 / -0.258	0.295 / -0.258
CCDC numbers	2150291	2150292

The X-ray structure of 2f

Compound **2f** crystalizes in the triclinic chiral space group (*P*1) with 4 crystallographically inequivalent molecules (*Z*' = 1, *Z* = 4, see Figure S1). Conformations of three molecules (A, B and C in Figure S2) are very similar (some are related by non-crystallographic inversion centers), but the conformation of the fourth molecule (D) exhibits significantly different conformation, preventing from crystallization in the centrosymmetric space group $P\bar{1}$.

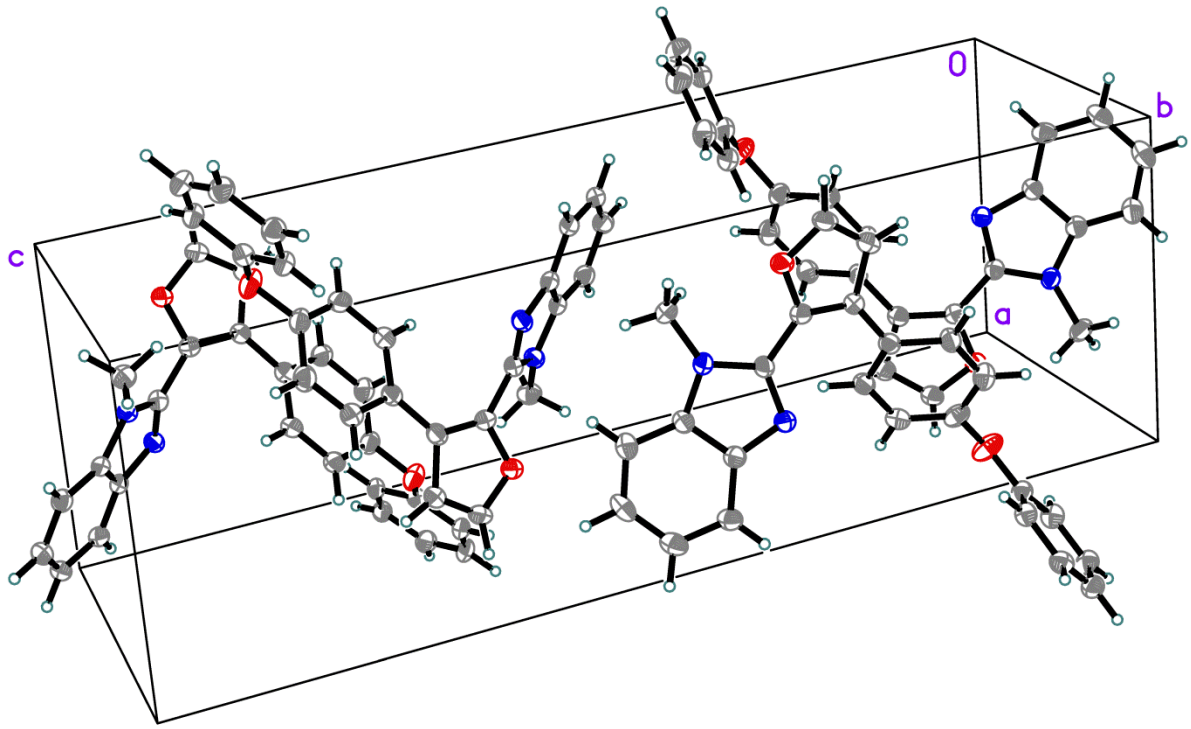


Figure S1. The unit cell with four crystallographically inequivalent molecules of **3f**. The displacement ellipsoids are set to 50% probability level.

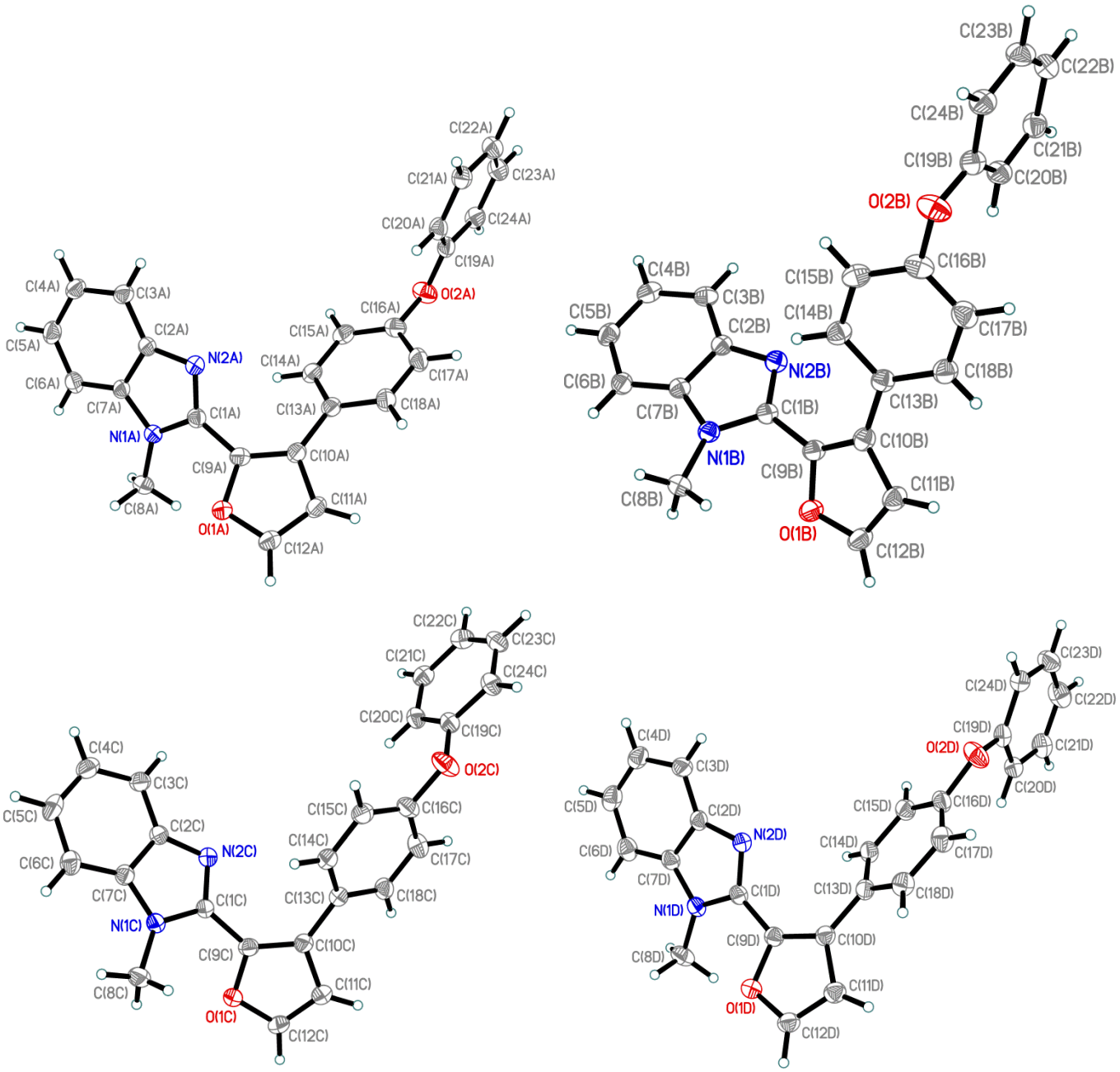


Figure S2. Four crystallographically inequivalent molecules of **2f** (p=50%).

Table S2. Bond lengths for **2f** (Å)

Bond	Molecule			
	A	B	C	D
O(1)-C(9)	1.377(3)	1.376(3)	1.378(3)	1.375(3)
O(1)-C(12)	1.363(3)	1.366(3)	1.368(3)	1.362(3)
O(2)-C(16)	1.396(3)	1.400(3)	1.398(3)	1.386(3)
O(2)-C(19)	1.381(3)	1.380(3)	1.379(3)	1.379(3)
N(1)-C(1)	1.374(3)	1.372(3)	1.378(3)	1.377(3)
N(1)-C(7)	1.383(3)	1.378(3)	1.383(3)	1.387(3)
N(1)-C(8)	1.457(3)	1.458(3)	1.459(3)	1.465(3)
N(2)-C(1)	1.317(3)	1.323(3)	1.320(3)	1.321(3)
N(2)-C(2)	1.385(3)	1.384(3)	1.384(3)	1.385(3)
C(1)-C(9)	1.460(3)	1.461(3)	1.459(3)	1.456(3)
C(2)-C(3)	1.405(3)	1.399(4)	1.406(3)	1.403(4)
C(2)-C(7)	1.405(3)	1.406(3)	1.407(4)	1.404(4)
C(3)-C(4)	1.388(4)	1.392(4)	1.381(4)	1.383(4)
C(4)-C(5)	1.404(4)	1.397(4)	1.408(5)	1.409(5)
C(5)-C(6)	1.382(4)	1.384(4)	1.388(4)	1.380(4)
C(6)-C(7)	1.398(4)	1.394(4)	1.399(4)	1.392(4)
C(9)-C(10)	1.366(4)	1.365(4)	1.373(4)	1.370(4)
C(10)-C(11)	1.439(3)	1.438(4)	1.440(3)	1.435(3)
C(10)-C(13)	1.472(4)	1.471(4)	1.470(4)	1.468(4)
C(11)-C(12)	1.351(4)	1.342(4)	1.341(4)	1.353(4)
C(13)-C(14)	1.409(4)	1.404(4)	1.395(4)	1.396(3)
C(13)-C(18)	1.394(4)	1.396(4)	1.400(4)	1.404(4)
C(14)-C(15)	1.382(4)	1.385(4)	1.387(4)	1.380(4)
C(15)-C(16)	1.383(4)	1.381(4)	1.382(4)	1.391(4)
C(16)-C(17)	1.387(4)	1.386(4)	1.385(4)	1.379(4)
C(17)-C(18)	1.392(4)	1.396(4)	1.388(4)	1.389(4)
C(19)-C(20)	1.396(4)	1.387(4)	1.396(4)	1.396(4)
C(19)-C(24)	1.388(4)	1.393(4)	1.392(4)	1.388(4)
C(20)-C(21)	1.388(4)	1.396(4)	1.392(4)	1.380(4)
C(21)-C(22)	1.383(4)	1.395(4)	1.385(4)	1.390(5)
C(22)-C(23)	1.390(4)	1.389(4)	1.395(4)	1.388(5)
C(23)-C(24)	1.393(4)	1.387(4)	1.389(4)	1.389(4)

Table S3. Bond angles for **2f** (°)

Angle	Molecule			
	A	B	C	D
C(12A)-O(1A)-C(9A)	106.5(2)	106.4(2)	106.2(2)	106.7(2)
C(19A)-O(2A)-C(16A)	120.1(2)	120.4(2)	120.7(2)	122.1(2)
C(1A)-N(1A)-C(7A)	105.7(2)	106.3(2)	105.9(2)	106.3(2)
C(1A)-N(1A)-C(8A)	129.4(2)	129.5(2)	128.4(2)	130.1(2)
C(7A)-N(1A)-C(8A)	124.8(2)	124.0(2)	125.3(2)	123.5(2)
C(1A)-N(2A)-C(2A)	104.6(2)	104.5(2)	104.4(2)	104.6(2)
N(1A)-C(1A)-C(9A)	121.8(2)	121.7(2)	122.0(2)	122.7(2)
N(2A)-C(1A)-N(1A)	113.9(2)	113.4(2)	113.8(2)	113.3(2)
N(2A)-C(1A)-C(9A)	124.3(2)	124.8(2)	124.2(2)	123.8(2)
N(2A)-C(2A)-C(3A)	130.4(2)	130.0(2)	129.6(3)	129.9(3)
N(2A)-C(2A)-C(7A)	110.0(2)	110.2(2)	110.5(2)	110.6(2)
C(3A)-C(2A)-C(7A)	119.5(2)	119.8(2)	119.9(3)	119.5(3)
C(4A)-C(3A)-C(2A)	117.7(2)	117.3(2)	117.9(3)	117.9(3)
C(3A)-C(4A)-C(5A)	121.5(2)	122.0(2)	121.2(3)	121.6(3)
C(6A)-C(5A)-C(4A)	122.0(3)	121.5(2)	122.1(3)	121.4(3)
C(5A)-C(6A)-C(7A)	116.2(2)	116.5(2)	116.2(3)	116.7(3)
N(1A)-C(7A)-C(2A)	105.8(2)	105.5(2)	105.4(2)	105.1(2)
N(1A)-C(7A)-C(6A)	131.1(2)	131.5(2)	131.9(3)	131.9(3)
C(6A)-C(7A)-C(2A)	123.1(2)	122.9(2)	122.5(2)	123.0(3)
O(1A)-C(9A)-C(1A)	115.5(2)	114.9(2)	116.0(2)	115.5(2)
C(10A)-C(9A)-O(1A)	110.5(2)	110.5(2)	110.5(2)	110.2(2)
C(10A)-C(9A)-C(1A)	133.9(2)	134.5(2)	133.4(2)	133.7(2)
C(9A)-C(10A)-C(11A)	105.4(2)	105.2(2)	105.0(2)	105.6(2)
C(9A)-C(10A)-C(13A)	128.6(2)	128.9(2)	129.5(2)	129.2(2)
C(11A)-C(10A)-C(13A)	125.8(2)	125.7(2)	125.5(2)	125.2(2)
C(12A)-C(11A)-C(10A)	106.9(2)	107.3(2)	107.4(2)	106.8(2)
C(11A)-C(12A)-O(1A)	110.7(2)	110.6(2)	110.9(2)	110.7(2)
C(14A)-C(13A)-C(10A)	120.4(2)	121.1(2)	121.8(2)	122.5(2)
C(14A)-C(13A)-C(18A)	118.1(3)	117.9(3)	118.7(2)	118.1(2)
C(18A)-C(13A)-C(10A)	121.3(2)	120.9(2)	119.5(2)	119.4(2)
C(15A)-C(14A)-C(13A)	120.7(3)	120.9(3)	120.3(3)	121.1(2)
C(14A)-C(15A)-C(16A)	119.9(2)	120.0(3)	120.1(2)	119.7(2)
C(15A)-C(16A)-O(2A)	117.0(3)	117.4(3)	117.6(3)	123.0(2)
C(15A)-C(16A)-C(17A)	120.8(3)	120.7(3)	120.8(3)	120.5(2)
C(17A)-C(16A)-O(2A)	121.9(3)	121.6(3)	121.2(3)	116.2(2)
C(16A)-C(17A)-C(18A)	119.1(3)	119.1(3)	119.1(3)	119.6(3)
C(17A)-C(18A)-C(13A)	121.3(3)	121.4(3)	121.0(2)	120.9(3)
O(2A)-C(19A)-C(20A)	124.0(2)	124.0(3)	124.3(2)	124.0(2)
O(2A)-C(19A)-C(24A)	115.3(2)	115.2(2)	114.6(2)	114.5(2)
C(20A)-C(19A)-C(24A)	120.7(3)	120.8(3)	121.1(3)	121.3(3)
C(19A)-C(20A)-C(21A)	119.0(3)	119.3(3)	118.5(3)	118.7(3)
C(22A)-C(21A)-C(20A)	121.1(3)	120.6(3)	121.4(3)	120.9(3)
C(21A)-C(22A)-C(23A)	119.4(3)	119.1(3)	119.2(3)	119.6(3)
C(22A)-C(23A)-C(24A)	120.5(3)	121.1(3)	120.6(3)	120.5(3)
C(19A)-C(24A)-C(23A)	119.3(3)	119.1(3)	119.3(3)	118.9(3)

The X-ray structure of 2i

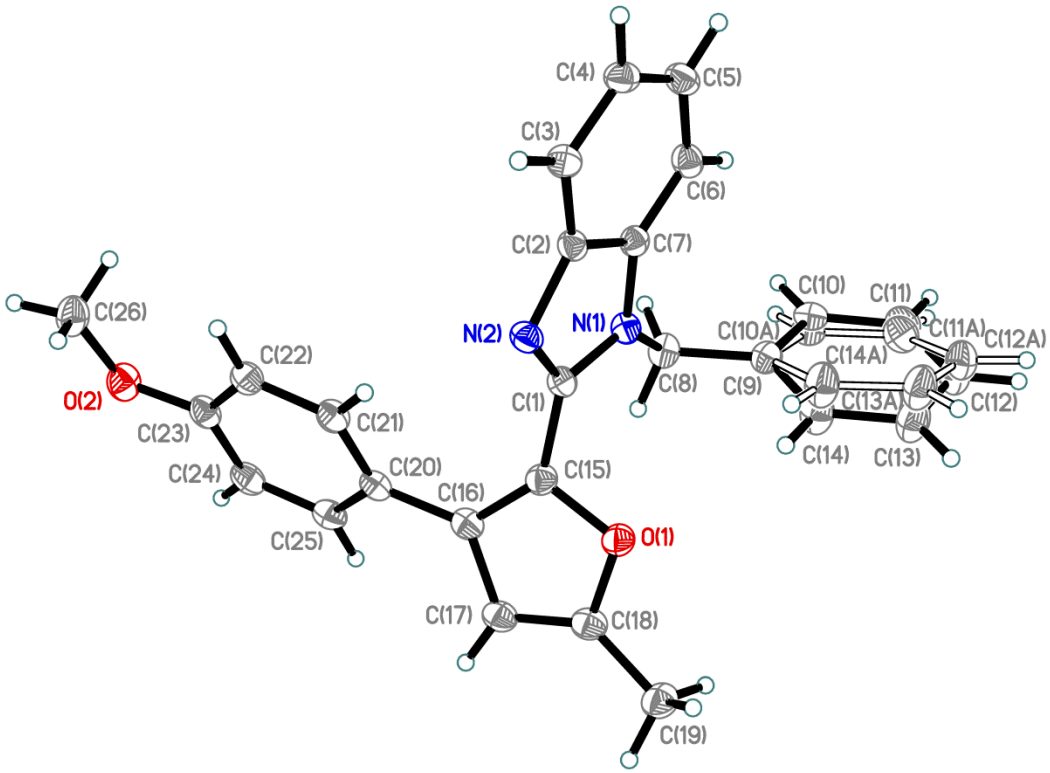


Figure S3. The structure of **2i** (p=50%). The Ph-group is disordered over two positions with the ratio of 0.787(10):0.213(10).

Table S4. Bond lengths for **2i** (Å)

N(1)-C(1)	1.3783(14)	C(9)-C(14)	1.3920(18)	O(1)-C(18)	1.3706(13)
N(1)-C(7)	1.3778(14)	C(9)-C(10A)	1.388(3)	C(16)-C(17)	1.4446(15)
N(1)-C(8)	1.4597(13)	C(9)-C(14A)	1.392(3)	C(16)-C(20)	1.4695(15)
C(1)-N(2)	1.3181(14)	C(10)-C(11)	1.396(2)	C(17)-C(18)	1.3499(16)
C(1)-C(15)	1.4676(15)	C(11)-C(12)	1.388(2)	C(18)-C(19)	1.4822(16)
N(2)-C(2)	1.3912(13)	C(12)-C(13)	1.387(2)	C(20)-C(21)	1.3954(16)
C(2)-C(3)	1.3989(15)	C(13)-C(14)	1.387(2)	C(20)-C(25)	1.4035(15)
C(2)-C(7)	1.4077(15)	C(10A)-C(11A)	1.396(3)	C(21)-C(22)	1.3888(16)
C(3)-C(4)	1.3879(15)	C(11A)-C(12A)	1.387(3)	C(22)-C(23)	1.3908(16)
C(4)-C(5)	1.4072(16)	C(12A)-C(13A)	1.386(3)	C(23)-C(24)	1.3976(17)
C(5)-C(6)	1.3831(16)	C(13A)-C(14A)	1.386(3)	C(23)-O(2)	1.3656(14)
C(6)-C(7)	1.3946(15)	C(15)-O(1)	1.3801(13)	C(24)-C(25)	1.3858(17)
C(8)-C(9)	1.5107(15)	C(15)-C(16)	1.3621(15)	O(2)-C(26)	1.4265(15)
C(9)-C(10)	1.3877(17)				

Table S5. Bond angles for **2i** (°)

C(1)-N(1)-C(8)	127.11(9)	C(13)-C(14)-C(9)	120.12(18)
C(7)-N(1)-C(1)	106.50(9)	C(9)-C(10A)-C(11A)	115.2(16)
C(7)-N(1)-C(8)	125.85(9)	C(12A)-C(11A)-C(10A)	128(2)
N(1)-C(1)-C(15)	120.49(9)	C(13A)-C(12A)-C(11A)	114.3(17)
N(2)-C(1)-N(1)	113.40(9)	C(14A)-C(13A)-C(12A)	120.0(12)
N(2)-C(1)-C(15)	126.00(10)	C(13A)-C(14A)-C(9)	123.5(7)
C(1)-N(2)-C(2)	104.51(9)	O(1)-C(15)-C(1)	113.54(9)
N(2)-C(2)-C(3)	129.85(10)	C(16)-C(15)-C(1)	135.98(10)
N(2)-C(2)-C(7)	110.22(9)	C(16)-C(15)-O(1)	110.40(9)
C(3)-C(2)-C(7)	119.93(10)	C(18)-O(1)-C(15)	106.96(8)
C(4)-C(3)-C(2)	117.54(10)	C(15)-C(16)-C(17)	105.27(10)
C(3)-C(4)-C(5)	121.64(10)	C(15)-C(16)-C(20)	127.79(10)
C(6)-C(5)-C(4)	121.65(10)	C(17)-C(16)-C(20)	126.94(10)
C(5)-C(6)-C(7)	116.45(10)	C(18)-C(17)-C(16)	107.54(10)
N(1)-C(7)-C(2)	105.38(9)	O(1)-C(18)-C(19)	115.53(10)
N(1)-C(7)-C(6)	131.85(10)	C(17)-C(18)-O(1)	109.81(10)
C(6)-C(7)-C(2)	122.77(10)	C(17)-C(18)-C(19)	134.65(11)
N(1)-C(8)-C(9)	113.84(9)	C(21)-C(20)-C(16)	120.79(10)
C(10)-C(9)-C(8)	119.9(2)	C(21)-C(20)-C(25)	117.83(10)
C(10)-C(9)-C(14)	119.1(2)	C(25)-C(20)-C(16)	121.37(10)
C(14)-C(9)-C(8)	120.89(13)	C(22)-C(21)-C(20)	121.74(10)
C(10A)-C(9)-C(8)	118.9(8)	C(21)-C(22)-C(23)	119.65(11)
C(10A)-C(9)-C(14A)	118.8(9)	C(22)-C(23)-C(24)	119.60(10)
C(14A)-C(9)-C(8)	122.2(4)	O(2)-C(23)-C(22)	124.25(11)
C(9)-C(10)-C(11)	121.4(4)	O(2)-C(23)-C(24)	116.15(10)
C(12)-C(11)-C(10)	118.6(5)	C(25)-C(24)-C(23)	120.21(10)
C(13)-C(12)-C(11)	120.7(4)	C(24)-C(25)-C(20)	120.96(11)
C(14)-C(13)-C(12)	120.1(3)	C(23)-O(2)-C(26)	116.61(9)

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

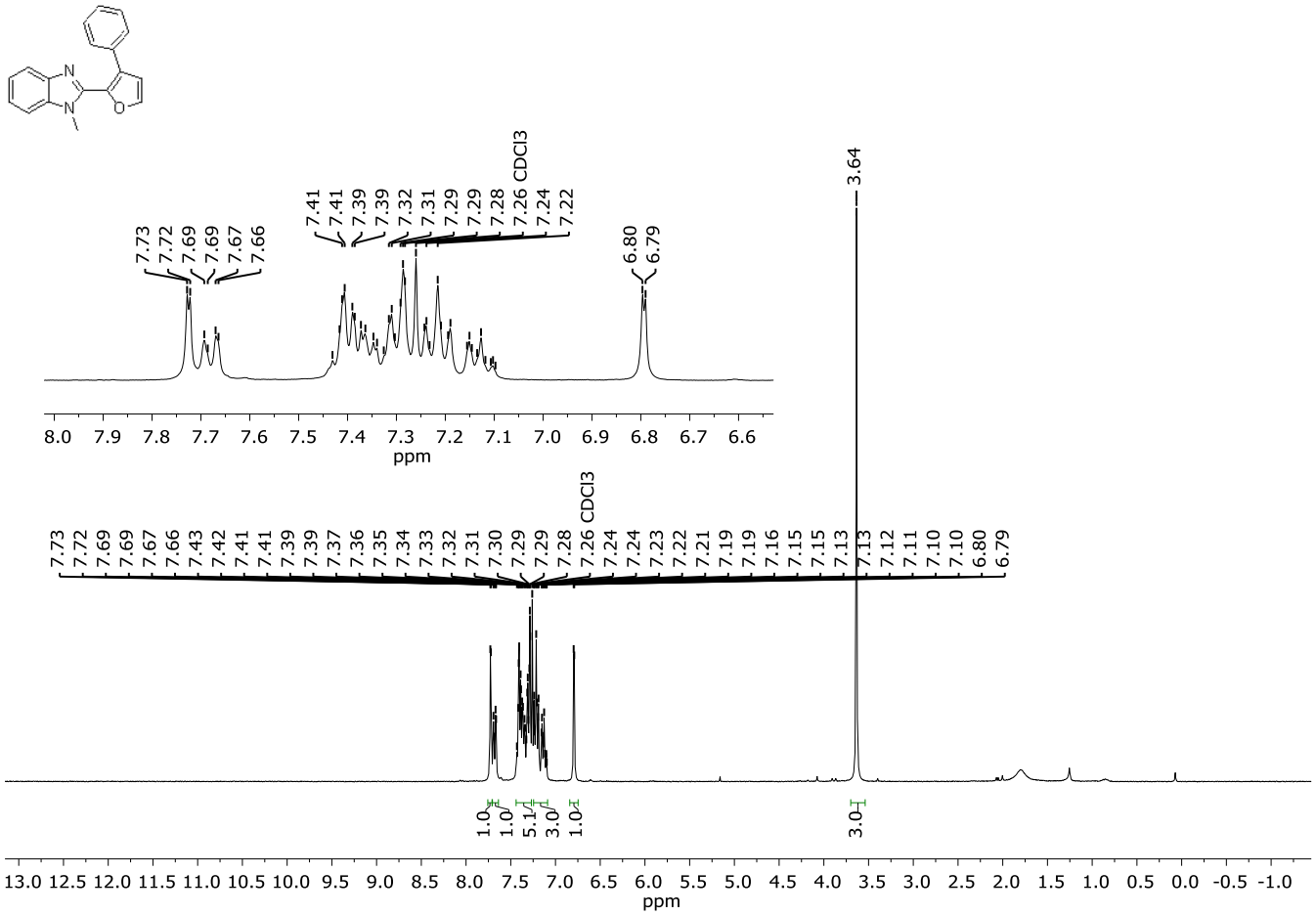


Figure S1. ^{1}H NMR spectrum of compound **2a** (300 MHz, $CDCl_3$).

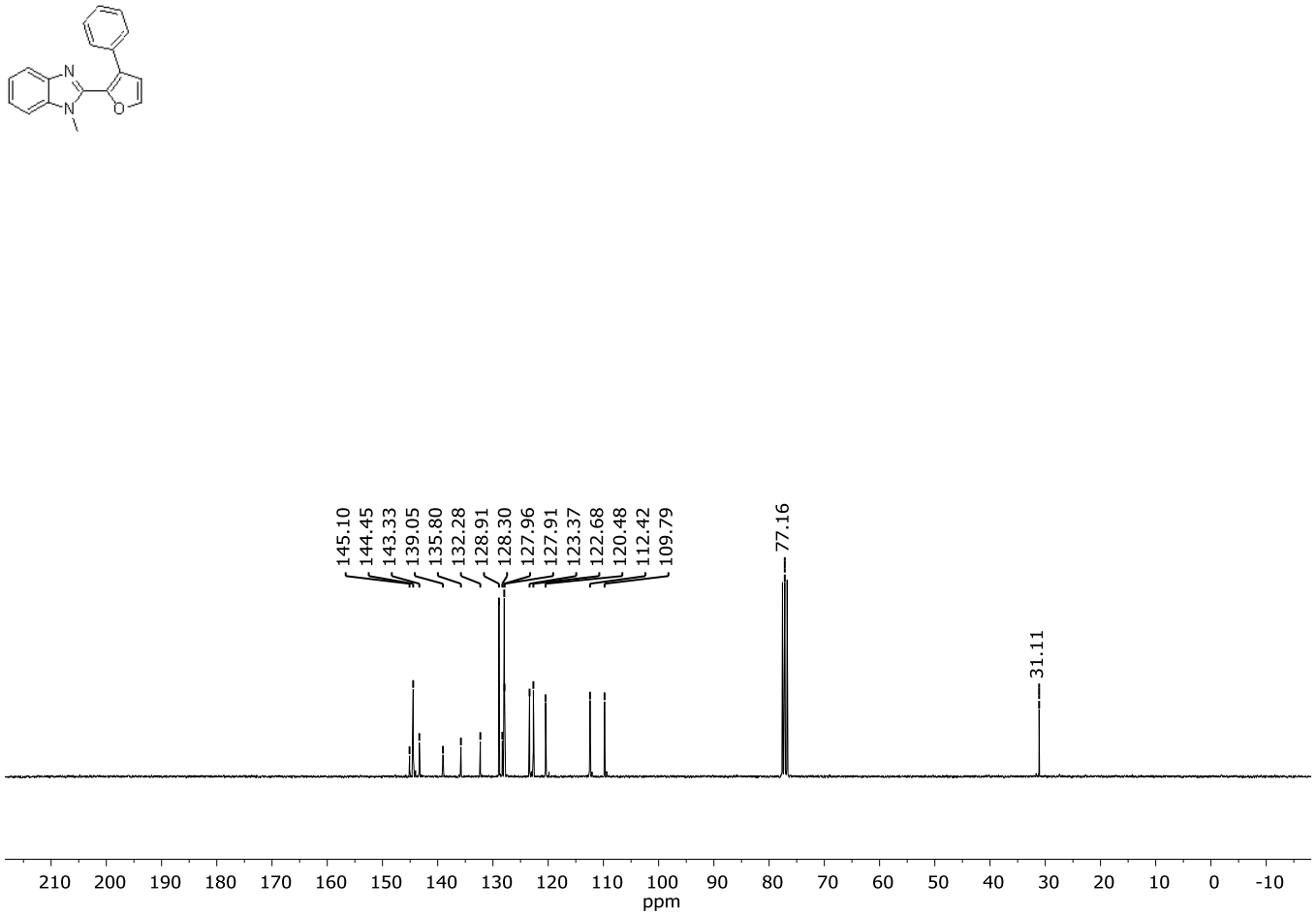


Figure S2. ^{13}C NMR spectrum of compound **2a** (75 MHz, $CDCl_3$).

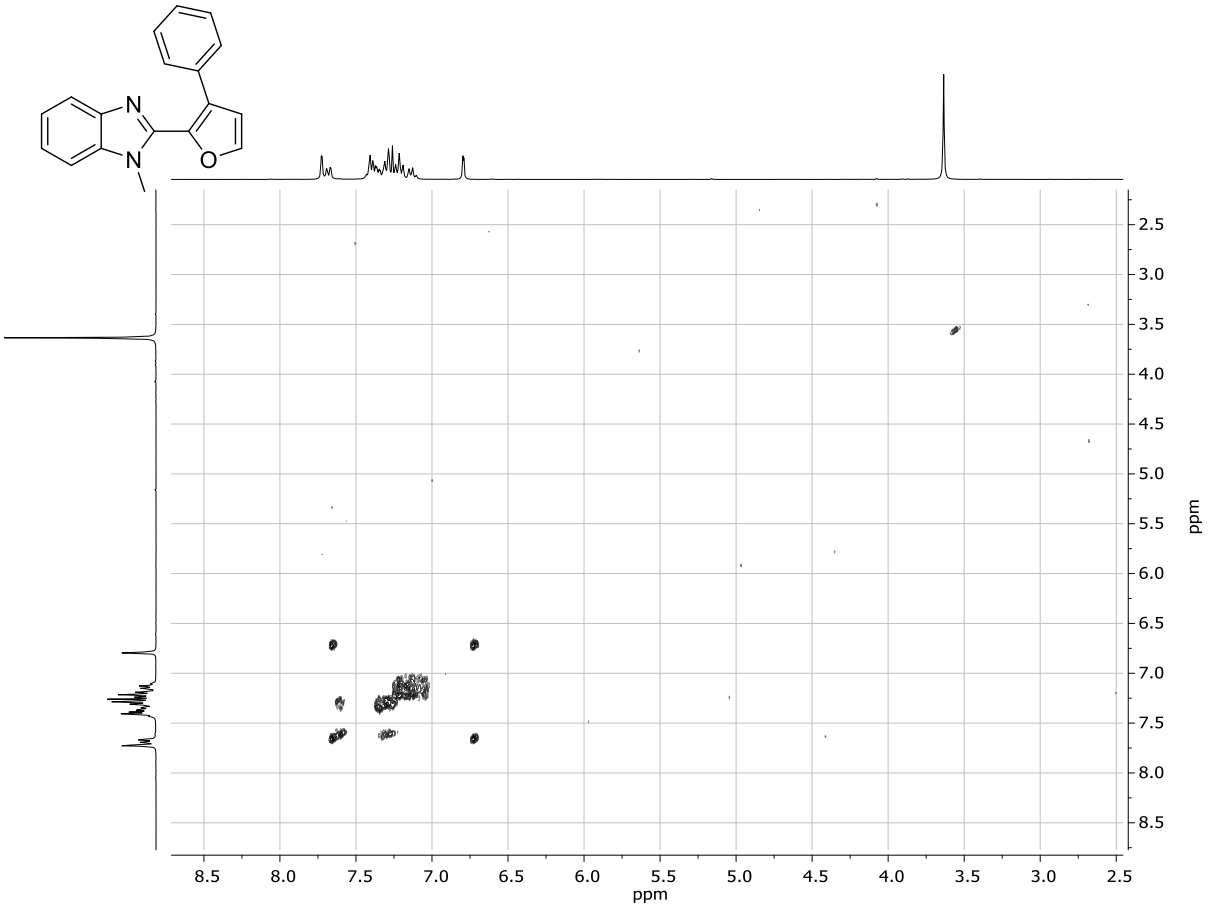


Figure S3. ^{1}H-^{1}H COSY spectrum of compound **2a** ($CDCl_3$)

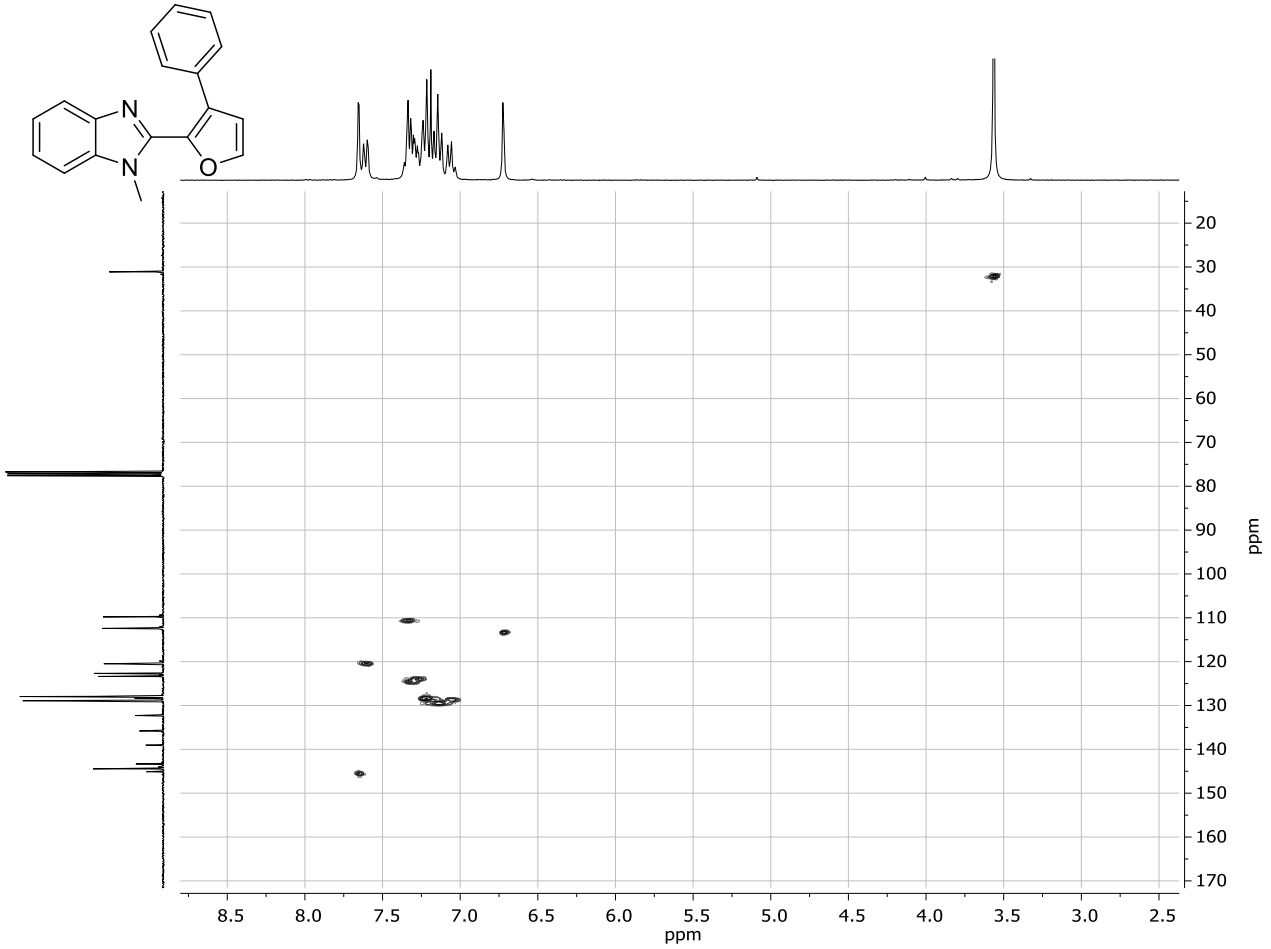


Figure S4. ^{1}H-^{13}C HSQC spectrum of compound **2a** ($CDCl_3$)

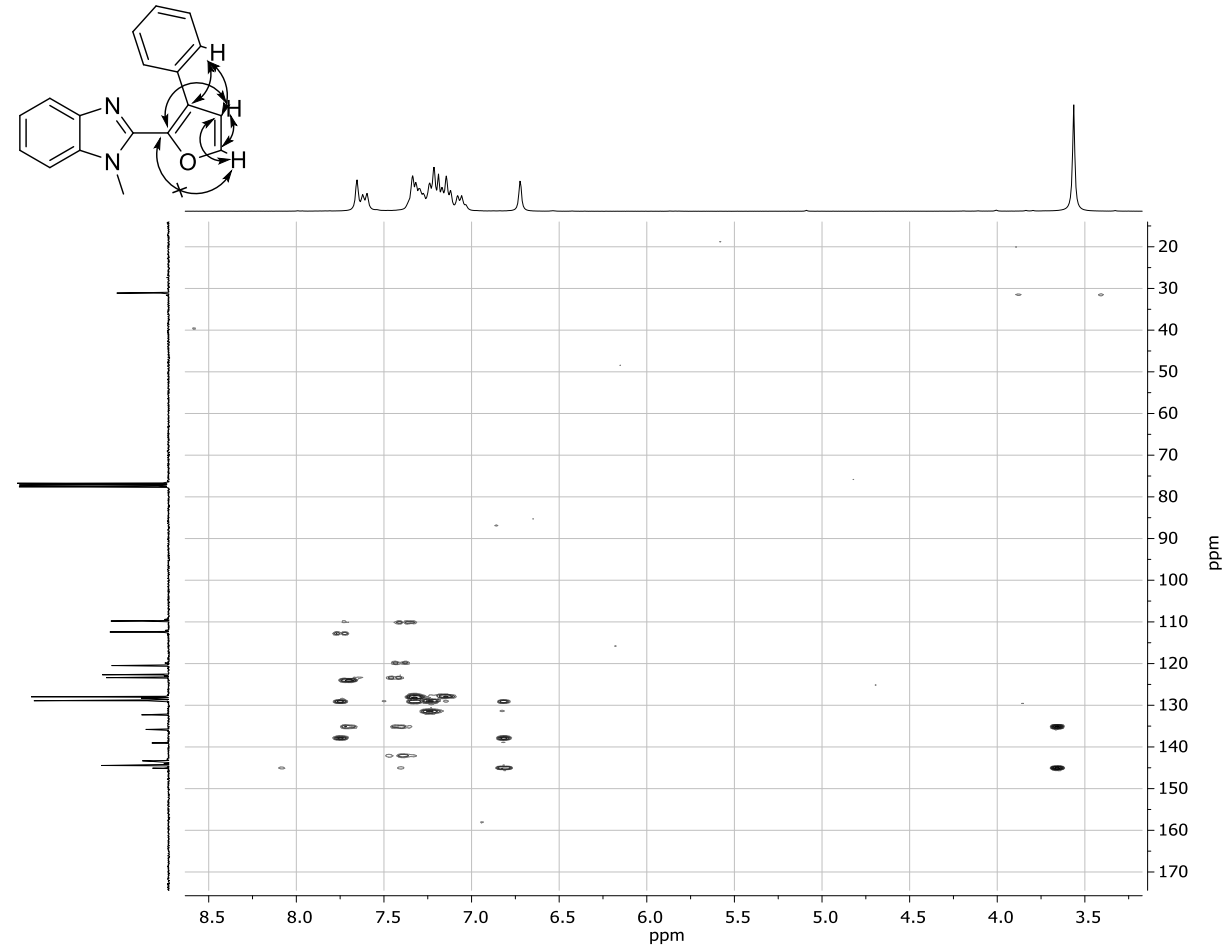


Figure S5. ^{1}H-^{13}C HMBC spectrum of compound **2a** ($CDCl_3$)

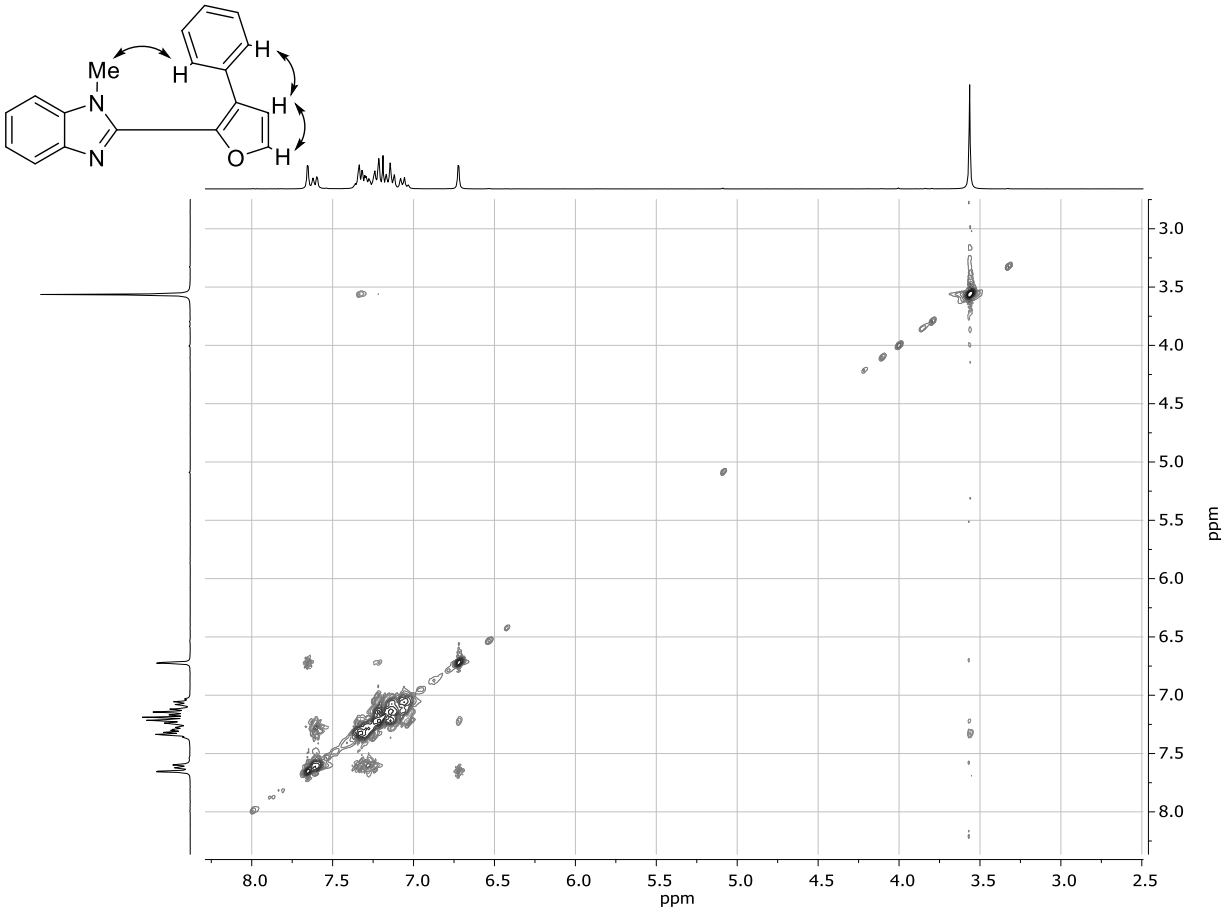


Figure S6. ^{1}H-^{1}H NOESY spectrum of compound **2a** ($CDCl_3$)

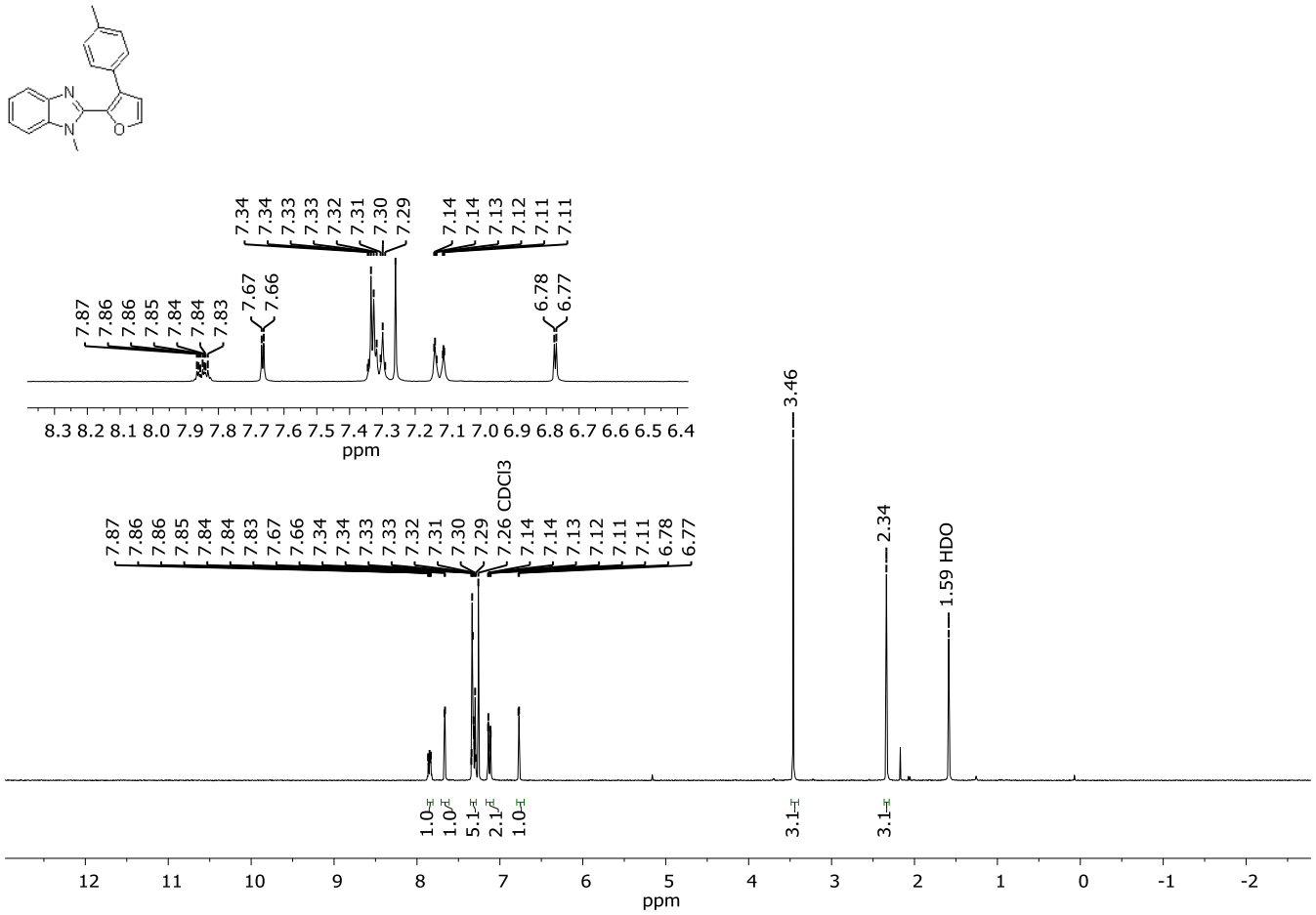


Figure S7. ^{1}H NMR spectrum of compound **2b** (300 MHz, $CDCl_3$).

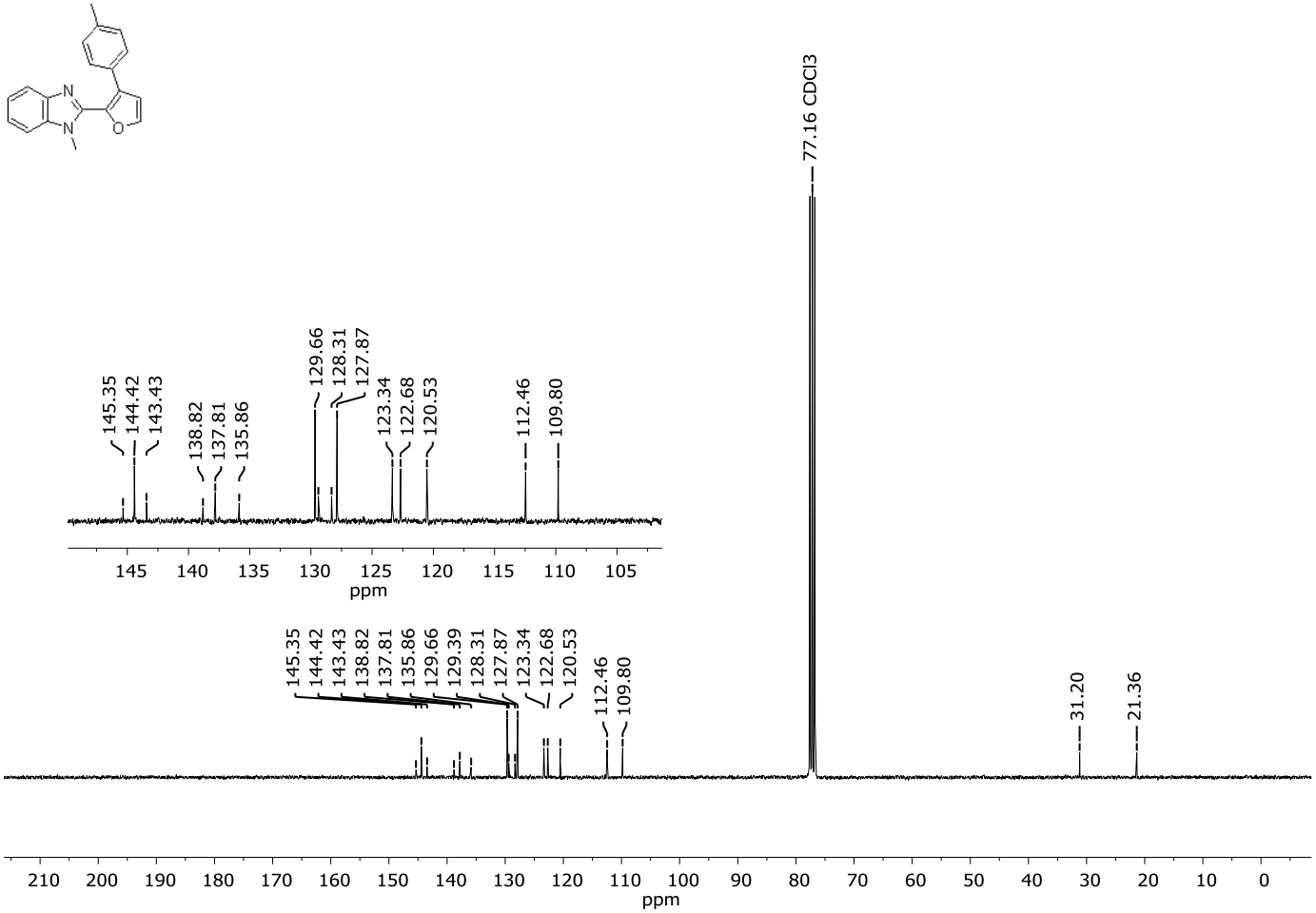


Figure S8. ^{13}C NMR spectrum of compound **2b** (75 MHz, $CDCl_3$).

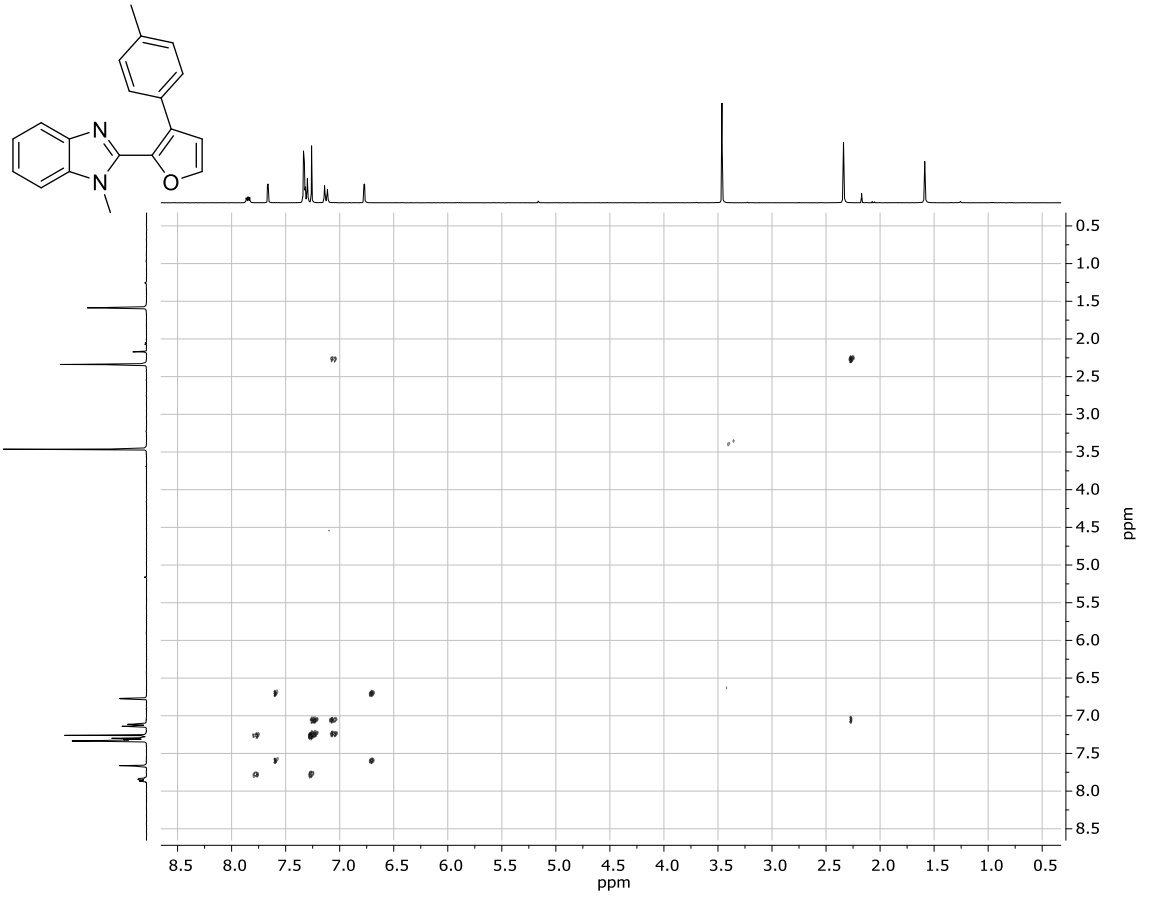


Figure S9. ^{1}H-^{1}H COSY spectrum of compound **2b** ($CDCl_3$).

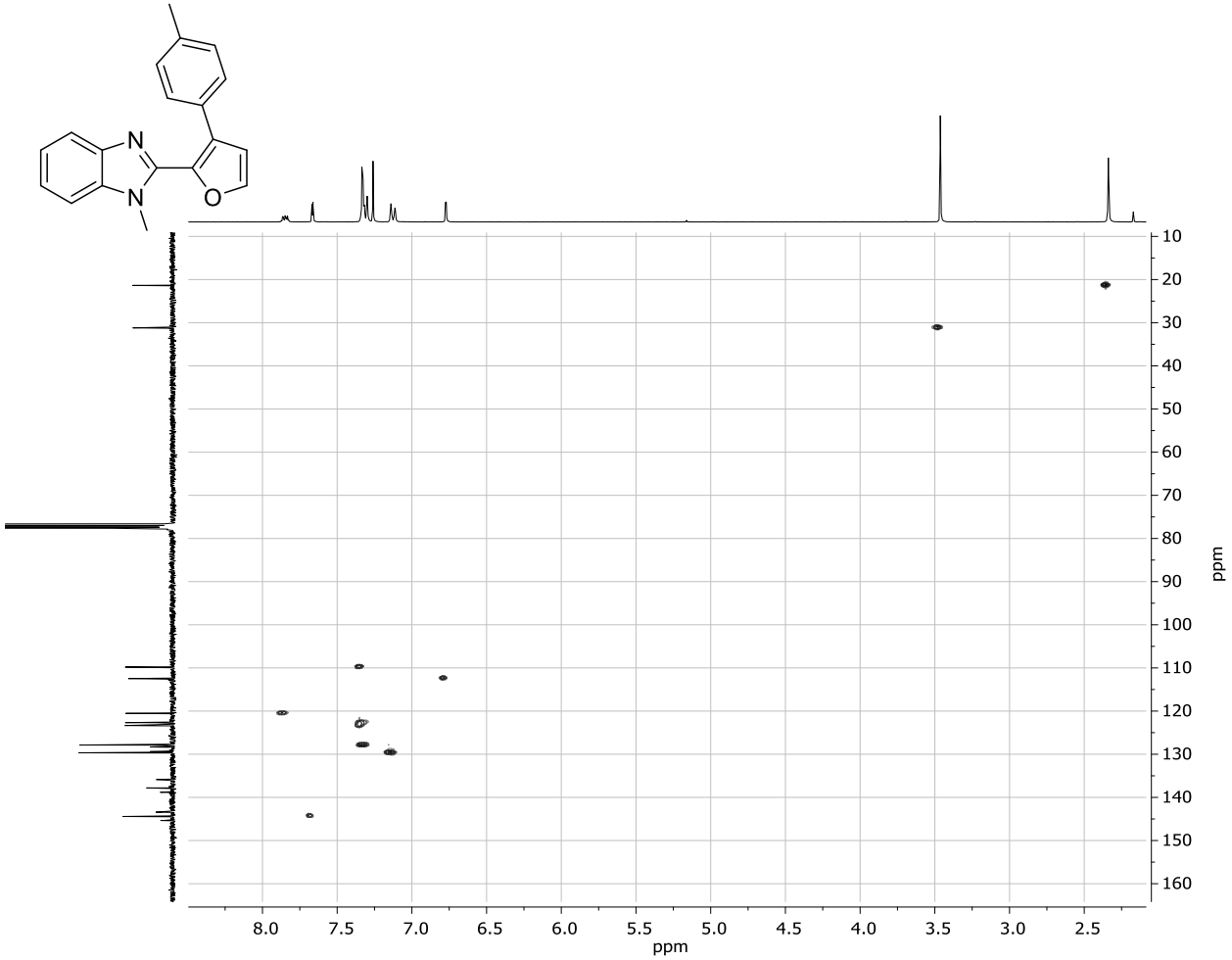


Figure S10. ^{1}H-^{13}C HSQC spectrum of compound **2b** ($CDCl_3$).

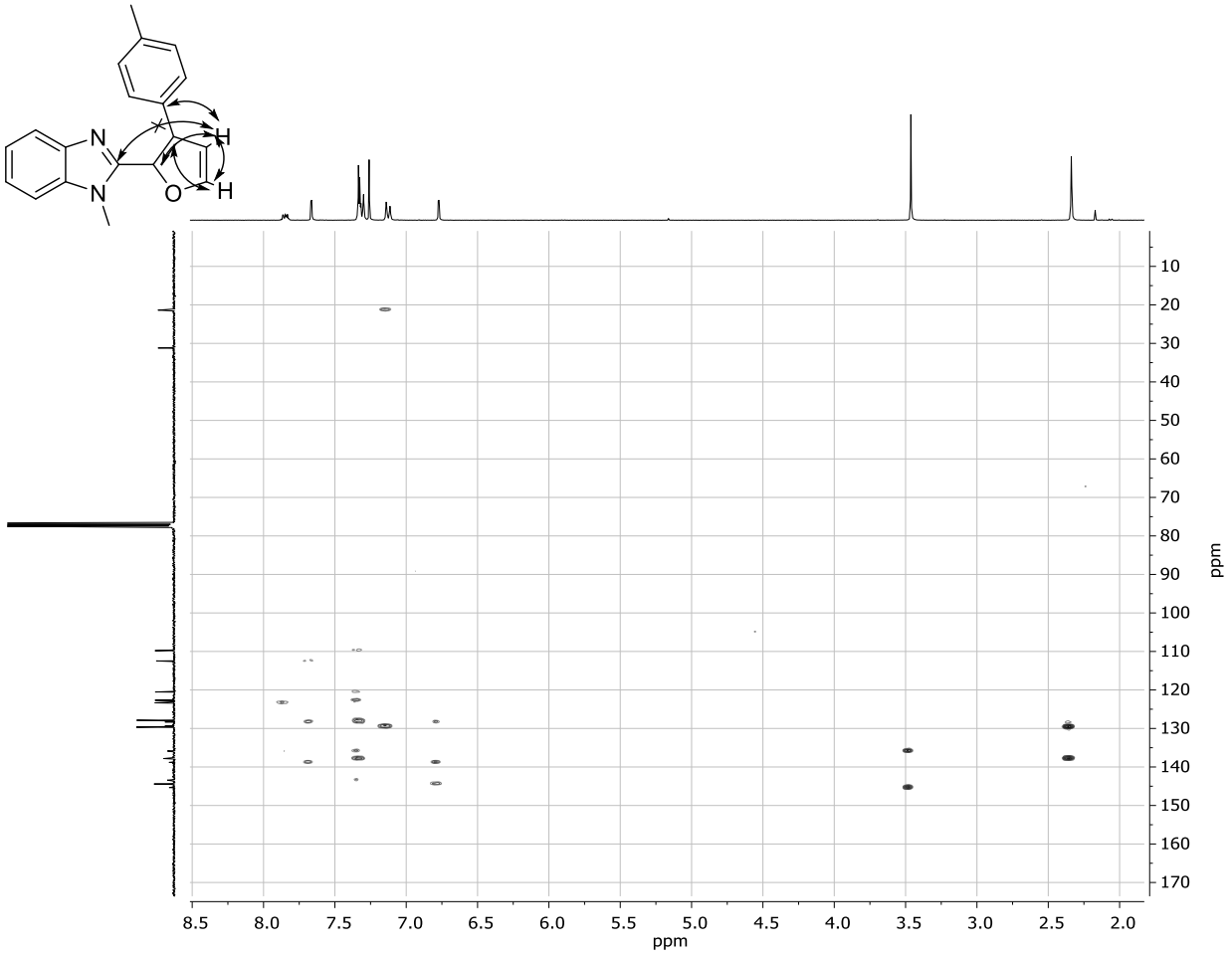


Figure S11. ^{1}H-^{13}C HMBC spectrum of compound **2b** ($CDCl_3$)

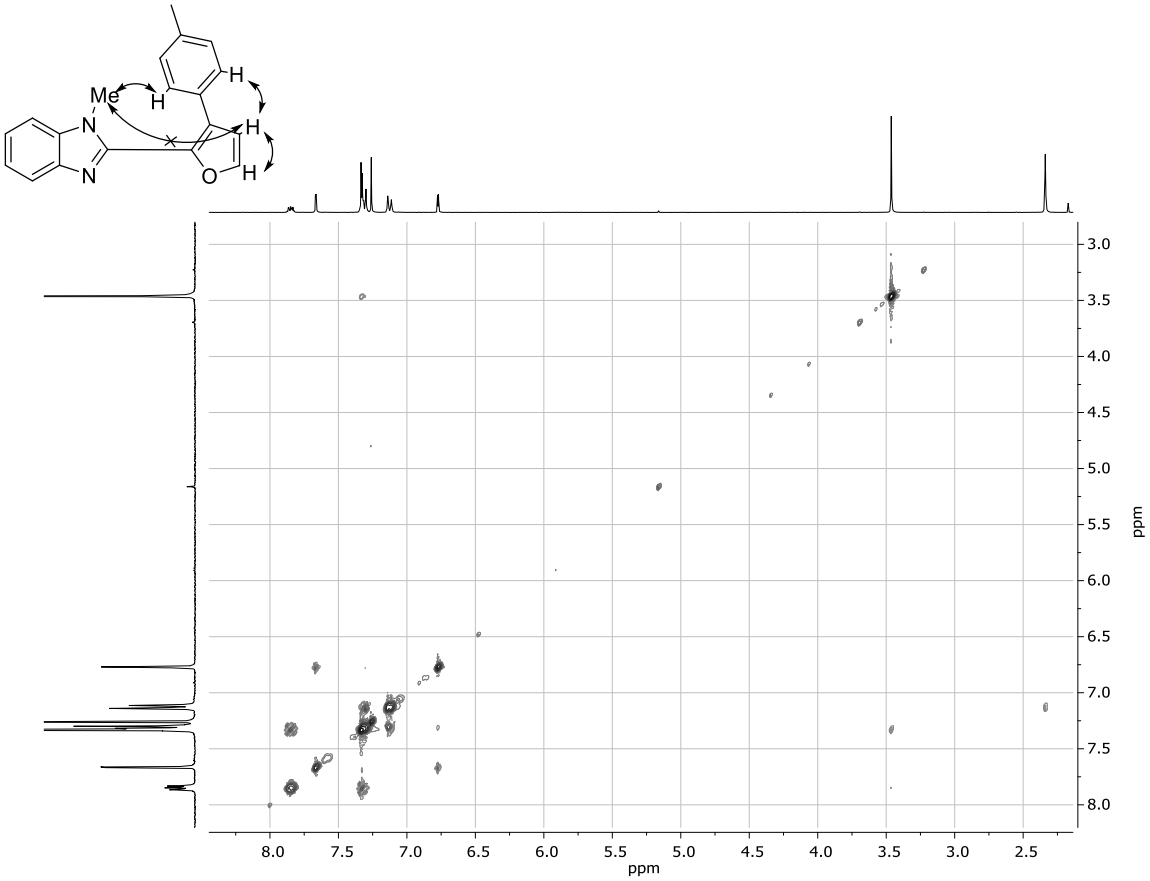


Figure S12. ^{1}H-^{1}H NOESY spectrum of compound **2b** ($CDCl_3$)

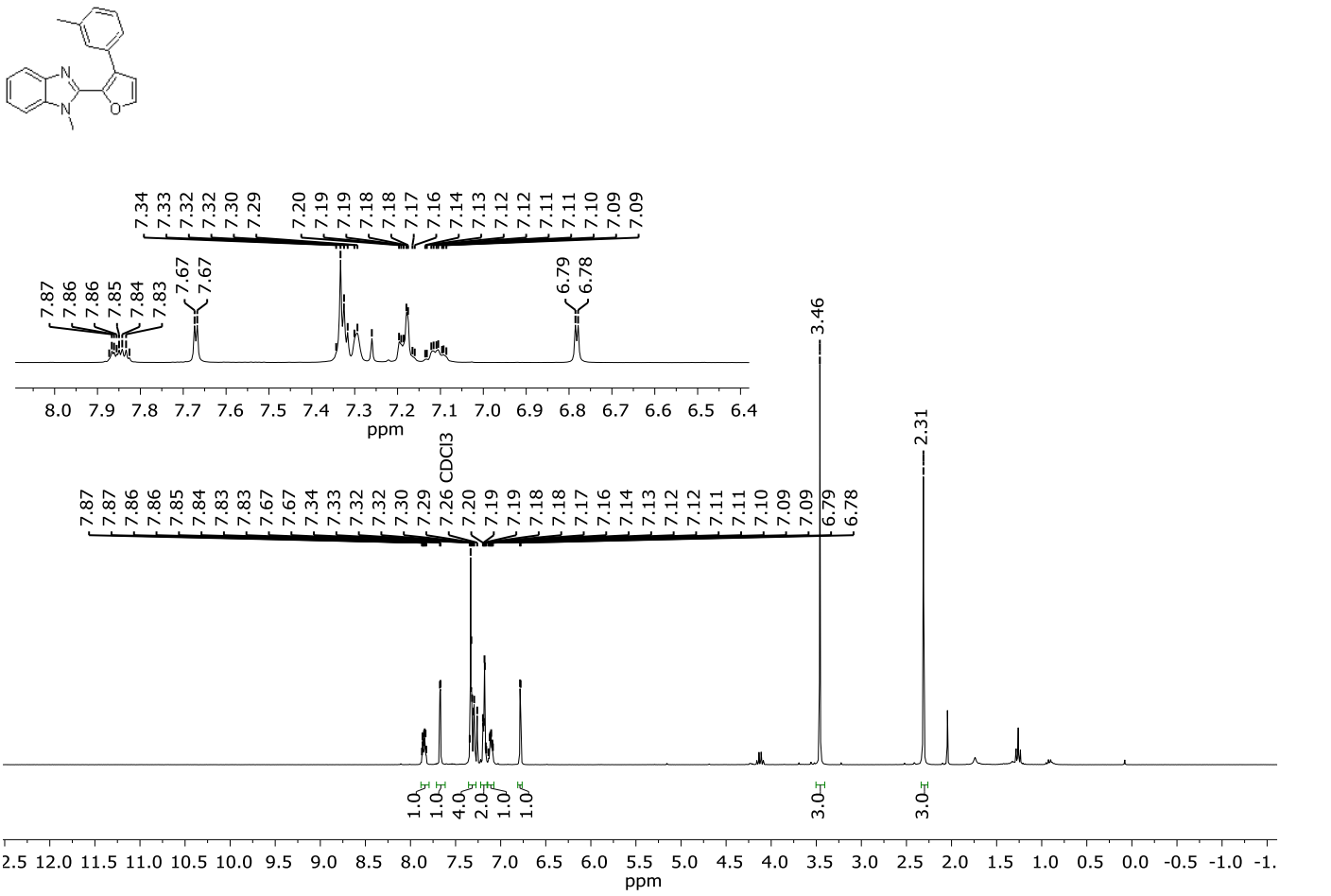


Figure S13. ^{1}H NMR spectrum of compound **2c** (300 MHz, $CDCl_3$)

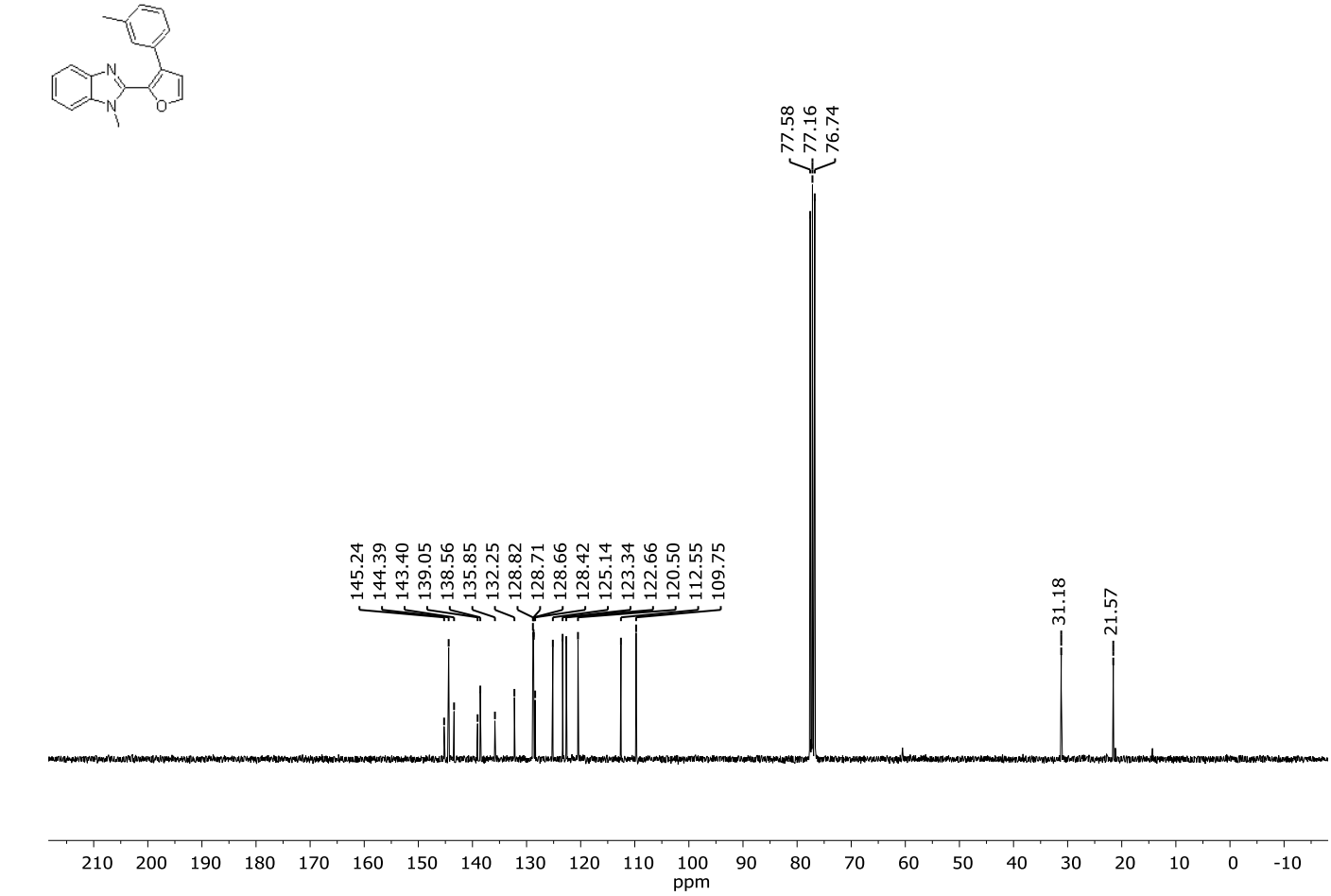


Figure S14. ^{13}C NMR spectrum of compound **2c** (75 MHz, $CDCl_3$).

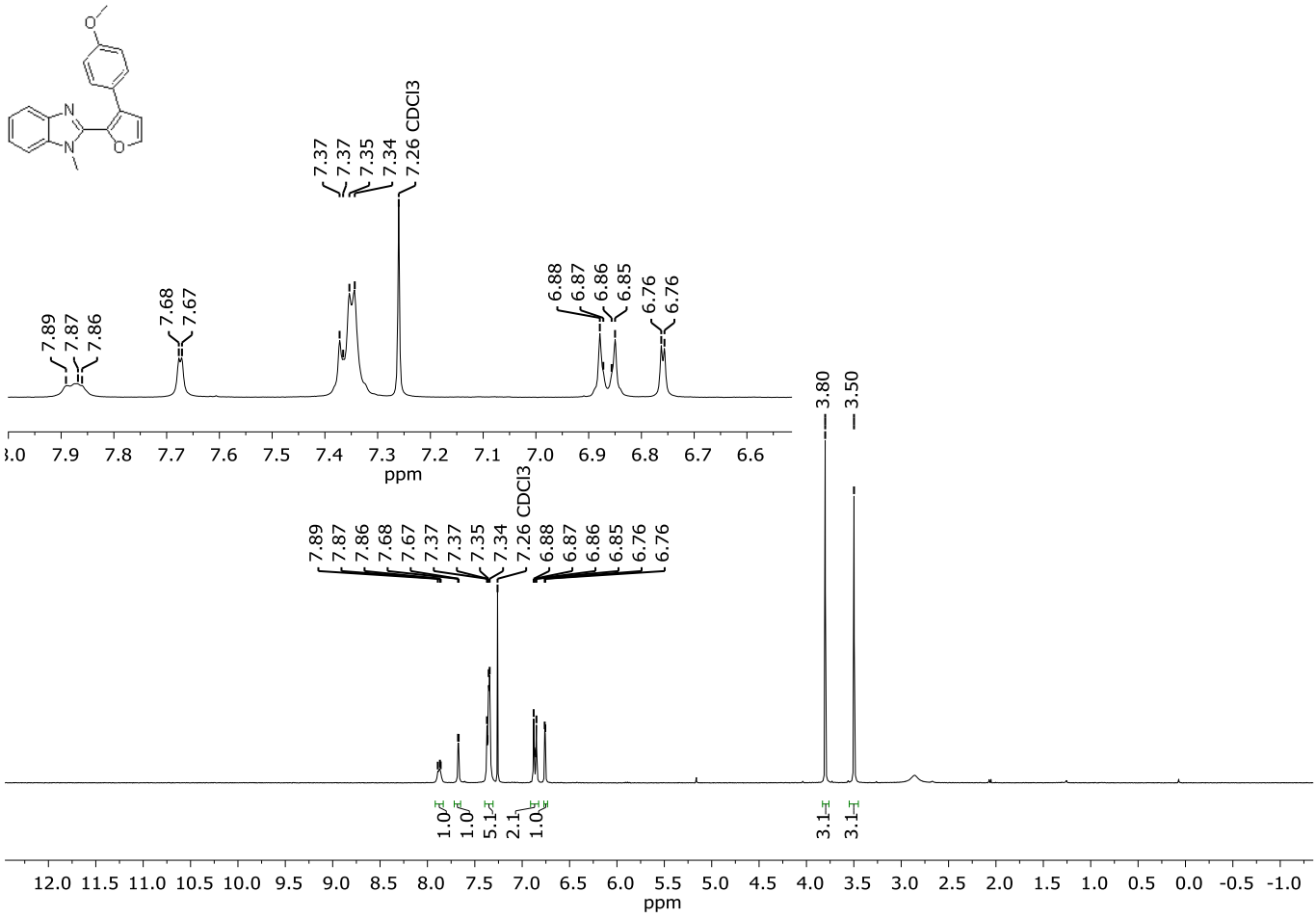


Figure S15. ^{1}H NMR spectrum of compound **2d** (300 MHz, $CDCl_3$).

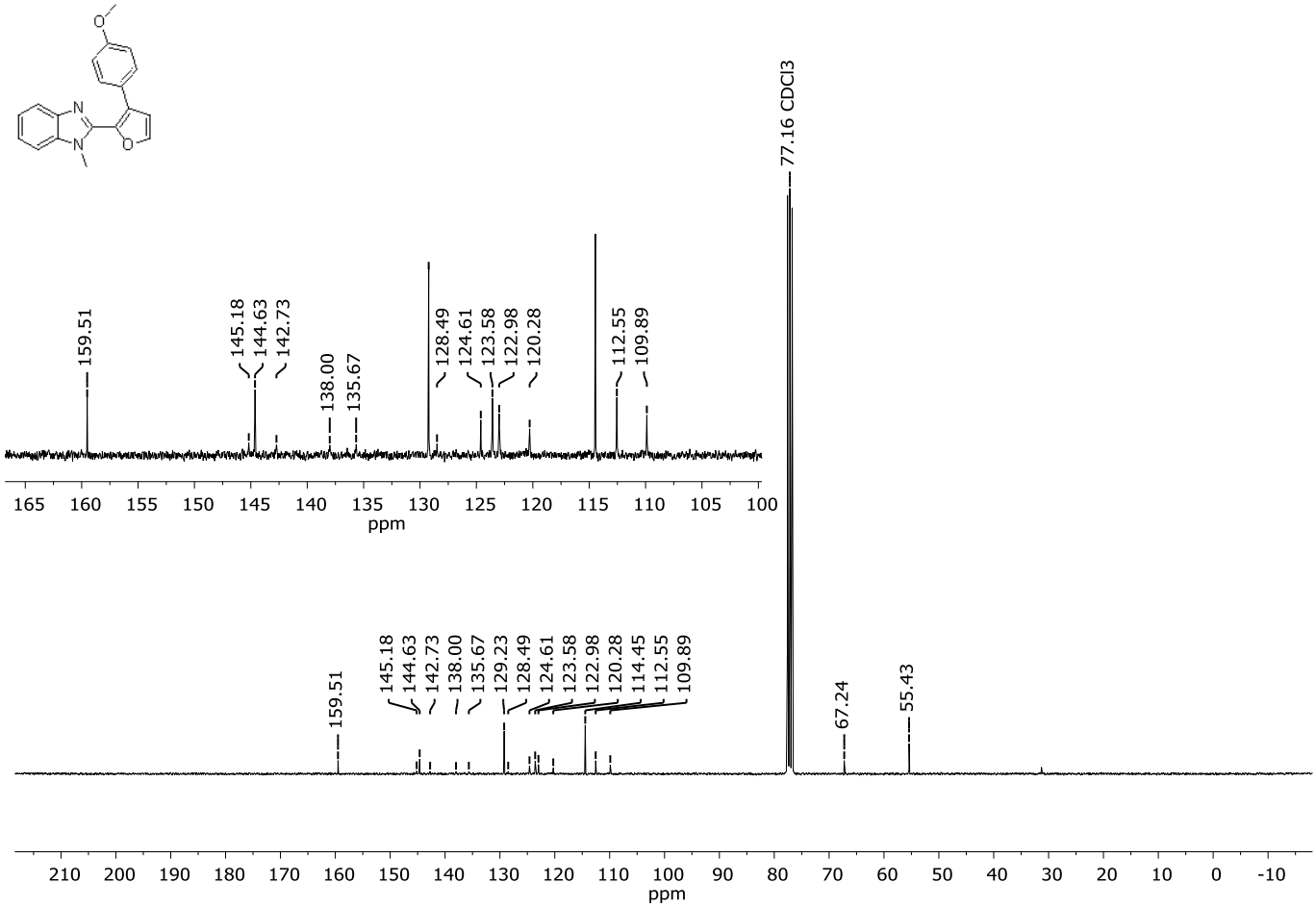


Figure S16. ^{13}C NMR spectrum of compound **2d** (75 MHz, $CDCl_3$).

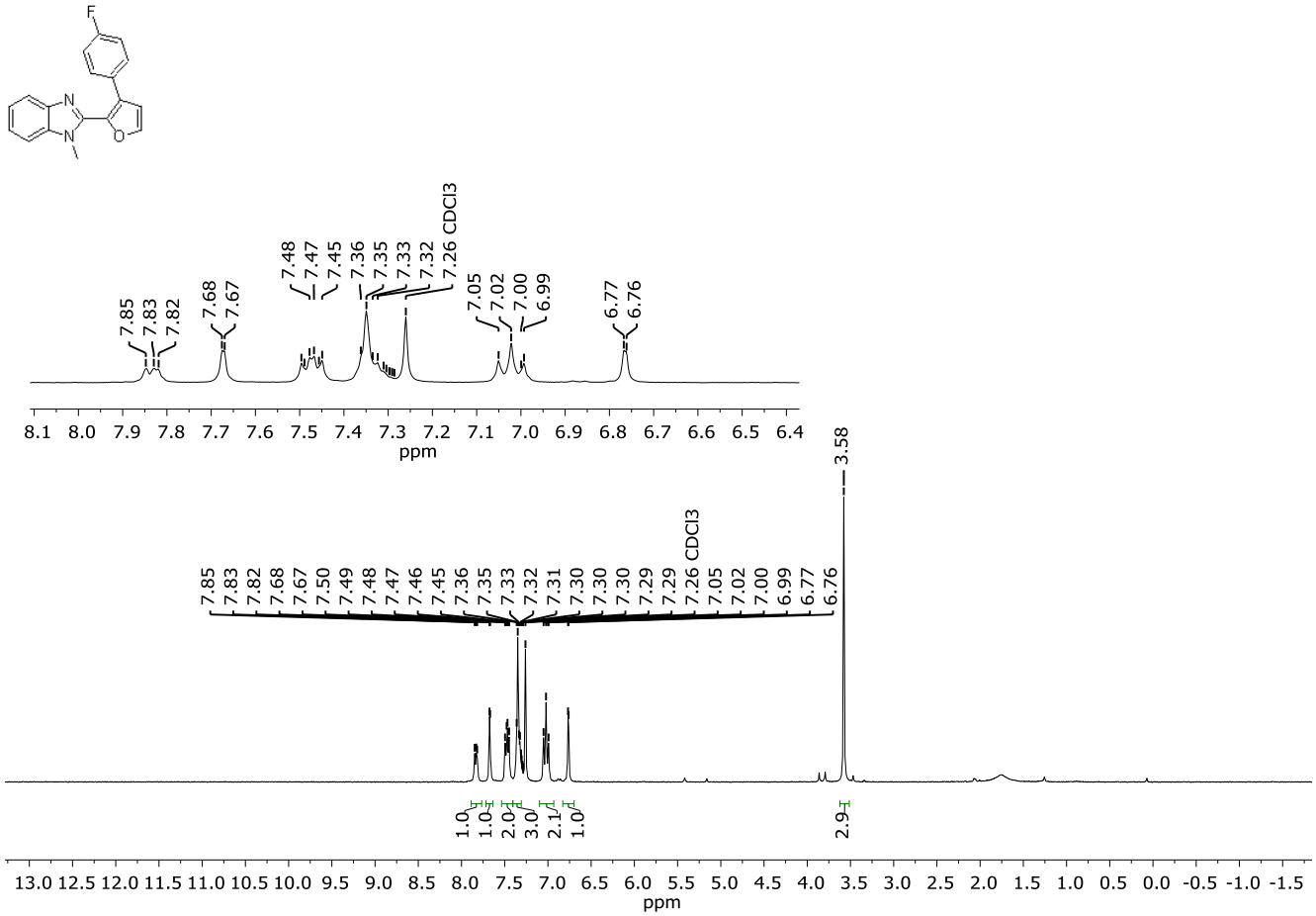


Figure S17. ^{1}H NMR spectrum of compound **2e** (300 MHz, $CDCl_3$).

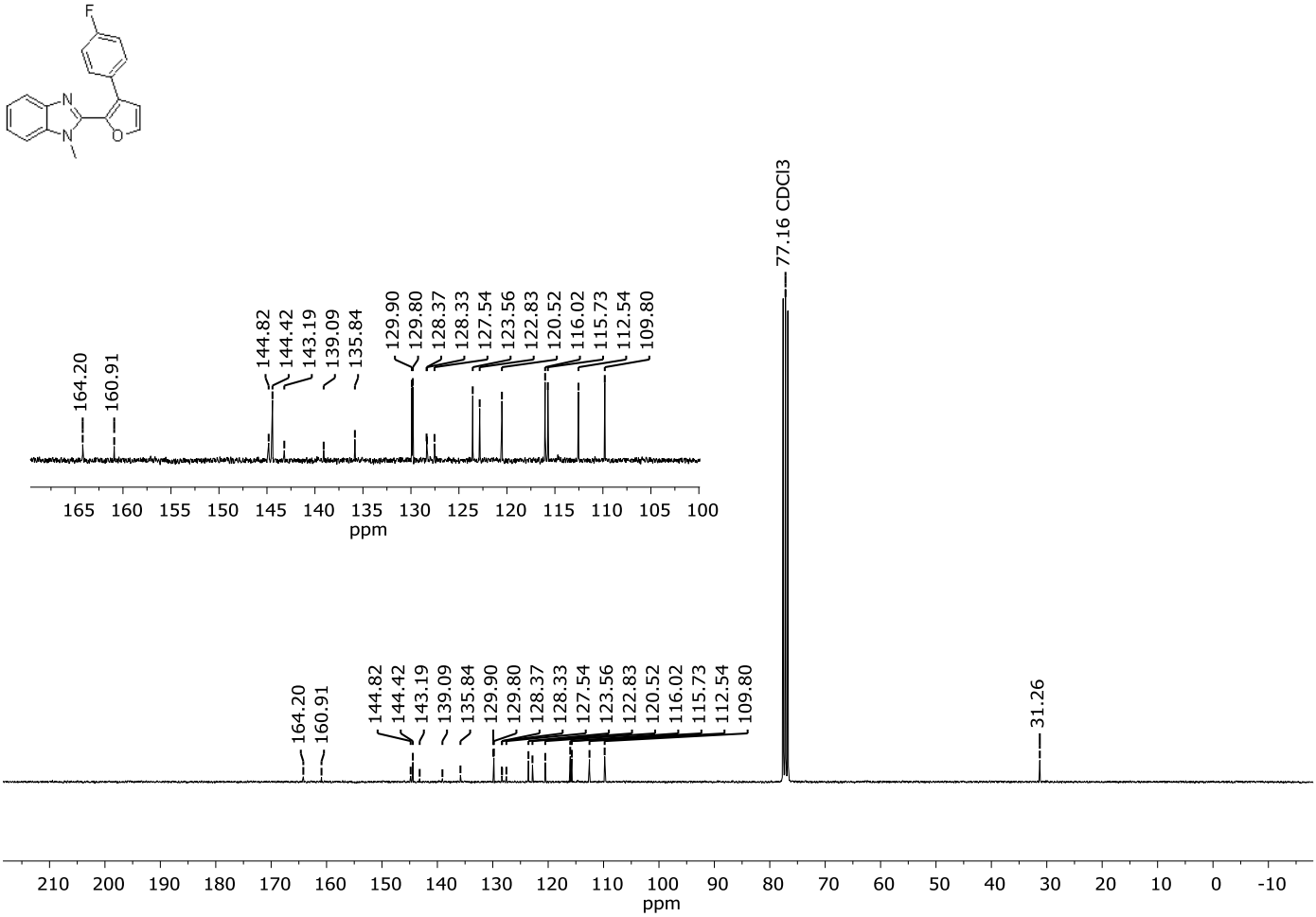


Figure S18. ^{13}C NMR spectrum of compound **2e** (75 MHz, $CDCl_3$).

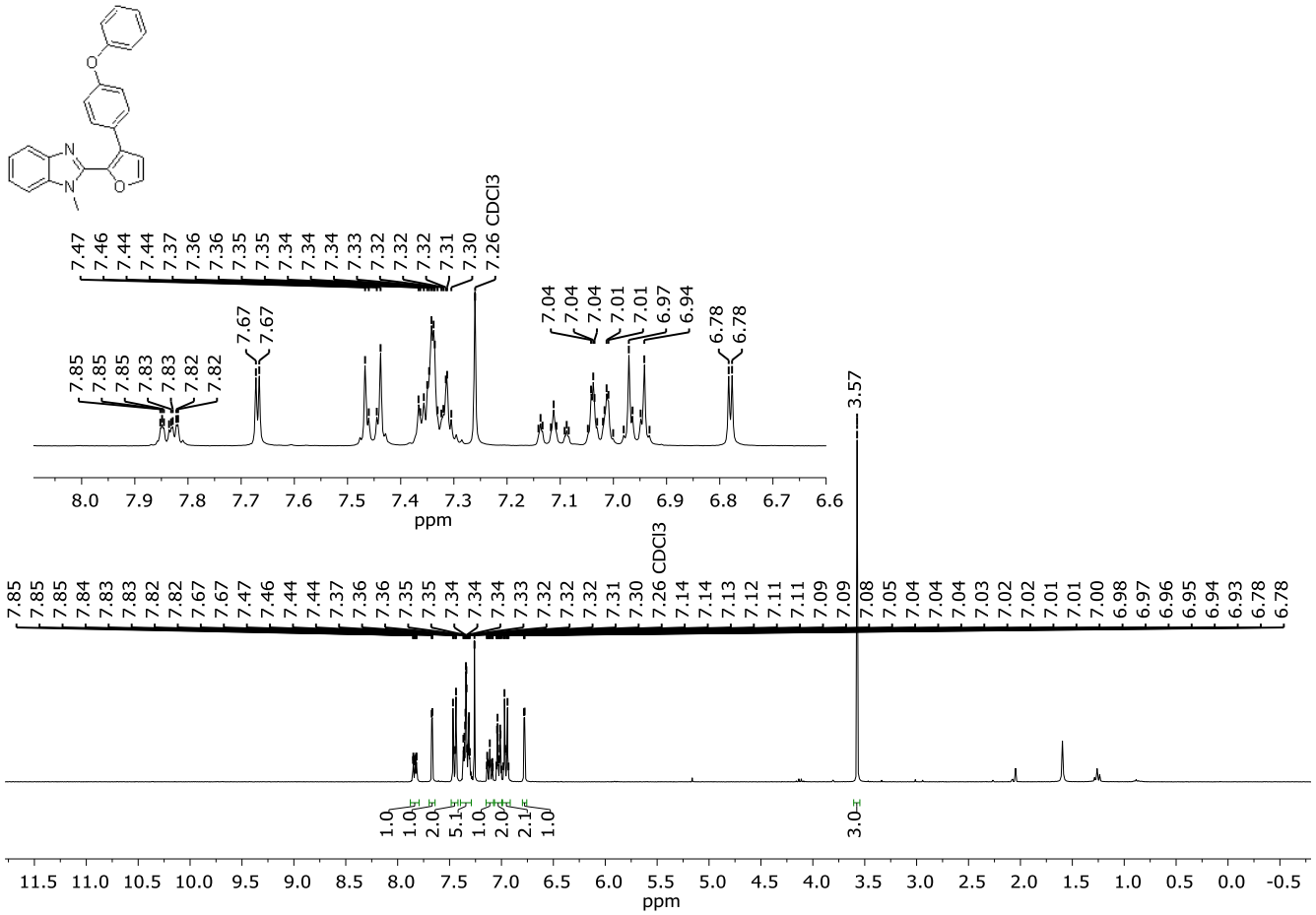


Figure S19. ^{1}H NMR spectrum of compound **2f** (300 MHz, $CDCl_3$).

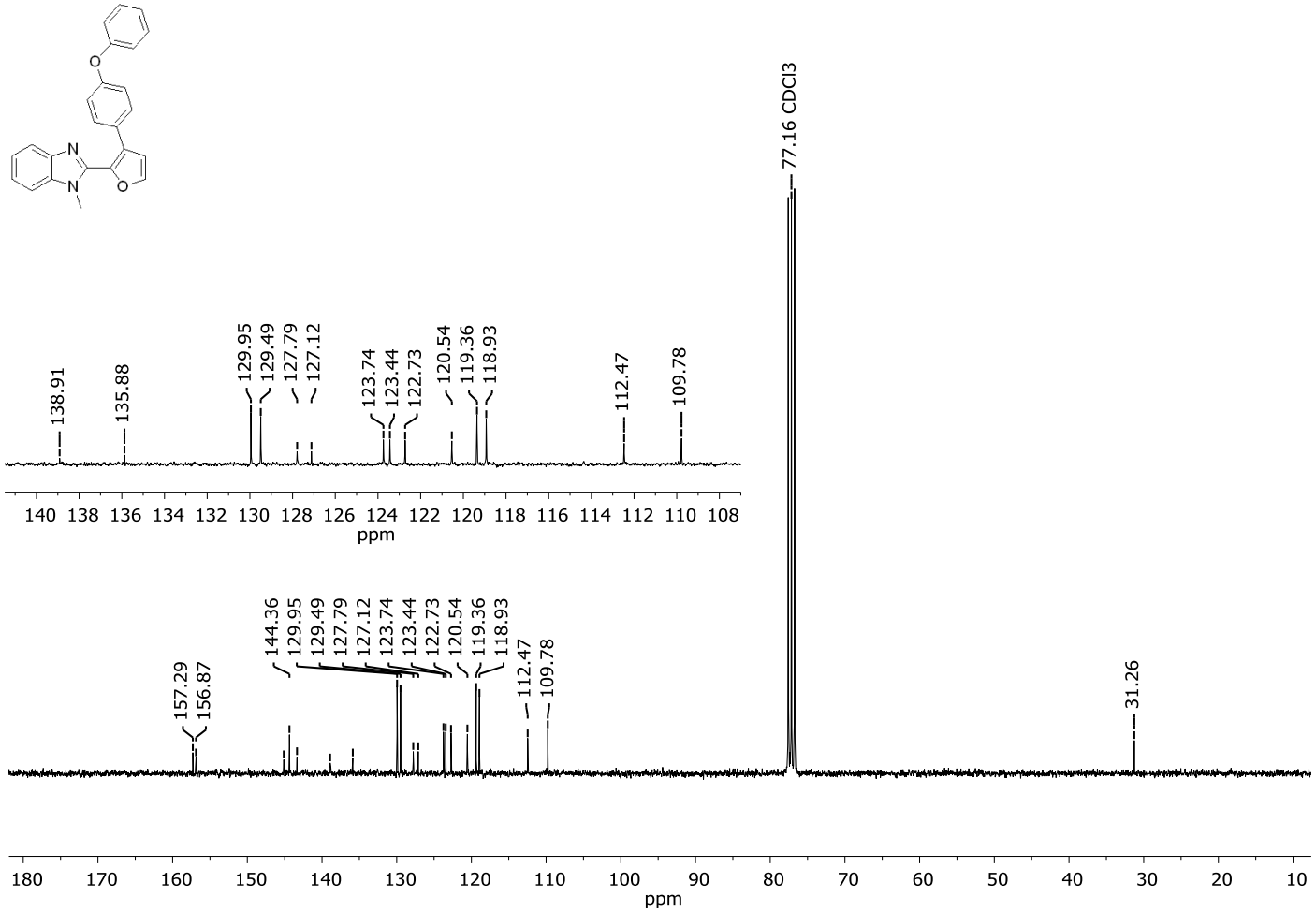


Figure S20. ^{13}C NMR spectrum of compound **2f** (75 MHz, $CDCl_3$).

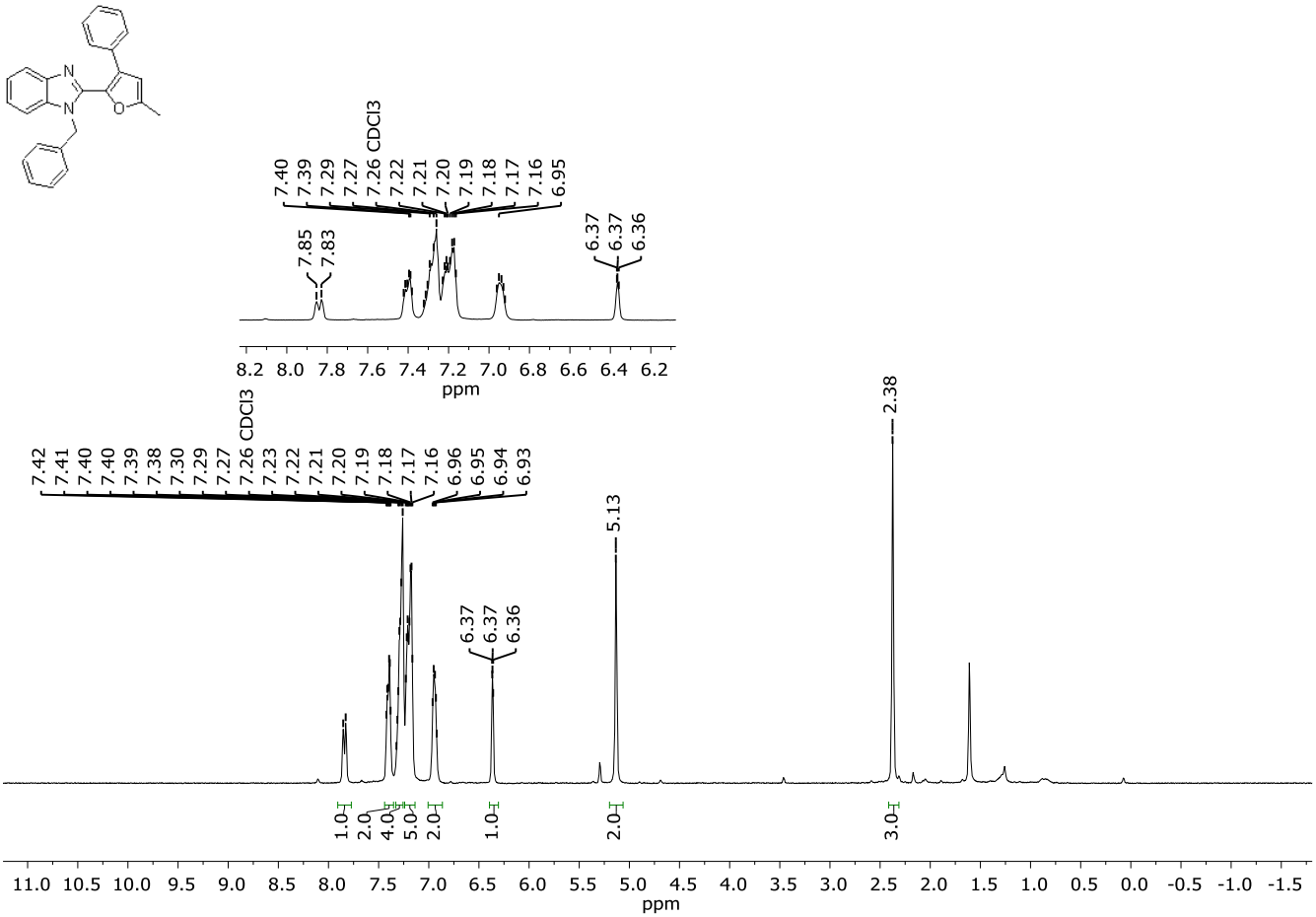


Figure S21. ^{1}H NMR spectrum of compound **2g** (300 MHz, $CDCl_3$).

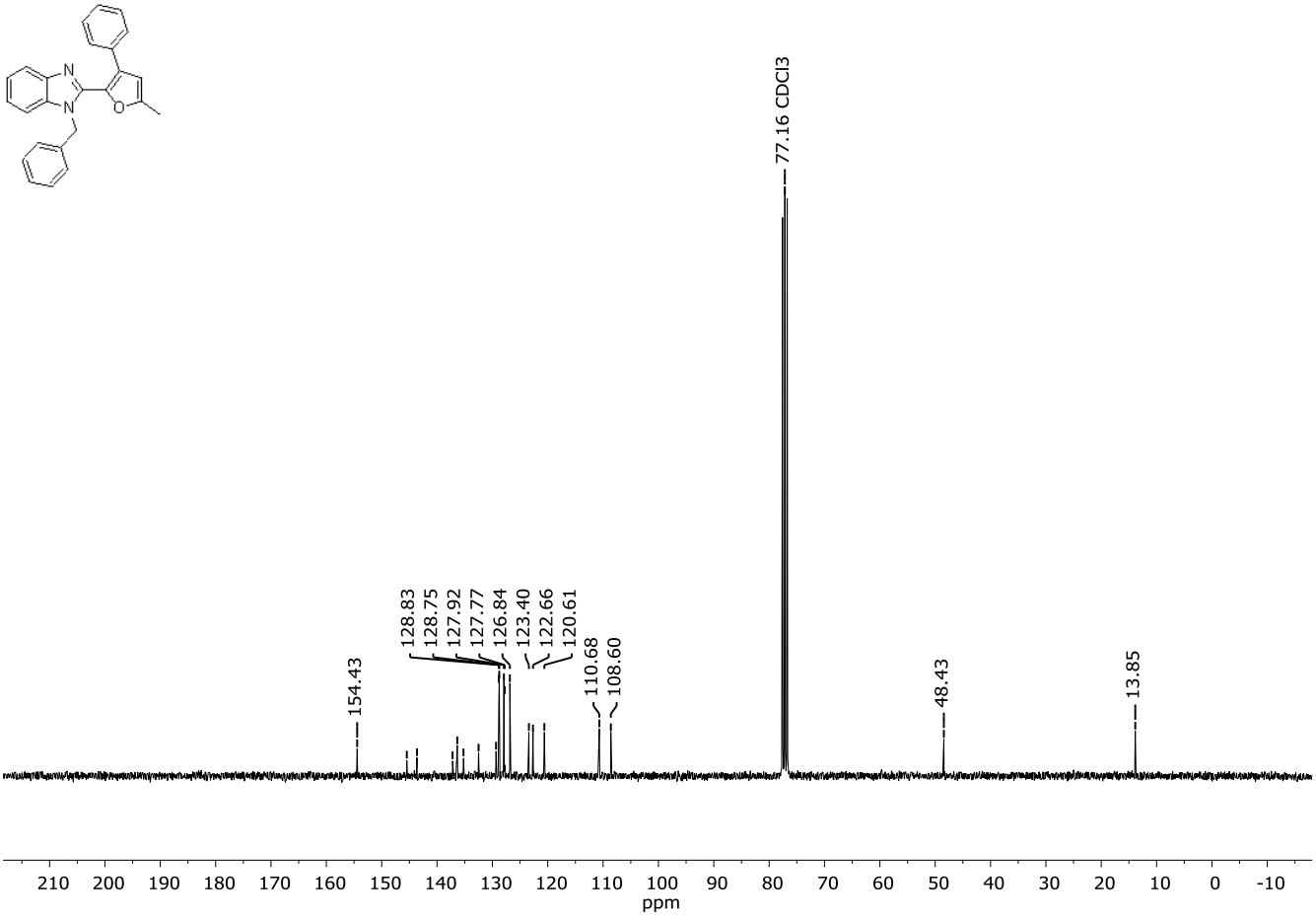


Figure S22. ^{13}C NMR spectrum of compound **2g** (75 MHz, $CDCl_3$).

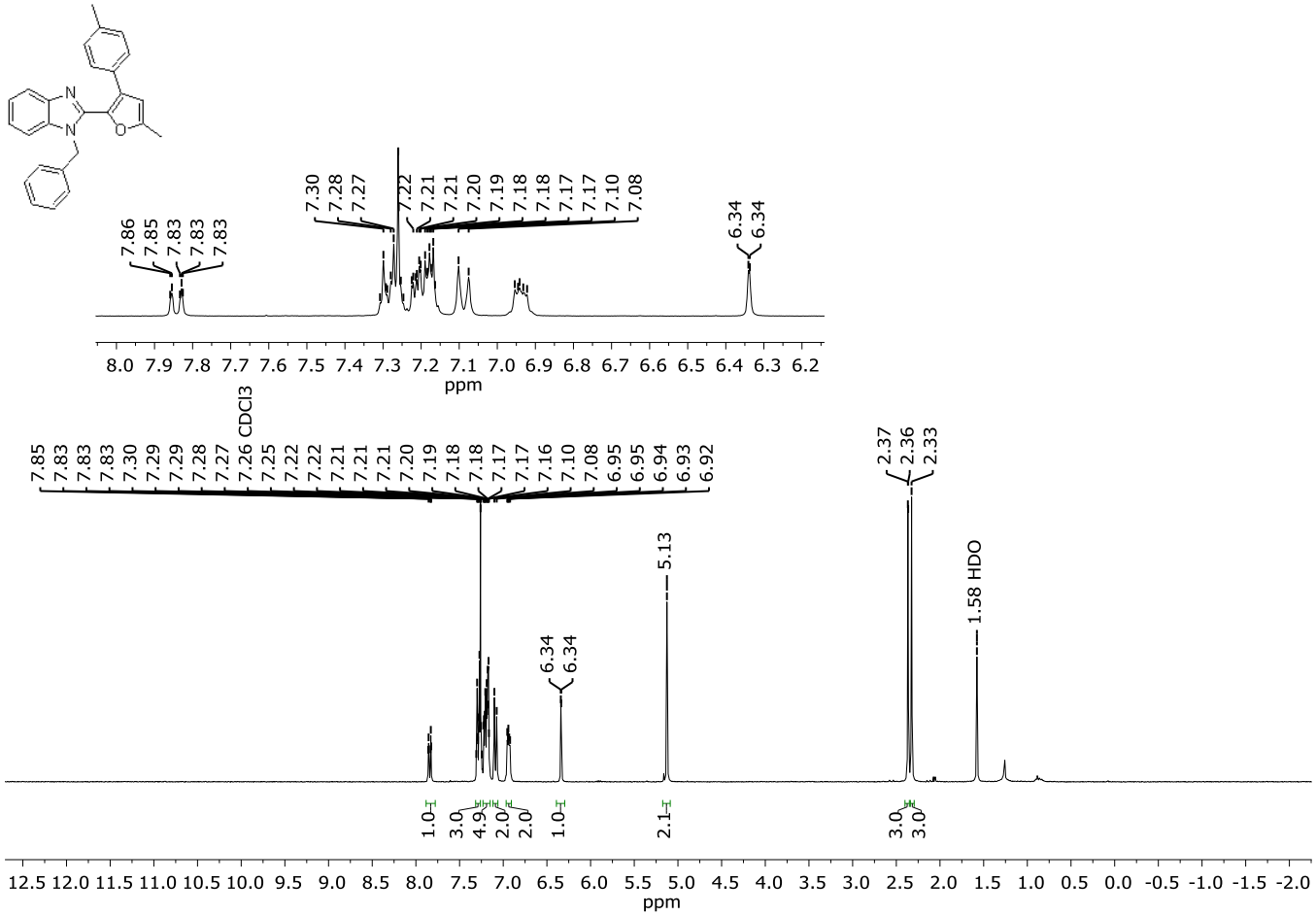


Figure S23. ^{1}H NMR spectrum of compound **2h** (300 MHz, $CDCl_3$).

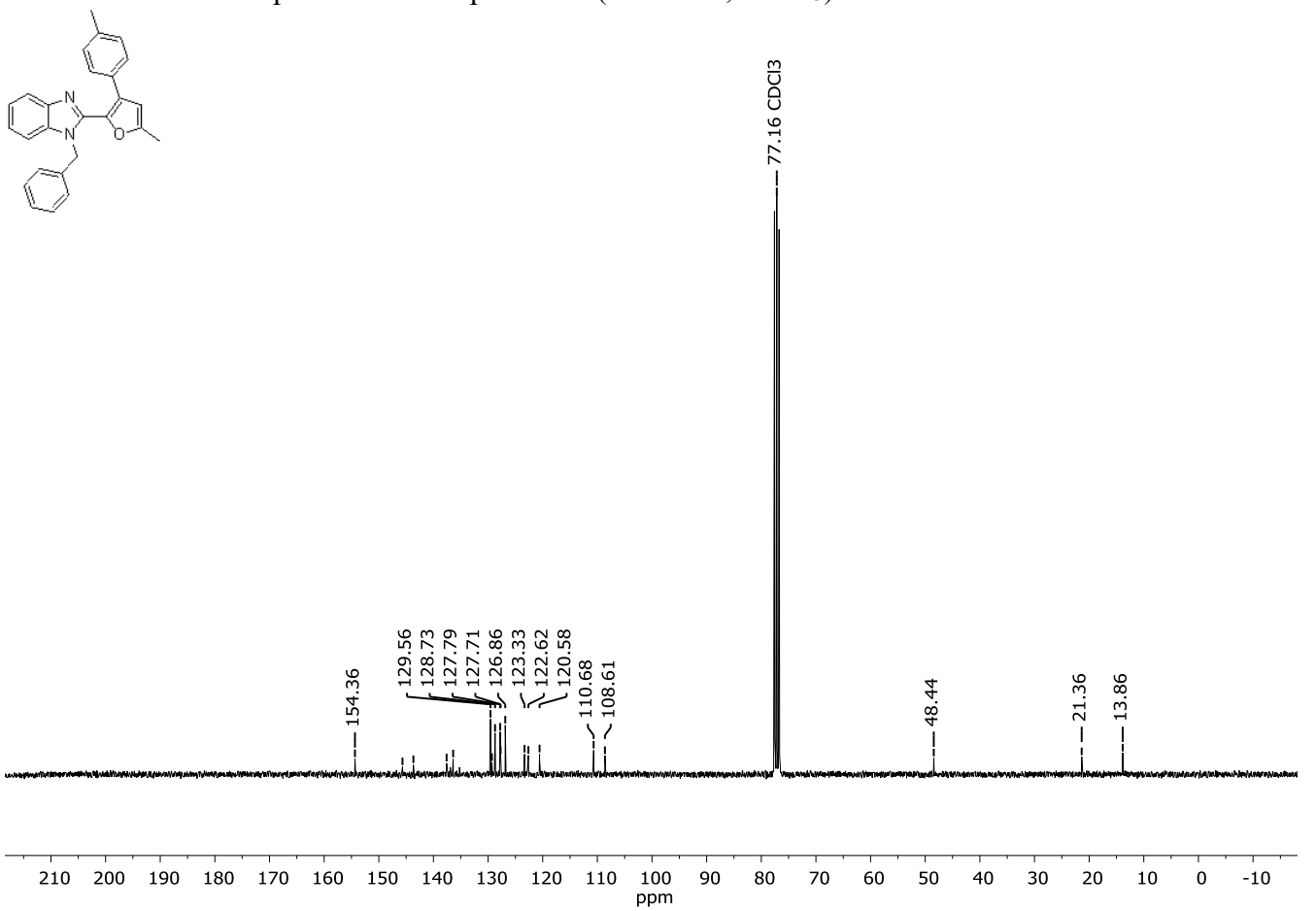


Figure S24. ^{13}C NMR spectrum of compound **2h** (75 MHz, $CDCl_3$).

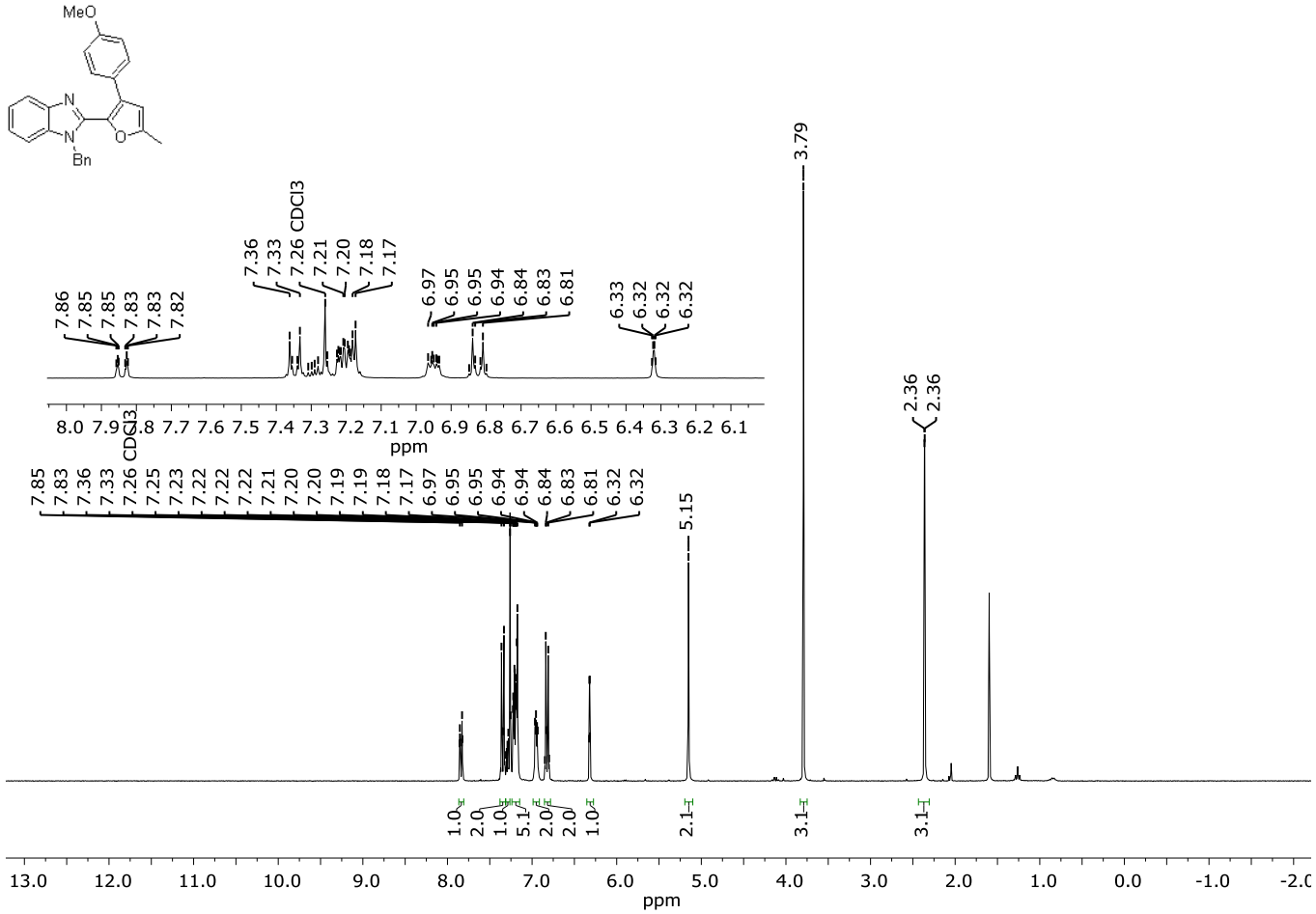


Figure S25. ^{1}H NMR spectrum of compound **2i** (300 MHz, $CDCl_3$).

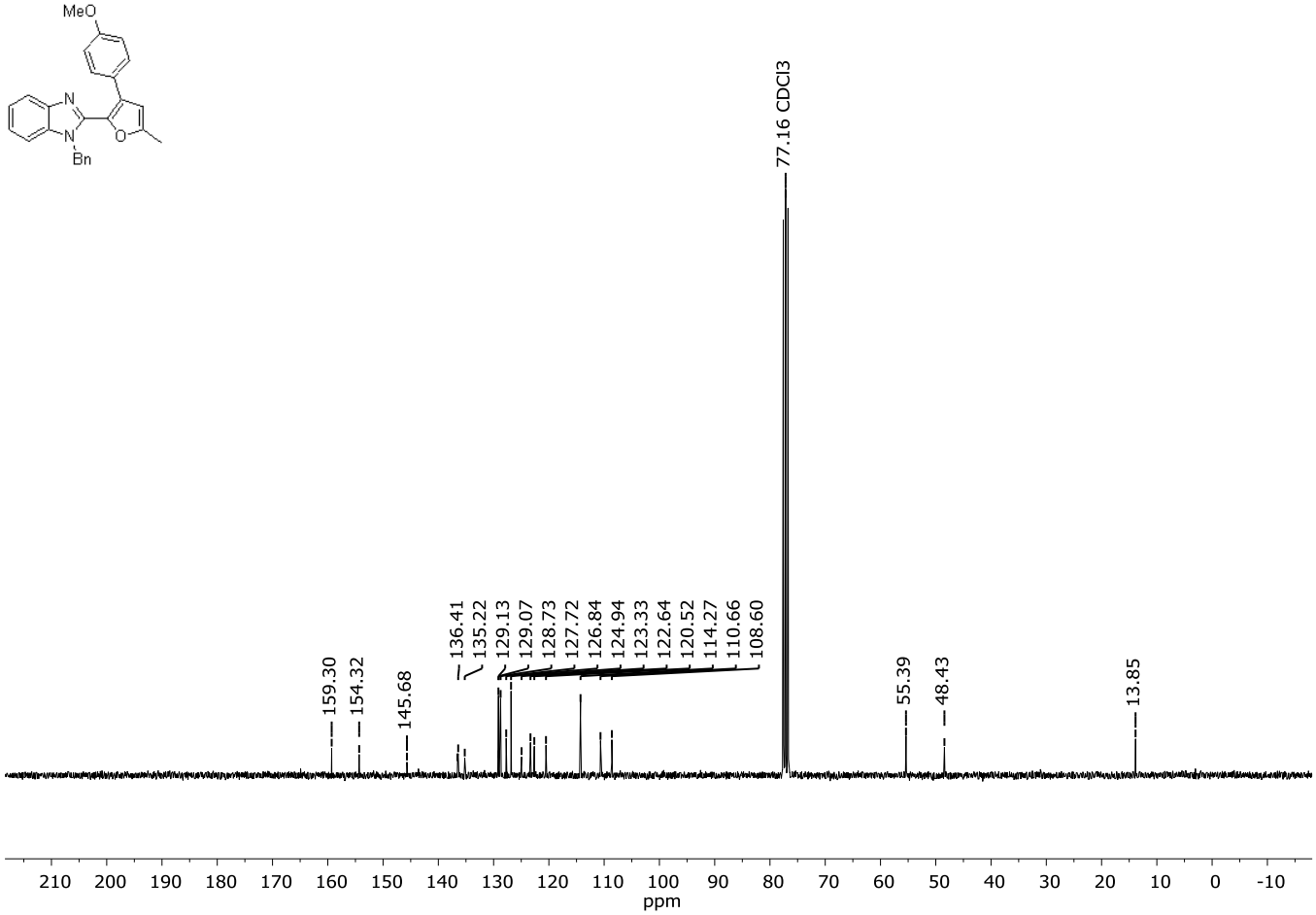


Figure S26. ^{13}C NMR spectrum of compound **2i** (75 MHz, $CDCl_3$).

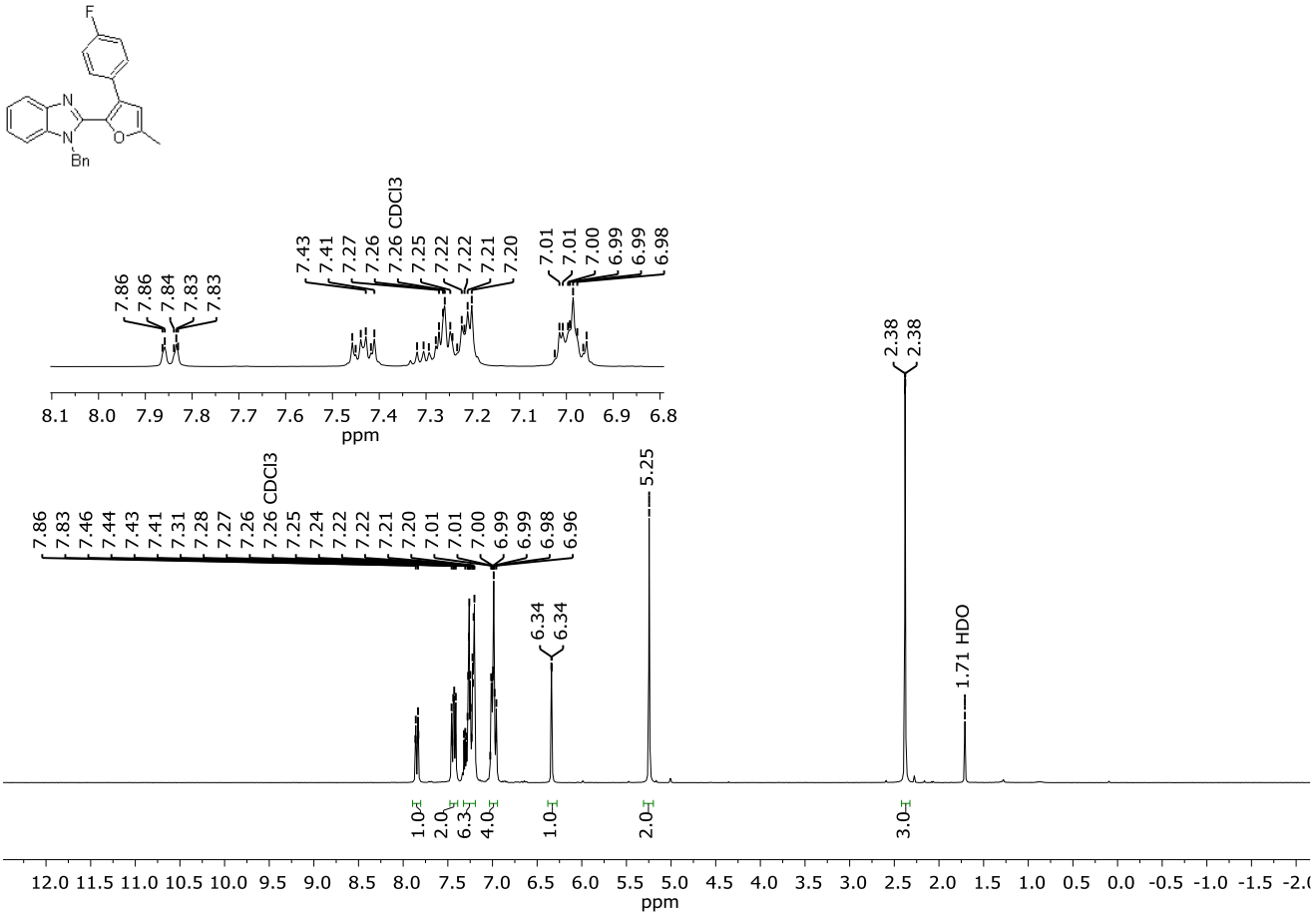


Figure S27. ^{1}H NMR spectrum of compound **2j** (300 MHz, $CDCl_3$).

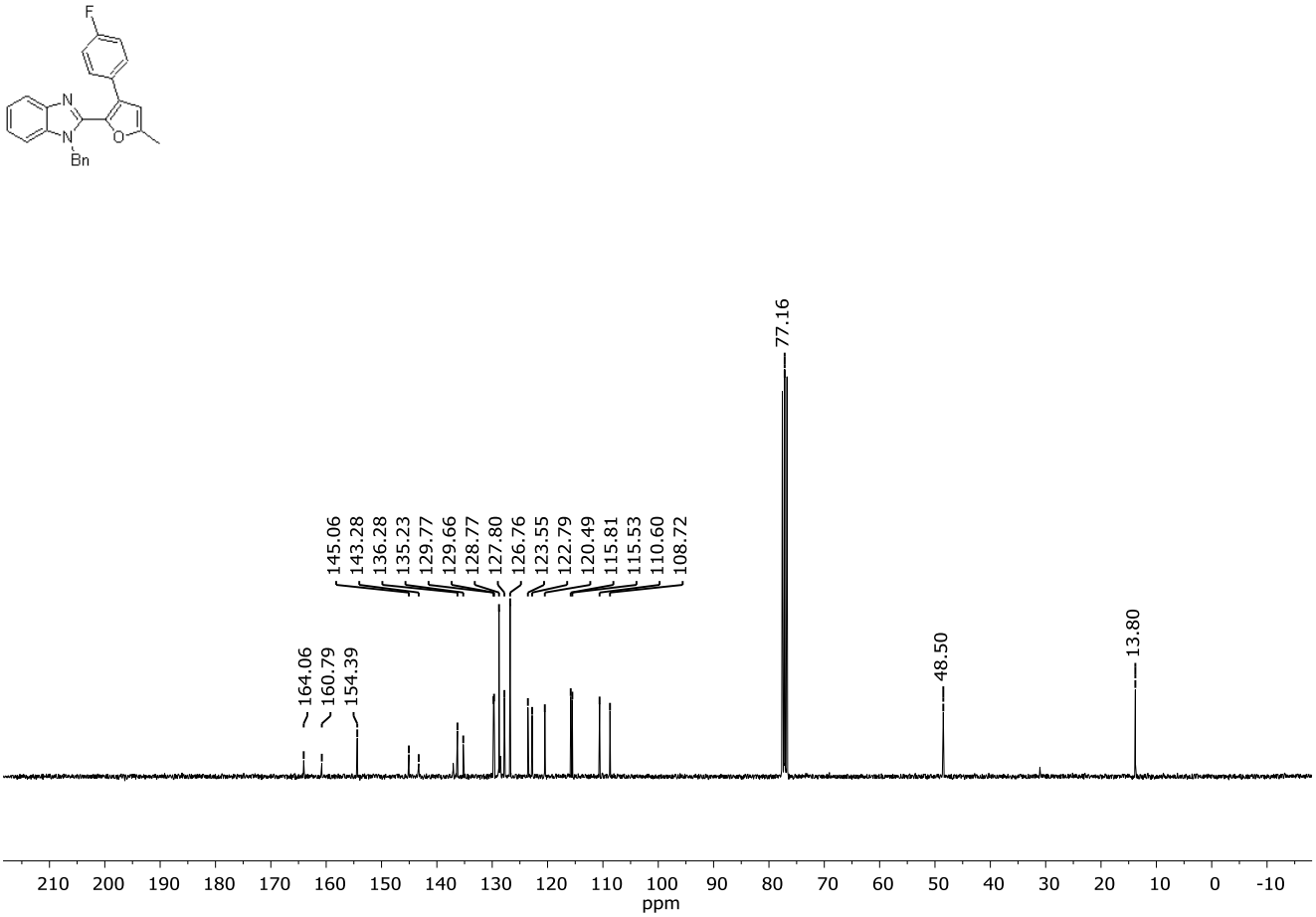


Figure S28. ^{13}C NMR spectrum of compound **2j** (75 MHz, $CDCl_3$).

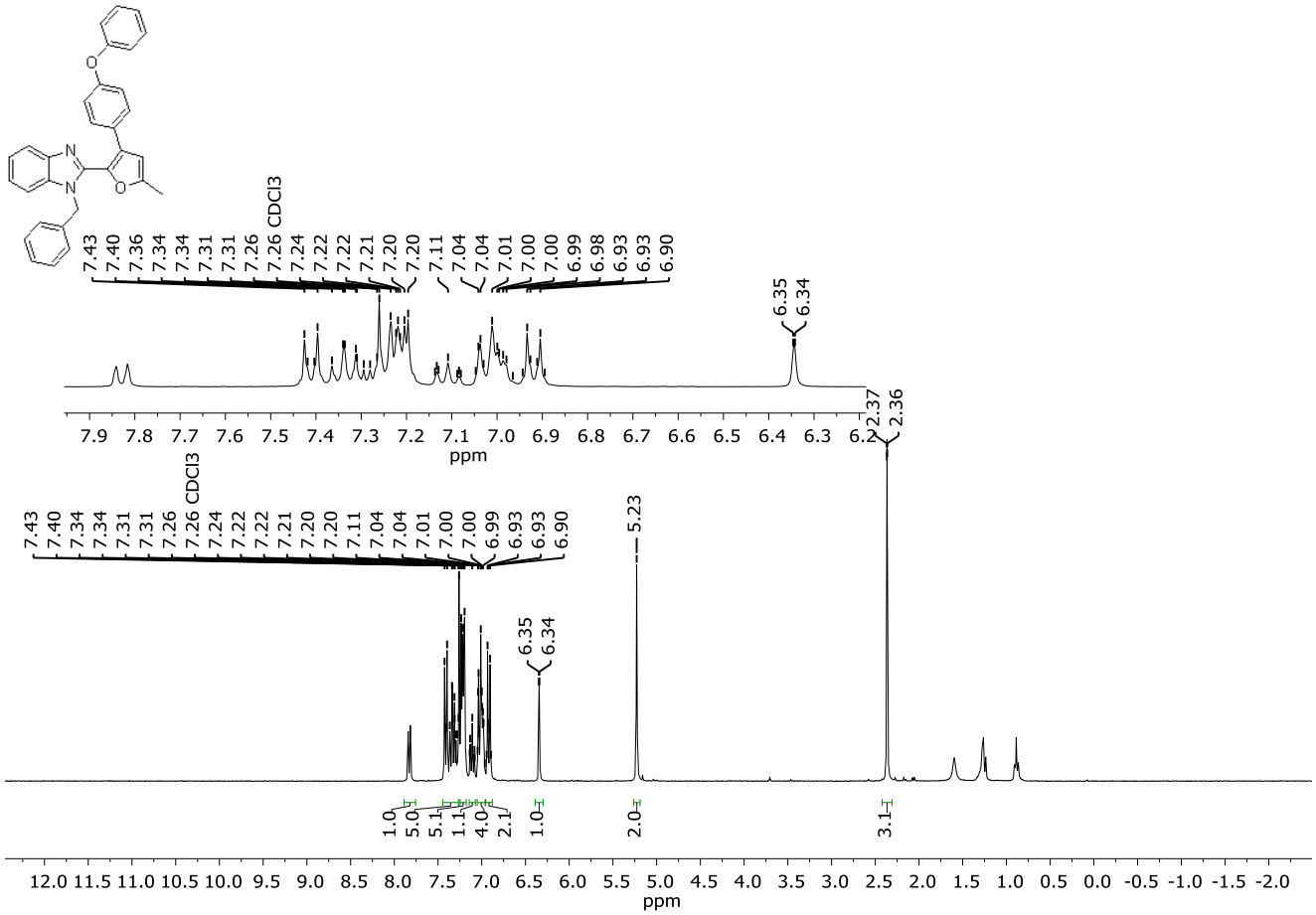


Figure S29. ^{1}H NMR spectrum of compound **2k** (300 MHz, $CDCl_3$).

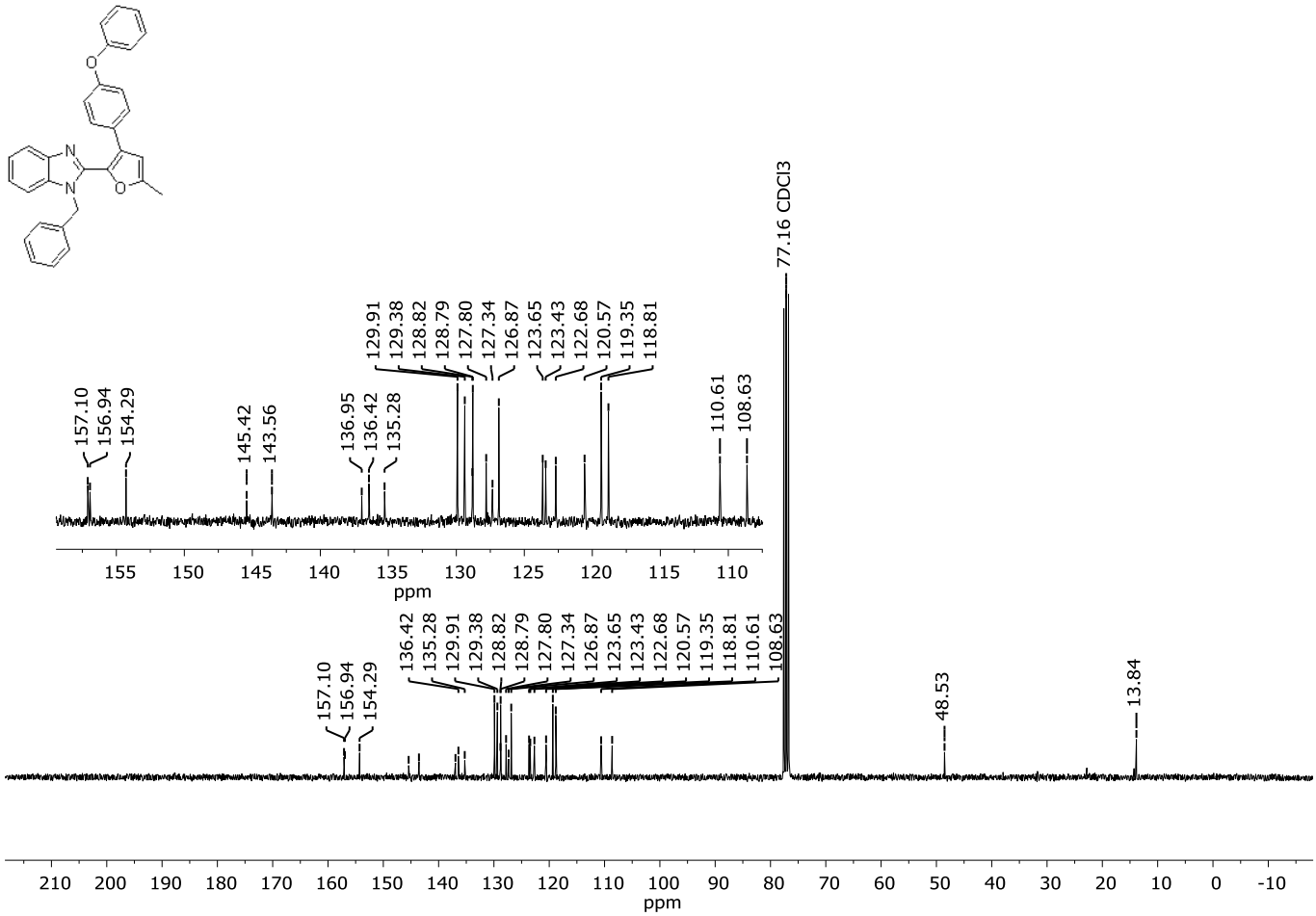


Figure S30. ^{13}C NMR spectrum of compound **2k** (75 MHz, $CDCl_3$).

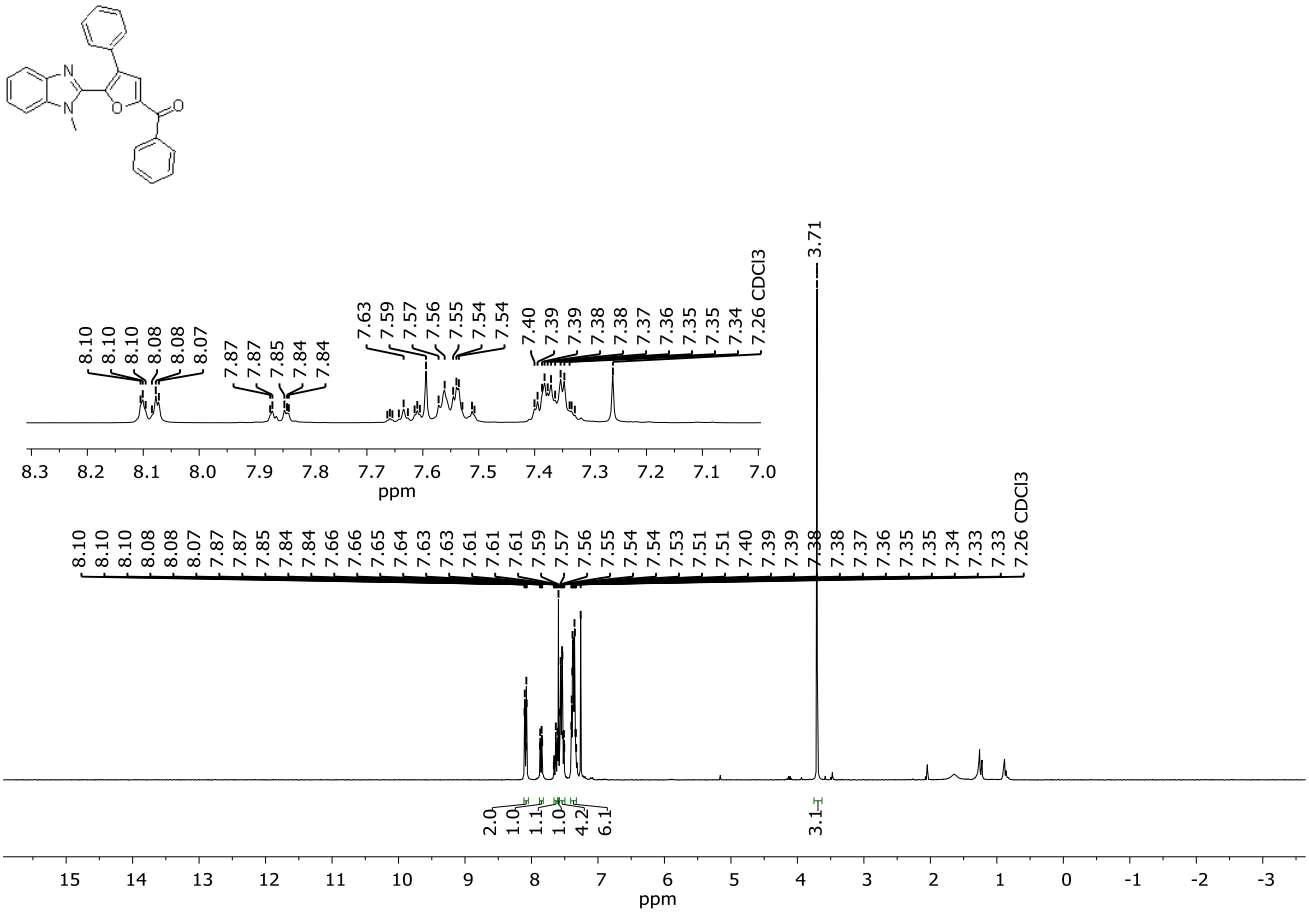


Figure S31. ^{1}H NMR spectrum of compound **2l** (300 MHz, $CDCl_3$).

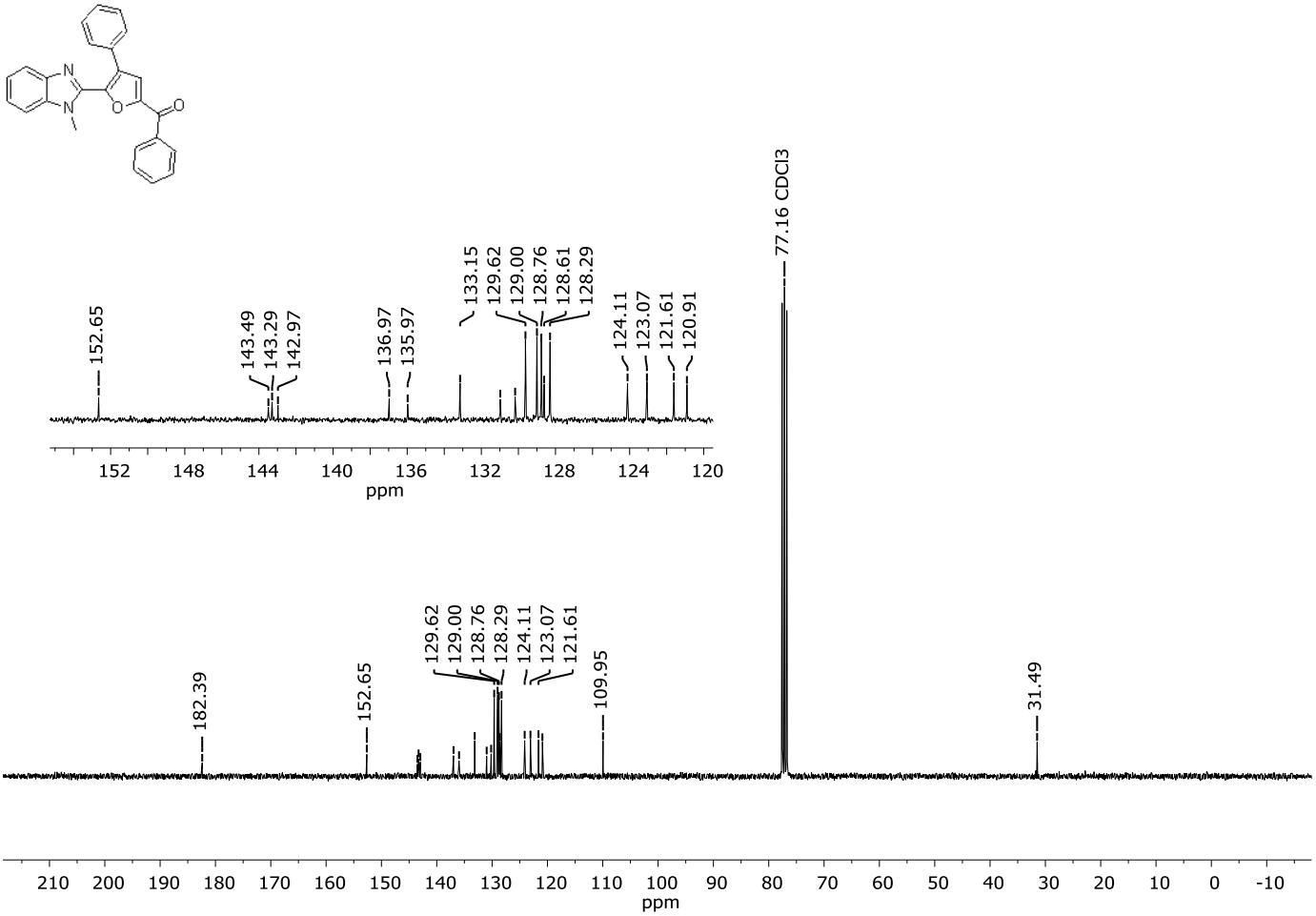


Figure S32. ^{13}C NMR spectrum of compound **2l** (75 MHz, $CDCl_3$).

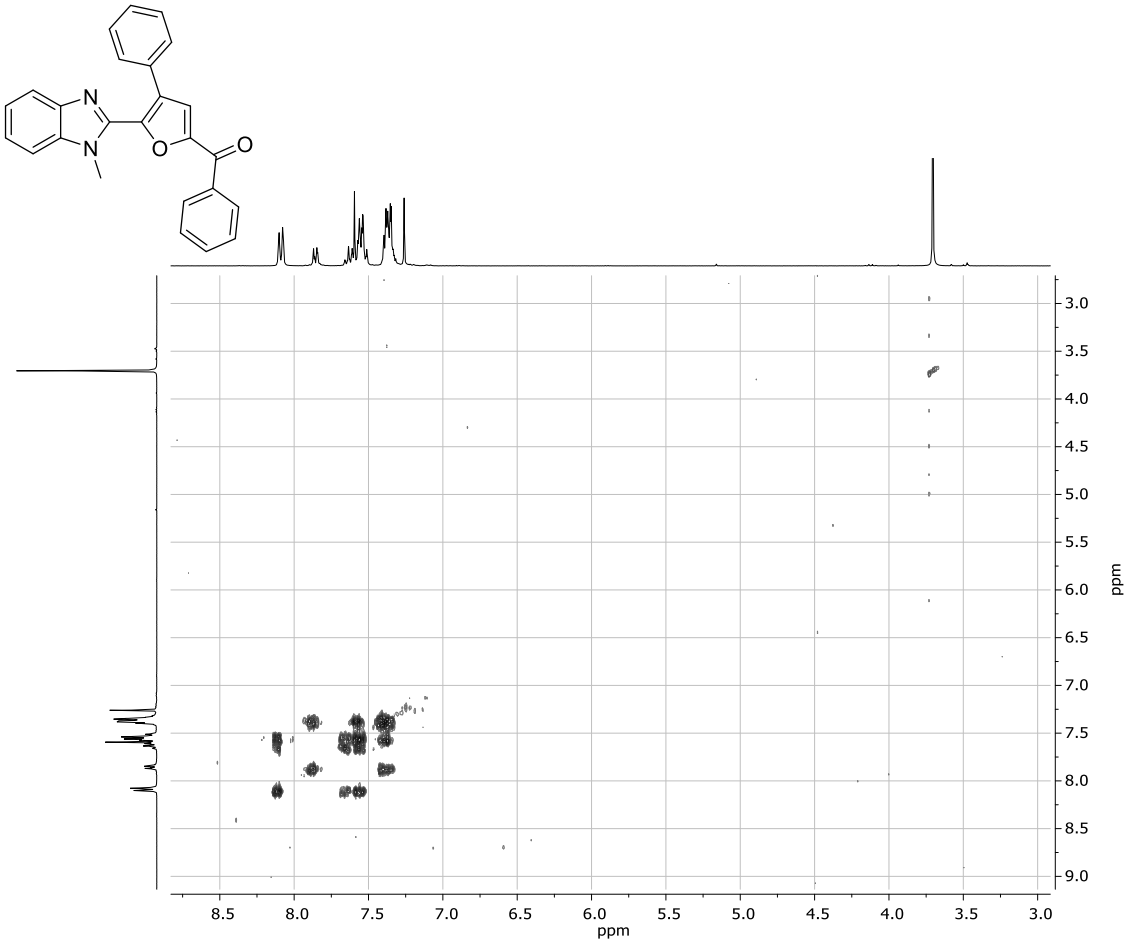


Figure S33. ^{1}H-^{1}H COSY spectrum of compound **2l** ($CDCl_3$).

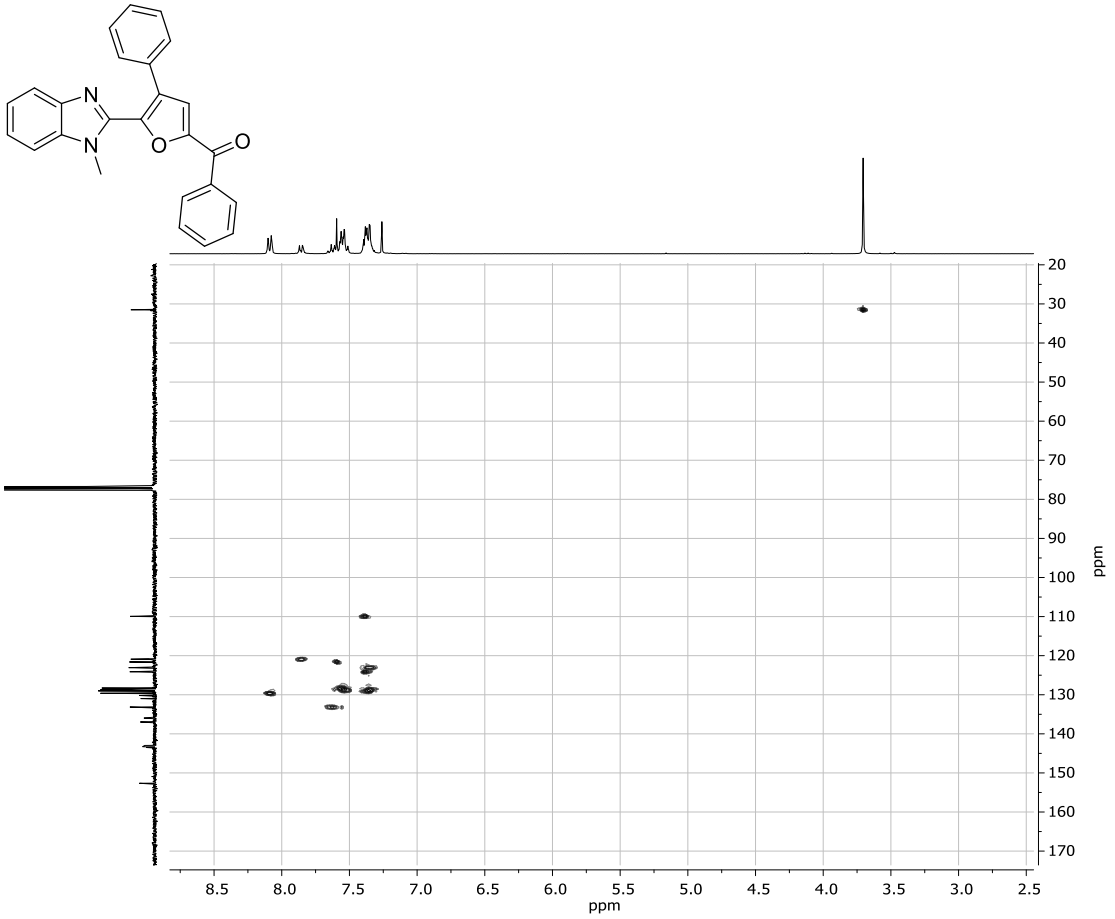


Figure S34. ^{1}H-^{13}C HSQC spectrum of compound **2l** ($CDCl_3$).

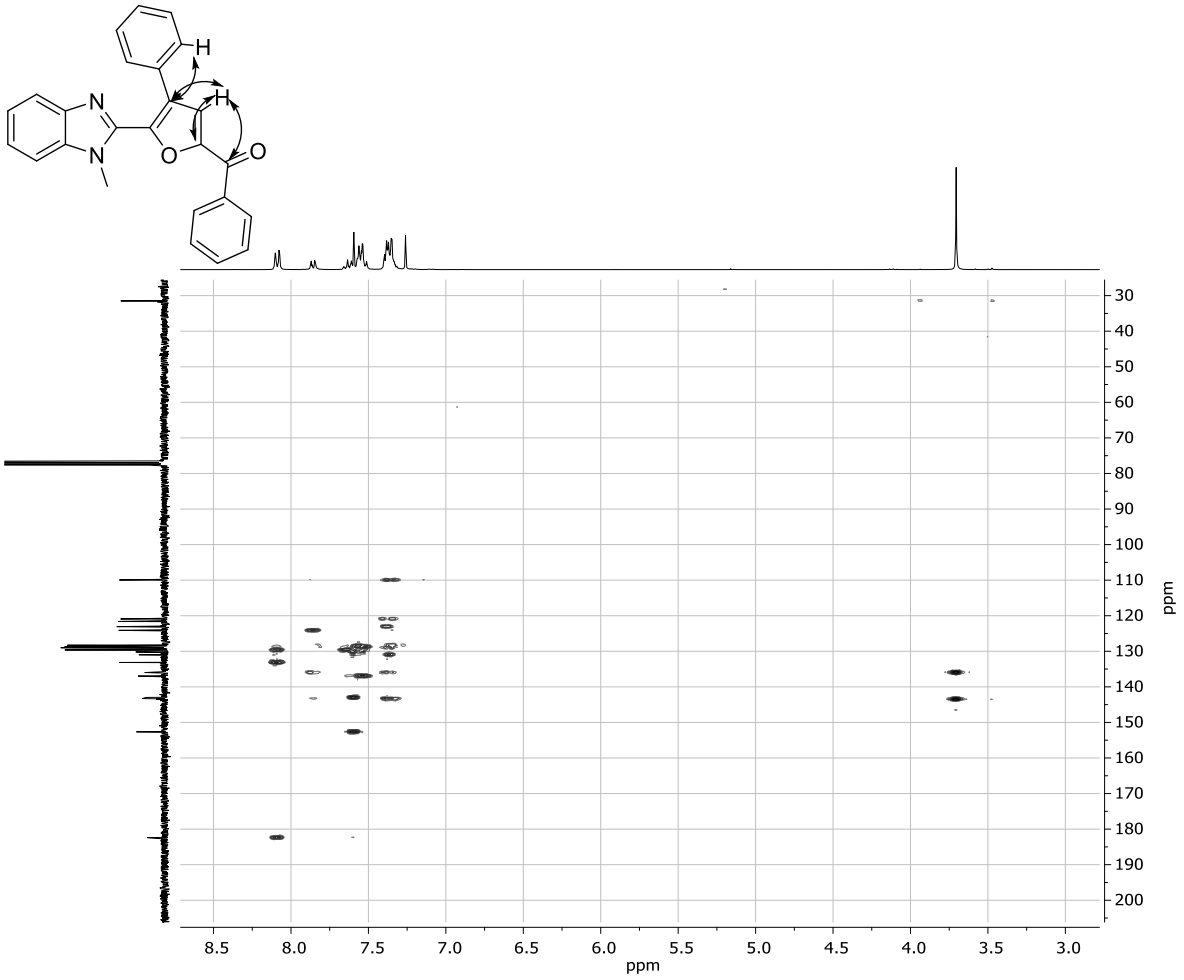


Figure S35. ^{1}H-^{13}C HMBC spectrum of compound **2l** ($CDCl_3$).

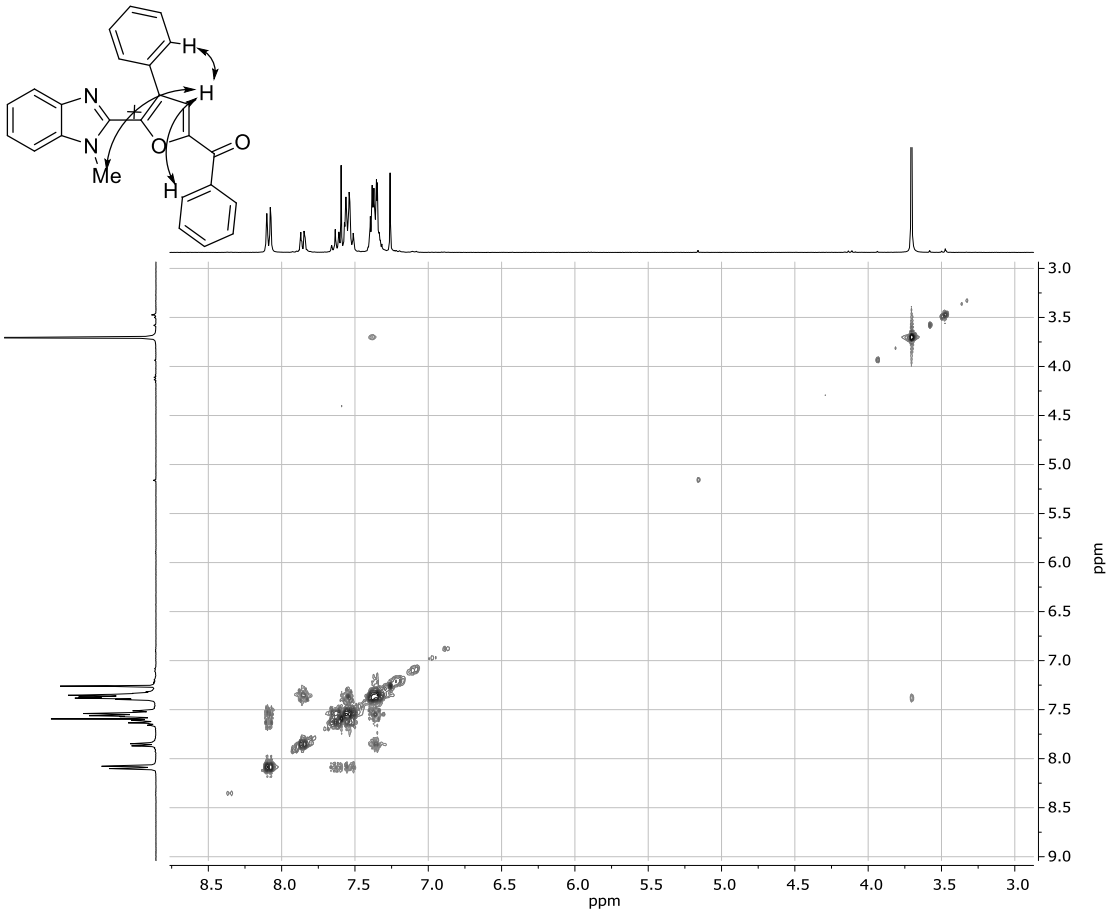


Figure S36. ^{1}H-^{1}H NOESY spectrum of compound **2l** ($CDCl_3$).

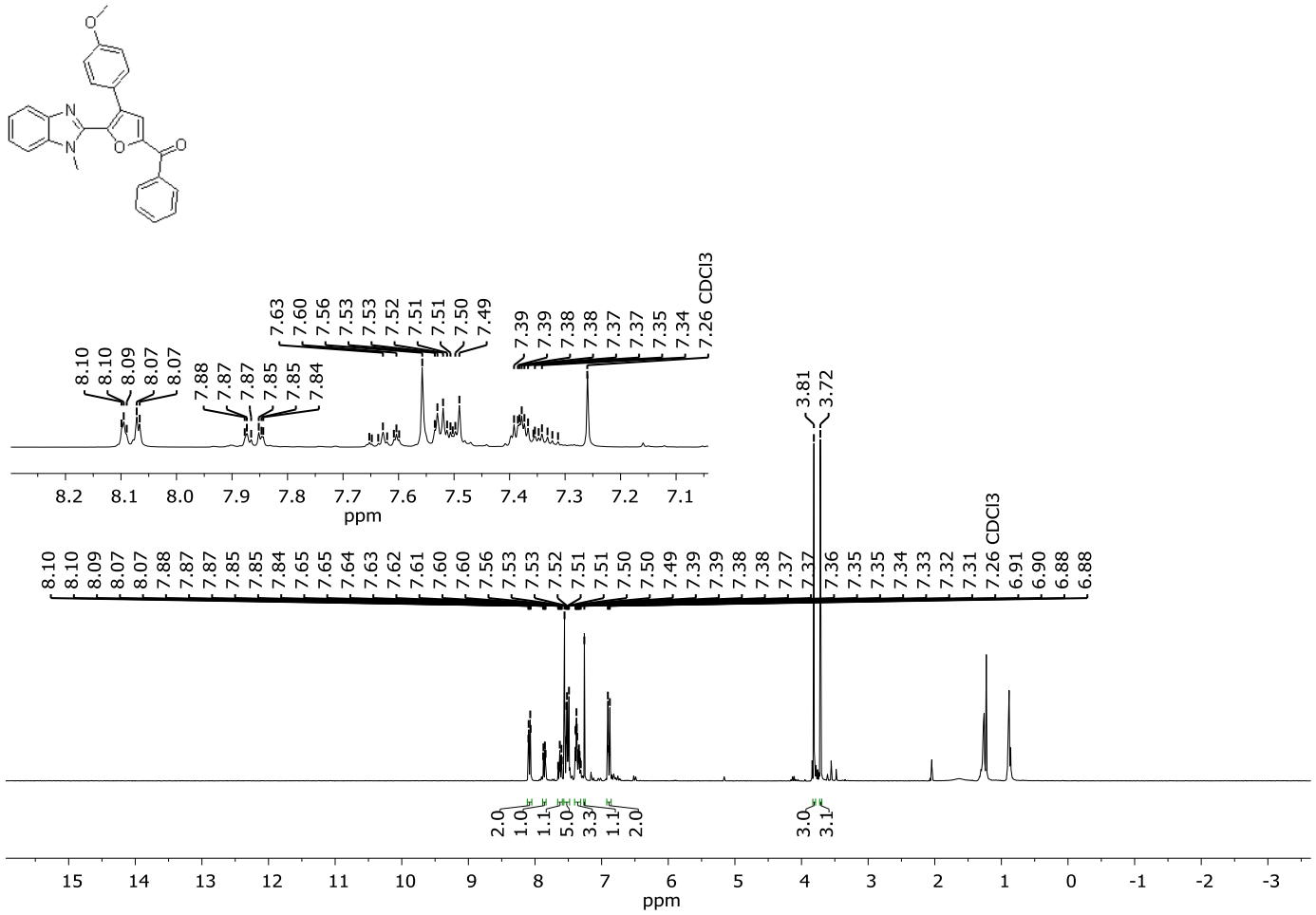


Figure S37. ^{1}H NMR spectrum of compound **2m** (300 MHz, $CDCl_3$).

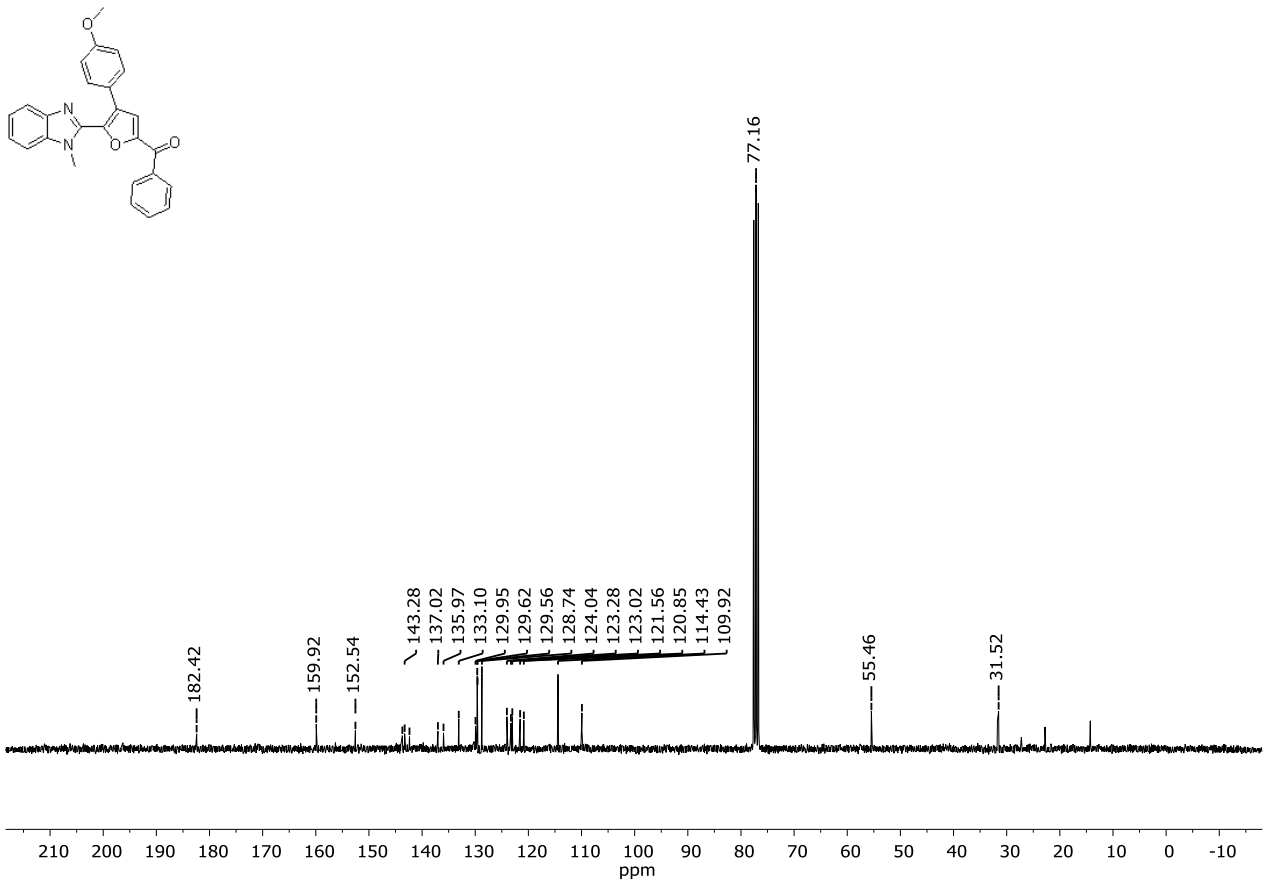


Figure S38. ^{13}C NMR spectrum of compound **2m** (75 MHz, $CDCl_3$).

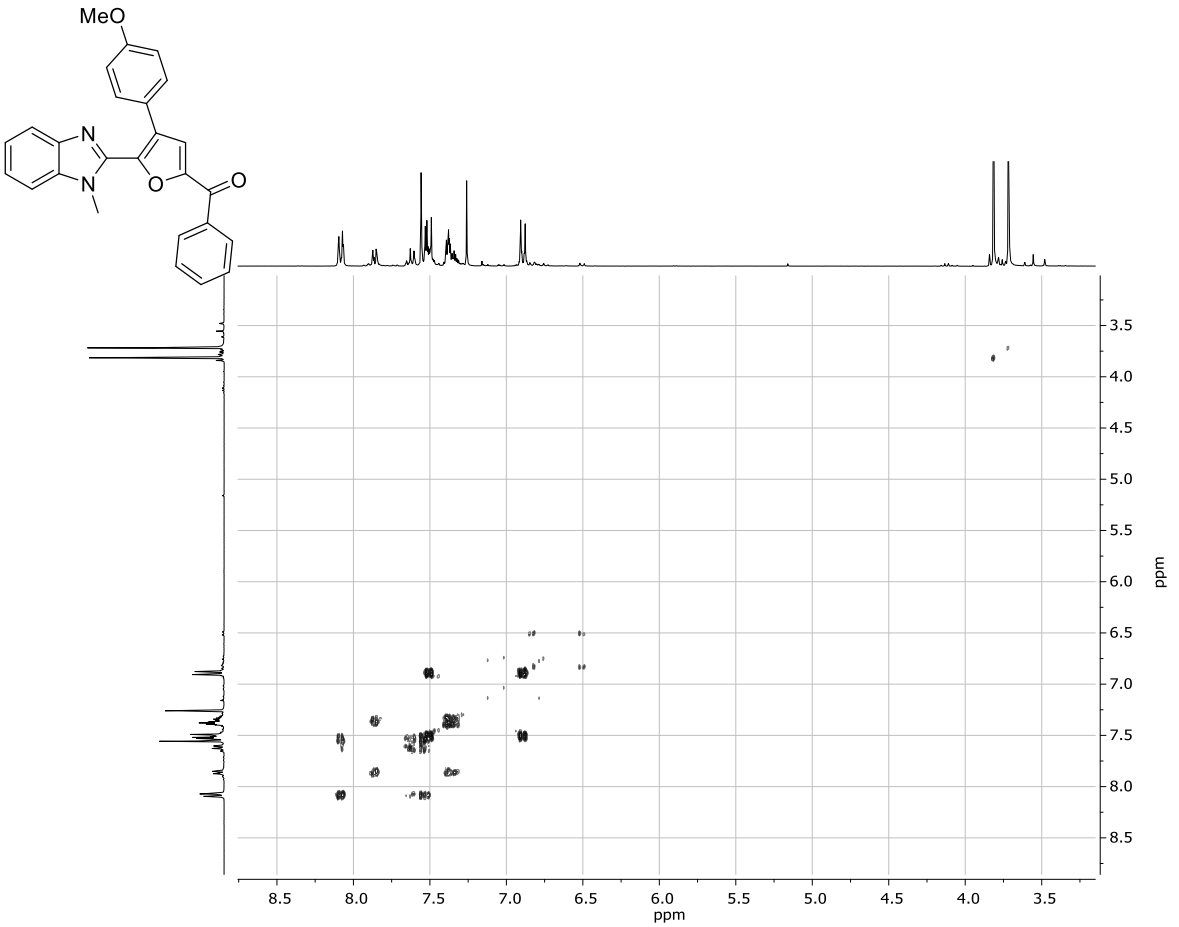


Figure S39. ^{1}H-^{1}H COSY spectrum of compound **2m** ($CDCl_3$).

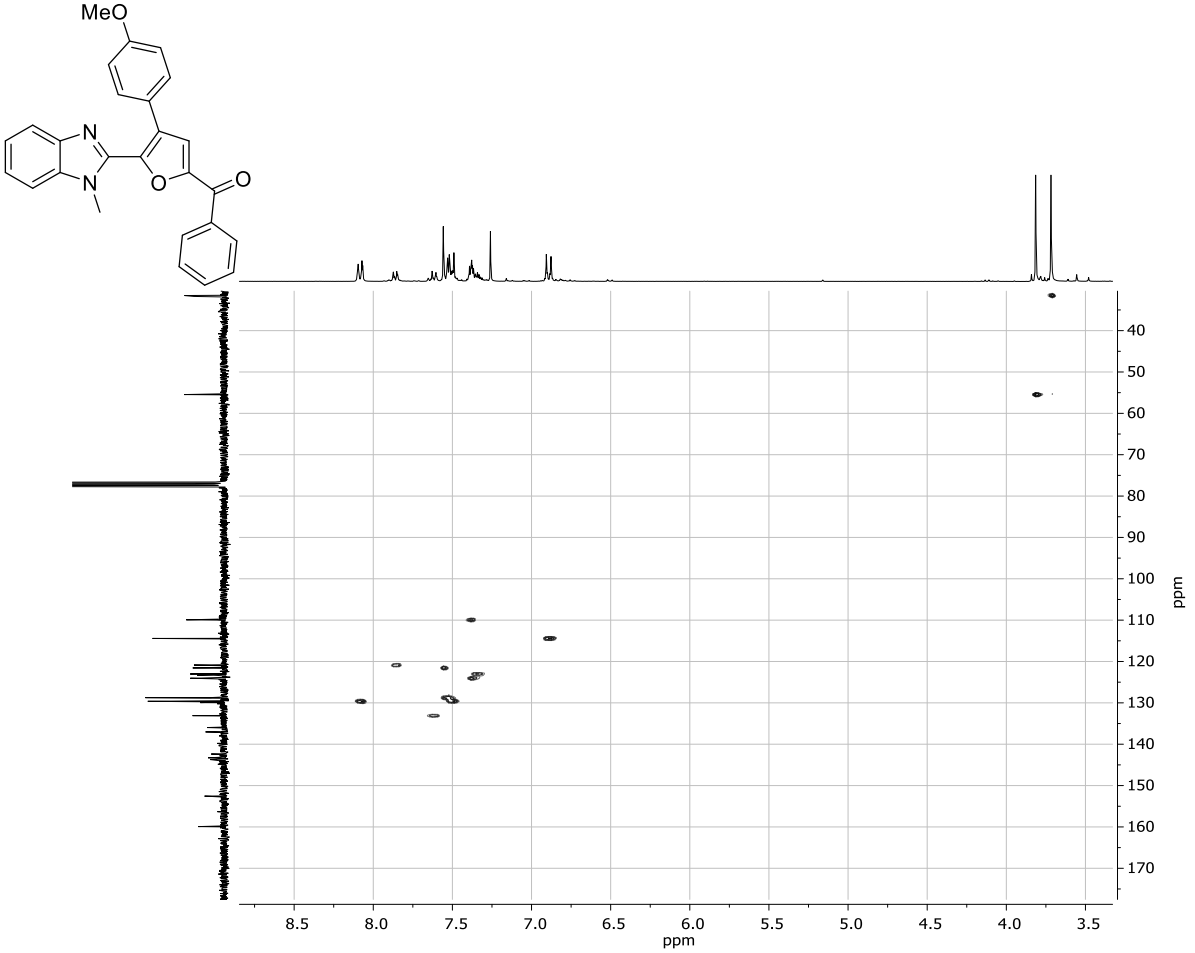


Figure S40. ^{1}H-^{13}C HSQC spectrum of compound **2m** ($CDCl_3$).

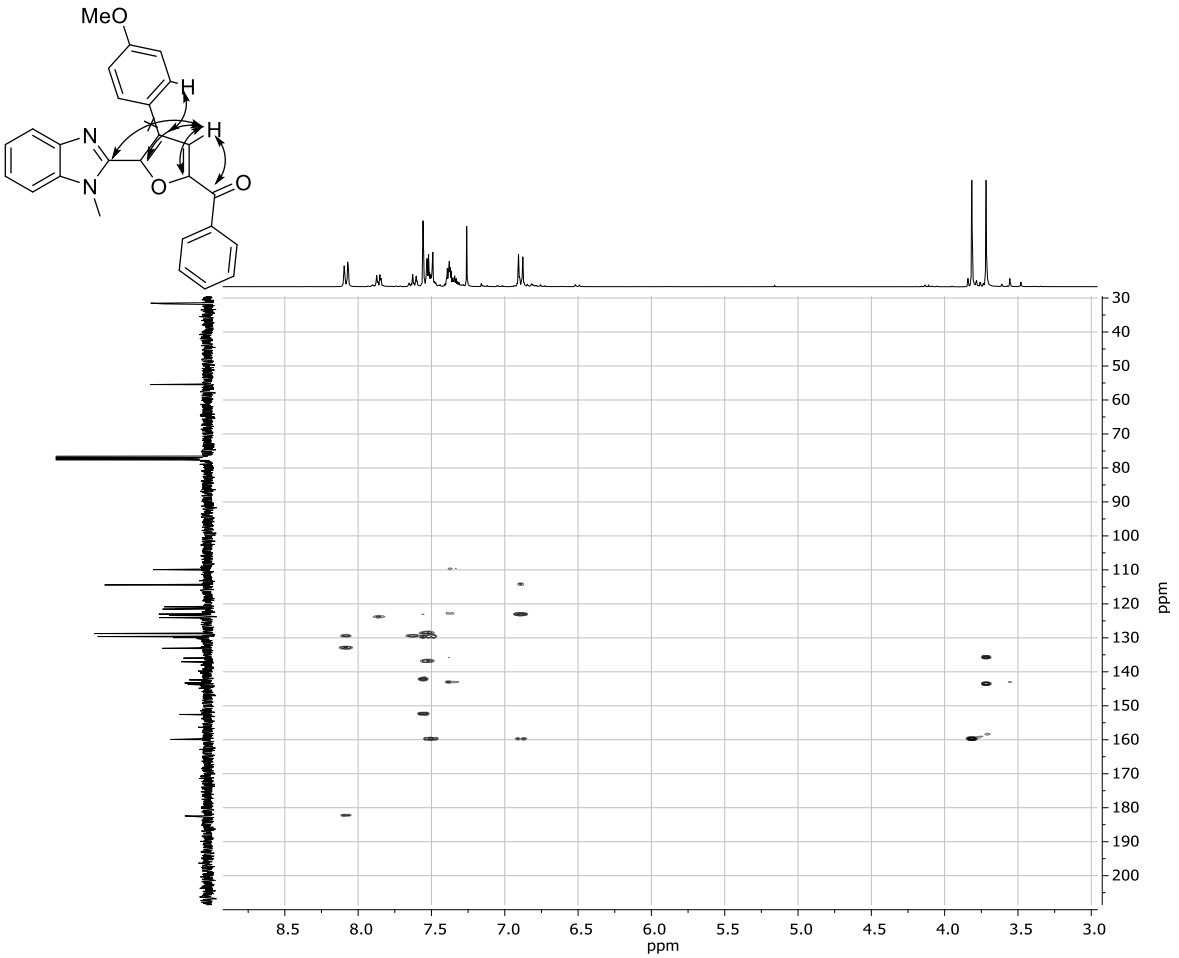


Figure S41. ^{1}H-^{13}C HMBC spectrum of compound **2m** ($CDCl_3$).

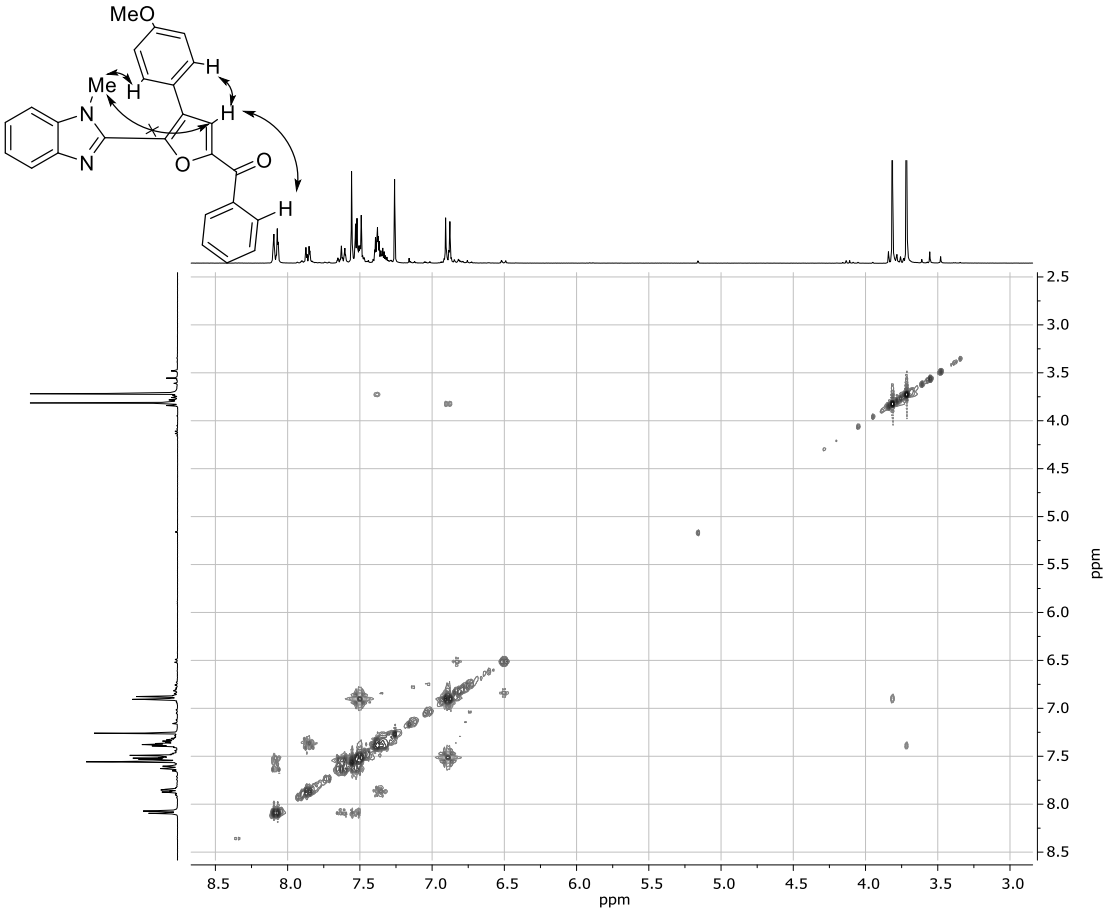


Figure S42. ^{1}H-^{1}H NOESY spectrum of compound **2m** ($CDCl_3$).

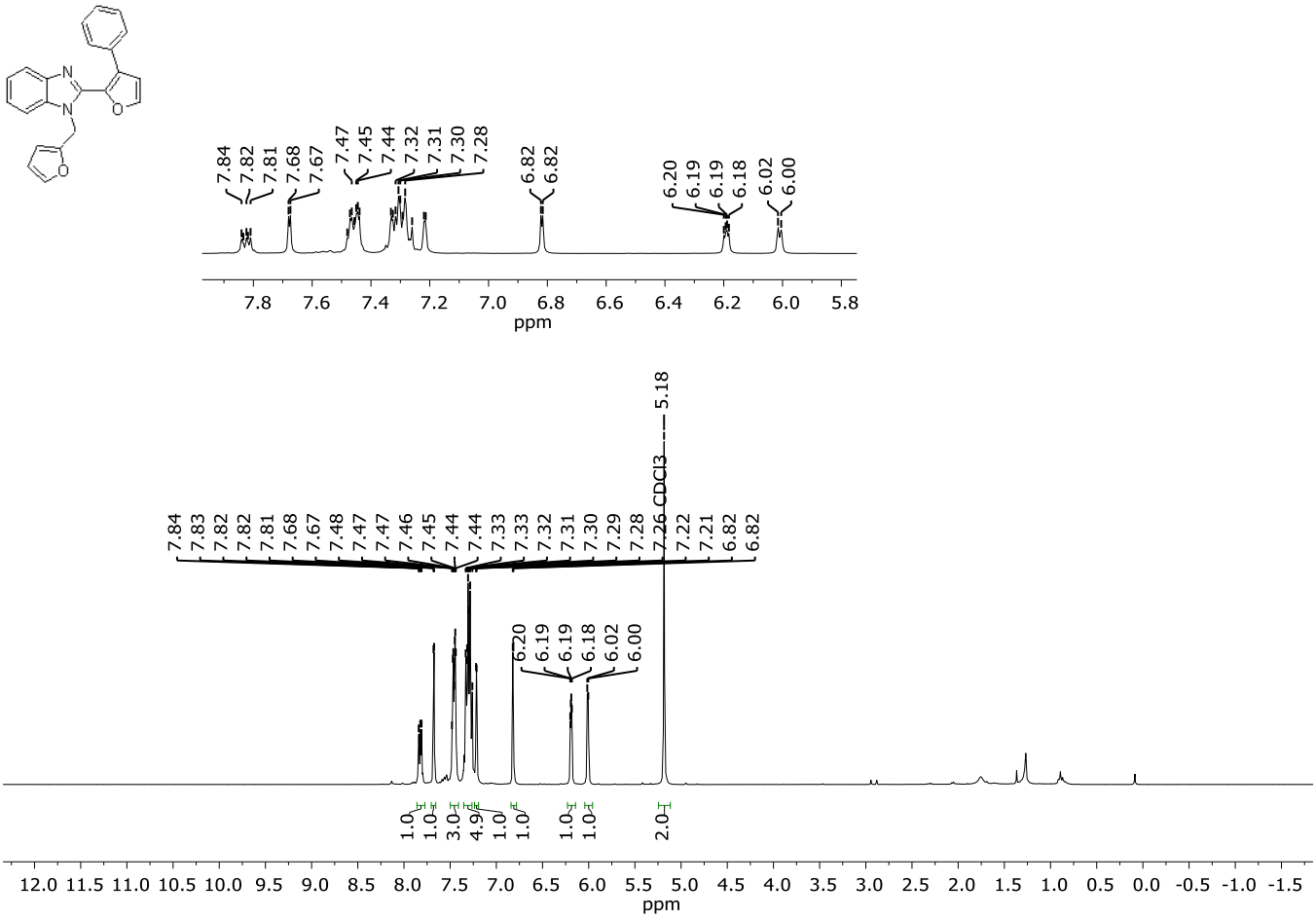


Figure S43. ^{1}H NMR spectrum of compound **2n** (300 MHz, $CDCl_3$).

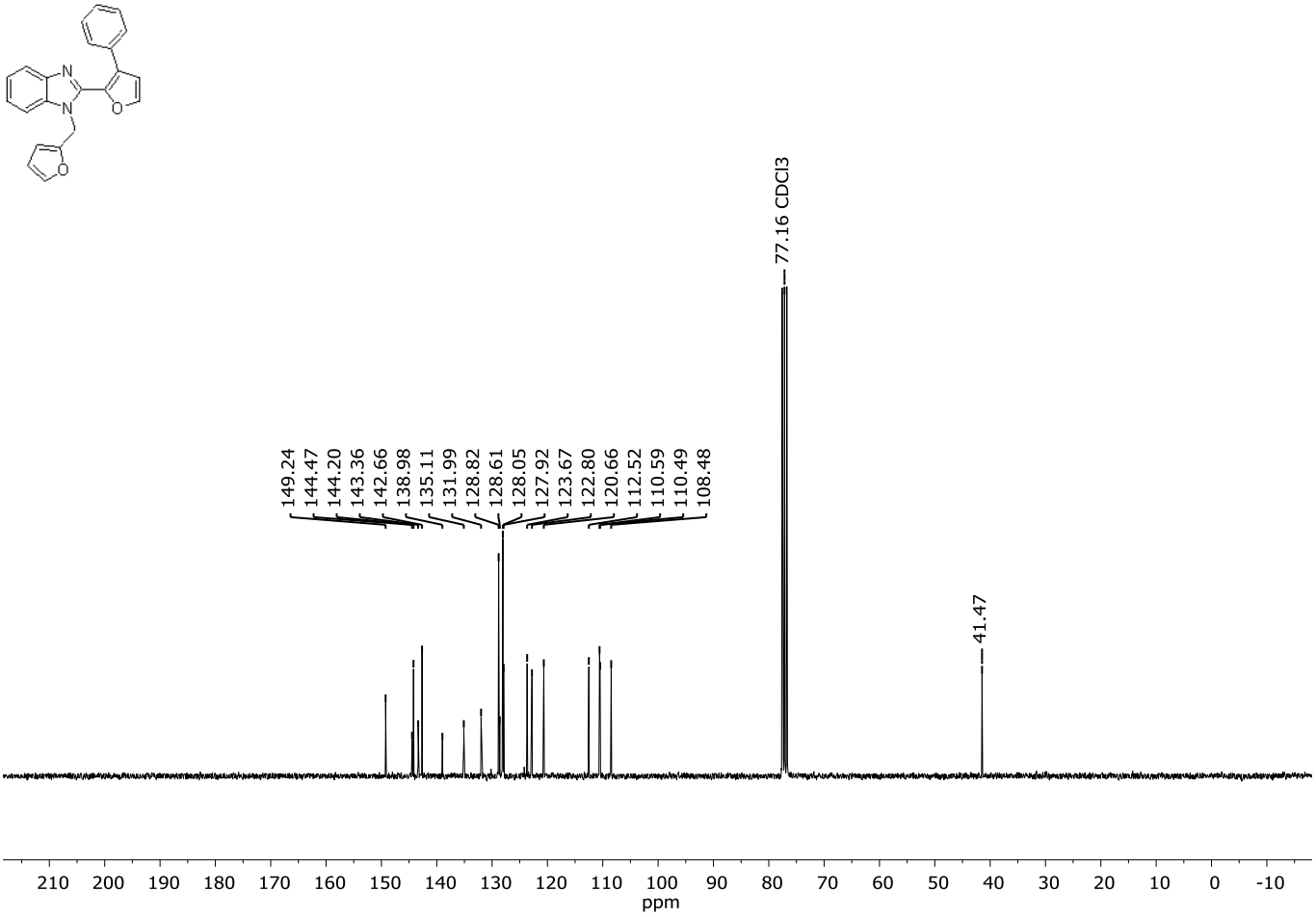


Figure S44. ^{13}C NMR spectrum of compound **2n** (75 MHz, $CDCl_3$)

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