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Synthesis of furo[2,3-*c*]quinolinones *via* intramolecular C(3)–H arylation of furan core under Pd/NHC-catalysis

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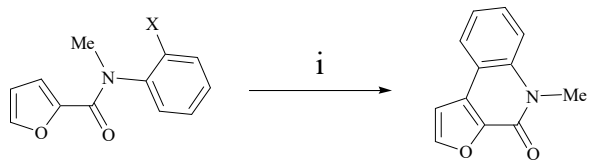
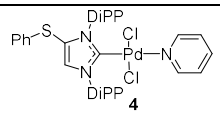
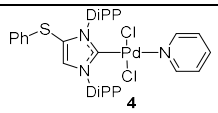
S1. Extended experimental data

Table S1. Optimization of the reaction conditions (extended experimental data)[a]



2a, X=Br
2'a, X=Cl
2"a, X=I

1a

Entry	[Pd] (mol%)	Ligand (mol%)	base, eq	Solvent	X	Yield of **1a** (%)[b]
1	$Pd(OAc)_2$ (5)	none	Cs_2CO_3, 1.5	toluene	Br	trace
2	$Pd(OAc)_2$ (5)	PPh_3 (15)	Cs_2CO_3, 1.5	toluene	Br	trace
3	$Pd(OAc)_2$ (5)	IMes·HCl (15)	Cs_2CO_3, 1.5	toluene	Br	trace
4	$Pd(OAc)_2$ (5)	IPr·HCl (15)	Cs_2CO_3, 1.5	toluene	Br	83
5	$Pd(OAc)_2$ (5)	IPr^{*OMe}·HCl (15)	Cs_2CO_3, 1.5	toluene	Br	trace
6	$Pd(OAc)_2$ (2)	IPr·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	75
7	$Pd(OAc)_2$ (1)	IPr·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	33
8	$Pd(OAc)_2$ (2)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	87
9	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	86
10	$Pd(OAc)_2$ (0.5)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	20
11	 **4** (0.5)	none	Cs_2CO_3, 1.5	toluene	Br	25
12	 **4** (1)	none	Cs_2CO_3, 1.5	toluene	Br	49
13	$PdCl_2$ (1)	IPr^{SPh}·HCl (15)	Cs_2CO_3, 1.5	toluene	Br	12
14	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 2	toluene	Br	84
15	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	K_2CO_3, 1.5	toluene	Br	41
16	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Na_2CO_3, 1.5	toluene	Br	14
17	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	NEt_3, 1.5	toluene	Br	trace
18	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	KOH, 1.5	toluene	Br	trace
19	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	KO^tBu, 1.5	toluene	Br	10
20	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	10
21	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	DMA	Br	trace
22	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	1,4-dioxane	Br	53
23	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	MeCN	Br	trace
24	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Br	87[c], 65[d]
25	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	Cl	trace
26	$Pd(OAc)_2$ (1)	IPr^{SPh}·HCl (5)	Cs_2CO_3, 1.5	toluene	I	88

[a]*Reagents and conditions*: **2a** (0.25 mmol), [Pd] (0.5 - 5 mol %), additive (0 – 15 mol %), base (0.5 mmol), solvent (1 mL), 110˚C, 16h. [b]Yield was determined by GC-MS.[c] for 24 h [d] for 12 h

S2. Synthetic procedures and characterization of isolated compounds

General Information

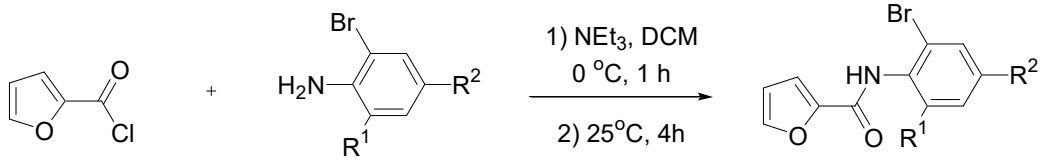
^{1}H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker Avance Neo 300 spectrometer. Chemical shifts (δ, ppm) are given relative to the residual signals of chloroform-*d* protons (7.26 ppm for ^{1}H NMR) or carbon signals in chloroform-*d* (77.16 ppm for ^{13}C NMR).

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. 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 performed 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.

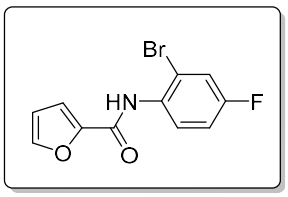
Melting points were determined in open capillary tubes using a Thiele apparatus and are uncorrected.

Materials. *N*-(2-bromophenyl)furan-2-carboxamide (**3a**)[S1], *N*-(2-bromo-4-methylphenyl)furan-2-carboxamide (**3b**),[S2] *N*-(2-bromo-4,6-dimethylphenyl)furan-2-carboxamide (**3c**)[S2], *N*-(2-bromophenyl)-*N*-methylfuran-2-carboxamide **(2a)**.[S3] *N*-(2-chlorophenyl)-*N*-methylfuran-2-carboxamide **(2'a)**[S4], *N*-(2-iodorophenyl)-*N*-methylfuran-2-carboxamide **(2"a)**,[S5] *N*-(2-bromophenyl)-*N*-ethylfuran-2-carboxamide (**2b**)[S6] were obtained as reported.

General procedure for the synthesis of amides 3d-f.

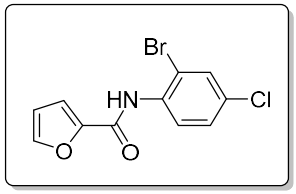


A solution of 2-furoyl chloride (1.44 g, 11 mmol) in DCM (5 ml) was added dropwise to the vigorously stirred ice-water cooled solution of the appropriate *o*-bromoaniline (10 mmol) and triethylamine (1.11 g, 11 mmol) in DCM (10 ml) within one hour. Then, the reaction mixture was stirred at 25 °C for 4 h, then diluted with water (50 ml) and extracted with DCM (3x5ml). The extract was sequentially washed with saturated aqueous solution of $NaHCO_3$ (2x15 ml) and water (2x15 ml), then dried over $MgSO_4$ and evaporated to dryness. The residue obtained was recrystallized from EtOH-water mixture (4:1).

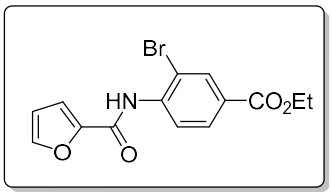


***N*-(2-Bromo-4-fluorophenyl)furan-2-carboxamide (3d).** Yield 2.10 g (74%), white powder, mp 76-77°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.58 (dd, J = 3.5, 1.8 Hz, 1H), 7.04 – 7.12 (m, 1H), 7.26 – 7.28 (m, 1H), 7.34 (dd, J_{H-F} = 7.8, J_{H-H} 2.9 Hz, 1H), 7.56 (dd, J = 1.8, 0.8 Hz, 1H), 8.47 (dd, J_{H-H} = 9.2, J_{H-F} = 5.6 Hz, 1H), 8.57 (s, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 112.9, 113.7 (d, J = 9.3 Hz), 115.5 (d, J = 21.7

Hz), 115.9, 119.6 (d, J = 25.6 Hz), 122.80 (d, J = 8.0 Hz), 132.1 (d, J = 3.3 Hz), 144.9, 147.6, 156.0, 158.68 (d, J = 248.1 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_8BrFNO_2^+$ 283.9717, found *m/z* 283.9730.

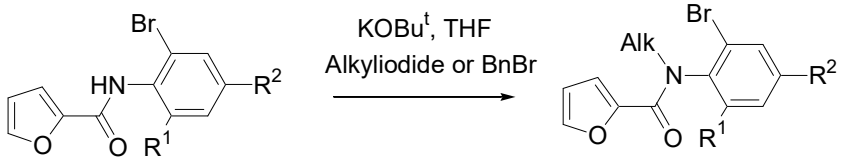


***N*-(2-Bromo-4-chlorophenyl)furan-2-carboxamide (3e).** Yield 2.24g (75%), white powder, mp 84-85˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.59 (dd, J = 3.6, 1.8 Hz, 1H), 7.27 – 7.36 (m, 2H), 7.58 (dd, J = 4.7, 2.1 Hz, 2H), 8.48 (d, J = 8.9 Hz, 1H), 8.66 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 112.9, 113.7, 116.1, 122.2, 128.7, 129.6, 132.0, 134.4, 145.0, 147.5, 156.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_8BrClNO_2^+$ 299.9421, found *m/z* 299.9410.

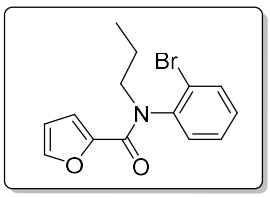


Ethyl 3-bromo-4-(furan-2-ylcarbonylamino)benzoate (3f). Yield 2.39g (71%), white powder, mp 145-146˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, J = 7.1 Hz, 3H), 4.31 (q, J = 7.2 Hz, 2H), 6.61 (dd, J = 3.6, 1.7 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 7.41 (dd, J = 3.6, 0.9 Hz, 1H), 7.71 (dd, J = 1.7, 0.8 Hz, 1H), 7.78 (dd, J = 8.4, 1.9 Hz, 1H), 8.11 (d, J = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 14.4, 61.8, 112.5, 119.9, 123.2, 129.7, 130.4, 132.2, 135.1, 142.5, 146.7, 147.3, 160.3, 164.7.ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}BrNO_4^+$ 338.0022, found *m/z* 338.0035.

General procedure for the synthesis of *N*-alkylamides 2c-l.

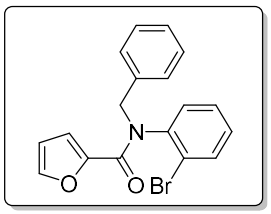


In a round bottomed flask, a mixture of the appropriate amide (8 mmol) and Bu^{t}OK (1.08 g, 9.6 mmol) in THF (20 ml) was stirred at room temperature for 15 min. Then the appropriate alkyl iodide or benzyl bromide (9.6 mmol) was slowly added to the mixture, and this was stirred for 12 h at 25˚C. The reaction mixture was then quenched with water (50 ml) and extracted with DCM (3x15 ml). The extract was dried with $MgSO_4$ and evaporated to dryness. The crude product was recrystallized from hexane-benzene (3:1) mixture.

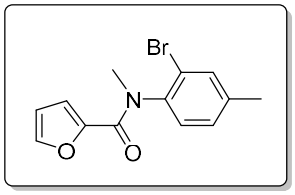


***N*-(2-Bromophenyl)-*N*-propylfuran-2-carboxamide (2c).** Yield 2.11 g (86%), white powder, mp 108-109˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.94 (t, J = 7.4 Hz, 3H), 1.49 – 1.81 (m, 3H), 3.24 – 3.50 (m, 2H), 4.00 – 4.22 (m, 1H), 5.83 (s, 1H), 6.19 (s, 1H), 7.23 – 7.32 (m, 2H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.68 (dd, J = 8.2, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 11.5, 20.8, 51.3, 111.1, 115.8, 124.3, 128.5, 129.8, 131.3,

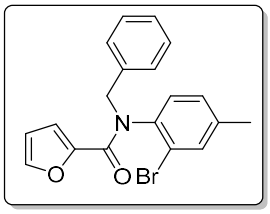
134.0, 141.6, 144.5, 147.4, 159.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{15}BrNO_2^+$ 308.0281, found *m/z* 308.0296.



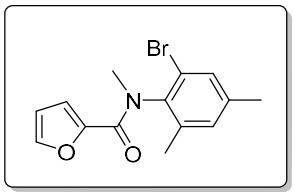
***N*-Benzyl-*N*-(2-bromophenyl)furan-2-carboxamide (2d).** Yield 2.11 g (74%), white powder, mp 104-105˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.23 (d, *J* = 14.3 Hz, 1H), 5.75 (d, *J* = 14.3 Hz, 1H), 5.83 (d, *J* = 3.6 Hz, 1H), 6.20 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.81 (dd, $J_{H\text{-}F}$ = 7.4, $J_{H\text{-}H}$ = 2.1 Hz, 1H), 7.12 – 7.33 (m, 8H), 7.67 (dd, $J_{H\text{-}F}$ = 7.6, $J_{H\text{-}H}$ = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 52.5, 111.3, 116.2, 124.1, 127.8, 128.3, 128.5, 129.7, 130.0, 131.8, 133.9, 136.7, 140.8, 144.8, 147.1, 159.1. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{15}BrNO_2^+$ 356.0281, found *m/z* 356.0293.



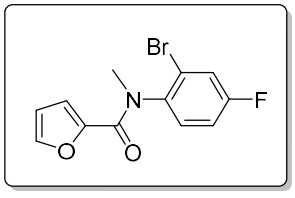
***N*-(2-Bromo-4-methylphenyl)-*N*-methylfuran-2-carboxamide (2e).** Yield 1.9 g (81%), white powder, mp 97-99 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.39 (s, 3H), 3.33 (s, 3H), 5.83 (d, *J* = 3.5 Hz, 1H), 6.19-6.21 (br. s, 1H), 7.11 – 7.22 (m, 2H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 1.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.0, 37.2, 111.2, 115.9, 123.2, 129.7, 134.3, 140.3, 140.5, 144.6, 147.1, 159.4 two signals are overlapped. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{13}BrNO_2^+$ 294.0124, found *m/z* 294.0134.



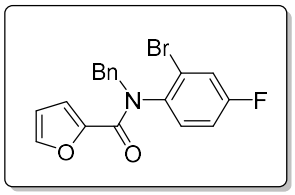
***N*-Benzyl-*N*-(2-bromo-4-methylphenyl)furan-2-carboxamide (2f).** Yield 2.24 g (76%), white powder, mp 126-127˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.35 (s, 3H), 4.18 (d, *J* = 14.3 Hz, 1H), 5.67 – 5.79 (m, 2H), 6.20 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.96 (ddd, *J* = 8.0, 1.9, 0.8 Hz, 1H), 7.21 – 7.30 (m, 5H), 7.35 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 21.0, 52.6, 111.2, 116.1, 123.7, 127.7, 128.5, 129.1, 129.7, 131.3, 134.3, 136.8, 138.2, 140.5, 144.8, 147.1, 159.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}BrNO_2^+$ 370.0437, found *m/z* 370.0451.



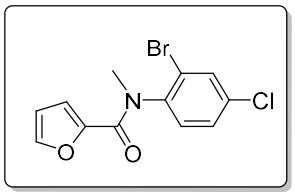
***N*-(2-Bromo-4,6-dimethylphenyl)-*N*-methylfuran-2-carboxamide (2g).** Yield 1.72 g (70%), white powder, mp 119-120˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (s, 3H), 2.34 (s, 3H), 3.27 (s, 3H), 5.73 (d, *J* = 3.5 Hz, 1H), 6.20 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.00 – 7.10 (m, 1H), 7.30 – 7.38 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 18.4, 21.0, 35.6, 111.3, 115.2, 124.0, 131.3, 131.9, 138.3, 138.8, 140.2, 144.7, 147.0, 159.4. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{15}BrNO_2^+$ 308.0281, found *m/z* 308.0290.



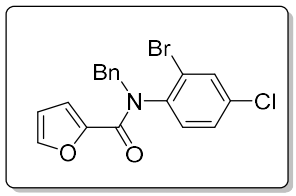
***N*-(2-bromo-4-fluorophenyl)-*N*-methylfuran-2-carboxamide (2h).** Yield 1.71 g (72%), white powder, mp 146-147˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.34 (s, 3H), 6.10 (s, 1H), 6.26 (s, 1H), 7.09 (td, J = $J_{H\text{-}H}$ = 8.7, $J_{H\text{-}F}$ = 8.2, $J_{H\text{-}H}$ = 2.9 Hz, 1H), 7.29 (dd, $J_{H\text{-}F}$ = 5.5, $J_{H\text{-}H}$ = 3.3 Hz, 2H), 7.41 (dd, $J_{H\text{-}F}$ = 7.8, $J_{H\text{-}H}$ = 2.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 37.3, 111.3, 116.0 (d, J = 22.0 Hz), 116.4, 121.1 (d, J = 25.2 Hz), 124.2 (d, J = 9.8 Hz), 131.1 (d, J = 9.0 Hz), 139.5 (d, J = 3.8 Hz), 144.8, 147.2, 159.3, 161.78 (d, J = 253.3 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{10}BrFNO_2^+$ 297.9873, found *m/z* 297.9874.



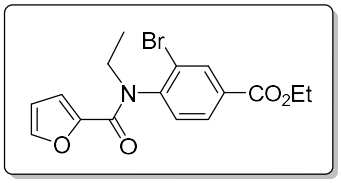
***N*-Benzyl-*N*-(2-bromo-4-fluorophenyl)furan-2-carboxamide (2i).** Yield 1.94 g (65%), white powder, mp 111-113˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1H NMR (300 MHz, Chloroform-d) δ 4.14 (d, J = 14.2 Hz, 1H), 5.70 (d, J = 14.2 Hz, 1H), 6.01 (s, 1H), 6.21 (s, 1H), 6.71 (dd, $J_{H\text{-}H}$ = 8.8, $J_{H\text{-}F}$ 5.5 Hz, 1H), 6.79 – 6.89 (m, 1H), 7.21-7.26 (m, 6H), 7.36 (dd, $J_{H\text{-}F}$ = 7.9, $J_{H\text{-}H}$ = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 52.5, 111.4, 115.3 (d, J = 21.9 Hz), 116.6, 121.1 (d, J = 25.2 Hz), 124.7, 124.8, 127.9, 128.6, 129.7, 132.7 (d, J = 9.0 Hz), 136.5, 137.2 (d, J = 3.7 Hz), 144.9, 147.1, 159.1, 161.83 (d, J = 253.3 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}BrFNO_2^+$ 374.0186, found *m/z* 374.0191.



***N*-(2-Bromo-4-chlorophenyl)-*N*-methylfuran-2-carboxamide (2j).** Yield 1.90 g (76%), white powder, mp 145-146˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.33 (s, 3H), 6.18 (s, 1H), 6.27 (s, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.30 (s, 1H), 7.35 (dd, J = 8.4, 2.3 Hz, 1H), 7.68 (d, J = 2.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 37.2, 111.3, 116.6, 124.2, 129.2, 130.8, 133.6, 134.9, 141.9, 144.8, 147.1, 159.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{10}BrClNO_2^+$ 313.9578, found *m/z* 313.9593.



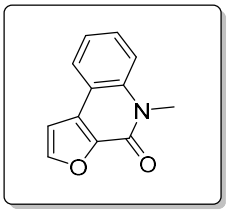
***N*-Benzyl-*N*-(2-bromo-4-chlorophenyl)furan-2-carboxamide (2k).** Yield 2.33 g (75%), white powder, mp 113-114˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.20 (d, J = 14.3 Hz, 1H), 5.72 (d, J = 14.3 Hz, 1H), 6.13 (s, 1H), 6.26 (dd, J = 3.7, 1.8 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 7.15 (dd, J = 8.5, 2.4 Hz, 1H), 7.21 – 7.36 (m, 6H), 7.67 (d, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 52.5, 111.4, 116.8, 124.7, 128.0, 128.5, 128.6, 129.7, 132.3, 133.5, 135.0, 136.4, 139.6, 145.0, 147.1, 158.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}BrClNO_2^+$ 389.9891, found *m/z* 389.9898.



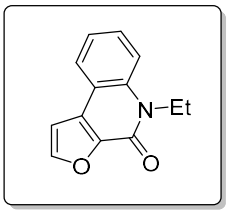
Ethyl 3-bromo-4-[*N*-ethyl-*N*-(furan-2-ylcarbonyl)amino)-benzoate (2l). Yield 2.07 g (71%), coloress crystalls, mp 99-100˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1 δ 1.22 (td, J = 7.2, 2.4 Hz, 3H), 1.41 (td, J = 7.2, 2.4 Hz, 3H), 3.50 – 3.70 (m, 1H), 4.09 – 4.24 (m, 1H), 4.41 (qd, J = 7.1, 2.3 Hz, 2H), 6.18 (s, 1H), 6.23 (s, 1H), 7.20 – 7.40 (m, 2H), 8.02 (dd, J = 8.2, 2.1 Hz, 1H), 8.34 (d, J = 2.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 12.8, 14.4, 44.7, 61.9, 111.3, 116.5, 124.3, 129.6, 131.0, 131.7, 135.1, 144.7,

145.4, 147.4, 158.6, 164.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}BrNO_4^+$ 366.0335, found *m/z* 366.0340.

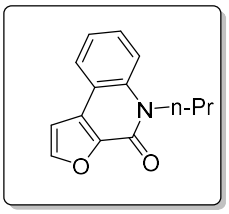
General procedure for the synthesis of compounds 1a-l. A mixture of the appropriate amide **2a-l** (0.25 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), IPr^{SPh}·HCl (6.7 mg, 0.0125 mmol), Cs_2CO_3 (122 mg, 0.375 mmol) and dry toluene (1.5 ml) was stirred at 110 °C under an argon atmosphere for 16 h. The mixture was then cooled to room temperature, diluted with DCM (3 ml) and filtered through a short pad of celite. The filtrate was rotary evaporated to dryness. The crude product obtained was purified by column chromatography on silica gel using a DCM-Et_2O (5:1) mixture as eluent.



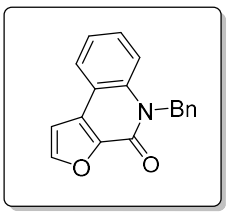
5-Methylfuro[2,3-*c*]quinolin-4(5*H*)-one (1a). Yield 0.40 g (80%), yellowish powder, mp 127-128 ˚C (lit[S5] mp 126.5-128.5 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): 3.84 (s, 3H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.35 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.57 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 29.5, 106.0, 115.5, 116.7, 122.7, 124.7, 129.0, 129.6, 138.1, 148.3, 154.0, 174.4. The spectral characteristics of the product obtained are similar to those described in the literature [S5].



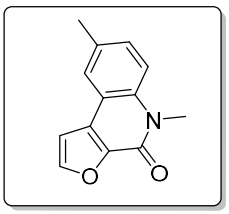
5-Ethylfuro[2,3-*c*]quinolin-4(5*H*)-one (1b). Yield 0.39 g (74%), reddish oil ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.41 (t, *J* = 7.1 Hz, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.32 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.44 – 7.59 (m, 2H), 7.82 (s, 1H), 7.82 – 7.89 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.2, 37.3, 105.9, 115.3, 117.0, 122.5, 124.9, 128.9, 129.5, 137.0, 142.5, 148.2, 153.6. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2^+$ 214.0863, found *m/z* 214.0869



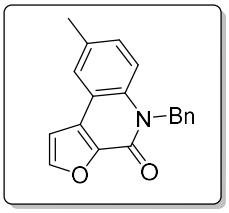
5-Propylfuro[2,3-*c*]quinolin-4(5*H*)-one (1c). Yield 0.43 g (76%), reddish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (t, *J* = 7.4 Hz, 3H), 1.75 – 1.92 (m, 2H), 4.13 – 4.63 (m, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.23 – 7.36 (m, 1H), 7.44 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.49 – 7.58 (m, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 11.4, 21.2, 43.7, 105.9, 115.5, 117.0, 122.5, 124.8, 128.8, 129.5, 137.2, 142.5, 148.2, 153.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_2^+$ 228.1019, found *m/z* 228.1027



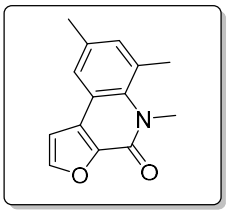
5-Benzylfuro[2,3-*c*]quinolin-4(5*H*)-one (1d). Yield 0.49 g (71%), yellowish powder, mp 181-182 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.68 (s, 2H), 7.10 (d, *J* = 1.9 Hz, 1H), 7.20 – 7.44 (m, 8H), 7.86 (dd, *J* = 9.1, 1.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 45.9, 106.1, 116.4, 116.9, 122.8, 124.7, 126.7, 127.4, 128.9, 130.1, 136.6, 137.5, 142.3, 148.6, 154.2 two signals are overlapped. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}NO_2^+$ 276.1019, found *m/z* 276.1030



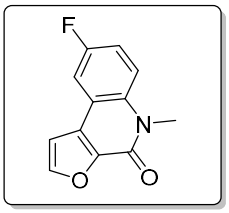
5,8-Dimethylfuro[2,3-*c*]quinolin-4(5*H*)-one (1e). Yield 0.40 g (75%), yellowish crystals, mp 200-201˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.48 (s, 1H), 3.81 (s, 3H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 1.2 Hz, 2H), 7.64 (dt, *J* = 1.7, 0.9 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.9, 29.5, 105.9, 115.3, 116.6, 124.6, 129.4, 130.1, 132.4, 136.1, 142.7, 148.1, 153.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2^+$ 214.0863, found *m/z* 214.0872.



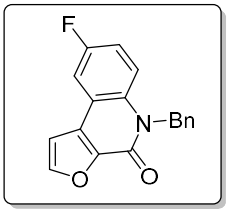
5-Benzyl-8-methylfuro[2,3-*c*]quinolin-4(5*H*)-one (1f). Yield 0.52 g (72%), yellowish powder, mp 143-144˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43 (s, 3H), 5.66 (s, 2H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.17 – 7.23 (m, 5H), 7.27 – 7.32 (m, 2H), 7.63 – 7.66 (m, 1H), 7.87 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.8, 45.8, 106.0, 116.3, 116.8, 124.6, 126.7, 127.4, 128.9, 129.9, 130.1, 132.4, 135.4, 136.7, 142.4, 148.5, 154.1. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_2^+$ 290.1176, found *m/z* 290.1175.



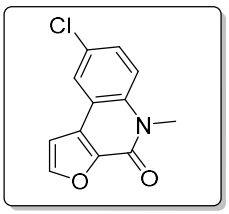
5,6,8-Trimethylfuro[2,3-*c*]quinolin-4(5*H*)-one (1g). Yield 0.37 g (65%), yellowish powder, mp 157-158˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.42 (s, 3H), 2.70 (s, 3H), 3.88 (s, 3H), 7.00 (d, *J* = 2.0 Hz, 1H), 7.11 – 7.20 (m, 2H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 20.6, 24.1, 37.1, 106.1, 118.2, 122.6, 126.3, 130.0, 132.7, 134.7, 137.7, 142.3, 148.1, 156.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_2^+$ 228.1019, found *m/z* 228.1020.



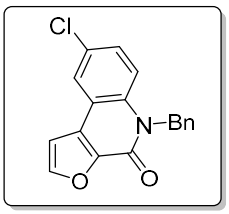
8-Fluoro-5-methylfuro[2,3-*c*]quinolin-4(5*H*)-one (1h). Yield 0.37 g (68%), yellowish crystals, mp 229-230˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3H), 7.02 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.32 (m, 1H), 7.43 (dd, $J_{H\text{-}H}$ = 9.3, $J_{H\text{-}F}$ = 4.5 Hz, 1H), 7.52 (dd, $J_{H\text{-}F}$ = 8.4, $J_{H\text{-}H}$ = 2.9 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 29.8, 106.0, 110.2 (d, *J* = 23.3 Hz), 116.5 (d, *J* = 23.5 Hz), 116.9, 117.1, 117.7 (d, *J* = 8.8 Hz), 128.8 (d, *J* = 3.1 Hz), 134.6, 143.0, 148.4, 153.6, 158.38 (d, *J* = 243.0 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_9FNO_2^+$ 218.0612, found *m/z* 218.0602.



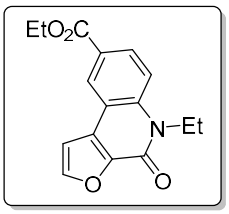
5-Benzyl-8-fluorofuro[2,3-*c*]quinolin-4(5*H*)-one (1i). Yield 0.49 g (67%), yellowish crystals, mp 173-174 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.67 (s, 2H), 7.03 – 7.08 (m, 1H), 7.09 – 7.17 (m, 1H), 7.19 – 7.24 (m, 3H), 7.28 – 7.35 (m, 3H), 7.52 (dd, $J_{H\text{-}F}$ = 8.3, $J_{H\text{-}H}$ = 2.9 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 46.2, 106.1, 110.3 (d, *J* = 23.0 Hz), 116.6 (d, *J* = 23.5 Hz), 118.0 (d, *J* = 8.4 Hz), 126.7, 127.6, 129.0, 129.4 (d, *J* = 3.1 Hz) 133.9, 136.3, 148.7, 153.8, 158.36 (d, *J* = 243.2 Hz). ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{13}FNO_2^+$ 294.0925, found *m/z* 294.0935



8-Chloro-5-methylfuro[2,3-*c*]quinolin-4(5*H*)-one (1j). Yield 0.41 g (71%), yellowish crystals, mp 210-211˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.81 (s, 3H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 9.1 Hz, 1H), 7.51 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 29.7, 105.9, 116.8, 117.9, 124.1, 128.4, 128.6, 128.9, 136.6, 142.9, 148.5, 153.7. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_9ClNO_2^+$ 234.0316, found *m/z* 234.0317



5-Benzyl-8-chlorofuro[2,3-c]quinolin-4(5*H*)-one (1k). Yield 0.56 g (72%), yellow powder, mp 167-168˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.65 (s, 2H), 7.07-7.25 (d, *J* = 2.1 Hz, 1H), 7.19-7.25 (m, 3H), 7.26-7.34 (m, 4H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 46.0, 106.0, 117.8, 118.2, 124.2, 126.7, 127.6, 128.4, 129.0, 129.1, 129.2, 136.0, 136.2, 148.9, 153.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{13}ClNO_2^+$ 310.0629, found *m/z* 310.0635.



Ethyl-5-methyl-4-oxo-4,5-dihydrofuro[2,3-*c*]quinoline-8-carboxylate (1l). Yield 0.55g (77%), white powder, mp 171-172˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 – 1.50 (m, 6H), 4.38 – 4.58 (m, 4H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 9.0, 2.1 Hz, 1H), 8.53 (d, *J* = 2.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.2, 14.5, 37.6, 61.4, 106.1, 115.2, 116.6, 124.5, 126.9, 129.6, 129.7, 140.0, 142.5, 148.6, 153.5, 166.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_4^+$ 286.1074, found *m/z* 286.1080.

S3. X-Ray structure determination

X-ray crystallographic data and refinement details.

X-ray diffraction data for **1g** and **1j** were collected at 100 K on a Rigaku Synergy-S diffractometer equipped with a HyPix6000HE 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.[S7] The structure was solved by direct methods using SHELXT [S8] and refined by the full-matrix least-squares minimization method on F^2 using SHELXL-2018 [S9] in the OLEX2 program. [S10] Positions of all atoms were found from the electron density-difference map. Non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were refined with relative isotropic displacement parameters taken as $U_{iso}(H)=1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H)=1.2U_{eq}(C)$ otherwise.

Crystal data, data collection and structure refinement details for **1g** and **1j** are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2300119 and 2300120; 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/structures/

Table S1. Crystal data, data collection and structure refinement details for **1g** and **1j.**

Identification code	**1g**	**1j**
Empirical formula	$C_{13}H_{11}NO_2$	$C_{12}H_8ClNO_2$
Formula weight	213.23	233.64
Temperature / K	100.0(5)	100.0(4)
Wavelength /Å	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a / Å	7.29862(7)	7.84250(10)
b / Å	10.87970(8)	10.07480(10)
c / Å	13.26532(11)	13.03250(10)
β / deg	105.5334(9)	100.5590(10)
Volume / $Å^3$	1014.882(15)	1012.282(18)
Z	4	4
Density (calculated) / $g·cm^{-3}$	1.396	1.533
Absorption coefficient μ / mm^{-1}	0.771	3.203
F(000)	448	480
Crystal size / mm	0.75 × 0.41 × 0.15	0.66 × 0.40 × 0.21
θ range for data collection / deg	5.339-79.754	5.586-79.691
Index ranges	-9<=h<=8,	-9<=h<=9,
	-13<=k<=13,	-12<=k<=12,
	-15<=l<=16	-16<=l<=15
Reflections		
Collected	15852	13518
Independent [R_{int}]	2202 [0.0211]	2190 [0.0276]
Observed (with I>2σ(I))	2152	2169
Data, restraints, parameters	2202, 0, 191	2190, 0, 170
Goodness-of-fit on F^2	1.064	1.042
R1, wR2 indices for I>2σ(I)	0.0347, 0.0962	0.0326, 0.0884
R1, wR2 indices for all data	0.0353, 0.0969	0.0329, 0.0886
Extinction coefficient	0.0090(9)	0.0026(4)
Largest diff. peak and hole / $ē·Å^{-3}$	0.302, -0.155	0.338, -0.366
CCDC deposition number	2300119	2300120

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

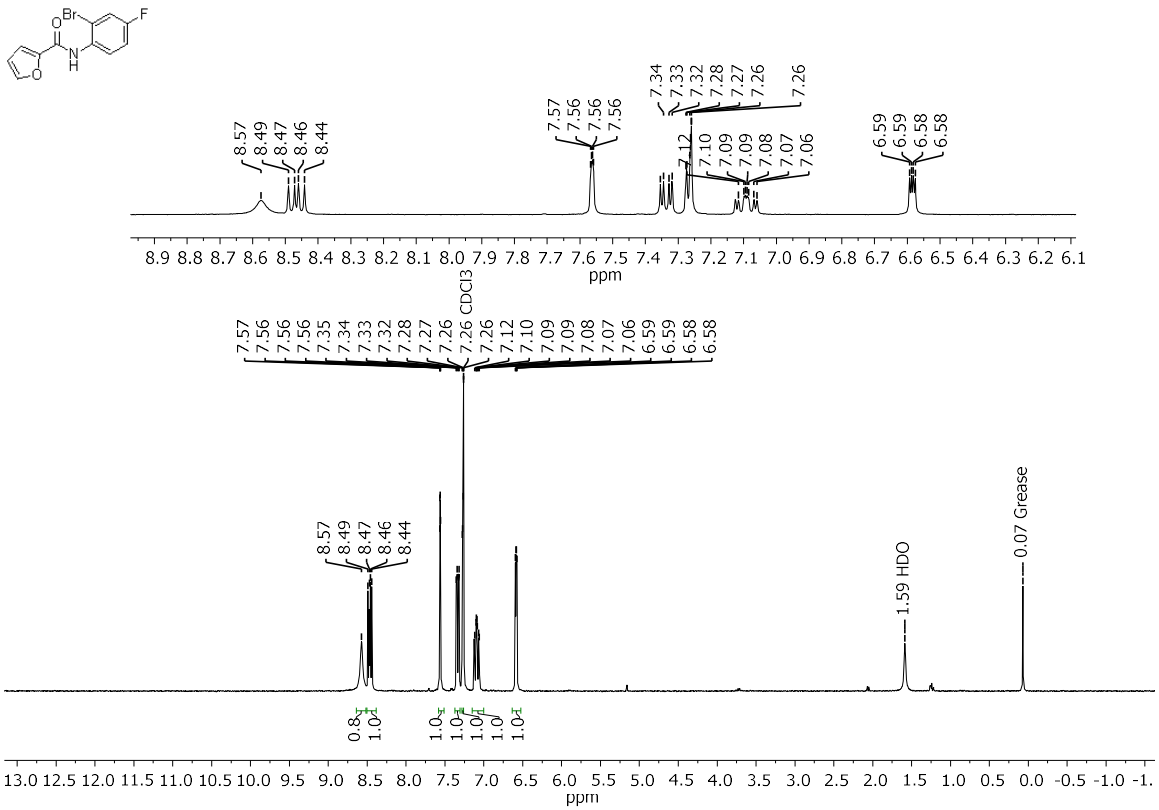


Figure S1. ^{1}H NMR spectrum of compound **3d** (300 MHz, $CDCl_3$).

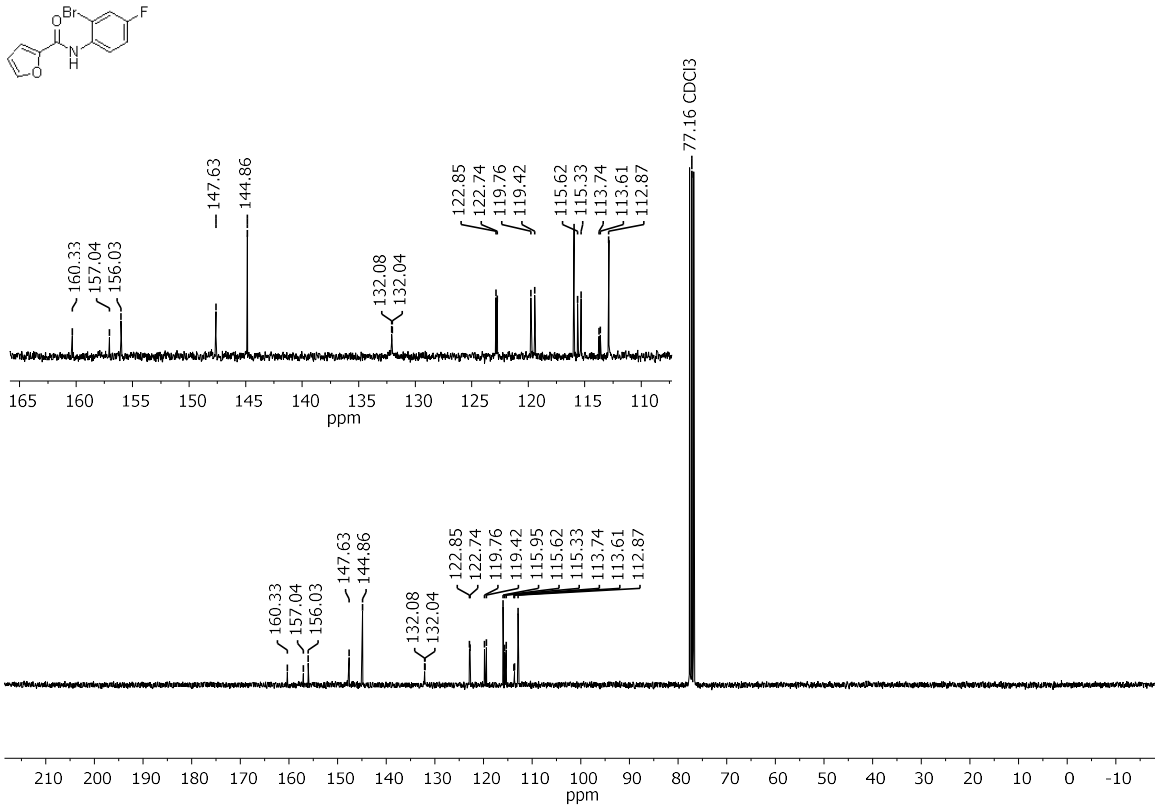


Figure S2. ^{13}C NMR spectrum of compound **3d** (75 MHz, $CDCl_3$).

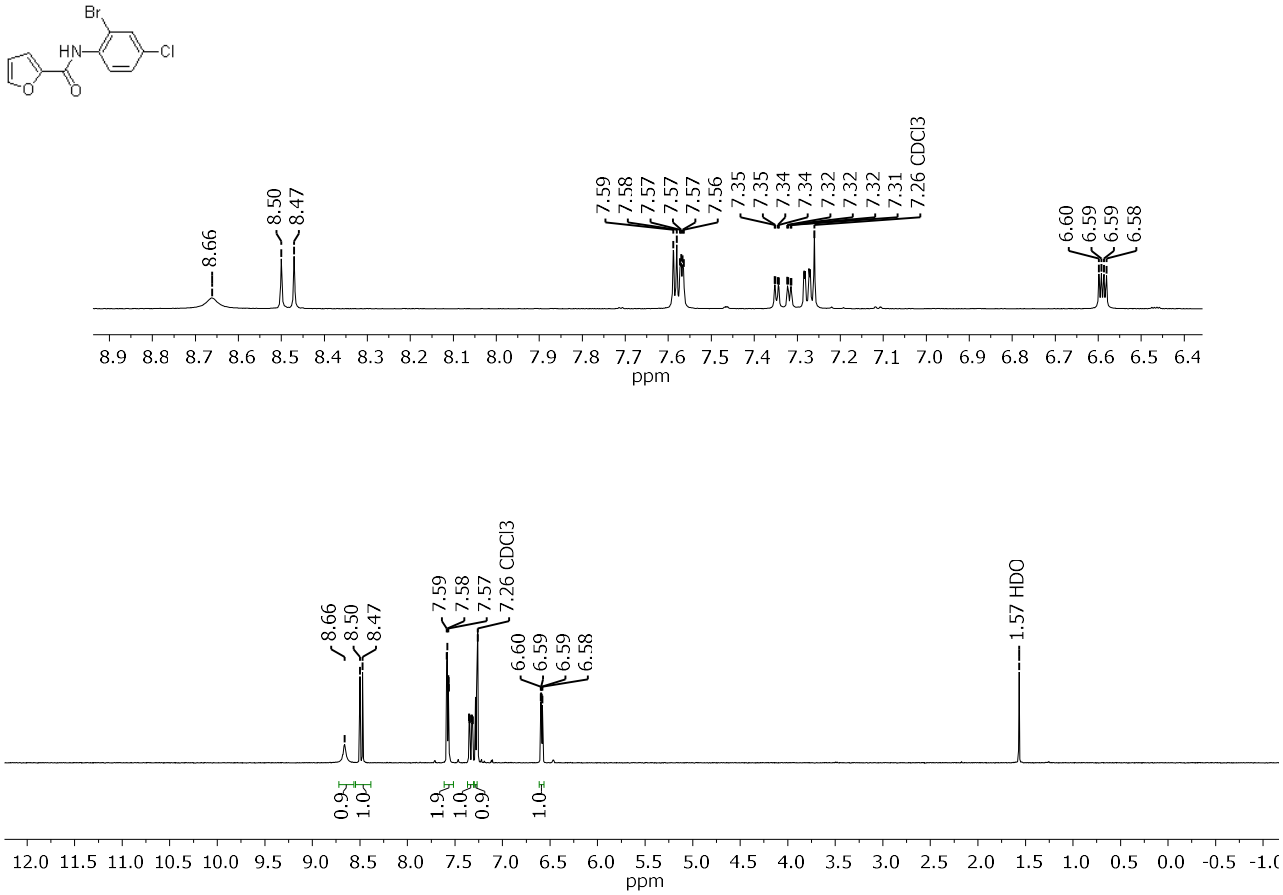


Figure S3. ^{1}H NMR spectrum of compound **3e** (300 MHz, $CDCl_3$).

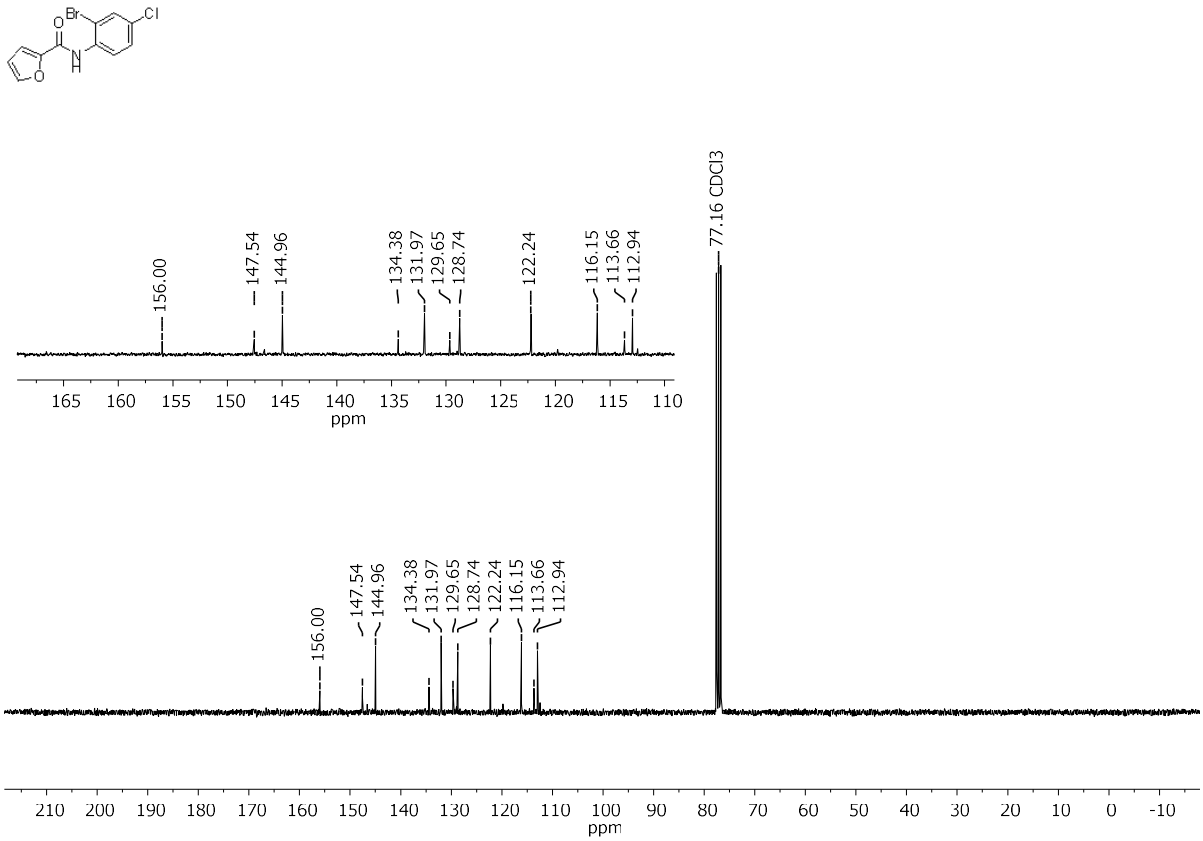


Figure S4. ^{13}C NMR spectrum of compound **3e** (75 MHz, $CDCl_3$).

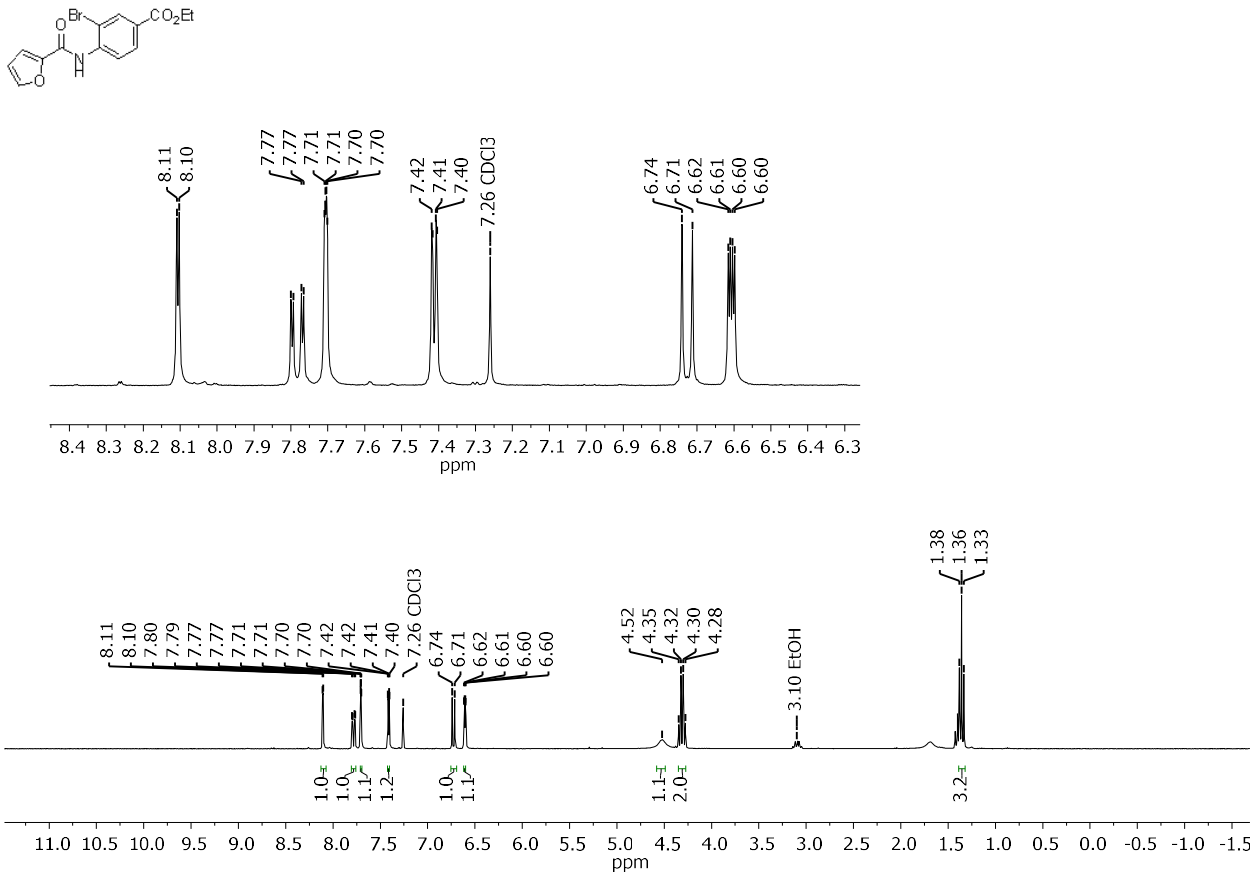


Figure S5. ^{1}H NMR spectrum of compound **3f** (300 MHz, $CDCl_3$).

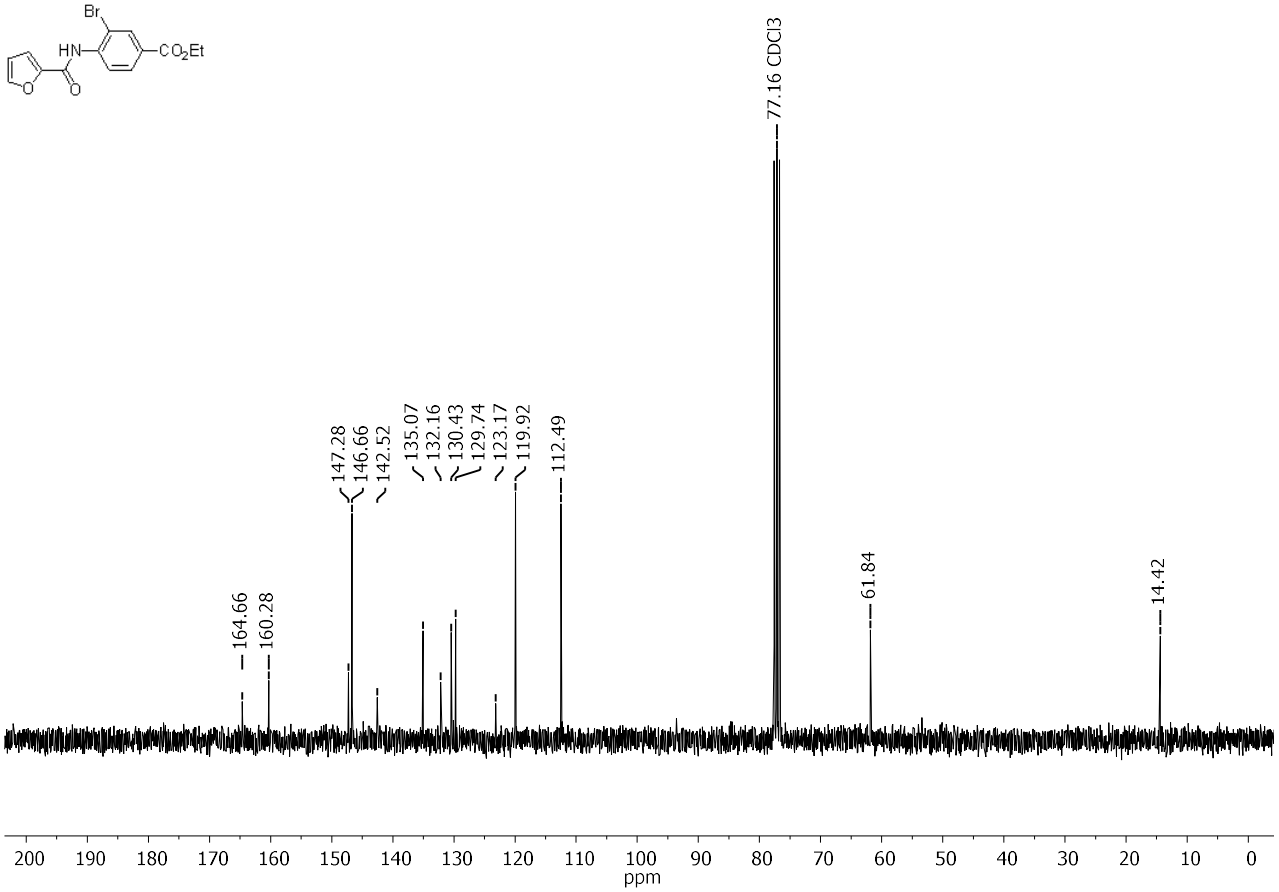


Figure S6. ^{13}C NMR spectrum of compound **3f** (75 MHz, $CDCl_3$).

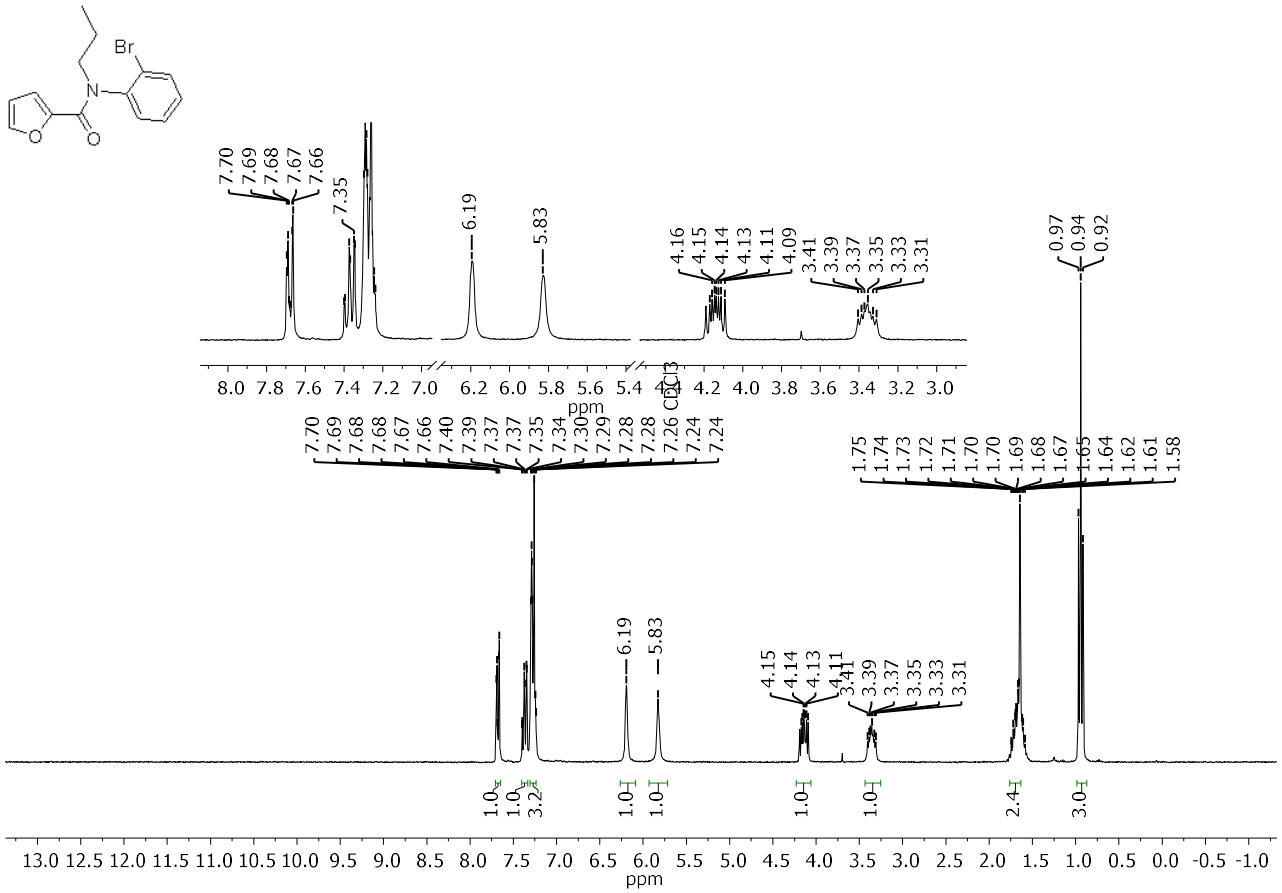


Figure S7. ^{1}H NMR spectrum of compound **2c** (300 MHz, $CDCl_3$).

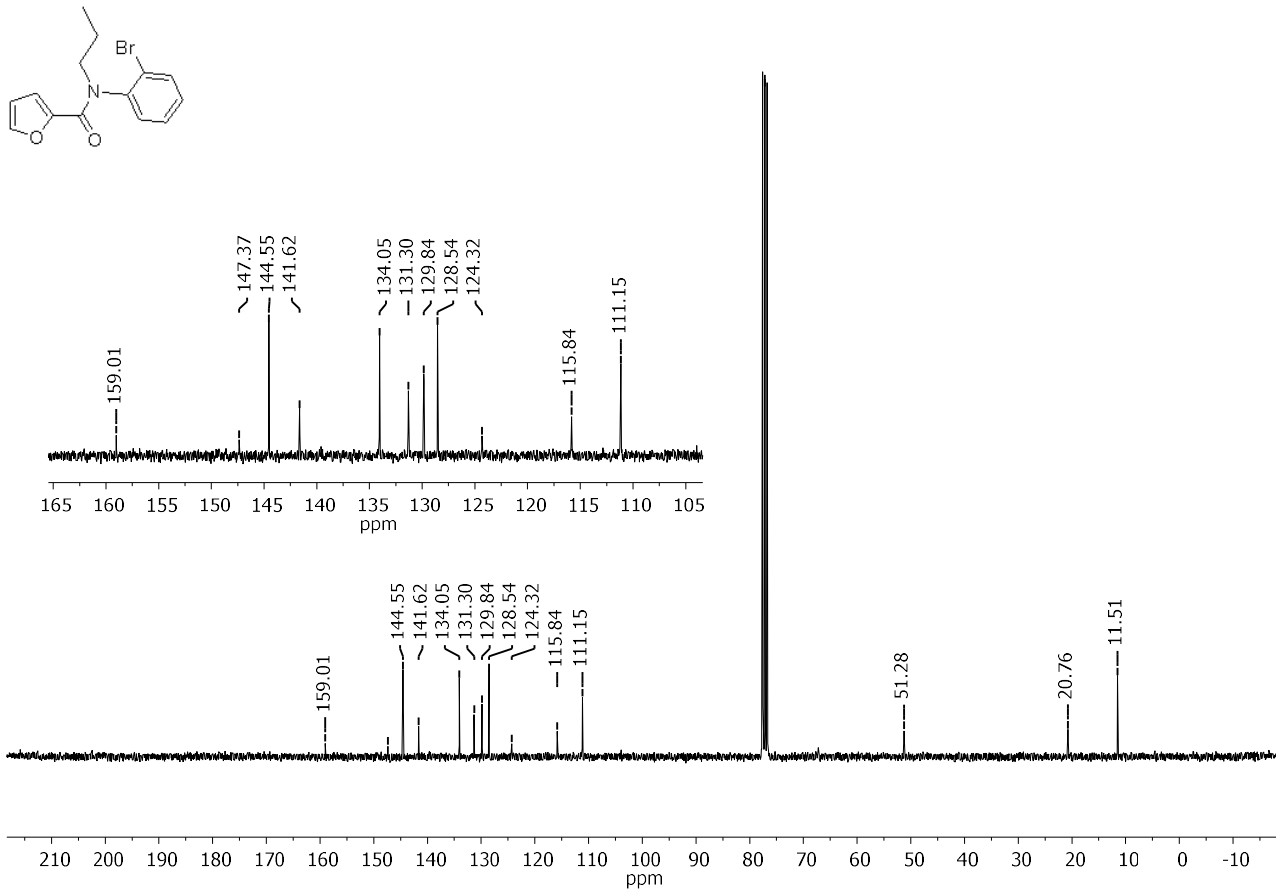


Figure S8. ^{13}C NMR spectrum of compound **2c** (75 MHz, $CDCl_3$).

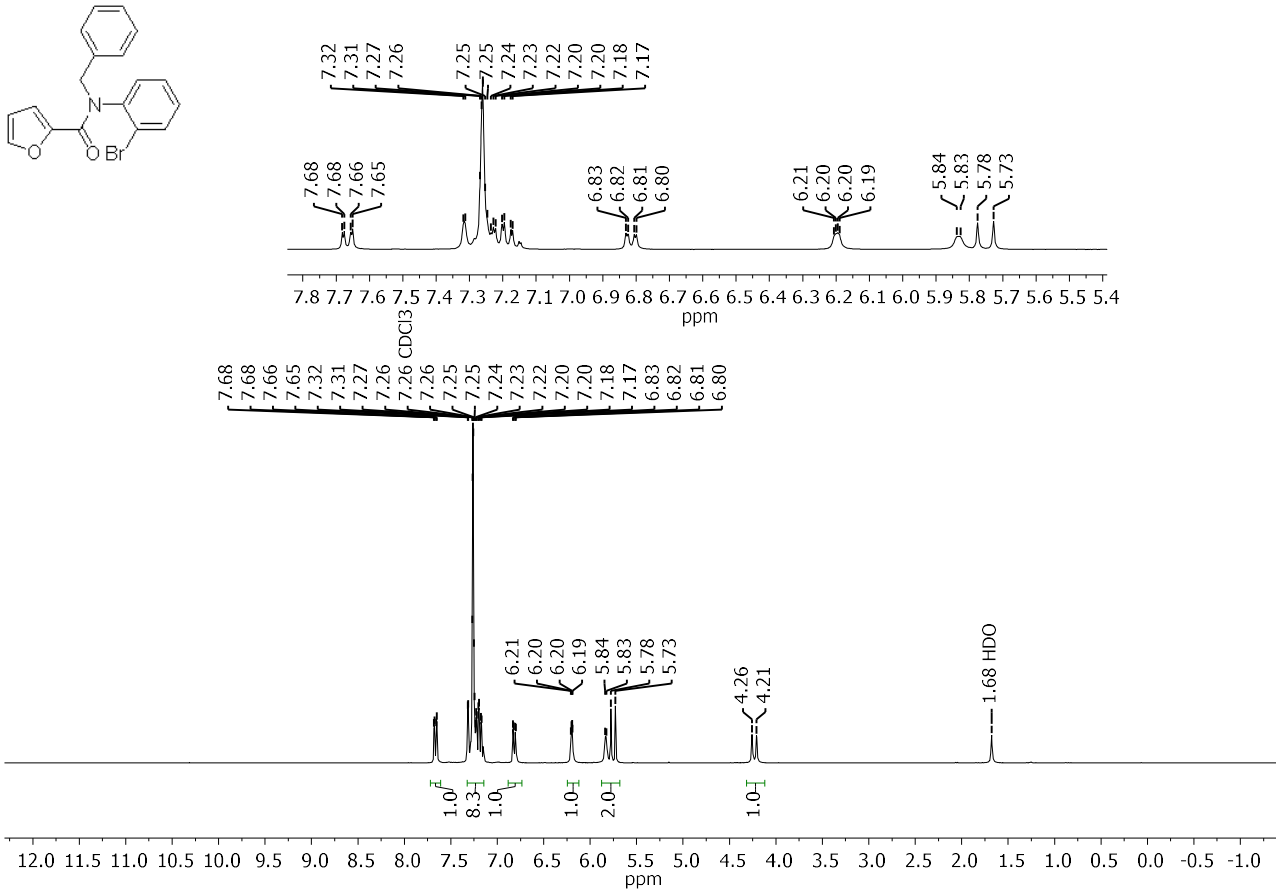


Figure S9. ^{1}H NMR spectrum of compound **2d** (300 MHz, $CDCl_3$).

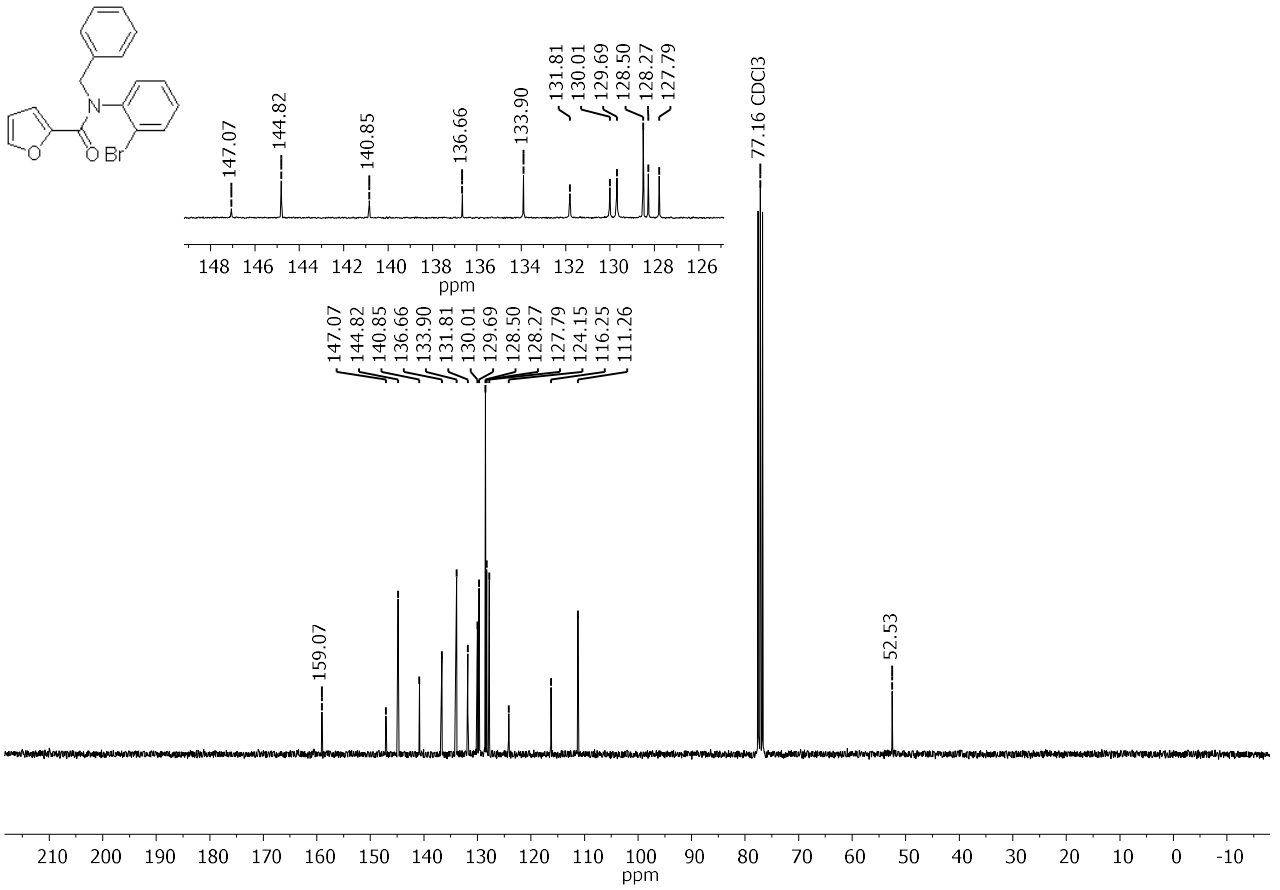


Figure S10. ^{13}C NMR spectrum of compound **2d** (75 MHz, $CDCl_3$).

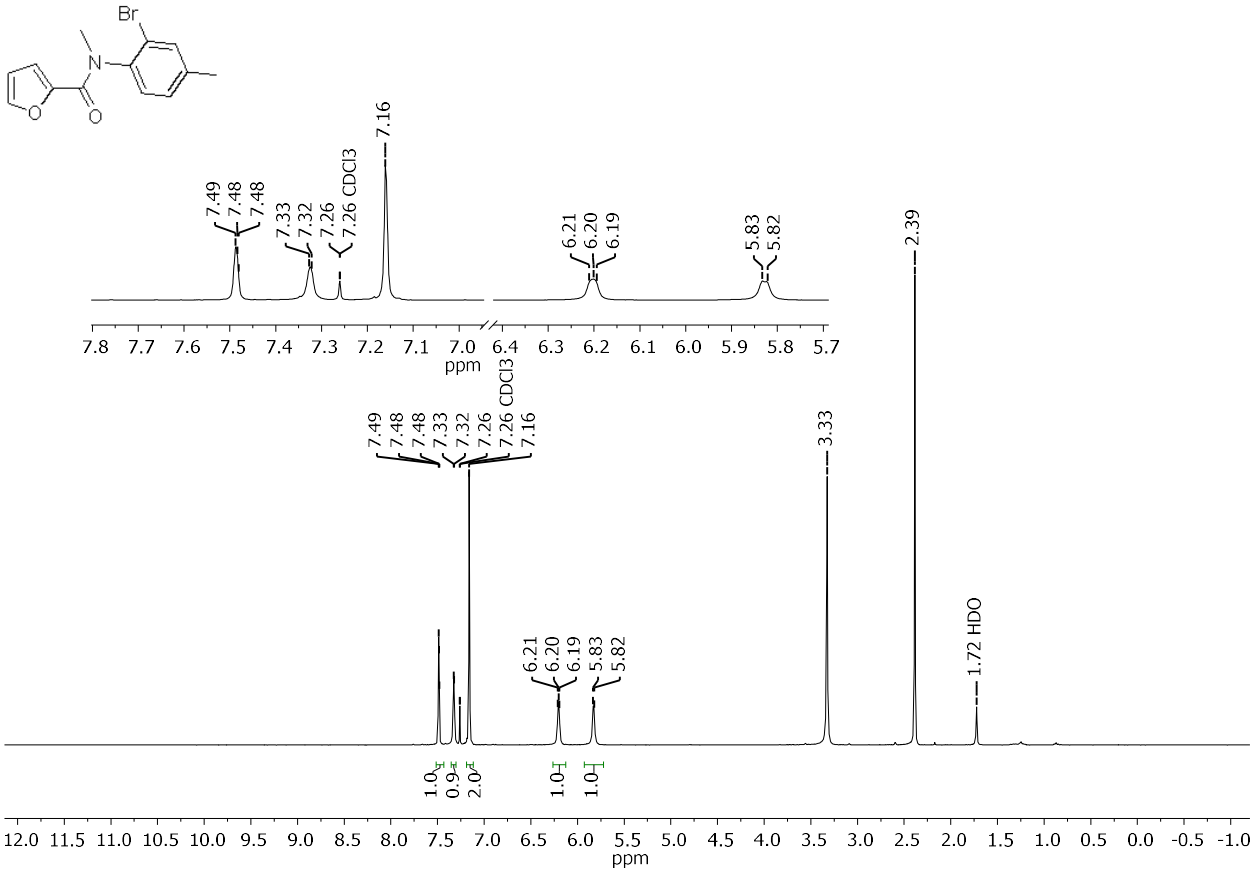


Figure S11. ^{1}H NMR spectrum of compound **2e** (300 MHz, $CDCl_3$).

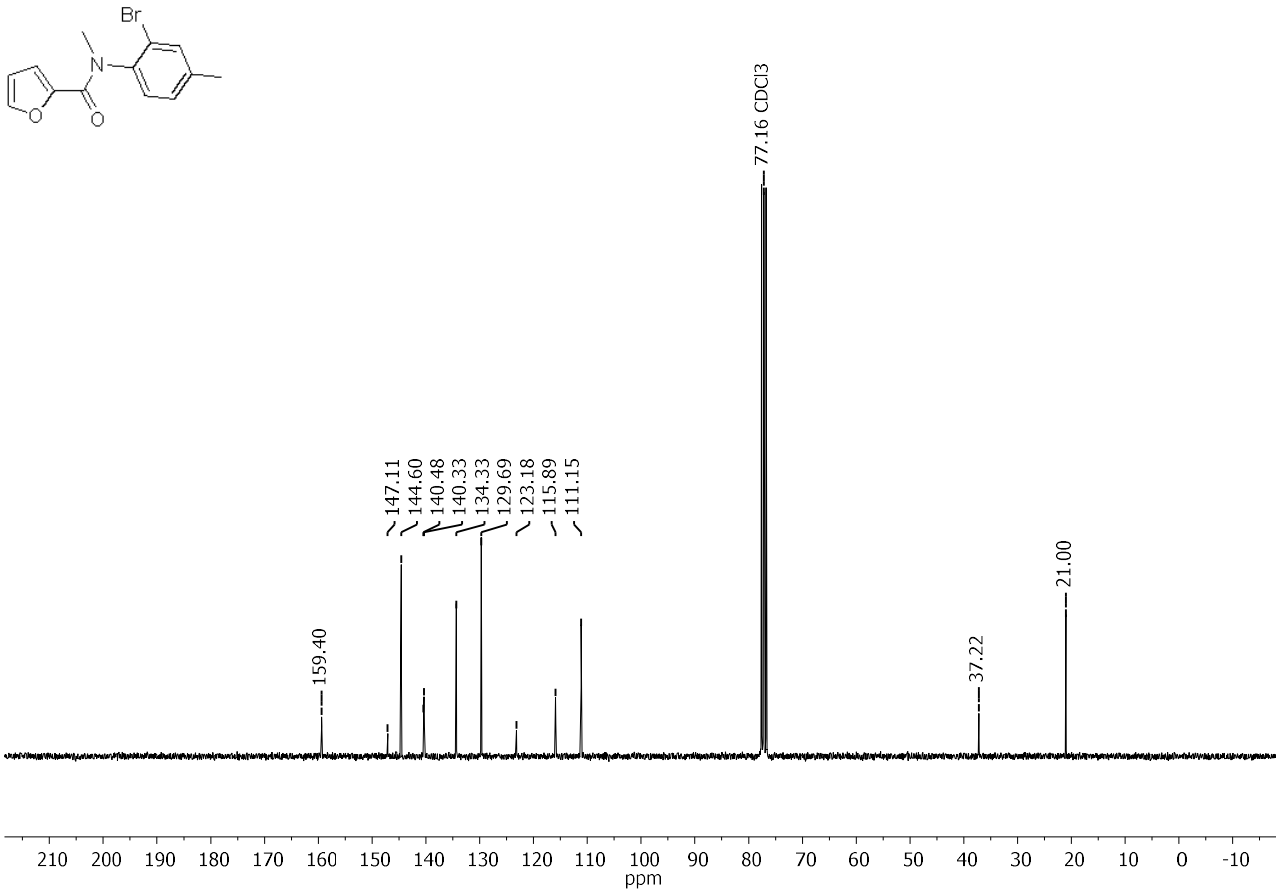


Figure S12. ^{13}C NMR spectrum of compound **2e** (75 MHz, $CDCl_3$).

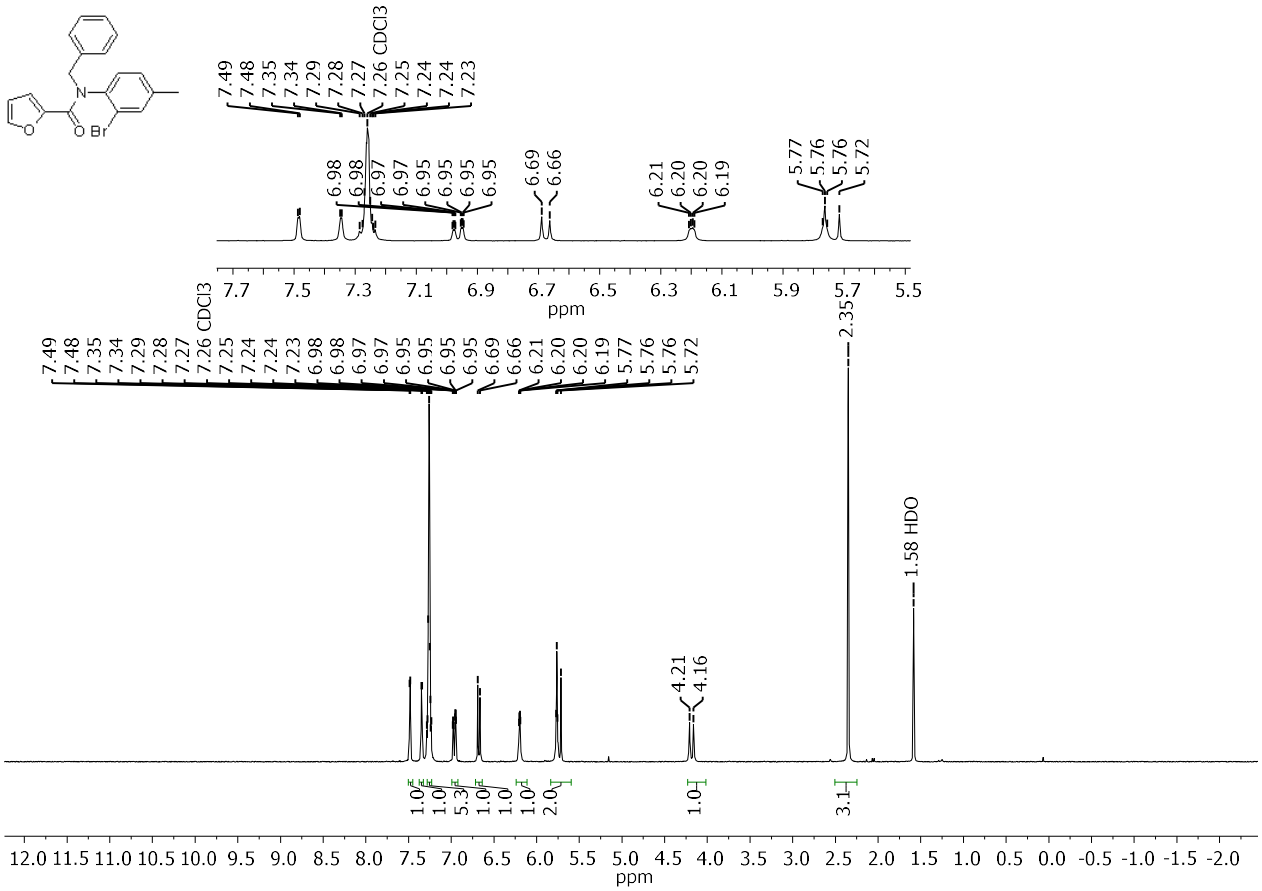


Figure S13. ^{1}H NMR spectrum of compound **2f** (300 MHz, $CDCl_3$).

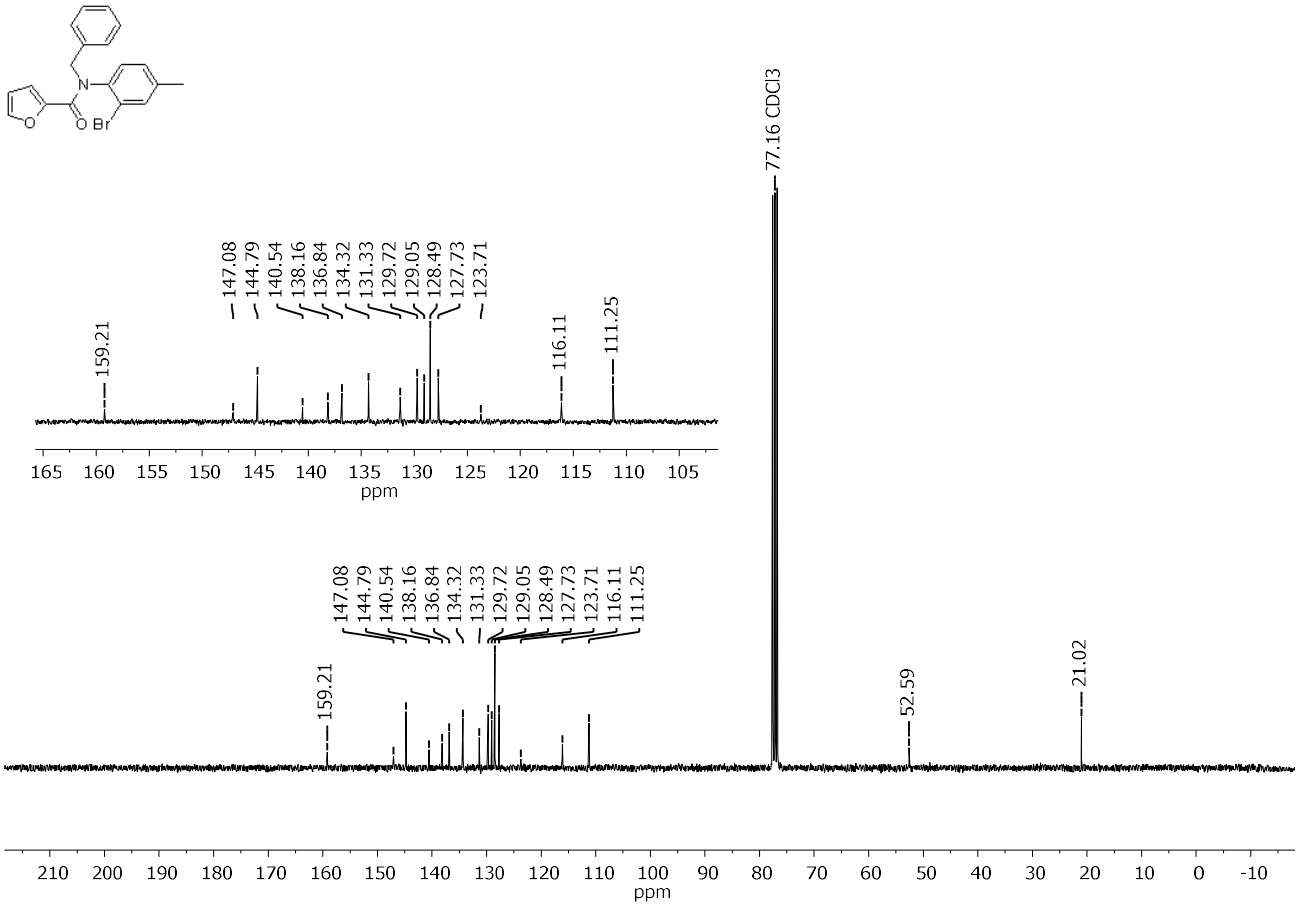


Figure S14. ^{13}C NMR spectrum of compound **2f** (75 MHz, $CDCl_3$).

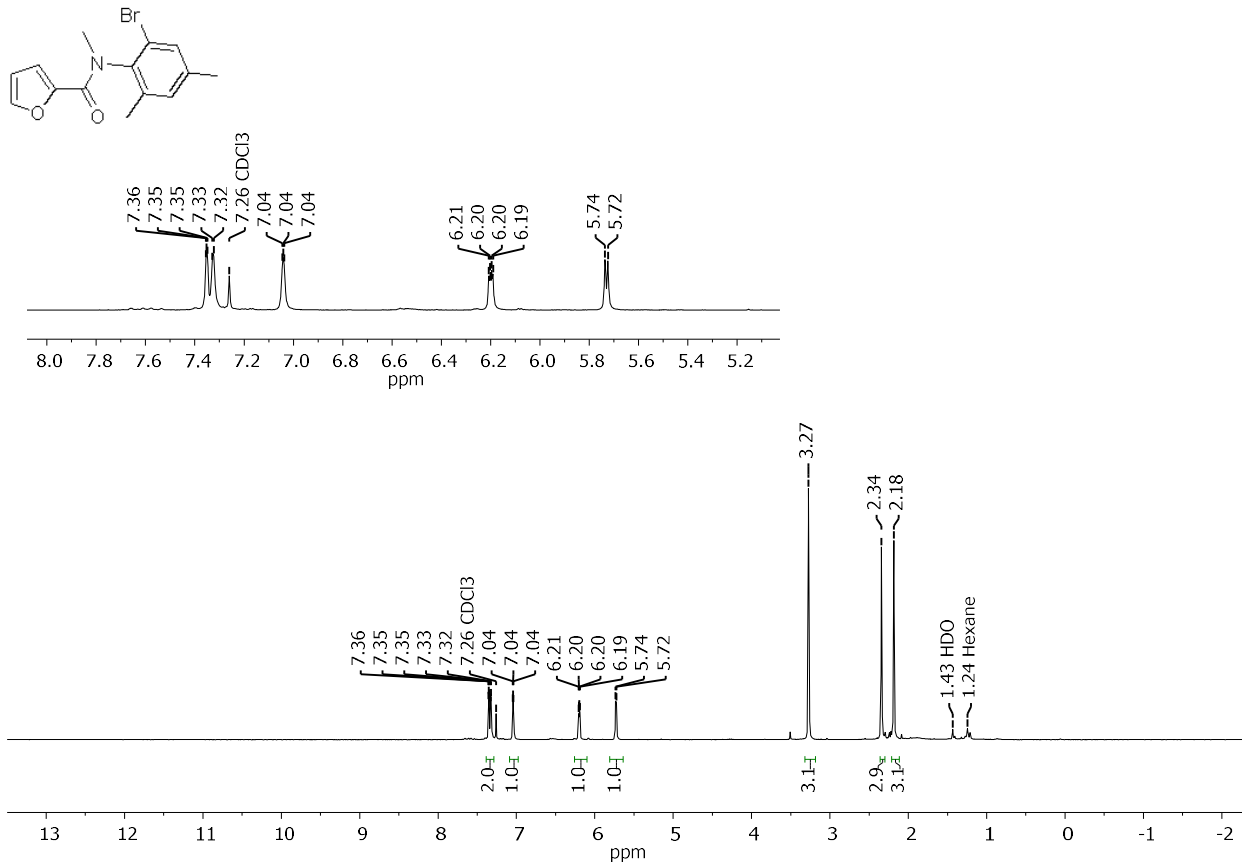


Figure S15. ^{1}H NMR spectrum of compound **2g** (300 MHz, $CDCl_3$).

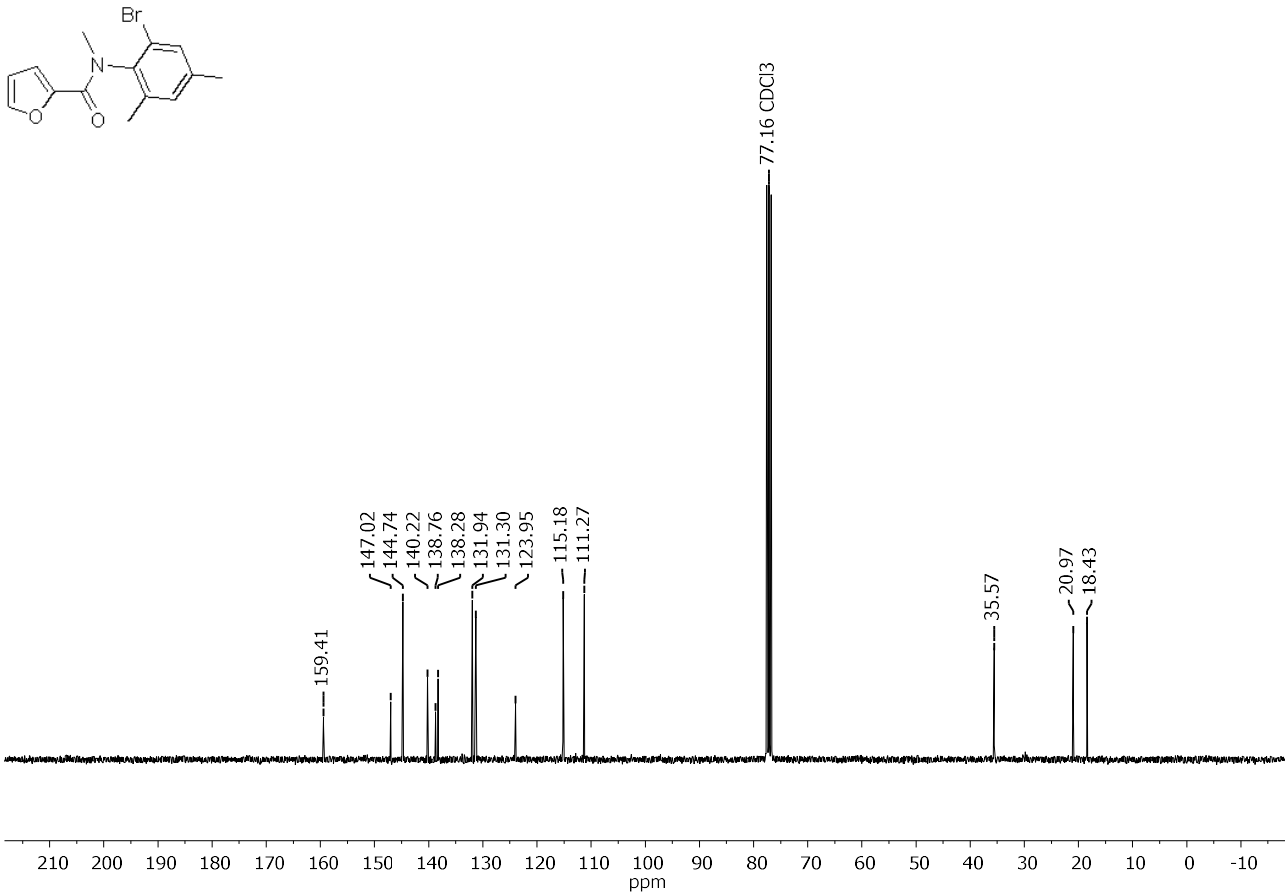


Figure S16. ^{13}C NMR spectrum of compound **2g** (75 MHz, $CDCl_3$).

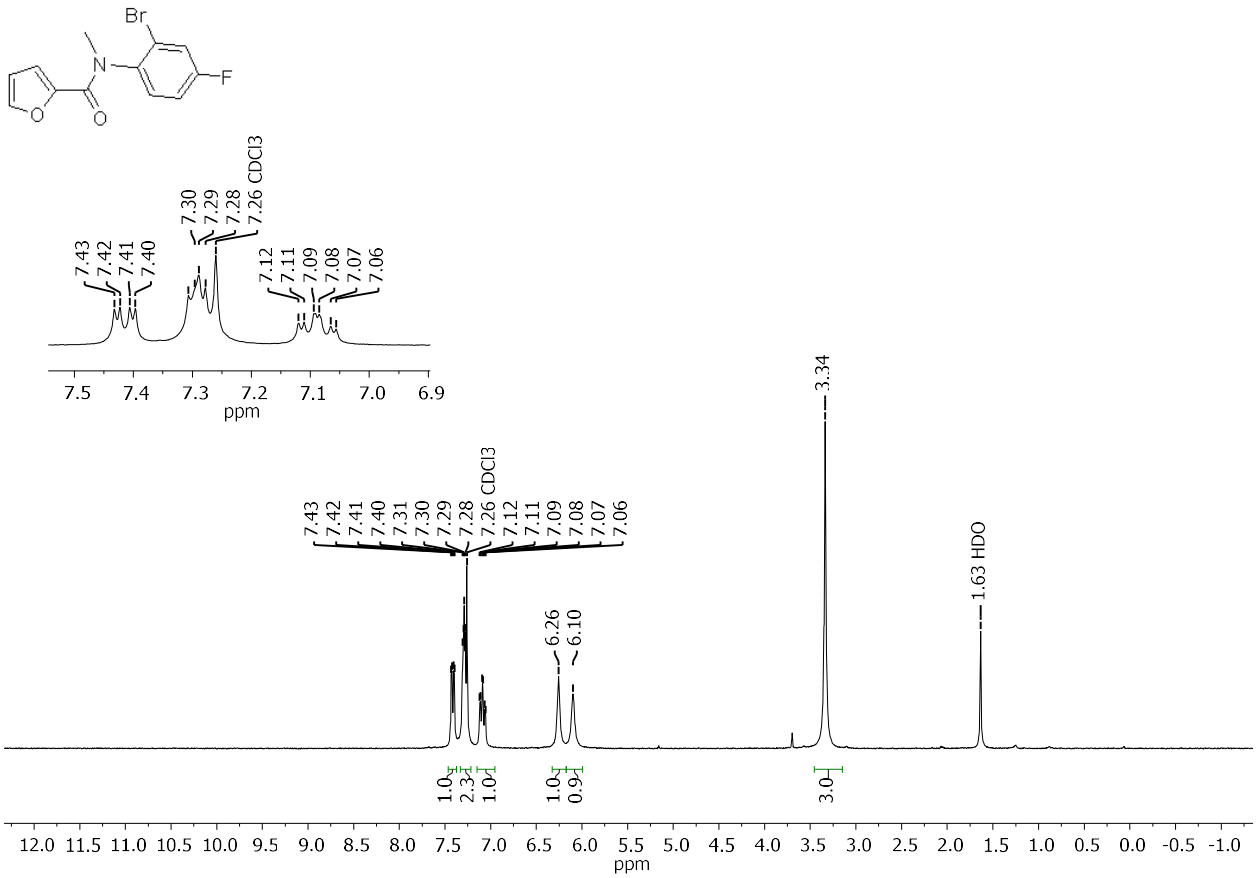


Figure S17. ^{1}H NMR spectrum of compound **2h** (300 MHz, $CDCl_3$).

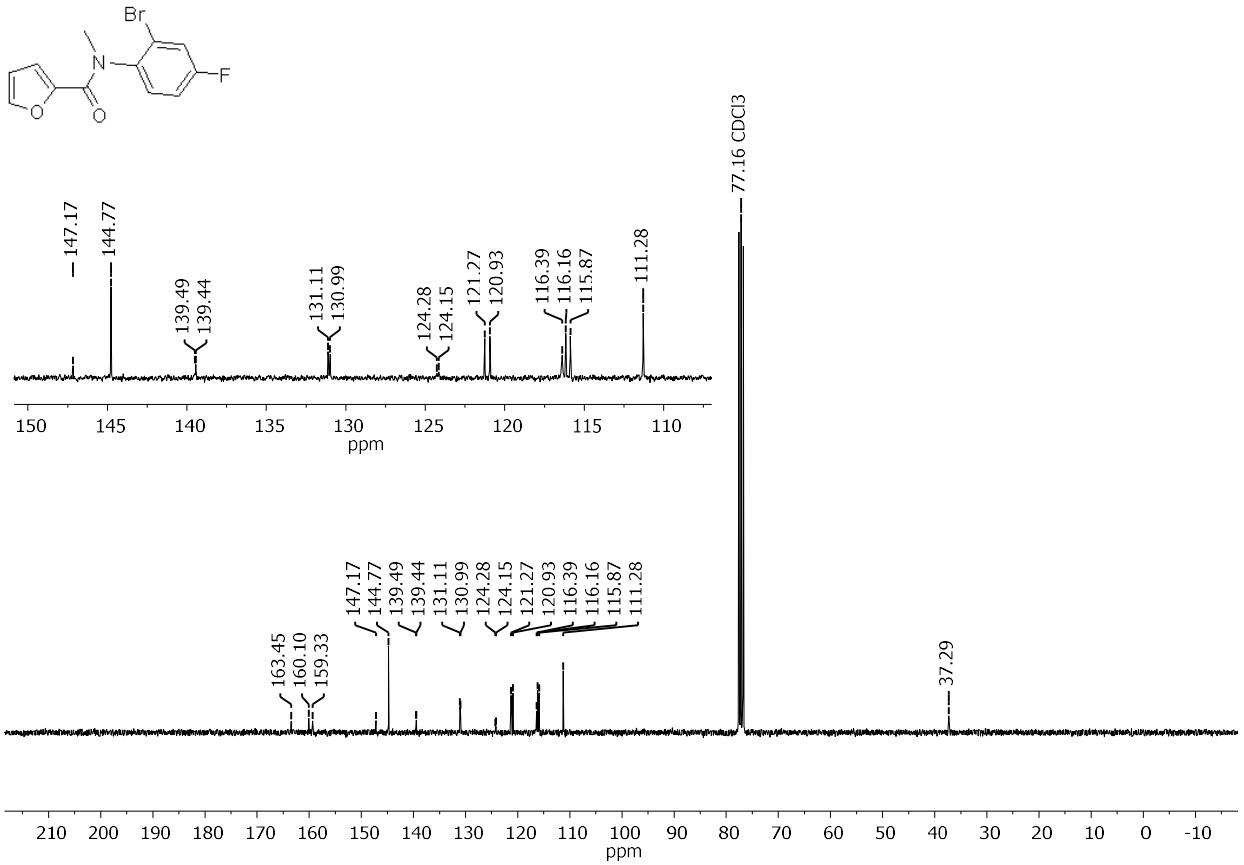


Figure S18. ^{13}C NMR spectrum of compound **2h** (75 MHz, $CDCl_3$).

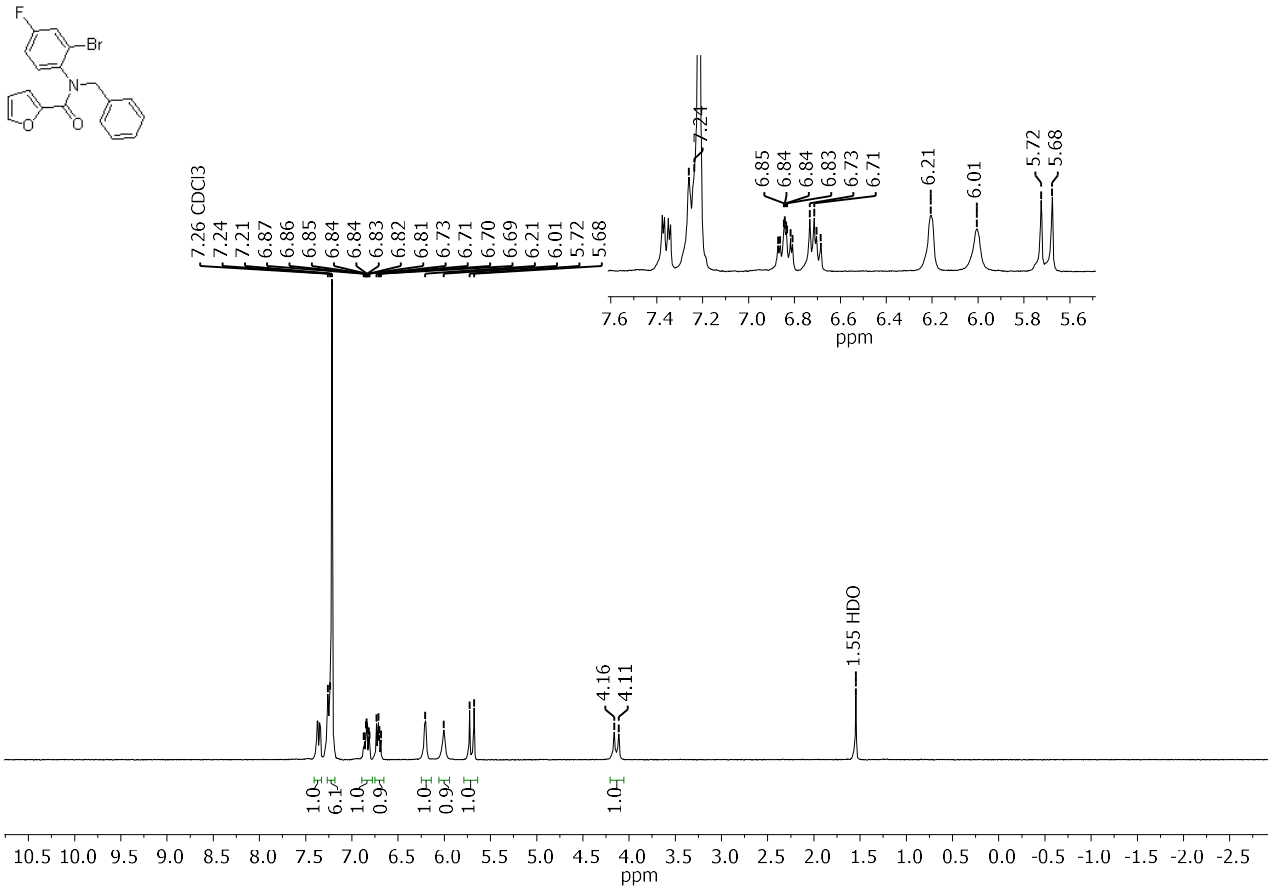


Figure S19. ^{1}H NMR spectrum of compound **2i** (300 MHz, $CDCl_3$).

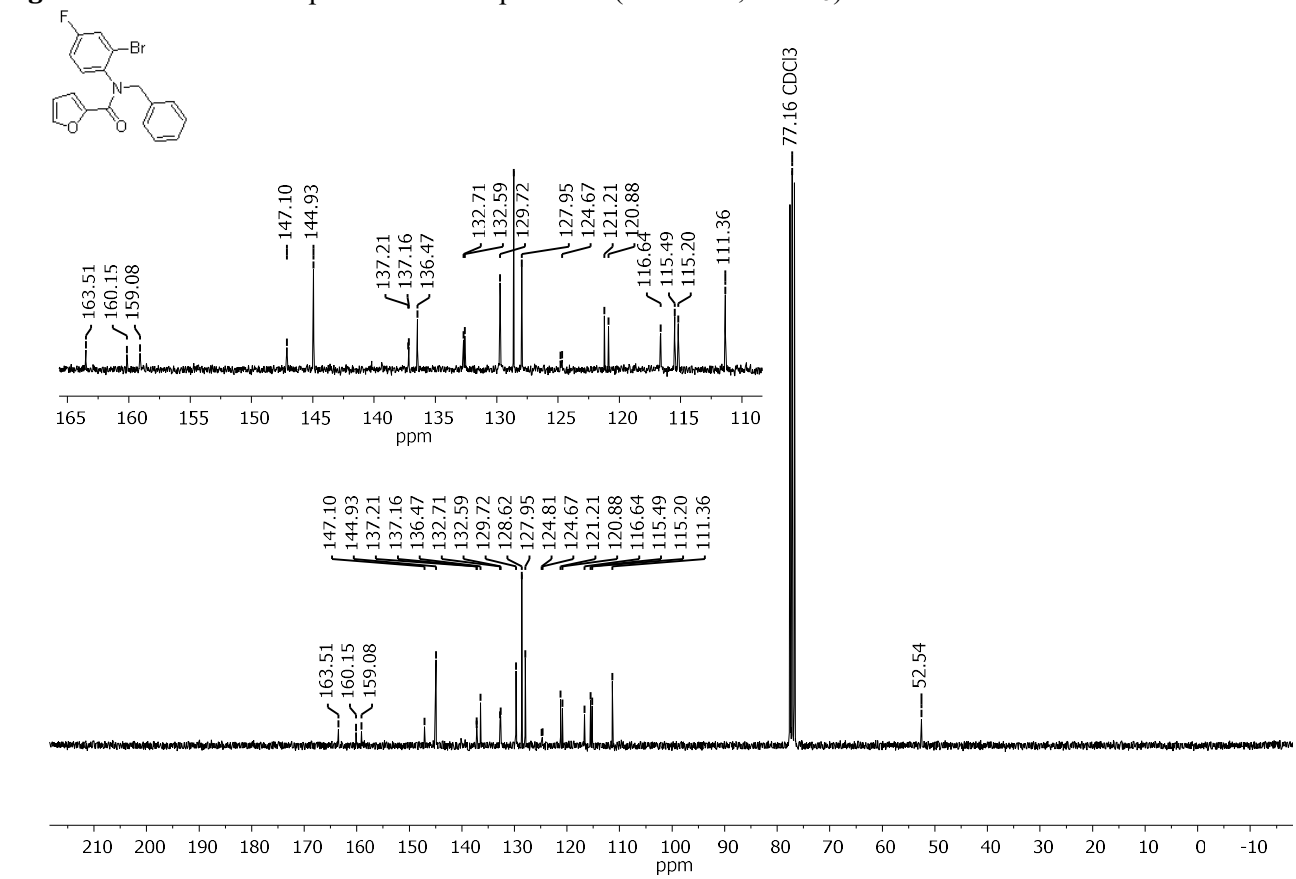


Figure S20. ^{13}C NMR spectrum of compound **2i** (75 MHz, $CDCl_3$).

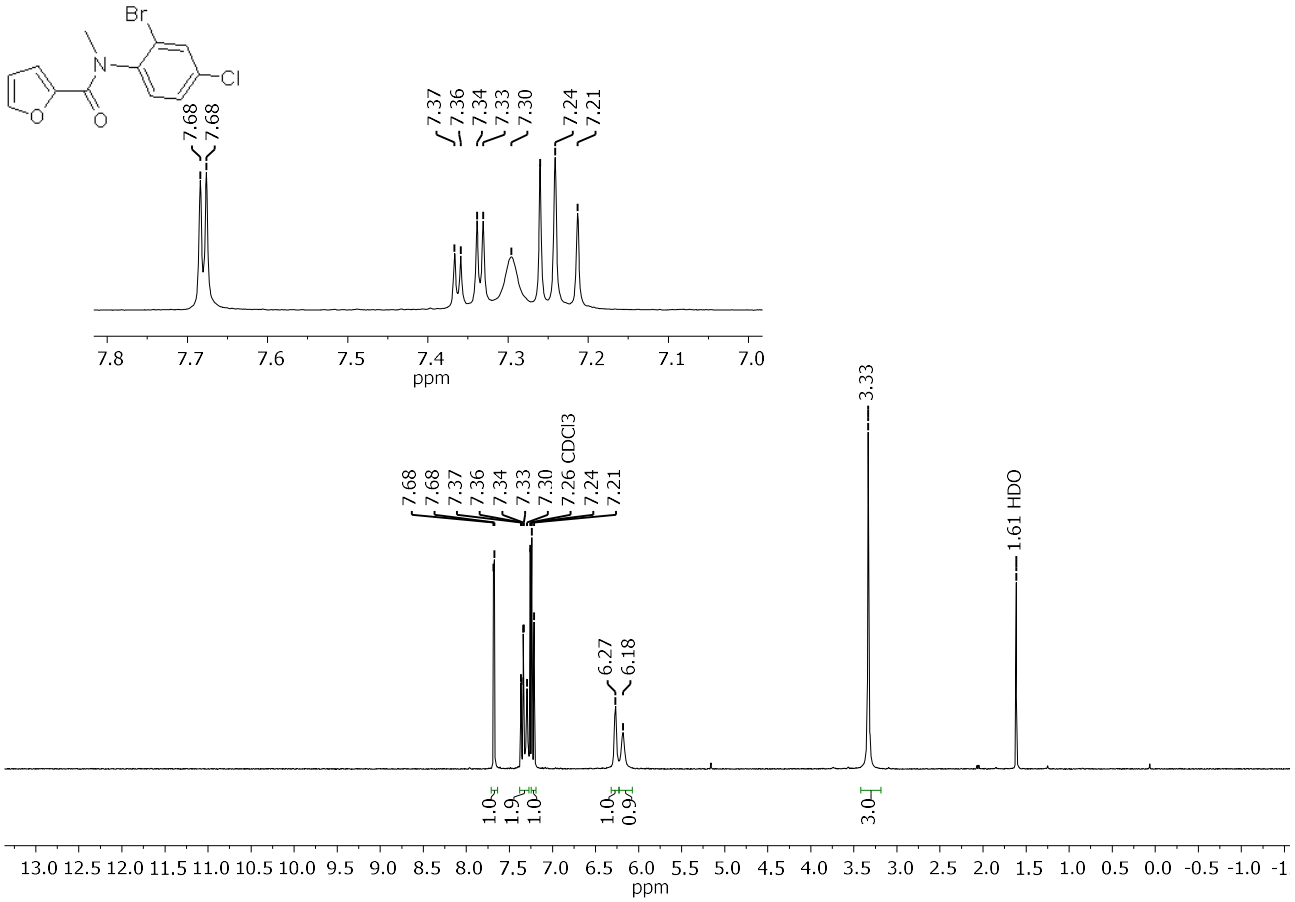


Figure S21. ^{1}H NMR spectrum of compound **2j** (300 MHz, $CDCl_3$).

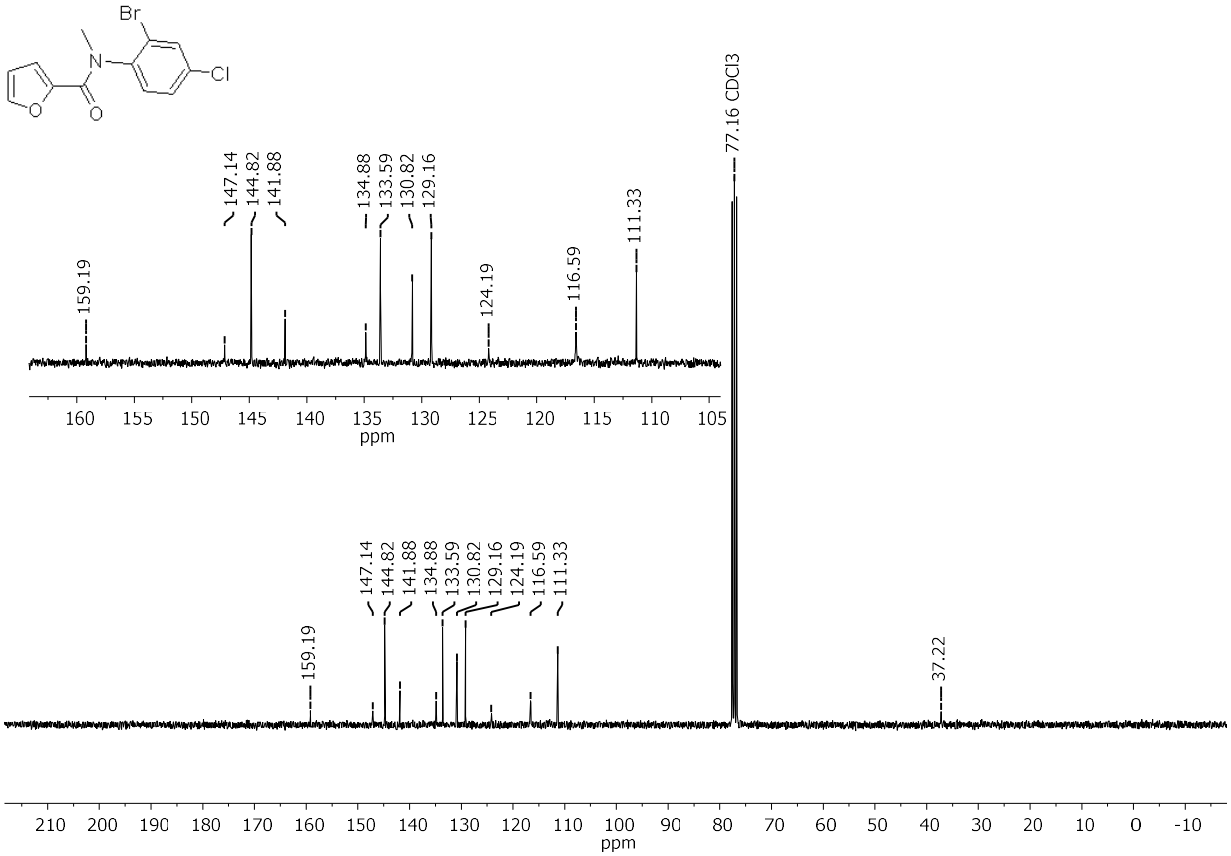


Figure S22. ^{13}C NMR spectrum of compound **2j** (75 MHz, $CDCl_3$).

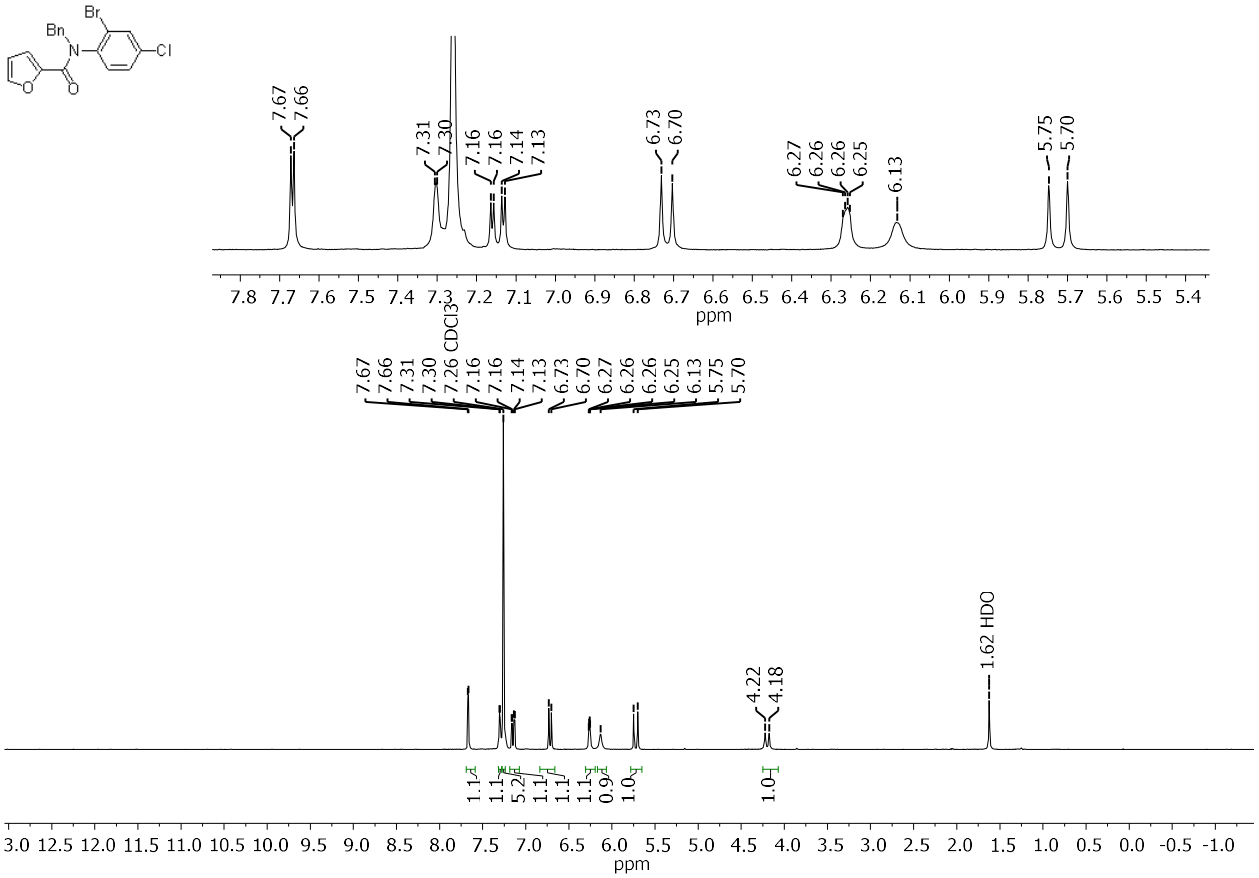


Figure S23. ^{1}H NMR spectrum of compound **2k** (300 MHz, $CDCl_3$).

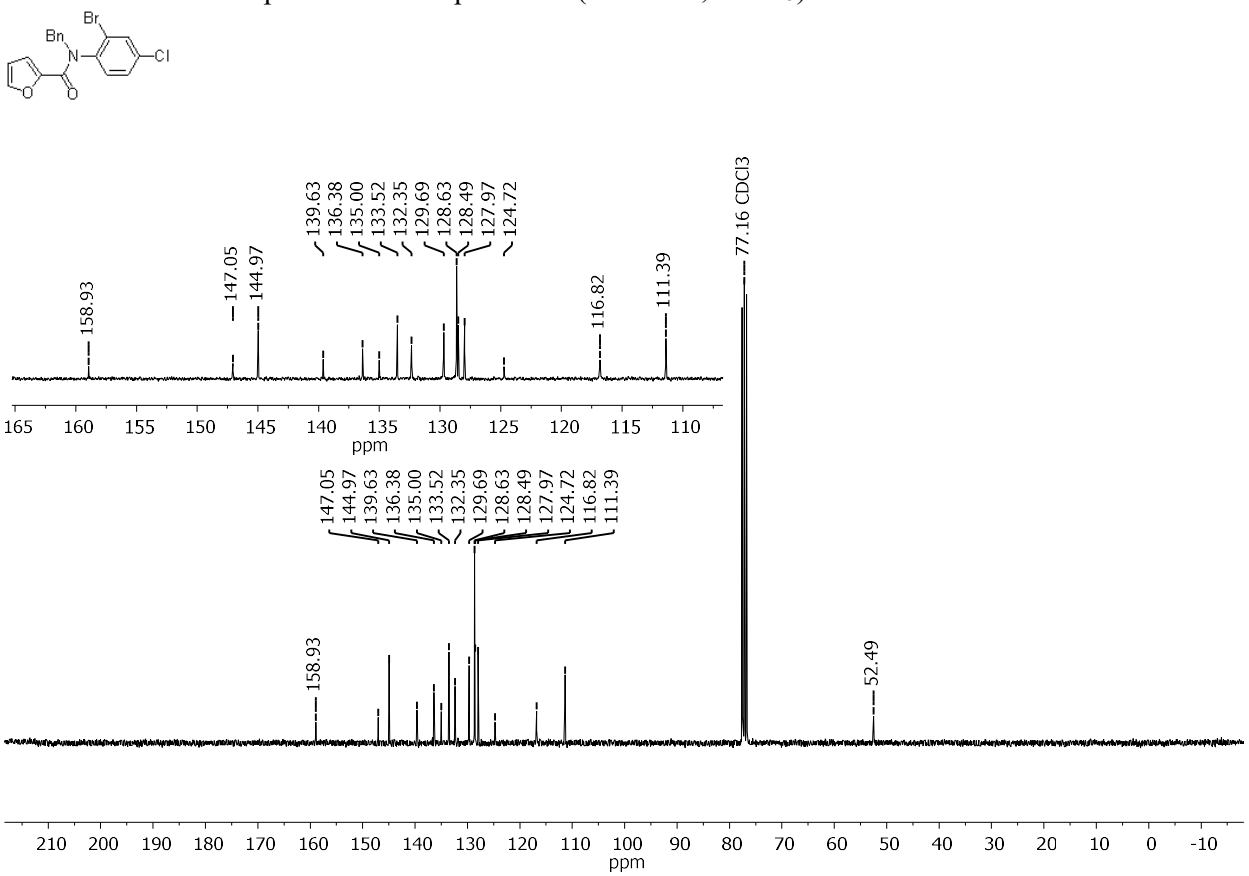


Figure S24. ^{13}C NMR spectrum of compound **2k** (75 MHz, $CDCl_3$).

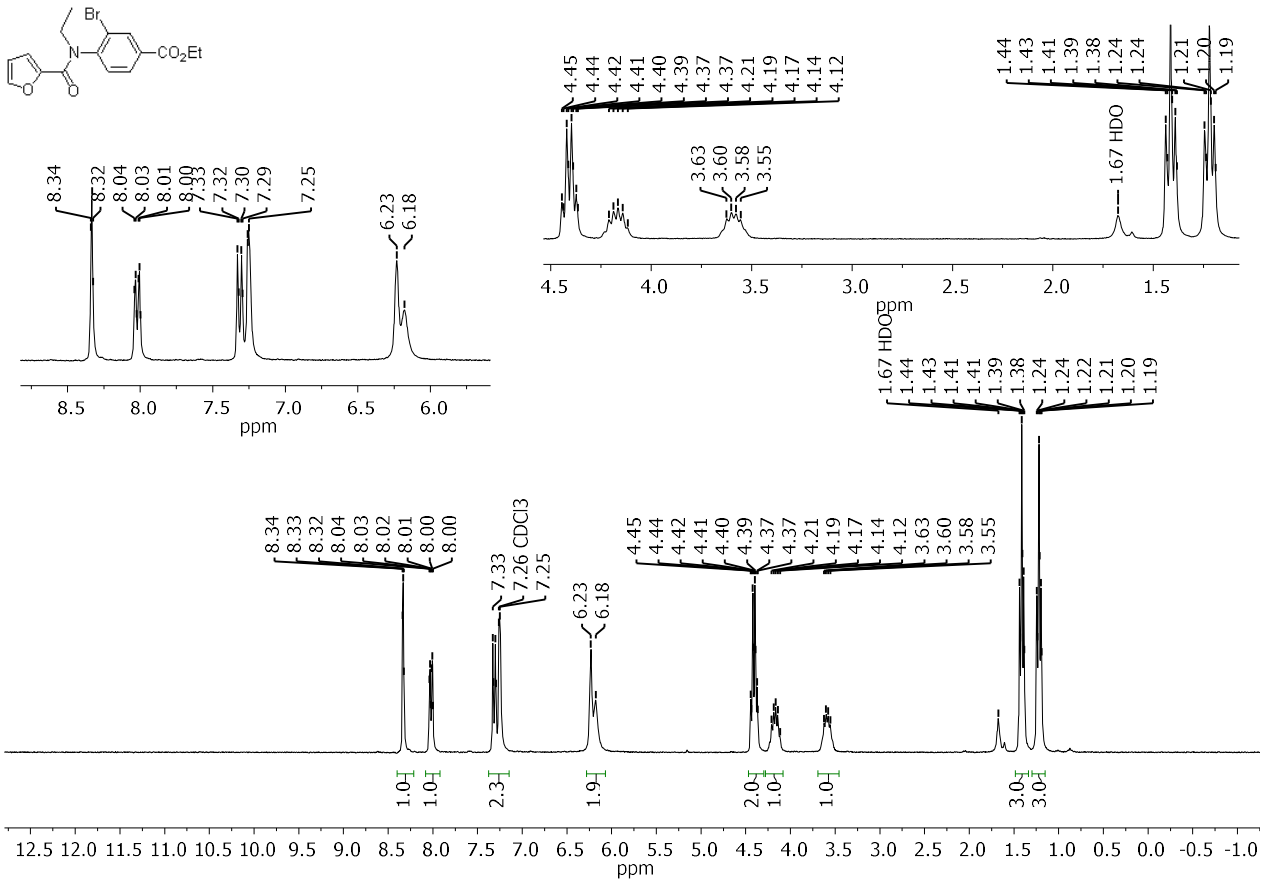


Figure S25. ^{1}H NMR spectrum of compound **2l** (300 MHz, $CDCl_3$).

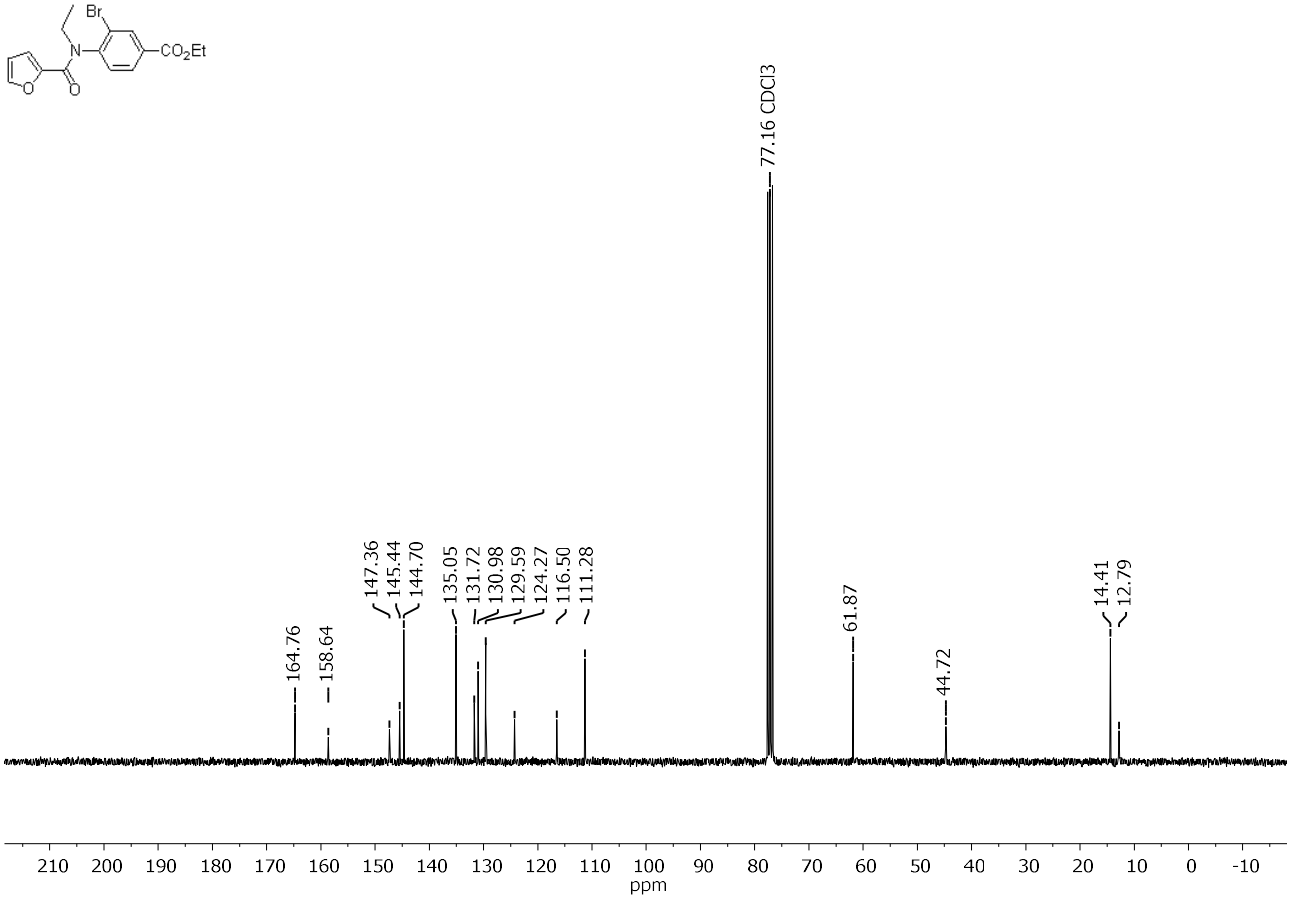


Figure S26. ^{13}C NMR spectrum of compound **2l** (75 MHz, $CDCl_3$).

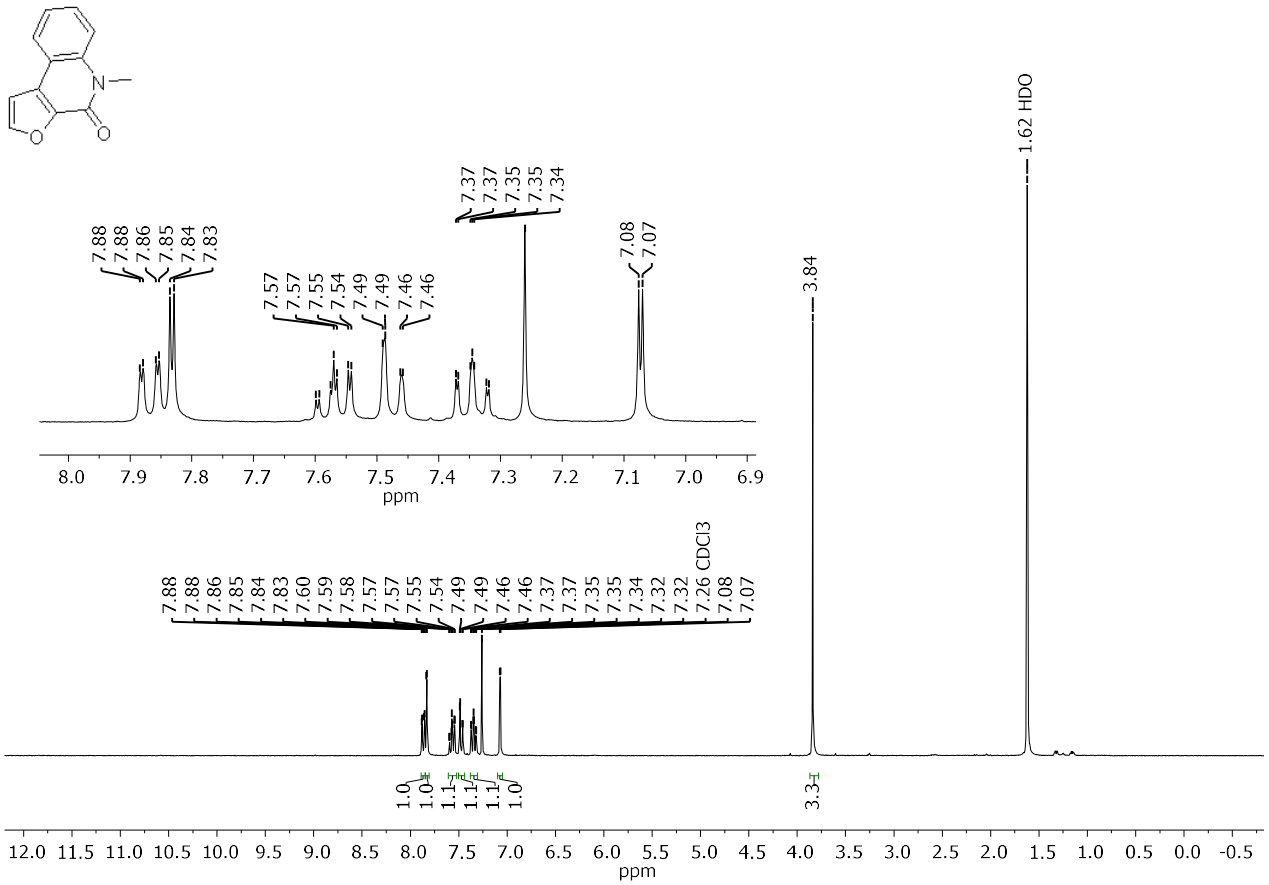


Figure S27. ^{1}H NMR spectrum of compound **1a** (300 MHz, $CDCl_3$).

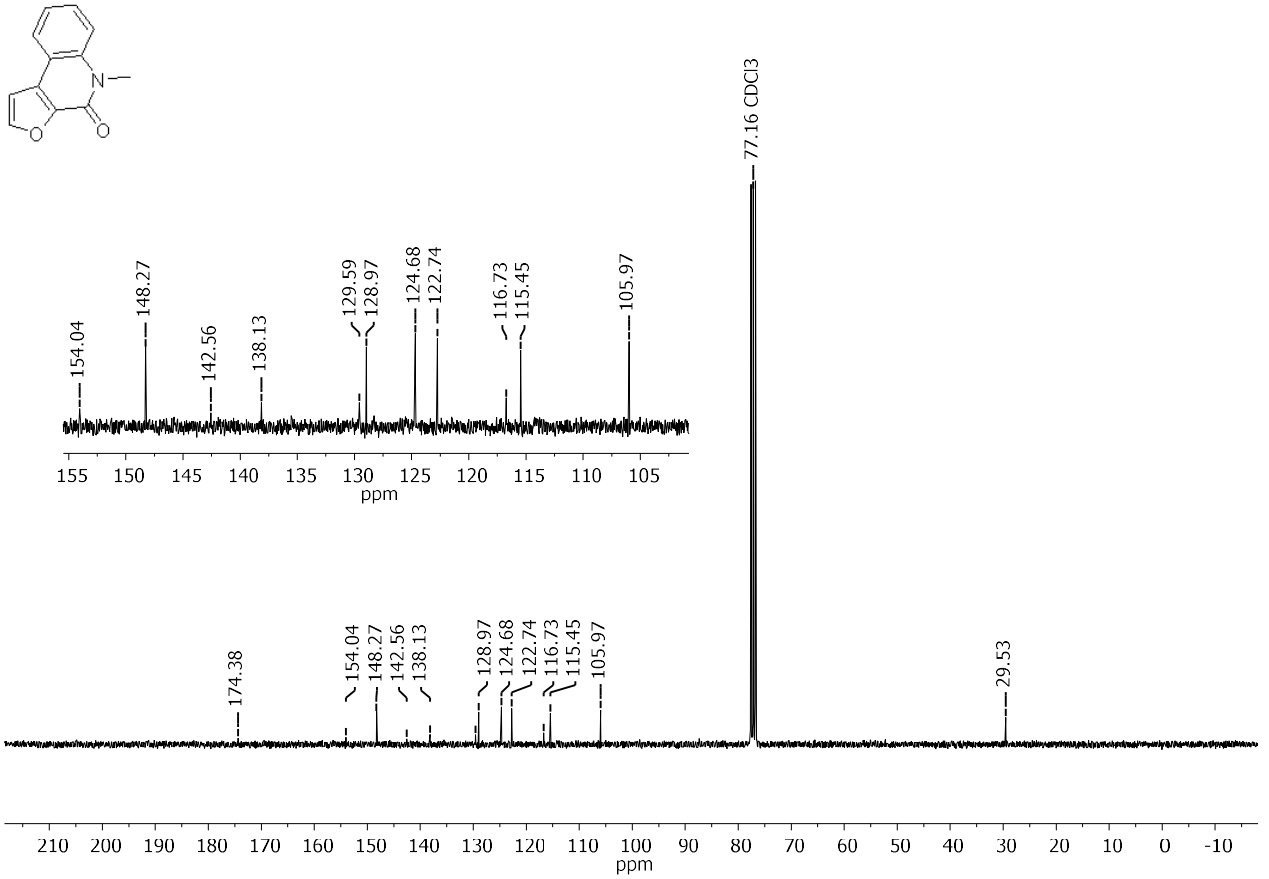


Figure S28. ^{13}C NMR spectrum of compound **1a** (75 MHz, $CDCl_3$).

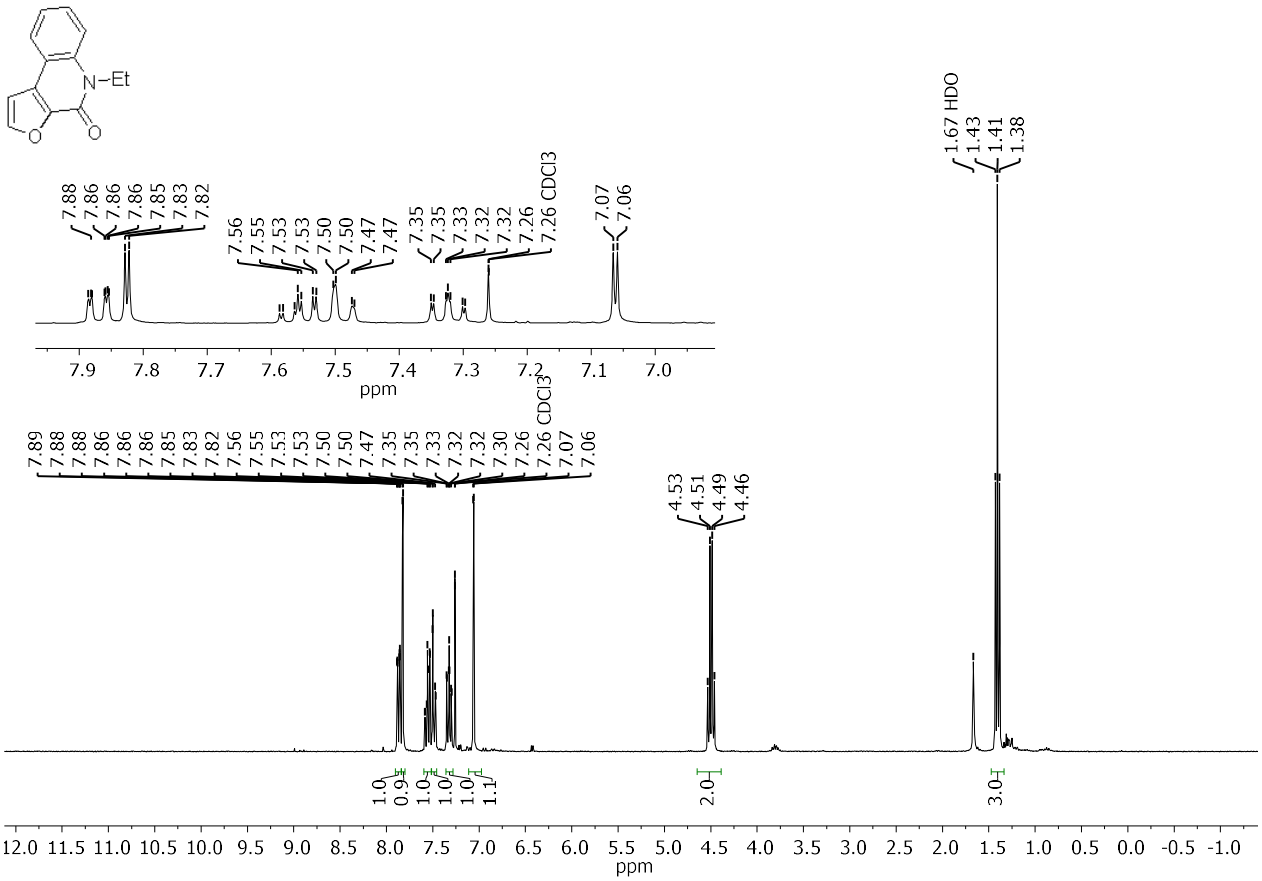


Figure S29. ^{1}H NMR spectrum of compound **1b** (300 MHz, $CDCl_3$).

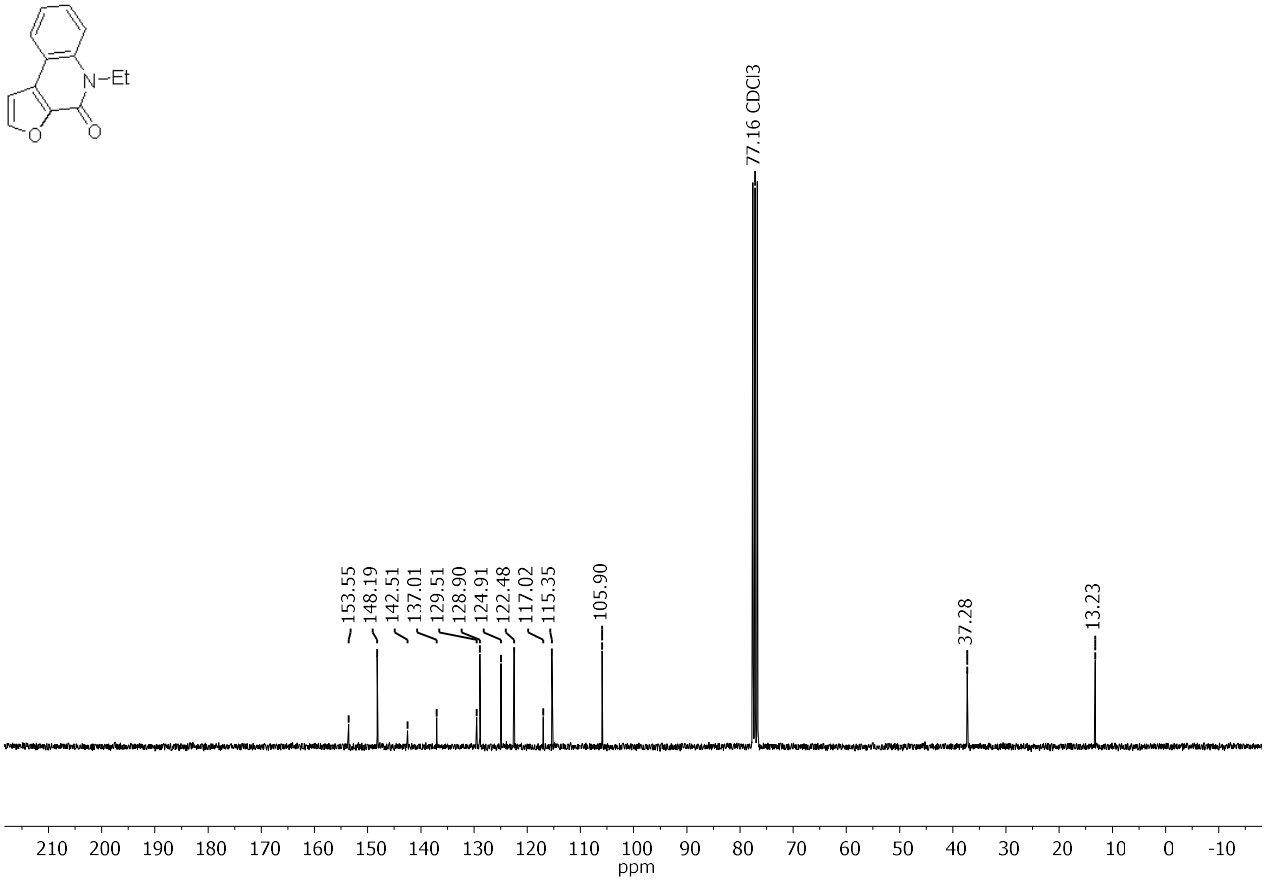


Figure S30. ^{13}C NMR spectrum of compound **1b** (75 MHz, $CDCl_3$).

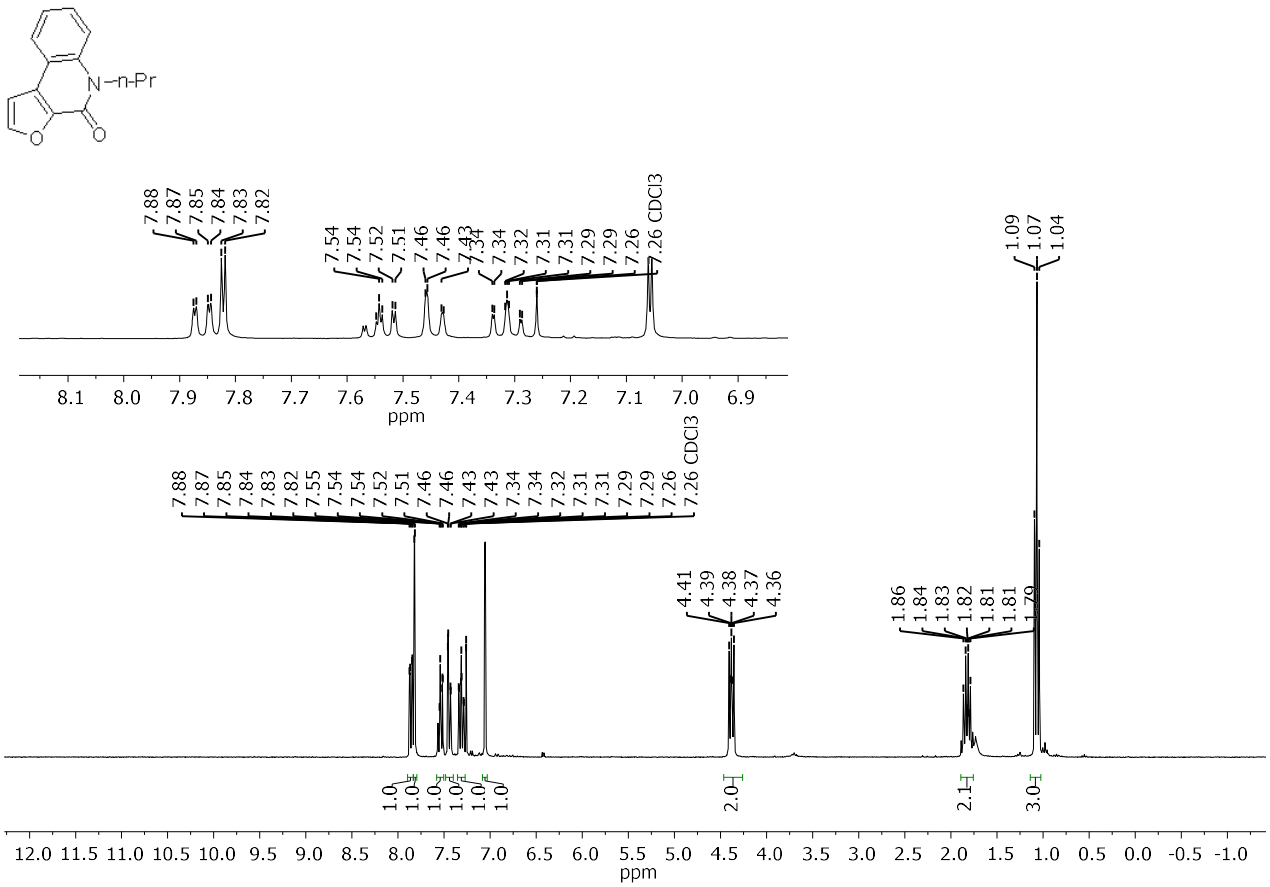


Figure S31. ^{1}H NMR spectrum of compound **1c** (300 MHz, $CDCl_3$)

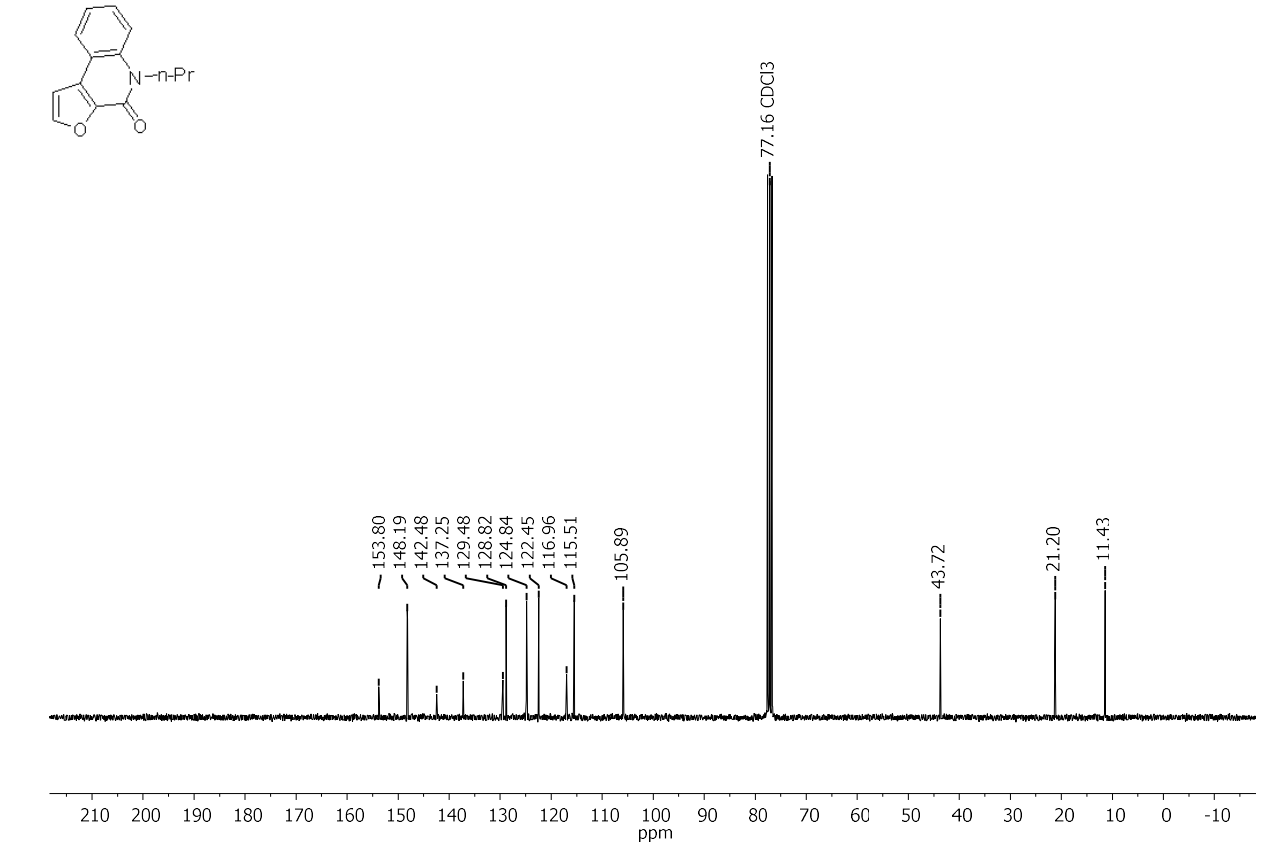


Figure S32. ^{13}C NMR spectrum of compound **1c** (75 MHz, $CDCl_3$).

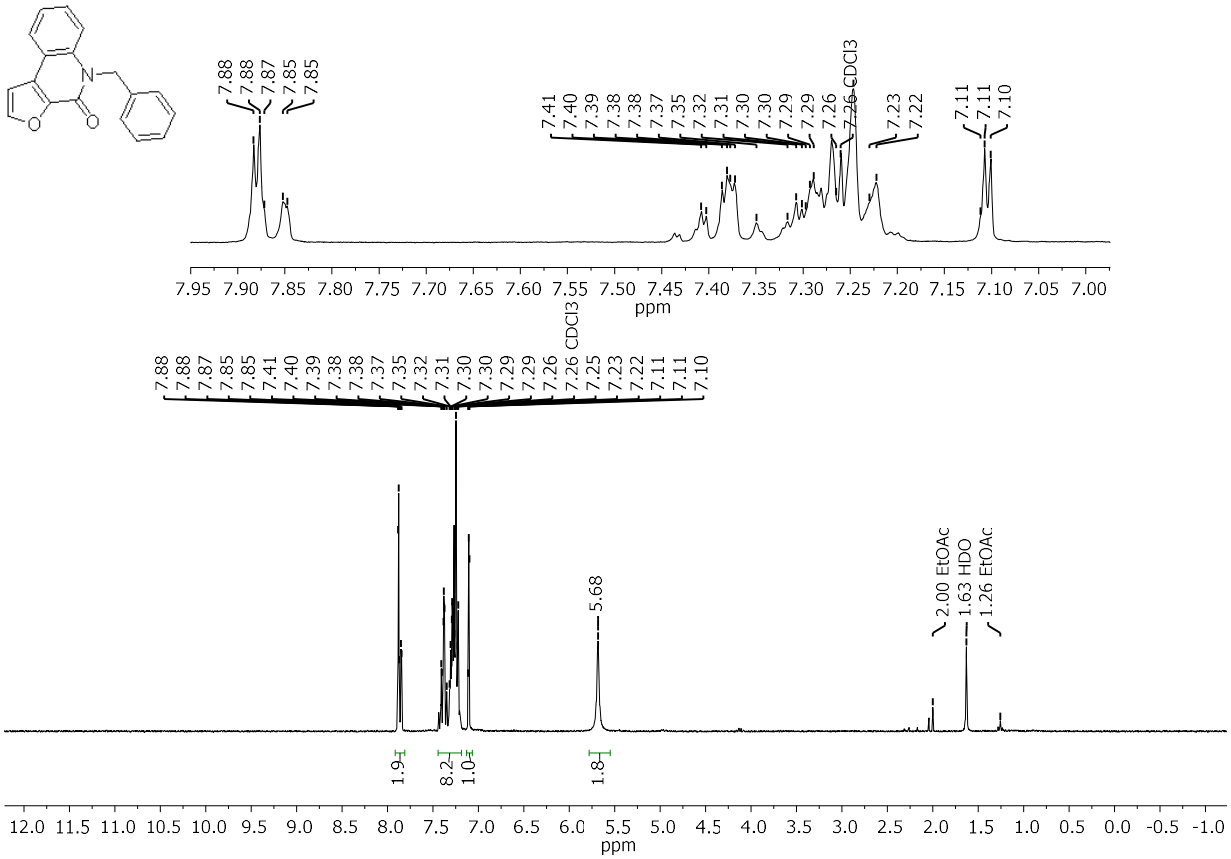


Figure S33. ^{1}H NMR spectrum of compound **1d** (300 MHz, $CDCl_3$).

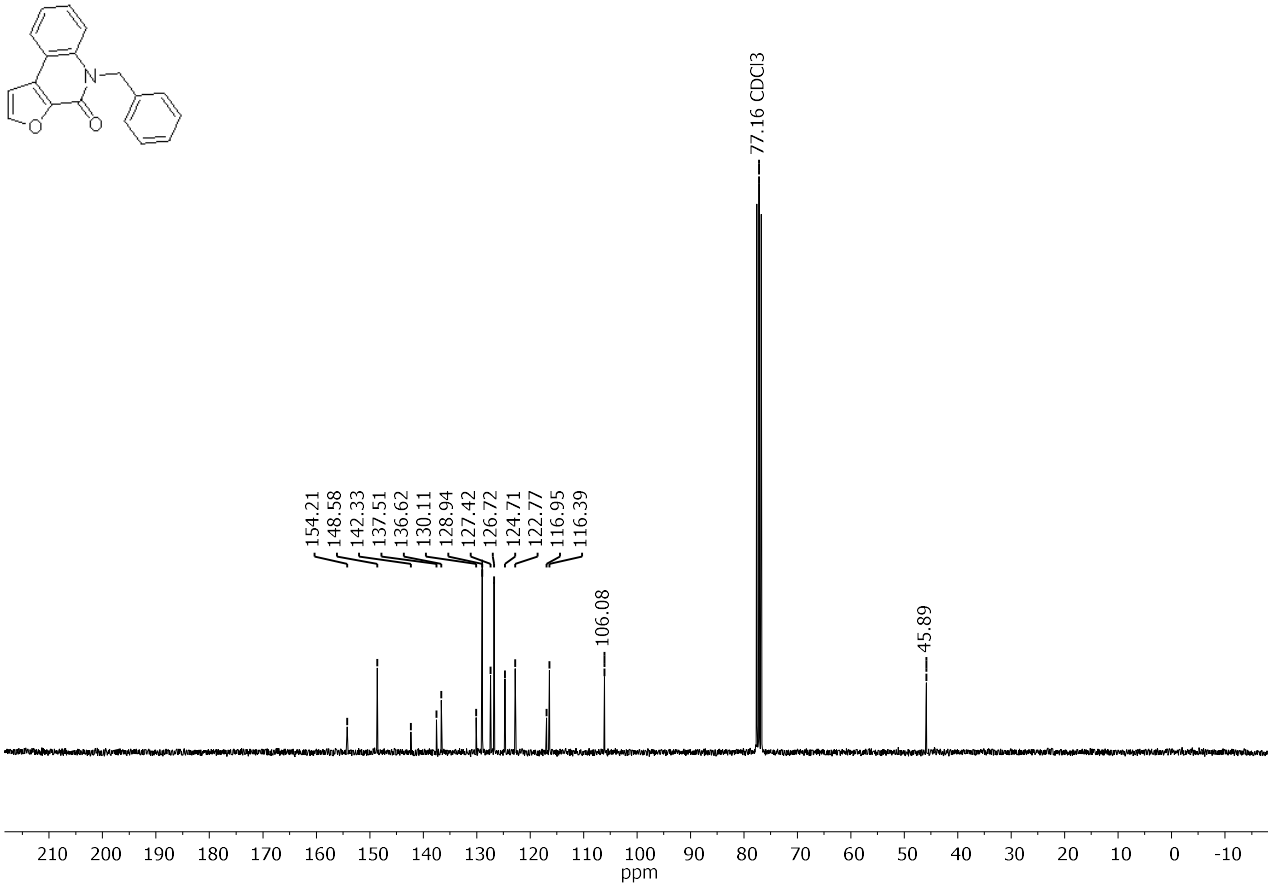


Figure S34. ^{13}C NMR spectrum of compound **1d** (75 MHz, $CDCl_3$).

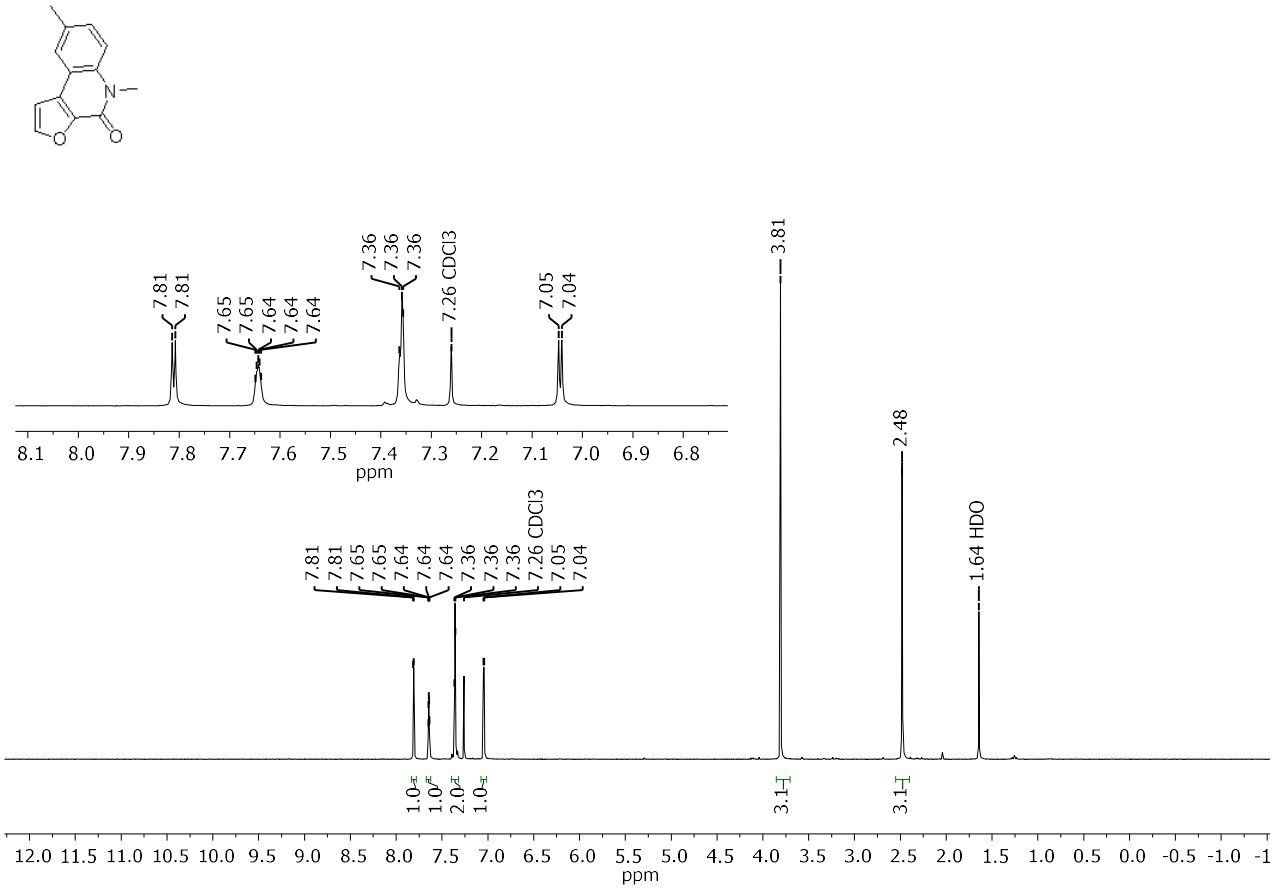


Figure S35. ^{1}H NMR spectrum of compound **1e** (300 MHz, $CDCl_3$).

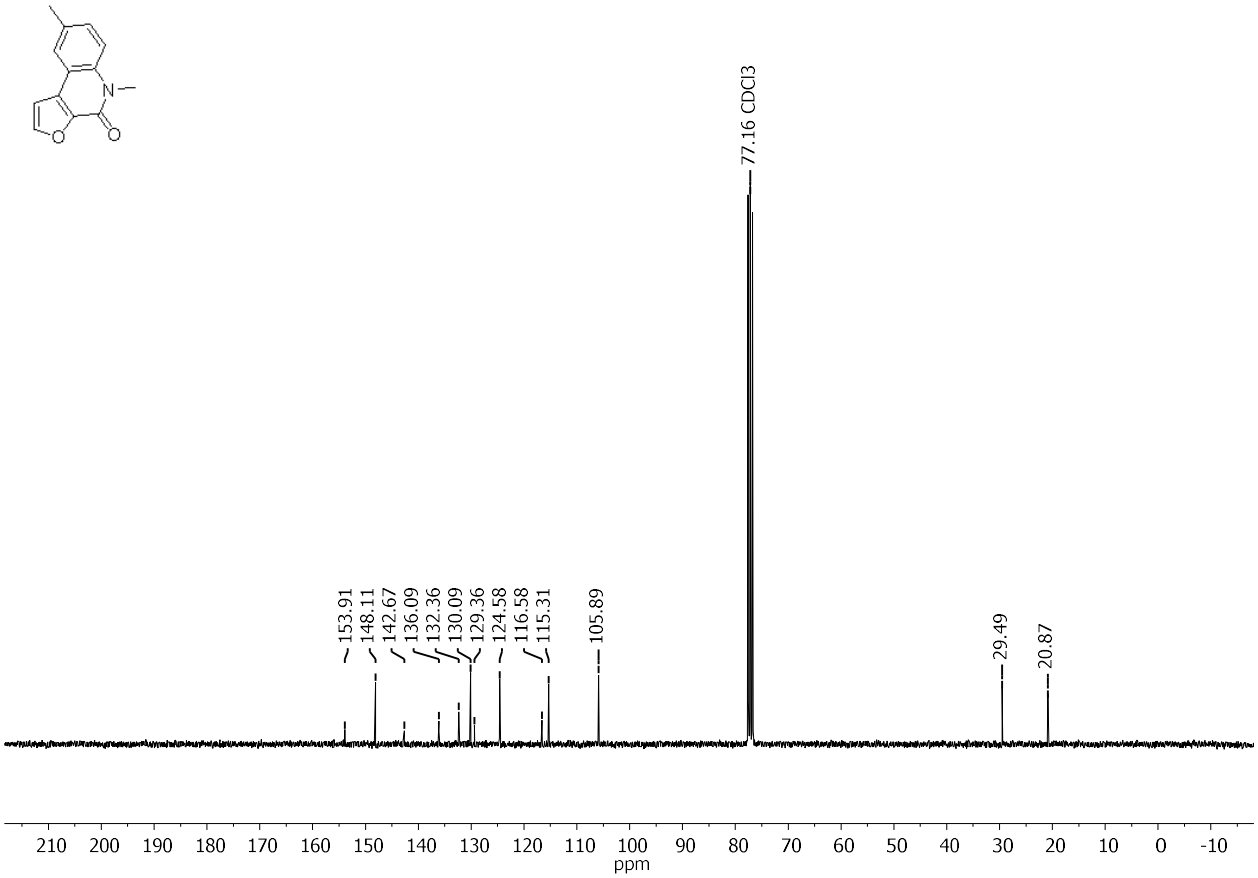


Figure S36. ^{13}C NMR spectrum of compound **1e** (75 MHz, $CDCl_3$).

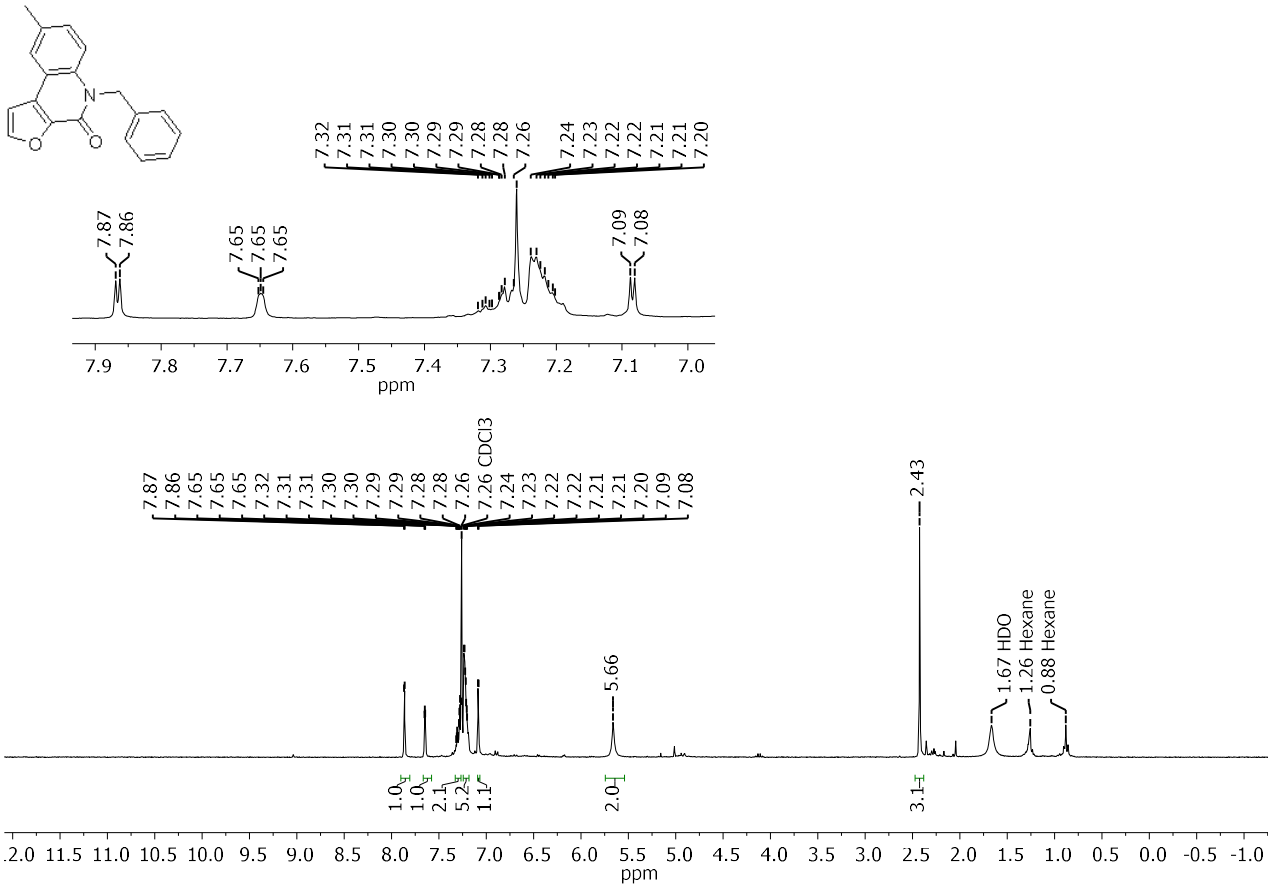


Figure S37. ^{1}H NMR spectrum of compound **1f** (300 MHz, $CDCl_3$).

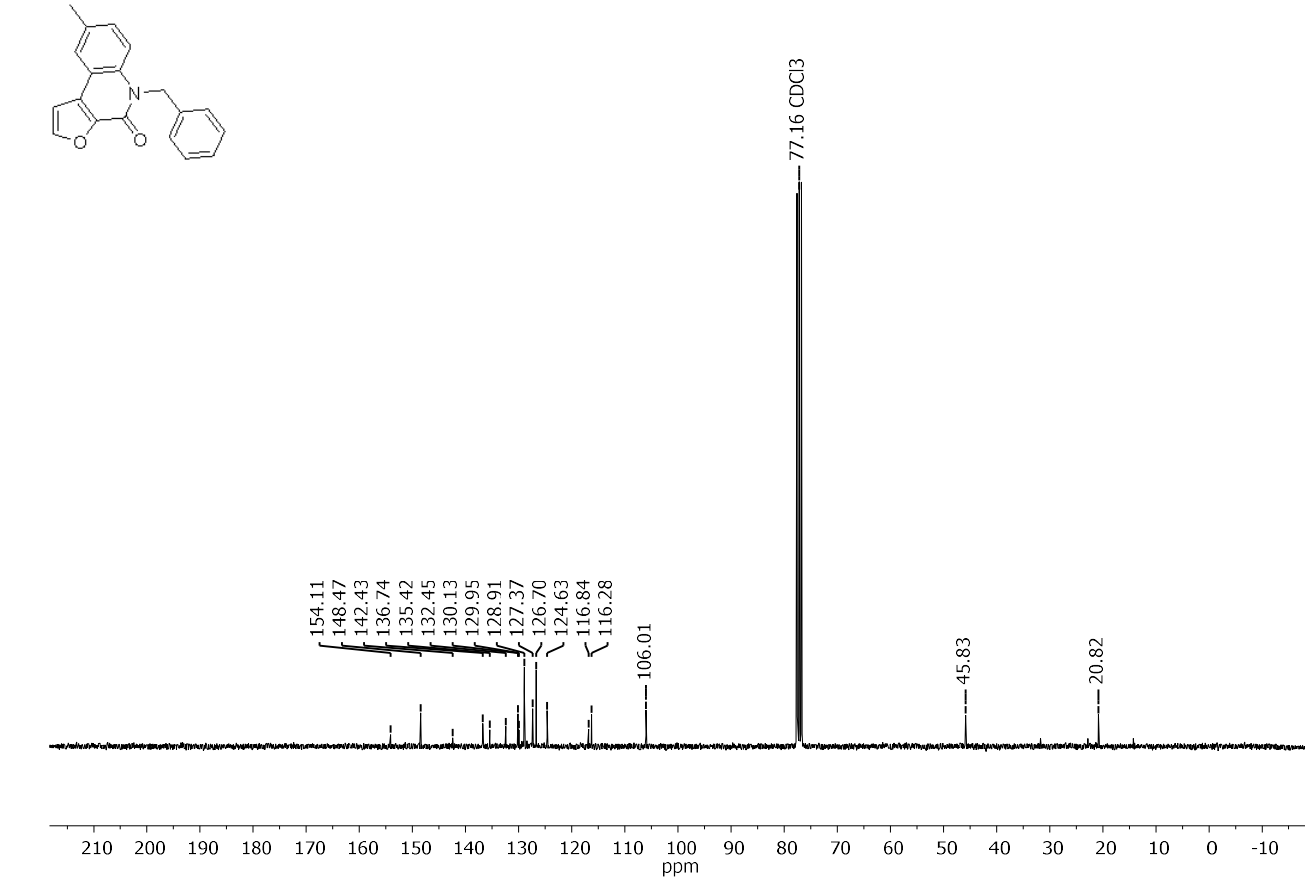


Figure S38. ^{13}C NMR spectrum of compound **1f** (75 MHz, $CDCl_3$).

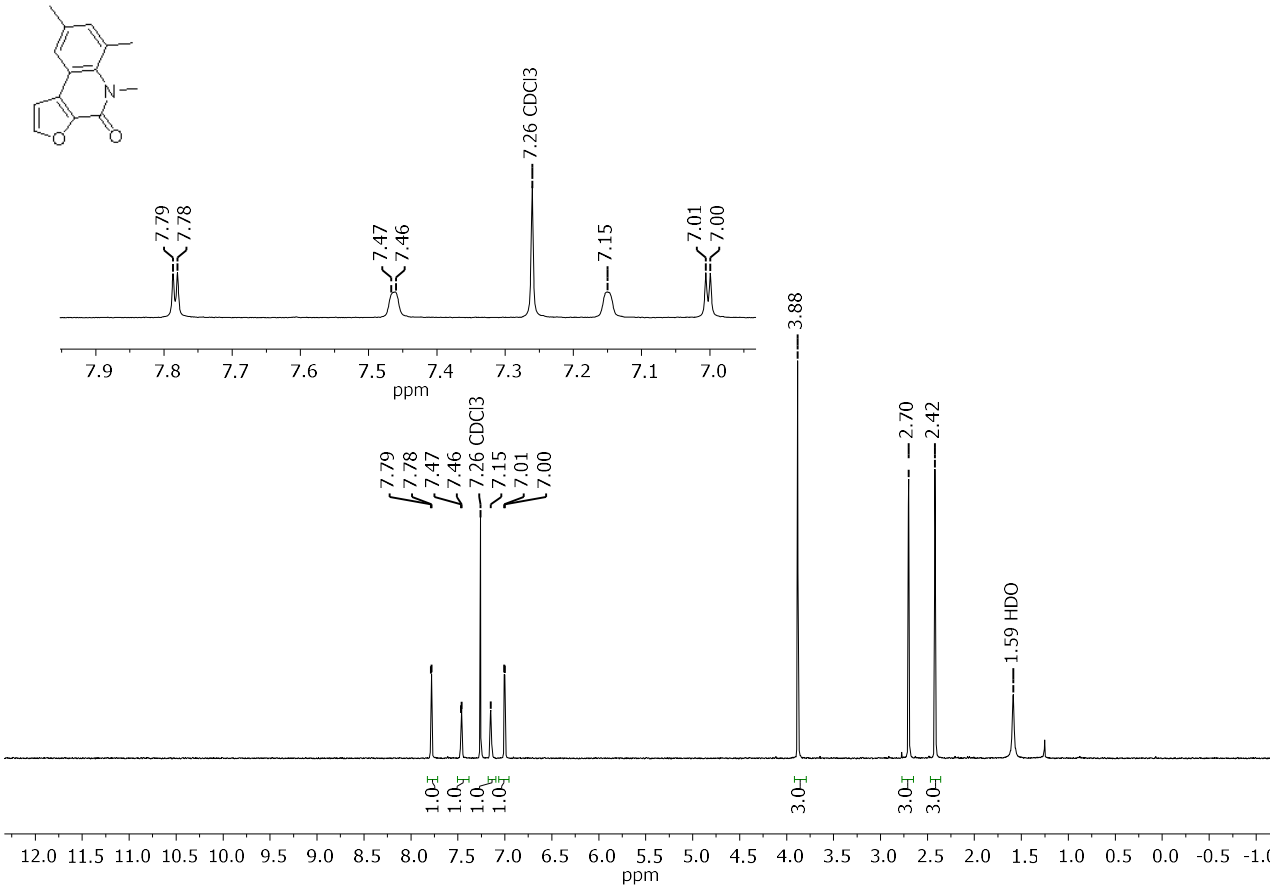


Figure S39. ^{1}H NMR spectrum of compound **1g** (300 MHz, $CDCl_3$).

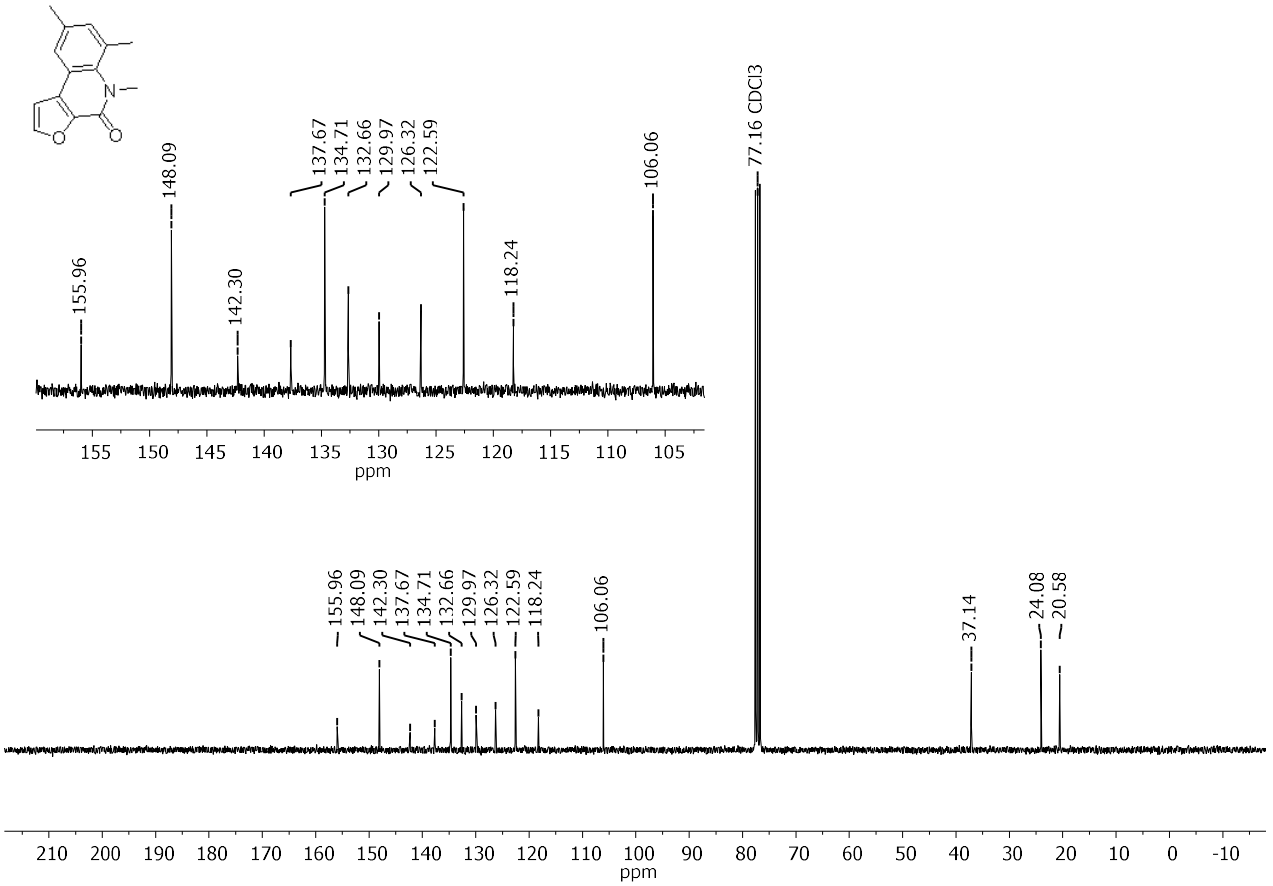


Figure S40. ^{13}C NMR spectrum of compound **1g** (300 MHz, $CDCl_3$).

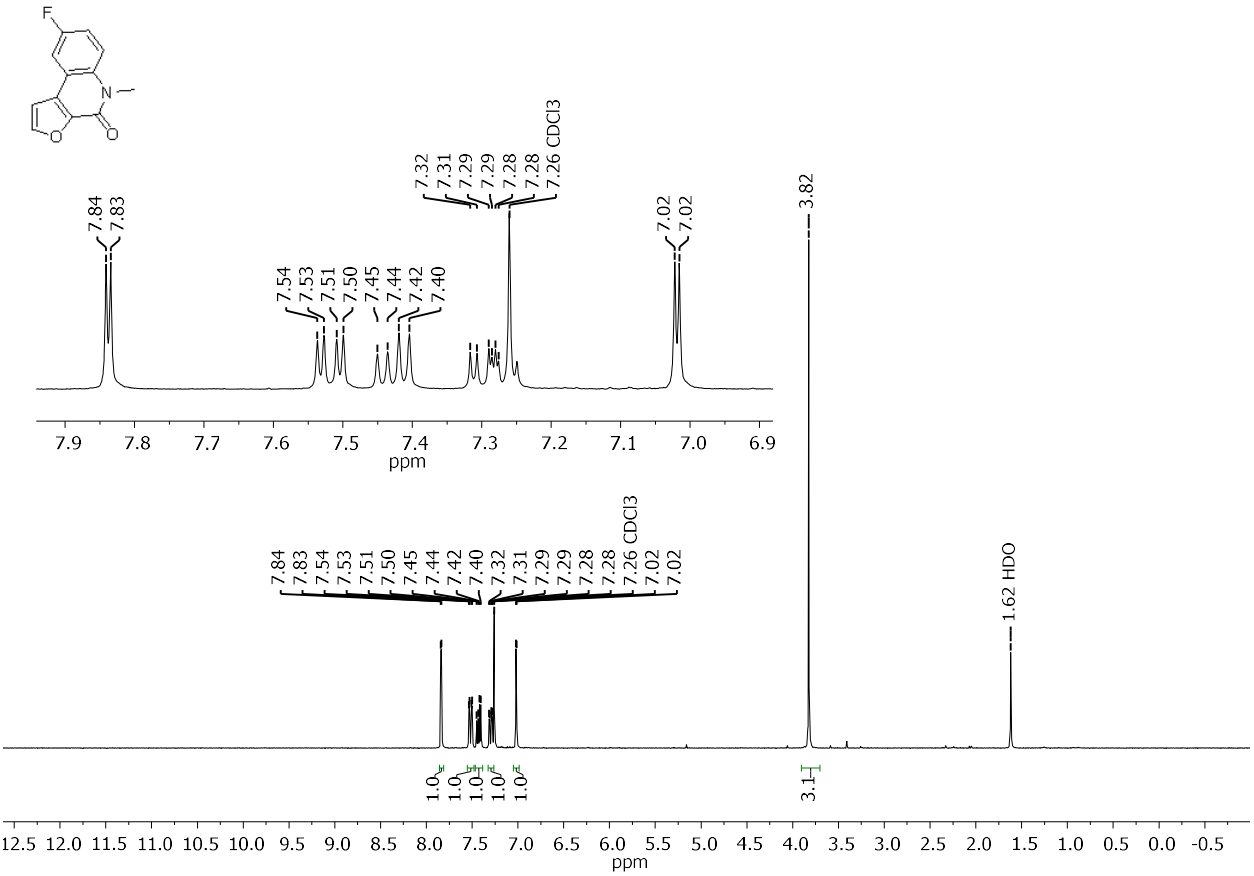


Figure S41. ^{1}H NMR spectrum of compound **1h** (300 MHz, $CDCl_3$).

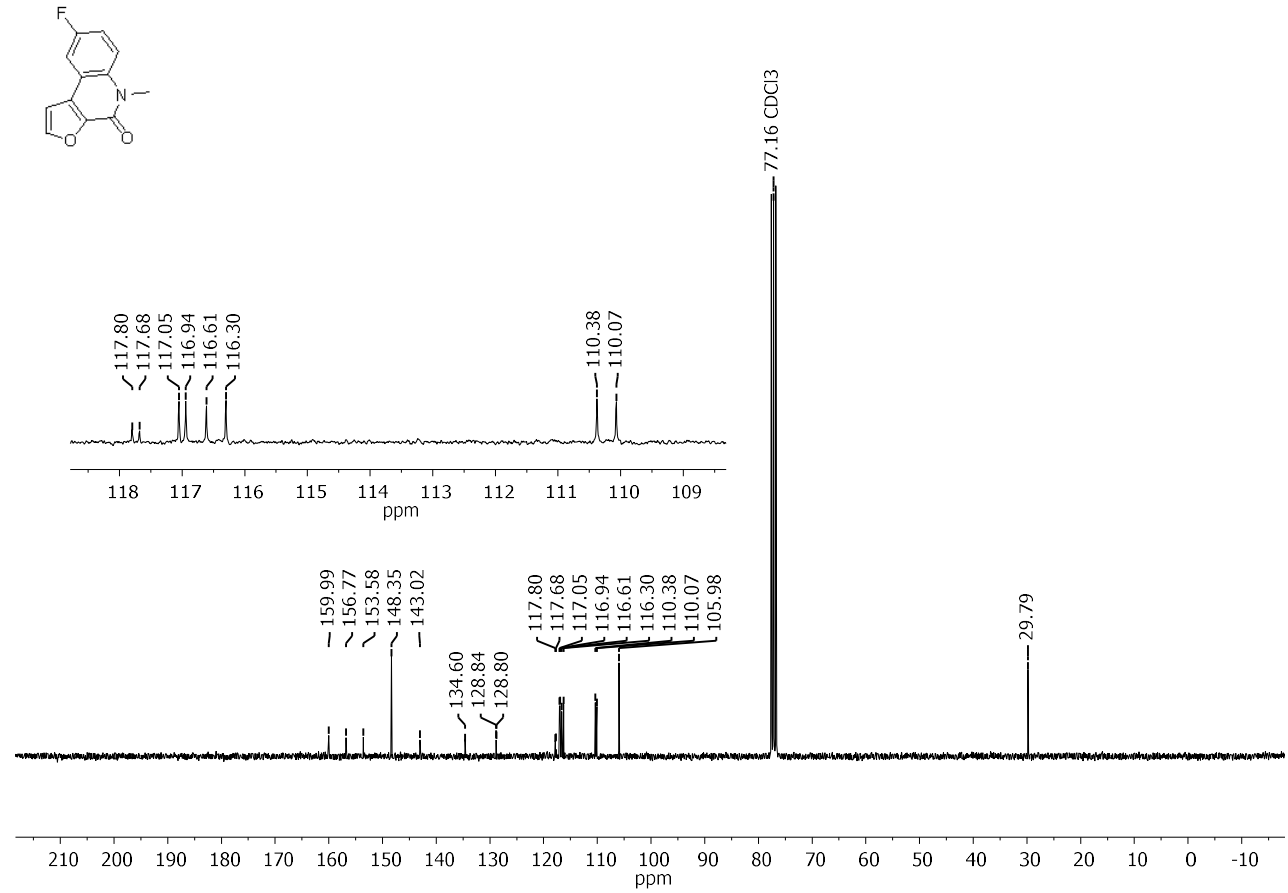


Figure S42. ^{13}C NMR spectrum of compound **1h** (75 MHz, $CDCl_3$).

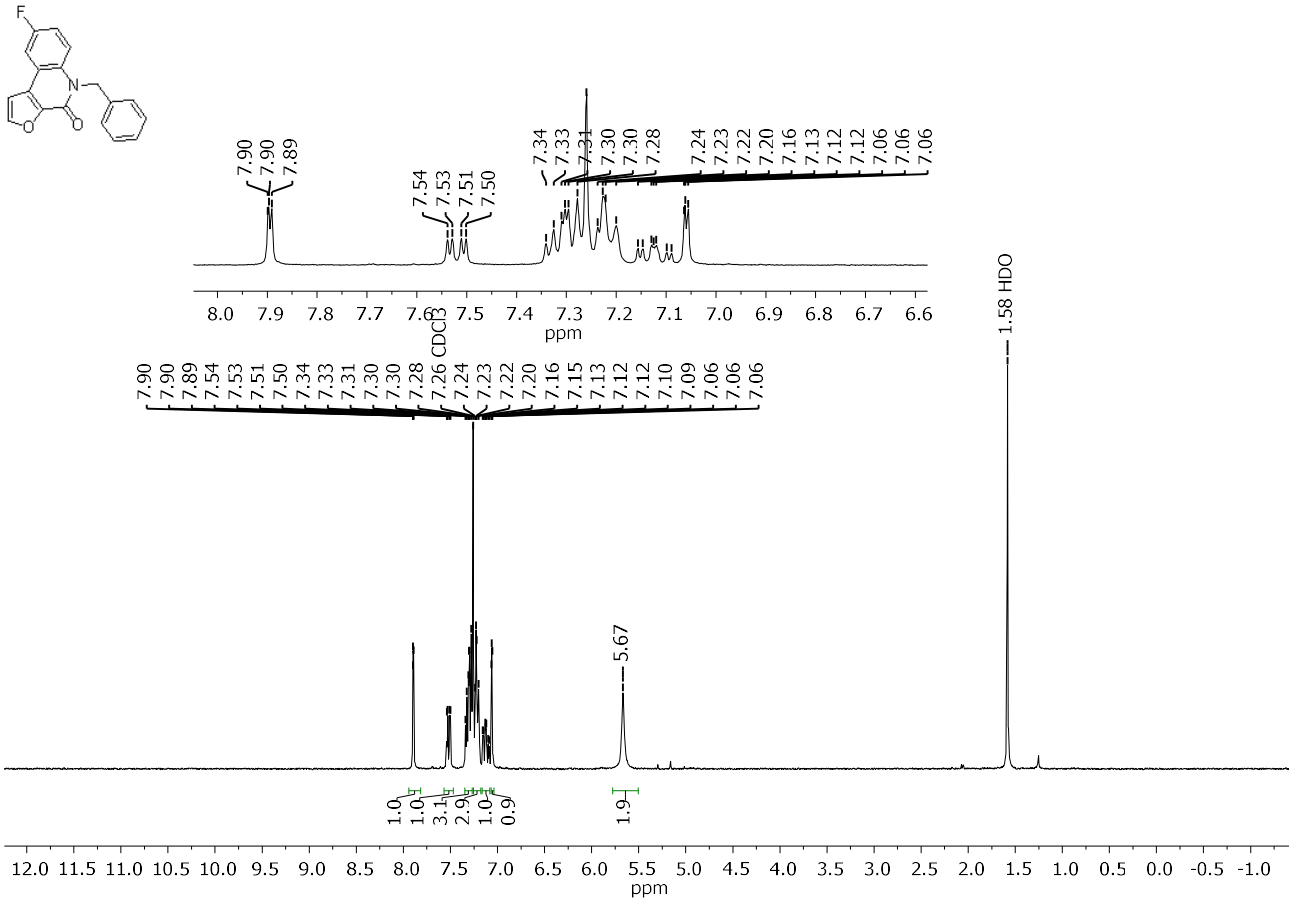


Figure S43. ^{1}H NMR spectrum of compound **1i** (300 MHz, $CDCl_3$).

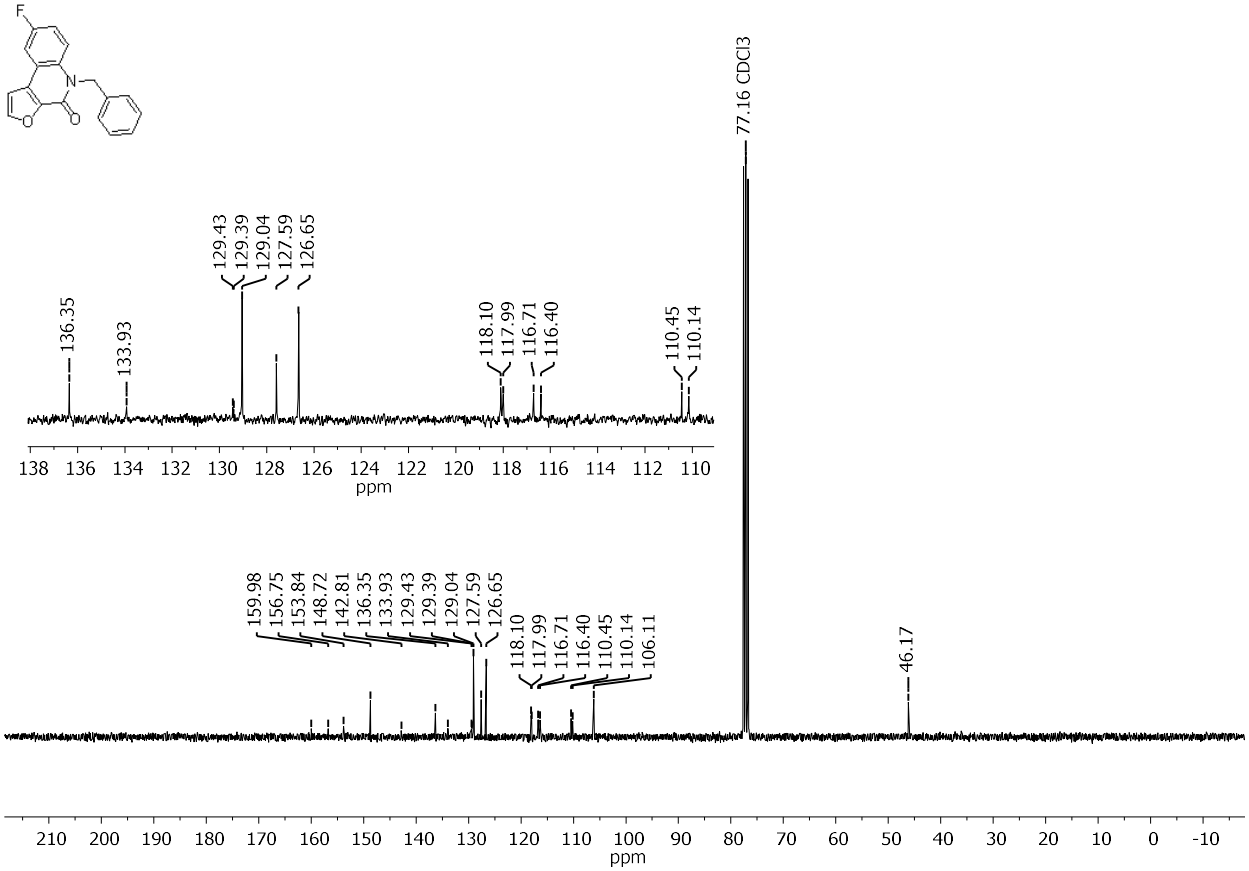


Figure S44. ^{13}C NMR spectrum of compound **1i** (75 MHz, $CDCl_3$).

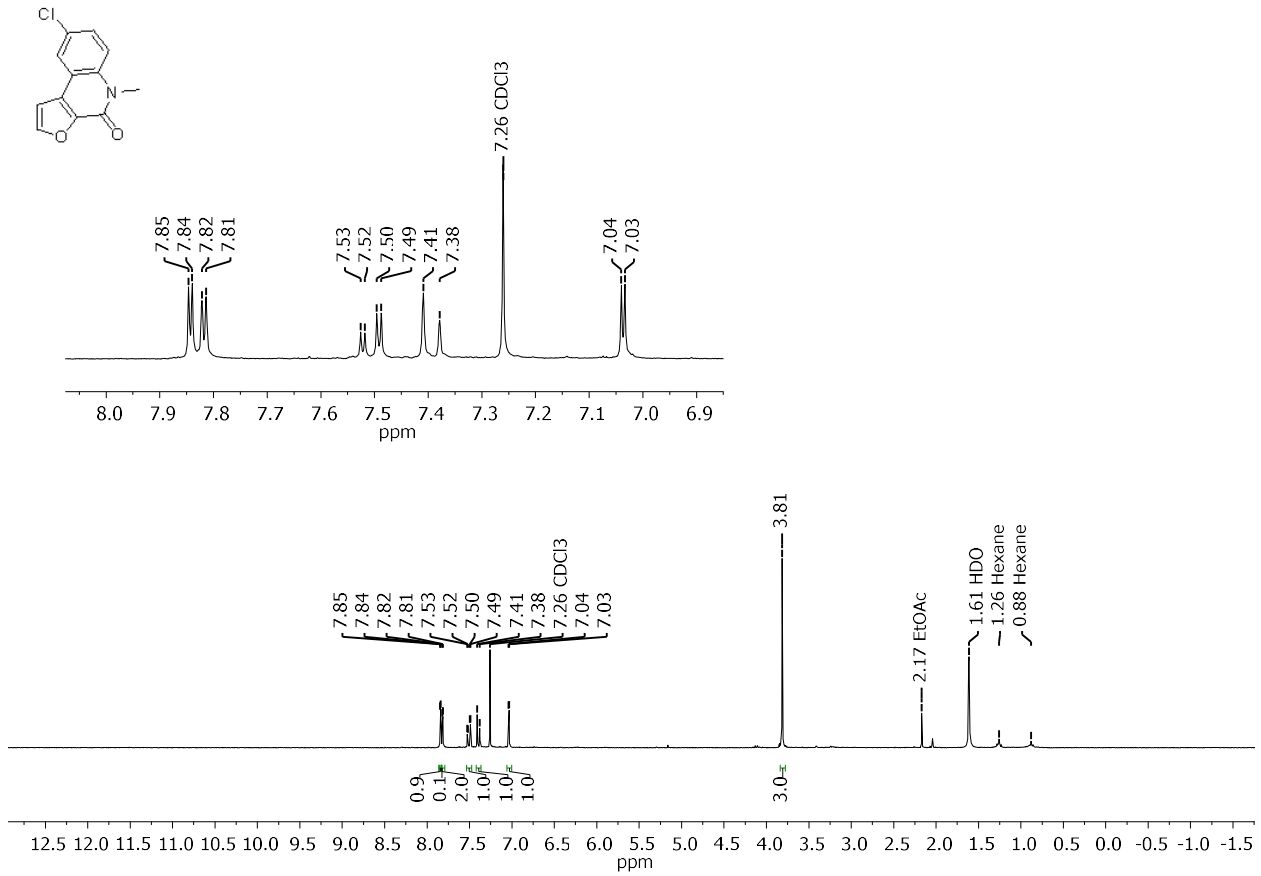


Figure S45. ^{1}H NMR spectrum of compound **1j** (300 MHz, $CDCl_3$).

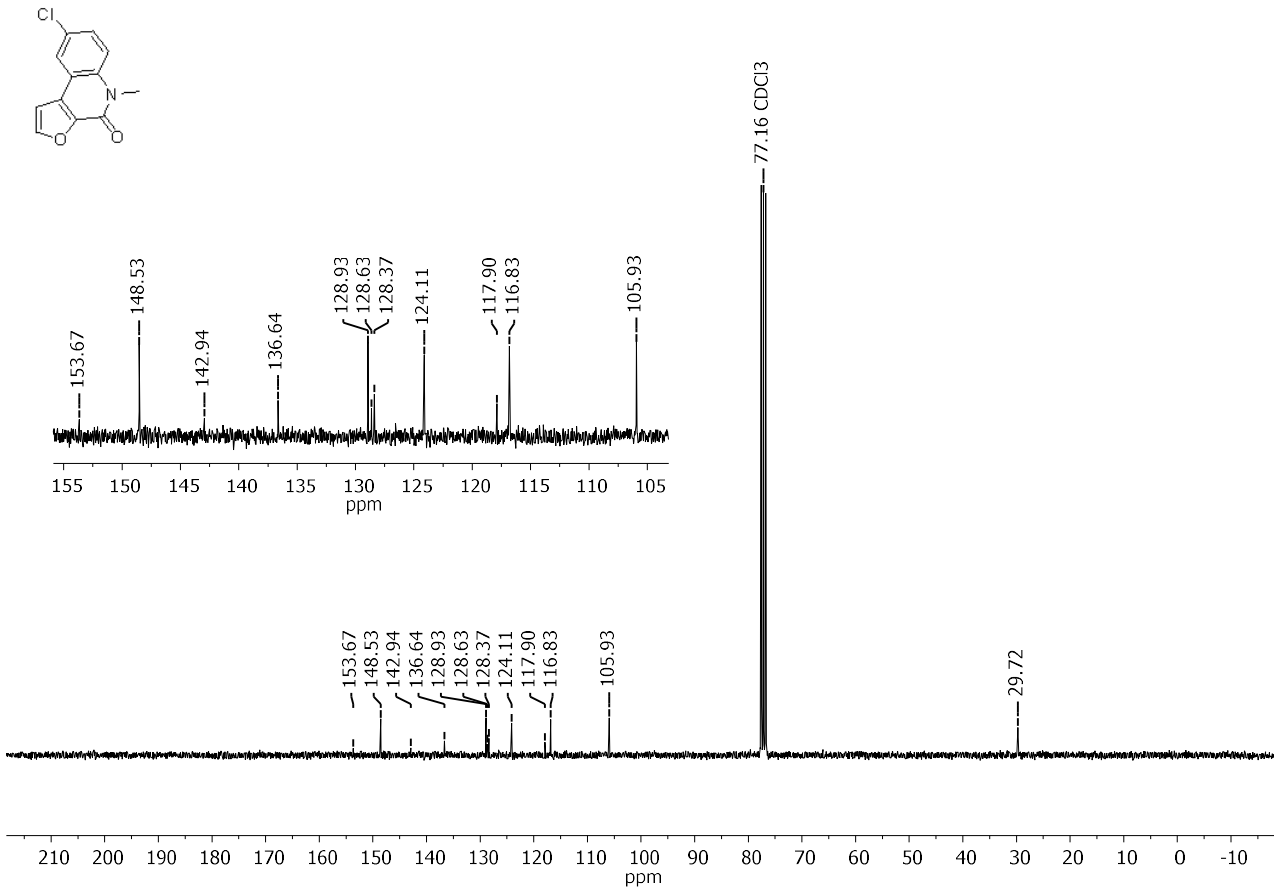


Figure S46. ^{13}C NMR spectrum of compound **1j** (75 MHz, $CDCl_3$).

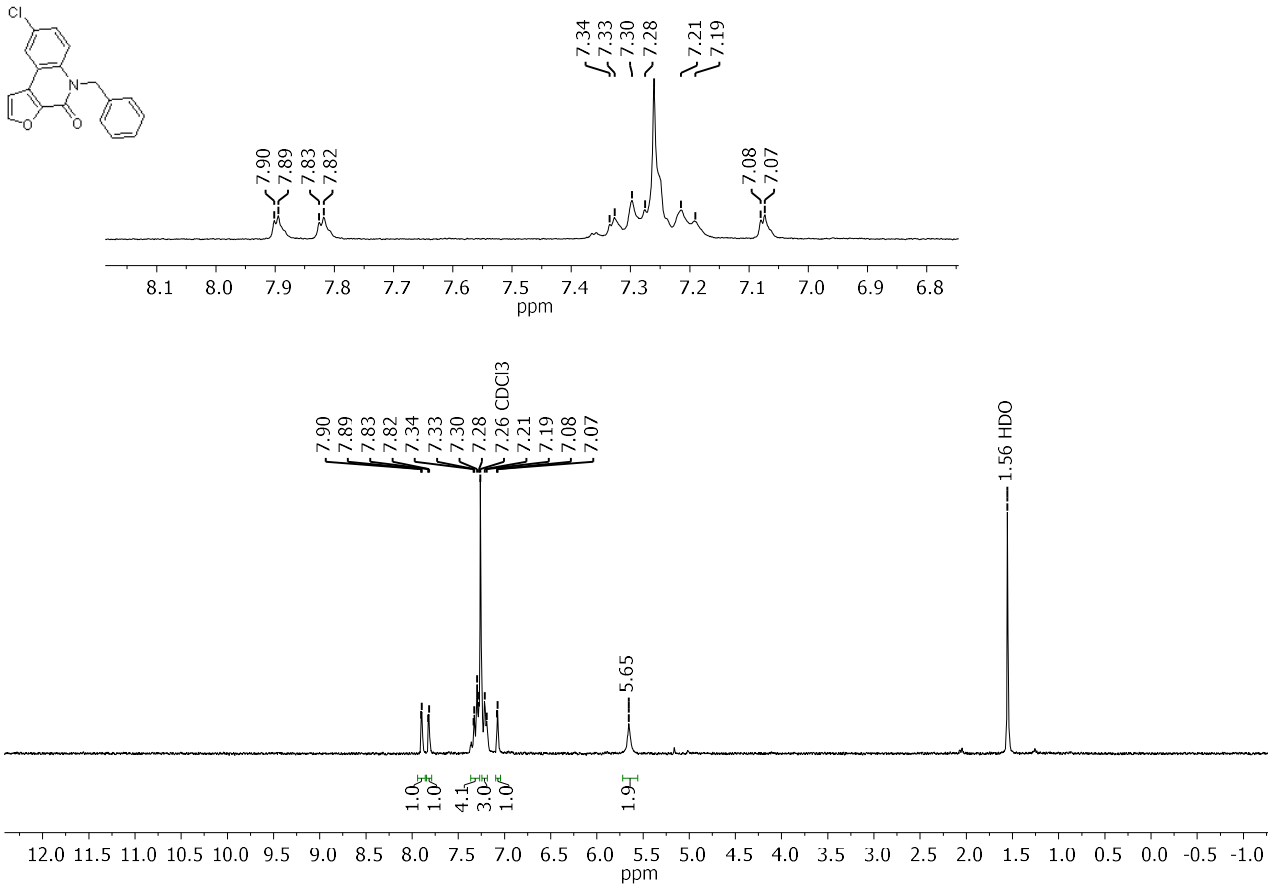


Figure S47. ^{1}H NMR spectrum of compound **1k** (300 MHz, $CDCl_3$).

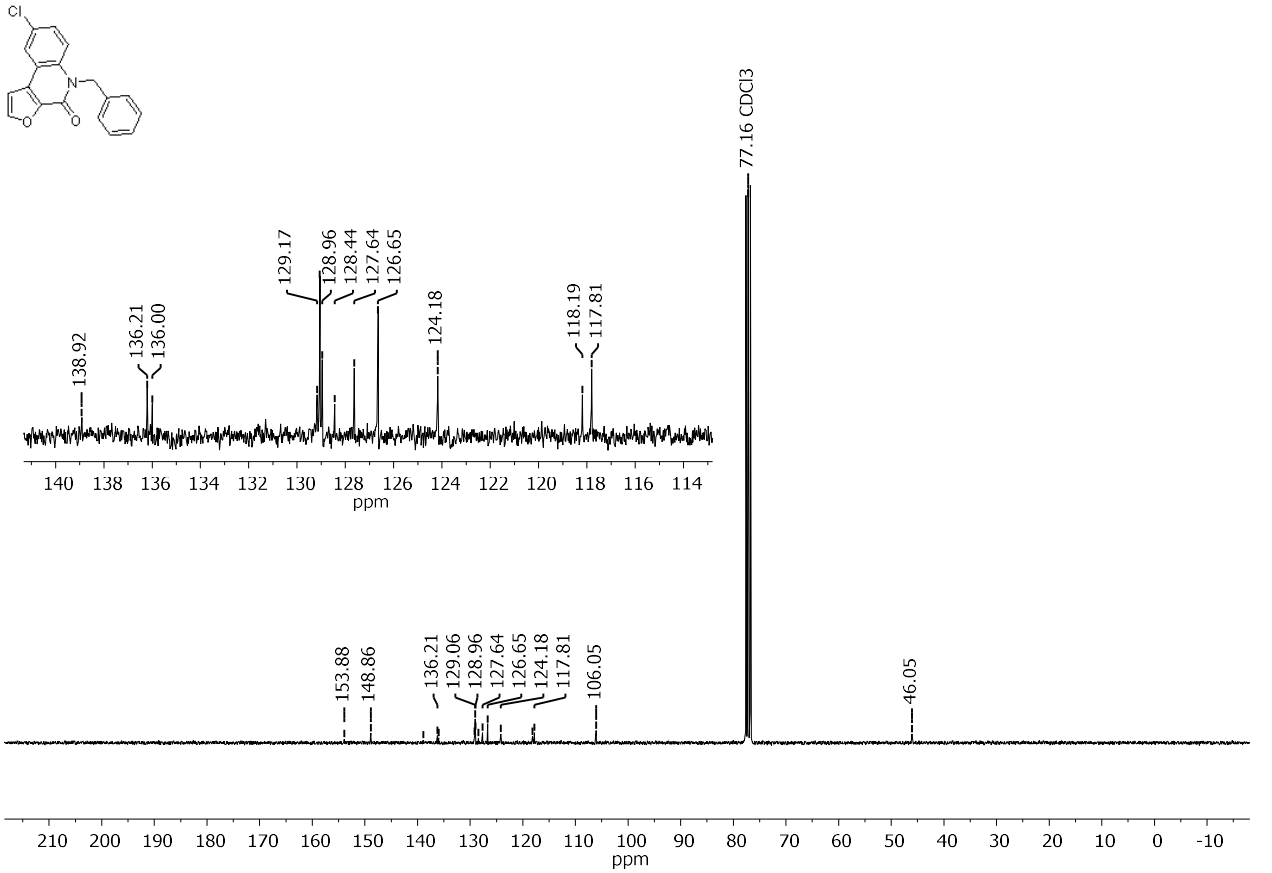


Figure S48. ^{13}C NMR spectrum of compound **1k** (75 MHz, $CDCl_3$).

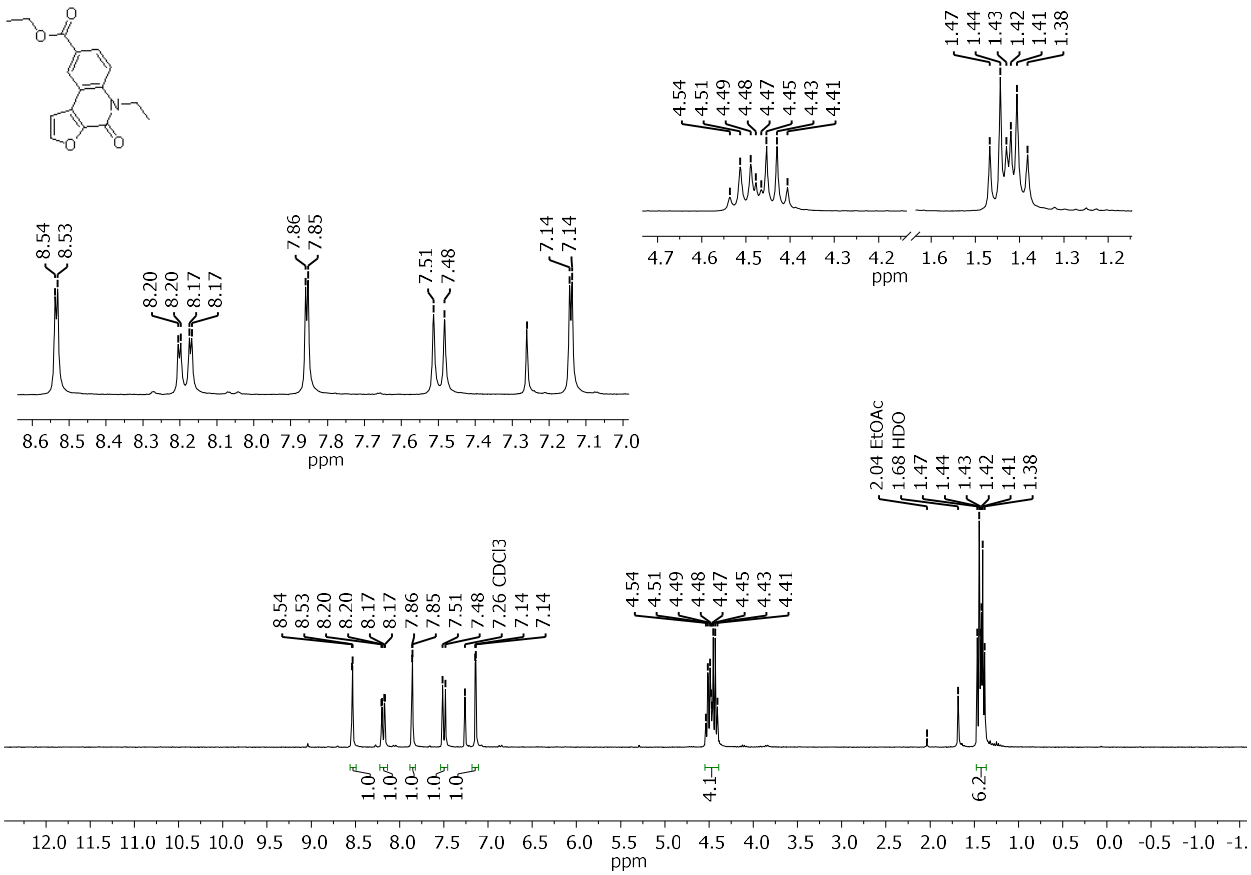


Figure S49. ^{1}H NMR spectrum of compound **1l** (300 MHz, $CDCl_3$).

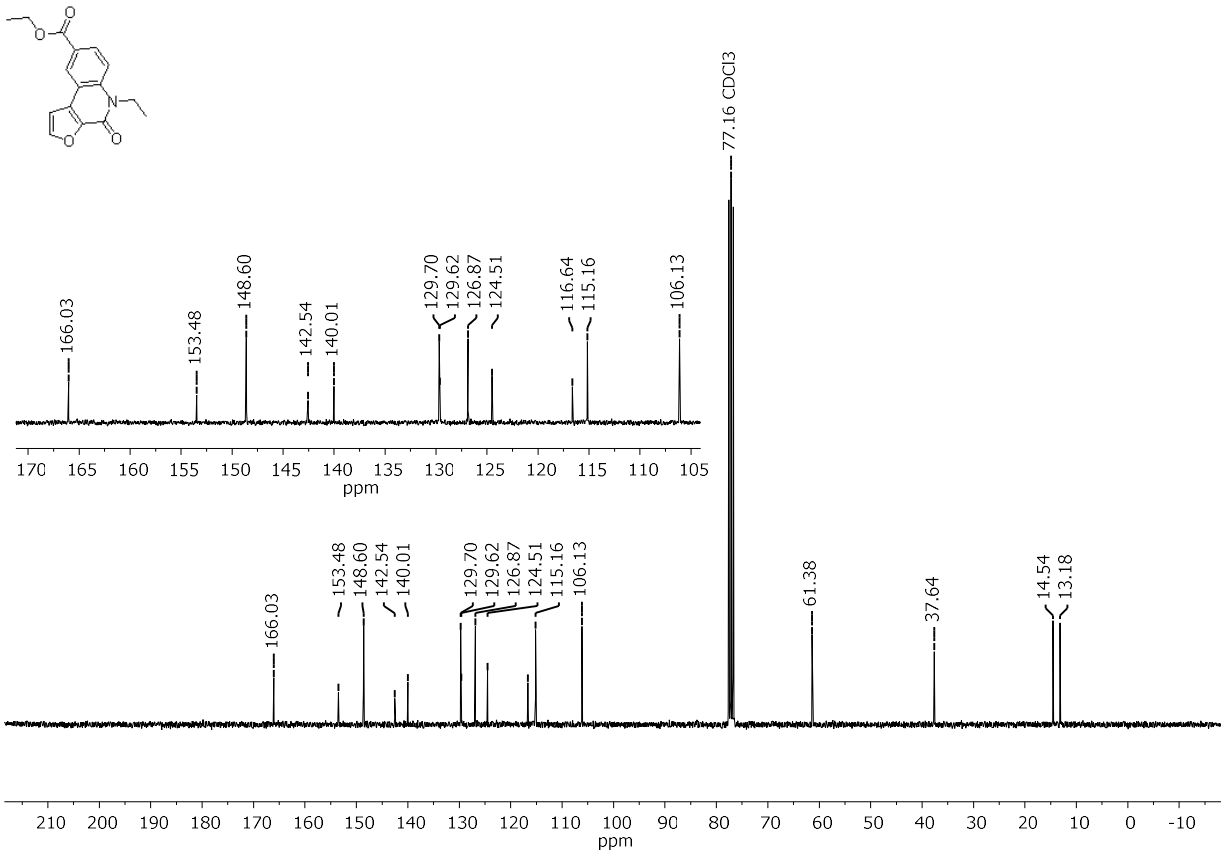


Figure S50. ^{13}C NMR spectrum of compound **1l** (75 MHz, $CDCl_3$)

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