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CH-alkylation of furan derivatives under photoinduced Pd catalysis

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S1. General information and materials

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).

GC-MS experiments were carried out using an Agilent 7890A GC system, furnished with an Agilent 5975C mass-selective detector (electron impact ionization, 70 eV) and a HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as carrier gas at a flow rate of 1.0 mL min^{-1}.

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*-benzo[*d*]imidazole (**1e**)[S1], 2-(furan-2-yl)benzo[*d*]oxazole (**1f**)[S2], 2-(furan-2-yl)benzo[*d*]thiazole (**1g**)[S3], 2-(2-furanyl)-1-methyl-1*H*-phenanthro[9,10-*d*]imidazole (**1h**)[S4], were synthesized according to previously described procedures. All other reagents are commercially available.

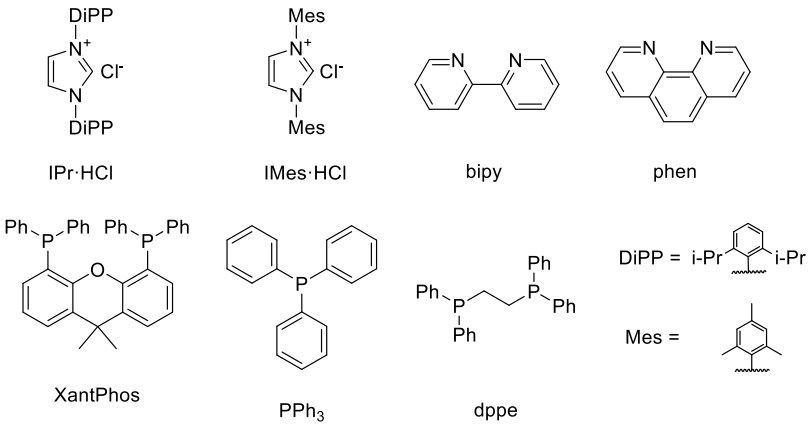


Figure S1. Ligands studied in the reaction between **1a** and **2a**.

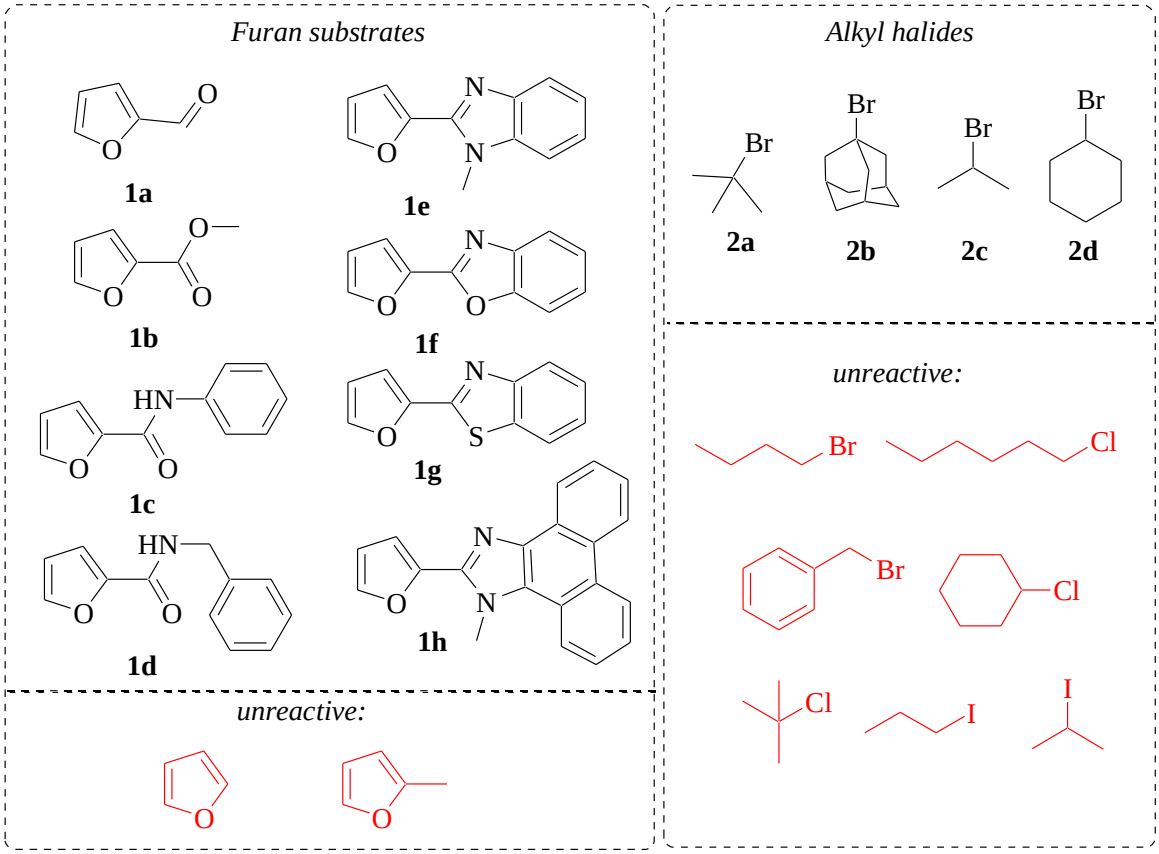


Figure S2. Structures of furan substrates and alkyl halides used in this study.

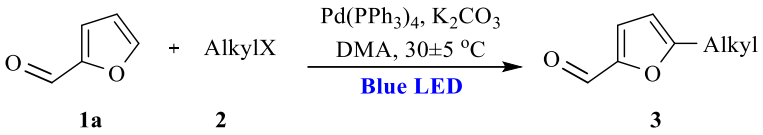
S2. Extended experimental data

Table S1. Optimization of the reaction conditions for alkylation of **1a** with **2a** (extended experimental data)[a]

Entry	[Pd] (mol%)	Additive (mol%)	Solvent	Base	Time (h)	Yield of **3a** (%)[b]
1	$Pd(OAc)_2$ (5)	none	DMA	K_2CO_3	24	trace
2	$Pd(OAc)_2$ (5)	$[Bu_4N]Br$ (20)	DMA	K_2CO_3	24	trace
3	$Pd(OAc)_2$ (5)	IPr·HCl (10)	DMA	K_2CO_3	24	trace
4	$Pd(OAc)_2$ (5)	IMes·HCl (10)	DMA	K_2CO_3	24	trace
5	$Pd(OAc)_2$ (5)	bipy (10)	DMA	K_2CO_3	24	0
6	$Pd(OAc)_2$ (5)	phen (10)	DMA	K_2CO_3	24	0
7	$Pd(OAc)_2$ (5)	XantPhos (10)	DMA	K_2CO_3	24	7
8	$Pd(OAc)_2$ (5)	PPh_3 (20)	DMA	K_2CO_3	24	40
9	$Pd(OAc)_2$ (5)	PPh_3 (30)	DMA	K_2CO_3	24	45
10	$PdCl_2$ (5)	PPh_3 (20)	DMA	K_2CO_3	24	39
11	$PdCl_2(PPh_3)_2$ (5)	PPh_3 (20)	DMA	K_2CO_3	24	40
12	$Pd(OAc)_2$ (5)	Dppe (10)	DMA	K_2CO_3	24	trace
13	$Pd(PPh_3)_4$ (5)	none	DMA	K_2CO_3	24	71
14	$Pd(PPh_3)_4$ (5)	none	DMA	K_2CO_3	36	72
15	$Pd(PPh_3)_4$ (10)	none	DMA	K_2CO_3	36	71
16	$Pd(PPh_3)_4$ (5)	PPh_3 (15)	DMA	K_2CO_3	24	70
17	$Pd(PPh_3)_4$ (2.5)	none	DMA	K_2CO_3	36	40
18	$Pd(PPh_3)_4$ (5)	$[Bu_4N]Br$ (5)	DMA	K_2CO_3	24	71
19	$Pd(PPh_3)_4$ (5)	$[Bu_4N]I$ (5)	DMA	K_2CO_3	24	56
20	$Pd(PPh_3)_4$ (5)	IPr·HCl (10)	DMA	K_2CO_3	24	65
21	$Pd(PPh_3)_4$ (5)	none	toluene	K_2CO_3	24	trace
22	$Pd(PPh_3)_4$ (5)	none	1,4-dioxane	K_2CO_3	24	trace
23	$Pd(PPh_3)_4$ (5)	none	THF	K_2CO_3	24	trace
24	$Pd(PPh_3)_4$ (5)	none	MeCN	K_2CO_3	24	12
25	$Pd(PPh_3)_4$ (5)	none	DMA	Na_2CO_3	24	35
26	$Pd(PPh_3)_4$ (5)	none	DMA	Cs_2CO_3	24	70
27	$Pd(PPh_3)_4$ (5)	none	DMA	Et_3N	24	0
28	$Pd(PPh_3)_4$ (5)	none	DMA	DBU	24	70
29	$Pd(PPh_3)_4$ (5)	none	DMA	K_2CO_3	24	trace[c]
30	none	PPh_3 (20)	DMA	K_2CO_3	24	0

[a]*Reagents and conditions*: **1a** (0.25 mmol), **2a** (0.5 mmol), [Pd] (0.0125 mmol, 5 mol %), additive (0 – 30 mol %), base (0.5 mmol), solvent (1 mL), two blue 40 W LED lamps at 30±5 °C. [b]Yield was determined by NMR. [c]In the dark.

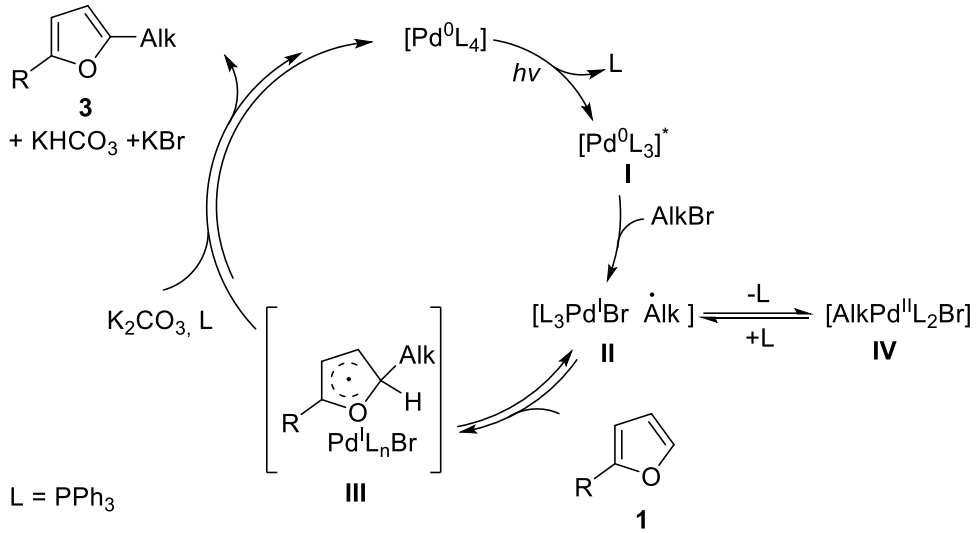
Table S2. Yields of alkylation products provided by various alkyl halides[a]



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

Entry	AlkHal	Yield of **3**, (%) [b]
1	^{n}Bu-Br	25
2	Bn-Br	0
3	^{n}Hept-Cl	0
4	Cy-Cl	0
5	^{t}Bu-Cl	trace, trace[c]
6	^{n}Pr-I	16
7	^{i}Pr-I	22

[a]*Reagents and conditions*: **1a** (0.25 mmol), **2** (0.5 mmol), $Pd(PPh_3)_4$ (0.0125 mmol, 5 mol %), K_2CO_3 (0.5 mmol), DMA (1 mL), two blue 40 W LED lamps 24 h. [b]Yield was determined by NMR. [c]In the presence of 5mol% $[Bu_4N]Br$.

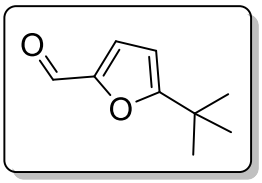


Scheme S1. Possible reaction mechanism.

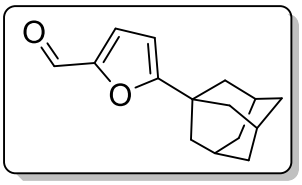
S3. Experimental procedures and characterization of synthesized compounds

Synthesis of compounds 3a-n (general procedure)

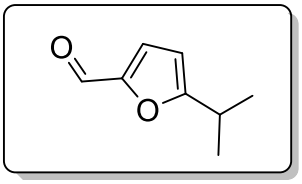
A mixture of compound **1a-h** (0.25 mmol), alkyl bromide (0.5 mmol), K_2CO_3 (0.069 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.0125 mmol, 5 mol %), and DMA (1 ml) was stirred under argon atmosphere and irradiation with blue LED lamps (2×40 W) at 30±5 °C for 24 h. Then the mixture was filtered through a short pad of Celite. The filtrate obtained was evaporated *in vacuo* to give crude product which was purified by column chromatography on silica-gel (hexane - EtOAc 10:1 as eluent).



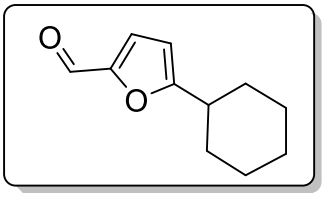
5-(*tert*-Butyl)furan-2-carbaldehyde (3a).[S5] Yield 0.025 g (66%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 9H), 6.22 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 9.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.9, 33.5, 106.0, 123.2, 151.9, 171.5, 177.4.



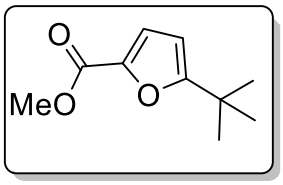
5-(Adamantan-1-yl)furan-2-carbaldehyde (3b).[S6] Yield 0.044 g (76%), white solid, mp = 75-76˚C (lit[6] mp=78˚C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.75-1.77 (m, 6H), 1.96-1.97 (m, 6H), 2.04 – 2.10 (m, 3H), 6.18 (d, J = 3.6 Hz, 1H), 7.16 (d, J = 3.6 Hz, 1H), 9.52 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.1, 35.4, 36.6, 40.8, 105.6, 123.4, 151.6, 171.6, 177.3.



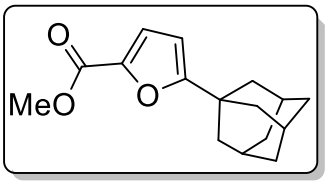
5-Isopropylfuran-2-carbaldehyde (3c).[S7] Yield 0.020 g (58%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.30 (s, 3H), 1.32 (s, 3H), 3.04 (dt, J = 13.8, 7.0 Hz, 1H), 6.22 (dd, J = 3.6, 0.9 Hz, 1H), 7.17 (dd, J = 3.6, 0.7 Hz, 1H), 9.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.9, 28.5, 106.8, 123.5, 151.8, 169.2, 177.3.



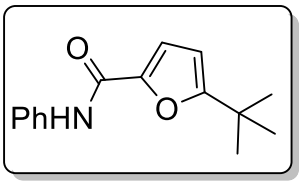
5-Cyclohexylfuran-2-carbaldehyde (3d).[S8] Yield 0.025 g (56%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.20 – 1.50 (m, 5H), 1.67 – 1.84 (m, 3H), 1.97 – 2.16 (m, 2H), 2.71 (td, J = 11.0, 3.6 Hz, 1H), 6.20 (dd, J = 3.5, 0.8 Hz, 1H), 7.16 (d, J = 3.6 Hz, 1H), 9.51 (s, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.8, 25.9, 31.2, 37.7, 106.9, 123.5, 151.7, 168.3, 177.2.



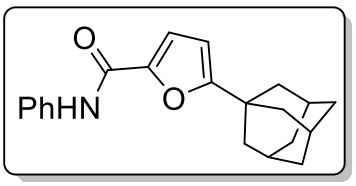
Methyl 5-(*tert*-butyl)furan-2-carboxylate (3e).[S9] Yield 0.024 g (53%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (s, 9H), 3.86 (s, 3H), 6.09 (d, J = 3.4 Hz, 1H), 7.07 (d, J = 3.5 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.0, 33.3, 51.8, 104.9, 119.1, 142.9, 159.5, 169.1.



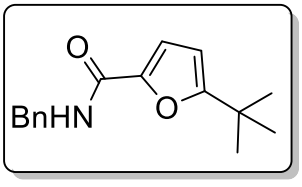
Methyl 5-(adamantan-1-yl)furan-2-carboxylate (3f). Yield 0.048 g (74%), white solid, mp=98-99˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69 – 1.80 (m, 6H), 1.94-1.96 (m, 6H), 2.02 – 2.10 (m, 3H), 3.86 (s, 3H), 6.05 (d, J = 3.5 Hz, 1H), 7.08 (d, J = 3.5 Hz, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.2, 35.2, 36.7, 40.9, 51.8, 104.5, 119.2, 142.6, 159.6, 169.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{21}O_3^+$ 261.1485, found *m/z* 261.1489



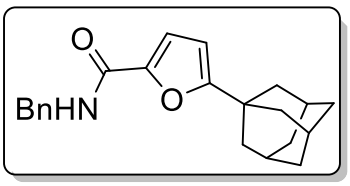
5-(*tert*-Butyl)-*N*-phenylfuran-2-carboxamide (3g). Yield 0.034 g (59%), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 9H), 6.15 (d, J = 3.4 Hz, 1H), 7.08 – 7.18 (m, 2H), 7.37 (dd, J = 8.4, 7.5 Hz, 2H), 7.61 – 7.71 (m, 2H), 7.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.1, 33.2, 77.2, 105.7, 116.4, 120.1, 124.5, 129.2, 137.6, 146.0, 156.5, 167.0. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_2^+$ 244.1332, found *m/z* 244.1340



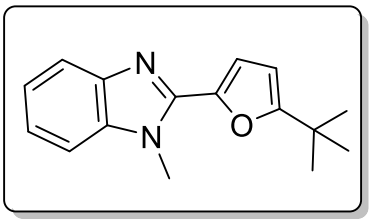
5-(Adamantan-1-yl)-*N*-phenylfuran-2-carboxamide (3h). Yield 0.051 g (64%), white solid, mp= 202-203 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.75-1.84 (m, 6H), 1.96-1.98 (m, 6H), 2.09-2.11 (m, 3H), 6.11 (d, J = 3.5 Hz, 1H), 7.02 – 7.18 (m, 2H), 7.31 – 7.44 (m, 2H), 7.63 – 7.72 (m, 2H), 7.92 (s, 1H). δ ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.2, 35.1, 36.7, 41.2, 105.3, 116.4, 120.1, 124.5, 129.2, 137.7, 145.7, 156.5, 167.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_2^+$ 322.1802, found *m/z* 322.1810



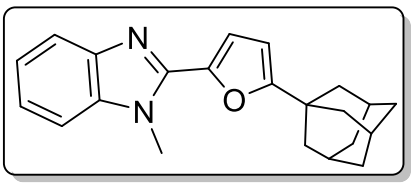
***N*-Benzyl-5-(*tert*-butyl)furan-2-carboxamide (3i).** Yield 0.034 g (53%), white solid, mp= 72-73 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 9H), 4.63 (d, J = 6.0 Hz, 2H), 6.09 (d, J = 3.5 Hz, 1H), 6.55 (s, 1H), 7.04 (d, J = 3.4 Hz, 1H), 7.25 – 7.42 (m, 5H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.1, 33.0, 43.1, 105.2, 115.5, 127.7, 128.0, 128.9, 138.5, 146.1, 158.7, 166.6. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}NO_2^+$ 258.1489, found *m/z* 258.1501



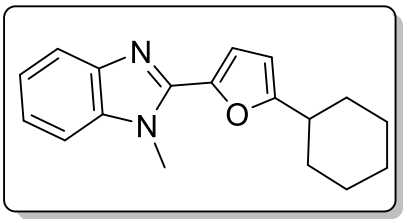
5-(Adamantan-1-yl)-*N*-benzylfuran-2-carboxamide (3j). Yield 0.052 g (62%), white solid, mp= 182-183 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.74-1.77 (m, 6H), 1.90-1.92 (m, 6H), 2.00 – 2.11 (m, 3H), 4.63 (d, J = 6.1 Hz, 2H), 6.05 (d, J = 3.5 Hz, 1H), 6.54 (s, 1H), 7.06 (d, J = 3.5 Hz, 1H), 7.27 – 7.46 (m, 5H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.2, 35.0, 36.7, 41.1, 43.1, 104.7, 115.5, 127.7, 128.1, 128.9, 138.6, 145.8, 158.8, 166.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_2^+$ 336.1958, found *m/z* 336.1949.



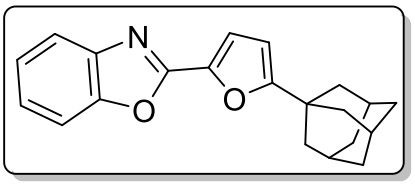
2-(5-*tert*-Butylfuran-2-yl)-1-methyl-1*H*-benz[*d*]imidazole (3k). Yield 0.046 g (72%), white solid, mp=105-106˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 9H), 4.05 (s, 3H), 6.19 (d, J = 3.4 Hz, 1H), 7.10 (d, J = 3.4 Hz, 1H), 7.27 – 7.38 (m, 3H), 7.74 – 7.80 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.2, 31.7, 33.1, 104.8, 109.3, 113.5, 119.7, 122.6, 122.7, 136.3, 143.3, 144.0, 145.1, 166.3. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd $C_{16}H_{19}N_2O^+$ 255.3405, found *m/z* 255.3402



2-[5-(Adamantan-1-yl)furan-2-yl]-1-methyl-1*H*-benz[*d*]imidazole (3l). Yield 0.072 g (87%), white solid, mp= 188-189 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.75 – 1.83 (m, 6H), 2.00-2.02 (m, 6H), 2.09-2.12 (m, 3H), 4.04 (s, 3H), 6.14 (d, J = 3.4 Hz, 1H), 7.11 (d, J = 3.4 Hz, 1H), 7.23 – 7.29 (m, 2H), 7.31 – 7.37 (m, 1H), 7.73 – 7.80 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.3, 31.8, 35.0, 36.8, 41.3, 104.4, 109.2, 113.4, 119.6, 122.5, 122.6, 136.3, 143.3, 143.7, 145.2, 166.6. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd $C_{22}H_{25}N_2O^+$ 333.4545, found *m/z* 333.4551.

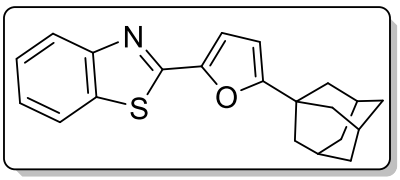


2-(5-Cyclohexylfuran-2-yl)-1-methyl-1*H*-benz[*d*]imidazole (3m). Yield 0.036 g (51%), white solid, mp= 110-111˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ. 1.27 – 1.52 (m, 5H), 1.69 – 1.88 (m, 3H), 2.07 – 2.16 (m, 2H), 2.77 (td, J = 11.0, 3.7 Hz, 1H), 4.03 (s, 3H), 6.18 (dd, J = 3.4, 0.9 Hz, 1H), 7.07 (d, J = 3.4 Hz, 1H), 7.26 – 7.37 (m, 3H), 7.73 – 7.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.0, 26.1, 31.6, 31.7, 37.5, 105.6, 109.2, 113.4, 119.7, 122.6, 122.7, 136.3, 143.3, 143.7, 145.2, 163.2. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd $C_{18}H_{21}N_2O^+$ 281.1648, found *m/z* 281.1649.

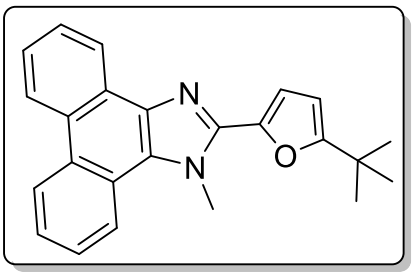


2-[5-(Adamantan-1-yl)furan-2-yl]benz[*d*]oxazole (3n). Yield 0.065 g (82%), white solid, mp= 176-177˚C. ^{1}H NMR ($CDCl_3$, 300]MHz): δ

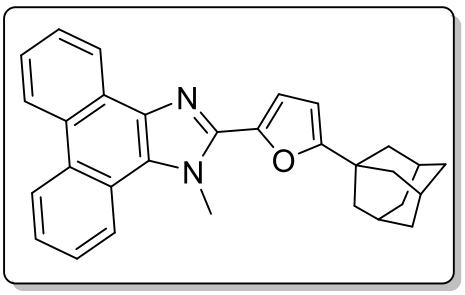
1.78-1.81 (m, 6H), 2.02-2.04 (m, 6H), 2.08-2.10 (m, 3H), 6.16 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 7.28 – 7.35 (m, 2H), 7.49 – 7.57 (m, 1H), 7.72 – 7.77 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.3, 35.2, 36.7, 41.0, 104.8, 110.5, 115.6, 120.0, 124.7, 124.9, 140.6, 142.0, 150.2, 155.9, 168.9. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd $C_{21}H_{22}NO_2^+$ 320.1645, found *m/z* 320.1647.



2-[5-(Adamantan-1-yl)furan-2-yl]benzo[*d*]thiazole (3o). Yield 0.047 g (56%), white solid, mp= 164-167 ˚C ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.79-1.81 (m, 6H), 2.00-2.03 (m, 6H), 2.06 – 2.13 (m, 3H), 6.15 (d, *J* = 3.5 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 7.28 – 7.40 (m, 1H), 7.40 – 7.52 (m, 1H), 7.84-7.87 (m, 1H), 7.97 – 8.07 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.3, 35.1, 36.8, 41.2, 105.2, 112.4, 121.6, 123.0, 124.9, 126.4, 134.3, 146.8, 154.1, 158.4, 167.8. ESI-MS(TOF) *m/z*: $[M+H]^+$ Calcd $C_{21}H_{22}NOS^+$ 336.1417, found *m/z* 336.1422.



2-(5-*tert*-Butylfuran-2-yl)-1-methyl-1*H*-phenanthro[9,10-*d*]imidazole (3p). Yield 0.048 g (54%), white solid, mp= 152-154 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.41 (s, 9H), 4.45 (s, 3H), 6.21 (d, J = 3.4 Hz, 1H), 7.06 (d, J = 3.4 Hz, 1H), 7.54 – 7.76 (m, 4H), 8.45 (dd, J = 7.9, 1.7 Hz, 1H), 8.59 – 8.71 (m, 1H), 8.77-8.79 (m, 1H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.25, 33.10, 35.73, 104.53, 113.35, 120.83, 122.82, 123.13, 123.71, 124.53, 124.92, 125.60, 126.72, 127.31, 127.35, 127.41, 128.23, 129.34, 137.98, 143.60, 143.96, 165.96. ESI-MS(TOF) m/z: [M+H]+ Calcd $C_{24}H_{23}N_2O^+$ 355.1805, found m/z 355.1809.



2-[5-(Adamantan-1-yl)furan-2-yl]-1-methyl-1*H*-phenanthro-[9,10-*d*]imidazole (3q). Yield 0.067 g (62%), white solid, mp= 105-108 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.75 – 1.89 (m, 6H), 1.97 – 2.17 (m, 9H), 6.17 (d, J = 3.4 Hz, 1H), 7.07 (d, J = 3.3 Hz, 1H), 7.55 – 7.74 (m, 4H), 8.44 – 8.49 (m, 1H), 8.64 – 8.71 (m, 1H), 8.71 – 8.86 (m, 2H).. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.4, 35.0, 35.8, 36.9, 41.4, 104.1, 113.3, 120.8, 122.8, 123.1, 123.7, 124.6, 124.9, 125.6, 126.7, 127.3, 127.4, 127.4, 128.2, 129.3, 138.0, 143.3, 144.1, 166.3. ESI-MS(TOF) m/z: [M+H]+ Calcd $C_{30}H_{29}N_2O^+$ 433.2274, found m/z 433.2281

S4. NMR spectra of the synthesized compounds

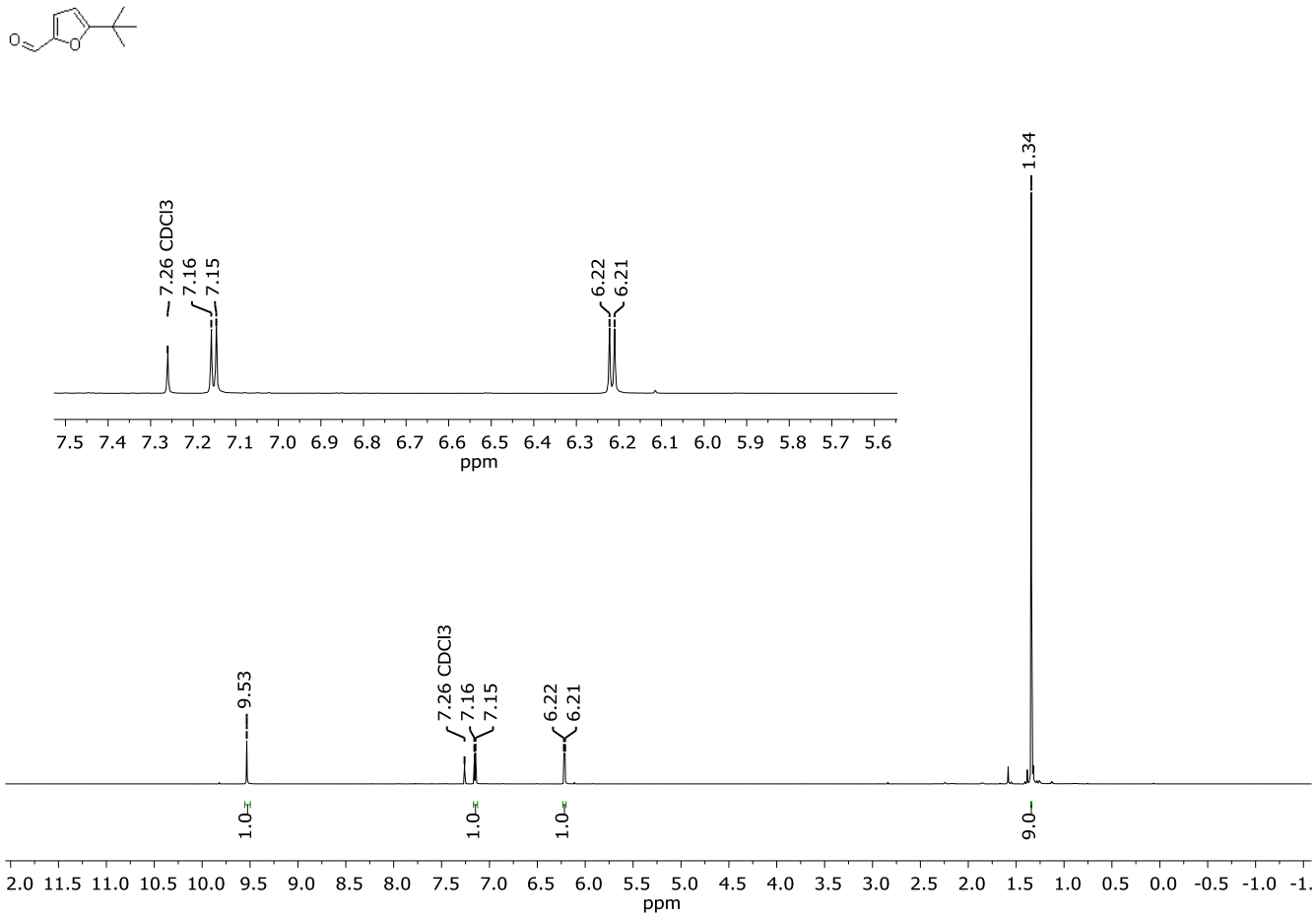


Figure S3. ^{1}H NMR spectrum of compound **3a** (300 MHz, $CDCl_3$).

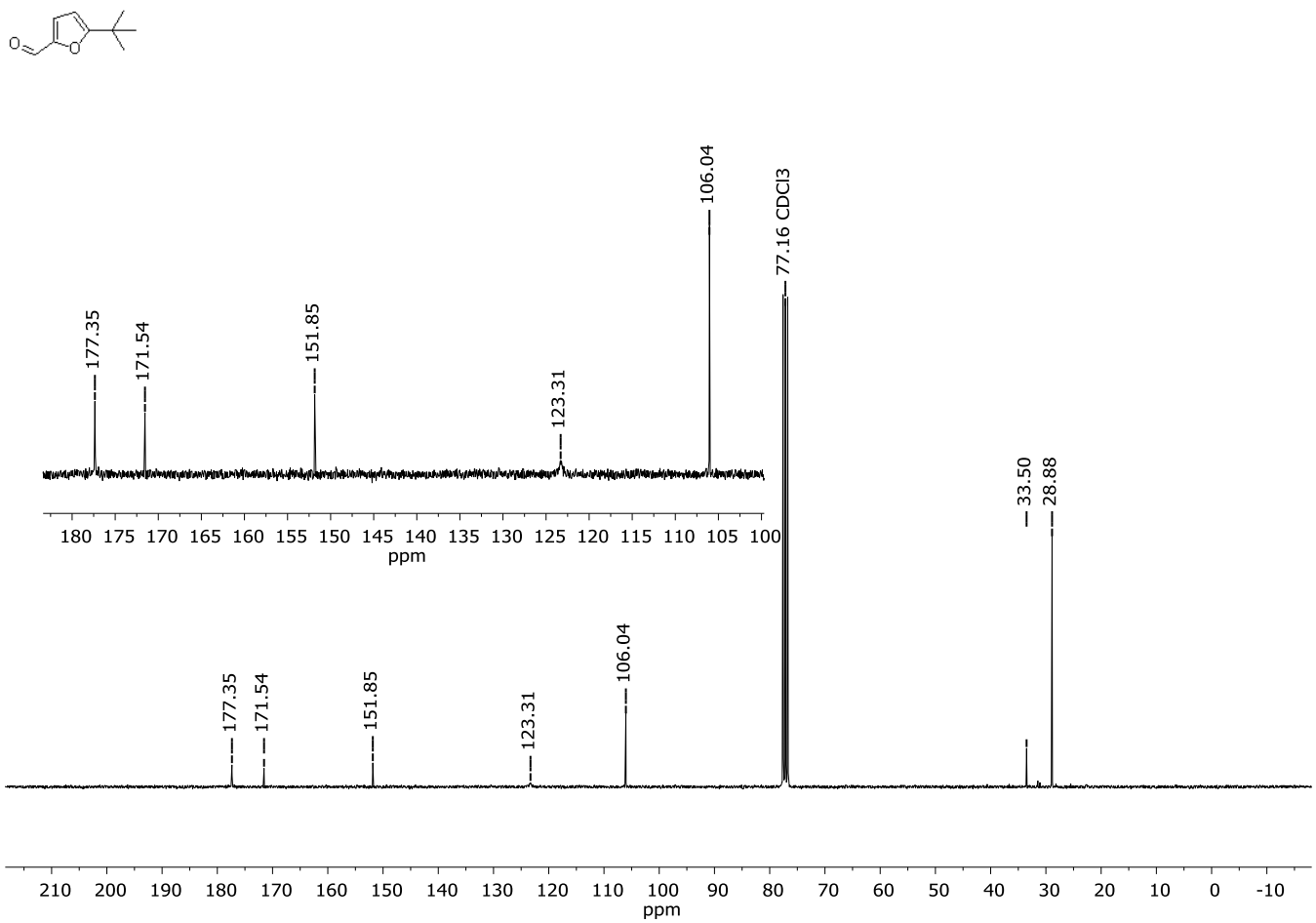


Figure S4. ^{13}C NMR spectrum of compound **3a** (75 MHz, $CDCl_3$).

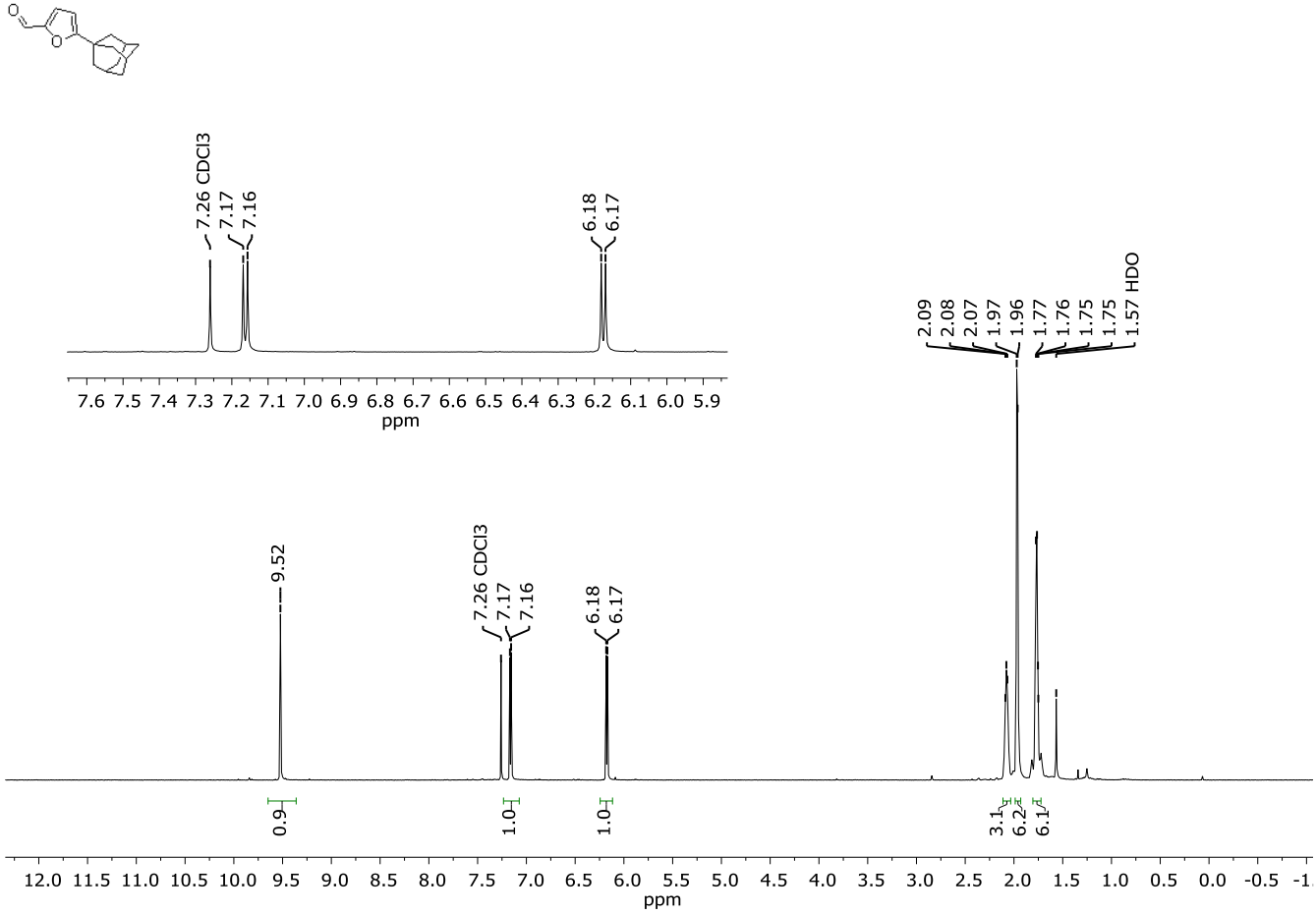


Figure S5. ^{1}H NMR spectrum of compound **3b** (300 MHz, $CDCl_3$).

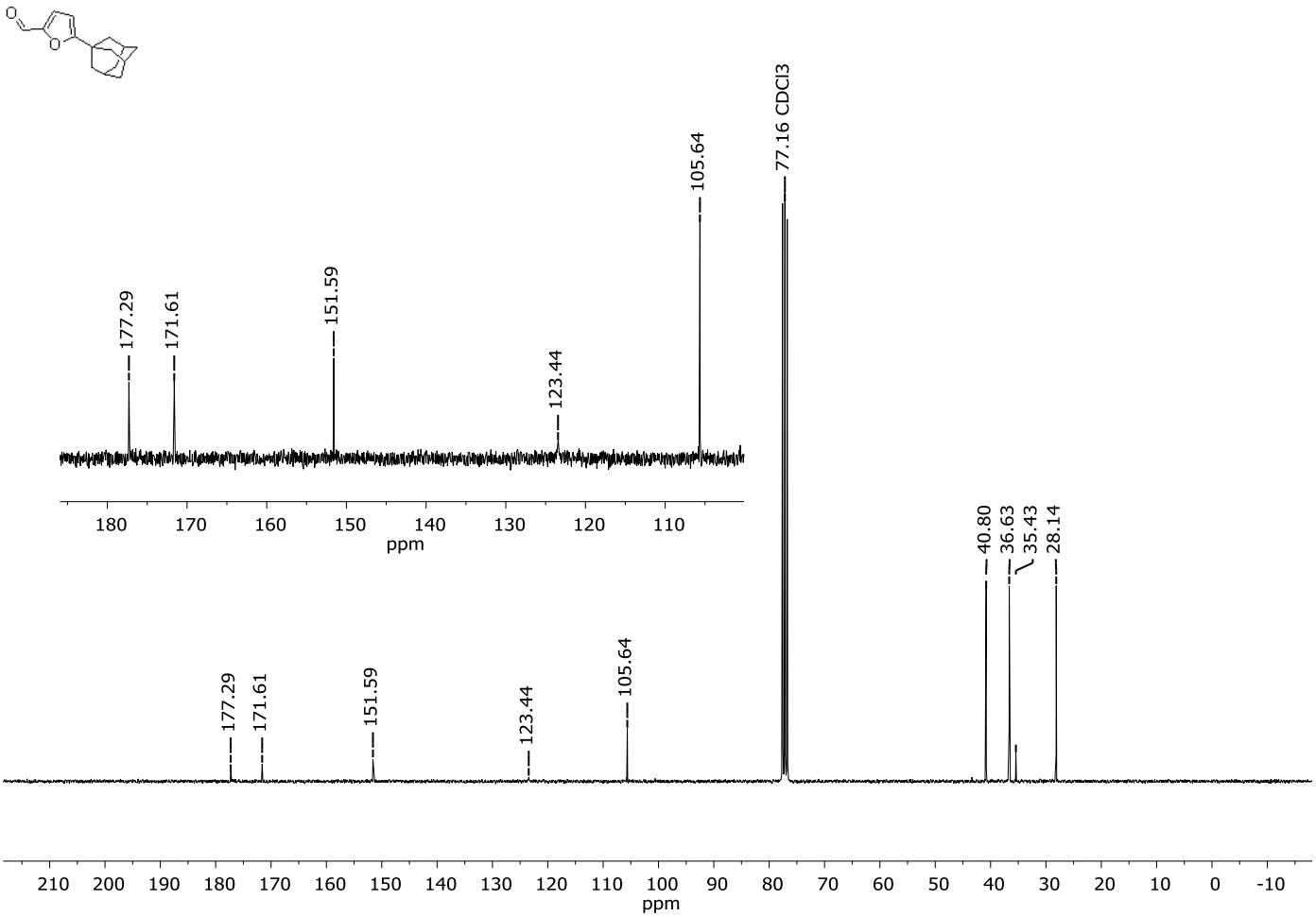


Figure S6. ^{13}C NMR spectrum of compound **3b** (75 MHz, $CDCl_3$).

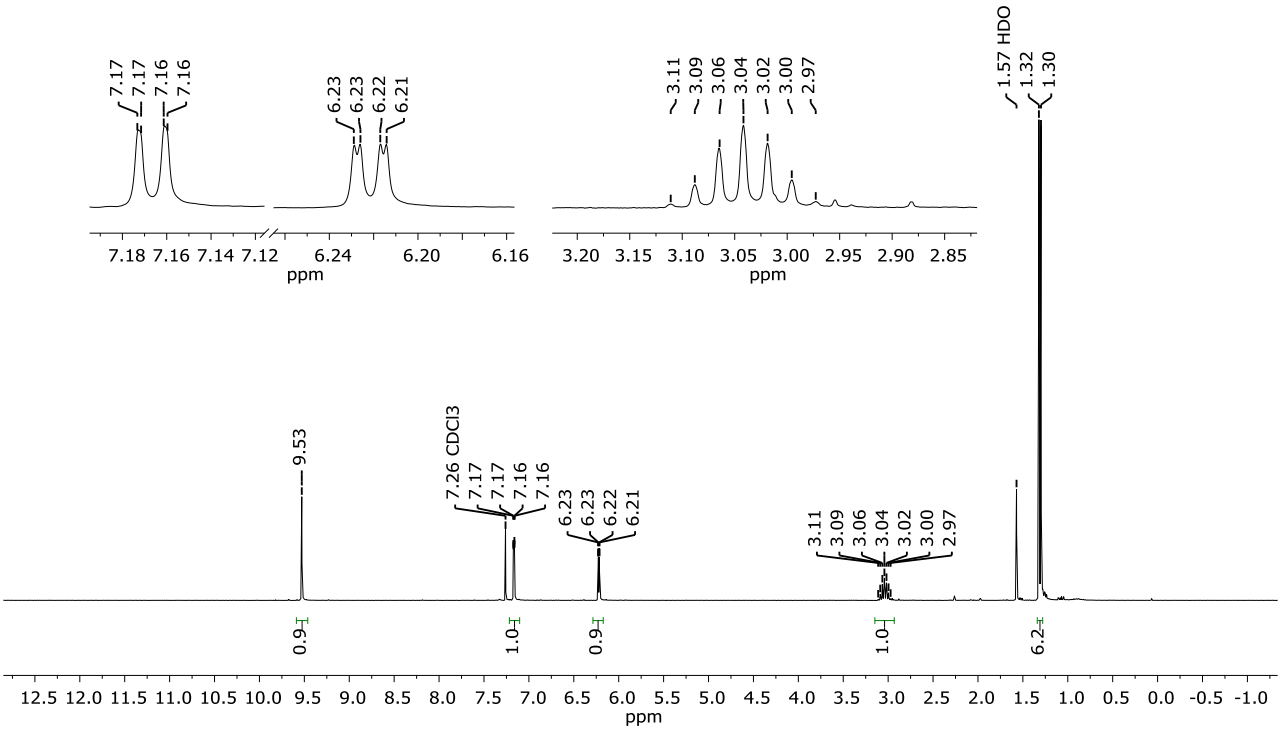


Figure S7. ^{1}H NMR spectrum of compound **3c** (300 MHz, $CDCl_3$)

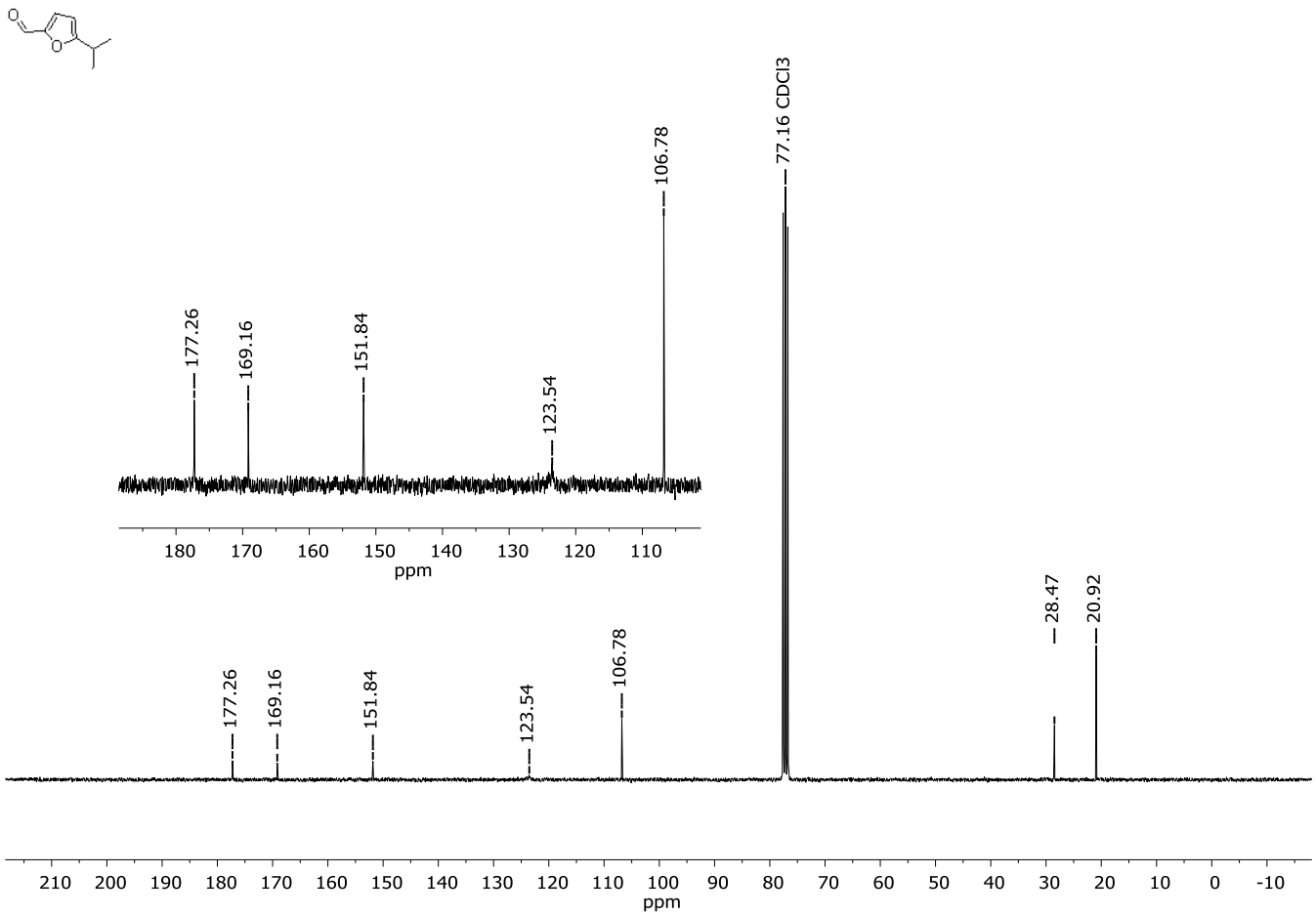


Figure S8. ^{13}C NMR spectrum of compound **3c** (75 MHz, $CDCl_3$).

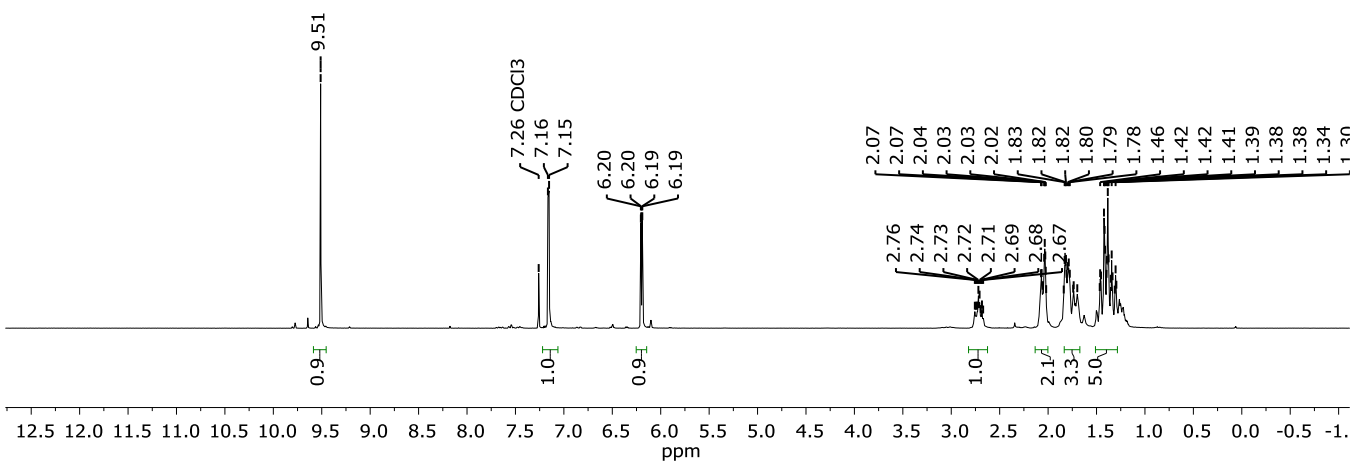


Figure S9. ^{1}H NMR spectrum of compound **3d**(300 MHz, $CDCl_3$)

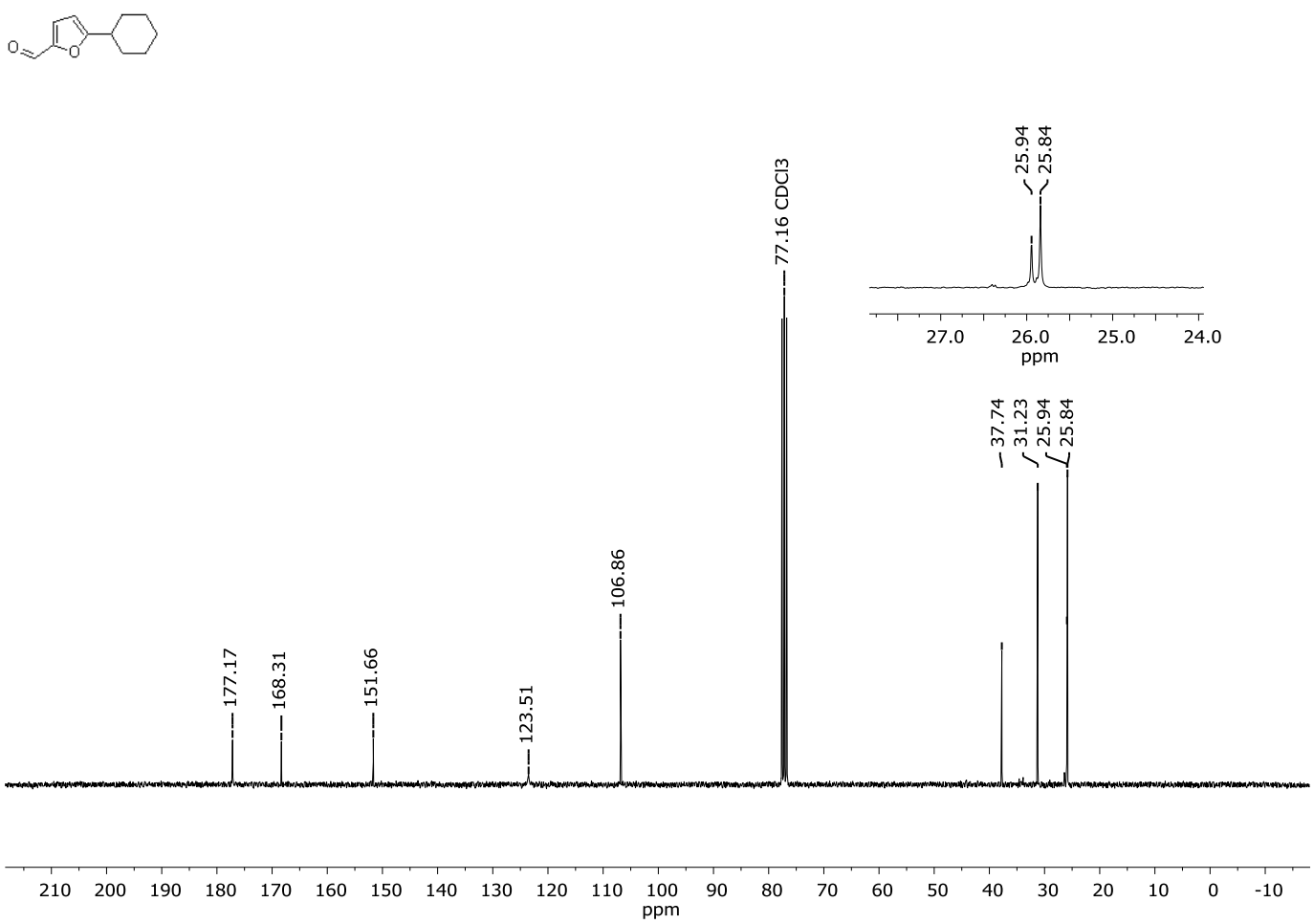


Figure S10. ^{13}C NMR spectrum of compound **3d** (75 MHz, $CDCl_3$).

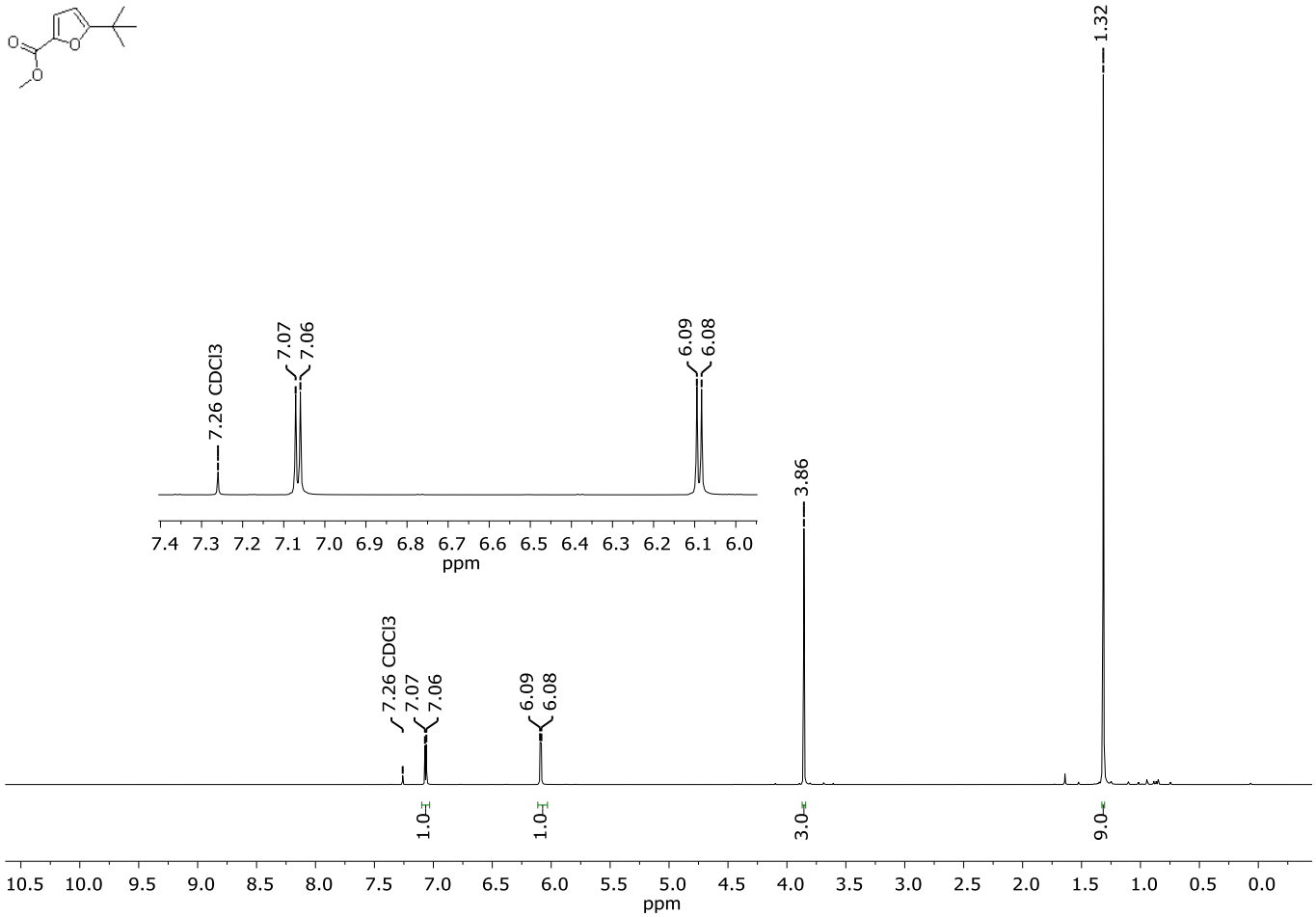
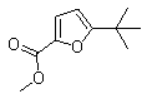


Figure S11. ^{1}H NMR spectrum of compound **3e** (300 MHz, $CDCl_3$).



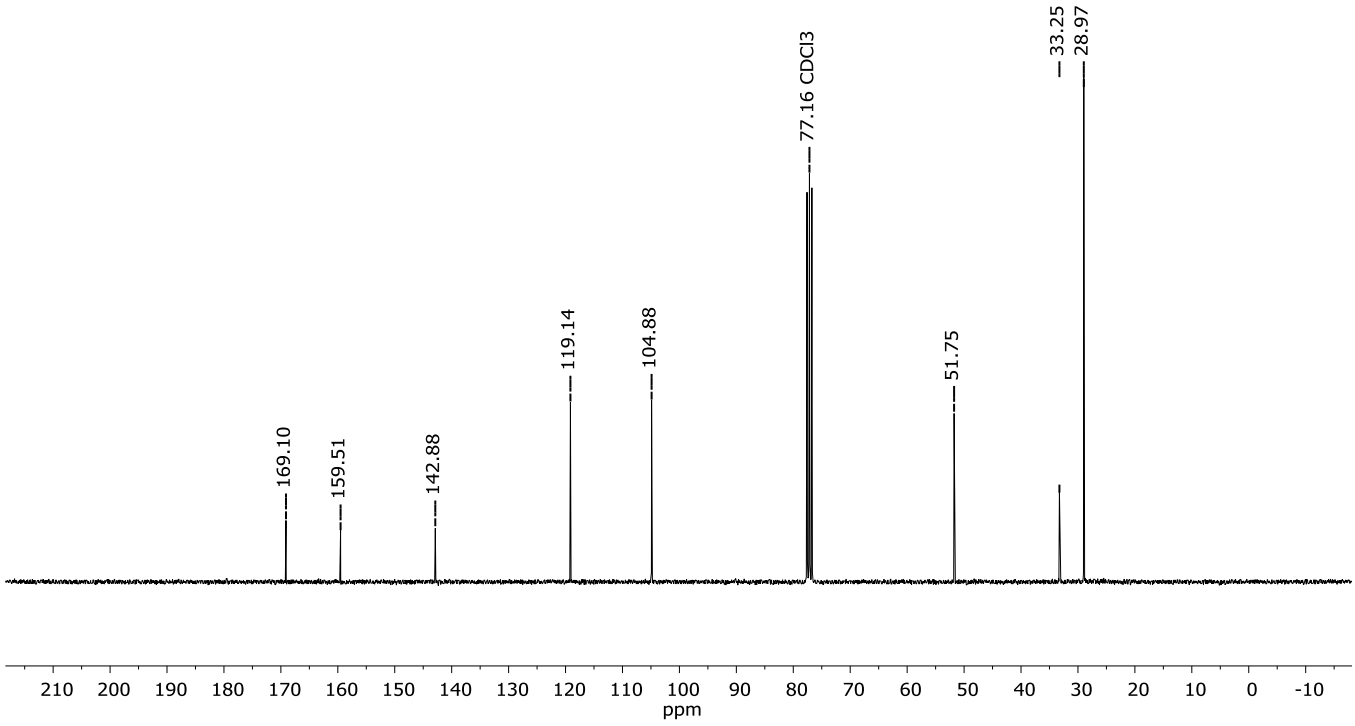
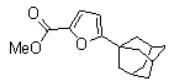


Figure S12. ^{13}C NMR spectrum of compound **3e** (75 MHz, $CDCl_3$).



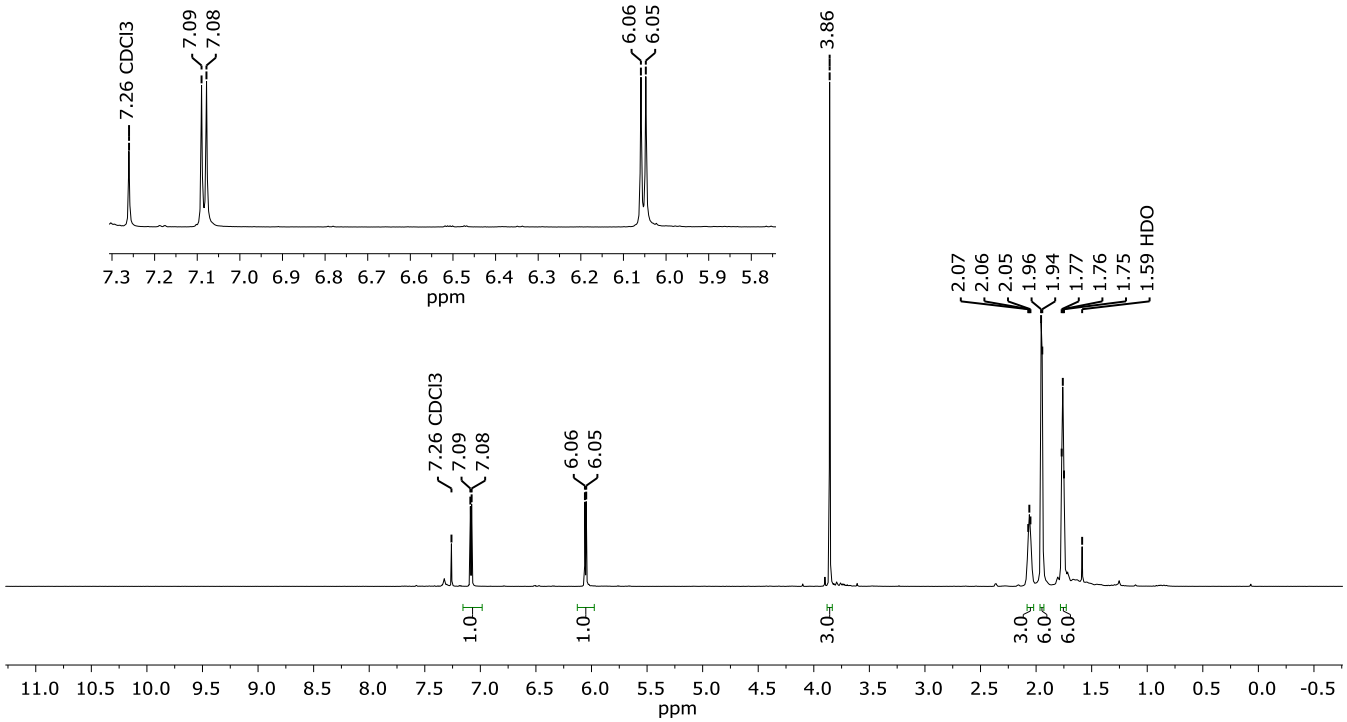


Figure S13. ^{1}H NMR spectrum of compound **3f** (300 MHz, $CDCl_3$).

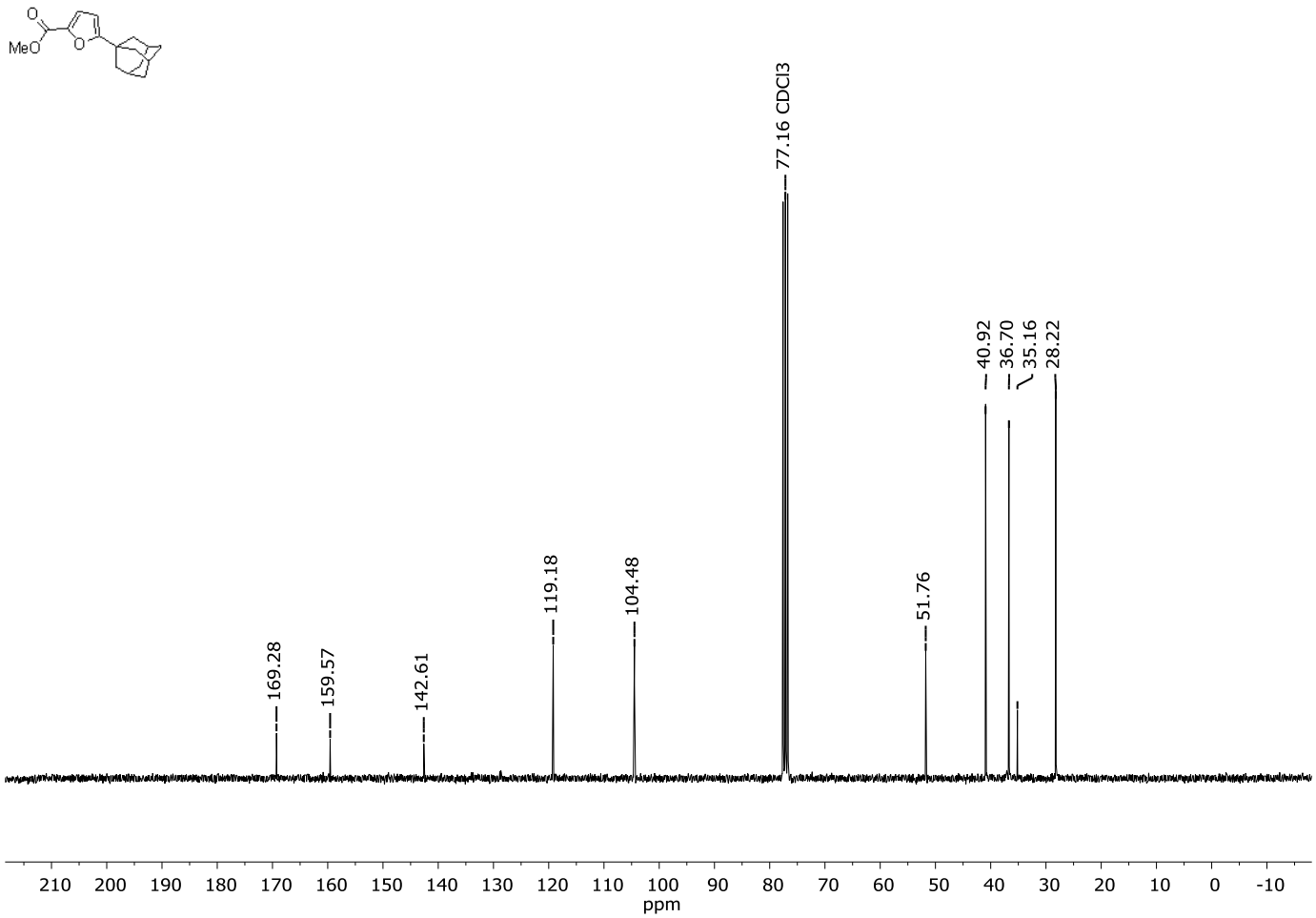


Figure S14. ^{13}C NMR spectrum of compound **3f** (75 MHz, $CDCl_3$).

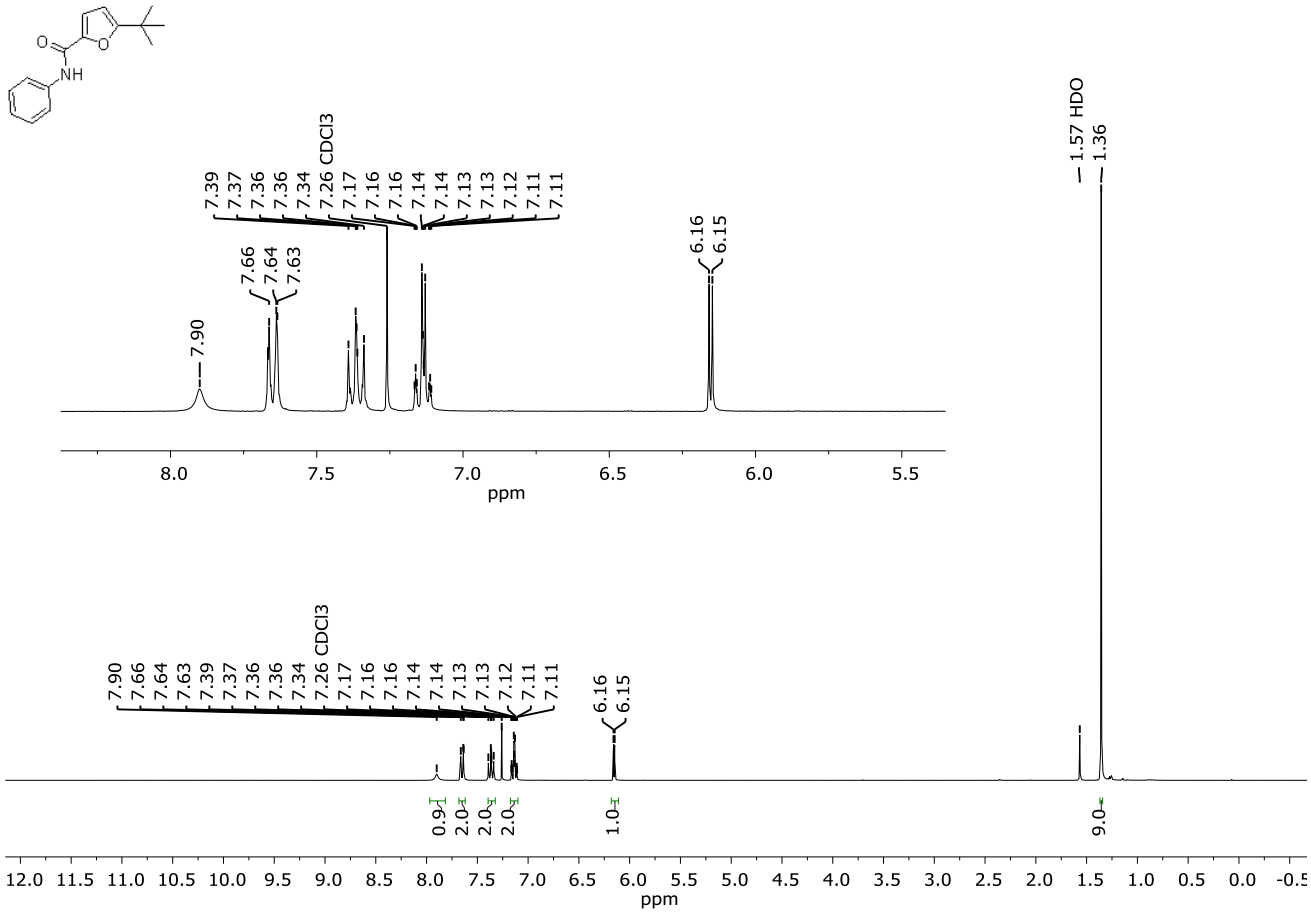


Figure S15. ^{1}H NMR spectrum of compound **3g** (300 MHz, $CDCl_3$).

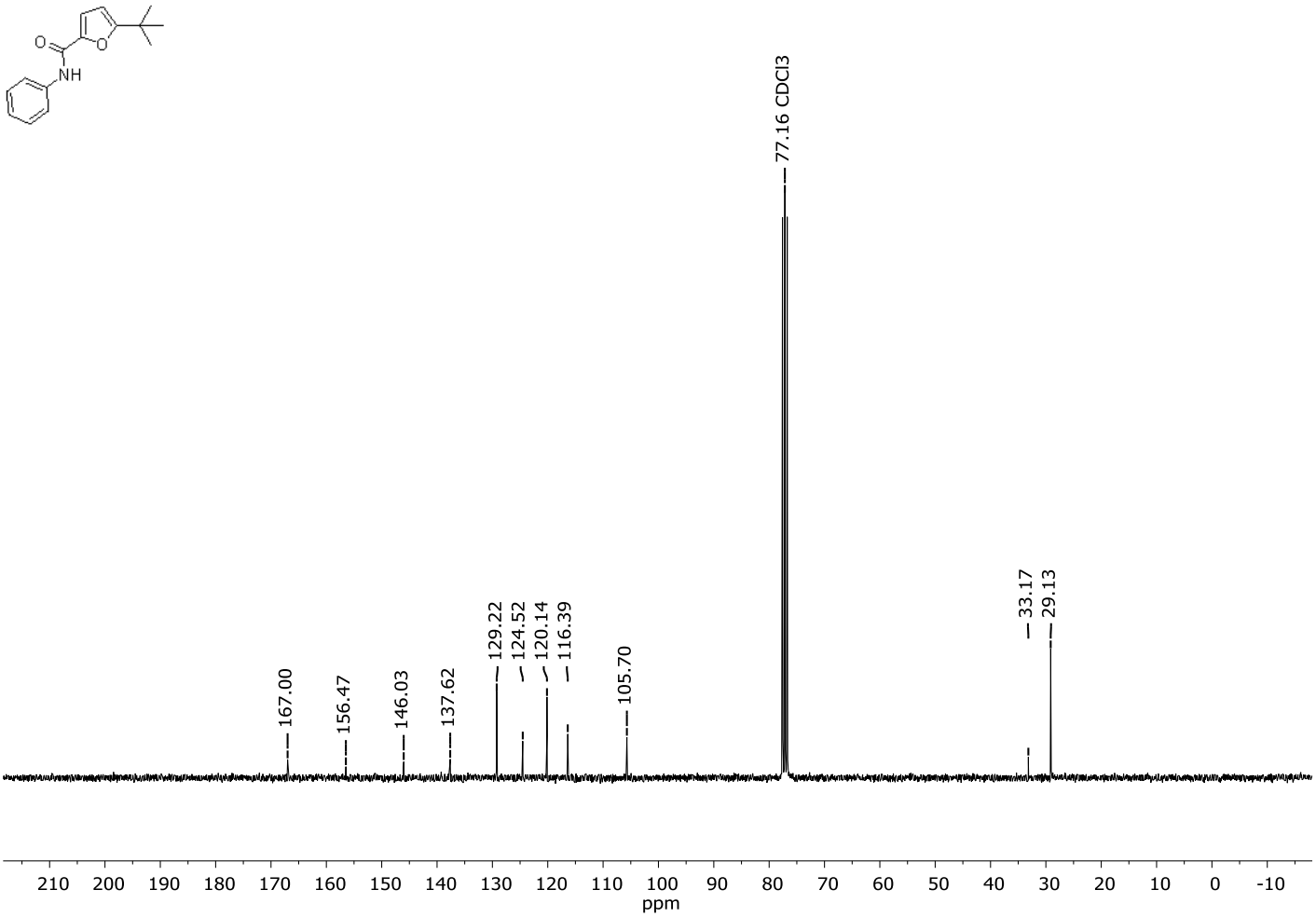


Figure S16. ^{13}C NMR spectrum of compound **3g** (75 MHz, $CDCl_3$).

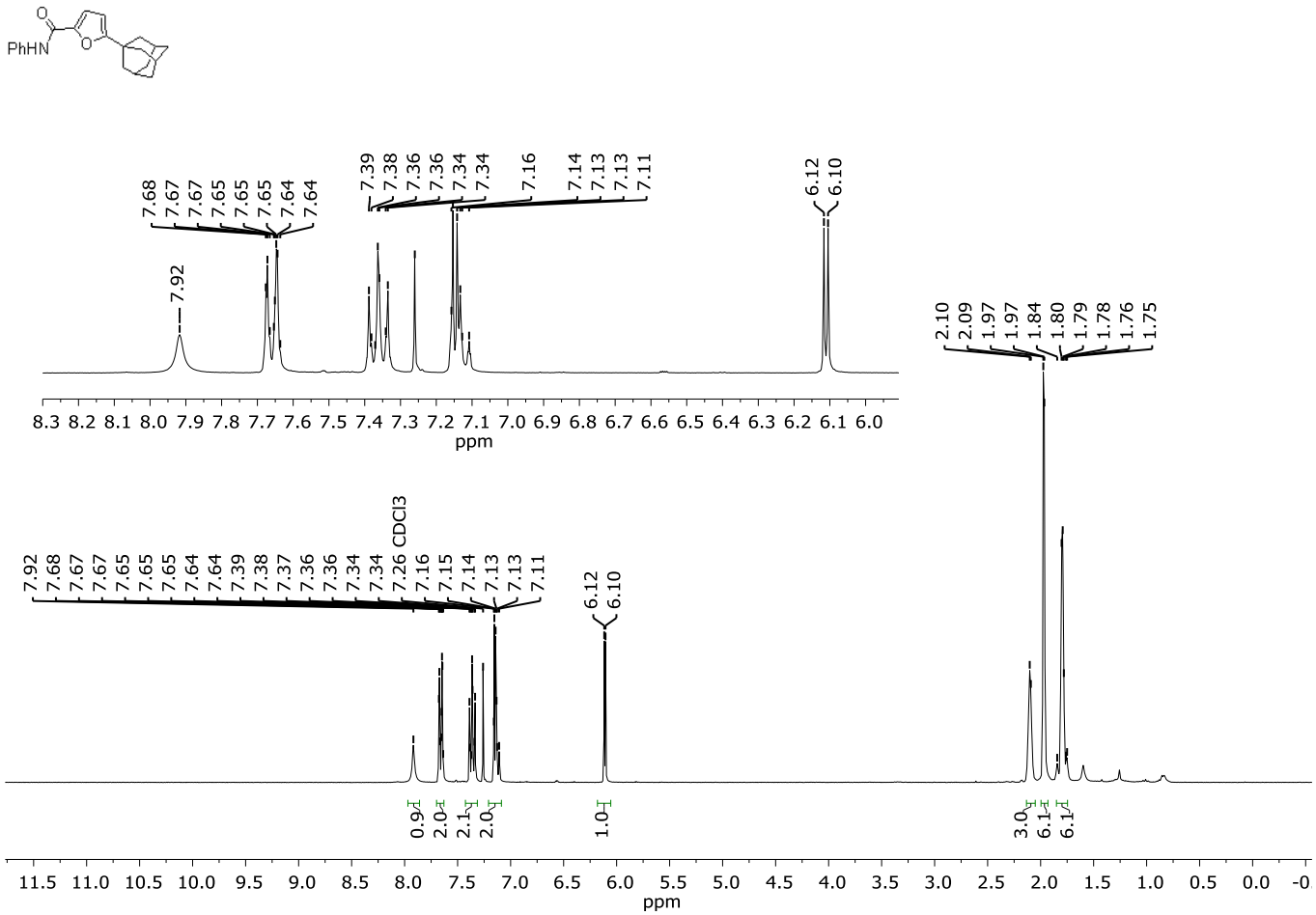


Figure S17. ^{1}H NMR spectrum of compound **3h** (300 MHz, $CDCl_3$).

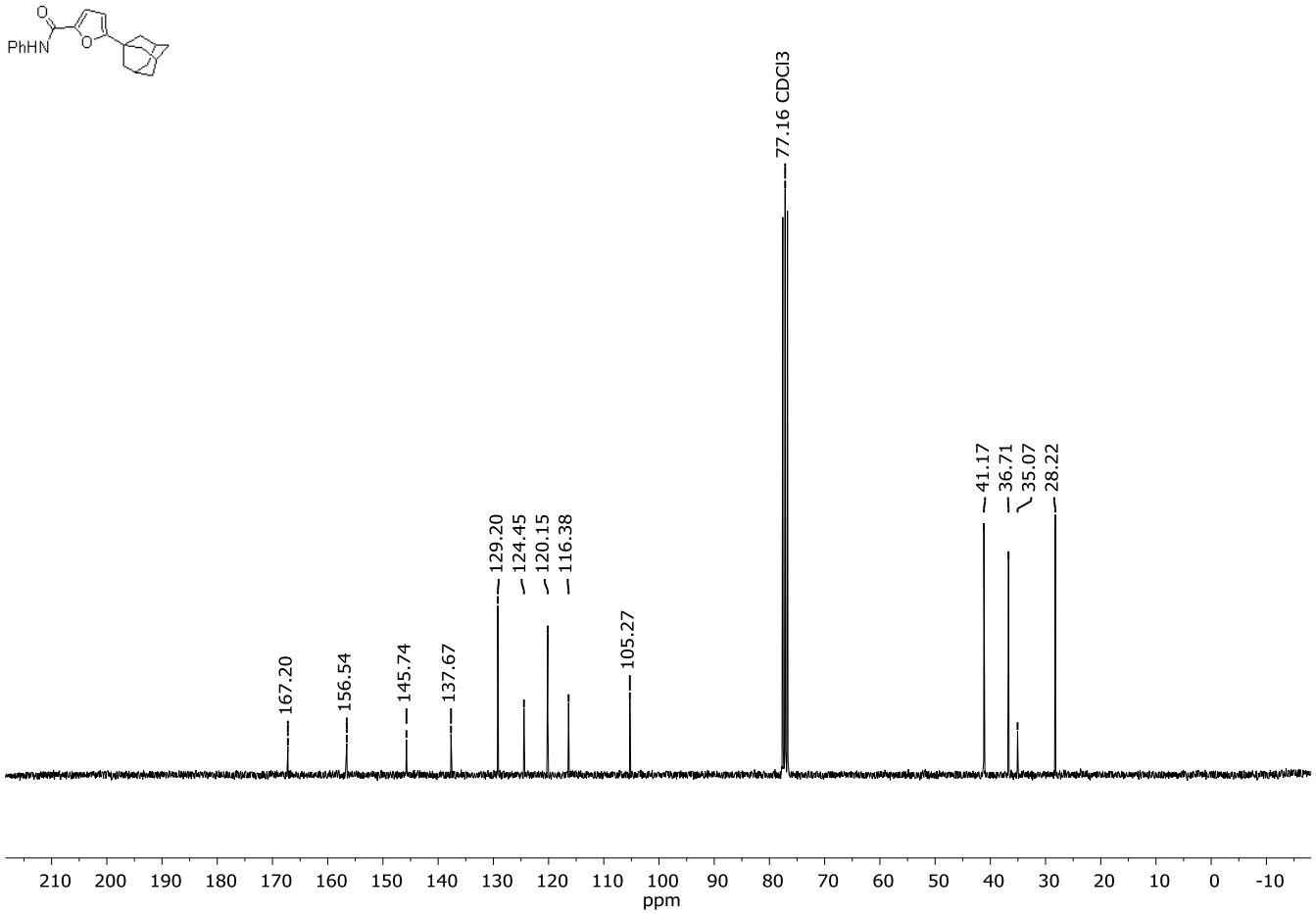


Figure S18. ^{13}C NMR spectrum of compound **3h** (75 MHz, $CDCl_3$).

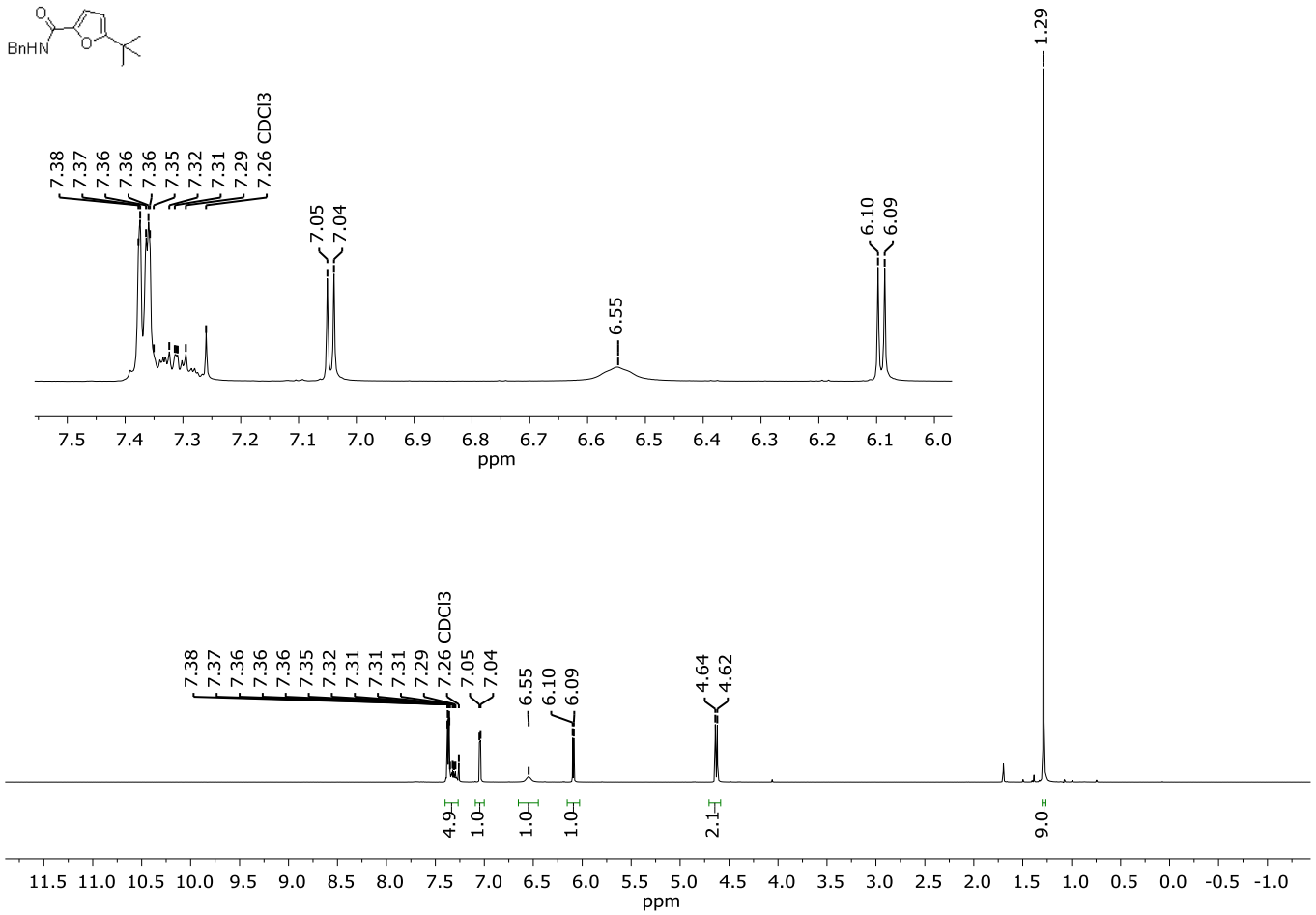


Figure S19. ^{1}H NMR spectrum of compound **3i**(300 MHz, $CDCl_3$).

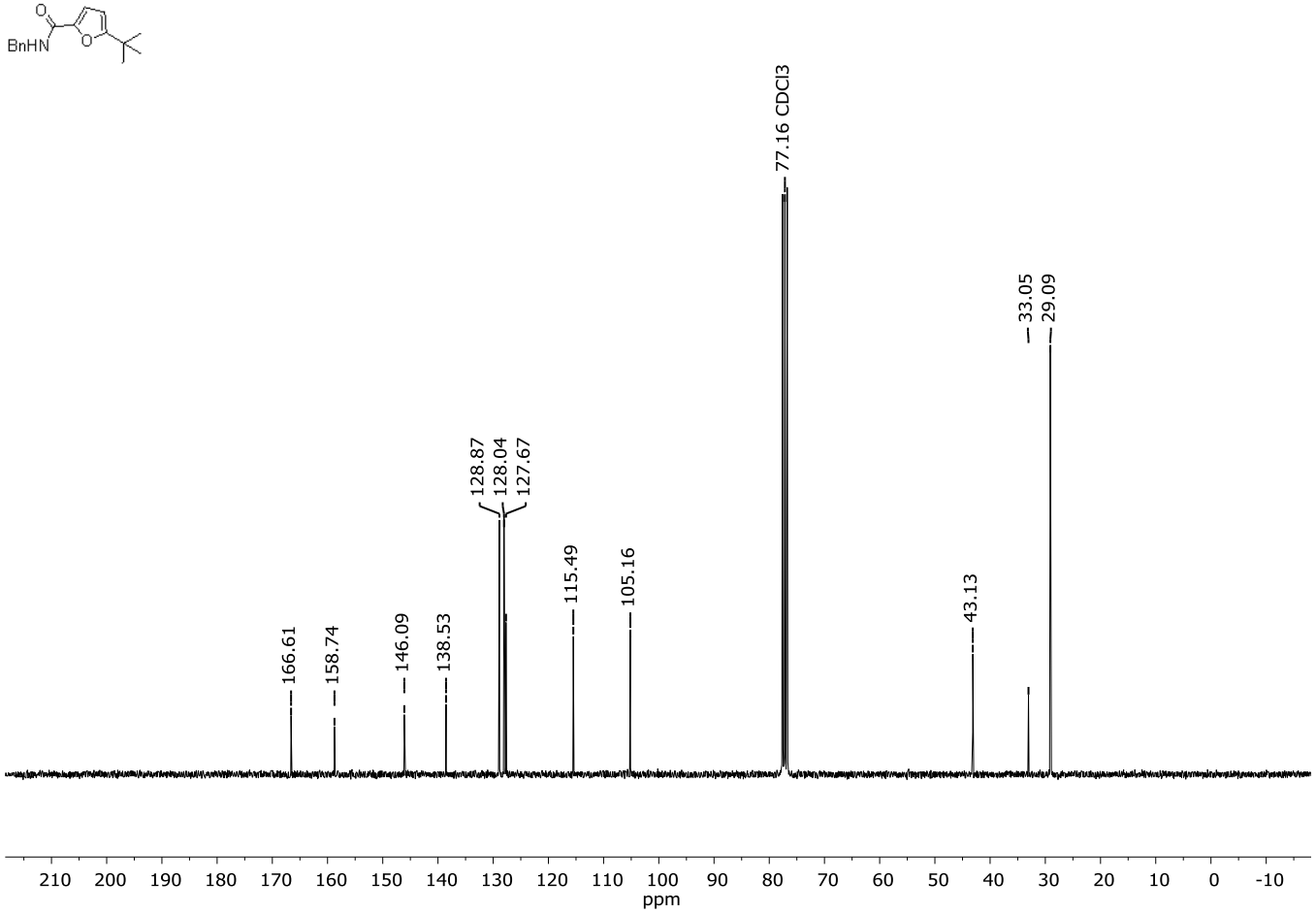


Figure S20. ^{13}C NMR spectrum of compound **3i** (75 MHz, $CDCl_3$).

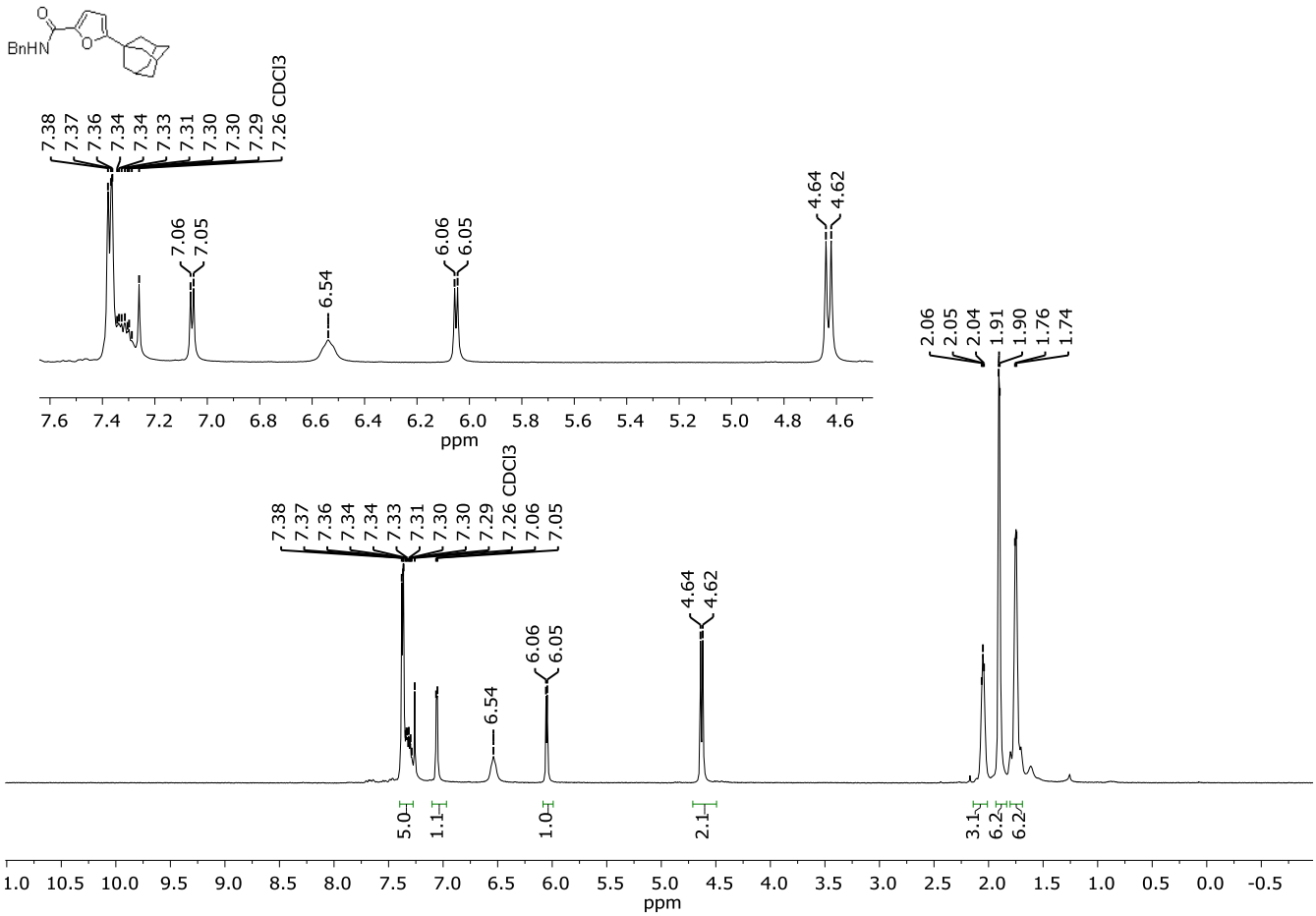


Figure S21. ^{1}H NMR spectrum of compound **3j** (300 MHz, $CDCl_3$).

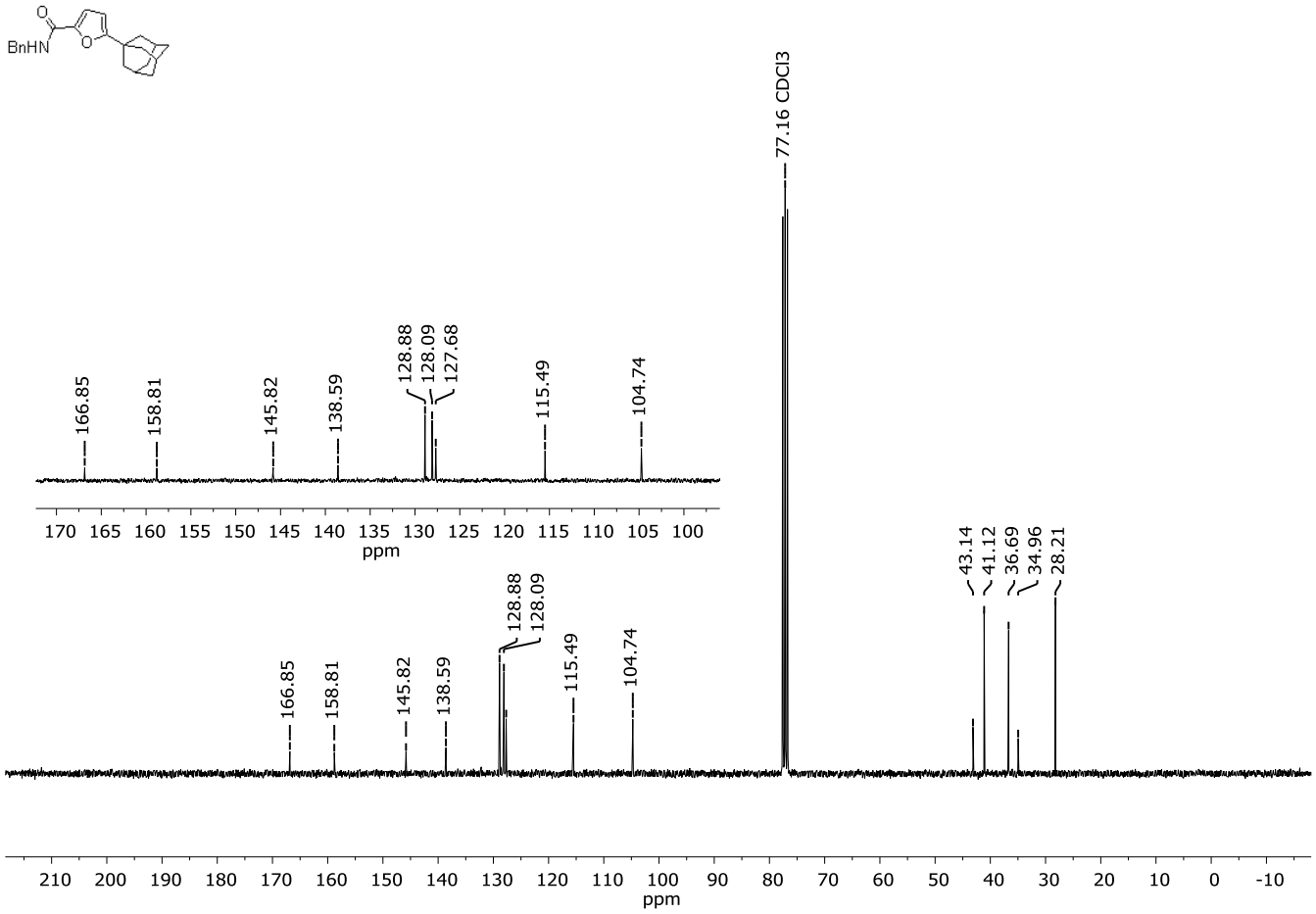


Figure S22. ^{13}C NMR spectrum of compound **3j** (75 MHz, $CDCl_3$).

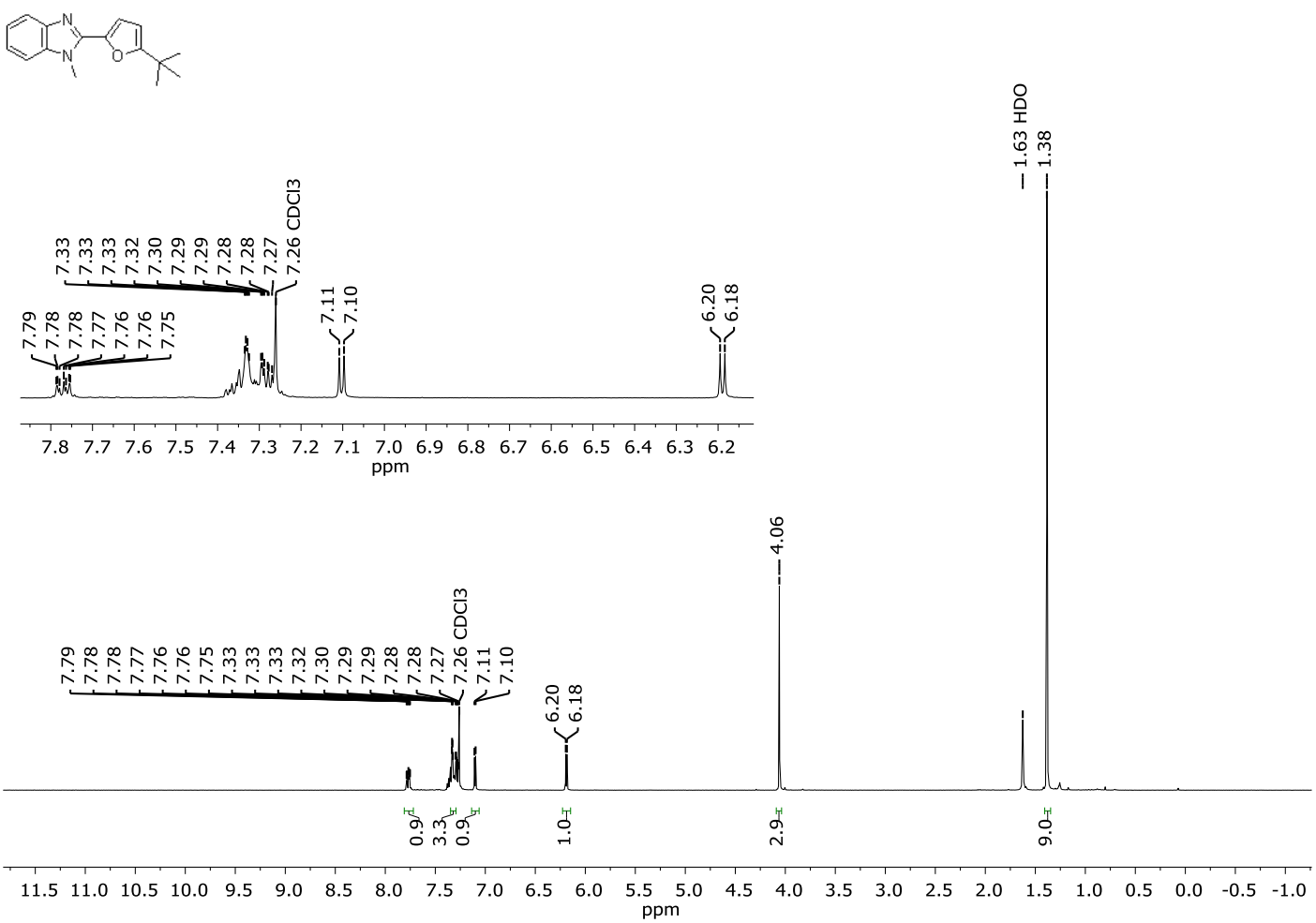


Figure S23. ^{1}H NMR spectrum of compound **3k** (300 MHz, $CDCl_3$).

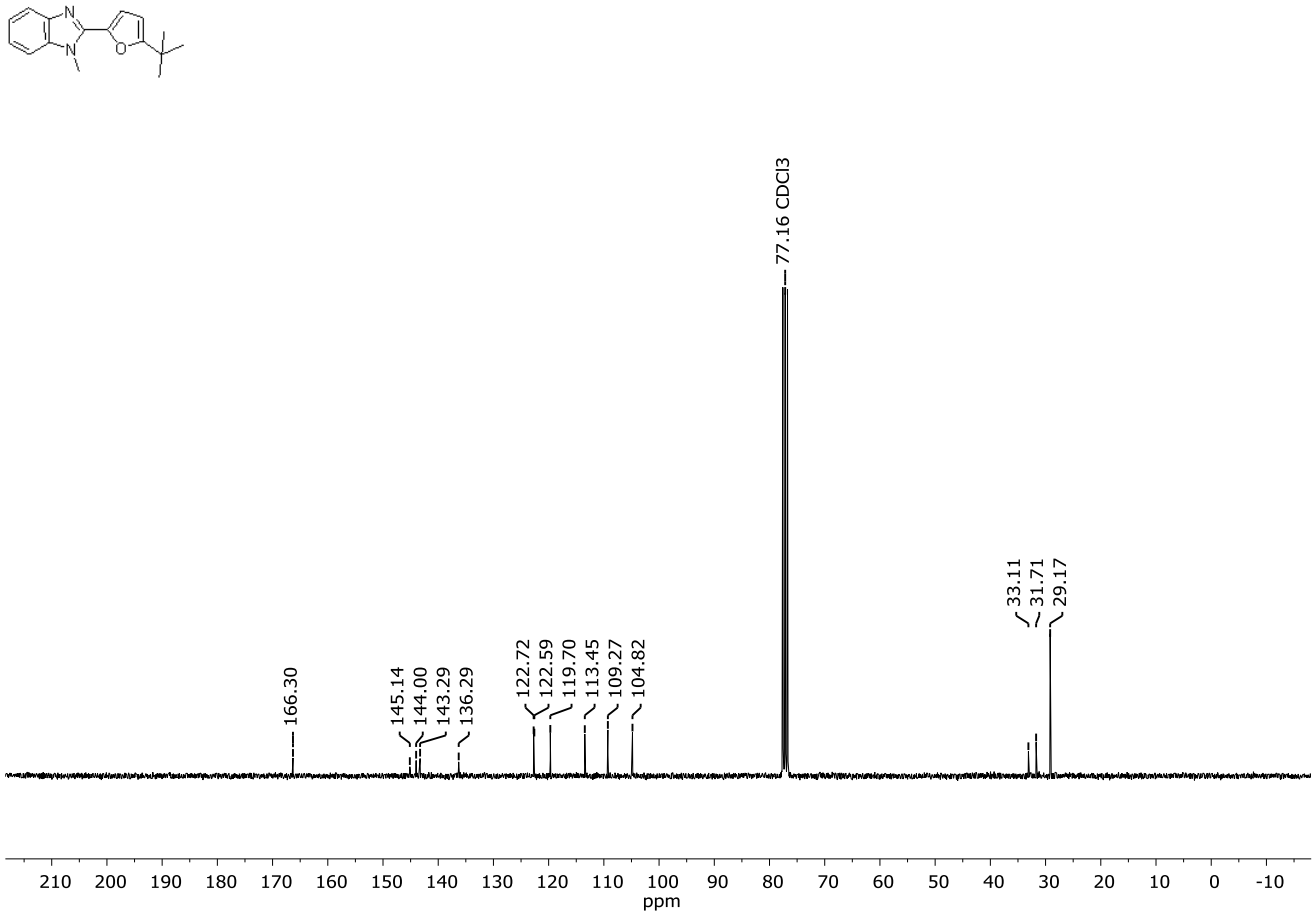


Figure S24. ^{13}C NMR spectrum of compound **3k** (75 MHz, $CDCl_3$).

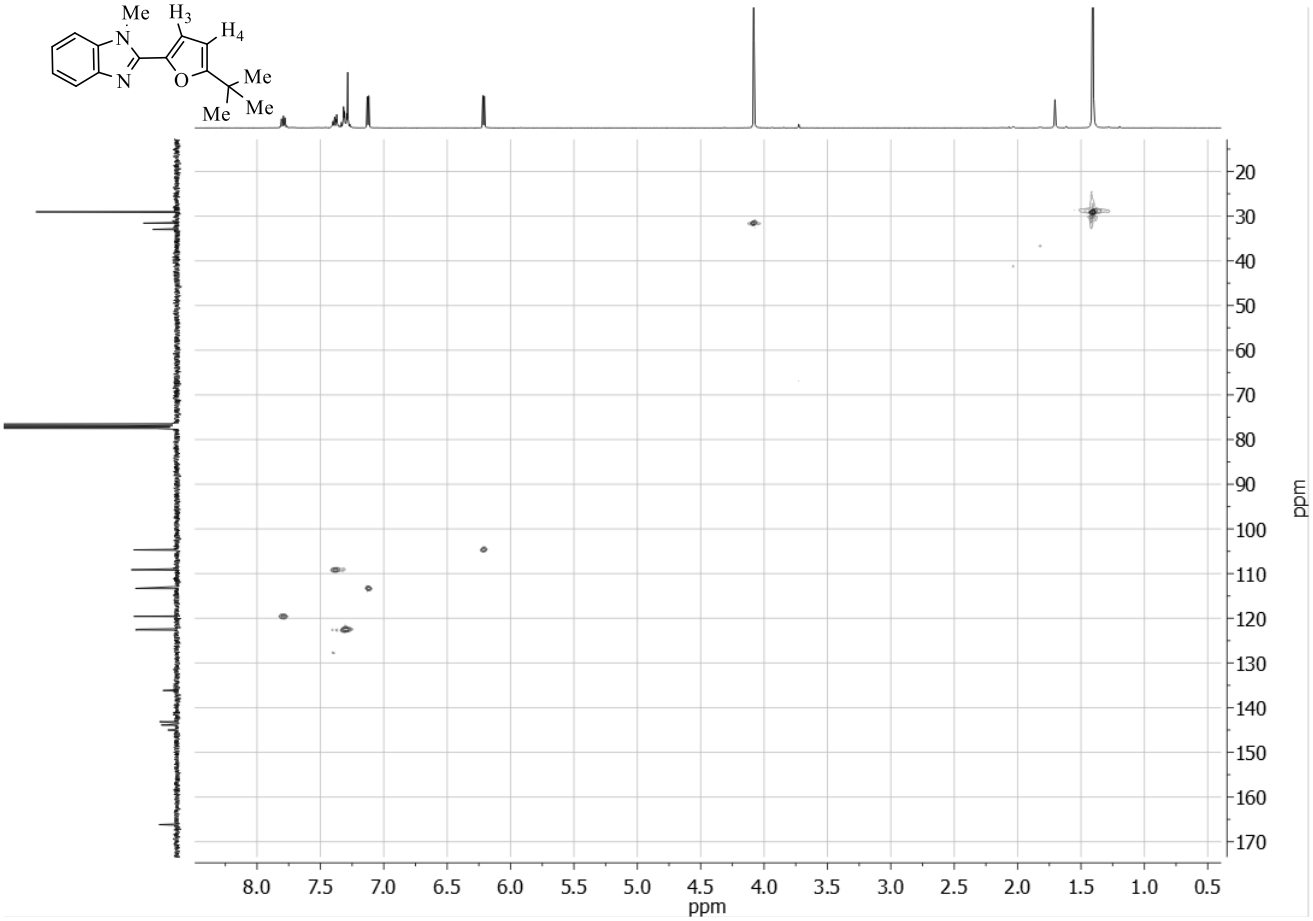


Figure S25. ^{1}H-^{13}C HSQC Spectra of compound **3k**

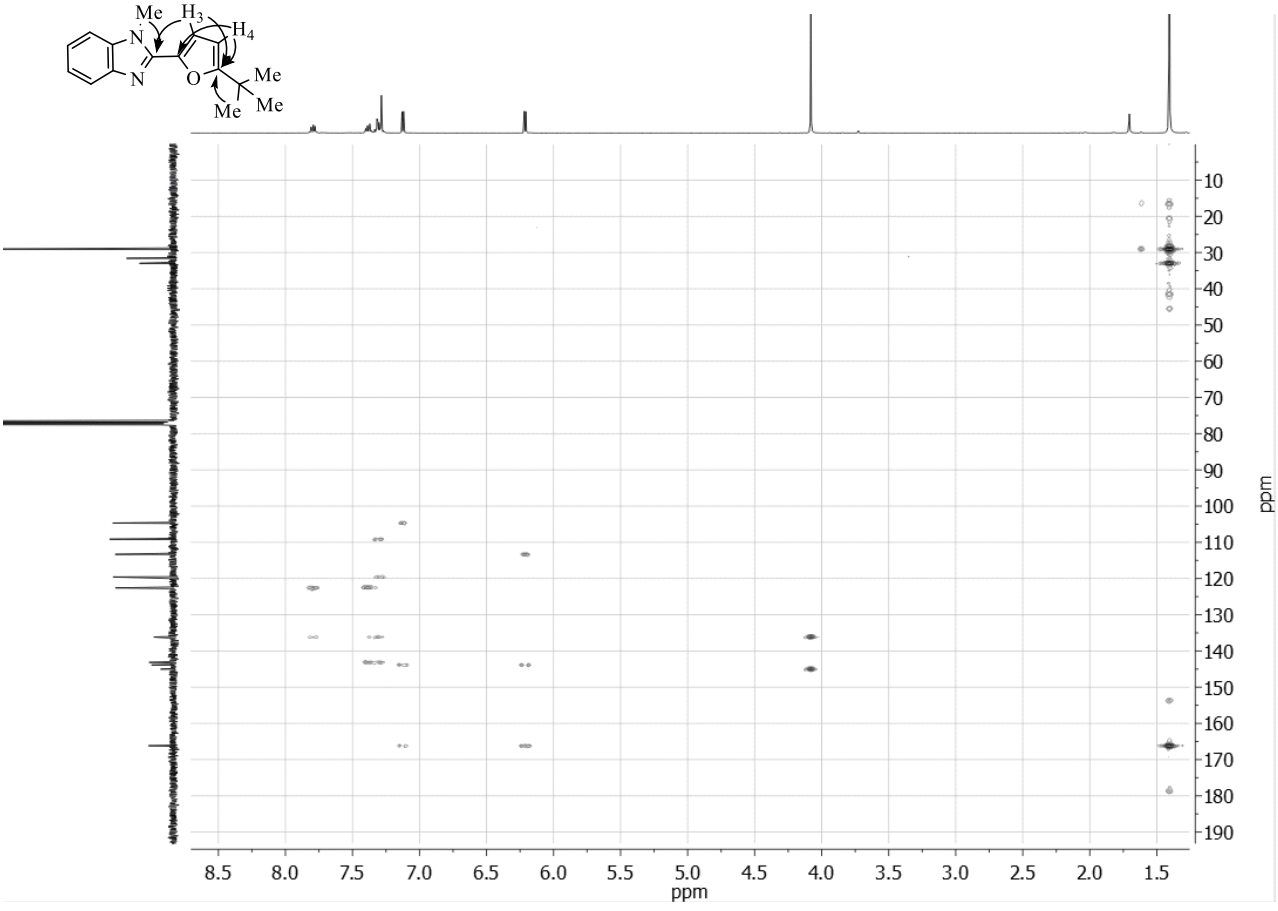


Figure S26. ^{1}H-^{13}C HMBC Spectra of compound **3k**

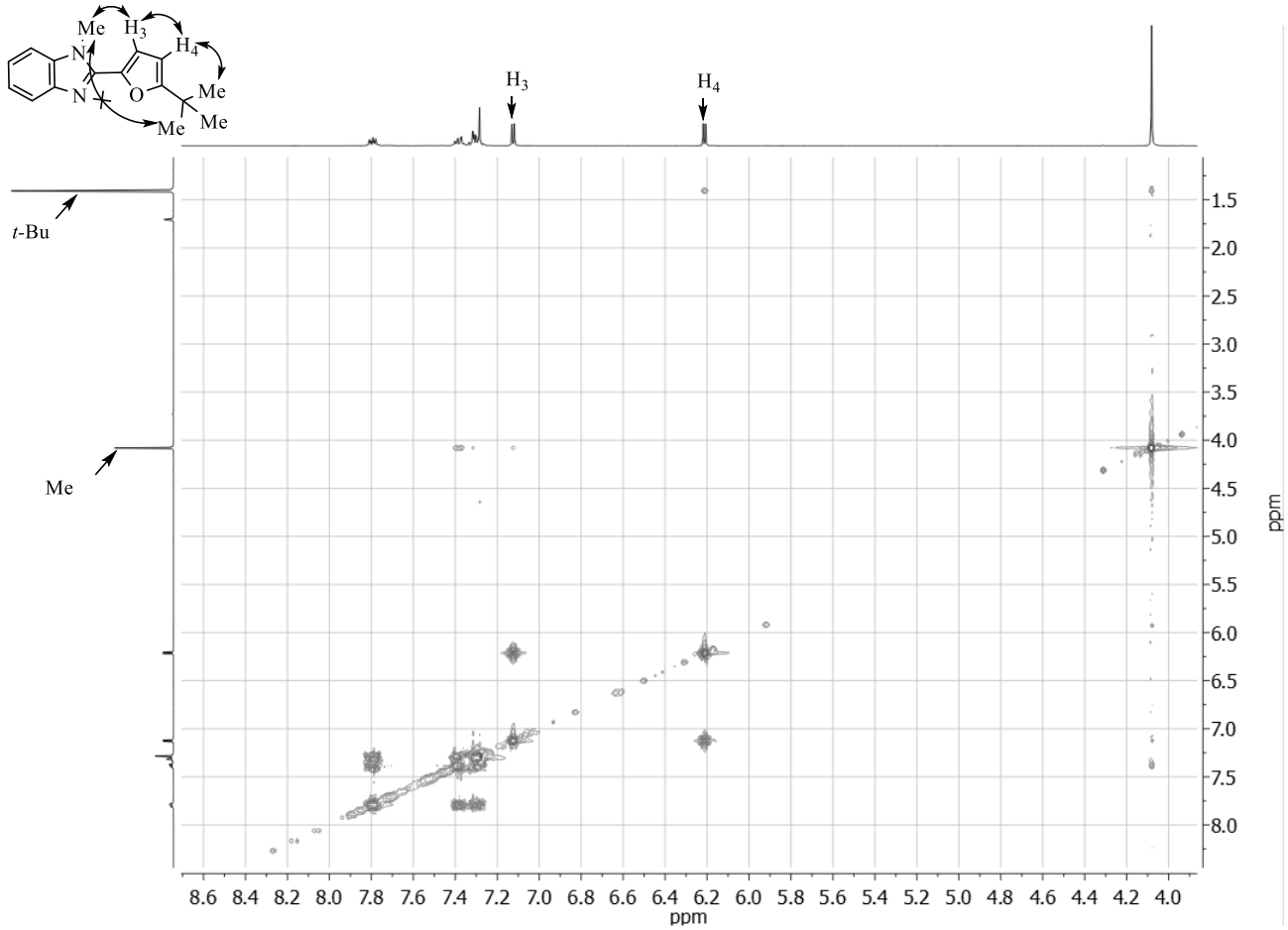


Figure S27. ^{1}H-^{1}H NOESY Spectra of compound **3k**

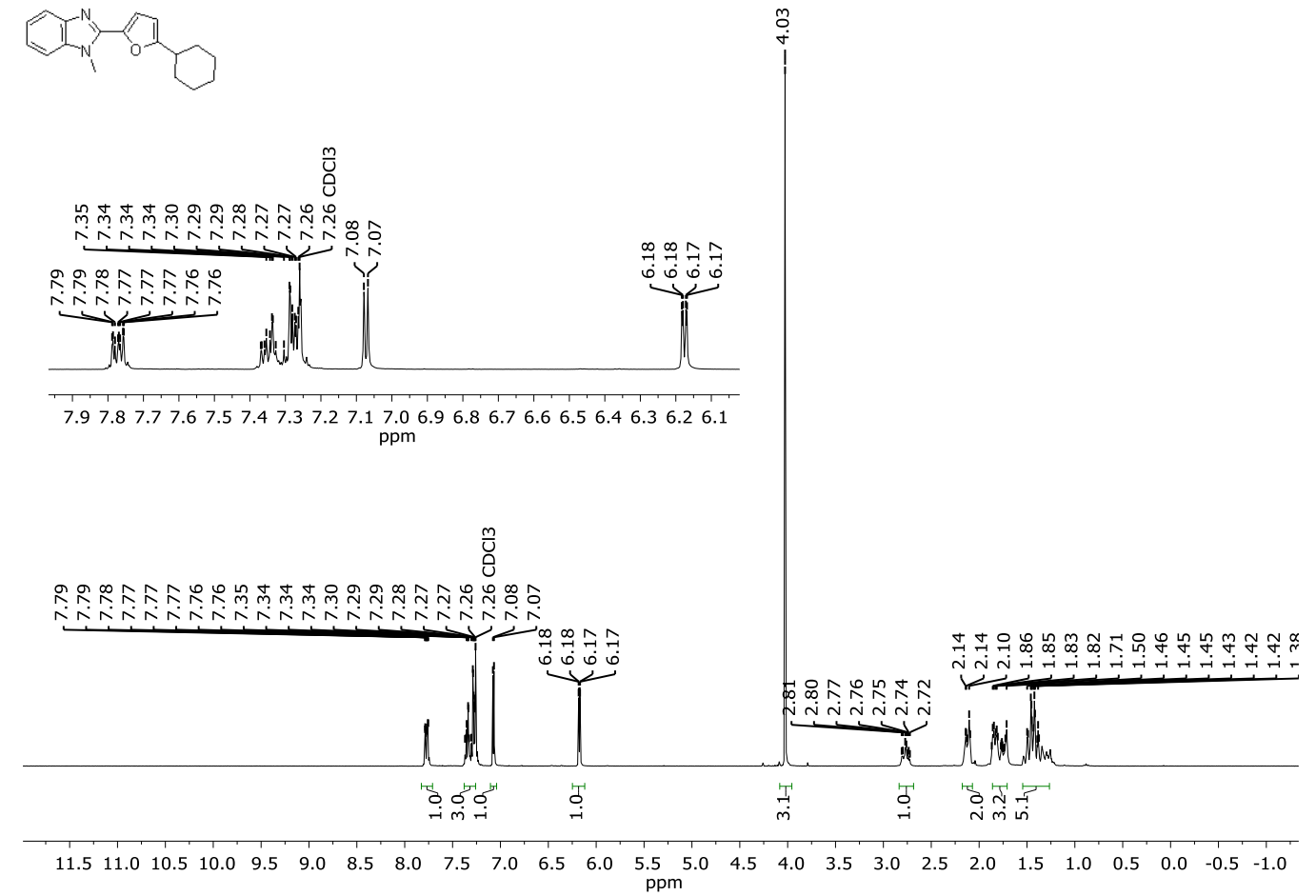


Figure S28. ^{1}H NMR spectrum of compound **3l** (300 MHz, $CDCl_3$).

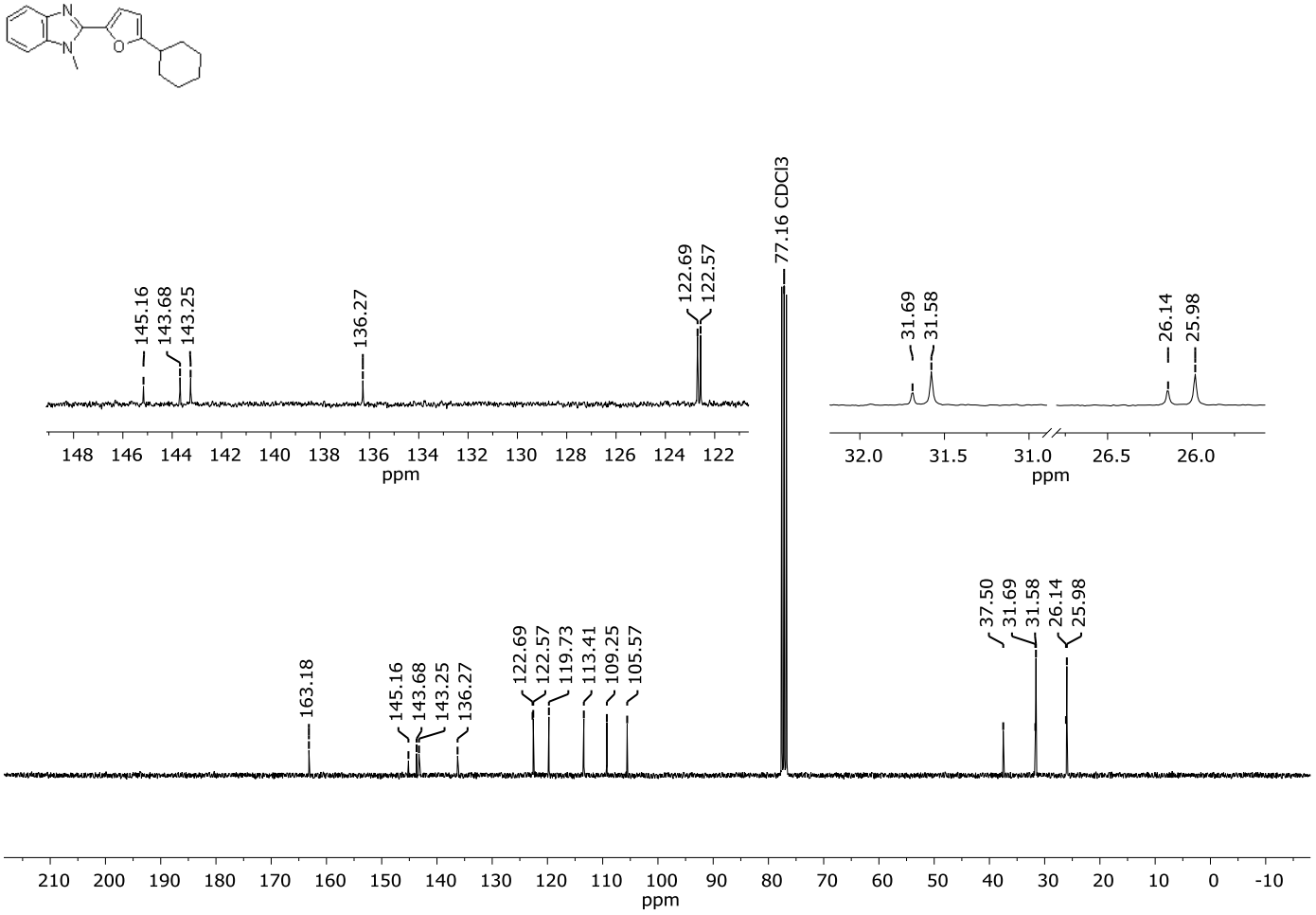


Figure S29. ^{13}C NMR spectrum of compound **3l** (75 MHz, $CDCl_3$).

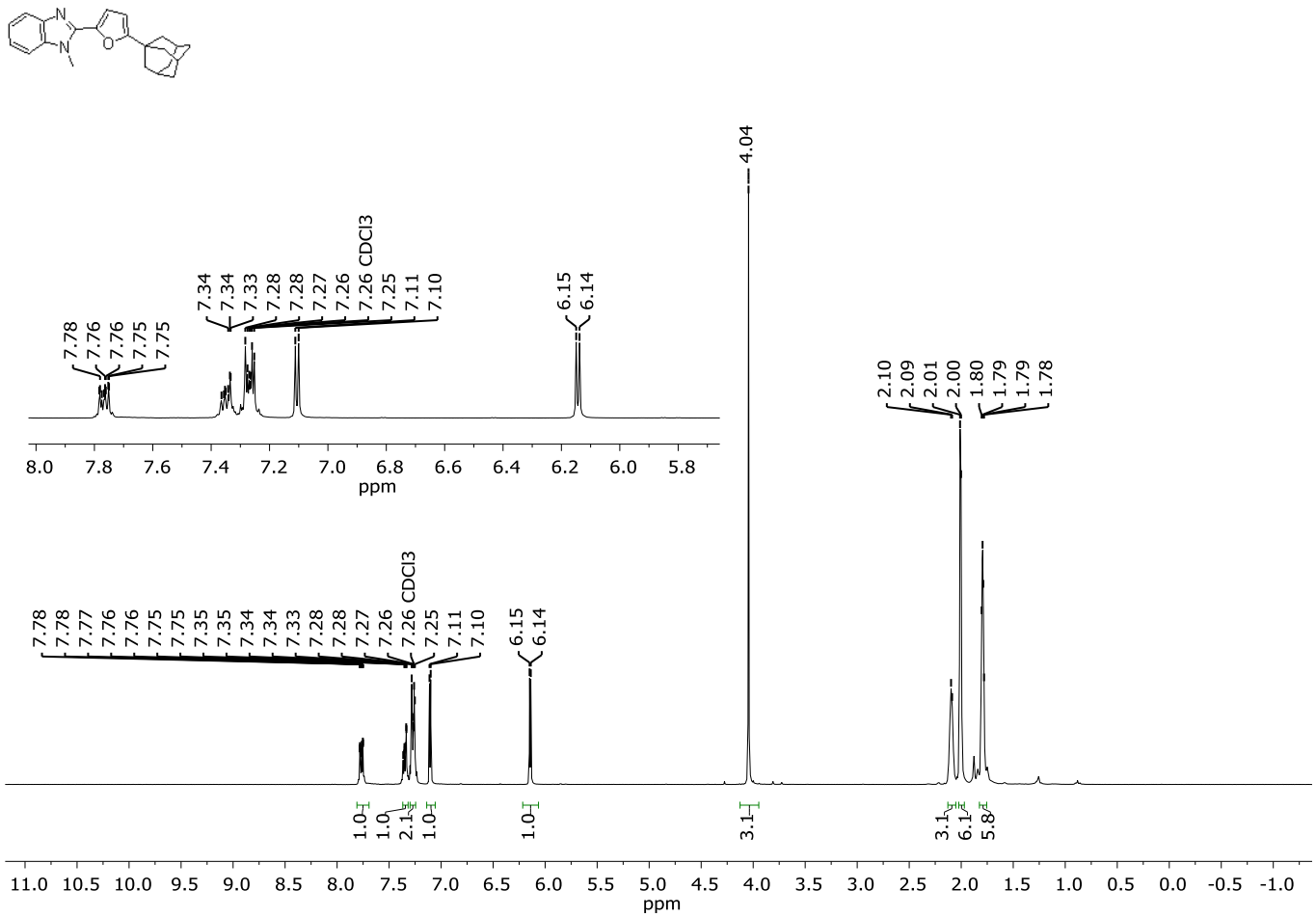


Figure S30. ^{1}H NMR spectrum of compound **3m** (300 MHz, $CDCl_3$).

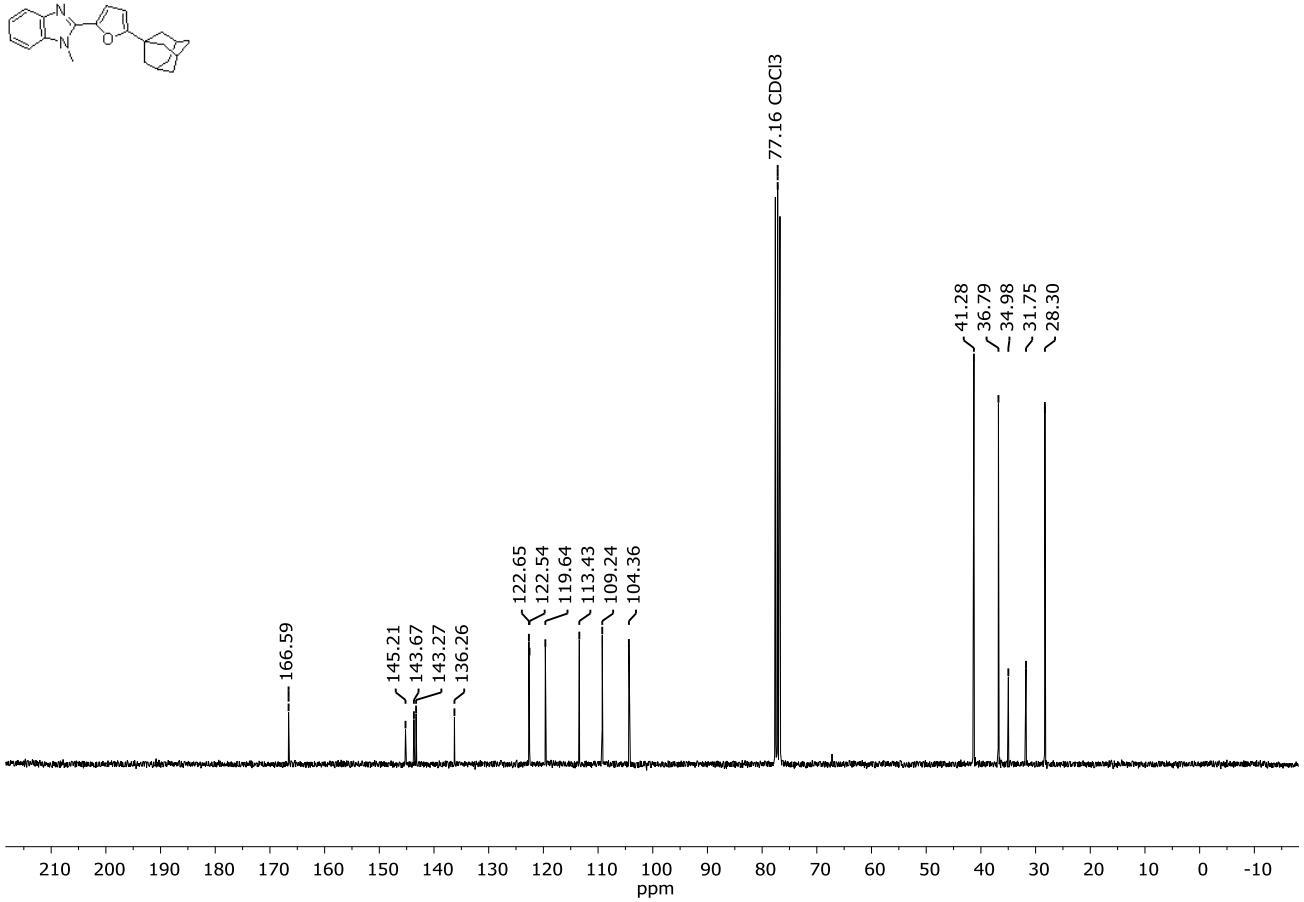


Figure S31. ^{13}C NMR spectrum of compound **3m** (75 MHz, $CDCl_3$).

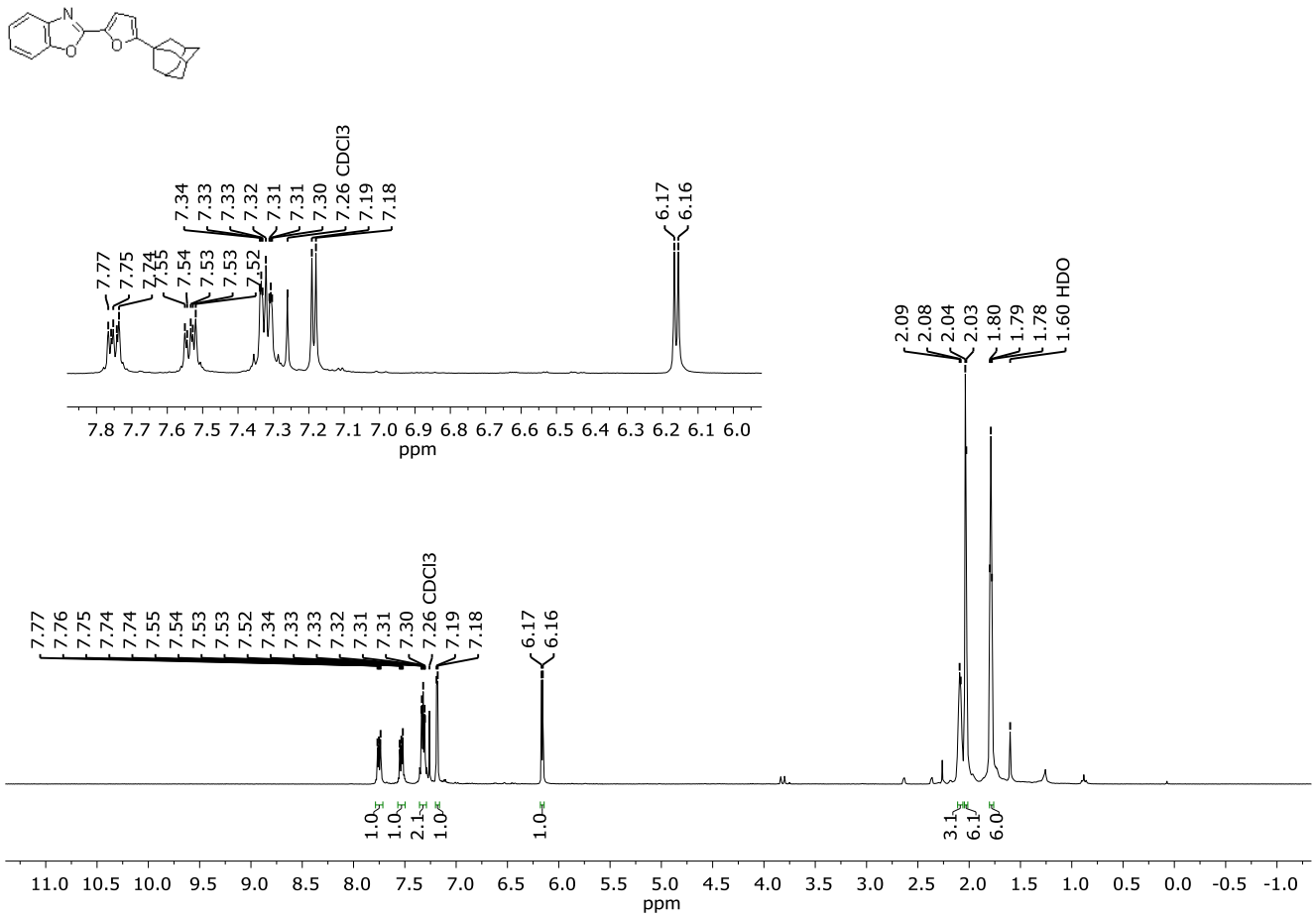


Figure S32. ^{1}H NMR spectrum of compound **3n** (300 MHz, $CDCl_3$).

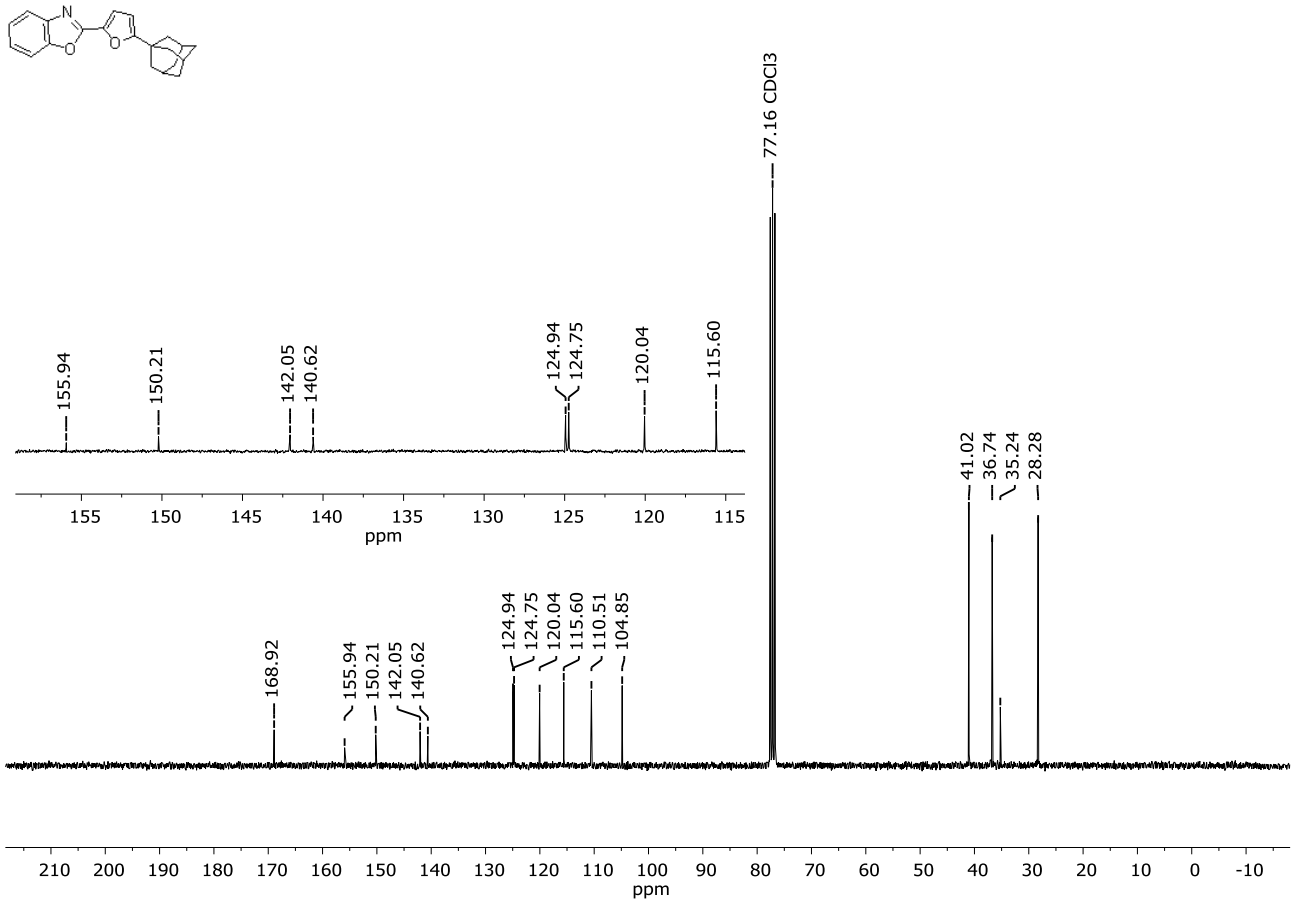


Figure S33. ^{13}C NMR spectrum of compound **3n** (75 MHz, $CDCl_3$).

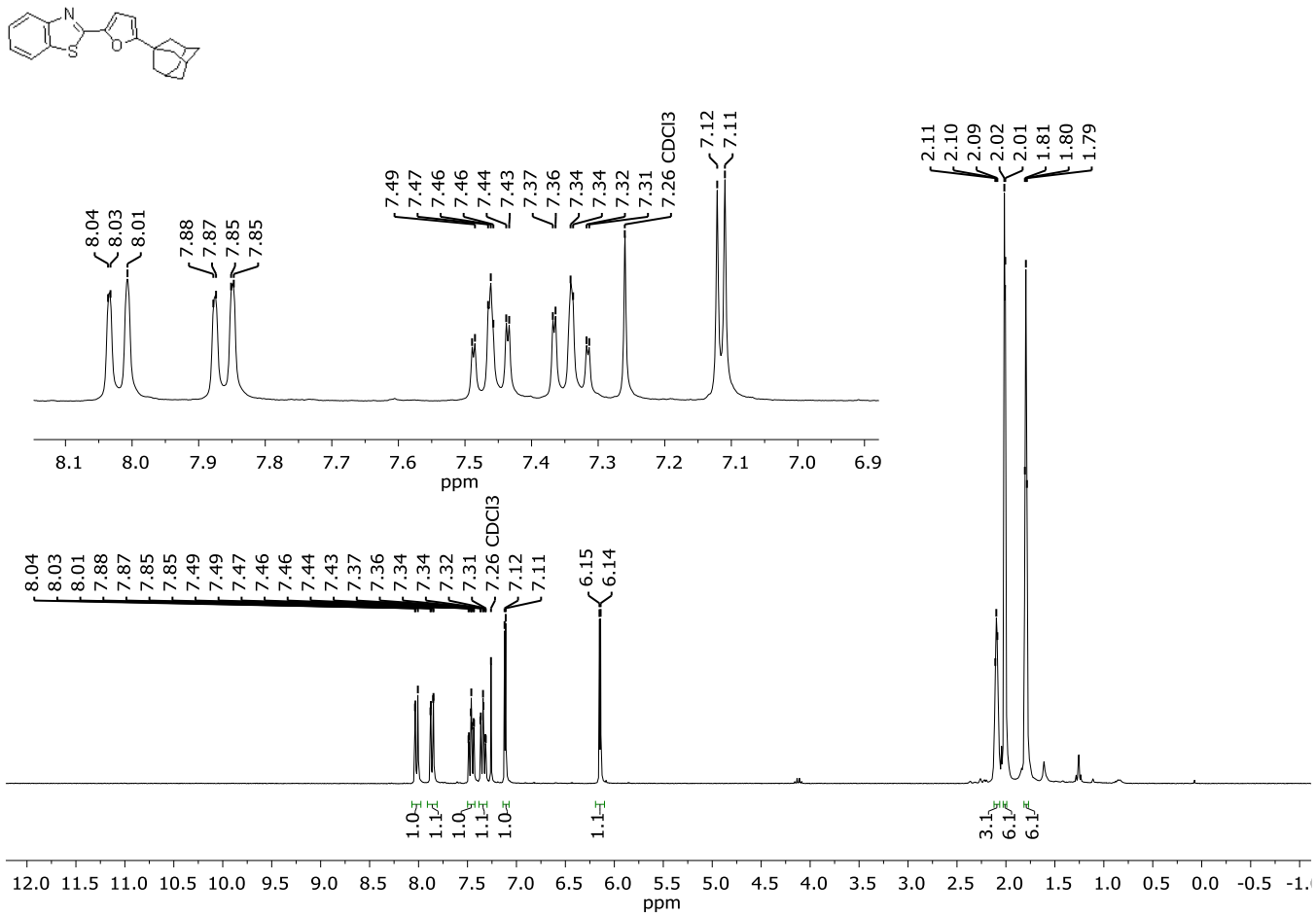


Figure S34. ^{1}H NMR spectrum of compound **3o** (300 MHz, $CDCl_3$).

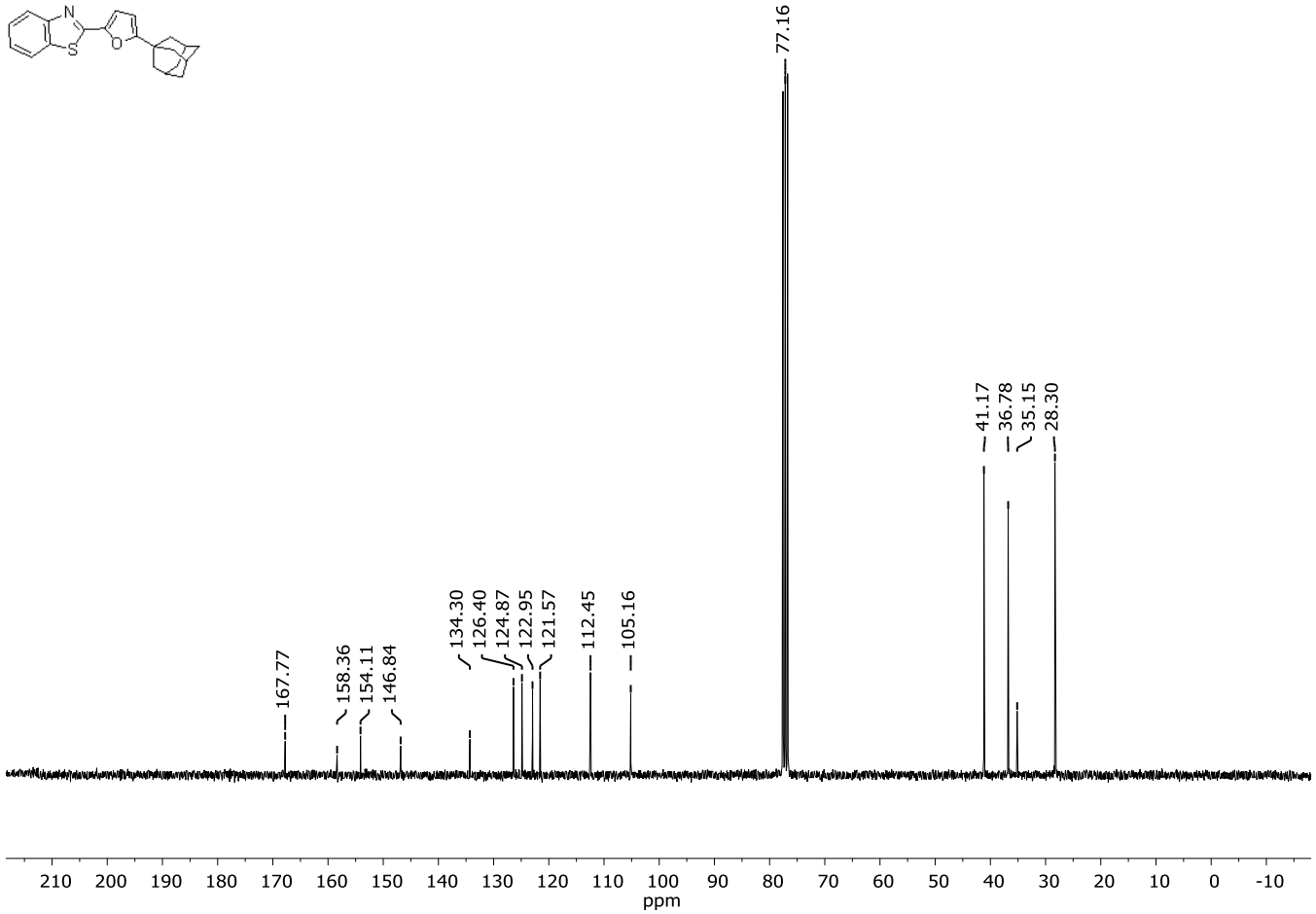


Figure S35. ^{13}C NMR spectrum of compound **3o** (75 MHz, $CDCl_3$).

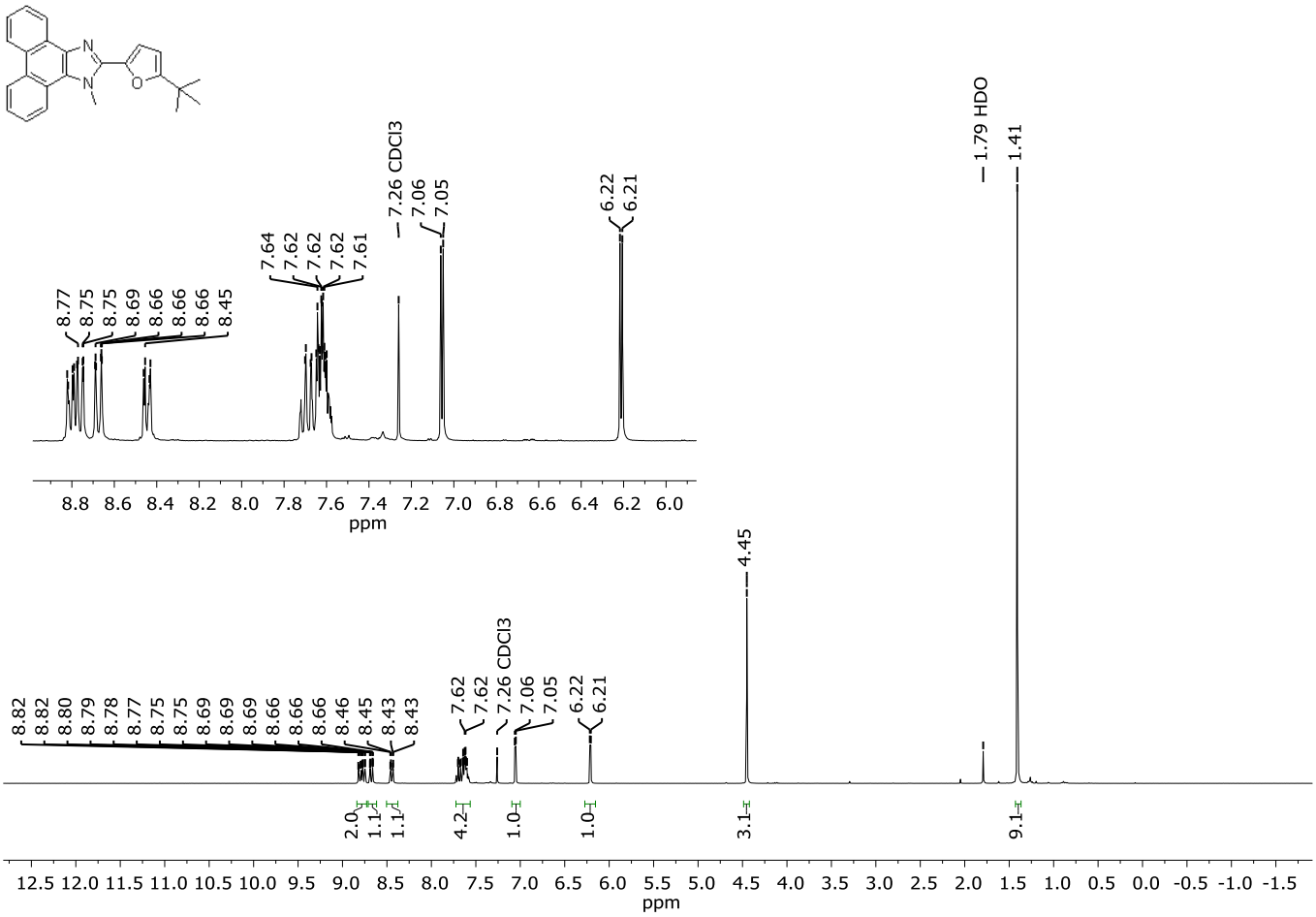


Figure S36. ^{1}H NMR spectrum of compound **3p** (300 MHz, $CDCl_3$).

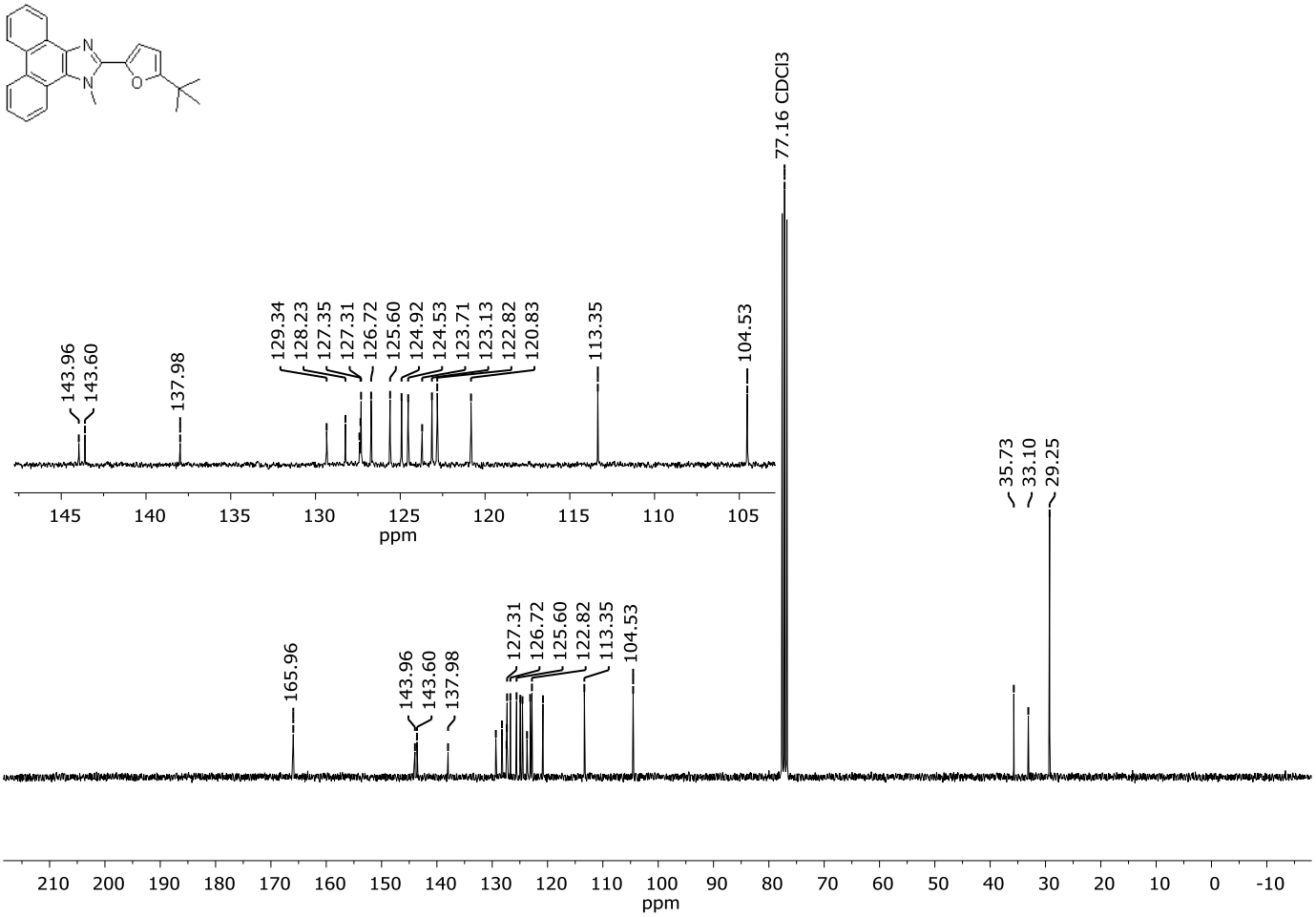


Figure S37. ^{13}C NMR spectrum of compound **3p** (75 MHz, $CDCl_3$).

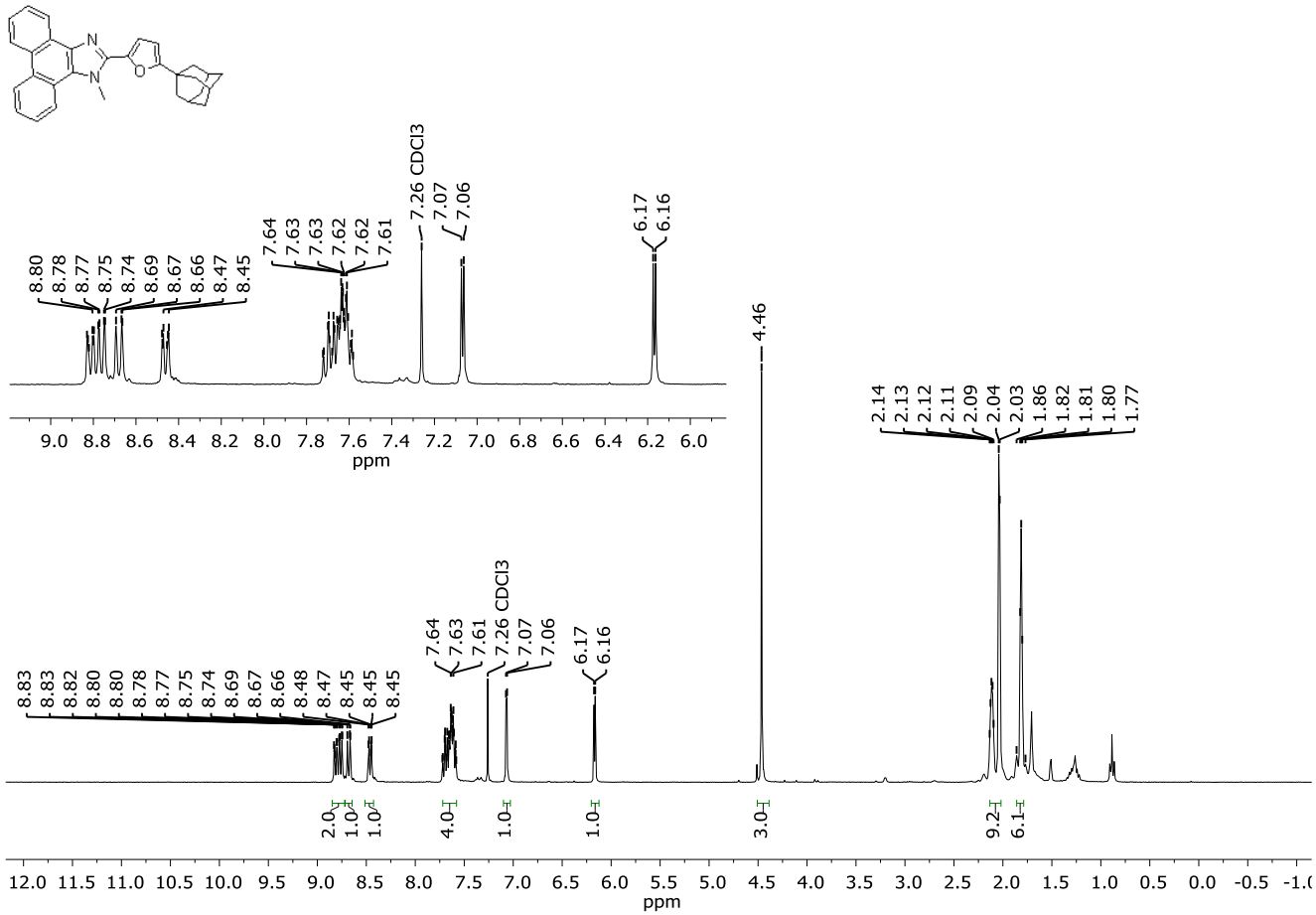


Figure S38. ^{1}H NMR spectrum of compound **3q** (300 MHz, $CDCl_3$).

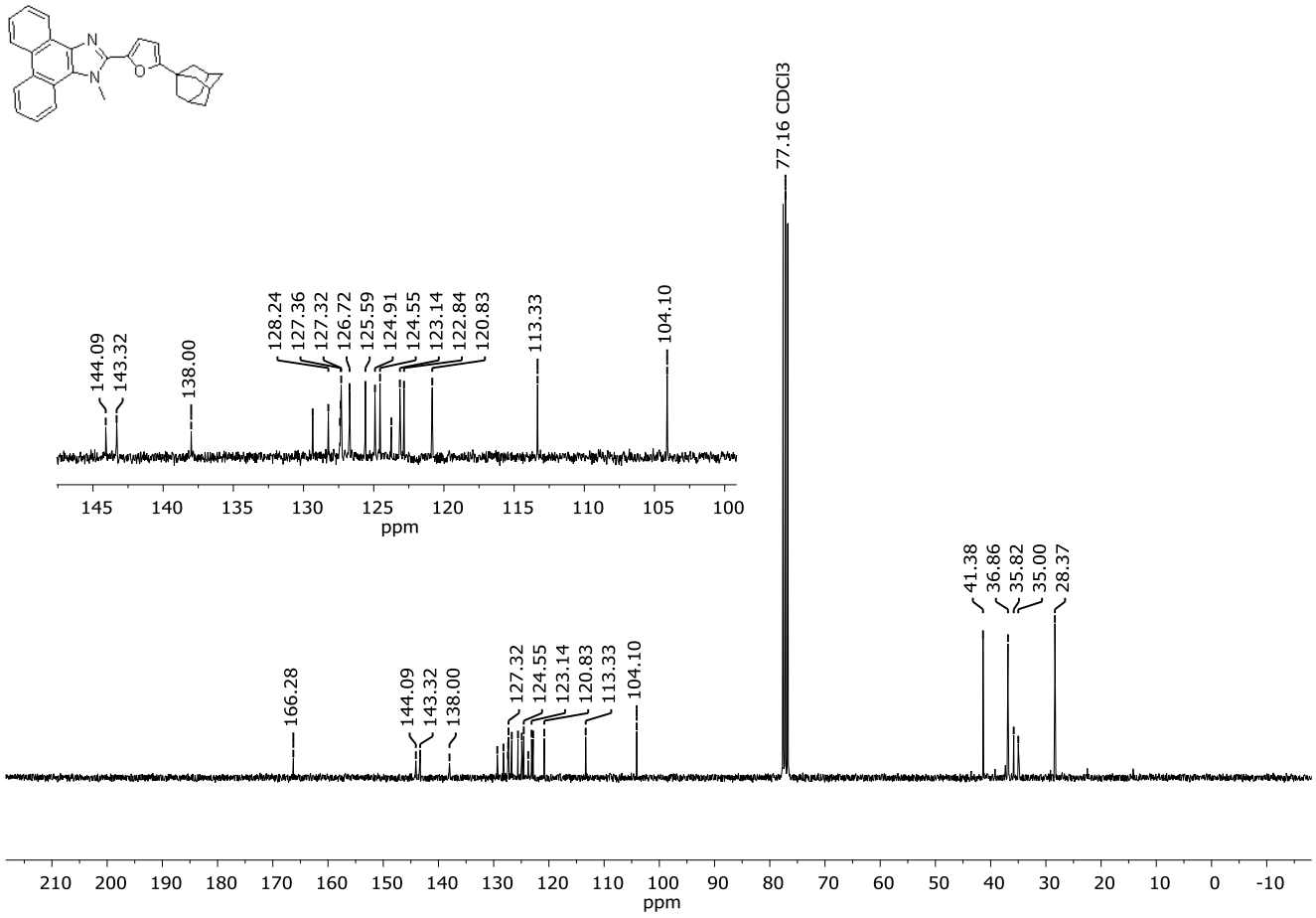


Figure S39. ^{13}C NMR spectrum of compound **3q** (75 MHz, $CDCl_3$).

S5. Literature references

S1 M. M. Elchaninov and A. A. Aleksandrov, *Russ. J. Org. Chem.*, 2018, **54**, 1200 [*Zh. Org. Khim*, 2018, **54**, 1189].

S2 Y. Wang, C. Wu, S. Nie, D. Xu, M. Yu and X. Yao, *Tetrahedron Lett.*, 2015, **56**, 6827.

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