

Supplementary Information

**One-pot furan synthesis through diethylzinc-mediated coupling reaction between
two α -bromocarbonyl compounds**

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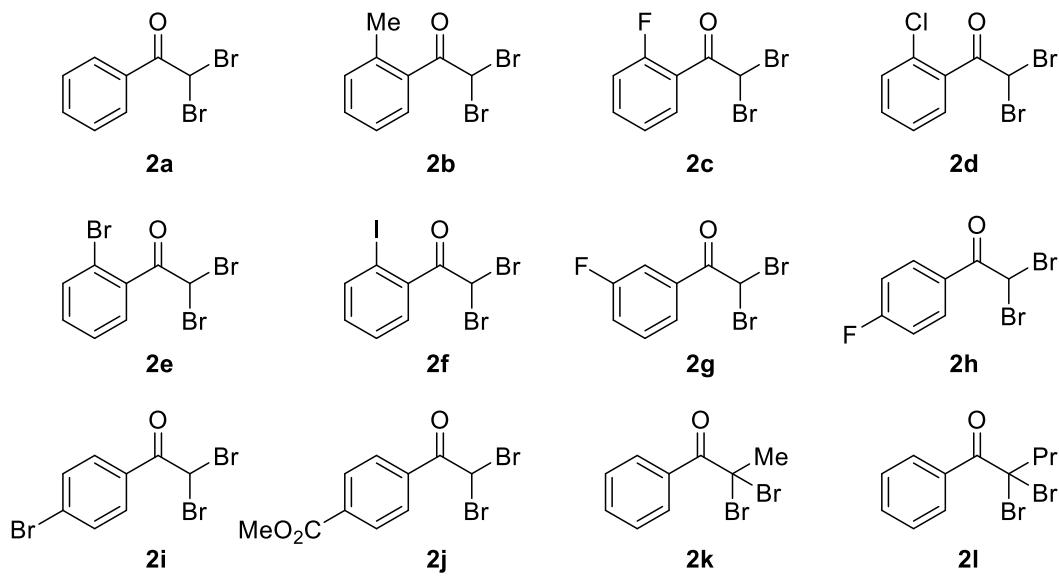
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General information

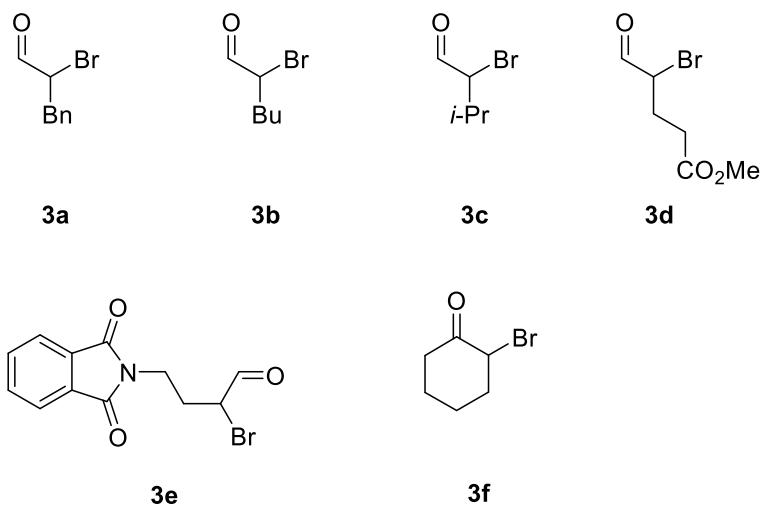
¹H NMR spectra were measured on JEOL JNM-FX300 (300 MHz) and JEOL JNM-ECX400 (400 MHz) spectrometers. ¹³C NMR spectra were measured on JEOL JNM-FX300 (75 MHz) and JEOL JNM-ECX400 (100 MHz) spectrometers. Chemical shifts were reported in ppm from tetramethylsilane (for CDCl₃) as an internal standard. ¹⁹F NMR spectra were measured on a JEOL JNM-ECX400 (376 MHz) and JEOL JNM-ECA500 (471 MHz) spectrometer. Chemical shifts were reported in ppm from benzotrifluoride as an internal standard. Data were reported as follow: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dt = doublet of triplet, td = triplet of doublet, tt = triplet of triplet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and integration. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60N (Kanto Chemical Co. Inc., 40-50 μm). HRMS analysis was performed on a Bruker Daltonics micrOTOF-QII instrument. ¹H-NMR yields were determined utilizing 1,1,2,2-tetrachloroethane as internal standard. A 1.0 M hexane solution of diethylzinc (Et₂Zn) was purchased from Tokyo Kasei, Inc. The commercially available aldehydes were distilled and stored under a nitrogen atmosphere at 5 °C. Toluene, hexane, CH₂Cl₂, 1,2-dichloroethane, benzotrifluoride, THF, MeCN, Et₂O, 1,4-dioxane, DME and AcOEt were dried over appropriate molecular sieves. KBA **5** was prepared according to the literature procedure.^[1]

Synthesis of dibromomethyl ketones 2

Dibromomethyl ketones **2a-2l** (except for **2j**) were prepared according to the literature procedure.^[2] Dibromomethyl ketone **2j** was prepared according to the literature procedure.^[3-5]



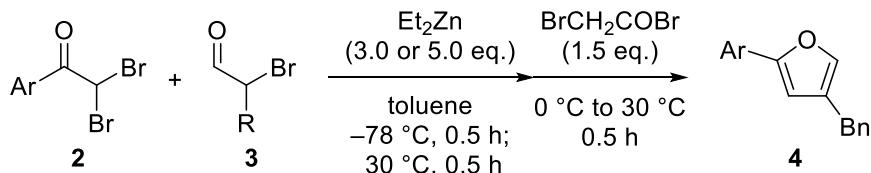
Synthesis of α -bromoaldehydes and α -bromoketones 3



α -Bromoaldehydes and α -bromoketone **3a-3f** were prepared according to the literature procedure.^[2]

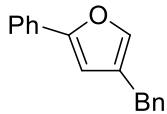
Synthesis of furans 4

General procedure (A)



A mixture of dibromomethyl ketone **2** (0.10 mmol, 1.0 eq.) and α -bromoaldehyde **3** (0.10 mmol, 1.0 eq.) in toluene (0.8 mL or 1.7 mL) was stirred at $-78\text{ }^\circ\text{C}$ under N_2 atmosphere. A 1.0 M hexane solution of Et_2Zn (0.3 or 0.5 mL, 0.3 or 0.5 mmol) was slowly added to the mixture. After stirring for 0.5 h at $-78\text{ }^\circ\text{C}$ and then 0.5 h at $30\text{ }^\circ\text{C}$, the reaction mixture was cooled at $0\text{ }^\circ\text{C}$, and bromoacetyl bromide (1.5 eq.) was added. After stirring for 0.5 h at $30\text{ }^\circ\text{C}$, the reaction mixture was quenched with NH_4Cl aq. and extracted with CH_2Cl_2 . The organic layer was dried with Na_2SO_4 , and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane) to give the corresponding furan **4**.

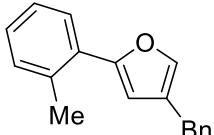
4-Benzyl-2-phenylfuran (**4a**)



Following the general procedure (A) using 2,2-dibromo-1-phenylethan-1-one^[1] (**2a**) (27.8 mg, 0.1 mmol), 2-bromo-3-phenylpronapal^[6] (**3a**) (21.3 mg, 0.1 mmol) and Et_2Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4a** as a pale yellow solid (11.5 mg, 0.049 mmol, 49% yield). Spectral data matched the literature value.^[7]

¹H-NMR (300 MHz, CDCl₃) δ 7.63-7.60 (m, 2H), 7.37-7.37 (m, 5H), 7.23-7.13 (m, 4H), 6.50 (s, 1H), 3.80 (s, 2H).

4-Benzyl-2-(2-methylphenyl)furan (4b)



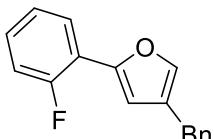
Following the general procedure (A) using 2,2-dibromo-1-(2-methylphenyl)ethan-1-one^[8] (**2b**) (29.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4b** as a pale yellow solid (12.4 mg, 0.050 mmol, 50% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 7.0 Hz, 1H), 7.34-7.26 (m, 5H), 7.22-7.18 (m, 4H), 6.40 (s, 1H), 3.83 (s, 2H), 2.46 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ 154.0, 140.4, 138.9, 134.6, 131.2, 130.4, 128.7, 128.6, 127.5, 127.0, 126.3, 126.1, 126.0, 110.4, 31.5, 22.1.

HRMS (APCI, positive) Calcd. For C₁₈H₁₇O: 249.1274 ([M + H]⁺), Found: 249.1272 ([M + H]⁺).

4-Benzyl-2-(2-fluorophenyl)furan (4c)



Following the general procedure (A) using 2,2-dibromo-1-(2-fluorophenyl)ethan-1-one^[9] (**2c**) (29.6 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.5 mL,

0.5 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4c** as colorless oil (13.8 mg, 0.055 mmol, 55% yield).

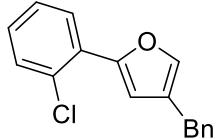
¹H-NMR (300 MHz, CDCl₃) δ 7.81-7.76 (m, 1H), 7.34-7.29 (m, 3H), 7.25-7.04 (m, 6H), 6.72 (d, *J* = 3.7 Hz, 1H), 3.82 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 158.6 (d, *J* = 250.2 Hz), 148.4 (d, *J* = 2.9 Hz), 140.3, 139.2, 128.7, 128.6, 128.3 (d, *J* = 7.7 Hz), 126.7, 126.4, 126.0 (d, *J* = 3.4 Hz), 124.4 (d, *J* = 3.8 Hz), 119.3 (d, *J* = 12.5 Hz), 116.0 (d, *J* = 22.0 Hz), 112.0 (d, *J* = 11.5 Hz), 31.5.

¹⁹F-NMR (471 MHz, CDCl₃) δ -115.4 (app s, 1F).

HRMS (APCI, positive) Calcd. For C₁₇H₁₄FO: 253.1023 ([M + H]⁺), Found: 253.1016 ([M + H]⁺).

4-Benzyl-2-(2-chlorophenyl)furan (4d)



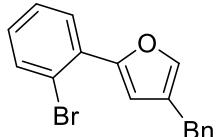
Following the general procedure (A) using 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one^[10] (**2d**) (31.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4d** as pale yellow oil (17.3 mg, 0.064 mmol, 64% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.34-7.28 (m, 5H), 7.22-7.15 (m, 3H), 7.01 (s, 1H), 3.84 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 150.5, 140.2, 139.4, 130.8, 130.1, 129.4, 128.7, 128.6, 128.1, 127.9, 127.0, 126.5, 126.4, 112.8, 31.5.

HRMS (APCI, positive) Calcd. For C₁₇H₁₄ClO: 269.0728, 271.0699 ([M + H]⁺), Found: 269.0729, 271.0698 ([M + H]⁺).

4-Benzyl-2-(2-bromophenyl)furan (4e)



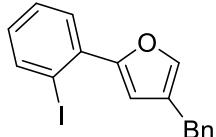
Following the general procedure (A) using 2,2-dibromo-1-(2-bromophenyl)ethan-1-one^[9] (**2e**) (35.6 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.5 mL, 0.5 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4e** as pale yellow oil (20.0 mg, 0.064 mmol, 64% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.36-7.26 (m, 6H), 7.23-7.18 (m, 1H), 7.13-7.07 (m, 1H), 7.06 (s, 1H), 3.84 (s, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 151.6, 140.2, 139.5, 134.2, 131.4, 128.75, 128.73, 128.6, 128.5, 127.5, 126.4, 126.2, 119.6, 112.5, 31.6.

HRMS (APCI, positive) Calcd. For C₁₇H₁₄BrO: 313.0223, 315.0203 ([M + H]⁺), Found: 313.0214, 315.0174 ([M + H]⁺).

4-Benzyl-2-(2-iodophenyl)furan (4f)



Following the general procedure (A) using 2,2-dibromo-1-(2-iodophenyl)ethan-1-one^[11] (**2f**)

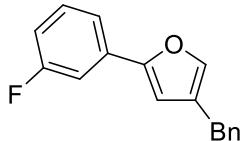
(40.3 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.5 mL, 0.5 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4f** as pale yellow oil (18.4 mg, 0.051 mmol, 51% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.94 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.39-7.27 (m, 6H), 7.23-7.20 (m, 1H), 6.98-6.93 (m, 2H), 3.84 (s, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 153.9, 140.9, 140.2, 139.6, 135.5, 129.3, 129.0, 128.7, 128.6, 128.2, 126.4, 125.9, 111.6, 94.3, 31.6.

HRMS (APCI, positive) Calcd. For C₁₇H₁₄IO: 361.0084 ([M + H]⁺), Found: 361.0076 ([M + H]⁺).

4-Benzyl-2-(3-fluorophenyl)furan (**4g**)



Following the general procedure (A) using 2,2-dibromo-1-(3-fluorophenyl)ethan-1-one^[12] (**2g**) (29.6 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4g** as pale yellow oil (10.6 mg, 0.042 mmol, 42% yield).

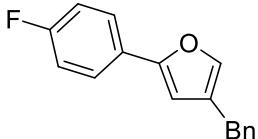
¹H-NMR (300 MHz, CDCl₃) δ 7.39-7.29 (m, 7H), 7.24-7.20 (m, 2H), 6.95-6.88 (m, 1H), 6.52 (s, 1H), 3.80 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 163.2 (d, *J* = 245.4 Hz), 153.2 (d, *J* = 2.9 Hz), 140.2, 139.7, 133.1 (d, *J* = 8.6 Hz), 130.3 (d, *J* = 8.6 Hz), 128.73, 128.68, 126.7, 126.5, 119.5 (d, *J* = 2.9 Hz), 114.1 (d, *J* = 22.0 Hz), 110.7 (d, *J* = 24.0 Hz), 107.8, 31.4.

¹⁹F-NMR (376 MHz, CDCl₃) δ -114.3 (app s, 1F).

HRMS (APCI, positive) Calcd. For C₁₇H₁₄FO: 253.1023 ([M + H]⁺), Found: 253.1022 ([M + H]⁺).

4-Benzyl-2-(4-fluorophenyl)furan (4h)



Following the general procedure (A) using 2,2-dibromo-1-(4-fluorophenyl)ethan-1-one^[13] (**2h**) (29.6 mg, 0.1 mmol) and 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.5 mL, 0.5 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4h** as pale yellow oil (11.6 mg, 0.046 mmol, 46% yield).

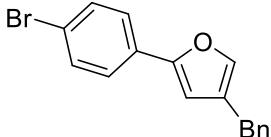
¹H-NMR (300 MHz, CDCl₃) δ 7.60-7.55 (m, 2H), 7.34-7.28 (m, 3H), 7.25-7.22 (m, 3H), 7.08-7.00 (m, 2H), 6.43 (s, 1H), 3.79 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 162.2 (d, *J* = 246.3 Hz), 153.6, 140.3, 139.2, 128.74, 128.66, 127.4 (d, *J* = 2.9 Hz), 126.5, 126.4, 125.6 (d, *J* = 7.6 Hz), 115.8 (d, *J* = 22.0 Hz), 106.5, 31.5.

¹⁹F-NMR (376 MHz, CDCl₃) δ -115.7 (tt, *J* = 8.7, 5.1 Hz, 1F).

HRMS (APCI, positive) Calcd. For C₁₇H₁₄FO: 253.1023 ([M + H]⁺), Found: 253.1025 ([M + H]⁺).

4-Benzyl-2-(4-bromophenyl)furan (4i)



Following the general procedure (A) using 2,2-dibromo-1-(4-bromophenyl)ethan-1-one^[9] (**2i**)

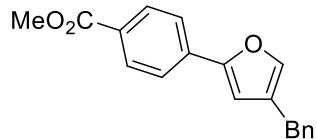
(35.6 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4i** as a yellow solid (15.7 mg, 0.052 mmol, 52% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.53-7.40 (m, 4H), 7.36-7.29 (m, 4H), 7.23-7.20 (m, 2H), 6.50 (s, 1H), 3.79 (s, 2H).

¹³C-NMR (75 MHz, CDCl₃) δ 153.3, 140.2, 139.5, 131.9, 129.9, 128.73, 128.67, 126.7, 126.4, 125.3, 121.1, 107.4, 31.4.

HRMS (APCI, positive) Calcd. For C₁₇H₁₄BrO: 313.0223, 315.0203 ([M + H]⁺), Found: 313.0224, 315.0225 ([M + H]⁺).

Methyl 4-(4-benzylfuran-2-yl)benzoate (**4j**)



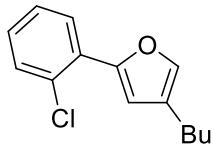
Following the general procedure (A) using methyl 4-(2,2-dibromoacetyl)benzoate^[5] (**2j**) (33.6 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4j** as white solid (21.8 mg, 0.075 mmol, 75% yield).

¹H-NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.35-7.30 (m, 4H), 7.25-7.18 (m, 2H), 6.64 (s, 1H), 3.91 (s, 3H), 3.81 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 166.9, 153.3, 140.3, 140.1, 134.9, 130.2, 128.72, 128.69, 128.6, 126.9, 126.5, 123.4, 109.0, 52.2, 31.4.

HRMS (APCI, positive) Calcd. For C₁₉H₁₇O₃: 293.1172 ([M + H]⁺), Found: 293.1180 ([M + H]⁺).

4-Butyl-2-(2-chlorophenyl)furan (4k)



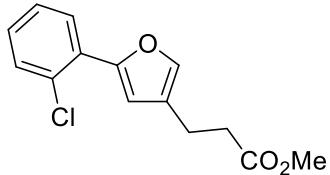
Following the general procedure (A) using 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one (**2d**) (31.2 mg, 0.1 mmol) and 2-bromohexanal (**3b**)^[14] (17.8 mg, 0.1 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4k** as colorless oil (11.7 mg, 0.049 mmol, 49% yield).

¹H-NMR (400 MHz, CDCl₃) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.31-7.27 (m, 2H), 7.19-7.14 (m, 1H), 7.03 (s, 1H), 2.47 (t, *J* = 7.8 Hz, 2H), 1.63-1.55 (m, 2H), 1.44-1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ 150.0, 138.5, 130.8, 129.9, 129.5, 127.9, 127.8, 127.6, 127.0, 112.8, 32.3, 24.8, 22.5, 14.1.

HRMS (APCI, positive) Calcd. For C₁₄H₁₆ClO: 235.0885, 237.0855 ([M + H]⁺), Found: 235.0879, 237.0837 ([M + H]⁺).

Methyl 3-(5-(2-chlorophenyl)furan-3-yl)propanoate (4l)



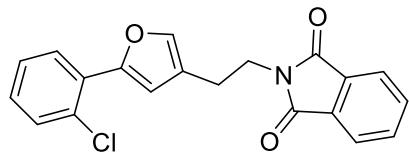
A mixture of 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one (**2d**) (31.2 mg, 0.1 mmol) and methyl 4-bromo-5-oxopentanoate (**3d**)^[15] (20.8 mg, 0.1 mmol) in toluene (0.8 mL) was stirred at -78 °C under N₂ atmosphere. A 1.0 M hexane solution of Et₂Zn (0.3 mL, 0.3 mmol) was slowly added to the mixture. After stirring for 0.5 h at -78 °C and then 1 h at 30 °C, the reaction mixture was cooled at 0 °C, and bromoacetyl bromide (1.5 eq.) was added. After stirring for 0.5 h at 30 °C, the reaction mixture was quenched with NH₄Cl aq. and extracted with CH₂Cl₂. The organic layer was dried with Na₂SO₄, and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane/CH₂Cl₂ = 2/1) to give the title compound **4l** as colorless oil (12.5 mg, 0.047 mmol, 47% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.32-7.27 (m, 2H), 7.21-7.15 (m, 1H), 7.03 (s, 1H), 3.70 (s, 3H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ 173.5, 138.8, 130.8, 130.1, 129.3, 128.1, 127.9, 127.0, 125.7 (two peaks overlap), 112.3, 51.8, 34.7, 20.6.

HRMS (APCI, positive) Calcd. For C₁₄H₁₄ClO₃: 265.0626, 267.0597 ([M + H]⁺), Found: 265.0625, 267.0599 ([M + H]⁺).

2-(2-(5-(2-Chlorophenyl)furan-3-yl)ethyl)isoindoline-1,3-dione (**4m**)

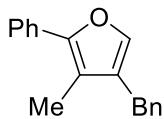


A mixture of 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one (**2d**) (21.6 mg, 0.069 mmol) and 2-bromo-4-(1,3-dioxoisooindolin-2-yl)butanal (**3e**)^[16] (20.5 mg, 0.069 mmol) in toluene (0.55 mL) was stirred at -78 °C under N₂ atmosphere. A 1.0 M hexane solution of Et₂Zn (0.21 mL, 0.21 mmol) was slowly added to the mixture. After stirring for 15 min at -78 °C and then 1 h at 30 °C, the reaction mixture was cooled at 0 °C, and bromoacetyl bromide (1.5 eq.) was added. After stirring for 0.5 h at 30 °C, the reaction mixture was quenched with NH₄Cl aq. and extracted with CH₂Cl₂. The organic layer was dried with Na₂SO₄, and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane/CH₂Cl₂ = 1/2) to give the title compound **4m** as white solid (9.6 mg, 0.027 mmol, 39% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.86-7.79 (m, 3H), 7.74-7.70 (m, 2H), 7.42-7.37 (m, 2H), 7.31-7.28 (m, 1H), 7.20-7.14 (m, 1H), 7.06 (s, 1H), 3.94 (t, *J* = 7.6 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H).
¹³C-NMR (100 MHz, CDCl₃) δ 168.4, 150.5, 139.4, 134.1, 132.2, 130.8, 130.2, 129.3, 128.1, 127.9, 126.9, 123.4, 123.2, 112.4, 38.3, 24.2.

HRMS (APCI, positive) Calcd. For C₂₀H₁₅ClNO₃: 352.0735, 354.0706 ([M + H]⁺), Found: 352.0735, 354.0733 ([M + H]⁺).

4-Benzyl-3-methyl-2-phenylfuran (**4n**)



Following the general procedure (A) using 2,2-dibromo-1-phenylpropan-1-one^[12] (**2k**) (29.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3

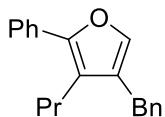
mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4n** as a white solid (11.7 mg, 0.047 mmol, 47% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.62-7.59 (m, 2H), 7.42-7.37 (m, 2H), 7.33-7.28 (m, 3H), 7.25-7.19 (m, 3H), 7.17 (s, 1H), 3.77 (s, 2H), 2.12 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ 149.4, 139.9, 138.8, 132.1, 128.7, 128.60, 128.57, 126.8, 126.7, 126.3, 125.6, 116.6, 30.2, 10.0.

HRMS (APCI, positive) Calcd. For C₁₈H₁₇O: 249.1274 ([M + H]⁺), Found: 249.1275 ([M + H]⁺).

4-Benzyl-2-phenyl-3-propylfuran (4o)



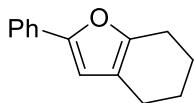
Following the general procedure (A) using 2,2-dibromo-1-phenylpentan-1-one^[17] (**2l**) (32.0 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol) and Et₂Zn (0.3 mL, 0.3 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **4o** as colorless oil (13.8 mg, 0.050 mmol, 50% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.42-7.28 (m, 5H), 7.24-7.16 (m, 3H), 7.11 (s, 1H), 3.77 (s, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 1.53-1.43 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ 149.4, 140.0, 139.1, 132.1, 128.8, 128.6, 128.5, 126.9, 126.6, 126.3, 125.5, 121.6, 30.3, 26.4, 23.3, 14.4.

HRMS (APCI, positive) Calcd. For C₂₀H₂₁O: 277.1587 ([M + H]⁺), Found: 277.1594 ([M + H]⁺).

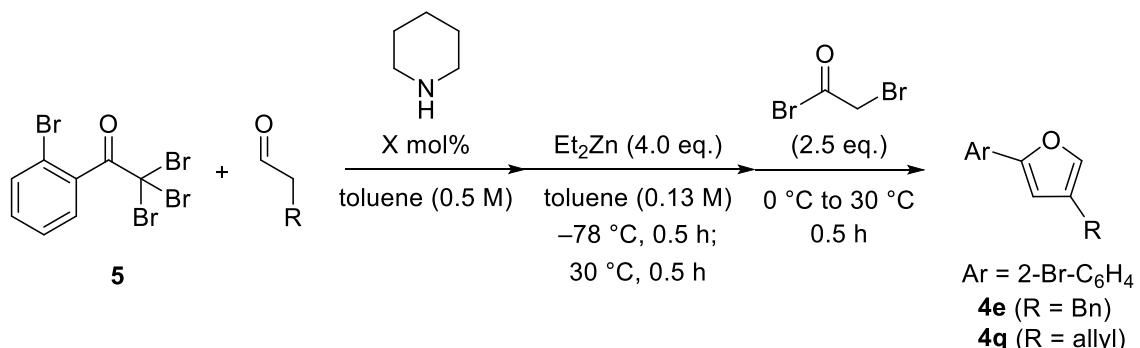
2-Phenyl-4,5,6,7-tetrahydrobenzofuran (**4p**)



A mixture of dibromomethyl ketone **2a** (27.8 mg, 0.10 mmol) and 2-bromocyclohexan-1-one^[18] (**3f**) (19.5 mg, 0.11 mmol) in DME (0.80 mL, 0.13 M) was stirred at $-78\text{ }^{\circ}\text{C}$. A 1.0 M hexane solution of Et_2Zn (0.3 mL, 0.3 mmol) was slowly added to the mixture at $-78\text{ }^{\circ}\text{C}$. After stirring for 0.5 h at $-78\text{ }^{\circ}\text{C}$ and then 2 h at $30\text{ }^{\circ}\text{C}$, 47% HBr aq. (120 μL , 1 mmol) was added to the mixture at $0\text{ }^{\circ}\text{C}$. After stirring for 2 h at reflux, the reaction mixture was quenched with NaHCO_3 aq. and extracted with CH_2Cl_2 . The organic layer was dried with Na_2SO_4 , and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane) to give the title compound **4p** as pale yellow oil (10.9 mg, 0.055 mmol, 55% yield). Spectral data matched the literature value.^[19]

¹H-NMR (300 MHz, CDCl_3) δ 7.63-7.60 (m, 2H), 7.37-7.31 (m, 2H), 7.22-7.17 (m, 1H), 6.47 (s, 1H), 2.68-2.64 (m, 2H), 2.48-2.44 (m, 2H), 1.91-1.83 (m, 2H), 1.79-1.71 (m, 2H).

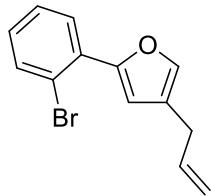
One-pot synthesis of furan **4e** from 3-phenylpropanal and KBA **5**



4-Benzyl-2-(2-bromophenyl)furan (4e)

A mixture of piperidine (0.49 μ L, 5 μ mol, 5 mol%), 3-phenylpropanal (13.4 mg, 0.1 mmol) and **5** (43.6 mg, 0.1 mmol) in toluene (0.2 mL, 0.5 M) was stirred at 0 °C under N₂ atmosphere for 5 h. To the mixture was added additional piperidine (0.49 μ L, 5 μ mol, 5 mol%). After stirring for 2 h at room temperature, the reaction mixture was diluted with toluene (0.6 mL, 0.17 M) at –78 °C. A 1.0 M hexane solution of Et₂Zn (0.4 mL, 0.4 mmol, 4.0 eq.) was slowly added to the mixture at –78 °C. After stirring for 0.5 h at –78 °C and then 0.5 h at 30 °C, the reaction mixture was cooled to 0 °C, and bromoacethyl bromide (21.8 μ L, 0.25 mmol, 2.5 eq.) was added. After stirring for 0.5 h at 30 °C, the reaction mixture was quenched with NH₄Cl aq. and extracted with CH₂Cl₂. The organic layer was dried with Na₂SO₄, and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane) to give the title compound **4e** as pale yellow oil (15.9 mg, 0.051 mmol, 51% yield).

4-Allyl-2-(2-bromophenyl)furan (4q)



A mixture of piperidine (0.49 μ L, 5 μ mol, 5 mol%), 4-pentenal (9.9 mL, 0.1 mmol) and **5** (43.6 mg, 0.1 mmol) in toluene (0.2 mL, 0.5 M) was stirred at 0 °C under N₂ atmosphere. After stirring for 4 h, the reaction mixture was diluted with toluene (0.6 mL, 0.17 M) at –78 °C. A 1.0 M hexane solution of Et₂Zn (0.4 mL, 0.4 mmol, 4.0 eq.) was slowly added to the mixture at –78 °C. After

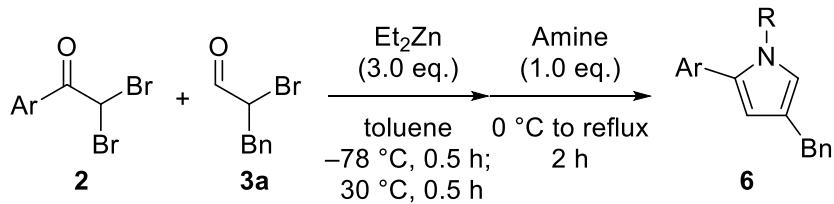
stirring for 0.5 h at $-78\text{ }^\circ\text{C}$ and then 0.5 h at $30\text{ }^\circ\text{C}$, the reaction mixture was cooled to $0\text{ }^\circ\text{C}$, and bromoacethyl bromide ($21.8\text{ }\mu\text{L}$, 0.25 mmol , 2.5 eq.) was added. After stirring for 0.5 h at $30\text{ }^\circ\text{C}$, the reaction mixture was quenched with NH_4Cl aq. and extracted with CH_2Cl_2 . The organic layer was dried with Na_2SO_4 , and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane) to give the title compound **4q** as pale yellow oil (10.2 mg, 0.039 mmol, 39% yield).

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.77 (dd, $J = 7.9, 1.6\text{ Hz}$, 1H), 7.63 (dd, $J = 8.1, 0.7\text{ Hz}$, 1H), 7.37-7.30 (m, 2H), 7.13-7.08 (m, 1H), 7.06 (s, 1H), 6.05-5.91 (m, 1H), 5.19-5.08 (m, 2H), 3.24 (d, $J = 6.4\text{ Hz}$, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 151.5, 139.1, 136.4, 134.2, 131.5, 128.8, 128.4, 127.5, 125.1, 119.6, 116.1, 112.4, 29.6.

HRMS (APCI, positive) Calcd. For $\text{C}_{13}\text{H}_{12}\text{BrO}$: 263.0067, 265.0046 ($[\text{M} + \text{H}]^+$), Found: 263.0066, 265.0050 ($[\text{M} + \text{H}]^+$).

Synthesis of pyrroles **6**

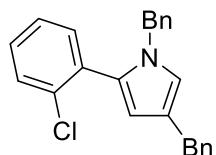


General procedure (B)

A mixture of dibromomethyl ketone **2** (0.10 mmol, 1.0 eq.) and 2-bromo-3-phenylpronapal (**3a**)

(0.10 mmol, 1.0 eq.) in toluene (0.80 mL, 0.13 M) was stirred at -78°C under N_2 atmosphere. A 1.0 M hexane solution of Et_2Zn (0.3 mL, 0.3 mmol) was slowly added to the mixture at -78°C . After stirring for 0.5 h at -78°C and then 0.5 h at 30°C , the reaction mixture was cooled at 0°C . To the mixture was added an amine (0.10 mmol, 1.0 eq.). After stirring for 2 h at reflux, the reaction mixture was quenched with NaHCO_3 aq. and extracted with CH_2Cl_2 . The organic layer was dried with Na_2SO_4 , and then concentrated. The resulting residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 50/1) to give the corresponding pyrrole **6**.

1,4-Dibenzyl-2-(2-chlorophenyl)-1*H*-pyrrole (6a)

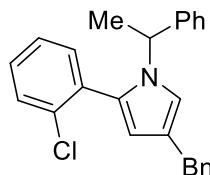


Following the general procedure (B) using **2d** (31.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol), and benzylamine (10.8 mg, 0.10 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **6a** as pale yellow oil (22.1 mg, 0.062 mmol, 62% yield).

¹H-NMR (300 MHz, CDCl_3) δ 7.41 (d, $J = 7.7$ Hz, 1H), 7.29-7.27 (m, 4H), 7.23-7.17 (m, 7H), 6.90 (d, $J = 5.9$ Hz, 2H), 6.49 (s, 1H), 6.06 (d, $J = 1.5$ Hz, 1H), 4.87 (s, 2H), 3.86 (s, 2H).
¹³C-NMR (100 MHz, CDCl_3) δ 142.3, 138.7, 134.9, 133.1, 132.6, 131.3, 129.6, 129.2, 128.8, 128.5, 128.4, 127.3, 127.0, 126.5, 125.8, 123.0, 120.3, 110.8, 51.0, 33.6.

HRMS (APCI, positive) Calcd. For C₂₄H₂₁ClN: 358.1358, 360.1328 ([M + H]⁺), Found: 358.1362, 360.1350 ([M + H]⁺).

4-Benzyl-2-(2-chlorophenyl)-1-(1-phenylethyl)-1*H*-pyrrole (6b)



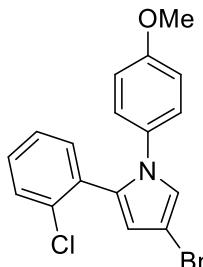
Following the general procedure (B) using **2d** (31.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol), and 1-phenylethylamine (12.2 mg, 0.10 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **6b** as pale yellow oil (22.1 mg, 0.059 mmol, 59% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 8.2 Hz, 1H), 7.29-7.28 (m, 4H), 7.24-7.12 (m, 7H), 6.89 (d, *J* = 6.4 Hz, 2H), 6.63 (s, 1H), 6.01 (d, *J* = 1.8 Hz, 1H), 5.05 (q, *J* = 7.0 Hz, 1H), 3.89 (s, 2H), 1.75 (d, *J* = 7.0 Hz, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ 142.5, 135.1, 133.3, 132.9, 131.4, 129.5, 129.2, 128.8, 128.4, 128.3, 127.1, 126.5, 126.0 (two peaks overlap), 125.7, 122.7, 116.5, 110.6, 55.1, 33.8, 21.8.

HRMS (APCI, positive) Calcd. For C₂₅H₂₃ClN: 372.1514, 374.1485 ([M + H]⁺), Found: 372.1516, 374.1486 ([M + H]⁺).

4-Benzyl-2-(2-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole (6c)

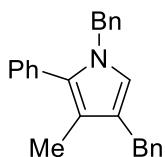


Following the general procedure (B) using **2d** (31.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal (**3a**) (21.3 mg, 0.1 mmol), and 4-methoxyaniline (12.3 mg, 0.10 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **6c** as pale yellow oil (24.2 mg, 0.065 mmol, 65% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.36-7.28 (m, 5H), 7.24-7.08 (m, 4H), 6.98-6.95 (m, 2H), 6.75-6.72 (m, 2H), 6.66-6.65 (m, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 3.92 (s, 2H), 3.75 (s, 3H).
¹³C-NMR (100 MHz, CDCl₃) δ 157.8, 141.9, 134.2, 133.8, 132.8, 132.7, 130.3, 129.8, 129.0, 128.6, 128.4, 126.3, 125.97, 125.94, 123.6, 121.4, 114.0, 112.7, 55.5, 33.6.

HRMS (APCI, positive) Calcd. For C₂₄H₂₁ClNO: 374.1307, 376.1277 ([M + H]⁺), Found: 374.1302, 376.1277 ([M + H]⁺).

1,4-Dibenzyl-3-methyl-2-phenyl-1*H*-pyrrole (6d)



Following the general procedure (B) using **2k** (29.2 mg, 0.1 mmol), 2-bromo-3-phenylpronapal

(**3a**) (21.3 mg, 0.1 mmol), and benzylamine (10.8 mg, 0.10 mmol) gave the crude product. Purification by flash column chromatography gave the title compound **6d** as pale yellow oil (18.2 mg, 0.054 mmol, 54% yield).

¹H-NMR (300 MHz, CDCl₃) δ 7.36-7.27 (m, 6H), 7.25-7.16 (m, 7H), 6.93 (d, *J* = 6.4 Hz, 2H), 6.39 (s, 1H), 4.94 (s, 2H), 3.83 (s, 2H), 1.95 (s, 3H)

¹³C-NMR (100 MHz, CDCl₃) δ 141.9, 139.4, 132.9, 131.8, 130.5, 128.8, 128.6, 128.4, 128.3, 127.2, 127.0, 126.6, 125.7, 122.4, 119.9, 116.2, 50.6, 32.2, 10.2.

HRMS (APCI, positive) Calcd. For C₂₅H₂₄N: 338.1903 ([M + H]⁺), Found: 338.1906 ([M + H]⁺).

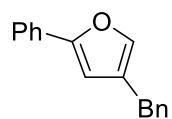
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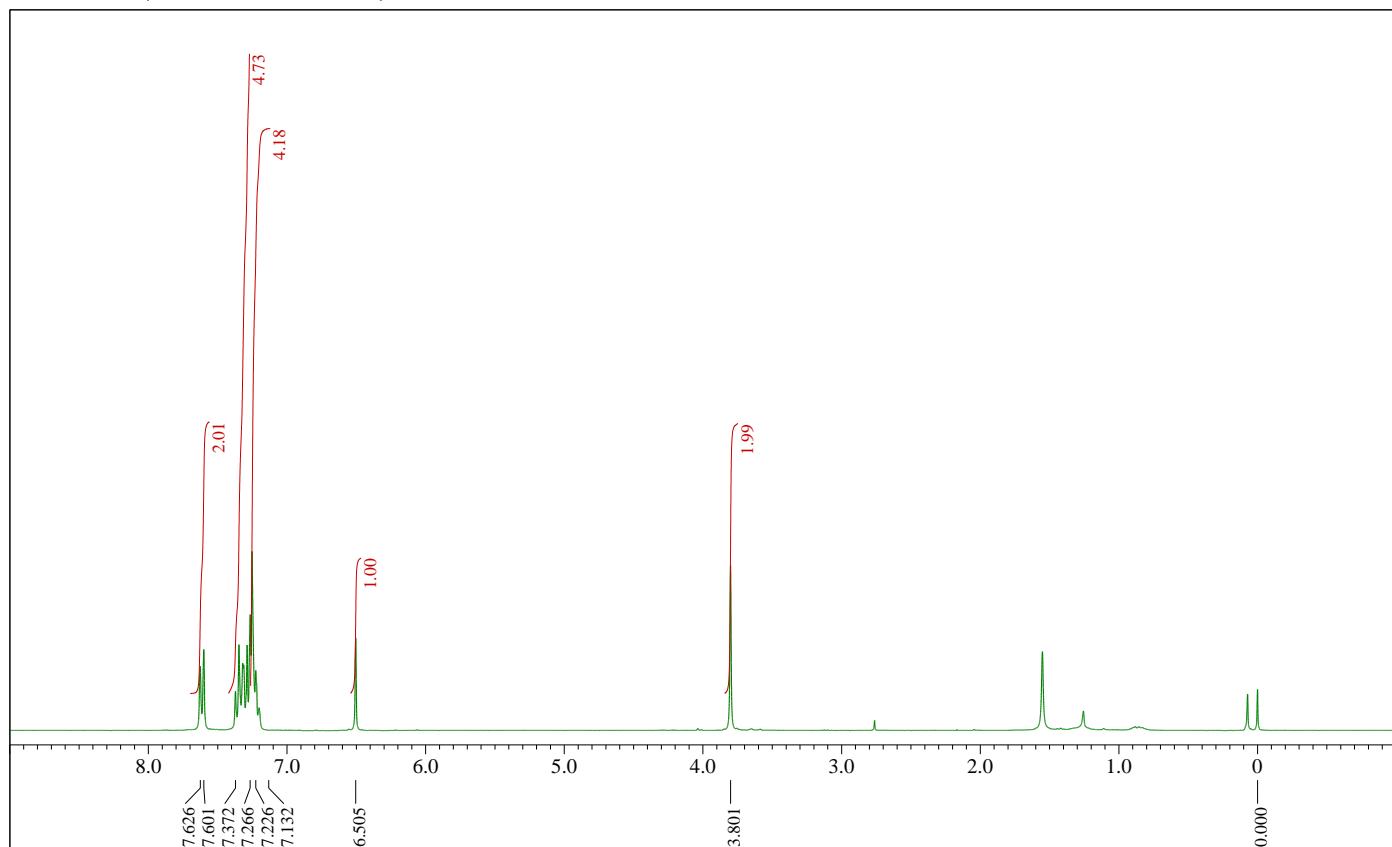
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¹H, ¹³C, ¹⁹F NMR spectra

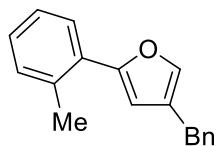
4-Benzyl-2-phenylfuran (4a)



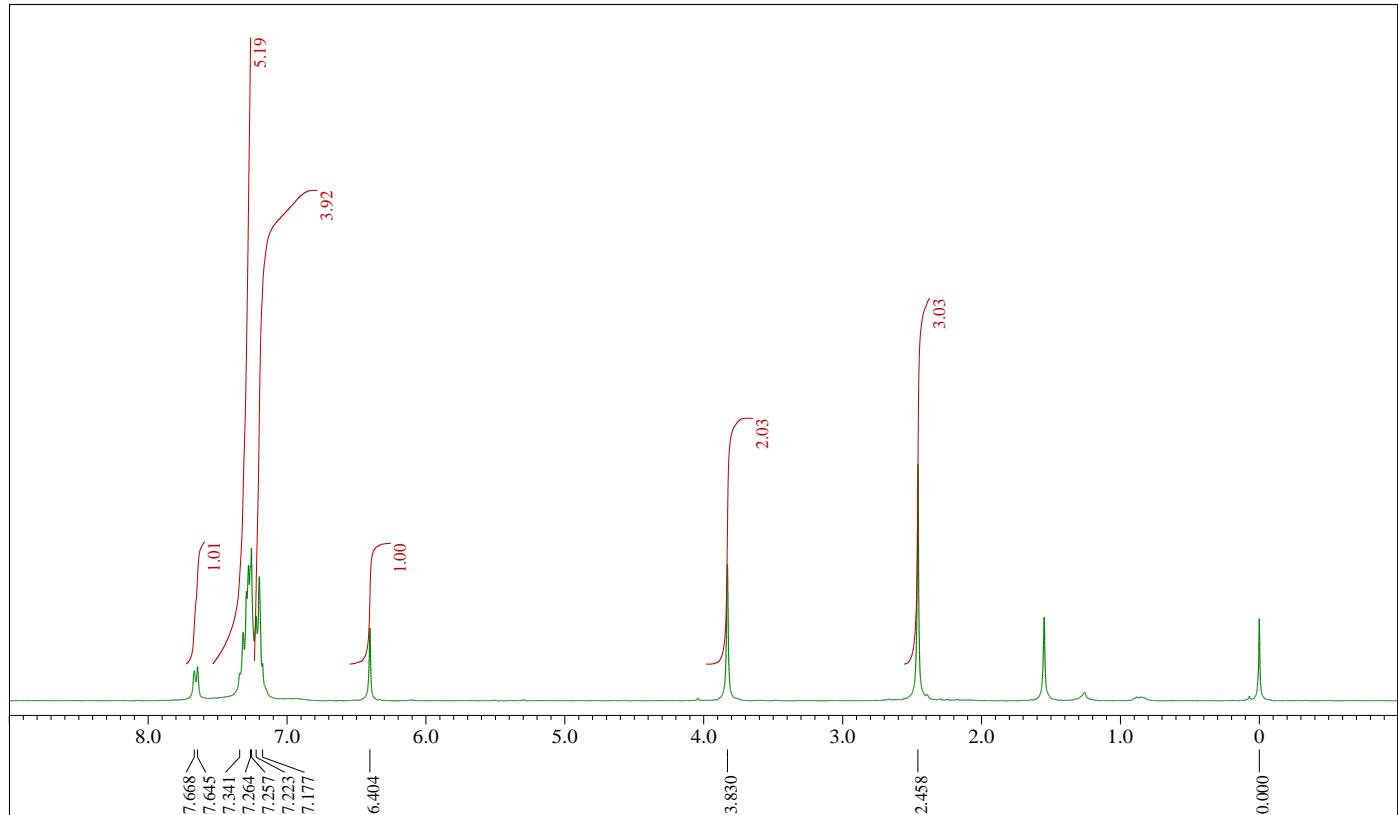
¹H-NMR (300 MHz, CDCl₃)



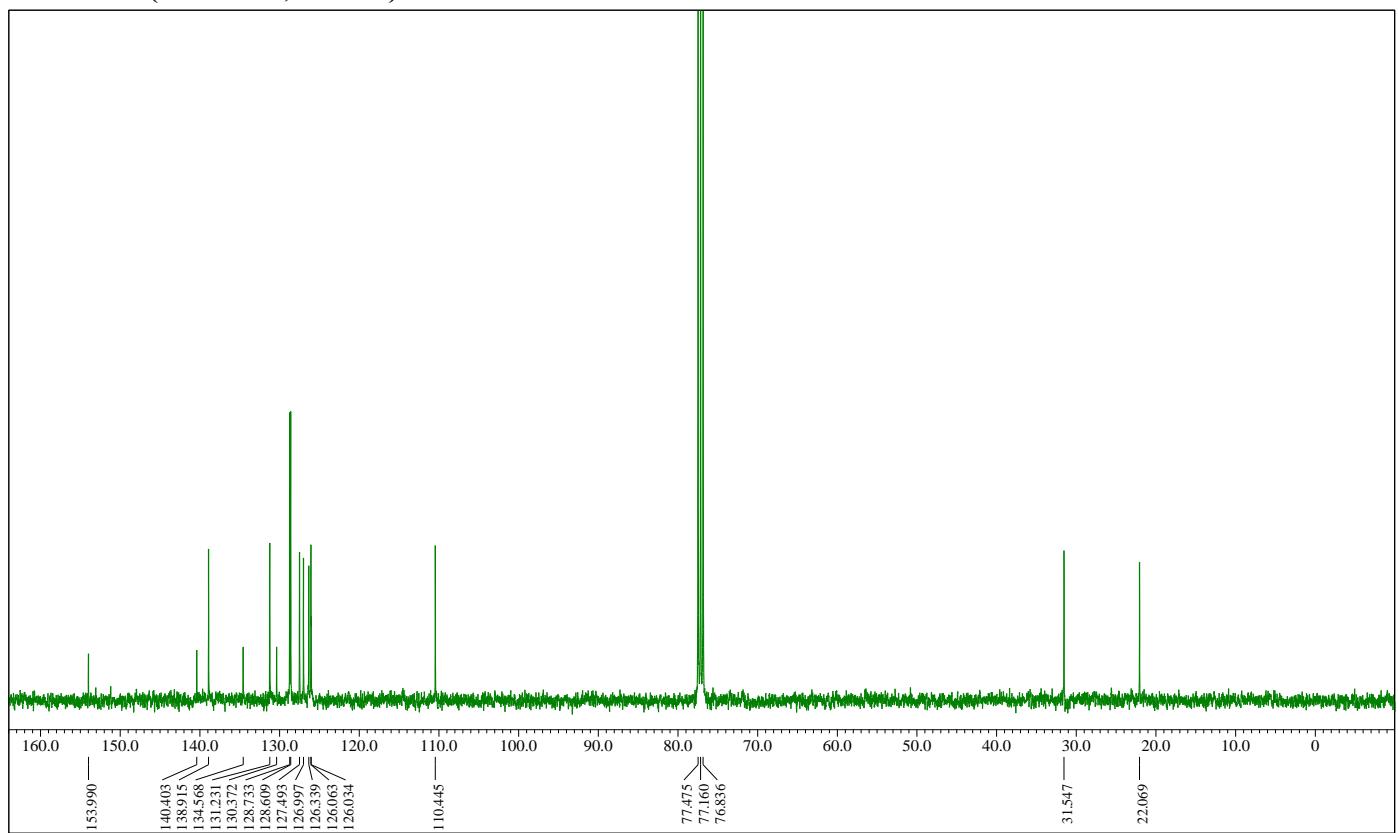
4-Benzyl-2-(2-methylphenyl)furan (4b)



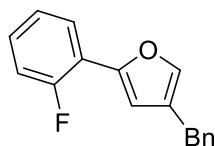
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



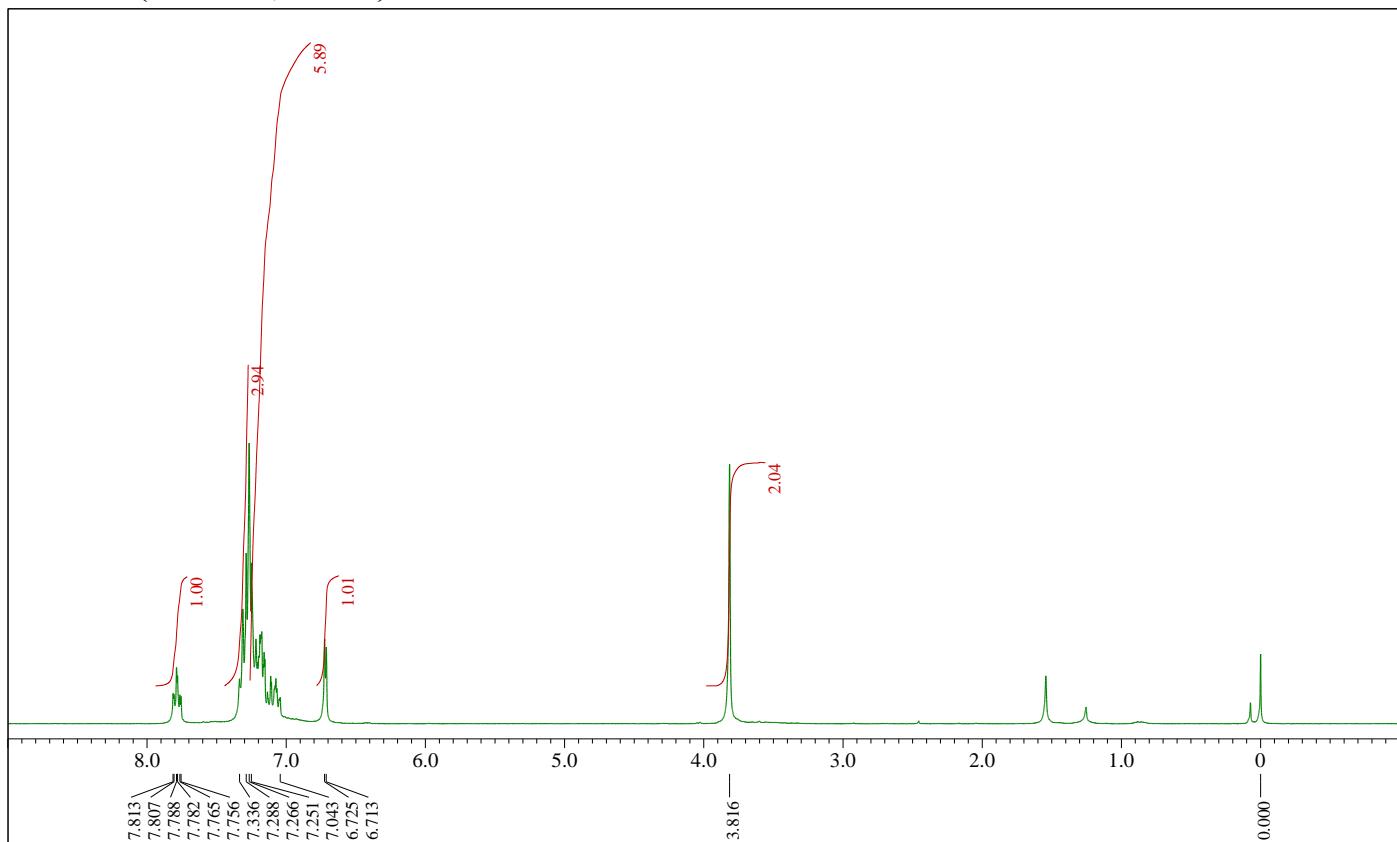
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)



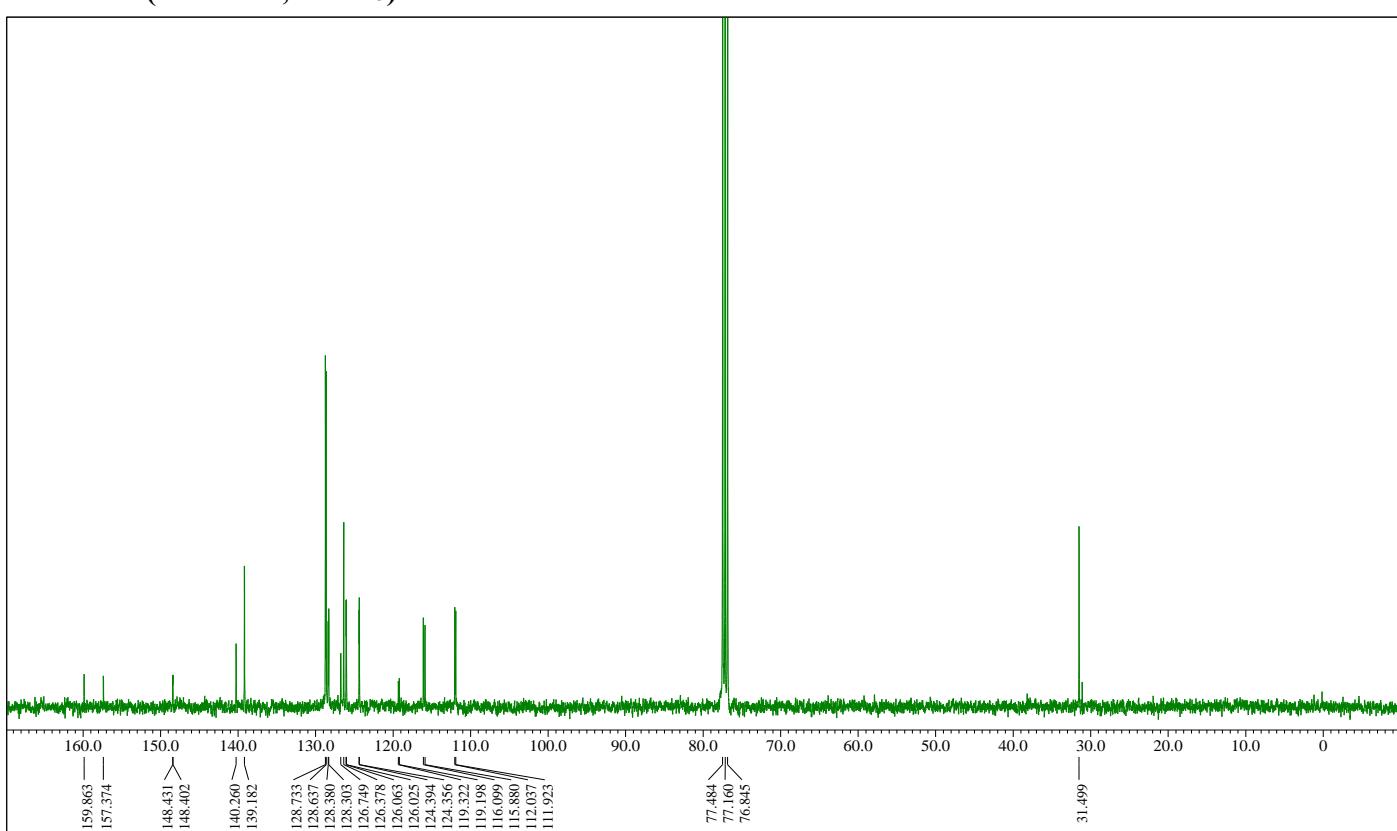
4-Benzyl-2-(2-fluorophenyl)furan (4c)



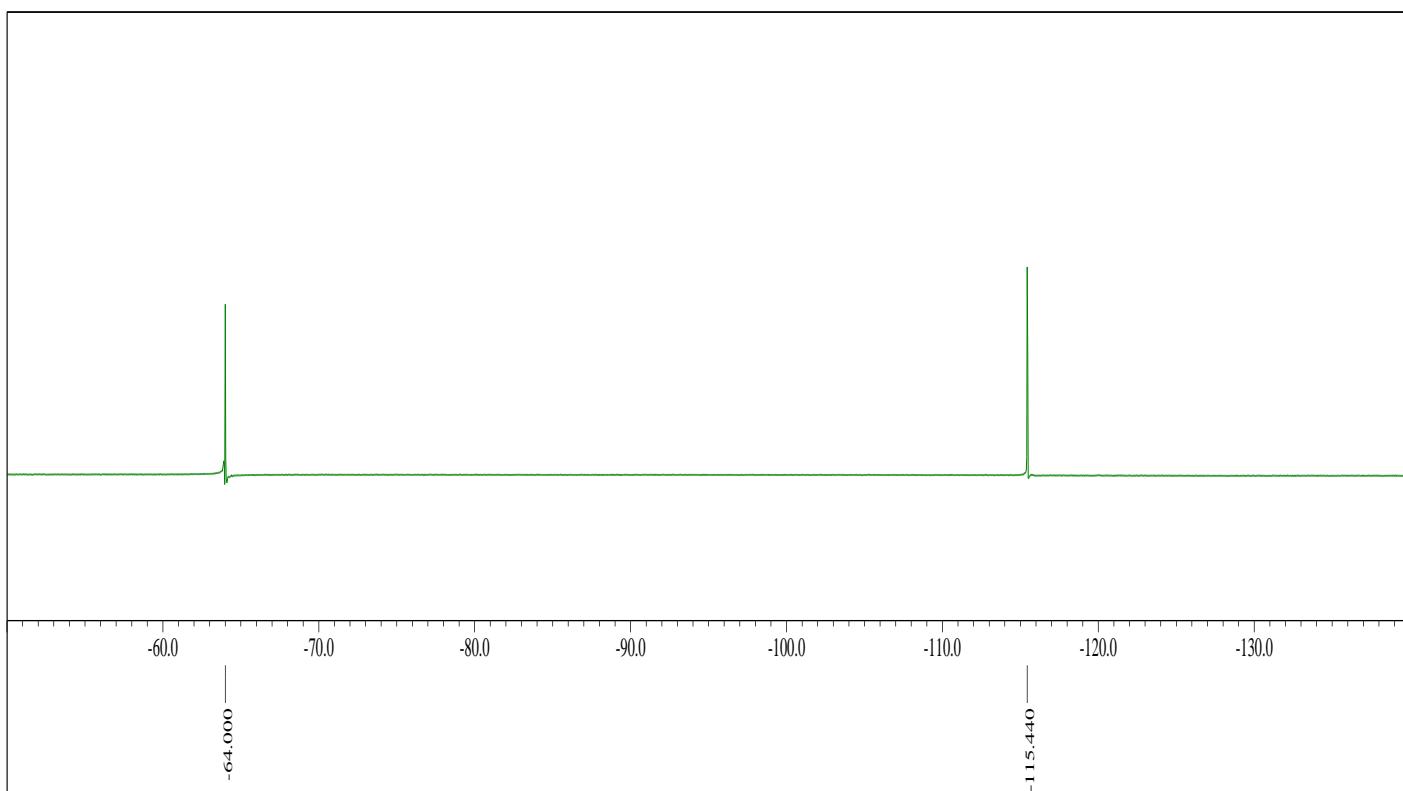
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



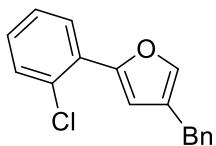
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)



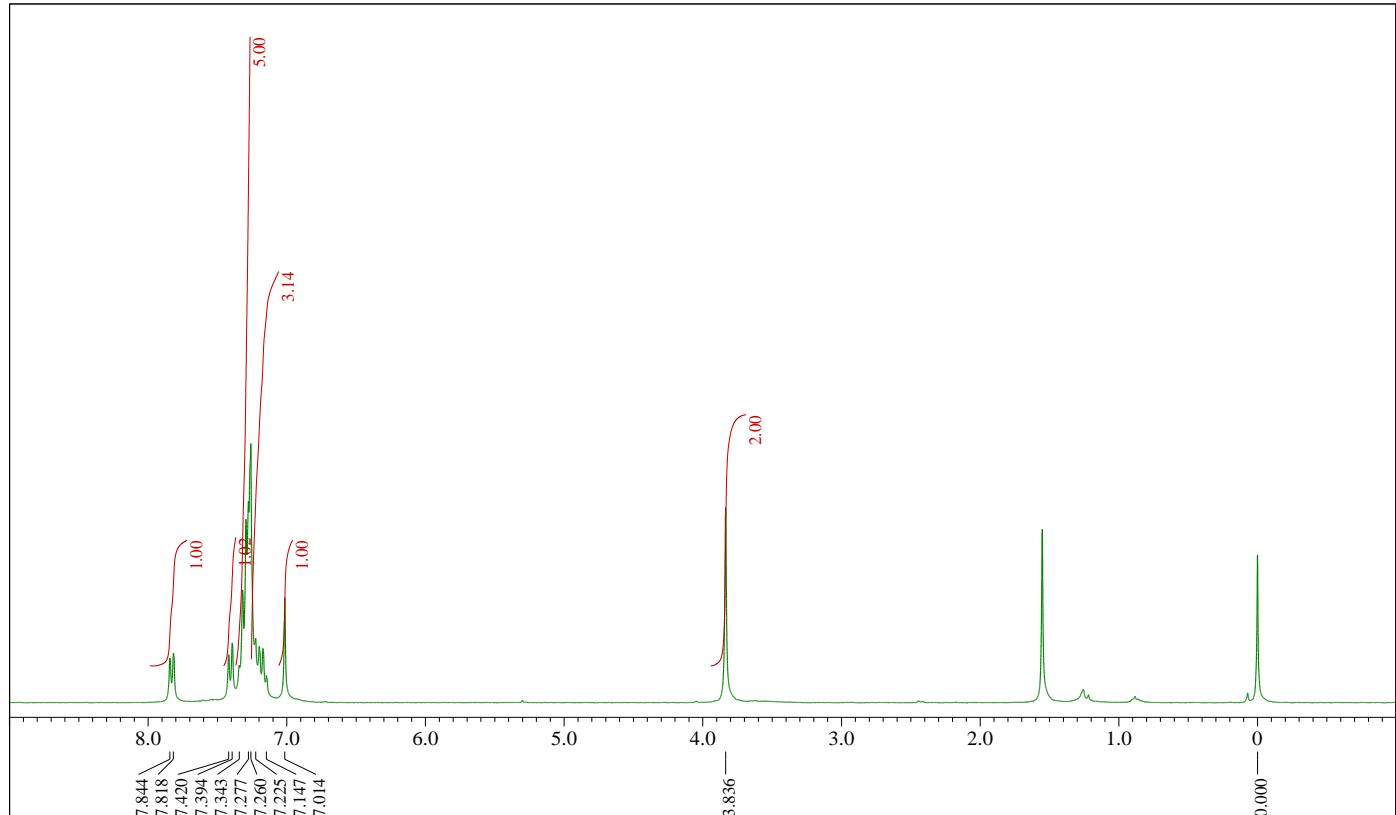
¹⁹F-NMR (471 MHz, CDCl₃)



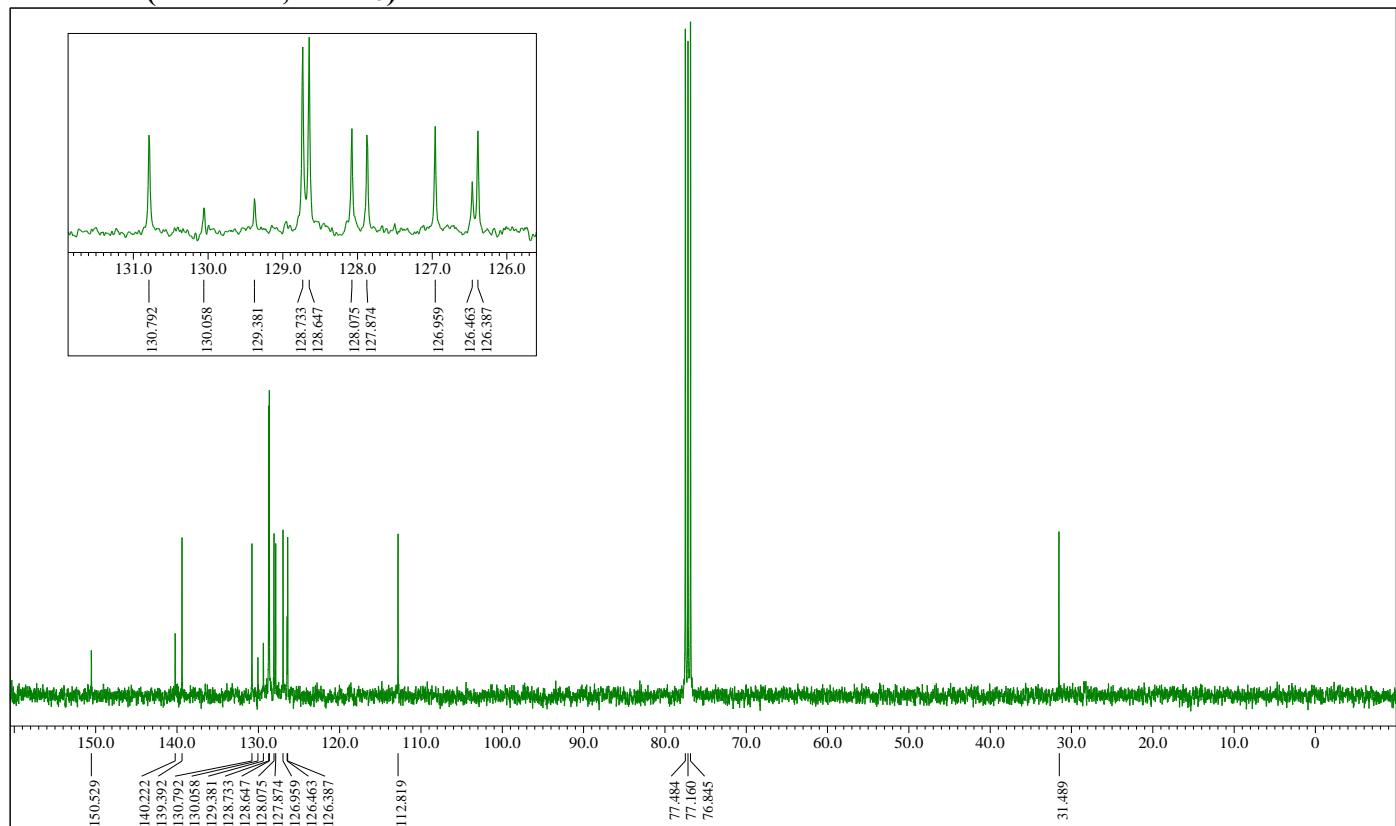
4-Benzyl-2-(2-chlorophenyl)furan (4d)



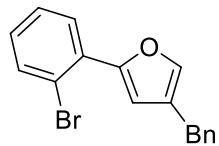
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



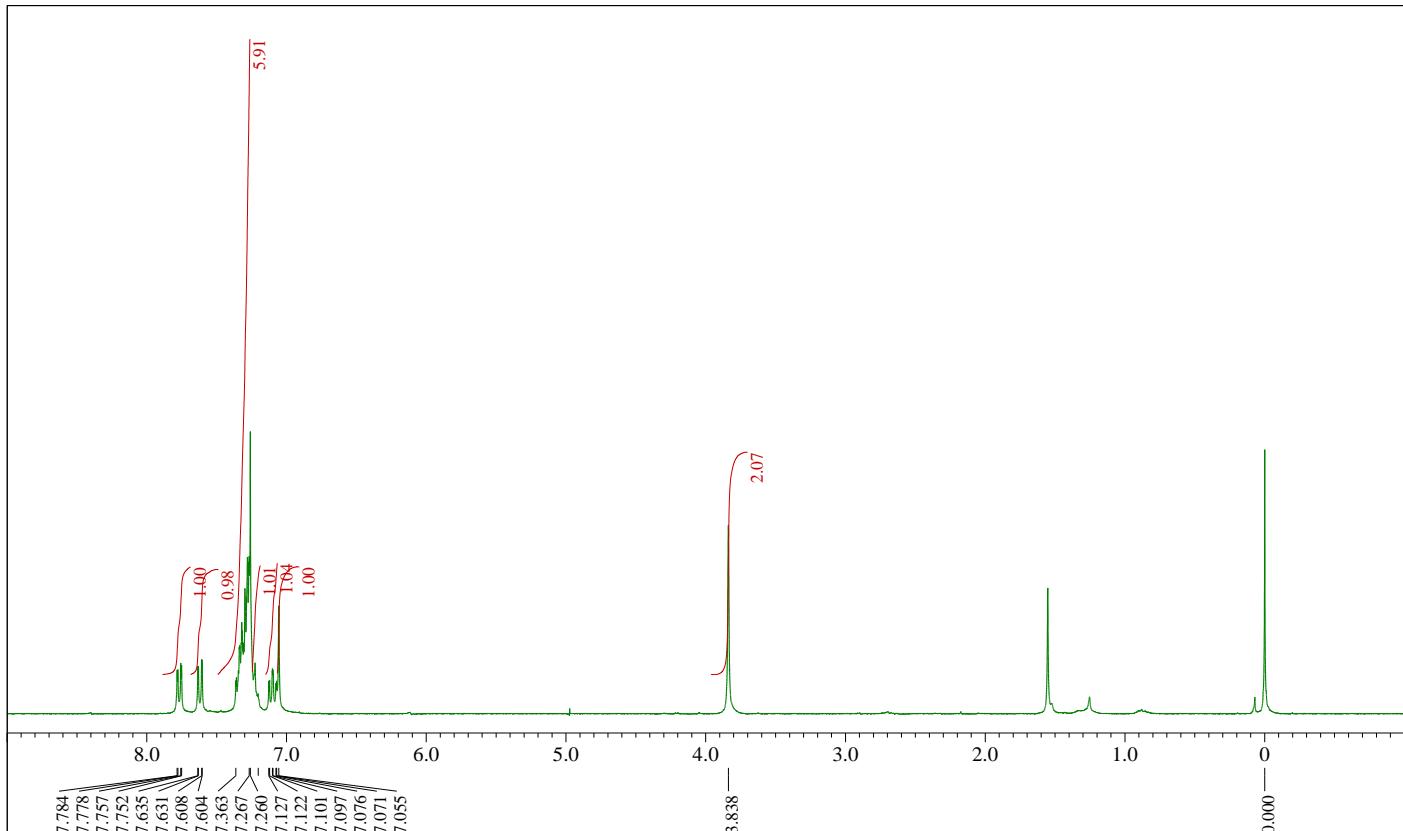
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)



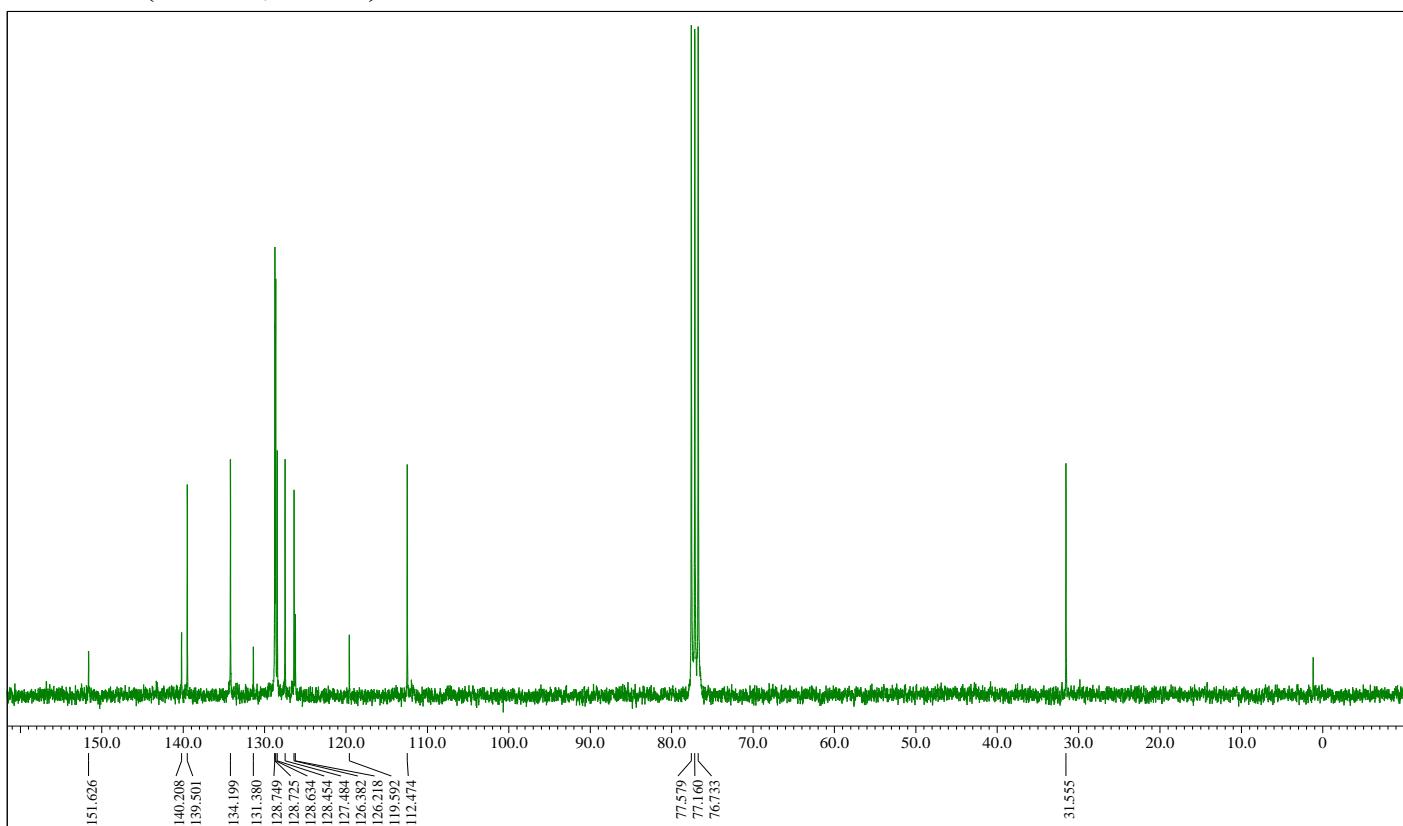
4-Benzyl-2-(2-bromophenyl)furan (4e)



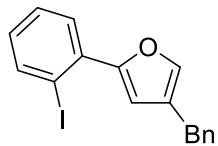
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



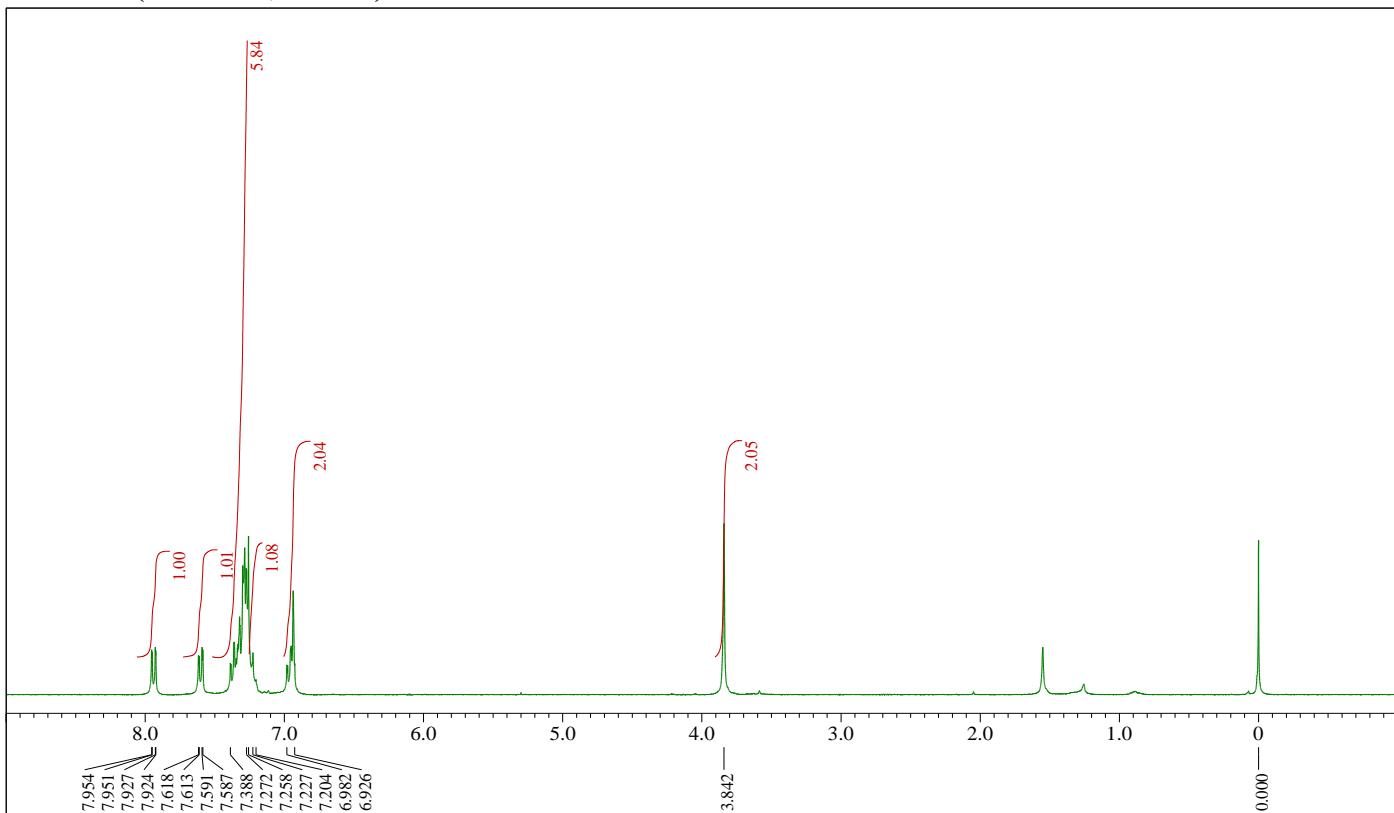
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



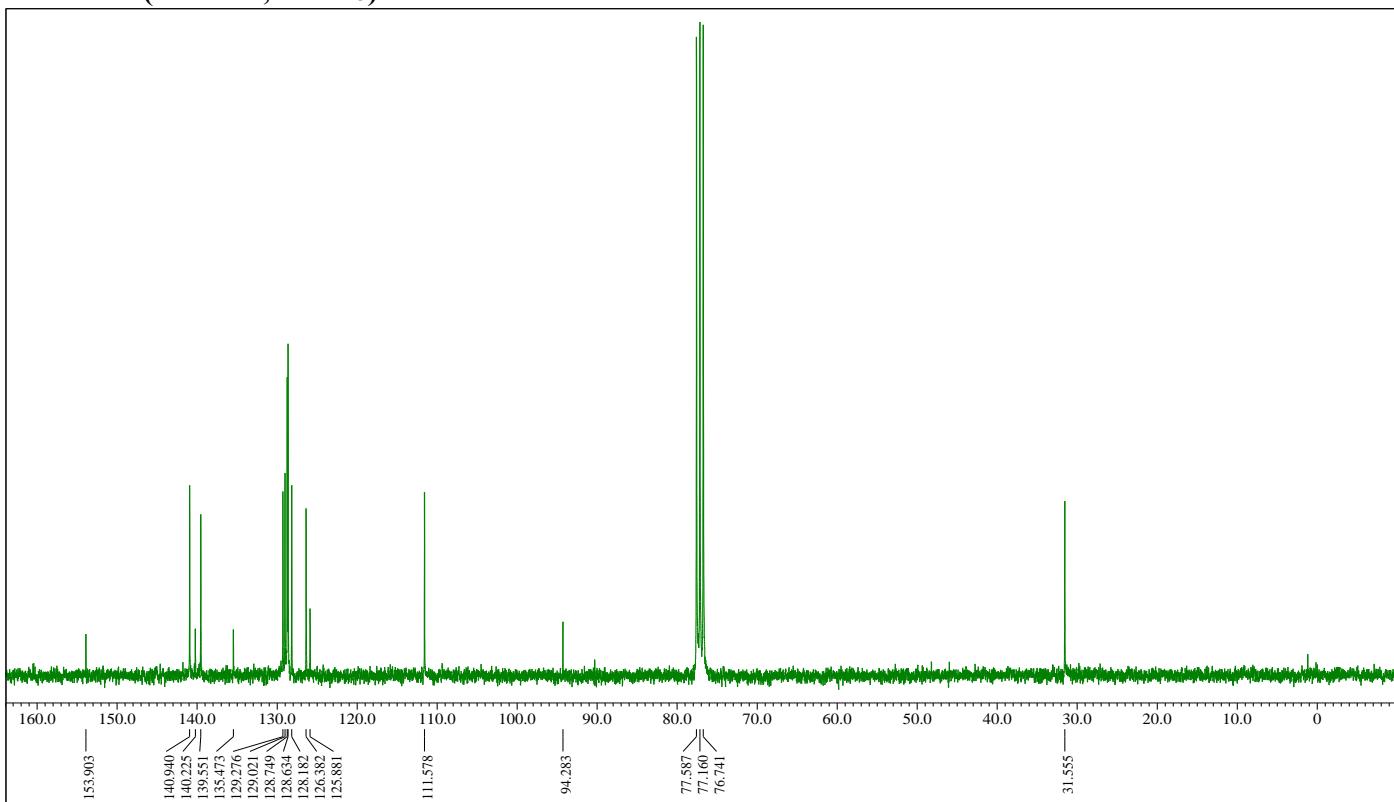
4-Benzyl-2-(2-iodophenyl)furan (4f)



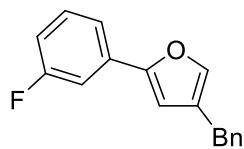
¹H-NMR (300 MHz, CDCl₃)



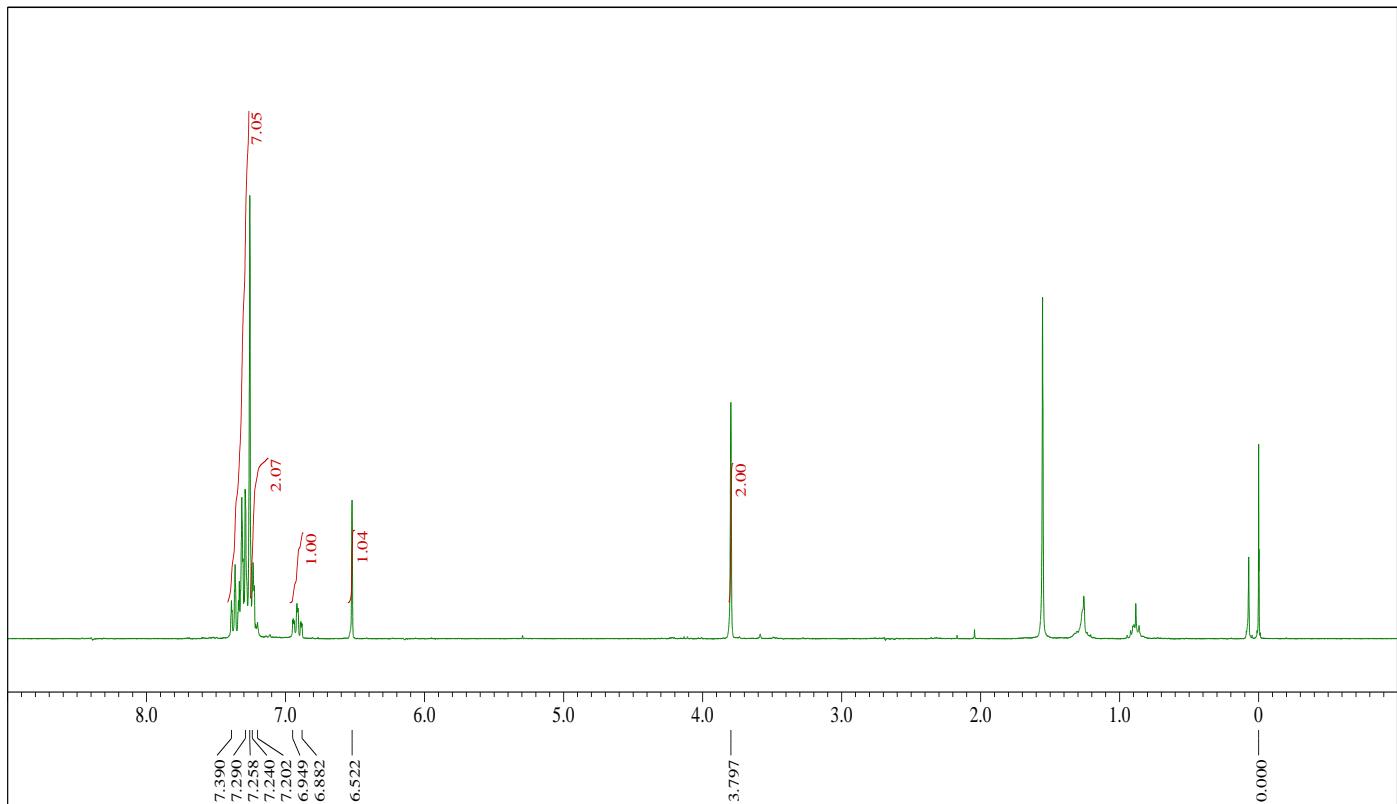
¹³C-NMR (75 MHz, CDCl₃)



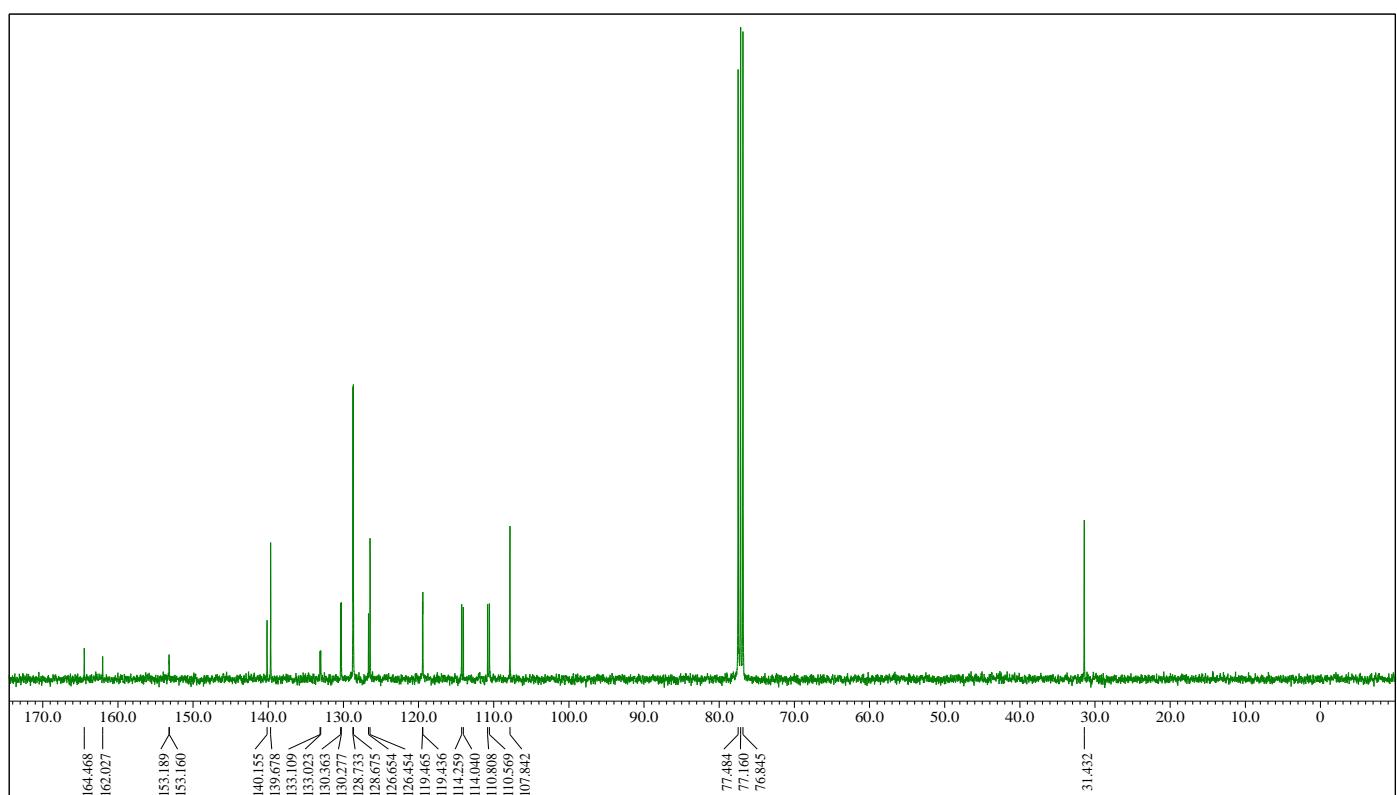
4-Benzyl-2-(3-fluorophenyl)furan (4g)



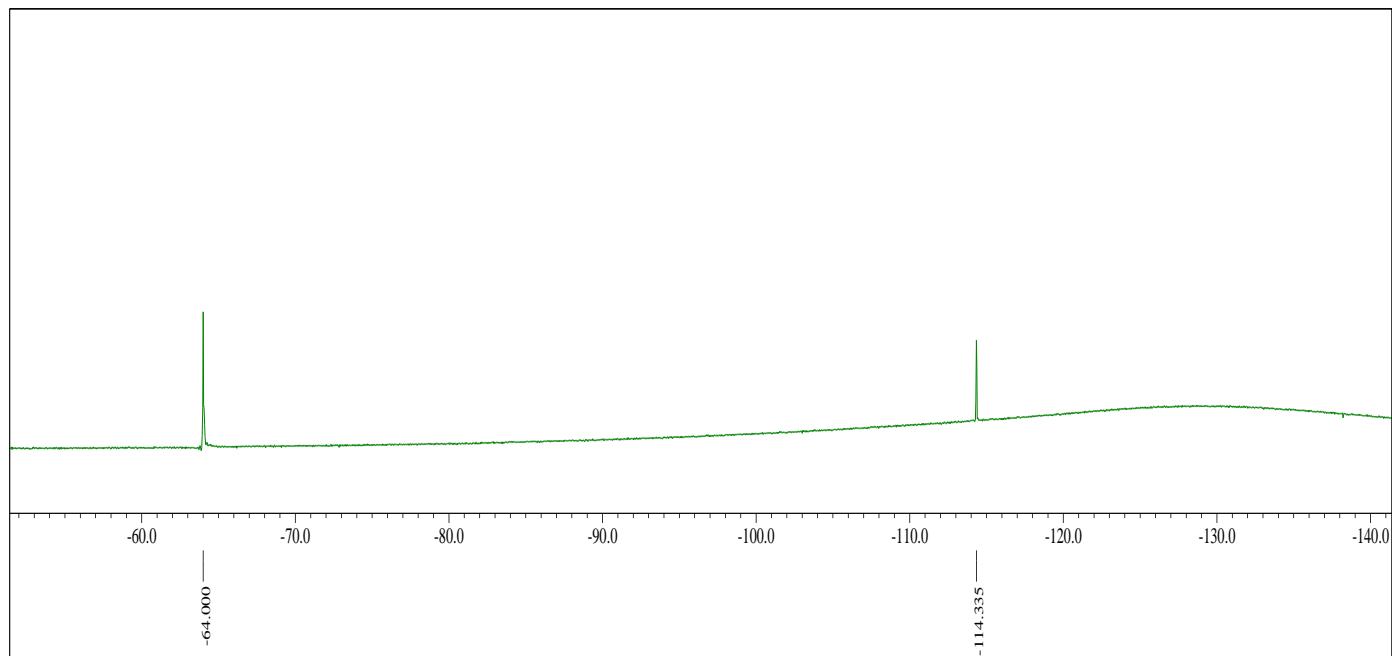
¹H-NMR (300 MHz, CDCl₃)



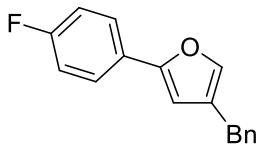
¹³C-NMR (100 MHz, CDCl₃)



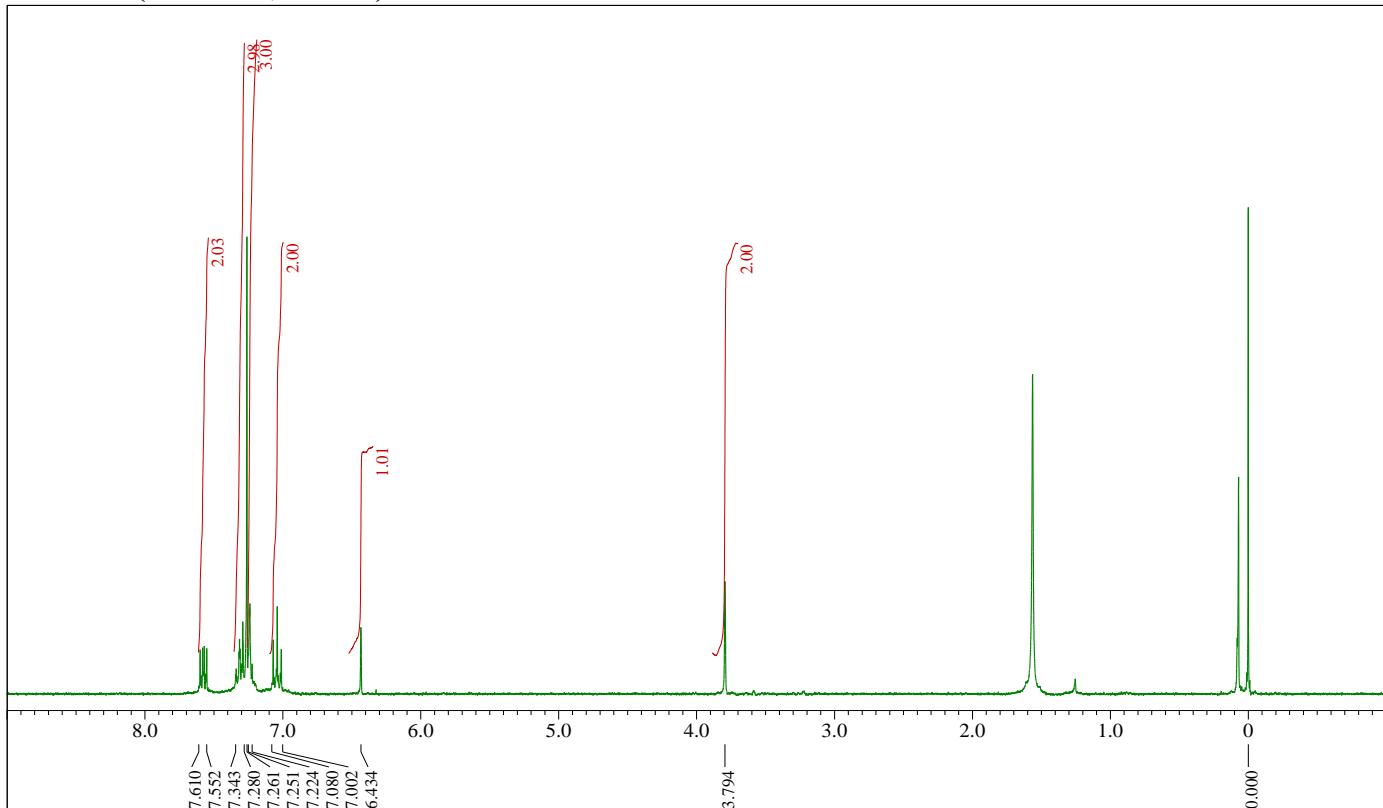
¹⁹F-NMR (376 MHz, CDCl₃)



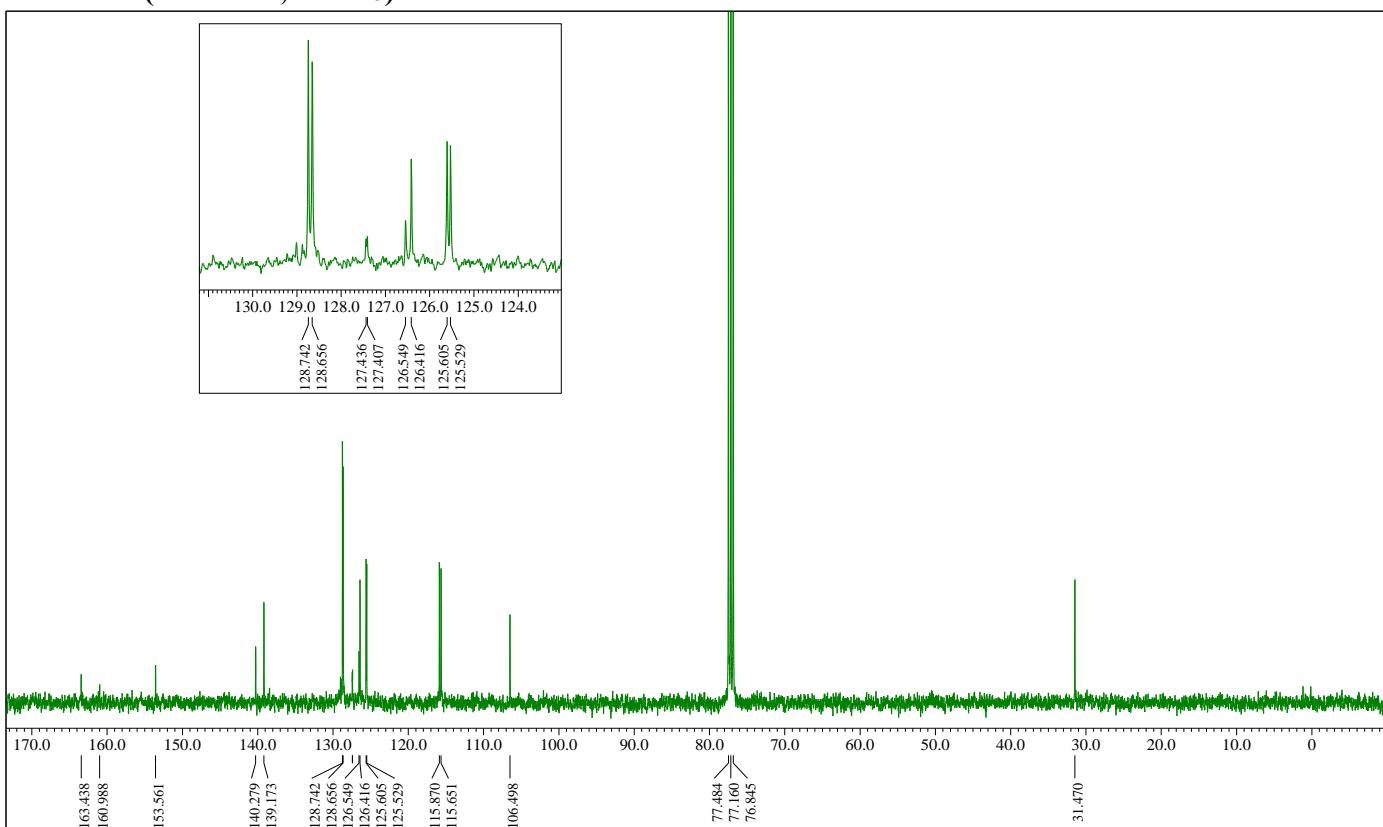
4-Benzyl-2-(4-fluorophenyl)furan (4h)



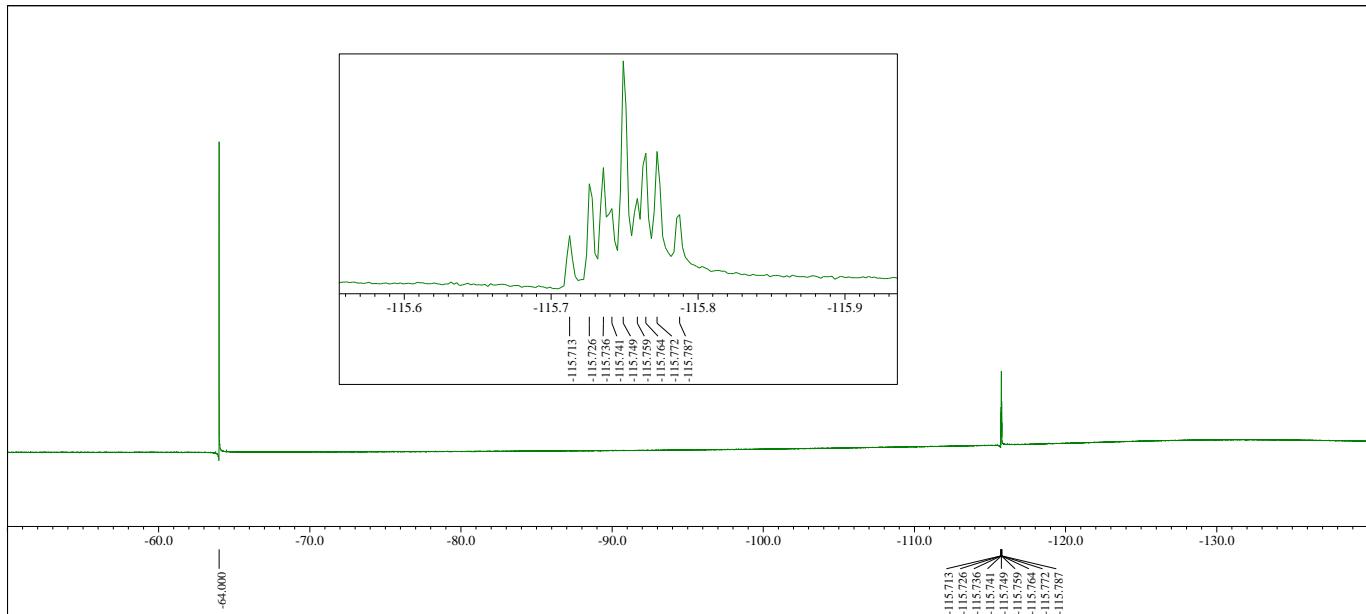
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



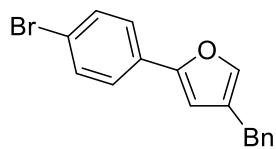
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)



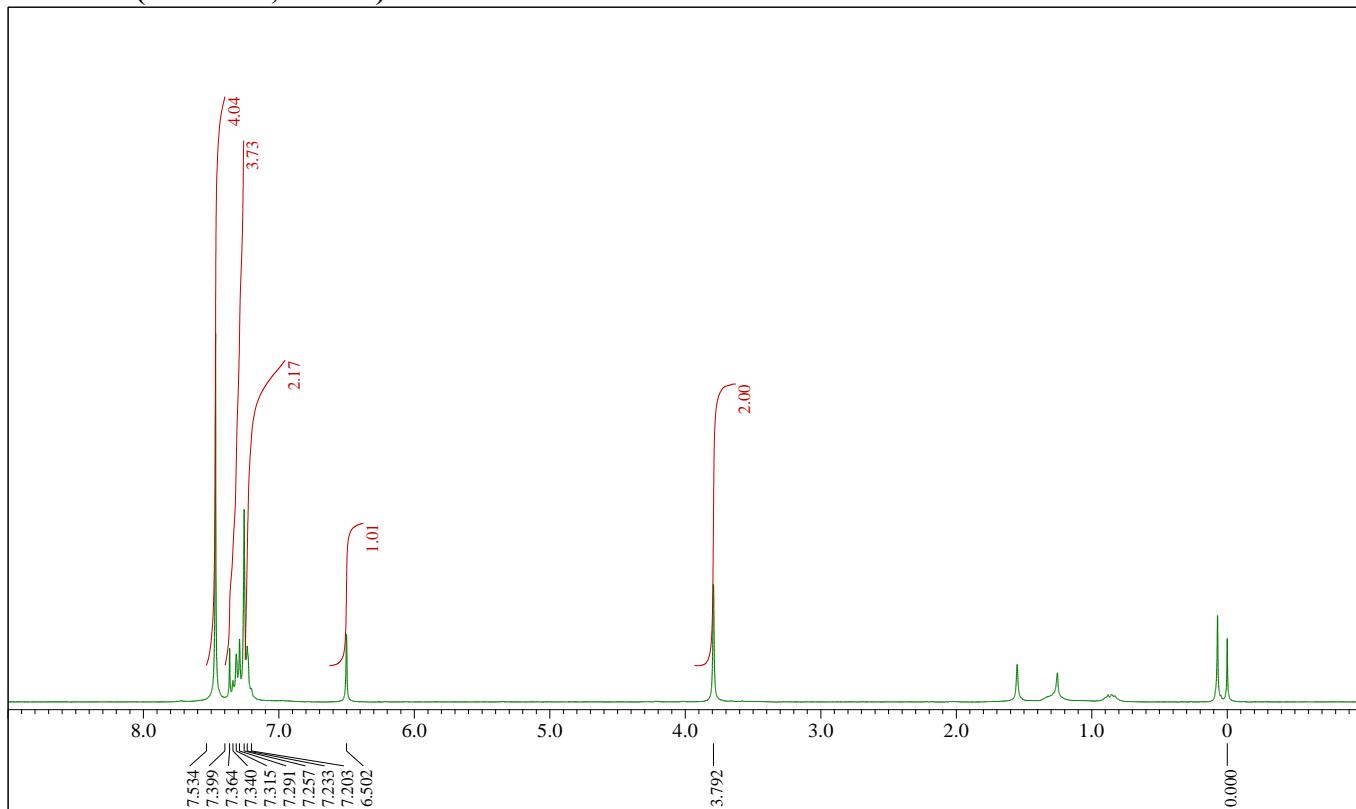
¹⁹F-NMR (376 MHz, CDCl₃)



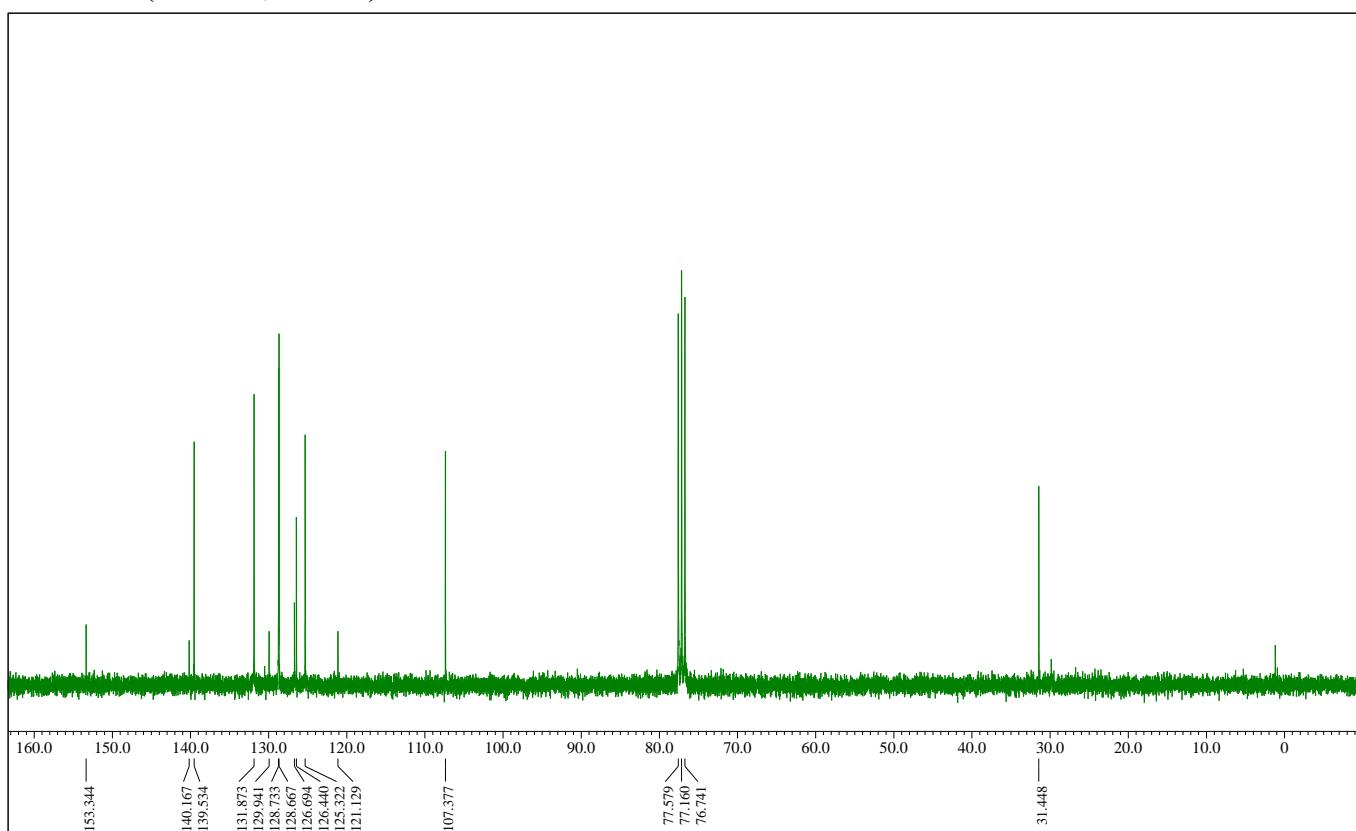
4-Benzyl-2-(4-bromophenyl)furan (4i)



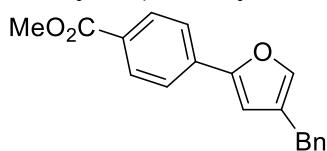
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



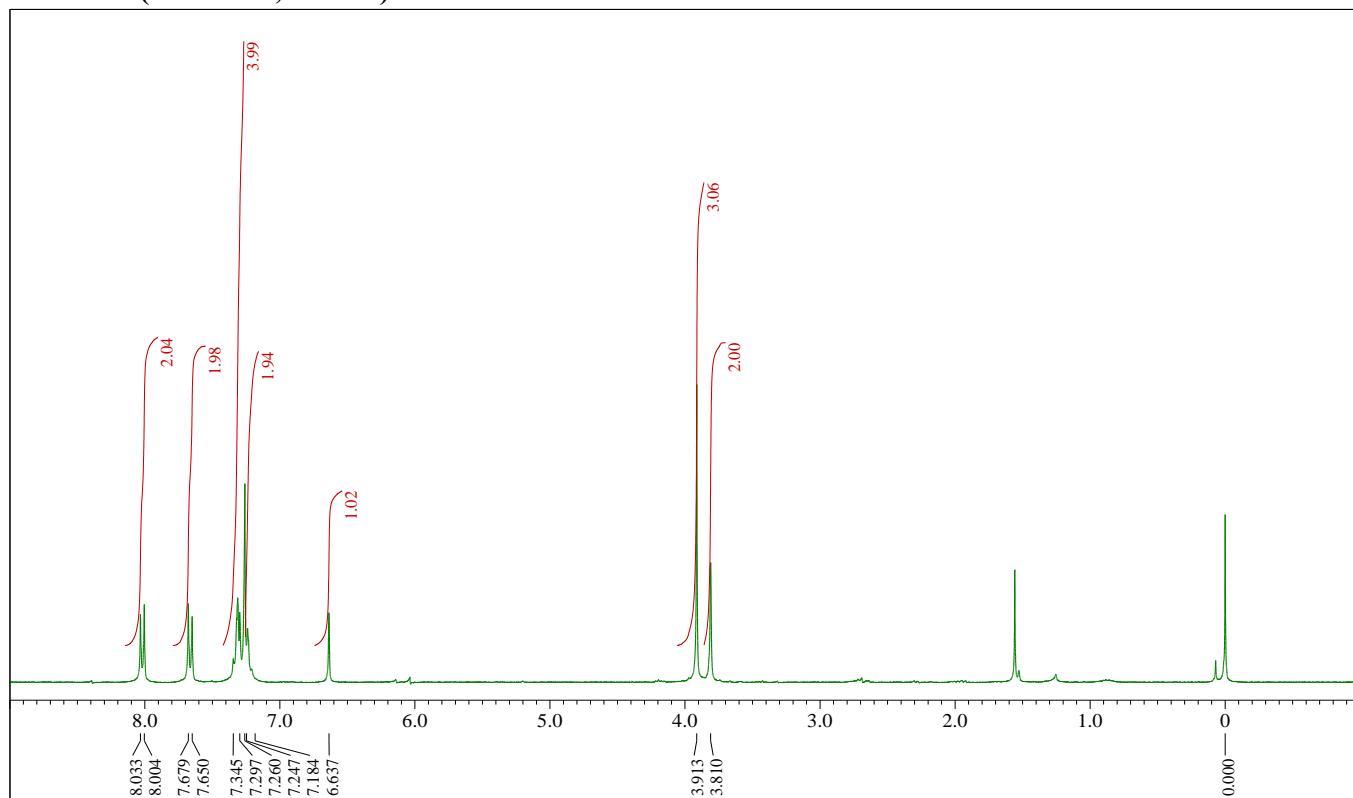
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)



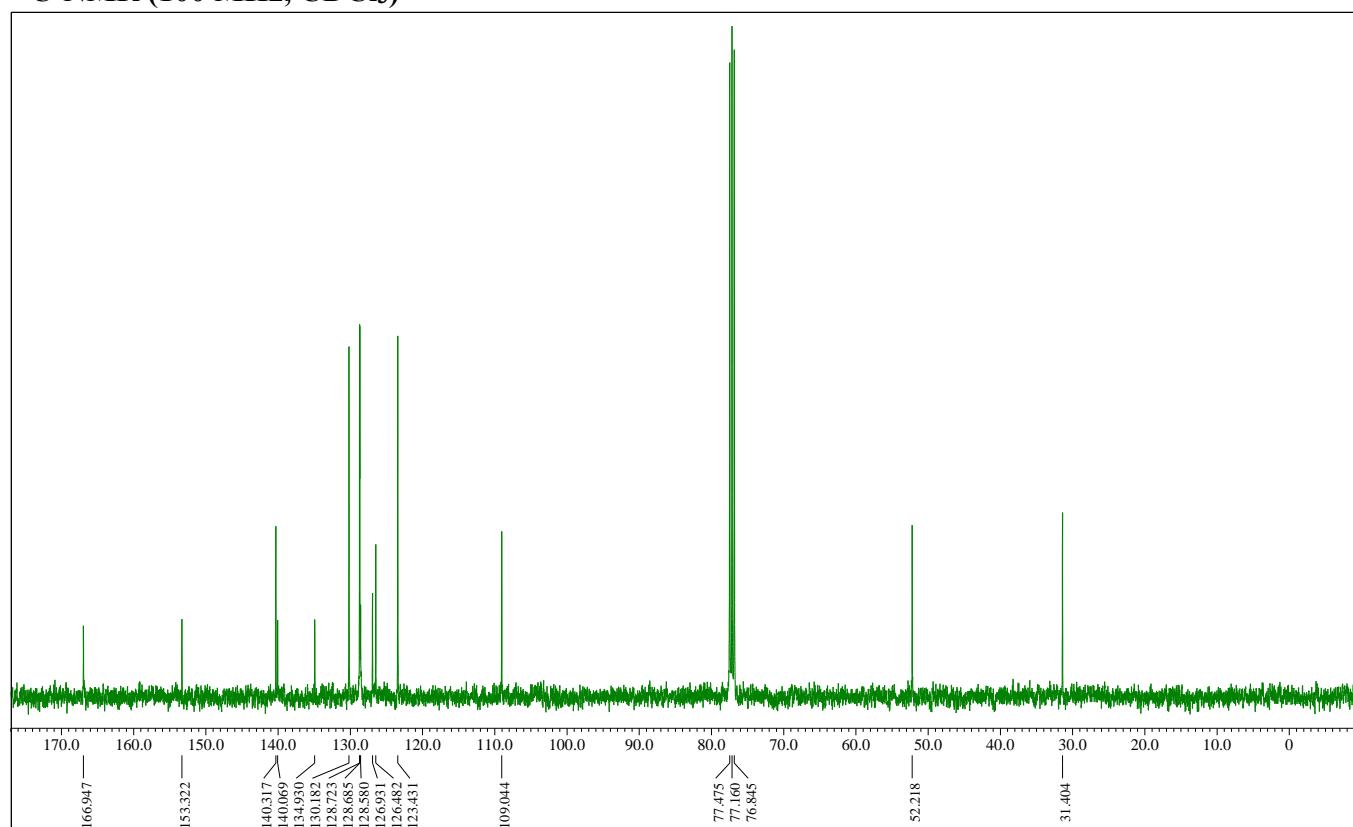
Methyl 4-(4-benzylfuran-2-yl)benzoate (4j)



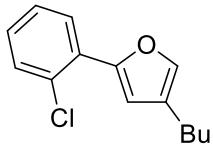
¹H-NMR (300 MHz, CDCl₃)



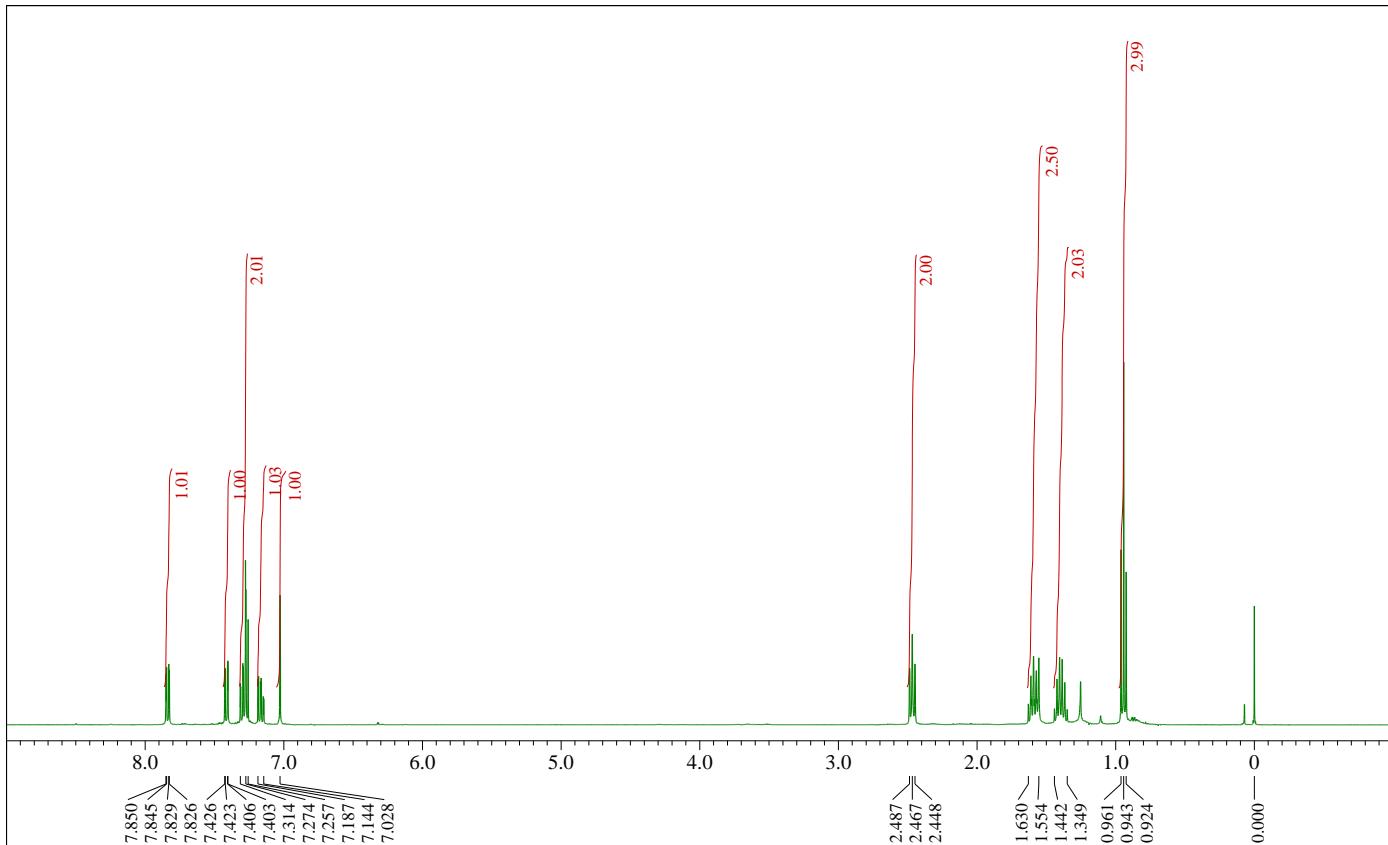
¹³C-NMR (100 MHz, CDCl₃)



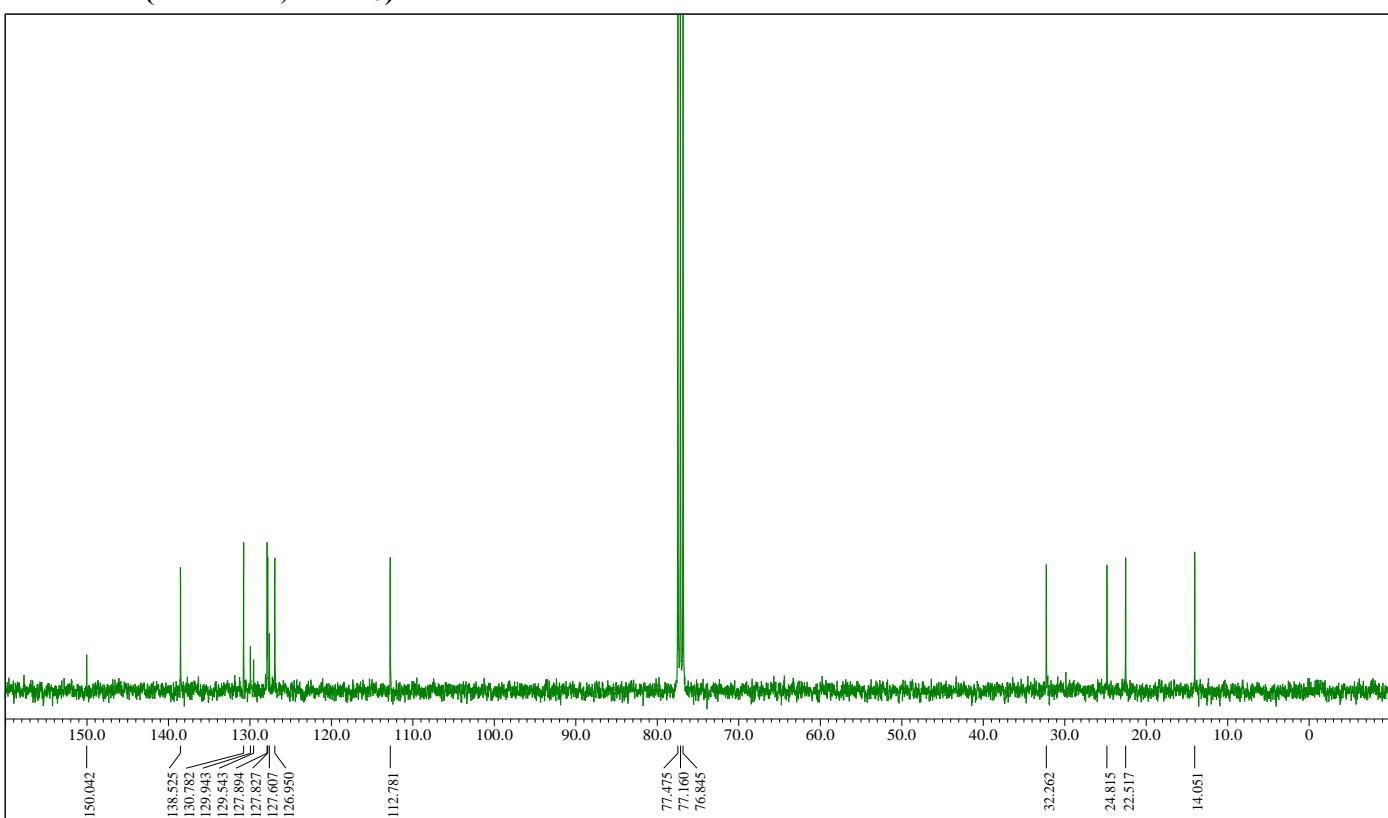
4-Butyl-2-(2-chlorophenyl)furan (4k)



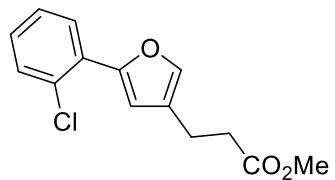
¹H-NMR (400 MHz, CDCl₃)



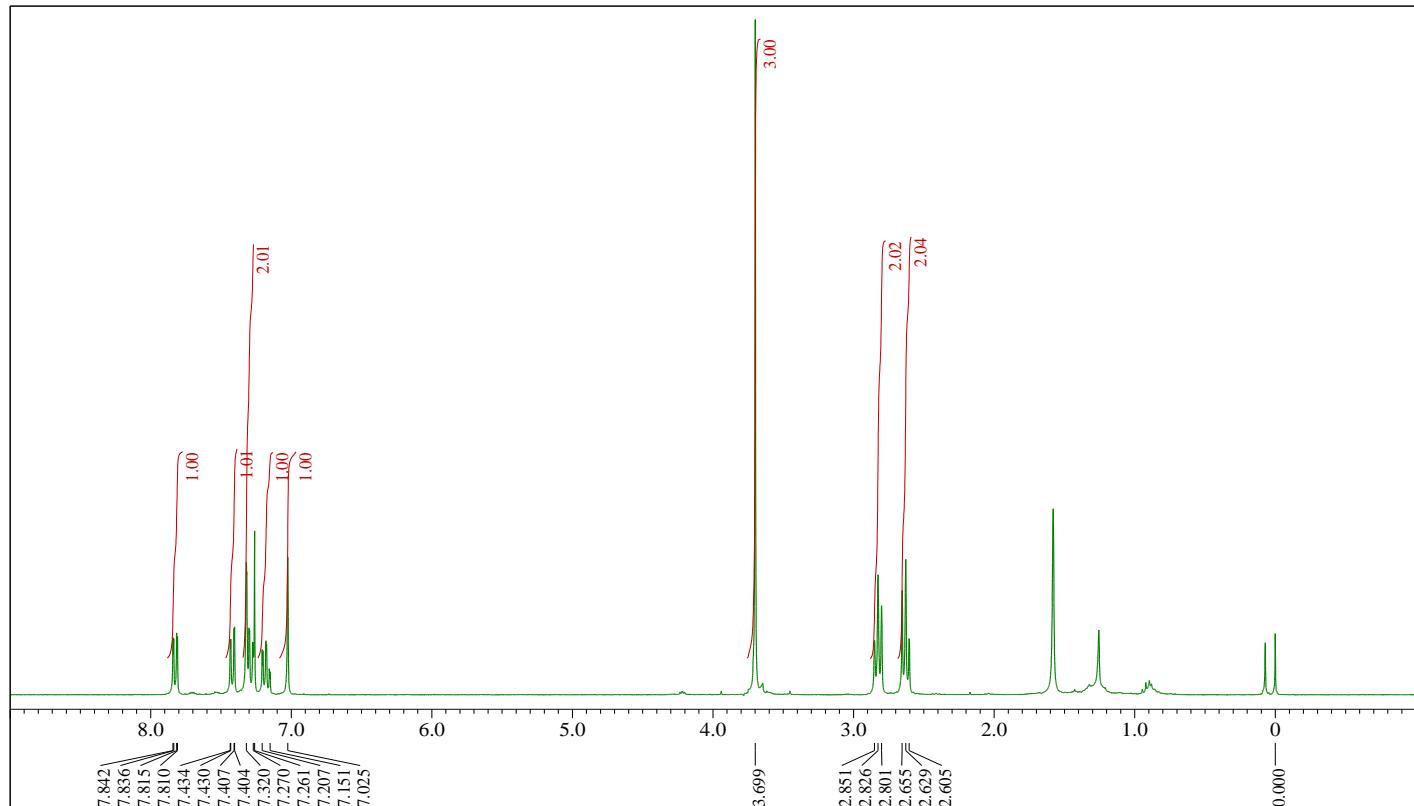
¹³C-NMR (100 MHz, CDCl₃)



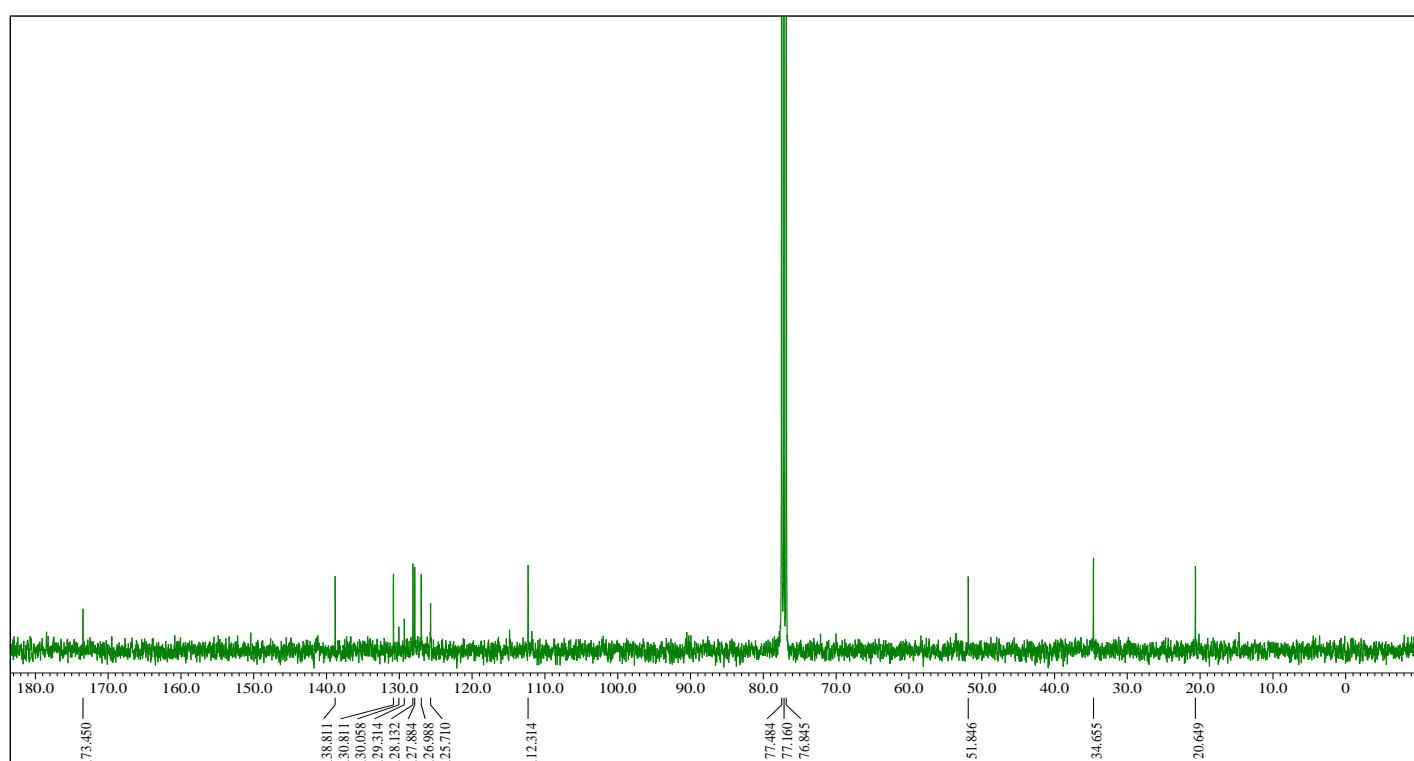
Methyl 3-(5-(2-chlorophenyl)furan-3-yl)propanoate (4l)



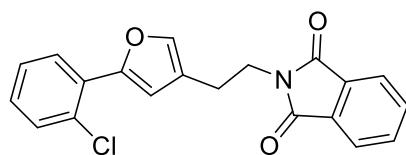
¹H-NMR (300 MHz, CDCl₃)



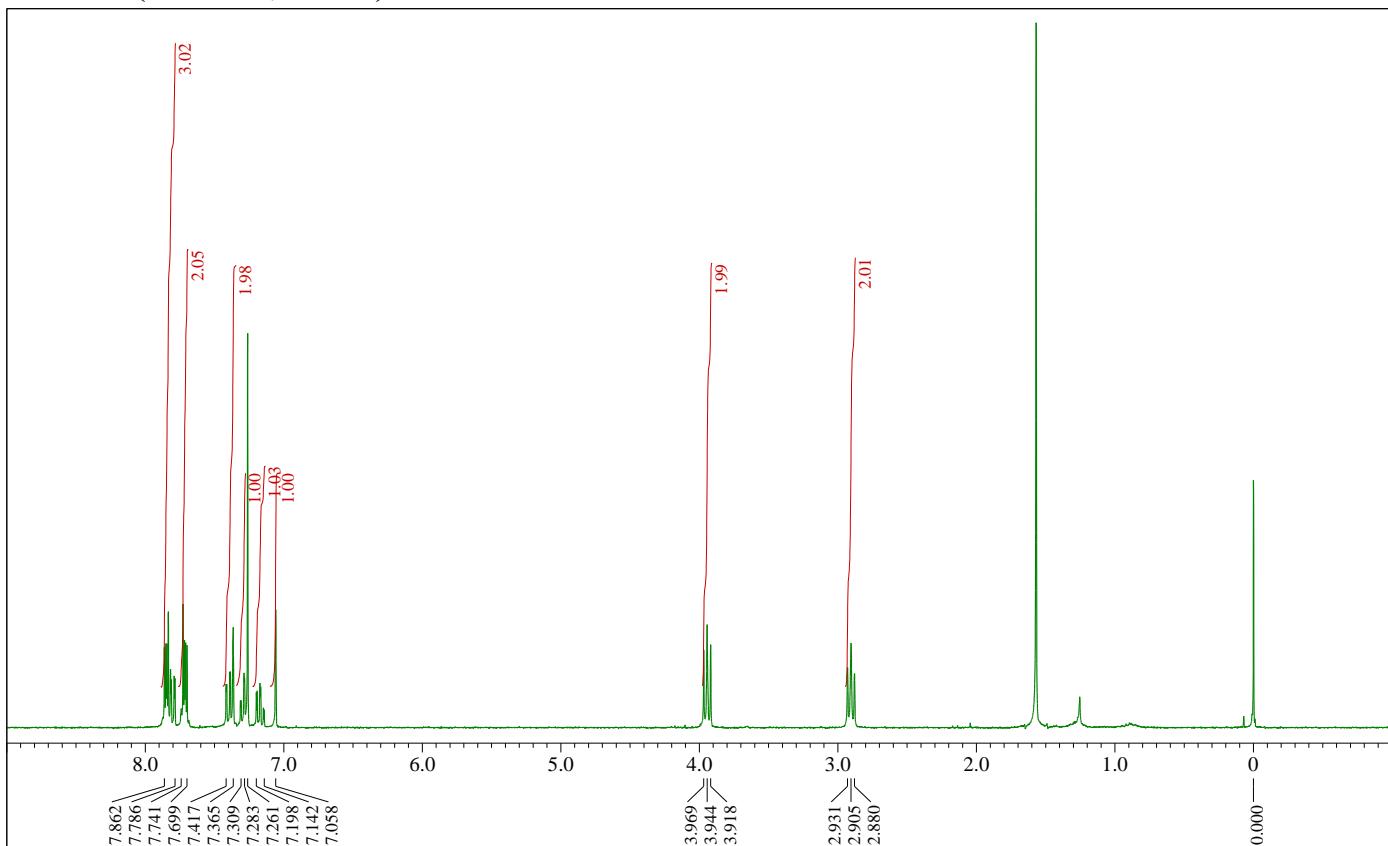
¹³C-NMR (100 MHz, CDCl₃)



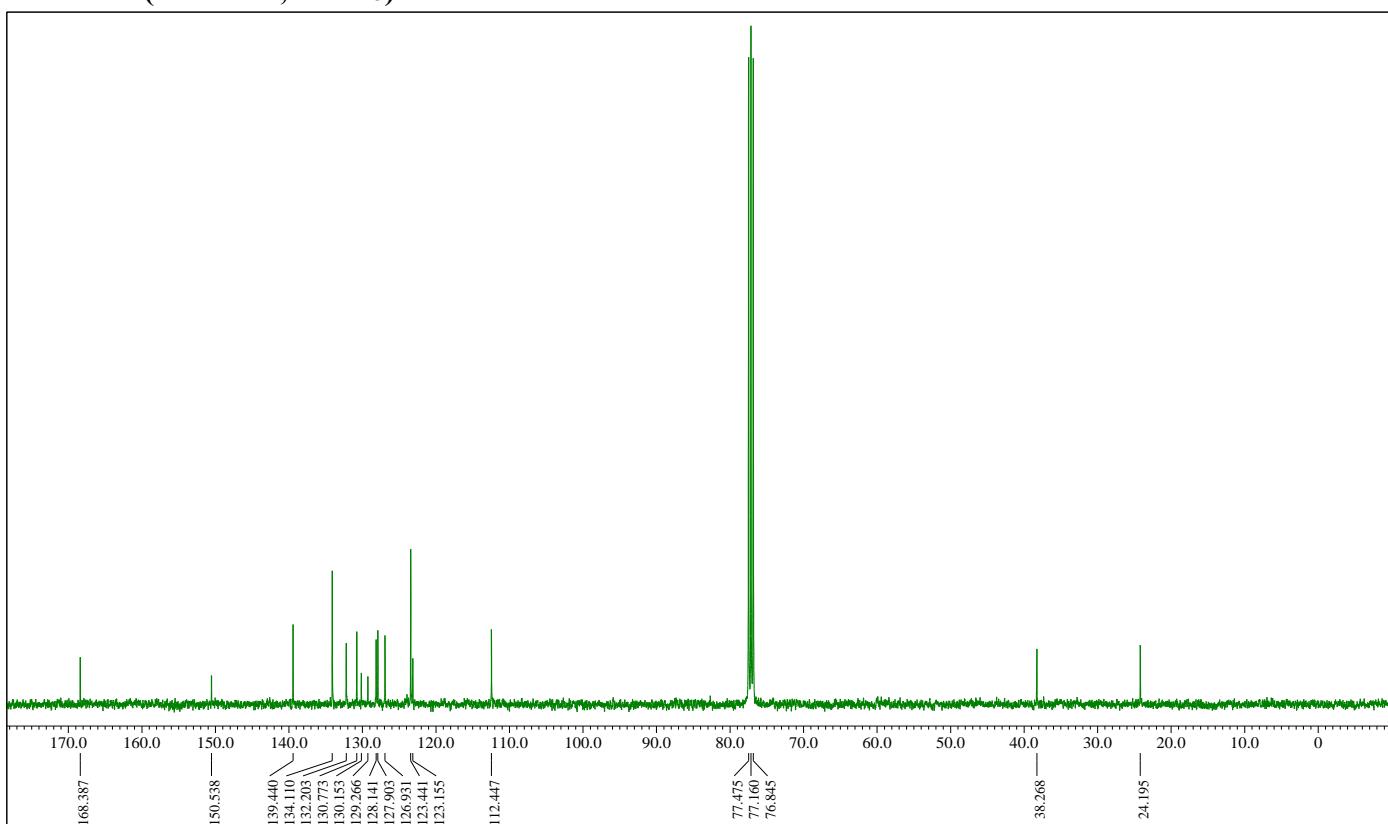
2-(2-(5-(2-Chlorophenyl)furan-3-yl)ethyl)isoindoline-1,3-dione (4m)



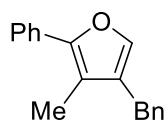
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



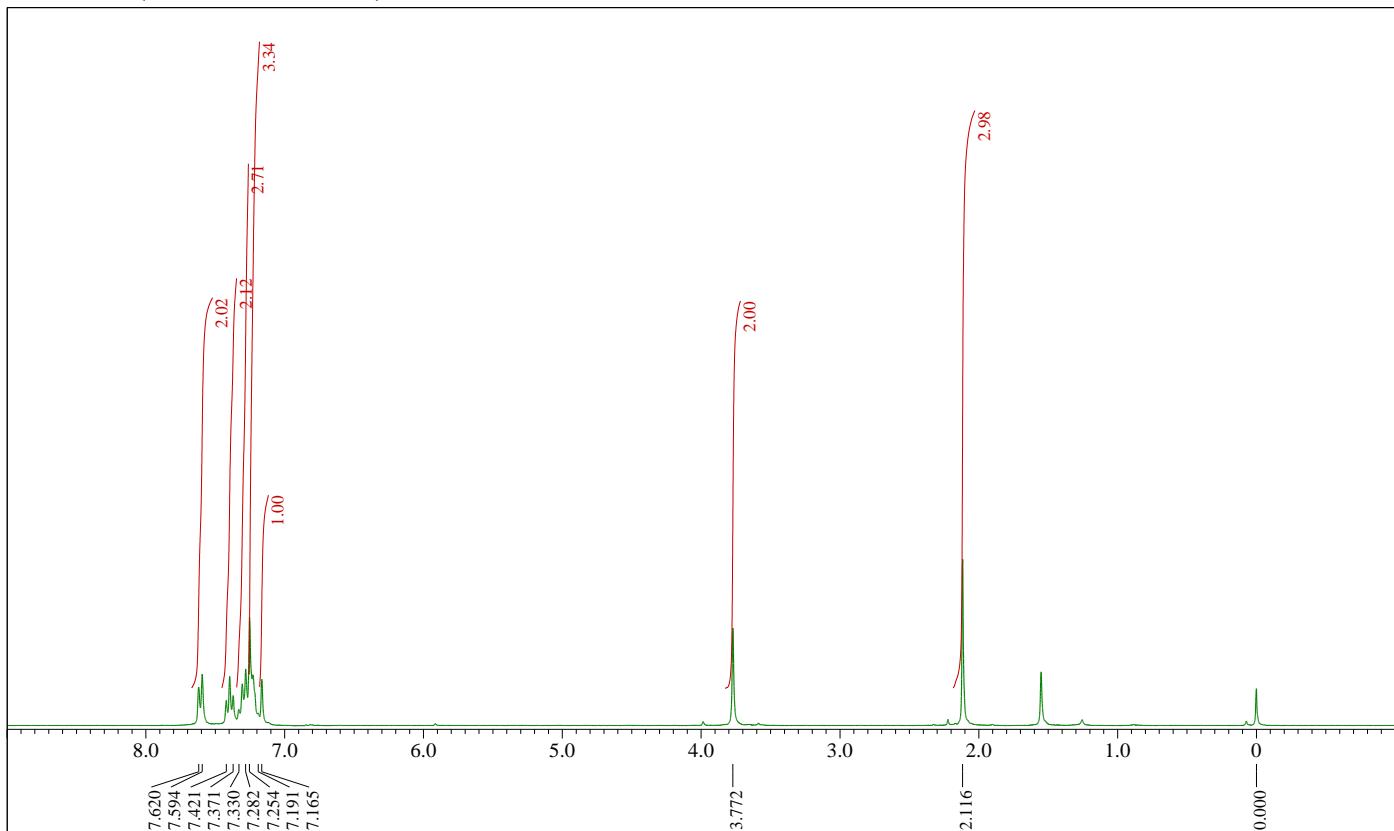
$^{13}\text{C-NMR}$ (100 MHz, CDCl_3)



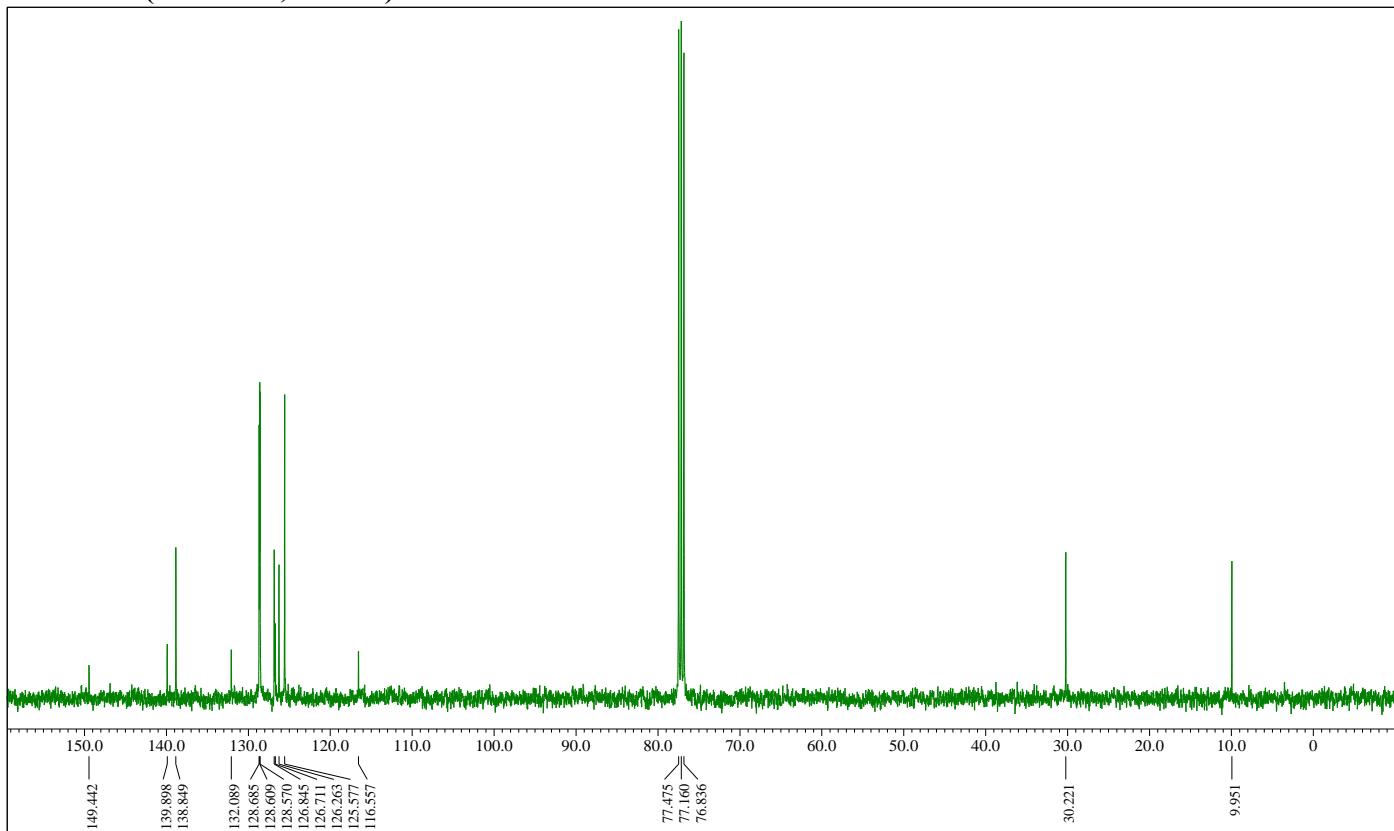
4-Benzyl-3-methyl-2-phenylfuran (4n)



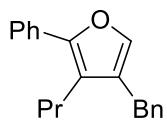
¹H-NMR (300 MHz, CDCl₃)



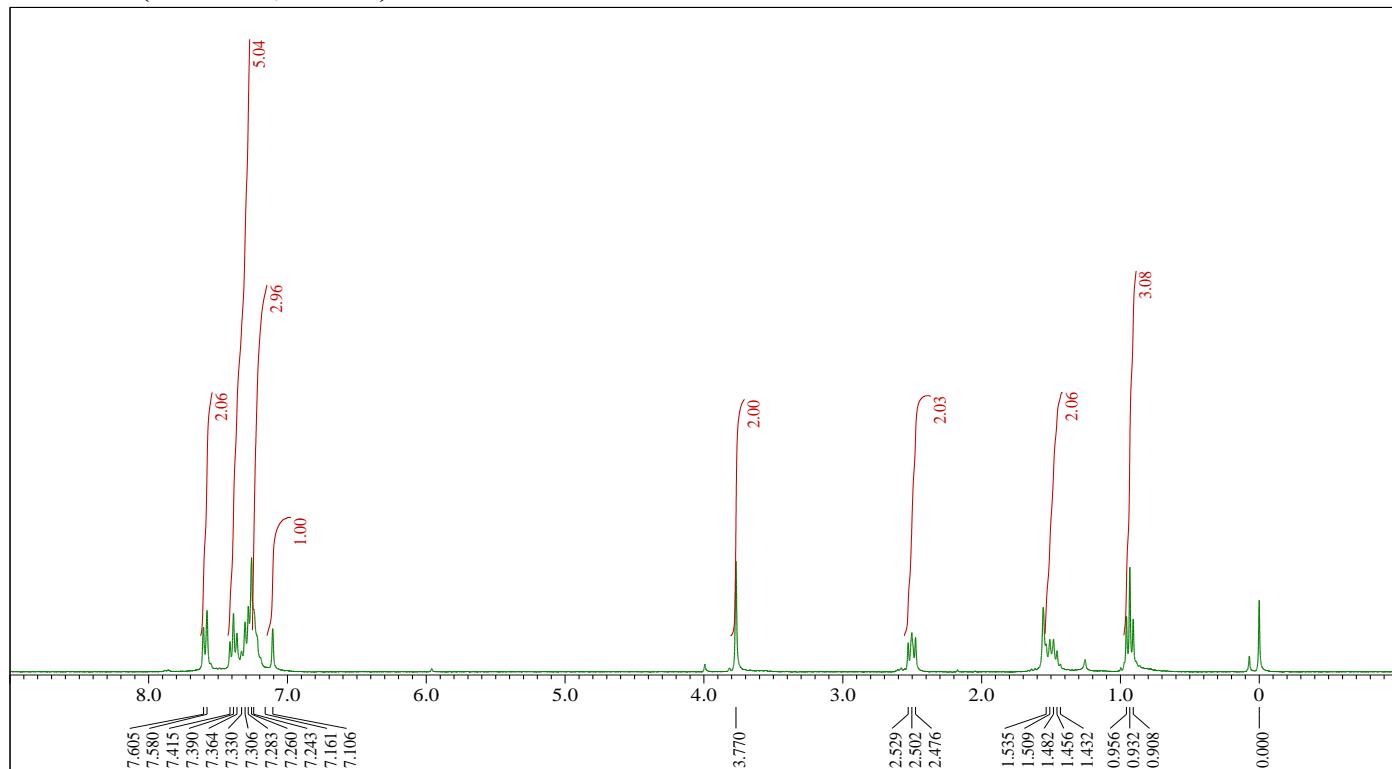
¹³C-NMR (100 MHz, CDCl₃)



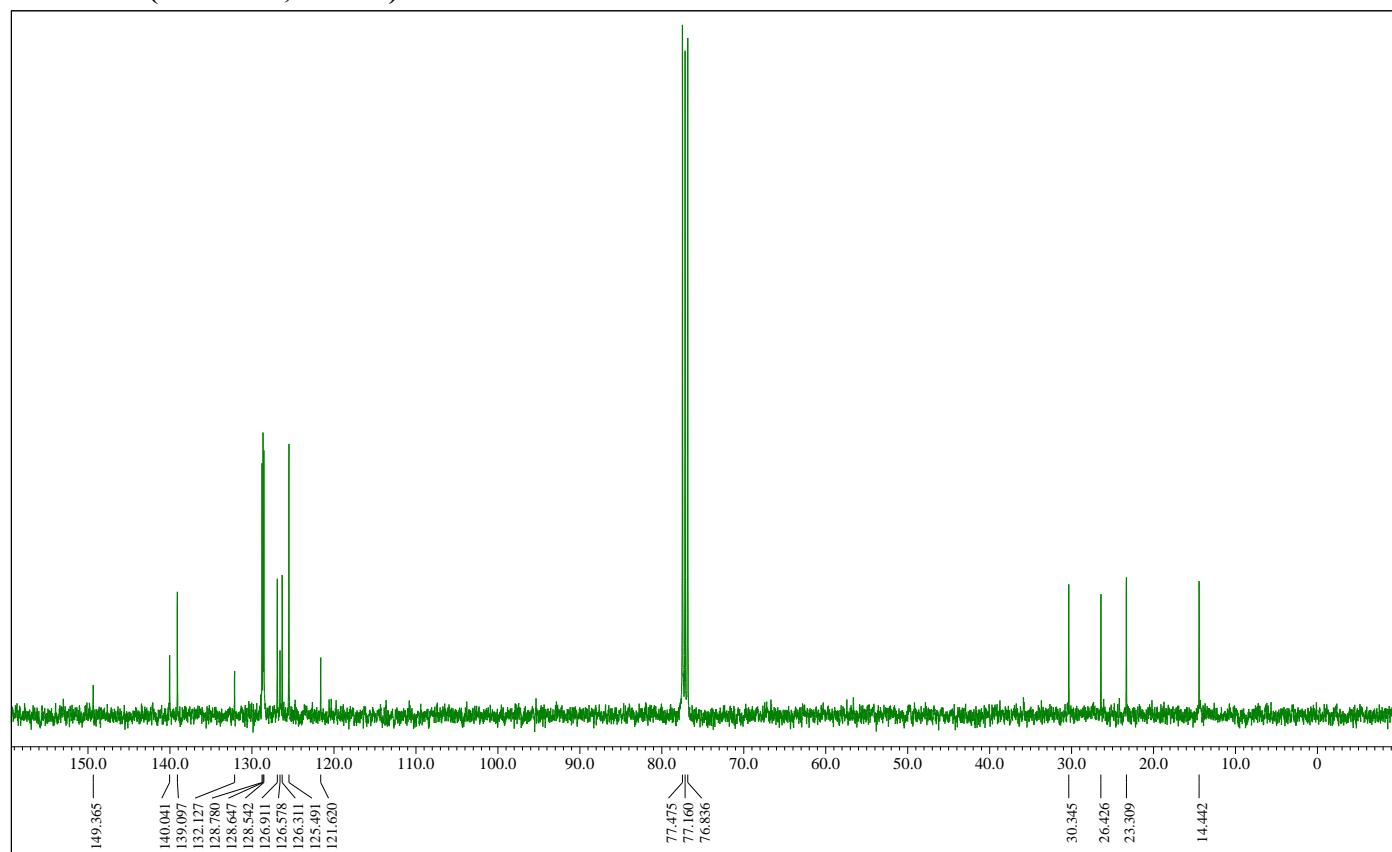
4-Benzyl-2-phenyl-3-propylfuran (4o)



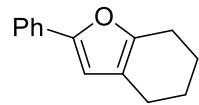
¹H-NMR (300 MHz, CDCl₃)



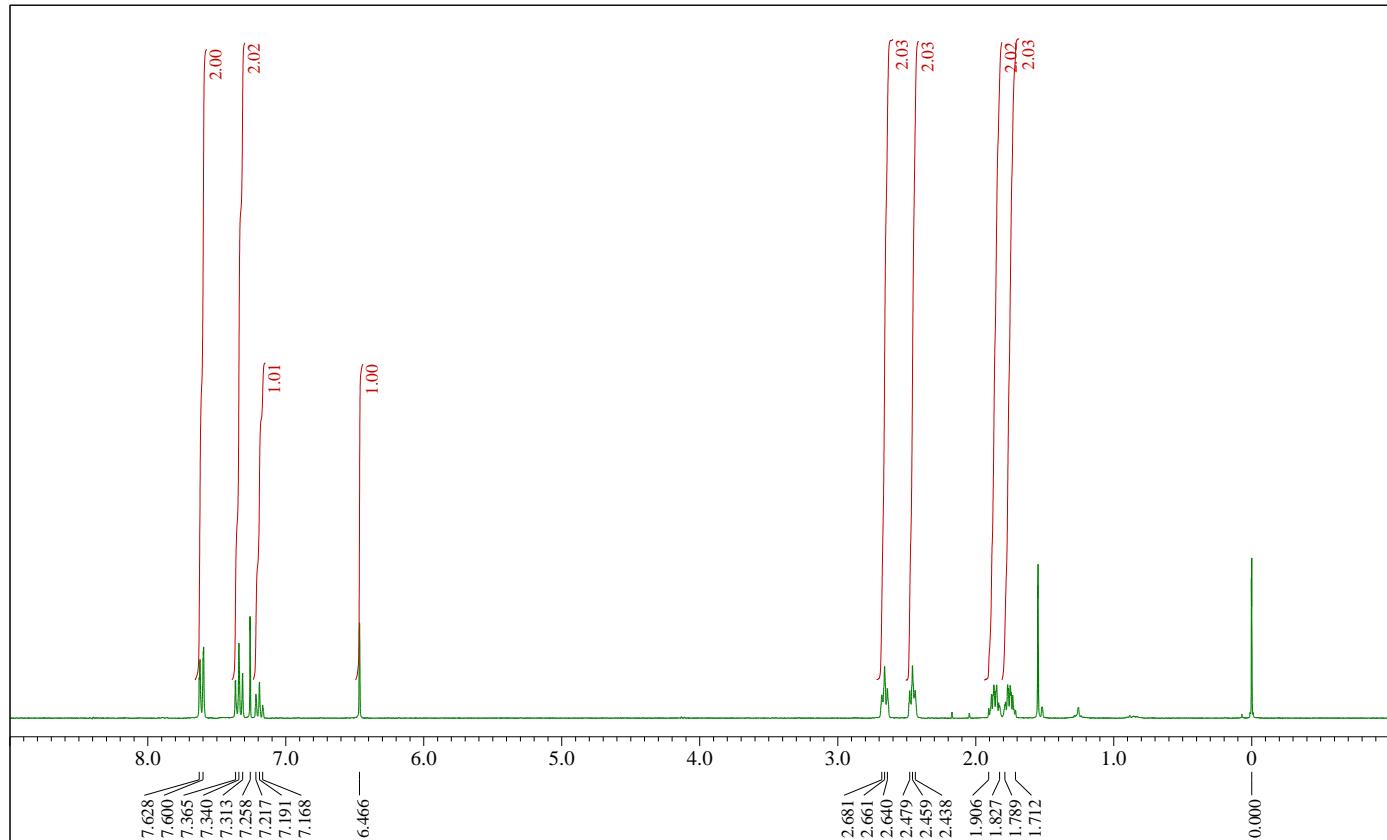
¹³C-NMR (100 MHz, CDCl₃)



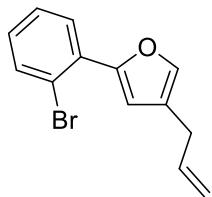
2-Phenyl-4,5,6,7-tetrahydrobenzofuran (4p)



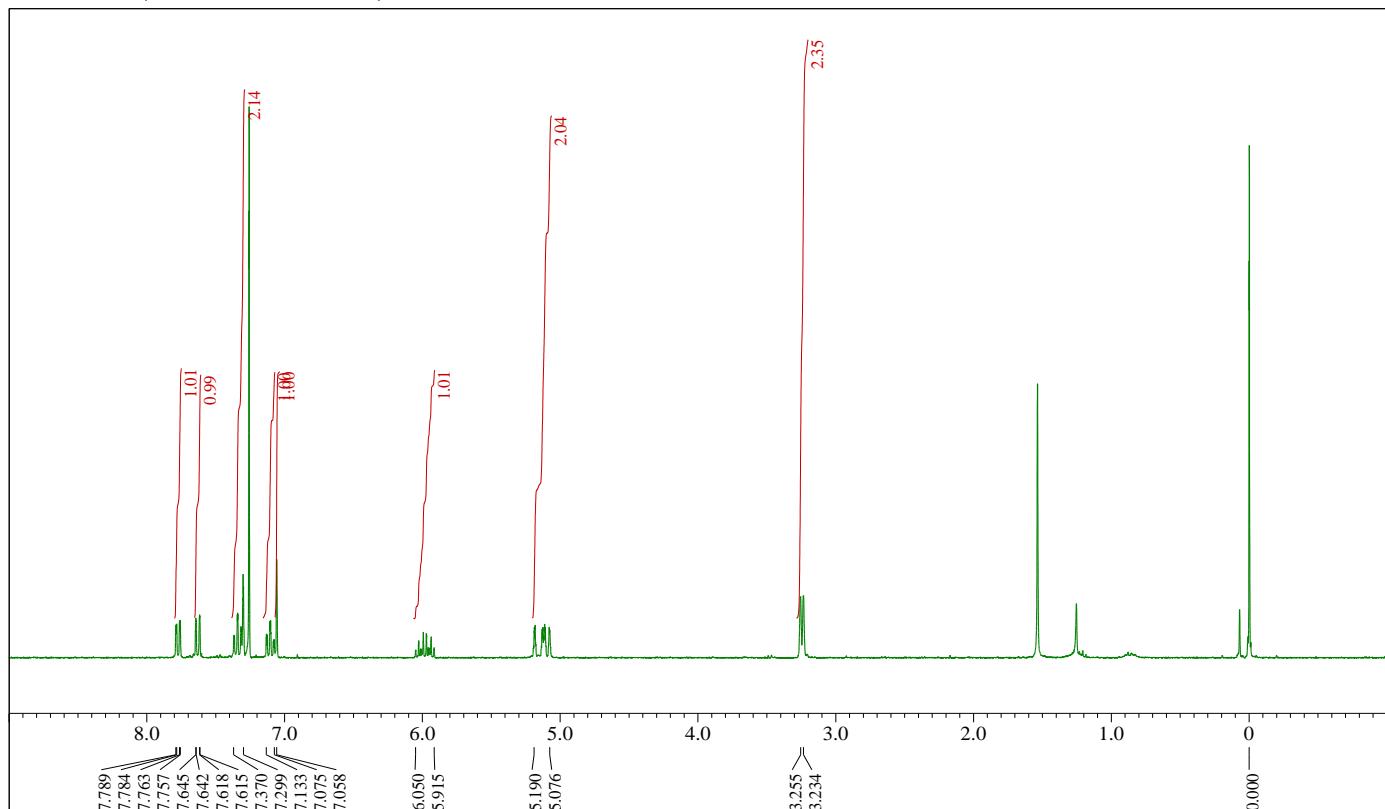
$^1\text{H-NMR}$ (300 MHz, CDCl_3)



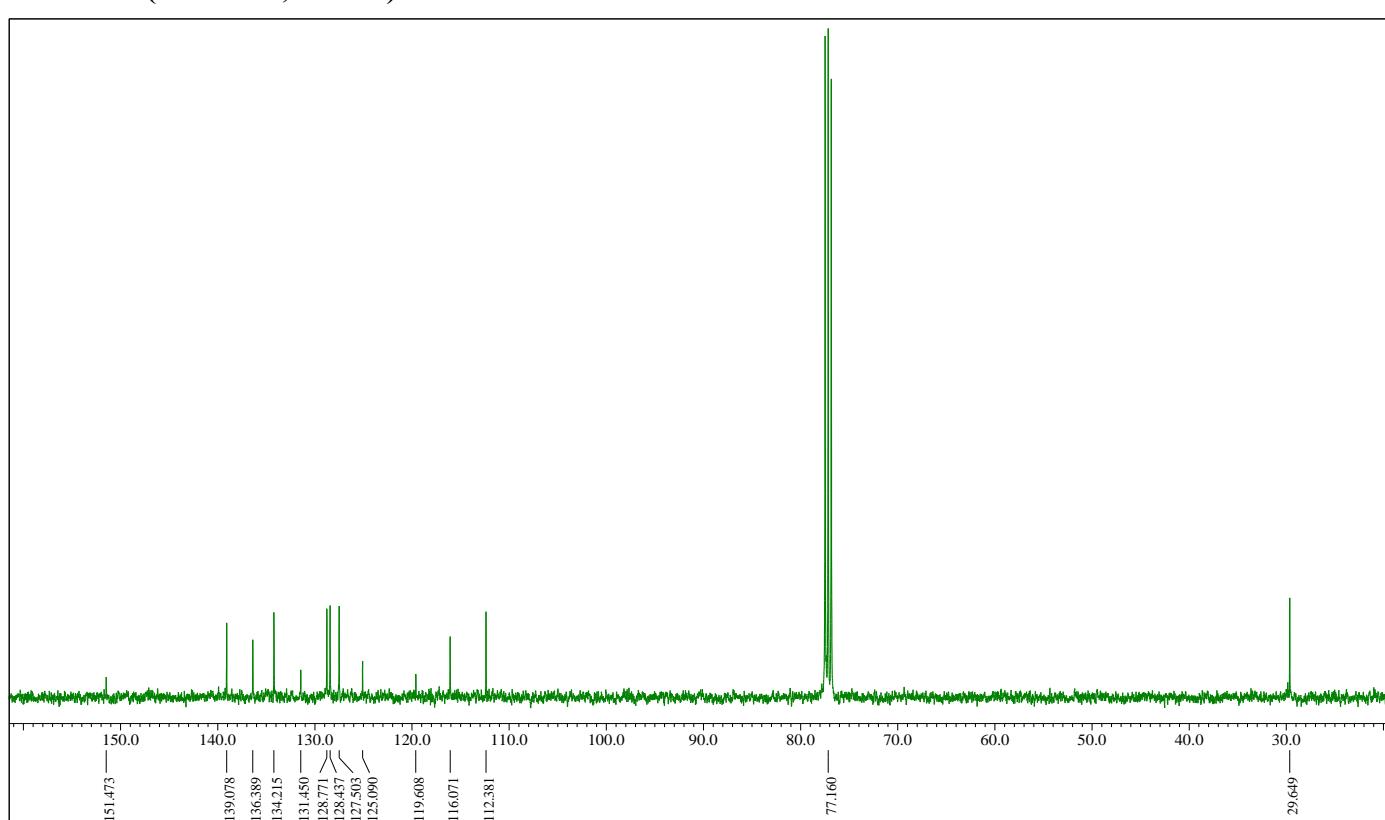
4-Allyl-2-(2-bromophenyl)furan (4q)



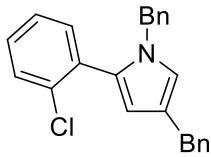
¹H-NMR (300 MHz, CDCl₃)



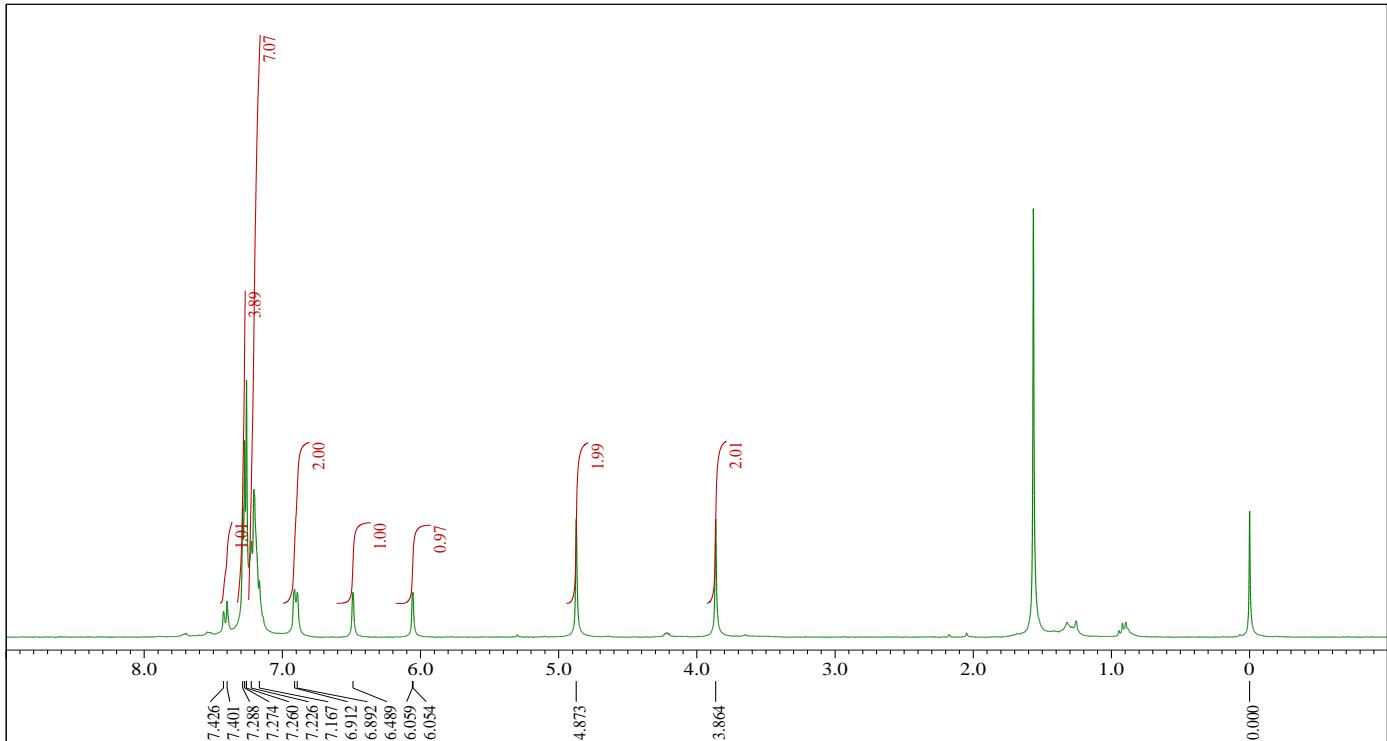
¹³C-NMR (100 MHz, CDCl₃)



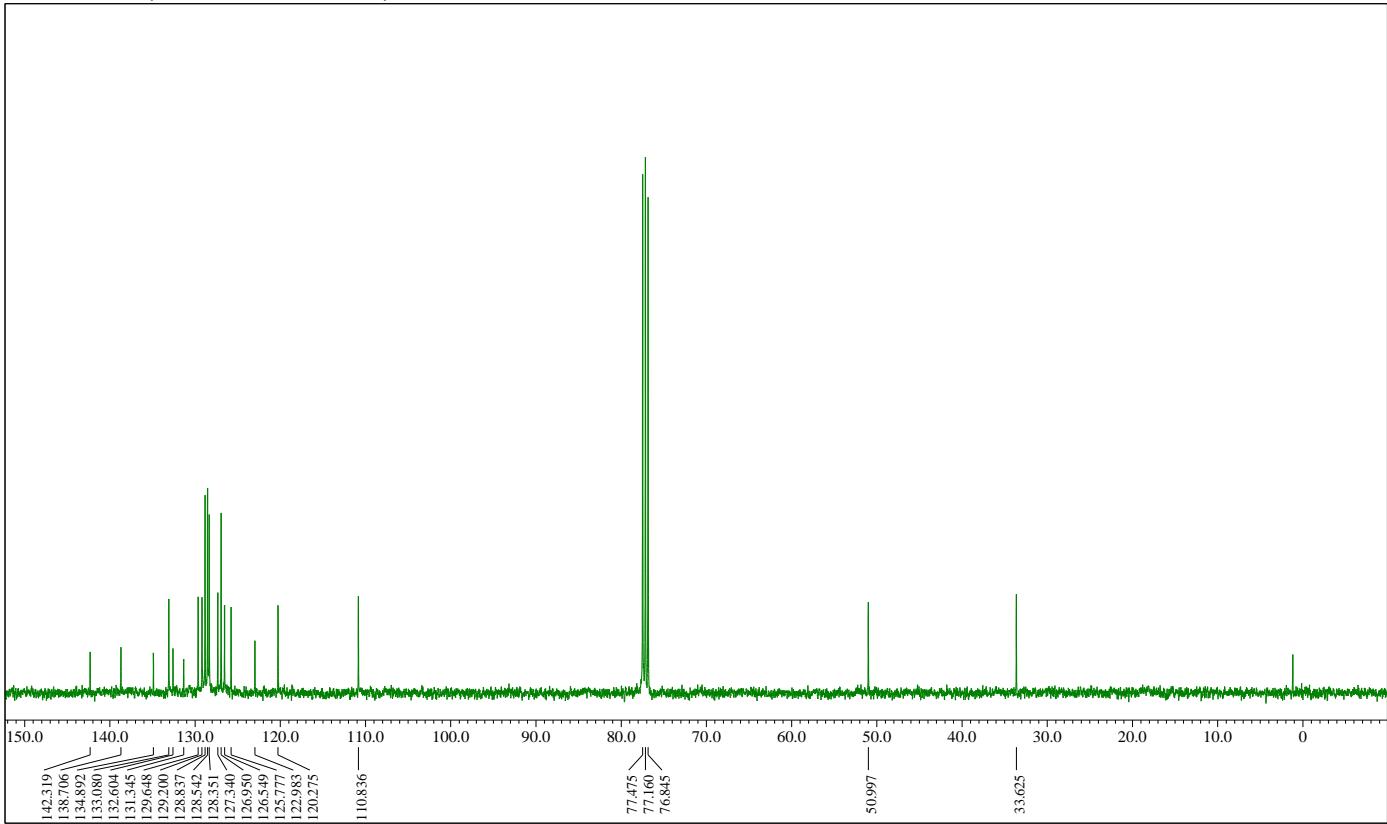
1,4-Dibenzyl-2-(2-chlorophenyl)-1*H*-pyrrole (6a)



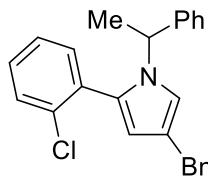
¹H-NMR (300 MHz, CDCl₃)



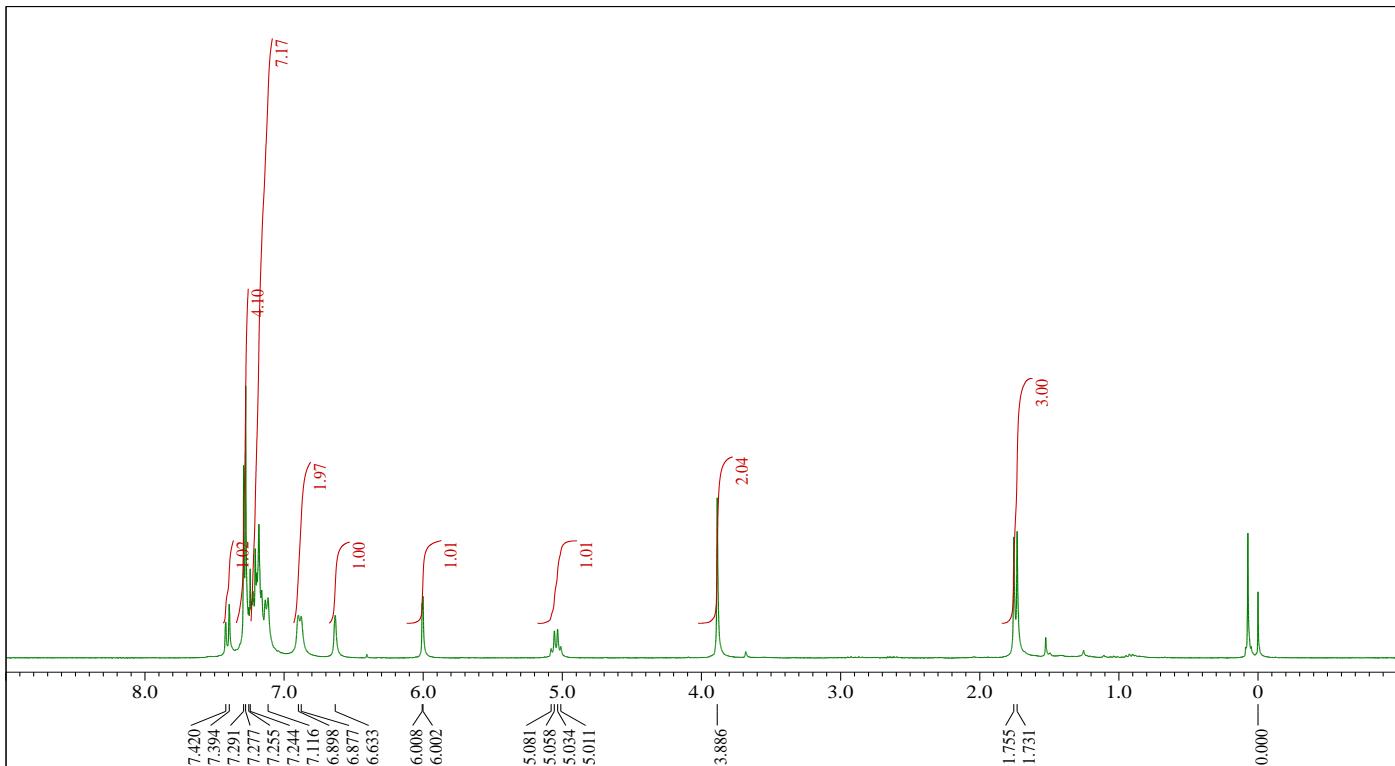
¹³C-NMR (100 MHz, CDCl₃)



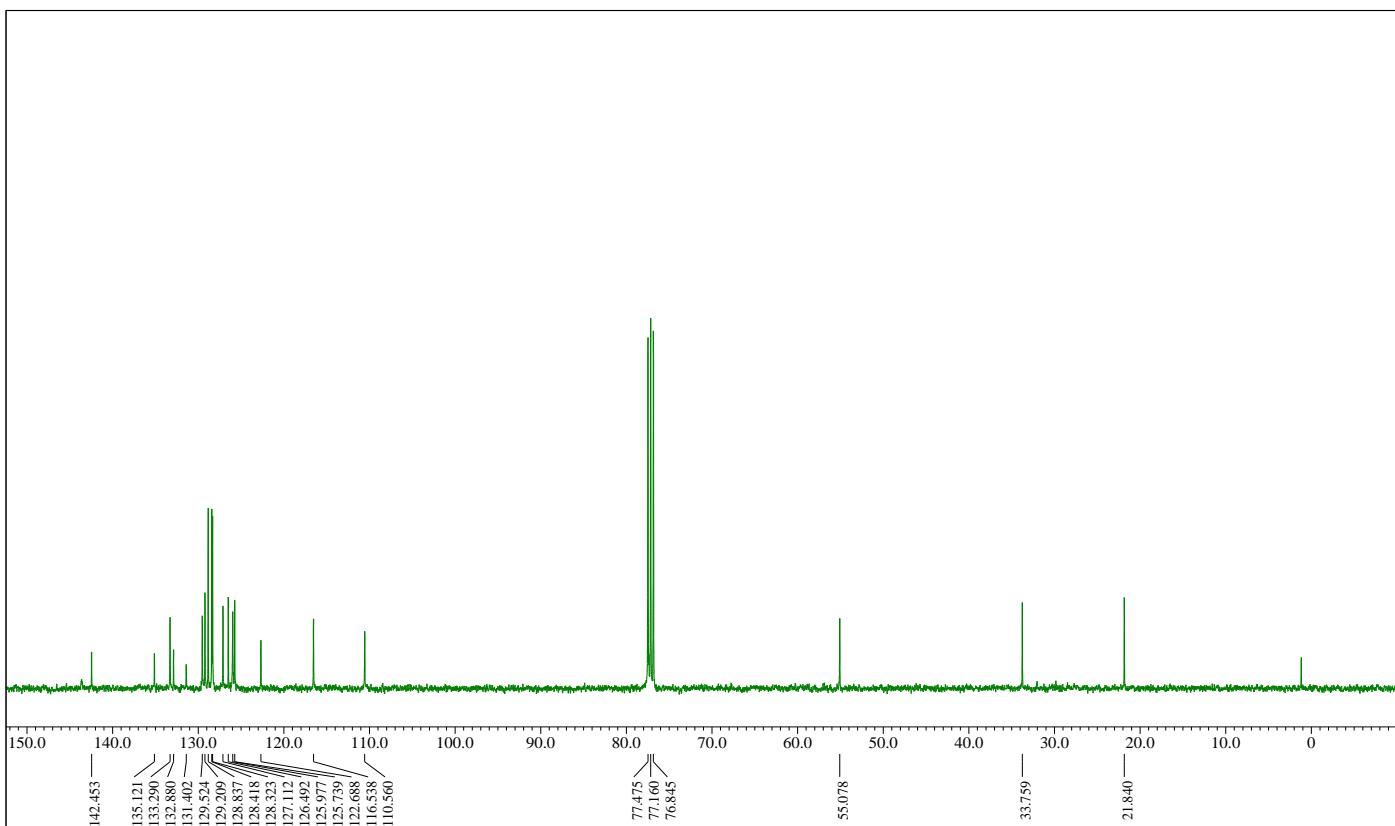
4-Benzyl-2-(2-chlorophenyl)-1-(1-phenylethyl)-1*H*-pyrrole (6b)



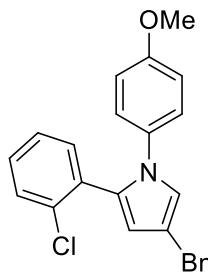
¹H-NMR (300 MHz, CDCl₃)



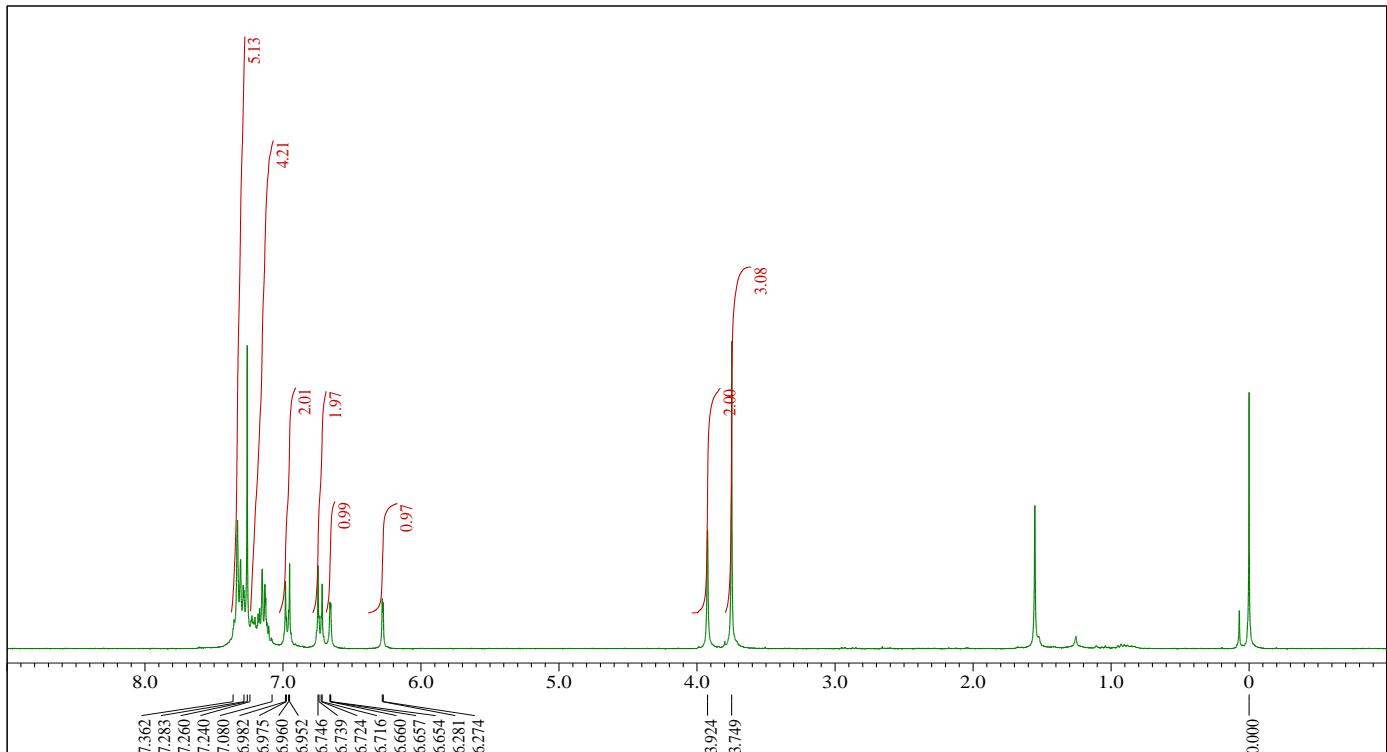
¹³C-NMR (100 MHz, CDCl₃)



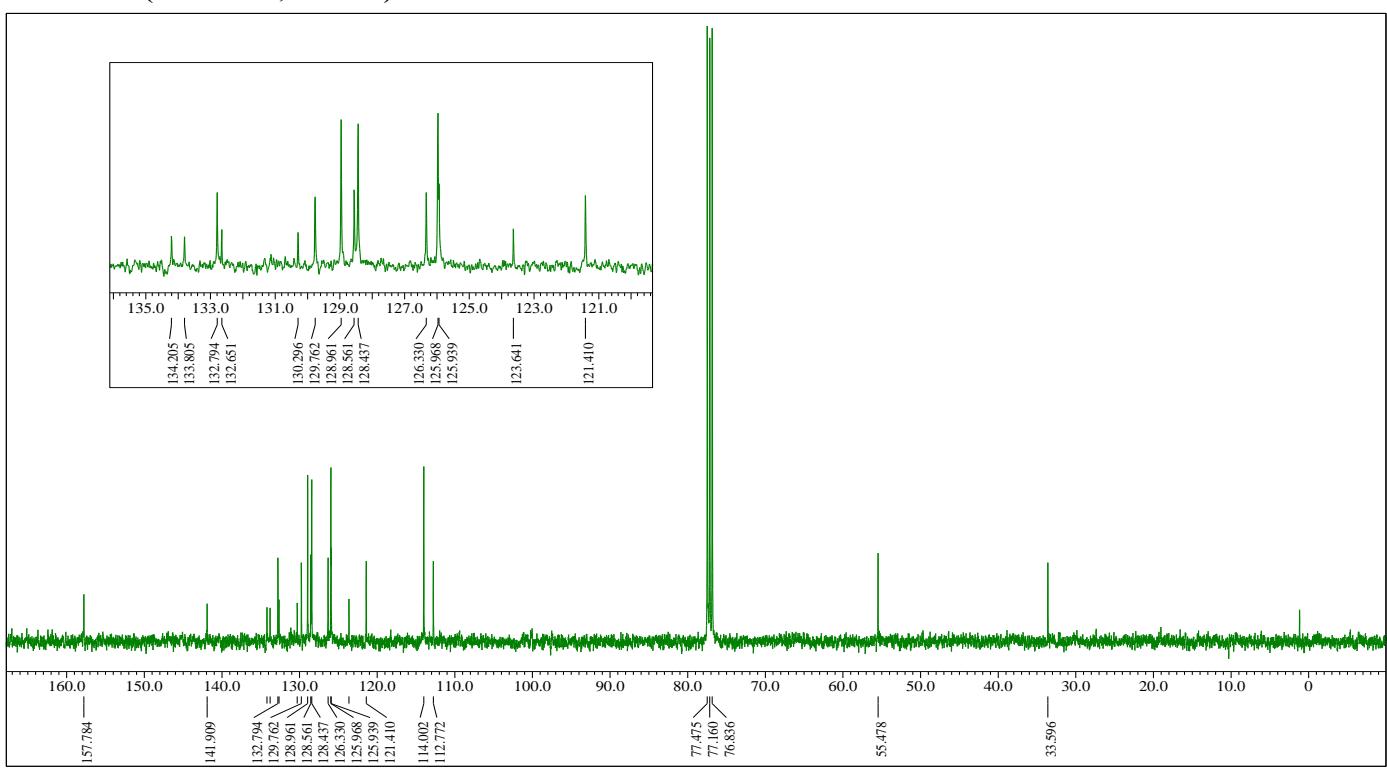
4-Benzyl-2-(2-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole (6c)



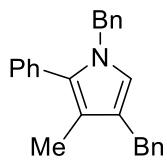
¹H-NMR (300 MHz, CDCl₃)



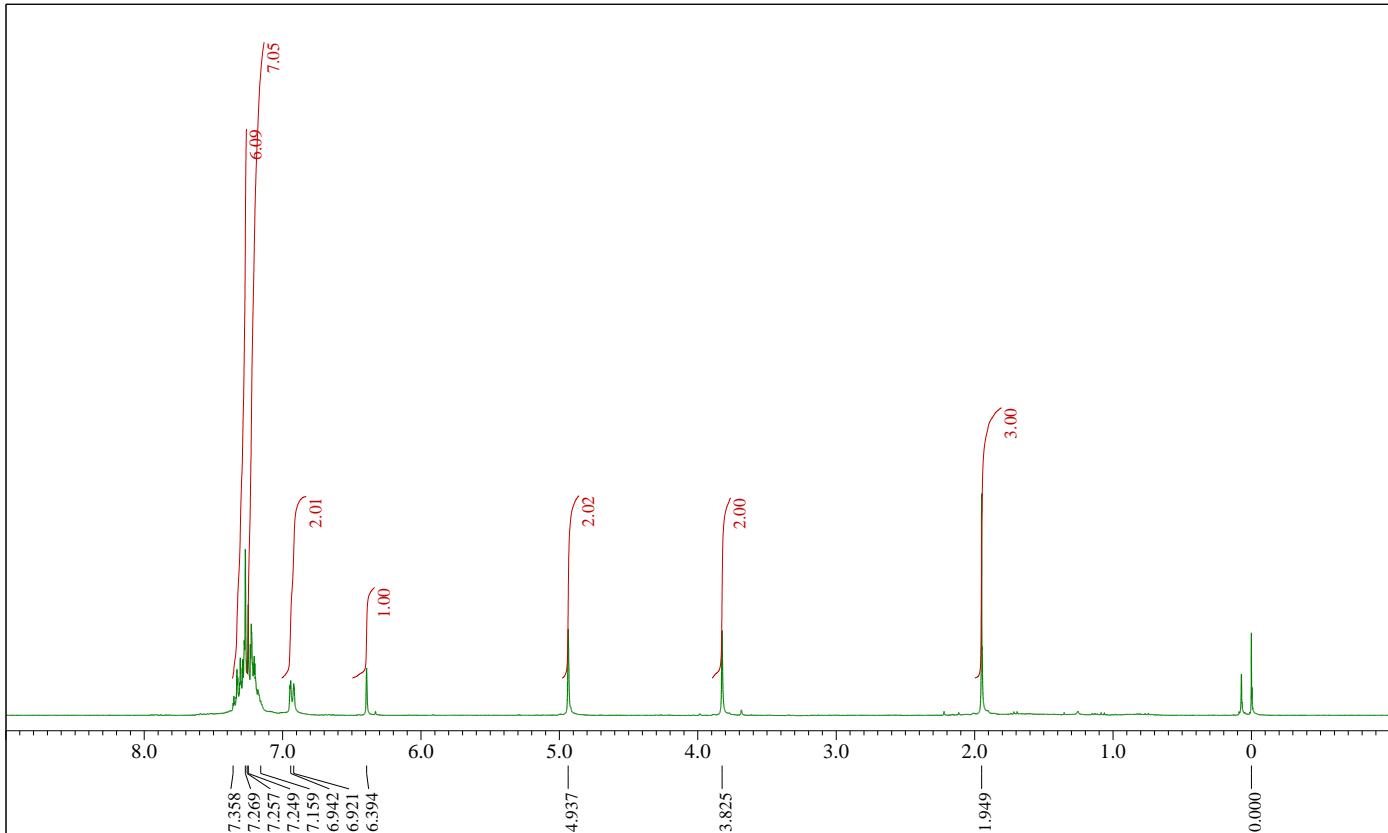
¹³C-NMR (100 MHz, CDCl₃)



1,4-Dibenzyl-3-methyl-2-phenyl-1*H*-pyrrole (6d)



¹H-NMR (300 MHz, CDCl₃)



¹³C-NMR (100 MHz, CDCl₃)

