Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Preparation of polysubstituted dihydrofurans through a $PhI(OAc)_2$-promoted haloenolcyclization of olefinic dicarbonyl compounds

Ji Liu,[a] Qing-Yun Liu,[a] Xing-Xiao Fang,[a] Gong-Qing Liu*[a] and Yong Ling*[a]

[a] *College of Pharmacy, Nantong University, 19 Qixiu Road, Nantong 226001, People's Republic of China*

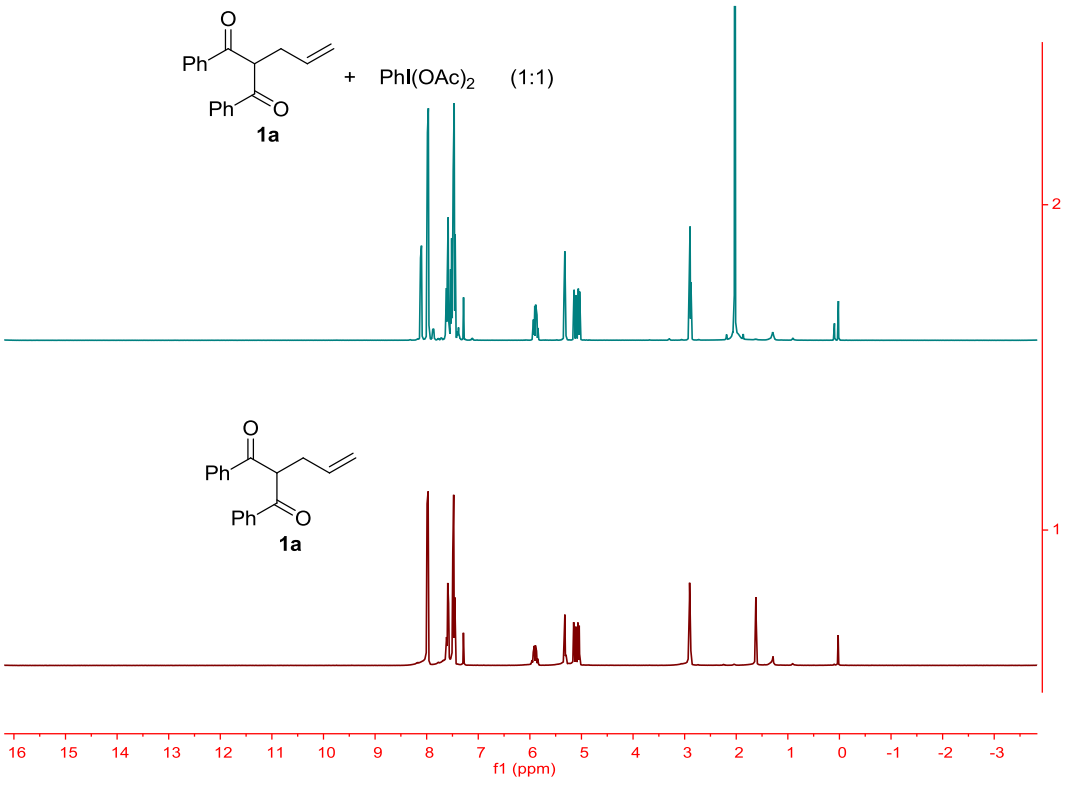
E-mail: gqliu@ntu.edu.cn; Lyyy111@sina.com

Contents

1. General information

Reagents were used as received without further purification unless otherwise indicated. Solvents were dried and distilled prior to use. Reactions were monitored with thin layer chromatography using silica gel GF_{254} plates. Organic solutions were concentrated *in vacuo* with a rotavapor. Flash column chromatography was performed using silica gel (200−300 meshes). Petroleum ether used had a boiling point range of 60−90 °C. Melting points were measured on a digital melting point apparatus without correction of the thermometer. Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) at 400 MHz (100 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were reported in ppm (δ) using TMS as internal standard, and spin−spin coupling constants (*J*) were given in Hz. High resolution mass spectrometry (HRMS) analyses were carried out on an FTICR HR-ESI-MS.

2. NMR experiments



3. General procedure for the preparation of olefinic dicarbonyl compounds.

Olefinic dicarbonyl compounds were prepared by allylation of dicarbonyl compounds according to the literature.[1-3]

4. General procedure for the preparation of 5-iodomethyl-4,5-dihydrofurans

The reaction was carried out in an open air system. In a 20 mL sealed tube were added olefinic 1,3-dicarbonyl compounds (0.5 mmol), $PhI(OAc)_2$ (0.5 mmol), and TMSI (0.5 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 12 h. CH_2Cl_2 (10 mL) was then added, and the mixture was washed with aqueous $Na_2S_2O_3$. The combined organic layer was dried (Na_2SO_4) and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products.

(5-(Iodomethyl)-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (2a). Compound **2a** was prepared according to the general procedure and isolated as a colorless solid (178 mg, 91% yield) after flash column chromatography (petroleum ether/ethyl acetate = 15/1); mp = 97.5–99.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.48 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.18 (m, 4H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 4.94 – 4.87 (m, 1H), 3.55 – 3.49 (m, 3H), 3.11 (dd, *J* = 15.5, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 193.2, 164.8, 138.8, 131.3, 130.1, 129.8, 129.3, 128.9, 127.68, 127.69, 111.7, 80.0, 39.2, 8.7. Spectral data are in agreement with literature values.[4]

(5-(Iodomethyl)-2-(4-methoxyphenyl)-4,5-dihydrofuran-3-yl)(4-methoxyphenyl) methanone (**2b**). Compound **2b** was prepared according to the general procedure and isolated as a colorless oil (203 mg, 90% yield) after flash column chromatography (petroleum ether /ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.55 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.67 – 6.64 (m, 4H), 4.88 – 4.84 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.51 – 3.45 (m, 3H),, 3.06 (dd, *J* = 15.3, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 192.0, 163.2, 162.3, 160.9, 131.5, 131.3, 130.9, 122.3, 113.2, 113.1, 110.0, 79.6, 55.33, 55.28, 39.7, 8.8. ESI–HRMS: calc. for $[C_{20}H_{19}IO_4+H]^+$: m/z = 451.0406, found: 451.0395.

(5-(Iodomethyl)-2-(*p*-tolyl)-4,5-dihydrofuran-3-yl)(p-tolyl)methanone (**2c**).

Compound **2c** was prepared according to the general procedure and isolated as a colorless oil (180 mg, 86% yield) after flash column chromatography (petroleum ether/ethyl acetate = 70/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.33 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.85 – 6.80 (m, 4H), 4.81 – 4.74 (m, 1H), 3.47 – 3.30 (m, 3H), 2.97 (dd, J = 15.4, 7.0 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 192.0, 163.1, 140.8, 139.3, 135.1, 128.2, 128.1, 127.4, 127.3, 125.9, 109.8, 78.8, 38.4, 20.4, 20.4, 7.7. ESI–HRMS: calc. for $[C_{20}H_{19}IO_2+H]^+$: m/z = 419.0508, found: 419.0508.

(4-Fluorophenyl)(2-(4-fluorophenyl)-5-(iodomethyl)-4,5-dihydrofuran-3-yl)methanone (**2d**). Compound **2d** was prepared according to the general procedure and isolated as a colorless solid (162 mg, 76% yield) after flash column chromatography (petroleum ether/ethyl acetate = 80/1); mp = 85.9–88.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.46 – 7.36 (m, 2H), 7.21 – 7.11 (m, 2H), 6.76 – 6.71 (m, 4H), 4.80 – 4.77 (m, 1H), 3.54 – 3.29 (m, 3H), 2.98 (dd, J = 15.5, 7.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm= -107.2, -108.4. ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 190.4, 164.4 (d, $J_{C\text{-}F}$ = 99.2 Hz), 162.5, 161.9 (d, $J_{C\text{-}F}$ = 98.4 Hz), 133.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.4 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.3 (d, $J_{C\text{-}F}$ = 4.3 Hz), 124.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 114.1 (d, $J_{C\text{-}F}$= 11.4 Hz), 113.9 (d, $J_{C\text{-}F}$= 11.3 Hz), 110.5. HRMS–ESI: calc. for $[C_{18}H_{13}F_2IO_2+H]^+$: m/z = 427.0007, found: 426.9993.

(4-Chlorophenyl)(2-(4-chlorophenyl)-5-(iodomethyl)-4,5-dihydrofuran-3-yl)methanone (**2e**). Compound **2e** was prepared according to the general procedure and isolated as a colorless solid (184 mg, 80% yield) after flash column chromatography (petroleum ether/ethyl acetate = 70/1); mp = 113.7-115.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.35 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 7.06 – 7.02 (m, 4H), 4.87 – 4.73 (m, 1H), 3.53 – 3.30 (m, 3H), 2.98 (dd, J = 15.6, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.4, 162.5, 137.0 136.0, 135.6, 129.5, 129.3, 127.2, 127.1, 127.0, 110.8, 78.9, 38.2, 7.7. HRMS–ESI: calc. for $[C_{18}H_{13}Cl_2IO_2+H]^+$: m/z = 458.9416, found: 458.9400.

(4-Bromophenyl)(2-(4-bromophenyl)-5-(iodomethyl)-4,5-dihydrofuran-3-yl)methanone (**2f**). Compound **2f** was prepared according to the general procedure and isolated as a colorless solid (222 mg, 81% yield) after flash column chromatography

(petroleum ether/ethyl acetate = 80/1); mp = 117.5-120.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.27 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.98 – 4.60 (m, 1H), 3.61 – 3.24 (m, 3H), 2.97 (dd, *J* = 15.6, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.5, 162.6, 136.4, 130.2, 130.1, 129.7, 129.4, 127.4, 125.4, 124.0, 110.9, 79.0, 38.2, 7.5. HRMS–ESI: calc. for $[C_{18}H_{13}Br_2IO_2+H]^+$: m/z = 546.8405, found: 546.8404.

1-(2-Ethyl-5-(iodomethyl)-4,5-dihydrofuran-3-yl)propan-1-one (**2g**). Compound **2g** was prepared according to the general procedure and isolated as a colorless oil (103 mg, 70% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 4.63 – 4.59 (m, 1H), 3.26 (q, *J* = 7.6 Hz, 2H), 3.05 (dd, *J* = 14.8, 10.3 Hz, 1H), 2.75 – 2.49 (m, 3H), 2.39 (q, *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 196.5, 170.8, 108.6, 79.1, 35.5, 33.6, 21.0, 10.1, 8.1, 6.9. HRMS–ESI: calc. for $[C_{10}H_{15}IO_2+H]^+$: m/z = 295.0195, found: 295.0186.

1-(5-(Iodomethyl)-2-phenyl-4,5-dihydrofuran-3-yl)ethanone (**2h**). Compound **2h** was prepared according to the general procedure and isolated as a colorless oil (51 mg, 31% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm= 7.63 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.47 (m, 3H), 4.83 – 4.76 (m, 1H), 3.61 (dd, *J* = 10.5, 5.1 Hz, 1H), 3.55 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.20 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.76 (dd, *J* = 15.2, 6.9 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ/ppm= 193.4, 164.5, 131.1, 130.9, 129.5, 128.7, 114.3, 80.0, 38.0, 29.4, 12.2. Spectral data are in agreement with literature values.[4]

(5-(Iodomethyl)-2-methyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**2h'**). Compound **2h'** was prepared according to the general procedure and isolated as a colorless oil (81 mg, 49% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm= 7.57 – 7.53 (m, 3H), 7.50 – 7.46 (m, 2H), 4.75 (m, 1H), 3.56 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.50 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.13 (dd, *J* = 14.6, 10.2 Hz, 1H), 2.69 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ/ppm= 192.1, 167.9, 141.1, 131.5, 128.8, 127.9, 112.2, 80.6, 37.6, 15.5, 11.8. HRMS–ESI: calc. for $[C_{13}H_{13}IO_2+H]^+$: m/z = 329.0038, found: 329.0027.

2-(Iodomethyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (2i). Compound **2i** was prepared according to the general procedure and isolated as a colorless oil (101 mg, 73% yield) after flash column chromatography (cyclohexane/ ethyl acetate = 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 4.91 – 4.77 (m, 1H), 3.46 – 3.23 (m, 2H), 3.11 – 2.91 (m, 1H), 2.59 (ddt, *J* = 14.9, 6.8, 1.9 Hz, 1H), 2.44 (ddt, *J* = 8.0, 5.9, 1.9 Hz, 2H), 2.38 – 2.31 (m, 2H), 2.09 – 2.01 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 195.4, 176.7, 112.9, 83.5, 36.4, 32.5, 23.9, 21.6, 8.3. Spectral data are in agreement with literature values.[5]

(5-(Iodomethyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**2j**). Compound **2j** was prepared according to the general procedure and isolated as a colorless oil (174 mg, 86% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.38 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.06 (m, 4H), 7.05 – 6.93 (m, 4H), 3.50 (d, *J* = 10.5 Hz, 1H), 3.45 (d, *J* = 10.5 Hz, 1H), 3.24 (d, *J* = 15.4 Hz, 1H), 3.17 (d, *J* = 15.4 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 192.4, 163.4, 137.8, 130.1, 129.0, 128.9, 128.3, 127.9, 126.6, 110.9, 84.1, 43.1, 25.1, 13.9. HRMS–ESI: calc. for $[C_{19}H_{17}IO_2+H]^+$: m/z = 405.0351, found: 405.0348.

(7-Iodo-2-phenyl-3a,4,5,6,7,7a-hexahydrobenzofuran-3-yl)(phenyl)methanone (**2k**). Compound **2k** was prepared according to the general procedure and isolated as a colorless oil (172 mg, 80% yield) after flash column chromatography (petroleum ether /ethyl acetate = 70/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.48 – 7.32 (m, 2H), 7.20 – 6.89 (m, 8H), 4.70 – 4.67 (m, 1H), 3.34 – 2.99 (m, 1H), 2.15 (dt, *J* = 15.1, 4.7 Hz, 2H), 1.86 – 1.69 (m, 1H), 1.63 – 1.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 192.9, 165.5, 138.3, 130.1, 129.5, 128.9, 128.5, 128.1, 126.7, 126.6, 118.3, 82.8, 43.4, 27.1, 26.2, 21.1, 19.6. Spectral data are in agreement with literature values.[6]

(2-(Iodomethyl)-6-phenyl-3,4-dihydro-2H-pyran-5-yl)(phenyl)methanone (**2l**). Compound **2l** was prepared according to the general procedure and isolated as a colorless oil (178 mg, 88% yield) after flash column chromatography (petroleum ether/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.44 (d, *J* = 7.2 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.11 – 7.08 (m, 1H), 7.03 – 6.85 (m, 5H), 4.22 – 4.08 (m,

1H), 3.36 (dd, *J* = 6.1, 3.5 Hz, 2H), 2.81 (ddd, *J* = 17.4, 6.2, 3.0 Hz, 1H), 2.39 (ddd, *J* = 17.4, 10.5, 6.9 Hz, 1H), 2.23 – 2.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 197.2, 159.1, 137.7, 133.9, 130.5, 128.47, 128.45, 128.2, 126.7, 110.9, 75.4, 26.2, 22.5, 5.7. HRMS–ESI: calc. for $[C_{19}H_{17}IO_2+H]^+$: m/z = 405.0351, found: 405.0347.

Ethyl 2-ethyl-5-(iodomethyl)-4,5-dihydrofuran-3-carboxylate (**2m**). Compound **2m** was prepared according to the general procedure and isolated as a colorless oil (118 mg, 76% yield) after flash column chromatography (petroleum ether/ethyl acetate = 80/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 4.63 – 4.56 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.23 (qd, *J* = 10.2, 5.9 Hz, 2H), 2.97 (dd, *J* = 14.8, 10.3 Hz, 1H), 2.65 – 4.51 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 170.9, 164.7, 99.7, 79.2, 58.6, 35.1, 20.3, 13.4, 10.2, 7.8. HRMS–ESI: calc. for $[C_{10}H_{15}IO_3+H]^+$: m/z = 311.0144, found: 311.0135.

5. Derivatizations of 2a.

General procedure for nucleophilic substitution of 2a. Compound **2a** was dissolved in 2 mL of DMF, the nucleophile of interest was added, and the reaction mixture was stirred for a given time. Then 20 mL of CH_2Cl_2 was added, and the reaction mixture was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding product.

(5-(Azidomethyl)-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**3**). Compound **3** was prepared according to the general procedure and isolated as a colorless oil (124 mg, 81% yield) after flash column chromatography (petroleum ether/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.48 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.13 – 7.07 (m, 4H), 5.09 – 5.02 (m, 1H), 3.62 (d, *J* = 5.0 Hz, 2H), 3.44 (dd, *J* = 15.3, 10.4 Hz, 1H), 3.13 (dd, *J* = 15.3, 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 193.2, 164.7, 138.7, 131.4, 130.2, 129.6, 129.3, 128.9, 127.73, 127.70, 111.7, 80.3, 54.5, 35.9. HRMS–ESI: calc. for $[C_{18}H_{15}N_3O_2+H]^+$: m/z =306.1243, found: 306.1241.

2-((4-Benzoyl-5-phenyl-2,3-dihydrofuran-2-yl)methyl)isoindoline-1,3-dione (**4**). Compound **4** was prepared according to the general procedure and isolated

as a colorless solid (155 mg, 76% yield) after flash column chromatography (petroleum ether/ethyl acetate = 60/1) ; mp = 132-134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.99 – 7.85 (m, 4H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.11 – 7.03 (m, 3H), 5.21 – 7.17 (m, 1H), 4.30 (dd, *J* = 14.2, 9.0 Hz, 1H), 3.88 (dd, *J* = 14.2, 3.8 Hz, 1H), 3.58 (dd, *J* = 15.3, 10.3 Hz, 1H), 3.06 (dd, *J* = 15.3, 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 193.3, 168.2, 165.4, 138.8, 134.3, 134.2, 132.0, 131.2, 130.0, 129.6, 128.9, 127.64, 127.61, 123.6, 123.5, 111.5, 78.6, 41.7, 36.2. HRMS–ESI: calc. for $[C_{26}H_{19}NO_4+H]^+$: m/z = 410.1392, found:410.1384.

(5-Methyl-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**5**). To a 100 mL flask was added tributyltinhydride (1.5 mmol), AIBN (0.025 mmol), **2a** (0.5 mmol) and 20 mL of toluene. The resulting solution was refluxed at 100 ℃ for 12 h. The residue obtained by concentration was purified by flash column chromatography to give the **5** as a colorless oil (88 mg, 92% yield) after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.34 (d, *J* = 8.4 Hz, 2H), 7.15 - 7.03 (m, 4H), 7.00 – 6.94 (m, 4H), 4.97 - 4.80 (m, 1H), 3.31 (dd, *J* = 14.7, 9.5 Hz, 1H), 2.87 (dd, *J* = 14.7, 8.2 Hz, 1H), 1.46 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 188.9, 161.2, 134.5, 126.2, 125.6, 125.2, 124.6, 124.1, 122.9, 107.3, 74.3, 35.3, 16.8. Spectral data are in agreement with literature values.[7]

6. General procedure for the preparation of furans

The mixture of iodomethyl dihydrofurans (0.5 mmol) and DBU (2 mmol) was stirred under nitrogen in 5 mL of benzene for 12 h at 60 °C. CH_2Cl_2 (10 mL) was then added, and the mixture was washed with diluted HCl. A few drops of H_2SO_4 (10 M) were added and the solution was stirred at room temperature until the completion of the reaction (TLC monitoring, usually 5 minutes). Then the solution was diluted with CH_2Cl_2 and washed with brine. The organic layer was dried (Na_2SO_4) and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products.

(5-Methyl-2-phenylfuran-3-yl)(phenyl)methanone (**6a**). Compound **6a** was prepared according to the general procedure and isolated as a colorless oil (116 mg, 89% yield) after flash column chromatography (petroleum ether/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.73 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.28 – 7.24 (m, 1H), 7.23 – 7.13 (m, 3H), 6.20 (d, *J* = 1.0 Hz, 1H), 2.29 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.9, 153.5, 150.1, 137.2, 131.6, 129.0, 128.6, 127.5, 127.18, 127.16, 126.2, 120.7, 108.7, 12.4. Spectral data are in agreement with literature values.[8]

(4-Methoxyphenyl)(2-(4-methoxyphenyl)-5-methylfuran-3-yl)methanone (**6b**). Compound **6b** was prepared according to the general procedure and isolated as a colorless oil (150 mg, 93% yield) after flash column chromatography (petroleum ether/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.77 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.29 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 189.7, 162.2, 158.7, 153.0, 149.3, 131.0, 130.1, 127.6, 122.0, 119.6, 112.7, 112.4, 108.6, 54.4, 54.2, 12.4. HRMS–ESI: calc. for $[C_{20}H_{18}O_4+H]^+$: m/z =323.1283, found: 323.1285.

(5-Methyl-2-(p-tolyl)furan-3-yl)(p-tolyl)methanone (**6c**). Compound **6c** was prepared according to the general procedure and isolated as a colorless oil (131 mg, 90% yield) after flash column chromatography (petroleum ether/ethyl acetate = 70/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.67 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.16 (s, 1H), 2.29 (s, 6H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.7, 153.3, 149.6, 142.4, 137.5, 134.7, 128.8, 127.9, 126.3, 126.0, 120.3, 108.7, 20.6, 20.3, 12.4. HRMS–ESI: calc. for $[C_{20}H_{18}O_2+H]^+$: m/z = 291.1385, found: 291.1386.

(4-Fluorophenyl)(2-(4-fluorophenyl)-5-methylfuran-3-yl)methanone (**6d**). Compound **6d** was prepared according to the general procedure and isolated as a colorless oil (142 mg, 95% yield) after flash column chromatography (petroleum ether/ethyl acetate = 80/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.78 (dd, *J* = 8.8, 5.5 Hz, 1H), 7.61 (dd, *J* = 8.9, 5.5 Hz, 1H), 7.03 – 6.85 (m, 4H), 6.19 (d, *J* = 1.0 Hz,

1H), 2.31 (d, J = 1.0 Hz, 1H),. ^{19}F NMR (376 MHz, $CDCl_3$) δ/ppm= -105.5, -111.7. ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 189.2, 165.8 (d, $J_{C\text{-}F}$ = 249.8 Hz), 161.8 (d, $J_{C\text{-}F}$ = 249.6 Hz), 152.7, 150.3, 133.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.2 (d, $J_{C\text{-}F}$ = 9.2 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 125.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 120.3, 114.5 (d, $J_{C\text{-}F}$ = 5.7 Hz), 114.3 (d, $J_{C\text{-}F}$ = 5.6 Hz), 108.6, 12.4. HRMS–ESI: calc. for $[C_{18}H_{12}F_2O_2+H]^+$: m/z = 299.0884, found: 299.0883.

(4-Chlorophenyl)(2-(4-chlorophenyl)-5-methylfuran-3-yl)methanone (**6e**). Compound **6e** was prepared according to the general procedure and isolated as a colorless solid (166 mg, 94% yield) after flash column chromatography (petroleum ether/ethyl acetate = 70/1). mp= 108.8-109.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.80 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 6.28 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.4, 153.5, 151.6, 139.3, 136.5, 134.7, 131.1, 128.7, 128.6, 128.5, 128.3, 121.7, 109.8, 13.4. HRMS–ESI: calc. for $[C_{18}H_{12}Cl_2O_2+H]^+$: m/z = 331.0293, found: 331.0290.

(4-Bromophenyl)(2-(4-bromophenyl)-5-methylfuran-3-yl)methanone (**6f**). Compound **6f** was prepared according to the general procedure and isolated as a colorless solid (200 mg, 95% yield) after flash column chromatography (petroleum ether/ethyl acetate = 70/1) ; mp = 115.0-116.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 6.27 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 190.6, 153.5, 151.7, 136.9, 131.7, 131.5, 131.2, 128.7, 128.6, 128.0, 123.1, 121.7, 109.9, 13.5. HRMS–ESI: calc. for $[C_{18}H_{12}Br_2O_2+H]^+$: m/z = 418.9282, found: 418.9271.

2-Methyl-6,7-dihydrobenzofuran-4(5H)-one (6g). Compound **6g** was prepared according to the general procedure and isolated as a colorless solid (68 mg, 90% yield) after flash column chromatography (petroleum ether/ethyl acetate = 60/1). mp = 37-38 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 6.25 (d, J = 1.1 Hz, 1H), 2.84 (t, J = 6.3 Hz, 2H), 2.54 – 2.43 (m, 2H), 2.31 (d, J = 1.1 Hz, 3H), 2.24 – 2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 194.6, 166.0, 152.6, 122.0, 101.9, 37.6, 23.3, 22.7, 13.4. Spectral data are in agreement with literature values.[9]

Phenyl(2-phenyl-3a,4,5,7a-tetrahydrobenzofuran-3-yl)methanone (**6h**). Compound **6h** was prepared according to the general procedure and isolated as a colorless oil (145 mg, 96% yield) after flash column chromatography (petroleum ether/ethyl acetate = 80/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.49 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.12 (m, 4H), 7.09 – 7.03 (m, 4H), 6.30 – 6.23 (m, 1H), 6.11 – 5.92 (m, 1H), 5.11 (d, *J* = 7.0 Hz, 1H), 3.63 (td, J = 9.0, 4.5 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.17 – 2.11 (m, 1H), 2.04 – 2.02 (m, 1H), 1.86 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 193.9, 166.4, 139.3, 134.8, 131.1, 130.4, 130.0, 129.5, 129.1, 127.62, 127.57, 123.5, 116.5, 78.3, 43.8, 23.9, 22.9. Spectral data are in agreement with literature values.[6]

Ethyl 2,5-dimethylfuran-3-carboxylate (**6i**). Compound **6i** was prepared according to the general procedure and isolated as a colorless oil (81 mg, 96% yield) after flash column chromatography (petroleum ether/ethyl acetate = 80/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 6.13 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.15 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 163.3, 156.5, 148.8, 113.0, 105.2, 58.9, 13.3, 12.6, 12.1. Spectral data are in agreement with literature values.[4]

7. General procedure for the preparation of 5-bromomethyl-4,5-dihydrofurans

The reaction was carried out in an open air system. In a 20 mL sealed tube were added olefinic 1,3-dicarbonyl compounds (0.5 mmol), $PhI(OAc)_2$ (0.5 mmol), and TMSBr (0.5 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 12 h. CH_2Cl_2 (10 mL) was then added, and the mixture was washed with aqueous $Na_2S_2O_3$. The combined organic layer was dried (Na_2SO_4) and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products.

(5-(Bromomethyl)-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**7a**). Compound **7a** was prepared according to the general procedure and isolated as a colorless oil (138 mg, 80% yield) after flash column chromatography (petroleum ether/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.47(d, *J* = 8.4 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 5.13 – 5.16 (m, 1H), 3.71 (dd, *J* = 10.3, 5.5 Hz, 1H), 3.68 (dd, *J*

= 10.3, 4.4 Hz, 1H), 3.52 (dd, *J* = 15.4, 10.2 Hz, 1H), 3.21 (dd, *J* = 15.4, 7.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 193.2, 165.0, 138.8, 131.3, 130.1, 129.6, 129.3, 128.9, 127.7, 127.7, 111.7, 79.8, 37.5, 34.6. HRMS–ESI: calc. for $[C_{18}H_{15}BrO_2+H]^+$: m/z = 343.0334, found: 343.0323.

(5-(Bromomethyl)-2-(4-methoxyphenyl)-4,5-dihydrofuran-3-yl)(4-methoxyphenyl)methanone (**7b**). Compound **7b** was prepared according to the general procedure and isolated as a colorless oil (143 mg, 71% yield) after flash column chromatography (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.45 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.95 – 4.92 (m, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.57 (d, *J* = 5.4 Hz, 2H), 3.37 (dd, *J* = 15.3, 10.1 Hz, 1H), 3.06 (dd, *J* = 15.3, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 191.0, 162.1, 161.3, 159.9, 130.4, 130.2, 129.9, 121.1, 112.2, 112.1, 108.9, 78.3, 54.29, 54.25, 37.1, 33.6. HRMS–ESI: calc. for $[C_{20}H_{19}BrO_4+H]^+$: m/z = 403.0545, found: 403.0540.

(5-(Bromomethyl)-2-(*p*-tolyl)-4,5-dihydrofuran-3-yl)(p-tolyl)methanone (**7c**). Compound **7c** was prepared according to the general procedure and isolated as a colorless oil (160 mg, 86% yield) after flash column chromatography (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.32 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 4.98 – 4.91 (m, 1H), 3.57 (d, *J* = 5.4 Hz, 2H), 3.37 (dd, *J* = 15.4, 10.1 Hz, 1H), 3.07 (dd, *J* = 15.4, 7.0 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 192.1, 163.2, 140.9, 139.3, 135.1, 128.2, 128.1, 127.4, 127.3, 125.8, 109.8, 78.5, 36.8, 33.5, 20.4, 20.3. HRMS–ESI: calc. for $[C_{20}H_{19}BrO_2+H]^+$: m/z = 371.0647, found: 371.0634.

(5-(Bromomethyl)-2-(4-fluorophenyl)-4,5-dihydrofuran-3-yl)(4-fluorophenyl)methanone (**7d**). Compound **7d** was prepared according to the general procedure and isolated as a colorless oil (144 mg, 76% yield) after flash column chromatography (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.44 – 7.37 (m, 2H), 7.21 – 7.12 (m, 2H), 6.76 – 6.71 (m, 4H), 5.01 – 4.97 (m, 1H), 3.62 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.57 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.40 (dd, *J* = 15.4, 10.3 Hz, 1H), 3.09 (dd, *J* = 15.4, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 191.4, 165.4 (d,

$J_{C\text{-}F}$ = 101.3 Hz), 163.6, 162.9 (d, $J_{C\text{-}F}$ = 100.5 Hz), 134.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.4 (d, $J_{C\text{-}F}$ = 5.6 Hz), 131.3 (d, $J_{C\text{-}F}$ = 5.9 Hz), 125.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.1 (d, $J_{C\text{-}F}$ = 10.6 Hz), 114.9 (d, $J_{C\text{-}F}$ = 10.5 Hz), 111.4, 79.7, 37.8, 34.7. HRMS–ESI: calc. for $[C_{18}H_{13}BrF_2O_2+H]^+$: m/z = 379.0145, found: 379.0133.

1-(5-(Bromomethyl)-2-ethyl-4,5-dihydrofuran-3-yl)propan-1-one (**7e**). Compound **7e** was prepared according to the general procedure and isolated as a colorless oil (84 mg, 68% yield) after flash column chromatography (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 5.76 – 5.58 (m, 1H), 4.99 – 4.73 (m, 1H), 3.56 – 3.29 (m, 2H), 3.15 – 3.00 (m, 1H), 2.84 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.41 (dd, *J* = 12.0, 6.1 Hz, 2H), 1.72 (t, *J* = 10.3 Hz, 3H), 1.35 – 1.15 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 196.4, 164.9, 108.0, 79.3, 36.5, 34.4, 33.8, 32.3, 21.0, 6.4. HRMS–ESI: calc. for $[C_{10}H_{15}BrO_2\text{-}H]^+$: m/z = 245.0117, found: 245.0158.

2-(Bromomethyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**7f**). Compound **7f** was prepared according to the general procedure and isolated as a colorless oil (70 mg, 60% yield) after flash column chromatography (cyclohexane/ ethyl acetate = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm= 5.09 – 4.90 (m, 1H), 3.52 (d, *J* = 5.4 Hz, 2H), 2.98 (ddt, *J* = 14.2, 10.2, 1.9 Hz, 1H), 2.69 (ddt, *J* = 14.8, 6.8, 1.9 Hz, 1H), 2.48 – 2.42 (m, 2H), 2.38 – 2.27 (m, 2H), 2.15 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ/ppm= 195.3, 176.8, 112.9, 83.2, 36.4, 34.2, 30.9, 23.8, 21.6. Spectral data are in agreement with literature values.[5]

(5-(Bromomethyl)-5-methyl-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (**7g**). Compound **7g** was prepared according to the general procedure and isolated as a colorless solid (110 mg, 62% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1) ; mp = 65.7-69.0 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ/ppm= 7.42 (d, *J* = 7.0 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.20 – 7.11 (m, 6H), 3.93 (d, *J* = 10.8 Hz, 1H), 3.91 (d, *J* = 10.8 Hz, 1H), 3.23 (d, *J* = 15.3 Hz, 1H), 3.08 (d, *J* = 15.3 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ/ppm= 192.7, 164.1, 139.4, 131.6, 130.5, 130.2, 129.4, 128.9, 128.14, 128.13, 111.9, 86.0, 43.1, 41.4, 25.3. Spectral data are in agreement with literature values.[10]

(5-(2-Bromopropan-2-yl)-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone

(**7h**). Compound **7h** was prepared according to the general procedure and isolated as a colorless solid (124 mg, 67% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1) ; mp = 134–135.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.40 – 7.39 (m, 2H), 7.14 – 7.06 (m, 3H), 7.04 – 6.85 (m, 5H), 4.19 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.36 (dd, *J* = 17.8, 5.9 Hz, 1H), 2.87 (dd, *J* = 17.8, 8.6 Hz, 1H), 1.57 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 196.0, 158.0, 137.7, 134.0, 130.5, 128.6, 128.4, 128.1, 126.71, 126.69, 108.8, 77.4, 50.7, 32.0, 25.6, 20.6. HRMS–ESI: calc. for $[C_{20}H_{19}BrO_2+H]^+$: m/z = 371.0647, found: 371.0638.

(7-Bromo-2-phenyl-3a,4,5,6,7,7a-hexahydrobenzofuran-3-yl)(phenyl)methanone (**7i**). Compound **7i** was prepared according to the general procedure and isolated as a colorless oil (123 mg, 64% yield) after flash column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.45 – 7.36 (m, 2H), 7.13 – 7.07 (m, 4H), 7.00 – 6.94 (m, 4H), 4.72 – 4.66 (m, 1H), 3.29 – 3.11 (m, 1H), 2.19 – 2.07 (m, 2H), 1.78 (d, *J* = 5.6 Hz, 1H), 1.57 – 1.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 193.3, 164.7, 138.7, 131.7, 130.3, 129.8, 129.5, 129.1, 128.6, 127.9, 127.8, 116.8, 86.0, 50.9, 44.8, 32.2, 25.5, 20.7. HRMS–ESI: calc. for $[C_{21}H_{19}BrO_2+H]^+$: m/z = 383.0647, found: 383.0646.

(2-(Bromomethyl)-6-phenyl-3,4-dihydro-2H-pyran-5-yl)(phenyl)methanone (**7j**). Compound **7j** was prepared according to the general procedure and isolated as a colorless oil (143 mg, 80% yield) after flash column chromatography (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm= 7.45 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 6.3 Hz, 2H), 7.12 – 7.08 (m, 3H), 7.05 – 6.91 (m, 5H), 4.29 – 4.27 (m, 1H), 3.58 (dd, *J* = 10.7, 6.7 Hz, 1H), 3.52 (dd, *J* = 10.7, 5.2 Hz, 1H), 2.87 – 2.80 (m, 1H), 2.45 – 2.40 (m, 1H), 2.18 – 2.12 (m, 1H), 1.80 – 1.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm= 197.3, 159.1, 137.7, 133.9, 130.5, 128.5, 128.4, 128.2, 126.67, 126.65, 111.0, 75.2, 32.5, 24.8, 22.4. HRMS–ESI: calc. for $[C_{19}H_{17}BrO_2+H]^+$: m/z = 357.0490, found: 357.0482.

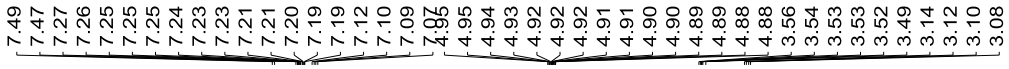
8. References

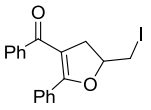
(1) Yang, N.-Y.; Li, Z.-L.; Ye, L.; Tan, B.; Liu, X.-Y. *Chem. Comm.* **2016**, *52*, 9052.

(2) Yang, W.; Huang, L.; Liu, H.; Wang, W.; Li, H. *Chem. Commun.* **2013**, *49*, 4667.

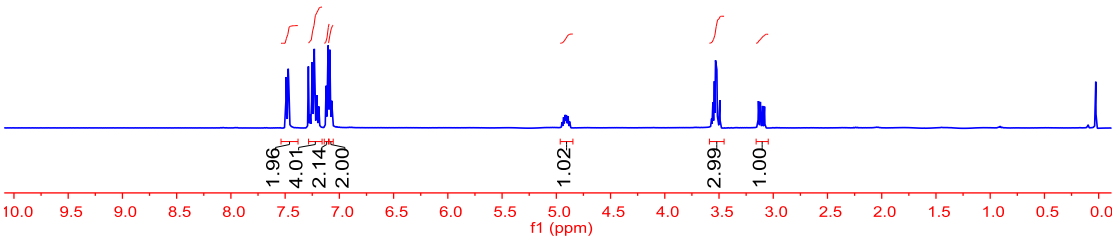
(3) Kalaitzakis, D.; Rozzell, J. D.; Smonou, I.; Kambourakis, S. *Adv. Synth. Catal.* **2006**, *348*, 1958.
(4) Tang, E.; Huang, X.; Xu, W.-M. *Tetrahedron* **2004**, *60*, 9963.
(5) Mphahlele, M. J.; Moekwa, T. B. *Org. Biomol. Chem.* **2005**, *3*, 2469.
(6) Antonioletti, R.; Cecchini, C.; Ciani, B.; Magnanti, S. *Tetrahedron Lett.* **1995**, *36*, 9019.
(7) Zhang, J.; Tang, Y.; Wei, W.; Wu, Y.; Li, Y.; Zhang, J.; Zheng, Y.; Xu, S. *Org. Lett.* **2017**, *19*, 3043.
(8) Han, X.; Widenhoefer, R. A. *J. Org. Chem.* **2004**, *69*, 1738.
(9) Tamaso, K.-i.; Hatamoto, Y.; Obora, Y.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2007**, *72*, 8820.
(10) Zhao, Y.; Jiang, X.; Yeung, Y.-Y. *Angew. Chem. Int. Ed* **2013**, *52*, 8597.

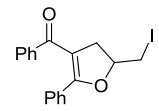
9. Copies of NMR spectra



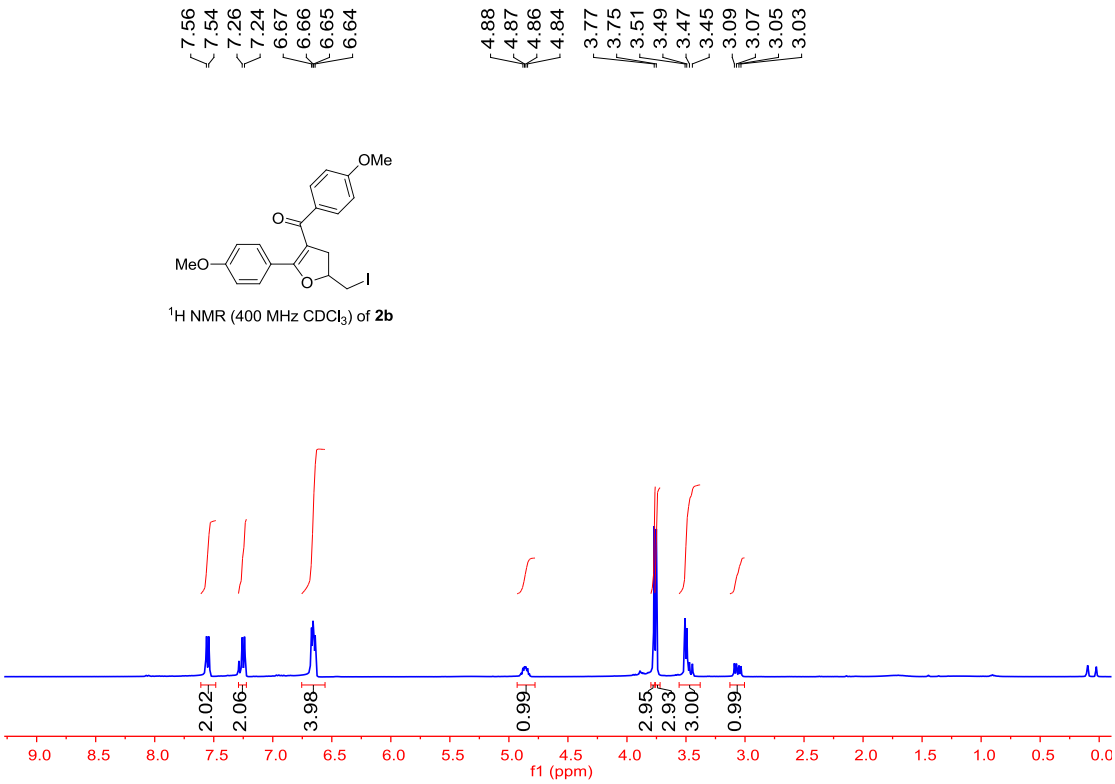


^{1}H NMR (400 MHz, $CDCl_3$) of **2a**

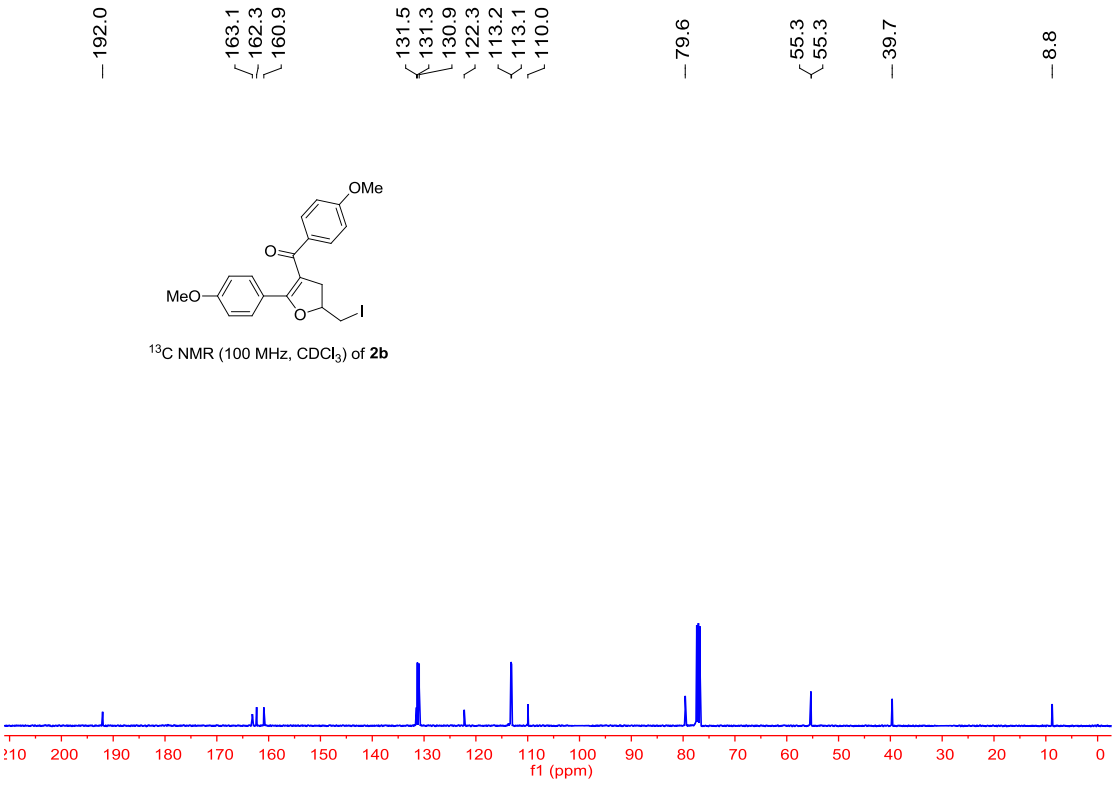




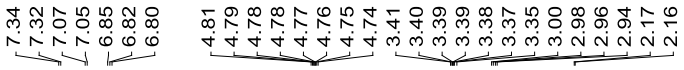
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**

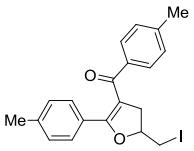


^{1}H NMR (400 MHz $CDCl_3$) of **2b**

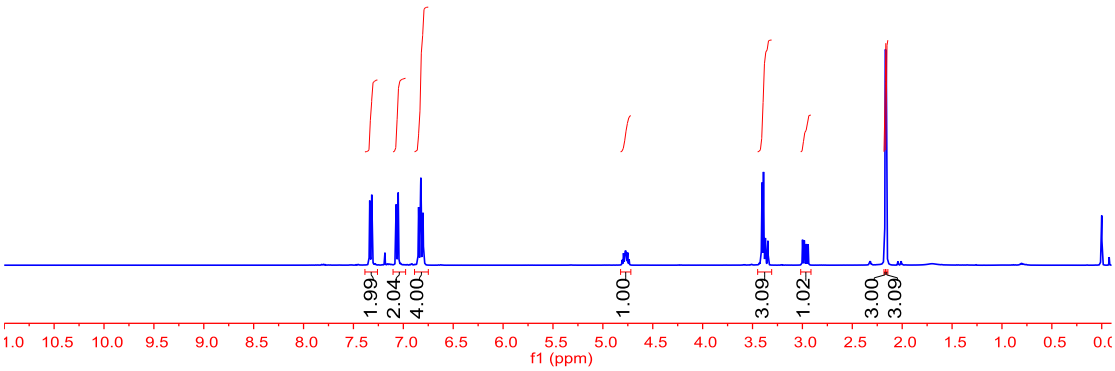


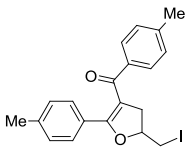
^{13}C NMR (100 MHz, $CDCl_3$) of **2b**



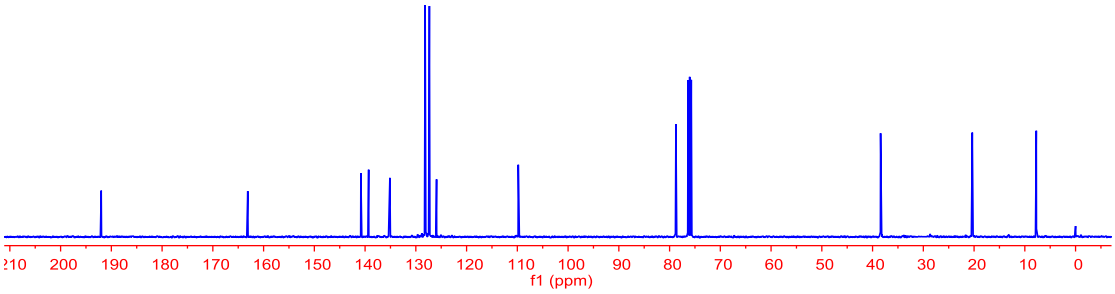


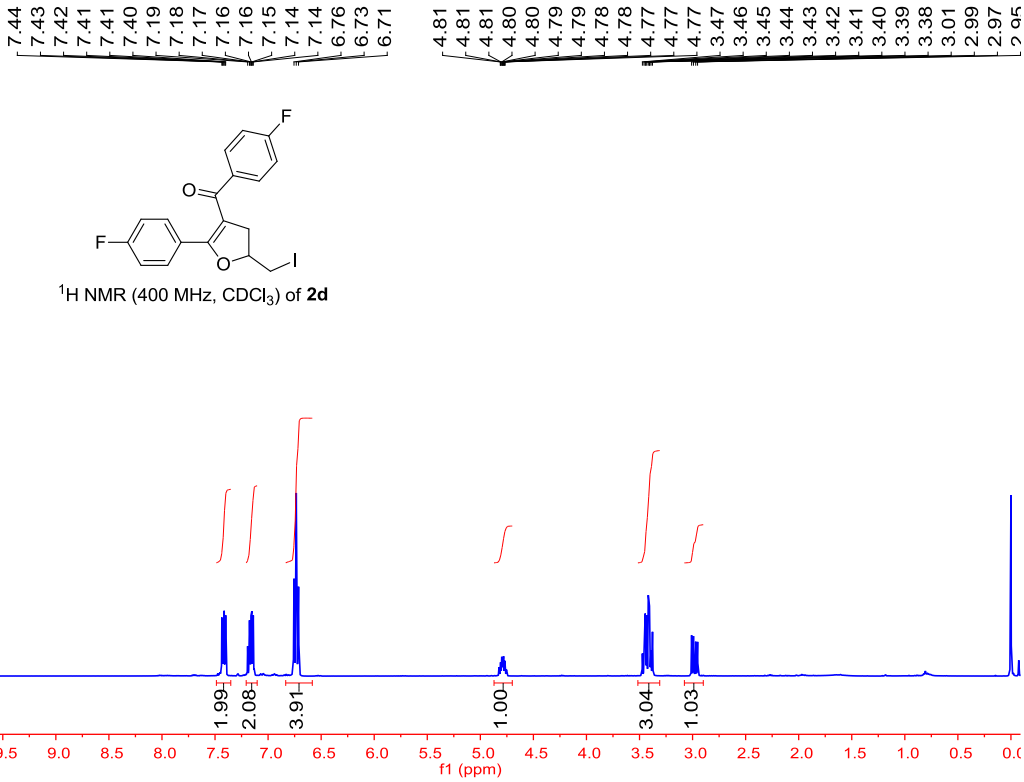
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



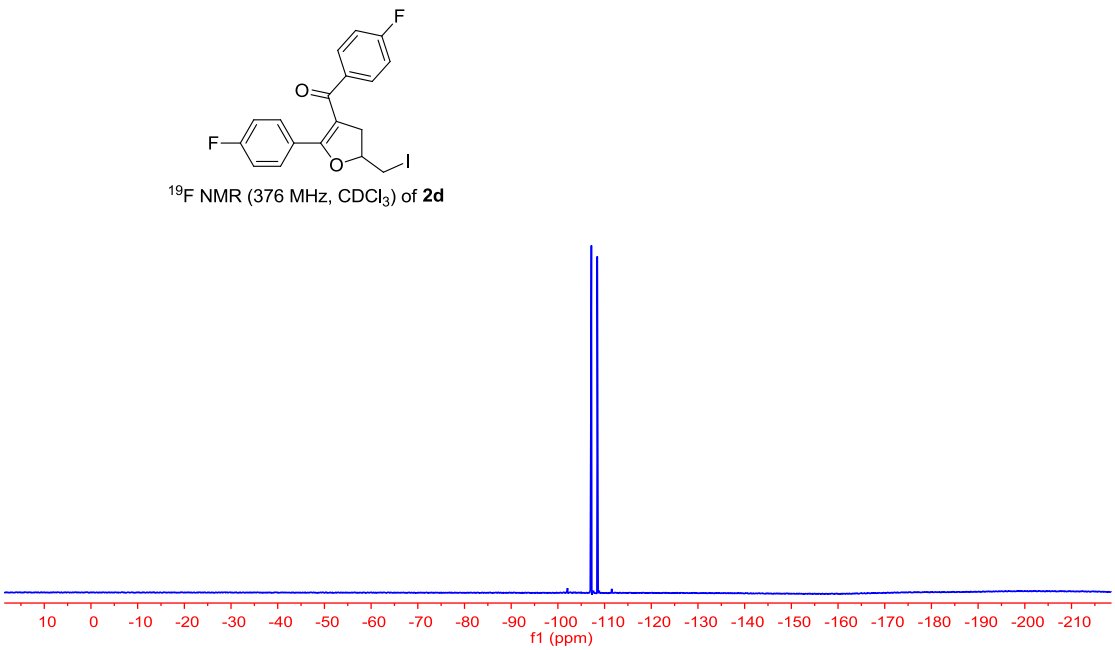


^{13}C NMR (100 MHz, $CDCl_3$) of **2c**

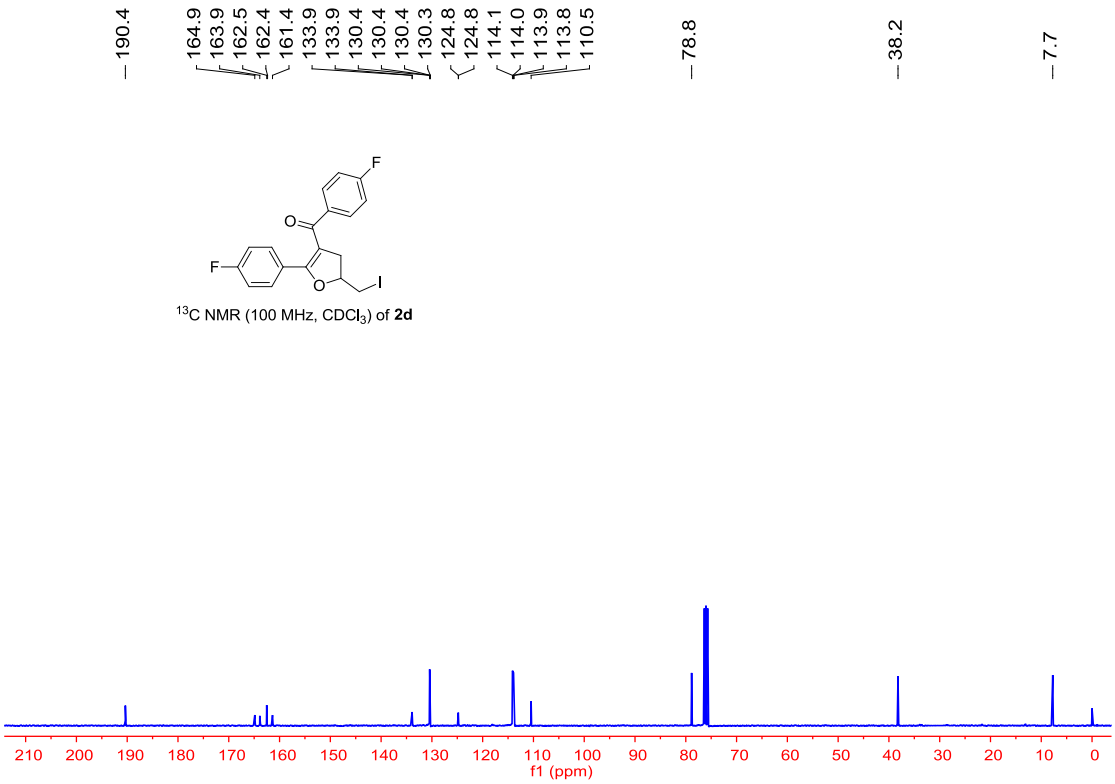




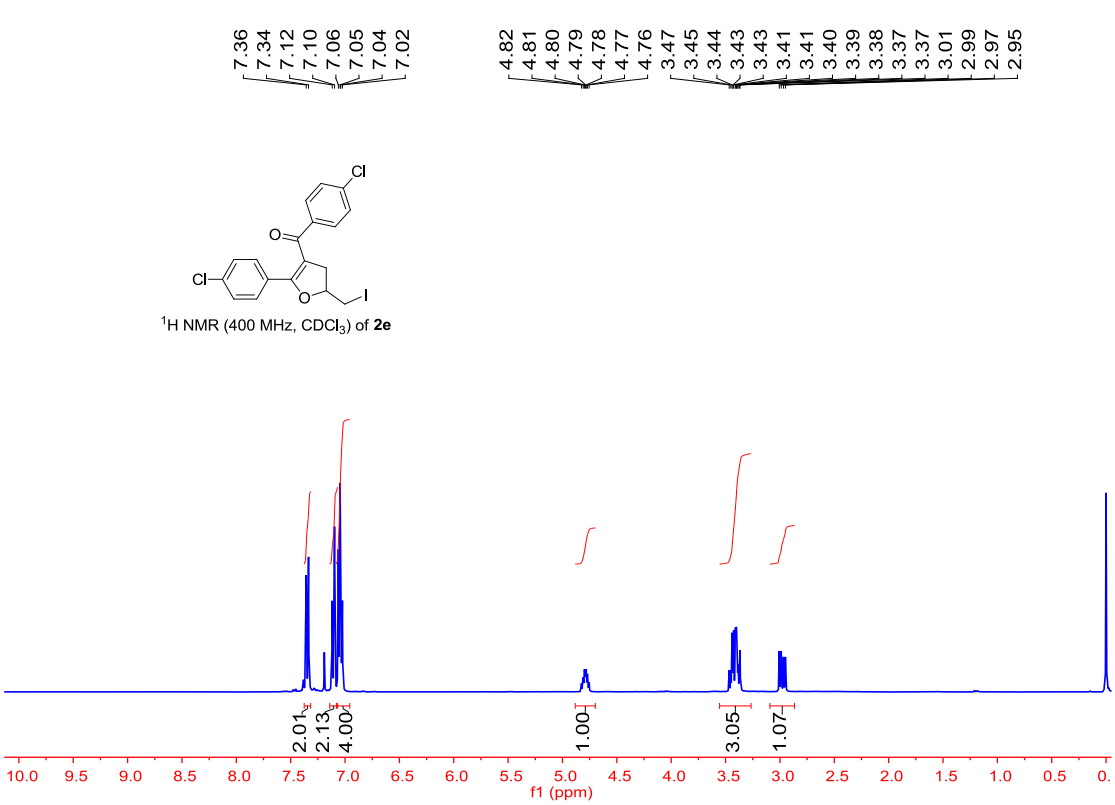
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



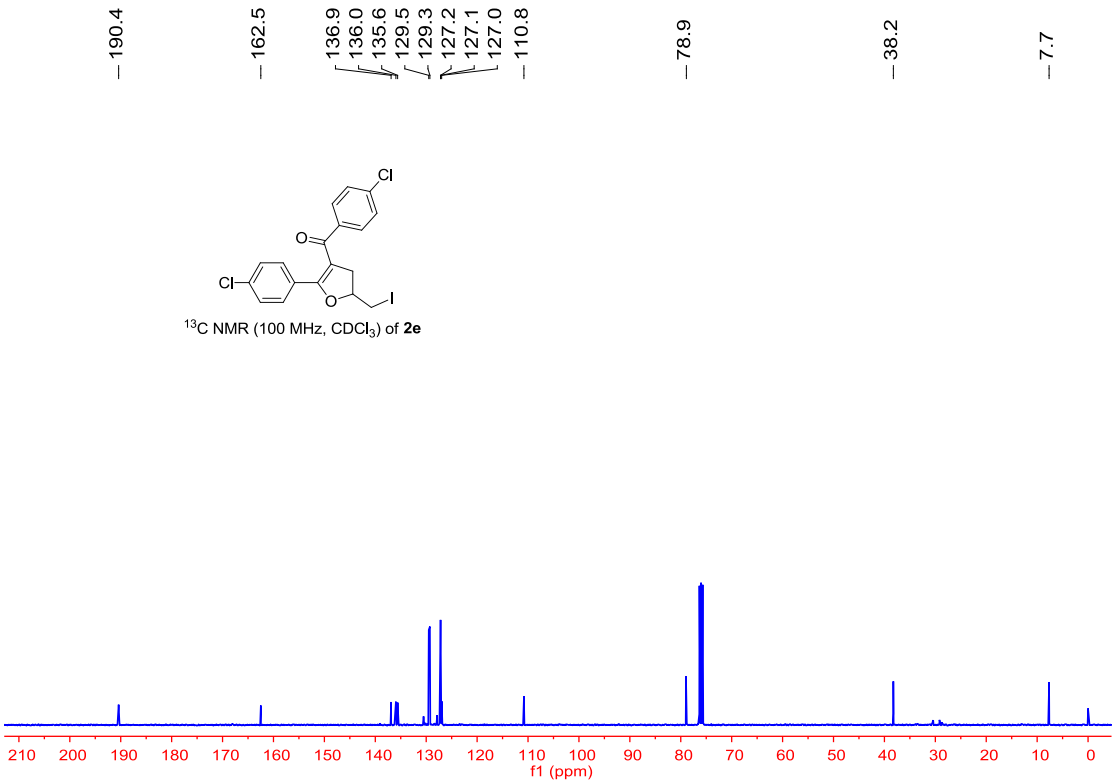
^{19}F NMR (376 MHz, $CDCl_3$) of **2d**



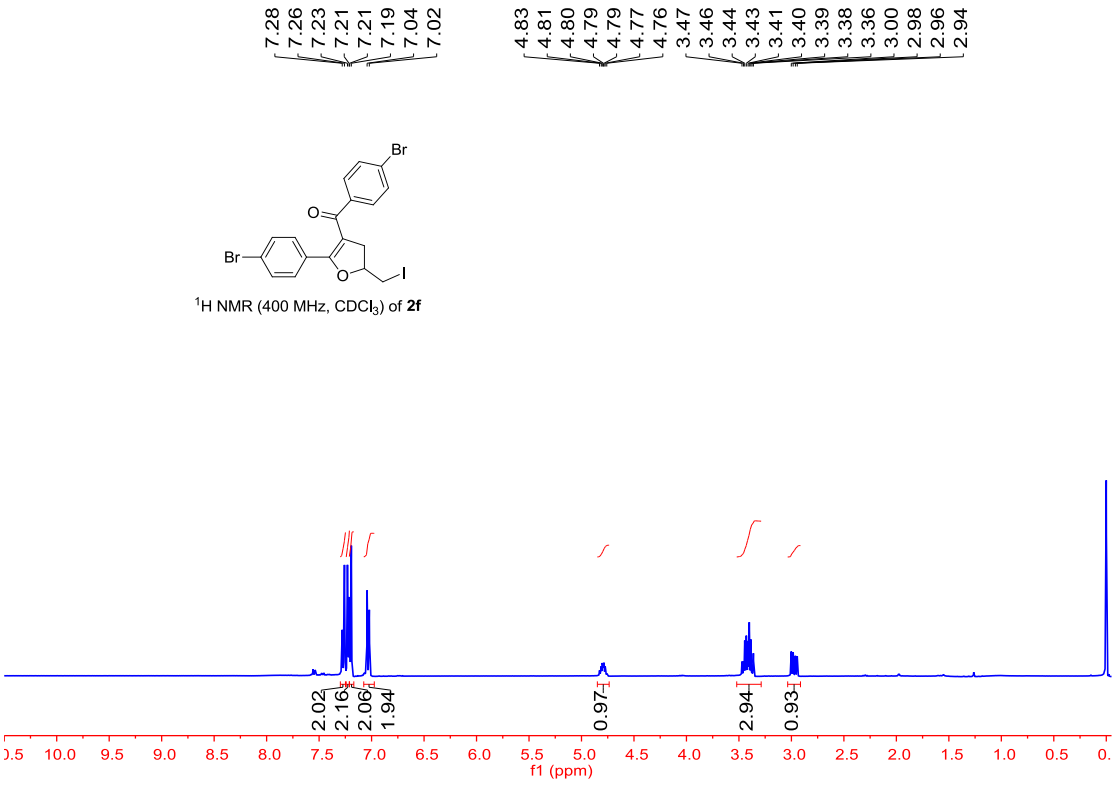
^{13}C NMR (100 MHz, $CDCl_3$) of **2d**



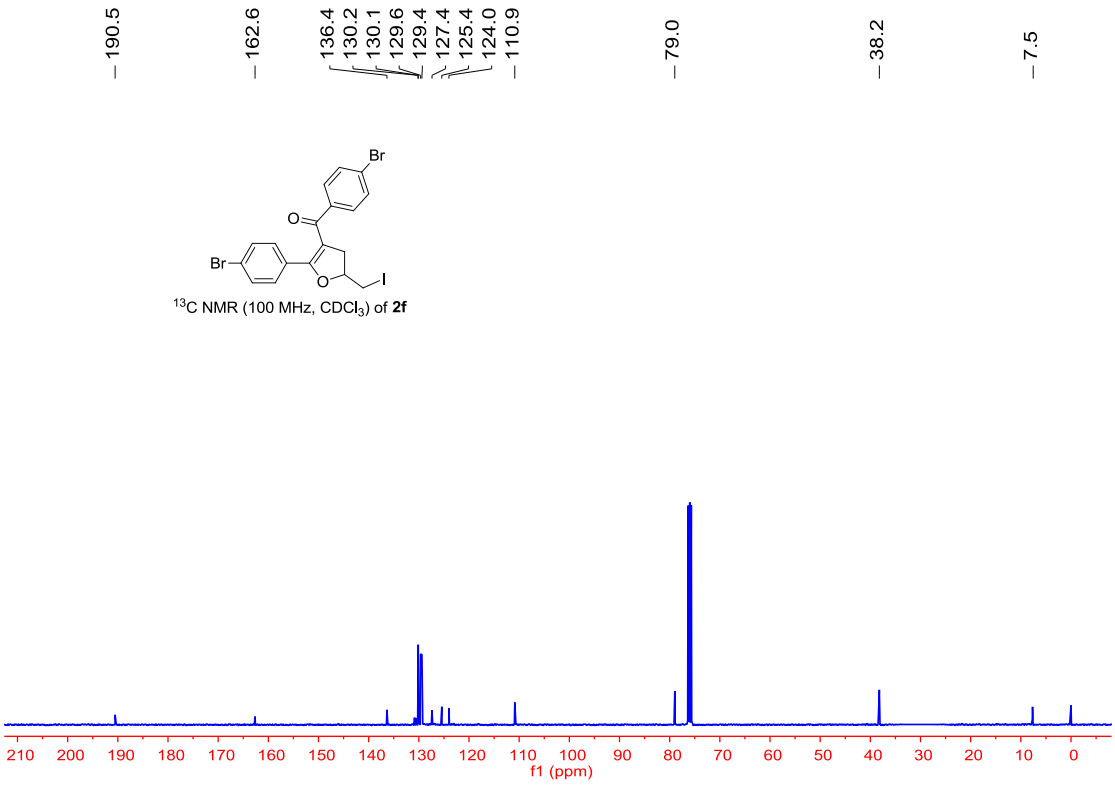
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



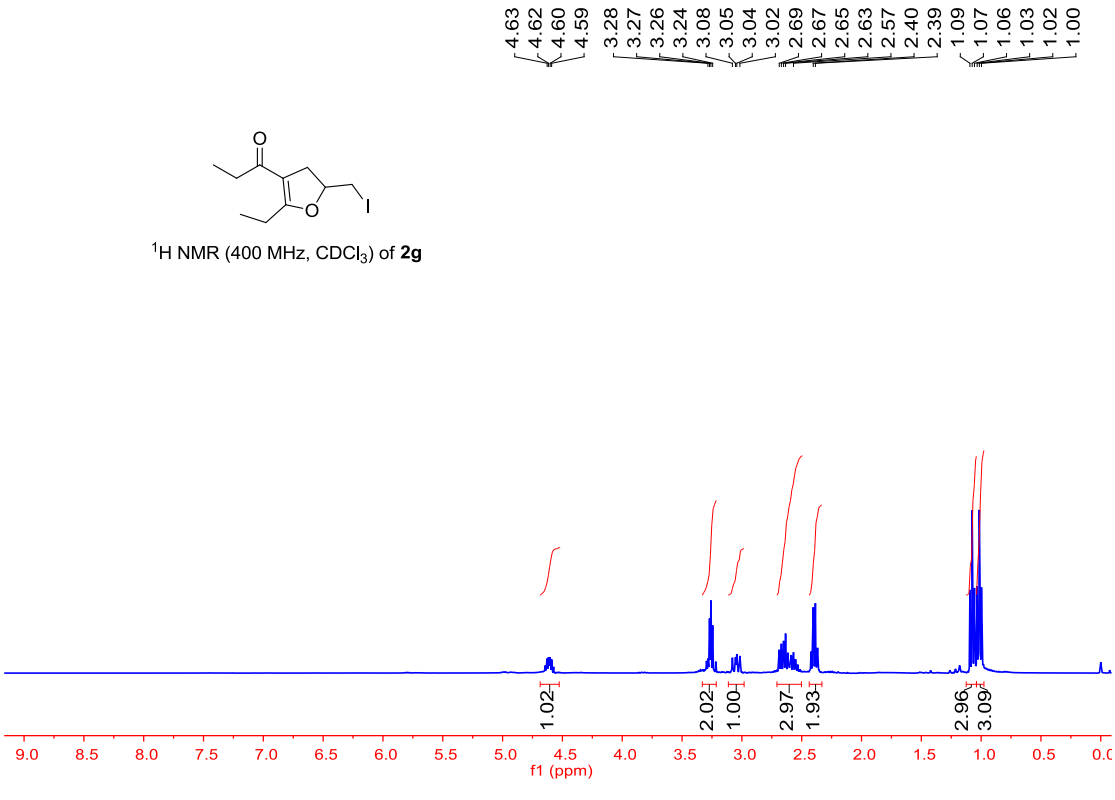
^{13}C NMR (100 MHz, $CDCl_3$) of **2e**



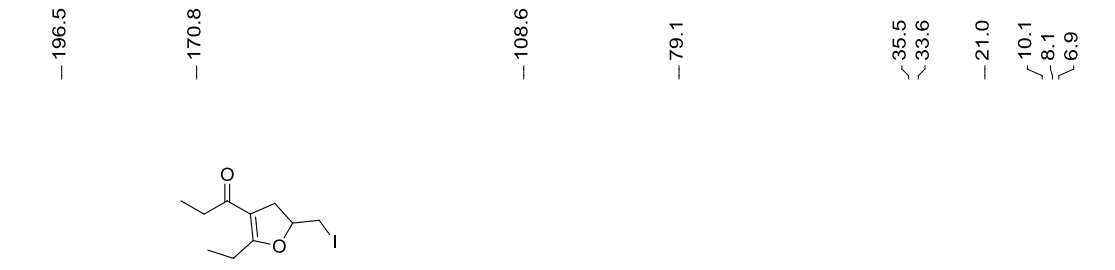
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



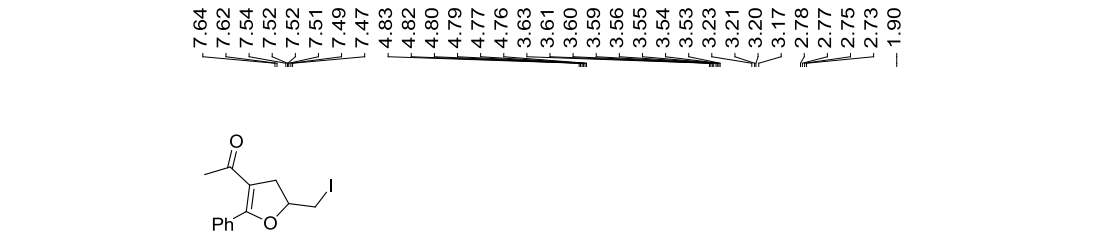
^{13}C NMR (100 MHz, $CDCl_3$) of **2f**



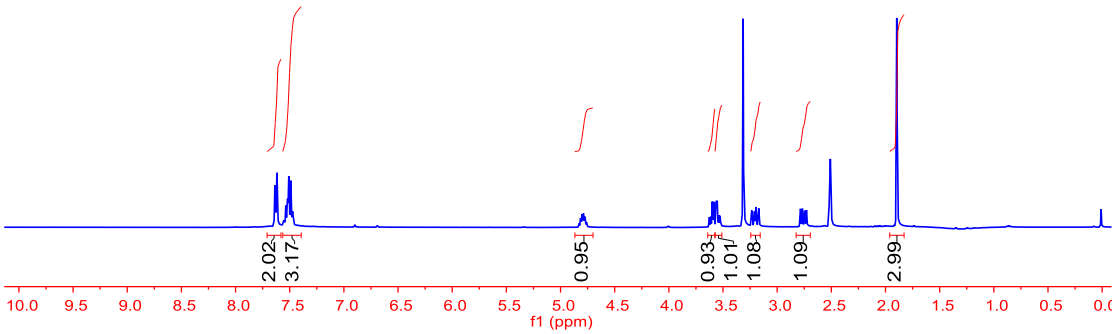
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**

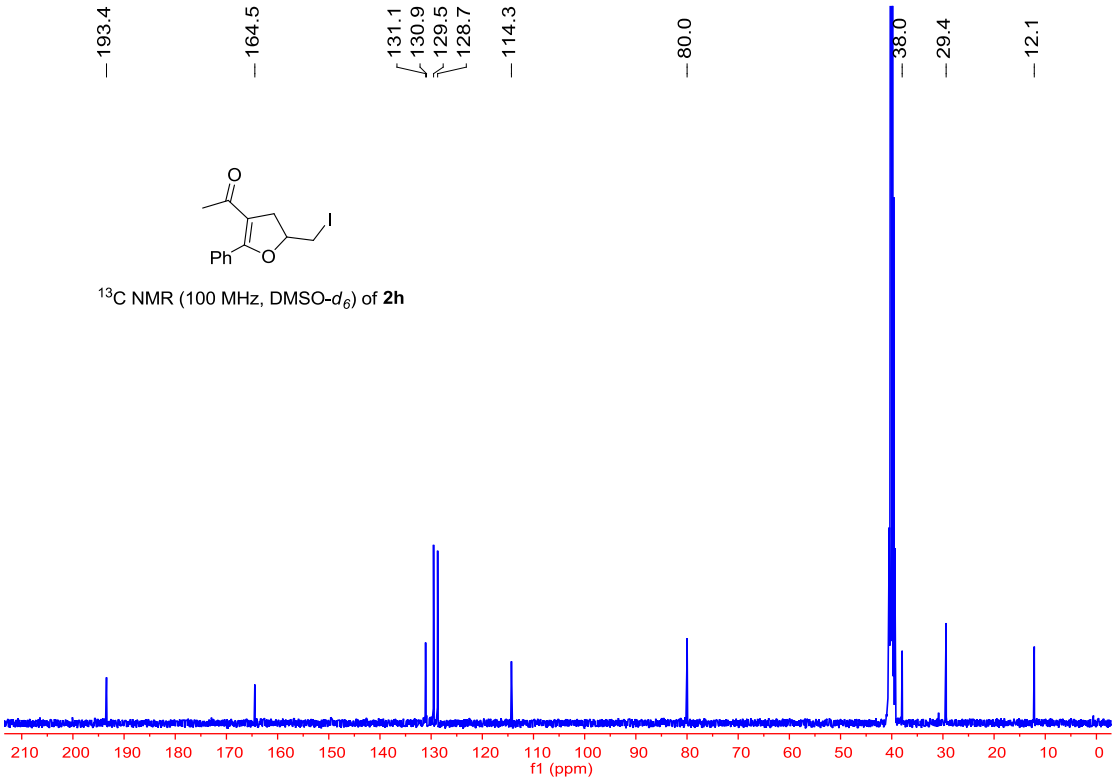


^{13}C NMR (100 MHz, $CDCl_3$) of **2g**

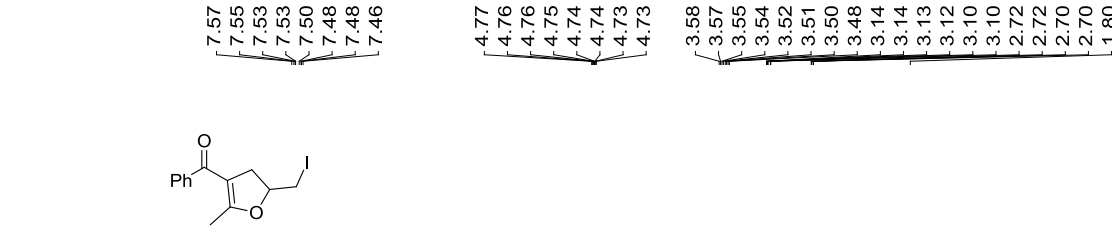


^{1}H NMR (400 MHz, DMSO-d_6) of **2h**

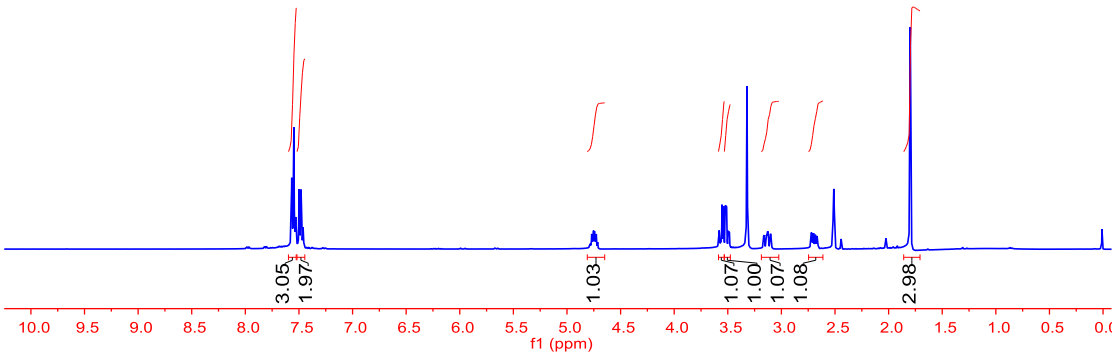


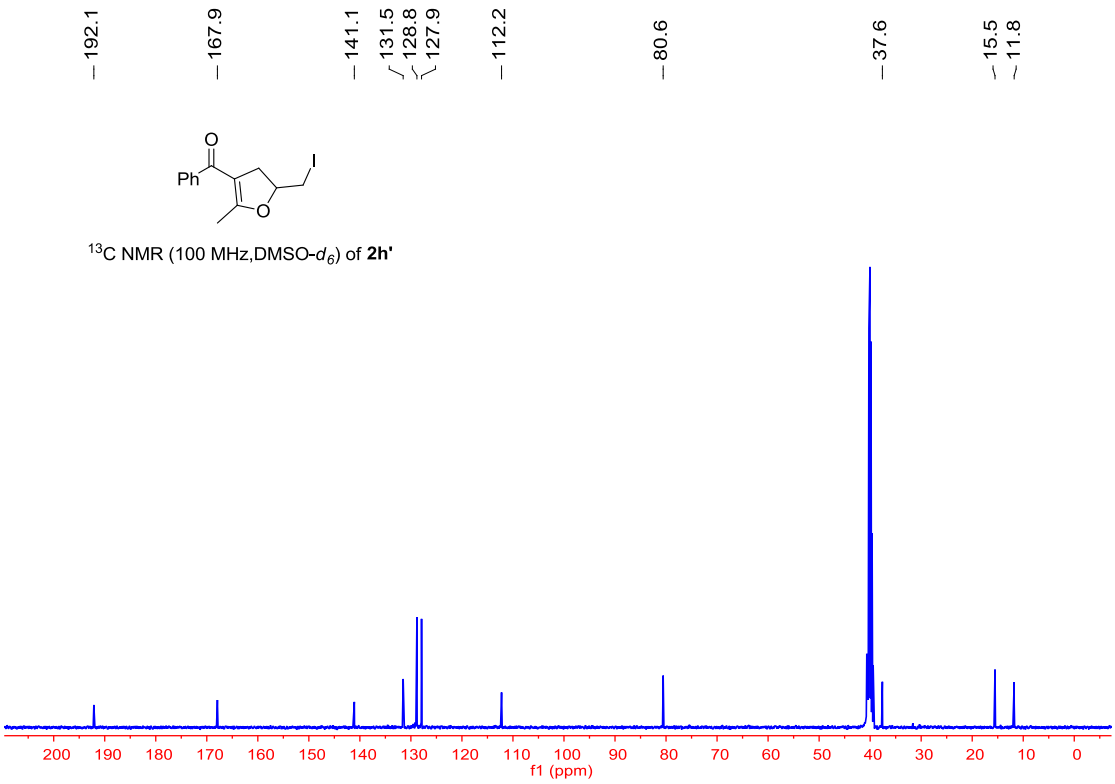


^{13}C NMR (100 MHz, DMSO-d_6) of **2h**

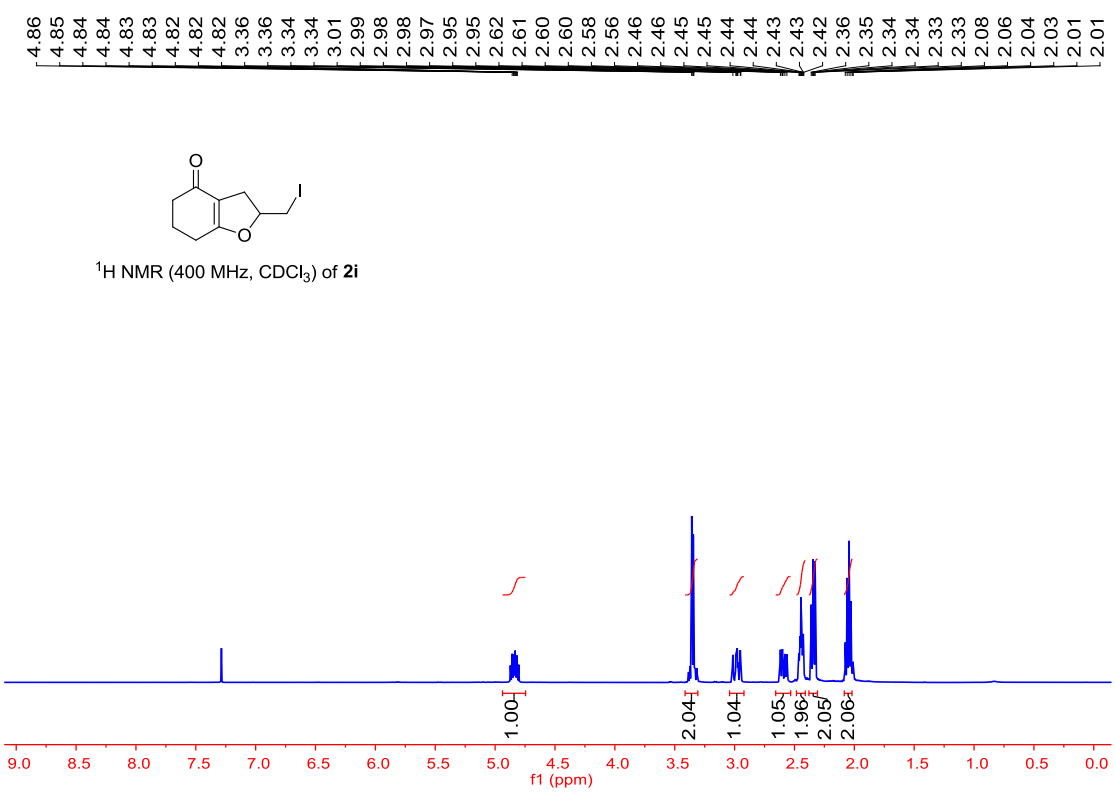


^{1}H NMR (400 MHz, DMSO-d_6) of **2h'**

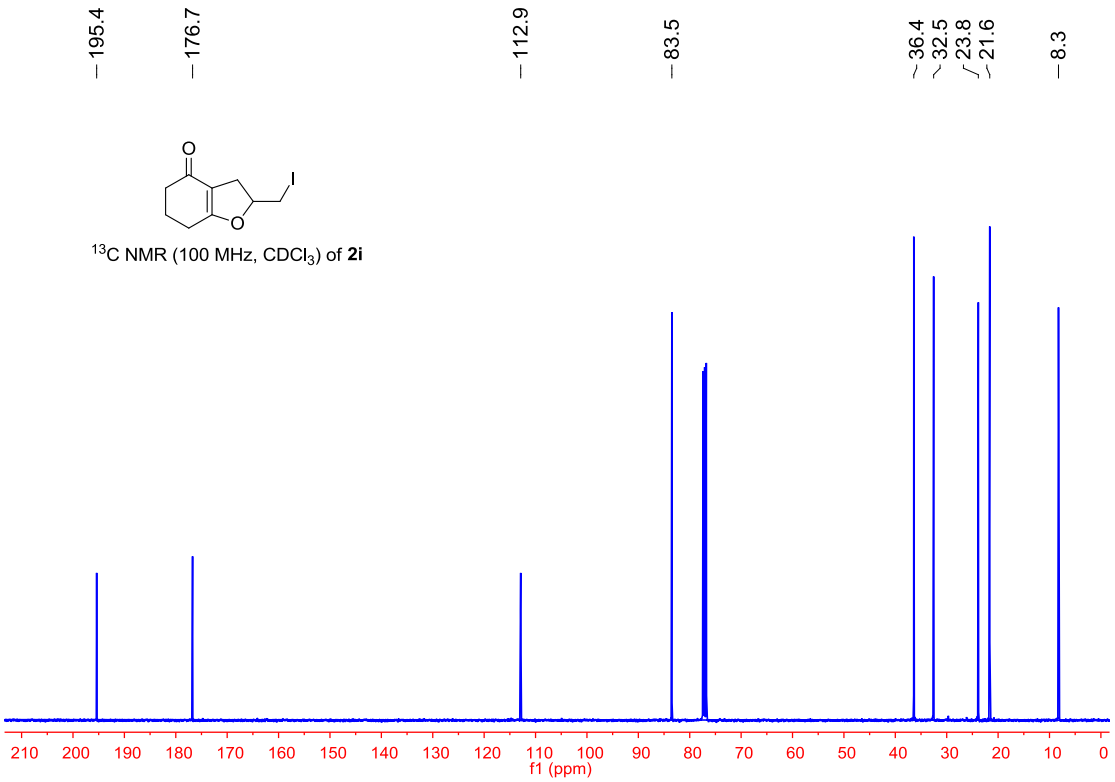




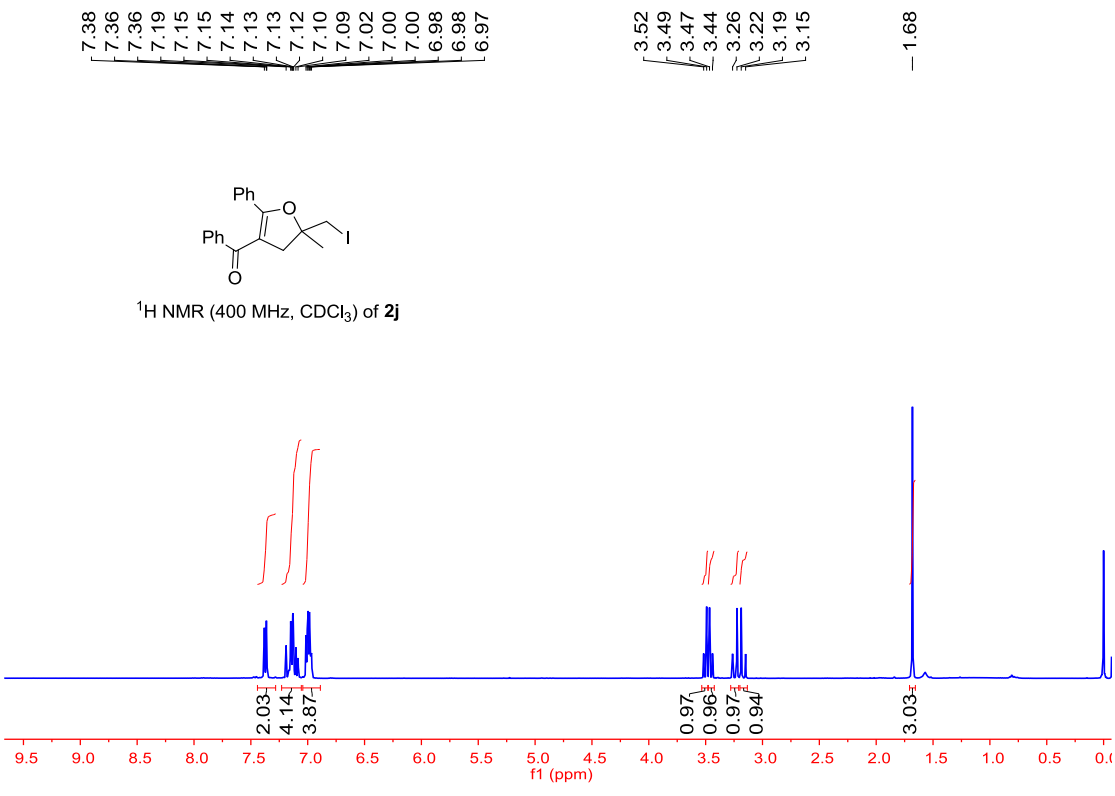
^{13}C NMR (100 MHz,DMSO-d_6) of **2h'**



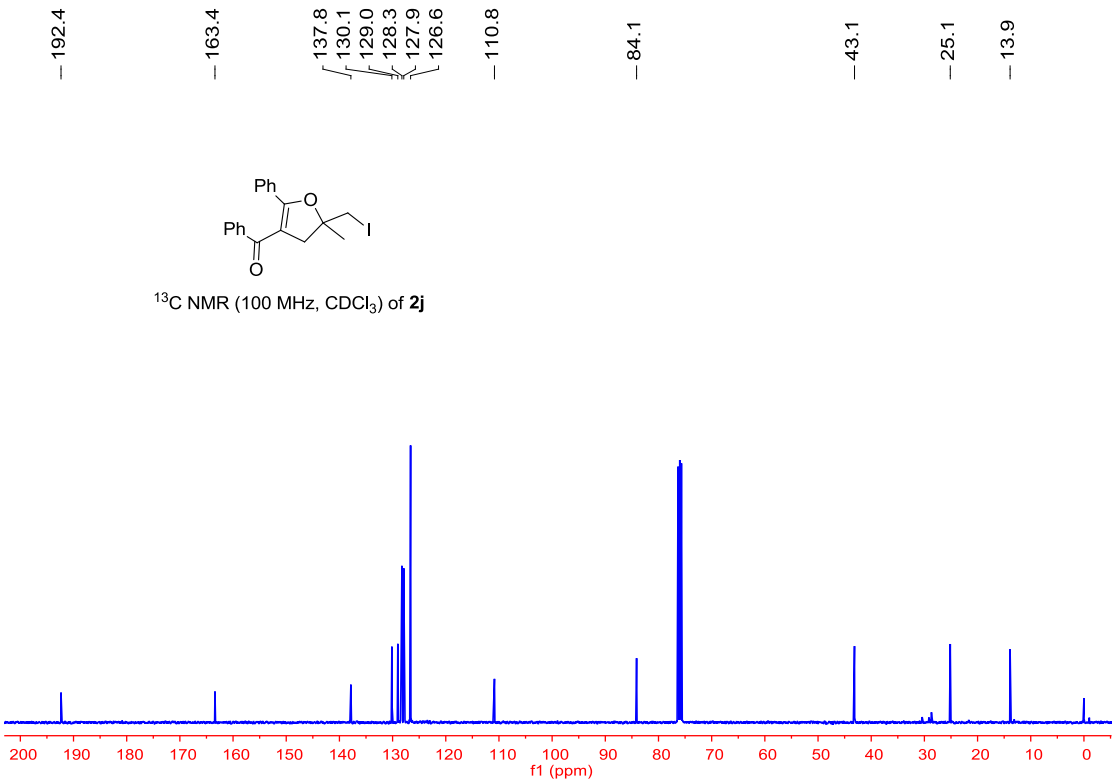
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



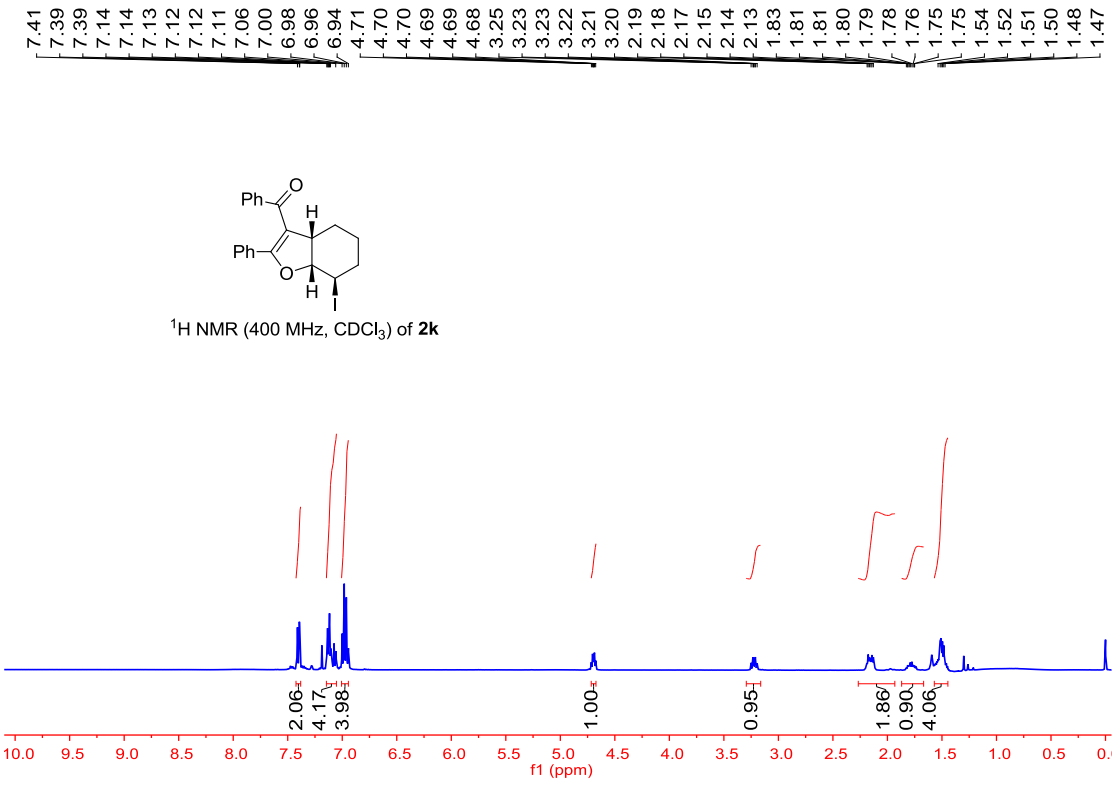
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



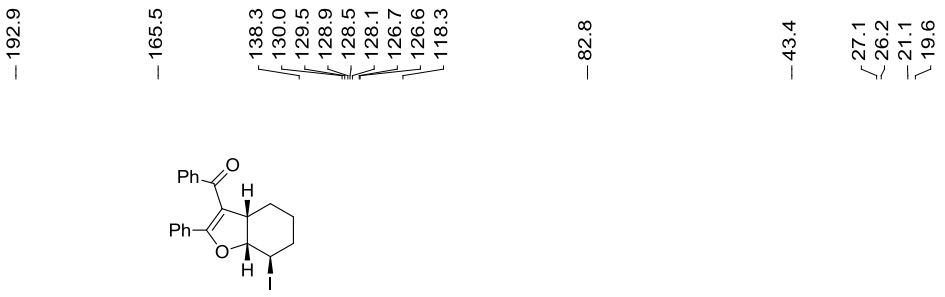
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



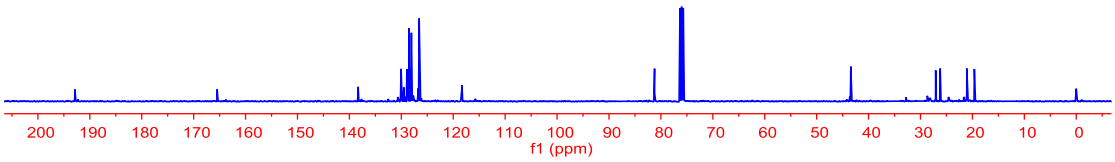
^{13}C NMR (100 MHz, $CDCl_3$) of **2j**

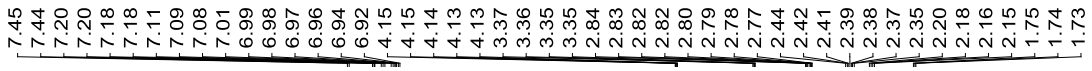


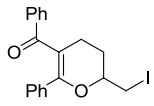
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



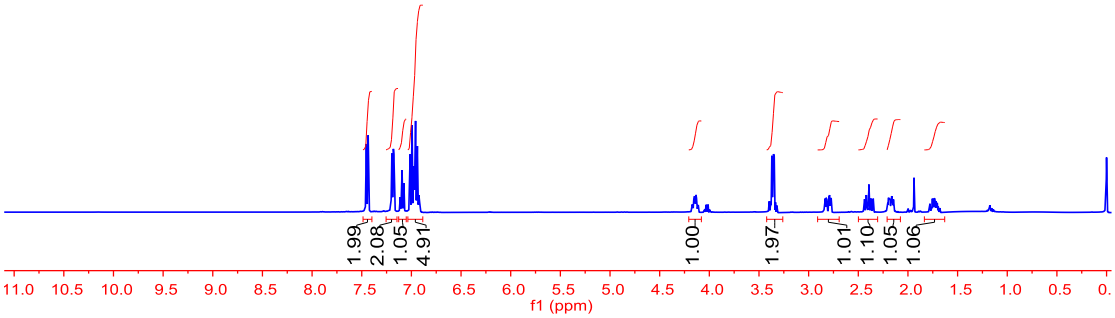
^{13}C NMR (100 MHz, $CDCl_3$) of **2k**

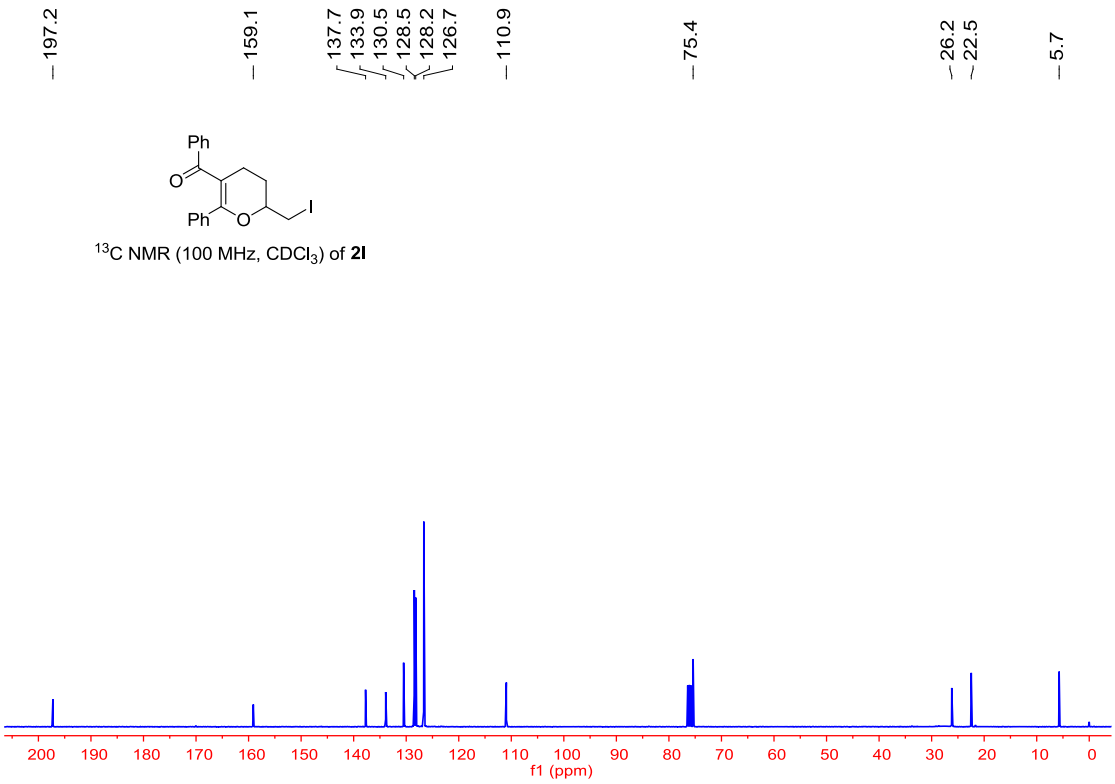




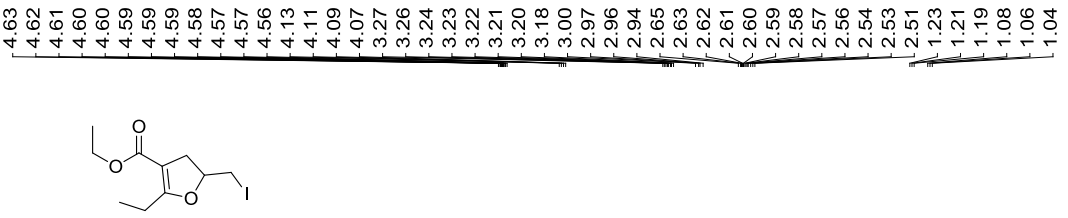


^{1}H NMR (400 MHz, $CDCl_3$) of **2l**

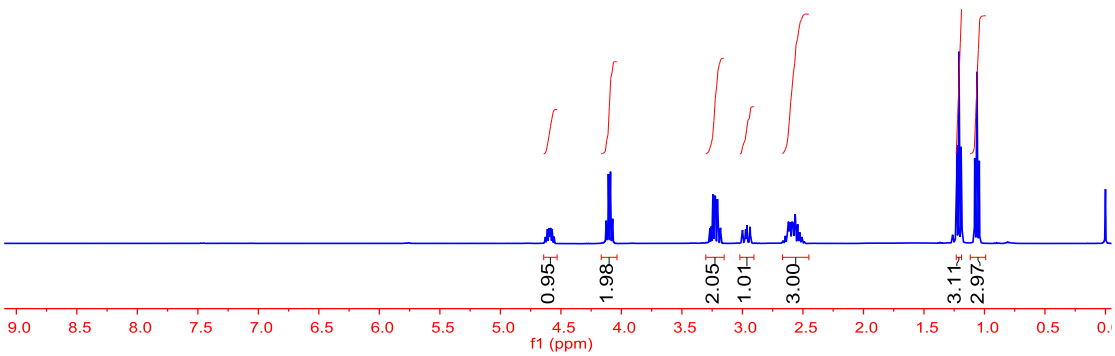


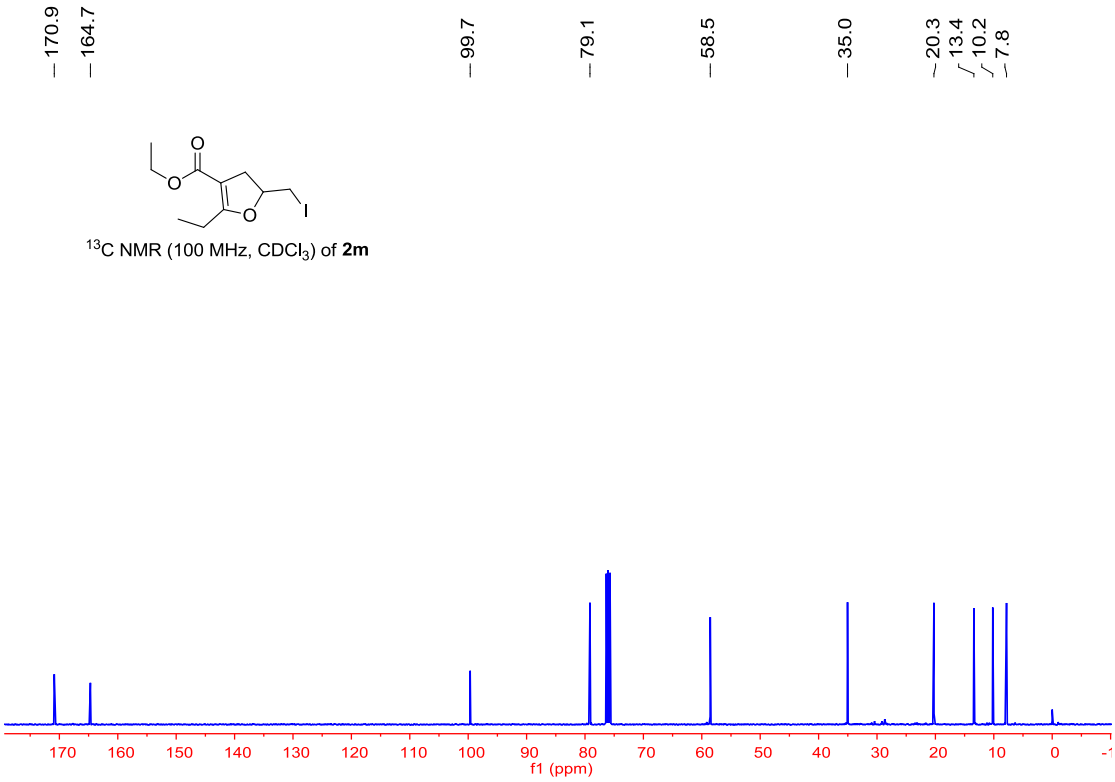


^{13}C NMR (100 MHz, $CDCl_3$) of **2l**

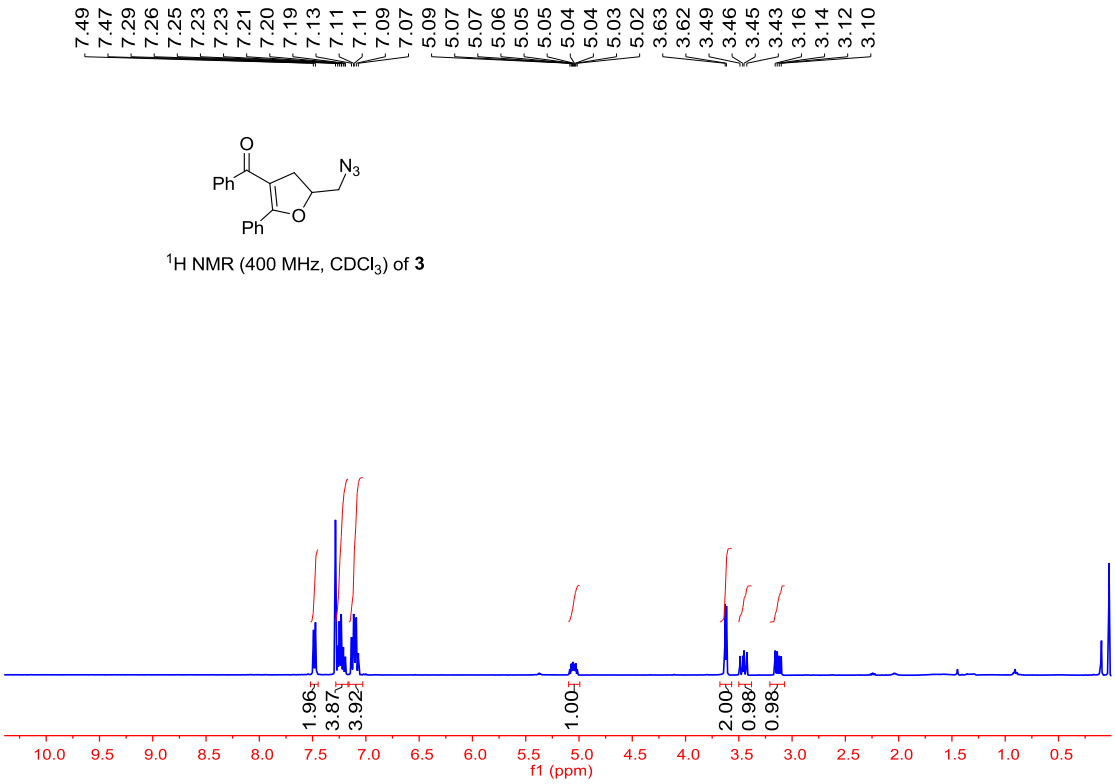


^{1}H NMR (400 MHz, $CDCl_3$) of **2m**

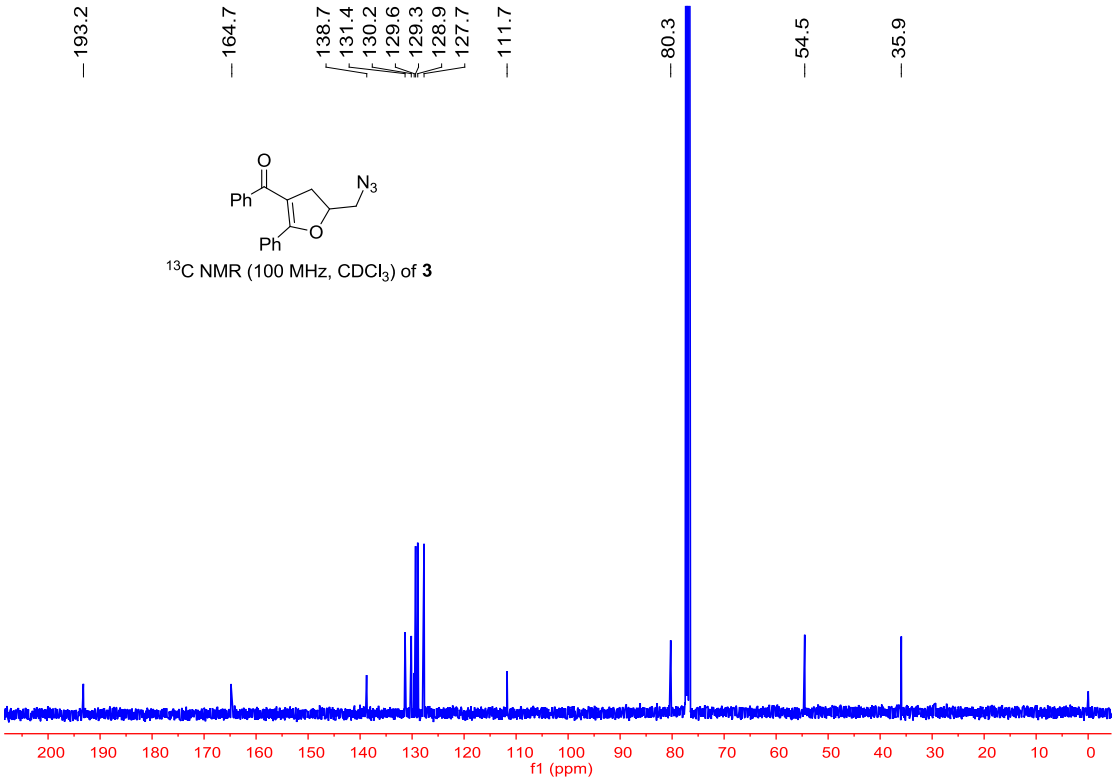




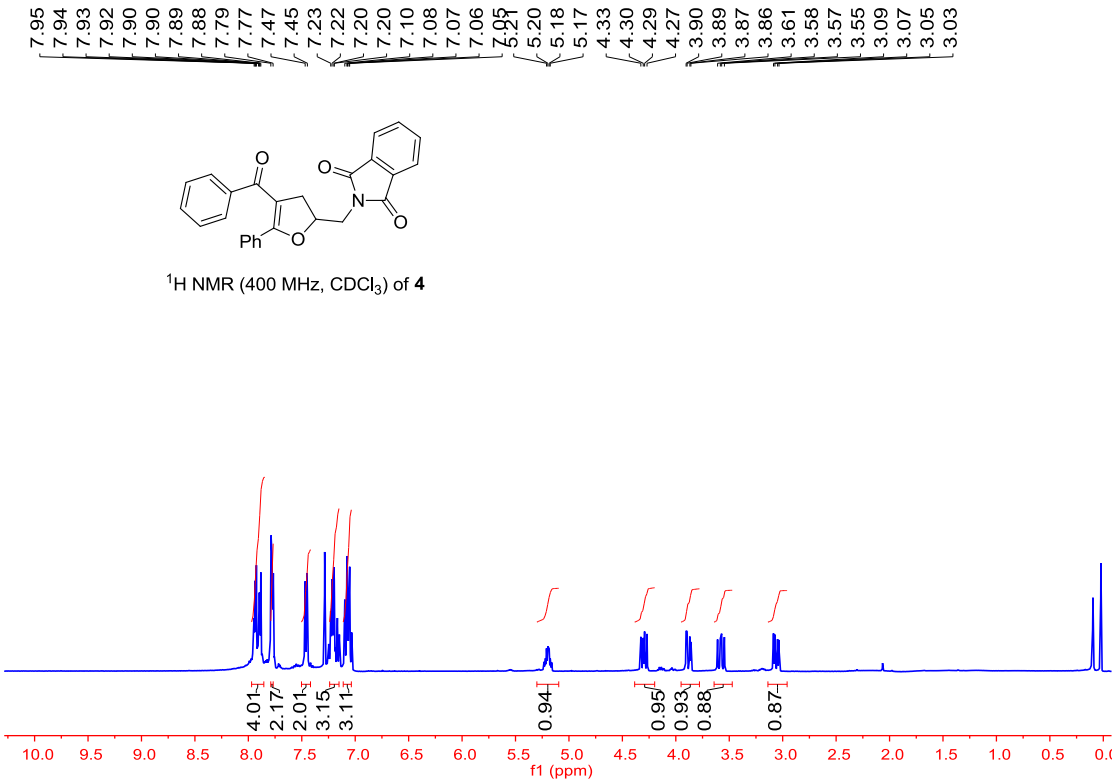
^{13}C NMR (100 MHz, $CDCl_3$) of **2m**



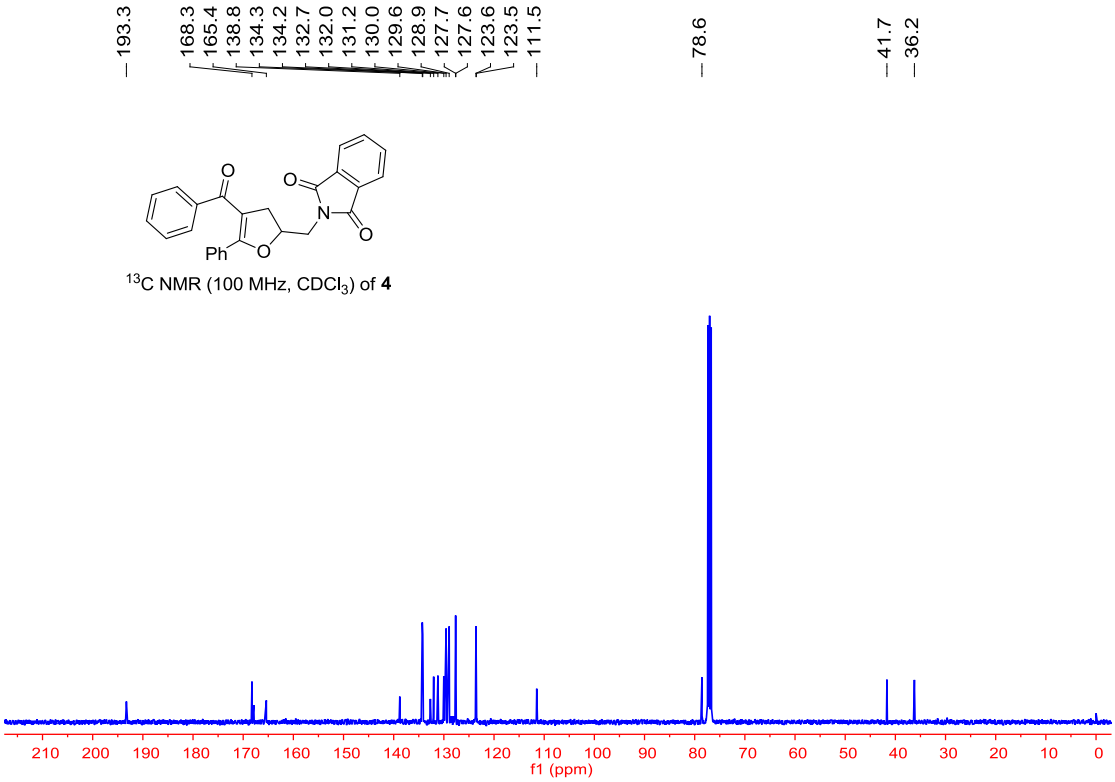
^{1}H NMR (400 MHz, $CDCl_3$) of **3**



^{13}C NMR (100 MHz, $CDCl_3$) of **3**

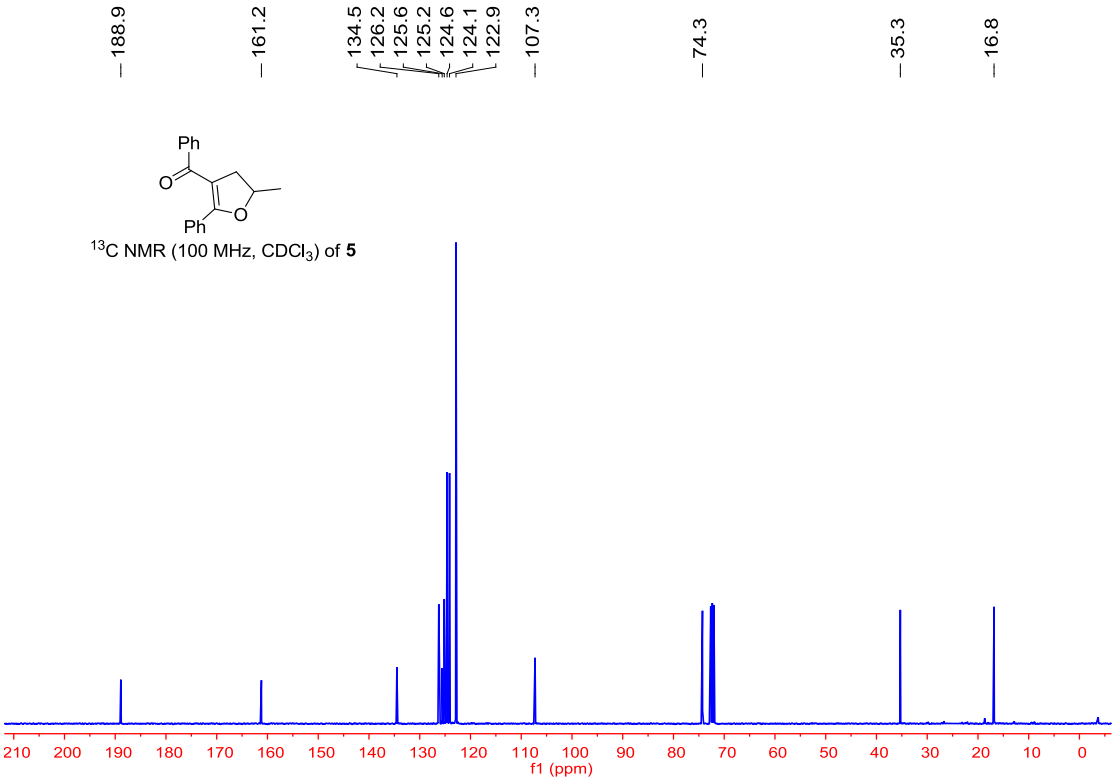


^{1}H NMR (400 MHz, $CDCl_3$) of **4**

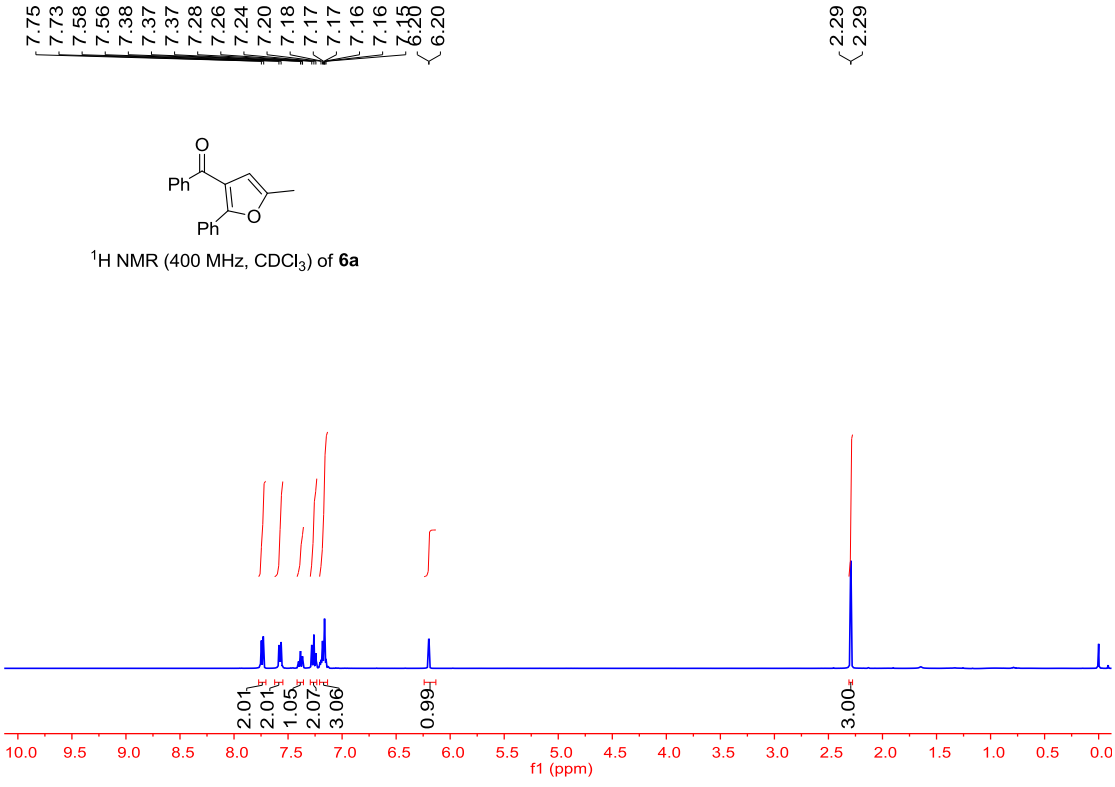


^{13}C NMR (100 MHz, $CDCl_3$) of **4**

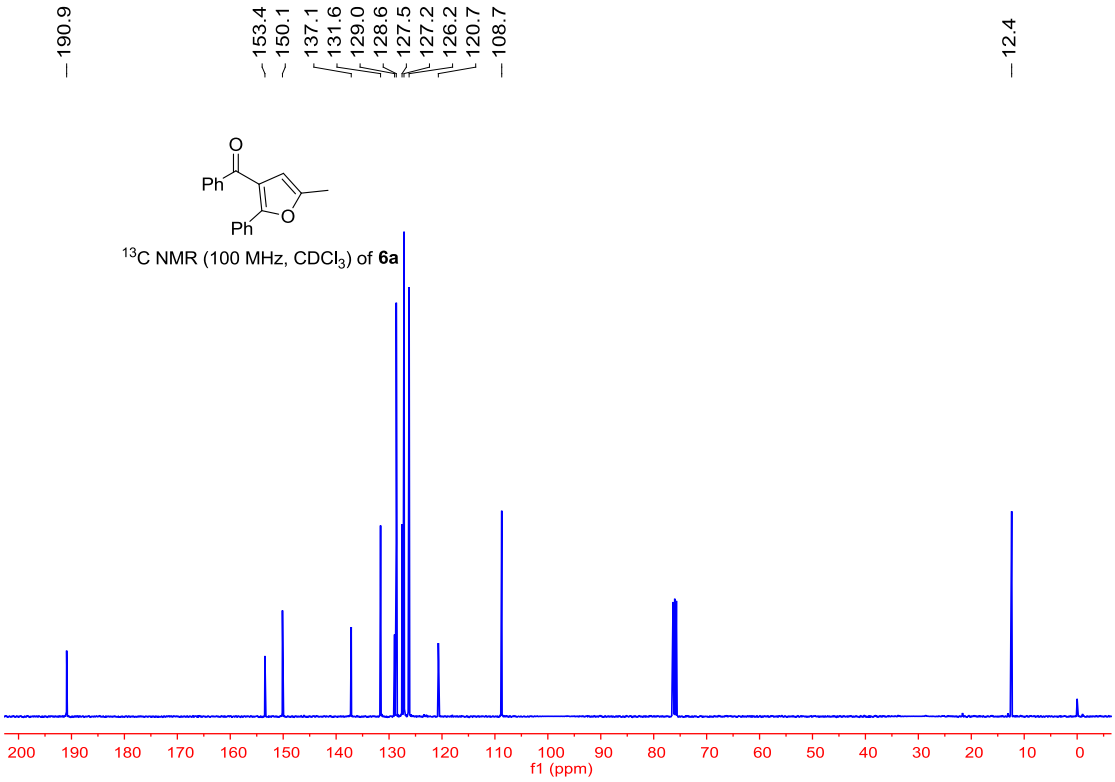
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



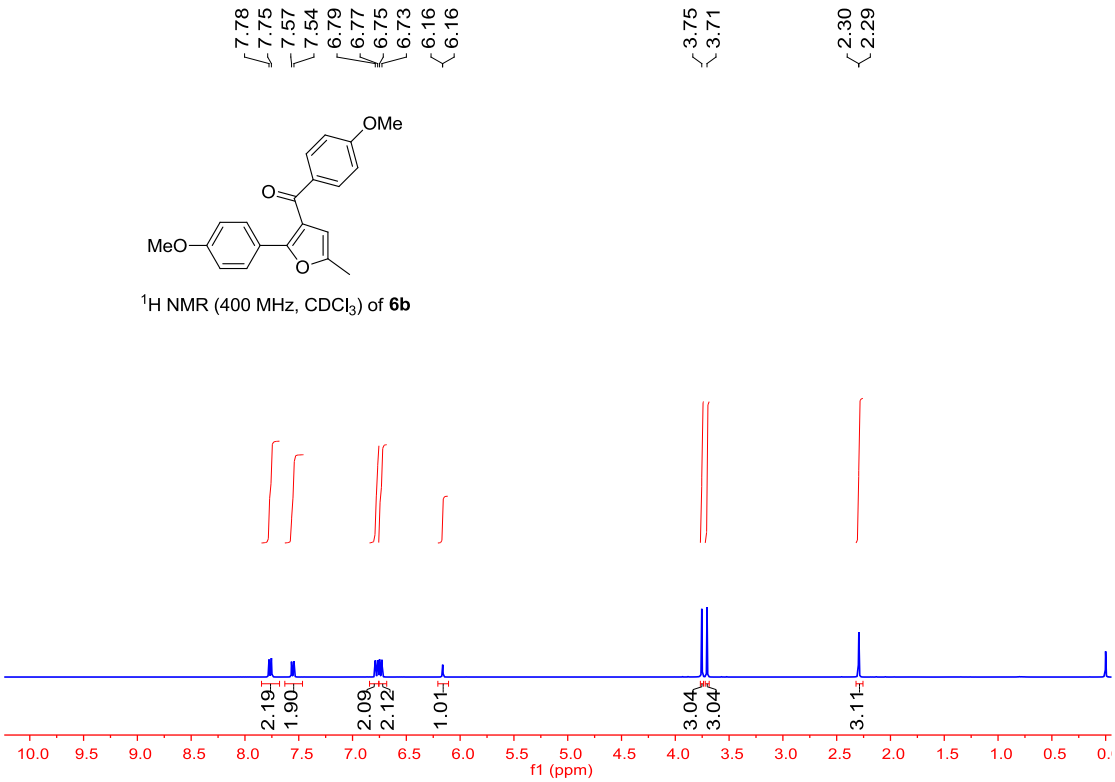
^{13}C NMR (100 MHz, $CDCl_3$) of **5**



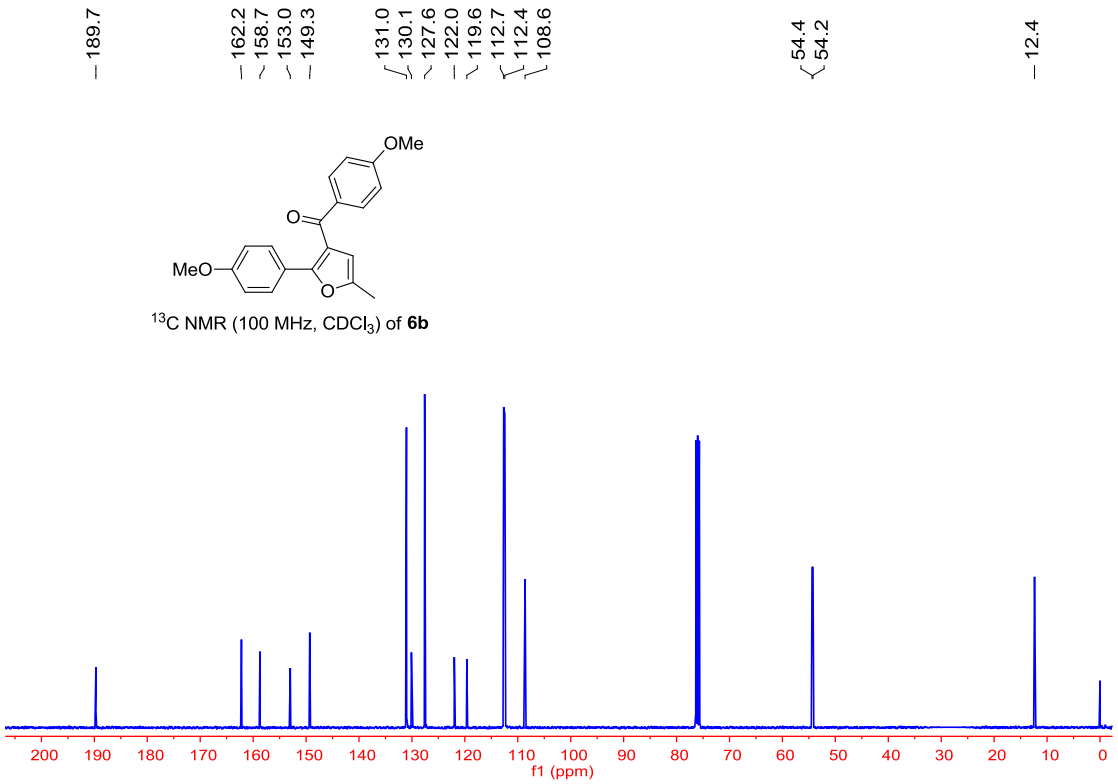
^{1}H NMR (400 MHz, $CDCl_3$) of **6a**



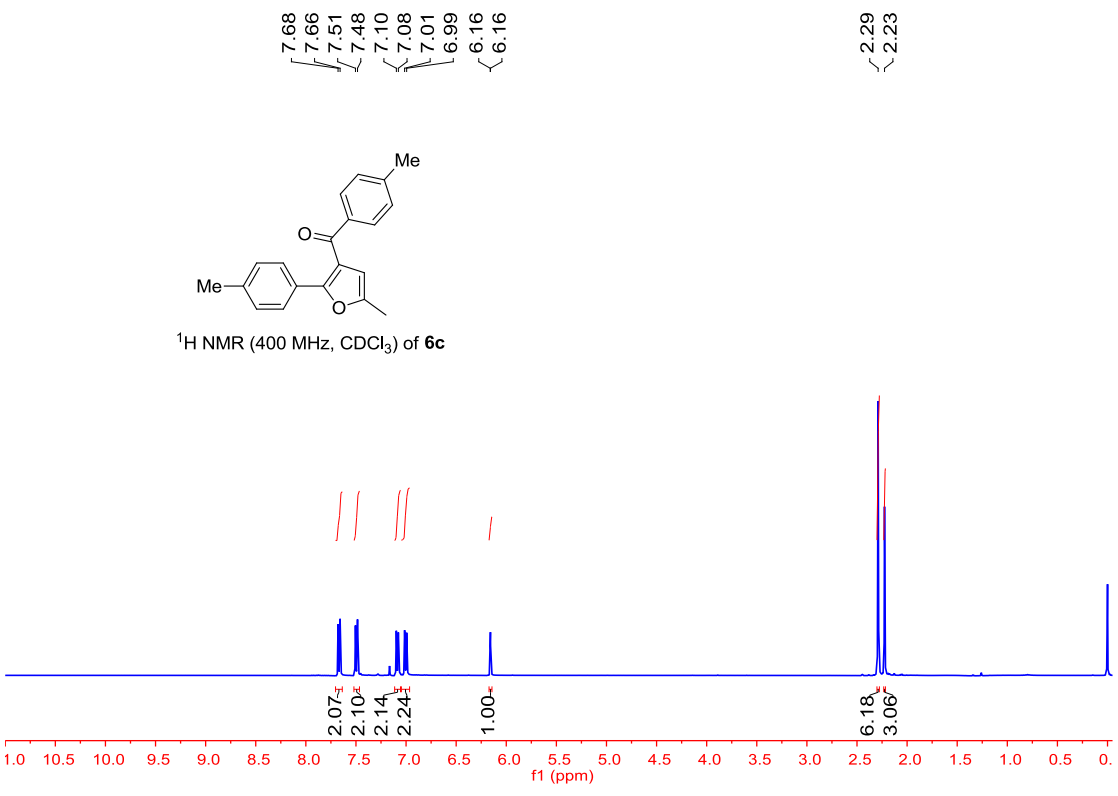
^{13}C NMR (100 MHz, $CDCl_3$) of **6a**



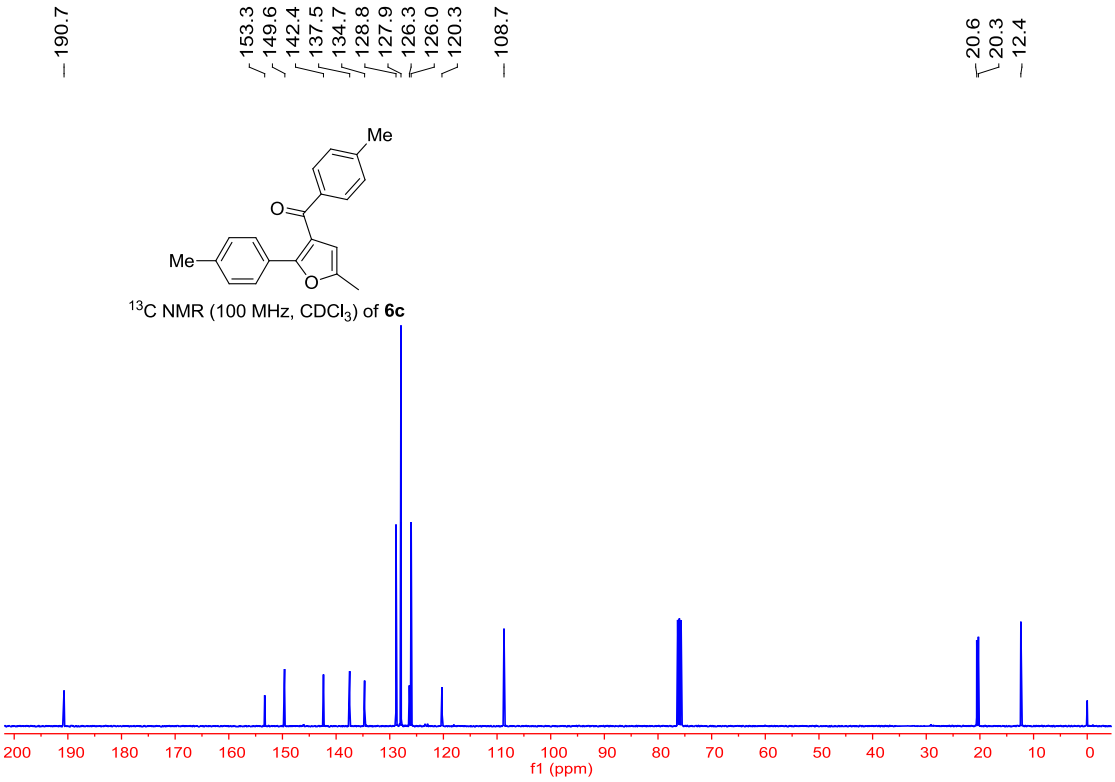
^{1}H NMR (400 MHz, $CDCl_3$) of **6b**



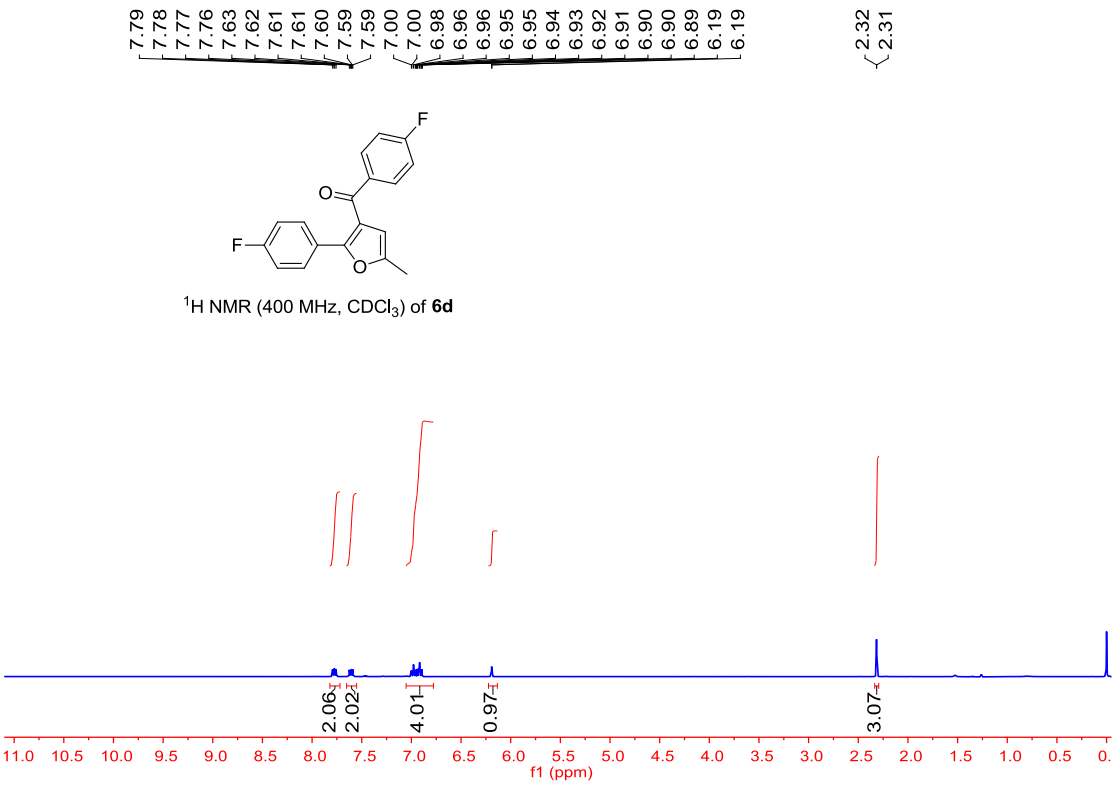
^{13}C NMR (100 MHz, $CDCl_3$) of **6b**



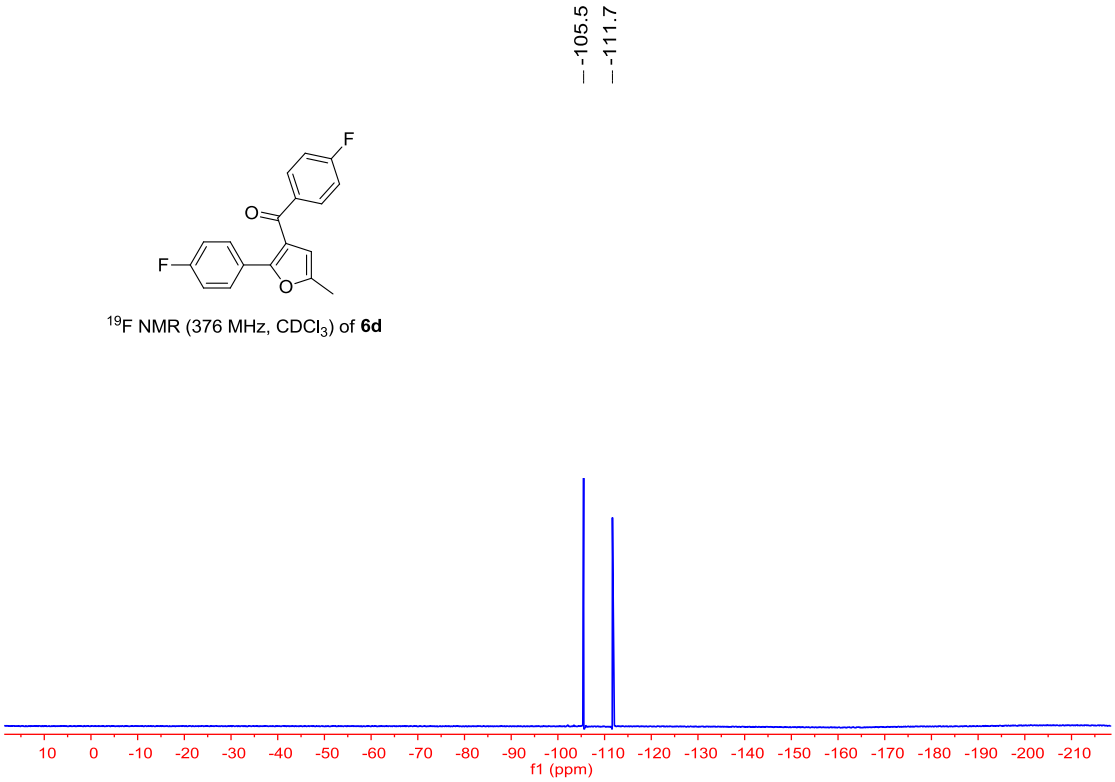
^{1}H NMR (400 MHz, $CDCl_3$) of **6c**



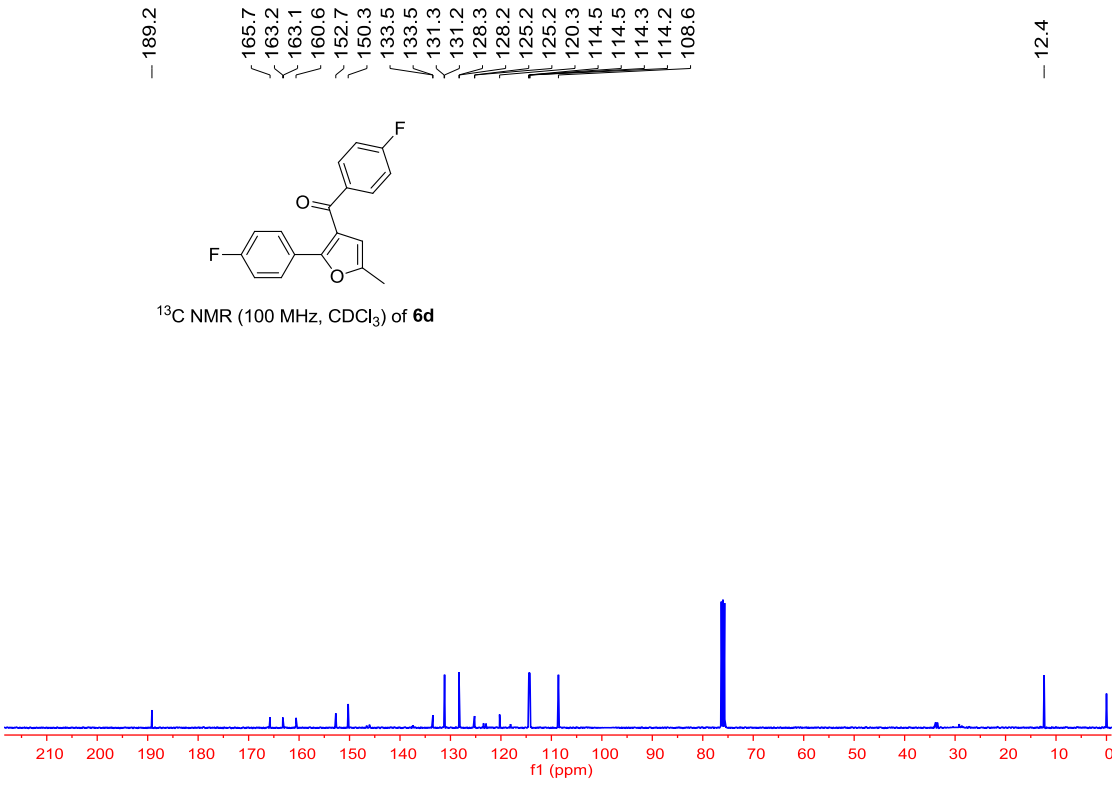
^{13}C NMR (100 MHz, $CDCl_3$) of **6c**



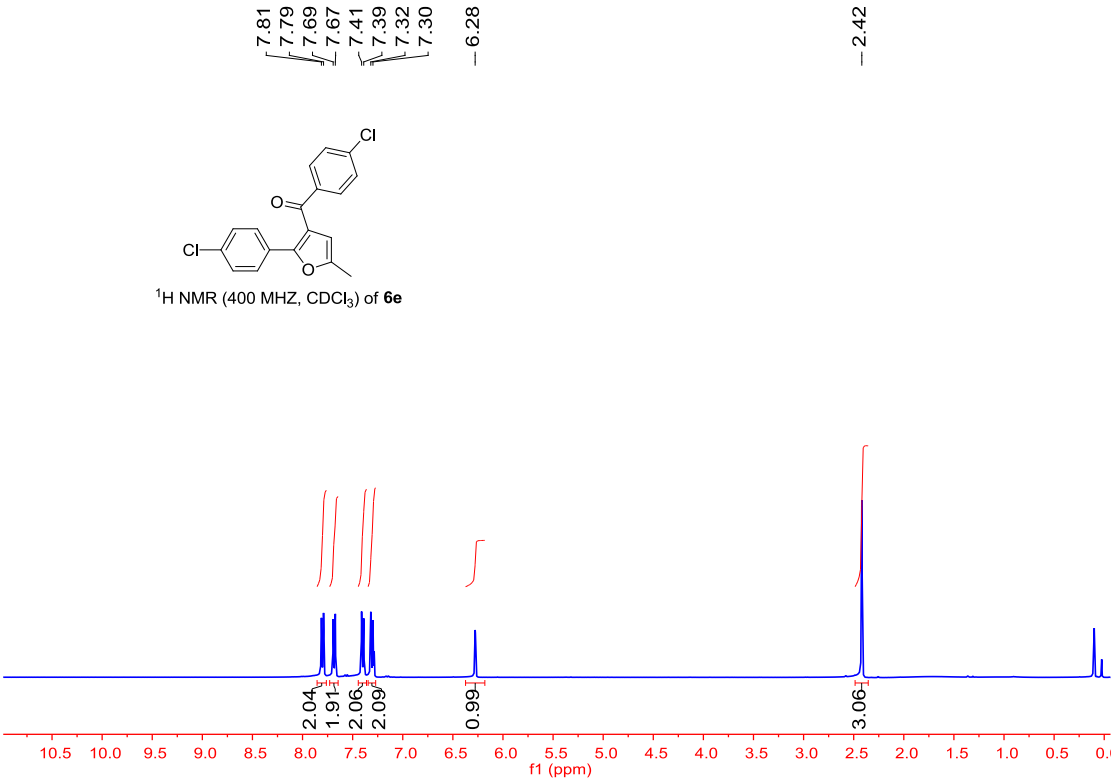
^{1}H NMR (400 MHz, $CDCl_3$) of **6d**



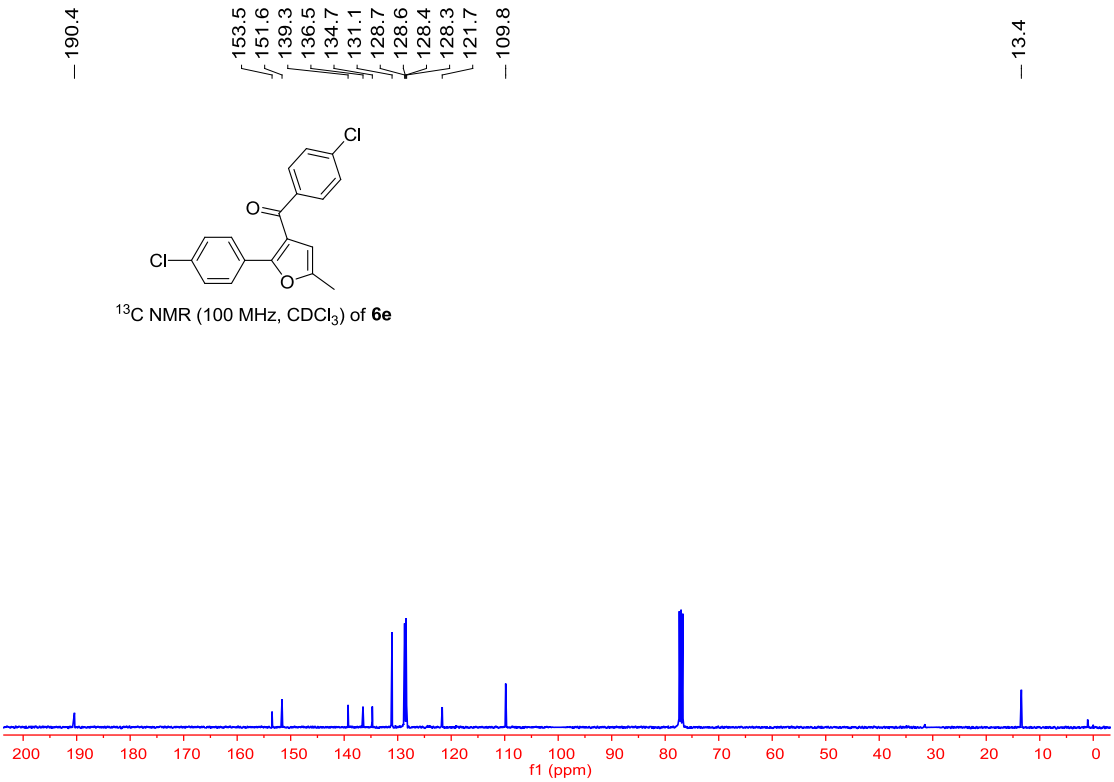
^{19}F NMR (376 MHz, $CDCl_3$) of **6d**



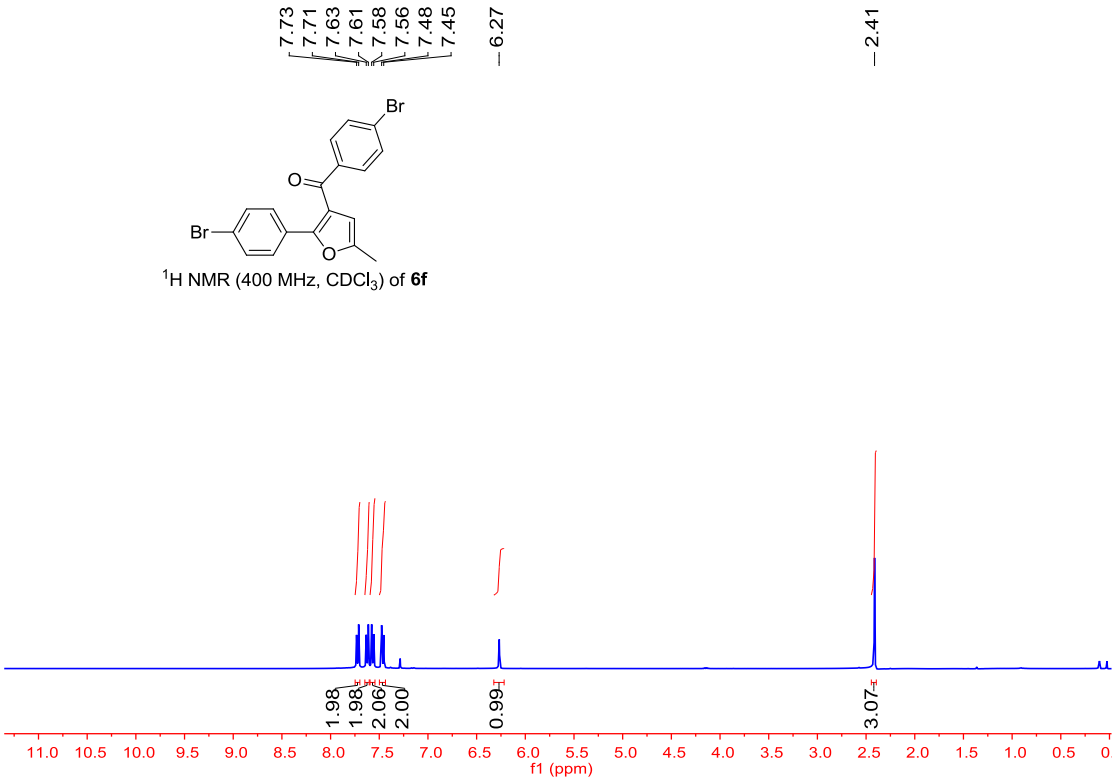
^{13}C NMR (100 MHz, $CDCl_3$) of **6d**



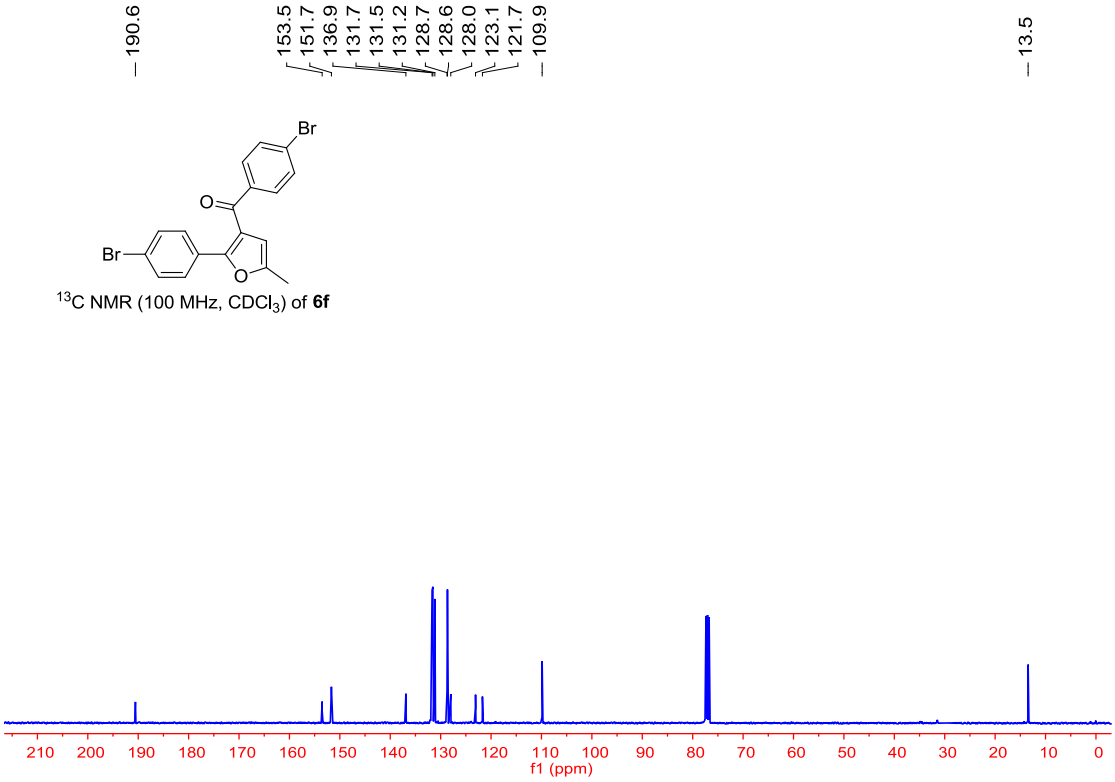
^{1}H NMR (400 MHZ, $CDCl_3$) of **6e**



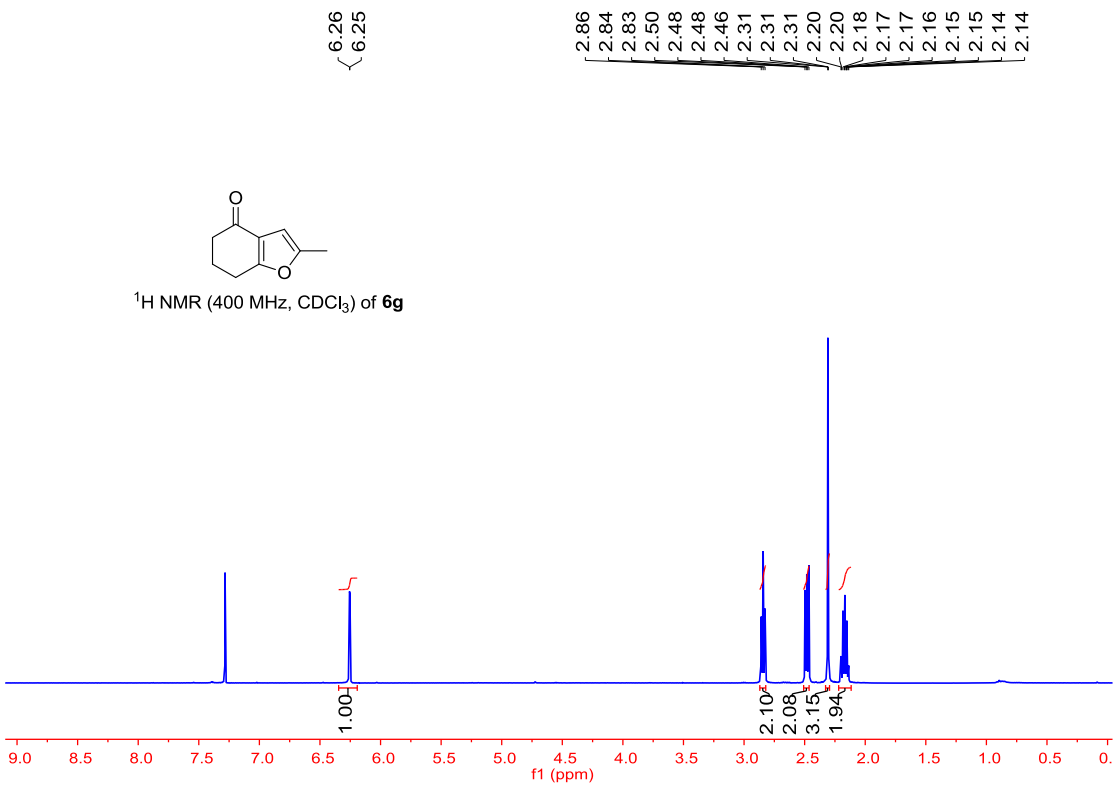
^{13}C NMR (100 MHz, $CDCl_3$) of **6e**



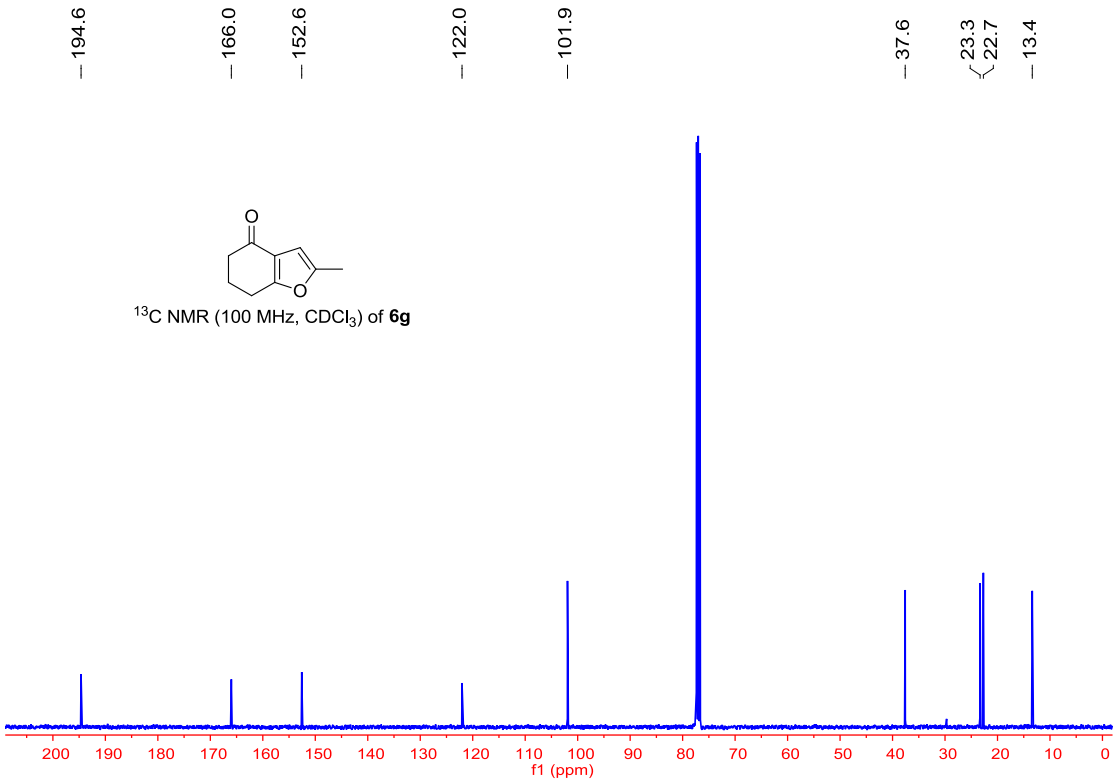
^{1}H NMR (400 MHz, $CDCl_3$) of **6f**



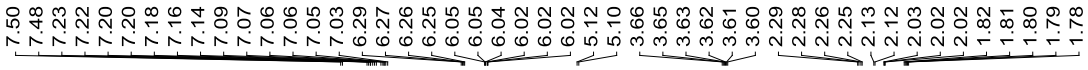
^{13}C NMR (100 MHz, $CDCl_3$) of **6f**

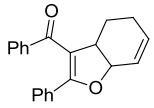


^{1}H NMR (400 MHz, $CDCl_3$) of **6g**

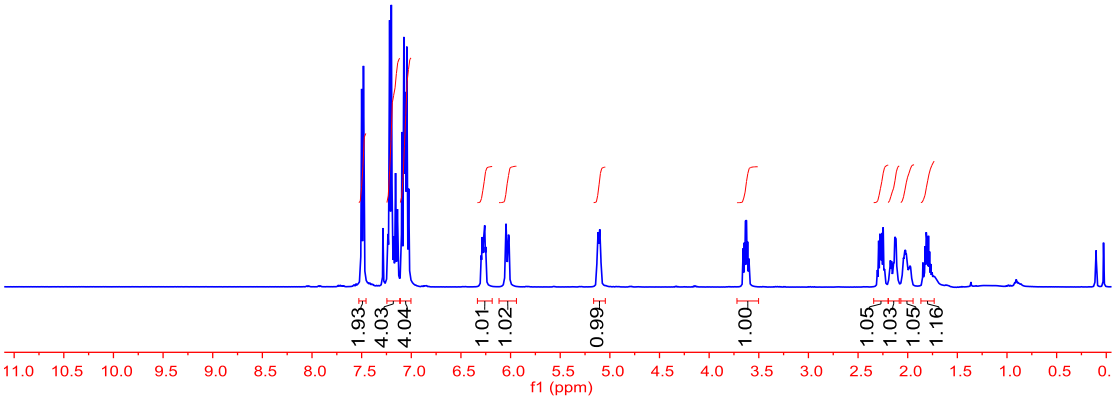


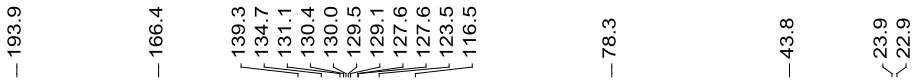
^{13}C NMR (100 MHz, $CDCl_3$) of **6g**

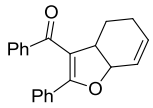




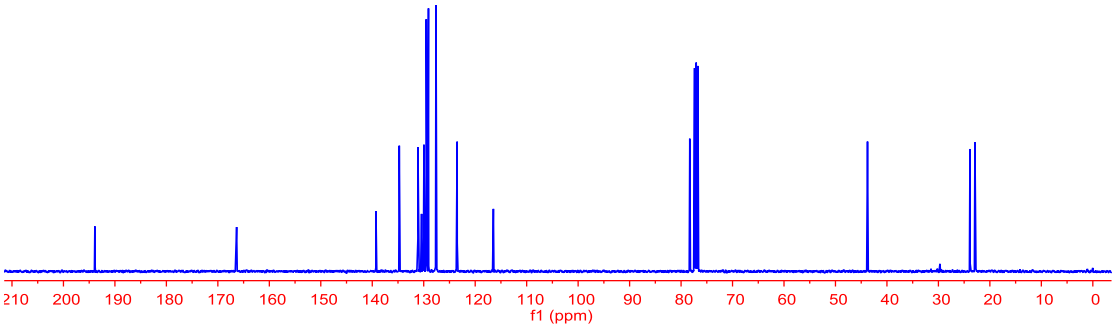
^{1}H NMR (400 MHz, $CDCl_3$) of **6h**

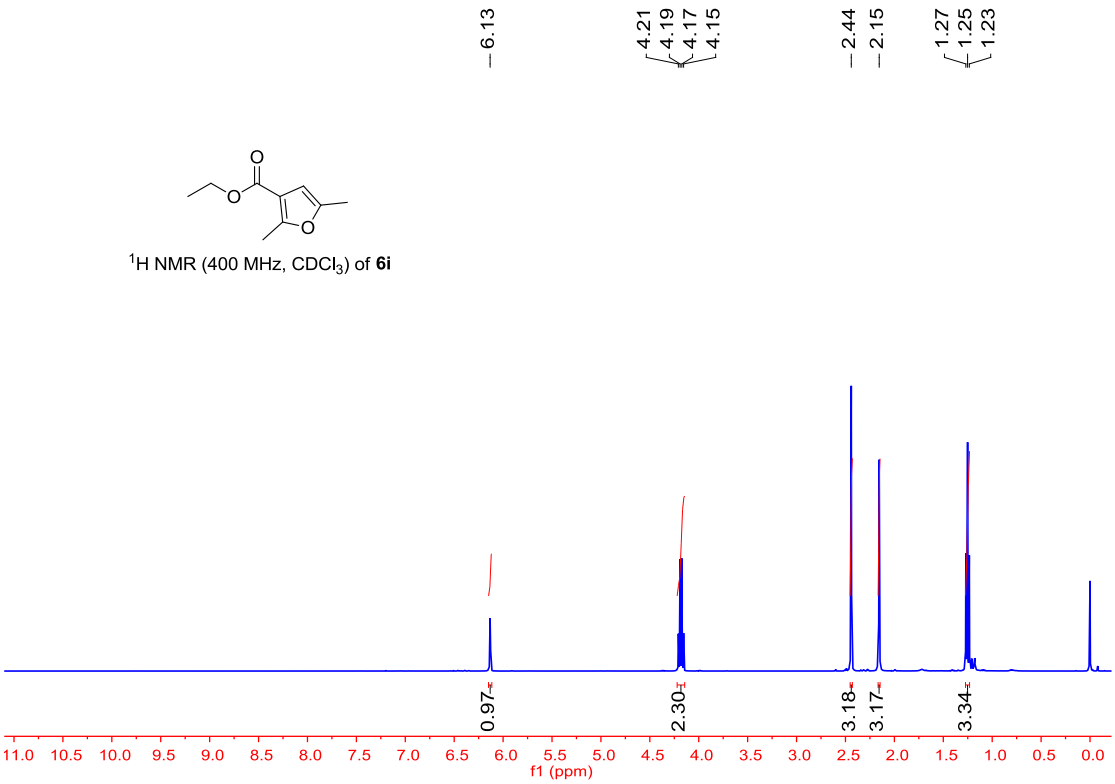




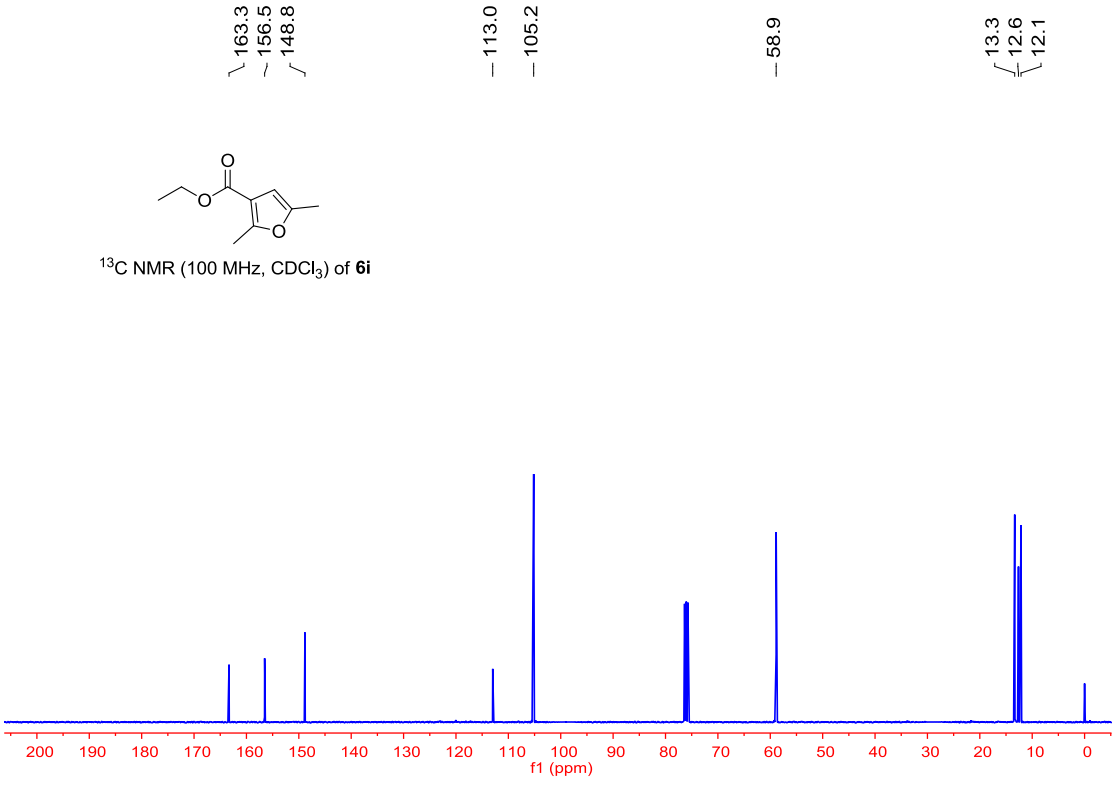


^{13}C NMR (100 MHz, $CDCl_3$) of **6h**

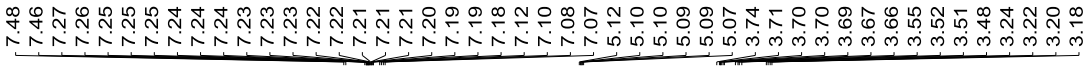


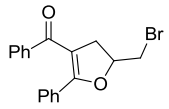


^{1}H NMR (400 MHz, $CDCl_3$) of **6i**

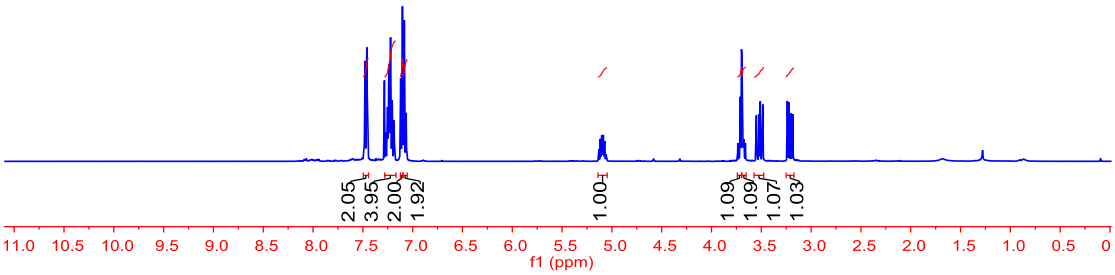


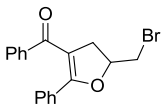
^{13}C NMR (100 MHz, $CDCl_3$) of **6i**



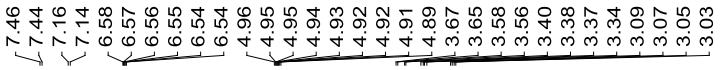


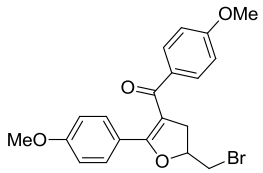
^{1}H NMR (400 MHz, $CDCl_3$) of **7a**



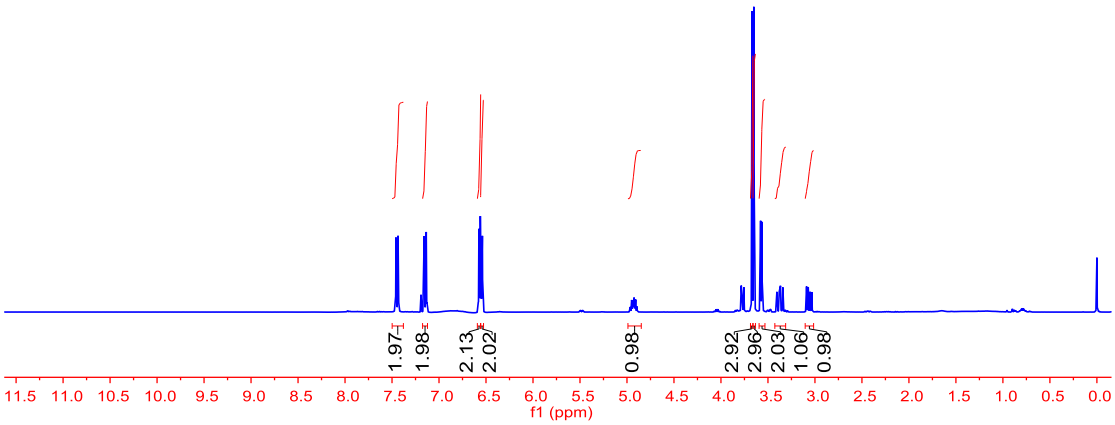


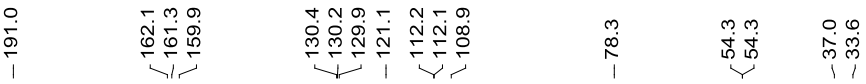
^{13}C NMR (100 MHz, $CDCl_3$) of **7a**

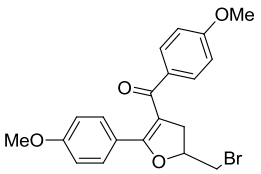




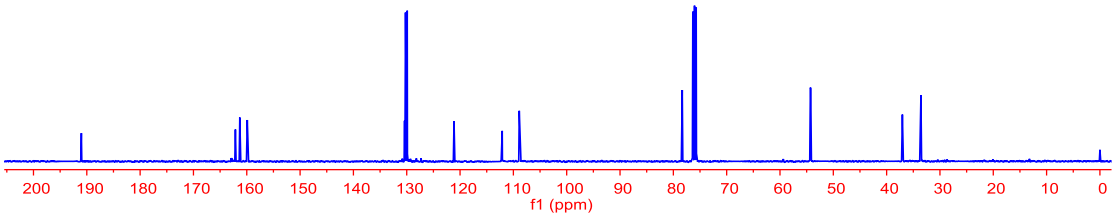
^{1}H NMR (400 MHz, $CDCl_3$) of **7b**

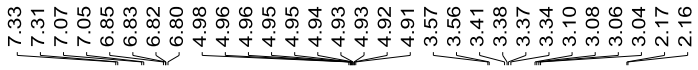


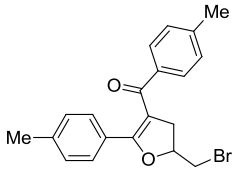




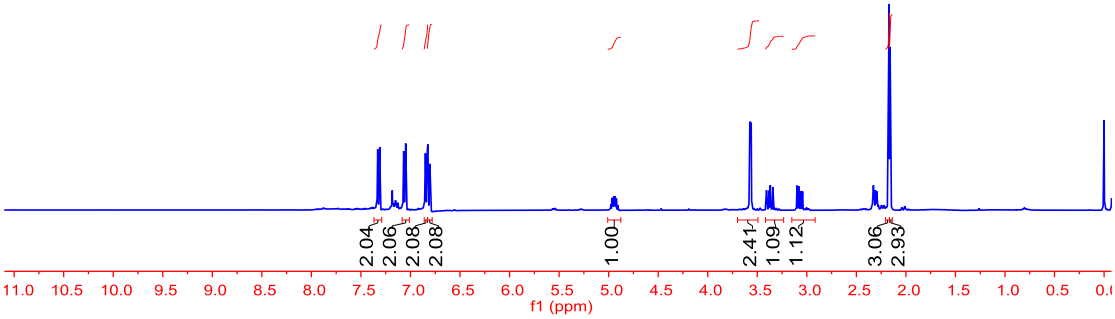
^{13}C NMR (100 MHz, $CDCl_3$) of **7b**

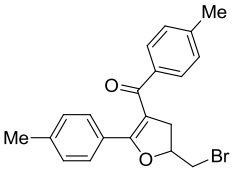




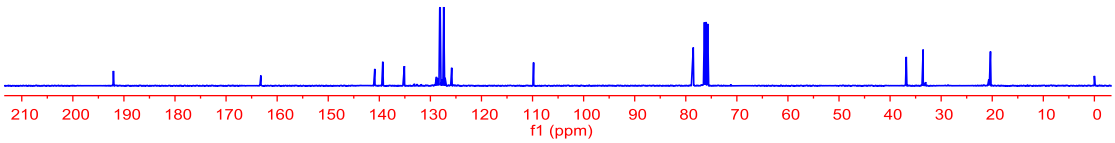


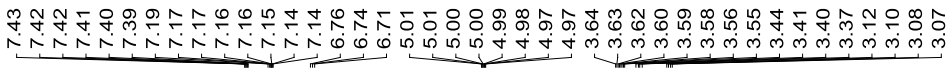
^{1}H NMR (400 MHz, $CDCl_3$) of **7c**

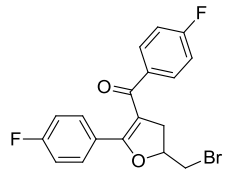




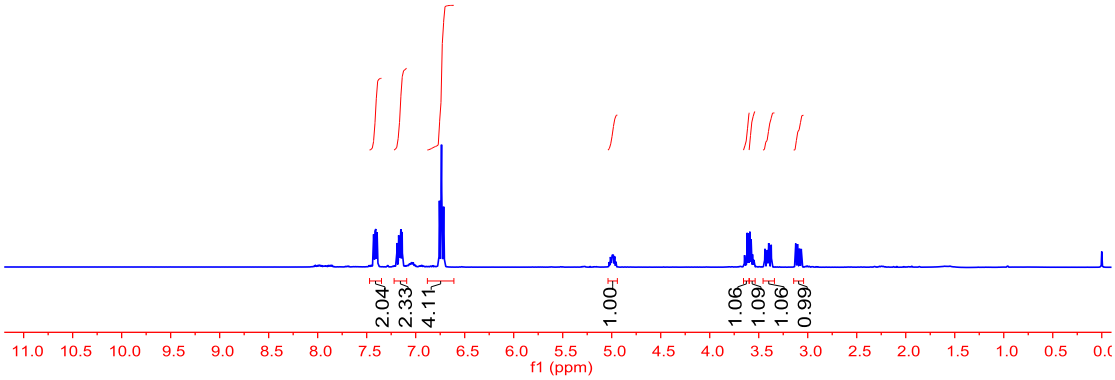
^{13}C NMR (100 MHz, $CDCl_3$) of **7c**

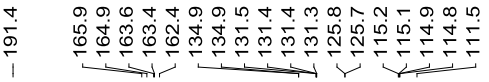


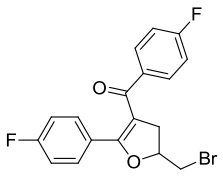




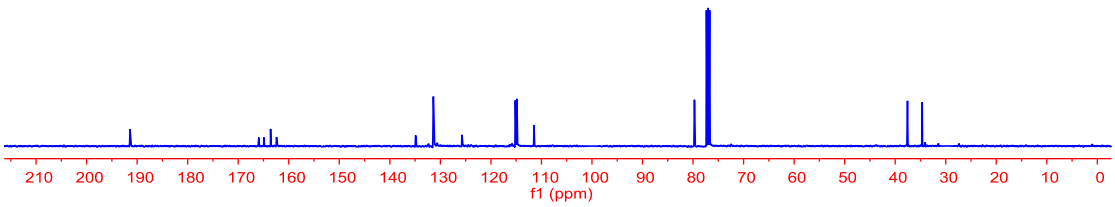
^{1}H NMR (400 MHz, $CDCl_3$) of **7d**

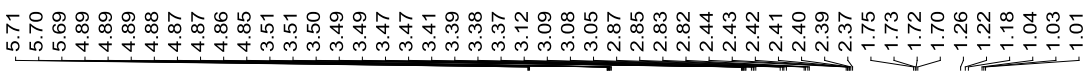


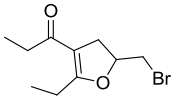




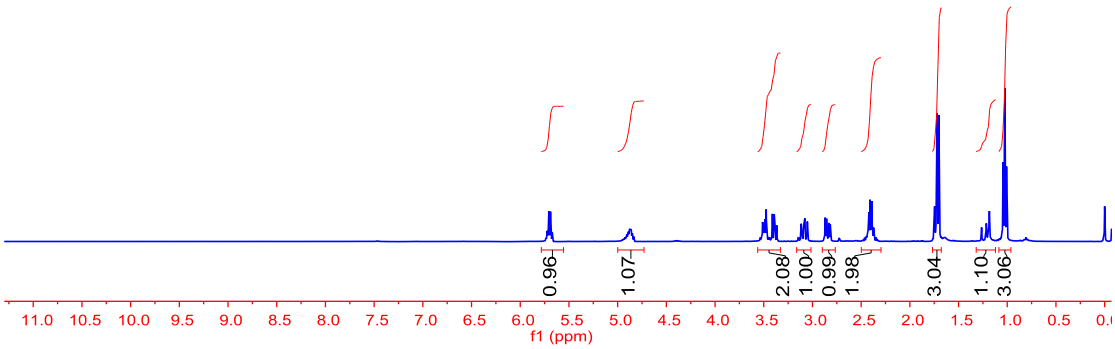
^{13}C NMR (100 MHz, $CDCl_3$) of **7d**

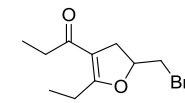




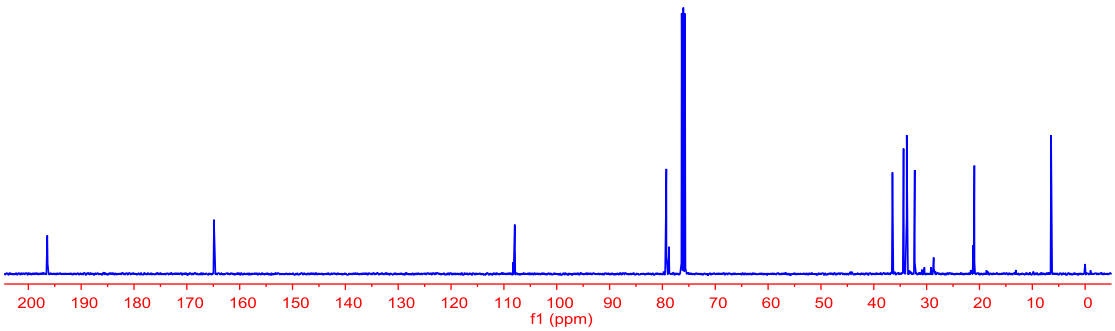


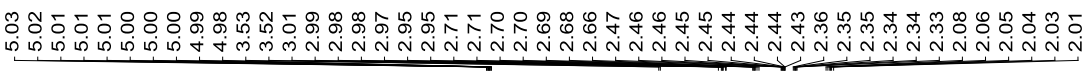
^{1}H NMR (400 MHz, $CDCl_3$) of **7e**

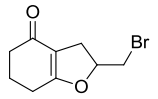




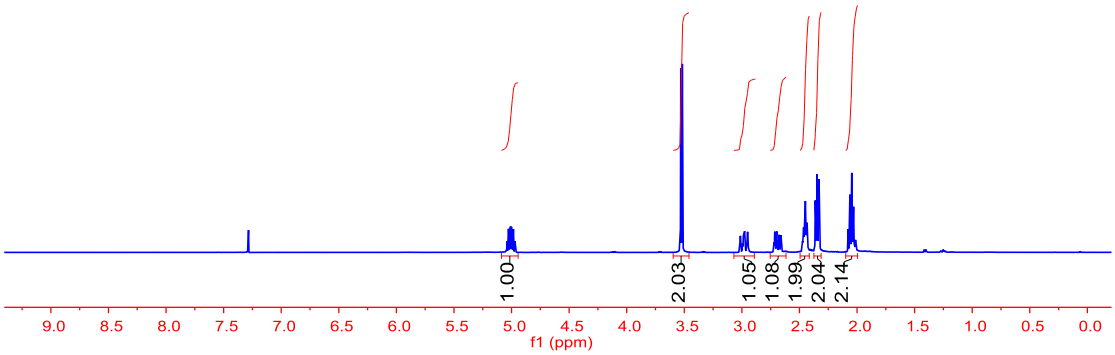
^{13}C NMR (100 MHz, $CDCl_3$) of **7e**

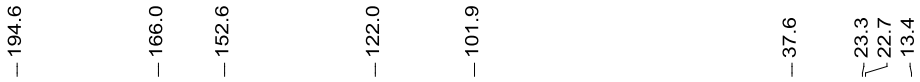


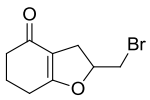




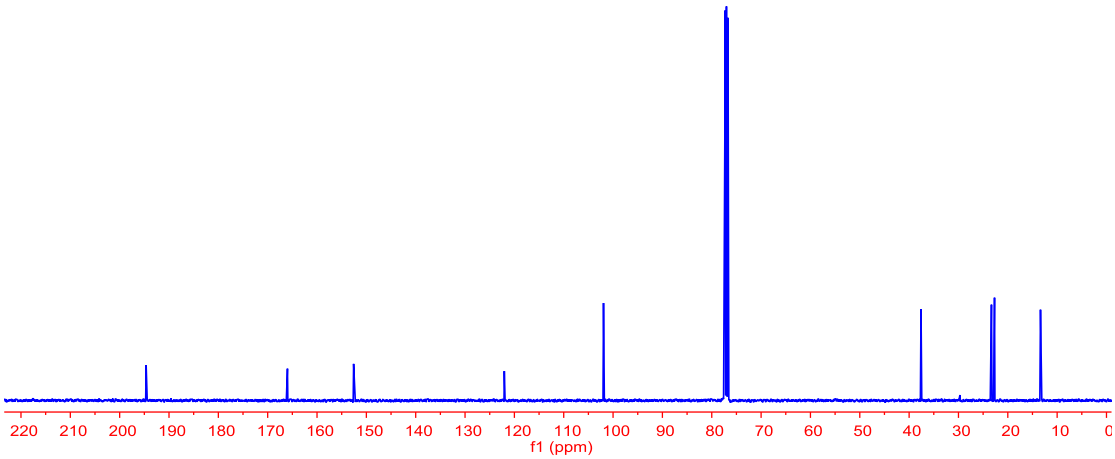
^{1}H NMR (400 MHz, $CDCl_3$) of **7f**

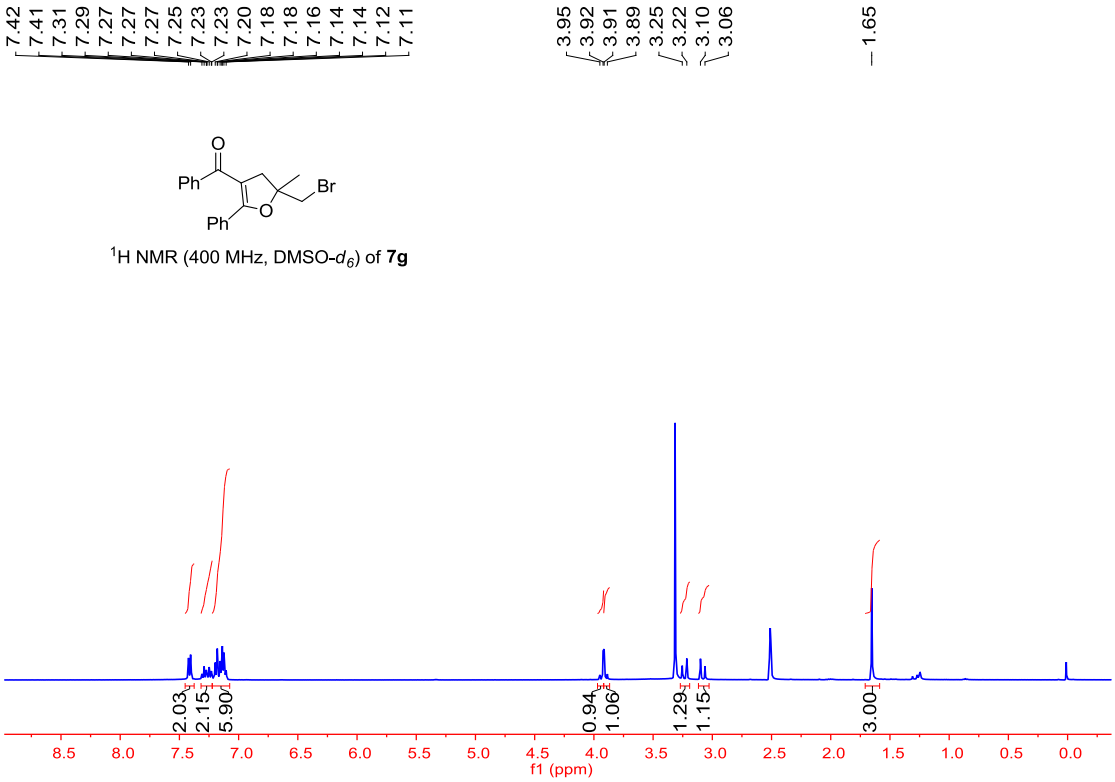




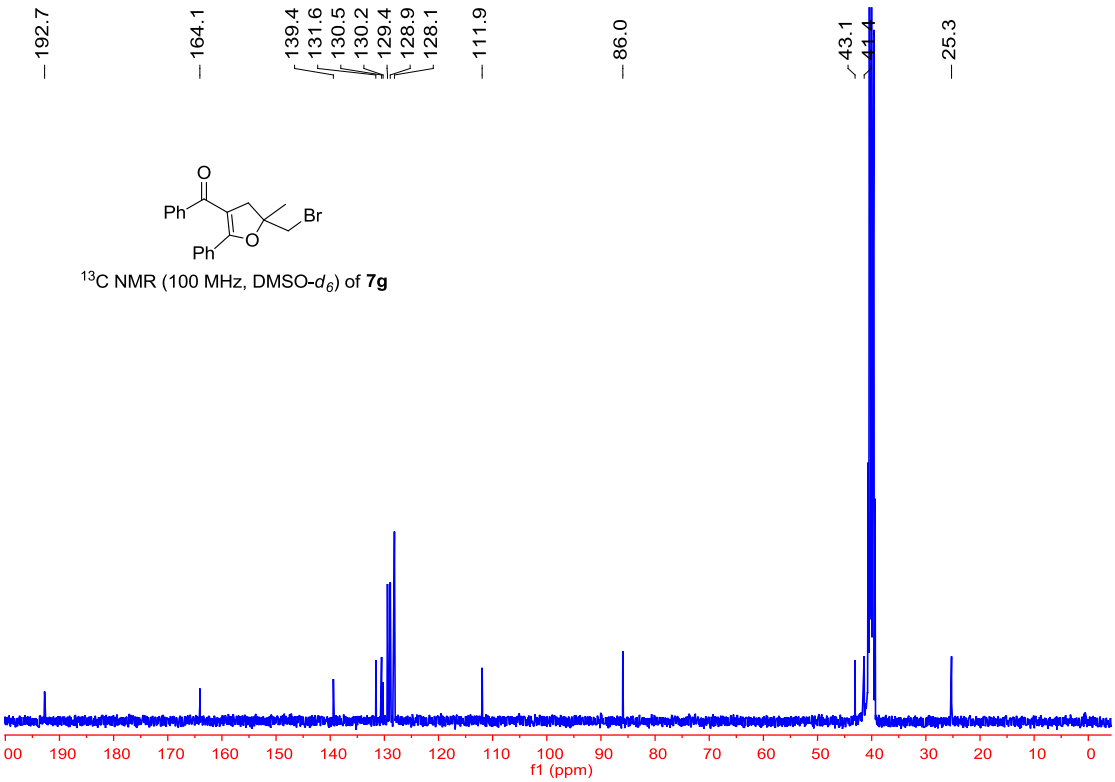


^{13}C NMR (100 MH, $CDCl_3$) of **7f**

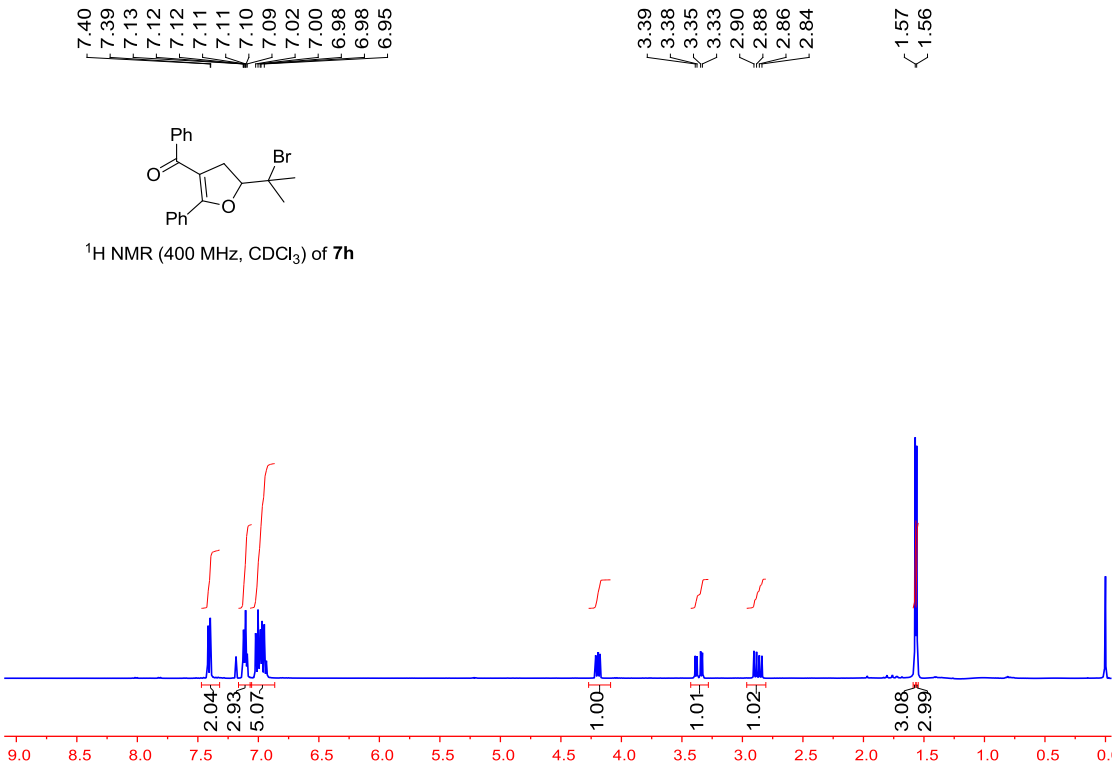




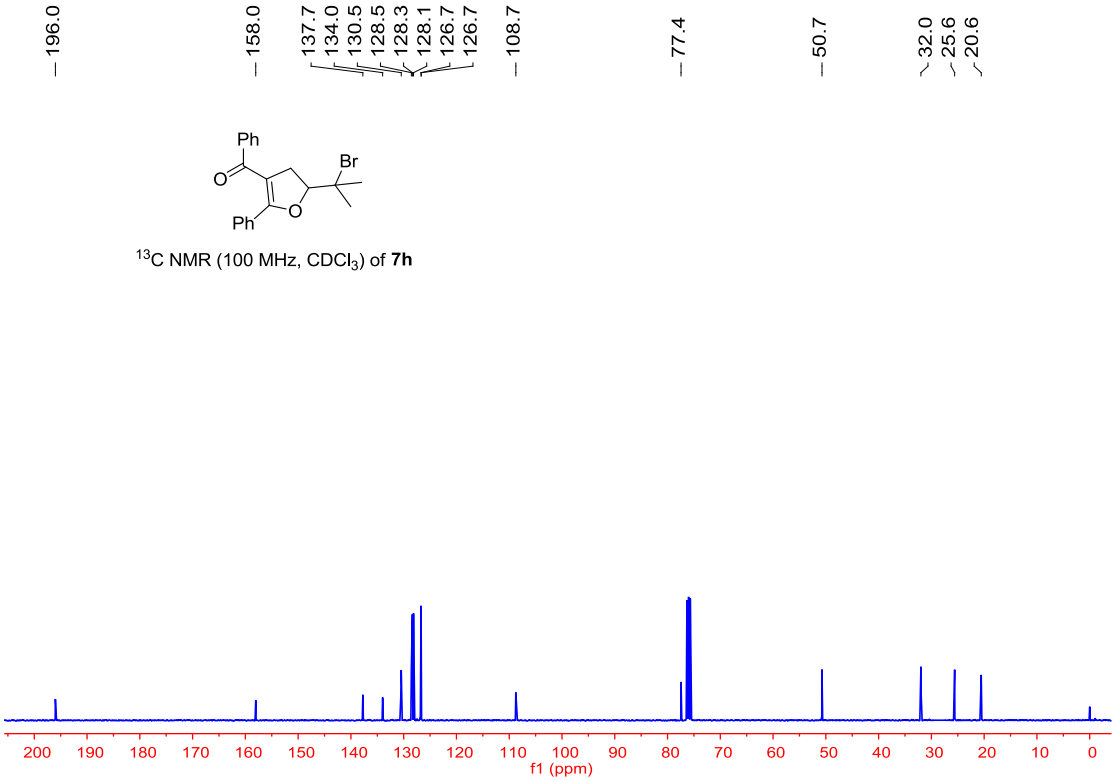
^{1}H NMR (400 MHz, DMSO-d_6) of **7g**



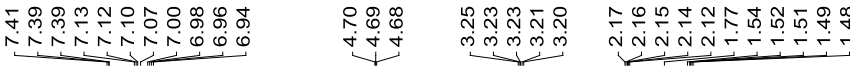
^{13}C NMR (100 MHz, DMSO-d_6) of **7g**

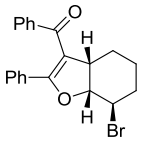


^{1}H NMR (400 MHz, $CDCl_3$) of **7h**

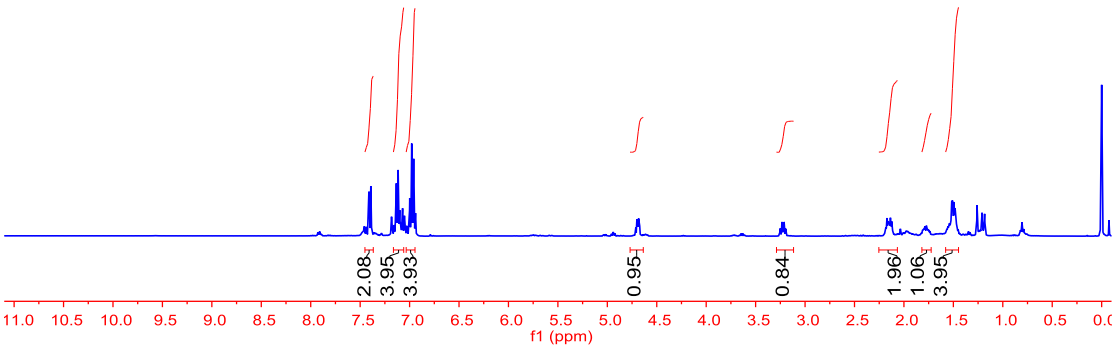


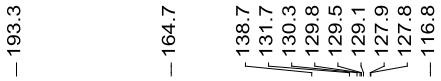
^{13}C NMR (100 MHz, $CDCl_3$) of **7h**

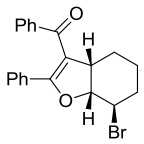




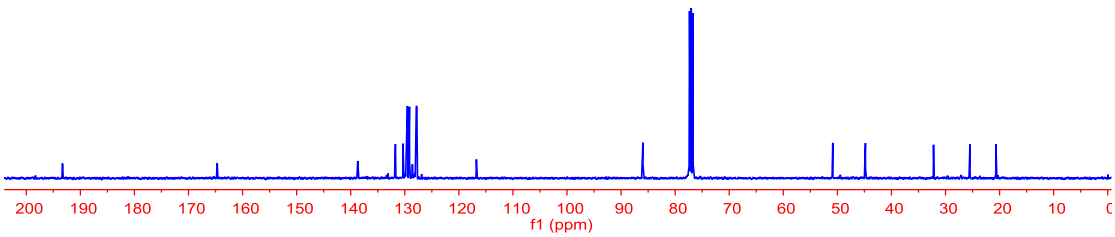
^{1}H NMR (400 MHz, $CDCl_3$) of **7i**

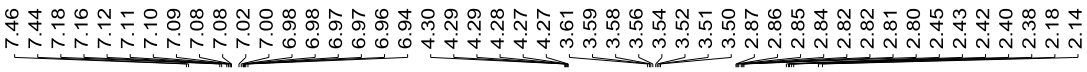


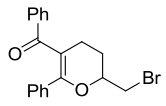




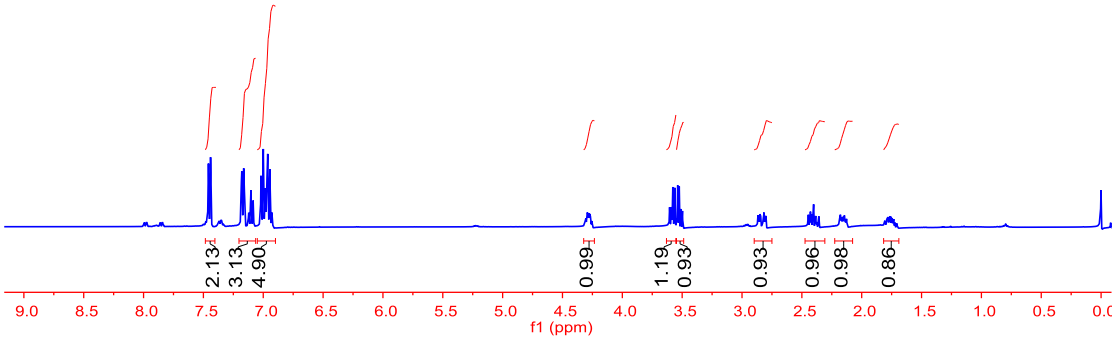
^{13}C NMR (100 MHz, $CDCl_3$) of **7i**

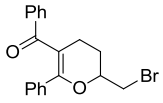






^{1}H NMR (400 MHz, $CDCl_3$) of **7j**





^{13}C NMR (100 MHz, $CDCl_3$) of **7j**