Supplementary Material

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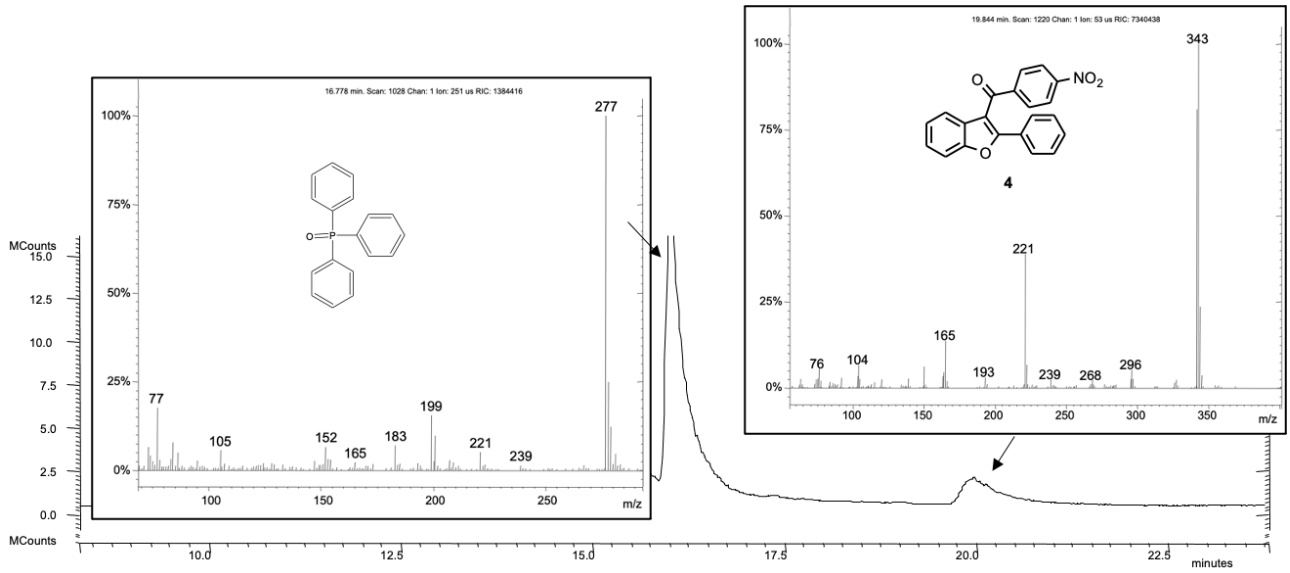
1. General Experimental Information. Experimental Procedures and Compounds Data

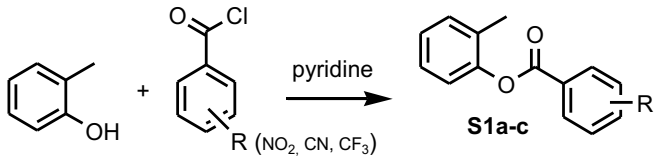
Starting materials, solvent and reagents were obtained from commercial suppliers (Sigma-Aldrich) and were used without further purification. All reactions were performed under N_2 atmosphere. Analytical thin layer chromatography (TLC) was carried out on silica gel 60 F254 plates (0.25 mm), visualized by exposure to UV light. Column chromatography purifications were performed using Aldrich silica gel (60-120) mesh size. Melting points were determined on a Stuart Scientific SMP 11 melting point apparatus and are uncorrected. Concentration and evaporation of the solvent after reaction or extraction were carried out on a rotary evaporator (Büchi Rotavapor) operating at reduced pressure. ^{1}H NMR and ^{13}C NMR spectra were recorded using a spectrometer (Varian INOVA) operating at a field of 14.4 T (600 MHz for ^{1}H, 150.8 MHz for ^{13}C) and using $CDCl_3$ as solvent. Chemical shifts are reported in ppm (δ) relative to TMS (tetramethylsilane) as an internal standard. The 150.8 MHz ^{13}C spectra were acquired under proton decoupling conditions with a 36000 Hz spectral width, 5.5 μs (60° tip angle) pulse width, 1 s acquisition time and 4 s delay time. The long relaxation time was needed to observe some quaternary carbons. Coupling constants *J* are expressed in hertz (Hz). Spin multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), m (multiplet) and apparent triplet (app t). GC/MS: low resolution mass spectrometric experiments were carried out on a Saturn 2000 ion-trap coupled with a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA) operating under EI conditions (electron energy 70 eV, emission current 20 mA, ion-trap temperature 200 °C, manifold temperature 80 °C, automatic gain control (AGC) target 21.000) with the ion trap operating in scan mode (scan range from m/z 40-600 at a scan rate of 1 scan/s). Aliquots of 1 μL of solutions 1.0 x 10^{-5} M in dichloromethane (DCM) have been introduced into the gas chromatographer inlet. An Agilent J&W VF-5ms Low-bleed/MS GC capillary column (30 m, 0.25 mm i.d., 0.25 mm film thickness) (Agilent Technologies Inc., Wilmington, DE, USA), was used. The oven temperature was programmed from 100°C (held for 2 min) to 325 °C at 30 °C/min (held for 10 min). The temperature was then ramped to 350 at 20 °C/min. The transfer line was maintained at 250 °C and the injector port (30:1 split) at 290 °C. HRMS: positive ESI-MS spectra were recorded with

a high-resolution LTQ Orbitrap Elite™ mass spectrometer (Thermo Fisher Scientific). The solutions were infused at a flow rate of 5.00 µL/min into the ESI source. Spectra were recorded in the range of m/z 100-1500 with a resolution of 240000. The instrumental conditions were as follows. Spray voltage 3500 V, capillary temperature 275 °C, sheath gas 5-10 (arbitrary units), auxiliary gas 3 (arbitrary units), sweep gas 0 (arbitrary units), probe heater temperature 50 °C.



1.1 **Figure S1**. GC/MS chromatogram of the crude reaction of **1** (1 equiv.) with **2a** (2.5 equiv.) and triethylamine (5 equiv.) in toluene at 40 °C for 2h.

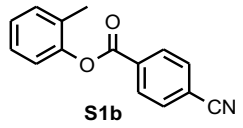
1.2 General procedure for the preparation of 2-methylphenyl benzoates S1a-c



Ortho-cresol (0.92 mmol) was taken in pyridine (10 mL) and to it the proper benzoyl chloride (0.92 mmol) was added drop wisely at 0 °C with stirring and kept overnight. The reaction mixture was warmed on a water bath for 10 min and decomposed with ice cold hydrochloric acid (1:1), followed by extraction with ether (3 x 15 mL). Combined organic layers were dried over $MgSO_4$ and filtered.

The solvent was removed in *vacuo* and the residue was chromatographed on silica gel. Compound **S1a** was synthesized according to known methods, whose analytical data were identical to those reported in precedent work.[1]

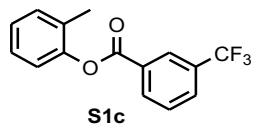
1.3 ***2-Methylphenyl-4-cyanobenzoate*** **(S1b)**



S1b

Column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) gave the title compound as white crystalline solid: (1.4 g, 65% yield); mp: 80-82 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.35 – 8.30 (m, 2H), 7.85 – 7.80 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 (td, *J* = 7.5, 1.4 Hz, 1H), 7.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 163.3 (Cq), 149.2 (Cq), 133.3 (Cq), 132.4 (CH), 131.4 (CH), 130.6 (CH), 130.0 (Cq), 127.2 (CH), 126.5 (CH), 121.7 (CH), 117.9 (Cq), 117.0 (Cq), 16.2 (CH_3) ppm; MS (EI, 70eV) *m/z* (%): 237 (10) [$M^{+\cdot}$], 130 (100), 102 (25).

1.4 ***2-Methylphenyl-3-trifluoromethylbenzoate*** **(S1c)**



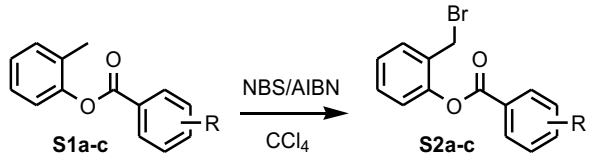
S1c

Column chromatography on silica gel (petroleum ether/ethyl acetate 9:0.5) gave the title compound as trasparent liquid: (2.1 g, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.49 (tt, *J* = 1.7, 0.8 Hz, 1H), 8.41 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.91 (ddt, *J* = 7.8, 1.8, 1.0 Hz, 1H), 7.68 (tt, *J* = 7.8, 0.8 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 (dd, *J* = 7.9, 1.3 Hz, 1H), 2.24 (s, 3H) ppm;

^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 163.6 (CO), 149.3 (Cq), 133.4 (CH), 131.3 (CH), 131.4 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 130.4 (Cq), 130.2 (Cq), 130.1 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 129.4 (CH), 127.1

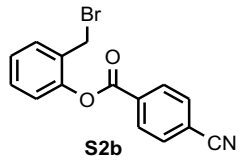
(CH), 127.0 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 126.4 (CH), 123.6 (CF_3, q, J = 271.8 Hz), 121.8 (CH), 16.2 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.80 ppm; MS (EI, 70eV) *m/z* (%): 280 (10) [$M^{+\cdot}$], 173 (100), 145 (22).

1.5 General procedure for the preparation of 2-(bromomethyl)phenyl benzoate S2a-c[1,2]



2-Methylphenyl benzoate **S1a-c** (1 equiv. mmol) and *N*-bromosuccinimide (NBS) (1.2 equiv.) were taken in dry carbon tetrachloride (CCl_4) (3 mL/mmol). The mixture was heated to 85 °C before azobisisobutyronitrile (AIBN) was added in few crystals. After heating at reflux for 1 h, more AIBN was added. The flask was kept at reflux for 5 h. The reaction mixture was cooled down to room temperature and precipitated succinimide was filtered off. The solvent was removed in *vacuo* and the residue was chromatographed on silica gel. Compounds **S2a** was synthesized according to known methods, whose analytical data were identical to those reported in precedent work.[1]

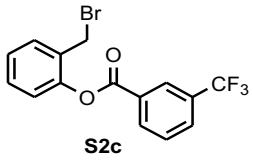
1.6 ***2-(Bromomethyl)phenyl-4-cianobenzoate*** **(S2b)**



Column chromatography on silica gel (petroleum ether/ethyl acetate 8:1) gave the title compound as colorless crystalline solid: (0,536 g, 63% yield); mp: 88-90 °C; ^1H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.34 – 8.30 (m, 2H), 7.83 – 7.78 (m, 2H), 7.45 – 7.340 (d, J = 7.3 Hz, 1H), 7.39 – 7.35 (*t*, J = 7.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 4.45 (s, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 163.1 (Cq), 149.0 (Cq), 133.1 (Cq), 132.7 (CH), 131.2 (CH), 131.1 (CH), 130.9 (Cq), 129.8 (CH),

126.9 (CH), 123.0 (CH), 117.9 (Cq), 117.4 (Cq), 27.6 (CH_3) ppm; MS (EI, 70eV) *m/z* (%): 236 (15) $[M\text{-}Br]^+$, 130 (100), 102 (25).

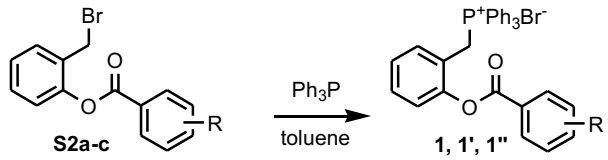
1.7 ***2-(Bromomethyl)phenyl-3-trifluoromethylbenzoate*** **(S2c)**



S2c

Column chromatography on silica gel (petroleum ether/ethyl acetate 8:1) gave the title compound as colorless crystalline solid: (0.533 g, 55% yield); mp: 102-104 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.54 (tt, *J* = 1.9, 0.9 Hz, 1H), 8.46 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.73 – 7.67 (m, 1H), 7.48 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.45-7.40 (m, 1H), 7.32 – 7.25 (m, 2H), 4.47 (s, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 163.4 (CO), 149.0 (Cq), 133.5 (CH), 131.5 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 131.0 (CH), 130.4 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 130.1 (CH), 130.1 (Cq), 129.8 (Cq), 129.5 (CH), 127.2 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 126.7 (CH), 123.6 (CF_3, q, *J* = 271.8 Hz), 123.0 (CH), 27.5 (CH_2) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.81 ppm; MS (EI, 70eV) *m/z* (%): 279 (15) $[M\text{-}Br]^+$, 173 (100), 145 (23).

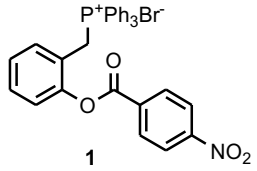
1.8 **General procedure for the preparation of *o*-benzoyloxybenzyltriphenyl phosphomium bromides 1, 1' and 1''**



S2a-c **1, 1', 1"**

A mixture of *o*-(bromomethyl)phenyl benzoate **S2a-c** (1.0 equiv.) and PPh_3·(1.0 equiv.) in toluene (1 mL/mmol) was stirred under reflux for 4 h. The solid formed was filtered and washed with toluene to give the desired solid compounds.[1,3]

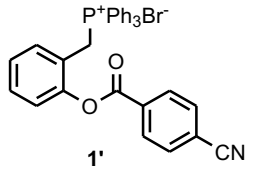
1.8.1 ***O-(4-nitrobenzoyloxy)benzyltriphenyl phosphomium bromide*** **(1)**



1

1 was obtained as a pale yellow solid: (0,590 g, 60% yield); ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.31 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.70 (ddd, *J* = 20.8, 13.8, 7.7 Hz, 9H), 7.55 (td, *J* = 7.9, 3.3 Hz, 6H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.58 (d, *J* = 14.3 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 162.0 (Cq), 151.0 (Cq), 149.4 (Cq, d, $J_{C\text{-}P}$ = 6.0 Hz), 135.1 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 134.2 (CH, d, $J_{C\text{-}P}$ = 15.1 Hz), 133.8 (Cq), 133.4 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 131.6 (CH), 130.2 (CH, d, $J_{C\text{-}P}$ = 15.1 Hz), 129.8 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 126.7 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 123.8 (CH), 122.6 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 119.7 (Cq, d, $J_{C\text{-}P}$ = 7.6 Hz), 117.7 (Cq, d, $J_{C\text{-}P}$ = 86.1 Hz), 26.4 (CH_2, d, $J_{C\text{-}P}$ = 48.3 Hz) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ 22.24 ppm; HRMS (ESI): *m/z* calcd. for $C_{32}H_{25}NO_4P^+$ $[M]^+$: 518.1521, found: 518.1554.

1.8.2 ***O-(4-cianobenzoyloxy)benzyltriphenyl phosphomium bromide*** **(1')**

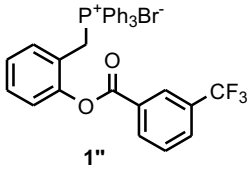


1'

1' was obtained as a cream solid: (0,589 g, 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.08 – 8.04 (m, 2H), 7.82 – 7.77 (m, 2H), 7.75 – 7.64 (m, 9H), 7.57 – 7.51 (m, 6H), 7.37 – 7.31 (m, 1H), 7.27 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.21 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.05 (tt, *J* = 7.6, 1.1 Hz, 1H), 5.55 (d, *J* = 14.4 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 162.2 (Cq), 149.41 (Cq), 149.37 (Cq), 135.1 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 134.2 (CH, d, $J_{C\text{-}P}$ = 10.6 Hz), 133.4 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 132.5 (CH), 132.27 (Cq), 130.9 (CH), 130.3 (CH, d, $J_{C\text{-}P}$ = 15.1 Hz), 129.8 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 126.6

(CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 122.6 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 119.6 (Cq, d, $J_{C\text{-}P}$ = 9.6 Hz), 117.8 (Cq, d, $J_{C\text{-}P}$ = 37.8 Hz), 117.3 (Cq, d, $J_{C\text{-}P}$ = 10.6 Hz), 26.3 (CH_2, d, $J_{C\text{-}P}$ = 48.3 Hz) ppm; ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.23 ppm; HRMS (ESI): *m/z* calcd. for $C_{33}H_{25}NO_2P^+$ $[M]^+$: 498.1623, found: 498.1649.

1.8.3 ***O-(3-trifluoromethylbenzoyloxy)benzyltriphenyl phosphomium bromide*** **(1'')**



1''

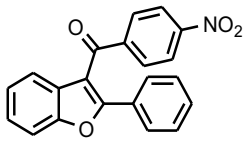
1'' was obtained as a white solid: (0,664 g, 65% yield); ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.24 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.75 – 7.66 (m, 4H), 7.68 – 7.62 (m, 6H), 7.58 – 7.51 (m, 6H), 7.41 (ddd, *J* = 7.9, 2.7, 1.6 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.21 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.10 (tt, *J* = 7.6, 1.1 Hz, 1H), 5.52 (d, *J* = 14.4 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 162.3 (Cq), 149.4 (Cq, d, $J_{C\text{-}P}$ = 4.5 Hz), 135.1 (CH, d, $J_{C\text{-}P}$ = 3.0 Hz), 134.2 (CH, d, $J_{C\text{-}P}$ = 10.6 Hz), 133.9 (CH), 133.3 (CH, d, $J_{C\text{-}P}$ = 6.0 Hz), 132.1 (Cq, d, $J_{C\text{-}P}$ = 10.6 Hz), 131.1 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 130.40 (CH, q, $J_{C\text{-}F}$ = 4.5 Hz), 130.2 (CH, d, $J_{C\text{-}P}$ = 12.1 Hz), 129.80 (CH, d, $J_{C\text{-}P}$ = 3.0 Hz), 129.49 (Cq), 128.5 (CH, d, $J_{C\text{-}P}$ = 12.1 Hz), 126.8 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 126.5 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 122.7 (CH, d, $J_{C\text{-}P}$ = 4.5 Hz), 123.5 (Cq, q, $J_{C\text{-}F}$ = 271.8 Hz), 119.8 (Cq, d, $J_{C\text{-}P}$ = 9.1 Hz), 117.6 (Cq, d, $J_{C\text{-}P}$ = 86.1 Hz), 26.1 (CH_2, d, $J_{C\text{-}P}$ = 48.3 Hz) ppm; ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.38 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.55 ppm; HRMS (ESI): *m/z* calcd. for $C_{33}H_{25}F_3O_2P^+$ $[M]^+$: 541.1544, found: 541.1575.

1.9 General procedure for the preparation of 2-phenylbenzofurans 3, 3' and 3-benzoyl-2-phenylbenzofuras 4-20

In a round bottom flask *o*-benzoyloxybenzyltriphenylphosphomium bromide **1**, **1'** or **1''** (1.0 equiv.) and the proper benzoyl chloride (2.5 equiv.) were added and dissolved in dichloromethane (25 mL/mmole). Then triethylamine (Et_3N) (5 equiv., 0,069 mL/mmole) was added dropwise and the reaction mixture was stirred under reflux for 2 h. DCM was removed under reduced pressure, and the reaction mixture heated to 160 °C for further 1 h. The crude mixture was purified by column chromatography on silica gel in petroleum ether/ethyl acetate to furnish the desired product.

The analytical data of compounds **3** and **3'** were identical to those reported in our precedent work.[4]

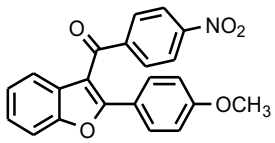
1.10 *3-(4-Nitrobenzoyl)-2-phenylbenzofuran* (4)



4

Accordingly to procedure, using phosphonium salt **1** (0.060 g, 0.10 mmol, 1.0 equiv.) and benzoyl chloride **2a** (0.035 g, 0.25 mmol, 2.5 equiv.), triethylamine (70 μL, 5 equiv.) and DCM (2 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 7:1. **4** was obtained as a yellow solid: (0.029 g, 85% yield); mp: 126-128 °C; ^1H and ^{13}C NMR data for this compound are consistent with previously reported literature data.[28] ^1H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ = 7.27 (t, *J* = 7.43 Hz, 2H), 7.31-7.35 (m, 2H), 7.42 (t, *J* = 7.72 Hz, 1H), 7.57 (d, *J* = 8.16 Hz, 2H), 7.61 (d, *J* = 8.29 Hz, 1H), 7.71 (d, *J* = 8.02 Hz, 1H), 7.89 (d, 2H, *J* = 8.22 Hz), 8.10 (d, *J* = 8.22 Hz, 2H) ppm; ^{13}C NMR (150.8 MHz, $CDCl_3$, 77.0 ppm): δ = 111.4, 115.5, 121.5, 123.4, 124.3, 125.9, 127.7, 128.5, 128.9, 129.0, 130.4, 130.5, 142.9, 149.9, 154.0, 159.7, 190.2 ppm; MS (EI, 70eV) *m/z* (%): 343 (100) [$M^{+\cdot}$], 221 (34), 150 (5).

1.11 ***2-(4-Methoxyphenyl)-3-(4-nitrobenzoyl)benzofuran*** **(5)**

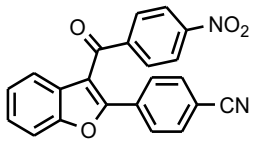


5

Accordingly to procedure, using phosphonium salt **1** (0.045 g, 0.075 mmol, 1.0 equiv.) and 4-methoxybenzoyl chloride **2b** (0.032 g, 0.19 mmol, 2.5 equiv.), triethylamine (52 μL, 5 equiv.) and DCM (2 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 6:1. **5** was obtained as a straw yellow solid: (0.016 g, 56% yield) ; mp: 130-132 °C; ^{1}H and ^{13}C NMR data for this compound are consistent with previously reported literature data.[1] ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ = 3.79 (s, OCH_3, 3H), 6.80 (ddd, *J* = 8.8, 2.6, 2.0 Hz, 2H), 7.31 (td, *J* = 7.3, 0.7 Hz, 1H), 7.39 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.8, 2.6, 2.0 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.91 (ddd, *J* = 8.8, 2.0, 1.6 Hz, 2H), 8.18 (ddd, *J* = 8.8, 2.0, 1.6 Hz, 2H) ppm; ^{13}C NMR (150.8 MHz, $CDCl_3$, 77.0 ppm): δ = 55.4, 111.3, 114.0, 114.4, 121.38, 121.43, 123.5, 124.2, 125.5, 127.9, 130.5, 130.6, 143.2, 149.9, 153.8, 160.2, 161.3, 190.3 ppm; MS (EI, 70eV) *m/z* (%): 373 (100) [$M^{+\cdot}$], 251 (23), 150 (3).

2-(4-Nitrophenyl)benzofuran **(3)**[4]: (0.01 g, 5% yield).

1.12 ***2-(4-Cyanophenyl)-3-(4-nitrobenzoyl)benzofuran*** **(6)**

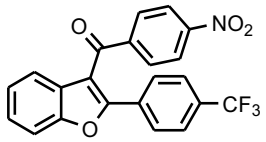


6

Accordingly to procedure, using phosphonium salt **1** (0.045 g, 0.075 mmol, 1.0 equiv.) and 4-cyanobenzoyl chloride **2d** (0.031 g, 0.19 mmol, 2.5 equiv.), triethylamine (53 μL, 5 equiv.) and DCM (2 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 6:1. **6** was obtained as a yellow solid: (0.024 g, 88% yield); mp: 174-177 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.28 – 8.21 (m, 2H), 8.04 – 7.99 (m, 2H), 7.92 – 7.86 (m, 2H), 7.68 – 7.62 (m, 3H), 7.46

(ddd, J = 8.4, 7.1, 1.3 Hz, 1H), 7.38 (dt, J = 7.9, 1.0 Hz, 1H), 7.30 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 189.9 (CO), 155.7 (Cq), 154.1 (Cq), 150.6 (Cq), 142.2 (Cq), 133.1 (Cq), 132.3 (CH), 130.7 (CH), 128.7 (CH), 127.4 (Cq), 126.8 (CH), 124.6 (CH), 123.9 (CH), 121.6 (CH), 118.1 (Cq), 117.5 (Cq), 113.6 (Cq), 111.8 (CH) ppm; MS (EI, 70eV) *m/z* (%): 368 (100) [$M^{+\cdot}$], 246 (45), 150 (13); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}N_2O_4$ $[M+H]^+$: 369.0875, found: 369.0866.

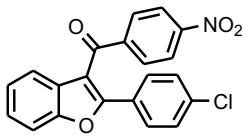
1.13 ***3-(4-Nitrobenzoyl)-2-(4-trifluoromethylphenyl)benzofuran*** **(7)**



7

Accordingly to procedure, using phosphonium salt **1** (0.060 g, 0.102 mmol, 1.0 equiv.) and 4-trifluoromethylbenzoyl chloride **2e** (0.053 g, 0.25 mmol, 2.5 equiv.), triethylamine (70 µL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 6:1. **7** was obtained as light yellow solid: (0.037 g, 90% yield); mp: 115-118 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.24 – 8.19 (m, 2H), 8.01 – 7.93 (m, 2H), 7.87 – 7.77 (m, 2H), 7.64 (dt, J = 8.3, 0.9 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.49 – 7.42 (m, 2H), 7.31 (ddd, J = 8.0, 7.4, 1.0 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm); δ 190.0 (CO), 156.8 (Cq), 154.1 (Cq), 150.4 (Cq), 142.4 (Cq), 132.4 (Cq), 131.9 (Cq, q, $J_{Cq\text{-}F}$ = 33.22 Hz), 130.7 (CH), 128.8 (CH), 127.4 (Cq), 126.5 (CH), 125.6 (CH, q, $J_{CH\text{-}F}$ = 3.02 Hz), 124.5 (CH), 123.8 (CH), 123.6 (CF_3, q, $J_{C\text{-}F}$ = 273.3 Hz), 121.6 (CH), 116.9 (Cq), 111.7 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.01 ppm; MS (EI, 70eV) *m/z* (%): 411 (100) [$M^{+\cdot}$], 289 (70), 150 (13); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}F_3NO_4$ $[M+H]^+$: 412.0796, found: 412.0776.

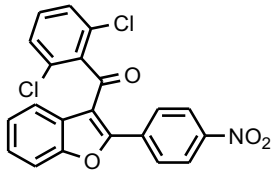
1.14 ***2-(4-Chlorophenyl)-3-(4-nitrobenzoyl)benzofuran*** **(8)**



8

Accordingly to procedure, using phosphonium salt **1** (0.045 g, 0.075 mmol, 1.0 equiv.) and 4-chlorobenzoyl chloride **2f** (0.033 g, 0.19 mmol, 2.5 equiv.), triethylamine (52 μL, 5 equiv.) and DCM (2 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 6:1. **8** was obtained as a yellow solid: (0.021 g, 72% yield); mp: 165-168 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.22 – 8.17 (m, 2H), 7.98 – 7.93 (m, 2H), 7.65 – 7.59 (m, 3H), 7.52 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.33 – 7.28 (m, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 190.0 (CO), 157.9 (Cq), 153.9 (Cq), 150.2 (Cq), 142.7 (Cq), 136.7 (Cq), 130.6 (CH), 129.9 (CH), 128.9 (CH), 127.6 (Cq), 127.5 (Cq), 126.1 (CH), 124.4 (CH), 123.7 (CH), 121.5 (CH), 115.8 (Cq), 111.5 (CH) ppm; MS (EI, 70eV) *m/z* (%): 377 (100) [$M^{+\cdot}$], 255 (30), 150 (3) ppm; HRMS (ESI): *m/z* calcd. for $C_{21}H_{13}ClNO_4$ $[M+H]^+$: 378.0533, found: 378.0522.

1.15 ***3-(2,6-Dichlorobenzoyl)-2-(4-nitrophenyl)benzofuran*** **(9)**

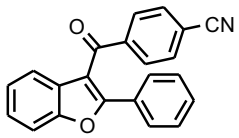


9

Accordingly to procedure, using phosphonium salt **1** (0.055 g, 0.092 mmol, 1.0 equiv.) and 2,6-dichorobenzoyl chloride **2g** (0.048 g, 0.229 mmol, 2.5 equiv.), triethylamine (65 μL, 5 equiv.) and DCM (2 mL). Light yellow solid, trace: (0.001 g, 3% yield); MS (EI, 70eV) *m/z* (%): 411 (100) [$M^{+\cdot}$], 266 (43), 173 (75); HRMS (ESI): *m/z* calcd. for $C_{21}H_{12}Cl_2NO_4$ $[M+H]^+$: 412.0143, found: 412.0143.

2-(4-Nitrophenyl)benzofuran **(3)**[4]: (0.003 g, 13% yield).

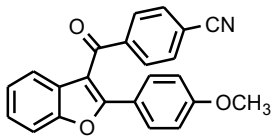
1.16 ***3-(4-Cyanobenzoyl)-2-phenylbenzofuran*** **(10)**



10

Accordingly to procedure, using phosphonium salt **1'** (0.060 g, 0.010 mmol, 1.0 equiv.) and benzoyl chloride **2a** (0.037 g, 0.259 mmol, 2.5 equiv.), triethylamine (72 μL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 9:1. **10** was obtained as a yellow solid: (0.019 g, 55% yield); mp: 160-162 °C; ^{1}H and ^{13}C NMR data for this compound are consistent with previously reported literature data.[28] ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ = 7.28 (t, *J* = 7.91 Hz, 2H), 7.34 (m, 2H), 7.39-7.44 (m, 1H), 7.56 (m, 4H), 7.61 (d, *J* = 8.30 Hz, 1H), 7.70 (d, *J* = 7.80 Hz, 1H), 7.82-7.86 (m, 2H) ppm; ^{13}C NMR (150.8 MHz, $CDCl_3$, 77.0 ppm): δ = 111.6, 115.6, 116.0, 118.1, 121.7, 124.5, 125.9, 127.9, 128.6, 129.1, 129.2, 130.2, 130.5, 132.2, 141.4, 154.2, 159.7, 190.8 ppm; MS (EI, 70eV) *m/z* (%): 323 (100) [$M^{+\cdot}$], 221 (33), 130 (12) 102 (17).

1.17 ***3-(4-Cyanobenzoyl)-2-(4-methoxyphenyl)benzofuran*** **(11)**



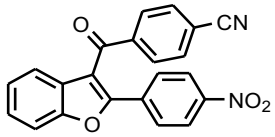
11

Accordingly to procedure, using phosphonium salt **1'** (0.060 g, 0.104 mmol, 1.0 equiv.) and 4-methoxybenzoyl chloride **2b** (0.044 g, 0.259 mmol, 2.5 equiv.), triethylamine (72 μL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 4:1. **11** was obtained as a yellow solid: (0.018 g, 50% yield); mp: 99-101 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 7.87 – 7.82 (m, 2H), 7.64 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.56 – 7.51 (m, 2H), 7.38 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.3, 1.0 Hz, 1H), 6.82 –

6.77 (m, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 190.6 (CO), 161.3 (Cq), 160.0 (Cq), 153.8 (Cq), 141.6 (Cq), 132.1 (CH), 130.6 (CH), 130.0 (CH), 128.0 (Cq), 125.5 (CH), 124.2 (CH), 121.5 (Cq), 121.4 (CH), 118.0 (Cq), 115.8 (Cq), 114.3 (Cq), 114.0 (CH), 111.2 (CH), 55.4 (OCH_3) ppm; MS (EI, 70eV) *m/z* (%): 353 (100) [$M^{+\cdot}$], 251 (33), 130 (12) 102 (17); HRMS (ESI): *m/z* calcd. for $C_{23}H_{16}NO_3$ $[M+H]^+$: 354.1130, found: 354.1120.

4-(Benzofuran-2-yl)-benzonitrile **(3')**[4]: (0.0016 g, 10% yield).

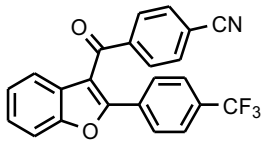
1.18 ***3-(4-Cyanobenzoyl)-2-(4-nitrophenyl)benzofuran*** **(12)**



12

Accordingly, to procedure, using phosphonium salt **1'** (0.060 g, 0.104 mmol, 1.0 equiv.), 4-nitrobenzoyl chloride **2c** (0.048 g, 0.259 mmol, 2.5 equiv.), triethylamine (72 μL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 6:0.5. **12** was obtained as a yellow solid: (0.033 g, 85% yield); mp: 70 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm) δ 8.17 – 8.14 (m, 2H), 7.91 – 7.87 (m, 4H), 7.67 – 7.63 (m, 2H), 7.58 (dt, J = 8.4, 0.8 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.31 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_{33}$, 77.0 ppm) δ 190.1$_5$ (CO), 154.9 (Cq), 154.2 (Cq), 148.3 (Cq), 140.6 (Cq), 134.9 (Cq), 132.6 (CH), 130.1 (CH), 128.9$_6$ (CH), 127.4 (Cq), 126.9 (CH), 124.7 (CH), 123.9 (CH), 121.6 (CH), 117.9 (Cq), 117.6 (Cq), 117.1 (Cq), 111.8 (CH) ppm; MS (EI, 70eV) *m/z* (%): 368 (100) [$M^{+\cdot}$], 266 (33), 130 (7); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}N_2O_4$ $[M+H]^+$: 369.0875, found: 369.0867.

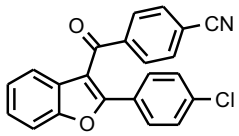
1.19 ***3-(4-Cyanobenzoyl)-2-(4-trifluoromethylphenyl)benzofuran*** **(13)**.



13

Accordingly, to procedure, using phosphonium salt **1'** (0.060 g, 0.104 mmol, 1.0 equiv.), 4-trifluoromethylbenzoyl chloride **2e** (0.054 g, 0.259 mmol, 2.5 equiv.), triethylamine (72 μL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 9:1. **13** was obtained as a white solid: (0.034 g, 83% yield); mp: 145-147 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 7.94 – 7.89 (m, 2H), 7.86 – 7.81 (m, 2H), 7.70 – 7.65 (m, 2H), 7.64 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.48 – 7.41 (m, 2H), 7.31 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 190.3 (CO), 156.6 (Cq), 154.0 (Cq), 140.8 (Cq), 132.4 (CH), 131.9 (Cq, q, J_{C-F} = 33.22 Hz), 130.1 (CH), 128.7 (CH), 127.5 (Cq), 126.4 (CH), 125.5 (CH, q, J_{CH-F} = 3.02 Hz), 124.5 (CH), 123.6 (CF_3, q, J_{C-F} = 273.31 Hz), 121.5 (CH), 117.7 (Cq), 116.8$_5$ (Cq), 116.7 (Cq), 111.7 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.99 ppm; MS (EI, 70eV) *m/z* (%): 391 (100) [$M^{+\cdot}$], 289 (33), 130 (7); HRMS (ESI): *m/z* calcd. for $C_{23}H_{13}F_3NO_2$ $[M+H]^+$: 392.0898, found: 392.0884.

1.20 ***2-(4-Chlorophenyl)-3-(4-cyanobenzoyl)benzofuran*** **(14)**

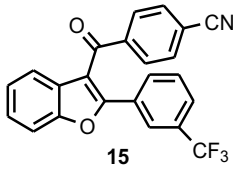


14

Accordingly to procedure, using phosphonium salt **1'** (0.060 g, 0.104 mmol, 1.0 equiv.), 4-chlorobenzoyl chloride **2f** (0.045 g, 0.259 mmol, 2.5 equiv.), triethylamine (72 μL, 5 equiv.) and DCM (2.5 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 9:1. **14** was obtained as a yellow solid: (0.029 g, 77% yield); mp: 164-166 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 7.90 – 7.87 (m, 2H), 7.67 – 7.63 (m, 2H), 7.63 – 7.58 (m, 3H), 7.51 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.33 – 7.27 (m, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 190.3 (CO), 157.7 (Cq), 153.9 (Cq), 141.1 (Cq), 136.6 (Cq), 132.3 (CH), 130.0 (CH), 129.9 (CH), 128.9 (CH), 127.7 (Cq), 127.5 (Cq), 126.0 (CH), 124.4 (CH), 121.5 (CH), 117.8 (Cq), 116.4 (Cq), 115.8 (Cq), 111.5 (CH) ppm; MS (EI, 70eV) *m/z* (%): 357 (100) [$M^{+\cdot}$], 255

(33), 130 (25), 102 (30); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}ClNO_2$ $[M+H]^+$: 358.0634, found: 358.0623.

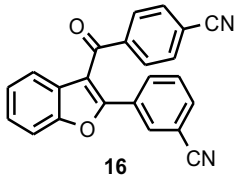
1.21 ***3-(4-Cyanobenzoyl)-2-(3-trifluoromethylphenyl)benzofuran*** **(15)**



15

Accordingly to procedure, using phosphonium salt **1'** (0.07 g, 0.121 mmol, 1.0 equiv.), 3-trifluoromethylbenzoyl chloride **2h** (0.063 g, 0.302 mmol, 2.5 equiv.), triethylamine (83 μL, 5 equiv.) and DCM (3 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 8:1. **15** was obtained as a pale yellow solid: (0.043 g, 92% yield); mp: 115-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 4H), 7.64 – 7.57 (m, 5H), 7.48 – 7.40 (m, 2H), 7.35 – 7.29 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2 (CO), 157.1 (Cq), 154.0 (Cq), 141.0 (Cq), 132.3 (CH), 131.6 (CH), 131.1 (Cq, $J_{C\text{-}F}$ = 33.22 Hz), 129.9 (CH), 129.8 (Cq), 129.1 (CH), 127.5 (Cq), 126.7 (CH, $J_{CH\text{-}F}$ = 3.02 Hz), 126.4 (CH), 125.7 (CH, $J_{CH\text{-}F}$ = 3.02 Hz), 124.5 (CH), 123.4 (CF_3, $J_{C\text{-}F}$ = 273.31 Hz), 121.7 (CH), 117.7 (Cq), 116.5 (Cq), 116.3 (Cq), 111.6 (CH) ppm; ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.98 ppm; MS (EI, 70eV) *m/z* (%): 391 (100) $[M^{+\cdot}]$, 289 (33), 130 (7); HRMS (ESI): *m/z* calcd. for $C_{23}H_{13}F_3NO_2$ $[M+H]^+$: 392.0898, found: 392.0880.

1.22 ***3-(4-Cyanobenzoyl)-2-(3-cyanophenyl)benzofuran*** **(16)**

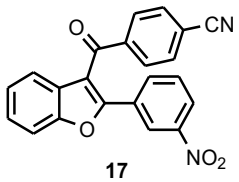


16

Accordingly to procedure, using phosphonium salt **1'** (0.07 g, 0.121 mmol, 1.0 equiv.), 3-cyanobenzoyl chloride **2i** (0.050 g, 0.302 mmol, 2.5 equiv.), triethylamine (83 μL, 5 equiv.) and DCM

(3 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 5:1. **16** was obtained as a white solid: (0.036 g, 86% yield); mp: 150-152 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.08 – 8.03 (m, 1H), 7.94 – 7.87 (m, 3H), 7.70 – 7.59 (m, 4H), 7.47 – 7.38 (m, 3H), 7.29 (ddd, *J* = 8.1, 7.2, 0.9 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 190.0 (CO), 155.8 (Cq), 153.9 (Cq), 140.8 (Cq), 133.2 (CH), 132.4 (CH), 132.3 (CH), 131.8 (CH), 130.4 (Cq), 130.0 (CH), 129.4 (CH), 127.3 (Cq), 126.5 (CH), 124.6 (CH), 121.6 (CH), 117.8 (Cq), 117.7 (Cq), 117.0 (Cq), 116.7 (Cq), 113.2 (Cq), 111.9 (CH) ppm; MS (EI, 70eV) *m/z* (%): 348 (100) [$M^{+\cdot}$], 246 (23), 130 (12); HRMS (ESI): *m/z* calcd. for $C_{23}H_{13}N_2O_2$ $[M+H]^+$: 349.0977, found: 349.0983.

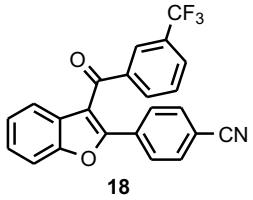
1.23 ***3-(4-Cyanobenzoyl)-2-(3-nitrophenyl)benzofuran*** **(17)**



17

Accordingly to procedure, using phosphonium salt **1'** (0.070 g, 0.121 mmol, 1.0 equiv.), 3-nitrobenzoyl chloride **2l** (0.056 g, 0.302 mmol, 2.5 equiv.), triethylamine (83 μL, 5 equiv.) and DCM (3 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 8:1. **17** was obtained as a pale yellow solid: (0.038 g, 86% yield); mp: 198-200 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.62 (t, J = 2.0 Hz, 1H), 8.21 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 8.04 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.69 – 7.65 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.33 – 7.27 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 190.0 (CO), 155.5 (Cq), 154.0 (Cq), 148.2 (Cq), 140.9 (Cq), 133.9 (CH), 132.4 (CH), 130.6 (Cq), 130.0 (CH), 129.7 (CH), 127.3 (Cq), 126.6 (CH), 124.6 (CH), 124.6 (CH), 123.3 (CH), 121.6 (CH), 117.6 (Cq), 117.2 (Cq), 116.7 (Cq), 111.7 (CH) ppm; MS (EI, 70eV) *m/z* (%): 368 (100) [$M^{+\cdot}$], 266 (33), 130 (7); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}N_2O_4$ $[M+H]^+$: 369.0875, found: 369.0800.

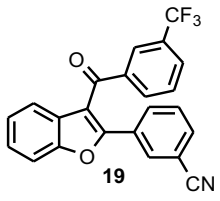
1.24 ***2-(4-Cyanophenyl)-3-(3-trifluoromethylphenyl)benzofuran*** **(18)**



18

Accordingly to procedure, using phosphonium salt **1''** (0.070 g, 0.113 mmol, 1.0 equiv.), 4-cyanobenzoyl chloride **2d** (0.047 g, 0.282 mmol, 2.5 equiv.), triethylamine (77 μL, 5 equiv.) and DCM (3 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 10:1. **18** was obtained as a pale yellow solid: (0.033 g, 75% yield); mp: 127-130 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.08 – 8.00 (m, 2H), 7.83 – 7.78 (m, 3H), 7.64 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.57 – 7.50 (m, 2H), 7.45 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 190.2 (CO), 155.5 (Cq), 154.2 (Cq), 138.0 (Cq), 133.3 (Cq), 132.9 (CH), 132.2 (CH), 131.3 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 130.0 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 129.4 (CH), 128.8 (CH), 127.6 (Cq), 126.7 (CH, q, $J_{C\text{-}F}$ = 4.5 Hz), 126.7 (CH), 124.6 (CH), 123.4 (CF_3, q, *J* = 271.8 Hz), 121.7 (CH), 118.2 (Cq), 117.6 (Cq), 113.3 (Cq), 111.7 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.93 ppm; MS (EI, 70eV) *m/z* (%): 391 (100) [$M^{+\cdot}$], 247 (35), 173 (10); HRMS (ESI): *m/z* calcd. for $C_{23}H_{13}F_3NO_2$ $[M+H]^+$: 392.0898, found: 392.0871.

1.25 ***2-(3-Cyanophenyl)-3-(3-trifluoromethylbenzoyl)benzofuran*** **(19)**

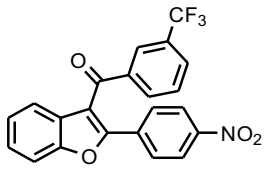


19

Accordingly to procedure, using phosphonium salt **1''** (0.070 g, 0.113 mmol, 1.0 equiv.), 3-cyanobenzoyl chloride **2i** (0.047 g, 0.282 mmol, 2.5 equiv.), triethylamine (77 μL, 5 equiv.) and DCM (3 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 10:1. **19** was obtained as a pale yellow solid: (0.027 g, 62% yield); mp: 172-174 °C; ^{1}H NMR (600 MHz,

$CDCl_3$, 7.26 ppm): δ 8.06 – 7.99 (m, 3H), 7.91 (ddd, J = 8.0, 1.8, 1.1 Hz, 1H), 7.81 – 7.72 (m, 1H), 7.67 – 7.38 (m, 6H), 7.37 – 7.30 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 190.1 (CO), 155.8 (Cq), 154.0 (Cq), 138.1 (Cq), 133.1 (CH), 132.9 (CH), 132.5 (CH), 131.9 (CH), 131.2 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 130.6 (Cq), 129.8 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 129.4 (CH), 129.4 (CH), 127.5 (Cq), 126.6 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 126.5 (CH), 124.6 (CH), 123.4 (CF_3, q, J = 271.8 Hz), 121.8 (CH), 117.8 (Cq), 117.2 (Cq), 113.1 (Cq), 111.6 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.93 ppm; MS (EI, 70eV) *m/z* (%): 391 (100) [$M^{+\cdot}$], 247 (35), 173 (10); HRMS (ESI): *m/z* calcd. for $C_{23}H_{13}F_3NO_2$ $[M+H]^+$: 392.0898, found: 392.0873.

1.26 ***2-(4-nitrophenyl)-3-(3-trifluoromethylbenzoyl)benzofuran*** **(20)**



20

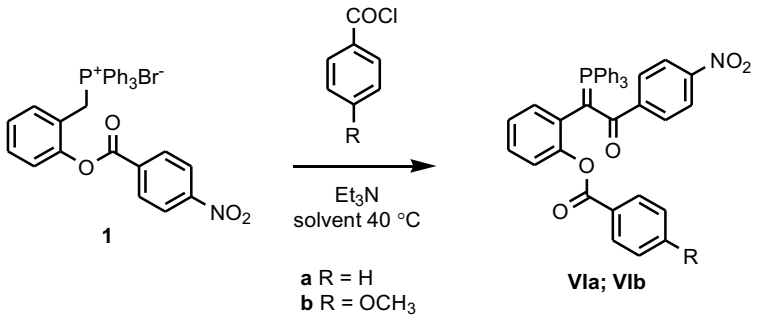
Accordingly to procedure, using phosphonium salt **1''** (0.070 g, 0.113 mmol, 1.0 equiv.), 4-nitrobenzoyl chloride **2c** (0.052 g, 0.282 mmol, 2.5 equiv.), triethylamine (77 μL, 5 equiv.) and DCM (2 mL). Purification by column chromatography on silica gel in petroleum ether/ethyl acetate 9:1. **20** was obtained as a yellow solid: (0.030 g, 67% yield); mp: 96-98 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm):

δ 8.21 – 8.17 (m, 2H), 8.09 (tt, J = 1.8, 0.8 Hz, 1H), 8.05 (dt, J = 7.8, 1.6 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.81 (ddt, J = 7.6, 1.7, 1.0 Hz, 1H), 7.66 (dt, J = 8.4, 0.8 Hz, 1H), 7.56 (tt, J = 7.8, 0.7 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.33 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm) δ 190.2 (CO), 154.9 (Cq), 154.2 (Cq), 148.1 (Cq), 137.9 (Cq), 135.1 (Cq), 133.0 (CH), 131.4 (Cq, q, $J_{C\text{-}F}$ = 33.2 Hz), 130.1 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 129.5 (CH), 129.0 (CH), 127.6 (Cq), 126.8 (CH), 126.7 (CH, q, $J_{C\text{-}F}$ = 3.0 Hz), 123.8 (CH), 123.4 (CF_3, q, J = 271.8 Hz), 124.6 (CH), 121.8 (CH), 118.1 (Cq), 111.7 (CH) ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.94 ppm; MS (EI, 70eV) *m/z*

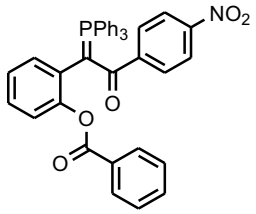
(%): 411 (100) [$M^{+\cdot}$], 266 (20), 173 (11); HRMS (ESI): *m/z* calcd. for $C_{22}H_{13}F_3NO_4$ $[M+H]^+$: 412.0796, found: 412.0769.

1.27 General procedure for the preparation of acyl ylide VIa and VIb

To a mixture of the corresponding *o*-benzoyloxybenzyltriphenylphosphomium bromide **1** (1.0 equiv.) and the proper benzoyl chloride (2.5 equiv.) in dichloromethane (25 mL/mmole) was added Et_3N (5 equiv., 0,069 mL/mmole) and stirred under reflux for 2 h. The crude mixture was purified by column chromatography on silica gel in petroleum ether/ethyl acetate to furnish the desired product.



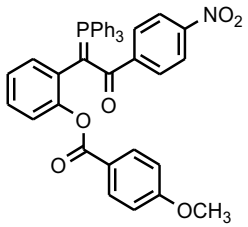
1.28 ***o-(Benzoyloxy)phenyl-4-nitrobenzoyl-methylene-triphenylphosphorane*** **(VIa)**



Accordingly to procedure, using phosphonium salt **1** (0.100 g, 0.167 mmol, 1.0 equiv.) and benzoyl chloride **2a** (0.059 g, 0.417 mmol, 2.5 equiv.), triethylamine (115 µL, 5 equiv.) and DCM (4 mL). Purification by column chromatography on silica gel in ethyl acetate/petroleum ether 3:2. Ylide **VIa** was obtained as an orange solid: (0.078 g, 75% yield); mp: 64-66 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.07 – 7.99 (m, 4H), 7.85 (dq, *J* = 8.0, 1.4 Hz, 2H), 7.68 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 – 7.49 (m, 8H), 7.47 – 7.41 (m, 3H), 7.29 – 7.23 (m, 4H), 7.12 – 7.05 (m, 1H),

6.87 (dt, J = 7.2, 1.1 Hz, 1H), 6.83 – 6.78 (m, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 182.29 (CO, d, J_{CP} = 6.04 Hz), 170.60 (Cq), 165.06 (Cq), 151.96 (Cq, d, J_{C-P} = 6.04 Hz), 147.93 (Cq, d, J_{C-P} = 12.08 Hz), 147.50 (Cq), 136.07 (CH, d, J_{C-P} = 3.02 Hz), 133.75 (CH, d, J_{C-P} = 9.06 Hz), 133.48 (CH, d, J_{C-P} = 46.81 Hz), 131.86 (CH, d, J_{C-P} = 3.02 Hz), 130.22 (CH, d, J_{C-P} = 45.30 Hz), 129.66 (Cq, d, J_{C-P} = 60.4 Hz), 129.37 (CH), 128.58 (CH, d, J_{C-P} = 12.08 Hz), 128.42 (CH, d, J_{C-P} = 19.63 Hz), 127.61 (CH, d, J_{C-P} = 3.02 Hz), 125.83 (Cq, d, J_{C-P} = 90.6 Hz), 125.38 (CH, d, J_{C-P} = 3.02 Hz), 123.00 (CH), 122.57 (CH), 69.52 (CP, d, J_{C-P} = 110.23 Hz) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ 17.96 (hept, J_{H-P} = 13.1 Hz) ppm; HRMS (ESI): *m/z* calcd. for $C_{39}H_{29}NO_5P$ $[M+H]^+$: 622.1783, found: 622.1781.

1.29 ***o-(4-Methoxybenzoyloxy)phenyl-4-nitro-benzoyl-methylene-triphenylphosphorane*** **(VIb)**



VIb

Accordingly to procedure, using phosphonium salt **1** (0.100 g, 0.167 mmol, 1.0 equiv.) and benzoyl chloride **2b** (0.071 g, 0.418 mmol, 2.5 equiv.), triethylamine (115 µL, 5 equiv.) and DCM (4 mL). Purification by column chromatography on silica gel in acetate/petroleum ether 3:2. Ylide **VIb** was obtained as a light orange solid: (0.059 g, 54% yield); mp: 205-207 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 7.26 ppm): δ 8.04 – 7.99 (m, 2H), 7.82 – 7.76 (m, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.51 (m, 9H), 7.49 – 7.42 (m, 3H), 7.30 – 7.24 (m, 3H), 7.09 – 7.03 (m, 1H), 7.00 – 6.94 (m, 2H), 6.85 (dt, J = 7.4, 1.0 Hz, 1H), 6.82 – 6.75 (m, 2H), 3.96 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 77.0 ppm): δ 182.3 (CO, d, J_{C-P} = 6.04 Hz), 164.77 (Cq), 163.91 (Cq), 152.13 (Cq, d, J_{C-P} = 6.04 Hz), 148.22 (Cq, d, J_{C-P} = 13.59 Hz), 147.45 (Cq), 135.96 (CH, d, J_{C-P} = 3.02 Hz), 133.72 (CH, d, J_{C-P} = 10.57 Hz), 132.48 (CH), 131.75 (CH, d, J_{C-P} = 3.02 Hz), 130.72 (Cq, d, J_{C-P} = 10.57 Hz), 129.32 (CH), 128.54 (CH, d, J_{C-P} = 13.59 Hz), 127.42 (CH, d, J_{C-P} = 3.02 Hz), 126.14 (Cq, d, J_{C-P} = 92.11 Hz), 125.2 (CH, d, J_{C-

$_P$ = 3.02 Hz), 123.09 (CH), 122.53 (CH), 121.86 (Cq), 113.67 (CH), 68.55 (CP, d, $J_{C\text{-}P}$ = 111.74 Hz), 55.64 (CH_3) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ 17.65 (hept, $J_{H\text{-}P}$ = 12.9 Hz) ppm; HRMS (ESI): *m/z* calcd. for $C_{40}H_{31}NO_6P$ $[M+H]^+$: 652.1889, found: 652.1883.

2. Biological Section

2.1. **Drugs.** 5′-O-(3-[^{35}S]thiotriphospate) ([^{35}S]GTPγS) (1250 Ci/mmol), was purchased from Perkin–Elmer Life Sciences, Inc. (Boston, MA, USA). Guanosine 5′- diphosphate (GDP), and guanosine 5′-O-(3-thiotriphosphate) (GTPγS) were obtained from Sigma/RBI (St. Louis, MO, USA). WIN-55,212-2 (WIN), and AM 251 were purchased from Tocris (Bristol, UK).

Drugs were dissolved in dimethyl sulfoxide (DMSO). The DMSO concentration used in the different assays never exceeded 0.1% (v/v) and had no effects on [^{35}S]GTPγS binding assays.

2.2. **Animals.** All experiments were carried out in accordance with European Council directives (63/2010) and in compliance with the animal policies approved by the Italian Ministry of Health and the Ethical Committee for Animal Experiments (CESA, University of Cagliari, Italy). We made all efforts to minimise pain and suffering, and to reduce the number of animals used. Adult male Sprague-Dawley rats (weight 275–300 g) (Envigo, Italy) were employed for [^{35}S]GTPγS binding experiments. Rats were housed in groups of six in standard temperature

2.3. **Tissue preparation and [^{35}S]GTP*γS* binding assay**.

Rats were sacrificed by decapitation. Brains were collected and cerebral cortices were rapidly dissected and placed on an ice-cold plate. Rat cortical tissue preparations and CB1-stimulated [^{35}S]GTP*γ*S binding assay in rat cortical membranes was carried out using a modified version of the method described by De Luca et al.[5]

Tissues were homogenated in 20 volumes (w/v) of ice-cold buffer (50 mM Tris–HCl, 1 mM EGTA, and 3 mM $MgCl_2$, pH 7.4).

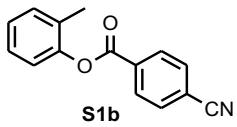
The homogenate was centrifuged at 48.000*g* at 4 °C for 10 min, the supernatant discarded, and the pellet resuspended in a homogenization buffer, and centrifuged again at 48.000*g* for 10 min. The final pellet was resuspended in a GTPγS assay buffer (50 mM Tris–HCl, 3 mM $MgCl_2$, 0.2 mM EGTA, 100 mM NaCl, pH 7.4), and the aliquots frozen at −80 °C until the day of experiment.

The Bradford protein assay was used for protein determination using bovine serum albumin (BSA) as a standard in accordance with the supplier protocol (Bio-Rad, Milan, Italy).

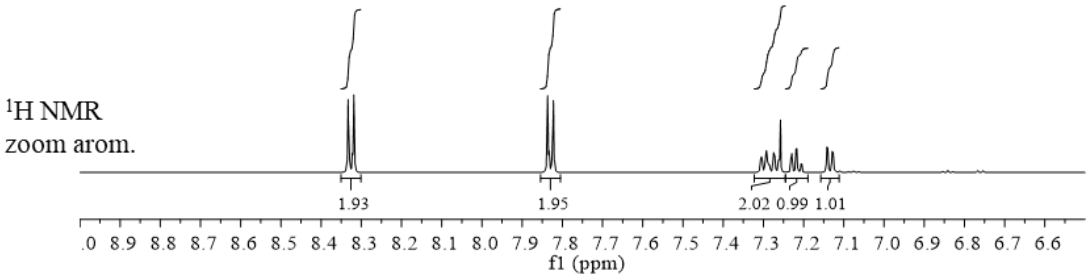
[^{35}S]GTPγS binding was measured as previously described.[35] Briefly, rat cortical membranes (5–10 μg of protein) were incubated with compounds at 30 °C in assay buffer containing 0.1% BSA in the presence of 0.05 nM [^{35}S]GTPγS and 30 μM GDP in a final volume of 1 ml. After 60 min incubation, samples were filtered using a Packard Unifilter-GF/B, washed twice with 1 ml of ice-cold 50 mM Tris–HCl, pH 7.4 buffer, and dried for 1 h at 30 °C. The radioactivity on the filters was counted in a liquid microplate scintillation counter (TopCount NXT, Packard, Meridien, CT) using 30 μl of scintillation fluid (Microscint 20, Packard, Meridien, CT). Nonspecific binding was measured in the presence of 10 μM unlabeled GTPγS. Basal binding was assayed in the absence of agonist and in the presence of GDP. Stimulation by the agonist was defined as a percentage increase above basal levels (i.e., {[dpm(agonist)−dpm(no agonist)]/dpm(no agonist)} × 100).

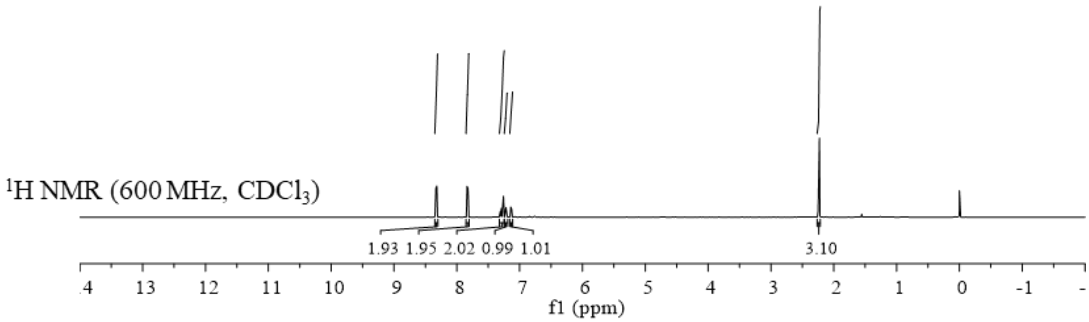
3. NMR Spectra

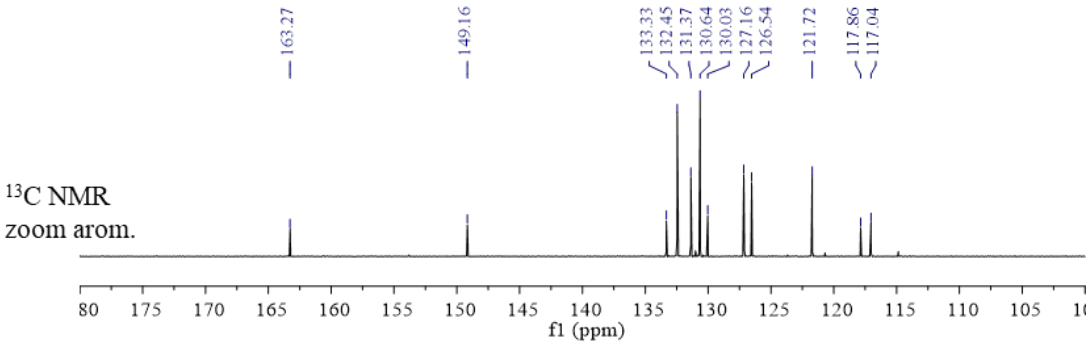
2-Methylphenyl-4-cyanobenzoate (S1b)

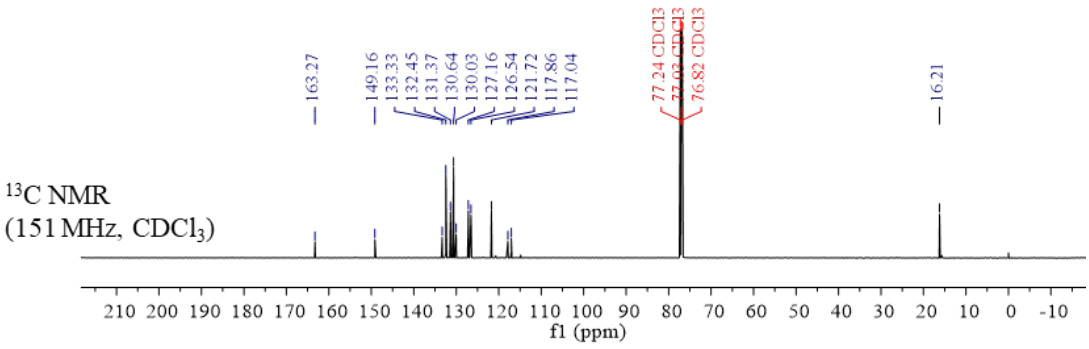


S1b

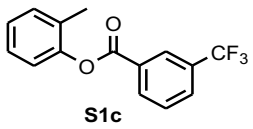




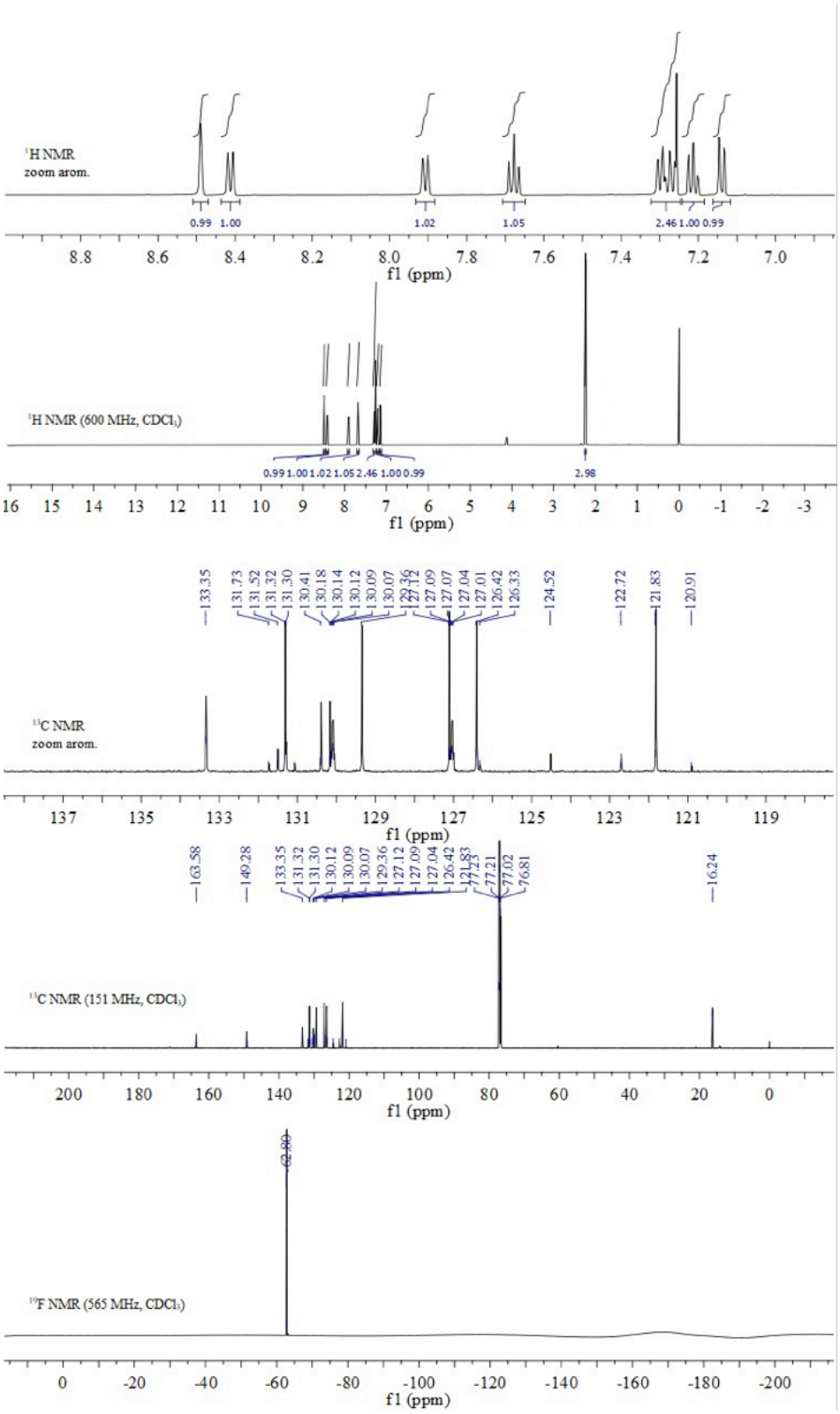




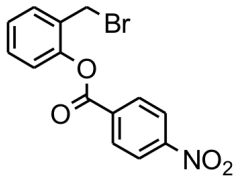
2-Methylphenyl-3-trifluoromethylbenzoate **(S1c)**



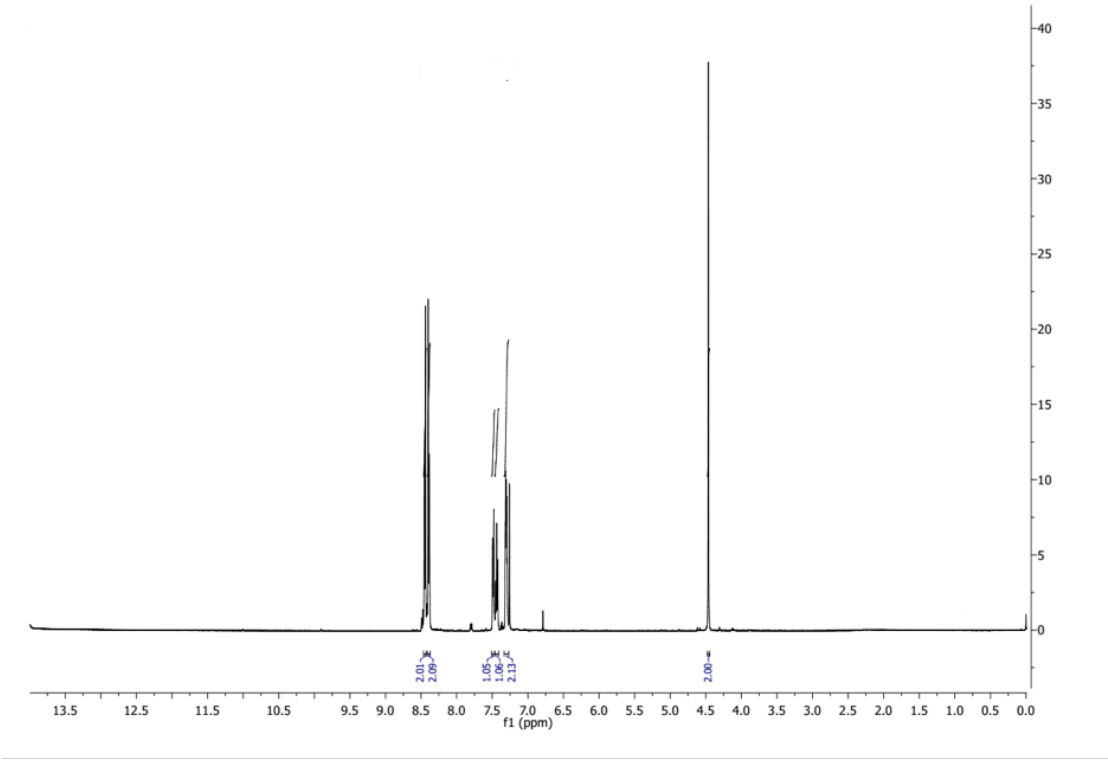
S1c

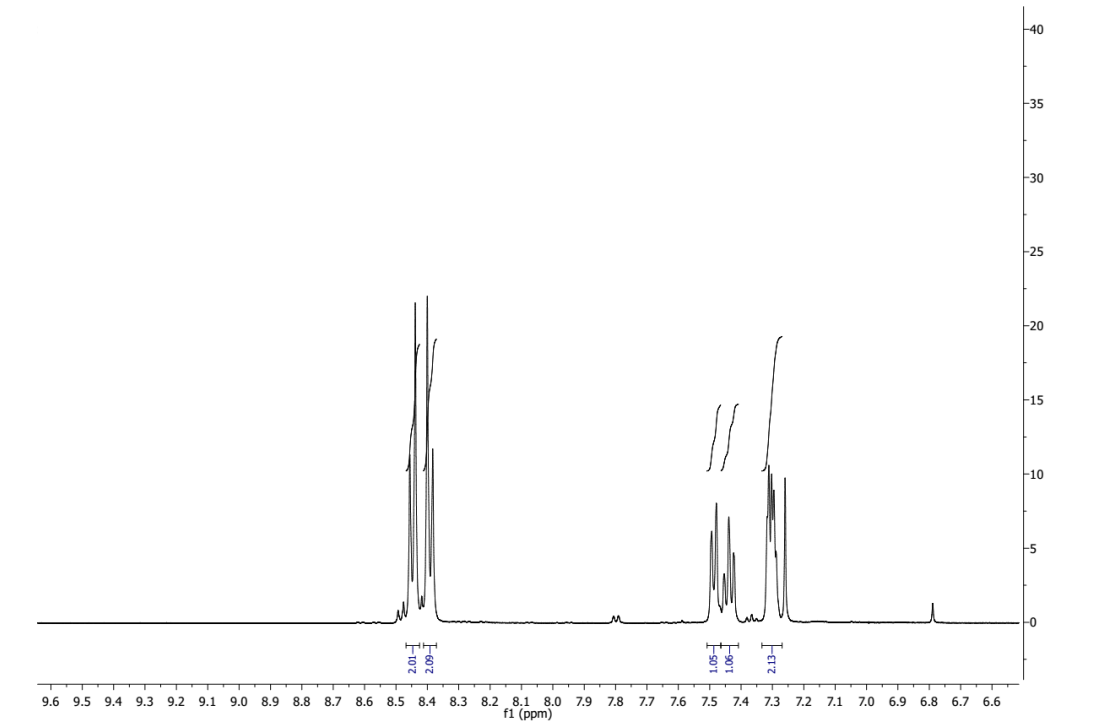


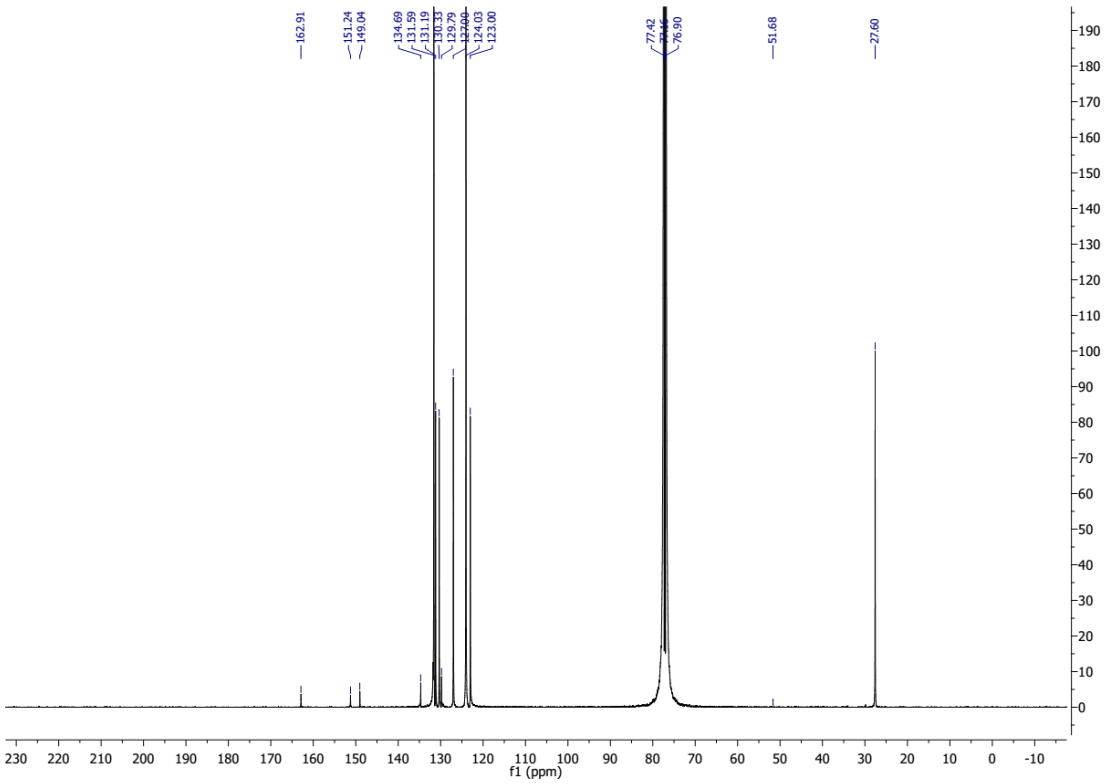
2-(Bromomethyl)phenyl-4-nitrobenzoate **(S2a)**



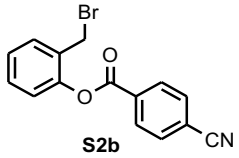
S2a



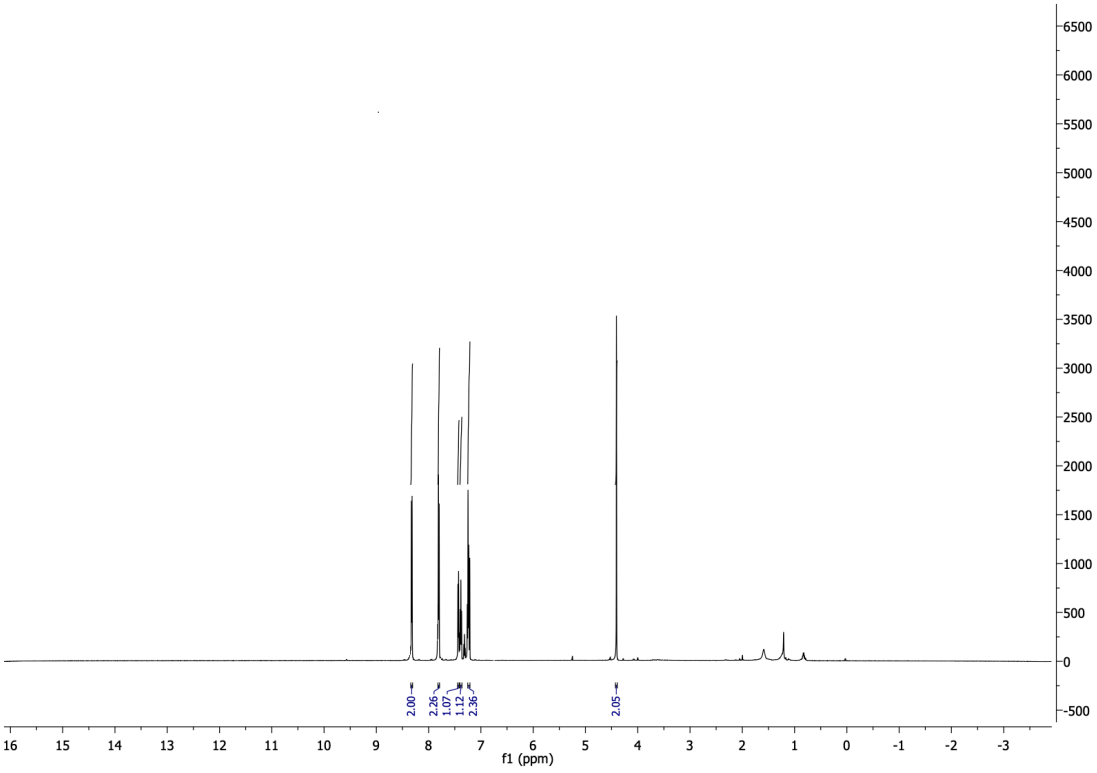


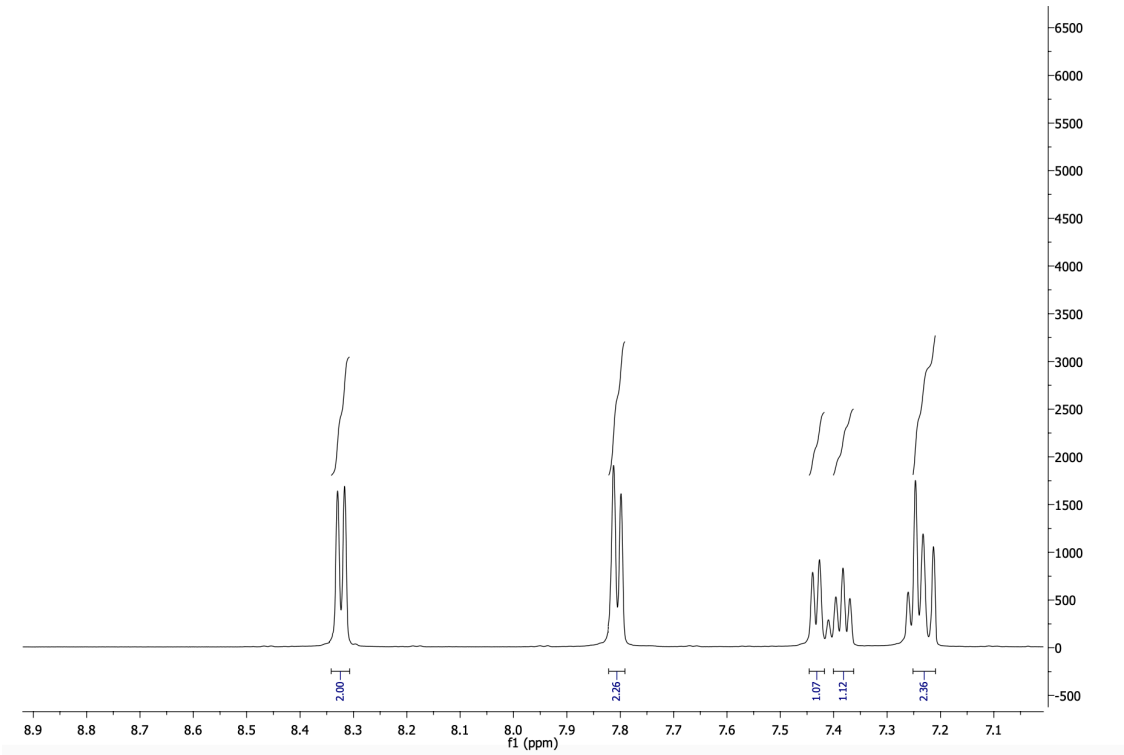

162.91
151.24
149.04
134.69
131.59
131.19
130.33
129.79
129.04
124.03
123.00
77.42
77.16
76.90
51.68
27.60
f1 (ppm)

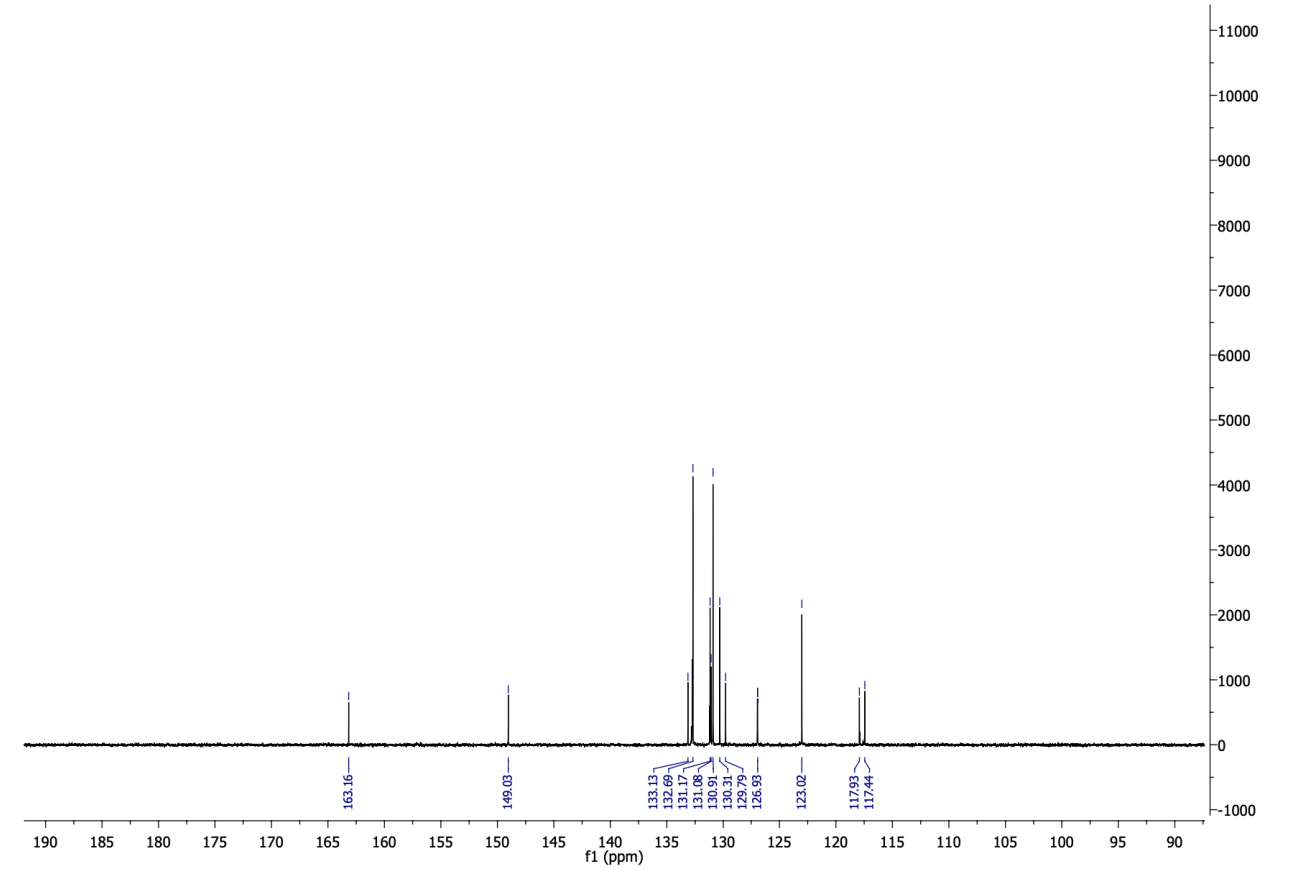
2-(Bromomethyl)phenyl-4-cyanobenzoate **(S2b)**



S2b






11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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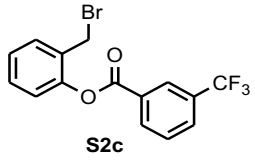
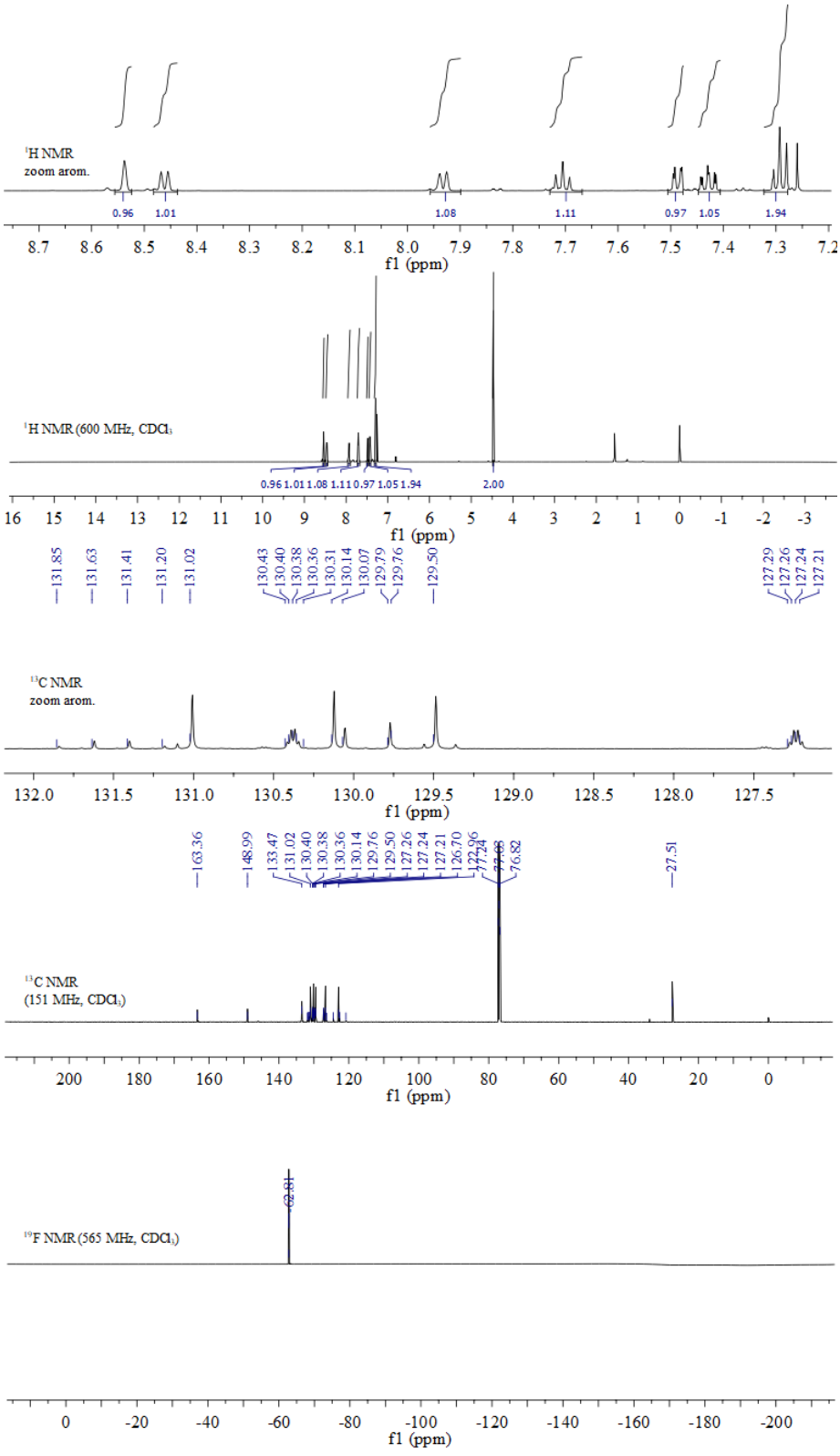
149.03
133.13
132.69
131.17
131.08
130.91
130.31
129.79
126.93
123.02
117.93
117.44
190
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
f1 (ppm)

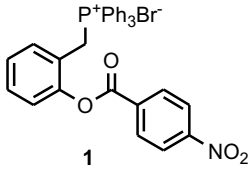
2-(Bromomethyl)phenyl-3-trifluoromethylbenzoate (S2c)



S2c

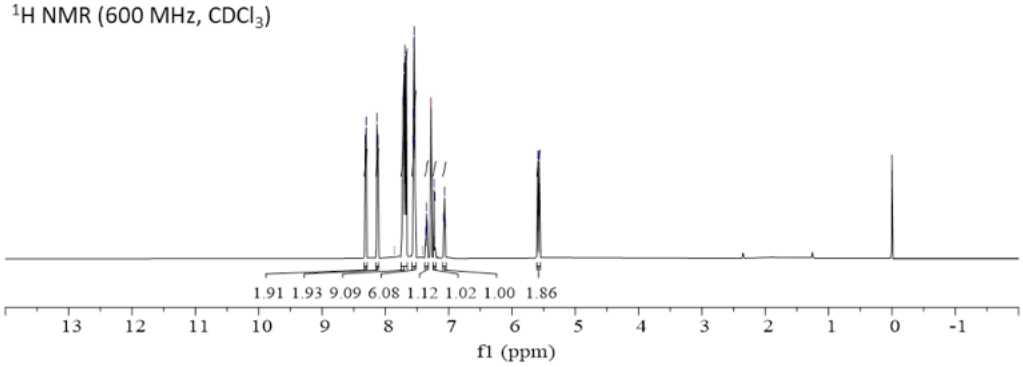


***O-(4-nitrobenzoyloxy)benzyltriphenyl phosphomium bromide* (1)**

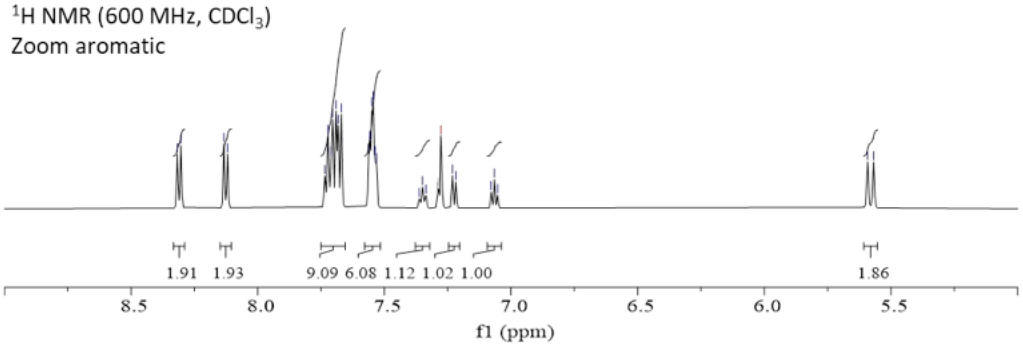


1

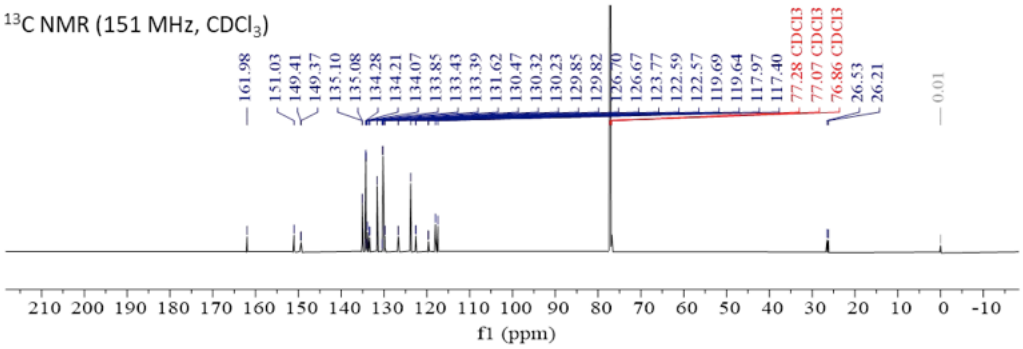
^{1}H NMR (600 MHz, $CDCl_3$)



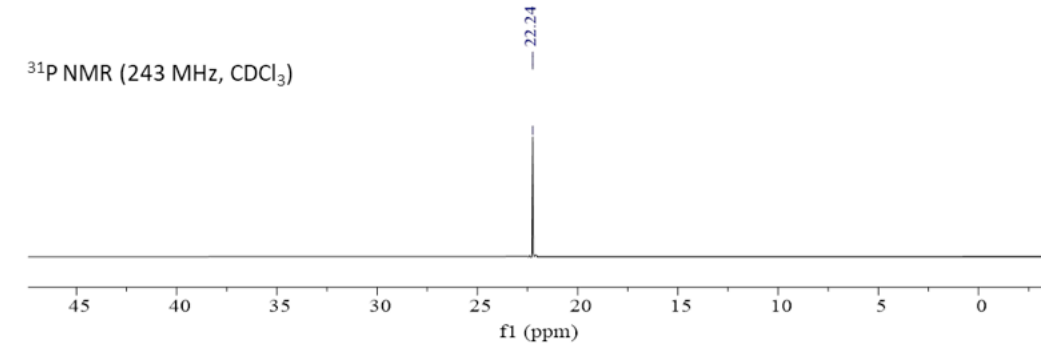
^{1}H NMR (600 MHz, $CDCl_3$)
Zoom aromatic



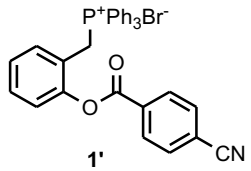
^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)

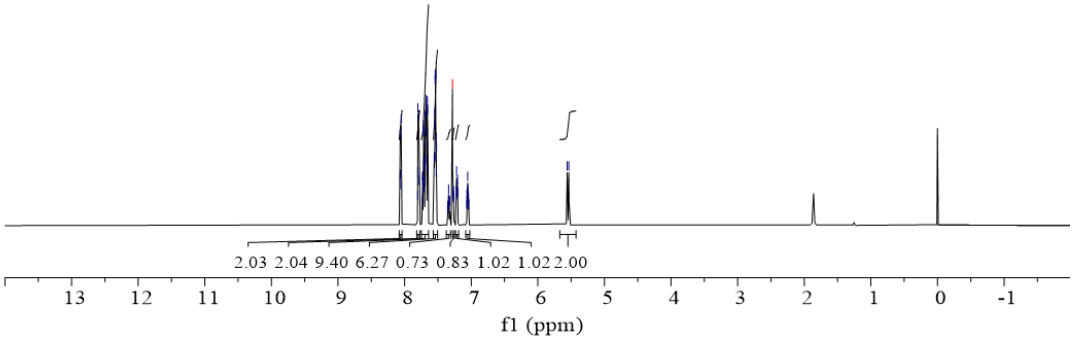


***O-(4-cianobenzoyloxy)benzyltriphenyl phosphomium bromide* (1')**

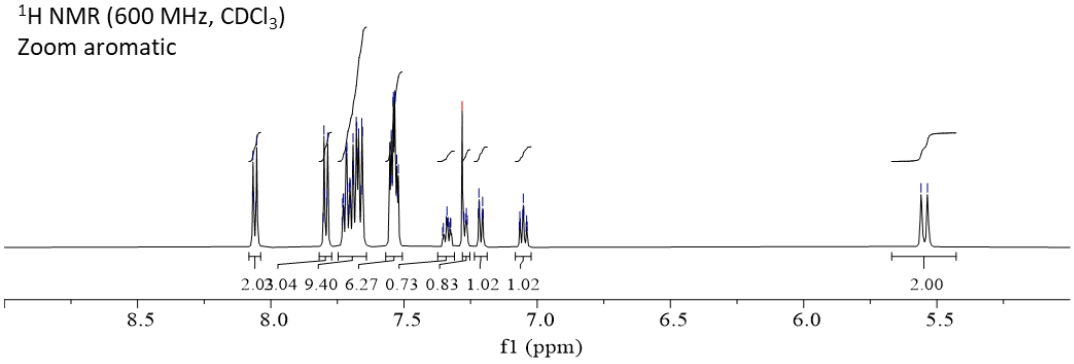


1'

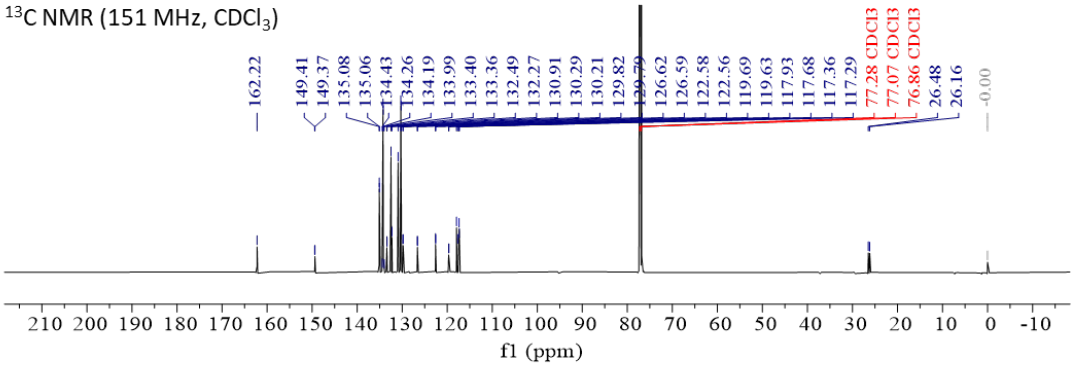
^{1}H NMR (600 MHz, $CDCl_3$)



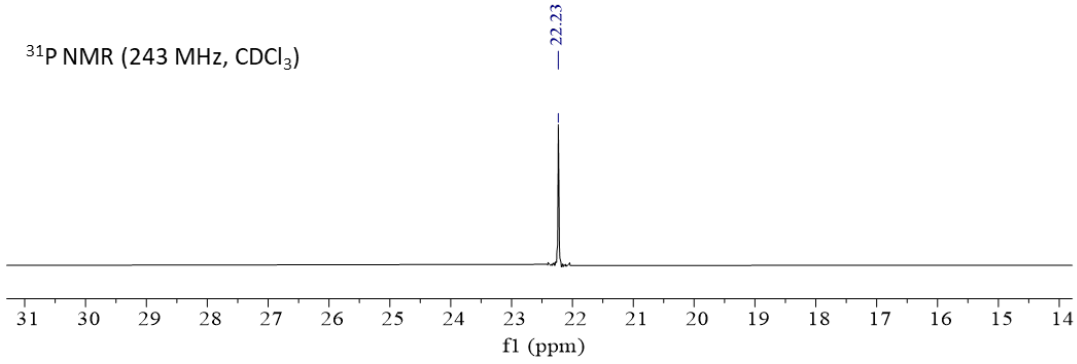
^{1}H NMR (600 MHz, $CDCl_3$)
Zoom aromatic



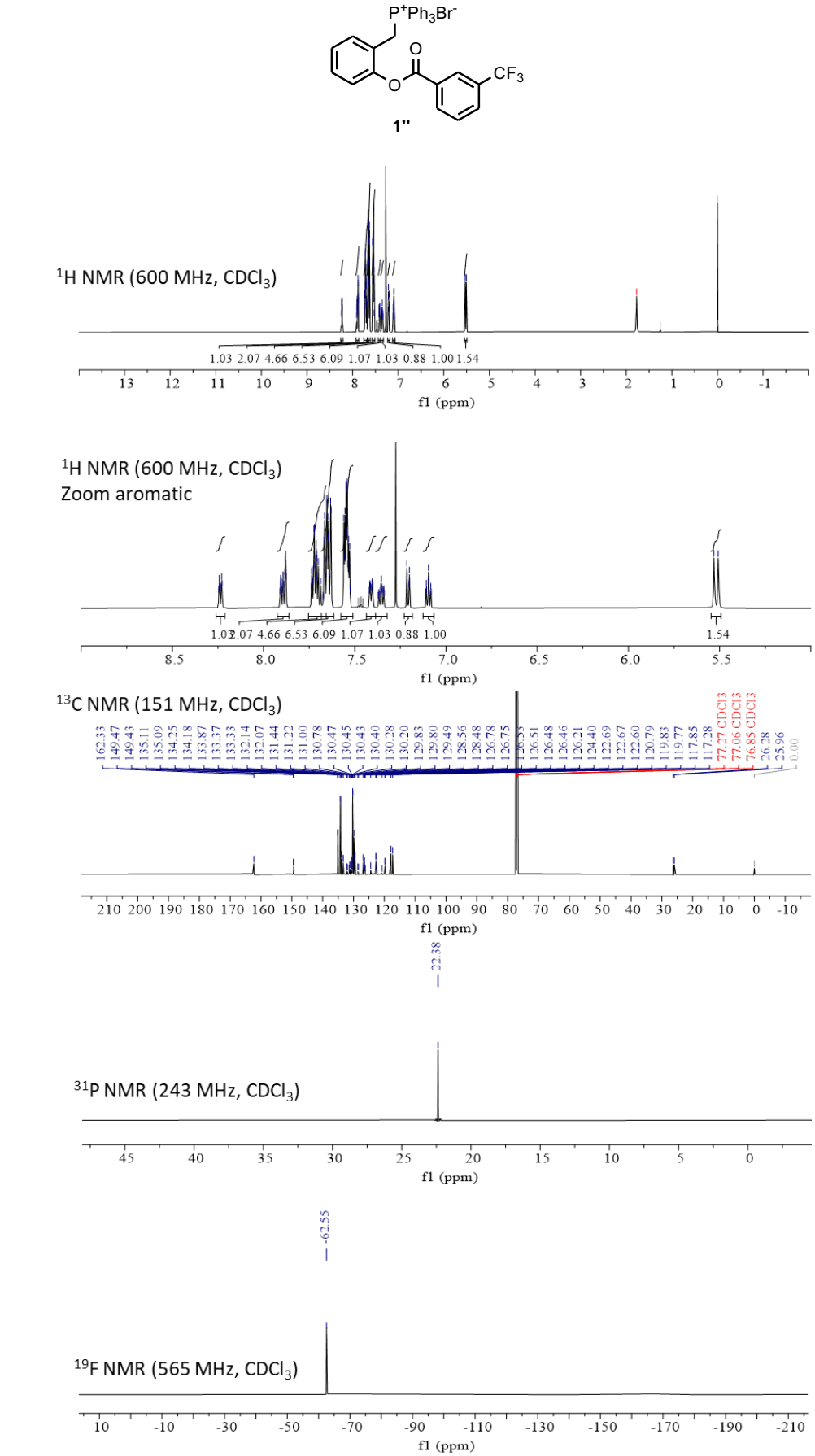
^{13}C NMR (151 MHz, $CDCl_3$)



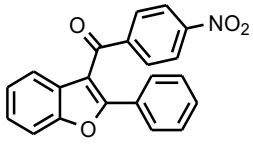
^{31}P NMR (243 MHz, $CDCl_3$)



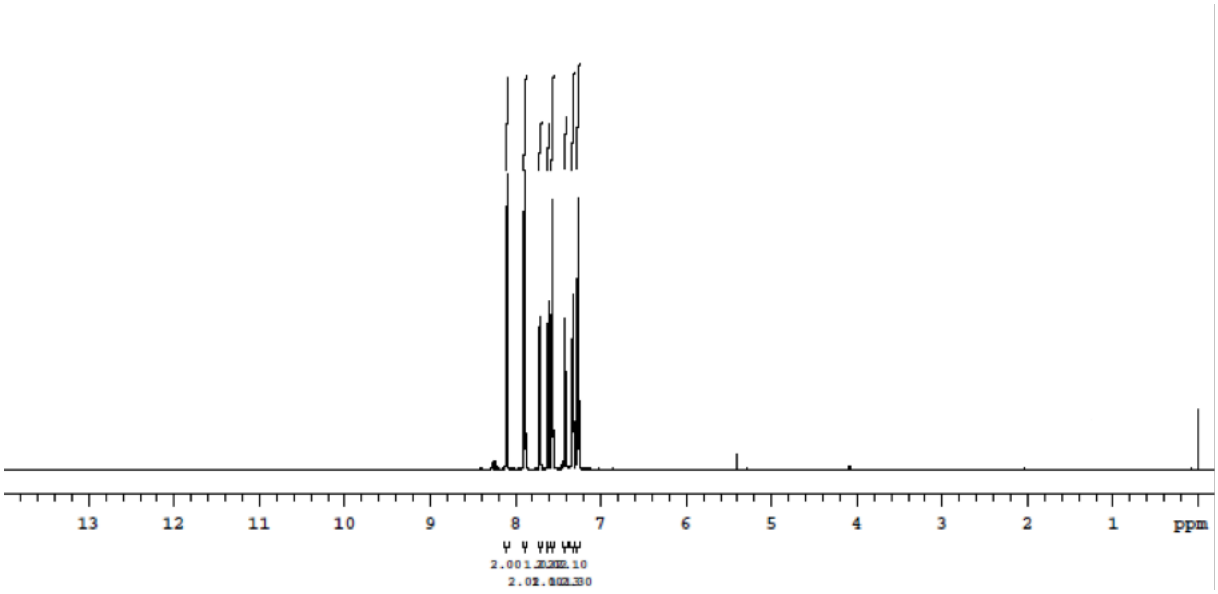
***O-(3-trifluoromethylbenzoyloxy)benzyltriphenyl phosphomium bromide* (1'')**



3-(4-nitrobenzoyl)-2-phenylbenzofuran **(4)**



4

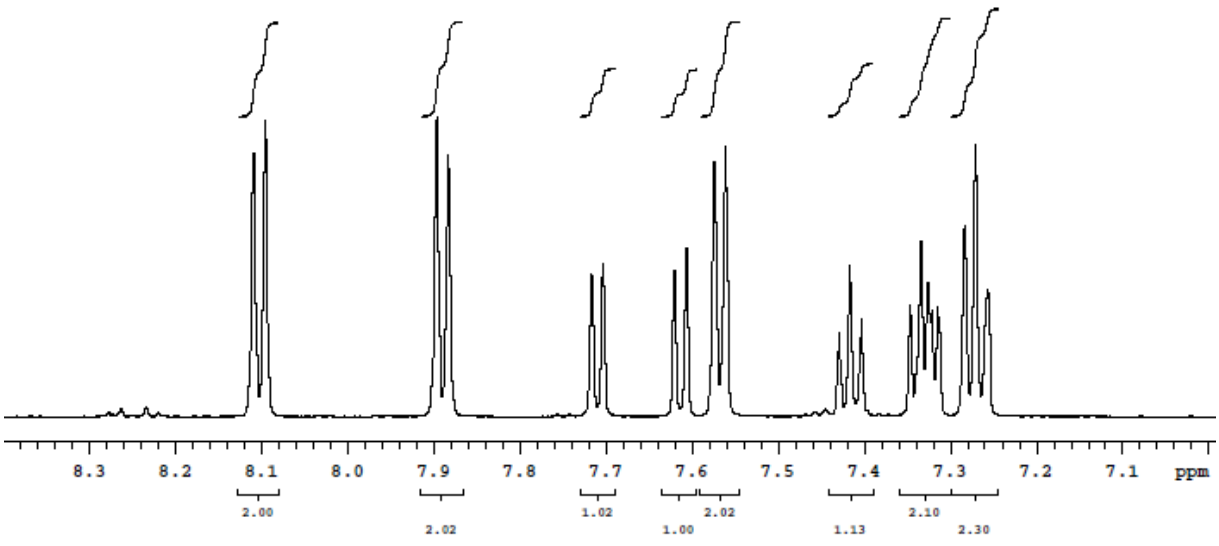


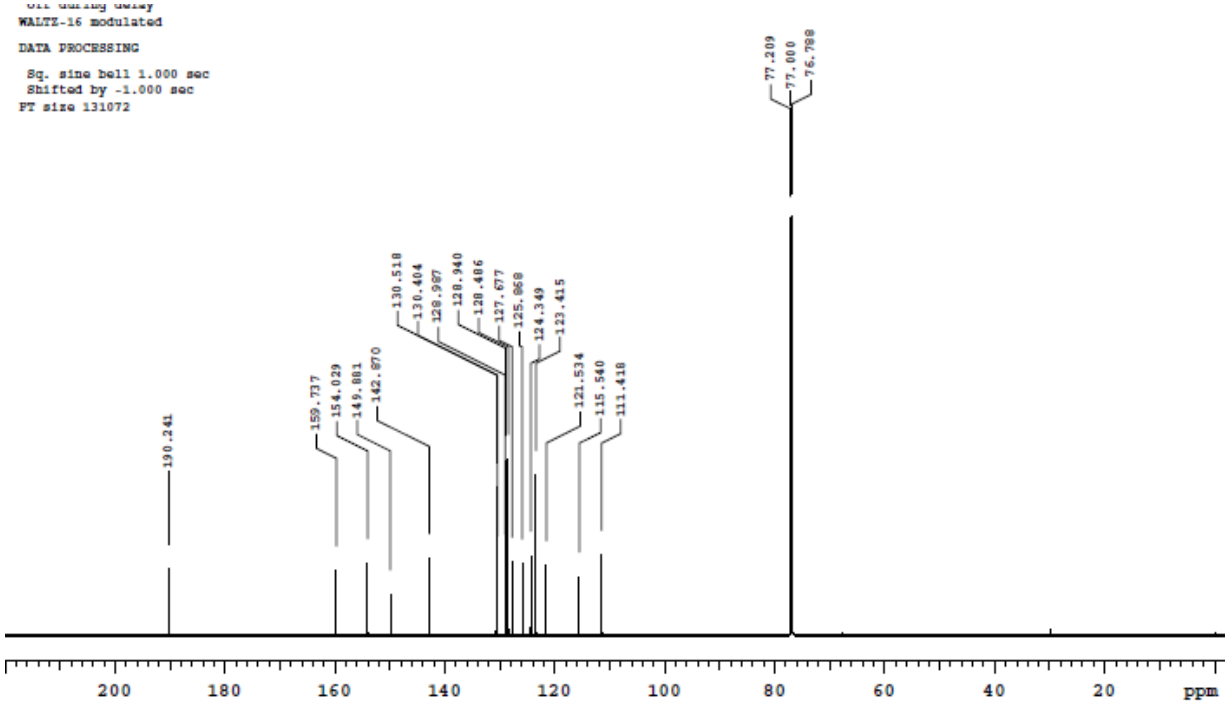
ACQUISITION PARAMETERS

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Acq. time 2.995 sec
Width 9611.9 Hz
OBSERVE H1, 599.7340946 MHz

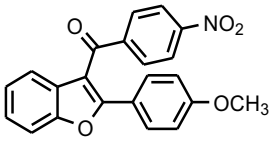
DATA PROCESSING

FT size 65536

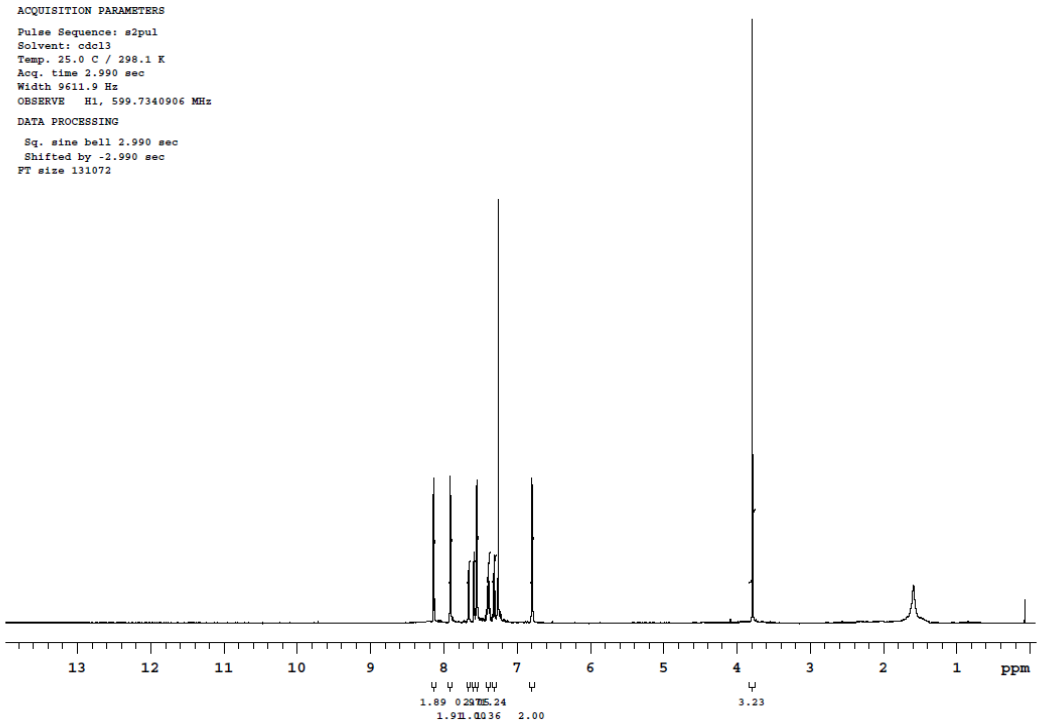


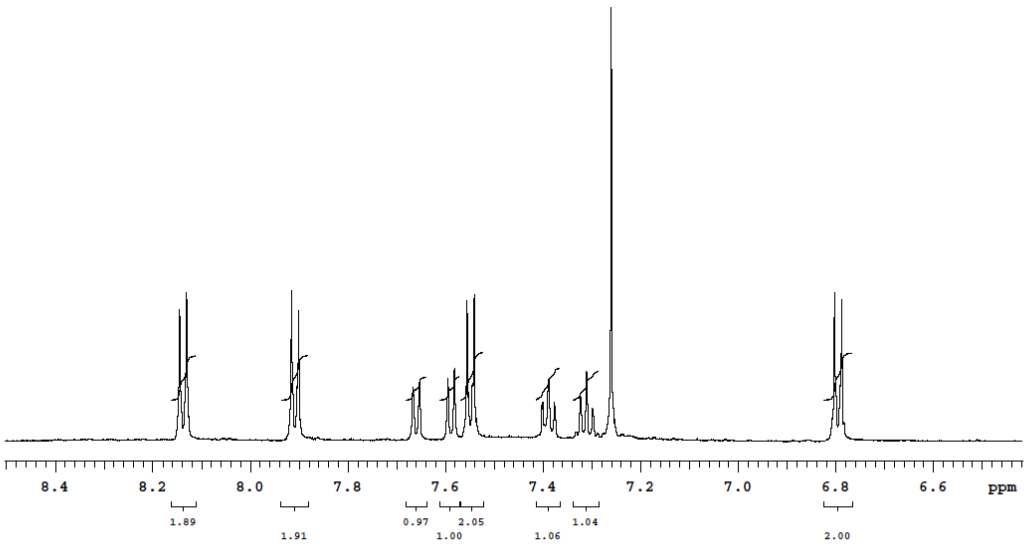

WALTZ-16 modulated
DATA PROCESSING
Sq. sine bell 1.000 sec
Shifted by -1.000 sec
FT size 131072
190.241
159.737
154.029
149.881
142.870
130.518
130.404
128.987
128.940
128.486
127.677
125.868
124.349
123.415
121.534
115.540
111.418
77.209
77.000
76.788
200
180
160
140
120
100
80
60
40
20
ppm

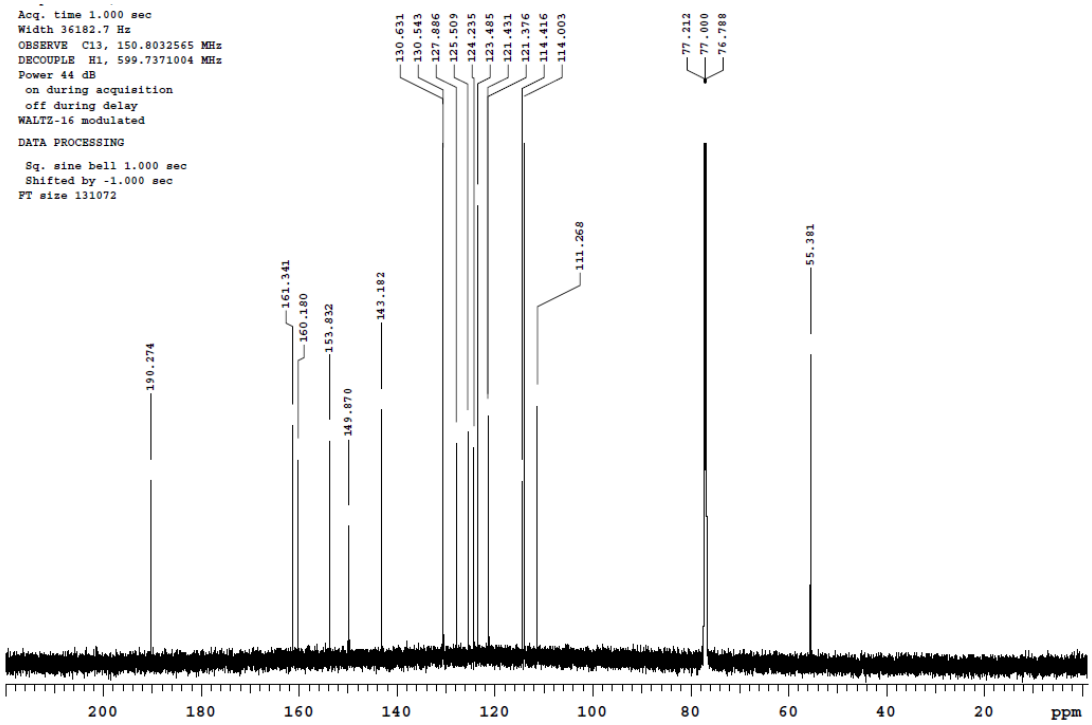
2-(4-methoxyphenyl)-3-(4-nitrobenzoyl)benzofuran (5)



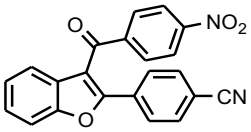
5



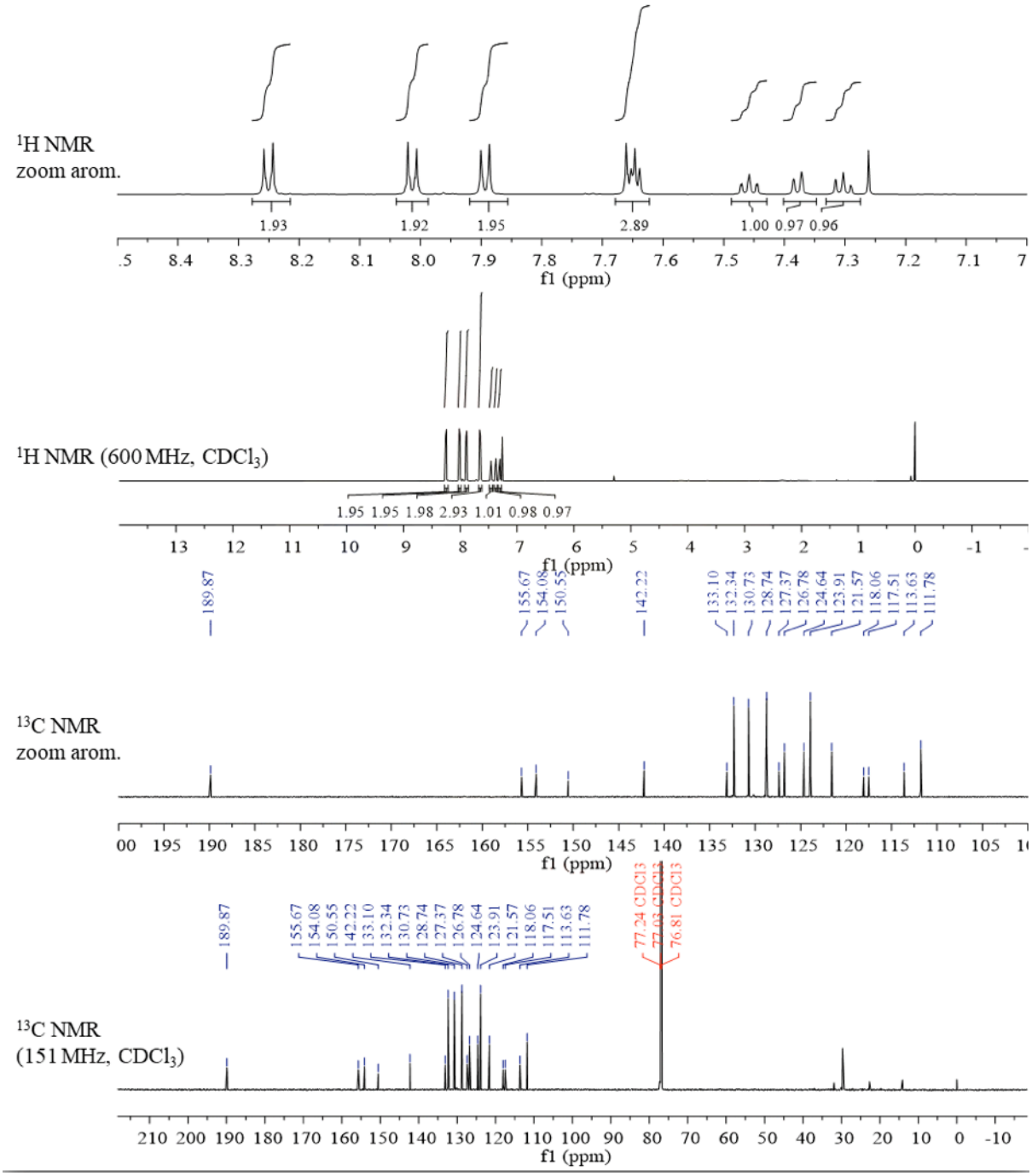



Acq. time 1.000 sec
Width 36182.7 Hz
OBSERVE C13, 150.8032565 MHz
DECOUPLE H1, 599.7371004 MHz
Power 44 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Sq. sine bell 1.000 sec
Shifted by -1.000 sec
FT size 131072
190.274
161.341
160.180
153.832
149.870
143.182
130.631
130.543
127.886
125.509
124.235
123.485
121.431
121.376
114.416
114.003
111.268
77.212
77.000
76.788
55.381
200
180
160
140
120
100
80
60
40
20
ppm

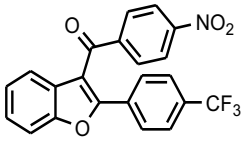
***2-(4-cianophenyl)-3-(4-nitrobenzoyl)benzofuran* (6)**



6

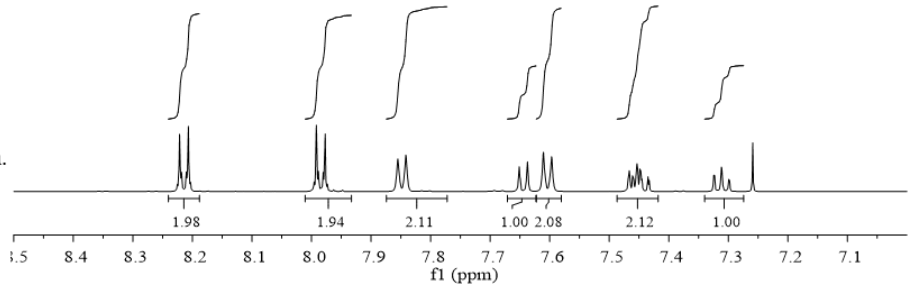


***3-(4-nitrobenzoyl)-2-(4-trifluoromethylphenyl)benzofuran* (7)**

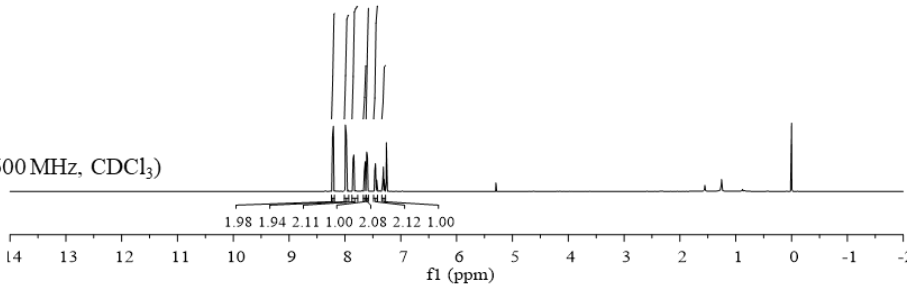


7

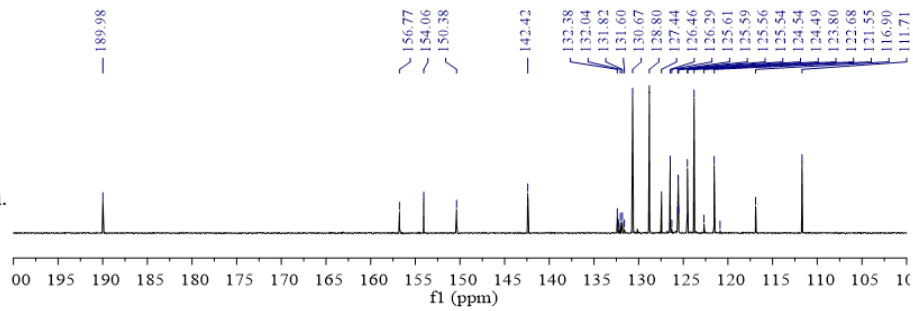
^{1}H NMR
zoom arom.



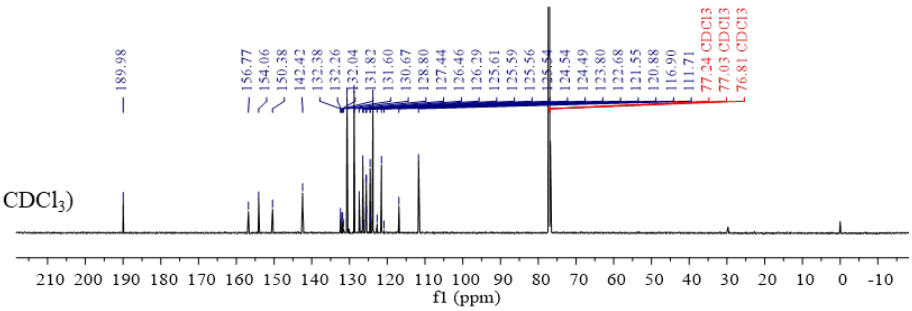
^{1}H NMR (600 MHz, $CDCl_3$)



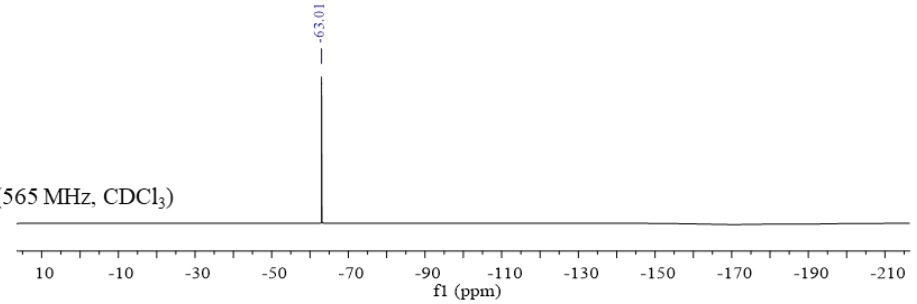
^{13}C NMR
zoom arom.



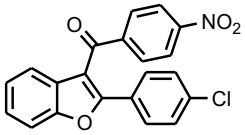
^{13}C NMR
(151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

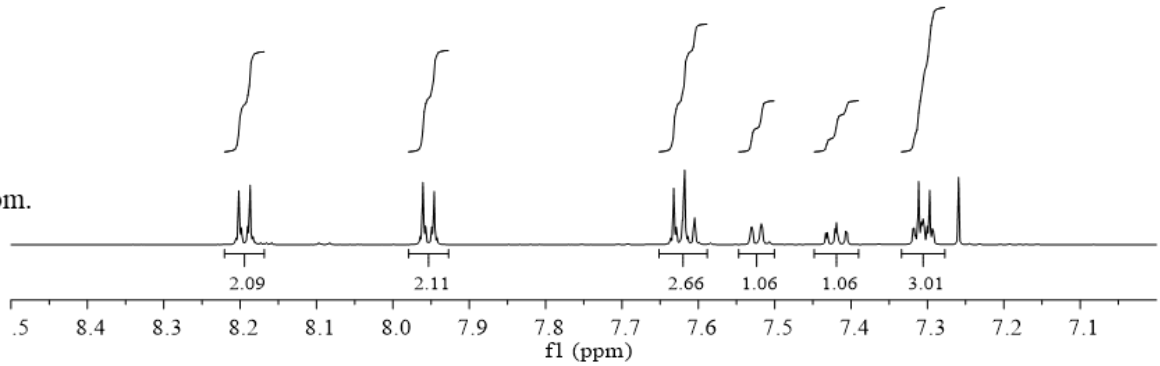


***2-(4-chlorophenyl)-3-(4-nitrobenzoyl)benzofuran* (8)**

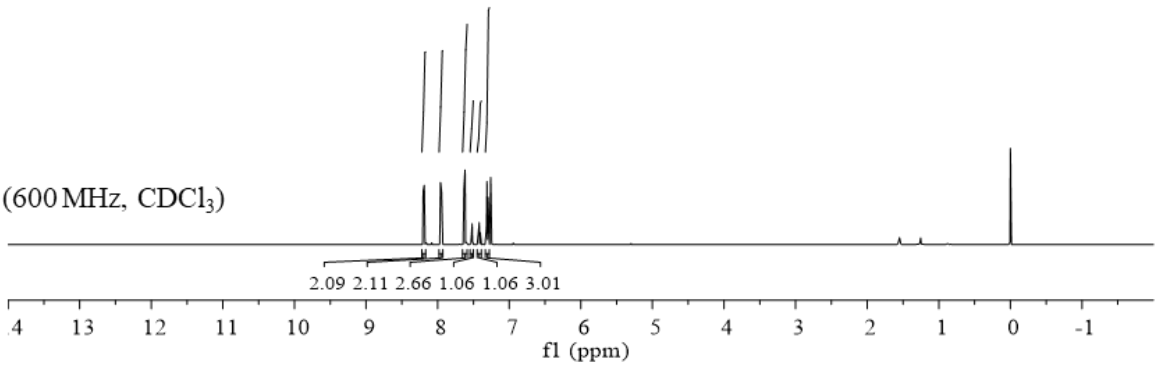


8

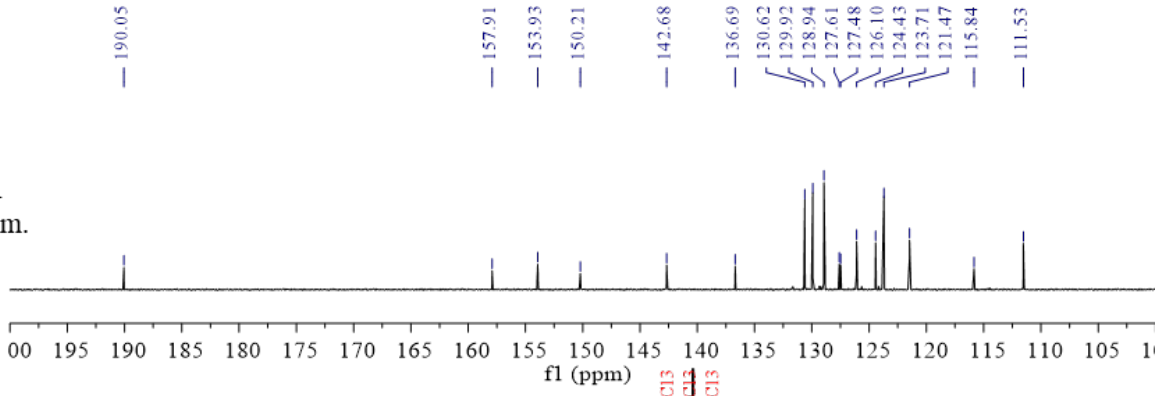
^{1}H NMR
zoom arom.



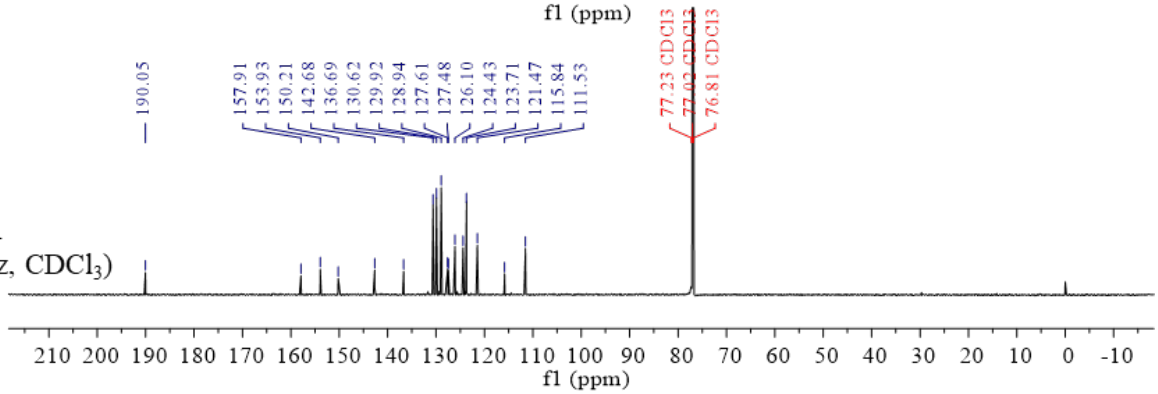
^{1}H NMR (600 MHz, $CDCl_3$)



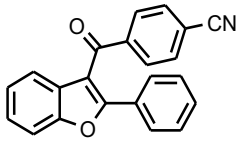
^{13}C NMR
zoom arom.



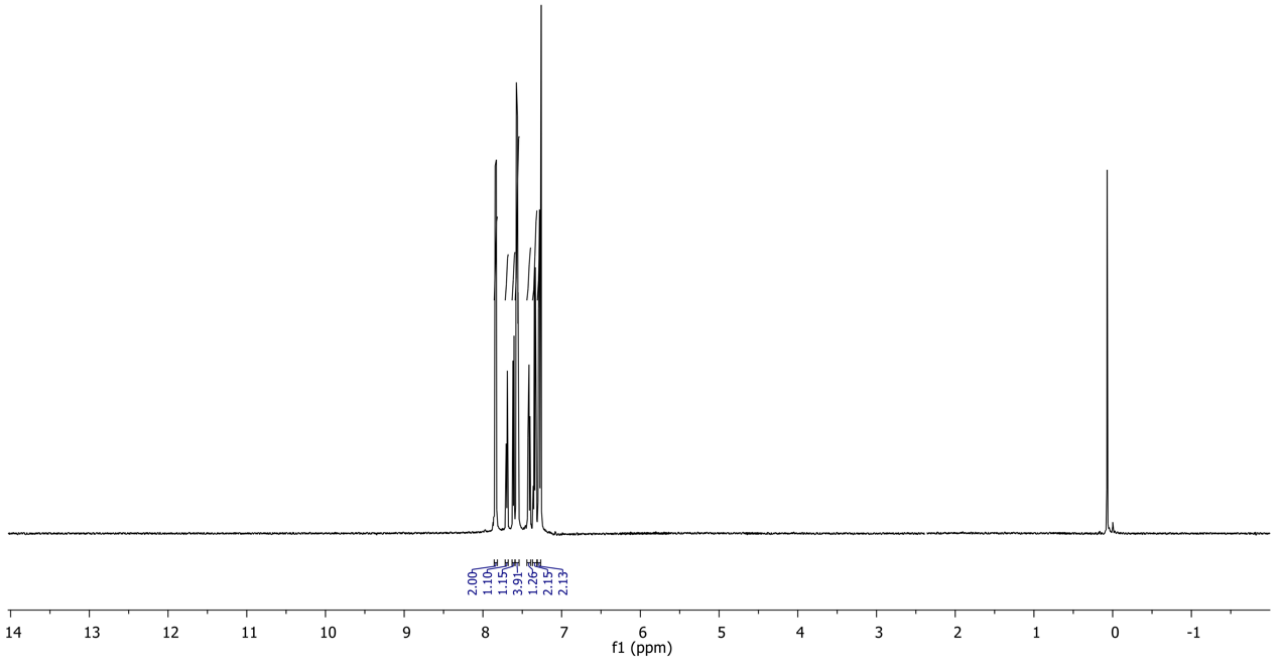
^{13}C NMR
(151 MHz, $CDCl_3$)

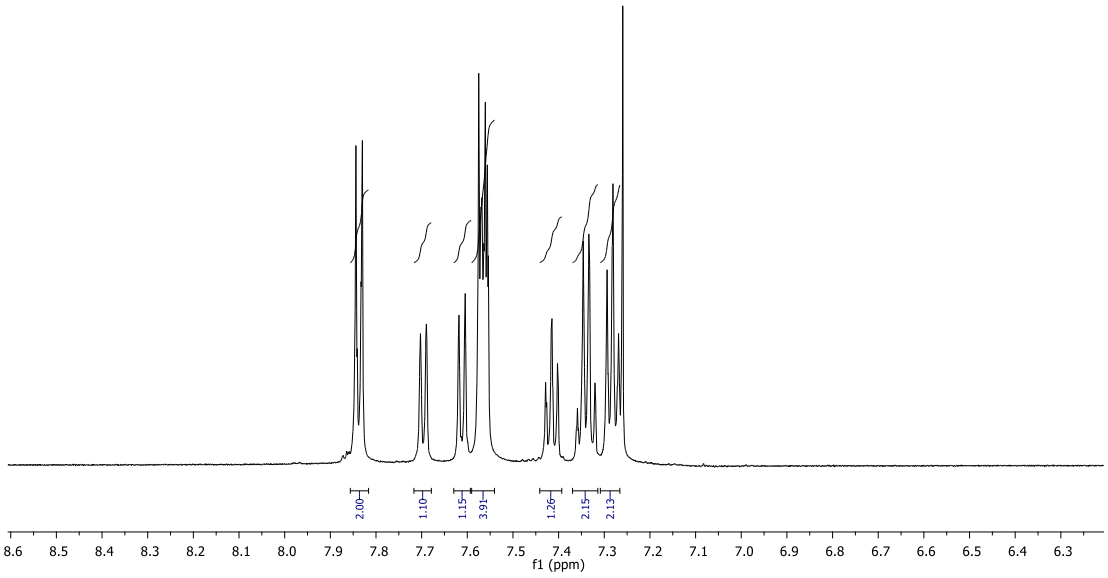


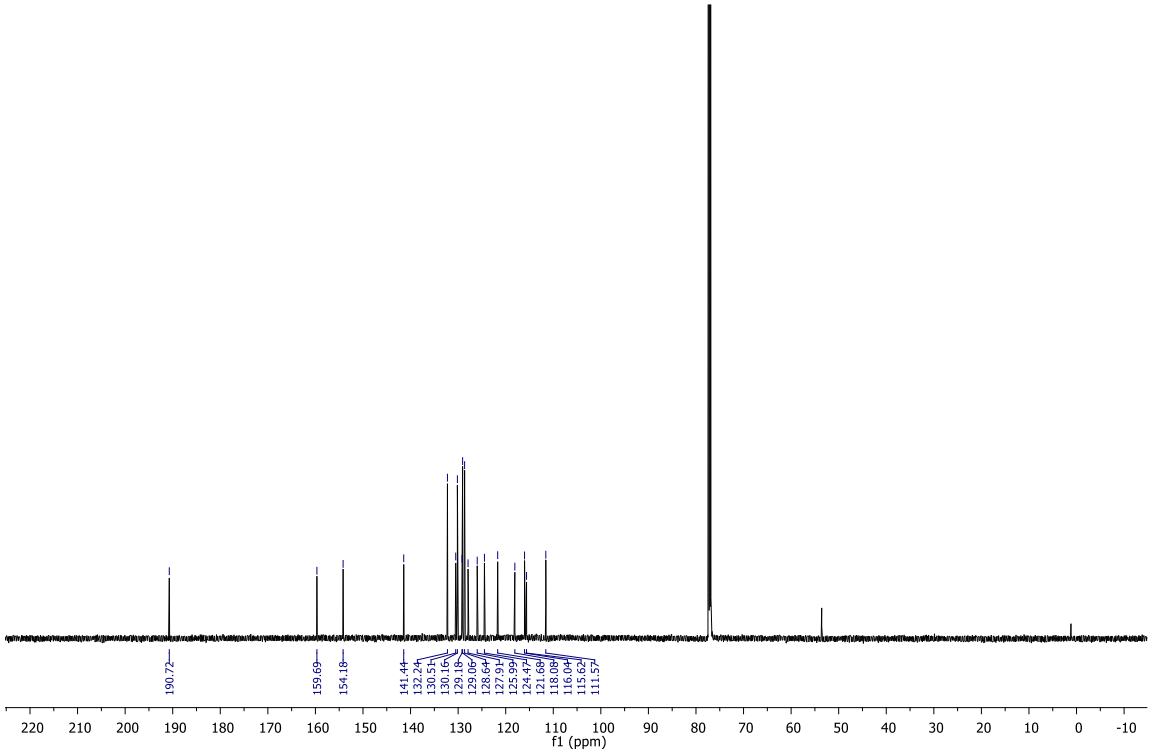
***3-(4-Cyanobenzoyl)-2-phenylbenzofuran* (10)**



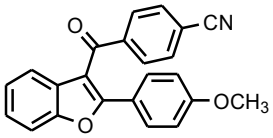
10





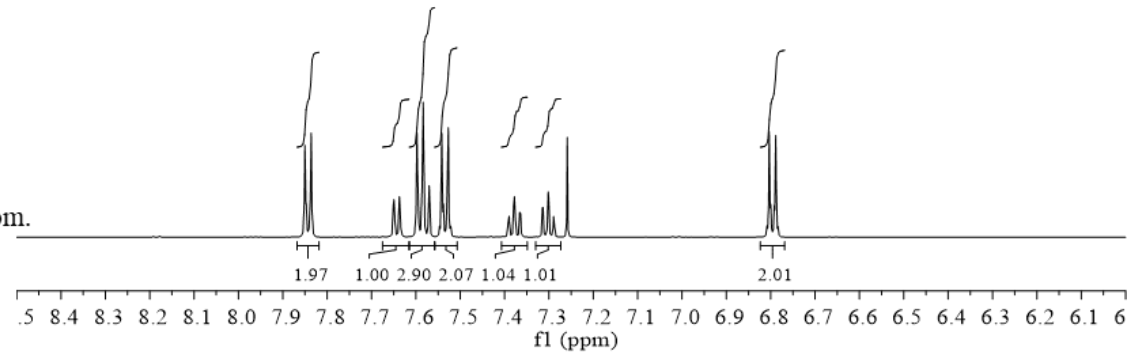

190.72
159.69
154.18
141.44
132.24
130.51
130.16
129.18
129.06
128.64
127.91
125.99
124.47
121.68
118.09
116.04
115.62
111.57
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

***3-(4-Cyanobenzoyl)-2-(4-methoxy)phenylbenzofuran* (11)**

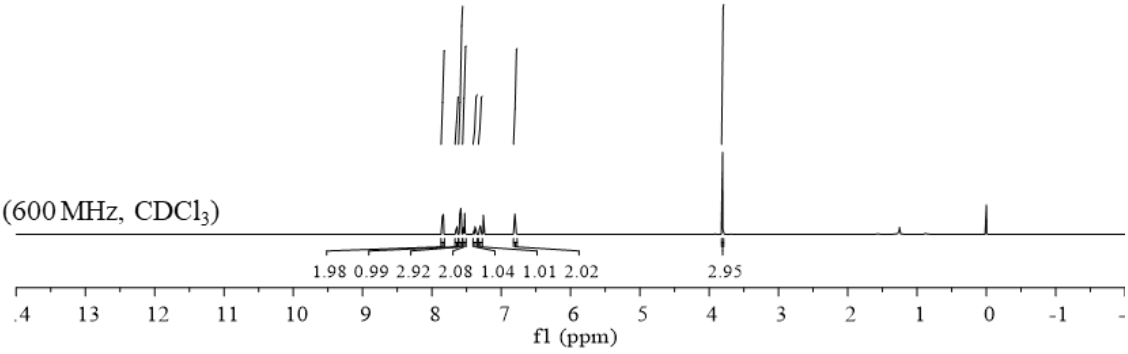


11

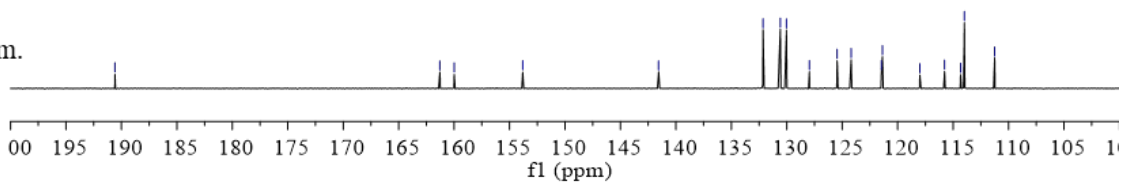
^{1}H NMR
zoom arom.

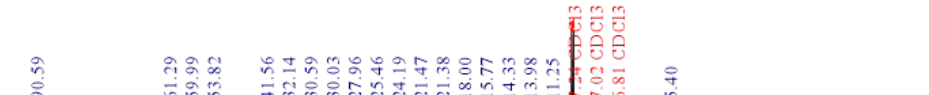


^{1}H NMR (600 MHz, $CDCl_3$)

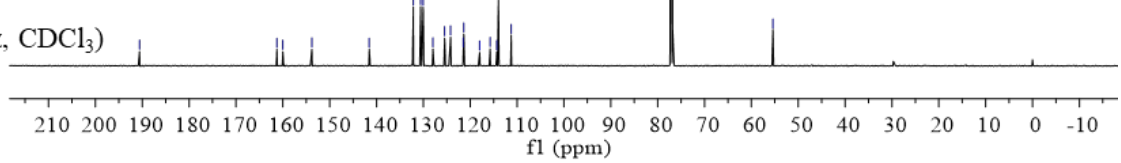


^{13}C NMR
zoom arom.

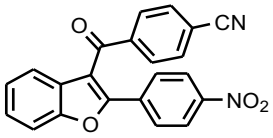




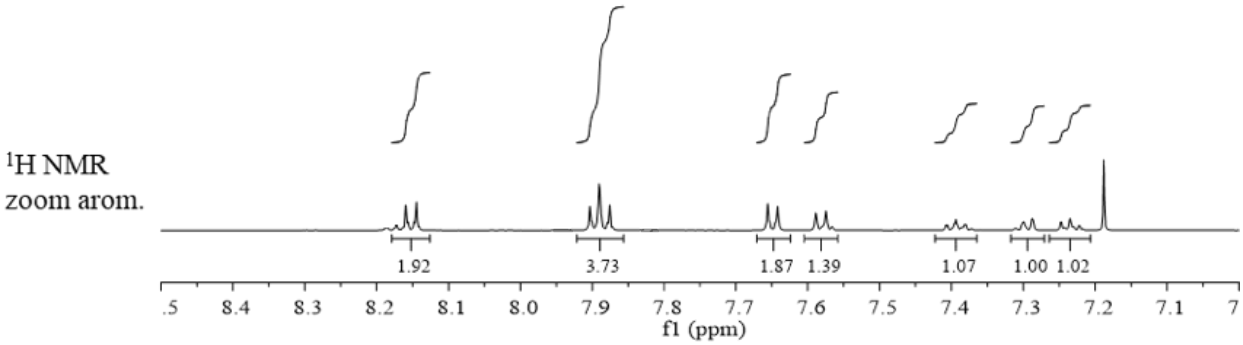
^{13}C NMR
(151 MHz, $CDCl_3$)

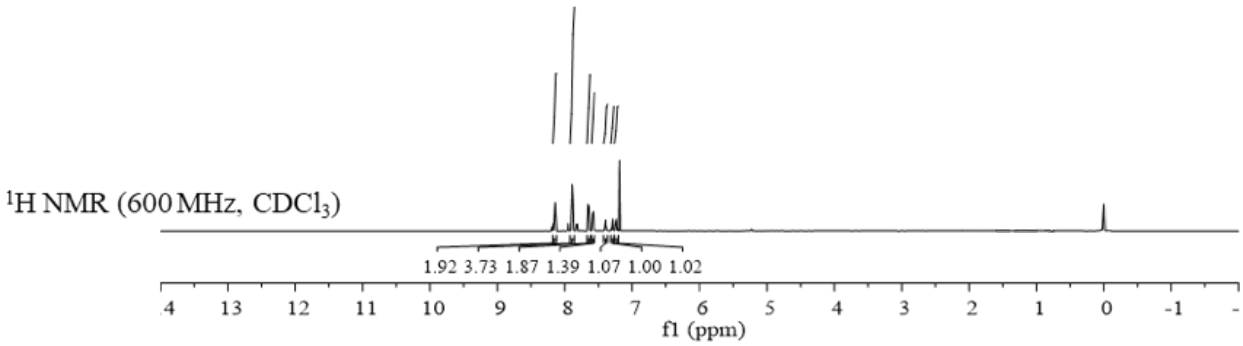


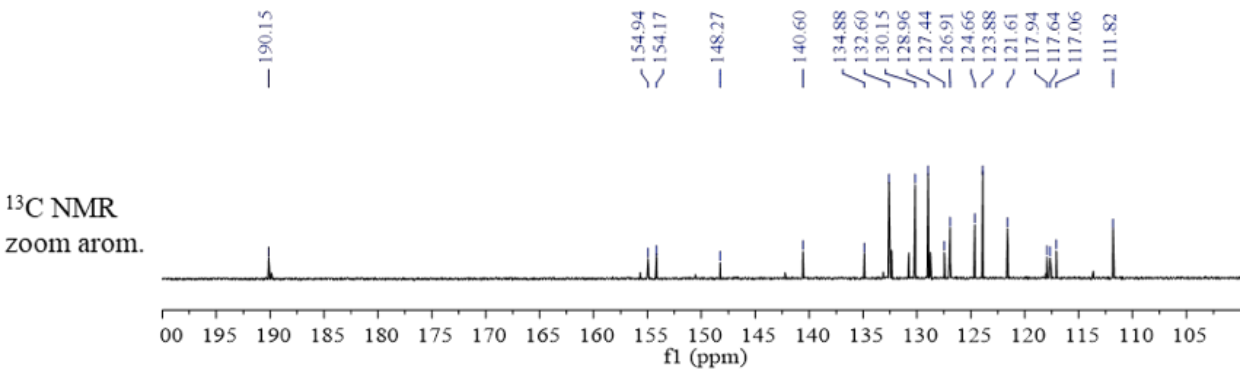
3-(4-Cyanobenzoyl)-2-(4-nitrophenyl)benzofuran **(12)**

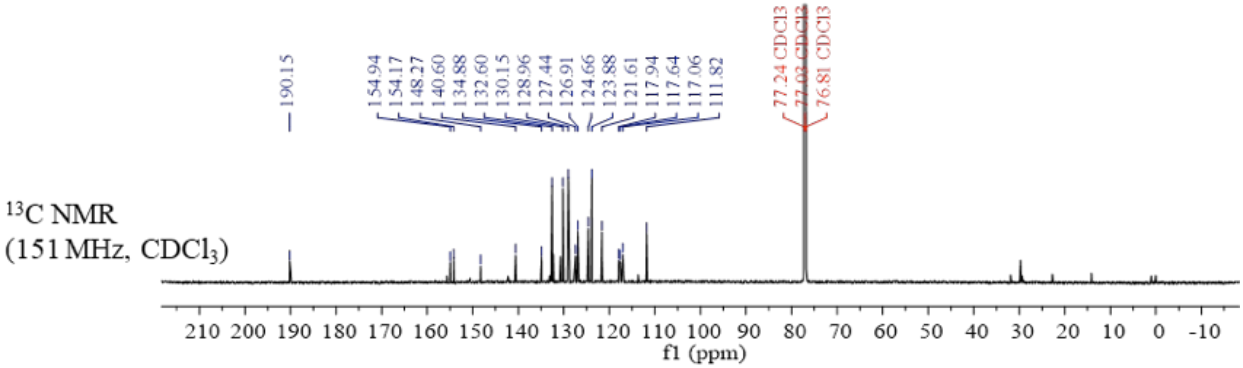


12

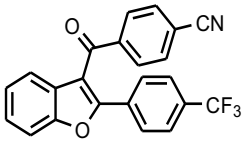






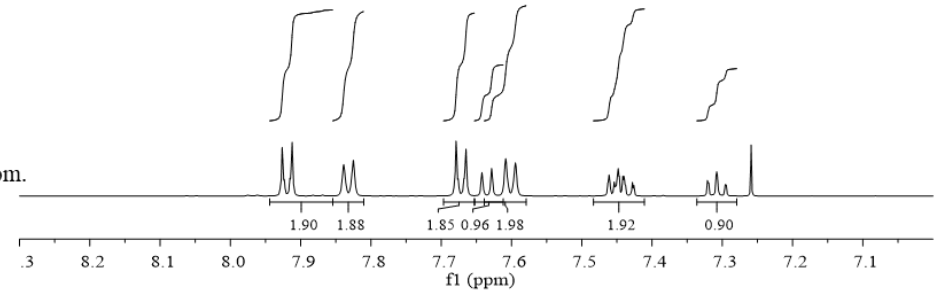


***3-(4-Cyanobenzoyl)-2-(4-trifluoromethyl)phenylbenzofuran* (13)**

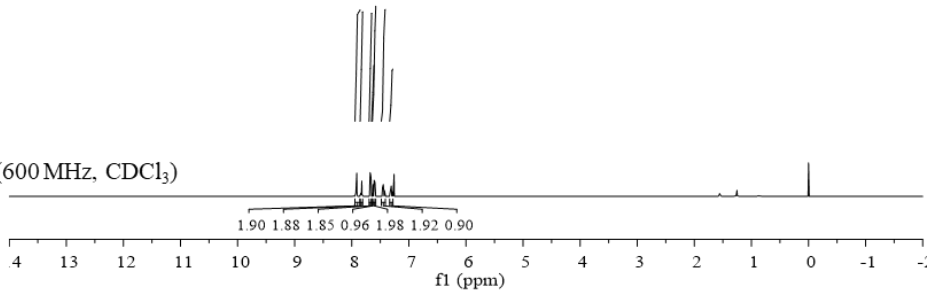


13

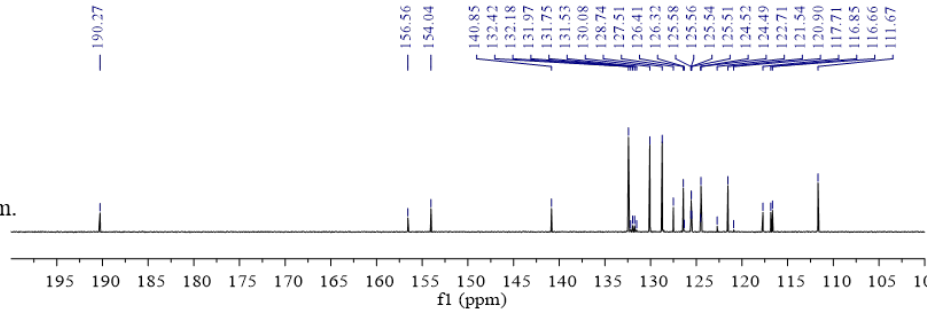
^{1}H NMR
zoom arom.



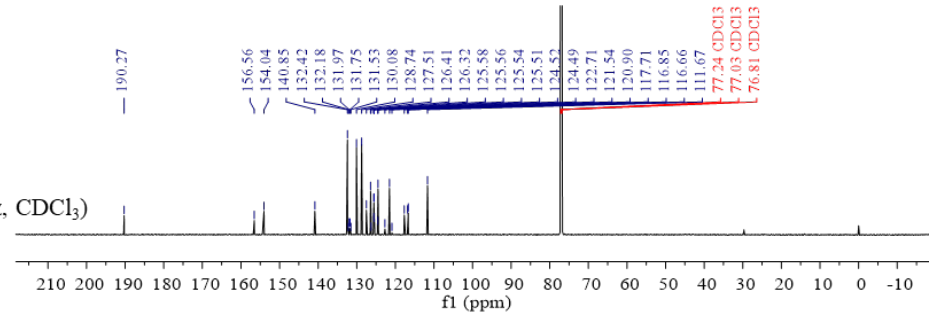
^{1}H NMR (600 MHz, $CDCl_3$)



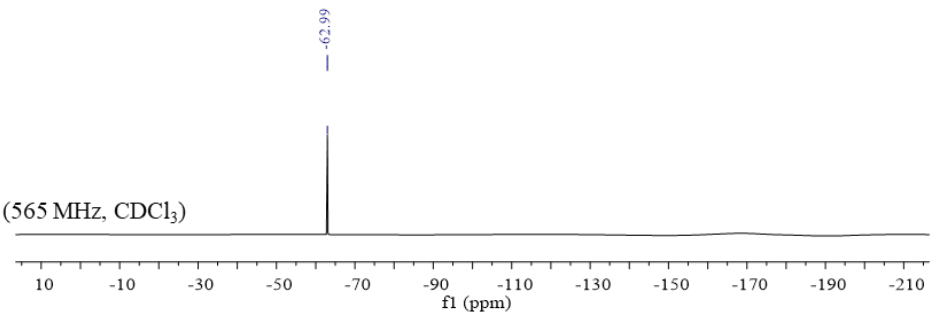
^{13}C NMR
zoom arom.



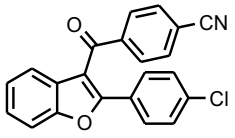
^{13}C NMR
(151 MHz, $CDCl_3$)



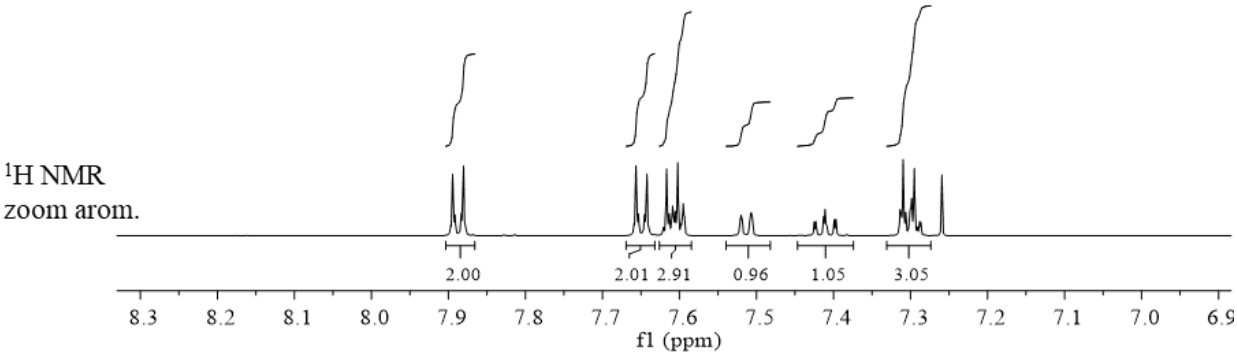
^{19}F NMR (565 MHz, $CDCl_3$)

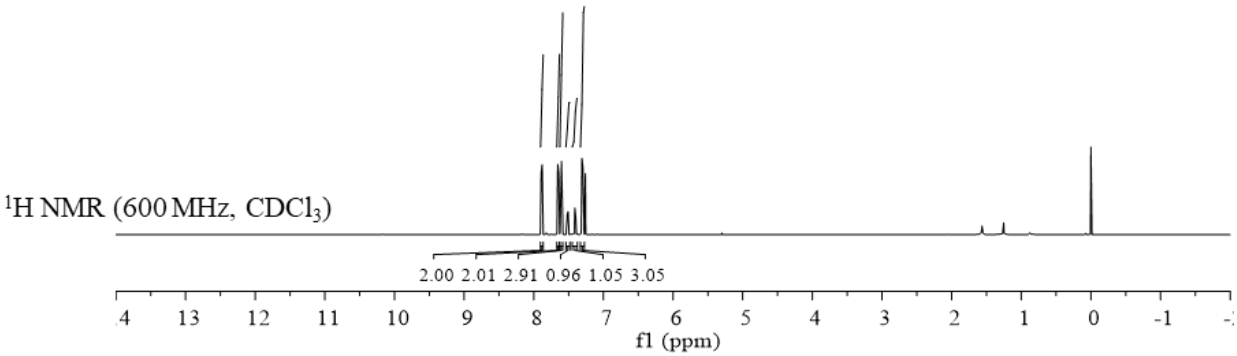


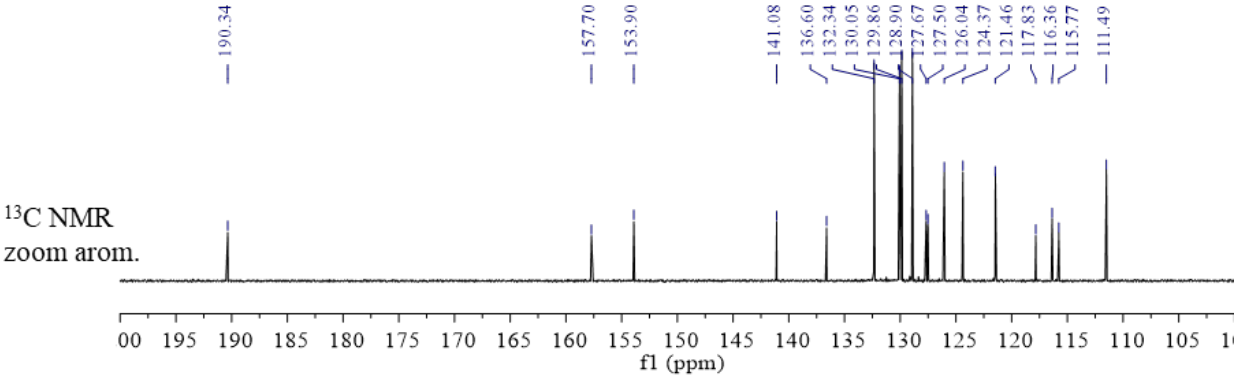
***3-(4-Cyanobenzoyl)-2-(4-chloro)phenylbenzofuran* (14)**

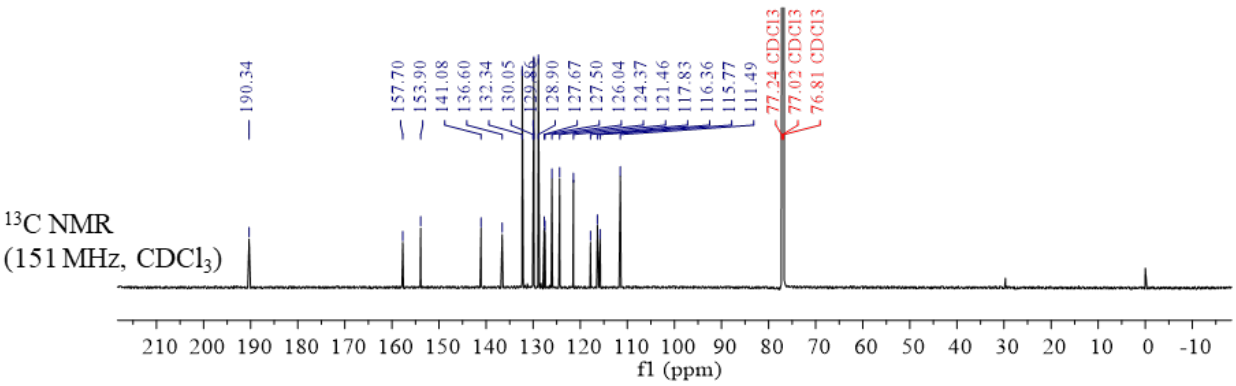


14

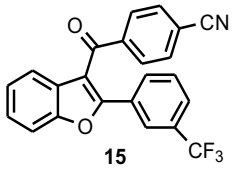






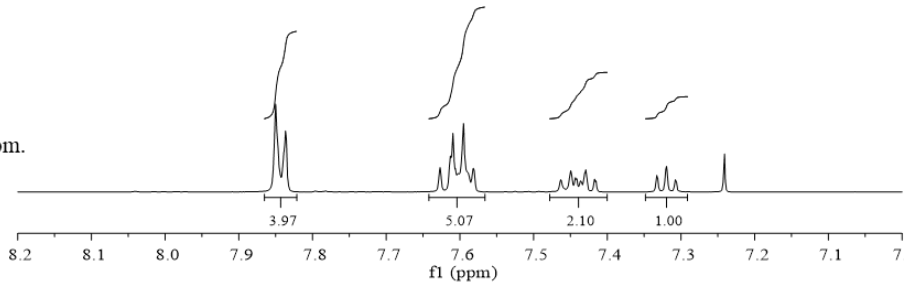


***3-(4-Cyanobenzoyl)-2-(3-trifluoromethylphenyl)benzofuran* (15)**

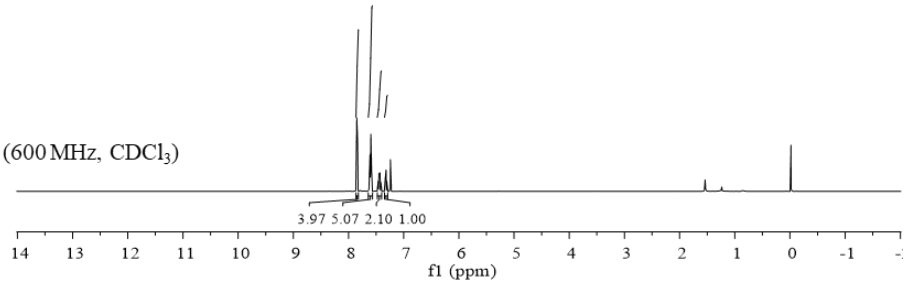


15

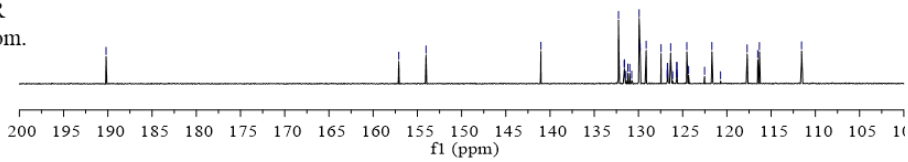
^{1}H NMR
zoom arom.

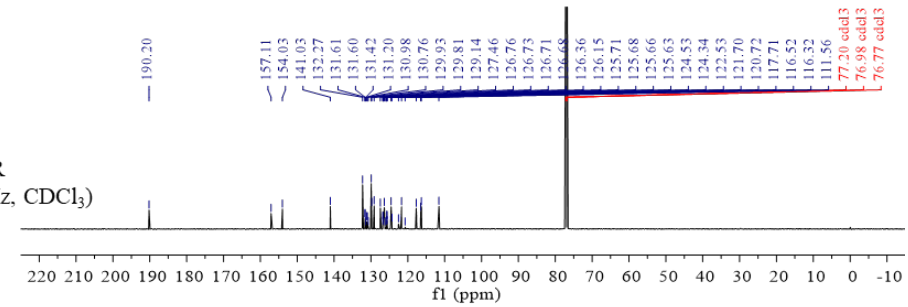


^{1}H NMR (600 MHz, $CDCl_3$)



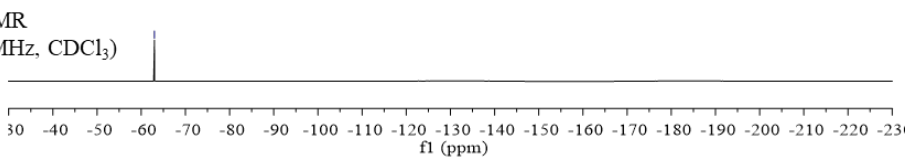
^{13}C NMR
zoom arom.



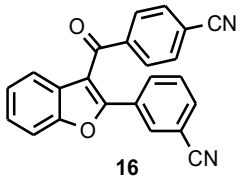


^{13}C NMR
(151 MHz, $CDCl_3$)

^{19}F NMR
(564 MHz, $CDCl_3$)

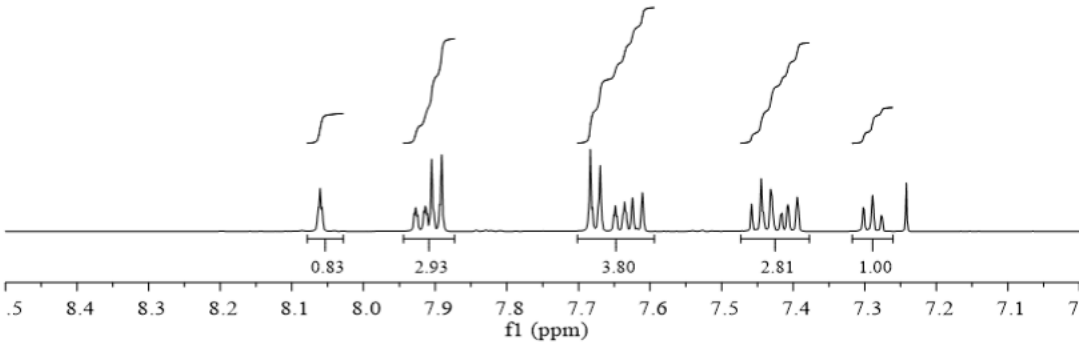


***3-(4-Cyanobenzoyl)-2-(3-cyanophenyl)benzofuran* (16)**

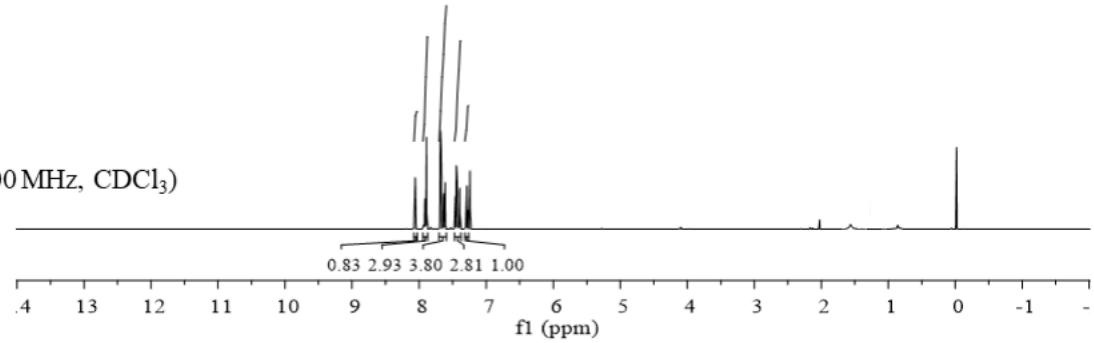


16

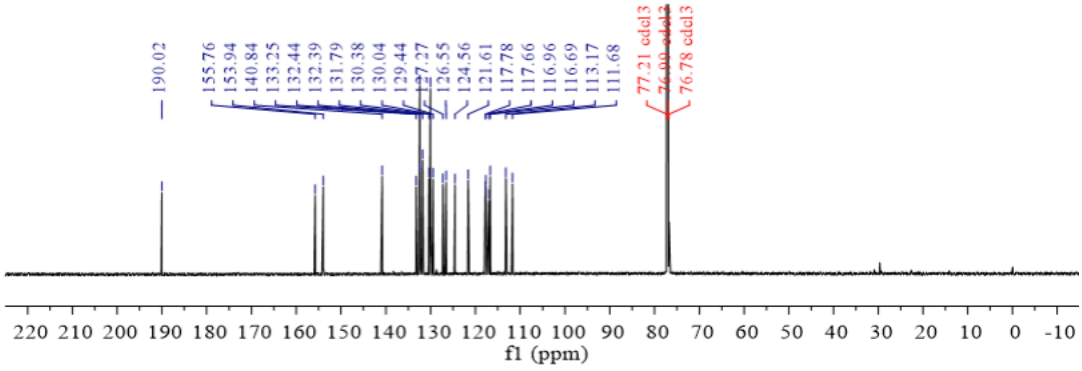
^{1}H NMR
zoom arom.



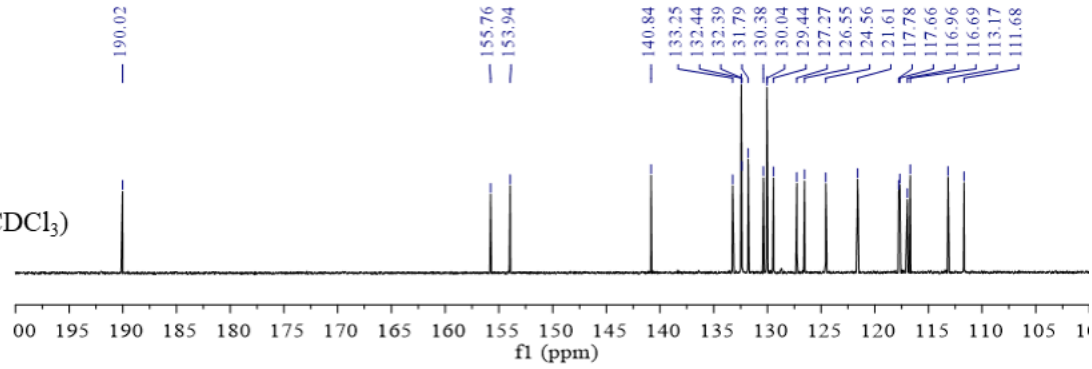
^{1}H NMR (600 MHz, $CDCl_3$)



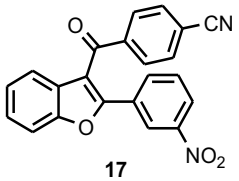
^{13}C NMR
zoom arom.



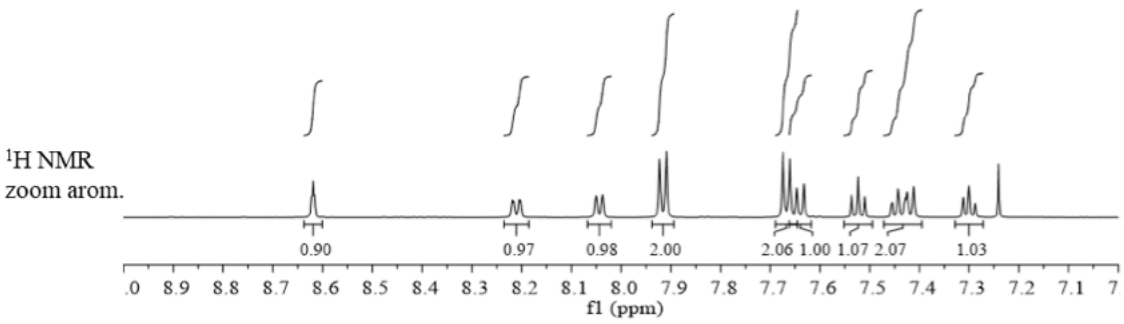
^{13}C NMR
(151 MHz, $CDCl_3$)

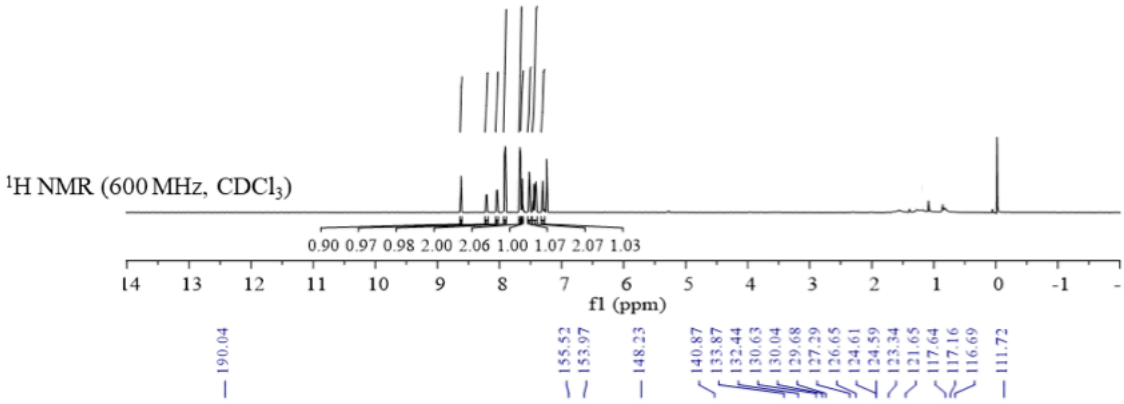


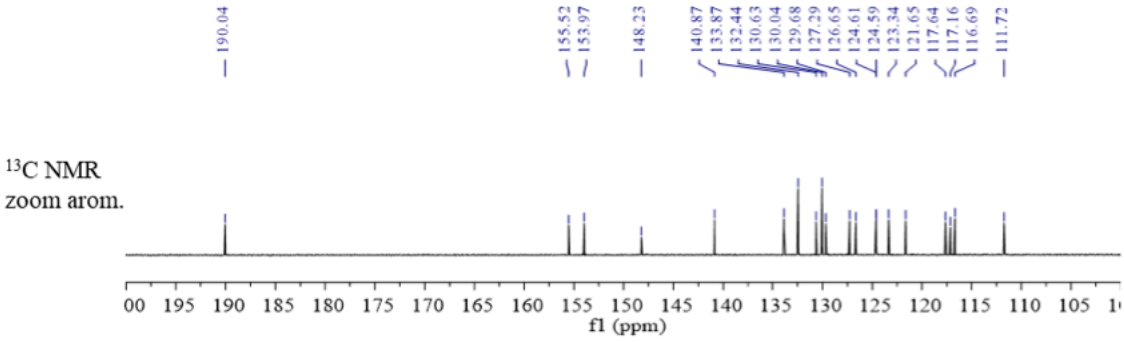
3-(4-Cyanobenzoyl)-2-(3-nitrophenyl)benzofuran **(17)**

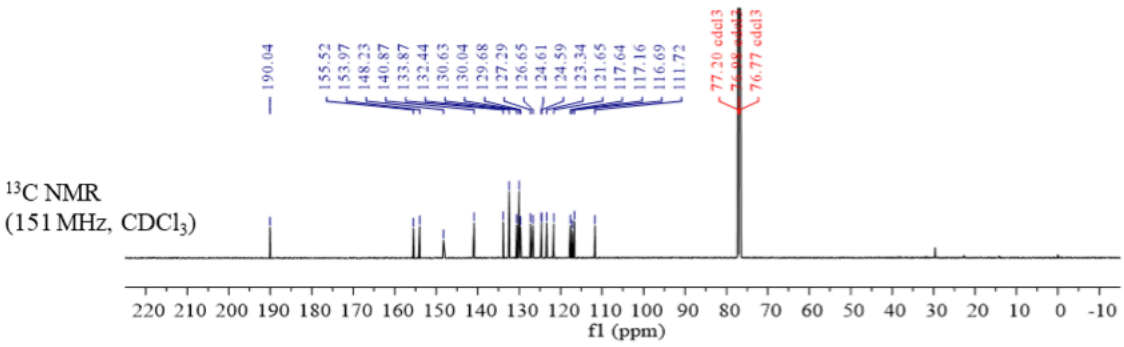


17

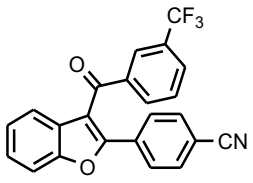




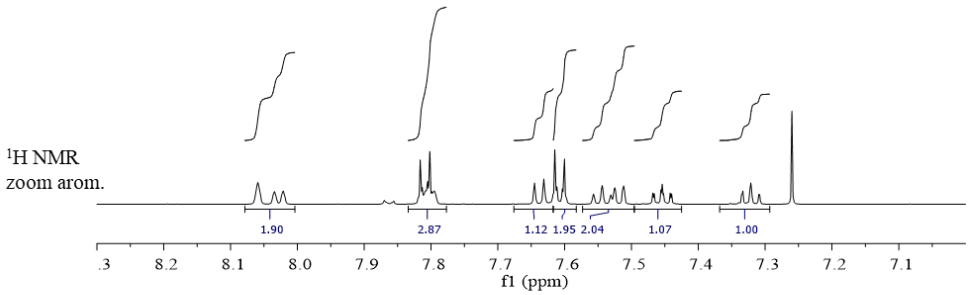


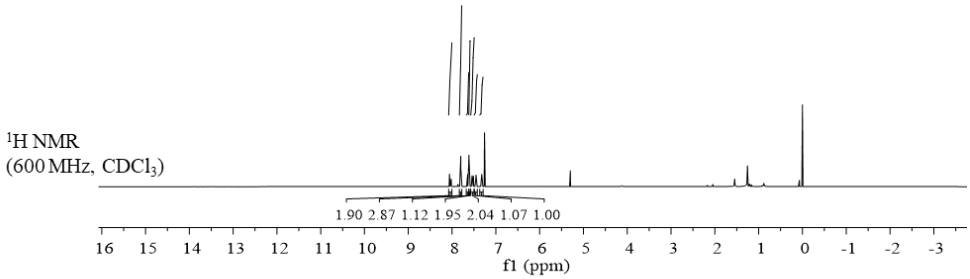


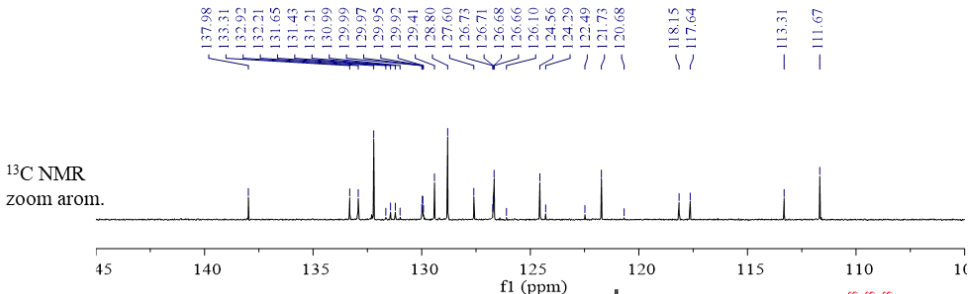
2-(4-Cyanophenyl)-3-(3-trifluoromethylphenyl)benzofuran (18)

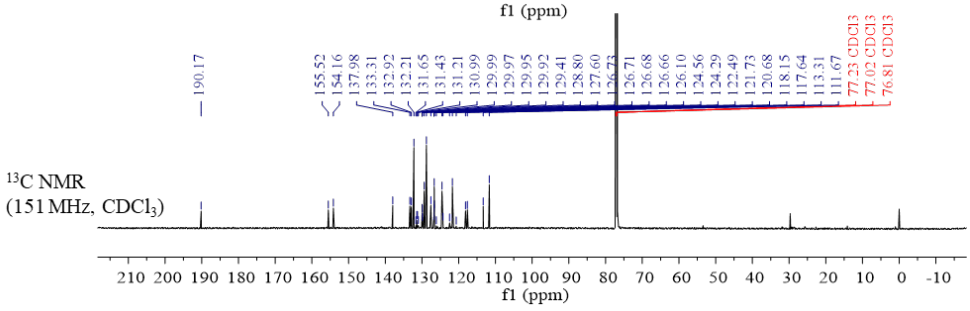


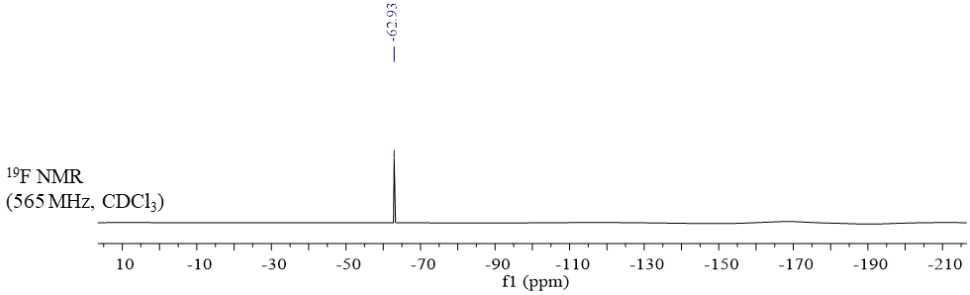
18



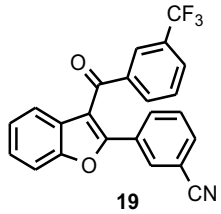






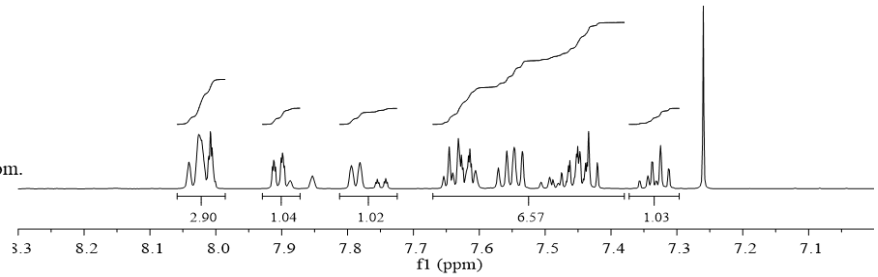


2-(3-Cyanophenyl)-3-(3-trifluoromethylbenzoyl)benzofuran (19)

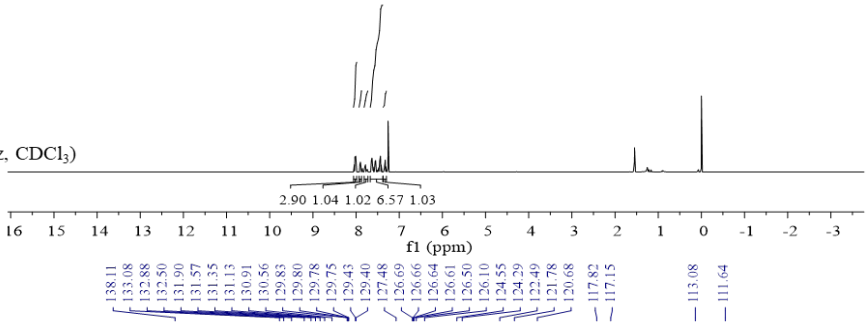


19

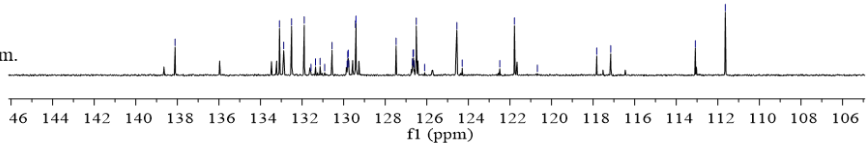
^{1}H NMR
zoom arom.



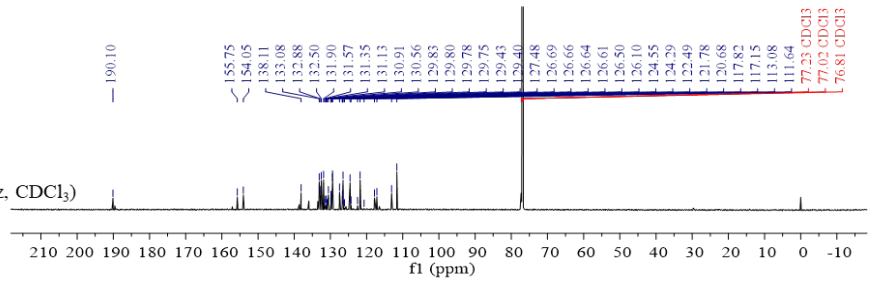
^{1}H NMR
(600 MHz, $CDCl_3$)



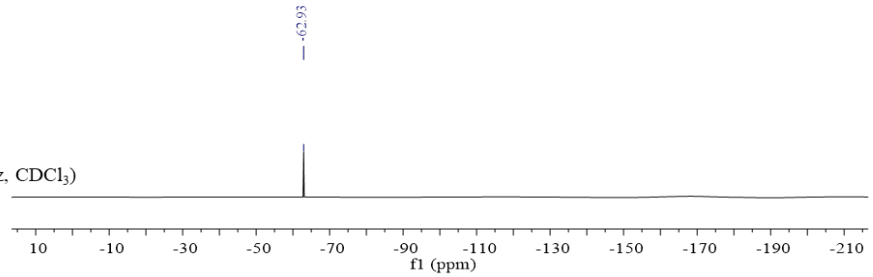
^{13}C NMR
zoom arom.



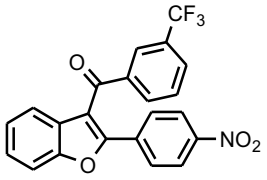
^{13}C NMR
(151 MHz, $CDCl_3$)



^{19}F NMR
(565 MHz, $CDCl_3$)

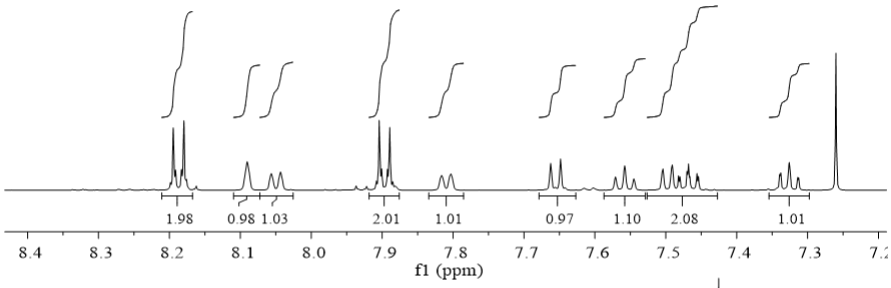


2-(4-nitrophenyl)-3-(3-trifluoromethylbenzoyl)benzofuran (20)

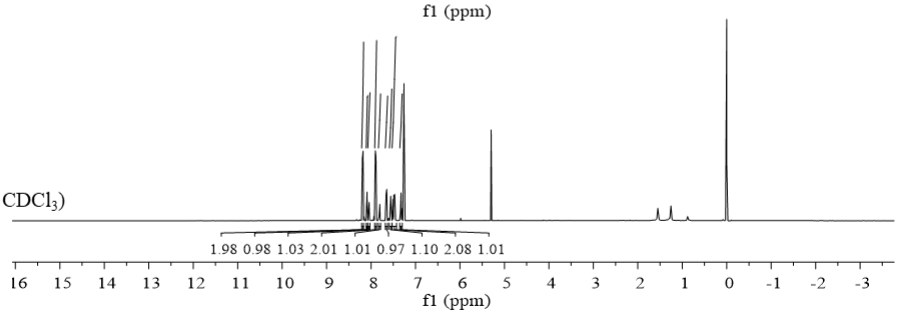


20

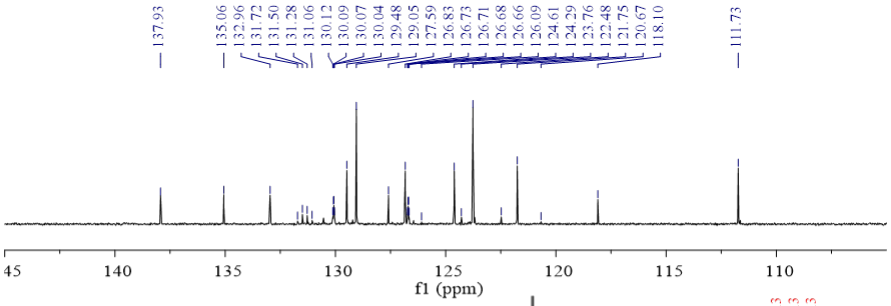
^{1}H NMR
zoom arom.



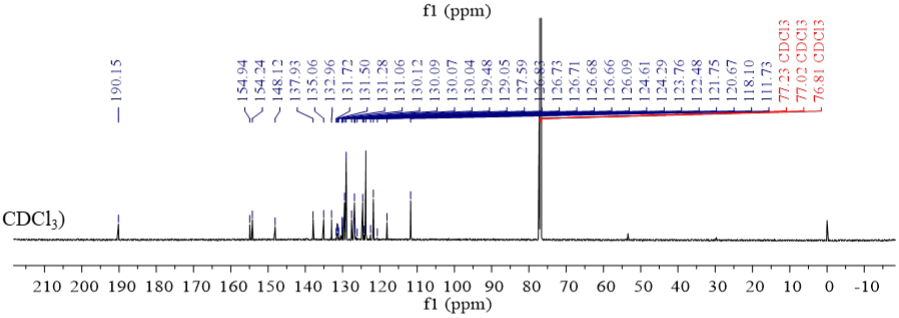
^{1}H NMR
(600 MHz, $CDCl_3$)



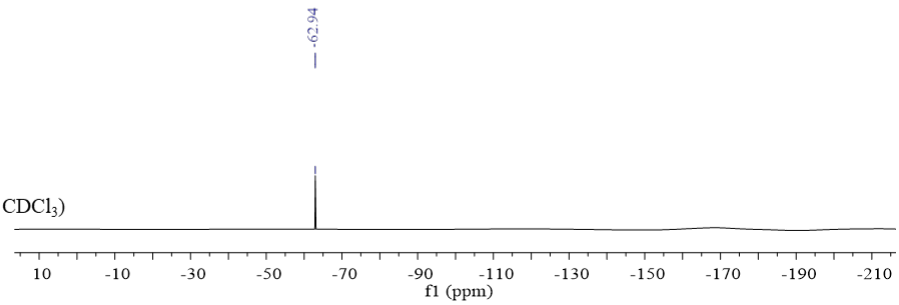
^{13}C NMR
zoom arom.



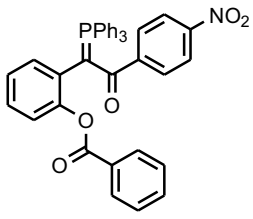
^{13}C NMR
(151 MHz, $CDCl_3$)



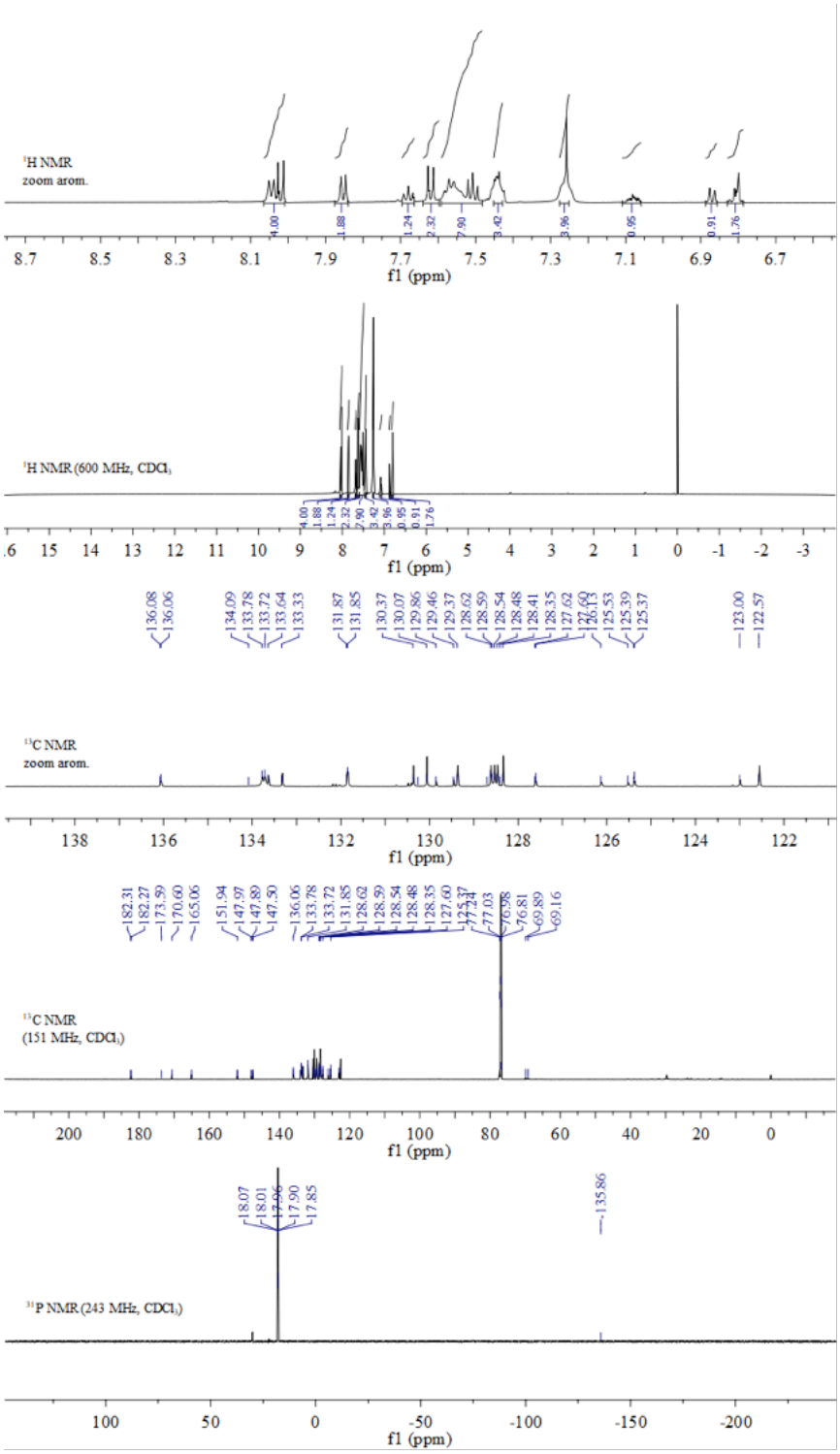
^{19}F NMR
(565 MHz, $CDCl_3$)



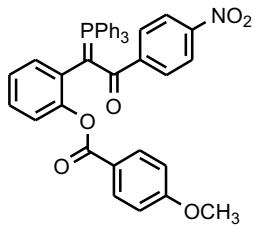
***o*-(Benzoyloxy)phenyl-4-nitro-benzoyl-methylene-triphenylphosphorane VIa**



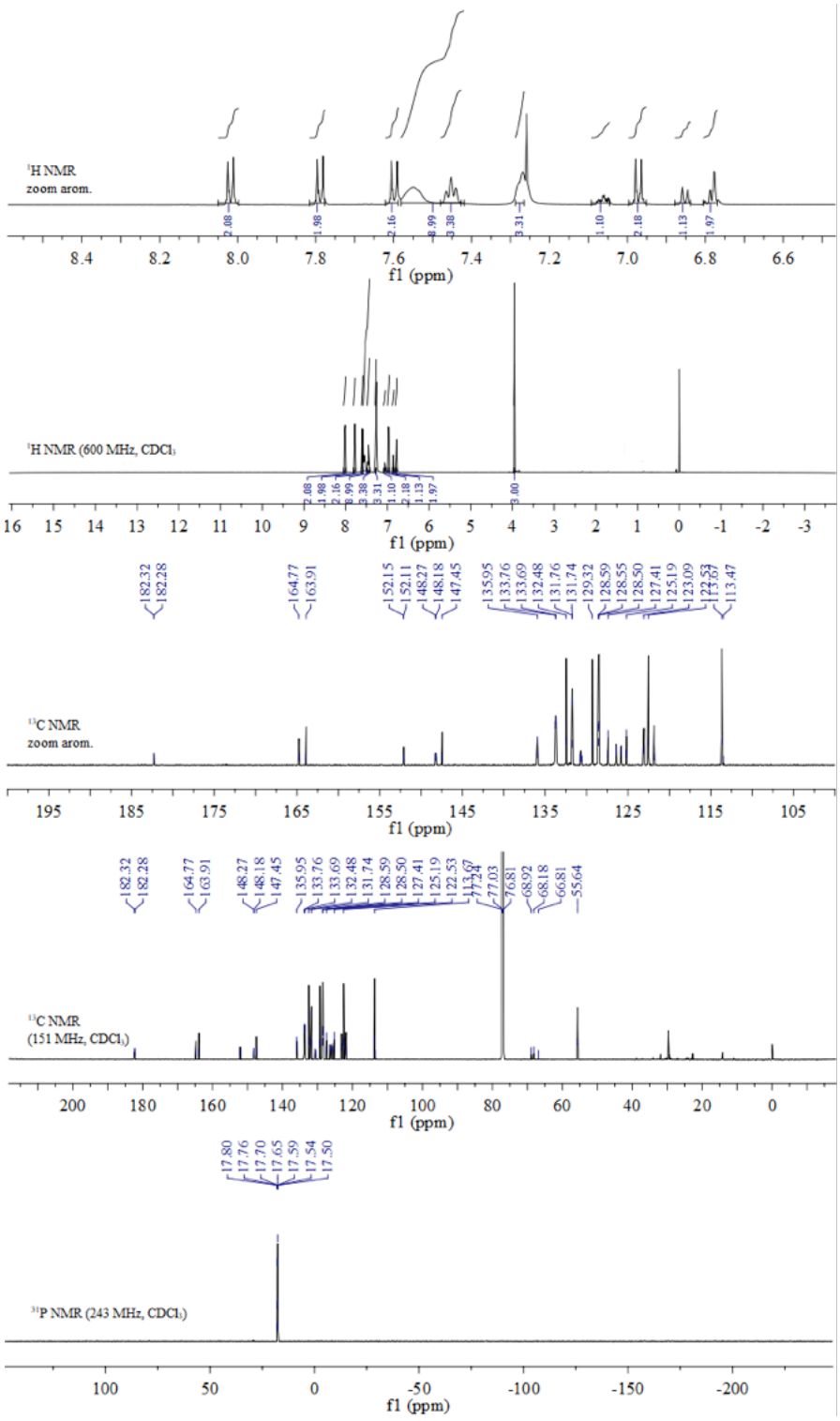
VIa



***o*-(4-methoxybenzoyloxy)phenyl-4-nitro-benzoyl-methylene-triphenylphosphorane VIb**



VIb



4. References

1. M. Begala, M. Mancinelli, G.L. Delogu, G.L. Tetrahedron Lett. 61 (2020) 151634.

2. P.K. Mandali, D.K. Chand. Synthesis 47 (2015) 1661-1668.

3. a) A. Hercouet, M. Le Corre. Tetrahedron Lett. 23 (1979) 2145-2148; (b) A. Hercouet, M. Le Corre. Tetrahedron 37(16) (1981) 2867-2873.

4. M. Begala, P. Caboni, M.J. Matos, G.L. Delogu. Tetrahedron Lett. 59 (2018) 1711-1714.

5. M.A. De Luca, M.P. Castelli, B. Loi, A. Porcu, M. Martorelli, C. Miliano, K. Kellett, C. Davidson, J.L. Stair, F. Schifano, G. Di Chiara. Neuropharmacology. 105 (2016) 630-638.