Supporting Information

Iridium/palladium dual photocatalysis for oxidative decarboxylative esterification of alcohols using *α*-keto acids

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Contents

1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received commercially. Commercially available metal salt precursors were used without additional purification. Most of the chemicals used in the catalytic reactions were purified according to standard procedure.[S1]

Chemicals: All reactants **1** and **2** were purchased from Sigma Aldrich, TCI India, Thermo Scientific and BLD Pharmatech India and used as received. Other reagents were purchased from Sigma Aldrich or TCI India and used as received.

Blue LED Setup: Reactions were irradiated with 40 W Kessil PR160L-456 nm LED (λ_{max}= 456 nm, average intensity of LED at 2x4 cm area is 137 mW/cm^2). Kessil PR160L-456 nm LED contains linear reflector and has upto 25% higher average intensity than Kessil PR160-456 nm LED. Distance between LED and reaction vessel surface was kept between 5-6 cm. 2 LEDs were used for irradiating 4 reaction vials and a cooling fan was used for maintaining the reaction temperature between 30-32 ºC .

Chromatography Techniques: Thin layer chromatography (TLC) was performed using silica gel percolated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Silica flash F60 (230-400 mesh)).

NMR Spectra: ^{1}H NMR (300, 400, 500 or 600 MHz), ^{13}C NMR (75, 101, 126 or 151 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform, dimethyl sulfoxide were used as NMR solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-d), δ 2.50 for ^{1}H (DMSO-d_6), δ 77.16 for ^{13}C (chloroform-d), δ 39.52 for ^{13}C (DMSO-d_6)]. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; quin, pentet (quintet); sext, sextet; m, multiplet; dq, doublet of quartet; qd, quartet of doublet.

Instrumental Techniques: GC-MS measurements were conducted on an Thermo Fischer TRACE 1300 GC system equipped with a ISQ QD single quadrupole mass spectrometer. GC analysis was carried out using a TG-5MS column (30 m, 0.25 mm, 0.25μ). High resolution mass

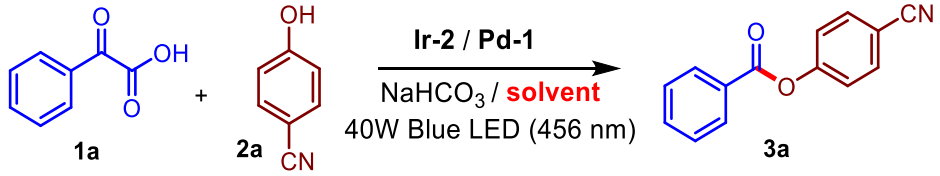
spectra (HRMS) were measured on Q-Tof micro-MS system by electron spray ionization (ESI) technique. Elemental analyses were performed on a Vario-EL cube elemental analyzer. Fourier transform infrared (FT-IR) analysis was carried out on a Perkin-Elmer Spectrometer. Optical absorption measurements were carried out by Shimadazu UV-vis-IR-3600 Plus spectrophotometer. The crystals were mounted on a Super Nova Dual Source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K_α radiation (λ= 0.71073 Å) and **Cu K_α** radiation (λ= 1.54178 Å) at 298K. X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature using Al K_α source (10 mA, 15kV) on a laboratory based commercial X-ray photoelectron spectrometer from Omicron Nanotechnology.

Computational Details: All molecular geometries were optimized in vacuum with M06 density functional paired with 6-31++G(p,d) basis set for C, H, N, O, F atoms and LanL2DZ, which has a double-ζ quality basis set with the Los Alamos effective core potential for Ir and Pd. The M06 density functional was used as it has been shown to be a tool to make reliable predictions for photo-redox reaction free energy changes and barriers. The CPCM technique has been chosen because continuum solvent models are reported to give satisfactory results for the solvent phase. All the calculations were conducted within the Gaussian 09 suite of programs.

2. Experimental Section

2.1 Optimization conditions

Table S1: Screening of solvent[a]



Entry	Solvent	Yield[b] (%) **3a**
1	**DMSO**	**88**
2	DMF	56
3	DMA	47
4	CH_3CN	37
5	THF	trace
6	1,4-Dioxane	7
7	DCE	19
8	Acetone	34
9	MeOH	trace
10	Toluene	NR
11	Water	NR
12	CCl_4	trace

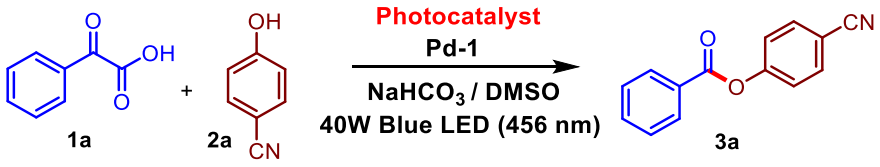
[a]Reaction conditions: α-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

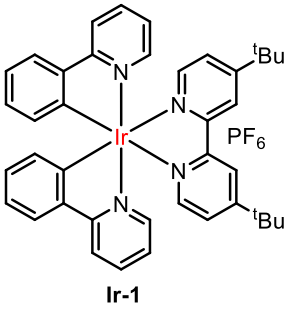
Table S2: Screening of additive[a]

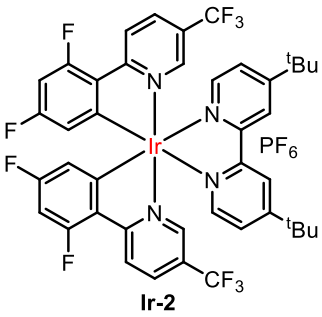
Entry	Additive	Yield[b] (%) **3a**
1	**$NaHCO_3$**	**88**
2	Cs_2CO_3	55
3	Na_2CO_3	59
4	K_2CO_3	57
5	NaOAc	23
6	NaH_2PO_4	56
7	Na_2HPO_4	64
8	K_2HPO_4	57
9	NaOH	9
10	NEt_3	11
11	$NaHSO_4$	NR
12	K_3PO_4	NR
13	^tBuOK	40

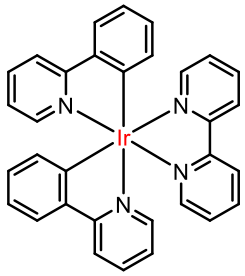
[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), addtive (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

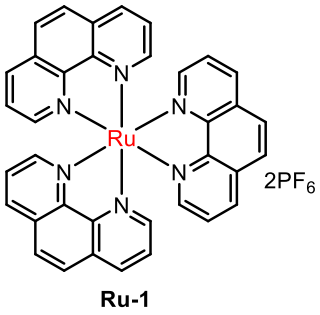
Table S3: Screening of photoredox catalyst[a]

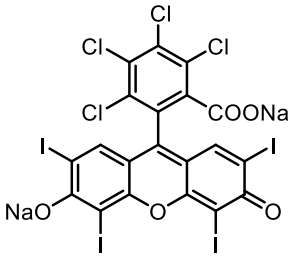


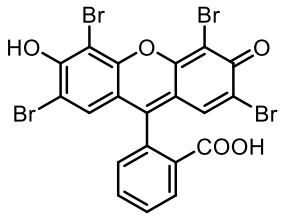








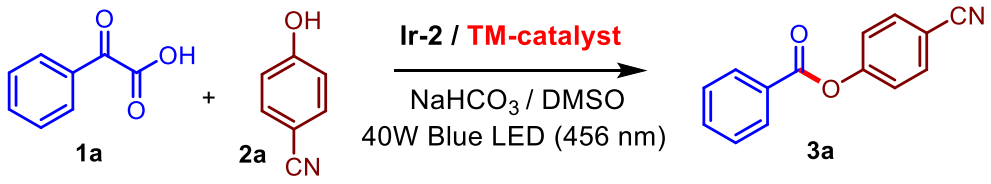




Entry	Photocatalyst	Yield[b] (%) **3a**
1	Ir-1	39
2	**Ir-2**	**88**
3	Ir-3	11
4	Ru-1	5
5	Rose Bengal	trace
6	Eosin-Y	trace

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), photocatalyst (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

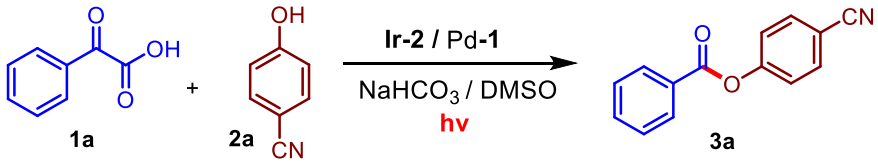
Table S4: Screening of transition metal catalyst[a]



Entry	TM-catalyst	Yield[b] (%) **3a**
1	$PdCl_2$	67
2	$Pd(OAc)_2$	49
3	**(4,4'-dtbbpy)$PdCl_2$ (Pd-1)**	**88**
4	$Pd(TFA)_2$	60
5	$Pd(PPh_3)_2Cl_2$	62
6	$Pd(PPh_3)_4$	11
7	$NiCl_2$	41
8	$Pd(acac)_2$	57
9	**$PdCl_2$ + (4,4'-dtbbpy)**	**84**
10	$Ni(TFA)_2$	43
11	$CuCl_2$	35
12	CuI	trace
13	$Rh(Ph_3P)_3Cl$	trace

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), TM-catalyst (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

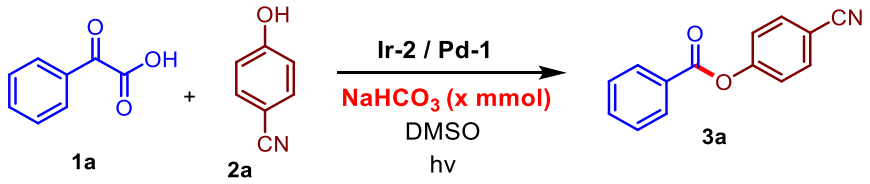
Table S5: Variation of light source and intensity[a]



Entry	Light source (Intensity)	Yield[b] (%) **3a**
1	PR160L-440 nm LED (100%)	63
2	PR160L-390 nm LED (100%)	32
3	**PR160L-456 nm LED (100%)**	**88**
4	PR160L-456 nm LED (50%)	64
5	CFL bulb	13

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

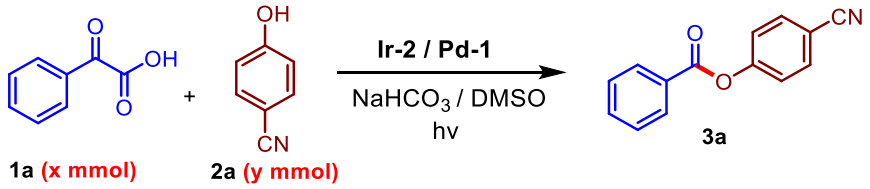
Table S6: Additive Equivalent[a,b]



Entry	**Additive $NaHCO_3$** (mmol)	**Yield (%)[b] 3a**
1	**0.3**	**88**
2	0.2	65
3	0.6	75

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (x mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

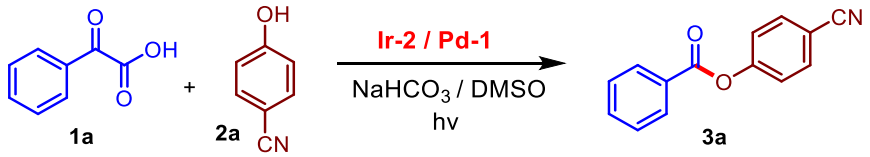
Table S7: Substrate Equivalent[a,b]



Entry	Keto Acid **1a** (mmol)	Alcohol **2a** (mmol)	Yield (%)[b] **3a**
1	0.3	0.3	80
2	**0.3**	**0.25**	**88**
3	0.45	0.25	90
4	0.3	0.45	76

[a]Reaction conditions: *α*-keto acid **1a** (x mmol), 4-hydroxybenzonitrile **2a** (y mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

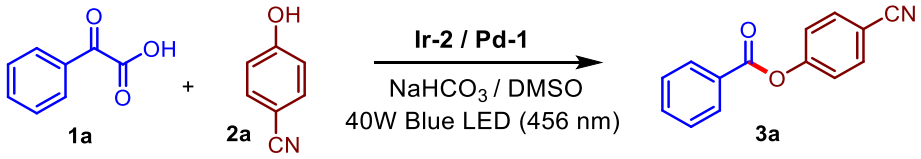
Table S8: Catalyst loading[a,b]



Entry	Photocatalyst (mol%)	TM-catalyst (mol%)	Yield (%)[b] **3a**
1	1	5	30
2	1.5	5	42
3	2	5	55
4	**5**	**5**	**88**
5	5	2	60
6	5	10	90

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

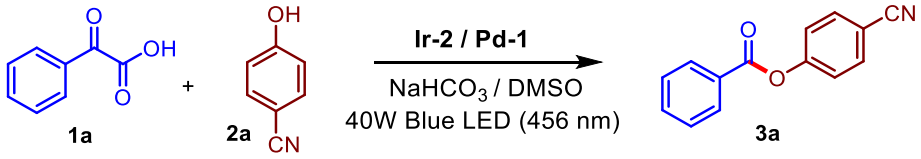
Table S9: Control experiment[a]

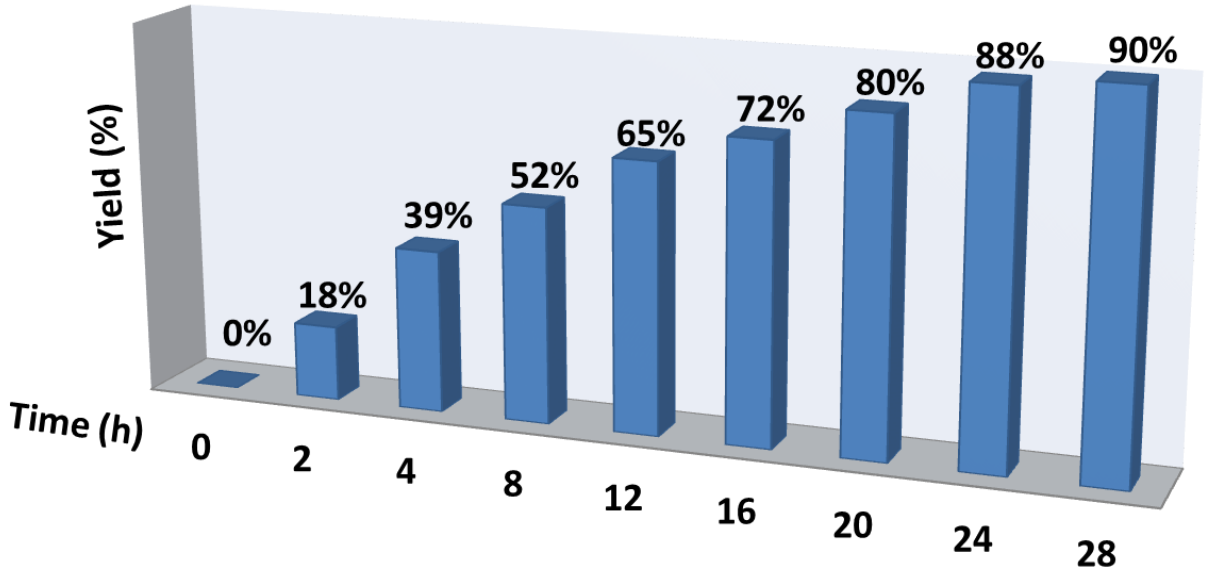


Entry	Condition	Yield (%)[b] **3a**
1	Without Ir-2	NR
2	Without Pd-1	20
3	Without $NaHCO_3$	9
4	Without blue LED	NR

[a]Reaction conditions: *α*-keto acid **1a** (0.3 mmol), 4-hydroxybenzonitrile **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.3 mmol), and solvent (1.5 mL) stirred at room temperature (RT) under 40W blue LED (456 nm) for 24 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

Table S10: Reaction Kinetics



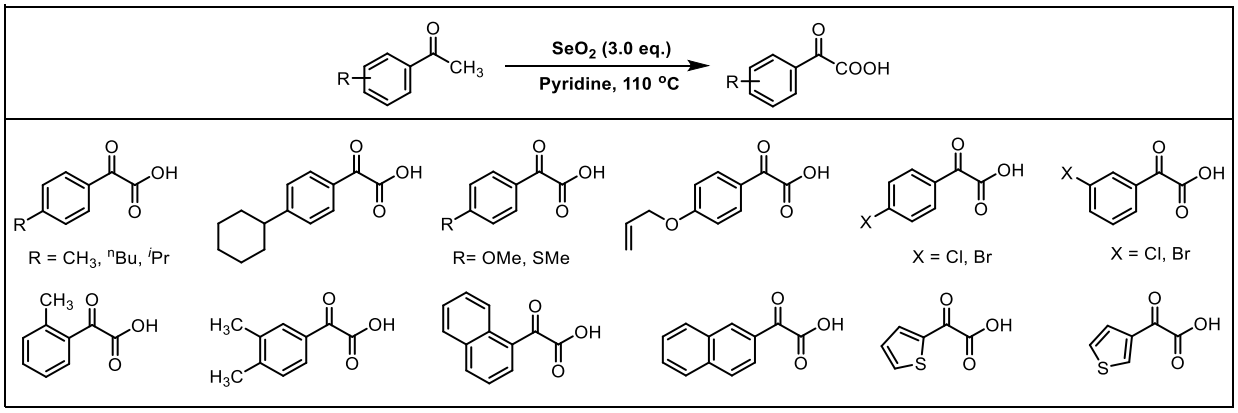


2.2 Synthesis and characterization of starting material

2.2.1 Photocatalyst preparation:

The photocatalysts, such as $[Ir(ppy)_2(dtbbpy)]PF_6$ (**Ir-1**), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (**Ir-2**), $[Ru(phen)_3](PF_6)_2$ (**Ru-1**) were synthesized according to literature report.[S2] The spectral data of the photocatalysts are consistent with the literature data. Other photocatalysts such as Eosin-Y, Rose-Bengal were purchased from commercial supplier and used as received.

2.2.2 General procedure for synthesis of glyoxalic acids[S3]

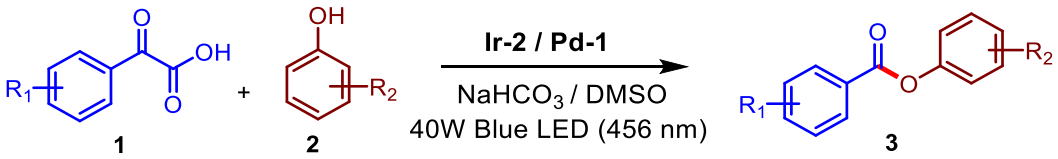


Scheme S1. Synthesis of glyoxalic acids.

Process: According to literature[S3], in a 50 mL round-bottom flask equipped with stirred bar and filled with argon, acetophenone derivatives (5 mmol, 1.0 equiv.) and selenium dioxide (15 mmol, 3 equiv.) were added followed by freshly-dried pyridine (15 mL). The reaction mixture was stirred at 110 °C in an oil bath for overnight (12-16 hr). After completion of the reaction, as determined by TLC, the mixture containing precipitated selenium was filtered through a pad of celite, the black selenium was washed several times with ethyl acetate. The combined filtrate was concentrated by rotary evaporator. The residue was transferred to a separatory funnel then 1 M HCl was gradually added to the solution for neutralize the leftover pyridine (a precipitate can be seen). The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were treated with 1 M NaOH and the solution was washed with water three times. The combined aqueous layers were acidified using 1 M HCl to about pH = 2 (a precipitate can be seen). The mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine solution, dried with Na_2SO_4 and concentrated under vacuo. The crude α-oxocarboxylic acid was used without further purification and spectral data are consistent with the

literal report. Remaining α-keto acids were purchased from commercial supplier and used as received.

2.2.3 General procedure for synthesis of ester

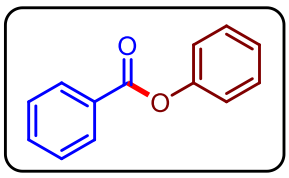


Scheme S2. Synthesis of ester(**3a-3zzw; 5a-5o; 7a-7p**).

Process: To a 15 mL clean, oven-dried screw cap reaction tube, α-keto acid **1a** (0.30 mmol), alcohol **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.30 mmol) in DMSO (1.5 mL) were added. The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 24h. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 24h, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

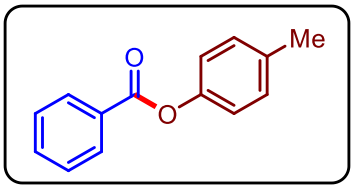
Characteristics of Isolated Products

phenyl benzoate (3b)



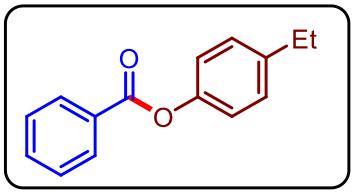
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2b** (24 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 98:2), White solid, 39.6 mg, Yield: 80%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23-8.20(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.46-7.41(t, *J* = 9 Hz, 2H), 7.30-7.26(t, *J* = 9 Hz, 1H), 7.24-7.21(d, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.4, 151.1, 133.7, 130.3, 129.8, 129.6, 128.7, 126.0, 121.9. **HRMS (ESI):** m/z Calcd for $C_{13}H_{11}O_2$ $[M+H]^+$: 199.0754; Found: 199.0755.

p-tolyl benzoate (3c)



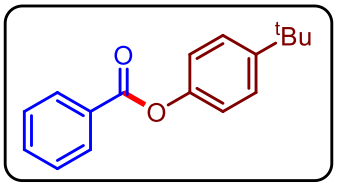
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2c** (27 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 44.0 mg, Yield: 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22-8.20(d, *J* = 8 Hz, 2H), 7.65-7.61(t, *J* = 8 Hz, 1H), 7.53-7.49(t, *J* = 8 Hz, 2H), 7.24-7.22(d, *J* = 8 Hz, 2H), 7.11- 7.09(d, *J* = 8 Hz, 2H), 2.38(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 148.9, 135.6, 133.6, 130.3, 130.1, 129.9, 128.7, 121.5, 21.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_2$: 213.0910; Found: 213.0912.

4-ethylphenyl benzoate (3d)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2d** (31 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 46.3 mg, Yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24-8.22(d, *J* = 8 Hz, 2H), 7.68-7.64(t, *J* = 8 Hz, 1H), 7.55-7.52(t, *J* = 8 Hz, 2H), 7.28-7.27(d, *J* = 8 Hz, 2H), 7.16-7.14(d, *J* = 8 Hz, 2H), 2.73-2.67(q, *J* = 8 Hz, 2H), 1.30-1.27(t, *J* = 8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 149.0, 142.0, 133.6, 130.3, 129.9, 129.0, 128.7, 121.6, 28.5, 15.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.

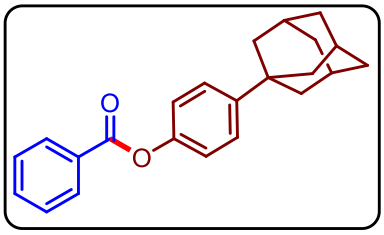
4-(tert-butyl)phenyl benzoate (3e)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2e** (47.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 50.8 mg, Yield: 80%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24-8.21(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.55-7.50(t, *J* = 9 Hz, 2H), 7.48-7.45(d, *J* = 9 Hz, 2H), 7.18-7.15(d, *J* = 9 Hz, 2H), 1.37(s, 9H). **^{13}C NMR** (75 MHz,

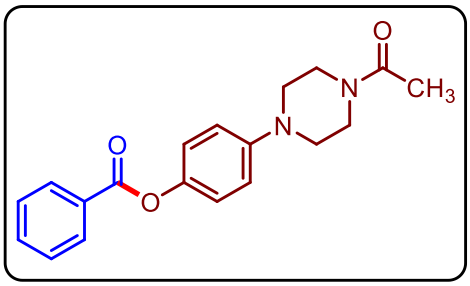
$CDCl_3$) δ 165.5, 148.8, 148.7, 133.6, 130.3, 129.8, 128.6, 126.5, 121.1, 34.6, 31.6. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{19}O_2$: 255.1380; Found: 255.1384.

4-((3r,5r,7r)-adamantan-1-yl)phenyl benzoate (3f)



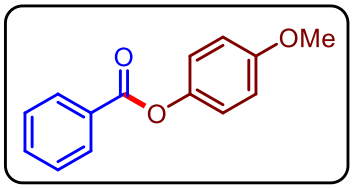
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2f** (57 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 65.5 mg, Yield: 79%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.19(d, *J* = 8 Hz, 2H), 7.65-7.61(t, *J* = 8 Hz, 1H), 7.53-7.49(t, *J* = 8 Hz, 2H), 7.42-7.40(d, *J* = 8 Hz, 2H), 7.17-7.15(d, *J* = 8 Hz, 2H), 2.11(br, 3H), 1.94(br, 6H), 1.77(br, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.5, 149.1, 148.8, 133.6, 130.3, 129.9, 128.7, 126.1, 121.2, 43.4, 36.9, 36.2, 29.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{23}H_{25}O_2$: 333.1849; Found: 333.1844.

4-(4-acetylpiperazin-1-yl)phenyl benzoate (3g)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2g** (45 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 70:30), White solid, 54.2 mg, Yield: 67%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.53-7.48(t, *J* = 9 Hz, 2H), 7.15-7.12(d, *J* = 9 Hz, 2H), 6.98-6.95(d, *J* = 9 Hz, 2H), 3.80-3.62(m, 4H), 3.19-3.12(m, 4H), 2.15(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.2, 165.7, 149.1, 144.7, 133.7, 130.3, 129.8, 128.7, 122.4, 117.9, 50.4, 50.0, 46.4, 41.5, 21.5. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{19}H_{21}N_2O_3$: 325.1547; Found: 325.1543.

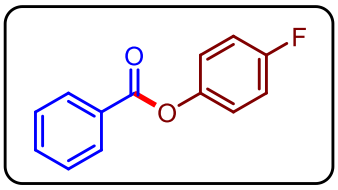
4-methoxyphenyl benzoate (3h)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2h** (31 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3

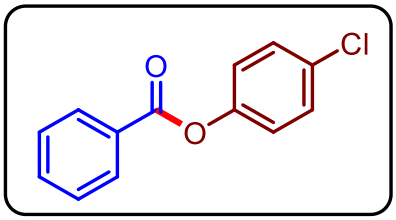
mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 94:6), White solid, 35.3 mg, Yield: 62%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.53-7.48(t, *J* = 9 Hz, 2H), 7.15-7.12(d, *J* = 9 Hz, 2H), 6.96-6.93(d, *J* = 9 Hz, 2H), 3.83(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.7, 157.5, 144.6, 133.6, 130.3, 129.8, 128.7, 122.6, 114.7, 55.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_3$: 229.0859; Found: 229.0853.

4-fluorophenyl benzoate (3i)



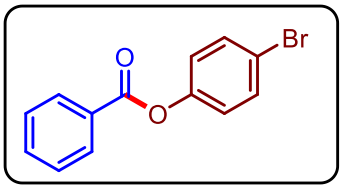
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2i** (28 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 42.1 mg, Yield: 78%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.67-7.63(t, *J* = 6 Hz, 1H), 7.55-7.49(t, *J* = 9 Hz, 2H), 7.21-7.08(m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.4, 162.1-158.8(d, *J* = 242.2 Hz, 1F), 146.9, 133.9, 130.3, 129.5, 128.8, 123.3-123.2(d, *J* = 8.2 Hz, 1F), 116.5-116.1(d, *J* = 24 Hz, 1F). **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}FO_2$: 217.0659; Found: 217.0655.

4-chlorophenyl benzoate (3j)



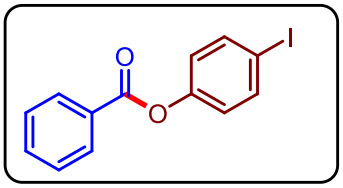
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2j** (32 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 46.9 mg, Yield: 81%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.67-7.63(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9Hz, 2H), 7.41-7.38(d, *J* = 9 Hz, 2H), 7.18-7.15(d, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.1, 149.6, 133.9, 131.4, 130.4, 129.7, 129.3, 128.8, 123.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}ClO_2$: 233.0364; Found: 233.0365.

4-bromophenyl benzoate (3k)



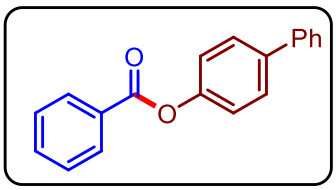
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2k** (43 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 52.9 mg, Yield: 77%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.68-7.63(t, *J* = 9 Hz, 1H), 7.56-7.49(m, 4H), 7.13-7.10(d, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.0, 150.1, 133.9, 132.7, 130.3, 129.3, 128.8, 123.7, 119.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}BrO_2$: 276.9859; Found: 276.9862.

4-iodophenyl benzoate (3l)



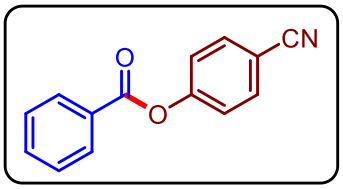
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2l** (55 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 62.1 mg, Yield: 77%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.75-7.72(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.01-6.98(d, *J* = 9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 151.0, 138.7, 133.9, 130.4, 129.4, 128.8, 124.1, 90.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}IO_2$: 324.9720; Found: 324.9724.

[1,1'-biphenyl]-4-yl benzoate (3m)



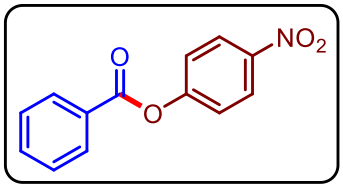
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2m** (42 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 57.5 mg, Yield: 84%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.25-8.22(d, *J* = 9 Hz, 2H), 7.66-7.59(m, 5H), 7.56-7.51(t, *J* = 9 Hz, 2H), 7.48-7.43(t, *J* = 9 Hz, 2H), 7.39-7.34(t, *J* = 9 Hz, 1H), 7.32-7.29(d, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.4, 150.5, 140.6, 139.2, 133.8, 130.4, 129.7, 129.0, 128.7, 128.4, 127.5, 127.3, 122.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{19}H_{15}O_2$: 275.1067; Found: 275.1075.

4-cyanophenyl benzoate (3a)



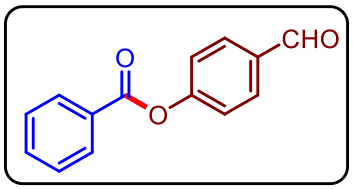
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 46.3 mg, Yield: 83% (88% GCMS). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.76-7.73(d, *J* = 9 Hz, 2H), 7.70-7.65(t, *J* = 9 Hz, 1H), 7.56-7.51(d, *J* = 9 Hz, 2H), 7.39-7.36(d, *J* = 9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 154.5, 134.3, 133.9, 130.5, 128.9, 123.1, 118.4, 110.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{10}NO_2$: 224.0706; Found: 224.0705.

4-nitrophenyl benzoate (3n)



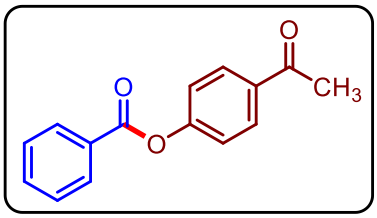
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2n** (35 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 43.1 mg, Yield: 71%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.35-8.32(d, *J* = 9 Hz, 2H), 8.22-8.19(d, *J* = 9 Hz, 2H), 7.71-7.66(t, *J* = 9 Hz, 1H), 7.57-7.52(t, *J* = 9 Hz, 2H), 7.44-7.41(d, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.4, 155.9, 145.6, 134.4, 130.5, 128.9, 128.7, 125.4, 122.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{10}NO_4$: 244.0604; Found: 244.0605.

4-formylphenyl benzoate (3o)



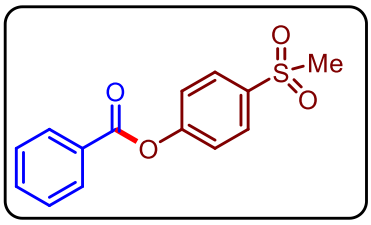
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2o** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 92:8), White solid, 40.6 mg, Yield: 72%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.03(s, 1H), 8.23-8.19(d, *J* = 9 Hz, 2H), 7.99-7.97(d, *J* = 6 Hz, 2H), 7.70-7.64(t, *J* = 9 Hz, 1H), 7.56-7.51(t, *J* = 9 Hz, 2H), 7.44-7.41(d, *J* = 9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.0, 164.6, 155.9, 134.3, 134.2, 131.4, 130.4, 129.1, 128.9, 122.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{11}O_3$: 227.0703; Found: 227.0701.

4-acetylphenyl benzoate (3p)



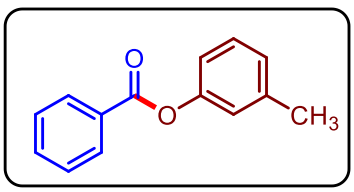
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2p** (34 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 92:8), White solid, 45.0 mg, Yield: 75%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 8.07-8.04(d, *J* = 9 Hz, 2H), 7.69-7.64(t, *J* = 9 Hz, 1H), 7.55-7.50(t, *J* = 9 Hz, 2H), 7.35-7.32(d, *J* = 9 Hz, 2H), 2.63(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.1, 164.8, 154.8, 135.0, 134.1, 130.4, 130.2, 129.2, 128.8, 122.1, 26.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{13}O_3$: 241.0859; Found: 241.0854.

4-(methylsulfonyl)phenyl benzoate (3q)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2q** (43 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 85:15), White solid, 53.8 mg, Yield: 78%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22-8.20(d, *J* = 8 Hz, 2H), 8.05-8.03(d, *J* = 8 Hz, 2H), 7.70-7.66(t, *J* = 8 Hz, 1H), 7.56-7.52(t, *J* = 8 Hz, 2H), 7.46-7.44(d, *J* = 8 Hz, 2H), 3.09(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.6, 155.2, 138.1, 134.3, 130.5, 129.4, 128.9, 123.0, 44.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_4S$: 277.0529; Found: 277.0524.

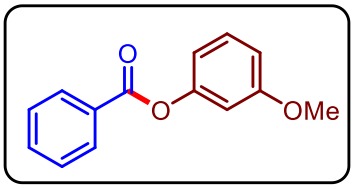
m-tolyl benzoate (3r)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2r** (27 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 42.9 mg, Yield: 81%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.19(d, *J* = 8 Hz, 2H), 7.65-7.62(t, *J* = 8 Hz, 1H), 7.53-7.49(t, *J* = 8 Hz, 2H), 7.33-7.29(t, *J* = 8 Hz, 1H), 7.10-7.08(d, *J* = 8 Hz, 1H), 7.04-7.01(m, 2H), 2.39(s, 3H). **^{13}C**

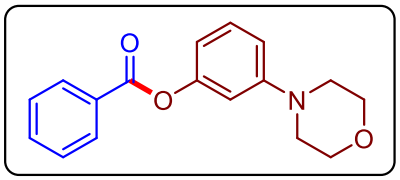
NMR (75 MHz, $CDCl_3$) δ 165.5, 151.1, 139.8, 133.7, 130.3, 129.8, 129.4, 128.7, 126.8, 122.5, 118.8, 21.5. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_2$: 213.0910; Found: 213.0913.

3-methoxyphenyl benzoate (3s)



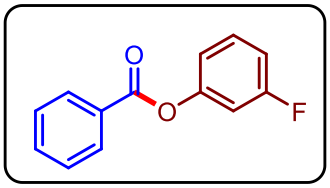
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2s** (31 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 92:8), White solid, 44.4 mg, Yield: 78%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H) 7.36-7.30(t, *J* = 9 Hz, 1H), 6.85-6.78(m, 3H), 3.82(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 160.7, 152.1, 133.7, 130.3, 130.0, 129.8, 128.7, 114.1, 112.0, 107.9, 55.6. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_3$: 229.0859; Found: 229.0860.

3-morpholinophenyl benzoate (3t)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2t** (45 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 85:15), White solid, 51.6 mg, Yield: 73%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 8 Hz, 2H), 7.66-7.61(t, *J* = 8 Hz, 1H), 7.54-7.48(t, *J* = 8 Hz, 2H), 7.34-7.29(t, *J* = 8 Hz, 1H), 6.84-6.80(d, *J* = 8 Hz, 1H), 6.75(s, 1H), 6.75-6.72(d, *J* = 8 Hz, 1H), 3.87-3.84(t, *J* = 8 Hz, 4H), 3.20-3.17(t, *J* = 8 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3, 152.6, 152.1, 133.7, 130.3, 130.0, 129.8, 128.7, 113.1, 113.0, 109.0, 66.9, 49.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{18}NO_3$: 284.1281; Found: 284.1288.

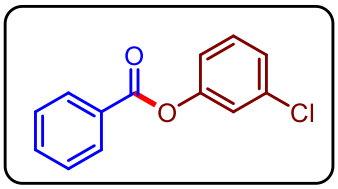
3-fluorophenyl benzoate (3u)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2u** (28 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 41.5 mg, Yield: 77%. **^{1}H NMR** (300

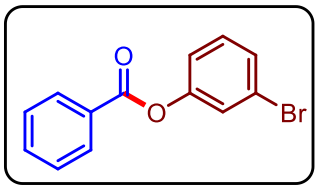
MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.68-7.63(t, *J* = 9 Hz, 1H), 7.55-7.50(t, *J* = 9 Hz, 2H), 7.43-7.35(m, 1H), 7.05-6.97(m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.9, 164.8-161.5 (d, *J* = 246 Hz, 1F), 152.0-151.9(d, *J* = 11.2 Hz, 1F), 134.0, 130.4-130.3(d, *J* = 9 Hz, 1F), 130.4, 128.8, 117.7, 113.2-113.0(d, *J* = 21 Hz, 1F), 110.2-109.9(d, *J* = 24 Hz, 1F). **HRMS (ESI):** m/z Calcd for $C_{13}H_{10}FO_2$ $[M+H]^+$: 217.0659; Found: 217.0657.

3-chlorophenyl benzoate (3v)



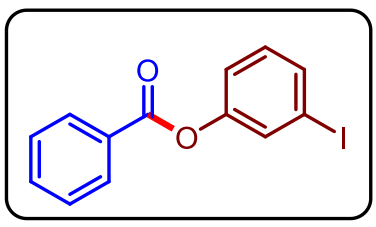
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2v** (32 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 45.8 mg, Yield: 79%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20-8.18(d, *J* = 8 Hz, 2H), 7.67-7.63(t, *J* = 8 Hz, 1H), 7.54-7.50(t, *J* = 8 Hz, 2H), 7.38-7.34(t, *J* = 8 Hz, 1H), 7.27-7.26(m, 2H), 7.15-7.13(d, *J* = 8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.9, 151.6, 134.9, 134.0, 130.4, 129.3, 128.8, 126.3, 122.6, 120.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}ClO_2$: 233.0364; Found: 233.0361.

3-bromophenyl benzoate (3w)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2w** (43 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 50.8 mg, Yield: 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20-8.18(d, *J* = 8 Hz, 2H), 7.67-7.64(t, *J* = 8 Hz, 1H), 7.54-7.50(t, *J* = 8 Hz, 2H), 7.43-7.41(m, 2H), 7.33-7.28(t, *J* = 8 Hz, 1H), 7.19-7.18(d, *J* = 4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 151.7, 134.0, 130.7, 130.4, 129.3, 128.8, 125.4, 122.6, 120.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}BrO_2$: 276.9859; Found: 276.9855.

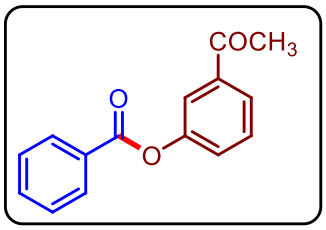
3-iodophenyl benzoate (3x)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2x** (55 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg,

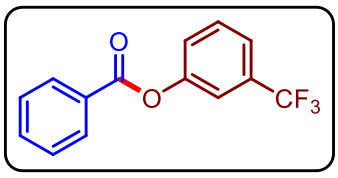
0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 57.3 mg, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19-8.17(d, *J* = 8 Hz, 2H), 7.67-7.63(t *J* = 8 Hz, 1H), 7.63-7.61(d, *J* = 8 Hz, 2H), 7.54-7.50(t, *J* = 8 Hz, 2H), 7.23-7.21(d, *J* = 8 Hz, 1H), 7.18-7.14(t, *J* = 8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.9, 151.4, 135.2, 134.0, 131.1, 130.9, 130.4, 129.2, 128.8, 121.5, 93.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}IO_2$: 324.9720; Found: 324.9723.

3-acetylphenyl benzoate (3y)



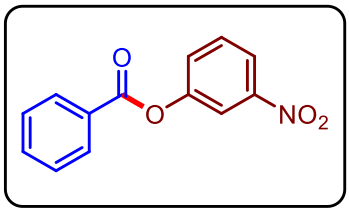
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2y** (34 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 92:8), White solid, 43.8 mg, Yield: 73%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22-8.21(d, *J* = 8 Hz, 2H), 7.88-7.87(d, *J* = 8 Hz, 1H), 7.81(s, 1H), 7.68-7.65(t, *J* = 8 Hz, 1H), 7.56-7.52(m, 3H), 7.45-7.44(d, *J* = 8 Hz, 1H), 2.62(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 165.1, 151.5, 139.0, 133.9, 130.4, 129.8, 129.5, 128.8, 126.6, 125.9, 121.8, 26.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{13}O_3$: 241.0859; Found: 241.0856.

3-(trifluoromethyl)phenyl benzoate (3z)



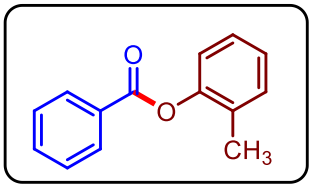
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2z** (41 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 44.5 mg, Yield: 67%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22-8.20(d, *J* = 8 Hz, 2H), 7.68-7.65(t, *J* = 8 Hz, 1H), 7.59-7.52(m, 5H), 7.45-7.44(m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.9, 151.2, 134.1, 132.9-131.6(q, *J* = 32.2 Hz, 3F), 130.4, 130.2, 129.1, 129.1-118.3(q, *J* = 271.5 Hz, 3F), 128.8, 125.5, 122.9-122.8(q, *J* = 3.7 Hz, 3F), 119.3-119.2(q, *J* = 3.7 Hz, 3F). **HRMS (ESI):** m/z Calcd for $C_{14}H_{10}F_3O_2$ $[M+H]^+$: 267.0627; Found: 267.0624.

3-nitrophenyl benzoate (3za)



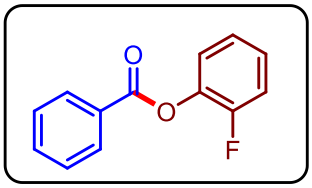
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2za** (35 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 40.1 mg, Yield: 66%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23-8.20(d, *J* = 9 Hz, 2H), 8.18-8.14(m, 2H), 7.71-7.66(t, *J* = 9 Hz, 1H), 7.63-7.59(m, 2H), 7.57-7.52(t, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.7, 151.4, 149.1, 134.4, 130.5, 130.3, 128.9, 128.7, 128.4, 121.0, 117.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}NO_4$: 244.0604; Found: 244.0600.

o-tolyl benzoate (3zb)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zb** (27 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 35.5 mg, Yield: 67%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.27-8.24(d, *J* = 9 Hz, 2H), 7.69-7.64(t, *J* = 9 Hz, 1H), 7.57-7.51(t, *J* = 9 Hz, 2H), 7.31-7.15(m, 4H), 2.26(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.0, 149.7, 133.7, 131.3, 130.4, 130.3, 129.6, 128.7, 127.1, 126.2, 122.1, 16.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_2$: 213.0910; Found: 213.0913.

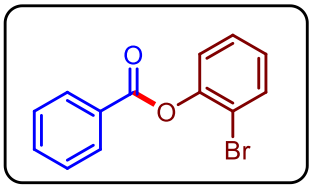
2-fluorophenyl benzoate (3zc)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zc** (28 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 31.3 mg, Yield: 58%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24-8.21(d, *J* = 9 Hz, 2H), 7.68-7.63(t, *J* = 9 Hz, 1H), 7.55-7.50(t, *J* = 9 Hz, 2H), 7.30-7.16(m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.3, 156.1-152.8(d, *J* = 248 Hz, 1F), 138.6-138.5(d, *J* = 12.7 Hz, 1F), 134.0, 130.5, 128.9, 128.8, 127.3-127.2(d, *J* = 7.5 Hz, 1F),

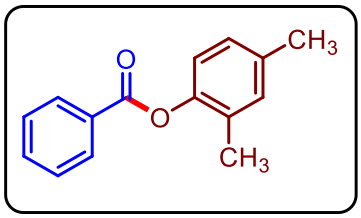
124.7-124.6(d, *J* = 3.7 Hz, 1F), 124.1, 117.1-116.8(d, *J* = 18 Hz, 1F). **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}FO_2$: 217.0659; Found: 217.0656.

2-bromophenyl benzoate (3zd)



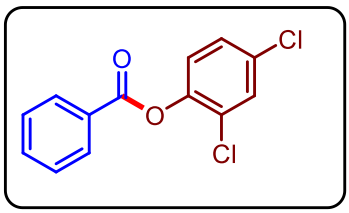
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zd** (43 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 44.7 mg, Yield: 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27-8.25(d, *J* = 8 Hz, 2H), 7.68-7.65(m, 2H), 7.55-7.52(t, *J* = 8 Hz, 2H), 7.41-7.37(t, *J* = 8 Hz, 1H), 7.30-7.28(d, *J* = 8 Hz, 1H), 7.19-7.16(t, *J* = 8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.4, 148.6, 134.0, 133.6, 130.6, 129.2, 128.8, 128.6, 127.5, 124.1, 116.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}BrO_2$: 276.9859; Found: 276.9855.

2,4-dimethylphenyl benzoate (3ze)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2ze** (31 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 47.5 mg, Yield: 84%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24-8.21(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.09-7.00(m, 3H), 2.34(s, 3H), 2.20(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 147.5, 135.8, 133.6, 131.9, 130.3, 130.0, 129.8, 128.7, 127.7, 121.8, 21.0, 16.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.

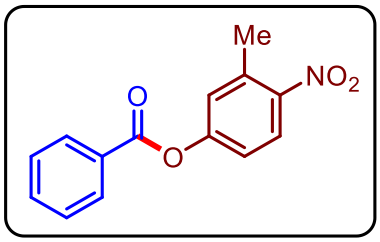
2,4-dichlorophenyl benzoate (3zf)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zf** (40 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 45.0 mg, Yield: 68%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24-8.21(d, *J* = 9 Hz, 2H), 7.70-7.65(t, *J* = 9

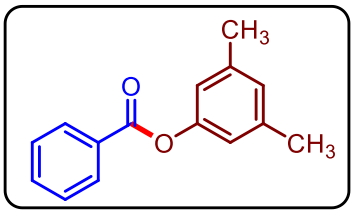
Hz, 1H), 7.56-7.50(m, 3H), 7.33-7.30(d, *J* = 9 Hz, 1H), 7.25-7.22(d, *J* = 9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 146.2, 134.2, 132.1, 130.6, 130.3, 128.9, 128.7, 128.2, 128.1, 124.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_9Cl_2O_2$: 266.9974; Found: 266.9977.

3-methyl-4-nitrophenyl benzoate (3zg)



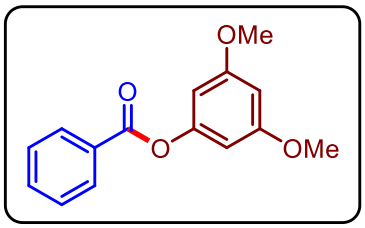
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zg** (38 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 39.8 mg, Yield: 62%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 8.13-8.10(d, *J* = 9 Hz, 1H), 7.70-7.65(t, *J* = 9 Hz, 1H), 7.56-7.51(t, *J* = 9 Hz, 2H), 7.24-7.21(m, 2H), 2.66(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.5, 154.1, 146.6, 136.3, 134.3, 130.4, 128.9, 128.8, 126.7, 125.9, 120.4, 21.0. **HRMS (ESI):** m/z Calcd for $C_{14}H_{12}NO_4$ $[M+H]^+$: 258.0761; Found: 258.0765.

3,5-dimethylphenyl benzoate (3zh)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zh** (31 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 48.0 mg, Yield: 85%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.53-7.48(t, *J* = 9 Hz, 2H), 6.91(s, 1H), 6.84(s, 2H), 2.35(s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.5, 151.0, 139.5, 133.6, 130.3, 129.9, 128.7, 127.8, 119.4, 21.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.

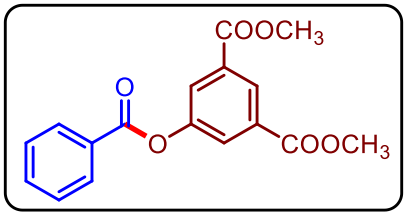
3,5-dimethoxyphenyl benzoate (3zi)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zi** (37 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by

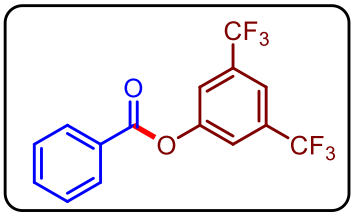
column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 56.1 mg, Yield: 87%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 6.41-6.38(m, 3H), 3.80(s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.2, 161.4, 152.7, 133.8, 130.3, 129.7, 128.7, 100.5, 98.6, 55.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_4$: 259.0965; Found: 259.0967.

dimethyl 5-(benzoyloxy)isophthalate (3zj)



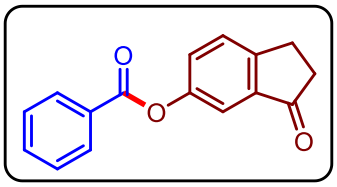
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zj** (52 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 54.1 mg, Yield: 69%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.62-8.61(t, *J* = 3 Hz, 1H), 8.22-8.19(d, *J* = 9 Hz, 2H), 8.10-8.09(d, *J* = 3 Hz, 2H), 7.69-7.64(t, *J* = 9 Hz, 1H), 7.56-7.51(t, *J* = 9 Hz, 2H), 3.96(s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.6, 164.9, 151.1, 134.2, 132.2, 130.4, 129.0, 128.9, 128.3, 127.5, 52.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{15}O_6$: 315.0863; Found: 315.0860.

3,5-bis(trifluoromethyl)phenyl benzoate (3zk)



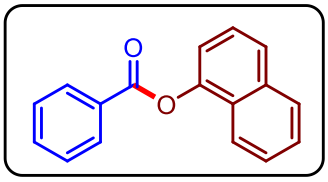
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zk** (57 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 54.2 mg, Yield: 65%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 7.81(s, 1H), 7.74(s, 2H), 7.72-7.67(t, *J* = 9 Hz, 1H), 7.58-7.53(t, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.5, 151.6, 134.5, 133.9-132.5(q, *J* = 34.5 Hz, 3F), 130.5, 129.0, 128.5, 128.4-117.5(q, *J* = 271.5 Hz, 3F), 122.9-122.8(q, *J* = 3 Hz, 3F), 120.0-119.8(sept, *J* = 3.7 Hz, 6F). **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_9F_6O_2$: 335.0501; Found: 335.0505.

3-oxo-2,3-dihydro-1H-inden-5-yl benzoate (3zn)



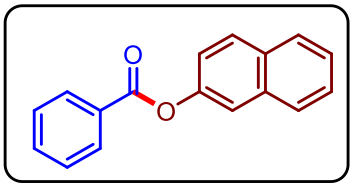
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zn** (37 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 49.7 mg, Yield: 79%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.19(d, *J* = 8 Hz, 2H), 7.67-7.63(d, *J* = 8 Hz, 1H), 7.58(s, 1H), 7.54-7.50(m, 3H), 7.45-7.43(d, *J* = 8 Hz, 1H), 3.18-3.15(m, 2H), 2.77-2.74(m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 206.1, 165.2, 152.5, 150.5, 138.5, 133.9, 130.3, 129.2, 128.8, 128.6, 127.7, 116.6, 37.0, 25.6. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{16}H_{13}O_3$: 253.0859; Found: 253.0856.

naphthalen-1-yl benzoate (3zl)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zl** (36 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 39.7 mg, Yield: 64%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42-8.39(d, *J* = 9 Hz, 2H), 8.03-8.00(m, 1H), 7.96-7.93(m, 1H), 7.85-7.82(d, *J* = 9 Hz, 1H), 7.74-7.69(t, *J* = 9 Hz, 1H), 7.63-7.54(m, 5H), 7.46-7.44(d, *J* = 6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3, 147.0, 134.8, 133.9, 130.4, 129.5, 128.8, 128.2, 127.1, 126.6, 126.2, 125.6, 121.4, 118.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{13}O_2$: 249.0910; Found: 249.0912.

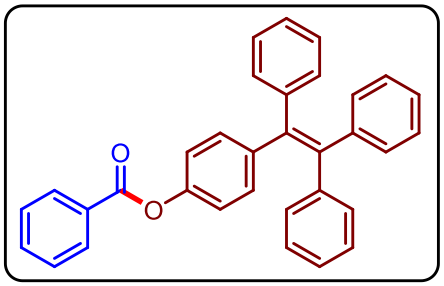
naphthalen-2-yl benzoate (3zm)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zm** (36 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 44.0 mg, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33-8.31(d, *J* = 8 Hz, 2H), 7.95-7.93(d, *J* = 8 Hz, 1H), 7.93-7.86(dd, *J* = 8 Hz, 8 Hz, 2H), 7.75(s, 1H), 7.70-7.66(t, *J* = 8 Hz, 1H), 7.58-7.52(m, 4H), 7.43-7.41(d, *J* = 8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.4, 148.7, 133.9, 133.7, 131.6, 130.3, 129.6, 129.5, 128.7,

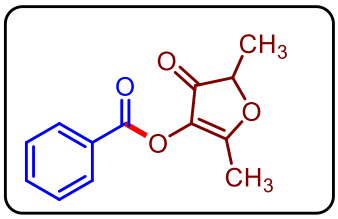
127.9, 127.7, 126.6, 125.8, 121.3, 118.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{13}O_2$: 249.0910; Found: 249.0915.

4-(1,2,2-triphenylvinyl)phenyl benzoate (3zo)



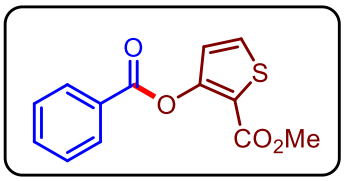
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zo** (87 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 98:2), White solid, 80.2 mg, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18-8.15(d, *J* = 8 Hz, 2H), 7.65-7.60(t, *J* = 8 Hz, 1H), 7.52-7.47(t, *J* = 8 Hz, 2H), 7.17-7.02(m, 17H), 6.99-6.96(d, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.2, 149.5, 143.8, 143.7, 143.6, 141.5, 140.2, 133.7, 132.5, 131.5, 131.47, 131.4, 130.3, 129.8, 129.2, 128.7, 128.0, 127.9, 127.8, 126.74, 126.69, 126.6, 121.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{33}H_{25}O_2$: 453.1849; Found: 453.1847.

2,5-dimethyl-4-oxo-4,5-dihydrofuran-3-yl benzoate (3zp)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zp** (32 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 93:7), White solid, 41.1 mg, Yield: 71%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14-8.11(d, *J* = 9 Hz, 2H), 7.63-7.58(t, *J* = 9 Hz, 1H), 7.49-7.44(d, *J* = 9 Hz, 2H), 4.66-4.59(q, *J* = 9 Hz, 1H), 2.21(s, 3H), 1.54-1.52(d, *J* = 6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 195.8, 180.4, 163.5, 134.0, 130.5, 129.2, 128.7, 128.2, 81.6, 16.5, 14.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{13}O_4$: 233.0808; Found: 233.0806.

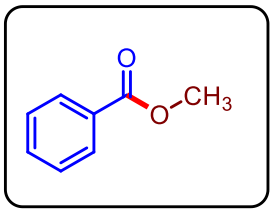
methyl 3-(benzoyloxy)thiophene-2-carboxylate (3zq)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zq** (39 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column

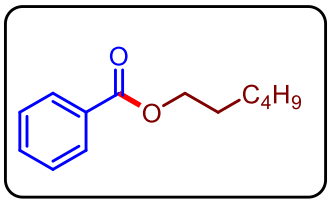
chromatography (Hexane/Ethyl acetate, 92:8), White solid, 44.5 mg, Yield: 68%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.25-8.22(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.55-7.50(m, 3H), 7.12-7.10(d, *J* = 6 Hz, 1H), 3.80(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.2, 161.2, 151.2, 133.9, 130.5, 130.0, 129.1, 128.8, 123.8, 118.8, 52.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{11}O_4S$: 263.0373; Found: 263.0371.

methyl benzoate (3zr)



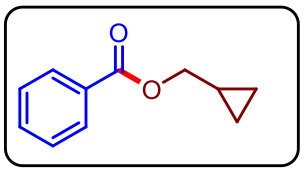
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zr** (8 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), White solid, 7.8 mg, Yield: 23%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05-8.03(d, *J* = 8 Hz, 2H), 7.57-7.53(t, *J* = 8 Hz, 1H), 7.45-7.41(t, *J* = 8 Hz, 2H), 3.91(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.2, 133.0, 130.2, 129.7, 128.5, 52.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_8H_9O_2$: 137.0597; Found: 137.0598.

hexyl benzoate (3zs)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zs** (25 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), White solid, 11.3 mg, Yield: 22%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06-8.03(d, *J* = 9 Hz, 2H), 7.57-7.52(t, *J* = 9 Hz, 1H), 7.45-7.40(t, *J* = 9 Hz, 2H), 4.34-4.29(t, *J* = 9 Hz, 2H), 1.81-1.72(quin, *J* = 9 Hz, 2H), 1.49-1.40(m, 2H), 1.37-1.31(m, 4H), 0.93-0.88(t, *J* = 9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.8, 132.9, 130.6, 129.6, 128.4, 65.2, 31.6, 28.8, 25.8, 22.7, 14.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{19}O_2$: 207.1380; Found: 207.1382.

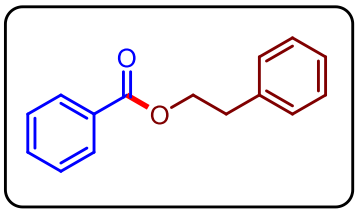
cyclopropylmethyl benzoate (3zt)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zt** (18 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in

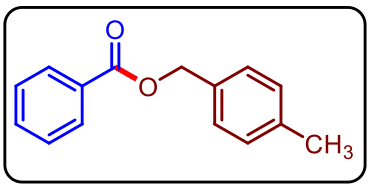
DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), White solid, 13.6 mg, Yield: 31%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06(d, *J* = 8 Hz, 2H), 7.57-7.53(t, *J* = 8 Hz, 1H), 7.46-7.42(t, *J* = 8 Hz, 2H), 4.17-4.15(d, *J* = 8 Hz, 2H), 1.30-1.23(m, 1H), 0.64-0.59(q, *J* = 8 Hz, 2H), 0.39-0.35(q, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.9, 132.9, 130.7, 129.7, 128.4, 69.8, 10.0, 3.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{11}H_{13}O_2$: 177.0910; Found: 177.0911.

phenethyl benzoate (3zu)



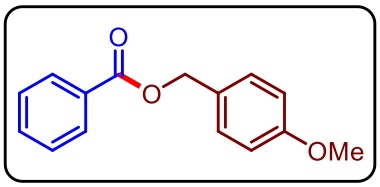
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zu** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 15.2 mg, Yield: 27%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06-8.03(d, *J* = 9 Hz, 2H), 7.59-7.54(t, *J* = 9 Hz, 1H), 7.47-7.42(t, *J* = 9 Hz, 2H), 7.37-7.24(m, 5H), 4.58-4.54(t, *J* = 9 Hz, 2H), 3.13-3.08(t, *J* = 9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.6, 138.0, 133.0, 130.4, 129.7, 129.1, 128.7, 128.5, 126.7, 65.6, 35.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1069.

4-methylbenzyl benzoate (3zv)



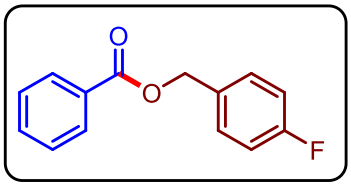
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zv** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 96:4), White solid, 19.7 mg, Yield: 35%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12-8.09(d, *J* = 9 Hz, 2H), 7.59-7.54(t, *J* = 9 Hz, 1H), 7.47-7.42(t, *J* = 9 Hz, 2H), 7.40-7.37(d, *J* = 9 Hz, 2H), 7.24-7.21(d, *J* = 9 Hz, 2H), 5.36(s, 2H), 2.39(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.5, 138.2, 133.2, 133.0, 130.3, 129.8, 129.4, 128.44, 128.42, 66.7, 21.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.

4-methoxybenzyl benzoate (3zw)



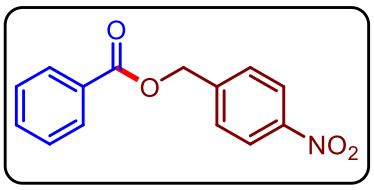
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zw** (34 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 95:5), White solid, 19.3 mg, Yield: 32%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08-8.05(d, *J* = 9 Hz, 2H), 7.57-7.53(d, *J* = 9 Hz, 1H), 7.45-7.40(t, *J* = 9 Hz, 2H), 7.41-7.38(d, *J* = 9 Hz, 2H), 6.94-6.91(d, *J* = 9 Hz, 2H), 5.31(s, 2H), 3.82(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.7, 159.8, 133.1, 130.4, 130.2, 129.8, 128.5, 128.3, 114.1, 66.7, 55.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_3$: 243.1016; Found: 243.1012.

4-fluorobenzyl benzoate (3zx)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zx** (32 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 96:4), White solid, 23.6 mg, Yield: 41%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08-8.05(d, *J* = 9 Hz, 2H), 7.58-7.53(t, *J* = 9 Hz, 1H), 7.46-7.41(m, 4H), 7.10-7.04(t, *J* = 9 Hz, 2H), 5.33(s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.5, 164.4-161.2(d, *J* = 245.2 Hz, 1F), 133.2, 132.1-132.0(d, *J* = 3.7 Hz, 1F), 130.4-130.3(d, *J* = 8.2 Hz, 1F), 130.2, 129.8, 128.5, 115.8-115.5(d, *J* = 21.7 Hz, 1F), 66.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{12}FO_2$: 231.0816; Found: 231.0814.

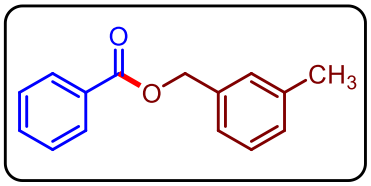
4-nitrobenzyl benzoate (3zy)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zy** (38 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 42.4 mg, Yield: 66%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.27-8.24(d, *J* = 9 Hz, 2H), 8.10-8.07(d, *J* = 9 Hz, 2H), 7.63-7.60(d, *J* = 9 Hz, 2H), 7.63-7.58(t, *J* = 9 Hz, 1H), 7.50-7.45(t, *J* = 9 Hz, 2H), 5.46(s, 2H). **^{13}C NMR** (75

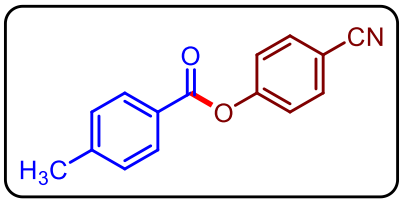
MHz, $CDCl_3$) δ 166.2, 147.8, 143.5, 133.5, 129.8, 129.6, 128.6, 128.4, 123.9, 65.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{12}NO_4$: 258.0761; Found: 258.0766.

3-methylbenzyl benzoate (3zz)



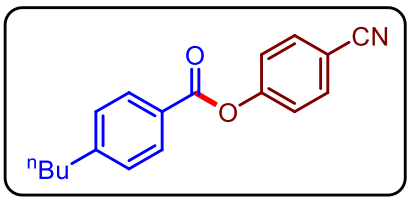
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **2zz** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 19.6 mg, Yield: 35%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19-8.17(d, *J* = 8 Hz, 2H), 7.63-7.59(t, *J* = 8 Hz, 1H), 7.51-7.47(t, *J* = 8 Hz, 2H), 7.38-7.35(m, 3H), 7.24-7.22(d, *J* = 8 Hz, 1H), 5.42(s, 2H), 2.45(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.4, 138.2, 136.0, 133.0, 130.2, 129.7, 129.0, 128.9, 128.5, 128.3, 125.3, 66.7, 21.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_2$: 227.1067; Found: 227.1064.

4-cyanophenyl 4-methylbenzoate (3zza)



Following General Procedure 2.2.3 using **1b** (50 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 37.4 mg, Yield: 63%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09-8.06(d, *J* = 9 Hz, 2H), 7.75-7.72(d, *J* = 9 Hz, 2H), 7.38-7.35(d, *J* = 9 Hz, 2H), 7.34-7.31(d, *J* = 9 Hz, 2H), 2.47(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.4, 154.4, 145.3, 133.8, 130.4, 129.6, 129.3, 125.9, 123.0, 109.7, 21.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{12}NO_2$: 238.0863; Found: 238.0869.

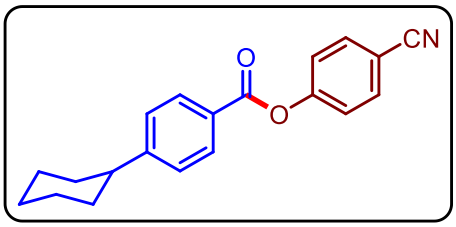
4-cyanophenyl 4-butylbenzoate (3zzb)



Following General Procedure 2.2.3 using **1c** (62.0 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 40.6 mg, Yield: 58%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.11-8.08(d, *J* = 9 Hz, 2H), 7.75-7.72(d, *J* = 9 Hz, 2H),

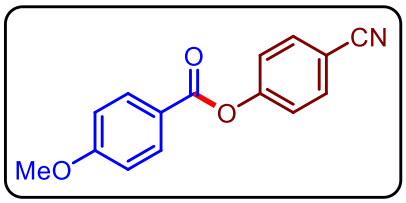
7.37-7.34(d, *J* = 9 Hz, 2H), 7.34-7.32(d, *J* = 6 Hz, 2H), 2.74-2.69(t, *J* = 9 Hz, 2H), 1.70-1.59(m, 2H), 1.44-1.32(sext, *J* = 9 Hz, 2H), 0.97-0.92(t, *J* = 9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.5, 154.5, 150.3, 133.9, 130.5, 129.0, 126.2, 123.1, 109.8, 36.0, 33.4, 22.5, 14.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{18}H_{18}NO_2$: 280.1332; Found: 280.1336.

4-cyanophenyl 4-cyclohexylbenzoate (3zzc)



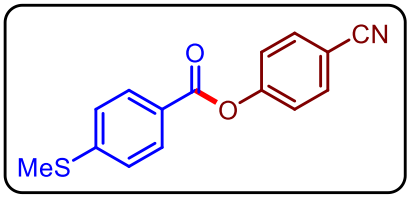
Following General Procedure 2.2.3 using **1d** (70 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 61.2 mg, Yield: 80%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12-8.09(d, *J* = 9 Hz, 2H), 7.75-7.72(d, *J* = 9 Hz, 2H), 7.37-7.35(d, *J* = 9 Hz, 2H), 7.37-7.34(d, *J* = 9 Hz, 2H), 2.64-2.56(m, 1H), 1.89-1.76(m, 5H), 1.48-1.25(m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.5, 155.2, 154.5, 133.8, 130.6, 127.4, 126.3, 123.1, 118.5, 109.8, 45.0, 34.2, 26.8, 26.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{20}H_{20}NO_2$: 306.1489; Found: 306.1488.

4-cyanophenyl 4-methoxybenzoate (3zzd)



Following General Procedure 2.2.3 using **1e** (54 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 85:15), White solid, 41.2 mg, Yield: 65%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14-8.11(d, *J* = 9 Hz, 2H), 7.73-7.70(d, *J* = 9 Hz, 2H), 7.36-7.33(d, *J* = 9 Hz, 2H), 7.00-6.97(d, *J* = 9 Hz, 2H), 3.89(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.4, 164.1, 154.5, 133.7, 132.6, 123.1, 120.9, 118.4, 114.1, 109.6, 55.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{12}NO_3$: 254.0812; Found: 254.0810.

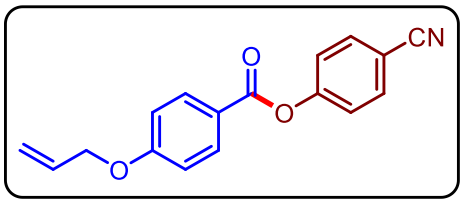
4-cyanophenyl 4-(methylthio)benzoate (3zze)



Following General Procedure 2.2.3 using **1f** (58.8 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$

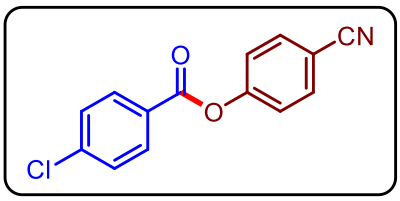
(25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 85:15), White solid, 38.4 mg, Yield: 57%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06(d, *J* = 8 Hz, 2H), 7.75-7.73(d, *J* = 8 Hz, 2H), 7.37-7.35(d, *J* = 8 Hz, 2H), 7.33-7.31(d, *J* = 8 Hz, 2H), 2.55(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.2, 154.4, 147.7, 133.8, 130.7, 125.2, 124.6, 123.1, 118.4, 109.9, 14.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{12}NO_2S$: 270.0583; Found: 270.0588.

4-cyanophenyl 4-(allyloxy)benzoate (3zzf)



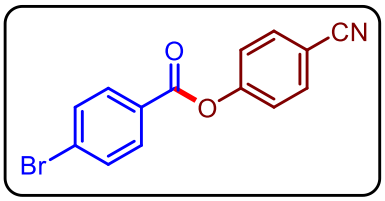
Following General Procedure 2.2.3 using **1g** (61.8 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 85:15), White solid, 47.0 mg, Yield: 67%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.15-8.12(d, *J* = 9 Hz, 2H), 7.75-7.72(d, *J* = 9 Hz, 2H), 7.37-7.34(d, *J* = 9 Hz, 2H), 7.03-7.00(d, *J* = 9 Hz, 2H), 6.13-6.01(m, 1H), 5.48-5.42(m, 1H), 5.37-5.33(m, 1H), 4.65-4.63(m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 163.5, 154.6, 133.8, 132.6, 132.4, 123.1, 121.1, 118.5, 118.5, 114.9, 109.8, 69.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{14}NO_3$: 280.0968; Found: 280.0966.

4-cyanophenyl 4-chlorobenzoate (3zzg)



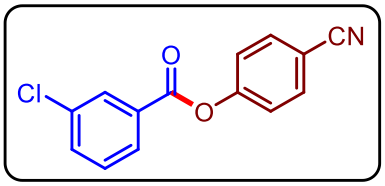
Following General Procedure 2.2.3 using **1h** (55 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 47.7 mg, Yield: 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14-8.12(d, *J* = 8 Hz, 2H), 7.76-7.74(d, *J* = 8 Hz, 2H), 7.52-7.50(d, *J* = 8 Hz, 2H), 7.38-7.35(d, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.7, 154.2, 141.0, 133.9, 131.8, 129.3, 127.3, 123.0, 118.3, 110.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_9ClNO_2$: 258.0316; Found: 258.0312.

4-cyanophenyl 4-bromobenzoate (3zzh)



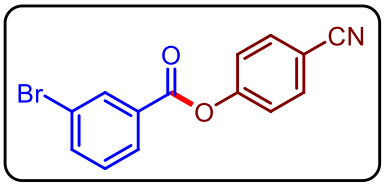
Following General Procedure 2.2.3 using **1i** (68 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 43.6 mg, Yield: 58%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06-8.03(d, *J* = 8 Hz, 2H), 7.76-7.74(d, *J* = 8 Hz, 2H), 7.69-7.67(d, *J* = 8 Hz, 2H), 7.37-7.35(d, *J* = 8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.8, 154.1, 133.9, 132.3, 131.9, 129.7, 127.7, 123.0, 118.3, 110.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_9BrNO_2$: 301.9811; Found: 301.9815.

4-cyanophenyl 3-chlorobenzoate (3zzi)



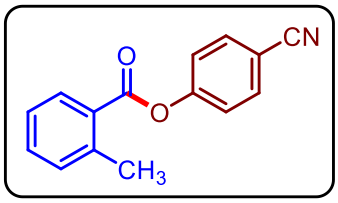
Following General Procedure 2.2.3 using **1j** (55 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 45.8 mg, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17(s, 1H), 8.09-8.07(d, *J* = 8 Hz, 1H), 7.77-7.75(d, *J* = 8 Hz, 2H), 7.66-7.64(d, *J* = 8 Hz, 1H), 7.51-7.47(t, *J* = 8 Hz, 1H), 7.38-7.36(d, *J* = 8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.3, 154.1, 135.1, 134.3, 134.0, 130.5, 130.4, 130.2, 128.6, 123.0, 118.3, 110.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_9ClNO_2$: 258.0316; Found: 258.0312.

4-cyanophenyl 3-bromobenzoate (3zzj)



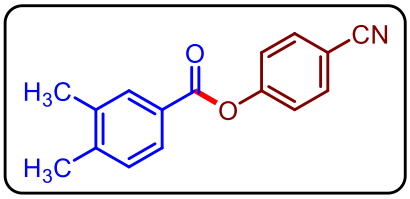
Following General Procedure 2.2.3 using **1k** (68 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 43.6 mg, Yield: 58%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33(s, 1H), 8.13-8.11(d, *J* = 8 Hz, 1H), 7.81-7.79(d, *J* = 8 Hz, 1H), 7.77-7.75(d, *J* = 8 Hz, 2H), 7.44-7.40(t, *J* = 8 Hz, 1H), 7.38-7.36(d, *J* = 8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.2, 154.1, 137.3, 134.0, 133.4, 130.7, 130.5, 129.0, 123.0, 118.3, 110.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_9BrNO_2$: 301.9811; Found: 301.9812.

4-cyanophenyl 2-methylbenzoate (3zzk)



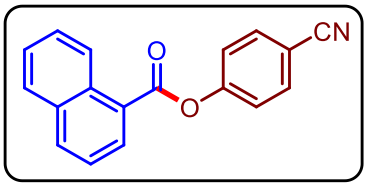
Following General Procedure 2.2.3 using **1l** (49.2 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 37.4 mg, Yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17-8.15(d, *J* = 8 Hz, 1H), 7.76-7.74(d, *J* = 8 Hz, 2H), 7.53-7.50(t, *J* = 8 Hz, 1H), 7.37-7.33(m, 4H), 2.67(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.9, 154.4, 142.0, 133.9, 133.5, 132.3, 131.4, 127.6, 126.2, 123.2, 118.5, 109.9, 22.1. **HRMS (ESI):** m/z Calcd for $C_{15}H_{12}NO_2$ $[M+H]^+$: 238.0863; Found: 238.0869.

4-cyanophenyl 3,4-dimethylbenzoate (3zzl)



Following General Procedure 2.2.3 using **1m** (53.4 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 88:12), White solid, 54 mg, Yield: 86%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94(s, 1H), 7.92-7.90(d, *J* = 8 Hz, 1H), 7.75-7.72(d, *J* = 8 Hz, 2H), 7.37-7.35(d, *J* = 8 Hz, 2H), 7.29-7.27(d, *J* = 8 Hz, 1H), 2.37(s, 3H), 2.35(s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.7, 154.6, 144.0, 137.4, 133.8, 131.4, 130.2, 128.1, 126.3, 123.1, 118.5, 109.8, 20.3, 19.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{16}H_{14}NO_2$: 252.1019; Found: 252.1014.

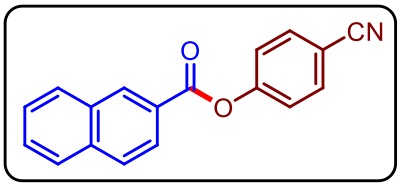
4-cyanophenyl 1-naphthoate (3zzm)



Following General Procedure 2.2.3 using **1n** (60 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 52.7 mg, Yield: 77%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01-8.99(d, *J* = 8 Hz, 1H), 8.49-8.48(d, *J* = 4 Hz, 1H), 8.16-8.14(d, *J* = 8 Hz, 1H), 7.96-7.94(d, *J* = 8 Hz, 1H), 7.79-7.77(d, *J* = 8 Hz, 2H), 7.69-7.65(t, *J* = 8 Hz, 1H), 7.61-7.57(t, *J* = 8 Hz, 2H), 7.45-7.43(d, *J* = 8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.9,

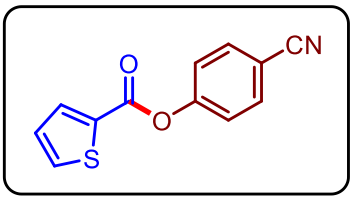
154.5, 135.2, 134.1, 133.9, 131.9, 131.8, 129.0, 128.7, 126.8, 125.6, 124.8, 124.6, 123.3, 118.5, 110.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{18}H_{12}NO_2$: 274.0863; Found: 274.0861.

4-cyanophenyl 2-naphthoate (3zzn)



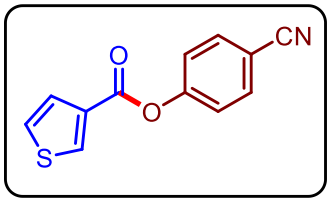
Following General Procedure 2.2.3 using **1o** (60 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 88:12), White solid, 43.8 mg, Yield: 64%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78(s, 1H), 8.18-8.16(d, *J* = 8 Hz, 1H), 8.02-8.00(d, *J* = 8 Hz, 1H), 7.98-7.96(d, *J* = 8 Hz, 1H), 7.95-7.93(d, *J* = 8 Hz, 1H), 7.79-7.76(d, *J* = 8 Hz, 2H), 7.68-7.65(t, *J* = 8 Hz, 1H), 7.62-7.59(t, *J* = 8 Hz, 1H), 7.44-7.42(d, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.7, 154.5, 136.2, 133.9, 132.6, 132.5, 129.7, 129.2, 128.8, 128.1, 127.2, 126.0, 125.4, 123.1, 118.5, 110.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{18}H_{12}NO_2$: 274.0863; Found: 274.0866.

4-cyanophenyl thiophene-2-carboxylate (3zzo)



Following General Procedure 2.2.3 using **1p** (46.5 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 41.4 mg, Yield: 72%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34-8.33(d, *J* = 1.8 Hz, 1H), 7.75-7.73(d, *J* = 8 Hz, 2H), 7.66-7.65(d, *J* = 4 Hz, 1H), 7.42-7.40(dd, *J* = 4 Hz, 1.8 Hz, 1H), 7.37-7.34(d, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 154.0, 135.6, 134.5, 133.9, 131.9, 128.4, 123.0, 118.4, 110.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_8NO_2S$: 230.0270; Found: 230.0274.

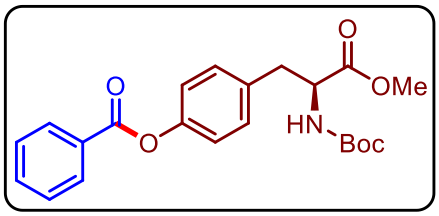
4-cyanophenyl thiophene-3-carboxylate (3zzp)



Following General Procedure 2.2.3 using **1q** (46.5 mg, 0.3 mmol, 1.2 equiv), **2a** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 43.7 mg, Yield: 76%. **^{1}H NMR**

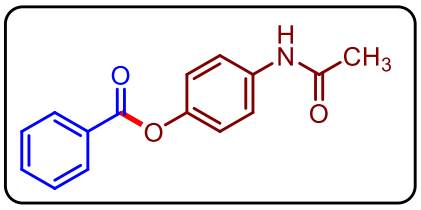
(400 MHz, $CDCl_3$) δ 8.34-8.33(d, *J* = 4 Hz, 1H), 7.75-7.73(d, *J* = 8 Hz, 2H), 7.66-7.65(d, *J* = 4 Hz, 1H), 7.42-7.40(m, 1H), 7.37-7.34(d, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 154.1, 135.0, 133.9, 132.0, 128.3, 126.9, 123.0, 118.4, 109.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_8NO_2S$: 230.0270; Found: 230.0272.

(S)-4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl benzoate (5a)



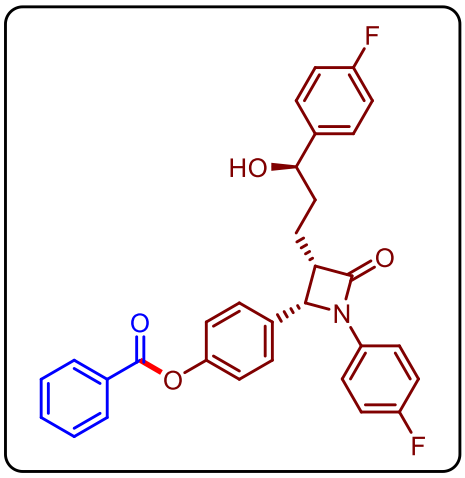
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4a** (73.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), $(dtbbpy)PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 56 mg, Yield: 56%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.21-7.11(m, 4H), 5.03-5.00(d, *J* = 9 Hz, 1H), 4.61-4.59(d, *J* = 9 Hz, 1H), 3.73(s, 3H), 3.13-3.09(t, *J* = 9 Hz, 1H), 1.43(s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4, 165.3, 155.2, 150.2, 133.9, 133.8, 130.5, 130.3, 129.7, 128.7, 121.9, 80.2, 54.6, 52.4, 37.9, 28.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{22}H_{26}NO_6$: 400.1755; Found: 400.1753.

4-acetamidophenyl benzoate (5b)



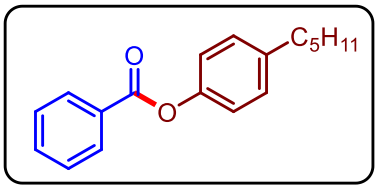
Following General Procedure 2.2.3 using **1a** (37.5 mg, 0.3 mmol, 1.2 equiv), **4b** (25 mg, 0.3 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), $(dtbbpy)PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 47.3 mg, Yield: 74%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.56-7.49(m, 4H), 7.37(br, 1H), 7.18-7.15(d, *J* = 9 Hz, 2H), 2.18(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 165.5, 147.3, 135.8, 133.8, 130.3, 129.6, 128.7, 122.3, 121.1, 24.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{14}NO_3$: 256.0968; Found: 256.0966.

4-((2S,3S)-1-(4-fluorophenyl)-3-((R)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-oxoazetidin-2-yl)phenyl benzoate (5c)



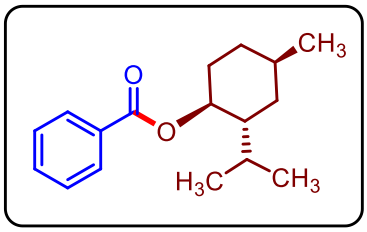
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4c** (102 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 60.4 mg, Yield: 47%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.67-7.62(t, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.40-7.37(d, *J* = 9 Hz, 2H), 7.32-7.22(m, 6H), 7.05-6.91(m, 4H), 4.74-4.70(t, *J* = 8 Hz, 1H), 4.67-4.66(d, *J* = 3 Hz, 1H), 3.14-3.09(m, 1H), 2.00-1.89(m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.6, 165.2, 164.0-160.7(d, *J* = 243.7 Hz, 1F), 160.8-157.6(d, *J* = 242.2 Hz, 1F), 151.2, 140.2-140.1(d, *J* = 3 Hz, 1F), 135.2, 134.0, 133.9, 130.3, 129.3, 128.8, 127.6, 127.5, 127.1, 122.8, 118.6-118.5(d, *J* = 7.5 Hz, 1F), 116.2-115.9(d, *J* = 23.2 Hz, 1F), 115.6-115.4(d, *J* = 21.9 Hz, 1F), 73.2, 61.0, 60.5, 36.7, 25.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{31}H_{26}F_2NO_4$: 514.1824; Found: 514.1827.

4-pentylphenyl benzoate (5d)



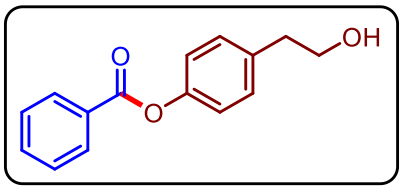
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4d** (41 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 97:3), White solid, 53.1 mg, Yield: 79%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.54-7.49(d, *J* = 9 Hz, 2H), 7.24-7.22(d, *J* = 6 Hz, 2H), 7.13-7.10(d, *J* = 9 Hz, 2H), 2.65-2.60(d, *J* = 9 Hz, 2H), 1.68-1.58(quin, *J* = 6 Hz, 2H), 1.36-1.31(m, 4H), 0.93-0.88(t, *J* = 9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.5, 149.0, 140.7, 133.6, 130.3, 129.9, 129.5, 128.7, 121.5, 35.5, 31.6, 31.3, 22.7, 14.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{18}H_{21}O_2$: 269.1536; Found: 269.1533.

(1S,2R,4R)-2-isopropyl-4-methylcyclohexyl benzoate (5e)



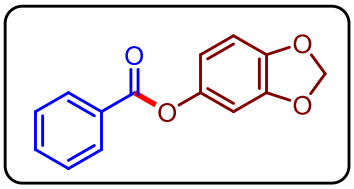
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4e** (39 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), White solid, 21 mg, Yield: 32%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06-8.04(d, *J* = 8 Hz, 2H), 7.57-7.52(t, *J* = 8 Hz, 1H), 7.46-7.41(t, *J* = 8 Hz, 2H), 4.98-4.89(td, *J* = 9 Hz, 3 Hz, 1H), 2.17-2.11(m, 1H), 2.03-1.92(m, 1H), 1.76-1.71(m, 2H), 1.61-1.51(m, 2H), 1.20-0.99(m, 3H), 0.94-0.91(m, 6H), 0.81-0.78(d, *J* = 9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.3, 132.8, 131.0, 129.7, 128.4, 75.0, 47.4, 41.1, 34.5, 31.6, 26.6, 23.8, 22.2, 20.9, 16.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{17}H_{25}O_2$: 261.1849; Found: 261.1848.

4-(2-hydroxyethyl)phenyl benzoate (5f)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4f** (34 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 46.7 mg, Yield: 77%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22-8.19(d, *J* = 9 Hz, 2H), 7.67-7.62(d, *J* = 9 Hz, 1H), 7.54-7.49(t, *J* = 9 Hz, 2H), 7.31-7.28(d, *J* = 9 Hz, 2H), 7.18-7.15(d, *J* = 9 Hz, 2H), 3.91-3.87(t, *J* = 6 Hz, 2H), 2.92-2.88(t, *J* = 6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 149.8, 136.4, 133.7, 130.3, 130.2, 129.8, 128.7, 128.6, 121.9, 63.8, 38.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{15}O_3$: 243.1016; Found: 243.1019.

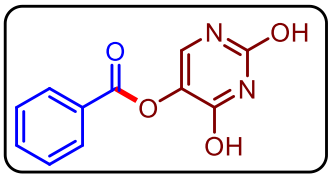
benzo[d][1,3]dioxol-5-yl benzoate (5g)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4g** (34.2 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 49.8 mg, Yield: 82%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19-8.16(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.53-7.48(t, *J* = 9

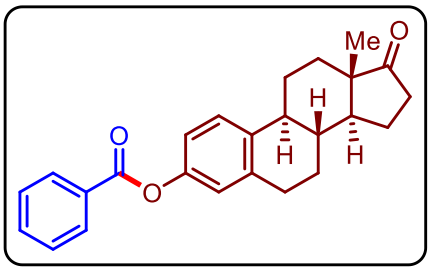
Hz, 2H), 6.84-6.81(d, *J* = 9 Hz, 1H), 6.74-6.73(d, *J* = 3 Hz, 1H), 6.67-6.64(d, *J* = 9 Hz, 1H), 6.01(s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.6, 148.2, 145.6, 145.4, 133.7, 130.3, 129.6, 128.7, 114.2, 108.2, 104.1, 101.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{11}O_4$: 243.0652; Found: 243.0656.

2,4-dihydroxypyrimidin-5-yl benzoate (5h)



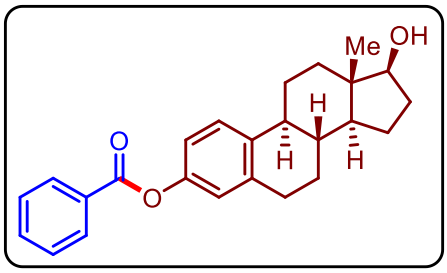
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4h** (31.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 45.4 mg, Yield: 78%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.53(s, 1H), 10.99(s, 1H), 8.07-8.05(d, *J* = 8 Hz, 2H), 7.75-7.73(m, 2H), 7.62-7.58(t, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 164.0, 159.3, 150.6, 134.3, 133.7, 129.8, 129.0, 128.1, 126.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{11}H_9N_2O_4$: 233.0557; Found: 233.0552.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl benzoate (5i)



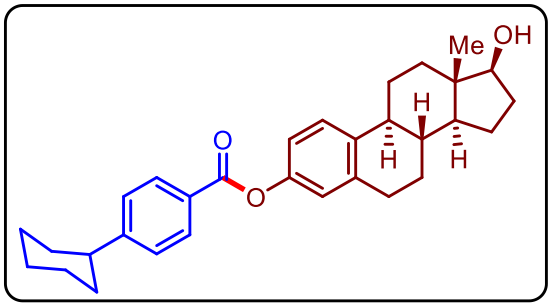
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4i** (67.3 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 70:30), White solid, 57.1 mg, Yield: 61%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21-8.18(d, *J* = 9 Hz, 2H), 7.66-7.61(t, *J* = 9 Hz, 1H), 7.53-7.48(t, *J* = 9 Hz, 2H), 7.35-7.32(d, *J* = 9 Hz, 1H), 7.00-6.97(d, *J* = 9 Hz, 1H), 6.95(s, 1H), 2.96-2.92(m, 2H), 2.56-2.47(q, *J* = 9 Hz, 1H), 2.46-2.41(m, 1H), 2.36-2.28(m, 1H), 2.21-2.12(m, 1H), 2.10-1.96(m, 3H), 1.61-1.40(m, 6H), 0.93(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 221.0, 165.6, 149.0, 138.2, 137.6, 133.7, 130.3, 129.8, 128.7, 126.6, 121.9, 119.0, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.5, 25.9, 21.7, 14.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{25}H_{27}O_3$: 375.1955; Found: 375.1994.

(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl benzoate (5j)



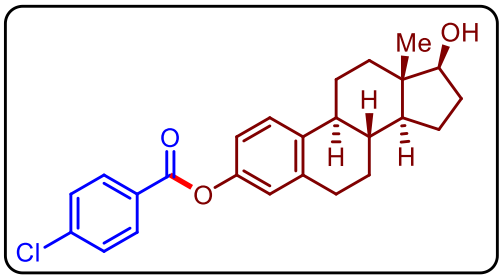
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 54.6 mg, Yield: 58%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.17(d, *J* = 9 Hz, 2H), 7.65-7.60(t, *J* = 9 Hz, 1H), 7.52-7.47(t, *J* = 9 Hz, 2H), 7.35-7.32(d, *J* = 9 Hz, 1H), 6.98-6.95(d, *J* = 9 Hz, 1H), 6.93(s, 1H), 3.77-3.71(t, *J* = 9 Hz, 1H), 2.90-2.87(m, 2H), 2.38-2.19(m, 2H), 2.17-2.07(m, 1H), 2.00-1.86(m, 2H), 1.75-1.58(m, 1H), 1.54-1.16(m, 7H), 0.79(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 148.9, 138.5, 138.2, 133.6, 130.3, 129.9, 128.7, 126.6, 121.8, 118.8, 82.1, 50.3, 44.3, 43.4, 38.7, 36.9, 30.8, 29.7, 27.2, 26.4, 23.3, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{25}H_{29}O_3$: 377.2111; Found: 377.2115.

(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-cyclohexylbenzoate (5k)



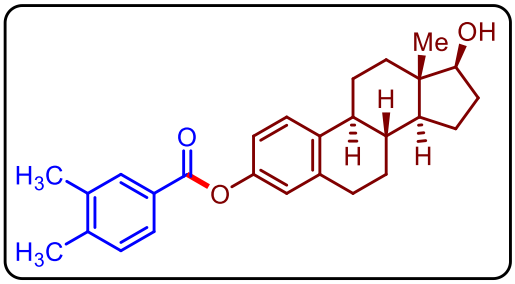
Following General Procedure 2.4.1 using **1d** (70 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), cat-**1** (5.6 mg, 2 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 66.5 mg, Yield: 58%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12-8.09(d, *J* = 9 Hz, 2H), 7.34-7.32(m, 3H), 6.96-6.94(d, *J* = 9 Hz, 1H), 6.91(s, 1H), 3.77-3.72(t, *J* = 8 Hz, 1H), 2.89-2.87(m, 2H), 2.62-2.56(m, 1H), 2.37-2.08(m, 3H), 2.00-1.76(m, 7H), 1.76-1.56(m, 1H), 1.53-1.20(m, 7H), 0.79(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 154.3, 148.9, 138.4, 138.1, 130.4, 127.2, 126.6, 121.8, 118.9, 82.1, 50.2, 44.9, 44.3, 43.4, 38.7, 36.8, 34.3, 30.8, 29.7, 27.2, 26.9, 26.3, 26.2, 23.3, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{31}H_{39}O_3$: 459.2894; Found: 459.2896.

(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-chlorobenzoate (5l)



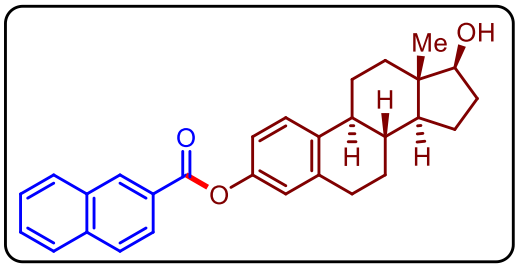
Following General Procedure 2.4.1 using **1h** (55 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), cat-**1** (5.6 mg, 2 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 55 mg, Yield: 54%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14-8.11(d, *J* = 9 Hz, 2H), 7.49-7.46(d, *J* = 9 Hz, 2H), 7.35-7.32(d, *J* = 9 Hz, 1H), 6.97-6.94(d, *J* = 9 Hz, 1H), 6.91(s, 1H), 3.77-3.71(t, *J* = 9 Hz, 1H), 2.89-2.87(m, 2H), 2.37-2.21(m, 2H), 2.17-2.07(m, 1H), 2.00-1.86(m, 2H), 1.76-1.66(m, 1H), 1.57-1.16(m, 7H), 0.79(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.8, 148.6, 140.2, 138.5, 138.4, 131.7, 129.0, 128.3, 126.6, 121.6, 118.7, 82.0, 50.2, 44.3, 43.4, 38.6, 36.8, 30.7, 29.7, 27.2, 26.3, 23.3, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{25}H_{28}ClO_3$: 411.1727; Found: 411.1729.

(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3,4-dimethylbenzoate (5m)



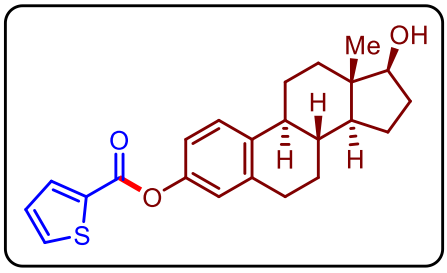
Following General Procedure 2.2.3 using **1m** (53.4 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 63.7 mg, Yield: 63%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95(s, 1H), 7.93-7.90(d, *J* = 9 Hz, 1H), 7.34-7.31(d, *J* = 9 Hz, 1H), 7.26-7.23(d, *J* = 9 Hz, 1H), 6.97-6.94(d, *J* = 9 Hz, 1H), 6.91(s, 1H), 3.77-3.72(t, *J* = 9 Hz, 1H), 2.89-2.87(m, 2H), 2.35(s, 3H), 2.34(s, 3H), 2.29-2.07(m, 3H), 2.00-1.87(m, 1H), 1.57-1.16(m, 7H), 0.79(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.9, 148.9, 143.1, 138.4, 138.0, 137.1, 131.3, 129.9, 127.9, 127.4, 126.5, 121.8, 118.9, 82.1, 50.2, 44.3, 43.4, 38.7, 36.8, 30.7, 29.7, 27.2, 26.3, 23.3, 20.2, 19.8, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{27}H_{33}O_3$: 405.2424; Found: 405.2423.

(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-naphthoate (5n)



Following General Procedure 2.2.3 using **1o** (60 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 50.2 mg, Yield: 47%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.78(s, 1H), 8.20-8.17(d, *J* = 9 Hz, 1H), 8.02-7.99(d, *J* = 9 Hz, 1H), 7.95-7.90(t, *J* = 9 Hz, 2H), 7.65-7.55(m, 2H), 7.38-7.35(d, *J* = 9 Hz, 1H), 7.04-7.01(d, *J* = 9 Hz, 1H), 6.98(s, 1H), 3.78-3.72(t, *J* = 9 Hz, 1H), 2.92-2.89(m, 2H), 2.39-2.23(m, 2H), 2.18-2.09(m, 1H), 2.00-1.89(m, 2H), 1.76-1.59(m, 1H), 1.56-1.17(m, 7H), 0.80(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 148.9, 138.5, 138.2, 135.9, 132.7, 132.0, 131.7, 129.1, 128.7, 128.5, 128.0, 126.9, 126.6, 125.7, 121.8, 118.9, 82.0, 50.2, 44.3, 43.4, 38.7, 36.8, 30.7, 29.7, 27.2, 26.3, 23.3, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{29}H_{31}O_3$: 427.2268; Found: 427.2265.

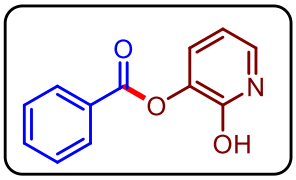
(8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl thiophene-2-carboxylate (5o)



Following General Procedure 2.2.3 using **1p** (46.5 mg, 0.3 mmol, 1.2 equiv), **4j** (67.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 60:40), White solid, 50 mg, Yield: 52%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97-7.96(d, *J* = 3 Hz, 1H), 7.66-7.64(d, *J* = 6 Hz, 1H), 7.34-7.31(d, *J* = 9 Hz, 1H), 7.18-7.15(dd, *J* = 6 Hz, 6Hz, 1H), 6.98-6.95(d, *J* = 9 Hz, 1H), 6.93(s, 1H), 3.77-3.71(t, *J* = 9 Hz, 1H), 2.89-2.86(m, 2H), 2.37-2.19(m, 2H), 2.16-2.07(m, 1H), 2.00-1.86(m, 2H), 1.75-1.60(m, 1H), 1.53-1.16(m, 7H), 0.79(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.0, 148.5, 138.5, 138.3, 134.7, 133.5, 133.3, 128.1, 126.6, 121.7, 118.8, 82.0, 50.2, 44.3, 43.4,

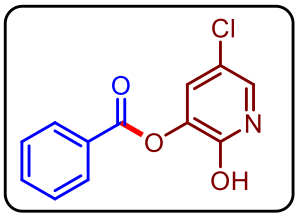
38.6, 36.8, 30.7, 29.7, 27.2, 26.3, 23.3, 11.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{23}H_{27}O_3S$: 383.1675; Found: 383.1674.

2-hydroxypyridin-3-yl benzoate (7a)



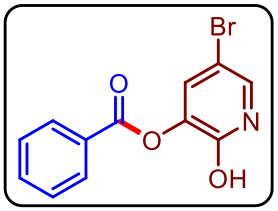
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 65:35), White solid, 43.7 mg, Yield: 81%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.09(s, 1H), 8.10-8.07(d, *J* = 9 Hz, 2H), 7.77-7.72(t, *J* = 9 Hz, 1H), 7.63-7.58(t, *J* = 9 Hz, 2H), 7.48-7.45(d, *J* = 9 Hz, 1H), 7.37-7.34(d, *J* = 9 Hz, 1H), 6.26-6.22(t, *J* = 6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.6, 157.2, 141.1, 134.1, 132.9, 130.7, 129.9, 129.0, 128.6, 104.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_{10}NO_3$: 216.0655; Found: 216.0654.

5-chloro-2-hydroxypyridin-3-yl benzoate (7b)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6b** (35.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 48.7 mg, Yield: 78%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.19(d, *J* = 8 Hz, 2H), 7.68-7.64(t, *J* = 8 Hz, 1H), 7.54-7.50(d, *J* = 8 Hz, 2H), 7.42-7.41(d, *J* = 4 Hz, 1H), 7.32-7.31(d, *J* = 4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.9, 158.6, 141.4, 134.2, 133.2, 130.7, 130.2, 128.8, 128.5, 113.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_9ClNO_3$: 250.0265; Found: 250.0262.

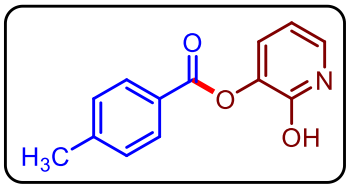
5-bromo-2-hydroxypyridin-3-yl benzoate (7c)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6c** (46.7 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 50.4 mg, Yield: 69%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.42(s, 1H), 8.09-8.06(d, *J* = 9 Hz, 2H), 7.78-7.73(t, *J* = 9 Hz, 1H),

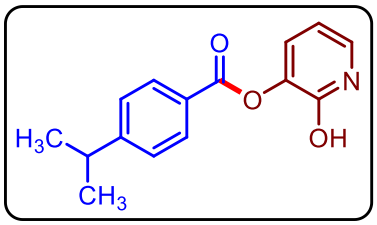
7.76-7.75(d, *J* = 3 Hz, 1H), 7.68-7.67(d, *J* = 3 Hz, 1H), 7.63-7.58(t, *J* = 9 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.4, 156.1, 141.2, 134.3, 133.9, 133.6, 129.9, 129.1, 128.2, 95.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_9BrNO_3$: 293.9760; Found: 293.9762.

2-hydroxypyridin-3-yl 4-methylbenzoate (7d)



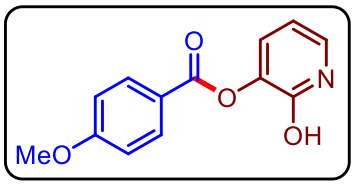
Following General Procedure 2.2.3 using **1b** (50 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 48.3 mg, Yield: 84%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.07(s, 1H), 7.98-7.96(d, *J* = 8 Hz, 2H), 7.46-7.44(d, *J* = 8 Hz, 1H), 7.41-7.39(d, *J* = 8 Hz, 2H), 7.35-7.33(d, *J* = 8 Hz, 1H), 6.25-6.21(t, *J* = 8 Hz, 1H), 2.42(s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.6, 157.2, 144.5, 141.2, 132.8, 130.6, 129.9, 129.5, 125.9, 104.0, 21.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{12}NO_3$: 230.0812; Found: 230.0816.

2-hydroxypyridin-3-yl 4-isopropylbenzoate (7e)



Following General Procedure 2.2.3 using **1r** (57.0 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 49.6 mg, Yield: 77%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.08(s, 1H), 8.02-7.99(d, *J* = 9 Hz, 2H), 7.48-7.45(d, *J* = 9 Hz, 2H), 7.45-7.42(d, *J* = 9 Hz, 1H), 7.36-7.33(d, *J* = 9 Hz, 1H), 6.26-6.21(t, *J* = 9 Hz, 1H), 3.07-2.94(hept, *J* = 9 Hz, 1H), 1.25-1.23(d, *J* = 6 Hz, 6H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.6, 157.2, 155.1, 141.2, 132.8, 130.6, 130.1, 126.9, 126.3, 104.0, 33.6, 23.5. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{15}H_{16}NO_3$: 258.1125; Found: 258.1122.

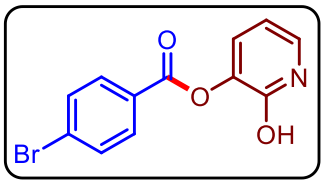
2-hydroxypyridin-3-yl 4-methoxybenzoate (7f)



Following General Procedure 2.2.3 using **1e** (54 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), **Ir-2** (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column

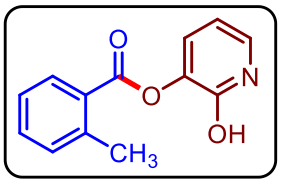
chromatography (Hexane/Acetone, 70:30), White solid, 44.9 mg, Yield: 73%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.01(s, 1H), 8.04-8.01(d, *J* = 9 Hz, 2H), 7.44-7.41(d, *J* = 9 Hz, 1H), 7.35-7.32(d, *J* = 9 Hz, 1H), 7.12-7.09(d, *J* = 9 Hz, 2H), 6.25-6.20(t, *J* = 9 Hz, 1H), 3.87(s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.8, 163.3, 157.4, 141.3, 132.7, 132.1, 130.7, 120.7, 114.3, 104.1, 55.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{12}NO_4$: 246.0761; Found: 246.0765.

2-hydroxypyridin-3-yl 4-bromobenzoate (7g)



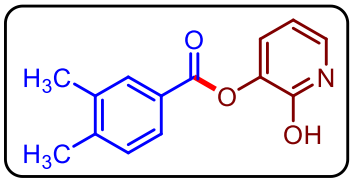
Following General Procedure 2.2.3 using **1i** (68 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 45.4 mg, Yield: 62%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.13(s, 1H), 8.01-7.99(d, *J* = 9 Hz, 2H), 7.83-7.80(d, *J* = 9 Hz, 2H), 7.50-7.47(d, *J* = 9 Hz, 1H), 7.38-7.35(d, *J* = 9 Hz, 1H), 6.26-6.22(t, *J* = 9 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.0, 157.1, 141.0, 133.0, 132.2, 131.8, 131.0, 128.2, 127.8, 104.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{12}H_9BrNO_3$: 293.9760; Found: 293.9761.

2-hydroxypyridin-3-yl 2-methylbenzoate (7h)



Following General Procedure 2.2.3 using **1l** (49.2 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 39.6 mg, Yield: 69%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.07(s, 1H), 8.02-7.99(d, *J* = 9 Hz, 1H), 7.59-7.54(t, *J* = 9 Hz, 1H), 7.47-7.44(d, *J* = 9 Hz, 1H), 7.41-7.38(d, *J* = 9 Hz, 2H), 7.36-7.33(d, *J* = 9 Hz, 1H), 6.26-6.21(t, *J* = 9 Hz, 1H), 2.56(s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 164.4, 157.2, 141.2, 140.0, 132.9, 132.7, 131.8, 130.8, 130.6, 128.2, 126.1, 104.0, 21.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{12}NO_3$: 230.0812; Found: 230.0817.

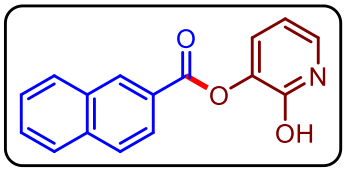
2-hydroxypyridin-3-yl 3,4-dimethylbenzoate (7i)



Following General Procedure 2.2.3 using **1m** (53.4 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5

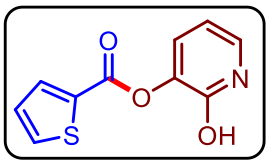
mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 34.7 mg, Yield: 57%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.07(s, 1H), 7.85(s, 1H), 7.81-7.78(d, *J* = 9 Hz, 1H), 7.45-7.42(d, *J* = 9 Hz, 1H), 7.37-7.33(m, 2H), 6.25-6.20(t, *J* = 9 Hz, 1H), 2.33(s, 3H), 2.31(s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.7, 157.2, 143.3, 141.2, 137.1, 132.7, 130.6, 120.0, 127.5, 126.1, 104.0, 19.7, 19.2. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{14}NO_3$: 244.0968; Found: 244.0966.

2-hydroxypyridin-3-yl 2-naphthoate (7j)



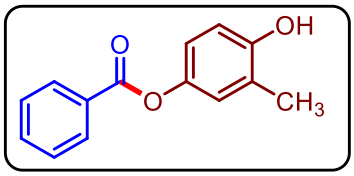
Following General Procedure 2.2.3 using **1o** (60.0 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 39.2 mg, Yield: 59%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 12.13(s, 1H), 8.80(s, 1H), 8.23-8.20(d, *J* = 9 Hz, 1H), 8.13-8.05(m, 3H), 7.75-7.63(m, 2H), 7.54-7.51(d, *J* = 9 Hz, 1H), 7.39-7.37(d, *J* = 6 Hz, 1H), 6.29-6.24(t, *J* = 9 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 163.7, 157.2, 141.2, 135.3, 132.9, 132.1, 131.6, 130.7, 129.5, 129.0, 128.6, 127.8, 127.2, 125.8, 125.0, 104.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{16}H_{12}NO_3$: 266.0812; Found: 266.0811.

2-hydroxypyridin-3-yl thiophene-2-carboxylate (7k)



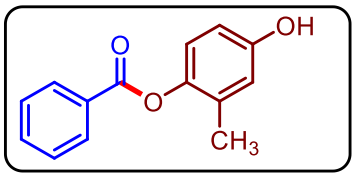
Following General Procedure 2.2.3 using **1p** (46.5 mg, 0.3 mmol, 1.2 equiv), **6a** (27.5 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Acetone, 70:30), White solid, 29.0 mg, Yield: 52%. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.10(s, 1H), 8.08-8.07(d, *J* = 5 Hz, 1H), 7.98-7.97(d, *J* = 5 Hz, 1H), 7.48-7.46(d, *J* = 8 Hz, 1H), 7.36-7.35(d, *J* = 5 Hz, 1H), 7.31-7.29(t, *J* = 5 Hz, 1H), 6.24-6.21(t, *J* = 8 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 159.0, 157.1, 140.7, 135.3, 135.2, 133.1, 131.4, 130.8, 128.7, 104.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{10}H_8NO_3S$: 222.0219; Found: 222.0220.

4-hydroxy-3-methylphenyl benzoate (7l)



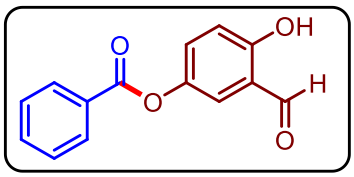
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6d** (30.8 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 29.2 mg, Yield: 51%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23-8.21(d, *J* = 8 Hz, 2H), 7.67-7.63(t, *J* = 8 Hz, 1H), 7.55-7.49(t, *J* = 8 Hz, 2H), 6.95-6.94(d, *J* = 3 Hz, 1H), 6.86-6.82(d, *J* = 8 Hz, 1H), 6.67-6.64(d, *J* = 8 Hz, 1H), 5.97(s, 1H), 2.22(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.6, 152.1, 143.9, 133.8, 130.3, 129.6, 128.7, 125.8, 123.7, 119.6, 115.8, 16.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_3$: 229.0859; Found: 229.0855.

4-hydroxy-2-methylphenyl benzoate (7m)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6d** (30.8 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:20), White solid, 12.6 mg, Yield: 22%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23-8.21(d, *J* = 8 Hz, 2H), 7.67-7.62(t, *J* = 8 Hz, 1H), 7.54-7.50(t, *J* = 8 Hz, 2H), 6.98-6.96(d, *J* = 8 Hz, 1H), 6.71-6.66(m, 2H), 5.11(s, 1H), 2.17(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.6, 153.6, 143.2, 133.7, 131.6, 130.3, 129.6, 128.8, 122.9, 117.8, 113.7, 16.5. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{13}O_3$: 229.0859; Found: 229.0858.

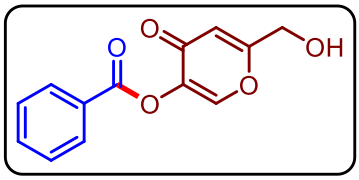
3-formyl-4-hydroxyphenyl benzoate (7n)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6e** (34.3 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 32.2 mg, Yield: 53%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.95(s, 1H), 9.86(s, 1H), 8.21-8.18(d, *J* = 9 Hz, 2H), 7.68-7.63(t, *J* = 9 Hz, 1H), 7.55-7.50(t, *J* = 9 Hz, 2H), 7.46-7.45(d, *J* = 3 Hz, 1H), 7.40-7.36(dd, *J* = 9 Hz, 3 Hz, 1H),

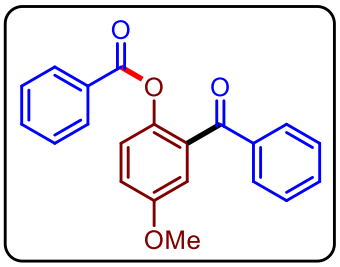
7.06-7.03(d, *J* = 9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 195.9, 165.3, 159.4, 143.3, 134.0, 130.9, 130.3, 129.1, 128.8, 125.6, 120.3, 118.8. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{11}O_4$: 243.0652; Found: 243.0652.

6-(hydroxymethyl)-4-oxo-4H-pyran-3-yl benzoate (7p)



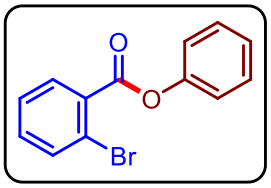
Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **6f** (35.3 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 80:20), White solid, 24.0 mg, Yield: 39%. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.65(s, 1H), 8.10-8.07(d, *J* = 9 Hz, 2H), 7.79-7.74(t, *J* = 9 Hz, 1H), 7.64-7.59(t, *J* = 9 Hz, 2H), 6.49(s, 1H), 5.81(s, 1H), 4.39(s, 2H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 171.8, 169.7, 163.2, 149.3, 140.5, 134.4, 129.9, 129.1, 127.9, 112.1, 59.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{11}O_5$: 247.0601; Found: 247.0600.

2-benzoyl-4-methoxyphenyl benzoate (9)



Following General Procedure 2.2.3 using **1a** (45 mg, 0.3 mmol, 1.2 equiv), **8** (56.8 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography (Hexane/Ethyl acetate, 90:10), White solid, 50.0 mg, Yield: 60%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.76(m, 4H), 7.52-7.49(t, *J* = 8 Hz, 1H), 7.47-7.43(t, *J* = 8 Hz, 1H), 7.38-7.28(m, 5H), 7.14-7.10(m, 2H), 3.85(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.8, 165.1, 157.2, 142.3, 137.7, 133.5, 133.1, 132.7, 130.1, 129.9, 129.0, 128.5, 128.4, 124.4, 118.0, 114.9, 56.0. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{21}H_{17}O_4$: 333.1121; Found: 333.1122.

phenyl 2-bromobenzoate (13)

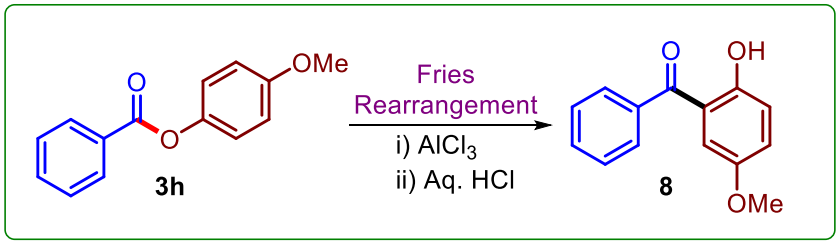


Following General Procedure 2.2.3 using **1s** (68.1 mg, 0.3 mmol, 1.2 equiv), **2b** (23.3 mg, 0.25 mmol, 1.0 equiv), Ir-2 (8.5 mg, 2.5 mol%), (dtbbpy)$PdCl_2$ (6.0 mg, 5 mol%) and $NaHCO_3$ (25 mg, 0.3 mmol) in DMSO (1.5 mL). The product was purified by column chromatography

(Hexane/Ethyl acetate, 95:5), White solid, 44.2 mg, Yield: 64%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03-8.00(d, *J* = 9 Hz, 1H), 7.75-7.72(d, *J* = 9 Hz, 1H), 7.47-7.36(m, 4H), 7.31-7.26(m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.7, 150.8, 134.7, 133.2, 131.9, 131.5, 129.6, 127.4, 126.2, 122.3, 121.7. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_{10}BrO_2$: 276.9859; Found: 276.9855.

2.3 Synthetic Application

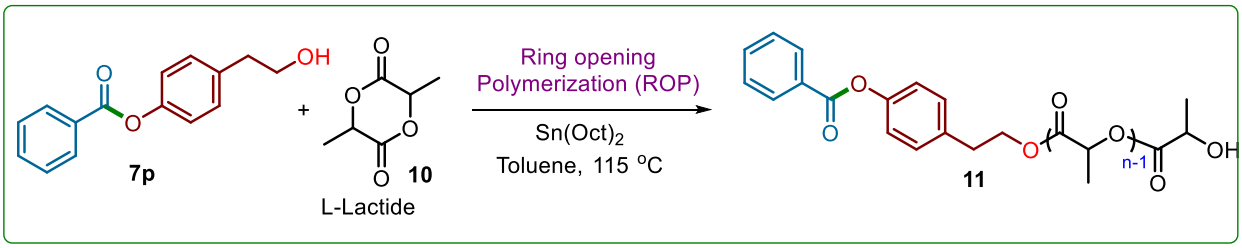
2.3.1 General procedure for the synthesis of (2-hydroxy-5-methoxyphenyl)(phenyl)methanone (8) [S4]



Scheme S3. Synthesis of (2-hydroxy-5-methoxyphenyl)(phenyl)methanone.

Process: Ester (4-methoxyphenyl benzoate) **3h** (114 mg, 0.50 mmol) in DMF (5 mL) was dissolved with $AlCl_3$ (100 mg, 0.75 mmol). The solution in sealed tube was stirred at 150-160 ^{o}C for 12 hr. The reaction mixture was cooled in ice, then mixed with 1 N HCl, after that extracted with $CHCl_3$, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (60-120 mesh size) using petroleum-ether/ethyl acetate (90:10) as an eluting system to give yellow oil (62 mg, 54%). Yellowish Liquid, 71.0 mg, Yield: 62%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.58(s, 1H), 7.72-7.68(d, *J* = 8 Hz, 2H), 7.62-7.57(t, *J* = 8 Hz, 1H), 7.53-7.49(t, *J* = 8 Hz, 2H), 7.17-7.13(dd, *J* = 8 Hz, 8 Hz, 1H), 7.07-7.06(d, *J* = 3 Hz, 1H), 7.04-7.01(d, *J* = 8 Hz, 1H), 3.70(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.3, 157.7, 151.6, 138.1, 132.1, 129.2, 128.5, 124.2, 119.4, 118.9, 116.5, 56.1. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{14}H_{23}O_3$: 229.0859; Found: 229.0864.

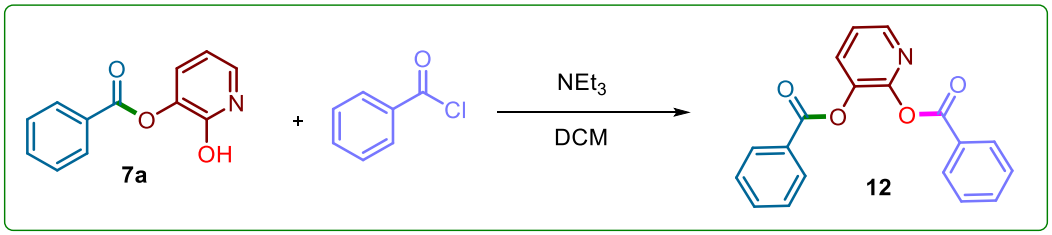
2.3.2 General procedure for synthesis of ring opening polymerization (ROP)[S5]



Scheme S4. Synthesis of poly(L-lactide) (PLLA) via ROP of L-lactide using **7p** initiator.

Process: To a 25 mL clean round bottom (R.B) flask equipped with a septum, ester (4-(2-hydroxyethyl)phenyl benzoate) **7p** (10 mg, 0.04 mmol) and L-lactide (~1.8 g, 12.4 mmol) were taken and added 3 mL of dry and degassed toluene to the R.B. Then, a solution of $Sn(Oct)_2$ (12.15 mg, 0.03 mmol) was added to the reaction vessel and the solution was degassed for 30 minute and the R.B was immersed in a preheated oil bath at 115 °C for 24 h. After that, the reaction was quenched by exposing to air. An off-white solid was produced after the solution was dissolved in DCM and purified by precipitating from cold methanol. To produce a pure polymer, the procedure was carried out three times. The polymer was then vacuum-dried for 48 hours at 40 °C (1.17 g, yield = 65 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20-8.19(d, *J* = 8 Hz, 2H), 7.65-7.62(t, *J* = 8 Hz, 1H), 7.53-7.50(t, *J* = 8 Hz, 2H), 7.26-7.25(d, *J* = 8 Hz, 2H), 7.16-7.14(d, *J* = 8 Hz, 2H), 5.19-5.14(m, 260H), 4.37-4.33(m, 5H), 3.76-3.74(t, *J* = 8 Hz, 2H), 2.98-2.96(t, *J* = 8 Hz, 2H), 1.58-1.57(m, 800H). Complete conversion was noted from the ^{1}H NMR of the crude. Molecular weight was calculated from ^{1}H NMR using the integration ratios of the aromatic protons (Ha) and the PLLA proton (Hb) = ~19,000 g/ mol (DP = 260), which gave a good match with the theoretical value (15000 g/mol).

2.3.3 General procedure for synthesis of pyridine-2,3-diyl dibenzoate (12)[S6]

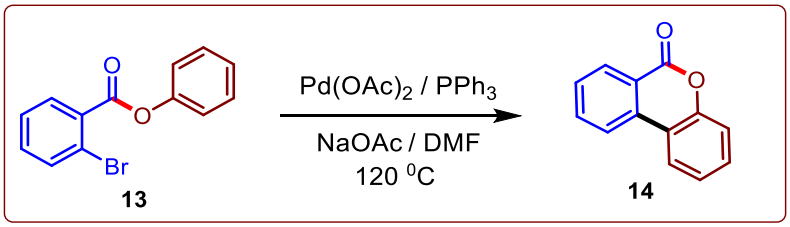


Scheme S5. Synthesis of pyridine-2,3-diyl dibenzoate.

Process: Ester (2-hydroxypyridin-3-yl benzoate) **7a** (215 mg, 1.0 mmol) was dissolved in 6 mL dry DCM with 175 µL of Et_3N (1.25 mmol). After 10 min, benzoyl chloride (116 mg, 1.0 mmol),

which was previously dissolved in 1 mL dry DCM, was added dropwise to the stirred solution of compound 7**a** under an inert atmosphere. After 12 h of stirring at room temperature, the reaction mixture was diluted with water (5 mL) and extracted with DCM (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (60-120 mesh size) using petroleum-ether/ethyl acetate (80:20) as an eluting system. White solid, 240 mg, Yield: 75%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38-8.36(d, *J* = 6 Hz, 1H), 8.14-8.11(d, *J* = 9 Hz, 2H), 8.05-8.02(d, *J* = 9 Hz, 2H), 7.87-7.84(d, *J* = 9 Hz, 1H), 7.60-7.52(m, 2H), 7.44-7.34(m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.1, 163.9, 150.7, 145.3, 139.0, 134.1, 134.0, 133.1, 130.5, 130.4, 128.73, 128.68, 128.6, 128.4, 123.3. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{19}H_{14}NO_4$: 320.0917; Found: 320.0919.

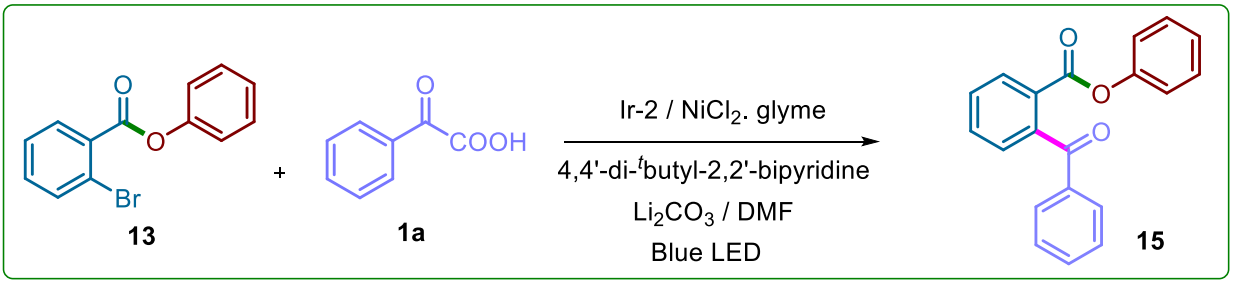
2.3.4 General procedure for synthesis of 6H-Benzo[c]chromen-6-ones (14)[S7]



Scheme S6. Synthesis of 6H-Benzo[c]chromen-6-ones.

Process: To a 15 mL clean, oven-dried screw cap reaction tube, bromo-ester **13** (70 mg, 0.25 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.1 equiv), NaOAc (2.5 equiv), PPh_3 (0.2 equiv) in DMF (3 mL) were added. The solution was then refluxed at 150 ºC temperature for 6h. After 6h, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate (90:10) as an eluting system. White solid, 29.6 mg, Yield: 60%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.41-8.38(d, *J* = 9 Hz, 1H), 8.13-8.11(d, *J* = 8 Hz, 1H), 8.07-8.04(d, *J* = 9 Hz, 1H), 7.85-7.80(t, *J* = 9 Hz, 1H), 7.61-7.55(t, *J* = 9 Hz, 1H), 7.51-7.45(t, *J* = 9 Hz, 1H), 7.38-7.31(m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.3, 151.4, 135.0, 134.9, 130.7, 130.6, 129.0, 124.7, 122.9, 121.8, 121.4, 118.2, 117.9. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{13}H_9O_2$: 197.0597; Found: 197.0597.

2.3.5 General procedure for synthesis of phenyl 2-benzoylbenzoate (15)[S8]



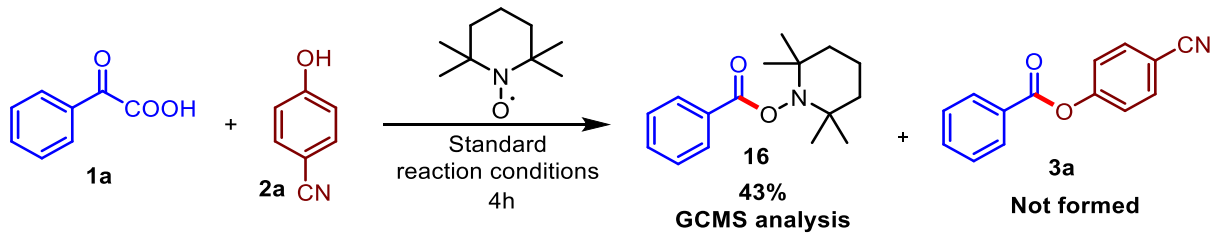
Scheme S7. Synthesis of phenyl 2-benzoylbenzoate.

Process: To a 40 mL clean, oven-dried screw cap reaction tube, phenyl 2-bromobenzoate **13** (138 mg, 0.50 mmol, 1.0 equiv), *α*-keto acid (150 mg, 1.00 mmol, 2.0 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ **Ir-2** (11.2 mg, 0.01 mmol, 0.02 equiv), $NiCl_2$·glyme (11.2 mg, 0.05 mmol, 0.10 equiv), 4,4′-di-tert-butyl-2,2′-bipyridine (20.1 mg, 0.075 mmol, 0.15 equiv), Li_2CO_3 (73.9 mg, 1.00 mmol, 2.0 equiv) and water (18 µL, 2.00 mmol, 2.0 equiv) in DMF (40 mL) were added. The reaction mixture was degassed for 30 minutes by bubbling argon stream, and then sealed with parafilm. The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 24h. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 24h, the reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate (95:5) as an eluting system. White solid, 98.5 mg, Yield: 65%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.24-8.21(d, *J* = 8 Hz, 1H), 7.81-7.79(d, *J* = 8 Hz, 2H), 7.75-7.63(m, 2H), 7.60-7.55(t, *J* = 8 Hz, 1H), 7.52-7.41(m, 3H), 7.30-7.25(t, *J* = 8 Hz, 2H), 7.22-7.14(m, 1H), 6.82-6.79(d, *J* = 8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.8, 164.8, 150.4, 142.0, 137.3, 133.4, 133.1, 130.8, 130.0, 129.7, 129.4, 128.9, 128.7, 128.3, 126.1, 121.3, 115.4. **HRMS (ESI):** m/z Calcd for $[M+H]^+$ $C_{20}H_{15}O_3$: 303.1016; Found: 303.1015.

3. Mechanistic studies

3.1 Radical trapping experiment

To a 30 mL clean Schlenk reaction tube, glyoxalic acid **1a** (0.3 mmol), alcohol **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.30 mmol) and TEMPO (2.00 equiv) were added in DMSO (1.5 mL). The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 4h of irradiation, a TEMPO-glyoxalic acid adduct **16** was observed, which was identified through GCMS & HRMS of the reaction mixture. Also after 24h of irradiation, any kind of our desired product **3a** was not formed. This observation further signifies that the reaction is likely to proceed through radical pathway.

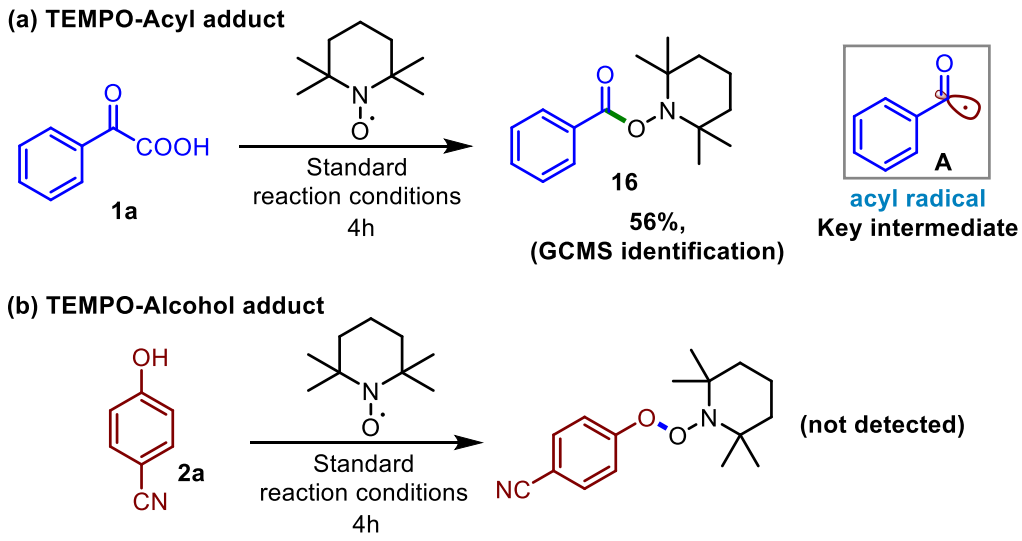


Scheme S8. Radical trapping experiment.

3.2 Individual TEMPO: Alcohol or TEMPO: *α*-keto Acid

To a 15 mL clean, oven-dried screw cap reaction tube, *α*-keto acid **1a** (0.30 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.30 mmol) and TEMPO (2.00 equiv) in DMSO (1.5 mL) were added. The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 24h. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 4h of irradiation, a TEMPO-glyoxalic acid adduct **16** was observed, which was identified through GCMS analysis of the reaction mixture.

To a 15 mL clean, oven-dried screw cap reaction tube, alcohol **2a** (0.30 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (5 mol%), $NaHCO_3$ (0.30 mmol) and TEMPO (2.00 equiv) in DMSO (1.5 mL) were added. The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 24h. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 4h of irradiation, there was no TEMPO-alcohol adduct observed.



Scheme S9. Identification of TEMPO adduct.

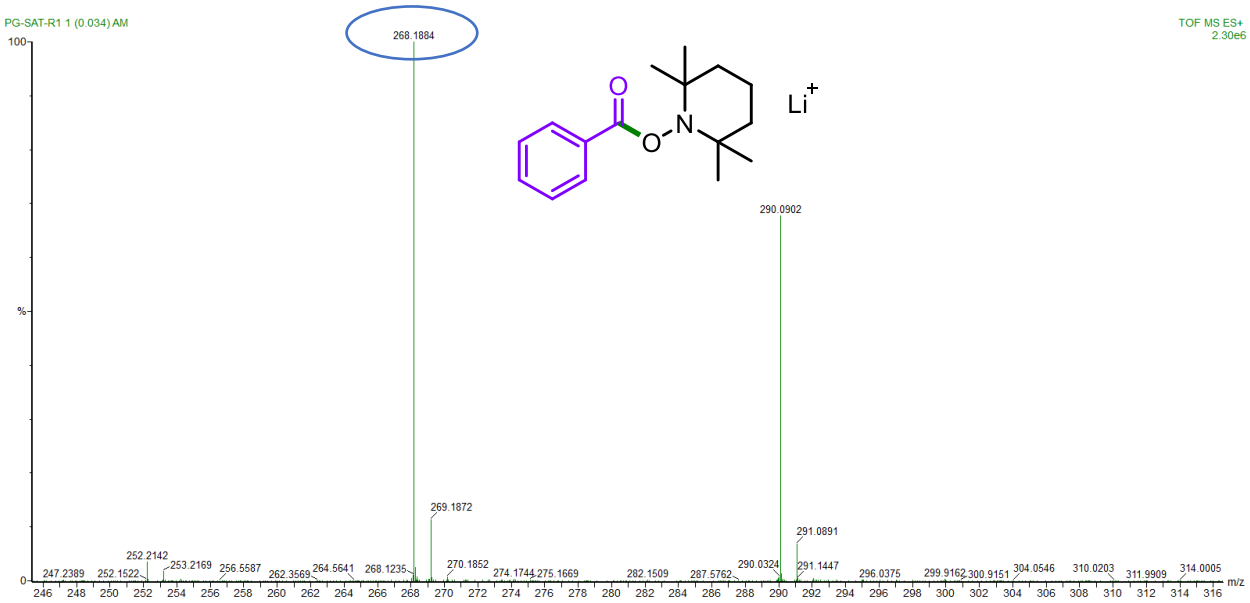


Figure S1: HRMS Chromatogram data of TEMPO: Glyoxalic acid adduct **16**.

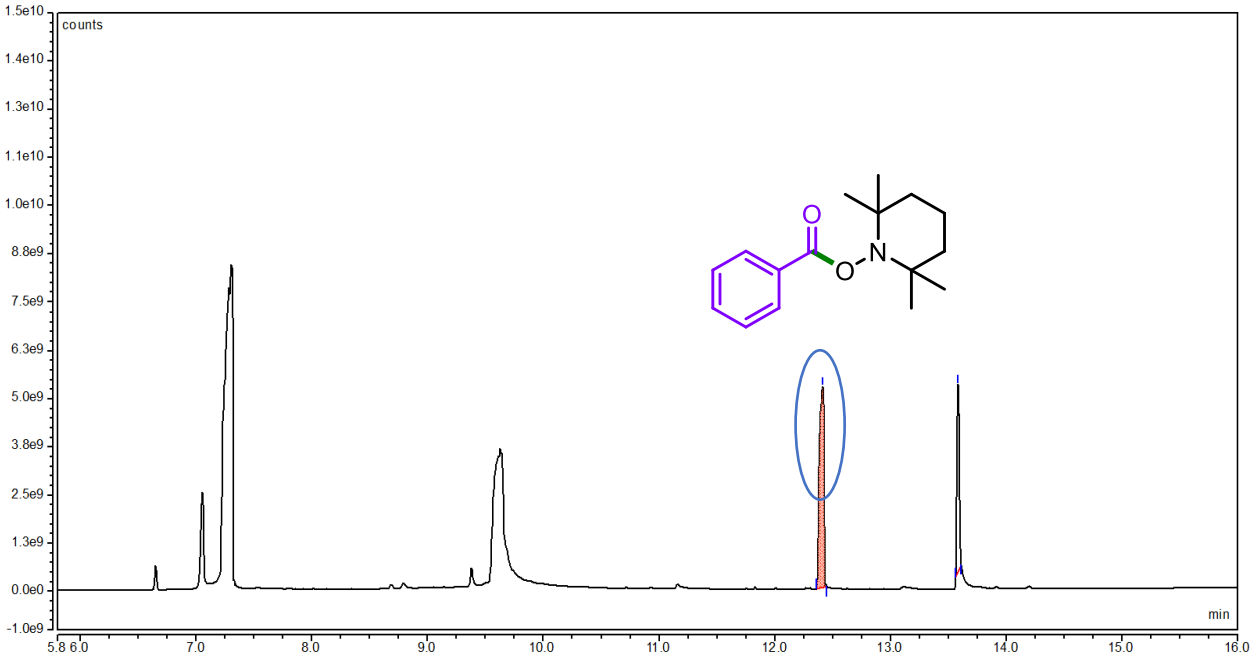


Figure S2: GCMS Chromatogram data for TEMPO: Glyoxalic acid adduct **16**.

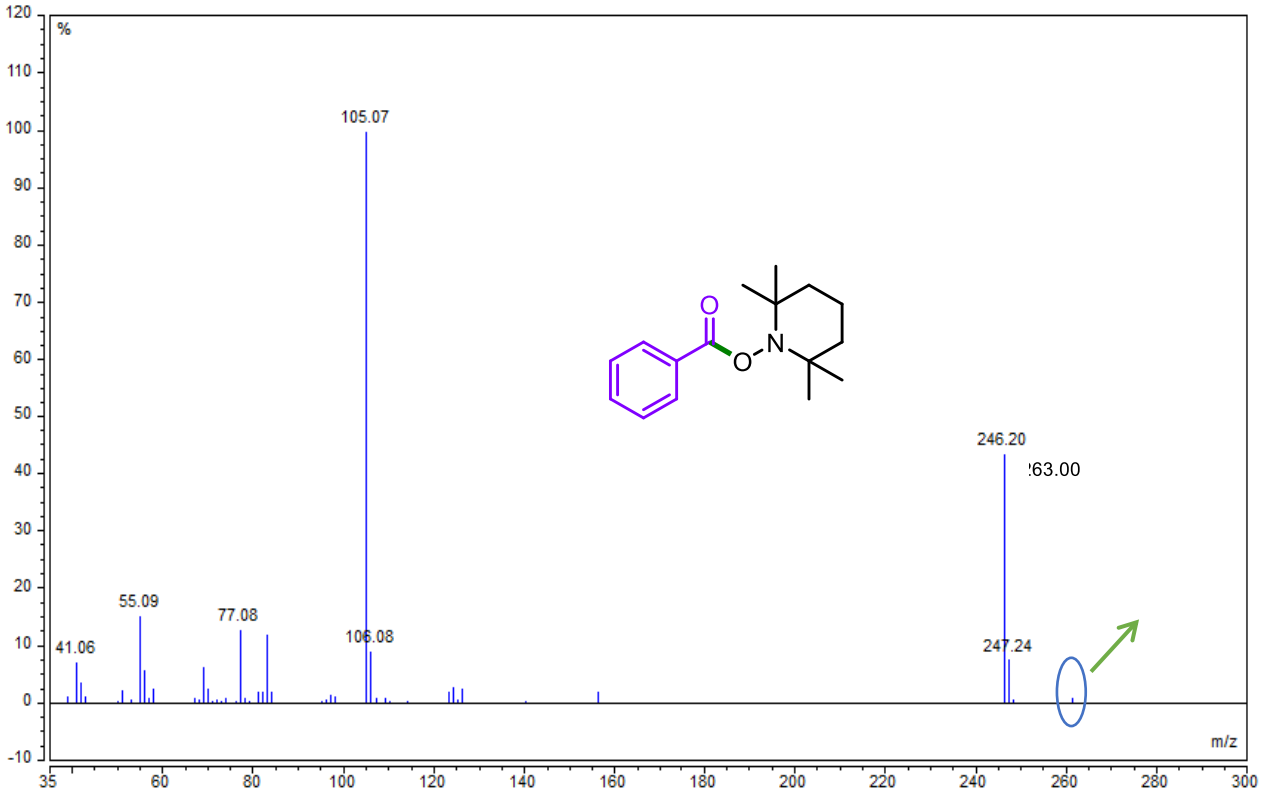


Figure S3: GCMS mass data for TEMPO: Glyoxalic acid adduct **16**.

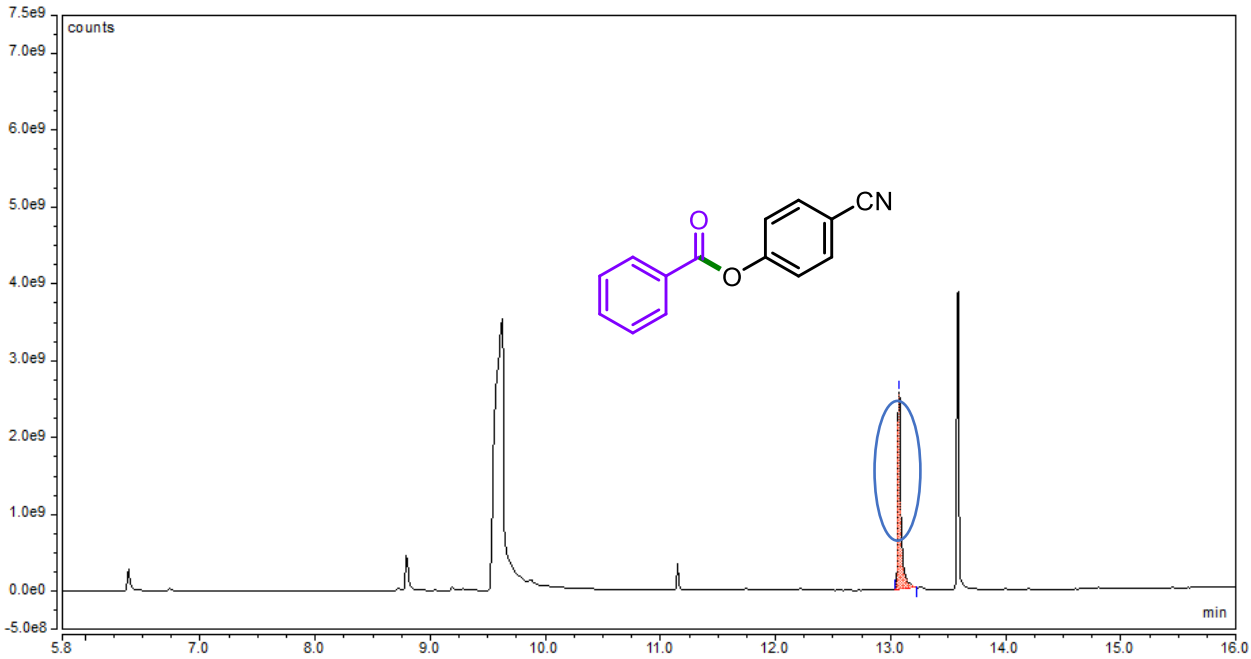


Figure S4: GCMS Chromatogram data for reaction mixture of ester **3a**.

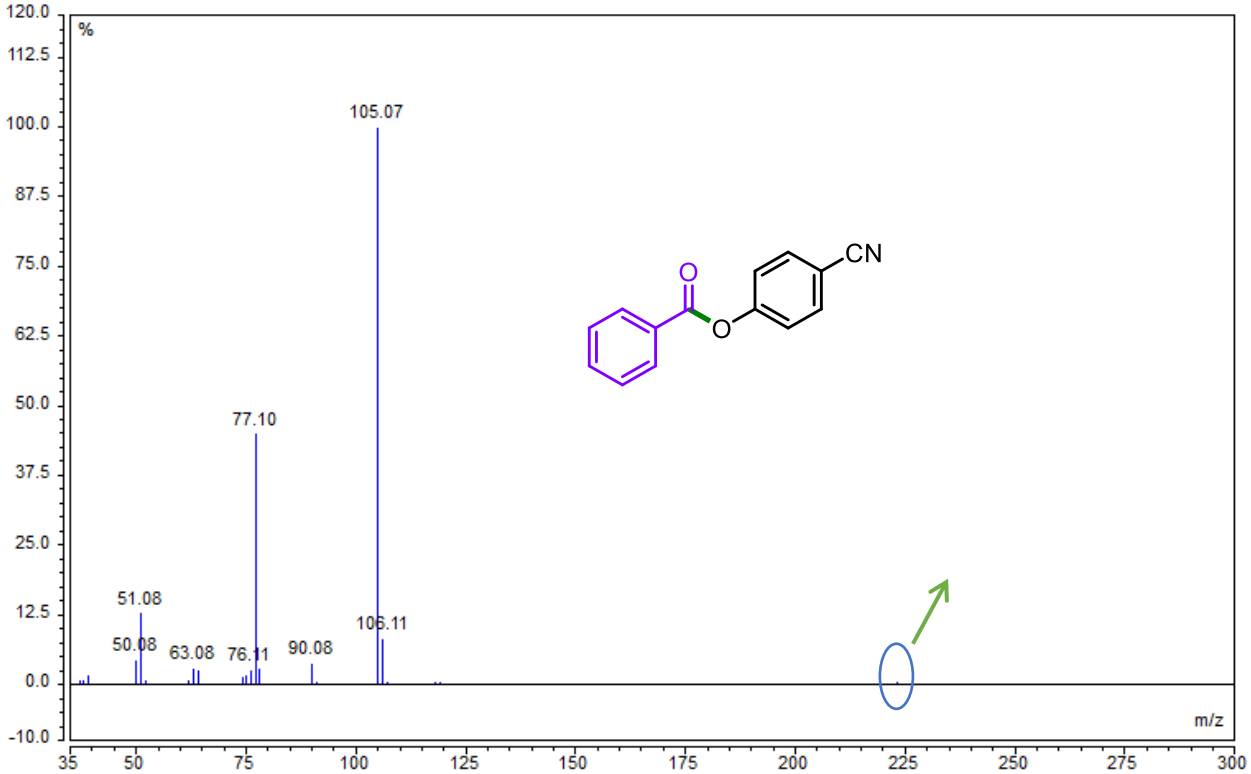
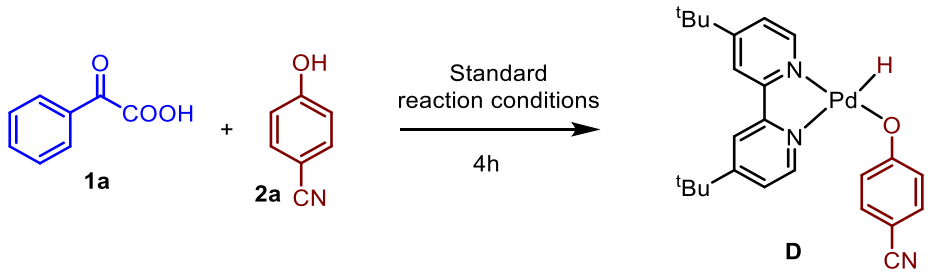


Figure S5: GCMS mass data for reaction mixture of ester **3a**.

3.3 Oxidative addition of Alcohols with Palladium complex



To a 30 mL clean Schlenk reaction tube, glyoxalic acid **1a** (0.3 mmol), alcohol **2a** (0.25 mmol), **Ir-2** (2.5 mol%), (4,4'-dtbbpy)$PdCl_2$ (22.5mg, 20.0 mol%), $NaHCO_3$ (0.30 mmol) were added in DMSO (1.5 mL). The solution was then photoirradiated with 40 W Kessil PR160L-456 nm LED at room temperature. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 4h of irradiation, oxidative additive product of alcohol with palladium complex that is intermediate **D** was observed and this was identified through the HRMS of the reaction mixture. These observations further support our proposed mechanistic catalytic pathway.

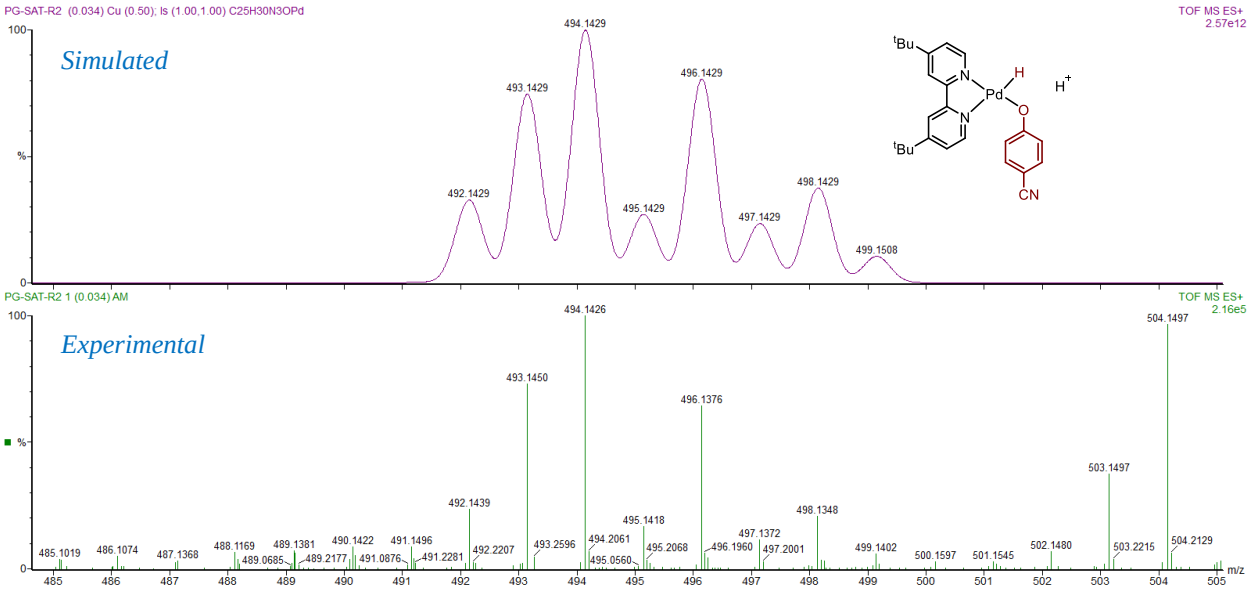
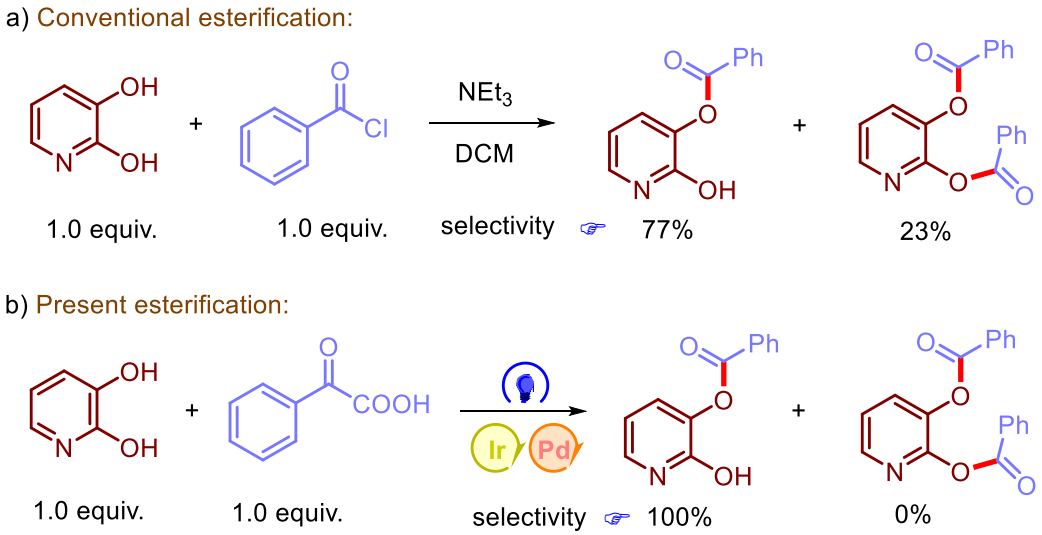
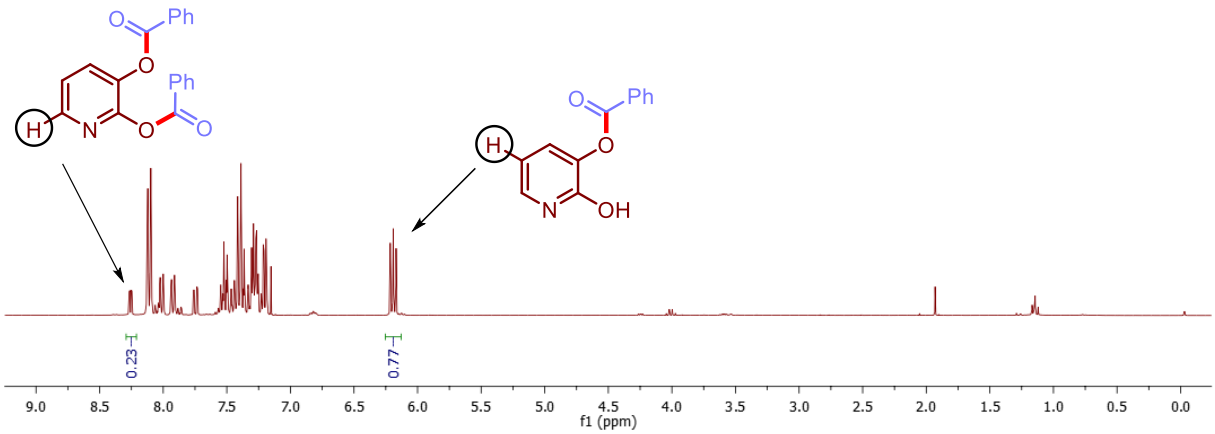


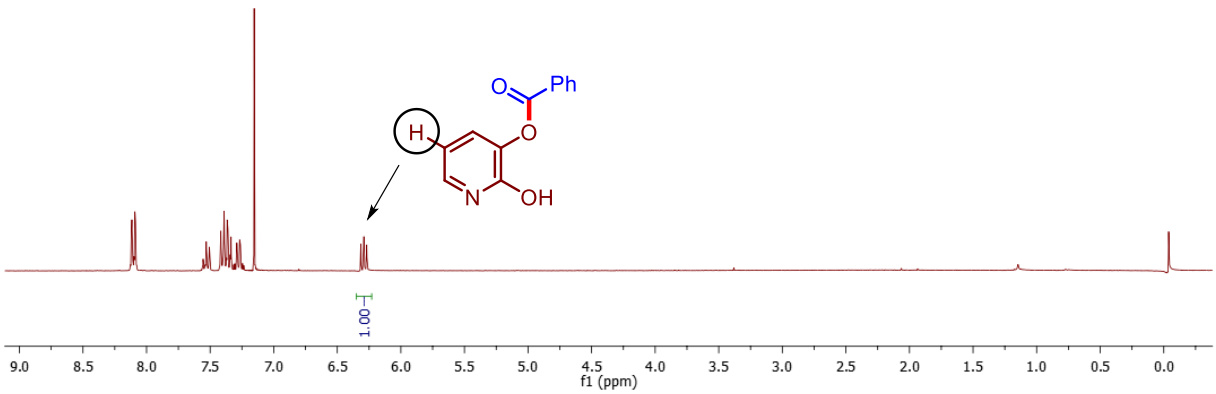
Figure S6: HRMS Chromatogram data for intermediate **D**.

3.4 Regio-selectivity comparisons between conventional esterification and present esterification of 2,3-dihydroxypyridine:



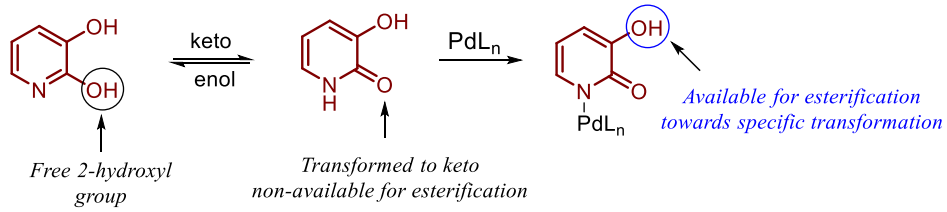


^{1}H NMR for conventional esterification reaction of 2,3-dihydroxypyridine.



^{1}H NMR for present esterification reaction of 2,3-dihydroxypyridine.

Representation of the lack of free hydroxyl groups at the 2-position in *N*-heterocyclic alcohols.



3.5 Fluorescence Quenching Experiments

For the fluorescence quenching experiment, we used 1.0 x 10^{-6} (M) solution of **Ir-2** in DMSO. For all sample, an appropriate amount of quencher was added for several times to that **Ir-2** solution in a screw-top 3.0 cm quartz cuvette. All **Ir-2** solution with or without quencher were excited at 350 nm and the emission intensity at 479 nm was observed and the emission spectrum of the sample was collected. I_0 is the luminescence intensity of the catalyst solution without the quencher and I is the intensity in presence of the quencher. For each quenching experiment, 10 μL of quencher solution (0.2 M) was added to 2.0 mL of **Ir-2** solution. From K(sv) value of Stern-Volmer quenching plot, we can say that the quenching efficiency of *α*-keto carboxylic acid **1** is more than the alcohol **2**. In this esterification reaction, *α*-keto acid was found to be the primary quencher.

To investigate the difference in reaction efficiency for pyridin-4-ol a series of fluorescence quenching studies were also performed. It is found that, other alcohols such as aromatic, aliphatic, pyridin-3-ol, where photoluminescence property of **Ir-2** was quenched. But in case of pyridin-4-ol, photoluminescence property of **Ir-2** was enhanced. In the contrary, heterocyclic 2 or 4 hydroxy group did not yield any esterification product. Also, this could be tautomerization of 2 or 4 hydroxy heterocyclic compounds and binding with the palladium center, which quenched the esterification reaction.

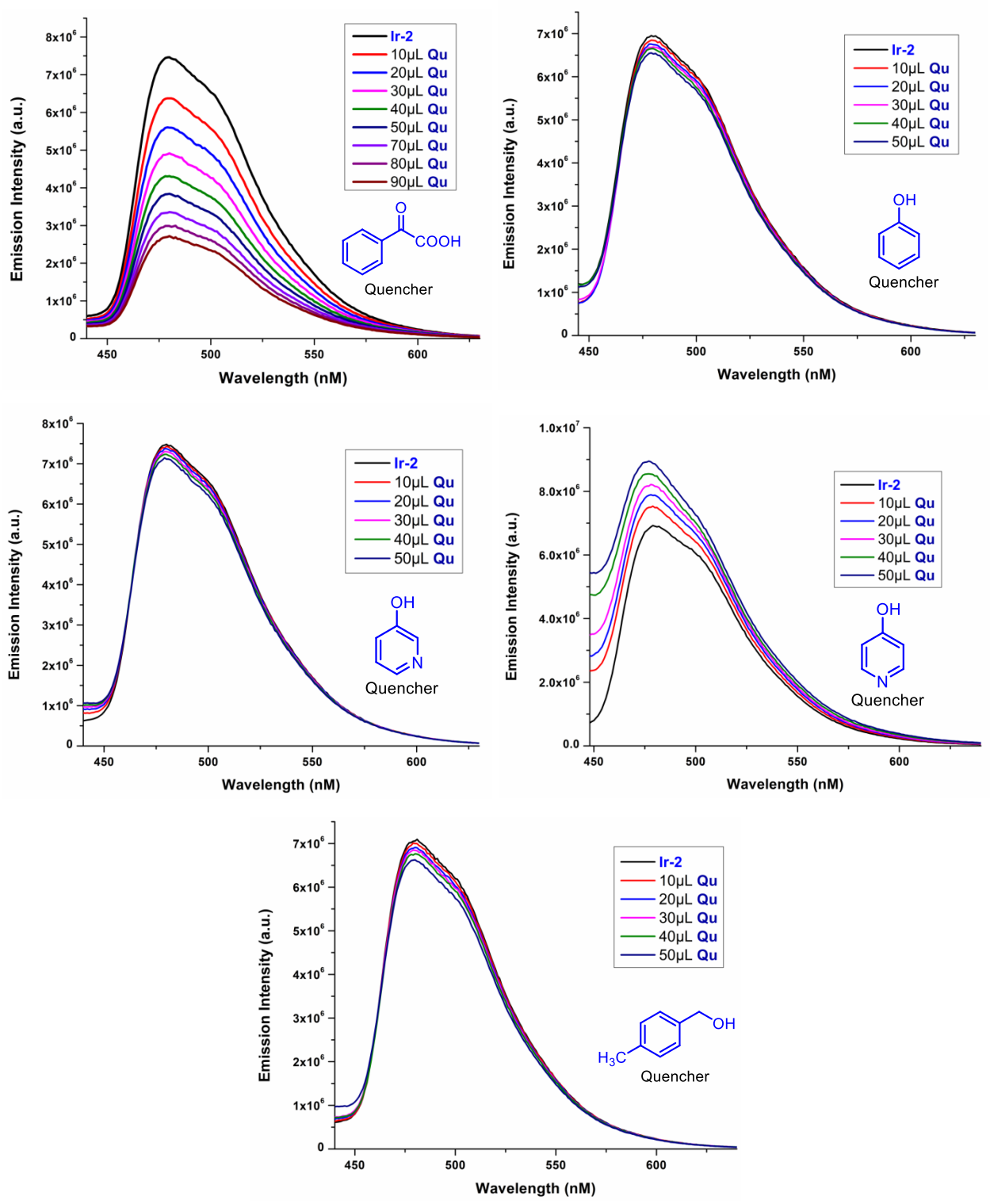


Figure S7. Photoluminescence fluorescence quenching experiments of keto acid & alcohols.

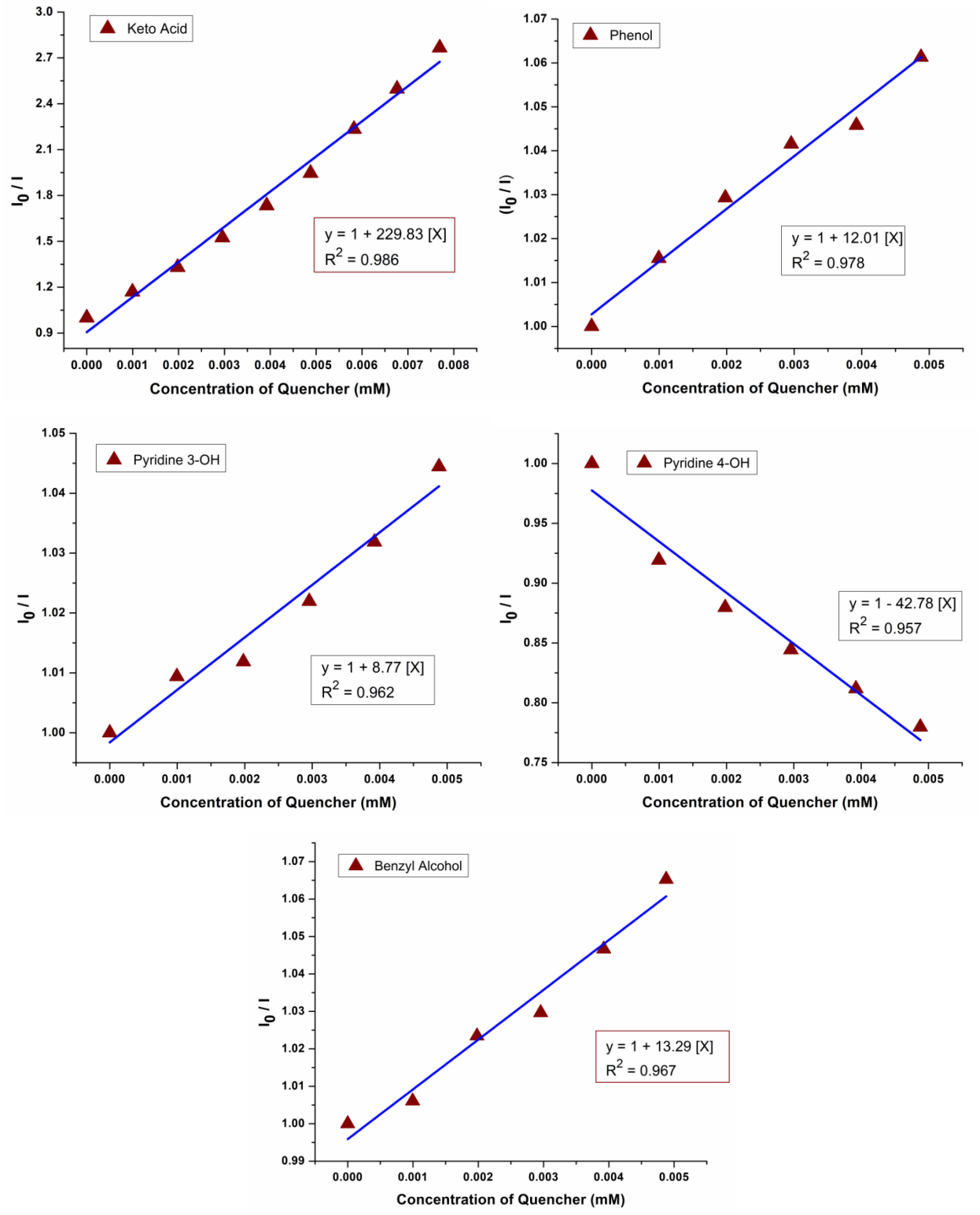


Figure S8: Stern-Volmer plot of **Ir-2** using keto acid & alcohols as quencher.

Quencher	Stern-Volmer constant (K_{sv})
α-Keto acid	229.83
Phenol	12.01
Pyridin-3-ol	8.77
Pyridin-4-ol	-
p-Tolylmethanol	13.29

3.6 XPS Data: Evidence of Pd^{2+}, Pd^{0} metal state[S9]

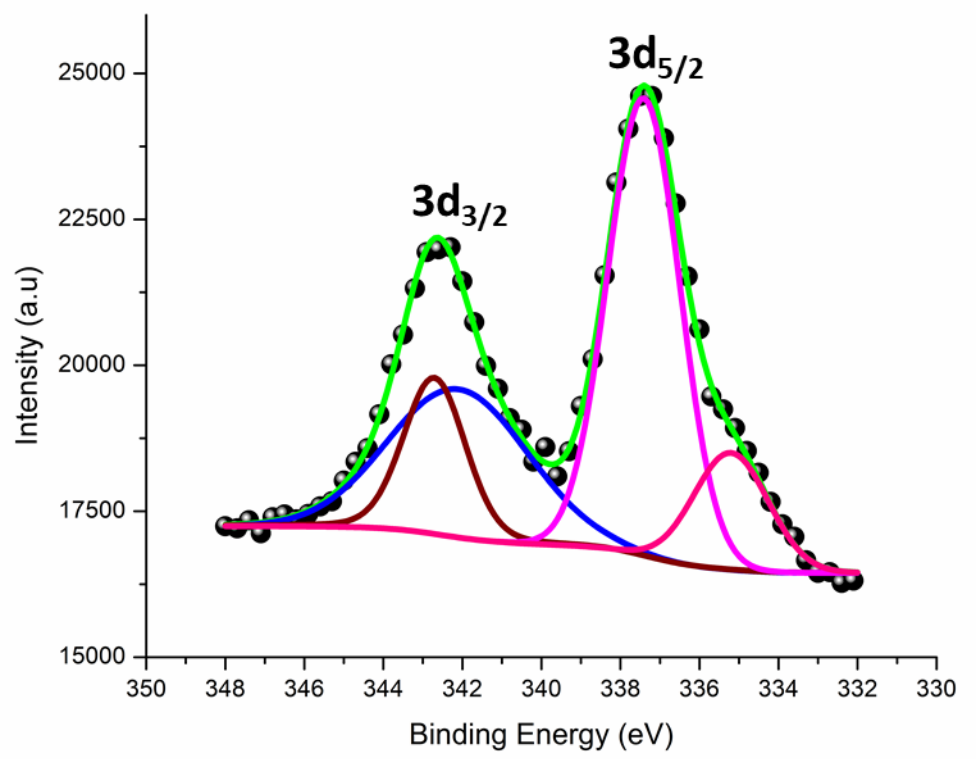


Figure S9. Pd 3d XPS spectra of Pd catalyst in present methodology

Binding energy:

Oxidation state	**$3d_{5/2}$ (eV)**	**$3d_{3/2}$ (eV)**
Pd(II)	337.39	342.77
Pd(0)	335.19	341.95

3.7 XPS Data: Evidence of Ir^{2+}, Ir^{3+} metal state[S10]

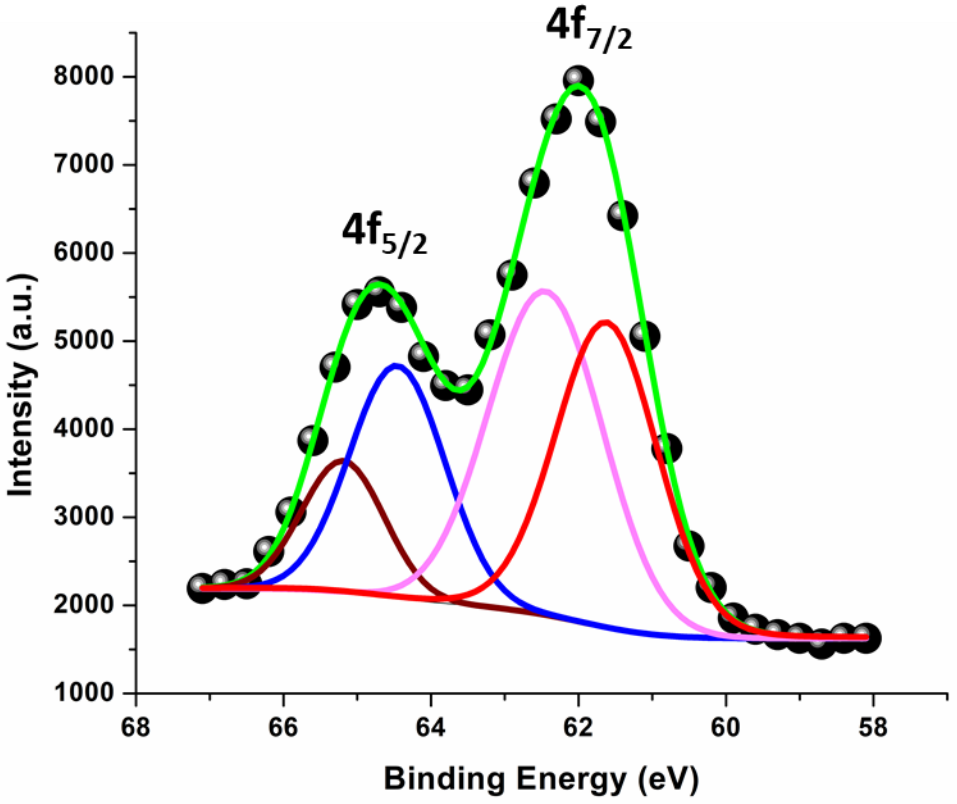


Figure S10. Ir 4f XPS spectra of Ir photocatalyst in present methodology

Binding energy:

Oxidation state	**$4f_{7/2}$ (eV)**	**$4f_{5/2}$ (eV)**
Ir(III)	62.52	65.29
Ir(II)	61.70	64.53

4. X-ray Crystal Structure

4.1 Crystal Structure of 3q

X-ray diffraction quality singles crystal of entry_**3q** were found by slow evaporating the chloroform solution of **3q**, and it was crystallized in the orthorhombic crystal system with **P n a 21** space group.

Crystallographic data (CCDC 2354489)

Compound reference	**Entry_3q**
Chemical formula	$C_{14}H_{12}O_4S$
Formula Mass	276.30
Crystal system	Orthorhombic
a/Å	8.6986(10)
b/Å	5.2970(8)
c/Å	27.895(3)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	1285.3(3)
Temperature/K	146
Space group	P n a 21
No. of formula units per unit cell, Z	4
Radiation type	MoK\a
No. of reflections measured	13857
No. of independent reflections	3131
R_{int}	0.0467
Final R_1 values ($I > 2\sigma(I)$)	0.0335
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0734
Final R_1 values (all data)	0.0451
Final $wR(F^2)$ values (all data)	0.0800
CCDC number	2354489

Crystal structure image of 3q:

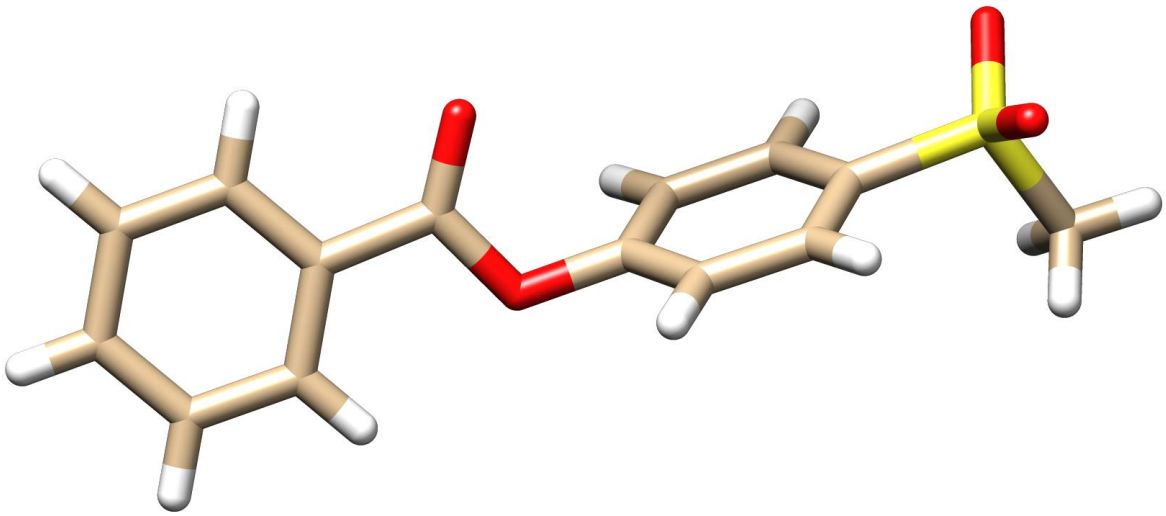
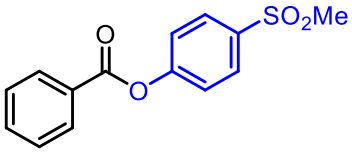


Figure S11: crystal structure of **Entry_3q** where thermal ellipsoids are shown at 50% probability.



4.2 Crystal Structure of 7e

X-ray diffraction quality singles crystal of entry_**7e** were found by slow evaporating the chloroform solution of **7e**, and it was crystallized in the orthorhombic crystal system with **P-1** space group.

Crystallographic data (CCDC 2354490)

Compound reference	**Entry_7e**
Chemical formula	$C_{15}H_{15}NO_3$
Formula Mass	257.28
Crystal system	triclinic
a/Å	7.402(2)
b/Å	12.593(4)
c/Å	15.571(5)
α/°	75.32(1)
β/°	76.785(10)
γ/°	82.923(11)
Unit cell volume/Å^3	1363.6(7)
Temperature/K	163
Space group	P-1

No. of formula units per unit cell, Z	2
Radiation type	MoK\a
No. of reflections measured	20198
No. of independent reflections	9081
R_{int}	0.0836
Final R_1 values ($I > 2\sigma(I)$)	0.0960
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2609
Final R_1 values (all data)	0.1531
Final $wR(F^2)$ values (all data)	0.3264
CCDC number	2354490

Crystal structure image of 7e:

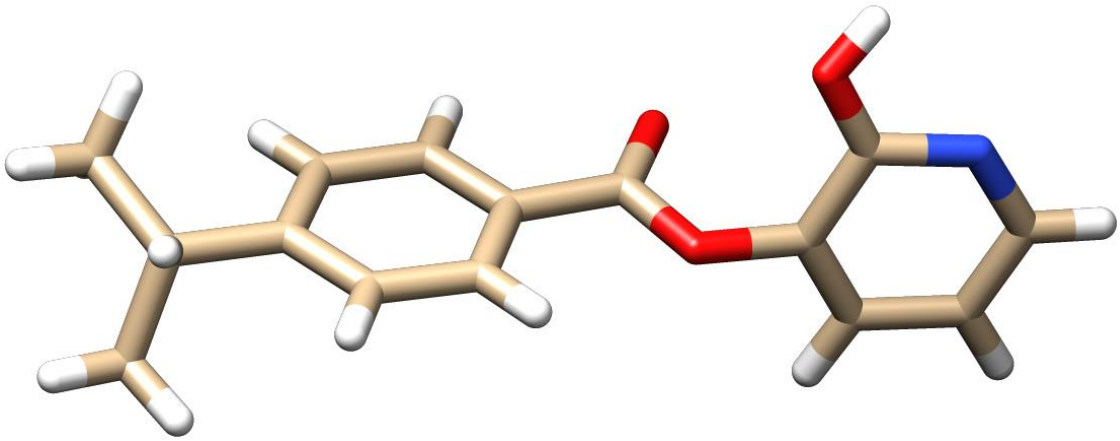
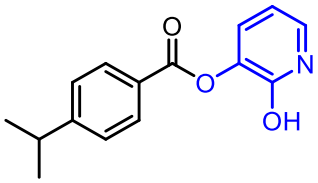


Figure S12: crystal structure of **Entry_7e** where thermal ellipsoids are shown at 50% probability.



5. Computational details:

All molecular geometries were optimized in vacuum with M06 density functional paired with 6-31++G(p,d) basis set for C, H, N, O, F atoms and LanL2DZ, which has a double-ζ quality basis set with the Los Alamos effective core potential for Ir and Pd. The M06 density functional was used as it has been shown to be a tool to make reliable predictions[S11] for photo-redox reaction free energy changes and barriers[S12]. Harmonic vibrational frequencies at the same level of theory were computed to characterize the structures as minima (all real frequencies) and transition states (one imaginary mode). Thermo-chemical information like zero-point corrections (ZPC) and thermal corrections to free energy were obtained from frequency calculations for 1 atmospheric pressure and 298 K temperature. To compensate for the damping of translational and rotational degrees of freedom in the solvent phase, Gibbs free energies were computed using solvent phase entropies, which in turn were derived by scaling gas phase entropies by an empirical factor of 0.5, which is a standard practice[S13]. The CPCM[S14] technique has been chosen because continuum solvent models are reported to give satisfactory results for the solvent phase. All the calculations were conducted within the Gaussian 09 suite of programs.[S15]

Energy barriers of single electron transfer steps, involved in this whole study, by using Marcus-Hush theory[S16]

λ is the reorganization energy, which has two components, inner sphere and outer sphere. However the first one is considered to be neglected, and hence, the total λ will be the outer sphere reorganization energy, which can be calculated by the equation:

$$\lambda_0 = (332 kcal/mol)(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R})(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon})$$

$$\lambda = \lambda_0 + \lambda_i$$

$$\Delta G^{0\#} = \frac{(\Delta G_r + \lambda)^2}{4\lambda}$$

Where a_1 is the radii of the oxidant, a_2 is the radii of the reductant, $R = a_1 + a_2$, ε_{op} is the optical dielectric constant (ε_{op} = 2.18), ε is the static dielectric constant for the solvent (ε = 46.68), and ΔGr is the free energy change of the reaction.

SET steps	a_1 (Å)	a_2 (Å)	R (Å)	λ (kcal/mol)	ΔG_r (kcal/mol)	ΔG_{SET} (kcal/mol)
Radical formation	7.09	3.41	10.50	19.20	-14.0	0.4
SET_{E-J}	7.25	7.09	14.34	10.95	-24.83	4.4
STE_{F-G}	5.32	7.09	12.41	28.08	1.62	7.8

Mechanistic Details:

In the reaction medium both α-keto acid (PhCOCOOH) and (-HCO_3^-) are present. They participate in an exoergic acid-base reaction which is favorable by 14.8 kcal/mol. The acid-base reaction produces H_2CO_3 and the deprotonated form of the α-keto acid, which serves as our starting reactive species. The photoexcitation of Ir(III) to *Ir(III) can plausibly initiate a reductive quenching process where the *IrIII can strip off an electron from the deprotonated keto-carboxylic acid, thus triggering decarboxylation and simultaneously yielding Ir(II). The decarboxylative redox process is facilitated by a single electron transfer (SET) which is predicted to be essentially barrierless (1.2 kcal/mol barrier) and is downhill by 16.0 kcal/mol. The SET facilitated decarboxylation yields a reactive acyl radical in the medium. The acyl radical sets into action the catalytic cycle for production of ester through a cross coupling reaction (see Figure 13). Some of the Ir(II) thus produced plausibly reduces Pd(II) to Pd(0). It must be noted that the optimized reaction uses 1.25 equiv of the phenyl-keto-carboxylic-acid. The excess acid produces enough Ir(II) to yield the requisite catalytic amount of Pd(0) from Pd(II).

The Pd(0)-complex (B) reacts with phenol to form an intermediate C, which is 9.3 kcal/mol more stable than the starting reactants. Subsequently, an oxidative addition occurs yielding intermediate, D. The oxidative addition process is 16.7 kcal/mol downhill and it proceeds through a transition state, TS-1 which lies 13.2 kcal/mol higher in energy than the previous intermediate C. In D the metal center is in formal II oxidation state. At this juncture the acyl radical A enters the reaction web. The acyl radical can endoergically bind to D leading to formation of metastable intermediate E which is 5 kcal/mol higher in free energy than D. Not

surprisingly, E, which has a formal Pd(III) center is predicted to undergo a highly exoergic reductive elimination involving C-O coupling by overcoming a barrier of 8.4 kcal/mol via TS-2 to yield F with formal I oxidation sate of Pd and the observed ester product (catalytic path-B). Ir(II) in the medium can reduce F by SET and converts it to G with a Pd(0) bearing a Pd-H bond. The barrier for SET leading to the formation of G is estimated to be only 7.8 kcal/mol. Alternatively, E can transform to G through a pathway which initiates through a SET from Ir(II) to E converting it to a five coordinate Pd(II) intermediate J (path-B). The overall barrier for the SET for J formation is only 4.4 kcal/mol. J is predicted to undergo reductive elimination, thus releasing the observed ester product and yielding simultaneously G. The intermediate G interacts with H2CO3 through hydrogen bonding interaction and releases H2 through a barrier less process and simultaneously releases the Pd(0) active catalytic form B. Thus in the last step the active catalytic form of the Pd complex is regenerated. Both the pathways described above are low barrier routes which are likely to be facile at room temperature. Moreover, both of these pathways satisfactorily delineates channels for ester formation as well as Pd(0) catalyst and Ir(III)-photocatalyst regeneration. Comparison of the two theoretically predicated paths for ester formation suggests that the one involving conversion of E to G via J (path-A) is expected to be more dominant than the other involving conversion of E to G via F (path-B). Both pathways involve a significantly exothermic step beyond intermediate E (E to F and E to J) and the relative barriers of from E to F and E to J are 8.4 kcal/mol and 4.4 kcal/mol respectively. Hence, conversion of E to J is likely to be several folds faster than E to F. The rater determining barrier for Pathway-B is the reductive elimination from J, with a barrier of 13.4 kcal/mol.

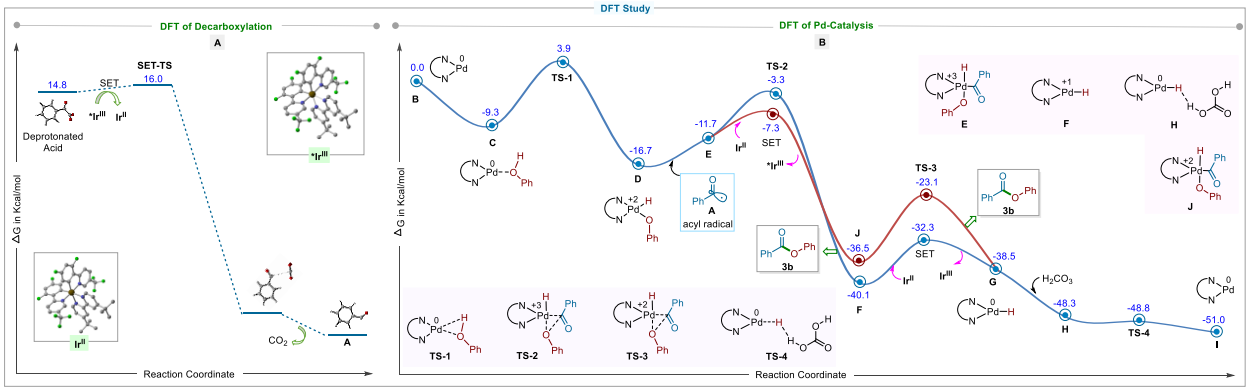


Figure S13: Plausible mechanistic cycles and Gibbs free energy profile (kcal/mol) of Ir-Pd catalyzed C-O cross-coupled decarboxylative ester synthesis at 298K.

Optimized cartesian coordinates:

Geometry of Ir^{III} in Cartesian Coordinates and in Angstroms:

C	2.17395500	0.08396600	0.73280600
C	0.93766400	-0.51476100	2.59931600
C	2.07196700	-0.58385200	3.38592400
C	3.32995300	-0.30851900	2.83293600
C	3.35034300	0.03196800	1.47967000
C	2.14673600	0.42662300	-0.70650500
C	0.83478100	0.76215000	-2.58743900
C	1.94043500	1.05753400	-3.36282300
C	3.22265200	1.03723200	-2.79711300
C	3.29645600	0.71167700	-1.44241300
H	-0.04909400	-0.73077900	3.00742800
H	1.96418900	-0.85888800	4.43170700
H	4.29491900	0.25951500	0.99754800
H	-0.17168800	0.77307200	-3.00440600
H	1.79115800	1.30303900	-4.41117000
H	4.26274200	0.67676400	-0.95075500
N	0.97798000	-0.19214800	1.29754300
N	0.92586500	0.45538400	-1.28443200
C	-2.65844400	0.62363100	2.08517200
C	-3.61508600	0.41639200	3.08916400
C	-4.11914800	-0.82983400	3.39995300

C	-3.63704700	-1.90251600	2.66166000
C	-2.69155200	-1.76695400	1.65482400
C	-2.18573700	-0.50219500	1.35482300
C	-2.08616200	1.90530800	1.71274500
C	-2.42344800	3.16419100	2.23458300
C	-1.79774200	4.29985800	1.76044700
C	-0.82785200	4.18249700	0.76209700
C	-0.52596300	2.92537100	0.27834900
H	-4.86060000	-0.95971000	4.18085600
H	-2.37920500	-2.66130600	1.11895000
H	-3.18078700	3.23893200	3.00380800
H	-2.05854900	5.27880700	2.15717600
H	0.21422600	2.78420100	-0.50508900
C	-2.41239200	-1.21336300	-2.11540100
C	-2.23161800	-0.00344800	-1.38825900
C	-3.02995900	1.09836200	-1.69478600
C	-3.97897800	0.99389900	-2.70191100
C	-4.18351300	-0.16731700	-3.43572600
C	-3.38908400	-1.25064300	-3.12107700
C	-1.54518700	-2.31498600	-1.73604900
C	0.20772200	-2.91600400	-0.28719100
C	0.23045900	-4.20877700	-0.76958800
C	-0.67482200	-4.56450400	-1.77224300

C	-1.55849700	-3.61966800	-2.25493100
H	-2.94716100	2.04442200	-1.16325300
H	-4.93293700	-0.22615000	-4.21750100
H	0.88310300	-2.59544700	0.50176700
H	-0.68332000	-5.57908900	-2.16512400
H	-2.26957000	-3.87872300	-3.02855500
Ir	-0.77512800	-0.07402900	-0.00855100
C	4.58285800	-0.39207400	3.69039000
C	4.44878200	0.59437400	4.85940700
H	5.34965700	0.55325400	5.48339400
H	4.33443400	1.62444500	4.49885600
H	3.59267500	0.36156100	5.50303300
C	4.71411000	-1.82339500	4.23045200
H	3.86394100	-2.10990600	4.86034900
H	4.79271600	-2.55185200	3.41350700
H	5.61974900	-1.90405800	4.84353800
C	5.84675900	-0.04944700	2.90546500
H	6.01441400	-0.74228300	2.07052600
H	5.82729100	0.97728000	2.51713300
H	6.71605800	-0.12686300	3.56791700
C	4.44500500	1.35426600	-3.64494800
C	4.29870600	2.77274100	-4.21303000
H	3.41627500	2.87527800	-4.85508800

H	4.22397800	3.51711200	-3.41027500
H	5.17758000	3.01894800	-4.82094800
C	4.52525000	0.33906500	-4.79373500
H	4.62567800	-0.68506600	-4.41263100
H	3.64444000	0.37502100	-5.44538500
H	5.40280500	0.55608400	-5.41443300
C	5.74153600	1.28222900	-2.84138200
H	5.76144000	2.01297200	-2.02226000
H	5.91581400	0.28032800	-2.42743700
H	6.58809100	1.51167300	-3.49810700
N	-1.13544100	1.82059300	0.73475400
N	-0.65240800	-1.99690300	-0.75173100
C	-0.12454500	5.40564100	0.25650400
F	-0.99890800	6.33767300	-0.13633800
F	0.67795300	5.13165900	-0.77996600
F	0.63089900	5.95472000	1.21864700
C	1.19710000	-5.22552900	-0.24239500
F	1.99090000	-5.68344500	-1.21985000
F	1.98455100	-4.72142500	0.71706300
F	0.55455800	-6.28165700	0.26864200
F	-4.07639700	1.45716800	3.79847800
F	-4.11119600	-3.11754700	2.93746000
F	-4.73647800	2.05444900	-2.98255400

F	-3.57702700	-2.37470500	-3.82891600

Geometry of $^{*}Ir^{III}$ in Cartesian Coordinates and in Angstroms:

C	-1.58776800	1.54698400	0.52961200
C	-0.10642700	1.62191200	2.31038000
C	-0.82915500	2.62342600	2.92986900
C	-1.98076700	3.13953200	2.31978400
C	-2.34708800	2.56844700	1.09999400
C	-1.93182200	0.91191100	-0.76145400
C	-1.24196000	-0.49998600	-2.46500600
C	-2.43149200	-0.33269900	-3.14797900
C	-3.44465100	0.47323500	-2.60960600
C	-3.15618800	1.10661000	-1.39961000
H	0.80611300	1.22034000	2.75164400
H	-0.47989400	3.00312400	3.88640400
H	-3.22474800	2.93466900	0.57866000
H	-0.45617200	-1.15017000	-2.84729500
H	-2.56841200	-0.85395400	-4.09157300
H	-3.90084800	1.74061700	-0.93017000
N	-0.46634500	1.09580300	1.13028200
N	-0.99618200	0.09155400	-1.28608300
C	1.55500000	-1.78479600	2.42585500
C	2.43836200	-2.08154600	3.51249000

C	3.65390400	-1.48537800	3.65799600
C	4.06188500	-0.53684900	2.68744700
C	3.27317800	-0.19334500	1.60505900
C	2.01802300	-0.77937700	1.45046900
C	0.29802100	-2.36206800	2.19264200
C	-0.35626300	-3.39211200	2.93812500
C	-1.58645000	-3.85621000	2.57029000
C	-2.21490300	-3.29314000	1.41856700
C	-1.55442100	-2.30808500	0.70047000
H	4.29846600	-1.73375400	4.49568700
H	3.65961700	0.53309700	0.89266000
H	0.14584600	-3.80739800	3.80381000
H	-2.08214500	-4.64285100	3.13243600
H	-2.01022900	-1.89210700	-0.19498600
C	2.56382100	-1.09602200	-2.08472500
C	1.64353300	-1.70500100	-1.18650900
C	1.44898200	-3.08516000	-1.23049900
C	2.15661200	-3.83904000	-2.15632200
C	3.06075200	-3.28426100	-3.05270500
C	3.24469700	-1.91751300	-2.99340800
C	2.70708400	0.34672000	-1.97437300
C	1.90626000	2.23124500	-0.81849300
C	2.73495700	3.07884900	-1.52582700

C	3.58642200	2.53243300	-2.48875800
C	3.57217400	1.16941300	-2.71348500
H	0.76627100	-3.59563900	-0.55402900
H	3.60339600	-3.89367400	-3.76742200
H	1.23430900	2.60815200	-0.05133800
H	4.25374400	3.17740200	-3.05674700
H	4.22779100	0.73102500	-3.45482200
Ir	0.69521800	-0.41950200	0.02418600
C	-2.76295600	4.26405700	2.98050900
C	-3.27268200	3.77168500	4.34229200
H	-3.83671500	4.57186600	4.83642400
H	-3.93994200	2.90808400	4.22826800
H	-2.45465300	3.48297200	5.01269300
C	-1.83041400	5.46776700	3.17705600
H	-0.98048600	5.23620600	3.82949900
H	-1.43503000	5.82644100	2.21806000
H	-2.38563100	6.29105600	3.64231600
C	-3.95885400	4.70861900	2.14217100
H	-3.65409800	5.09152200	1.15930000
H	-4.68800200	3.90064500	1.99811100
H	-4.47959500	5.52320800	2.65796600
C	-4.77872700	0.61501600	-3.32434600
C	-5.41443900	-0.77708700	-3.45472800

H	-4.80356900	-1.45726600	-4.05965400
H	-5.56732200	-1.24089400	-2.47144200
H	-6.39197300	-0.69026000	-3.94420100
C	-4.53491300	1.20979400	-4.71840300
H	-4.07027000	2.20172800	-4.65185100
H	-3.89238600	0.57278200	-5.33746000
H	-5.49148900	1.32045100	-5.24315400
C	-5.74515200	1.52413700	-2.56855700
H	-5.98596200	1.13229700	-1.57165500
H	-5.35556900	2.54538900	-2.46395500
H	-6.68686200	1.59329800	-3.12433400
N	-0.35617300	-1.84386500	1.03991300
N	1.89453700	0.90757300	-1.03159000
C	-3.56601200	-3.76408000	1.00154900
F	-3.57124100	-5.07866200	0.74040300
F	-4.00746200	-3.13119500	-0.10005700
F	-4.47467800	-3.56012300	1.96890600
C	2.72597700	4.55891700	-1.28701500
F	2.35502300	5.21752300	-2.39300800
F	1.88019400	4.90271200	-0.30660100
F	3.94218900	5.00206100	-0.95315500
F	2.05664400	-2.98257100	4.42942200
F	5.25620900	0.03063300	2.85217900

F	1.96691700	-5.15664900	-2.19237800
F	4.11475500	-1.37994700	-3.85934600

Geometry of Ir^{II} in Cartesian Coordinates and in Angstroms:

Ir	0.81484900	-0.05267700	0.00122400
C	-0.87580400	-0.92762400	-2.49429700
C	-2.11645500	-0.10964000	-0.67154300
C	-2.00850300	-1.21057500	-3.22150700
H	0.11424200	-1.13457300	-2.90288200
C	-3.31092600	-0.39006100	-1.39203400
C	-3.28829800	-0.94104300	-2.65137300
H	-1.90285200	-1.63718800	-4.21488400
H	-4.26040400	-0.17470100	-0.91177700
C	-2.08353600	0.43692400	0.64281600
C	-0.75501700	1.06693400	2.47829500
C	-3.23265100	0.87792000	1.35696500
C	-1.84357100	1.49317600	3.20319300
H	0.25189100	1.13668600	2.89189100
C	-3.14322200	1.40945600	2.62204700
H	-4.19941400	0.79930200	0.86957300
H	-1.68852000	1.89138200	4.20169500
N	-0.89596400	-0.40467600	-1.25600600
N	-0.83830700	0.56122600	1.23587600

C	1.95351900	1.83074900	-1.93206800
C	0.34386700	2.86206100	-0.55899200
C	2.16021600	3.04838700	-2.60019700
C	0.51401700	4.07773100	-1.19279600
H	-0.36399100	2.73273100	0.25651500
C	1.44362100	4.16902900	-2.23130700
H	2.88208800	3.10150000	-3.40486400
H	1.59918100	5.11639000	-2.74342100
C	2.23288400	-0.51787400	-1.34713700
C	2.61930800	0.56478300	-2.18980700
C	2.83470100	-1.76586200	-1.53660800
C	3.58042200	0.33221300	-3.18186400
H	2.58343800	-2.62485700	-0.91642500
C	4.17483800	-0.89688900	-3.38072900
H	4.91631700	-1.04600800	-4.15790900
N	1.04475600	1.77507500	-0.91304500
C	1.59929300	-2.09020700	1.95597000
C	-0.11537500	-2.86097400	0.53997300
C	1.59274100	-3.32167200	2.63154500
C	-0.15475300	-4.08561600	1.17840800
H	-0.77192800	-2.62785900	-0.29542500
C	0.71840300	-4.31681900	2.24323800
H	2.27527900	-3.48352100	3.45561900

H	0.70679300	-5.27370700	2.76096700
C	2.26282900	0.18314900	1.37860600
C	2.45289000	-0.94585900	2.22785400
C	3.05370900	1.31858600	1.58502600
C	3.41941300	-0.87151700	3.23825800
H	2.95892100	2.20761600	0.96366800
C	4.20020600	0.24545900	3.45275900
H	4.94113600	0.27347200	4.24387500
N	0.73649000	-1.89519400	0.91472800
C	-4.54505200	-1.27910800	-3.44013700
C	-5.82278100	-0.92284200	-2.68409900
H	-5.88153300	0.15164800	-2.46651200
H	-6.69607300	-1.18541600	-3.29412100
H	-5.90282800	-1.47374800	-1.73795700
C	-4.53562900	-0.50019800	-4.76229900
H	-3.66505800	-0.74862300	-5.38050500
H	-5.43650200	-0.73460100	-5.34500400
H	-4.51887600	0.58176300	-4.57790000
C	-4.56193000	-2.78577300	-3.73136200
H	-3.69221400	-3.10054300	-4.32008000
H	-4.56072300	-3.36325400	-2.79781700
H	-5.46391100	-3.05197000	-4.29846400
C	-4.34680800	1.90905400	3.40780000

C	-4.14327700	3.39099100	3.75188300
H	-5.01064800	3.77111600	4.30787400
H	-3.25374400	3.55215600	4.37212100
H	-4.03007900	3.99224800	2.84039400
C	-5.65260600	1.77624800	2.62707200
H	-5.63310200	2.35781500	1.69616000
H	-5.87757500	0.73063100	2.37942600
H	-6.48299200	2.15550600	3.23573500
C	-4.47519200	1.09518000	4.70217100
H	-3.58229700	1.18130600	5.33275100
H	-5.33398300	1.44877400	5.28836500
H	-4.62826800	0.03111700	4.47996000
C	3.99015000	1.32559900	2.60382200
C	3.77752700	-1.92698500	-2.53652900
C	-0.27559400	5.28472800	-0.79744700
F	-1.01280300	5.74169100	-1.82420600
F	0.53166500	6.29511000	-0.43148900
F	-1.10721600	5.04402700	0.22006500
F	4.34432200	-3.12863600	-2.70998500
F	3.96496900	1.33091300	-3.99970800
C	-1.11062200	-5.15597400	0.75689400
F	-1.92548100	-5.50527500	1.76690000
F	-0.46055600	-6.27344400	0.39035300

F	-1.87903900	-4.78168100	-0.26992200
F	4.74084800	2.42028000	2.79099900
F	3.62265900	-1.92108500	4.05826400

Geometry of deprotonated acid in Cartesian Coordinates and in Angstroms:

C	3.02649500	-0.52311200	0.06261100
C	2.00957700	-1.48306000	0.01188700
C	0.66974400	-1.08797900	-0.03487600
C	0.33366900	0.27408500	-0.03506200
C	1.35843300	1.23078100	0.01318000
C	2.69690700	0.83810200	0.06355400
H	4.06865400	-0.83286400	0.10098000
H	2.26087400	-2.54119400	0.00696700
H	-0.12432700	-1.82657300	-0.08910500
H	1.07492800	2.27948200	0.00984900
H	3.48393400	1.58829300	0.10434900
C	-1.10989100	0.73547700	-0.07317000
O	-1.36178200	1.93348800	-0.19547200
C	-2.19091000	-0.35712600	0.04023700
O	-2.41593300	-0.95345500	-1.04482600
O	-2.66331000	-0.53380200	1.18739800

Geometry of acid radical in Cartesian Coordinates and in Angstroms:

C	-3.20799000	-1.01422100	0.00011900
C	-1.97887800	-1.68101200	-0.00006200
C	-0.79042700	-0.94870900	-0.00019300
C	-0.83670600	0.45354600	-0.00012400
C	-2.07537100	1.12421400	0.00014800
C	-3.25664100	0.38668900	0.00024700
H	-4.13225500	-1.58522400	0.00023500
H	-1.94772800	-2.76638000	-0.00012400
H	0.17401500	-1.44703900	-0.00034400
H	-2.09179500	2.20975000	0.00021400
H	-4.21550800	0.89705300	0.00043600
C	0.43000400	1.21742200	-0.00025800
O	0.59350100	2.40111100	-0.00024600
C	3.53005700	-0.61980200	0.00009400
O	4.25440000	0.29677200	0.00041200
O	2.81822300	-1.54999900	-0.00019600

Geometry of radical in Cartesian Coordinates and in Angstroms:

C	-2.16773200	0.26604800	0.00019100
C	-1.70934400	-1.04978600	-0.00003200
C	-0.34194400	-1.30321900	-0.00016500
C	0.56102500	-0.23804800	-0.00007600
C	0.09932700	1.08524900	0.00014900

C	-1.26635800	1.33287100	0.00028200
H	-3.23725300	0.46461600	0.00029700
H	-2.41752700	-1.87458700	-0.00010100
H	0.04473700	-2.32062900	-0.00033900
H	0.82299400	1.89775700	0.00021300
H	-1.63477000	2.35612600	0.00045600
C	2.00796400	-0.51827800	-0.00021400
O	2.91552400	0.25346200	-0.00016800

Geometry of B in Cartesian Coordinates and in Angstroms:

C	-0.75703400	0.20678100	0.06707900
C	-2.55132800	1.46086800	0.74026400
C	-3.43281900	0.41339100	0.52606700
C	-2.95383700	-0.81844000	0.06083000
C	-1.58142300	-0.89813100	-0.16716700
C	0.69682400	0.14375700	-0.20431800
C	2.57743400	1.20591800	-0.96789600
C	3.37772600	0.11520300	-0.66780200
C	2.81129600	-1.03771400	-0.10882200
C	1.43546100	-0.99967000	0.11161000
H	-2.91032000	2.41854300	1.11522600
H	-4.49076700	0.56585200	0.73015800
H	-1.13445400	-1.80737000	-0.56085900

H	3.00575400	2.09773000	-1.42363900
H	4.44374900	0.17156600	-0.87930400
H	0.92066700	-1.84201300	0.56710700
N	-1.23258000	1.37694900	0.52617800
N	1.25546200	1.24458100	-0.74236100
C	-3.91067600	-1.97662500	-0.19026000
C	-4.65360500	-2.31110700	1.10962300
H	-5.33972700	-3.15219600	0.94477600
H	-3.94964100	-2.59497600	1.90235500
H	-5.24748200	-1.46494400	1.47456800
C	-4.92147800	-1.56757900	-1.26952800
H	-5.51508900	-0.69635400	-0.96782400
H	-4.41177700	-1.31699500	-2.20864900
H	-5.61711100	-2.39377100	-1.46803900
C	-3.18394500	-3.23373400	-0.66402300
H	-2.66127900	-3.07088800	-1.61539700
H	-2.45428300	-3.58784600	0.07605700
H	-3.91166400	-4.03925400	-0.82178000
C	3.68341000	-2.23504700	0.24437500
C	4.72211600	-1.80801100	1.28981600
H	5.38204200	-1.01676100	0.91452700
H	4.23205600	-1.43359500	2.19760800
H	5.35099400	-2.66408400	1.56857300

C	4.39864100	-2.73333200	-1.01781800
H	3.67493000	-3.04409100	-1.78227600
H	5.04297400	-1.96351400	-1.45856700
H	5.03093400	-3.59745300	-0.77472000
C	2.87023100	-3.39222200	0.82204600
H	2.36800300	-3.11371500	1.75744900
H	2.11178700	-3.75275900	0.11470400
H	3.53820500	-4.23329800	1.04559000
Pd	0.23085600	3.12990500	0.06046000

Geometry of C in Cartesian Coordinates and in Angstroms:

C	0.47799000	0.73182200	0.19928600
C	-1.64235000	1.32397400	0.78810000
C	-1.42505300	2.65931900	0.45302100
C	-0.17645800	3.05527800	-0.02556500
C	0.78539400	2.04626600	-0.14733100
C	1.48281400	-0.34310800	0.01659200
C	1.97803500	-2.47299400	-0.68839500
C	3.31411300	-2.32718800	-0.35952600
C	3.77577800	-1.12430100	0.19018200
C	2.81869400	-0.12890700	0.36932500
H	-2.61463500	1.00893600	1.17336600
H	-2.23709400	3.37001800	0.57831100

H	1.77274900	2.26926900	-0.54923700
H	1.60814800	-3.39841800	-1.12334600
H	3.98859600	-3.16213100	-0.53752000
H	3.08359700	0.82717600	0.81328200
N	-0.72414500	0.36742300	0.67399700
N	1.05796000	-1.50840700	-0.51016800
C	0.15593400	4.48857900	-0.42261800
C	-1.02058800	5.43514500	-0.19153700
H	-0.73626600	6.45316600	-0.48591200
H	-1.89701400	5.15076400	-0.78802100
H	-1.31757400	5.46606100	0.86481700
C	1.34305500	4.98401800	0.41296800
H	1.10824100	4.95256200	1.48472600
H	2.24261600	4.37918200	0.24762600
H	1.58554900	6.02141800	0.14668900
C	0.52349500	4.52915200	-1.91143100
H	1.39637500	3.90501700	-2.13738300
H	-0.31072700	4.17498600	-2.53037600
H	0.76065800	5.55831800	-2.21266900
C	5.24182700	-0.95717400	0.56593400
C	6.10476700	-1.12899400	-0.69079500
H	5.97636100	-2.11857900	-1.14495800
H	5.84963800	-0.37631600	-1.44784500

H	7.16695900	-1.01295800	-0.43765000
C	5.62240300	-2.02440600	1.60028800
H	5.00577800	-1.93310000	2.50351200
H	5.49538700	-3.04024700	1.20776200
H	6.67480500	-1.90843700	1.89145000
C	5.53274000	0.41737000	1.16451900
H	5.30433200	1.22780900	0.46009200
H	4.96527200	0.59111200	2.08795200
H	6.59863000	0.48857200	1.41392800
Pd	-1.01458900	-1.94217900	-0.74001000
C	-4.01872900	-1.61833700	-0.13332500
C	-3.71249500	-1.69032700	1.22341100
C	-5.06960400	-0.83035700	-0.59087000
C	-4.47989300	-0.96747800	2.12801100
H	-2.85797600	-2.28968600	1.53311000
C	-5.82665100	-0.10427400	0.32803000
H	-5.29257400	-0.77861700	-1.65628100
C	-5.53938400	-0.17065700	1.68796700
H	-4.24171300	-1.01992500	3.18801200
H	-6.64707400	0.51481400	-0.02811500
H	-6.13364400	0.39483000	2.40136300
O	-3.24494800	-2.36311700	-0.98921400
H	-3.47843700	-2.17808800	-1.90674700

Geometry of D in Cartesian Coordinates and in Angstroms:

C	0.41858200	0.68166300	-0.19131300
C	-1.84453900	1.06609300	-0.43338600
C	-1.66438100	2.43929900	-0.37543400
C	-0.38006100	2.97027700	-0.21701000
C	0.66798600	2.05439100	-0.12711000
C	1.49532700	-0.33375300	-0.10204500
C	2.06878600	-2.57652300	-0.16098200
C	3.40699100	-2.29216900	0.03555500
C	3.82744100	-0.96463000	0.17821400
C	2.83429400	0.00874700	0.10164600
H	-2.83713200	0.62781400	-0.54505700
H	-2.53774800	3.08208800	-0.45032600
H	1.68575500	2.41000700	-0.01039000
H	1.71846700	-3.59841500	-0.26943000
H	4.11282800	-3.11793900	0.07939400
H	3.09838100	1.05557500	0.20505400
N	-0.82847600	0.20451300	-0.34234500
N	1.12232500	-1.62756800	-0.22712100
C	-0.17322900	4.47869000	-0.15240100
C	-0.68010900	5.10864900	-1.45624800
H	-0.53790200	6.19654000	-1.42610300

H	-0.13192600	4.71716400	-2.32272000
H	-1.74708100	4.91752200	-1.61907500
C	-0.96465800	5.04197300	1.03532200
H	-2.04063800	4.85627700	0.94094400
H	-0.62787100	4.59691800	1.98029800
H	-0.81902100	6.12801500	1.09943800
C	1.29563700	4.85779700	0.02593700
H	1.71175100	4.46112200	0.96142300
H	1.91485300	4.50694100	-0.81009500
H	1.38739600	5.94981900	0.06499400
C	5.29820400	-0.64022400	0.40110600
C	6.10350700	-1.12837500	-0.81034000
H	6.00940100	-2.21056200	-0.95829600
H	5.77061000	-0.63221700	-1.73087900
H	7.16802900	-0.90273100	-0.66683100
C	5.78469800	-1.35689700	1.66744900
H	5.20877600	-1.04010700	2.54621300
H	5.70110300	-2.44664300	1.58483900
H	6.84079400	-1.11903100	1.84832200
C	5.54286300	0.85754000	0.57316500
H	5.25405900	1.42790100	-0.31920200
H	5.00413400	1.26403100	1.43900600
H	6.61208900	1.03408900	0.74053300

Pd	-0.90280100	-2.01894000	-0.48975400
C	-3.72404900	-1.68864700	-0.06763400
C	-3.46460700	-1.41254300	1.29459000
C	-4.96235500	-1.24989000	-0.59417200
C	-4.37833100	-0.70670600	2.07025300
H	-2.52082100	-1.76147400	1.71682800
C	-5.86782800	-0.55148500	0.19395000
H	-5.17442300	-1.47190300	-1.63847500
C	-5.58570000	-0.26085900	1.53146100
H	-4.14387000	-0.50477800	3.11504700
H	-6.80999800	-0.22261700	-0.24360900
H	-6.29725300	0.28987600	2.14236400
O	-2.88136500	-2.31511200	-0.85925800
H	-0.77674800	-3.55425000	-0.58863900

Geometry of E in Cartesian Coordinates and in Angstroms:

C	2.02612700	-0.76452300	-0.50079000
C	0.88329900	-2.74758500	-0.19820900
C	2.03899800	-3.42315500	0.14204900
C	3.26524900	-2.74645000	0.16441000
C	3.22778200	-1.39521900	-0.16707300
C	1.99664500	0.67637600	-0.85083500
C	1.04484100	2.32912800	-2.09606300

C	1.78775700	3.31078800	-1.45438700
C	2.69387900	2.95259600	-0.45032600
C	2.79908600	1.59188500	-0.16547900
H	-0.07766900	-3.25496200	-0.22301300
H	1.97200800	-4.48112600	0.38339300
H	4.13928400	-0.80518800	-0.19968500
H	0.32984400	2.59531700	-2.87422500
H	1.63703600	4.35211100	-1.73099900
H	3.45350200	1.23992000	0.62785900
N	0.86173000	-1.44193000	-0.51520100
N	1.13548400	1.03229200	-1.80583400
C	4.54832800	-3.48484600	0.51762100
C	4.40824900	-4.09225200	1.91945400
H	5.32827800	-4.62715900	2.18795200
H	4.23608500	-3.31227000	2.67206200
H	3.57967200	-4.80756500	1.97950100
C	4.77644300	-4.60218200	-0.50913800
H	3.95334300	-5.32627900	-0.51831400
H	4.87568600	-4.19101700	-1.52173500
H	5.69834200	-5.14826800	-0.27069500
C	5.76597600	-2.56325600	0.51056300
H	5.94178200	-2.12169500	-0.47883200
H	5.66754900	-1.75058100	1.24204600

H	6.66070800	-3.13875400	0.77685400
C	3.45946400	4.02393200	0.31481600
C	2.44450600	4.89272000	1.07063200
H	1.75432700	5.40013400	0.38658100
H	1.84382600	4.28289800	1.75783100
H	2.96633200	5.66220600	1.65493500
C	4.25576800	4.89196100	-0.66662000
H	4.98655000	4.29007700	-1.22215100
H	3.60769200	5.39118600	-1.39591100
H	4.80182500	5.67233500	-0.12058900
C	4.43365900	3.42784100	1.32847800
H	3.91661200	2.83777100	2.09600100
H	5.18656400	2.79010400	0.84629400
H	4.96657500	4.23781900	1.84153200
Pd	-0.98129300	-0.50373700	-0.96736400
C	-1.13886400	0.61124200	0.93591500
O	-0.29690200	1.44794400	1.11052600
C	-2.33412800	0.36812700	1.75943100
C	-3.04603200	-0.82891600	1.65724800
C	-2.78333800	1.38879500	2.60894500
C	-4.20074100	-1.01256700	2.40859900
H	-2.69012300	-1.60067100	0.97688300
C	-3.94547900	1.20521500	3.34445300

H	-2.22130200	2.31826600	2.66558900
C	-4.65257200	0.00534300	3.24428000
H	-4.76303500	-1.93857100	2.31744900
H	-4.30774300	1.99794600	3.99502400
H	-5.56854000	-0.13059400	3.81504500
O	-2.69460300	0.50433700	-1.38104900
C	-3.91483200	0.01979000	-1.26354100
C	-4.24350400	-1.34828400	-1.36772000
C	-4.97244400	0.92582500	-1.01919900
C	-5.55823900	-1.78165400	-1.23571000
H	-3.43582100	-2.05471800	-1.56165800
C	-6.28017100	0.48022400	-0.88553000
H	-4.72498600	1.98292300	-0.93966000
C	-6.59080500	-0.87808900	-0.98697600
H	-5.77828200	-2.84461600	-1.33028700
H	-7.07117800	1.20485800	-0.69623200
H	-7.61701400	-1.22275000	-0.88217100
H	-1.32615500	-1.67483400	-2.00230000

Geometry of F in Cartesian Coordinates and in Angstroms:

C	0.73726100	0.15863000	-0.07899000
C	2.65805500	1.38333200	-0.39028100
C	3.45745300	0.25595200	-0.28041600

C	2.87098400	-0.99282700	-0.04126700
C	1.48113500	-1.01753700	0.06163600
C	-0.74323900	0.17450000	0.02018300
C	-2.65122100	1.42520700	0.29362000
C	-3.46422700	0.30620800	0.21932700
C	-2.89162800	-0.95611300	0.02387700
C	-1.50262600	-0.99586000	-0.07558000
H	3.08625200	2.37067800	-0.55904500
H	4.53584000	0.36324300	-0.37342300
H	0.96834000	-1.95088400	0.27176600
H	-3.07891200	2.41633400	0.43770000
H	-4.54106900	0.43075100	0.30659200
H	-0.99823400	-1.94080100	-0.25031200
N	1.32795100	1.34193900	-0.29574400
N	-1.31888700	1.37577700	0.19668300
C	3.74026900	-2.23622600	0.10310300
C	4.54053200	-2.44004800	-1.19000100
H	5.16684800	-3.33773100	-1.10633600
H	3.87061900	-2.57052300	-2.04954000
H	5.20118800	-1.59200600	-1.40486300
C	4.70390400	-2.04237100	1.28094300
H	5.36396200	-1.17928100	1.13522400
H	4.15428500	-1.89050500	2.21865700

H	5.33749500	-2.93132200	1.39703700
C	2.91535700	-3.49613500	0.35988700
H	2.33287500	-3.42332100	1.28758700
H	2.22751800	-3.71224100	-0.46799900
H	3.58715700	-4.35719800	0.46103600
C	-3.77265400	-2.19409300	-0.08275200
C	-4.71917600	-2.03314600	-1.27939800
H	-5.36929500	-1.15639600	-1.17604900
H	-4.15571400	-1.92521400	-2.21499200
H	-5.36320100	-2.91756100	-1.36907100
C	-4.59113100	-2.34109200	1.20653600
H	-3.93418400	-2.44314700	2.07976500
H	-5.24870800	-1.48115100	1.37977000
H	-5.22348700	-3.23652700	1.14899300
C	-2.95821200	-3.47100600	-0.28231100
H	-2.36548500	-3.43997400	-1.20579600
H	-2.28121600	-3.66174900	0.56056800
H	-3.63776900	-4.32857100	-0.35739800
Pd	0.00957900	3.20621000	0.03217500
H	0.99581200	4.46116700	-0.14517800

Geometry of G in Cartesian Coordinates and in Angstroms:

C	0.66387700	0.08913500	-0.35224700

C	2.63494700	1.15105500	-0.92429300
C	3.38462300	0.02566800	-0.65922500
C	2.75451300	-1.13822000	-0.14450500
C	1.38194100	-1.07071100	0.01243800
C	-0.76483700	0.20291900	-0.15884500
C	-2.54241100	1.61315800	0.27935300
C	-3.46148700	0.57925500	0.22802000
C	-3.00644800	-0.73781400	-0.01541200
C	-1.64665600	-0.89808300	-0.22012900
H	3.10979000	2.07193900	-1.26546100
H	4.45890200	0.05400800	-0.83869600
H	0.83272300	-1.89658800	0.46233000
H	-2.86665000	2.63609500	0.47779300
H	-4.51509700	0.79699500	0.39375700
H	-1.23357900	-1.87094200	-0.47667900
N	1.29428700	1.21895300	-0.80662500
N	-1.22356200	1.45560800	0.13460200
C	3.59168600	-2.35203900	0.23314700
C	4.35330800	-2.85191300	-1.00171300
H	4.97538900	-3.72195800	-0.74491700
H	3.65356400	-3.14901900	-1.79367700
H	5.01202400	-2.07805200	-1.41417100
C	4.59907900	-1.96431500	1.32488400

H	5.27360700	-1.16786400	0.98908100
H	4.07579100	-1.59893000	2.21751000
H	5.21224600	-2.83192200	1.61244300
C	2.74283500	-3.50588800	0.76225200
H	2.20403400	-3.22691600	1.67673000
H	2.00576500	-3.83881100	0.01956900
H	3.38882700	-4.36141000	1.00279100
C	-4.00549000	-1.88825300	-0.07077500
C	-5.04912100	-1.61462600	-1.16150000
H	-5.60868100	-0.69143900	-0.96909400
H	-4.56610200	-1.51282000	-2.14203000
H	-5.77191800	-2.44157500	-1.21543000
C	-4.71038900	-2.01011300	1.28680100
H	-3.98184300	-2.21298900	2.08241500
H	-5.24347000	-1.08884000	1.55086700
H	-5.44113300	-2.83174000	1.26735900
C	-3.33957400	-3.22773500	-0.37974200
H	-2.84306800	-3.21849900	-1.35876800
H	-2.59324000	-3.49501400	0.37929500
H	-4.09854500	-4.02193200	-0.39615400
Pd	0.37010100	3.05270300	0.18469200
H	1.55858900	4.14308800	0.46041800

Geometry of H in Cartesian Coordinates and in Angstroms:

C	-1.01380600	-0.64718800	-0.50890400
C	-0.22597900	-2.61814000	-1.37890300
C	-1.27736100	-3.33823900	-0.84373000
C	-2.25439600	-2.68358600	-0.06376000
C	-2.09071500	-1.31414600	0.09783300
C	-0.78083000	0.78150200	-0.30769100
C	0.77245000	2.46723800	-0.09512800
C	-0.20903200	3.43238000	0.04817800
C	-1.56660300	3.05620300	0.02725400
C	-1.82781400	1.70634200	-0.16650600
H	0.55467400	-3.11746800	-1.95408200
H	-1.33058900	-4.41082400	-1.02729000
H	-2.76906100	-0.74071900	0.72633200
H	1.82881600	2.73364500	-0.06996200
H	0.08993400	4.46984300	0.18719400
H	-2.84946400	1.34266000	-0.24641700
N	-0.07314300	-1.29116600	-1.24184400
N	0.52086200	1.15872000	-0.24333500
C	-3.38804100	-3.47813600	0.57243300
C	-4.19851400	-4.18007900	-0.52489200
H	-5.02251200	-4.75773700	-0.08162100
H	-4.62675100	-3.44674100	-1.22096100

H	-3.57980400	-4.87161900	-1.10944500
C	-2.80403700	-4.53048500	1.52402900
H	-2.14243800	-5.22969300	0.99864600
H	-2.21577000	-4.05162100	2.31724000
H	-3.61030700	-5.11293400	1.99355400
C	-4.34187900	-2.59105600	1.37079800
H	-3.82871400	-2.08257400	2.19712600
H	-4.81051000	-1.82705800	0.73637000
H	-5.14338500	-3.20554000	1.80264500
C	-2.65698100	4.10800900	0.18812100
C	-2.52613700	5.15772400	-0.92284700
H	-1.55535900	5.66661800	-0.89070100
H	-2.62503700	4.69112100	-1.91155100
H	-3.31035200	5.92161800	-0.82128400
C	-2.50378600	4.79028300	1.55382600
H	-2.59804500	4.05705600	2.36530400
H	-1.52697400	5.27777800	1.65853200
H	-3.28034100	5.55688500	1.68852700
C	-4.05898400	3.50608500	0.11105300
H	-4.23973600	3.02243500	-0.85785100
H	-4.22495200	2.76179200	0.90088000
H	-4.80903600	4.29860900	0.23490200
Pd	2.06744400	-0.39984000	-0.55806000

H	3.25778000	-1.56185600	-0.57400900
H	4.17013100	-1.03272400	0.48568700
O	4.91116700	-0.98340100	1.20788100
C	5.93817100	-0.25803000	0.88745100
O	6.91293200	-0.06172300	1.59224500
O	5.84859900	0.29165600	-0.35201100
H	6.66540500	0.79648900	-0.45736300

Geometry of J in Cartesian Coordinates and in Angstroms:

C	1.93438500	-0.88500000	-0.46010100
C	0.91832800	-2.82022600	0.26518600
C	2.12570600	-3.38353900	0.63302300
C	3.31833200	-2.67353400	0.43469700
C	3.19068200	-1.41092100	-0.12890200
C	1.83141300	0.46610600	-1.05613200
C	0.77557800	1.86412100	-2.50381400
C	1.48955100	2.96380700	-2.05161100
C	2.45632400	2.79630100	-1.04897300
C	2.63749200	1.50498600	-0.57412300
H	-0.01859600	-3.35711800	0.39095900
H	2.12299000	-4.38227000	1.06486900
H	4.06466400	-0.80405800	-0.34893100
H	0.02112700	1.97925700	-3.28296600

H	1.26862000	3.94643200	-2.46528500
H	3.31169400	1.30035200	0.25301500
N	0.80624100	-1.59193100	-0.26653600
N	0.93002600	0.62975900	-2.02247400
C	4.65919300	-3.29359300	0.80716800
C	4.65623300	-3.64655300	2.29964200
H	5.62157100	-4.08596000	2.58709000
H	4.48876800	-2.75139100	2.91207200
H	3.87191400	-4.37149100	2.54735400
C	4.87281100	-4.56708400	-0.02107800
H	4.08662500	-5.30943600	0.16084800
H	4.87313900	-4.33686000	-1.09430600
H	5.83778300	-5.02800000	0.23250500
C	5.82927100	-2.34814700	0.54144100
H	5.90761000	-2.08390200	-0.52098800
H	5.74302400	-1.41997400	1.12114500
H	6.76840400	-2.83687700	0.83188400
C	3.16783300	4.00302800	-0.45107100
C	2.12105100	4.84222800	0.29470400
H	1.35452200	5.23056200	-0.38691400
H	1.61295600	4.22953400	1.05079400
H	2.59949200	5.69710200	0.79401600
C	3.82032000	4.84147300	-1.55509600

H	4.57118700	4.25453000	-2.10091100
H	3.08814500	5.20927200	-2.28399200
H	4.32133400	5.71634700	-1.11745100
C	4.25353400	3.60081100	0.54631600
H	3.83366200	3.07250200	1.41135300
H	5.01424300	2.95823600	0.08237000
H	4.75845200	4.50097900	0.92145400
Pd	-1.12155800	-0.84424000	-0.60243100
C	-0.78596100	0.64564500	0.90613700
O	0.34925500	1.04375500	1.18300400
C	-1.92690700	1.27879200	1.66814900
C	-3.12457700	0.58988800	1.86563100
C	-1.79453200	2.57128500	2.18608700
C	-4.17157300	1.17843500	2.56979400
H	-3.23065900	-0.41116900	1.45253100
C	-2.84423400	3.17152800	2.87410700
H	-0.84888200	3.09073900	2.03398800
C	-4.03731500	2.47296600	3.06893700
H	-5.10243100	0.63019600	2.70625800
H	-2.73662200	4.18453300	3.26204300
H	-4.86342500	2.94174200	3.60254600
O	-3.00729600	-0.07601700	-1.00405300
C	-4.11149500	-0.75944500	-0.97978500

C	-4.20114500	-2.13662600	-0.64990400
C	-5.33817900	-0.09477400	-1.25907000
C	-5.42625000	-2.79399300	-0.61930800
H	-3.26672000	-2.65993100	-0.44276600
C	-6.55182900	-0.76544400	-1.22303100
H	-5.28645100	0.96655600	-1.49892500
C	-6.61931100	-2.12649500	-0.90443200
H	-5.44868200	-3.85491800	-0.36477600
H	-7.46807700	-0.21572800	-1.44503000
H	-7.57454600	-2.64828200	-0.87569000
H	-1.34308900	-2.03933100	-1.73441800

Geometry of TS1 in Cartesian Coordinates and in Angstroms:

C	1.09168900	0.80215300	-0.04734100
C	-0.42265100	2.52562200	0.03730200
C	0.58473900	3.48350000	0.11142800
C	1.91917300	3.07844600	0.08983200
C	2.15435700	1.70167200	0.00508500
C	1.28855300	-0.66733600	-0.12925100
C	0.35954500	-2.73327400	-0.54896700
C	1.55524300	-3.38265400	-0.29647500
C	2.68689300	-2.64428600	0.06751700
C	2.52220700	-1.26342400	0.14627200

H	-1.47265700	2.81725000	0.03656200
H	0.30921600	4.53177300	0.17482000
H	3.17683400	1.33480700	-0.04185500
H	-0.53120100	-3.28942100	-0.82975300
H	1.58953500	-4.46610600	-0.38105200
H	3.35548200	-0.63643900	0.44615500
N	-0.18435000	1.22048400	-0.03887600
N	0.21341900	-1.40312500	-0.46829800
C	3.08888200	4.05400700	0.13900200
C	2.62092800	5.50247200	0.26419800
H	3.49289000	6.16673200	0.29932900
H	2.00725000	5.81039700	-0.59200900
H	2.04284300	5.66723800	1.18256000
C	3.97378100	3.72720900	1.34869300
H	3.40402100	3.79755200	2.28404200
H	4.40140500	2.71918500	1.28912900
H	4.80892900	4.43742100	1.40480700
C	3.90770500	3.91983200	-1.15163000
H	4.31844100	2.91086100	-1.27784000
H	3.29300800	4.14557500	-2.03224000
H	4.75089000	4.62264400	-1.13589700
C	4.00453200	-3.34615900	0.36711100
C	4.44294700	-4.14193800	-0.86889900

H	3.71578600	-4.91552700	-1.14186100
H	4.57452300	-3.48203300	-1.73581900
H	5.40045000	-4.64115800	-0.67206300
C	3.80465300	-4.29991300	1.55207500
H	3.48564800	-3.75243700	2.44816300
H	3.05133400	-5.06832400	1.34185800
H	4.74752000	-4.81238900	1.78304600
C	5.11682300	-2.36171500	0.72455500
H	5.33043500	-1.66690300	-0.09824300
H	4.87577800	-1.77721200	1.62203600
H	6.04037000	-2.91512400	0.93325500
Pd	-1.71717500	-0.45390600	-0.68928100
C	-4.70083000	-0.18298800	-0.27699600
C	-4.42922300	-0.51461000	1.05959500
C	-6.01677100	0.17189500	-0.62514600
C	-5.44202300	-0.49052600	2.01499300
H	-3.40523700	-0.78567000	1.32651000
C	-7.01616200	0.20268800	0.33879200
H	-6.22242200	0.42461600	-1.66316100
C	-6.74191800	-0.12987900	1.66719400
H	-5.20749300	-0.75317700	3.04555800
H	-8.02663400	0.48663100	0.04841200
H	-7.52931300	-0.10717800	2.41702000

O	-3.77403800	-0.17322400	-1.24197600
H	-2.91718800	-1.32441500	-1.22218000

Geometry of TS2 in Cartesian Coordinates and in Angstroms:

C	2.10124700	-0.69004800	-0.52478000
C	1.17787400	-2.79116700	-0.29842800
C	2.38358000	-3.33219300	0.10600100
C	3.52157000	-2.52099100	0.20219000
C	3.34698400	-1.17911600	-0.12479400
C	1.92550000	0.73928600	-0.87776900
C	0.95363800	2.27290600	-2.24745200
C	1.49170400	3.33127900	-1.52780200
C	2.29657500	3.07909500	-0.41327500
C	2.51908400	1.73719300	-0.10198900
H	0.28541500	-3.40553700	-0.38539500
H	2.42576200	-4.39363100	0.33763600
H	4.18097600	-0.48351300	-0.10288500
H	0.31356800	2.46300200	-3.10852400
H	1.25352400	4.34863500	-1.83077500
H	3.10852300	1.45224700	0.76565100
N	1.02351700	-1.49264600	-0.60624500
N	1.15709500	0.99329300	-1.94016800

C	4.85866500	-3.11527400	0.62229900
C	4.71202600	-3.75191600	2.01032900
H	5.67172200	-4.17879100	2.32884900
H	4.40689100	-3.00643900	2.75575500
H	3.97045900	-4.55946700	2.01880900
C	5.26683400	-4.18707700	-0.39709500
H	4.53372800	-5.00018100	-0.45605900
H	5.37219500	-3.75492600	-1.40033400
H	6.23146000	-4.62657600	-0.11190900
C	5.96473900	-2.06405100	0.68666600
H	6.14283400	-1.59492400	-0.28943200
H	5.73963000	-1.27512400	1.41603300
H	6.90243300	-2.54074200	0.99733100
C	2.82409500	4.22873200	0.43512200
C	1.62341300	4.91960000	1.09608200
H	0.93022200	5.32759900	0.35090300
H	1.05931900	4.21195200	1.71699700
H	1.96531800	5.74614900	1.73340000
C	3.57579300	5.22890500	-0.45088700
H	4.42664400	4.74951400	-0.95226400
H	2.93137800	5.66421700	-1.22293500
H	3.96136300	6.05479300	0.16103200
C	3.77632900	3.75286100	1.53065700

H	3.28096000	3.08437000	2.24624300
H	4.64971600	3.23274600	1.11493800
H	4.14412700	4.61868500	2.09494000
Pd	-0.87840500	-0.72318000	-1.14007400
C	-1.66855300	0.83211700	0.24804000
O	-1.15833500	1.91061500	0.08343300
C	-2.40483800	0.35233600	1.43727700
C	-2.69903100	-0.99608600	1.64938500
C	-2.84726100	1.31576500	2.35021400
C	-3.46080000	-1.37358400	2.74868100
H	-2.33456900	-1.73738100	0.93923100
C	-3.60489200	0.93329900	3.45079100
H	-2.60538300	2.36112400	2.16896800
C	-3.91995800	-0.41069800	3.64557200
H	-3.70264200	-2.42249600	2.90313900
H	-3.95965500	1.68444900	4.15308200
H	-4.52352400	-0.70861300	4.50022300
O	-2.68887900	0.36314300	-1.20513500
C	-3.91912700	-0.16810500	-1.04367300
C	-4.20164800	-1.50302400	-1.34885600
C	-4.94444400	0.65797500	-0.56196700
C	-5.48858700	-2.00203300	-1.17071400
H	-3.38893600	-2.12969500	-1.71767900

C	-6.22246500	0.14647500	-0.37353700
H	-4.71225300	1.69775500	-0.33720900
C	-6.50421400	-1.18668600	-0.67357700
H	-5.69714400	-3.04190900	-1.41619200
H	-7.00698400	0.79579800	0.01068600
H	-7.50526200	-1.58469500	-0.52431900
H	-1.13477500	-2.01140100	-2.11229400

Geometry of TS3 in Cartesian Coordinates and in Angstroms:

C	1.99607500	0.97555200	0.47348600
C	1.64006500	-1.21519100	1.03597000
C	2.99663800	-1.50433100	0.99445900
C	3.90152900	-0.50304300	0.63970500
C	3.37257500	0.76276400	0.39714900
C	1.43570700	2.33271400	0.25189200
C	1.81917200	4.55006600	-0.11866700
C	0.46231300	4.85766900	-0.07650300
C	-0.46341100	3.83362800	0.14076000
C	0.05672500	2.54749700	0.29454500
H	0.92403100	-1.99728100	1.29713600
H	3.32053500	-2.52410600	1.19059500
H	3.99559600	1.60984800	0.13002600
H	2.54902200	5.34460200	-0.28878400

H	0.14995700	5.89023700	-0.20994000
H	-0.58855500	1.68751600	0.45367900
N	1.12562300	-0.00518700	0.77716700
N	2.31398500	3.32844700	0.04756000
C	5.37634600	-0.82922100	0.44637700
C	5.92791300	-1.57108600	1.66859500
H	6.99086200	-1.80475900	1.51588800
H	5.83913300	-0.95664700	2.57468400
H	5.40634900	-2.51789600	1.85110200
C	5.49551700	-1.71726100	-0.80021600
H	4.96116400	-2.66641900	-0.67220700
H	5.05420000	-1.22090200	-1.67352100
H	6.55231700	-1.93933400	-1.00847900
C	6.22329400	0.42437900	0.23256500
H	5.94029200	0.95705800	-0.68349700
H	6.13777100	1.12290000	1.07579000
H	7.27947000	0.13924500	0.13639000
C	-1.96851600	4.07333200	0.17546300
C	-2.56787500	3.58570600	-1.15054400
H	-2.17091300	4.16953400	-1.99226500
H	-2.34341000	2.53010300	-1.34850600
H	-3.66100300	3.70662200	-1.13297100
C	-2.30616900	5.55485300	0.34932400

H	-1.85807100	5.97059500	1.26258500
H	-1.97506100	6.15851800	-0.50575200
H	-3.39515500	5.67160200	0.42528400
C	-2.60091500	3.30552600	1.34182900
H	-2.47424700	2.22116800	1.24746600
H	-2.16653000	3.61984500	2.30078400
H	-3.68160800	3.50181600	1.37201900
Pd	0.27909200	-0.81503300	-1.40409700
C	-1.66818900	-0.33963200	-1.16544200
O	-1.82668900	0.38958400	-2.13550300
C	-2.56114500	-0.32490400	0.02923600
C	-2.13882000	-0.74227300	1.29090500
C	-3.88335700	0.09774300	-0.15000700
C	-3.02948700	-0.74046200	2.36238000
H	-1.10530900	-1.04898000	1.42655400
C	-4.77309400	0.09316300	0.91812600
H	-4.19415500	0.41405900	-1.14460800
C	-4.34679700	-0.32792900	2.17883000
H	-2.69175400	-1.07224500	3.34219300
H	-5.80270800	0.41558200	0.76953100
H	-5.04216900	-0.33394200	3.01656100
O	-1.86885000	-2.10430600	-1.73284400
C	-1.91791300	-3.08876200	-0.85279500

C	-0.74789800	-3.67274700	-0.32365700
C	-3.15932600	-3.58618300	-0.39926200
C	-0.81834000	-4.67934300	0.63263000
H	0.21036600	-3.29746000	-0.69899200
C	-3.22006100	-4.59191800	0.55886700
H	-4.06594300	-3.13770800	-0.80410900
C	-2.05339200	-5.14470700	1.09117800
H	0.10401400	-5.10578300	1.02879500
H	-4.19231900	-4.94291400	0.90526800
H	-2.10555100	-5.92606900	1.84738900
H	1.87323100	-1.18550100	-2.04703200

Geometry of TS4 in Cartesian Coordinates and in Angstroms:

C	-1.17419000	-0.46564200	-0.46454700
C	-1.04680200	-2.58772900	-1.31032000
C	-2.27829000	-2.93137900	-0.77945400
C	-3.00754800	-1.98948500	-0.02902200
C	-2.41989300	-0.73810600	0.11922900
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C	1.51782200	1.89581100	0.03646600
C	0.90183300	3.13356100	0.10126800
C	-0.49707500	3.23055600	-0.01514000
C	-1.18226400	2.03686800	-0.21046600

H	-0.46476400	-3.31482900	-1.87790100
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H	-2.89265000	0.03663400	0.71941000
H	2.59852700	1.79095600	0.13206800
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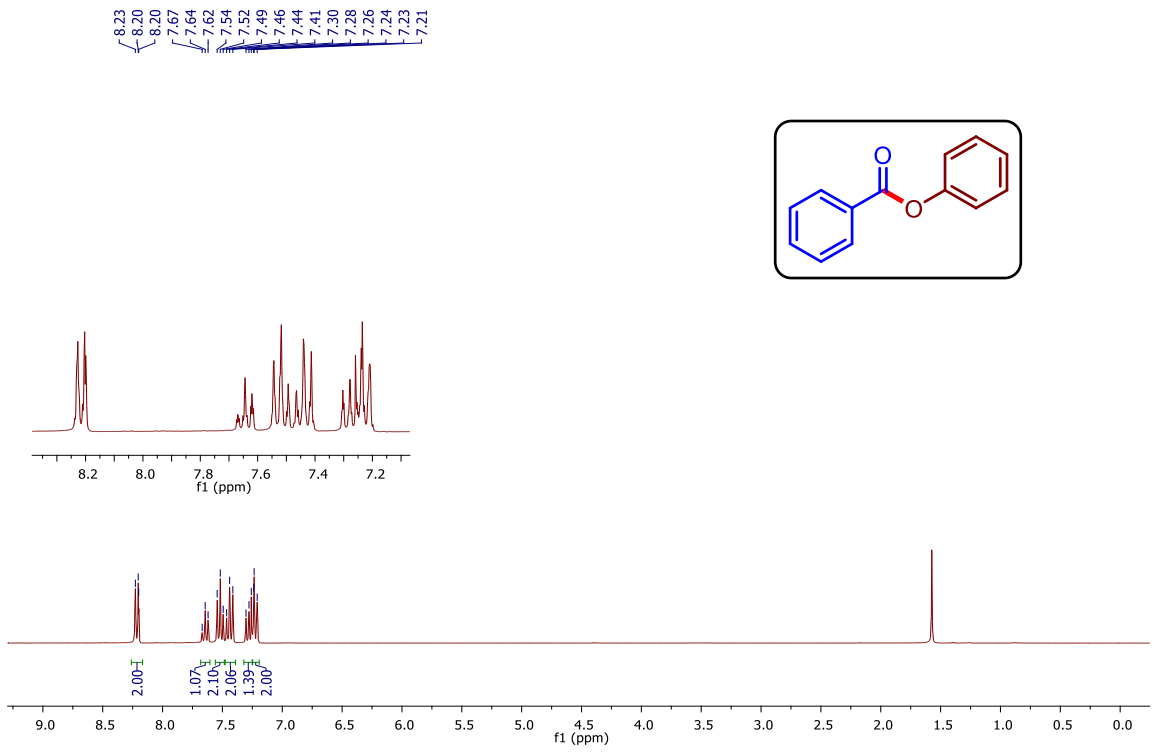

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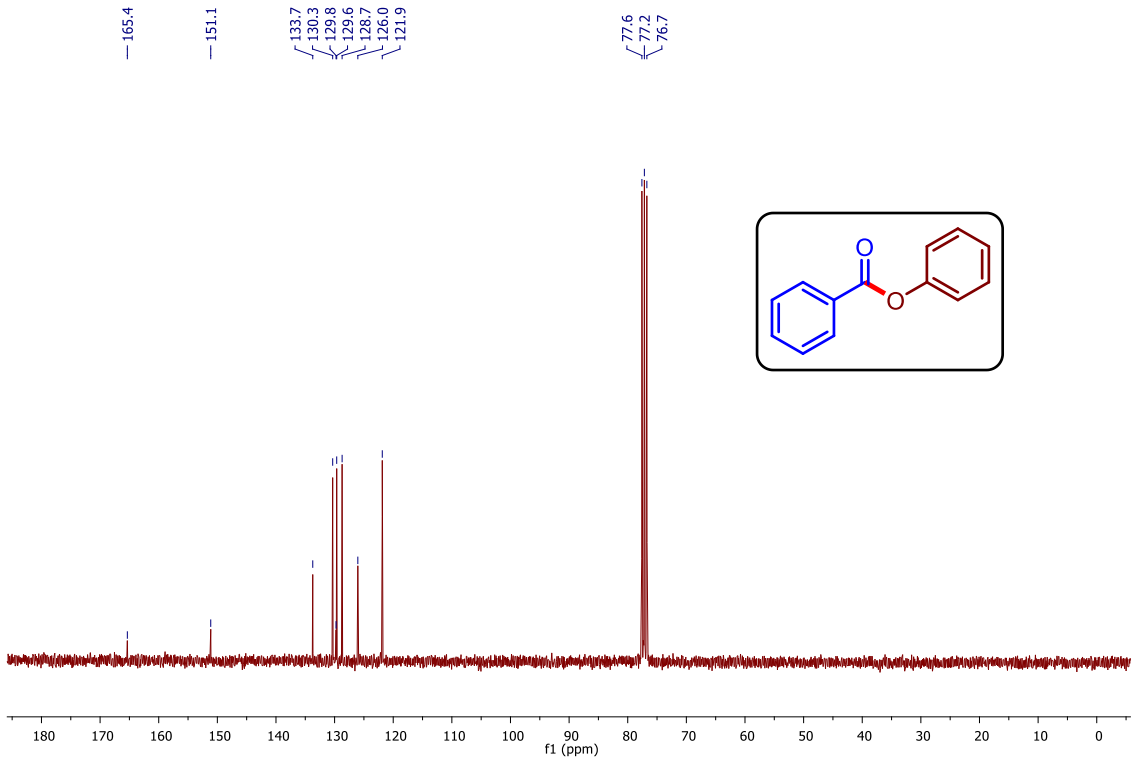

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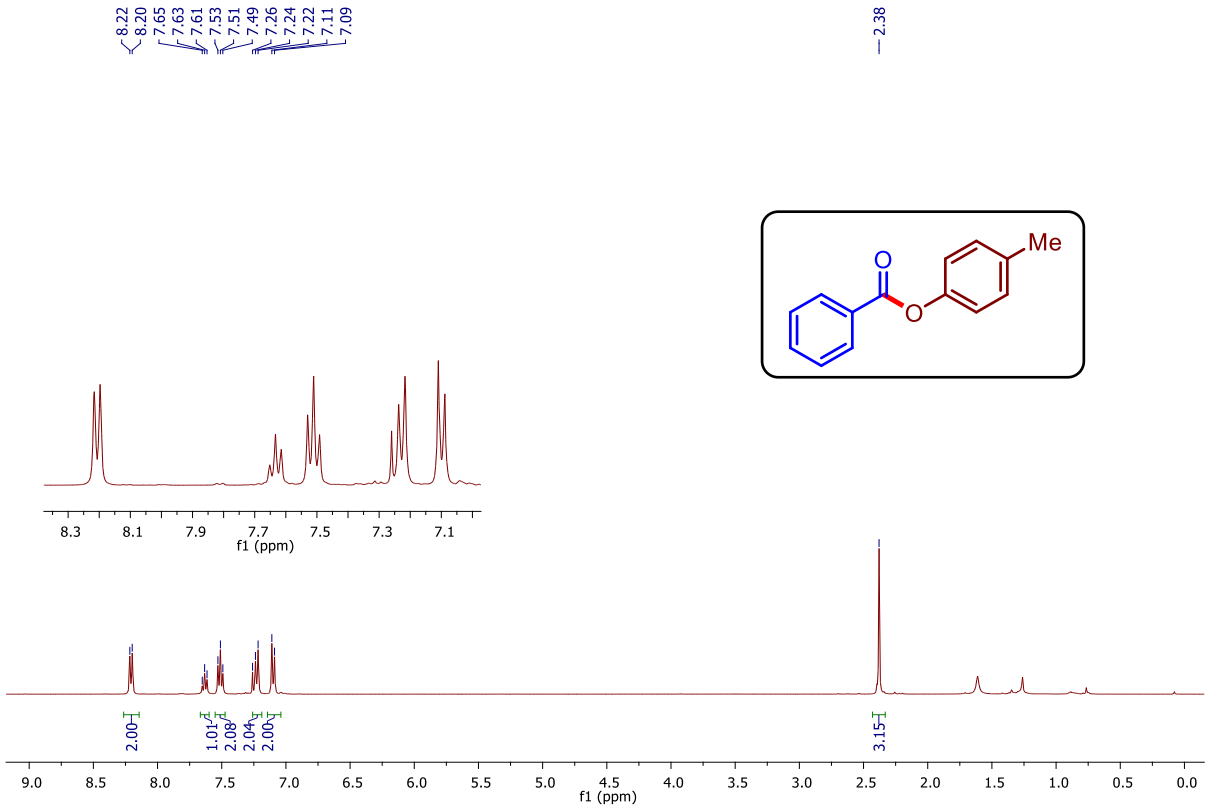

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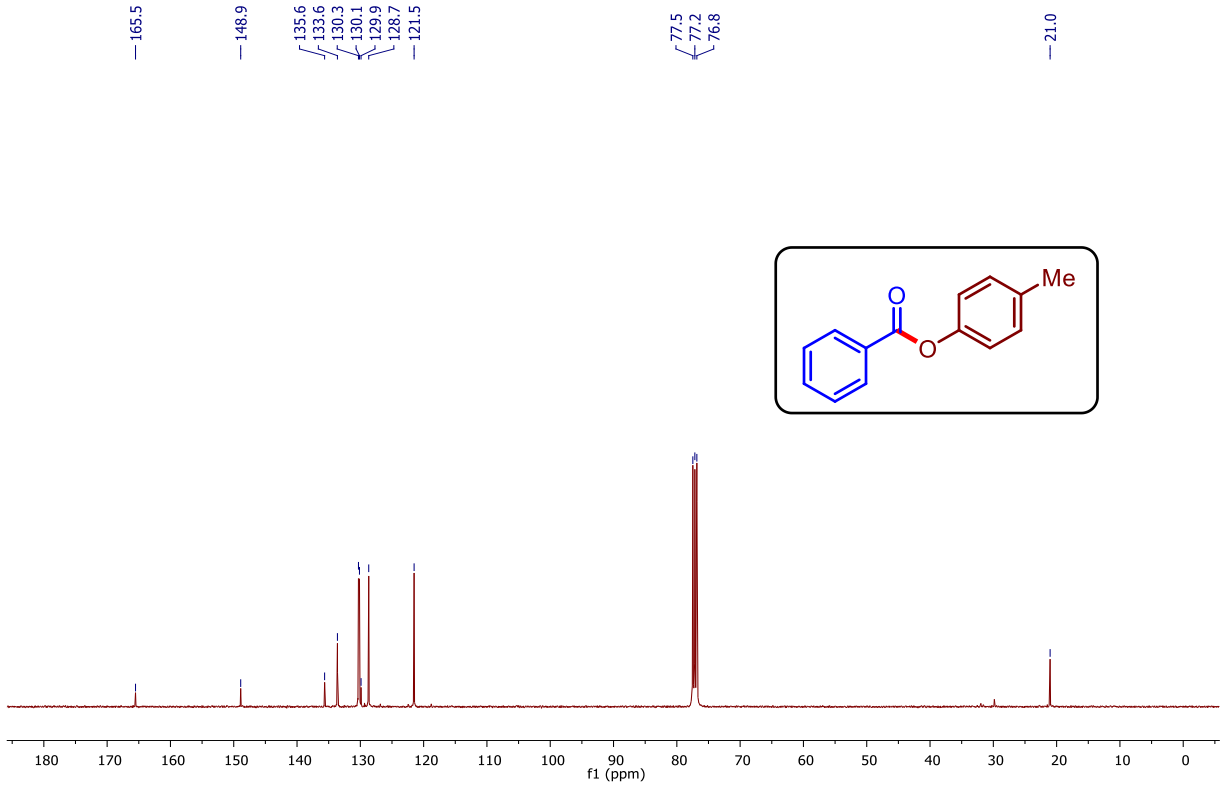

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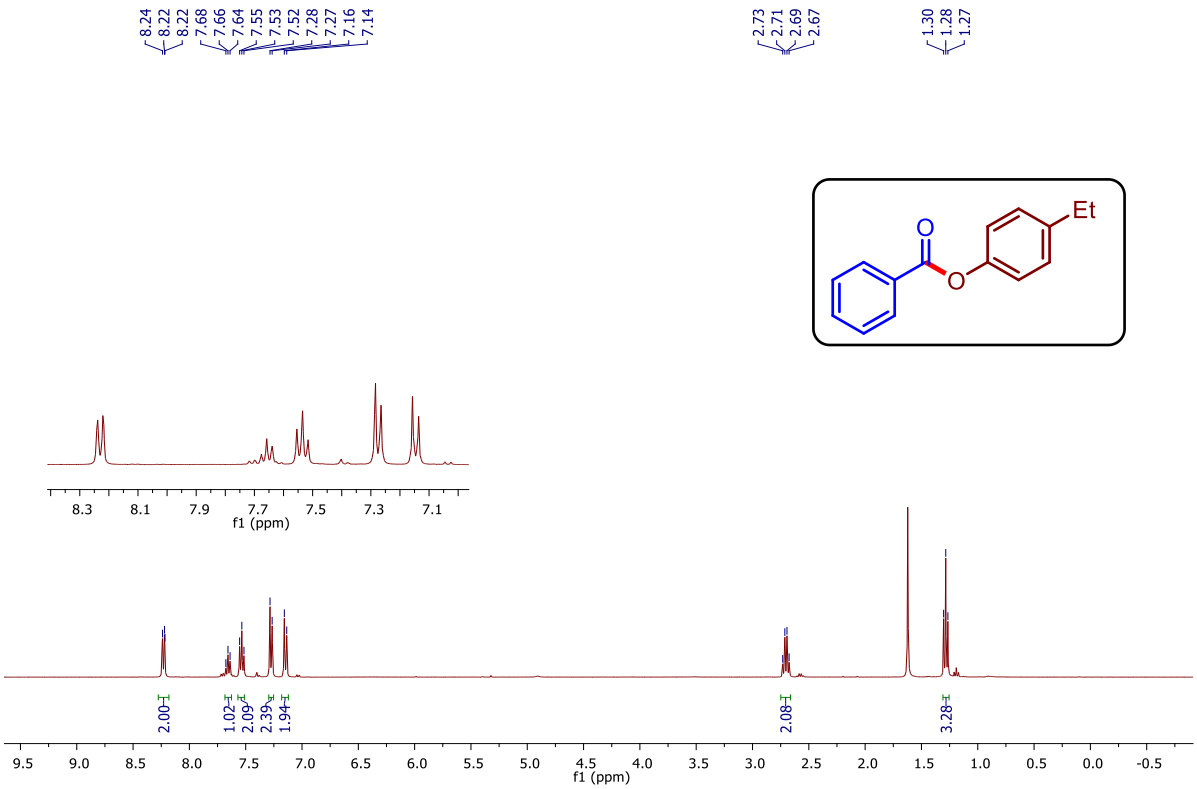

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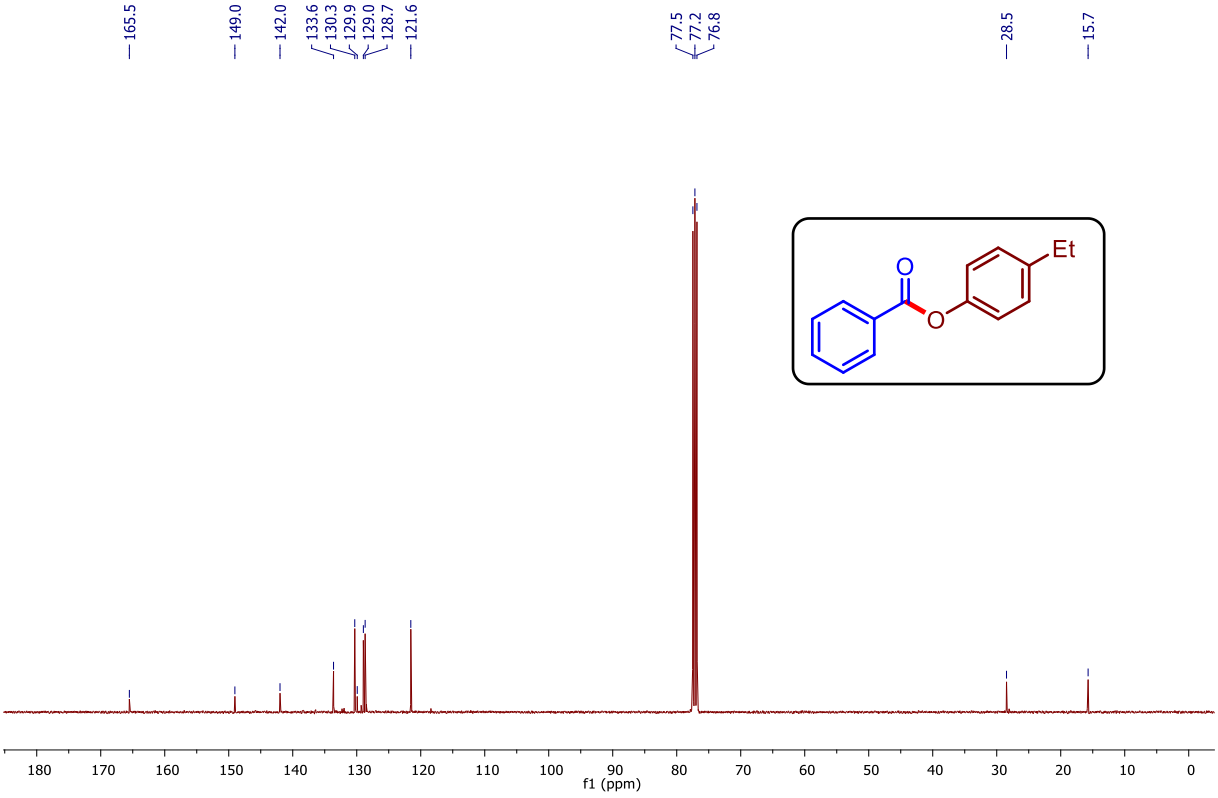

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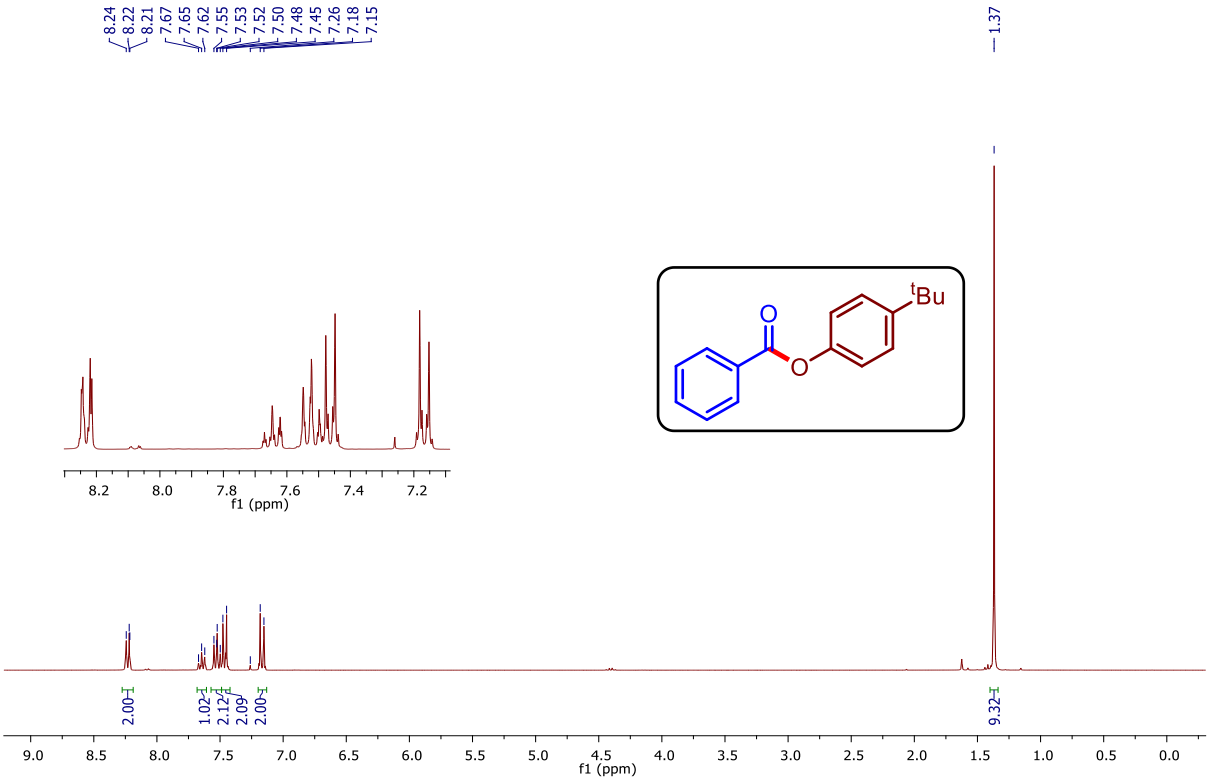

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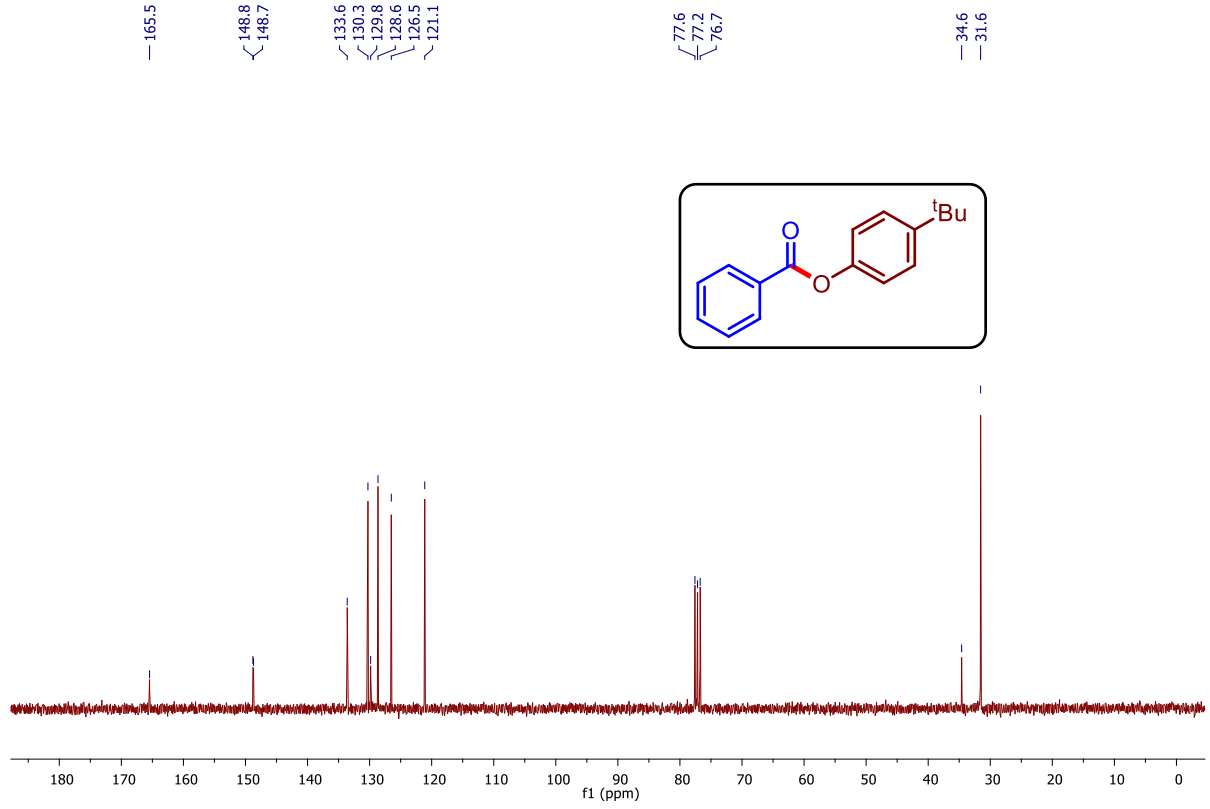

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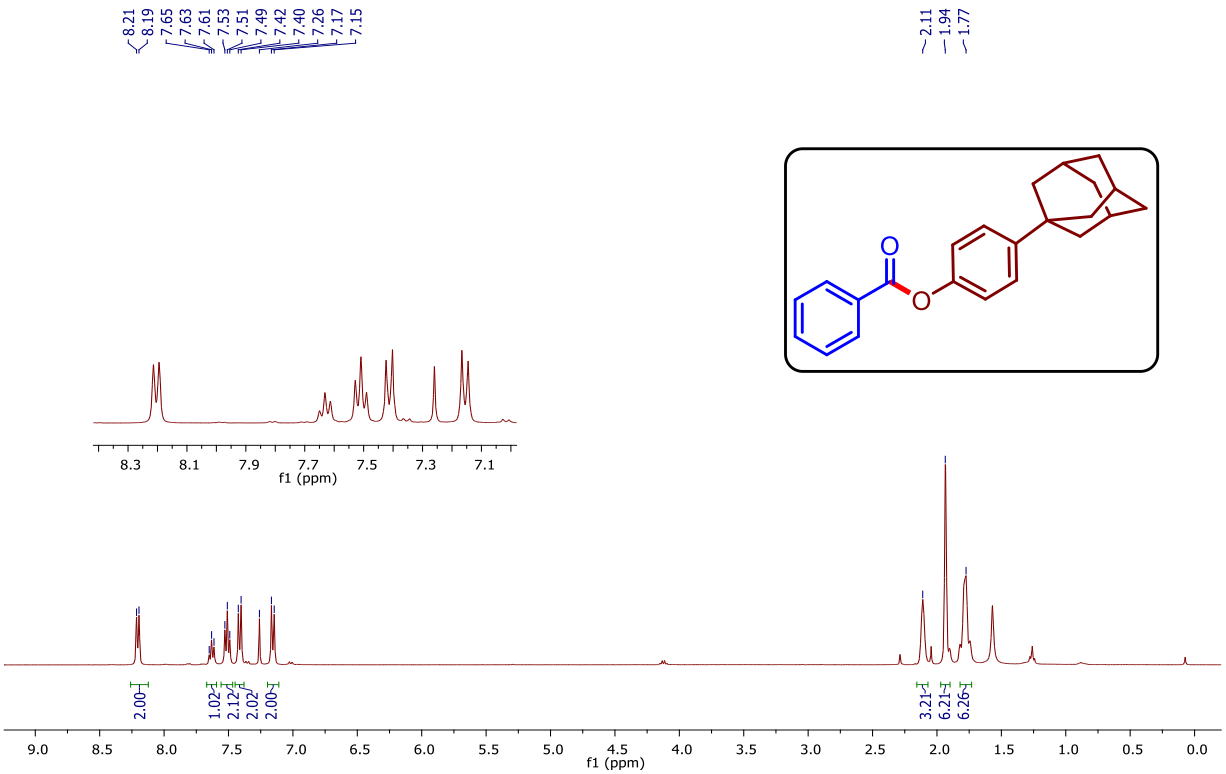

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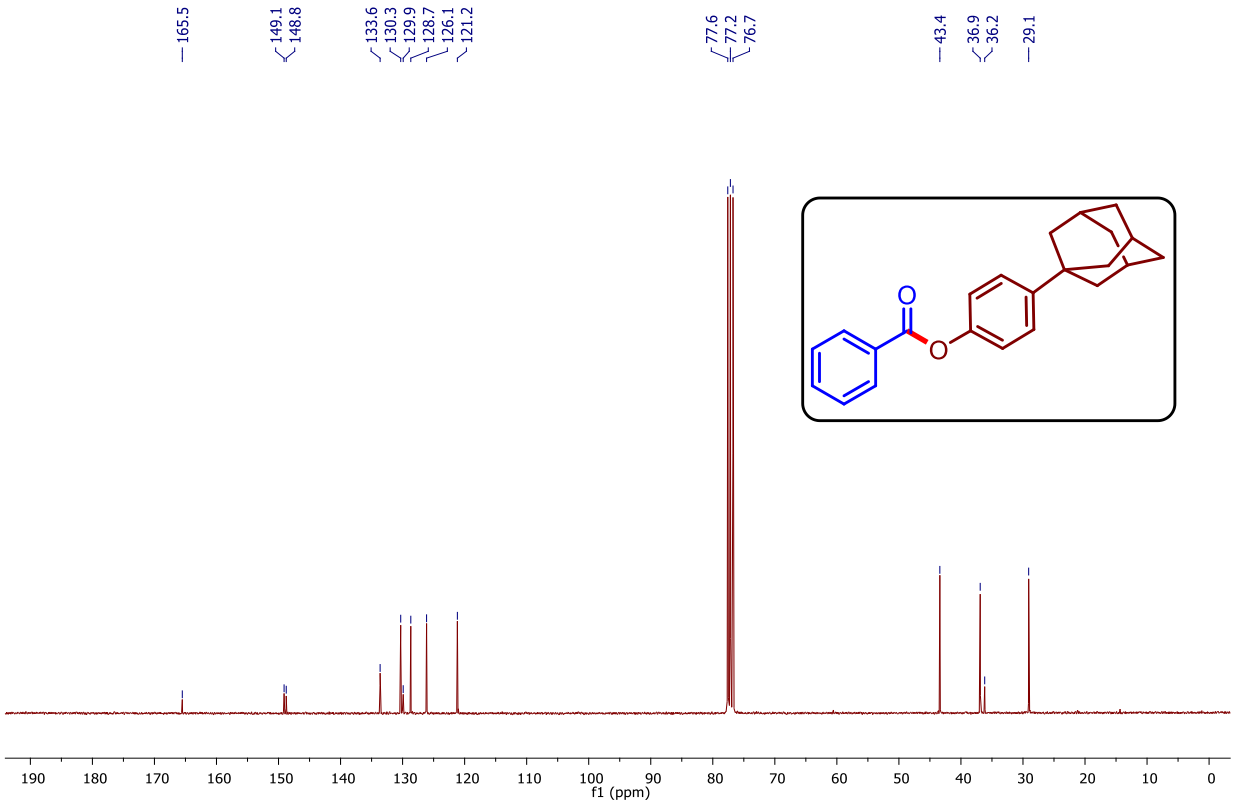

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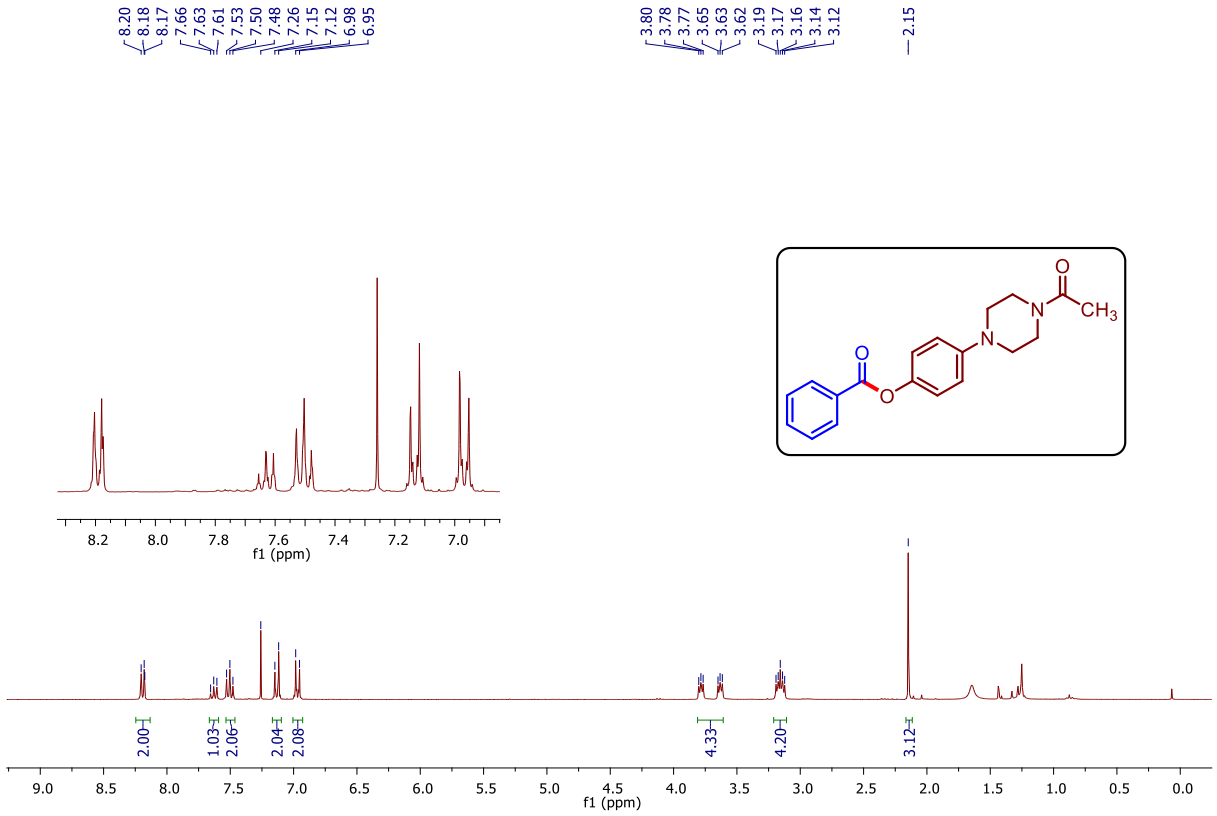

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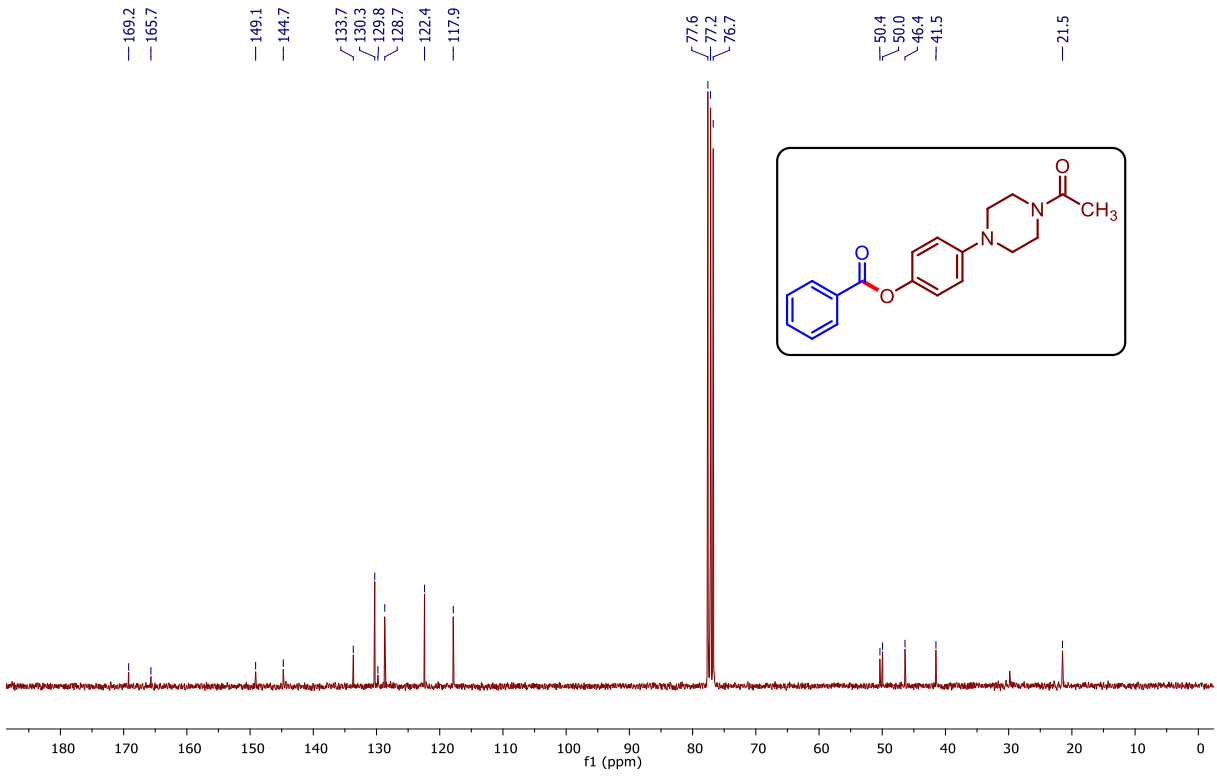

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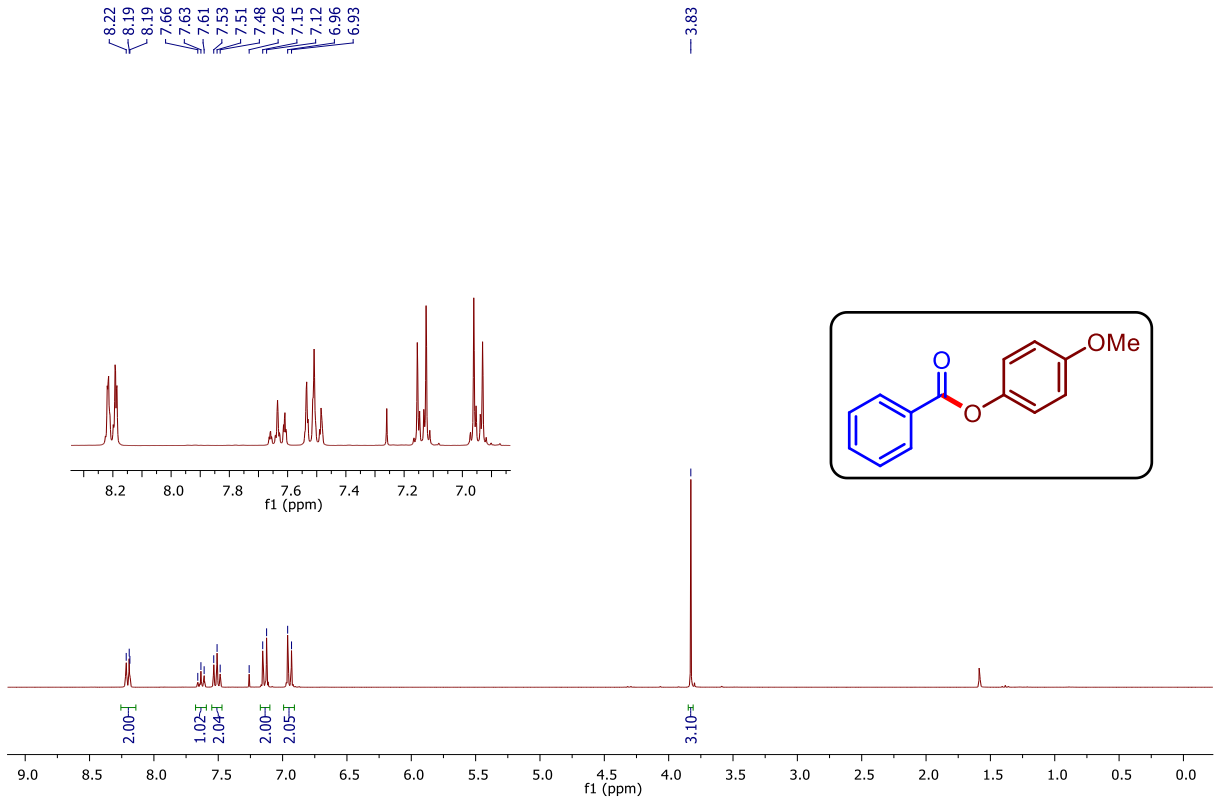

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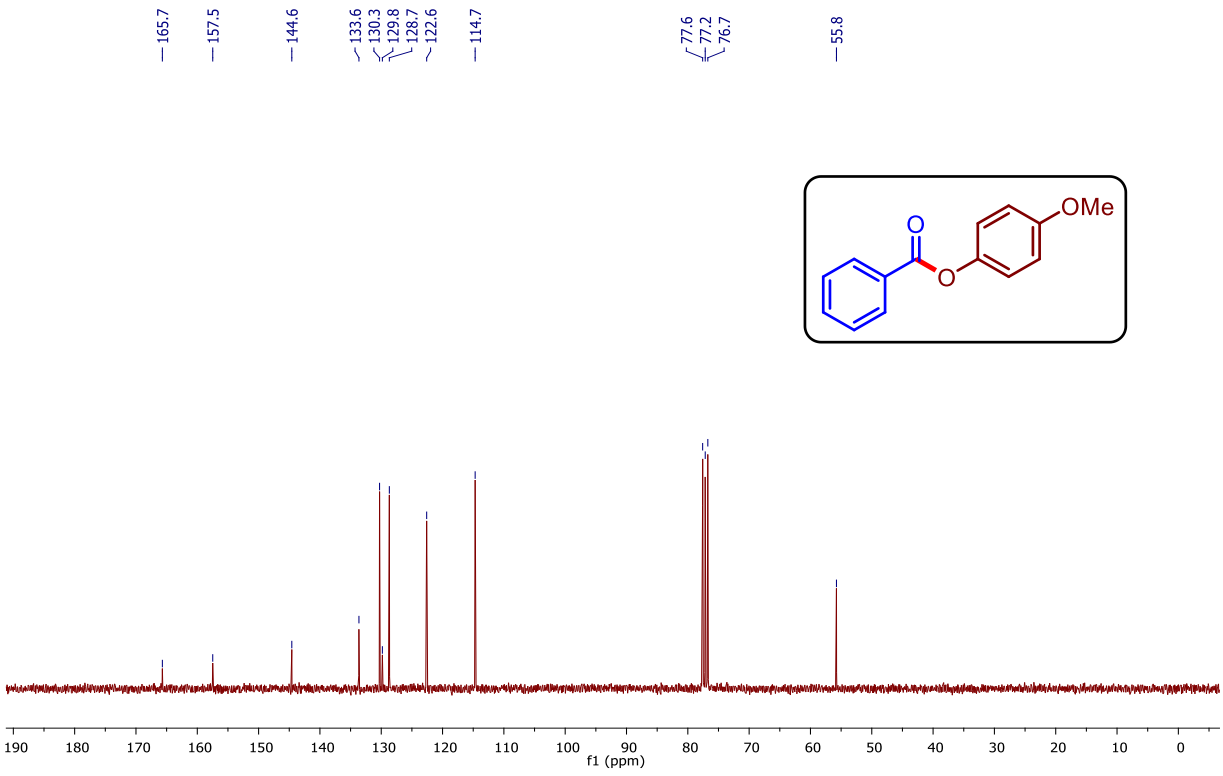

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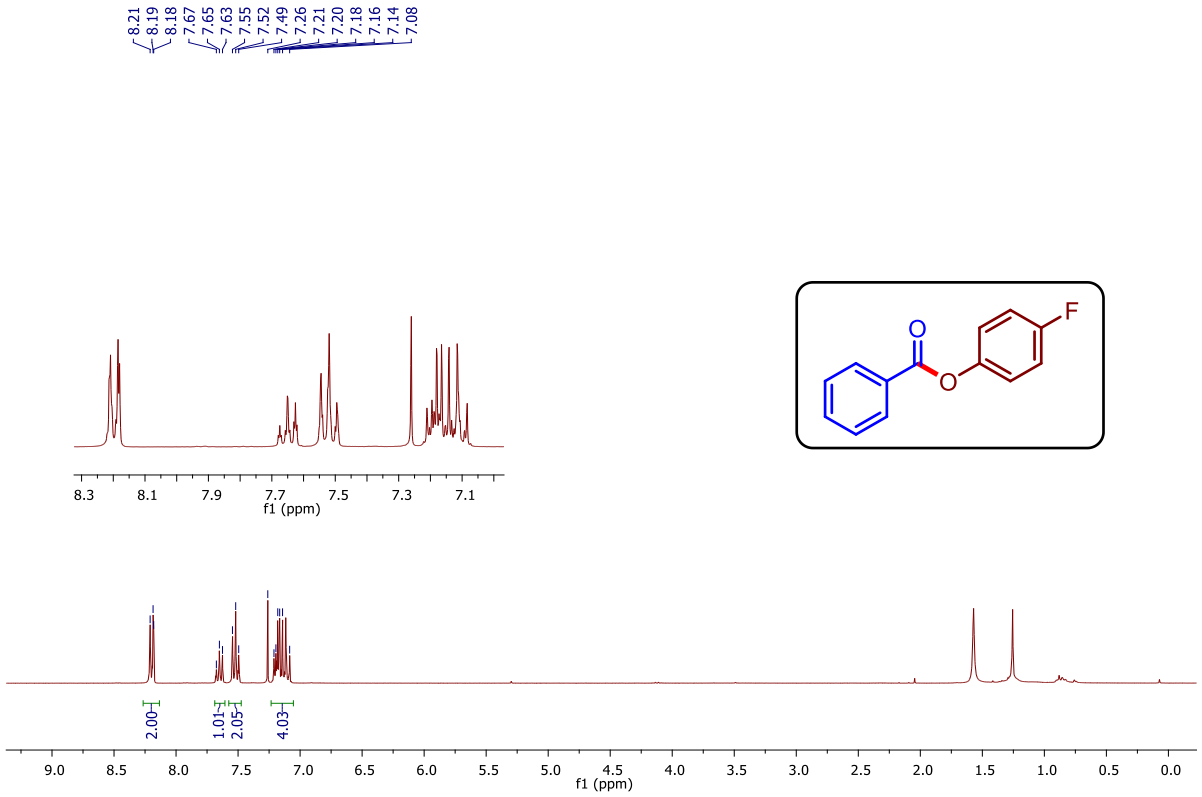

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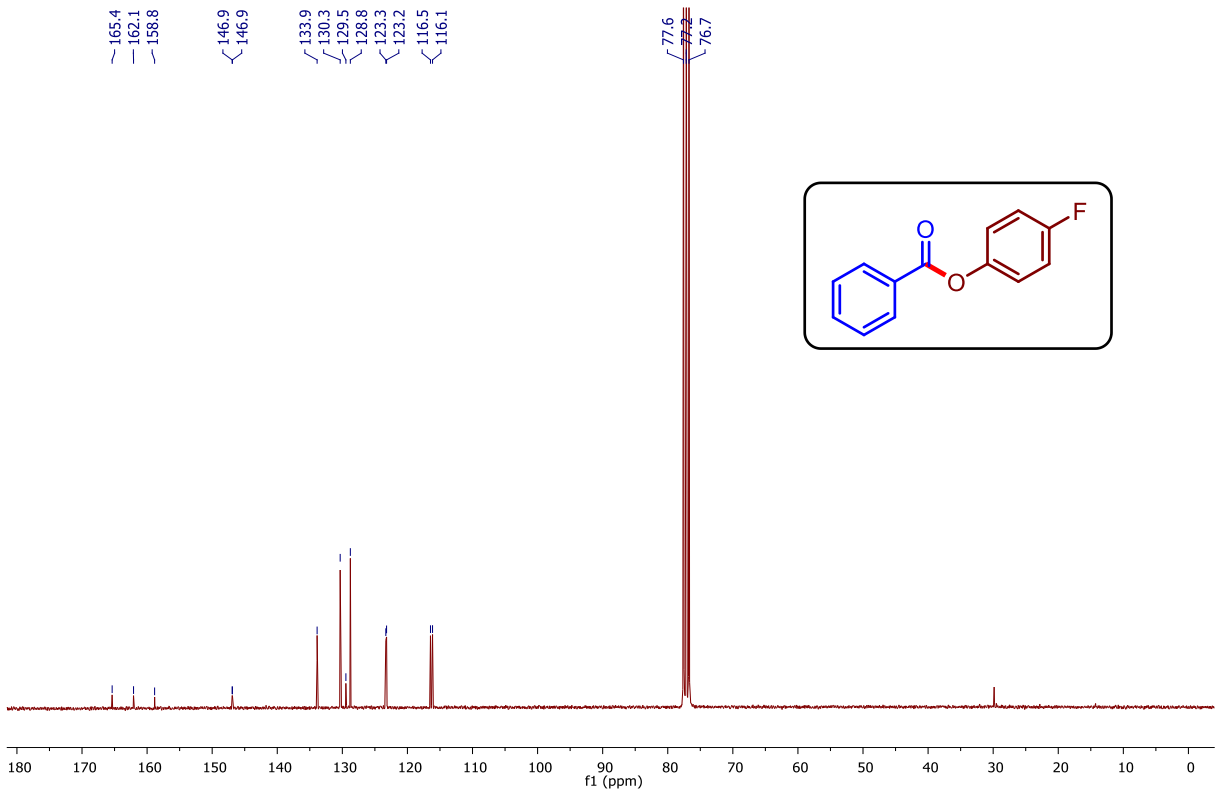

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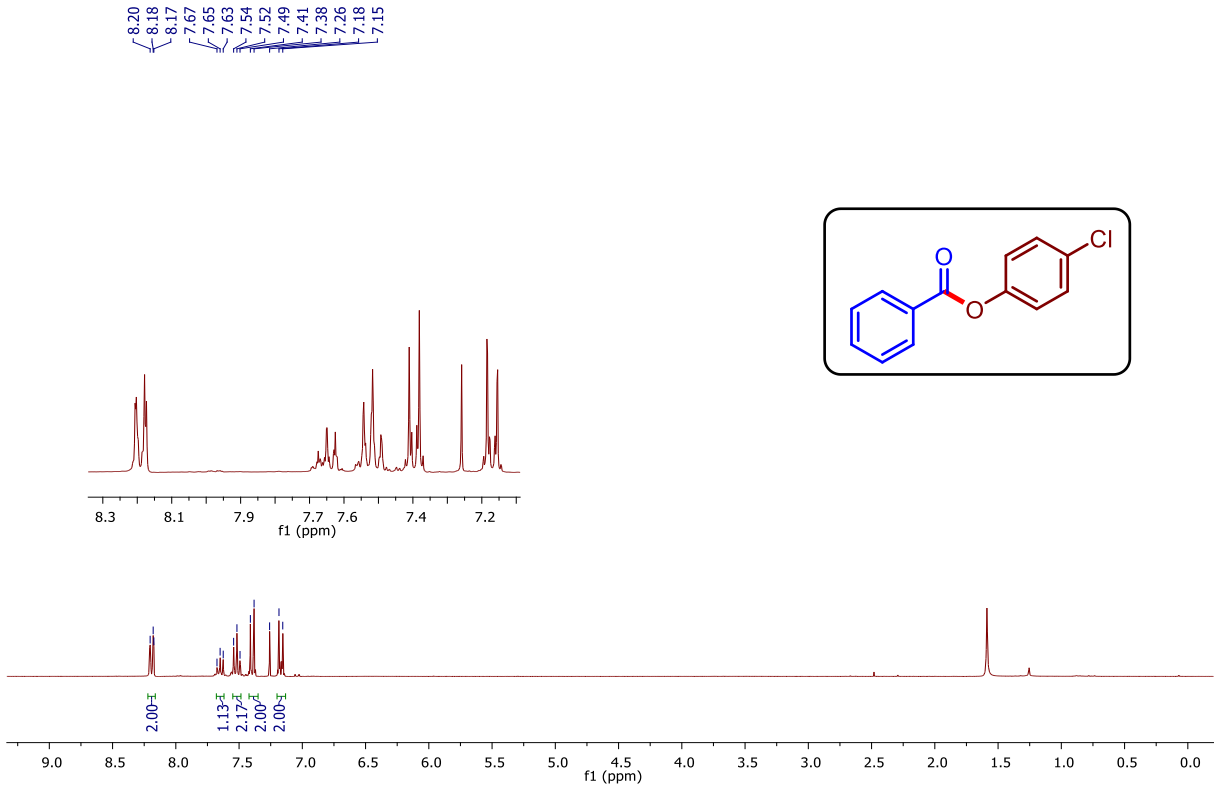

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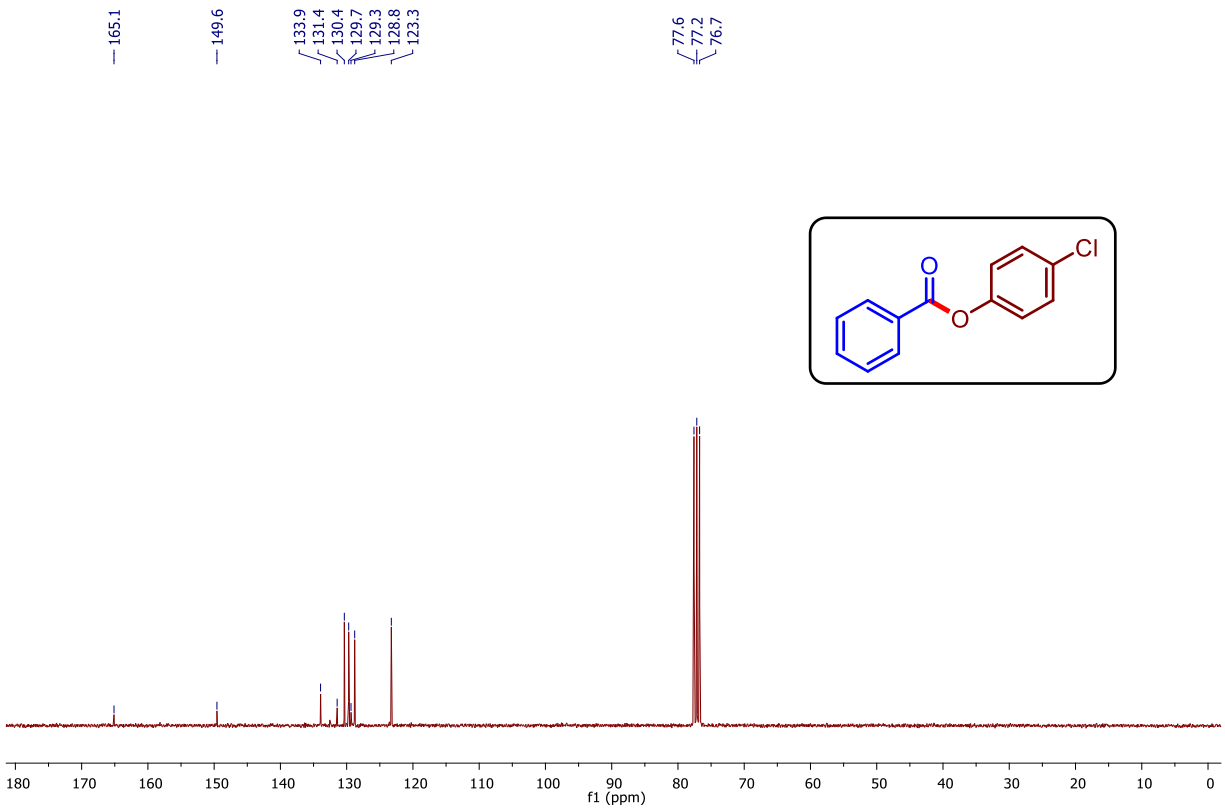

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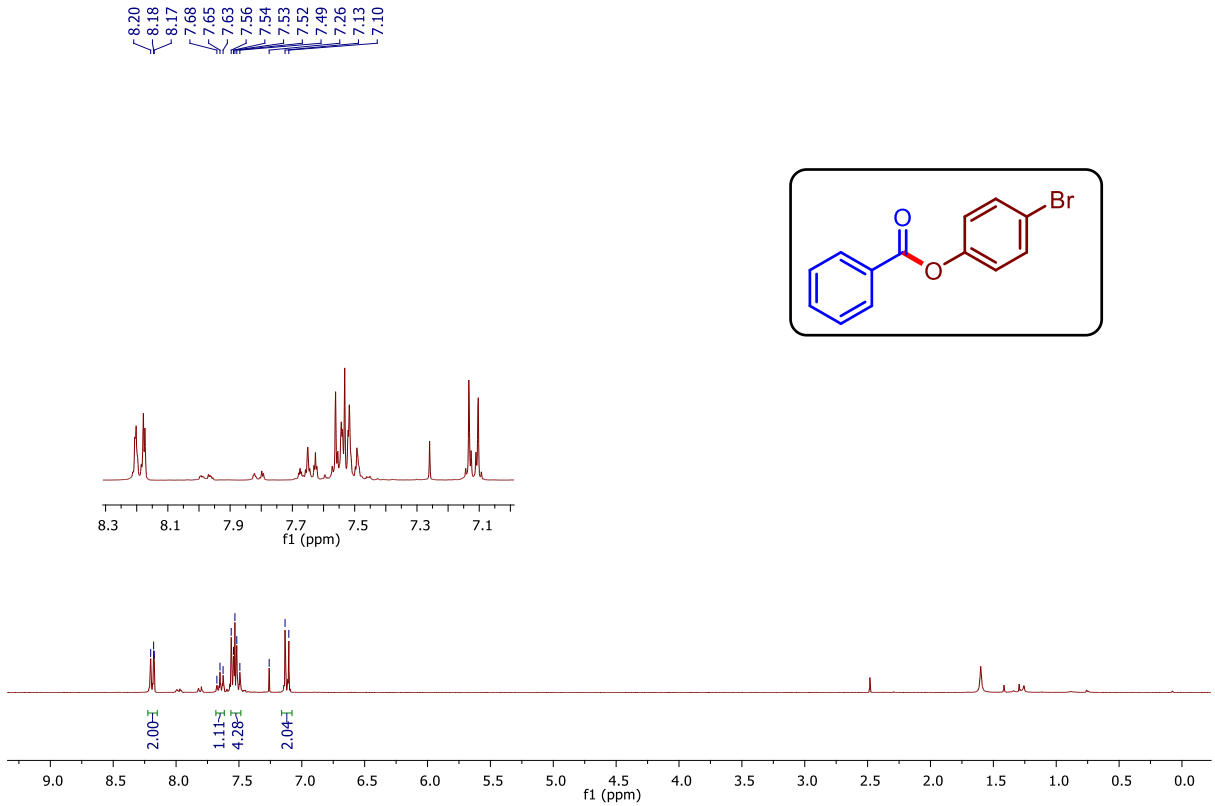

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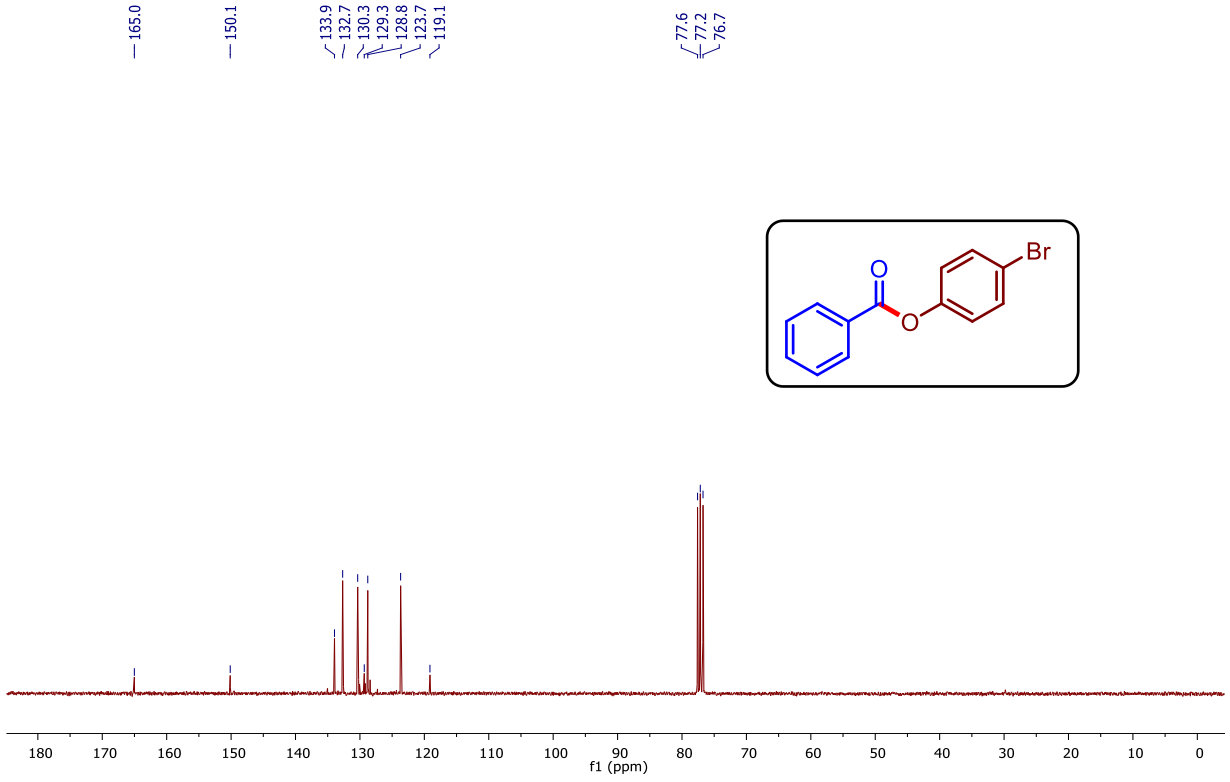

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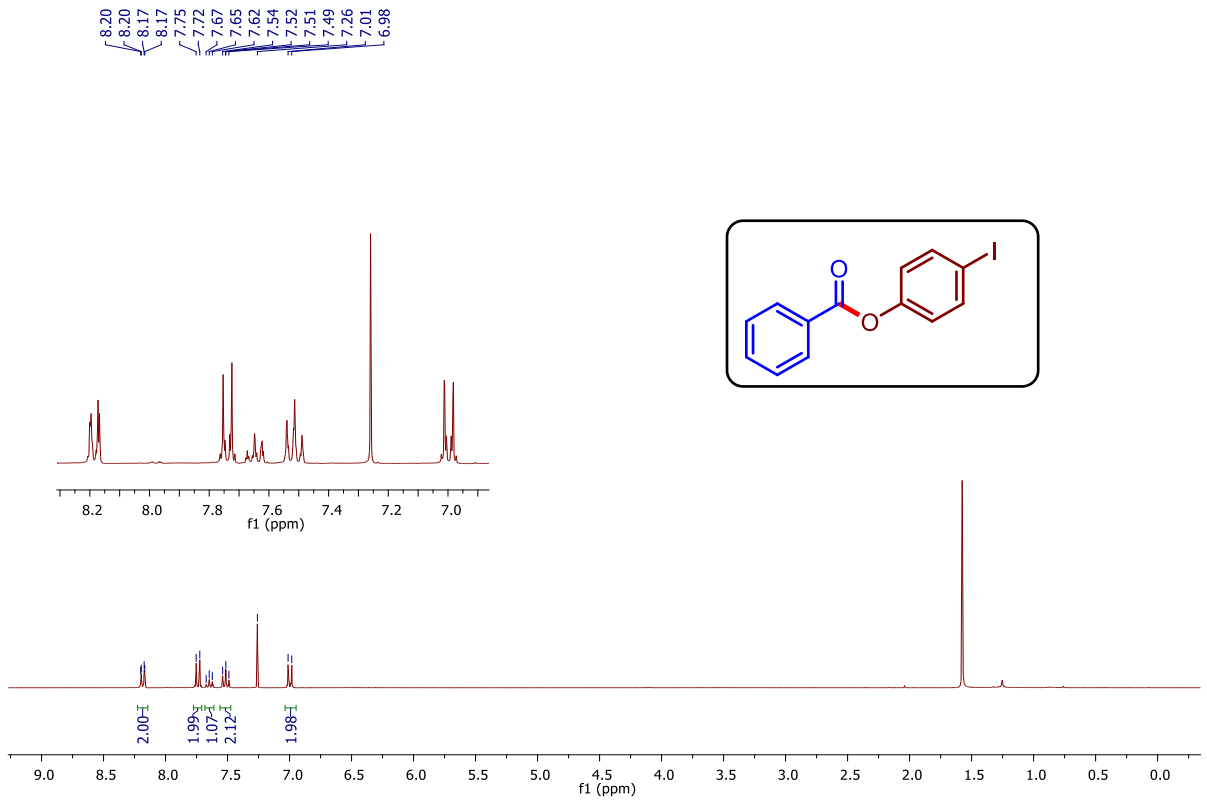

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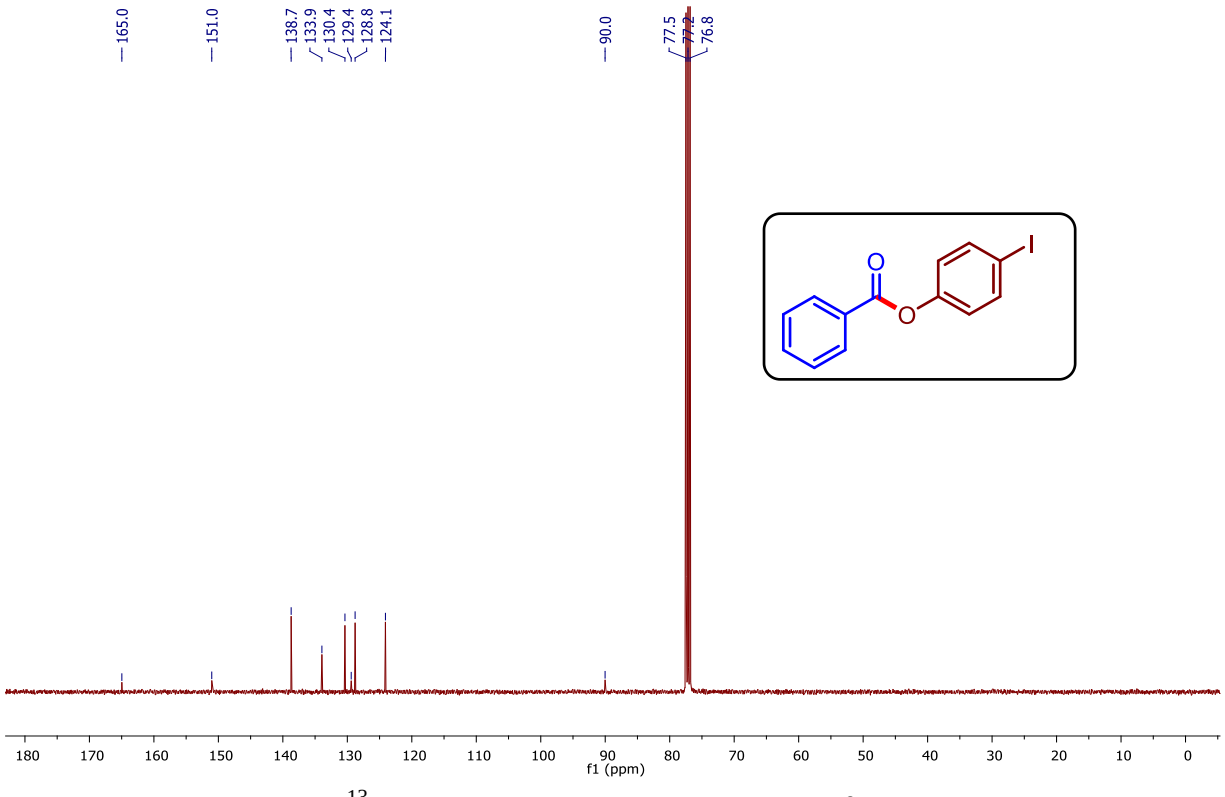

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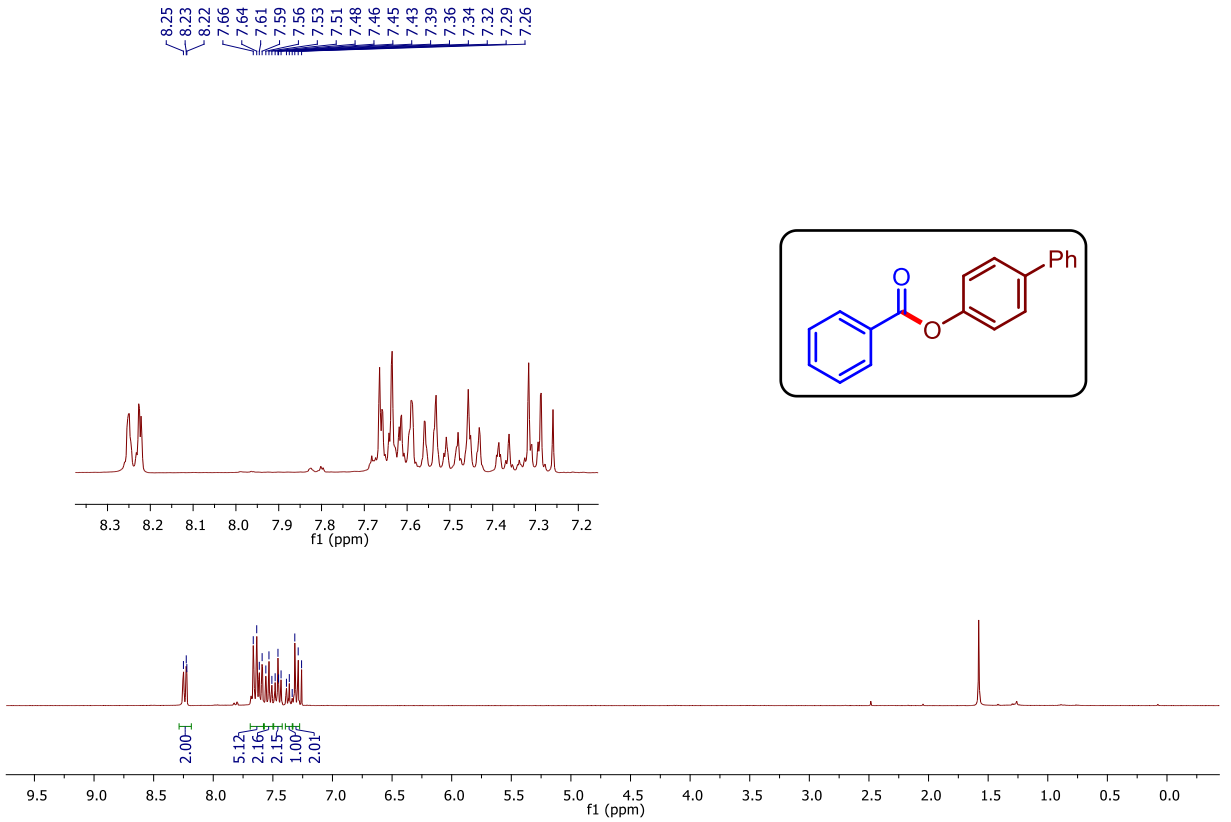

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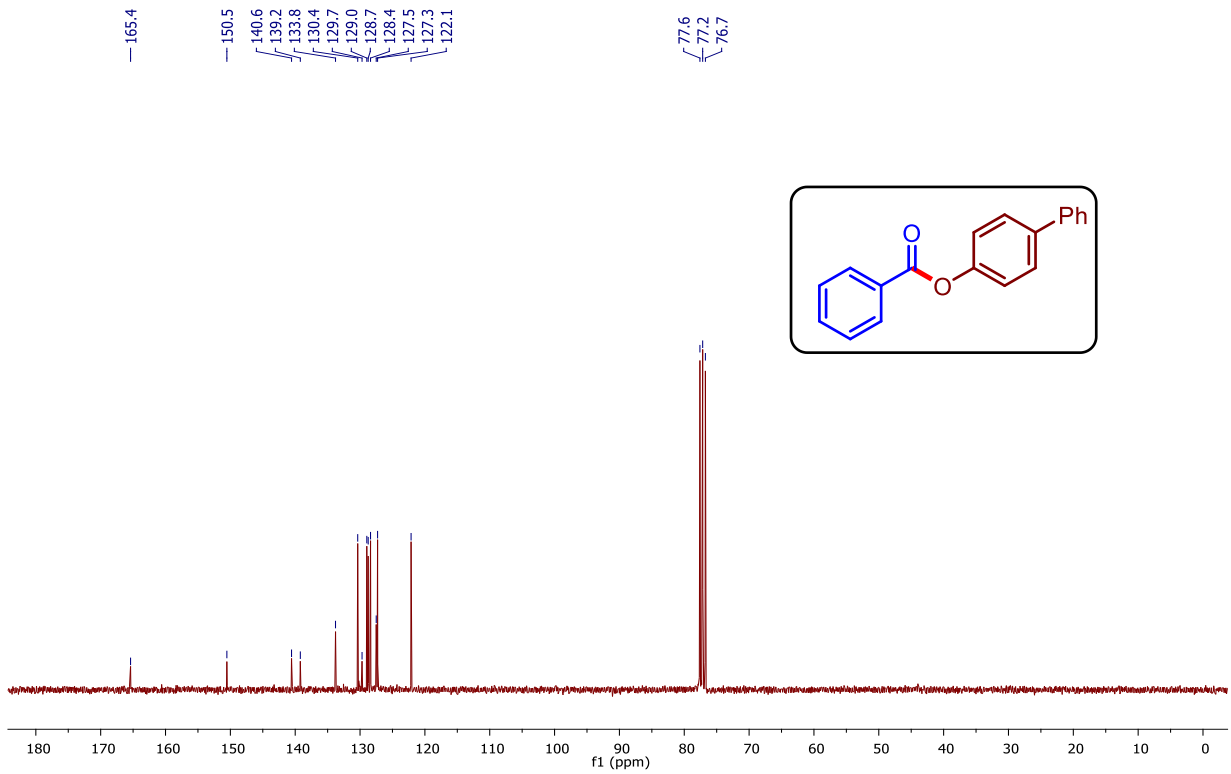

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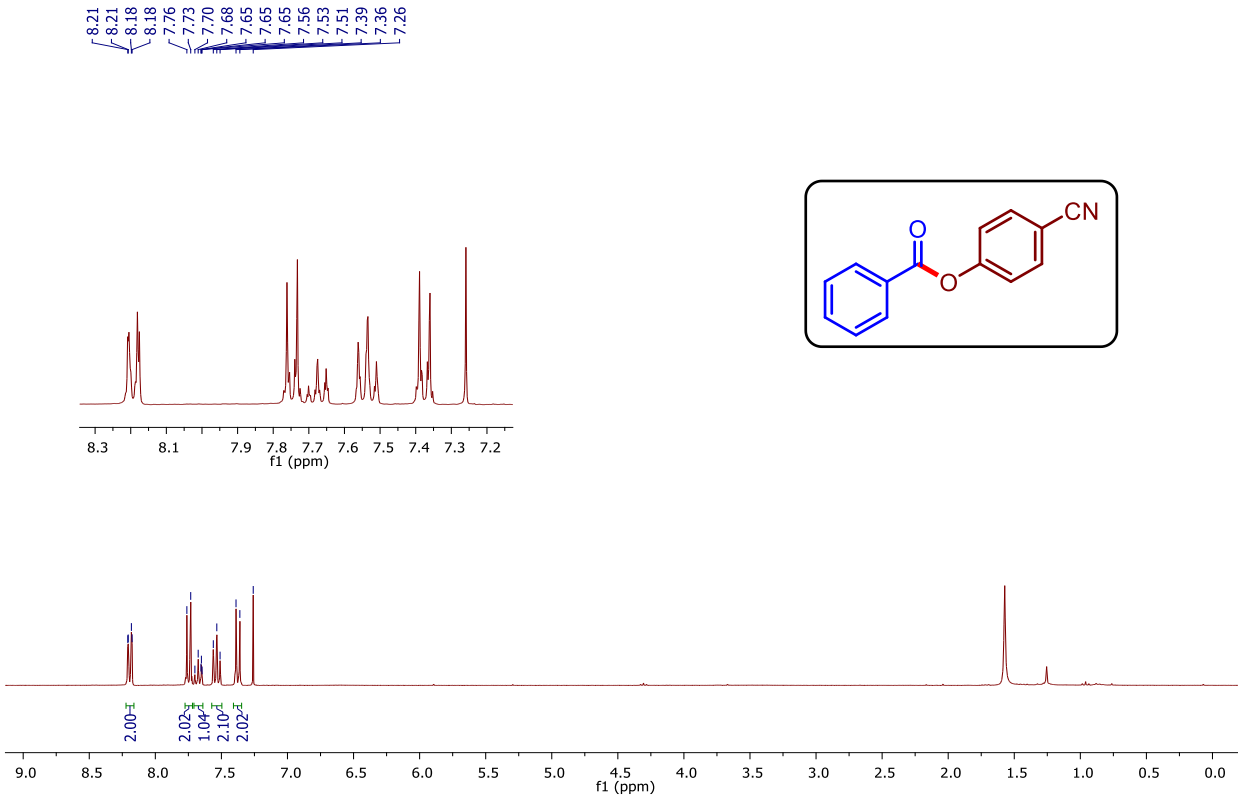
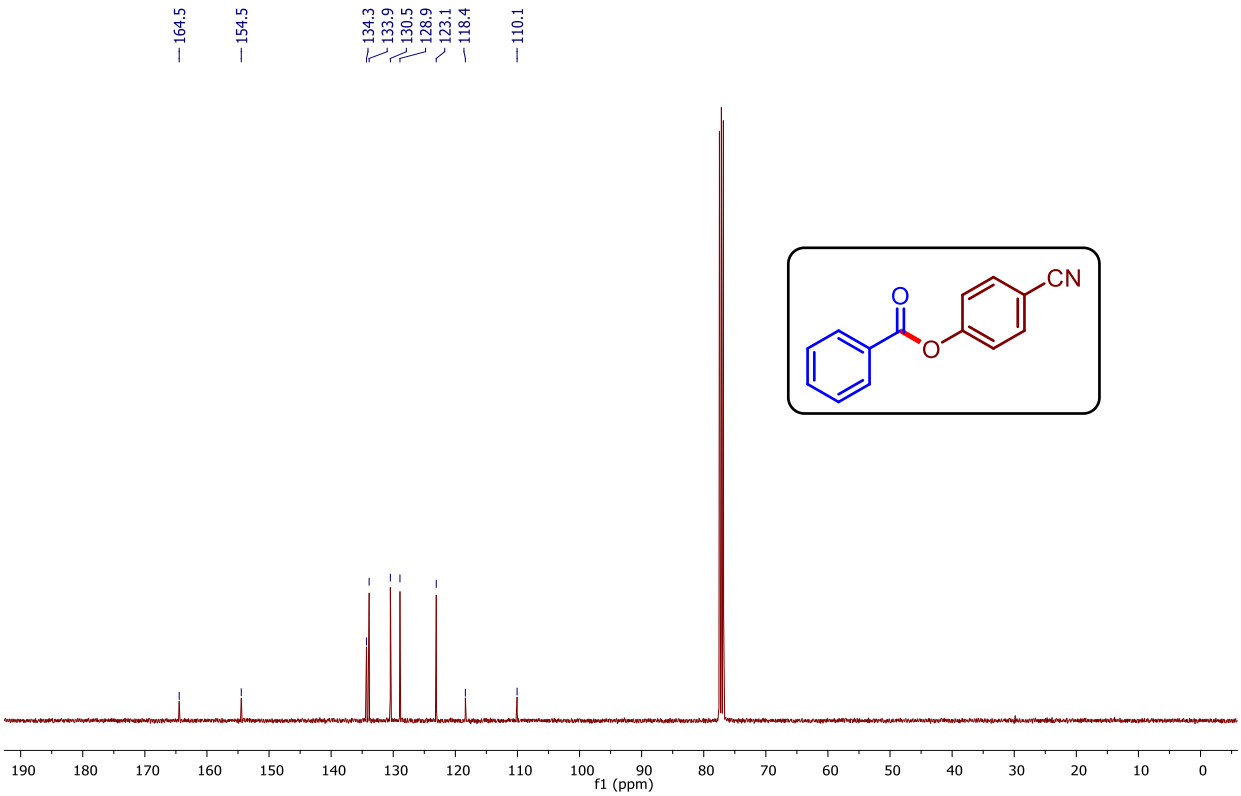
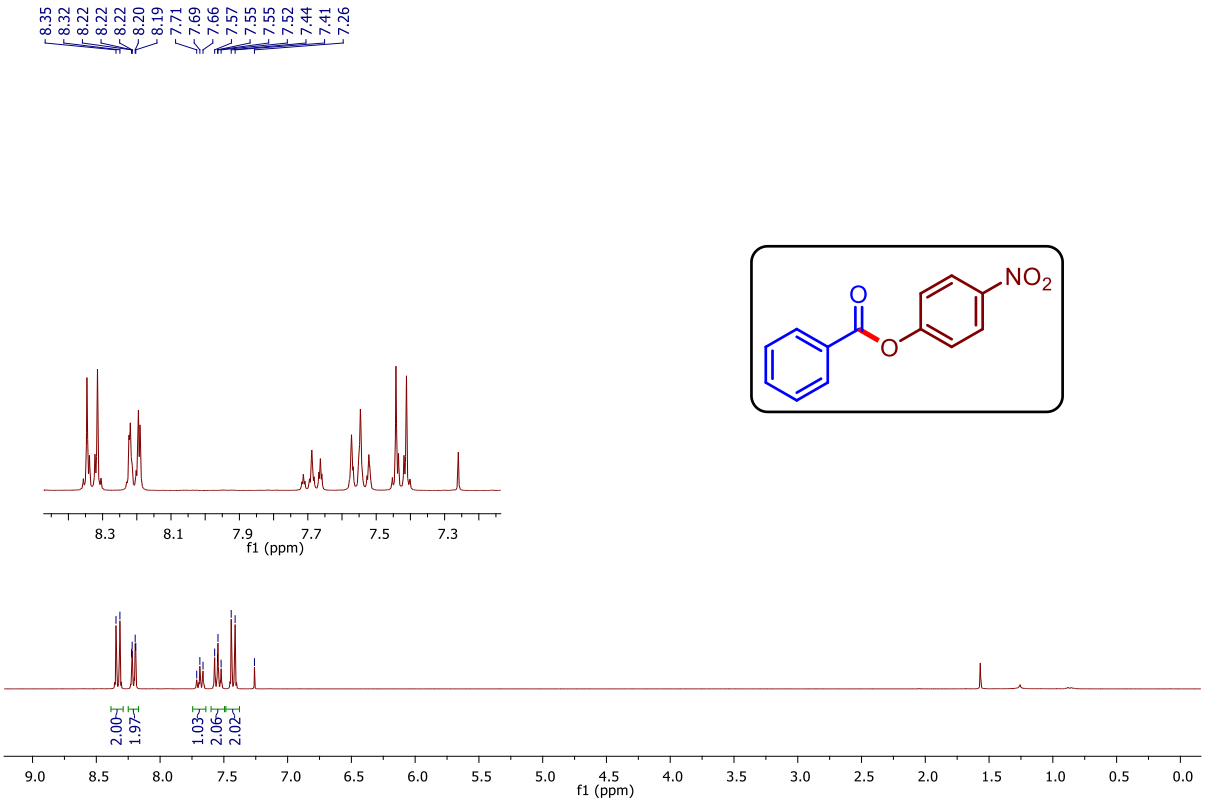


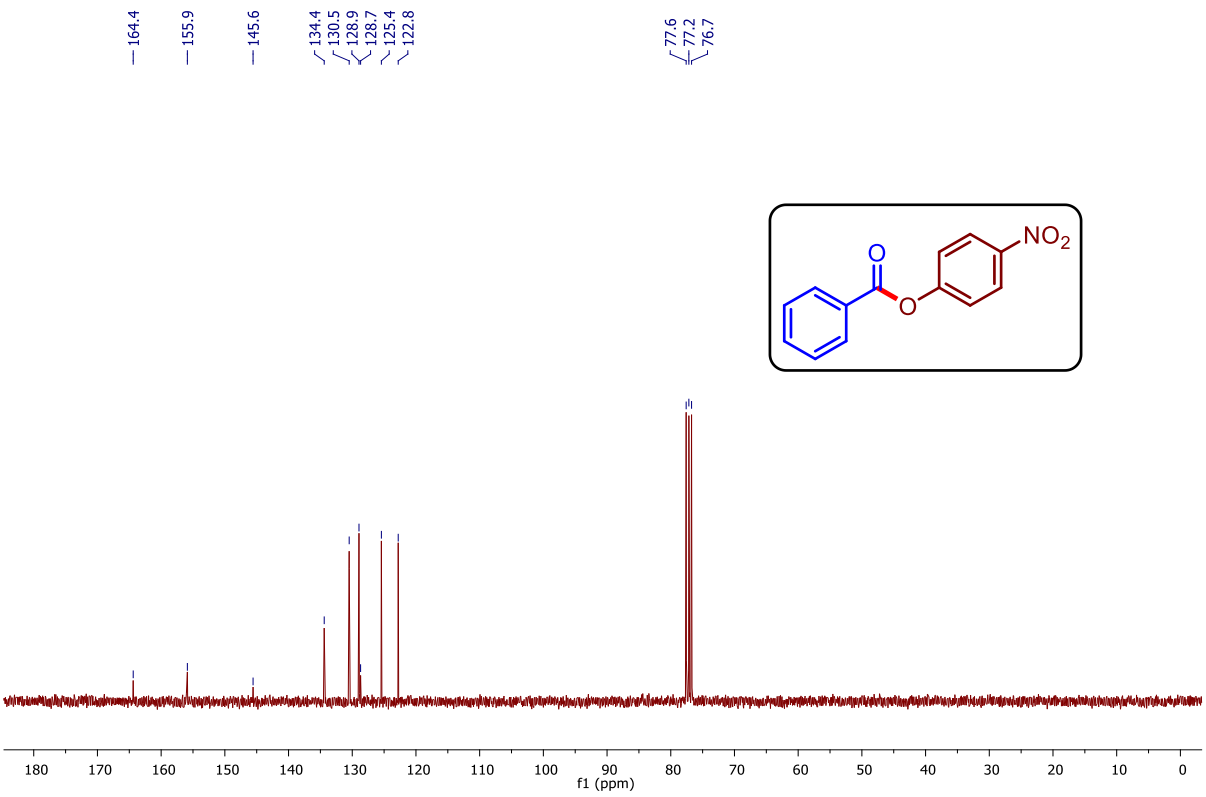
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3a



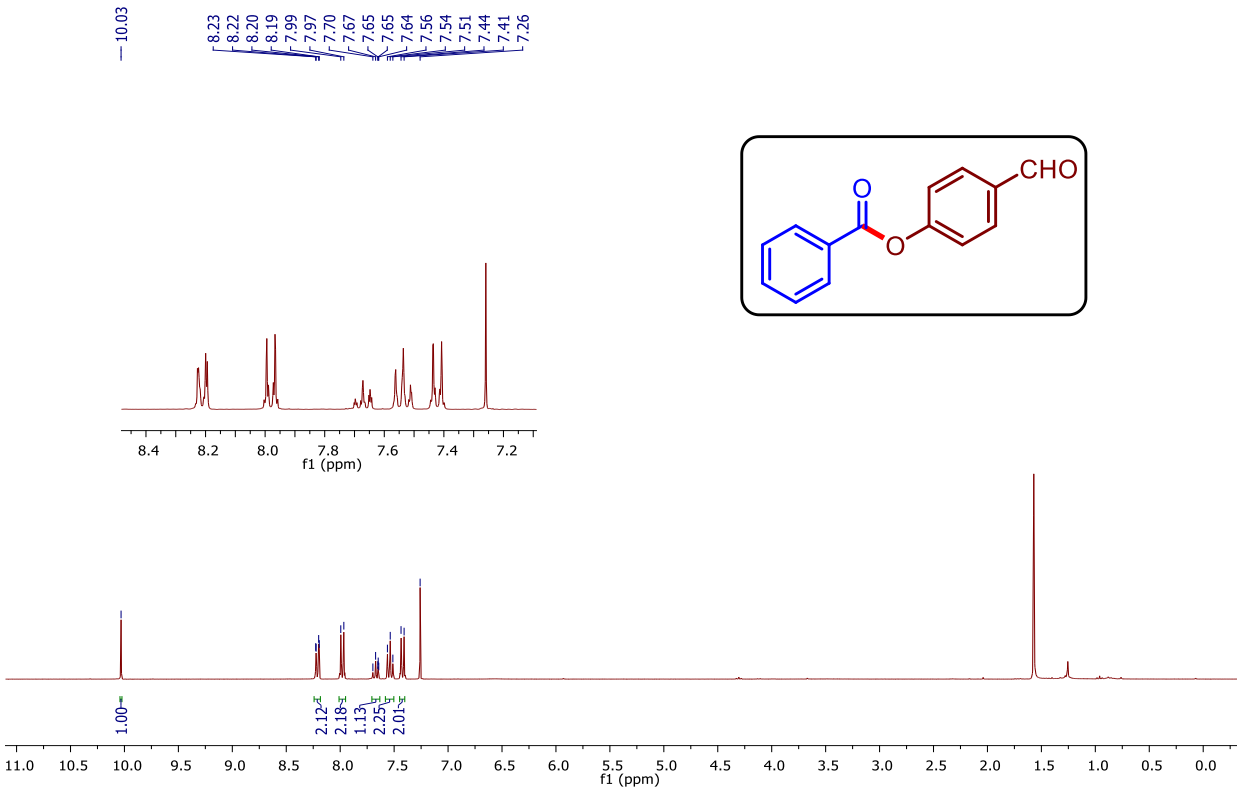
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3a



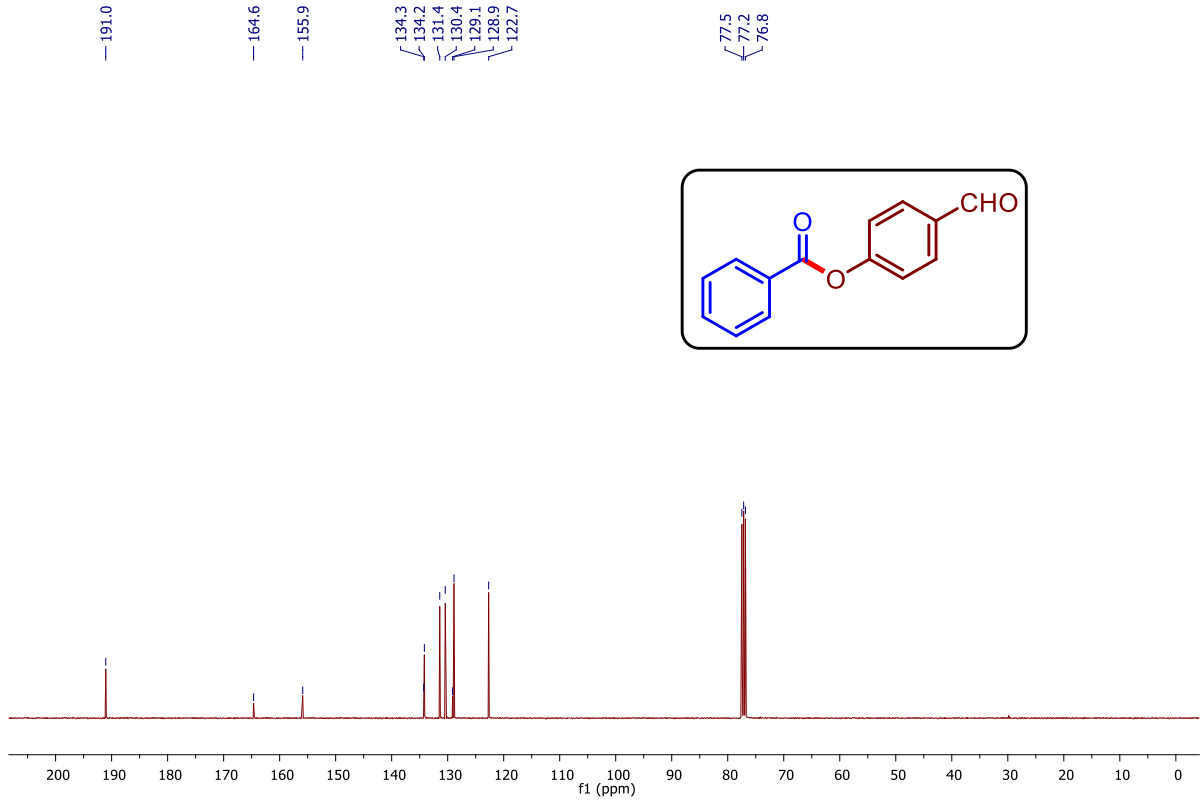
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3n



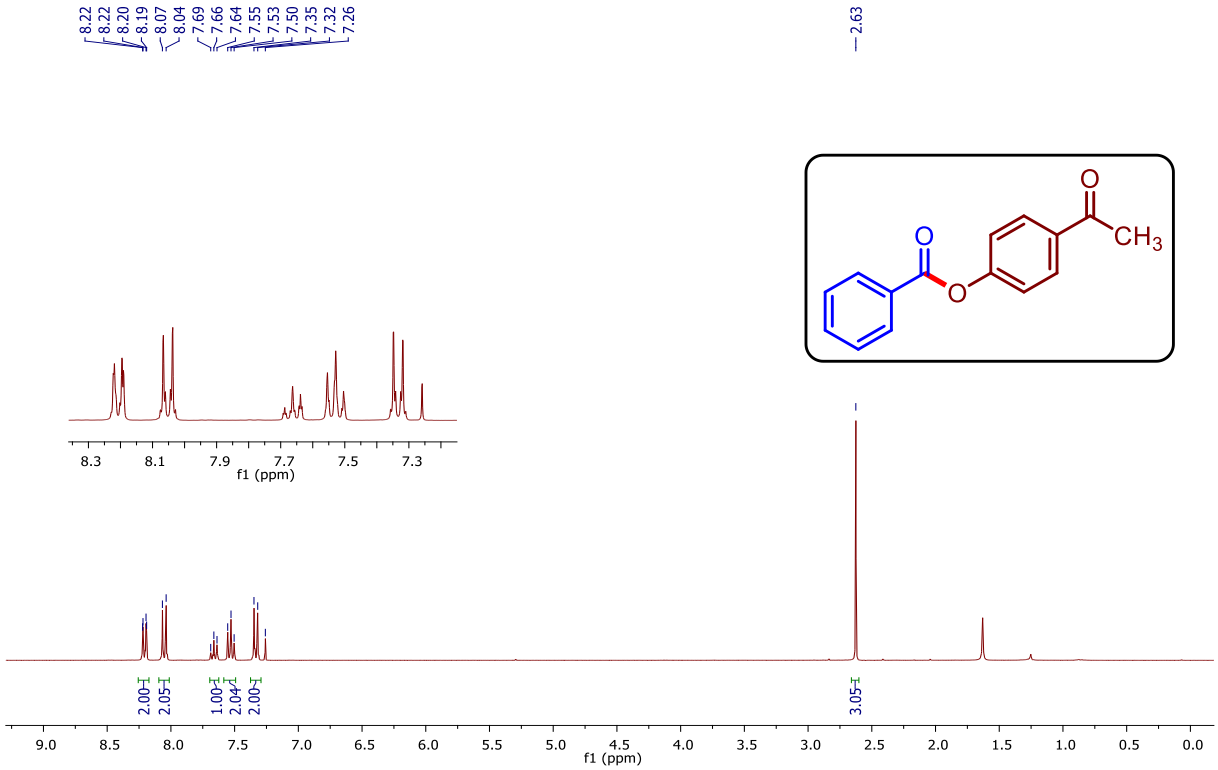
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3n



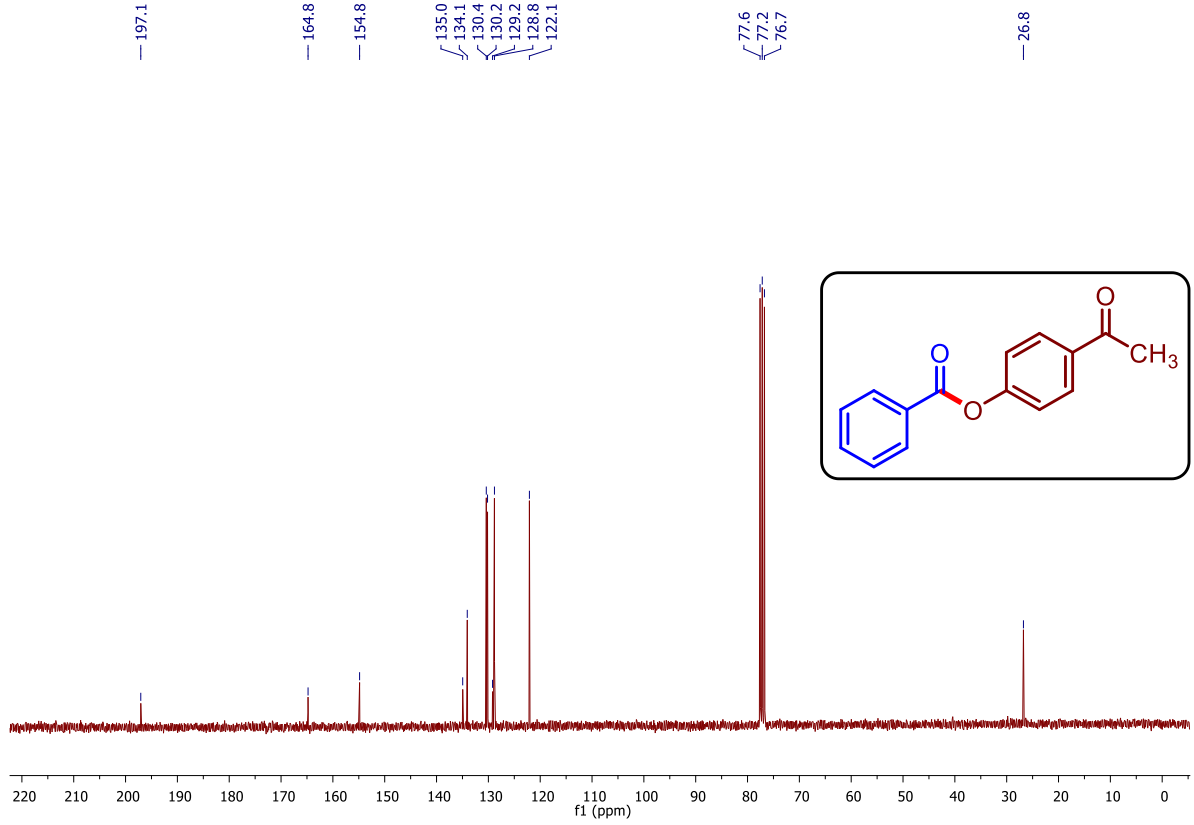
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3o



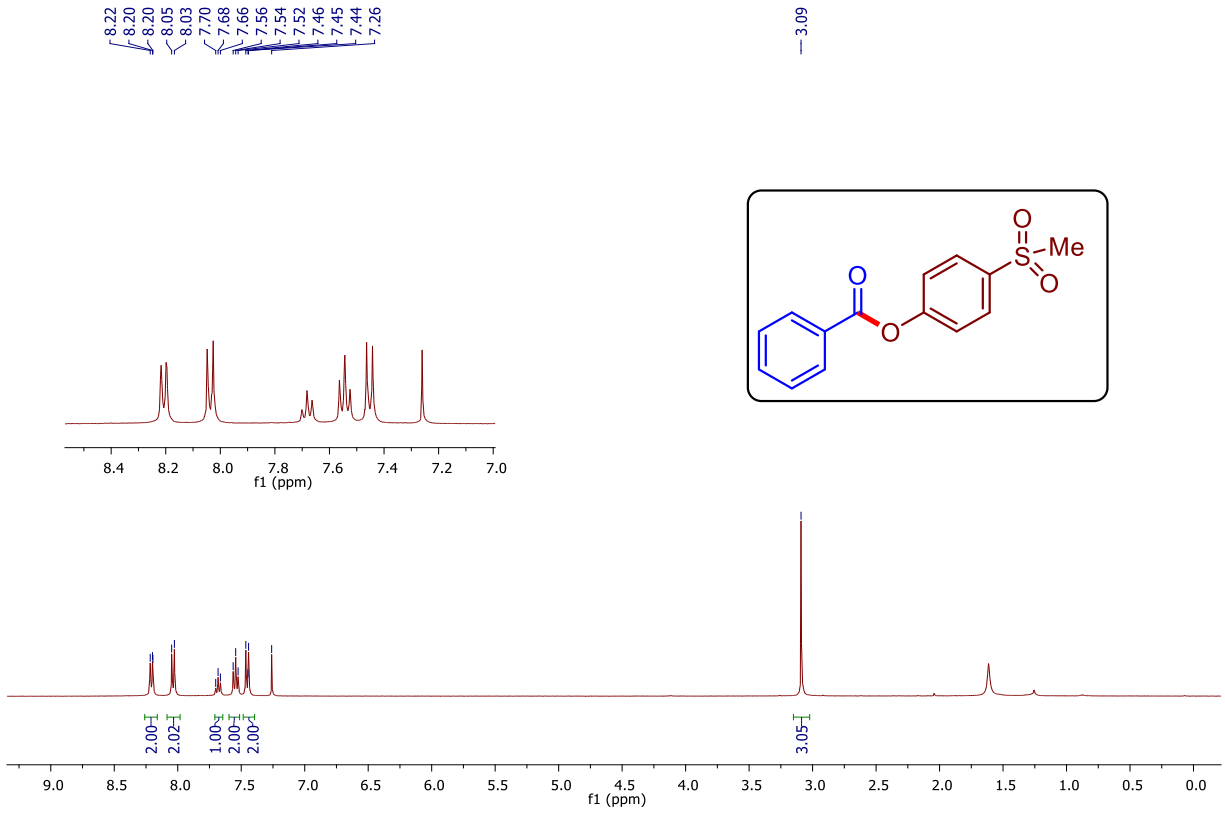
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3o



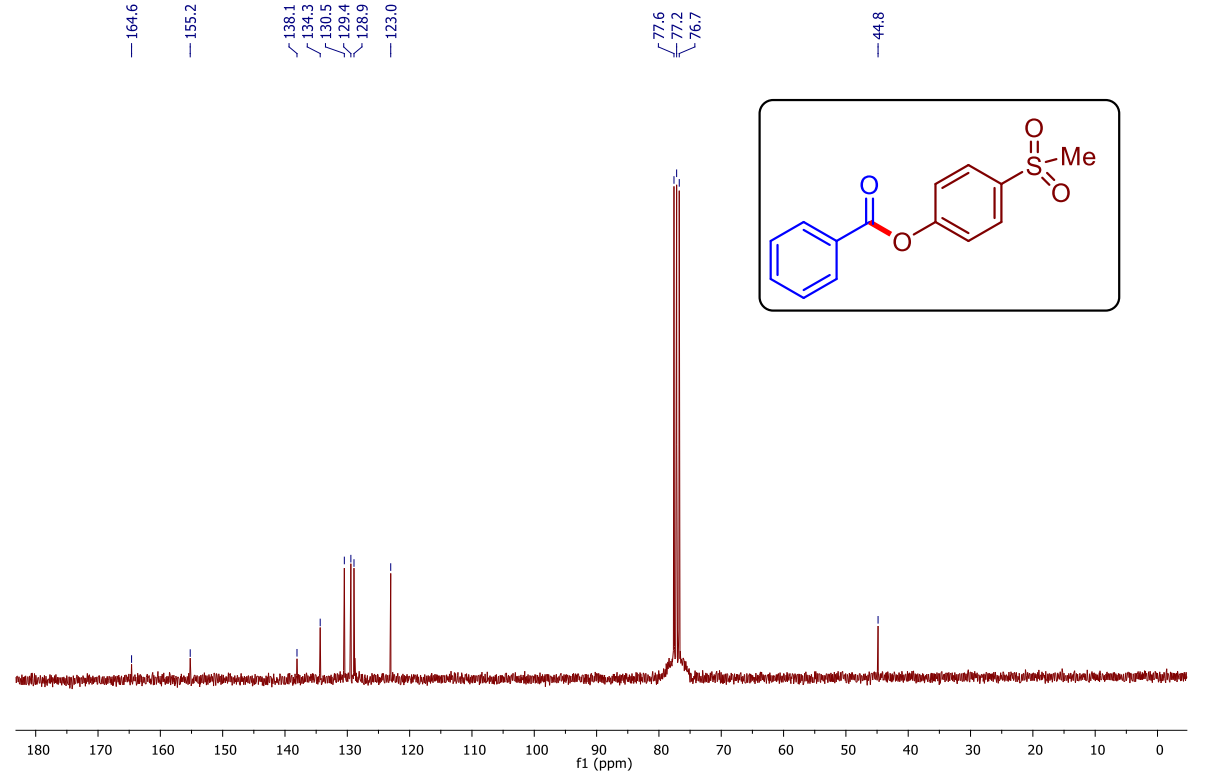
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3p



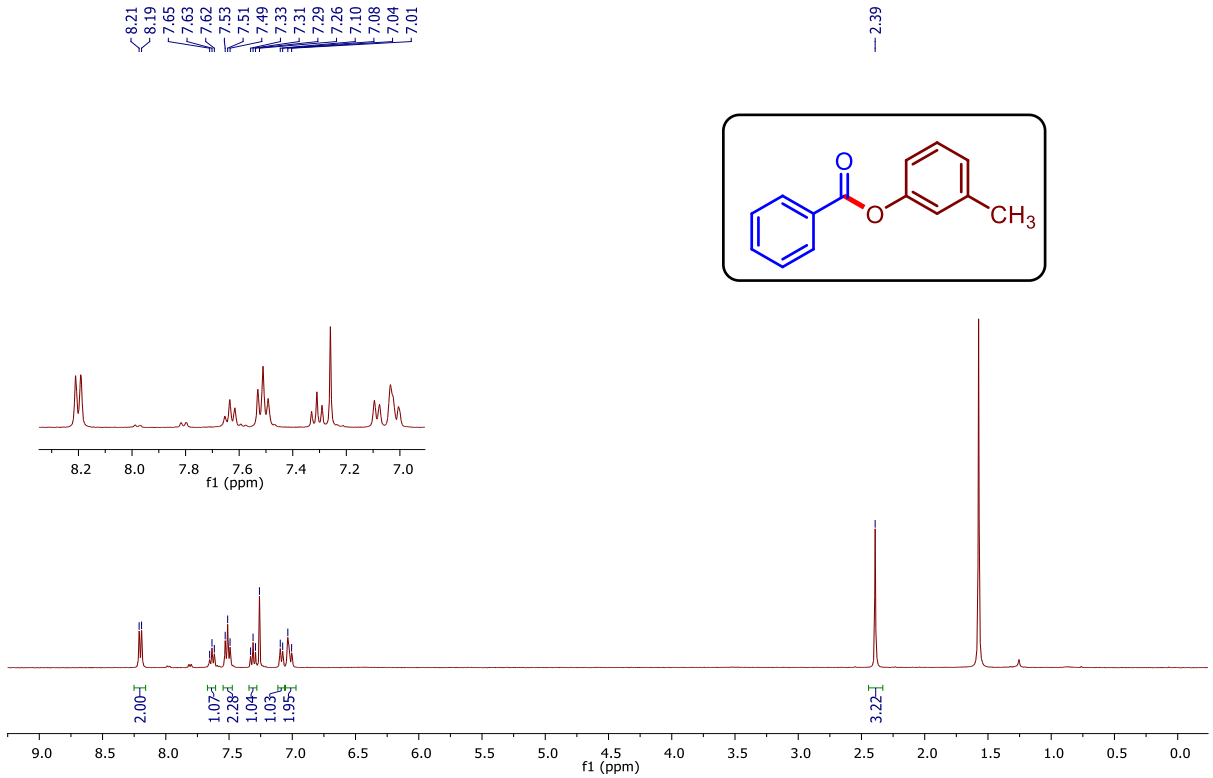
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3p



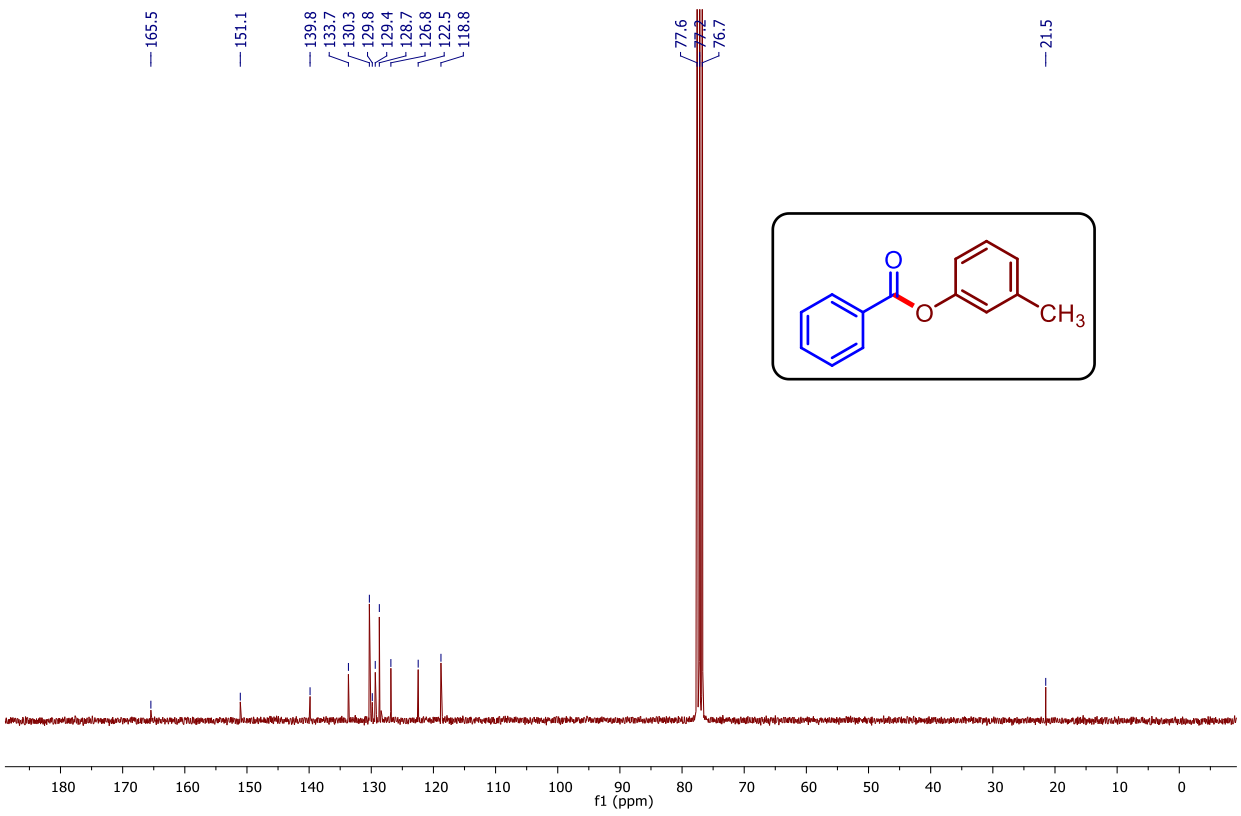
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3q



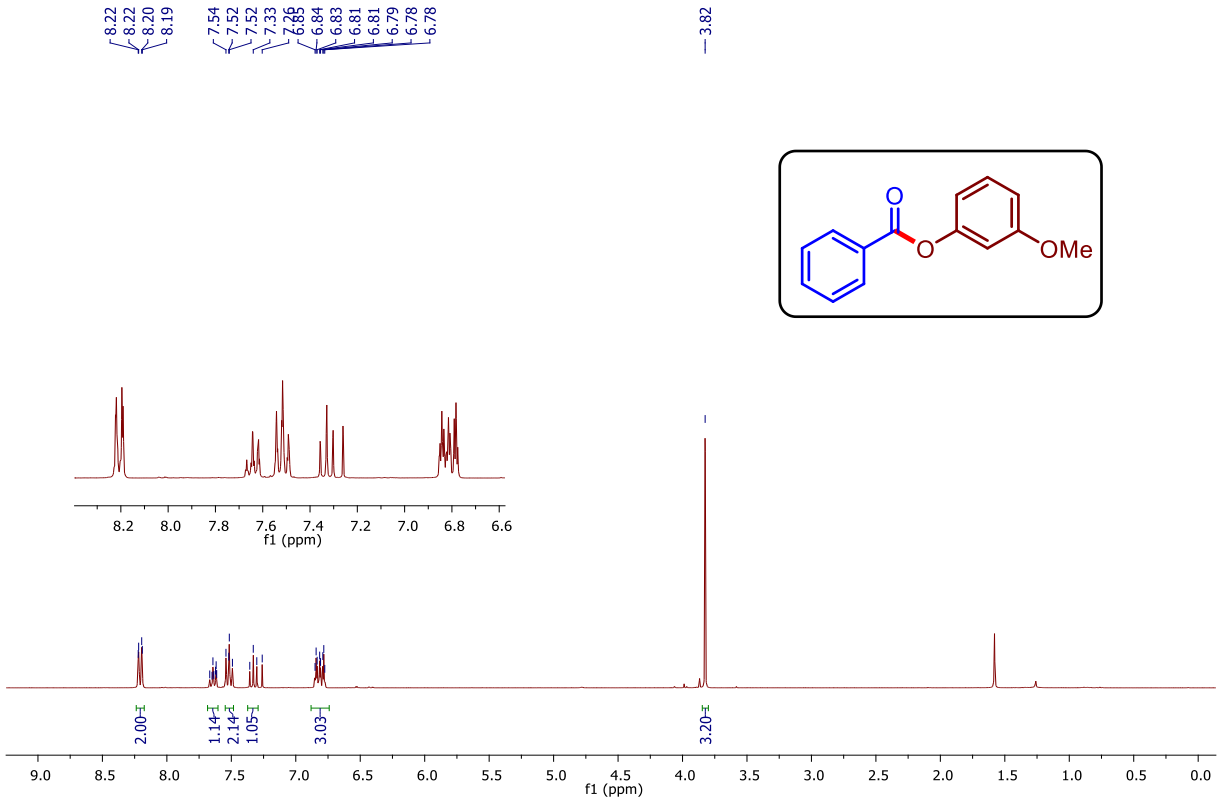
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3q



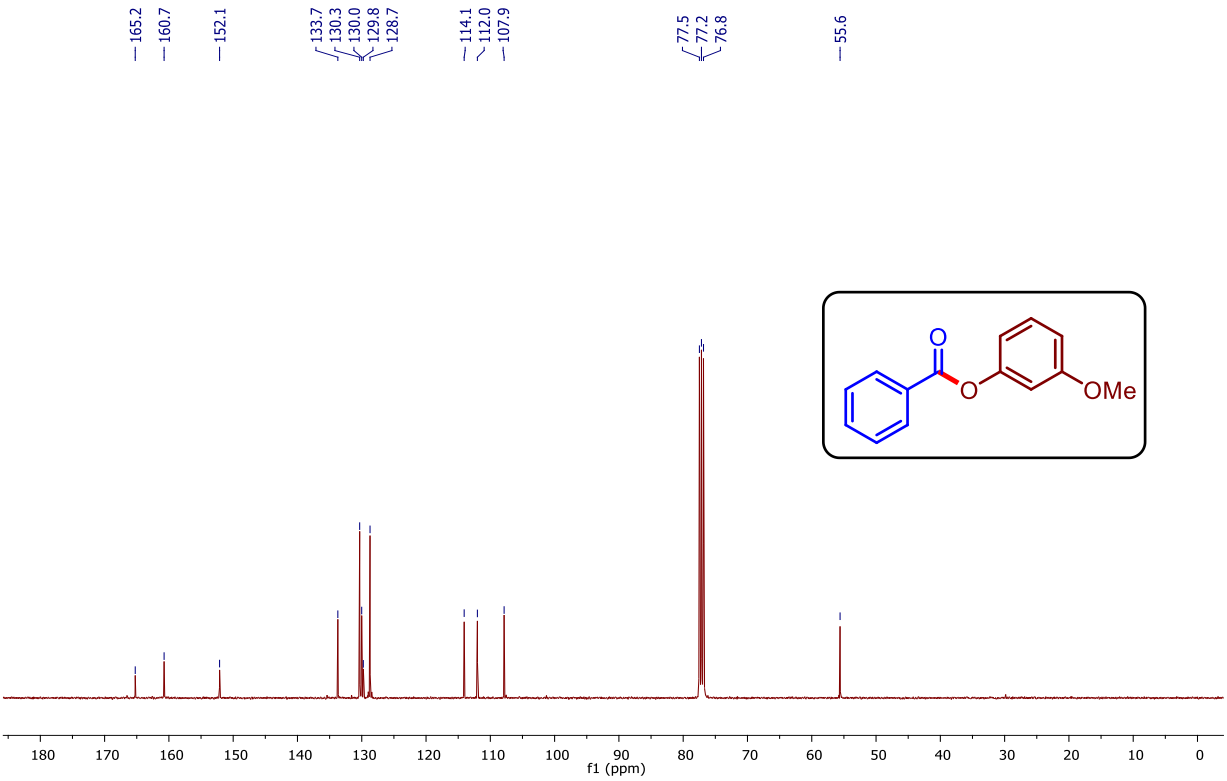
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3r



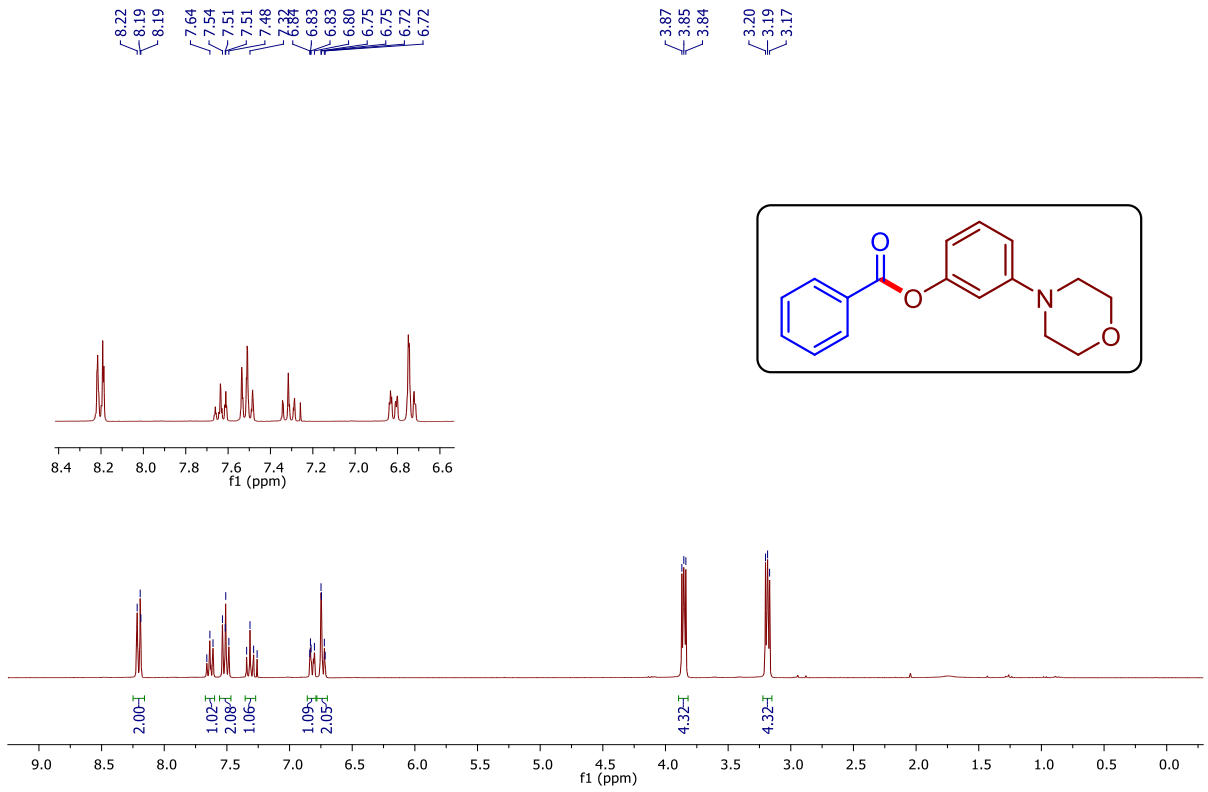
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3r



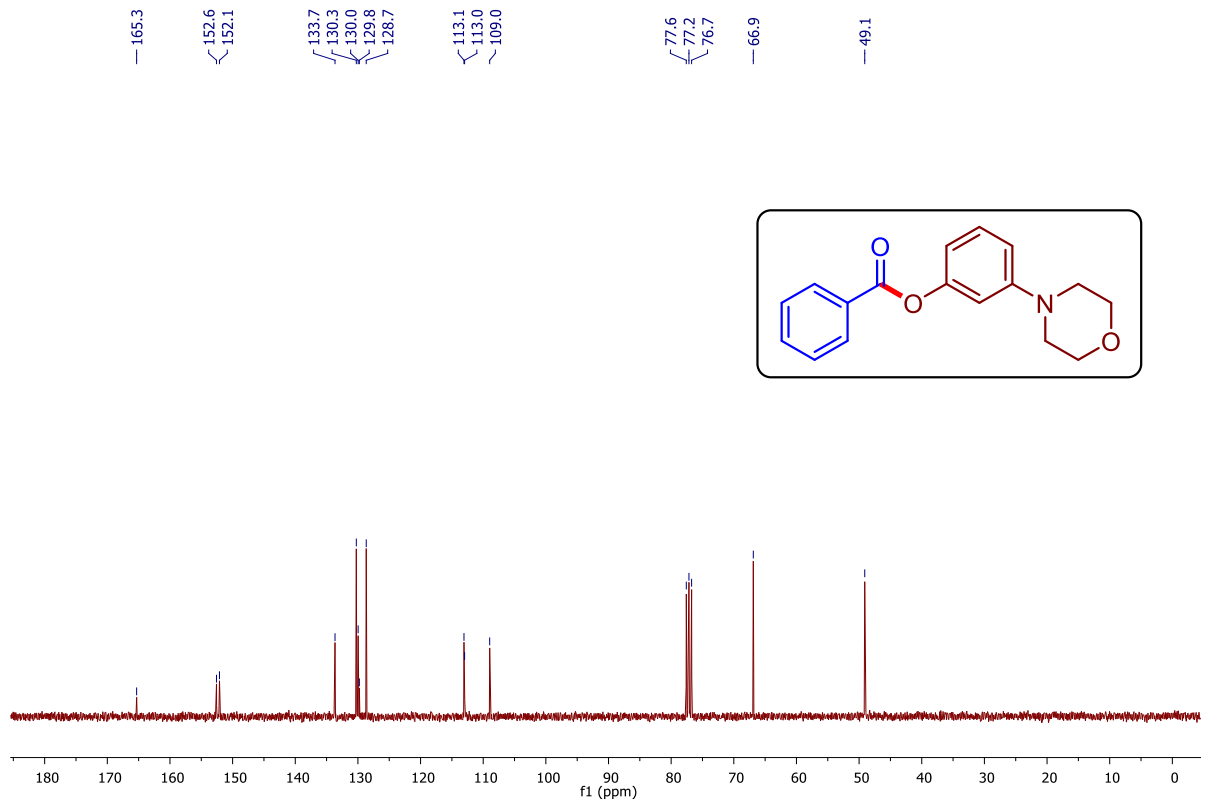
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3s



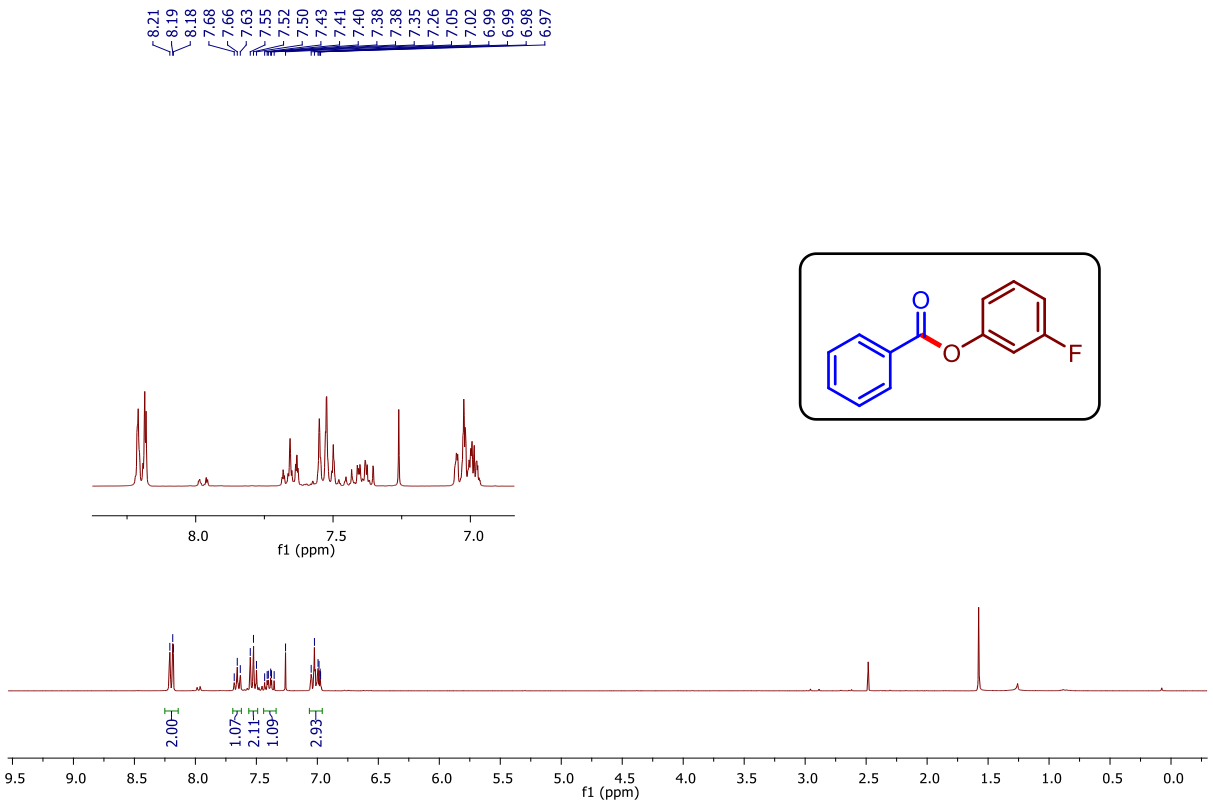
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3s



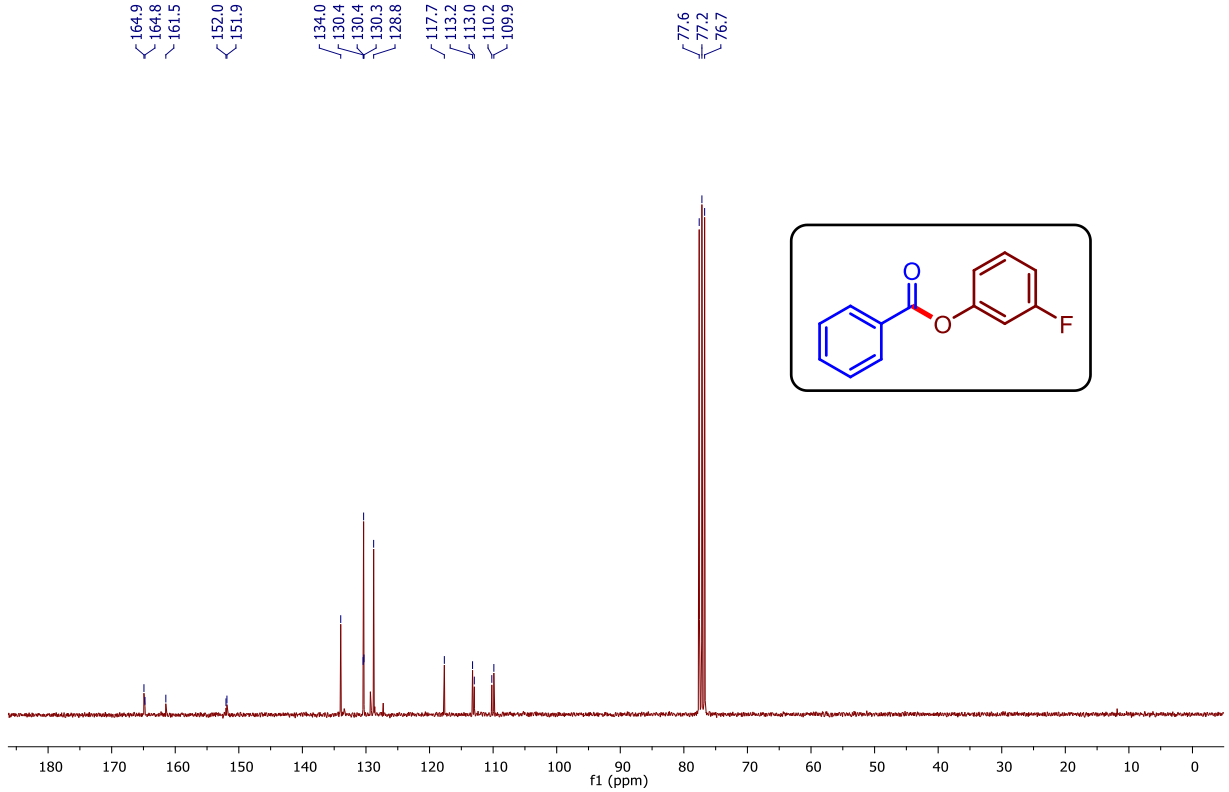
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3t



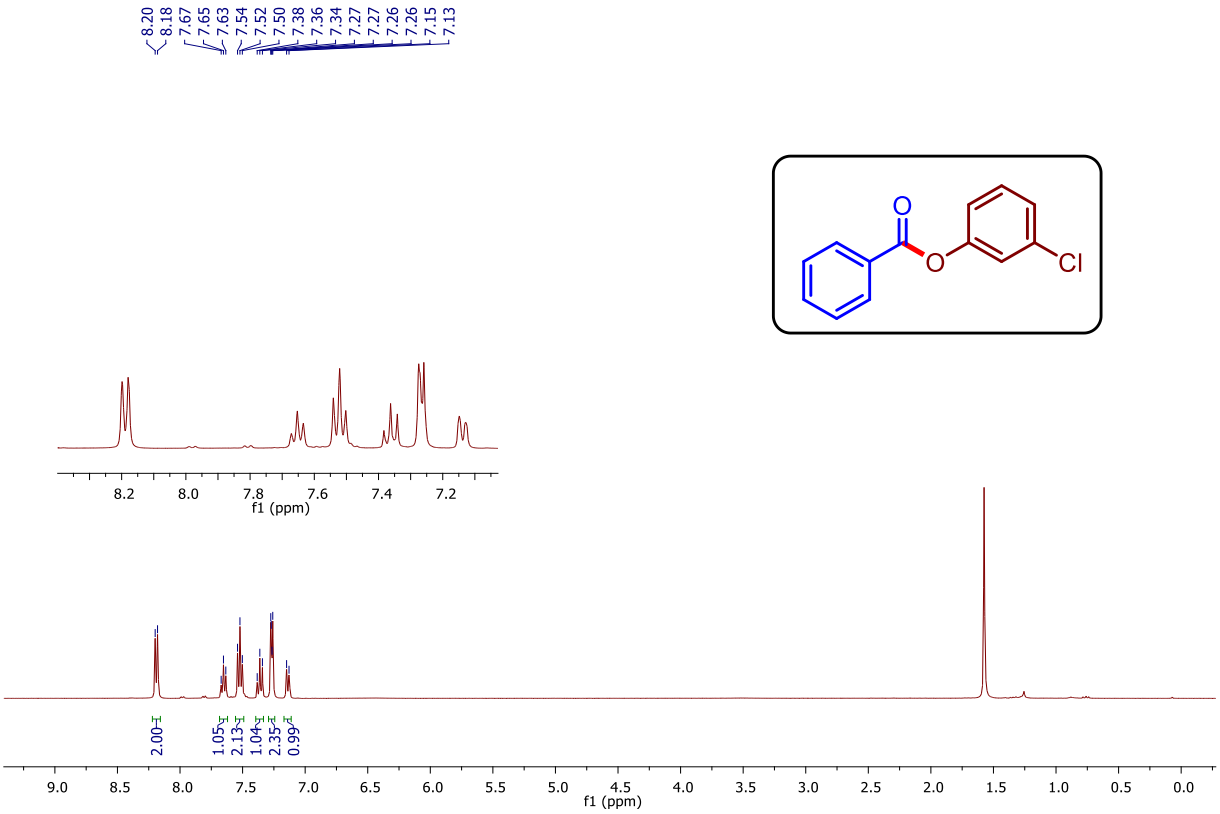
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3t



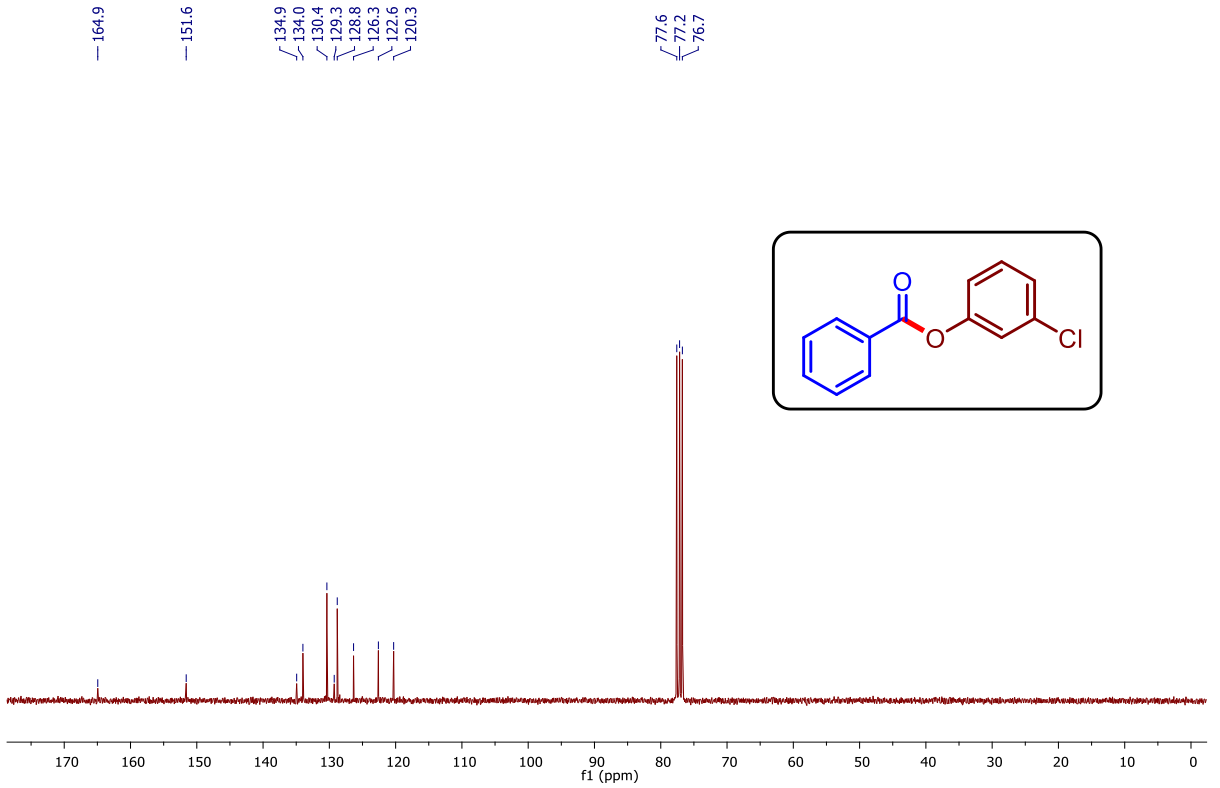
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3u



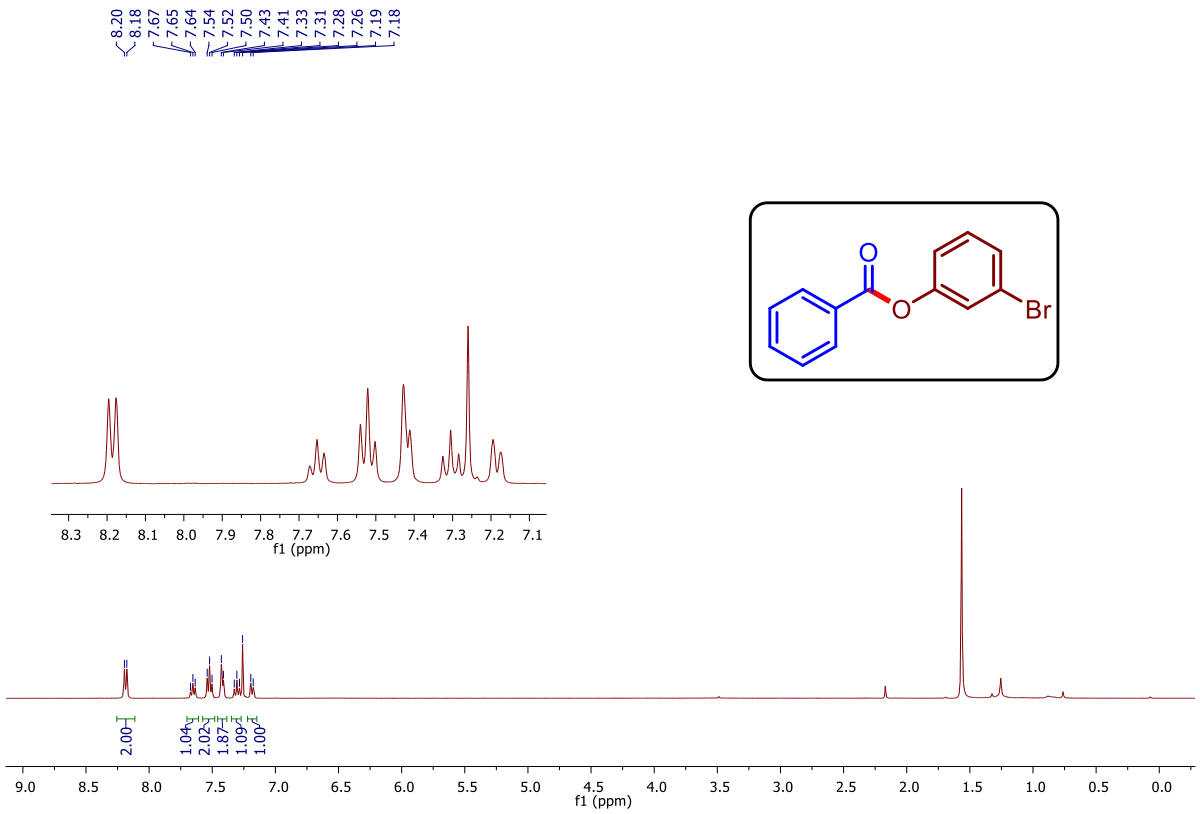
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3u



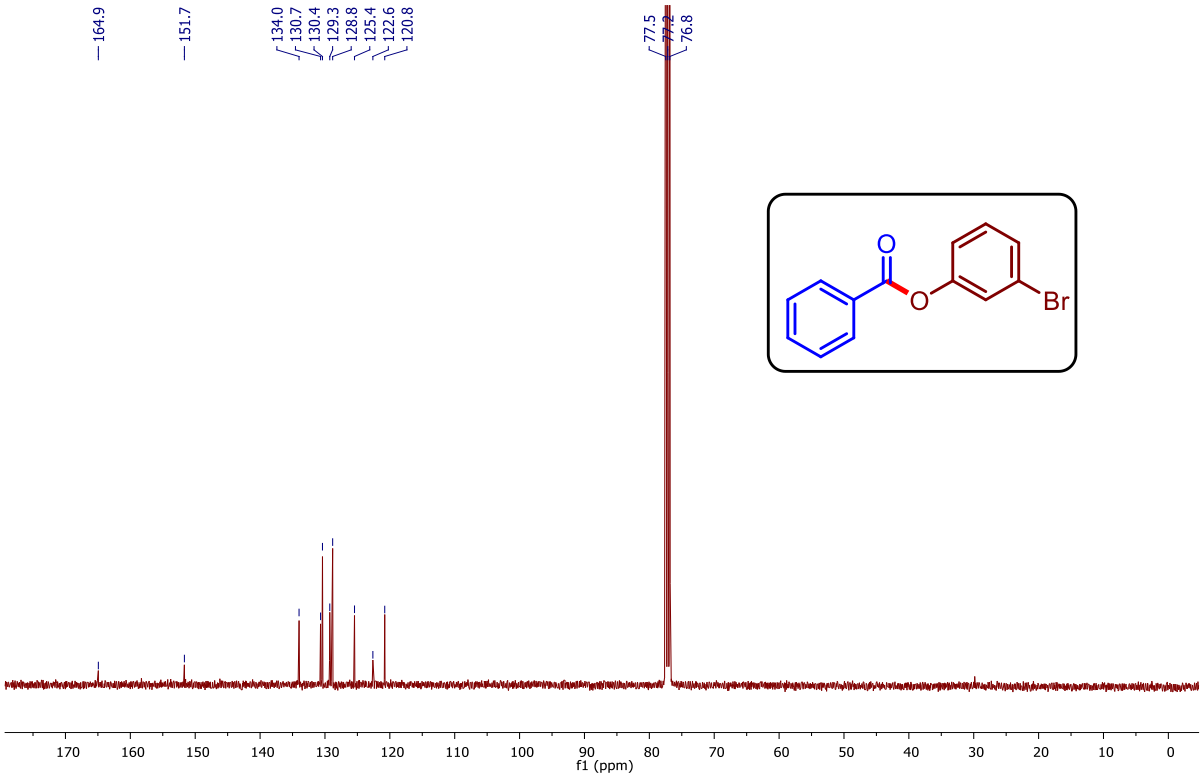
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3v



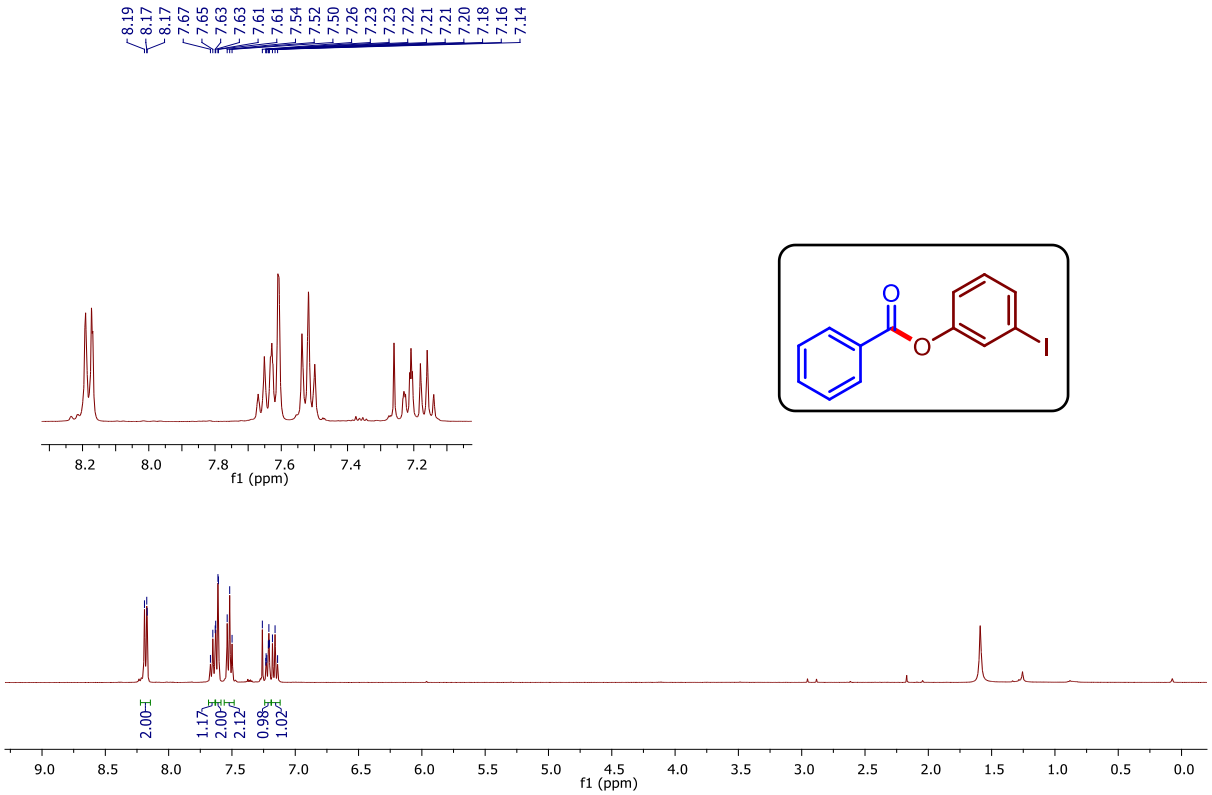
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3v



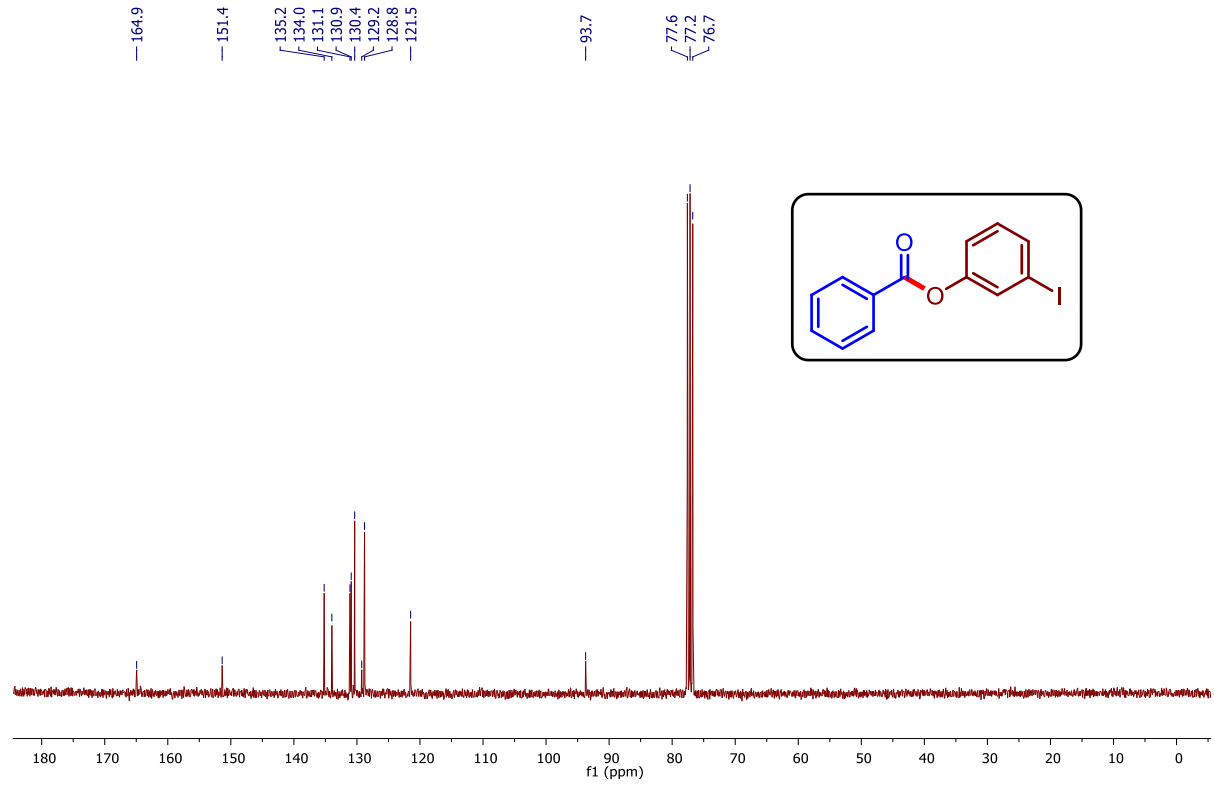
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3w



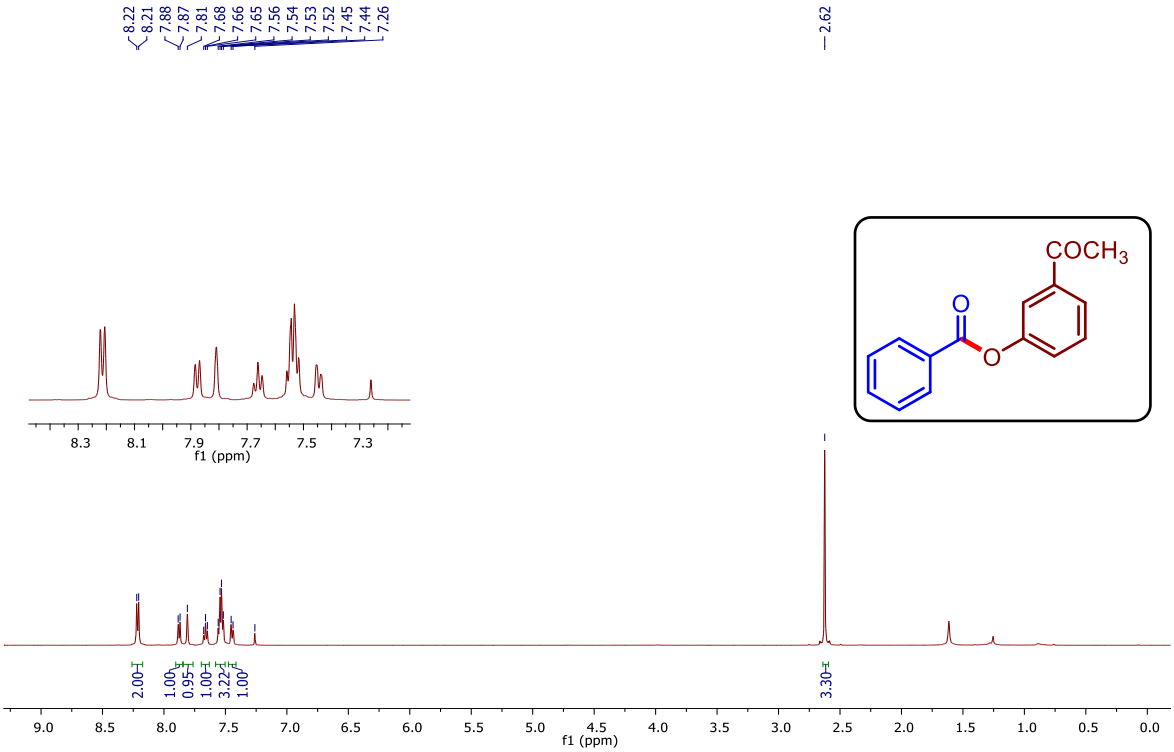
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3w



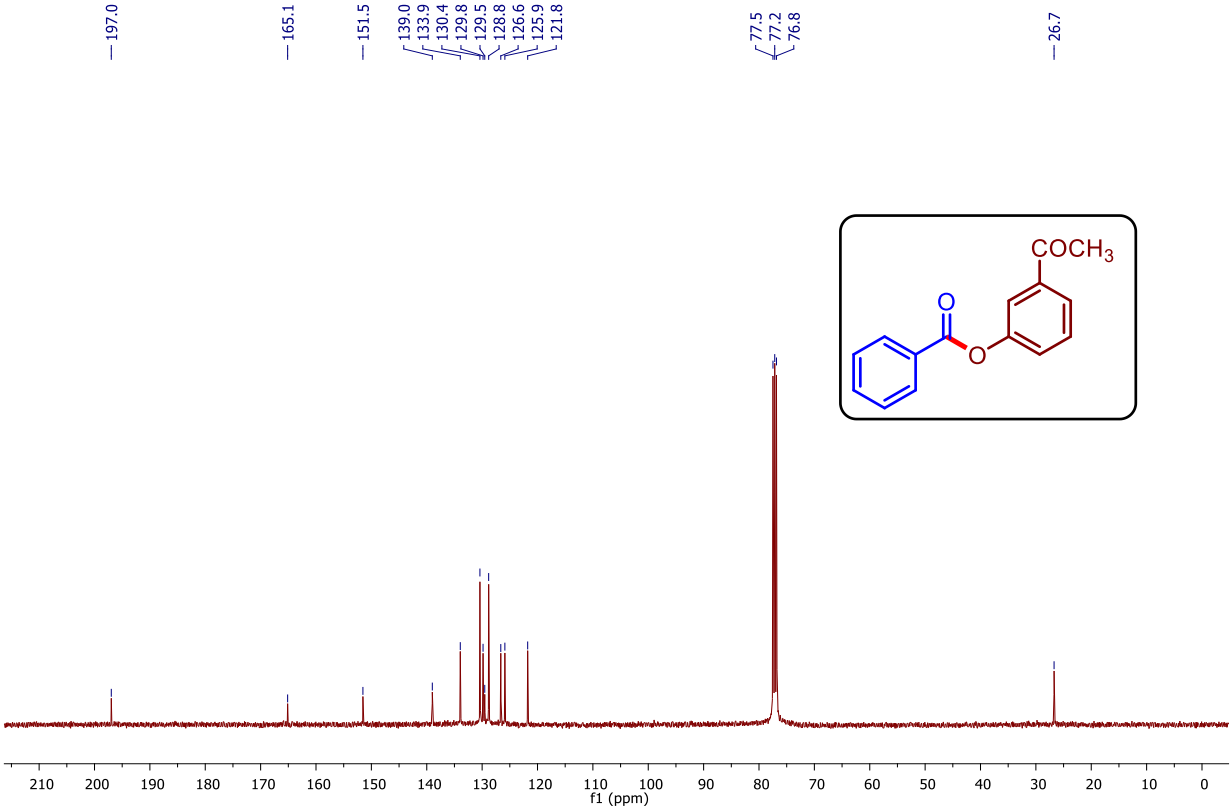
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3x



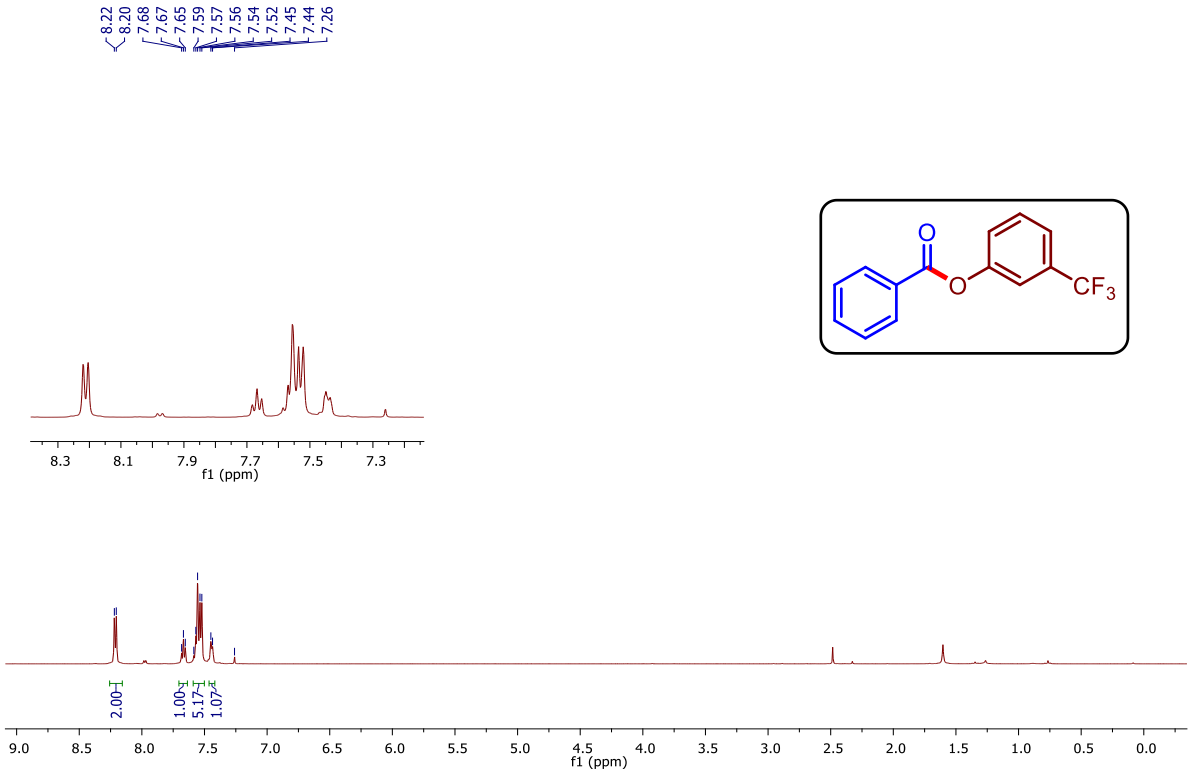
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3x



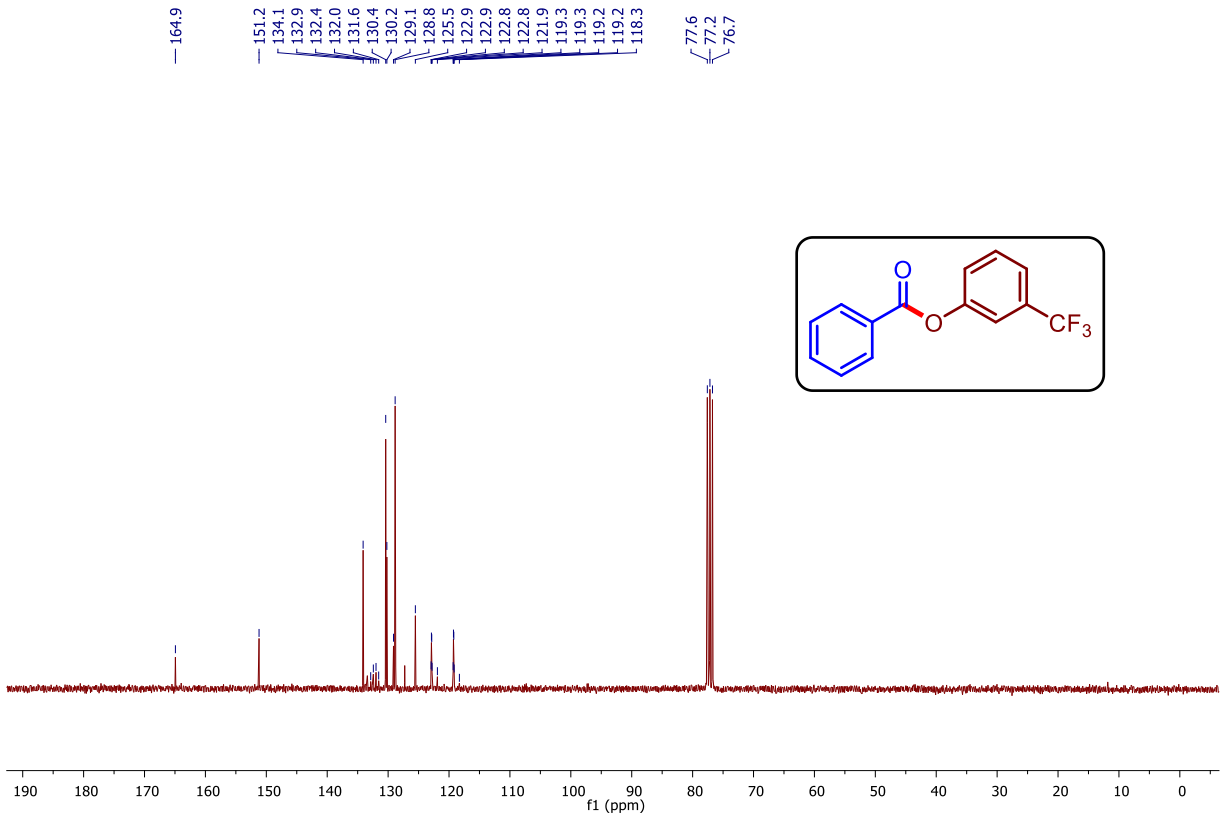
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of 3y



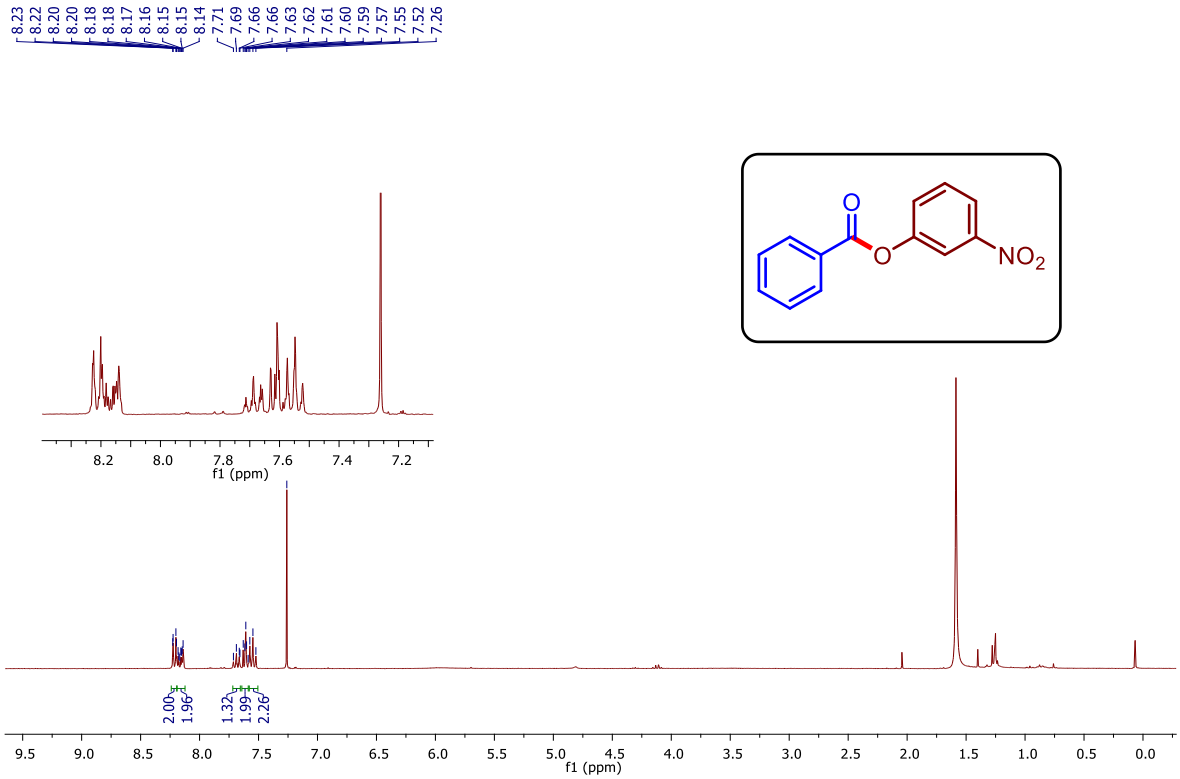
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3y



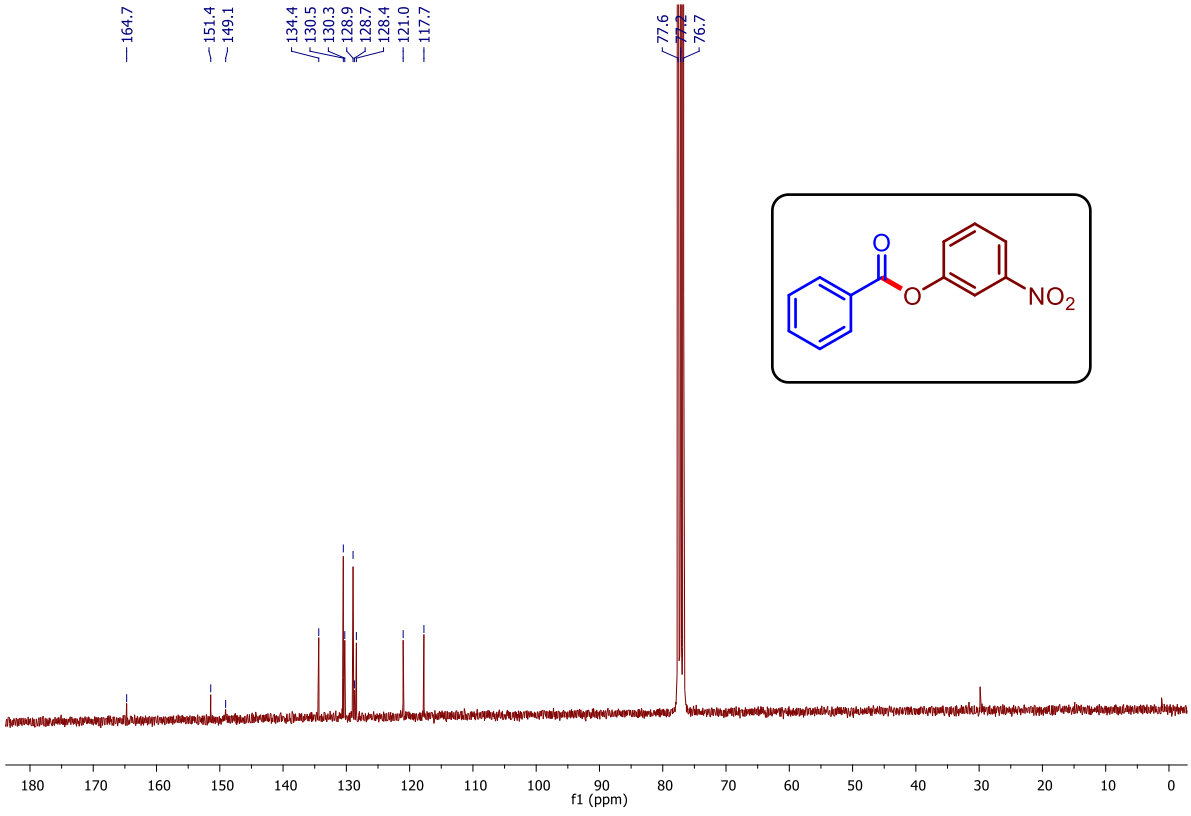
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of 3z



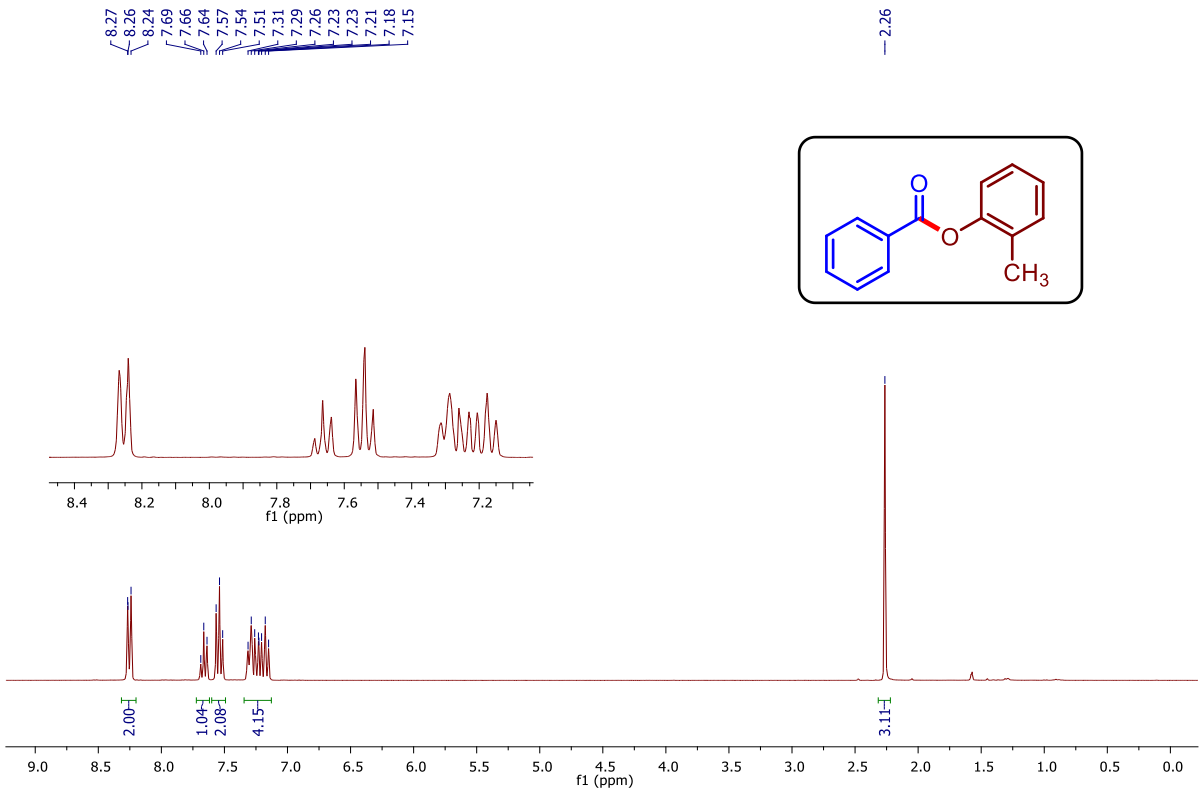
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3z



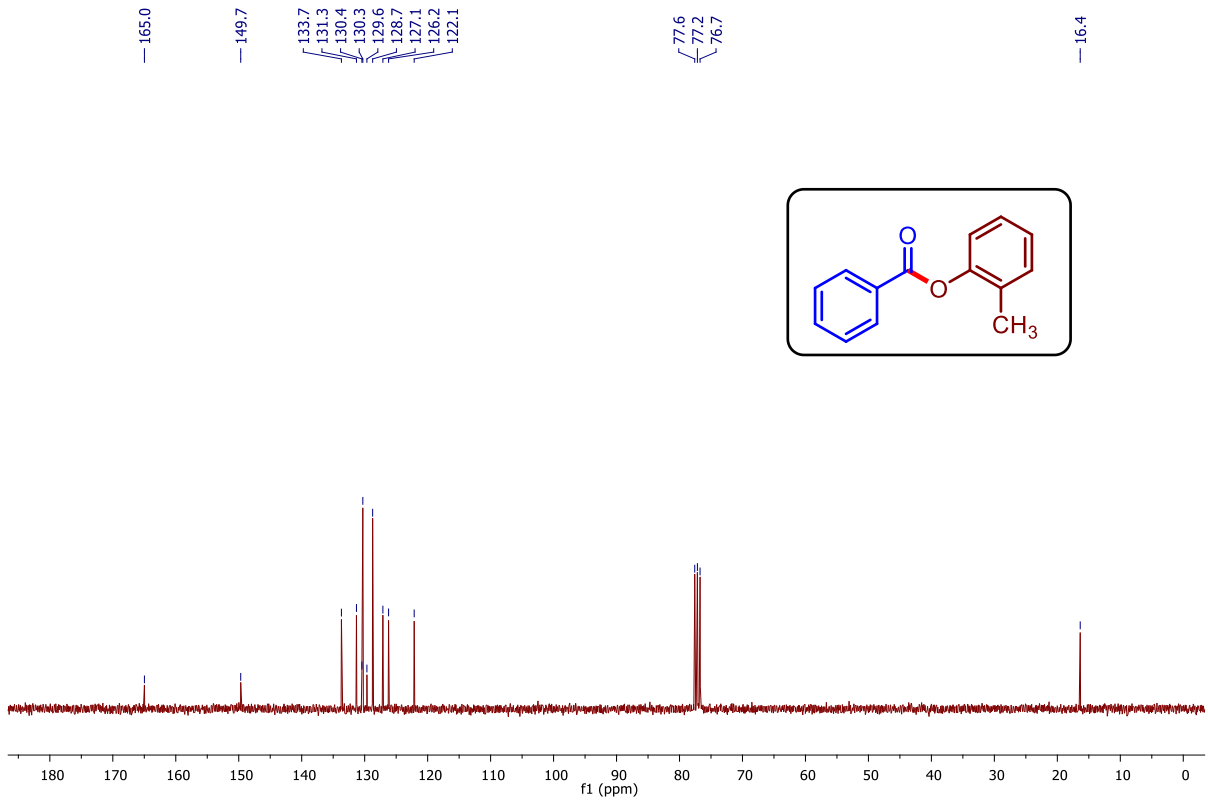
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3za



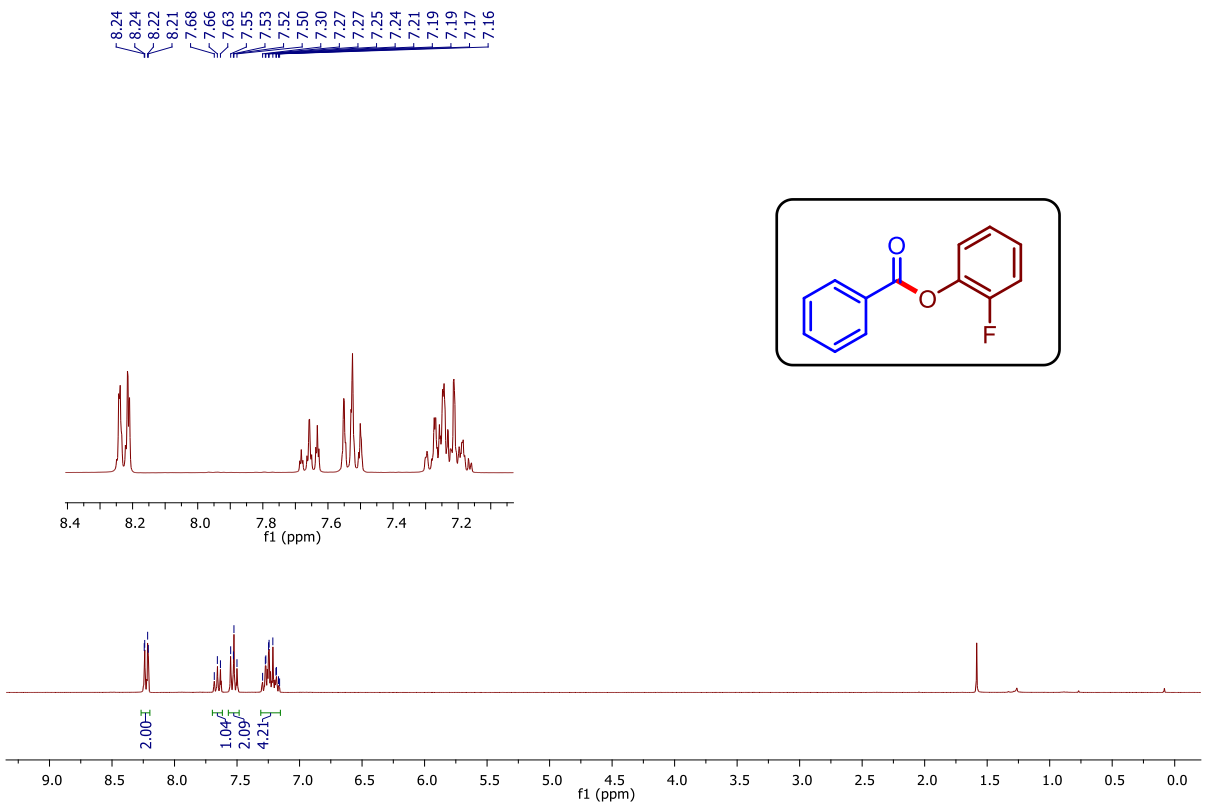
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3za



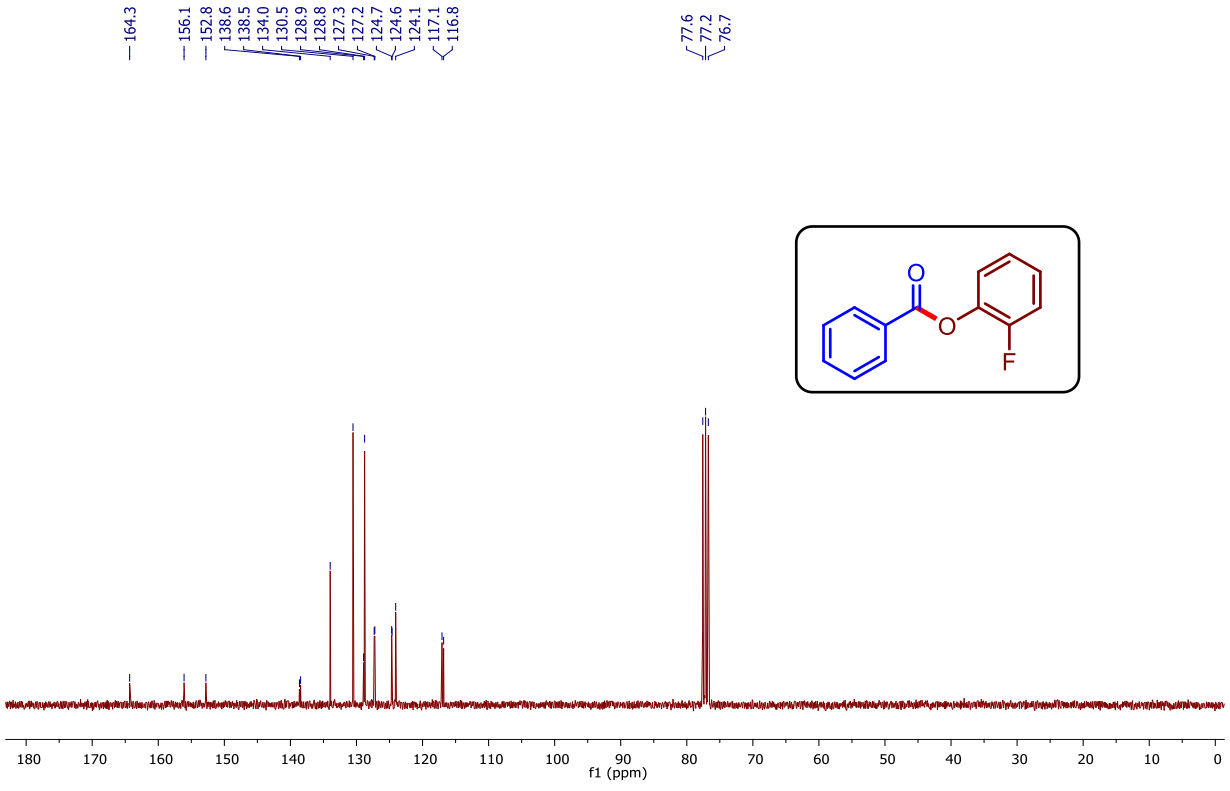
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zb



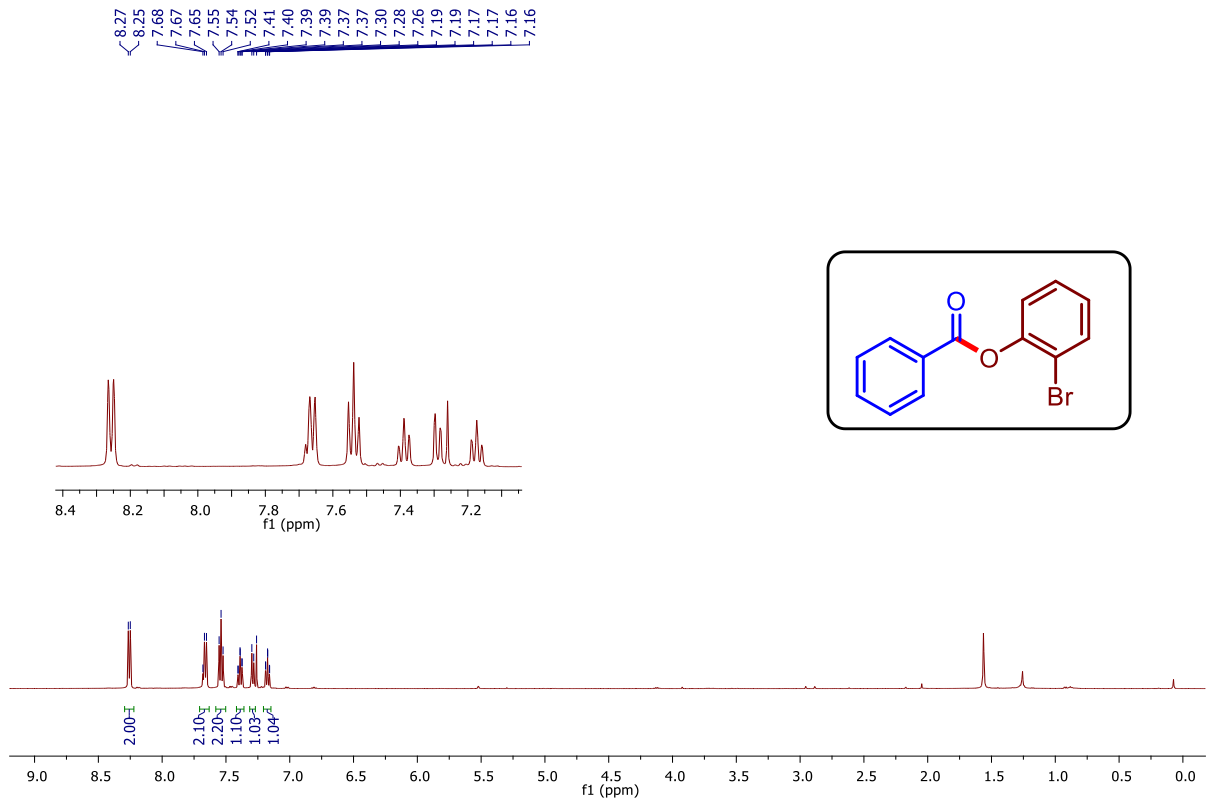
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zb



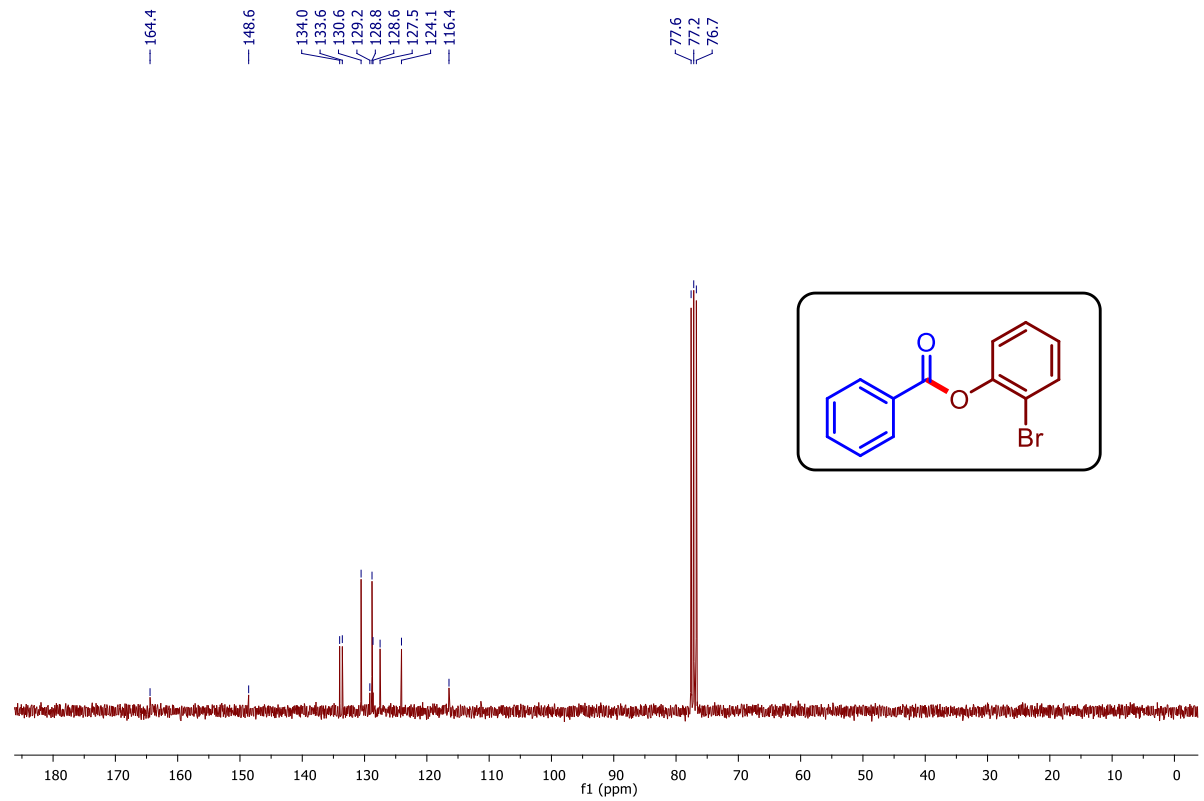
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zc



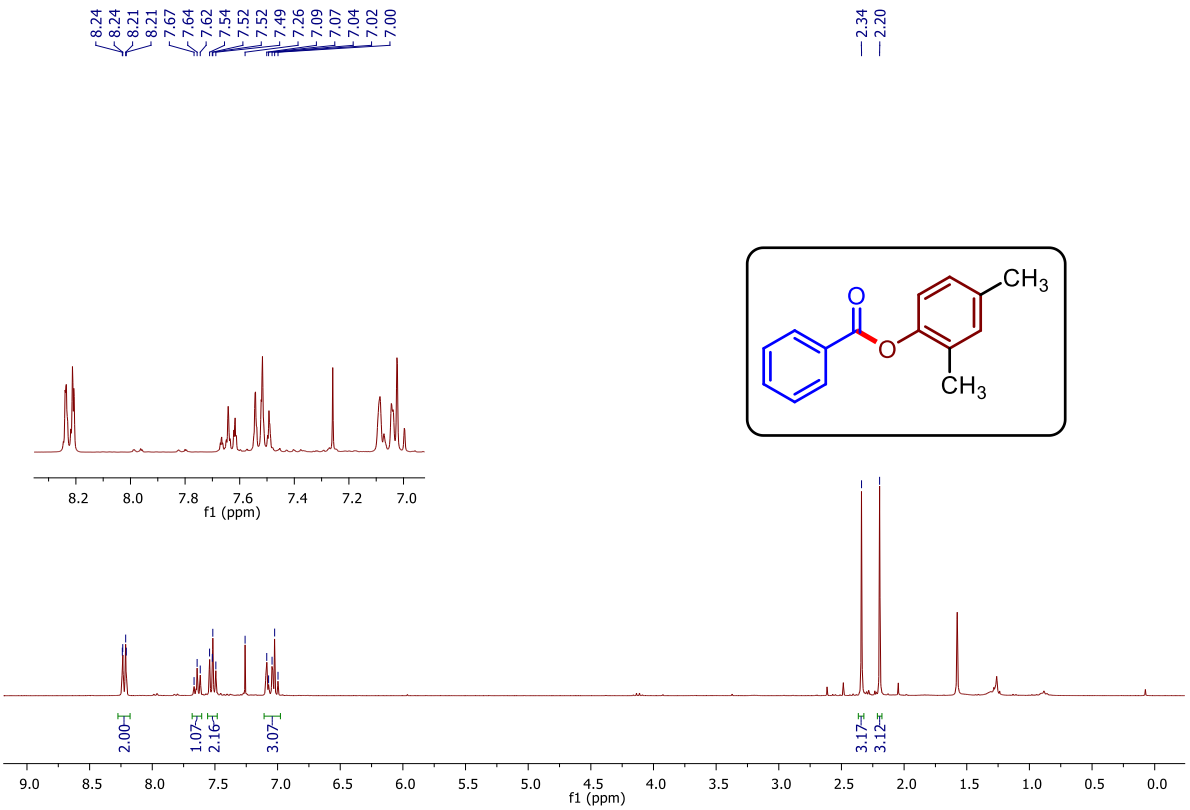
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zc



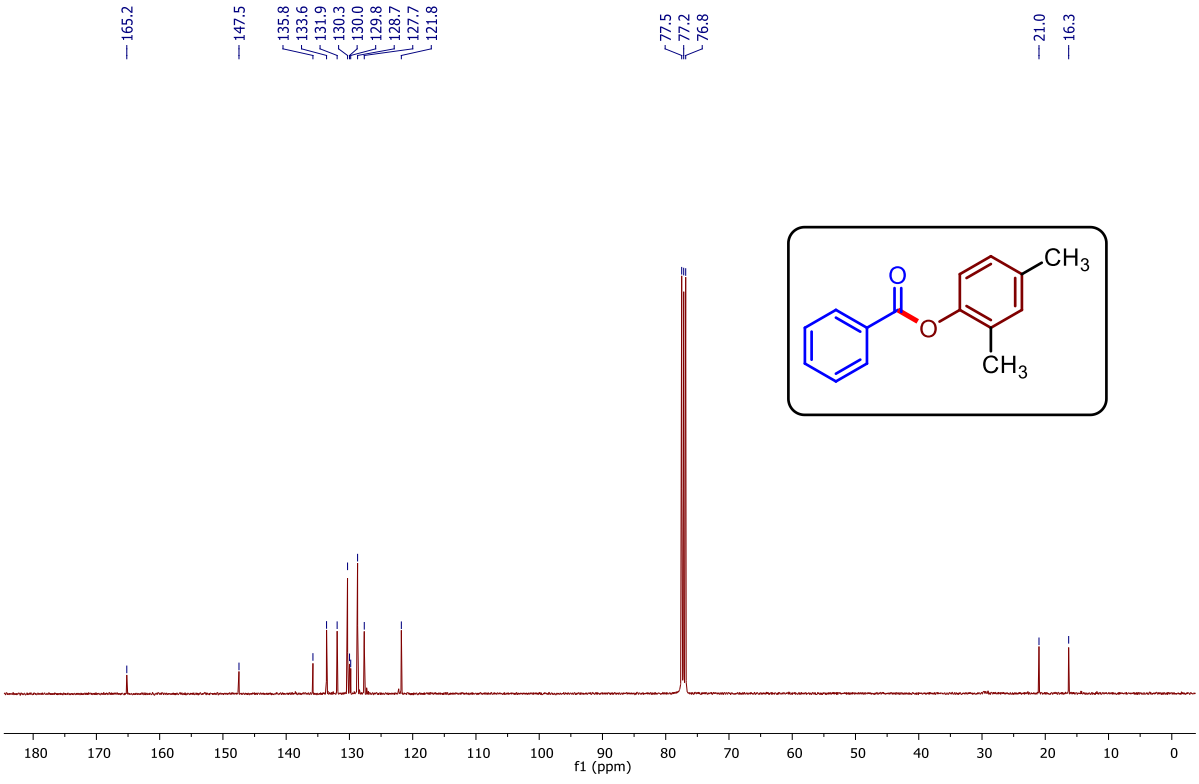
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of 3zd



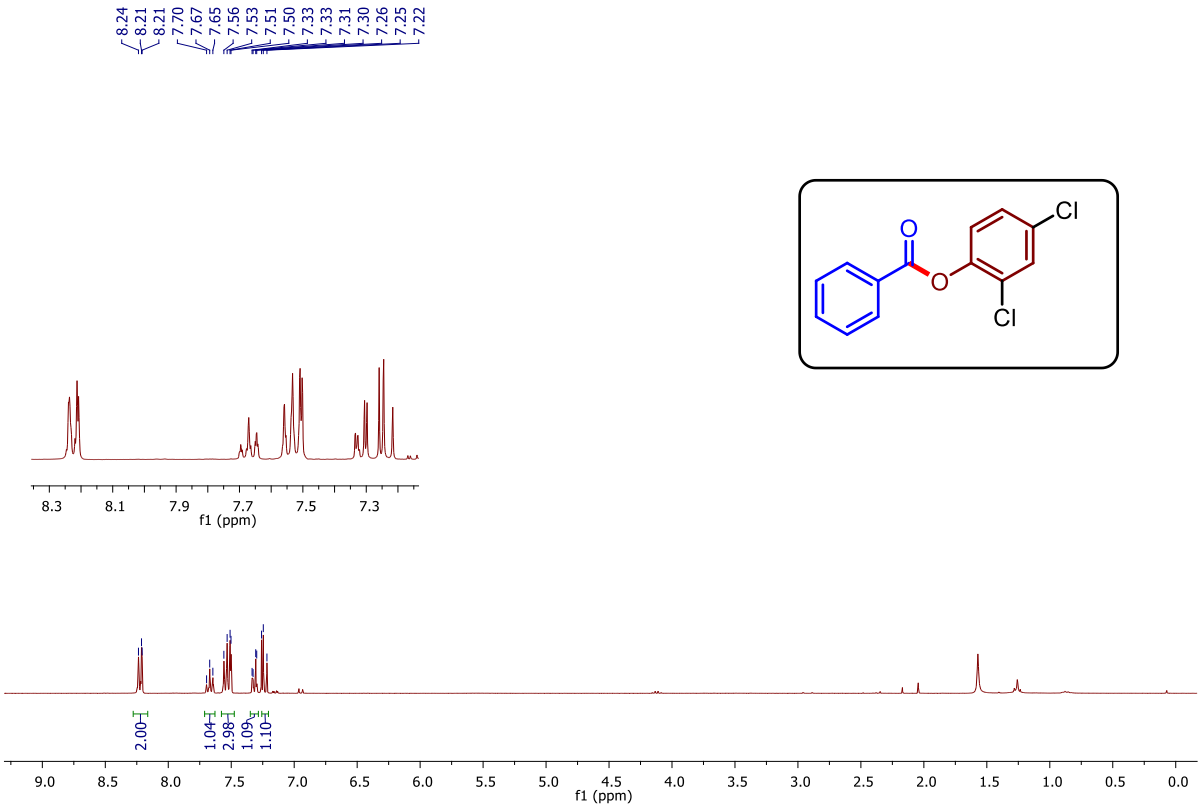
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zd



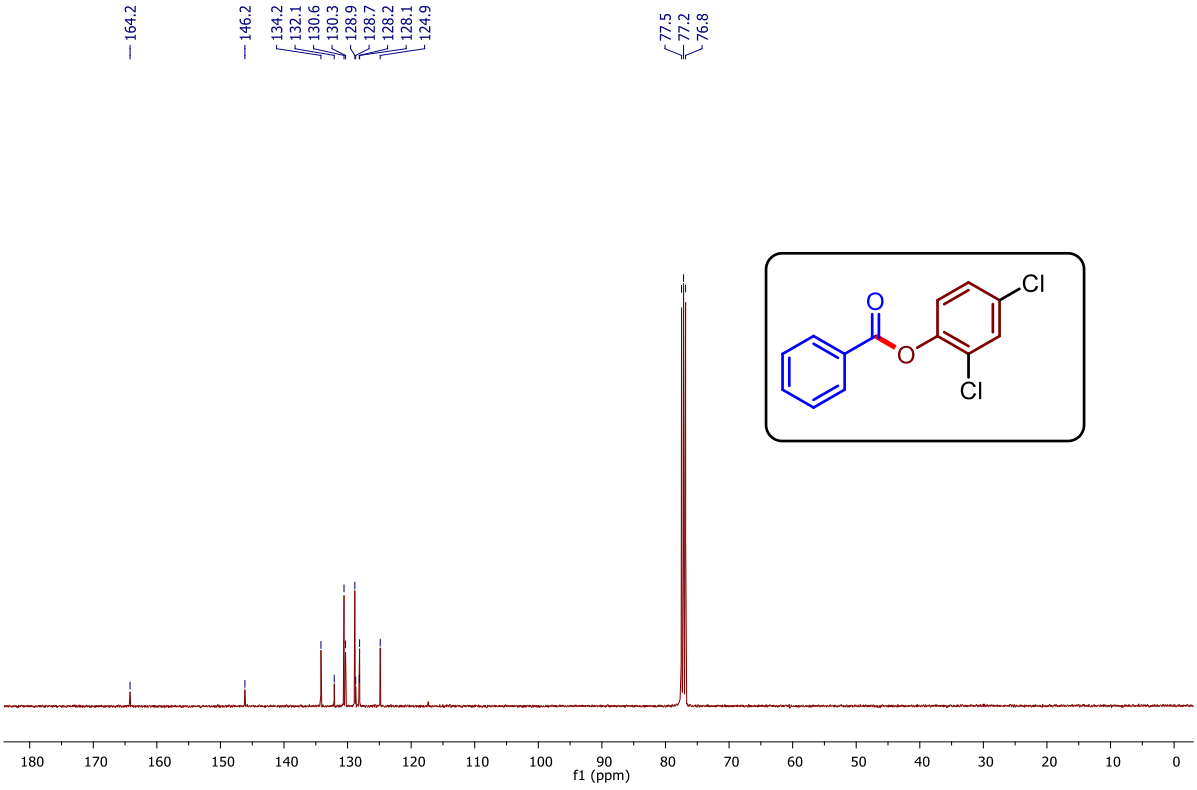
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3ze



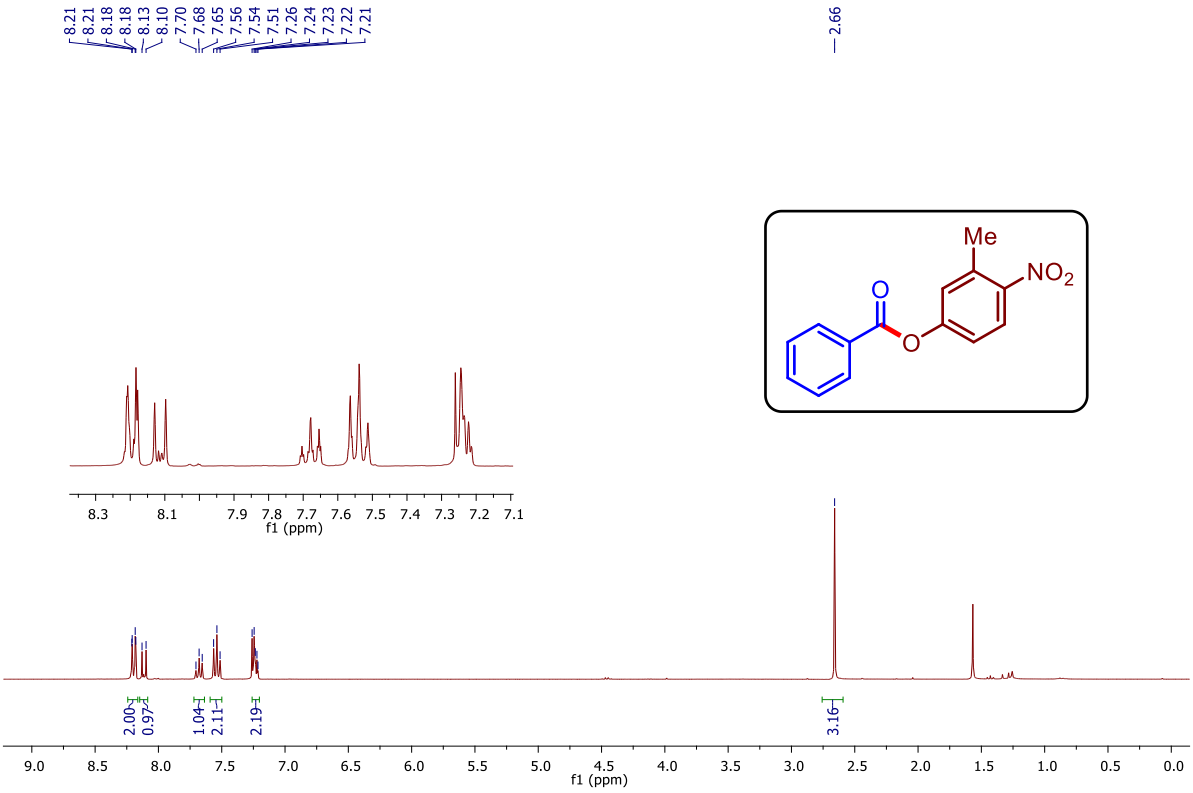
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3ze



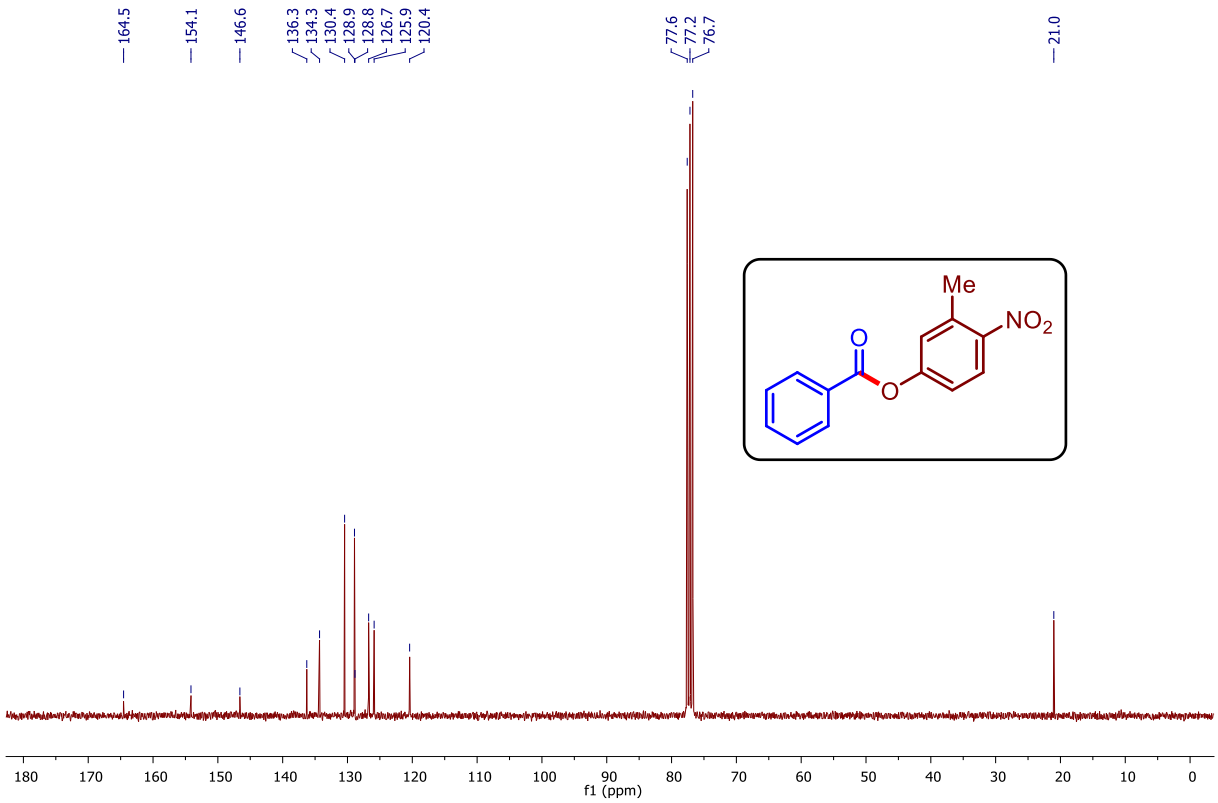
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zf



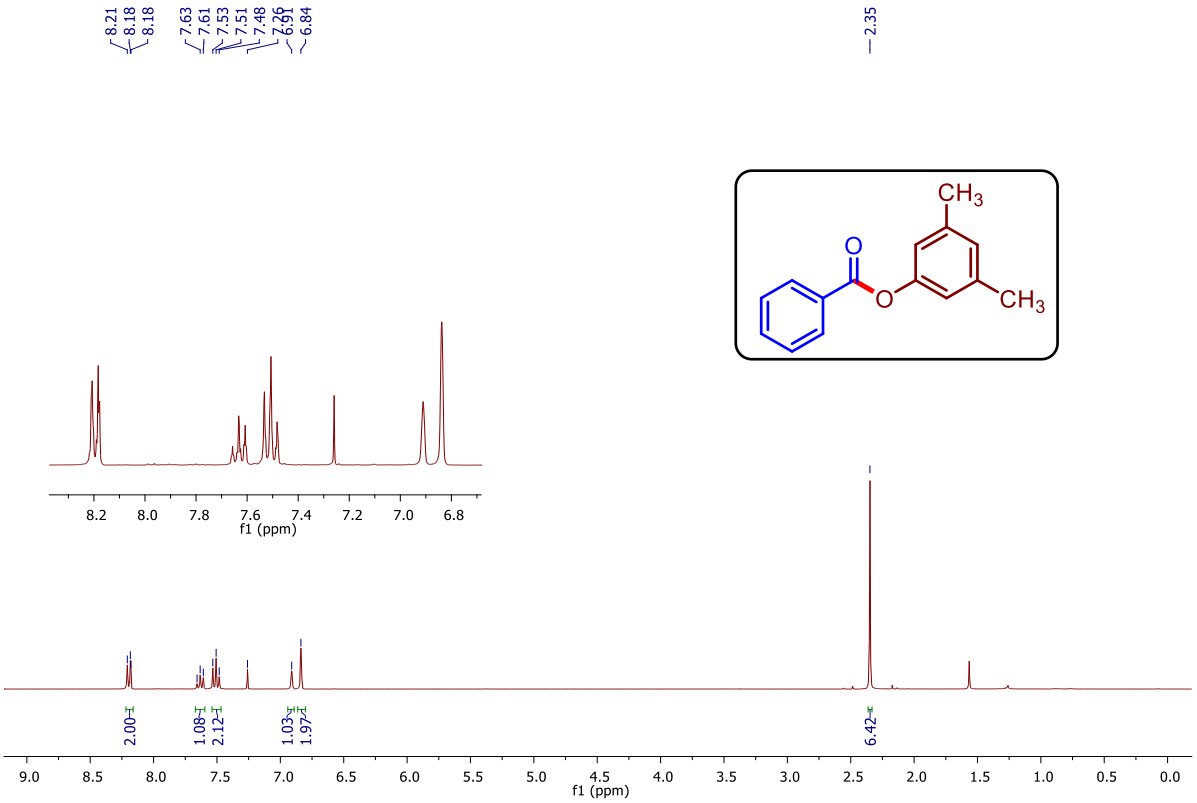
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3zf



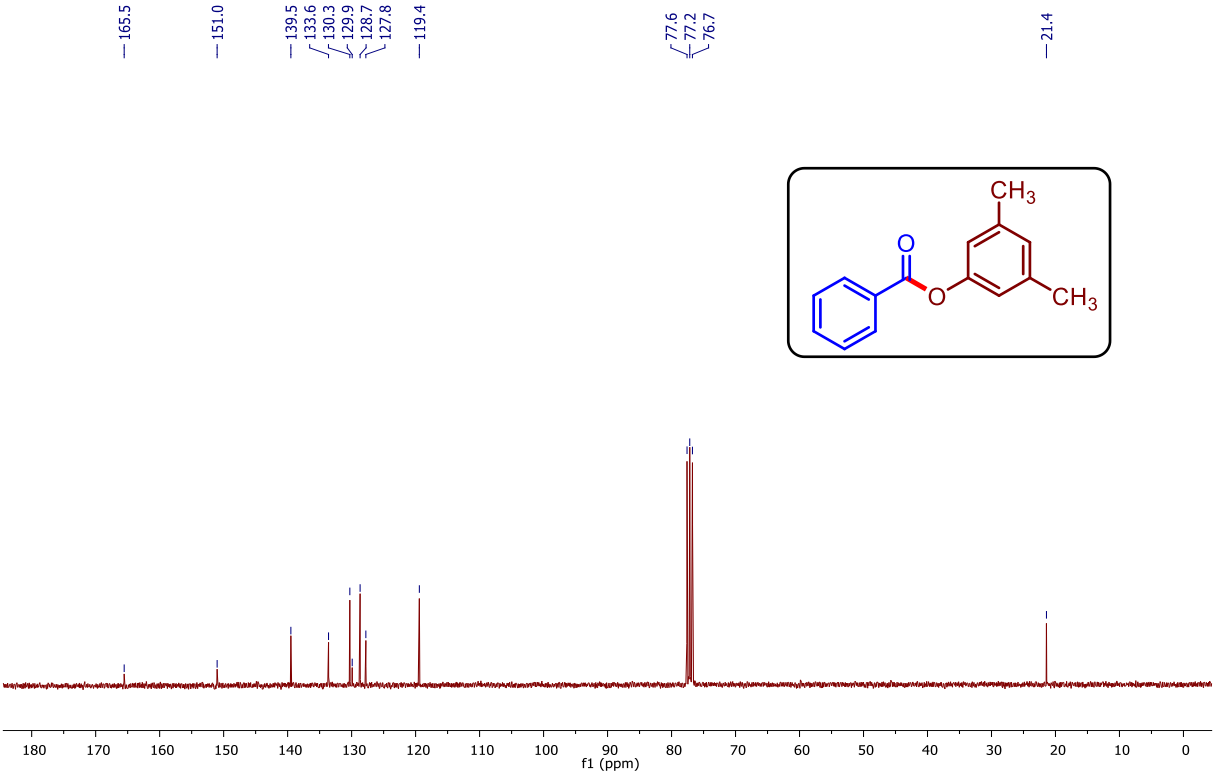
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zg



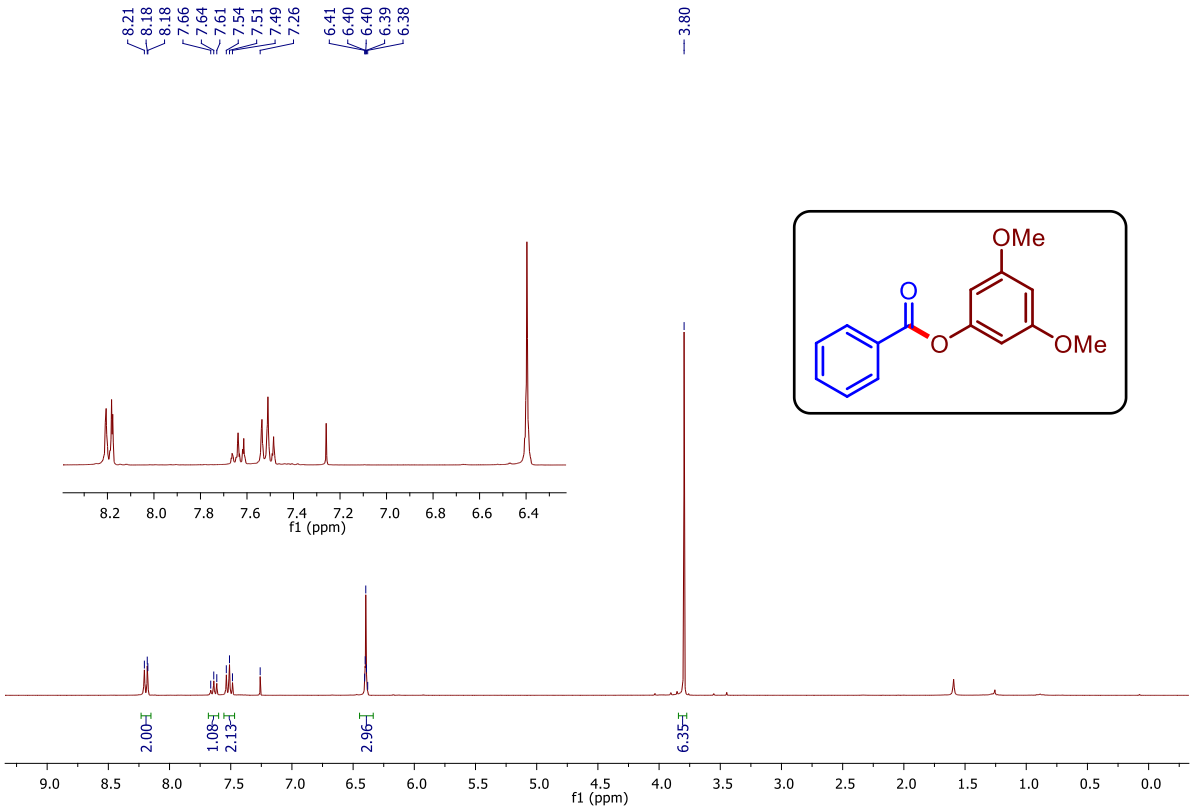
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zg



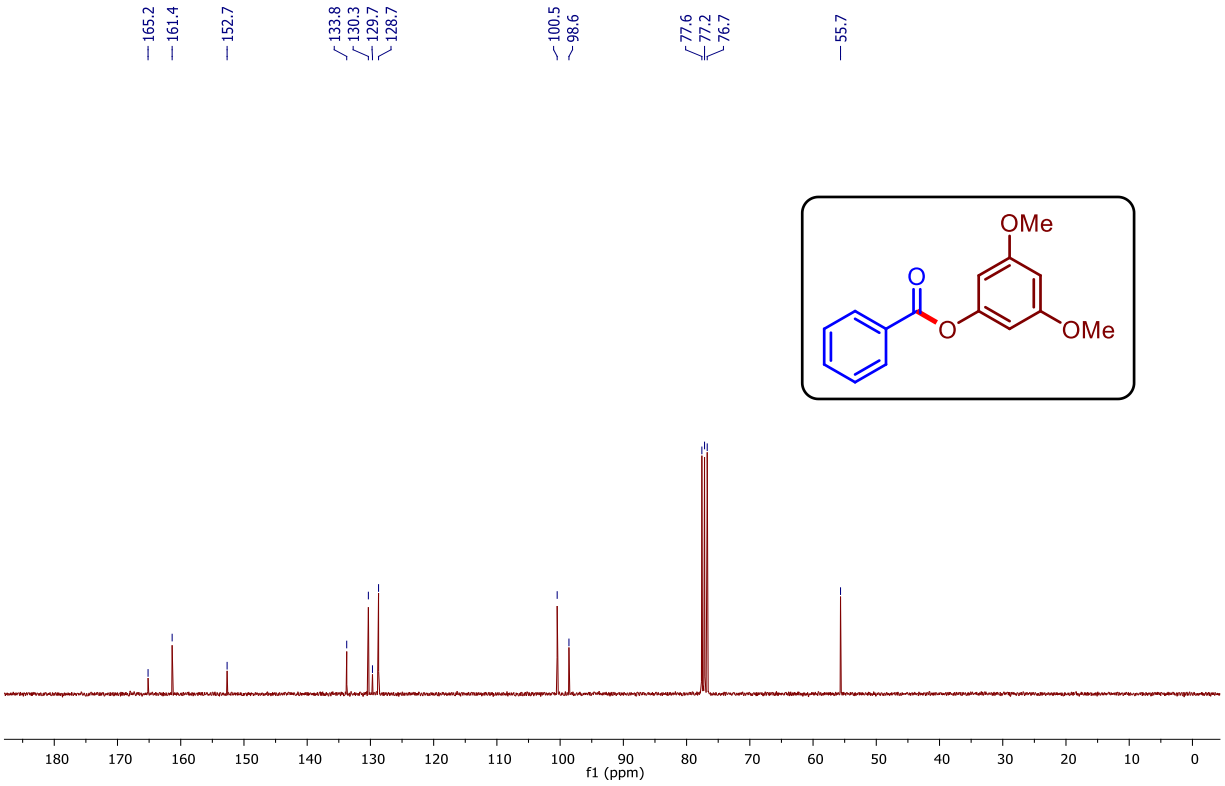
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zh



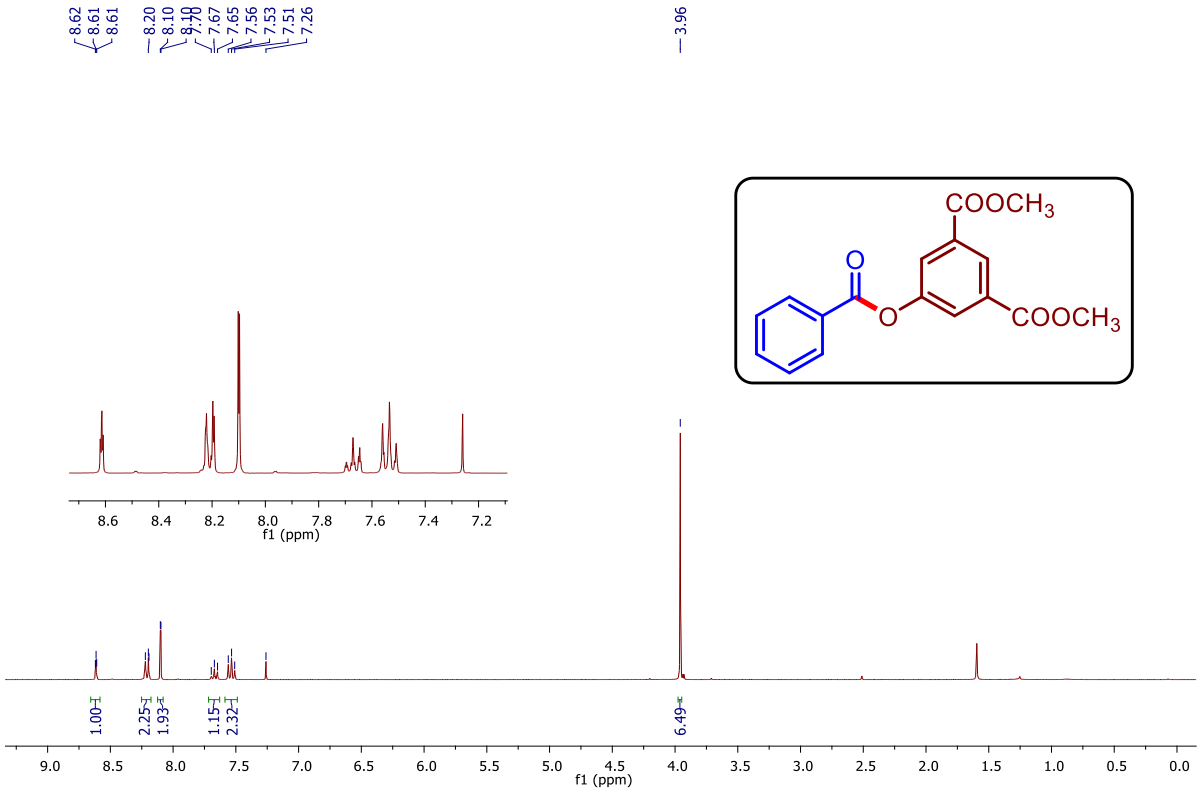
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zh



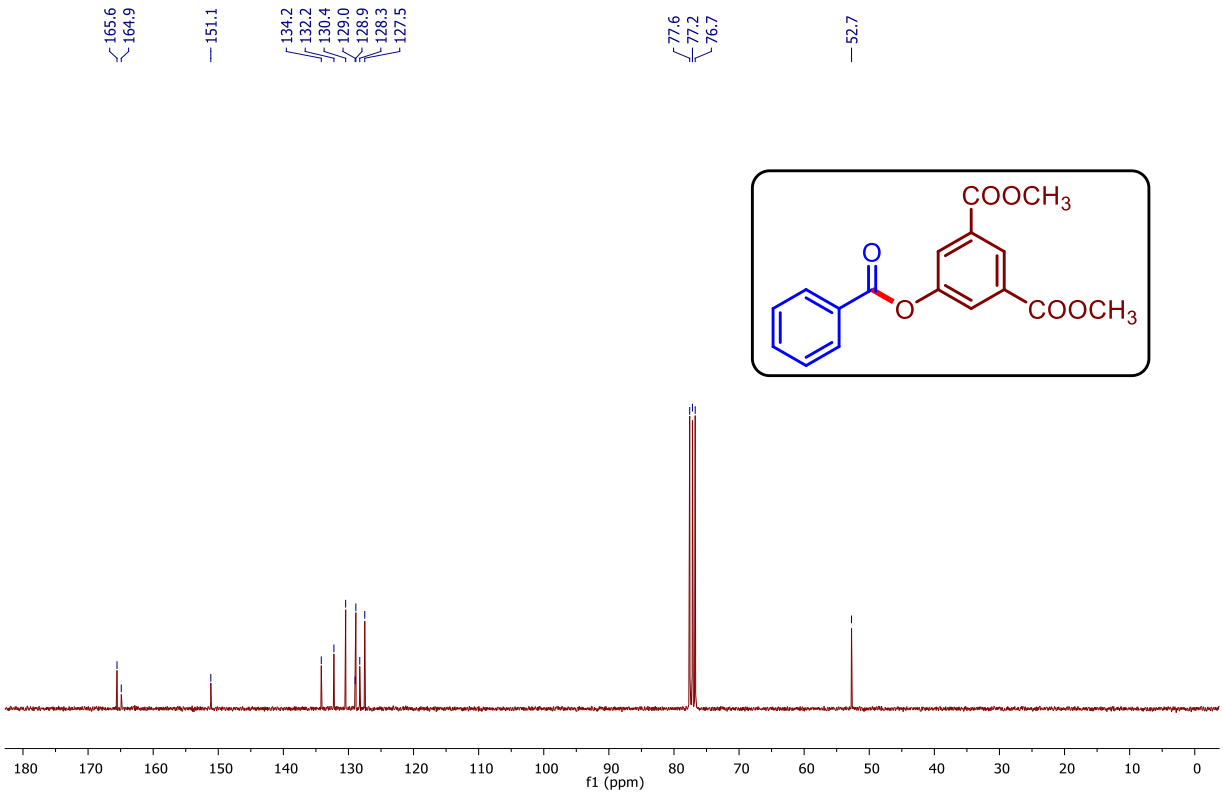
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zi



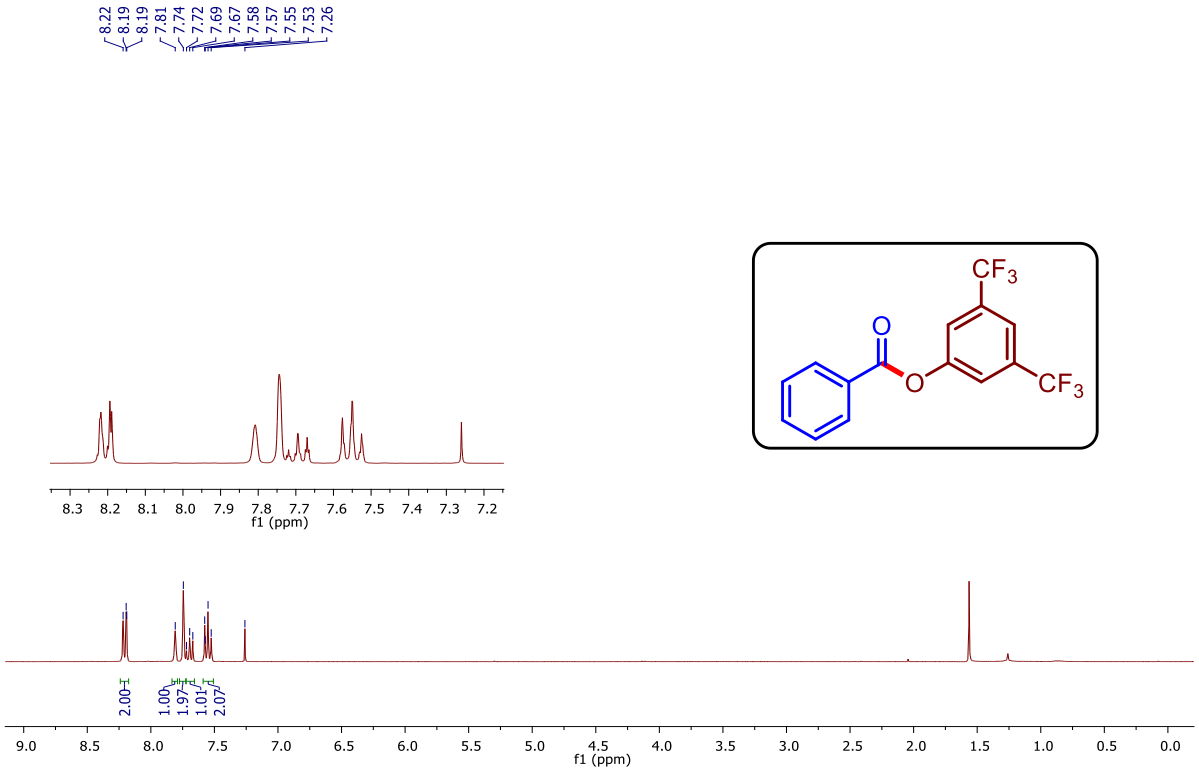
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zi



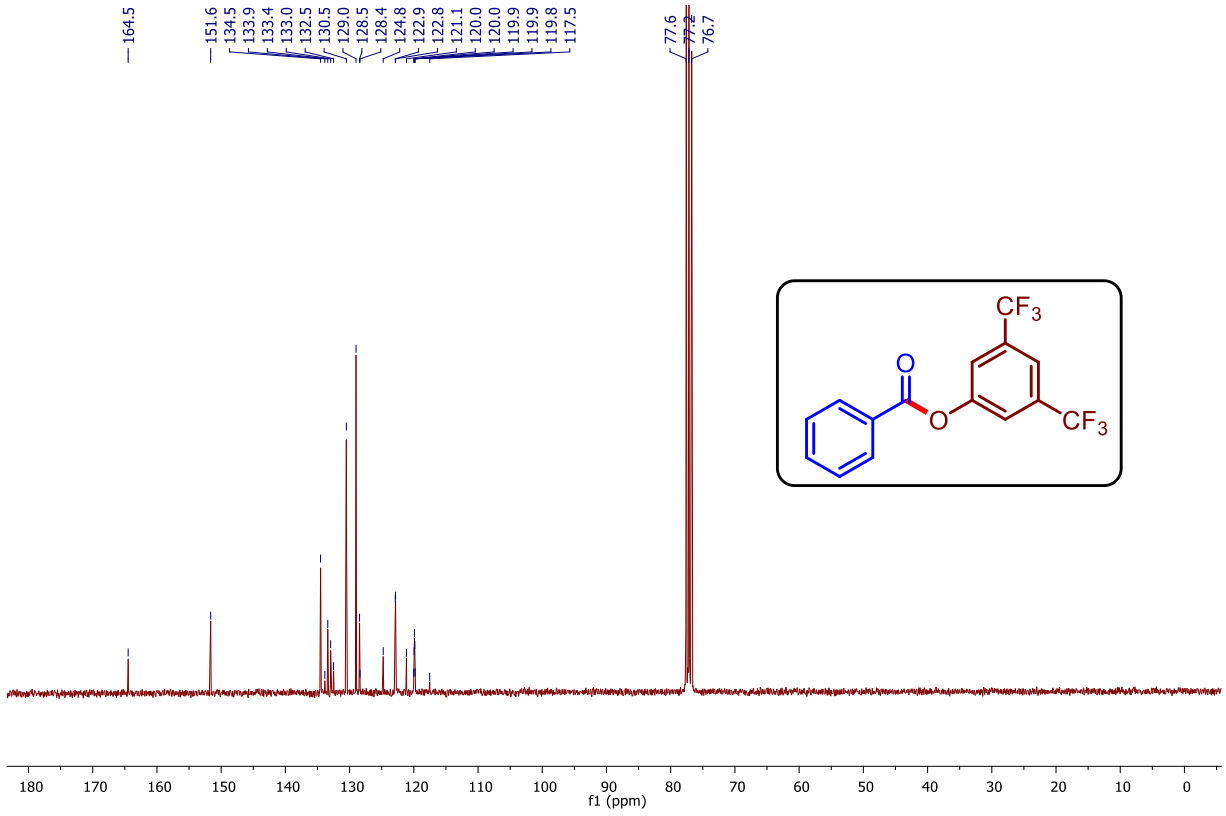
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zj



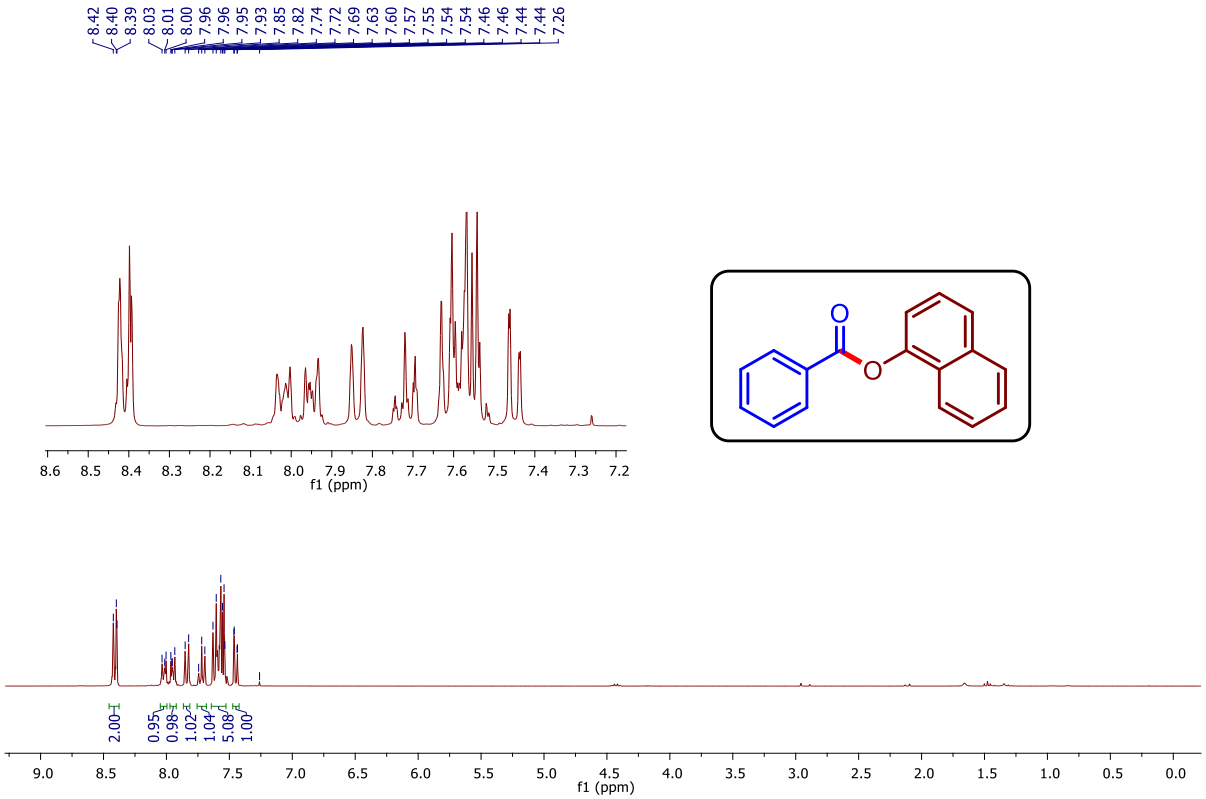
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zj



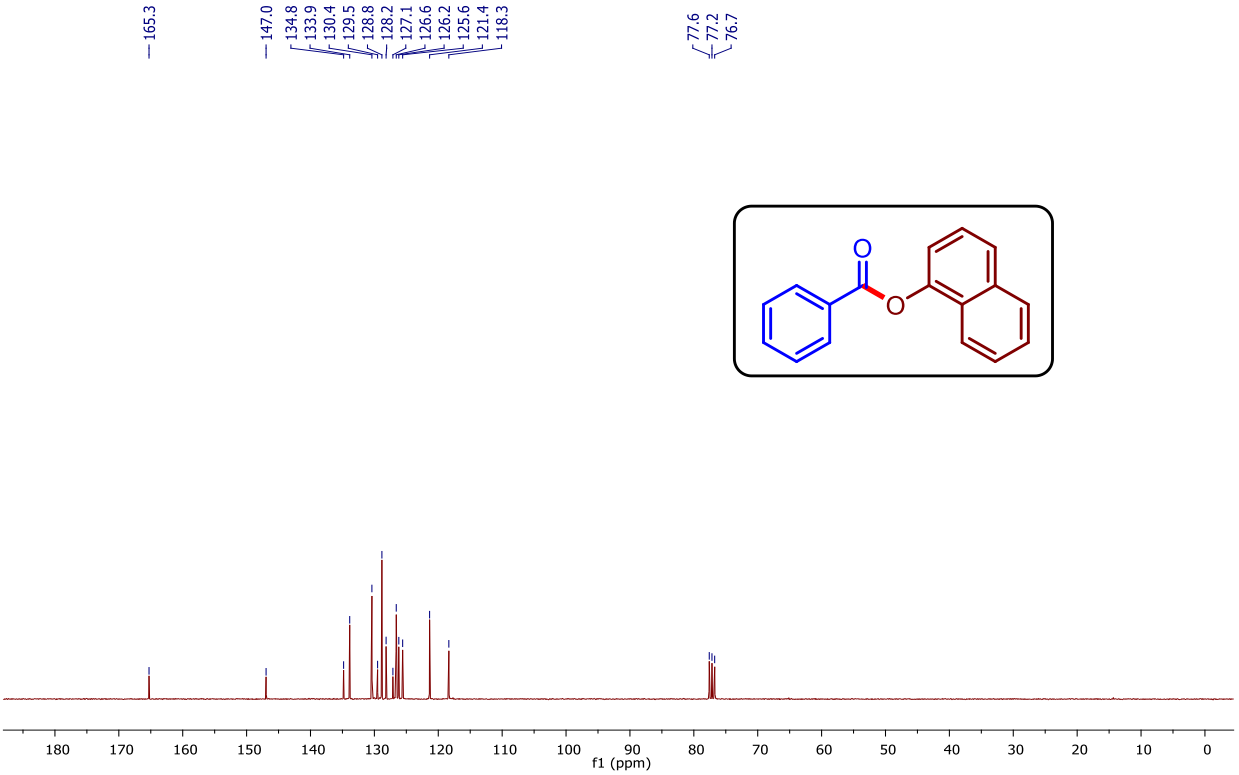
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zk



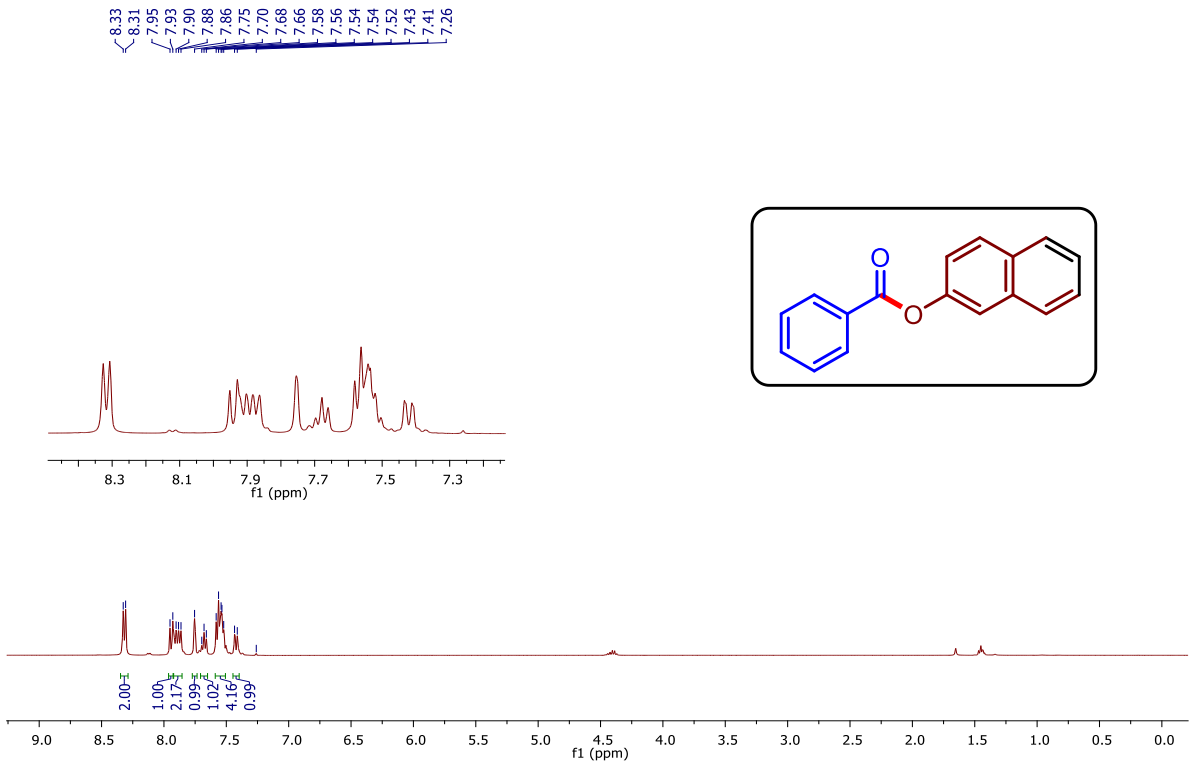
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zk



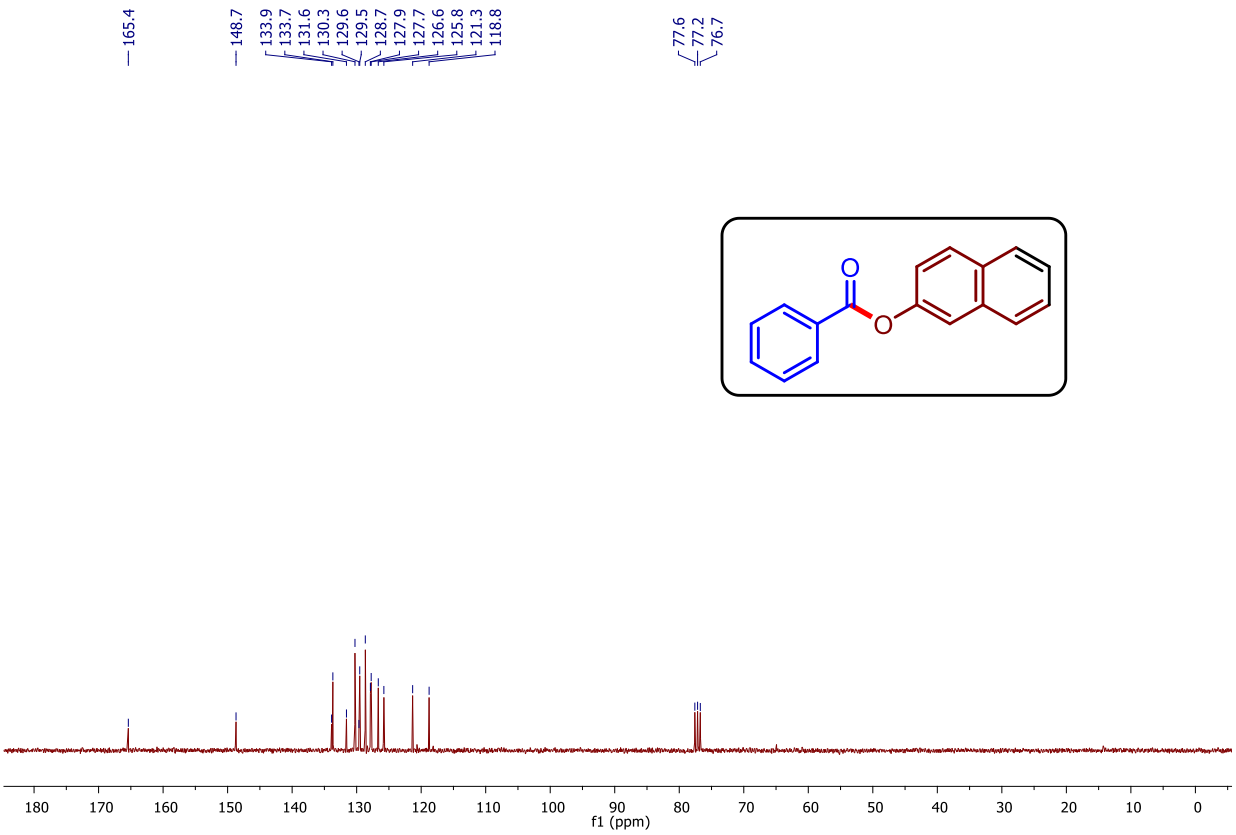
^{1}H NMR(300 MHz, $CDCl_3$, 298 K) of 3zl



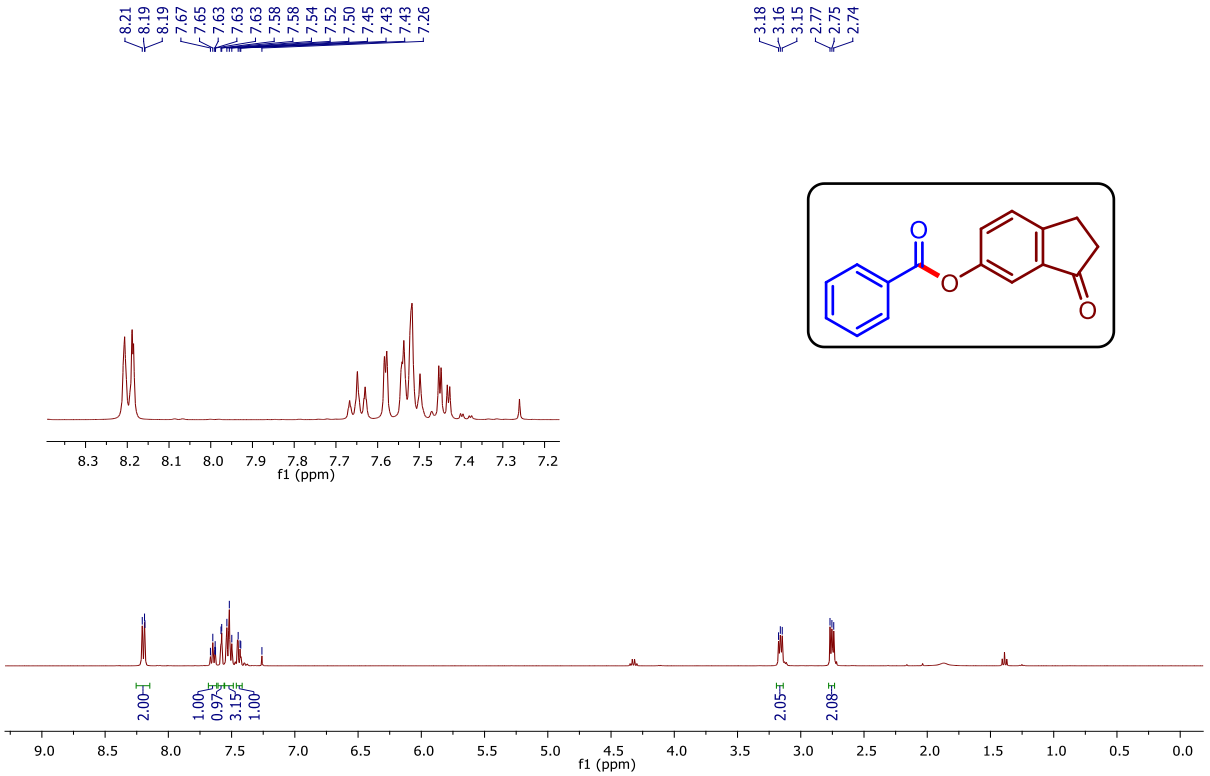
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zl



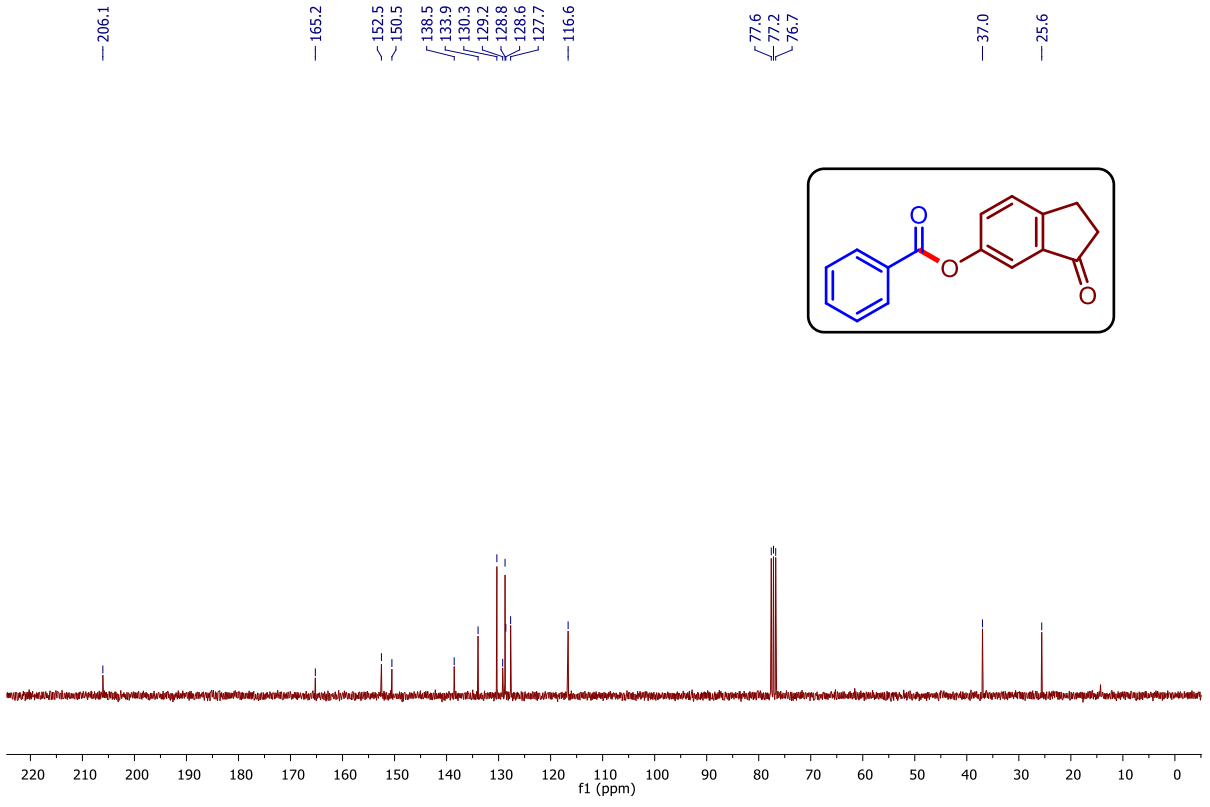
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zm



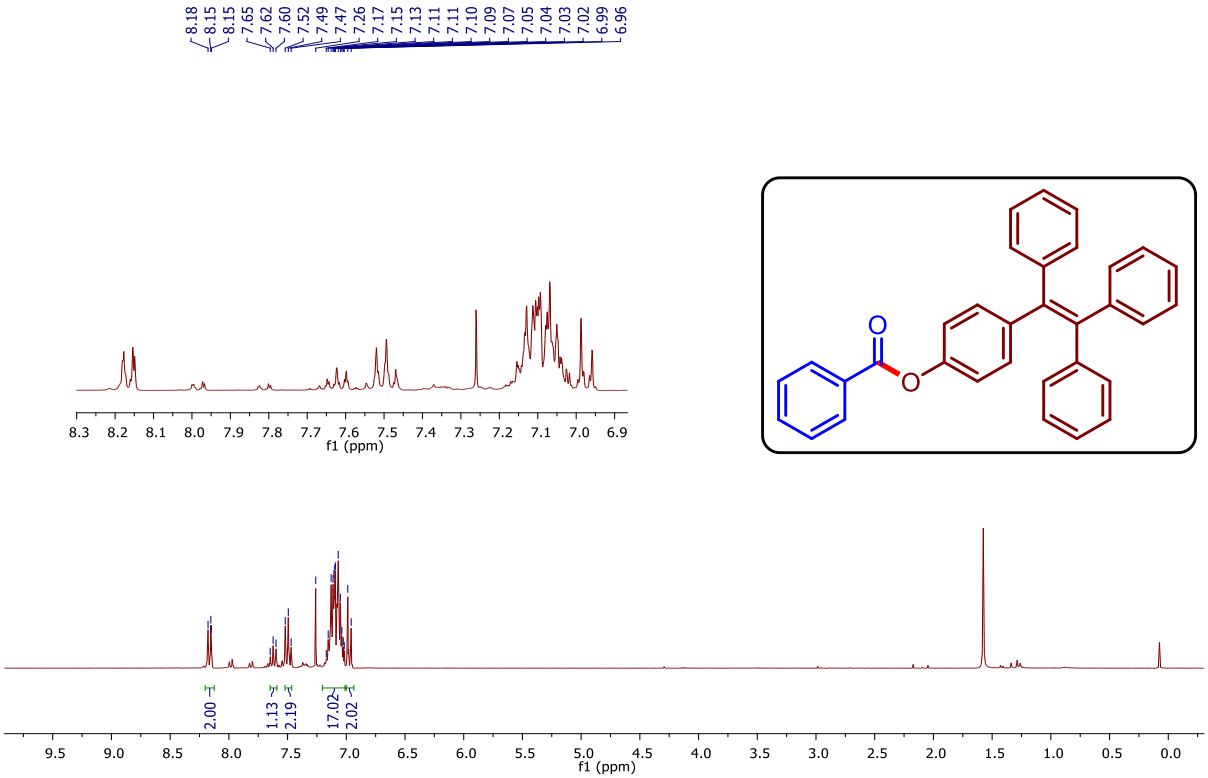
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zm



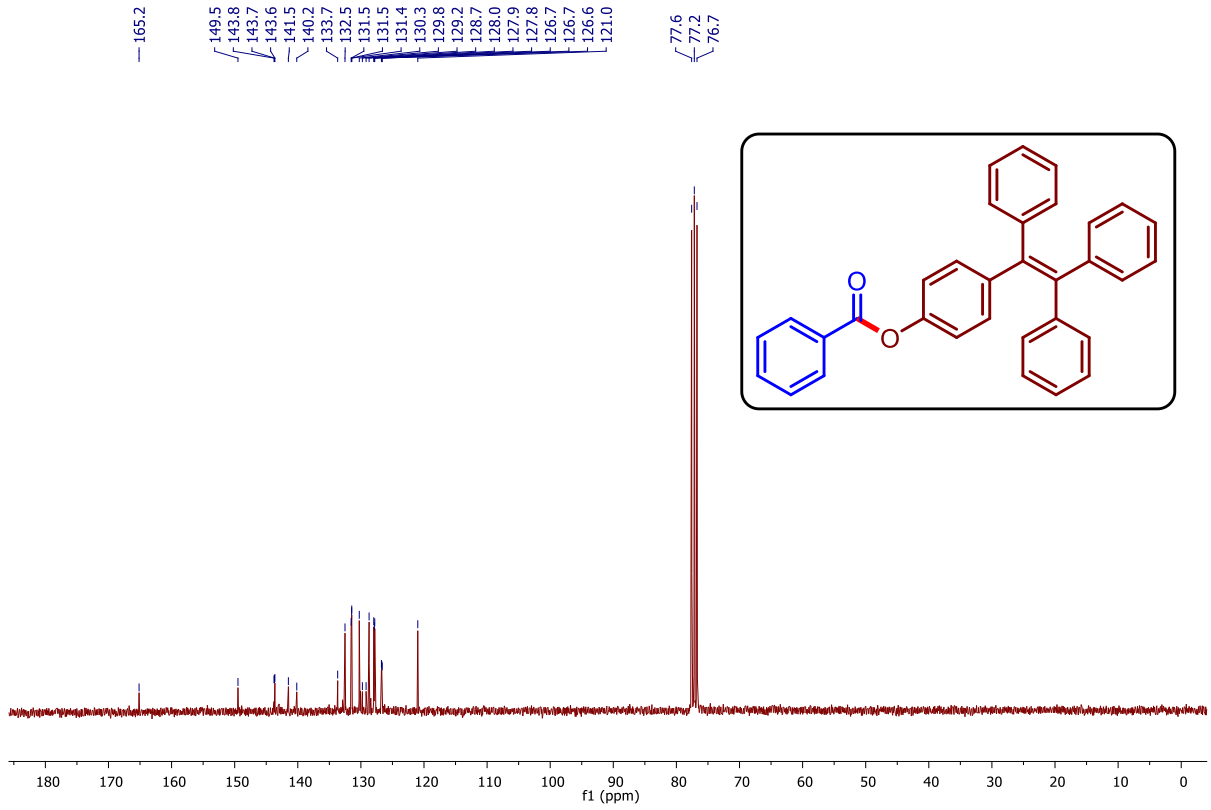
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zn



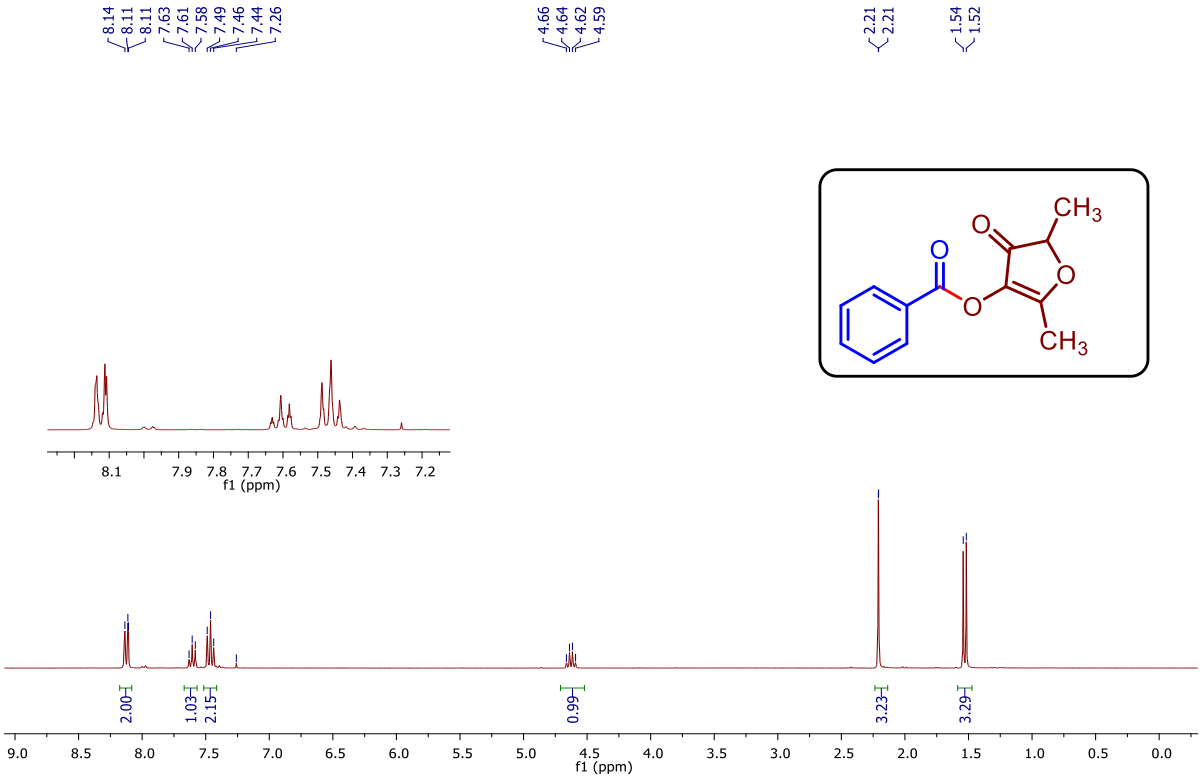
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zn



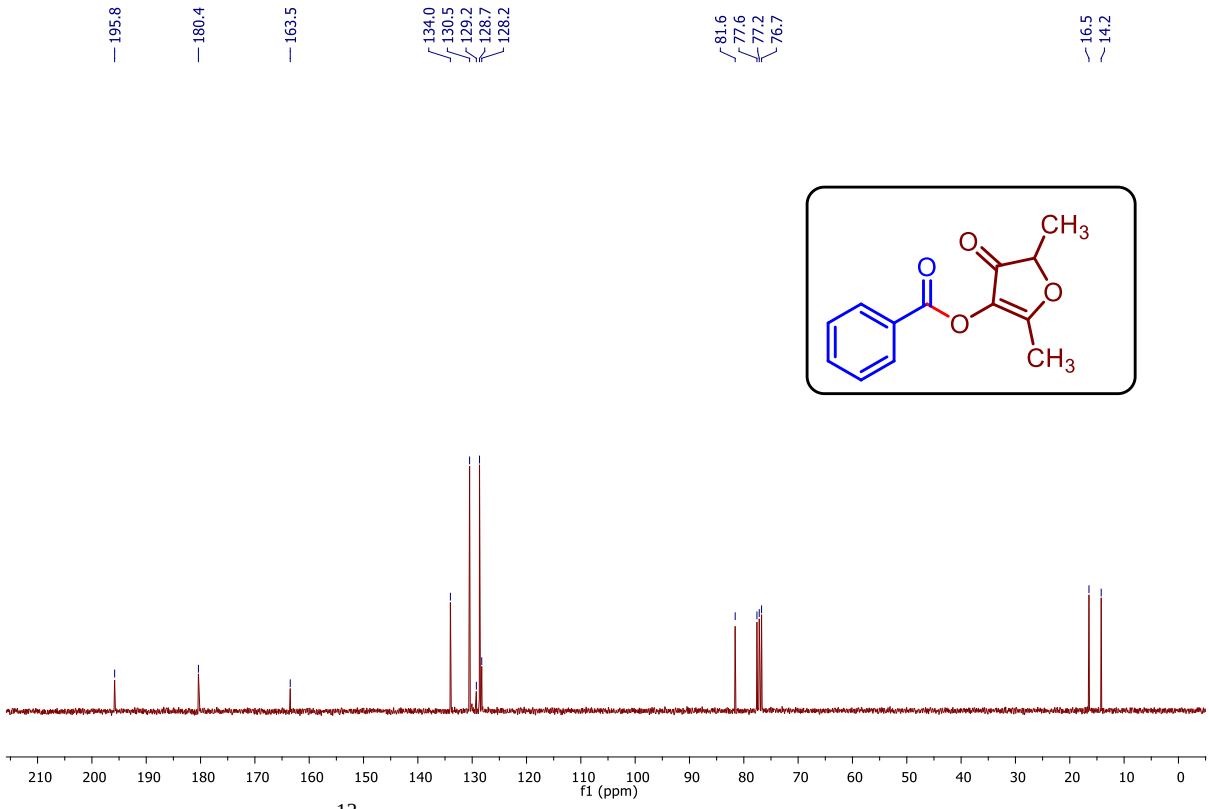
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zo



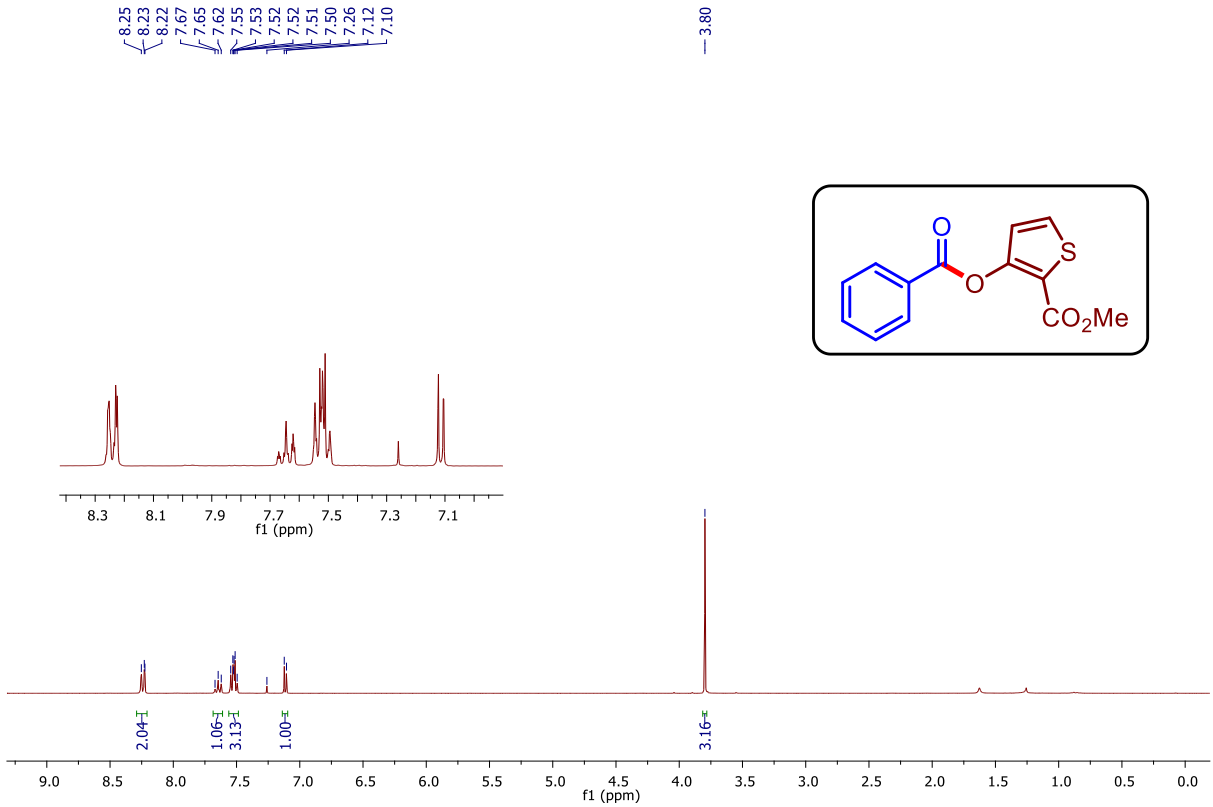
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zo



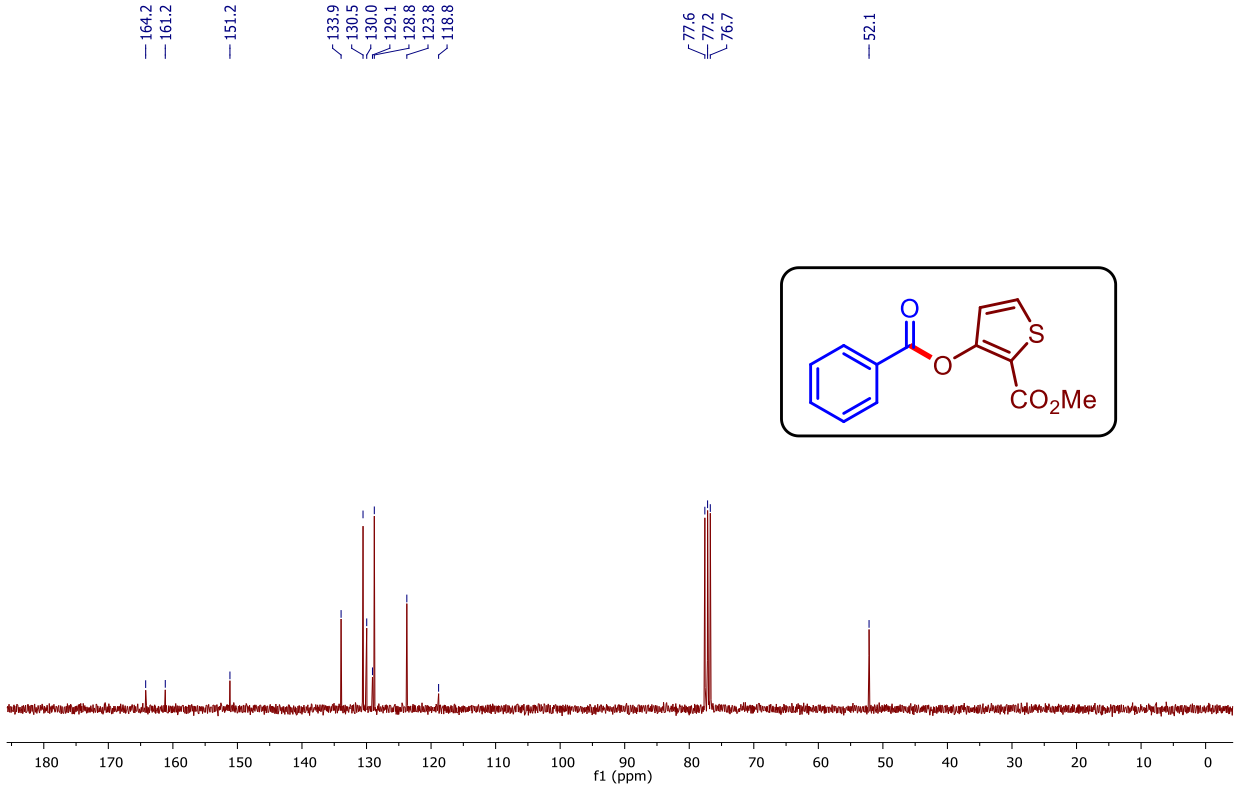
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zp



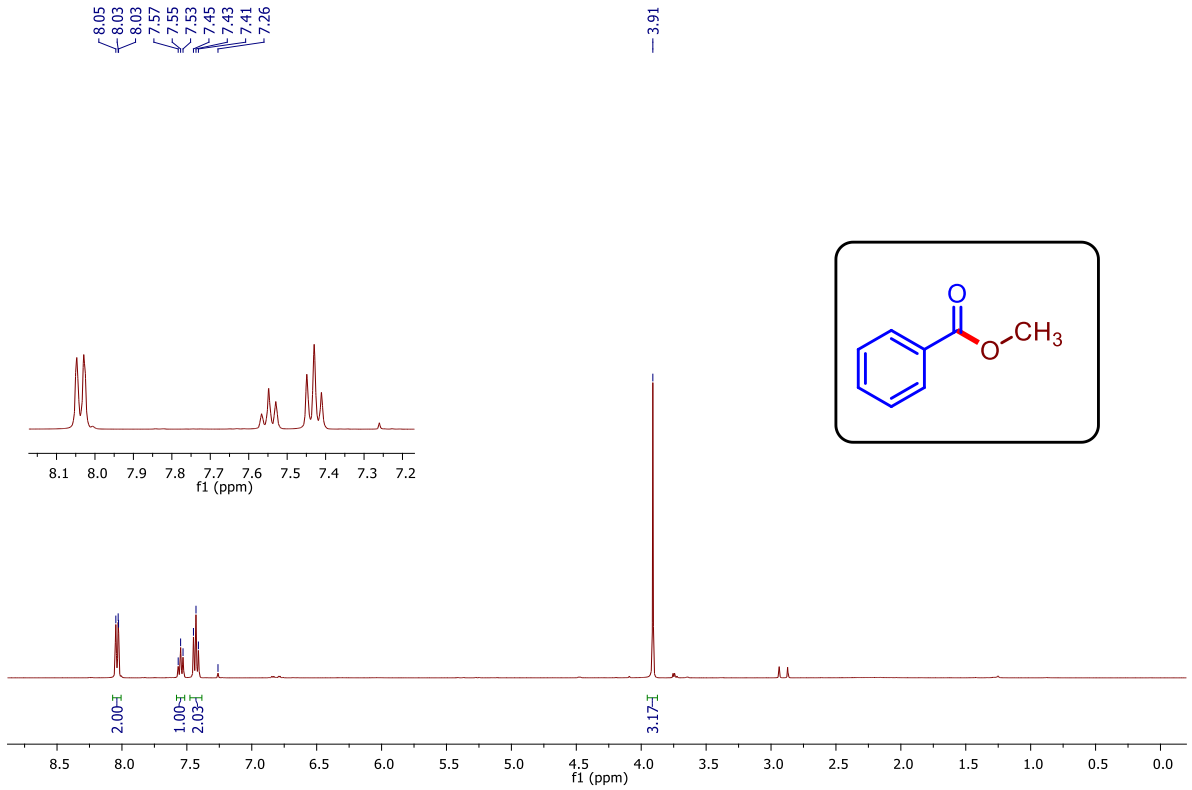
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zp



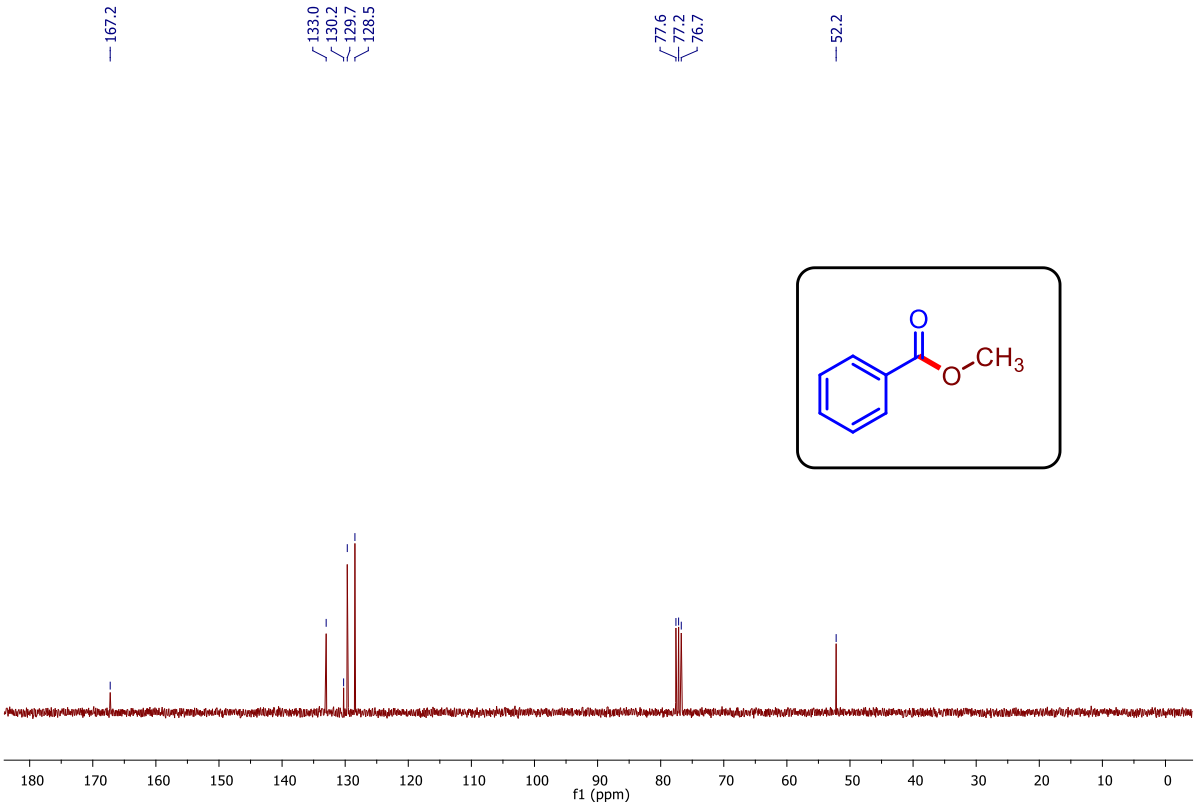
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zq



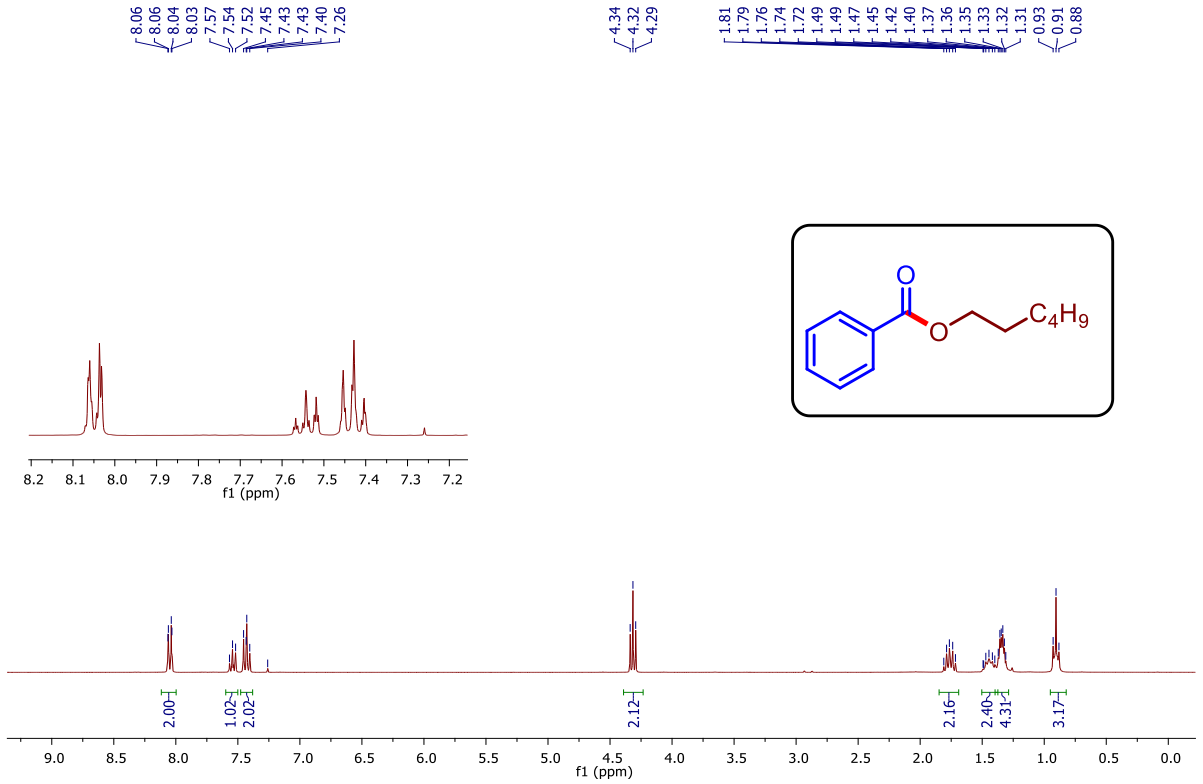
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zq



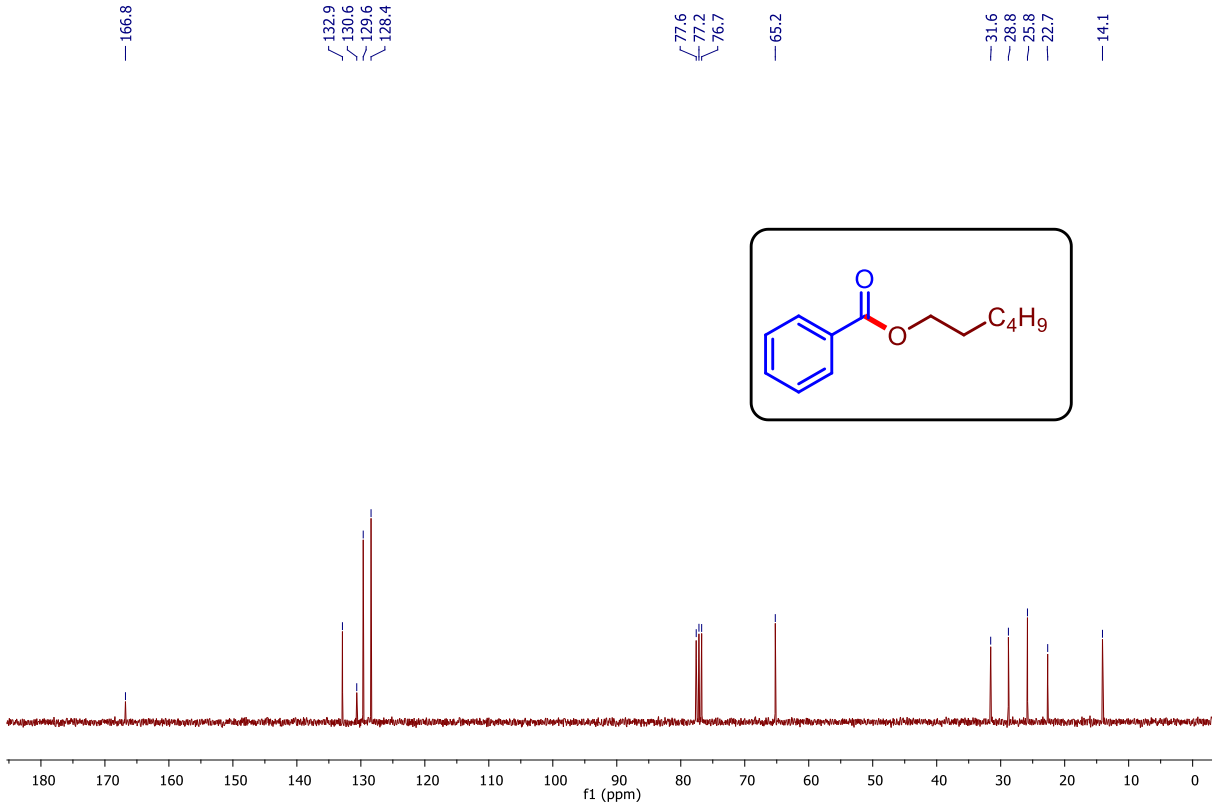
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zr



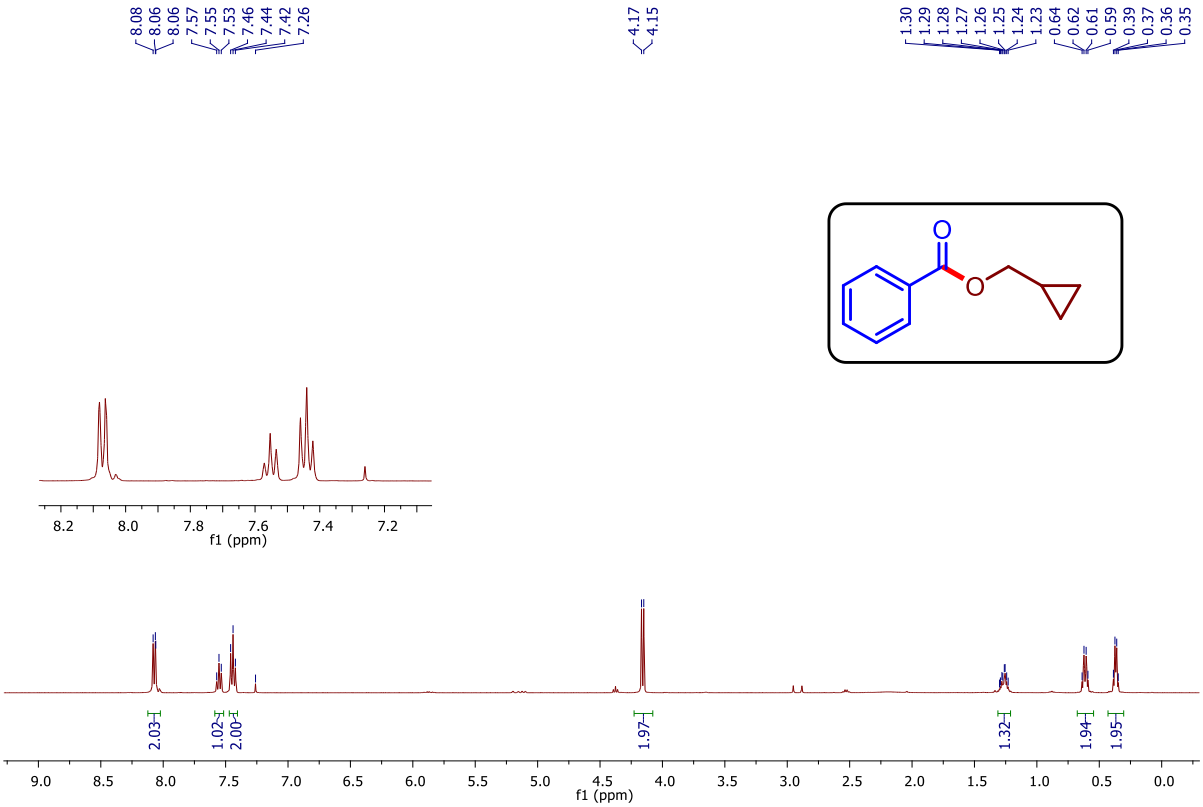
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zr



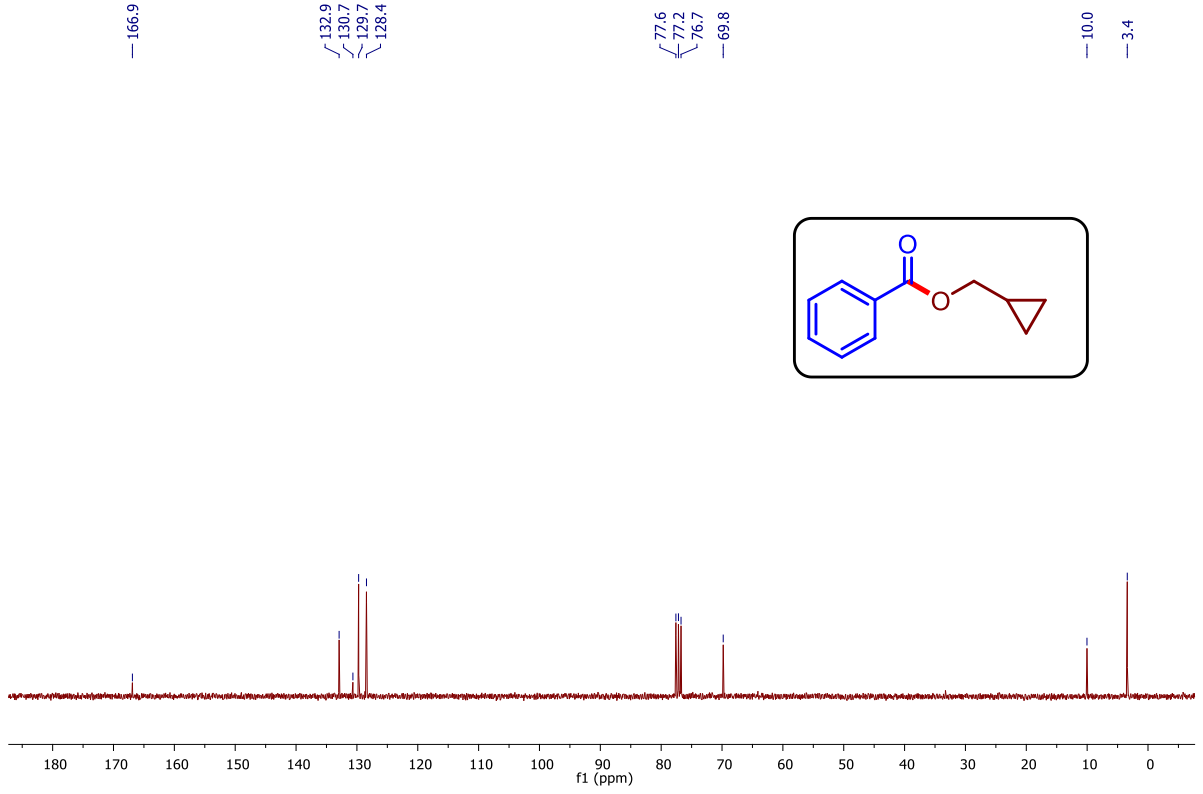
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zs



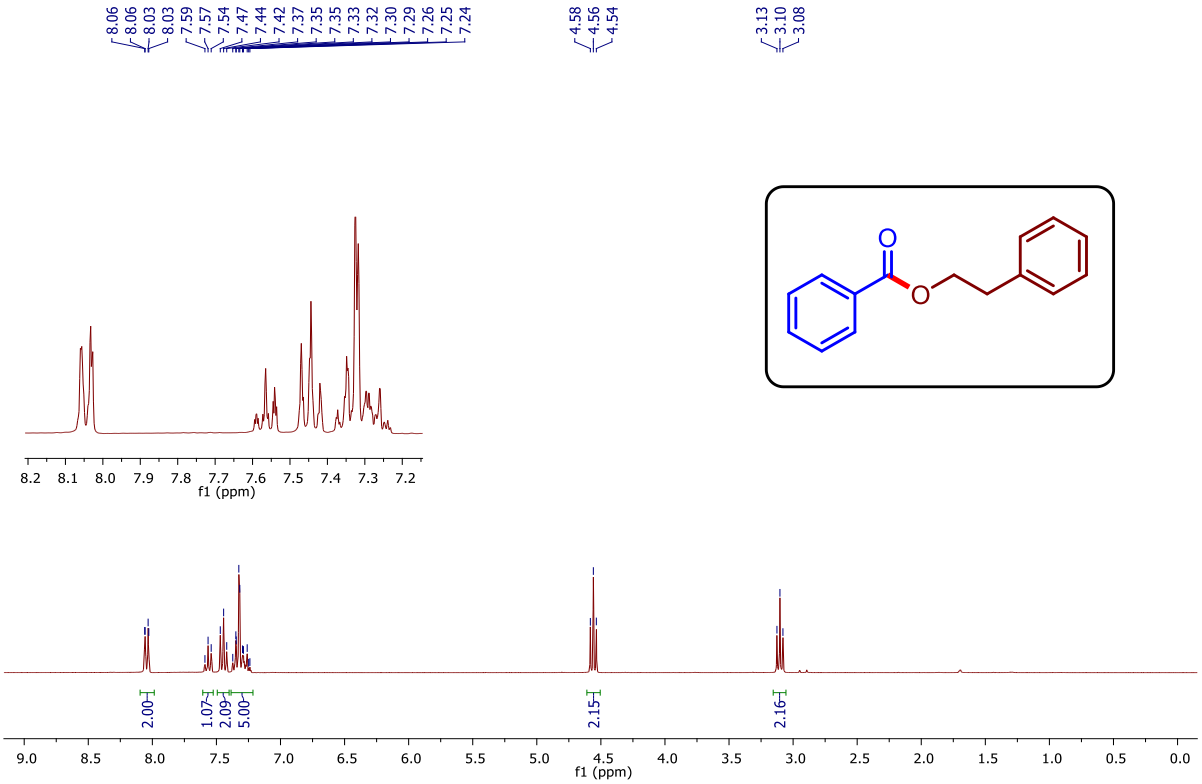
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zs



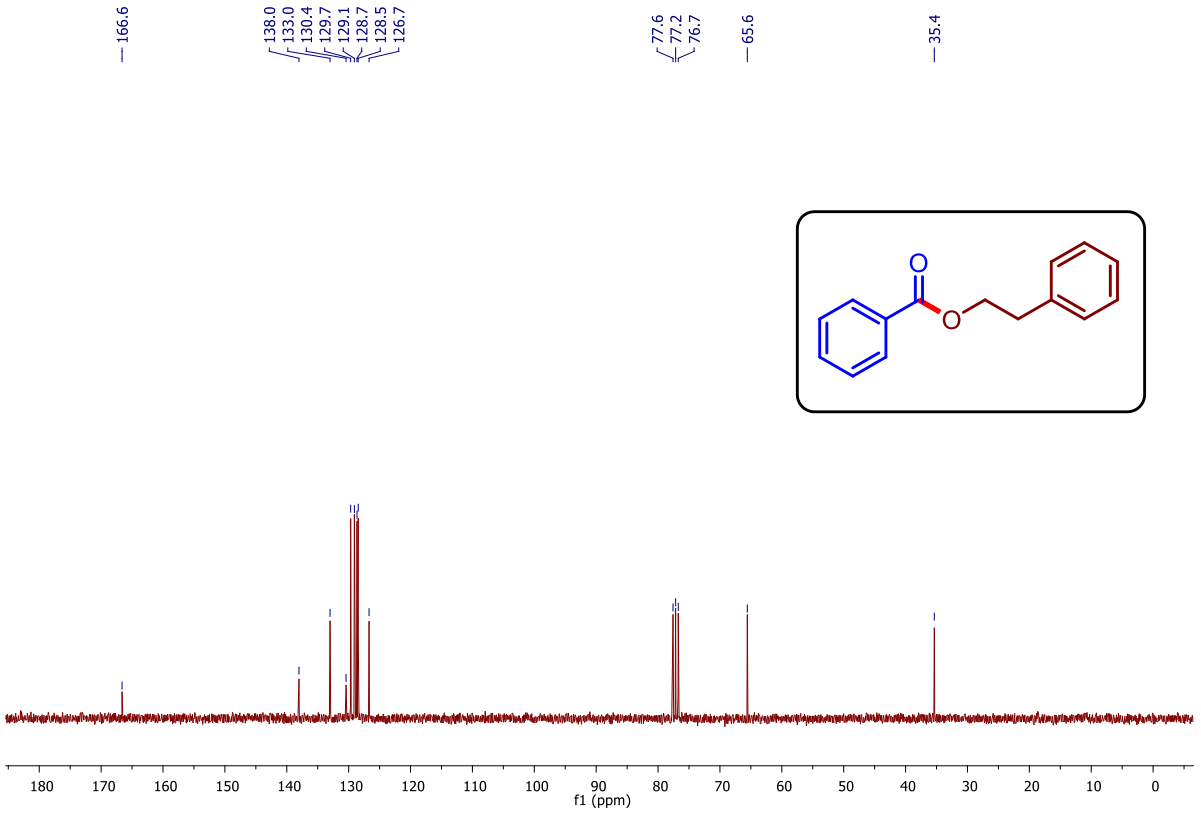
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zt



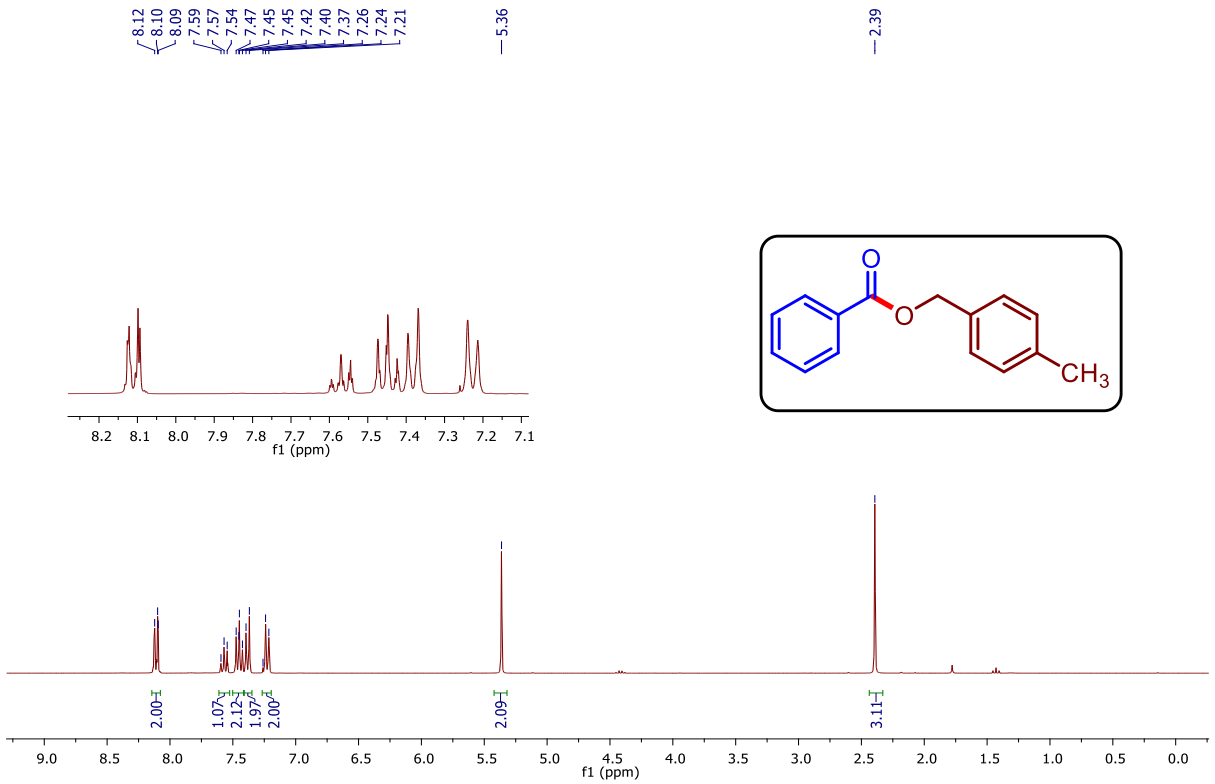
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zt



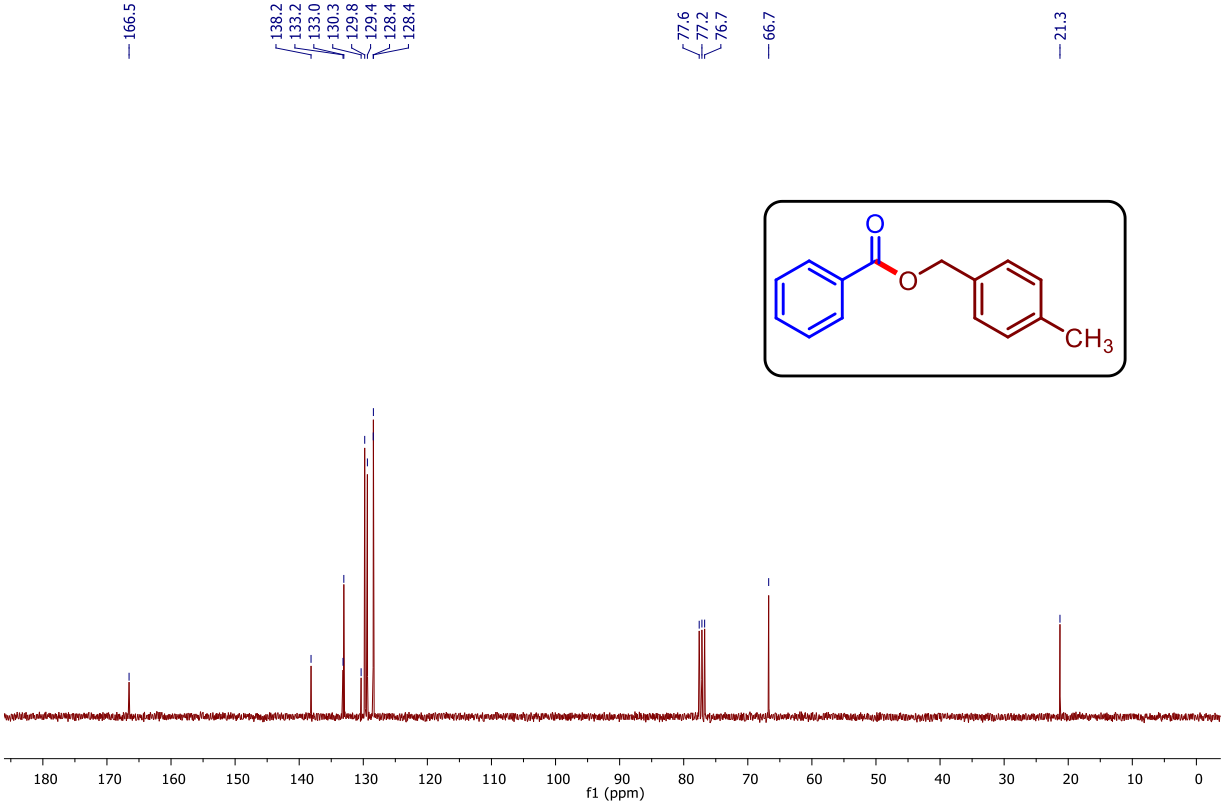
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zu



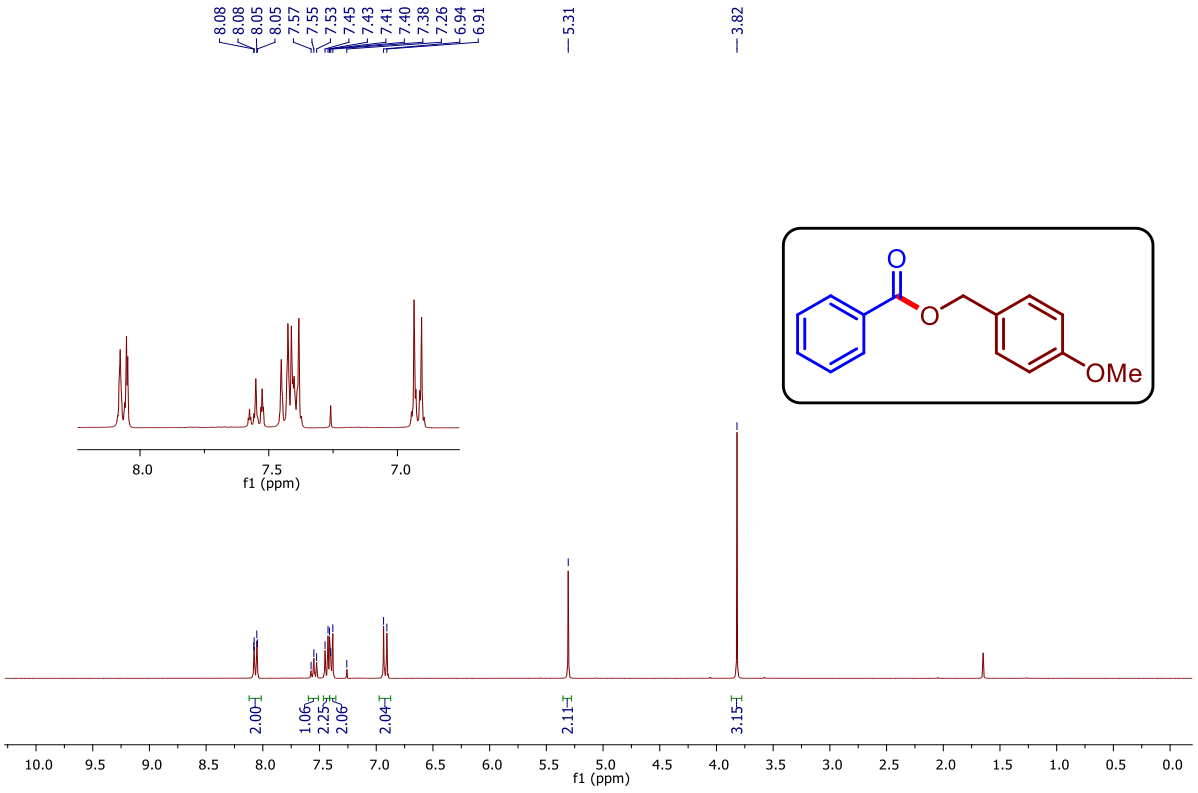
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zu



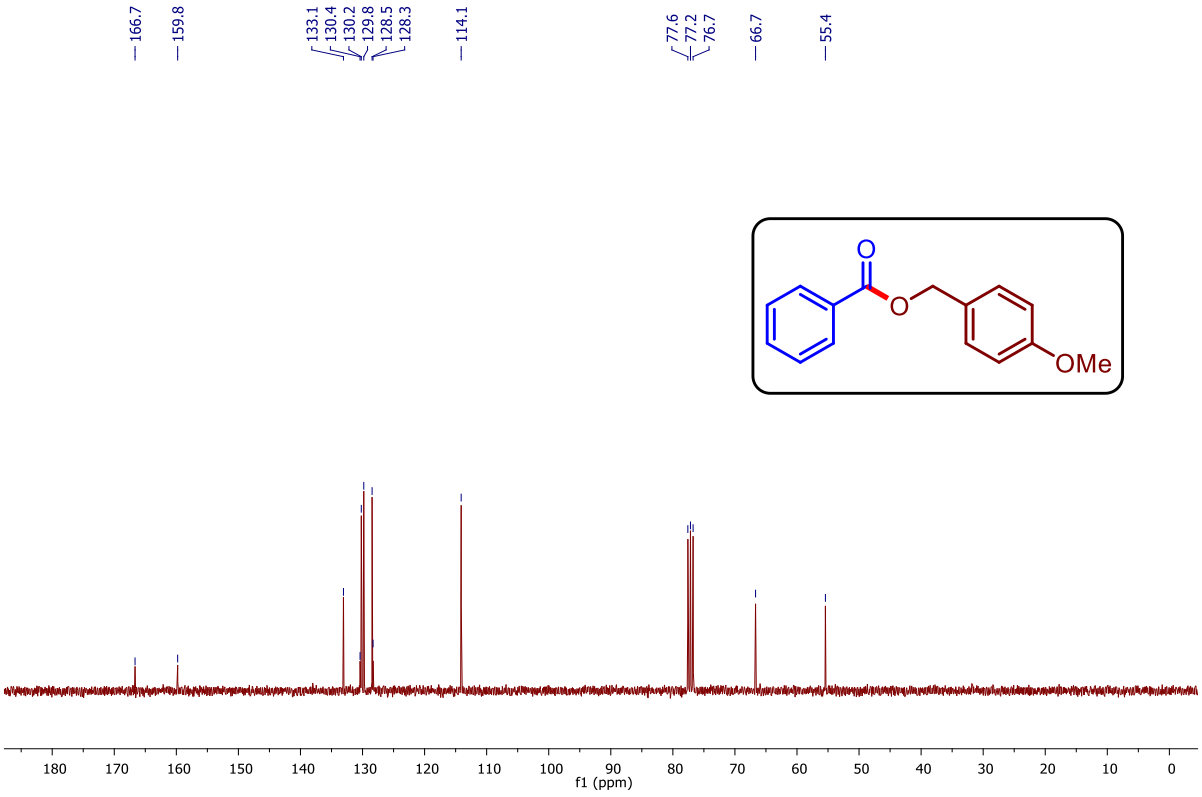
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zv



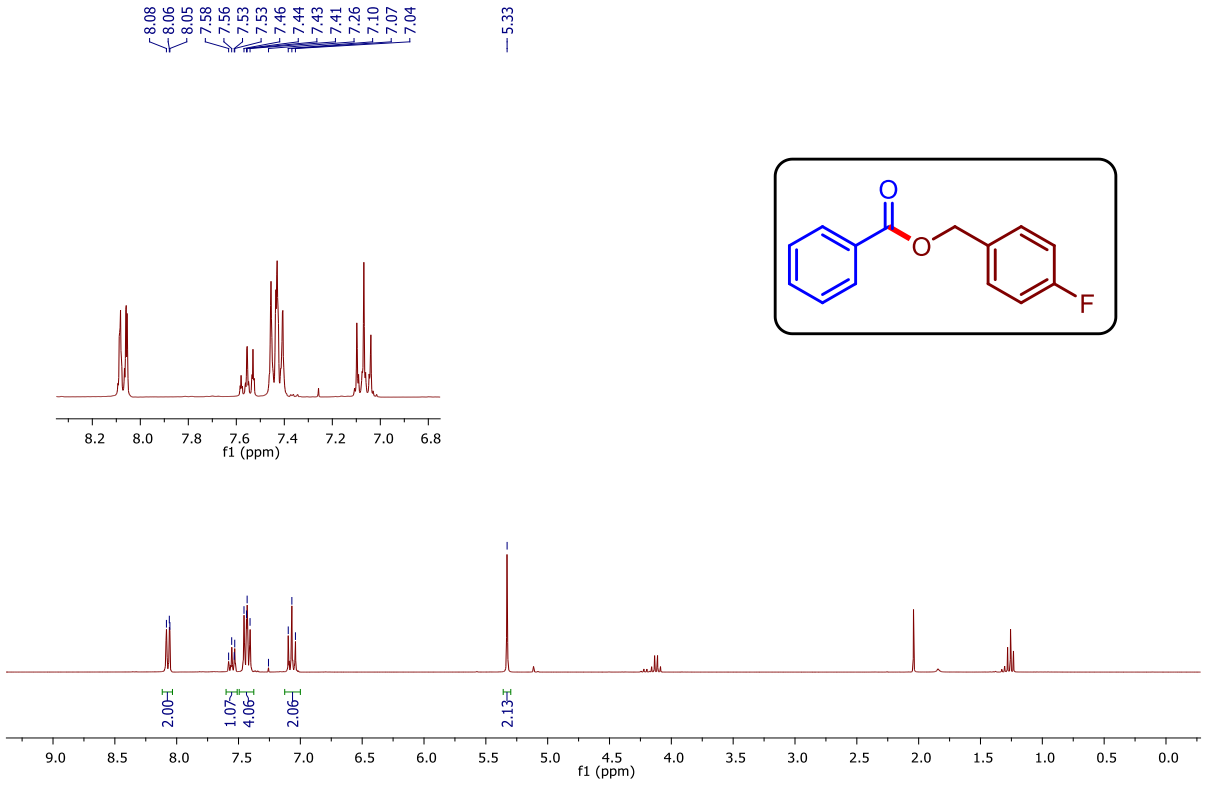
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zv



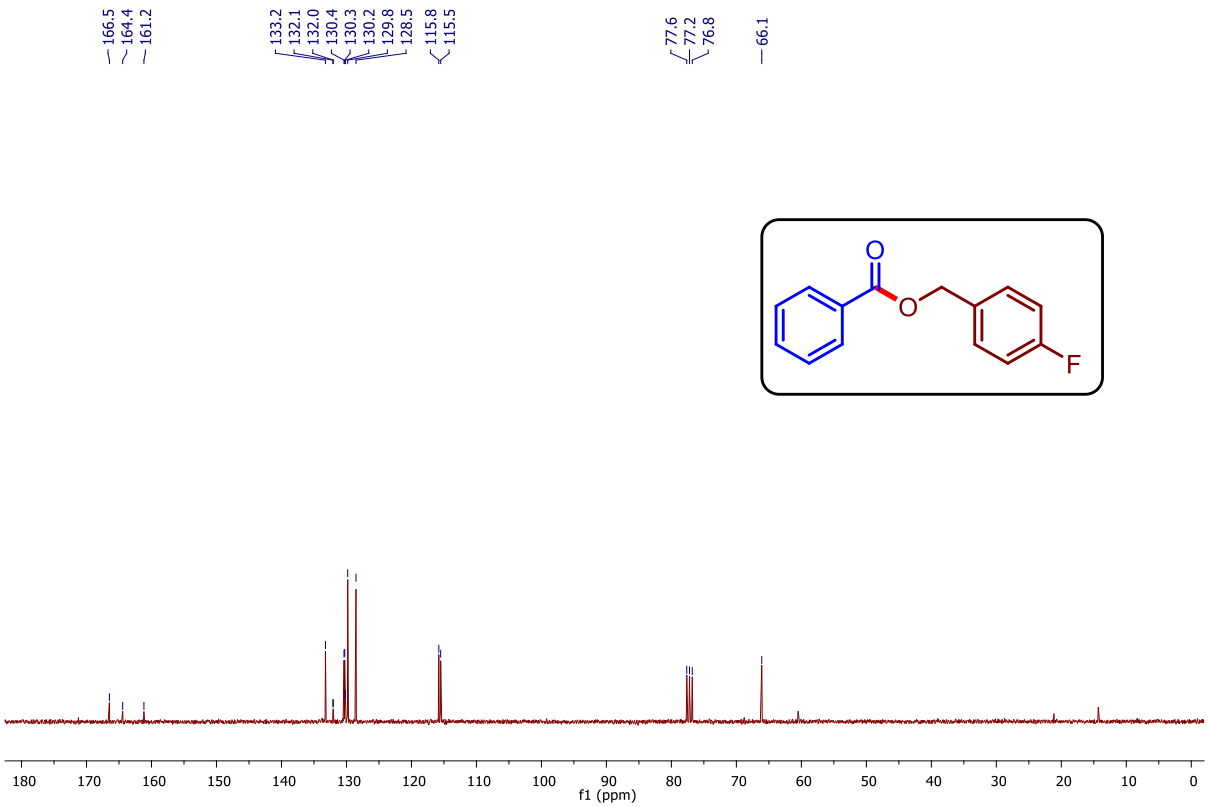
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zw



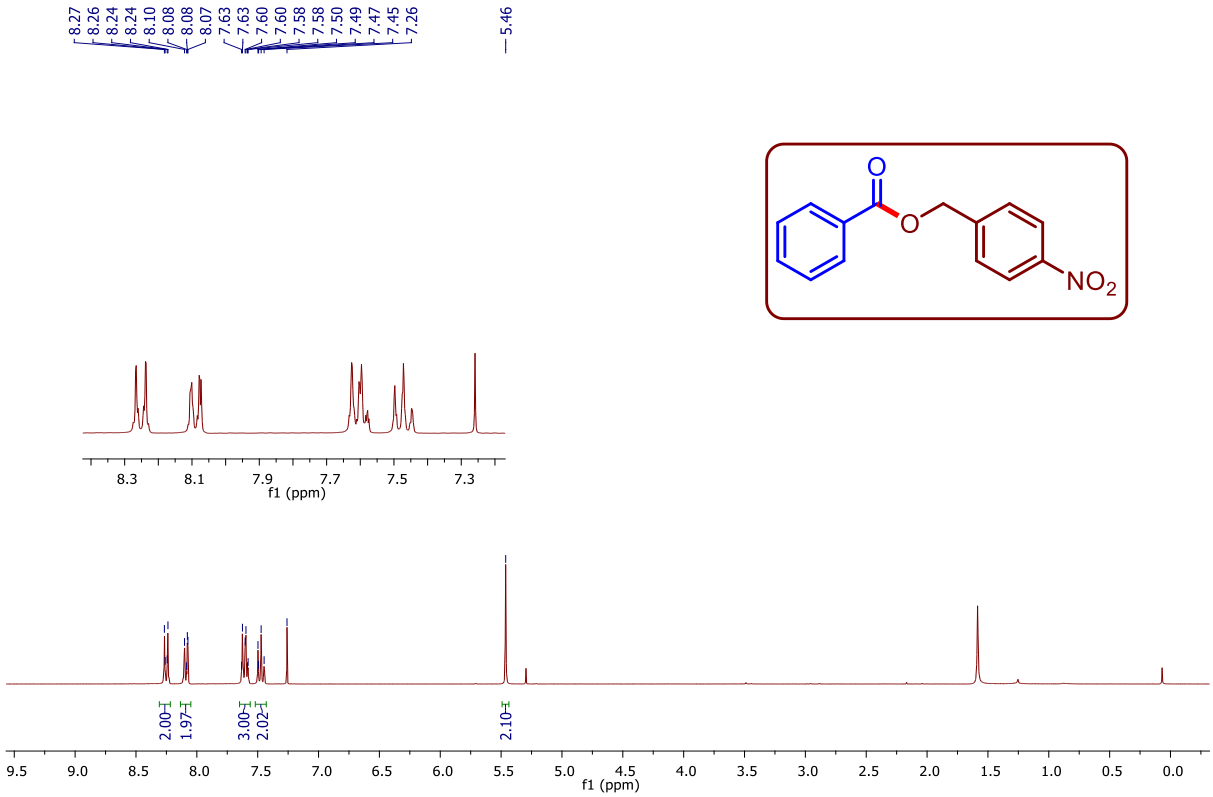
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zw



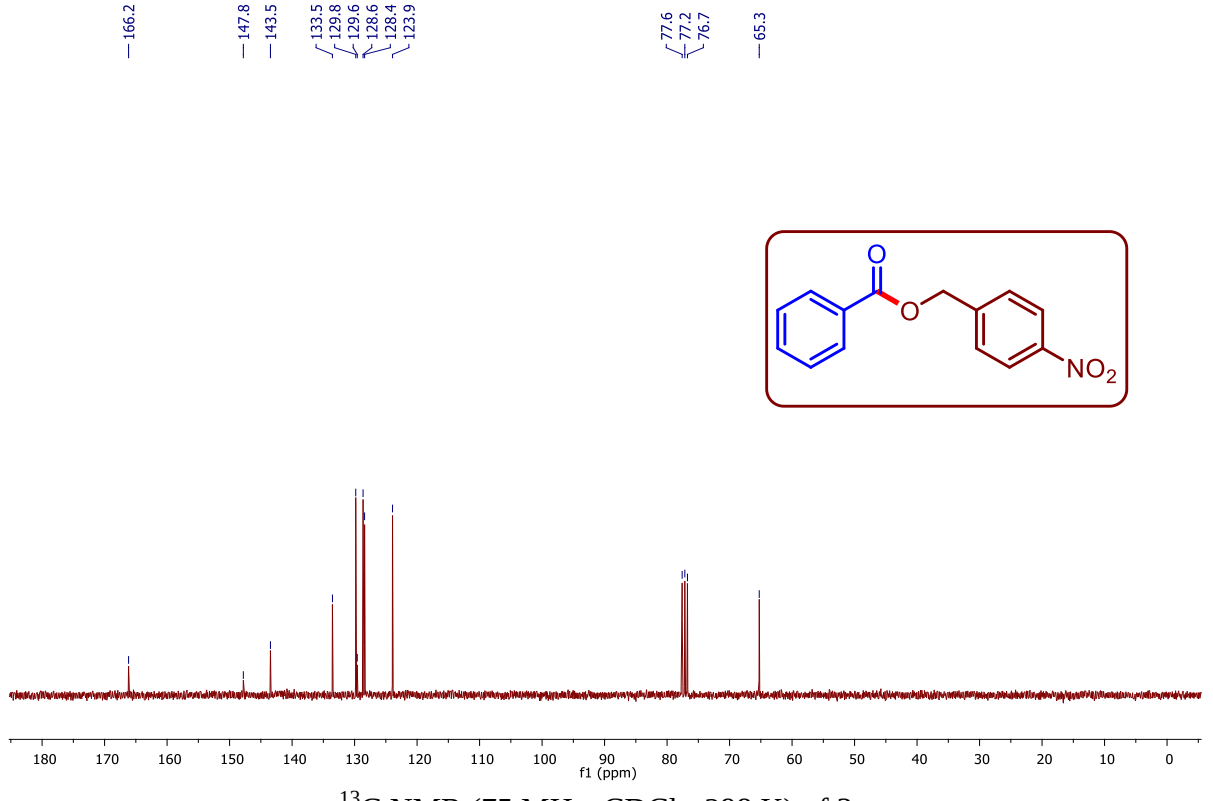
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zx



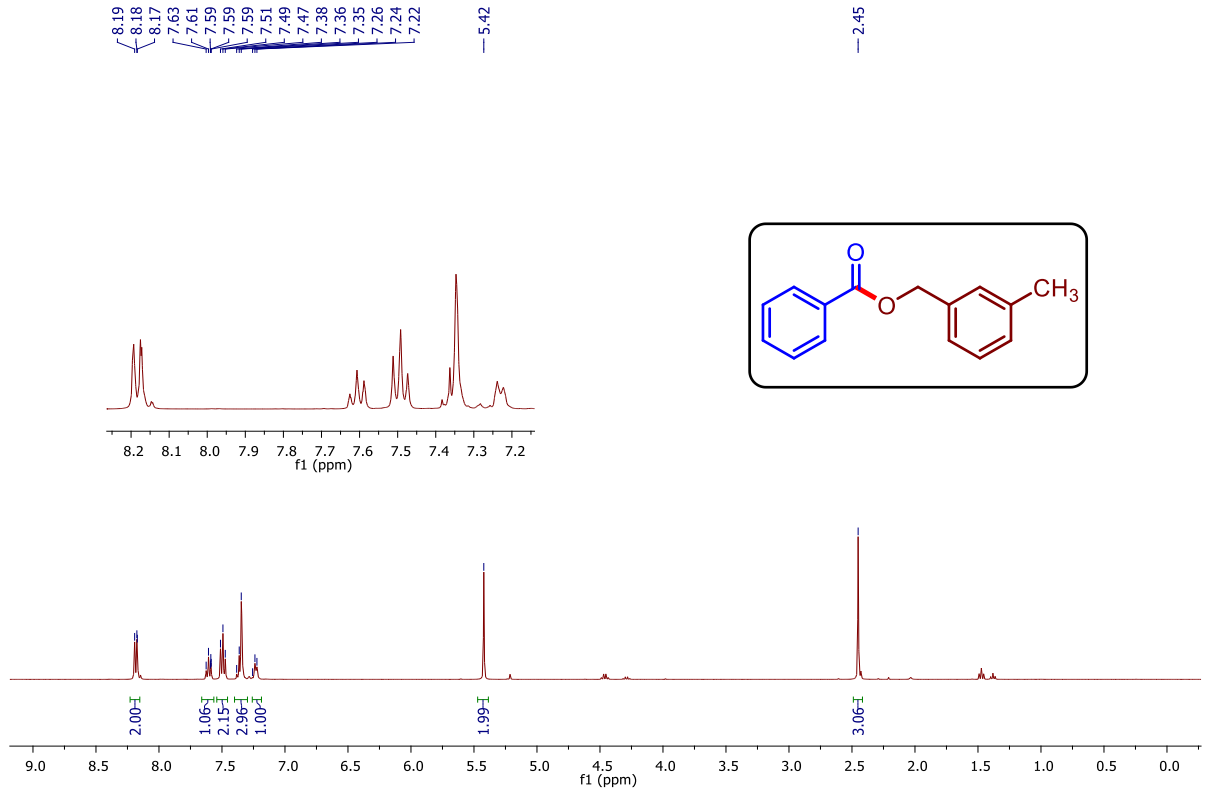
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zx



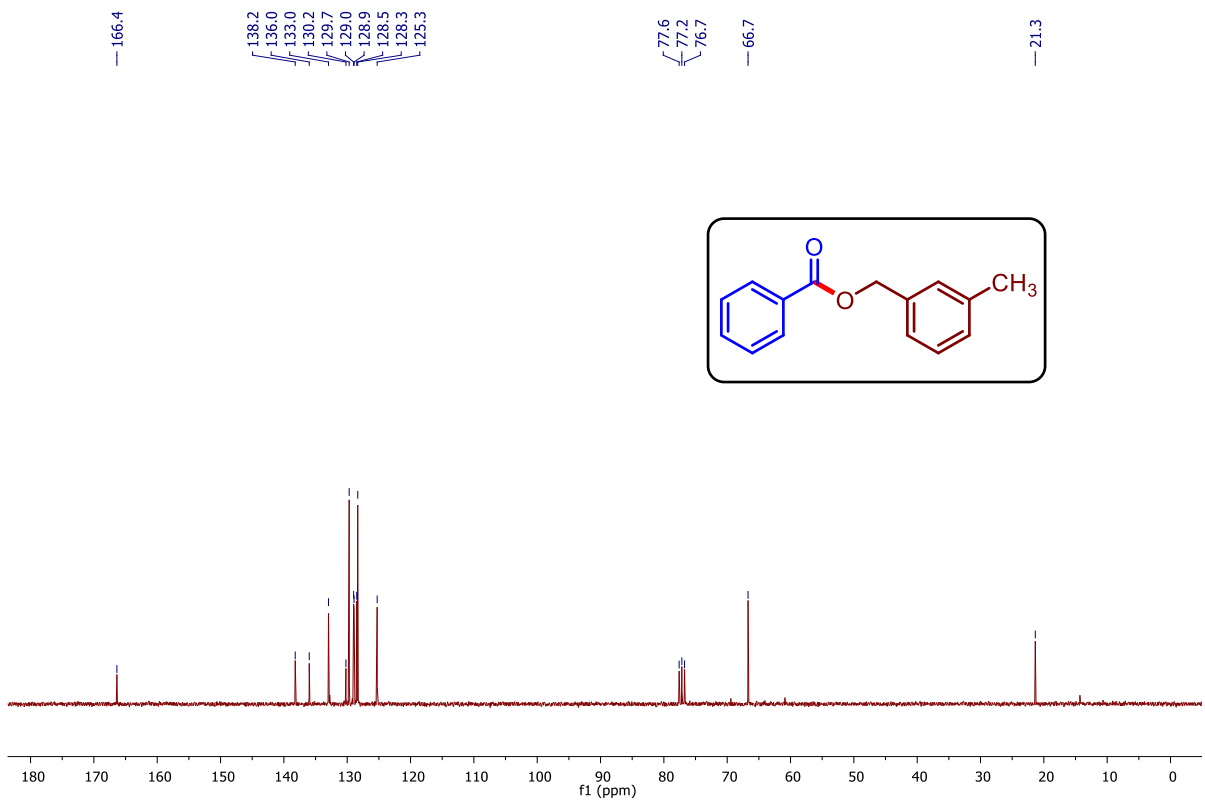
^{1}H NMR (75 MHz, $CDCl_3$, 298 K) of 3zy



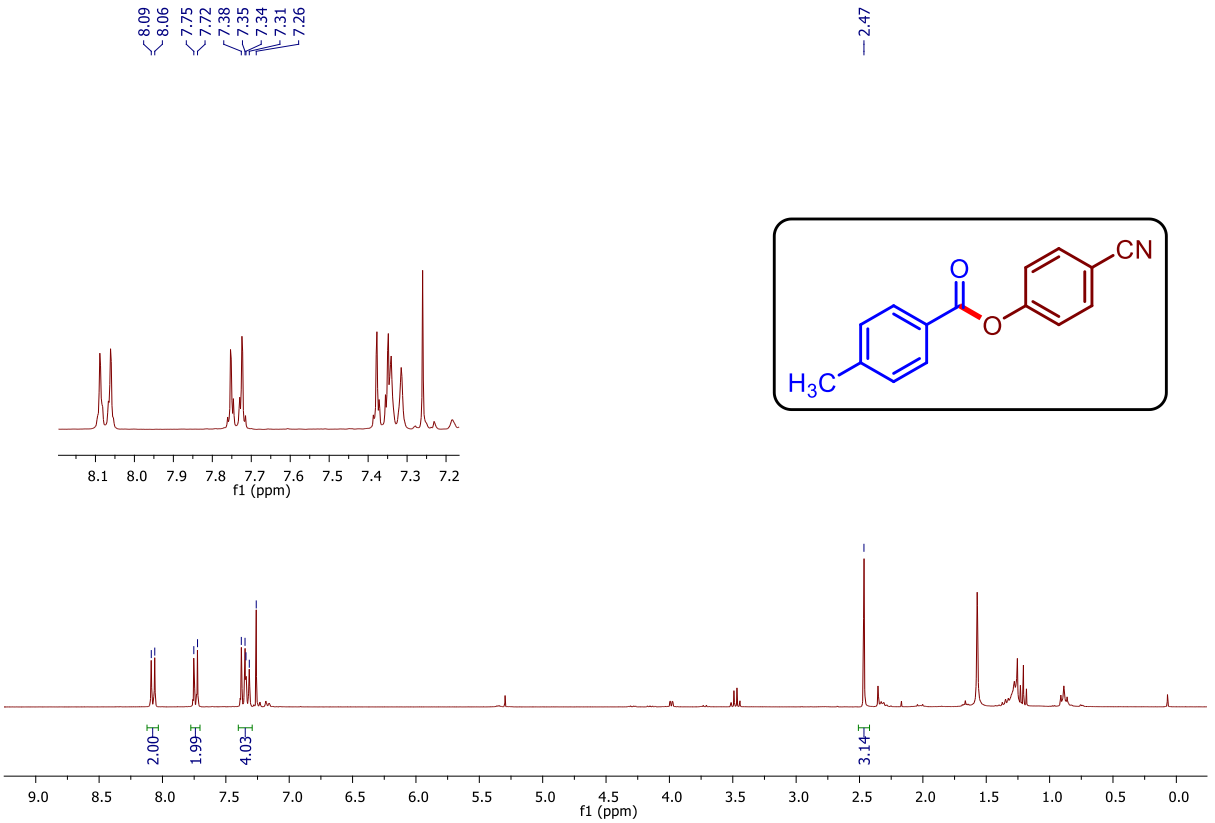
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zy



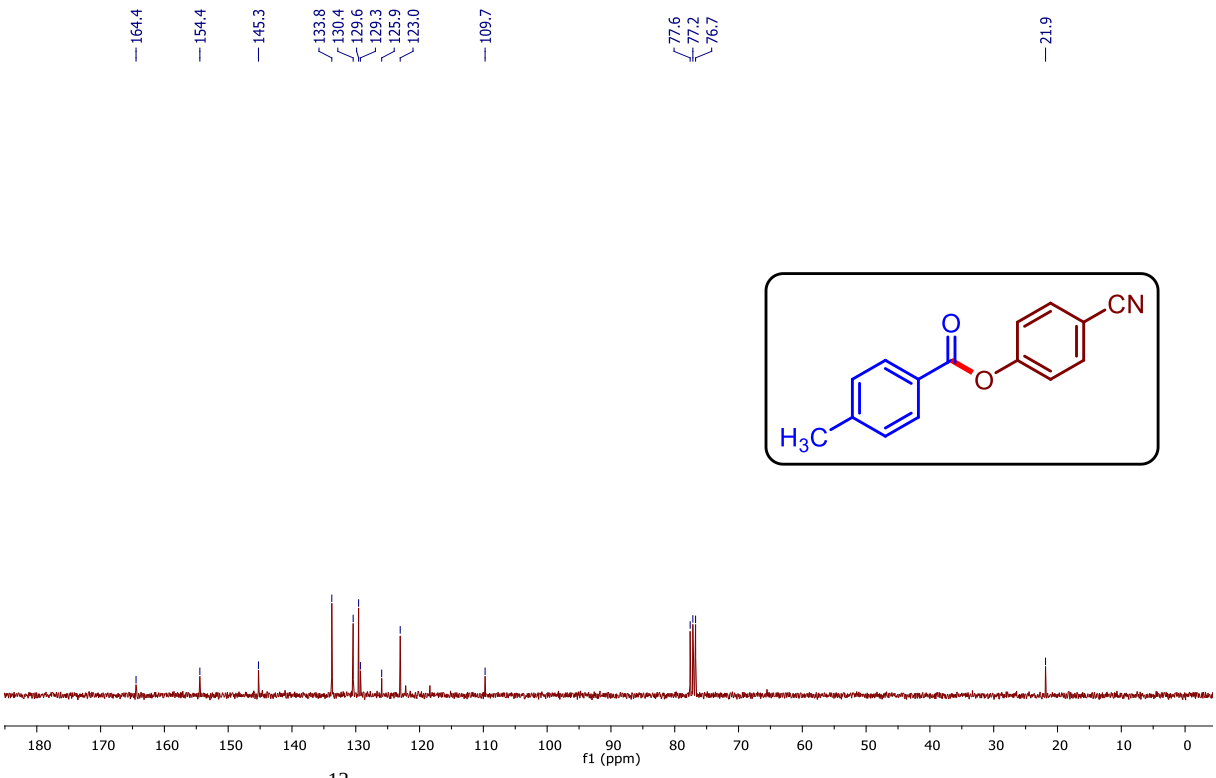
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zz



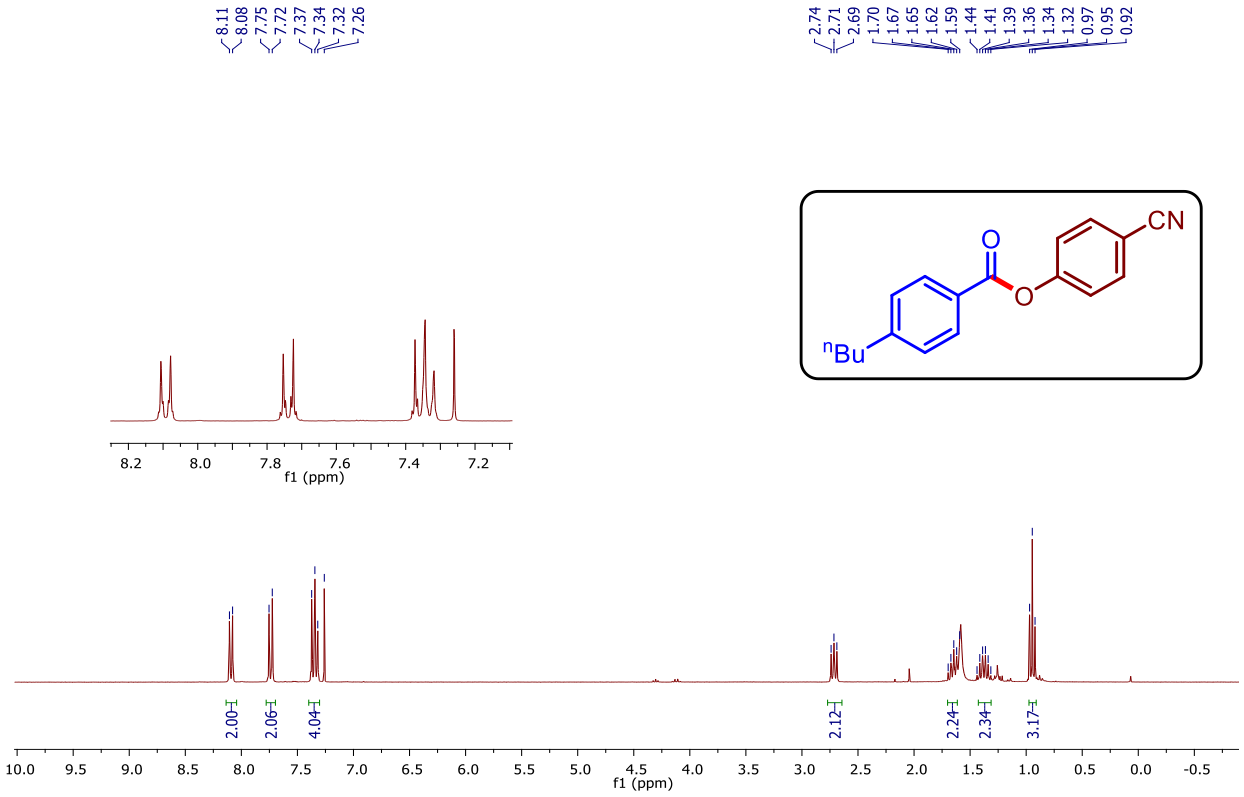
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zz



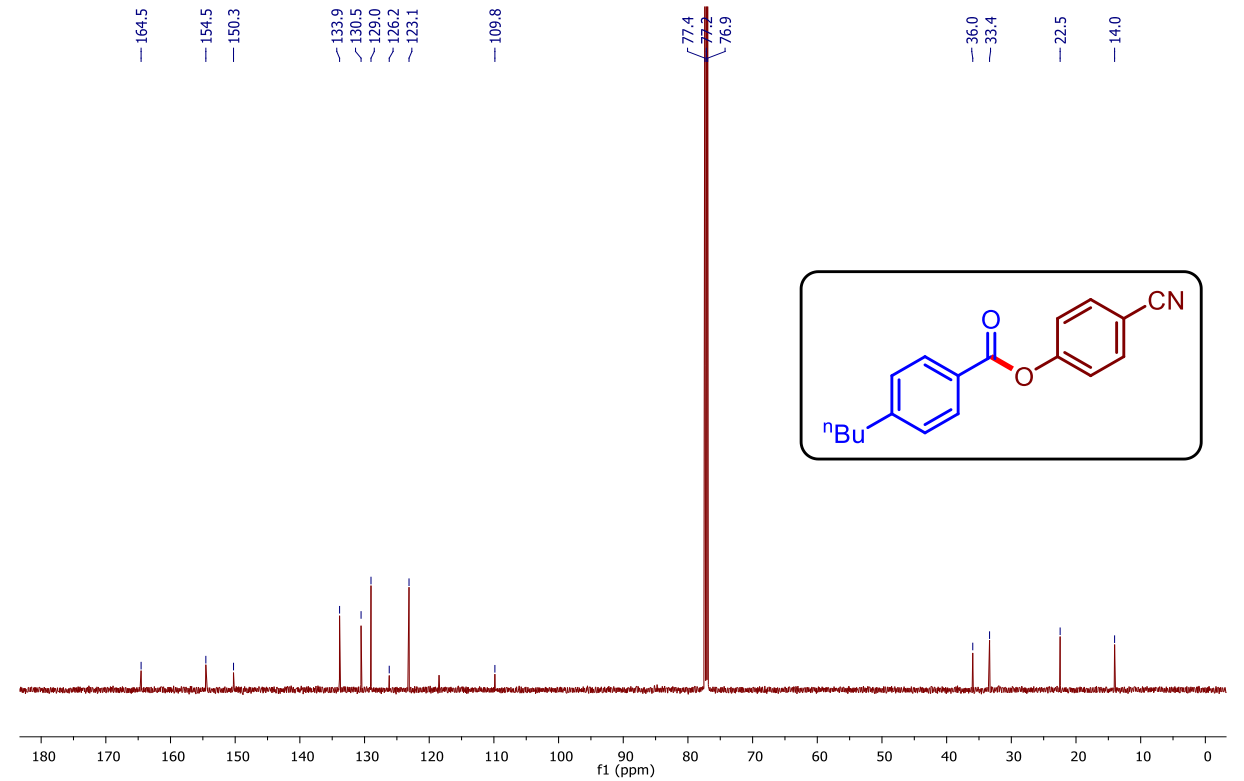
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zza



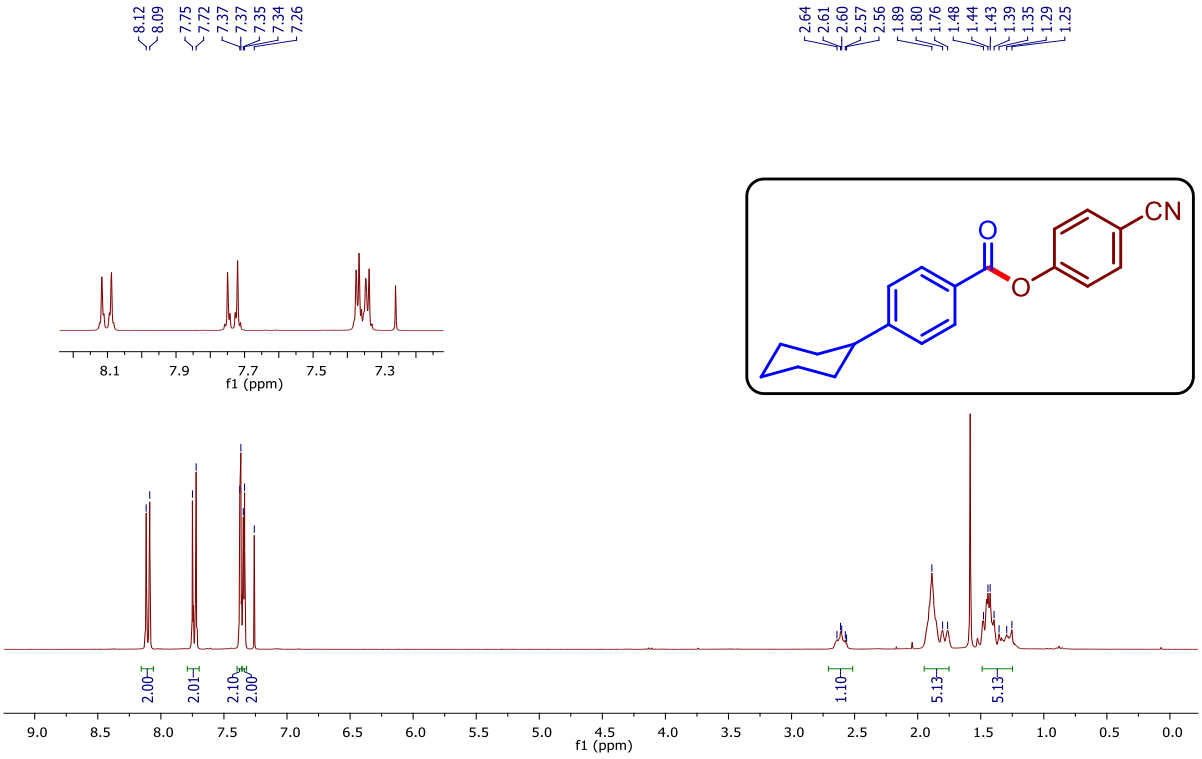
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zza



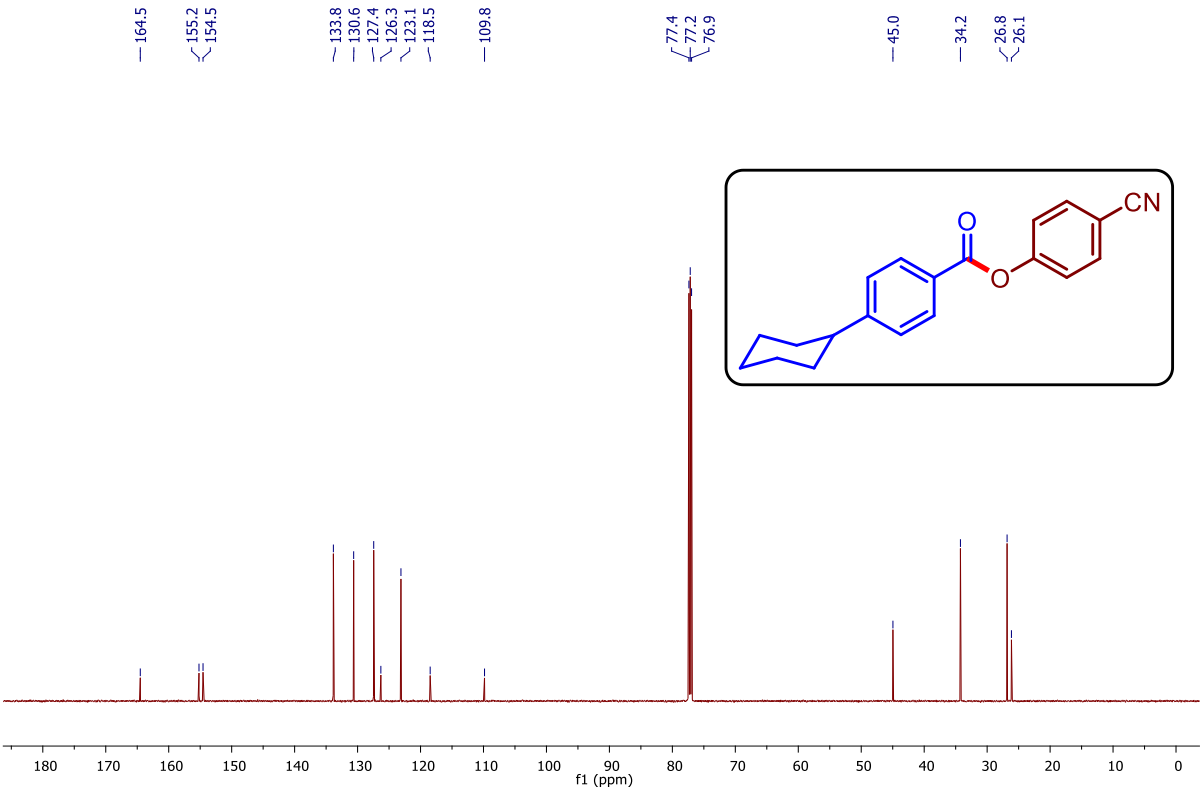
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zzb



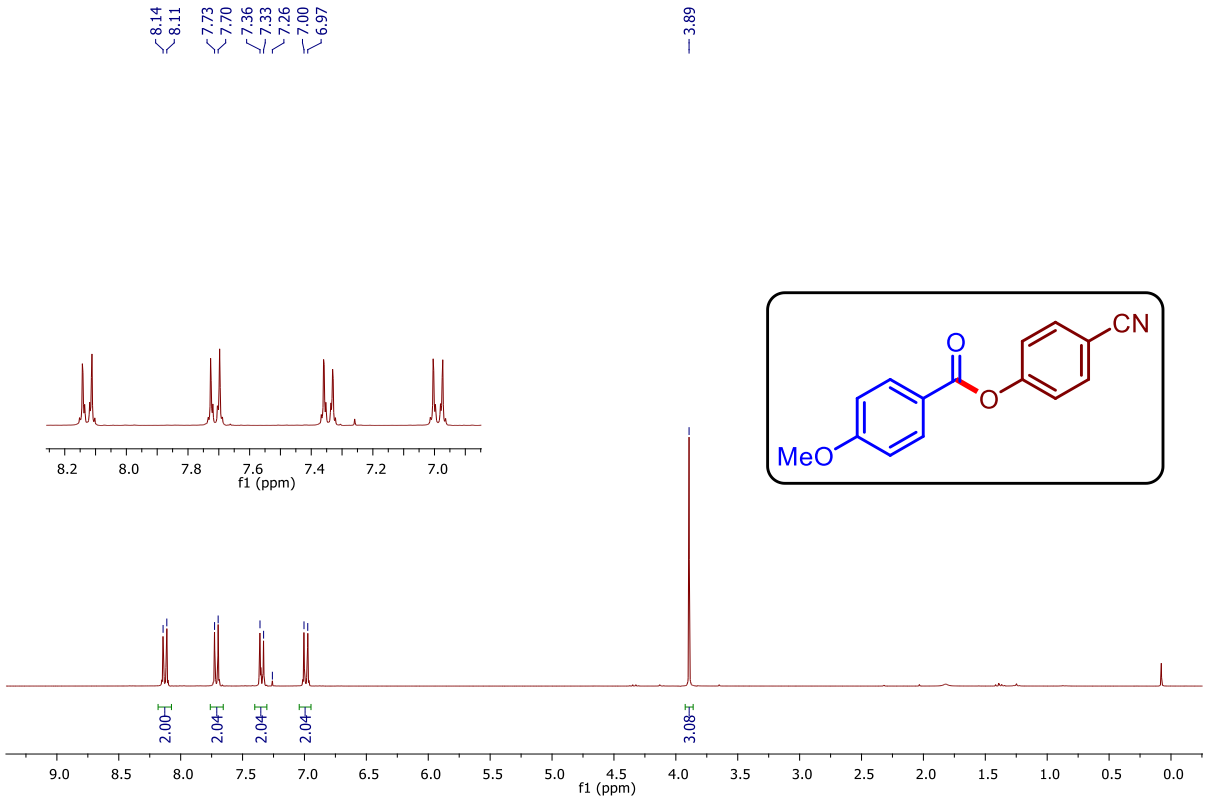
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzb



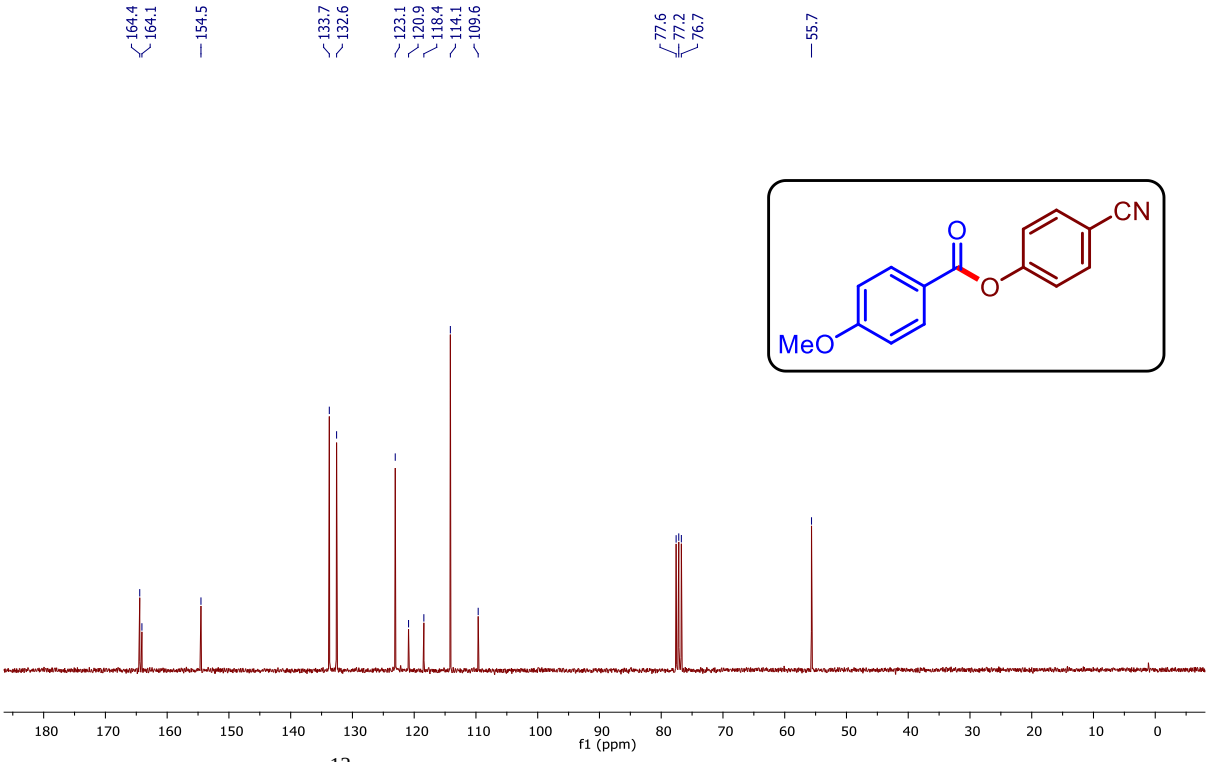
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zzc



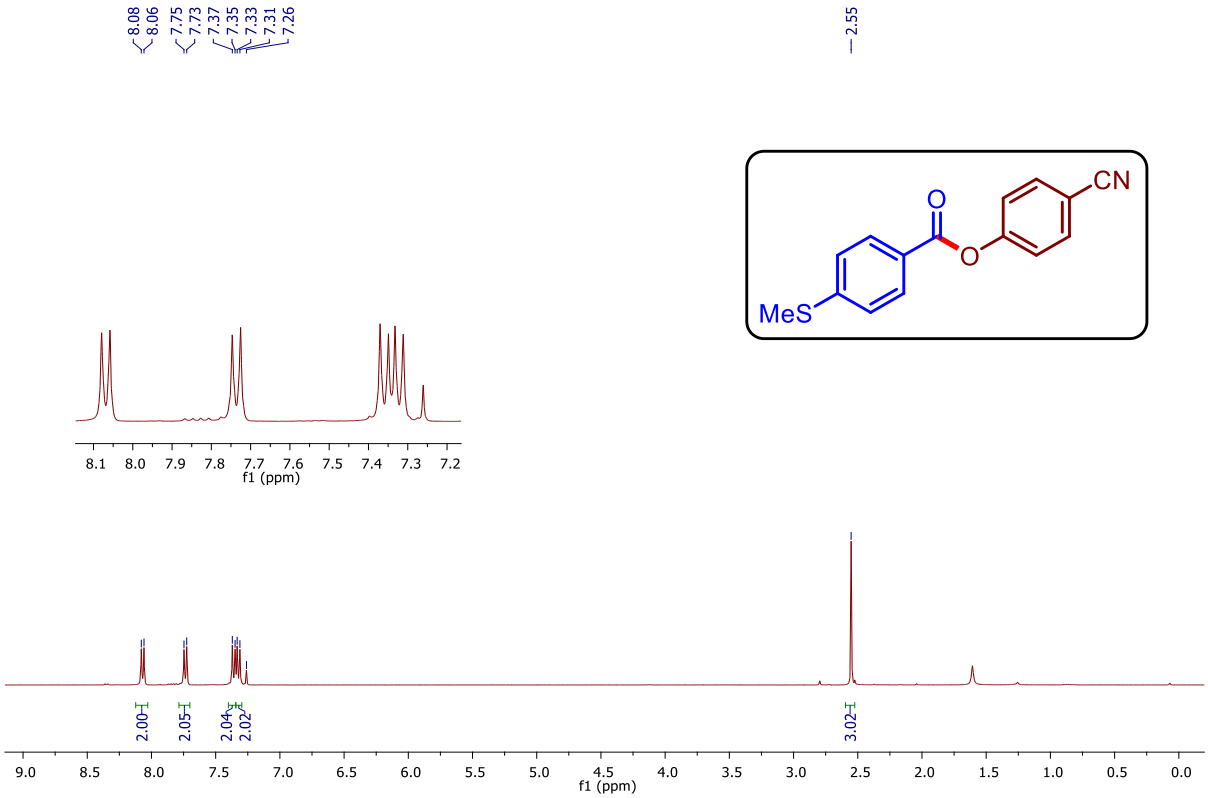
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzc



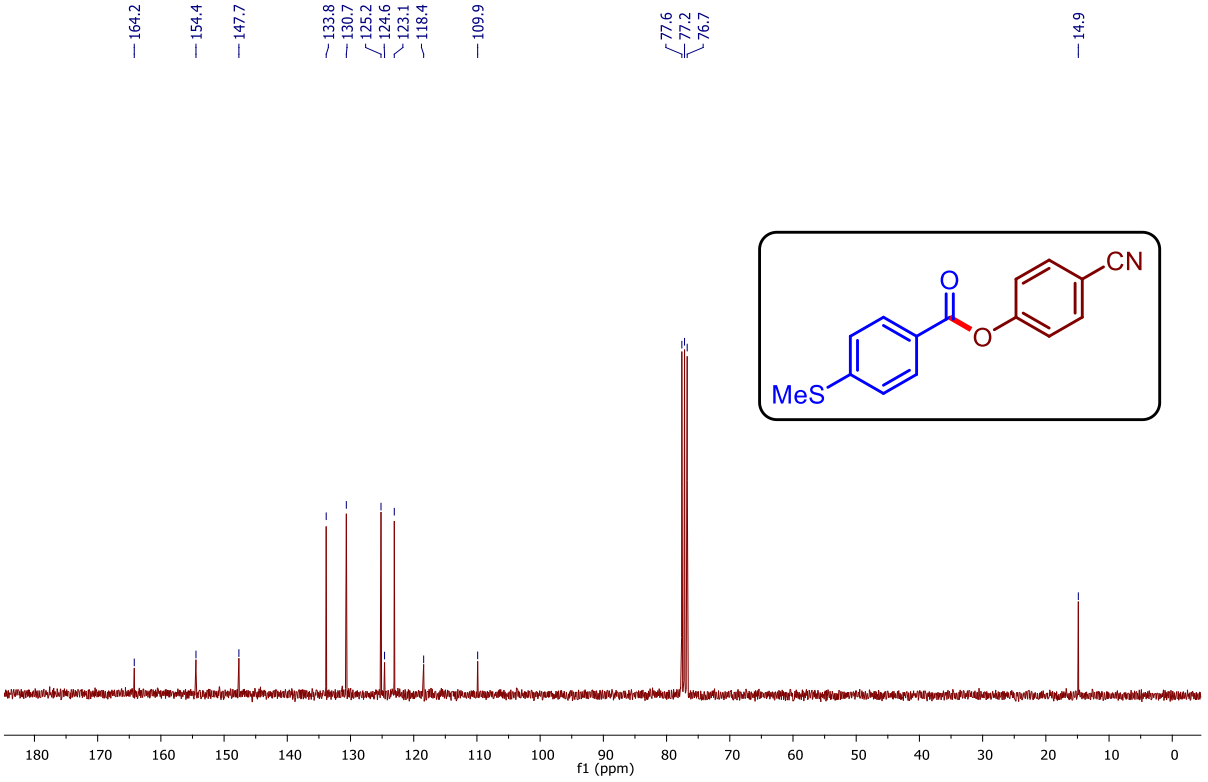
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zzd



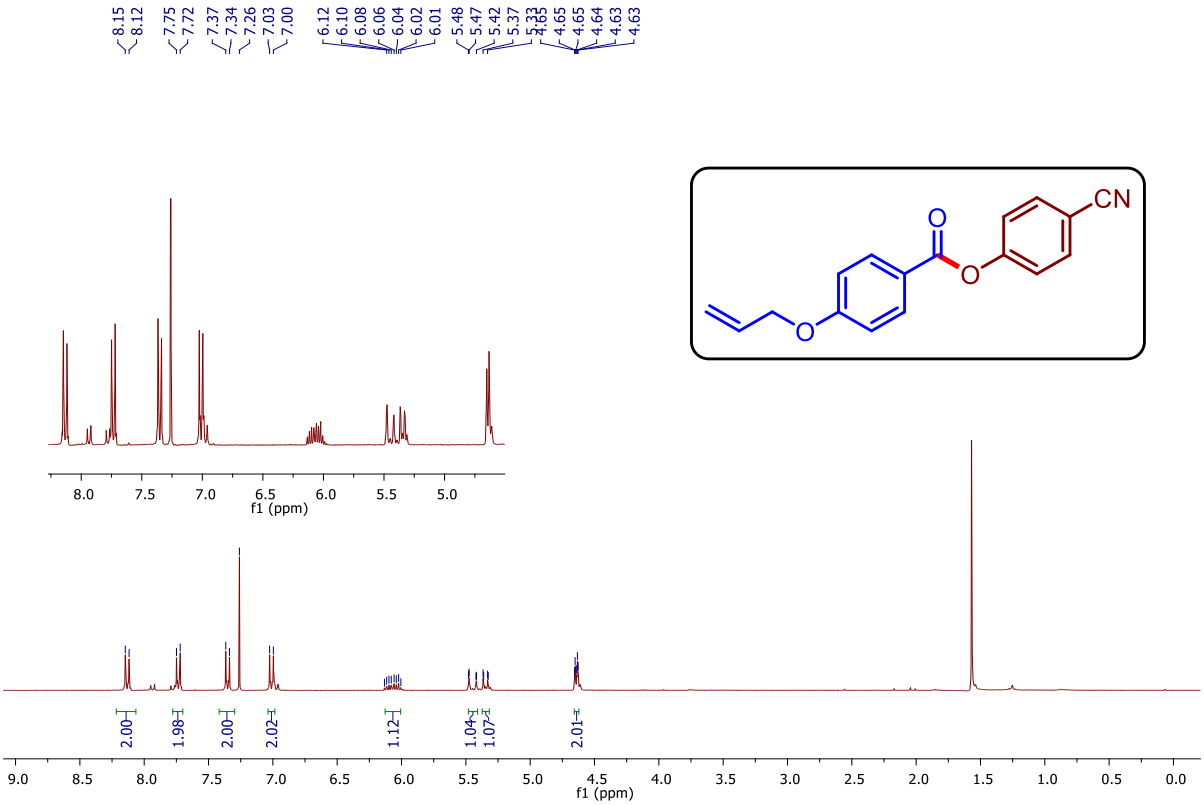
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zzd



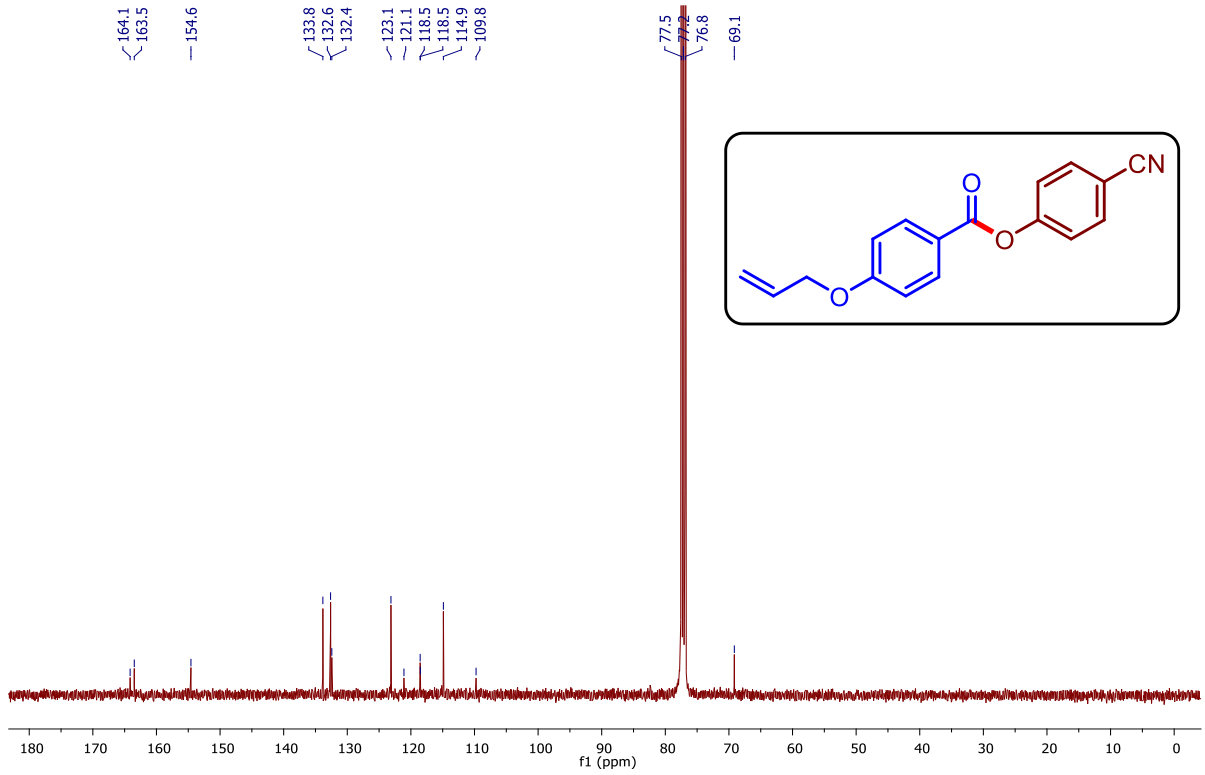
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zze



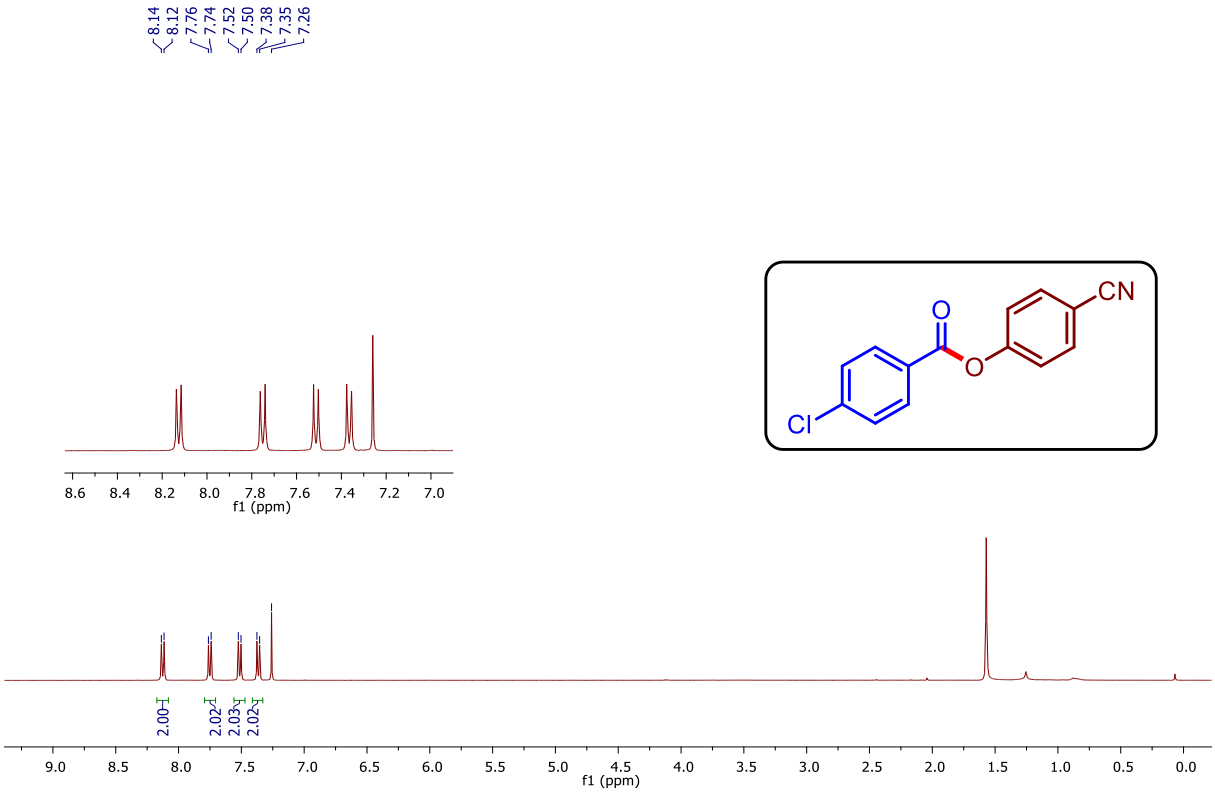
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zze



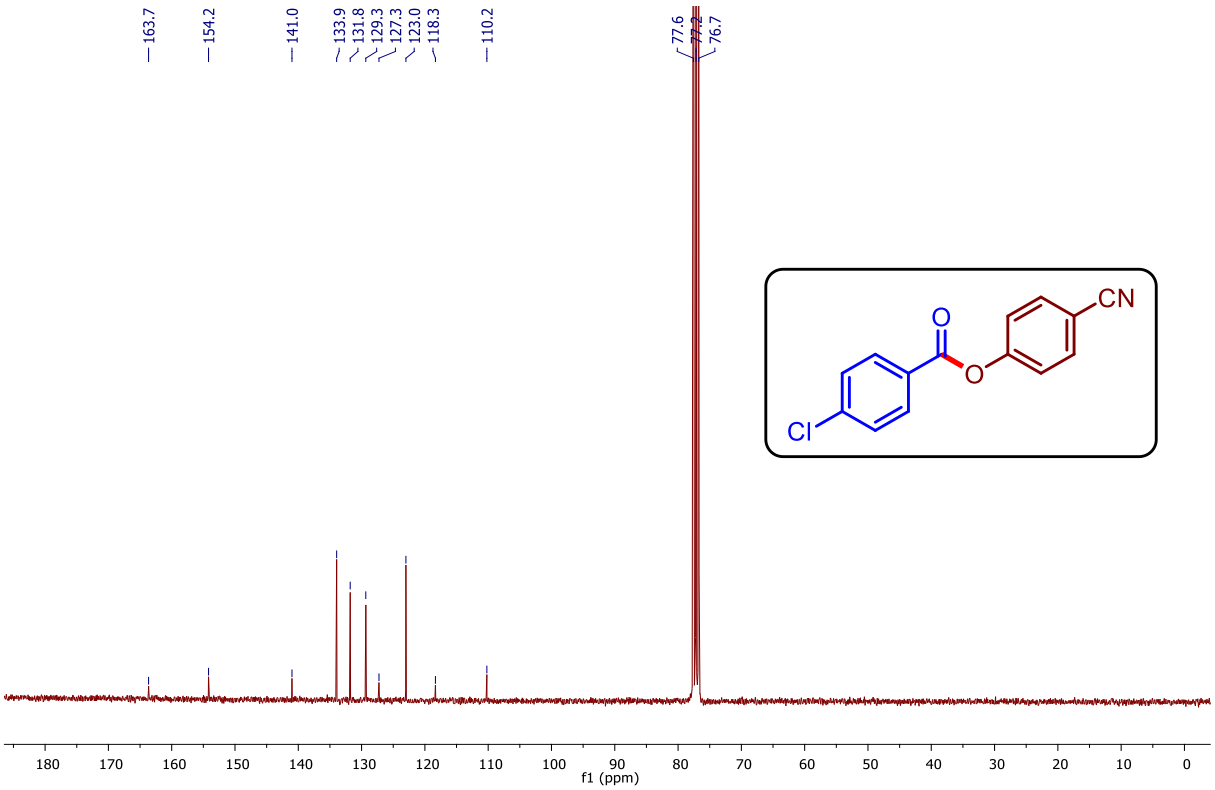
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 3zzf



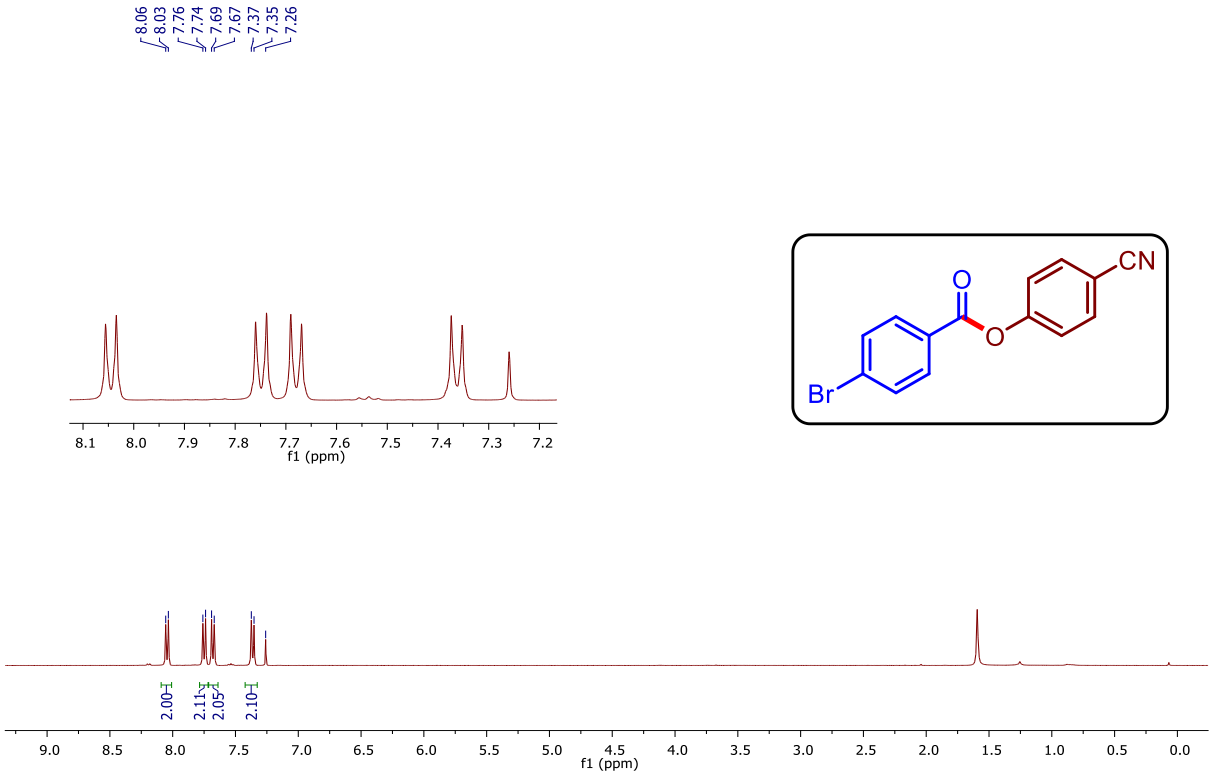
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3zzf



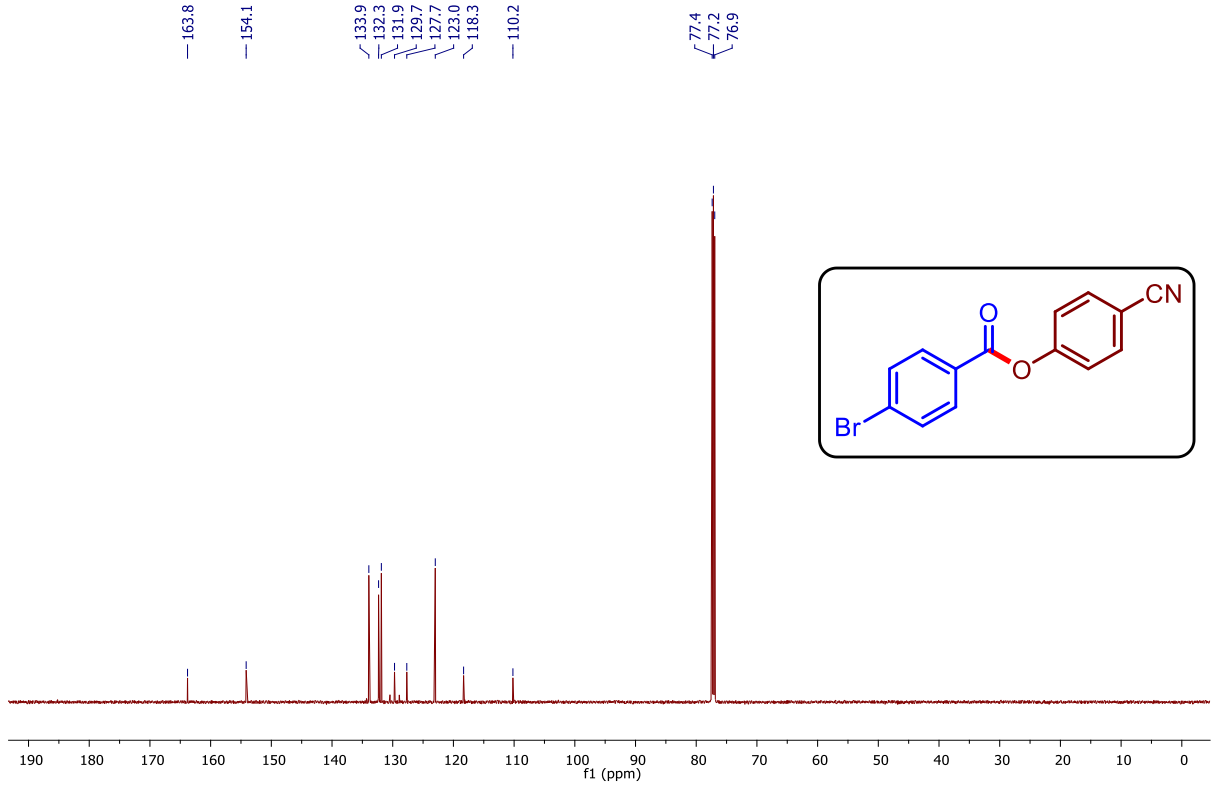
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzg



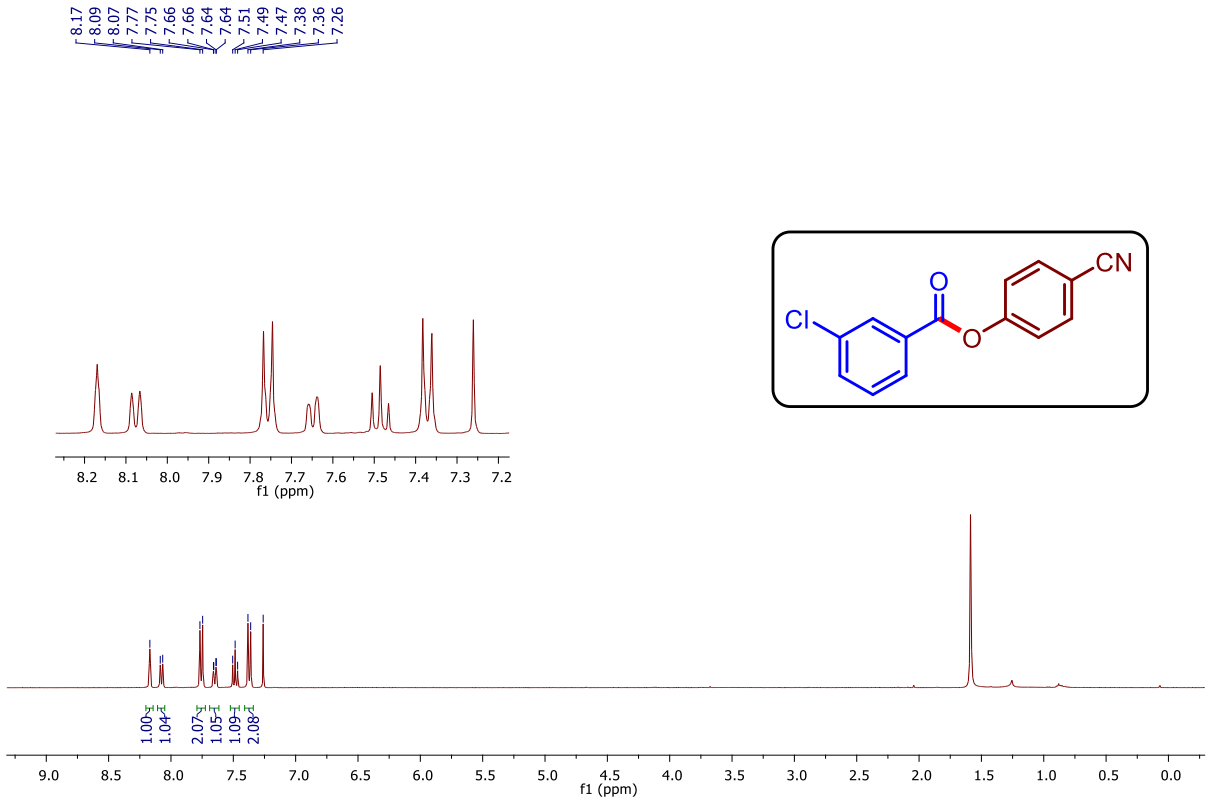
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zzg



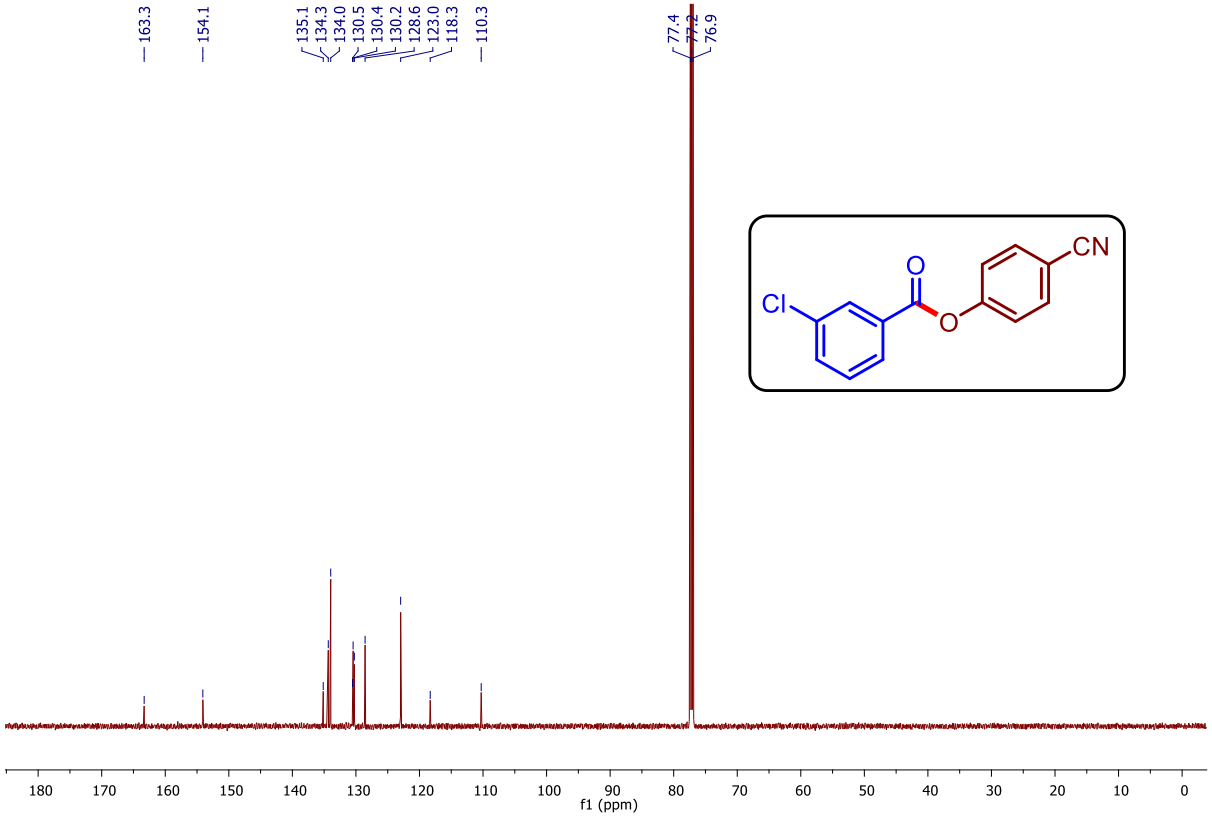
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzh



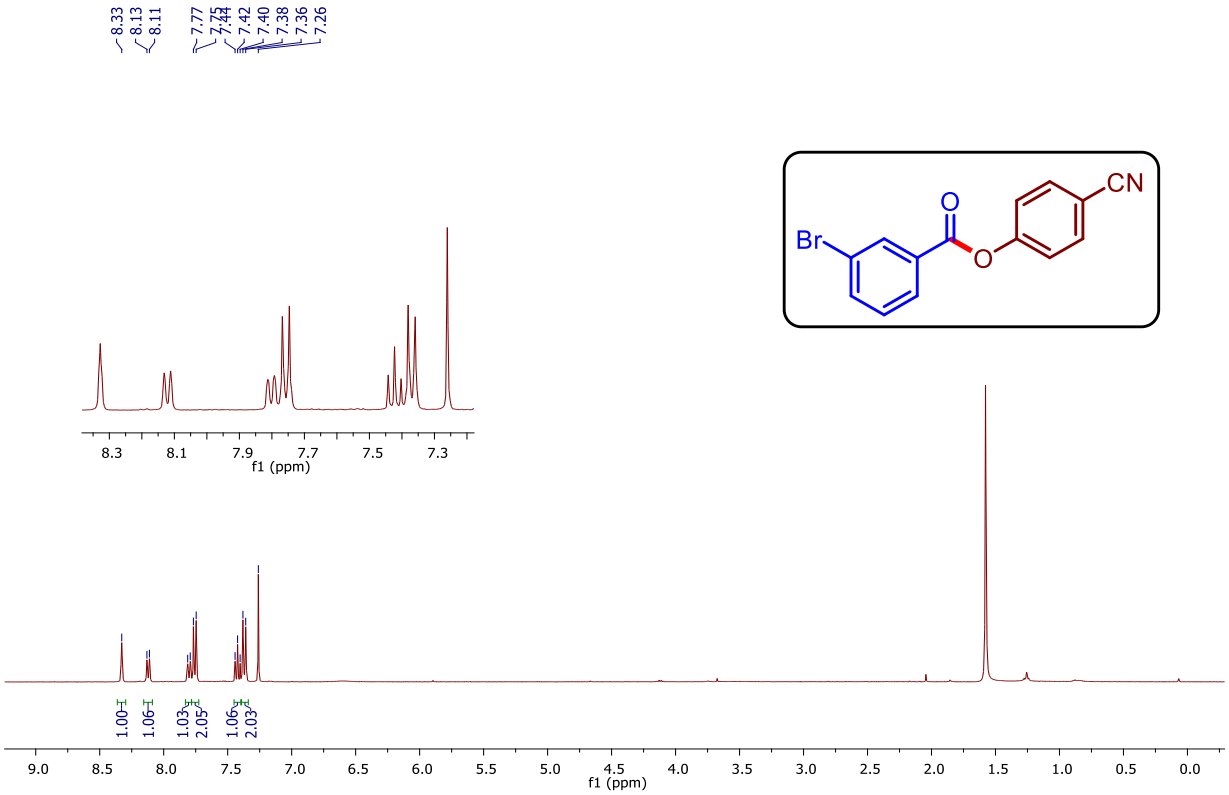
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzh



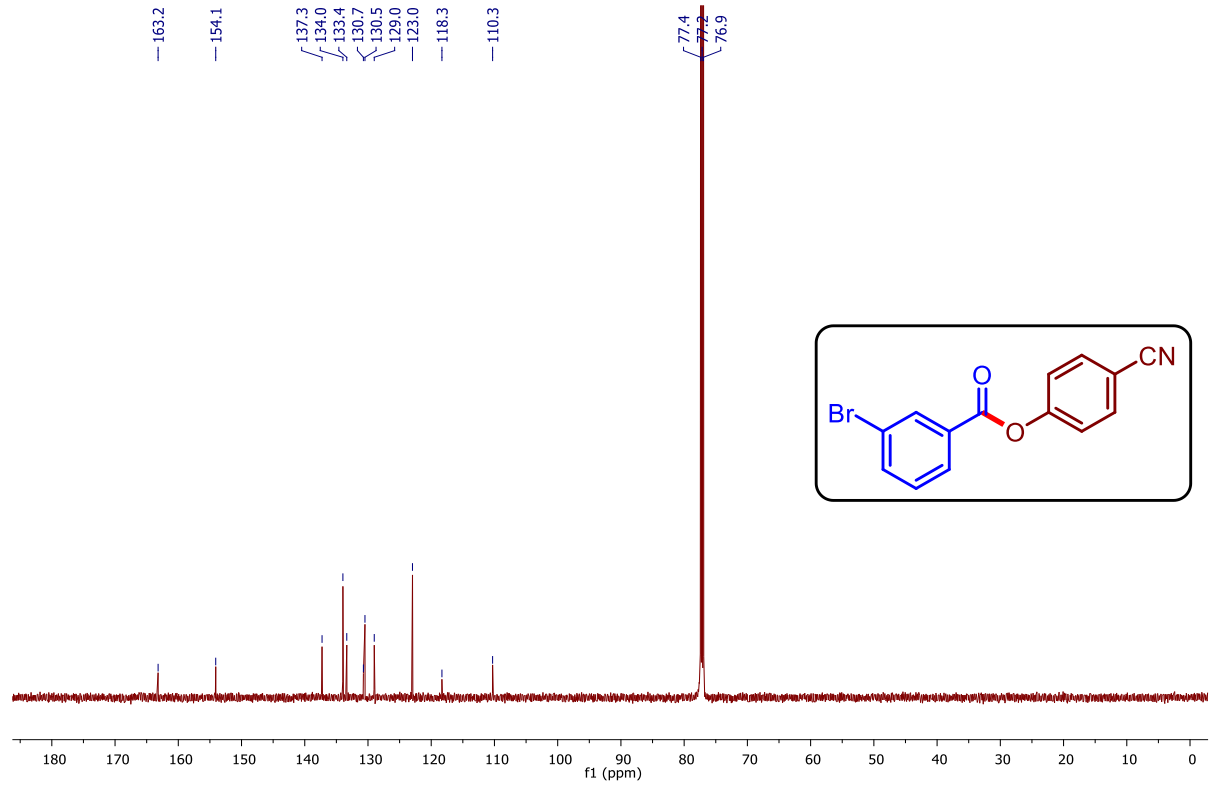
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzi



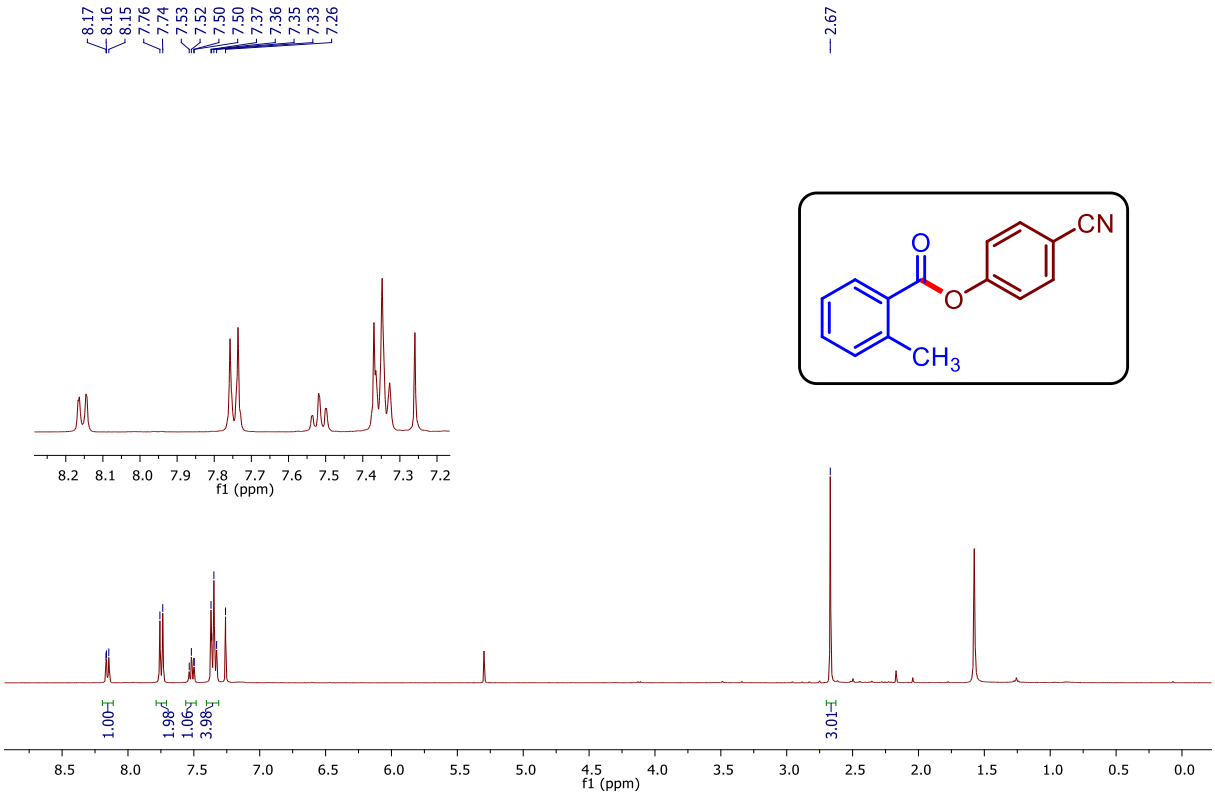
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzi



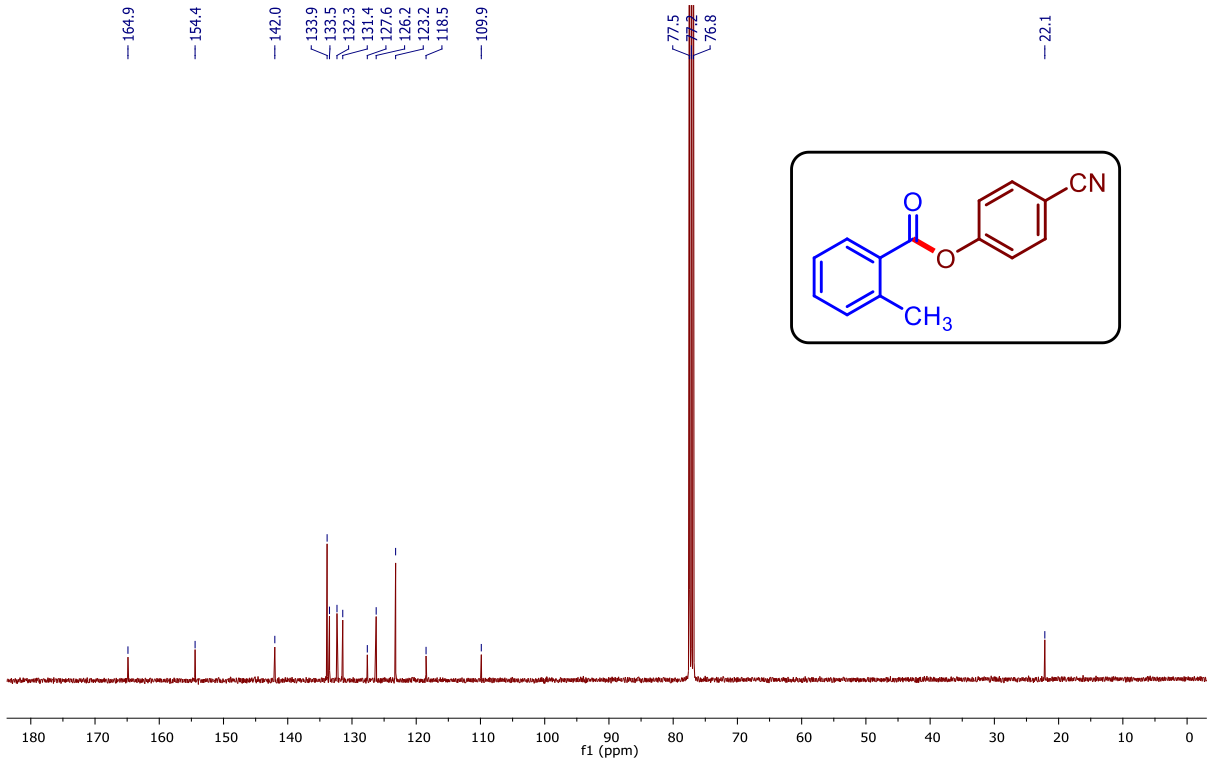
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzj



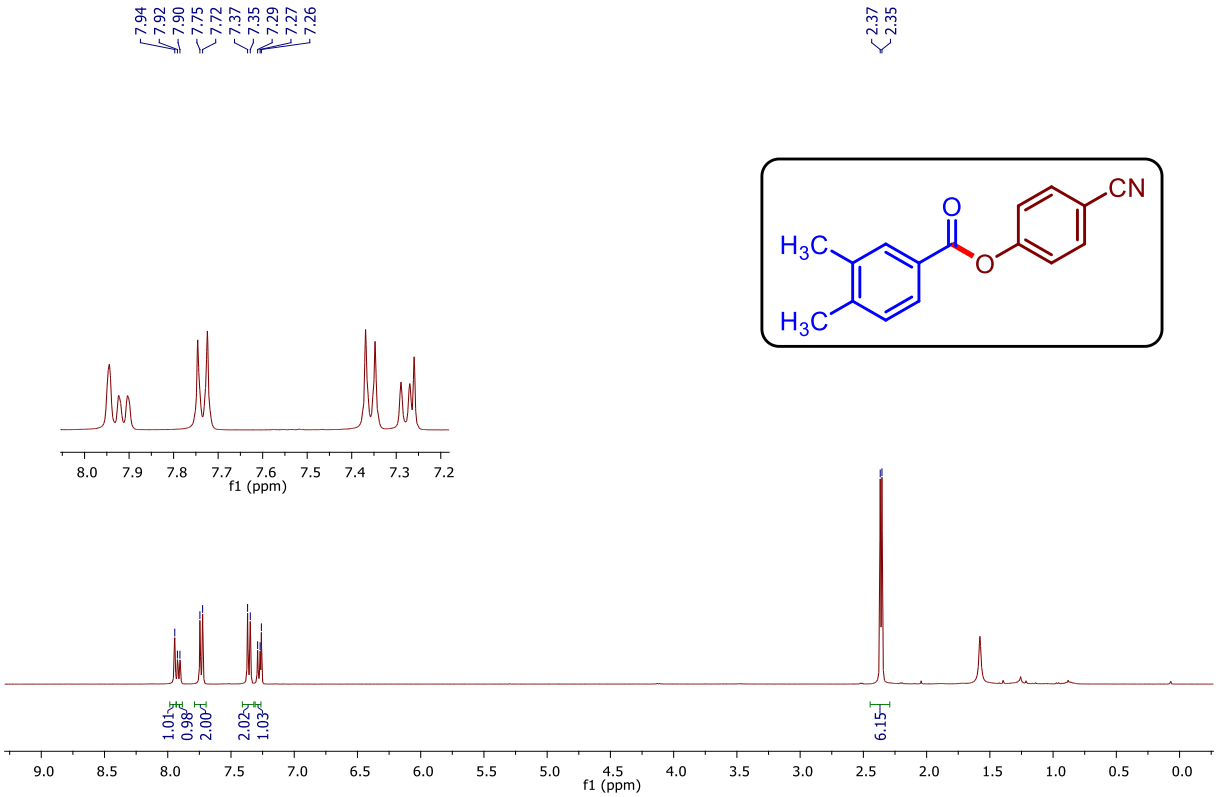
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzj



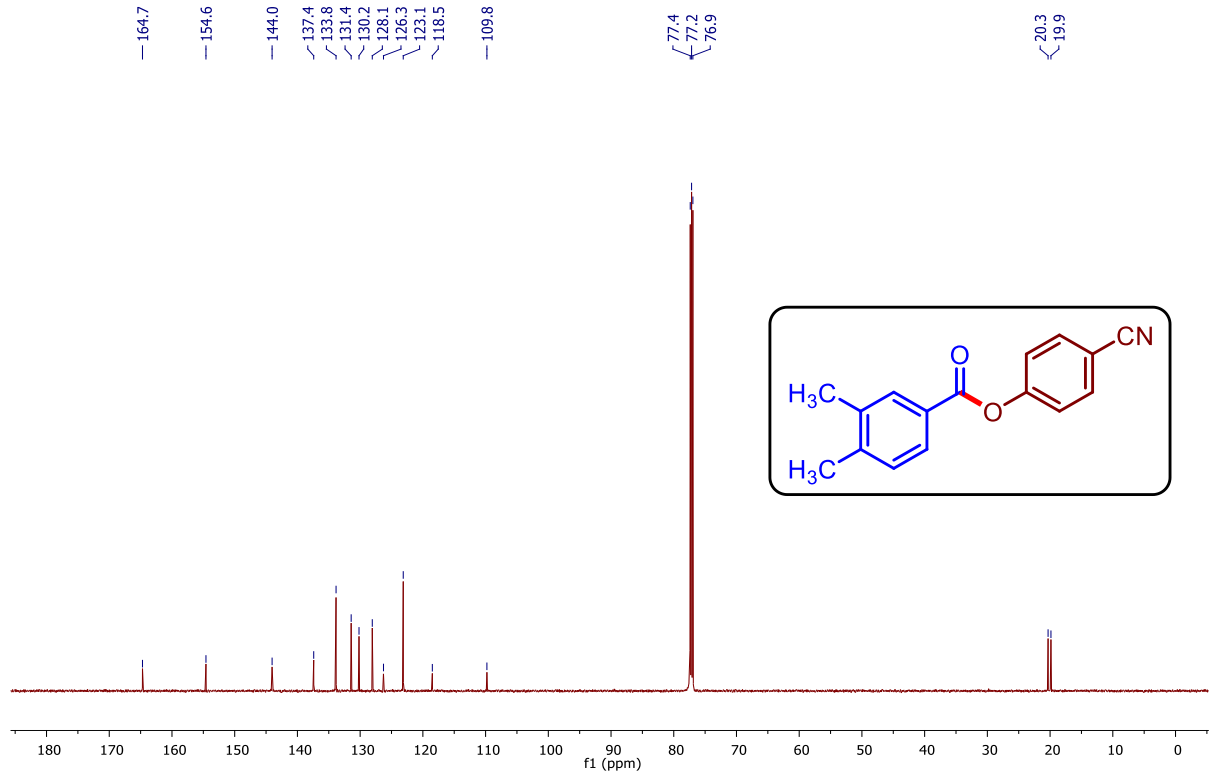
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzk



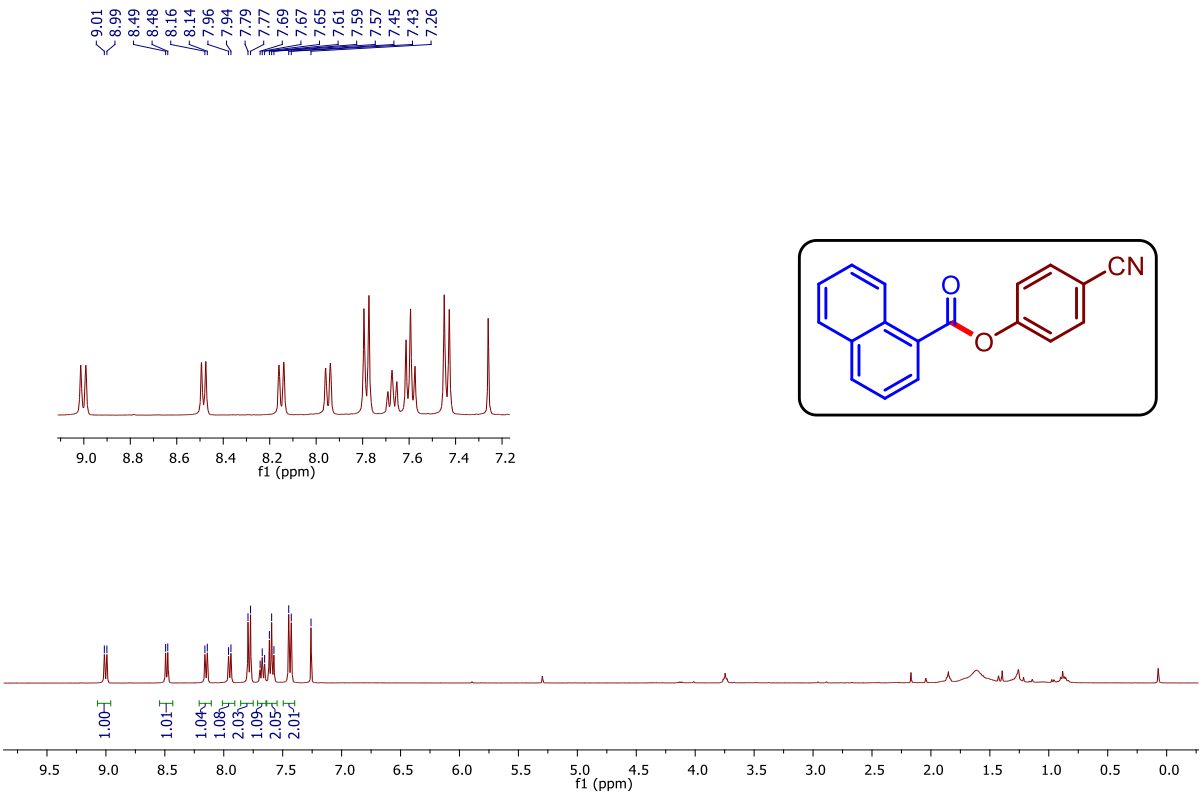
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zzk



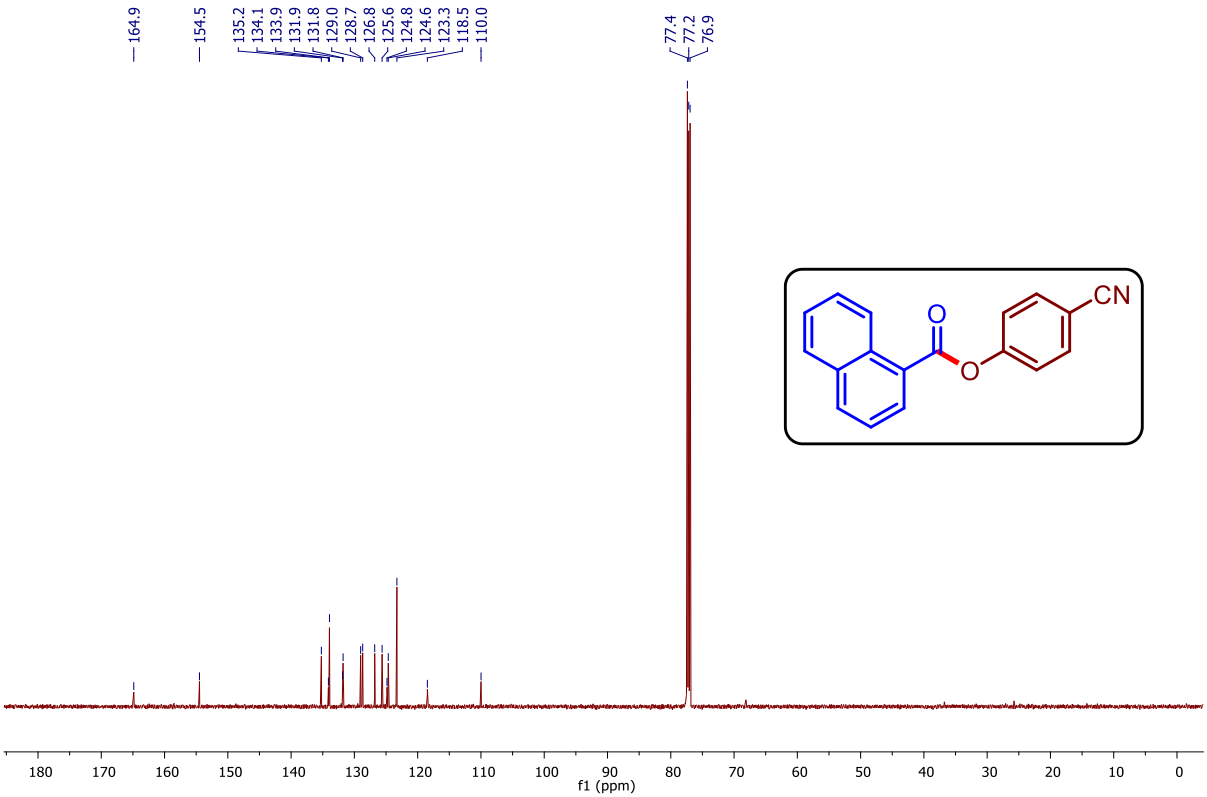
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzl



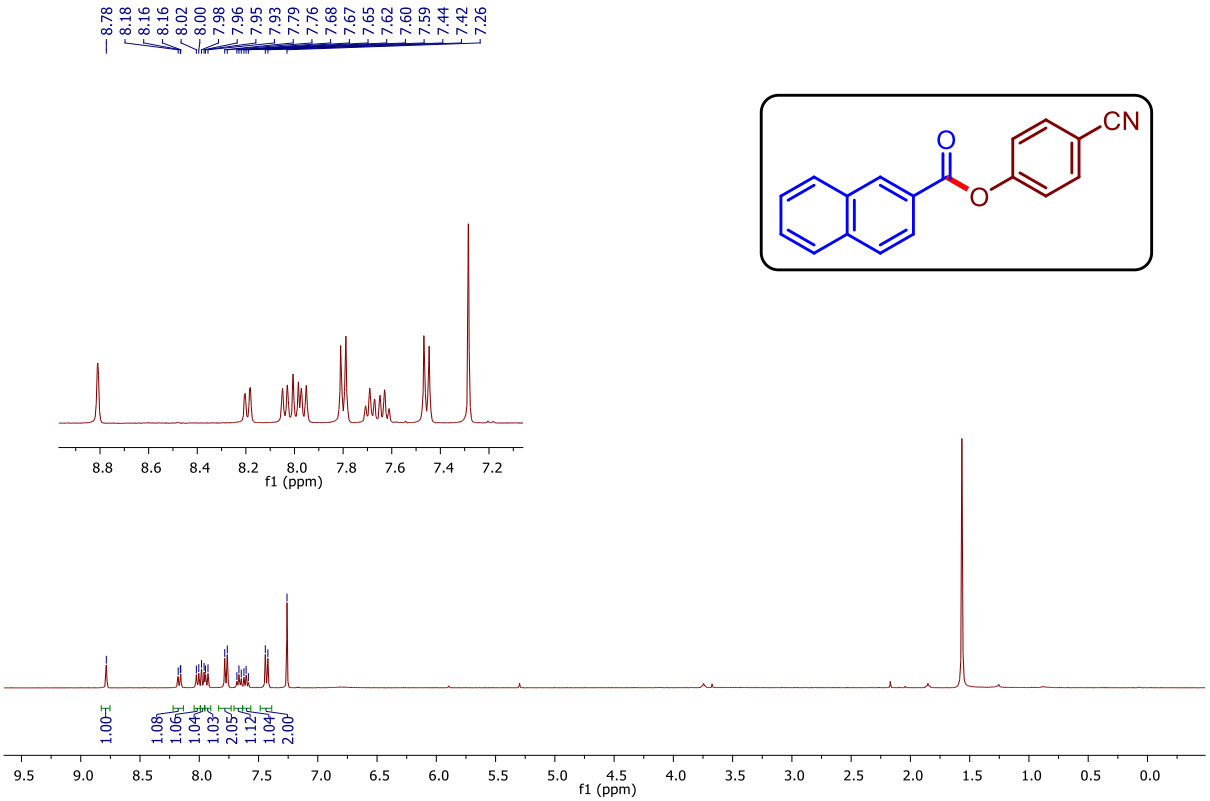
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzl



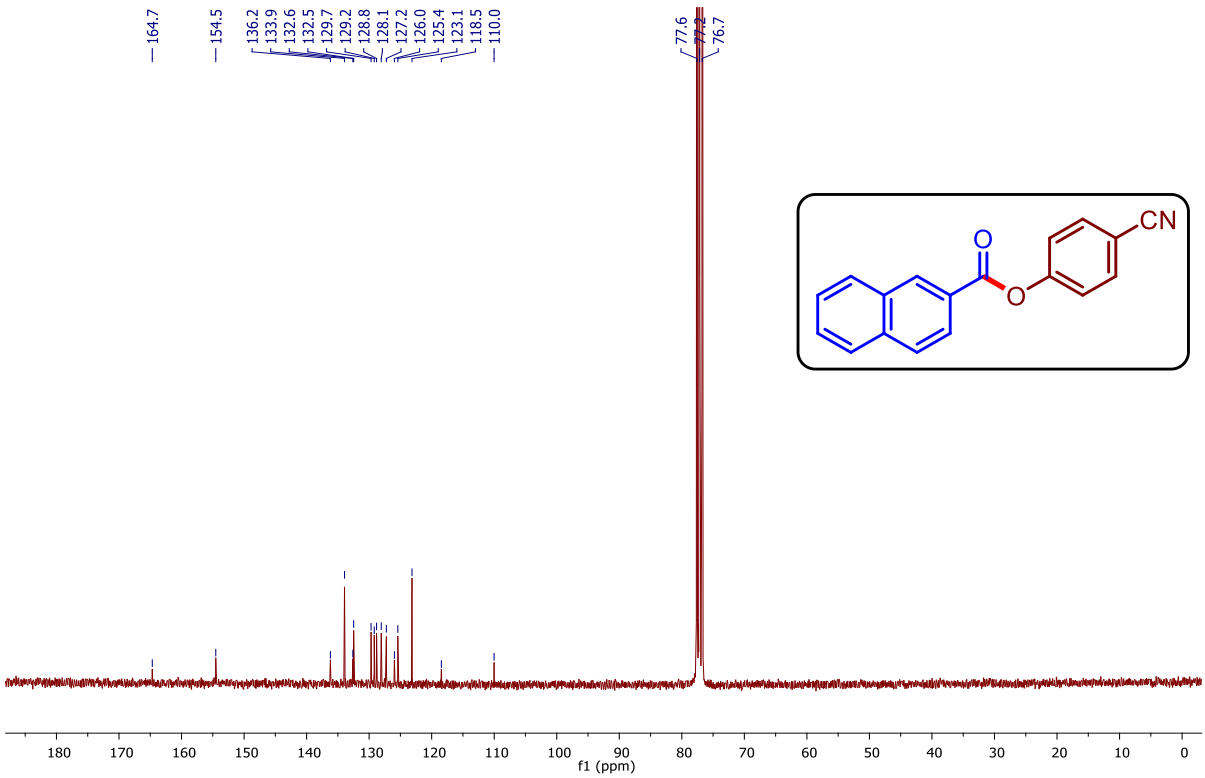
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzm



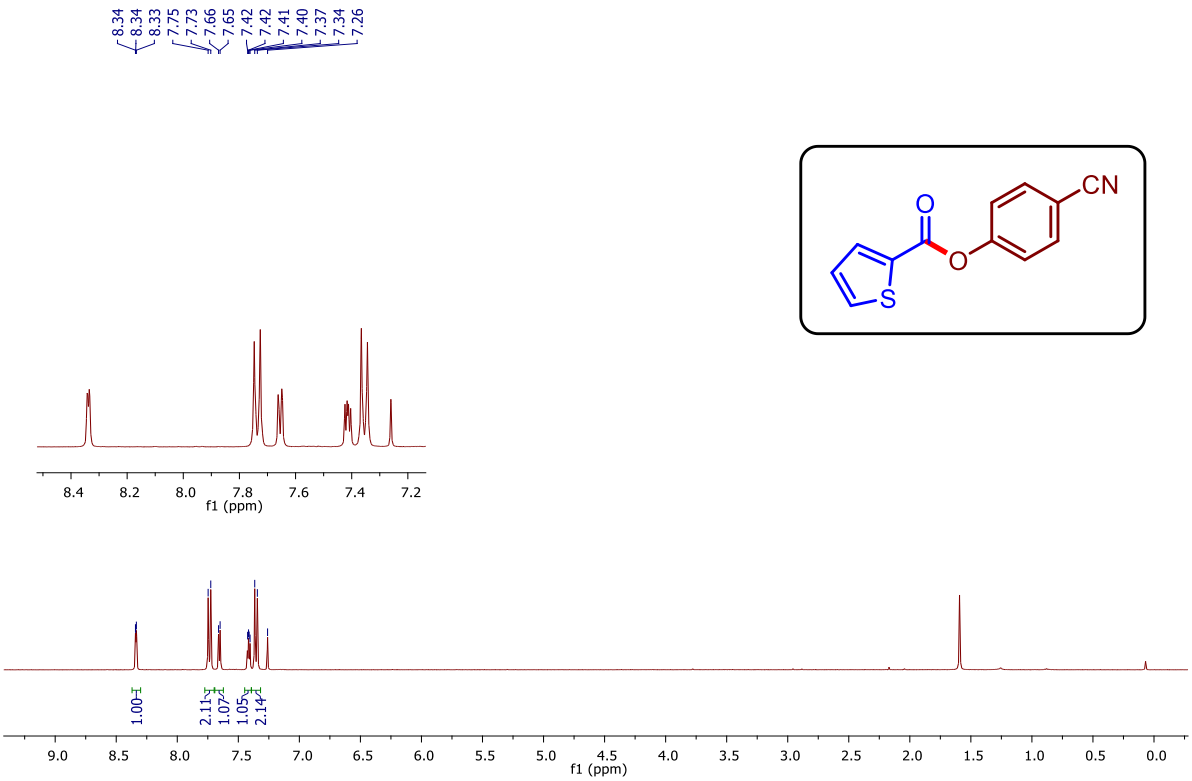
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of 3zzm



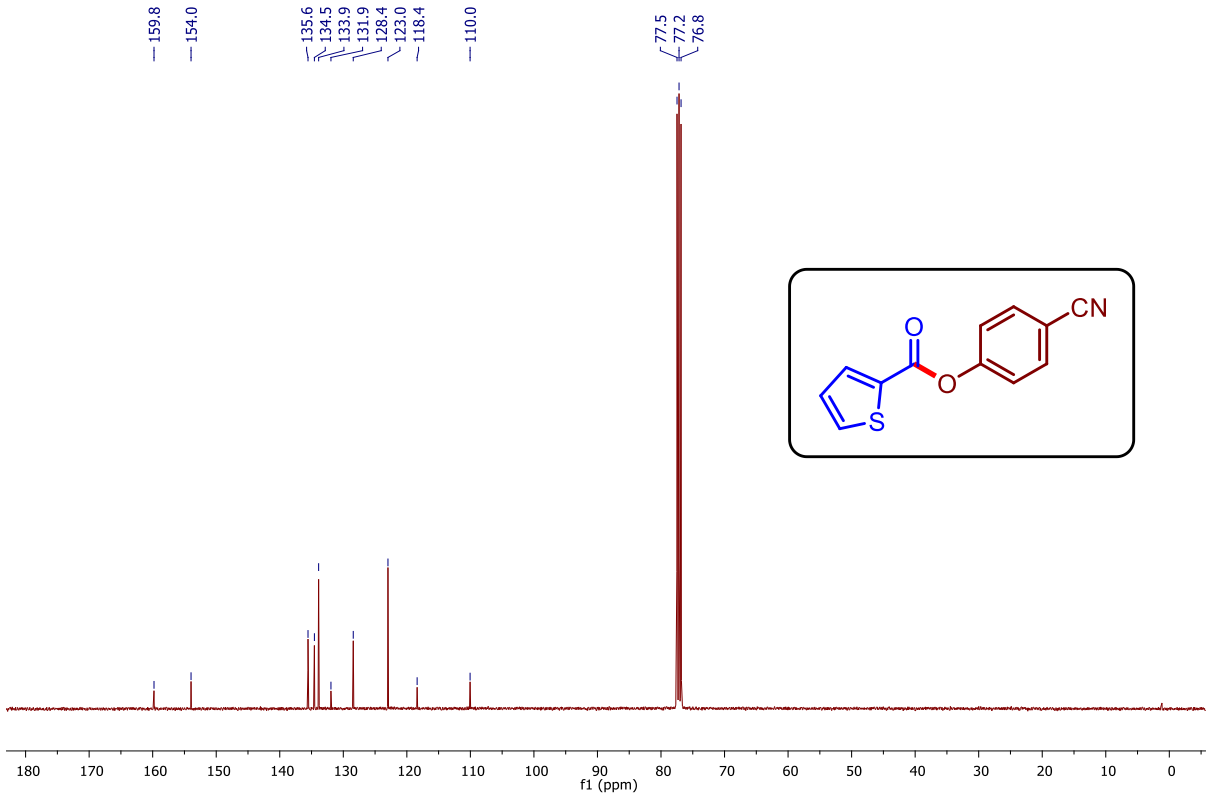
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzn



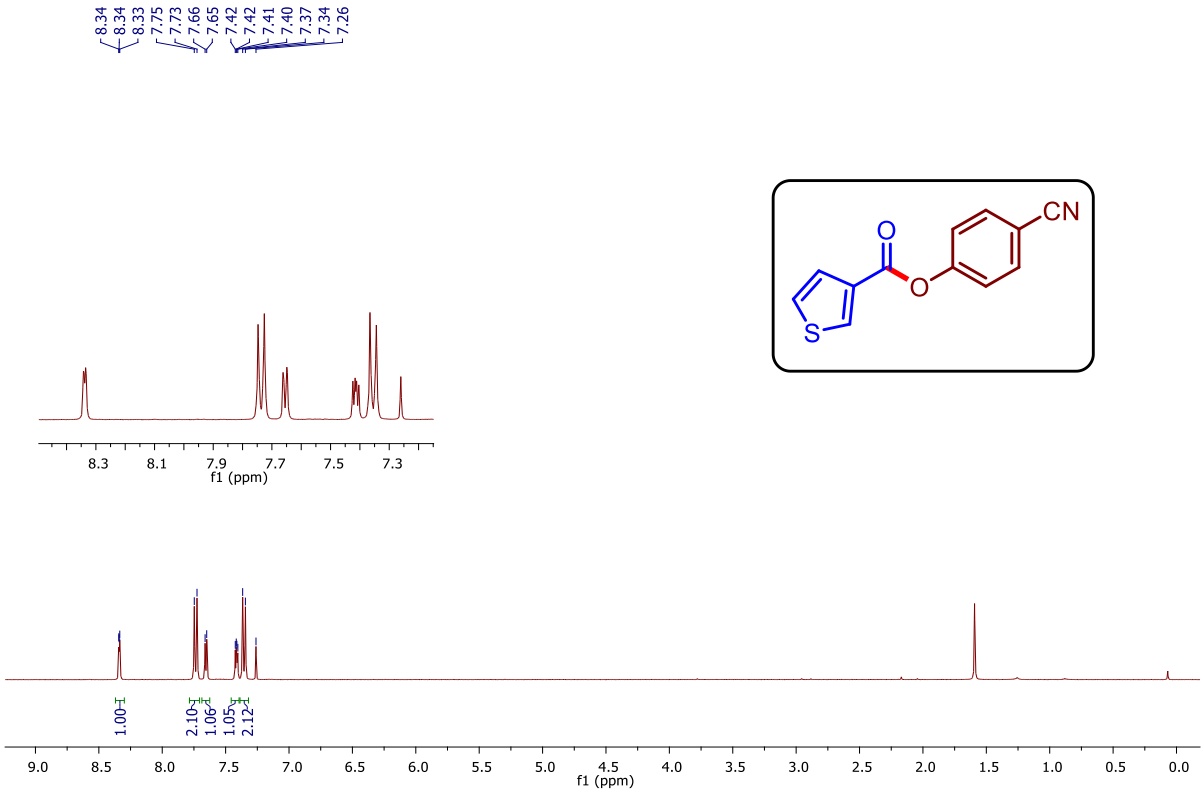
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 3zzn



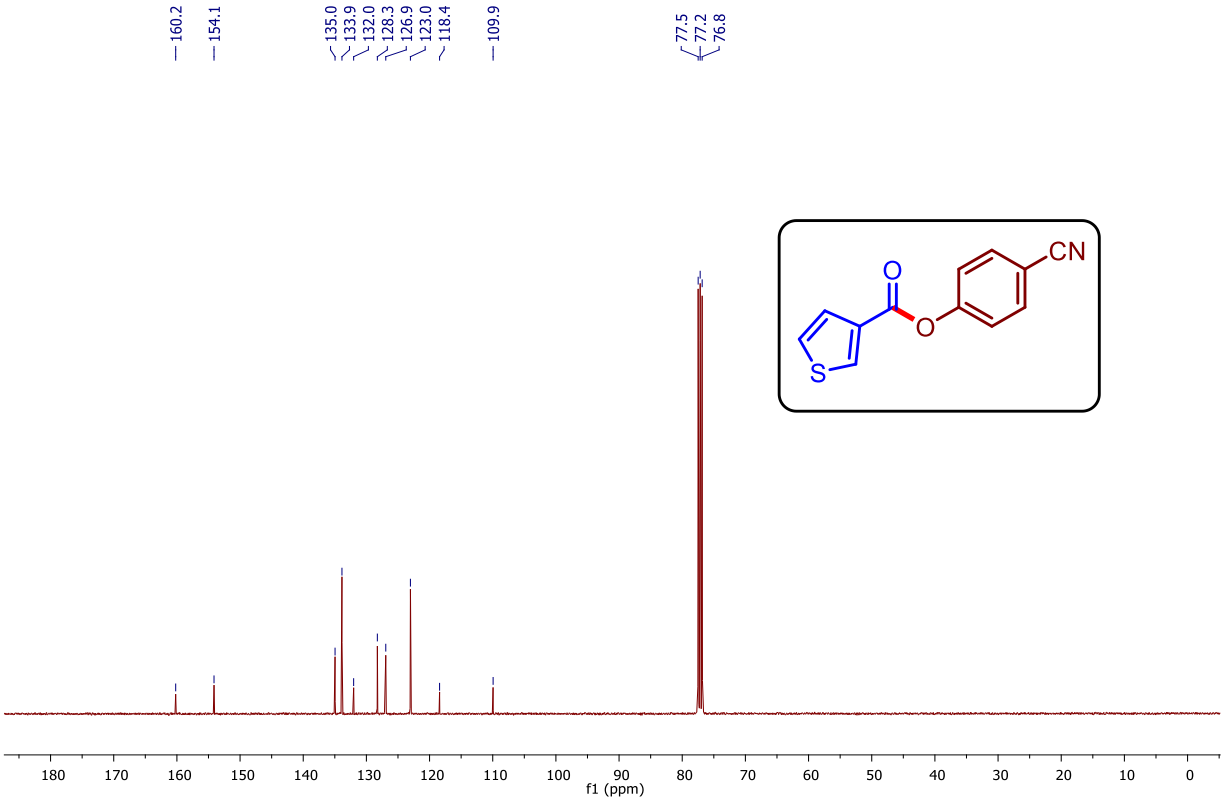
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzo



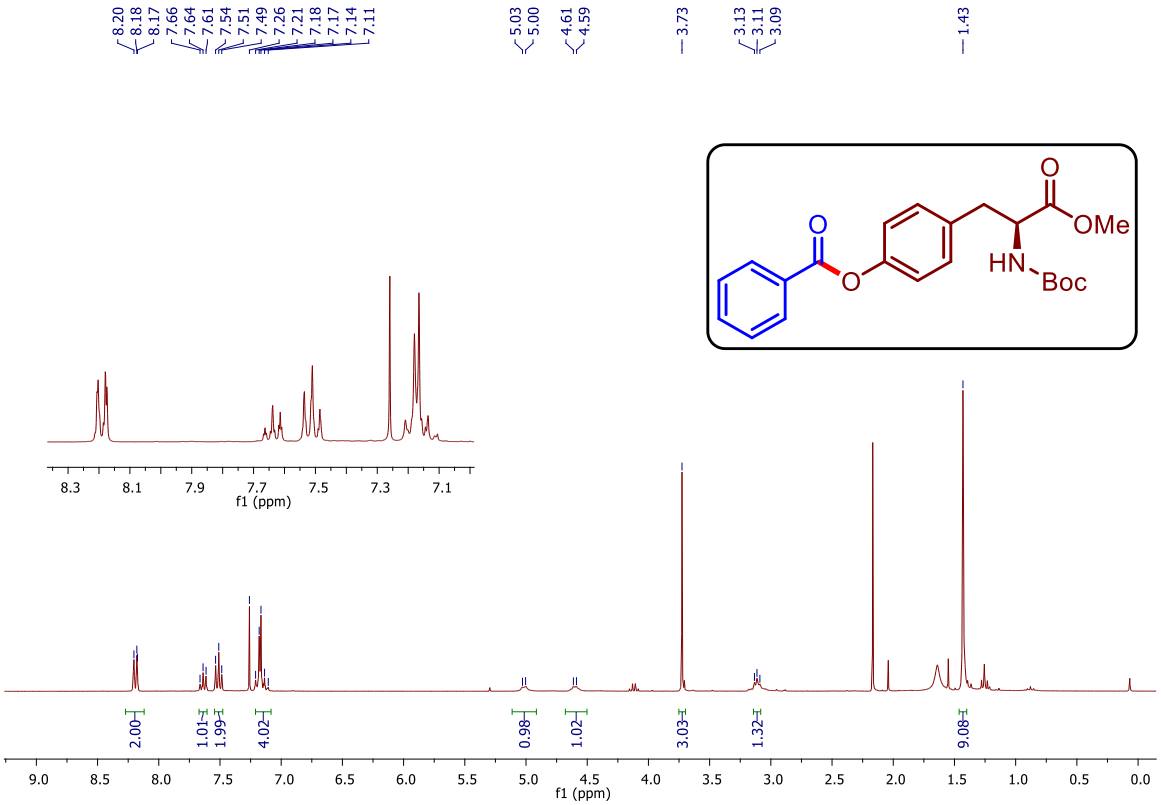
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3zzo



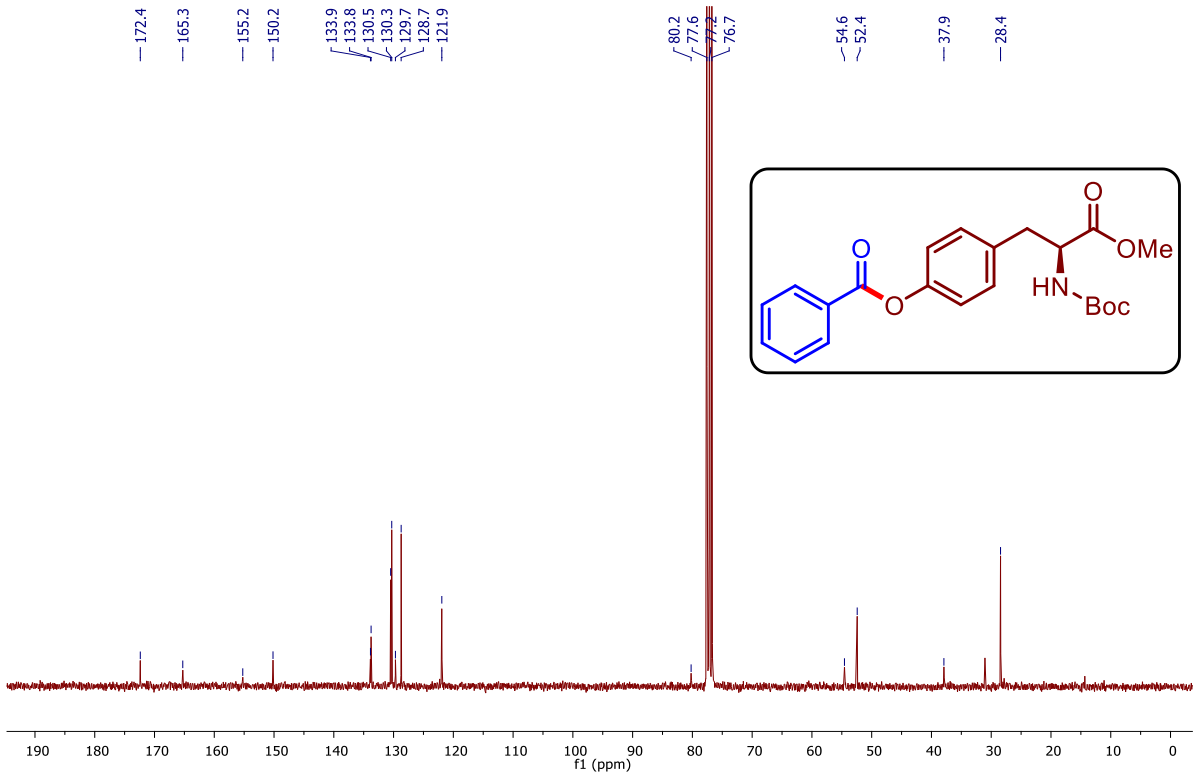
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 3zzp



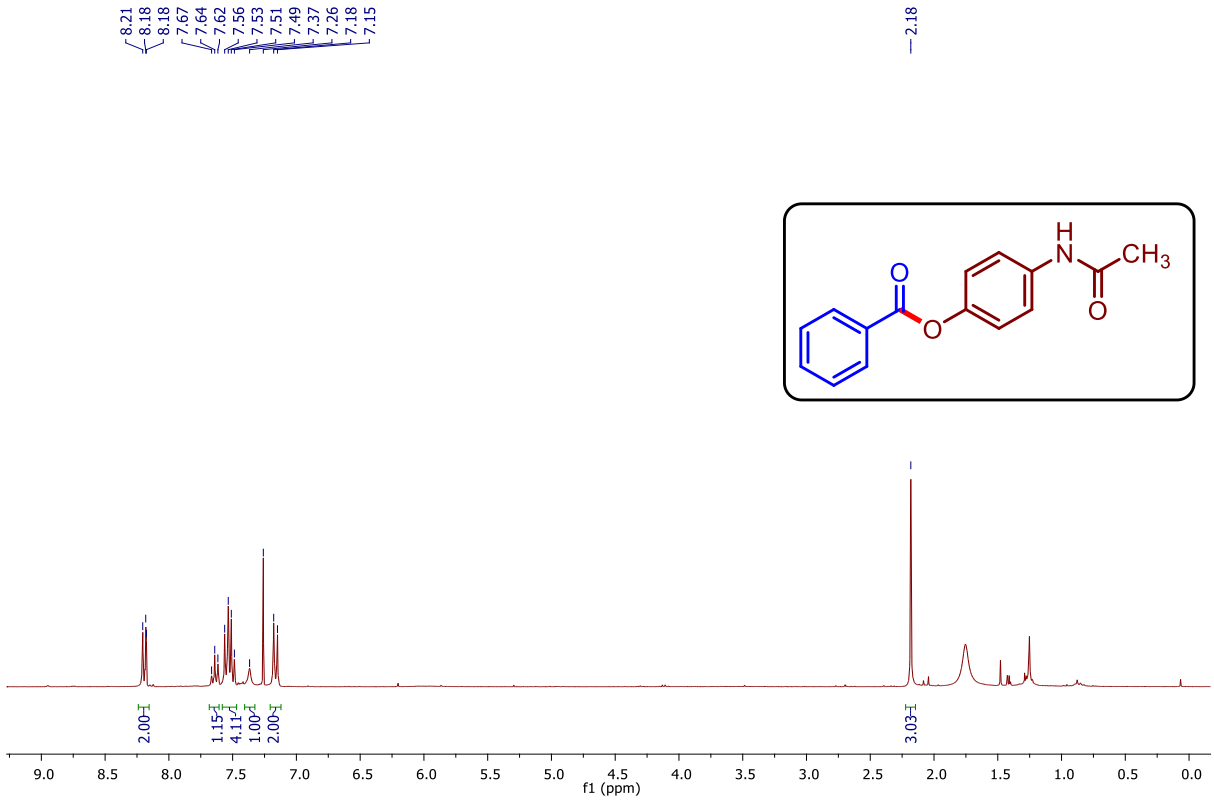
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 3zzp



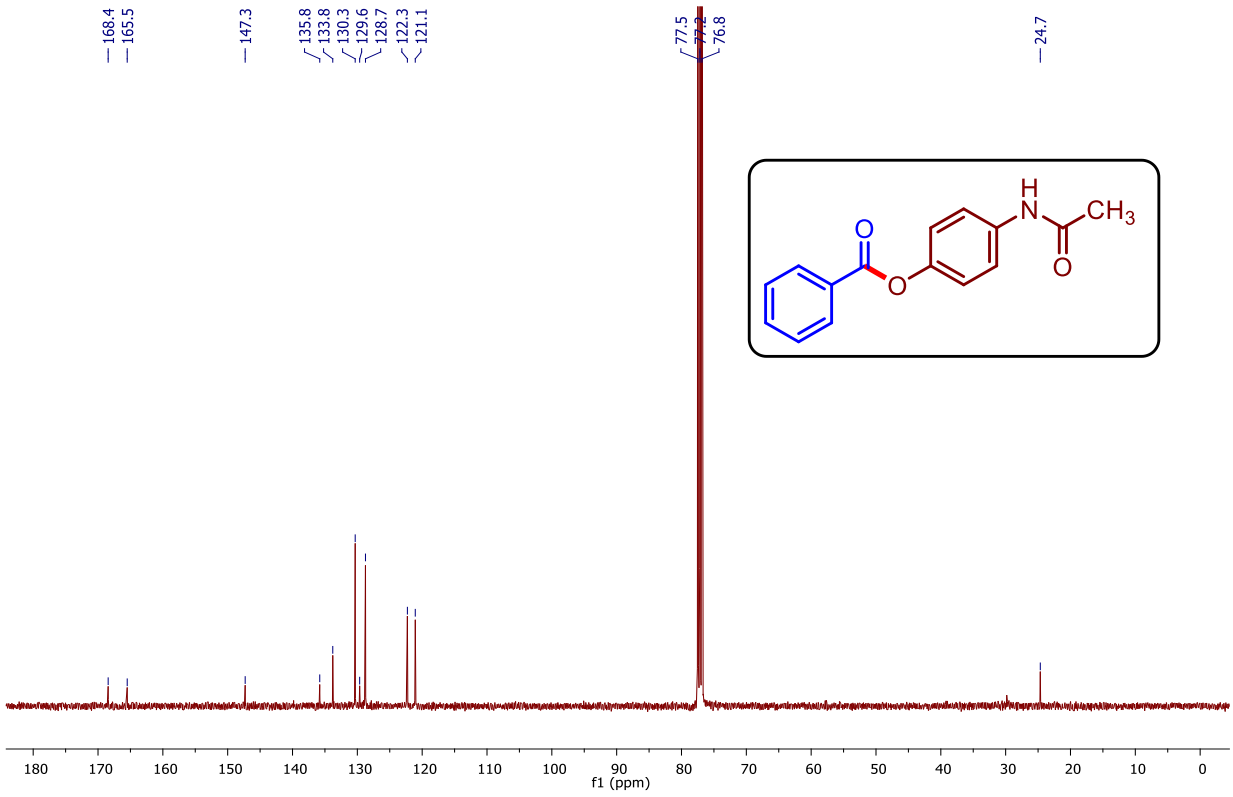
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5a



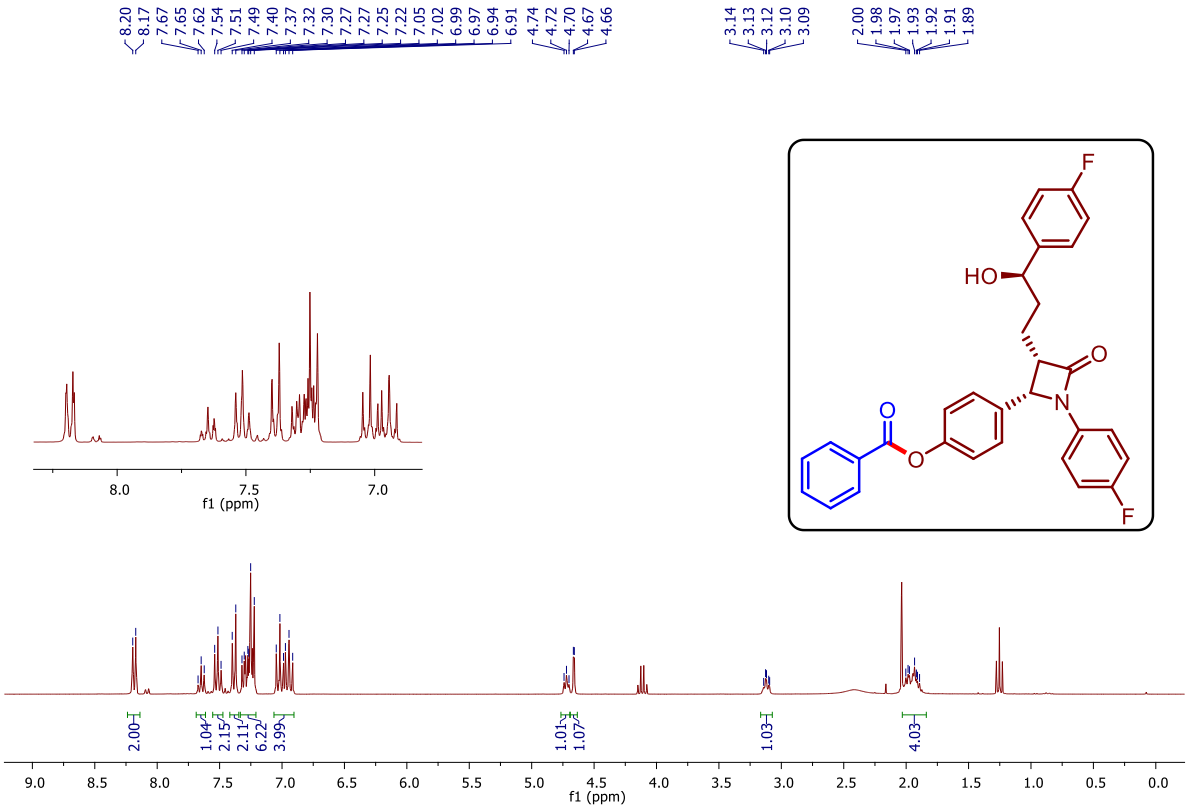
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5a



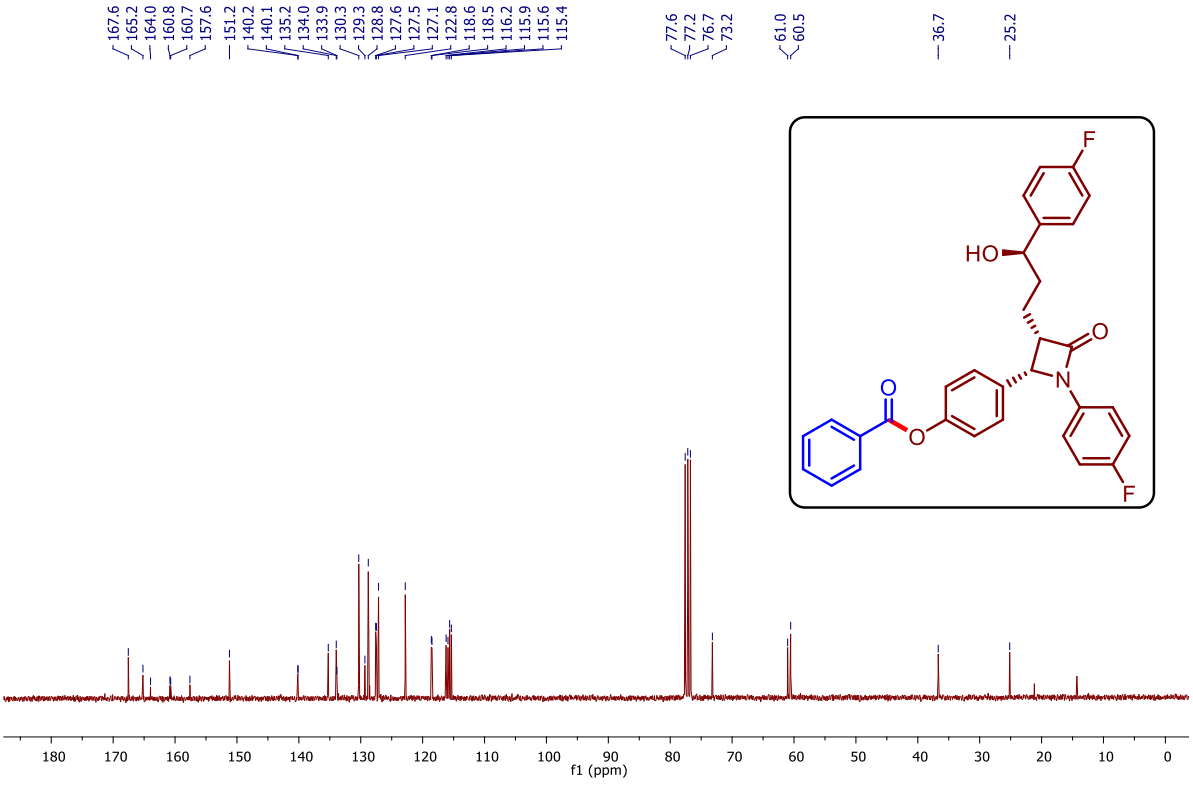
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5b



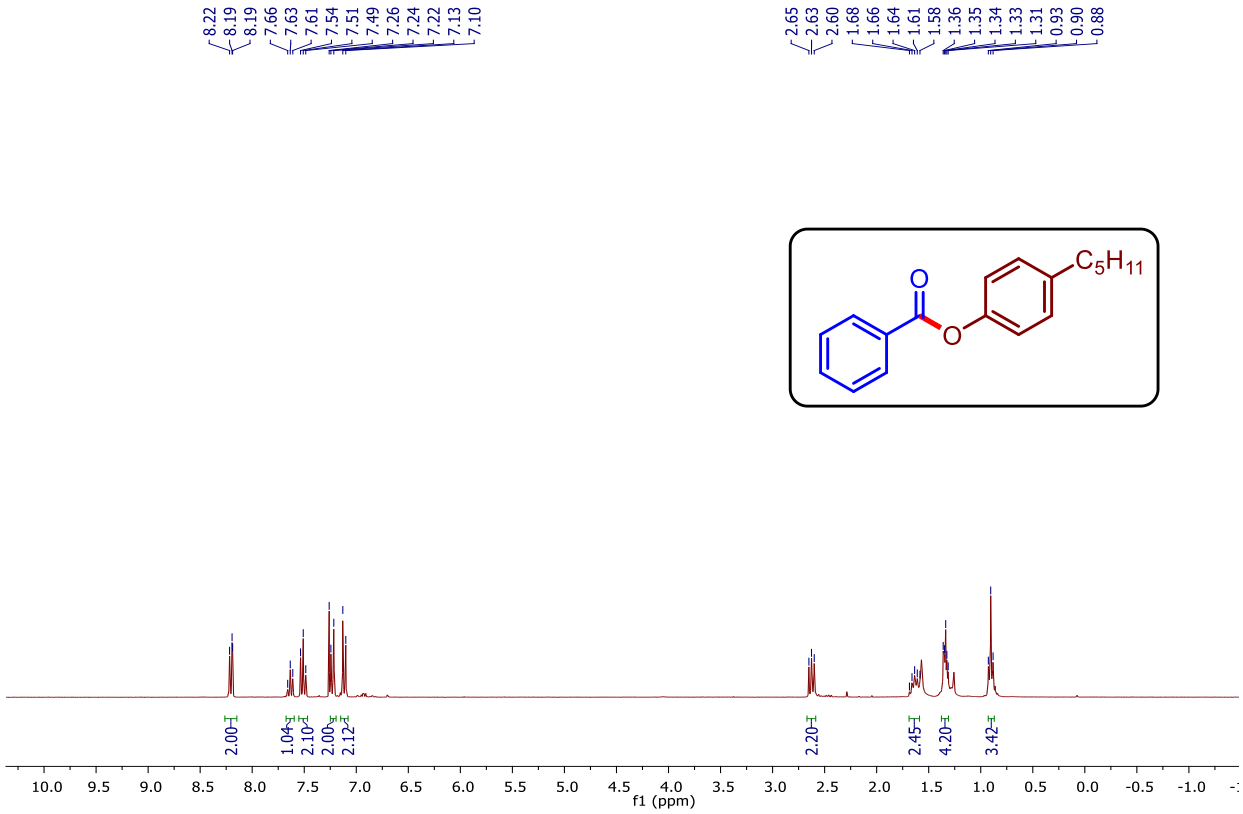
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 5b



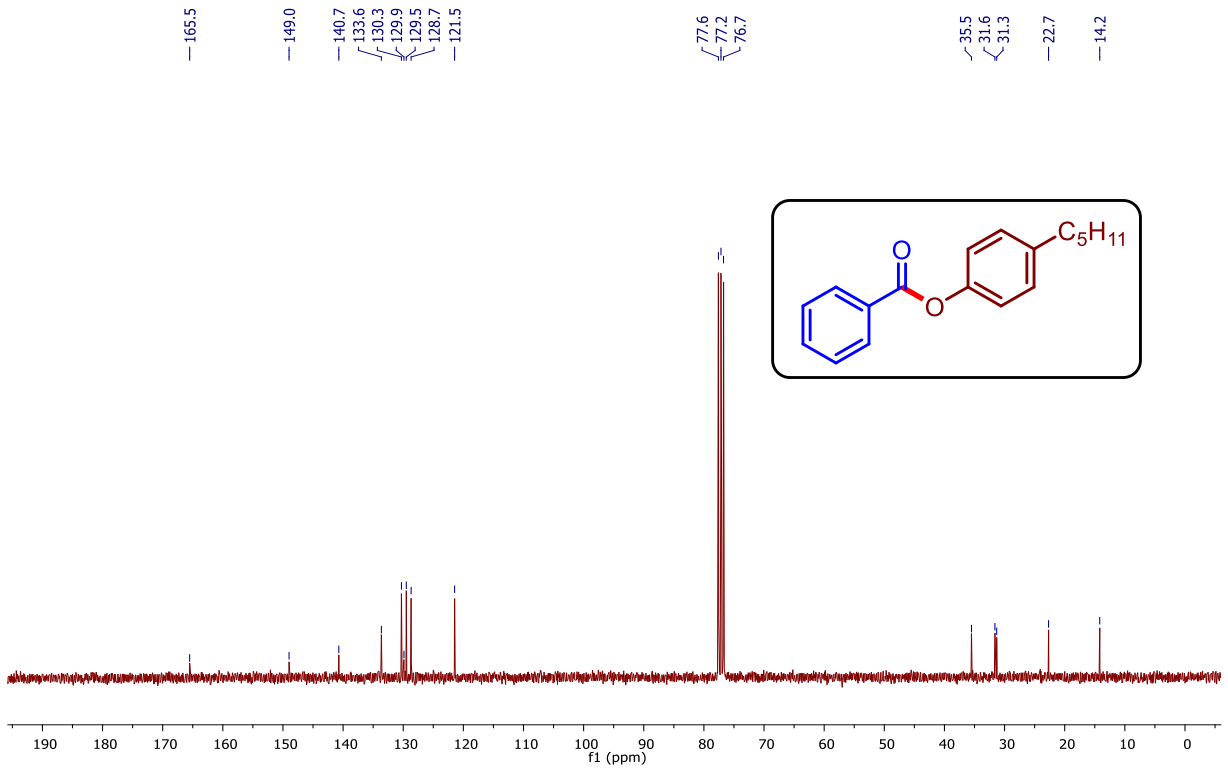
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5c



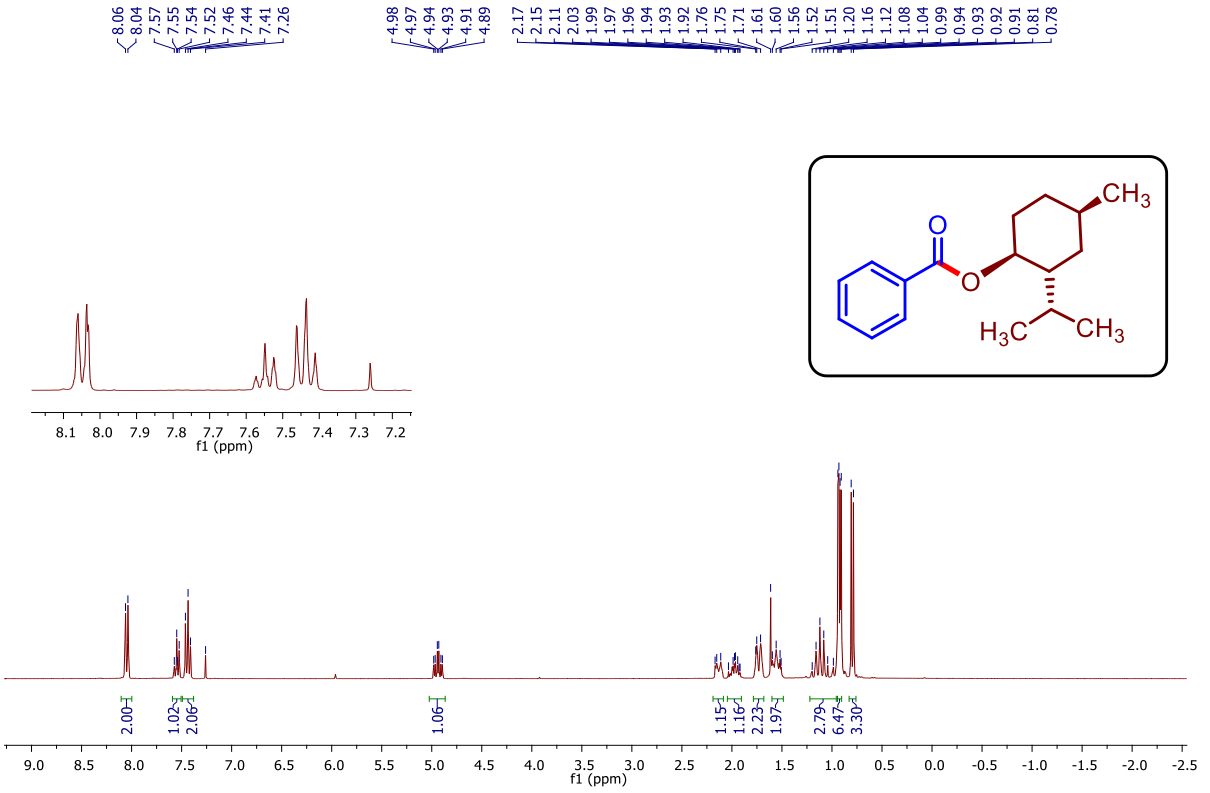
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5c



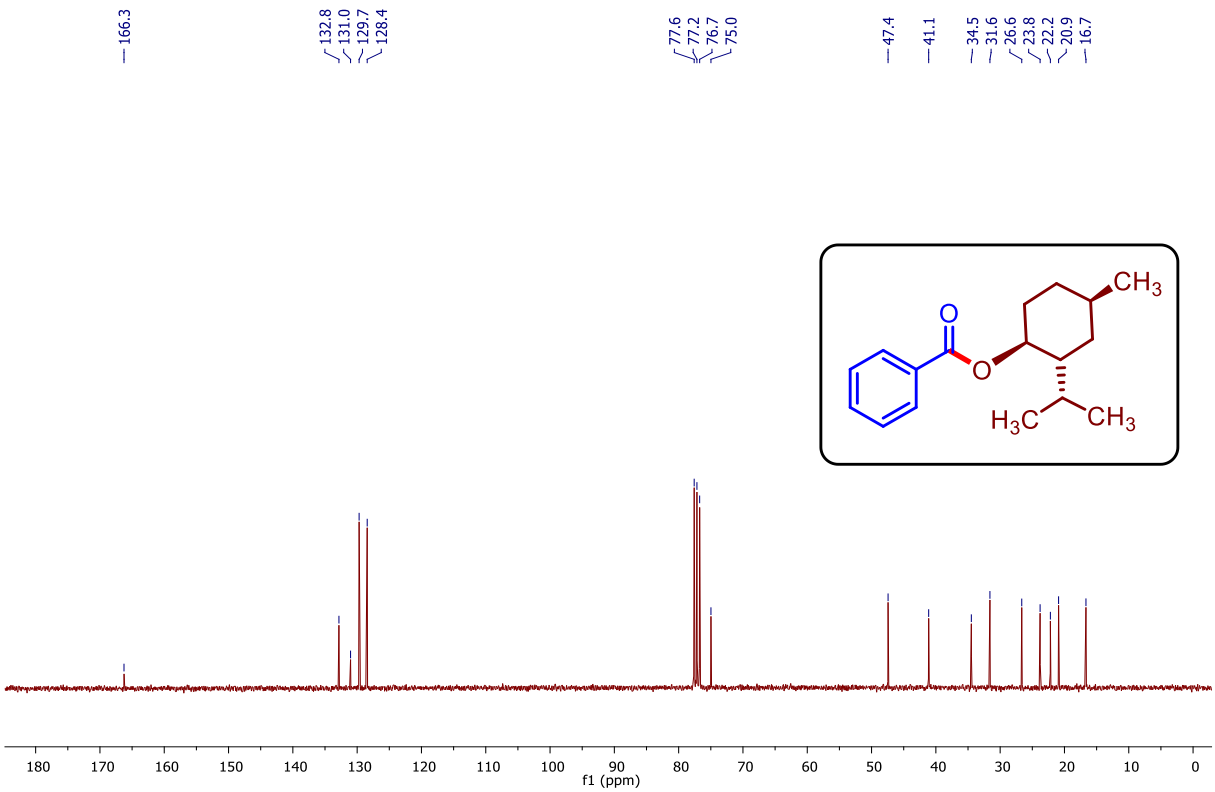
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5d



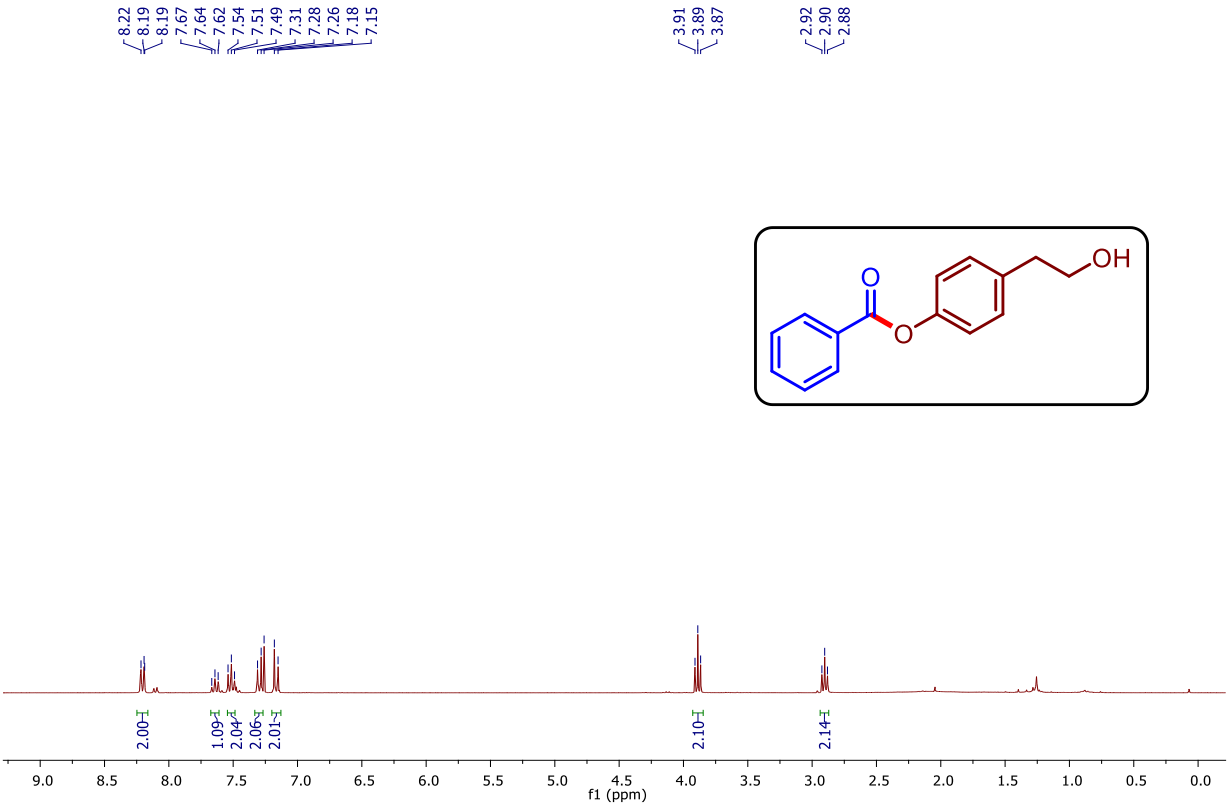
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5d



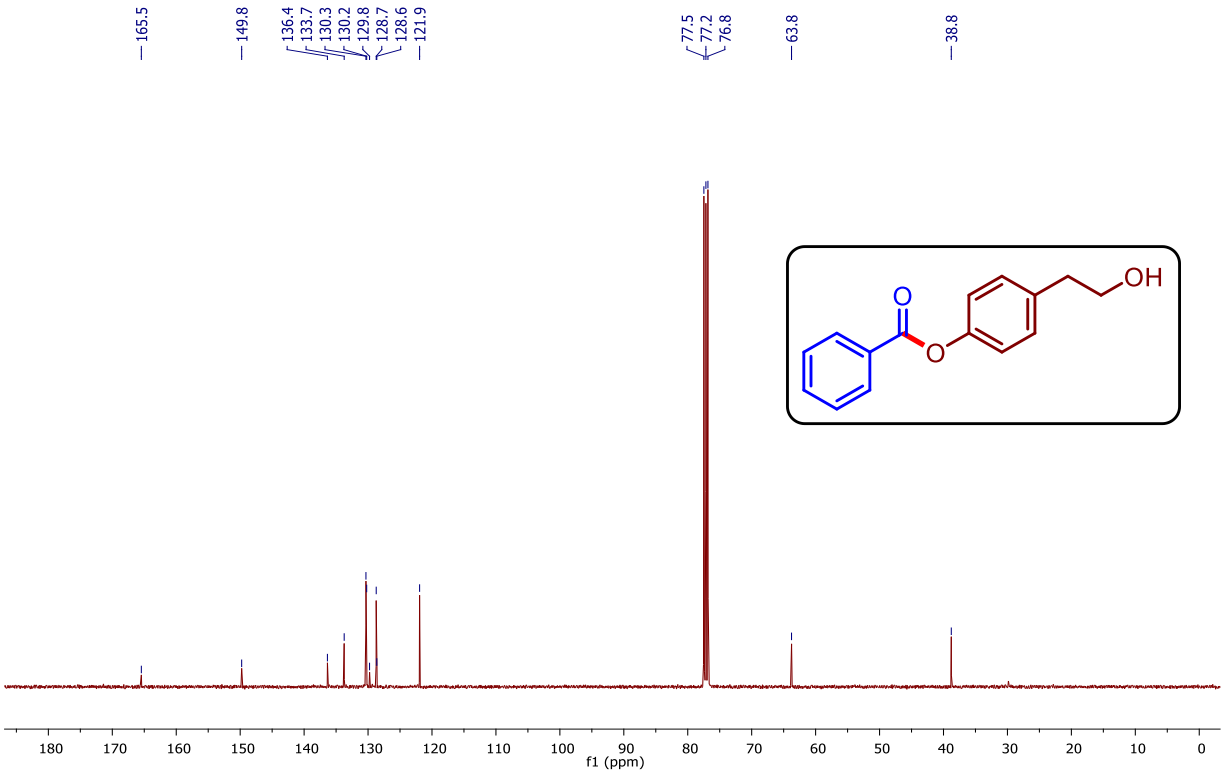
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5e



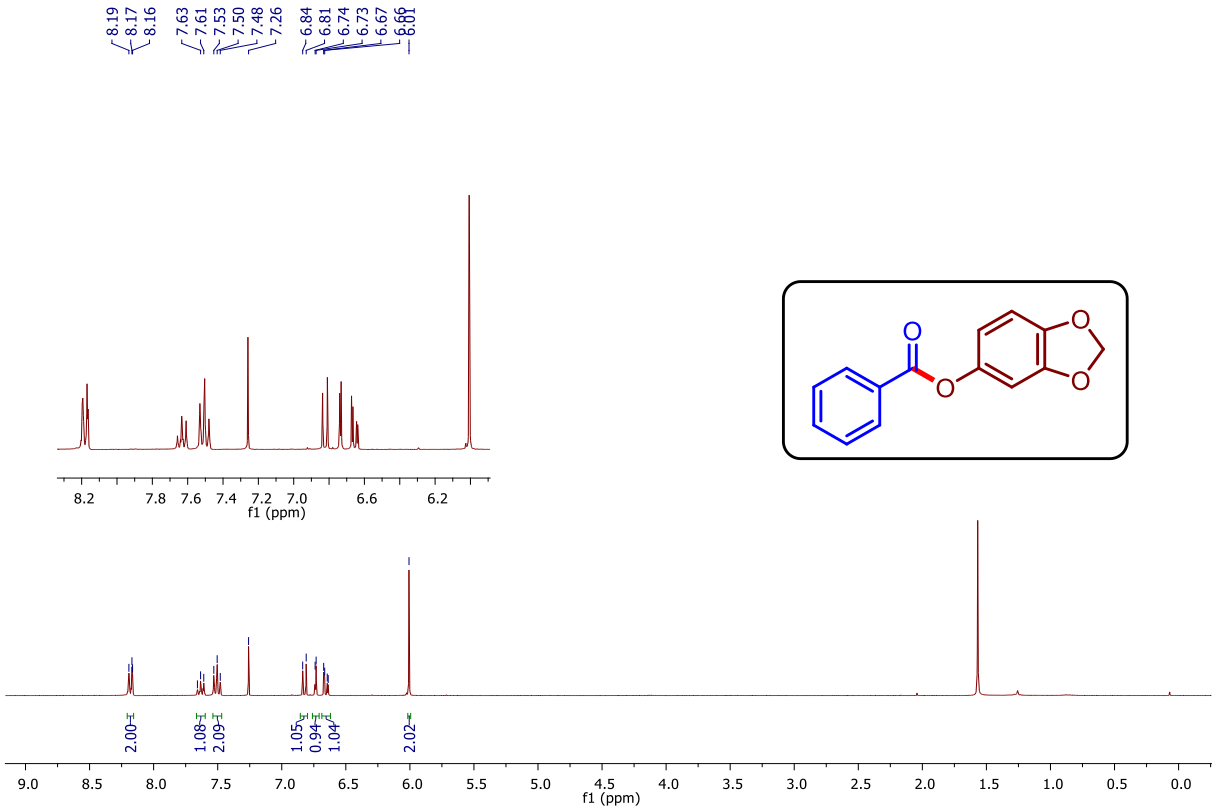
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5e



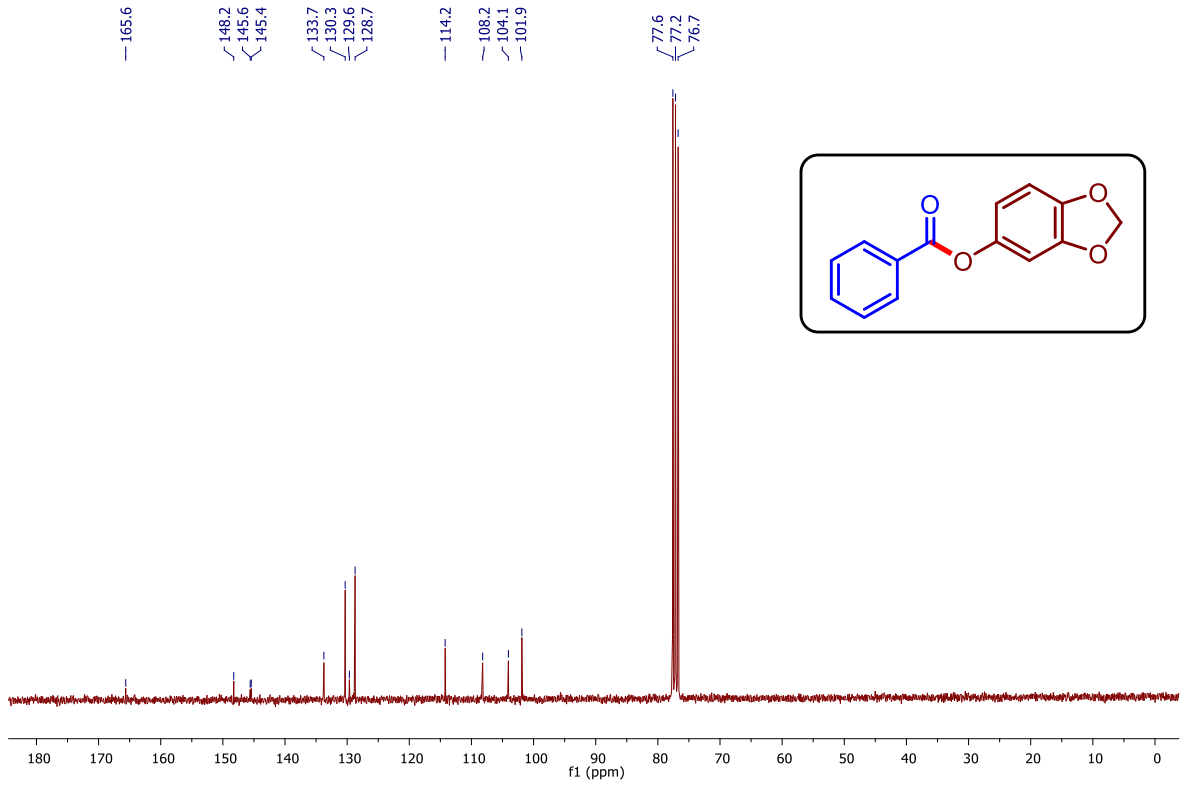
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 7f



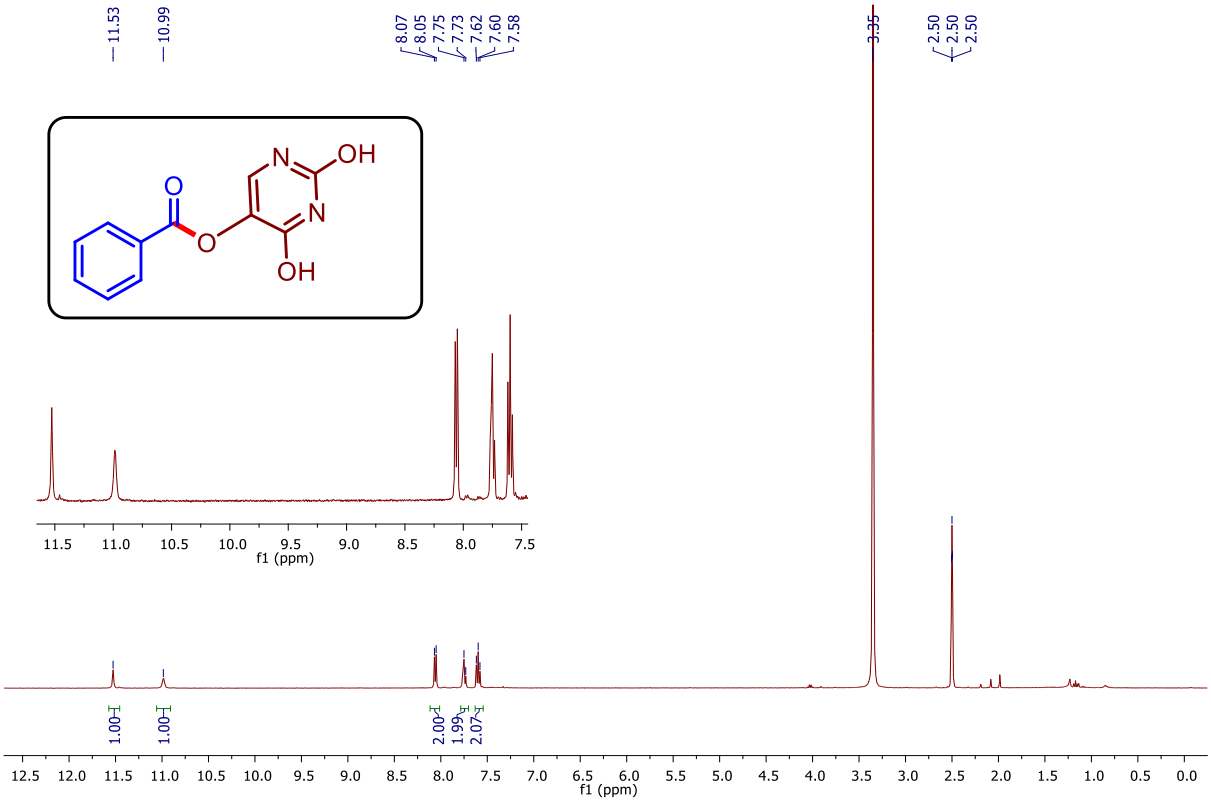
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 7f



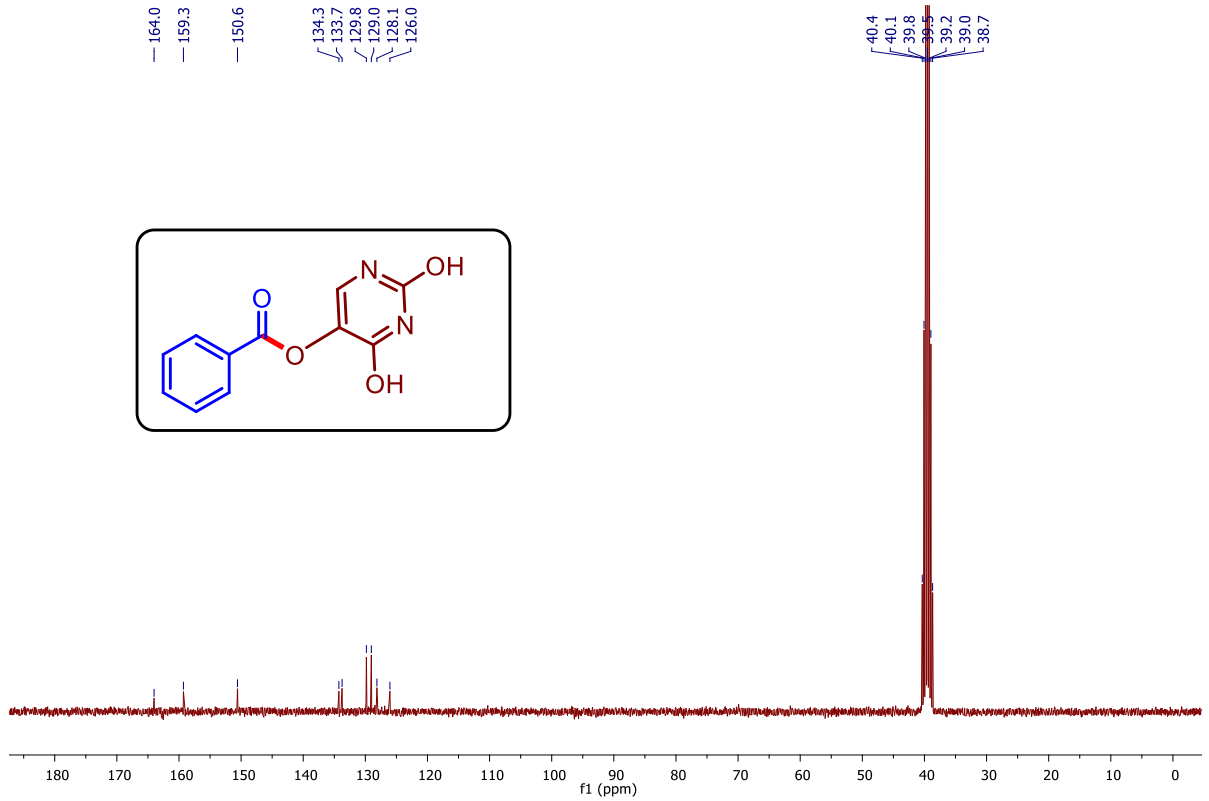
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5g



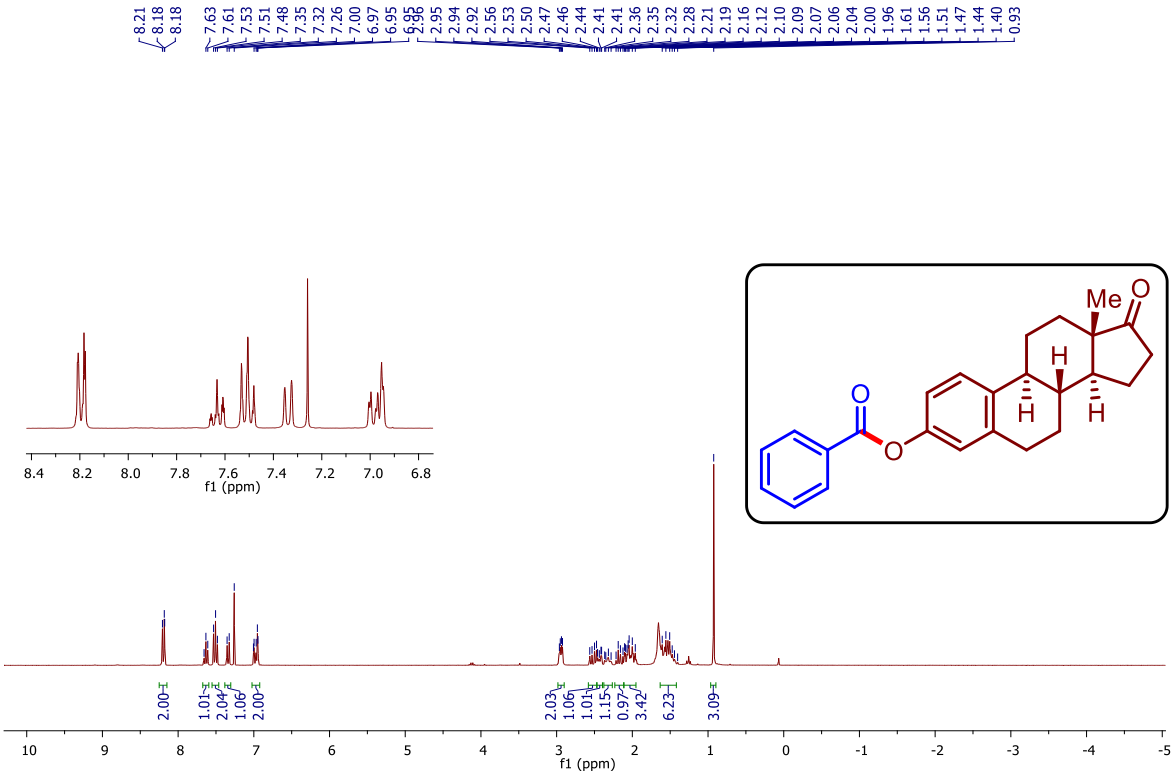
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5g



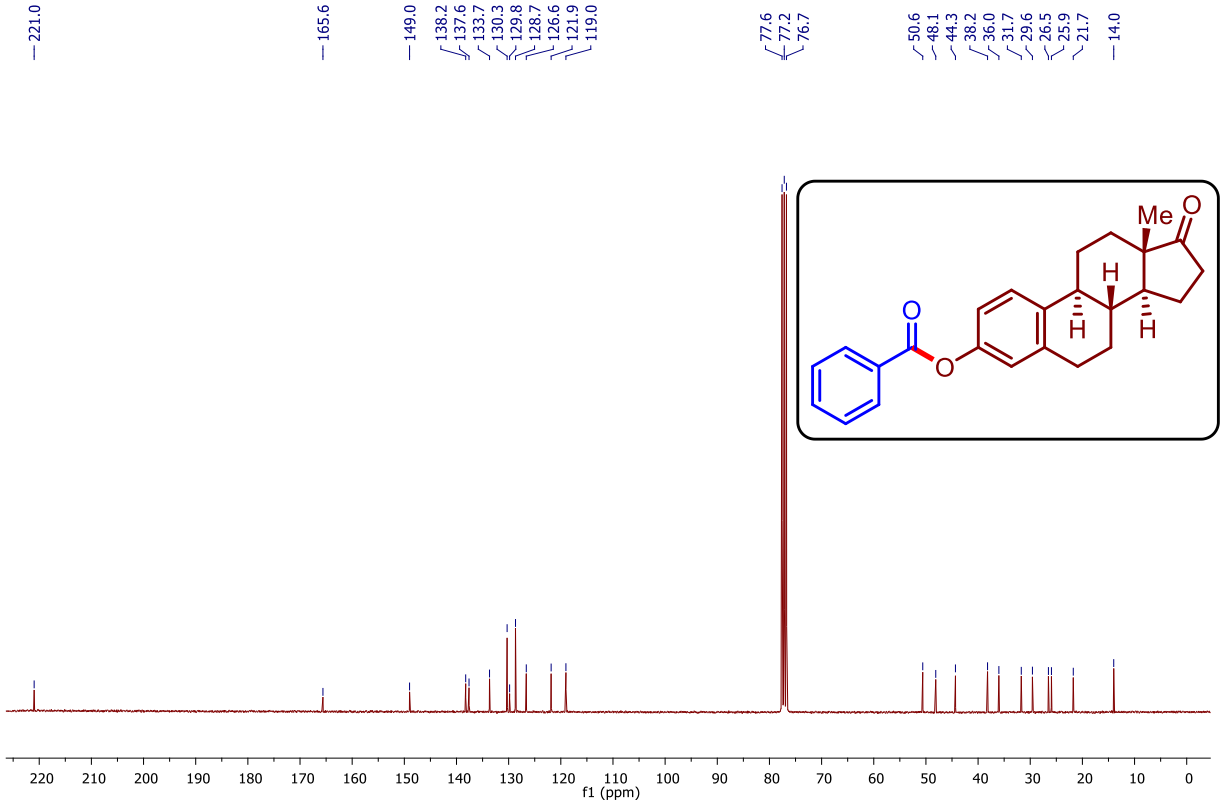
^{1}H NMR (400 MHz, DMSO-d6, 298 K) of 5h



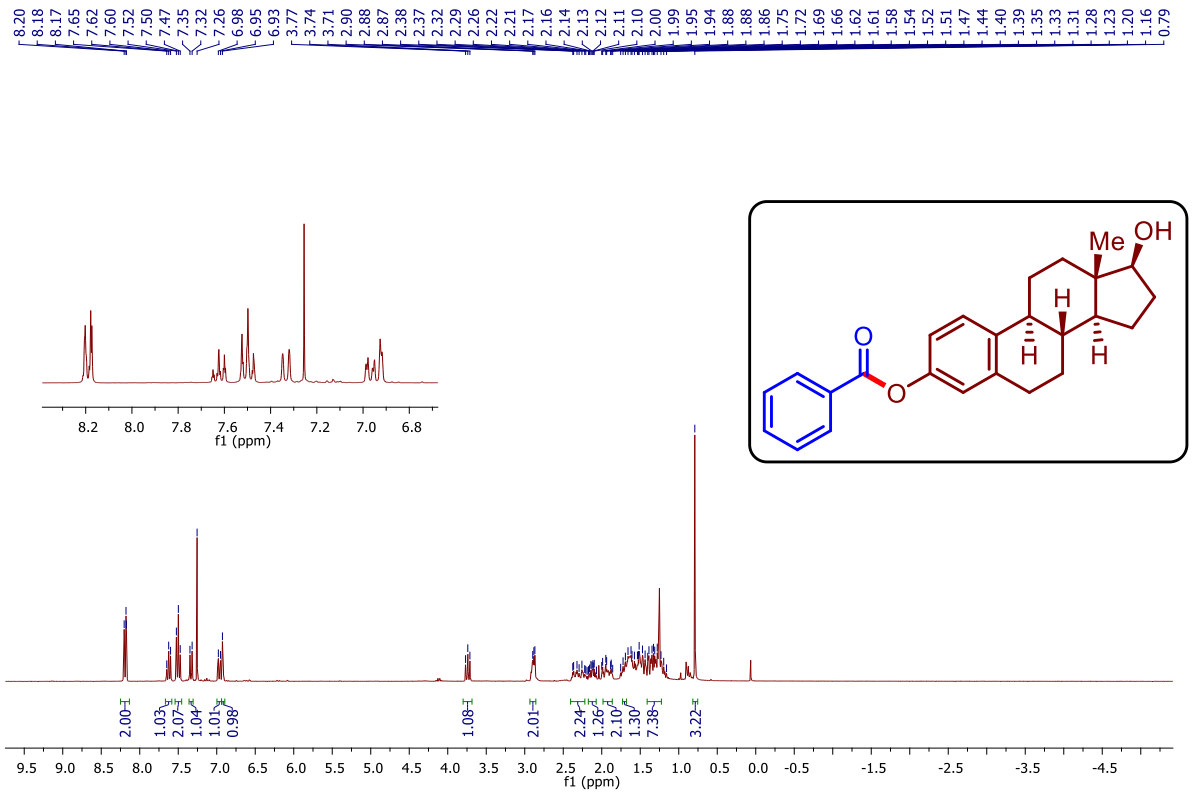
^{13}C NMR (75 MHz, DMSO-d6, 298 K) of 5h



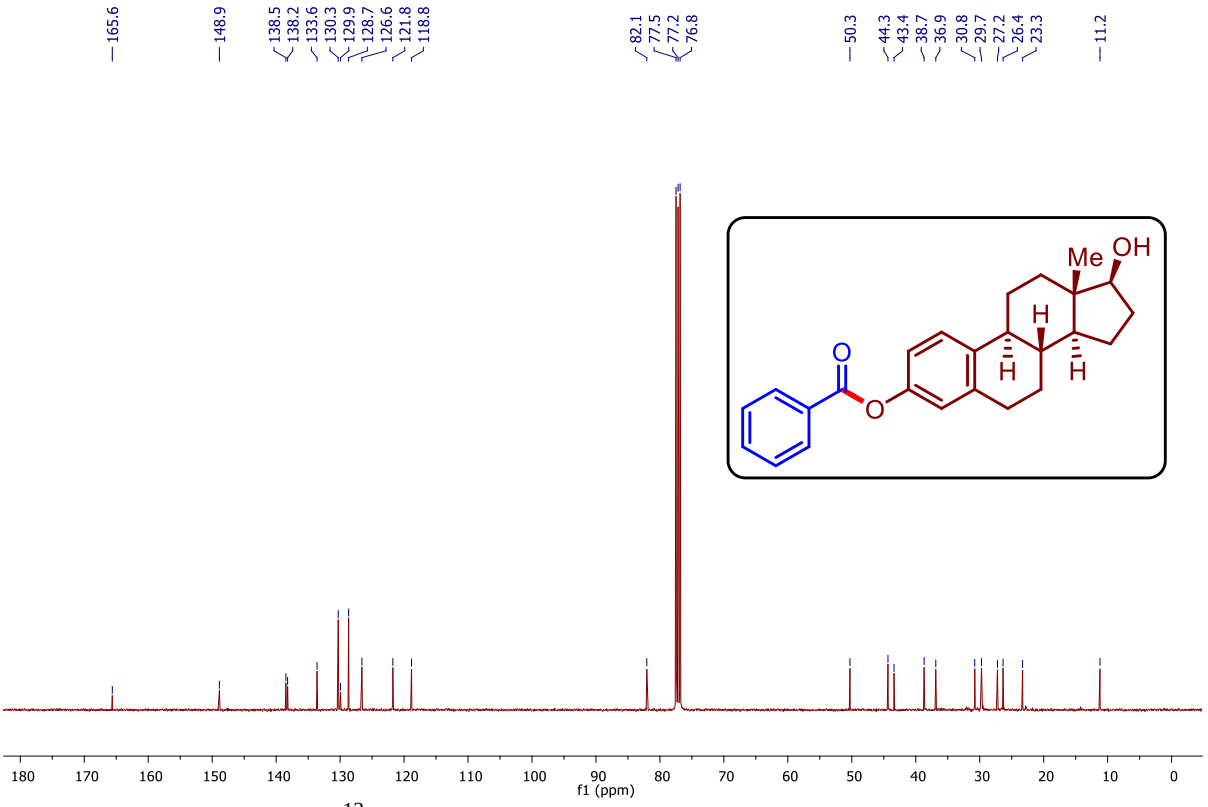
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5i



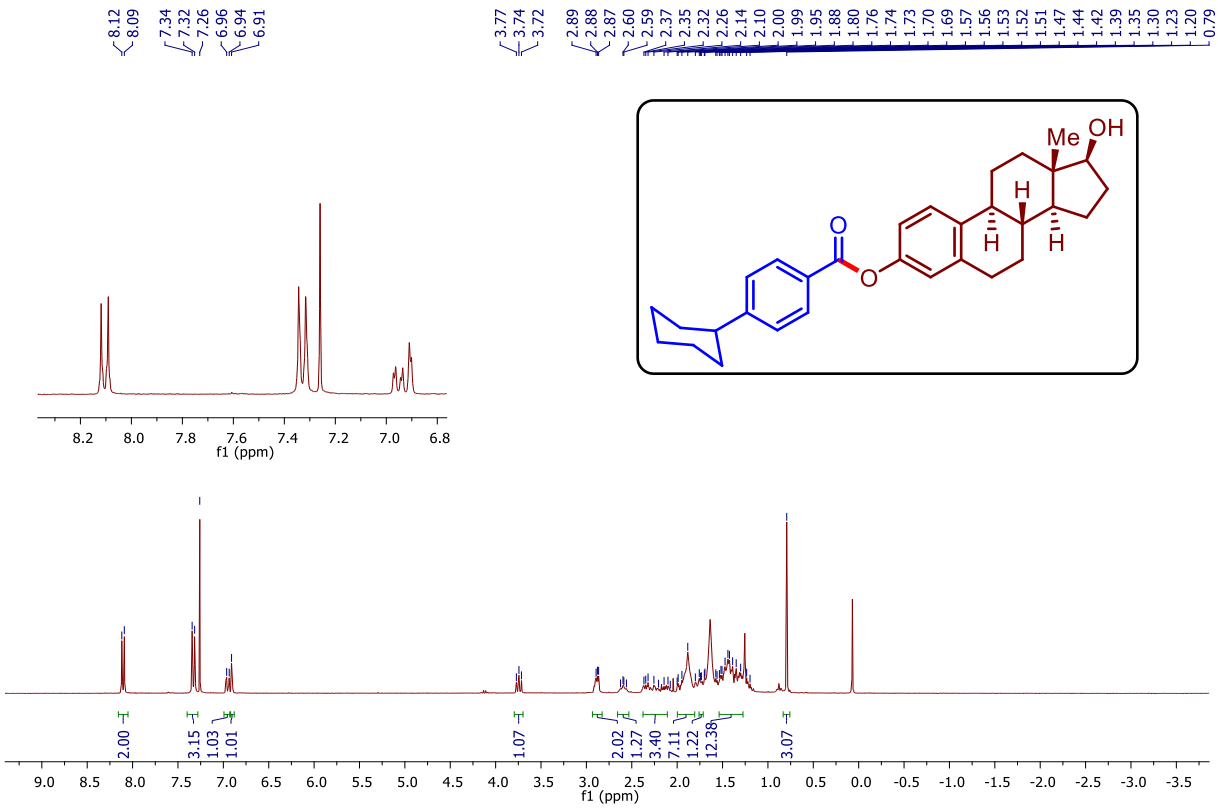
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5i



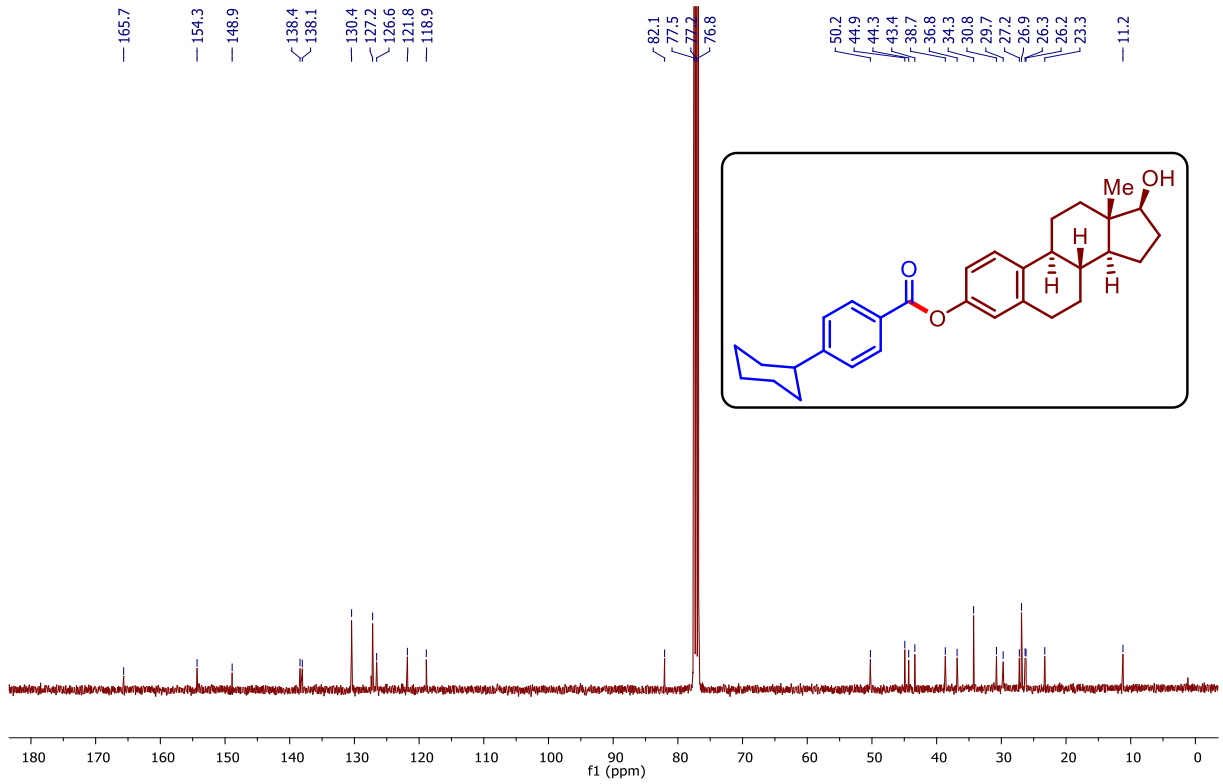
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5j



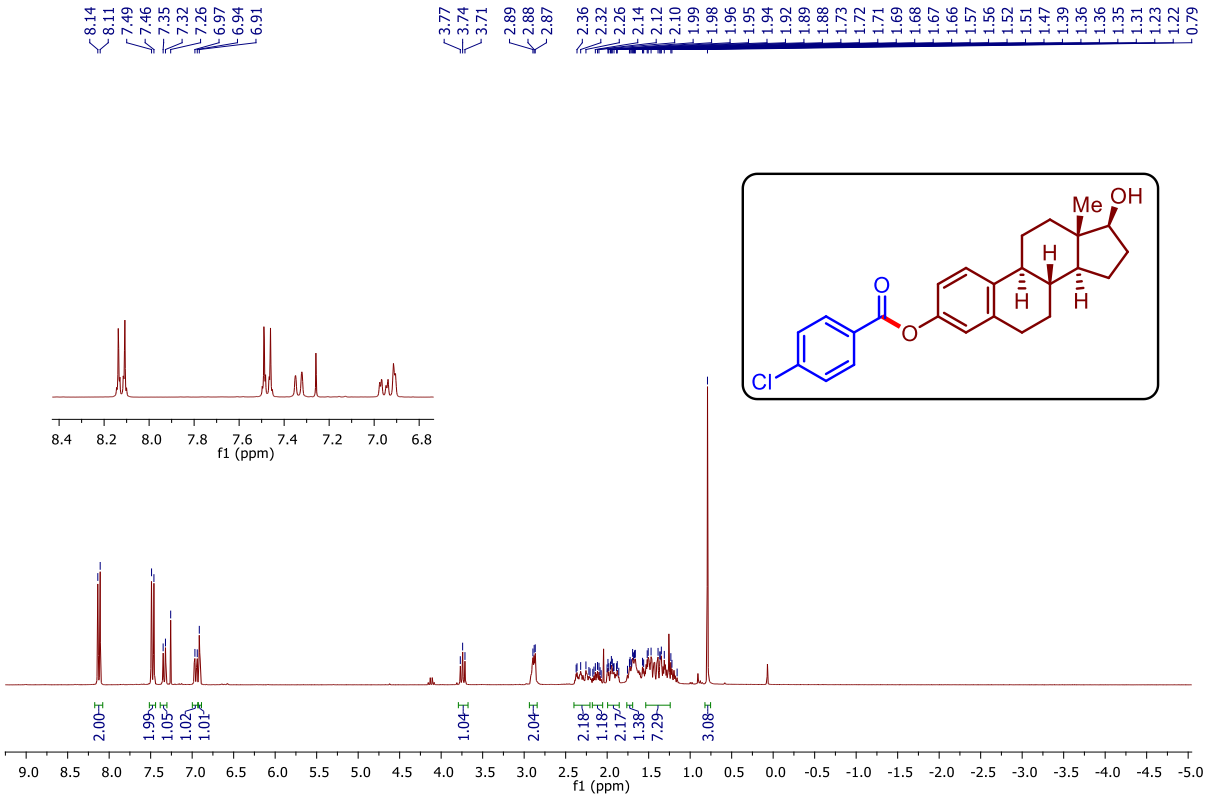
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 5j



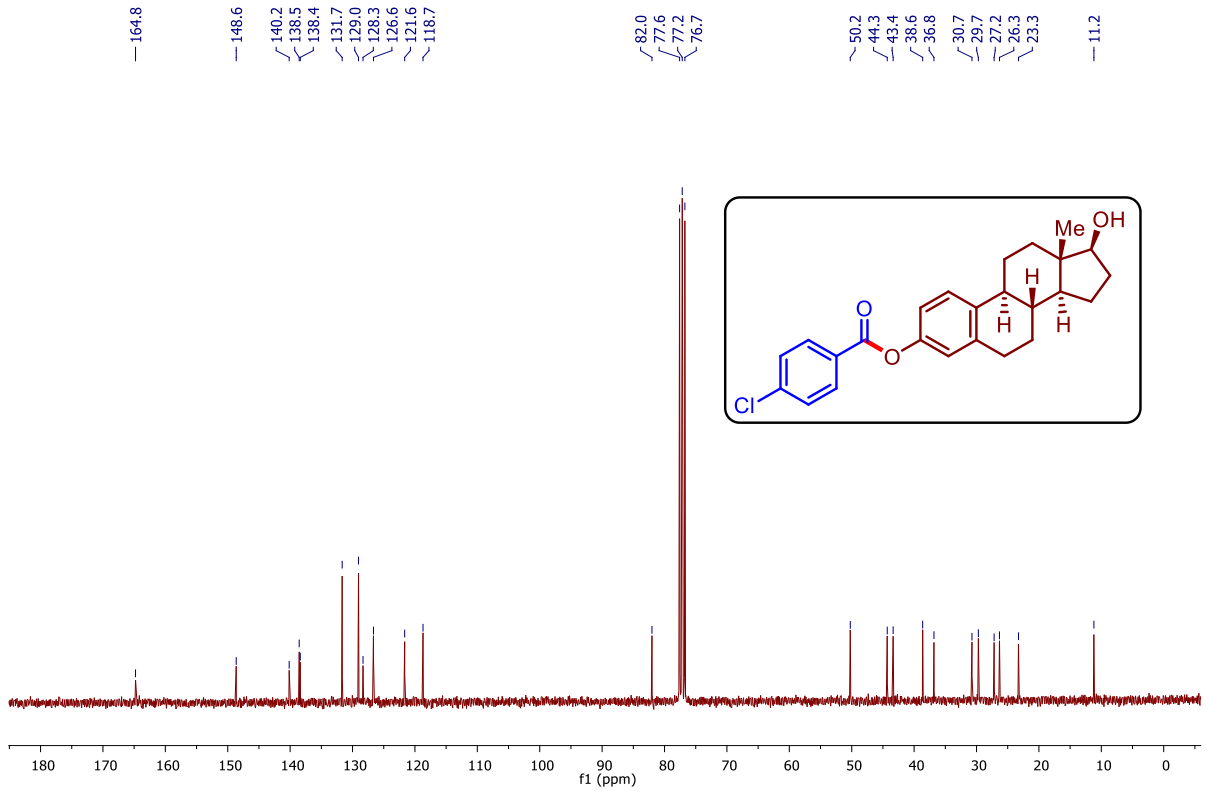
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5k



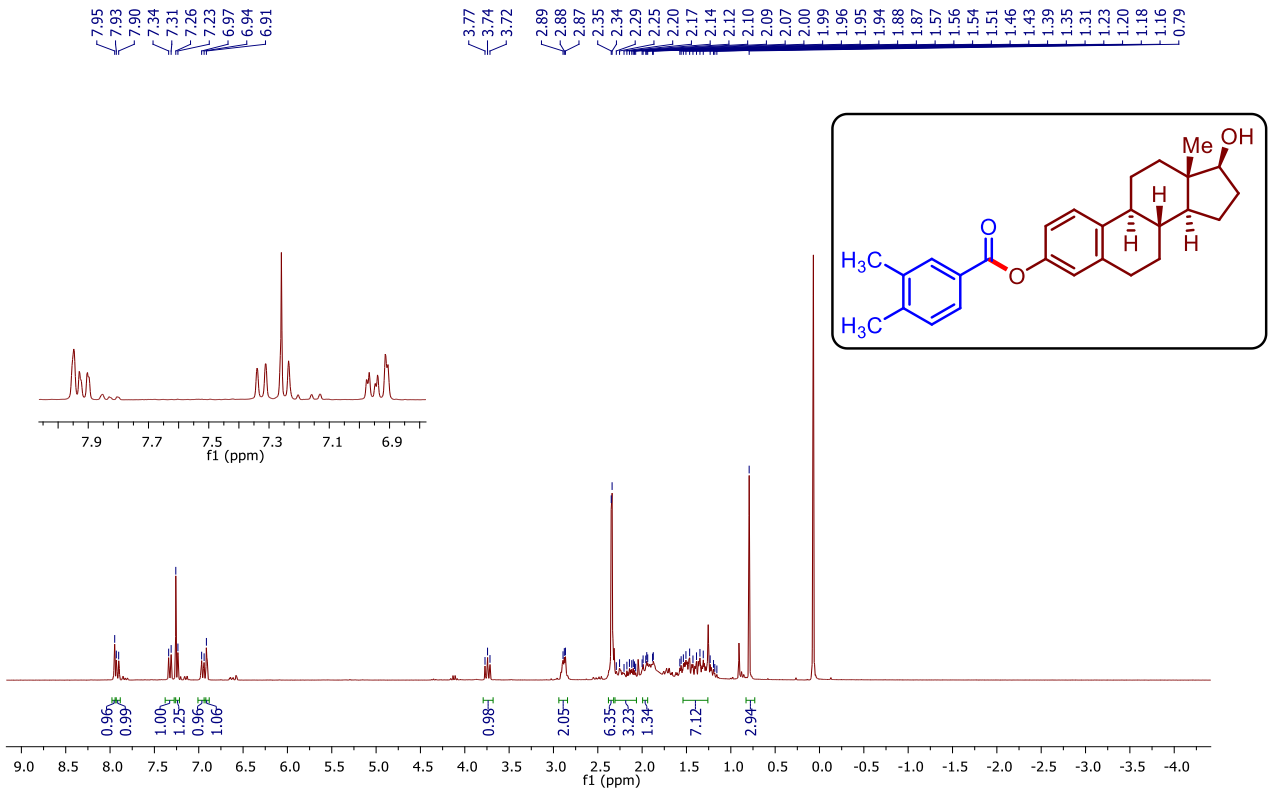
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 5k



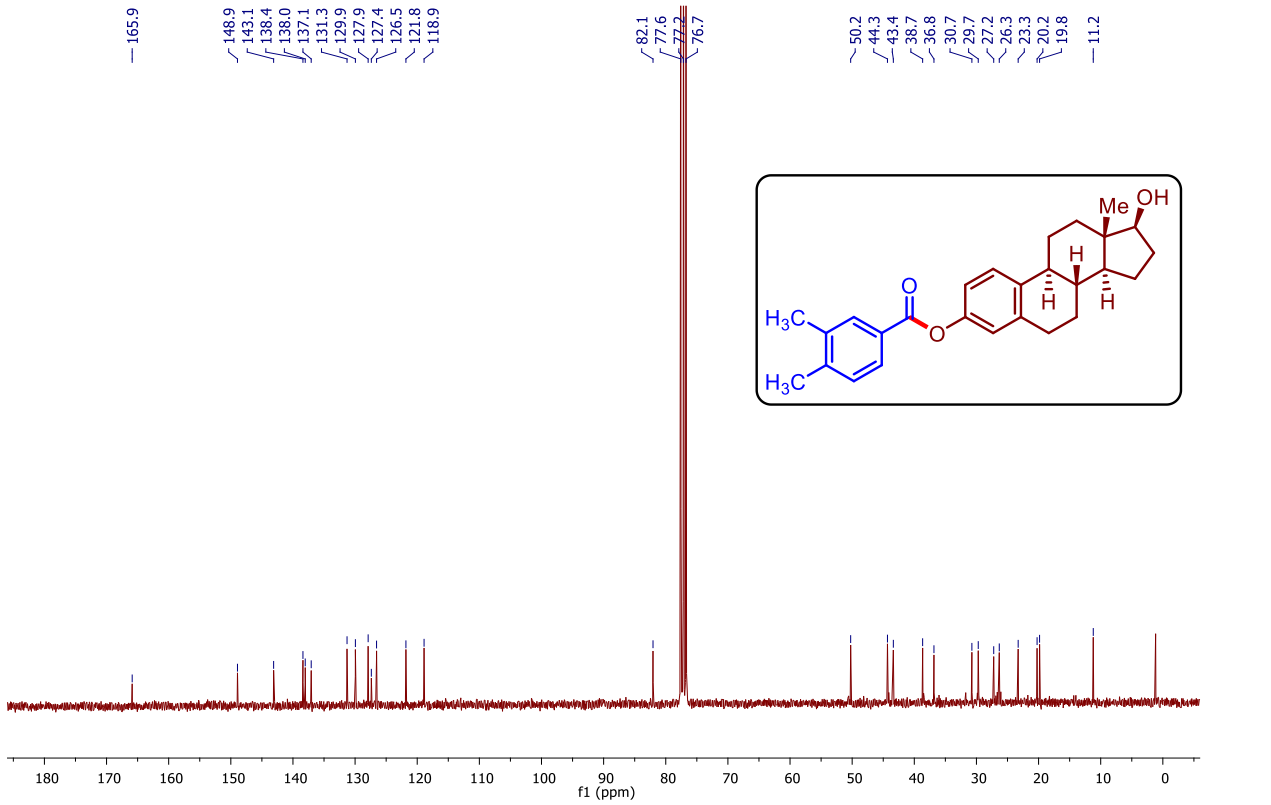
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5l



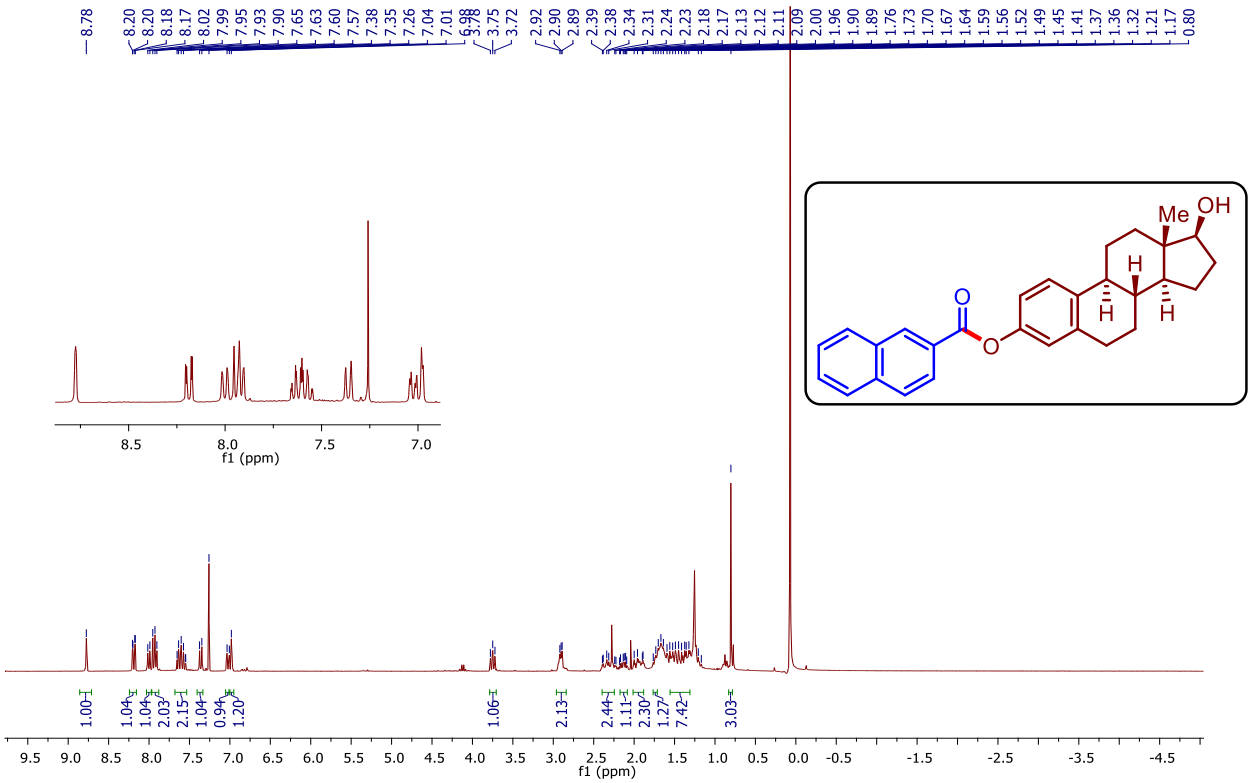
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5l



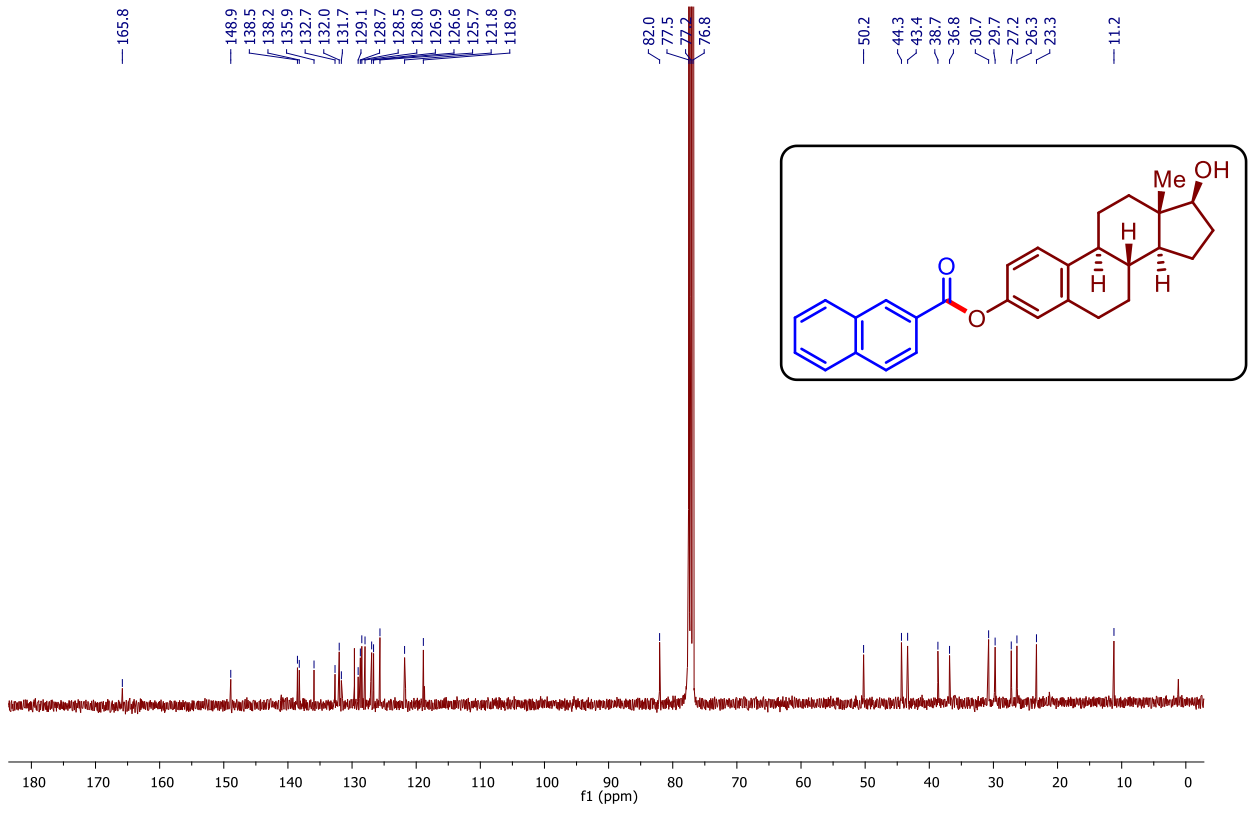
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5m



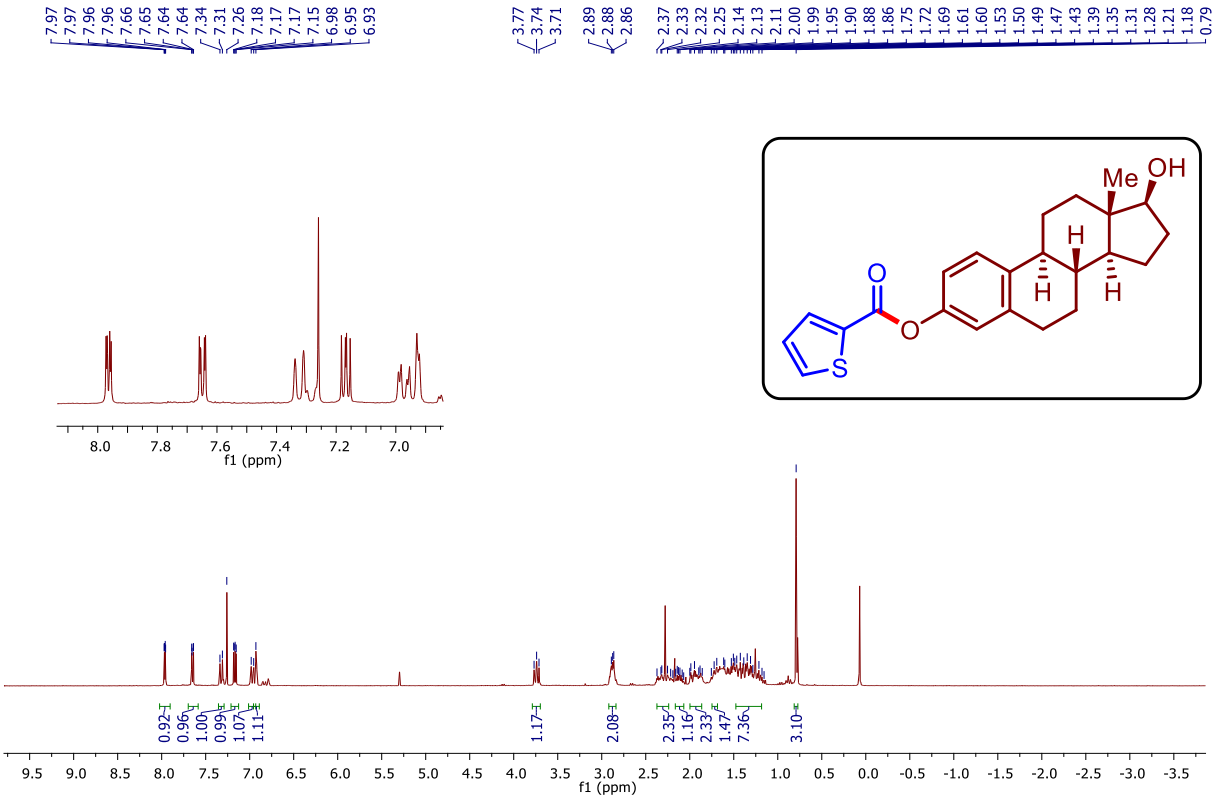
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5m



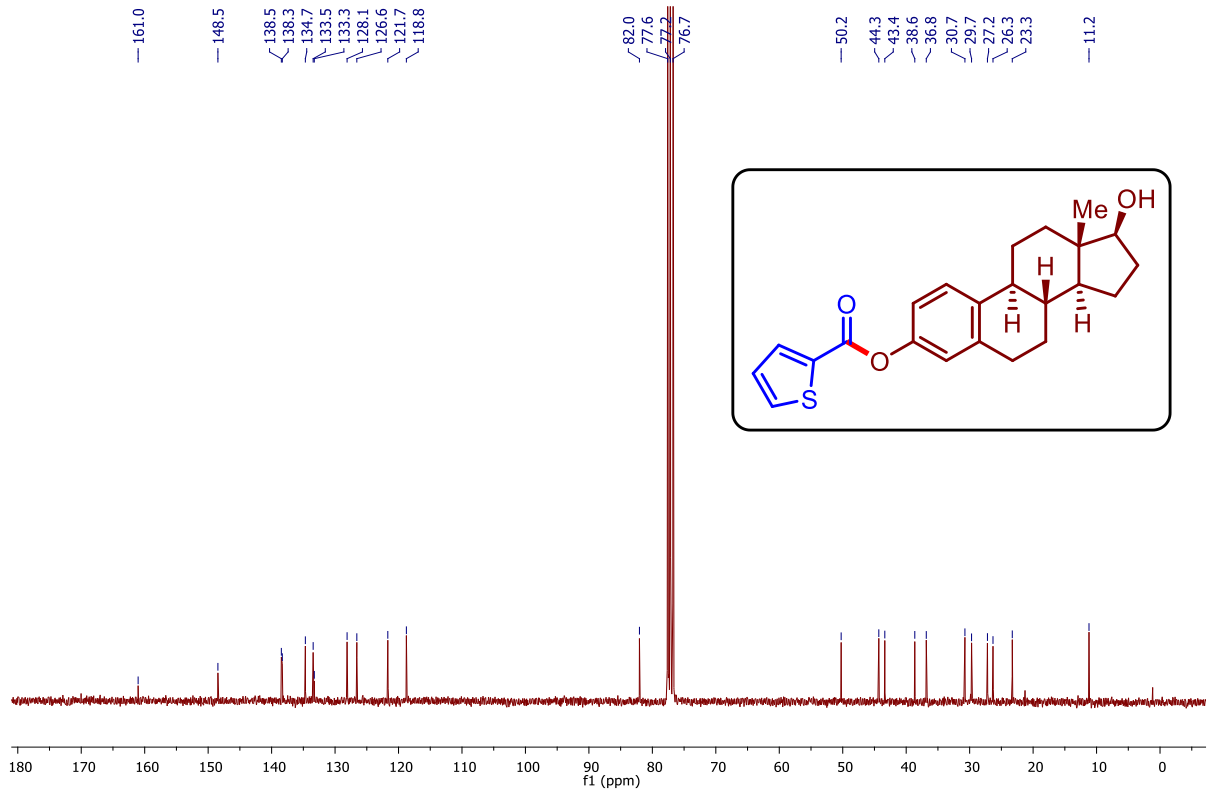
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5n



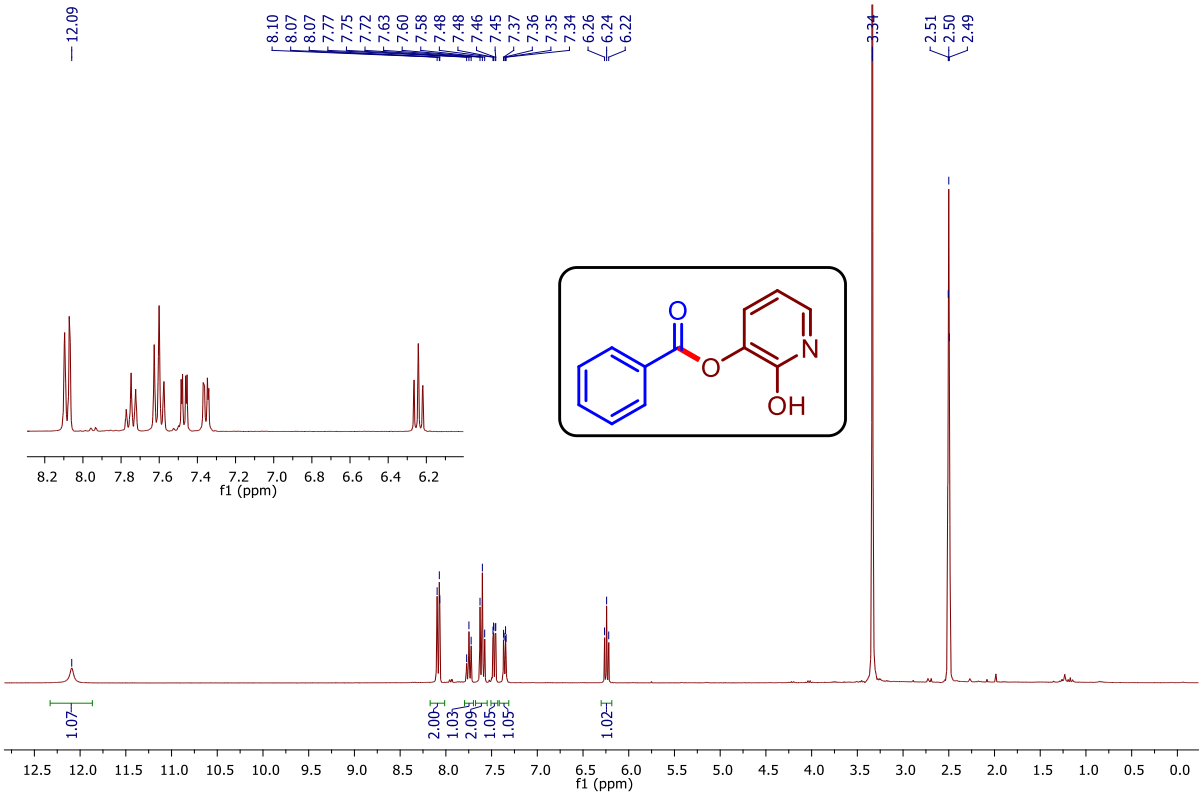
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of 5n



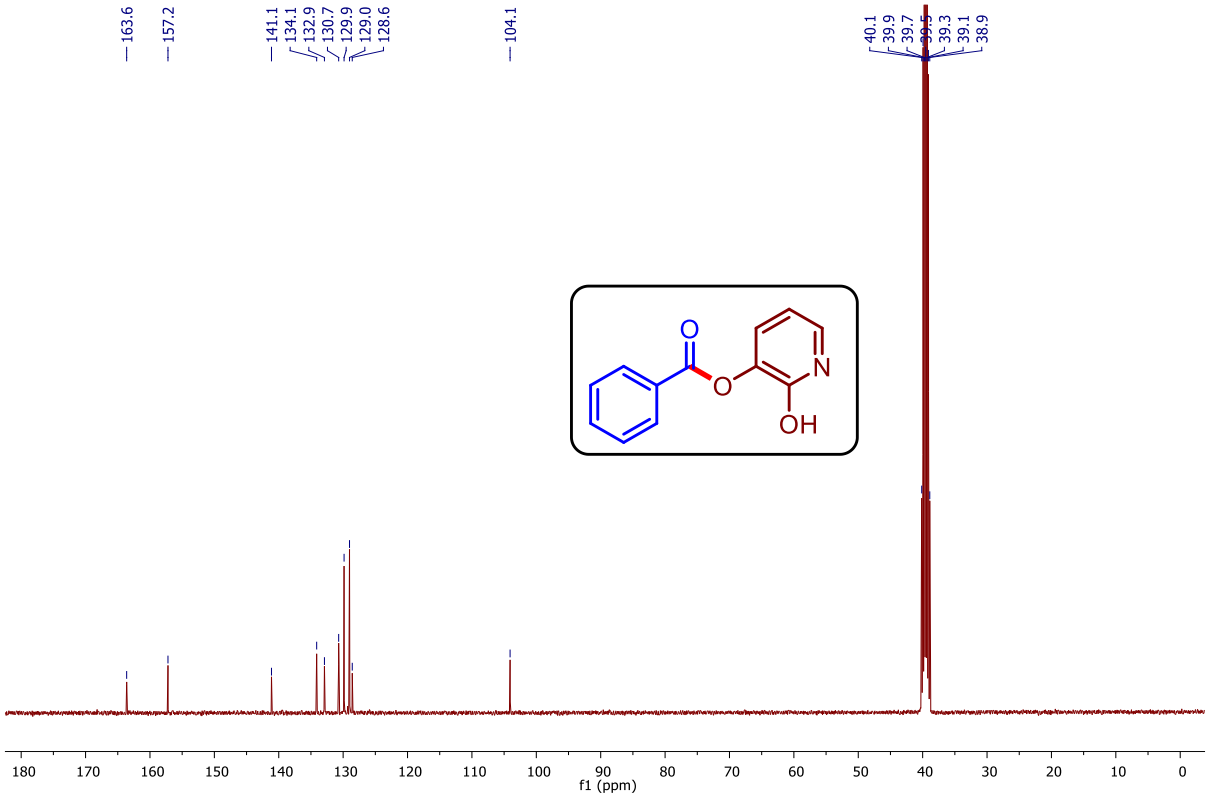
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 5o



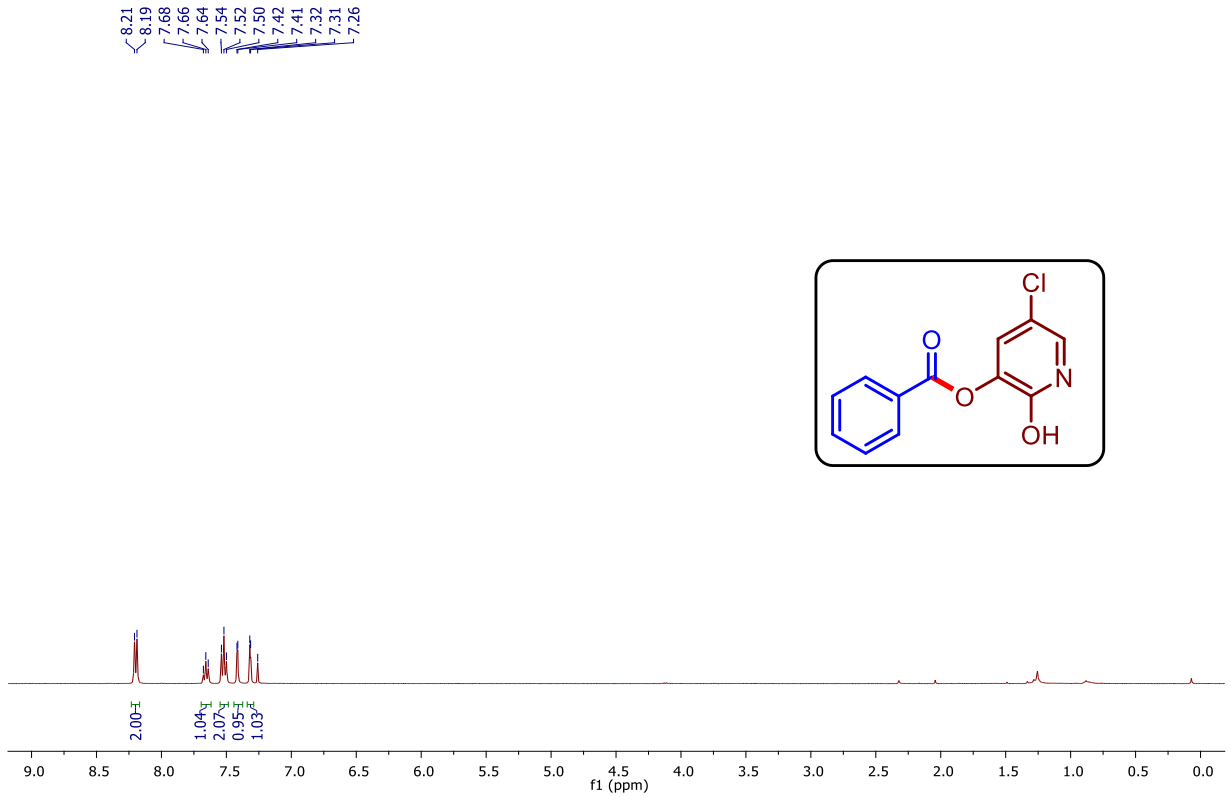
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 5o



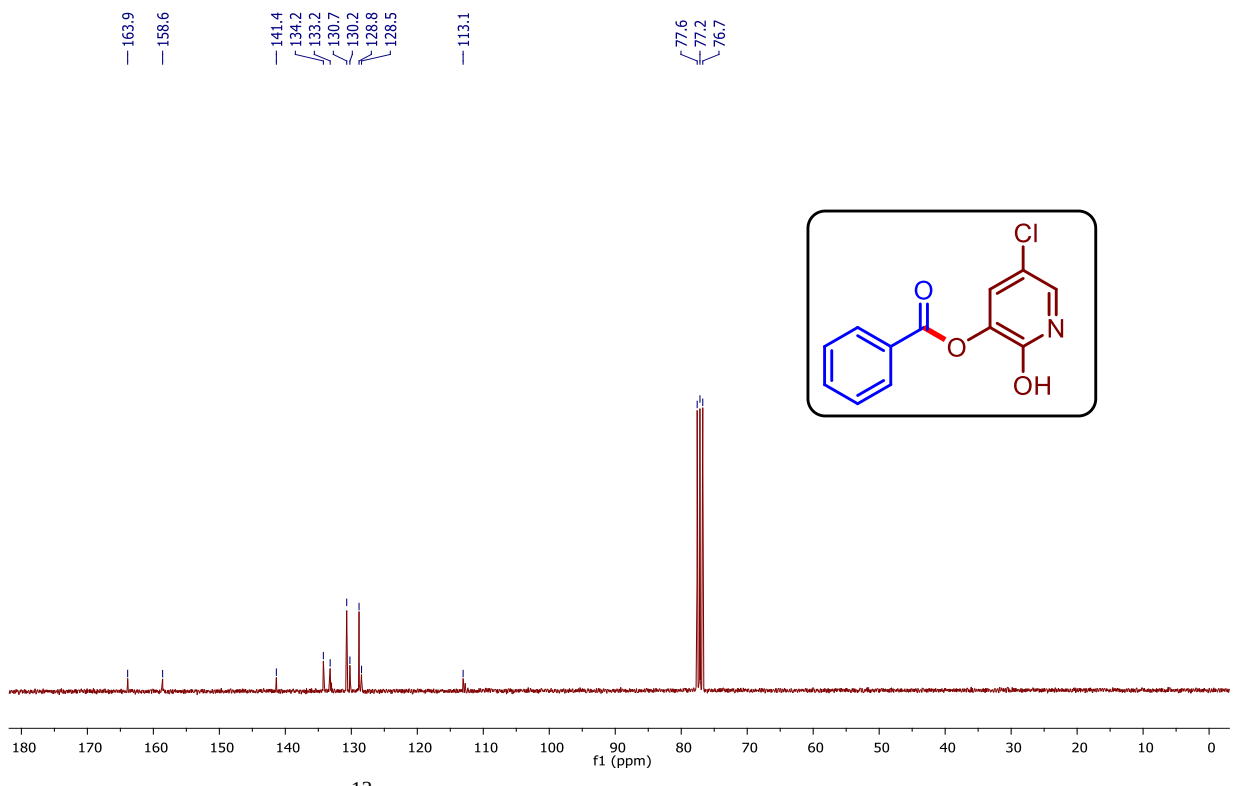
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7a



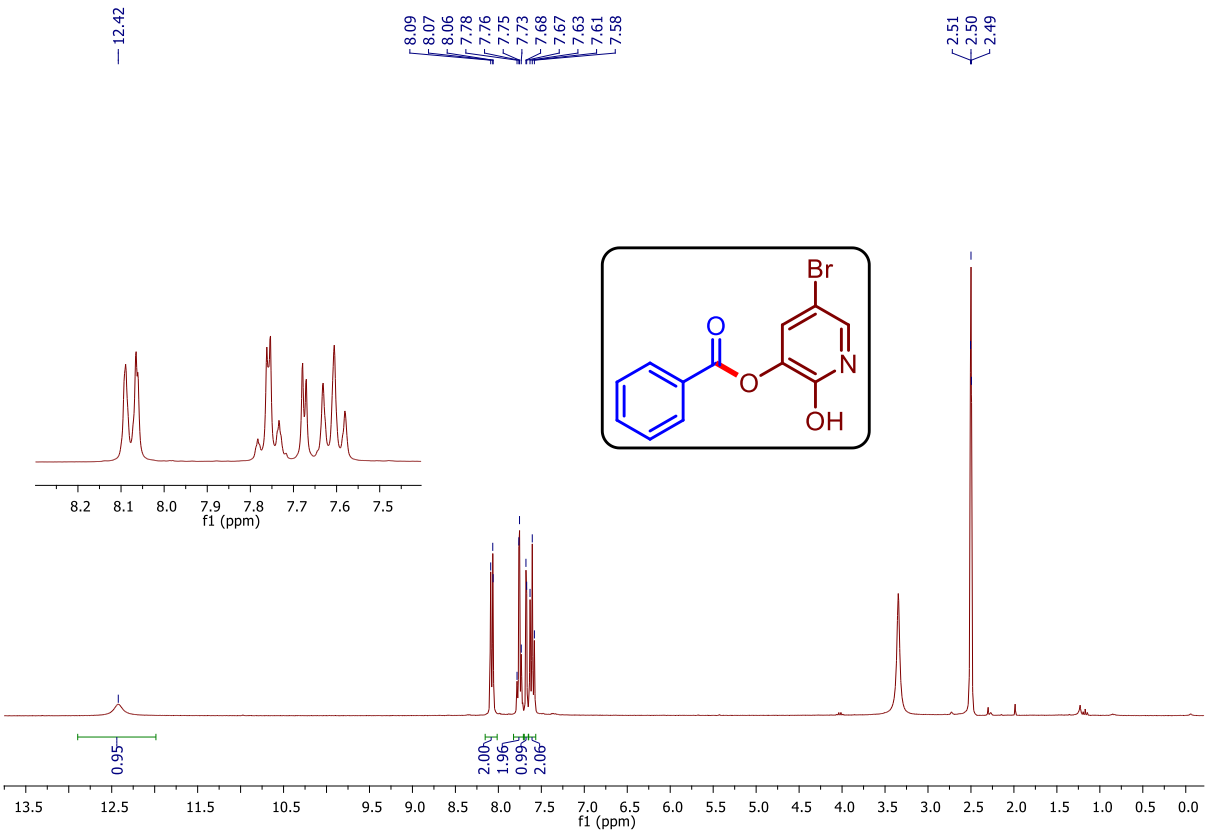
^{13}C NMR (101 MHz, DMSO-d_6, 298 K) of 7a



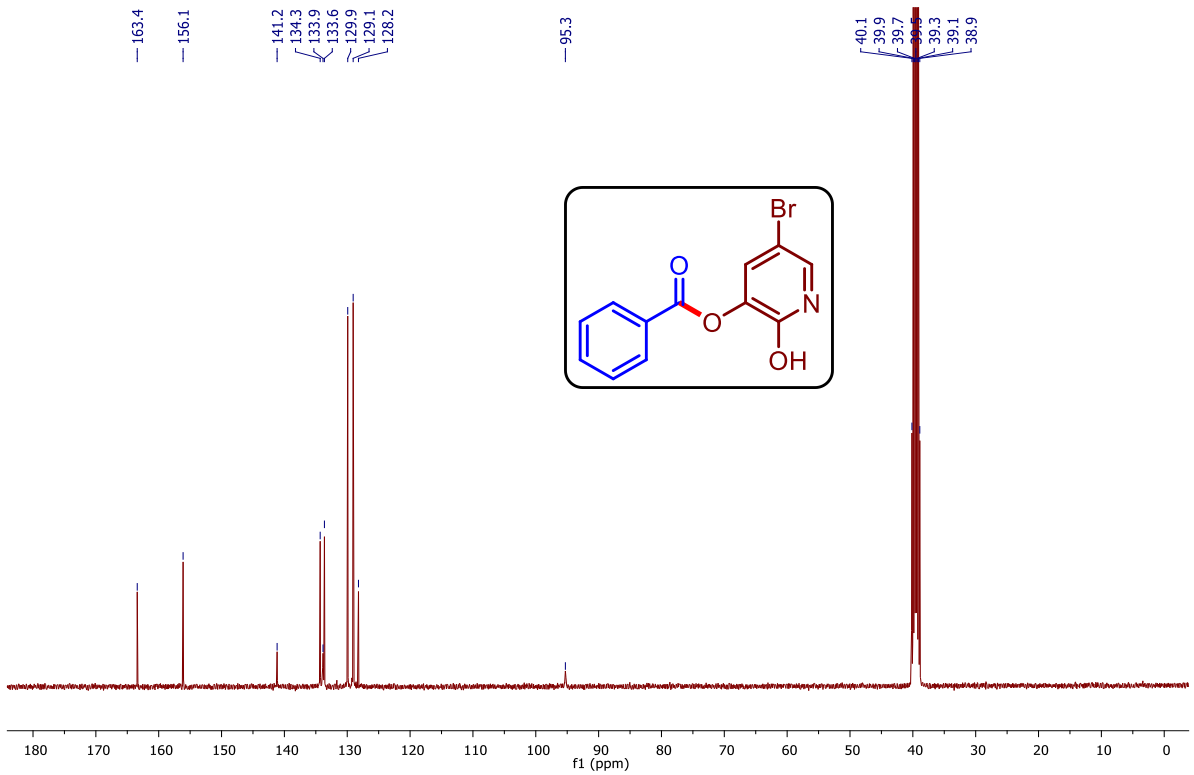
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 7b



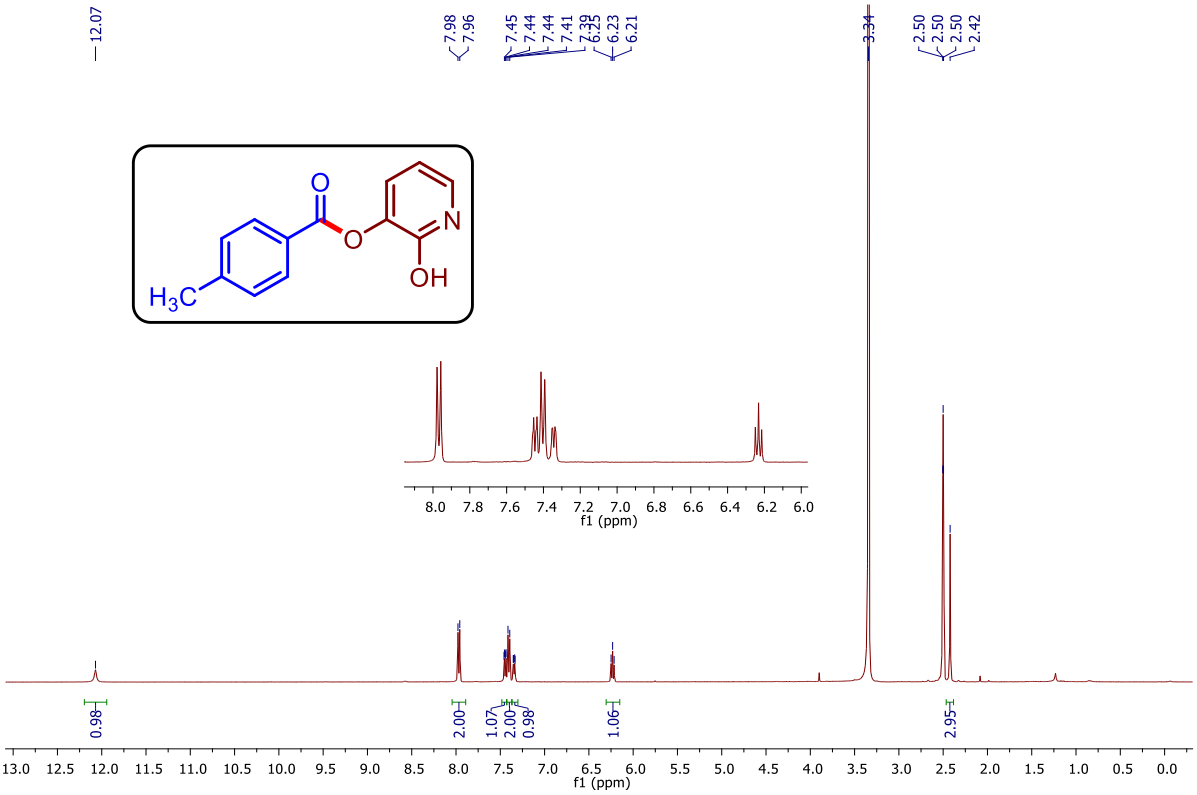
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 7b



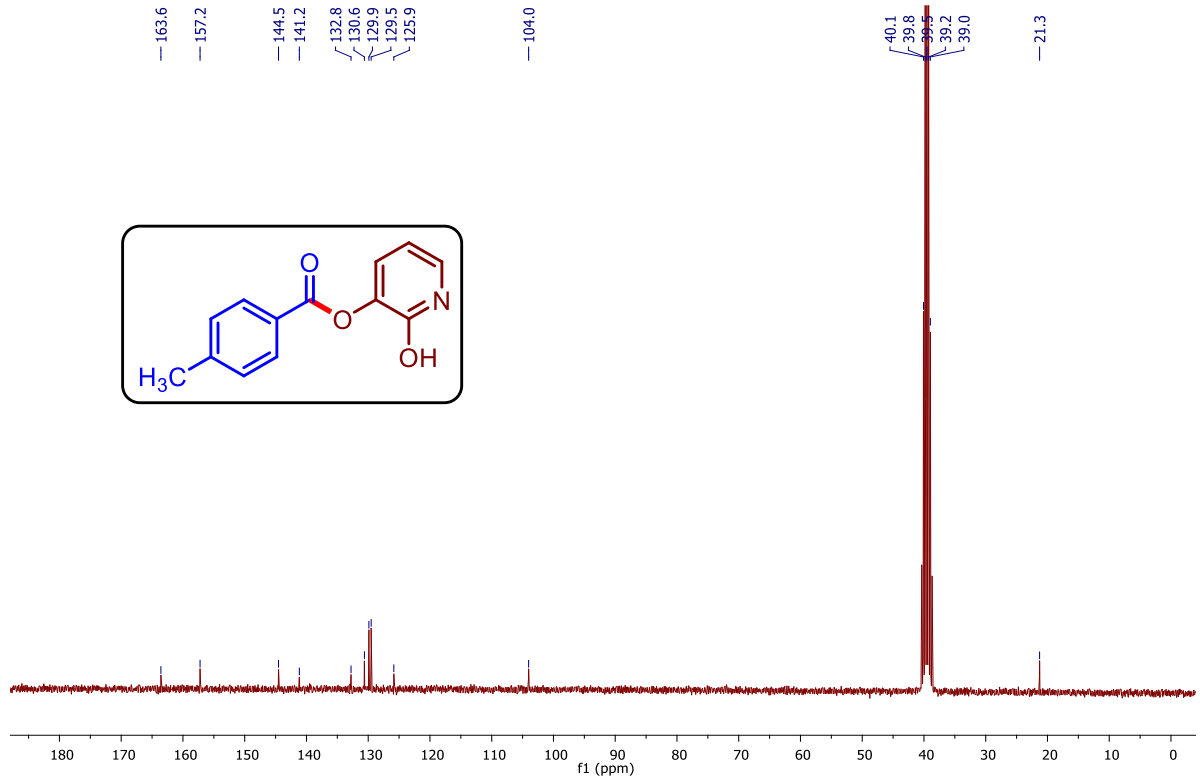
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7c



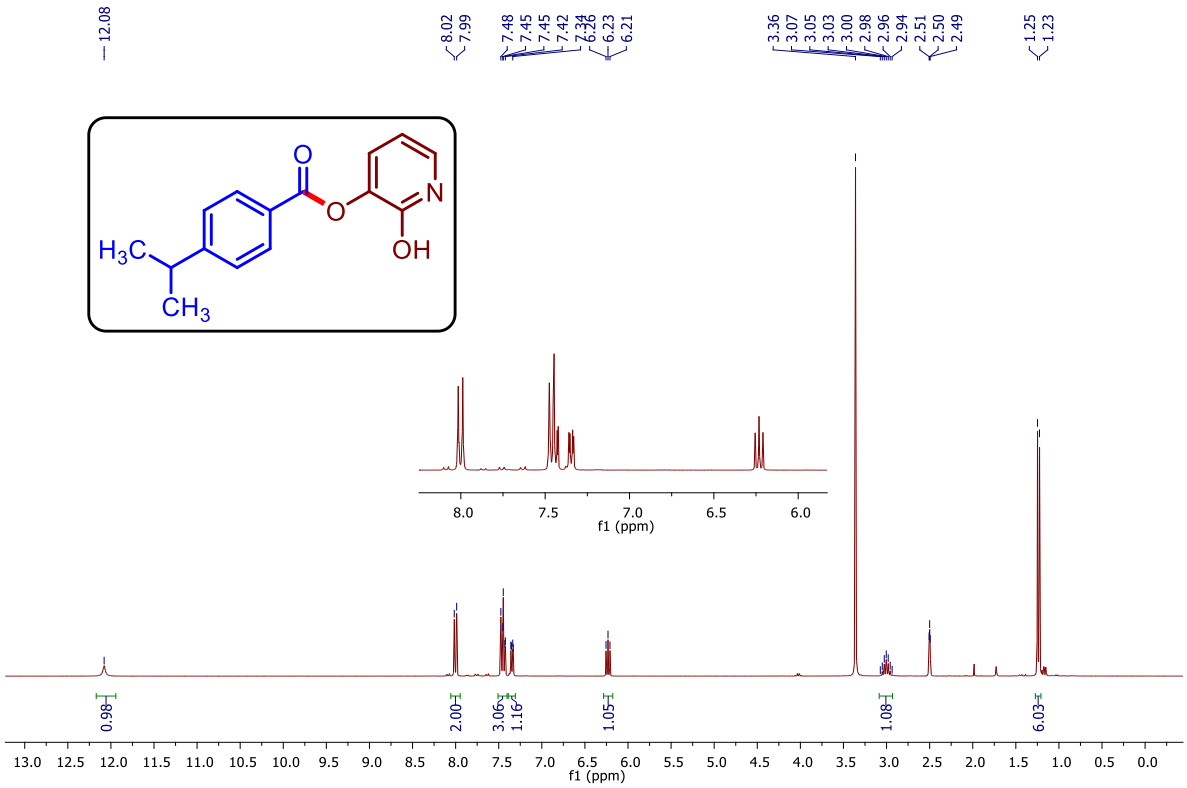
^{13}C NMR (101 MHz, DMSO-d_6, 298 K) of 7c



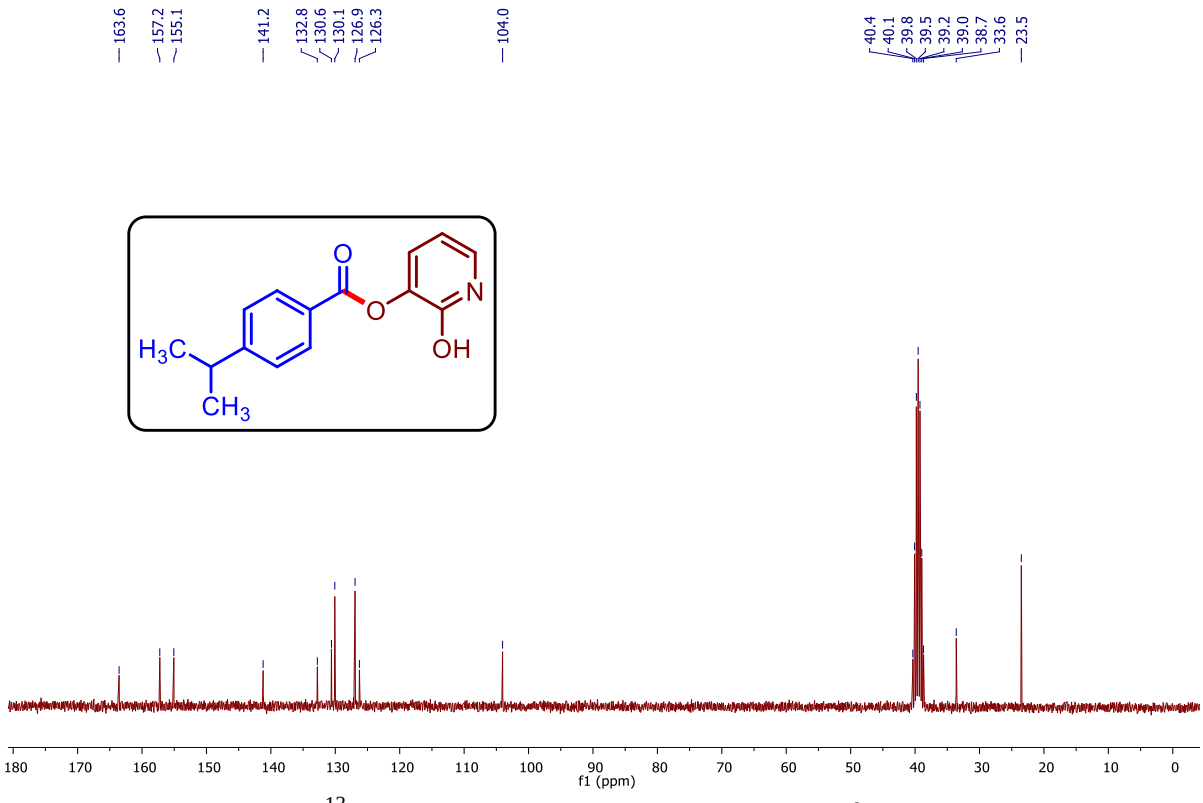
^{1}H NMR (400 MHz, DMSO-d_6, 298 K) of 7d



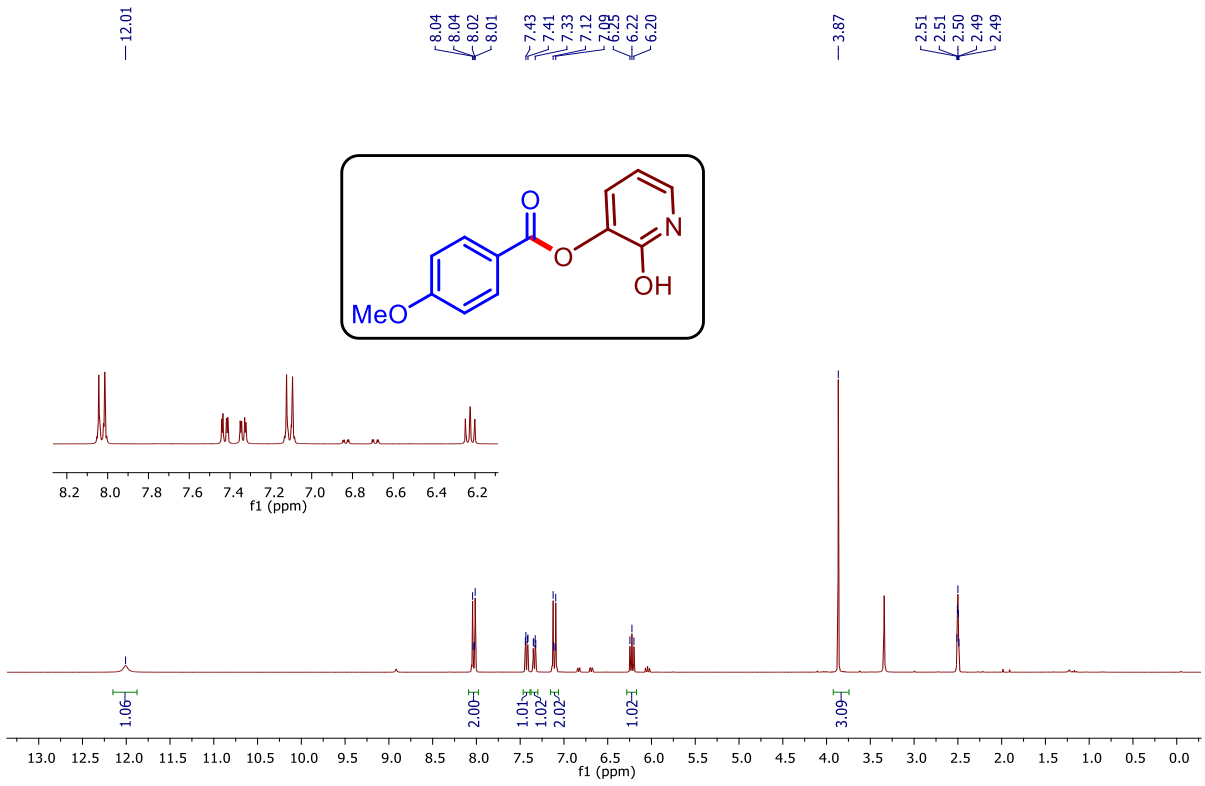
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7d



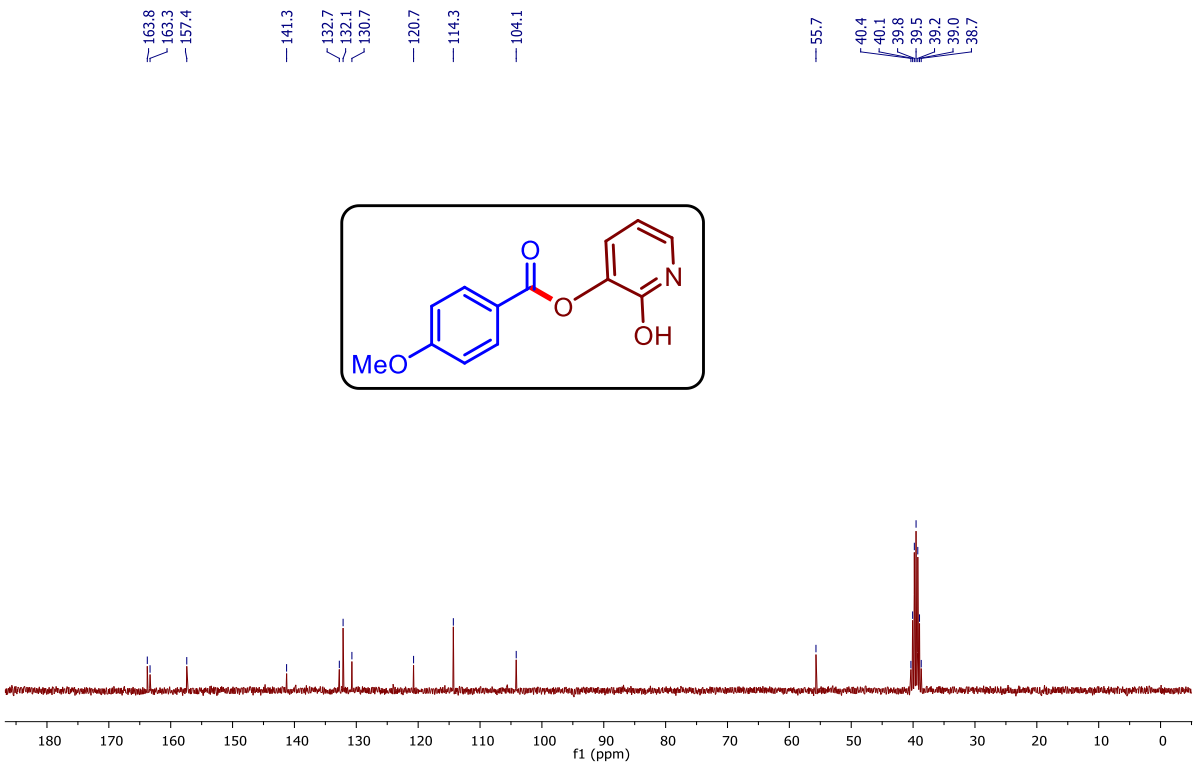
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7e



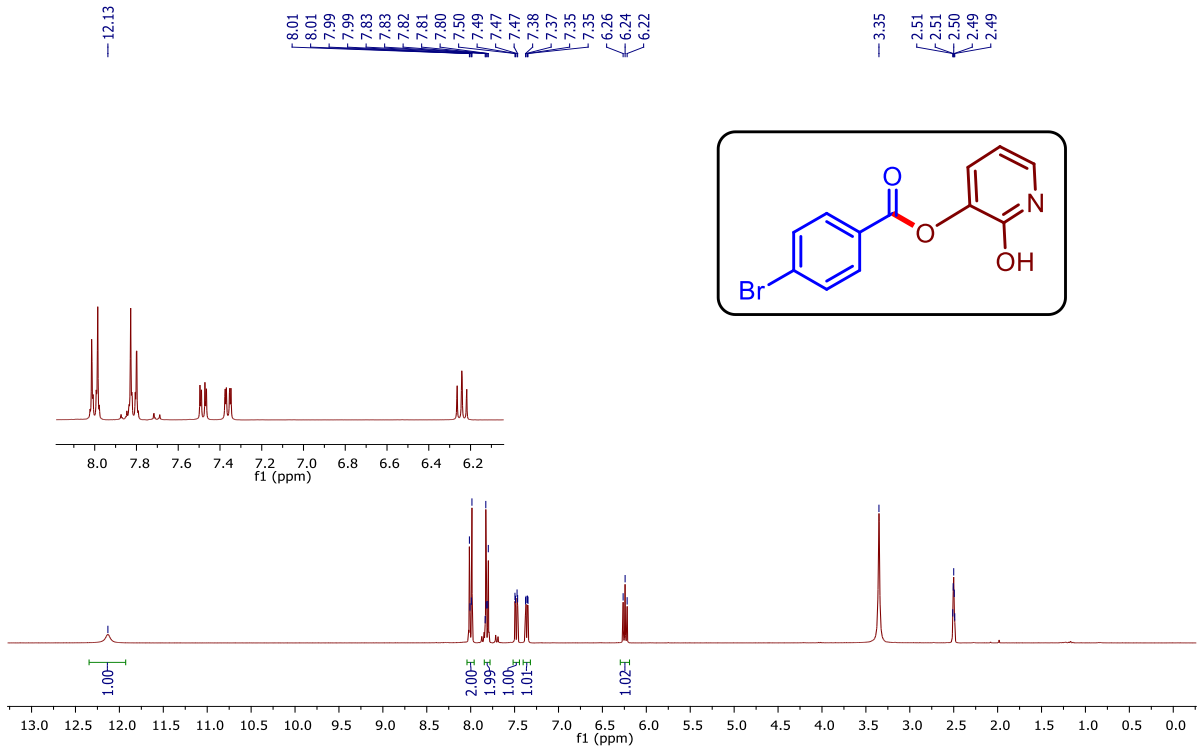
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7e



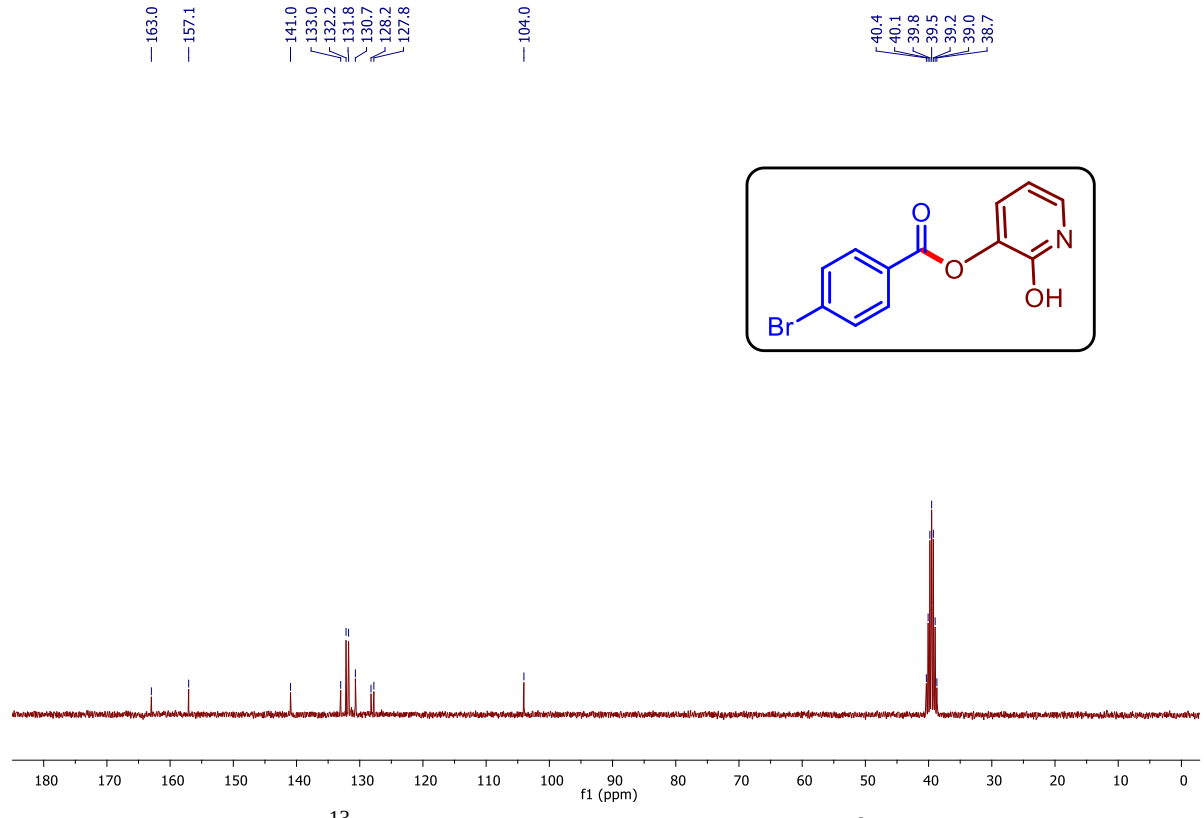
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7f



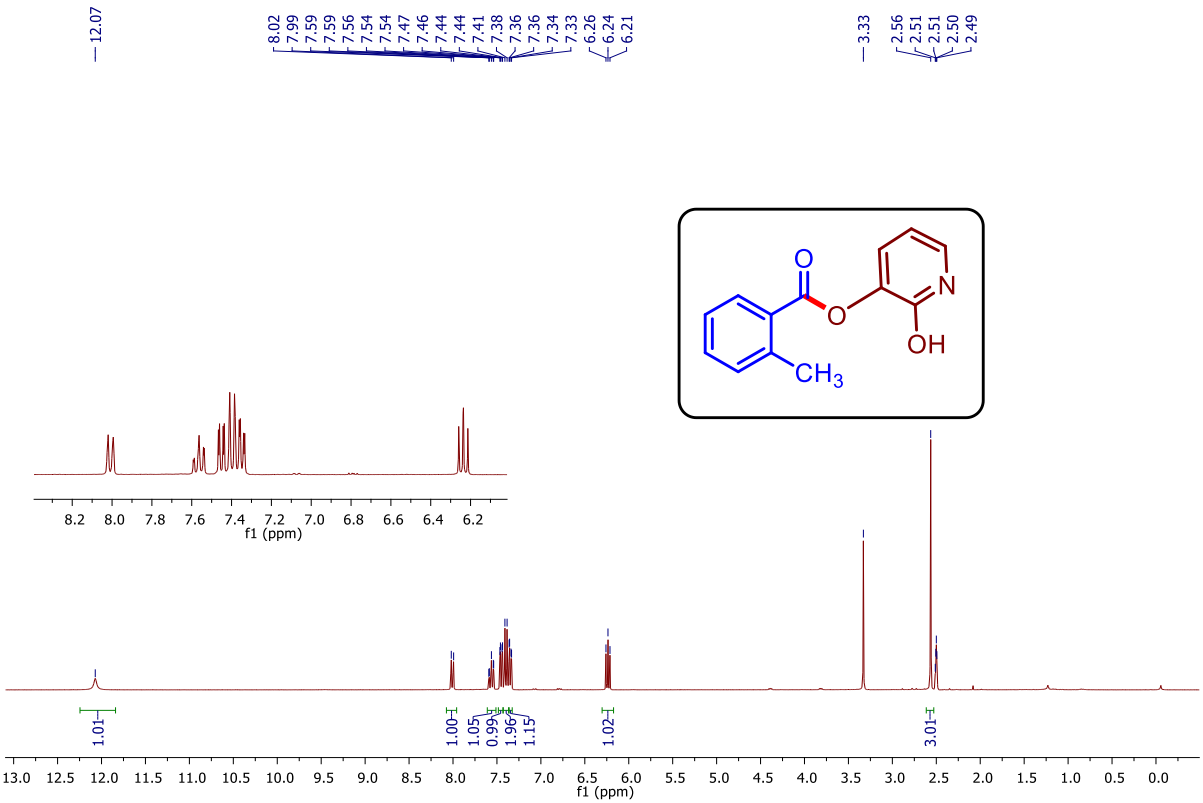
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7f



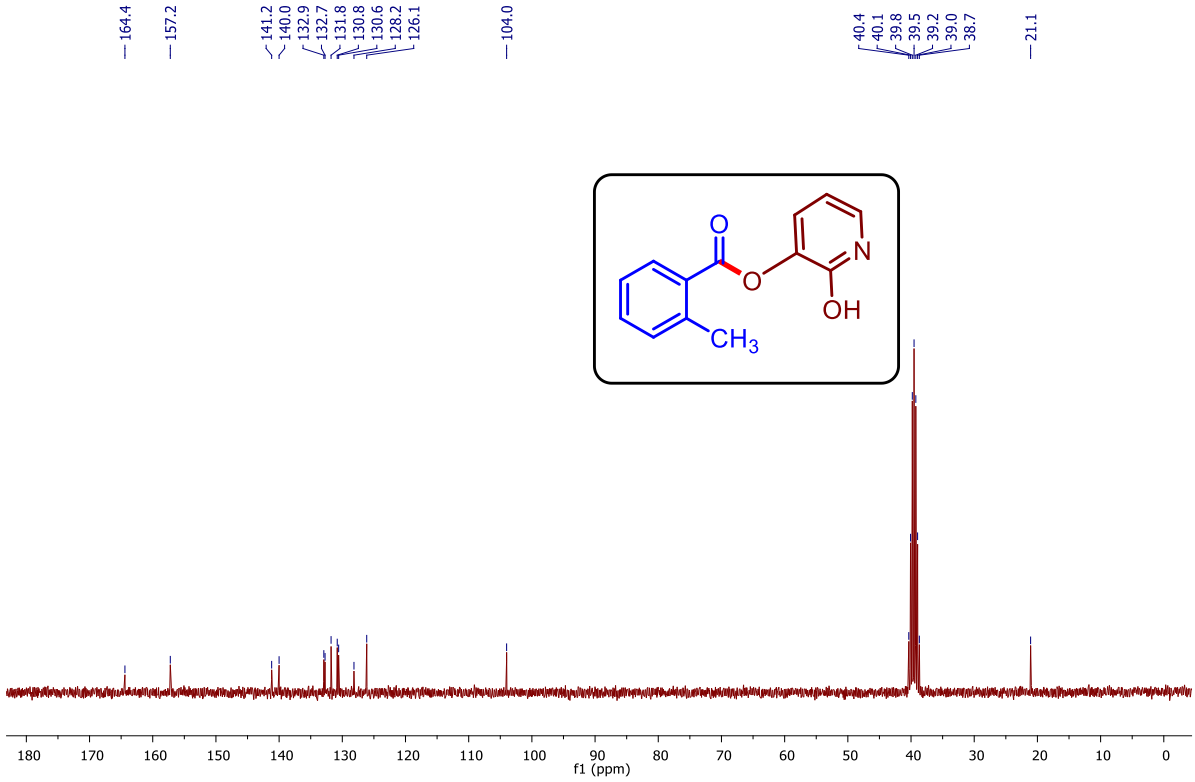
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7g



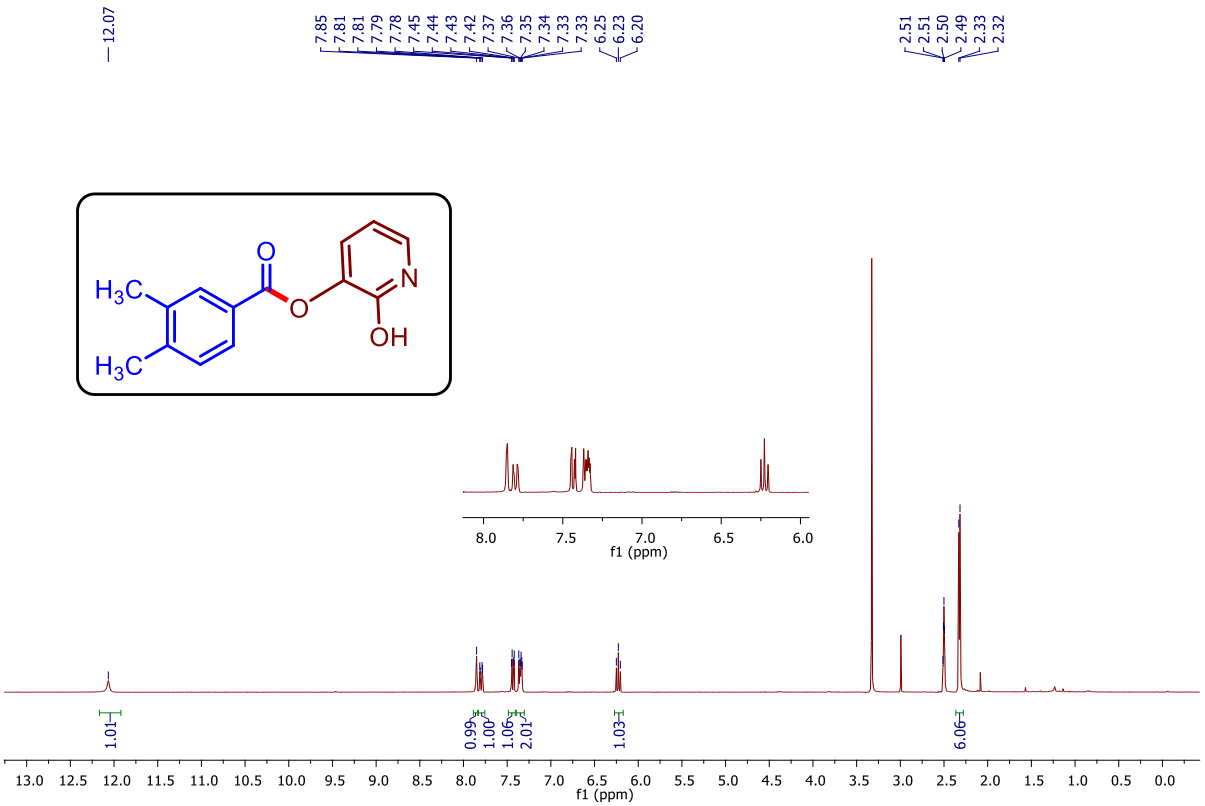
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7g



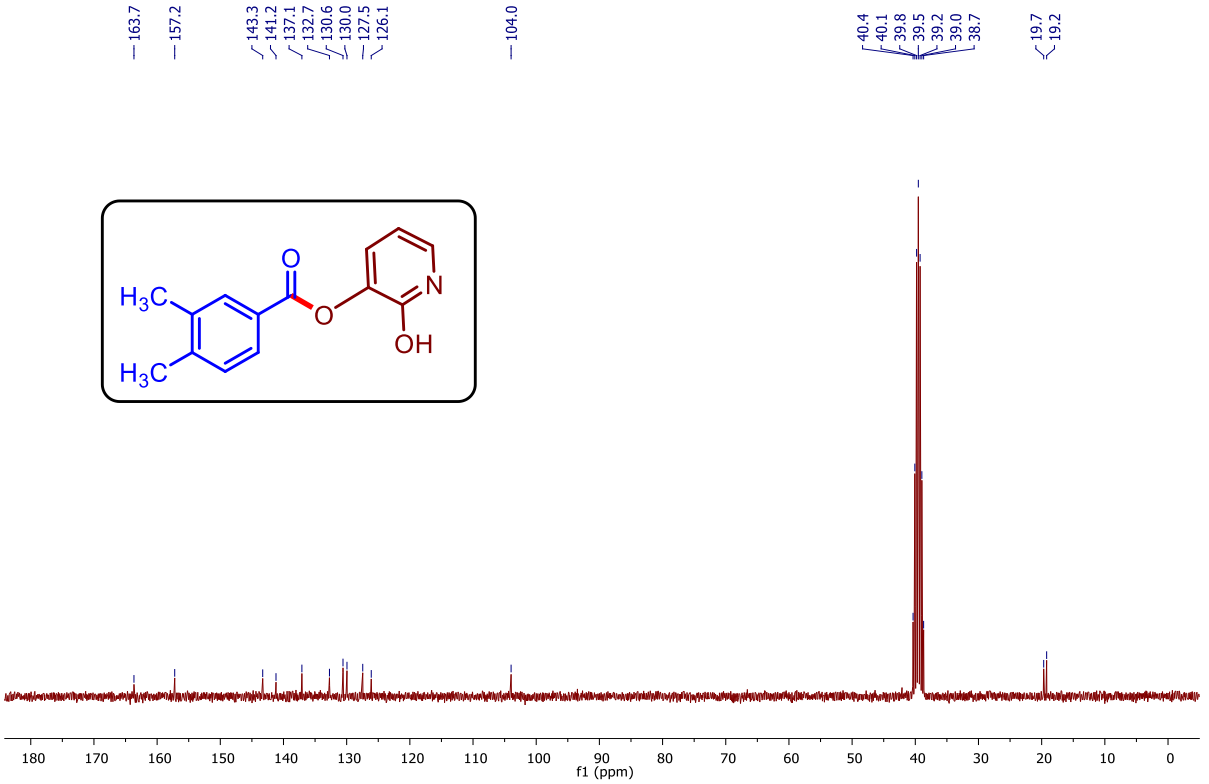
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7h



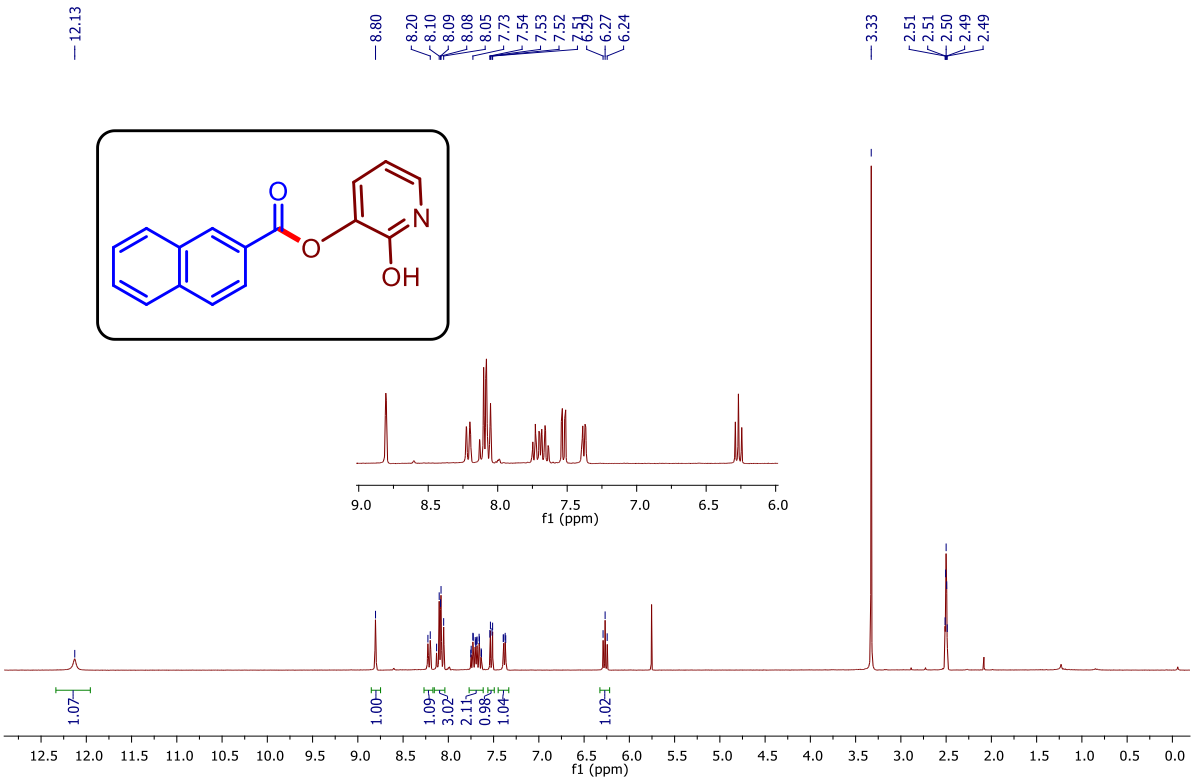
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7h



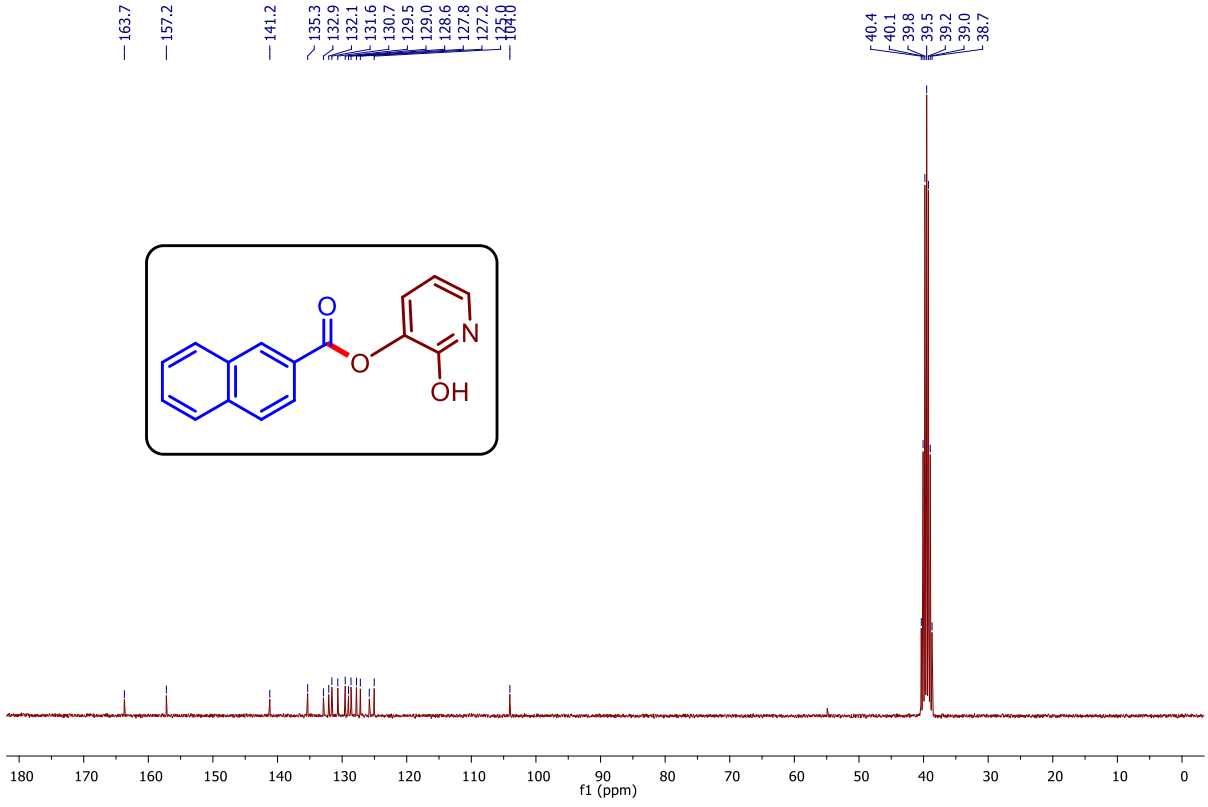
^{1}H NMR (300 MHz, DMSO-d$_6$, 298 K) of 7i



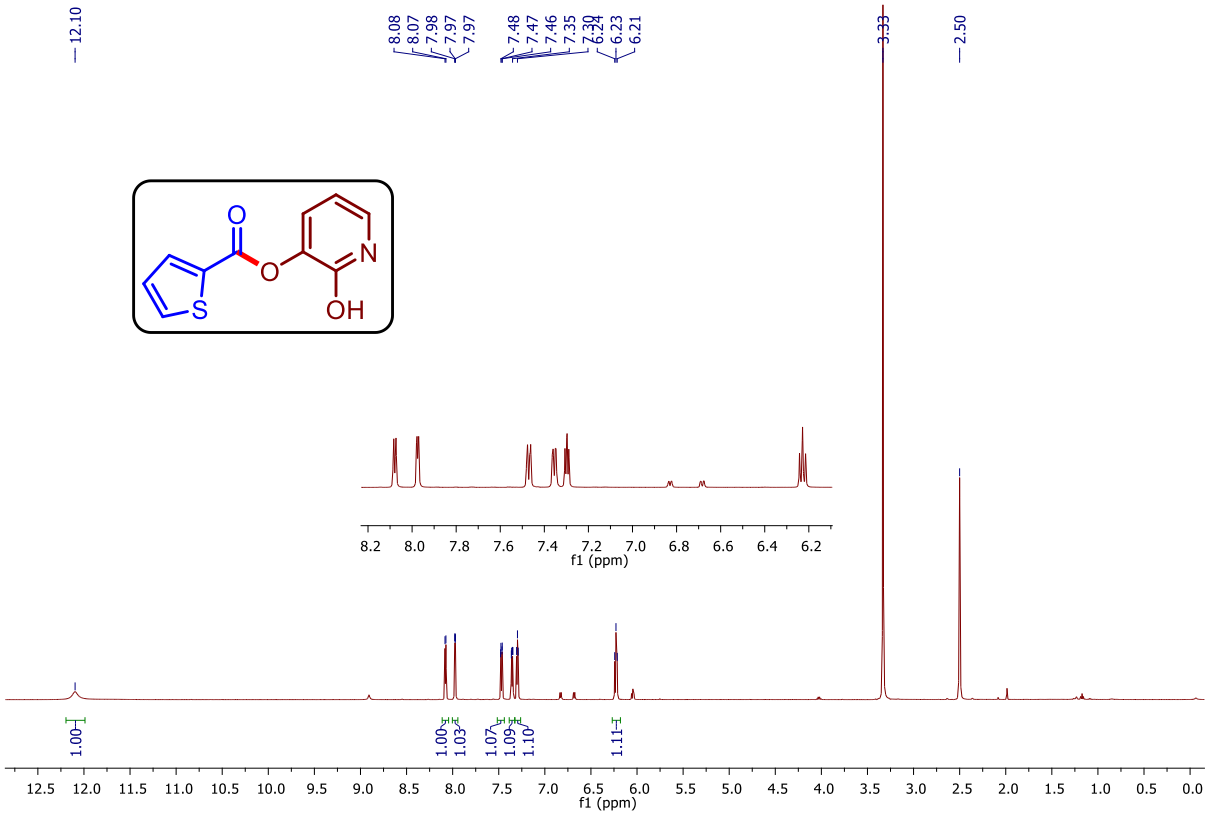
^{13}C NMR (75 MHz, DMSO-d$_6$, 298 K) of 7i



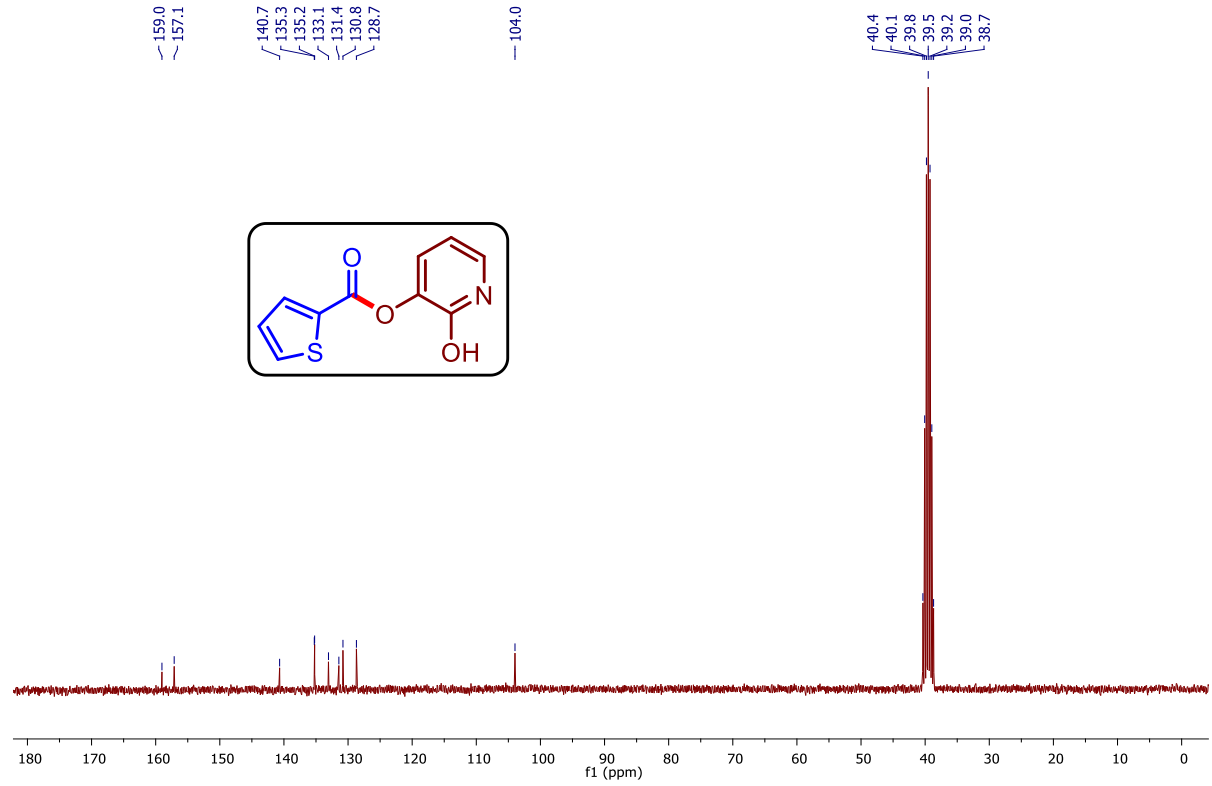
^{1}H NMR (300 MHz, DMSO-d_6, 298 K) of 7j



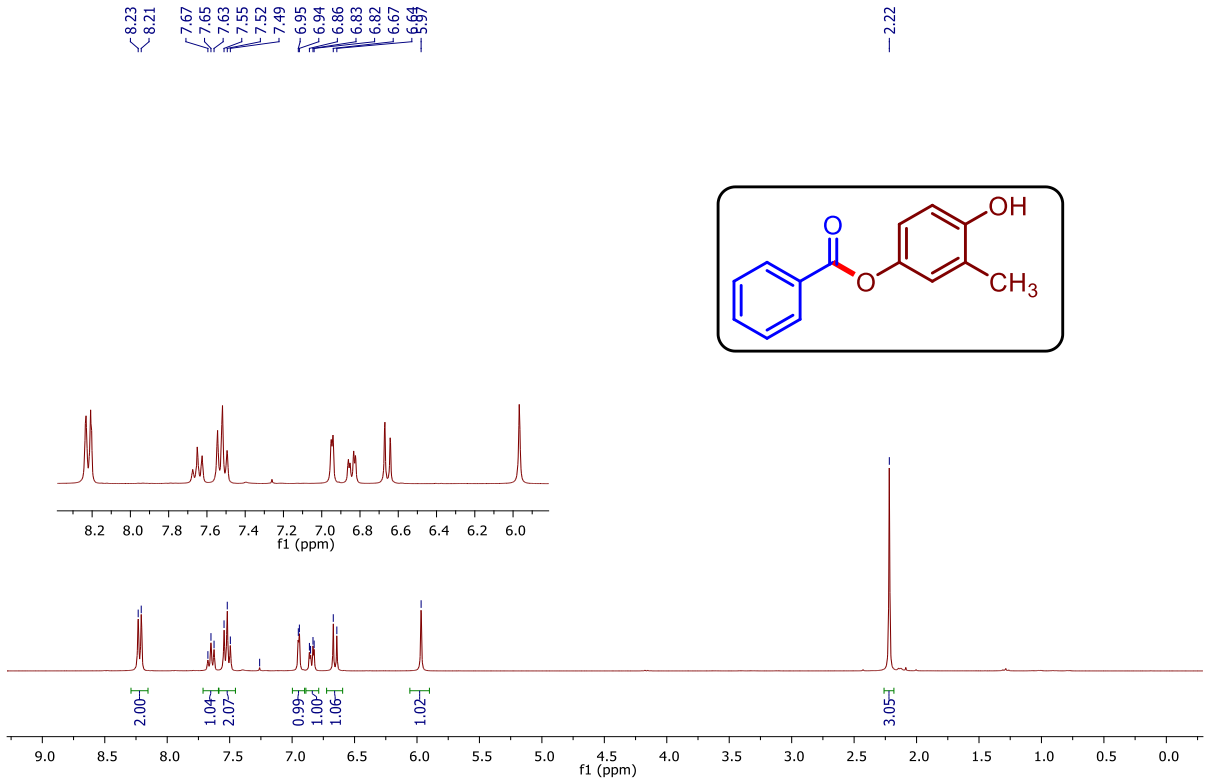
^{13}C NMR (75 MHz, DMSO-d_6, 298 K) of 7j



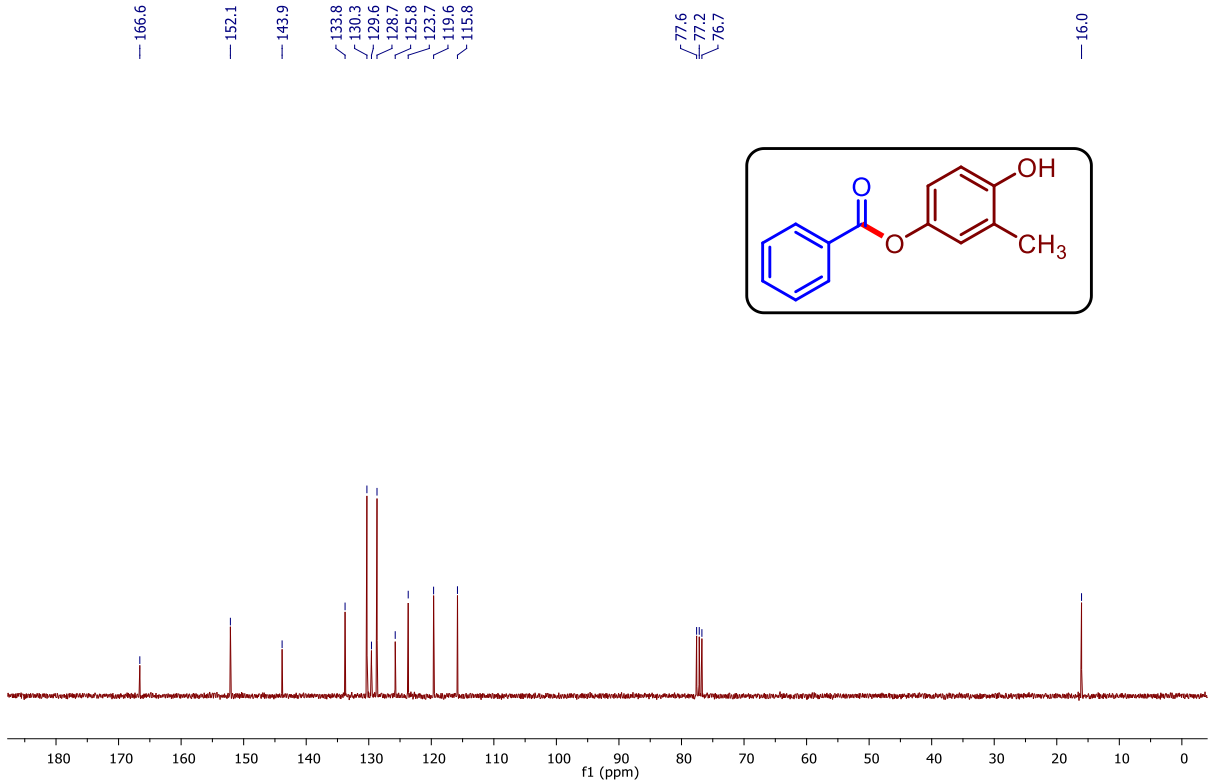
^{1}H NMR (500 MHz, DMSO-d$_6$, 298 K) of 7k



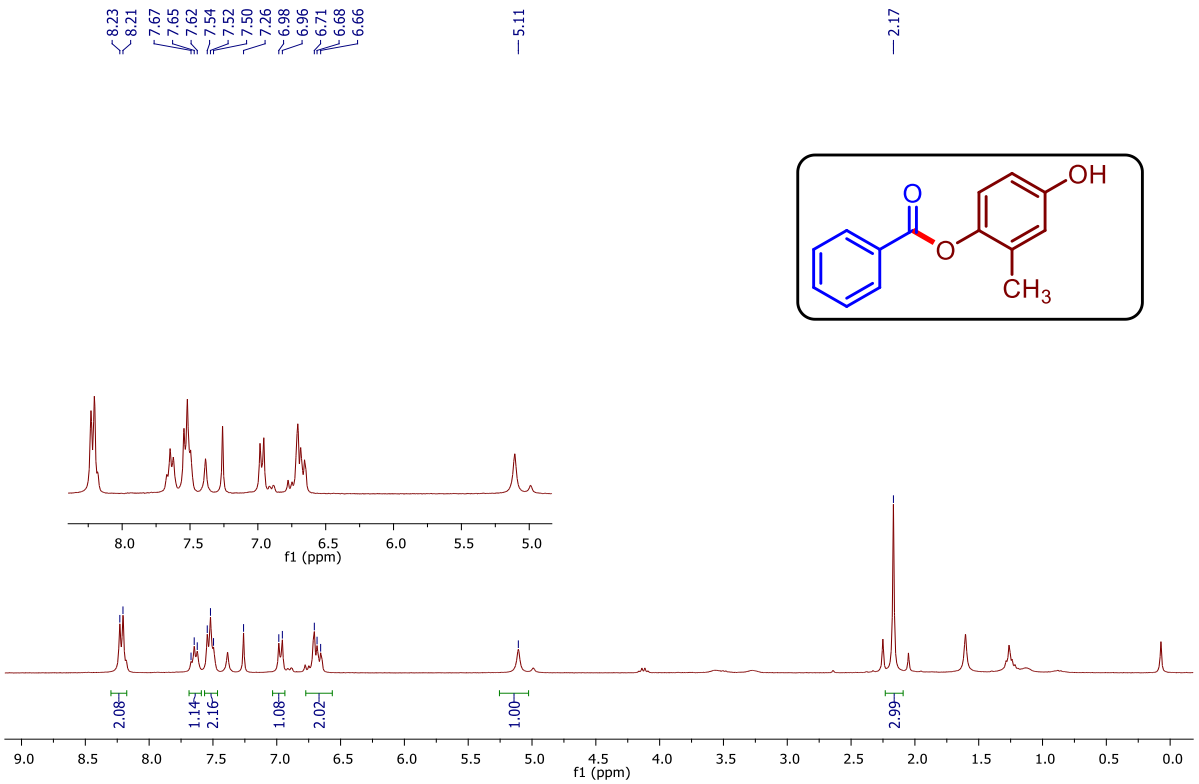
^{13}C NMR (75 MHz, DMSO-d$_6$, 298 K) of 7k



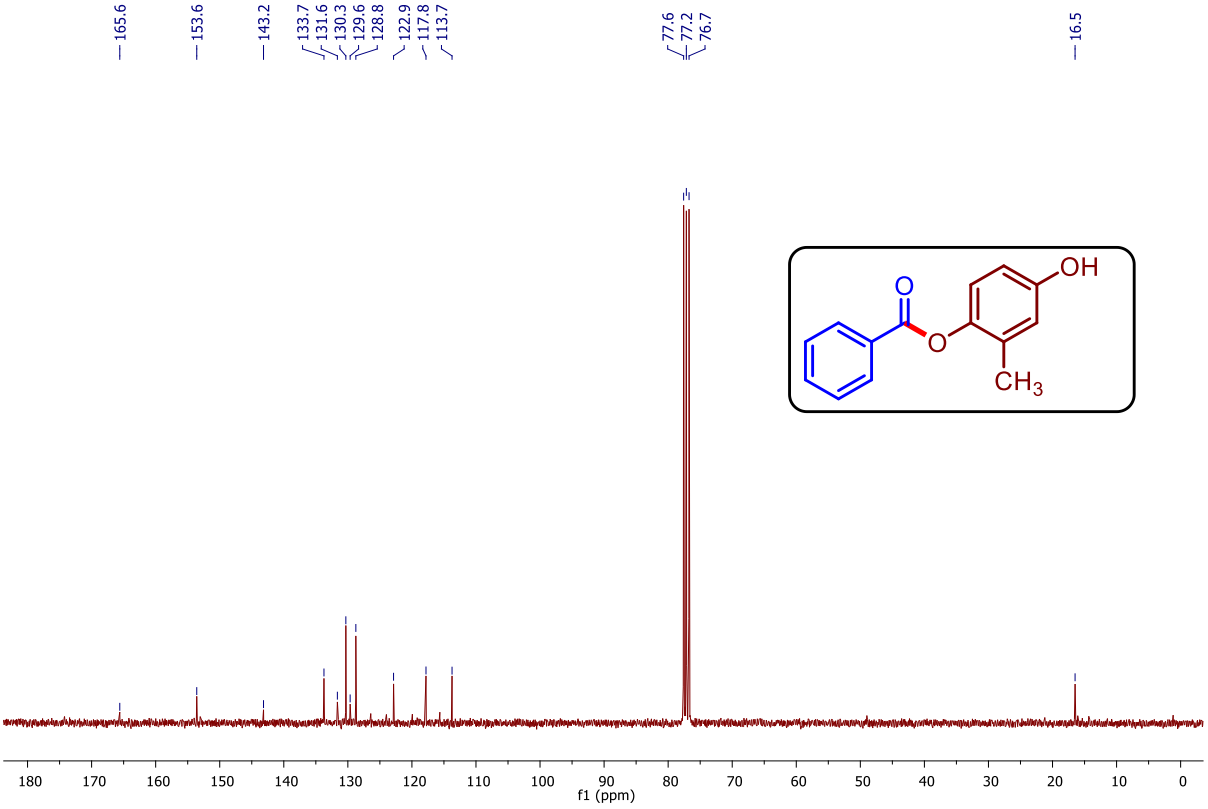
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 7l



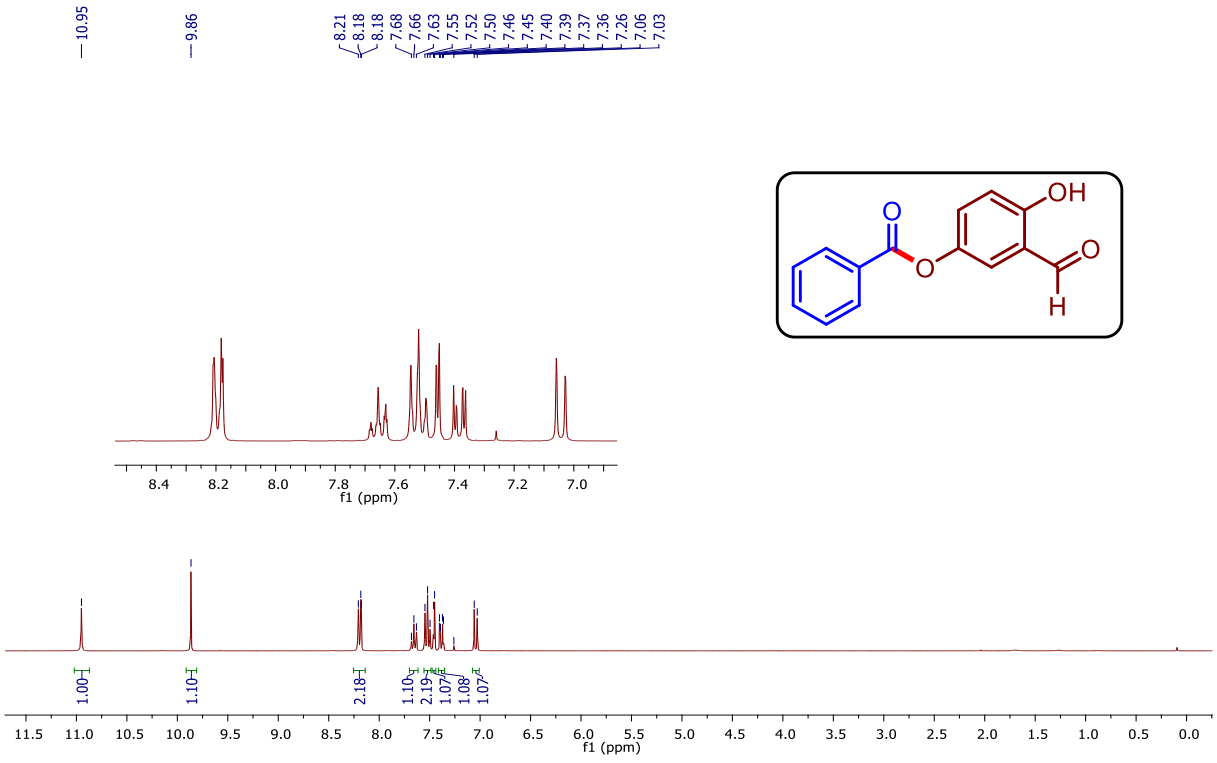
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 7l



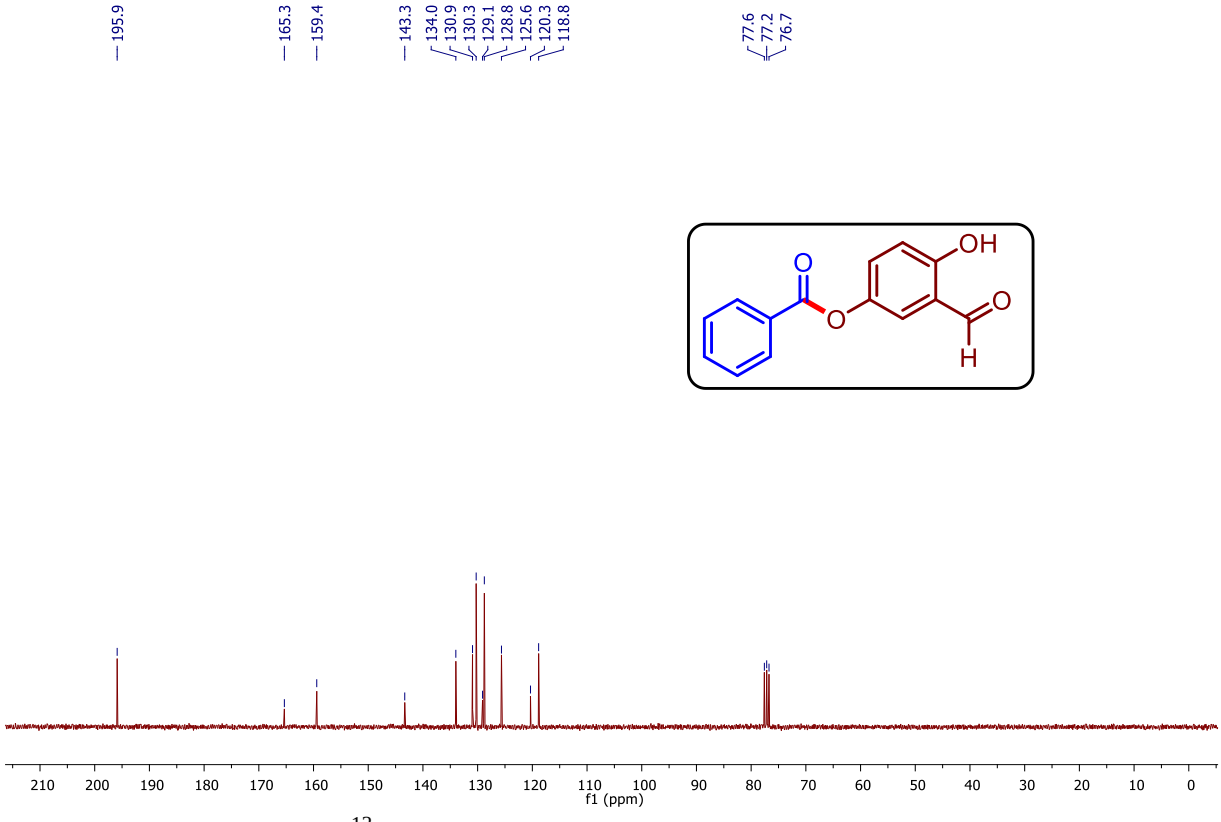
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 7m



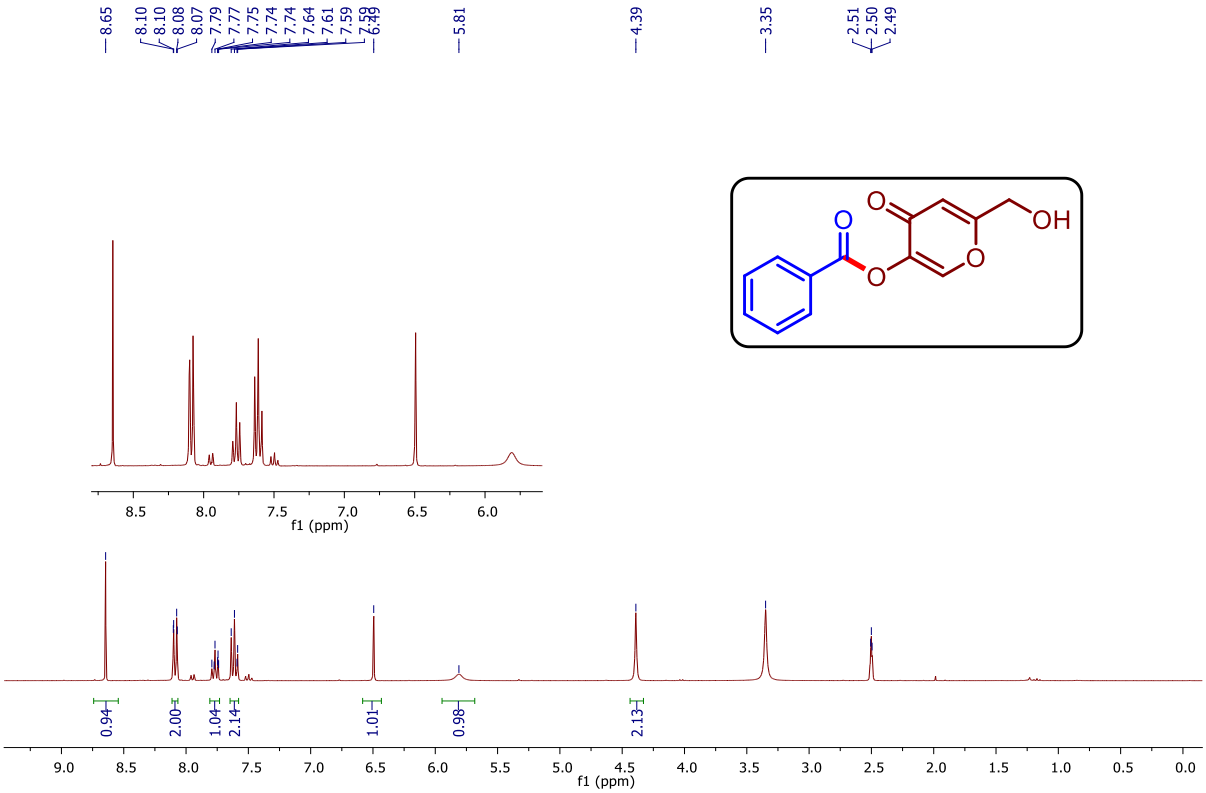
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 7m



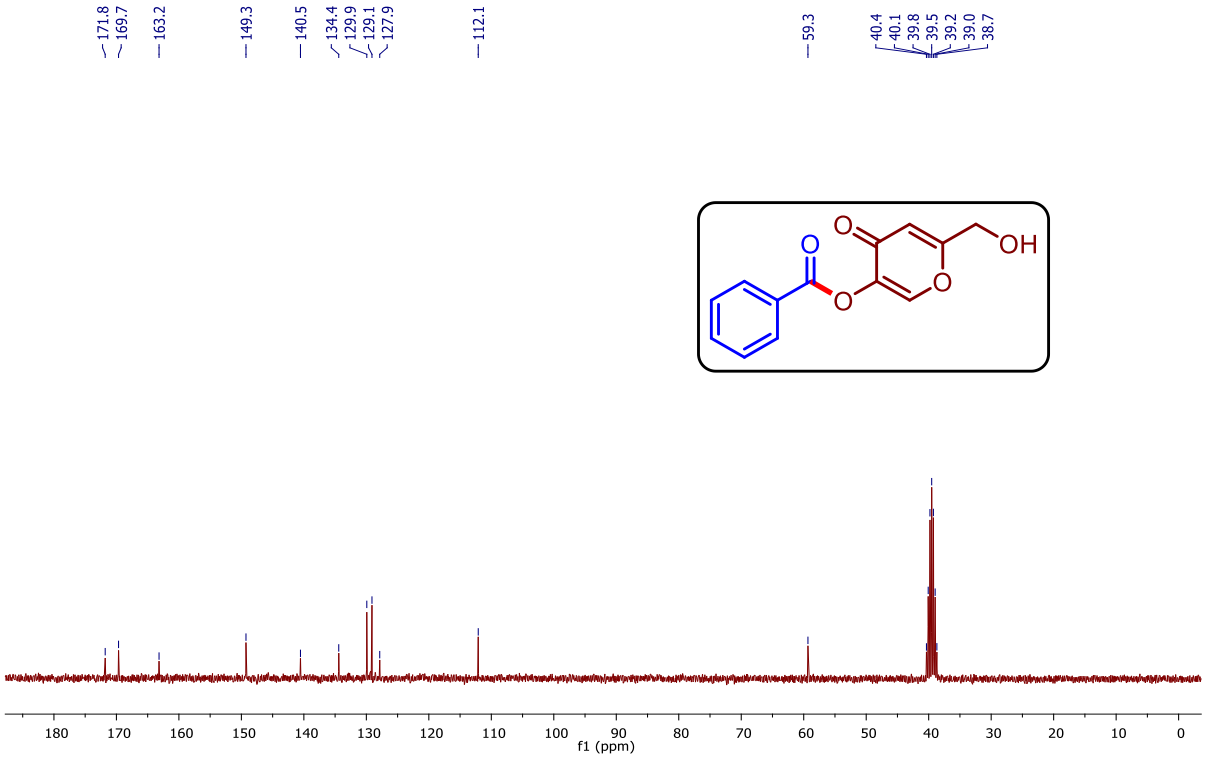
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 7n



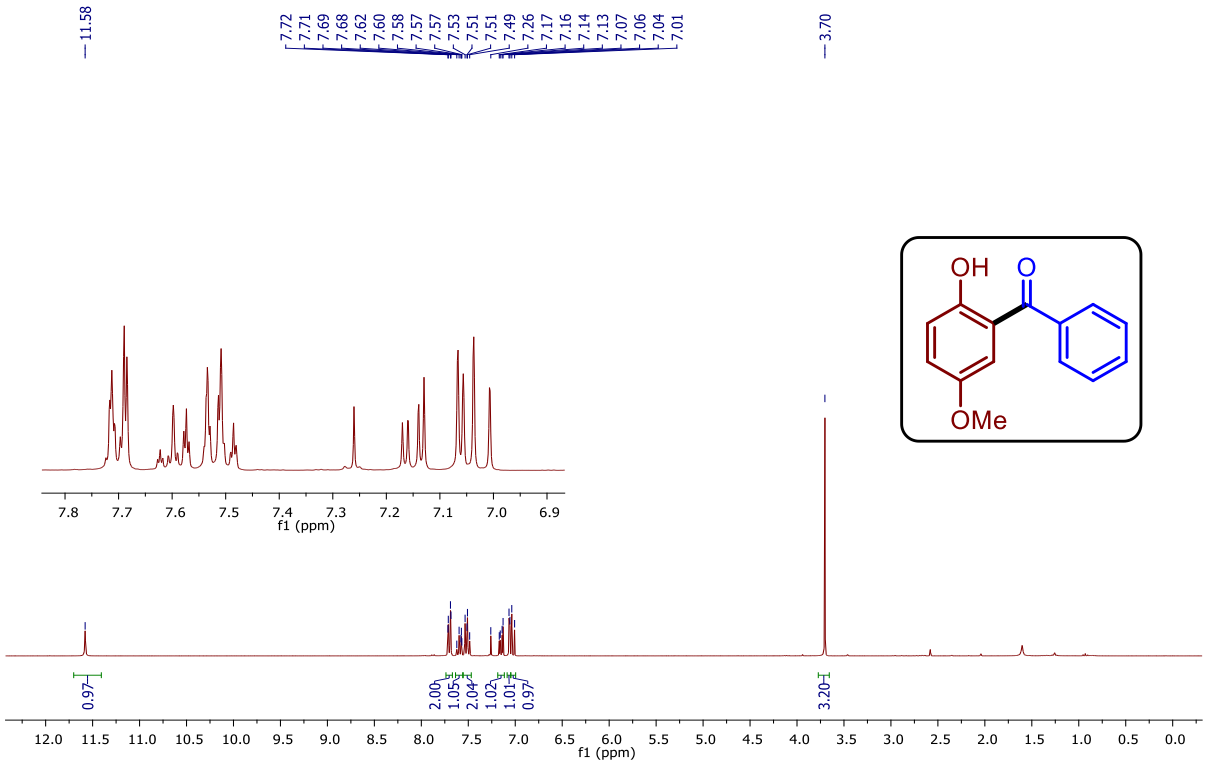
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 7n



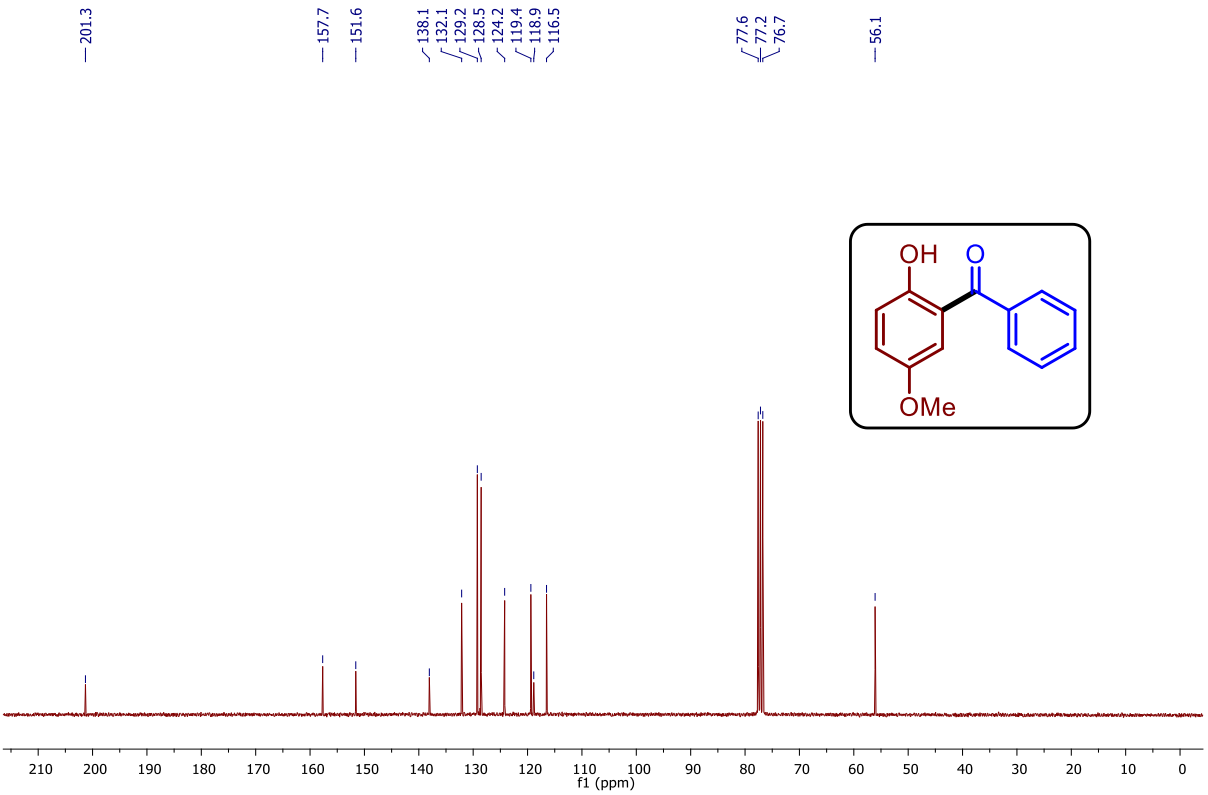
^{1}H NMR (300 MHz, DMSO-d$_6$, 298 K) of 7p



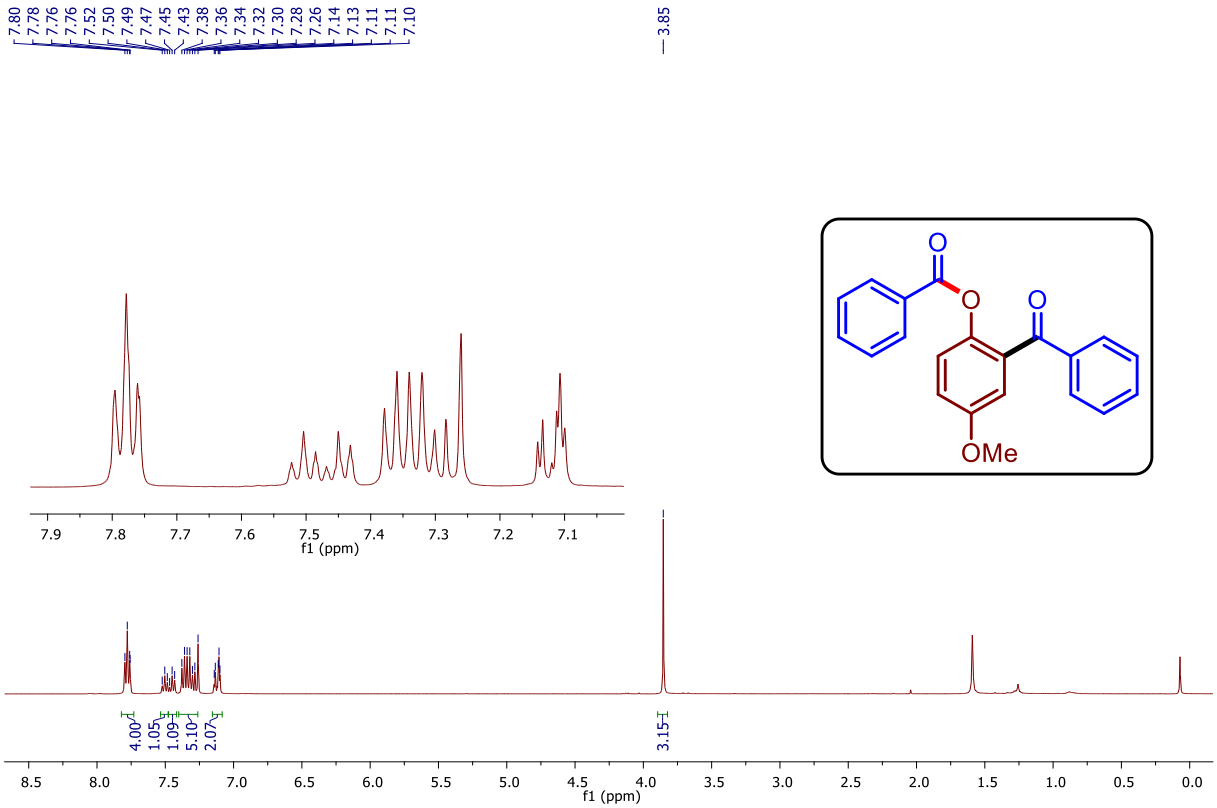
^{13}C NMR (101 MHz, DMSO-d$_6$, 298 K) of 7p



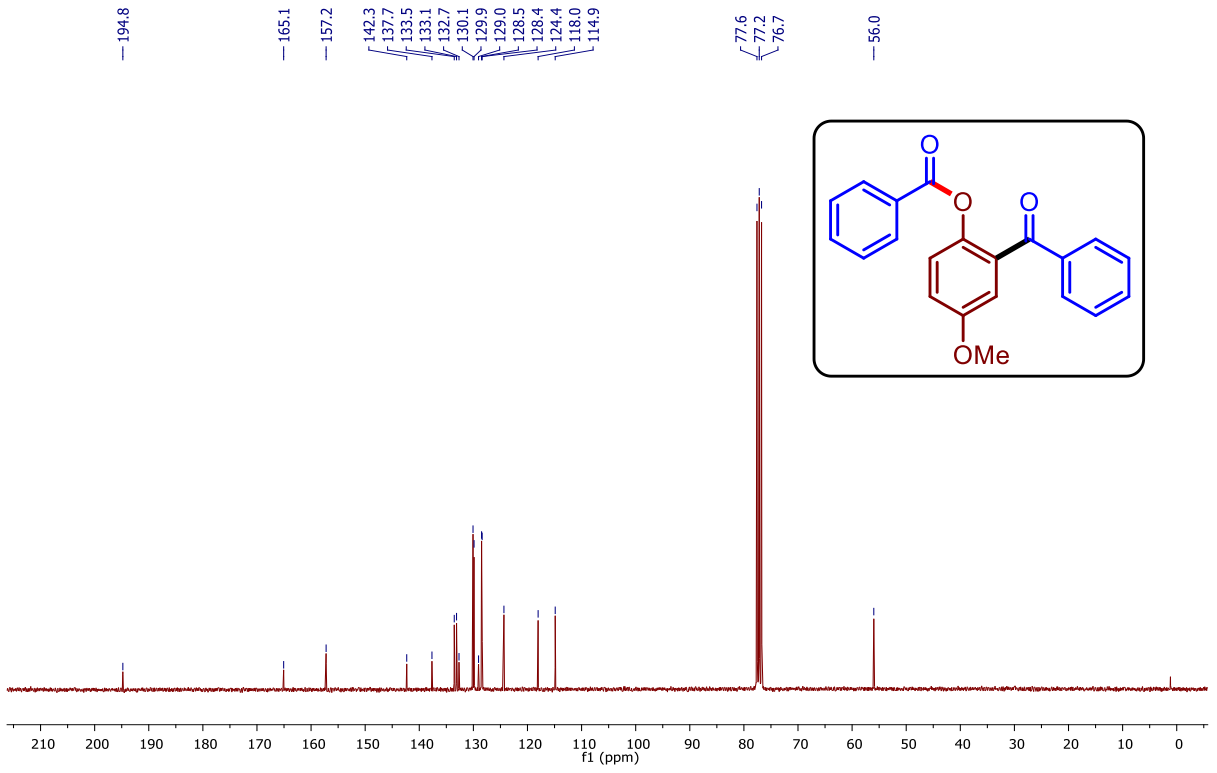
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 8



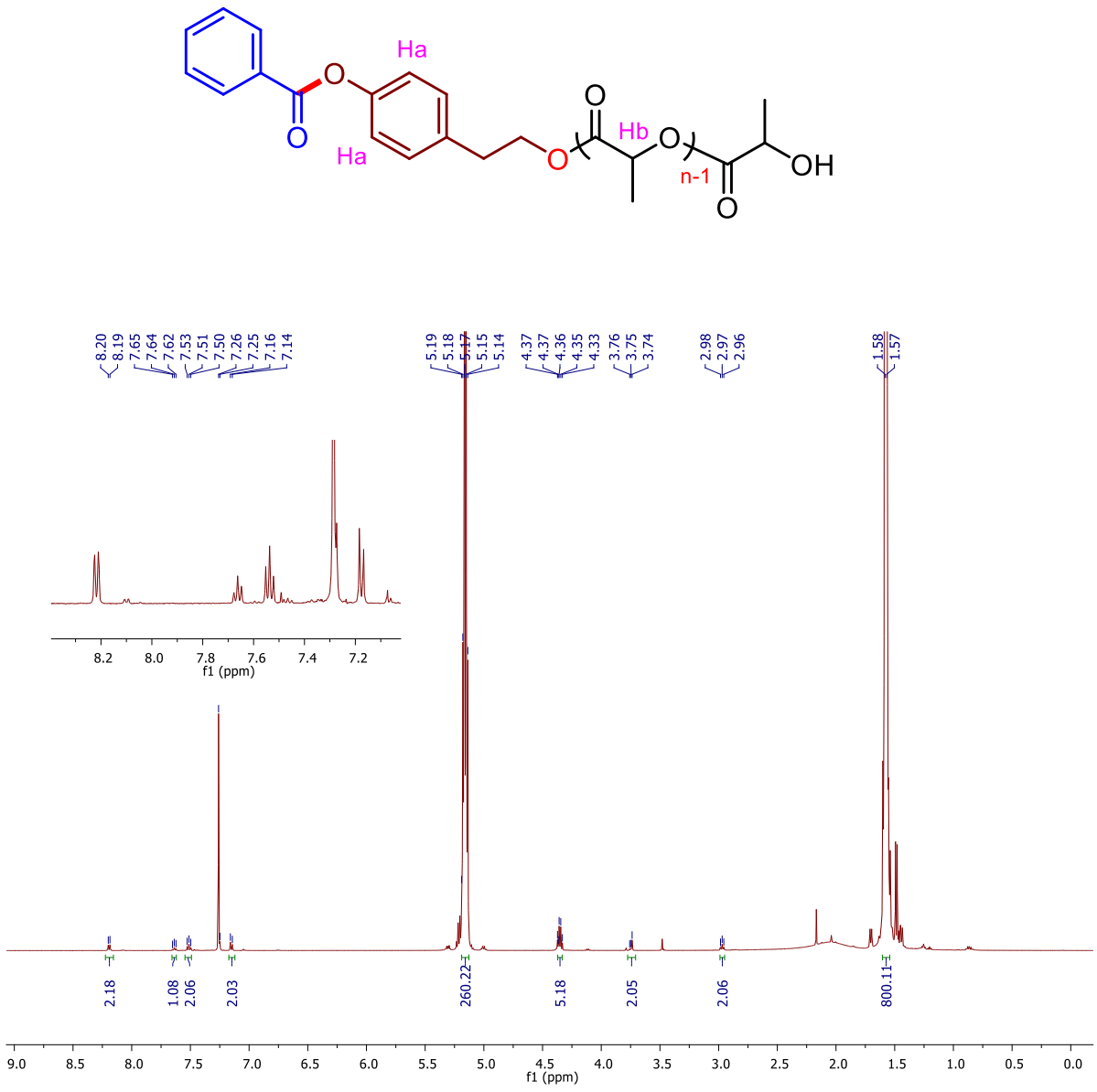
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 8



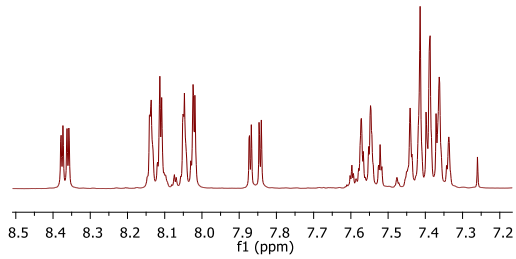
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of 9

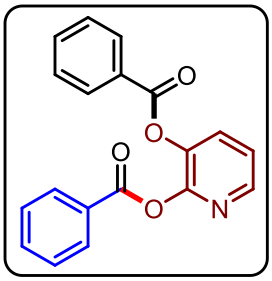


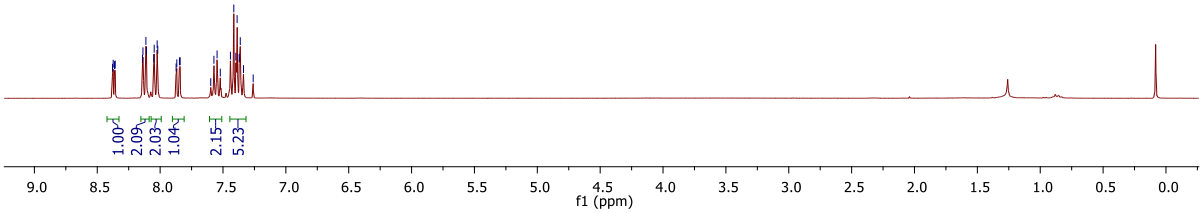
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 9



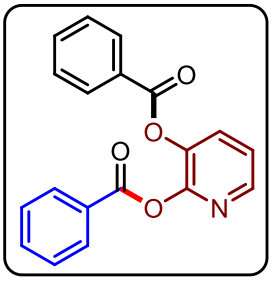
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of 11

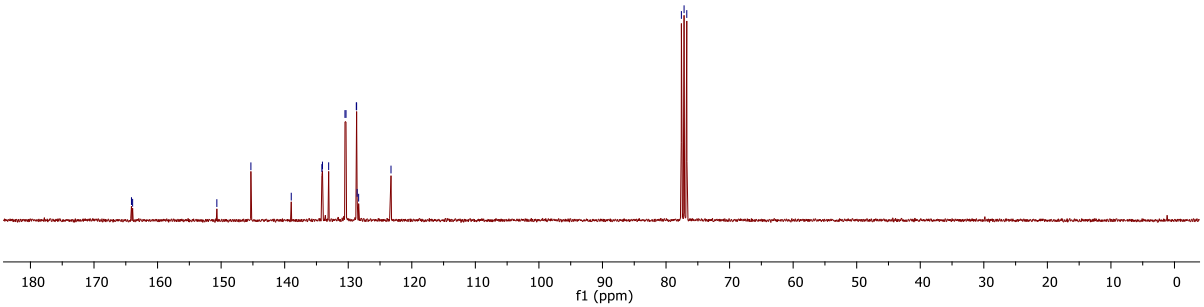




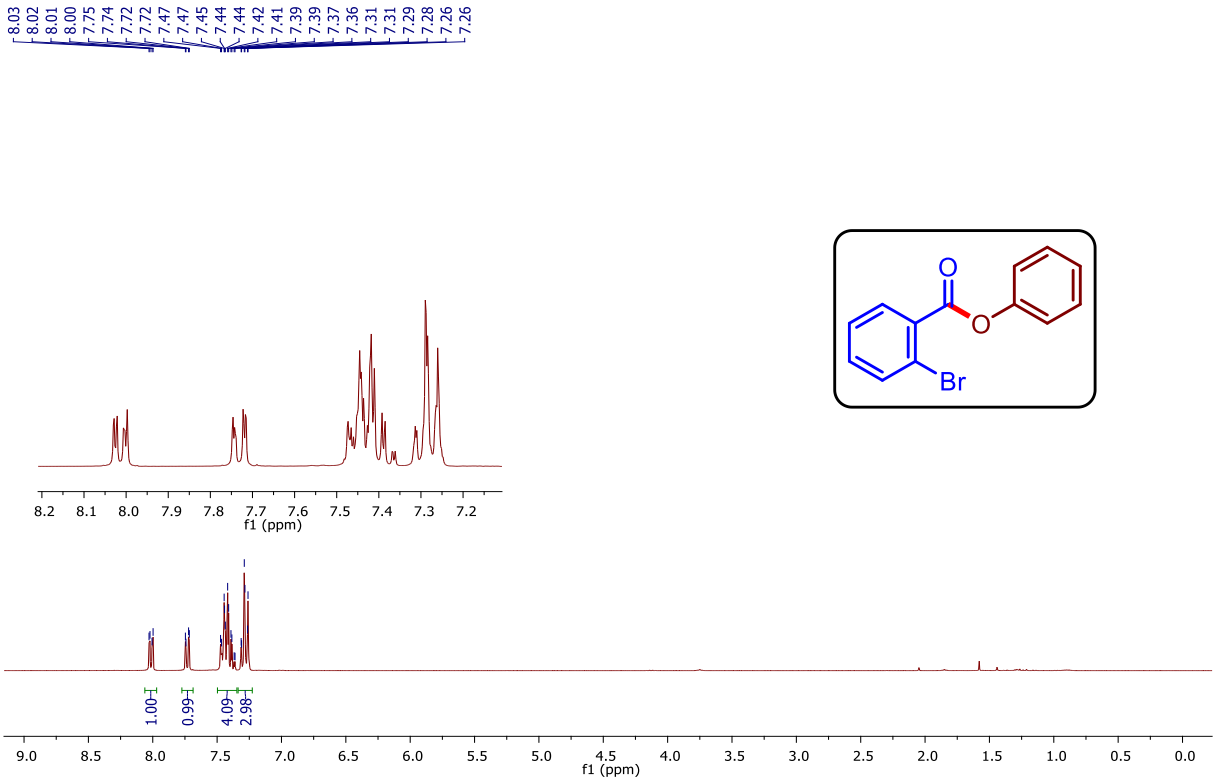


^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 12

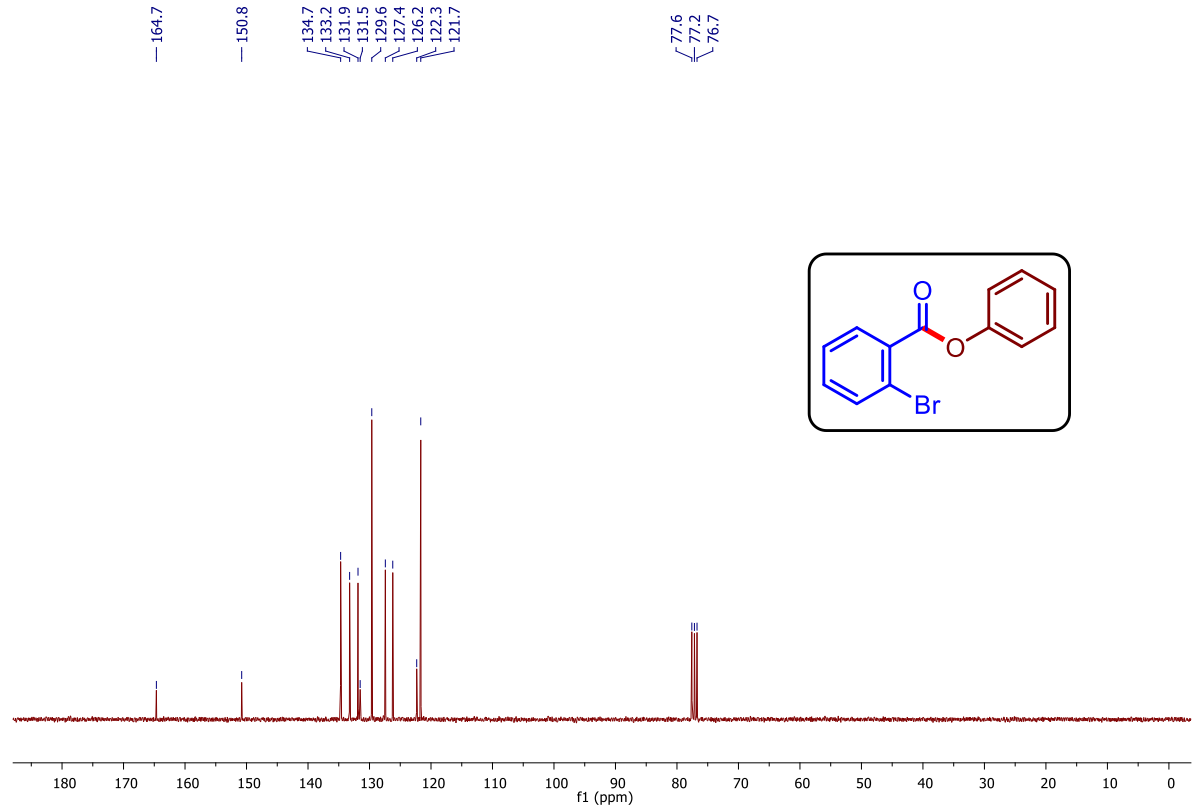




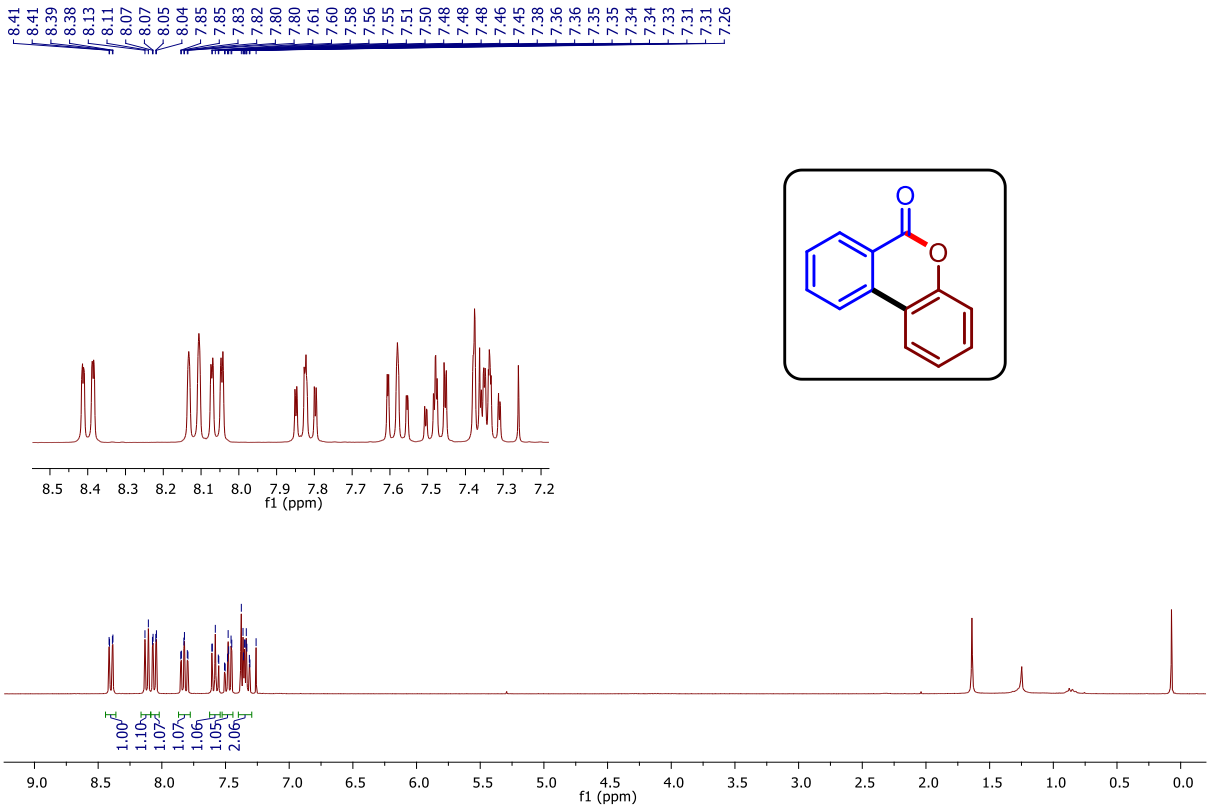
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 12



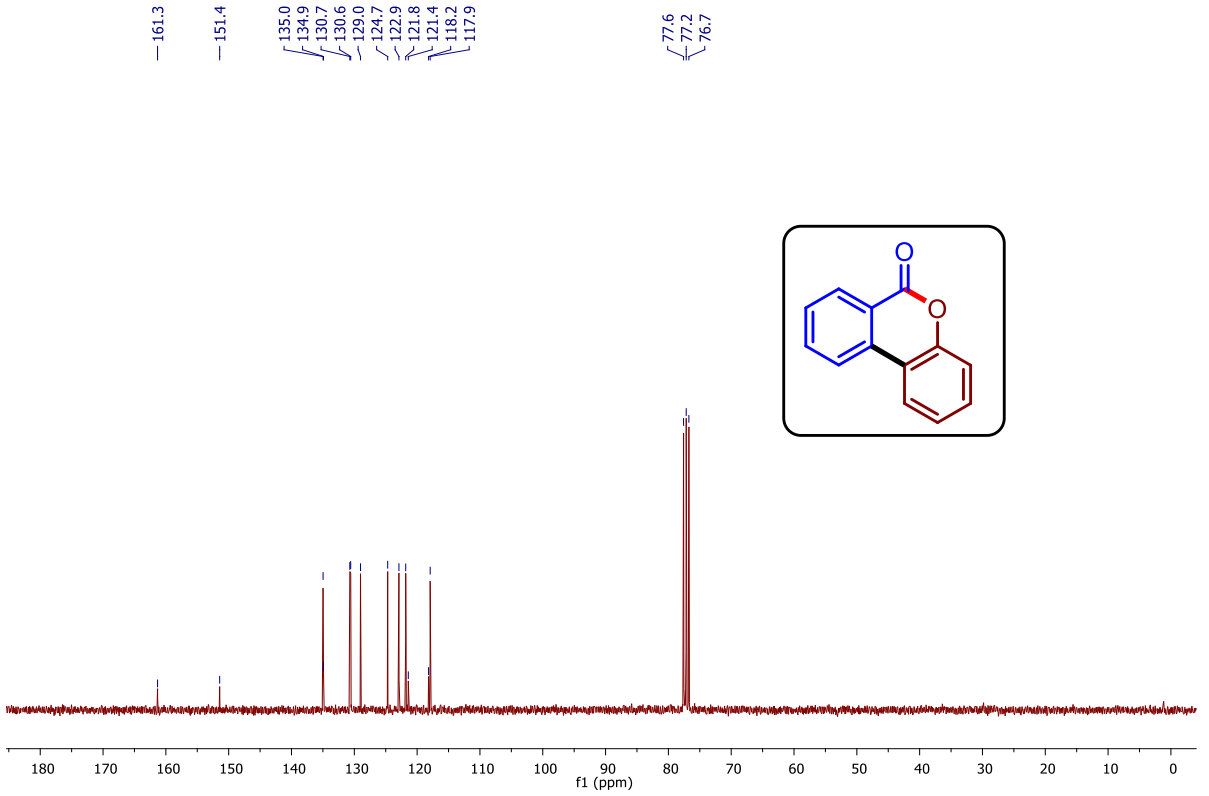
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 13



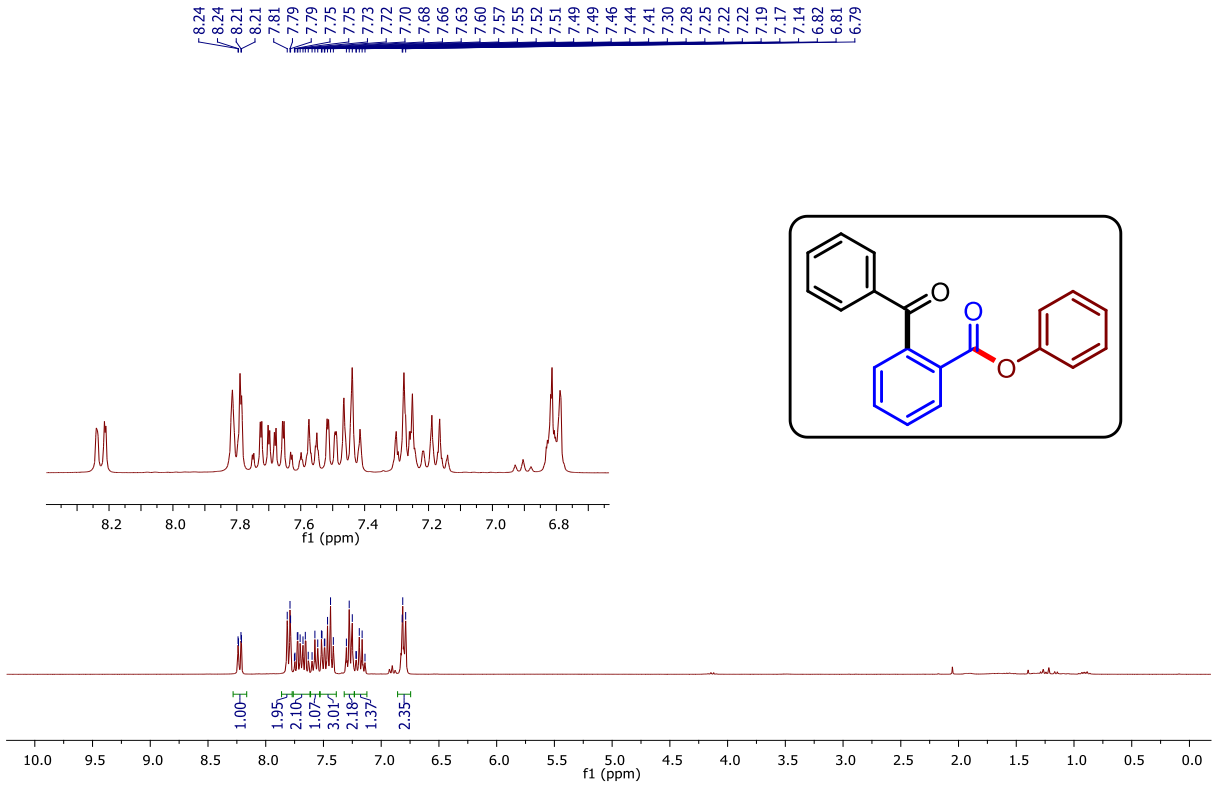
^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 13



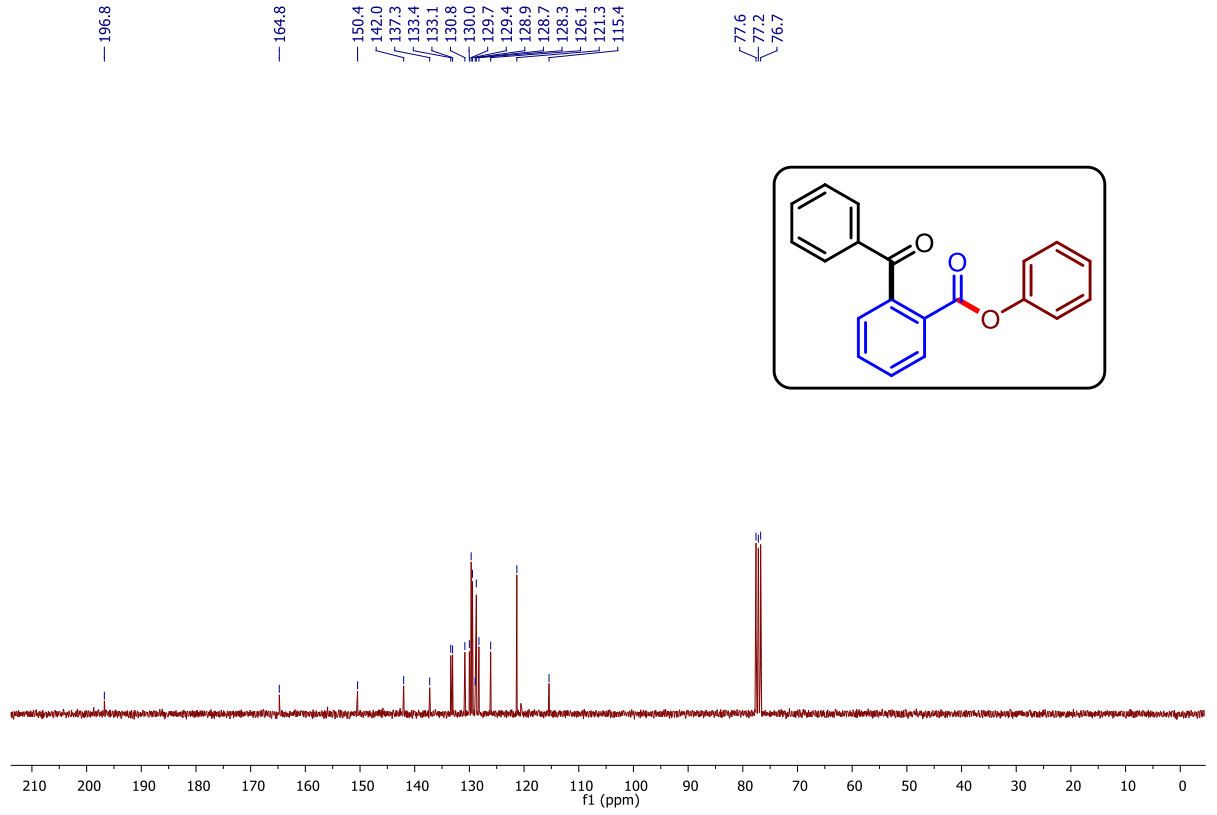
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 14



^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 14



^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of 15



^{13}C NMR (75 MHz, $CDCl_3$, 298 K) of 15