Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Photocatalytic selective oxidation of toluene under encapsulated air conditions

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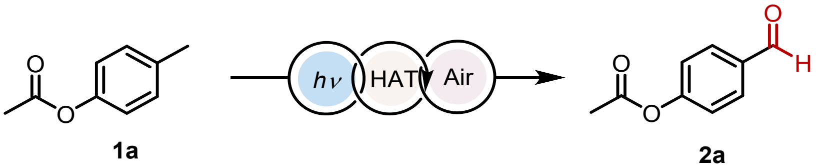
1. Materials and Characterizations.

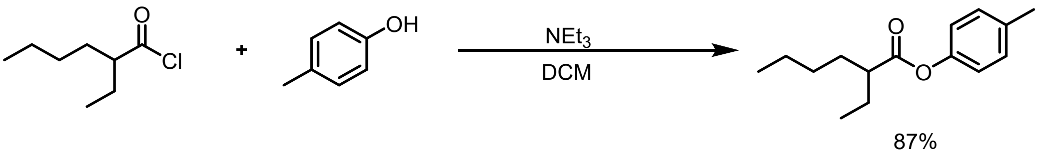
Unless otherwise stated, the chemicals used are all purchased from reagent companies. ^{1}H NMR spectra was recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). LED (395 nm, 10W) was purchased from Taobao.com.

2. General procedure for the photochemical reaction

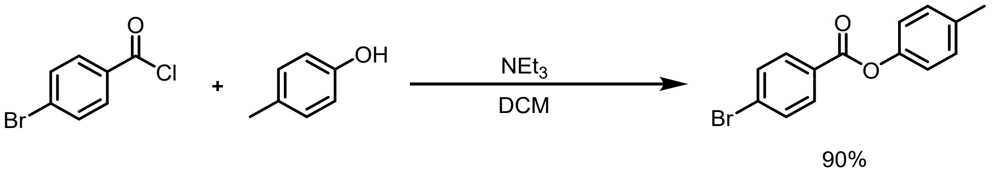


4-Acetoxytoluene (14.4 μL, 0.1 mmol), $FeCl_3$ (0.05 mg, 3×10^{-4} mmol) and MeCN (2.0 mL) was added to an oven-dried quartz tube equipped with magnetic stirring bar. The vessel placed 2 cm away from one purple 10 W LED (395 nm). The reaction mixture was irradiated with for 4 h under encapsulated air atmosphere at 25 °C. After irradiation, the reaction mixture was transferred to a 25 mL round-bottom flask and the solvent was concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1).

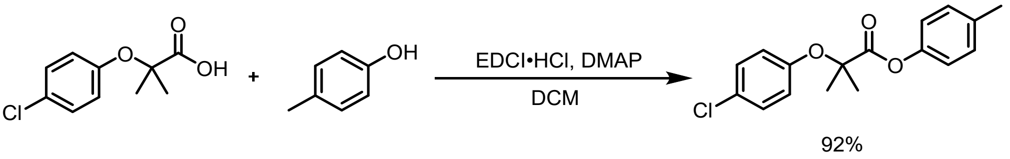
3. Preparation of bio-active molecules containing toluene moieties



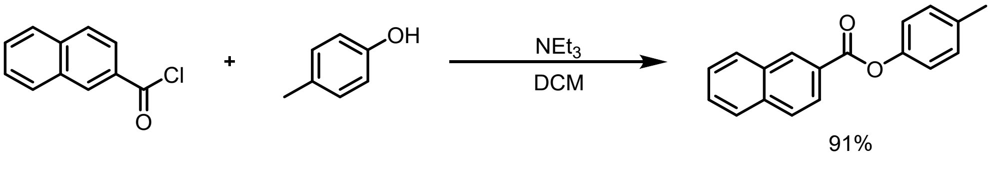
p-cresol (108.1 mg, 2 mmol, 1.0 equiv.), NEt_3 (556.0 μL, 4 mmol, 2.0 equiv.) and DCM (20 mL) was added to a 100 mL round-bottom flask equipped with magnetic stirring bar. The reaction was stirred at 0 °C and slowly add 2-ethylhexanoyl chloride (363.8 μL, 2.1 mmol, 1.05 equiv.), the reaction mixture was stirred for 12 h. Then the solvent was concentrated in vacuo and the residue was obtained was purified by chromatography on silica gel, eluted with petroleum/ethyl acetate (20:1) to afford the desired product in 87% yield as white solid. The spectral data obtained were identical with those reported in literature.



p-cresol (108.1 mg, 2 mmol, 1.0 equiv.), NEt_3 (556.0 µL, 4 mmol, 2.0 equiv.) and DCM (20 mL) was added to a 100 mL round-bottom flask equipped with magnetic stirring bar. The reaction was stirred at 0 °C and slowly add 4-bromobenzoyl chloride (460.8 mg, 2.1 mmol, 1.05 equiv.), the reaction mixture was stirred for 12 h. Then the solvent was concentrated in vacuo and the residue was obtained was purified by chromatography on silica gel, eluted with petroleum/ethyl acetate (20:1) to afford the desired product in 90% yield as yellow solid. The spectral data obtained were identical with those reported in literature.



To a solution of the p-cresol (108.1 mg, 1 mmol, 1.0 equiv.), EDCI·HCl (383.4 mg, 2 mmol, 2.0 equiv.), DMAP (122.2 mg, 0.1 mmol, 0.1 equiv) and DCM (10 mL) was added to a 100 mL round-bottom flask equipped with magnetic stirring bar. Then, 2-(4-chlorophenoxy) -2-methylpropanoic acid (118.06 mg, 0.55 mmol, 1.1 equiv.) under 0 °C and stirred overnight at room temperature. After reaction, the mixture was filtered and the filtrate was concentrated in vacuo. Finally, the residue was purified by chromatography on silica gel, eluted with petroleum/ethyl acetate to afford the desired product in 92% yield as yellow solid. The spectral data obtained were identical with those reported in literature.

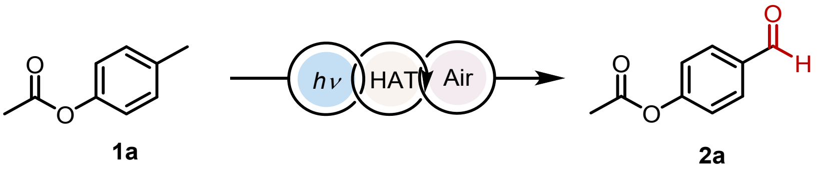


p-cresol (108.1 mg, 2 mmol, 1.0 equiv.), NEt_3 (556.0 µL, 4 mmol, 2.0 equiv.) and

DCM (20 mL) was added to a 100 mL round-bottom flask equipped with magnetic stirring bar. The reaction was stirred at 0 °C and slowly add 2-naphthoyl chloride (400.32 mg, 2.1 mmol, 1.05 equiv.), the reaction mixture was stirred for 12 h. Then the solvent was concentrated in vacuo and the residue was obtained was purified by chromatography on silica gel, eluted with petroleum/ethyl acetate (20:1) to afford the desired product in 91% yield as white solid. The spectral data obtained were identical with those reported in literature.

4. Optimization of the light wavelength.

Table S1 Optimization of the light wavelength.



Entry	Variation from standard conditions	Yield^{b} (%)
1	254 nm	99
2	365 nm	99
3	400 nm	71
4	420 nm	37
5	435 nm	11
6	475 nm	< 5%
7	500 nm	0
8	660 nm	0

Note: When utilizing lamps with wavelengths below 390 nm, it is recommended to employ quartz flasks to prevent light absorption by glass.

5. Absolute fluorescence quantum yield of $FeCl_3$

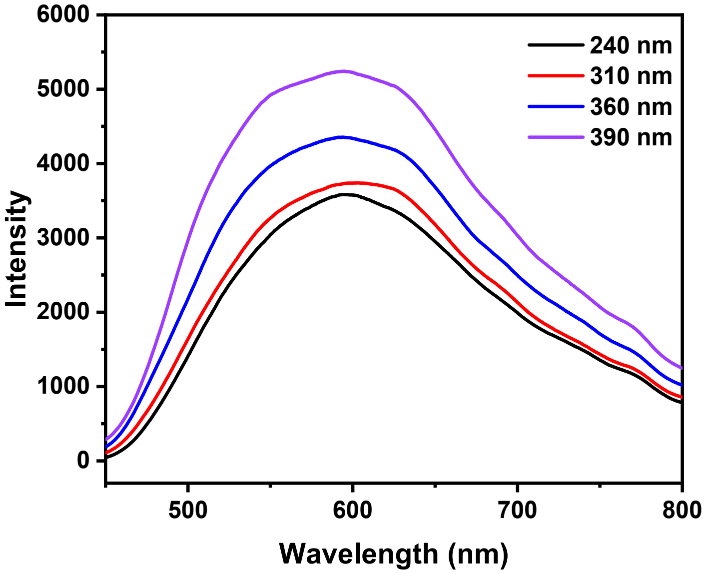
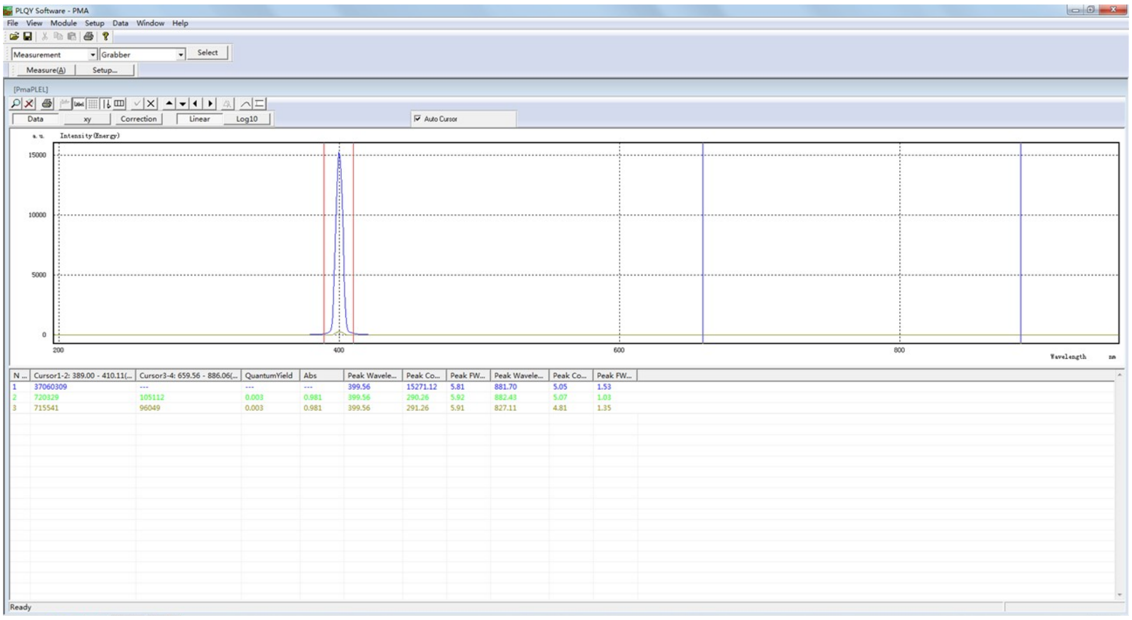


Fig. S1 Fluorescence spectra of catalysts at different wavelengths.



N ...	Cursor1-2: 389.00 - 410.11(...	Cursor3-4: 659.56 - 886.06(...	QuantumYield	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...
1	37060309	---	---	---	399.56	15271.12	5.81	881.70	5.05	1.53
2	720329	105112	0.003	0.981	399.56	290.26	5.92	882.43	5.07	1.03
3	715541	96049	0.003	0.981	399.56	291.26	5.91	827.11	4.81	1.35

Fig. S2 Absolute fluorescence quantum yield of $FeCl_3$.

6. Kinetic isotopic effect of the reaction

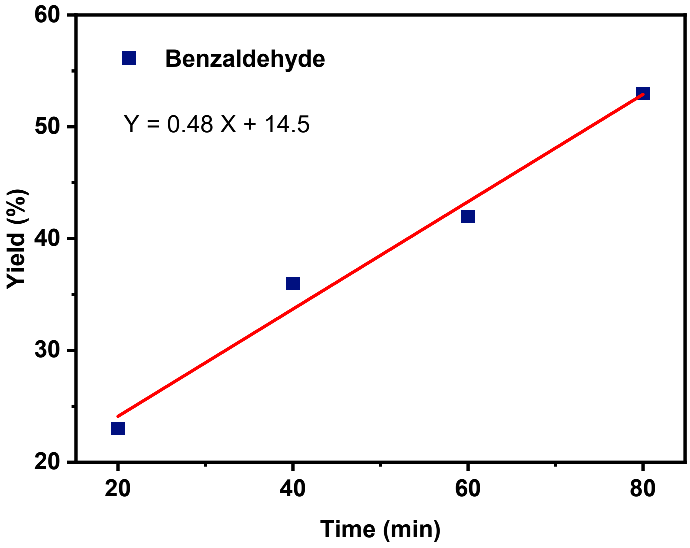


Fig. S3 Variation of benzaldehyde yield over time.

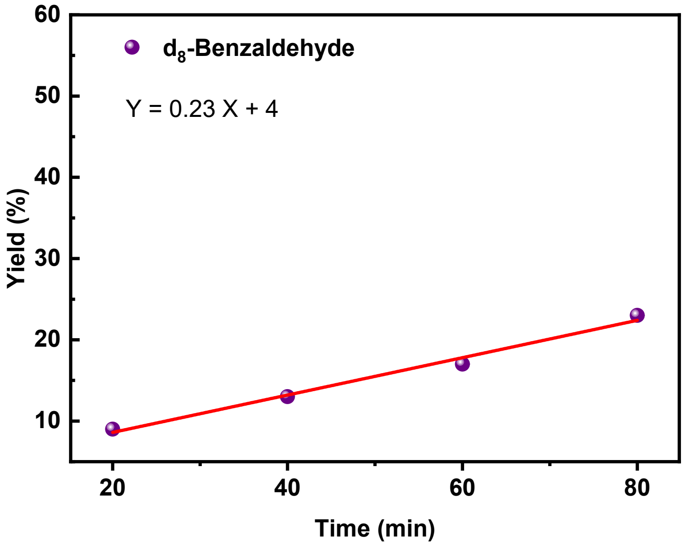
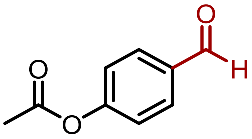


Fig. S4 Variation of d_8-benzaldehyde yield over time.

7. Light on/off experiment

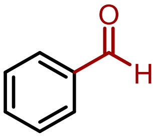
Four standard reaction mixtures in an oven-dried 10 mL quartz tube were charged with 4-Acetoxytoluene (14.4 μL, 0.1 mmol), $FeCl_3$ (0.05 mg, 3.0×10^{-4} mmol) and MeCN (2.0 mL) was added to an oven-dried quartz tube equipped with magnetic stirring bar. The vessel placed 2 cm away from one. The mixtures were then stirred and irradiated with purple 10 W LED (395 nm) at room temperature. After 1 h, the light was turned off, and one vial was removed from the irradiation setup for analysis. The remaining three vials were stirred in the absence of light for an additional 1 h. Then, one vial was removed for analysis, and the light was turned back on to irradiate the remaining two mixtures. After an additional 1 h of irradiation, the light was turned off, and one vial was removed for analysis. The remaining one vials were stirred in the absence of light for an additional 1 h and then it was analyzed. The yield was determined by ^1H NMR spectroscopy using dibromomethane as the internal standard.

8. Characterization Data for Products



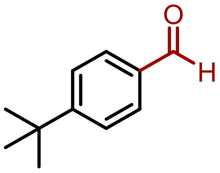
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2b** as a colorless oil (95% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 2.34 (s, 3H).



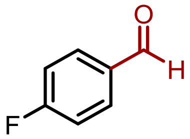
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2c** as a colorless oil (71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.02 (s, 1H), 7.92 – 7.86 (m, 2H), 7.68 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H).



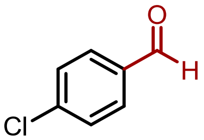
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2d** as a colorless oil (69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.84 – 7.80 (m, 2H), 7.57 – 7.54 (m, 2H), 1.35 (s, 9H).



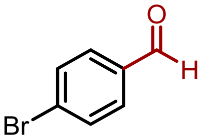
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2e** as a colorless oil (77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.96 – 7.89 (m, 2H), 7.26 – 7.19 (m, 2H).



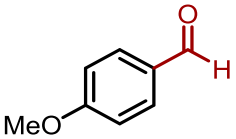
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2f** as a colorless oil (82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.85 – 7.81 (m, 2H), 7.55 – 7.51 (m, 2H).



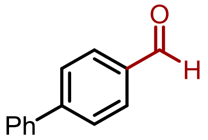
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2g** as a colorless oil (88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.78 – 7.74 (m, 2H), 7.72 – 7.67 (m, 2H).



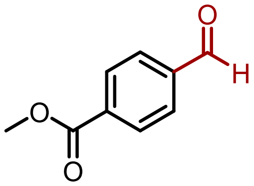
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2h** as a colorless oil (91% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.89 (s, 1H), 7.87 – 7.82 (m, 2H), 7.04 – 6.98 (m, 2H), 3.90 (s, 3H).



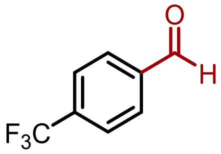
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2i** as a colorless oil (80% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 7.99 – 7.94 (m, 2H), 7.79 – 7.74 (m, 2H), 7.67 – 7.62 (m, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H).



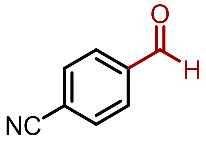
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2j** as a colorless oil (89% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 3H).



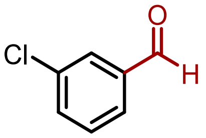
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2k** as a colorless oil (67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H).



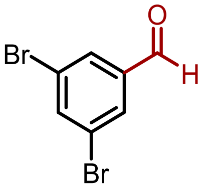
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2l** as a colorless oil (73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.03 – 7.99 (m, 2H), 7.89 – 7.84 (m, 2H).



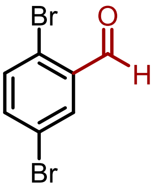
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2m** as a colorless oil (81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.88 – 7.85 (m, 1H), 7.78 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.61 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H).



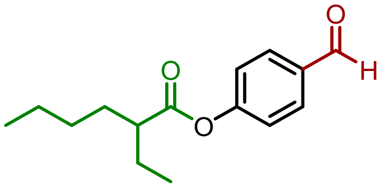
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2n** as a colorless oil (79% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 7.94 (d, *J* = 1.8 Hz, 2H), 7.93 – 7.91 (m, 1H).



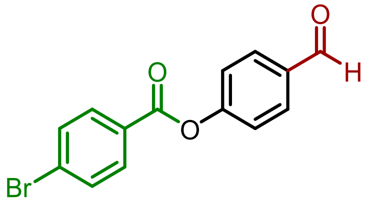
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2o** as a colorless oil (72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 8.03 (s, 1H), 7.59 – 7.53 (m, 2H).



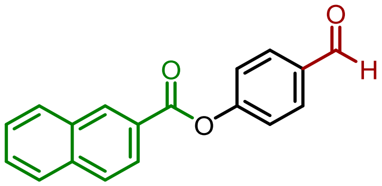
Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2p** as a colorless oil (70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.95 – 7.91 (m, 2H), 7.27 – 7.24 (m, 2H), 2.59 – 2.50 (m, 1H), 1.85 – 1.75 (m, 2H), 1.73 – 1.62 (m, 2H), 1.40 – 1.36 (m, 4H), 1.03 (t, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.1, 174.3, 155.6, 133.9, 131.3, 122.5, 47.4, 31.7, 29.7, 25.5, 22.7, 14.0, 11.9.



Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2q** as a colorless oil (69% yield).

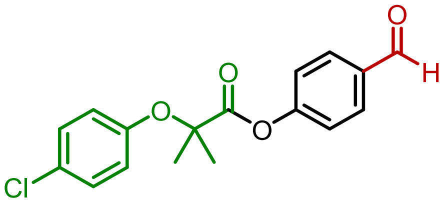
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.10 – 8.04 (m, 2H), 8.02 – 7.97 (m, 2H), 7.71 – 7.66 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.0, 163.9, 155.4, 134.2, 132.2, 131.8, 131.4, 129.4, 127.8, 122.5.



Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2r** as a colorless oil (72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.05 (s, 1H), 8.81 (s, 1H), 8.19 (dd, *J* = 8.6, 1.7

Hz, 1H), 8.05 – 7.98 (m, 4H), 7.96 – 7.93 (m, 1H), 7.69 – 7.59 (m, 2H), 7.51 – 7.46 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.1, 164.8, 155.8, 136.0, 134.1, 132.5, 132.3, 131.4, 129.6, 129.0, 128.6, 127.9, 127.1, 126.1, 125.4, 122.7.



Following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **2s** as a colorless oil (67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.04 – 9.96 (m, 1H), 7.98 – 7.88 (m, 2H), 7.29 – 7.17 (m, 4H), 6.95 – 6.85 (m, 2H), 1.75 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 190.8, 172.2, 155.1, 153.9, 134.3, 131.3, 129.4, 127.8, 122.2, 120.5, 79.6, 25.3.

9. Spectra of prepared compounds

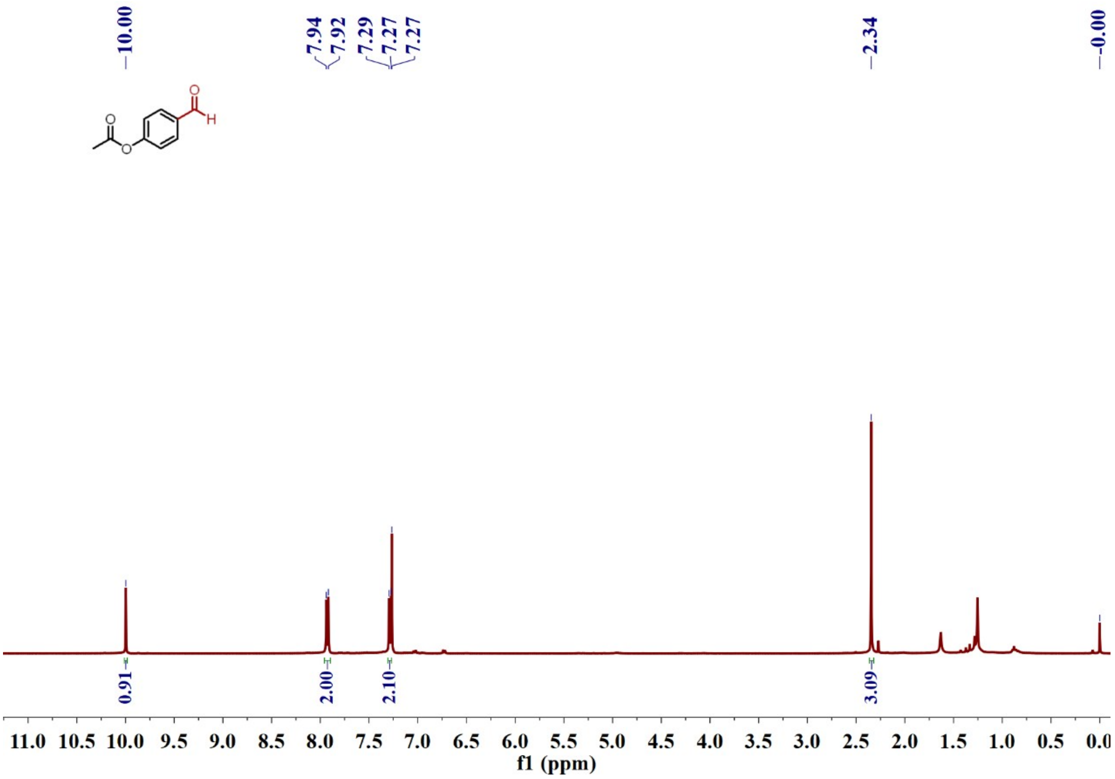


Fig. S5 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2b**.

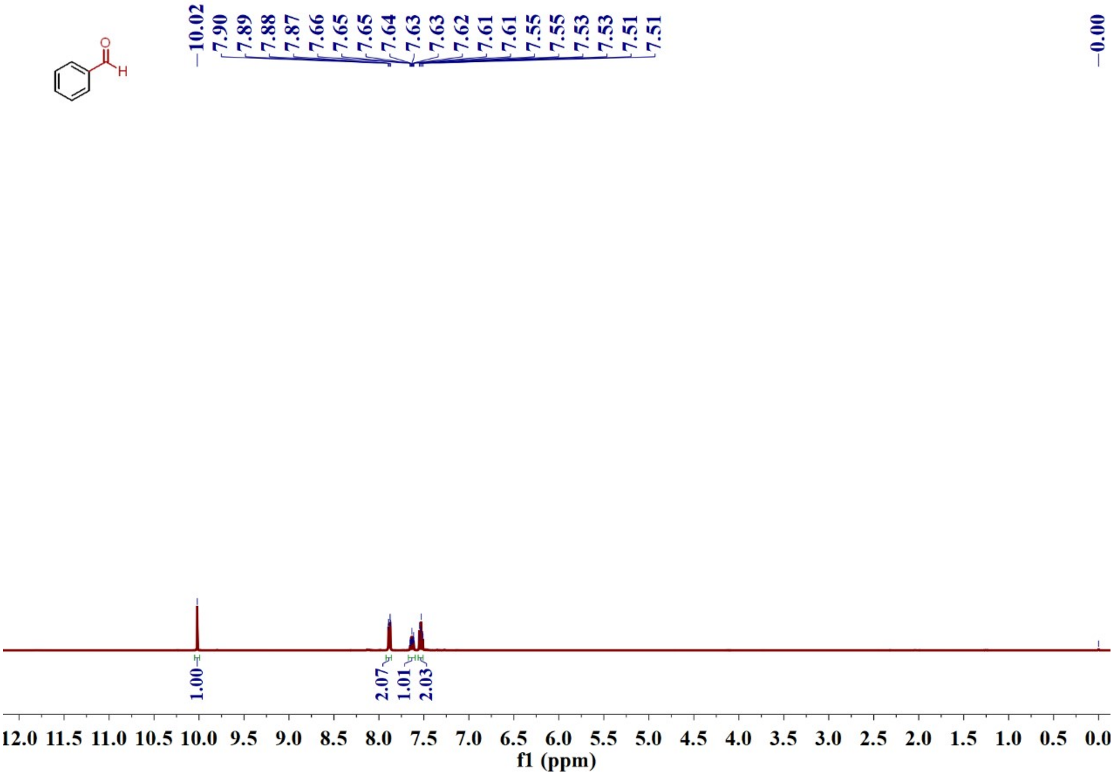


Fig. S6 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2c**.

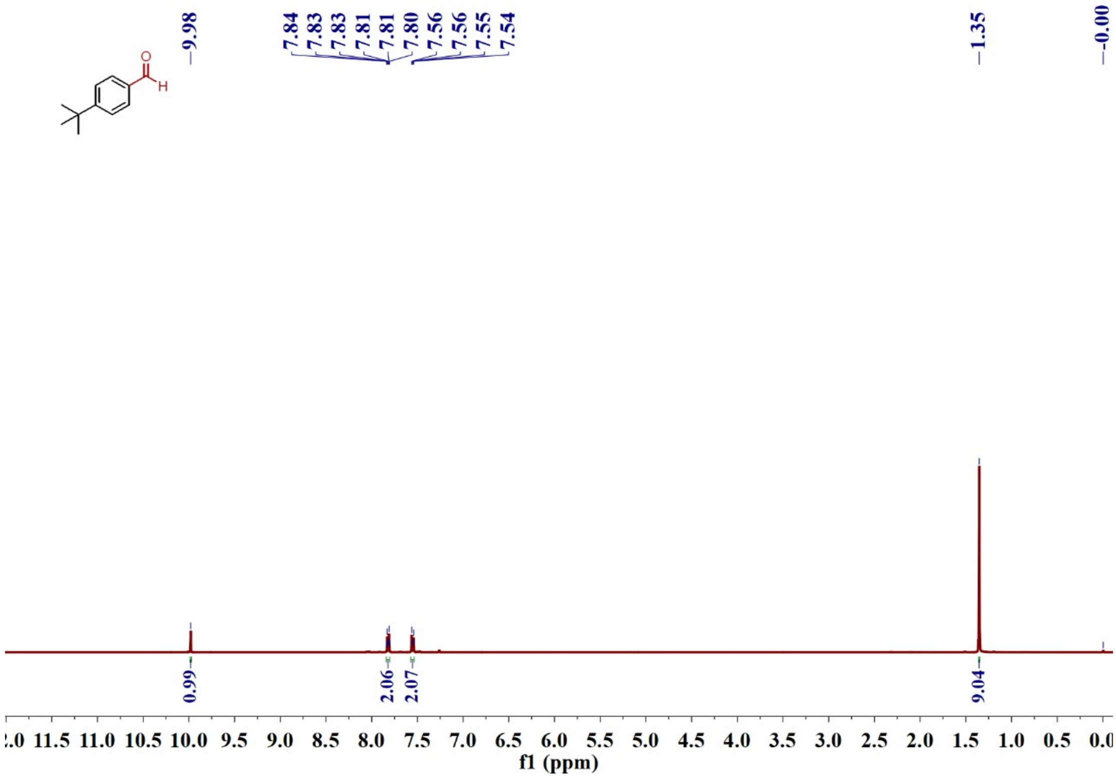


Fig. S7 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2d**.

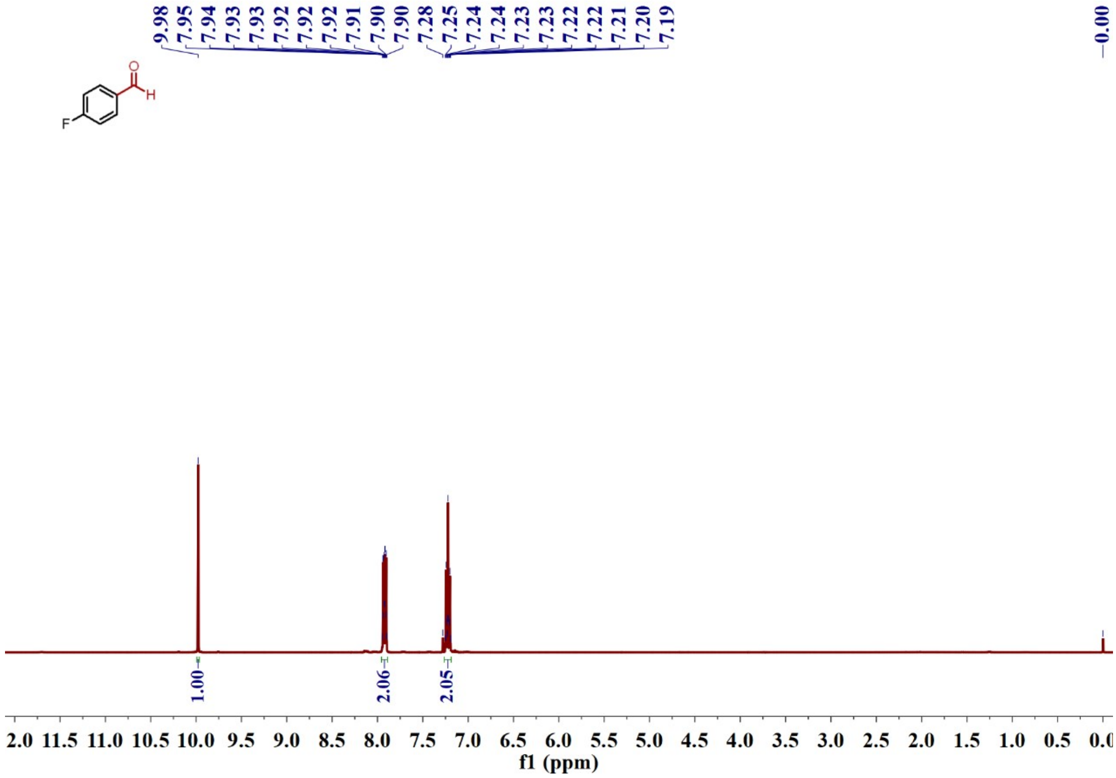


Fig. S8 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2e**.

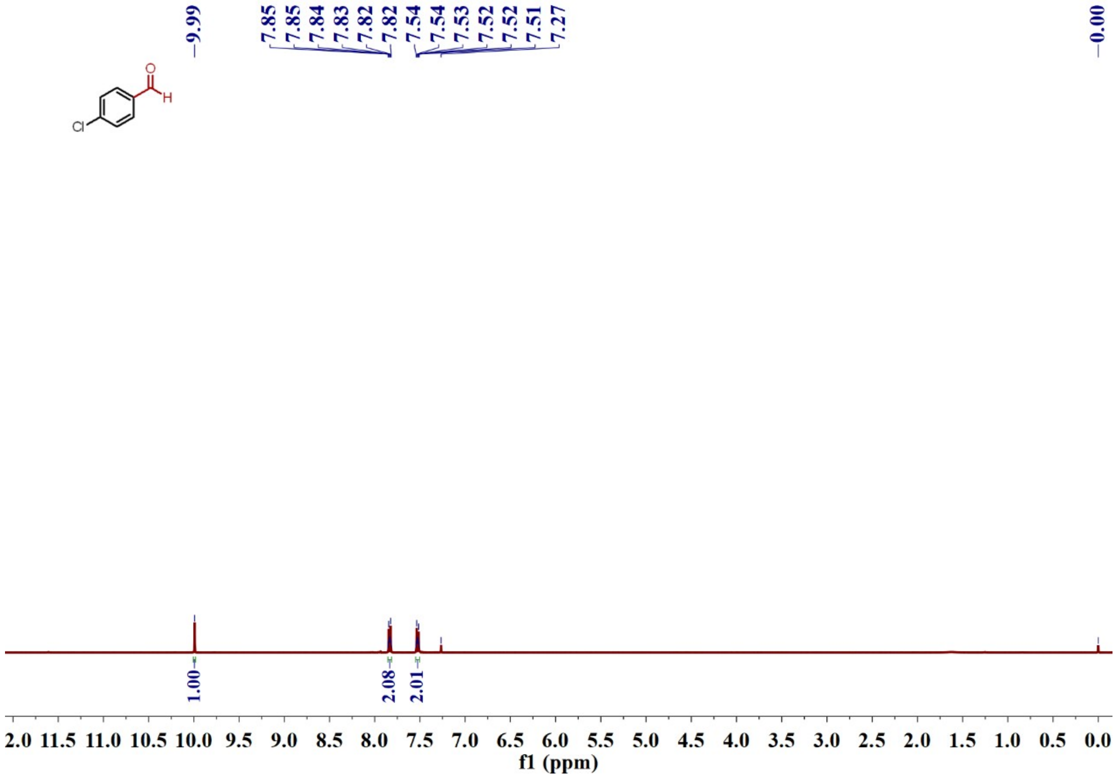


Fig. S9 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2f**.

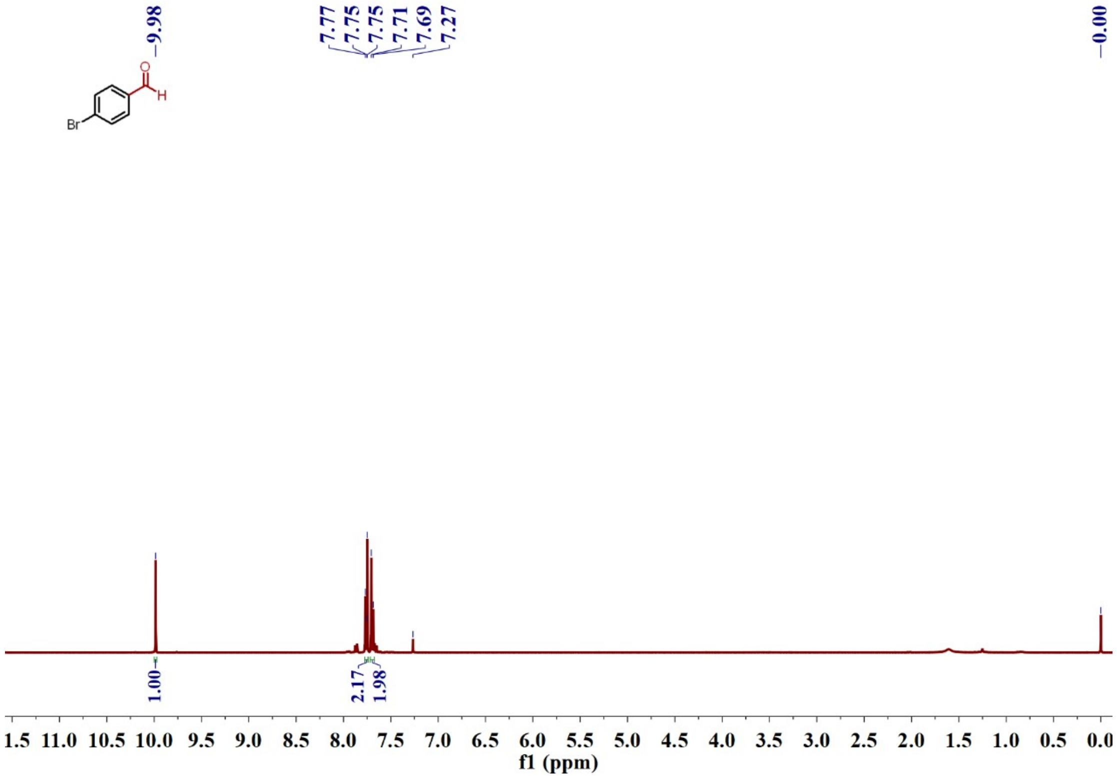


Fig. S10 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2g**.

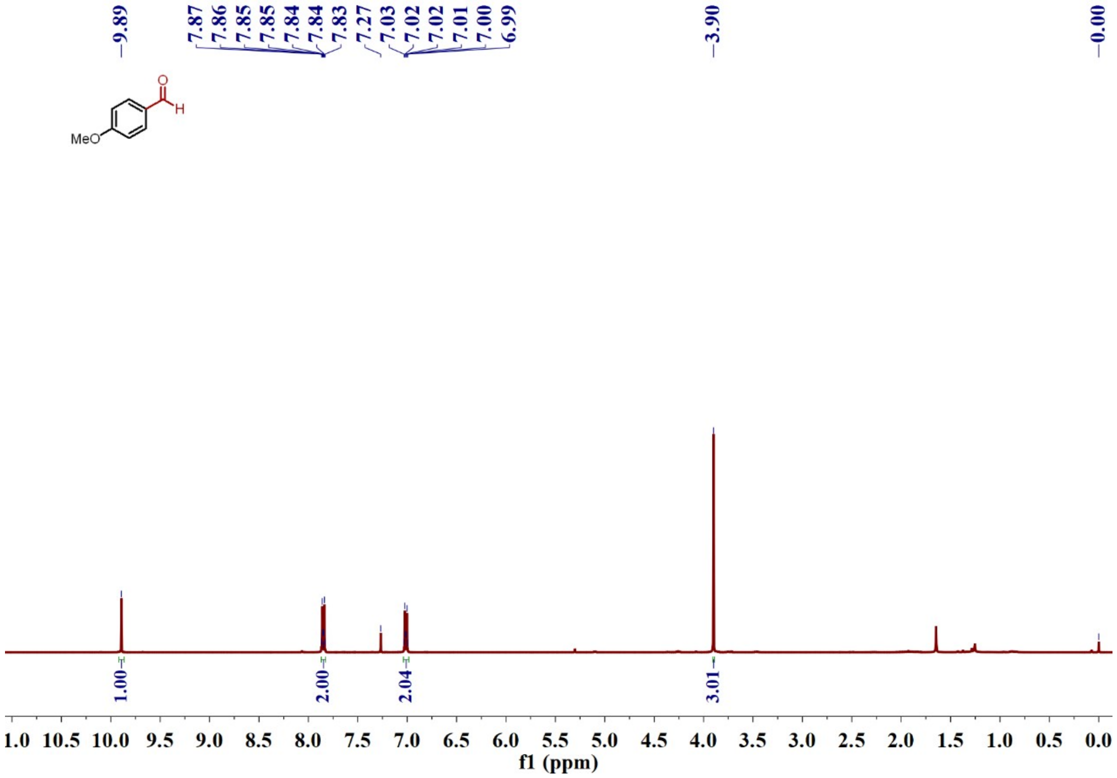


Fig. S11 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2h**.

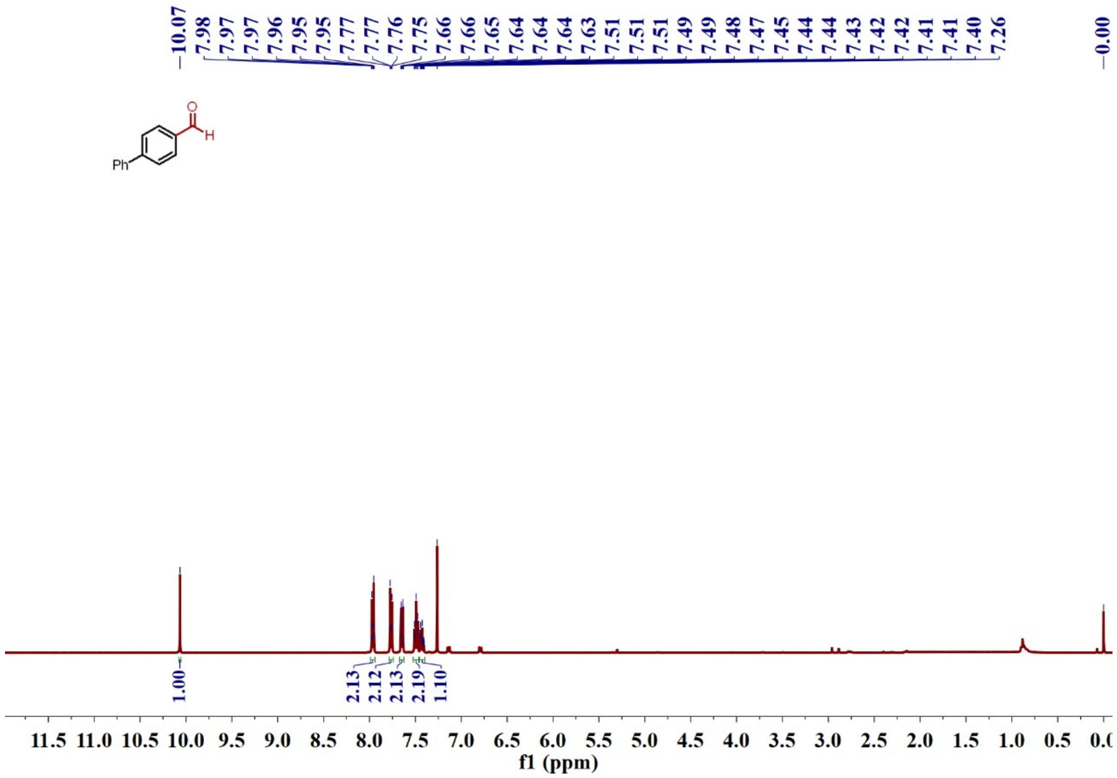


Fig. S12 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2i**.

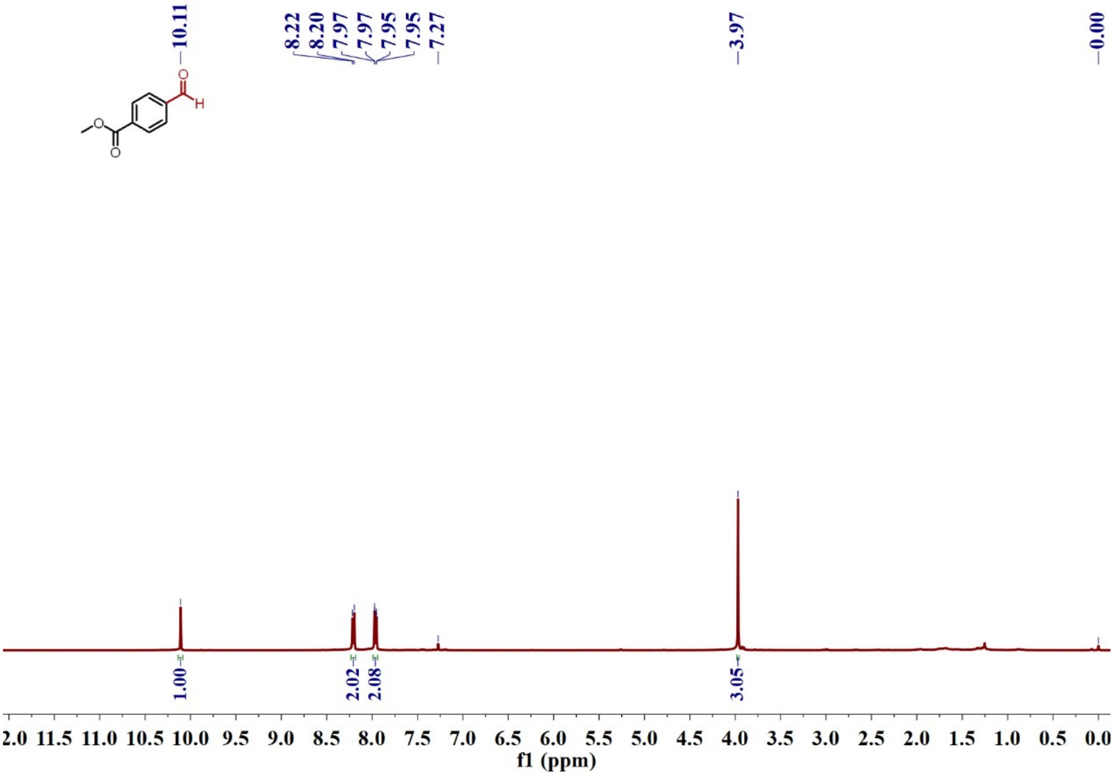


Fig. S13 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2j**.

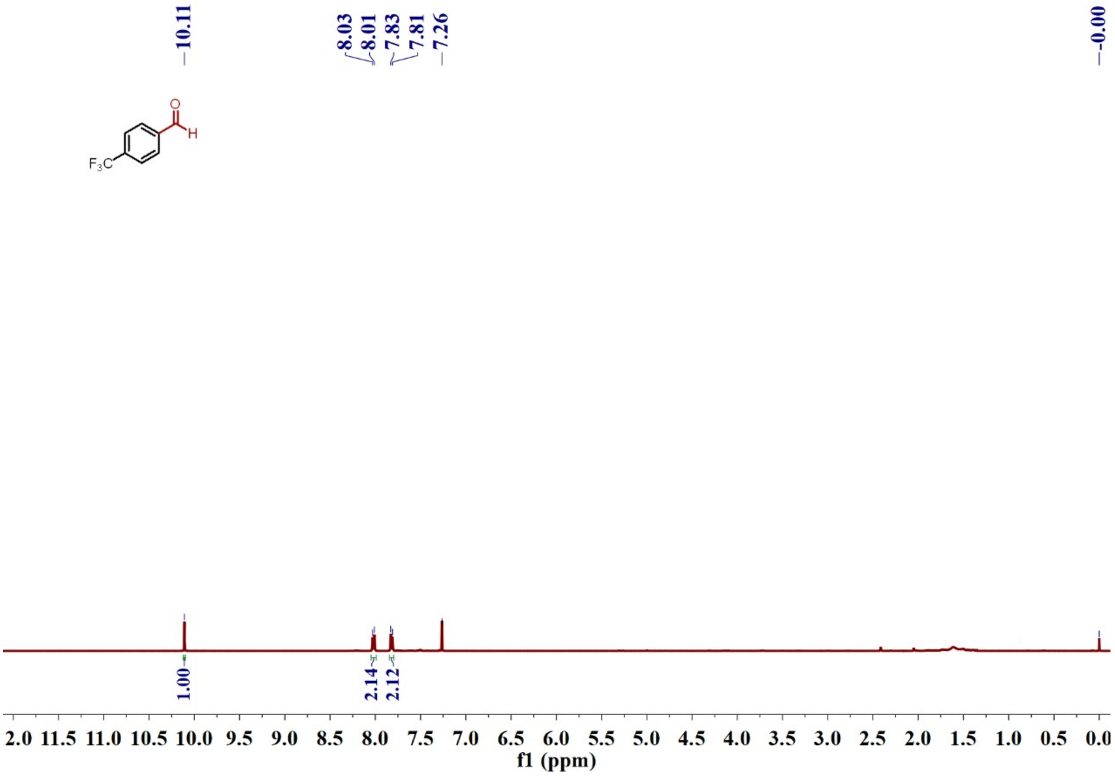


Fig. S14 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2k**.

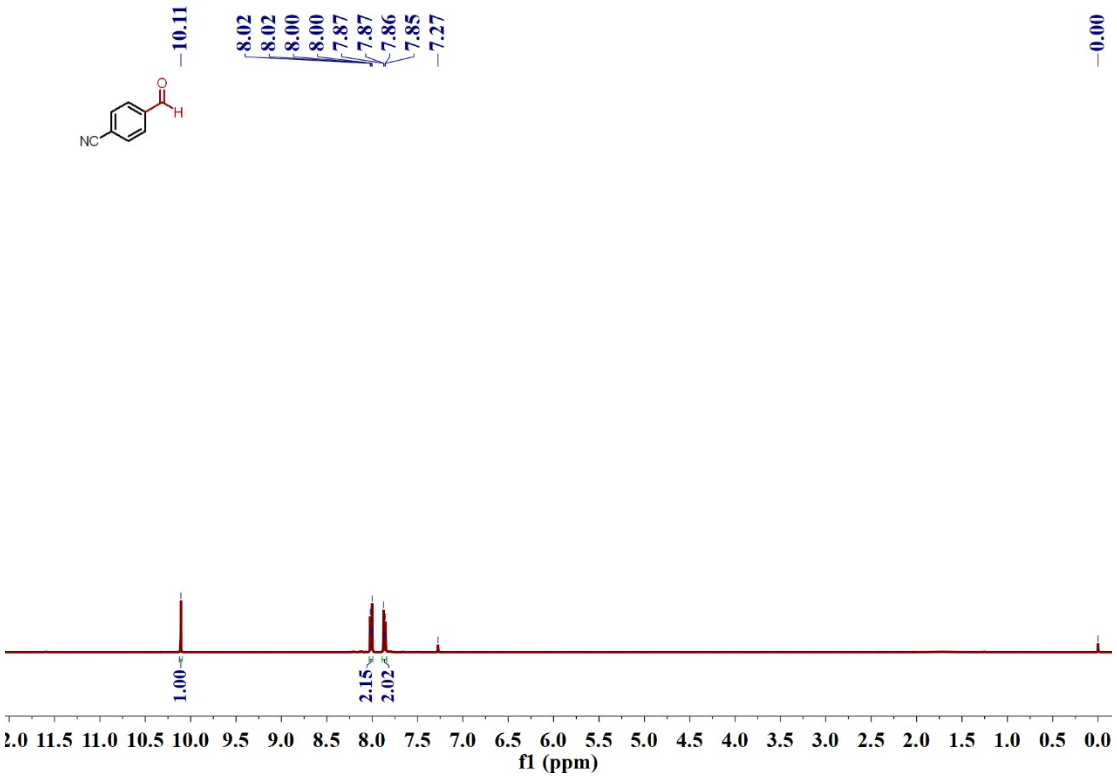


Fig. S15 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2l**.

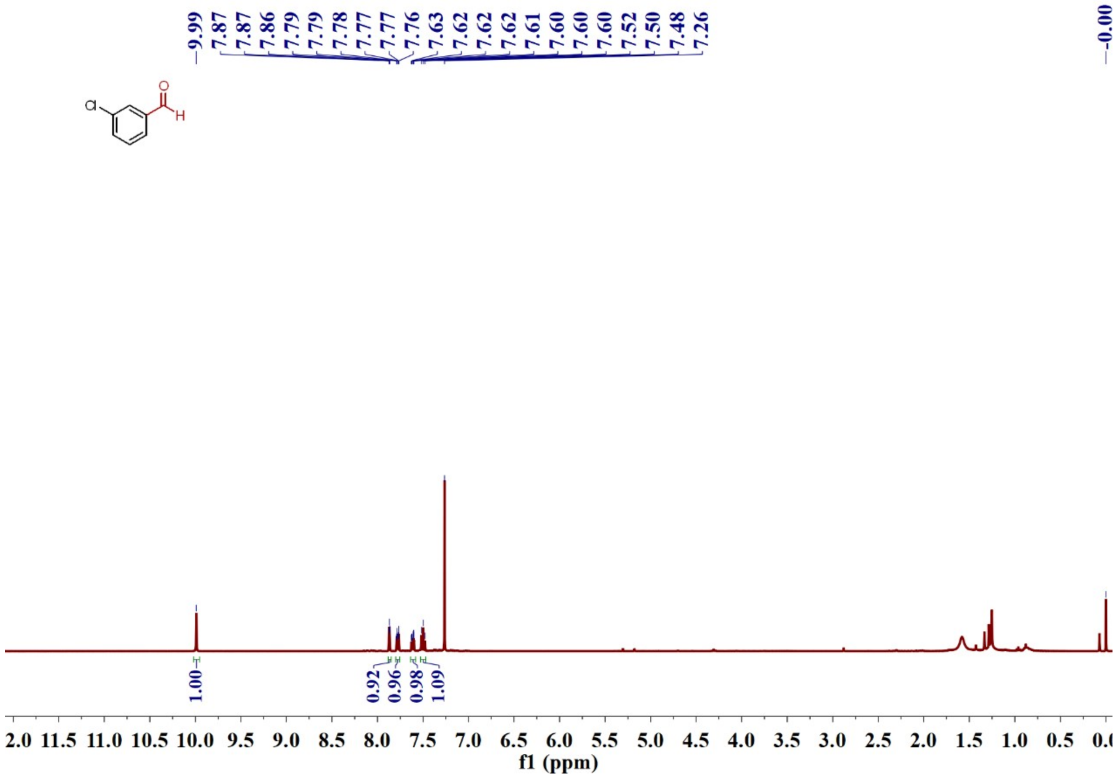


Fig. S16 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2m**.

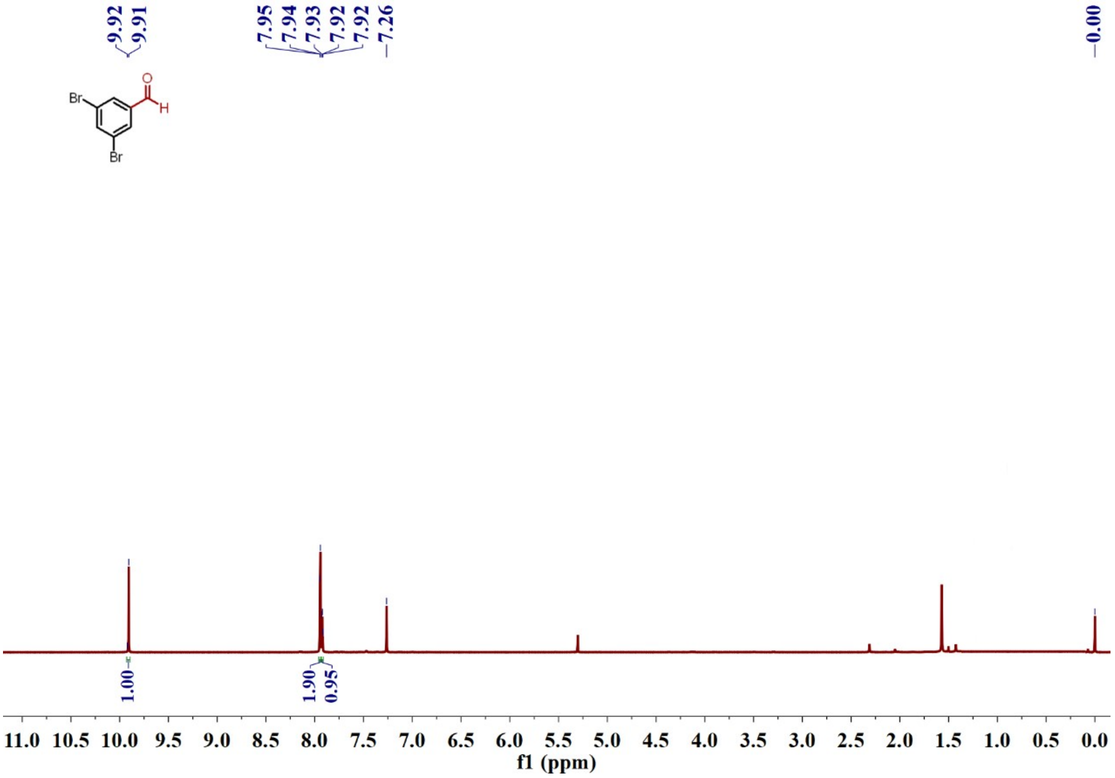


Fig. S17 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2n**.

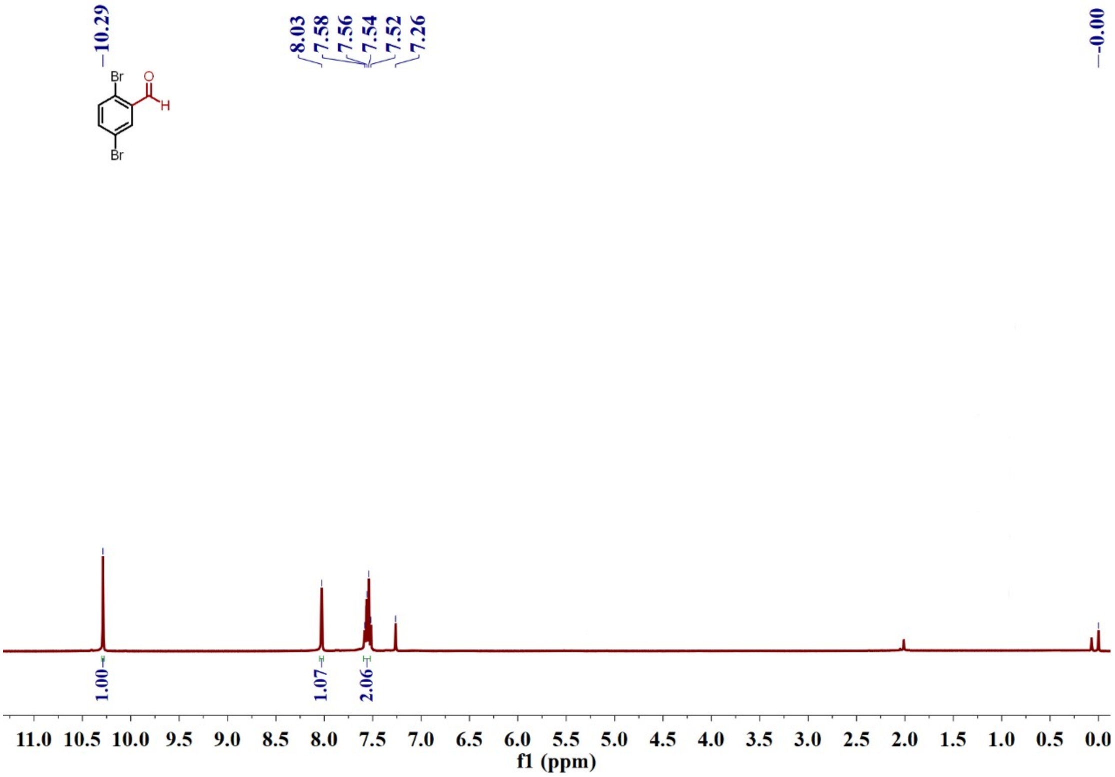


Fig. S18 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2o**.

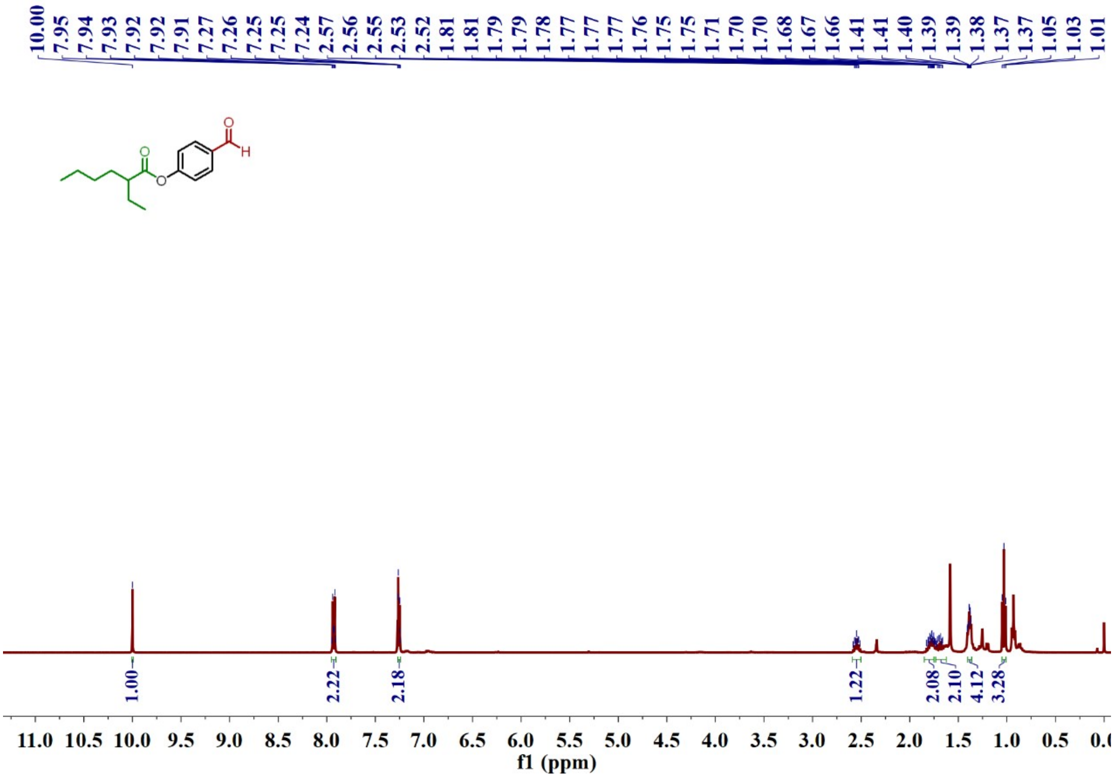


Fig. S19 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2p**.

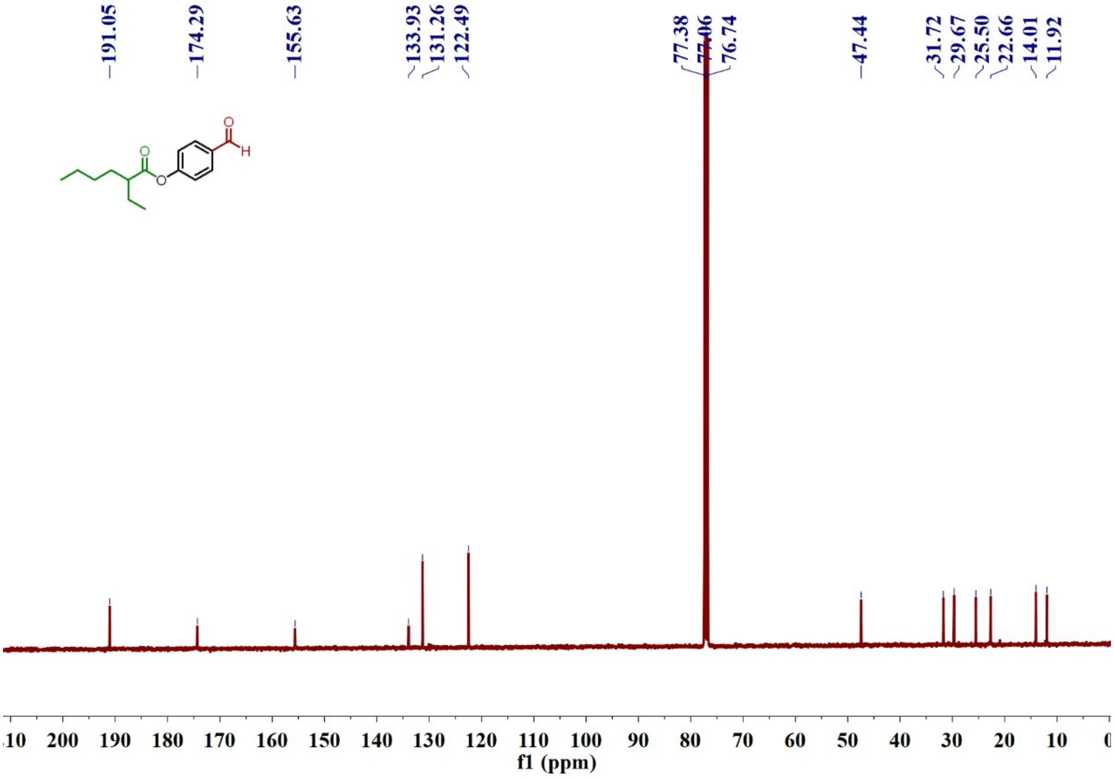


Fig. S20 ^{13}C NMR (101 MHz, Chloroform-d) spectrum of compound **2p**.

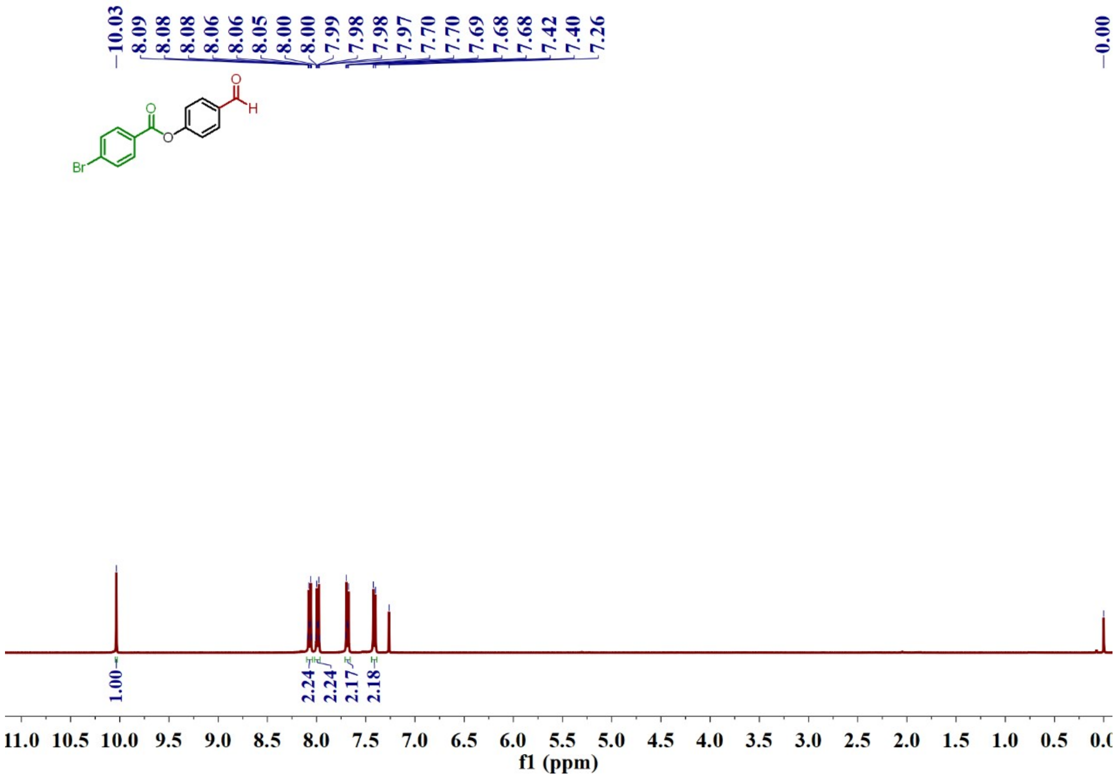


Fig. S21 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2q**.

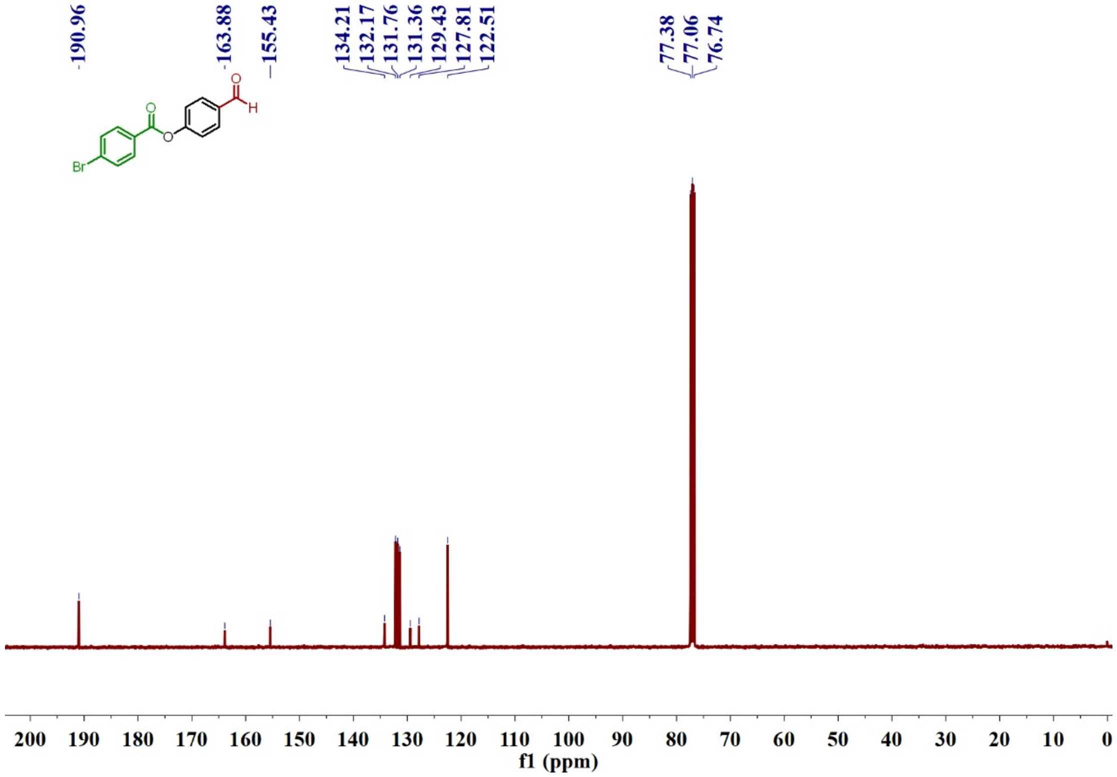


Fig. S22 ^{13}C NMR (101 MHz, Chloroform-d) spectrum of compound **2q**.

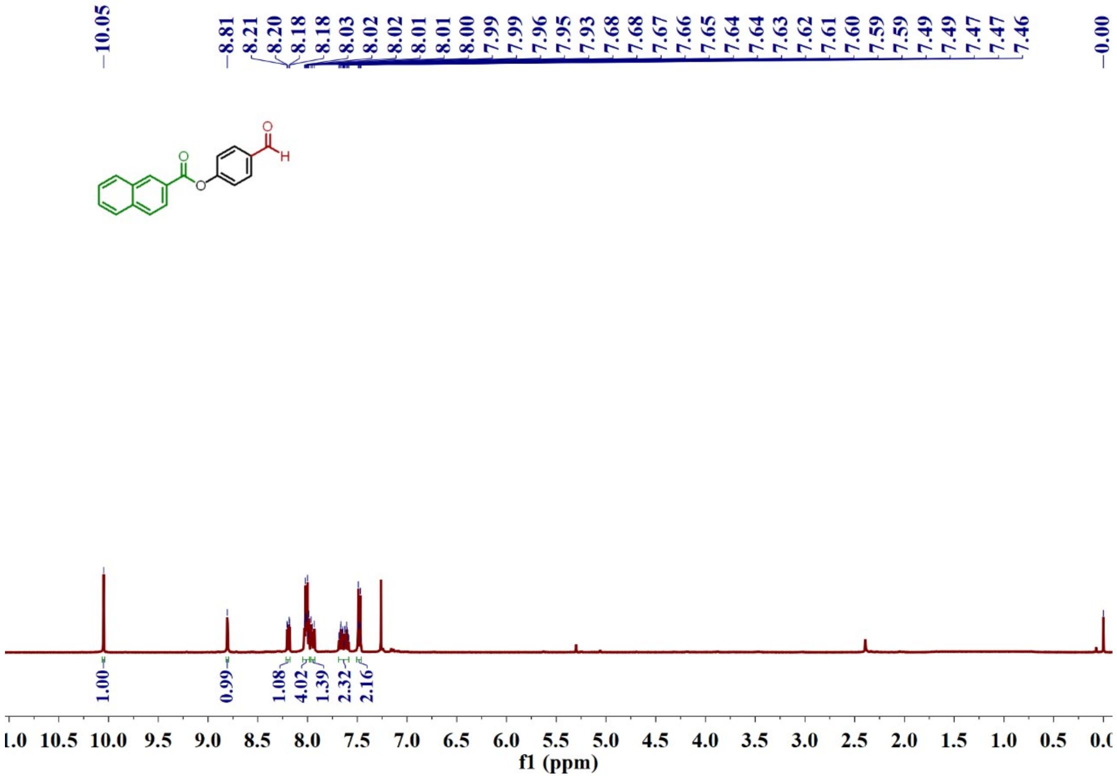


Fig. S23 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2r**.

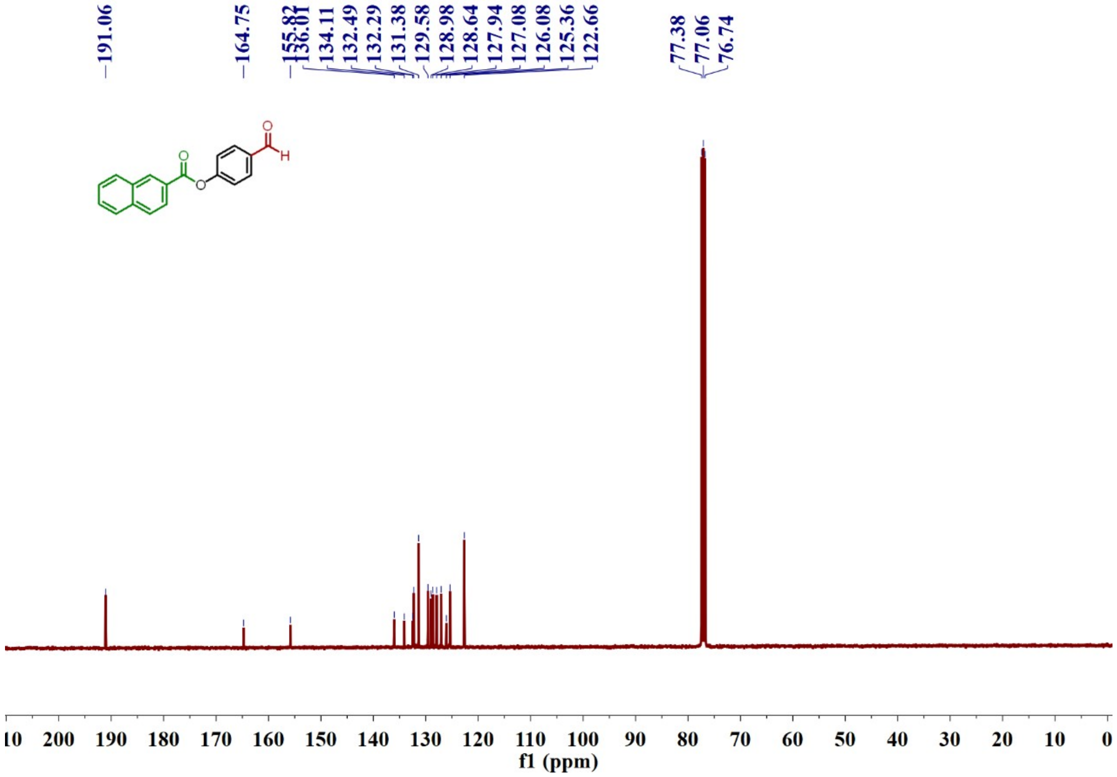


Fig. S24 ^{13}C NMR (101 MHz, Chloroform-d) spectrum of compound **2r**.

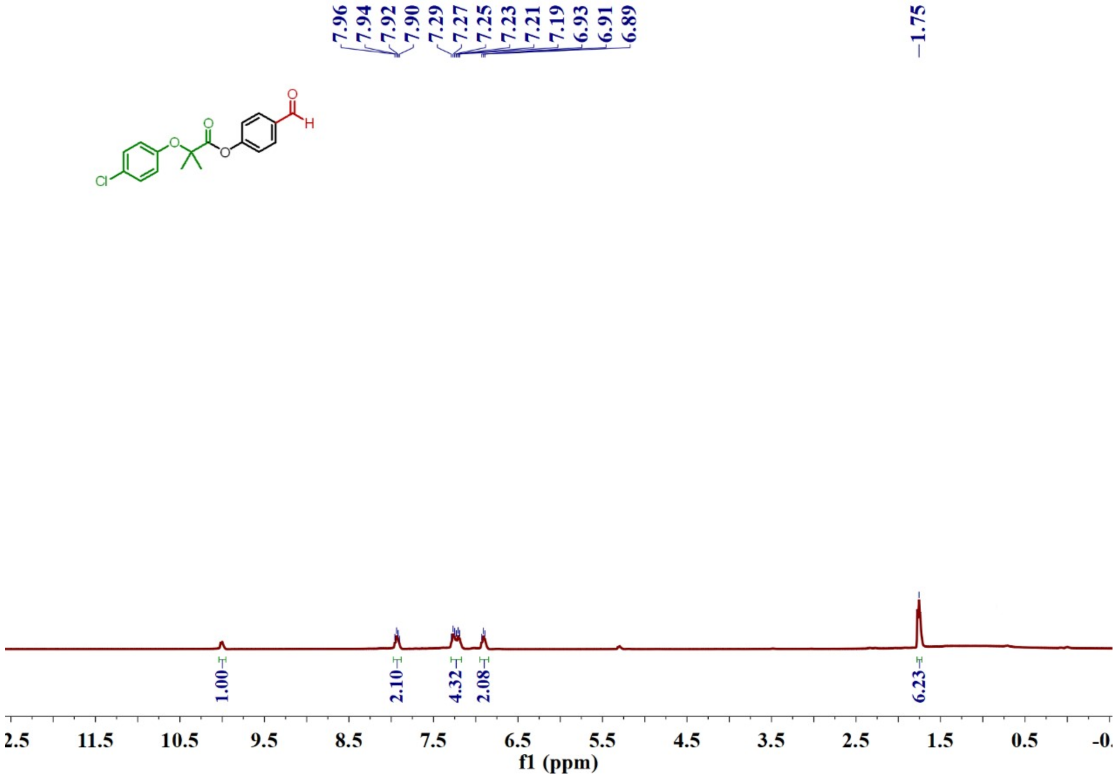


Fig. S25 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **2s**.

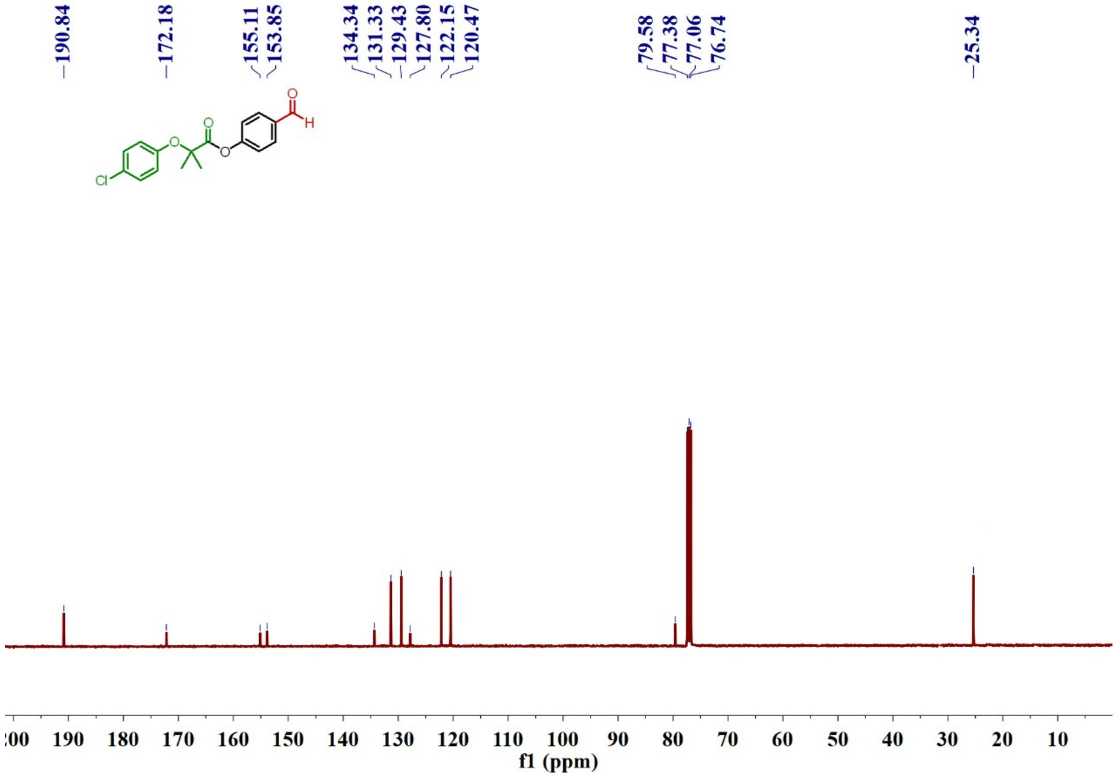


Fig. S26 ^{13}C NMR (101 MHz, Chloroform-d) spectrum of compound **2s**.