SUPPORTING INFORMATION

ortho-C(sp^3)−H Arylation of Aromatic Aldehydes Using 2-Amino-*N*-methyl-acetamide as L,L-Type Transient Directing Group

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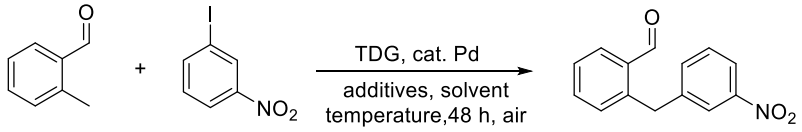
1. General Information

All reagents and all solvents were obtained from commercial sources and used as received without further purification unless otherwise stated. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Petroleum ether refers to the fraction boiling in the 60-90°C range. Reaction products were purified via column chromatography on silica gel (300-400 mesh). GC yields were detemined on GC-9680II via standard curve method with toluene as an internal standard. ^{1}H NMR spectra were recorded on Bruker DPX-500 instrument (500 MHz) in Chloroform-*d* and MeOD with tetramethylsilane (TMS) as an internal standard. Chemical shifts δ were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-500 (125 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. ^{19}F NMR spectra were recorded on Bruker DPX-500 instrument (470 MHz) and Chemical shifts were reported in ppm. High resolution mass spectra (HRMS) data were measured on an ESI-microTOF II spectrometer. X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Yields refers to isolated yield of analytically pure material unless otherwise noted. The known compounds were identified by comparison of their physical and spectral data with those reported in the literature.

2. Experimental Procedures

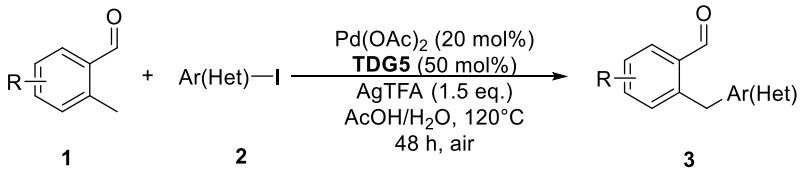
2.1 Optimization of the Reaction Conditions



1a **2a** **3a**

A reaction tube (10 mL) with magnetic stir bar was charged with 2-Methylbenzaldehyde **1a** (12.0 mg, 0.1 mmol), palladium catalyst (0.01 mmol), **TDG** (0.05 mmol) and solvent (1mL) in air. The reaction mixture was stirred at room temperature for 10 min. Then 1-iodo-3-nitrobenzene **2a** (29.9 mg, 0.12 mmol) and siliver salts (0.15 mmol) were added into the tube followed by heating to desired temperature for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through a silica gel plug, and evaporated all solvents under reduced pressure. The resultant residue was dissolved in DCM (1 mL), added toluene (9.2 mg, 0.1 mmol) as an internal standard and analyzed by GC to abtained the yield.

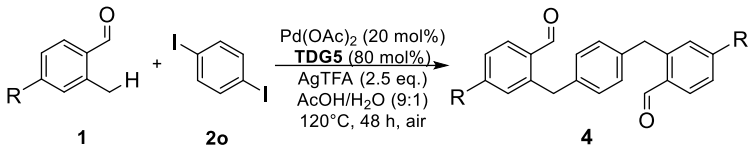
2.2 General Procedure for the Synthesis of 2-Benzylbenzaldehydes 3



1 **2** **3**

A reaction tube (25 mL) with magnetic stir bar was charged with aldehyde substrate **1** (0.5 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), 2-Amino-*N*-methyl-acetamide (**TDG5**, 22.0 mg, 0.25 mmol), HOAc (4.5 mL) and H_2O (0.5 mL) in air. The reaction mixture was stirred at room temperature for 10 min. Then aryl iodide **2** (0.6 mmol) and AgTFA (165 mg, 0.75 mmol) were added into the tube followed by heating to 120°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered throught a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product.

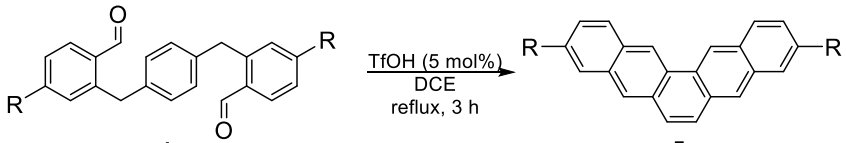
2.3 General Procedure for Further Arylation with 1,4-Diiodobenzene



1 **2o** **4**

A reaction tube (25 mL) with magnetic stir bar was charged with aldehyde substrate **1** (1.25 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), 2-Amino-*N*-methyl-acetamide (**TDG5**, 35.2 mg, 0.4 mmol), HOAc (4.5 mL) and H_2O (0.5 mL) in air. The reaction mixture was stirred at room temperature for 10 min. Then aryl iodide **2o** (165 mg, 0.5 mmol) and AgTFA (275 mg, 1.25 mmol) were added into the tube followed by heating to 120°C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered throught a silica gel plug, and concentrated in *vacuo*. The crude reaction mixture was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product.

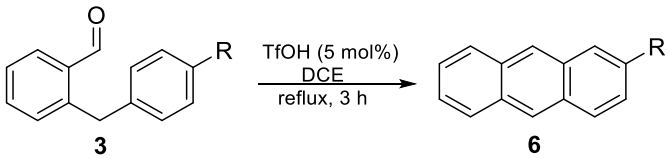
2.4 General Procedure for Cycloaromatization of Further Arylation Products



4 **5**

A round bottom flask (50 mL) with magnetic stir bar was charged with further arylation product **4** (0.2 mmol), TfOH (1.5 mg, 0.01 mmol) and DCE (25mL). The reaction mixture was heated to reflux for 3 h to remove water. The progress of the reactions was monitored by TLC until completion. After cooling to ambient temperature, the reaction mixture was concentrated in *vacuo* and purified by flash silica gel column chromatography using petroleum ether as the eluent to afford the desired product.

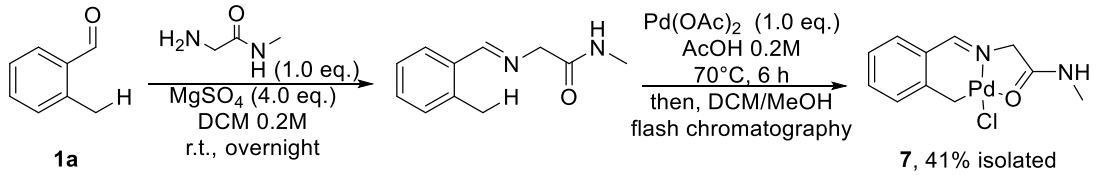
2.5 General Procedure for Cycloaromatization of Arylation Products



3 **6**

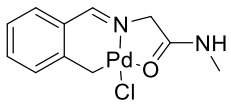
A round bottom flask (50 mL) with magnetic stir bar was charged with arylation product **3** (0.2 mmol), TfOH (1.5 mg, 0.01 mmol) and DCE (25mL). The reaction mixture was heated to reflux for 3 h to remove water. The progress of the reactions was monitored by TLC until completion. After cooling to ambient temperature, the reaction mixture was concentrated in *vacuo* and purified by flash silica gel column chromatography using petroleum ether as the eluent to afford the desired product.

2.6 Procedure for the Synthesis of Palladacycle 7 and Its arylation



1a **7**, 41% isolated

To a solution of **1a** (60.0 mg, 0.5 mmol) and 2-Amino-*N*-methyl-acetamide (44.0 mg, 0.5 mmol) in DCM (2.5 mL) was added $MgSO_4$ (240.7 mg, 2.0 mmol). The reaction mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered and concentrated in *vacuo* to give the imine as a colorless oil. To a solution of imine in AcOH (2.5 mL) was added $Pd(OAc)_2$ (112.0 mg, 0.5 mmol), and the resulting suspension was stirred for 6 h at 70°C. The reaction mixture was cooled to room temperature and purified by flash chromatography using DCM/MeOH as eluent to afford **7** (67.6 mg, 41%) as a yellow solid. Stereochemistry was confirmed by X-Ray analysis of the crystal obtained using chloroform/acetonitrile as recrystallization solvents.

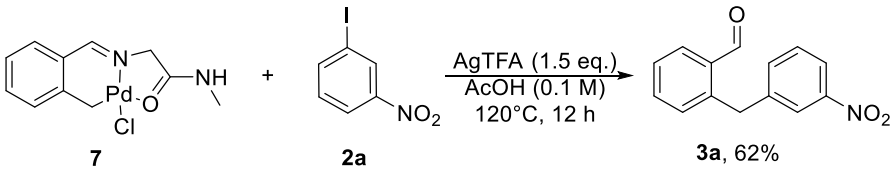


Palladacycle 7

^{1}H NMR (500 MHz, Methanol-d_4) δ 8.22 (s, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 4.71 (s, 2H), 3.44 (s, 2H), 2.80 (s, 3H).

^{13}C NMR (126 MHz, Methanol-d_4) δ 163.57, 144.69, 134.64, 133.30, 132.89, 129.19, 127.10, 124.69, 63.96, 56.09, 25.58.

HRMS (ESI): *m/z* calculated for $C_{11}H_{13}ClN_2NaOPd^+$ $[M+Na]^+$ 352.9643; found 352.9642.

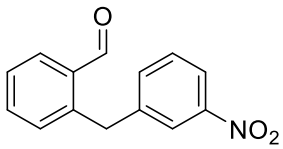


7 **2a** **3a**, 62%

A sealed tube with magnetic stir bar was charged with **2a** (37.4 mg, 0.15 mmol), AgTFA (33 mg, 0.15 mmol) and **7** (33.0 mg, 0.1 mmol) in air. Then, AcOH (1 mL) was added as solvent. The reaction mixture was stirred at room temperature for 10 minutes, then at 120°C for 12 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a silica plug, and concentrated in *vacuo*. The crude reaction mixture

was purified by flash chromatography using petroleum ether/ethyl acetate as eluent to afford **3a** (14.9 mg, 62%) as a colorless oil.

3. Analytical data

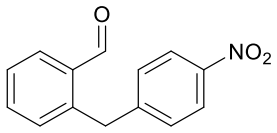


2-(3-nitrobenzyl)benzaldehyde (3a)

Following the general procedure, compound **3a** was isolated as a colorless oil (91.9 mg, 76% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 4.55 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.82, 148.43, 142.44, 140.78, 135.15, 134.79, 134.15, 133.89, 131.96, 129.31, 127.74, 123.57, 121.44, 38.09.

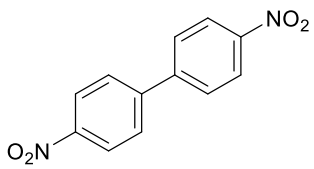


2-(4-nitrobenzyl)benzaldehyde (3b)

When reaction completed, the crude reaction mixture was purified by flash silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 150:1), only afford a mixture of the desired product **3b** and an inseparable by-product **S1**. The yield of compound 3b was determined by ^{1}H NMR (59.0 mg, 49%). The physical and spectral data are in accordance with literature values[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 7.86 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 (td, *J* = 7.5, 1.6 Hz, 1H), 7.51 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 3H), 4.55 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.78, 148.11, 146.55, 140.62, 134.78, 134.09, 133.93, 131.99, 129.58, 127.74, 123.71, 38.38.

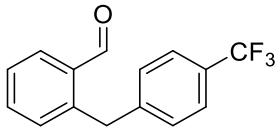


4,4'-dinitrobiphenyl (S1)

The yield of compound **S1** was determined by ^{1}H NMR (8.9 mg, 6%) based on 1-iodo-4-nitrobenzene. The spectral data are in accordance with literature values[3].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 4H), 7.79 (d, *J* = 8.8 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.08, 145.02, 128.37, 124.43.

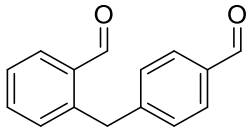


2-(4-(trifluoromethyl)benzyl)benzaldehyde (3c)

Following the general procedure, compound **3c** was isolated as a colorless oil (95.0 mg, 72% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[4].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 3H), 4.51 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.66, 144.44, 141.61, 134.04, 133.94, 133.77, 131.84, 129.14, 128.73, 128.48, 127.44, 125.49, 125.46, 125.43, 125.40, 38.11.

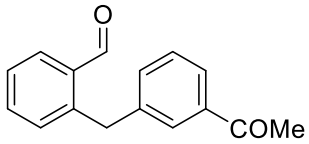


2-(4-formylbenzyl)benzaldehyde (3d)

Following the general procedure, compound **3d** was isolated as a yellow oil (72.0 mg, 64% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 9.96 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.23 (m, 3H), 4.54 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.68, 192.00, 147.66, 141.36, 134.05, 133.96, 133.89, 131.92, 130.06, 129.49, 128.98, 127.51, 38.54.

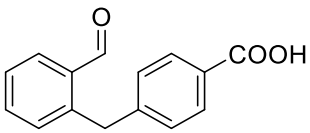


2-(3-acetylbenzyl)benzaldehyde (3e)

Following the general procedure, compound **3e** was isolated as a yellow oil (83.3 mg, 70% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.85 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.26 (s, 1H), 4.51 (s, 2H), 2.56 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.34, 192.70, 142.12, 140.95, 137.40, 134.08, 133.87, 133.69, 133.44, 131.76, 128.82, 128.61, 127.33, 126.52, 38.08, 26.73.



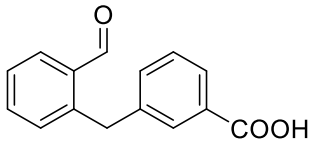
4-(2-formylbenzyl)benzoic acid (3f)

Following the general procedure, compound **3f** was isolated as a yellow solid (71.0 mg, 59% yield)

by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.23 (m, 3H), 4.52 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.71, 172.11, 146.77, 141.66, 134.08, 133.93, 133.60, 131.88, 130.54, 129.00, 127.43, 38.38.

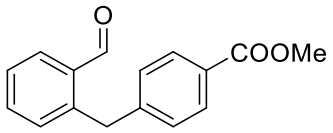


3-(2-formylbenzyl)benzoic acid (3g)

Following the general procedure, compound **3g** was isolated as a yellow solid (80.0 mg, 66% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.04 (s, 1H), 10.20 (s, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.91 (s, 1H), 7.85 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 4.51 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.74, 172.24, 142.06, 140.86, 134.41, 134.11, 133.88, 133.44, 131.78, 130.49, 129.64, 128.77, 128.28, 127.35, 37.97.

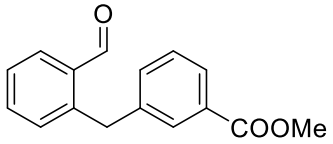


methyl 4-(2-formylbenzyl)benzoate (3h)

Following the general procedure, compound **3h** was isolated as a yellow oil (66.0 mg, 52% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.50 (s, 2H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.54, 167.01, 145.74, 141.82, 134.01, 133.95, 133.33, 131.81, 129.88, 128.86, 128.27, 127.35, 52.07, 38.25.

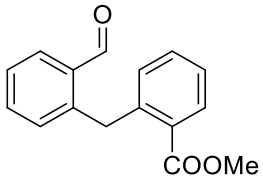


methyl 3-(2-formylbenzyl)benzoate (3i)

Following the general procedure, compound **3i** was isolated as a yellow oil (86.3 mg, 68% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.90 – 7.82 (m, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 4.8 Hz, 2H), 7.25 (s, 1H), 4.50 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.61, 167.13, 142.20, 140.69, 134.05, 133.89, 133.51, 133.18, 131.74, 130.44, 129.93, 128.65, 127.64, 127.27, 52.16, 37.97.



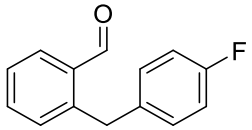
methyl 2-(2-formylbenzyl)benzoate (3j)

Following the general procedure, compound **3j** was isolated as a yellow oil (30.5 mg, 24% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 150:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.84 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.57, 175.54, 145.90, 145.51, 141.58, 134.00, 133.88, 132.29, 132.26, 131.98, 131.17, 130.95, 126.78, 126.51, 52.03, 36.27. C17H18ClO2+ [M+H] + 289.0990, 289.0988.

HRMS (ESI): *m/z* calculated for $C_{16}H_{15}O_3^+$ $[M+H]^+$ 255.1016; found 255.1018.



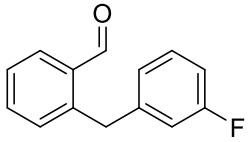
2-(4-fluorobenzyl)benzaldehyde (3k)

Following the general procedure, compound **3k** was isolated as a yellow oil (56.7 mg, 53% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 500:1). The physical and spectral data are in accordance with literature values[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.16 – 7.03 (m, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 4.42 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.54, 162.46, 142.77, 135.99, 133.98, 133.89, 132.90, 131.61, 130.27, 130.21, 127.17, 115.44, 115.27, 37.37.

^{19}F NMR (470 MHz, $CDCl_3$) δ -116.96.



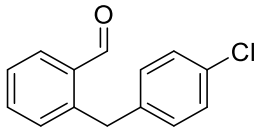
2-(3-fluorobenzyl)benzaldehyde (3l)

Following the general procedure, compound **3l** was isolated as a yellow oil (77.7 mg, 73% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 500:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.86 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.55 (td, *J* = 7.4, 1.4 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.19 (m, 3H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.89 (td, *J* = 8.3, 2.6 Hz, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 4.45 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.54, 163.99, 162.04, 142.92, 142.86, 142.03, 134.04, 133.93, 133.05, 131.77, 130.00, 129.93, 127.33, 124.51, 124.48, 115.81, 115.64, 113.32, 113.15, 37.90, 37.89.

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.22.

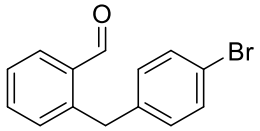


2-(4-chlorobenzyl)benzaldehyde (3m)

Following the general procedure, compound **3m** was isolated as a yellow oil (67.9 mg, 59% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 500:1). The physical and spectral data are in accordance with literature values[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.41 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.58, 142.33, 138.81, 134.01, 133.89, 133.18, 132.11, 131.68, 130.19, 128.68, 127.26, 37.58.

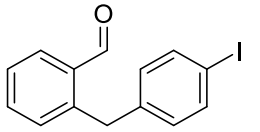


2-(4-bromobenzyl)benzaldehyde (3n)

Following the general procedure, compound **3n** was isolated as a yellow oil (92.1 mg, 67% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[4].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.85 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 0.9 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 4.40 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.56, 142.21, 139.32, 133.99, 133.90, 133.21, 131.67, 131.62, 130.58, 127.26, 120.17, 37.64.

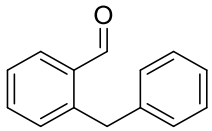


2-(4-iodobenzyl)benzaldehyde (3o)

Following the general procedure, compound **3o** was isolated as a yellow oil (41.9 mg, 26% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[4].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.84 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.56, 142.15, 140.02, 137.60, 133.99, 133.89, 133.22, 131.69, 130.92, 127.27, 91.55, 37.74.



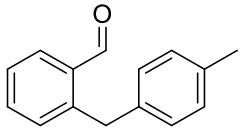
2-benzylbenzaldehyde (3p)

Following the general procedure, compound **3p** was isolated as a colorless oil (55.8 mg, 57% yield)

by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[5].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.21 – 7.18 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 4.45 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.47, 143.04, 140.33, 133.99, 132.10, 131.72, 128.84, 128.63, 127.06, 126.35, 38.08.

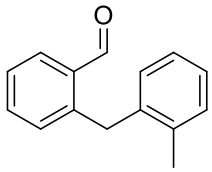


2-(4-methylbenzyl)benzaldehyde (3q)

Following the general procedure, compound **3q** was isolated as a yellow oil (70.0 mg, 67% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 4.40 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.44, 143.38, 137.27, 135.87, 133.96, 133.94, 131.85, 131.63, 129.31, 128.68, 126.96, 37.64, 21.04.

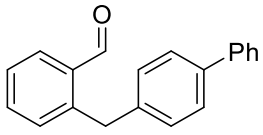


2-(2-methylbenzyl)benzaldehyde (3r)

Following the general procedure, compound **3r** was isolated as a yellow oil (50.4 mg, 48% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 4.43 (s, 2H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.66, 142.69, 138.24, 136.53, 134.07, 133.96, 132.38, 130.80, 130.28, 129.46, 126.82, 126.64, 126.22, 35.73, 19.66.

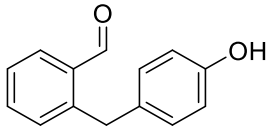


2-([1,1'-biphenyl]-4-ylmethyl)benzaldehyde (3s)

Following the general procedure, compound **3s** was isolated as a yellow oil (100.6 mg, 74% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 150:1). The physical and spectral data are in accordance with literature values[4].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 3H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 4.48 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.52, 142.93, 140.91, 139.45, 139.30, 134.03, 132.36, 131.78, 129.24, 128.80, 127.36, 127.21, 127.14, 127.07, 37.78.

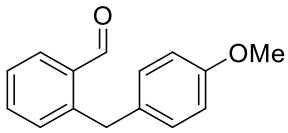


2-(4-hydroxybenzyl)benzaldehyde (3t)

Following the general procedure, compound **3t** was isolated as a yellow oil (71.0 mg, 67% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.36 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.85, 154.18, 143.64, 134.12, 133.83, 132.40, 132.05, 131.60, 129.93, 127.00, 115.51, 37.26.

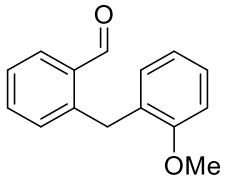


2-(4-methoxybenzyl)benzaldehyde (3u)

Following the general procedure, compound **3u** was isolated as a yellow oil (77.4 mg, 68% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.85 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.38 (s, 2H), 3.76 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.47, 158.12, 143.57, 133.96, 133.92, 132.43, 131.98, 131.55, 129.78, 126.95, 114.04, 77.34, 77.09, 76.84, 55.29, 37.21.

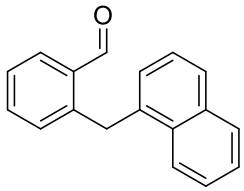


2-(2-methoxybenzyl)benzaldehyde (3v)

Following the general procedure, compound **3v** was isolated as a yellow oil (26.0 mg, 23% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 300:1). The physical and spectral data are in accordance with literature values[6].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.90 – 6.82 (m, 2H), 4.41 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.49, 157.03, 143.34, 134.06, 133.87, 131.34, 130.28, 130.11, 128.79, 127.81, 126.71, 120.66, 110.34, 55.27, 31.89.



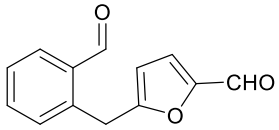
2-(naphthalen-1-ylmethyl)benzaldehyde (3w)

Following the general procedure, compound **3w** was isolated as a yellow oil (18.5 mg, 15% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 300:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.98 – 7.92 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.02 (m, 2H), 4.92 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.73, 142.70, 136.06, 135.50, 133.99, 132.42, 132.01, 131.16, 129.21, 128.81, 127.37, 127.17, 126.93, 126.25, 125.81, 125.63, 123.85, 35.22.

HRMS (ESI): *m/z* calculated for $C_{18}H_{15}O^+$ $[M+H]^+$ 247.1117; found 247.1115.

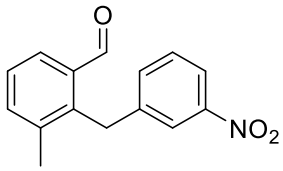


5-(2-formylbenzyl)furan-2-carbaldehyde (3x)

Following the general procedure, compound **3x** was isolated as a yellow oil (20.3 mg, 19% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 100:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.53 (s, 1H), 7.85 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 3.6 Hz, 1H), 6.20 (d, *J* = 3.5 Hz, 1H), 4.55 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.73, 177.25, 160.97, 152.24, 137.78, 134.47, 134.14, 133.81, 131.81, 127.97, 110.22, 31.83.

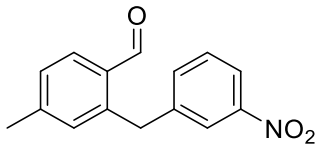


3-methyl-2-(3-nitrobenzyl)benzaldehyde (3aa)

Following the general procedure, compound **3aa** was isolated as a yellow solid (82 mg, 64% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 4.62 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.27, 148.46, 141.87, 139.07, 138.30, 136.40, 134.67, 134.39, 132.70, 129.29, 127.65, 122.89, 121.26, 33.37, 19.61.

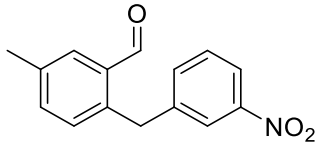


4-methyl-2-(3-nitrobenzyl)benzaldehyde (3ab)

Following the general procedure, compound **3ab** was isolated as a yellow solid (99.7 mg, 78% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.10 (s, 1H), 4.51 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.42, 148.38, 145.30, 142.63, 140.73, 135.18, 135.08, 132.80, 131.62, 129.26, 128.43, 123.53, 121.36, 38.04, 21.85.

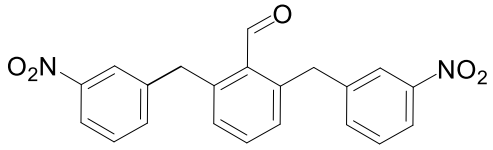


5-methyl-2-(3-nitrobenzyl)benzaldehyde (3ac)

Following the general procedure, compound **3ac** was isolated as a yellow solid (86.7 mg, 68% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.97 (s, 1H), 7.65 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 4.50 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.96, 148.38, 142.80, 137.79, 137.62, 135.22, 135.11, 134.90, 133.70, 131.97, 129.25, 123.48, 121.34, 37.68, 20.86.



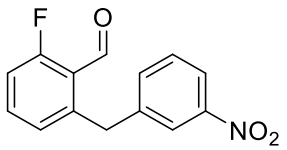
2,6-bis(3-nitrobenzyl)benzaldehyde (3ad)

Following the general procedure, compound **3ad** was isolated as a yellow oil (101.5 mg, 54% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.06 (dt, *J* = 6.9, 2.3 Hz, 2H), 7.95 (s, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.27 (d, *J* = 7.6 Hz, 2H), 4.48 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.19, 148.48, 142.35, 142.23, 134.85, 134.07, 132.09, 131.39, 129.55, 123.36, 121.62, 38.69.

HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_2O_5^+$ $[M+H]^+$ 377.1132; found 377.1134.



2-fluoro-6-(3-nitrobenzyl)benzaldehyde (3ae)

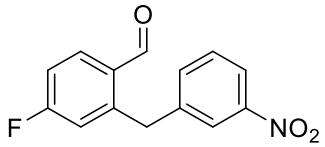
Following the general procedure, compound **3ae** was isolated as a yellow oil (68.1 mg, 53% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical

and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.99 (s, 1H), 7.60 – 7.52 (m, 2H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.14 (dd, *J* = 10.3, 8.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 4.51 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.75, 188.66, 167.93, 165.88, 148.38, 142.59, 141.92, 135.80, 135.72, 135.29, 129.24, 127.71, 127.68, 123.60, 122.18, 122.13, 121.47, 115.42, 115.25, 38.45, 38.43.

^{19}F NMR (470 MHz, $CDCl_3$) δ -120.12.



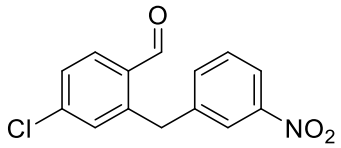
4-fluoro-2-(3-nitrobenzyl)benzaldehyde (3af)

Following the general procedure, compound **3af** was isolated as a yellow oil (87.8 mg, 68% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.07 (dd, *J* = 8.0, 2.3 Hz, 1H), 8.01 (s, 1H), 7.89 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.17 (td, *J* = 8.0, 2.3 Hz, 1H), 6.97 (dd, *J* = 9.5, 2.6 Hz, 1H), 4.56 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.13, 166.79, 164.73, 148.47, 144.43, 144.36, 141.48, 137.45, 137.37, 135.16, 130.52, 130.50, 129.53, 123.63, 121.73, 119.06, 118.88, 114.88, 114.71, 37.86.

^{19}F NMR (470 MHz, $CDCl_3$) δ -102.33.

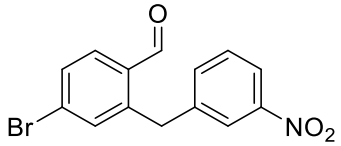


4-chloro-2-(3-nitrobenzyl)benzaldehyde (3ag)

Following the general procedure, compound **3ag** was isolated as a yellow oil (77.0 mg, 56% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 8.00 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.27 (s, 1H), 4.53 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.39, 148.49, 142.63, 141.49, 140.59, 135.81, 135.08, 132.27, 131.94, 129.52, 128.04, 123.60, 121.75, 37.73.

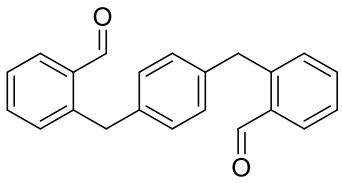


4-bromo-2-(3-nitrobenzyl)benzaldehyde (3ah)

Following the general procedure, compound **3ah** was isolated as a yellow oil (98.0 mg, 61% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[1].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 8.00 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.43 (m, 3H), 4.52 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.61, 148.49, 142.61, 141.51, 135.78, 135.06, 134.90, 132.65, 131.09, 129.53, 129.49, 123.59, 121.76, 37.67.

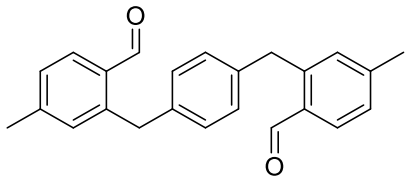


2,2'-(1,4-phenylenebis(methylene))dibenzaldehyde (4oa)

Following the general procedure, compound **4oa** was isolated as a yellow oil (86.3 mg, 55% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[7].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.04 (s, 4H), 4.40 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.47, 143.02, 138.30, 133.98, 132.07, 131.70, 128.99, 127.04, 37.62.

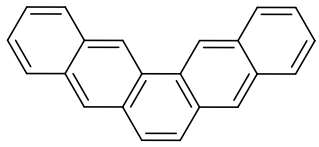


2,2'-(1,4-phenylenebis(methylene))bis(4-methylbenzaldehyde) (4ob)

Following the general procedure, compound **4ob** was isolated as a yellow oil (130.0 mg, 76% yield) by silica gel column chromatography (eluent : petroleum ether/ ethyl acetate = 75:1). The physical and spectral data are in accordance with literature values[7].

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.05 (s, 2H), 7.04 (s, 4H), 4.35 (s, 4H), 2.37 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.07, 145.00, 143.02, 138.37, 132.48, 132.32, 131.70, 128.90, 127.82, 37.54, 21.84.

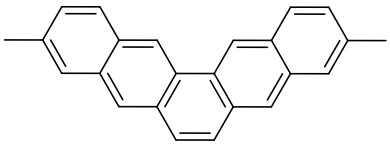


pentacene (5oa)

Following the general procedure, compound **5oa** was isolated as a white solid (53.4 mg, 96% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[7].

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 2H), 8.27 (s, 2H), 8.16 (d, *J* = 7.4 Hz, 2H), 8.04 (d, *J* = 7.1 Hz, 2H), 7.66 (s, 2H), 7.58 (ddd, *J* = 6.8, 4.0, 1.7 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.40, 132.21, 130.71, 129.12, 128.44, 127.75, 127.59, 126.89, 126.07, 125.95, 121.96.

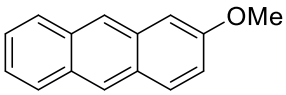


3,10-dimethylpentaphene (5ob)

Following the general procedure, compound **5ob** was isolated as a white solid (54.4 mg, 89% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[7].

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 2H), 8.17 (s, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 2H), 7.63 (s, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 2.59 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.65, 132.55, 130.76, 130.64, 128.54, 128.47, 128.21, 127.52, 126.39, 126.04, 121.50, 21.98.

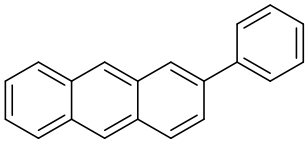


2-methoxyanthracene (6a)

Following the general procedure, compound **6a** was isolated as a white solid (32.8 mg, 79% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[8].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.26 (s, 1H), 7.94 (t, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.42 (dt, *J* = 21.3, 6.7 Hz, 2H), 7.18 (s, 1H), 7.15 (d, *J* = 9.4 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.20, 132.74, 132.23, 130.38, 129.88, 128.32, 128.29, 127.63, 126.27, 125.57, 124.48, 124.22, 120.60, 103.59, 55.31.



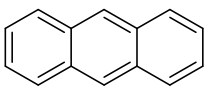
2-phenylanthracene (6b)

Following the general procedure, compound **6b** was isolated as a yellow solid (44.2 mg, 87% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[9].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.44 (s, 1H), 8.20 (s, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.04 – 7.99 (m, 2H), 7.81 – 7.73 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.09, 137.85, 132.10, 131.91, 131.86, 130.91, 128.94, 128.80, 128.26, 128.19, 127.47, 127.39, 126.60, 126.05, 125.70, 125.57, 125.53, 125.43.

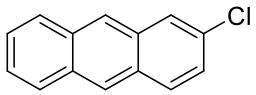
HRMS (ESI): *m/z* calculated for $C_{20}H_{15}^{+}$ $[M+H]^{+}$ 255.1168; found 255.1169.



anthracene (6c)

Following the general procedure, compound **6c** was isolated as a white solid (25.2 mg, 71% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[8].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.03 – 7.97 (m, 4H), 7.49 – 7.43 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 131.73, 128.21, 126.26, 125.38.



2-chloroanthracene (6d)

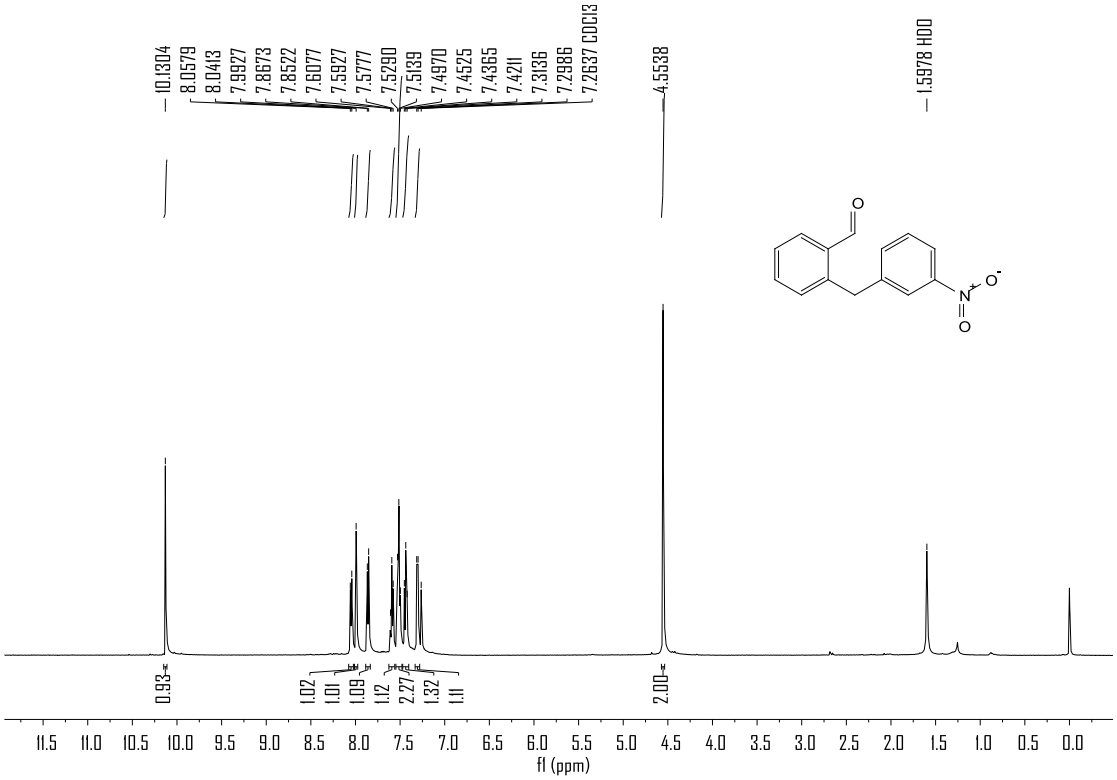
Following the general procedure, compound **6c** was isolated as a white solid (24.6 mg, 58% yield) by silica gel column chromatography (eluent : petroleum ether). The physical and spectral data are in accordance with literature values[8].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.32 (s, 1H), 8.02 – 7.96 (m, 3H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.38 (d, *J* = 9.0 Hz, 1H).

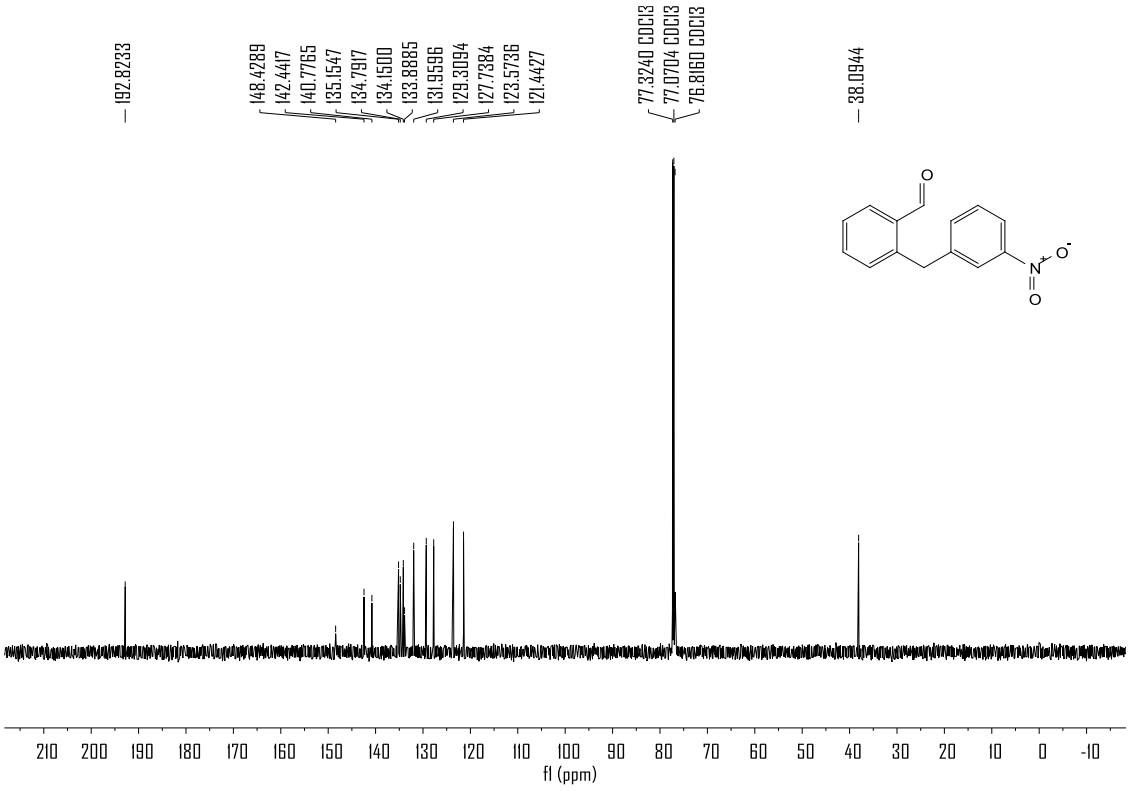
^{13}C NMR (126 MHz, $CDCl_3$) δ 132.23, 131.81, 131.76, 131.11, 129.94, 129.74, 128.27, 128.10, 126.65, 126.56, 126.38, 126.07, 125.74, 125.43.

4. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of Compounds

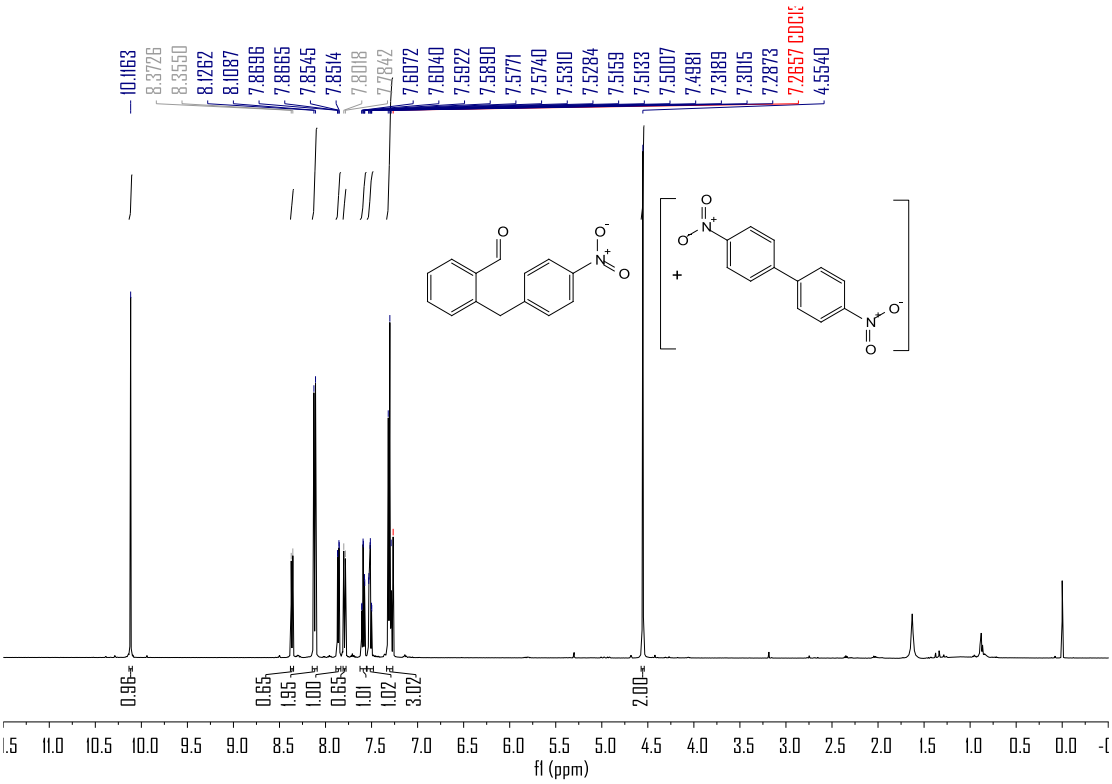
^{1}H NMR spectrum of compound 3a ($CDCl_3$, 500 MHz)



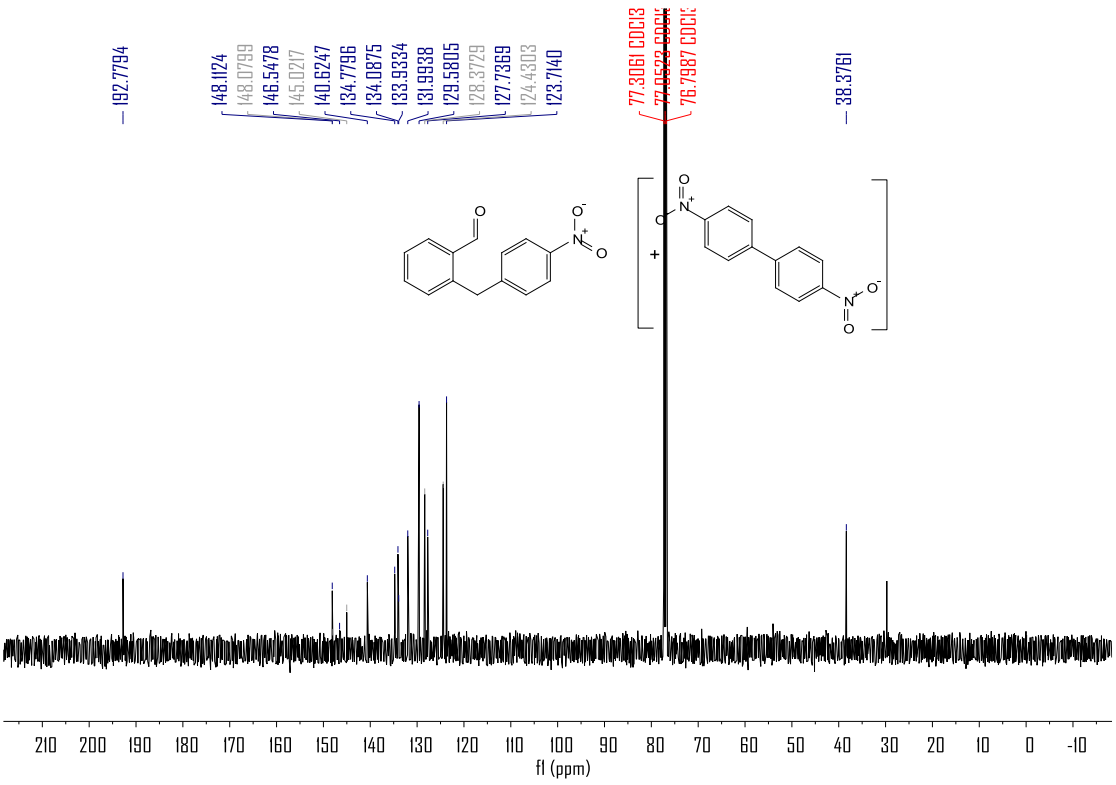
^{13}C NMR spectrum of compound 3a ($CDCl_3$, 126 MHz)



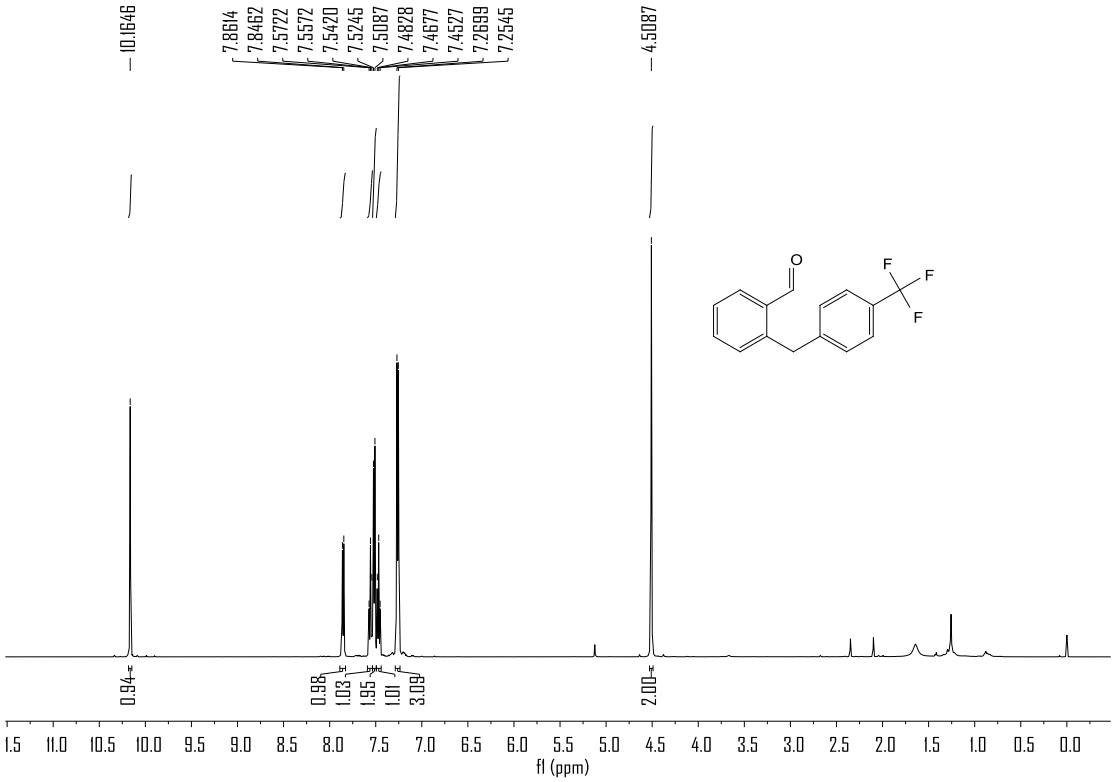
^{1}H NMR spectrum of compound 3b and S1 ($CDCl_3$, 500 MHz)



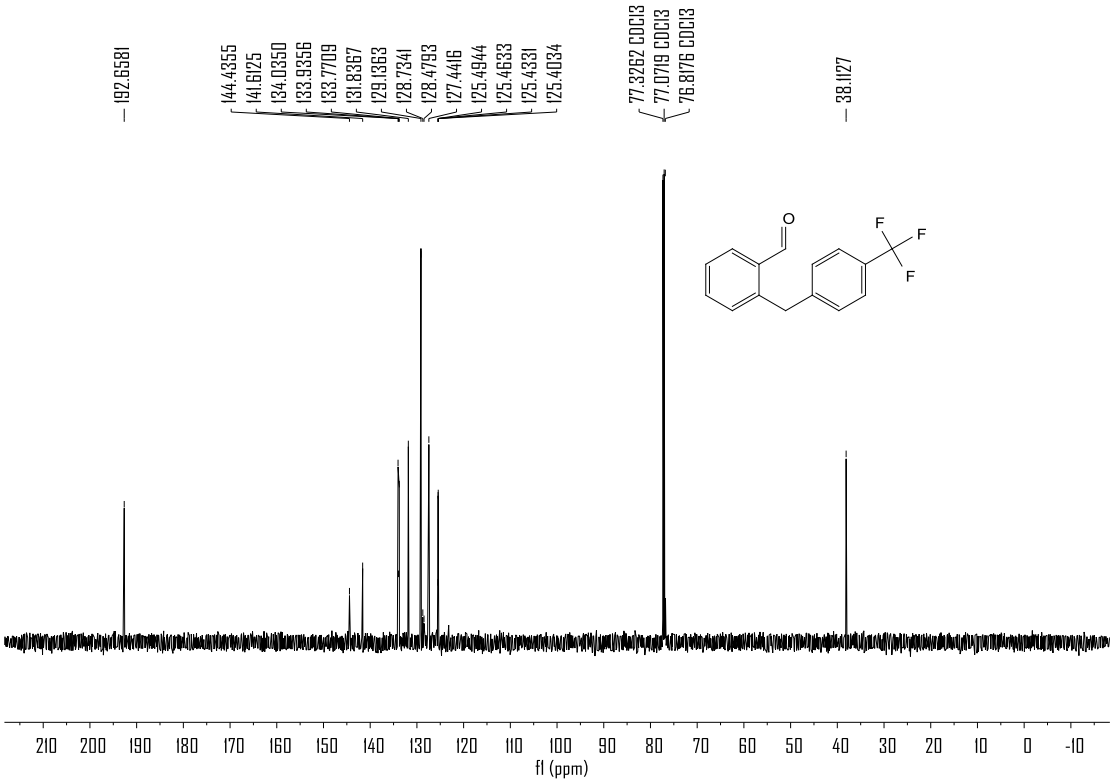
^{13}C NMR spectrum of compound 3b and S1 ($CDCl_3$, 126 MHz)



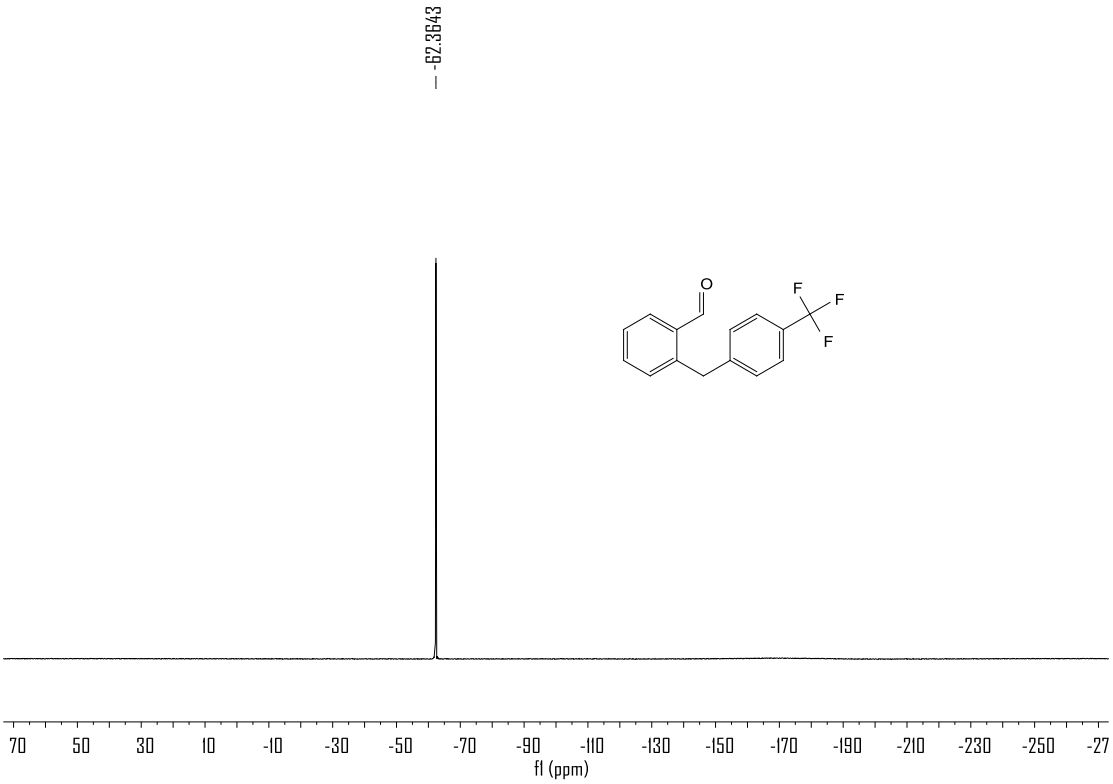
^{1}H NMR spectrum of compound 3c ($CDCl_3$, 500 MHz)



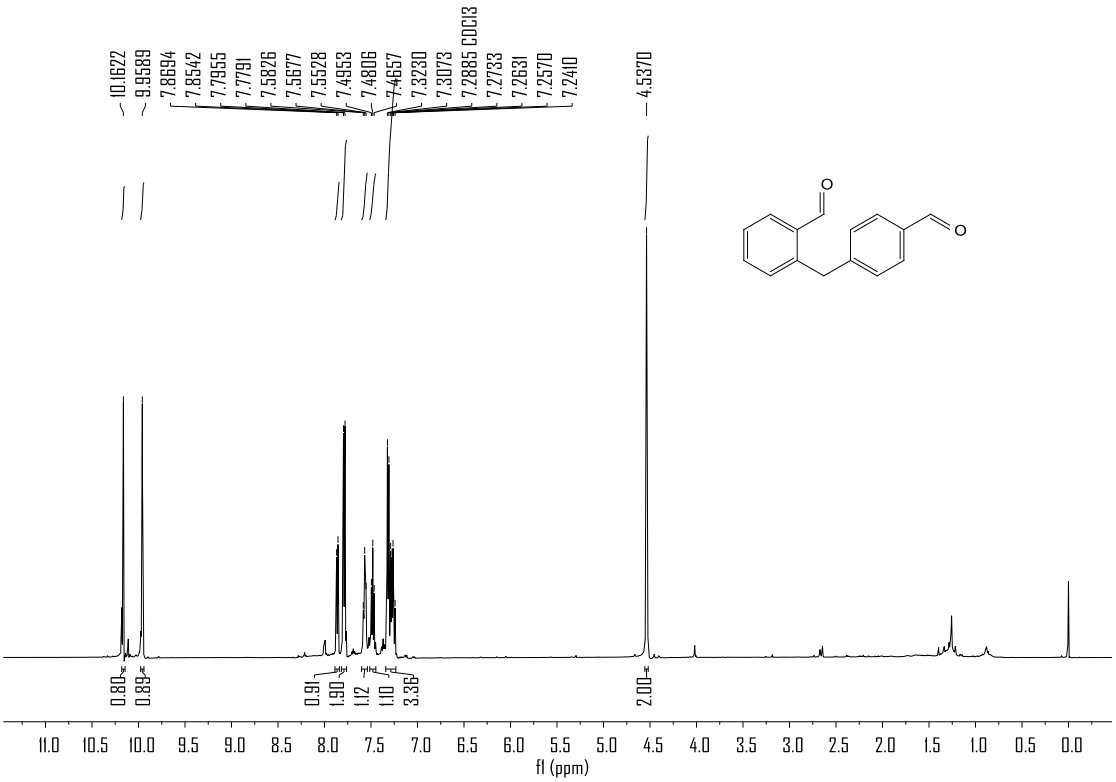
^{13}C NMR spectrum of compound 3c ($CDCl_3$, 126 MHz)



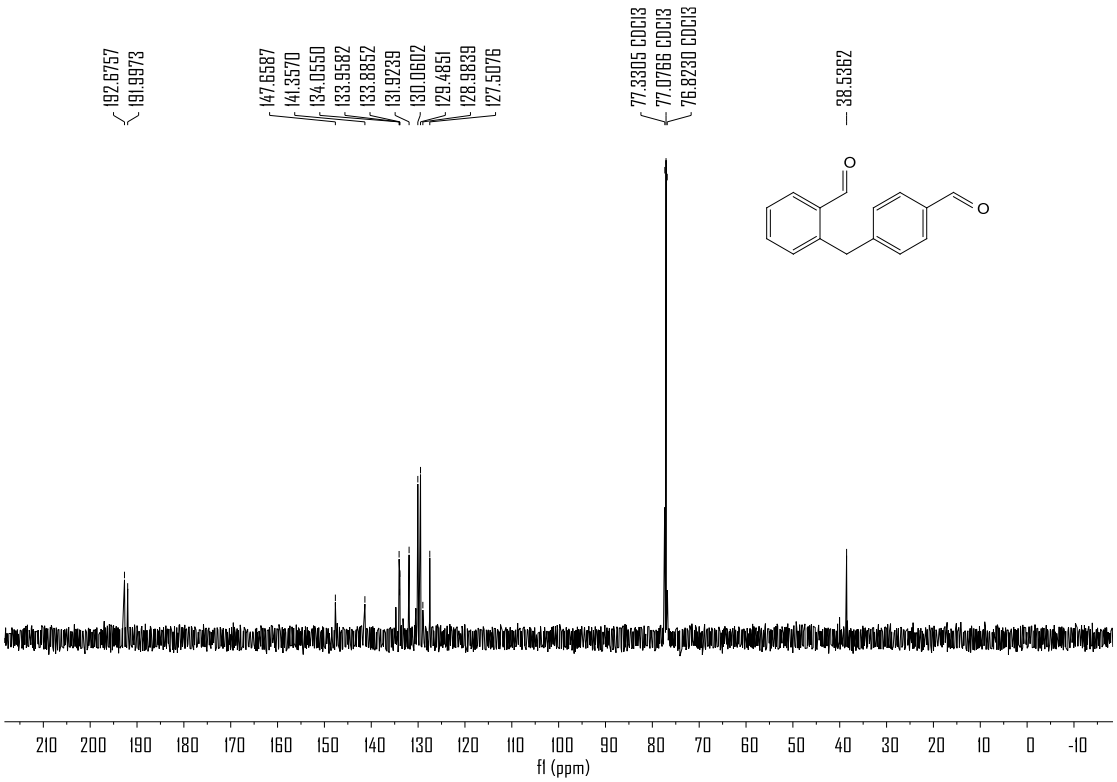
^{19}F NMR spectrum of compound 3c ($CDCl_3$, 470 MHz)



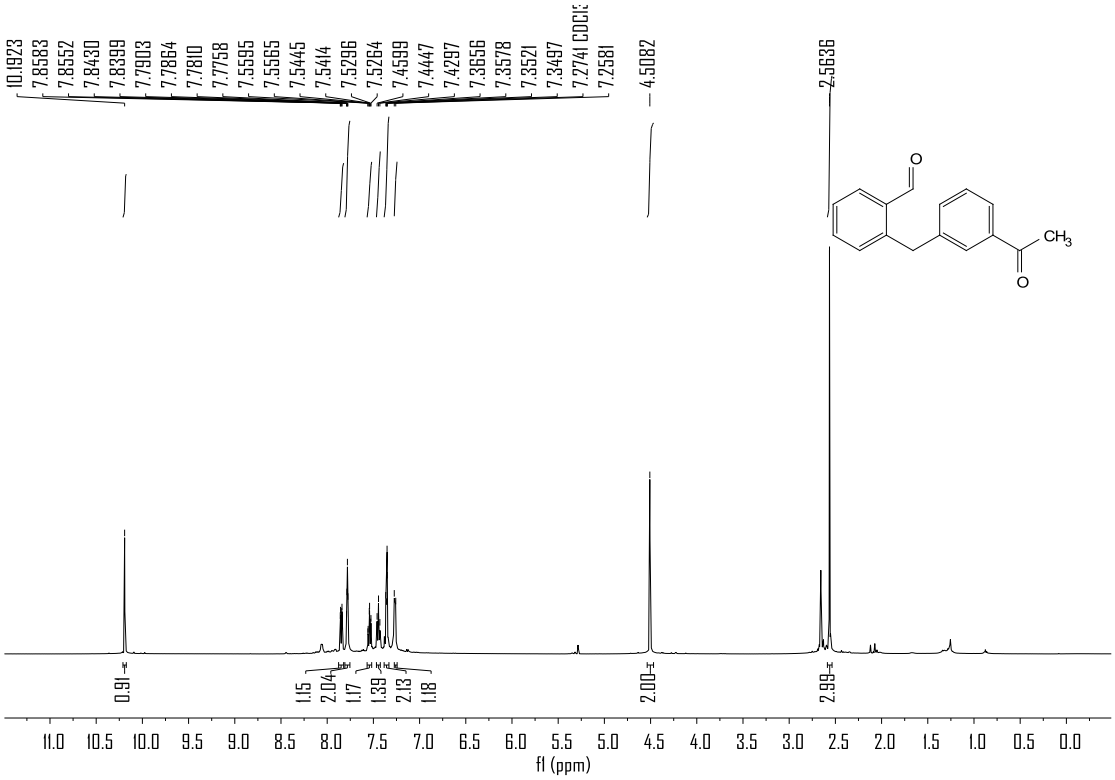
^{1}H NMR spectrum of compound 3d ($CDCl_3$, 500 MHz)



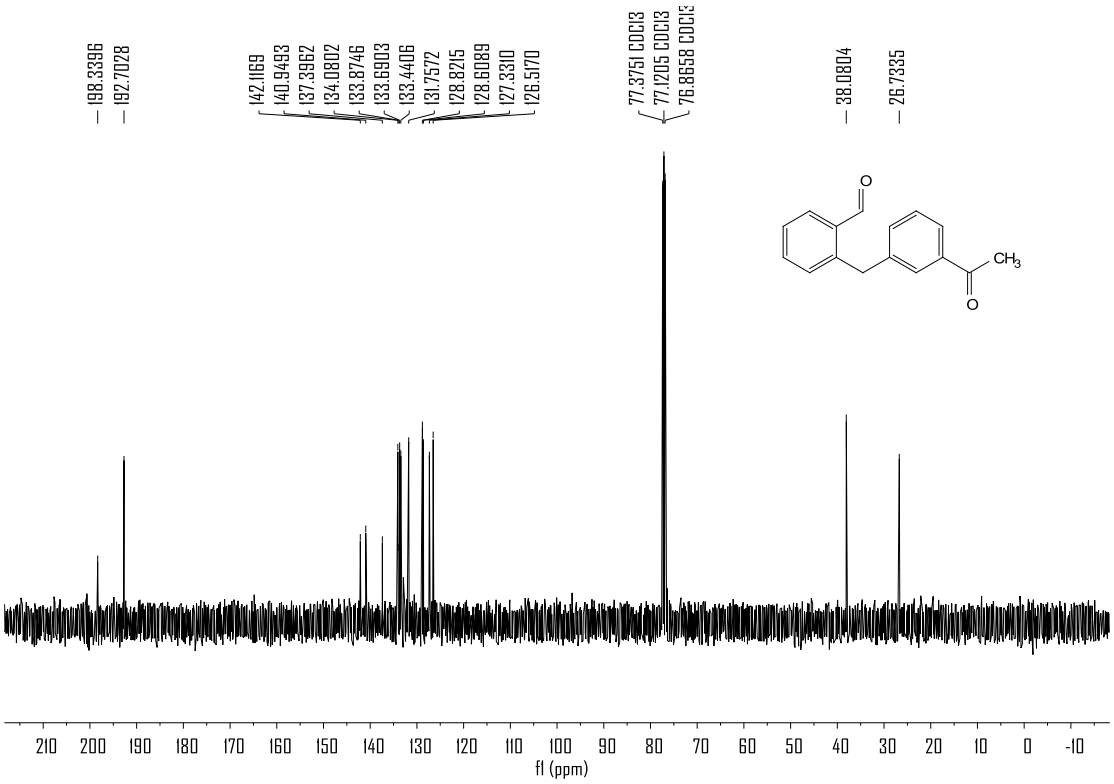
^{13}C NMR spectrum of compound 3d ($CDCl_3$, 126 MHz)



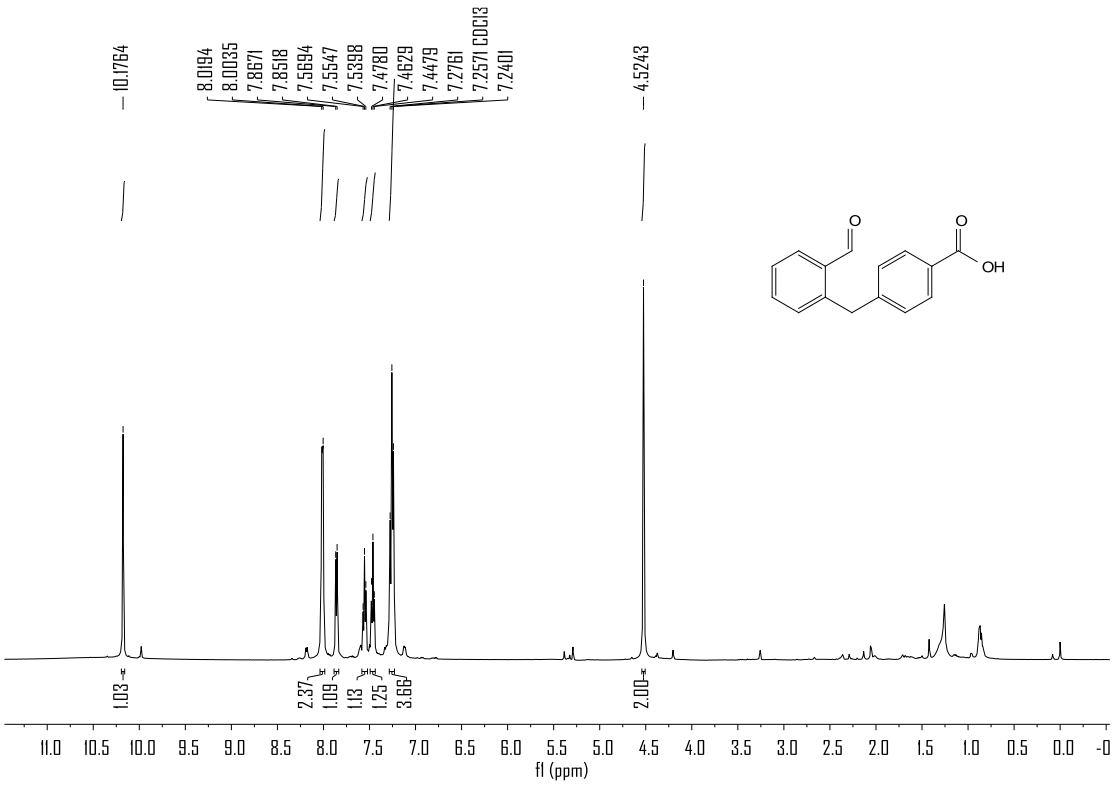
^{1}H NMR spectrum of compound 3e ($CDCl_3$, 500 MHz)



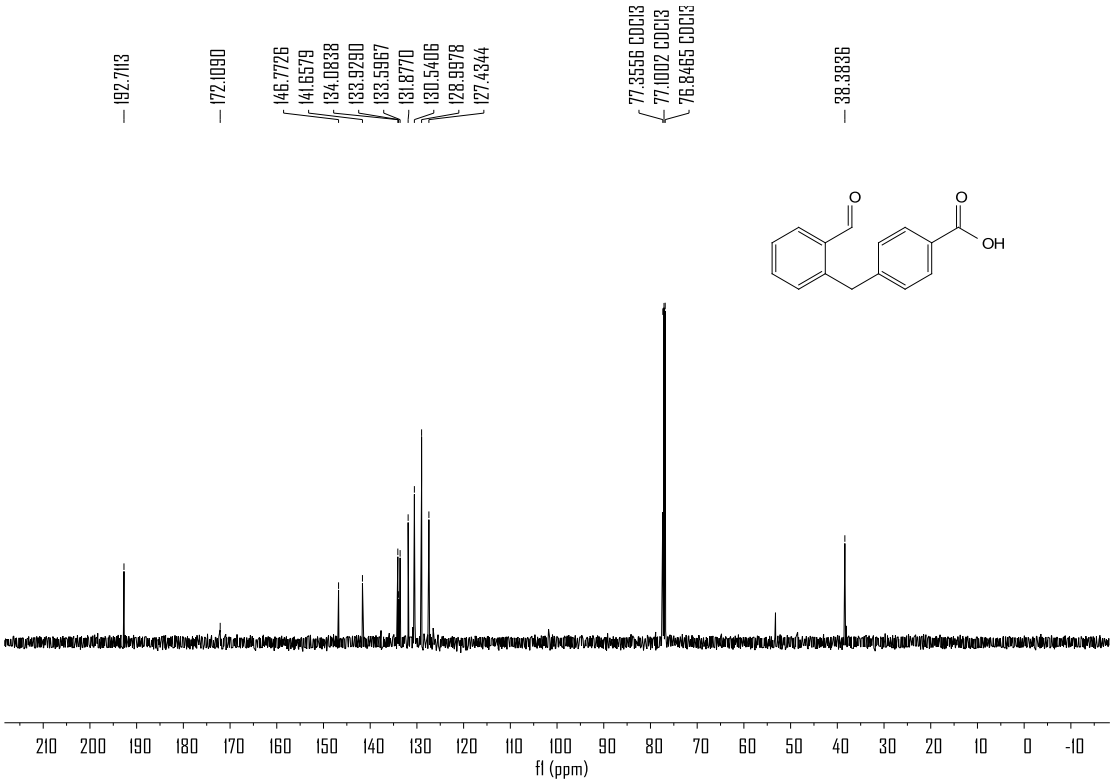
^{13}C NMR spectrum of compound 3e ($CDCl_3$, 126 MHz)



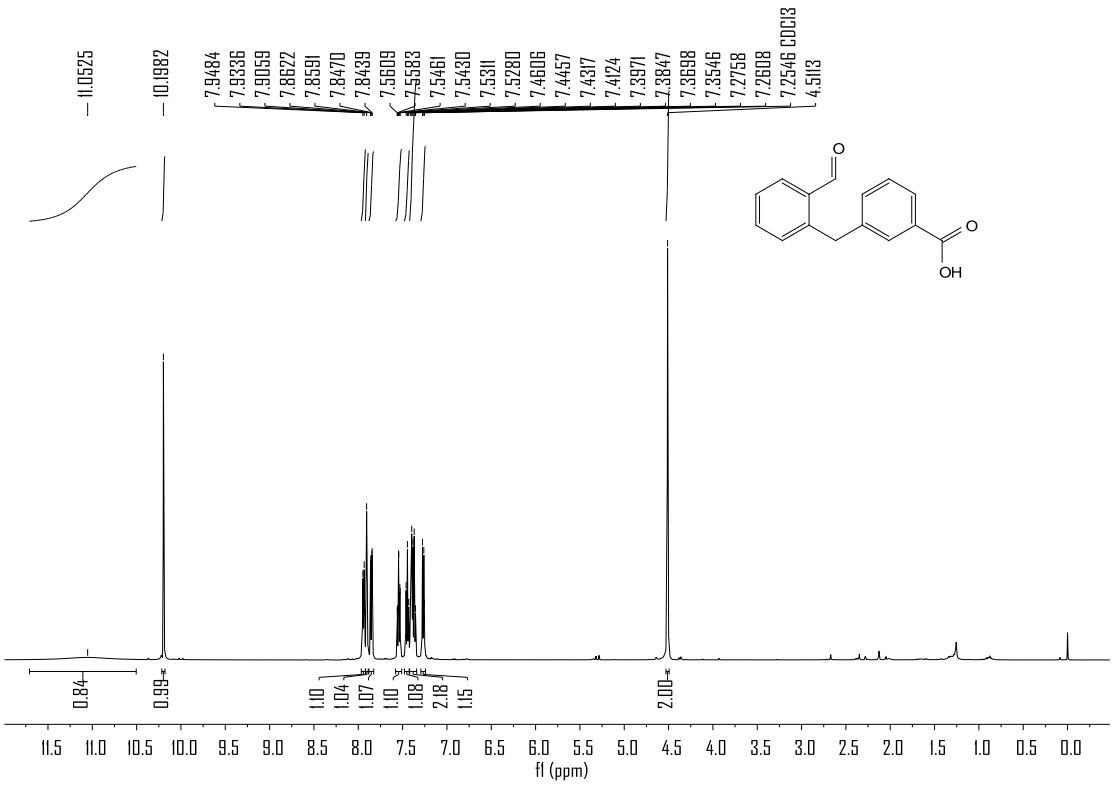
^{1}H NMR spectrum of compound 3f ($CDCl_3$, 500 MHz)



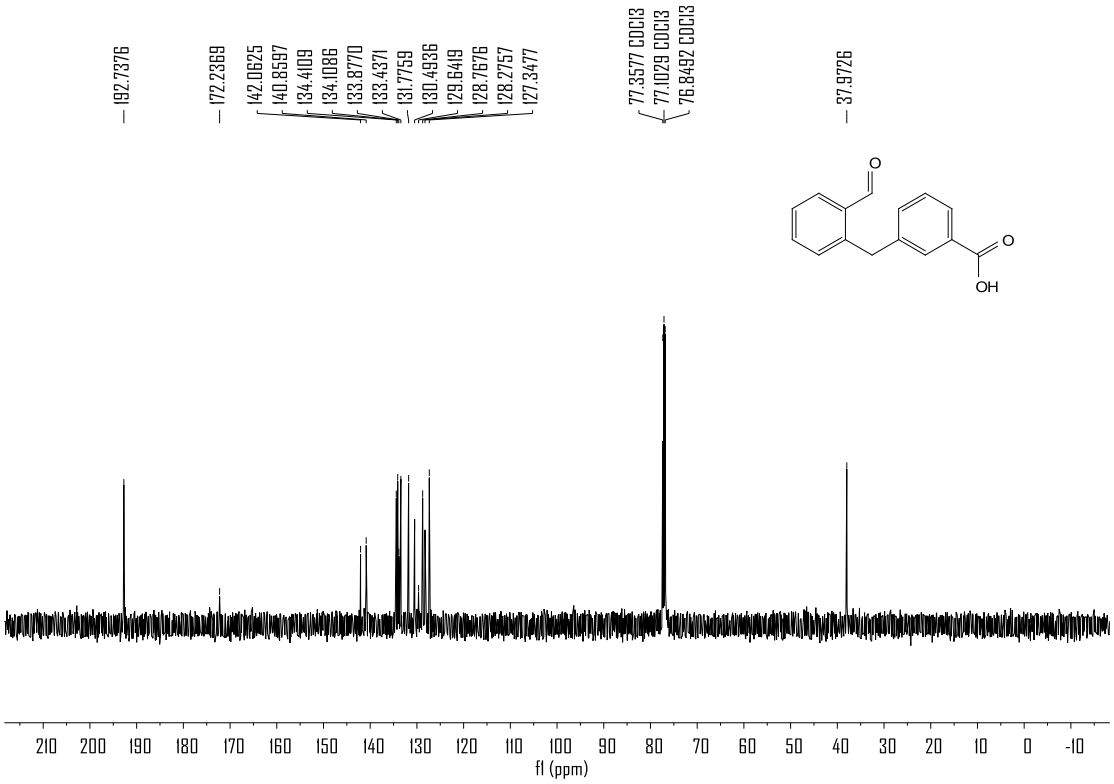
^{13}C NMR spectrum of compound 3f ($CDCl_3$, 126 MHz)



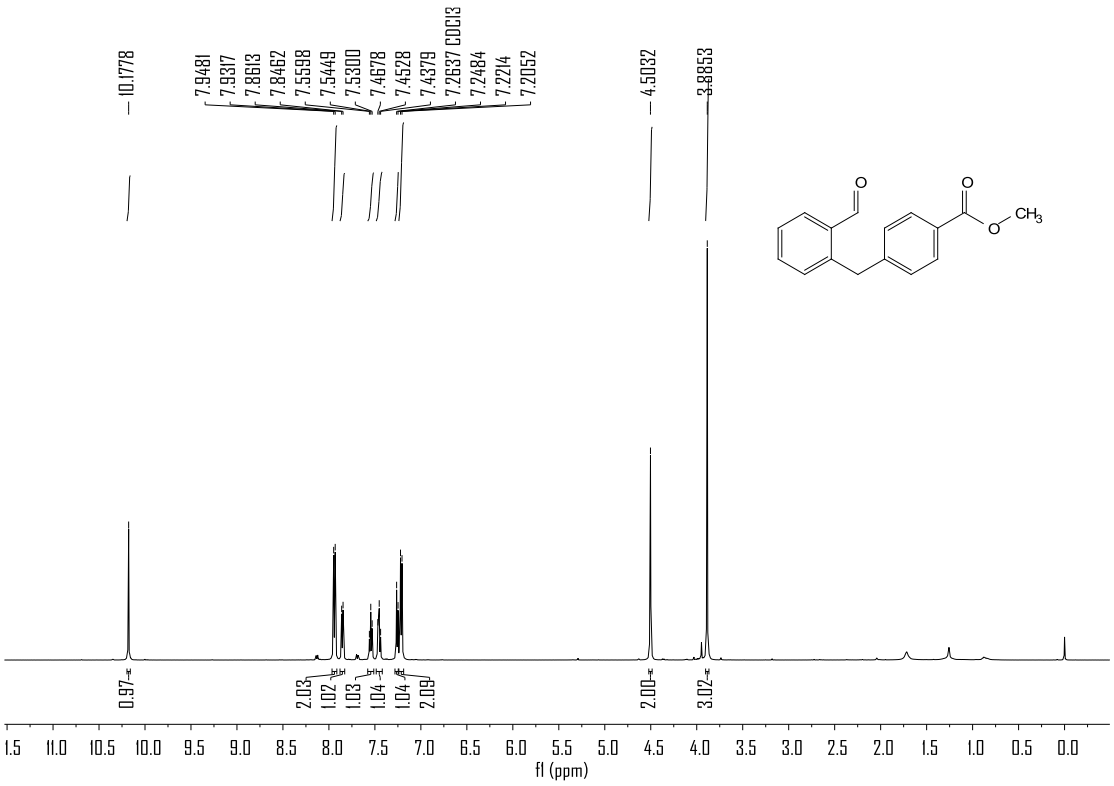
^{1}H NMR spectrum of compound 3g ($CDCl_3$, 500 MHz)



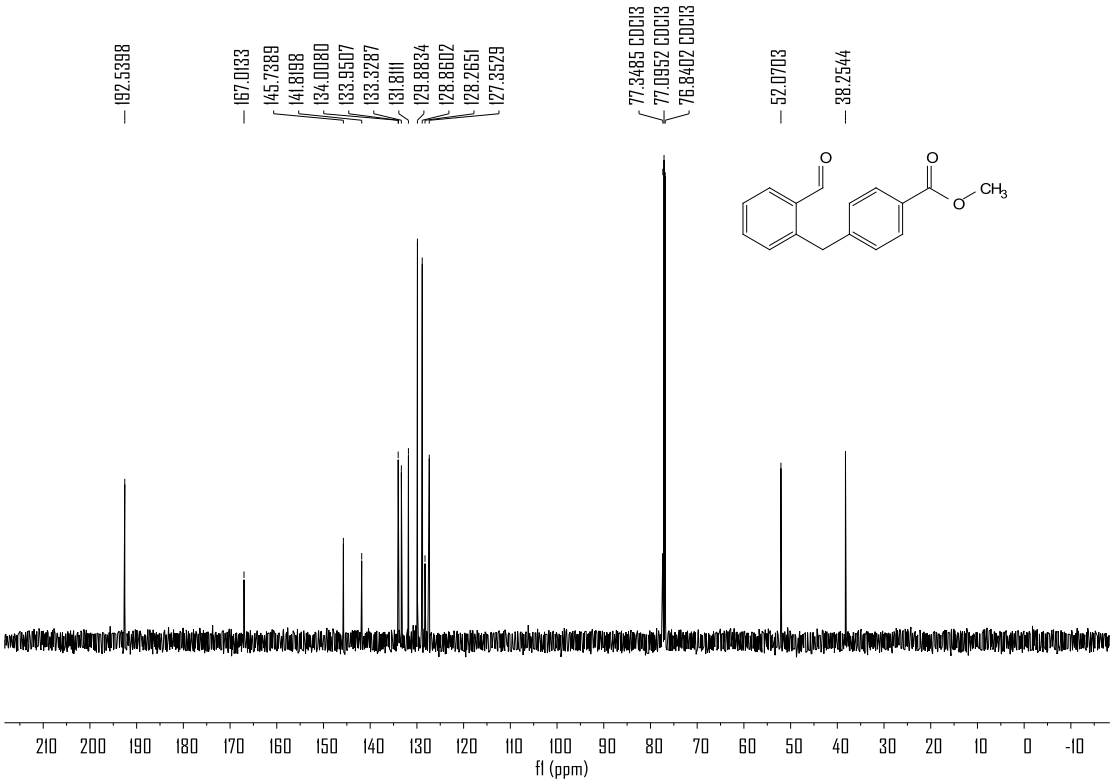
^{13}C NMR spectrum of compound 3g ($CDCl_3$, 126 MHz)



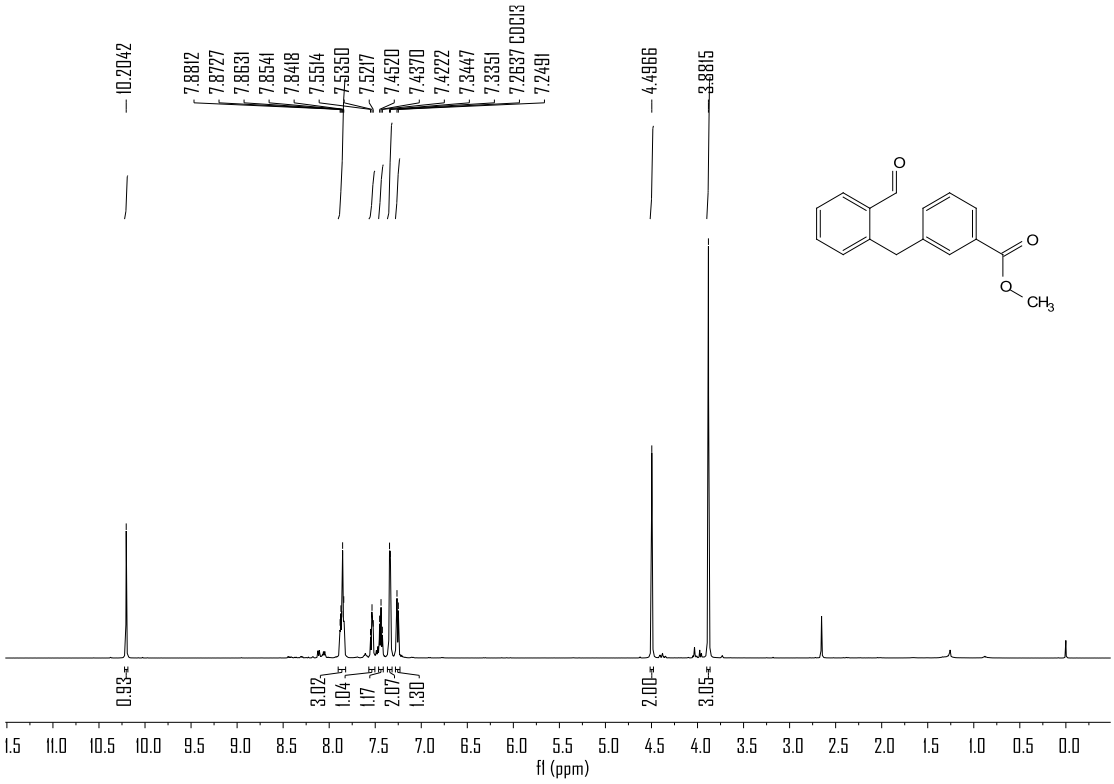
^{1}H NMR spectrum of compound 3h ($CDCl_3$, 500 MHz)



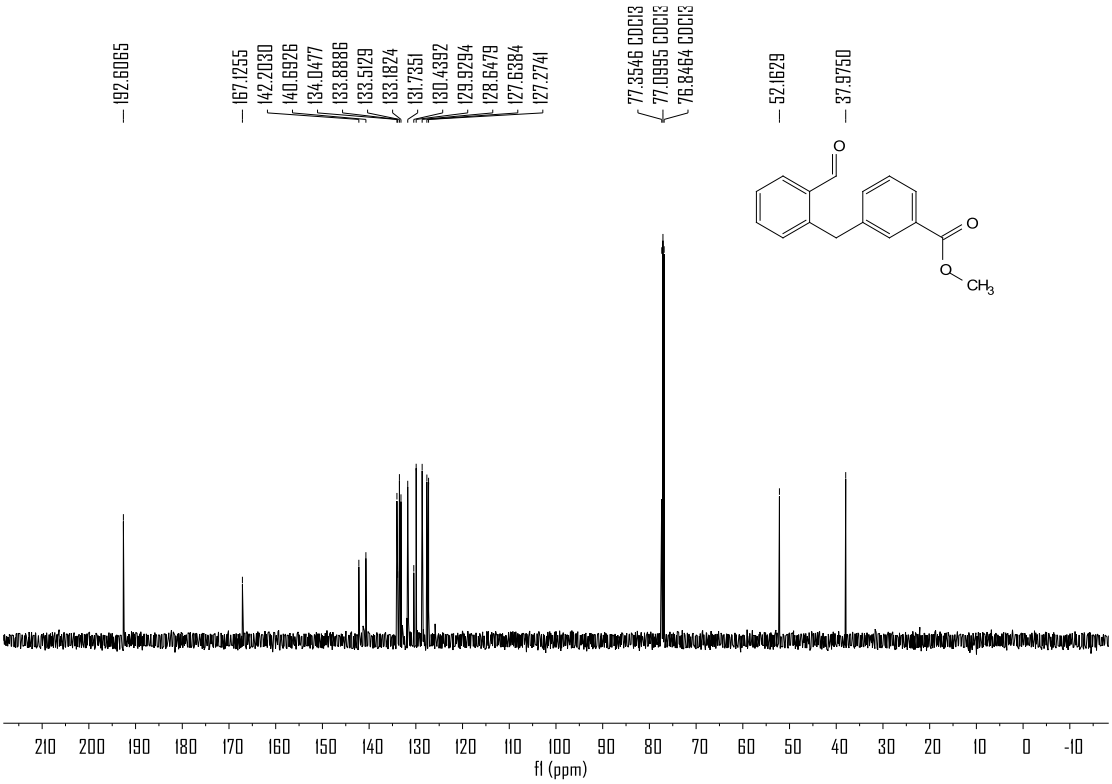
^{13}C NMR spectrum of compound 3h ($CDCl_3$, 126 MHz)



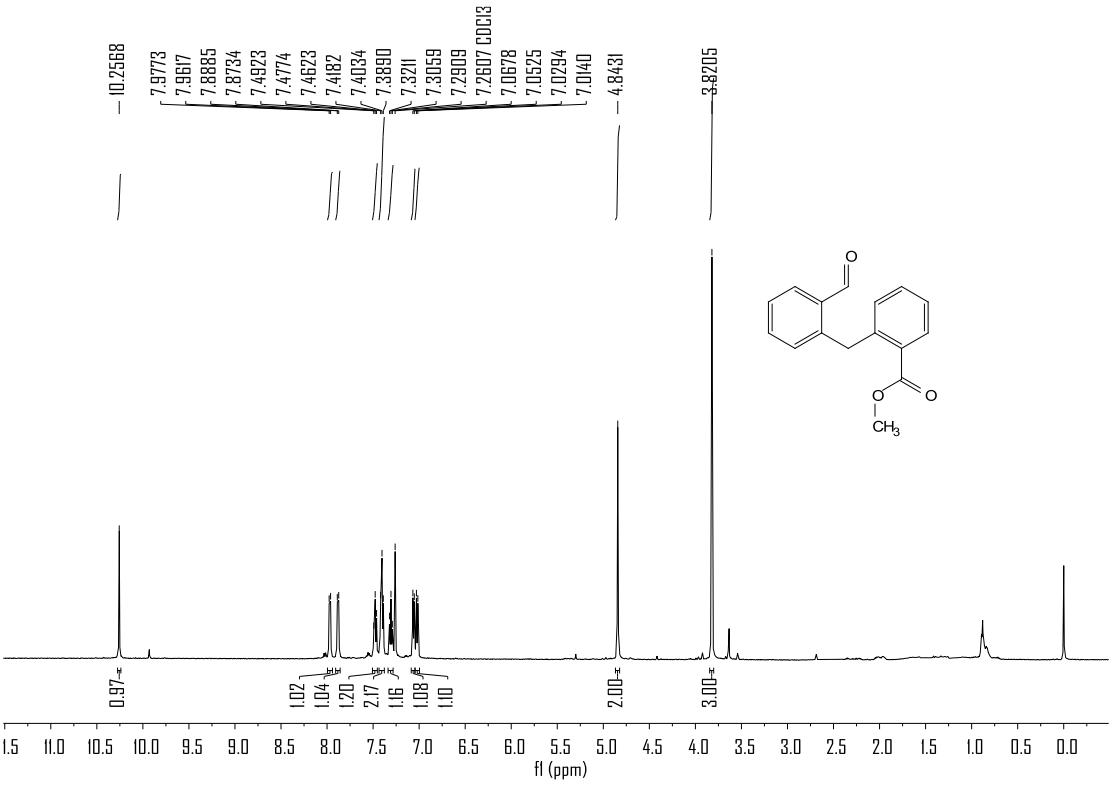
^{1}H NMR spectrum of compound 3i ($CDCl_3$, 500 MHz)



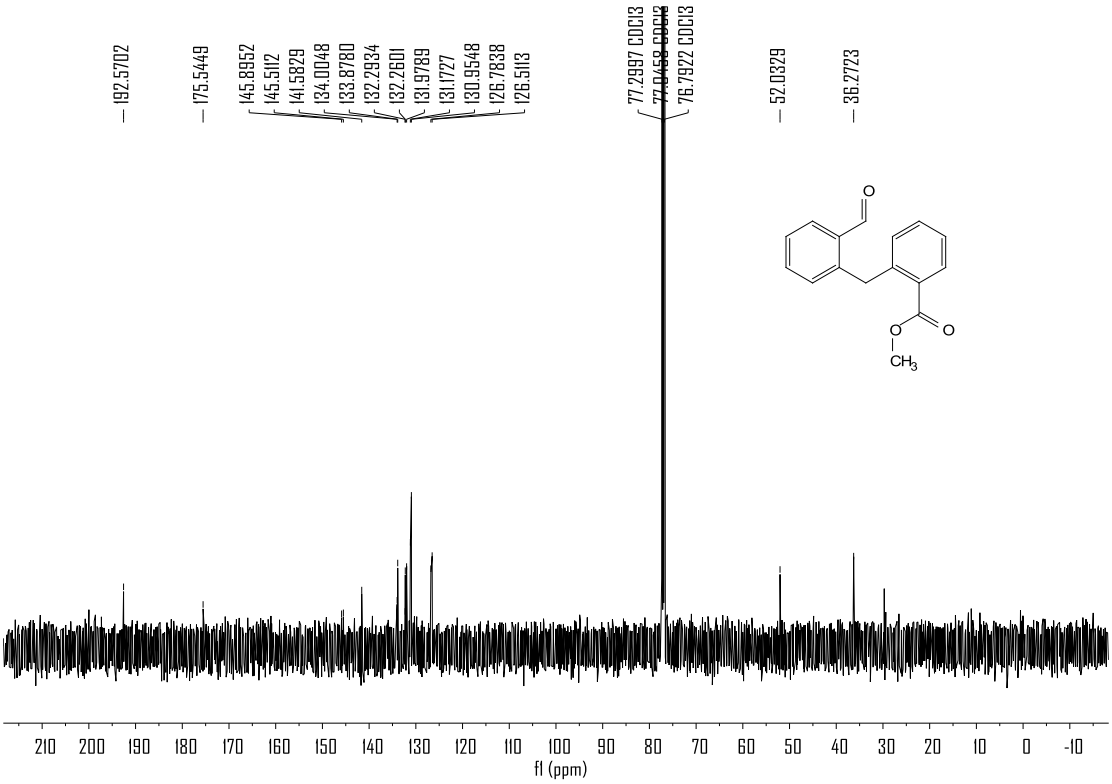
^{13}C NMR spectrum of compound 3i ($CDCl_3$, 126 MHz)



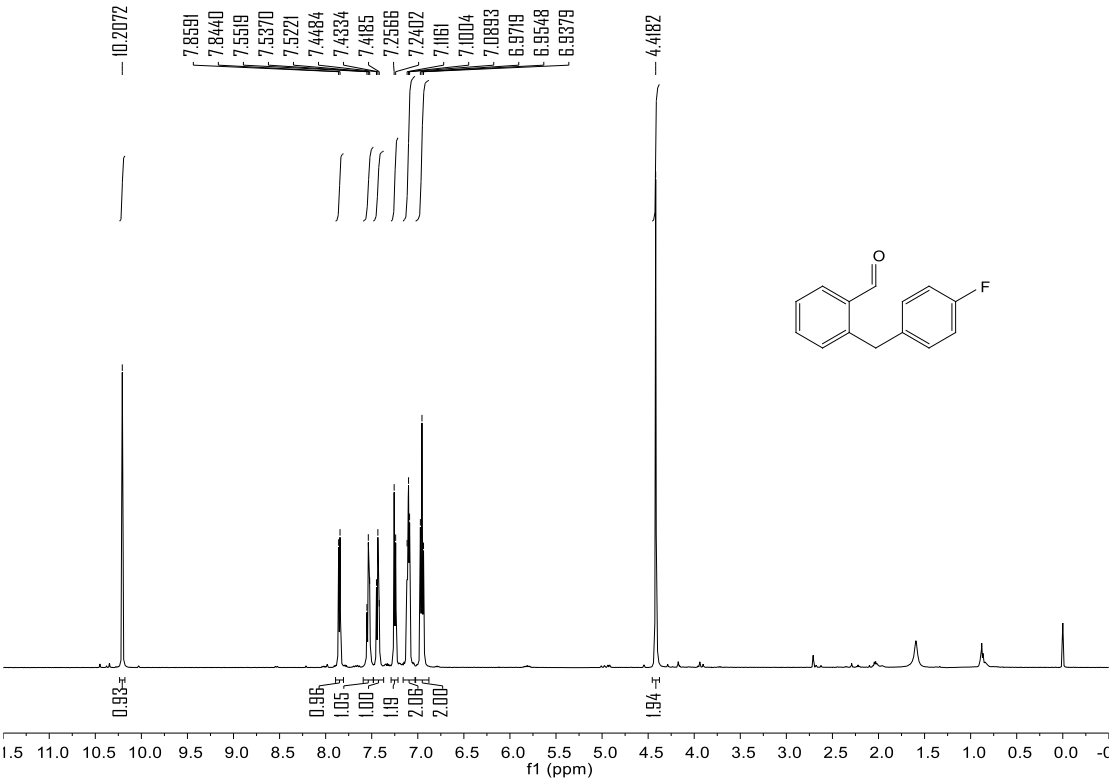
^{1}H NMR spectrum of compound 3j ($CDCl_3$, 500 MHz)



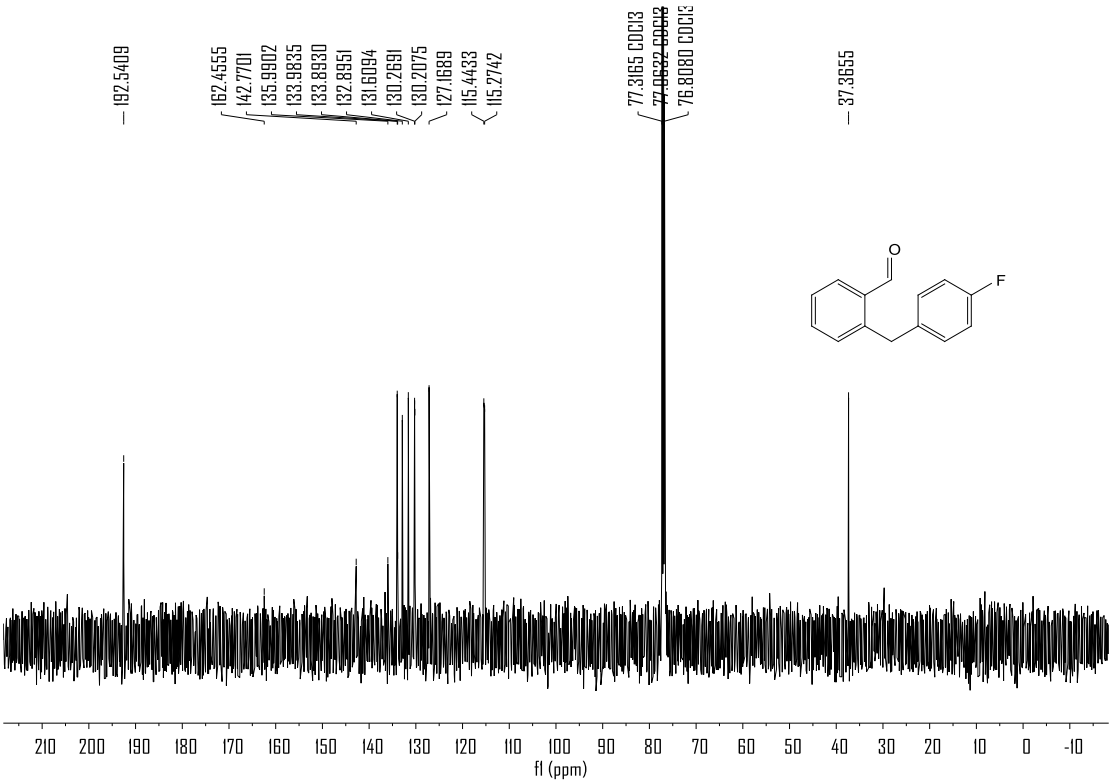
^{13}C NMR spectrum of compound 3j ($CDCl_3$, 126 MHz)



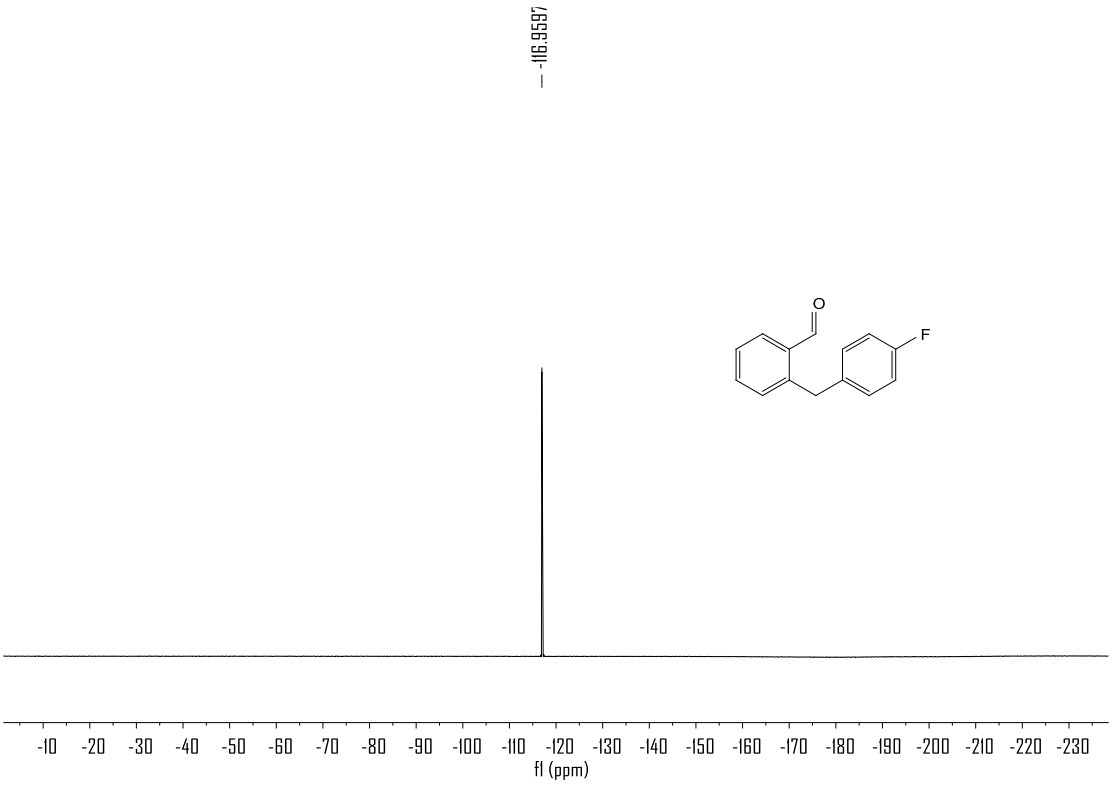
^{1}H NMR spectrum of compound 3k ($CDCl_3$, 500 MHz)



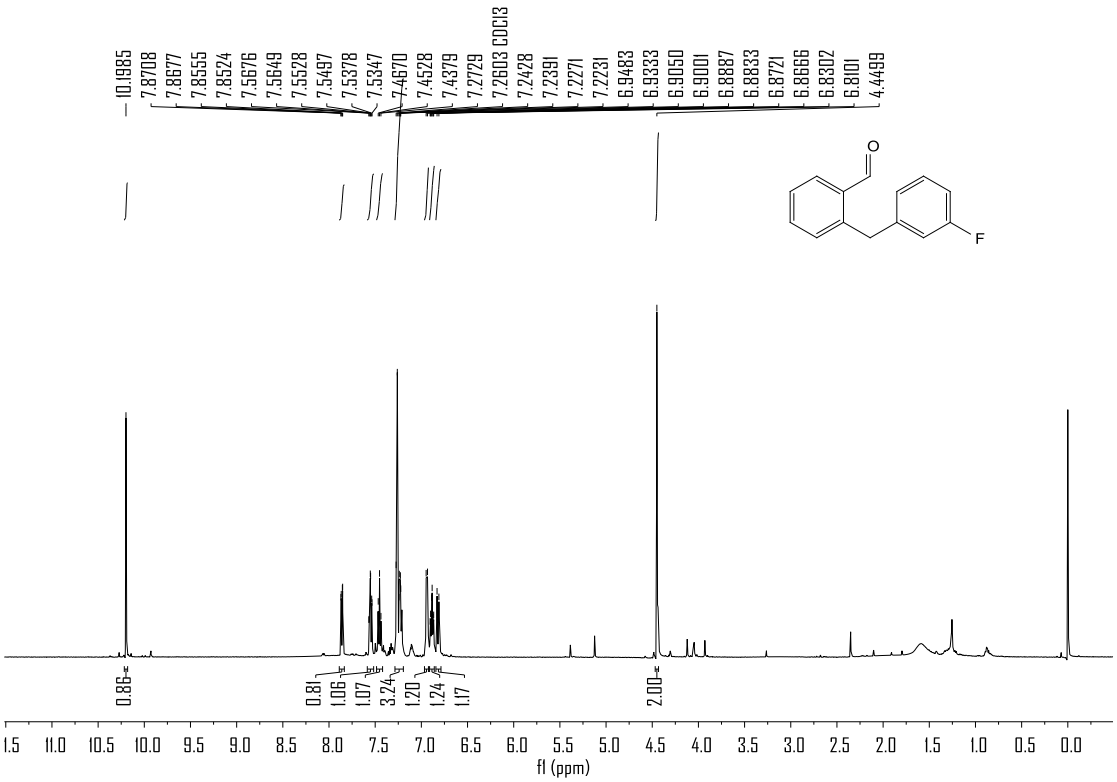
^{13}C NMR spectrum of compound 3k ($CDCl_3$, 126 MHz)



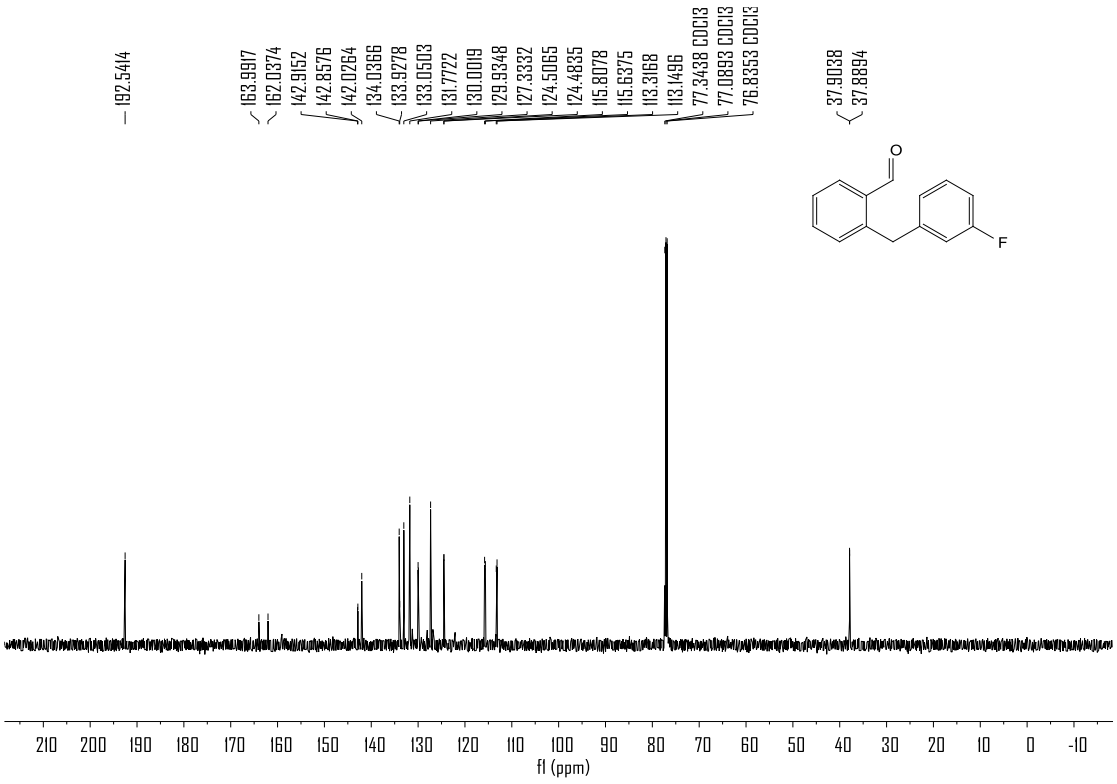
^{19}F NMR spectrum of compound 3k ($CDCl_3$, 470 MHz)



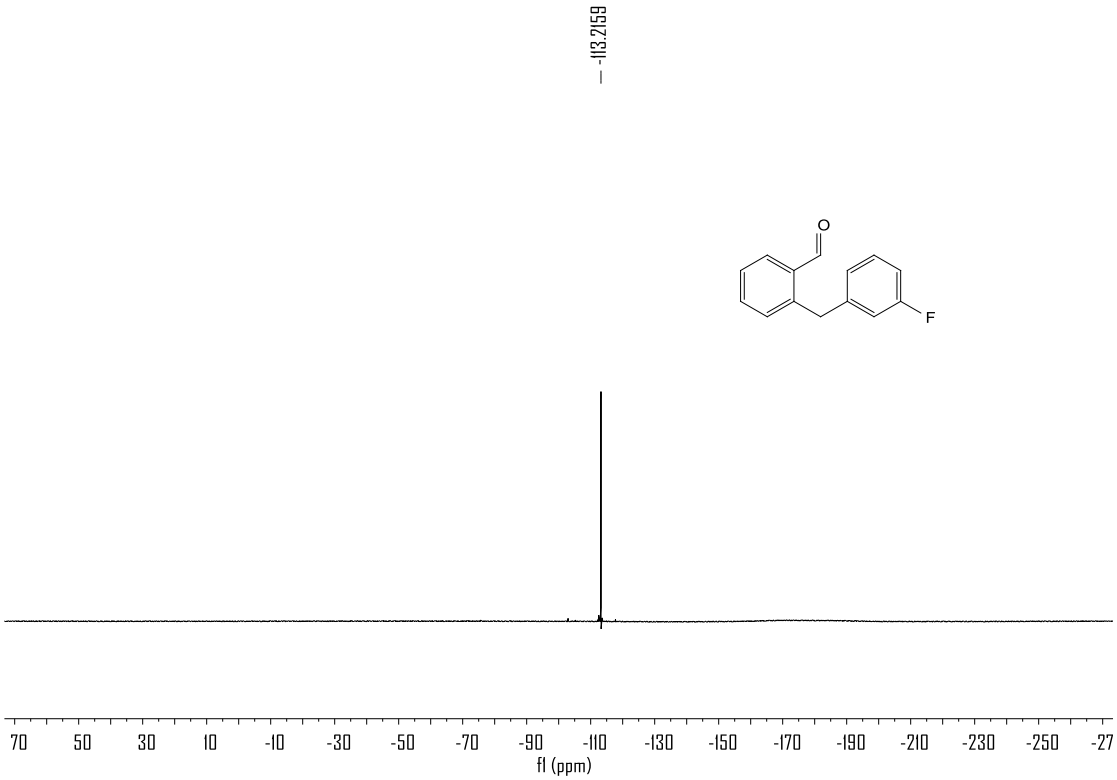
^{1}H NMR spectrum of compound 3l ($CDCl_3$, 500 MHz)



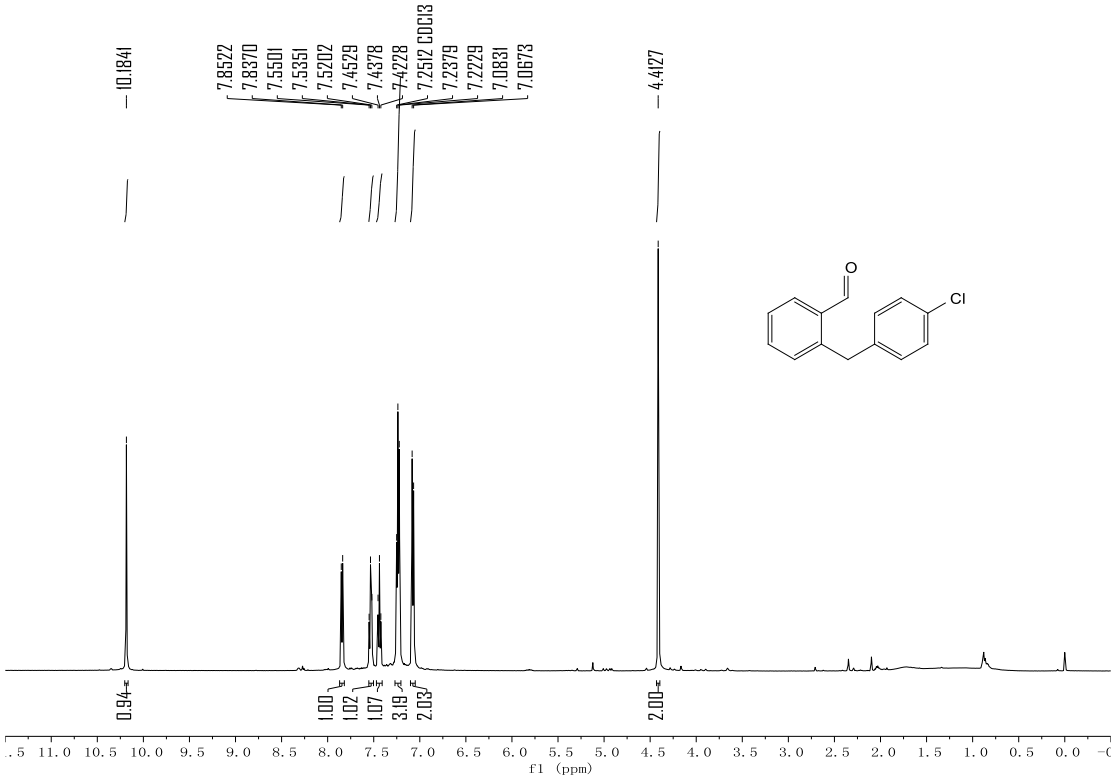
^{13}C NMR spectrum of compound 3l ($CDCl_3$, 126 MHz)



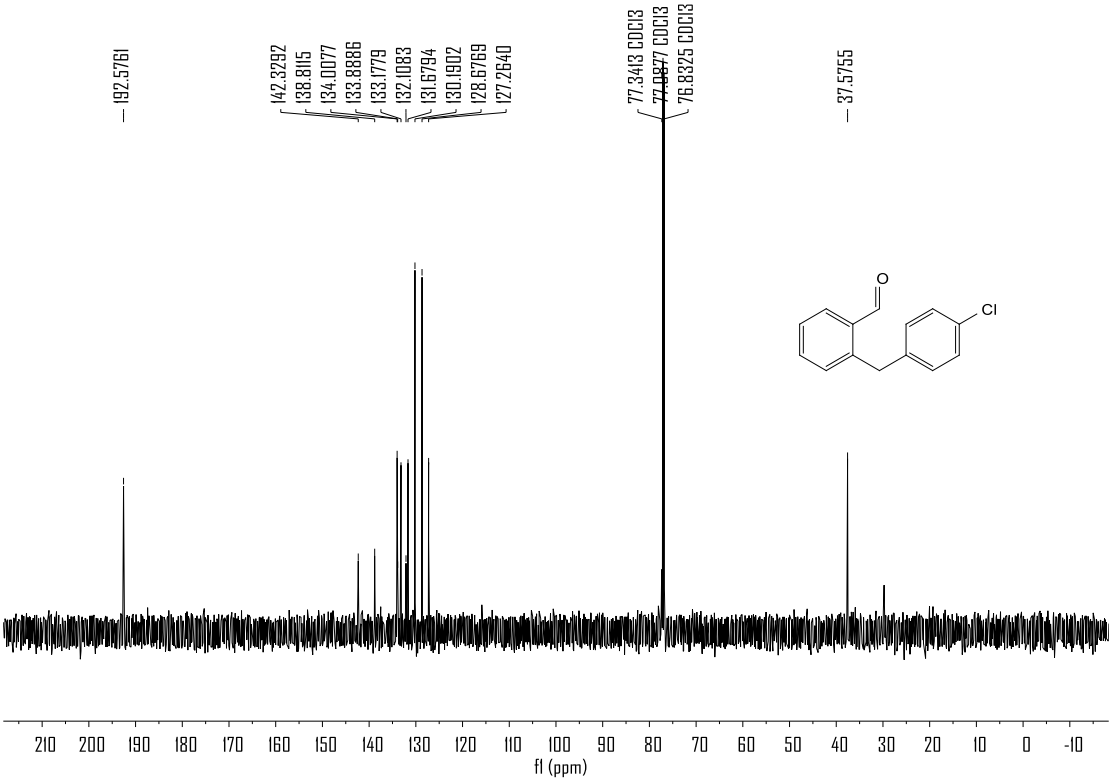
^{19}F NMR spectrum of compound 3l ($CDCl_3$, 470 MHz)



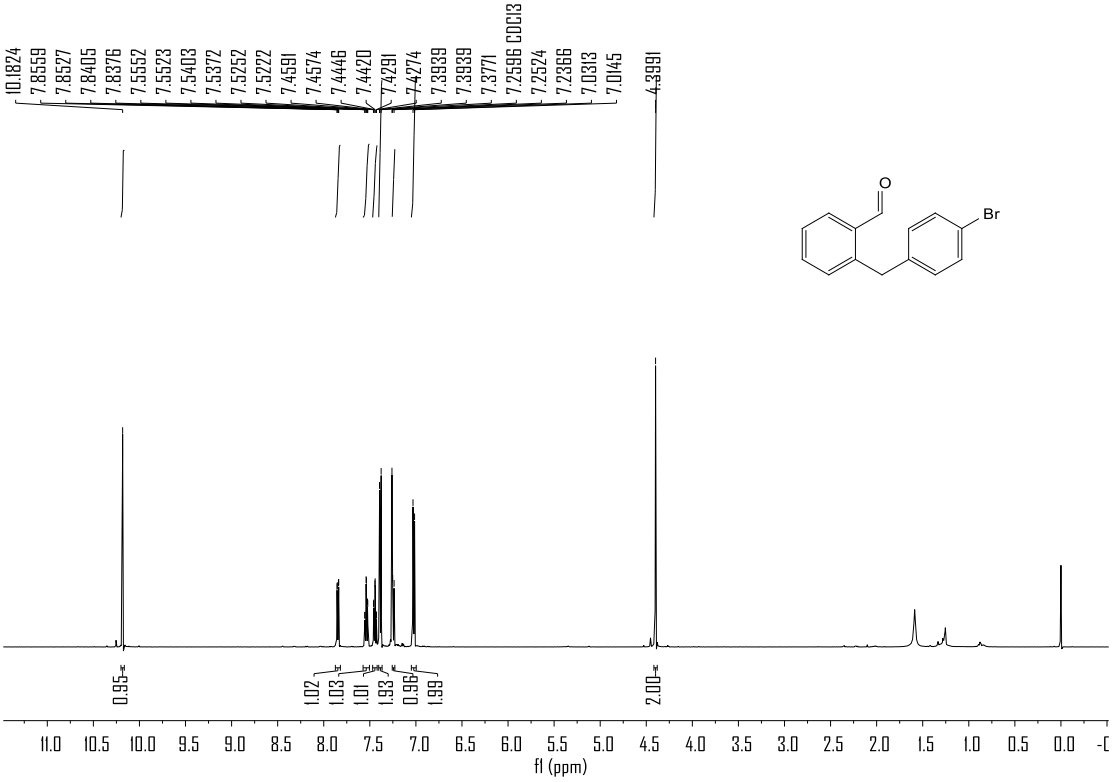
^{1}H NMR spectrum of compound 3m ($CDCl_3$, 500 MHz)



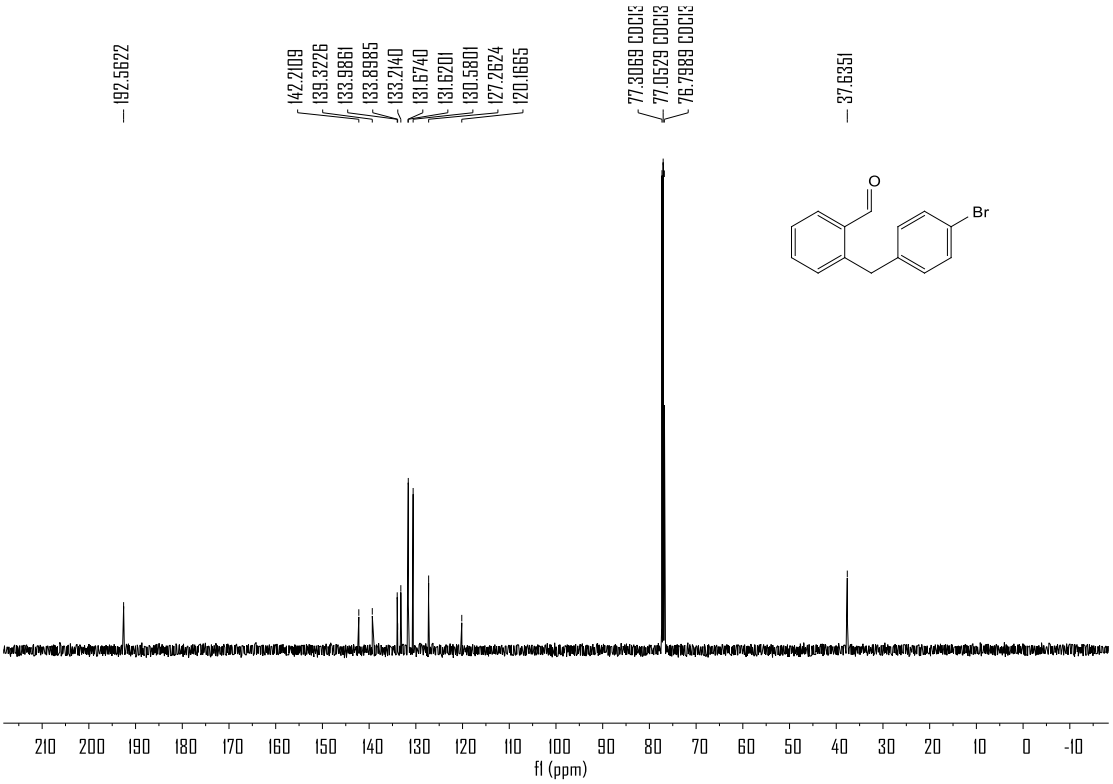
^{13}C NMR spectrum of compound 3m ($CDCl_3$, 126 MHz)



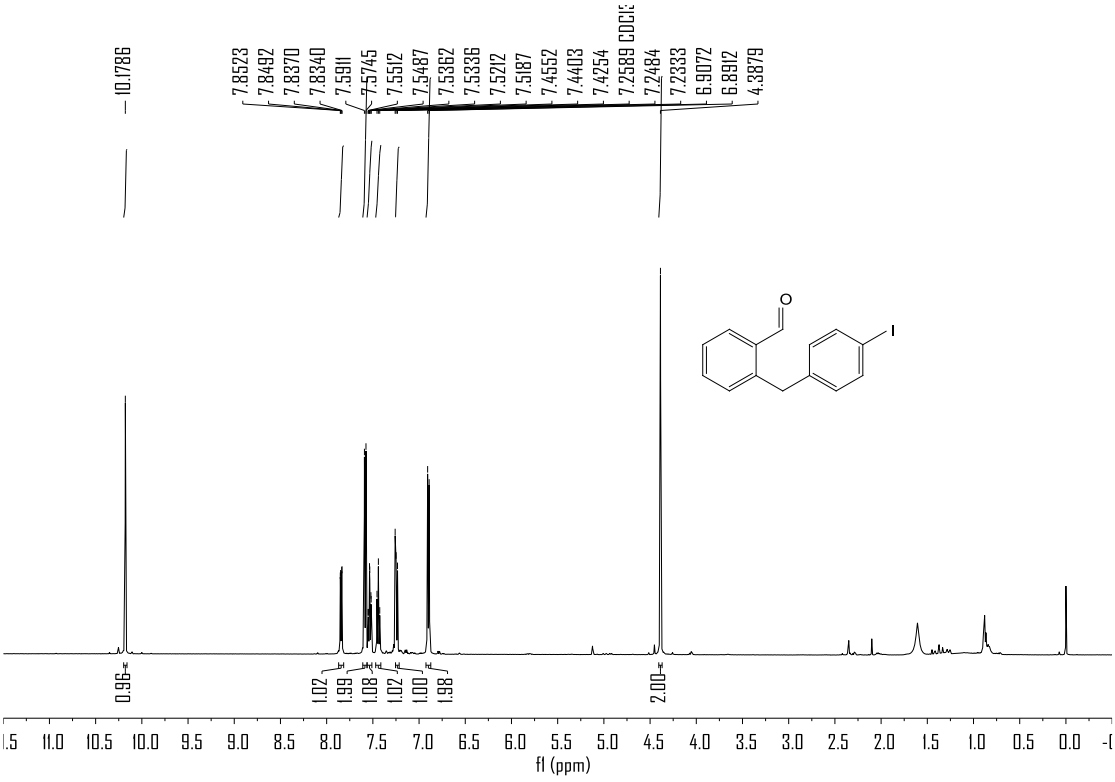
^{1}H NMR spectrum of compound 3n ($CDCl_3$, 500 MHz)



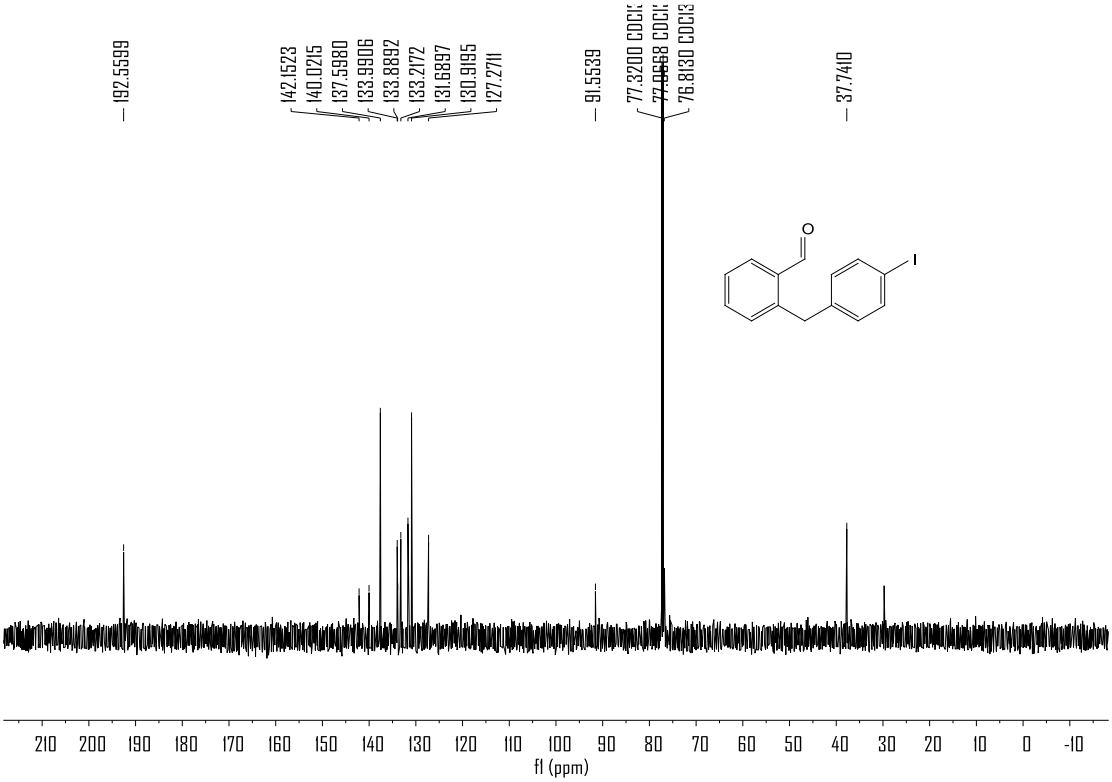
^{13}C NMR spectrum of compound 3n ($CDCl_3$, 126 MHz)



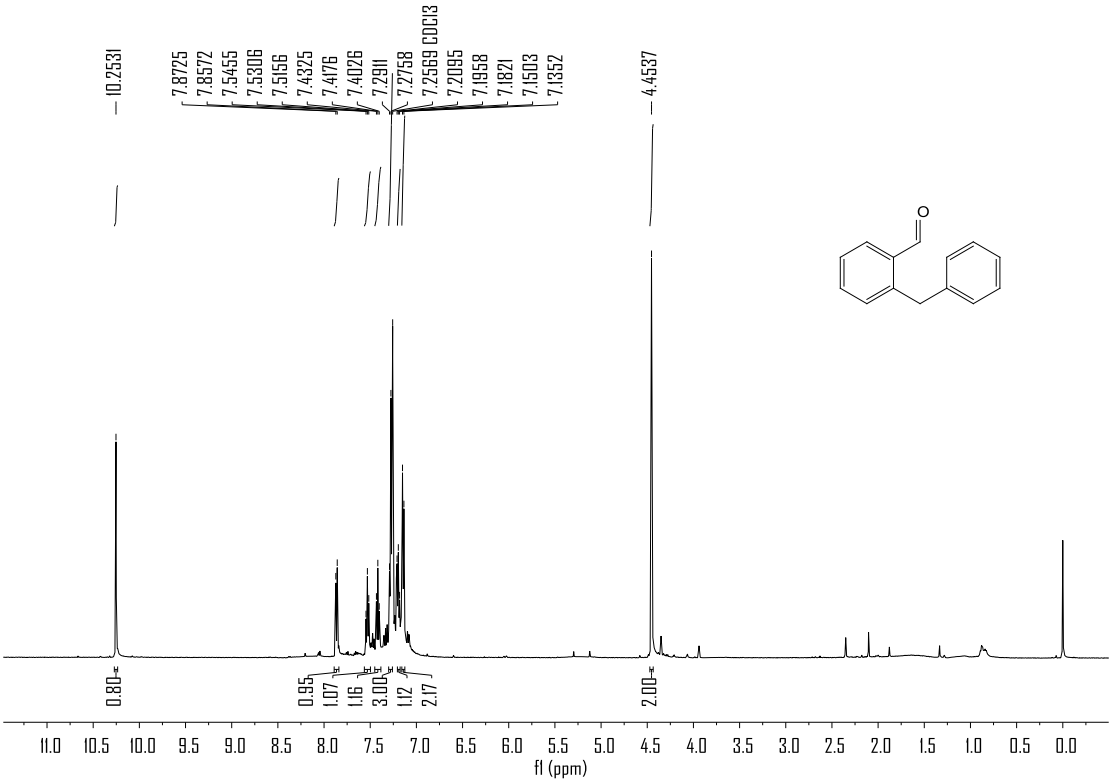
^{1}H NMR spectrum of compound 3o ($CDCl_3$, 500 MHz)



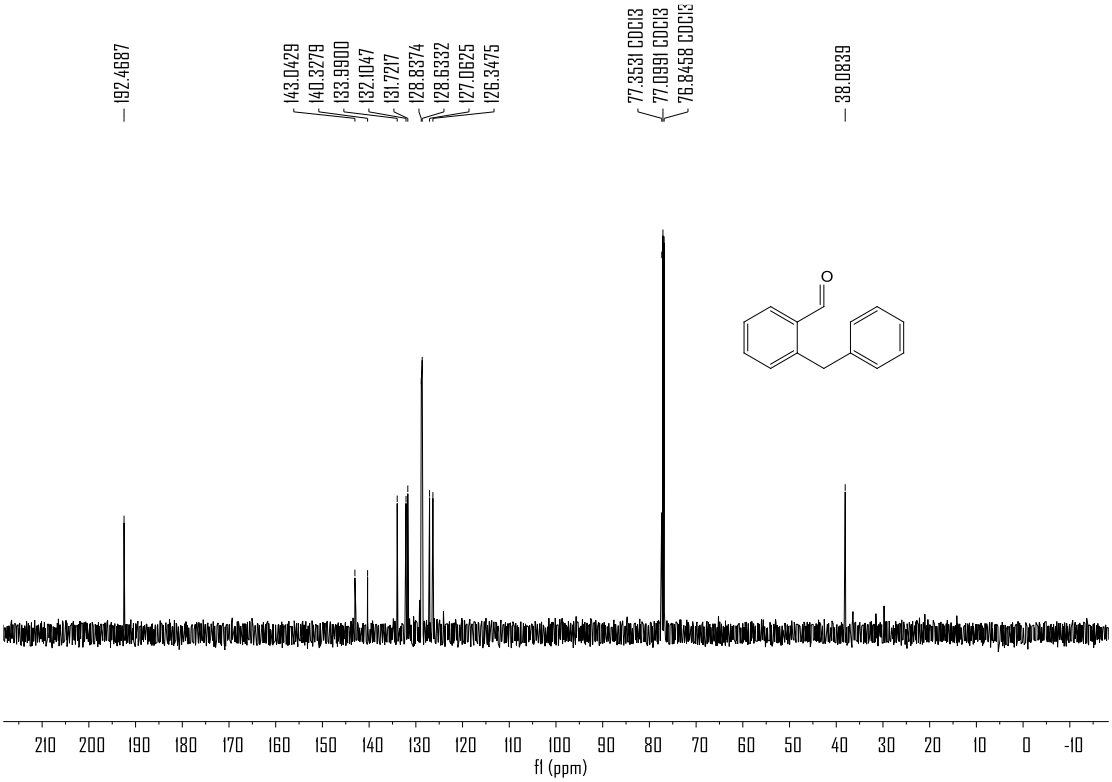
^{13}C NMR spectrum of compound 3o ($CDCl_3$, 126 MHz)



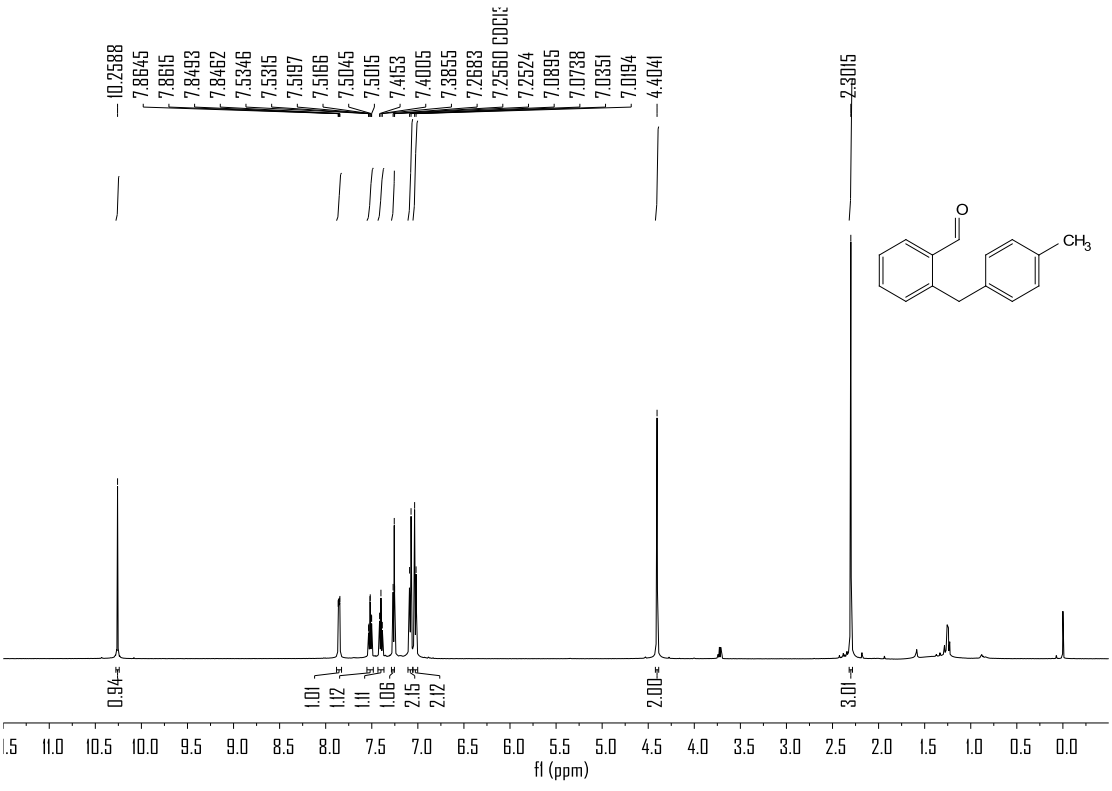
^{1}H NMR spectrum of compound 3p ($CDCl_3$, 500 MHz)



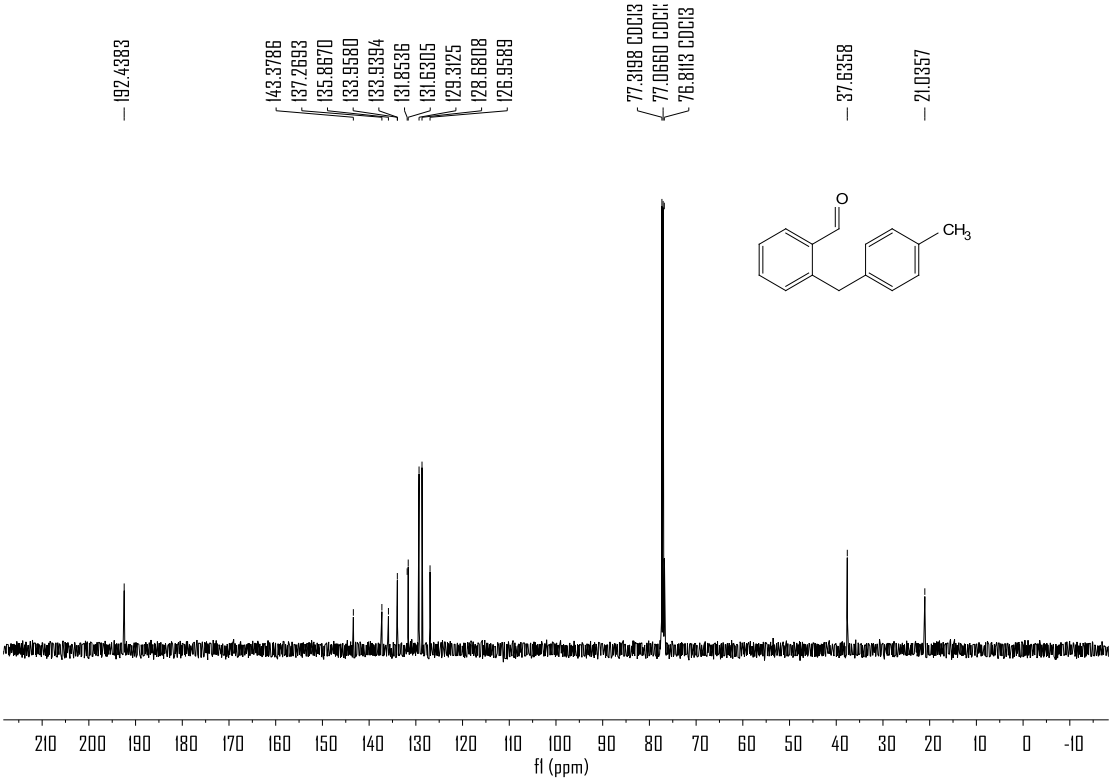
^{13}C NMR spectrum of compound 3p ($CDCl_3$, 126 MHz)



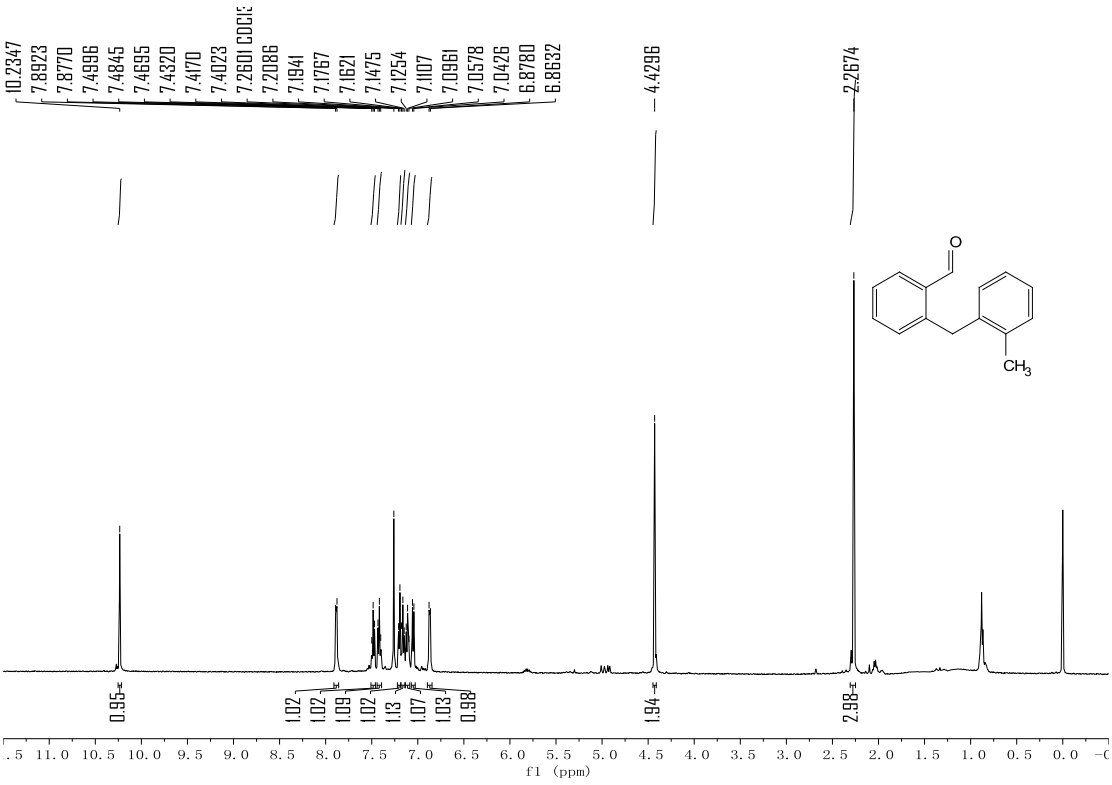
^{1}H NMR spectrum of compound 3q ($CDCl_3$, 500 MHz)



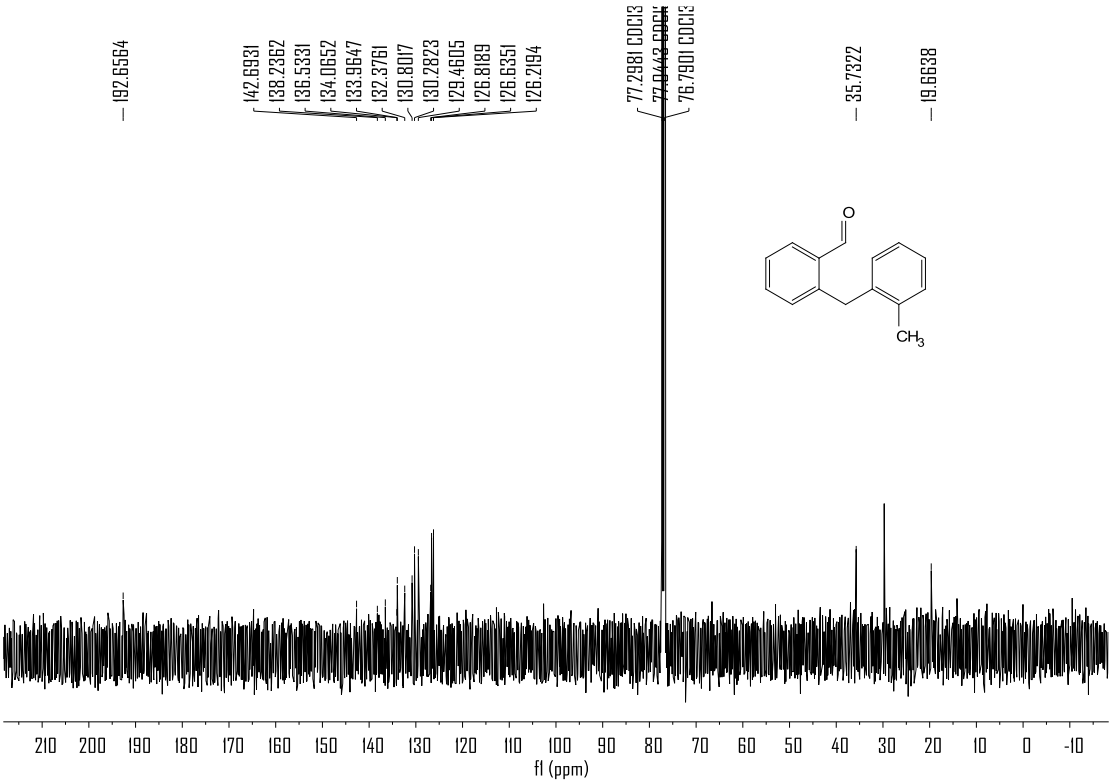
^{13}C NMR spectrum of compound 3q ($CDCl_3$, 126 MHz)



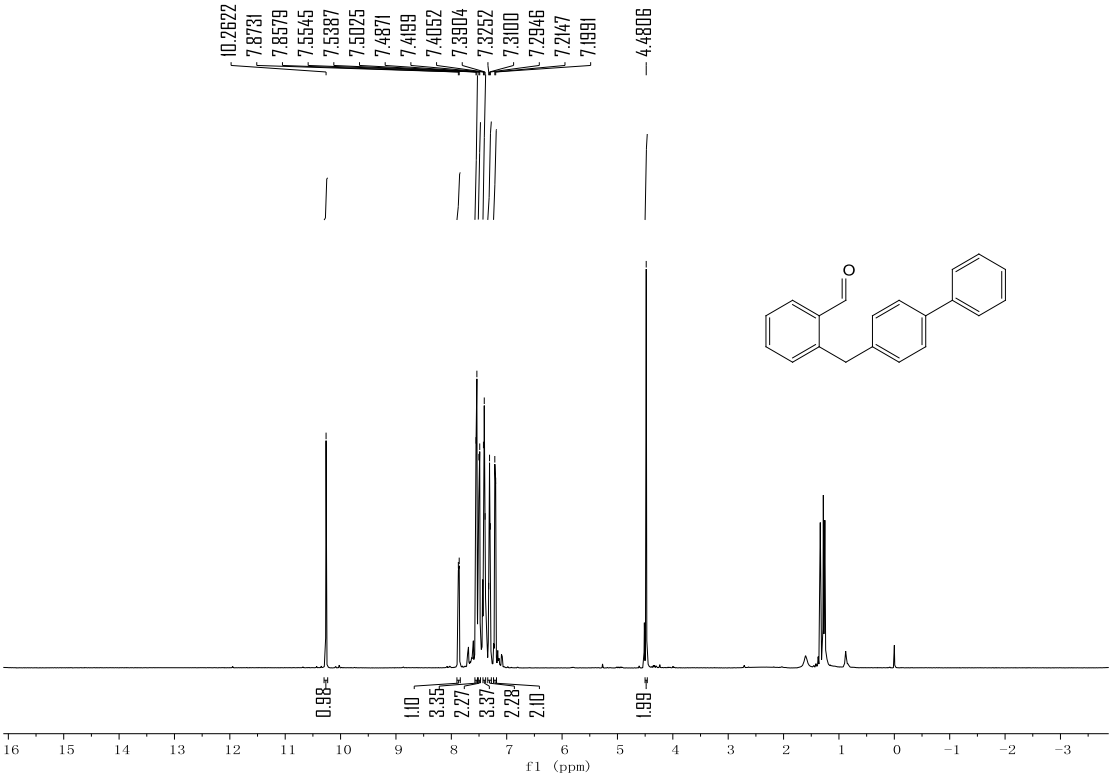
^{1}H NMR spectrum of compound 3r ($CDCl_3$, 500 MHz)



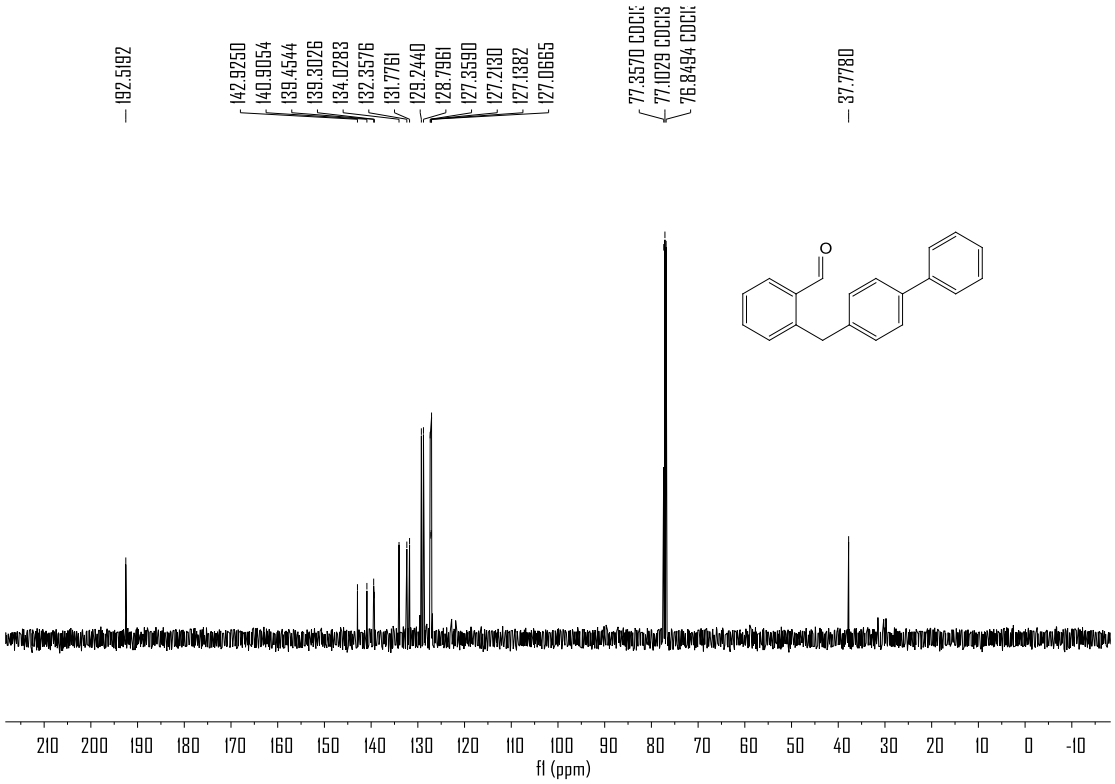
^{13}C NMR spectrum of compound 3r ($CDCl_3$, 126 MHz)



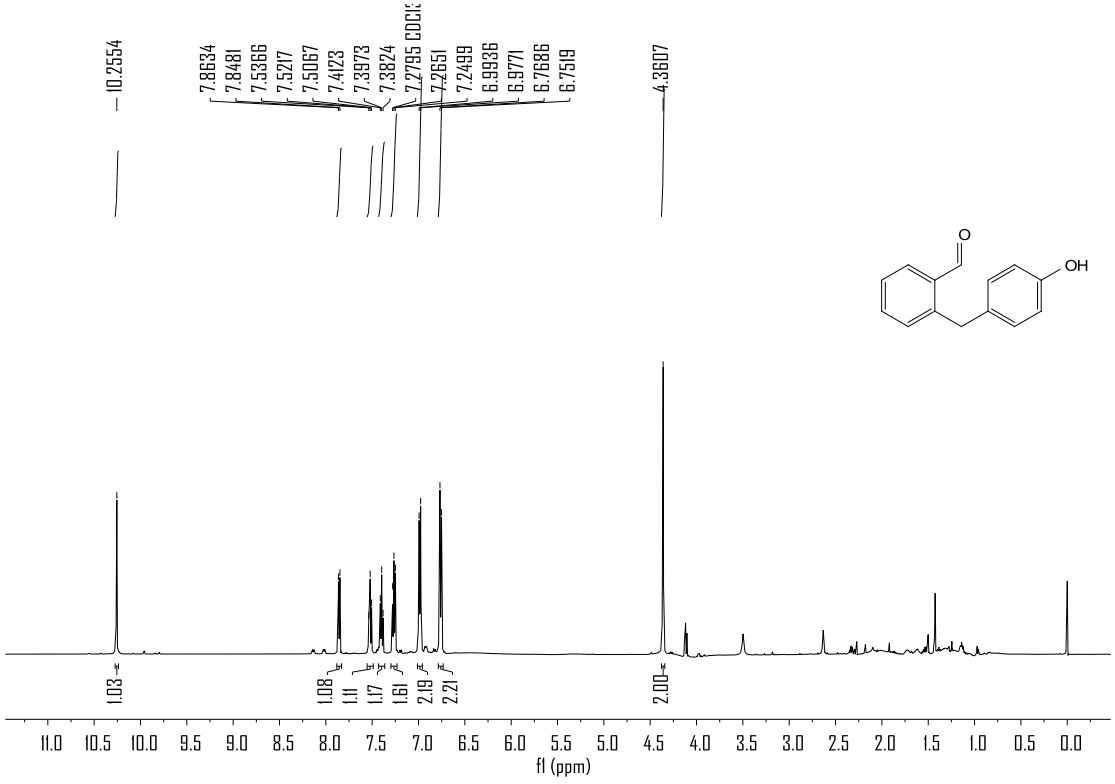
^{1}H NMR spectrum of compound 3s ($CDCl_3$, 500 MHz)



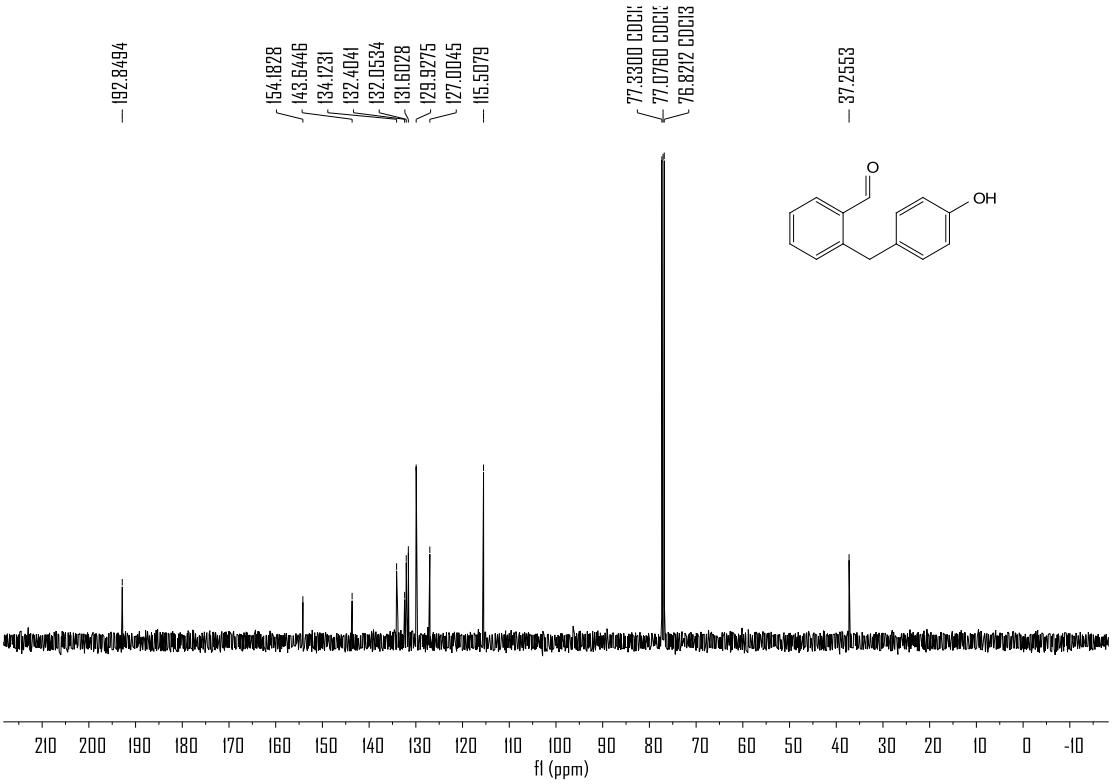
^{13}C NMR spectrum of compound 3s ($CDCl_3$, 126 MHz)



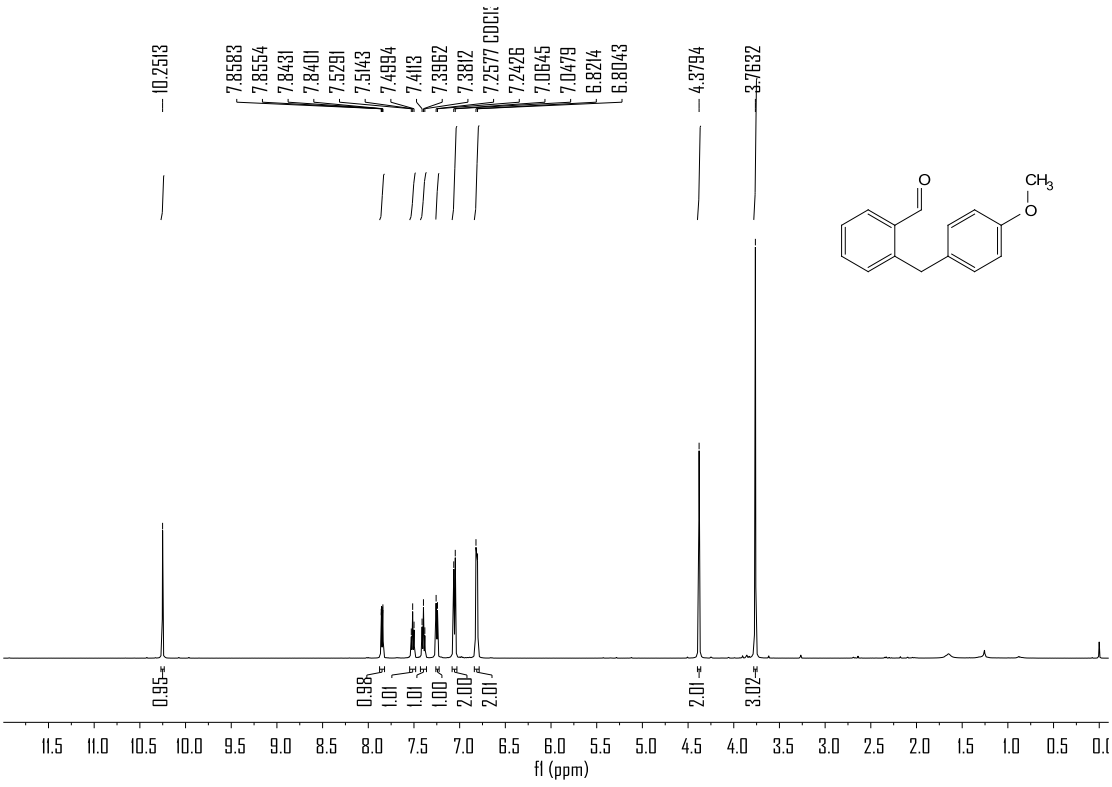
^{1}H NMR spectrum of compound 3t ($CDCl_3$, 500 MHz)



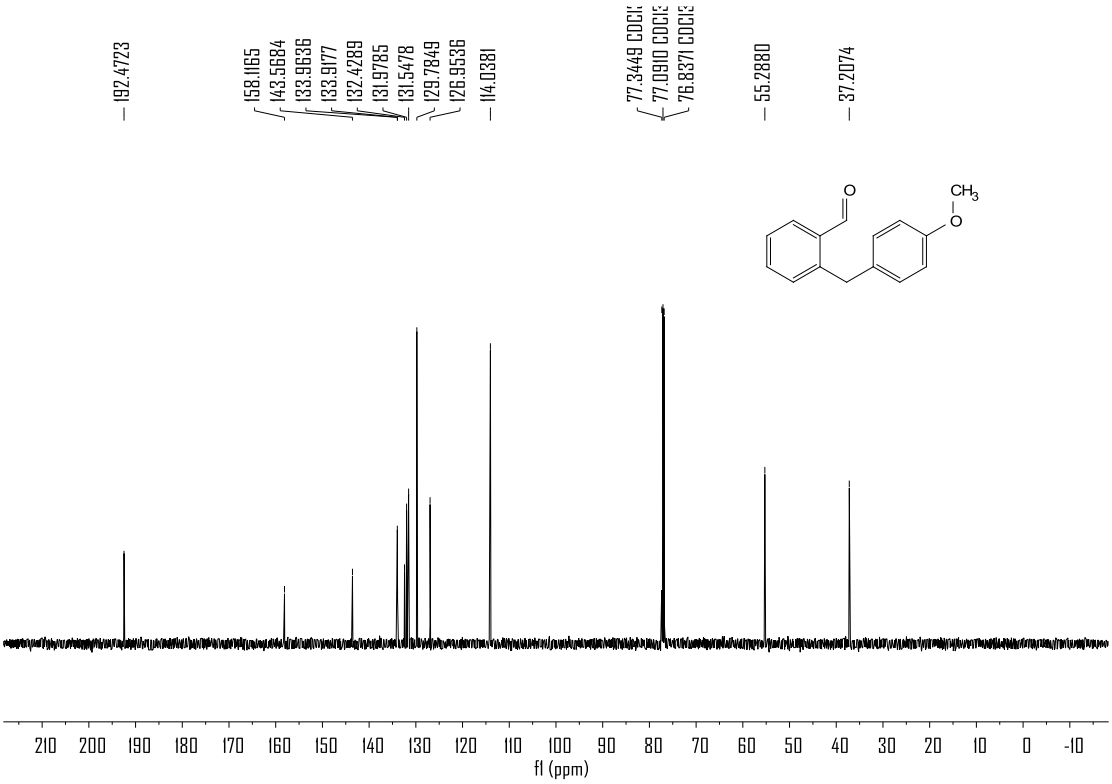
^{13}C NMR spectrum of compound 3t ($CDCl_3$, 126 MHz)



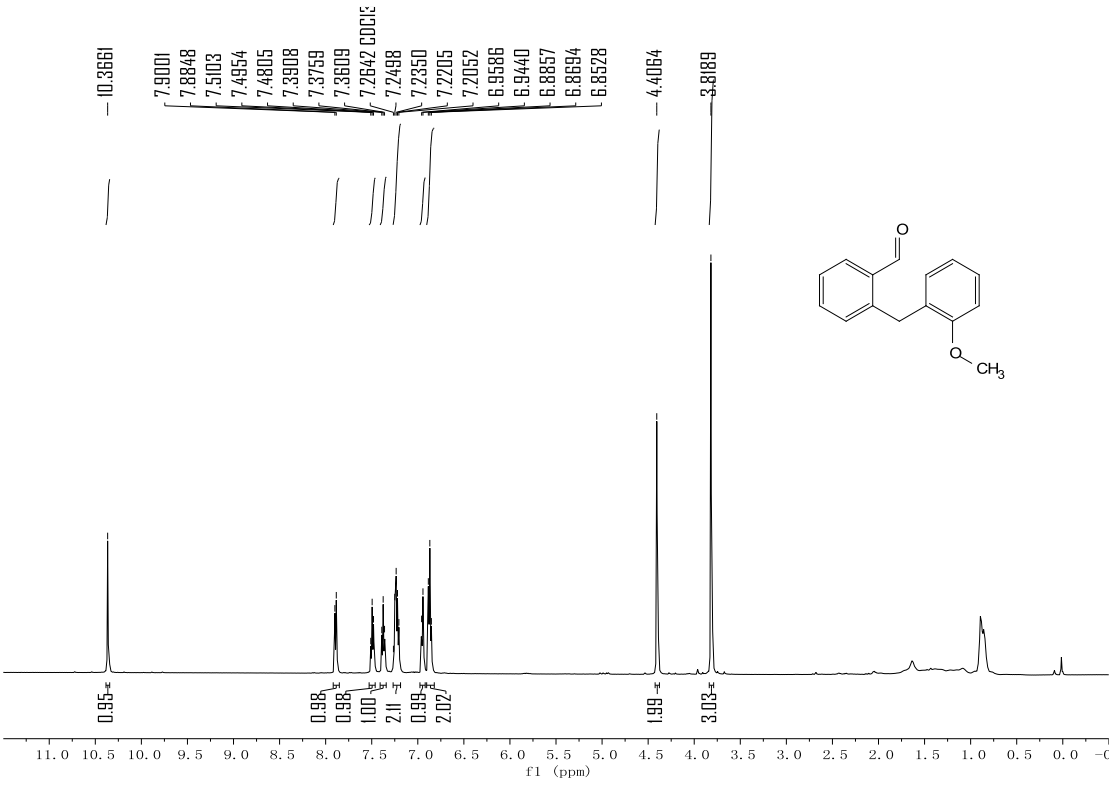
^{1}H NMR spectrum of compound 3u ($CDCl_3$, 500 MHz)



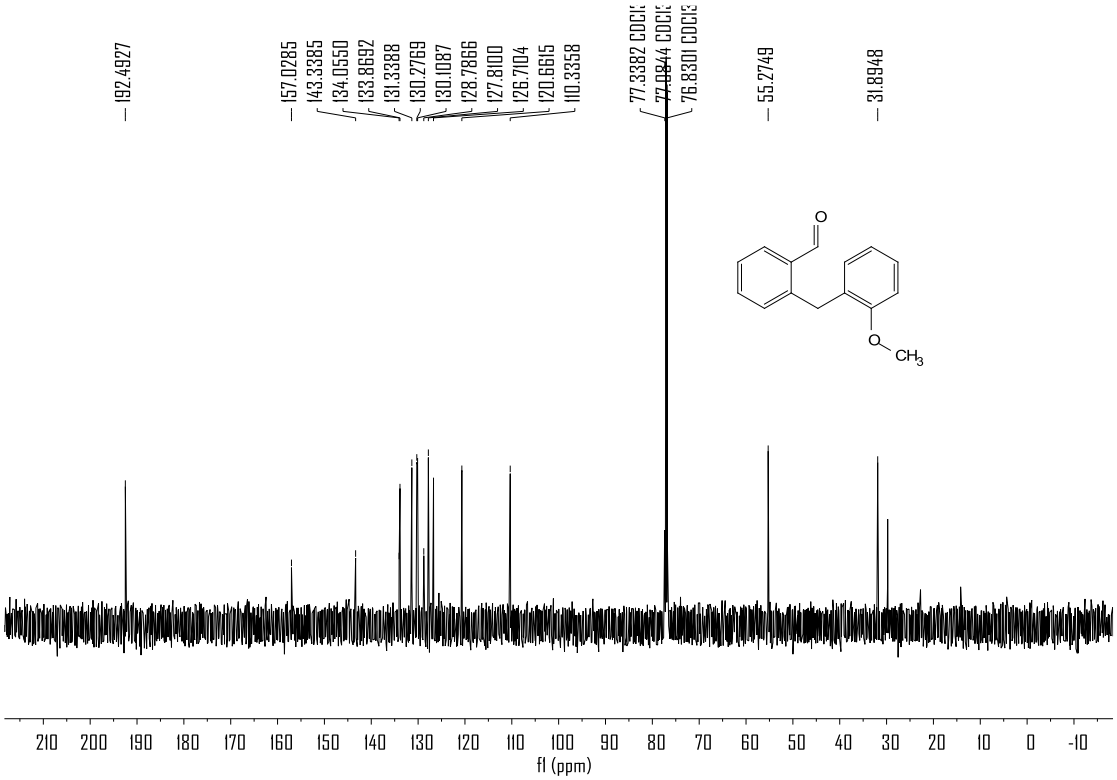
^{13}C NMR spectrum of compound 3u ($CDCl_3$, 126 MHz)



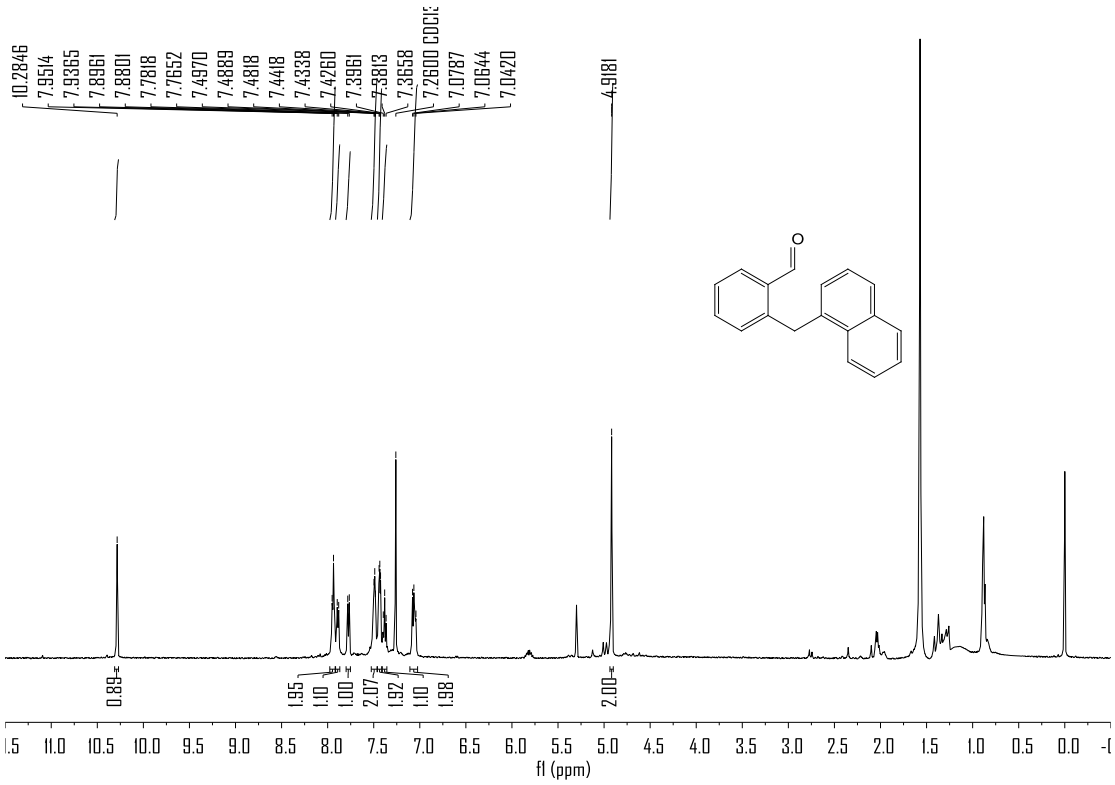
^{1}H NMR spectrum of compound 3v ($CDCl_3$, 500 MHz)



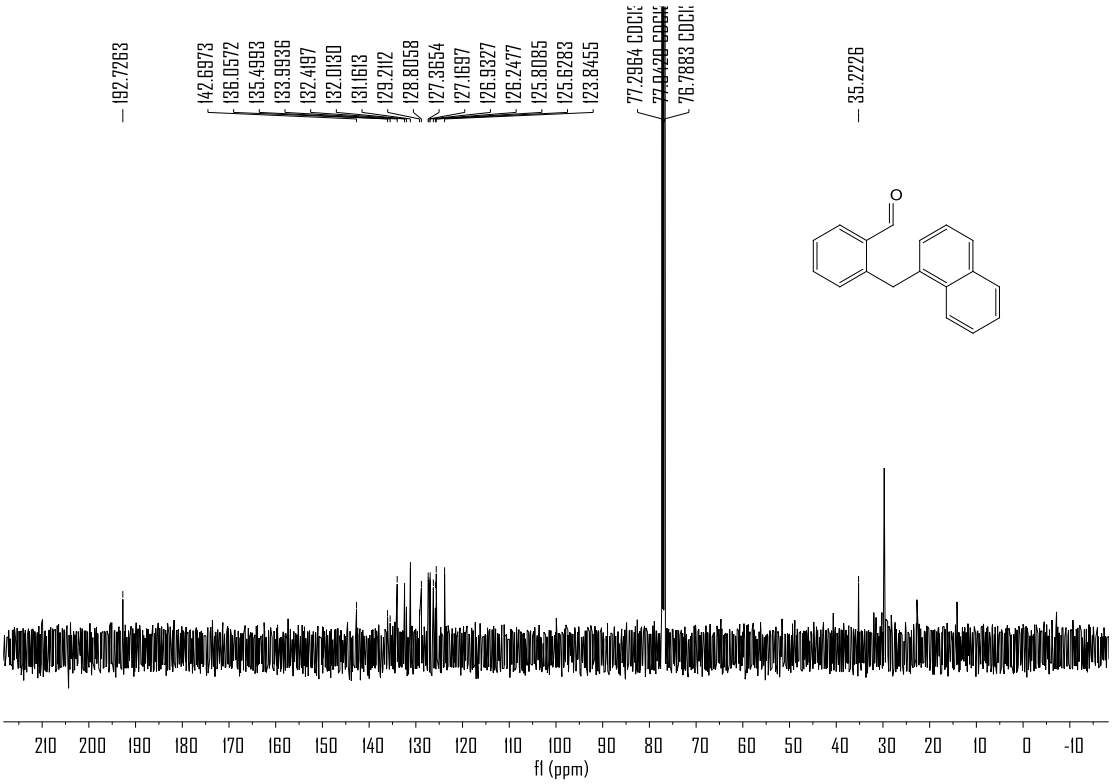
^{13}C NMR spectrum of compound 3v ($CDCl_3$, 126 MHz)



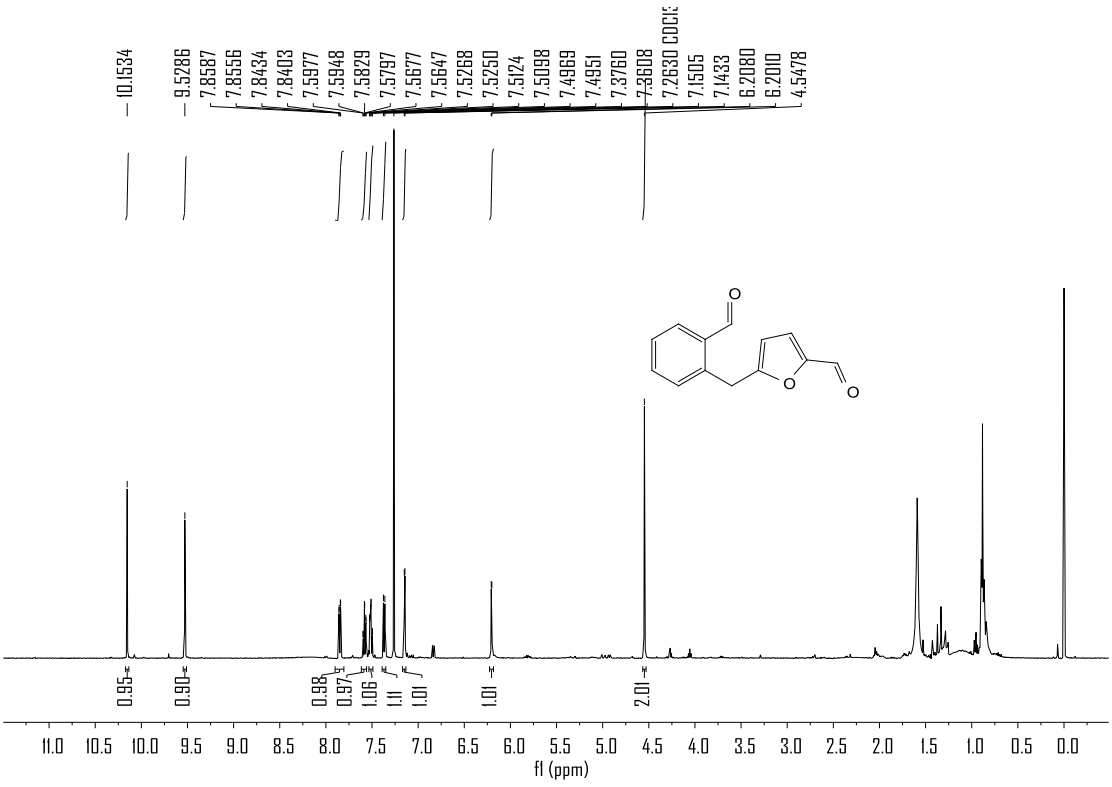
^{1}H NMR spectrum of compound 3w ($CDCl_3$, 500 MHz)



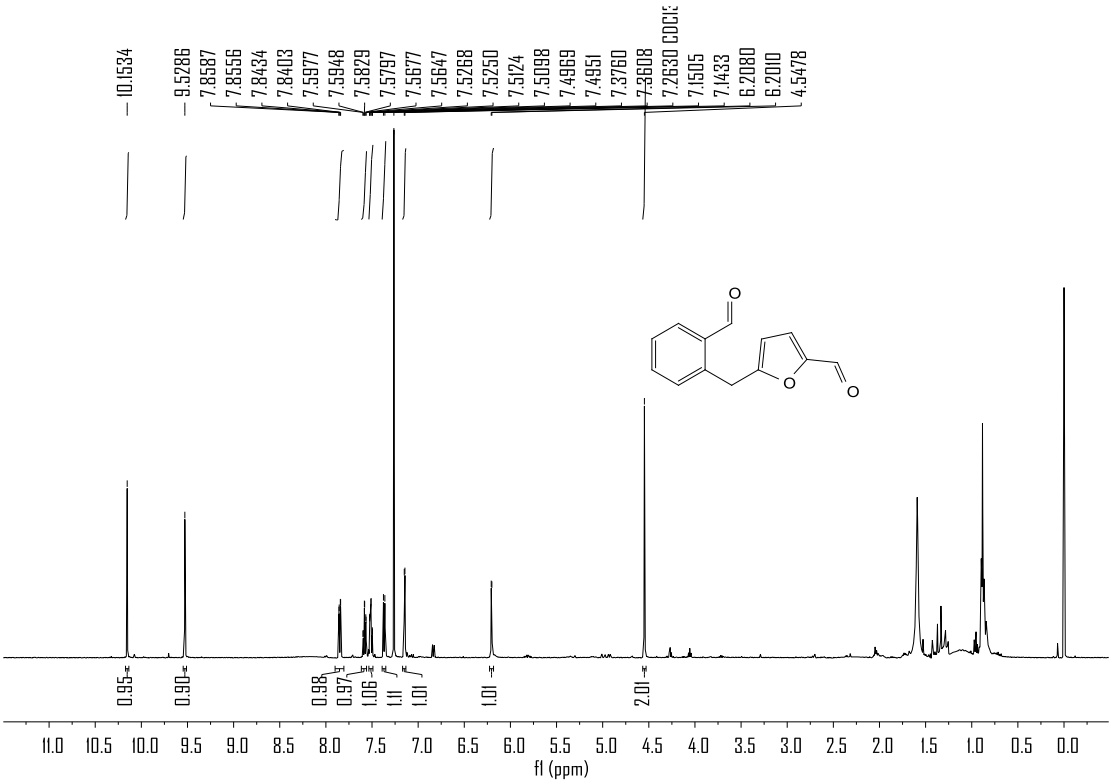
^{13}C NMR spectrum of compound 3w ($CDCl_3$, 126 MHz)



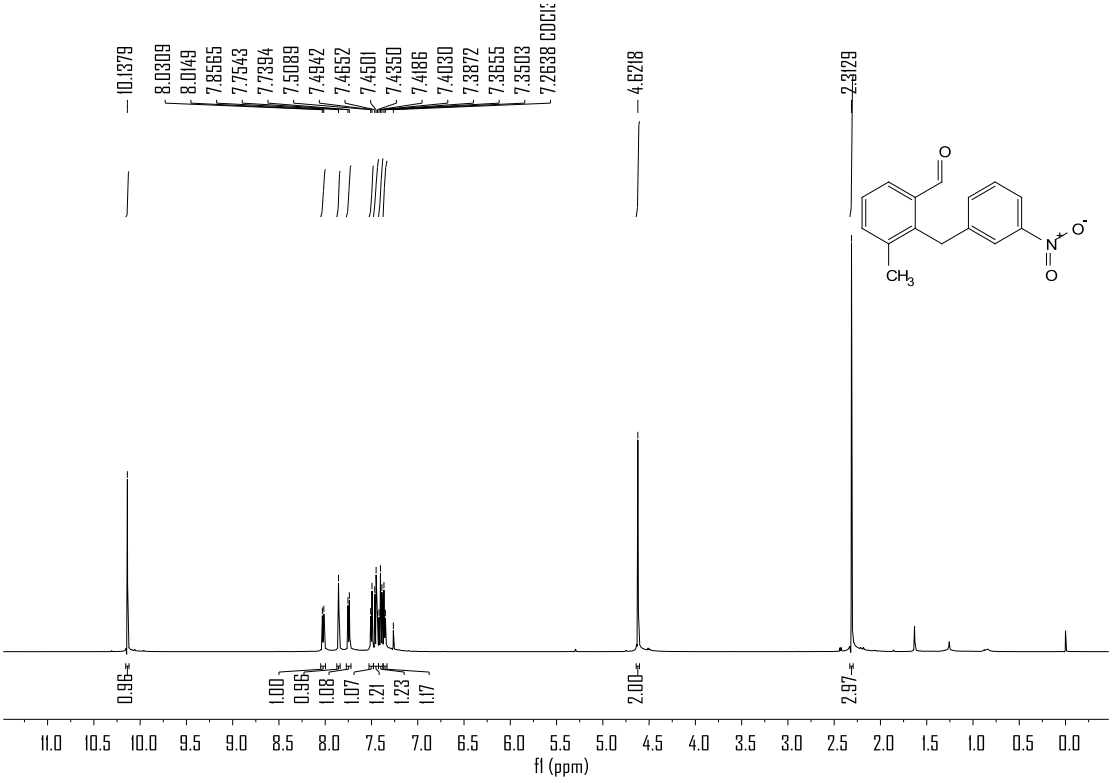
^{1}H NMR spectrum of compound 3x ($CDCl_3$, 500 MHz)



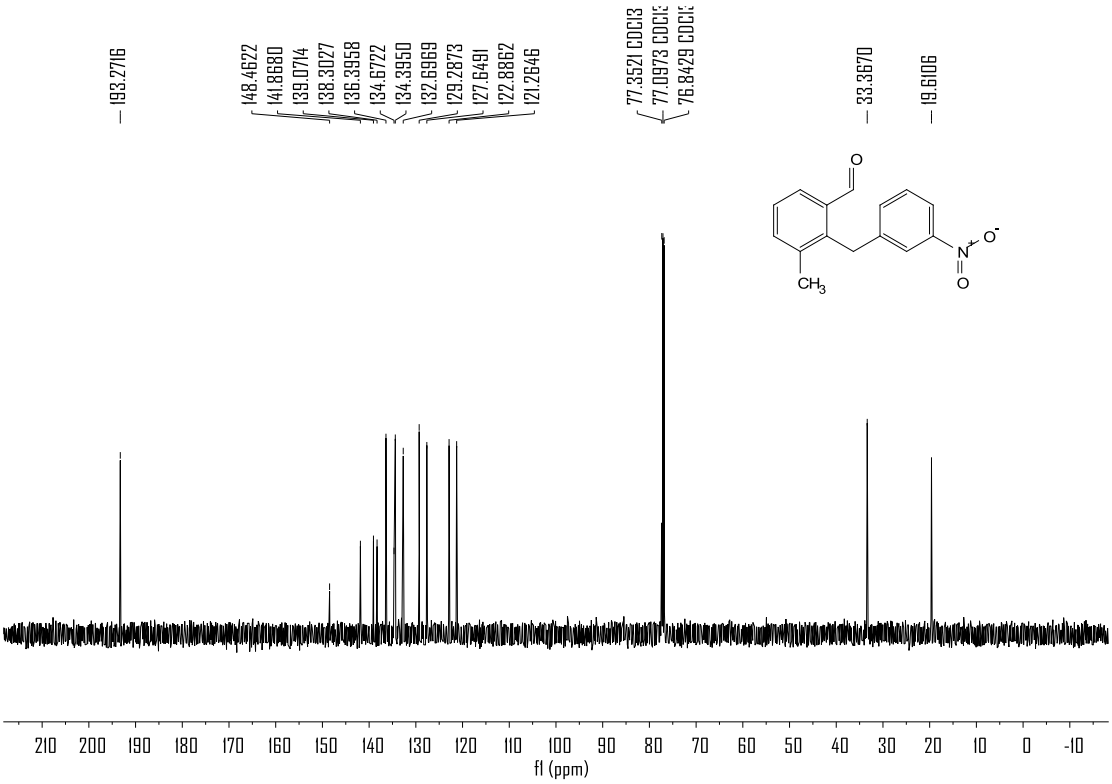
^{13}C NMR spectrum of compound 3x ($CDCl_3$, 126 MHz)



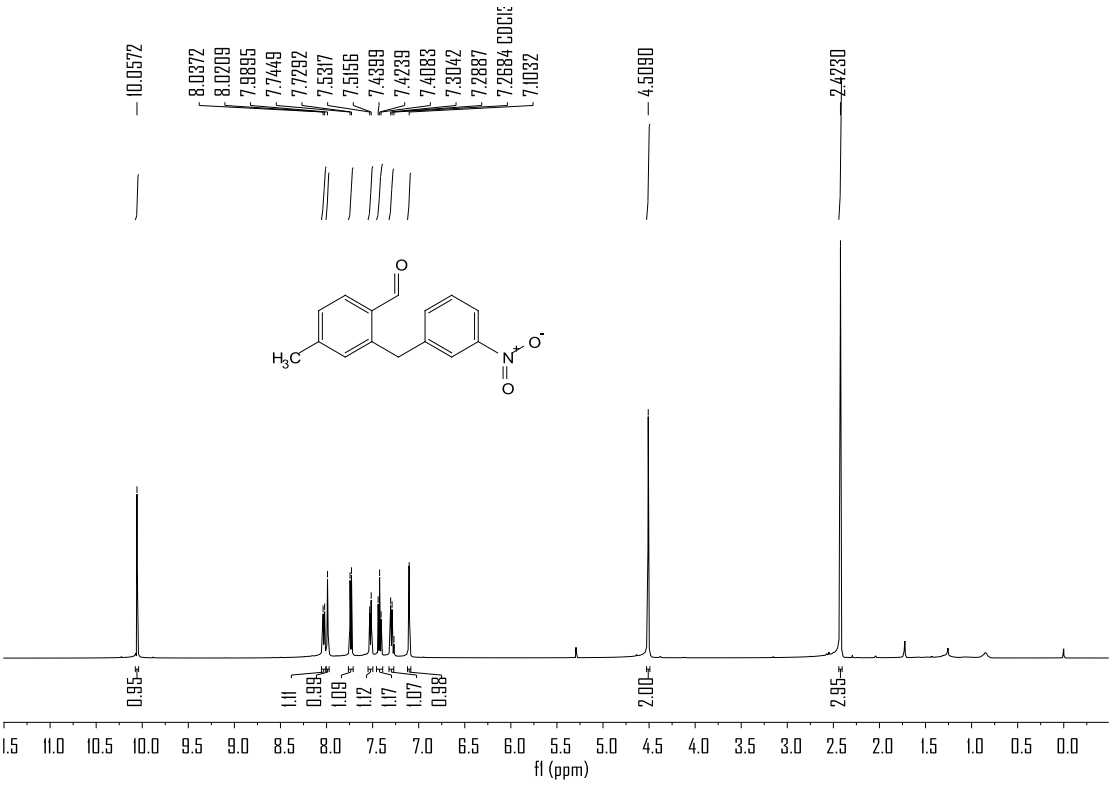
^{1}H NMR spectrum of compound 3aa ($CDCl_3$, 500 MHz)



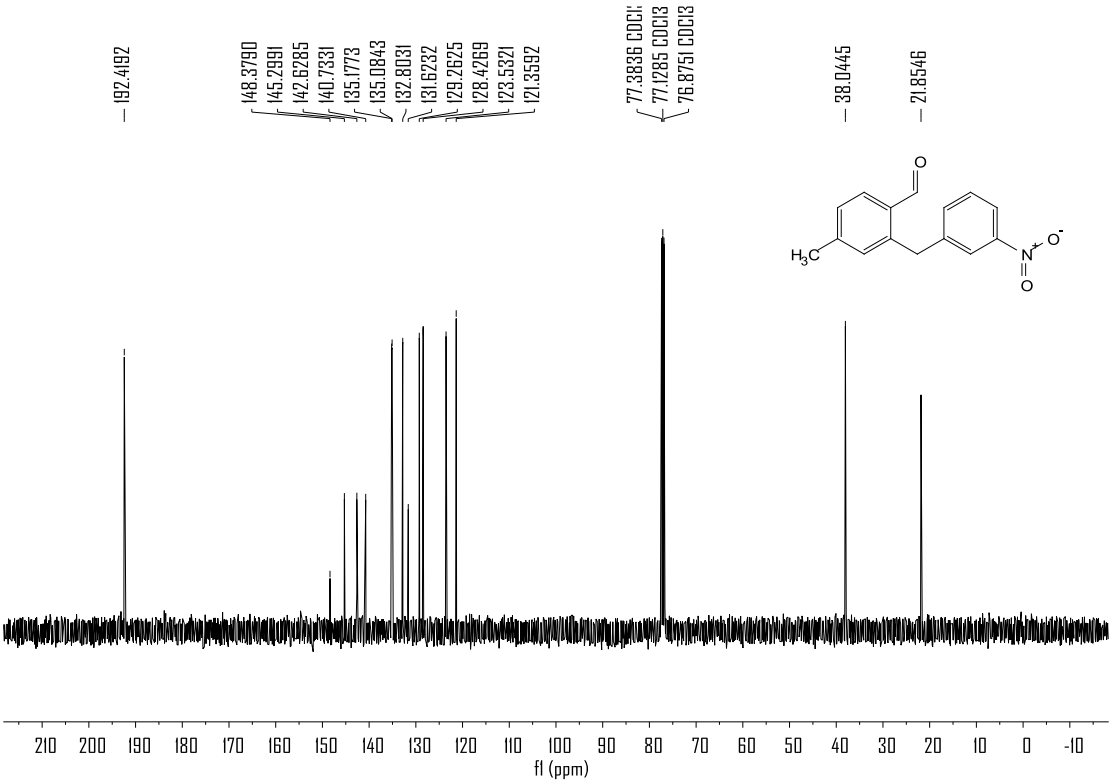
^{13}C NMR spectrum of compound 3aa ($CDCl_3$, 126 MHz)



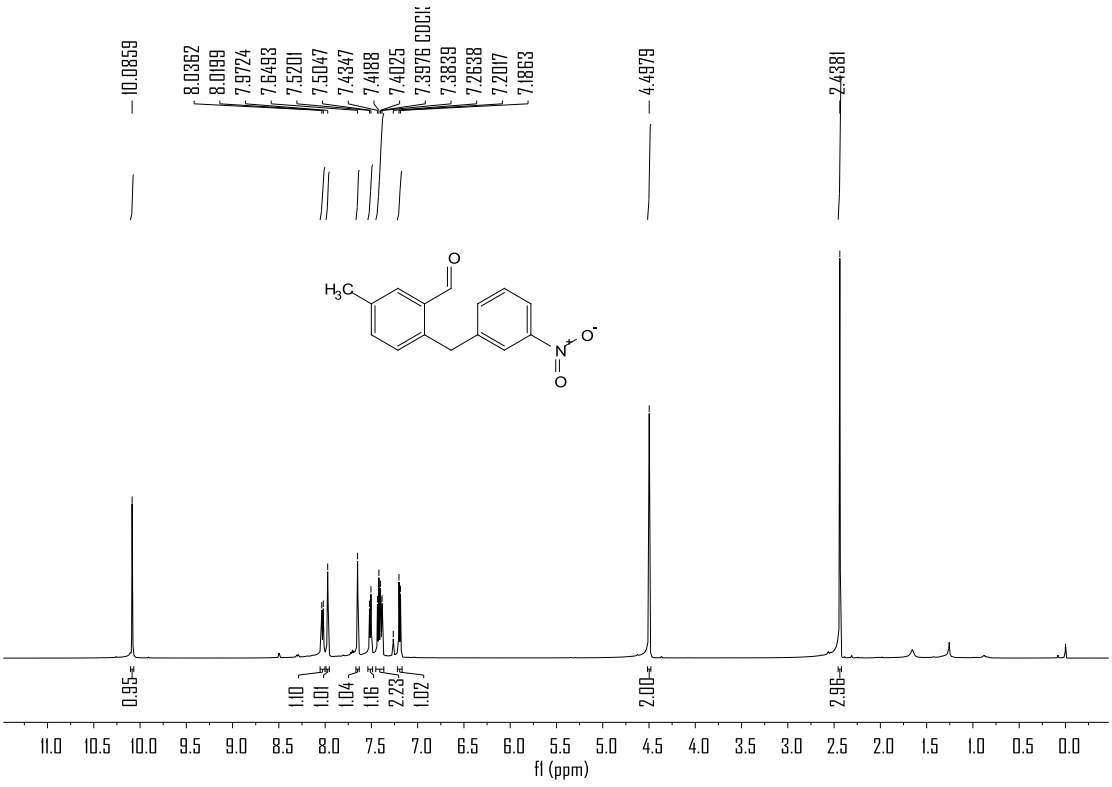
^{1}H NMR spectrum of compound 3ab ($CDCl_3$, 500 MHz)



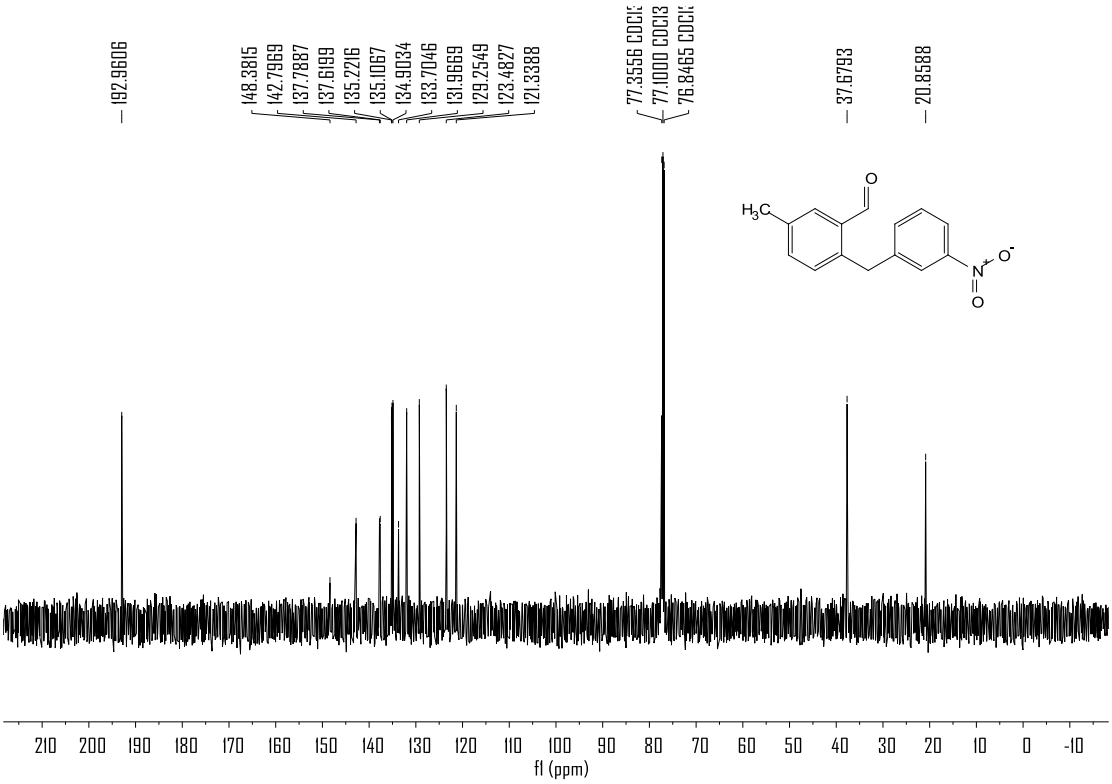
^{13}C NMR spectrum of compound 3ab ($CDCl_3$, 126 MHz)



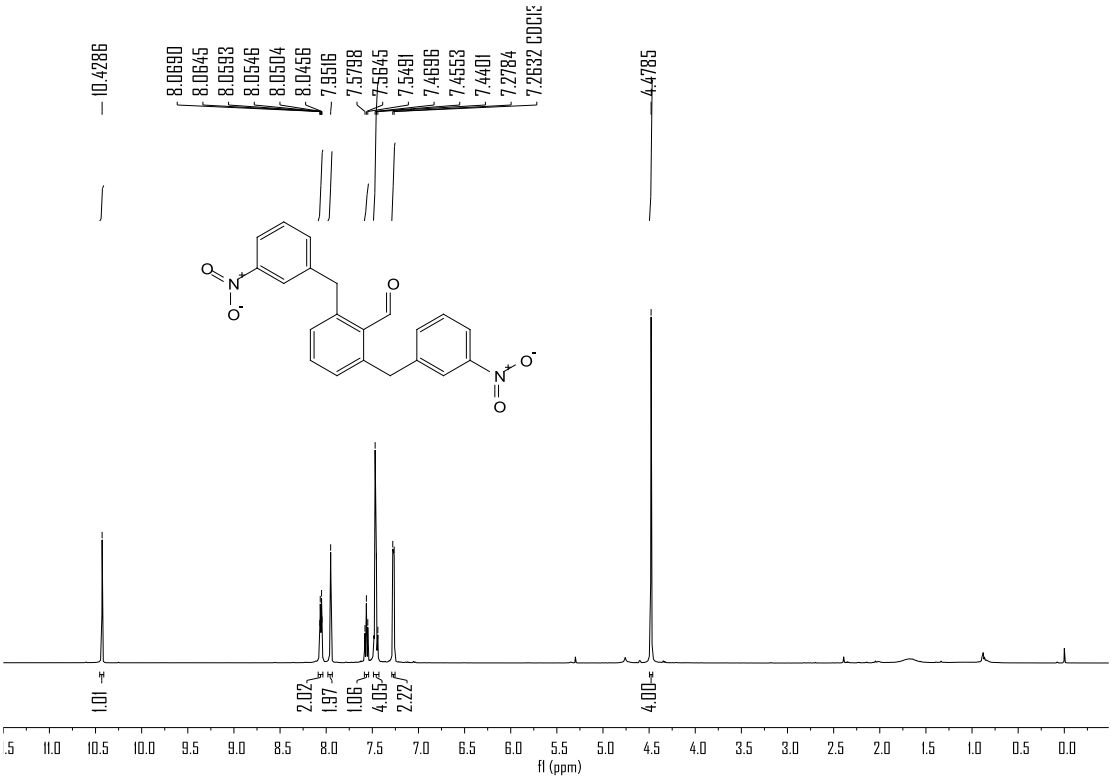
^{1}H NMR spectrum of compound 3ac ($CDCl_3$, 500 MHz)



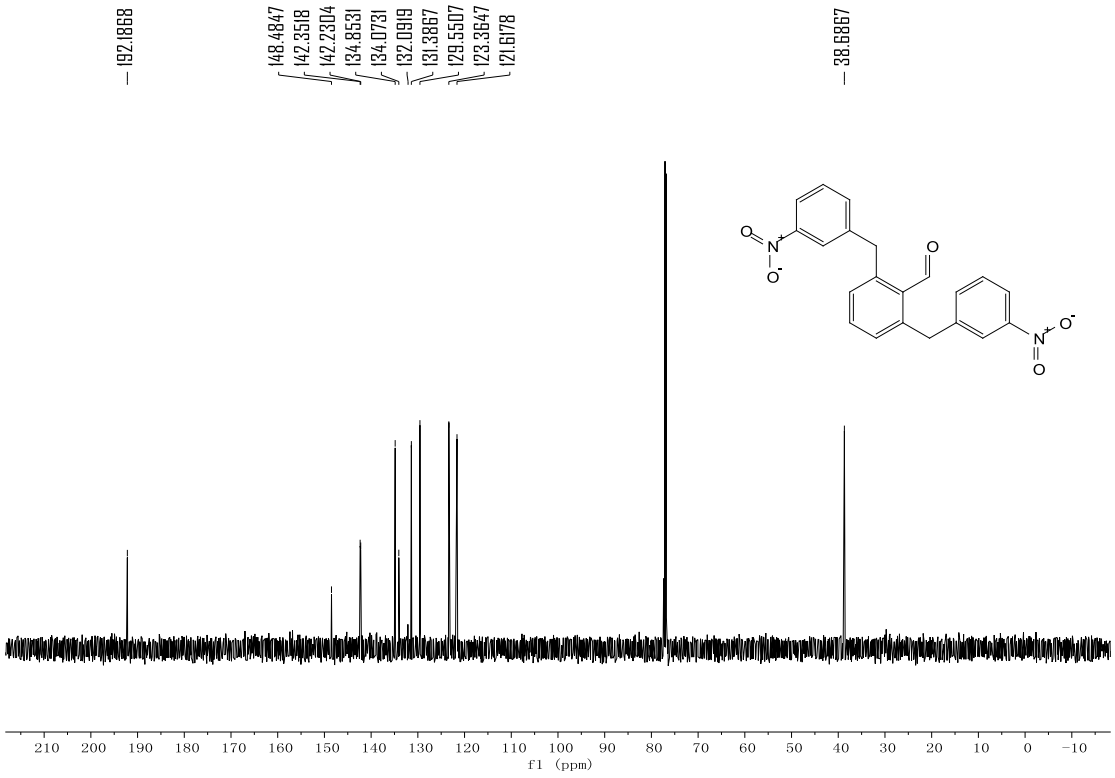
^{13}C NMR spectrum of compound 3ac ($CDCl_3$, 126 MHz)



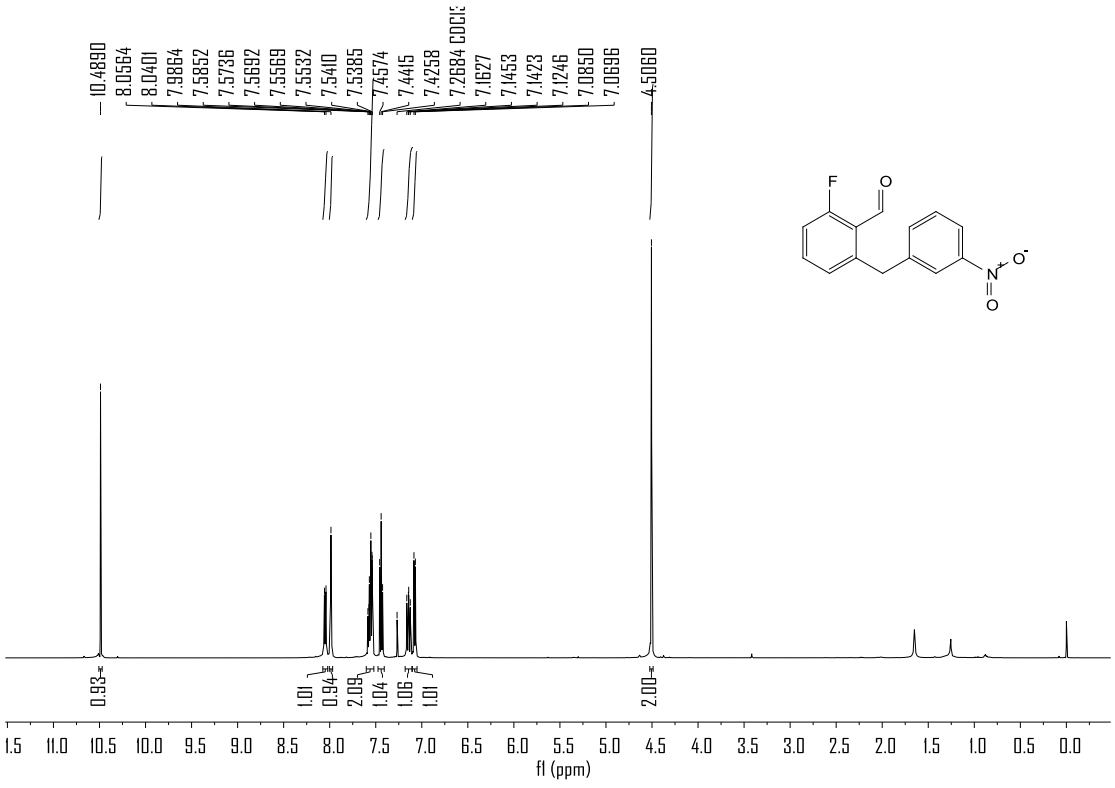
^{1}H NMR spectrum of compound 3ad ($CDCl_3$, 500 MHz)



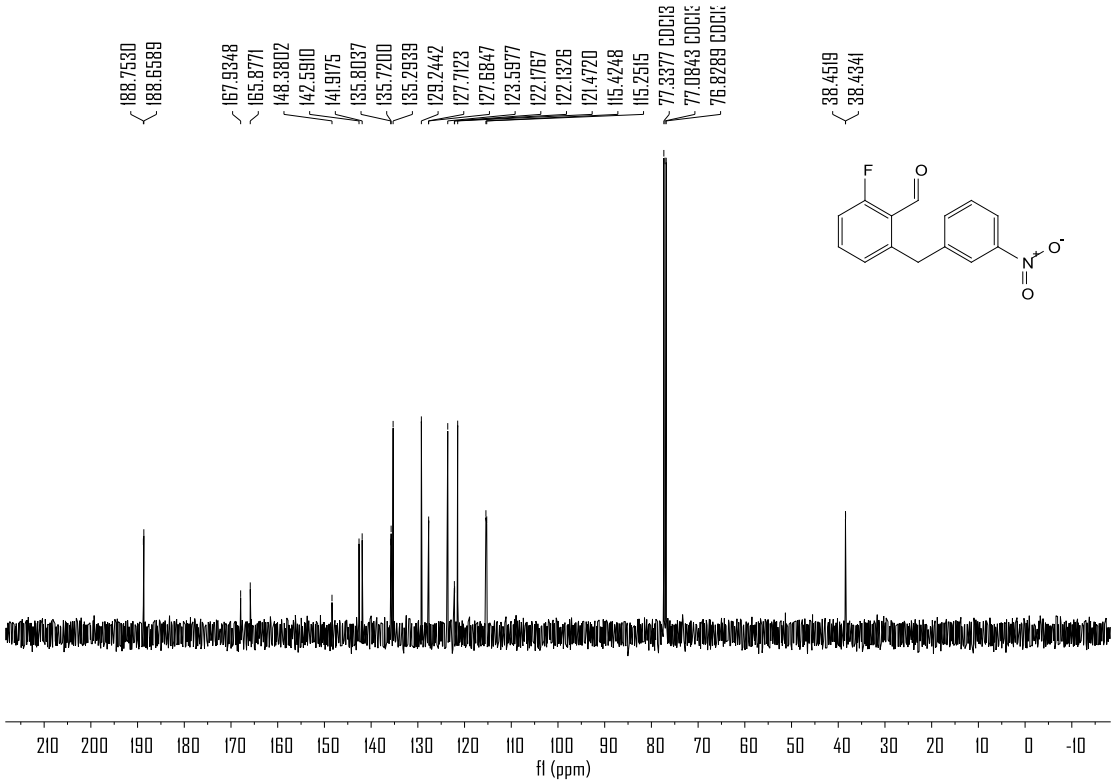
^{13}C NMR spectrum of compound 3ad ($CDCl_3$, 126 MHz)



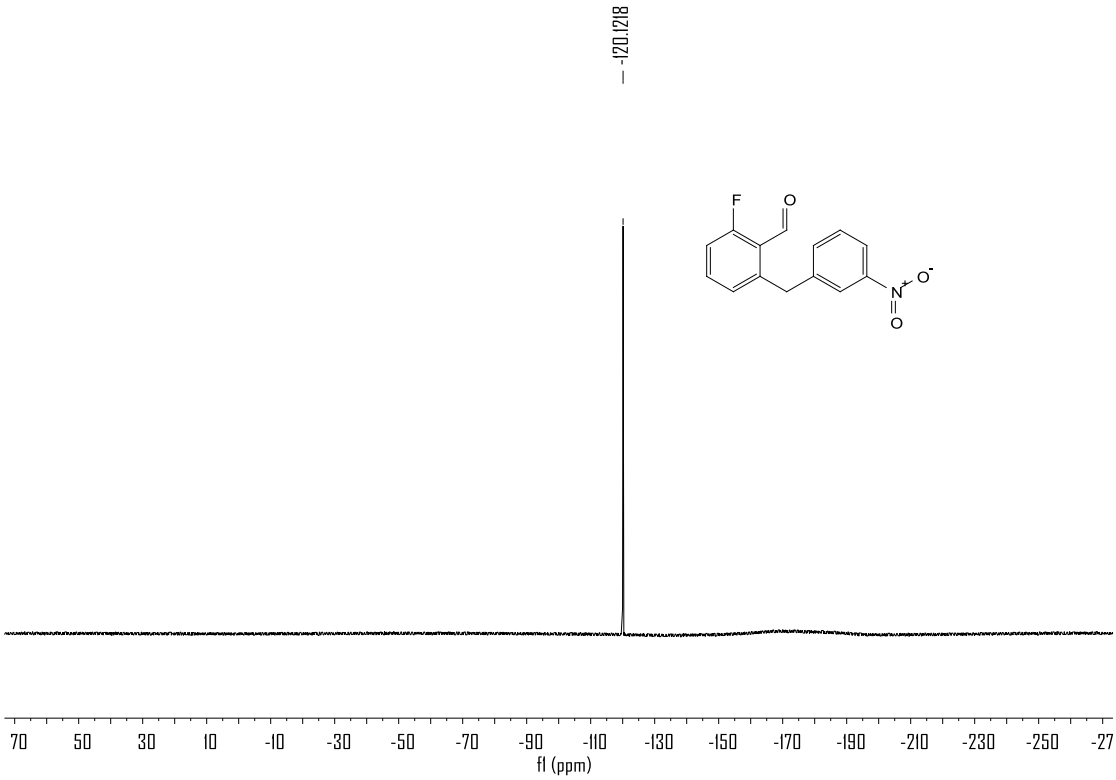
^{1}H NMR spectrum of compound 3ae ($CDCl_3$, 500 MHz)



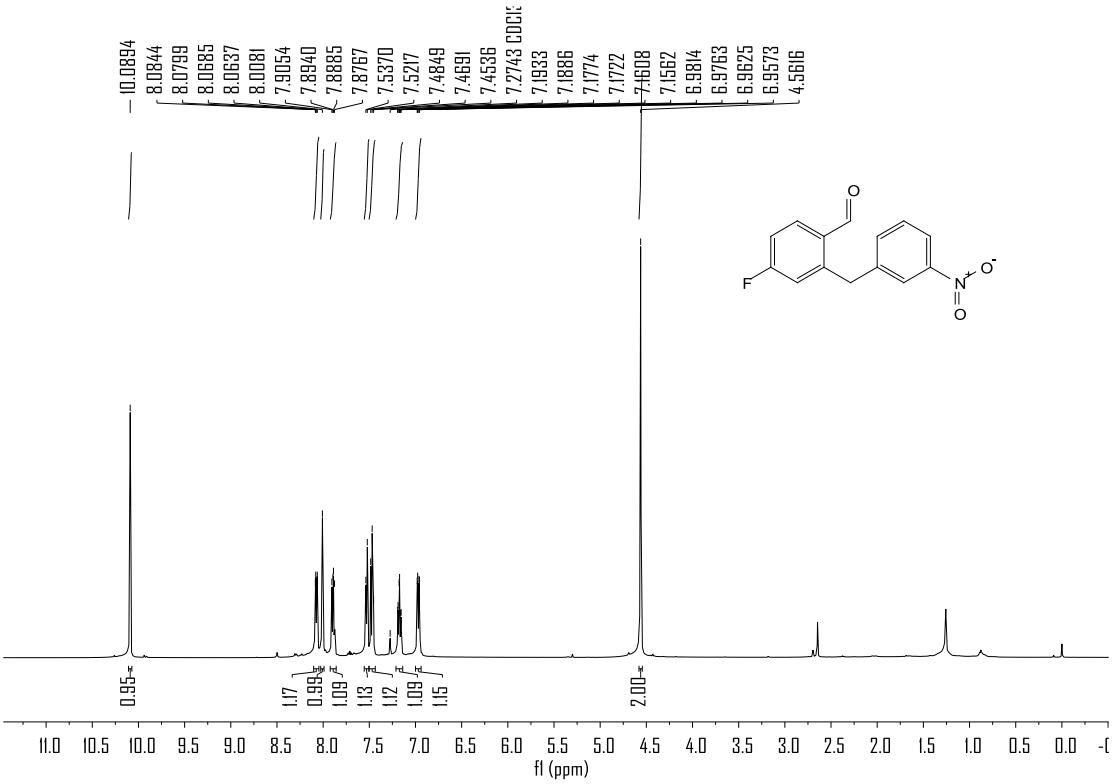
^{13}C NMR spectrum of compound 3ae ($CDCl_3$, 126 MHz)



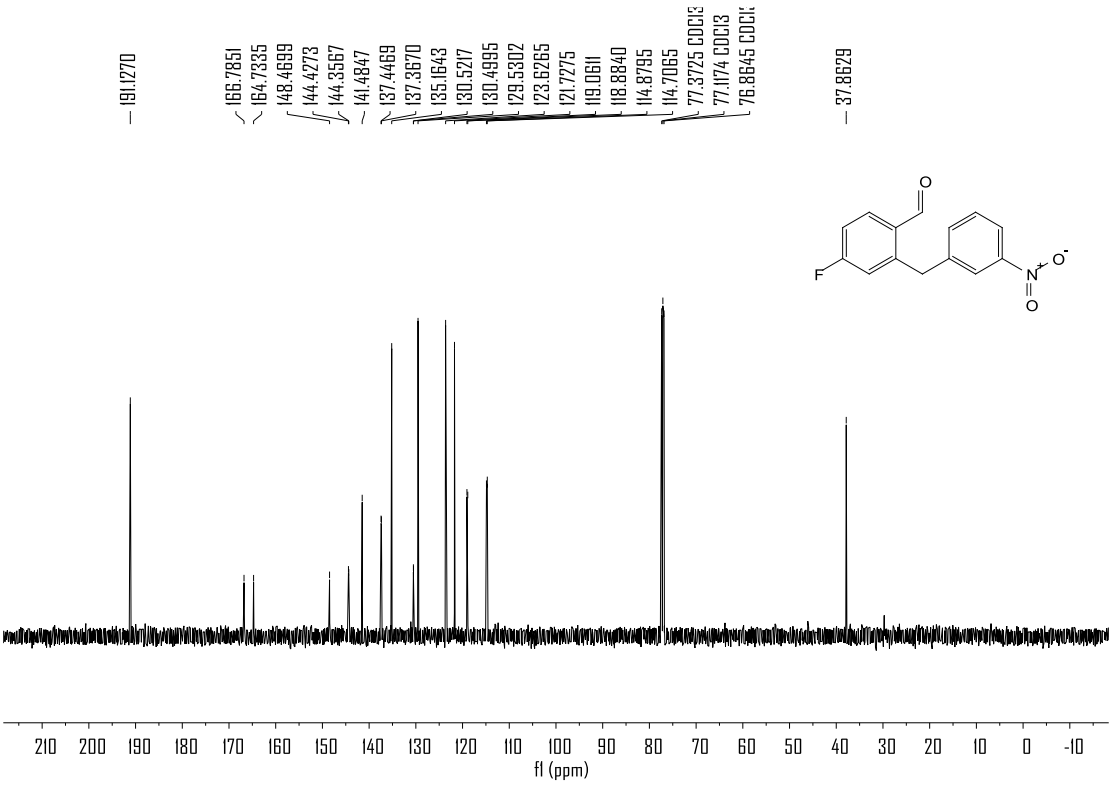
^{19}F NMR spectrum of compound 3ae ($CDCl_3$, 470 MHz)



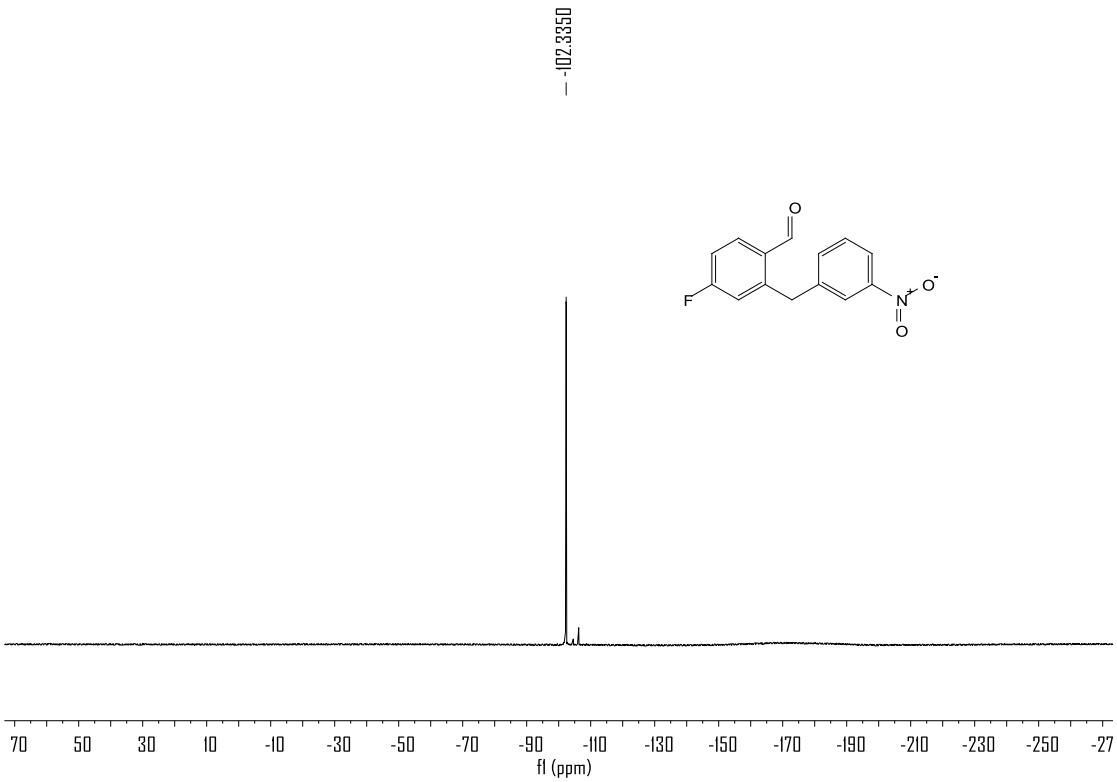
^{1}H NMR spectrum of compound 3af ($CDCl_3$, 500 MHz)



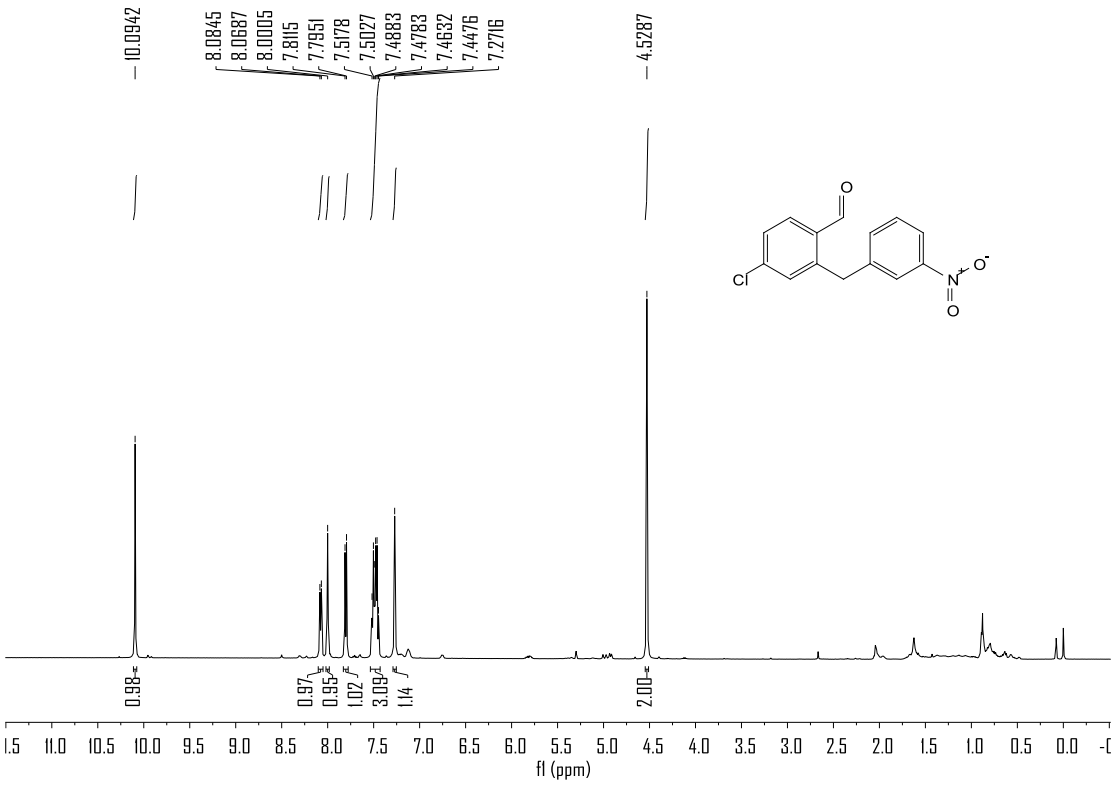
^{13}C NMR spectrum of compound 3af ($CDCl_3$, 126 MHz)



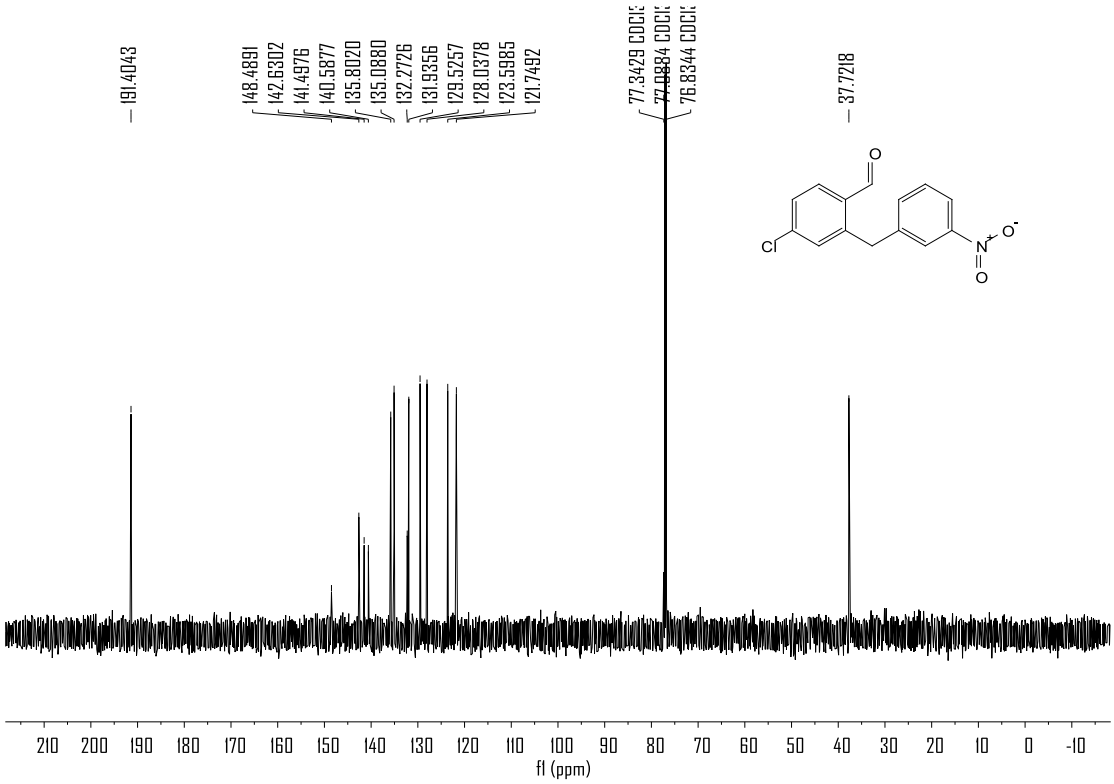
^{19}F NMR spectrum of compound 3af ($CDCl_3$, 470 MHz)



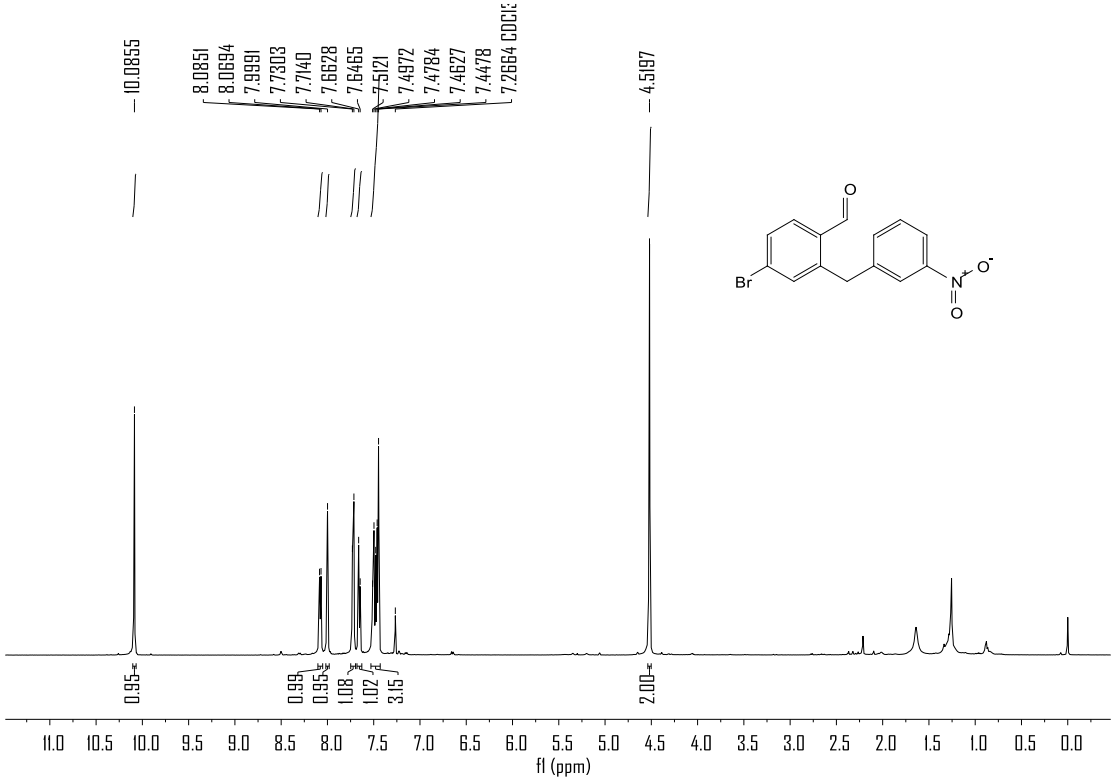
^{1}H NMR spectrum of compound 3ag ($CDCl_3$, 500 MHz)



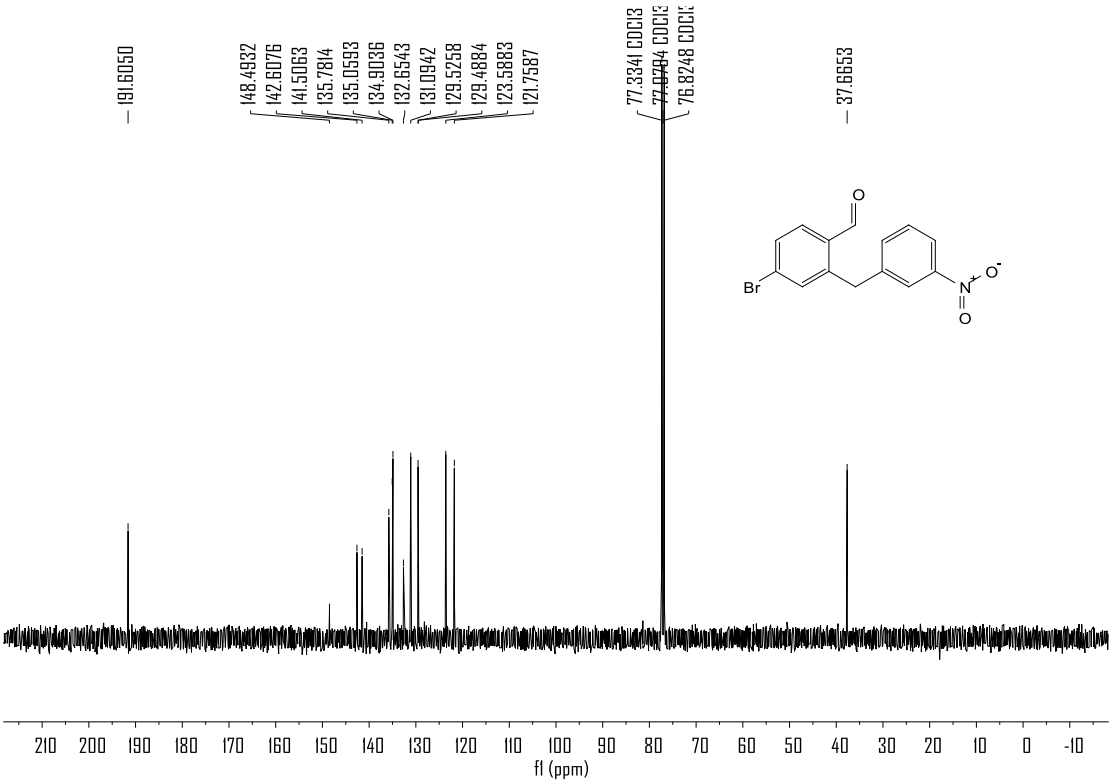
^{13}C NMR spectrum of compound 3ag ($CDCl_3$, 126 MHz)



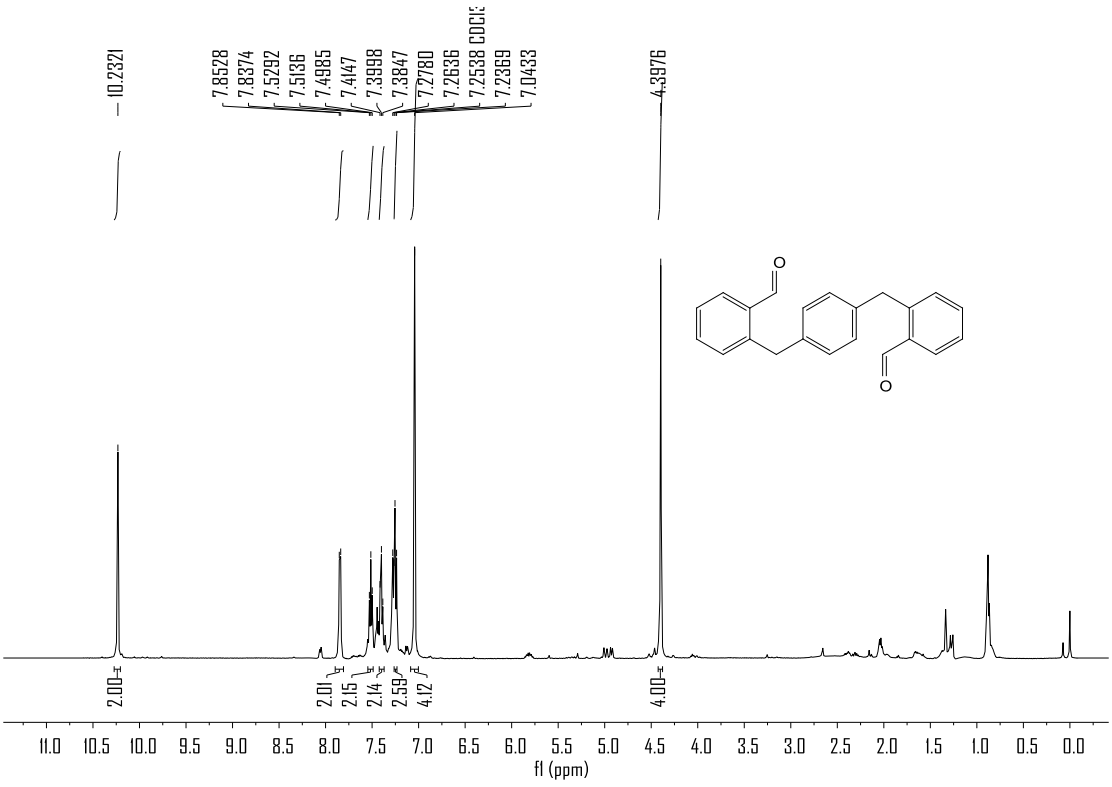
^{1}H NMR spectrum of compound 3ah ($CDCl_3$, 500 MHz)



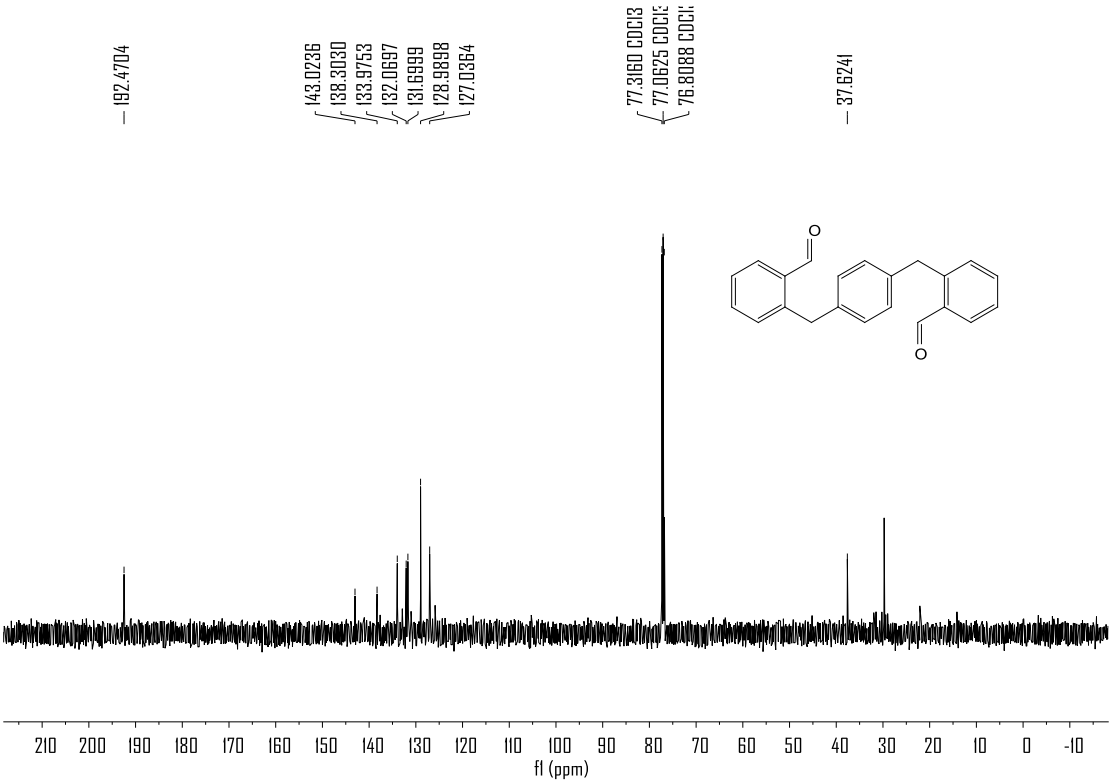
^{13}C NMR spectrum of compound 3ah ($CDCl_3$, 126 MHz)



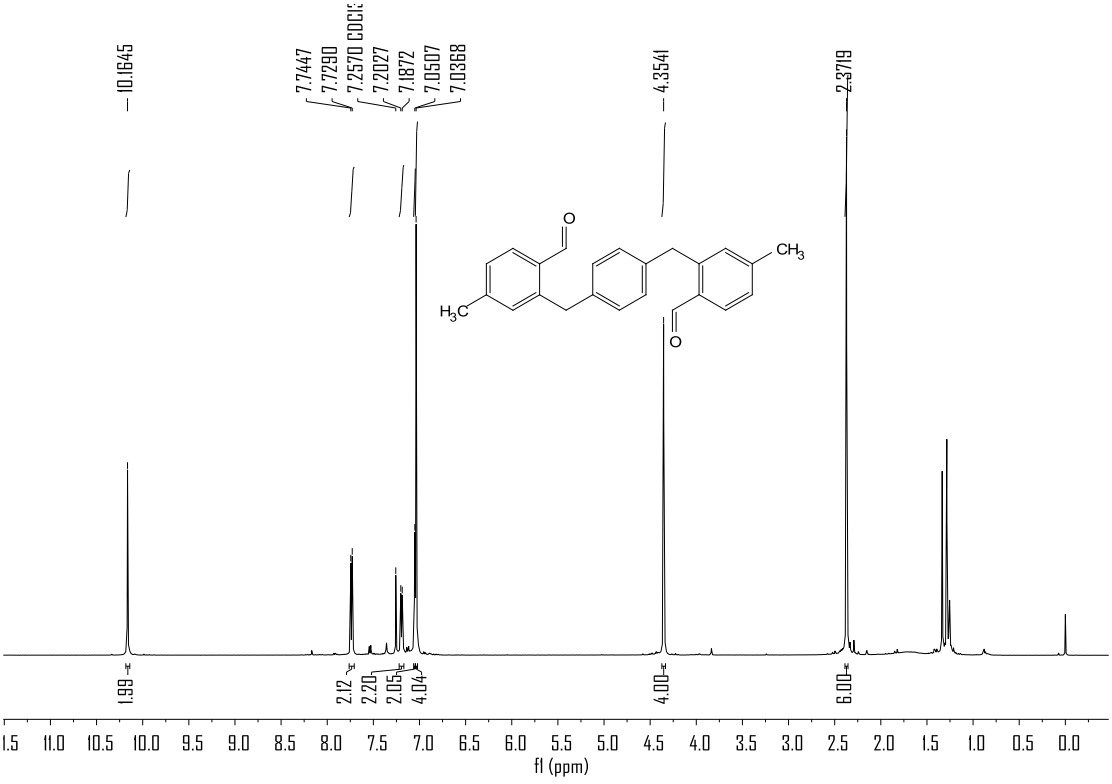
^{1}H NMR spectrum of compound 4oa ($CDCl_3$, 500 MHz)



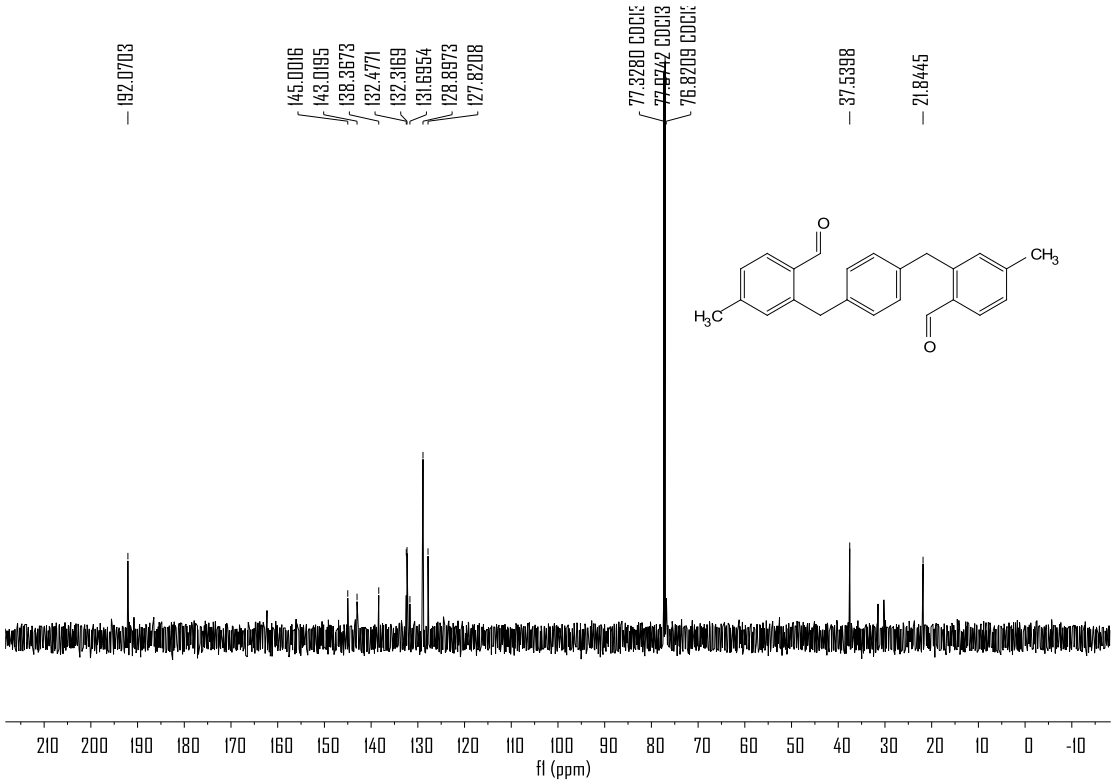
^{13}C NMR spectrum of compound 4oa ($CDCl_3$, 126 MHz)



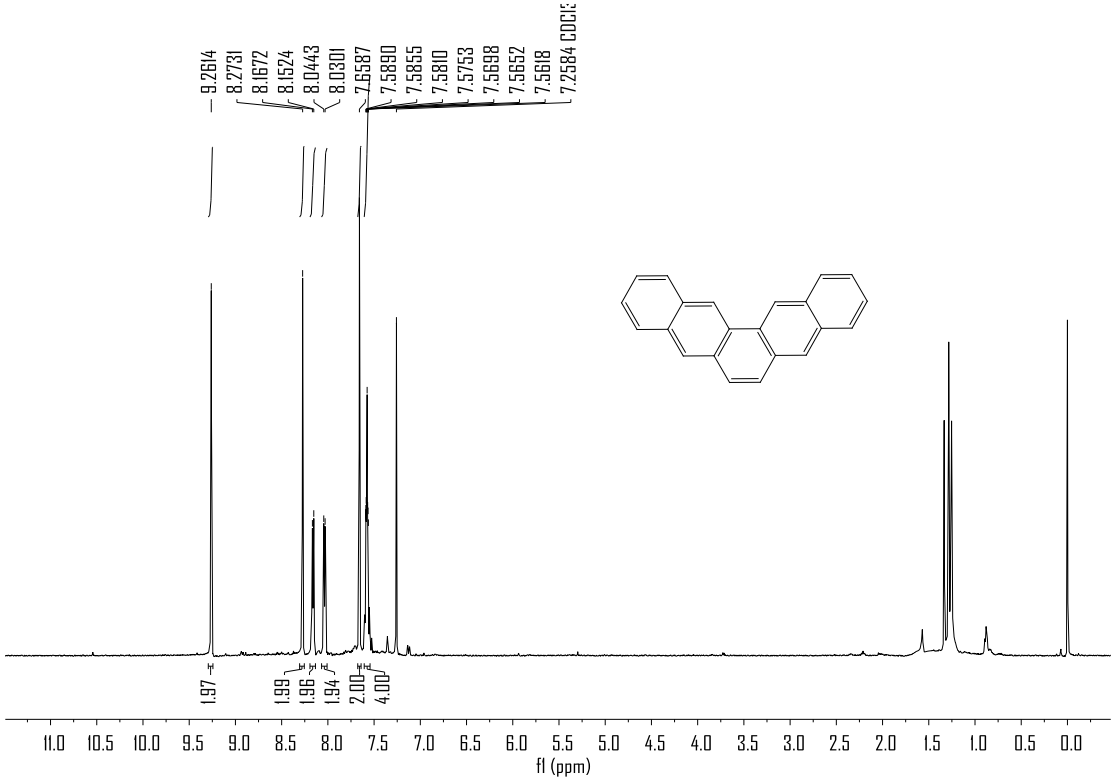
^{1}H NMR spectrum of compound 4ob ($CDCl_3$, 500 MHz)



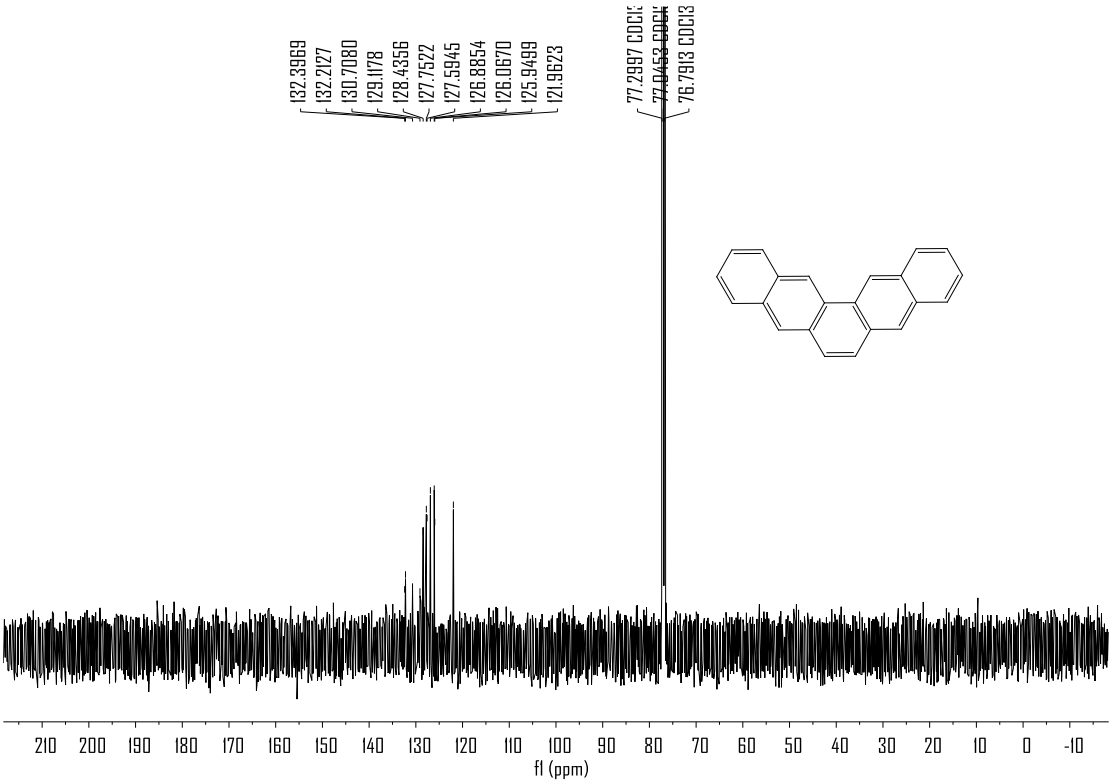
^{13}C NMR spectrum of compound 4ob ($CDCl_3$, 126 MHz)



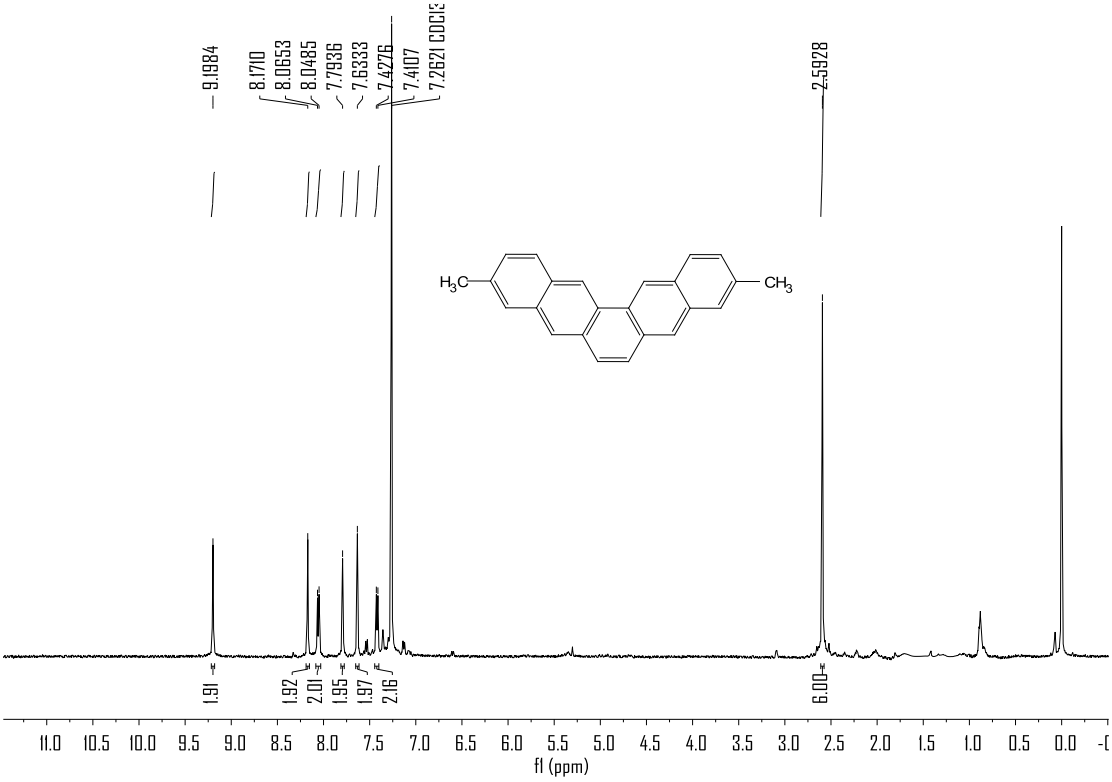
^{1}H NMR spectrum of compound 5oa ($CDCl_3$, 500 MHz)



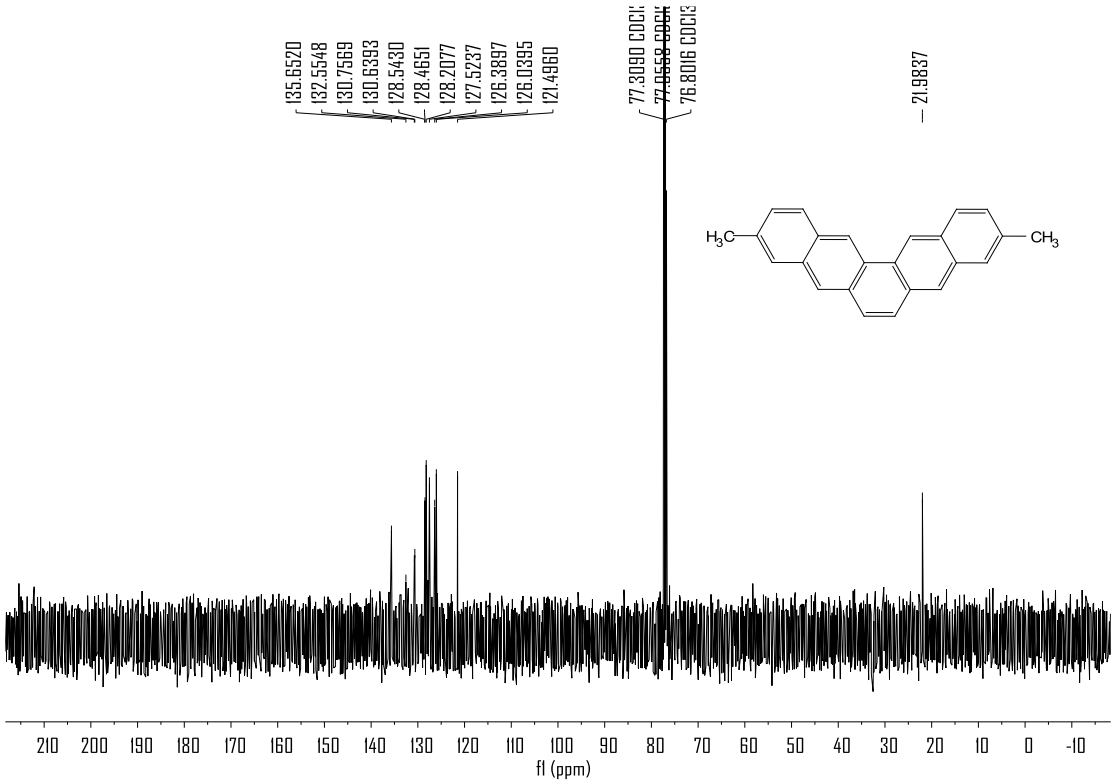
^{13}C NMR spectrum of compound 5oa ($CDCl_3$, 126 MHz)



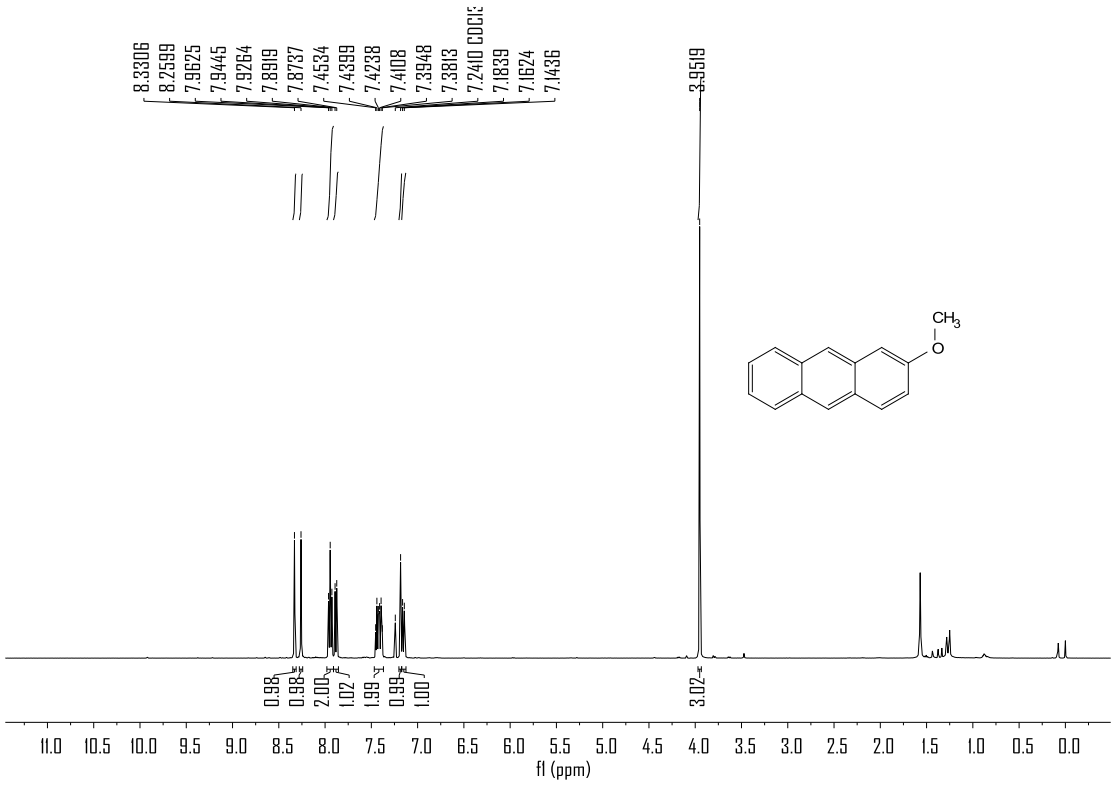
^{1}H NMR spectrum of compound 5ob ($CDCl_3$, 500 MHz)



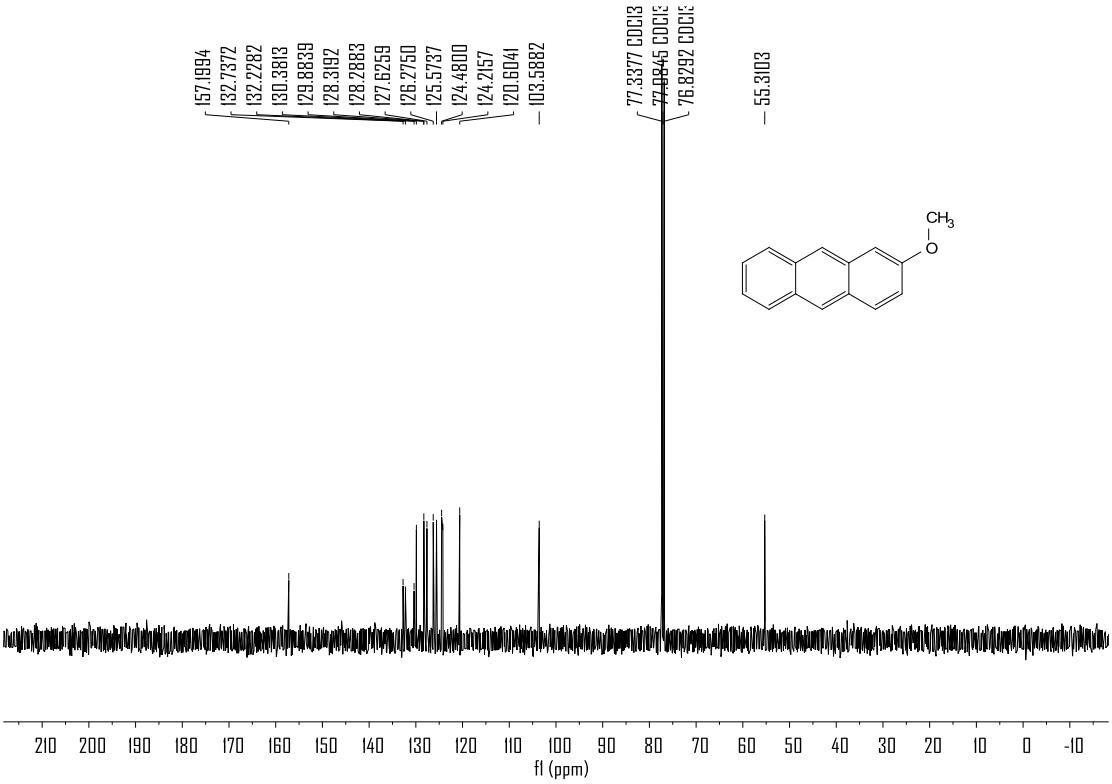
^{13}C NMR spectrum of compound 5ob ($CDCl_3$, 126 MHz)



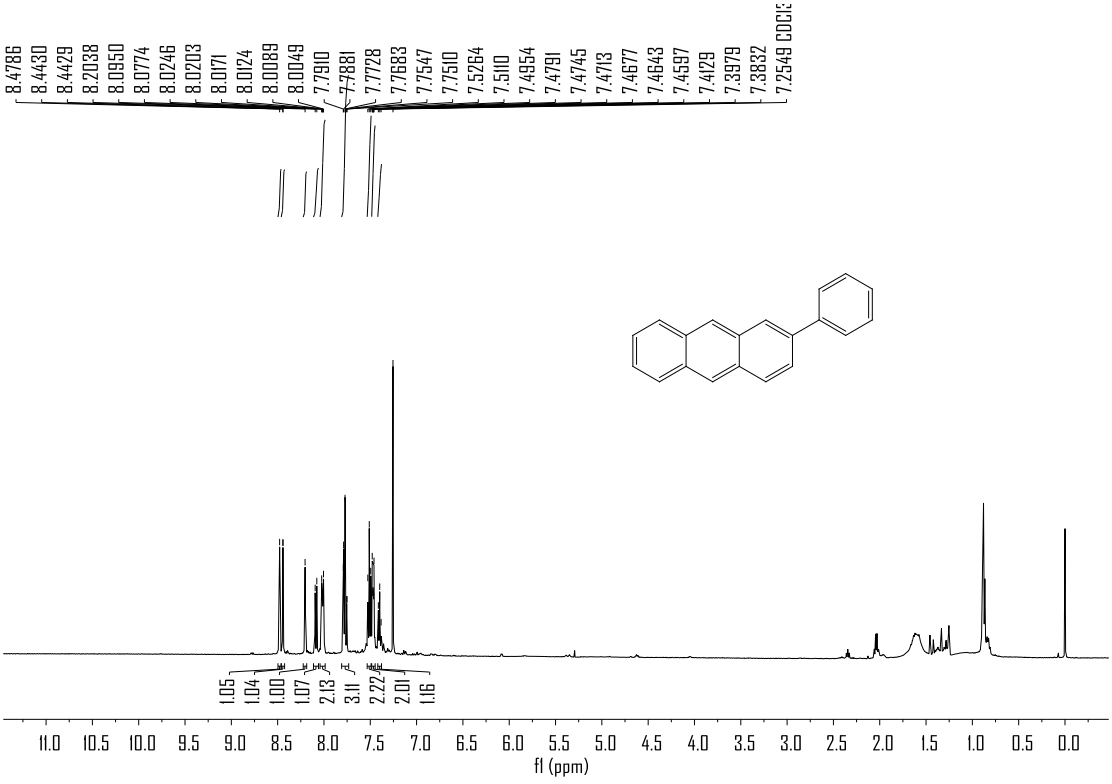
^{1}H NMR spectrum of compound 6a ($CDCl_3$, 500 MHz)



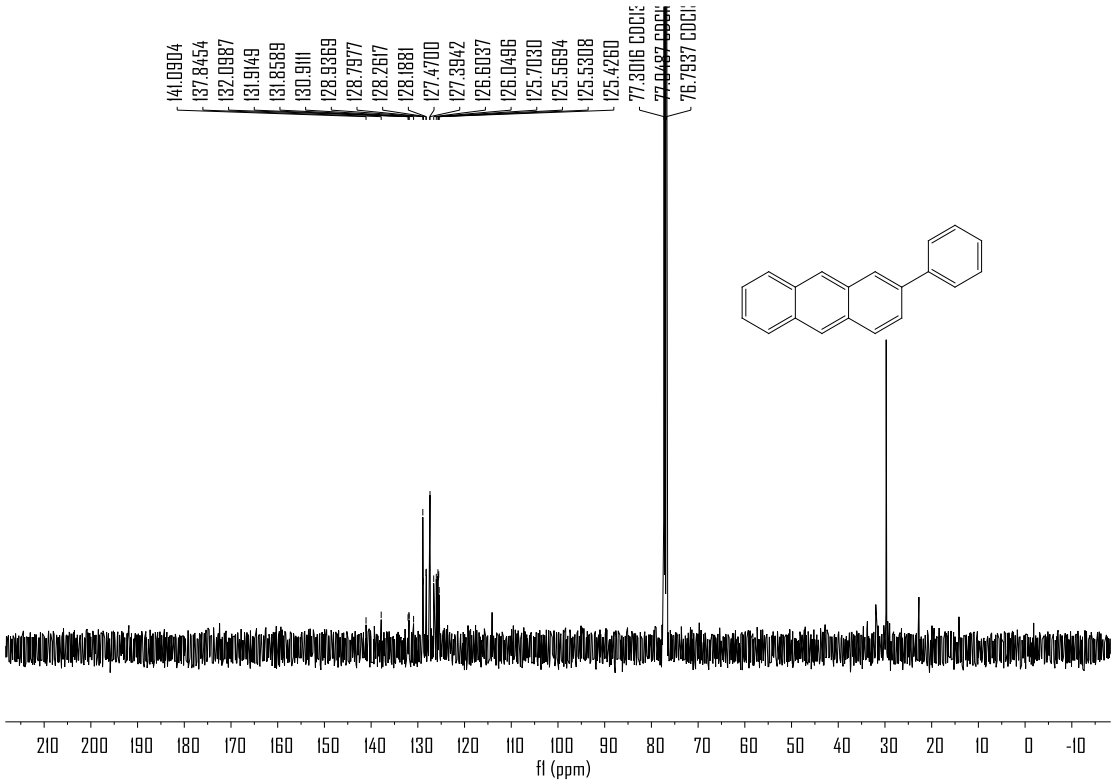
^{13}C NMR spectrum of compound 6a ($CDCl_3$, 126 MHz)



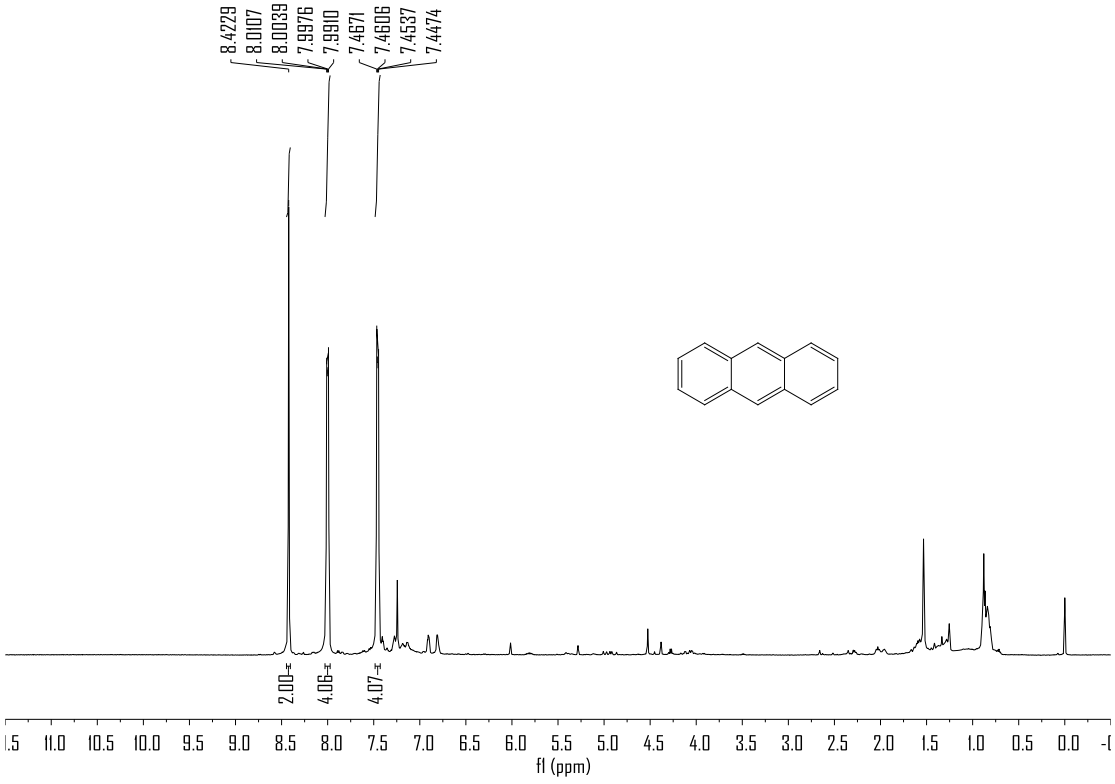
^{1}H NMR spectrum of compound 6b ($CDCl_3$, 500 MHz)



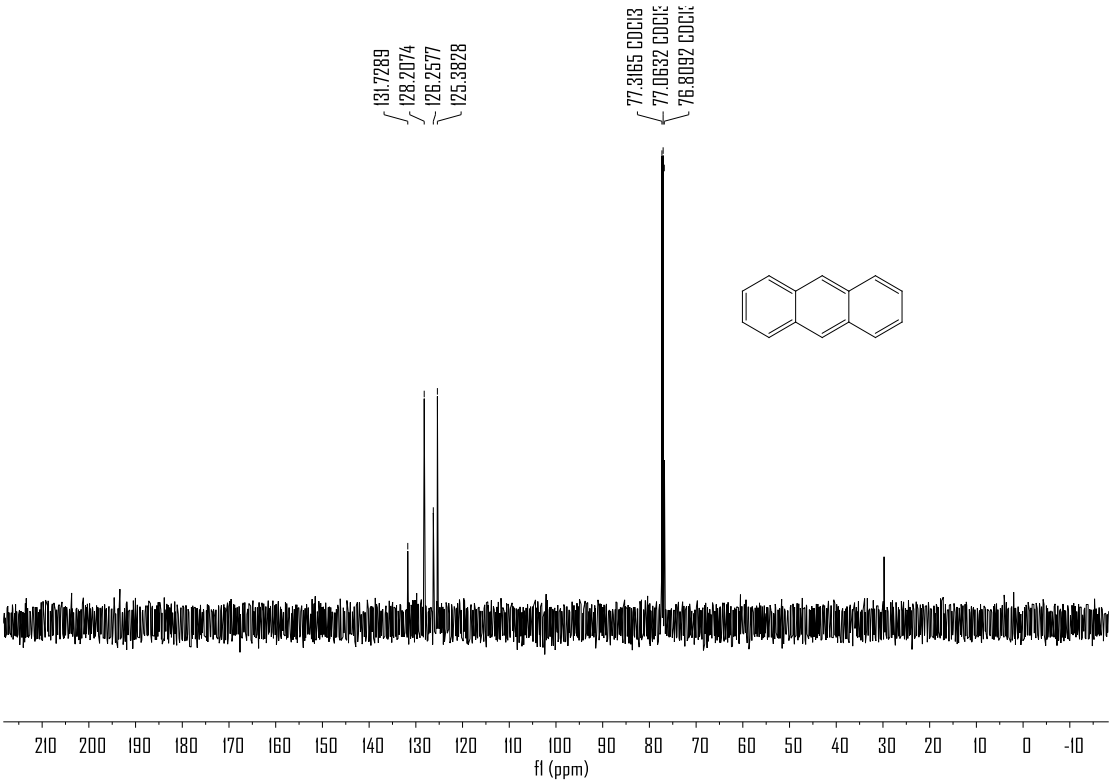
^{13}C NMR spectrum of compound 6b ($CDCl_3$, 126 MHz)



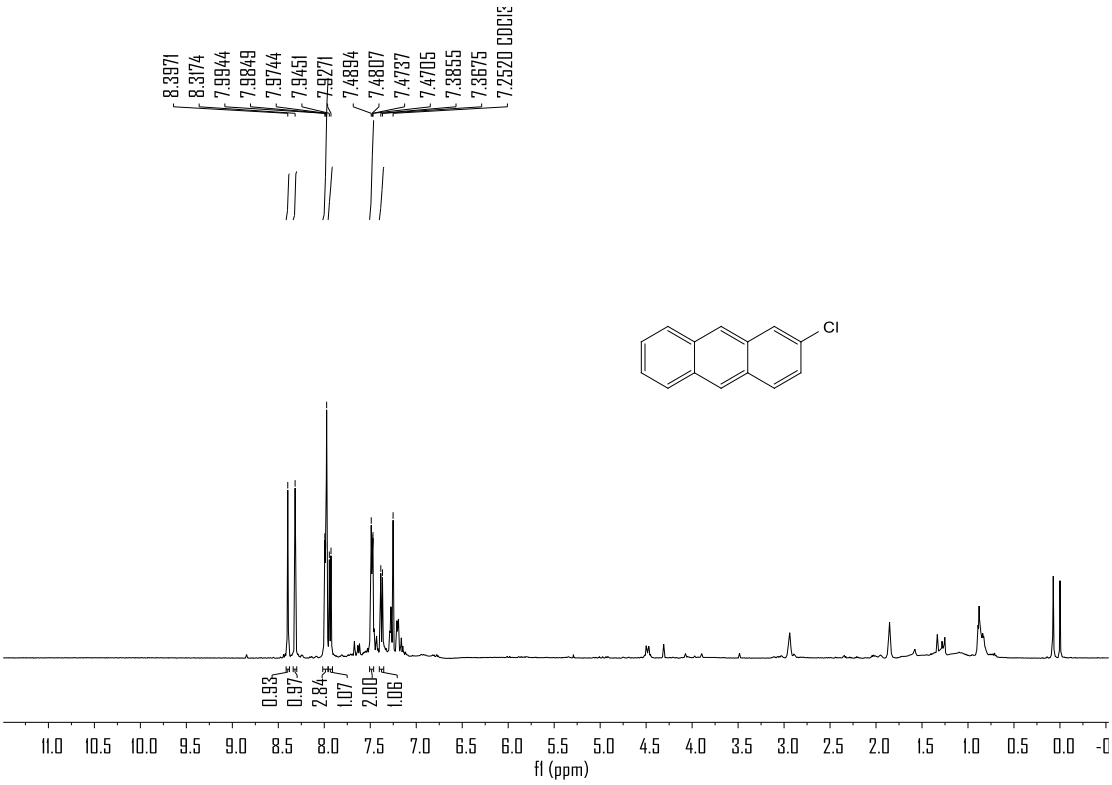
^{1}H NMR spectrum of compound 6c ($CDCl_3$, 500 MHz)



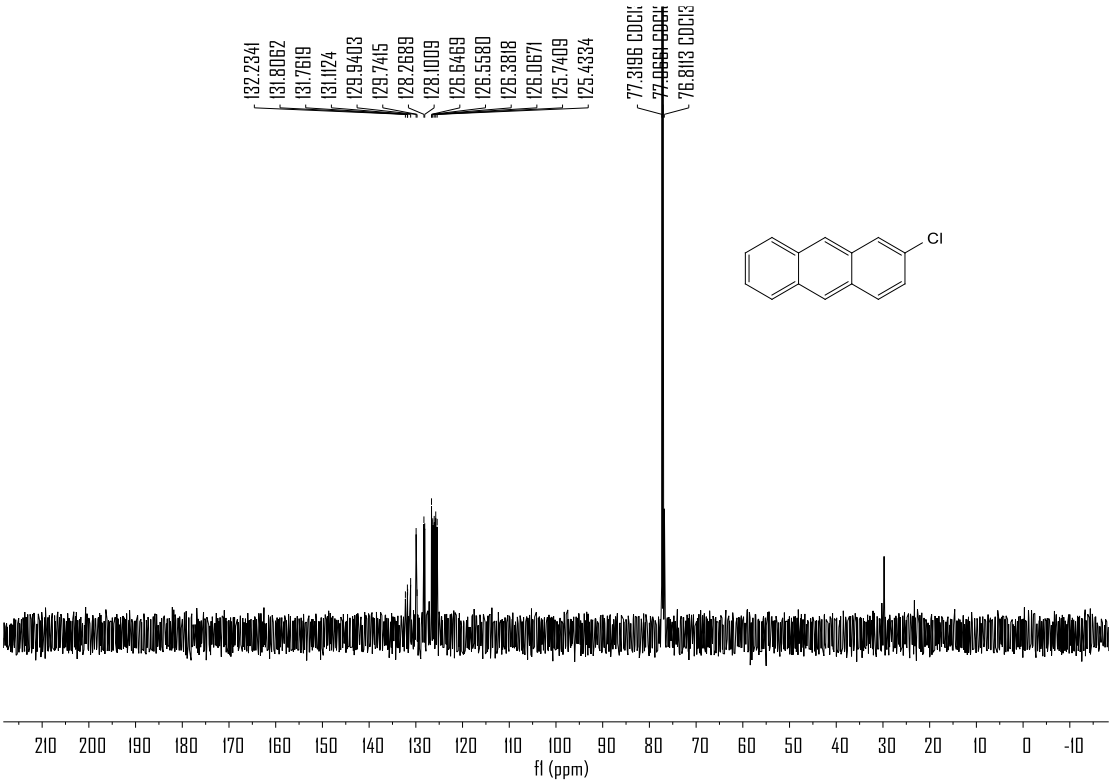
^{13}C NMR spectrum of compound 6c ($CDCl_3$, 126 MHz)



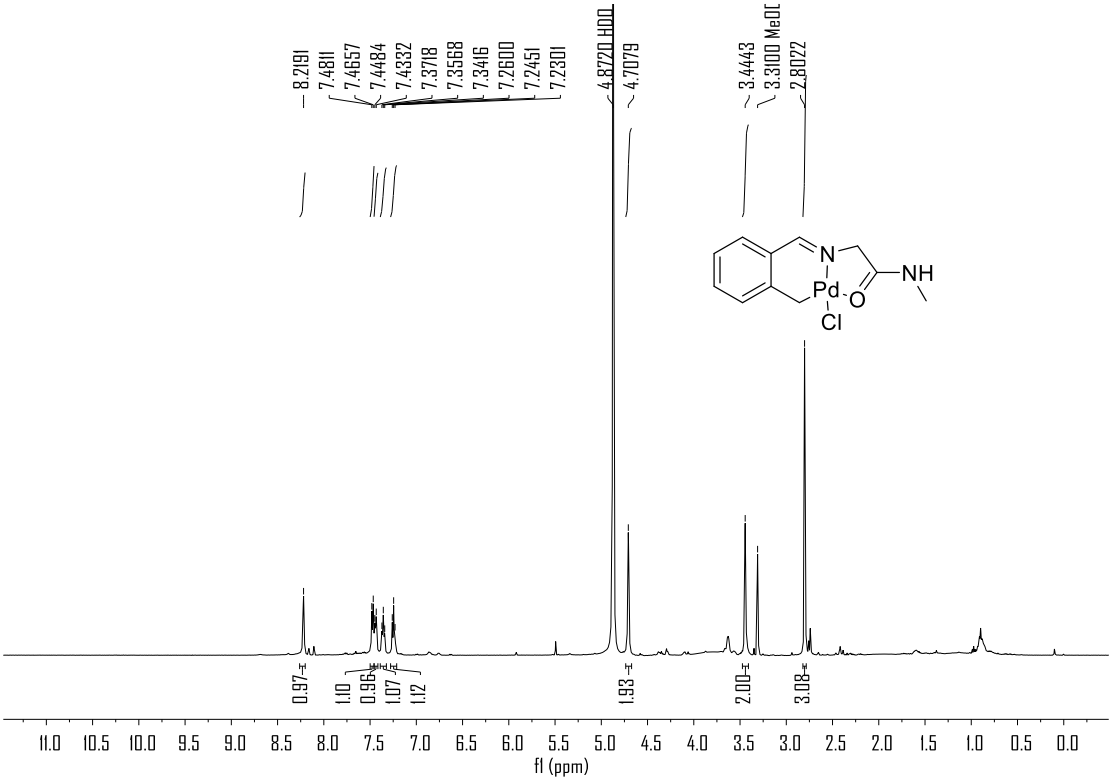
^{1}H NMR spectrum of compound 6d ($CDCl_3$, 500 MHz)



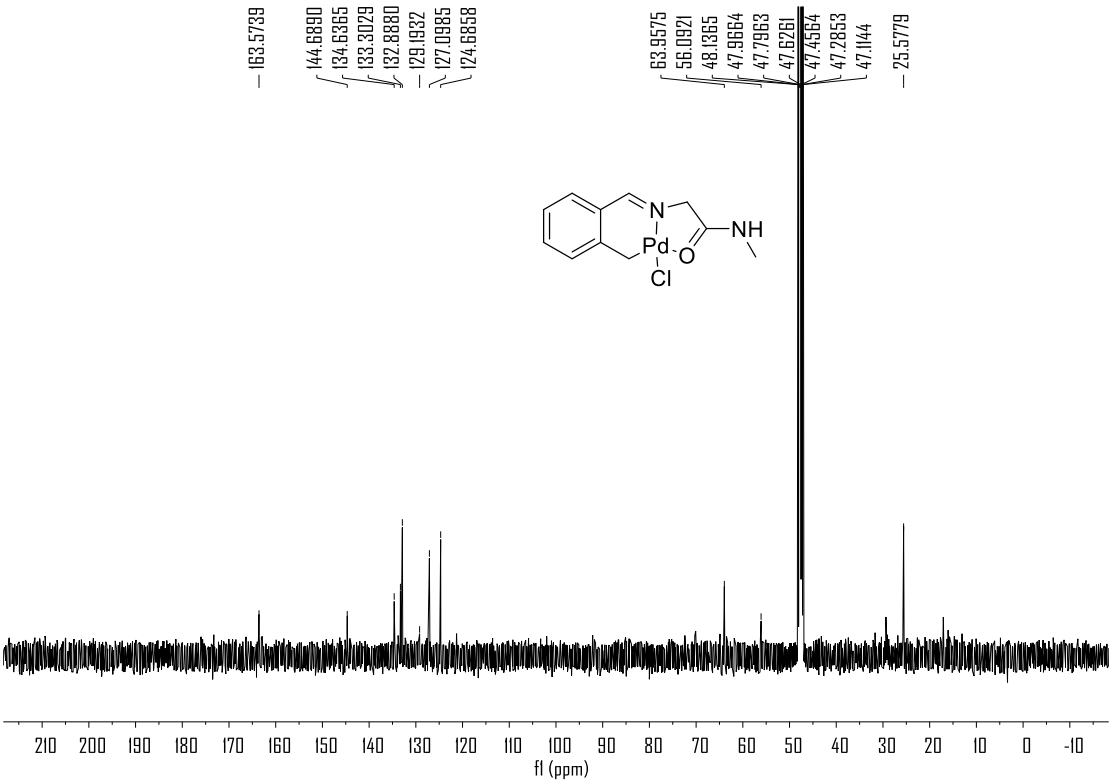
^{13}C NMR spectrum of compound 6d ($CDCl_3$, 126 MHz)



^{1}H NMR spectrum of compound 7 (MeOD, 500 MHz)



^{13}C NMR spectrum of compound 7 (MeOD, 126 MHz)



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