SUPPORTING INFORMATION

Pd-Catalyzed C(sp^3)−H Biarylation via Transient Directing Group Strategy

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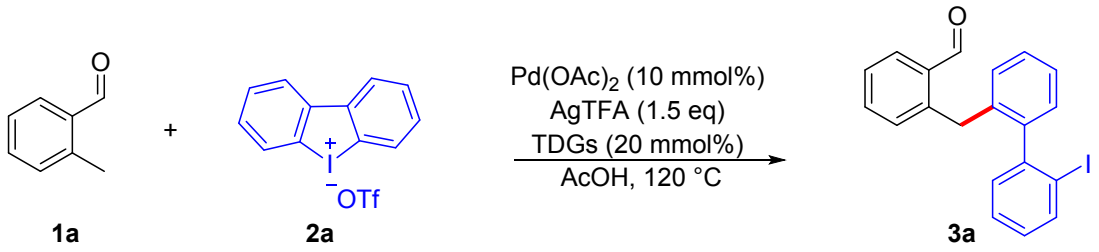
I. General information

All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 60-90 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H reree and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz or 600 MHz using $CDCl_3$ as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.03 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.52 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a SGW® X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer.

II. Optimization Studies

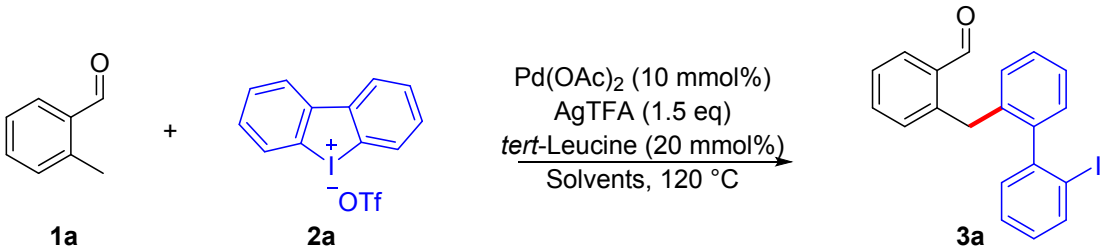
Table S1: Optimization of TDGs



Entry[a]	TDGs	Yield(%)[b]
1	Glycine	18
2	*beta*-Alanine	nr
3	Valine	21
4	*tert*-Leucine	31
5	Phenylalanine	27
6	Phenylglycine	24
7	4-Aminobutyric acid	nr
8	Anthranilic acid	nr

[a]Reaction conditions: 0.2 mmol **1a**, 0.22 mmol **2a**, 10 mol% $Pd(OAc)_2$, 10 mol% TDGs, 1.5 equiv AgTFA, 1.0 mL AcOH, 120 °C, 12 h. [b]Isolated yields.

Table S2: Optimization of solvents

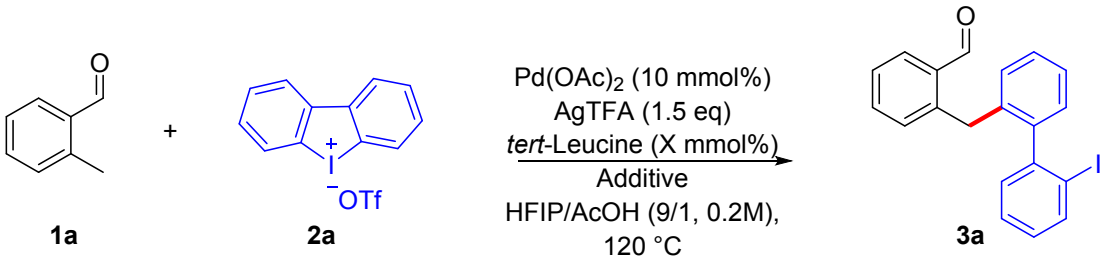


Entry[a]	Solvents	Yield(%)[b]
1	HFIP/AcOH (1/1)	33
2	HFIP/AcOH (4/1)	39
3	HFIP/AcOH (9/1)	42
4	HFIP/AcOH (19/1)	25
5	HFIP	trace

6	*i*-PrOH/AcOH (9/1)	trace
7	*n*-BuOH/AcOH (9/1)	trace
8	TFE/AcOH (9/1)	40
9	HFIP/TFA(9/1)	33

[a]Reaction conditions: 0.2 mmol **1a**, 0.22 mmol **2a**, 10 mol% $Pd(OAc)_2$, 10 mol% TDGs, 1.5 equiv AgTFA, 1.0 mL Solvent, 120 °C, 12 h. [b]Isolated yields. HFIP=1,1,1,3,3,3- hexafluoro-2-propanol; TFE= 2,2,2-trifluoroethanol; TFA= trifluoroacetic acid

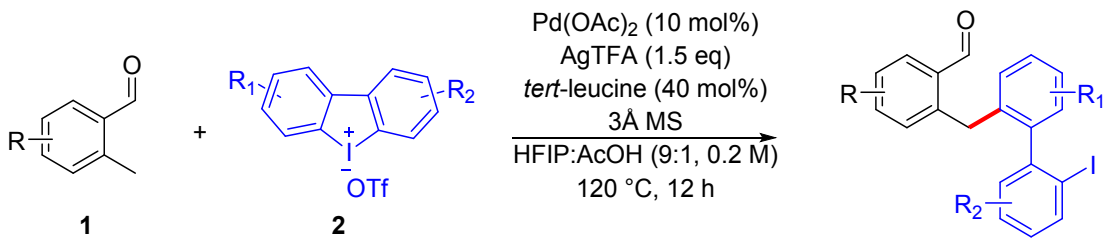
Table S3: Condition optimization



Entry[a]	X	Additive	Yield(%)[b]
1	40		49
2	60		47
3	100		34
4	40	3Å MS	56
5	40	$MgSO_4$ (2 eq)	45
6[c]	40	3Å MS	60
7[d]	40	3Å MS	65

[a]Reaction conditions: 0.2 mmol **1a**, 0.22 mmol **2a**, 10 mol% $Pd(OAc)_2$, 10 mol% TDGs, 1.5 equiv AgTFA, 1.0 mL Solvent, 120 °C, 12 h. [b]Isolated yields. [c]0.4 mmol **1a**, 0.2 mmol **2a**, [d]0.8 mmol **1a**, 0.2 mmol **2a**.

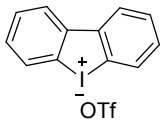
III. Representative Procedure for Biarylation



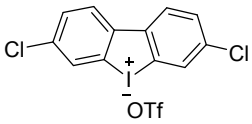
Synthesis of 2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(3a). To a 15 mL pressure vessel equipped with a magnetic stir bar were introduced 2-methylbenzaldehyde **1a** (92 μL, 0.8 mmol), cyclic diaryliodonium salt **2a** (86 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), AgTFA (66 mg, 0.3 mmol), *tert*-leucine (10.6 mg,0.08 mmol) and 3Å MS (120 mg). Next, the mixture of HFIP (0.9 mL) and HOAc (0.1 mL) were added into the above mixture. The reaction was then stirred at room temperature for 10 min before heated to 120 ˚C in oil bath for 12h. After cooling to room temperature, the reaction mixture was diluted with DCM (10 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EtOAc = 200:1) to yield the desired product **3a** (52 mg, 65%) as a White solid.

For 4 mmol scale reaction: To a 100 mL pressure vessel equipped with a magnetic stir bar were introduced 2-methylbenzaldehyde **1a** (1.84 mL, 16 mmol), cyclic diaryliodonium salt **2a** (1.71 g, 4 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), AgTFA (1.32 g, 6 mmol), *tert*-leucine (210 mg,1.6 mmol) and 3Å MS (2.4 g). Next, the mixture of HFIP (18 mL) and HOAc (2 mL) were added into the above mixture. The reaction was then stirred at room temperature for 10 min before heated to 120 ˚C in oil bath for 12h. After cooling to room temperature, the reaction mixture was diluted with DCM (100 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EtOAc = 200:1) to yield the desired product **3a** (1.05 g, 66%) as a White solid.

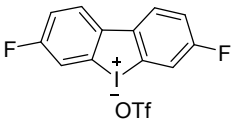
IV. Synthesis and characterization of cyclic diaryliodonium salts



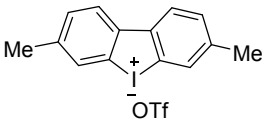
2a



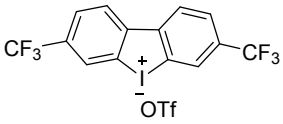
2b



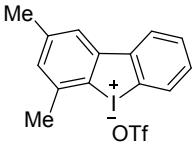
2c



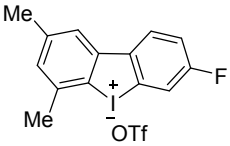
2d



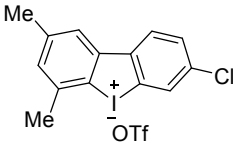
2e



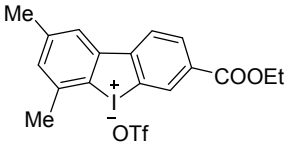
2f



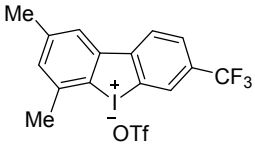
2g



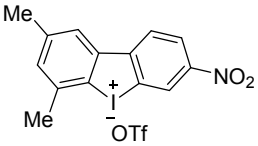
2h



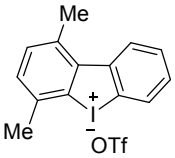
2i



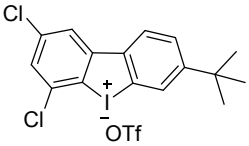
2j



2k



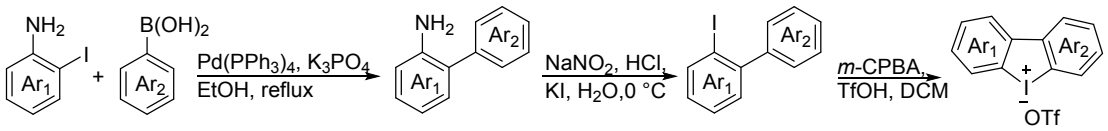
2l



2m

General procedure for the preparation of cyclic diaryliodoniums

These diphenyleneiodoniums were synthesized according to previous work[1].



To a stirred solution of 2-iodoaniline derivative (5.0 mmol) in EtOH (20 mL) was added phenylboronic acid (7.5 mmol, 1.5 equiv), K_3PO_4 (3.18 g, 15.0 mmol, 3.0 equiv), $Pd(PPh_3)_4$ (288.5 mg, 0.25 mmol, 5 mol%). The reaction proceeded at a reflux for 12h under argon atmosphere before EtOH was removed by rotary evaporation. The residue was extracted with EtOAc, and the combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated by rotary evaporation. The crude product was purified by column chromatography to afford the desired 2-aminobiaryl derivative.

2-Aminobiaryl derivative (5 mmol) was suspended water (5 mL) at 0 °C and HCl (12 N; 1 mL) was added. After slow addition of a solution of $NaNO_2$ (10 mmol) in water (2 mL), the reaction mixture was stirred for 20 min at 0 °C. A solution of ice cooled KI (12.5 mmol) in water (2 mL) was added, and then it was allowed to warm to r.t. and stirred overnight before 1M aqueous $Na_2S_2O_3$ was added until the color of the mixture didn't change. The phases were separated, and the aqueous phase extracted with EtOAc (20 mL× 3). The combined organic layers were washed with H_2O (20 mL ×2) and brine (20 mL×1), dried over anhydrous Na_2SO_4, concentrated in a vacuo. The residue was purified by column chromatography
to yield 2-iodobiaryl derivative.

In a 50 mL round bottom flask, 1.4 equiv (7 mmol) of *m*-chloroperbenzoic acid (*m*-CPBA) was taken. A solution of 2-iodobiaryl derivative (5 mmol) in anhydrous DCM (20 mL) was added, followed by dropwise addition of TfOH (3 equiv) with constant stirring at ice-bath. The solution was stirred for 3h at r.t. before DCM was removed by rotary evaporation. Et_2O (20 mL) was added to the remained solid, and the mixture was stirred for 20 min, and filtered. The collected solid was washed with Et_2O three times, dried in high vacuo to provide the required cyclic diaryliodonium salts.

^1H and ^{13}C NMR spectra for the following known cyclic diaryliodonium salts showed good agreement with the literature data.

Diphenyleniodonium trifluoromethanesulfonate (2a)[1],

3,7-Dichlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2b)[2]

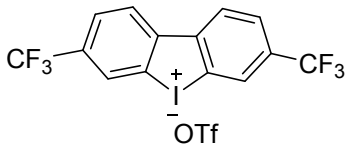
3,7-Difluorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2c)[1]

3,7-Dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2d)[1]

2,4-Dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2f)[1]

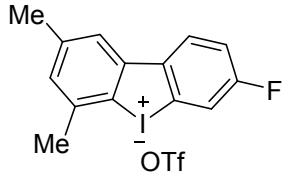
3-Chloro-6,8-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2h)[3],

1,4-Dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2l)[4]



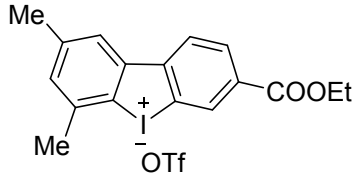
2e

3,7-bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2e): white solid (2.1g, 74% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.87 (d, J = 8.8 Hz, 2H), 8.58 (q, J = 3.6, 2.8 Hz, 2H), 8.40 – 8.24 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 144.65, 131.49 (q, $J_{C\text{-}F}$= 33.0 Hz), 129.1, 128.3, 127.9 (q, $J_{C\text{-}F}$= 7.8 Hz), 123.9, 123.6 (q, $J_{C\text{-}F}$= 272.4 Hz); HRMS m/z (ESI) calcd for $C_{14}H_6F_6I$ [M-OTf] $^{+}$: 414.9413, found: 414.9408, error 1.1 ppm.



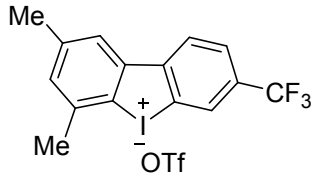
2g

7-fluoro-2,4-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2g) : white solid (1.8g, 76% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.44 – 8.38 (m, 1H), 8.11 (m, 1H), 8.07 (d, J = 3.6 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.38 (s, 1H), 2.62 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.9 (d, $J_{C\text{-}F}$= 252.4 Hz), 141.8, 141.4, 139.7, 139.2, 132.5, 129.1 (d, $J_{C\text{-}F}$= 8.6 Hz), 125.6, 123.3, 121.9 (d, $J_{C\text{-}F}$= 10.6 Hz), 119.6 (d, $J_{C\text{-}F}$= 22.8 Hz), 118.8 (d, $J_{C\text{-}F}$= 28.6 Hz), 25.0, 21.0; HRMS m/z (ESI) calcd for $C_{14}H_{11}FI$ [M-OTf] $^{+}$: 324.9884, found: 324.9884, error 0.0 ppm.



2i

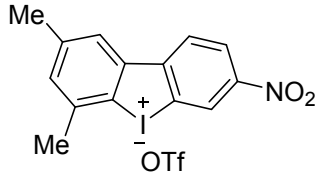
7-(ethoxycarbonyl)-2,4-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2i): white solid (1.6g, 60% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.88 – 8.78 (m, 1H), 8.51 – 8.37 (m, 1H), 8.31 – 8.21 (m, 1H), 8.14 (t, J = 9.8 Hz, 1H), 7.44 (t, J = 4.9 Hz, 1H), 4.40 (q, 2H), 2.63 (s, 3H), 2.47 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.3, 146.8, 141.9, 141.3, 139.5, 133.7, 132.4, 131.6, 127.8, 126.3, 124.0, 122.23, 122.12, 62.16, 25.08, 21.00, 14.60; HRMS m/z (ESI) calcd for $C_{17}H_{16}O_2I$ [M-OTf] $^{+}$: 379.0189, found: 379.0189, error 0.0 ppm.



2j

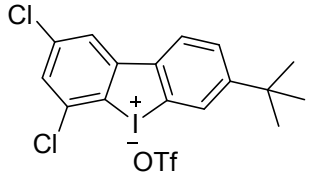
2,4-dimethyl-7-(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2j): white solid (1.7g, 65% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70 – 8.58 (m, 2H), 8.33 – 8.21 (m, 2H), 7.51 (s, 1H), 2.68 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.89, 141.99, 141.20, 139.52, 133.94, 130.37 (q, $J_{C\text{-}F}$= 33.1 Hz), 128.64, 128.41, 126.54, 124.36, 123.65 (q, $J_{C\text{-}F}$= 272.8 Hz), 122.22, 120.09, 25.11, 21.01; HRMS m/z (ESI) calcd for $C_{15}H_{11}F_3I$

[M-OTf] $^{+}$: 374.9852, found: 374.9847, error 1.3 ppm.



2k

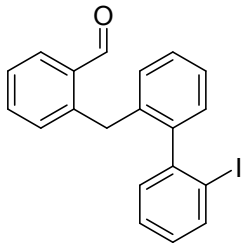
2,4-dimethyl-7-nitrodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2k): white solid (1.1g, 44% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.13 (m, 1H), 8.75 – 8.49 (m, 2H), 8.38 – 8.14 (m, 1H), 7.59 – 7.39 (m, 1H), 2.67 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.62, 147.65, 142.17, 140.53, 139.71, 134.42, 128.23, 127.37, 127.07, 126.51, 125.18, 121.76, 25.03, 20.98; HRMS m/z (ESI) calcd for $C_{14}H_{11}NO_2I$ [M-OTf] $^{+}$: 351.9829, found: 351.9829, error 0.0 ppm.



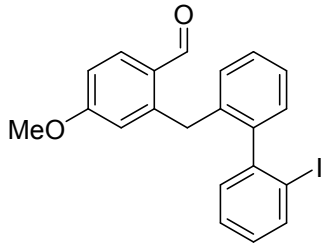
2m

7-(tert-butyl)-2,4-dichlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2m) : white solid (1.4g, 50% yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (m, 1H), 8.51 (m, 1H), 8.36 (t, J = 1.5 Hz, 1H), 8.02 (m, 1H), 7.98 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 156.44, 145.55, 138.97, 137.64, 134.31, 129.37, 129.28, 128.87, 127.90, 125.70, 124.40, 123.43, 36.29, 31.25; HRMS m/z (ESI) calcd for $C_{16}H_{14}Cl_2I$ [M-OTf] $^{+}$: 402.9511, found: 402.9511, error 0.5 ppm.

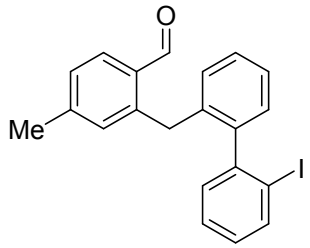
V. Characterization Data of Biarylated Compounds



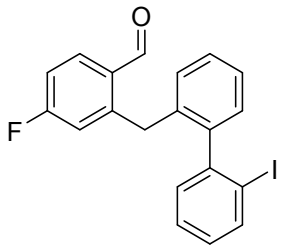
2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3a) White solid (52 mg, 65% yield). Mp: 89 - 90 °C; R_f = 0.17 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.92 (dd, J = 7.9, 0.8 Hz, 1H), 7.80 (dd, J = 7.7, 1.2 Hz, 1H), 7.45 (td, J = 7.5, 1.4 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.18 – 7.11 (m, 3H), 7.06 – 6.97 (m, 2H), 4.31 – 4.07 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 145.9, 144.0, 142.5, 139.0, 138.0, 134.1, 133.8, 131.9, 130.5, 129.9, 129.8, 129.3, 128.9, 128.3, 128.0, 126.8, 126.4, 100.2, 35.5; HRMS m/z (ESI) calcd for $C_{20}H_{15}IONa$ [M+Na] $^{+}$: 421.0060, found: 421.0049, error 2.5 ppm. IR (cm^{-1}): 1694, 1595, 1461, 1001, 755.



2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-methoxybenzaldehyde (3b) Colorless oil (54 mg, 63% yield); R_f = 0.28 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.93 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 (dd, *J* = 6.3, 2.6 Hz, 1H), 7.04 (td, *J* = 7.4, 1.4 Hz, 2H), 6.85 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.63 (d, *J* = 2.5 Hz, 1H), 4.19 (d, *J* = 7.2 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3, 163.8, 145.9, 145.1, 143.9, 139.0, 137.7, 133.3, 129.9, 129.8, 129.2, 128.9, 128.3, 128.0, 127.7, 126.3, 117.1, 112.1, 100.1, 55.4, 35.6; HRMS m/z (ESI) calcd for $C_{21}H_{17}IO_2Na$ $[M+Na]^+$: 451.0165, found: 451.0162, error 0.8 ppm. IR (cm^{-1}): 1682, 1597, 1565, 1460, 1250, 755.

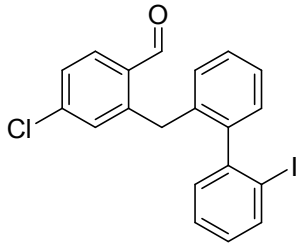


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-methylbenzaldehyde (3c) Colorless oil (58 mg, 70% yield); R_f = 0.16 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.00 – 7.85 (m, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.35 (td, *J* = 7.5, 0.9 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.03 (m, 2H), 6.91 (s, 1H), 4.18 (d, *J* = 2.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 145.9, 144.6, 143.9, 142.4, 138.9, 138.0, 132.7, 131.8, 130.9, 129.9, 129.8, 129.3, 128.9, 128.2, 128.0, 127.6, 126.2, 100.2, 35.5, 21.7; HRMS m/z (ESI) calcd for $C_{21}H_{17}IO_2Na$ $[M+Na]^+$: 435.0216, found: 435.0221, error 1.14 ppm. IR (cm^{-1}): 1682, 1600, 1459, 1213, 820, 767, 752.

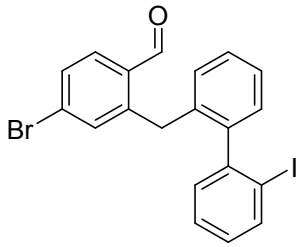


4-fluoro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3d) Colorless oil (70 mg, 84% yield); R_f = 0.47 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.14 (dt, *J* = 4.4, 1.6 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.02 (m, 2H), 6.79 (dd, *J* = 9.8, 2.4 Hz, 1H), 4.22 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 165.8 (d, $J_{C\text{-}F}$ = 256.5 Hz), 146.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 145.6, 144.0, 139.0, 137.0, 133.4 (d, $J_{C\text{-}F}$ = 9.9 Hz), 130.6, 130.07, 129.9, 129.5, 129.0, 128.4, 128.0, 126.7, 118.6

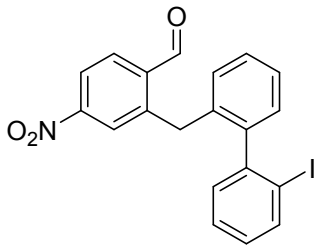
(d, J_{C-F} = 22.1 Hz), 114.1 (d, J_{C-F} = 22.1 Hz), 100.1, 35.3.; HRMS m/z (ESI) calcd for $C_{20}H_{14}FIONa$ $[M+Na]^+$: 438.9966, found: 438.9974, error 2.03 ppm. IR (cm^{-1}): 1689, 1600, 1583, 1246, 828, 765, 756.



4-chloro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3e) Colorless oil (64 mg, 74% yield); R_f = 0.47 (PE/EtOAc = 50:1); ^1H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.91 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.30 (m, 4H), 7.15 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.11 – 7.01 (m, 3H), 4.31 – 4.08 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 145.6, 144.2, 144.0, 140.1, 139.0, 137.0, 132.3, 131.8, 131.8, 130.1, 129.9, 129.5, 129.1, 128.4, 128.0, 127.2, 126.7, 100.1, 35.3; HRMS m/z (ESI) calcd for $C_{20}H_{14}ClIONa$ $[M+Na]^+$: 454.9670, found: 454.9679, error 2.07 ppm. IR (cm^{-1}): 1685, 1589, 1560, 1459, 1209, 1085, 1001, 899, 814, 756.

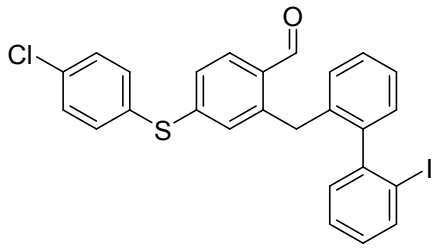


4-bromo-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3f) White solid (71 mg, 75% yield); Mp: 65 - 67 °C; R_f = 0.47 (PE/EtOAc = 50:1); ^1H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.11 – 7.01 (m, 2H), 4.27 – 4.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 145.5, 144.2, 144.0, 139.0, 137.0, 134.7, 132.75, 131.7, 130.2, 130.0, 129.9, 129.4, 129.1, 129.0, 128.4, 128.0, 126.7, 100.1, 35.3; HRMS m/z (ESI) calcd for $C_{20}H_{14}BrIONa$ $[M+Na]^+$: 498.9165, found: 498.9174, error 1.91 ppm. IR (cm^{-1}): 1690, 1584, 1460, 1209, 1016, 819, 759.

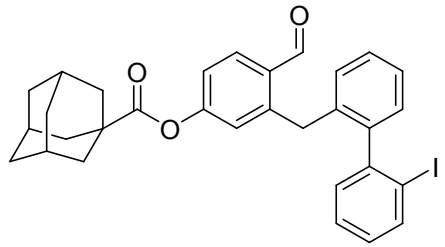


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-nitrobenzaldehyde (3g) White solid (55 mg, 62% yield). Mp: 123 - 125 °C; R_f = 0.45 (PE/EtOAc = 20:1); ^1H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.12 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.37 (m, 2H), 7.31 (td, *J* = 7.5, 0.9 Hz, 1H), 7.14 (dd, *J* = 6.4, 2.1 Hz, 2H), 7.10 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.01 (td, *J* = 7.7, 1.6 Hz, 1H), 4.33 (dd, *J* = 46.4, 16.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$)

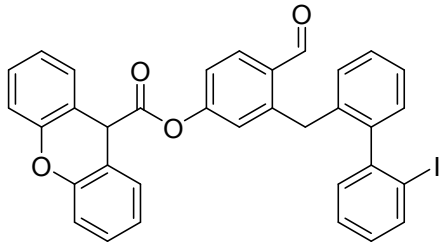
δ 189.8, 150.3, 145.4, 144.2, 144.1, 139.2, 137.9, 136.4, 131.0, 130.4, 129.9, 129.7, 129.2, 128.7, 128.2, 127.2, 126.7, 121.6, 100.1, 35.8.; HRMS m/z (ESI) calcd for $C_{20}H_{14}INO_3Na$ $[M+Na]^+$: 465.9911, found: 465.9909, error 0.4 ppm. IR (cm^{-1}): 1691, 1518, 1350, 809, 754, 741.



4-((4-chlorophenyl)thio)-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3h) Colorless oil (58 mg, 53% yield). R_f = 0.25 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.90 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.29 (m, 7H), 7.13 – 6.98 (m, 5H), 6.80 (d, *J* = 1.7 Hz, 1H), 4.22 – 4.04 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 145.6, 145.4, 143.9, 143.3, 139.0, 137.2, 135.4, 135.2, 131.5, 131.2, 129.9, 129.9, 129.8, 129.4, 129.0, 128.3, 128.0, 126.5, 125.1, 100.1, 35.2.; HRMS m/z (ESI) calcd for $C_{26}H_{18}ClISONa$ $[M+Na]^+$: 562.9704, found: 562.9707, error 0.6 ppm. IR (cm^{-1}): 1686, 1585, 1474, 1092, 1013, 820, 754.

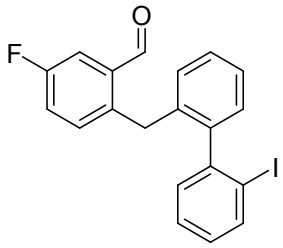


4-formyl-3-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl(3r,5r,7r)-adamantane-1-carboxylate (3i) White solid (61 mg, 53% yield). Mp: 129 - 131 °C; R_f = 0.40 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.91 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.08 – 7.00 (m, 3H), 6.80 (d, *J* = 2.2 Hz, 1H), 4.19 (q, *J* = 16.3 Hz, 2H), 2.09 (s, 3H), 2.02 (d, *J* = 2.5 Hz, 6H), 1.81 – 1.72 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 175.4, 155.2, 145.7, 144.4, 143.9, 139.0, 137.4, 132.1, 131.4, 130.0, 129.8, 129.3, 129.0, 128.4, 128.1, 126.5, 124.8, 120.2, 100.1, 41.1, 38.6, 36.3, 35.4, 27.8.; HRMS m/z (ESI) calcd for $C_{31}H_{29}IO_3Na$ $[M+Na]^+$: 599.1054, found: 599.1050, error 0.62 ppm. IR (cm^{-1}): 2907, 2850, 1746, 1682, 1605, 1459, 1229, 1205, 1180, 1042, 755.

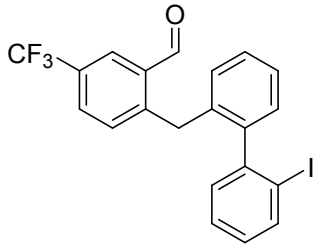


4-formyl-3-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl 9*H*-xanthene-9-carboxylate (3j)

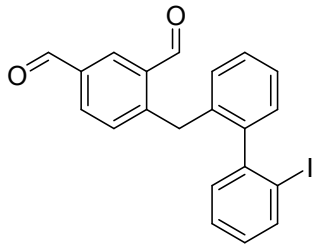
Colorless oil (70 mg, 56% yield). R_f = 0.23 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.85 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.31 (dd, *J* = 5.5, 3.6 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.21 (dd, *J* = 8.2, 0.8 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.13 – 7.08 (m, 2H), 7.00 (dd, *J* = 5.2, 3.8 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.65 (d, *J* = 2.2 Hz, 1H), 5.22 (s, 1H), 4.15 (d, *J* = 1.8 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 169.2, 154.6, 151.3, 145.6, 144.5, 143.9, 138.9, 137.2, 132.1, 131.8, 129.9, 129.5, 129.4, 128.9, 128.9, 128.3, 128.0, 126.5, 124.3, 123.5, 119.7, 117.4, 117.2, 100.0, 45.6, 35.5.; HRMS m/z (ESI) calcd for $C_{34}H_{24}IO_4$ $[M+H]^+$: 623.0714, found: 623.0741, error 4.37 ppm. IR (cm^{-1}): 2922, 2850, 1749, 1636, 1480, 1456, 1258, 1118, 751.



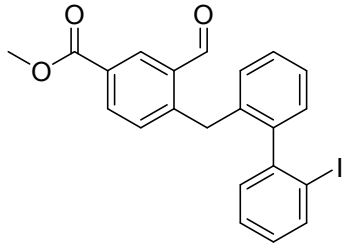
5-fluoro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3k) Colorless oil (52 mg, 63% yield). R_f = 0.47 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (d, *J* = 2.4 Hz, 1H), 7.93 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.50 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.20 – 7.11 (m, 4H), 7.08 – 7.00 (m, 2H), 4.17 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4 (d, $J_{C\text{-}F}$ = 1.7 Hz), 161.5 (d, $J_{C\text{-}F}$ = 248.5 Hz), 145.7, 143.9, 139.0, 138.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 137.6, 135.4 (d, $J_{C\text{-}F}$ = 5.8 Hz), 133.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.9, 129.8, 129.2, 129.1, 128.4, 128.1, 126.6, 120.8 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 100.1, 34.8.; HRMS m/z (ESI) calcd for $C_{20}H_{14}FIONa$ $[M+Na]^+$: 438.9966, found: 438.9971, error 1.3 ppm. IR (cm^{-1}): 1691, 1492, 1420, 1238, 759.



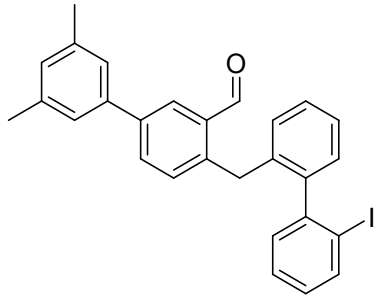
2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-5-(trifluoromethyl)benzaldehyde (3l) Colorless oil (70 mg, 75% yield). R_f = 0.19 (PE/EtOAc = 100:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.09 – 7.03 (m, 2H), 4.30 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 146.3, 145.6, 144.1, 139.1, 137.0, 134.2, 132.6, 130.2, 129.9, 129.8 (q, $J_{C\text{-}F}$ = 3.4 Hz), 129.5, 129.4 (q, $J_{C\text{-}F}$ = 33.2 Hz), 129.2, 128.5, 128.2, 127.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.9, 123.6 (q, $J_{C\text{-}F}$ = 271.4 Hz), 100.1, 35.5; HRMS m/z (ESI) calcd for $C_{21}H_{15}OF_3I$ $[M+H]^+$: 467.0114, found: 467.0099, error 3.3 ppm. IR (cm^{-1}): 1697, 1617, 1461, 1332, 1168, 1129, 755.



4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)isophthalaldehyde (3m) Colorless oil (55 mg, 64% yield). R_f = 0.30 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 10.05 (s, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 – 7.05 (m, 1H), 7.05 – 7.01 (m, 1H), 4.32 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 190.5, 149.0, 145.5, 144.0, 139.1, 136.8, 134.9, 134.4, 132.9, 132.7, 132.4, 130.1, 129.9, 129.5, 129.1, 128.4, 128.1, 126.8, 100.1, 35.8.; HRMS m/z (ESI) calcd for $C_{21}H_{15}O_2Na$ $[M+Na]^+$: 449.0009, found: 449.0015, error 1.4 ppm. IR (cm^{-1}): 1694, 1604, 1459, 1157, 1001, 755.



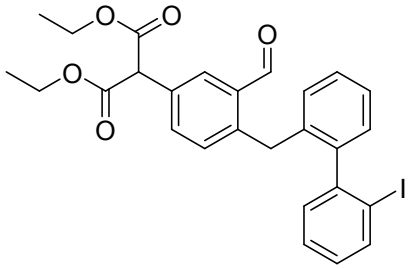
Methyl-3-formyl-4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzoate (3n) Colorless oil (72 mg, 79% yield). R_f = 0.33 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.43 (d, *J* = 1.9 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.03 (m, 2H), 4.34 – 4.23 (m, 2H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 166.0, 147.3, 145.6, 144.1, 139.0, 137.1, 134.1, 134.0, 132.2, 132.2, 130.0, 129.9, 129.4, 129.0, 128.9, 128.4, 128.0, 126.7, 100.1, 52.3, 35.7.; HRMS m/z (ESI) calcd for $C_{22}H_{17}IO_3Na$ $[M+Na]^+$: 479.0115, found: 479.0102, error 2.7 ppm. IR (cm^{-1}): 1724, 1693, 1608, 1435, 1289, 1198, 1115, 1001, 756.



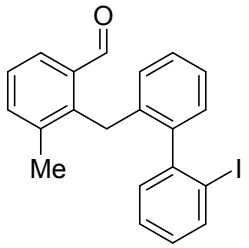
4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-3',5'-dimethyl-[1,1'-biphenyl]-3-carbaldehyde (3o)

Colorless oil (39 mg, 39% yield). R_f = 0.33 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.26 (s, 2H), 7.23 – 7.19 (m, 2H), 7.18 – 7.14 (m, 1H), 7.07 (m, 3H), 4.32 – 4.19 (m, 2H), 2.42 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 145.9, 144.0,

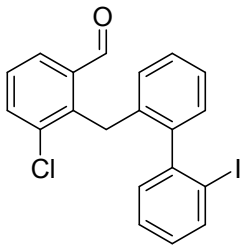
141.2, 139.9, 139.5, 139.0, 138.5, 138.0, 134.2, 132.4, 132.2, 130.0, 129.8, 129.4, 129.3, 129.0, 128.8, 128.8, 128.3, 128.1, 126.4, 124.8, 100.2, 35.2, 21.4.; HRMS m/z (ESI) calcd for $C_{28}H_{23}IONa$ $[M+Na]^+$: 525.0686, found: 525.0709, error 4.6 ppm. IR (cm^{-1}): 1686, 1604, 1459, 1164, 1017, 1000, 842, 753.



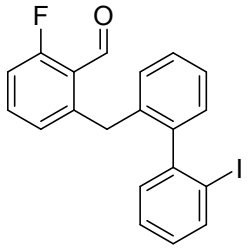
Diethyl-2-(3-formyl-4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)malonate (3p) Colorless oil (67 mg, 60% yield). R_f = 0.14 (PE/EtOAc = 20:1); ^1H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.91 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.17 – 7.11 (m, 3H), 7.07 – 7.01 (m, 2H), 4.66 (s, 1H), 4.35 – 4.14 (m, 6H), 1.36 – 1.19 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 167.6, 145.7, 144.0, 142.5, 138.9, 137.6, 134.4, 134.0, 132.2, 131.5, 131.5, 129.9, 129.8, 129.4, 128.9, 128.3, 128.0, 126.4, 100.1, 62.0, 61.9, 57.2, 35.1, 13.9; HRMS m/z (ESI) calcd for $C_{27}H_{25}IO_5Na$ $[M+Na]^+$: 579.0639, found: 579.0640, error 0.2 ppm. IR (cm^{-1}): 2981, 1732, 1690, 1461, 1302, 1234, 1176, 1148, 1031, 756.



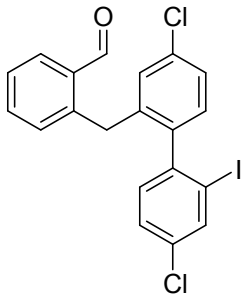
2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-3-methylbenzaldehyde (3q) Colorless oil (59 mg, 72% yield); R_f = 0.16 (PE/EtOAc = 100:1); ^1H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.47 (dt, *J* = 15.5, 5.5 Hz, 2H), 7.40 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.22 (dd, *J* = 7.4, 6.6 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.11 (td, *J* = 7.7, 1.6 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 4.22 – 4.06 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 146.2, 144.0, 140.2, 139.1, 139.0, 137.0, 135.9, 135.0, 129.6, 129.4, 129.0, 128.4, 128.3, 127.1, 126.9, 126.1, 100.0, 31.5, 19.6.; HRMS m/z (ESI) calcd for $C_{21}H_{17}IONa$ $[M+Na]^+$: 435.0199, found: 435.0216, error 4.2 ppm. IR (cm^{-1}): 1686, 1538, 1459, 1238, 1001, 755.



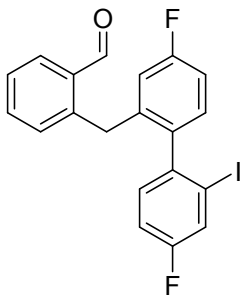
3-chloro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3r) White solid (54 mg, 63% yield). Mp: 68- 70 °C; R_f = 0.45 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.65 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.46 (m, 1H), 7.38 (m, 2H), 7.29 (m, 1H), 7.27 – 7.21 (m, 1H), 7.16 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.10 (m, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 4.30 (dd, *J* = 86.4, 16.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 146.0, 143.8, 139.6, 139.1, 136.9, 136.3, 136.3, 134.9, 129.7, 129.5, 129.1, 128.4, 128.3, 128.3, 128.1, 127.2, 126.3, 100.0, 31.9.; HRMS m/z (ESI) calcd for $C_{20}H_{14}ClIONa$ $[M+Na]^+$: 454.9670, found: 454.9676, error 1.4 ppm. IR (cm^{-1}): 1697, 1681, 1586, 1459, 1242, 1001, 755.



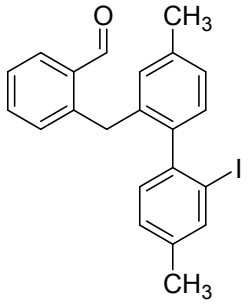
2-fluoro-6-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3s) White solid (58 mg, 70% yield). Mp: 72- 74 °C; R_f = 0.18 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.39 (m, 1H), 7.35 – 7.30 (m, 3H), 7.19 (m, 1H), 7.15 – 7.12 (m, 1H), 7.07 – 6.97 (m, 3H), 6.89 (d, *J* = 7.7 Hz, 1H), 4.32 – 4.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6 (d, J_{C-F} = 10.4 Hz), 165.7 (d, J_{C-F} = 258.6 Hz), 145.8, 144.2, 144.2, 138.9, 137.6, 134.7 (d, J_{C-F} = 10.4 Hz), 130.1, 129.9, 129.4, 128.8, 128.1, 127.9, 127.7 (d, J_{C-F} = 3.4 Hz), 126.3, 122.6 (d, J_{C-F} = 5.4 Hz), 114.1 (d, J_{C-F} = 22.8 Hz), 100.2, 36.0 (d, J_{C-F} = 2.0 Hz); HRMS m/z (ESI) calcd for $C_{20}H_{15}OFI$ $[M+H]^+$: 417.0146, found: 417.0137, error 2.1 ppm. IR (cm^{-1}): 1702, 1608, 1462, 1245, 1000, 756.



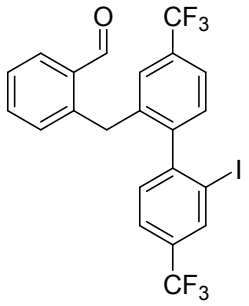
2-((4,4'-dichloro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4a) Colorless oil (57 mg, 61% yield). R_f = 0.20 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.81 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (m, 1H), 7.34 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 4.18 (dd, *J* = 60.4, 16.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 143.4, 141.3, 141.0, 140.2, 138.4, 134.4, 134.0, 134.0, 133.8, 132.6, 132.0, 131.1, 130.5, 129.2, 128.4, 127.3, 126.6, 100.0, 35.7.; HRMS m/z (ESI) calcd for $C_{20}H_{13}Cl_2IONa$ $[M+Na]^+$: 488.9280, found: 488.9286, error 1.2 ppm. IR (cm^{-1}): 1693, 1643, 1456, 1098, 999, 817, 752.



2-((4,4'-difluoro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4b) Colorless oil (62 mg, 72% yield). R_f = 0.15 (PE/EtOAc = 100:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.81 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.64 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.07 (td, *J* = 8.3, 2.5 Hz, 2H), 6.97 (td, *J* = 8.3, 2.6 Hz, 1H), 6.63 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.16 (dd, *J* = 62.2, 16.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 162.6 (d, J_{C-F} = 246.8 Hz), 161.3 (d, J_{C-F} = 252.0 Hz), 141.2, 141.1 (d, J_{C-F} = 3.4 Hz), 140.9 (d, J_{C-F} = 7.4 Hz), 138.9 (d, J_{C-F} = 3.3 Hz), 134.0, 133.8, 132.3, 132.0, 131.6 (d, J_{C-F} = 8.5 Hz), 130.8 (d, J_{C-F} = 8.0 Hz), 127.2, 125.9 (d, J_{C-F} = 23.6 Hz), 116.0 (d, J_{C-F} = 22.6 Hz), 115.3 (d, J_{C-F} = 20.7 Hz), 113.2 (d, J_{C-F} = 21.1 Hz), 99.9 (d, J_{C-F} = 8.1 Hz), 35.8.; HRMS m/z (ESI) calcd for $C_{20}H_{13}F_2IONa$ $[M+Na]^+$: 456.9850, found: 456.9871, error 4.9 ppm. IR (cm^{-1}): 1697, 1591, 1471, 1199, 856, 818, 750.

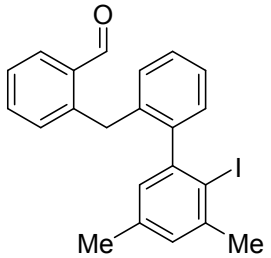


2-((2'-iodo-4,4'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4c) Colorless oil (55 mg, 65% yield). R_f = 0.15 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.82 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.76 (d, *J* = 0.7 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (m, 3H), 7.03 (t, *J* = 8.1 Hz, 2H), 6.80 (s, 1H), 4.18 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 142.9, 142.9, 141.1, 139.4, 138.9, 137.9, 137.9, 134.0, 133.7, 131.9, 130.1, 130.0, 129.9, 129.7, 128.8, 127.1, 126.7, 100.4, 35.3, 21.3, 20.5.; HRMS m/z (ESI) calcd for $C_{22}H_{19}IONa$ $[M+Na]^+$: 449.0352, found: 449.0373, error 4.9 ppm. IR (cm^{-1}): 1694, 1597, 1473, 1207, 818, 751.

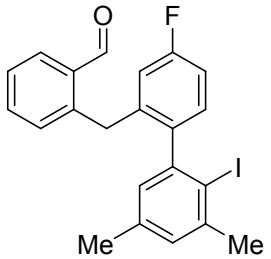


2-((2'-iodo-4,4'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4d)

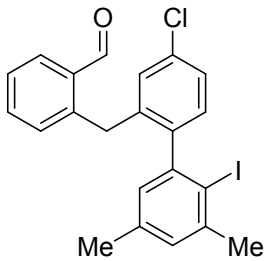
Colorless oil (71 mg, 67% yield). R_f = 0.18 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.17 (s, 1H), 7.78 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.61 (dd, *J* = 13.6, 5.0 Hz, 2H), 7.53 – 7.40 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 15.5, 4.9 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 4.28 (dd, *J* = 78.0, 16.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 148.5, 146.2, 140.4, 139.1, 135.9 (d, J_{C-F} = 3.8 Hz), 133.9, 133.8, 133.6, 132.0, 131.5 (q, J_{C-F} = 33.2 Hz), 130.9 (q, J_{C-F} = 32.4 Hz), 130.0, 129.2, 127.4, 126.2 (q, J_{C-F} = 3.7 Hz), 125.0 (q, J_{C-F} = 3.4 Hz), 123.9 (q, J_{C-F} = 272.6 Hz), 123.4 (q, J_{C-F} = 4.0 Hz), 122.7 (q, J_{C-F} = 272.7 Hz), 99.1, 35.9.; HRMS m/z (ESI) calcd for $C_{22}H_{13}F_6IONa$ $[M+Na]^+$: 556.9807, found: 556.9811, error 0.7 ppm. IR (cm^{-1}): 1698, 1601, 1321, 1169, 1127, 1085, 834, 755.



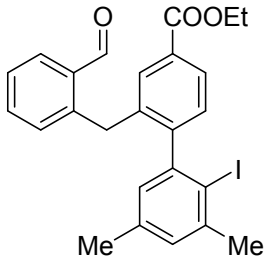
2-((2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4e) Colorless oil (45 mg, 53% yield). R_f = 0.15 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.81 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.04 (dd, *J* = 1.4, 0.6 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.84 – 6.63 (m, 1H), 4.21 (dd, *J* = 47.4, 16.3 Hz, 2H), 2.50 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 146.5, 145.2, 142.7, 142.0, 138.0, 137.5, 134.1, 133.6, 131.9, 129.9, 129.8, 129.5, 129.2, 128.0, 128.0, 126.6, 126.3, 103.0, 35.4, 29.4, 20.6.; HRMS m/z (ESI) calcd for $C_{22}H_{19}IONa$ $[M+Na]^+$: 449.0352, found: 449.0359, error 1.6 ppm. IR (cm^{-1}): 1693, 1596, 1210, 1006, 773, 753.



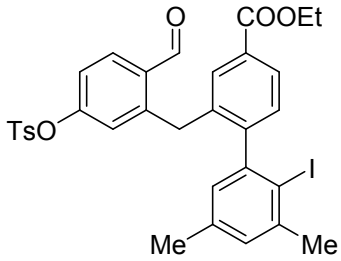
2-((4-fluoro-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4f)
Colorless oil (46 mg, 52% yield). R_f = 0.17 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.82 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.98 (td, *J* = 8.3, 2.6 Hz, 1H), 6.76 (d, *J* = 1.5 Hz, 1H), 6.66 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.17 (dd, *J* = 67.5, 16.4 Hz, 2H), 2.50 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 162.4 (d, J_{C-F} = 246.4 Hz) , 145.6, 142.2, 141.7, 141.1 (d, J_{C-F} = 3.2 Hz), 140.6 (d, J_{C-F} = 7.3 Hz), 137.7, 134.1, 133.8, 132.0, 131.2 (d, J_{C-F} = 8.1 Hz), 130.9, 129.7, 128.3, 127.0, 115.9 (d, J_{C-F} = 22.2 Hz), 113.1 (d, J_{C-F} = 21.4 Hz), 103.4, 35.5, 29.4, 20.6.; HRMS m/z (ESI) calcd for $C_{22}H_{18}FIONa$ $[M+Na]^+$: 467.0279, found: 467.0277, error 0.4 ppm. IR (cm^{-1}): 1695, 1598, 1493, 1452, 1210, 1006, 858, 748.



2-((4-chloro-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4g)
Colorless oil (60 mg, 65% yield). R_f = 0.17 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 7.5, 2.7 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 1.0 Hz, 1H), 4.17 (dd, *J* = 71.0, 16.4 Hz, 2H), 2.49 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 145.3, 143.5, 142.1, 141.6, 140.1, 137.6, 134.0, 133.7, 133.7, 132.0, 131.1, 131.0, 129.7, 129.1, 128.0, 126.9, 126.5, 102.8, 35.3, 29.4, 20.6.; HRMS m/z (ESI) calcd for $C_{22}H_{18}ClIONa$ $[M+Na]^+$: 482.9961, found: 482.9983, error 4.8 ppm. IR (cm^{-1}): 1688, 1596, 1450, 1209, 1105, 1009, 761.

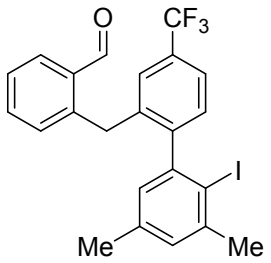


Ethyl-2-(2-formylbenzyl)-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate(4h)
Colorless oil (63 mg, 63% yield). R_f = 0.38 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.77 (d, *J* = 1.3 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 1.4, 0.4 Hz, 1H), 4.39 – 4.14 (m, 4H), 2.46 (s, 3H), 2.18 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 166.3, 149.6, 145.5, 142.1, 142.0, 138.5, 137.6, 134.0, 133.6, 131.8, 130.8, 130.6, 130.1, 129.8, 127.7,127.6, 126.7, 101.9, 60.9, 35.3, 29.3, 20.6, 14.3; HRMS m/z (ESI) calcd for $C_{25}H_{27}INO_3[M+NH_4]^+$: 516.1030, found: 516.1022, error 1.6 ppm. IR (cm^{-1}): 1716, 1696, 1598, 1451, 1288, 1251, 1177, 1109, 1007, 858, 771, 754.

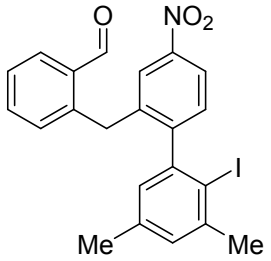


Ethyl-2-(2-formyl-5-(tosyloxy)benzyl)-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (4i) Colorless oil (68 mg, 51% yield). R_f = 0.11 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.66 (dd, *J* = 18.9, 8.4 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 1.5 Hz, 1H), 6.97 (dd, *J* = 8.5, 2.3 Hz,

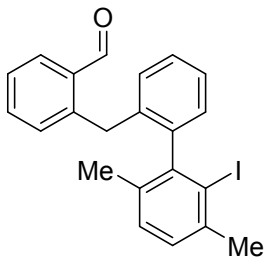
1H), 6.72 (d, J = 2.3 Hz, 1H), 6.48 (d, J = 1.6 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.17 (dd, J = 99.6, 16.2 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 166.2, 153.2, 149.6, 145.7, 145.3, 144.5, 142.2, 137.8, 137.5, 132.5, 132.3, 132.2, 130.6, 130.2, 130.1, 129.9, 129.9, 128.3, 128.0, 127.6, 125.1, 120.6, 101.8, 61.1, 34.9, 29.2, 21.7, 20.5, 14.3.; HRMS m/z (ESI) calcd for $C_{32}H_{29}IO_6SNa$ $[M+Na]^+$: 691.0622, found: 691.0628, error 0.8 ppm. IR (cm^{-1}): 1716, 1696, 1599, 1377, 1287, 1190, 1177, 1091, 964, 834, 814, 741.



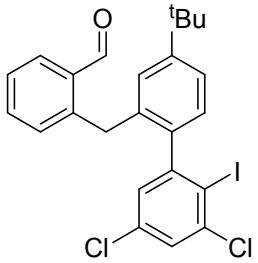
2-((2'-iodo-3',5'-dimethyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4j) Colorless oil (64 mg, 65% yield). R_f = 0.19 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.24 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 0.5 Hz, 1H), 6.69 (s, 1H), 4.28 (dd, J = 83.1, 16.4 Hz, 2H), 2.49 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 148.5, 145.2, 142.2, 141.3, 139.1, 137.8, 134.0, 133.7, 131.9, 131.4, 130.4, 130.1 (q, J_{C-F} = 32.4 Hz), 129.9, 129.2, 127.0, 126.0 (q, J_{C-F} = 3.7 Hz), 124.1 (q, J_{C-F} = 272.8 Hz), 123.3 (q, J_{C-F} = 3.8 Hz), 102.0, 35.4, 29.3, 20.6.; HRMS m/z (ESI) calcd for $C_{23}H_{18}F_3IONa$ $[M+Na]^+$: 517.0222, found: 517.0247, error 5.0 ppm. IR (cm^{-1}): 1693, 1599, 1333, 1163, 1123, 1097, 1007, 834, 756.



2-((2'-iodo-3',5'-dimethyl-4-nitro-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4k) Colorless oil (60 mg, 64% yield). R_f = 0.41 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.15 (dd, J = 8.3, 2.4 Hz, 1H), 7.84 (d, J = 2.2 Hz, 1H), 7.81 (dd, J = 7.6, 1.4 Hz, 1H), 7.51 (td, J = 7.5, 1.5 Hz, 1H), 7.44 (td, J = 7.5, 1.1 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.09 (dd, J = 1.5, 0.6 Hz, 1H), 6.78 – 6.64 (m, 1H), 4.29 (dd, J = 110.9, 16.4 Hz, 2H), 2.50 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 151.4, 147.6, 144.5, 142.4, 140.5, 140.4, 138.0, 134.1, 133.8, 132.6, 132.1, 130.9, 130.2, 127.5, 127.4, 124.0, 121.4, 101.3, 35.7, 29.2, 20.6.; HRMS m/z (ESI) calcd for $C_{22}H_{22}IN_2O_3$ $[M+NH_4]^+$: 489.0670, found: 489.0664, error 1.2 ppm. IR (cm^{-1}): 1697, 1518, 1344, 1261, 1099, 1008, 809, 751.



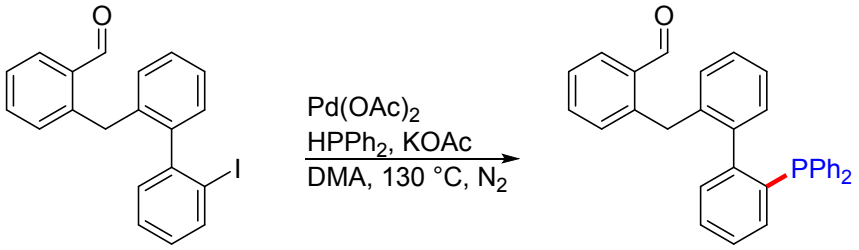
2-((2'-iodo-3',6'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4l) Colorless oil (31 mg, 37% yield). R_f = 0.14 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.21 – 7.09 (m, 3H), 7.05 – 6.99 (m, 2H), 4.10 (dd, *J* = 42.8, 16.2 Hz, 2H), 2.50 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 145.4, 144.6, 141.9, 139.9, 137.7, 134.8, 134.4, 133.7, 132.3, 129.9, 129.7, 129.5, 129.3, 128.7, 128.0, 126.9, 126.8, 108.2, 35.2, 29.5, 21.3.; HRMS m/z (ESI) calcd for $C_{22}H_{19}IONa$ $[M+Na]^+$: 449.0373 found: 449.0367, error 1.4 ppm. IR (cm^{-1}): 1696, 1597, 1466, 1207, 809, 752.



2-((4-(tert-butyl)-3',5'-dichloro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4m) White solid (75 mg, 72% yield). Mp: 132 - 134 °C; R_f = 0.60 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.81 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.38 (dt, *J* = 7.4, 3.7 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.07 (dd, *J* = 9.7, 4.7 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 4.23 (q, *J* = 16.4 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 151.9, 150.2, 142.2, 140.8, 140.0, 137.0, 134.5, 134.1, 133.7, 131.7, 131.1, 129.1, 128.1, 127.6, 126.9, 126.9, 123.5, 102.9, 36.1, 34.7, 31.3.; HRMS m/z (ESI) calcd for $C_{24}H_{21}Cl_2IONa$ $[M+Na]^+$: 544.9906, found: 544.9914, error 1.5 ppm. IR (cm^{-1}): 1695, 1597, 1372, 1211, 1107, 1009, 813, 755.

VI. Further Transformation of 3a

1. Procedure for the Synthesis of Compound 5[5]



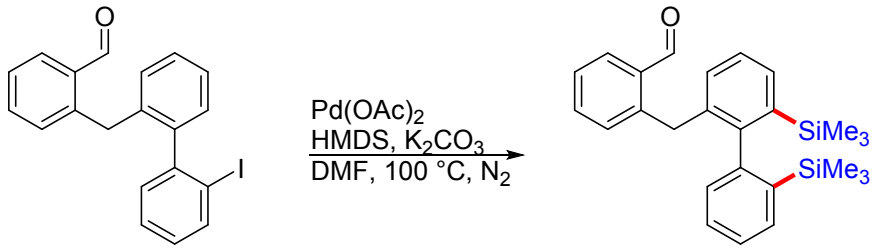
3a **5**

A 20 mL Schlenk tube was charged with **3a** (80 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol)

and KOAc (22 mg, 0.22 mmol). The tube was evacuated and filled with N_2 with three times. Next, diphenylphosphine (38 μL, 0.22 mmol) and DMA (1 mL) were added into the tube via syringe. The reaction was then stirred for 12 h at 130 ˚C in oil bath. After cooling to room temperature, the reaction mixture was diluted with EtOAc (10 mL),filtered through a pad of Celite, and the filtrate was washed with H_2O (10 mL×2) and brine (10 mL) before it was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **5** as a white solid.

2-((2'-(diphenylphosphaneyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (5) White solid (52 mg, 57% yield). Mp: 125 - 127 °C; R_f = 0.13 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.27 (m, 9H), 7.15 (m, 8H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 4.19 (dd, *J* = 86.5, 16.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 146.8, 146.5, 143.1, 140.8, 138.0, 137.0, 136.8, 134.1, 134.0, 133.9, 133.9, 133.8, 133.7, 133.6, 131.8, 130.8, 130.0, 129.8, 128.9, 128.7, 128.5, 128.5, 128.4, 128.2, 128.2, 127.8, 127.6, 126.6, 125.5, 35.7.; HRMS m/z (ESI) calcd for $C_{32}H_{26}OP$ $[M+H]^+$: 457.1716, found: 457.1716, error 0.0 ppm. IR (cm^{-1}): 1694, 1596, 1434, 1207, 753, 696.

2. Procedure for the Synthesis of Compound 6[6]



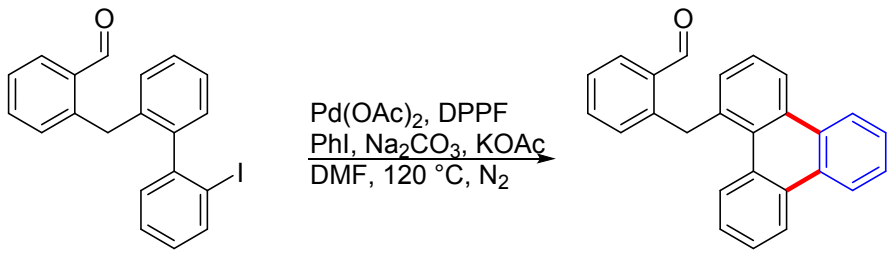
3a **6**

A 25 mL Schlenk-type tube equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), **3a** (80 mg, 0.2 mmol), and DMF (1 mL). Then the tube was evacuated and backfilled with nitrogen (3 times). Hexamethyldisilane (HMDS) (123 μL, 0.6 mmol) were added into the tube via microsyringe. The mixture was first stirred at room temperature for 10 minutes and then stirred at 100 °C (preheated oil bath) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **6** as a Colorless oil.

2-((2',6-bis(trimethylsilyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (6) Colorless oil (65 mg, 78% yield). R_f = 0.37 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.76 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.60 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.5, 1.4 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 7.6, 0.7 Hz, 1H), 4.05 (dd, *J* = 112.9, 16.4 Hz, 2H), -0.02 (s, 9H), -0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 148.8, 147.1, 143.4, 139.7, 139.6, 137.9, 134.8, 133.9, 133.5, 132.6, 131.3, 130.5, 129.9, 129.9, 128.1, 126.9, 126.6, 126.5, 35.9, 0.5, 0.3.; HRMS m/z (ESI) calcd for $C_{26}H_{33}OSi_2$

[M+H]$^+$: 417.2064, found: 417.2056, error 2.0 ppm. IR (cm^{-1}): 2954, 1697, 1599, 1412, 837, 757, 732.

3. Procedure for the Synthesis of Compound 7[7]

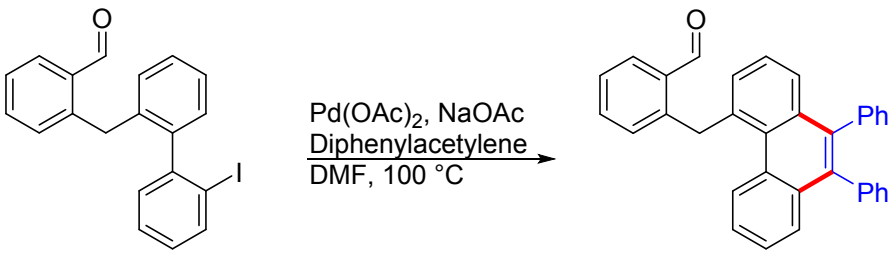


3a **7**

A 15 mL pressure vessel equipped with a magnetic stir bar was charged with **3a** (80mg, 0.2 mmol), $Pd(OAc)_2$ (2.3 mg, 5 mol %), DPPF (5.5 mg, 5 mol%), Na_2CO_3 (42.4 mg, 0.4 mmol), KOAc (59 mg, 0.6 mmol), followed by iodobenzene (33 µL, 0.3 mmol), and DMF (4 mL) as solvent. The reaction tube was backfilled with nitrogen and sealed. After the reaction mixture was stirred at 120 °C in oil bath for 12 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (15 mL) and washed with brine (5 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **7** as a white solid.

2-(triphenylen-1-ylmethyl)benzaldehyde(7) White solid (44 mg, 63% yield). Mp: 121 - 123 °C; R_f = 0.14 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.66 – 8.55 (m, 4H), 8.27 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.52 (m, 1H), 7.50 (td, *J* = 7.5, 1.6 Hz, 1H), 7.45 (dd, *J* = 7.4, 6.6 Hz, 1H), 7.39 (m, 1H), 7.30 (dd, *J* = 16.3, 7.4 Hz, 2H), 5.20 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 143.9, 136.9, 134.0, 133.8, 132.5, 131.8, 131.5, 131.2, 131.1, 130.7, 130.3, 130.0, 129.6, 128.4, 127.4, 127.3, 127.0, 126.9, 126.5, 125.7, 123.6, 123.4, 123.1, 121.5, 40.4.; HRMS m/z (ESI) calcd for $C_{26}H_{22}NO$ [M+NH_4]$^+$: 364.1696, found: 364.1685, error 3.1 ppm. IR (cm^{-1}): 1693, 1597, 1203, 744.

4. Procedure for the Synthesis of Compound 8[8]



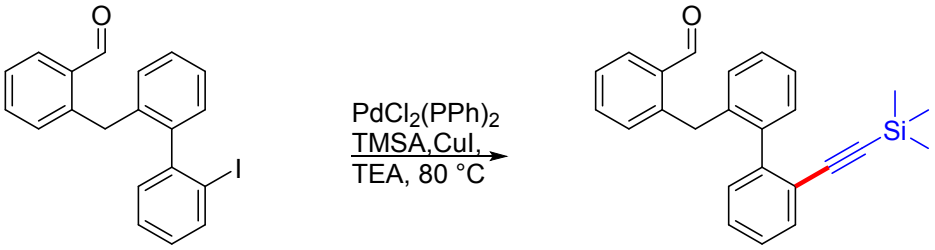
3a **8**

A mixture of **3a** (80 mg, 0.2 mmol), diphenylacetylene (72 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), NaOAc (32.8 mg, 0.4 mmol), *n*-Bu_4NCl (167 mg, 0.6 mmol) and DMF (1 mL) in a pressure vessel at room temperature was purged with nitrogen. The sealed tube was kept in an oil bath at 110 ºC in oil bath for 24 h. After being cooled to room temperature, hydrochloric

acid (1 M, 10 mL) was carefully added. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent of the filtrate was removed under reduced pressure. The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **8** as a white solid.

2-((9,10-diphenylphenanthren-4-yl)methyl)benzaldehyde (8) White solid (60 mg, 66% yield). Mp: 161 - 163 °C; R_f = 0.16 (PE/EtOAc = 100:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.61 – 8.40 (m, 1H), 8.01 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.43 (m, 3H), 7.36 (t, *J* = 6.9 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.20 (m, 6H), 5.37 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 143.8, 140.0, 139.6, 137.6, 137.3, 136.1, 134.2, 133.7, 133.2, 132.8, 131.4, 131.1, 131.0, 130.5, 129.9, 127.7, 127.6, 127.3, 127.0, 127.0, 126.4, 126.2, 125.9, 125.1, 41.2.; HRMS m/z (ESI) calcd for $C_{34}H_{24}ONa$ $[M+Na]^+$: 471.1719, found: 471.1765, error 9.6 ppm. IR (cm^{-1}): 1693, 1597, 1439, 1196, 764, 748, 723, 700.

5. Procedure for the Synthesis of Compound 9

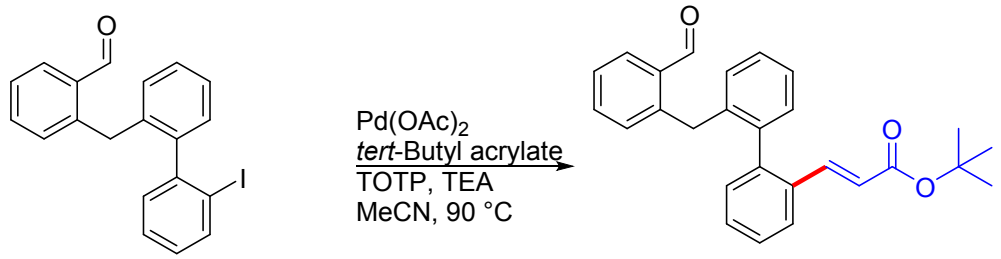


3a **9**

To a 25 mL Schlenk-type tube, $PdCl_2(PPh_3)_2$ (4.2 mg, 0.006 mmol) and CuI (2.3 mg, 0.012 mmol) were added to the dissolved biaryl iodide (80 mg, 0.2 mmol) in NEt_3 (0.5 mL) under nitrogen atmosphere and stirred another 10 minutes in room temperature. Then, trimethylsilylacetylene (34 μL, 0.24 mmol) was added to reaction mixture and stirred another 6h at 80°C in oil bath. After completion, the reaction mixture was filtered through celite pad and washed with EtOAc, evaporated solvent under reduced pressure. The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **9** as a colorless oil.

2-((2'-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (9) Colorless oil (47 mg, 64% yield). R_f = 0.28 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.80 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 – 7.22 (m, 6H), 7.22 – 7.19 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.99 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.31 (s, 2H), 0.24 – 0.02 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 144.5, 143.3, 140.5, 138.5, 133.9, 133.6, 132.0, 131.7, 130.1, 130.1, 129.3, 129.1, 128.3, 127.8, 127.1, 126.6, 126.0, 122.9, 104.1, 97.9, 35.3.; HRMS m/z (ESI) calcd for $C_{25}H_{24}OSiNa$ $[M+Na]^+$: 391.1489, found: 391.1483, error 1.5 ppm. IR (cm^{-1}): 2157, 1697, 1598, 1470, 1249, 1208, 863, 843, 758.

6. Procedure for the Synthesis of Compound 10



3a **10**

A dry Schlenk tube equipped with a stir bar was charged with **3a** (80 mg, 0.2 mmol), *tert*-butyl acrylate (58 µL 0.4 mmol), Et_3N (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), tri-*o*-tolylphopine (12.2 mg, 0.04 mmol) and CH_3CN (1.5 mL). The reaction mixture was stirred at 90 °C in oil bath for 6 h. After completion, the reaction mixture was filtered through celite pad and washed with EtOAc, evaporated solvent under reduced pressure. The residue was purified by column chromatography (PE/EtOAc =50:1) on silica gel to provide the desired products **10** as a colorless oil.

***tert*-butyl (*E*)-3-(2'-(2-formylbenzyl)-[1,1'-biphenyl]-2-yl)acrylate (10)** Colorless oil (52 mg, 78% yield). R_f = 0.14 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.73 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.66 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 3H), 7.25 (d, *J* = 16.0 Hz, 1H), 7.20 –7.14 (m, 2H), 7.11 – 7.03 (m, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 16.3 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 165.9, 142.7, 141.9, 141.2, 139.6, 138.5, 133.8, 133.6, 133.1, 131.6, 130.6, 130.3, 130.3, 129.8, 129.5, 128.1, 127.8, 126.6, 126.5, 125.9, 120.7, 80.2, 35.2, 28.1.; HRMS m/z (ESI) calcd for $C_{27}H_{26}O_3Na$ $[M+Na]^+$: 421.1774, found: 421.1768, error 1.6 ppm. IR (cm^{-1}): 1704, 1633, 1598, 1320, 1203, 1149, 983, 867, 754.

7. Procedure for the Synthesis of Compound 11[9]

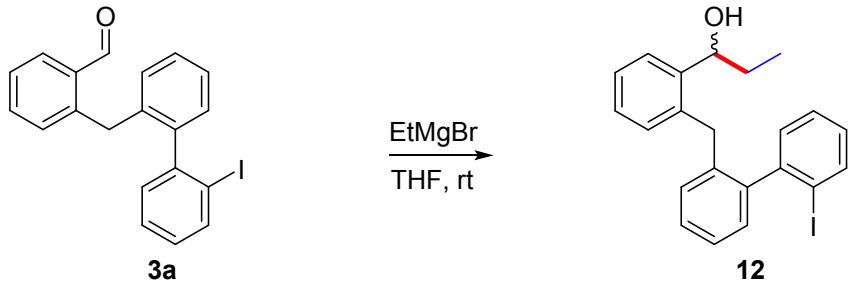
3a **11**

Trifluoromethanesulfonic acid (2.7 µL, 0.03 mmol) was added to a HFIP (2 mL) solution of **3a** (80 mg, 0.2 mmol) at 0 °C. After stirring at the same temperature for 20 min, the reaction was quenched with phosphate buffer (pH 7). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were washed with brine and dried (Na_2SO_4).The solvent of the filtrate was removed under reduced pressure.The residue was purified by column chromatography (PE/EtOAc =200:1) on silica gel to provide the desired products **11** as a light yellow solid.

1-(2-iodophenyl)anthracene (11) Light yellow solid (55 mg, 72%). Mp: 155 - 157 °C; R_f = 0.66 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.13 – 8.06 (m, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 8.94 – 6.98 (m, 1H), 7.58 – 7.50

(m, 1H), 7.44 (m, 1H), 7.33 (d, J = 6.7 Hz, 1H), 7.21 (td, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 142.3, 139.3, 131.7, 131.7, 131.6, 131.0, 129.9, 129.1, 128.6, 128.5, 128.0, 127.9, 126.6, 126.4, 125.6, 125.4, 124.9, 124.7, 100.6.; HRMS m/z (EI) calcd for $C_{20}H_{13}I$ $[M]^+$: 380.0062, found: 380.0057, error 1.3 ppm. IR (cm^{-1}): 3046, 1016, 884, 756, 750, 735, 726.

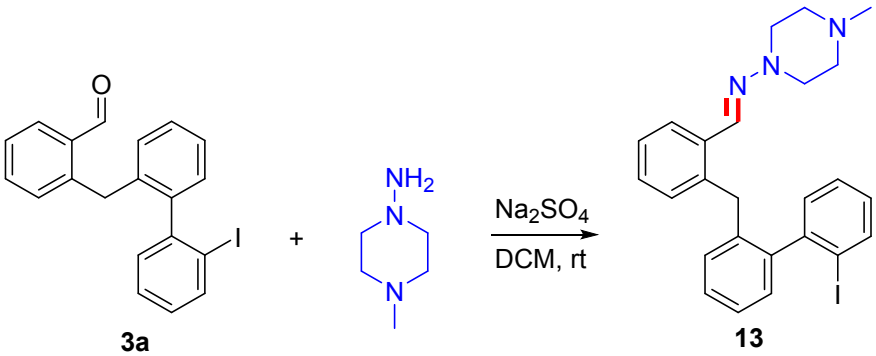
8. Procedure for the Synthesis of Compound 12



Ethylmagnesium bromide (in THF 2 M, 0.12 mL, 0.24 mmol) was added to a anhydrous THF (1 mL) solution of **3a** (80 mg, 0.2 mmol) at 0 °C. The reaction mixture was stirred at rt for 12 h. Then the reaction was quenched with saturated aqueous NH_4Cl. The resulting solution was extracted with DCM, and the organic layer was dried over Na_2SO_4. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography to afford the expected secondary alcohol **12** as a white solid.

1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)propan-1-ol (12) White solid (56 mg, 65% yield). Mp: 100 - 102 °C; R_f = 0.28 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (m, 1H), 7.45 (m, 1H), 7.35 (m, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 7.20 – 6.95 (m, 6H), 4.61 (m, 1H), 3.94 – 3.48 (m, 2H), 1.73 – 1.36 (m, 2H), 0.90 – 0.63 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 146.1, 144.1, 144.0, 143.0, 142.8, 139.1, 138.9, 138.6, 138.2, 136.9, 136.6, 130.7, 130.6, 130.0, 129.9, 129.7, 129.6, 129.2, 129.1, 128.9, 128.8, 128.2, 128.0, 127.9, 127.3, 127.2, 126.8, 126.7, 126.2, 126.1, 125.7, 125.6, 100.2, 100.1, 71.4, 71.3, 36.1, 36.1, 31.1, 30.9, 10.3, 10.2; HRMS m/z (ESI) calcd for $C_{22}H_{21}IONa$ $[M+Na]^+$: 451.0529, found: 451.0518, error 2.4 ppm. IR (cm^{-1}): 3377, 1461, 1453, 1441, 1429, 1017, 1001, 973, 769, 755.

9. Procedure for the Synthesis of Compound 13

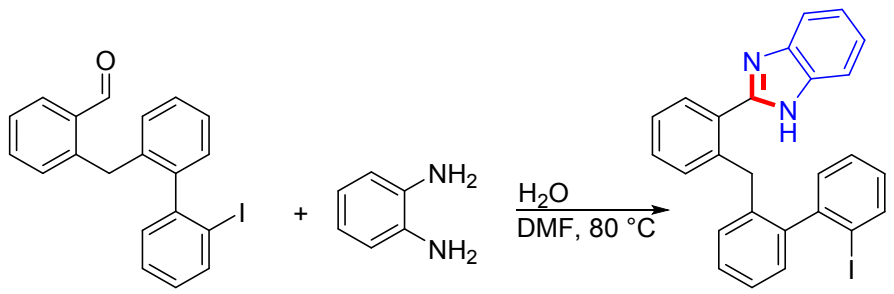


1-Amino-4-methylpiperazine (35 mg, 0.3 mmol) and **3a** (80 mg, 0.2 mmol) was dissolved in the DCM (2 mL) and Na_2SO_4(57 mg, 0.4 mmol) was added. The reaction mixture was stirred at rt for 12 h. The solvents were removed under reduced pressure and the residue was purified

by flash column chromatography (DCM/MeOH = 50:1) to afford the desired products **13** as a colorless syrup.

(*E*)-1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)-*N*-(4-methylpiperazin-1-yl)methanimine(13) Colorless syrup (93 mg, 94% yield). R_f = 0.31 (DCM/MeOH = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 (s, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.22 – 7.17 (m, 1H), 7.13 (m, 3H), 7.06 – 7.00 (m, 1H), 6.99 – 6.94 (m, 2H), 3.87 (dd, *J* = 40.4, 16.7 Hz, 2H), 3.21 – 3.03 (m, 4H), 2.63 – 2.51 (m, 4H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 143.9, 138.9, 138.0, 137.0, 134.5, 134.4, 130.9, 129.8, 129.5, 129.1, 128.9, 128.2, 128.1, 128.1, 126.6, 126.1, 125.5, 100.0, 54.3, 51.0, 45.8, 36.5.; HRMS m/z (ESI) calcd for $C_{25}H_{27}IN_3$ $[M+H]^+$: 496.1244, found: 496.1229, error 3.0 ppm. IR (cm^{-1}): 3419, 2795, 1459, 1448, 1364, 1283, 1000, 754.

10. Procedure for the Synthesis of Compound 14[10]

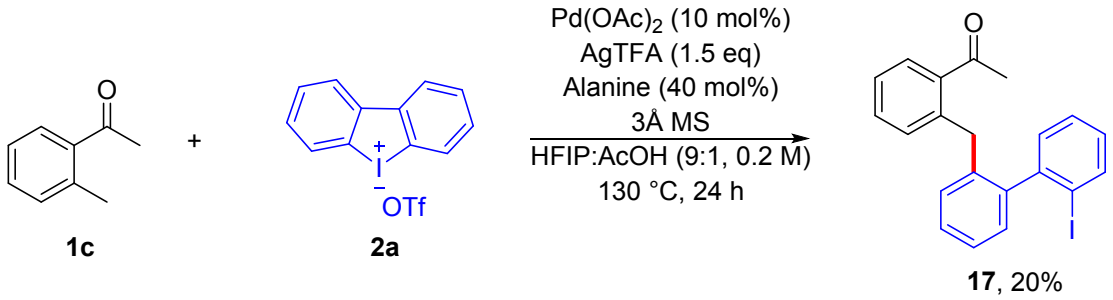


3a **14**

o-Phenylenediamine (21.6 mg, 0.2 mmol) and an **3a** (88 mg, 0.22 mmol) were dissolved in DMF (1.8 mL) and H_2O (0.2 mL). The resulting reaction mixture was stirred at 80 °C in oil bath in an open flask for overnight.Then the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (PE/EtOAc =10:1) on silica gel to afford the corresponding benzimidazole **14** as a white solid.

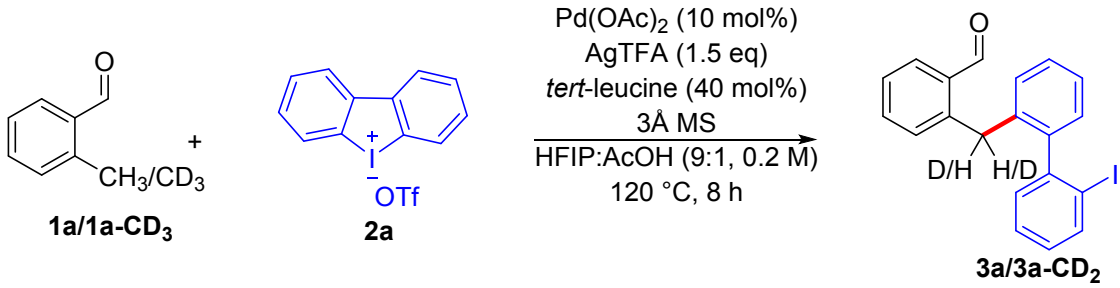
2-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)-1*H*-benzo[d]imidazole (14) White solid (80 mg, 82% yield). Mp: 224- 226°C; R_f = 0.26 (PE/EtOAc = 10:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.54 (s, 1H), 7.83 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.65 (dd, *J* = 6.7, 2.4 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.39–7.34 (m, 2H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.24–7.15 (m, 4H), 7.10 (m, 2H), 7.03 (td, *J* = 7.7, 1.5 Hz, 1H), 6.97 (m, 2H), 4.30 (dd, *J* = 82.2, 15.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.5, 145.5, 143.6, 143.6, 139.6, 138.6, 138.4, 134.2, 131.1, 130.1, 129.9, 129.5, 129.3, 129.2, 129.2, 129.1, 129.0, 127.8, 126.2, 125.7, 122.2, 121.2, 118.8, 111.1, 100.4.; HRMS m/z (ESI) calcd for $C_{26}H_{20}IN_2$ $[M+H]^+$: 487.0666, found: 487.0649, error 3.4 ppm. IR (cm^{-1}): 3044, 2669, 1445, 1416, 1373, 1269, 1001, 764, 753, 743.

VII. Control Experiments



Synthesis of 1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)ethan-1-one--1-(o-tolyl)-ethan-1-one (17). To a 15 mL pressure vessel equipped with a magnetic stir bar were introduced 2'-methylacetophenone (104 μL, 0.8 mmol), cyclic diaryliodonium salt **2a** (86 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), AgTFA (66 mg, 0.3 mmol), alanine (7.1 mg,0.08 mmol) and 3Å MS (120 mg). Next, the mixture of HFIP (0.9 mL) and HOAc (0.1 mL) were added into the above mixture. The reaction was then stirred at room temperature for 10 min before heated to 130 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with DCM (10 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EtOAc = 200:1) to yield the desired product **17** as a White solid.

1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)ethan-1-one--1-(*o*-tolyl)-ethan-1-one (17).White solid (17 mg, 20% yield). Mp: 67- 69°C; R_f = 0.16 (PE/EtOAc = 100:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.31 (m, 4H), 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.11 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.07–6.98 (m, 3H), 4.06 (dd, *J* = 53.8, 16.2 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 146.1, 144.2, 139.8, 138.8, 138.6, 138.5, 132.0, 131.1, 130.1, 129.8, 129.8, 128.6, 128.4, 127.9, 127.8, 126.0, 125.9, 100.3, 36.9, 29.7.; HRMS m/z (ESI) calcd for $C_{21}H_{17}IONa$ $[M+Na]^+$: 435.0216, found: 435.0206, error 2.4 ppm. IR (cm^{-1}): 1674, 1429, 1351, 1266, 1255, 1015, 999, 774, 766, 750.



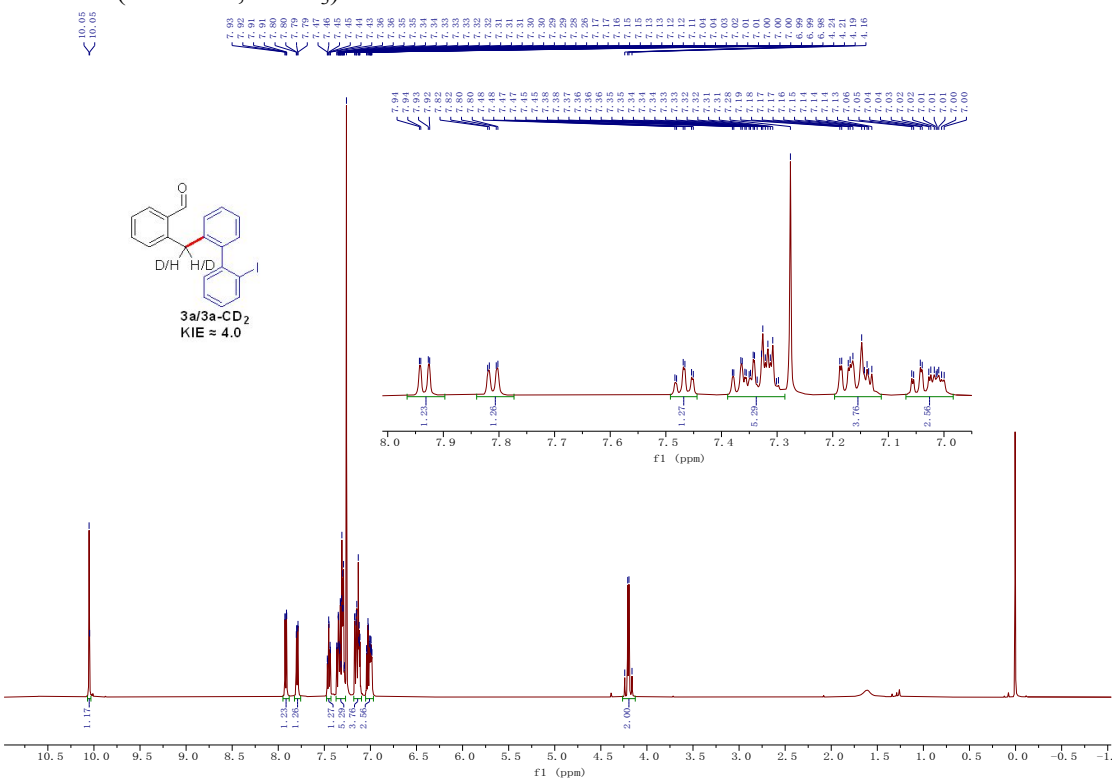
Deuteration Experiments

To a 15 mL pressure vessel equipped with a magnetic stir bar were introduced 2-methylbenzaldehyde **1a** (48 mg, 0.4 mmol) and **1a-CD$_3$** (49 mg, 0.4 mmol), cyclic diaryliodonium salt **2a** (86 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), AgTFA (66 mg, 0.3 mmol), *tert*-leucine (10.6 mg,0.08 mmol) and 3Å MS (120 mg). Next, the mixture of HFIP (0.9 mL) and HOAc (0.1 mL) were added into the above mixture. The reaction was then stirred at room temperature for 10 min before heated to 120 ˚C in oil bath for 8 h. After cooling to room temperature, the reaction mixture was diluted with DCM (10 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash

chromatography on silica gel and analyzed for its isotopic distribution.

The KIE value for this reaction was estimated to be $k_H/k_D \approx 4.0$ by ^{1}H NMR spectra.

^{1}H NMR (500 MHz, $CDCl_3$)



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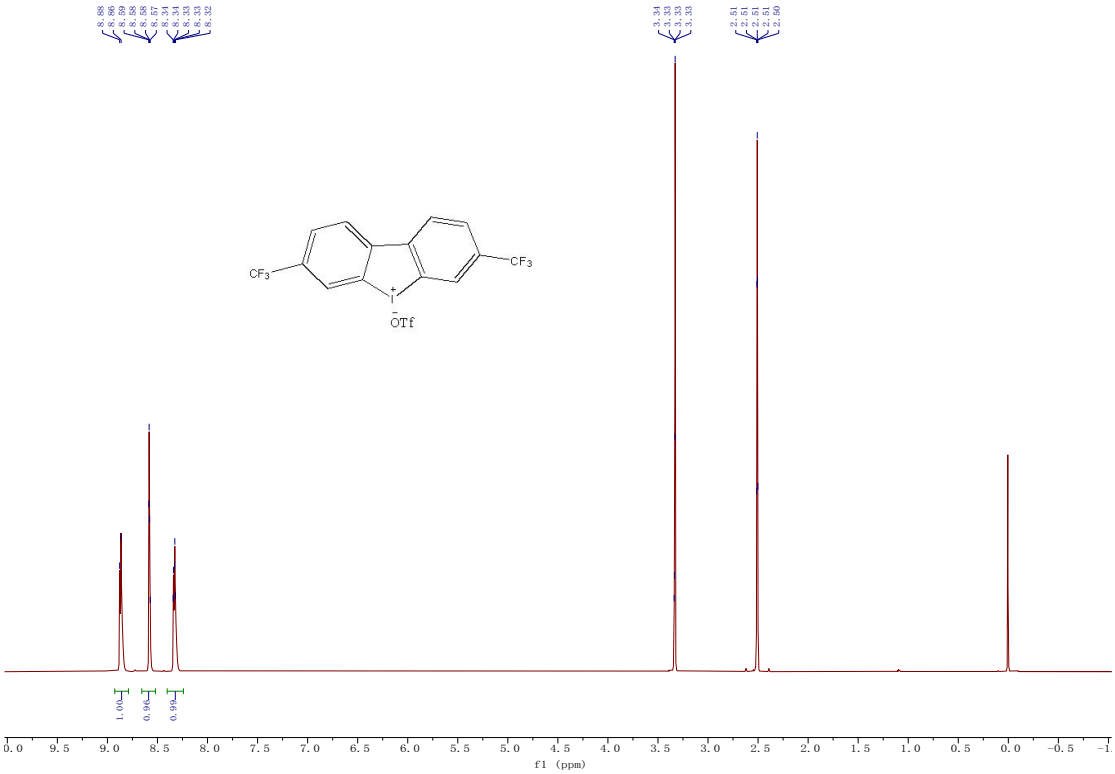
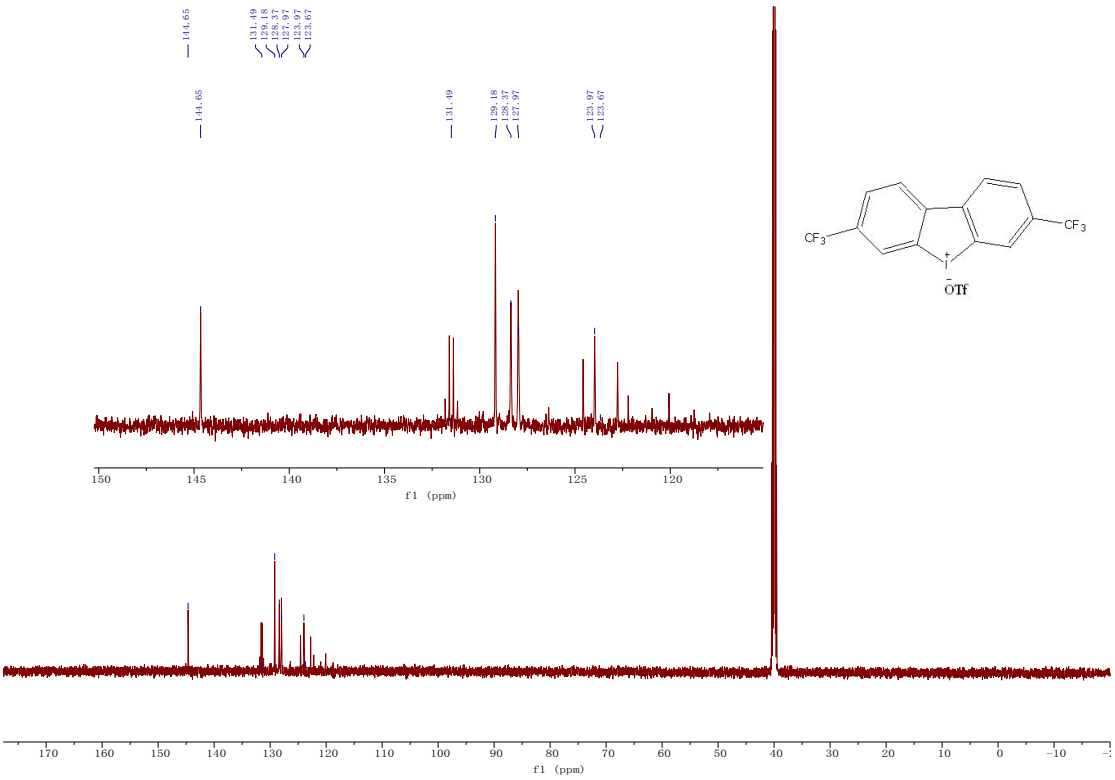
IX. NMR Spectra

3,7-bis(trifluoromethyl)dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2e)

^{1}H NMR (600 MHz, DMSO-d_6)

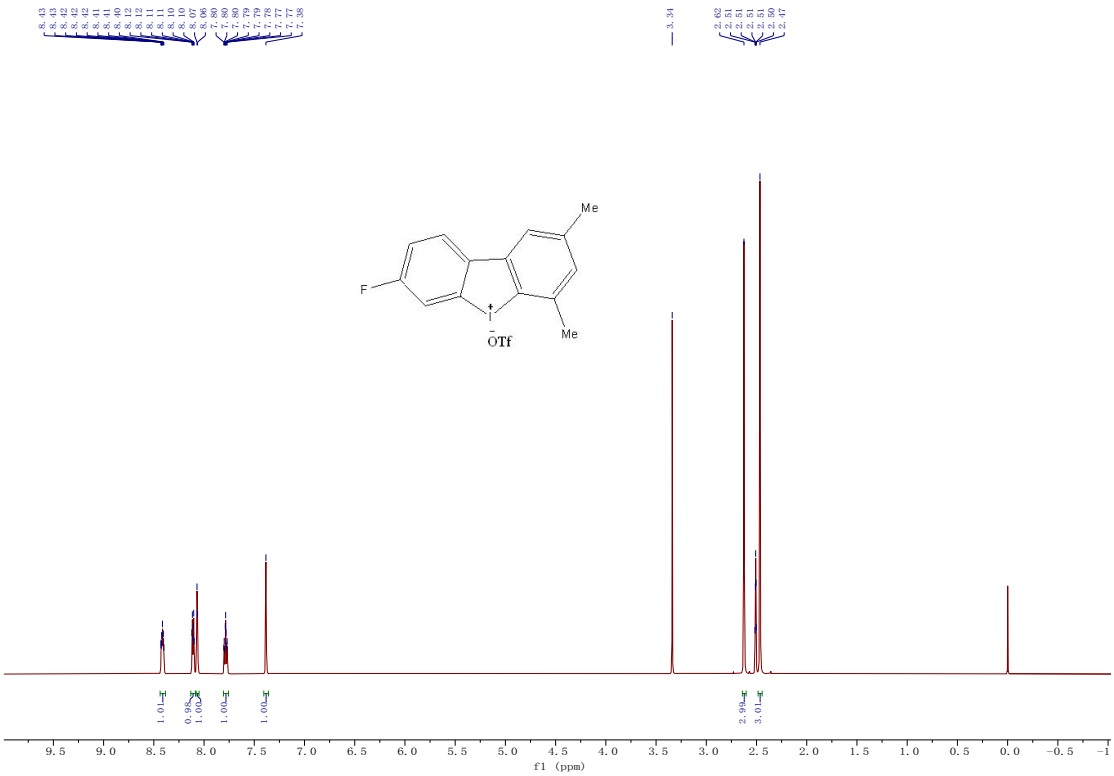


^{13}C NMR (151 MHz, DMSO-d_6)

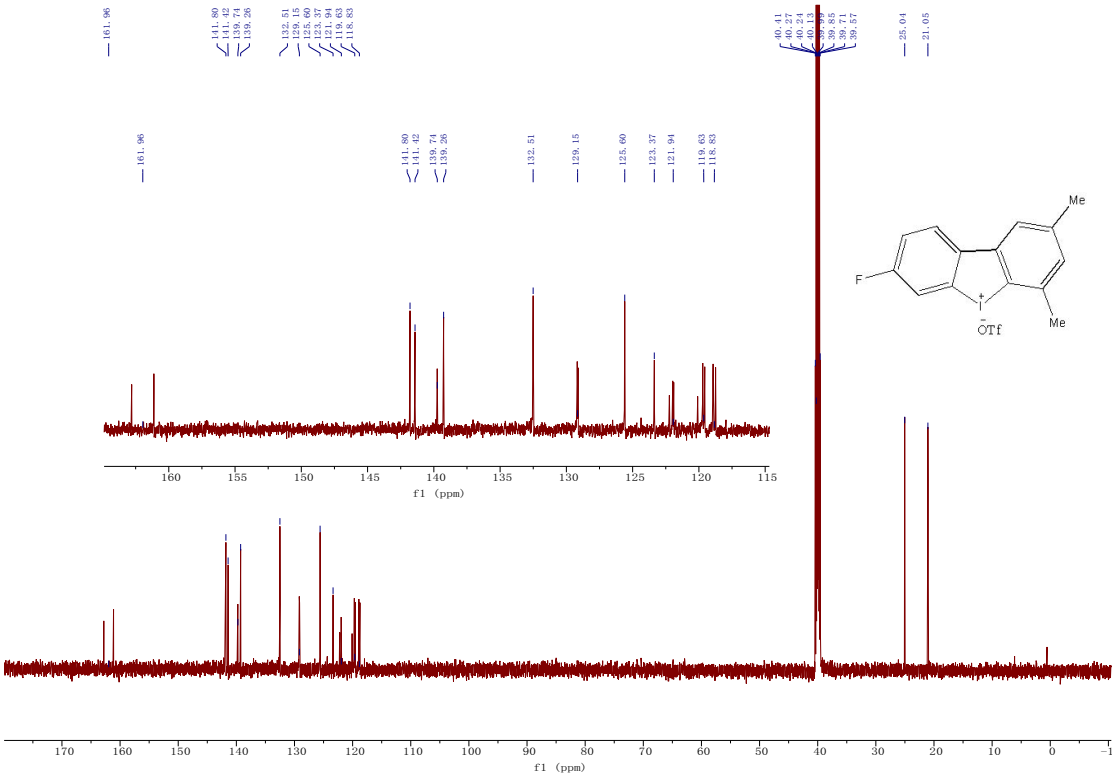


7-fluoro-2,4-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2g)

^{1}H NMR (600 MHz, DMSO-d_6)

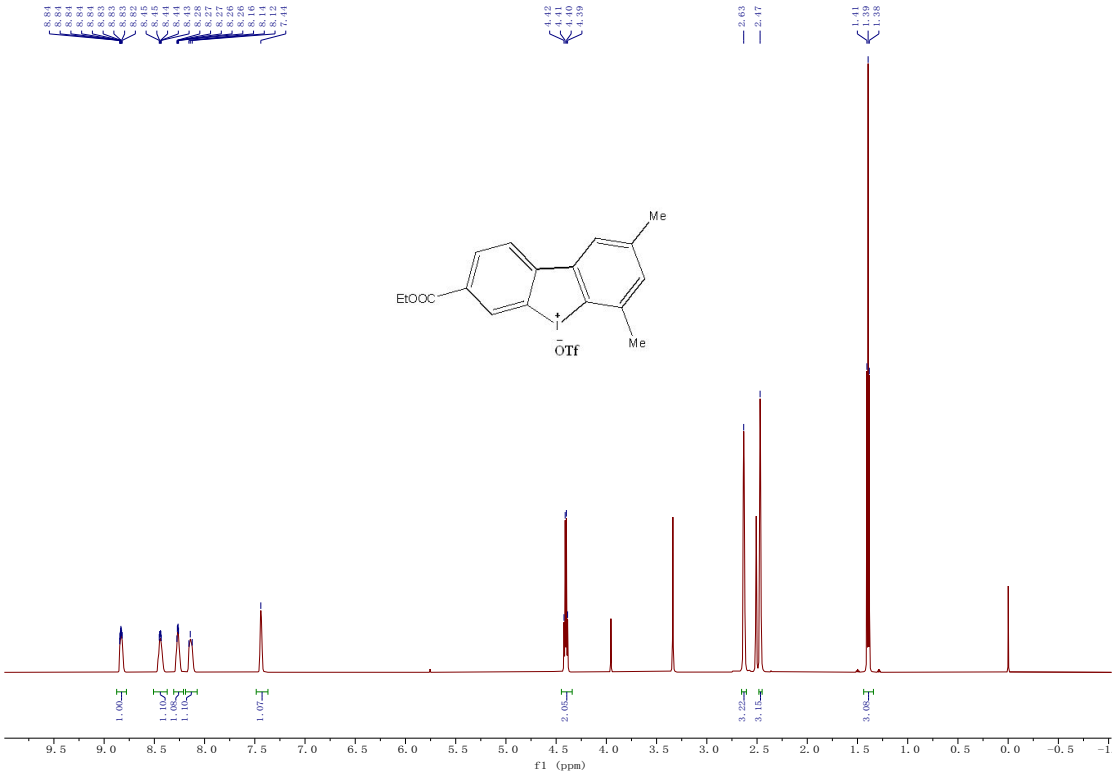


^{13}C NMR (151 MHz, DMSO-d_6)

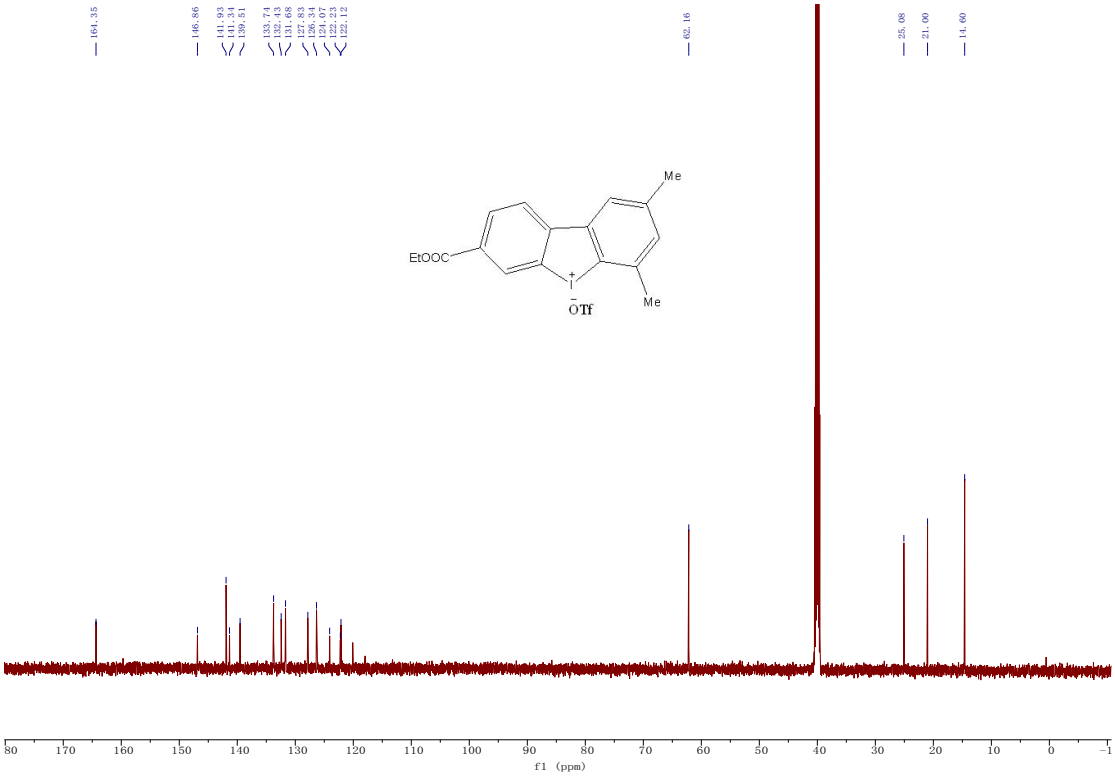


7-(ethoxycarbonyl)-2,4-dimethyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2i)

^{1}H NMR (600 MHz, DMSO-d_6)

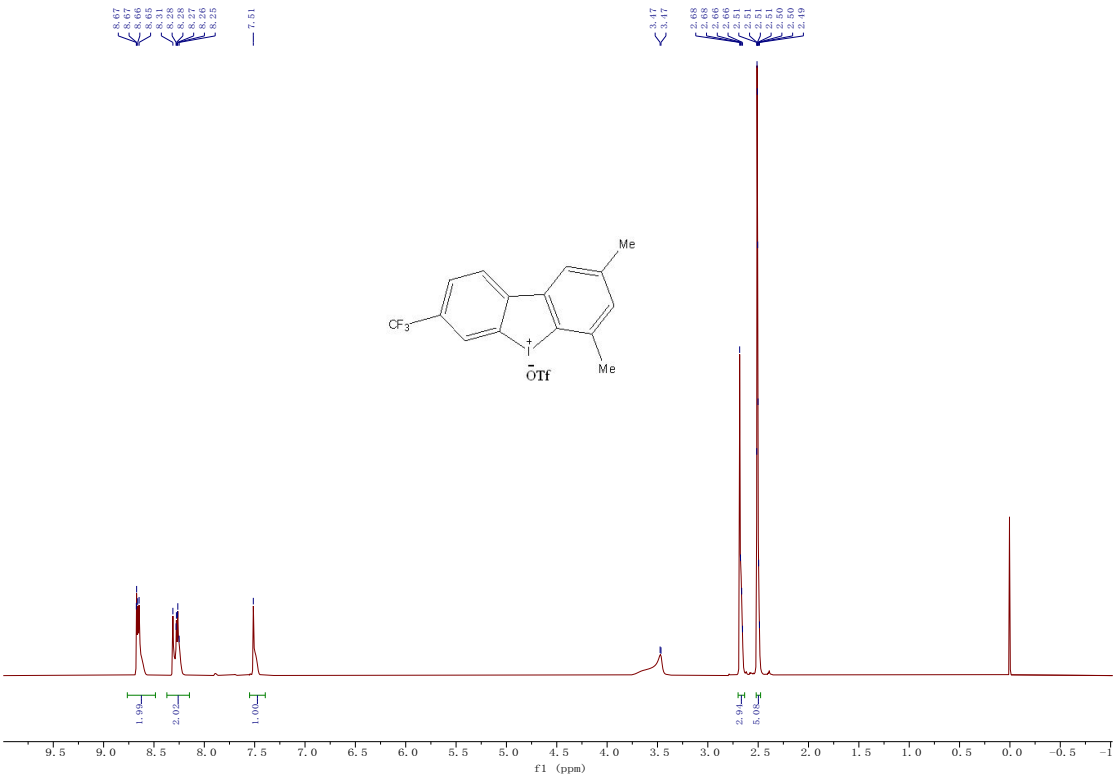


^{13}C NMR (151 MHz, DMSO-d_6)

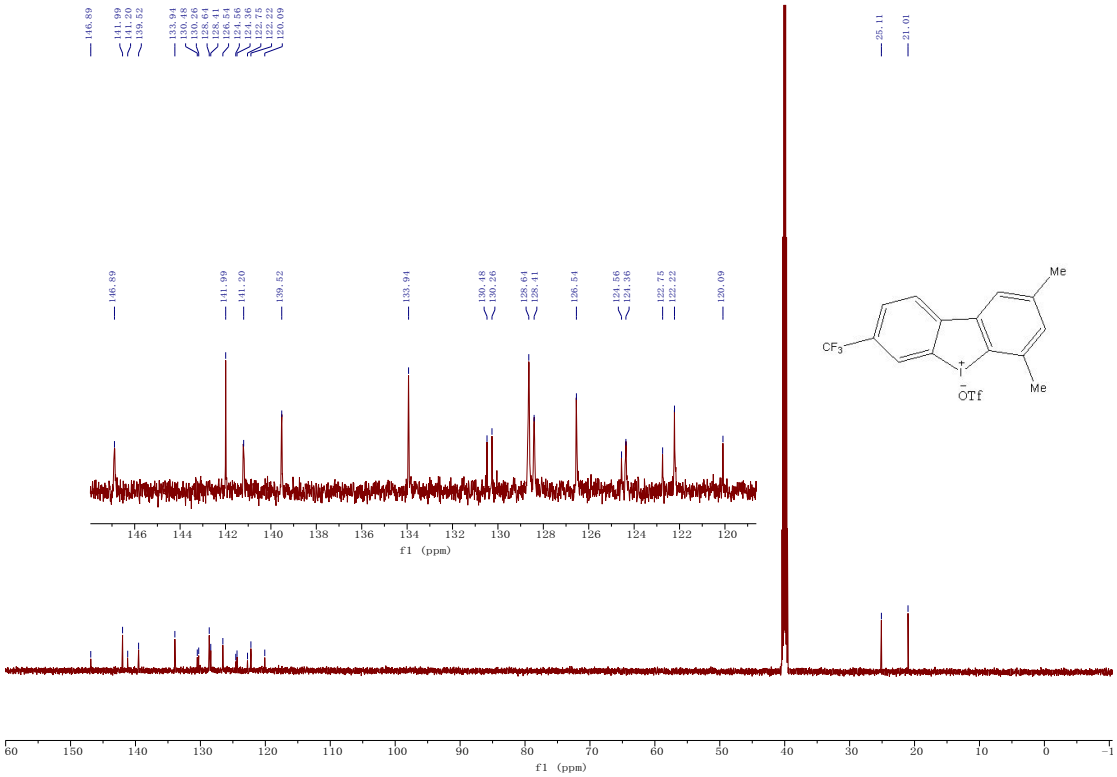


2,4-dimethyl-7-(trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2j)

^{1}H NMR (600 MHz, DMSO-d_6)

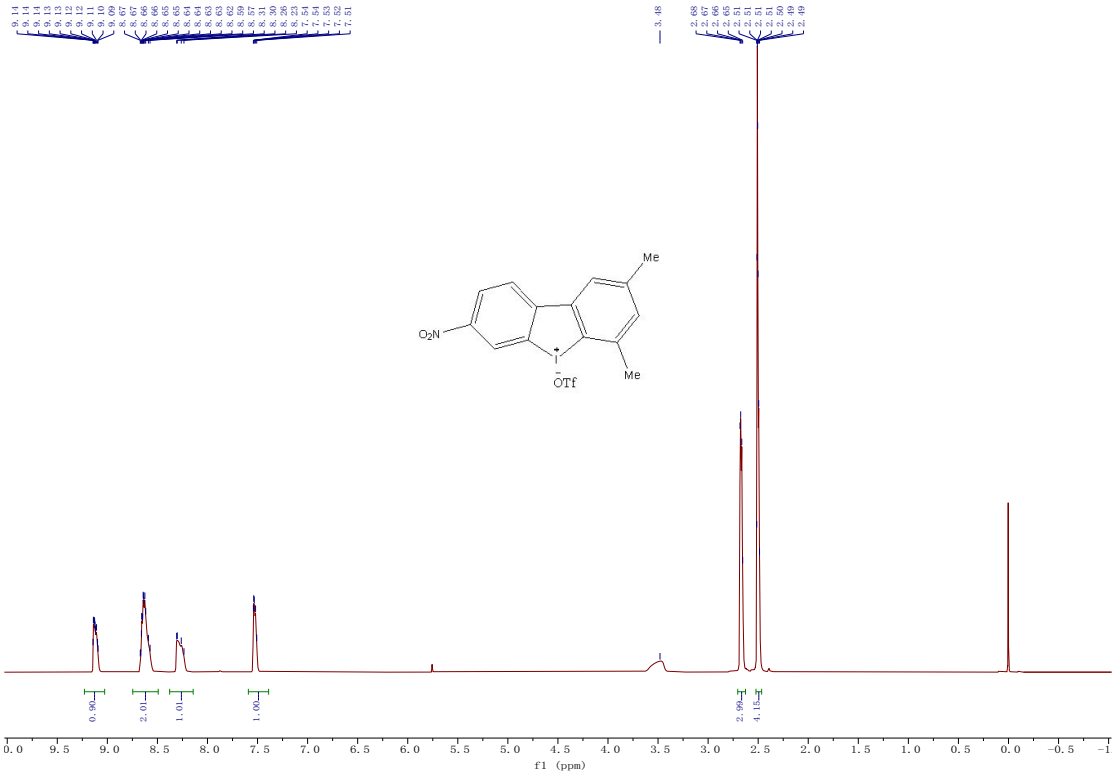


^{13}C NMR (151 MHz, DMSO-d_6)

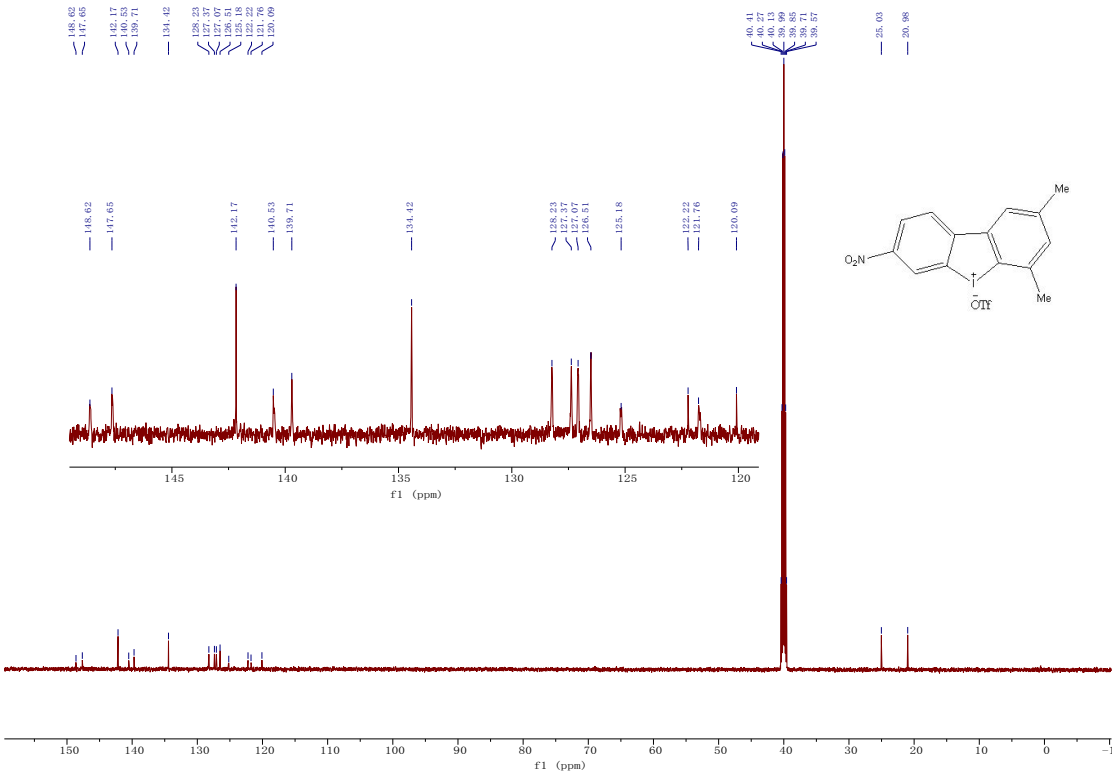


2,4-dimethyl-7-nitrodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2k)

^{1}H NMR (600 MHz, DMSO-d_6)

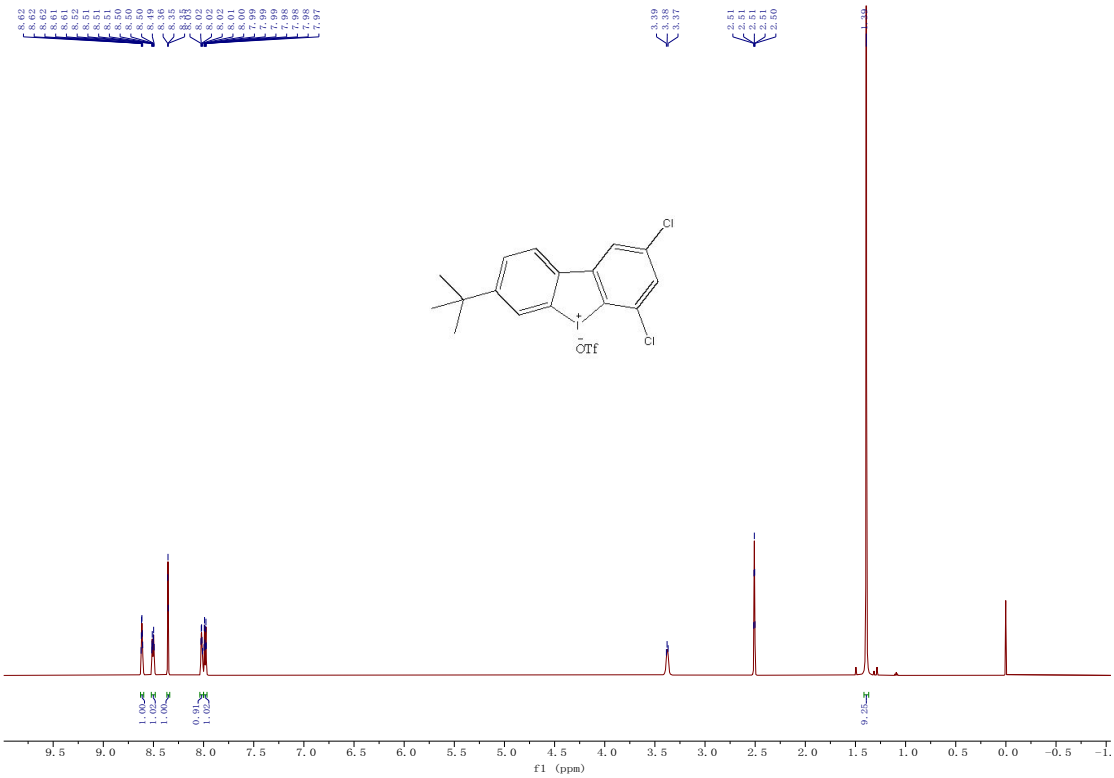


^{13}C NMR (151 MHz, DMSO-d_6)

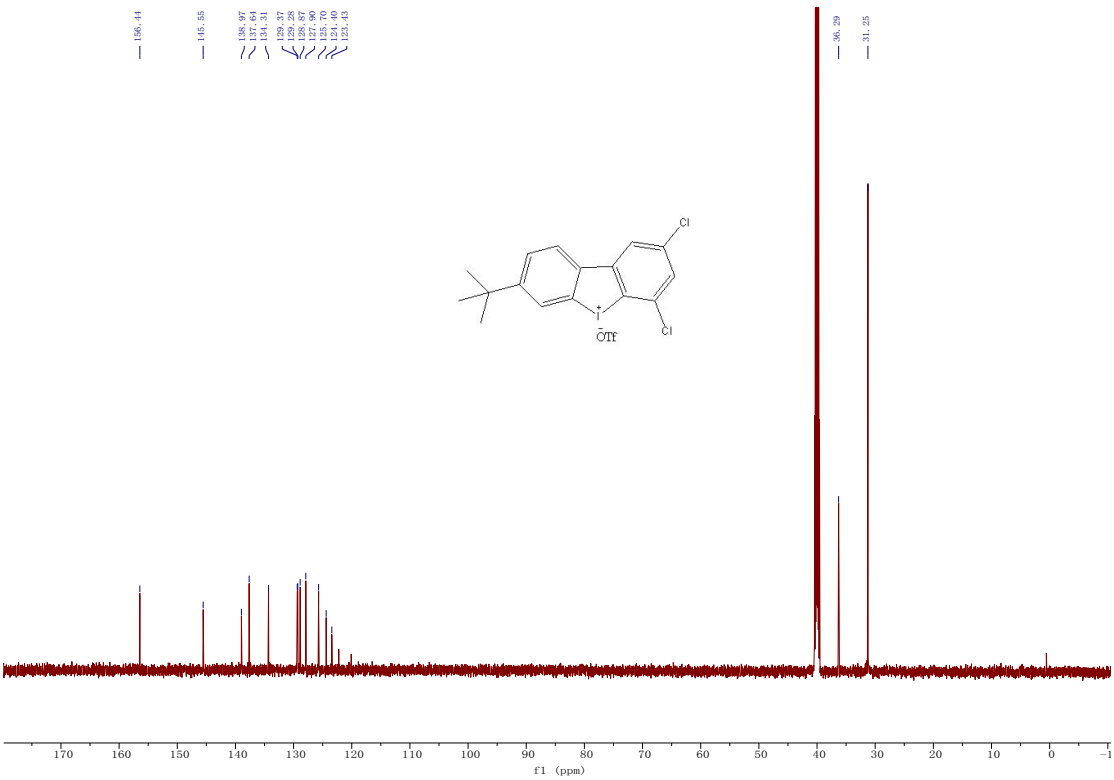


7-(tert-butyl)-2,4-dichlorodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2m)

^{1}H NMR (600 MHz, DMSO-d_6)

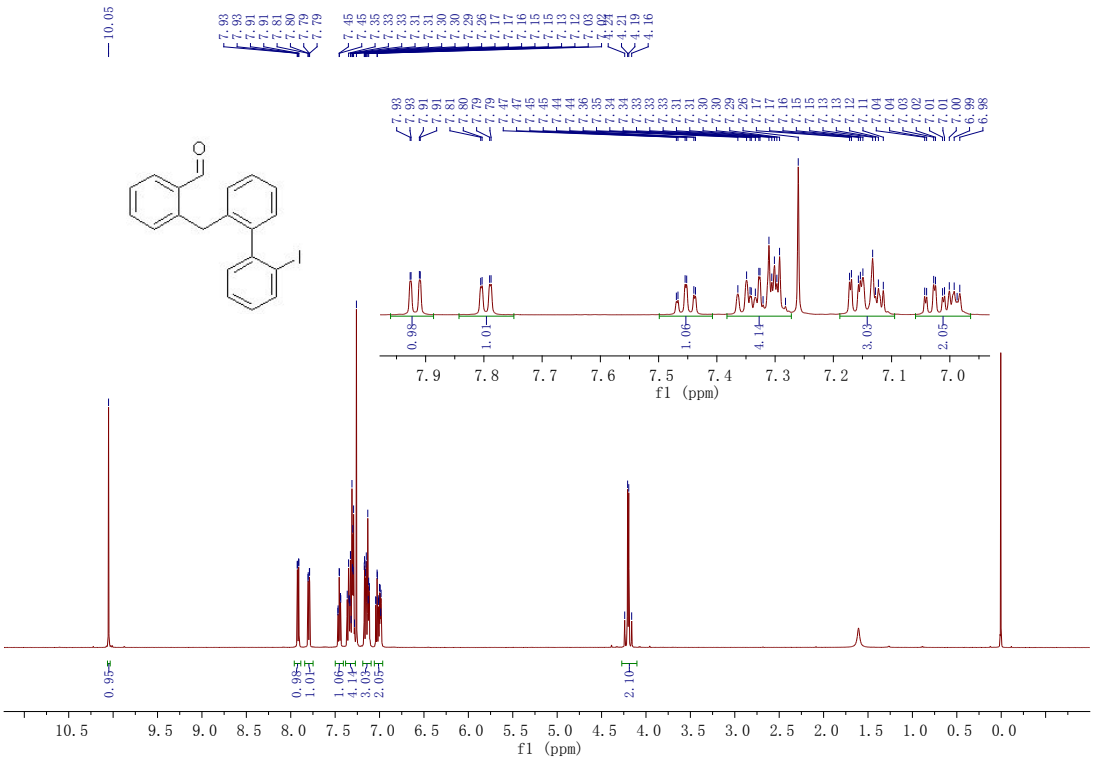


^{13}C NMR (151 MHz, DMSO-d_6)

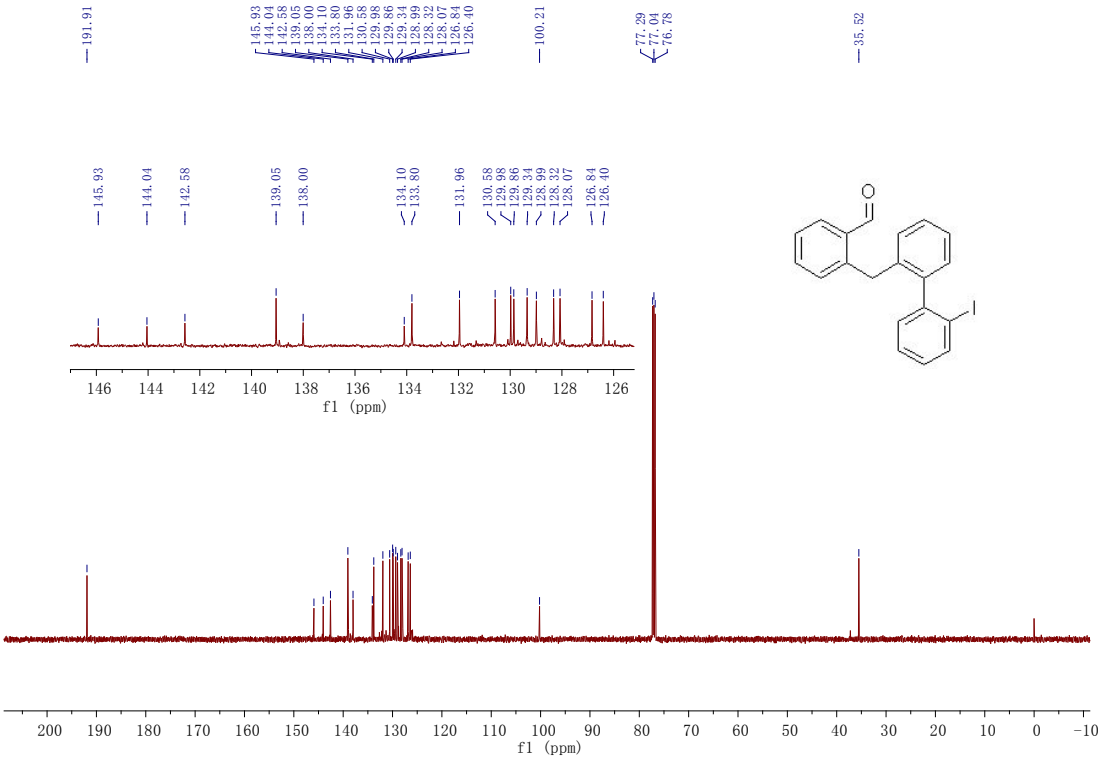


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(3a)

^{1}H NMR (500 MHz, $CDCl_3$)

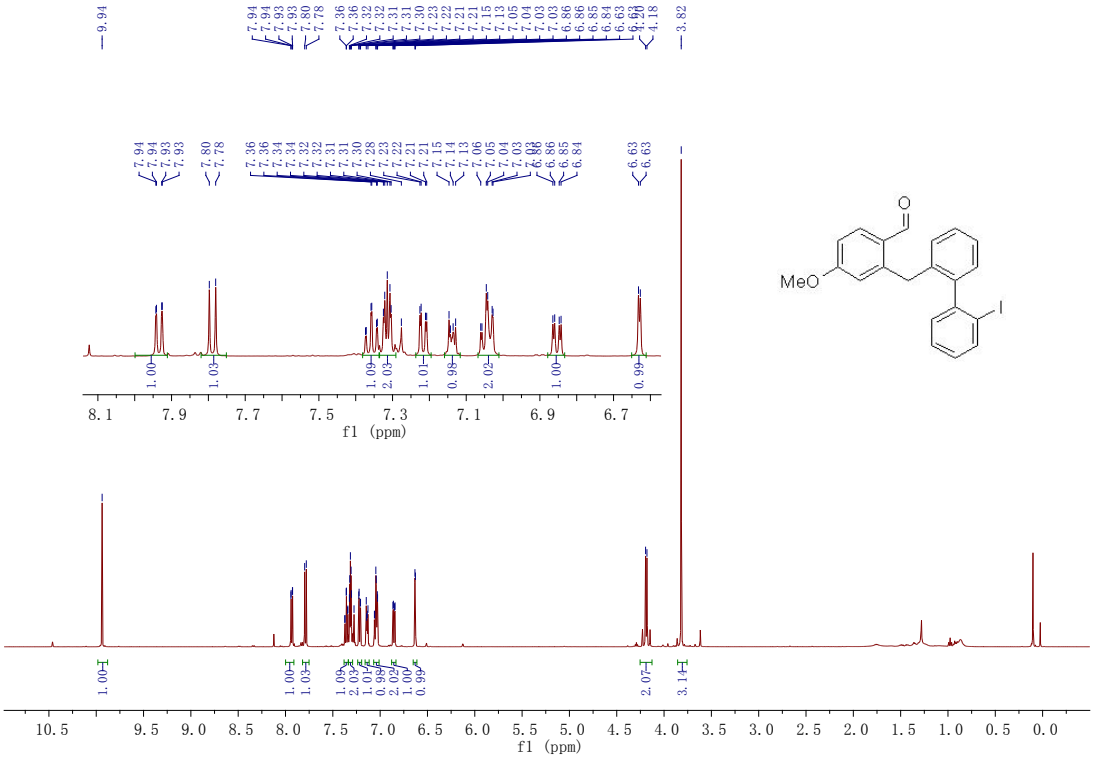


^{13}C NMR (126 MHz, $CDCl_3$)

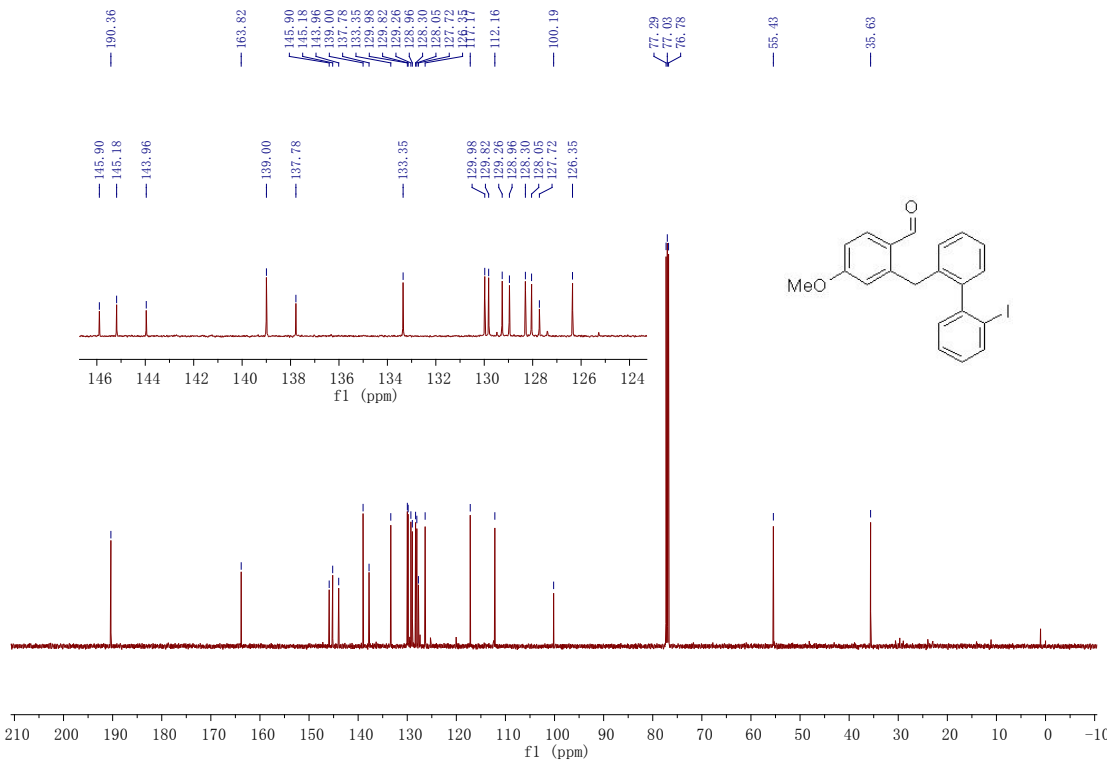


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-methoxybenzaldehyde (3b)

^{1}H NMR (500 MHz, $CDCl_3$)

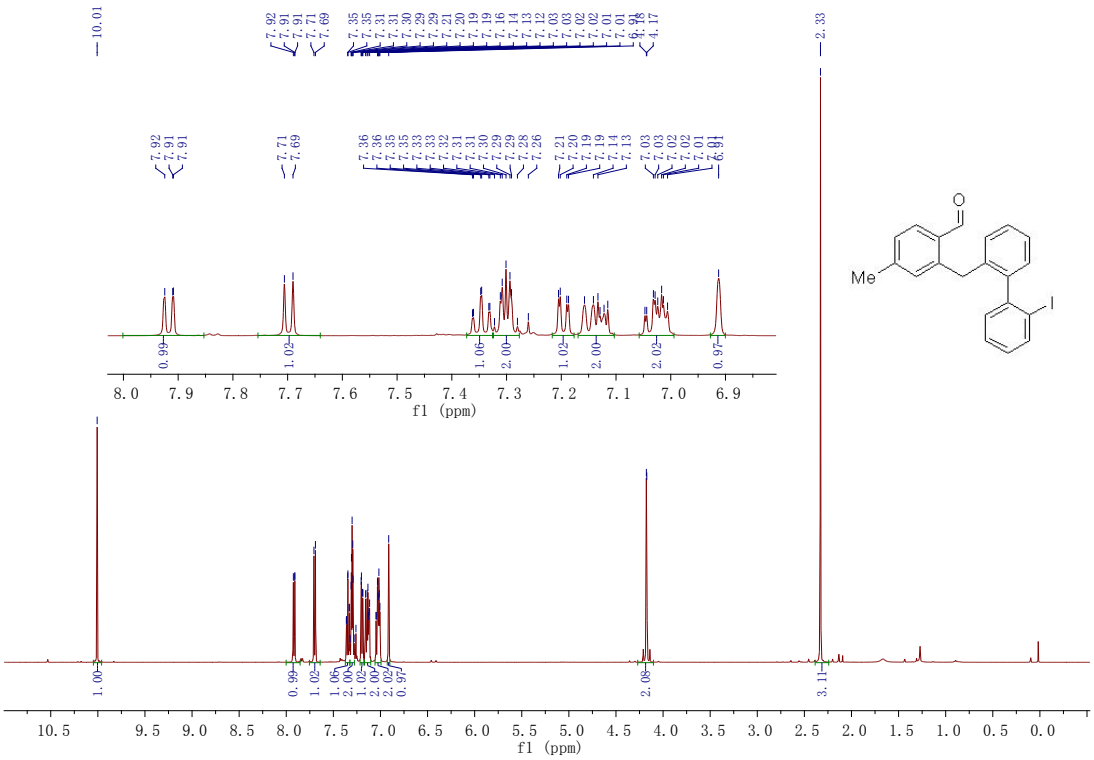


^{13}C NMR (126 MHz, $CDCl_3$)

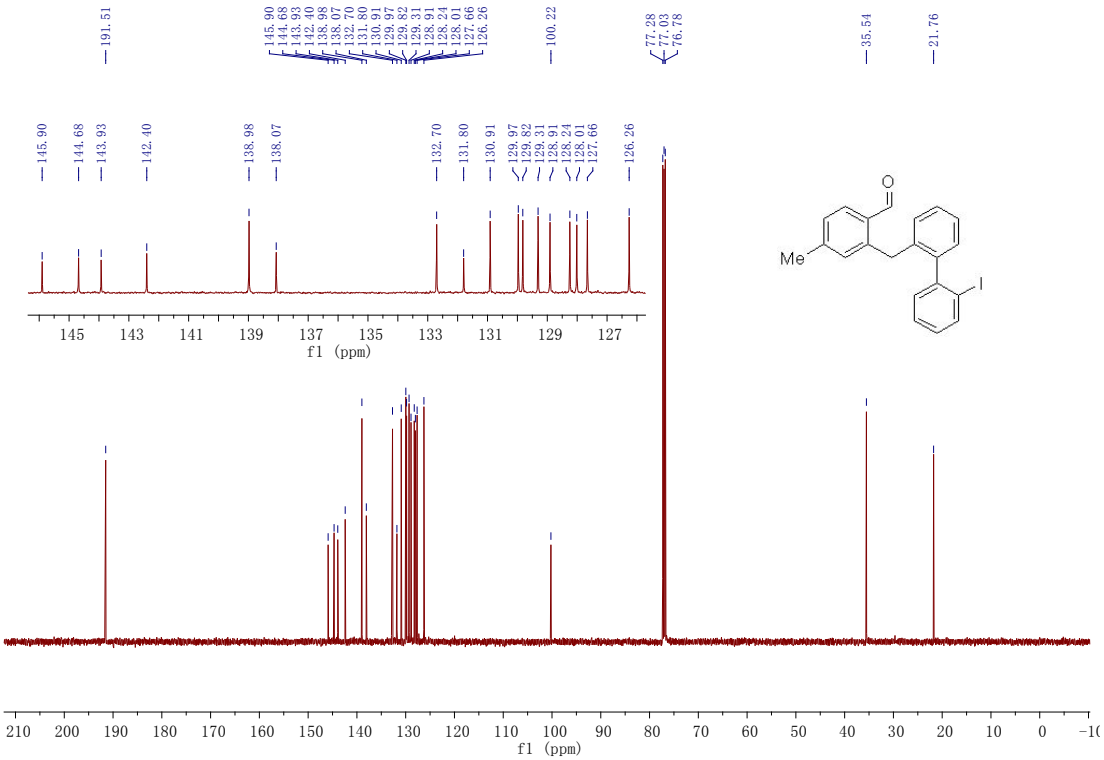


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-methylbenzaldehyde(3c)

^{1}H NMR (500 MHz, $CDCl_3$)

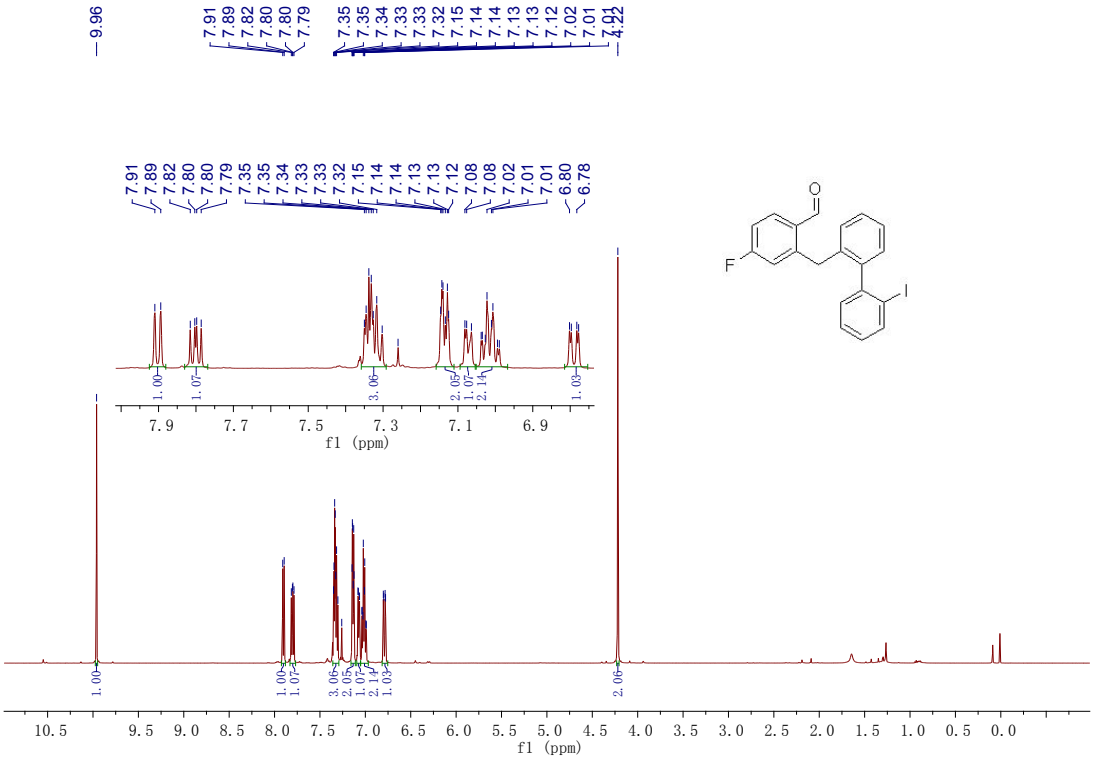


^{13}C NMR (126 MHz, $CDCl_3$)

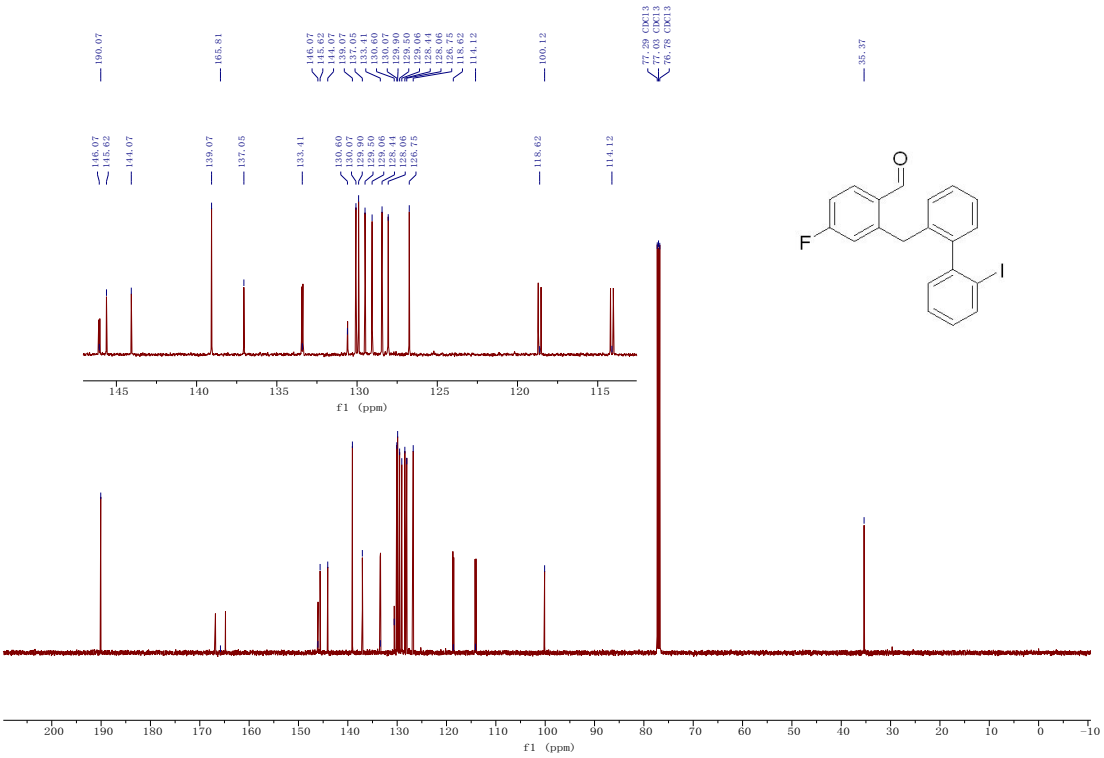


4-fluoro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3d)

^{1}H NMR (500 MHz, $CDCl_3$)

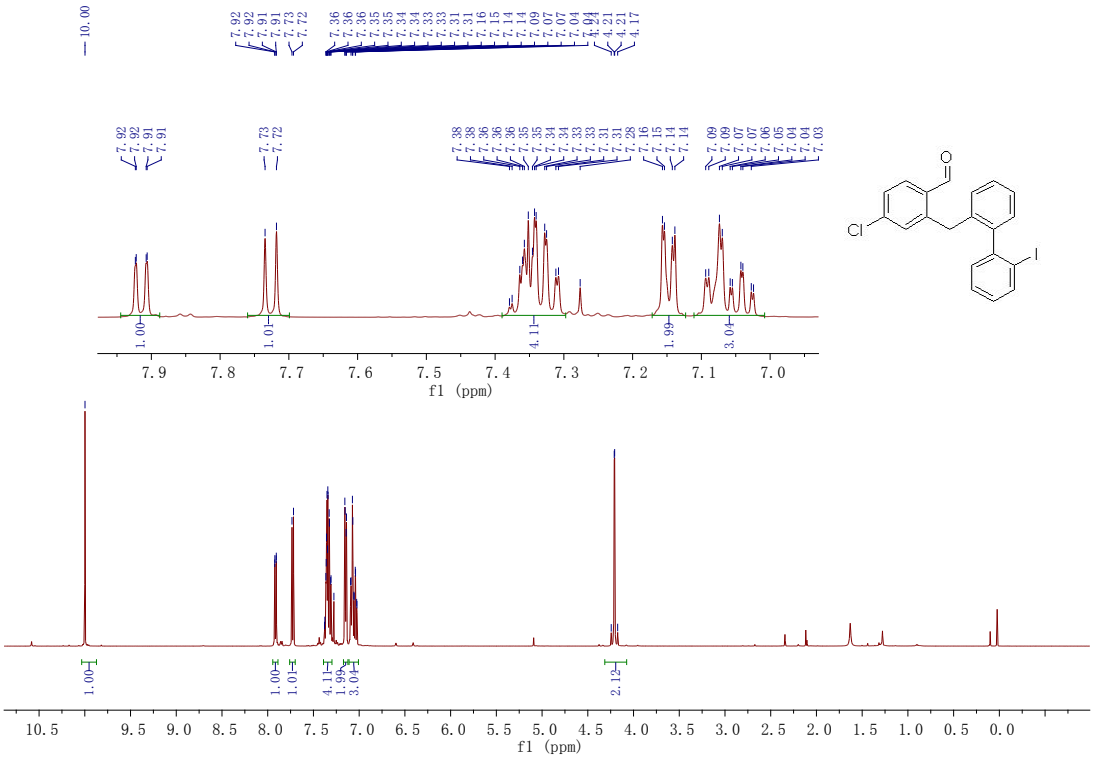


^{13}C NMR (126 MHz, $CDCl_3$)

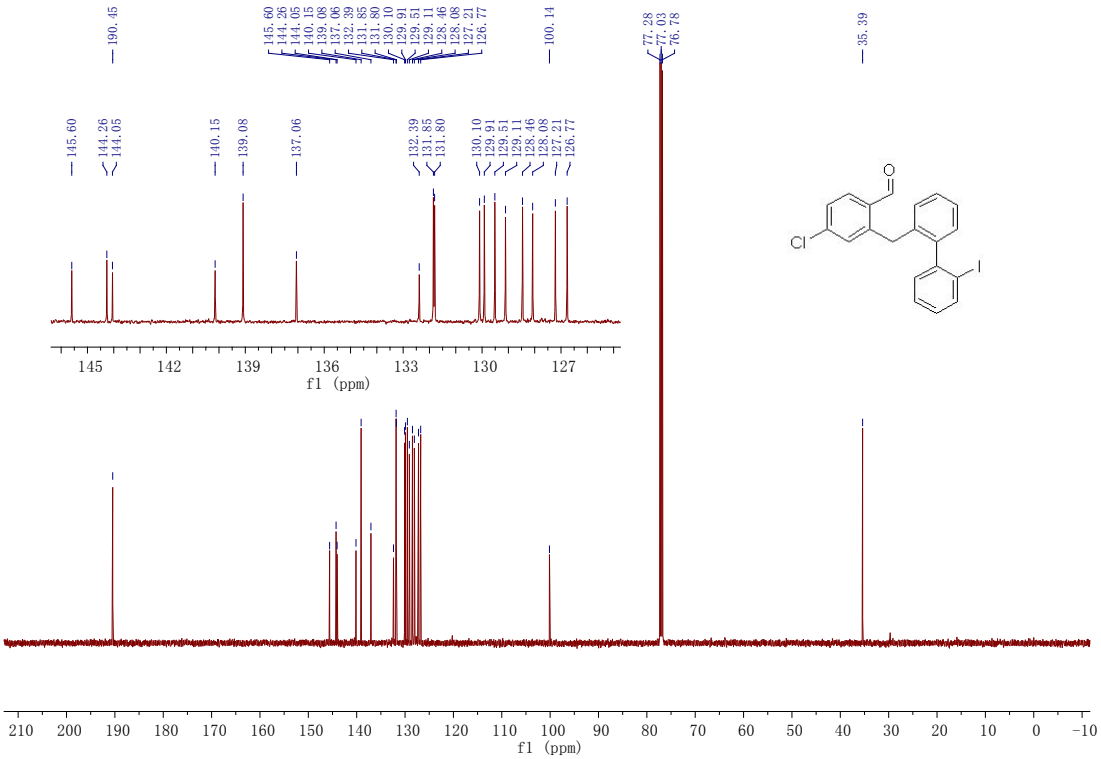


4-chloro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(3e)

^{1}H NMR (500 MHz, $CDCl_3$)

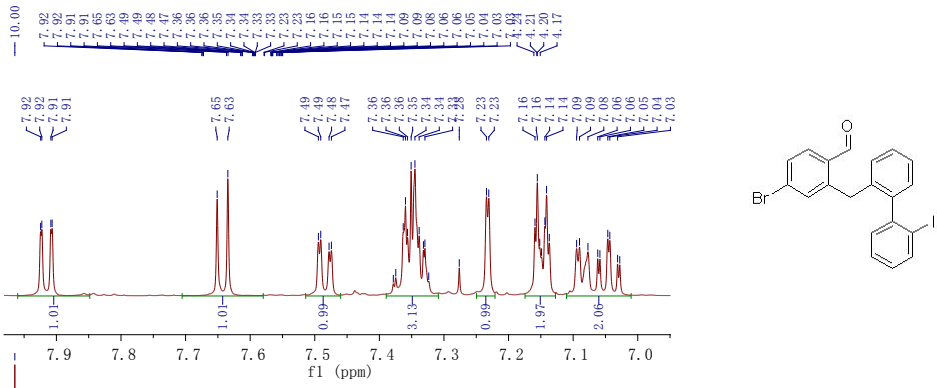


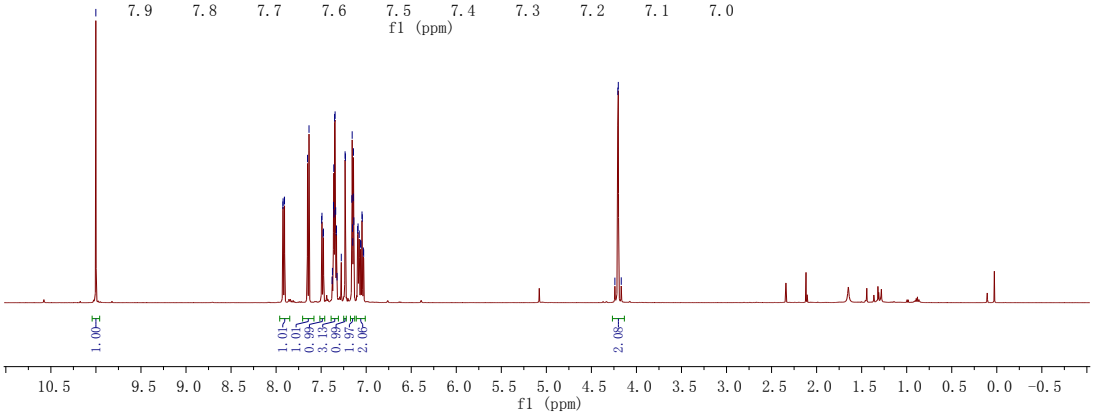
^{13}C NMR (126 MHz, $CDCl_3$)



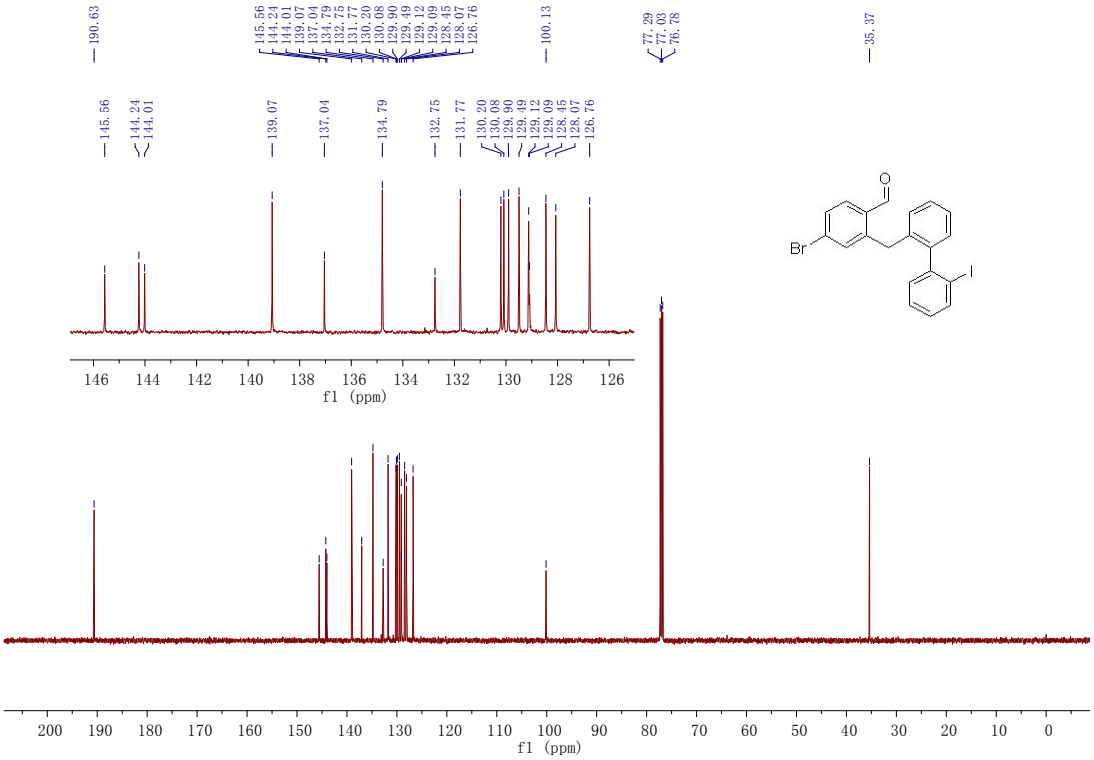
4-bromo-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3f)

^{1}H NMR (500 MHz, $CDCl_3$)



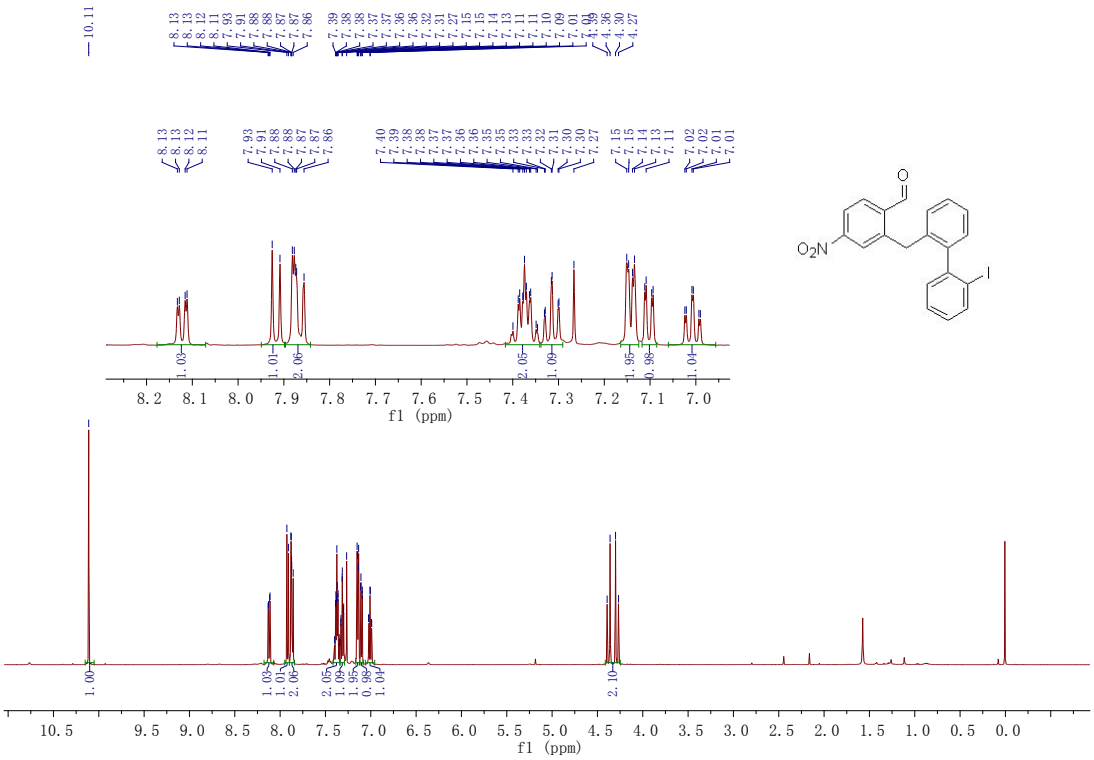


^{13}C NMR (126 MHz, $CDCl_3$)

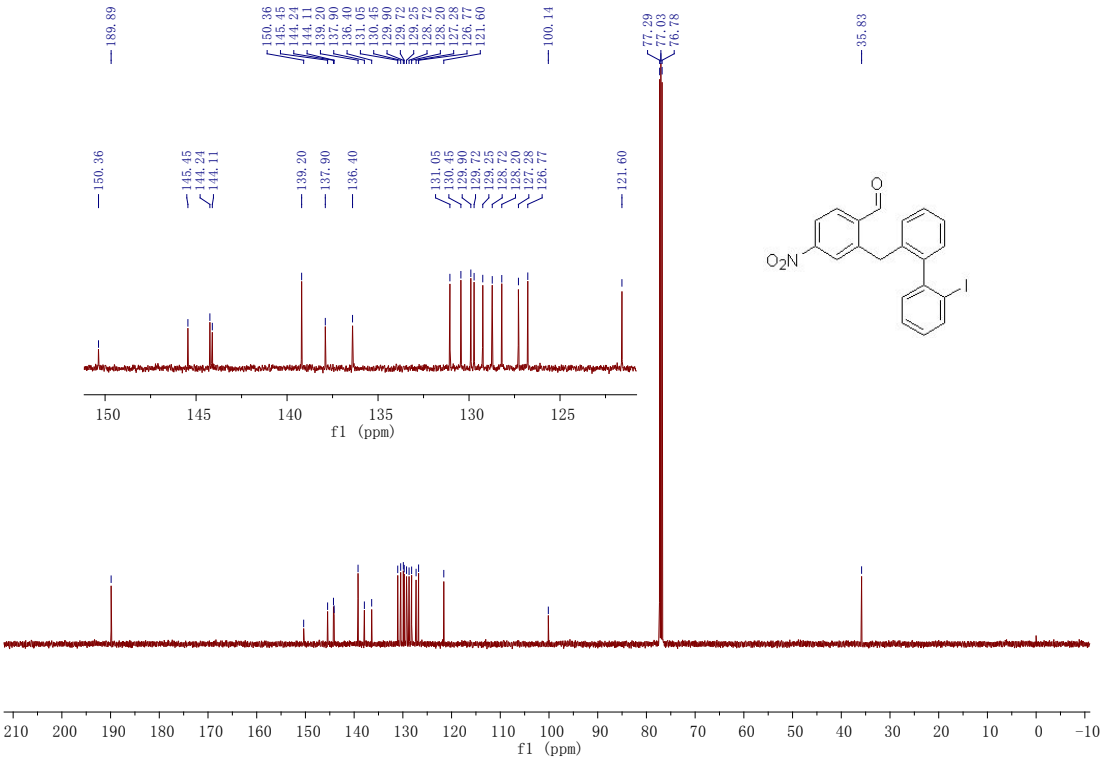


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-4-nitrobenzaldehyde(3g)

^{1}H NMR (500 MHz, $CDCl_3$)

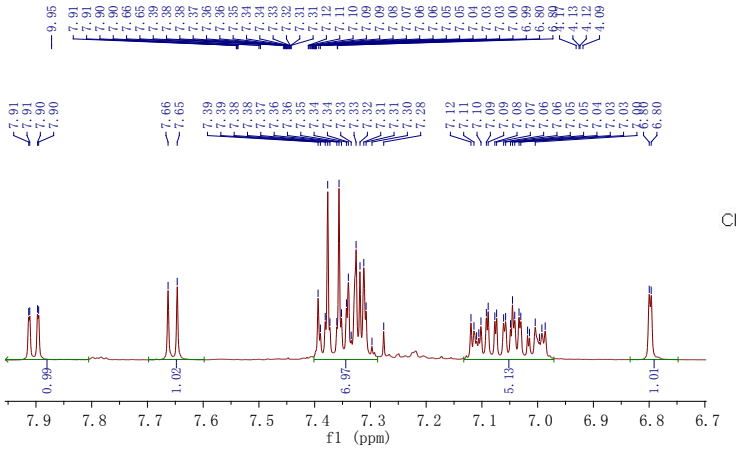


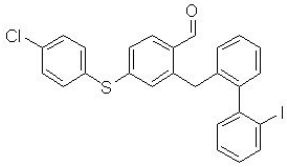
^{13}C NMR (126 MHz, $CDCl_3$)

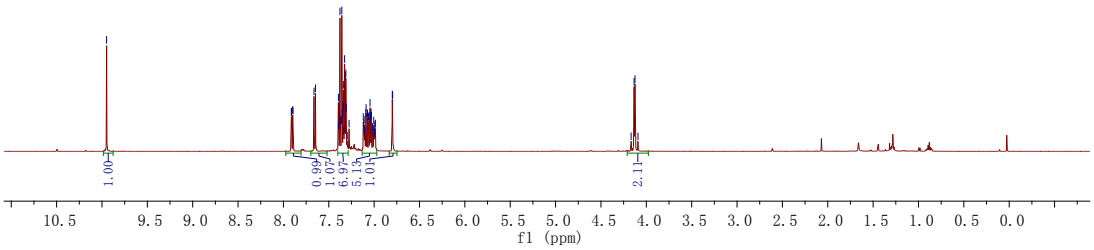


4-((4-chlorophenyl)thio)-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(3h)

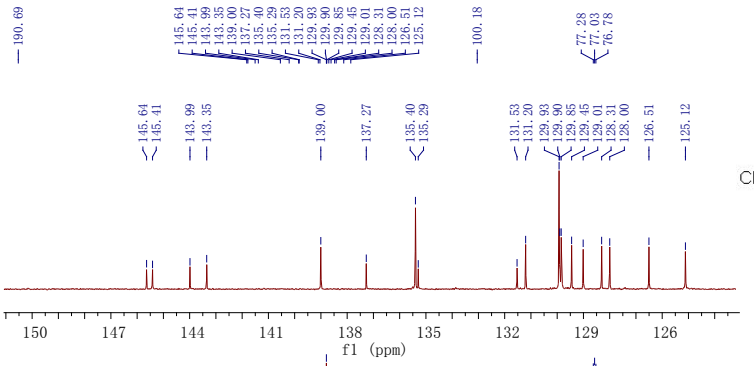
^{1}H NMR (500 MHz, $CDCl_3$)

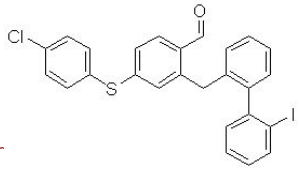


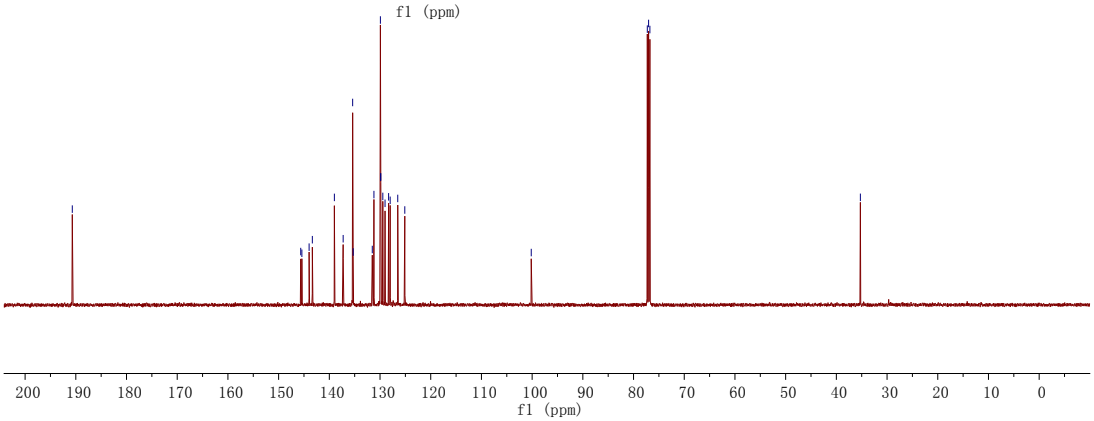




^{13}C NMR (126 MHz, $CDCl_3$)

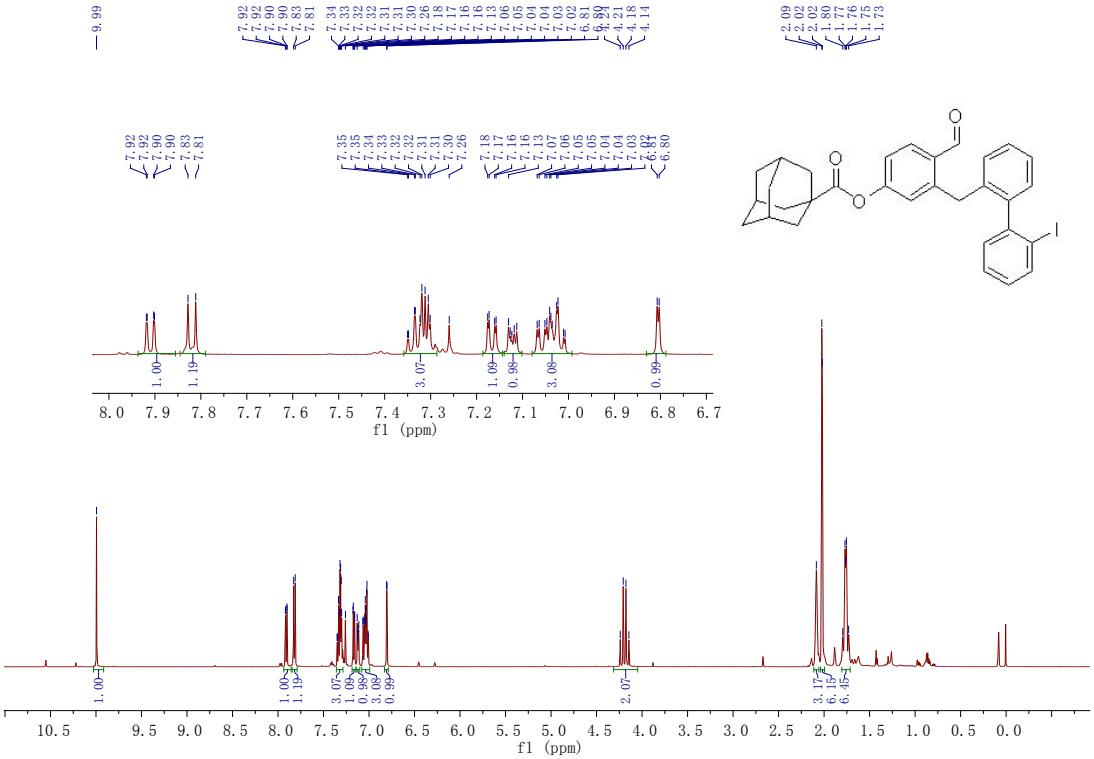




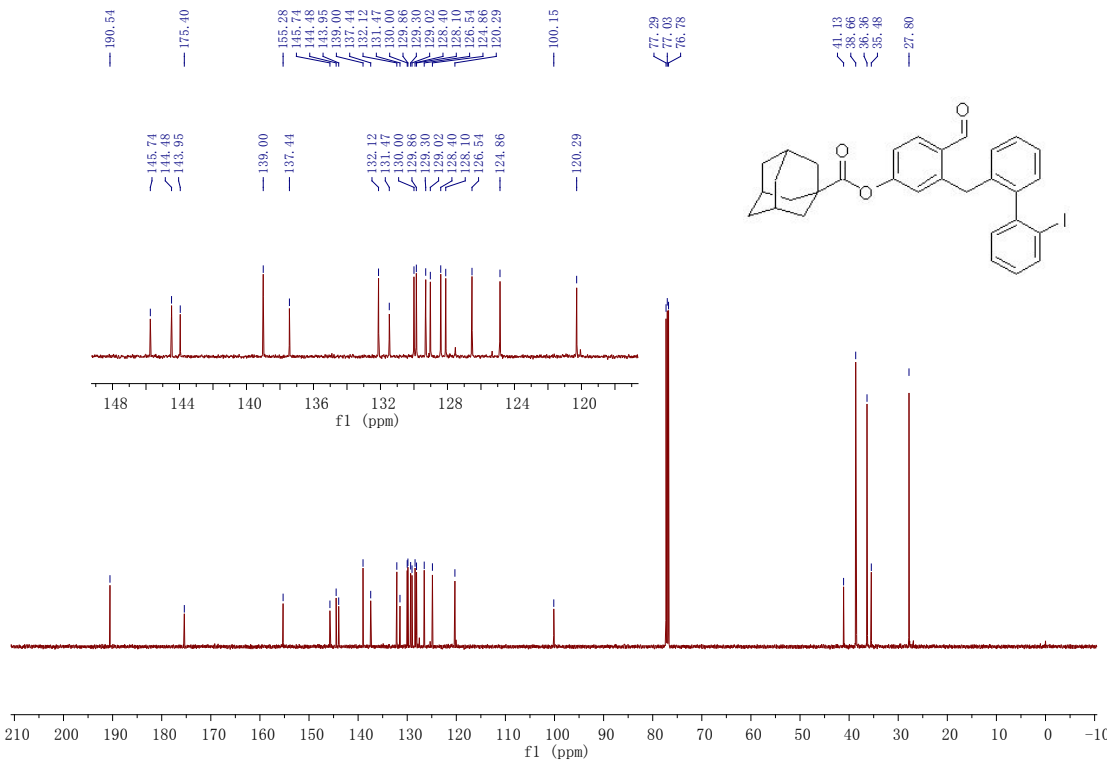


4-formyl-3-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl(3r,5r,7r)-adamantane-1-carboxylate(3i)

^{1}H NMR (500 MHz, $CDCl_3$)

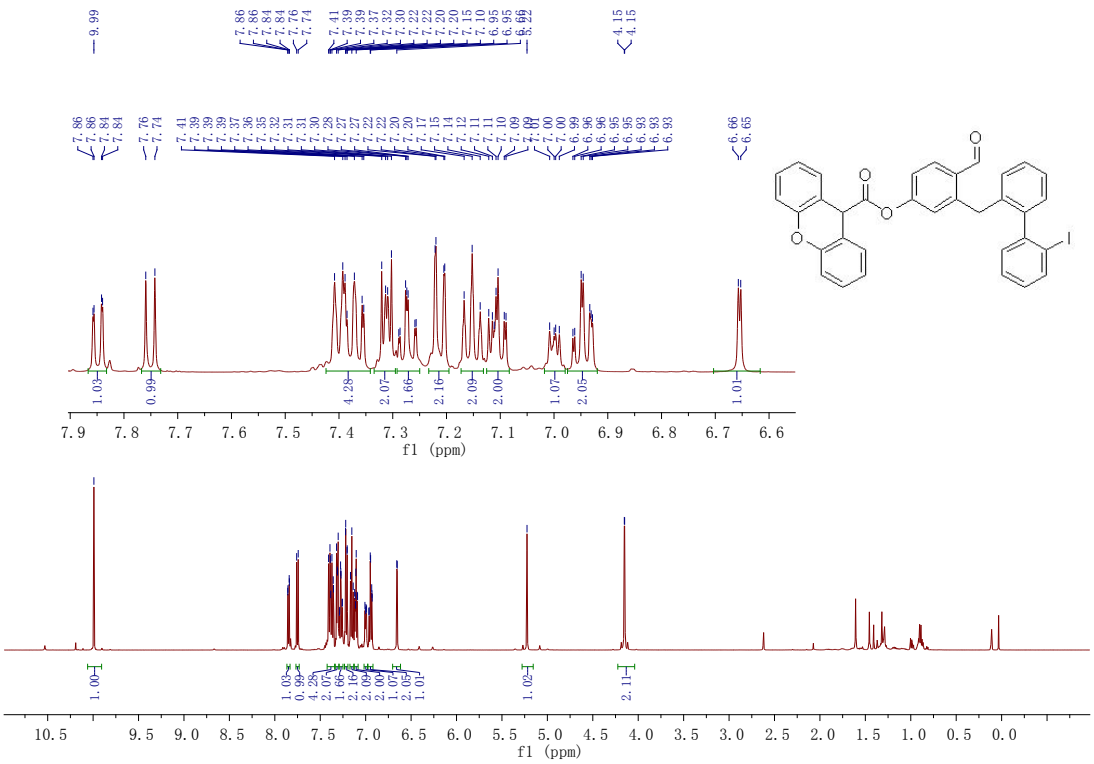


^{13}C NMR (126 MHz, $CDCl_3$)

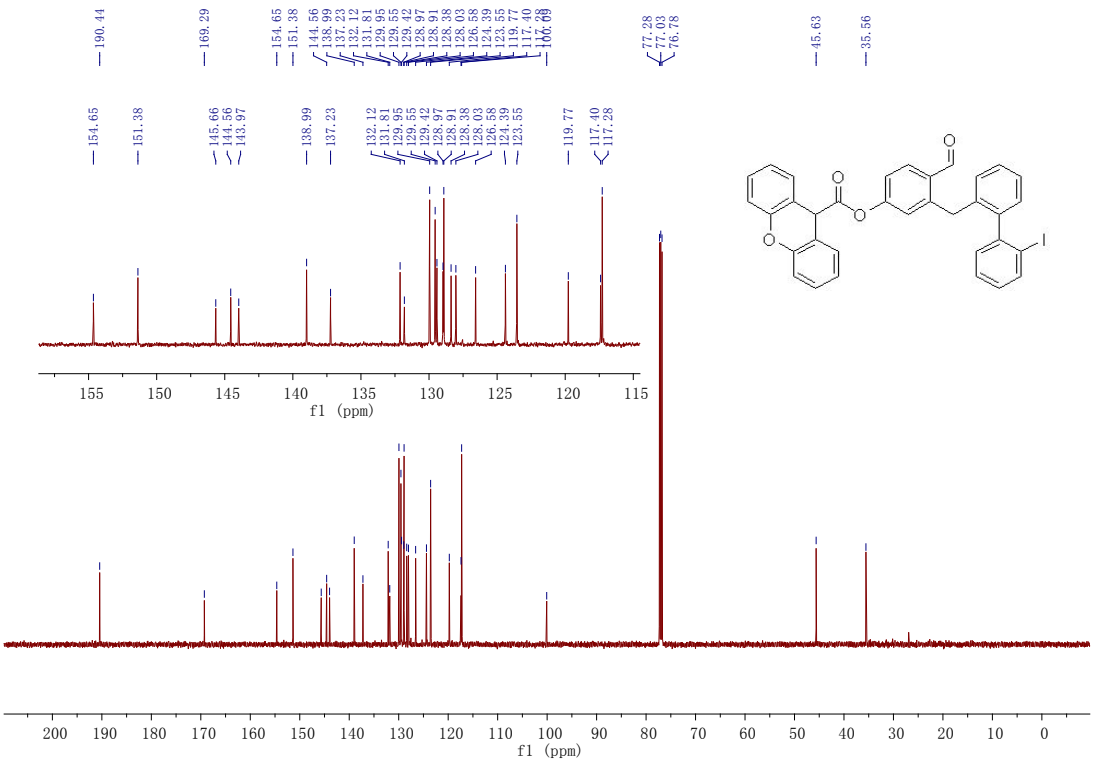


4-formyl-3-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl 9*H*-xanthene-9-carboxylate(3j)

^{1}H NMR (500 MHz, $CDCl_3$)

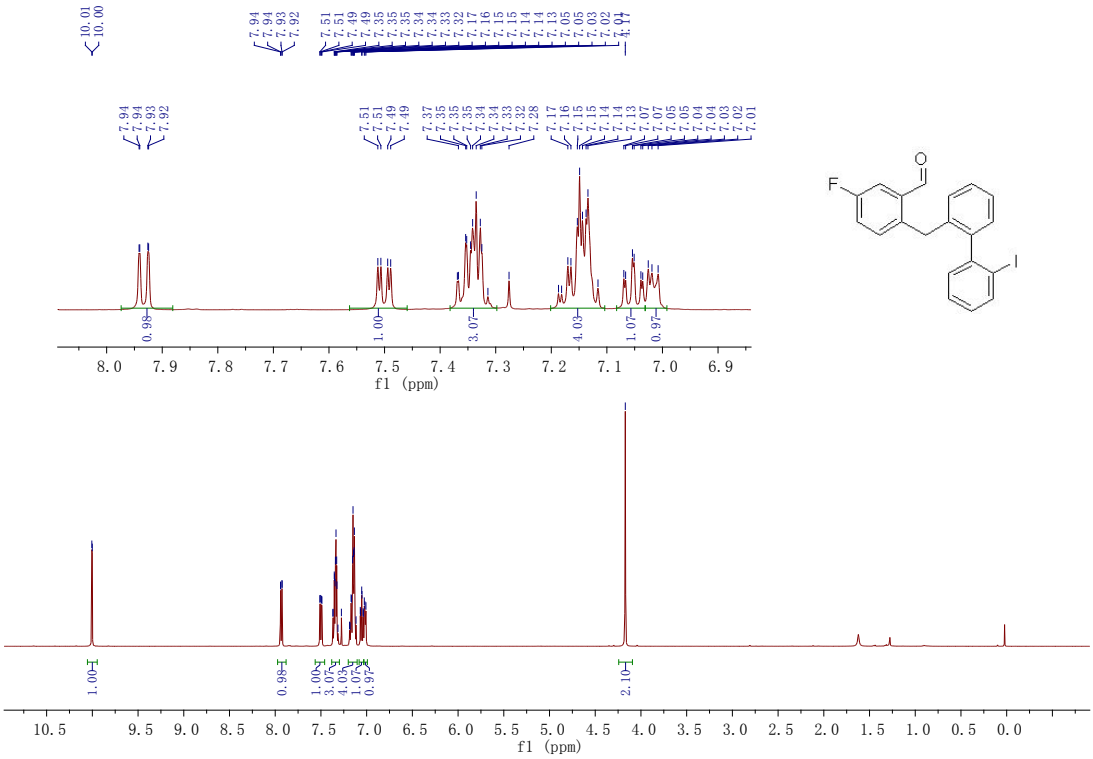


^{13}C NMR (126 MHz, $CDCl_3$)

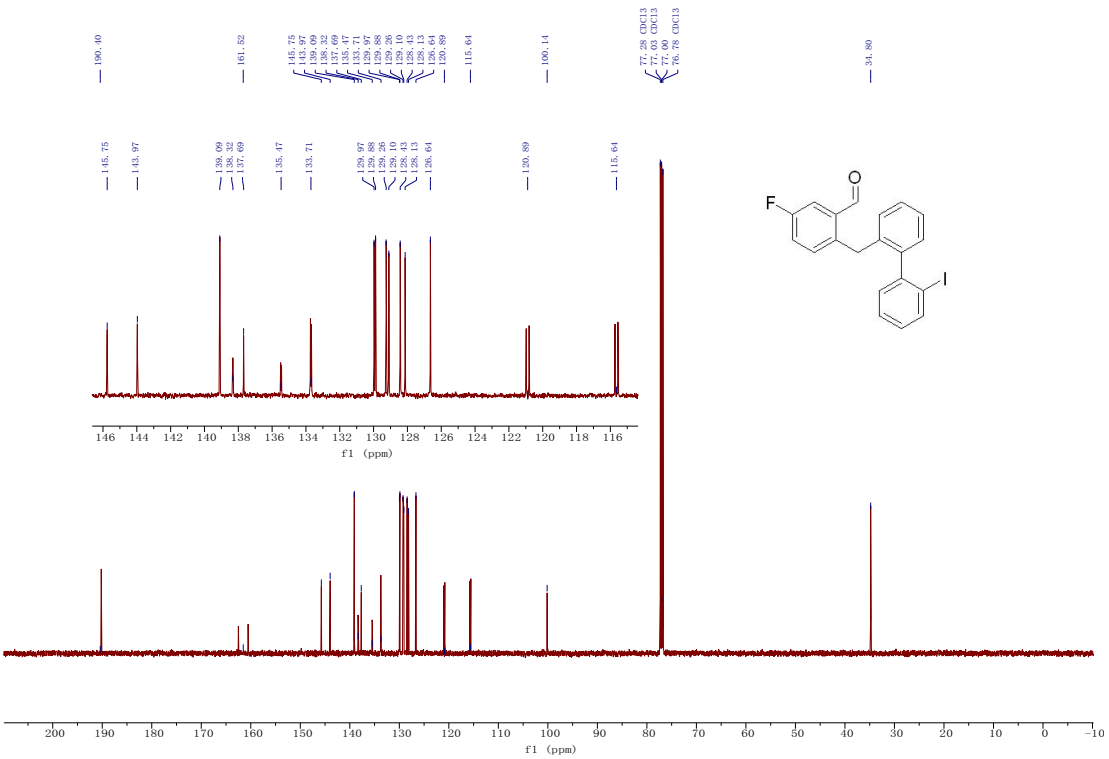


5-fluoro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(3k)

^{1}H NMR (500 MHz, $CDCl_3$)

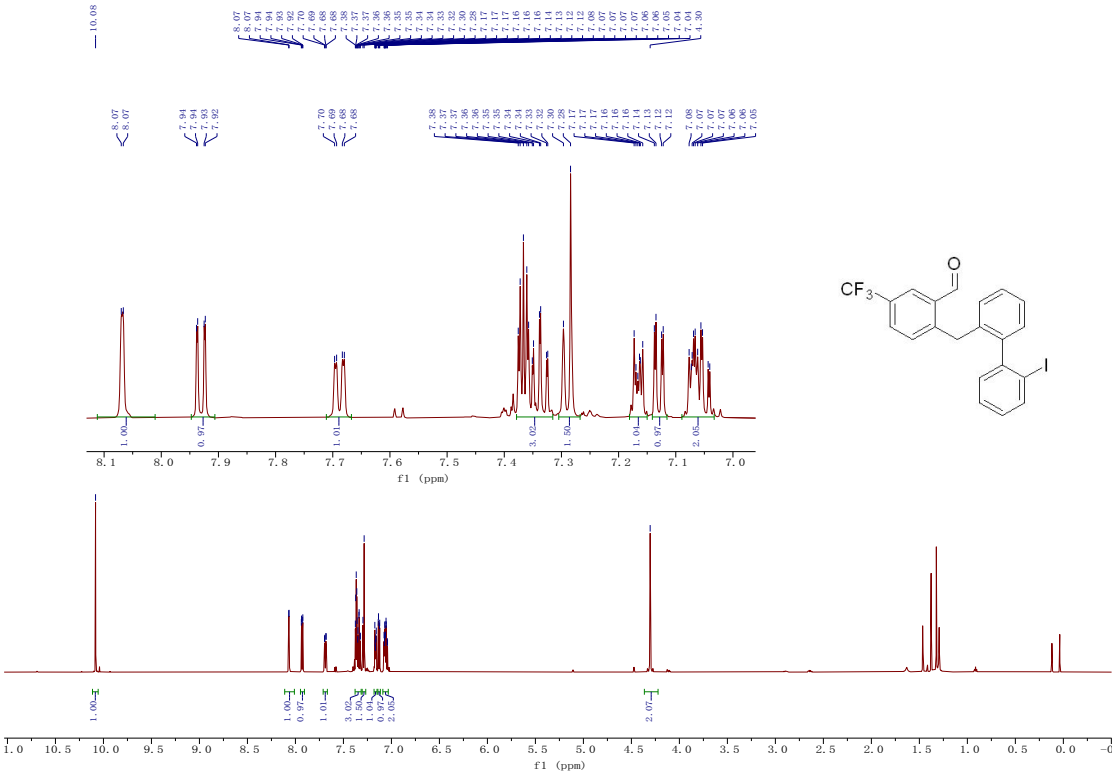


^{13}C NMR (126 MHz, $CDCl_3$)

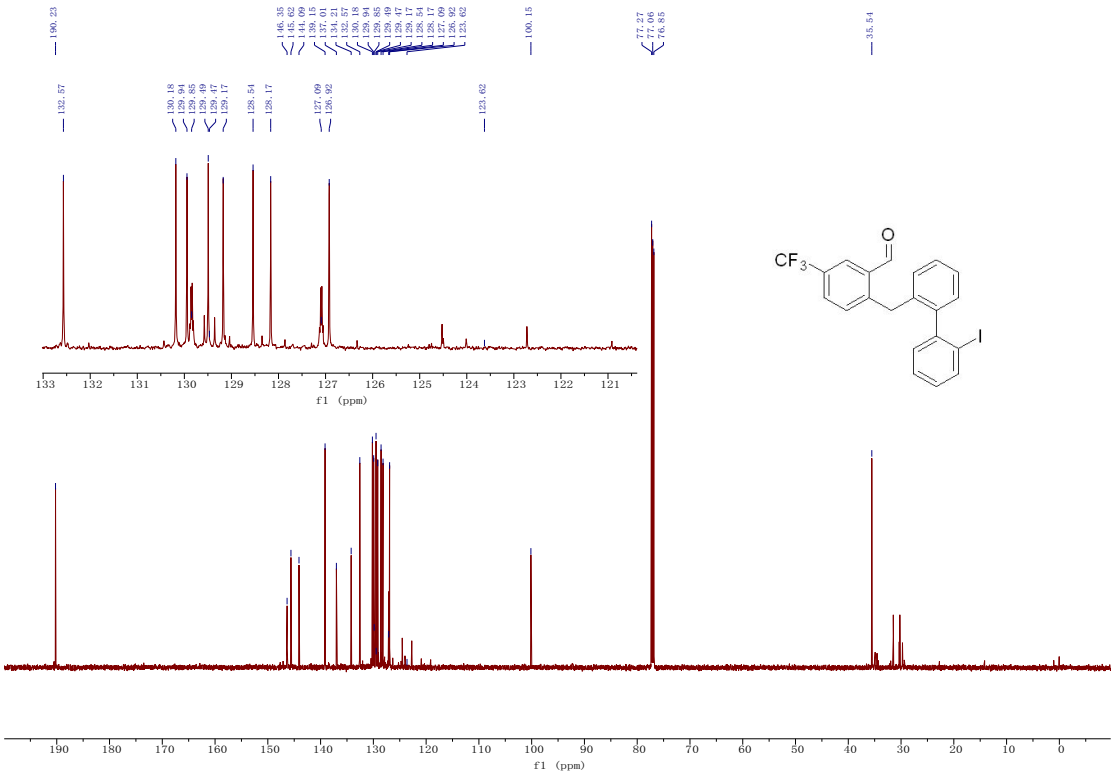


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-5-(trifluoromethyl)benzaldehyde (3l)

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

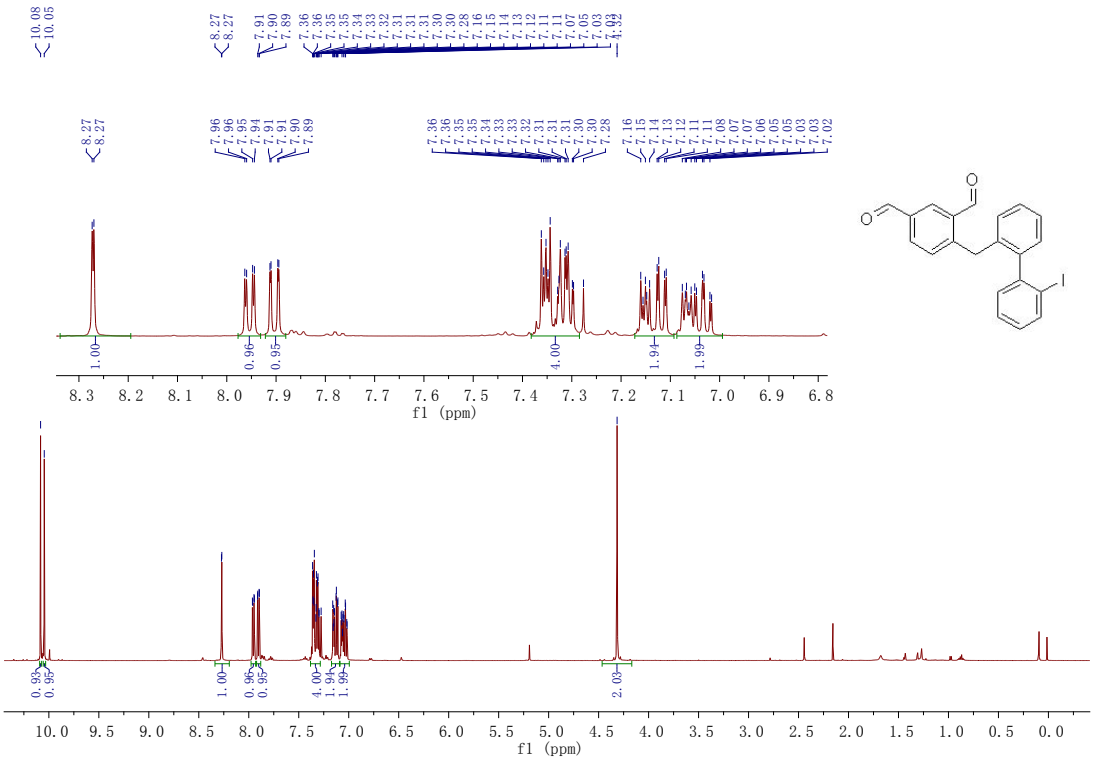


^{13}C NMR (151 MHz, $CDCl_3$)

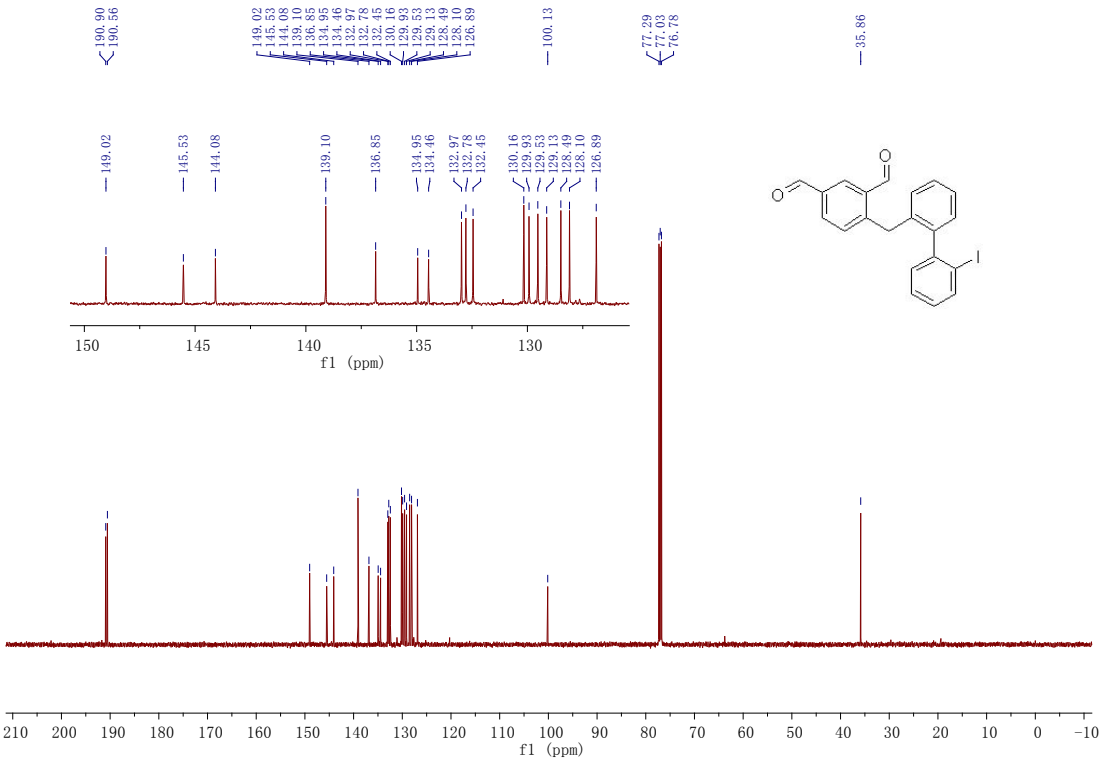


4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)isophthalaldehyde (3m)

^{1}H NMR (500 MHz, $CDCl_3$)

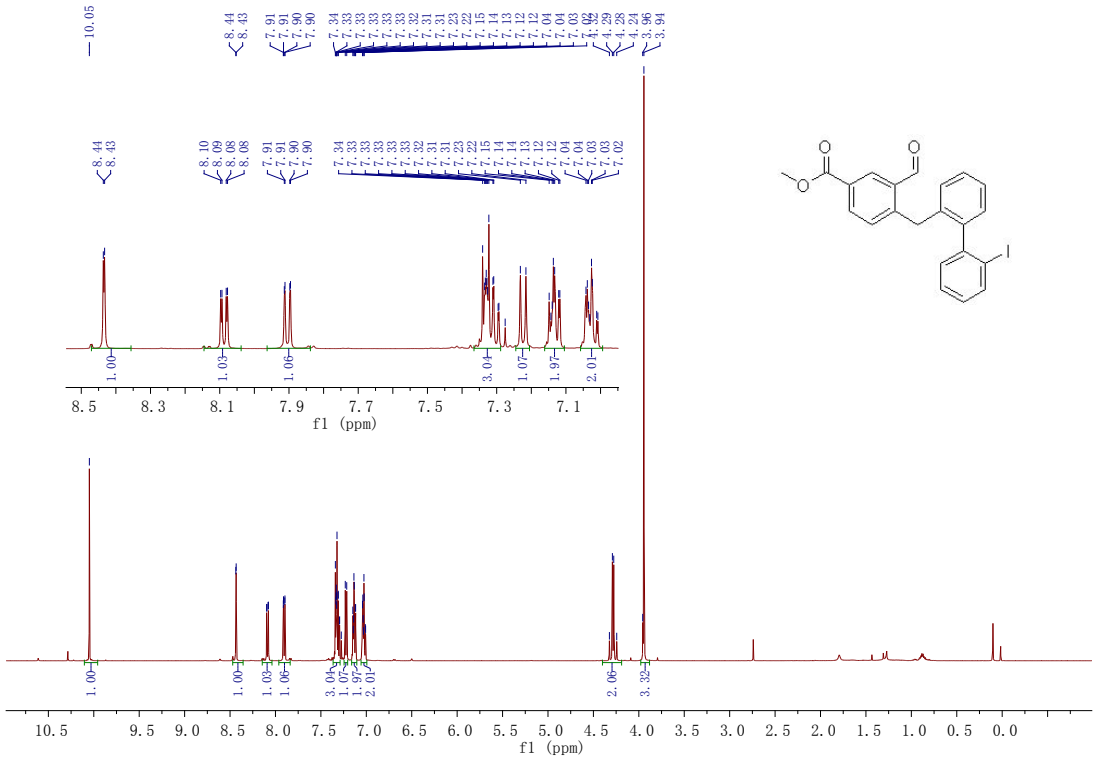


^{13}C NMR (126 MHz, $CDCl_3$)

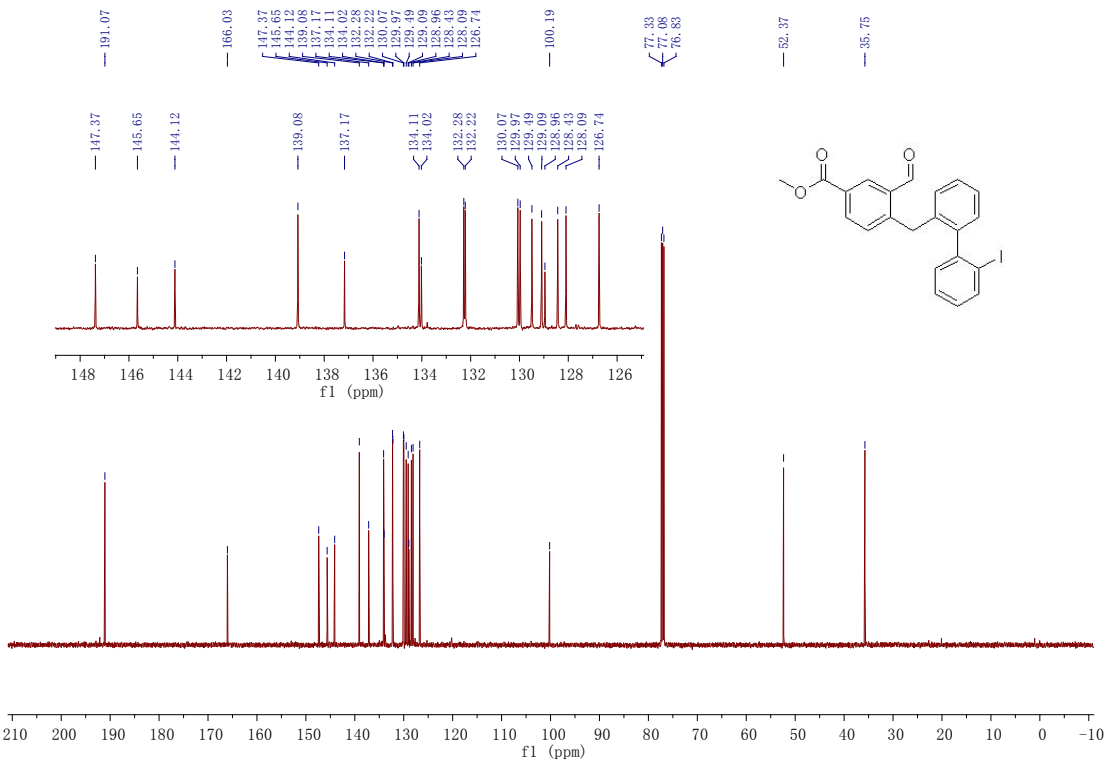


Methyl-3-formyl-4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzoate(3n)

^{1}H NMR (500 MHz, $CDCl_3$)

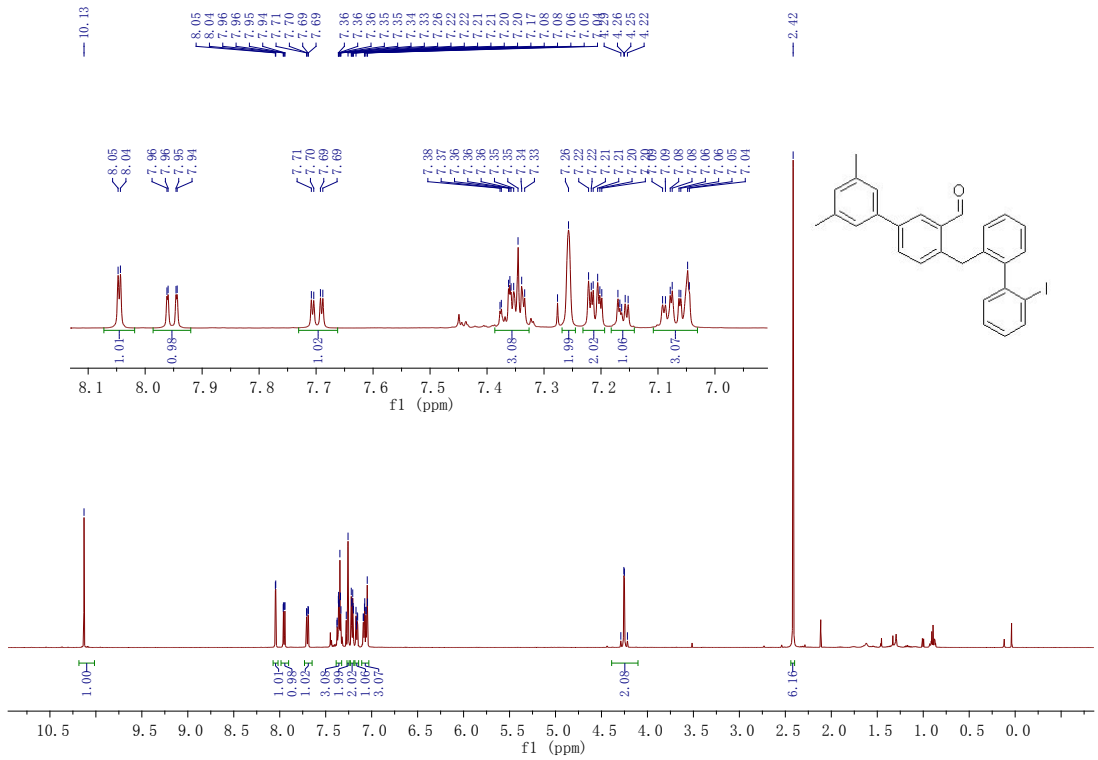


^{13}C NMR (126 MHz, $CDCl_3$)

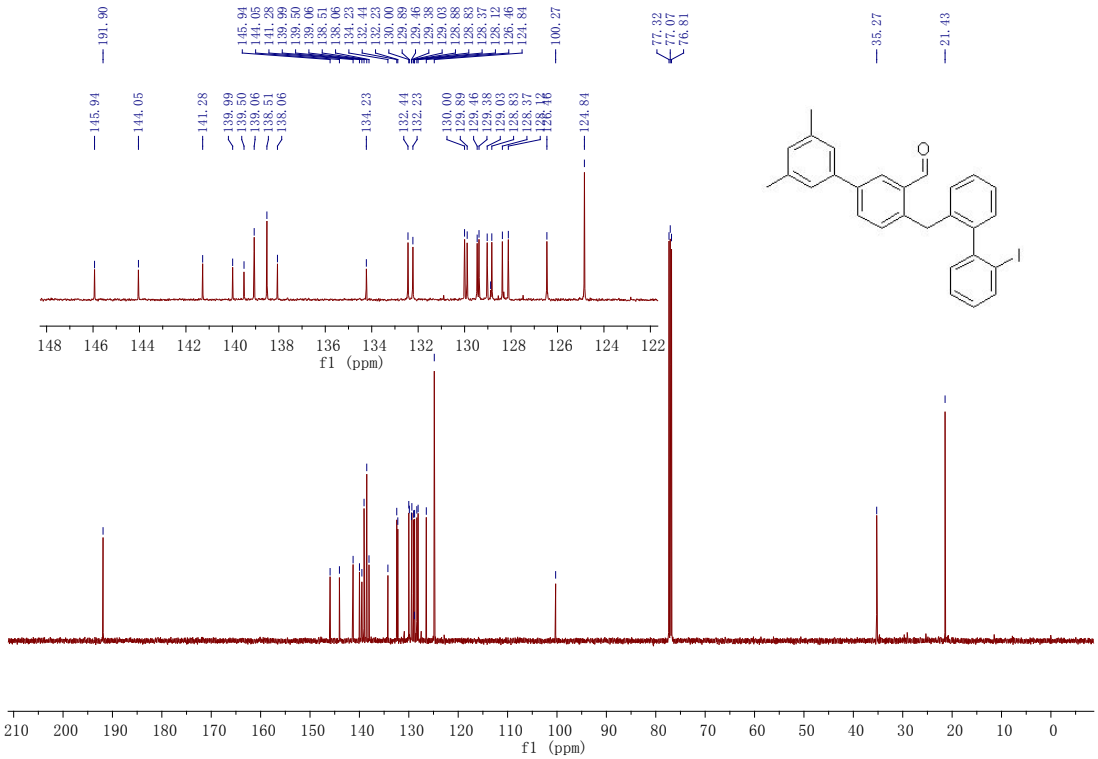


4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-3',5'-dimethyl-[1,1'-biphenyl]-3-carbaldehyde(3o)

^{1}H NMR (500 MHz, $CDCl_3$)

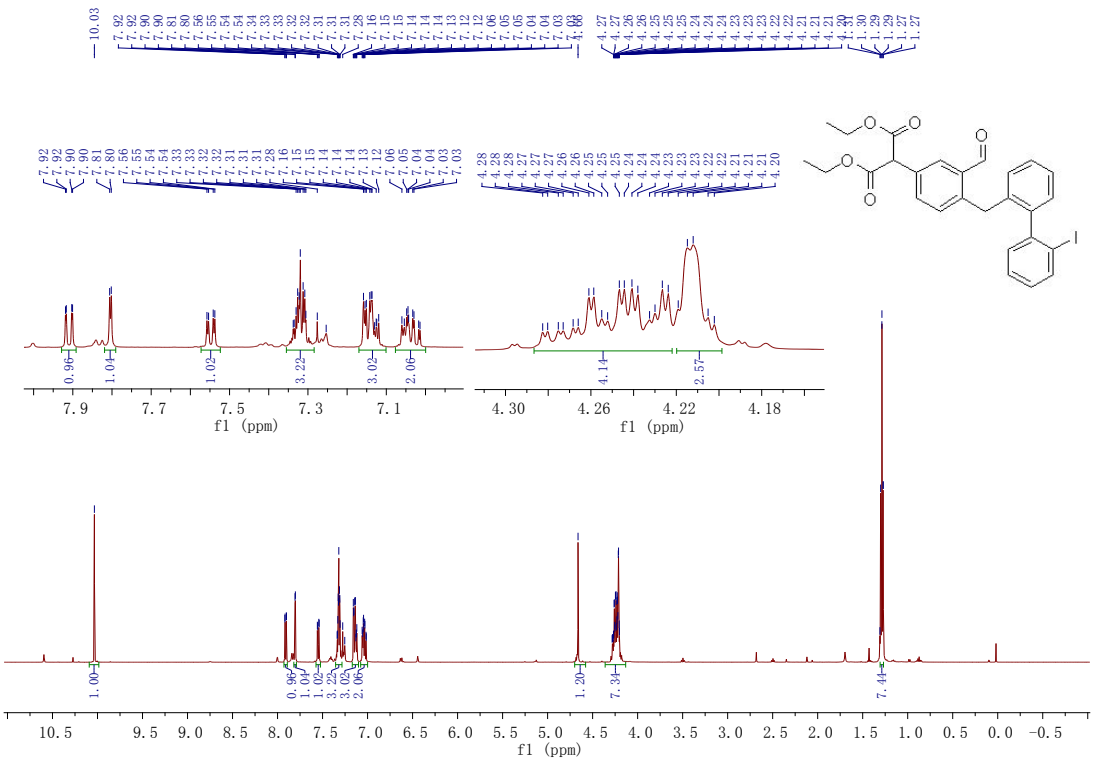


^{13}C NMR (126 MHz, $CDCl_3$)

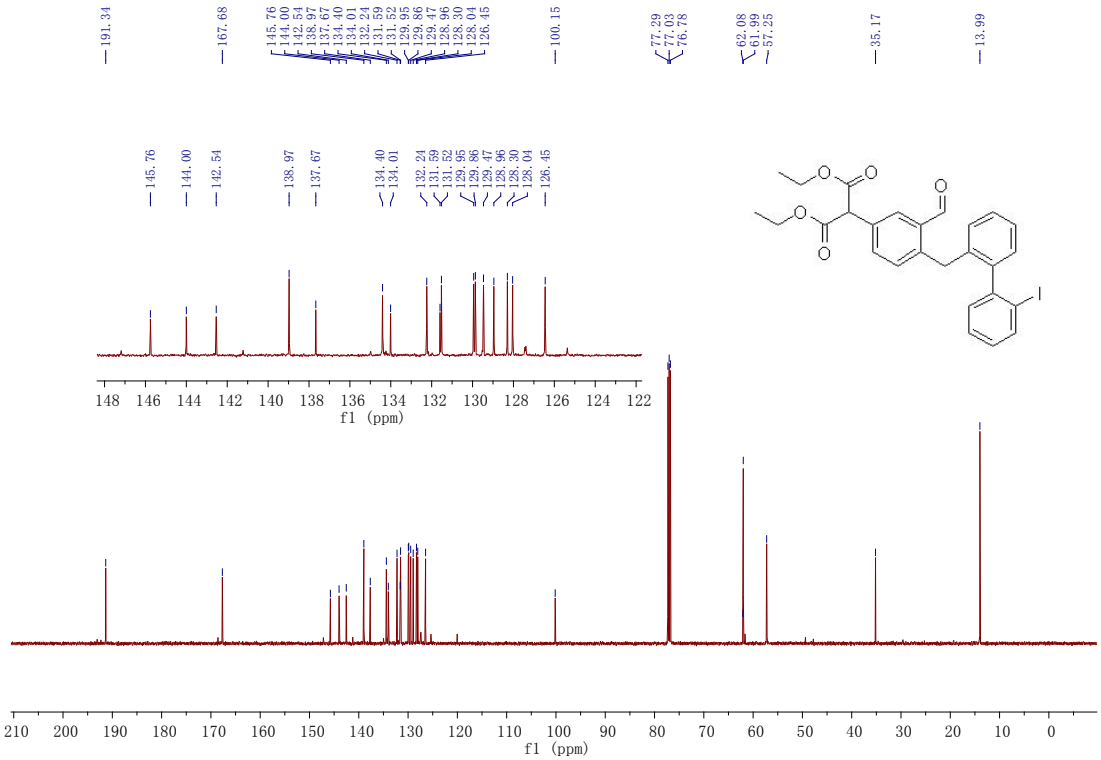


Diethyl-2-(3-formyl-4-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)malonate(3p)

^{1}H NMR (500 MHz, $CDCl_3$)

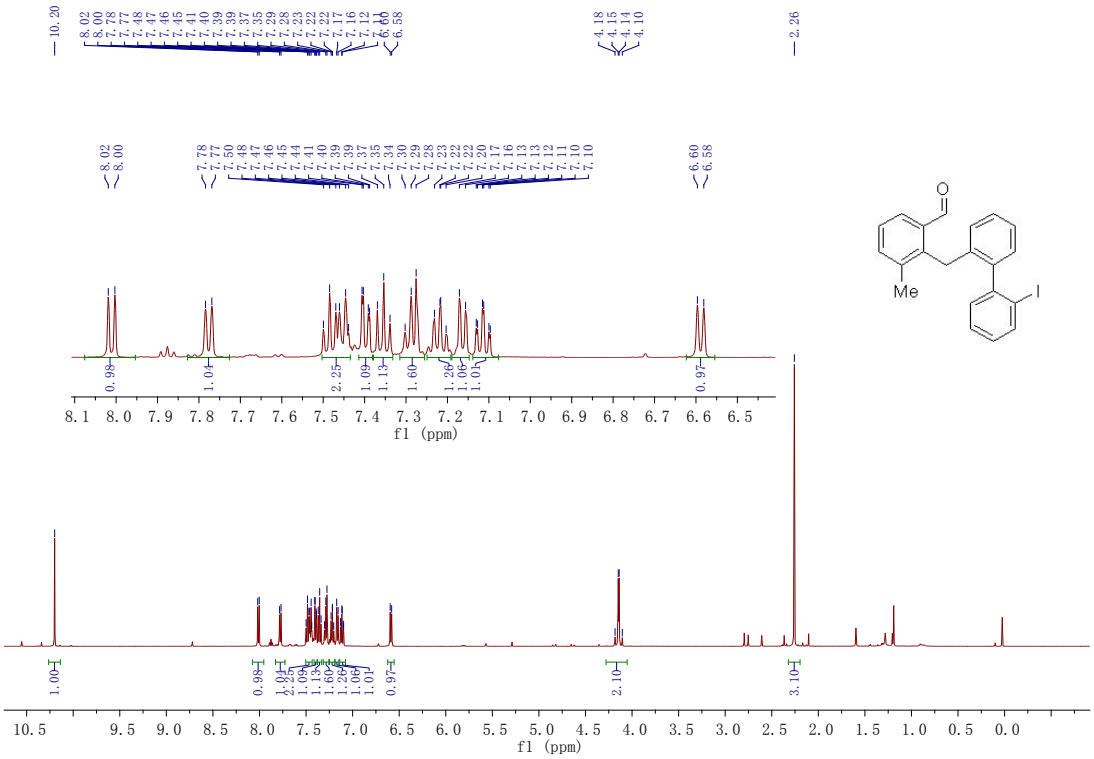


^{13}C NMR (126 MHz, $CDCl_3$)

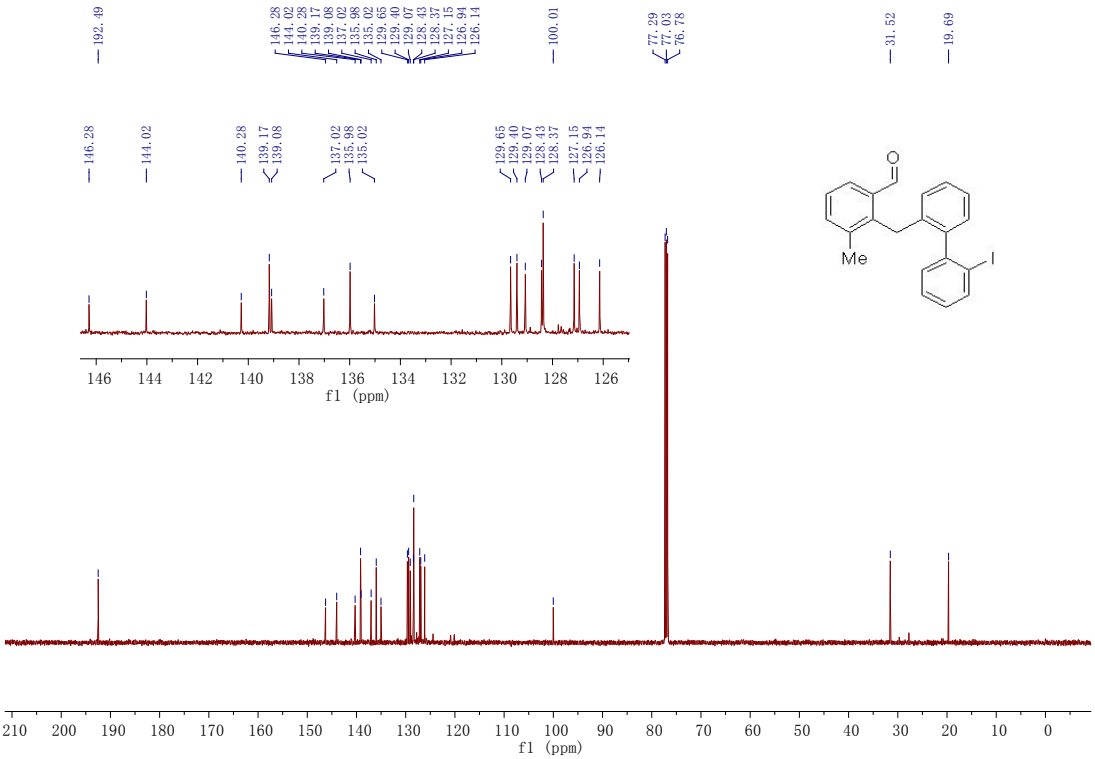


2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)-3-methylbenzaldehyde(3q)

^{1}H NMR (500 MHz, $CDCl_3$)

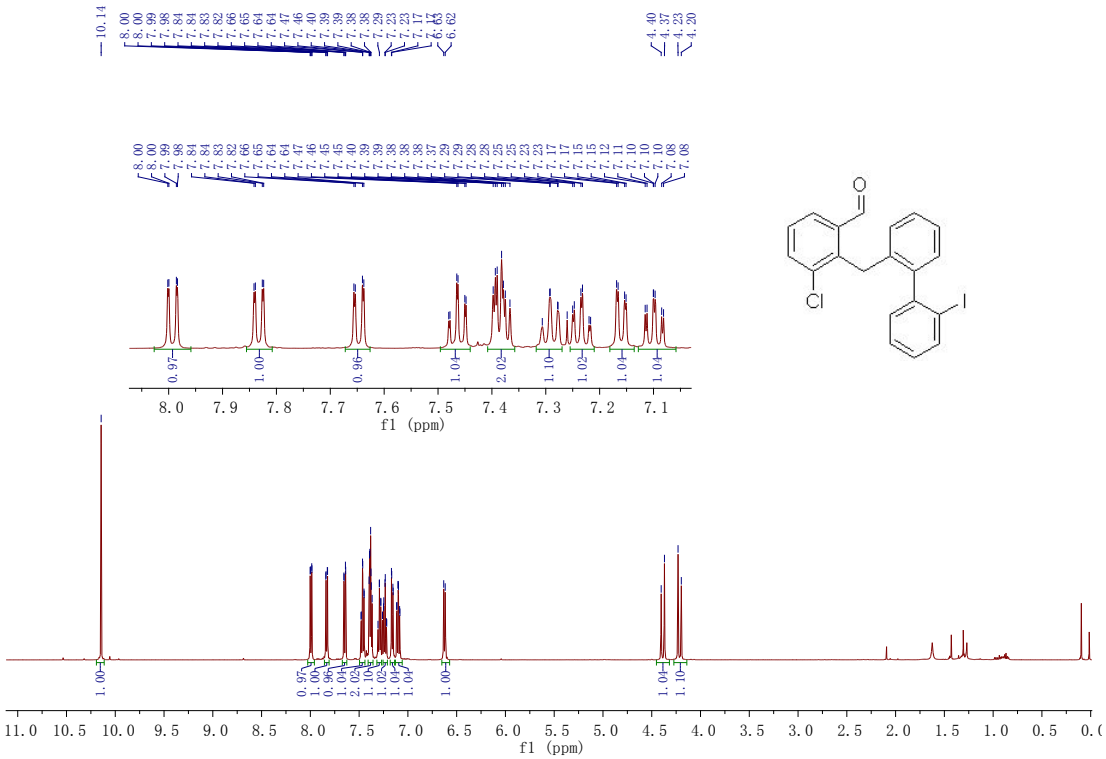


^{13}C NMR (126 MHz, $CDCl_3$)

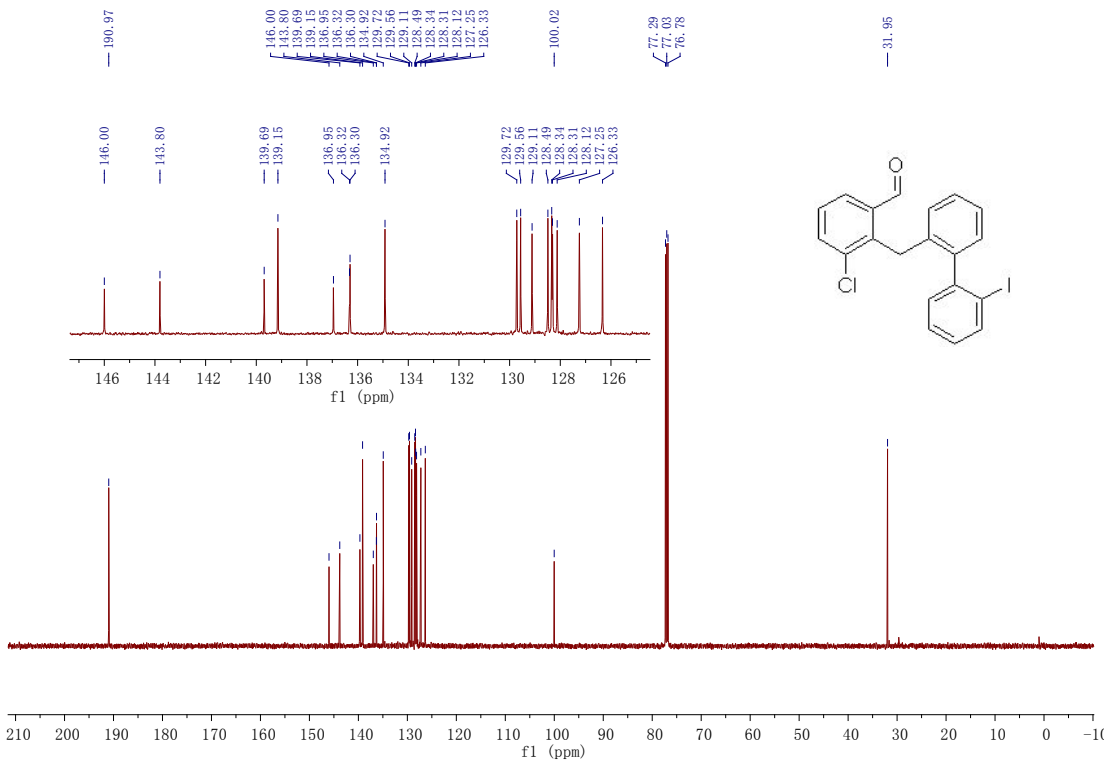


3-chloro-2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3r)

^{1}H NMR (500 MHz, $CDCl_3$)

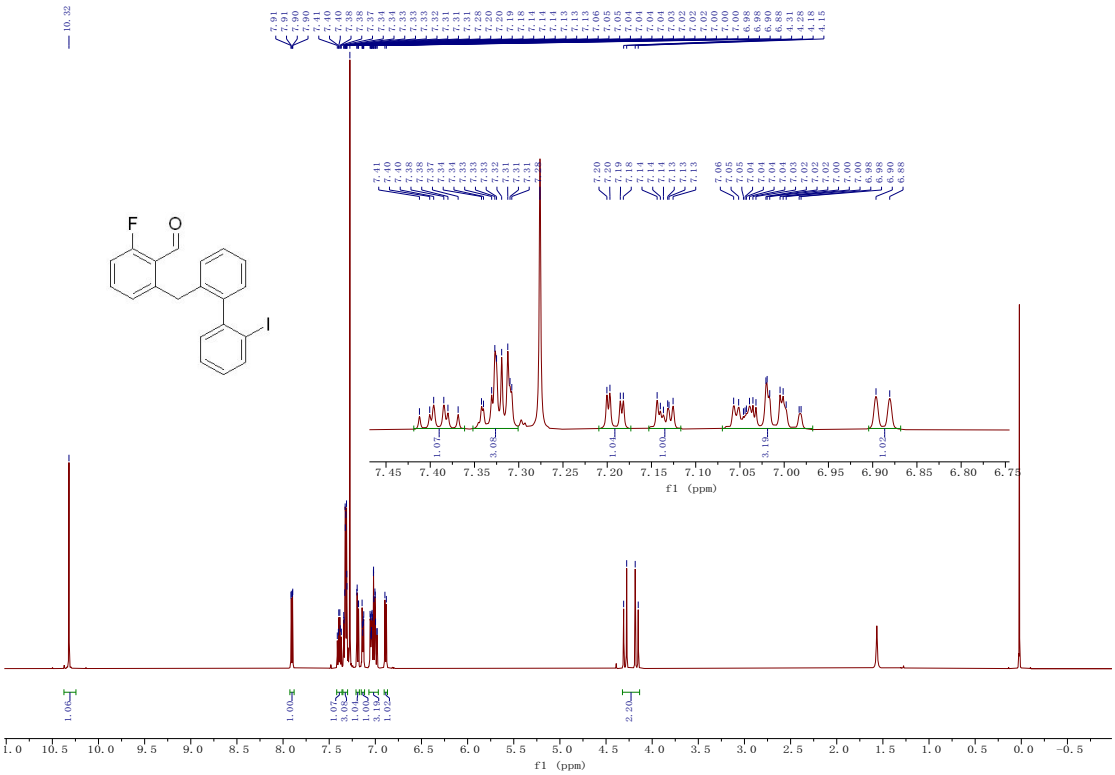


^{13}C NMR (126 MHz, $CDCl_3$)



2-fluoro-6-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (3s)

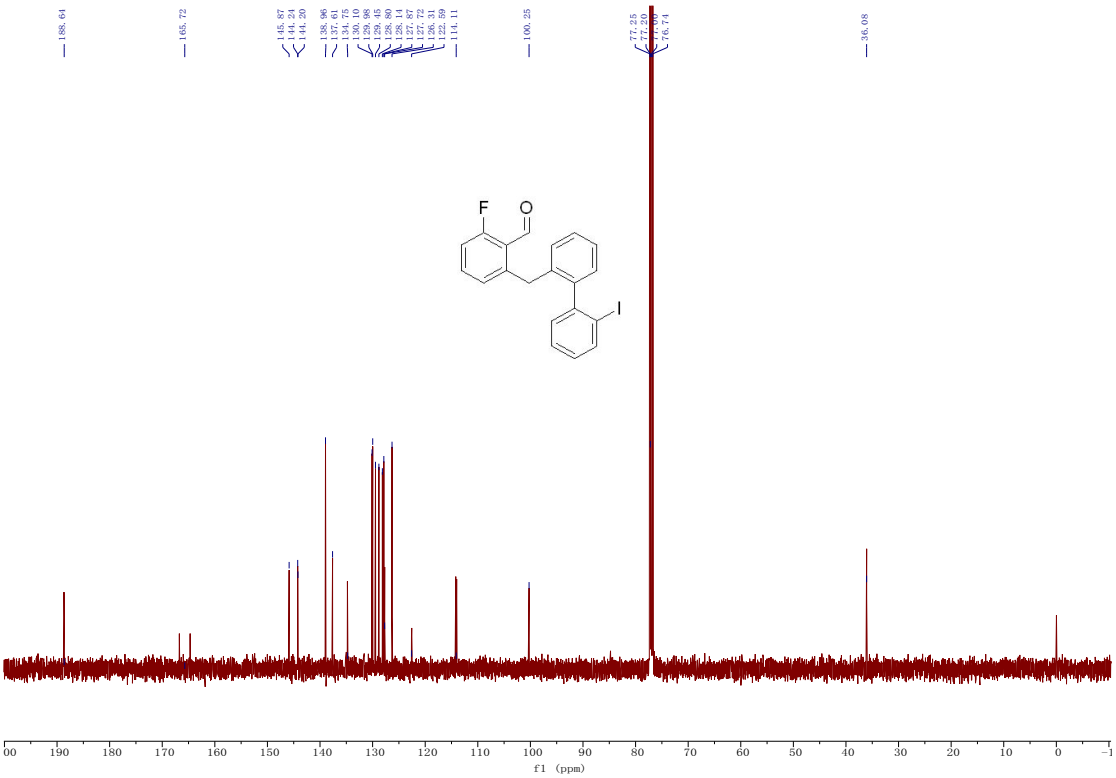
^{1}H NMR (500 MHz, $CDCl_3$)

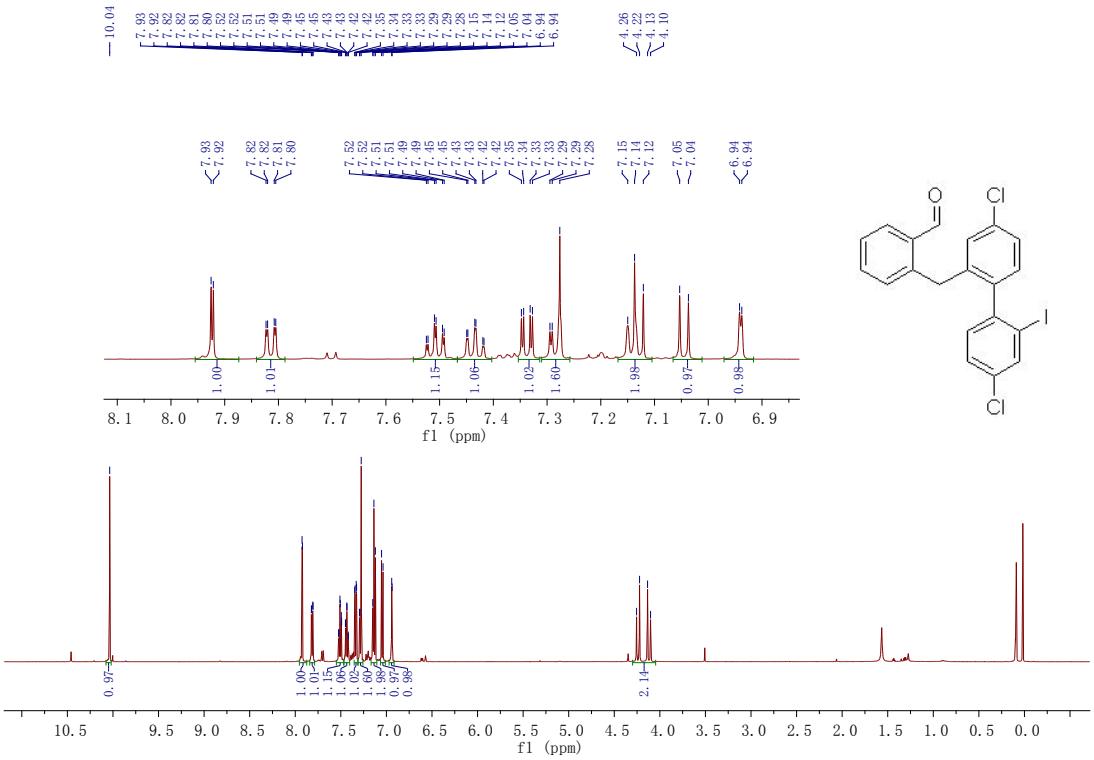


^{13}C NMR (126 MHz, $CDCl_3$)

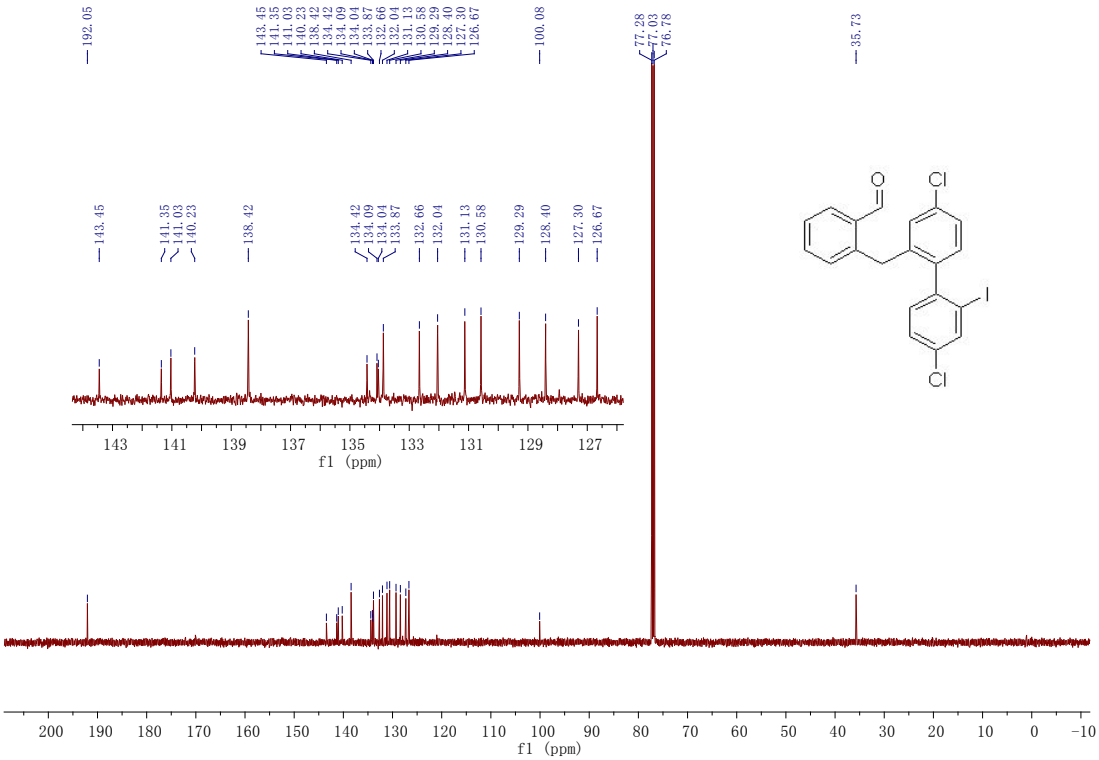
2-((4,4'-dichloro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4a)

^{1}H NMR (500 MHz, $CDCl_3$)



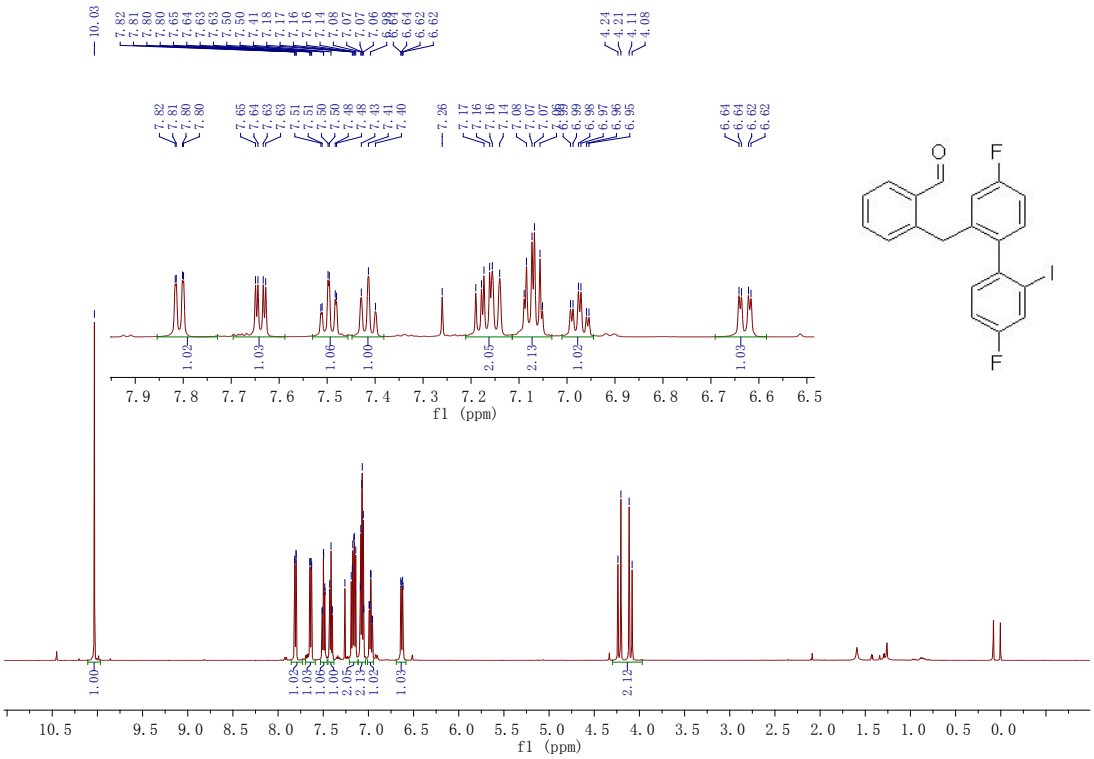


^{13}C NMR (126 MHz, $CDCl_3$)

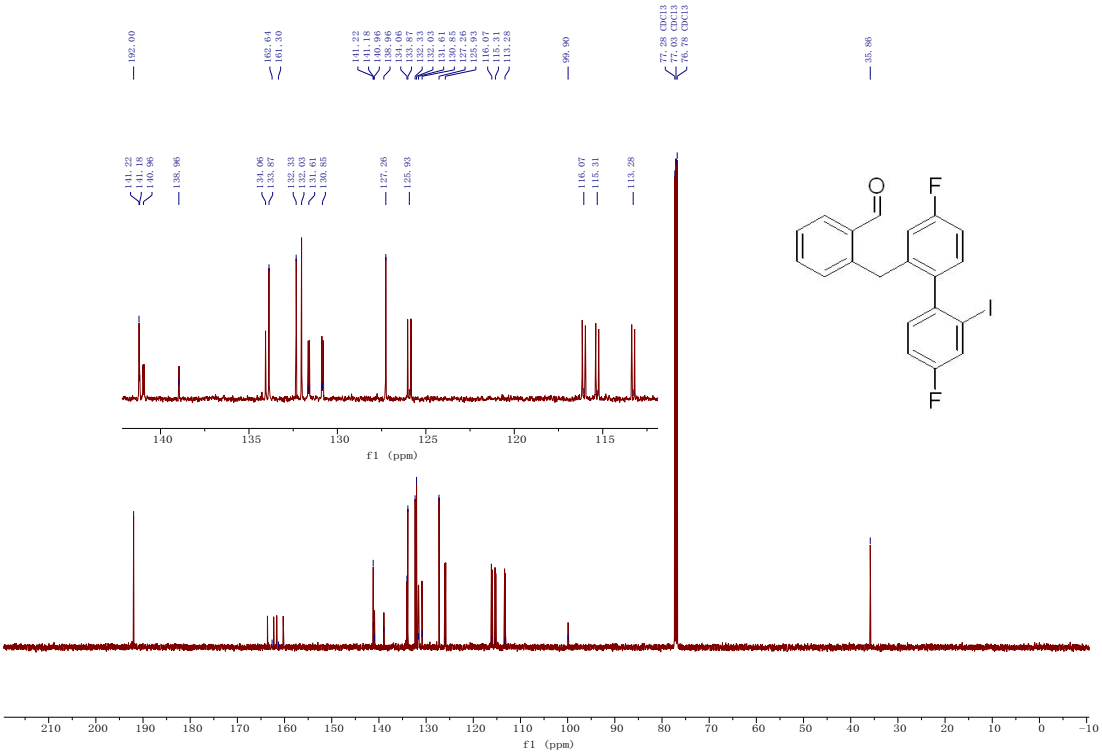


2-((4,4'-difluoro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4b)

^{1}H NMR (500 MHz, $CDCl_3$)

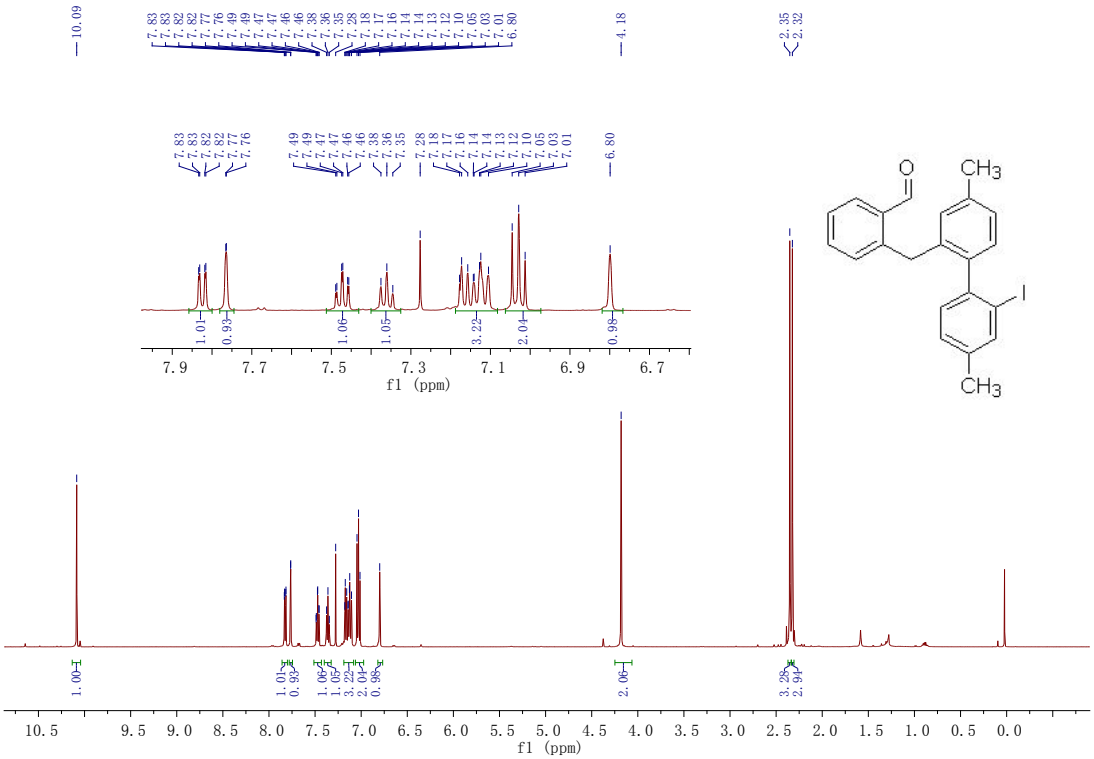


^{13}C NMR (126 MHz, $CDCl_3$)

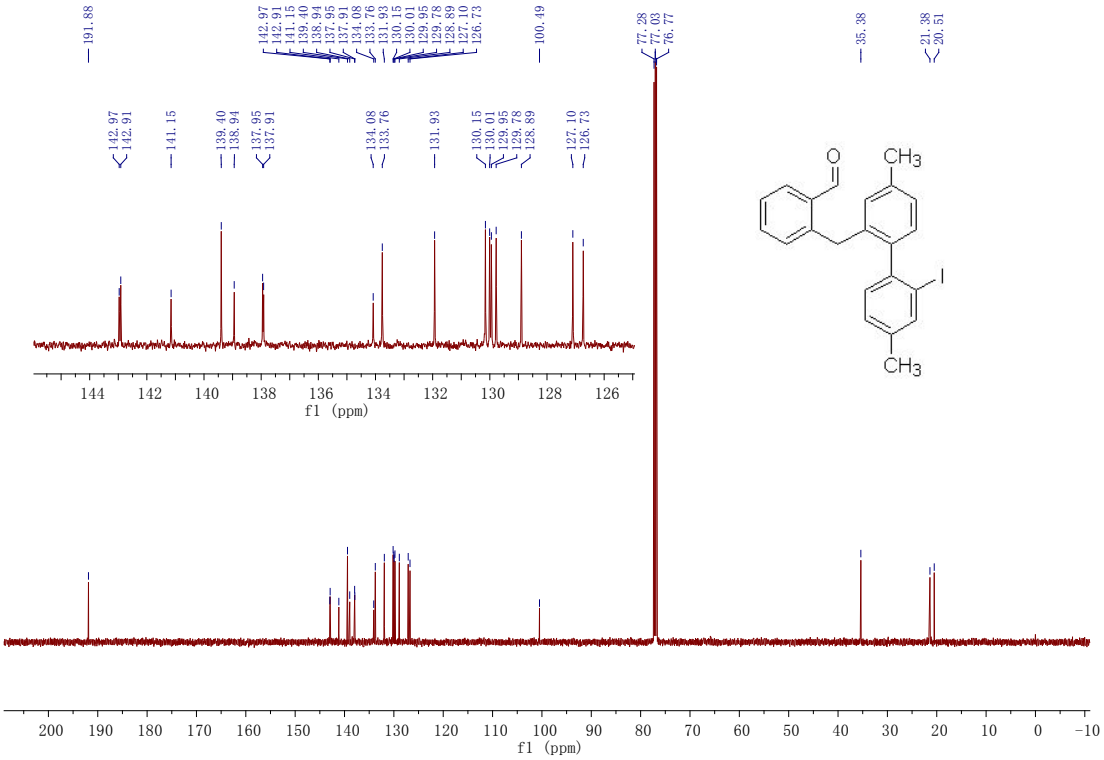


2-((2'-iodo-4,4'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4c)

^{1}H NMR (500 MHz, $CDCl_3$)

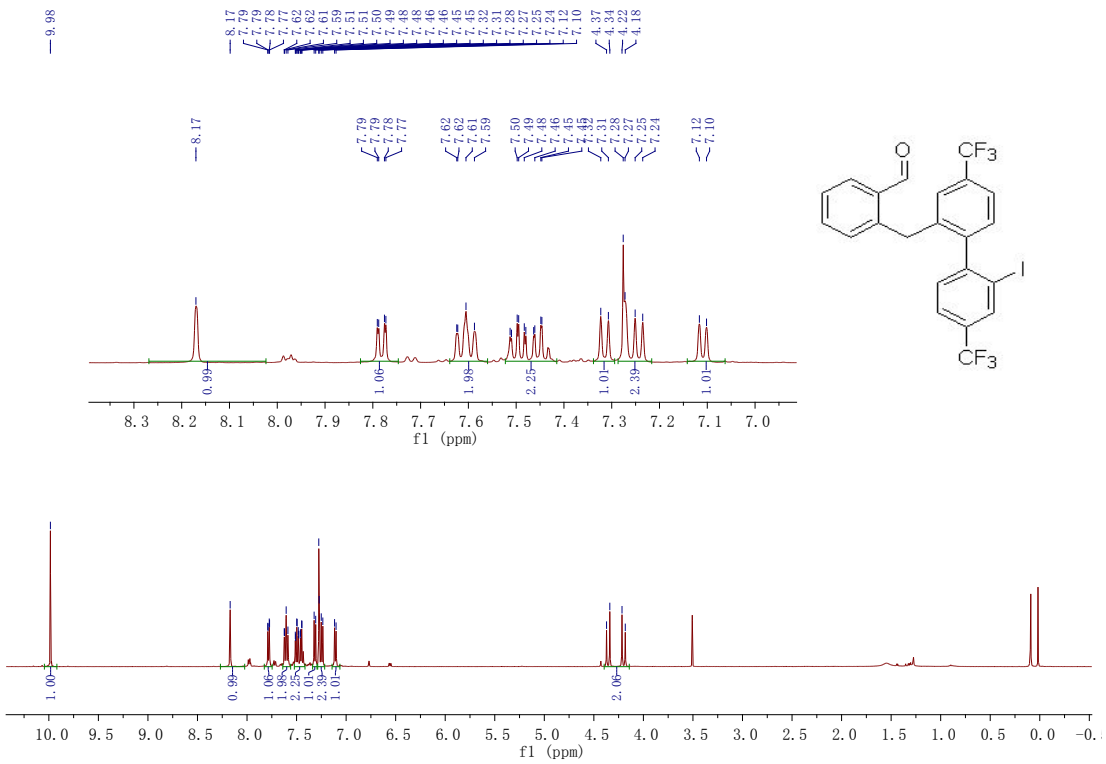


^{13}C NMR (126 MHz, $CDCl_3$)

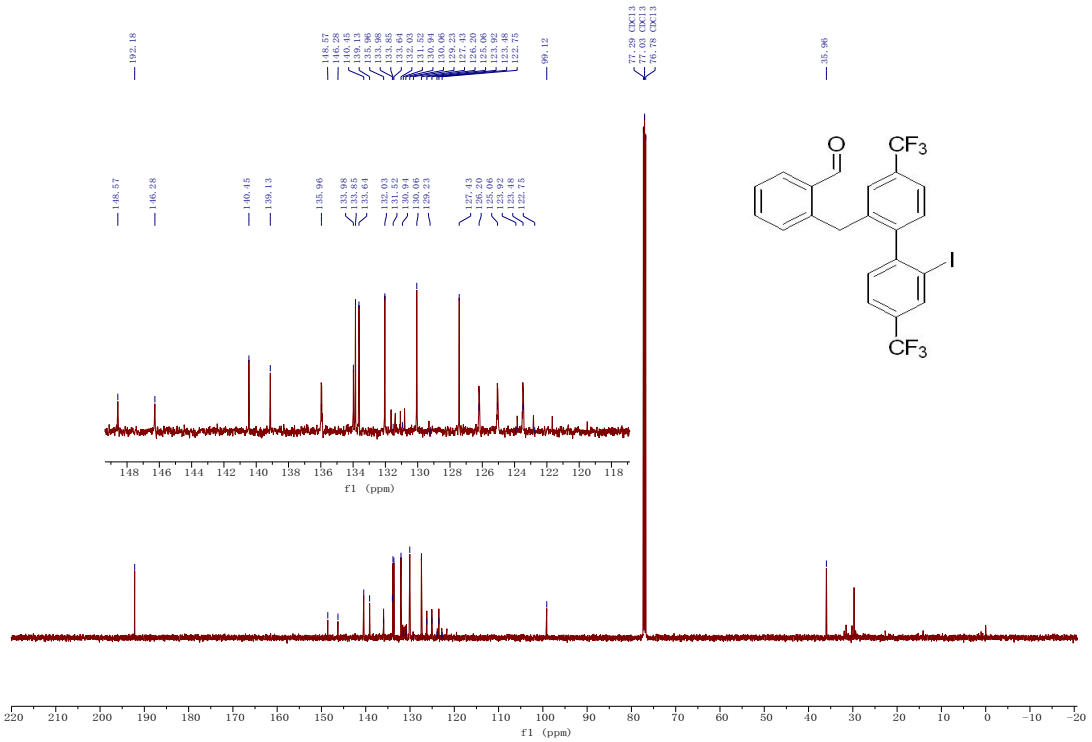


2-((2'-iodo-4,4'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4d)

^{1}H NMR (500 MHz, $CDCl_3$)

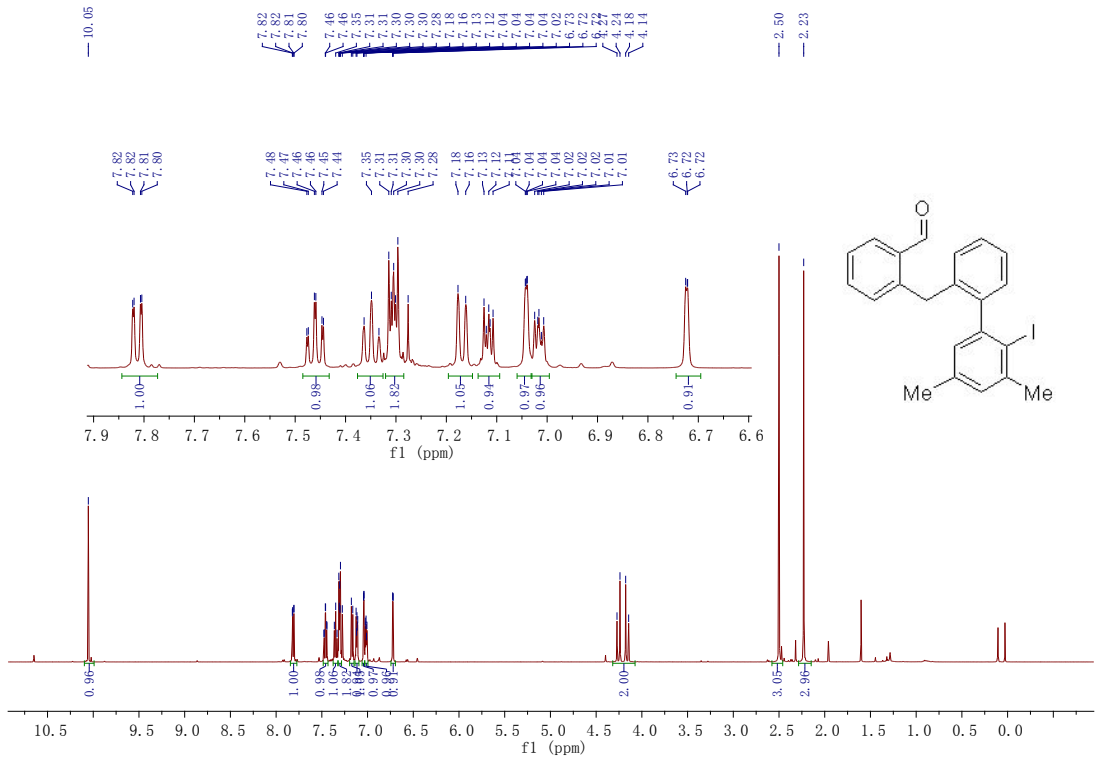


^{13}C NMR (126 MHz, $CDCl_3$)

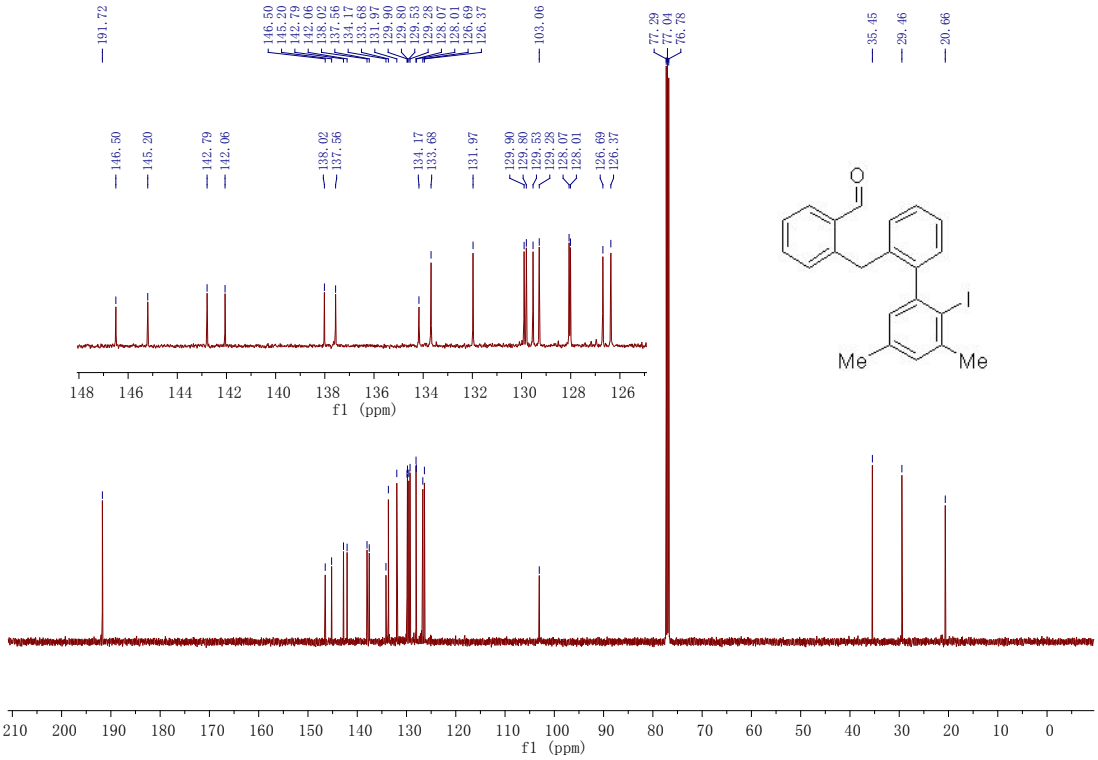


2-((2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4e)

^{1}H NMR (500 MHz, $CDCl_3$)

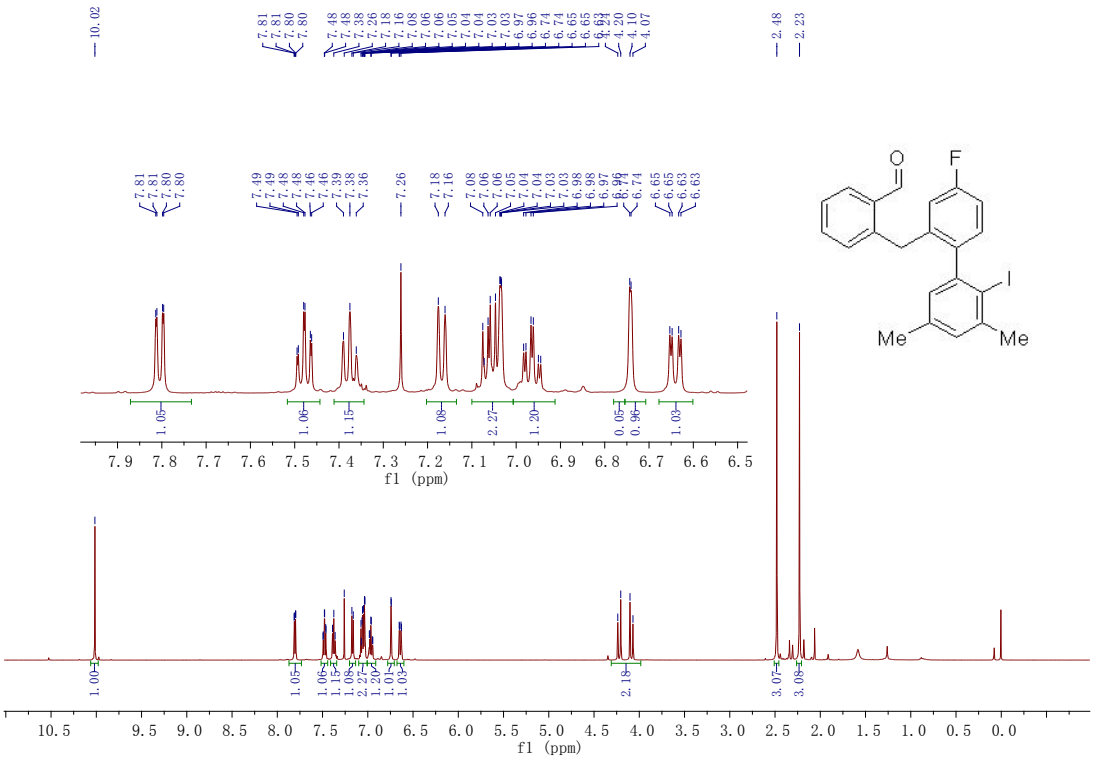


^{13}C NMR (126 MHz, $CDCl_3$)

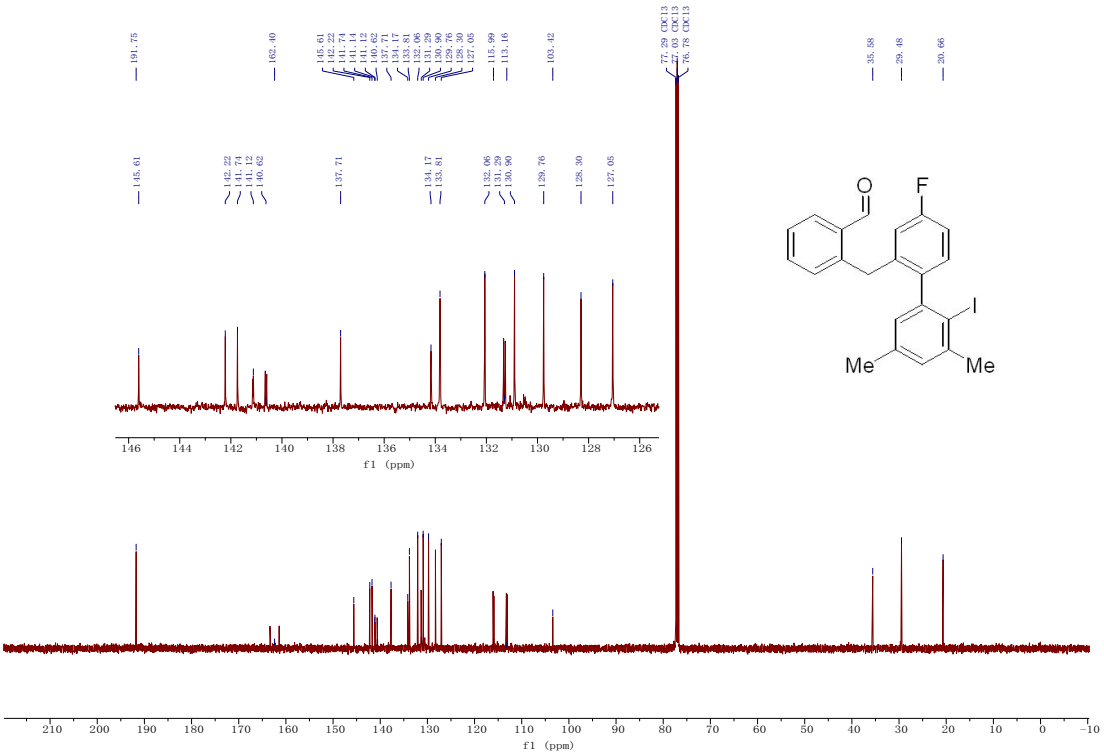


2-((4-fluoro-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4f)

^{1}H NMR (500 MHz, $CDCl_3$)

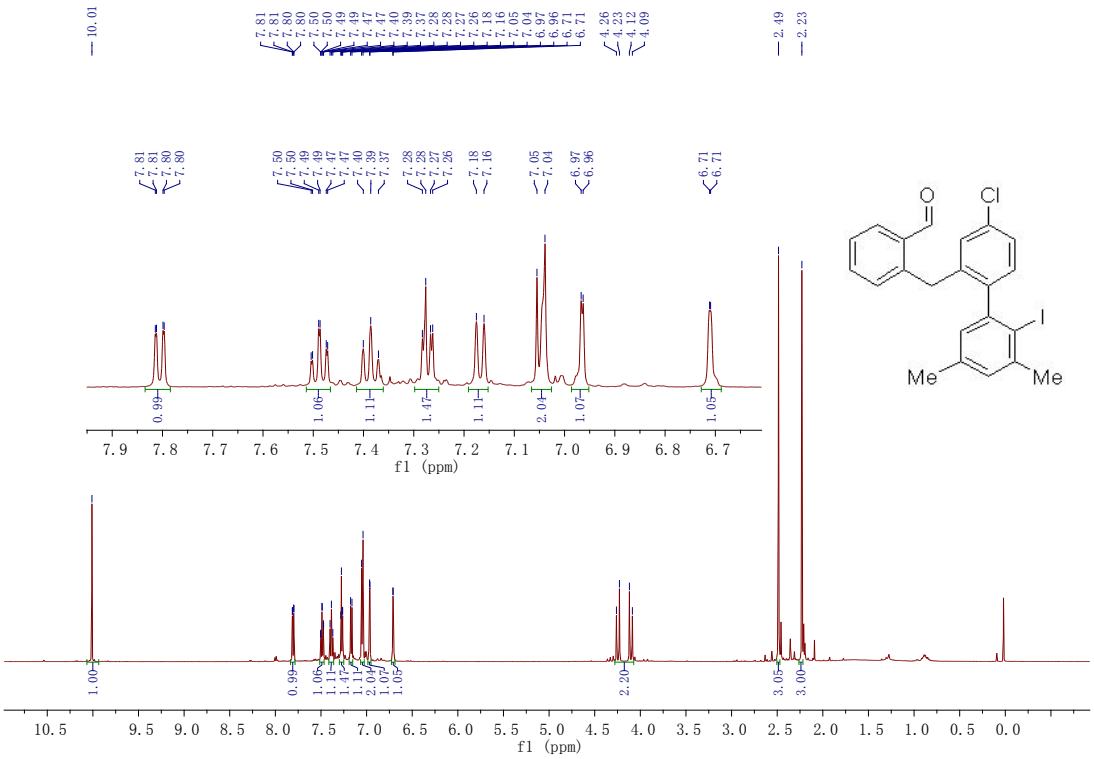


^{13}C NMR (126 MHz, $CDCl_3$)

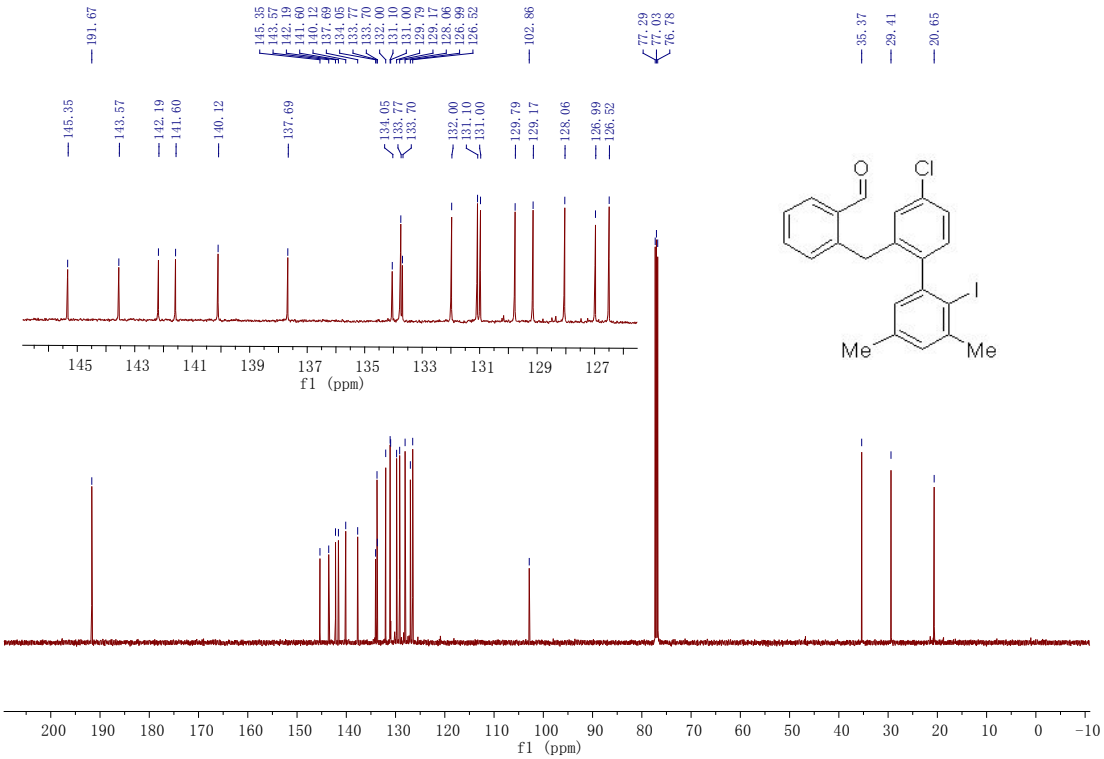


2-((4-chloro-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4g)

^{1}H NMR (500 MHz, $CDCl_3$)

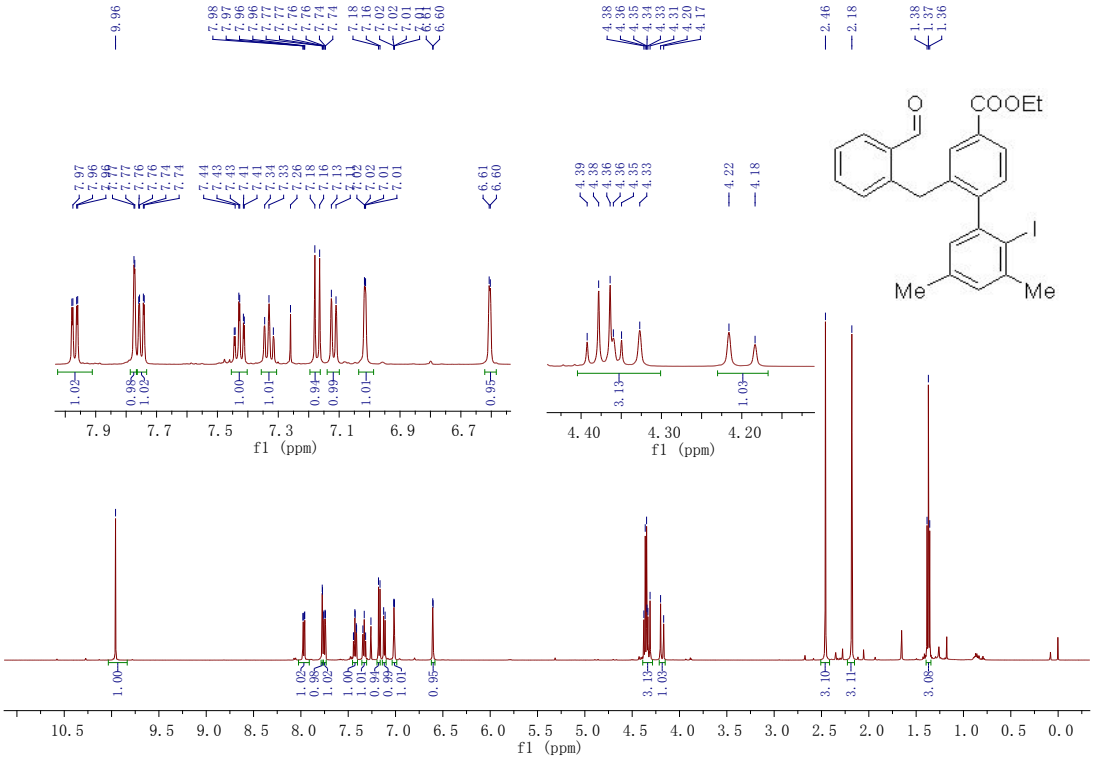


^{13}C NMR (126 MHz, $CDCl_3$)

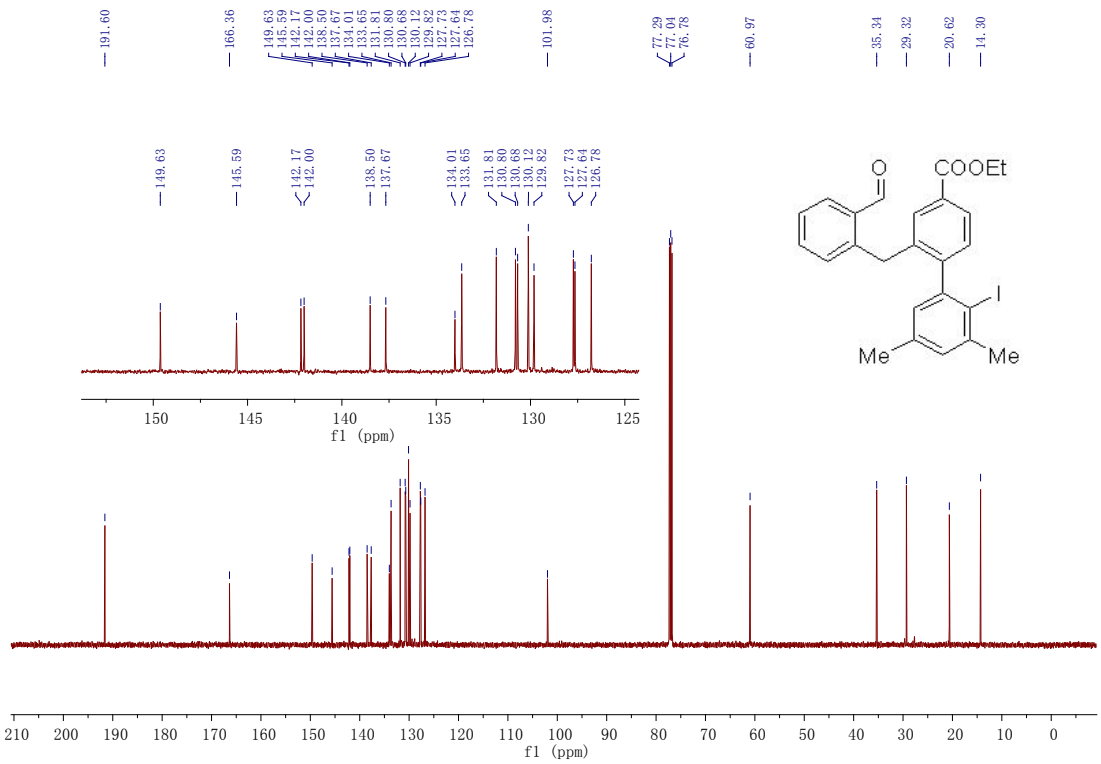


Ethyl-2-(2-formylbenzyl)-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate(4h)

^{1}H NMR (500 MHz, $CDCl_3$)

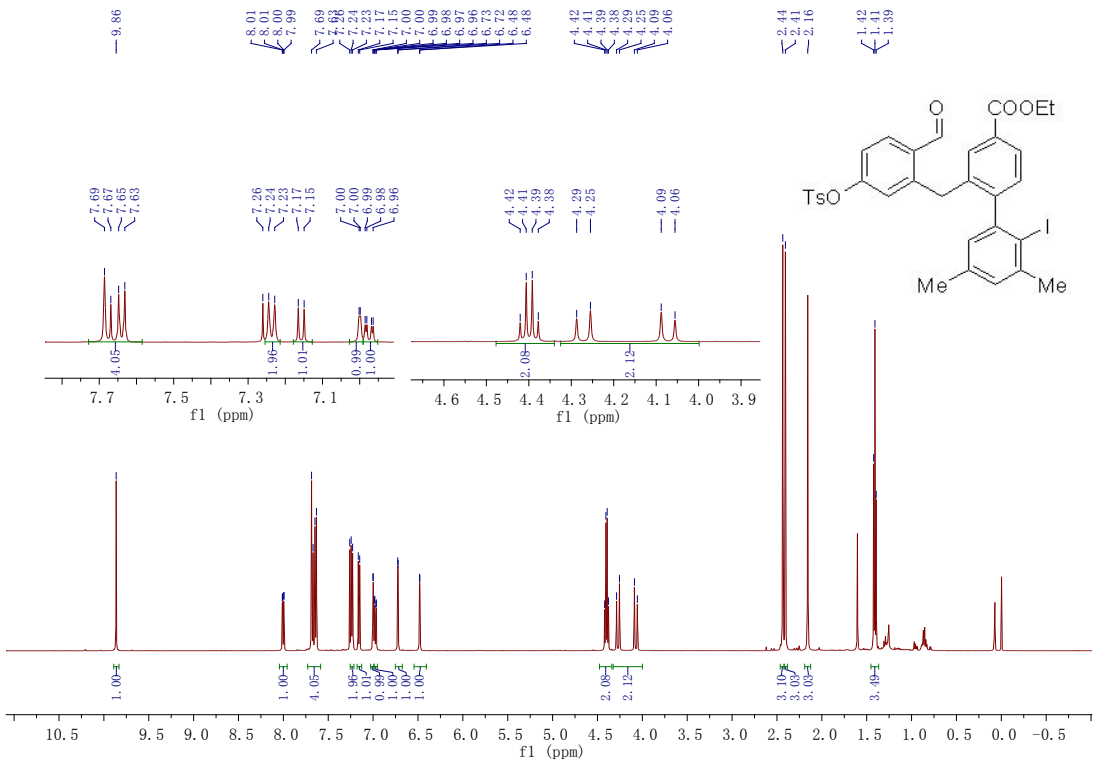


^{13}C NMR (126 MHz, $CDCl_3$)

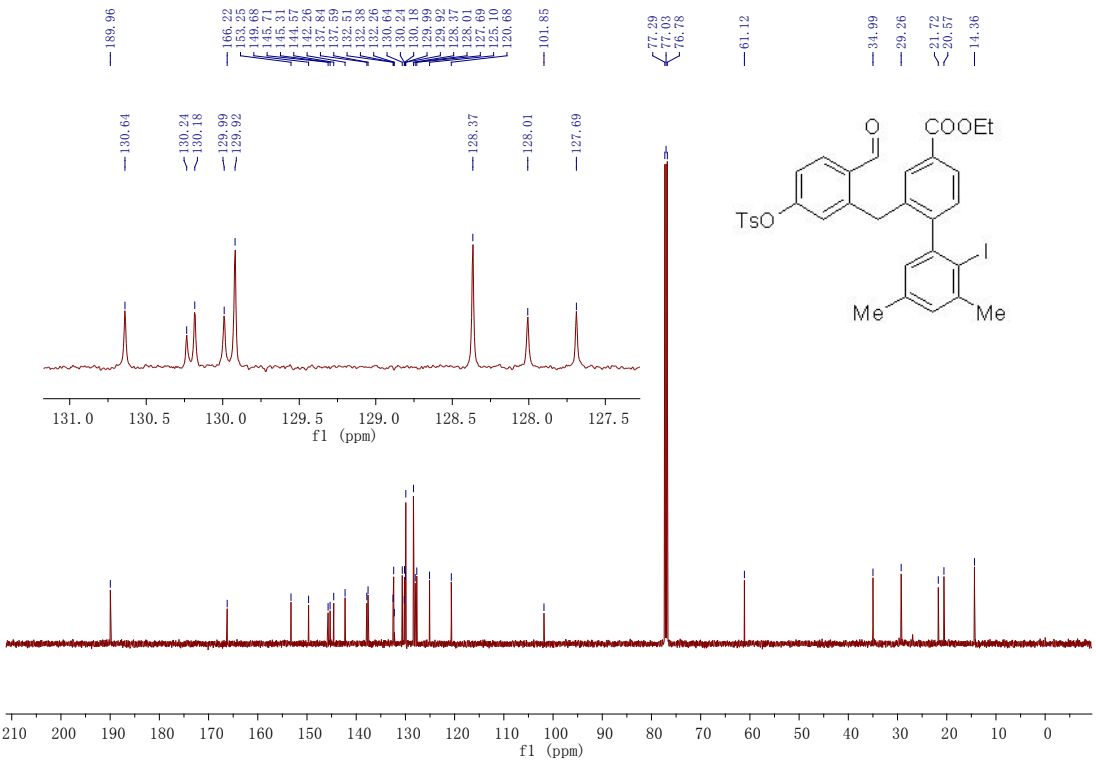


Ethyl-2-(2-formyl-5-(tosyloxy)benzyl)-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate(4i)

^{1}H NMR (500 MHz, $CDCl_3$)

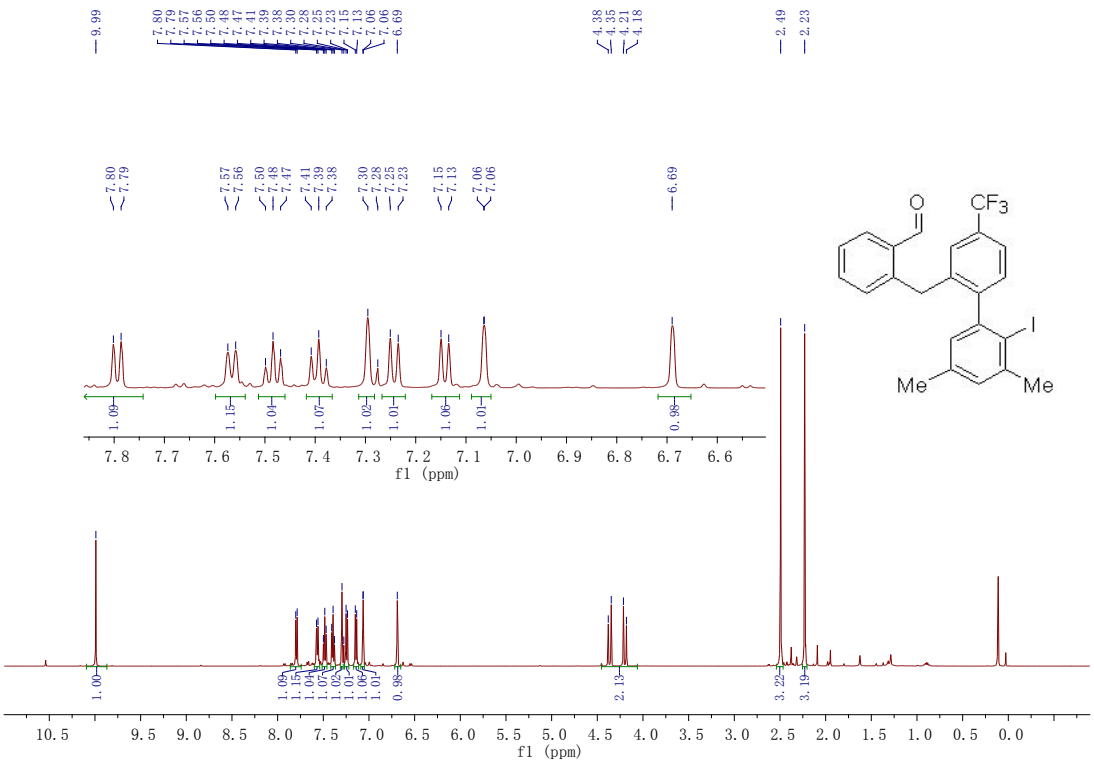


^{13}C NMR (126 MHz, $CDCl_3$)

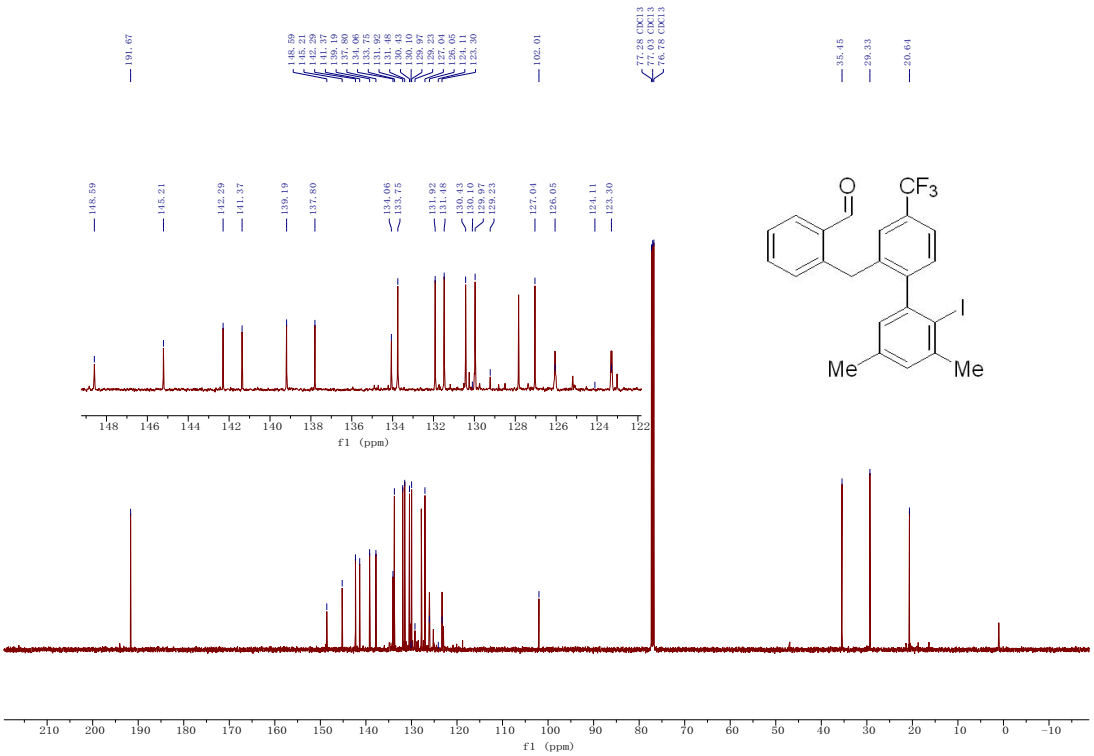


2-((2'-iodo-3',5'-dimethyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4j)

^{1}H NMR (500 MHz, $CDCl_3$)

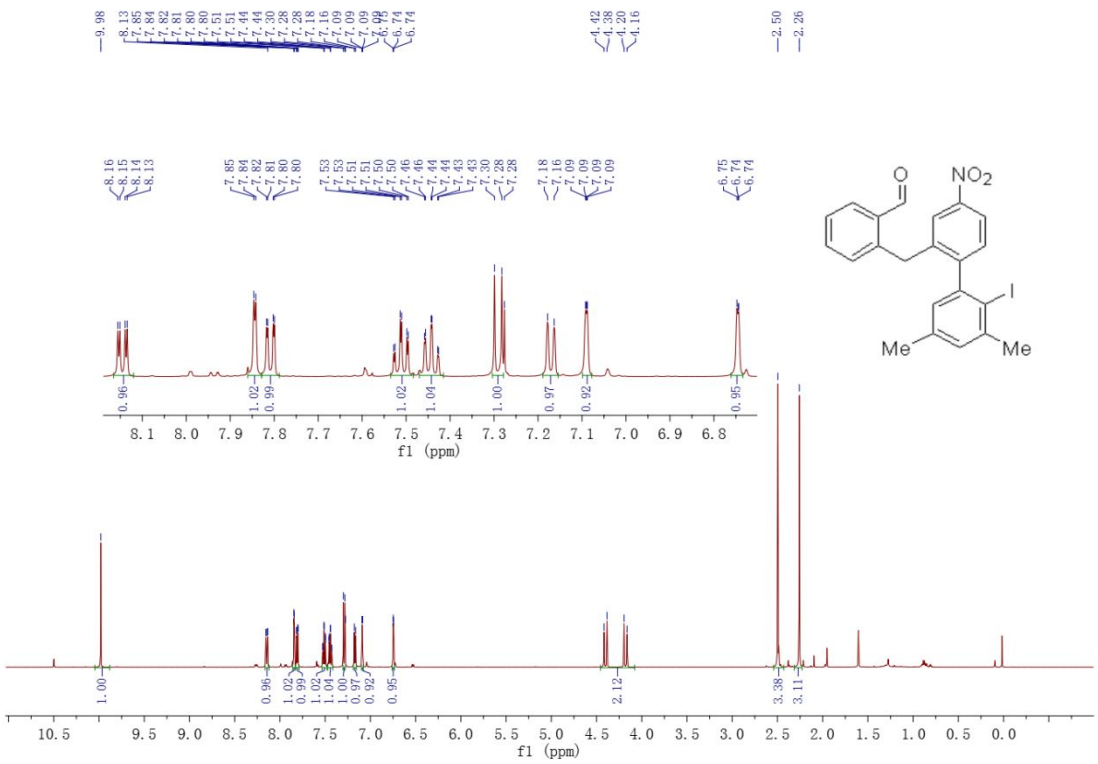


^{13}C NMR (126 MHz, $CDCl_3$)

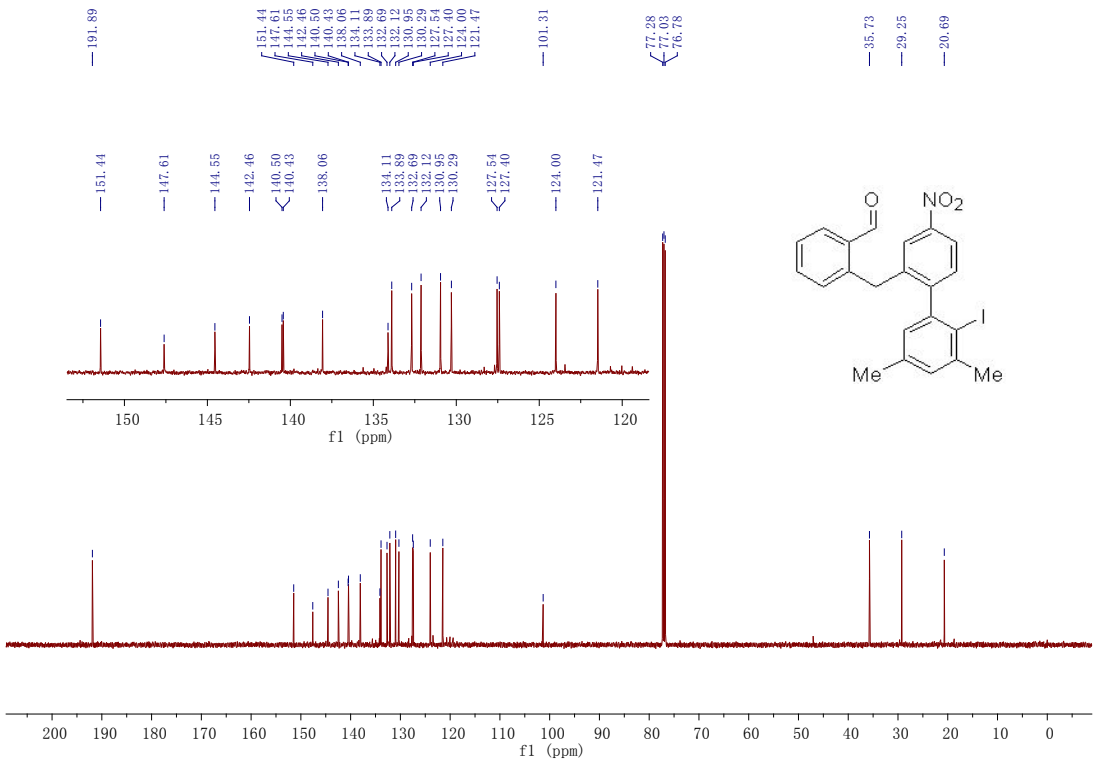


2-((2'-iodo-3',5'-dimethyl-4-nitro-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4k)

^{1}H NMR (500 MHz, $CDCl_3$)

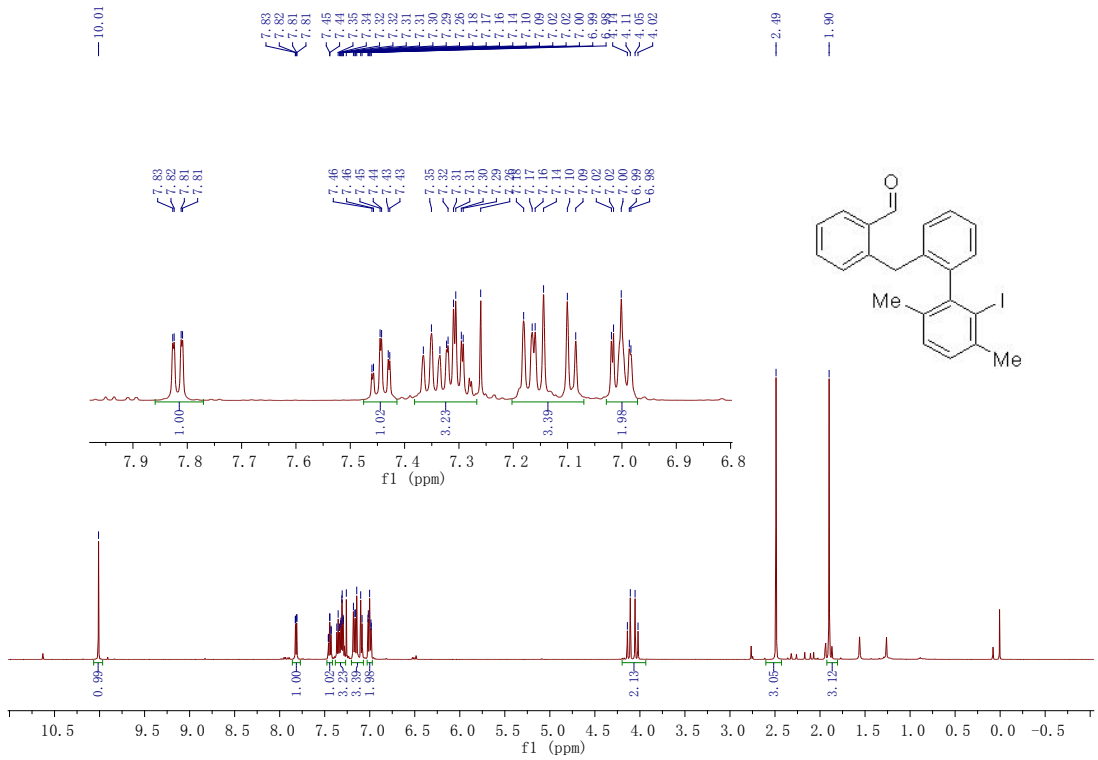


^{13}C NMR (126 MHz, $CDCl_3$)

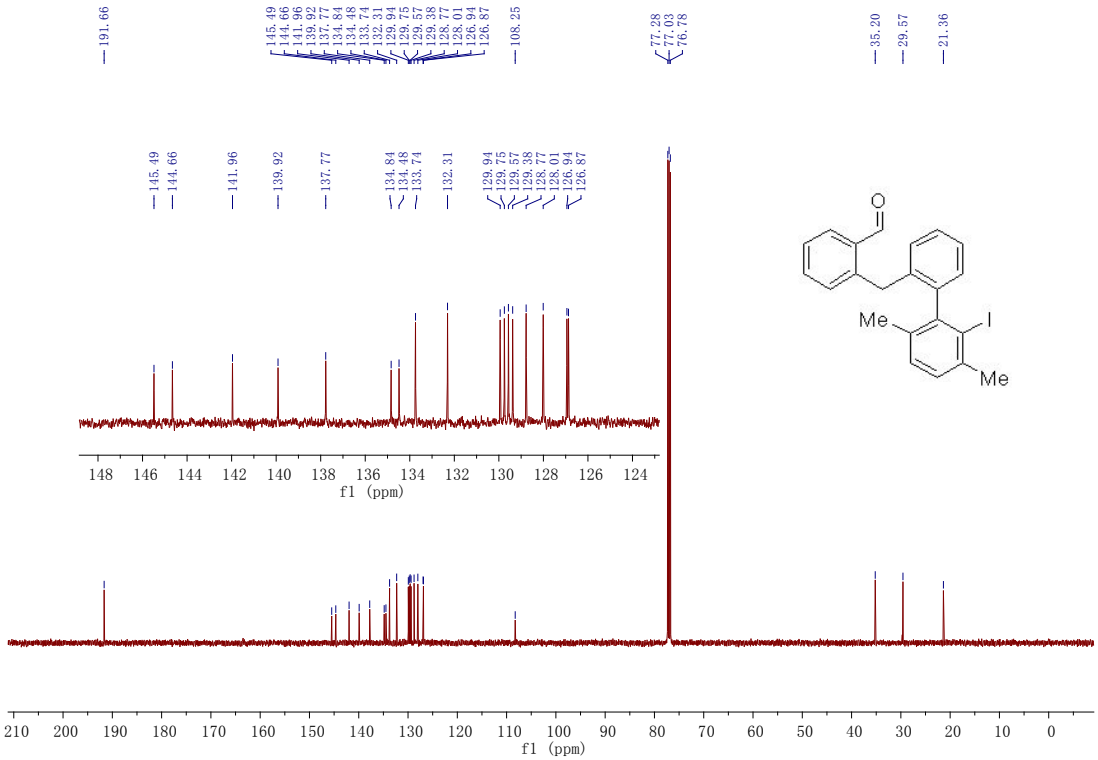


2-((2'-iodo-3',6'-dimethyl-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde (4l)

^{1}H NMR (500 MHz, $CDCl_3$)

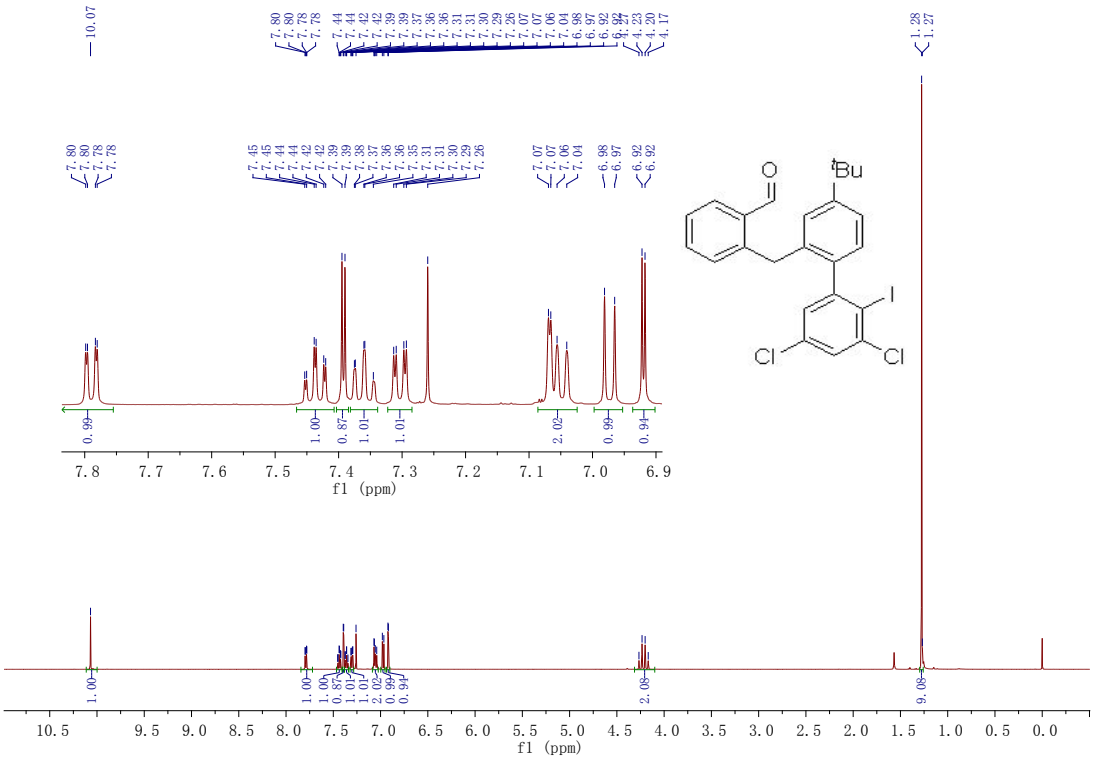


^{13}C NMR (126 MHz, $CDCl_3$)

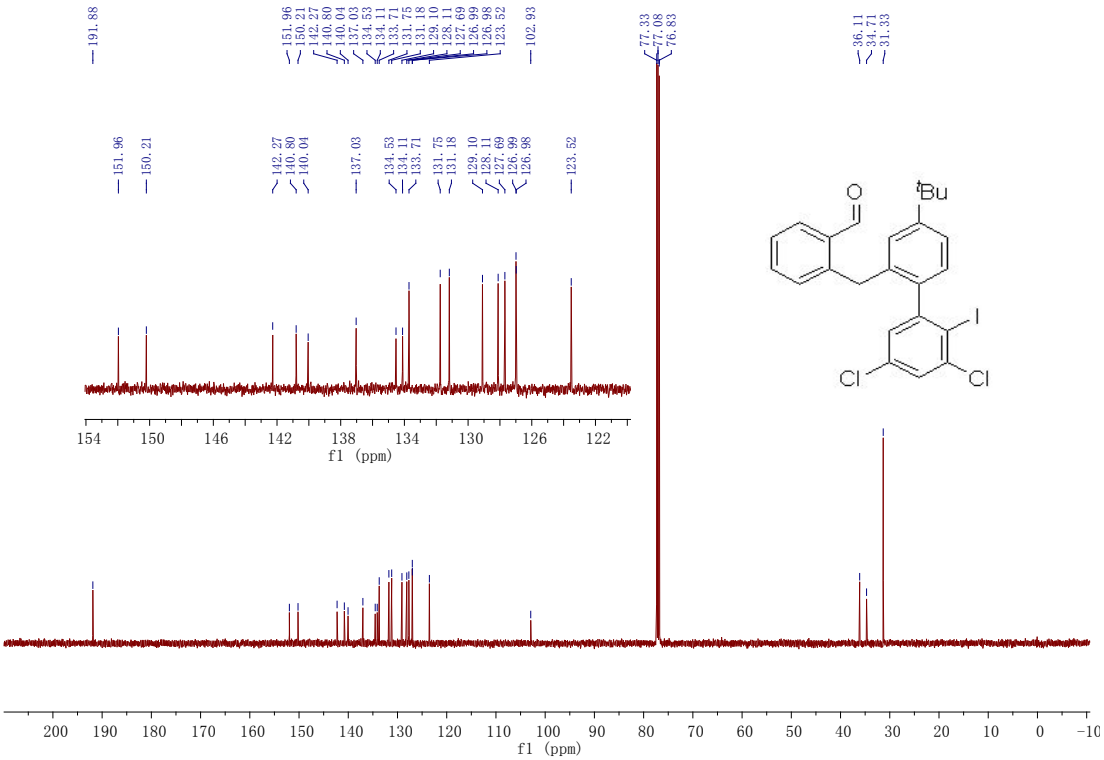


2-((4-(tert-butyl)-3',5'-dichloro-2'-iodo-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(4m)

^{1}H NMR (500 MHz, $CDCl_3$)

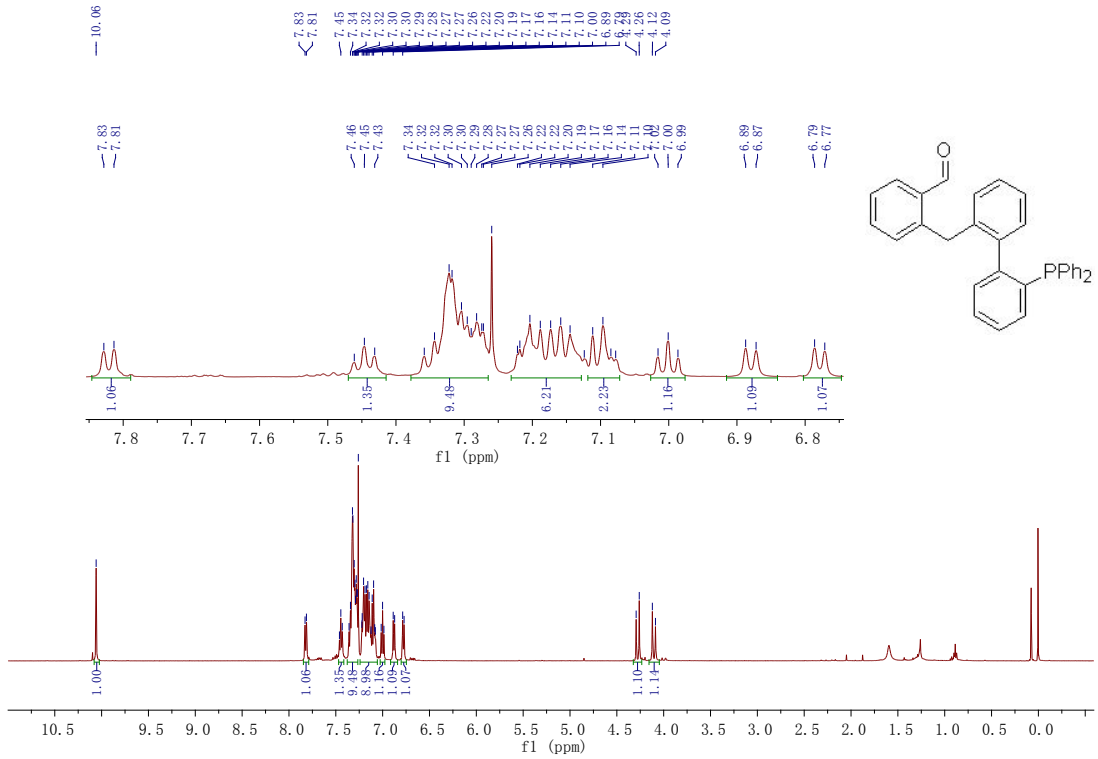


^{13}C NMR (126 MHz, $CDCl_3$)

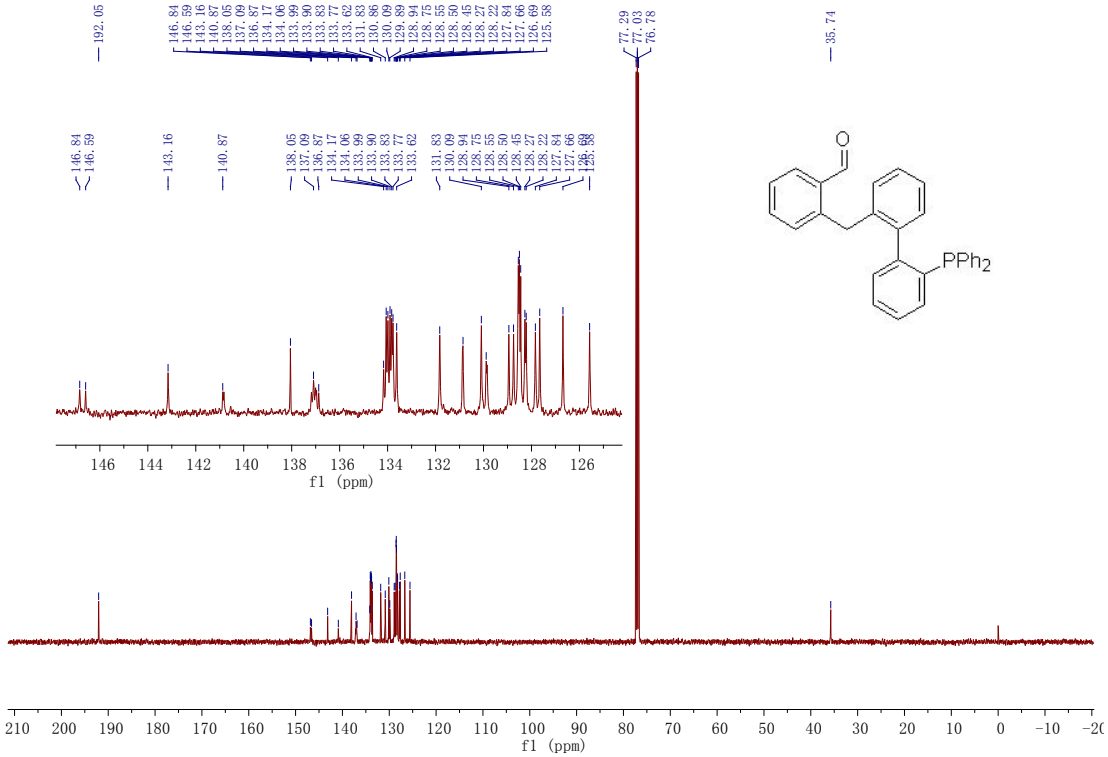


2-((2'-(diphenylphosphaneyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(5)

^{1}H NMR (500 MHz, $CDCl_3$)

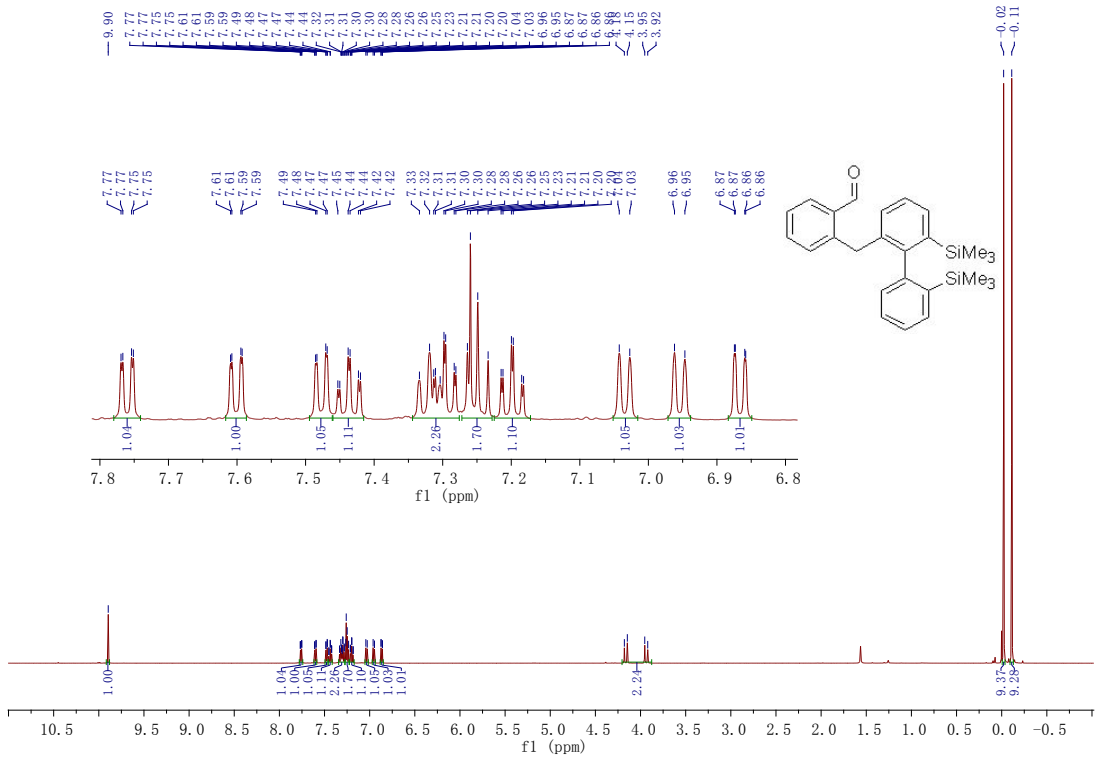


^{13}C NMR (126 MHz, $CDCl_3$)

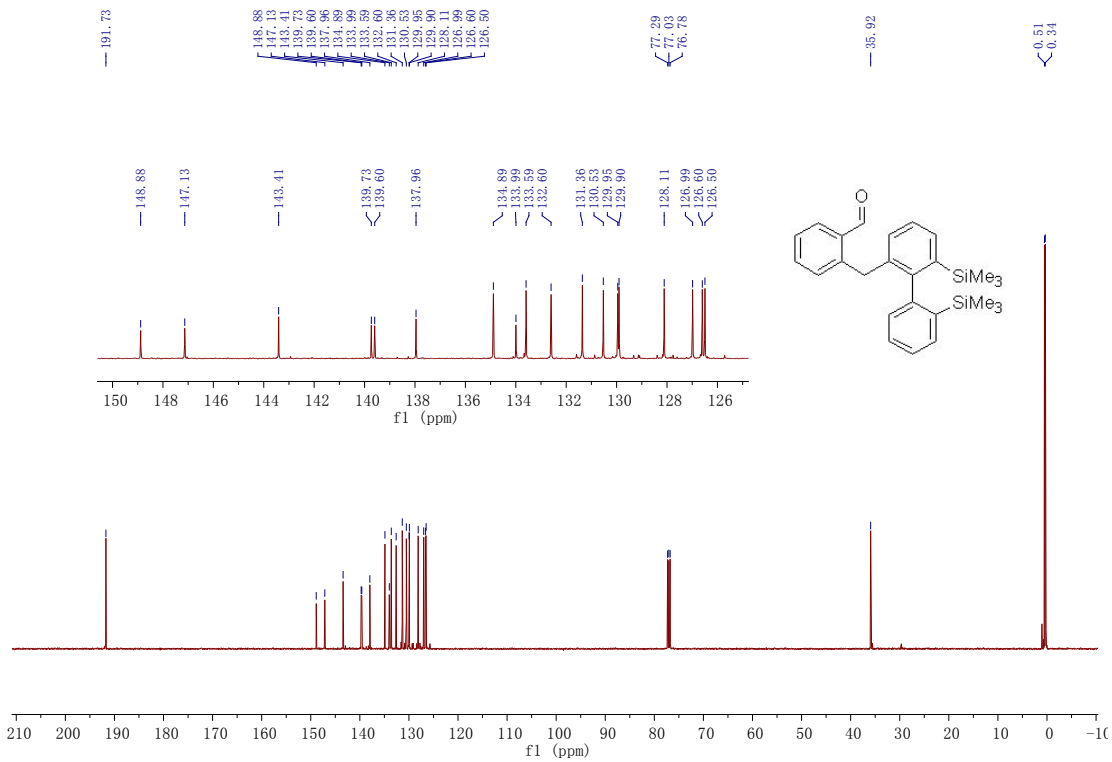


2-((2',6-bis(trimethylsilyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(6)

^{1}H NMR (500 MHz, $CDCl_3$)

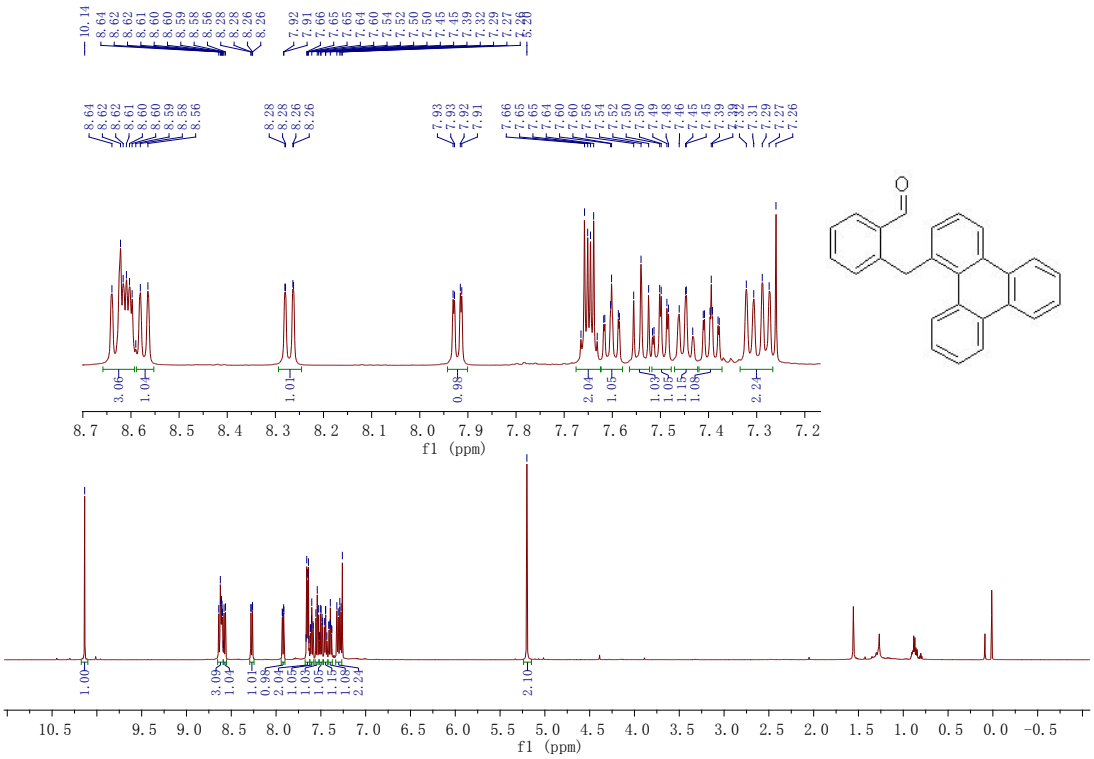


^{13}C NMR (126 MHz, $CDCl_3$)

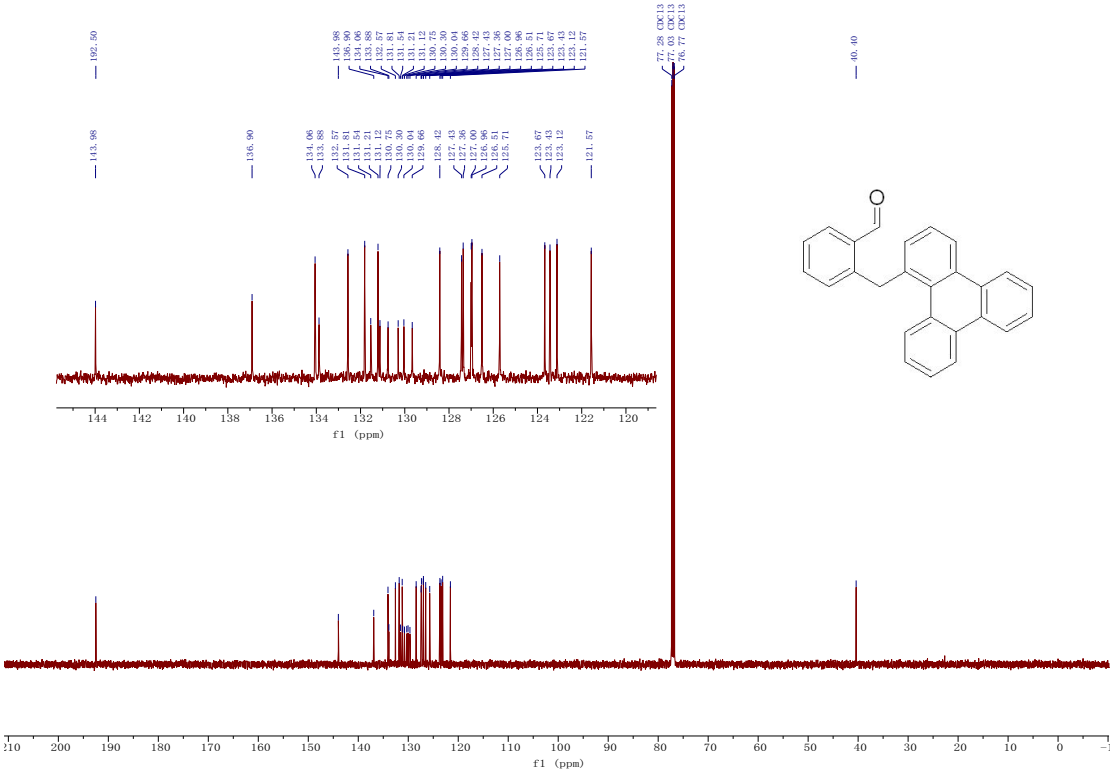


2-(triphenylen-1-ylmethyl)benzaldehyde(7)

^{1}H NMR (500 MHz, $CDCl_3$)

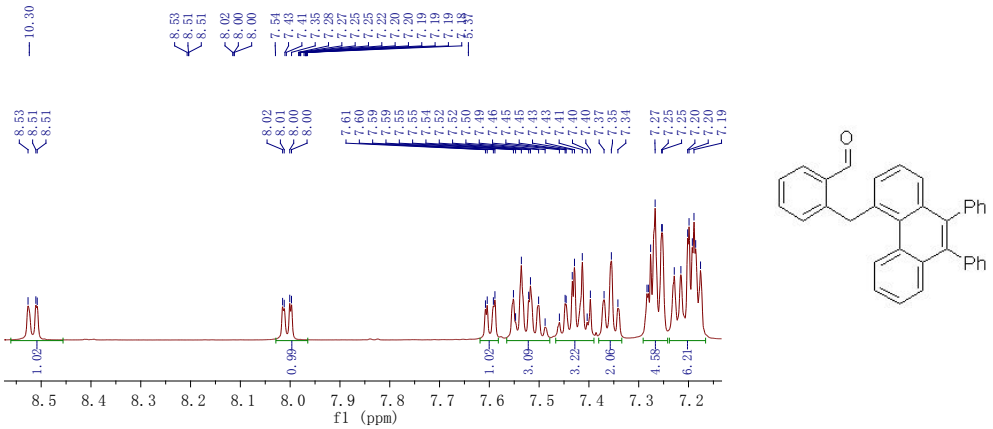


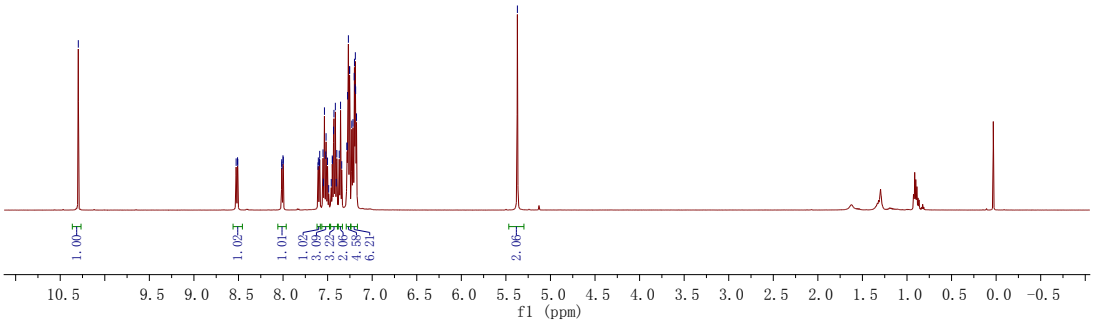
^{13}C NMR (126 MHz, $CDCl_3$)



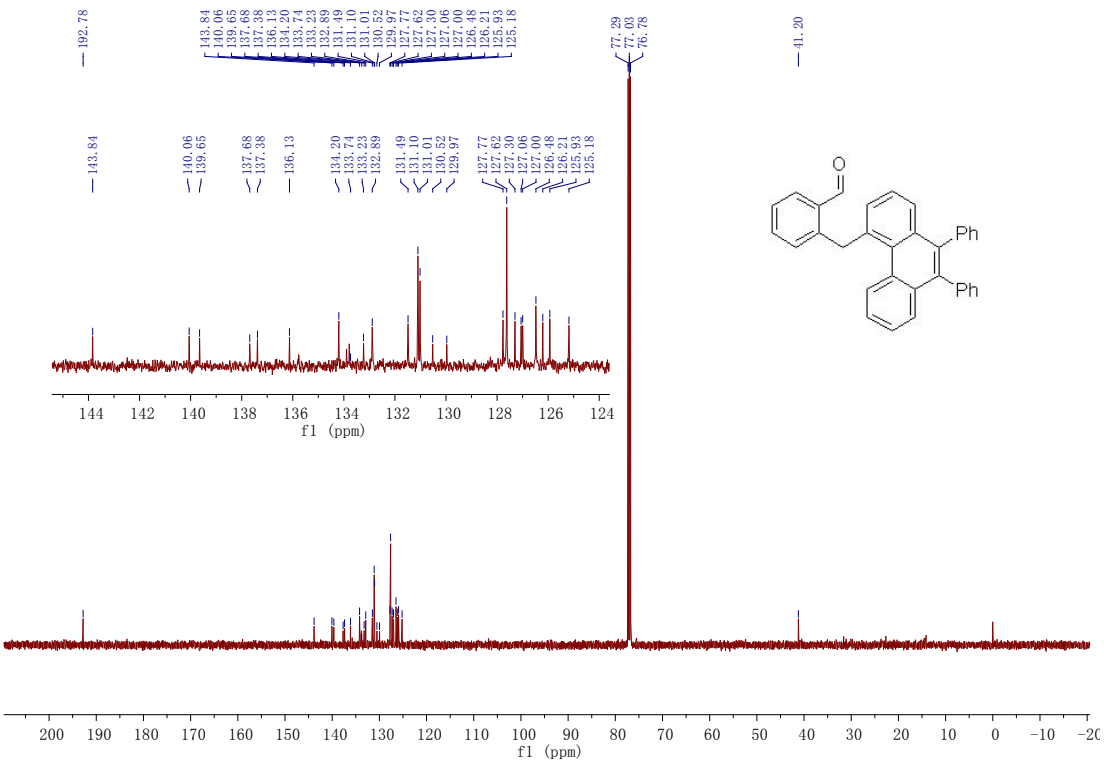
2-((9,10-diphenylphenanthren-4-yl)methyl)benzaldehyde(8)

^{1}H NMR (500 MHz, $CDCl_3$)



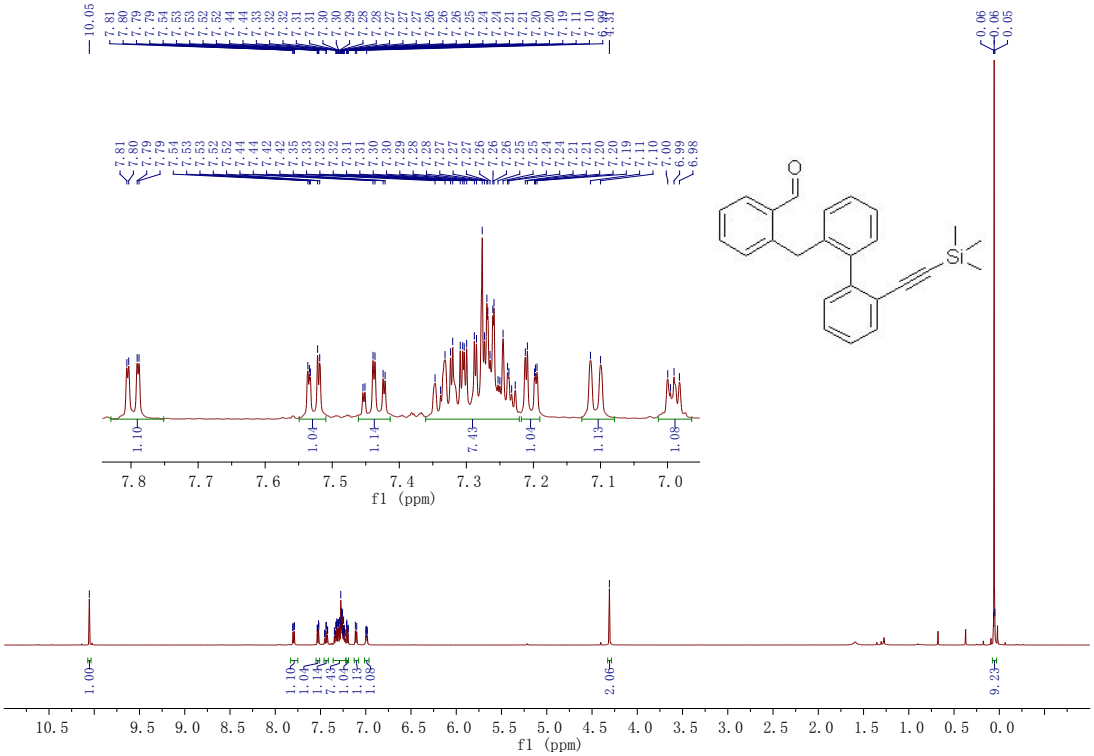


^{13}C NMR (126 MHz, $CDCl_3$)

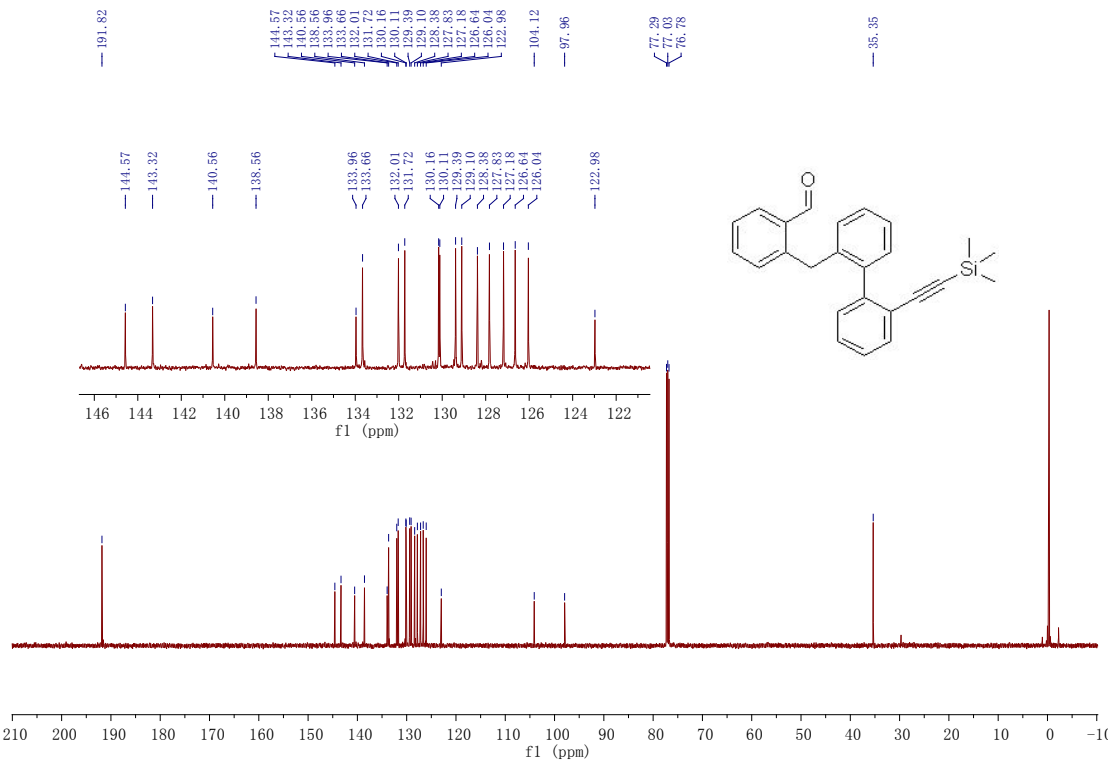


2-((2'-((trimethylsilyl)ethynyl)-[1,1'-biphenyl]-2-yl)methyl)benzaldehyde(9)

^{1}H NMR (500 MHz, $CDCl_3$)

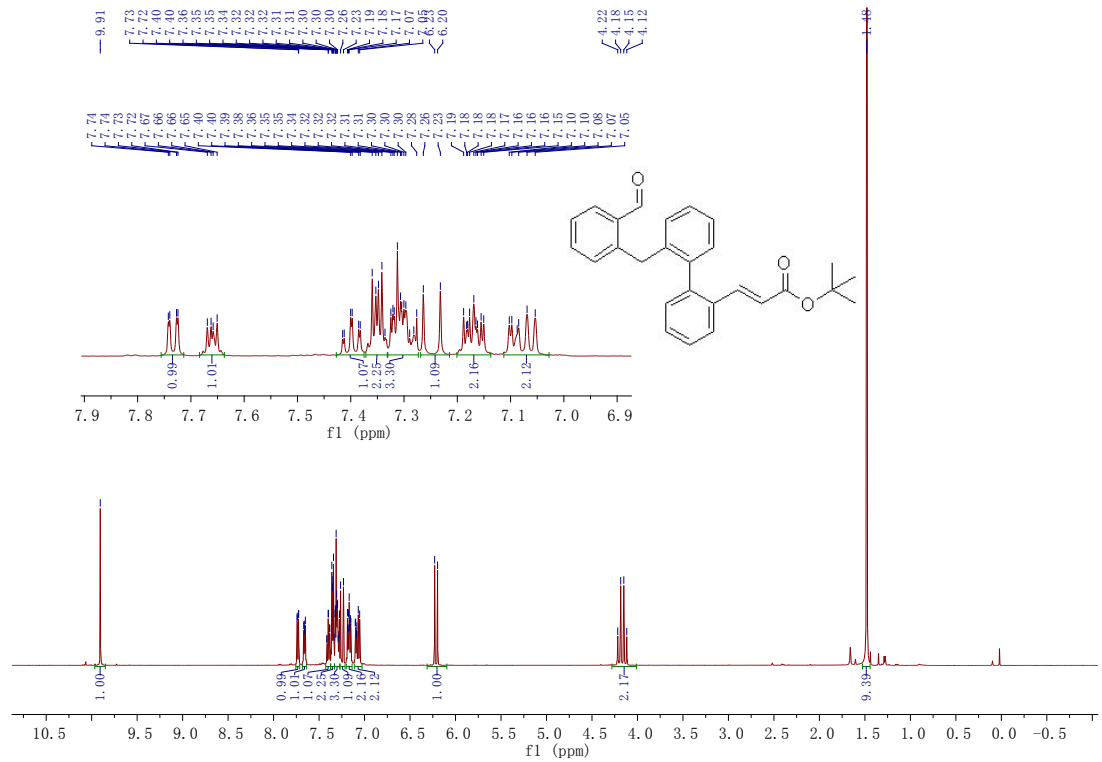


^{13}C NMR (126 MHz, $CDCl_3$)

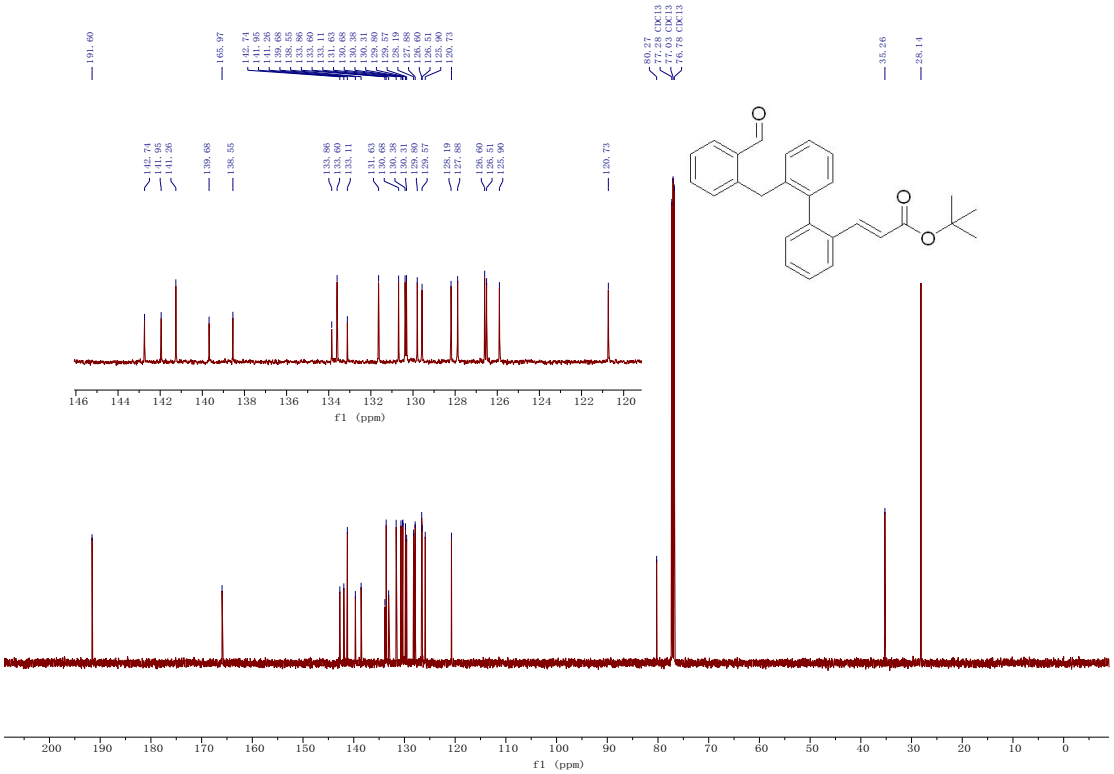


***tert*-butyl (*E*)-3-(2'-(2-formylbenzyl)-[1,1'-biphenyl]-2-yl)acrylate(10)**

^{1}H NMR (500 MHz, $CDCl_3$)

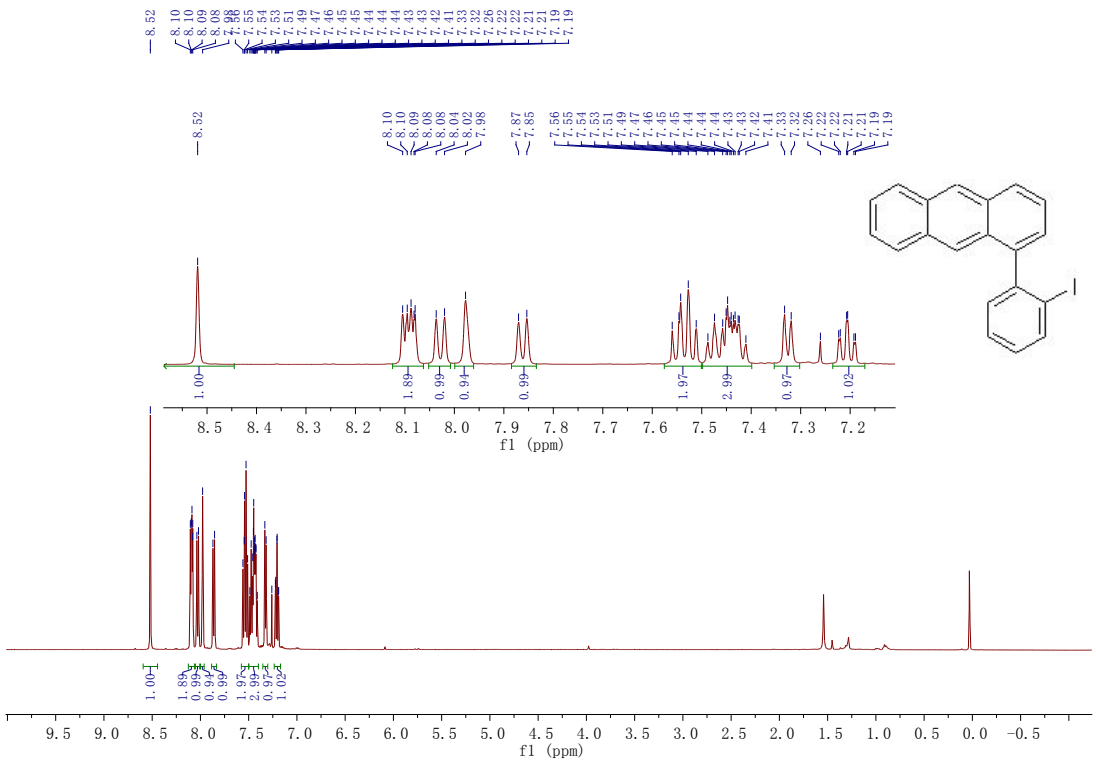


^{13}C NMR (126 MHz, $CDCl_3$)

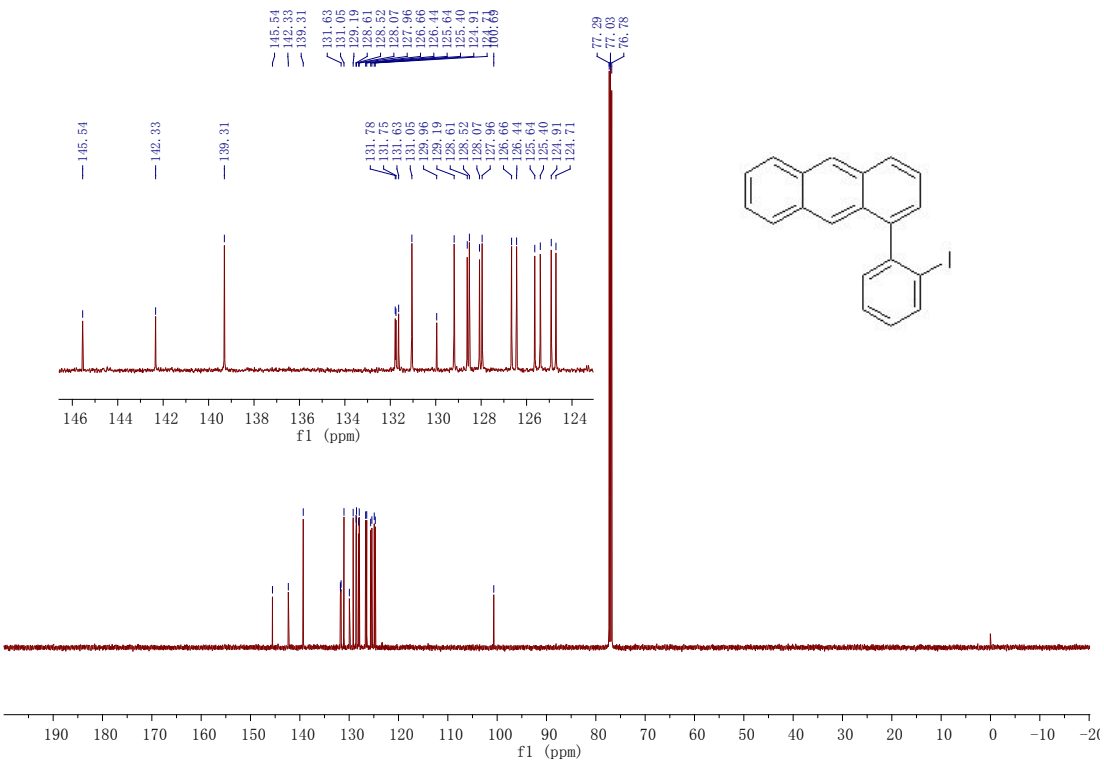


1-(2-iodophenyl)anthracene(11)

^{1}H NMR (500 MHz, $CDCl_3$)

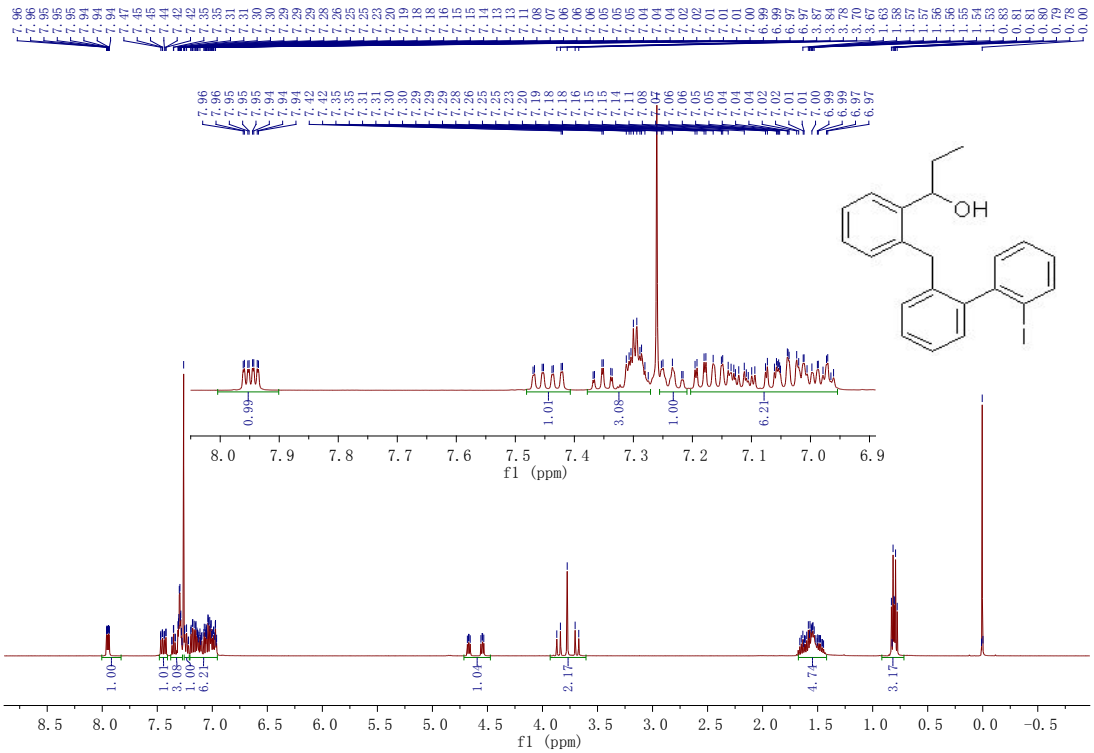


^{13}C NMR (126 MHz, $CDCl_3$)

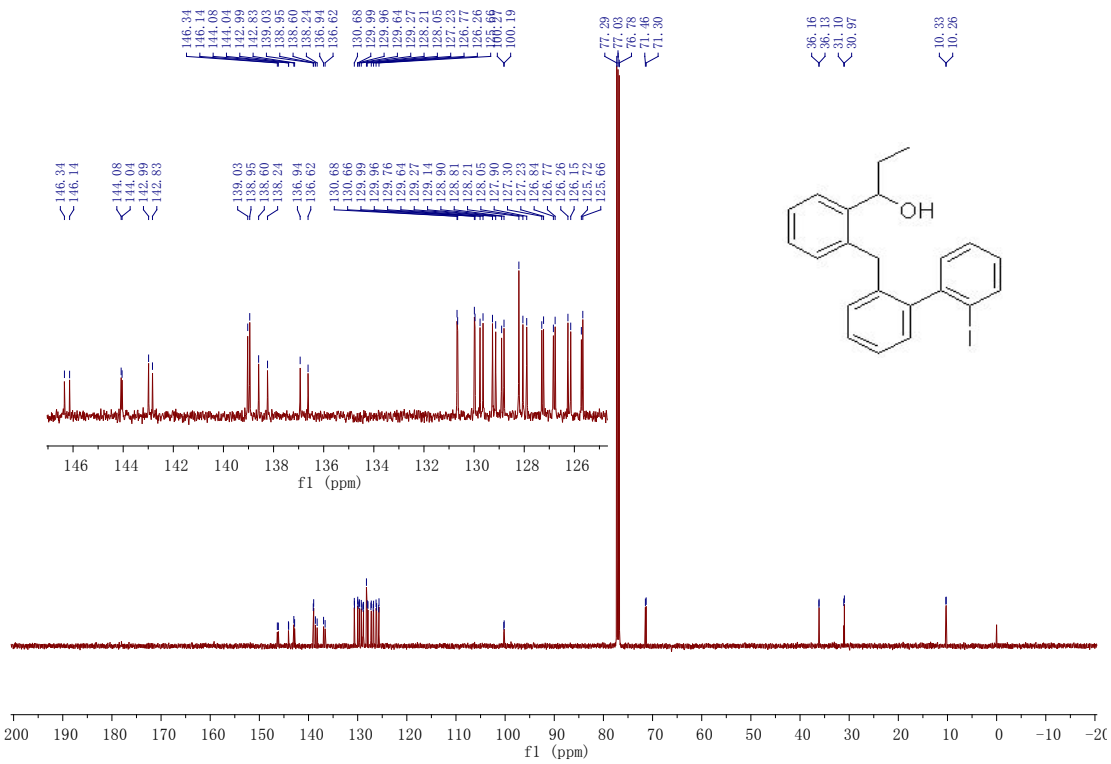


1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)propan-1-ol(12)

^{1}H NMR (500 MHz, $CDCl_3$)

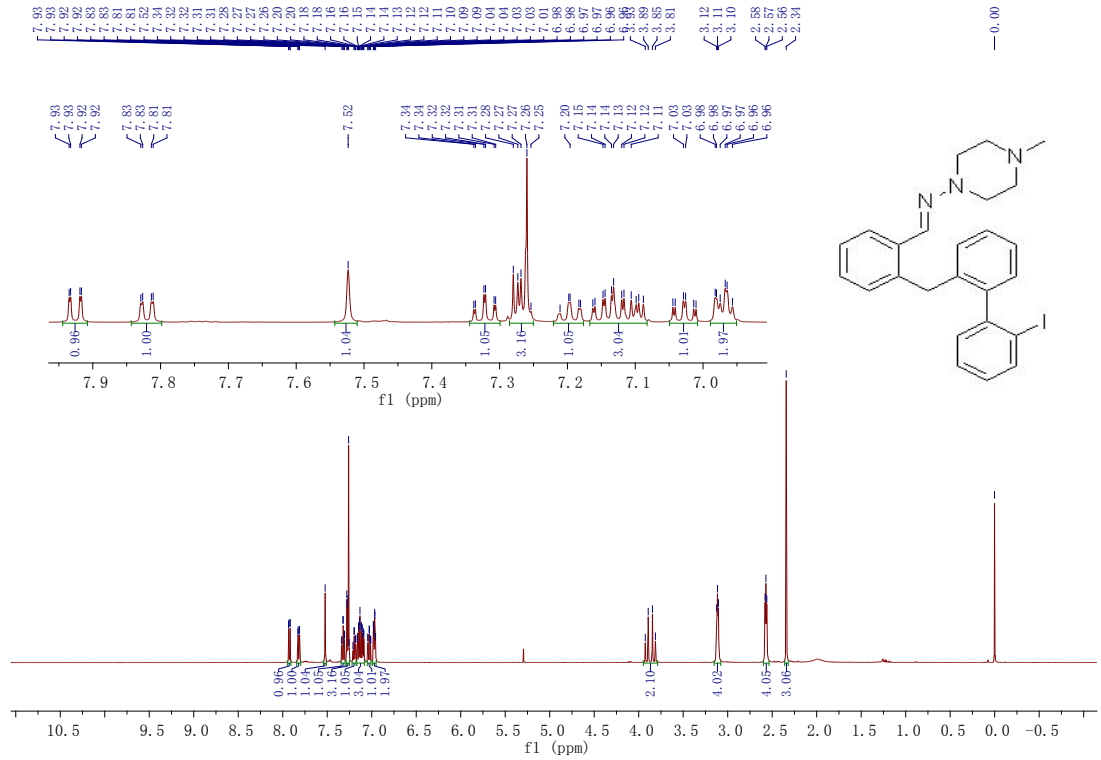


^{13}C NMR (126 MHz, $CDCl_3$)

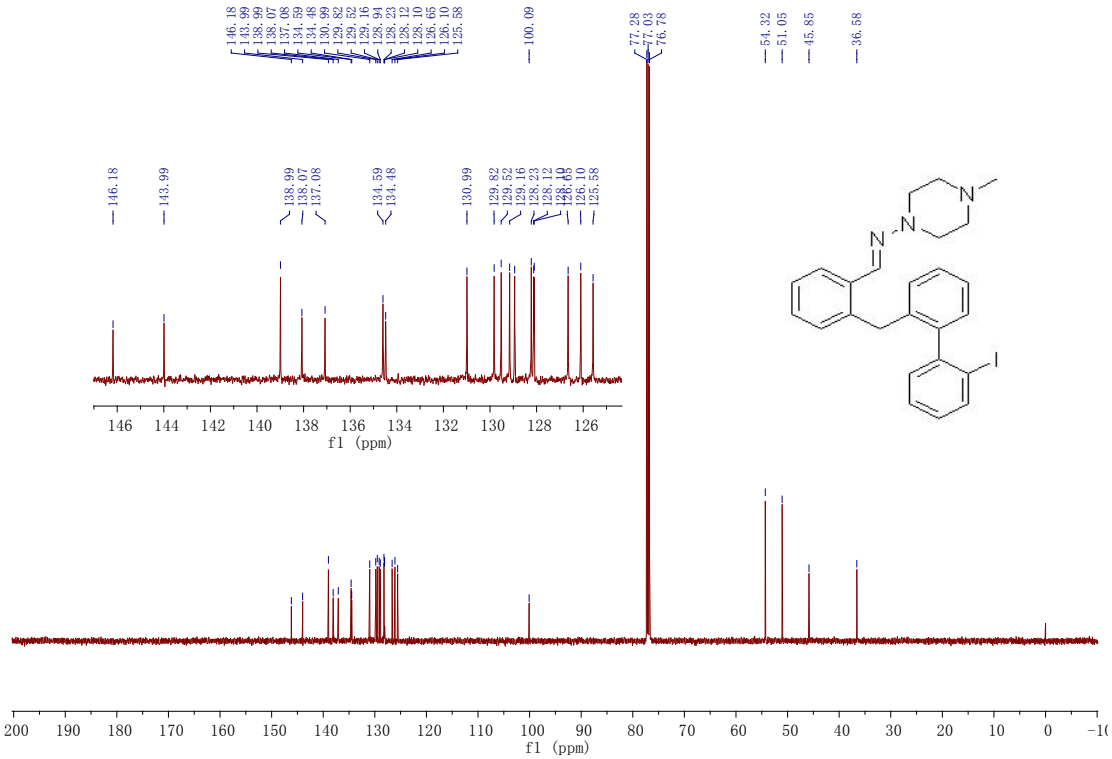


(*E*)-1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)-*N*-(4-methylpiperazin-1-yl)methanimine (13)

^{1}H NMR (500 MHz, $CDCl_3$)

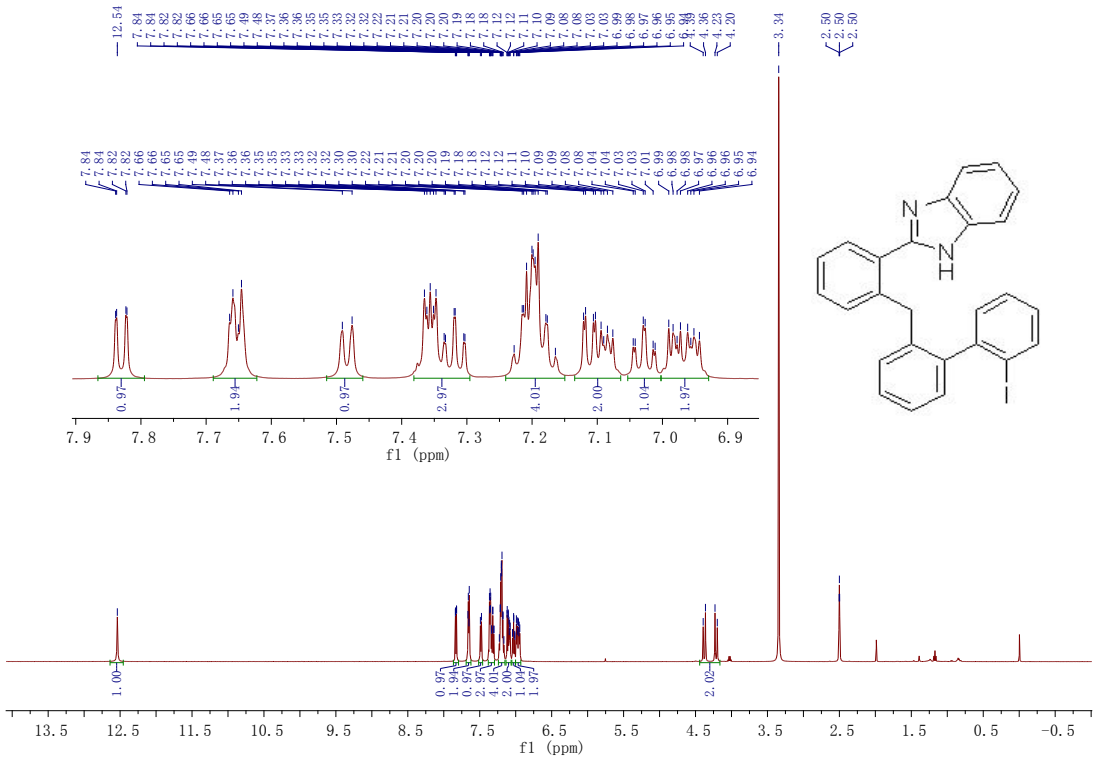


^{13}C NMR (126 MHz, $CDCl_3$)

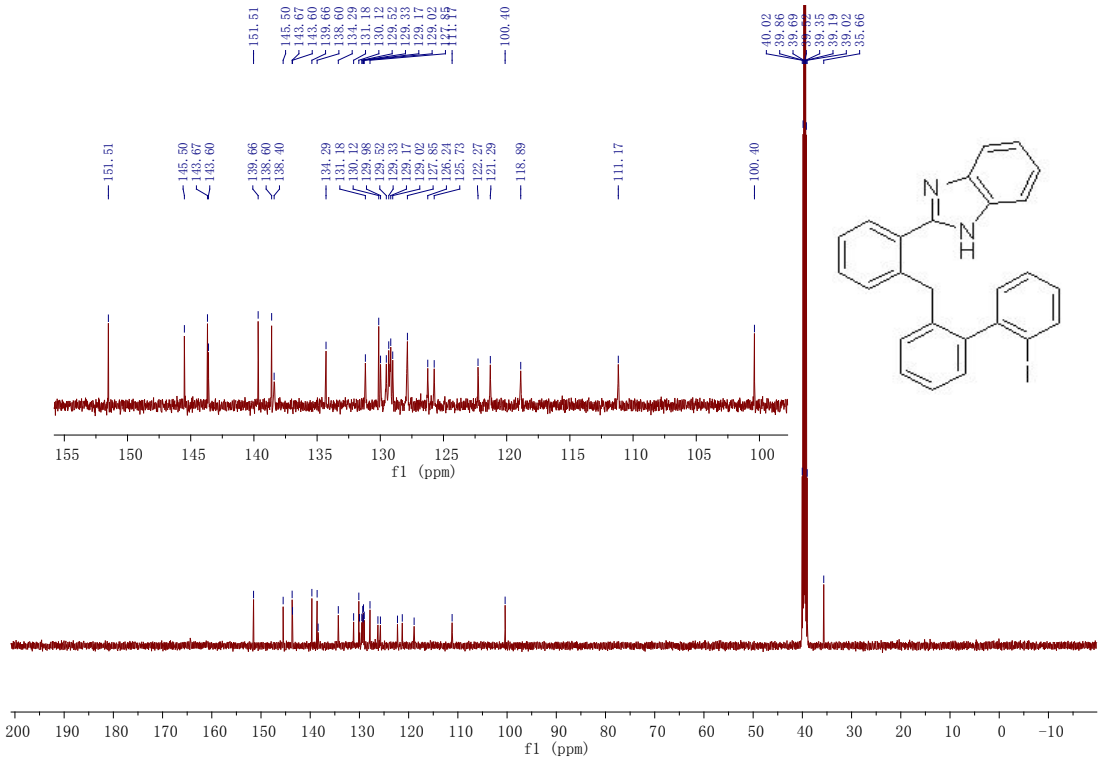


2-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)-1*H*-benzo[d]imidazole(14)

^{1}H NMR (500 MHz, DMSO-d_6)

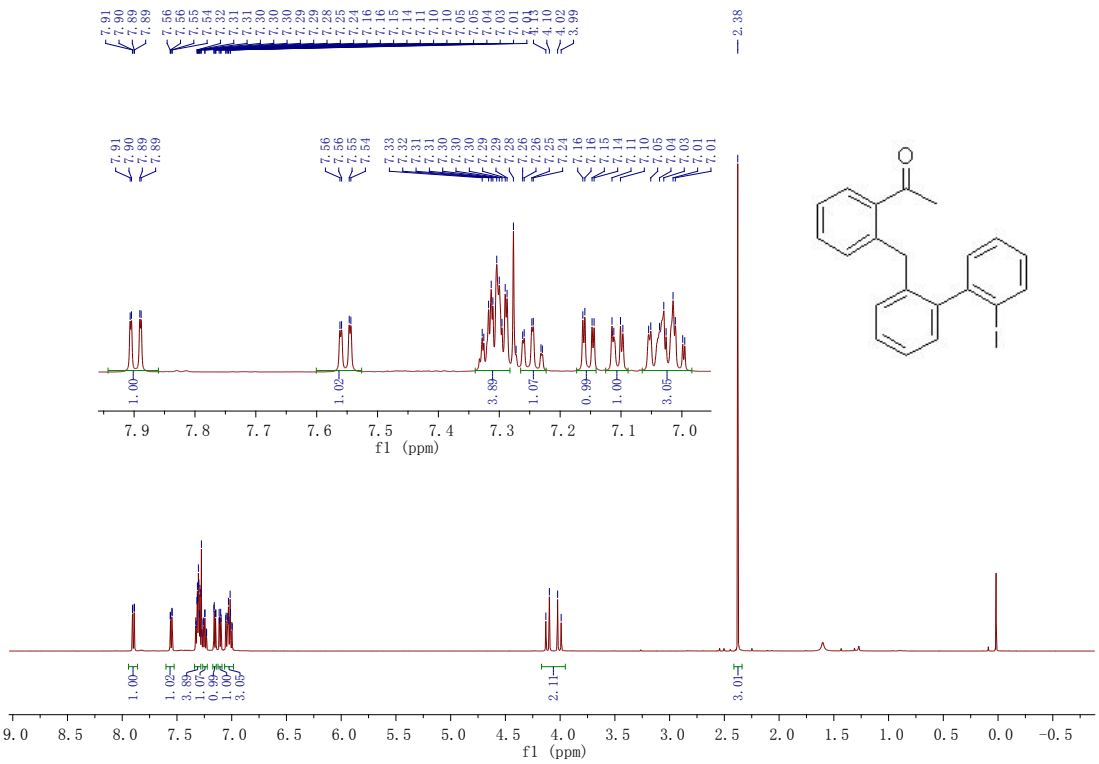


^{13}C NMR (126 MHz, DMSO-d_6)



1-(2-((2'-iodo-[1,1'-biphenyl]-2-yl)methyl)phenyl)ethan-1-one--1-(*o*-tolyl)-ethan-1-one(17)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)