

Supplementary information

NHCs-catalyzed enantioselective synthesis of biaryl axially chiral imides

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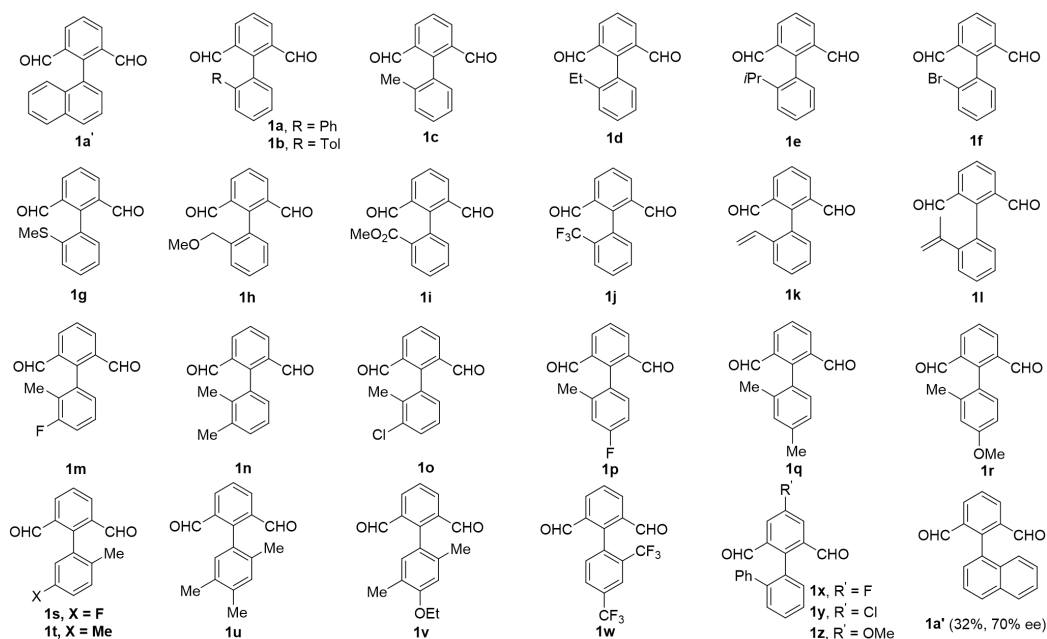
I. General Information.

All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^1H , ^{13}C , ^{19}F spectra were recorded with Varian 500 MHz (Inova-500) or Bruker 600 MHz (Avance-600) instrument. Chemical shifts were referenced to $\delta_{\text{TMS}} = 0.00$ ppm (^1H , ^{13}C). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane- d_2 (δ (^1H) = 5.32 ppm, δ (^{13}C) = 53.8 ppm), chloroform- d_1 (δ (^1H) = 7.26 ppm, δ (^{13}C) = 77.2 ppm) or methanol- d_4 (δ (^1H) = 3.31 ppm, δ (^{13}C) = 49.0 ppm) were used as solvents. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = triplet of doublet, td = doublet of triplet, bs = broad singlet. High-pressure liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound. High-resolution mass spectra HRMS (ESI-TOF) were recorded on Bruker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 $\times$ 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light. Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{25} = (c: \text{g}/100 \text{ mL in } \text{CH}_2\text{Cl}_2)$.

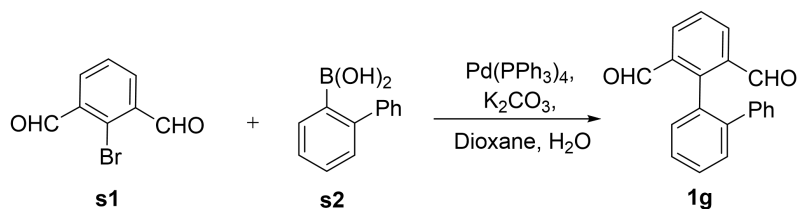
II. Experimental Section

2.1 Synthesis of Starting Materials

2.1.1 List of starting materials

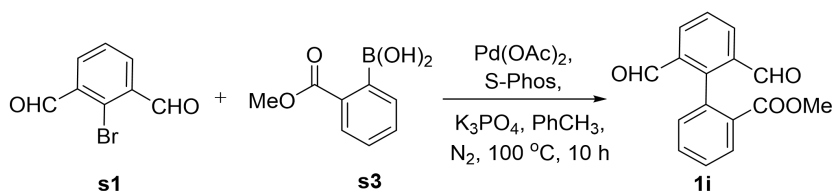


2.1.2 General procedure for the synthesis of Substrates 1a', 1a-h and 1j-w.^[1] Preparation of 1a is shown as a representative example.



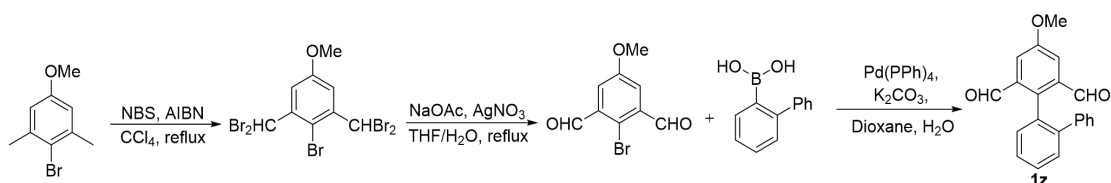
A 250 mL round-bottom Schlenk flask was charged with 2-bromoisophthalaldehyde (2.13 g, 10.0 mmol), 2-biphenylboronic acid (4.536 g, 22.9 mmol), K_2CO_3 (9.59 g, 68.9 mmol) and $\text{Pd(PPh}_3)_4$ (0.21 g, 0.18 mmol) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane (112 mL) and water (15 mL) were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous MgSO_4 . The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (2.3 g, yield: 81 %).

2.1.3 Procedure for the synthesis of Substrates 1i.



A 25 mL round-bottom Schlenk flask was charged with 2-bromoisophthalaldehyde **s1** (0.639 g, 3.0 mmol), 2-methoxycarbonylphenylboronic acid **s3** (1.35 g, 2.5 equiv), S-Phos (0.124 g, 10 mol%), K_3PO_4 (3.82 g, 6.0 equiv) and Pd(OAc)_2 (0.034 g, 5 mol%) and was evacuated and charged with argon three times. Then degassed toluene (12 mL) were added and the reaction was heated at 100 °C for 10 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous MgSO_4 . The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (0.57 g, yield: 71 %).

2.1.4 General procedure for the synthesis of Substrates 1x-z.^[5b] Preparation of 1z is shown as a representative example.



2-bromo-5-methoxy-1,3-dimethylbenzene (5 mmol), NBS (4.5 equiv.) and AIBN (50 mol%) cat. were dissolved in CCl_4 (50 mL) and refluxed for 16 h. The mixture was cooled and the precipitated succinimide was removed by filtration. The solvent was removed under reduced pressure to give a brown oil which was purified by flash column chromatography (petroleum ether) to give the

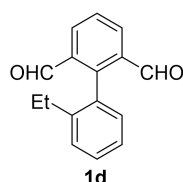
corresponding brominated compound (69% yield);

2-bromo-1,3-bis(dibromomethyl)-5-methoxybenzene (3.4 mmol), sodium acetate (8.5 equiv.) and silver nitrate (16.1 equiv.) were dissolved in a mixture of THF and H₂O (5:1). The mixture was heated at reflux for 24 h. The inorganic precipitate was filtered, washed, and the solvent was removed in vacuo. The crude mixture was purified by flash column chromatography (ethyl acetate : petroleum ether = 1:10 to 1:20) to give the 2-bromo-5-methoxyisophthalaldehyde (92% yield);

2-bromo-5-methoxyisophthalaldehyde (3.1 mmol), 2-biphenylboronic acid (2.29 equiv), K₂CO₃ (9.59 g, 6.89 equiv) and Pd(PPh₃)₄ (0.018 mmol) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane (33 mL) and water (5 mL) were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : petroleum ether = 1:20 to 1:10) and washed with ethanol to give compound as a light yellow solid (0.5 g, yield: 51 %).

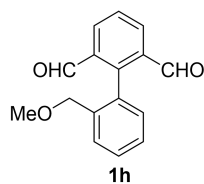
2.1.5 Characterization data of the substrates

2'-ethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



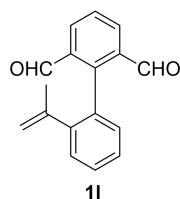
1d: light green solid; ¹H NMR (600 MHz, Chloroform-*d*) δ 9.71 (d, *J* = 0.8 Hz, 2H), 8.27 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.1, 147.9, 143.0, 134.9, 132.7, 131.7, 130.9, 129.7, 128.9, 128.6, 126.1, 26.7, 14.7. HRMS (ESI-TOF) (*m/z*): Calcd for C₁₆H₁₄NaO₂, ([M + Na]⁺), 261.0886; found 261.0882.

2'-(methoxymethyl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



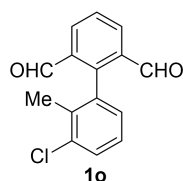
1h: white solid; ¹H NMR (600 MHz, Chloroform-*d*) δ 9.64 (d, *J* = 1.0 Hz, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.68 (td, *J* = 7.8, 1.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.34 – 7.28 (m, 1H), 4.06 (s, 2H), 3.06 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.6, 146.2, 136.9, 134.9, 132.9, 132.2, 130.8, 129.7, 129.4, 128.6, 128.2, 72.8, 58.1. HRMS (ESI-TOF) (*m/z*): Calcd for C₁₆H₁₄NaO₃, ([M + Na]⁺), 277.0835; found 277.0827.

2'-(prop-1-en-2-yl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



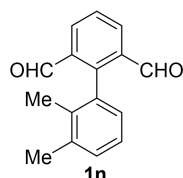
11: white solid; ^1H NMR (600 MHz, Chloroform-*d*) δ 9.76 (s, 2H), 8.24 (d, J = 7.7 Hz, 2H), 7.65 (t, J = 7.7 Hz, 1H), 7.50 (td, J = 7.6, 1.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.30 – 7.22 (m, 1H), 5.02 (t, J = 1.6 Hz, 1H), 4.82 (s, 1H), 1.56 (t, J = 1.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.8, 147.7, 144.6, 144.5, 134.6, 132.5, 131.5, 129.9, 129.5, 128.8, 128.5, 127.2, 118.4, 23.2. HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{17}\text{H}_{14}\text{NaO}_2$, ($[\text{M} + \text{Na}]^+$), 273.0886; found 273.0887.

3'-chloro-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



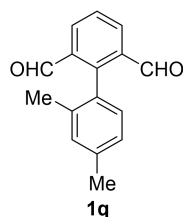
10: white solid; ^1H NMR (600 MHz, Chloroform-*d*) δ 9.71 (s, 2H), 8.28 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.3, 146.7, 135.9, 134.5, 134.3, 133.0, 130.3, 129.1, 128.9, 126.8, 117.1, 18.00. HRMS(ESI-TOF) (m/z): Calcd for $\text{C}_{15}\text{H}_{11}\text{ClNaO}_2$, ($[\text{M} + \text{Na}]^+$), 281.0340; found 281.0341.

2'-ethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1n: white solid; ^1H NMR (600 MHz, Chloroform-*d*) δ 9.70 (s, 2H), 8.26 (d, J = 7.7 Hz, 2H), 7.66 (s, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 2.37 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.0, 148.7, 137.7, 135.5, 134.7, 132.5, 132.2, 130.8, 128.6, 128.3, 125.6, 20.4, 17.1. HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_{14}\text{NaO}_2$, ($[\text{M} + \text{Na}]^+$), 261.0886; found 261.0882.

2',4'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde

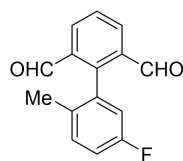


1q: white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.79 (s, 2H), 8.32 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 7.7 Hz, 1H), 7.26 (s, 1H), 7.23 – 7.20 (m, 2H), 2.49 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (150 MHz,

Chloroform-*d*) δ 190.9, 148.1, 139.1, 136.6, 134.8, 132.6, 131.1, 130.6, 129.1, 128.3, 126.7, 21.2, 20.3.

HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ($[M + Na]^+$), 261.0886; found 261.0887.

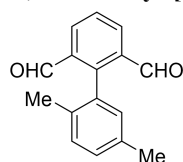
5'-fluoro-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1s

1s: light yellow solid; 1H NMR (600 MHz, Chloroform-*d*) δ 9.72 (d, $J = 0.9$ Hz, 2H), 8.28 (d, $J = 7.7$ Hz, 2H), 7.70 (td, $J = 7.8, 0.9$ Hz, 1H), 7.33 (dd, $J = 8.6, 5.6$ Hz, 1H), 7.14 (td, $J = 8.4, 2.7$ Hz, 1H), 7.00 (dd, $J = 8.6, 2.8$ Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.3, 160.8 ($J = 247.6$ Hz), 146.3, 134.3, 134.0 ($J = 8.1$ Hz), 133.0, 132.7 ($J = 3.5$ Hz), 131.9 (d, $J = 8.2$ Hz), 128.9, 117.5 ($J = 21.3$ Hz), 116.3 (d, $J = 20.9$ Hz), 19.6. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.45 (s, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{11}FNaO_2$, ($[M + Na]^+$), 265.0635; found 265.0635.

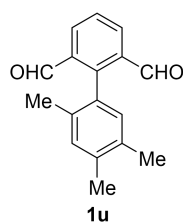
2',5'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1t

1t: light yellow solid; 1H NMR (600 MHz, Chloroform-*d*) δ 9.71 (s, 2H), 8.26 (d, $J = 7.7$ Hz, 2H), 7.65 (t, $J = 7.7$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.05 (s, 1H), 2.36 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.1, 148.3, 135.6, 134.6, 133.7, 132.6, 131.9, 131.3, 130.2, 130.1, 128.4, 20.9, 19.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ($[M + Na]^+$), 261.0886; found 261.0894.

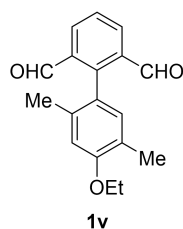
2',4',5'-trimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1u

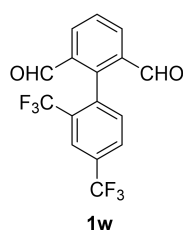
1u: white solid; 1H NMR (600 MHz, Chloroform-*d*) δ 9.72 (d, $J = 0.9$ Hz, 2H), 8.24 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.3, 148.4, 137.8, 134.7, 134.2, 134.0, 132.5, 131.9, 131.6, 129.3, 128.2, 19.7, 19.5, 19.2. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}NaO_2$, ($[M + Na]^+$), 275.1043; found 275.1038.

4'-ethoxy-2',5'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



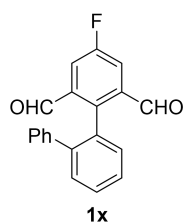
1v: light green solid; ^1H NMR (600 MHz, Chloroform-*d*) δ 9.74 (d, J = 0.9 Hz, 2H), 8.23 (d, J = 7.7 Hz, 2H), 7.63 (dd, J = 8.2, 7.2 Hz, 1H), 6.98 (s, 1H), 6.76 (s, 1H), 4.10 (d, J = 7.0 Hz, 2H), 2.22 (s, 3H), 2.00 (s, 3H), 1.48 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.5, 157.7, 148.4, 135.3, 135.1, 132.8, 132.5, 128.1, 124.6, 123.1, 112.5, 63.7, 20.5, 15.8, 14.9. HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{18}\text{H}_{18}\text{NaO}_3$, ($[\text{M} + \text{Na}]^+$), 305.1148; found 305.1168.

2',4'-bis(trifluoromethyl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



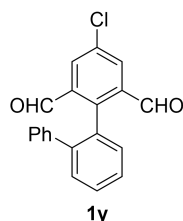
1w: white solid; ^1H NMR (600 MHz, Chloroform-*d*) δ 9.68 (s, 2H), 8.27 (d, J = 7.7 Hz, 2H), 8.13 (s, 1H), 7.95 (dd, J = 8.0, 1.8 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.2, 141.1, 137.1, 134.7, 134.1, 132.6, 131.8 (J = 34.3 Hz), 130.5 (J = 30.4 Hz), 131.0, 128.6 (J = 3.6 Hz), 123.1 (J = 271.7 Hz), 122.9 (J = 272.3 Hz), 123.7 – 123.6 (m, J = 4.7 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -59.73 (s, 1CF₃), -62.93 (s, 1CF₃). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{16}\text{H}_8\text{F}_6\text{NaO}_2$, ($[\text{M} + \text{Na}]^+$), 369.0321; found 369.0324.

4-fluoro-[1,1':2',1''-terphenyl]-2,6-dicarbaldehyde



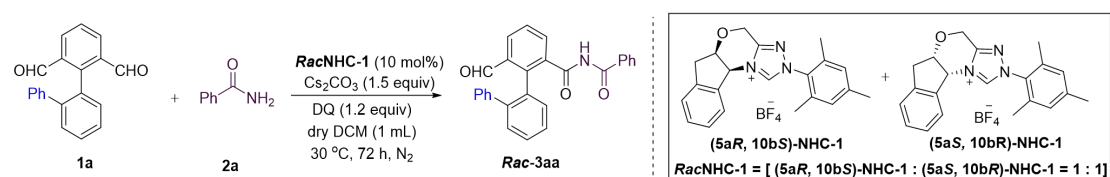
1x: white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.78 (d, J = 3.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.63 (td, J = 7.6, 1.4 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.39 (dd, J = 7.6, 1.3 Hz, 1H), 7.19 – 7.17 (m, 3H), 6.95 (dd, J = 6.7, 2.9 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.2, 162.2 (J = 250.4 Hz), 143.4 (J = 3.5 Hz), 143.1, 139.4, 136.9 (J = 5.7 Hz), 132.0, 130.5, 130.2, 130.0, 129.3, 128.5, 127.6 (J = 13.8 Hz), 119.1, 118.9. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.76. (s, 1F). HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{20}\text{H}_{13}\text{FNaO}_2$, ($[\text{M} + \text{Na}]^+$), 327.0792; found 327.0788.

4-chloro-[1,1':2',1''-terphenyl]-2,6-dicarbaldehyde



1y: white solid; ¹H NMR (500 MHz, Chloroform-*d*) δ 9.77 (s, 2H), 8.03 (s, 2H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.38 – 7.36 (m, 1H), 7.19 – 7.18 (m, 3H), 6.97 – 6.95 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 189.2, 145.4, 142.9, 139.3, 136.1, 135.3, 132.1, 131.9, 130.5, 130.1, 130.1, 129.3, 128.6, 127.6, 127.6. HRMS (ESI-TOF) (*m/z*): Calcd for C₂₀H₁₃ClNaO₂, ([*M* + Na]⁺), 343.0496; found 343.0498.

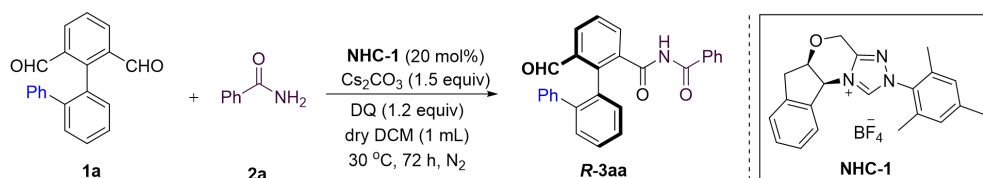
2.2 General Synthetic Procedure of 3.



Racemic Synthesis:

Preparation of **RacNHC-1**: (5a*R*, 10b*S*)-NHC-1 (100 mg) and (5a*S*, 10b*R*)-NHC-1 (100 mg) are completely dissolved in dry DCM and concentrated to remove DCM.

Representative Synthesis of Product (Rac)-3aa. In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **RacNHC-1** (10 mol%, 4.18 mg), Cs₂CO₃ (49.0 mg, 1.5 equiv), [1,1':2',1''-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg) and anhydrous dichloromethane (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of Benzamide **2a** (36.3 mg, 3.0 equiv) and 3,3',5,5'-tetra-*tert*-butyldiphenylquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 30 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 4:1 (v/v) to give the racemic product **Rac-3aa**.

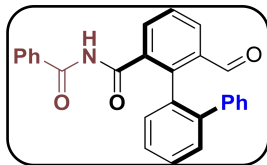


Asymmetric Synthesis:

Representative Synthesis of Product R-3aa (standard conditions A): In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **NHC-1** (20 mol%, 8.36 mg), Cs₂CO₃ (49.0 mg, 1.5 equiv), [1,1':2',1''-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg) and anhydrous dichloromethane (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of Benzamide **2a** (36.3 mg, 3.0 equiv) and 3,3',5,5'-tetra-*tert*-butyldiphenylquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction

mixture was stirred at 30 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 4:1 (v/v) to give the product *R*-**3aa**.

(*R*)-*N*-benzoyl-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3aa**)**

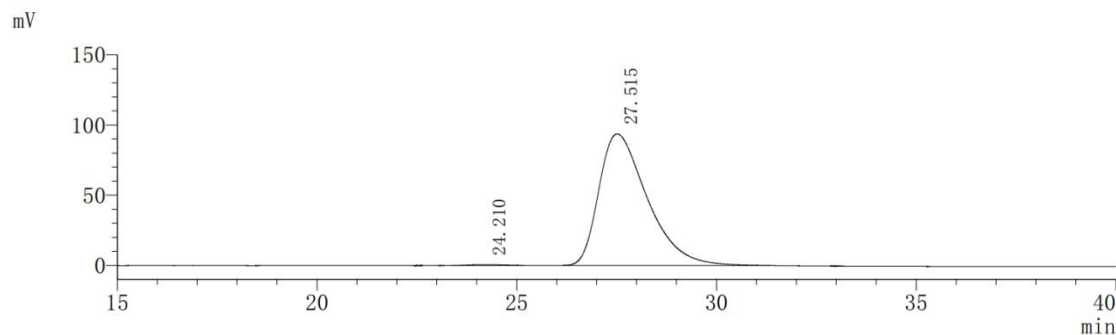
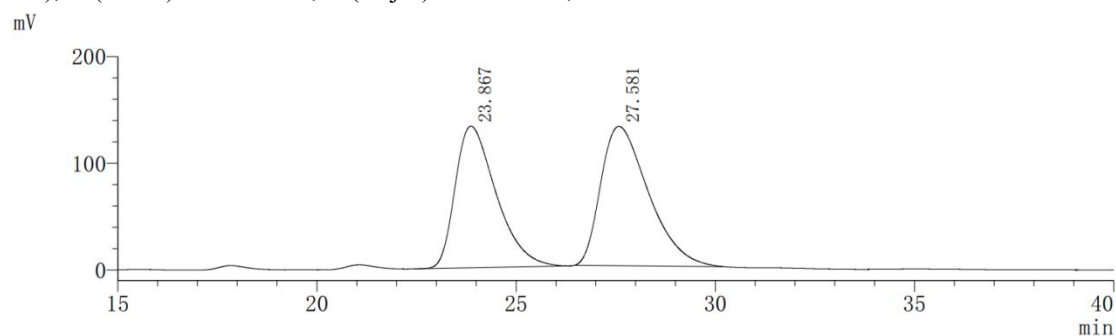


The title compound **3aa** was obtained as a yellow solid (30.4 mg, 75%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 0.9 Hz, 1H), 8.79 (s, 1H), 7.97 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.51 – 7.43 (m, 4H), 7.40 – 7.35 (m, 3H), 7.15 (s, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 168.7, 165.2, 142.7, 142.6, 139.7, 136.9, 134.6, 133.5, 133.2, 132.5, 131.2, 130.7, 130.0, 129.8, 129.6, 129.0, 128.5, 128.1, 127.9, 127.9, 127.5.

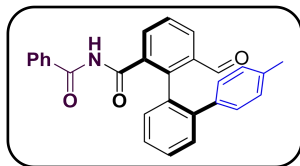
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₂₀NO₃, ([*M* + *H*]⁺), 406.1438; found 406.1428.

[α]_D²⁰ = -51.7 (*c* = 1.52, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 24.21 min, *t*_R (major) = 27.52 min, 99% ee.



(R)-N-benzoyl-6-formyl-4''-methyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ba)

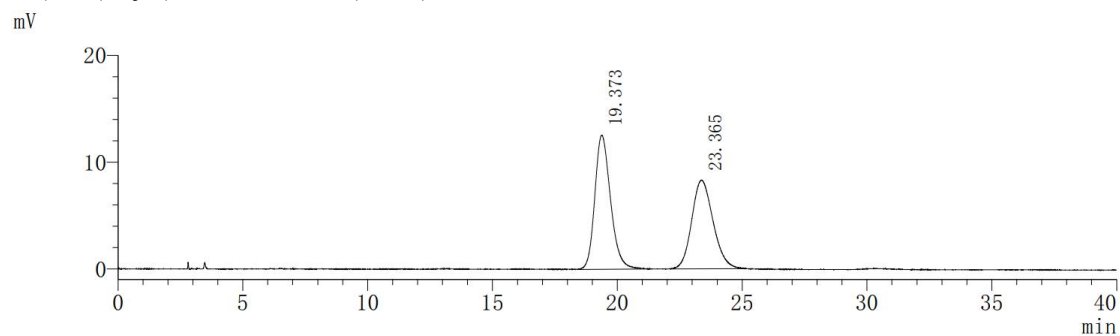


The title compound **3ba** was obtained as a yellow solid (24.3 mg, 58%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 8.77 (s, 1H), 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.45 – 7.41 (m, 3H), 7.39 – 7.33 (m, 3H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.20 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 191.1, 168.6, 165.1, 142.9, 142.6, 137.3, 136.7, 136.7, 134.5, 133.4, 133.3, 133.3, 132.4, 131.3, 130.7, 130.0, 129.6, 129.6, 129.3, 129.0, 128.1, 127.9, 127.7, 21.2.

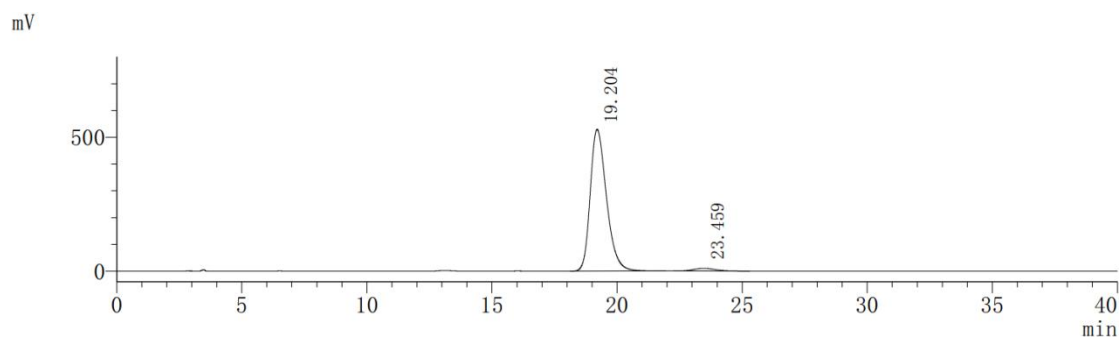
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₁NNaO₃, ([*M* + Na]⁺), 442.1414; found 442.1419.

[α]_D²⁰ = -86.7 (*c* = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 19.20 min, *t*_R (minor) = 23.46 min, 95% ee.

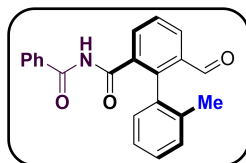


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	19.373	M	1.1120	551764	12570	52.8151
2	23.365	M	1.5260	492945	8298	47.1849



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	19.204	M	1.1672	23957937	529571	97.4260
2	23.459	M	1.5825	632981	10409	2.5740

(R)-N-benzoyl-6-formyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3ca)

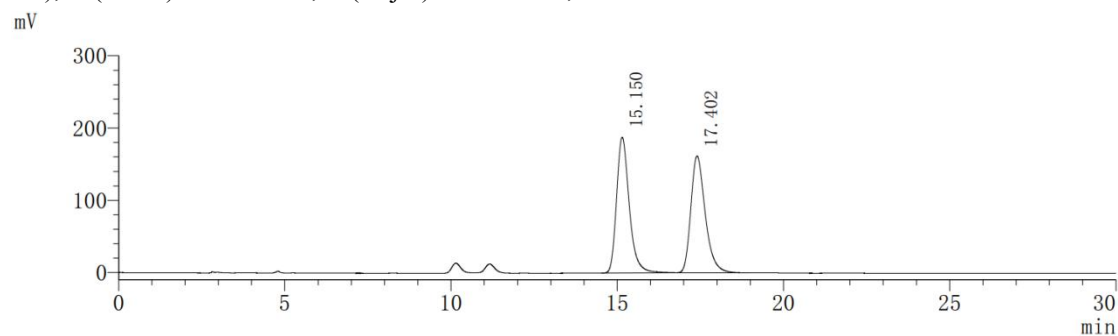


The title compound **3ca** was obtained as a yellow solid (24.7 mg, 72%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (s, 1H), 8.48 (s, 1H), 8.18 – 8.16 (m, 1H), 7.98 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 5.9, 3.0 Hz, 1H), 7.39 – 7.38 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.25 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 2.09 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.4, 168.6, 165.1, 141.7, 137.5, 136.8, 134.4, 134.4, 133.9, 133.4, 132.5, 131.0, 130.3, 130.0, 129.5, 128.9, 128.6, 127.7, 126.4, 20.3.

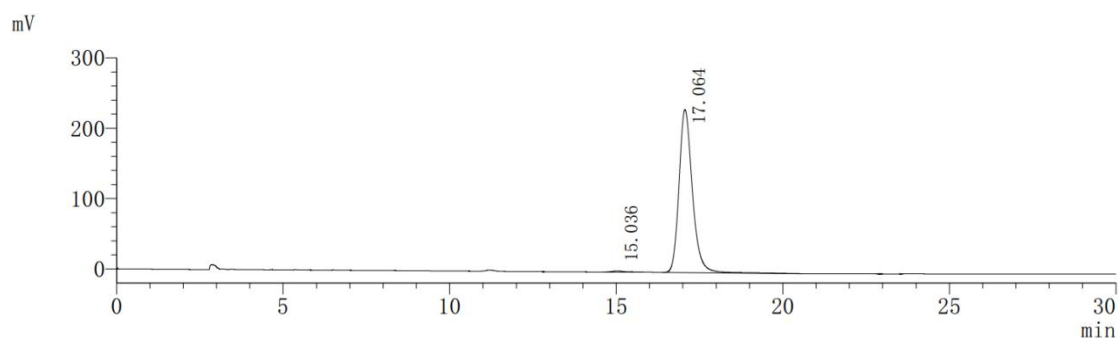
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₂H₁₈NO₃, ([M + H]⁺), 344.1281; found 344.1291.

[α]_D²⁰ = -22.5 (*c* = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 15.04 min, *t*_R (major) = 17.06 min, 99% ee.

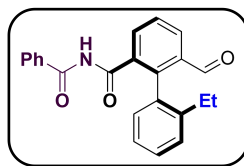


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.150	M	0.6748	4988500	187820	50.6111
2	17.402	M	0.7755	4868029	161574	49.3889



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.036	M	0.5956	42974	1677	0.6565
2	17.064	M	0.7136	6502538	231817	99.3435

(R)-N-benzoyl-2'-ethyl-6-formyl-[1,1'-biphenyl]-2-carboxamide (3da)

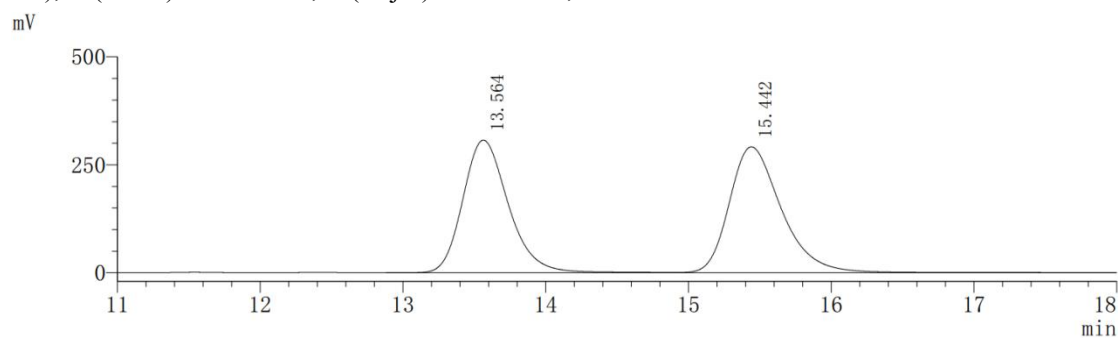


The title compound **3da** was obtained as a yellow solid (25.0 mg, 70%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (d, *J* = 0.8 Hz, 1H), 8.47 (s, 1H), 8.18 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.66 (td, *J* = 7.8, 0.9 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.40 – 7.33 (m, 6H), 7.26 – 7.24 (m, 1H), 7.22 – 7.19 (m, 1H), 2.48 – 2.36 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.4, 168.1, 165.0, 143.4, 141.5, 136.6, 134.7, 134.2, 133.7, 133.4, 132.6, 130.4, 130.1, 129.8, 129.6, 128.9, 128.6, 127.7, 126.4, 26.3, 14.5.

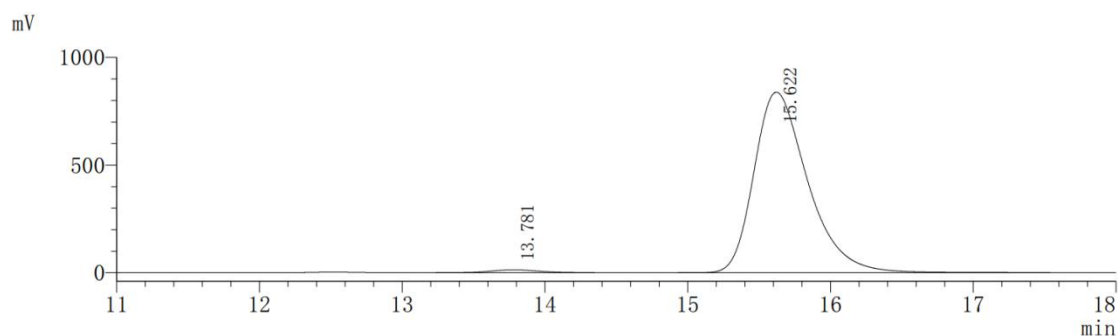
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₀NO₃, ([M + H]⁺), 358.1438; found 358.1445.

[α]_D²⁰ = 39.8 (*c* = 1.3, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 13.78 min, t_R (major) = 15.62 min, 97% ee.

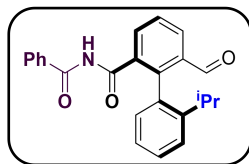


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.564	M	0.5710	6840949	307128	47.8647
2	15.442	M	0.6485	7451319	291587	52.1353



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.781	M	0.6096	306626	13342	1.3778
2	15.622	M	0.6711	21948915	838586	98.6222

(R)-N-benzoyl-6-formyl-2'-isopropyl-[1,1'-biphenyl]-2-carboxamide (3ea)

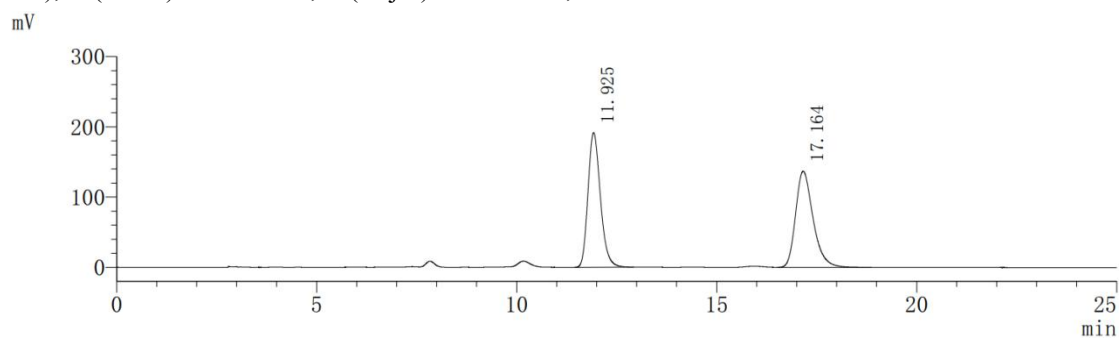


The title compound **3ea** was obtained as a white solid (28.5 mg, 77%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.60 (s, 1H), 8.54 (s, 1H), 8.18 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 7.0, 1.7 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 7.23 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.18 (td, *J* = 7.3, 1.4 Hz, 1H), 2.75 – 2.68 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.3, 167.6, 165.0, 148.5, 141.7, 136.4, 135.0, 134.2, 133.4, 133.0, 132.7, 130.3, 130.2, 130.1, 128.9, 128.6, 127.7, 126.9, 126.3, 30.5, 24.6, 23.3.

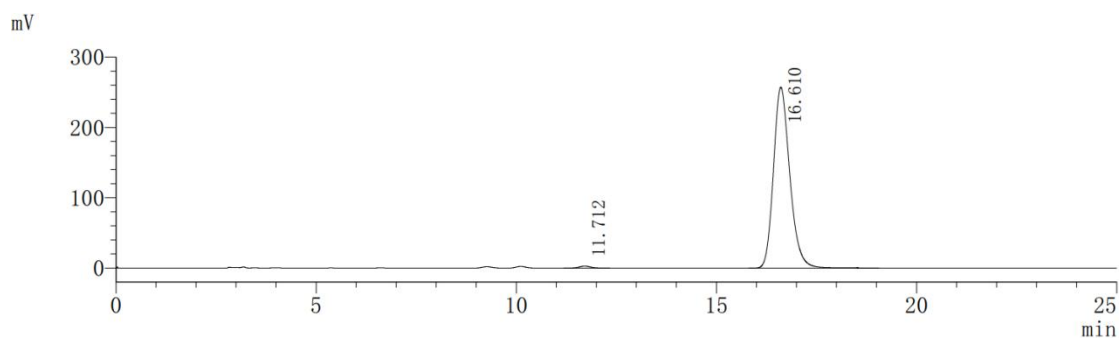
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₂NO₃, ([*M* + *H*]⁺), 372.1594; found 372.1596.

[α]_D²⁰ = 43.4 (*c* = 1.4, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 11.71 min, *t*_R (major) = 16.61 min, 98% ee.

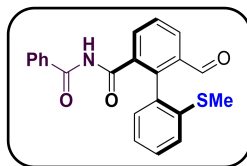


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.925	M	0.5606	4141259	191719	49.8980
2	17.164	M	0.7804	4158187	136984	50.1020



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.712	M	0.5117	58382	2923	0.7928
2	16.610	M	0.7334	7305458	257390	99.2072

(R)-N-benzoyl-6-formyl-2'-(methylthio)-[1,1'-biphenyl]-2-carboxamide (3ga)

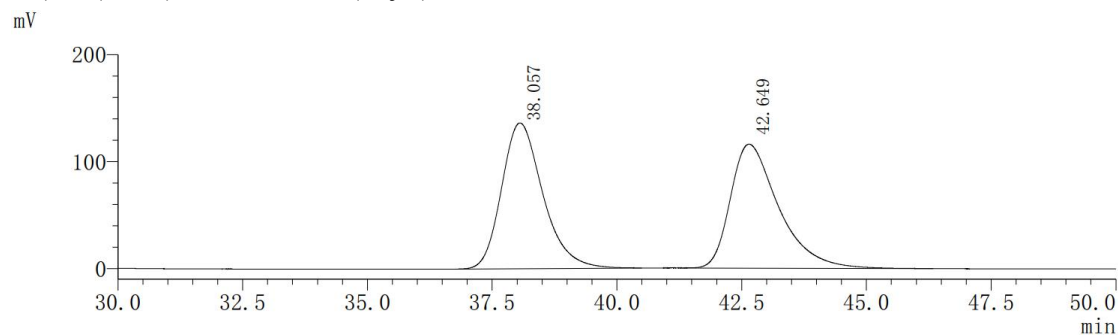


The title compound **3ga** was obtained as a light yellow solid (28.1 mg, 75%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 8.81 (s, 1H), 8.18 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.04 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.49 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.27 – 7.22 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 166.8, 165.0, 139.7, 138.0, 136.8, 134.8, 134.6, 133.1, 133.1, 132.4, 130.8, 130.2, 130.2, 129.5, 128.8, 127.7, 125.7, 123.5, 14.7.

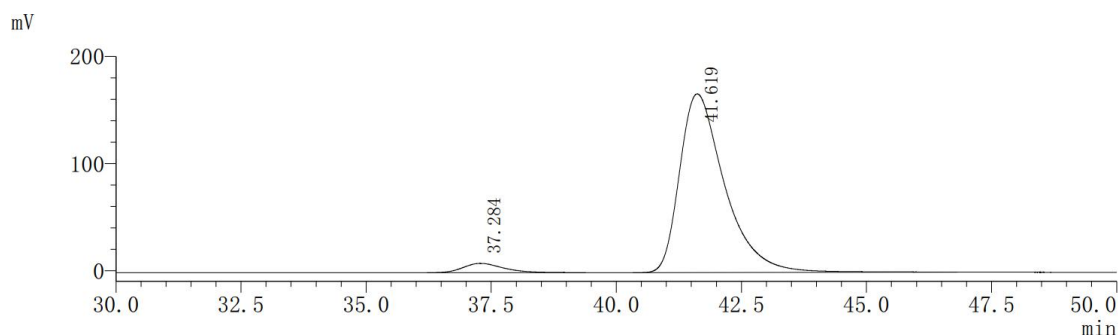
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₂H₁₈NO₃S, ([M + Na]⁺), 376.1002; found 376.1003.

[α]_D²⁰ = 60.8 (*c* = 1.4, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 37.28 min, t_R (major) = 41.62 min, 91% ee.

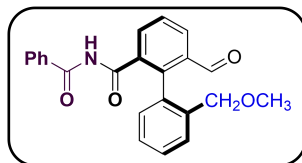


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	38.057	M	1.4857	7841392	136344	50.1366
2	42.649	M	1.7254	7798678	115971	49.8634



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	37.284	M	1.4225	483989	8683	4.4187
2	41.619	M	1.5986	10469121	166881	95.5813

(R)-N-benzoyl-6-formyl-2'-(methoxymethyl)-[1,1'-biphenyl]-2-carboxamide (3ha)



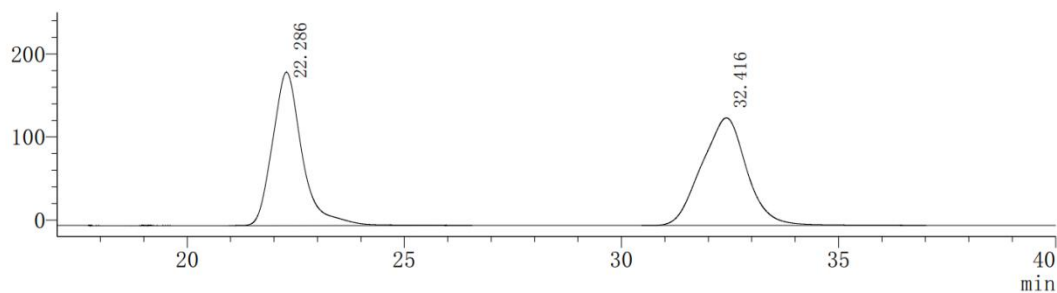
The title compound **3ha** was obtained as a light yellow oil (24.6 mg, 66%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.80 (s, 1H), 9.63 (d, J = 0.9 Hz, 1H), 8.15 (dd, J = 7.9, 1.5 Hz, 1H), 8.03 (dd, J = 7.7, 1.5 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.51 – 7.48 (m, 1H), 7.46 – 7.32 (m, 8H), 4.29 – 4.24 (m, 2H), 2.95 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.2, 167.6, 165.9, 140.6, 137.6, 135.7, 135.5, 134.9, 133.3, 133.2, 132.8, 130.6, 129.9, 129.9, 129.8, 129.6, 128.9, 128.3, 128.0, 74.1, 58.8.

HRMS (ESI-TOF) (m/z): Calcd for C₂₃H₁₉NNaO₃, ([M + Na]⁺), 396.1206; found 396.1207.

[α]_D²⁰ = 47.8 (c = 1.2, CH₂Cl₂).

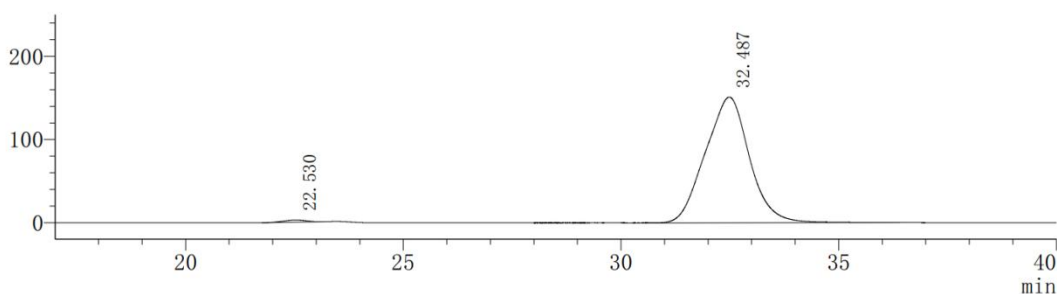
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 22.53 min, t_R (major) = 32.49 min, 98% ee.

mV



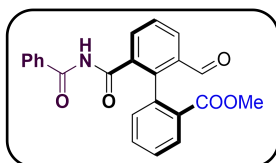
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.286	M	1.2212	8737901	184760	48.2250
2	32.416	M	2.0306	9381109	129632	51.7750

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.530	M	1.0322	98765	2745	0.9176
2	32.487	M	1.9652	10664757	151208	99.0824

methyl (*R*)-2'-(benzoylcarbamoyl)-6'-formyl-[1,1'-biphenyl]-2-carboxylate (3ia**)**

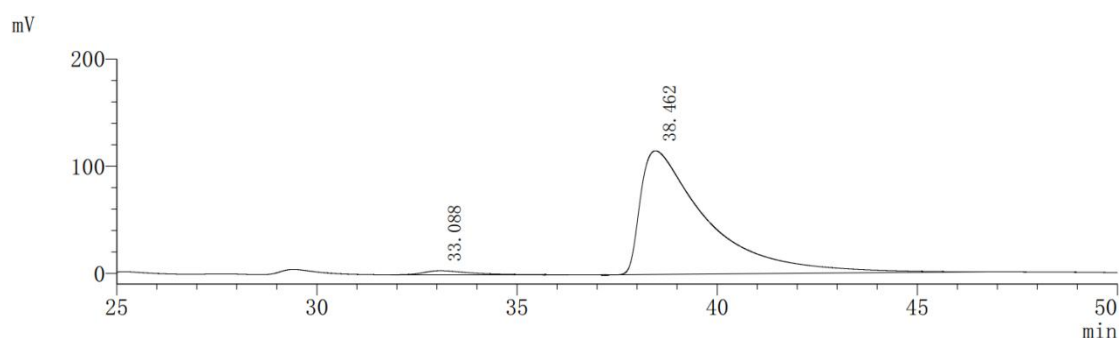
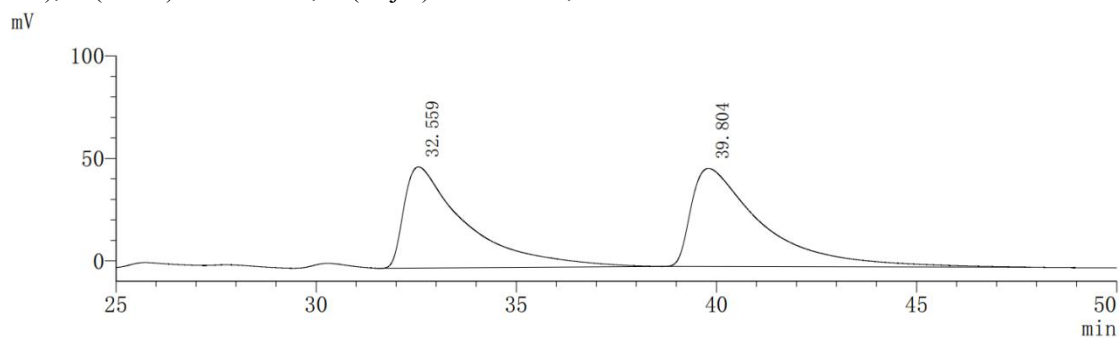


The title compound **3ia** was obtained as a light yellow solid (23.6 mg, 61%). **¹H NMR (600 MHz, Chloroform-*d*)** δ 9.57 (d, J = 0.7 Hz, 1H), 9.43 (s, 1H), 8.10 (dd, J = 7.8, 1.4 Hz, 1H), 7.92 (dd, J = 7.6, 1.4 Hz, 1H), 7.80 (dd, J = 7.8, 1.3 Hz, 1H), 7.66 (td, J = 7.7, 0.8 Hz, 1H), 7.58 (td, J = 7.6, 1.3 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.46 (td, J = 7.7, 1.3 Hz, 1H), 7.38 – 7.34 (m, 3H), 3.71 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 190.4, 168.9, 167.5, 165.1, 141.3, 137.0, 136.1, 134.0, 133.4, 133.1, 132.9, 132.9, 131.8, 131.2, 130.4, 129.8, 129.3, 128.8, 128.7, 127.8, 53.0.

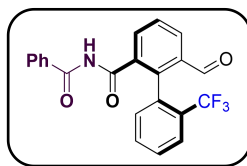
HRMS (ESI-TOF) (m/z): Calcd for C₂₃H₁₇NNaO₅, ([M + Na]⁺), 410.0999; found 410.0995.

[α]_D²⁰ = 60.6 (c = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IA-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 33.09 min, t_R (major) = 38.46 min, 95% ee.



(R)-N-benzoyl-6-formyl-2'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3ja)



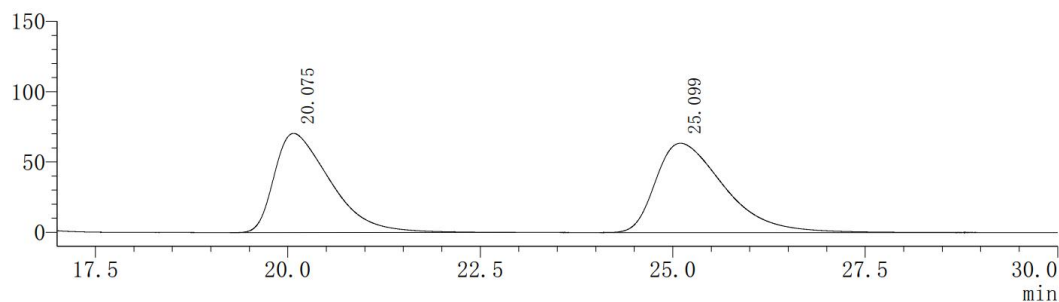
The title compound **3ja** was obtained as a light yellow oil (25.4 mg, 64%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 8.59 (s, 1H), 8.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.59 – 7.56 (m, 1H), 7.55 – 7.51 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.2, 167.4, 165.3, 139.5, 136.5, 134.9, 133.6, 133.3, 132.9, 132.5, 132.3, 132.0, 130.3, 129.3, 129.1, 129.1, 128.1, 127.8, 126.5 (q, *J* = 5.1 Hz), 124.0 (q, *J* = 272.1 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -58.32 (s, 1CF₃).

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₂H₁₄F₃NNaO₃, ([M + Na]⁺), 420.0818; found 420.0812.

[α]_D²⁰ = -14.3 (c = 1.3, CH₂Cl₂).

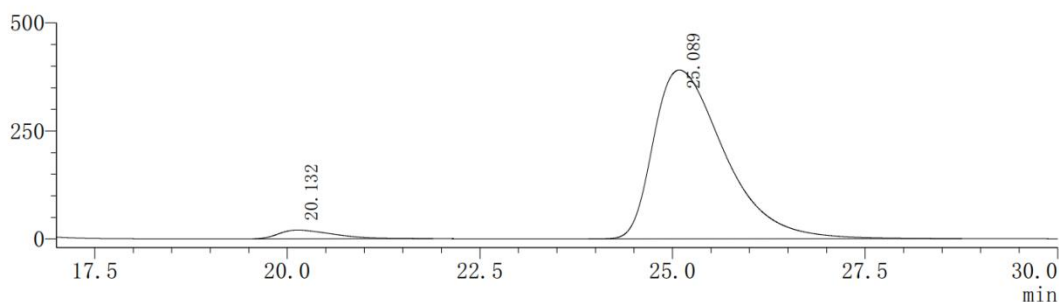
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 20.13 min, *t*_R (major) = 25.09 min, 92% ee.

mV



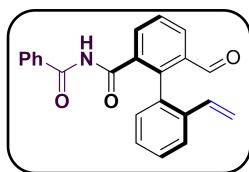
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.075	M	1.3383	3567902	70523	47.5353
2	25.099	M	1.5935	3937889	63487	52.4647

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.132	M	1.3119	998697	20419	3.8351
2	25.089	M	1.6320	25042246	390674	96.1649

(R)-N-benzoyl-6-formyl-2'-vinyl-[1,1'-biphenyl]-2-carboxamide (3ka)



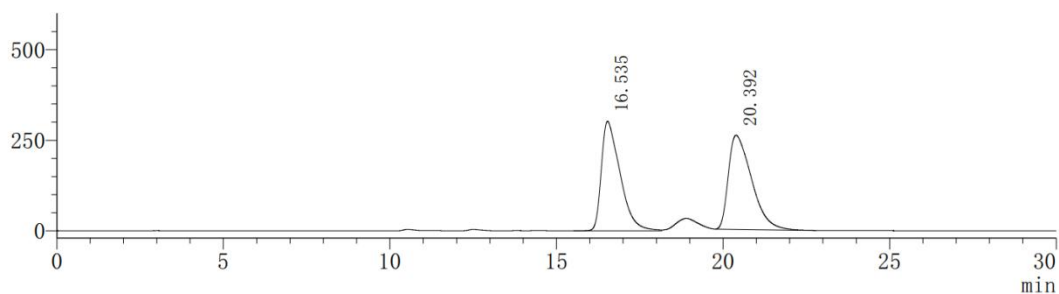
The title compound **3ka** was obtained as a light yellow solid (25.2 mg, 71%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.58 (d, *J* = 0.8 Hz, 1H), 8.40 (s, 1H), 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.96 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.42 – 7.36 (m, 5H), 7.30 – 7.28 (m, 2H), 6.43 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.62 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.20 (dd, *J* = 11.0, 0.9 Hz, 1H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.3, 168.6, 165.0, 140.8, 137.8, 137.2, 134.8, 134.1, 133.8, 133.4, 133.1, 132.5, 130.9, 129.9, 129.6, 128.9, 128.8, 128.3, 127.7, 125.9, 117.8.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₁₇NNaO₃, ([M + Na]⁺), 378.1101; found 378.1096.

[α]_D²⁰ = -16.4 (*c* = 1.3, CH₂Cl₂).

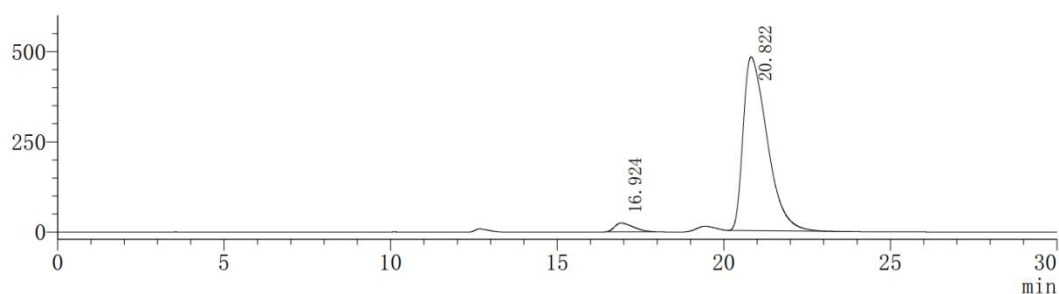
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 16.92 min, *t*_R (major) = 20.82 min, 93% ee.

mV



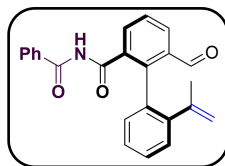
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.535	M	1.0598	11838743	302544	48.5038
2	20.392	M	1.2798	12569148	259582	51.4962

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.924	M	1.0700	911365	24075	3.6305
2	20.822	M	1.3159	24191383	481336	96.3695

(R)-N-benzoyl-6-formyl-2'-(prop-1-en-2-yl)-[1,1'-biphenyl]-2-carboxamide (3la)



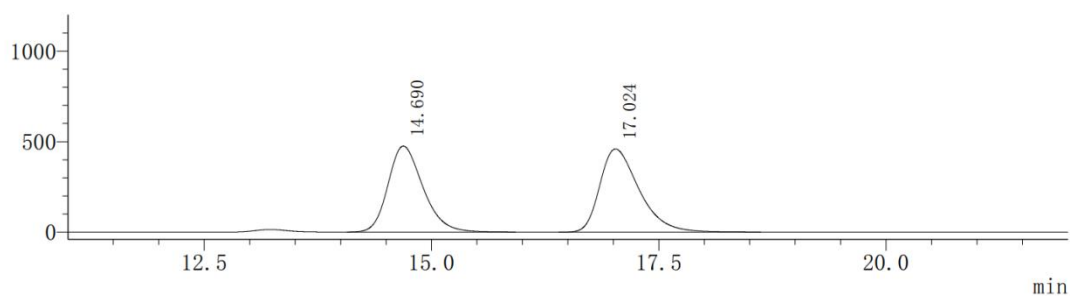
The title compound **3la** was obtained as a light yellow solid (22.9 mg, 62%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.66 (d, *J* = 0.9 Hz, 1H), 8.68 (s, 1H), 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 (td, *J* = 7.8, 0.9 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.46 – 7.44 (m, 2H), 7.40 – 7.37 (m, 4H), 7.34 – 7.28 (m, 2H), 5.05 (t, *J* = 1.6 Hz, 1H), 4.86 (t, *J* = 1.2 Hz, 1H), 1.67 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.3, 168.1, 165.1, 144.5, 144.0, 142.4, 136.2, 134.6, 134.2, 133.4, 132.6, 132.3, 130.9, 130.3, 129.6, 129.3, 128.9, 128.4, 127.8, 127.7, 119.1, 23.2.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₀NO₃, ([*M* + *H*]⁺), 370.1438; found 370.1444.

[α]_D²⁰ = -60.0 (*c* = 1.1, CH₂Cl₂).

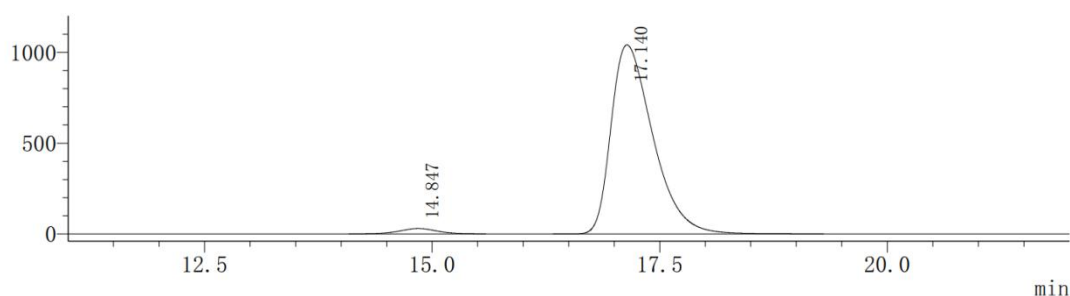
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 14.85 min, *t*_R (major) = 17.14 min, 95% ee.

mV



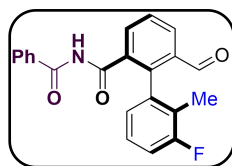
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.690	M	0.6940	12708618	474618	47.9161
2	17.024	M	0.7740	13814012	458871	52.0839

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.847	M	0.7341	832646	29595	2.4444
2	17.140	M	0.8258	33231306	1040465	97.5556

(R)-N-benzoyl-3'-fluoro-6-formyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3ma)

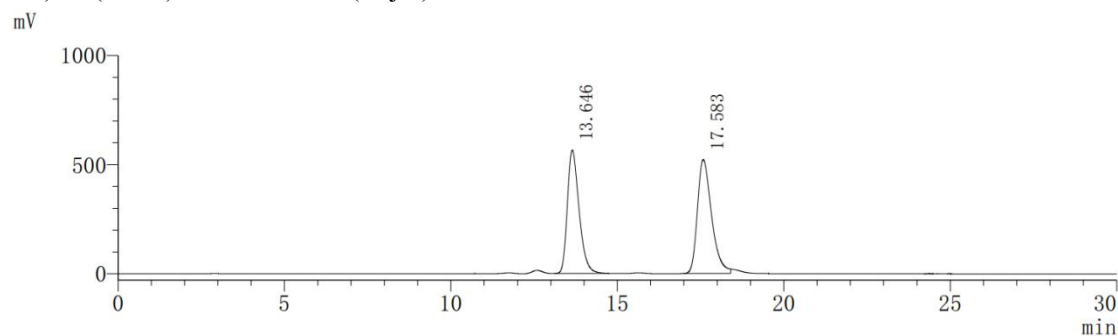


The title compound **3ma** was obtained as a light yellow oil (20.2 mg, 56%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.64 (d, *J* = 0.8 Hz, 1H), 8.54 (s, 1H), 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.50 (m, 2H), 7.44 – 7.41 (m, 2H), 7.15 – 7.11 (m, 1H), 7.06 – 7.02 (m, 2H), 1.99 (d, *J* = 2.4 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 169.4, 165.1, 161.6 (d, *J* = 245.3 Hz), 140.2 (d, *J* = 2.7 Hz), 137.3, 136.7 (d, *J* = 4.6 Hz), 134.4, 133.7, 133.1, 132.2, 129.7, 129.0, 128.8, 127.8, 127.2 (d, *J* = 8.9 Hz), 126.0 (d, *J* = 3.3 Hz), 125.3 (d, *J* = 17.2 Hz), 115.8 (d, *J* = 22.7 Hz), 12.4 (d, *J* = 4.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -114.34 (s, 1F).

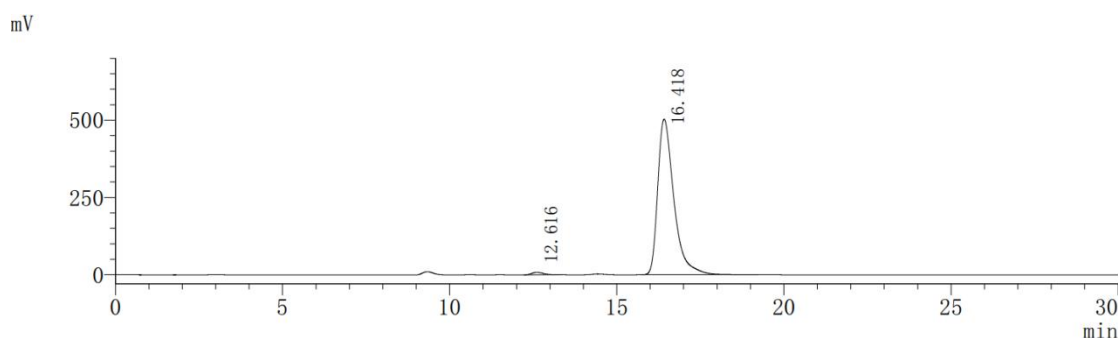
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₂H₁₇FO₃, ([*M* + *H*]⁺), 362.1187; found 362.1183.

[α]_D²⁰ = -28.8 (*c* = 1.0, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 12.62 min, *t*_R (major) = 16.42 min, 98% ee.

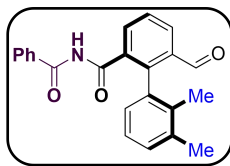


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.646	M	0.6355	13868040	565883	47.2612
2	17.583	M	0.7613	15475384	522526	52.7388



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.616	M	0.6457	203770	8095	1.1924
2	16.418	M	0.8409	16884574	503055	98.8076

(R)-N-benzoyl-6-formyl-2',3'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3na)

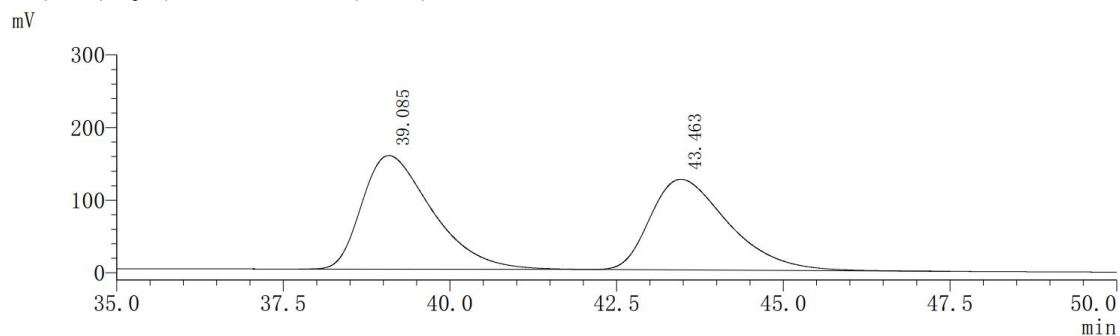


The title compound **3na** was obtained as a white solid (23.6 mg, 66%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 8.42 (s, 1H), 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.04 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.30 (m, 2H), 7.19 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.15 – 7.11 (m, 2H), 2.18 (s, 3H), 1.96 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.5, 168.2, 165.0, 142.3, 138.6, 136.6, 136.0, 134.5, 134.4, 133.4, 132.6, 131.0, 130.0, 128.8, 128.6, 128.2, 127.6, 126.3, 20.5, 17.2.

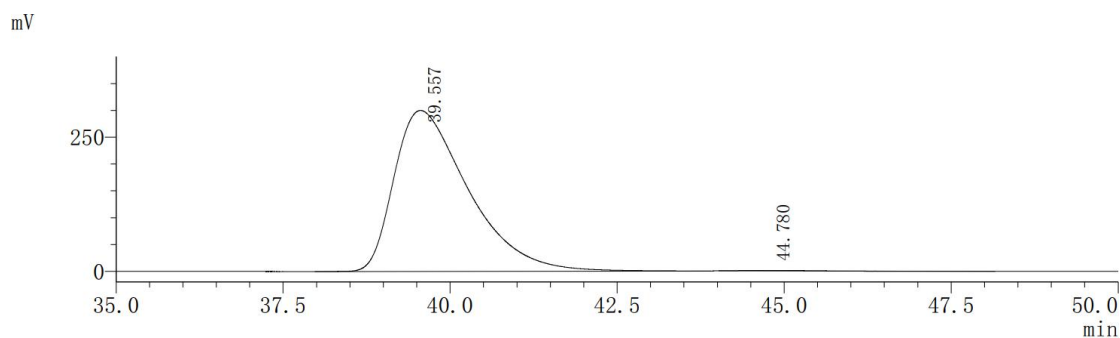
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₀NO₃, ([*M* + *H*]⁺), 358.1438; found 358.1443.

[α]_D²⁰ = -40.0 (*c* = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IC-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (major) = 39.56 min, *t*_R (minor) = 44.78 min, 99% ee.

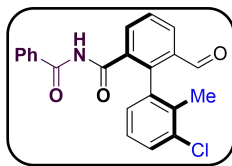


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	39.085	M	1.9331	11455212	156504	52.9145
2	43.463	M	2.1318	10193305	124834	47.0855



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	39.557	M	2.0211	23129665	299890	99.7274
2	44.780	M	1.7929	63234	1133	0.2726

(R)-N-benzoyl-3'-chloro-6-formyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3oa)

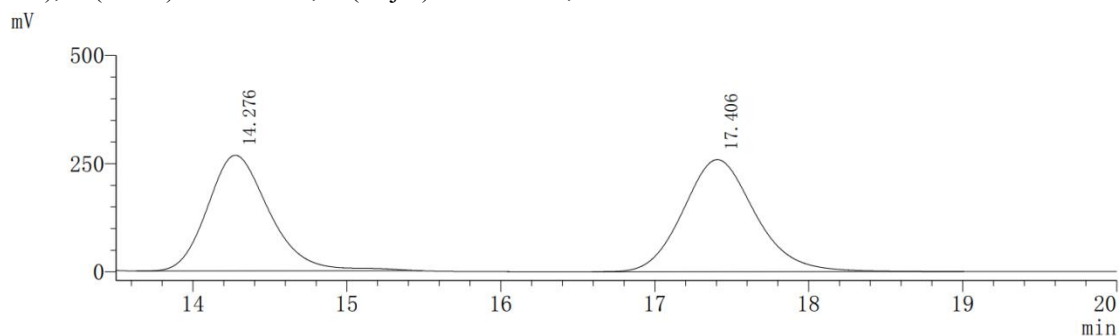


The title compound **3oa** was obtained as a light yellow oil (23.4 mg, 62%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.64 (d, J = 0.8 Hz, 1H), 8.48 (s, 1H), 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.88 (dd, J = 7.7, 1.4 Hz, 1H), 7.67 (td, J = 7.7, 0.9 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.51 – 7.49 (m, 2H), 7.45 – 7.42 (m, 2H), 7.38 (dd, J = 7.9, 1.4 Hz, 1H), 7.16 (dd, J = 7.6, 1.4 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 2.10 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 190.9, 169.2, 165.1, 140.9, 137.2, 136.4, 136.1, 135.8, 134.3, 133.7, 133.2, 132.2, 130.1, 129.8, 129.1, 128.9, 128.8, 127.7, 126.9, 18.1.

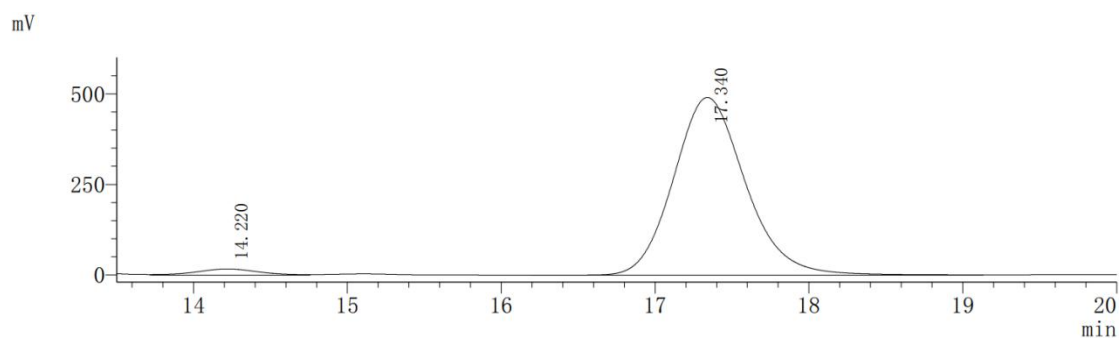
HRMS (ESI-TOF) (m/z): Calcd for C₂₂H₁₆ClNNaO₃, ($[M + Na]^+$), 400.0711; found 400.0701.

$[\alpha]_D^{20}$ = -40.3 (c = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 14.22 min, t_R (major) = 17.34 min, 94% ee.

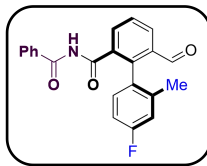


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.276	M	0.7250	7496575	267138	47.0839
2	17.406	M	0.8478	8425162	258790	52.9161



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.220	M	0.7345	508450	17534	3.0747
2	17.340	M	0.8442	16028306	490728	96.9253

(R)-N-benzoyl-4'-fluoro-6-formyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3pa)



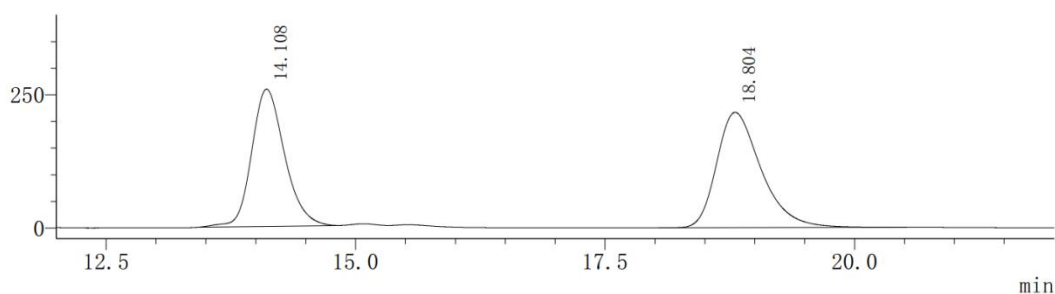
The title compound **3pa** was obtained as a light yellow oil (20.2 mg, 56%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.64 (d, J = 0.8 Hz, 1H), 8.59 (s, 1H), 8.15 (dd, J = 7.8, 1.4 Hz, 1H), 7.85 (dd, J = 7.7, 1.4 Hz, 1H), 7.65 (td, J = 7.8, 0.8 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.53 (m, 2H), 7.45 – 7.42 (m, 2H), 7.20 (dd, J = 8.4, 5.8 Hz, 1H), 6.93 (dd, J = 9.5, 2.6 Hz, 1H), 6.85 (td, J = 8.4, 2.7 Hz, 1H), 2.06 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.2, 169.5, 165.1, 163.1 (d, J = 247.0 Hz), 140.7, 140.3 (d, J = 8.0 Hz), 137.5, 134.6, 133.7, 133.1, 132.2, 131.8 (d, J = 8.2 Hz), 130.3 (d, J = 3.4 Hz), 129.8, 129.1, 128.7, 127.8, 117.4 (d, J = 21.0 Hz), 113.2 (d, J = 21.3 Hz), 20.5. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -112.86 (s, 1F).

HRMS (ESI-TOF) (m/z): Calcd for C₂₂H₁₇FNO₃, ([M + H]⁺), 362.1187; found 362.1190.

[α]_D²⁰ = -46.7 (c = 1.0, CH₂Cl₂).

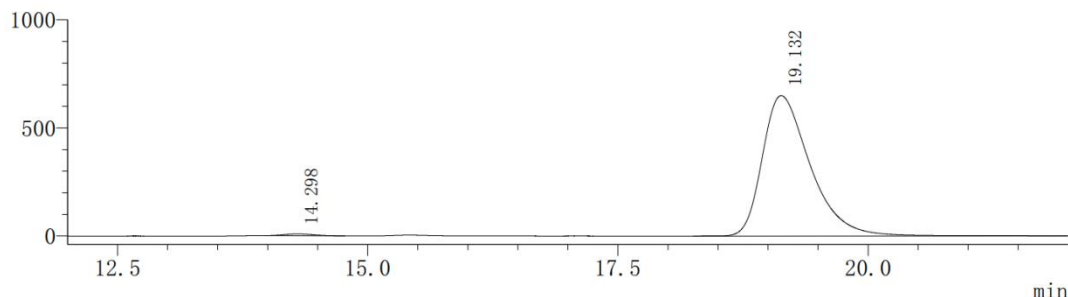
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 14.30 min, t_R (major) = 19.13 min, 98% ee.

mV



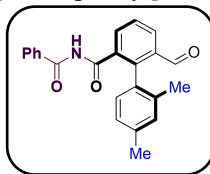
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.108	M	0.5915	5910171	257451	46.8270
2	18.804	M	0.7971	6711125	216394	53.1730

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.298	M	0.5662	171112	8134	0.7839
2	19.132	M	0.8501	21658079	649360	99.2161

(R)-N-benzoyl-6-formyl-2',4'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3qa)

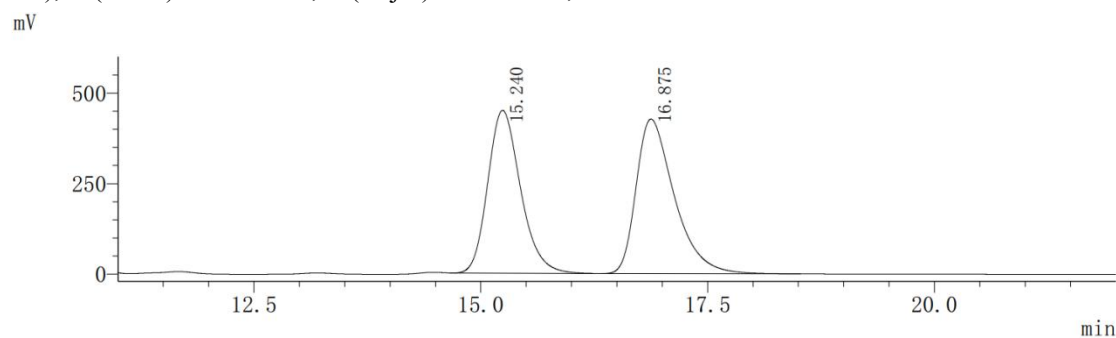


The title compound **3qa** was obtained as a light yellow oil (22.1 mg, 62%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (s, 1H), 8.48 (s, 1H), 8.16 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.39 – 7.34 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 2.30 (s, 3H), 2.05 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.5, 168.0, 165.0, 141.8, 139.6, 137.3, 136.5, 134.7, 134.5, 133.3, 132.7, 132.0, 131.3, 130.3, 130.2, 128.8, 128.6, 127.7, 127.3, 21.3, 20.2.

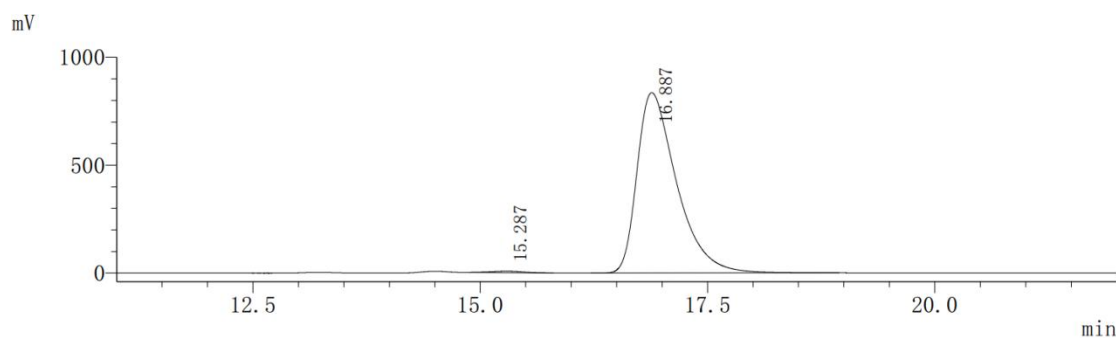
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₀NO₃, ([M + H]⁺), 358.1438; found 358.1429.

[α]_D²⁰ = -30.3 (*c* = 1.1, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t_R* (minor) = 15.29 min, *t_R* (major) = 16.89 min, 99% ee.

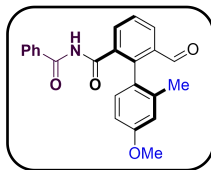


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.240	M	0.6516	11307605	449463	47.5237
2	16.875	M	0.7506	12486012	426748	52.4763



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.287	M	0.6688	176756	7105	0.6927
2	16.887	M	0.7734	25339620	835759	99.3073

(R)-N-benzoyl-6-formyl-4'-methoxy-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3ra)

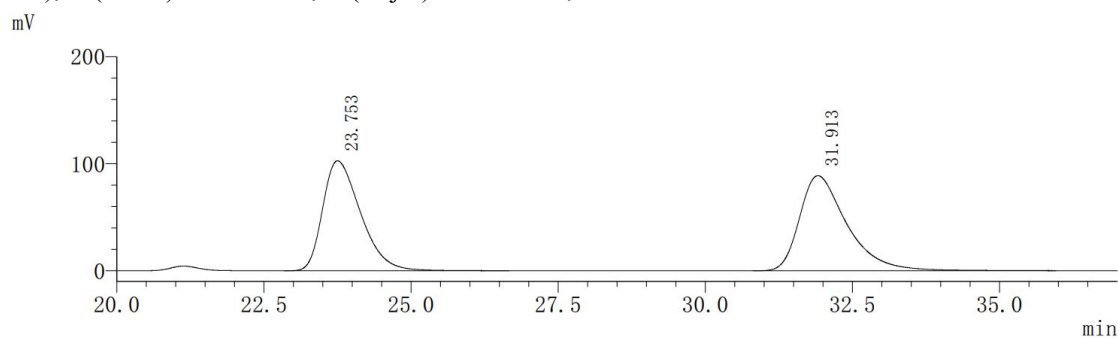


The title compound **3ra** was obtained as a light yellow oil (24.2 mg, 65%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.63 (s, 1H), 8.54 (s, 1H), 8.16 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.04 – 8.02 (m, 1H), 7.64 (t, *J* = 7.7 Hz, 0H), 7.57 – 7.51 (m, 1H), 7.39 – 7.38 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.76 (s, 3H), 2.07 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.6, 168.2, 165.0, 160.5, 141.6, 139.1, 136.9, 135.0, 134.3, 133.4, 132.7, 131.6, 130.1, 128.8, 128.5, 127.7, 126.3, 116.4, 112.1, 55.4, 20.6.

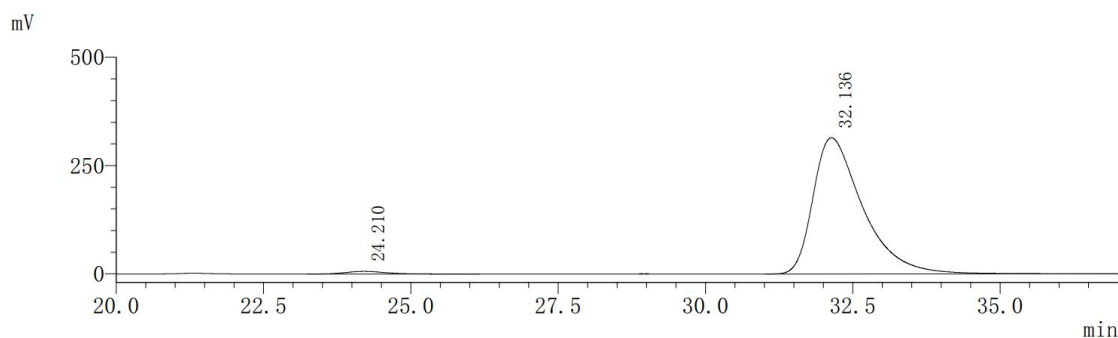
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₀NO₄, ([*M* + *H*]⁺), 374.1387; found 374.1377.

[α]_D²⁰ = -41.2 (*c* = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 24.21 min, *t*_R (major) = 32.14 min, 97% ee.

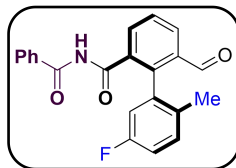


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	23.753	M	1.1762	4612951	102860	48.0294
2	31.913	M	1.4285	4991480	88953	51.9706



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	24.210	M	1.2026	287935	6041	1.5311
2	32.136	M	1.4924	18517263	314410	98.4689

(R)-N-benzoyl-5'-fluoro-6-formyl-2'-methyl-[1,1'-biphenyl]-2-carboxamide (3sa)

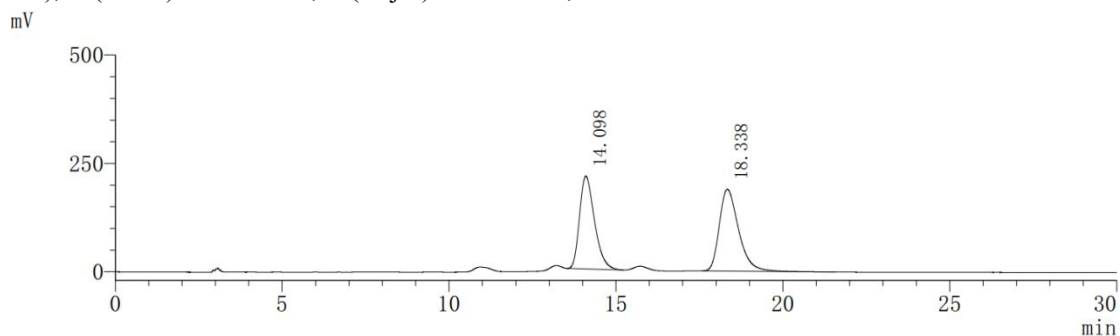


The title compound **3sa** was obtained as a light yellow oil (22.8 mg, 63%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.65 (d, J = 0.8 Hz, 1H), 8.59 (s, 1H), 8.16 (dd, J = 7.8, 1.4 Hz, 1H), 7.86 (dd, J = 7.7, 1.4 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.60 – 7.55 (m, 3H), 7.45 – 7.42 (m, 2H), 7.18 (dd, J = 8.1, 5.7 Hz, 1H), 7.00 – 6.96 (m, 2H), 2.03 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.0, 169.2, 165.1, 160.8 (d, J = 245.3 Hz), 140.5 (d, J = 1.9 Hz), 137.1, 136.0 (d, J = 7.4 Hz), 134.2, 133.7, 133.3 (d, J = 3.4 Hz), 133.2, 132.2, 132.1 (d, J = 8.0 Hz), 129.8, 129.1, 128.8, 127.8, 117.1 (d, J = 21.8 Hz), 116.1 (d, J = 20.6 Hz), 19.5. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -116.68 (s, 1F).

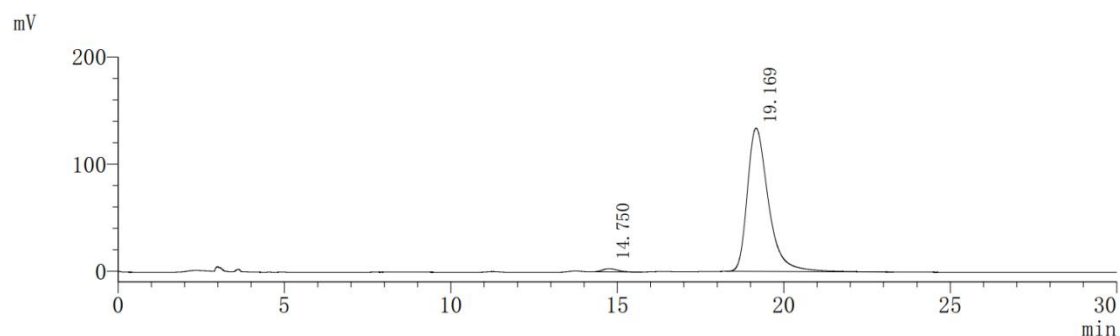
HRMS (ESI-TOF) (m/z): Calcd for C₂₂H₁₆FNNaO₃, ([M + Na]⁺), 384.1006; found 384.1008.

[α]_D²⁰ = -43.8 (c = 1.1, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 14.75 min, t_R (major) = 19.17 min, 97% ee.

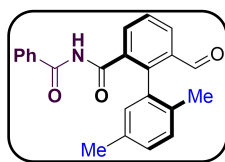


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.098	M	0.8142	668450	214214	46.7467
2	18.338	M	1.0405	7614920	188924	53.2533



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.750	M	0.7923	96278	3072	1.6048
2	19.169	M	1.1098	5903070	133857	98.3952

(R)-N-benzoyl-6-formyl-2',5'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3ta)

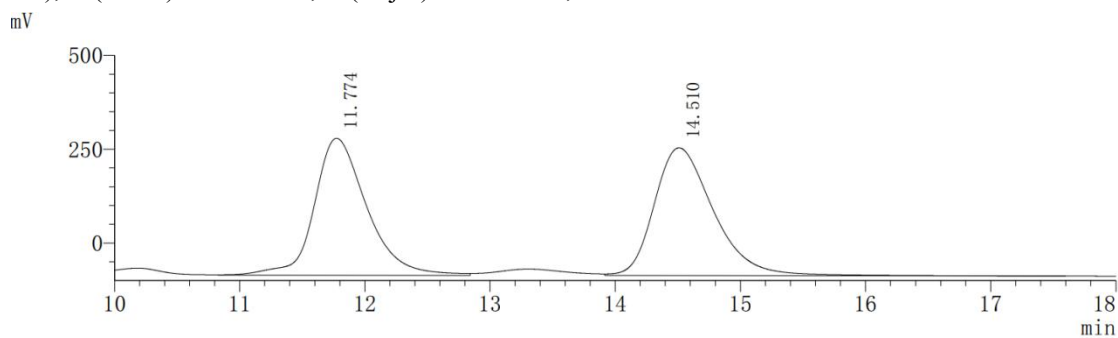


The title compound **3ta** was obtained as a light yellow oil (19.6 mg, 55%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.60 (s, 1H), 8.44 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 2.15 (s, 3H), 2.05 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.5, 168.1, 165.0, 141.8, 136.5, 136.3, 134.5, 134.4, 134.3, 134.2, 133.3, 132.7, 131.2, 130.9, 130.3, 130.2, 128.8, 128.7, 127.6, 20.8, 19.8.

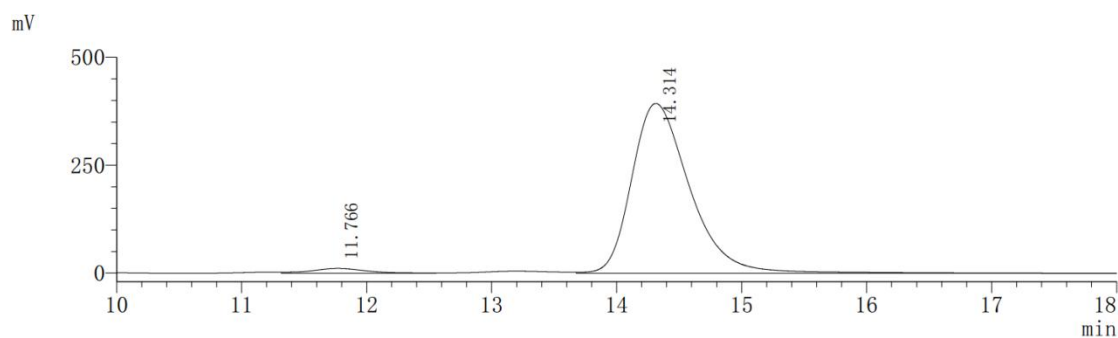
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₀NO₃, ([*M* + *H*]⁺), 358.1438; found 358.1446.

[α]_D²⁰ = -50.9 (*c* = 1.0, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 11.77 min, *t*_R (major) = 14.31 min, 95% ee.

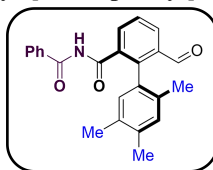


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.774	M	0.7235	10663039	365100	48.5910
2	14.510	M	0.8460	11281423	340693	51.4090



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.766	M	0.7712	358001	11376	2.7229
2	14.314	M	0.8246	12789608	393479	97.2771

(R)-N-benzoyl-6-formyl-2',4',5'-trimethyl-[1,1'-biphenyl]-2-carboxamide (3ua)

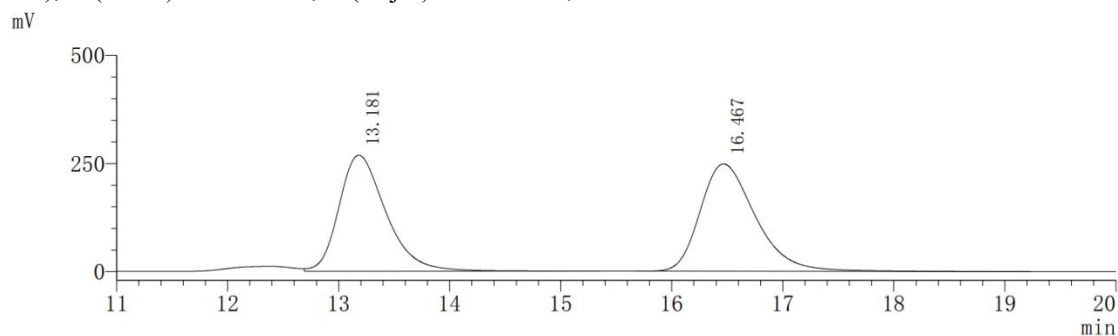


The title compound **3ua** was obtained as a light yellow oil (22.6 mg, 61%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (s, 1H), 8.46 (s, 1H), 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.12 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.55 – 7.52 (m, 1H), 7.37 – 7.34 (m, 2H), 7.29 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.05 (s, 1H), 7.00 (s, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.6, 167.6, 165.0, 141.9, 138.4, 136.2, 135.1, 135.0, 134.6, 134.6, 133.2, 132.9, 132.6, 131.5, 130.4, 128.7, 128.6, 127.6, 19.7, 19.6, 19.2.

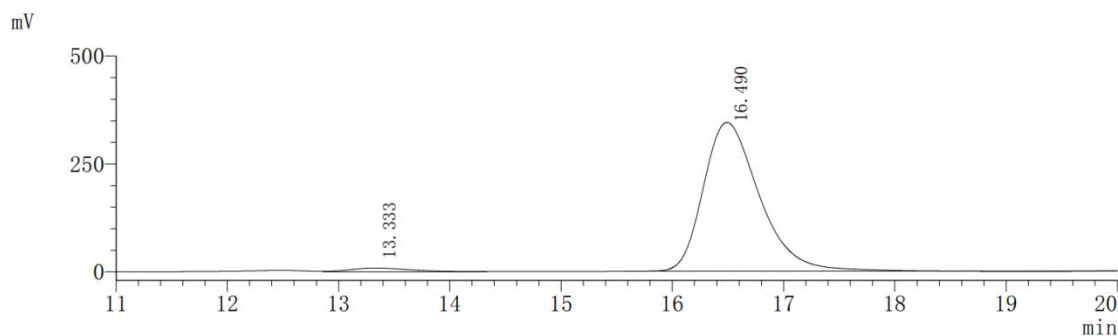
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₂NO₃, ([*M* + *H*]⁺), 372.1594; found 372.1601.

[α]_D²⁰ = -44.2 (*c* = 1.1, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 13.33 min, *t*_R (major) = 16.49 min, 94% ee.

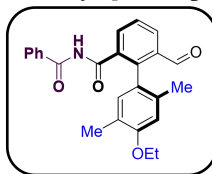


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.181	M	0.7567	7936469	268666	47.9418
2	16.467	M	0.8942	8617905	248217	52.0582



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.333	M	0.9818	344758	8790	2.7996
2	16.490	M	0.9022	11969584	344599	97.2004

(R)-N-benzoyl-4'-ethoxy-6-formyl-2',5'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3va)



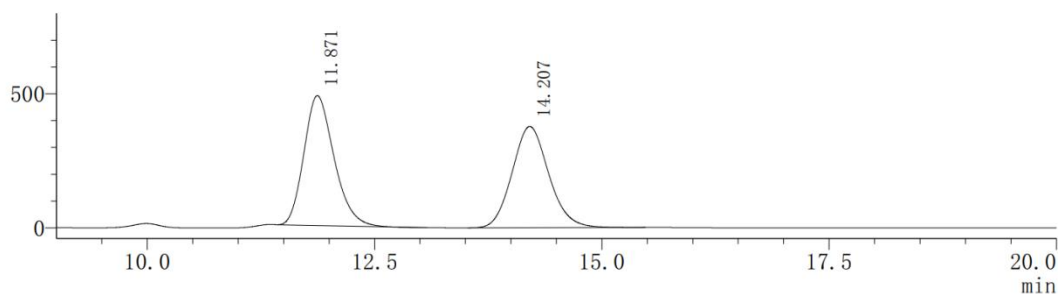
The title compound **3va** was obtained as a light yellow oil (24.1 mg, 60%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.62 (s, 1H), 8.54 (s, 1H), 8.16 (td, *J* = 7.2, 1.4 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.02 (s, 1H), 6.67 (s, 1H), 4.05 – 3.88 (m, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.8, 167.4, 165.0, 158.2, 141.9, 136.3, 136.2, 135.2, 135.0, 133.1, 132.9, 132.4, 130.5, 128.7, 128.5, 127.5, 125.6, 125.2, 113.5, 63.8, 20.4, 15.8, 15.0.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₄NO₄, ([M + H]⁺), 402.1700; found 402.1701.

[α]_D²⁰ = -41.4 (*c* = 1.2, CH₂Cl₂).

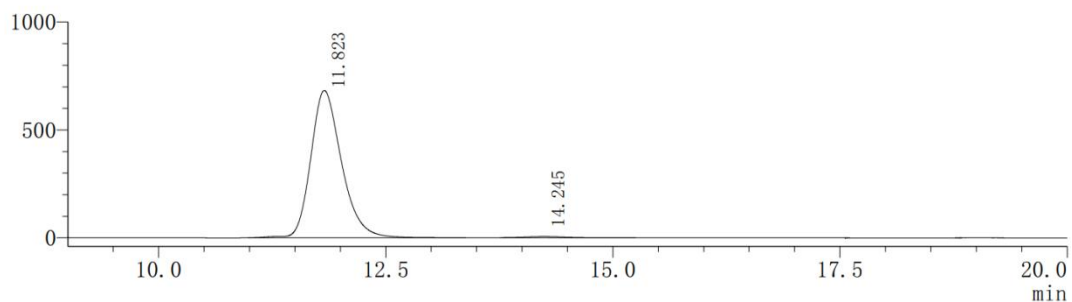
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (major) = 11.82 min, t_R (minor) = 14.25 min, 98% ee.

mV



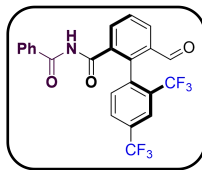
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.871	M	0.6081	11191622	484637	51.4144
2	14.207	M	0.7370	10575855	377574	48.5856

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	11.823	M	0.6084	16150615	682646	98.9399
2	14.245	M	0.7907	173054	5912	1.0601

(R)-N-benzoyl-6-formyl-2',4'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3wa)



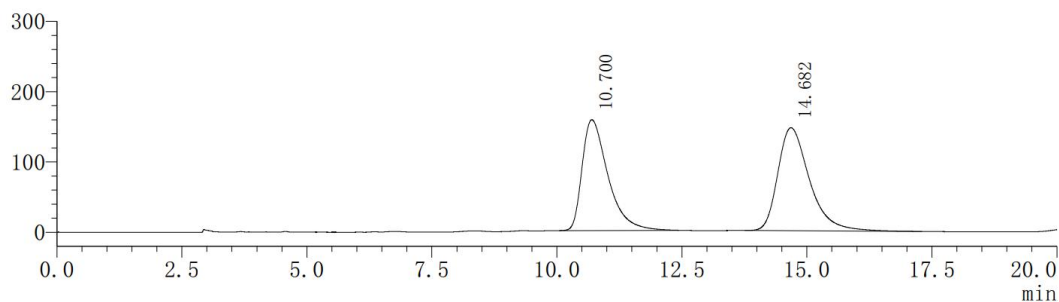
The title compound **3wa** was obtained as a light yellow oil (25.6 mg, 55%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.63 (s, 1H), 8.71 (s, 1H), 8.18 (dd, J = 7.8, 1.3 Hz, 1H), 7.99 (s, 1H), 7.86 (td, J = 7.7, 1.4 Hz, 1H), 7.77 (dd, J = 8.0, 1.8 Hz, 1H), 7.73 – 7.69 (m, 3H), 7.63 – 7.57 (m, 2H), 7.47 (t, J = 7.8 Hz, 2H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 189.7, 167.7, 165.4, 138.1, 136.3, 134.8, 133.9, 133.1, 132.6, 132.2, 131.5 (q, J = 33.7 Hz), 130.4 (q, J = 30.8 Hz), 129.5, 129.2, 129.1, 128.4 (q, J = 3.0 Hz), 128.1, 127.9, 123.7 – 123.5 (m), 123.3 (q, J = 271.1 Hz), 123.2 (q, J = 272.7 Hz). **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -58.96, -62.95 (s, 2CF₃).

HRMS (ESI-TOF) (m/z): Calcd for C₂₃H₁₄F₆NO₃, ([M + H]⁺), 466.0872; found 466.0874.

[α]_D²⁰ = -42.1 (c = 1.3, CH₂Cl₂).

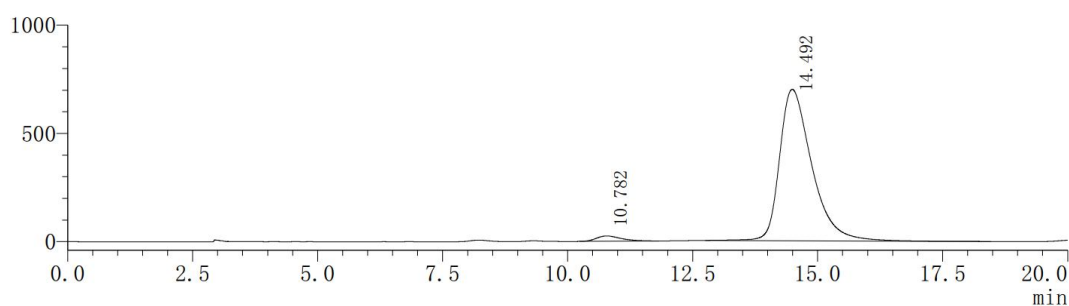
HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 10.78 min, t_R (major) = 14.49 min, 95% ee.

mV



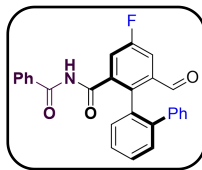
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.700	M	0.9158	5667402	157584	46.7275
2	14.682	M	1.1180	6461219	146555	53.2725

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.782	M	0.8958	850983	24636	2.6390
2	14.492	M	1.1408	31395785	699444	97.3610

(R)-N-benzoyl-4-fluoro-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3xa)

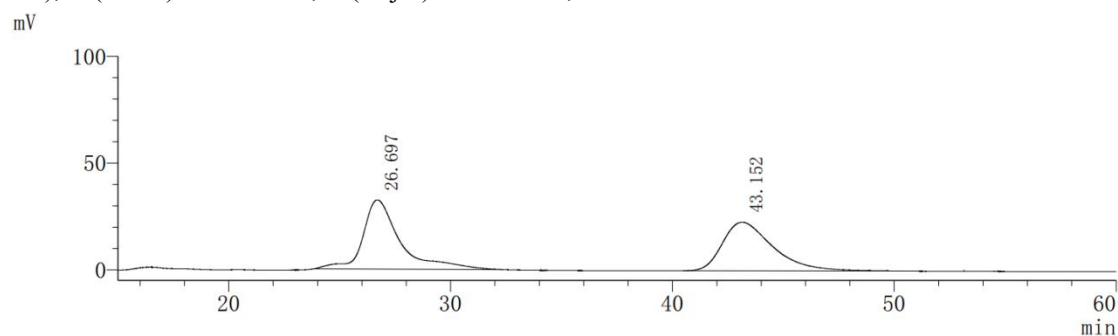


The title compound **3xa** was obtained as a light yellow oil (19.0 mg, 45%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (d, *J* = 3.1 Hz, 1H), 8.90 (s, 1H), 7.62 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.57 – 7.54 (m, 1H), 7.48 – 7.45 (m, 3H), 7.43 – 7.33 (m, 4H), 7.18 – 7.13 (m, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 189.6, 167.8, 165.1, 161.8 (d, *J* = 249.8 Hz), 143.0, 139.5, 139.0 (d, *J* = 6.1 Hz), 138.5 (d, *J* = 3.6 Hz), 136.4 (d, *J* = 6.1 Hz), 133.7, 132.6, 132.1, 131.3, 130.7, 129.8, 129.7, 129.1, 128.6, 128.0, 127.9, 127.6, 120.3 (d, *J* = 23.9 Hz), 116.2 (d, *J* = 22.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -111.56 (s, 1F).

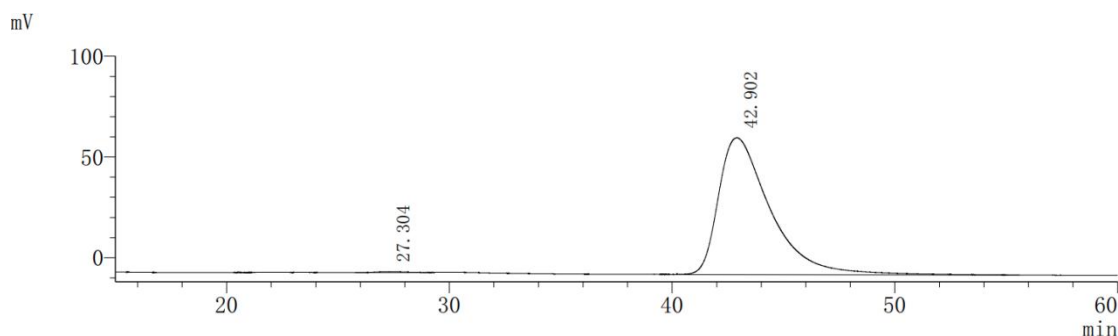
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₈FNNaO₃, ([M + Na]⁺), 446.1163; found 446.1170.

[α]_D²⁰ = -96.7 (*c* = 1.0, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-H column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (minor) = 27.30 min, *t*_R (major) = 42.90 min, 99% ee.

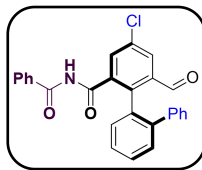


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	26.697	M	2.5555	3786152	32414	51.2986
2	43.152	M	3.8719	3594466	22781	48.7014



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	27.304	M	1.5107	38592	469	0.3502
2	42.902	M	3.9755	10982679	67891	99.6498

(R)-N-benzoyl-4-chloro-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ya)

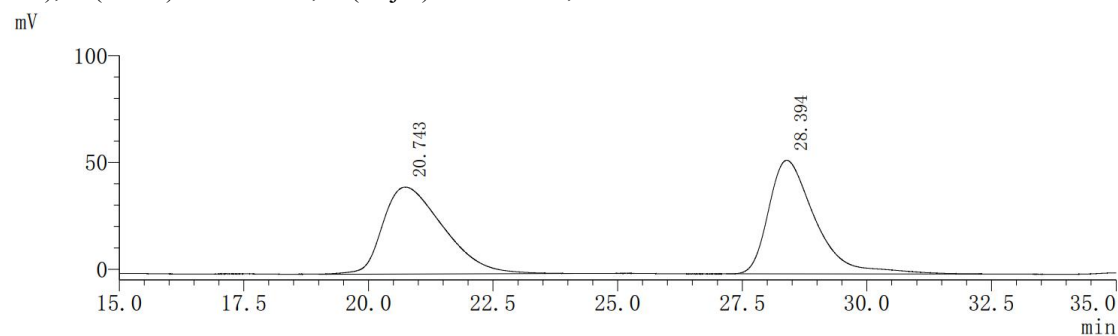


The title compound **3ya** was obtained as a light yellow oil (18.0 mg, 41%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.60 (s, 1H), 9.00 (s, 1H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.69 (d, *J* = 2.3 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.57 – 7.54 (m, 1H), 7.47 – 7.44 (m, 2H), 7.42 – 7.37 (m, 3H), 7.36 – 7.33 (m, 1H), 7.19 – 7.15 (m, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 189.6, 167.8, 165.1, 142.8, 140.7, 139.5, 138.6, 135.7, 134.6, 133.7, 132.6, 132.5, 132.1, 131.1, 130.7, 129.9, 129.8, 129.6, 129.1, 128.6, 128.0, 127.9, 127.7.

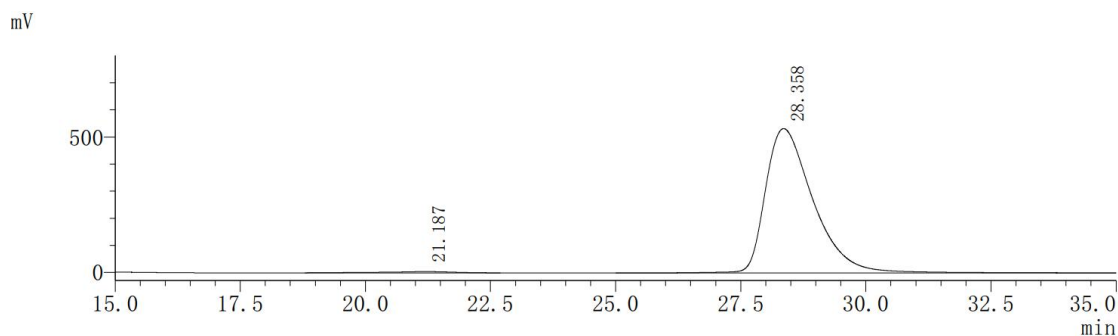
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₈ClNNaO₃, ([*M* + Na]⁺), 462.0867; found 462.0866.

[α]_D²⁰ = -103.2 (*c* = 0.9, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 21.19 min, *t*_R (major) = 28.36 min, 97% ee.

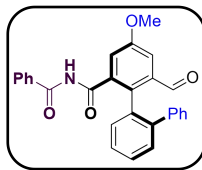


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.743	M	2.2098	3431869	40685	49.7716
2	28.394	M	1.6468	3463359	53203	50.2284



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.187	M	2.1623	468699	4674	1.3058
2	28.358	M	1.7110	35424719	532494	98.6942

(R)-N-benzoyl-6-formyl-4-methoxy-[1,1':2'',1'''-terphenyl]-2-carboxamide (3za)

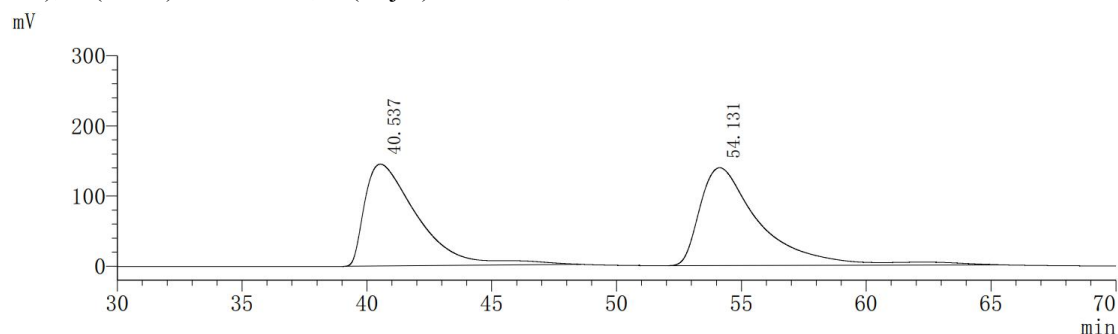


The title compound **3za** was obtained as a light yellow oil (22.2 mg, 51%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.66 (s, 1H), 8.65 (s, 1H), 7.56 – 7.50 (m, 3H), 7.48 – 7.45 (m, 3H), 7.43 – 7.36 (m, 5H), 7.17 – 7.15 (m, 3H), 7.13 – 7.11 (m, 2H), 3.86 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 165.0, 159.1, 143.0, 139.8, 137.9, 135.8, 135.1, 133.4, 133.2, 132.5, 131.7, 130.8, 129.7, 129.6, 129.0, 128.5, 128.1, 127.9, 127.8, 127.5, 120.6, 113.4, 55.9.

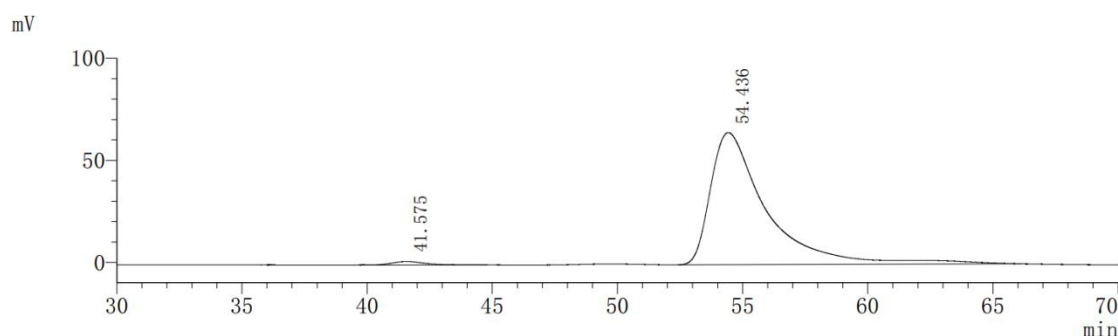
HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₂₂NO₄, ([M + H]⁺), 436.1543; found 436.1552.

[α]_D²⁰ = -60.3 (c = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 41.58 min, t_R (major) = 54.44 min, 97% ee.

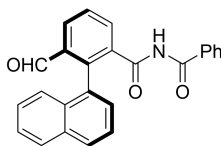


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	40.537	M	3.7830	21431168	145300	47.6418
2	54.131	M	3.9746	23552782	139487	52.3582



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	41.575	M	2.1043	158448	1721	1.5461
2	54.436	M	3.5588	10089669	64762	98.4539

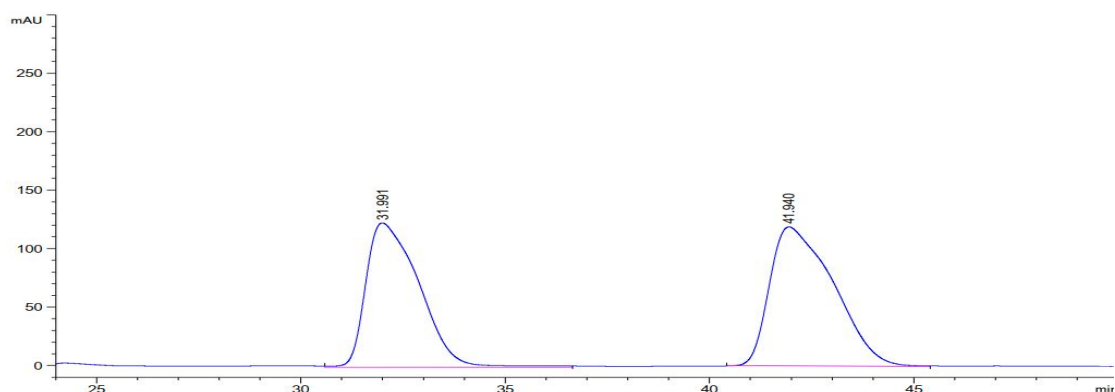
(R)-N-benzoyl-3-formyl-2-(naphthalen-1-yl)benzamide (3a'a)



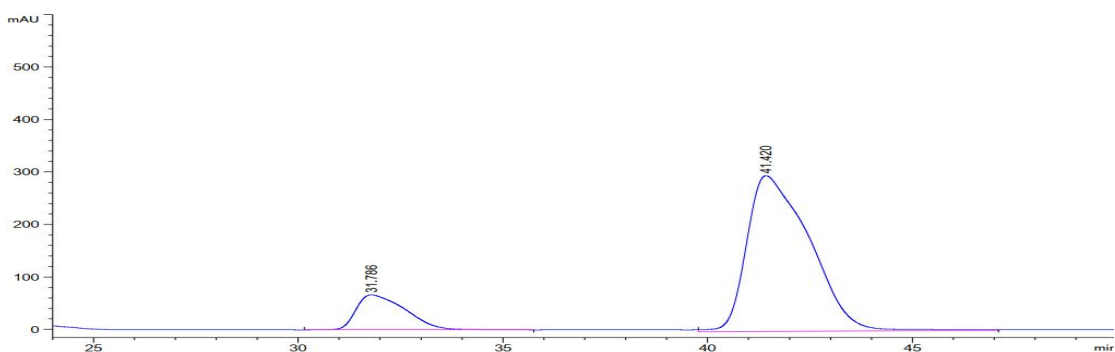
¹H NMR (600 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 8.26 (dd, J = 7.8, 1.4 Hz, 1H), 8.13 (s, 1H), 8.08 (dd, J = 7.7, 1.4 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.76 – 7.74 (m, 1H), 7.52 – 7.45 (m, 5H), 7.42 (t, J = 7.5 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.90 – 6.88 (m, 2H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ = 191.0, 167.8, 164.6, 140.1, 137.6, 135.2, 134.3, 133.5, 133.1, 132.9, 132.5, 131.9, 129.9, 129.6, 129.0, 128.9, 128.9, 128.5, 127.9, 127.1, 126.9, 125.5, 125.3.

HRMS (ESI-TOF) (m/z): Calcd for C₂₅H₁₈NO₃, ([M + H]⁺), 380.1281; found 380.1280.

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 31.79 min, t_R (major) = 41.42 min, 70% ee.

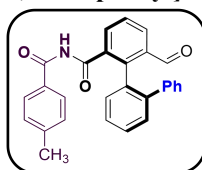


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	31.991	MM	1.5102	1.12002e4	123.60742	46.5666
2	41.940	MM	1.8031	1.28517e4	118.79055	53.4334



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	31.786	MM	1.1870	5536.58838	66.58951	14.8525
2	41.420	MM	1.7841	3.17405e4	296.51199	85.1475

(R)-6-formyl-N-(4-methylbenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ab)

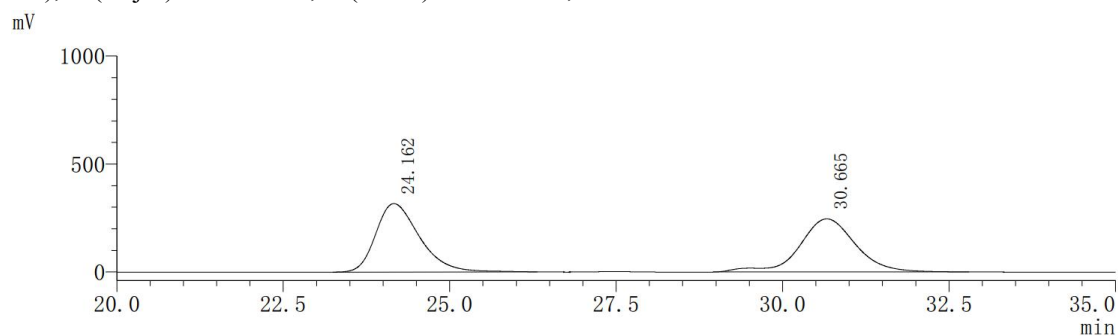


The title compound **3ab** was obtained as a light yellow solid (31.4 mg, 75%). **¹H NMR (600 MHz, Chloroform-*d*)** δ 9.67 (s, 1H), 8.92 (s, 1H), 7.94 (dd, J = 7.8, 1.4 Hz, 1H), 7.76 (dd, J = 7.7, 1.4 Hz, 1H), 7.48 (t, J = 8.0 Hz, 3H), 7.46 – 7.41 (m, 3H), 7.36 (td, J = 7.4, 1.7 Hz, 1H), 7.17 – 7.13 (m, 7H), 2.35 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.0, 169.2, 165.1, 144.5, 142.7, 142.6, 139.8, 137.1, 134.4, 133.6, 133.0, 131.1, 130.5, 129.8, 129.8, 129.7, 129.6, 129.5, 128.4, 128.0, 128.0, 127.8, 127.5, 21.8.

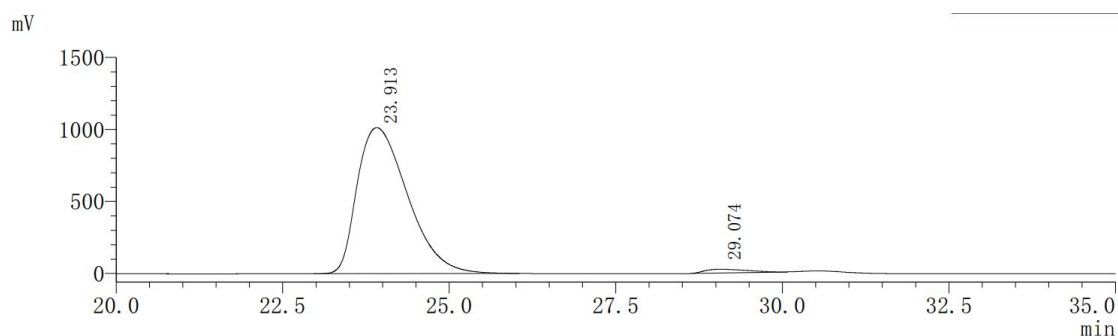
HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₂₂NO₃, ([M + H]⁺), 420.1594; found 420.1599.

[α]_D²⁰ = -67.3 (c = 1.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (major) = 23.91 min, t_R (minor) = 29.07 min, 96% ee.

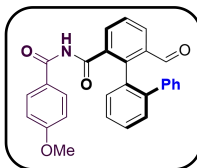


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	24.162	M	1.1775	14507667	316913	50.1507
2	30.665	M	1.4466	14420466	246050	49.8493



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	23.913	M	1.3651	53427488	1013807	97.9613
2	29.074	M	1.1768	1111883	25899	2.0387

(R)-6-formyl-N-(4-methoxybenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ac)

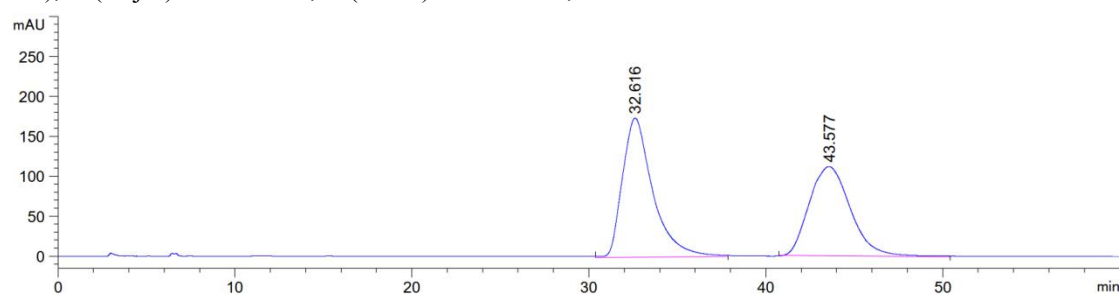


The title compound **3ac** was obtained as a yellow oil (26.5 mg, 61%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.65 (d, *J* = 0.8 Hz, 1H), 9.10 (s, 1H), 7.92 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.74 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.47 (td, *J* = 7.6, 0.8 Hz, 2H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (td, *J* = 7.4, 1.6 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.16 – 7.14 (m, 3H), 6.80 – 6.78 (m, 2H), 3.74 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 164.7, 163.9, 142.7, 142.5, 139.9, 137.3, 134.3, 133.7, 132.8, 131.0, 130.4, 130.3, 129.9, 129.6, 129.5, 128.4, 128.0, 127.8, 127.5, 124.3, 114.2, 55.6.

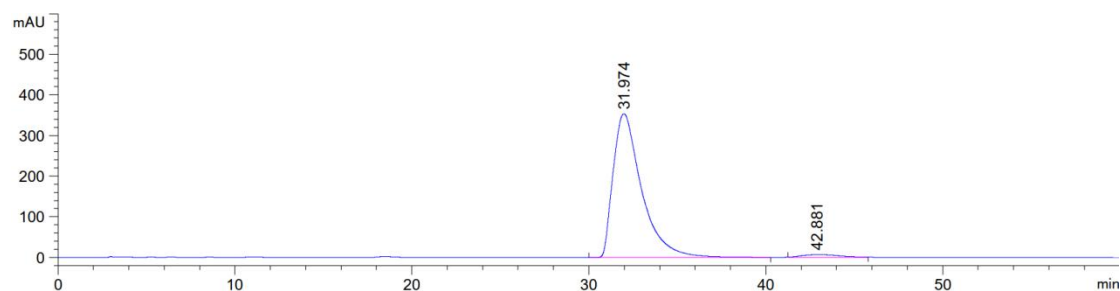
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₁NNaO₄, ([M + Na]⁺), 458.1363; found 458.1365.

[α]_D²⁰ = -69.2 (*c* = 1.3, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 31.97 min, *t*_R (minor) = 42.88 min, 94% ee.

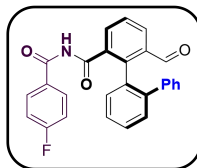


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	32.616	MM	1.9857	2.07468e4	174.13799	53.2752
2	43.577	MM	2.7159	1.81959e4	111.66368	46.7248



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	31.974	MM	1.7544	3.95059e4	353.61603	96.9957
2	42.881	MM	2.6650	1223.62463	7.65247	3.0043

(R)-N-(4-fluorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ad)

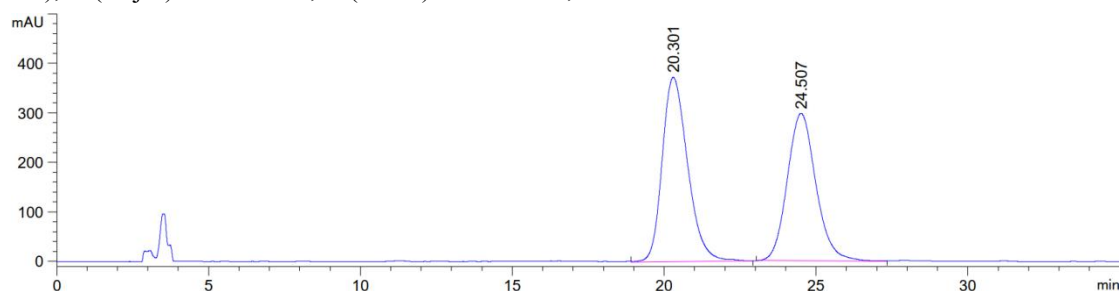


The title compound **3ad** was obtained as a yellow solid (30.0 mg, 71%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 9.19 (s, 1H), 7.95 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.37 – 7.32 (m, 1H), 7.15 – 7.12 (m, 5H), 7.00 – 6.96 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 169.7, 165.9 (d, *J* = 254.2 Hz), 164.4, 142.6 (d, *J* = 3.5 Hz), 139.6, 136.8, 134.5, 133.5, 133.0, 131.3, 130.7 (d, *J* = 9.4 Hz), 130.5, 130.0, 129.7, 129.6, 128.5, 128.5, 128.1, 127.8, 127.6, 116.1 (d, *J* = 21.9 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -104.29 (s, 1F).

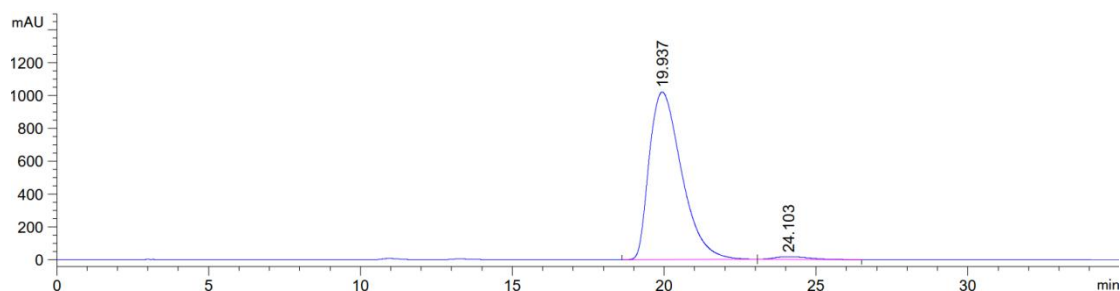
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉FNO₃, ([M + H]⁺), 424.1343; found 424.1343.

[α]_D²⁰ = -61.1 (*c* = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 19.94 min, *t*_R (minor) = 24.10 min, 97% ee.

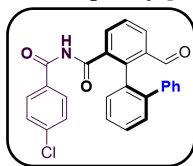


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.301	MM	0.9719	2.16919e4	372.00159	52.6353
2	24.507	MM	1.0942	1.95198e4	297.31589	47.3647



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	19.937	MM	1.1543	7.56467e4	1021.05798	98.3424
2	24.103	MM	1.2128	1275.05811	16.33311	1.6576

(R)-N-(4-chlorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ae)

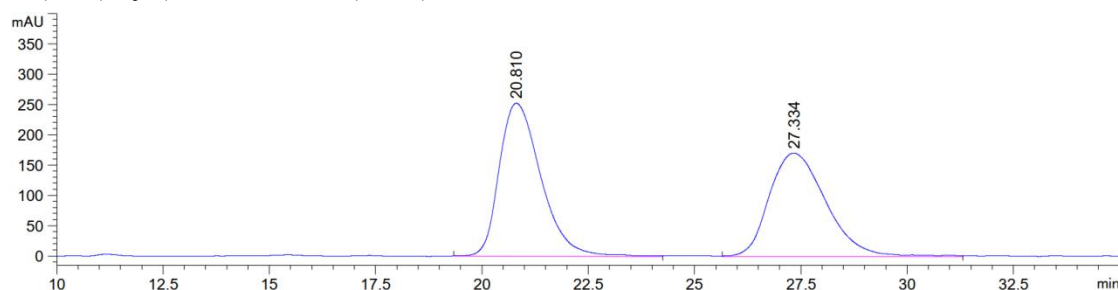


The title compound **3ae** was obtained as a yellow solid (28.5 mg, 65%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 9.21 (s, 1H), 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.47 (m, 1H), 7.45 – 7.43 (m, 2H), 7.42 – 7.41 (m, 1H), 7.36 – 7.33 (m, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.15 – 7.13 (m, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 169.6, 164.6, 142.6, 140.0, 139.6, 136.7, 134.5, 133.5, 133.1, 131.2, 130.6, 130.6, 130.1, 129.8, 129.7, 129.6, 129.5, 129.3, 128.5, 128.1, 127.8, 127.6.

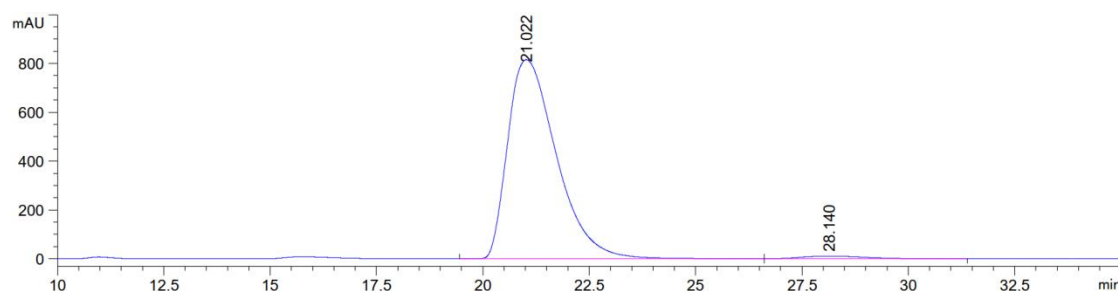
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉ClNO₃, ([*M* + *H*]⁺), 440.1048; found 440.1051.

[α]_D²⁰ = -117.5 (*c* = 1.4, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 21.02 min, *t*_R (minor) = 28.14 min, 97% ee.

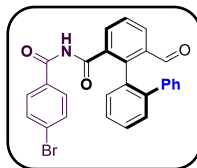


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.810	MM	1.1377	1.72043e4	252.02365	52.1164
2	27.334	MM	1.5460	1.58070e4	170.40355	47.8836



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.022	MM	1.1917	6.48145e4	815.13727	98.3672
2	28.140	MM	1.3464	1075.83472	10.66915	1.6328

(R)-N-(4-bromobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3af)

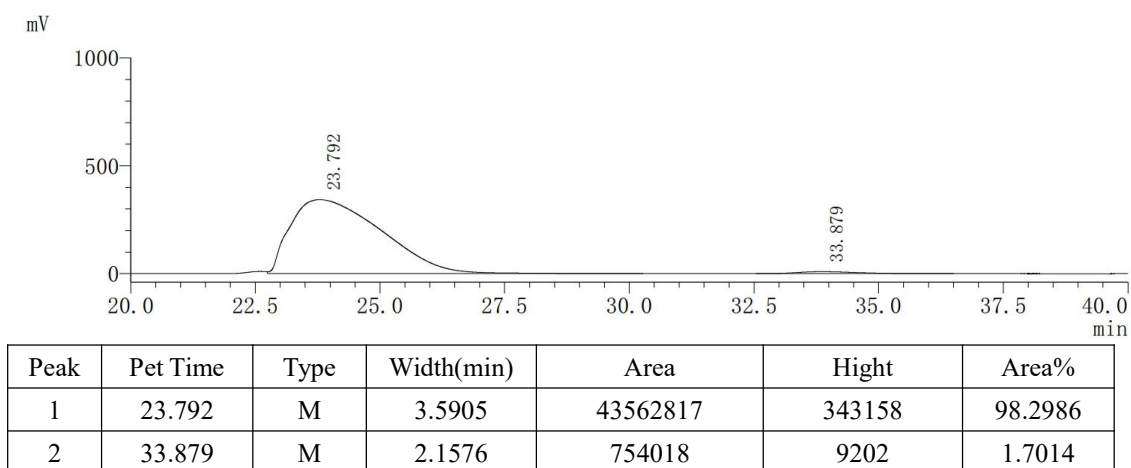
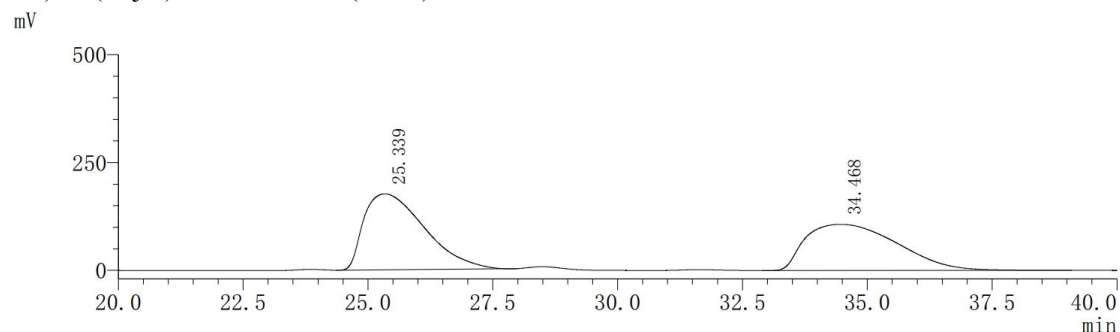


The title compound **3af** was obtained as a yellow solid (35.7 mg, 74%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 9.22 (s, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.45 – 7.41 (m, 7H), 7.36 – 7.33 (m, 1H), 7.16 – 7.12 (m, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 169.8, 164.8, 142.7, 142.6, 139.6, 136.8, 134.5, 133.5, 133.0, 132.2, 131.1, 131.0, 130.5, 130.0, 129.7, 129.6, 129.6, 128.7, 128.5, 128.1, 127.8, 127.6.

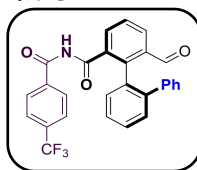
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉BrNO₃, ([M + H]⁺), 484.0543; found 484.0540.

[α]_D²⁰ = -63.2 (*c* = 1.8, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (major) = 23.79 min, *t*_R (minor) = 33.88 min, 97% ee.



(R)-6-formyl-N-(4-(trifluoromethyl)benzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ag)

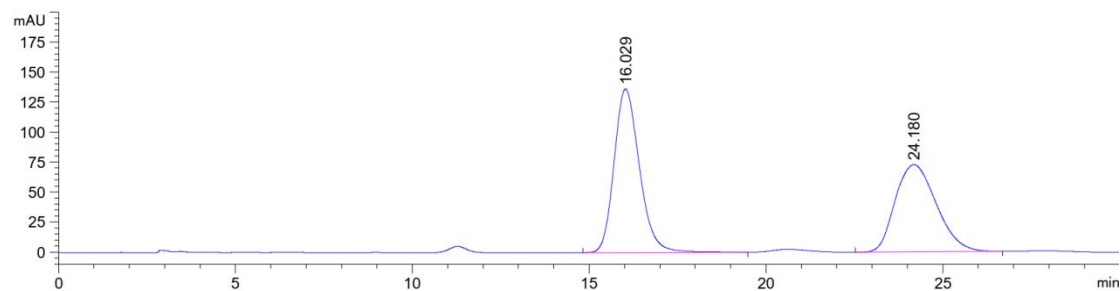


The title compound **3ag** was obtained as a white solid (36.9 mg, 78%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 0.9 Hz, 1H), 9.14 (s, 1H), 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.78 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (td, *J* = 7.7, 0.8 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.38– 7.35 (m, 1H), 7.16– 7.11 (m, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.8, 169.1, 164.5, 142.7, 142.7, 139.5, 136.5, 135.6, 134.9 (q, *J* = 32.7 Hz), 134.7, 133.5, 133.2, 131.2, 130.7, 130.4, 129.7, 129.7, 128.6, 128.5, 128.2, 127.9, 127.7, 126.0 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 271.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -63.25 (s, 1CF₃).

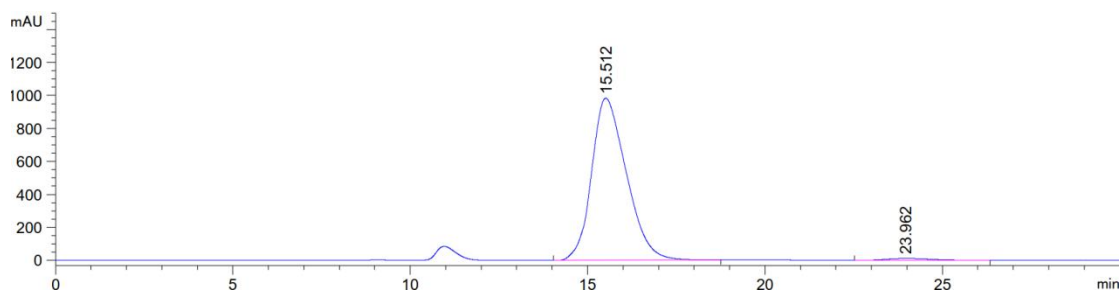
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₁₉F₃NO₃, ([M + H]⁺), 474.1312; found 474.1311.

[α]_D²⁰ = -61.3 (c = 1.8, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); *t*_R (major) = 23.80 min, *t*_R (minor) = 33.88 min, 97% ee.

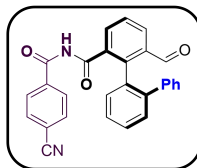


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	16.029	M	0.7744	6775.11914	136.19400	53.5267
2	24.180	M	1.2502	5882.34570	72.75662	46.4733



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	15.512	M	1.0680	6.69160e4	982.00677	98.5061
2	23.962	M	1.1984	1014.80737	11.65987	1.4939

(R)-N-(4-cyanobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ah)

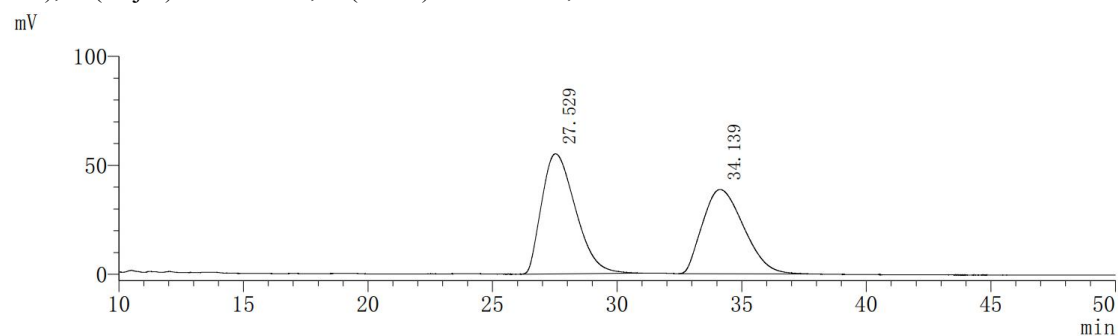


The title compound **3ah** was obtained as a yellow solid (23.6 mg, 55%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 9.15 (s, 1H), 8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.60 – 7.58 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.41 – 7.39 (m, 1H), 7.38 – 7.35 (m, 1H), 7.15 – 7.14 (m, 3H), 7.11 – 7.09 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.5, 168.9, 164.1, 142.5, 142.4, 139.2, 136.0, 135.9, 134.6, 133.2, 133.1, 132.4, 131.1, 130.5, 130.4, 129.6, 129.5, 128.4, 128.4, 128.1, 127.7, 127.6, 117.5, 116.6.

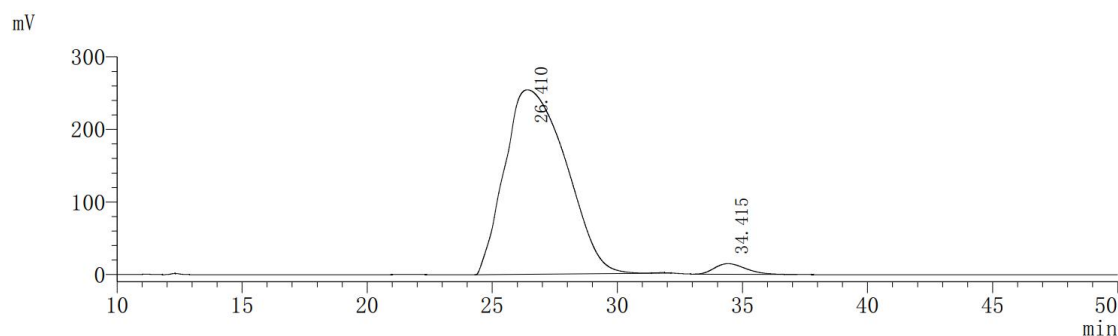
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₁₈N₂NaO₃, ([*M* + Na]⁺), 453.1210; found 453.1208.

[α]_D²⁰ = -91.3 (*c* = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (85:15 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 26.41 min, *t*_R (minor) = 34.42 min, 94% ee.

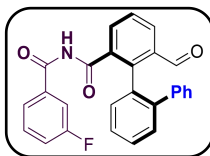


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	27.529	M	2.5394	5202125	55134	53.8915
2	34.139	M	3.1569	4450832	38713	46.1085



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	26.410	M	4.8866	43402014	254246	97.1551
2	34.415	M	2.3252	1270884	14624	2.8449

(R)-N-(3-fluorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ai)

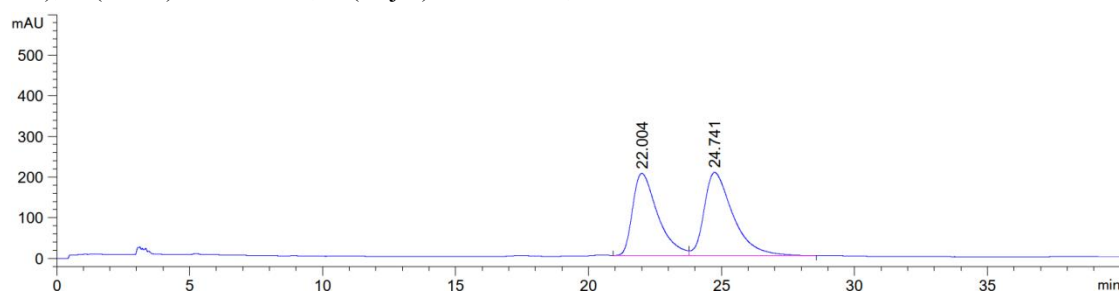


The title compound **3ai** was obtained as a white solid (30.5 mg, 72%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.57 (s, 1H), 8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.44 – 7.34 (m, 3H), 7.28 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.17 – 7.15 (m, 3H), 7.11 – 7.09 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 167.7, 163.9 (d, *J* = 1.2 Hz), 162.9 (d, *J* = 248.0 Hz), 142.7, 142.6, 139.6, 136.3, 134.8 (d, *J* = 7.4 Hz), 134.8, 133.6, 133.3, 131.3, 130.9, 130.7 (d, *J* = 8.0 Hz), 130.4, 130.0, 129.7, 128.6, 128.3, 128.0, 127.7, 123.3 (d, *J* = 3.2 Hz), 120.6 (d, *J* = 21.6 Hz), 115.2 (d, *J* = 23.0 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -110.74 (s, 1F).

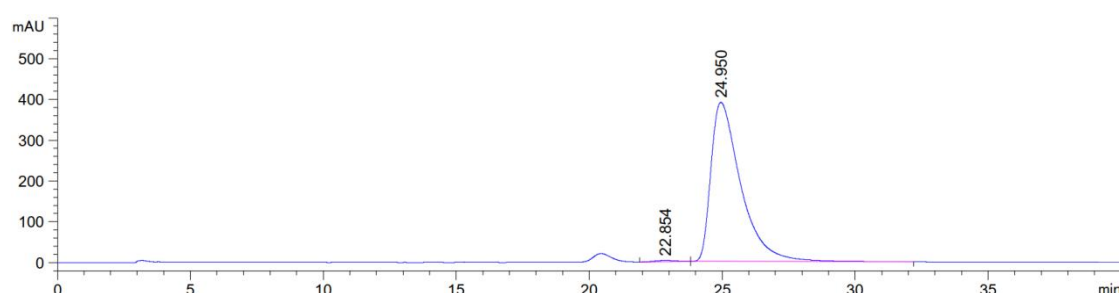
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₈FNNaO₃, ([*M* + Na]⁺), 446.1163; found 446.1153.

[α]_D²⁰ = -70.7 (*c* = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t_R* (minor) = 22.85 min, *t_R* (major) = 24.95 min, 99% ee.

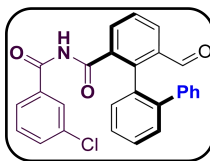


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	22.004	M	0.9894	1.32369e4	202.03552	46.1421
2	24.741	M	1.1356	1.54503e4	204.92700	53.8579



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	22.854	M	0.7368	177.62236	3.23916	0.5775
2	24.950	M	1.1832	3.05799e4	390.23392	99.4225

(R)-N-(3-chlorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3aj)

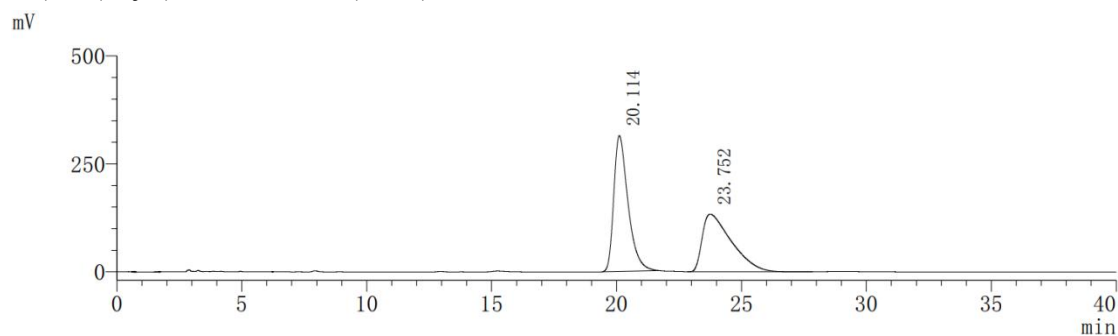


The title compound **3aj** was obtained as a white solid (28.5 mg, 65%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 8.76 (s, 1H), 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 – 7.48 (m, 5H), 7.43 – 7.38 (m, 3H), 7.28 (t, *J* = 8.2 Hz, 1H), 7.15 – 7.13 (m, 3H), 7.10 – 7.09 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 190.8, 167.9, 163.9, 142.5, 142.4, 139.3, 136.2, 135.1, 134.5, 134.1, 133.4, 133.3, 133.1, 131.1, 130.7, 130.2, 130.1, 129.8, 129.5, 128.4, 128.1, 127.9, 127.5, 125.8.

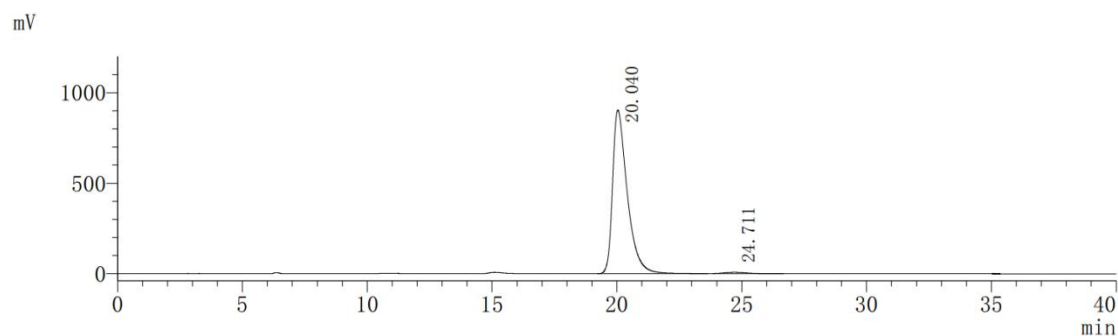
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉ClNO₃, ([*M* + *H*]⁺), 440.1048; found 440.1037.

[α]_D²⁰ = -61.3 (*c* = 1.4, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 20.04 min, *t*_R (minor) = 24.71 min, 98% ee.

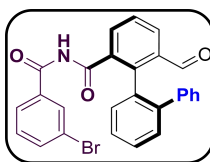


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.114	M	1.0222	12465883	314524	53.6283
2	23.752	M	2.2114	10779079	133351	46.3717



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.040	M	1.0269	36979689	904353	98.9009
2	24.711	M	1.6080	410977	6794	1.0991

(R)-N-(3-bromobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ak)

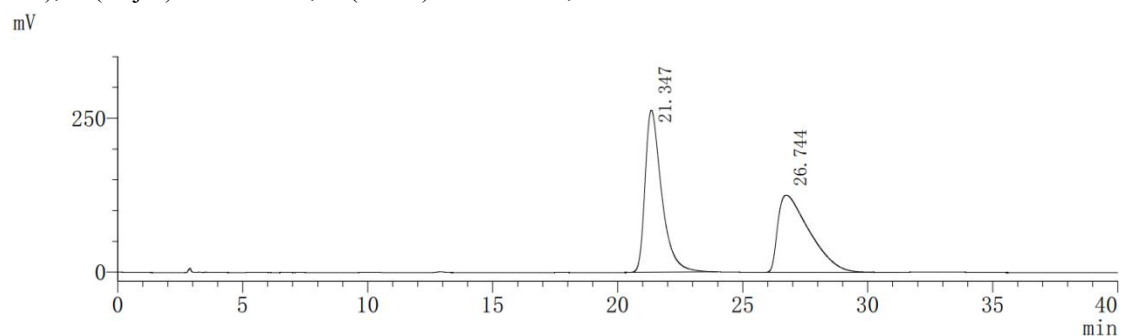


The title compound **3ak** was obtained as a white solid (36.7 mg, 76%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.18 (s, 1H), 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.41 – 7.40 (m, 2H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 – 7.09 (m, 7H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 168.5, 164.1, 142.6, 142.6, 139.5, 136.5, 136.3, 134.6, 134.4, 133.4, 133.3, 131.2, 131.0, 130.8, 130.4, 130.3, 129.8, 129.7, 128.5, 128.2, 127.9, 127.6, 126.5, 123.1.

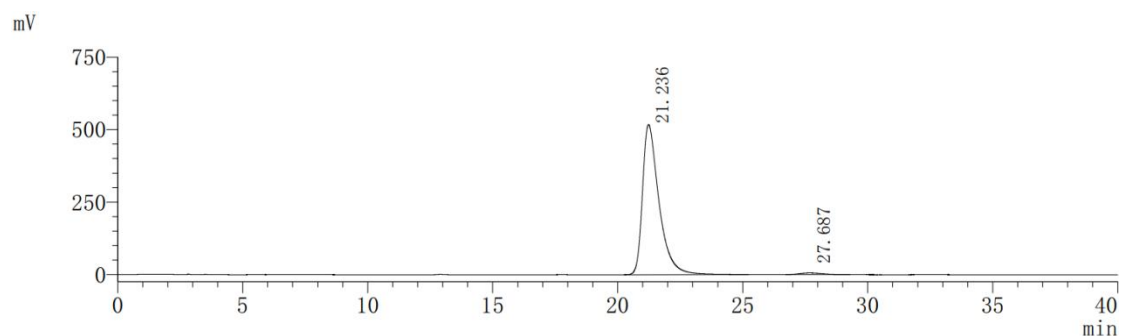
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉BrNO₃, ([*M* + *H*]⁺), 484.0543; found 484.0537.

[α]_D²⁰ = -47.6 (*c* = 1.8, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (major) = 21.24 min, *t*_R (minor) = 27.69 min, 97% ee.

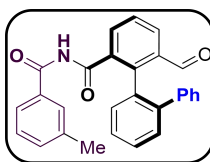


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.347	M	1.1674	12129101	263300	52.4377
2	26.744	M	2.4111	11001381	125345	47.5623



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.236	M	1.1497	23777182	517636	98.5153
2	27.687	M	1.6045	358334	5694	1.4847

(R)-6-formyl-N-(3-methylbenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3al)

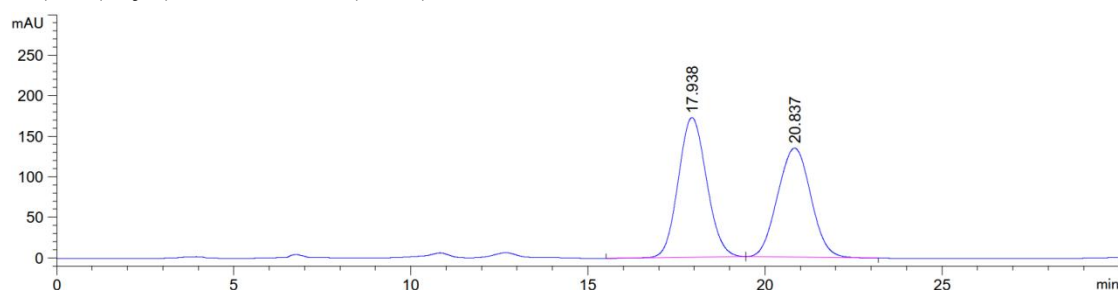


The title compound **3al** was obtained as a yellow solid (29.8 mg, 71%). **¹H NMR (500 MHz, Chloroform-*d*)** ¹H NMR (500 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 0.8 Hz, 1H), 8.77 (s, 1H), 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.42 (m, 5H), 7.38 – 7.33 (m, 3H), 7.26 – 7.23 (m, 1H), 7.14 (s, 7H), 2.35 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.0, 168.6, 165.3, 142.7, 142.6, 139.7, 139.0, 136.9, 134.5, 134.3, 133.5, 133.2, 132.5, 131.2, 130.6, 129.9, 129.7, 129.6, 128.8, 128.5, 128.5, 128.1, 127.8, 127.5, 124.9, 21.4.

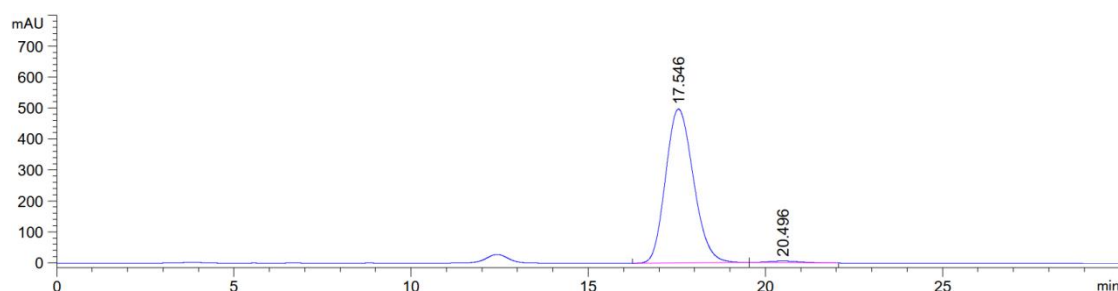
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₁NNaO₃, ([M + Na]⁺), 442.1414; found 442.1403.

[α]_D²⁰ = -120.1 (*c* = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t_R* (major) = 17.55 min, *t_R* (minor) = 20.50 min, 98% ee.

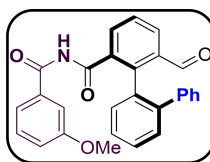


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.938	M	0.8703	9588.98145	172.30843	52.2190
2	20.837	M	1.0439	8774.01367	134.53415	47.7810



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.546	M	0.8580	2.71352e4	496.94574	98.7650
2	20.496	M	0.9385	339.31244	5.29588	1.2350

(R)-6-formyl-N-(3-methoxybenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3am)

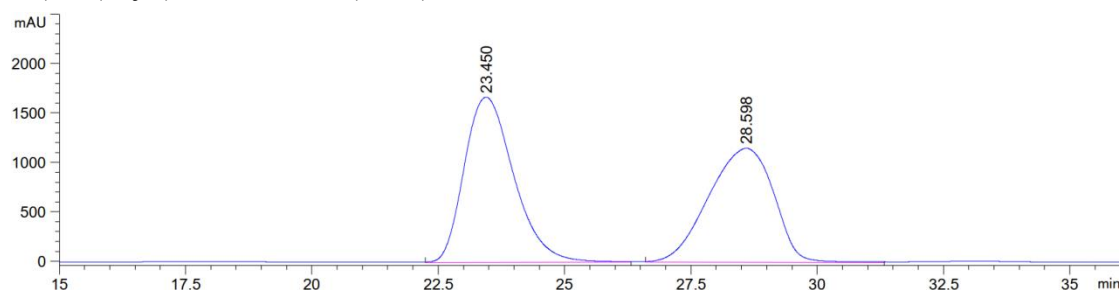


The title compound **3am** was obtained as a yellow oil (30.9 mg, 71%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 0.8 Hz, 1H), 8.93 (s, 1H), 7.95 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.37 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 7.16 – 7.12 (m, 5H), 7.07 – 7.05 (m, 2H), 3.79 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 191.0, 169.1, 165.1, 160.1, 142.6, 139.7, 137.0, 134.5, 133.7, 133.4, 133.0, 131.1, 130.6, 130.0, 129.8, 129.8, 129.6, 128.4, 128.0, 127.8, 127.5, 119.9, 119.6, 113.0, 55.7.

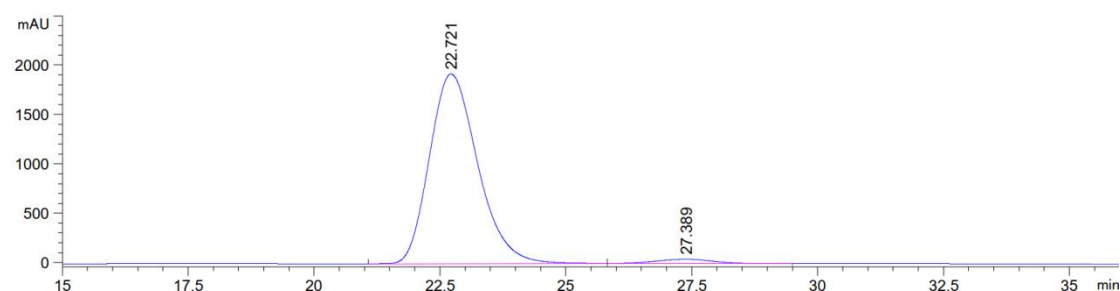
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₂NO₄, ([M + H]⁺), 436.1543; found 436.1547.

[α]_D²⁰ = -125.4 (*c* = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (major) = 22.72 min, t_R (minor) = 27.39 min, 95% ee.

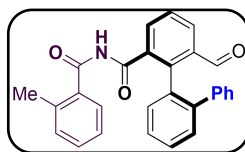


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	23.450	MM	1.1421	1.14615e5	1672.50244	52.5840
2	28.598	MM	1.4938	1.03350e5	1153.12048	47.4160



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	22.721	BB	1.0423	1.27747e5	1919.96448	97.4577
2	27.389	BB	1.1908	3332.48389	43.20620	2.5423

(R)-6-formyl-N-(2-methylbenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3an)

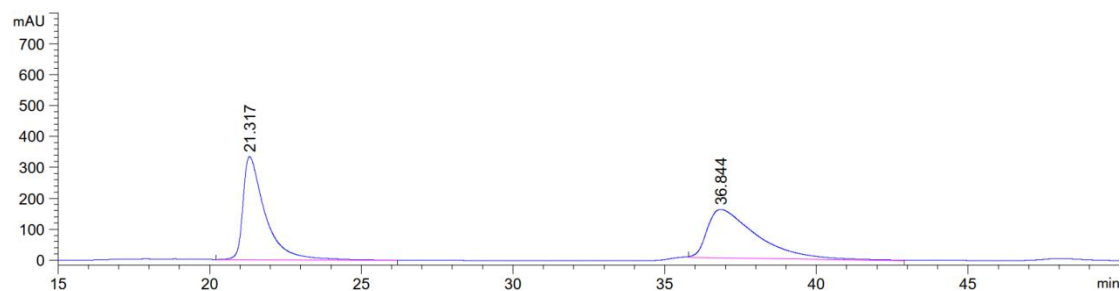


The title compound **3an** was obtained as a white solid (31.4 mg, 75%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.69 (d, J = 0.9 Hz, 1H), 8.31 (s, 1H), 7.96 (dd, J = 7.8, 1.5 Hz, 1H), 7.80 (dd, J = 7.7, 1.4 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.41 – 7.36 (m, 2H), 7.34 (td, J = 7.7, 1.5 Hz, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.16 – 7.12 (m, 4H), 7.11 – 7.09 (m, 2H), 7.04 (dd, J = 7.8, 1.4 Hz, 1H), 2.41 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 190.9, 167.5, 167.5, 142.6, 142.6, 139.6, 137.8, 136.6, 134.6, 133.6, 133.4, 131.7, 131.6, 131.0, 130.7, 130.1, 129.7, 129.7, 128.4, 128.2, 127.8, 127.5, 127.0, 125.9, 20.2.

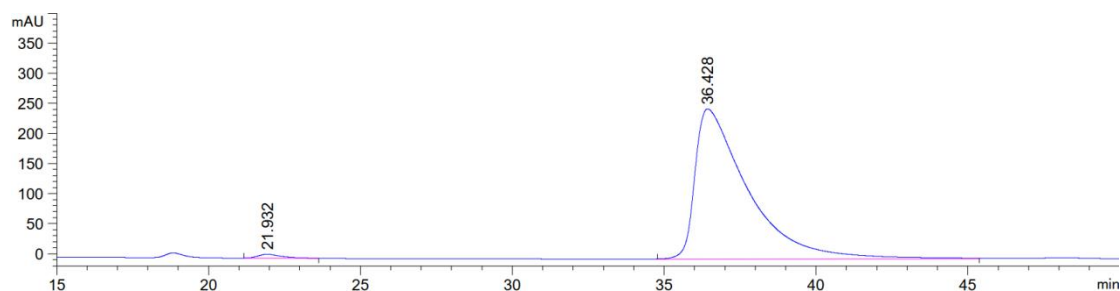
HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₂₂NO₃, ([M + H]⁺), 420.1594; found 420.1605.

[α]_D²⁰ = -96.2 (c = 1.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IF column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 21.93 min, t_R (major) = 36.43 min, 98% ee.

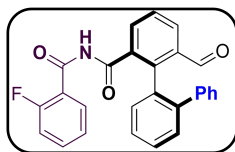


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.317	MM	0.7320	1.68544e4	332.73495	48.9302
2	36.844	MM	1.8823	1.75914e4	155.76401	51.0698



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.932	MM	0.9568	376.20032	6.55281	1.2233
2	36.428	MM	2.0248	3.03756e4	250.02936	98.7767

(R)-N-(2-fluorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ao)

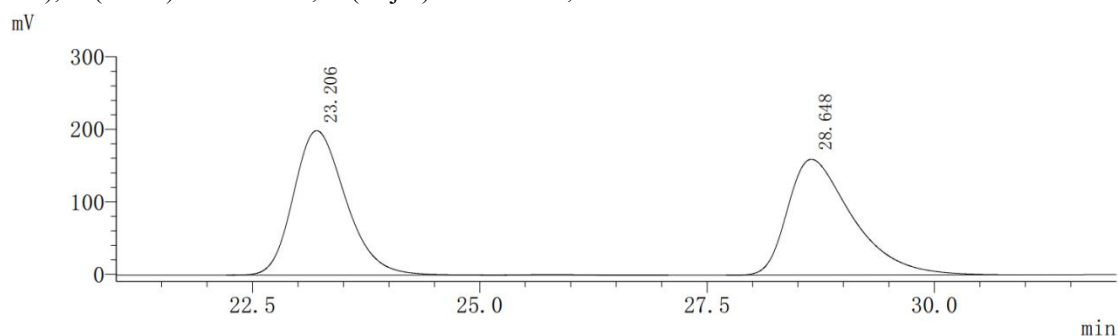


The title compound **3ao** was obtained as a white solid (30.5 mg, 72%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.76 (d, *J* = 1.8 Hz, 1H), 8.73 (d, *J* = 13.0 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.96 (td, *J* = 7.8, 1.8 Hz, 1H), 7.74 (dt, *J* = 7.8, 1.7 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.52 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.11 (m, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 167.2, 161.2 (d, *J* = 3.0 Hz), 160.4 (d, *J* = 247.7 Hz), 143.1, 142.2, 139.7, 136.8, 135.1 (d, *J* = 9.5 Hz), 134.6, 133.0, 132.4, 132.4, 131.1, 130.3, 129.8, 129.7, 129.3, 128.2, 127.9, 127.4, 127.2, 125.3 (d, *J* = 3.3 Hz), 120.0 (d, *J* = 10.6 Hz), 116.3 (d, *J* = 24.5 Hz). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -111.83 (s, 1F).

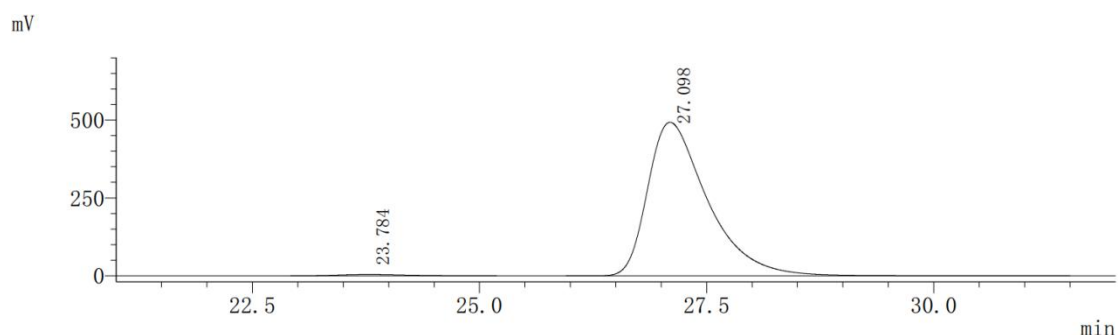
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉FN₃, ([M + H]⁺), 424.1343; found 424.1332.

[α]_D²⁰ = -40.3 (c = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 23.78 min, t_R (major) = 27.10 min, 98% ee.

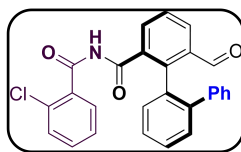


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	23.206	M	1.0436	8027075	199238	50.3373
2	28.648	M	1.2875	7919499	159705	49.6627



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	23.784	M	1.2659	233895	4574	1.0237
2	27.098	M	1.1669	22613407	493132	98.9763

(R)-N-(2-chlorobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ap)

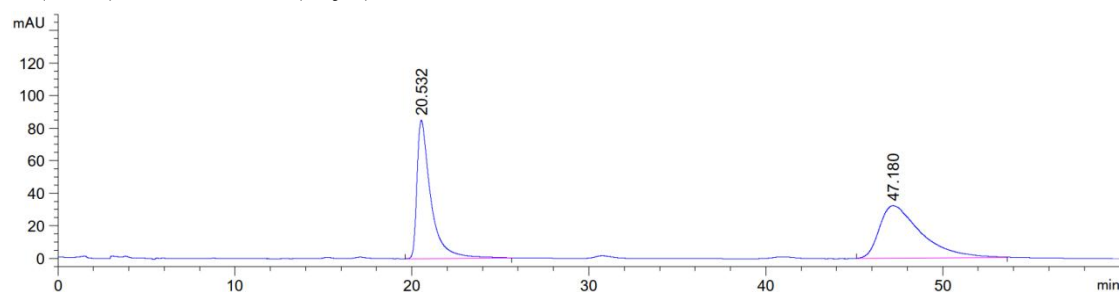


The title compound **3ap** was obtained as a white solid (31.2 mg, 72%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 8.35 (s, 1H), 8.00 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.37 (m, 7H), 7.32 (td, *J* = 7.3, 1.7 Hz, 1H), 7.15 – 7.13 (m, 3H), 7.12 – 7.08 (m, 2H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 191.0, 166.5, 165.3, 143.3, 142.3, 139.7, 136.2, 134.8, 133.9, 133.14, 133.06, 132.5, 131.1, 130.8, 130.7, 130.5, 130.3, 130.0, 129.8, 129.7, 128.4, 128.2, 127.8, 127.5, 127.3.

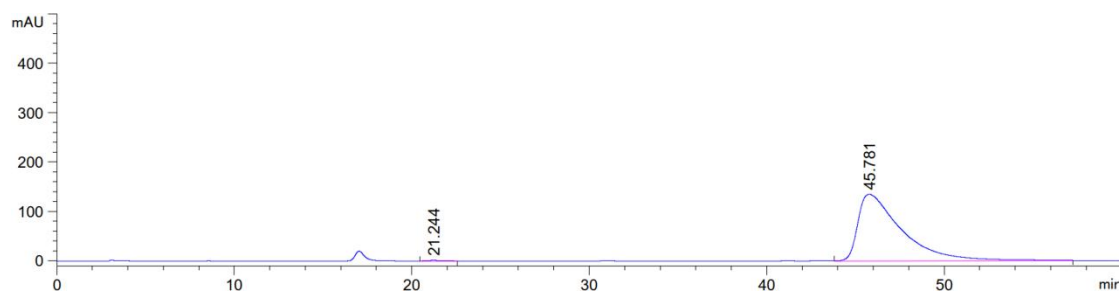
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₉ClNO₃, ([*M* + *H*]⁺), 440.1048; found 440.1037.

[α]_D²⁰ = -62.1 (*c* = 1.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IF column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t_R* (minor) = 21.24 min, *t_R* (major) = 45.78 min, 99% ee.

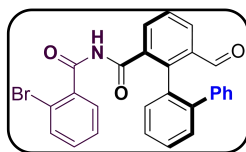


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.532	MM	0.7896	4604.29004	85.04762	46.5102
2	47.180	MM	2.7290	5295.24609	32.33969	53.4898



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.244	MM	1.2195	125.27692	1.71209	0.5331
2	45.781	MM	2.8702	2.33751e4	135.73512	99.4669

(R)-N-(2-bromobenzoyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3aq)

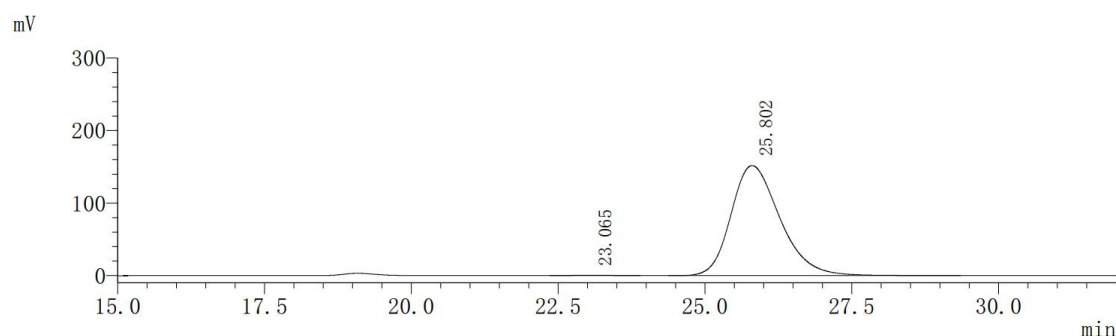
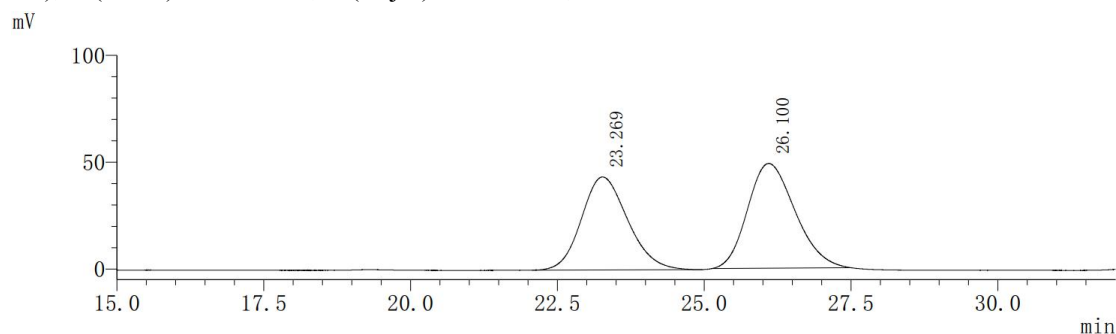


The title compound **3aq** was obtained as a yellow solid (37.2 mg, 77%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.29 (s, 1H), 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.84 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.51 – 7.45 (m, 3H), 7.41 – 7.29 (m, 5H), 7.16 – 7.09 (m, 5H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 191.0, 166.4, 166.2, 143.2, 142.3, 139.7, 136.3, 136.0, 134.8, 133.6, 133.2, 133.1, 132.4, 131.1, 130.7, 130.4, 129.7, 129.5, 128.5, 128.3, 127.9, 127.8, 127.5, 119.2.

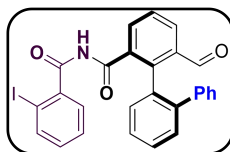
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₈BrNNaO₃, ([*M* + Na]⁺), 506.0362; found 506.0368.

[α]_D²⁰ = -7.2 (*c* = 1.8, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 23.07 min, *t*_R (major) = 25.80 min, 99% ee.



(*R*)-6-formyl-*N*-(2-iodobenzoyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ar)



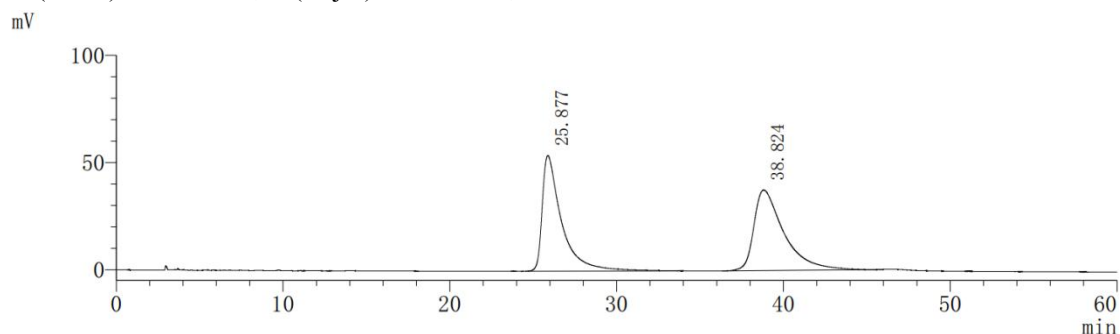
The title compound **3ar** was obtained as a white solid (36.1 mg, 68%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.18 (s, 1H), 7.98 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.51 – 7.47 (m, 3H), 7.40 – 7.37 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.18 – 7.09 (m, 7H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 167.5, 166.4, 143.1, 142.4, 140.3, 140.3, 139.6, 136.0, 134.8, 133.4, 133.2, 132.2, 131.1, 130.8, 130.4, 129.8, 129.7, 128.5, 128.4, 128.3, 128.3, 128.0, 127.6, 91.9.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₁₈INNaO₃, ([*M* + Na]⁺), 554.0224; found 554.0228.

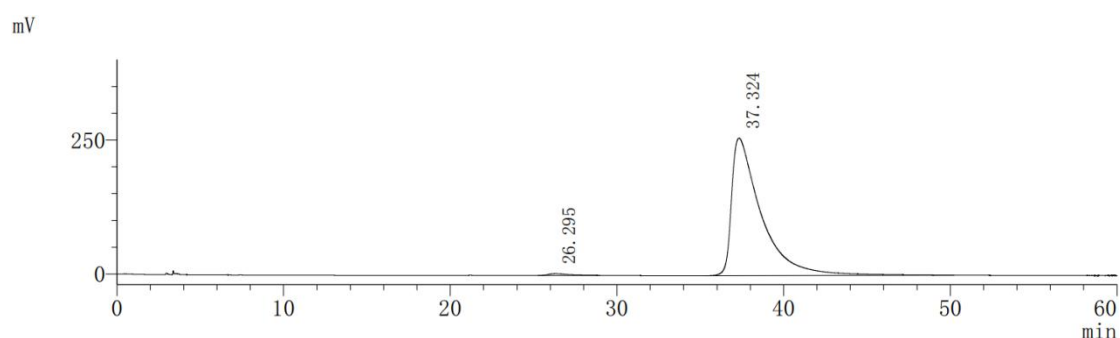
[α]_D²⁰ = -3.2 (*c* = 1.8, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IF column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm);

t_R (minor) = 26.30 min, *t_R* (major) = 37.32 min, 98% ee.

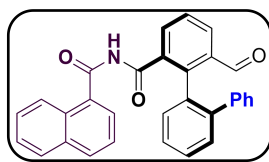


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	25.877	M	1.8846	4372999	53991	48.1931
2	38.824	M	3.0741	4700902	37602	51.8069



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	26.295	M	1.8730	300320	3471	0.9380
2	37.324	M	2.9813	31717306	256600	99.0620

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)-1-naphthamide (3as)

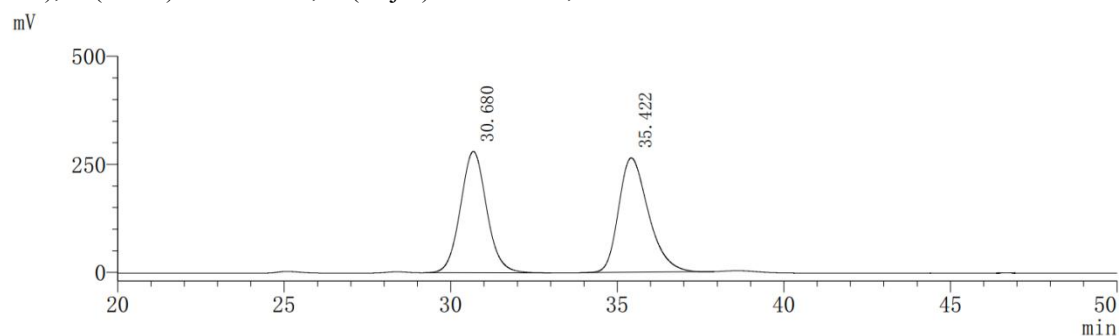


The title compound **3as** was obtained as a yellow solid (32.3 mg, 71%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.70 (d, *J* = 0.8 Hz, 1H), 8.51 (s, 1H), 8.27 – 8.25 (m, 1H), 7.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.58 – 7.53 (m, 2H), 7.50 (td, *J* = 7.8, 0.8 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.31 (td, *J* = 7.3, 1.6 Hz, 2H), 7.15 – 7.12 (m, 3H), 7.10 – 7.07 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 191.0, 167.5, 167.0, 142.6, 142.5, 139.5, 136.5, 134.6, 133.9, 133.6, 133.3, 132.8, 131.4, 131.1, 130.7, 130.2, 130.2, 129.7, 129.6, 128.7, 128.5, 128.3, 128.0, 127.8, 127.5, 126.9, 126.3, 125.0, 124.4.

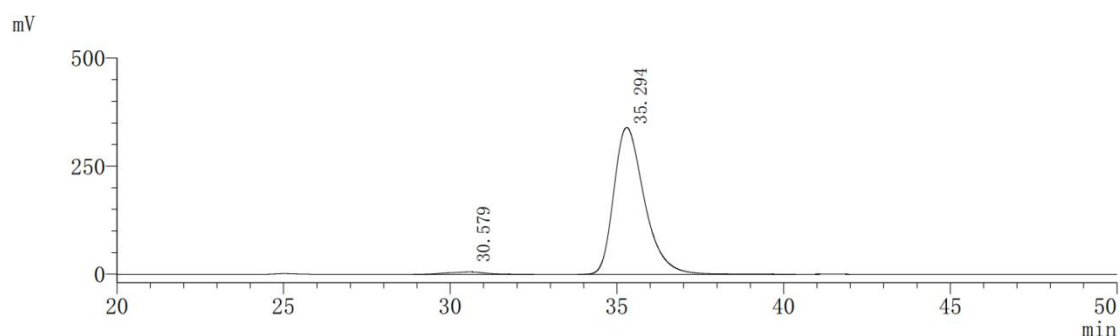
HRMS (ESI-TOF) (*m/z*): Calcd for C₃₁H₂₂NO₃, ([*M* + *H*]⁺), 456.1594; found 456.1596.

[α]_D²⁰ = -76.2 (*c* = 1.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 30.58 min, *t*_R (major) = 35.29 min, 96% ee.

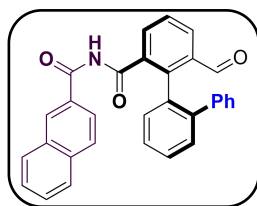


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	30.680	M	1.4251	15393260	280828	48.2766
2	35.422	M	1.6220	16492268	264830	51.7234



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	30.579	M	2.1454	436970	5559	1.9710
2	35.294	M	1.6417	21732639	339717	98.0290

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)-2-naphthamide (3at)

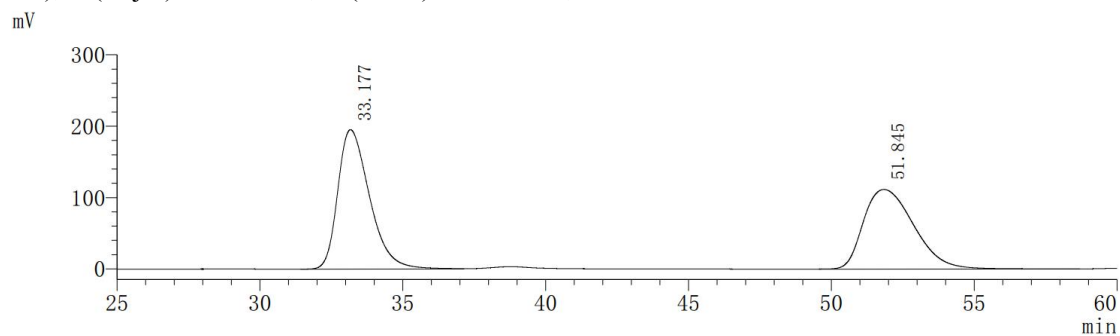


The title compound **3at** was obtained as a yellow oil (24.1 mg, 53%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.70 (s, 1H), 8.97 (s, 1H), 8.07 (d, J = 1.8 Hz, 1H), 7.98 (dd, J = 7.8, 1.4 Hz, 1H), 7.86 – 7.82 (m, 4H), 7.65 (dd, J = 8.6, 1.9 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.54 – 7.49 (m, 2H), 7.47 (d, J = 7.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.16 – 7.13 (m, 5H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 191.0, 168.9, 165.3, 142.6, 142.6, 139.7, 136.9, 135.7, 134.5, 133.4, 133.3, 132.4, 131.2, 130.6, 130.0, 129.8, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.5, 128.1, 128.0, 127.9, 127.5, 127.3, 123.7.

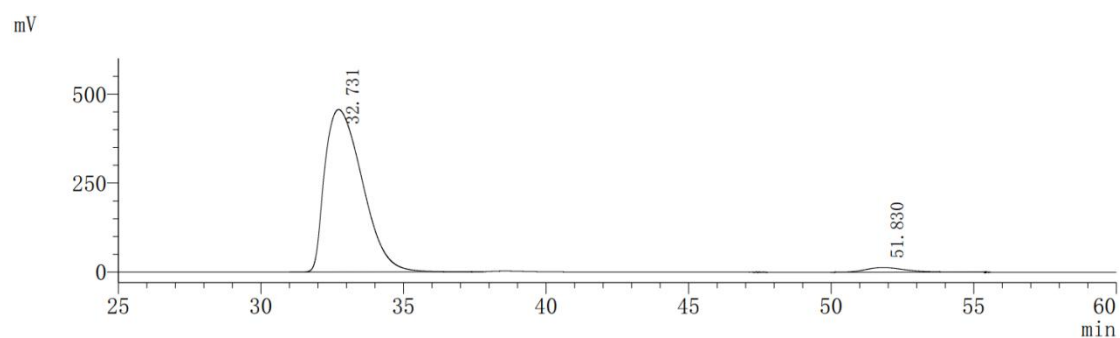
HRMS (ESI-TOF) (m/z): Calcd for C₃₁H₂₂NO₃, ([M + H]⁺), 456.1594; found 456.1590.

[α]_D²⁰ = -77.7 (c = 1.2, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 32.73 min, t_R (minor) = 51.83 min, 94% ee.

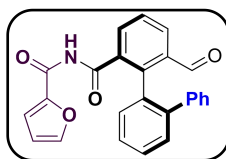


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	33.177	M	1.9936	15138872	195385	52.5619
2	51.845	M	3.1447	13663090	111581	47.4381



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	32.731	M	2.3708	41811614	456607	97.0231
2	51.830	M	2.4502	1282872	13190	2.9769

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)furan-2-carboxamide (3au)



The title compound **3au** was obtained as a white solid (30.8 mg, 78%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 8.75 (s, 1H), 7.97 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.43 – 7.38 (m, 3H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.17 – 7.12 (m, 5H), 6.54 (dd, *J* = 3.6, 1.7 Hz, 1H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 191.0, 167.3, 154.8, 146.0, 145.5, 142.9, 142.6, 139.8, 136.6, 134.5, 133.2, 133.2, 131.2, 130.6, 130.0, 129.8, 129.6, 128.4, 128.0, 127.8, 127.4, 118.3, 113.4.

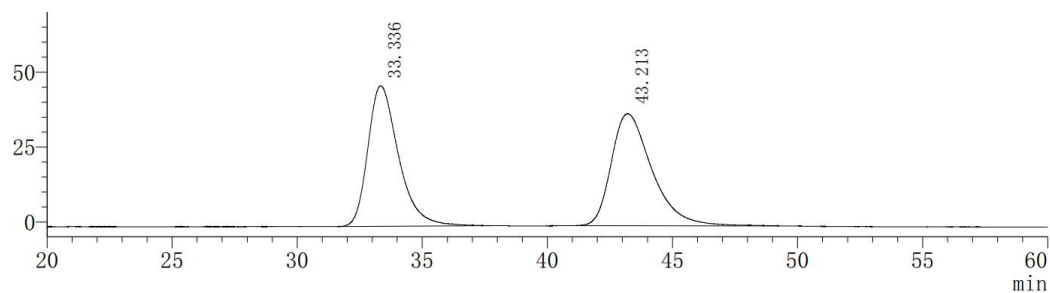
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₁₈NO₄, ([*M* + *H*]⁺), 396.1230; found 396.1236.

[α]_D²⁰ = -115.2 (*c* = 1.5, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak IC column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm);

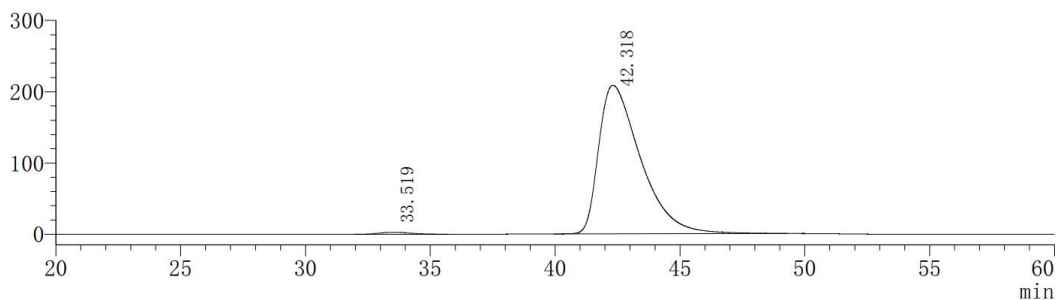
*t*_R (minor) = 33.52 min, *t*_R (major) = 42.32 min, 98% ee.

mV



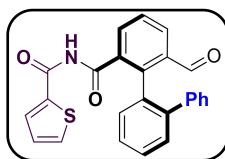
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	33.336	M	2.1939	4006919	46922	48.6265
2	43.213	M	2.8411	4233274	37400	51.3735

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	33.519	M	2.3091	253207	2935	1.0277
2	42.318	M	3.0360	24384505	208612	98.9723

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)thiophene-2-carboxamide (3av)

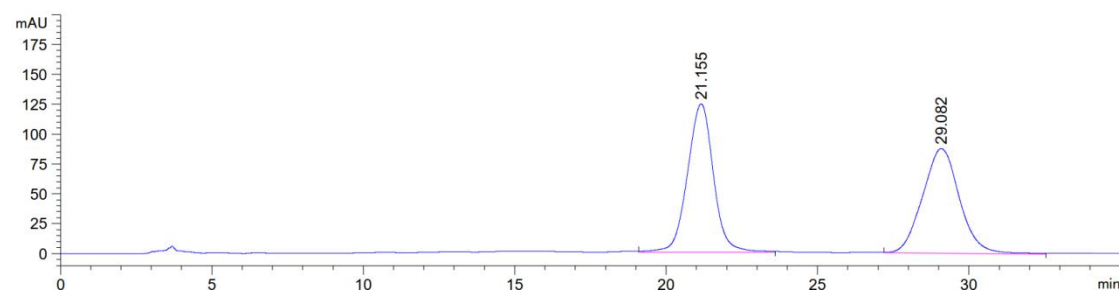


The title compound **3av** was obtained as a white solid (32.9 mg, 80%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 9.63 (d, *J* = 0.8 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.47 – 7.44 (m, 3H), 7.43 – 7.33 (m, 3H), 7.24 – 7.22 (m, 2H), 7.16 – 7.11 (m, 3H), 6.66 (dd, *J* = 5.0, 3.8 Hz, 1H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 190.9, 171.4, 159.9, 142.7, 142.5, 139.9, 137.3, 137.1, 134.2, 134.1, 133.7, 132.4, 131.6, 131.0, 130.2, 129.8, 129.5, 129.3, 128.4, 128.4, 127.8, 127.8, 127.4.

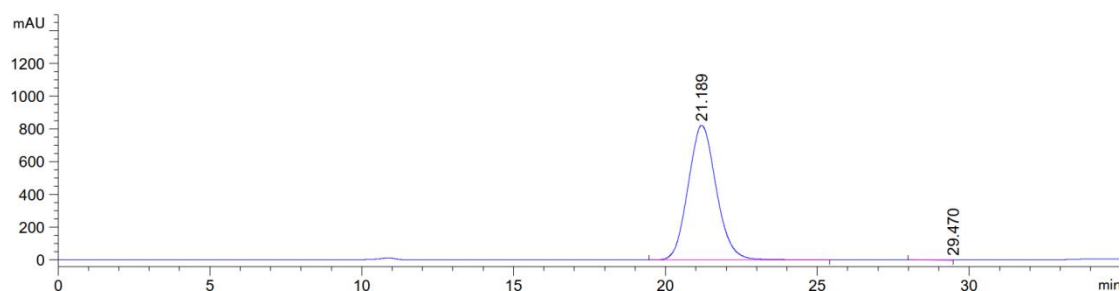
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₁₈NO₃S, ([M + H]⁺), 412.1002; found 412.1010.

[α]_D²⁰ = -133.0 (*c* = 1.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 21.19 min, *t*_R (major) = 29.47 min, 99% ee.

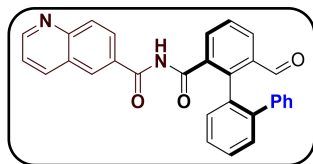


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.155	MM R	0.9967	7416.22070	124.01254	49.7207
2	29.082	MM R	1.4251	7499.54492	87.70899	50.2793



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.189	MM R	0.9924	5.29945e4	822.77960	99.7805
2	29.470	MM R	0.6379	116.55227	3.04531	0.2195

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)quinoline-6-carboxamide (3aw)



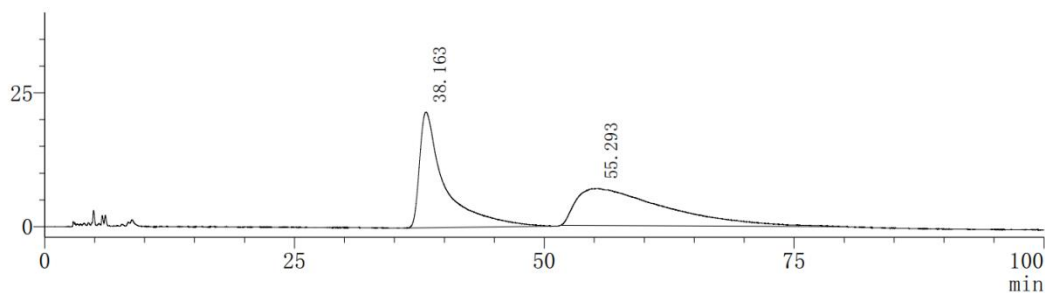
The title compound **3aw** was obtained as a yellow solid (18.7 mg, 41%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 9.13 (s, 1H), 9.00 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.13 – 8.07 (m, 3H), 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.34 (td, *J* = 7.1, 2.2 Hz, 1H), 7.12 (s, 5H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 168.7, 164.9, 153.1, 150.2, 142.7, 142.6, 139.6, 137.3, 136.6, 134.7, 133.4, 133.4, 131.3, 130.7, 130.6, 130.4, 130.3, 129.7, 129.3, 128.5, 128.2, 127.9, 127.6, 127.5, 127.4, 122.4.

HRMS (ESI-TOF) (*m/z*): Calcd for C₃₀H₂₁N₂O₃, ([M + H]⁺), 457.1547; found 457.1557.

[α]_D²⁰ = -126.2 (*c* = 0.9, CH₂Cl₂).

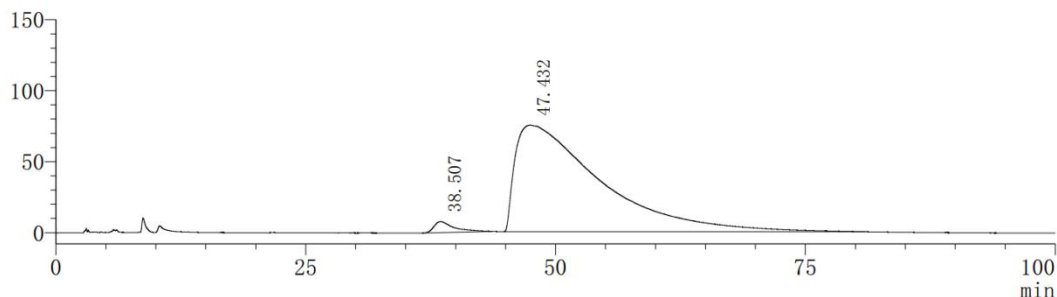
HPLC analysis: Daicel Chiralpak AD-H column (85:15 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 38.51 min, *t*_R (major) = 47.43 min, 95% ee.

mV



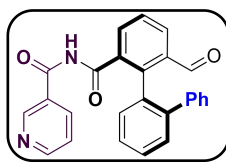
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	38.163	M	3.4921	3802931	21616	46.8770
2	55.293	M	11.1016	4309643	6920	53.1230

mV



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	38.507	M	3.0677	1071160	7737	2.3416
2	47.432	M	15.2503	44673678	75076	97.6584

(R)-N-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)nicotinamide (3ax)

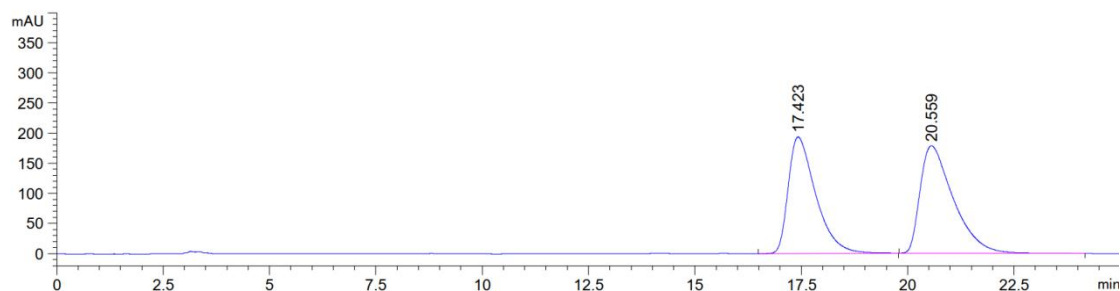


The title compound **3ax** was obtained as a yellow solid (26.4 mg, 65%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 9.13 (s, 1H), 8.67 (s, 1H), 8.63 (d, *J* = 3.9 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.83 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.38 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.20 – 7.17 (m, 1H), 7.07 – 7.05 (m, 3H), 7.03 – 7.01 (m, 2H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 168.6, 164.3, 153.8, 149.0, 142.7, 142.6, 139.5, 136.4, 135.8, 134.7, 133.31, 133.28, 131.26, 130.8, 130.4, 129.8, 129.7, 128.5, 128.2, 127.9, 127.6, 123.6.

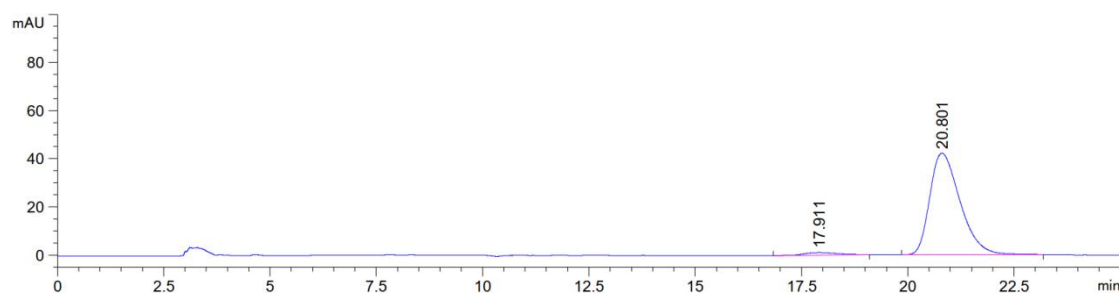
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₁₉N₂O₃, ([M + H]⁺), 407.1390; found 407.1386.

[α]_D²⁰ = -108.6 (*c* = 1.3, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 17.91 min, *t*_R (major) = 20.80 min, 95% ee.

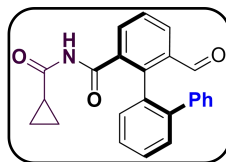


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.423	MM R	0.6810	8673.96191	193.50725	47.2799
2	20.559	MM R	0.7996	9672.03223	178.08861	52.7201



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.911	MM R	0.8364	53.60511	1.06814	2.4999
2	20.801	MM R	0.7578	2090.67334	42.21397	97.5001

(R)-N-(cyclopropanecarbonyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ay)

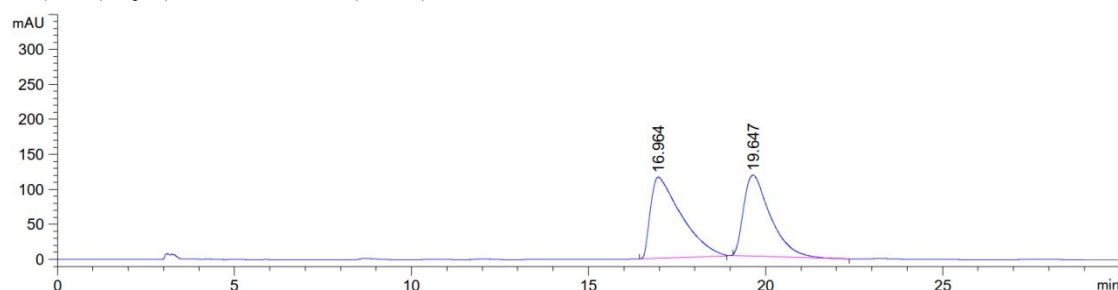


The title compound **3ay** was obtained as a white solid (12.9 mg, 35%). **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.81 (s, 1H), 8.03 (dd, J = 7.9, 1.5 Hz, 1H), 7.79 (s, 1H), 7.71 (dd, J = 7.7, 1.4 Hz, 1H), 7.57 (td, J = 7.5, 1.4 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.48 (td, J = 7.4, 1.6 Hz, 2H), 7.34 (dd, J = 7.6, 1.3 Hz, 1H), 7.18 – 7.13 (m, 3H), 7.09 – 7.07 (m, 2H), 2.54 – 2.49 (m, 1H), 1.13 – 1.07 (m, 2H), 0.99 – 0.92 (m, 2H). **¹³C NMR (125 MHz, Chloroform-*d*)** δ 191.2, 175.5, 166.6, 143.6, 142.1, 139.8, 136.4, 135.1, 133.1, 132.8, 131.3, 130.7, 130.5, 129.9, 129.8, 128.5, 128.2, 127.9, 127.6, 14.6, 11.1, 10.9.

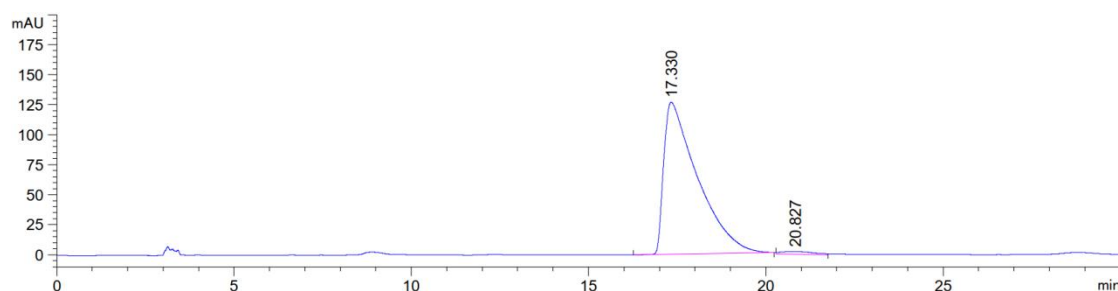
HRMS (ESI-TOF) (m/z): Calcd for C₂₄H₂₀NO₃, ([M + H]⁺), 370.1438; found 370.1447.

[α]_D²⁰ = -70.8 (c = 0.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak OD-3 column (93:7 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 17.33 min, t_R (minor) = 20.83 min, 97% ee.

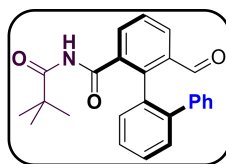


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	16.964	MM R	1.0100	7038.58398	116.14294	53.4668
2	19.647	MM R	0.8828	6125.82715	115.65082	46.5332



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.330	MM R	0.9226	8370.72949	126.56844	98.2594
2	20.827	MM R	1.0553	148.27992	2.34175	1.7406

(*R*)-6-formyl-*N*-pivaloyl-[1,1':2',1''-terphenyl]-2-carboxamide (3az)

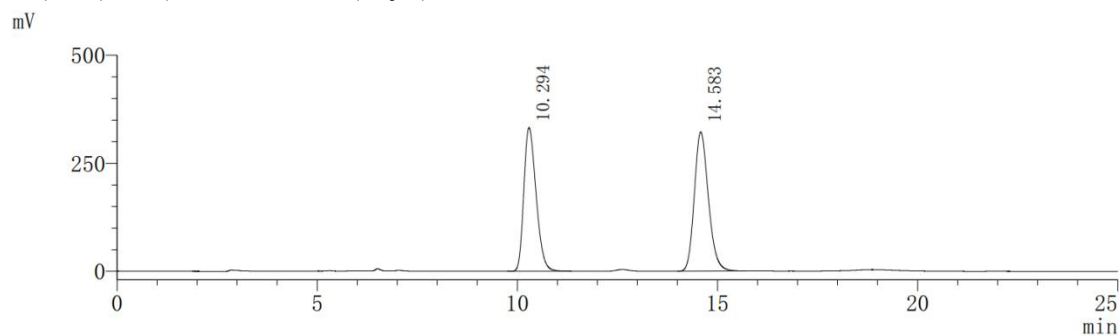


The title compound **3az** was obtained as a white solid (12.3 mg, 32%). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.61 (d, *J* = 0.8 Hz, 1H), 8.20 (s, 1H), 7.91 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.47 (td, *J* = 7.7, 0.8 Hz, 1H), 7.43 (td, *J* = 7.3, 1.7 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.19 – 7.13 (m, 5H), 1.06 (s, 9H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 190.9, 176.3, 169.0, 142.8, 142.0, 139.6, 137.2, 134.3, 133.4, 133.0, 131.1, 130.7, 129.8, 129.7, 128.5, 128.1, 127.8, 127.6, 40.2, 26.9.

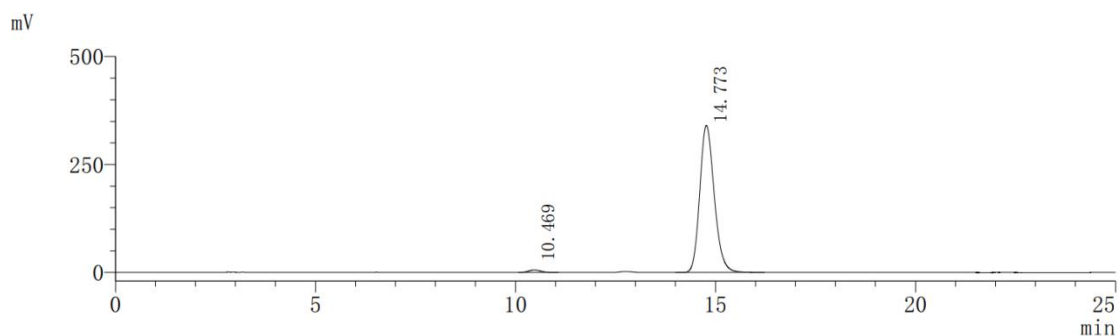
HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₄NO₃, ([*M* + *H*]⁺), 386.1751; found 386.1757.

[α]_D²⁰ = -57.6 (*c* = 0.6, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); *t*_R (minor) = 10.47 min, *t*_R (major) = 14.77 min, 97% ee.



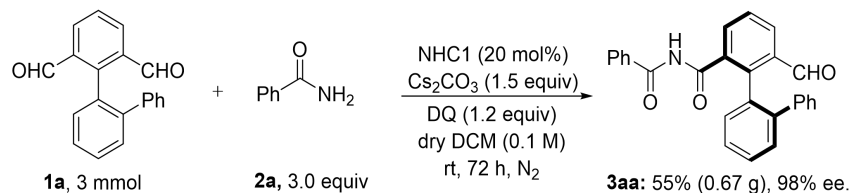
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.294	M	0.5596	7059704	332237	47.2598
2	14.583	M	0.6364	7878361	322097	52.7402



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.469	M	0.5636	125183	5911	1.4355
2	14.773	M	0.6556	8595391	340556	98.5645

III Synthetic Applications

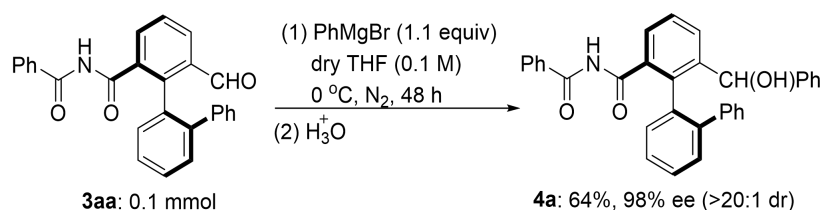
3.1 Scale-up synthesis:



In a nitrogen-filled glovebox, a flame-dried 100 mL Schlenk reaction tube equipped with a magnetic stir bar was charged with **NHC-1** (20 mol%, 0.252 g), Cs_2CO_3 (1.466g, 4.5 mmol), [1,1':2',1''-terphenyl]-2,6-dicarbaldehyde **1a** (0.858 g, 3 mmol) and anhydrous dichloromethane (30.0 mL). The mixture was stirred for 5 minutes, followed by the addition of Benzamide **2a** (1.09 g, 3.0 equiv) and 3,3',5,5'-tetra-*tert*-butyldiphenylquinone (1.469 g, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at rt for 72 h. The mixture was concentrated under reduced pressure and purified by *via* column chromatography on silica gel (hexanes/EtOAc = 4:1) to afford 0.67 g product **3aa** in 55% yield with 98% ee.

3.2 Synthetic Transformation

3.2.1,

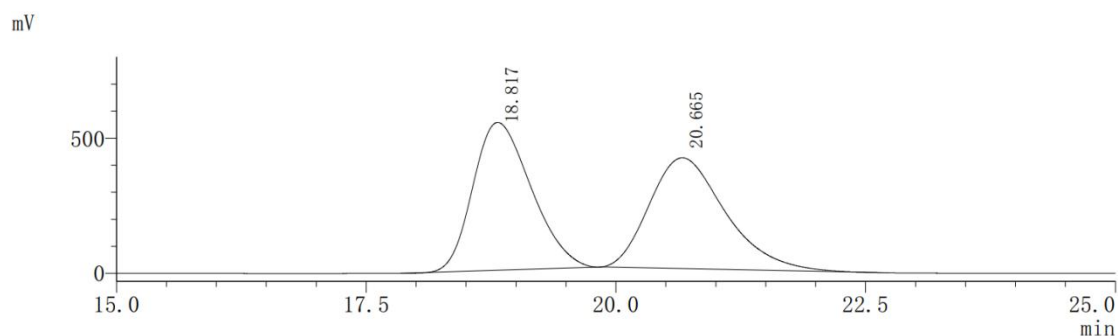


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **3aa** (0.1 mmol, 40.5 mg) and anhydrous tetrahydrofuran (1.0 mL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. 1 mol/L PhMgBr in THF (110 μL , 1.1 equiv) was added dropwise and stirring at 0 $^\circ\text{C}$ for 48 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3 $\times$ 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : acetone = 2:1) to afford the desired product **4a** as a colorless oil. (yield: 64 %, 98% ee). **^1H NMR (500 MHz, Chloroform-*d*)** δ 8.95 (s, 1H), 7.64 – 7.62 (m, 2H), 7.54 (dd, J = 7.7, 1.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.43 – 7.41 (m, 2H), 7.39 (td, J = 7.4, 1.7 Hz, 1H), 7.36 – 7.25 (m, 8H), 7.20 – 7.17 (m, 2H), 7.15 – 7.11 (m, 1H), 7.01 (dd, J = 7.0, 1.9 Hz, 2H), 5.47 (d, J = 2.7 Hz, 1H), 1.00 (d, J = 3.1 Hz, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 170.0, 165.4, 143.3, 143.2, 141.1, 140.6, 137.5, 136.3, 136.1, 133.2, 132.7, 131.2, 130.7, 130.2, 129.9, 128.93, 128.89, 128.6, 128.4, 128.3, 128.2, 128.0, 127.6, 127.3, 127.2, 126.0, 71.5.

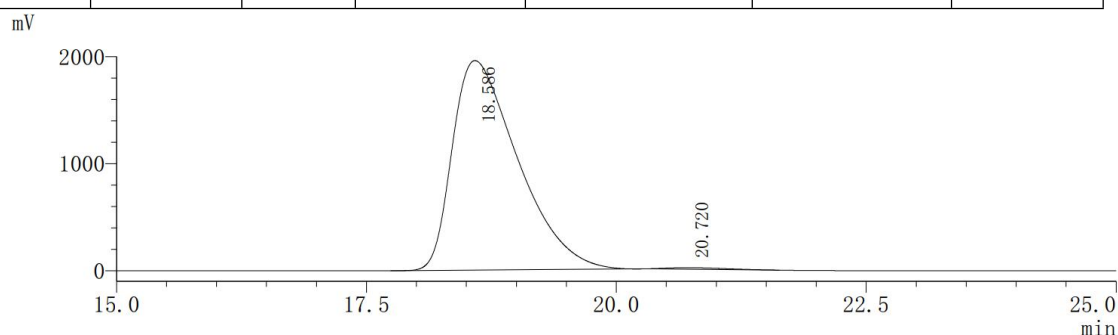
HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{33}\text{H}_{25}\text{NNaO}_3$, $([\text{M} + \text{Na}]^+)$, 506.1727; found 506.1720.

$[\alpha]_D^{19}$ = -16.1 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 $^\circ\text{C}$, 254 nm); t_R (major) = 18.59 min, t_R (minor) = 20.72 min, 98% ee.

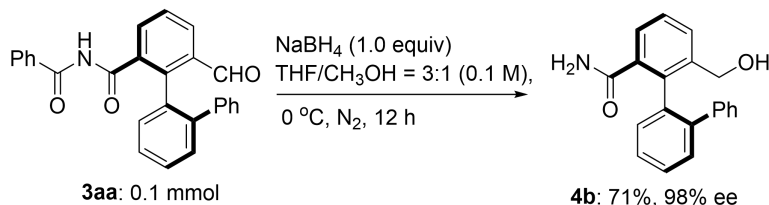


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.817	M	1.0895	22101900	546307	50.5197
2	20.665	M	1.3879	21647145	409452	49.4803



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.586	M	1.2129	89212100	1958699	99.3606
2	20.720	M	1.0880	574092	14200	0.6394

3.2.2,

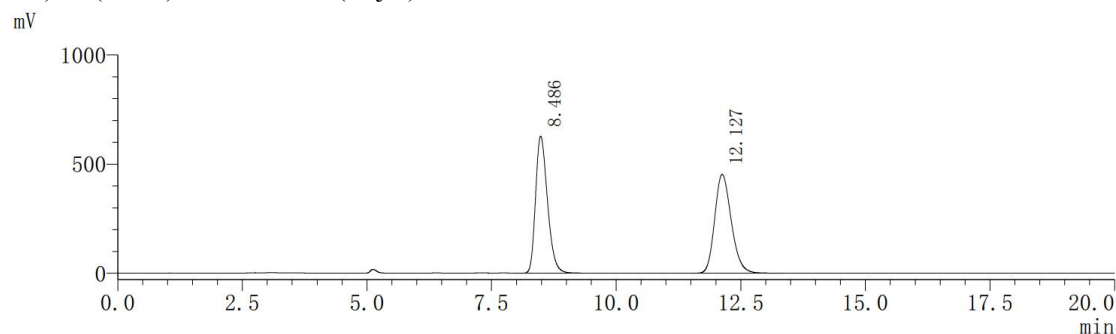


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **3aa** (0.1 mmol, 40.5 mg), NaBH₄ (0.1 mmol, 3.8 mg) and dry THF/CH₃OH = 3:1 (1.0 mL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. Reaction mixture was stirred at 0 °C for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH₂Cl₂ (3×5 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 1 : 2) to give the desired product **4b** as a colorless oil. (yield: 71%, 98% ee). **¹H NMR (500 MHz, Chloroform-*d*)** δ 7.61 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.41 – 7.38 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 5H), 5.73 (s, 1H), 5.34 (s, 1H), 4.27 (dd, *J* = 13.5, 5.6 Hz, 1H), 4.16 (dd, *J* = 13.5, 4.3 Hz, 1H), 1.53 (t, *J* = 6.0 Hz, 1H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 170.9, 141.0, 140.4, 139.7, 137.8, 136.4, 135.4, 130.7, 130.1, 130.1, 129.4, 128.9, 128.2, 128.0, 127.8, 127.7, 127.3, 62.8.

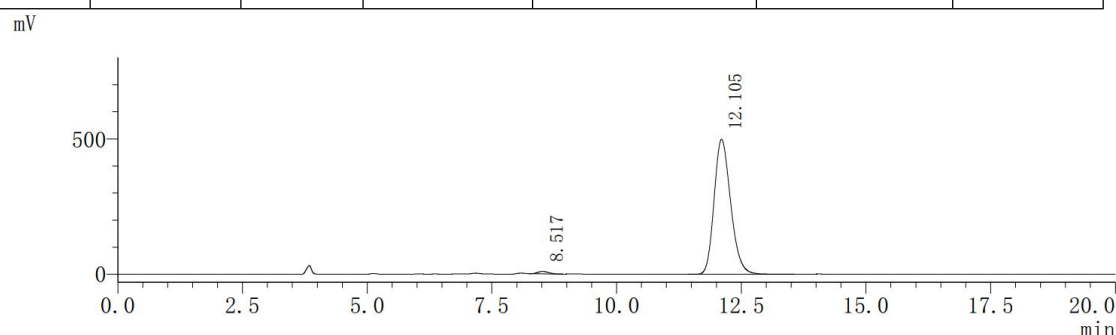
HRMS (ESI-TOF) (m/z): Calcd for C₂₀H₁₇NNaO₂, ([M + Na]⁺), 326.1151; found 326.1151.

[α]_D¹⁹ = -3.4 (c = 1.0, CH₂Cl₂).

HPLC analysis: Daicel Chiralpak AD-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 8.52 min, t_R (major) = 12.11 min, 98% ee.

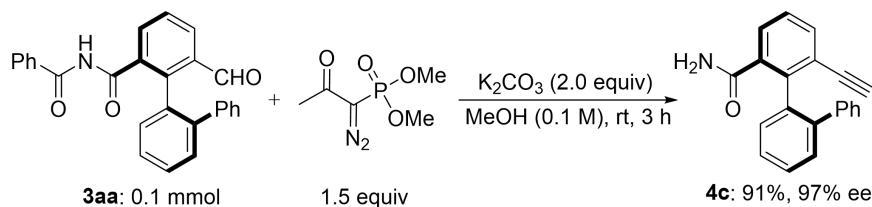


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.486	M	0.4323	10411603	628313	49.8492
2	12.127	M	0.6033	10474578	453208	50.1508



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.517	M	0.4093	138949	9117	1.1922
2	12.105	M	0.6033	11515489	498355	98.8078

3.2.3,

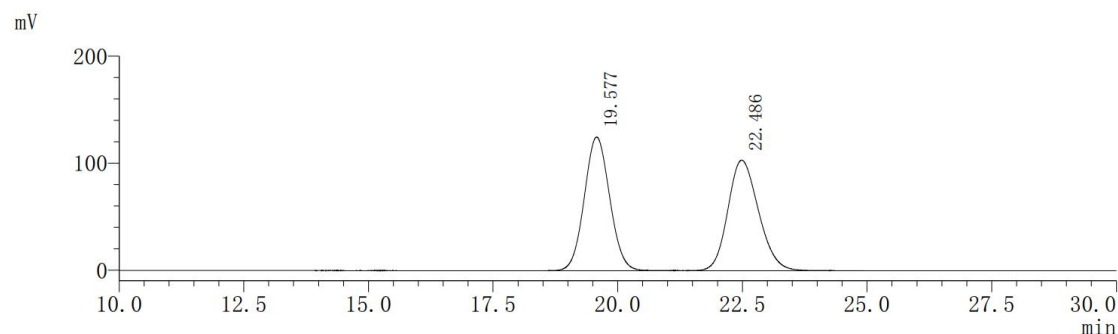


To a solution of **3aa** (0.1 mmol, 40.5 mg) in 1.0 mL MeOH was added K_2CO_3 (0.2 mmol, 27.6 mg), P-(1-diazo-2-oxopropyl)-dimethylester (0.15 mmol, 22.5 μ L) is slowly added. the reaction mixture was stirred at rt for 3 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3 $\times$ 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 2 : 1) to give the desired **4c** (yield: 91 %, 97% ee). **1H NMR (500 MHz, Chloroform-*d*)** δ 7.66 (dd, J = 7.8, 1.4 Hz, 1H), 7.61 (dd, J = 7.8, 1.4 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.39 (dd, J = 7.6, 1.4 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.15 (s, 5H), 5.74 (s, 1H), 5.11 (s, 1H), 2.97 (s, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 169.3, 142.4, 141.5, 140.3, 136.9, 135.1, 134.9, 130.4, 130.2, 129.4, 129.4, 129.4, 128.9, 127.8, 127.4, 127.0, 123.9, 82.3, 81.6.

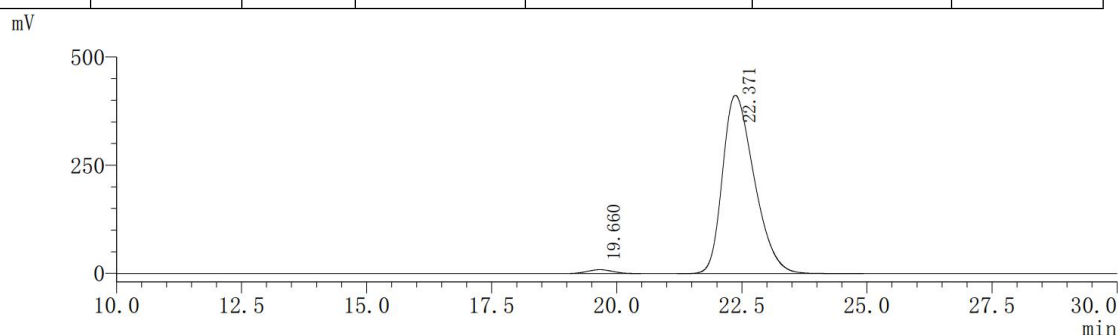
HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{15}NNaO$, ($[M + Na]^+$), 320.1046; found 320.1041.

$[\alpha]_D^{19}$ = +64.6 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 19.66 min, t_R (major) = 22.37 min, 97% ee.

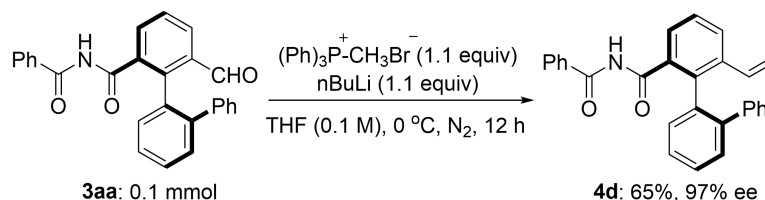


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.577	M	0.9354	4436156	124887	50.0560
2	22.486	M	1.1237	4426235	103336	49.9440



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.660	M	0.9138	305685	8824	1.6528
2	22.371	M	1.1674	18189318	412259	98.3472

3.2.4,



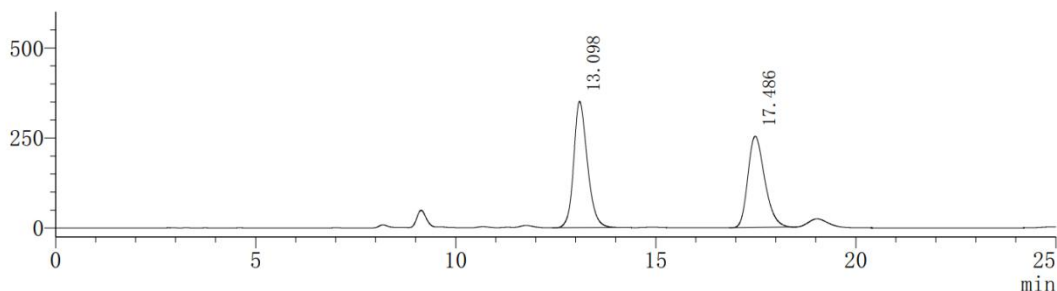
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with methyltriphenylphosphonium bromide (0.11 mmol, 39.3 mg), anhydrous tetrahydrofuran (0.5 mL) and nBuLi of 2.5 mol/L in hexane (0.11 mmol, 45 μ L) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The mixture was stirred at 0 °C for 30 minutes, followed by tetrahydrofuran solution (0.5 mL) dissolved in **3aa** (0.1 mmol, 40.5 mg) was added dropwise and stirring at 0 °C for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH₂Cl₂ (3 $\times$ 5 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 2 : 1) to give the desired **4d** (yield: 65 %, 97% ee). **¹H NMR (500 MHz, Chloroform-*d*)** δ 8.35 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.34 (m, 8H), 7.15 – 7.06 (m, 5H), 6.48 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.60 (d, *J* = 17.4 Hz, 1H), 5.15 (d, *J* = 11.0 Hz, 1H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 167.6, 165.0, 142.1, 140.2, 138.0, 137.7, 136.1, 135.7, 135.0, 133.1, 133.0, 131.3, 130.9, 129.5, 129.0, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.2, 116.3.

HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₂₁NNaO₂, ([M + Na]⁺), 426.1465; found 426.1467.

[α]_D¹⁹ = -14.1 (c = 1.3, CH₂Cl₂).

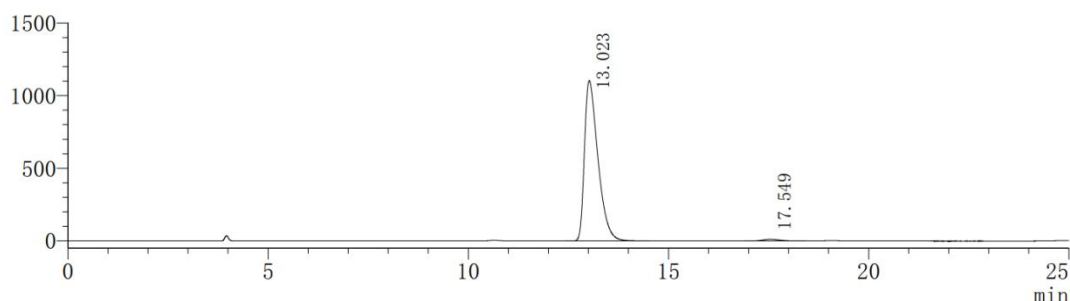
HPLC analysis: Daicel Chiralpak AD-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (major) = 13.02 min, t_R (minor) = 17.55 min, 97% ee.

mV



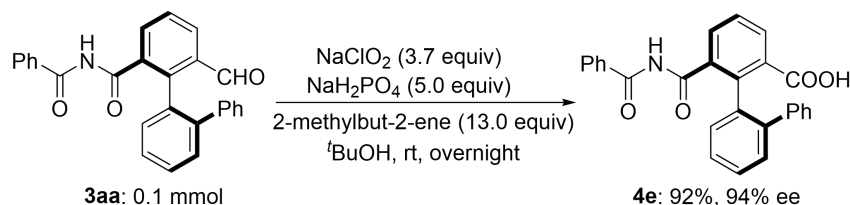
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	13.098	M	0.6093	8357967	350734	52.9130
2	17.486	M	0.7684	7437721	253749	47.0870

mV



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	13.023	M	0.6063	25758281	1103584	98.6528
2	17.549	M	0.7778	351763	11715	1.3472

3.2.5,

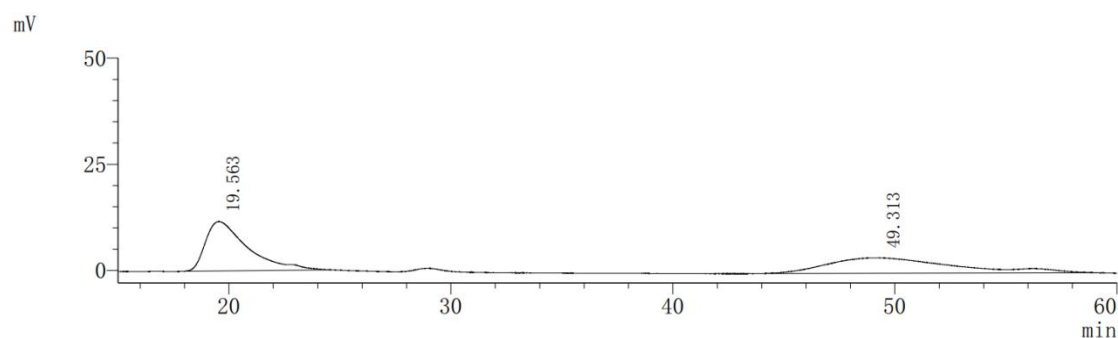


To a stirred solution of compound **3aa** (40.5 mg, 0.1 mmol) and 2-methylbut-2-ene (138 μ l, 1.3 mmol) in t BuOH (1.5 mL) were added a saturated solution of NaClO_2 (41.8 mg, 0.37 mmol) and NaH_2PO_4 (60.0 mg, 0.5 mmol). The mixture was stirred overnight at room temperature. The mixture was quenched with saturated NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, concentrated, and purified by silica gel column chromatography (DCM : MeOH = 20:1) to give compound **4e** (yield: 92 %, 94% ee) as a white solid. **^1H NMR (500 MHz, Methanol- d_4)** δ 7.72 (d, J = 7.5 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.48 – 7.46 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 – 7.27 (m, 5H), 7.11 – 7.06 (m, 3H). **^{13}C NMR (150 MHz, Methanol- d_4)** δ 168.8, 166.7, 141.6, 140.7, 137.4, 137.2, 135.5, 132.8, 132.7, 130.5, 130.1, 129.8, 129.7, 128.3, 128.1, 127.8, 127.8, 127.4, 126.7, 126.4.

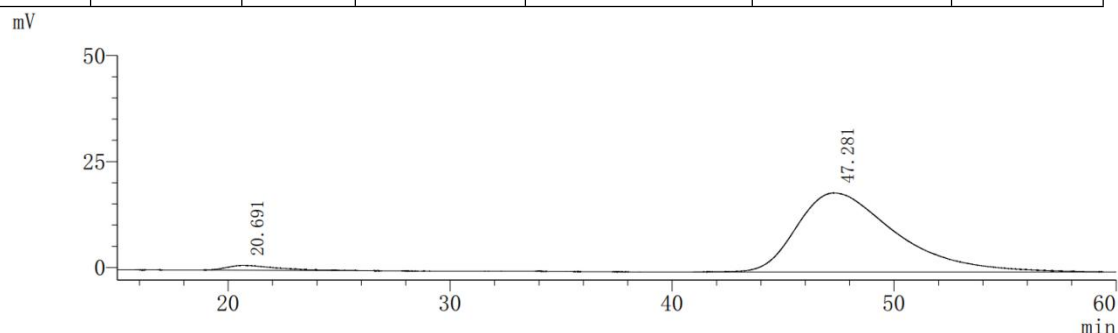
HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{27}\text{H}_{19}\text{NNaO}_4$, ($[\text{M} + \text{Na}]^+$), 444.1206; found 444.1213.

$[\alpha]_D^{19}$ = -7.6 (c = 1.9, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 °C, 256 nm); t_R (minor) = 20.69 min, t_R (major) = 47.28 min, 94% ee.

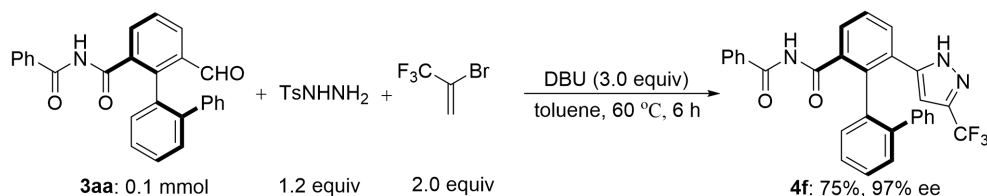


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.563	M	3.2402	1534123	11612	51.5380
2	49.313	M	11.6459	1442563	3629	48.4620



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.691	M	2.9165	172726	1118	2.9085
2	47.281	M	7.4747	5766023	18647	97.0915

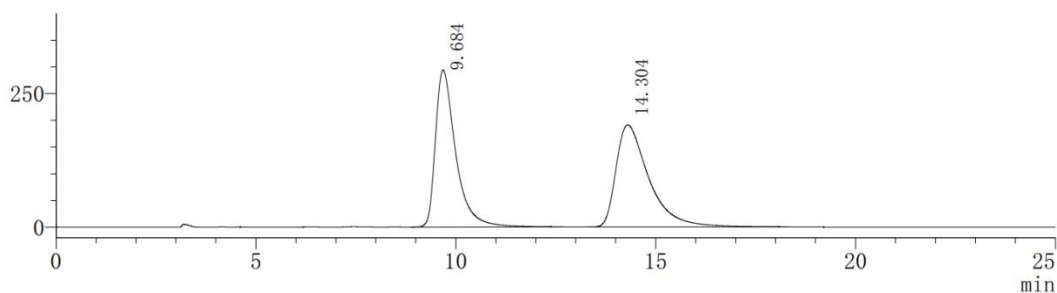
3.2.6^[2],



To a 10 mL round-bottom flask equipped with a magnetic stirring bar and a refluxing condenser was added aldehyde **3aa** (0.1 mmol, 40.5 mg), 4-methylbenzenesulfonohydrazide (0.12 mmol, 22.3 mg), toluene (1 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.3 mmol, 45 μ L), and 2-bromo-3,3,3-trifluoropropene (0.2 mmol, 21 μ L). The resulting mixture was vigorously stirred at 60 $^{\circ}$ C for 6 h. Then the mixture was added water (2 mL), extracted with EtOAc (5 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The obtained crude product was then purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 1/1) to provide the product **4f** (yield: 75 %, 97% ee) as a white solid. **¹H NMR (500 MHz, Chloroform-*d*)** δ 9.41 (s, 1H), 9.11 (s, 1H), 7.71 – 7.69 (m, 2H), 7.63 (dd, J = 7.7, 1.4 Hz, 1H), 7.54 (td, J = 7.4, 1.3 Hz, 1H), 7.48 (dd, J = 7.5, 1.5 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 7.31 (dd, J = 7.6, 1.4 Hz, 1H), 7.11 – 7.08 (m, 1H), 7.05 – 7.02 (m, 2H), 6.88 – 6.86 (m, 2H), 5.83 (s, 1H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 169.0, 164.2, 141.9, 140.7, 138.4, 136.6, 136.2, 134.4, 132.5, 131.0, 129.7, 129.6, 129.3, 128.6, 127.9, 127.83, 127.75, 127.3, 127.1, 127.02, 126.95, 126.81, 126.79, 125.9, 120.0 (q, J = 267.0 Hz), 102.8. **¹⁹F NMR (565 MHz, Chloroform-*d*)** δ -62.40 (s, 1CF₃). **HRMS (ESI-TOF) (m/z)**: Calcd for $\text{C}_{30}\text{H}_{20}\text{F}_3\text{N}_3\text{NaO}_2$, ($[\text{M} + \text{Na}]^+$), 534.1400; found 534.1396. $[\alpha]_{\text{D}}^{19}$ = -23.8 (c = 1.9, CH_2Cl_2).

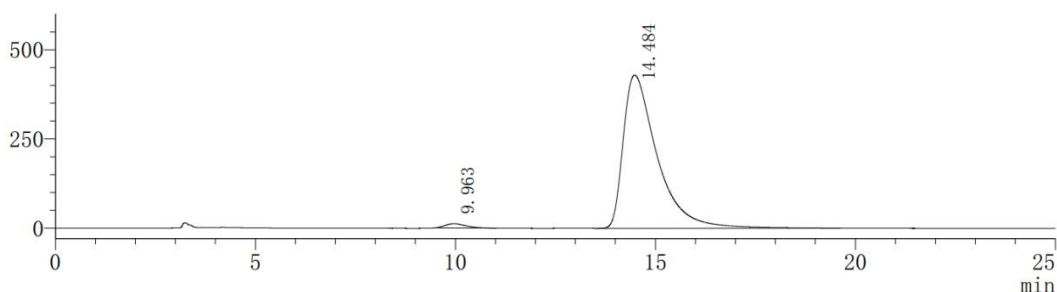
HPLC analysis: Daicel Chiralpak IC column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 9.96 min, t_R (major) = 14.48 min, 97% ee.

mV



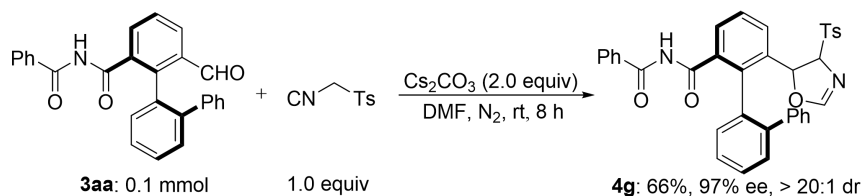
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.684	M	0.8744	10384318	293840	48.6597
2	14.304	M	1.4478	10956385	191217	51.3403

mV



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.963	M	0.9538	423464	11905	1.6462
2	14.484	M	1.4751	25299925	429353	98.3538

3.2.7^[3],

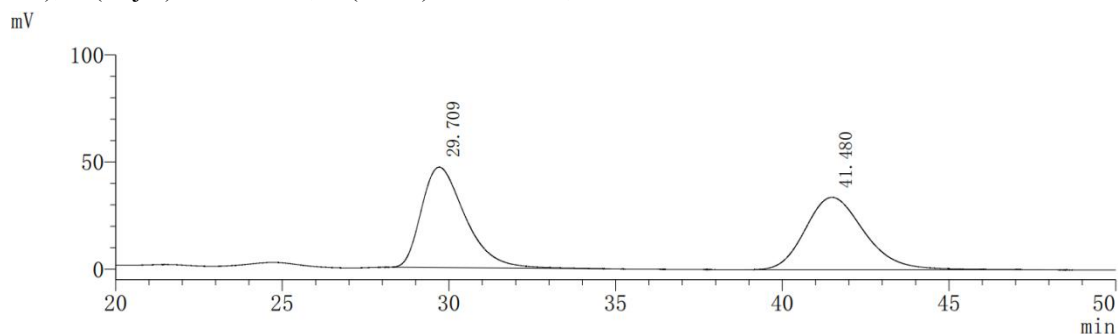


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3aa** (40.5 mg, 0.1 mmol), TosMIC (19.5 mg, 0.1 mmol), DMF (0.5 mL), Cs_2CO_3 (65 mg, 0.2 mmol). The reaction mixture was stirred at 25 °C for about 8 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 3:2) afforded **4g** as white solid in 66% yield (97% ee, > 20:1 dr). **¹H NMR (600 MHz, Chloroform-*d*)** δ 8.40 (s, 1H), 7.65 – 7.61 (m, 4H), 7.55 (t, J = 7.5 Hz, 1H), 7.51 – 7.45 (m, 5H), 7.42 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 7.14 – 7.12 (m, 5H), 7.02 (s, 1H), 5.89 (d, J = 5.8 Hz, 1H), 5.21 (d, J = 5.8 Hz, 1H), 2.45 (s, 3H). **¹³C NMR (150 MHz, Chloroform-*d*)** δ 167.1, 164.7, 159.4, 145.6, 142.1, 139.6, 138.7, 137.0, 136.3, 133.8, 133.1, 132.7, 132.7, 132.0, 131.0, 130.1, 129.7, 129.7, 129.6, 129.5, 129.2, 128.9, 128.7, 128.1, 128.1, 127.6, 127.2, 92.5, 76.6, 21.7.

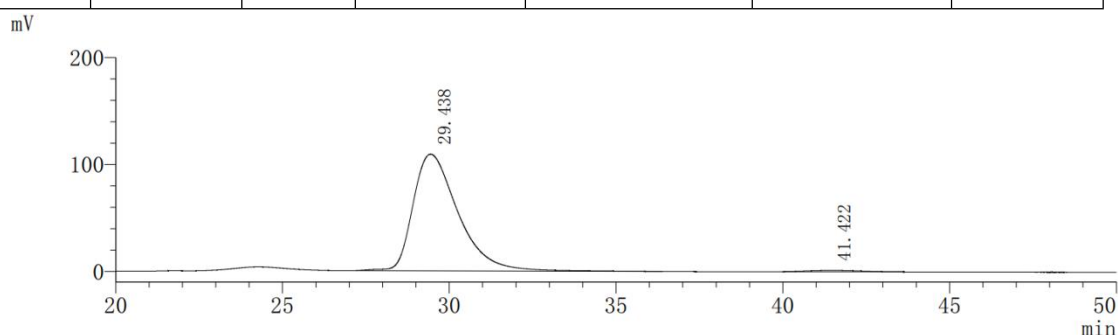
HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{36}\text{H}_{29}\text{N}_2\text{O}_5\text{S}$, ($[\text{M} + \text{H}]^+$), 601.1792; found 601.1750.

$[\alpha]_{\text{D}}^{19}$ = -14.3 (c = 1.9, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (70:30 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 29.44 min, t_R (minor) = 41.42 min, 97% ee.



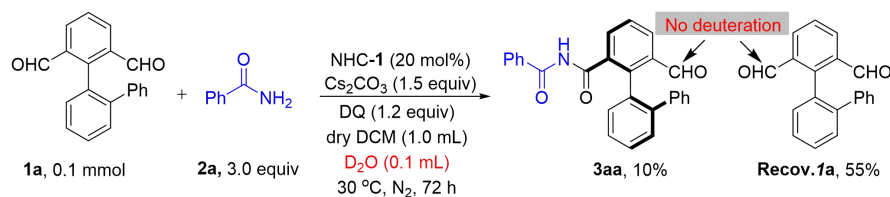
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.709	M	2.3304	4293524	46913	50.7417
2	41.480	M	3.1845	4168010	33799	49.2583



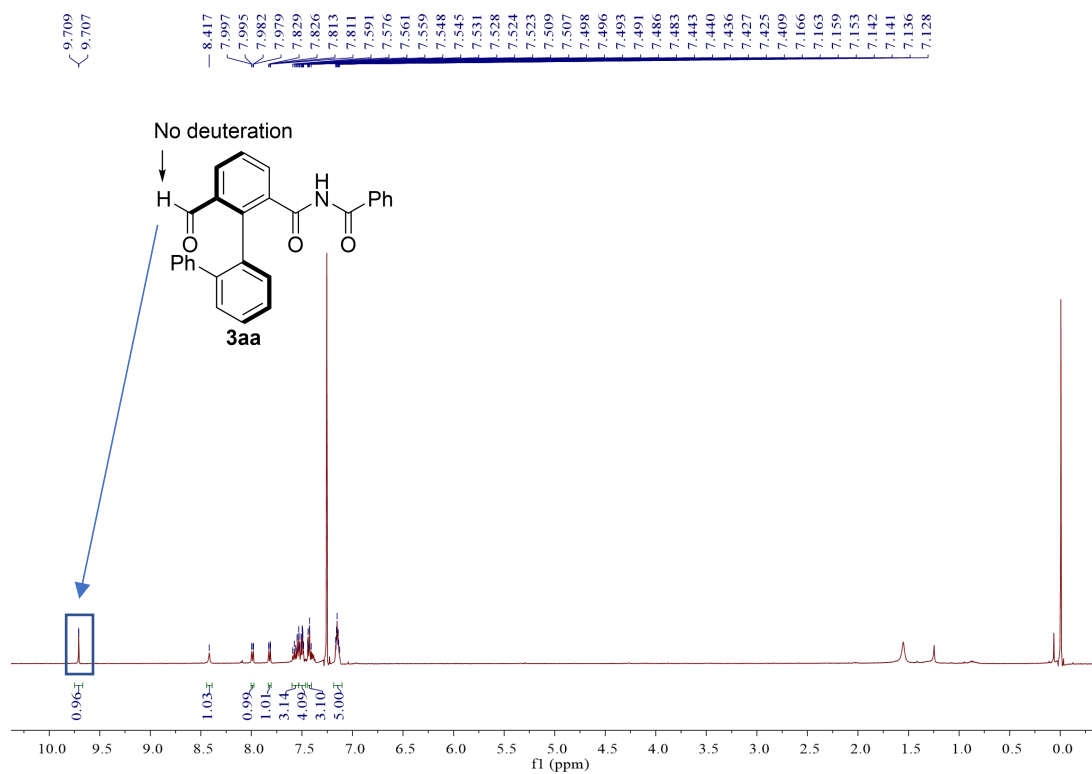
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.438	M	2.3842	10260935	109132	98.6702
2	41.422	M	6.2410	138293	1292	1.3298

IV. Mechanistic Studies

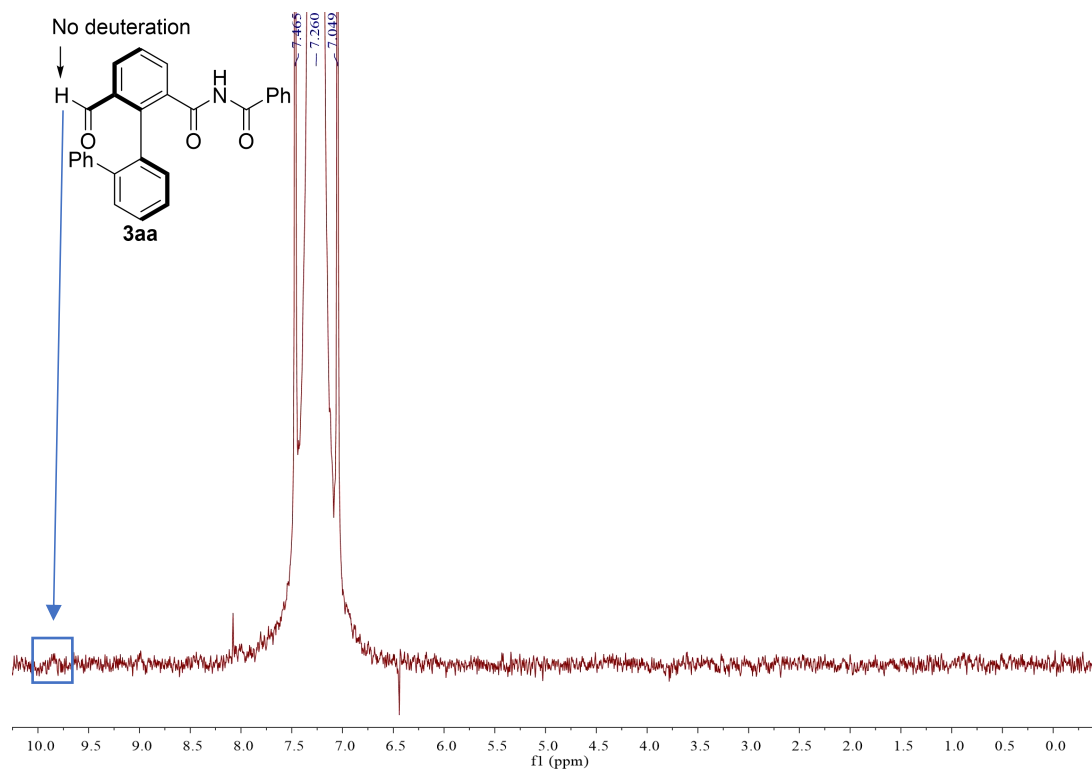
4.1 Deuterium labeling experiment



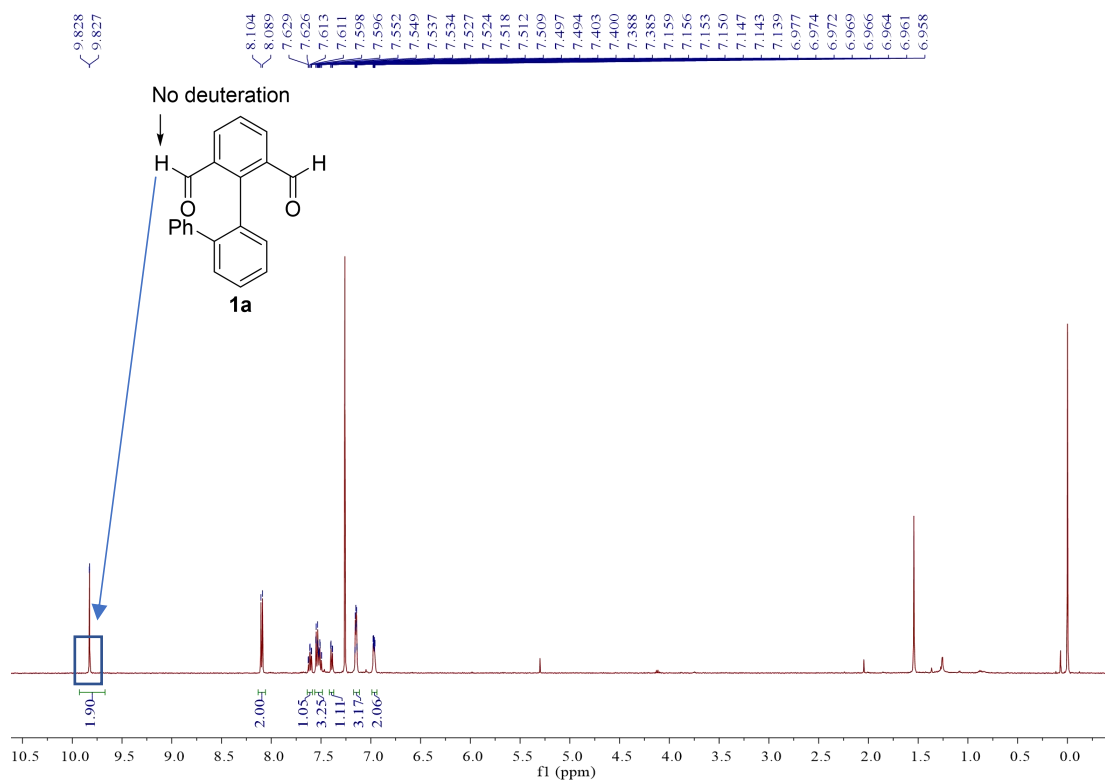
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **NHC-1** (20 mol%, 8.36 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), [1,1':2',1''-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg), anhydrous dichloromethane (1.0 mL), and D_2O (0.1 mL). The mixture was stirred for 5 minutes, followed by the addition of Benzamide **2a** (36.3 mg, 3.0 equiv) and 3,3',5,5'-tetra-*tert*-butyldiphenylquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 30 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 2:1 (v/v) to give the product **R-3aa**.



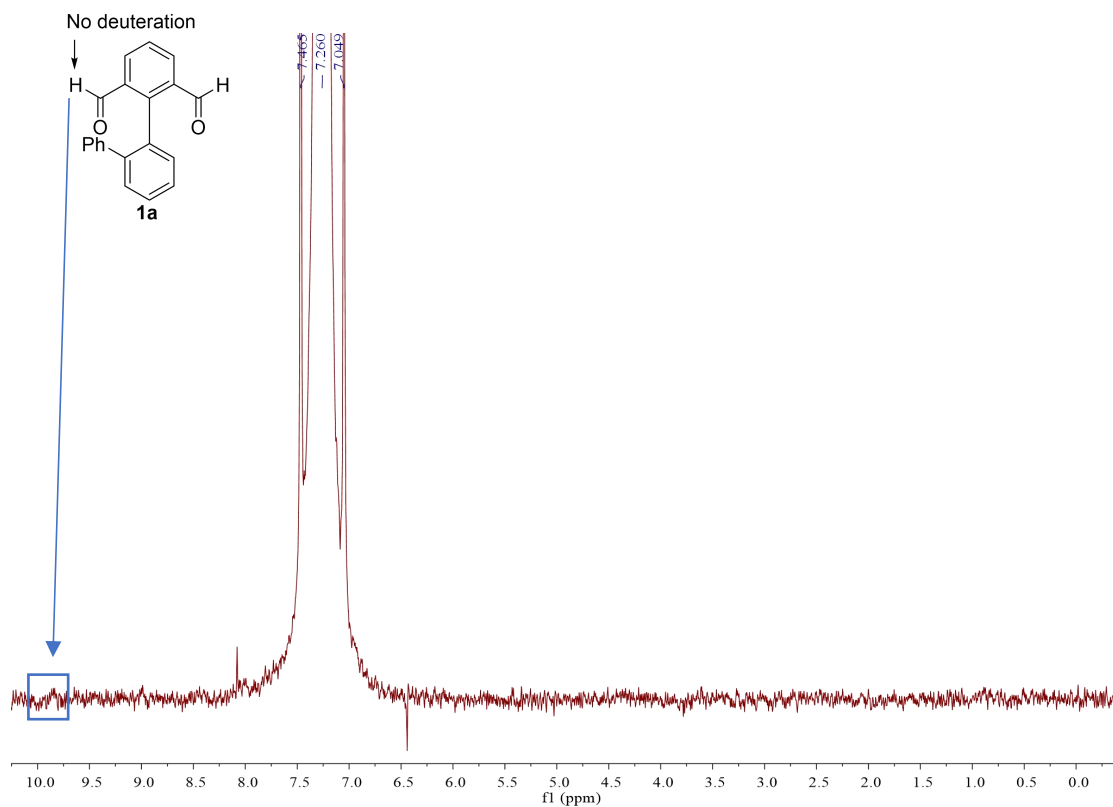
¹H NMR (500 MHz, CDCl₃) spectrum of 3aa.



²H NMR (77 MHz, CDCl₃) spectrum of 3aa.



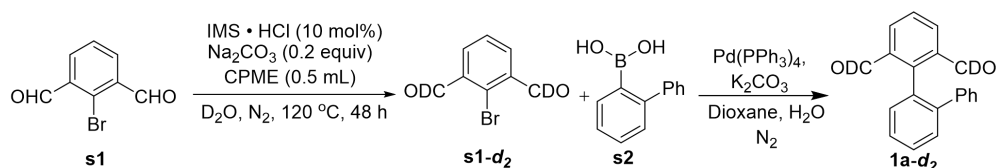
¹H NMR (500 MHz, CDCl₃) spectrum of *Recov. 1a*.



²H NMR (77 MHz, CDCl₃) spectrum of *Recov. 1a*.

4.2 Parallel Kinetic Isotope Effect Experiment

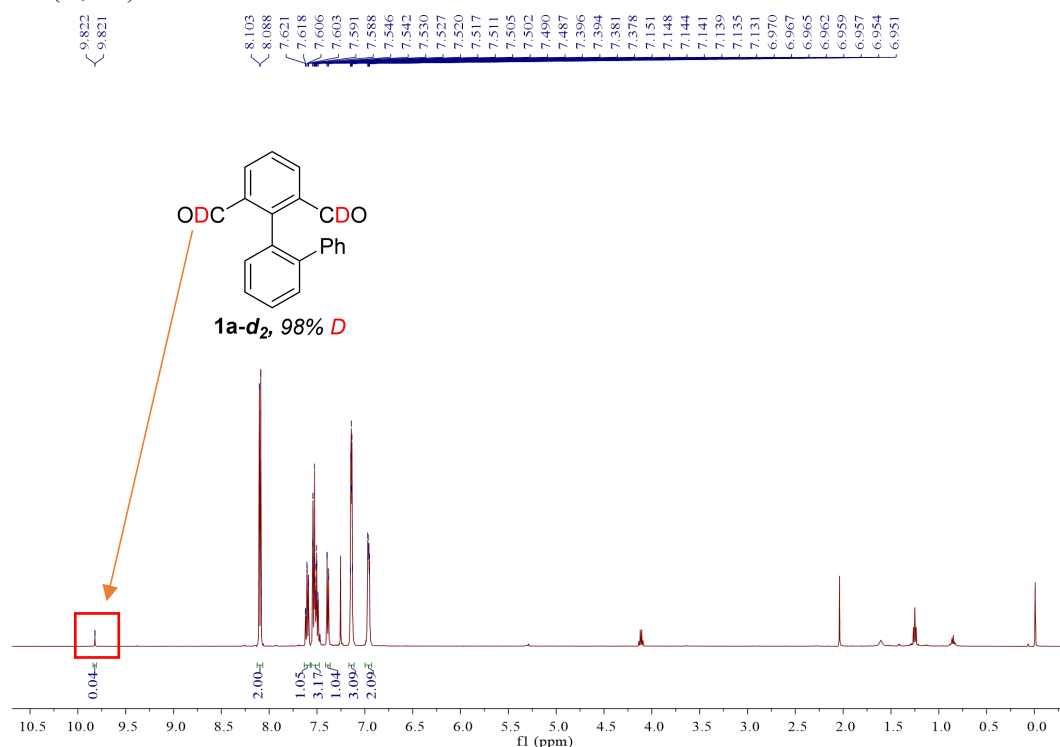
4.2.1 Procedure for synthesis of 1a-d₂^[4]



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with aldehyde **s1** (0.5 mmol), IMes • HCl (17.0 mg, 0.05 mmol), Na₂CO₃ (11.0 mg, 0.1 mmol), CPME (0.5 mL) and D₂O (2.5 mL). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 120 °C for 48 h, and extracted with AcOEt, and the organic layers were dried over MgSO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE : EA = 10:1), **s1-d₂** was obtained in 90% yield, with 98% D.

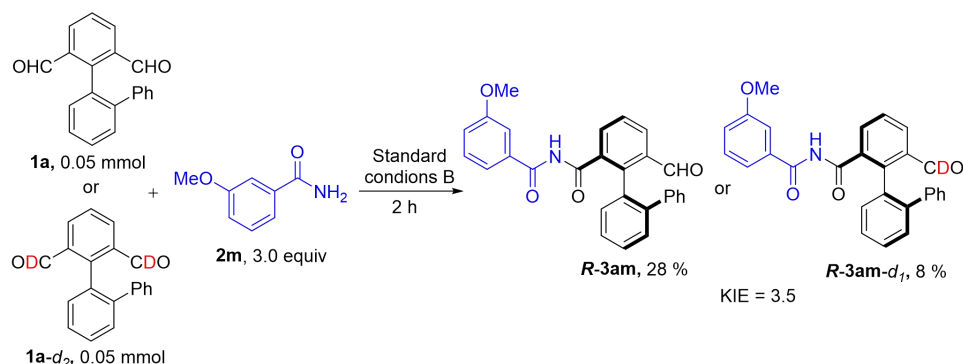
A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with 2-bromoisophthalaldehyde **s1-d₂**, 2-biphenylboronic acid **s2** (2.29 equiv), K₂CO₃ (6.89 equiv) and Pd(PPh₃)₄ (0.018 equiv) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane : water = 7 : 1 were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (yield: 75 %).

¹H NMR (500 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 0.8 Hz, 0.04 H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.15 – 7.13 (m, 3H), 6.97 – 6.95 (m, 2H).

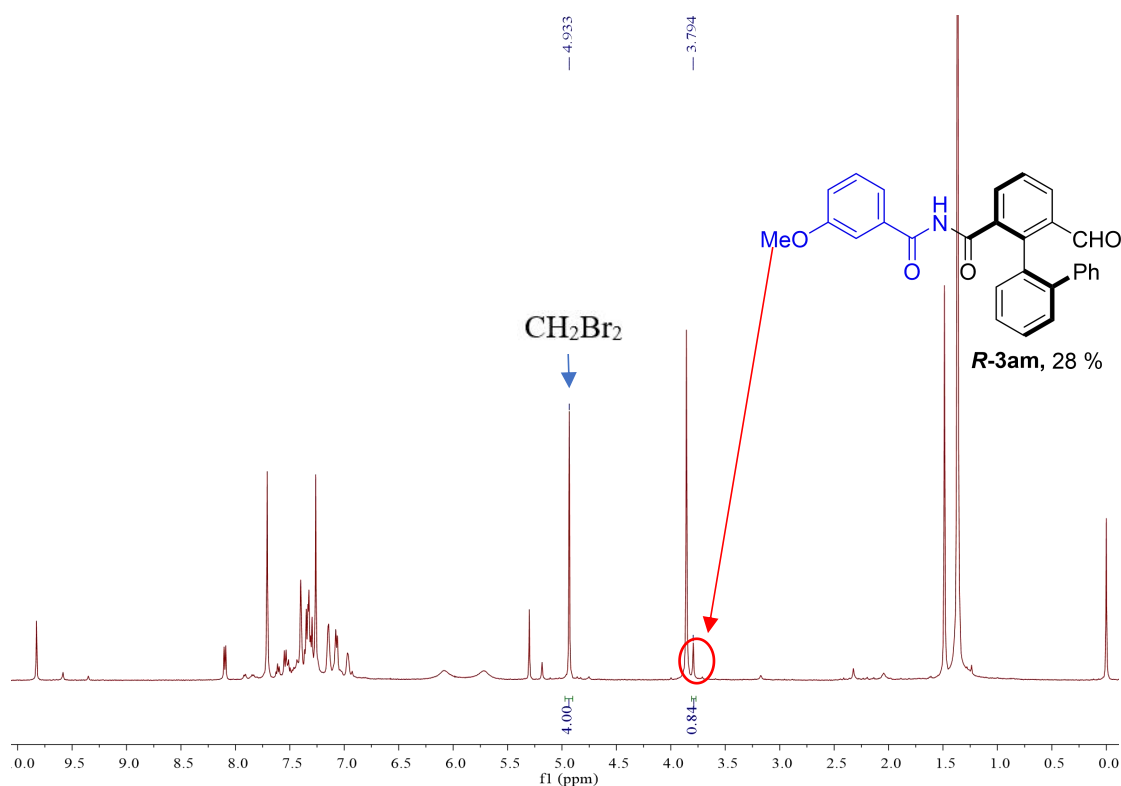


¹H NMR (500 MHz, CDCl₃) spectrum of **1a-d₂**.

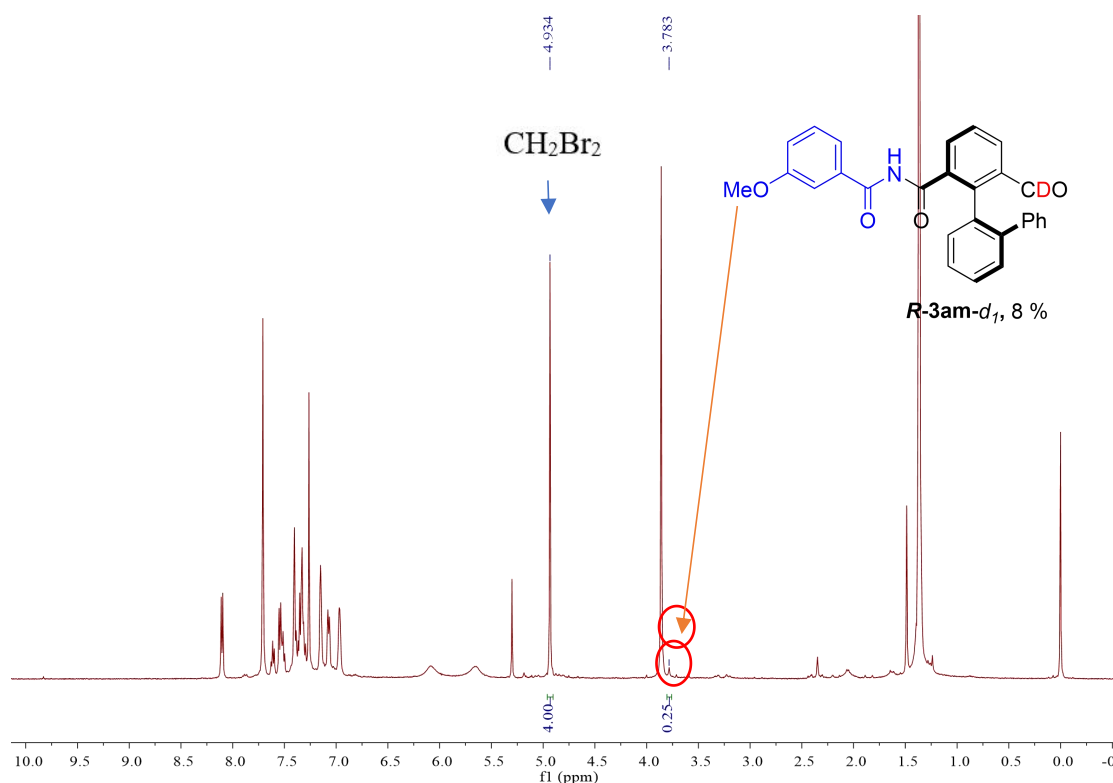
4.2.2 Experiment Procedure for the Isotope Experiments



In a nitrogen-filled glovebox, two flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-1** (20 mol%, 4.18 mg), Cs₂CO₃ (25.0 mg, 1.5 equiv), **1a** or **1a-d₂** (0.05 mmol, 14.3 mg), and anhydrous dichloromethane (0.5 mL), was added. The mixture was stirred for 5 minutes, followed by the addition of 3-methoxybenzamide **2m** (22.6 mg, 3.0 equiv) and 3,3',5,5'-tetra-*tert*-butyldiphenylquinone (24 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 30 °C for 2 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 2:1 (v/v) to give the product **R-3am**, yield: 28%; **R-3am-d₁**, yield: 8%. The KIE was determined by ¹H NMR analysis to be 3.5.



¹H NMR (500 MHz, CDCl₃) using CH₂Br₂ (0.1 mmol, 7.0 μL) as an internal standard of the reaction mixture (**R-3am**)



¹H NMR (500 MHz, CDCl₃) using CH₂Br₂ (0.1 mmol, 7.0 μL) as an internal standard of the reaction mixture (*R*-3am-*d*₁)

4.3 Feasibility of kinetic resolution

Across all our reaction systems, including racemic reactions, no bis-substituted byproducts were detected even upon prolonged reaction time. We attribute this absence to the pronounced steric hindrance of the mono-substituted amide. Consequently, the enantioselectivity of this process is primarily governed by a desymmetrization mechanism.

To further probe the possibility of kinetic resolution, we first shortened the reaction time to 6 hours, observing a slight decrease in ee from 99% to 97%. This suggests a marginal enrichment of enantiopurity over time. More notably, when enantiomerically enriched (*R*)-**3aa** (91% ee) was resubjected to the standard conditions for 24 hours, its ee increased to 95% without any detectable bis-substituted species. This finding confirms that the chiral NHC catalyst can still bind the mono-substituted product; however, the resulting Breslow intermediate is sterically impeded from further conversion. While this recognition event does not lead to a second functionalization and may contribute to catalyst poisoning, it nonetheless enables a measurable enhancement of enantioselectivity.

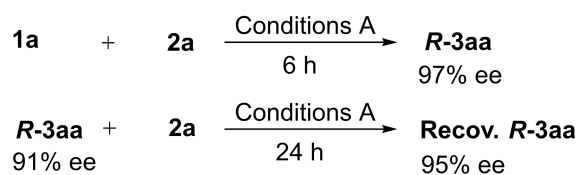
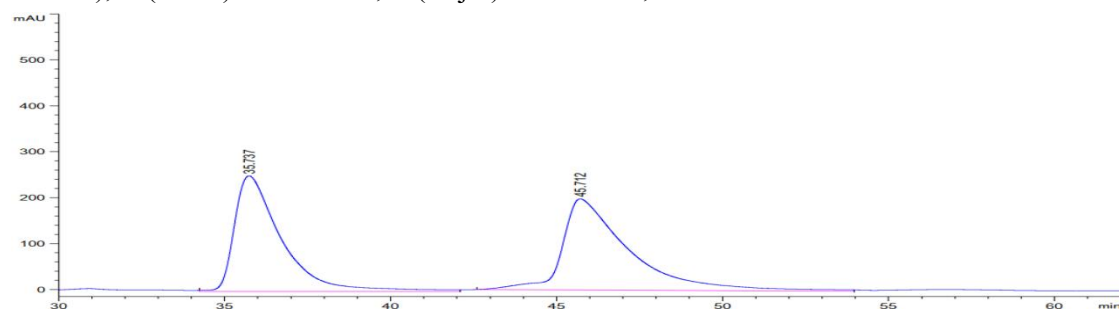


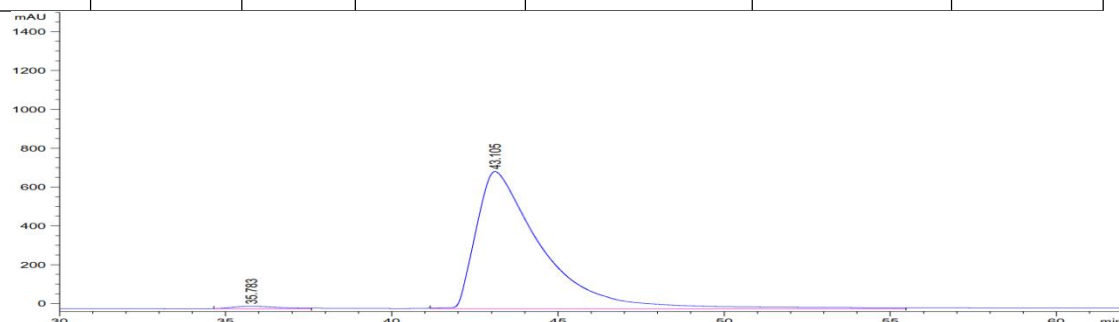
Figure S1 Feasibility of kinetic resolution

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C,

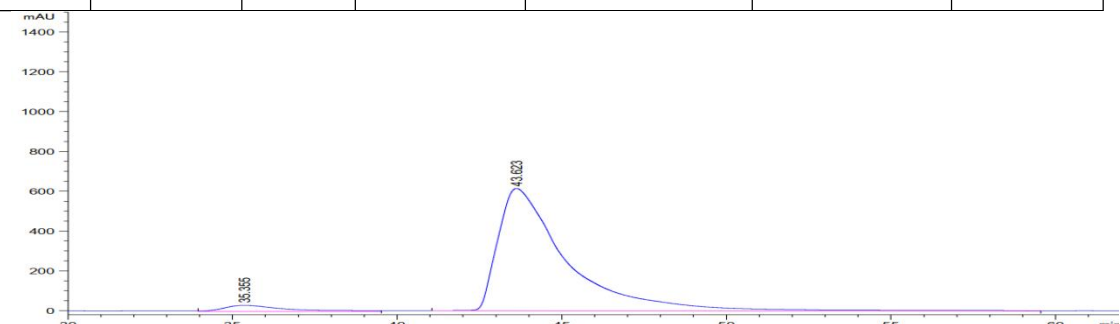
256 nm); t_R (minor) = 35.78 min, t_R (major) = 43.11 min, 97% ee.



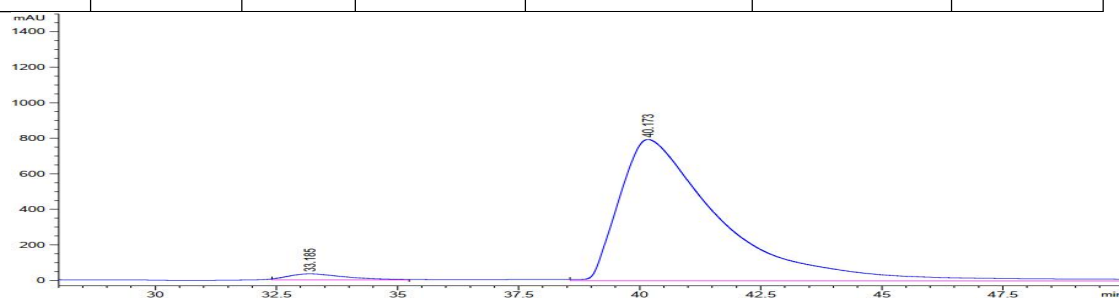
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	35.737	MM	1.6450	2.48297e4	251.56958	47.3418
2	45.712	MM	2.3200	2.76180e4	198.40315	52.6582



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	35.783	MM	1.6942	1352.16016	13.30180	1.3682
2	43.105	MM	2.3011	9.74787e4	706.02216	98.6318



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	35.355	MM	2.1602	3928.98828	30.31310	4.2571
2	43.623	MM	1.9861	8.83639e4	613.61267	95.7429



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	33.185	MM	1.3833	2801.20972	33.75088	2.3587
2	40.173	MM	2.4313	1.15960e5	794.90350	97.6413

4.4 Proposed Reaction Mechanism

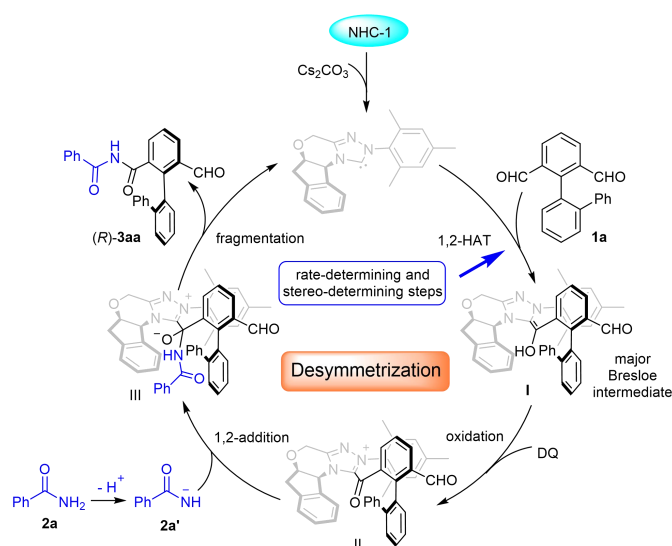


Figure S2 Proposed Reaction Mechanism

V Determination of Rotational Barrier and half-life for C-C Bond.^[6]

Following the procedure of Curran,^[6c] compound **3aa** (5 mg) was dissolved in toluene (5 mL) to make a 1 mg/mL solution in a sealed tube. The tube was kept in a pre-equilibrated metal bath maintained at 90 °C. At 60 min time intervals, the sealed tube was taken out briefly (1-2 min) from the metal bath and a 70 µL aliquot was diluted with ⁱPrOH (0.5 mL) taken out via syringe and injected onto the analytical HPLC column to determine the er. This er was plotted against time, and the barrier to rotation was calculated from the plot. In the y-axis of the graph, “m” stands for the % of the minor enantiomer, and “M” denotes the % of the major enantiomer. All the data have been recorded at 363.15 K (90 °C). The rate value can be inserted into **Equation 2** to give $\Delta G^\ddagger_{363.15\text{ K}}$ and into **Equation 1** to give the half-life to racemisation.

k_B = Boltzmann’s constant [$1.381 \times 10^{-23} \text{ J K}^{-1}$],

T = temperature in K,

h = Planck’s constant [$6.626 \times 10^{-34} \text{ J s}$],

R = gas constant [$8.3145 \text{ J mol}^{-1}$].

Then the simplified equation for racemization is:

$$\ln [(M + m) / (M - m)] = k_{\text{rac}}t + c = 2k_{\text{rot}}t + c$$

$$k_{\text{rot}} = (\text{slope}/2)$$

$$t_{1/2\text{rac}} = \ln(2)/k_{\text{rac}} \quad \text{Equation 1}$$

The experimental data is shown for **3aa** below:

Time (min)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M + m) / (M - m)	$\ln [(M + m) / (M - m)]$
0	98.9189	1.0811	100	97.8378	1.02210	0.021859
60	98.1476	1.8524	100	96.2952	1.03847	0.037748
120	96.9276	3.0724	100	93.8552	1.06547	0.063416
180	95.4358	4.5642	100	90.8716	1.10045	0.095719
240	94.0070	5.9930	100	88.0410	1.13583	0.127364

300	92.4263	7.5737	100	84.8526	1.17851	0.164251
360	90.7133	9.2867	100	81.4266	1.22810	0.205468
420	89.4563	10.5437	100	78.9126	1.26722	0.236826
480	88.1060	11.8940	100	76.2120	1.31213	0.271652
540	86.7547	13.2453	100	73.5094	1.36037	0.307757
600	85.7219	14.2781	100	71.4438	1.39970	0.336258
660	84.3010	15.6990	100	68.6020	1.45768	0.376846
720	83.1276	16.8724	100	66.2552	1.50932	0.411659
780	81.7851	18.2149	100	63.5702	1.57306	0.453023
840	80.6421	19.3579	100	61.2842	1.63174	0.489647
900	79.2690	20.7310	100	58.5380	1.70829	0.535493

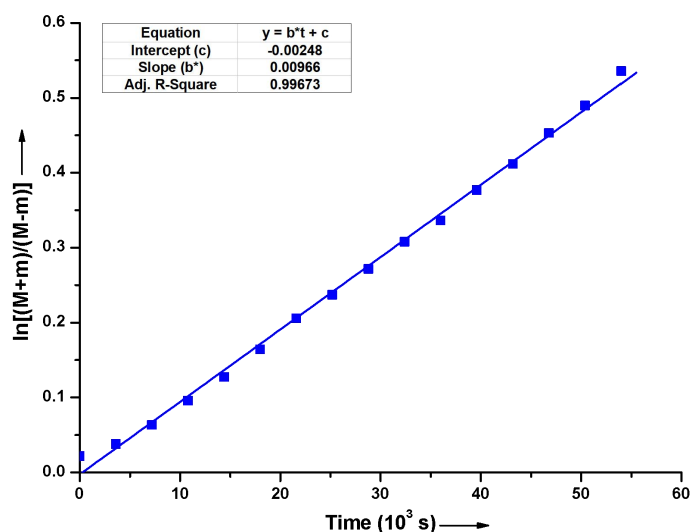


Figure S3. Plot for the Determination of Rotational Barrier and Half-Life for C-C Bond in **3aa**.

So, from plot, $k_{\text{rot}} = [(0.00966 \times 10^{-3})/2] = 4.83 \times 10^{-6} \text{ s}^{-1}$

$$k_{\text{rot}}^{\ddagger} = [(k_{\text{rot}} \times h)/k_B T] = 0.638 \times 10^{-18}$$

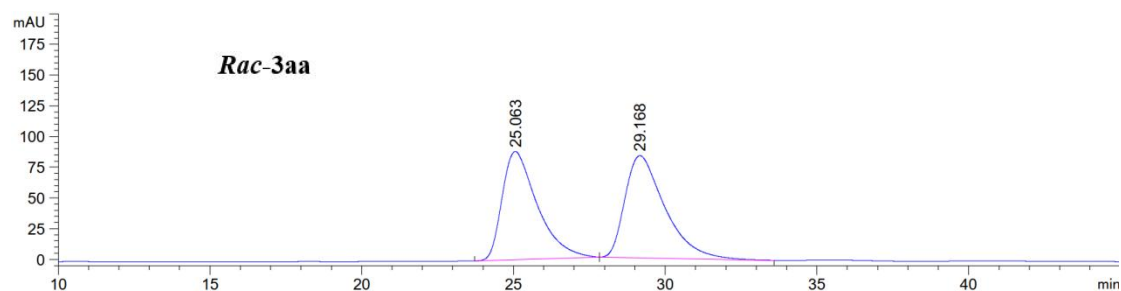
$$\Delta G_{\text{rot}}^{\ddagger} = -RT \ln k_{\text{rot}}^{\ddagger} \quad \text{Equation 2}$$

$$= 126.501 \text{ kJ/mol} = 30.2 \text{ kcal/mol}$$

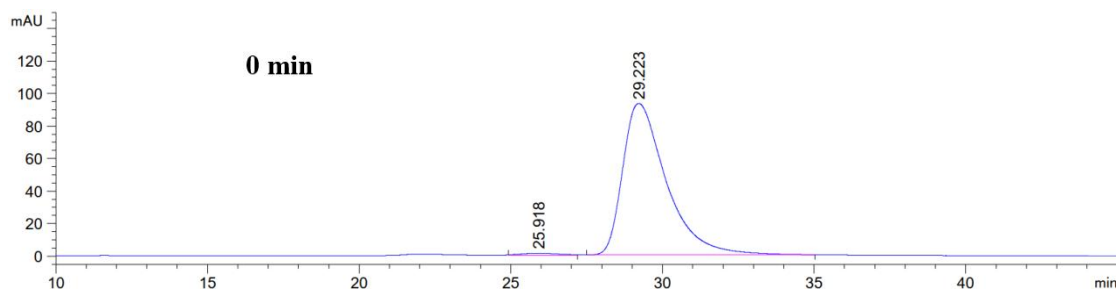
$$t_{1/2\text{rac}} = \ln(2)/k_{\text{rac}} = 19.93 \text{ h}$$

HPLC data for the Analysis of C-C Bond Rotational Barrier:

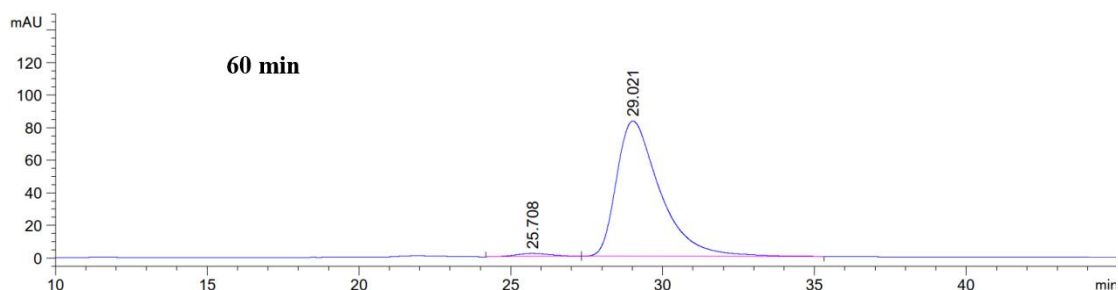
HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm)



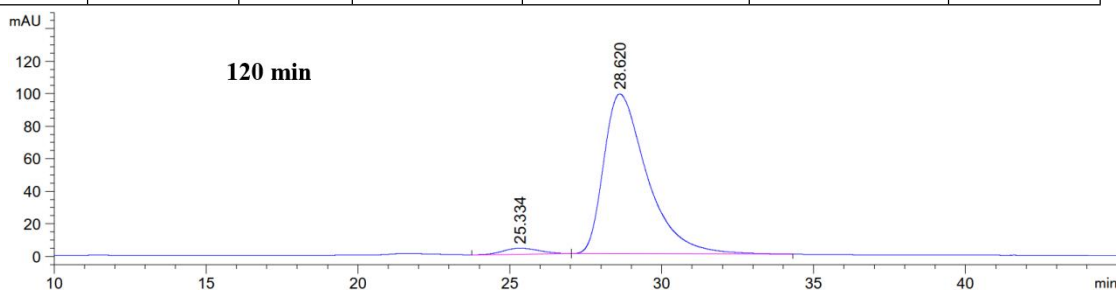
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.063	BB	1.2149	7078.86572	88.05233	48.2206
2	29.168	BB	1.3466	7601.29150	83.14301	51.7794



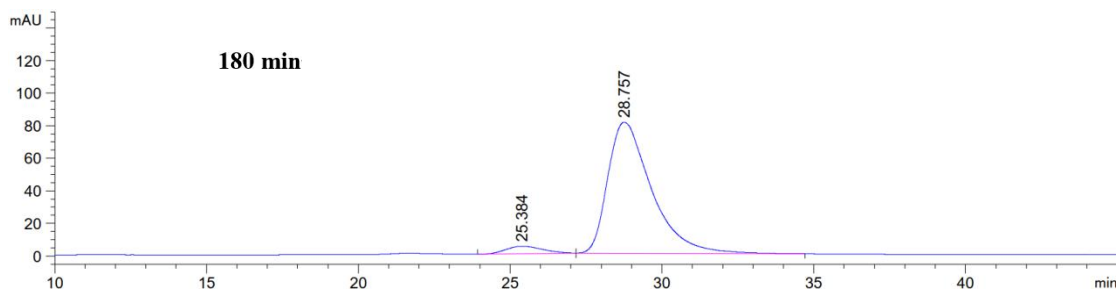
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.918	BB	1.4156	101.82645	1.19882	1.0811
2	29.223	BB	1.4783	9317.23535	93.12170	98.9189



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.708	BB	0.9594	156.70174	1.92569	1.8524
2	29.021	BB	1.4409	8302.80273	83.08090	98.1476

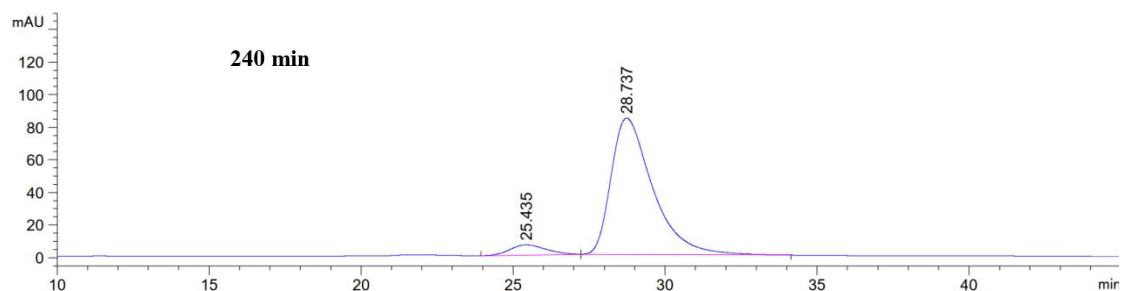


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.334	BB	0.9851	310.94925	3.80239	3.0724
2	28.620	BB	1.4806	9809.80469	98.35349	96.9276

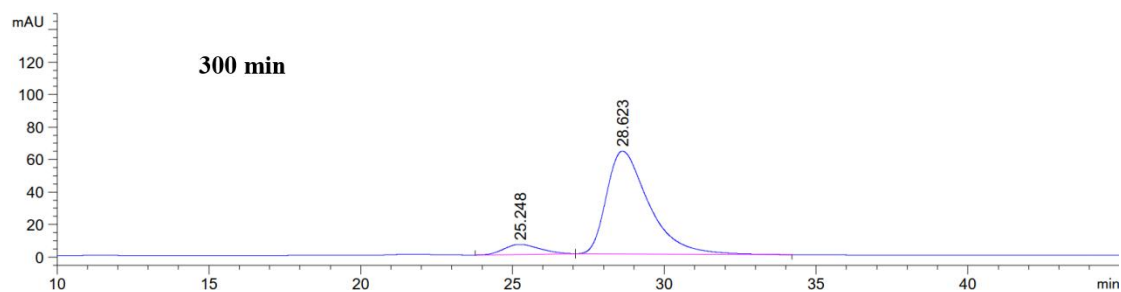


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
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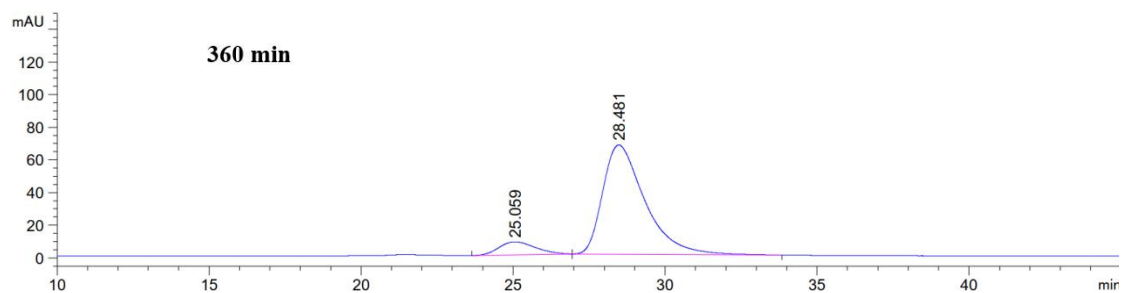
1	25.384	BB	1.0594	386.16815	4.65709	4.5642
2	28.757	BB	1.4761	8074.60693	80.44025	95.4358



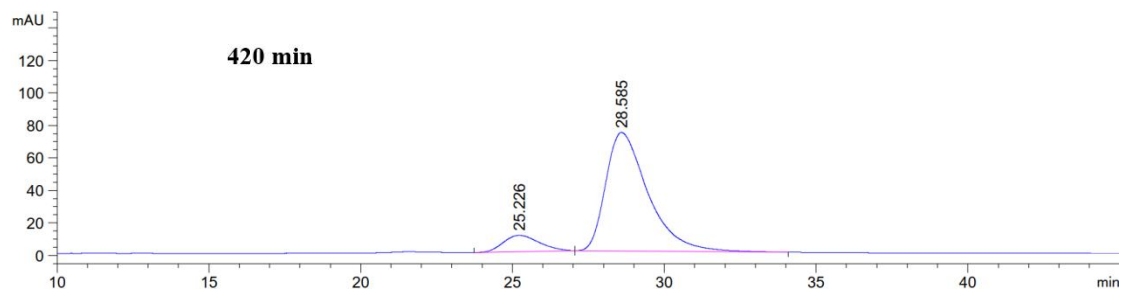
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.435	BB	0.9718	508.45535	6.23255	5.9930
2	28.737	BB	1.4156	7976.38477	83.64233	94.0070



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.248	BB	1.0274	503.14087	6.16357	7.5737
2	28.623	BB	1.4204	6140.14355	63.31292	92.4263

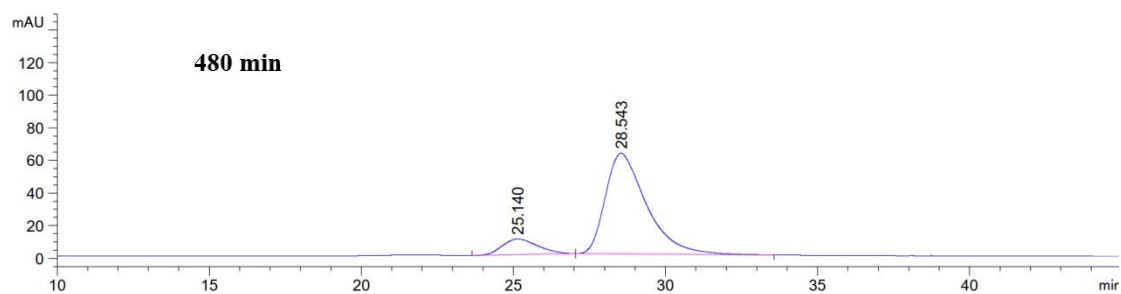


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.059	BB	1.1309	661.30133	7.99555	9.2867
2	28.481	BB	1.4460	6459.68262	67.04990	90.7133

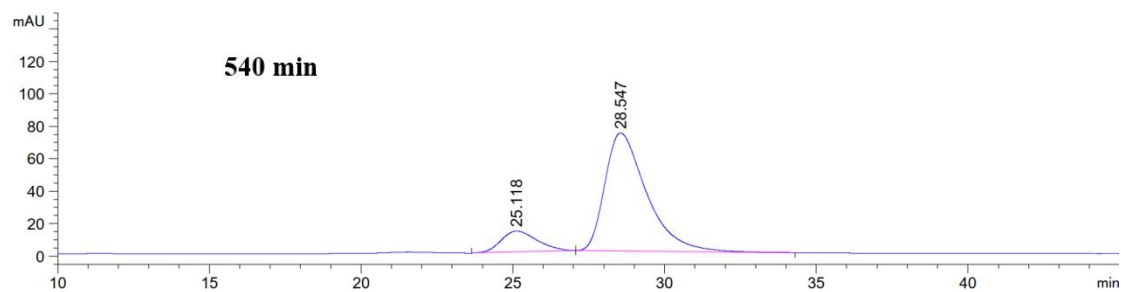


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
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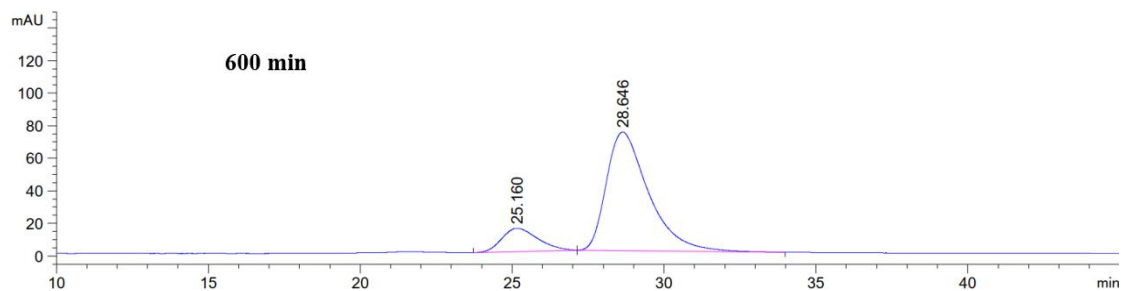
1	25.226	BB	1.1908	836.21613	10.14340	10.5437
2	28.585	BB	1.4163	7094.72949	73.03577	89.4563



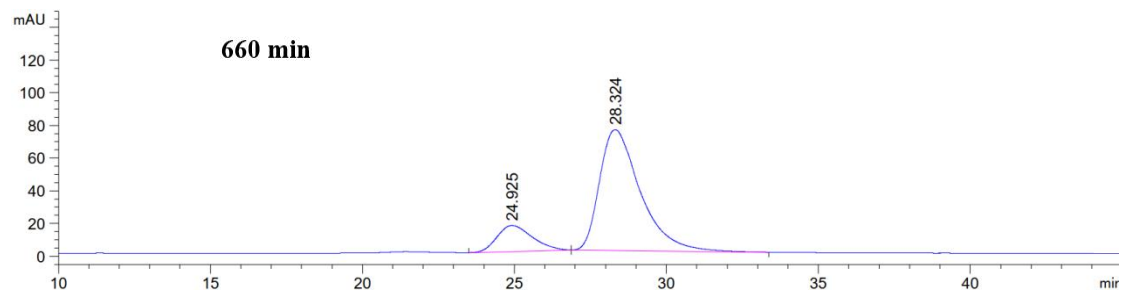
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.140	BB	1.1047	784.89056	9.66279	11.8940
2	28.543	BB	1.3986	5814.16553	61.91508	88.1060



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.118	BB	1.1205	1064.56787	12.91742	13.2453
2	28.547	BB	1.4045	6972.72949	72.73010	86.7547

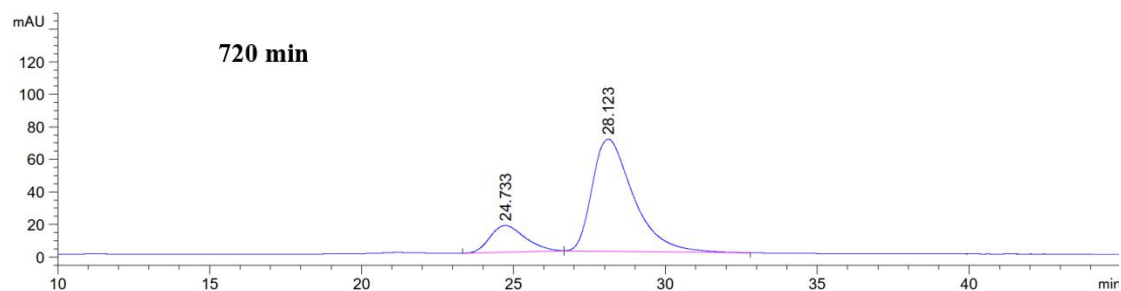


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	25.160	BB	1.1520	1172.22192	14.26033	14.2781
2	28.646	BB	1.3997	7037.72021	72.87468	85.7219

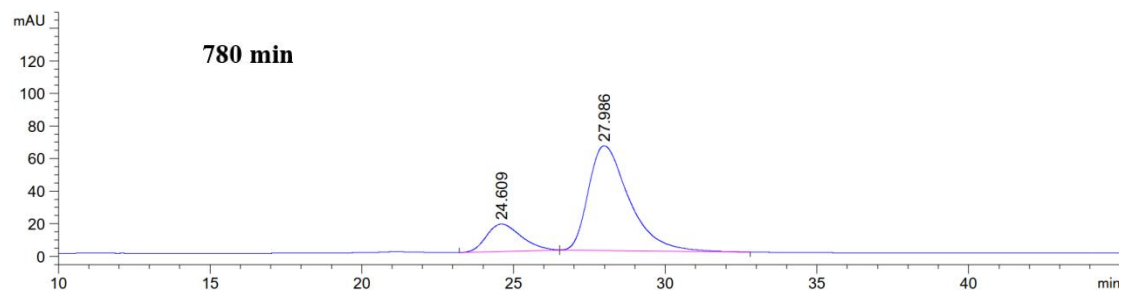


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
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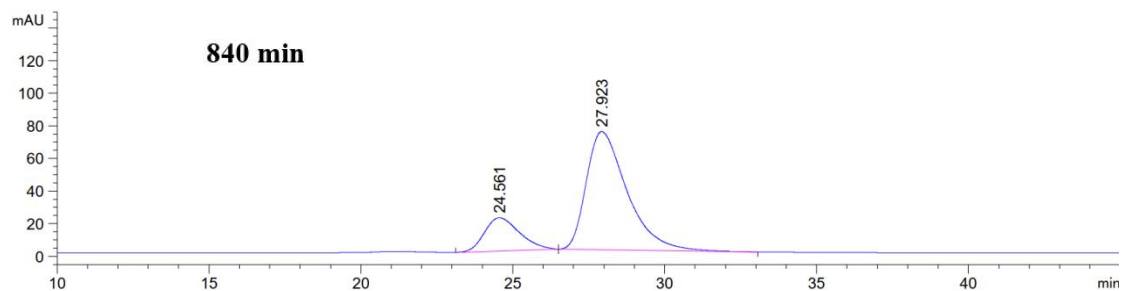
1	24.925	BB	1.1987	1284.38293	15.96337	15.6990
2	28.324	BB	1.3490	6896.94531	73.95615	84.3010



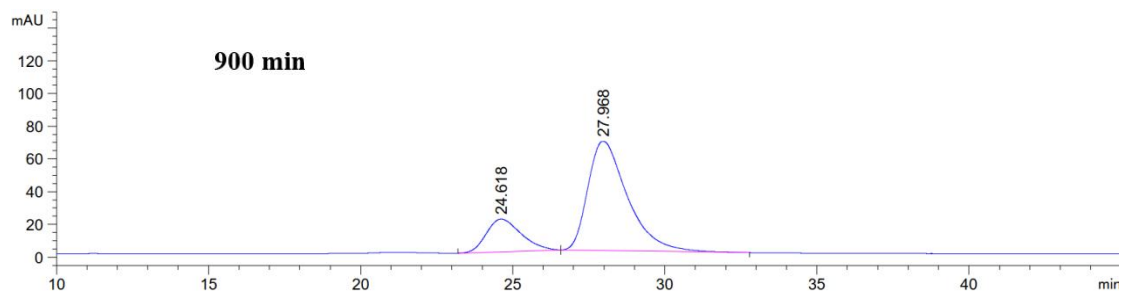
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	24.733	BB	1.1292	1318.41089	16.53558	16.8724
2	28.123	BB	1.3587	6495.60107	68.97516	83.1276



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	24.609	BB	1.1750	1335.67822	16.82759	18.2149
2	27.986	BB	1.3681	5997.20557	64.18481	81.7851



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	24.561	BB	1.1802	1624.11853	20.37078	19.3579
2	27.923	BB	1.4012	6765.83398	72.53531	80.6421



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
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1	24.618	BB	1.1753	1586.20251	19.99938	20.7310
2	27.968	BB	1.3544	6065.16162	66.85517	79.2690

VI. Modeling the CD spectrum to identify the sense of enantioselectivity

The instrument employed for the ECD analysis is MOS-500, Bio-Logic (France). Light source: 150W xenon lamp; wavelength range: 200-450 nm; wavelength accuracy: ± 0.1 nm; scanning speed: up to 12000 nm/min. *Ent-3aa* (using (**5aS**, **10R**)-NHC-1 as chiral catalyst) was dissolved in dichloromethane (DCM) to prepare a 1 mM sample solution. Transfer 250 μ L of the sample solution into a quartz colorimetric cell with a 1 mm optical path for testing. Then the ECD spectra from the tests were calculated by the TD-DFT method, which has been proven to be useful in predicting ECD spectra and assigning the AC of organic molecules.^[7] Gaussian 16 package of programs is applied for theoretical calculation.^[8] Geometries optimization and the Gibbs energy calculations were performed at the level of b3lyp/6-311+g(d,p). Calculations of ECD were performed based on the optimized conformations, and then the ECD spectra was obtained by Multiwfn.^[9] As shown in Figure S2, the simulated spectra are in good agreement with the experimental spectral data. Finally, the absolute configuration of the products was determined by electronic circular dichroism (ECD) analysis of *ent-3aa*, which was assigned as *S*. Accordingly, the absolute configurations of all other products were assigned by analogy as *R*.

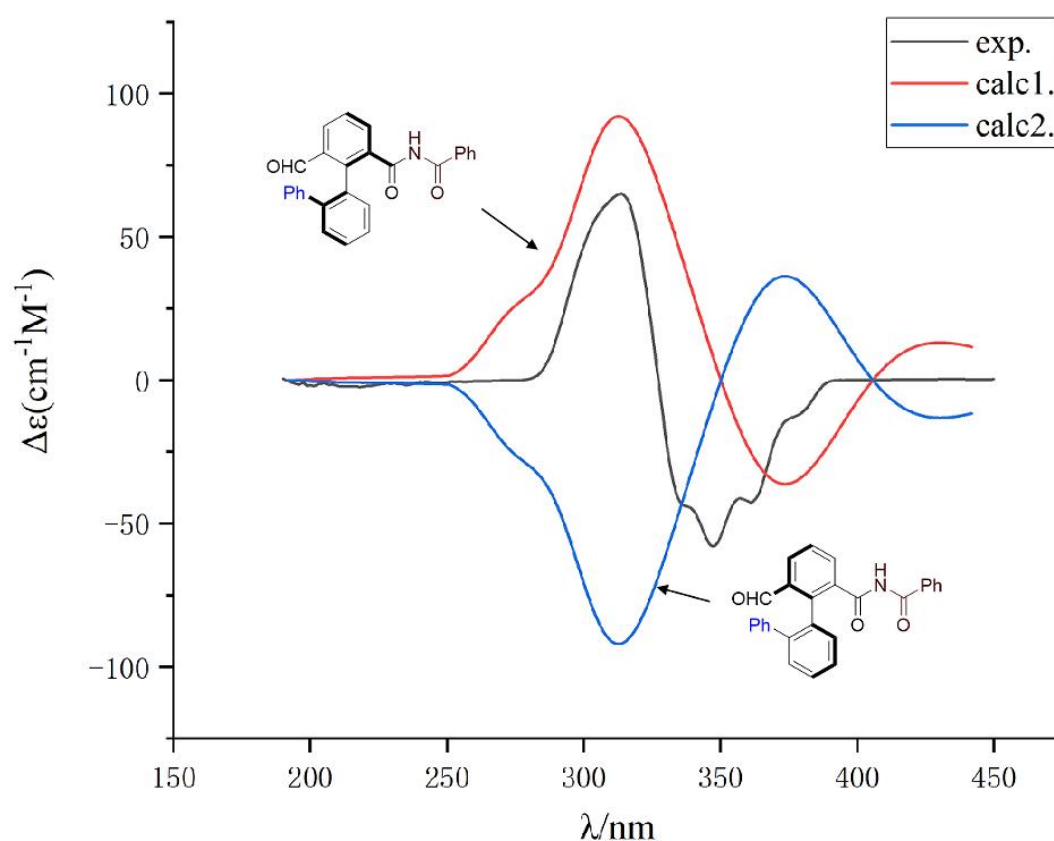
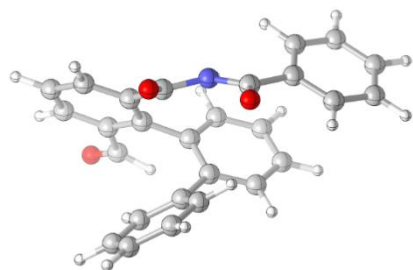


Figure S4. Experimental ECD spectra (black line) and simulated spectra (red line) proving *Sa*-conformer for *ent-3aa* absolute configuration.

Table S1. Optimized geometries labeled with Gibbs free energies (Hartree) and cartesian coordinates for the 2 conformations.

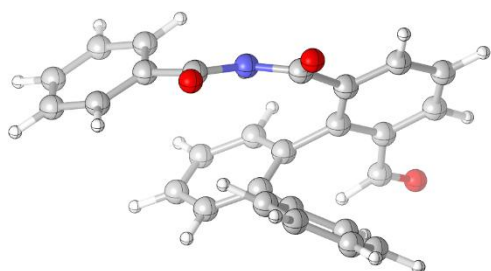
calc.1



C	-1.80883600	-1.14809600	-2.18776200
C	-1.43735400	-2.26772400	-1.44652200
C	-0.28831300	-2.21943200	-0.65724700
C	0.49997900	-1.06039500	-0.59671400
C	0.14404300	0.06489200	-1.37430900
C	-1.01879400	-0.00047300	-2.15299700
H	-2.71467700	-1.16384800	-2.78545500
H	-2.04550000	-3.16649000	-1.46503300
H	-0.00765300	-3.07683000	-0.05098100
H	-1.29585000	0.86758900	-2.74341600
C	1.62830900	-1.00305100	0.38372700
C	1.58614200	-0.13973300	1.50228200
C	2.76673500	-1.81852400	0.20964900
C	2.67202200	-0.08789900	2.38333900
C	3.82391300	-1.77971000	1.12999800
C	3.78259200	-0.91172900	2.21184300
H	2.62026800	0.61448200	3.20838000
H	4.67427700	-2.42986000	0.95136400
H	4.60816100	-0.86734400	2.91542800
C	0.94993400	1.31206200	-1.34984900
C	0.33833600	2.54260500	-1.07274900
C	2.33108000	1.28157300	-1.59554000
C	1.09414500	3.71296400	-1.02811000
H	-0.72003200	2.57843100	-0.83921600
C	3.08261200	2.45257900	-1.56066100
H	2.81401300	0.33647000	-1.82202300
C	2.46616800	3.67220800	-1.27286000
H	0.60915800	4.65318700	-0.78390200
H	4.15028100	2.41292000	-1.75701300
H	3.05496700	4.58414900	-1.23323500
C	2.92796000	-2.68736800	-0.98431100

O	3.84518600	-3.47638900	-1.12340000
H	2.16255400	-2.56861400	-1.77371100
C	0.45369200	0.80307600	1.83766300
O	0.65488900	1.87393500	2.37060700
N	-0.82713600	0.31142700	1.55727300
H	-0.86033000	-0.63100300	1.19277200
C	-1.96856200	1.07701400	1.28668900
O	-1.99923000	2.29172800	1.32987900
C	-3.13973700	0.25388500	0.84109900
C	-4.05801400	0.86209000	-0.02283000
C	-3.33063100	-1.07901700	1.22467500
C	-5.13202200	0.13555400	-0.52763500
H	-3.90333100	1.90150400	-0.29174500
C	-4.41613500	-1.80114000	0.73165200
H	-2.64951900	-1.55050500	1.92707400
C	-5.31019700	-1.19946000	-0.15464900
H	-5.83288300	0.60833100	-1.20950800
H	-4.56440600	-2.83155700	1.04118100
H	-6.15070800	-1.76569700	-0.54576800

calc.2



C	1.80829600	1.14906300	2.18801300
C	1.43648100	2.26855900	1.44675100
C	0.28749200	2.21988600	0.65744000
C	-0.50039500	1.06057000	0.59682500
C	-0.14412000	-0.06458500	1.37441300
C	1.01862900	0.00117500	2.15320900
H	2.71402100	1.16517700	2.78588500
H	2.04430400	3.16755200	1.46532100
H	0.00659800	3.07718600	0.05114200
H	1.29591700	-0.86679000	2.74365300
C	-1.62865100	1.00282100	-0.38369000
C	-1.58612100	0.13960700	-1.50232200
C	-2.76738200	1.81784400	-0.20956100
C	-2.67194400	0.08751500	-2.38342800

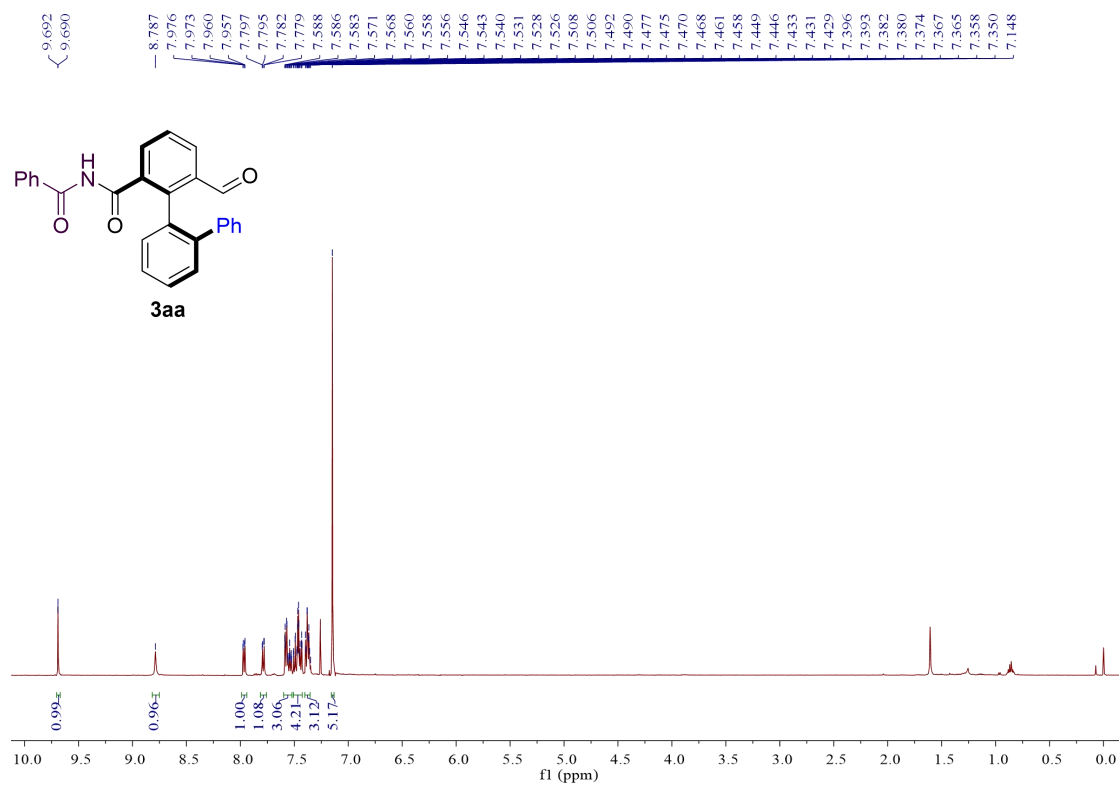
C	-3.82451900	1.77875500	-1.12994500
C	-3.78282000	0.91093000	-2.21188000
H	-2.61991600	-0.61472900	-3.20856300
H	-4.67512100	2.42858500	-0.95127900
H	-4.60836100	0.86628200	-2.91548500
C	-0.94967100	-1.31198100	1.34998000
C	-0.33771800	-2.54235100	1.07294400
C	-2.33084000	-1.28180800	1.59550300
C	-1.09324100	-3.71289300	1.02822300
H	0.72070000	-2.57789000	0.83959900
C	-3.08208500	-2.45300700	1.56057000
H	-2.81403100	-0.33679900	1.82187700
C	-2.46530900	-3.67247000	1.27282400
H	-0.60801400	-4.65299800	0.78404700
H	-4.14978500	-2.41360200	1.75681600
H	-3.05386600	-4.58456000	1.23311900
C	-2.92892100	2.68662000	0.98441800
O	-3.84636500	3.47539000	1.12343600
H	-2.16354600	2.56805000	1.77387900
C	-0.45344200	-0.80295700	-1.83773800
O	-0.65440100	-1.87369200	-2.37102900
N	0.82727000	-0.31122300	-1.55706500
H	0.86034800	0.63111000	-1.19234600
C	1.96879000	-1.07675500	-1.28678500
O	1.99955300	-2.29146700	-1.33014700
C	3.13994700	-0.25364100	-0.84116600
C	4.05847800	-0.86203800	0.02236800
C	3.33069700	1.07938100	-1.22440400
C	5.13259900	-0.13559700	0.52708900
H	3.90388000	-1.90151900	0.29105100
C	4.41629500	1.80141700	-0.73145000
H	2.64940900	1.55107000	-1.92650000
C	5.31063400	1.19952300	0.15442400
H	5.83363600	-0.60854300	1.20866200
H	4.56443300	2.83193500	-1.04071100
H	6.15123500	1.76568800	0.54545500

Proposed Reaction Mechanism

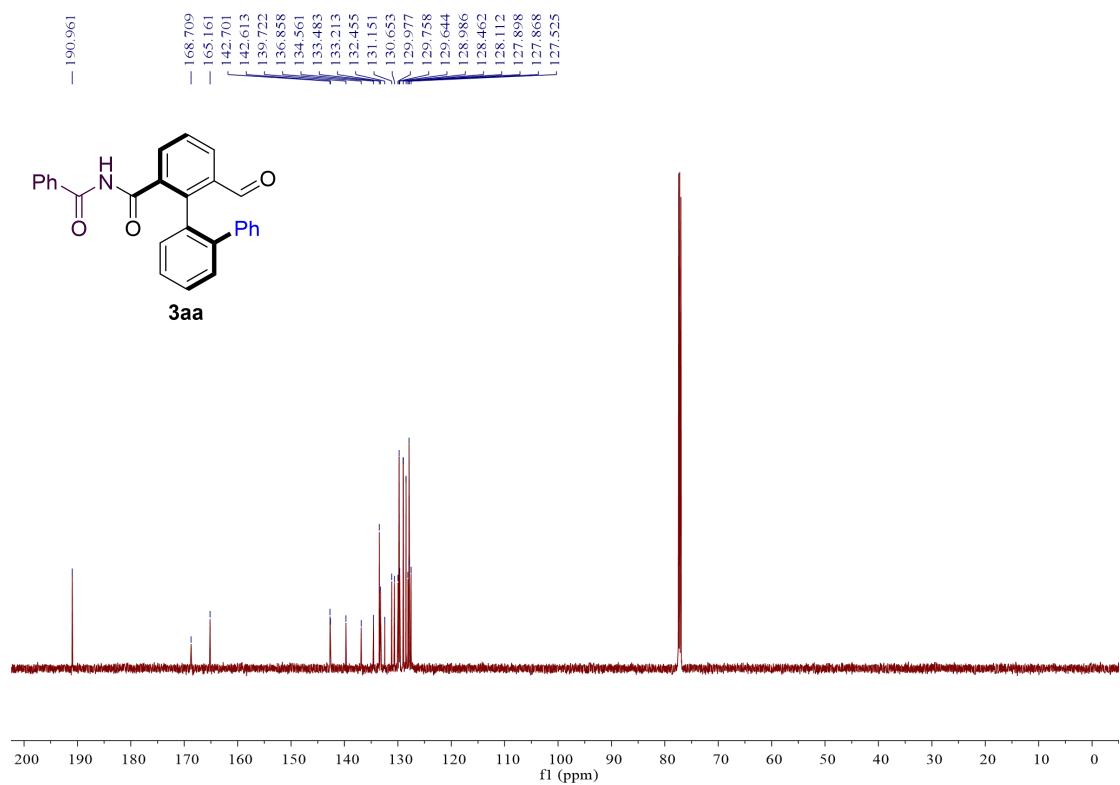
VII. References

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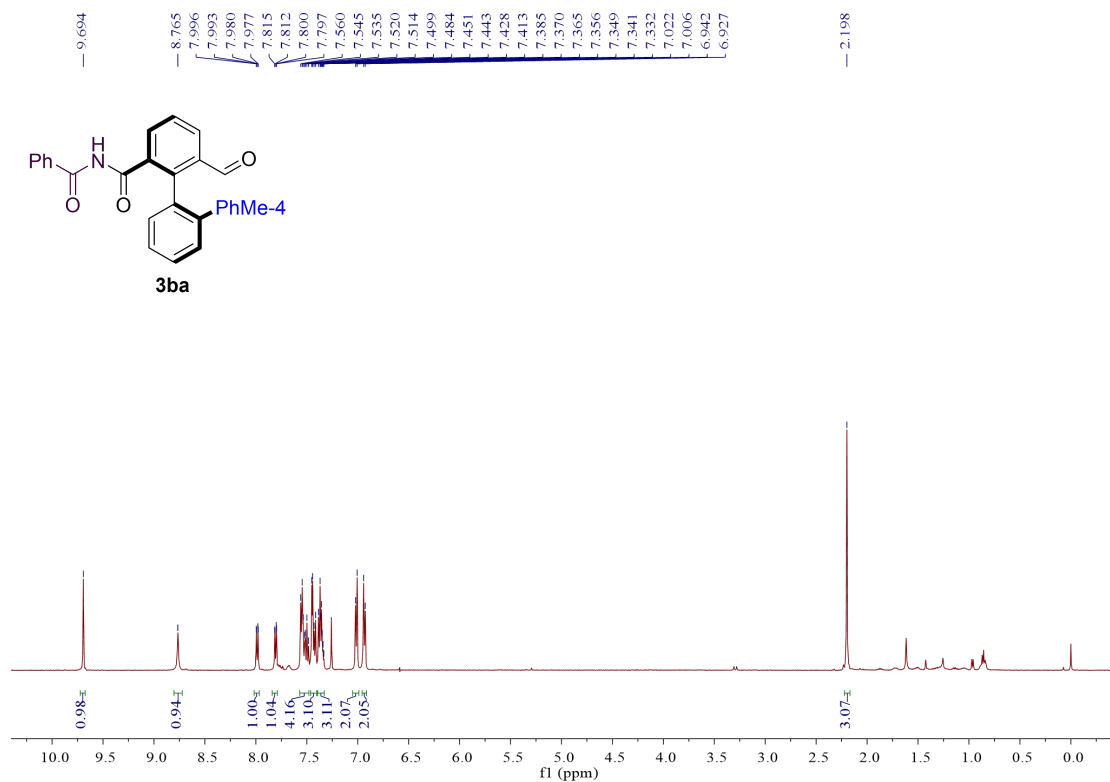
VIII. ^1H , ^{13}C , ^{19}F NMR Spectra of New Compounds.



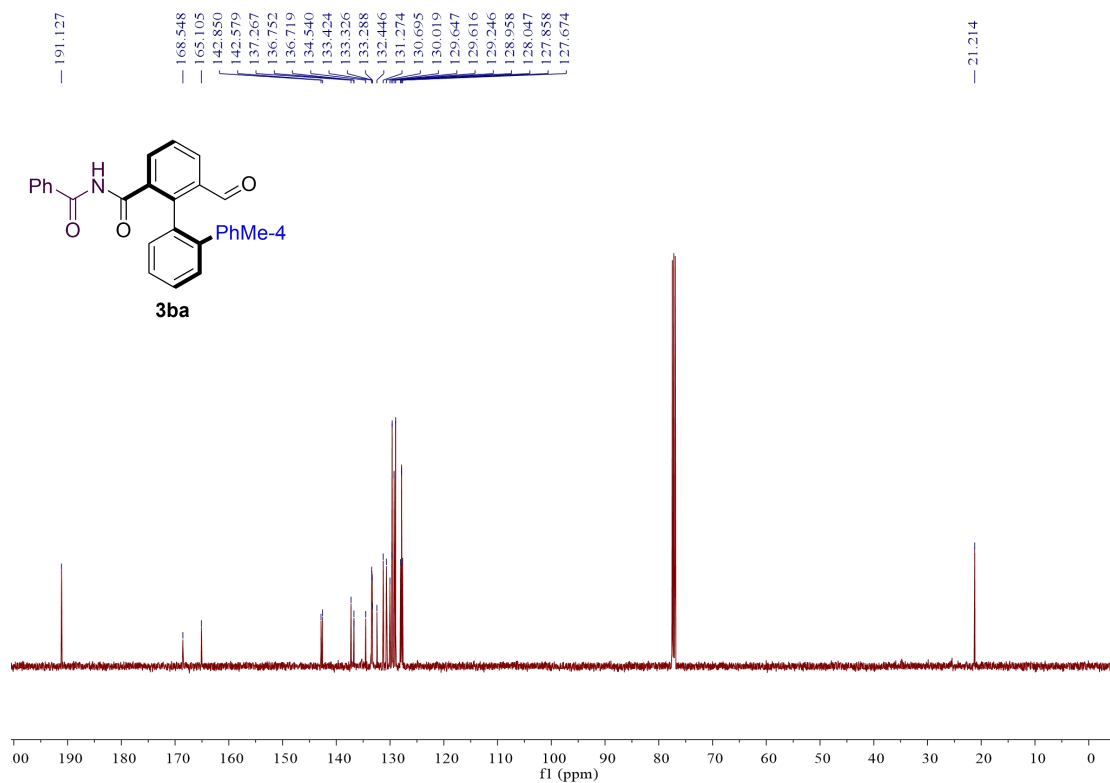
^1H NMR (500 MHz, CDCl_3) spectrum of 3aa.



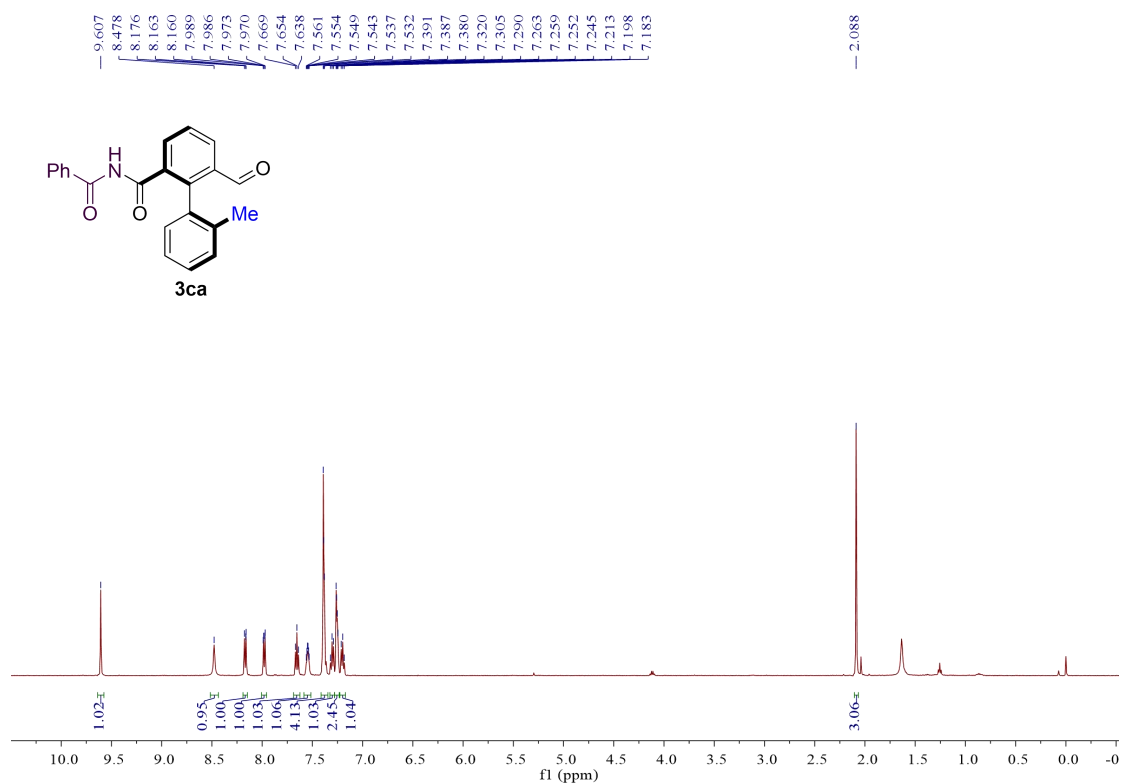
^{13}C NMR (150 MHz, CDCl_3) spectrum of 3aa.



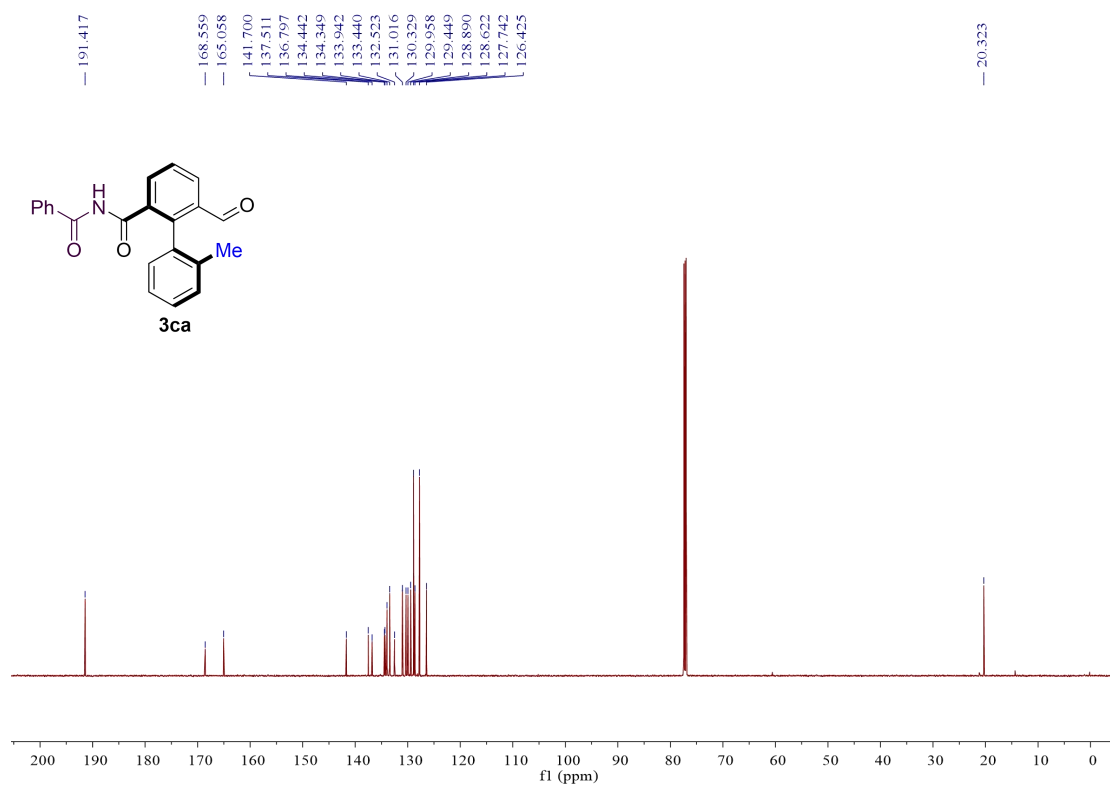
^1H NMR (500 MHz, CDCl_3) spectrum of **3ba**.



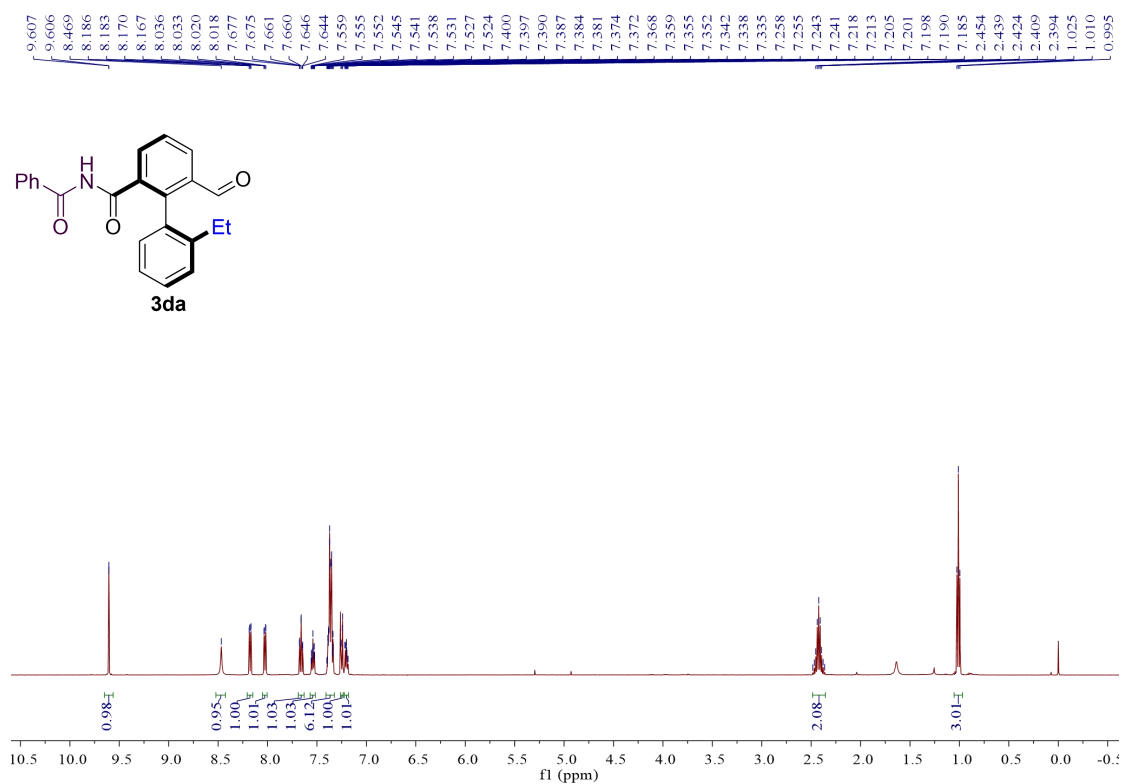
^{13}C NMR (125 MHz, CDCl_3) spectrum of **3ba**.



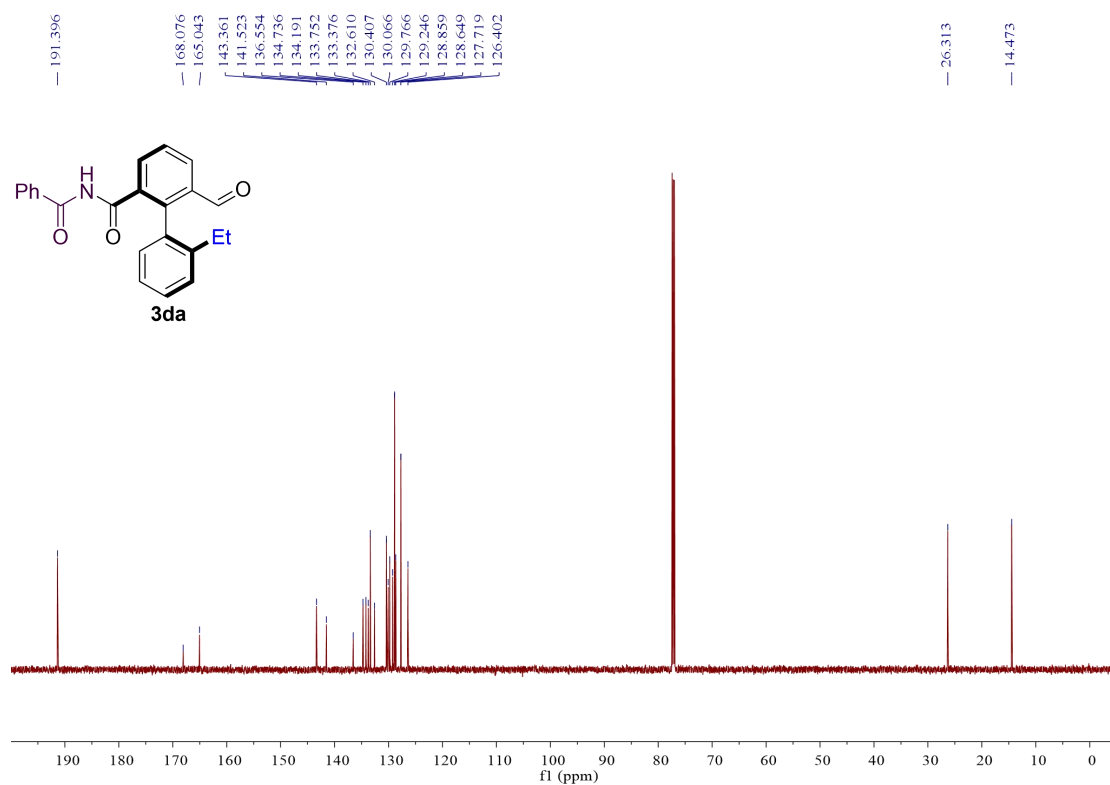
^1H NMR (500 MHz, CDCl_3) spectrum of **3ca**.



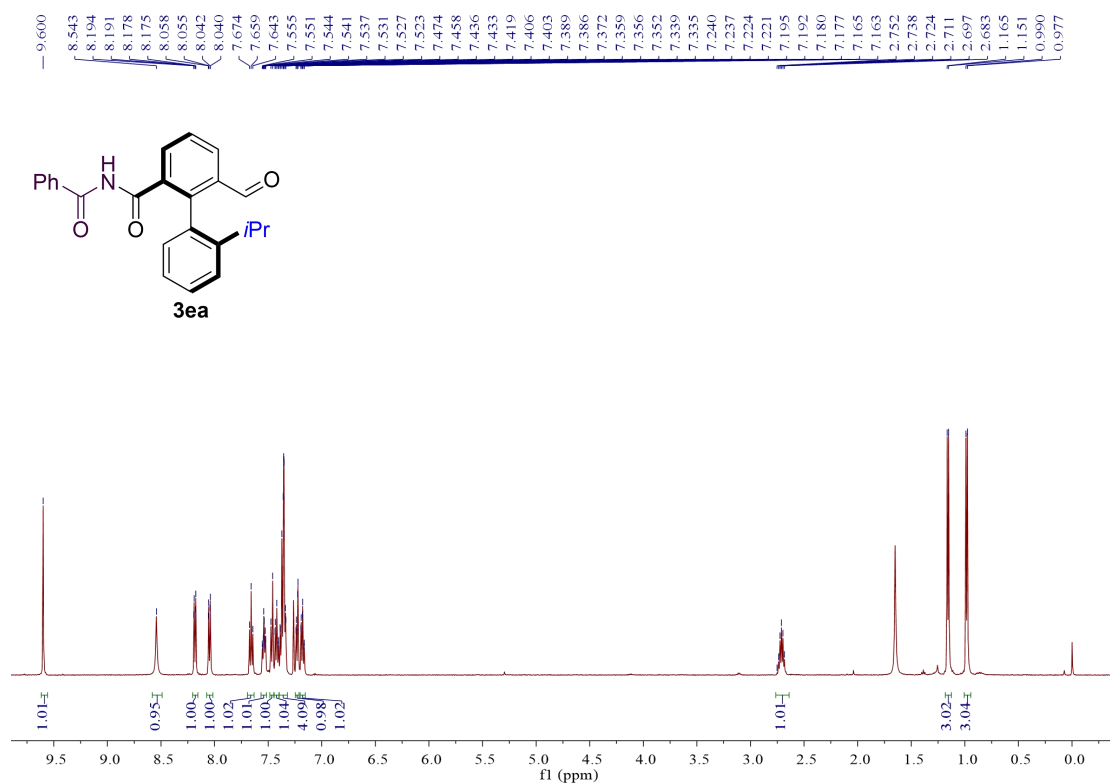
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ca**.



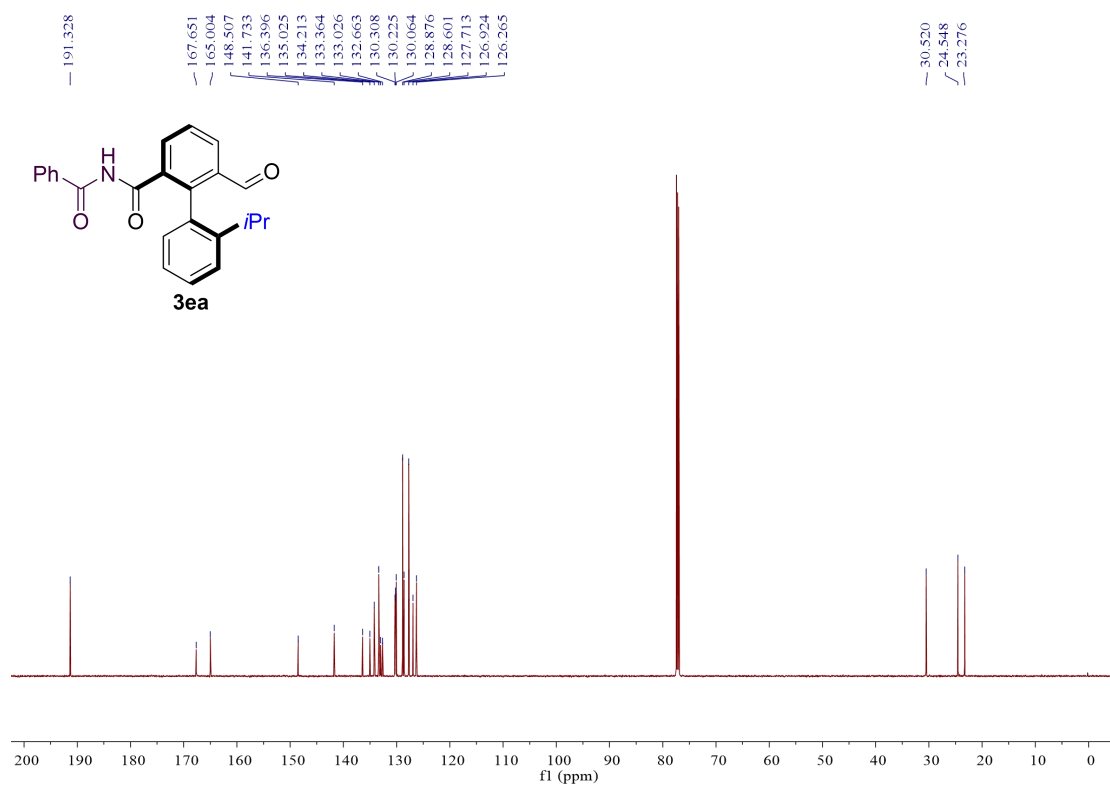
¹H NMR (500 MHz, CDCl₃) spectrum of 3da.



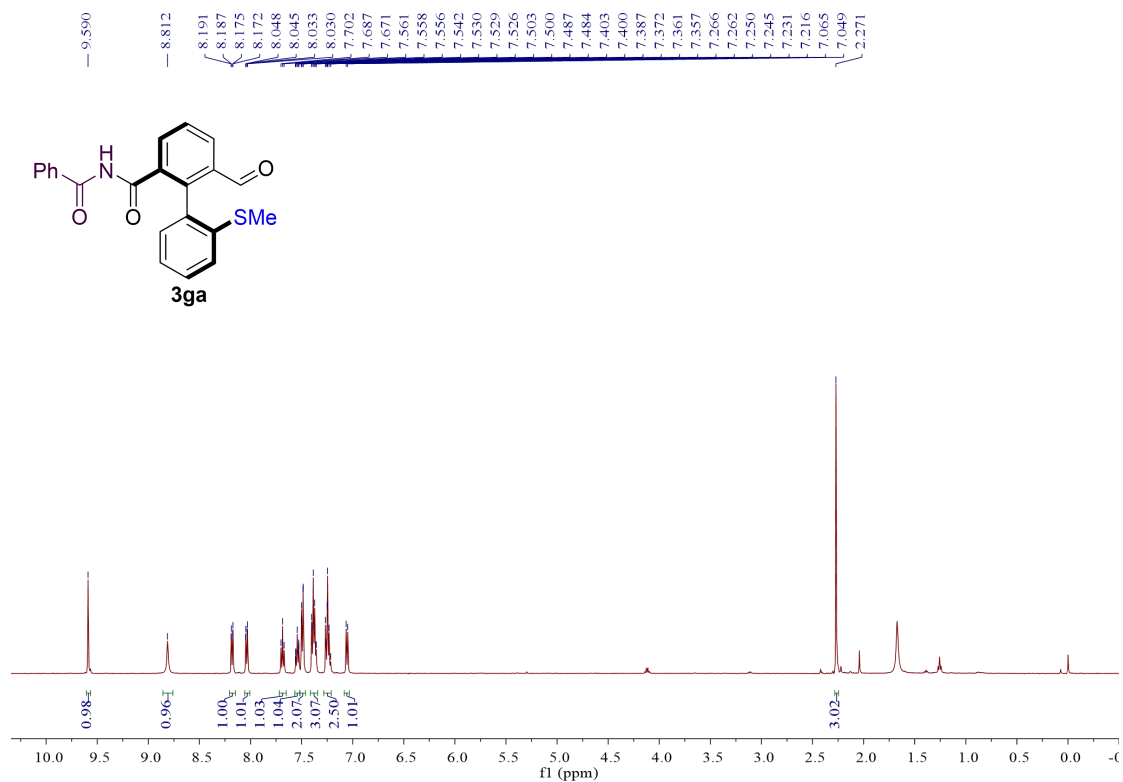
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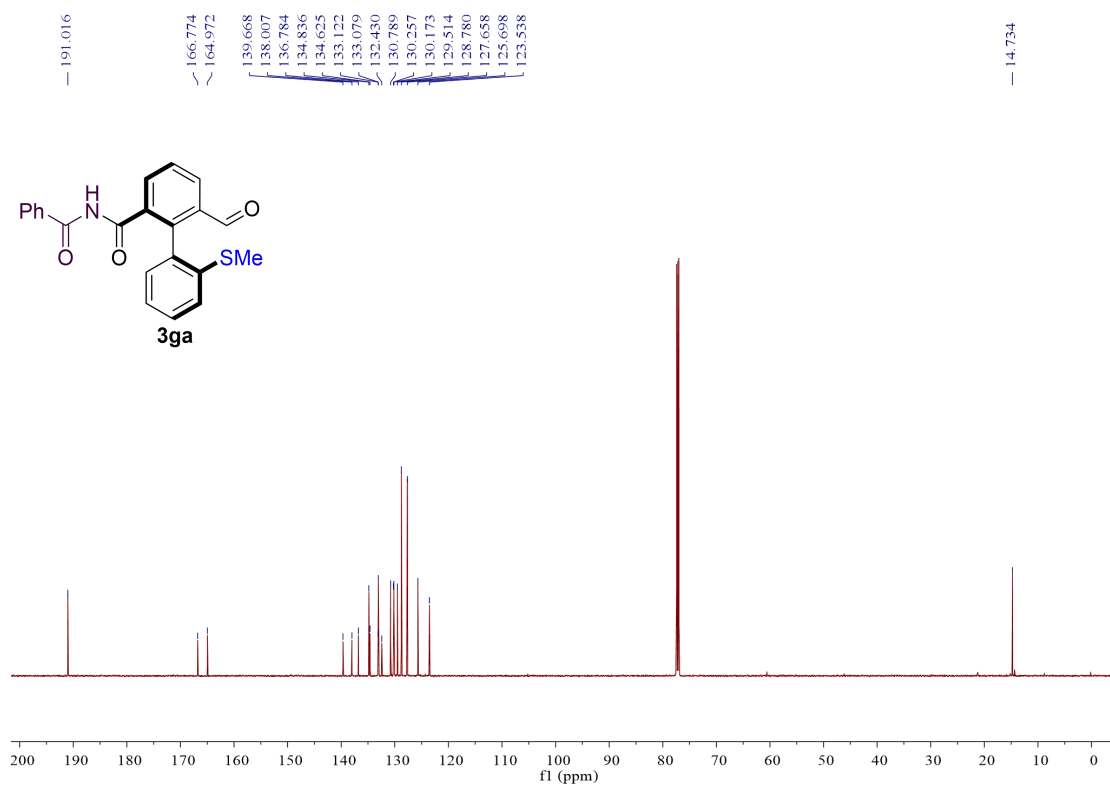
^1H NMR (500 MHz, CDCl_3) spectrum of **3ea**.



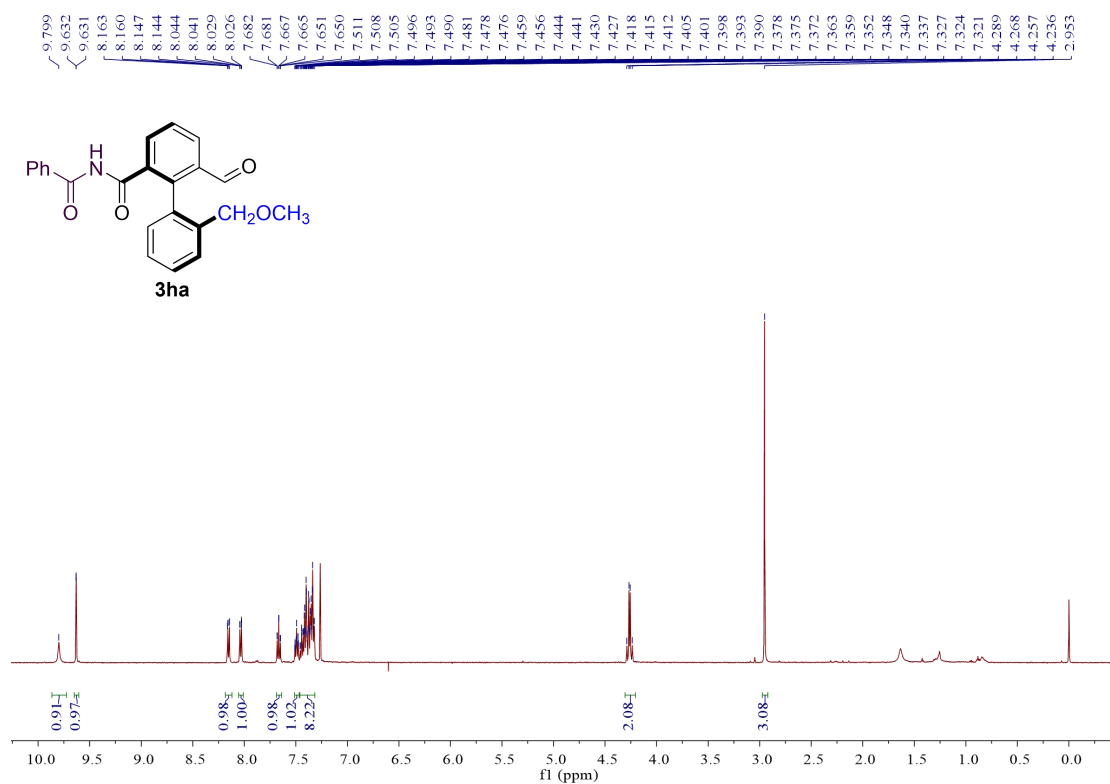
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ea**.



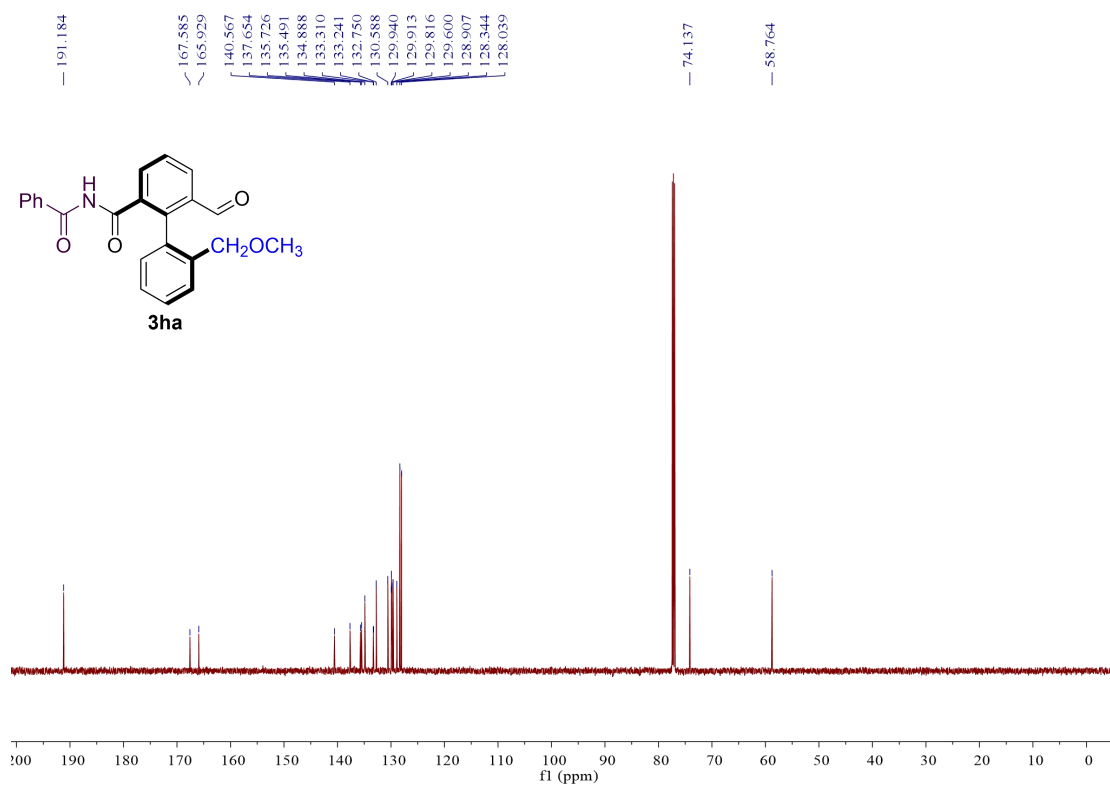
^1H NMR (500 MHz, CDCl_3) spectrum of **3ga**.



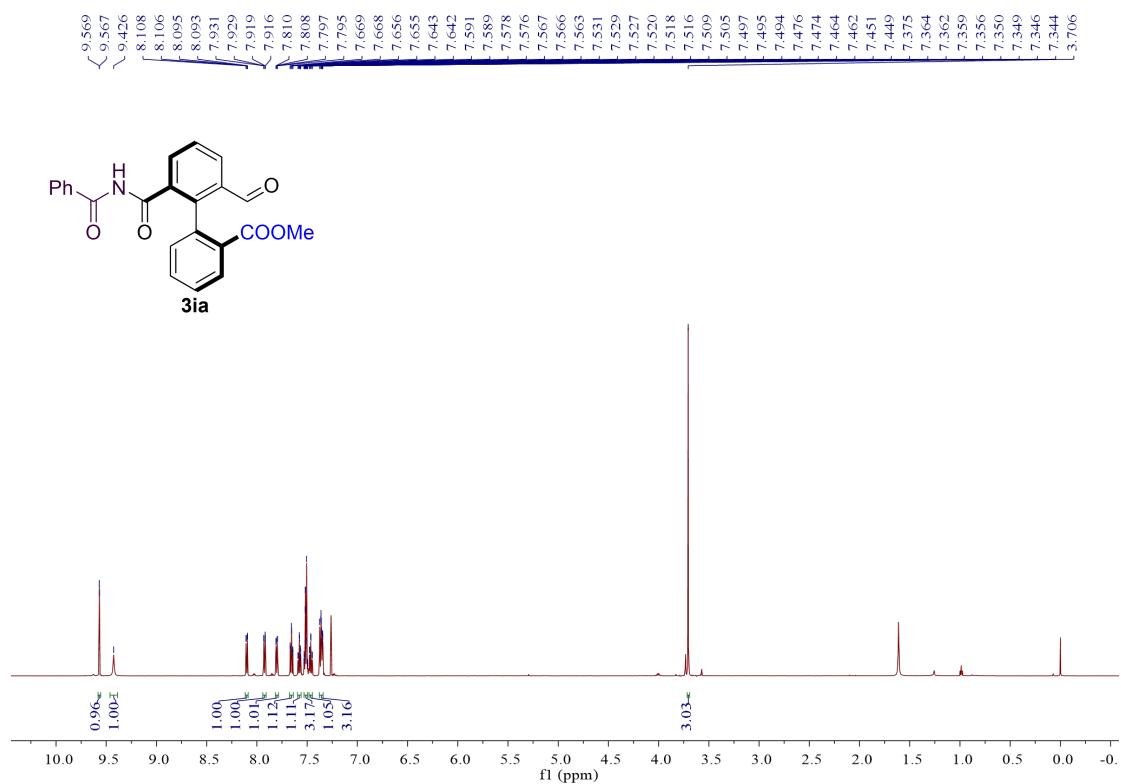
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ga**.



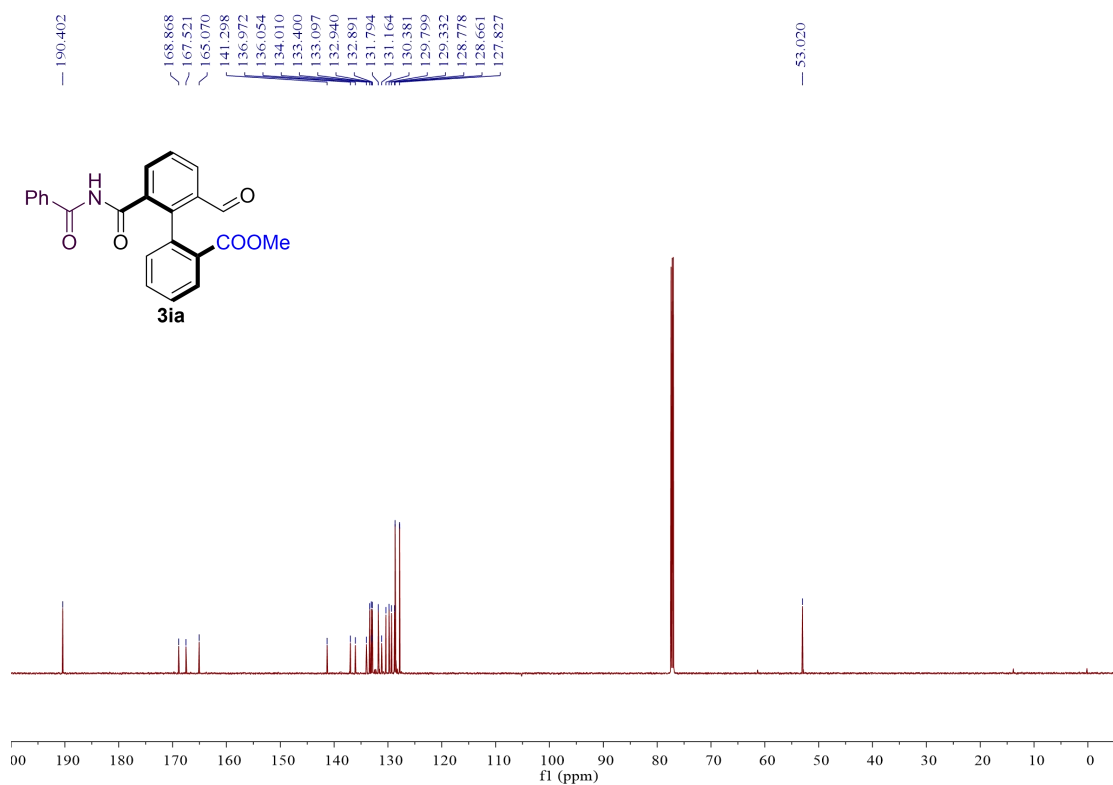
^1H NMR (500 MHz, CDCl_3) spectrum of **3ha**.



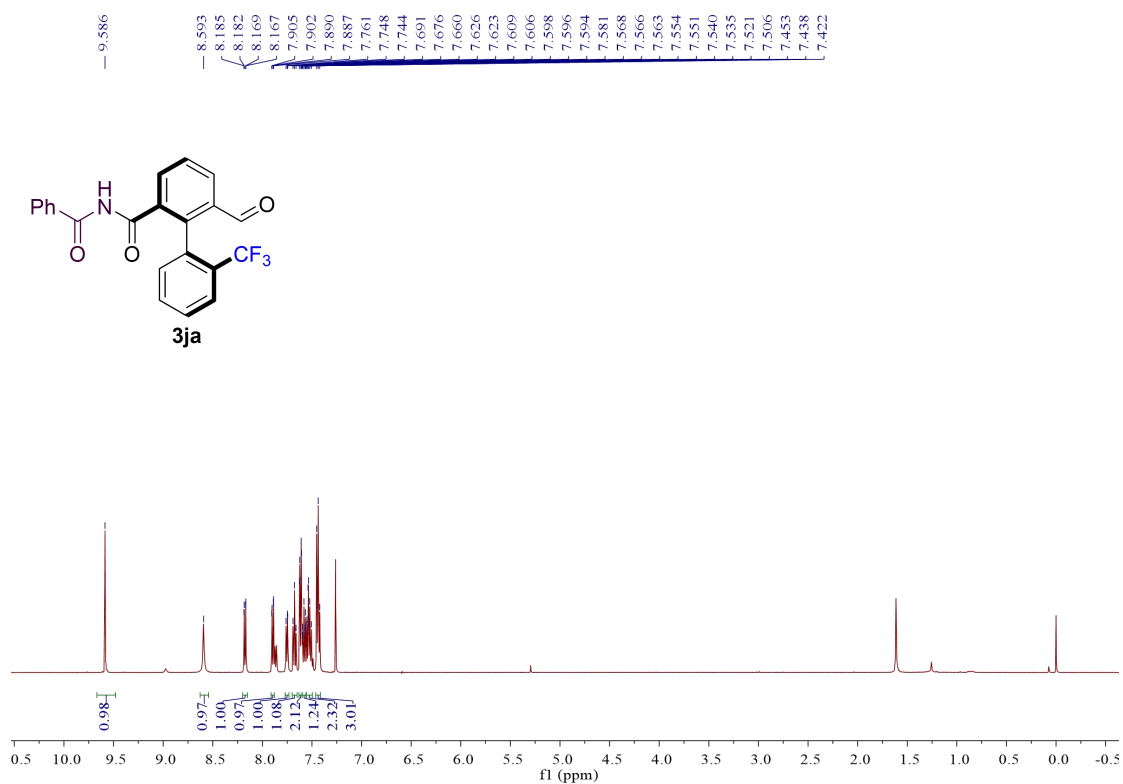
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ha**.



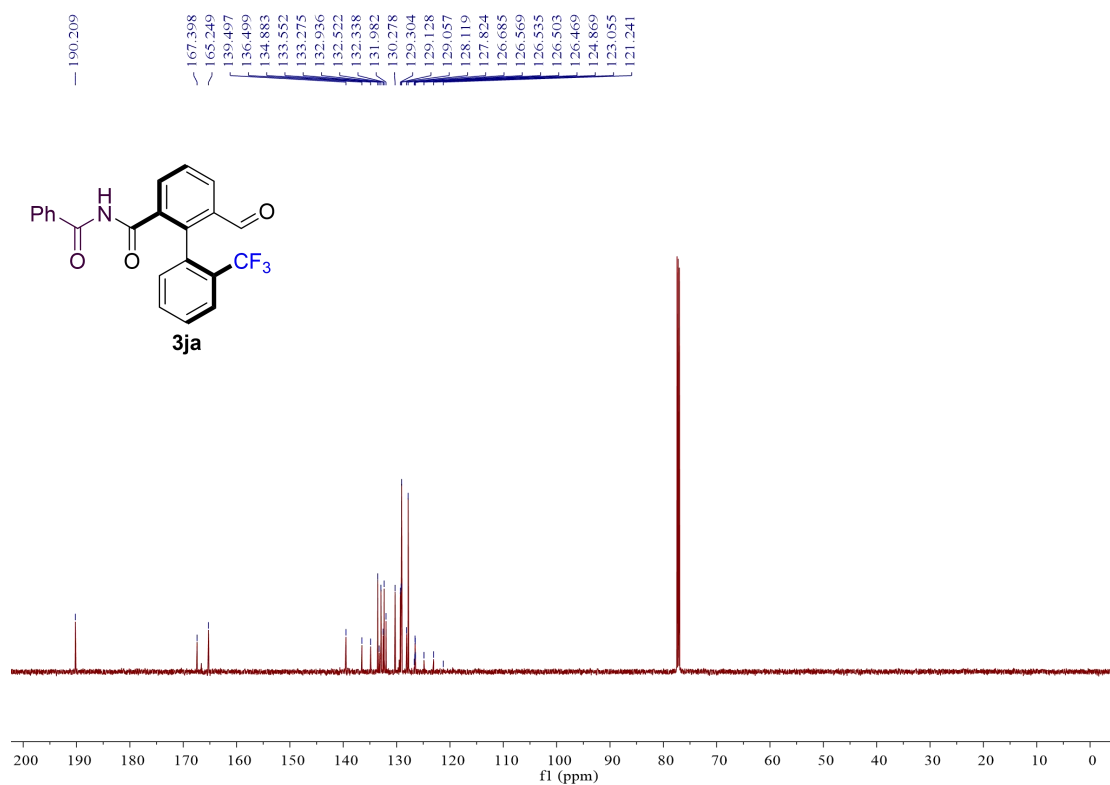
^1H NMR (600 MHz, CDCl_3) spectrum of **3ia**.



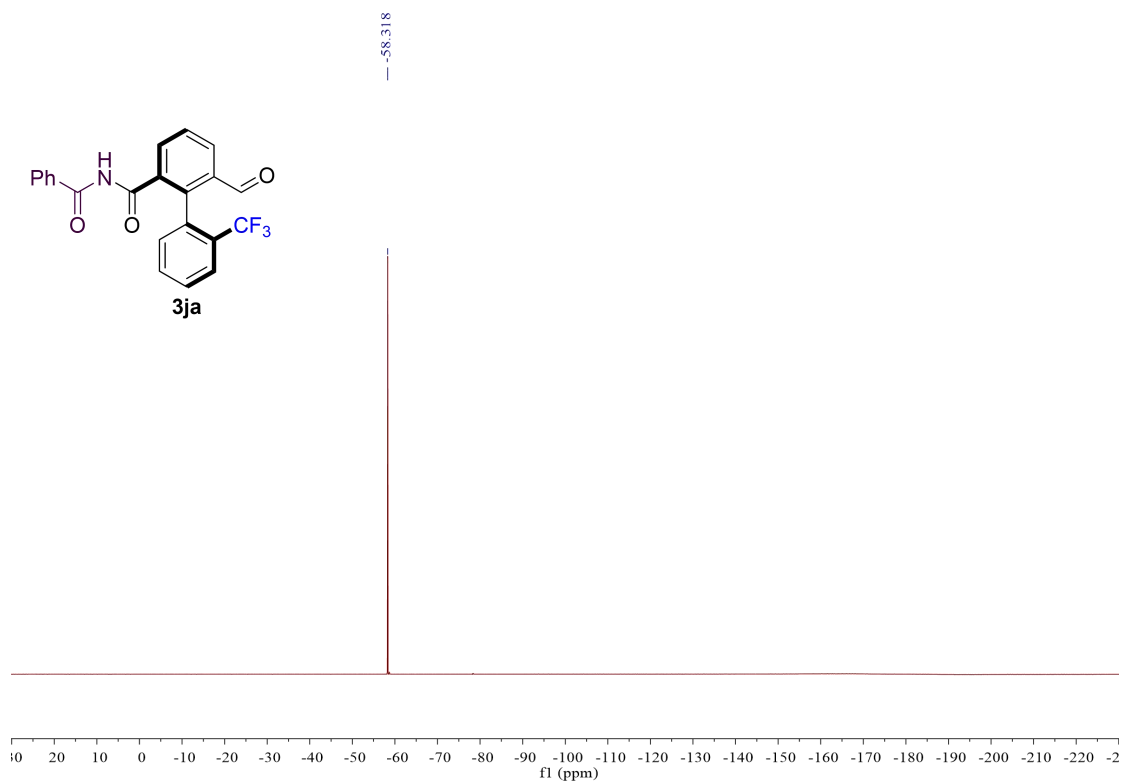
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ia**.



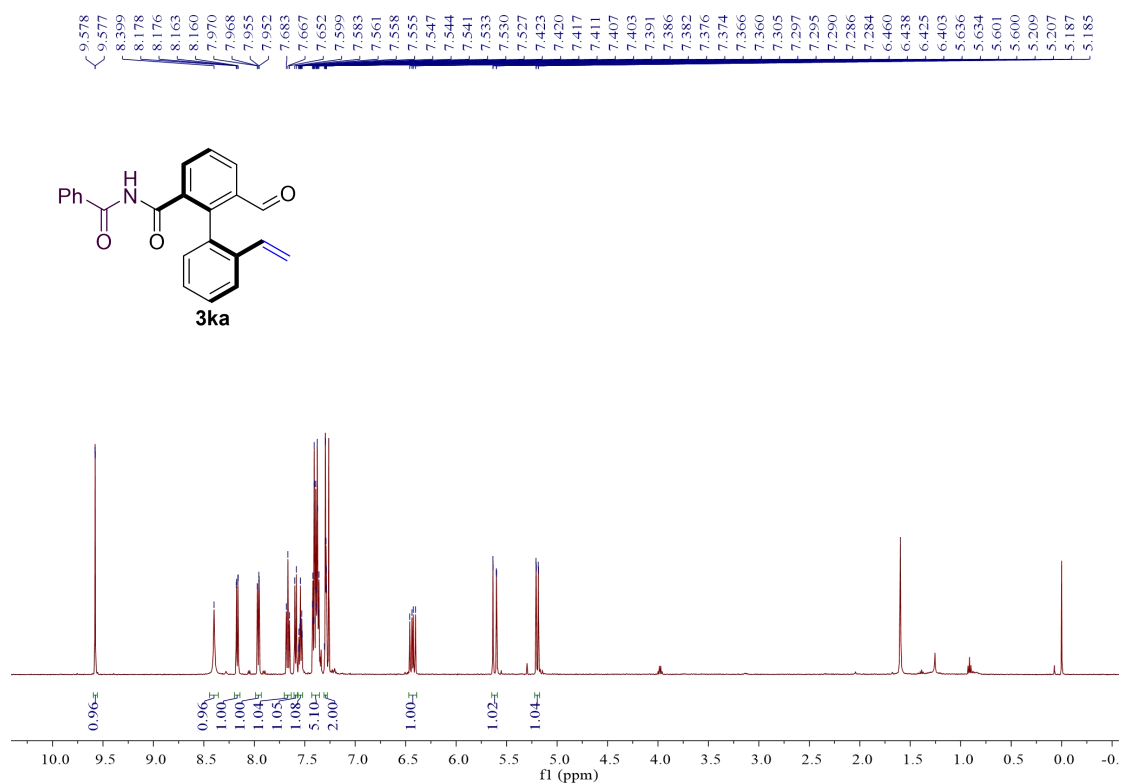
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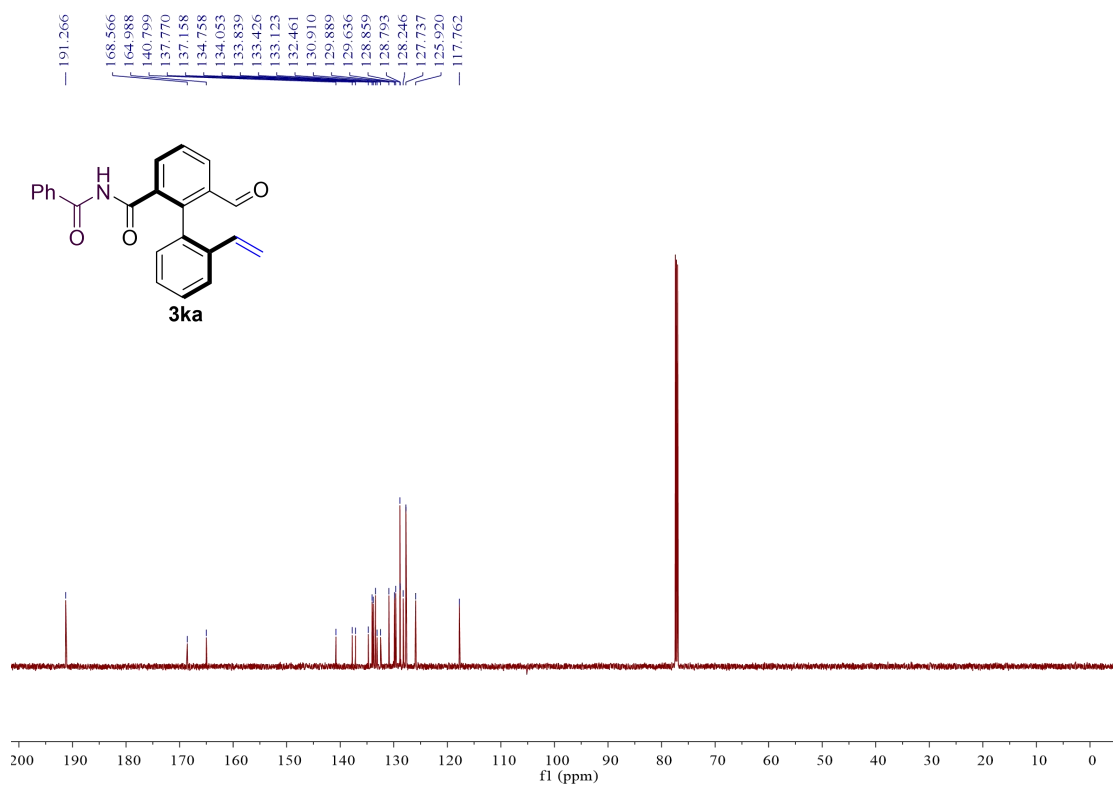
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ja**.



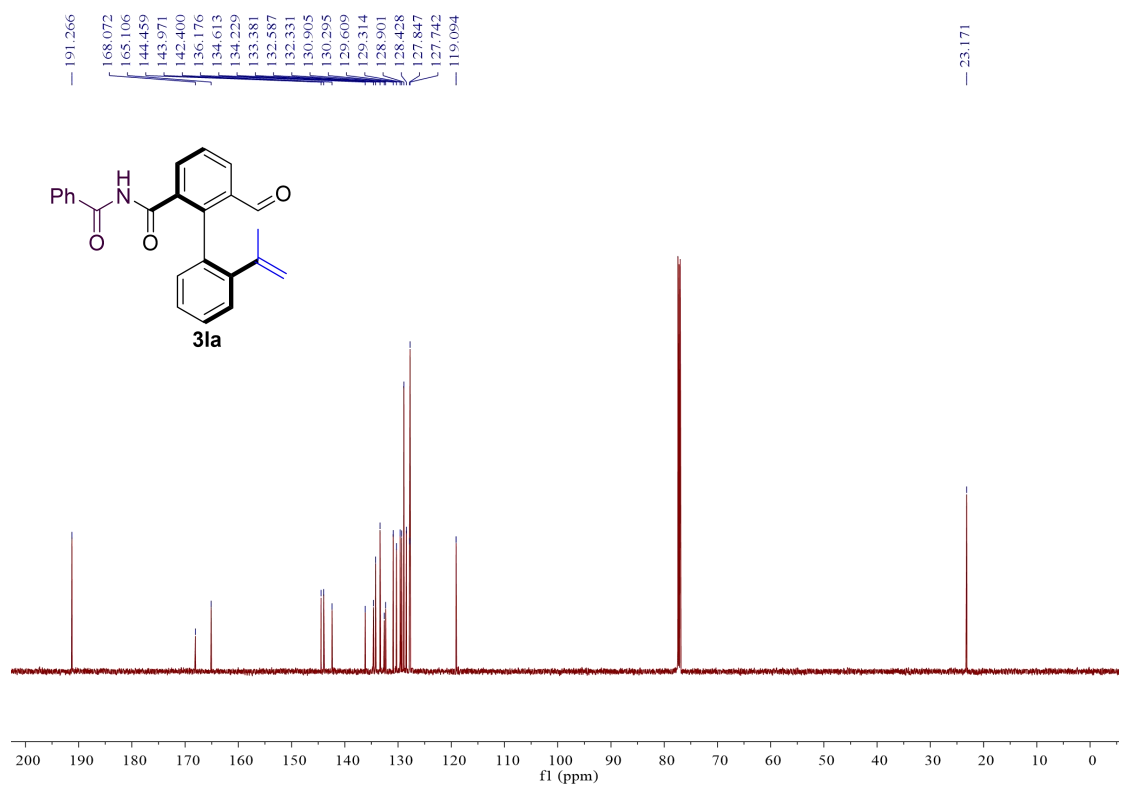
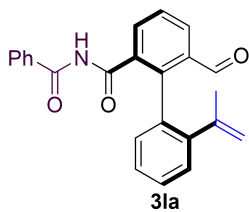
¹⁹F NMR (565 MHz, CDCl₃) spectrum of 3ja.

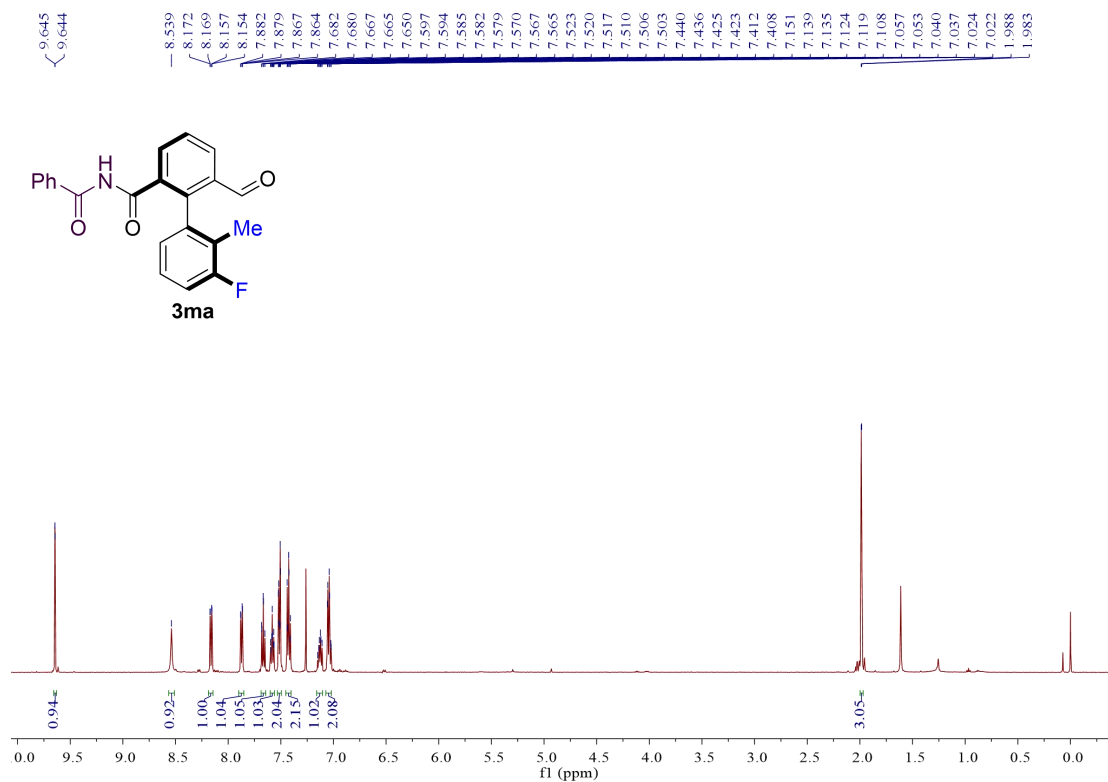


^1H NMR (500 MHz, CDCl_3) spectrum of **3ka**.

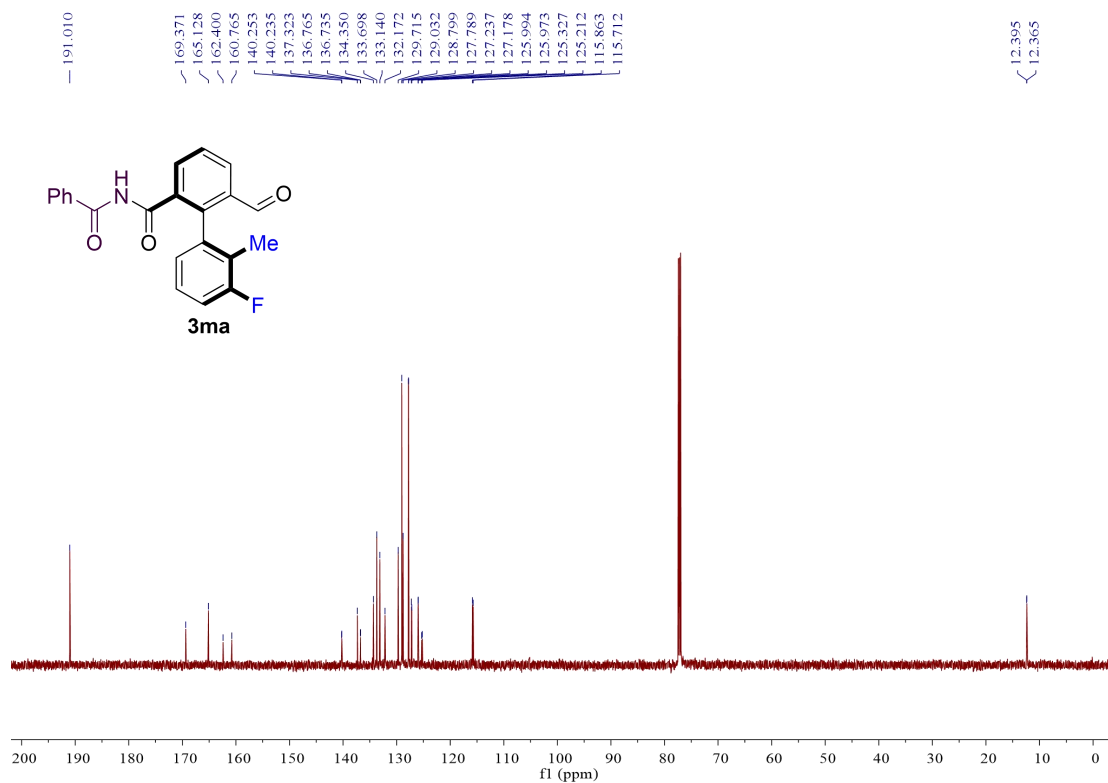


^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ka**.

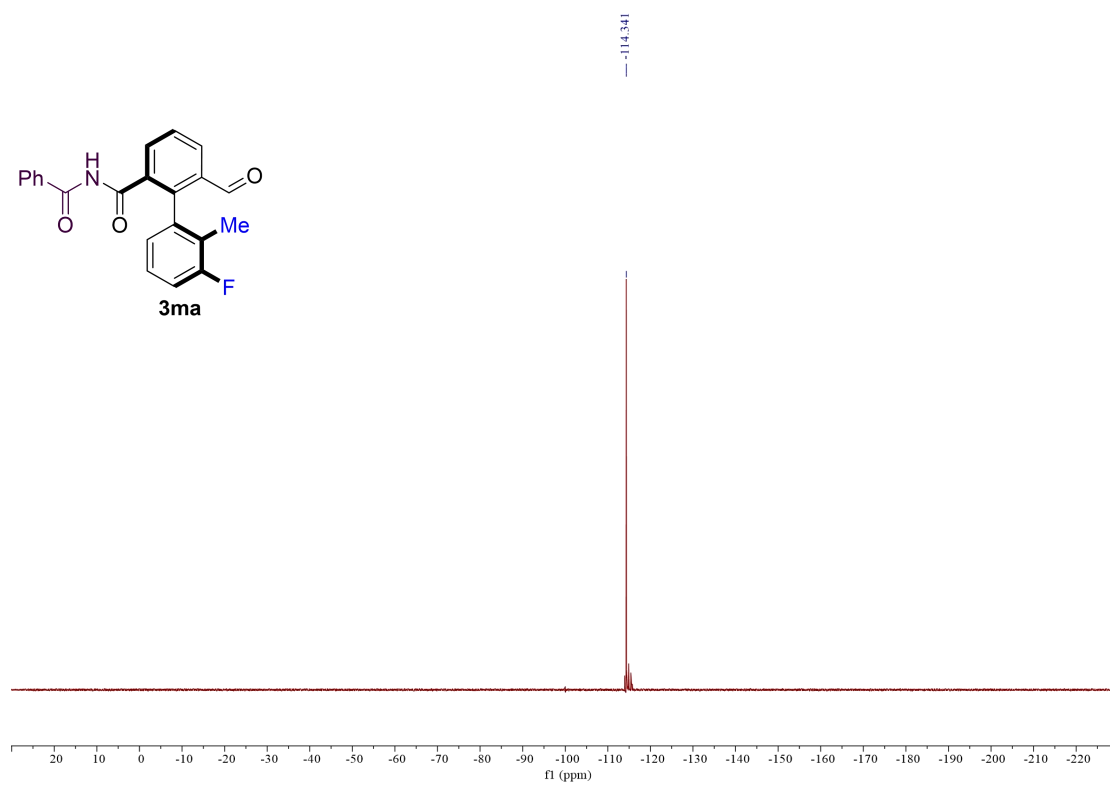




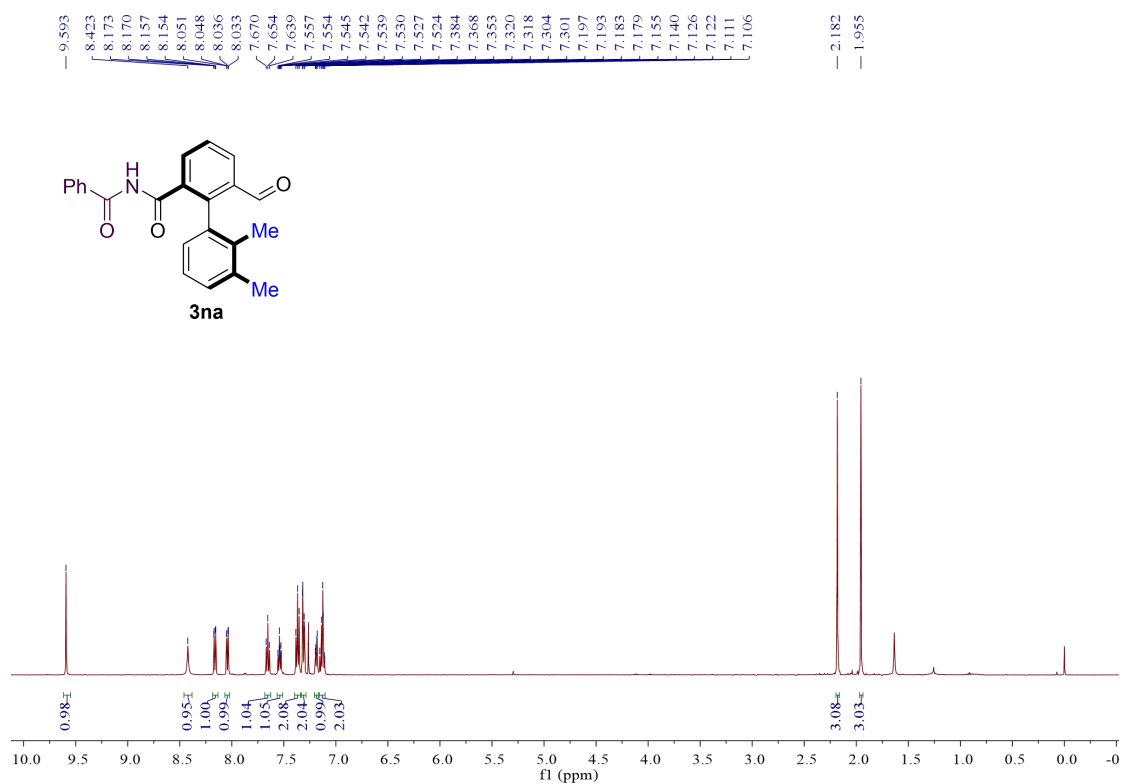
¹H NMR (500 MHz, CDCl₃) spectrum of 3ma.



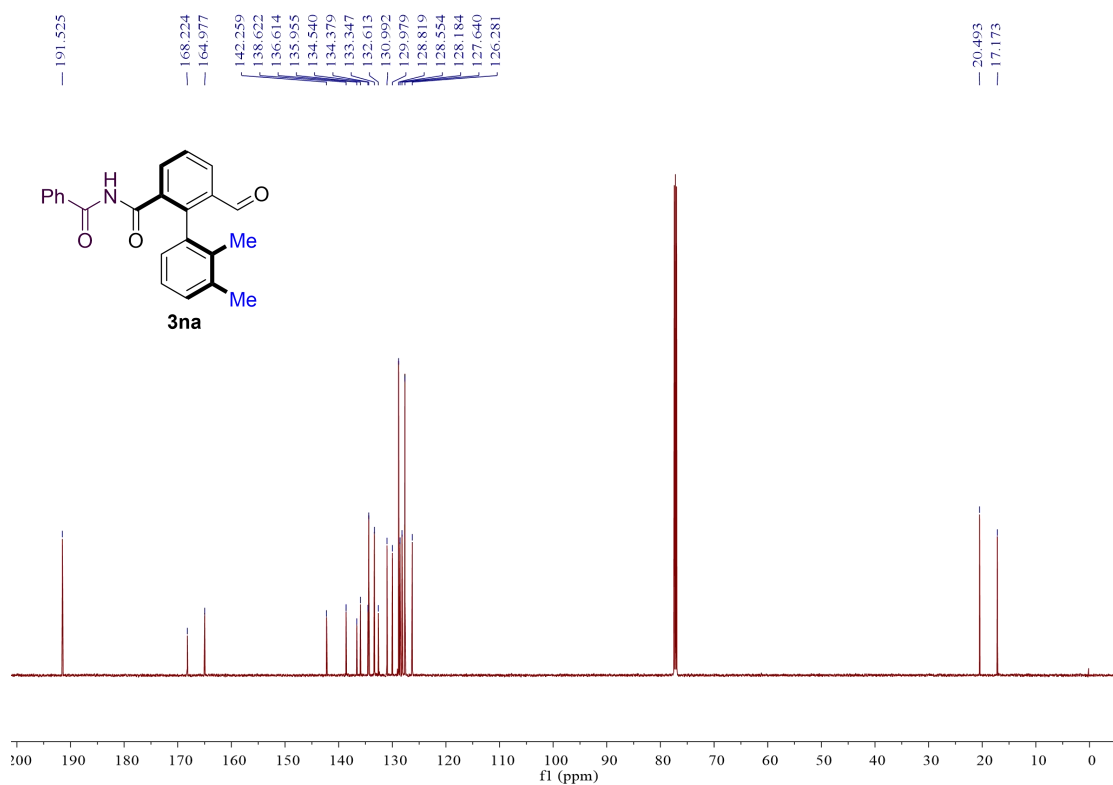
¹³C NMR (150 MHz, CDCl₃) spectrum of 3ma.



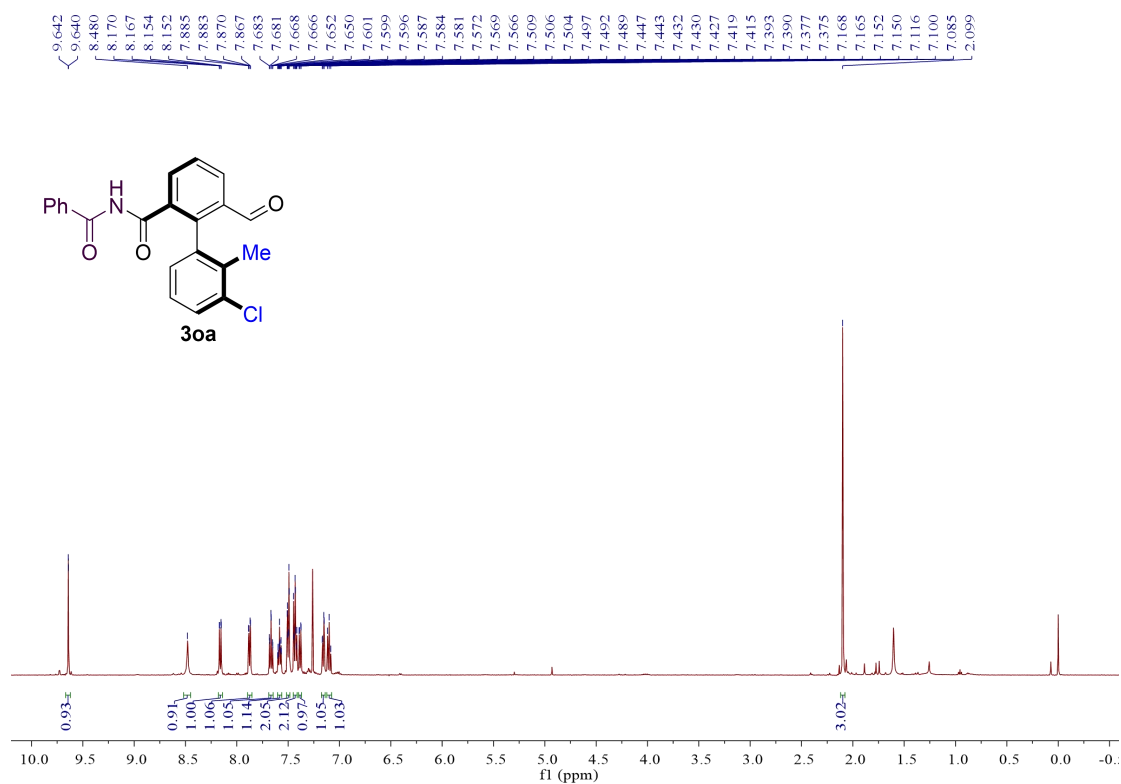
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3ma.**



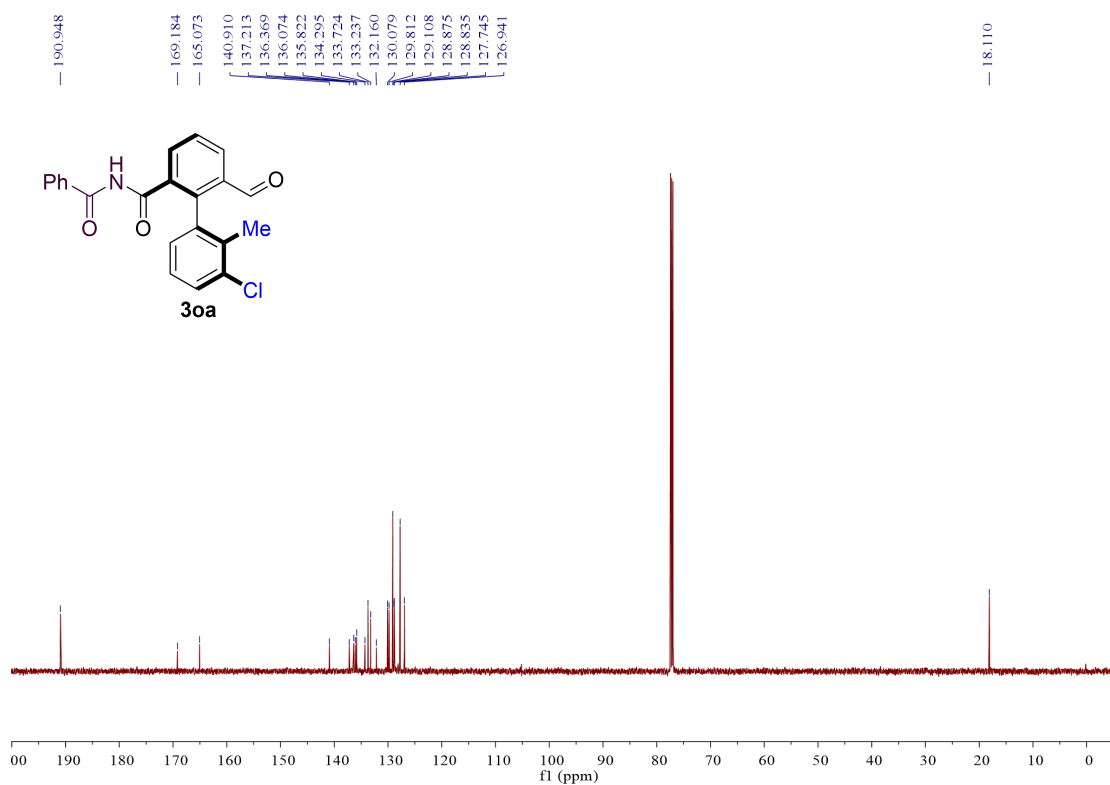
¹H NMR (500 MHz, CDCl₃) spectrum of 3na.



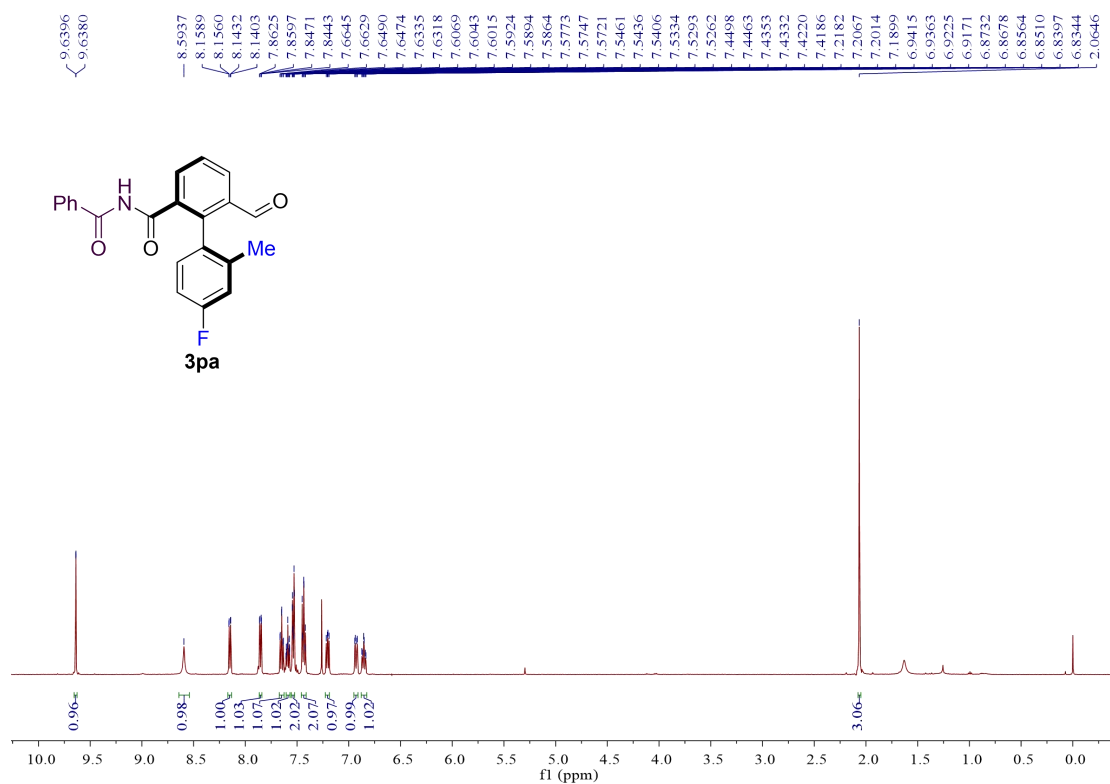
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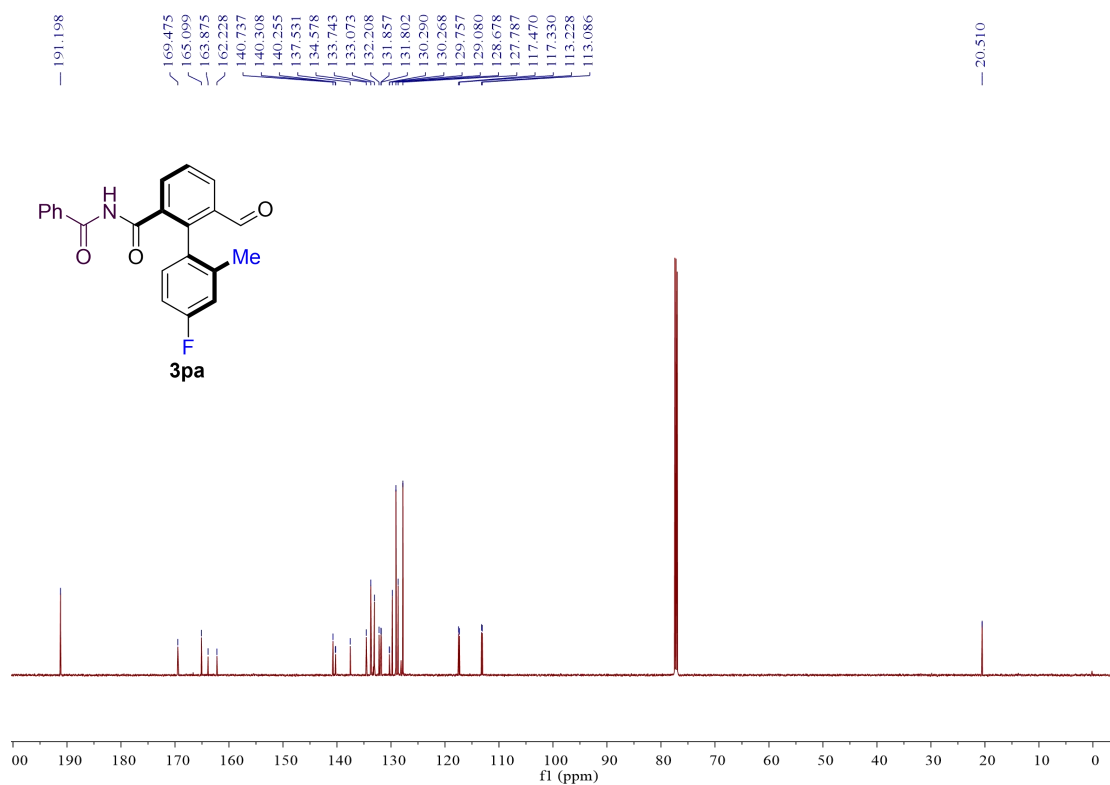
¹H NMR (500 MHz, CDCl₃) spectrum of **30a**.



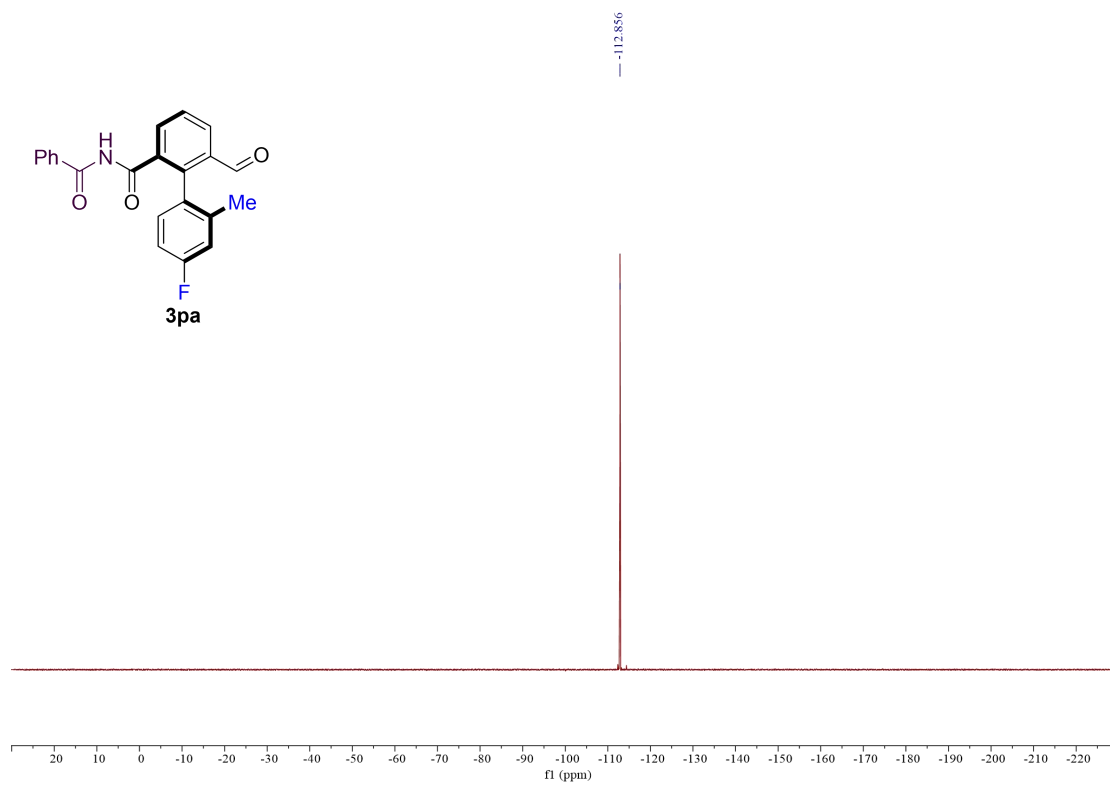
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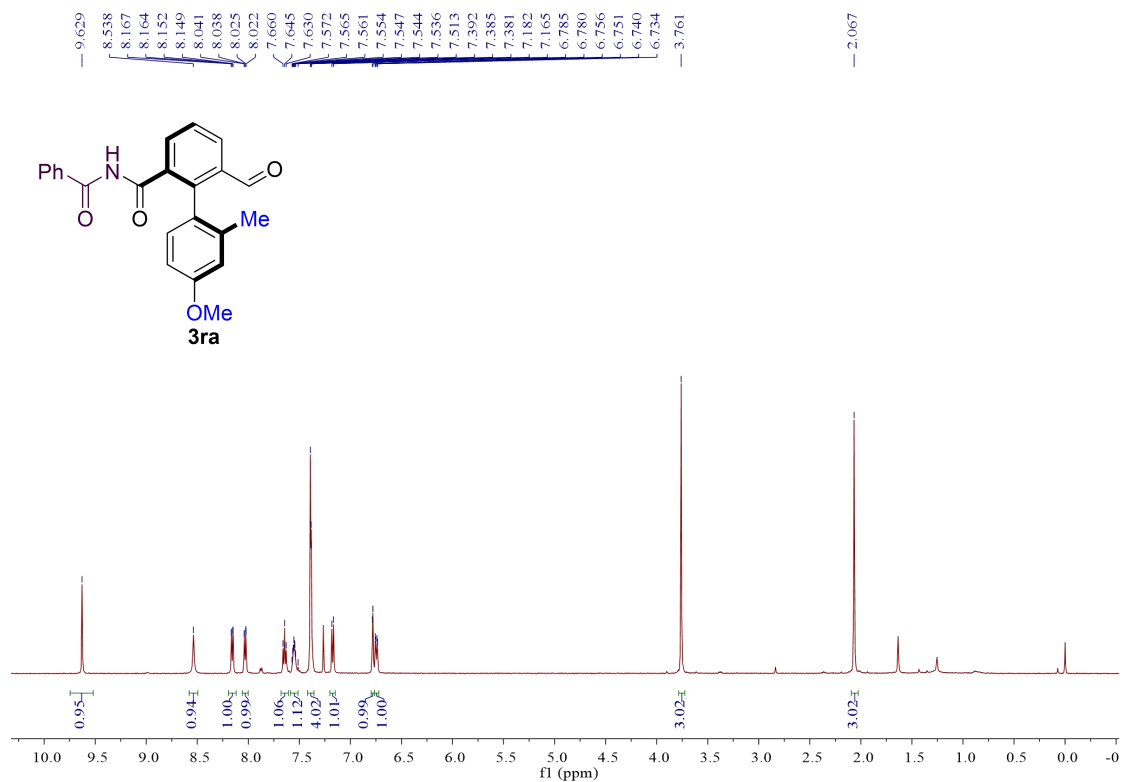
¹H NMR (500 MHz, CDCl₃) spectrum of 3pa.



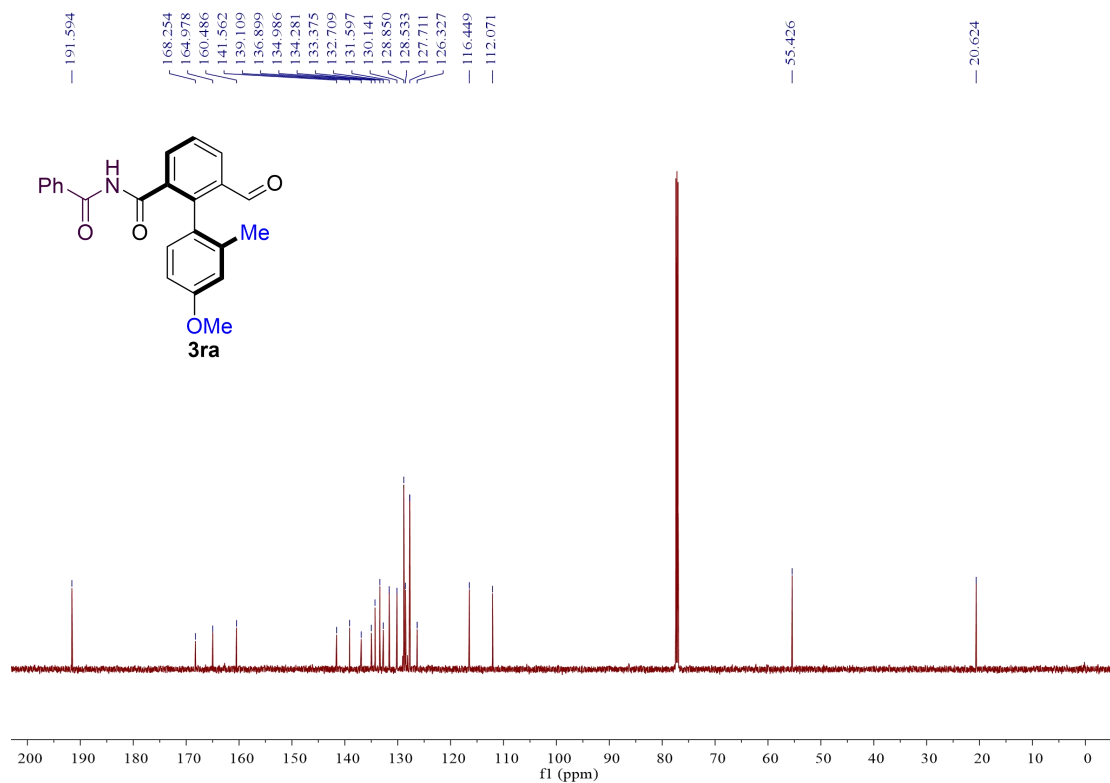
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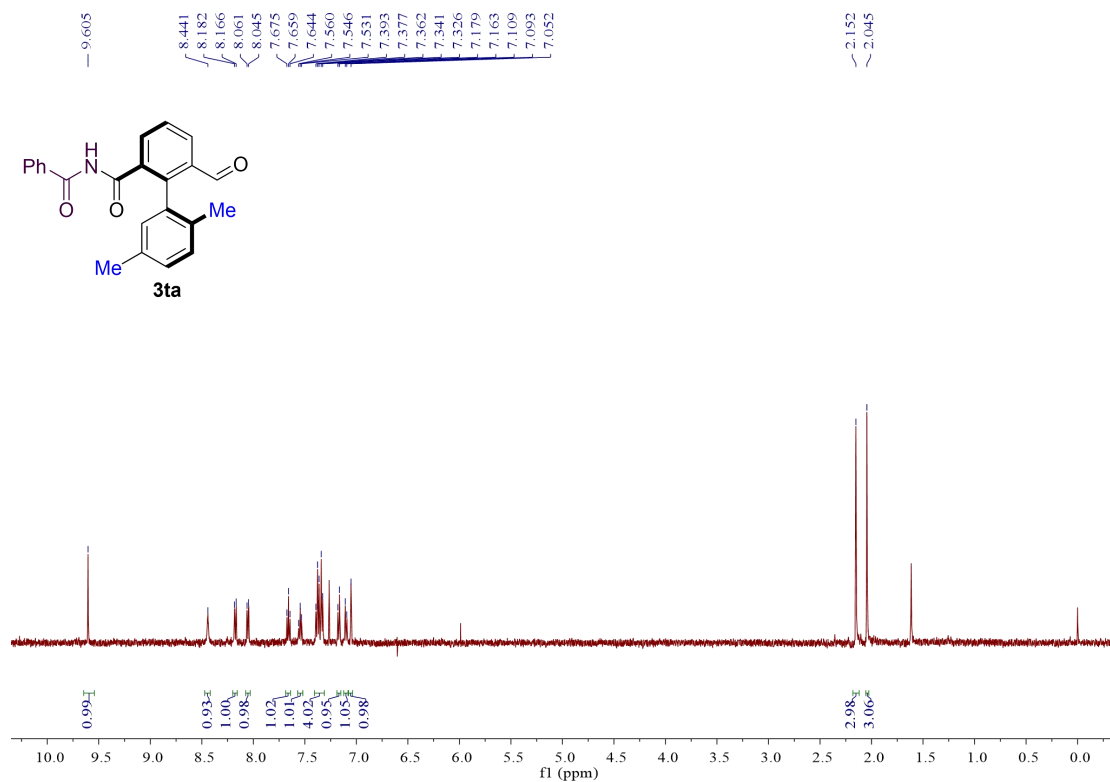
¹⁹F NMR (565 MHz, CDCl₃) spectrum of 3pa.



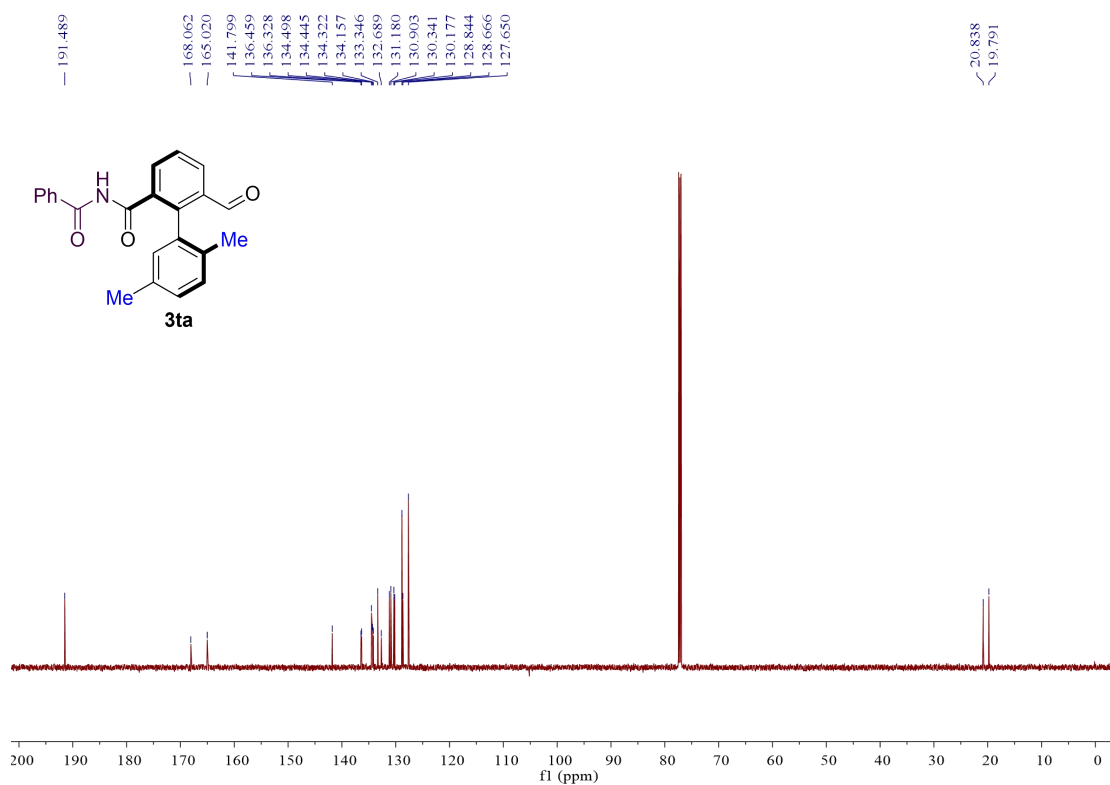
¹H NMR (500 MHz, CDCl₃) spectrum of **3ra.**



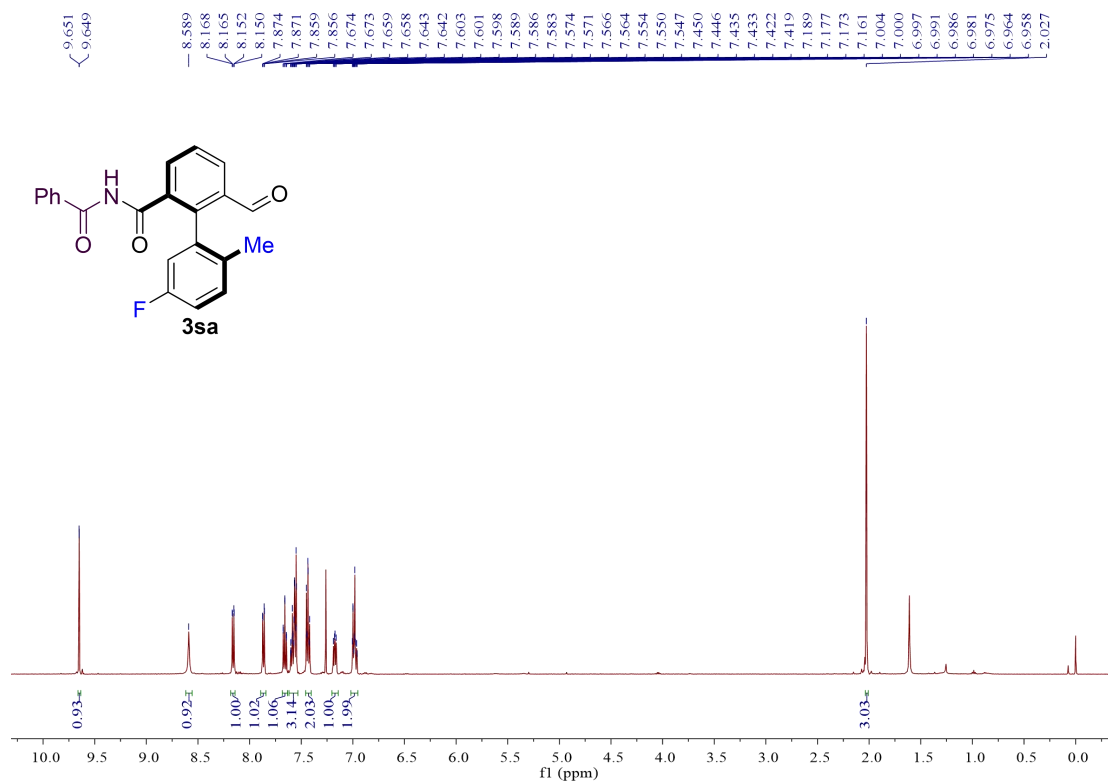
¹³C NMR (150 MHz, CDCl₃) spectrum of **3ra.**



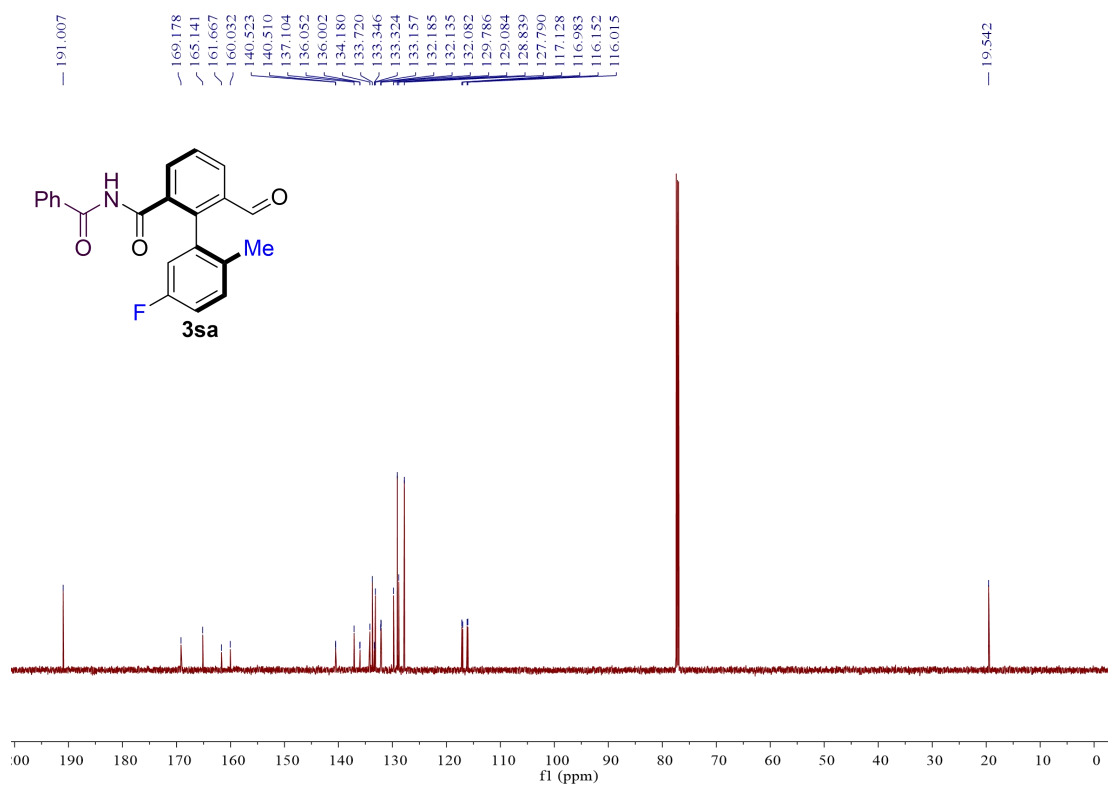
^1H NMR (500 MHz, CDCl_3) spectrum of **3ta**.



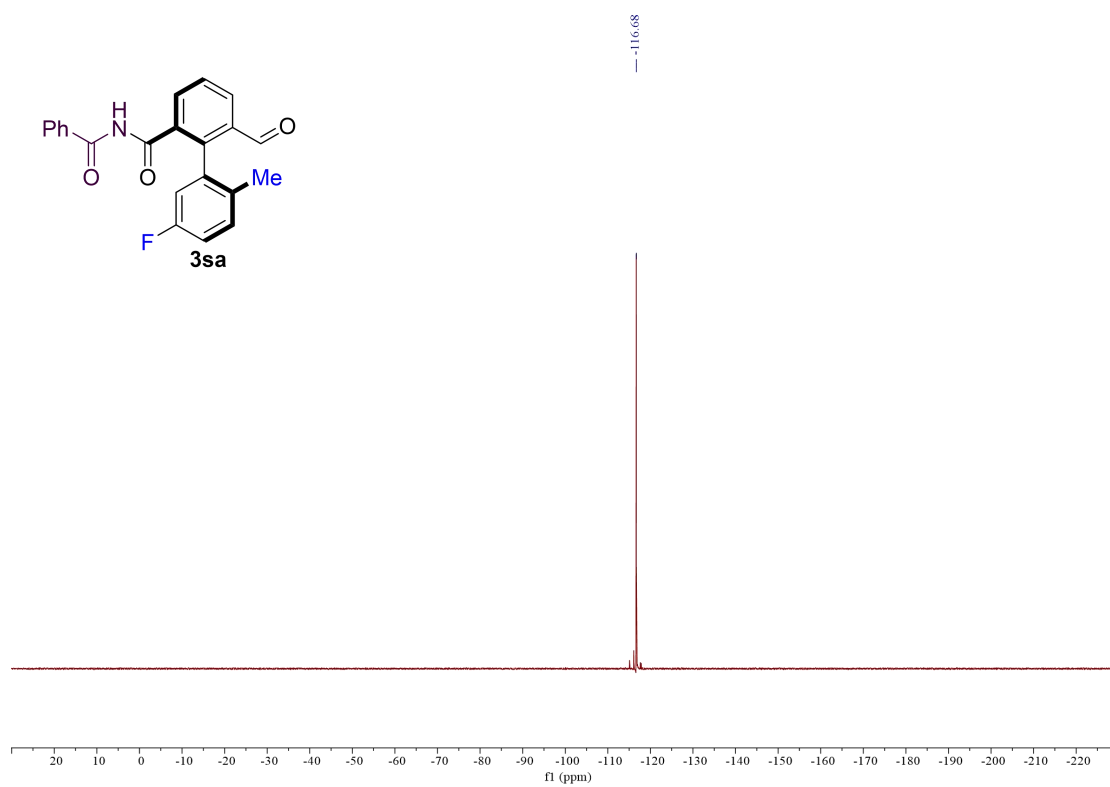
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ta**.



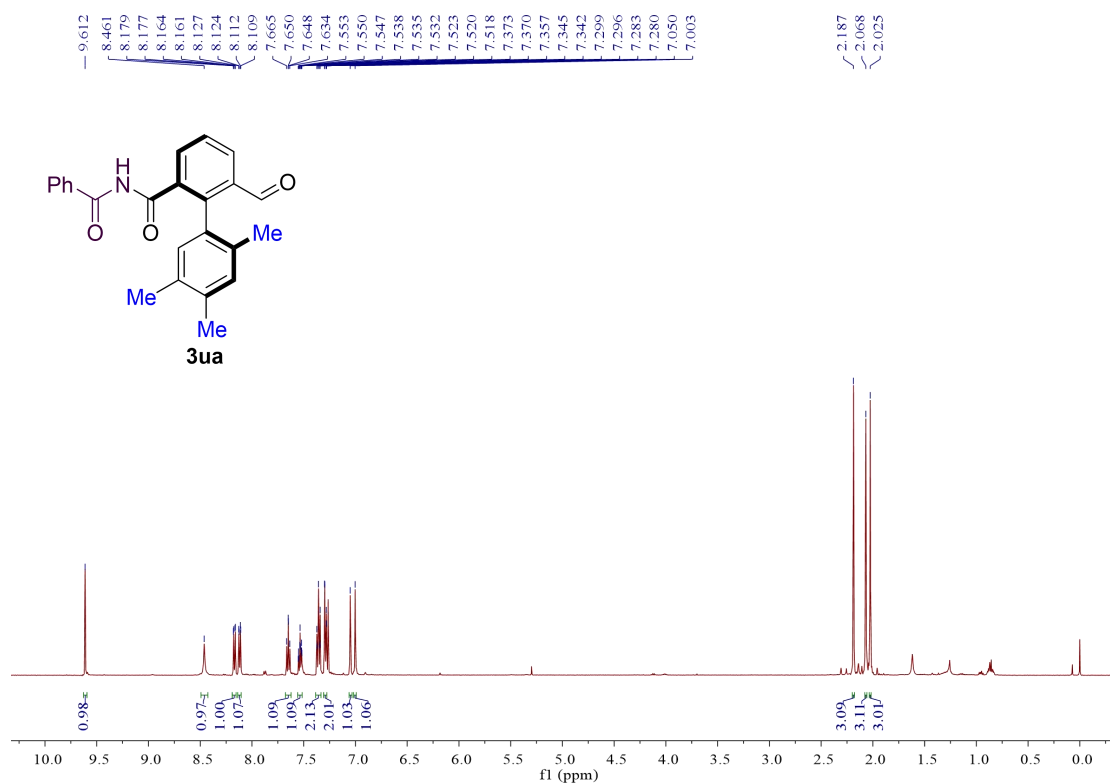
¹H NMR (500 MHz, CDCl₃) spectrum of 3sa.



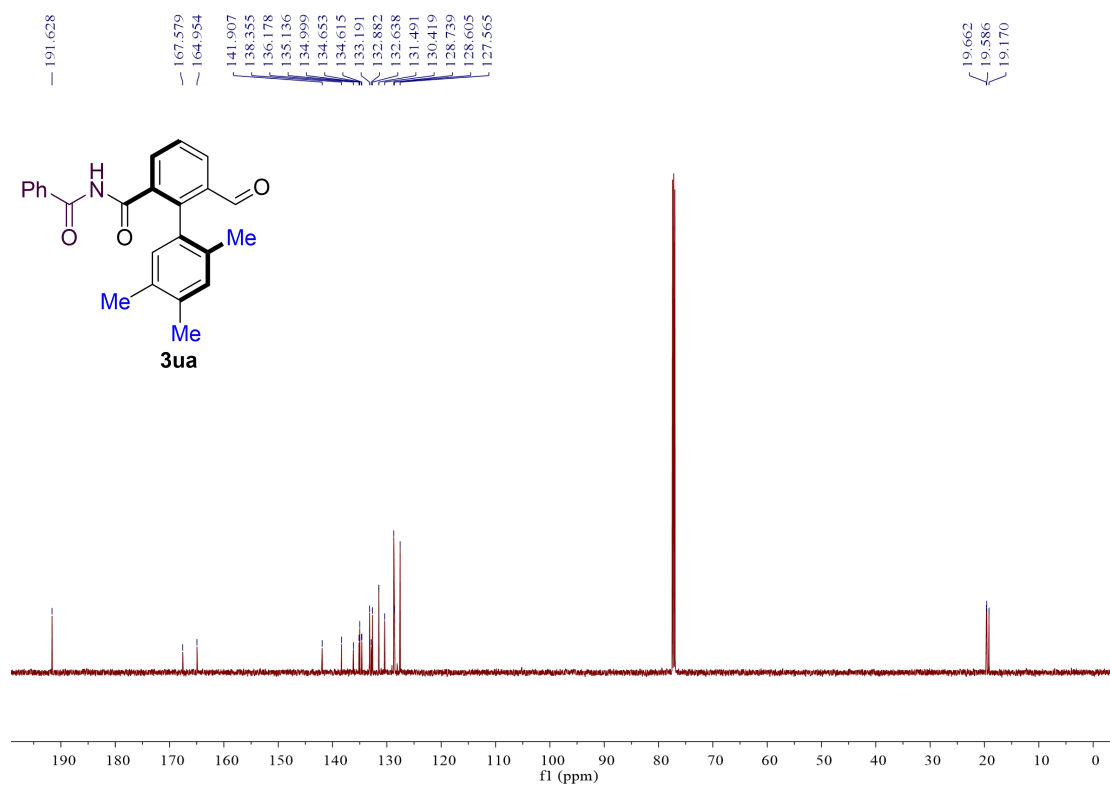
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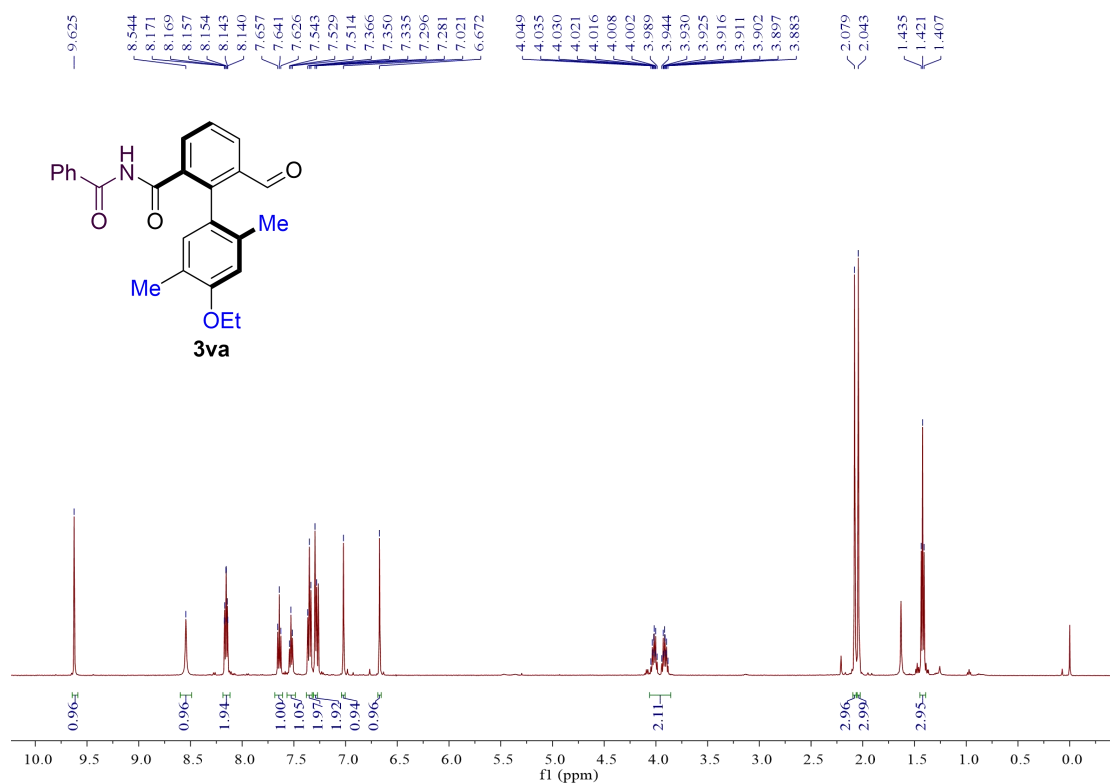
^{19}F NMR (565 MHz, CDCl_3) spectrum of 3sa.



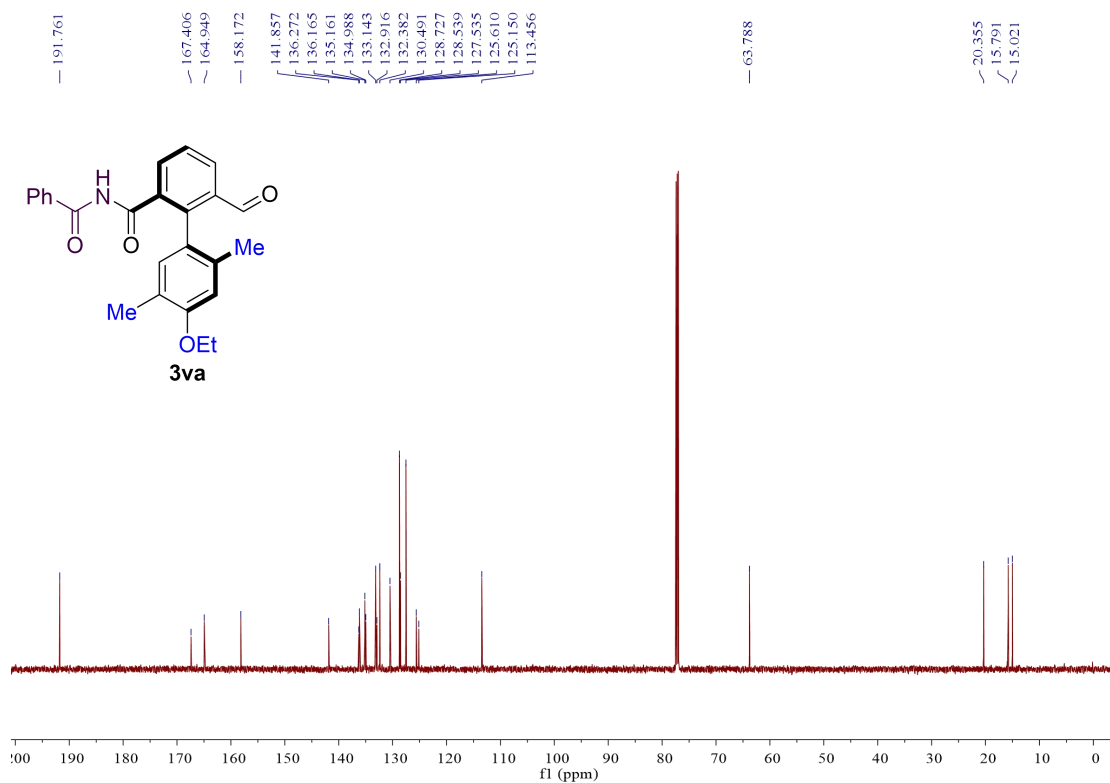
¹H NMR (500 MHz, CDCl₃) spectrum of 3ua.



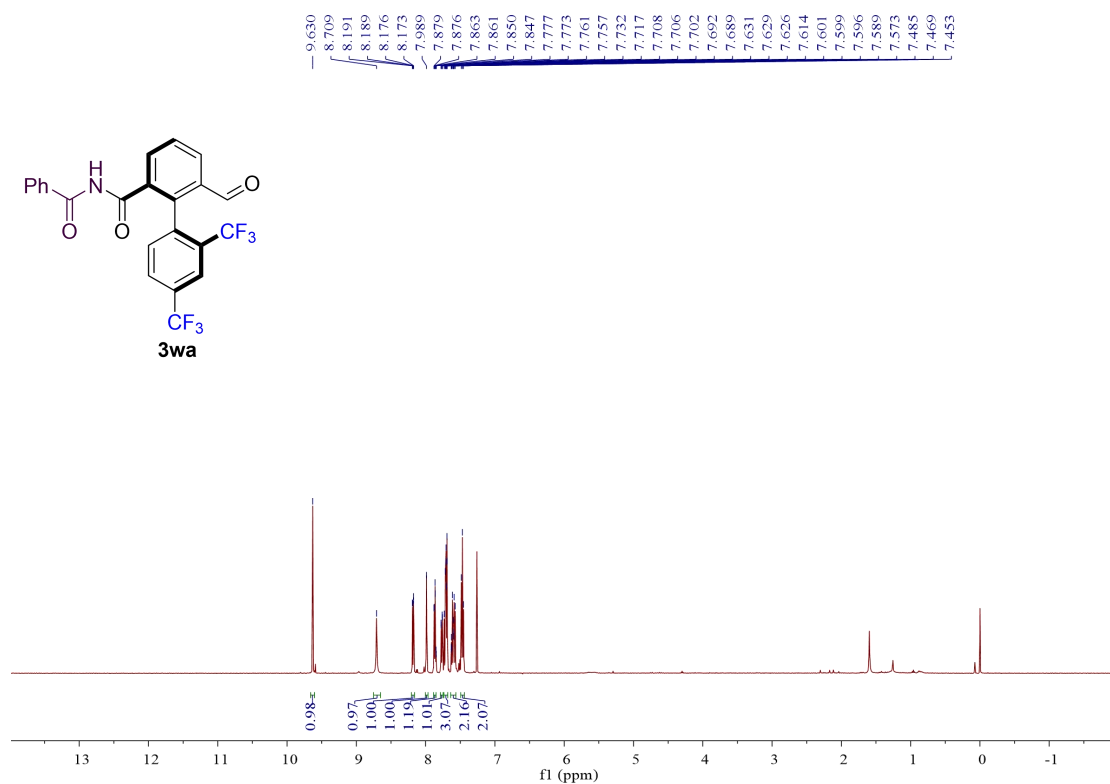
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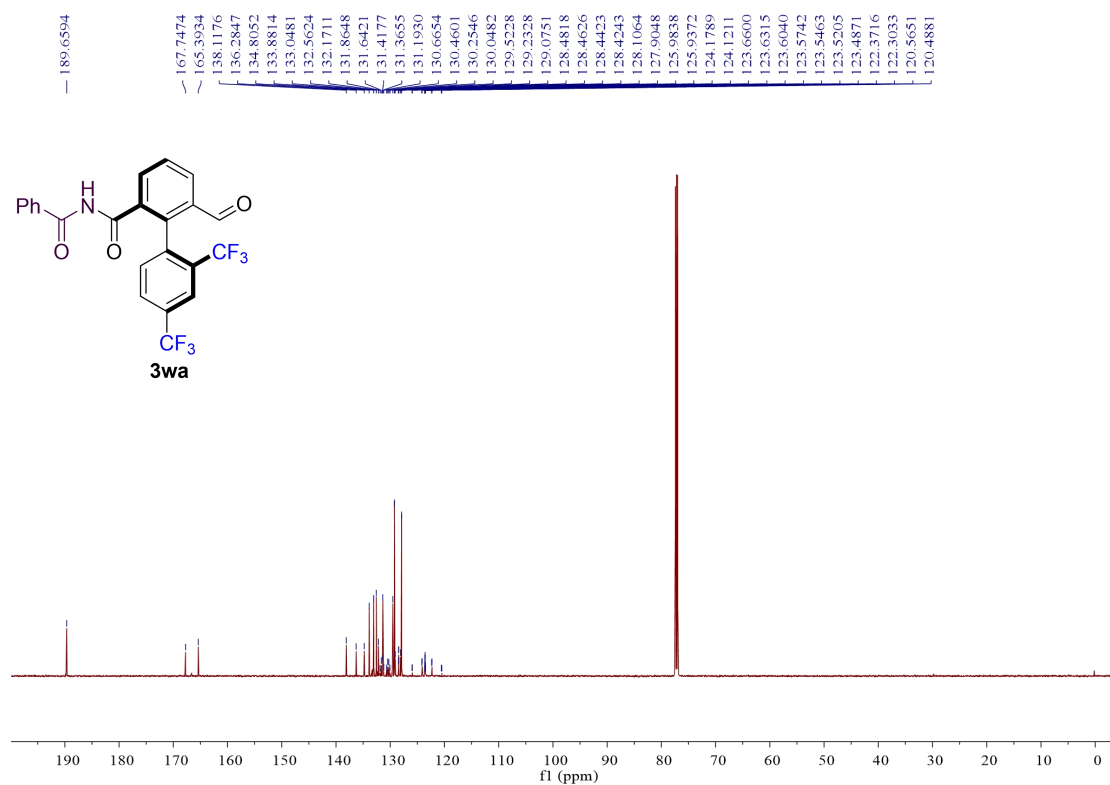
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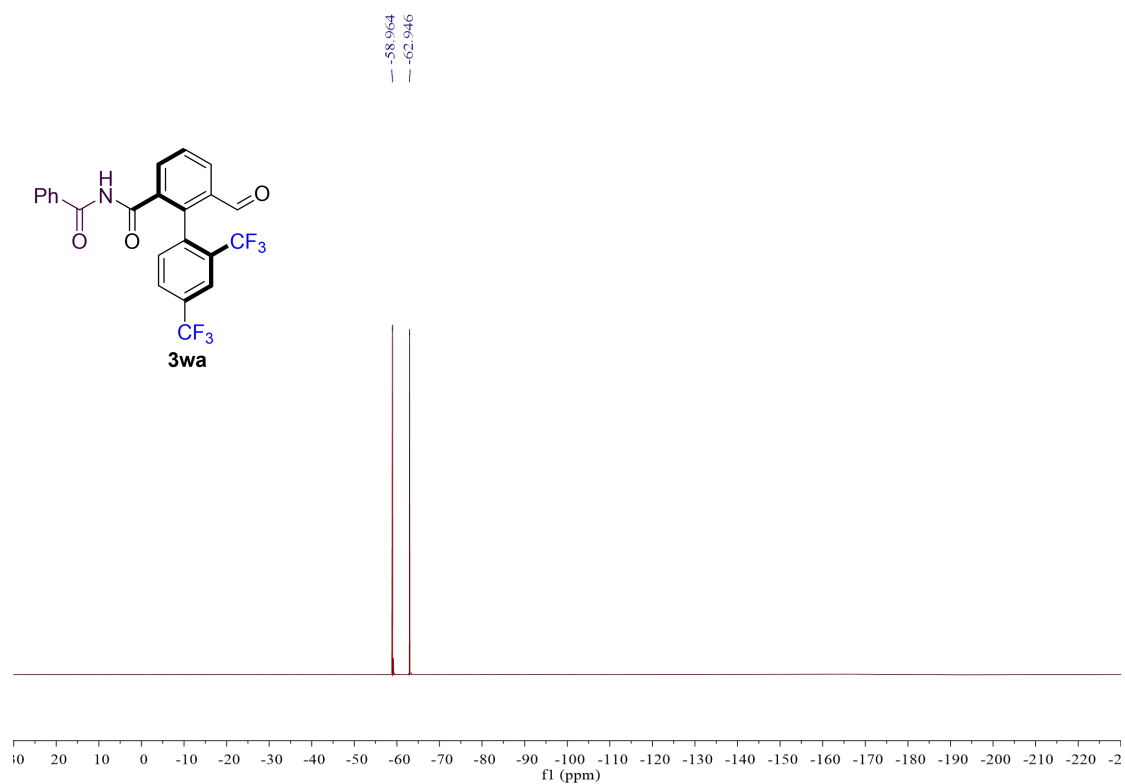
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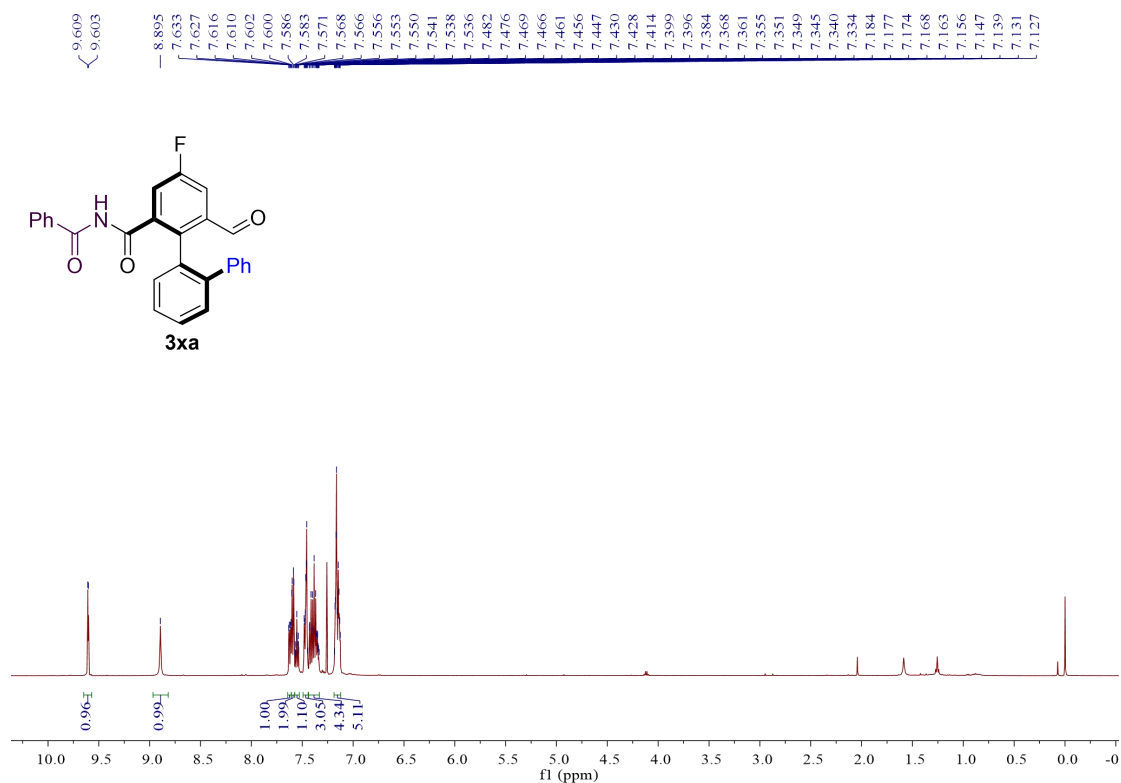


^1H NMR (500 MHz, CDCl_3) spectrum of **3wa**.

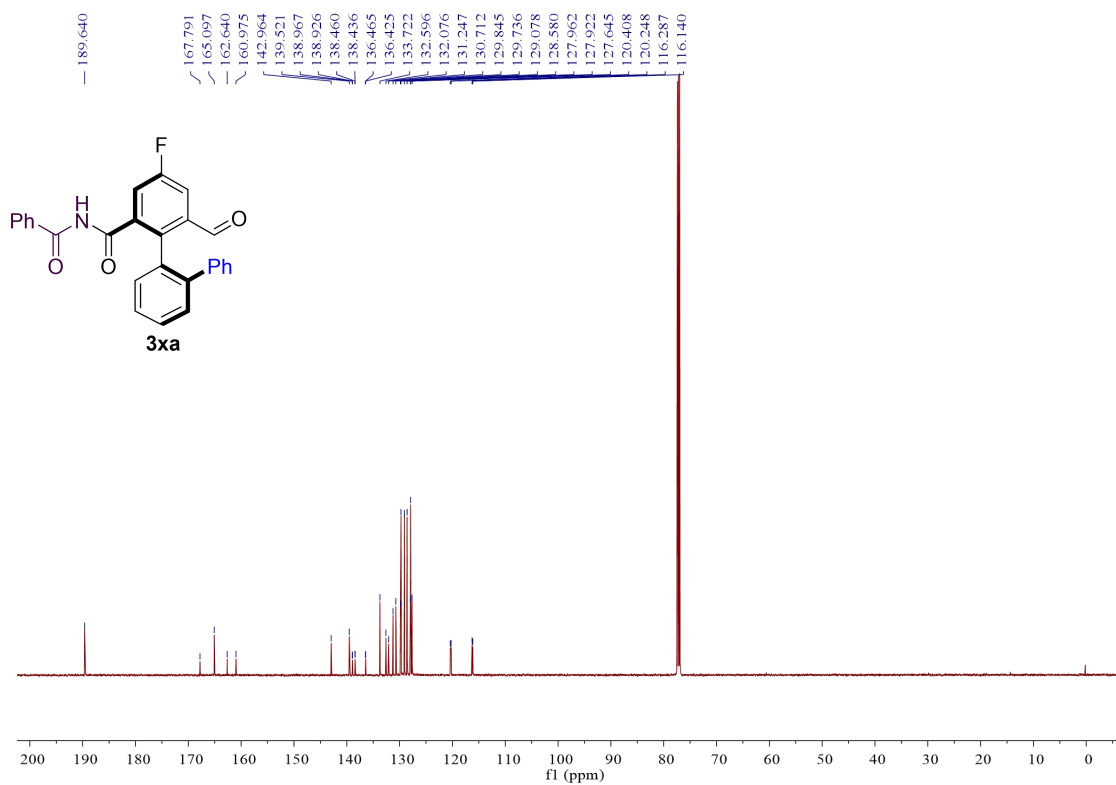


^{13}C NMR (150 MHz, CDCl_3) spectrum of **3wa**.

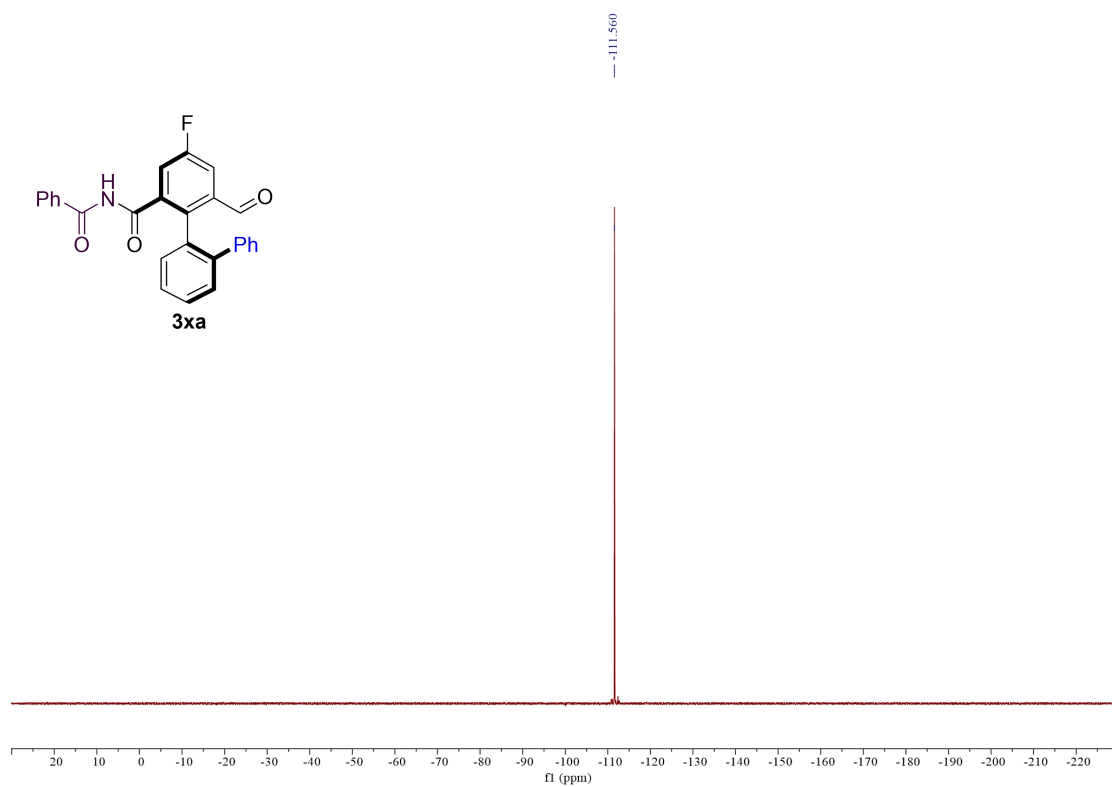




¹H NMR (500 MHz, CDCl₃) spectrum of 3xa.

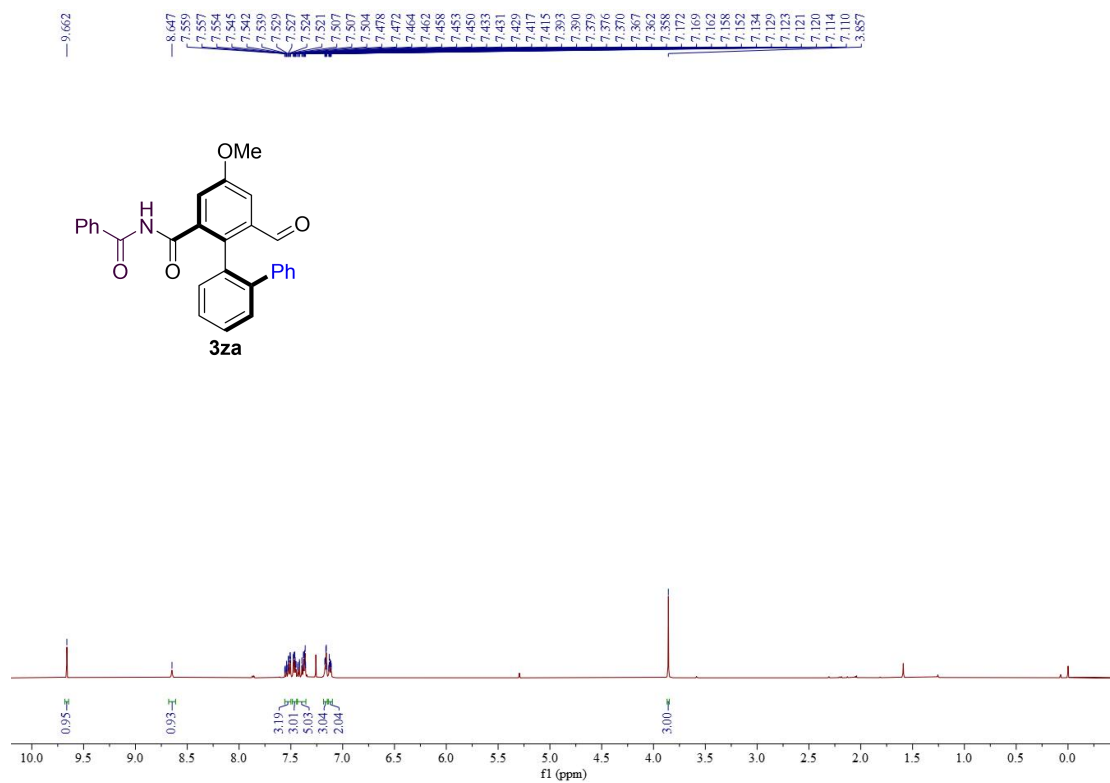


¹³C NMR (150 MHz, CDCl₃) spectrum of 3xa.

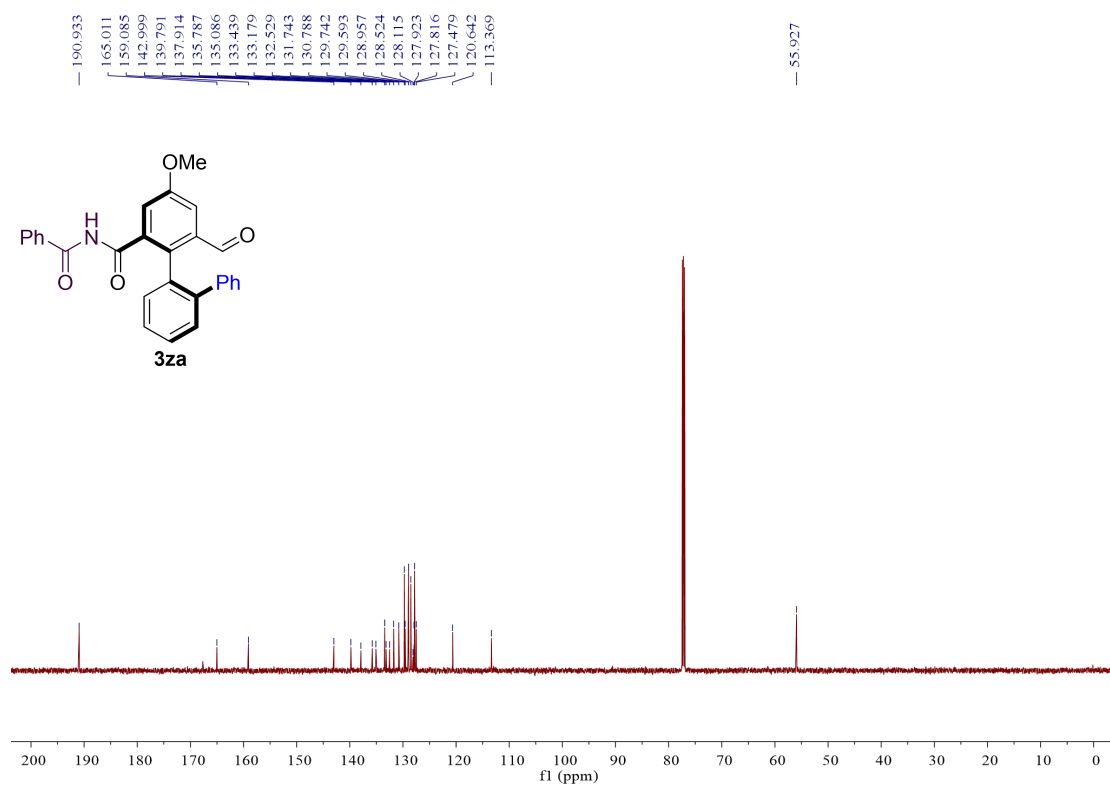


^{19}F NMR (565 MHz, CDCl_3) spectrum of **3xa.**

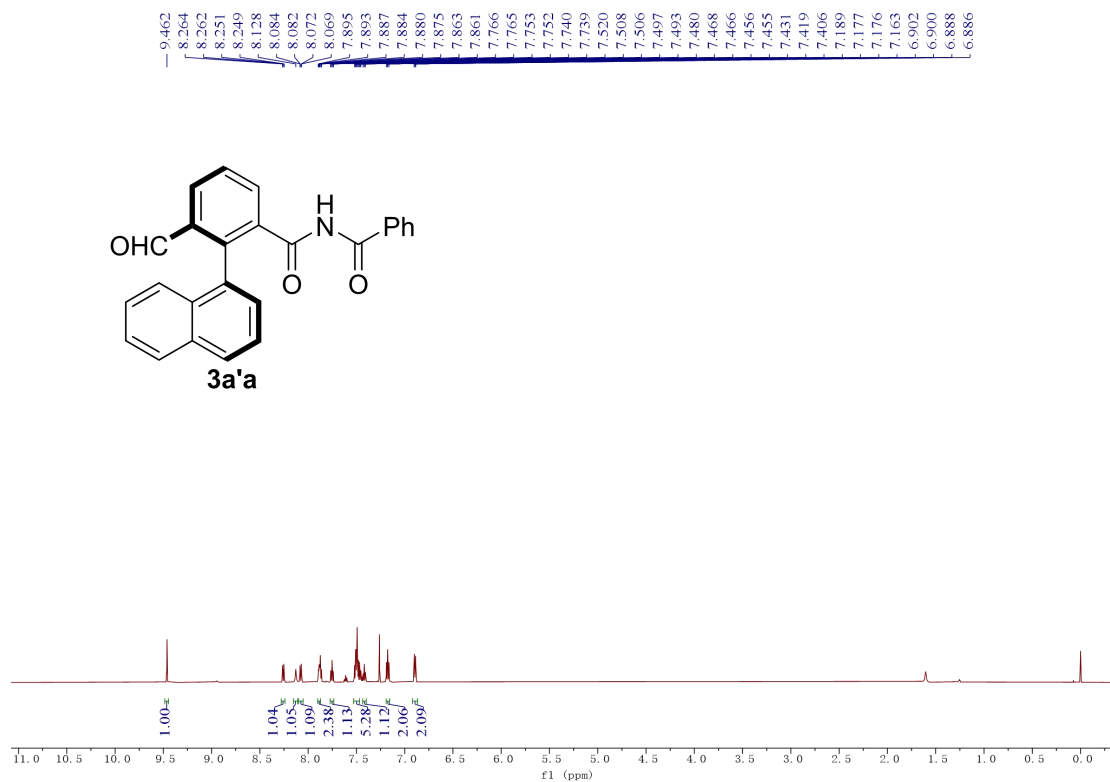




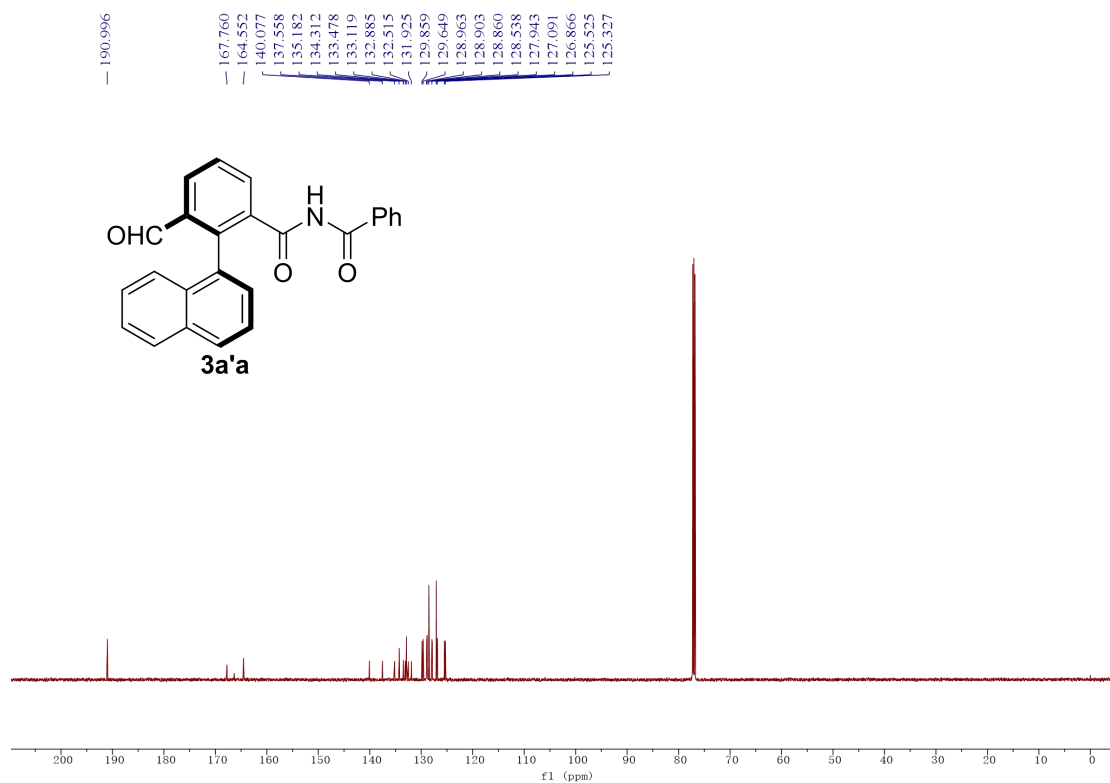
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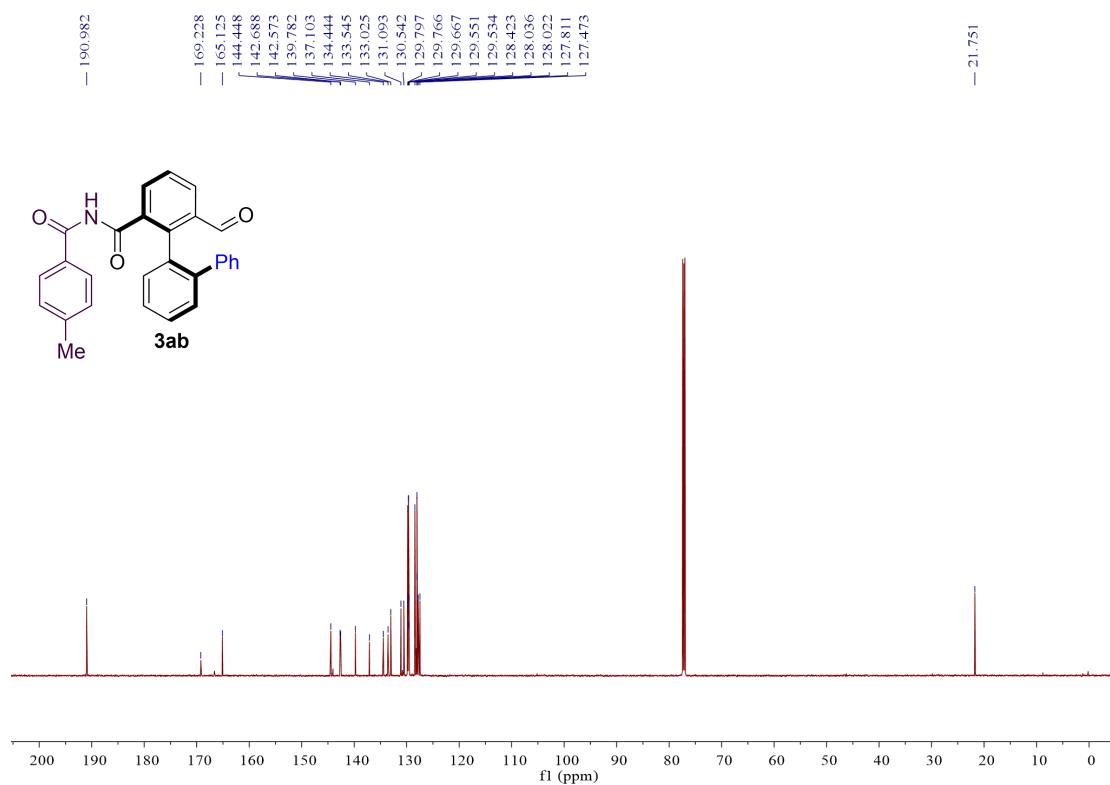
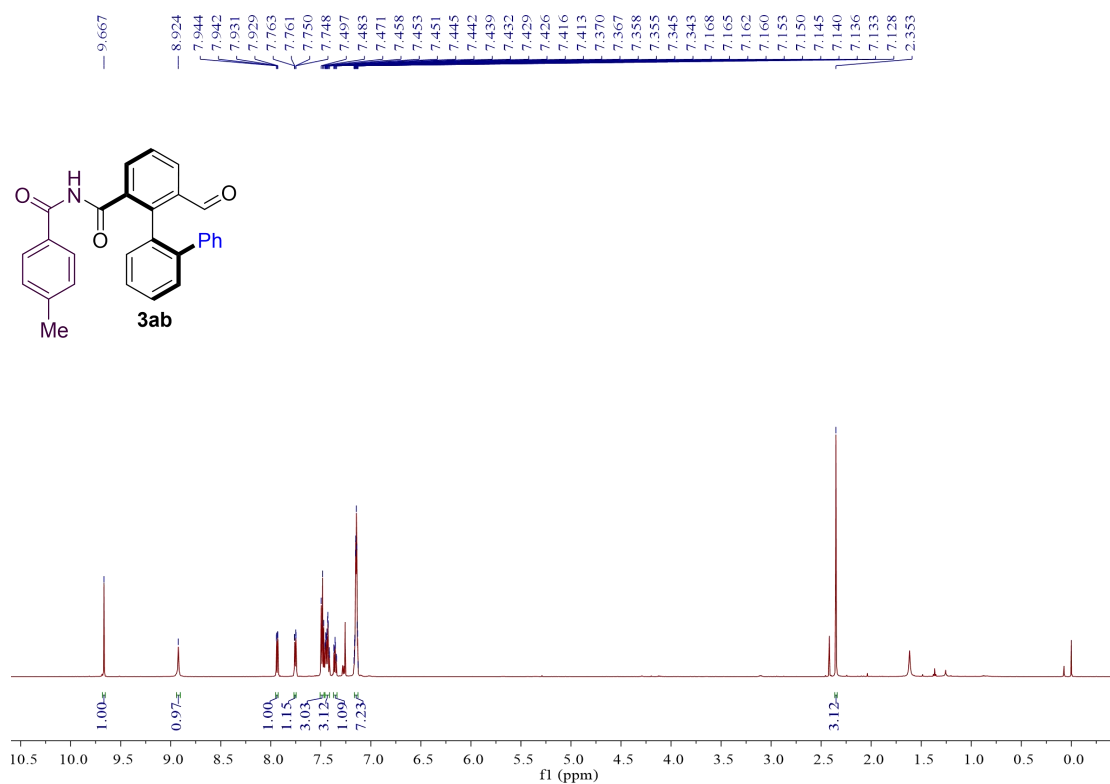
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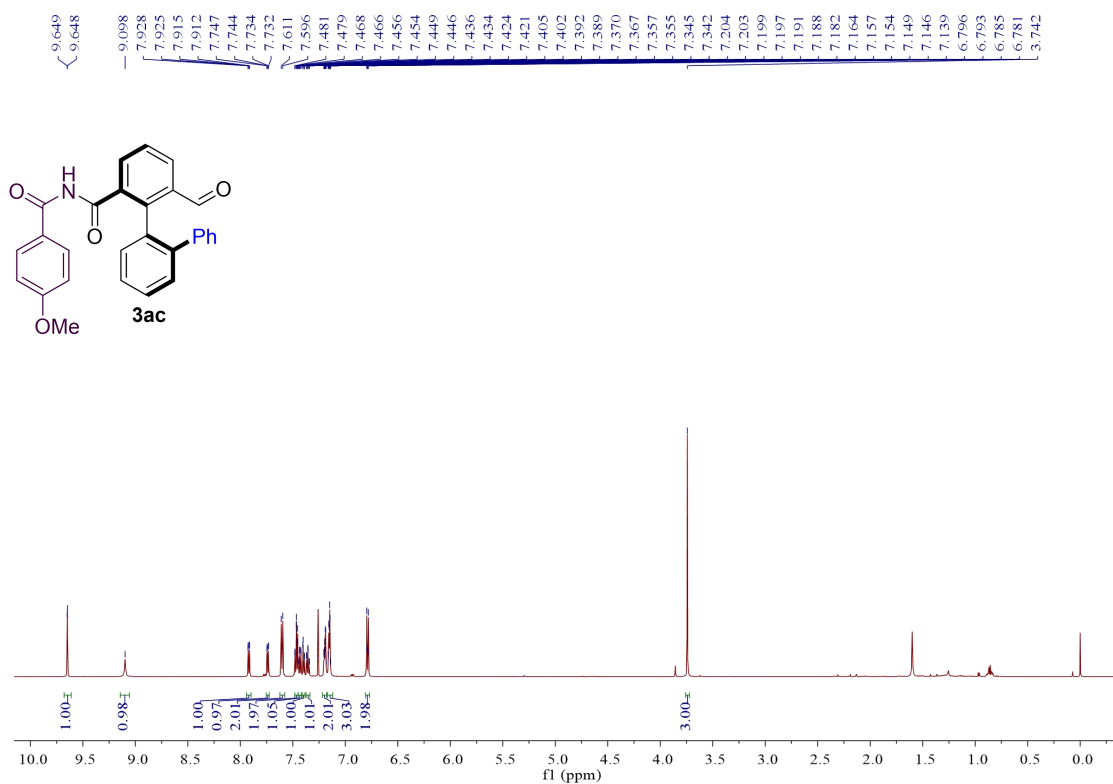


¹H NMR (600 MHz, CDCl₃) spectrum of 3a'a.

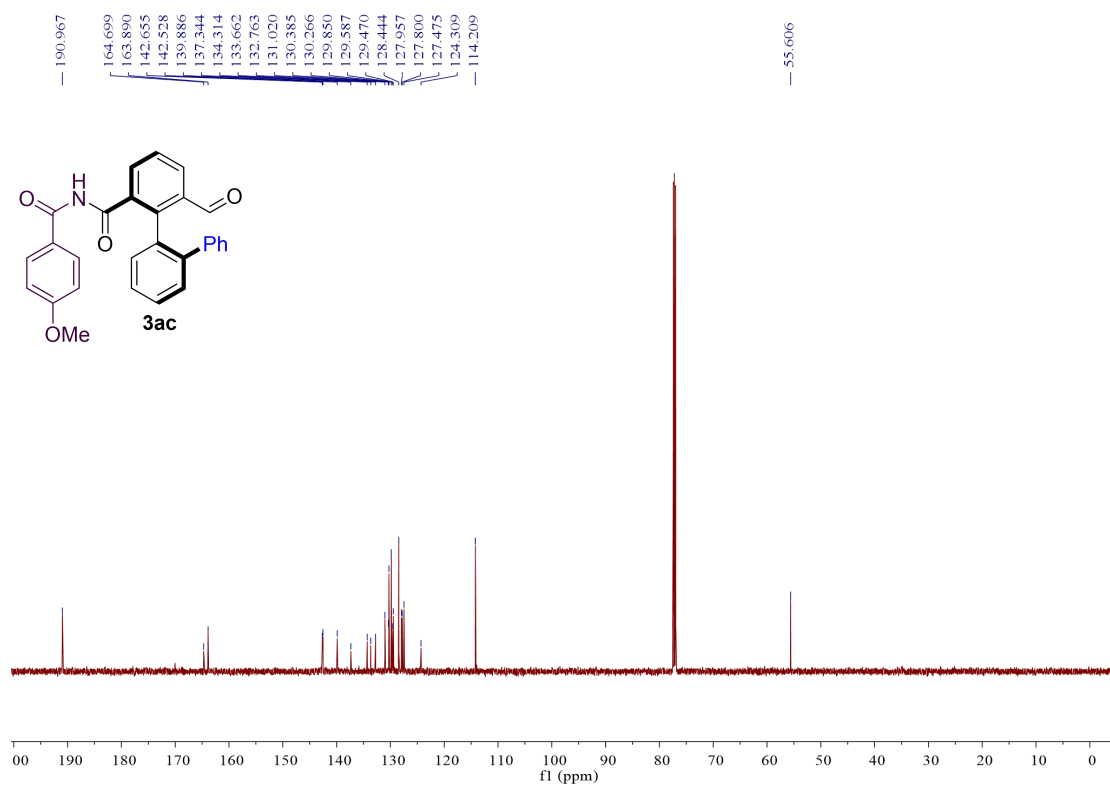


¹³C NMR (150 MHz, CDCl₃) spectrum of 3a'a.

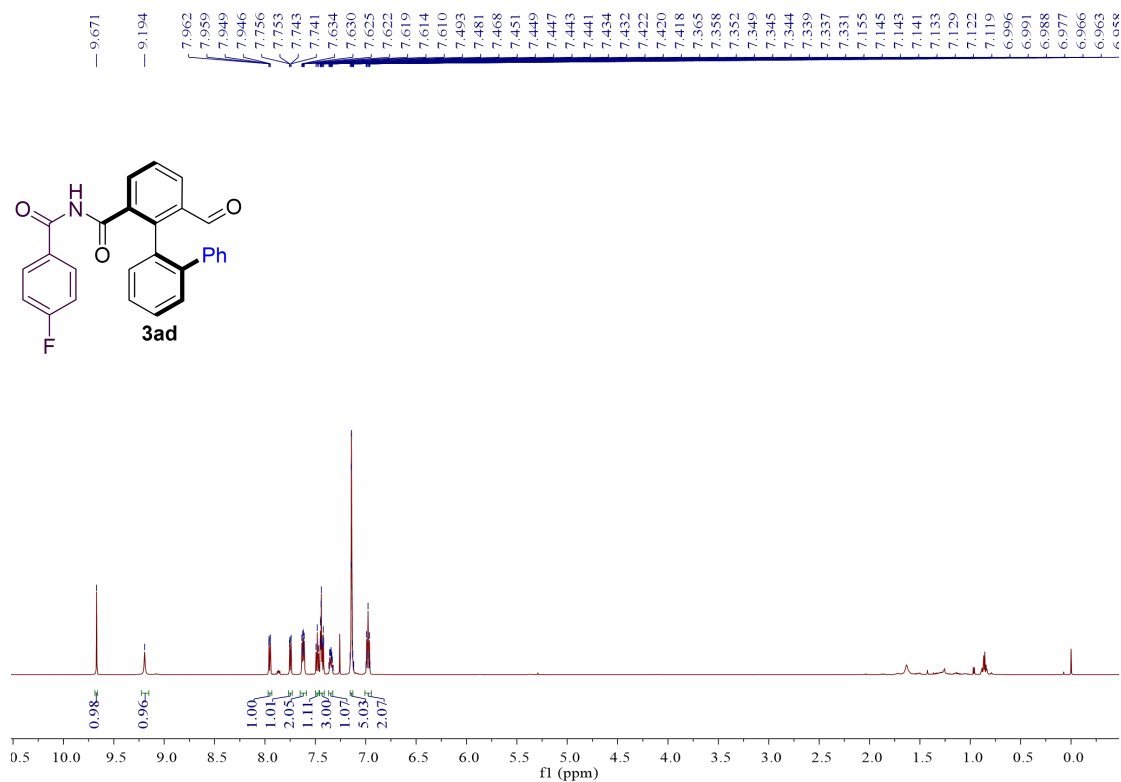




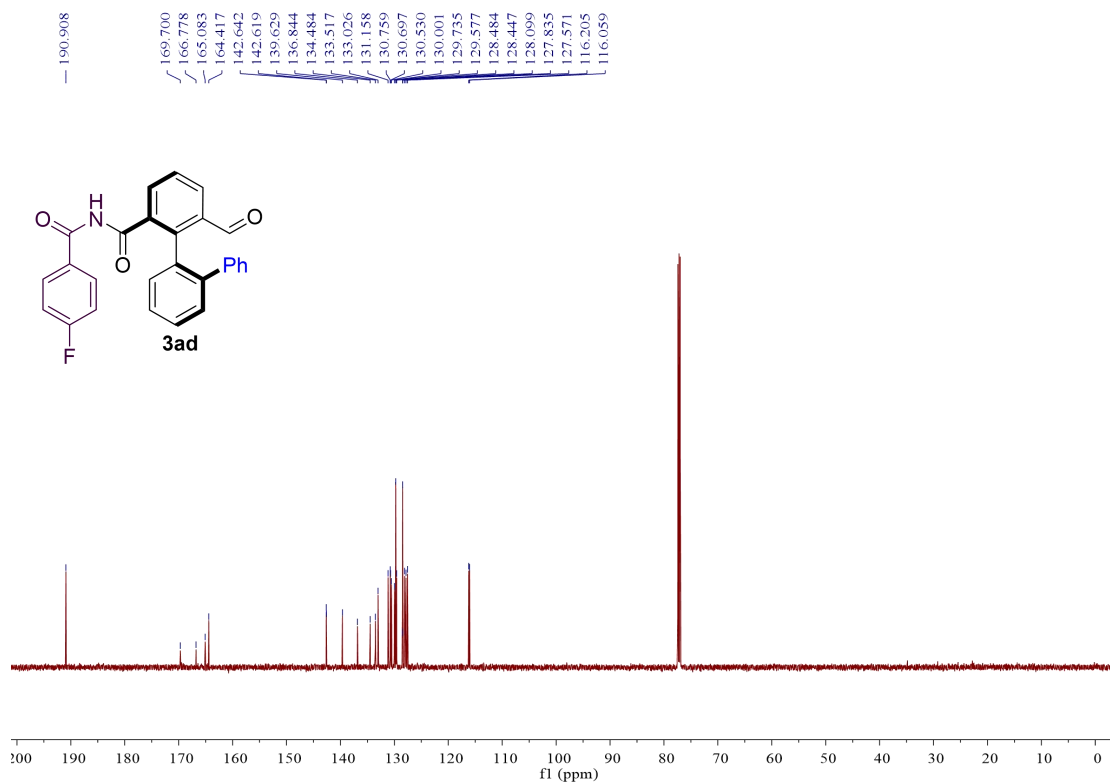
^1H NMR (600 MHz, CDCl_3) spectrum of **3ac**.



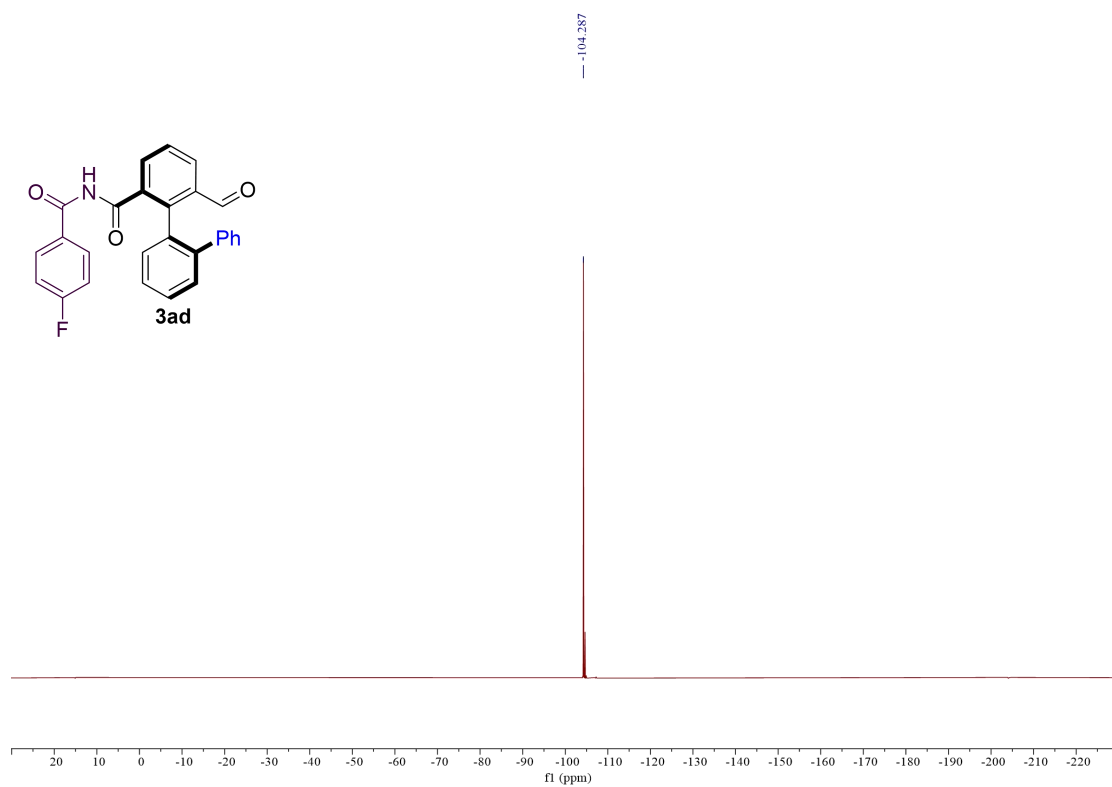
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ac**.



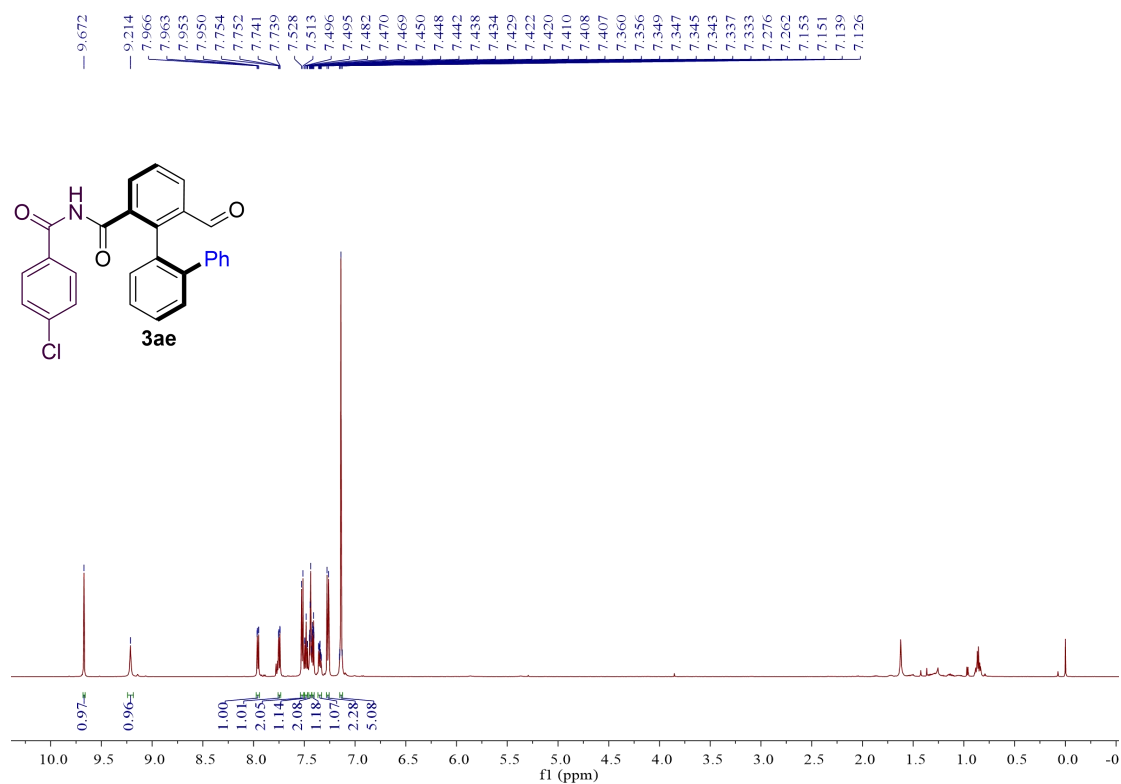
¹H NMR (600 MHz, CDCl₃) spectrum of 3ad.



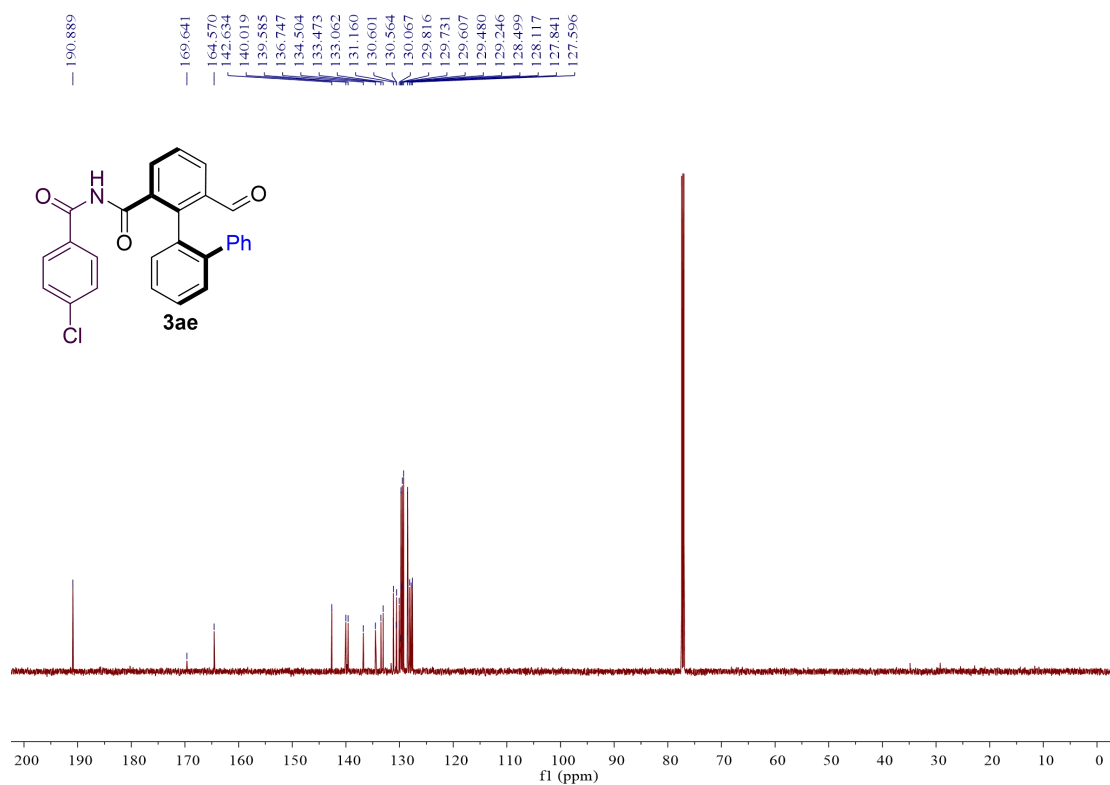
¹³C NMR (150 MHz, CDCl₃) spectrum of 3ad.



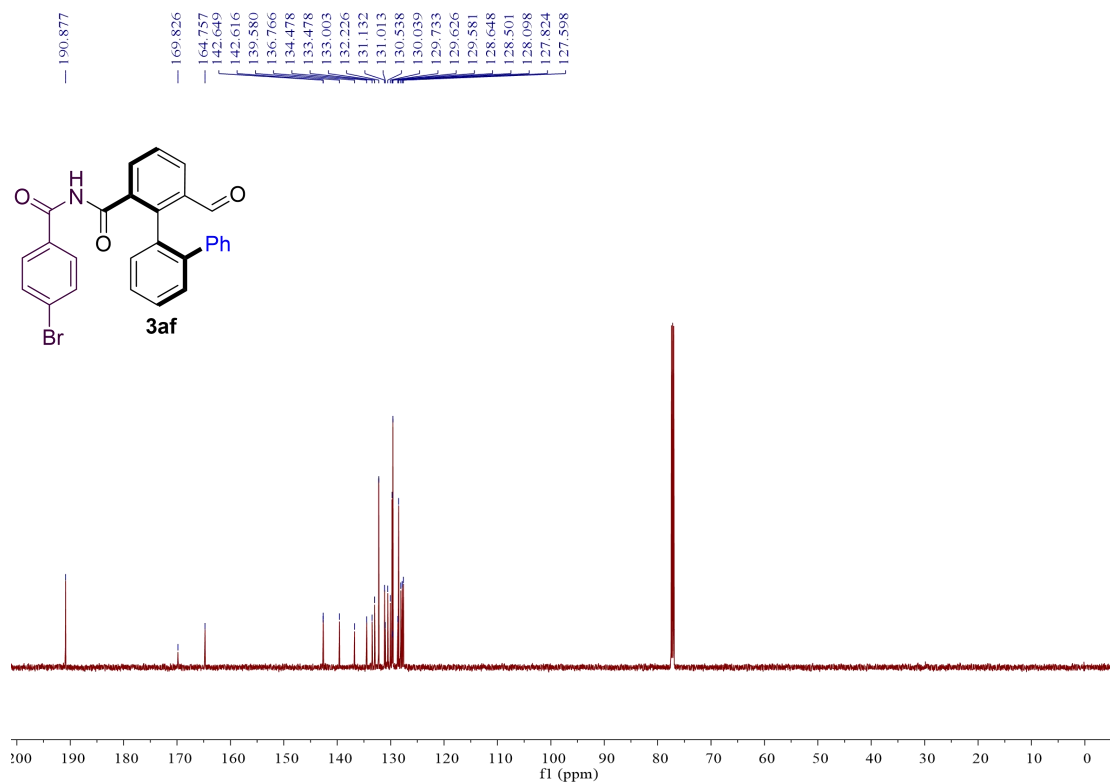
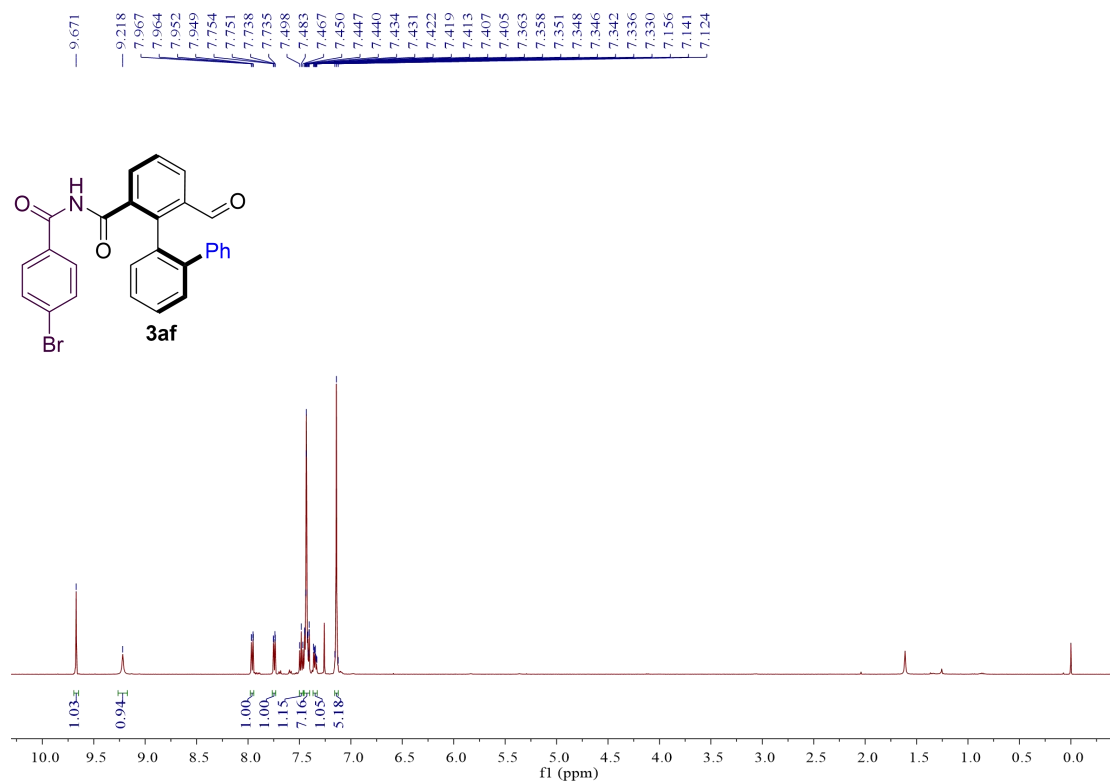
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3ad.**

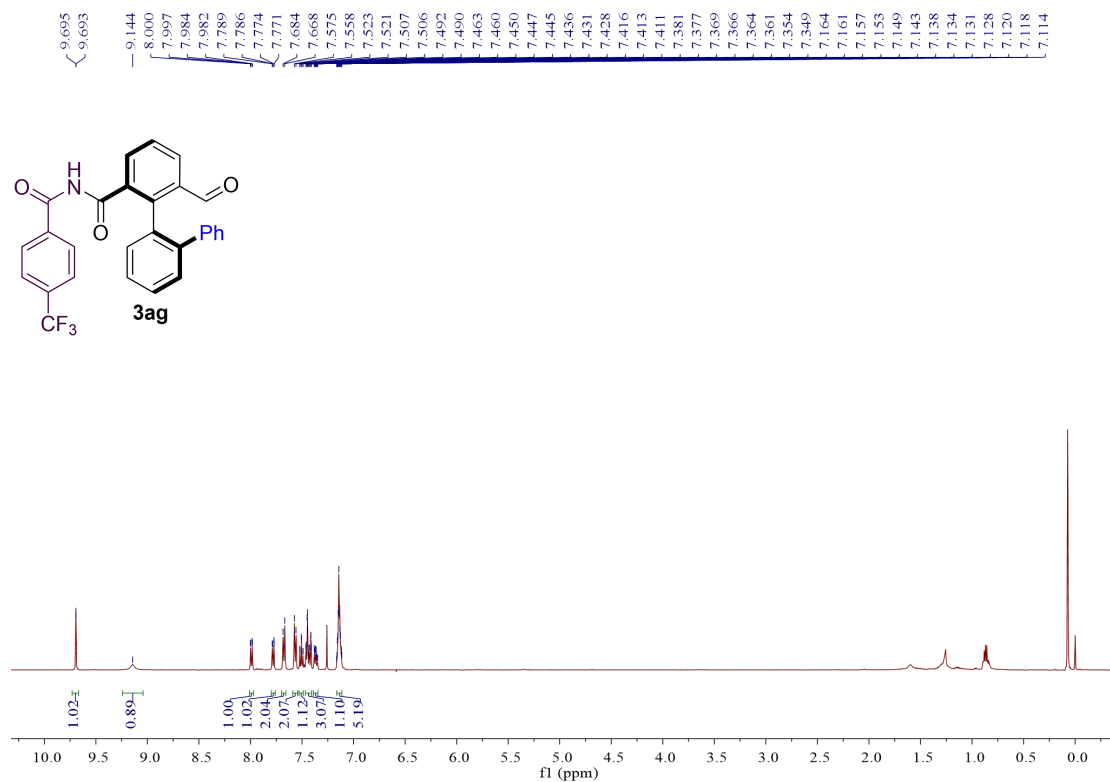


¹H NMR (600 MHz, CDCl₃) spectrum of 3ae.

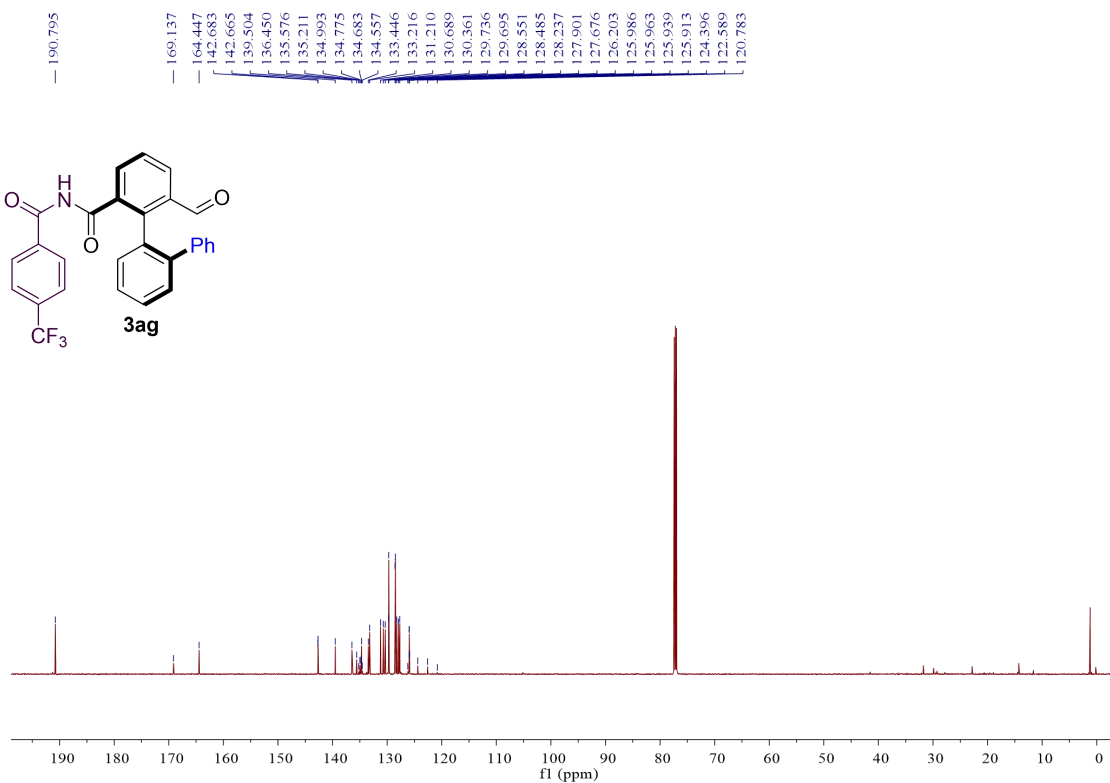


¹³C NMR (150 MHz, CDCl₃) spectrum of 3ae.

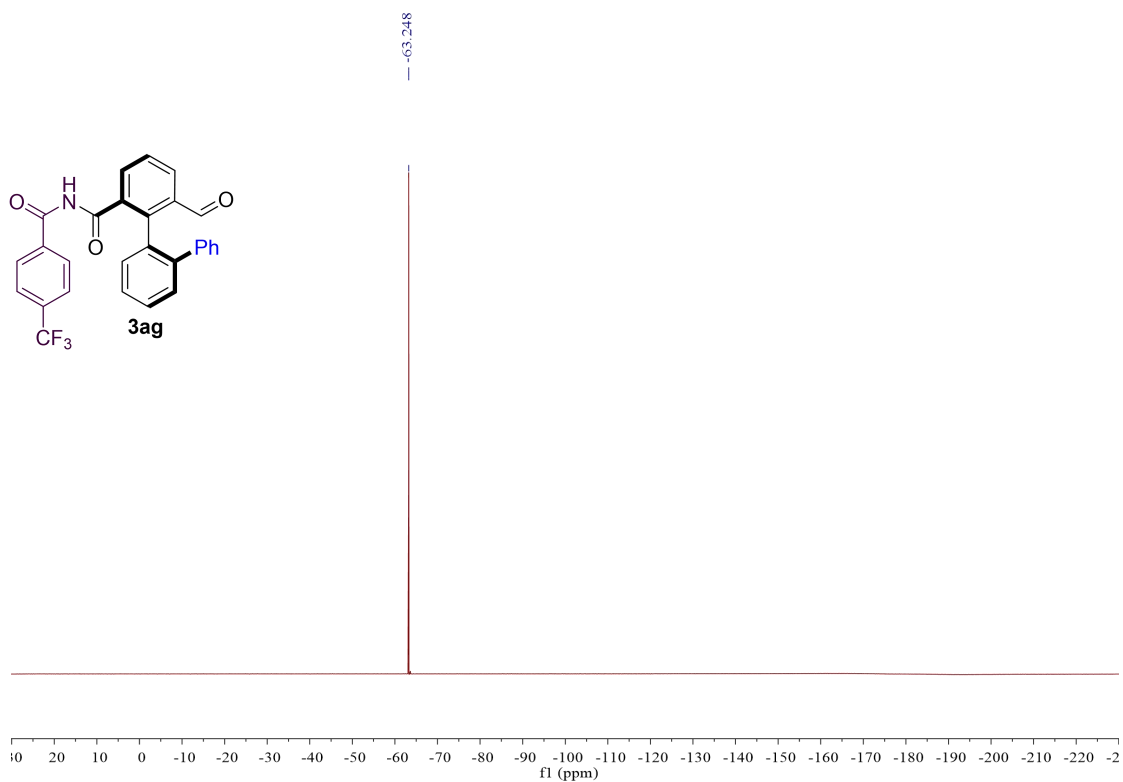




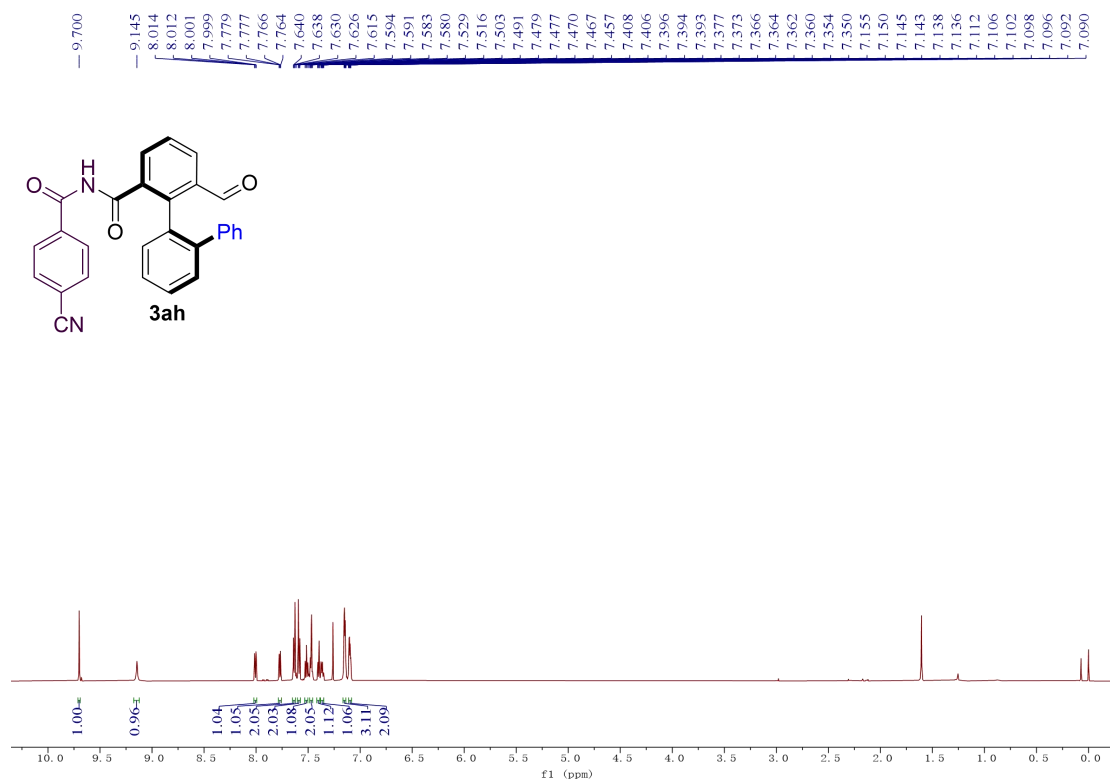
¹H NMR (500 MHz, CDCl₃) spectrum of **3ag**.



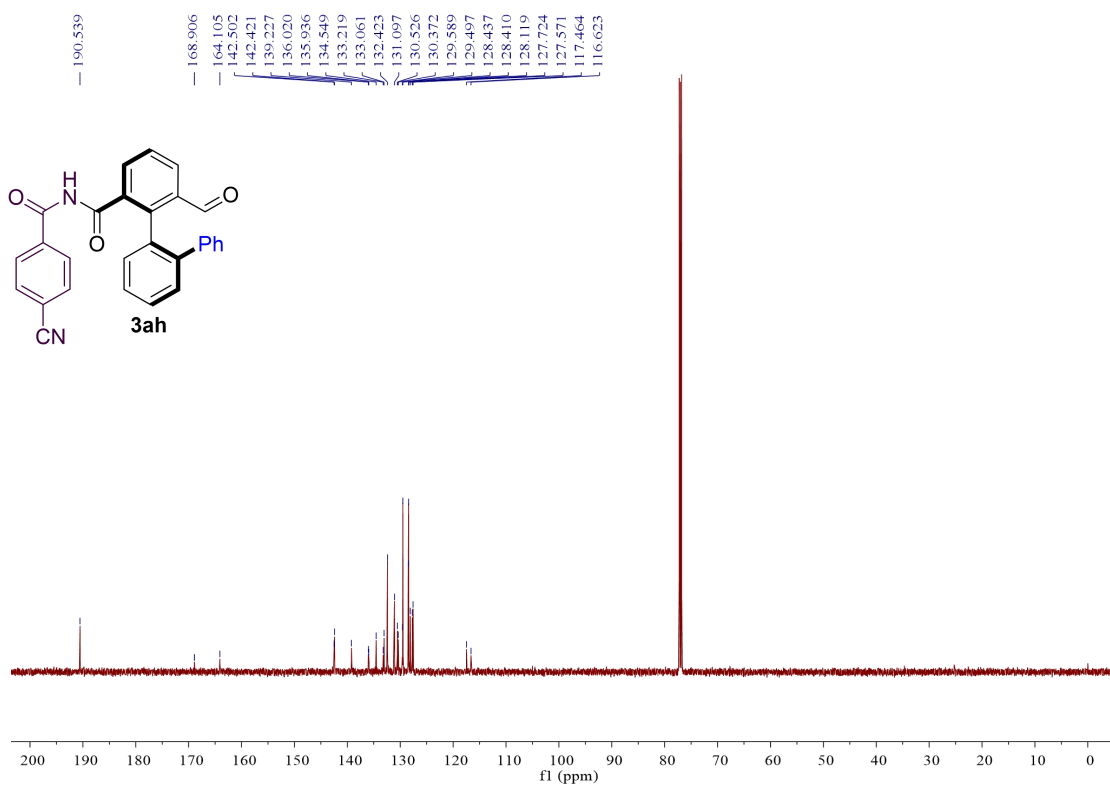
¹³C NMR (150 MHz, CDCl₃) spectrum of **3ag**.



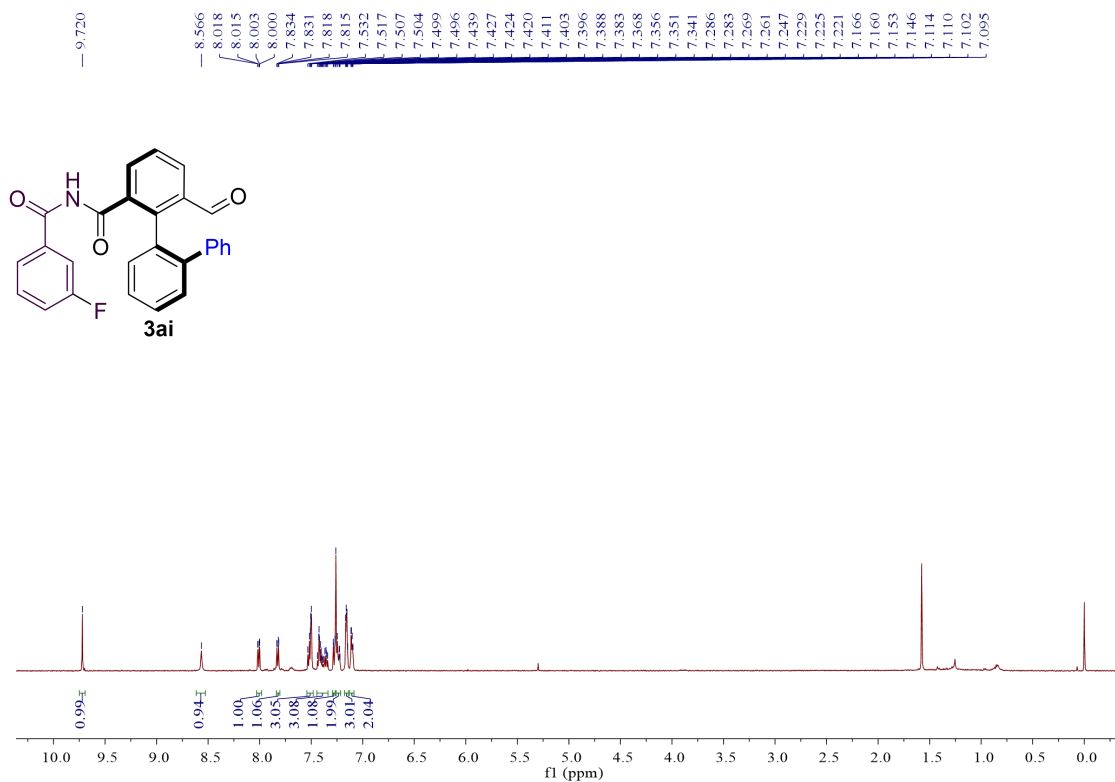
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3ag.**



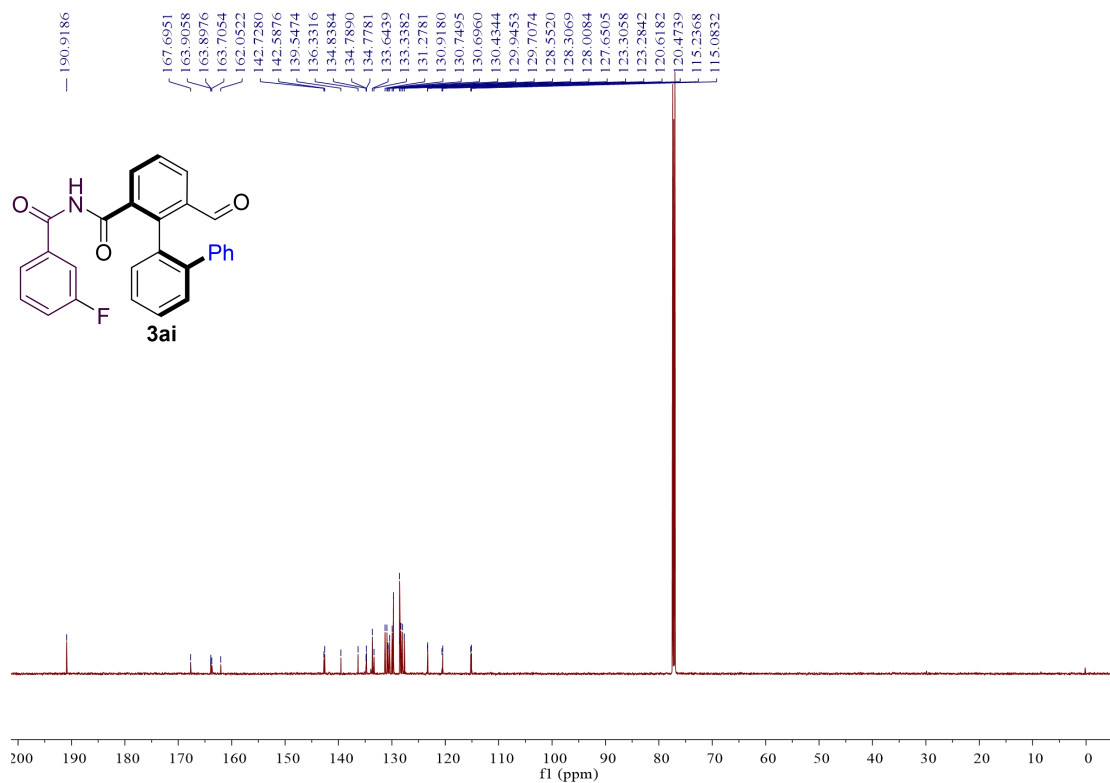
¹H NMR (500 MHz, CDCl₃) spectrum of 3ah.



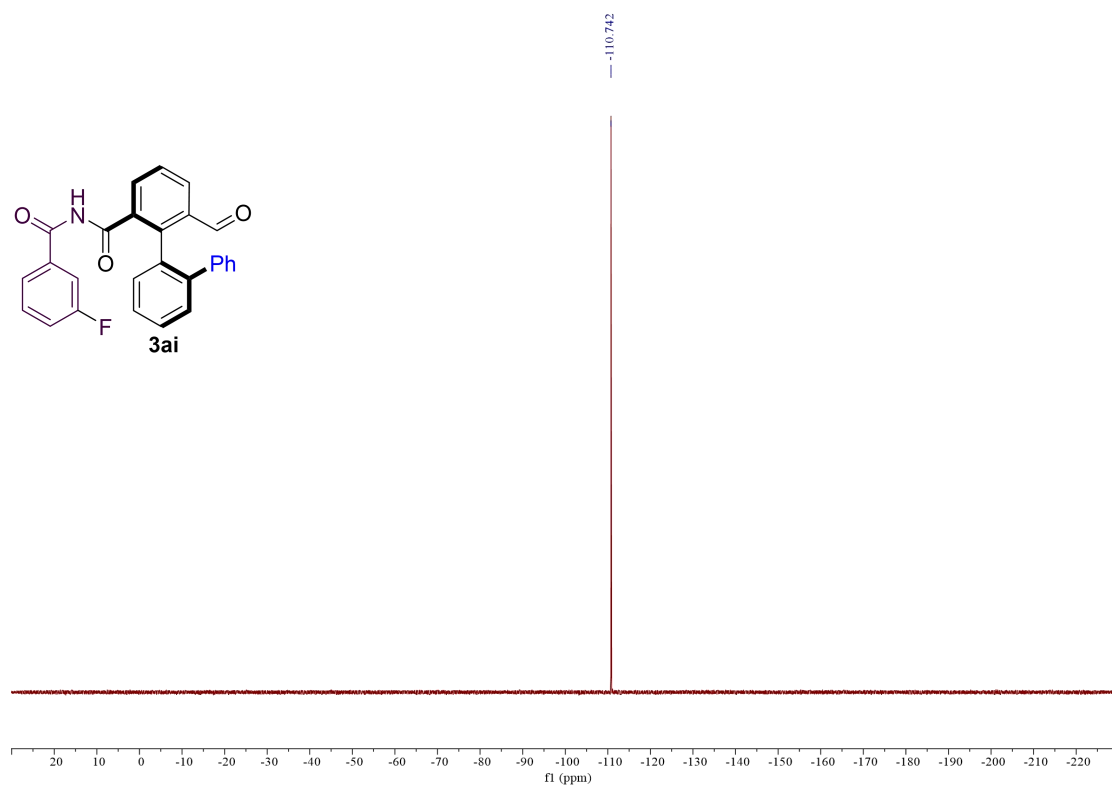
¹³C NMR (150 MHz, CDCl₃) spectrum of 3ah.



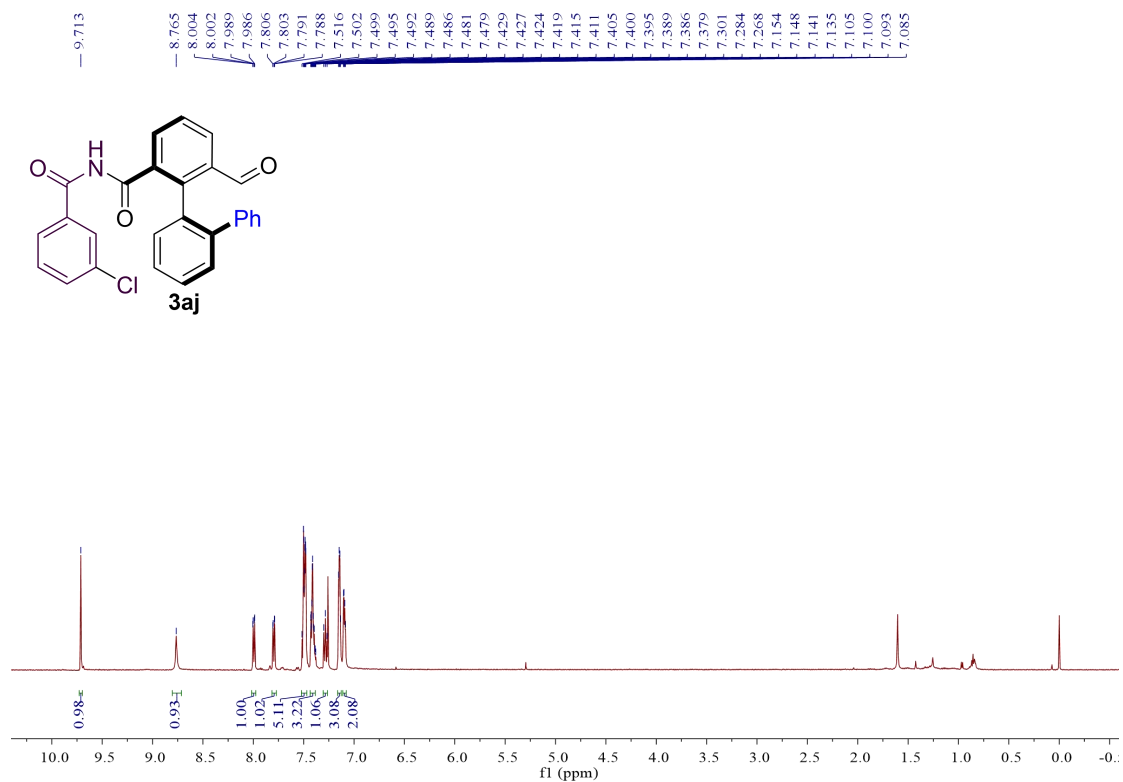
^1H NMR (500 MHz, CDCl_3) spectrum of **3ai**.



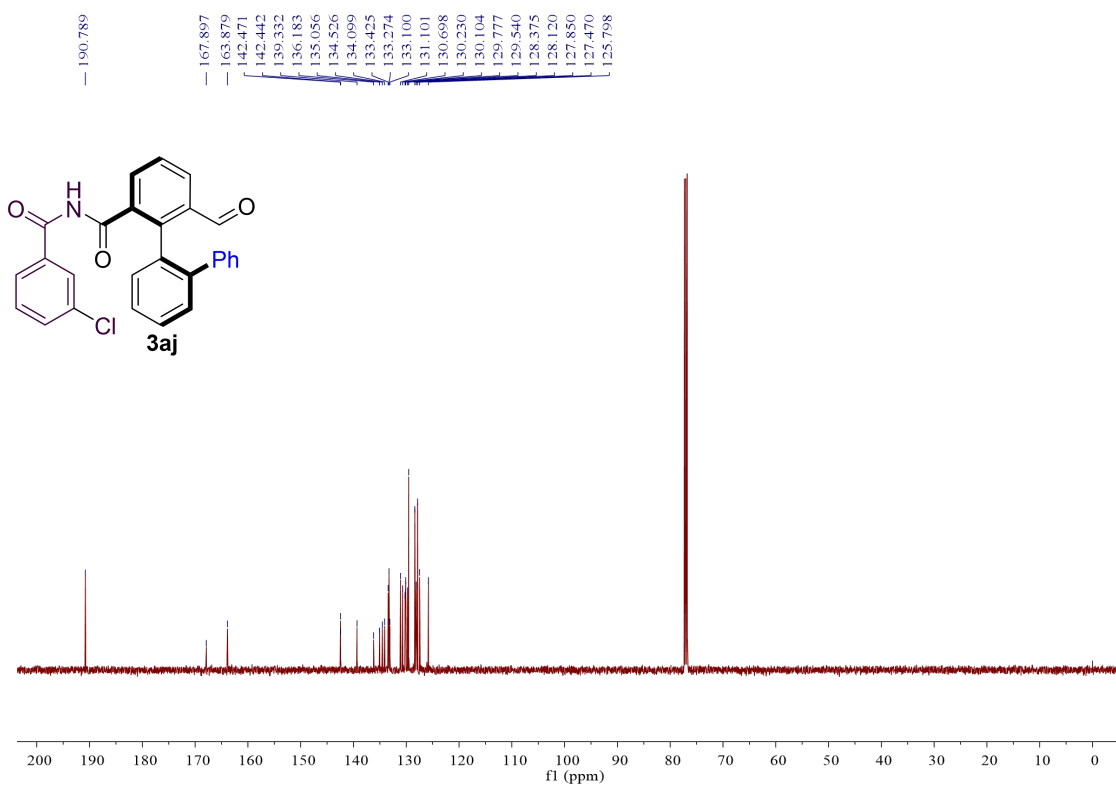
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ai**.



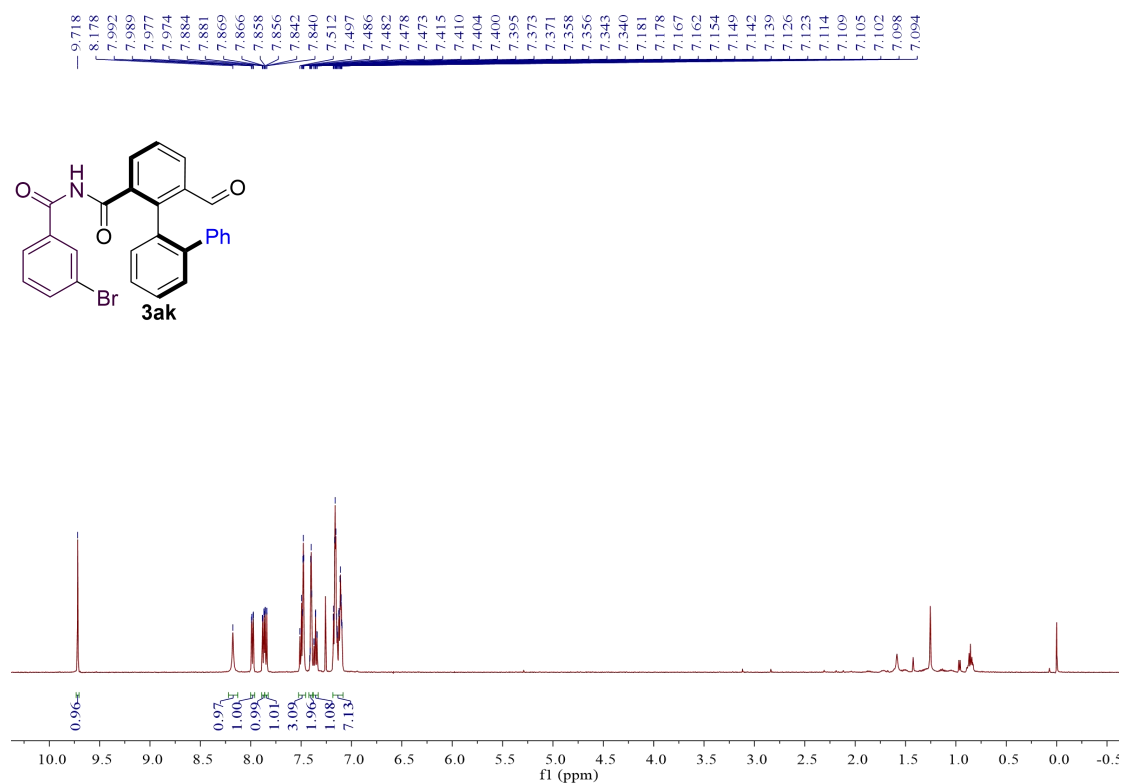
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3ai.**



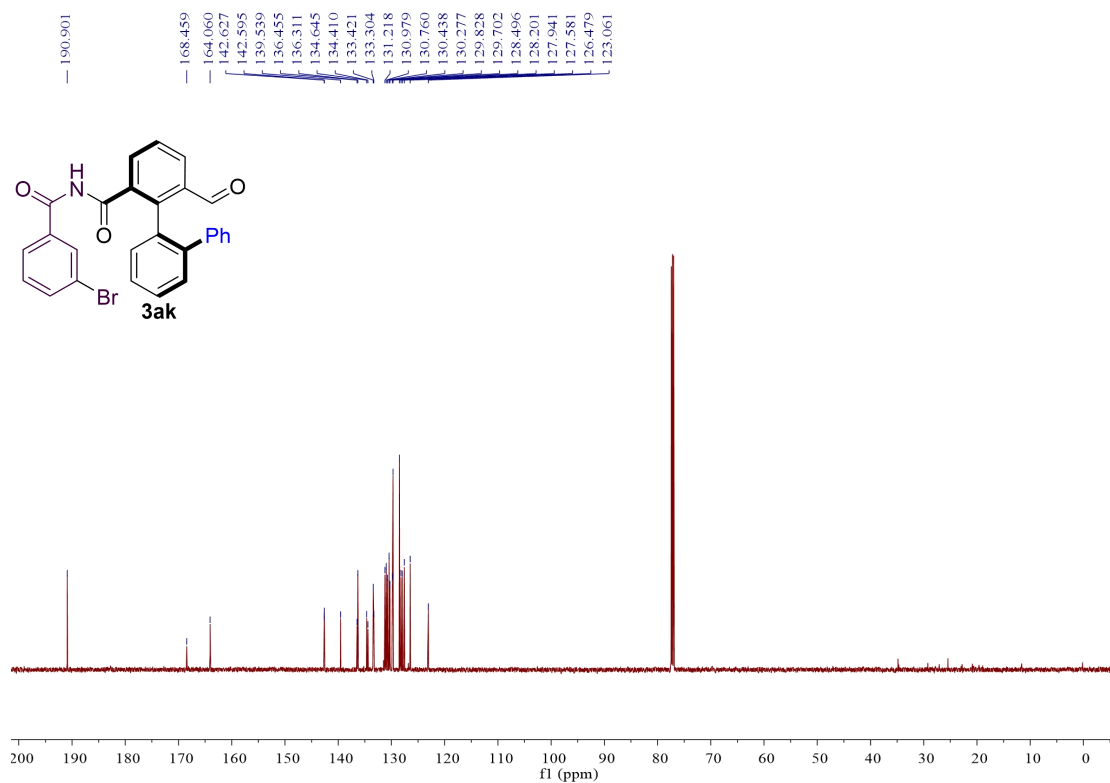
¹H NMR (500 MHz, CDCl₃) spectrum of 3aj.



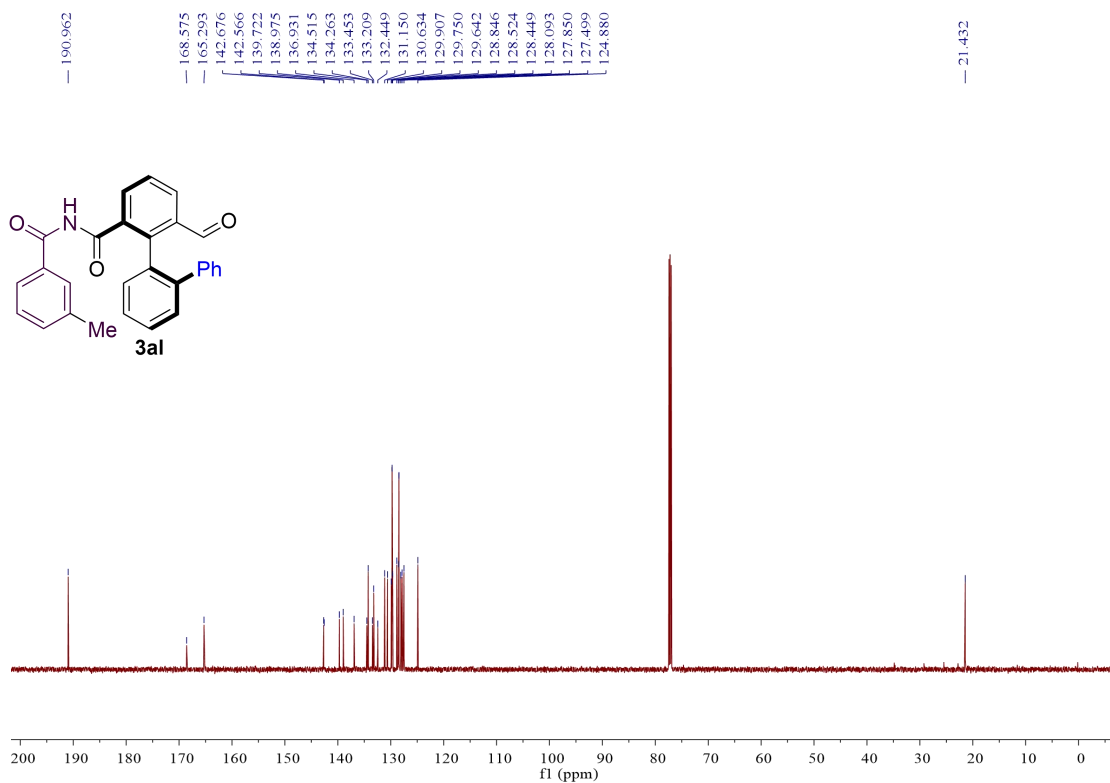
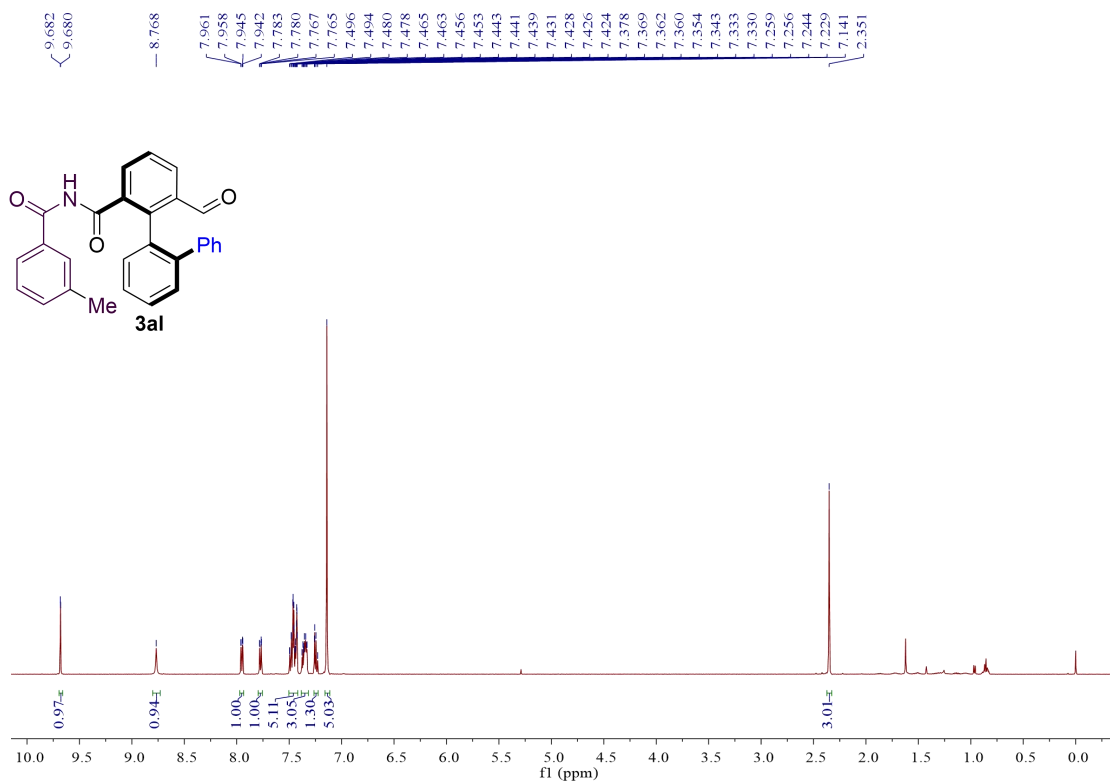
¹³C NMR (125 MHz, CDCl₃) spectrum of 3aj.

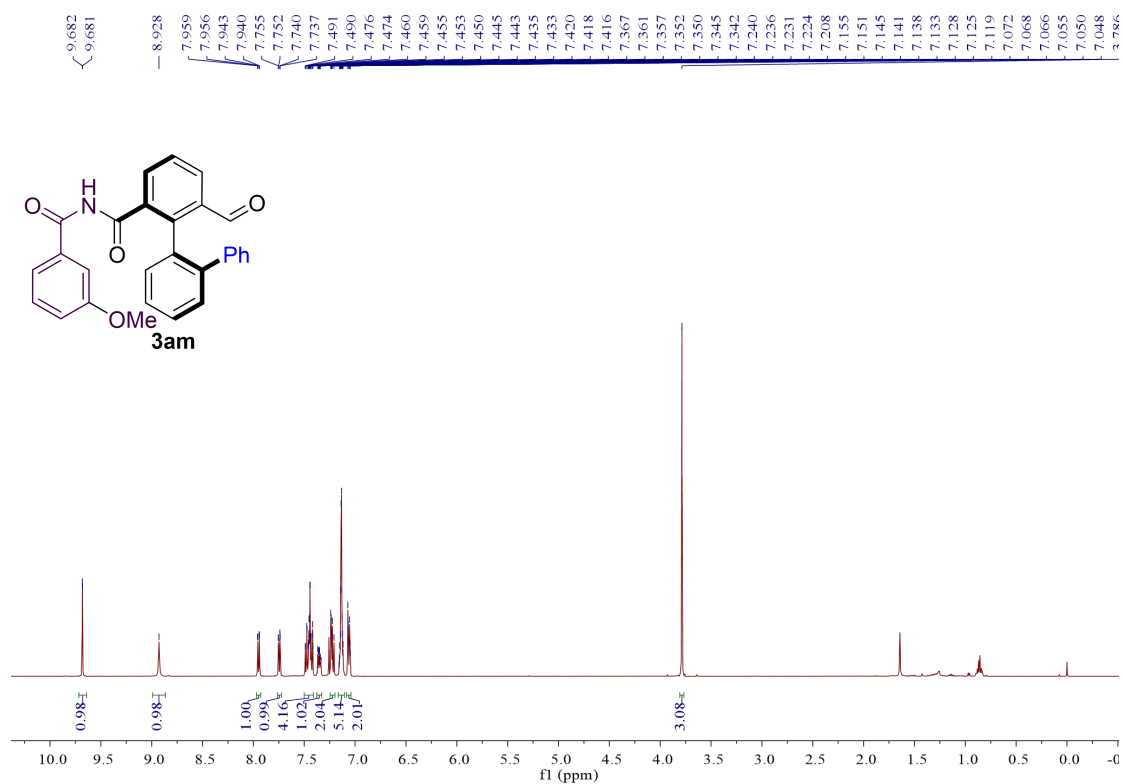


¹H NMR (500 MHz, CDCl₃) spectrum of **3ak.**

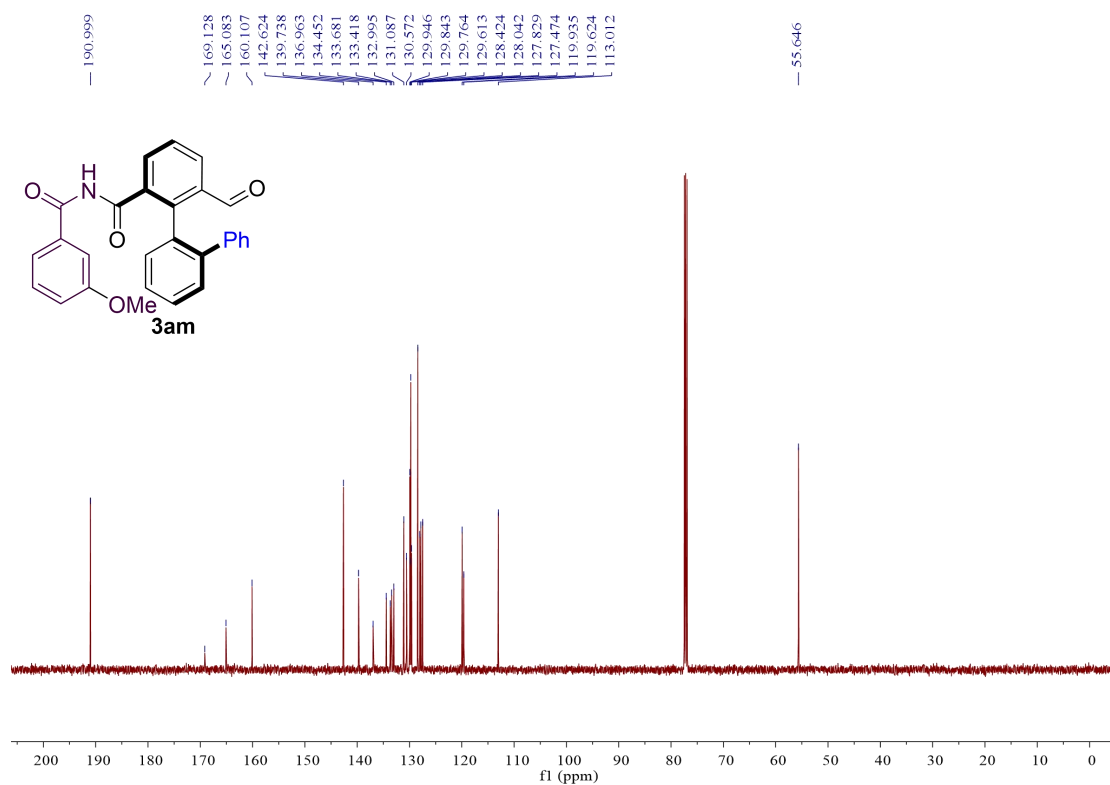


¹³C NMR (150 MHz, CDCl₃) spectrum of **3ak.**

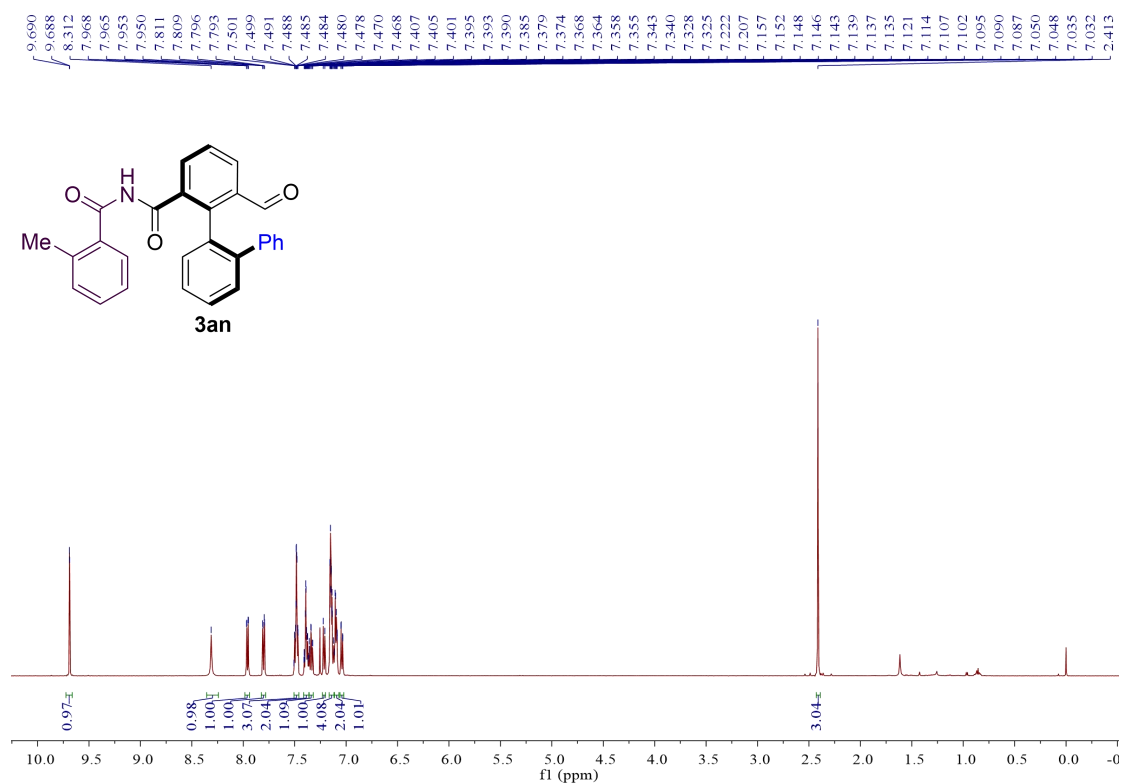




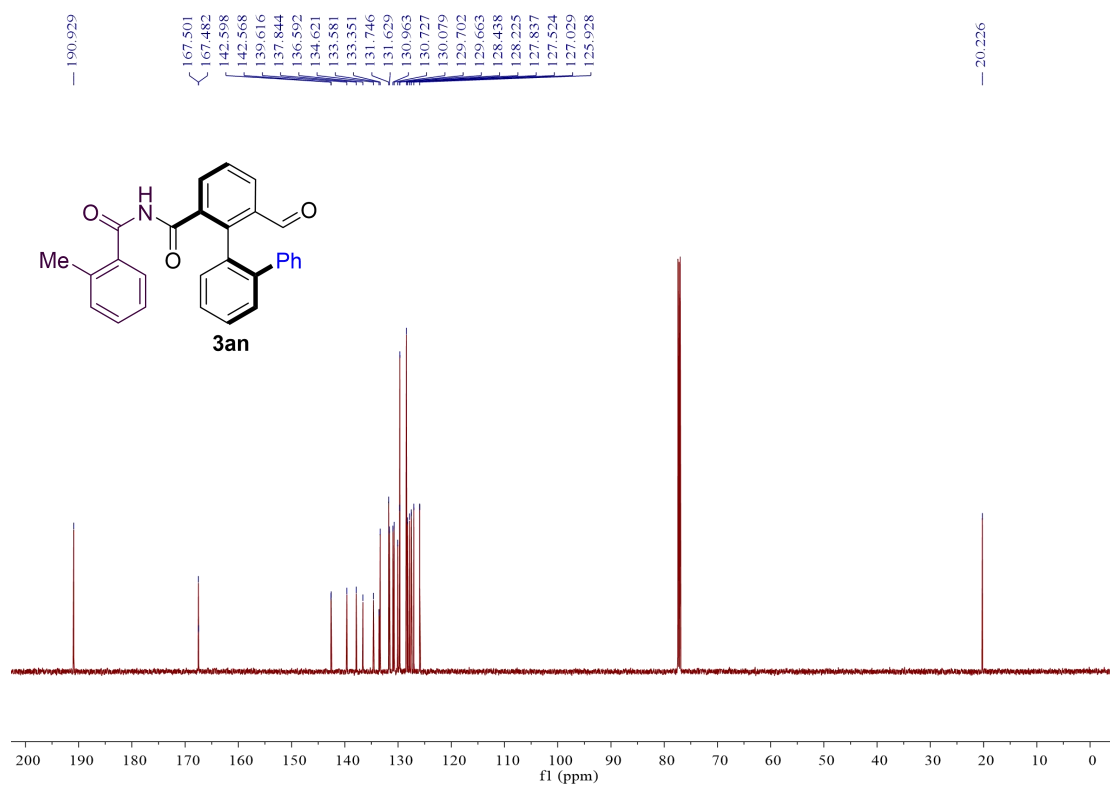
¹H NMR (500 MHz, CDCl₃) spectrum of 3am.



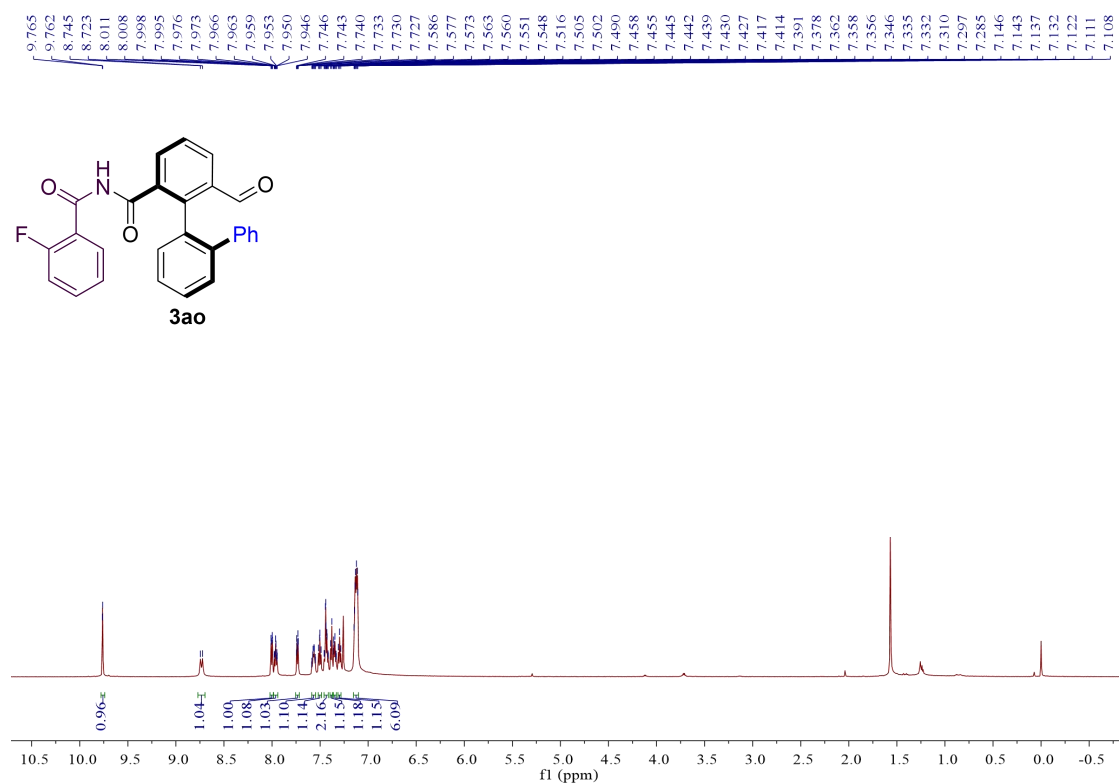
¹³C NMR (125 MHz, CDCl₃) spectrum of 3am.



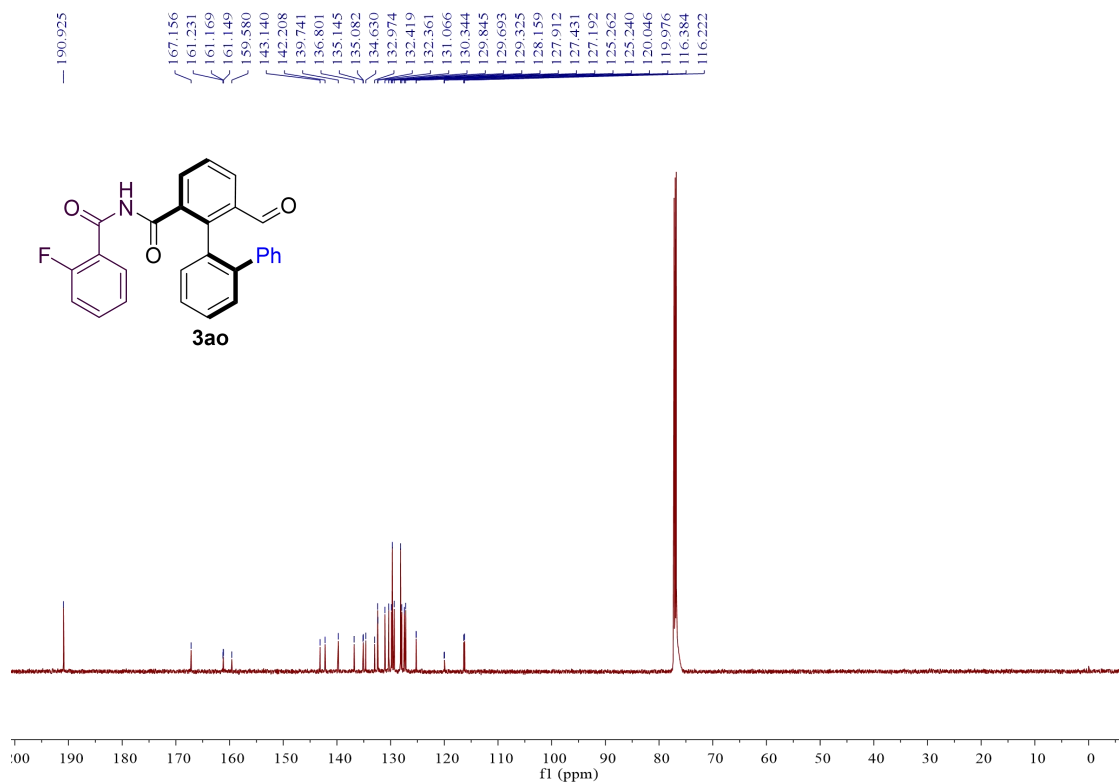
¹H NMR (500 MHz, CDCl₃) spectrum of 3an.



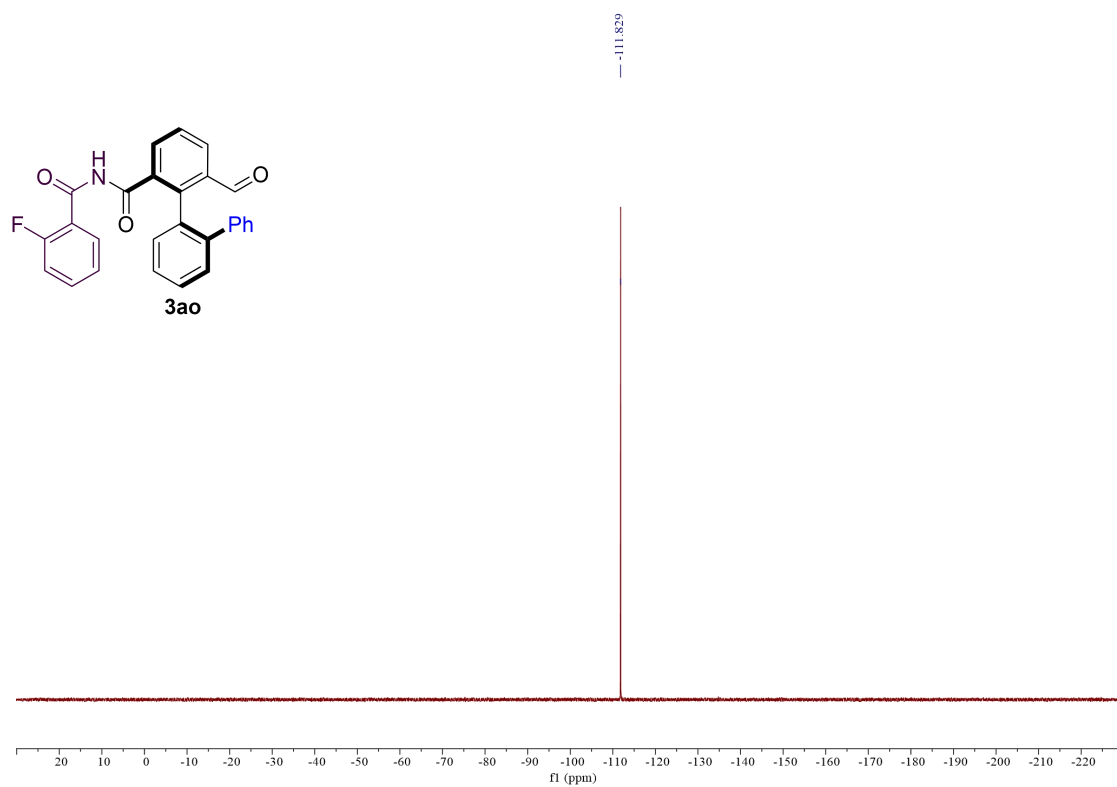
¹³C NMR (150 MHz, CDCl₃) spectrum of 3an.



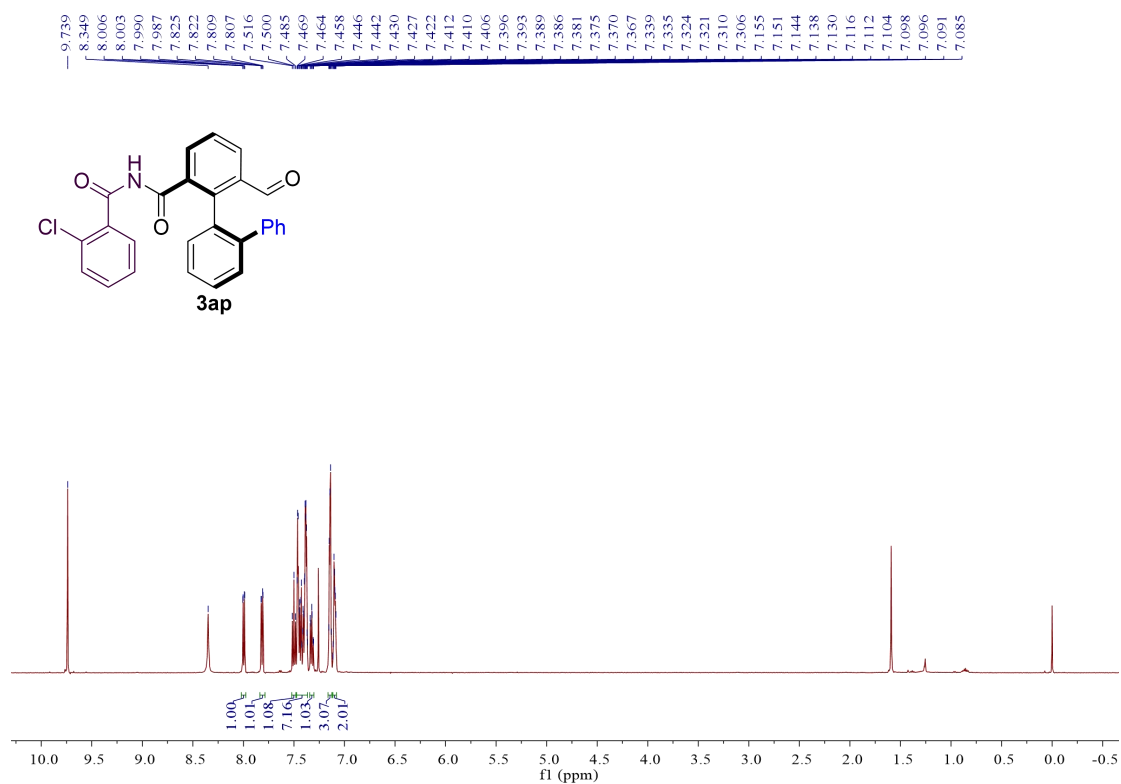
¹H NMR (600 MHz, CDCl₃) spectrum of 3ao.



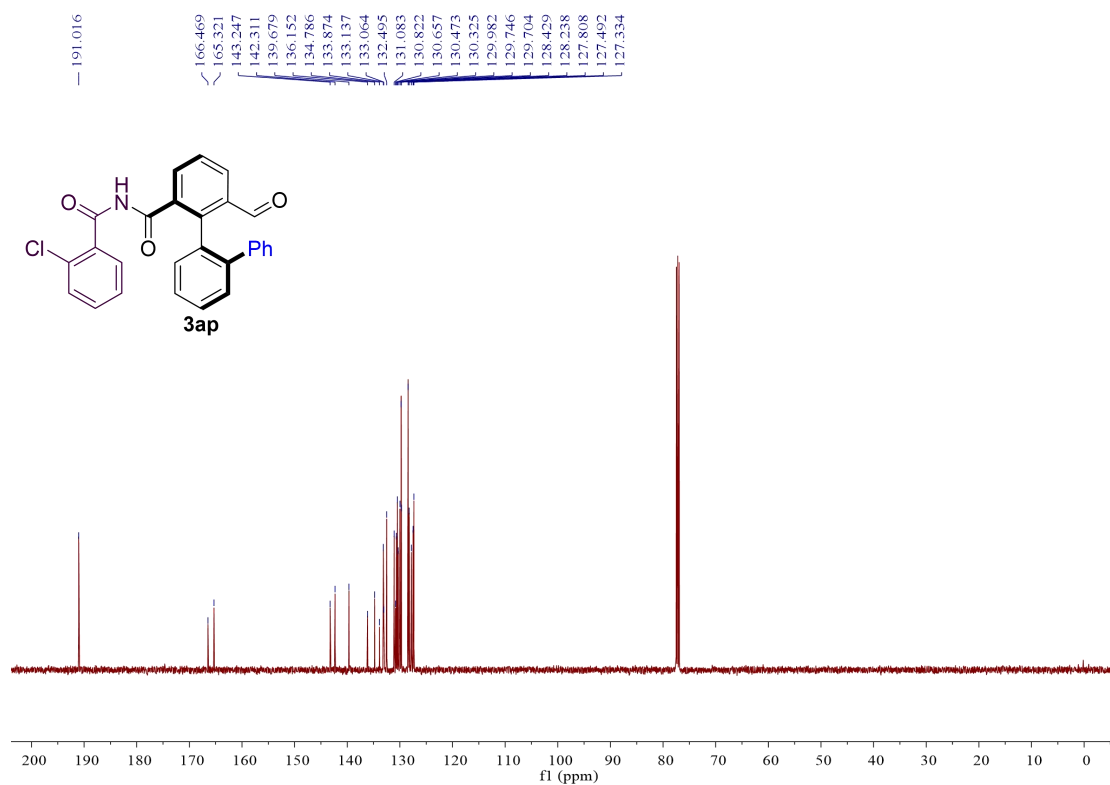
¹³C NMR (150 MHz, CDCl₃) spectrum of 3ao.



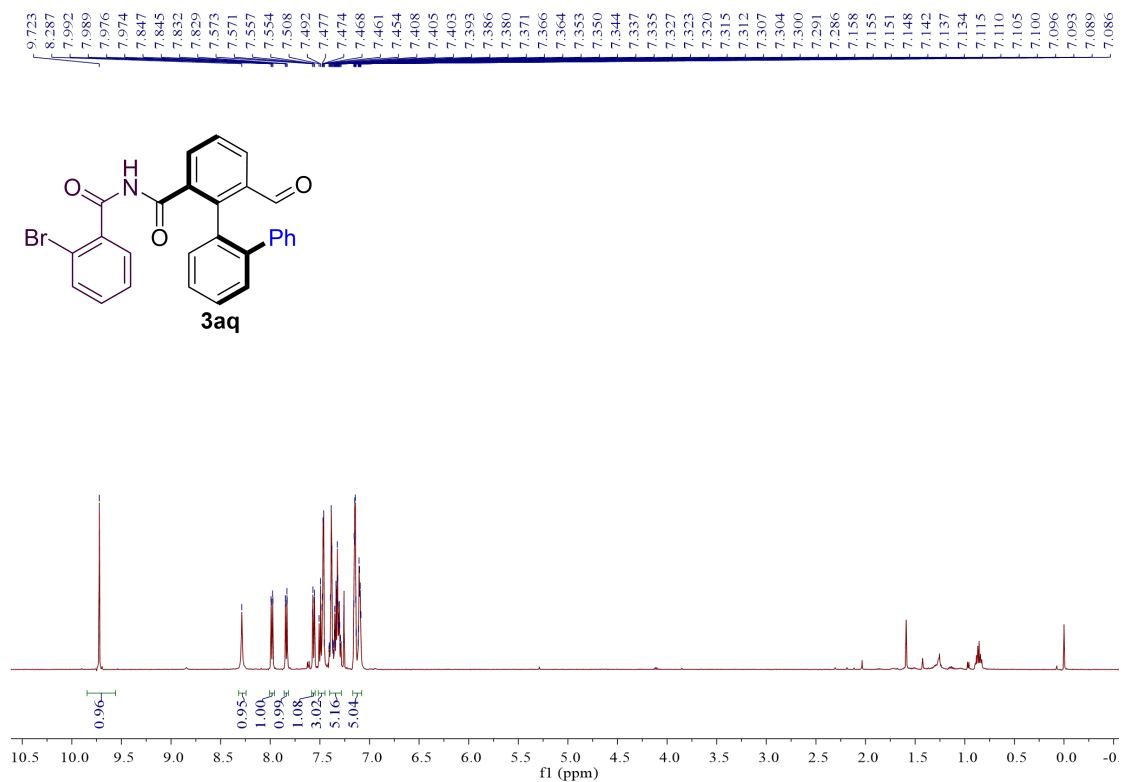
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3ao.**



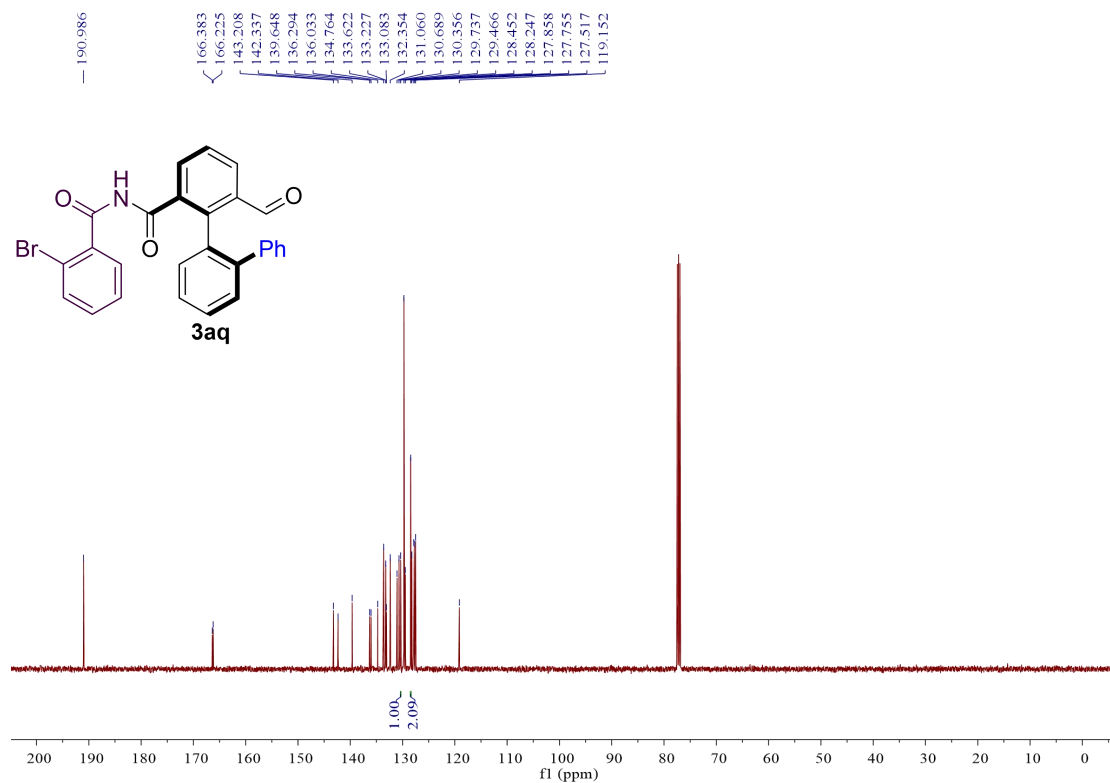
¹H NMR (500 MHz, CDCl₃) spectrum of **3ap.**



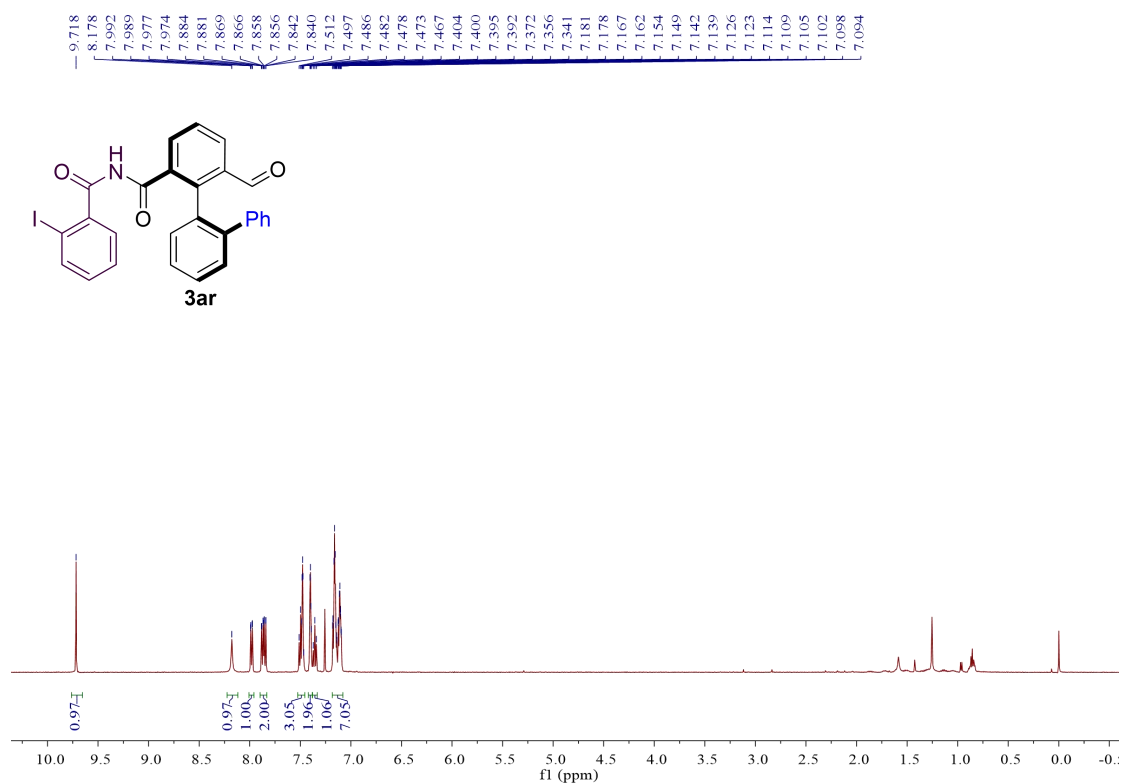
¹³C NMR (125 MHz, CDCl₃) spectrum of **3ap.**



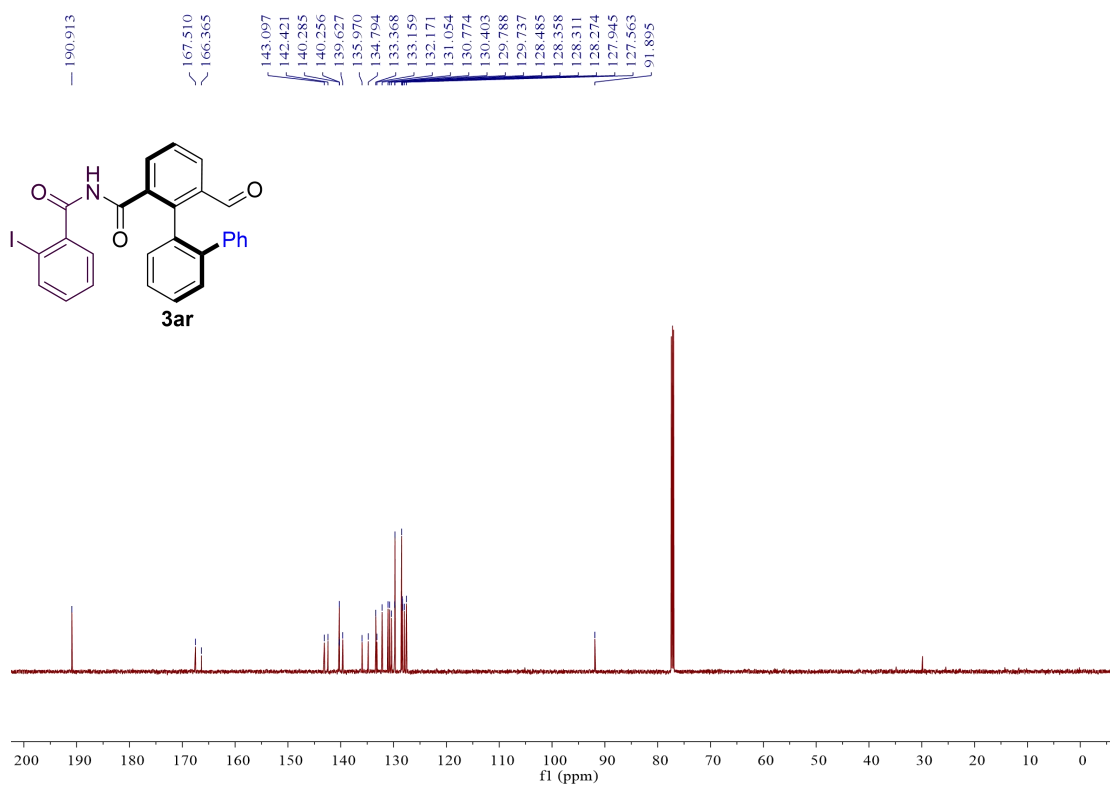
¹H NMR (500 MHz, CDCl₃) spectrum of **3aq.**



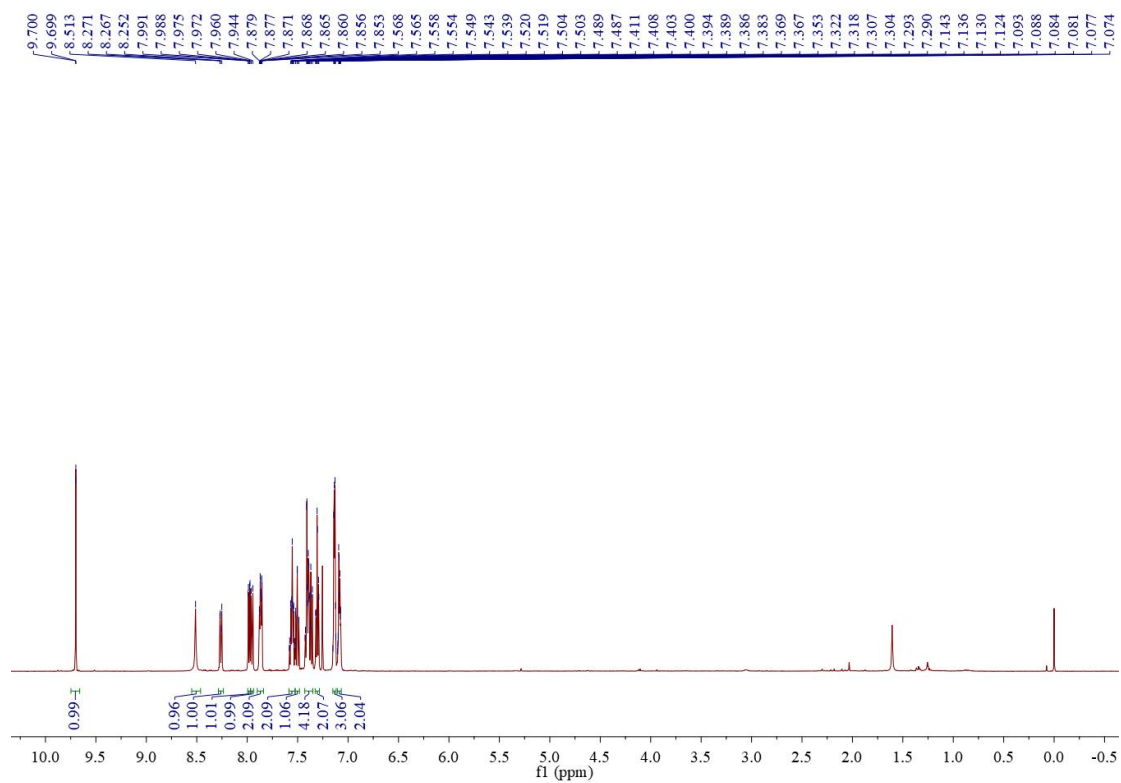
¹³C NMR (125 MHz, CDCl₃) spectrum of **3aq.**



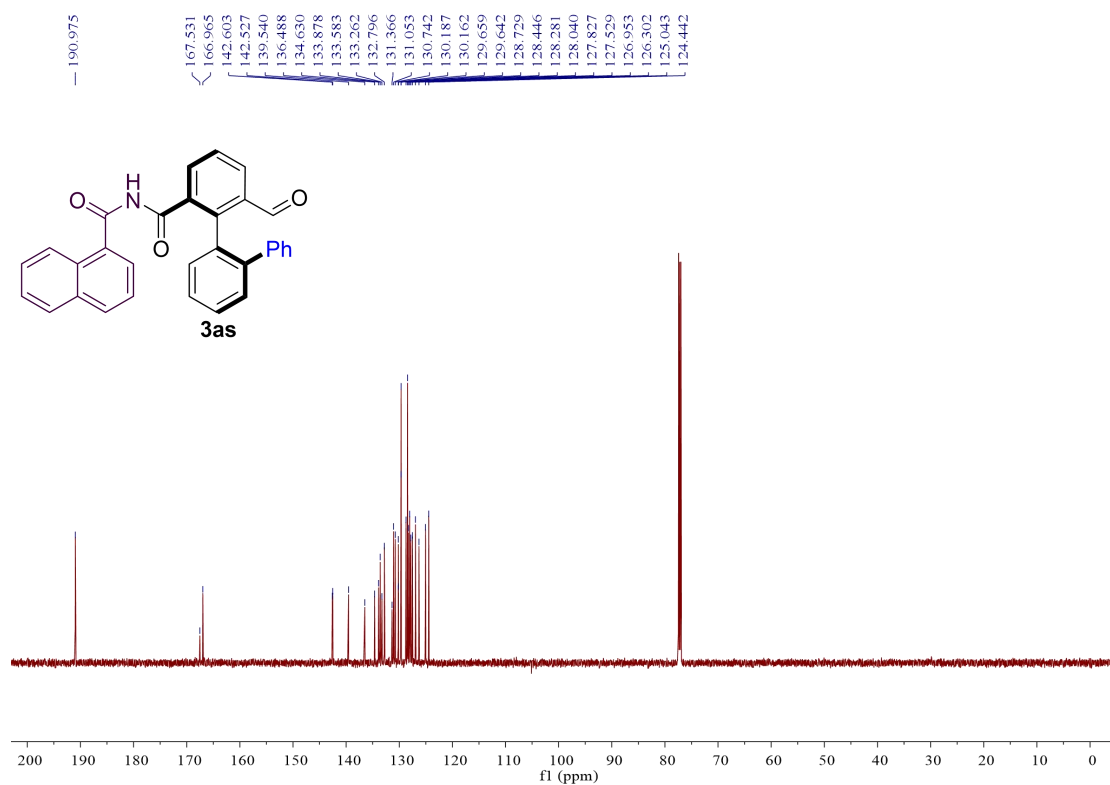
¹H NMR (500 MHz, CDCl₃) spectrum of 3ar.



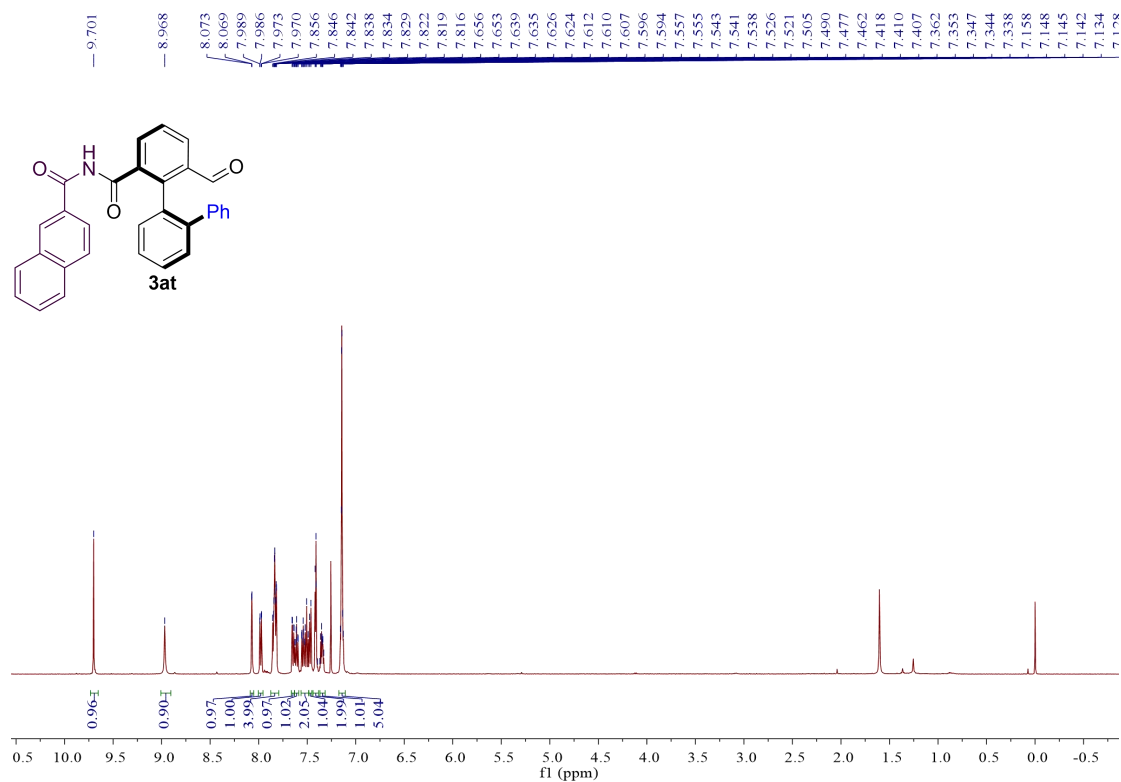
¹³C NMR (150 MHz, CDCl₃) spectrum of 3ar.



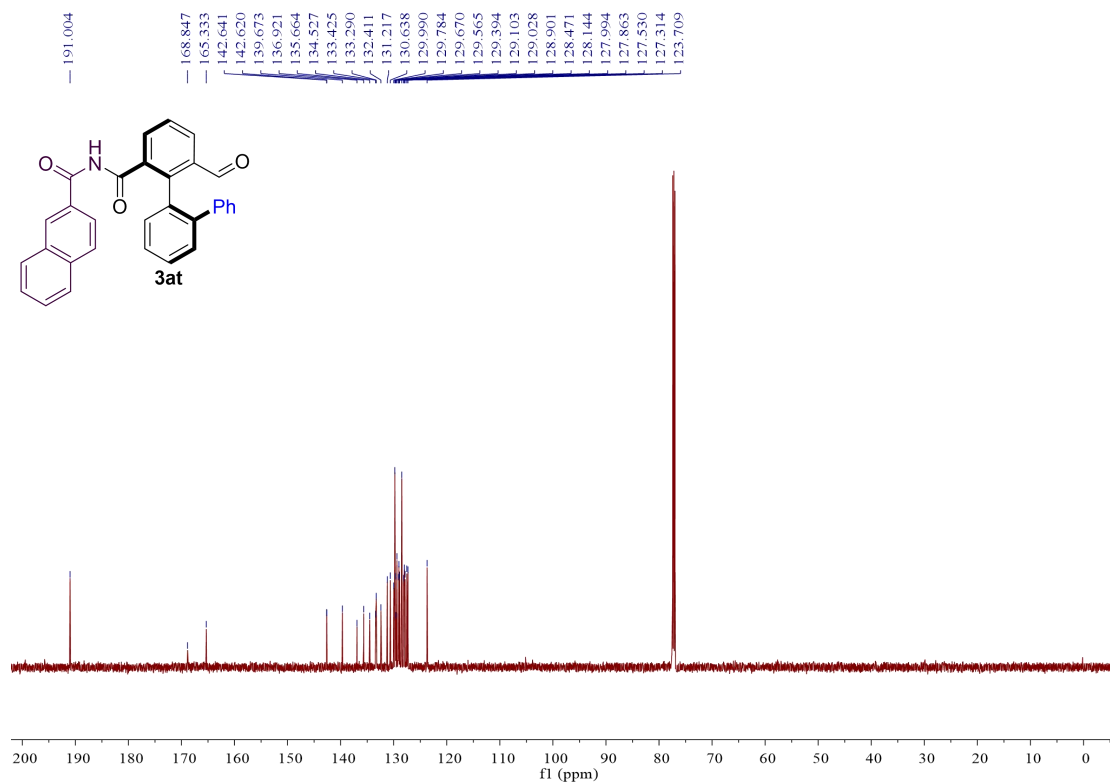
¹H NMR (500 MHz, CDCl₃) spectrum of 3as.



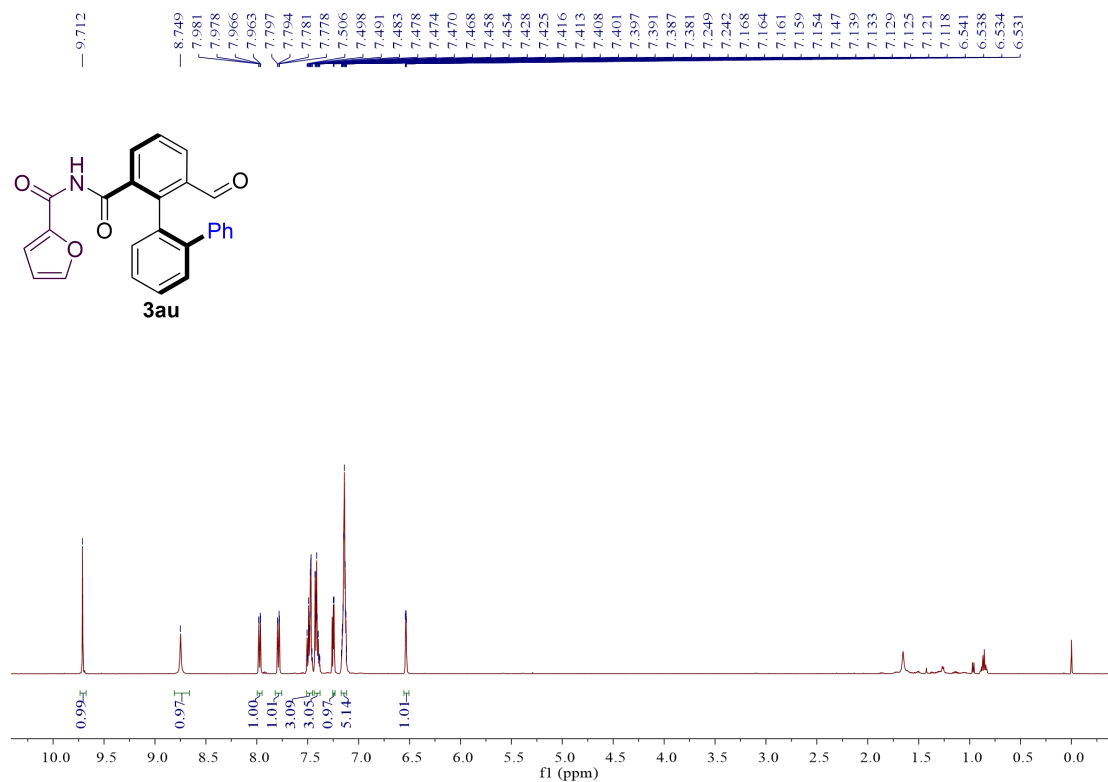
¹³C NMR (150 MHz, CDCl₃) spectrum of 3as.



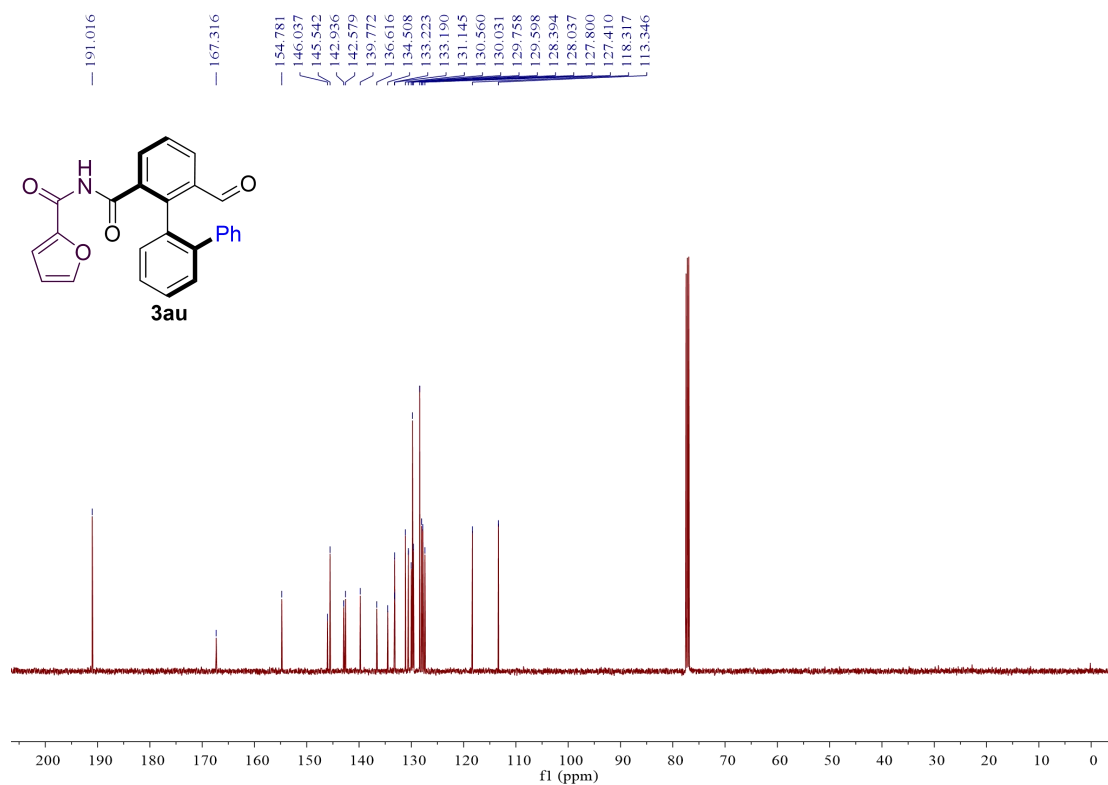
¹H NMR (500 MHz, CDCl₃) spectrum of 3at.



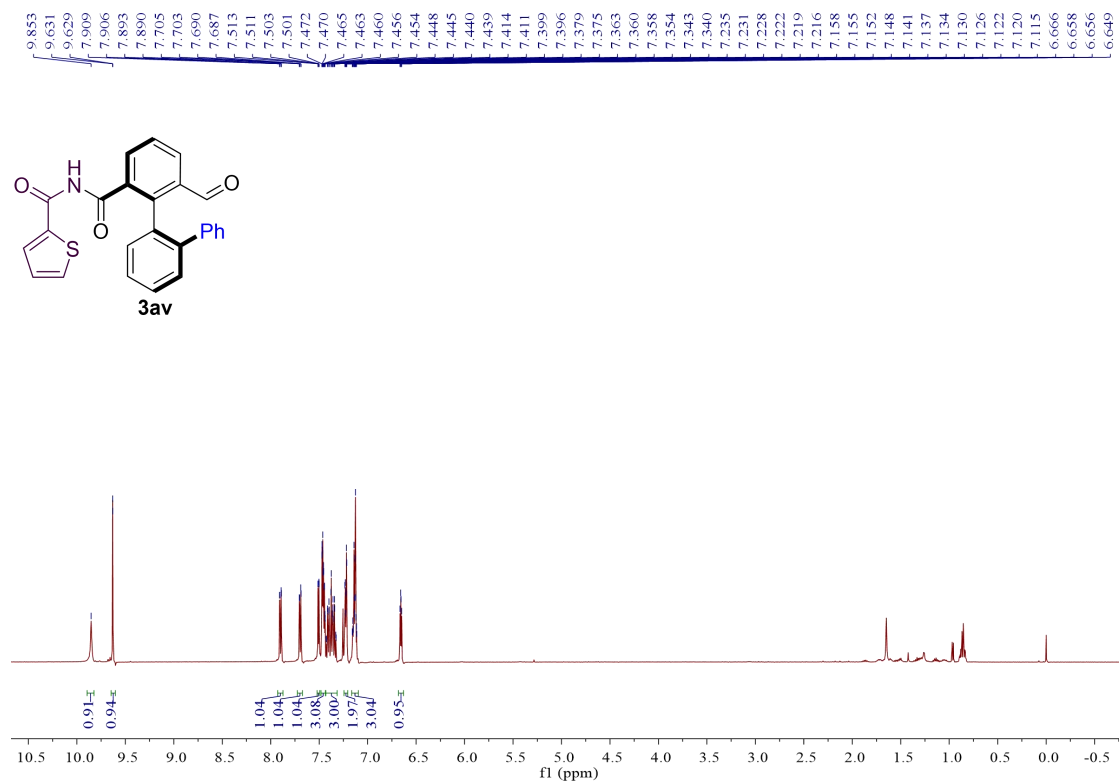
¹³C NMR (150 MHz, CDCl₃) spectrum of 3at.



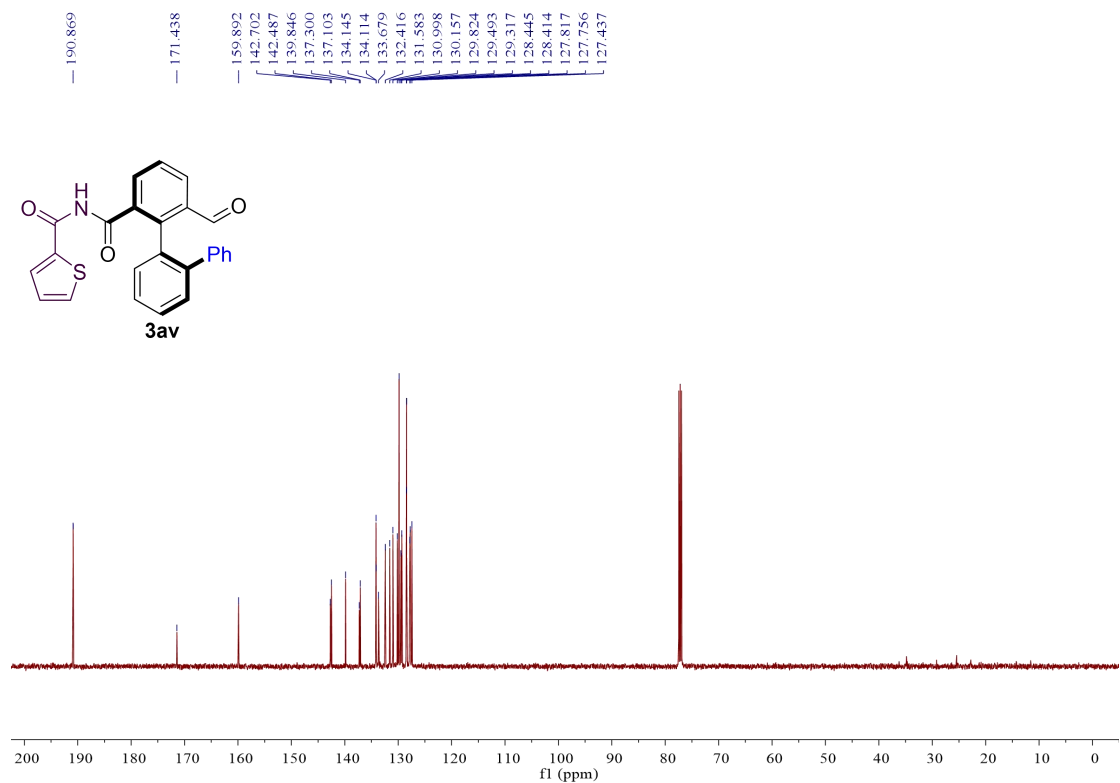
^1H NMR (500 MHz, CDCl_3) spectrum of **3au**.



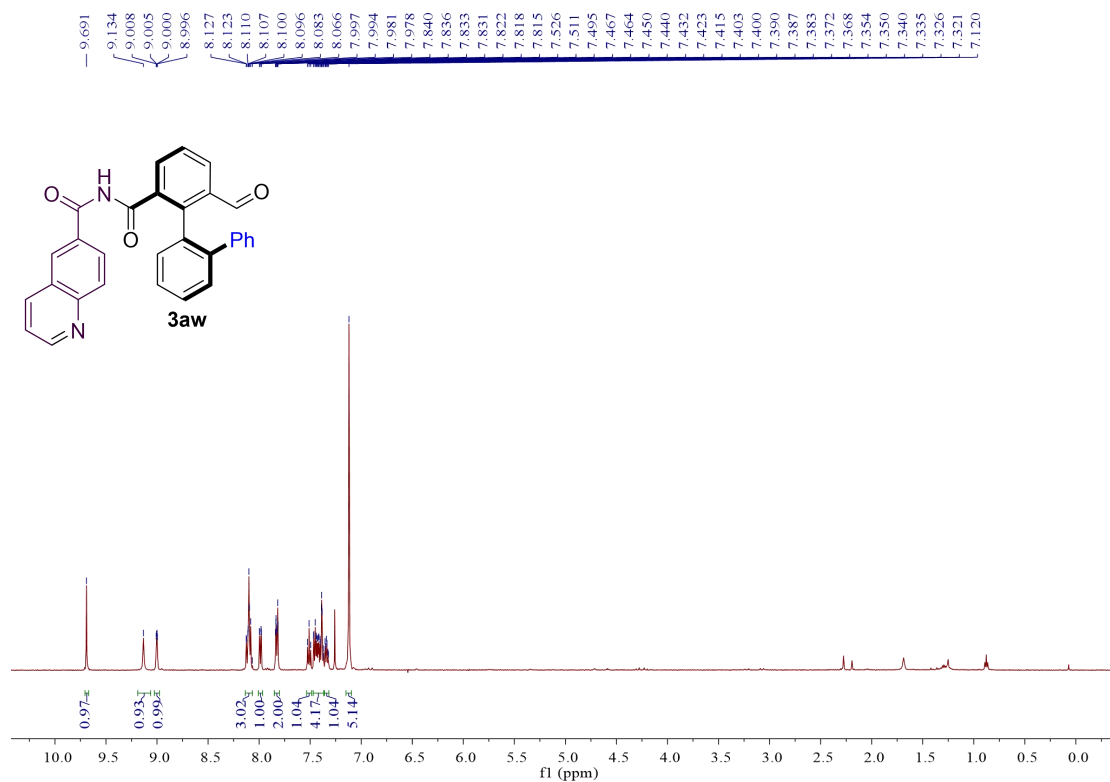
^{13}C NMR (125 MHz, CDCl_3) spectrum of **3au**.



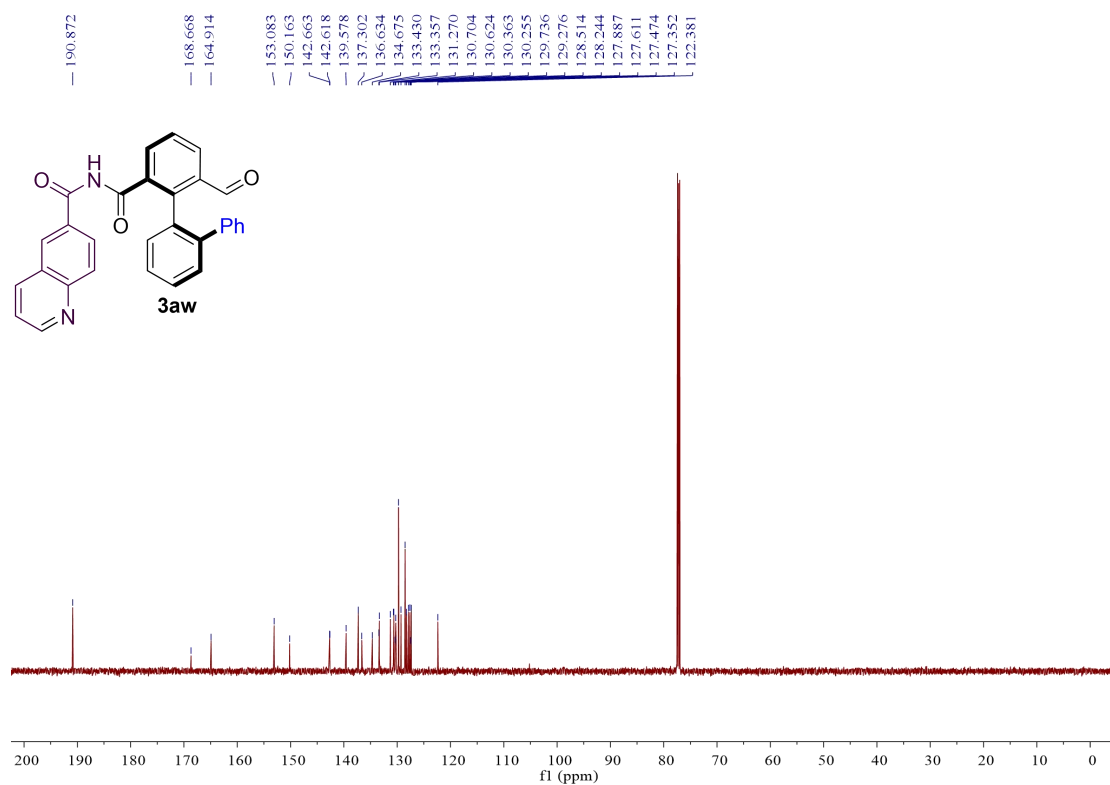
^1H NMR (500 MHz, CDCl_3) spectrum of **3av**.



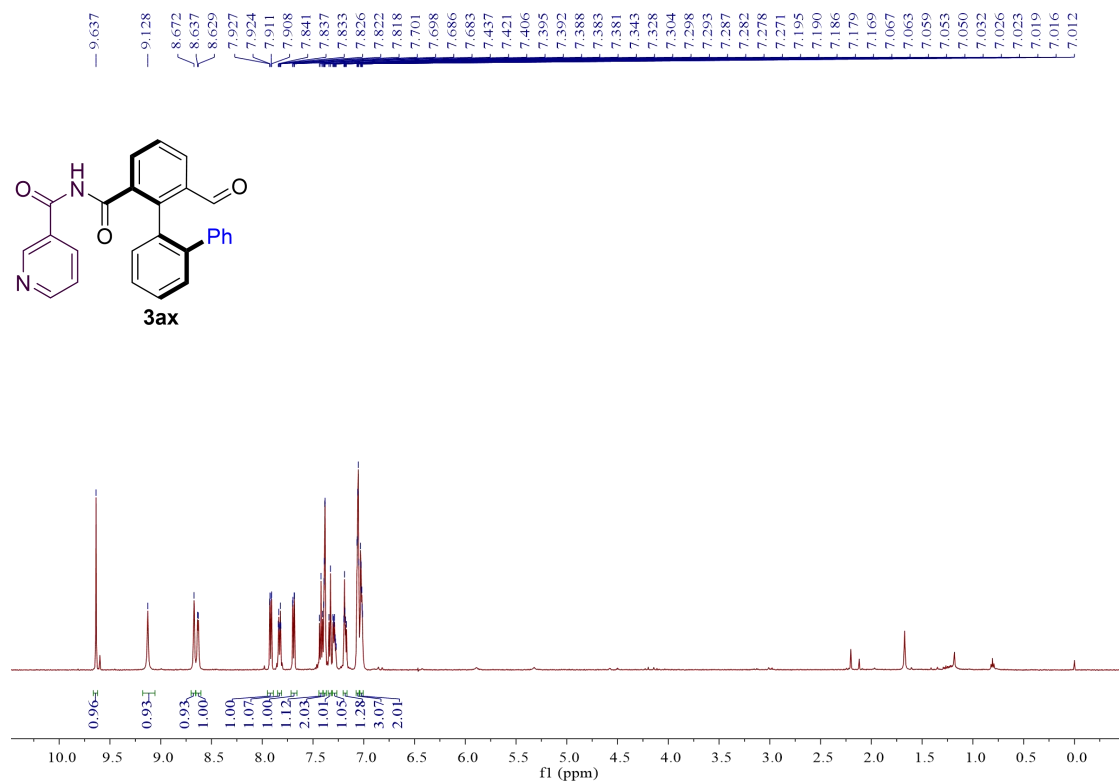
^{13}C NMR (125 MHz, CDCl_3) spectrum of **3av**.



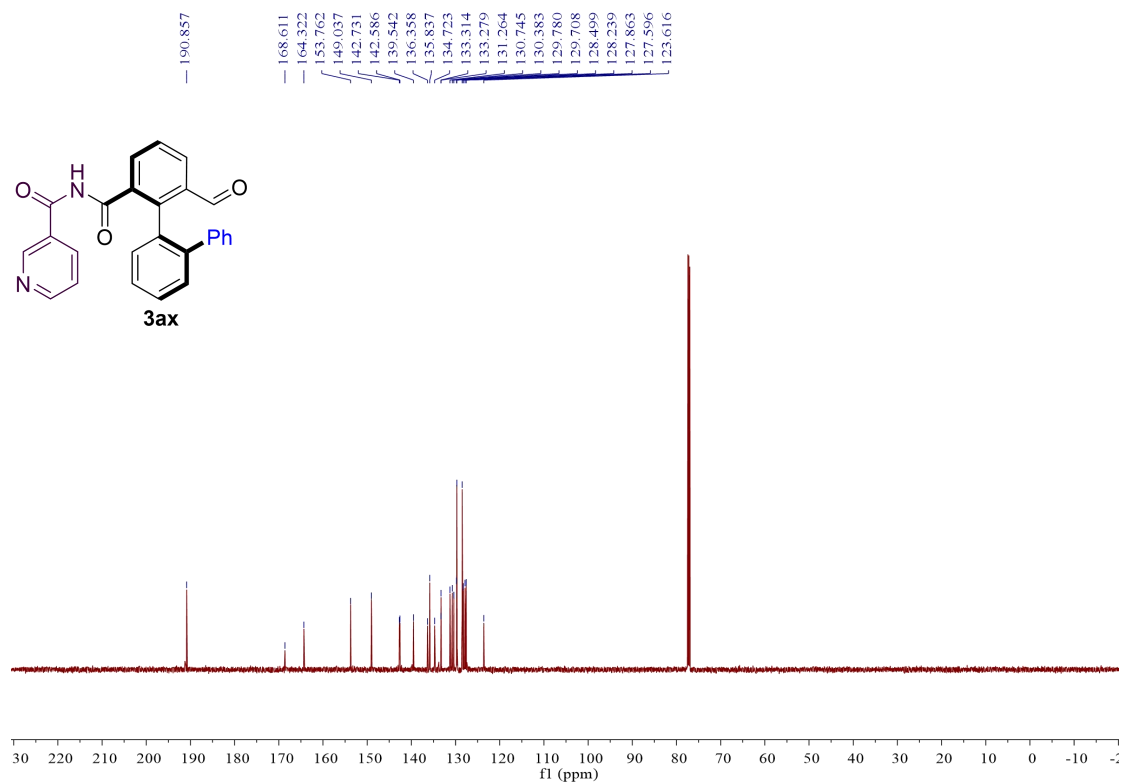
¹H NMR (500 MHz, CDCl₃) spectrum of 3aw.



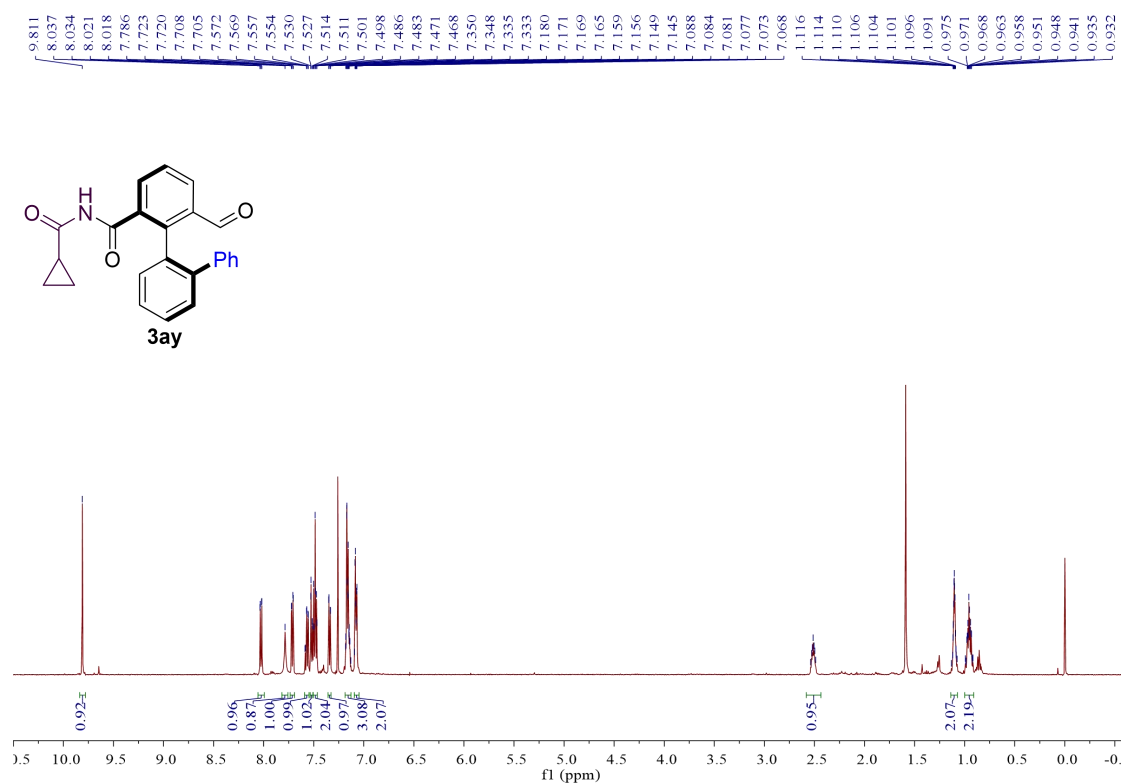
¹³C NMR (150 MHz, CDCl₃) spectrum of 3aw.



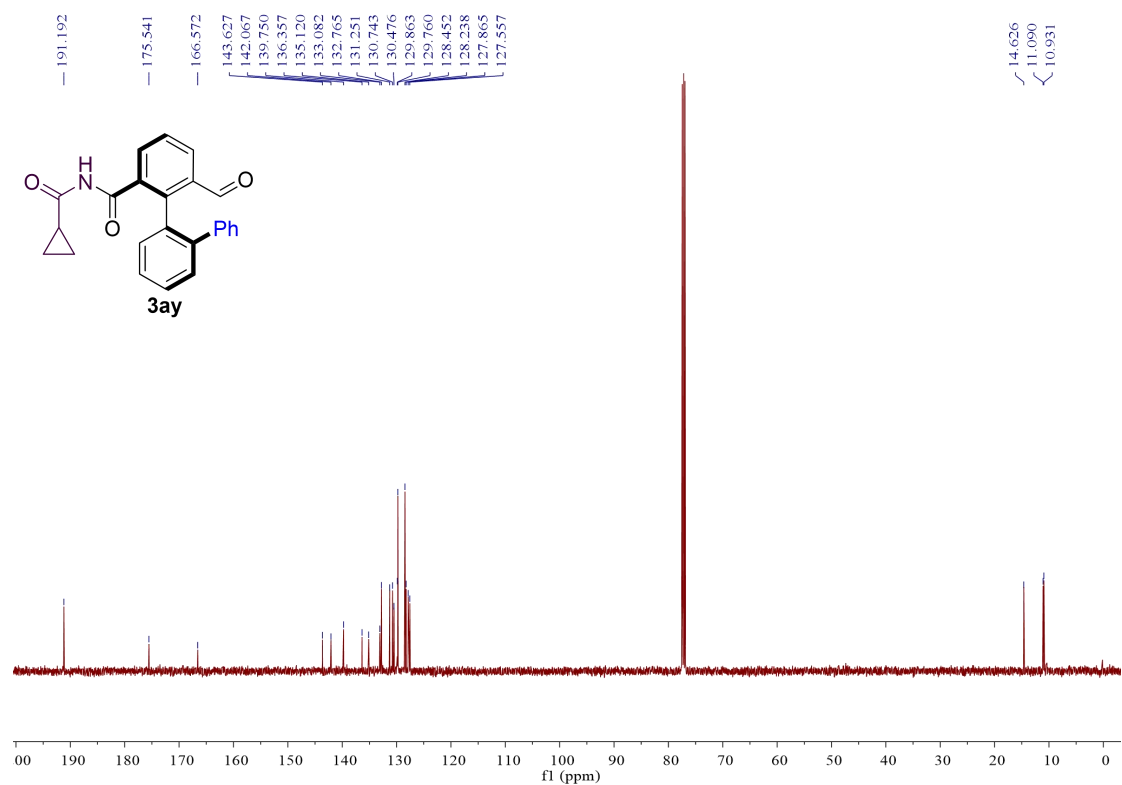
^1H NMR (500 MHz, CDCl_3) spectrum of **3ax**.



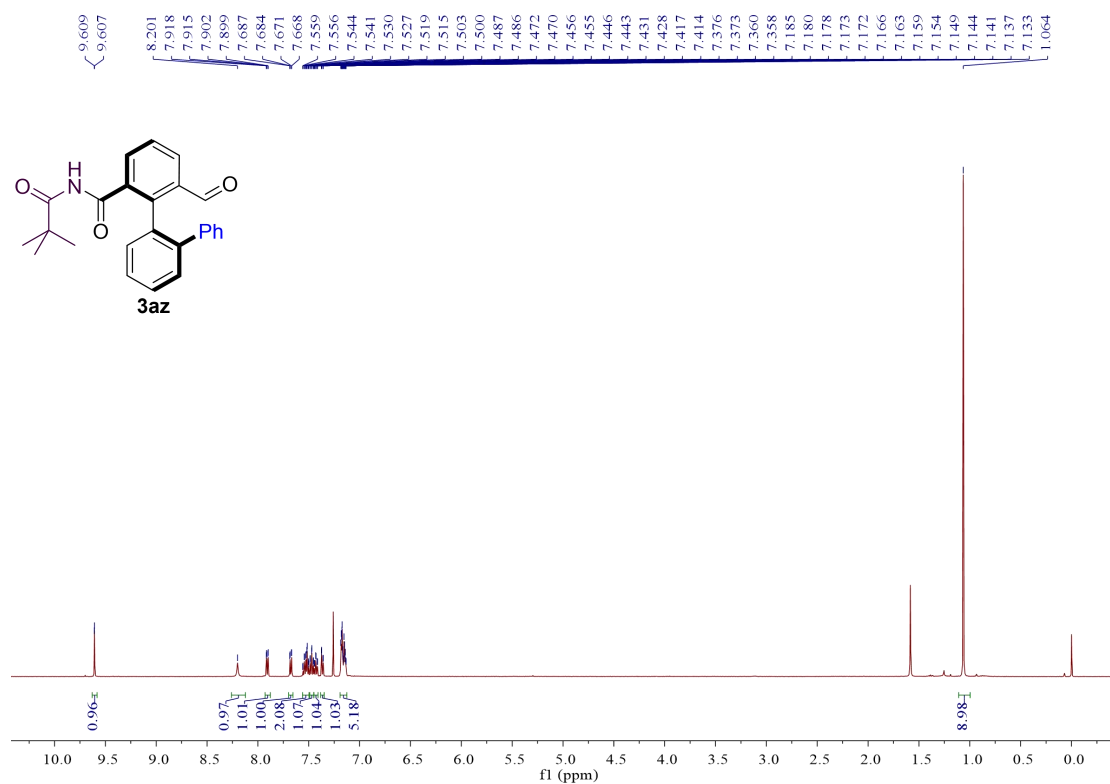
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3ax**.



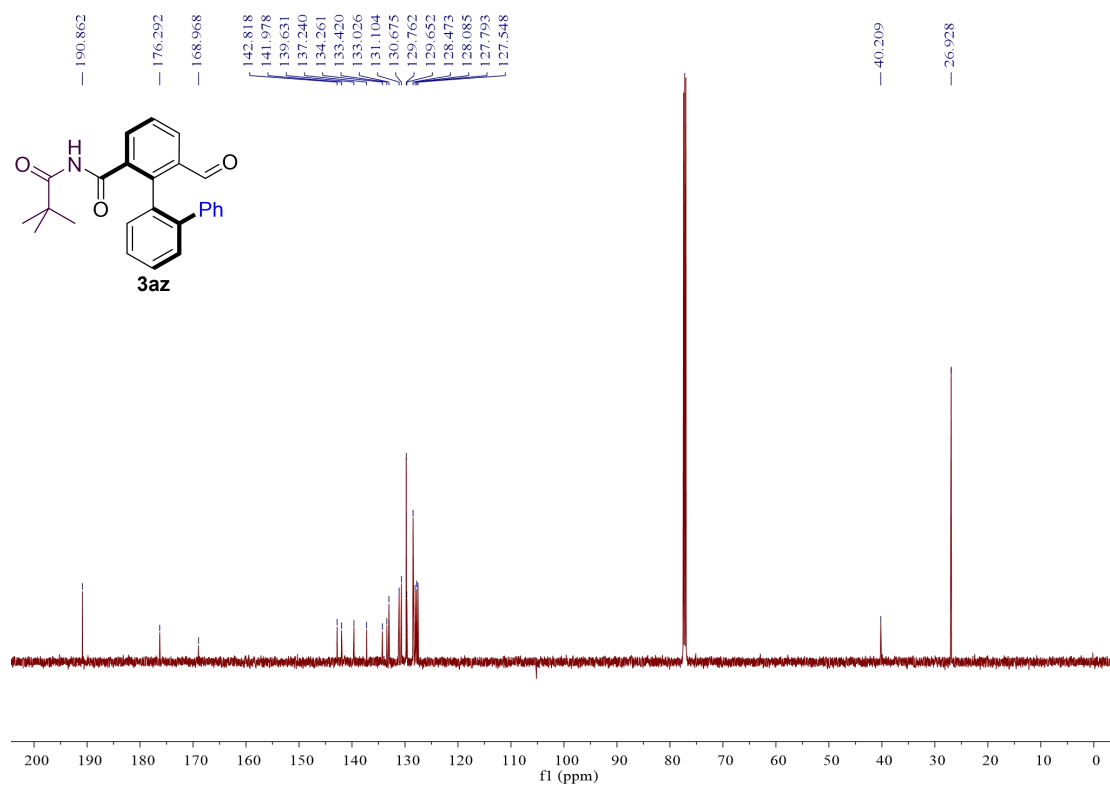
^1H NMR (500 MHz, CDCl_3) spectrum of **3ay**.



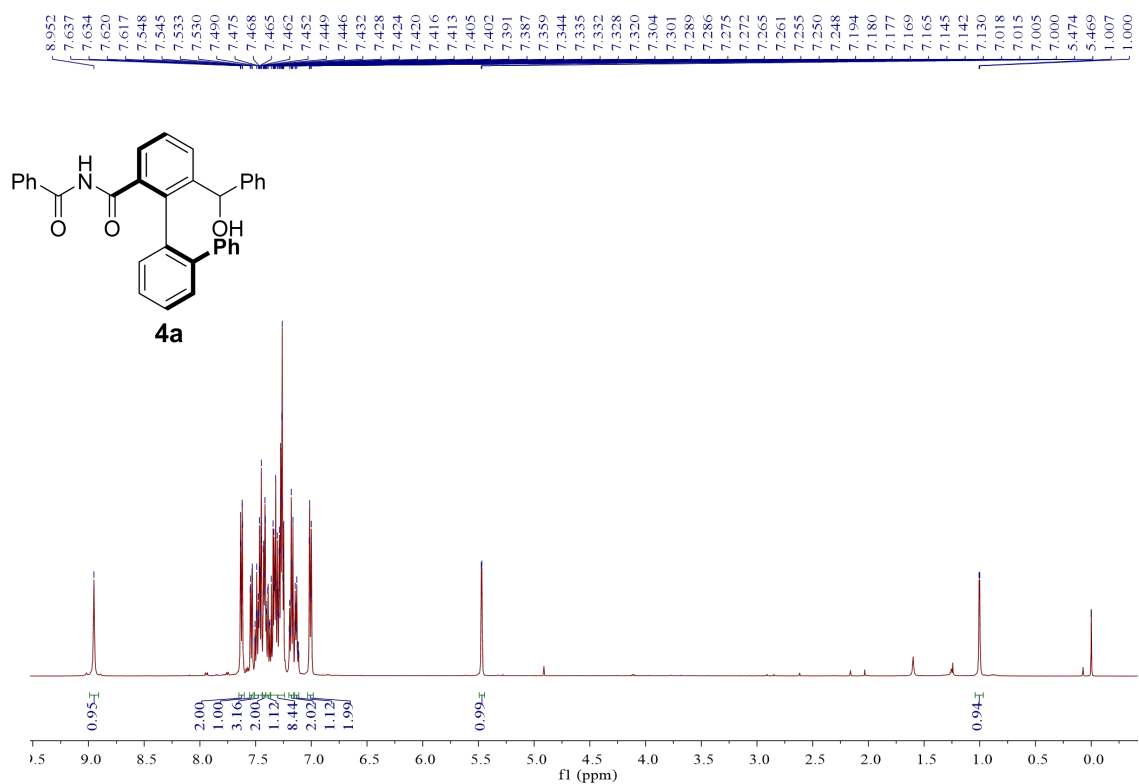
^{13}C NMR (125 MHz, CDCl_3) spectrum of **3ay**.



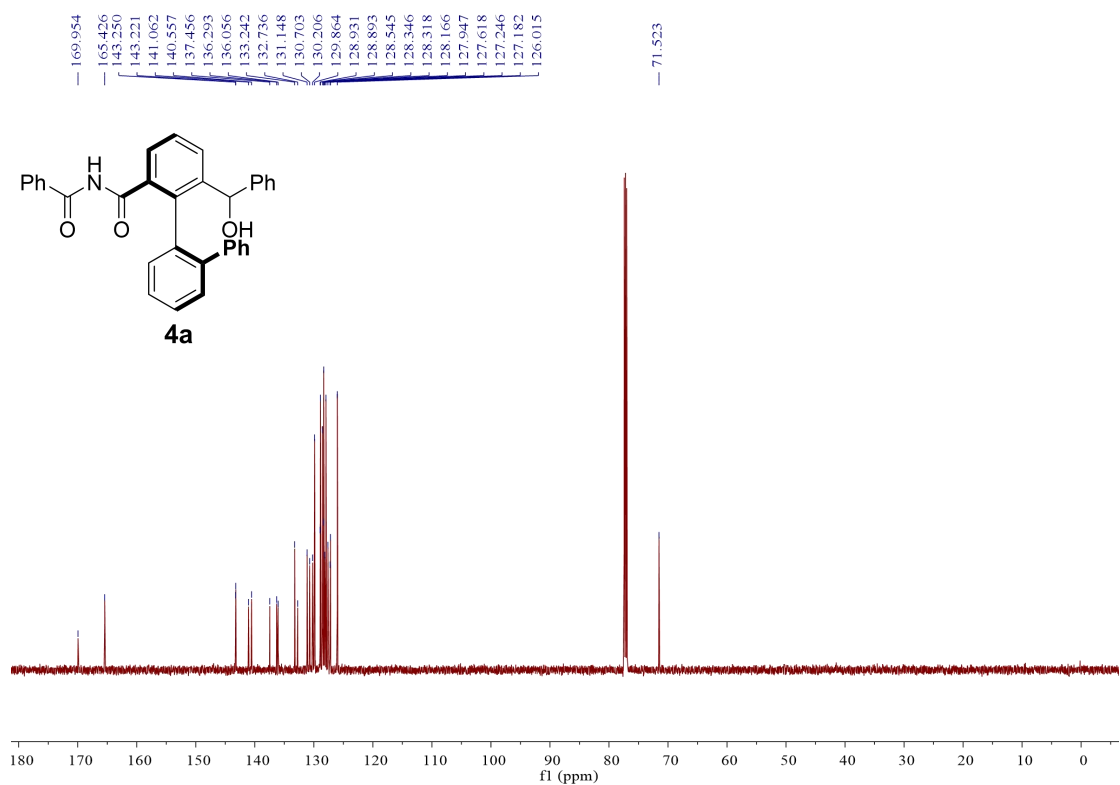
^1H NMR (500 MHz, CDCl_3) spectrum of **3az**.



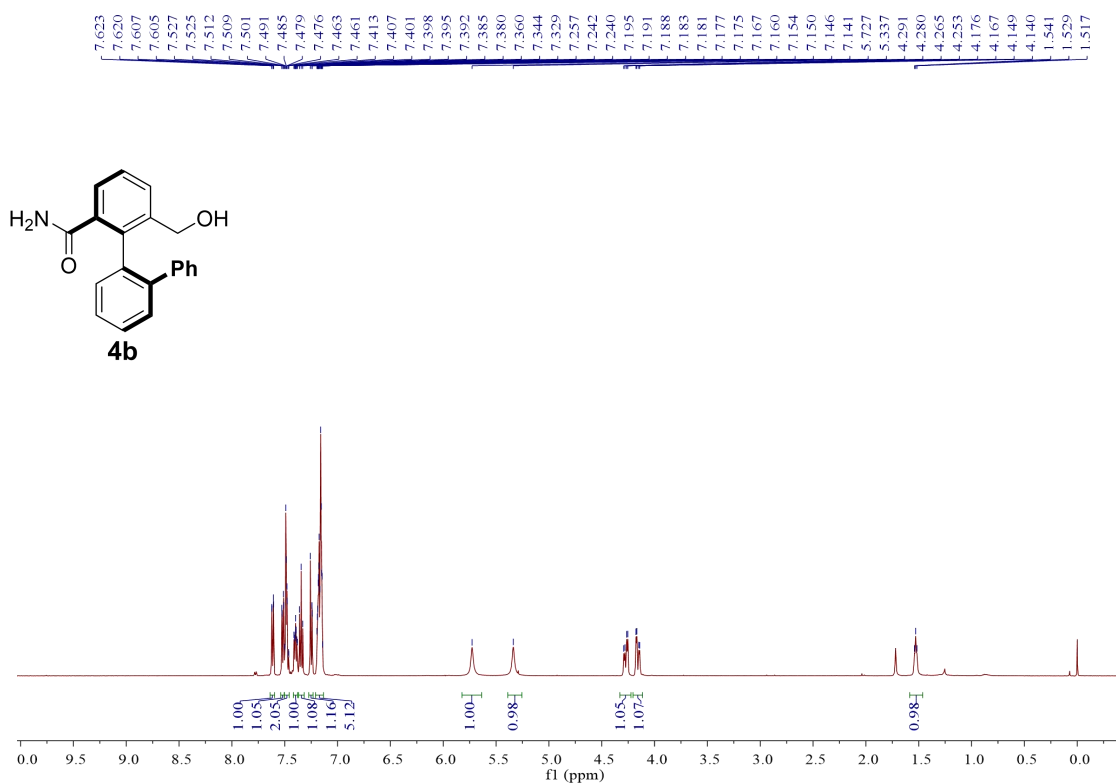
^{13}C NMR (150 MHz, CDCl_3) spectrum of **3az**.



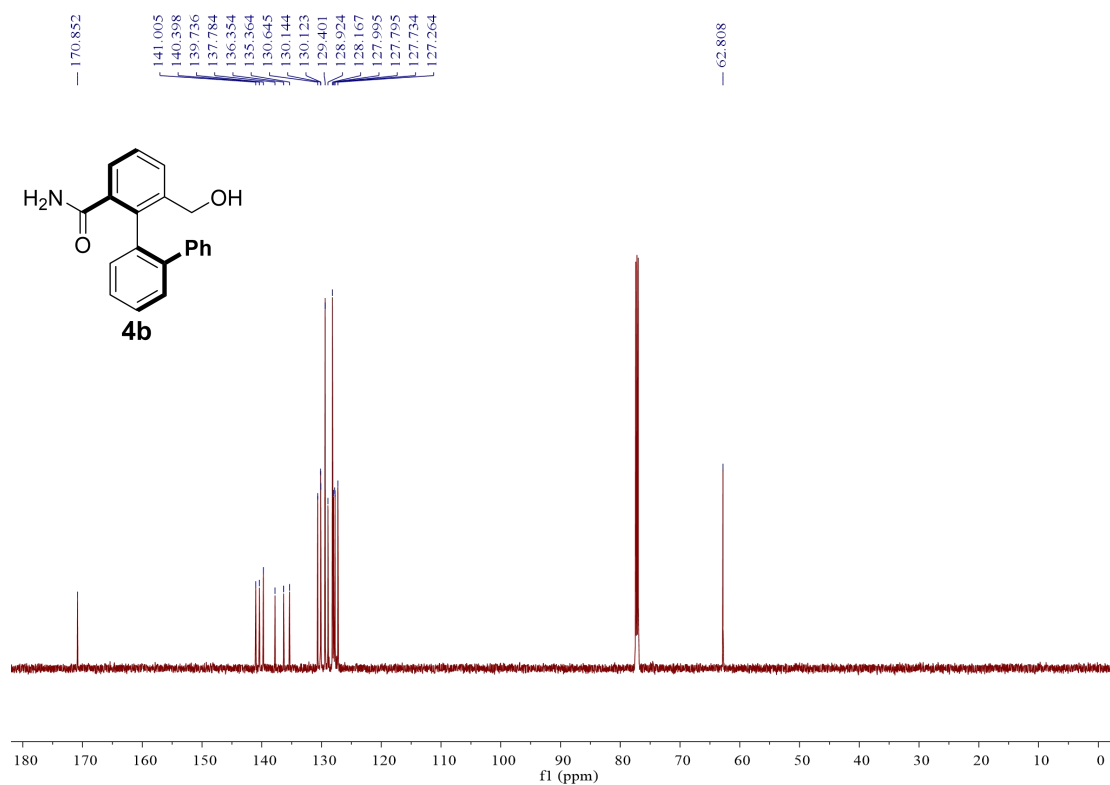
¹H NMR (500 MHz, CDCl₃) spectrum of 4a.



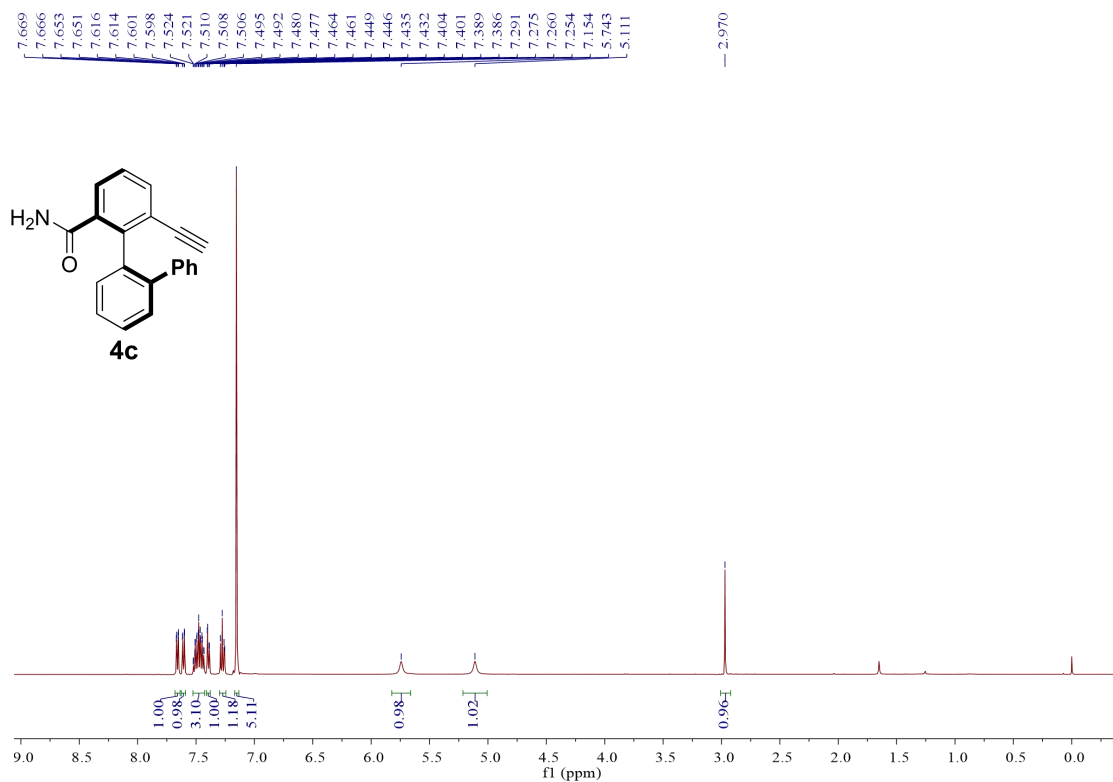
¹³C NMR (150 MHz, CDCl₃) spectrum of 4a.



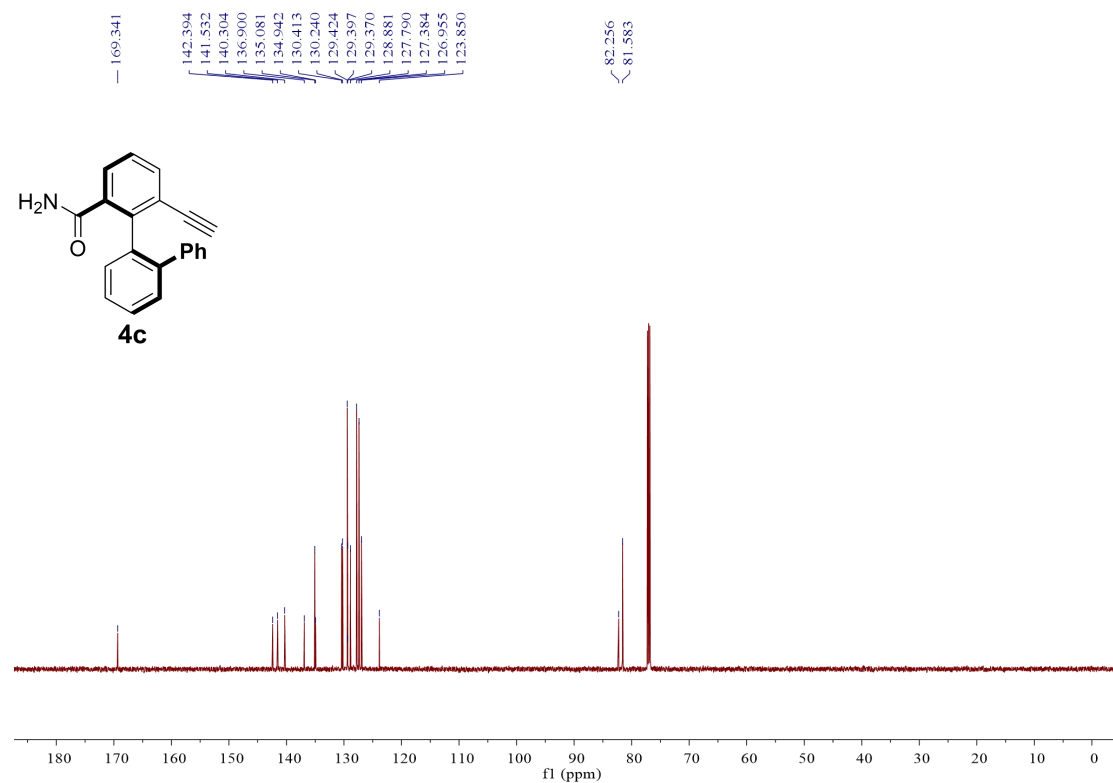
¹H NMR (500 MHz, CDCl₃) spectrum of 4b.



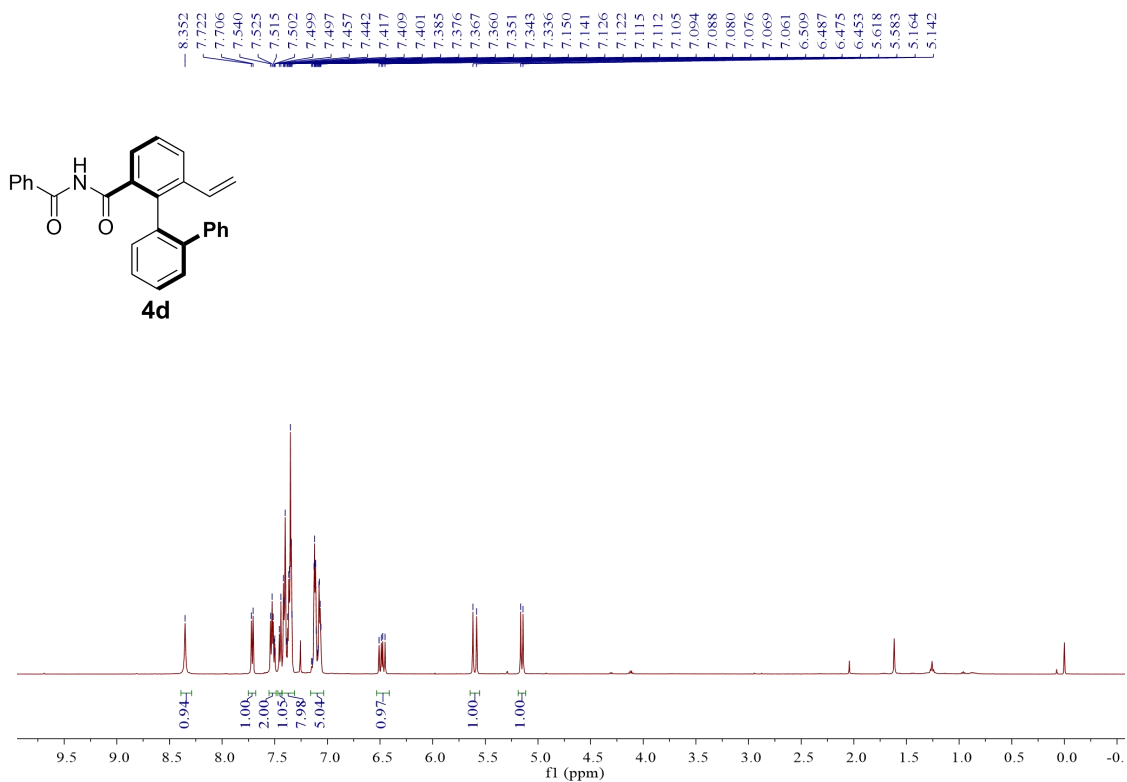
¹³C NMR (150 MHz, CDCl₃) spectrum of 4b.



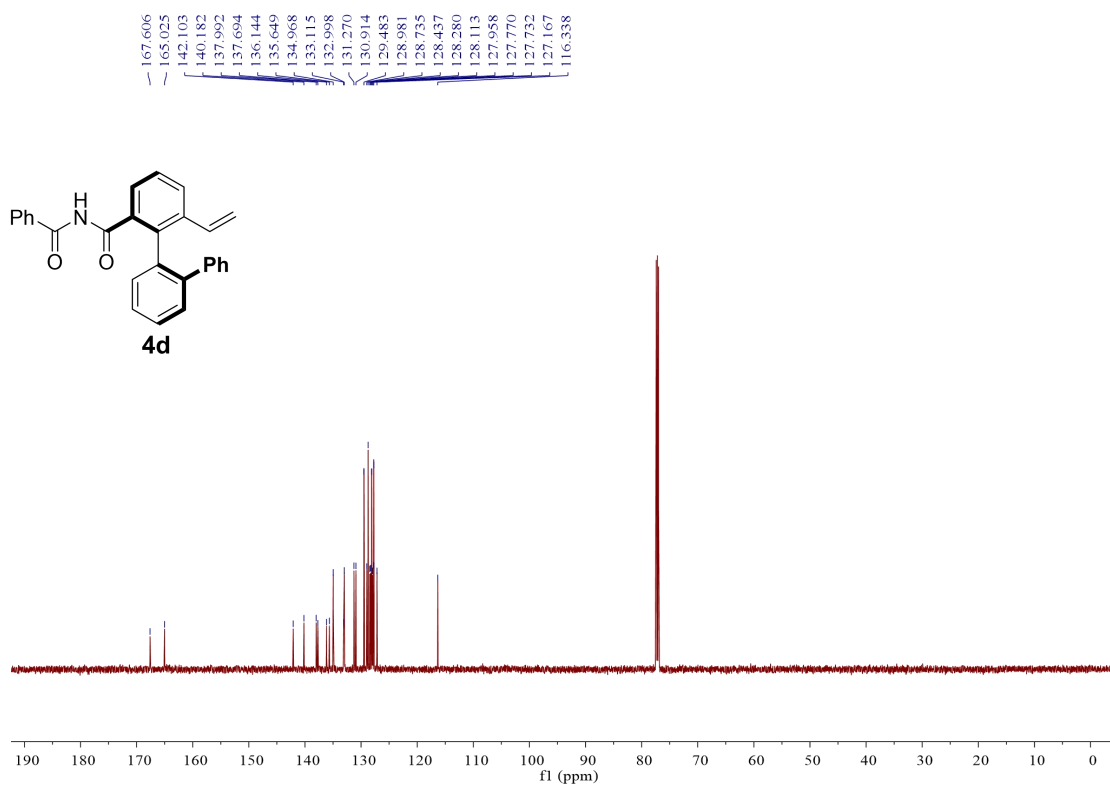
¹H NMR (500 MHz, CDCl₃) spectrum of 4c.



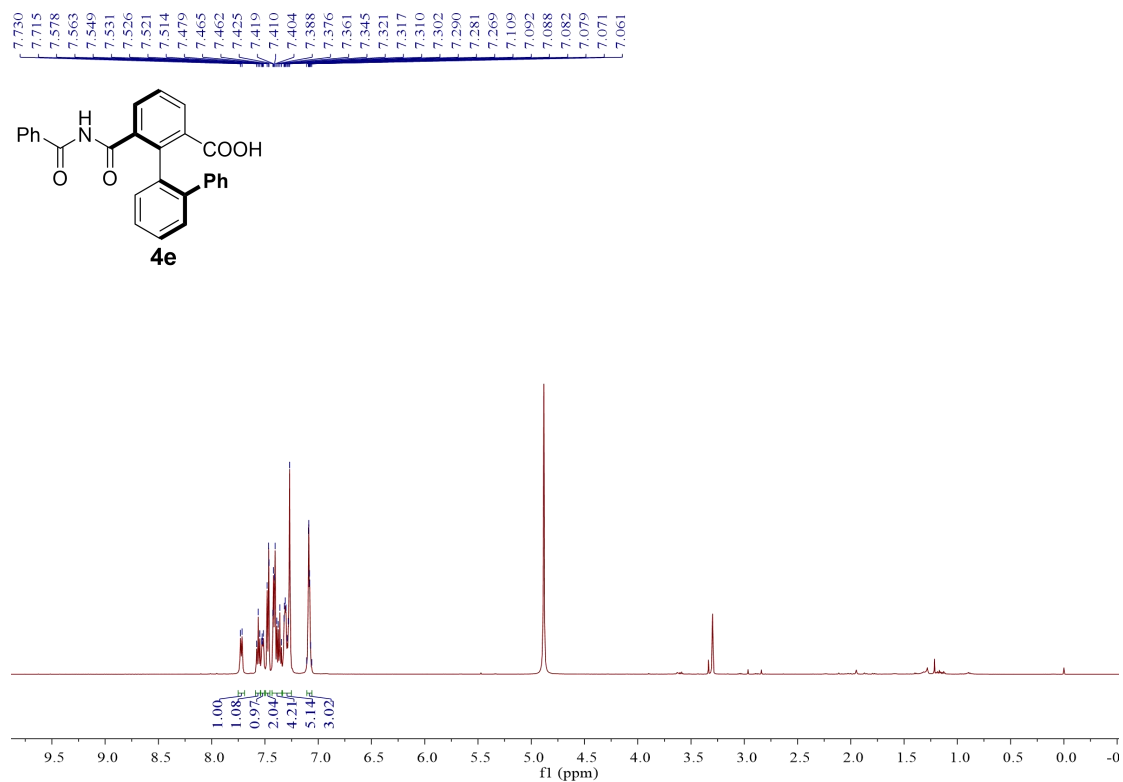
¹³C NMR (150 MHz, CDCl₃) spectrum of 4c.



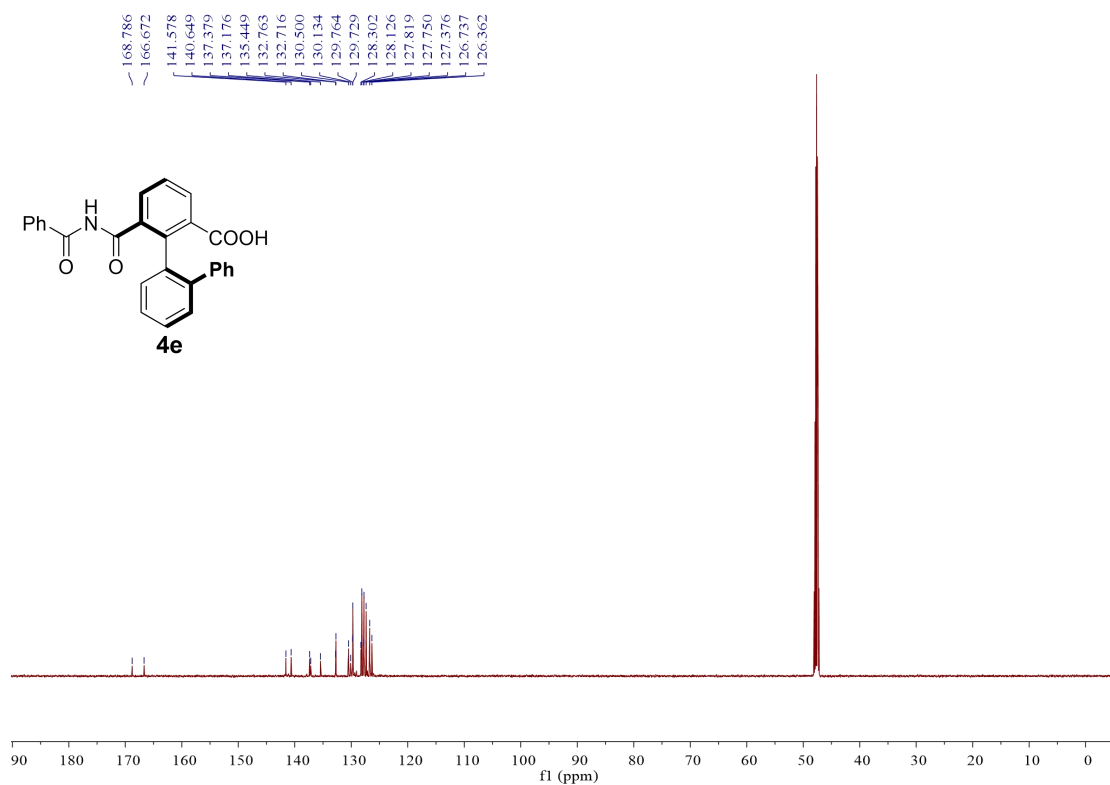
^1H NMR (500 MHz, CDCl_3) spectrum of **4d**.



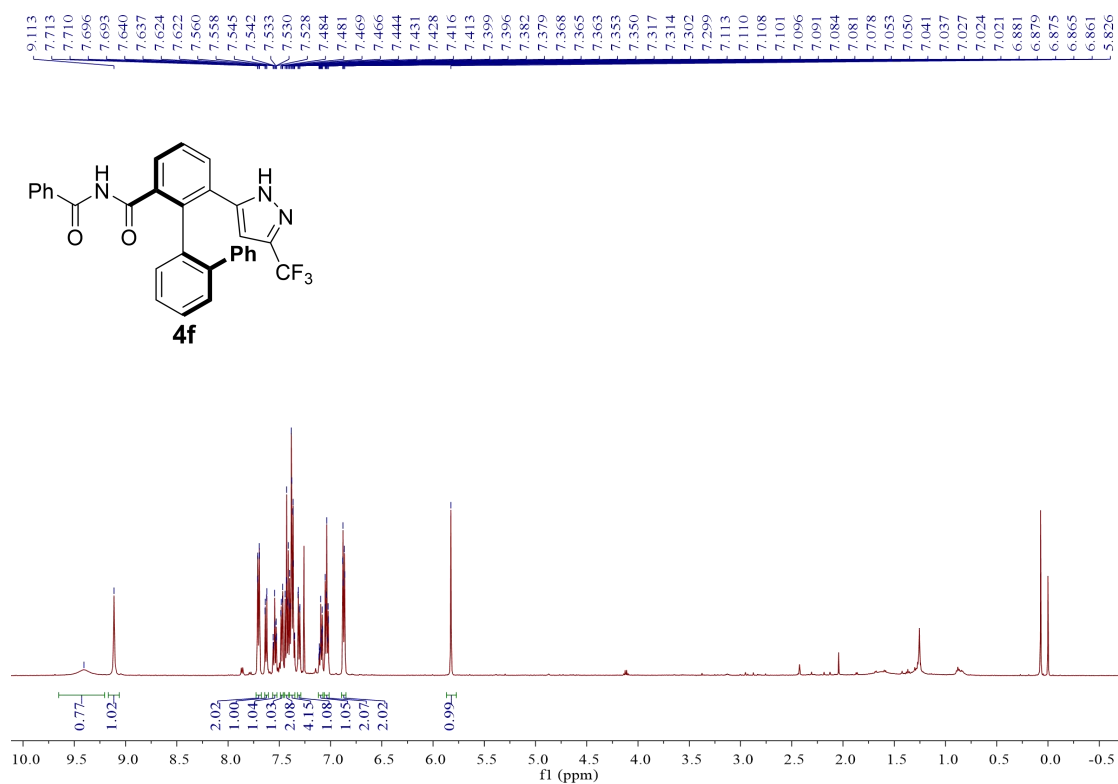
^{13}C NMR (150 MHz, CDCl_3) spectrum of **4d**.



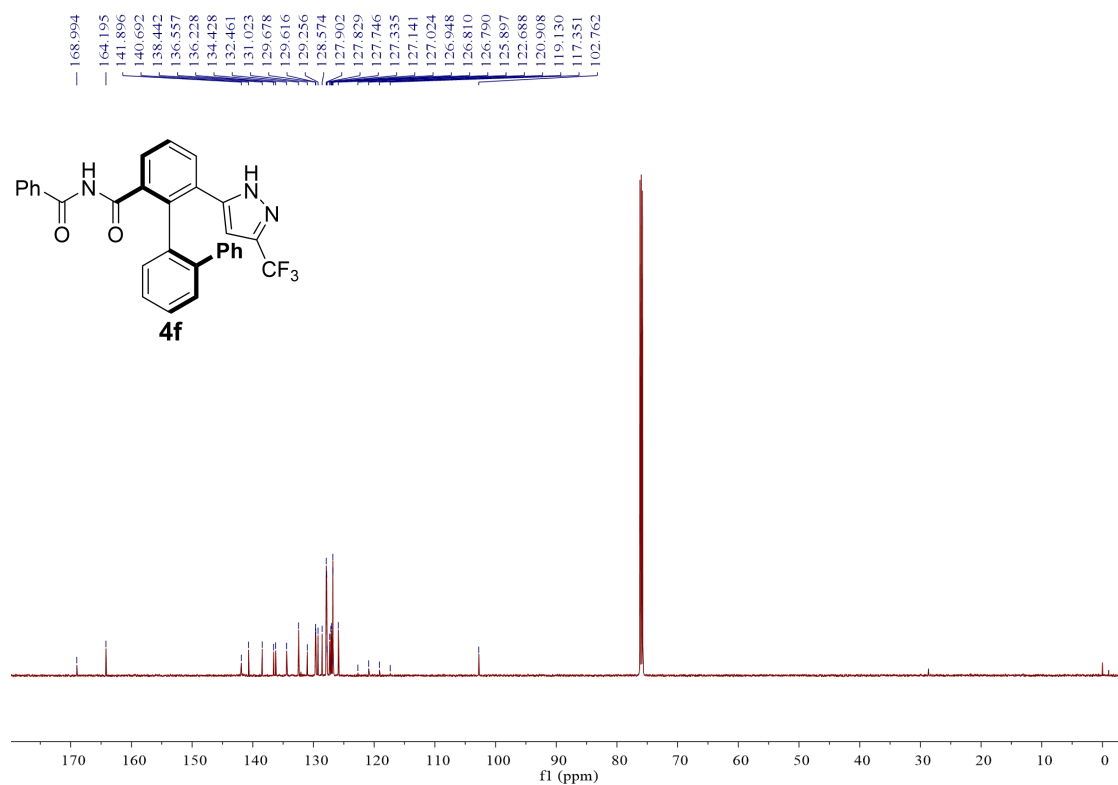
¹H NMR (500 MHz, Methanol-*d*₄) spectrum of 4e.



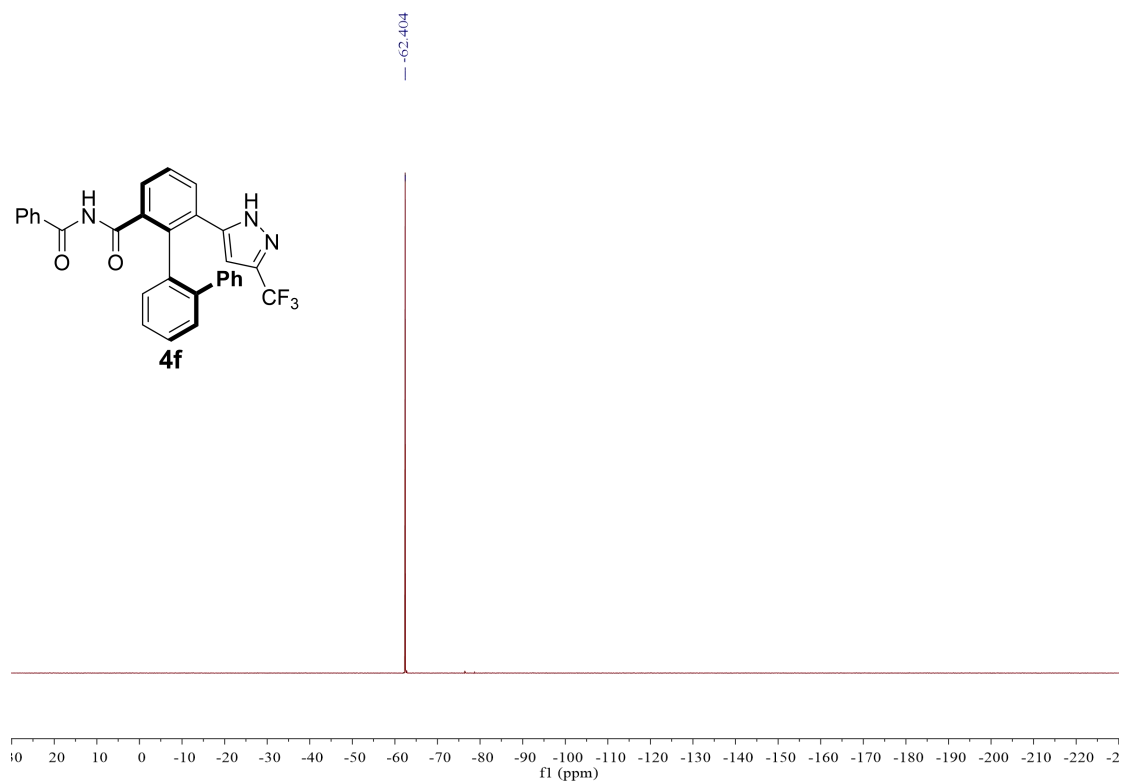
¹³C NMR (150 MHz, Methanol-*d*₄) spectrum of 4e.

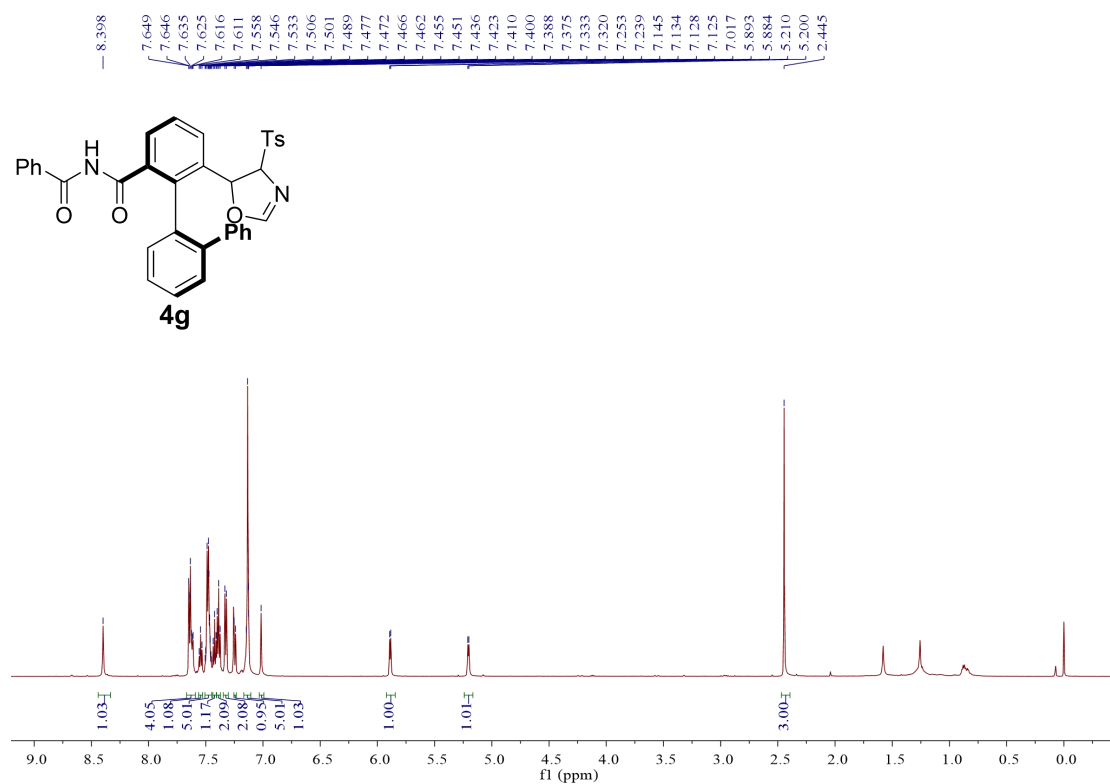


¹H NMR (500 MHz, CDCl₃) spectrum of 4f.

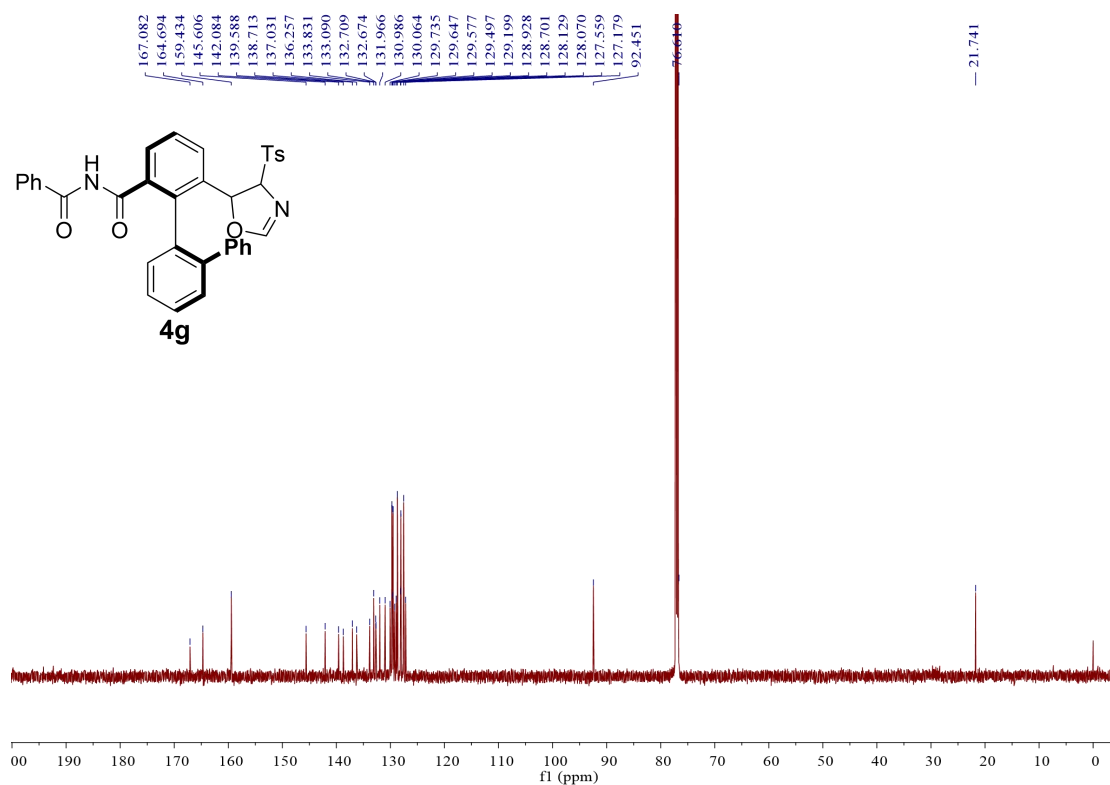


¹³C NMR (150 MHz, CDCl₃) spectrum of 4f.

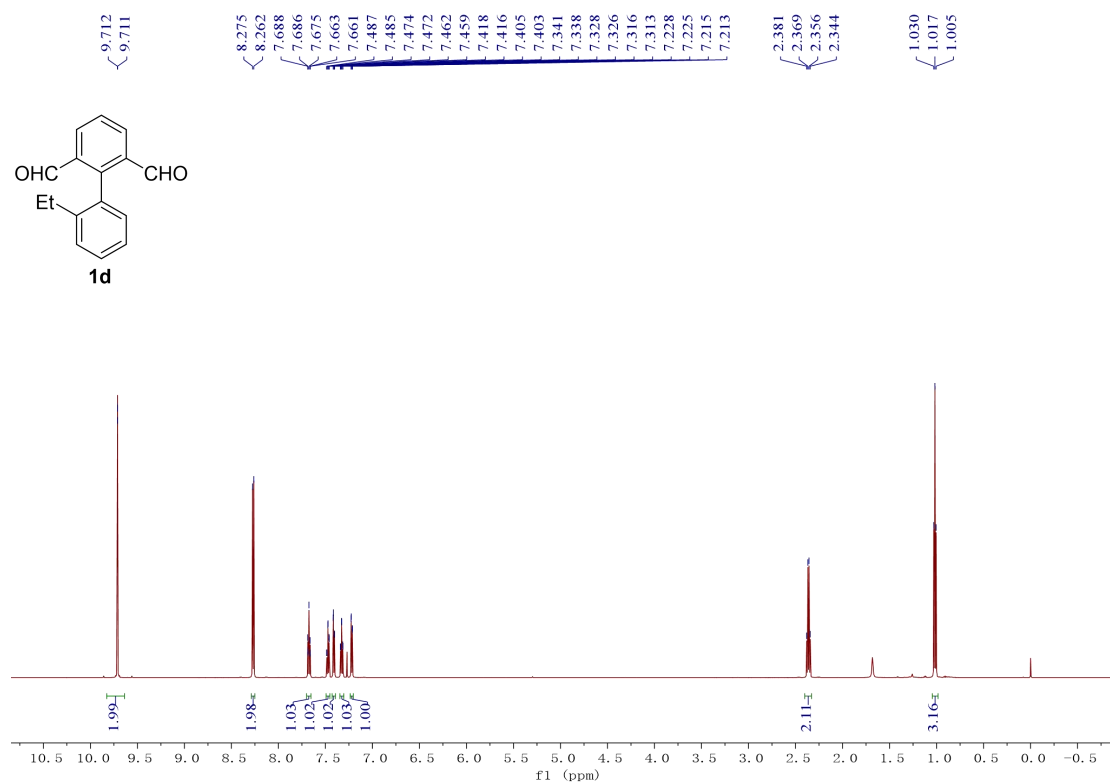




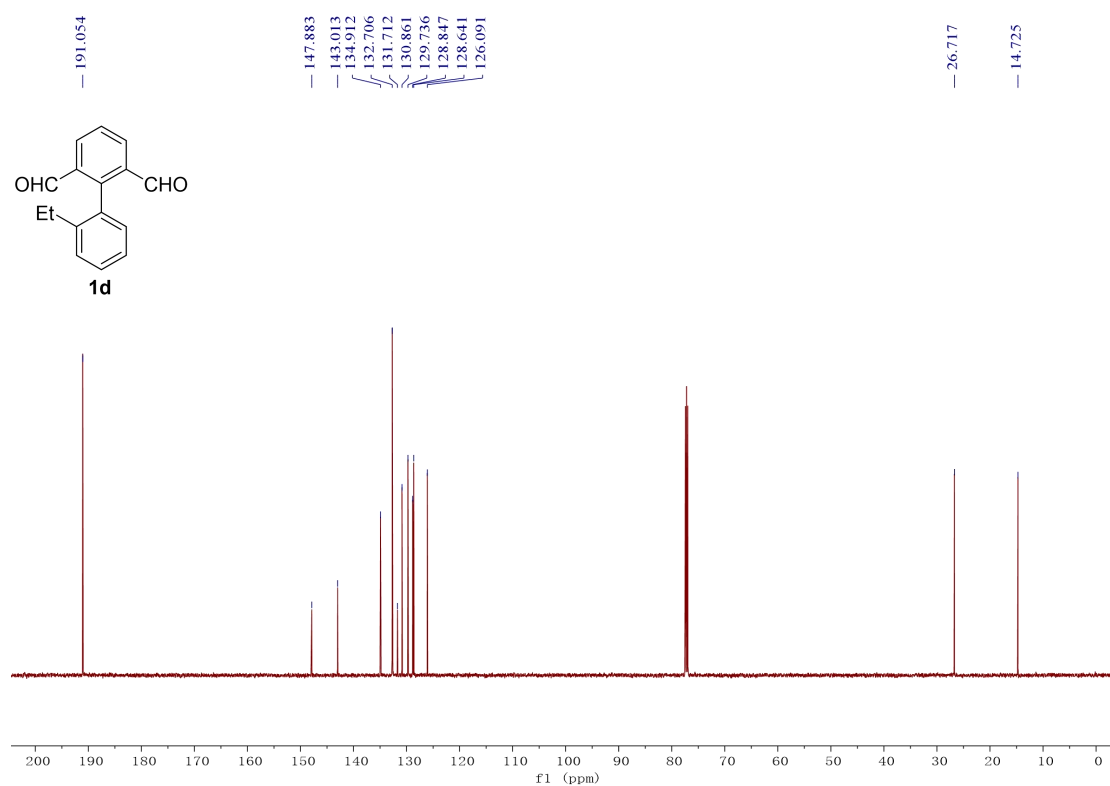
^1H NMR (500 MHz, CDCl_3) spectrum of **4g**.



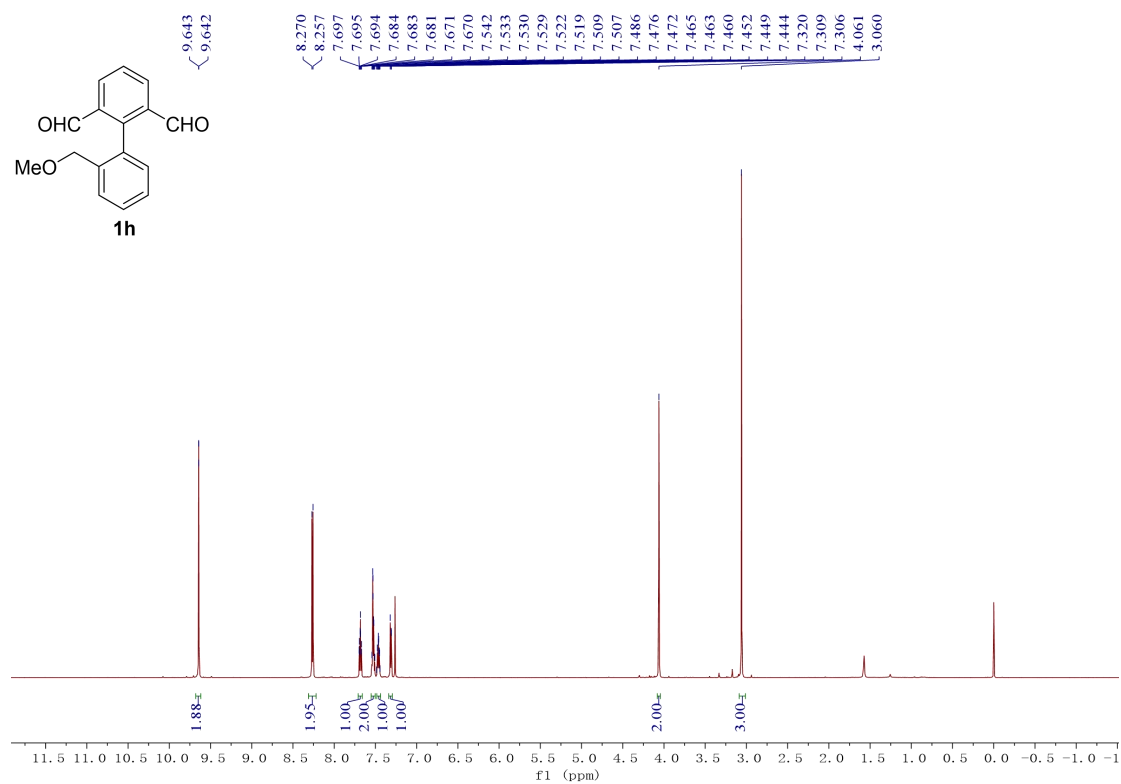
^{13}C NMR (150 MHz, CDCl_3) spectrum of **4g**.



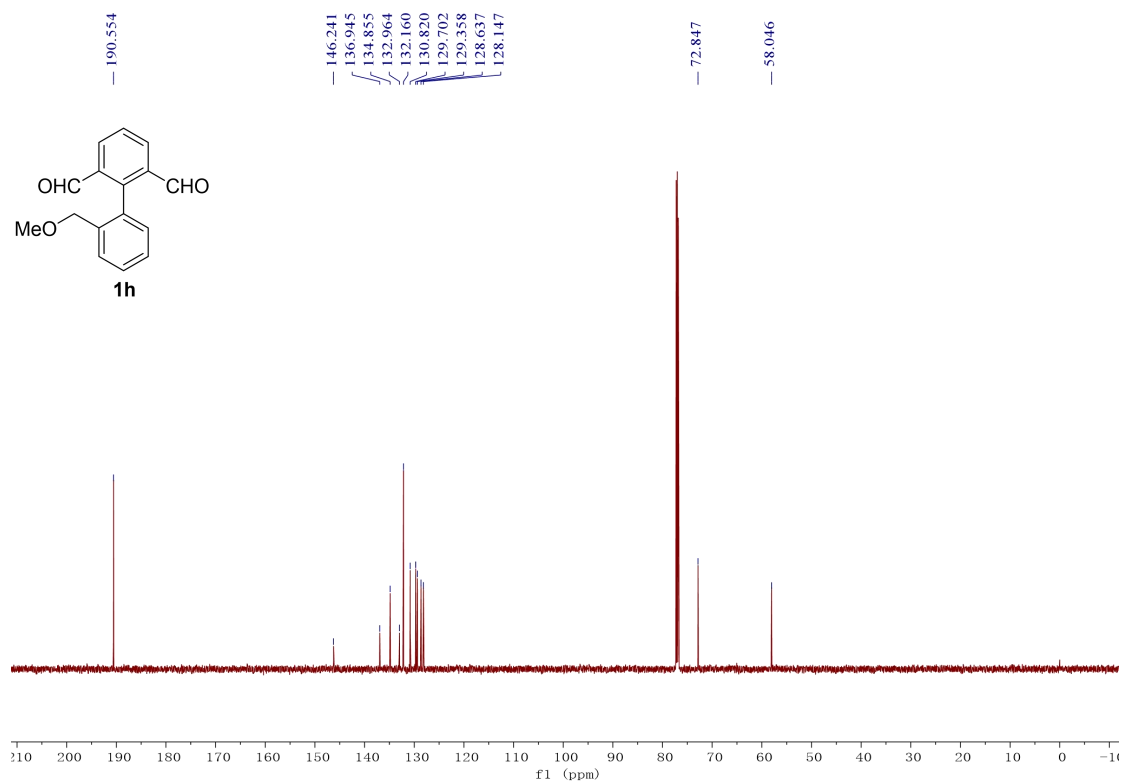
^1H NMR (600 MHz, CDCl_3) spectrum of **1d**.



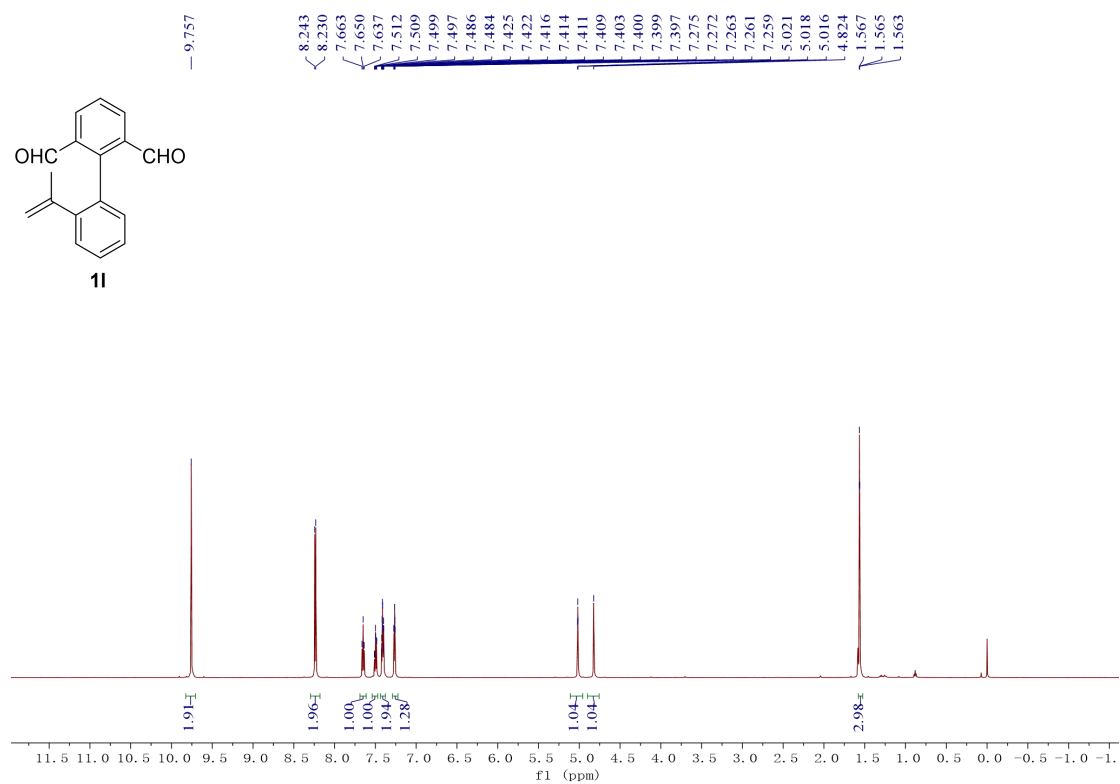
^{13}C NMR (150 MHz, CDCl_3) spectrum of **1d**.



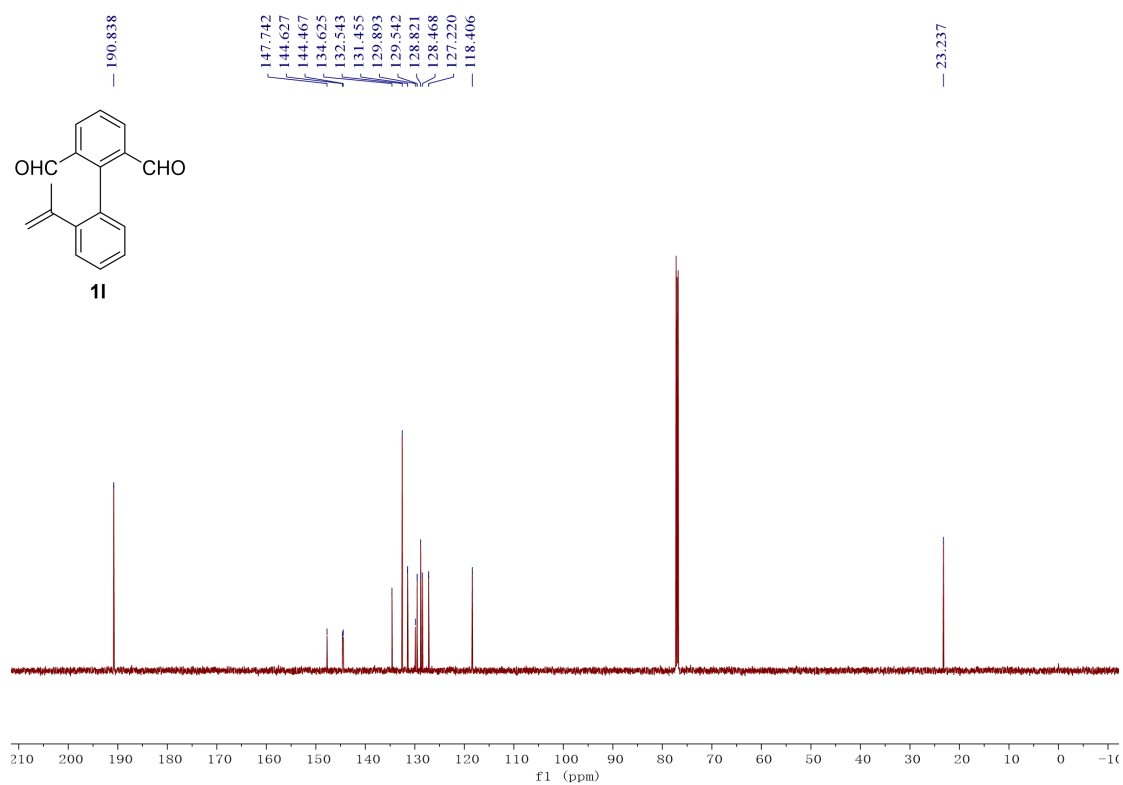
¹H NMR (600 MHz, CDCl₃) spectrum of **1h.**



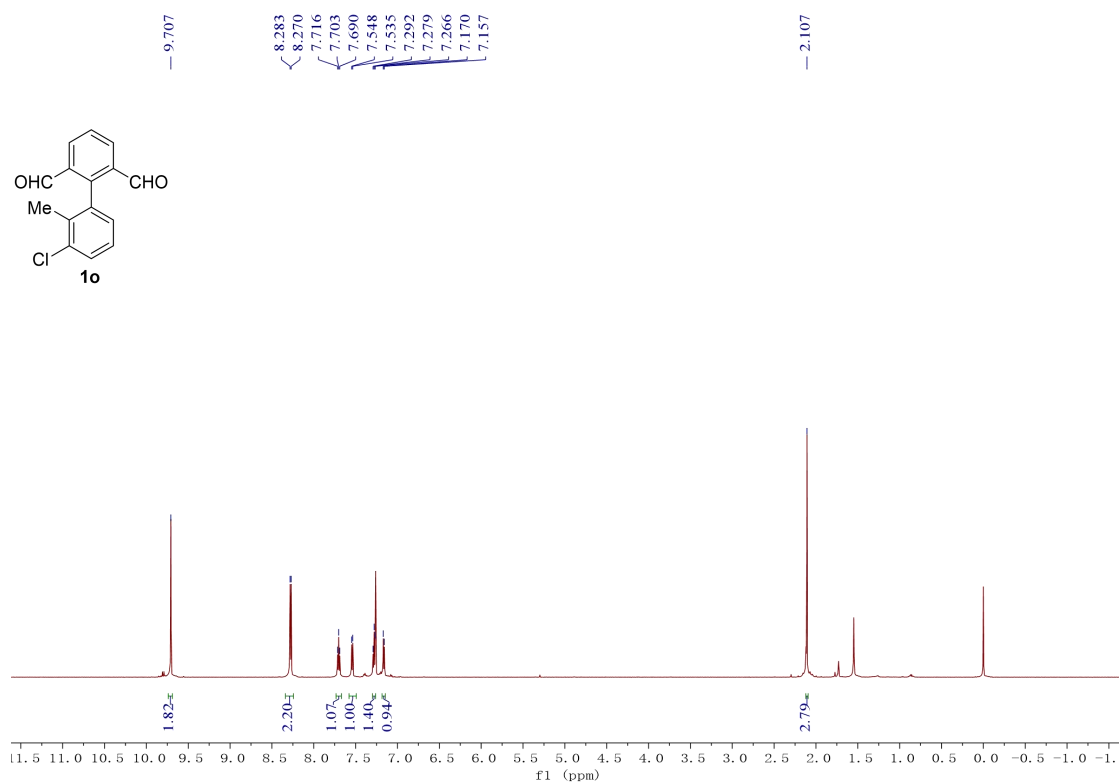
¹³C NMR (150 MHz, CDCl₃) spectrum of **1h.**



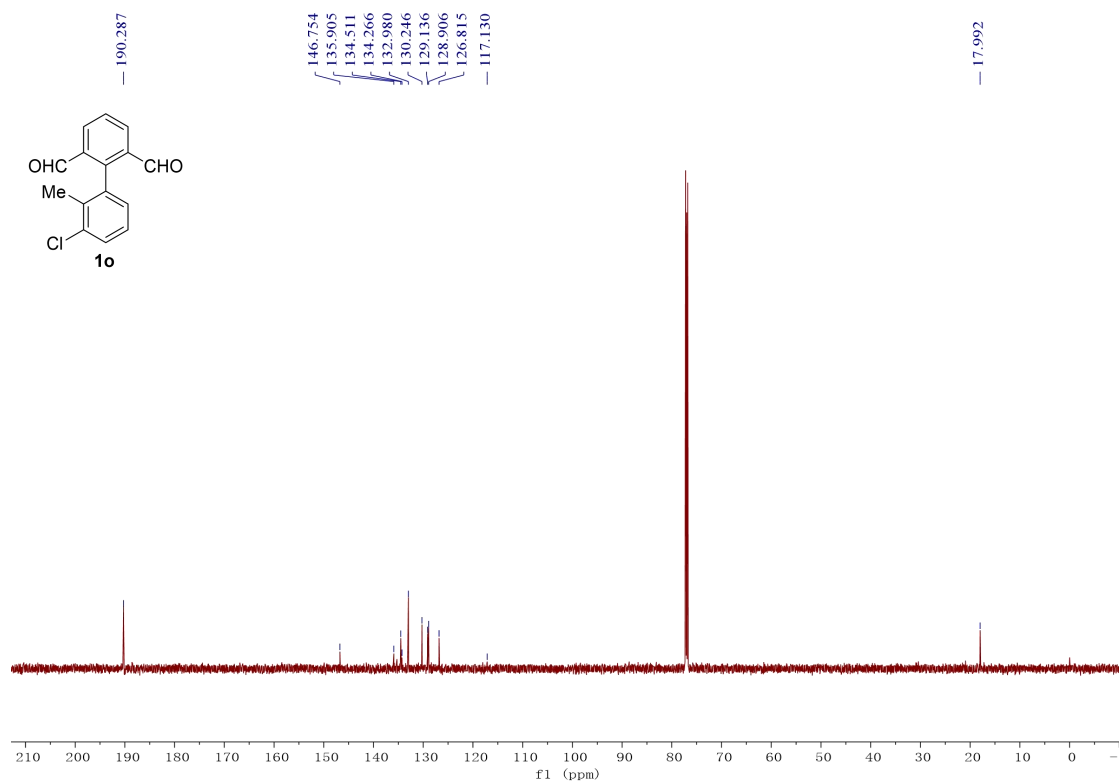
¹H NMR (600 MHz, CDCl₃) spectrum of **1l.**



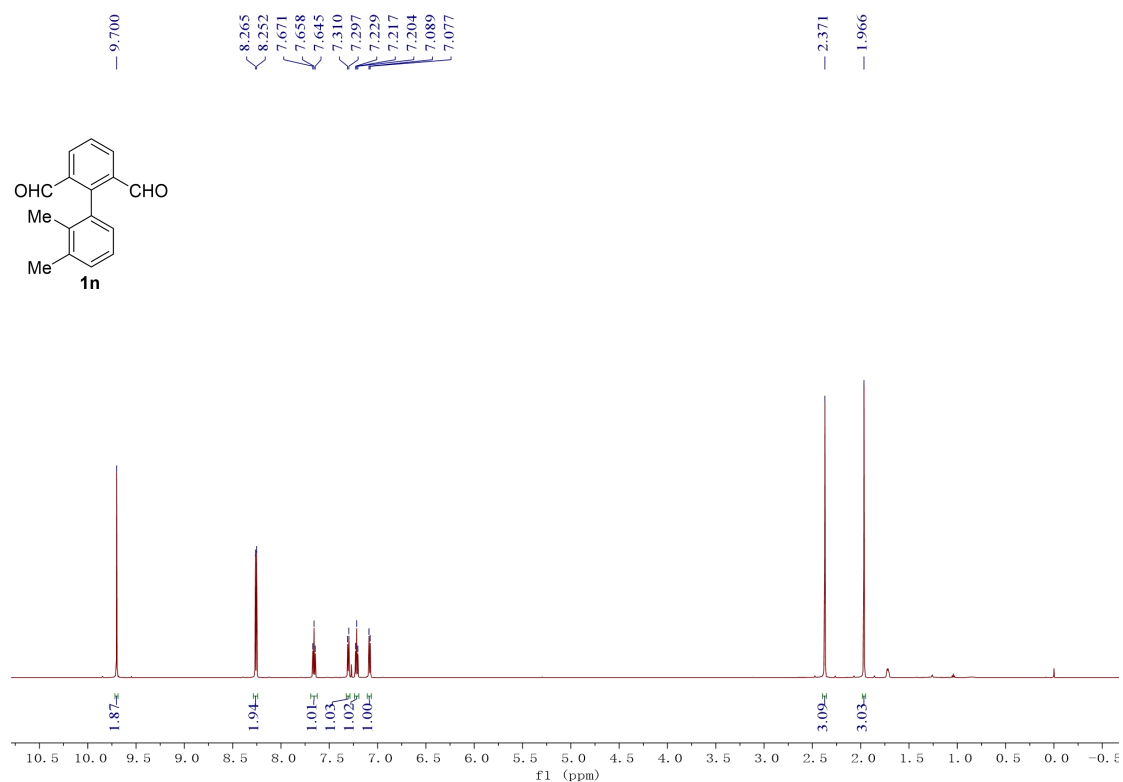
¹³C NMR (150 MHz, CDCl₃) spectrum of **1l.**



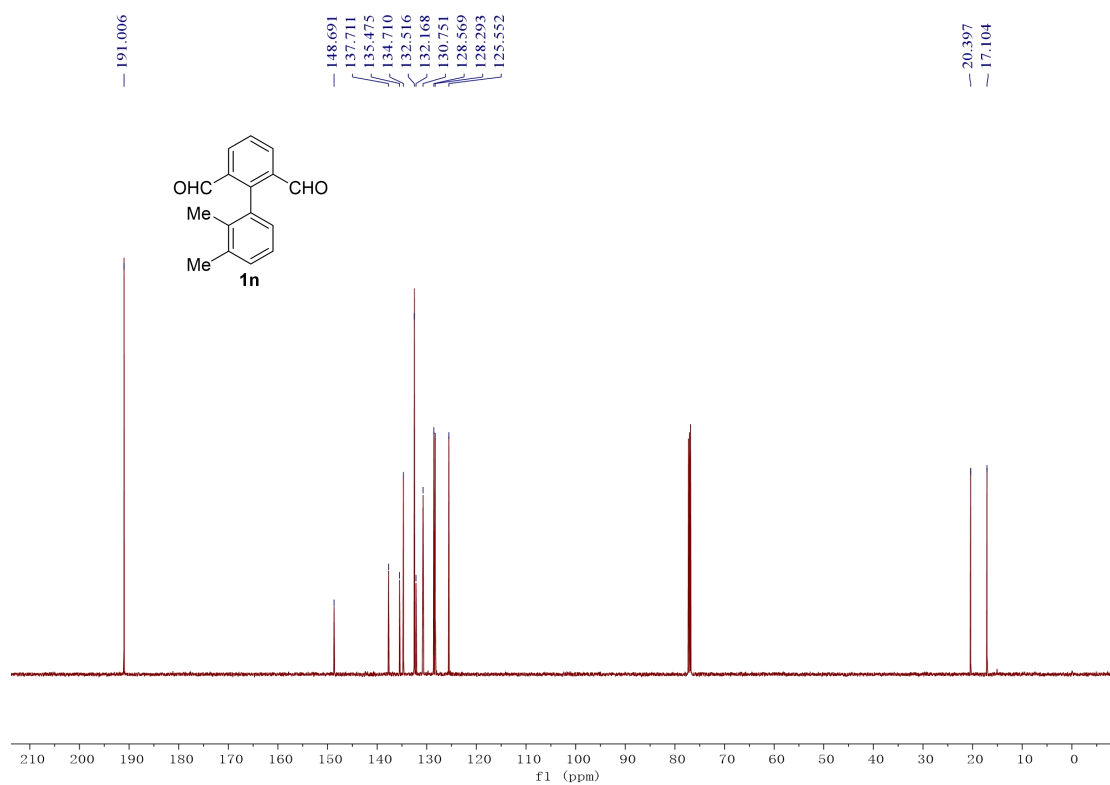
¹H NMR (600 MHz, CDCl₃) spectrum of 1o.



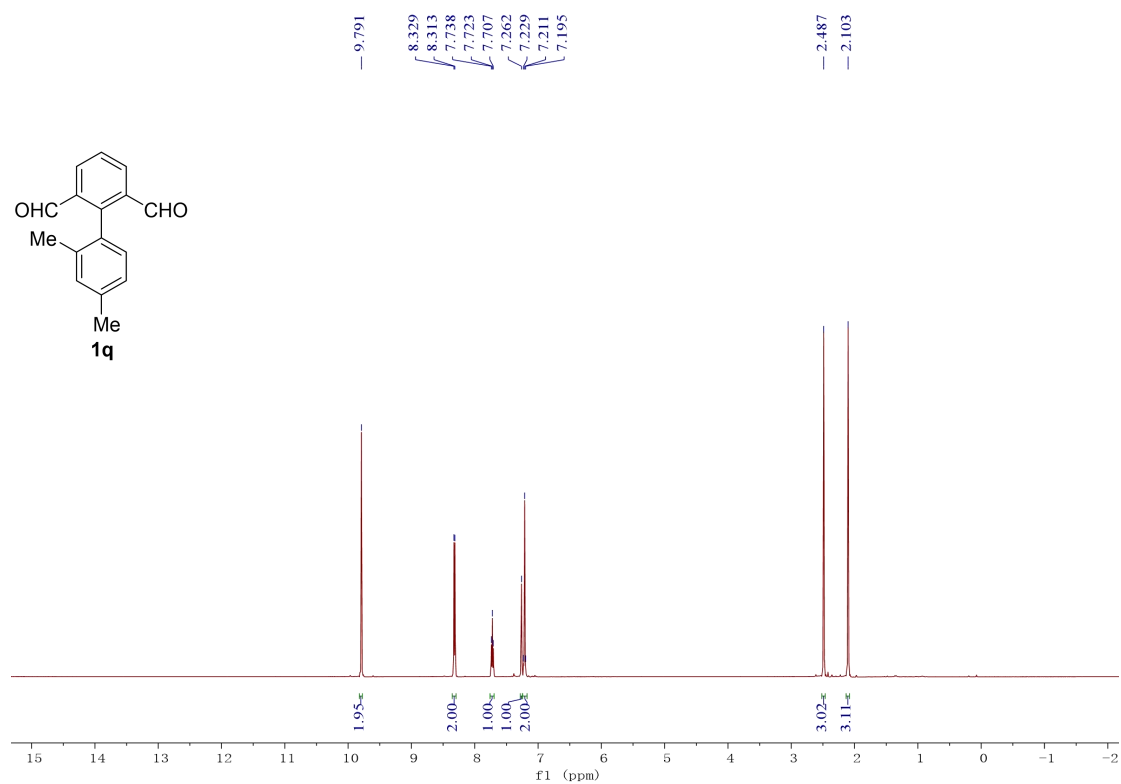
¹³C NMR (150 MHz, CDCl₃) spectrum of 1o.



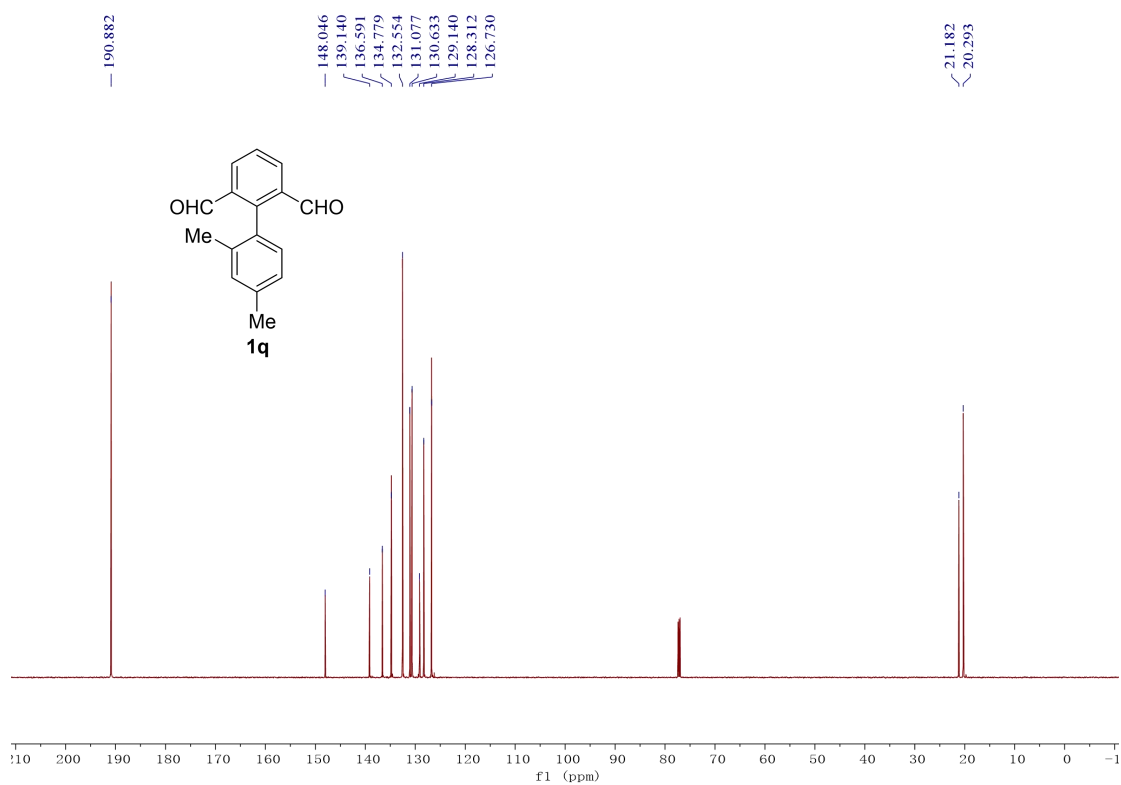
^1H NMR (600 MHz, CDCl_3) spectrum of **1n**.



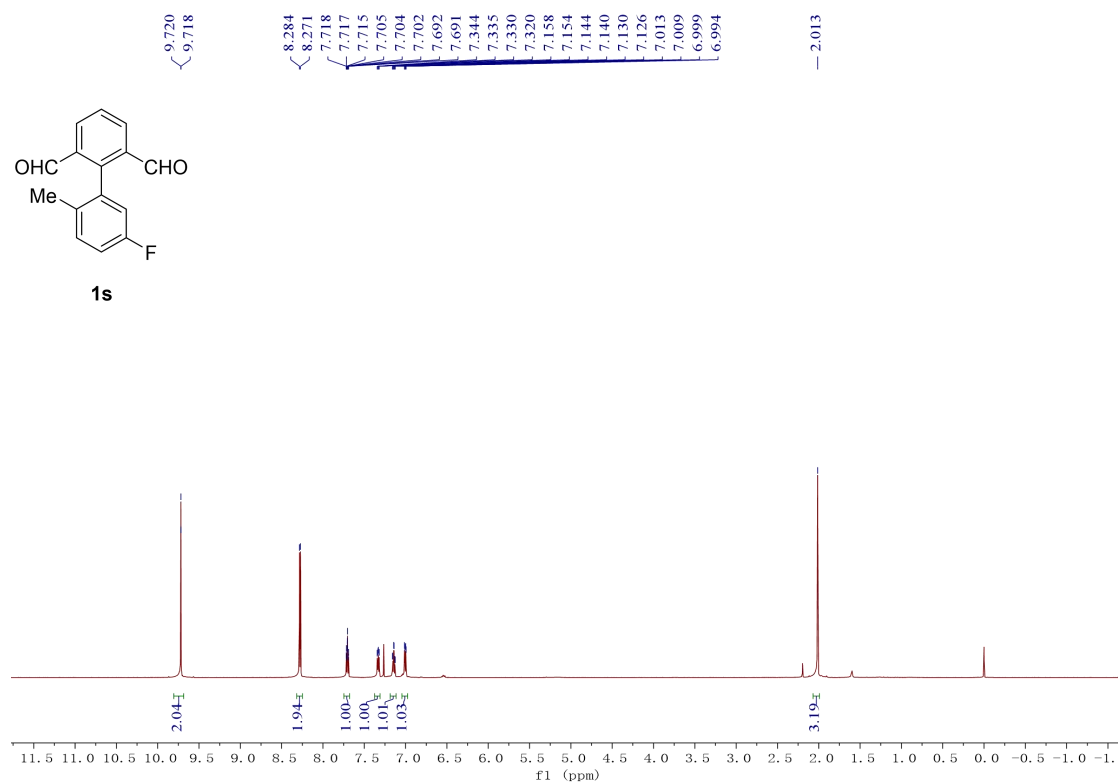
^{13}C NMR (150 MHz, CDCl_3) spectrum of **1n**.



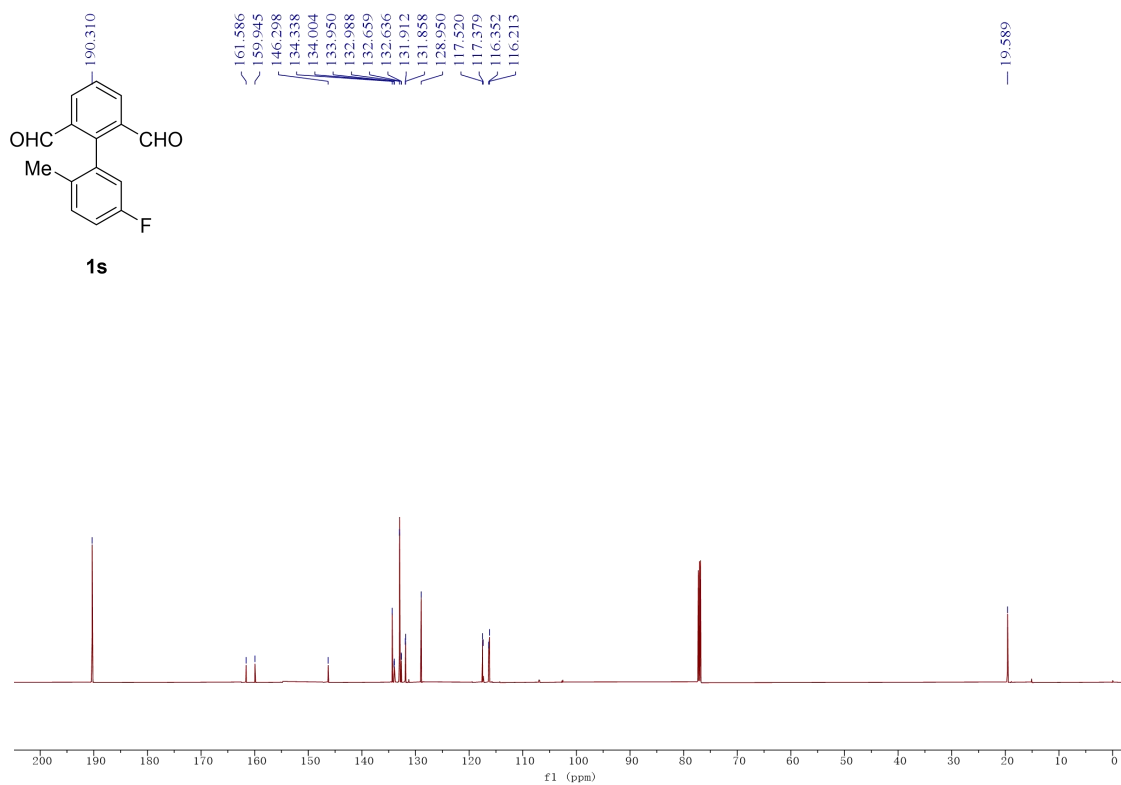
¹H NMR (500 MHz, CDCl₃) spectrum of 1q.



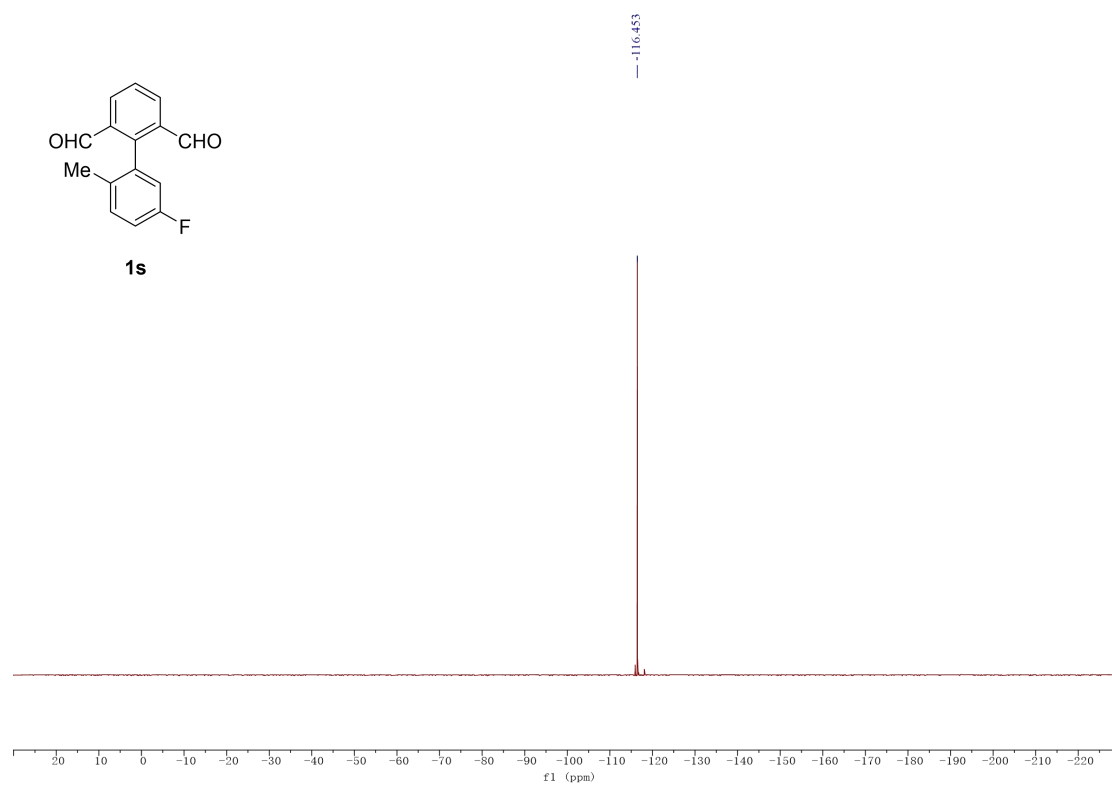
¹³C NMR (150 MHz, CDCl₃) spectrum of 1q.



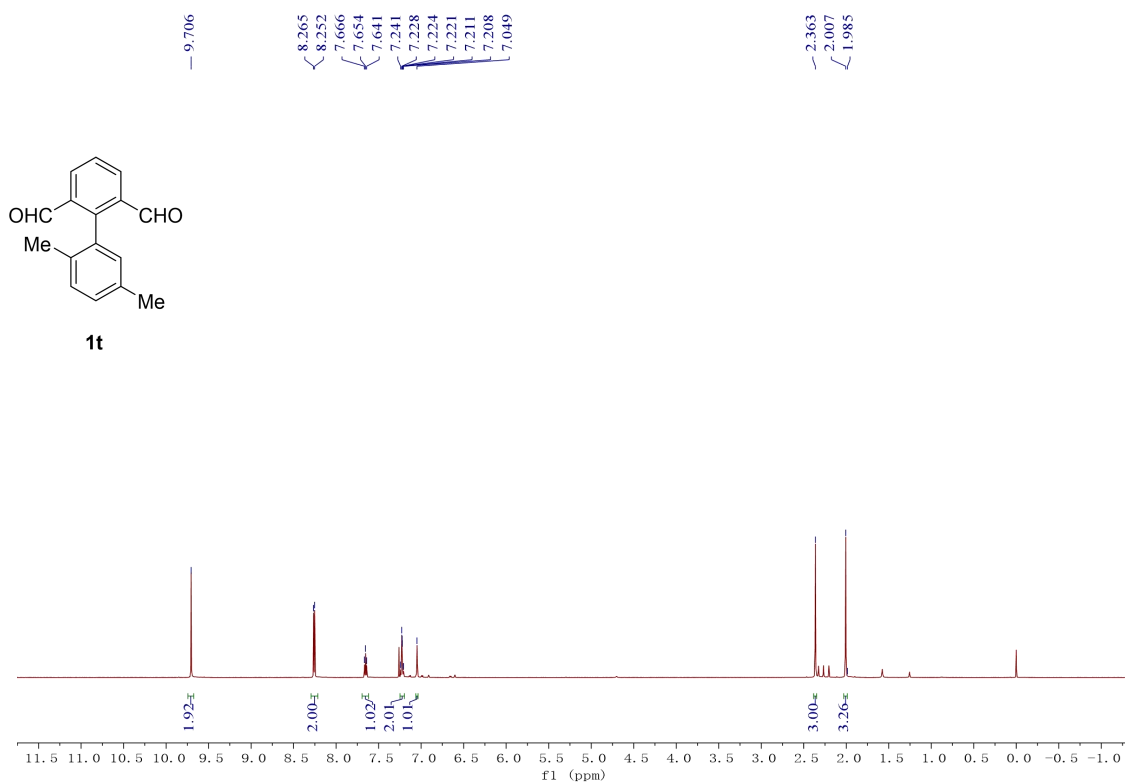
¹H NMR (600 MHz, CDCl₃) spectrum of **1s.**



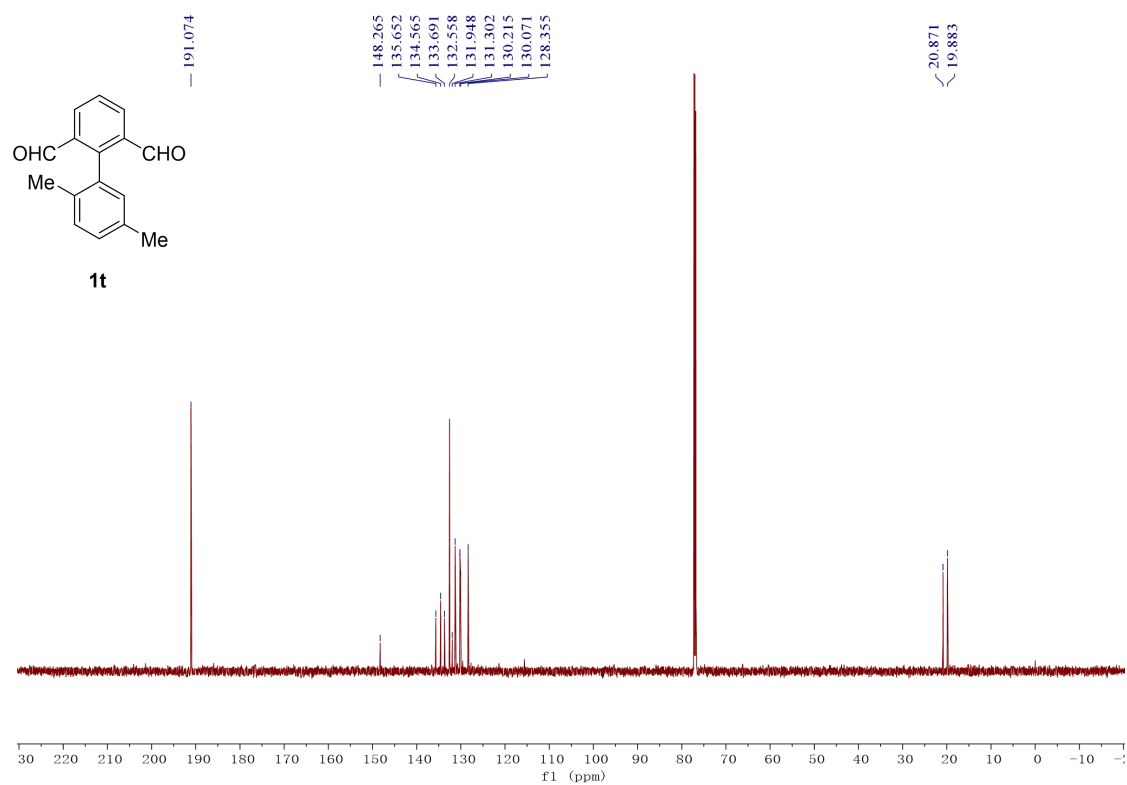
¹³C NMR (150 MHz, CDCl₃) spectrum of **1s.**



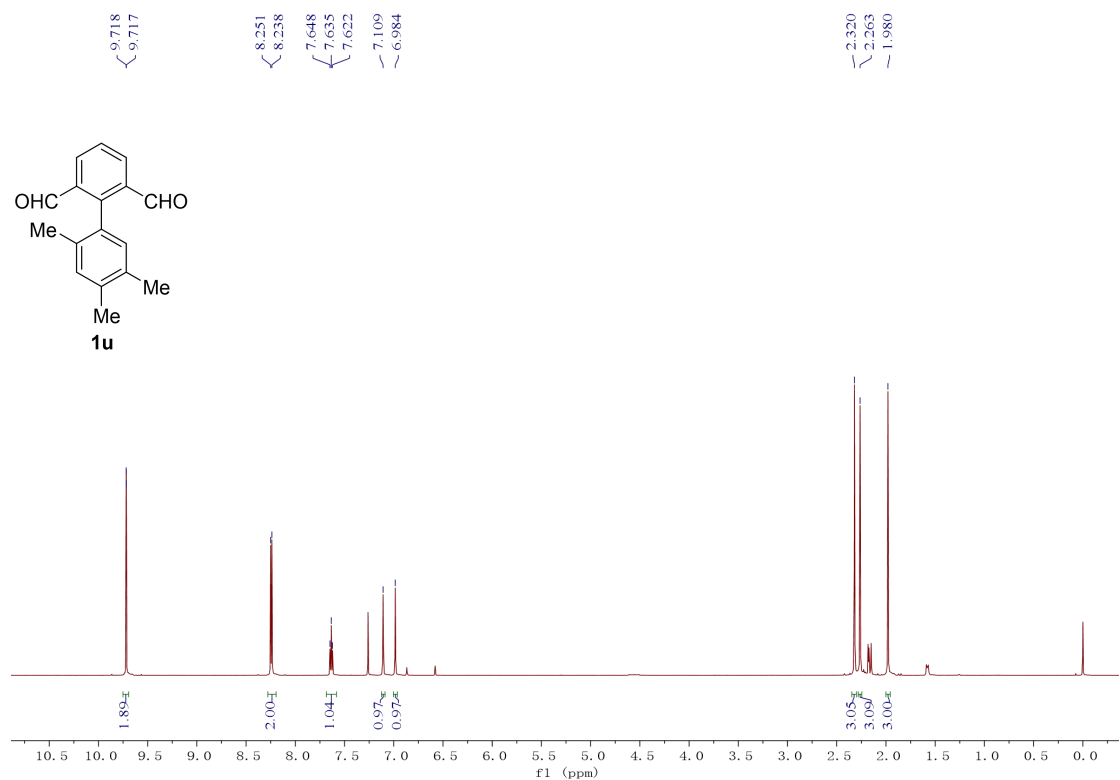
^{19}F NMR (565 MHz, CDCl_3) spectrum of **1s.**



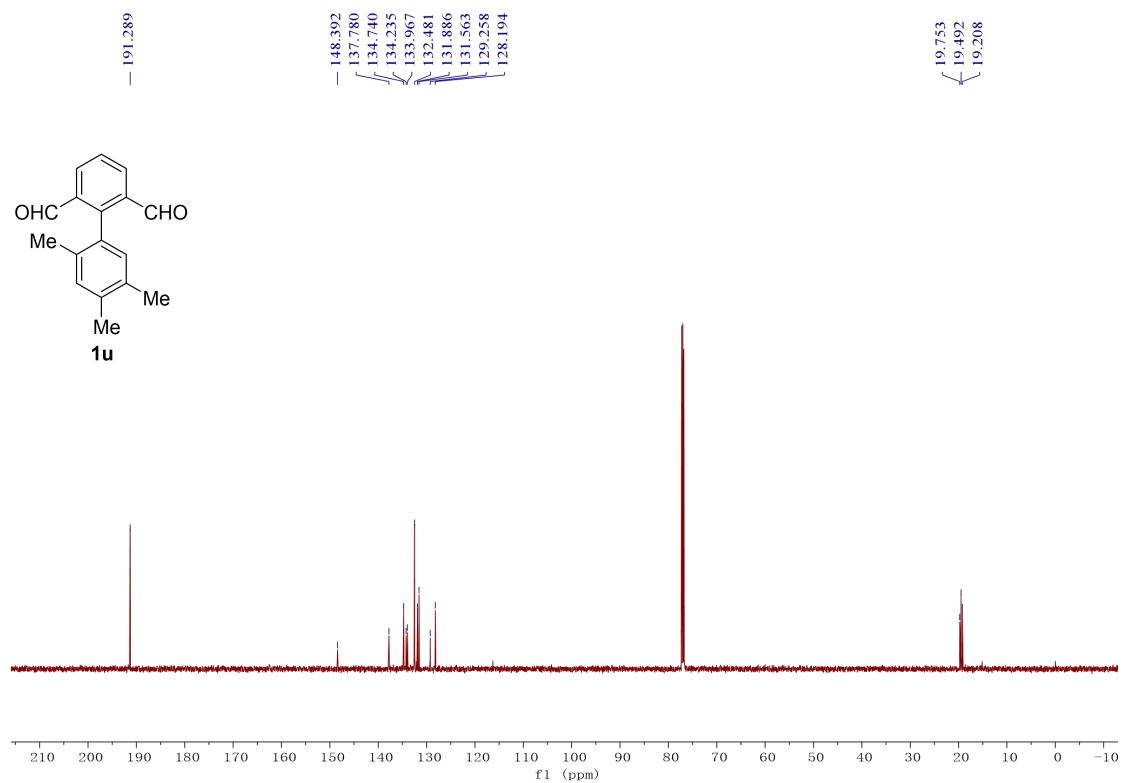
¹H NMR (600 MHz, CDCl₃) spectrum of **1t.**



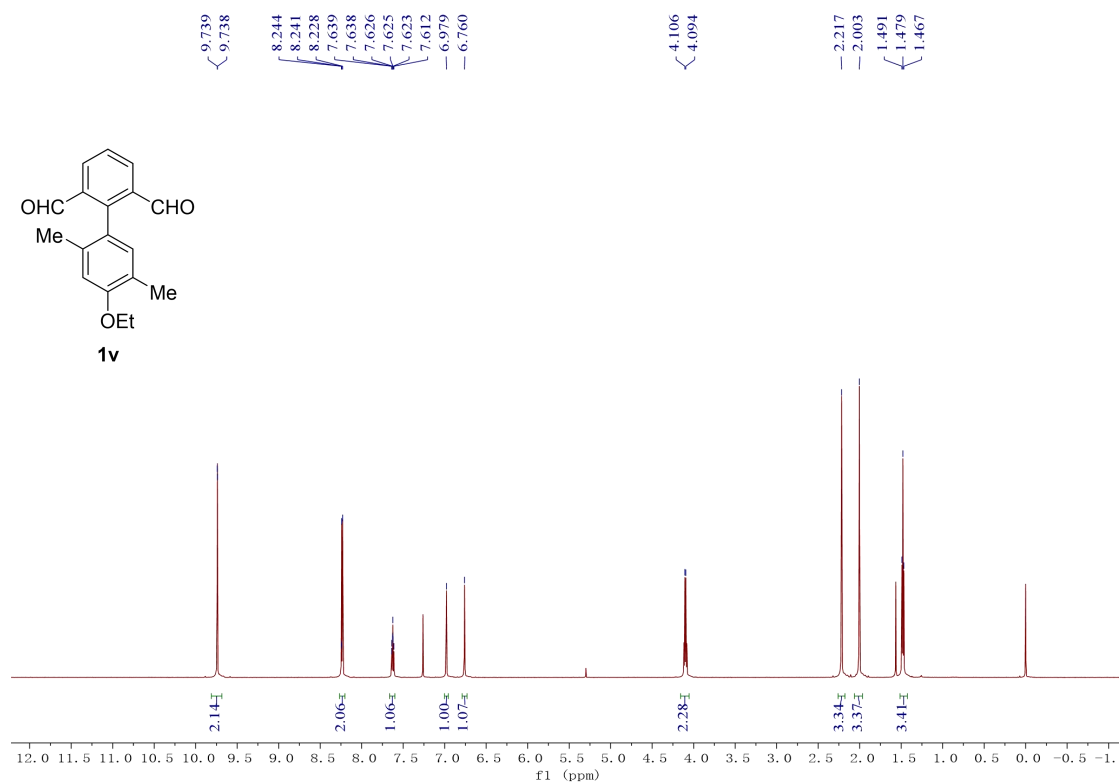
¹³C NMR (150 MHz, CDCl₃) spectrum of **1t.**



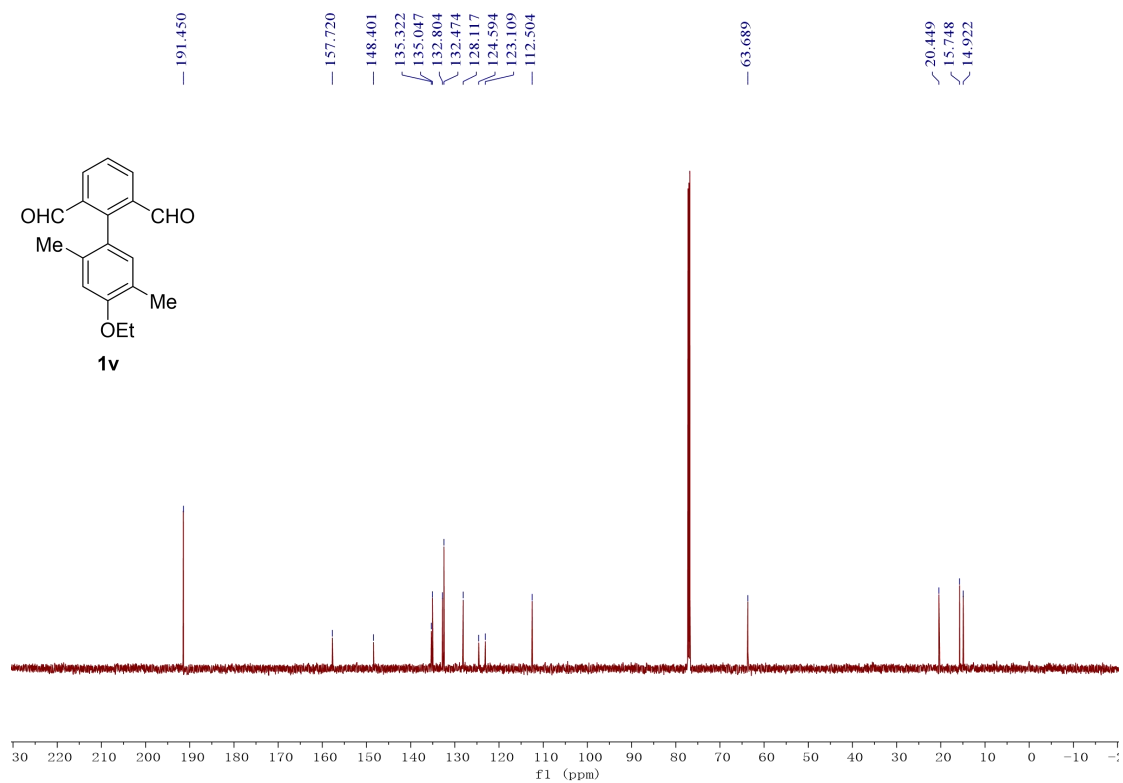
¹H NMR (600 MHz, CDCl₃) spectrum of **1u.**



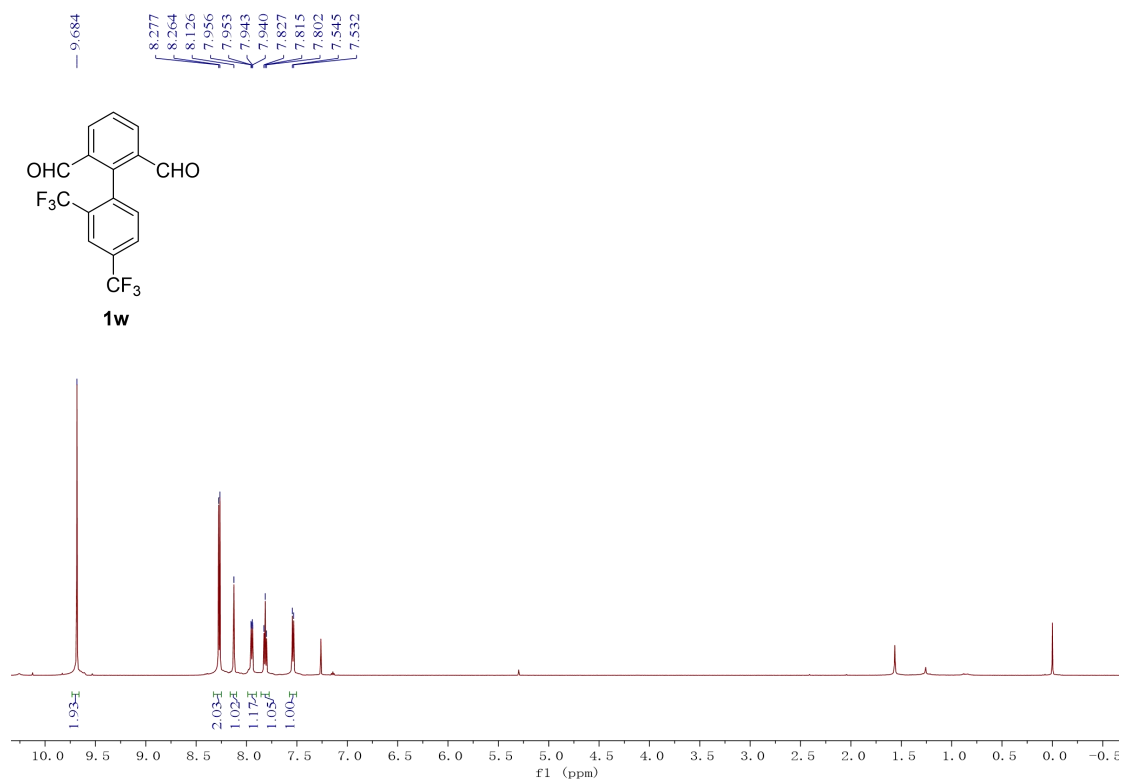
¹³C NMR (150 MHz, CDCl₃) spectrum of **1u.**



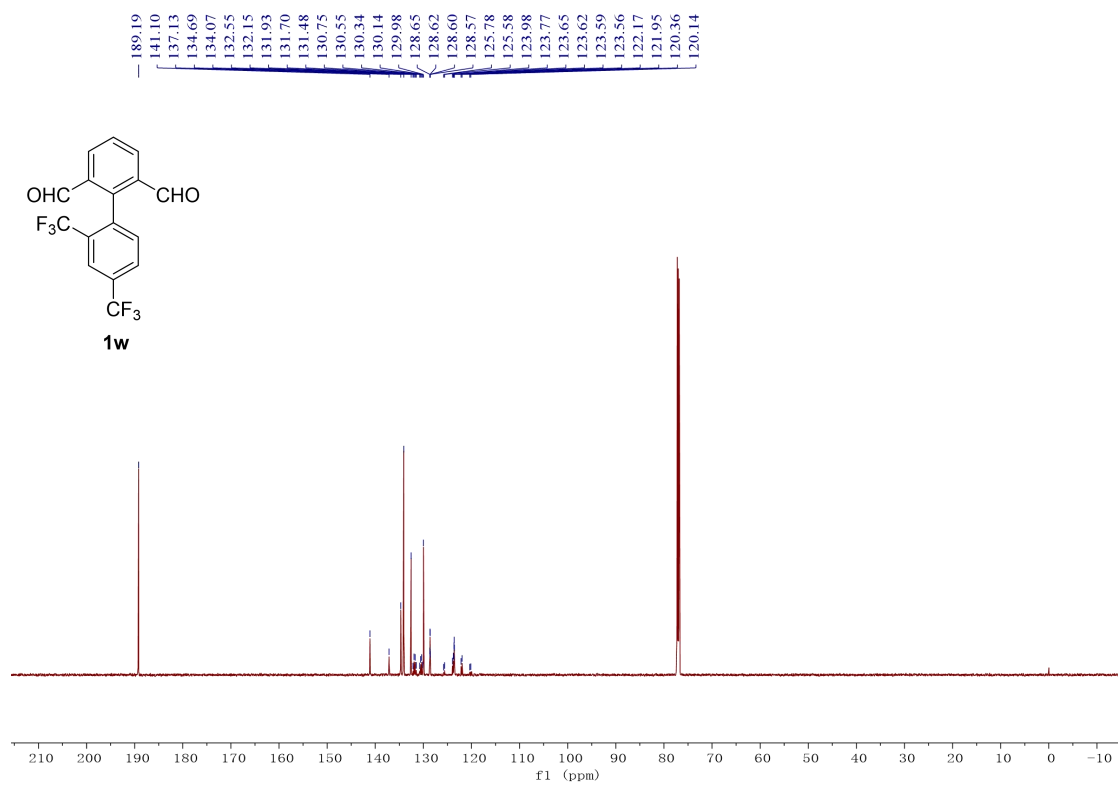
^1H NMR (600 MHz, CDCl_3) spectrum of **1v**.



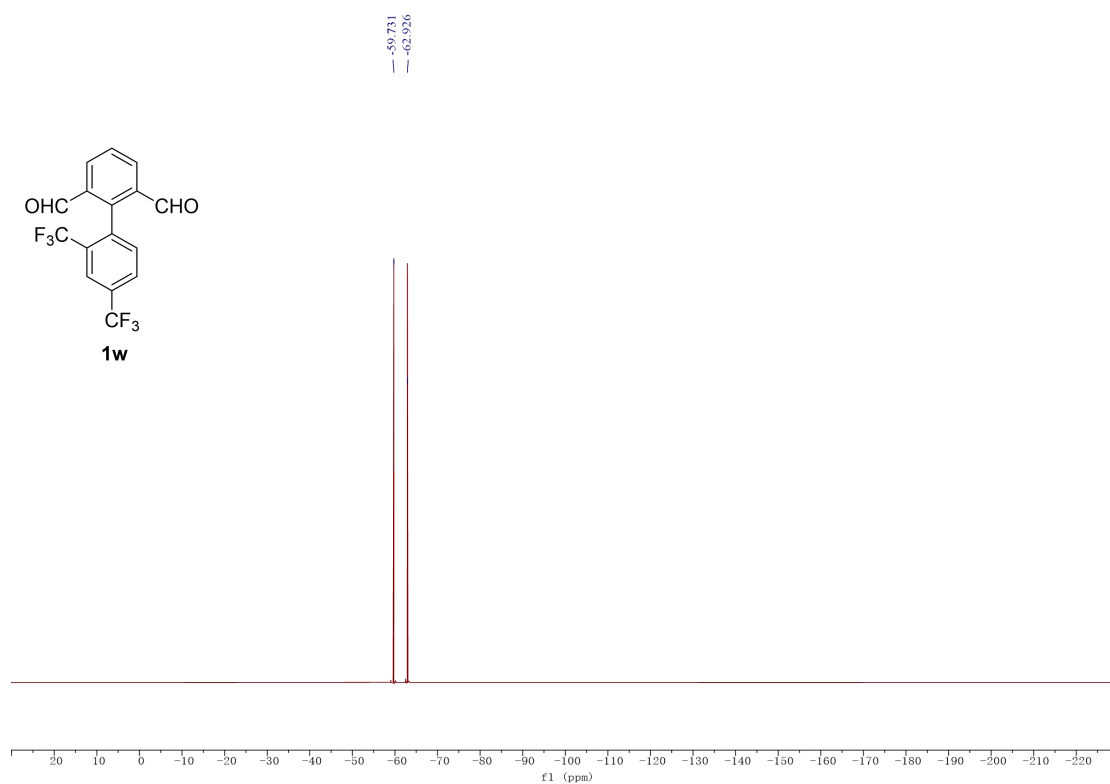
^{13}C NMR (150 MHz, CDCl_3) spectrum of **1v**.

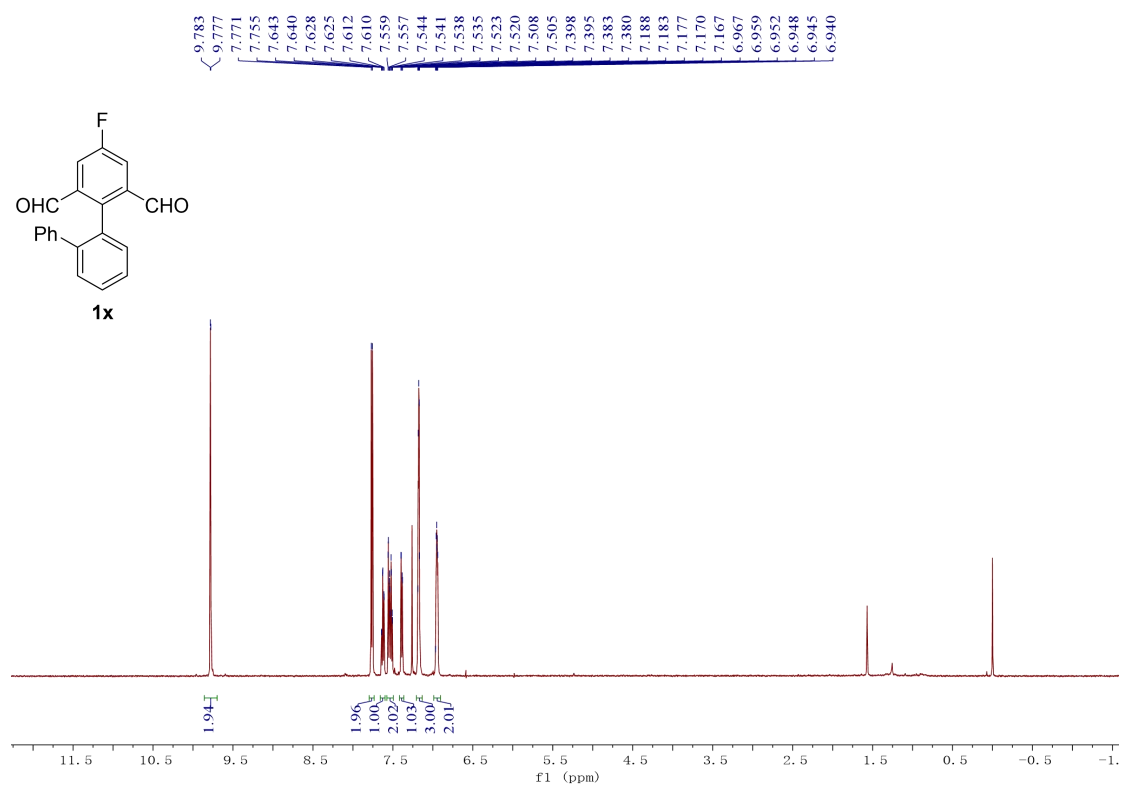


^1H NMR (600 MHz, CDCl_3) spectrum of **1w**.

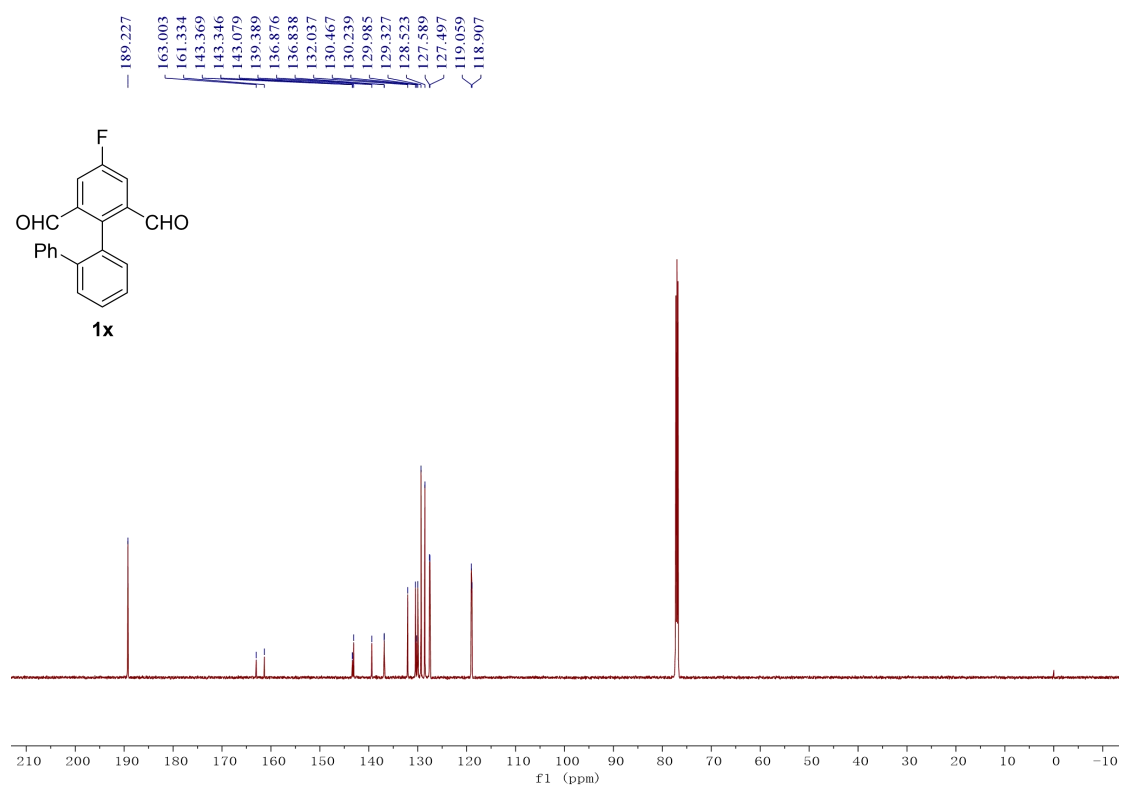


^{13}C NMR (150 MHz, CDCl_3) spectrum of **1w**.

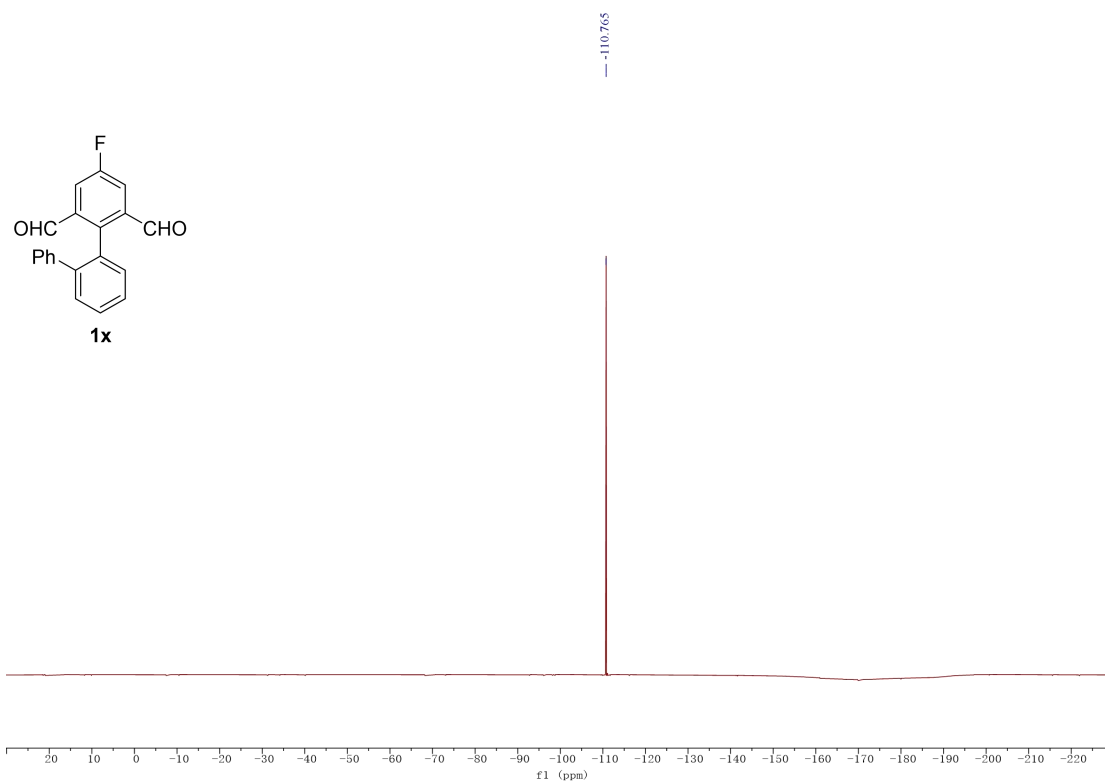


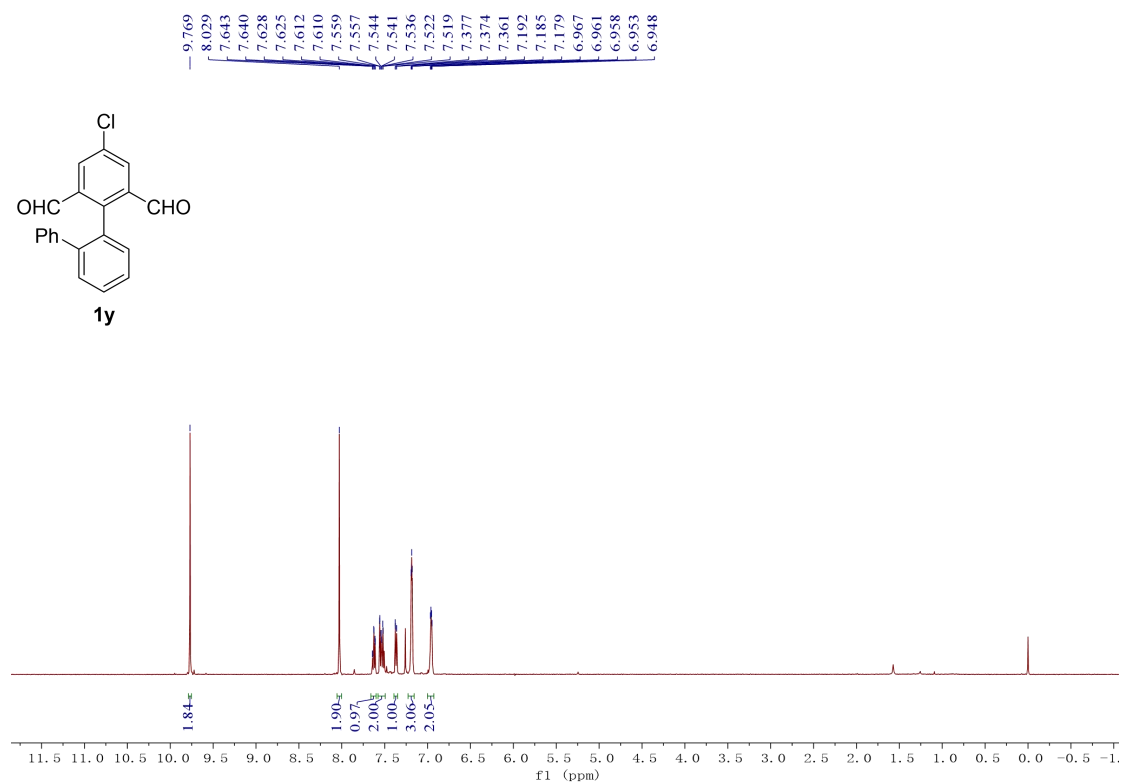


¹H NMR (500 MHz, CDCl₃) spectrum of **1x.**

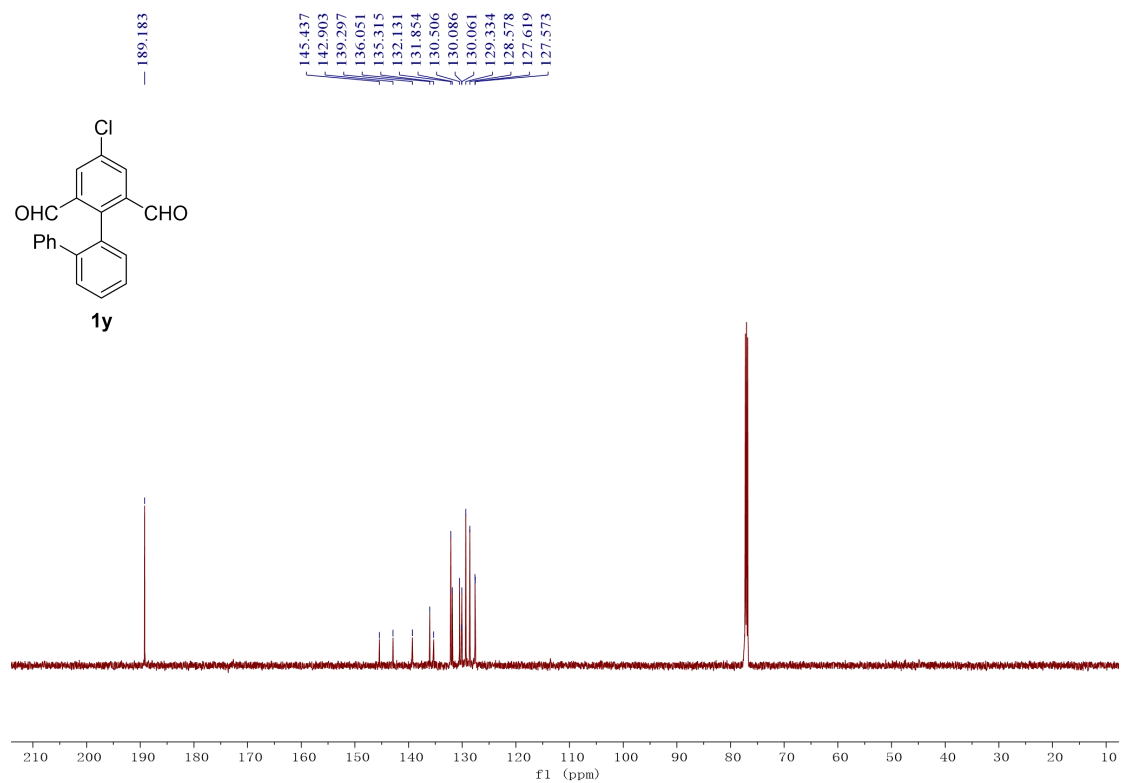


¹³C NMR (150 MHz, CDCl₃) spectrum of **1x.**





¹H NMR (500 MHz, CDCl₃) spectrum of **1y.**



¹³C NMR (150 MHz, CDCl₃) spectrum of **1y.**