Supporting Information

Silver/palladium relay catalyzed 1,3-dipole annulation/allylation reactions to access fully substituted allyl imidazolidines

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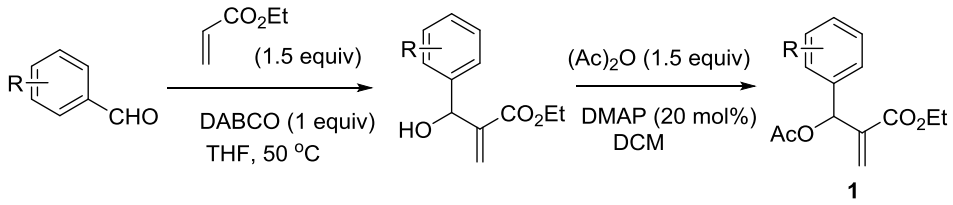
1. General Experimental Details.

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification.

2. General Procedure for the Synthesis of Baylis−Hillman acetates 1.



A 50 mL round-bottom flask was charged with appropriate benzaldehyde (3 mL, 30 mmol), ethyl acrylate (1.5 equiv, 45 mmol), DABCO (1.0 equiv, 30 mmol) in 5mL THF. The solution was stirred at room temperature for several days. The reaction was subsequently diluted with ethyl acetate (50 mL) and washed with brine (30 mL) and dried over $MgSO_4$, then concentrated to give a yellow liquid. The mixture was directly purified by flash column chromatography to give the corresponding Baylis−Hillman product.

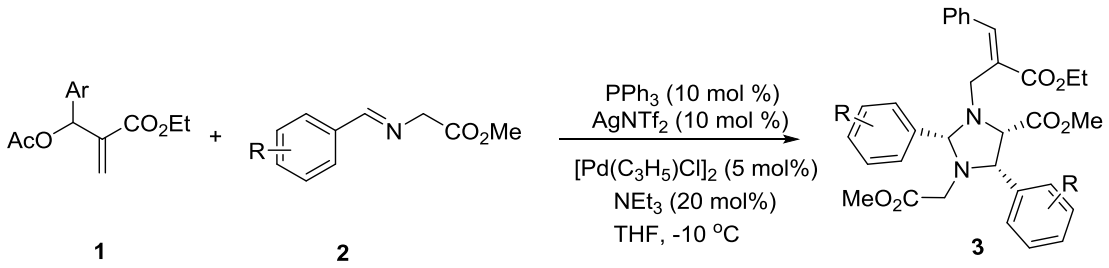
A 100 mL round-bottom flask was charged with appropriate Baylis−Hillman products, DMAP (0.2 equiv, 6 mmol) and dichloromethane (50 mL). The solution was cooled to 0 ℃ by an ice bath, then acetic anhydride (1.5 equiv, 45 mmol) was added dropwise into the flask within 10 min. After stirred for 2 h, 50 mL of 1M HCl, was added into the solution, and the mixture was extracted with dichloromethane (30 mL) for 3 times. The organic layer was separated, washed with 1M HCl, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give the compounds **1**.[1]

3. General Procedure for the Synthesis of glycine imino ester 2.

2

To a stirred solution of aldehydes (2.5 mL, 15 mmol) in dichloromethane (50 mL) was added, and glycine hydrochloride (1.1 equiv, 18 mmol). The mixture was stirred at RT for overnight. After completion under reduced pressure, washed with brine and extracted with Et_2O. The combined organic phases were dried over anhydrous $MgSO_4$, filtered and dried under reduced pressure. The glycine imino ester **2** was obtained pure as a yellow oil with 85% yield.[2]

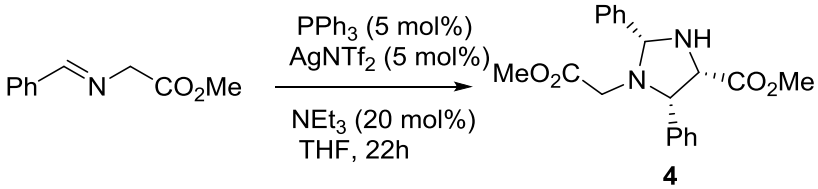
4. General procedure for synthesis of 3.



1 **2** **3**

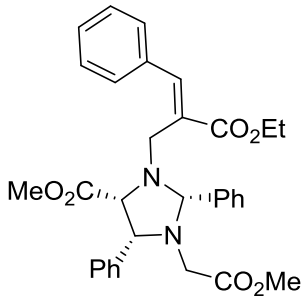
$AgNTf_2$ (0.02 mmol) and PPh_3 (0.02 mmol) were added under nitrogen to a 10 mL Schlenk tube. The freshly distilled anhydrous THF (1 mL) was added into the tube. After being stirred for 1h at -10 ℃, the $[Pd(C_3H_5)Cl]_2$ (5 mol%), the Baylis−Hillman acetates **1** (0.2 mmol) and glycine imino ester **2** (0.8 mmol) in THF (2 mL) were added subsequently，then at -10 ℃, NEt_3 (0.04 mmol) were added to the reaction. The reaction mixture was stirred at -10 ℃ for 8h. When the reaction was completed as monitored by TLC, the mixture was filtered through celite and the filtrate was concentrated to dryness. The residue was purified by column chromatography on silicagel (petroleum ether /ethyl acetate 10 : 1) to give off the products **3**.

5. General Procedure for the Synthesis of Imidazolidine 4.



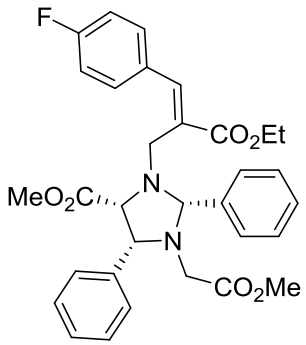
4

To the $AgNTf_2$ (97 mg, 0.25 mmol, 5 mol %) catalyst in THF (15 mL), PPh_3 (65.6 mg, 0.25 mmol, 5 mol %) was added. The mixture was stirred at room temperature for 1h, then glycine imino ester (886 mg, 5.0 mmol) and NEt_3 (139 μL, 20 mol %) were added. The reaction was allowed to proceed for 22 h at room temperature, after which 10 mL H_2O was added to quench the reaction. The organic layer was diluted with 10 mL EtOAc and water layer was extracted with EtOAc (10 mL×2). The combined organic layer was dried over $MgSO_4$ and concentrated. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give the compounds **4**.[3]



Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-phenylallyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3a.

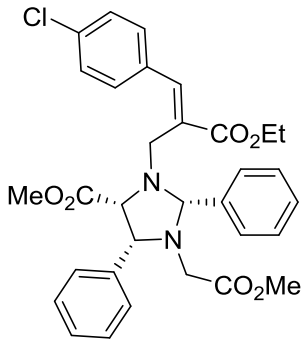
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.30 (t, *J* = 7.1 Hz, 3H) , 3.02 (s, 3H), 3.08 (d, *J* = 17.5 Hz, 1H), 3.20 (d, *J* = 17.4 Hz, 1H), 3.52-3.55 (m, 4H), 3.76 (d, *J* = 11.7 Hz, 1H), 4.10 (d, *J* = 9.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.70 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.32 – 7.16 (dq, *J* = 14.0, 6.6 Hz, 7H), 7.49 – 7.37 (m, 6H), 7.65 (s, 1H), 7.73 (d, *J* = 5.6 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 47.0, 47.3, 50.9, 51.1, 61.0, 65.9, 68.7, 85.5, 128.0, 128.1, 128.2, 128.8, 128.9, 129.0, 129.9, 130.4, 134.7, 137.5, 139.3, 143.9, 168.4, 171.0, 171.8 ppm. **IR (KBr)**: 2922, 1735, 1698, 1456, 1434, 1196, 1090, 698, 515 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{35}N_2O_6$ $[M+H]^+$: 543.2490, found: 543.2493.



Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(4-fluorophenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3b.

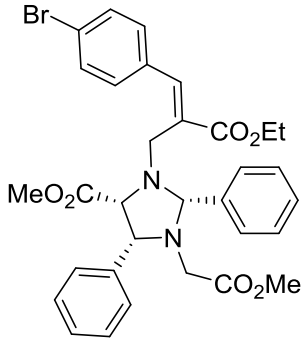
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.01 (s, 3H), 3.09 (d, *J* =17.4 Hz, 1H), 3.22 (d, *J* =17.3 Hz, 1H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.54 (s, 3H), 3.79 (d, *J* = 11.6 Hz, 1H), 4.18 (d, *J* = 9.9 Hz, 1H), 4.25 (q, *J* = 6.9 Hz, 2H), 4.75 (s, 1H), 4.88 (d, *J* = 9.9 Hz, 1H), 6.84 (t, *J* = 8.7 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.47 – 7.40 (m, 5H), 7.56 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.63 (s, 1H), 7.76 – 7.74 (m, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 46.9, 47.3, 50.9, 51.1, 61.0, 65.9, 68.5, 85.6,

115.0, 115.3, 127.3 (d, *J* = 1.3 Hz), 128.0, 128.2, 128.8, 129.1, 129.8, 130.8 (d, *J* = 3.1 Hz), 132.8, 132.9, 137.5, 139.2, 143.1, 168.3, 170.8, 171.7 ppm. **IR (KBr)**: 2918, 1738, 1697, 1507, 1455, 1193, 1084, 701, 523 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}FN_2O_6$ $[M+H]^+$: 561.2395, found: 543.2397.



Methyl (*Z*)-3-(3-(4-chlorophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2,5-diphenylimidazolidine-4-carboxylate 3c.

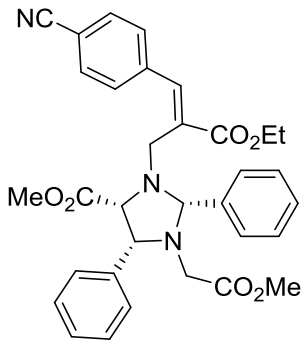
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.00 (s, 3H), 3.08 (d, *J* =17.3 Hz, 1H), 3.21 (d, *J* =17.3 Hz, 1H), 3.47 (d, *J* = 11.7 Hz, 1H), 3.54 (s, 3H), 3.75 (d, *J* = 11.7 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.72 (s, 1H), 4.84 (d, *J* = 9.9 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.49 – 7.38 (m, 7H), 7.57 (s, 1H),7.70 (dd, *J* = 6.5, 3.0 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 47.0, 47.3, 50.9, 51.1, 61.1, 65.8, 68.7, 85.5, 128.0, 128.2, 128.4, 128.7, 129.1, 129.8, 132.0, 133.1, 135.0, 137.5, 139.1, 142.8, 168.2, 170.9, 171.7 ppm. **IR (KBr)**: 2950, 1736, 1699, 1490, 1456, 1196, 1086, 700, 511 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}ClN_2O_6$ $[M+H]^+$: 577.2100, found: 577.2102.



Methyl (*Z*)-3-(3-(4-bromophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3d.

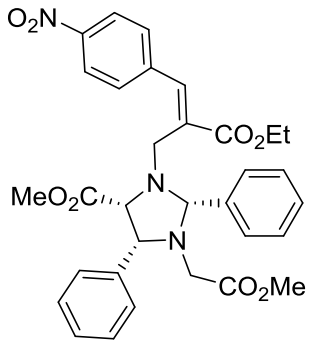
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.01 (s, 3H), 3.08 (d, *J* =17.3 Hz, 1H), 3.21 (d, *J* =17.3 Hz, 1H), 3.48 (d, *J* = 11.7 Hz, 1H), 3.55 (s, 3H),

3.75 (d, *J* = 11.7 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.73 (s, 1H), 4.85 (d, *J* = 9.9 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.43 (dt, J = 5.9, 2.3 Hz, 7H), 7.56 (s, 1H), 7.70 (dd, J = 6.5, 2.9 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 46.9, 47.3, 50.9, 51.1, 61.1, 65.8, 68.7, 85.4, 123.5, 128.0, 128.2, 128.4, 128.7, 129.1, 129.8, 131.4, 132.2, 133.5, 137.5, 139.1, 142.8, 168.2, 170.9, 171.7 ppm. **IR (KBr)**: 2923, 1736, 1699, 1456, 1435, 1196, 1071, 700, 508 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}BrN_2O_6$ $[M+H]^+$: 621.1595, found: 621.1598.



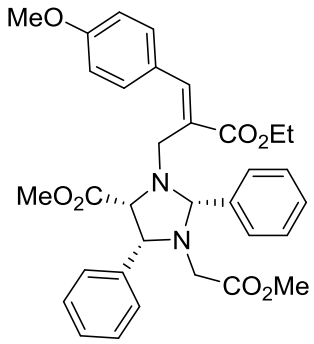
Methyl (*Z*)-3-(3-(4-cyanophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3e.

Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.01 (s, 3H), 3.07 (d, *J* =17.4 Hz, 1H), 3.21 (d, *J* =17.5 Hz, 1H), 3.45 (d, *J* = 11.7 Hz, 1H), 3.55 (s, 3H), 3.75 (d, *J* = 11.7 Hz, 1H), 4.14 (d, *J* = 9.9 Hz, 1H), 4.29 – 4.22 (m, 2H), 4.74 (s, 1H), 4.88 (d, *J* = 9.9 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.45 – 7.39 (m, 7H), 7.60 (s, 1H), 7.71 – 7.64 (m, 4H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.7, 47.3, 51.0, 51.1, 61.4, 65.7, 68.7, 85.4, 112.1, 118.8, 128.1, 128.3, 128.7, 129.2, 129.7, 130.9, 131.9, 137.4, 139.0, 141.9, 167.7, 170.8, 171.6 ppm. **IR (KBr)**: 2922, 1737, 1704, 1458, 1377, 1194, 1082, 701, 557 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{33}H_{34}N_3O_6$ $[M+H]^+$: 568.2442, found: 568.2444.



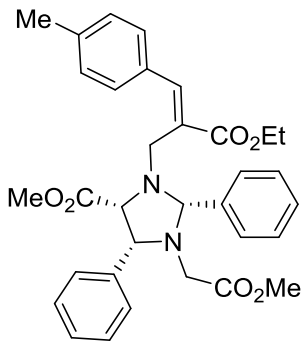
Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(4-nitrophenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3f.

Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.02 (s, 3H), 3.08 (d, *J* =17.5 Hz, 1H), 3.22 (d, *J* =17.5 Hz, 1H), 3.45 (d, *J* = 11.7 Hz, 1H), 3.56 (s, 3H), 3.75 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 9.9 Hz, 1H), 4.30 – 4.23 (m, 2H), 4.75 (s, 1H), 4.89 (d, *J* = 9.9 Hz, 1H), 7.35 – 7.24 (m, 3H), 7.46 – 7.40 (m, 5H), 7.64 (s, 1H), 7.71 (t, *J* = 6.2 Hz, 4H), 7.99 (d, *J* = 8.7 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.7, 47.3, 51.0, 51.1, 61.5, 65.7, 68.7, 85.4, 123.3, 128.1, 128.2, 128.4, 128.7, 129.3, 129.7,131.2, 137.4, 138.9, 140.9, 141.5, 147.5, 167.6, 170.8, 171.6 ppm. **IR (KBr)**: 2950, 1736, 1704, 1519, 1344, 1197, 1086, 699, 516 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}N_3O_8$ $[M+H]^+$: 588.2340, found: 588.2342.



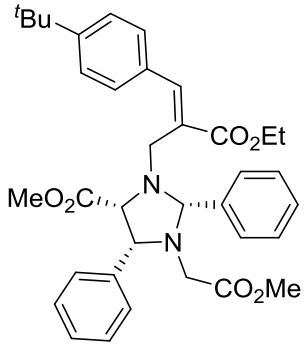
Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(4-methoxyphenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3g.

Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.00 (s, 3H), 3.10 (d, *J* =17.2 Hz, 1H), 3.22 (d, *J* =17.2 Hz, 1H), 3.49 (d, *J* = 11.6 Hz, 1H), 3.55 (s, 3H), 3.82 (d, *J* = 13.6 Hz, 4H), 4.23 (m, 3H), 4.74 (s, 1H), 4.86 (d, *J* = 9.8 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.43 (dt, *J* = 13.9, 6.9 Hz, 5H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.64 (s, 1H), 7.77 (d, *J* = 6.3 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3 (s), 47.1, 47.5, 50.8, 51.1, 55.2, 60.9, 65.9, 68.5, 85.7, 113.6, 125.2, 127.4, 128.0, 128.2, 128.8, 128.9, 129.9, 132.7, 137.5, 139.4, 144.2, 160.3, 168.8, 170.9 , 171.8 ppm. **IR (KBr)**: 2949, 1736, 1694, 1510, 1455, 1174, 1086, 700, 525 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{33}H_{37}N_2O_7$ $[M+H]^+$: 573.2595, found: 573.2598.



Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(p-tolyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3h.

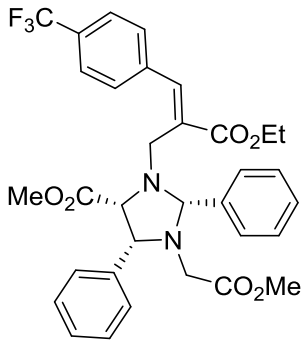
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.33 (s, 3H), 3.08 (d, *J* =17.4 Hz, 1H), 3.20 (d, *J* =17.3 Hz, 1H), 3.02 (s, 3H), 3.53 (d, J = 9.9 Hz, 4H), 3.78 (d, *J* = 11.7 Hz, 1H), 4.10 (d, *J* = 9.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.72 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.42 (dd, *J* = 13.9, 5.6 Hz, 7H), 7.63 (s, 1H), 7.73 (d, *J* = 5.1 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 21.4, 47.0, 47.4, 50.8, 51.1, 60.9, 65.9, 68.7, 85.5, 127.1, 128.0, 128.1, 128.8, 128.9, 128.9, 129.9, 130.6, 131.9, 137.5, 139.0, 139.4, 144.0, 168.6, 170.9, 171.7 ppm. **IR (KBr)**: 2948, 1737, 1699, 1455, 1435, 1198, 1088, 701, 514 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{33}H_{37}N_2O_6$ $[M+H]^+$: 557.2646, found: 557.2647.



Methyl (*Z*)-3-(3-(4-(tert-butyl)phenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3i.

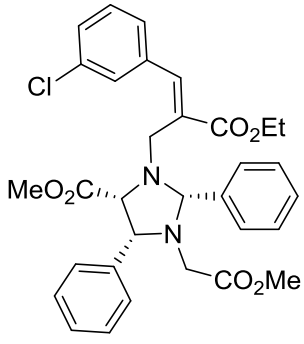
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.34 – 1.28 (m, 12H), 3.01 (s, 3H), 3.10 (d, *J* =17.3 Hz, 1H), 3.22 (d, *J* =17.3 Hz, 1H), 3.50 (d, *J* = 11.6 Hz, 1H), 3.54 (s, 3H), 3.79 (d, *J* = 11.6 Hz, 1H), 4.22 (m, 3H), 4.73 (s, 1H), 4.86 (d, *J* = 9.8 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.47 – 7.41 (m, 7H), 7.67 (s, 1H), 7.79 – 7.76 (m, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 31.2, 34.7, 47.0, 47.4, 50.9, 51.1, 60.9, 65.9, 68.4, 85.6, 125.1, 127.1, 128.0, 128.2, 128.8, 130.0, 130.3, 131.9, 137.5,

139.4, 144.2, 152.0, 168.6, 170.9, 171.8 ppm. **IR (KBr)**: 2919, 1737, 1698, 1456, 1434, 1193, 1085, 700, 553 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{36}H_{43}N_2O_6$ $[M+H]^+$: 599.3116, found: 599.3119.



Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(4-(trifluoromethyl)phenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3j.

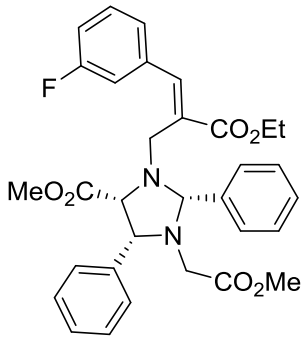
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.02 (s, 3H), 3.08 (d, *J* =17.4 Hz, 1H), 3.21 (d, *J* =17.4 Hz, 1H), 3.48 (d, *J* = 11.8 Hz, 1H), 3.55 (s, 3H), 3.74 (d, *J* = 11.8 Hz, 1H), 4.14 (d, *J* = 9.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.73 (s, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 7.30 (dt, *J* = 6.9, 5.3 Hz, 3H), 7.46 – 7.38 (m, 7H), 7.63 (d, *J* = 8.3 Hz, 3H), 7.70 (dd, *J* = 6.3, 2.7 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.8, 47.2, 50.9, 51.1, 61.2, 65.8, 68.7, 85.3, 125.1 (d, *J* = 3.8 Hz), 128.1, 128.3, 128.7, 129.1, 129.8, 130.1, 130.5, 130.5, 137.4, 138.1, 139.1, 142.3, 167.9, 170.8, 171.7 ppm. **IR (KBr)**: 2950, 1737, 1703, 1456, 1435, 1165, 1066, 700, 516 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{33}H_{34}F_3N_2O_6$ $[M+H]^+$: 611.2363, found: 611.2366.



Methyl (*Z*)-3-(3-(3-chlorophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3k.

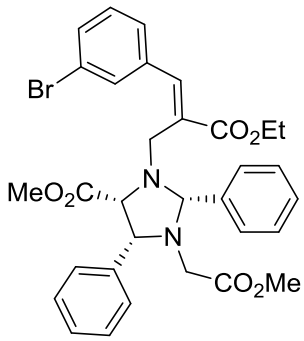
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.10 – 3.04 (m, 4H), 3.21 (d, *J* =17.4 Hz, 1H), 3.52 (d, *J* = 15.8 Hz, 4H), 3.75 – 3.71 (m, 1H), 4.08 (d,

J = 9.8 Hz, 1H), 4.24 (dd, *J* = 13.4, 6.4 Hz, 2H), 4.71 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.36 (t, *J* = 7.1 Hz, 4H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.70 (s, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.9, 47.2, 50.9, 51.1, 61.1, 65.8, 68.4, 85.4, 128.0, 128.2, 128.5, 128.8, 129.0, 129.6, 129.8, 129.9, 133.9, 136.5, 137.6, 139.1, 142.1, 168.0, 170.9, 171.6 ppm. **IR (KBr)**: 2987, 1736, 1703, 1455, 1434, 1197, 1084, 701, 547 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}ClN_2O_6$ $[M+H]^+$: 577.2100, found: 577.2104.



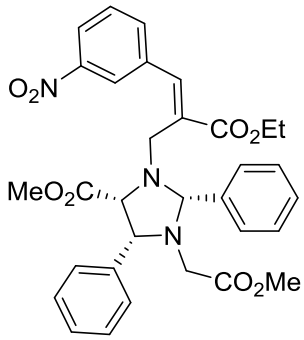
Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(3-fluorophenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2,5-diphenylimidazolidine-4-carboxylate 3l.

Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.10 – 3.04 (m, 4H), 3.21 (d, *J* =17.4 Hz, 1H), 3.52 (d, *J* = 13.9 Hz, 4H), 3.74 (d, *J* = 11.8 Hz, 1H), 4.10 (d, *J* = 9.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.73 (s, 1H), 4.84 (d, *J* = 9.9 Hz, 1H), 6.96 (td, *J* = 8.4, 2.0 Hz, 1H), 7.16 (dt, *J* = 13.8, 6.9 Hz, 1H), 7.40 – 7.22 (m, 8H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.59 (s, 1H), 7.73 – 7.71 (m, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.9, 47.3, 50.9, 51.1, 61.1, 65.9, 68.8, 85.6, 115.8 (d, *J* = 21.3 Hz), 116.9 (d, *J* = 22.1 Hz), 126.1 (d, *J* = 2.9 Hz), 128.0, 128.2, 128.8, 129.0, 129.3, 129.8, 136.8 (d, *J* = 8.1 Hz), 137.6, 139.0, 142.4 (d, *J* = 2.2 Hz), 168.0, 170.9, 171.6 ppm. **IR (KBr)**: 2920, 1735, 1701, 1456, 1435, 1195, 1089, 699, 519 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}FN_2O_6$ $[M+H]^+$: 561.2395, found: 561.2397.



Methyl (*Z*)-3-(3-(3-bromophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3m.

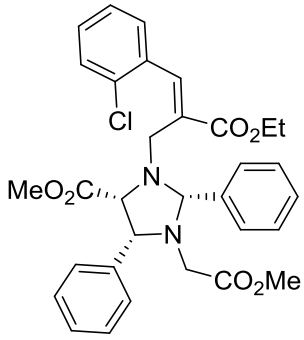
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.10 – 3.04 (m, 4H), 3.20 (d, *J* =17.4 Hz, 1H), 3.55 – 3.49 (m, 4H), 3.73 (d, *J* = 11.9 Hz, 1H), 4.08 (d, *J* = 9.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.71 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.38 (d, *J* = 5.6 Hz, 4H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.50 (s, 1H), 7.55 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 5.0 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.9, 47.1, 50.9, 51.1, 61.1, 65.8, 68.8, 85.4, 122.0, 128.0, 128.2, 128.8, 128.9, 129.0, 129.7, 129.8, 129.9, 131.7, 132.8, 136.8, 137.6, 139.1, 141.9, 167.9, 170.9, 171.6 ppm. **IR (KBr)**: 2987, 1736, 1702, 1456, 1434, 1195, 1075, 699, 548 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}BrN_2O_6$ $[M+H]^+$: 621.1595, found: 621.1598.



Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(3-nitrophenyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3n.

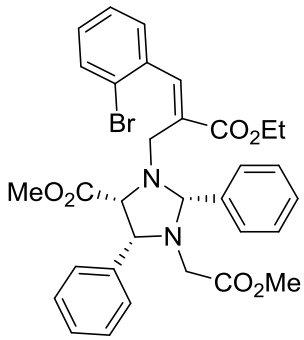
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.33 (t, *J* = 7.1 Hz, 3H), 3.09 – 3.03 (m, 4H), 3.21 (d, *J* =17.5 Hz, 1H), 3.45 (d, *J* = 11.9 Hz, 1H), 3.55 (s, 3H), 3.74 (d, *J* = 11.8 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.72 (s, 1H), 4.86 (d, *J* = 9.9 Hz, 1H), 7.31 (ddd, *J* = 12.6, 6.5, 3.8 Hz, 7H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.68 – 7.64 (m, 3H), 8.15 – 8.07 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.8,

47.2, 51.0, 51.2, 61.4, 65.7, 68.8, 85.4, 123.3, 124.8, 128.1, 128.2, 128.8, 129.1, 129.4, 129.7, 130.7, 136.2, 136.4, 137.5, 138.9, 141.3, 147.9, 167.6, 170.9, 171.6 ppm. **IR (KBr)**: 2950, 1736, 1704, 1529, 1350, 1197, 1093, 701, 519 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}N_3O_8$ $[M+H]^+$: 588.2340, found: 588.2343.



Methyl (*Z*)-3-(3-(2-chlorophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2,5-diphenylimidazolidine-4-carboxylate 3o.

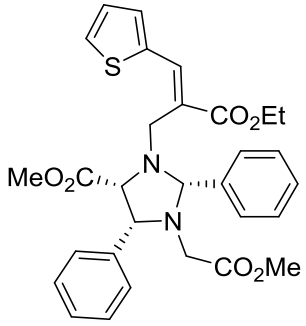
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.08 – 3.04 (m, 4H), 3.18 (d, *J* =17.4 Hz, 1H), 3.48 (d, *J* = 12.0 Hz, 1H), 3.54 (s, 3H), 3.65 (d, *J* = 12.0 Hz, 1H), 4.09 (d, *J* = 9.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.69 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.28 (dq, *J* = 13.8, 7.0 Hz, 4H), 7.40 – 7.34 (m, 3H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.78 (d, *J* = 5.4 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.9, 47.2, 50.9, 51.1, 61.1, 65.9, 68.5, 85.2, 126.7, 128.0, 128.2, 128.7, 128.9, 129.0, 129.8, 130.2, 132.0, 133.0, 134.0, 137.5, 139.2, 140.0, 168.0, 170.9, 171.7 ppm. **IR (KBr)**: 2922, 1737, 1703, 1456, 1435, 1196, 1087, 700, 521 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}ClN_2O_6$ $[M+H]^+$: 577.2100, found: 577.2104.



Methyl (*Z*)-3-(3-(2-bromophenyl)-2-(ethoxycarbonyl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3p.

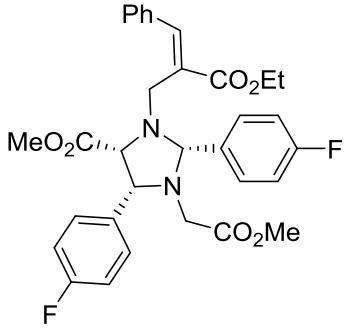
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.31 (t, *J* = 7.2 Hz, 3H), 3.08 – 3.04 (m,

4H), 3.18 (d, *J* =17.4 Hz, 1H), 3.47 (d, *J* = 12.1 Hz, 1H), 3.54 (s, 3H), 3.64 (d, *J* = 12.0 Hz, 1H), 4.10 (d, *J* = 9.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.69 (s, 1H), 4.83 (d, *J* = 9.8 Hz, 1H), 7.10 – 7.07 (m, 2H), 7.38 – 7.25 (m, 6H), 7.51 – 7.43 (m, 3H), 7.74 (ddd, *J* = 13.9, 8.4, 5.4 Hz, 4H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.2, 46.9, 47.1, 50.9, 51.1, 61.1, 65.9, 68.5, 85.1, 124.3, 127.4, 128.0, 128.2, 128.7, 128.9, 129.8, 130.0, 130.1, 132.2, 134.8, 137.5, 139.3, 142.3, 168.0, 170.9, 171.8 ppm. **IR (KBr)**: 2920, 1737, 1704, 1457, 1434, 1196, 1087, 699, 519 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{34}BrN_2O_6$ $[M+H]^+$: 621.1595, found: 621.1597.



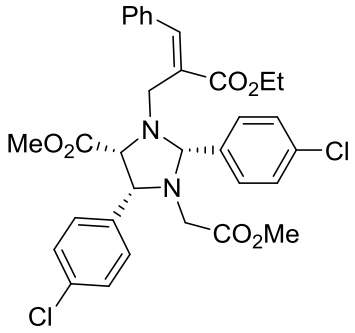
Methyl (*Z*)-3-(2-(ethoxycarbonyl)-3-(thiophen-2-yl)allyl)-1-(2-methoxy-2-oxoethyl)-2, 5-diphenylimidazolidine-4-carboxylate 3q.

Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 1.28 (t, *J* = 7.2 Hz, 3H), 3.02 (s, 3H), 3.11 (d, *J* = 17.4 Hz, 1H), 3.21 (d, *J* = 17.4 Hz, 1H), 3.56 (s, 3H), 3.69 (d, *J* = 12.2 Hz, 1H), 3.92 (d, *J* = 12.2 Hz, 1H), 4.13 (d, *J* = 9.7 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.79 (s, 1H), 4.86 (d, *J* = 9.7 Hz, 1H), 6.96 – 6.93 (m, 1H), 7.31 – 7.24 (m, 3H), 7.43 – 7.35 (m, 7H), 7.67 (s, 2H), 7.74 (d, J = 3.5 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 46.9, 47.7, 50.9, 51.1, 60.9, 65.9, 68.8, 85.3, 125.3, 127.8, 128.0, 128.7, 128.9, 129.4, 130.0, 133.3, 135.0, 137.4, 137.5, 139.5, 168.1, 171.0, 171.7 ppm. **IR (KBr)**: 2949, 1734, 1697, 1456, 1434, 1199, 1093, 699, 511 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{30}H_{33}N_2O_6S$ $[M+H]^+$: 549.2054, found: 549.2057.



Methyl (Z)-3-(2-(ethoxycarbonyl)-3-phenylallyl)-2, 5-bis(4-fluorophenyl)-1-(2-methoxy-2-oxoethyl)imidazolidine-4-carboxylate 3r.

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 3.02 (d, *J* = 17.2 Hz, 1H), 3.08 (s, 3H), 3.14 (d, *J* = 17.3 Hz, 1H), 3.55 (s, 4H), 3.74 (d, *J* = 11.6 Hz, 1H), 4.06 (d, *J* = 9.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.68 (s, 1H), 4.78 (d, *J* = 9.8 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.32 – 7.19 (m, 4H), 7.40 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.68 (dd, *J* = 8.2, 5.4 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.3, 46.9, 47.1, 51.0, 51.2, 61.0, 65.2, 68.5, 84.5, 114.8 (d, *J* = 6.0 Hz), 115.1 (d, *J* = 6.1 Hz) 128.1, 128.2, 128.9, 130.2, 130.4, 131.4, 131.5, 133.0 (d, *J* = 3.0 Hz), 134.7, 135.0 (d, *J* = 2.9 Hz), 143.7, 161.3 (d, *J* = 50.2 Hz), 164.5 (d, *J* = 50.8 Hz), 168.3, 170.7, 171.6. **IR (KBr)**: 2950, 1735, 1698, 1507, 1435, 1196, 1094, 730, 527 cm^{-}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{33}F_2N_2O_6$ $[M+H]^+$: 579.2301, found: 579.2304.

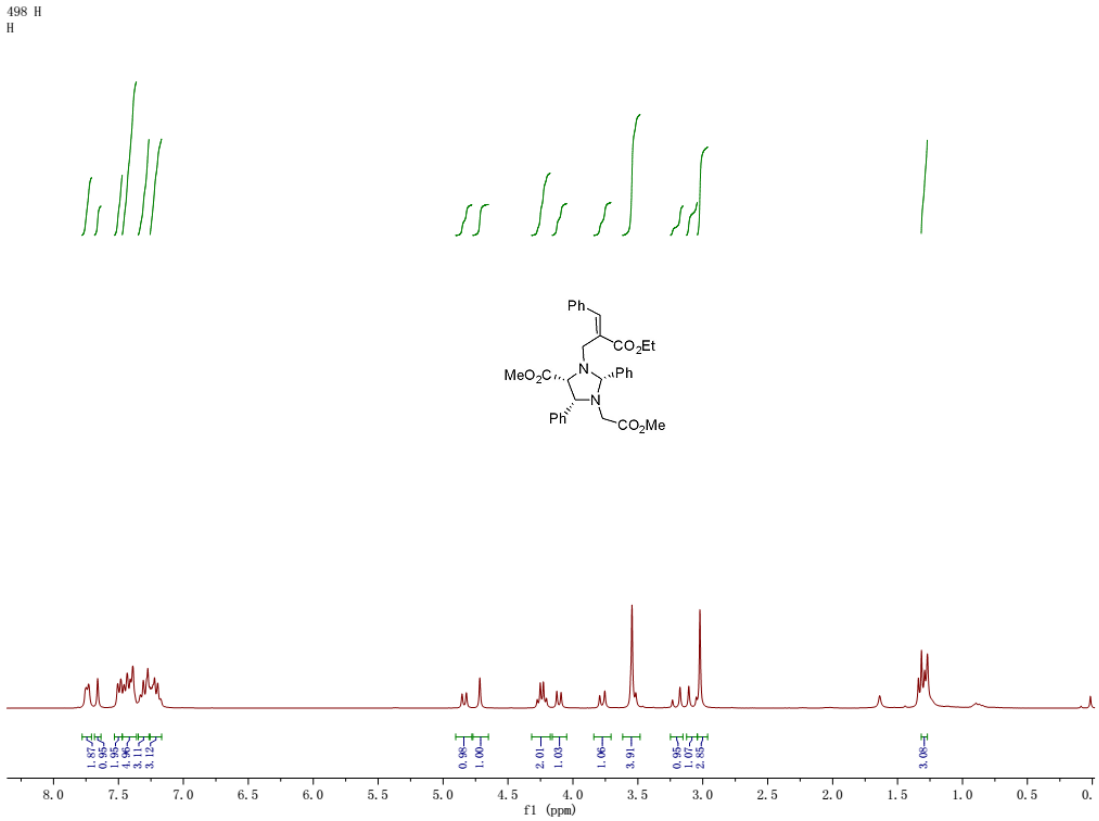


Methyl (2R, 4R, 5R)-2, 5-bis(4-chlorophenyl)-3-((*E*)-2-(ethoxycarbonyl)-3-phenylallyl)-1-(2-methoxy-2-oxoethyl)imidazolidine-4-carboxylate 3s.

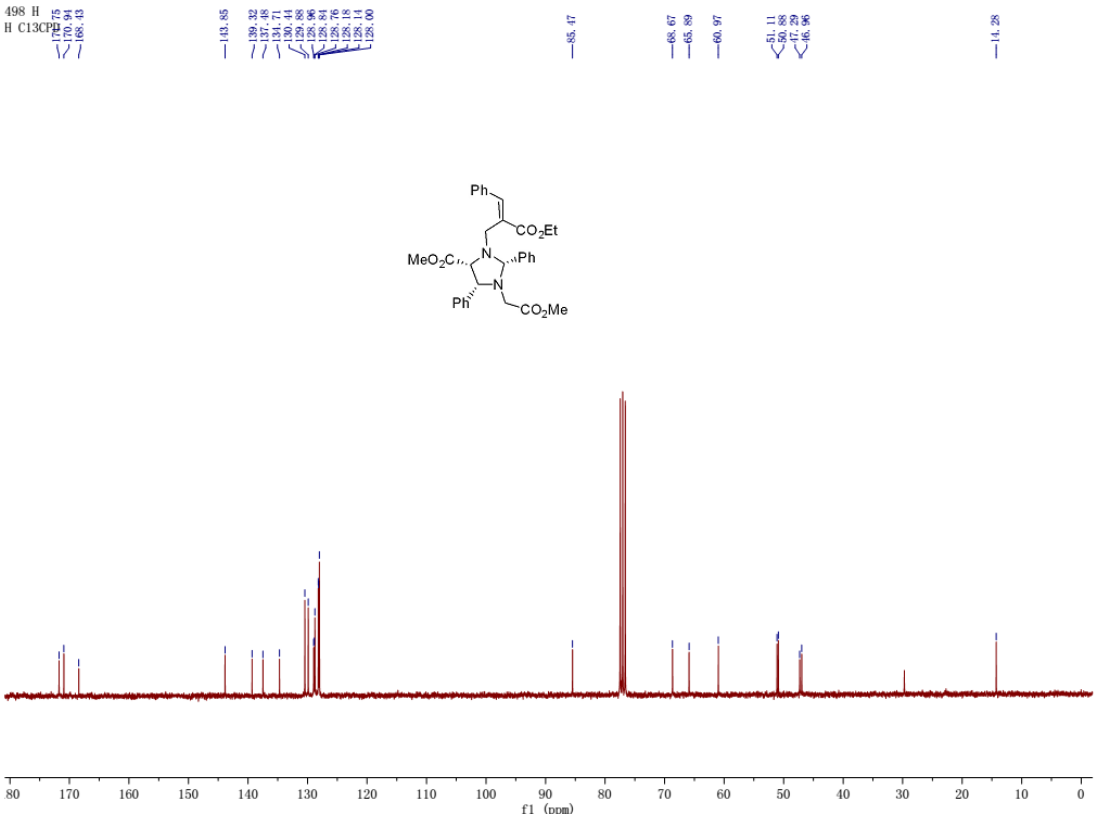
Yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* 1.32 (t, *J* = 7.1 Hz, 3H), 3.16 – 2.99 (m, 5H), 3.57 – 3.53 (m, 4H), 3.75 (d, *J* = 12.2 Hz, 1H), 4.07 (d, *J* = 9.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.68 (s, 1H), 4.79 (d, *J* = 9.7 Hz, 1H), 7.37 – 7.21 (m, 9H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.61 (s, 1H), 7.65 (d, *J* = 4.6 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* 14.3, 46.8, 47.1, 51.1, 51.3, 61.0, 65.3, 68.6, 84.4, 128.1, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.0, 130.0, 130.0, 130.2, 130.2, 131.1, 131.1, 133.8, 134.7 (d, J = 1.0 Hz), 135.9, 137.9, 143.8, 168.3, 170.6, 171.5 ppm. **IR (KBr)**: 2950, 1735, 1699, 1489, 1434, 1197, 1086, 698, 516 cm^{-1}. **HRMS** (ESI, m/z): Calcd for $C_{32}H_{32}Cl_2N_2O_6$ $[M+H]^+$: 611.1710, found: 611.1713.

1. H. Huang, B. Sun, Y. Huang et al. *J. Am. Chem. Soc.*, 2018, **140**, 10402-10406.
2. A. Zubia,, L. Mendoza, S. Vivanco, E. Aldaba, T. Carrascal, B. Lecea, A. Arrieta, T. Zimmerman, F. Vidal-Vanaclocha and F. P. Coss ́o, *Angew. Chem. Int. Ed.*, 2005, **44**, 2903.
3. B. Yu, X.-F. Bai, J.-Y. Lv, et al. *Adv. Syn. Catal.*, 2017, **359**, 3577-3584.

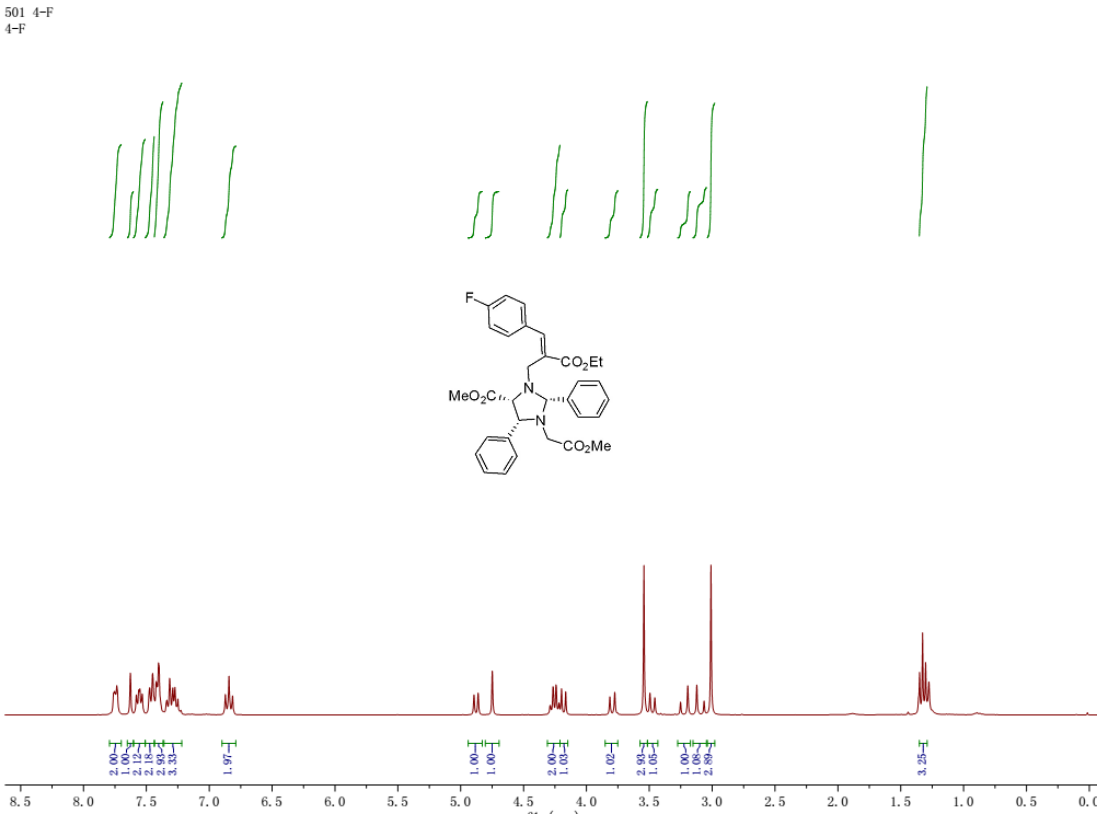
6. Copies of ^{1}H NMR, ^{13}C NMR Spectra.



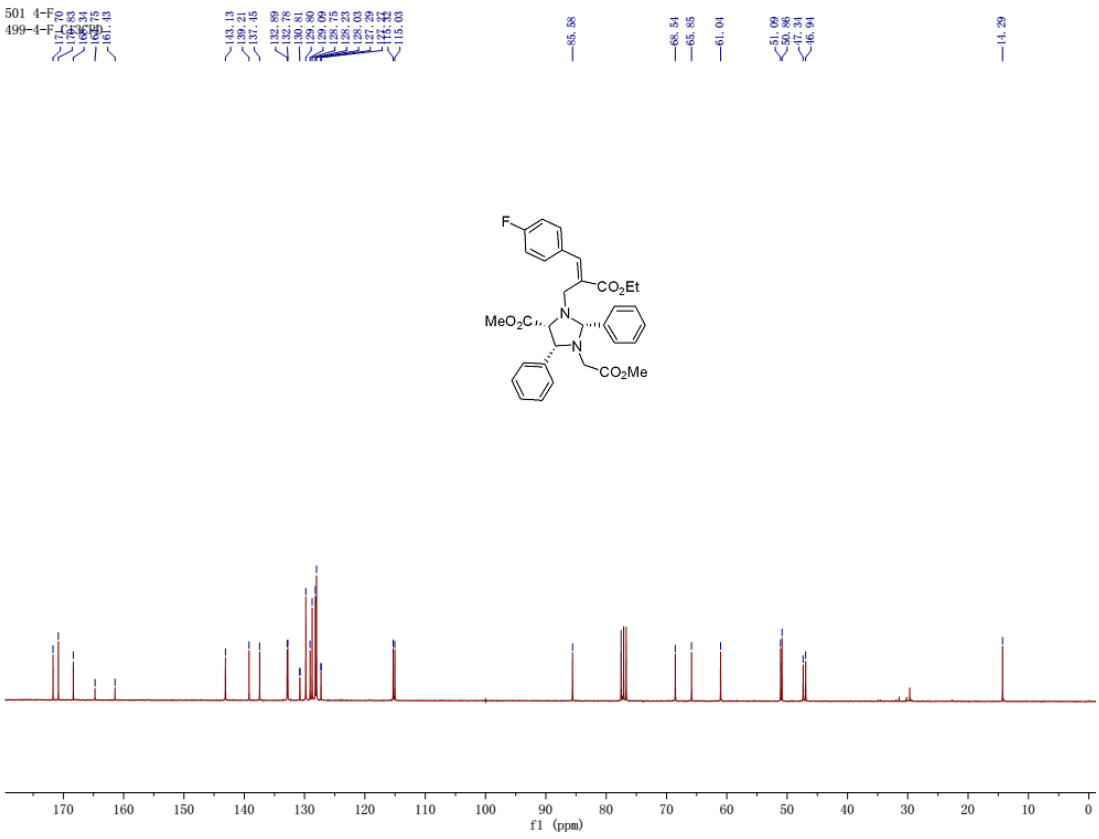
Compound 3a ^{1}H NMR



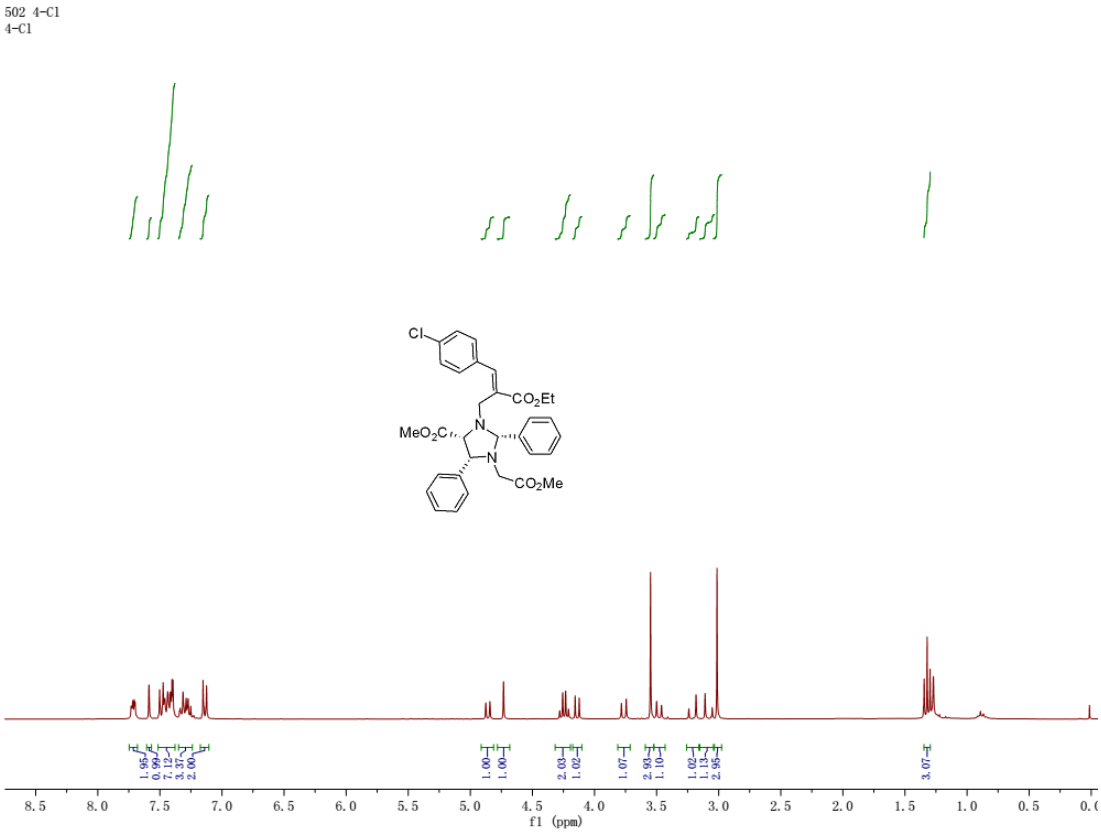
Compound 3a ^{13}C NMR



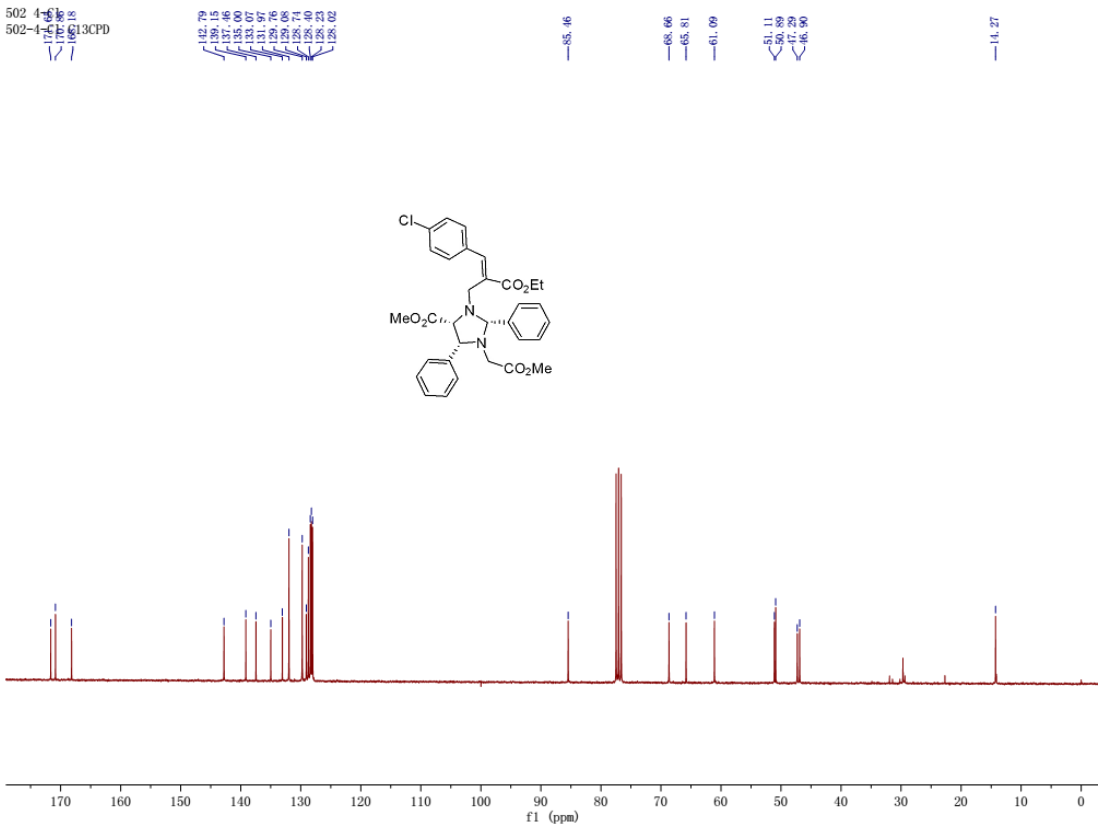
Compound 3b ^{1}H NMR



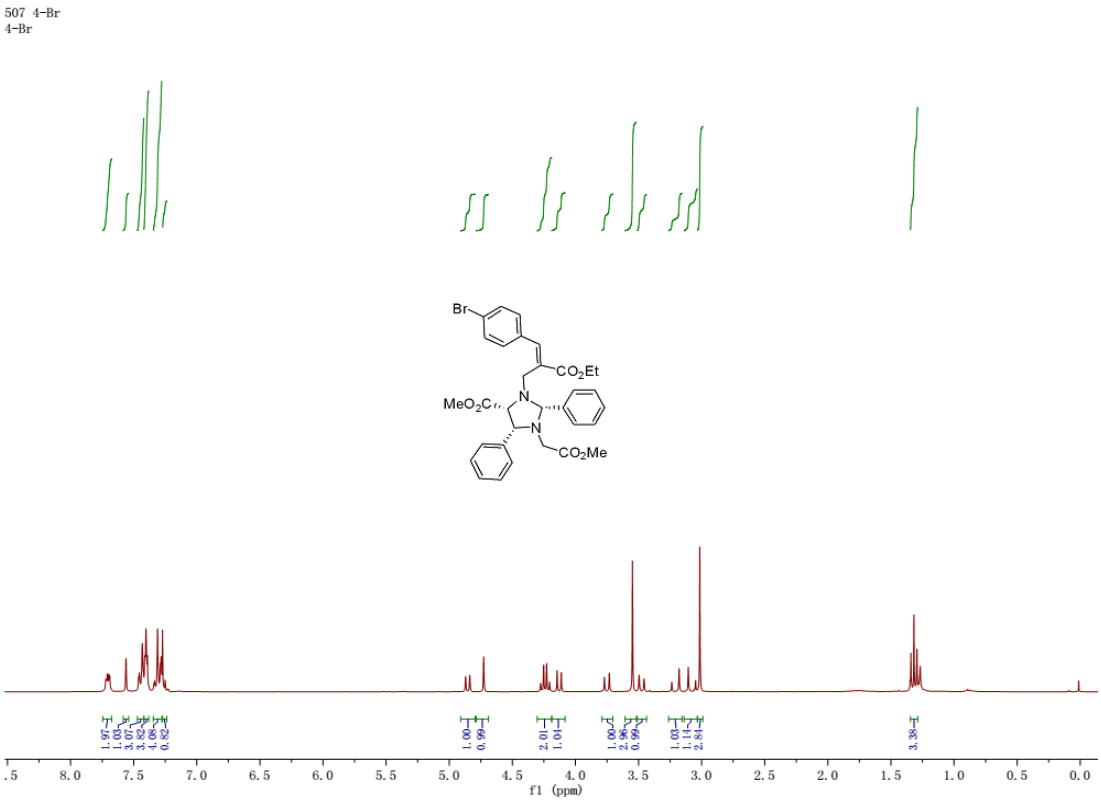
Compound 3b ^{13}C NMR



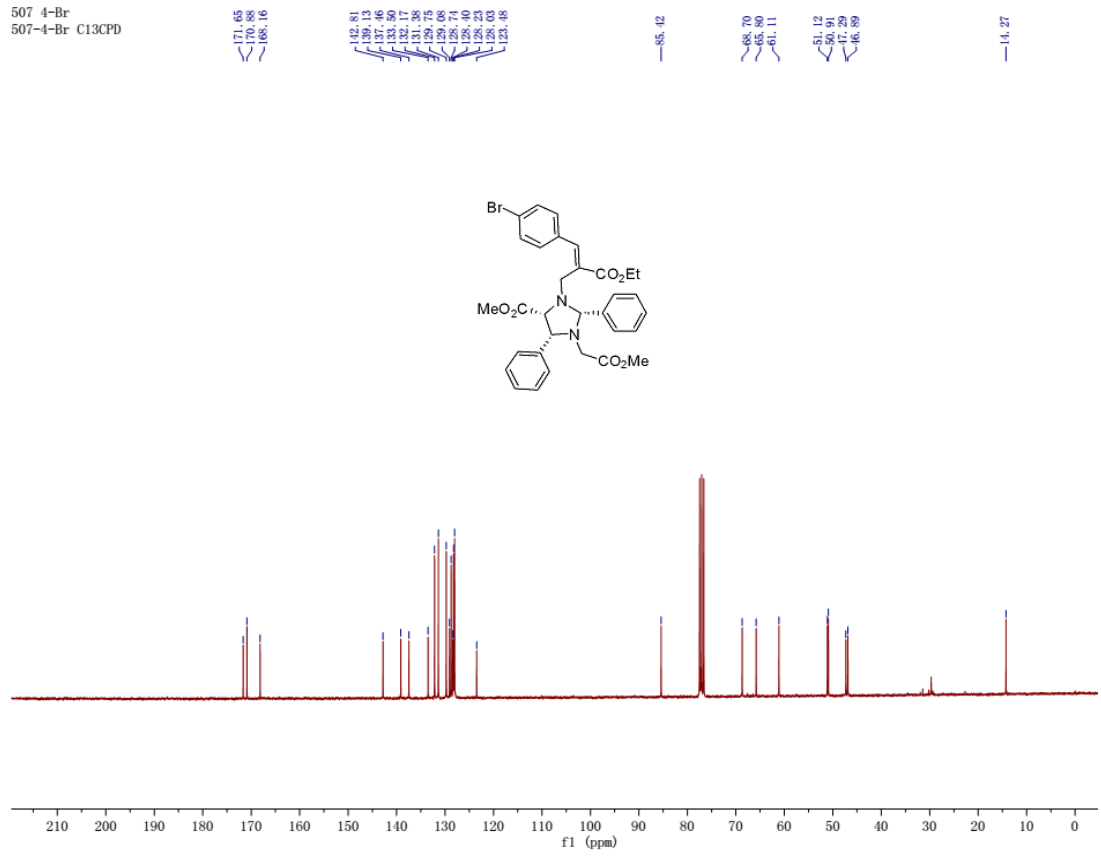
Compound 3c ^{1}H NMR



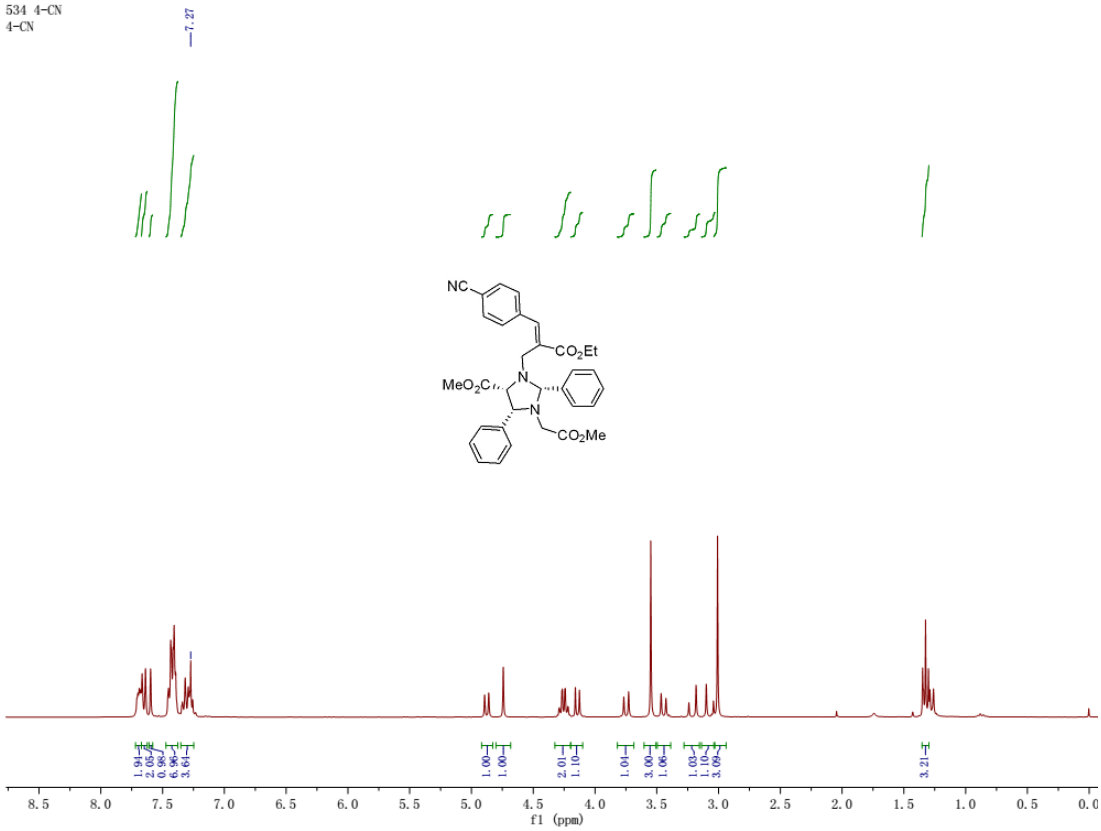
Compound 3c ^{13}C NMR



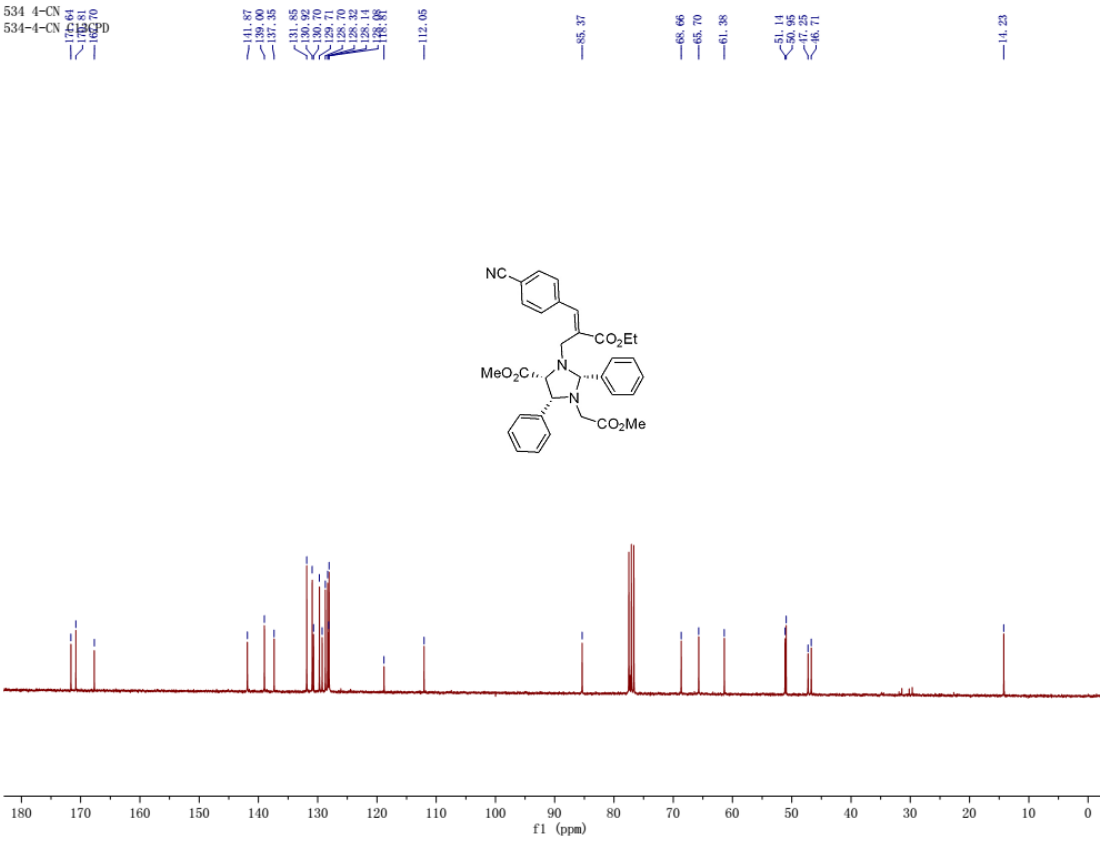
Compound 3d ^{1}H NMR



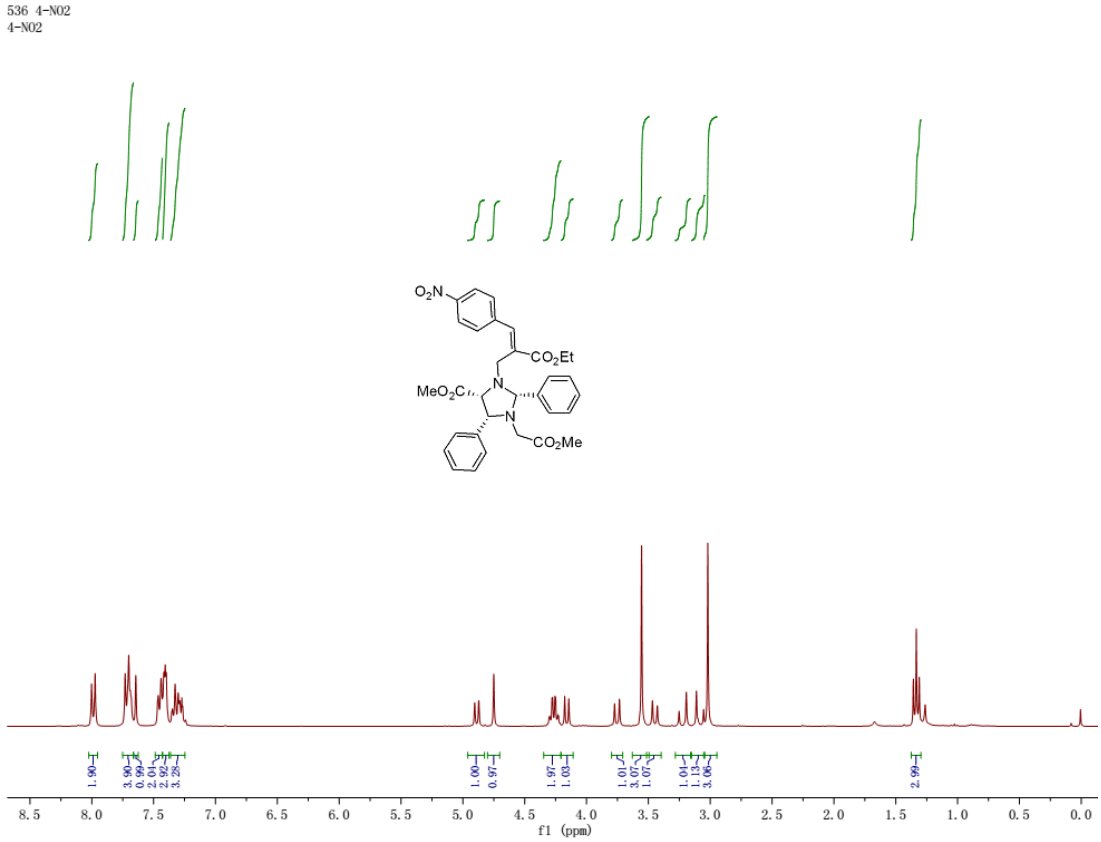
Compound 3d ^{13}C NMR



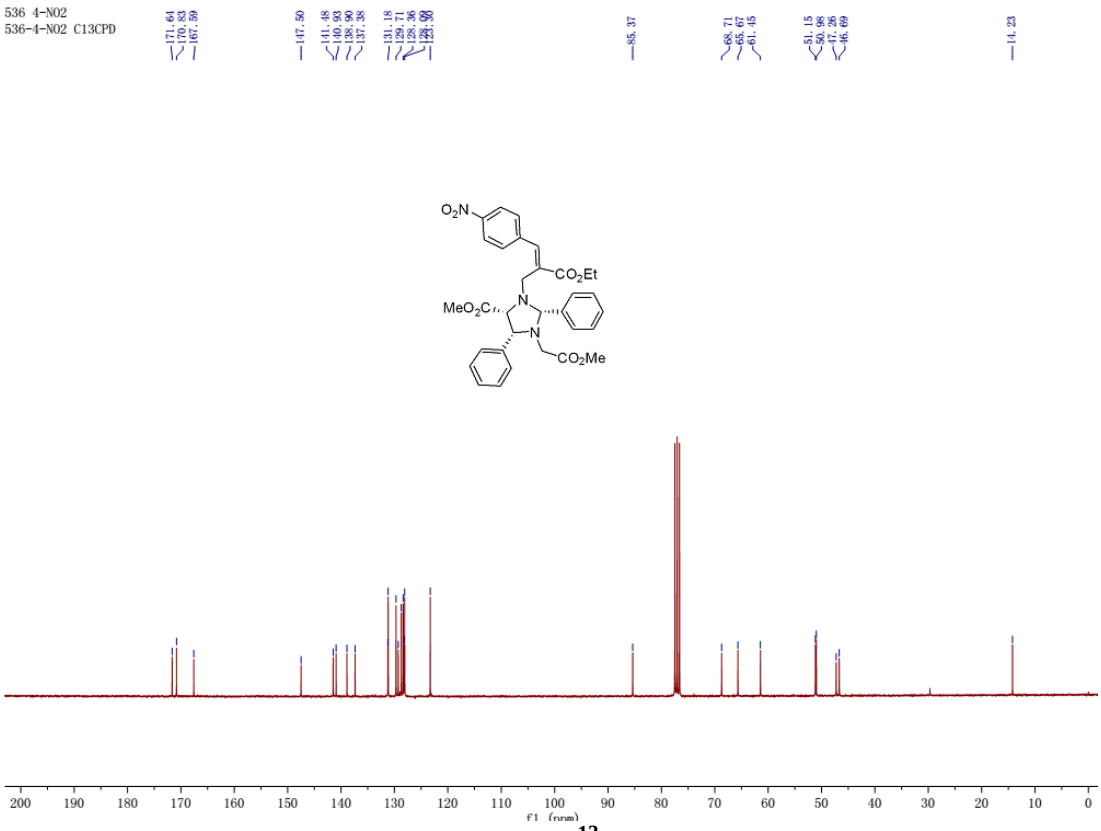
Compound 3e ^{1}H NMR



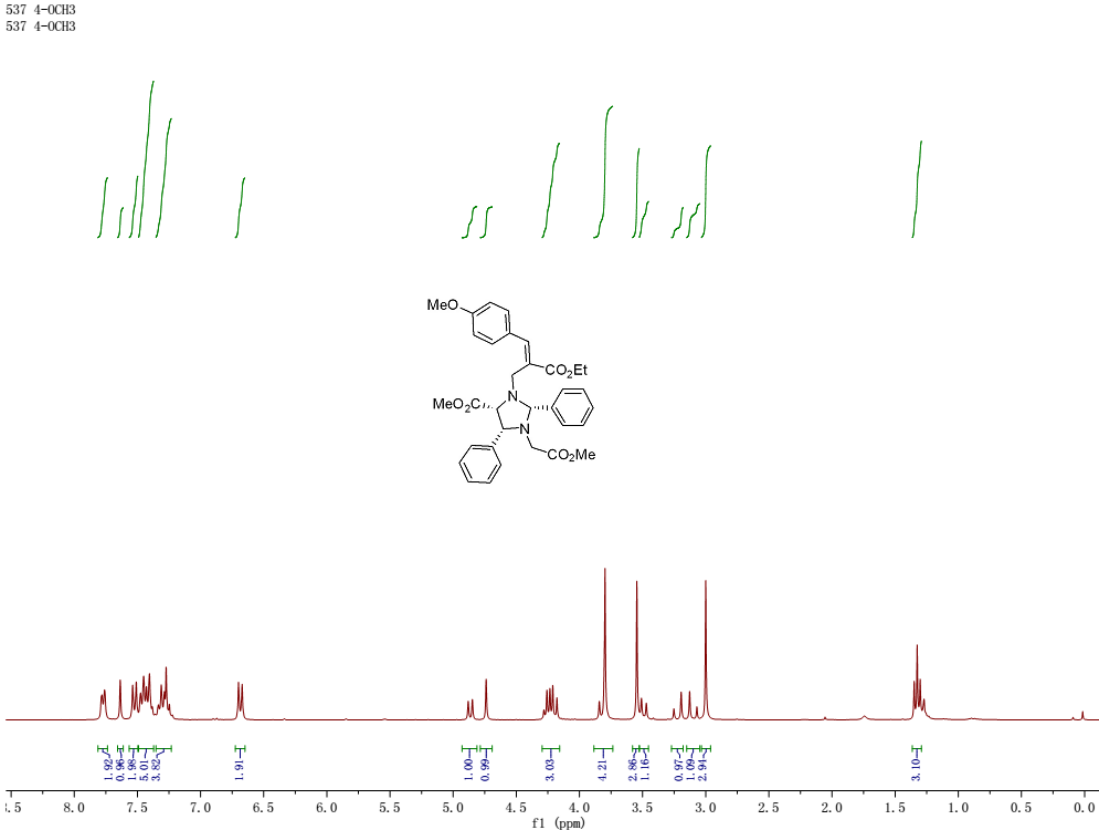
Compound 3e ^{13}C NMR



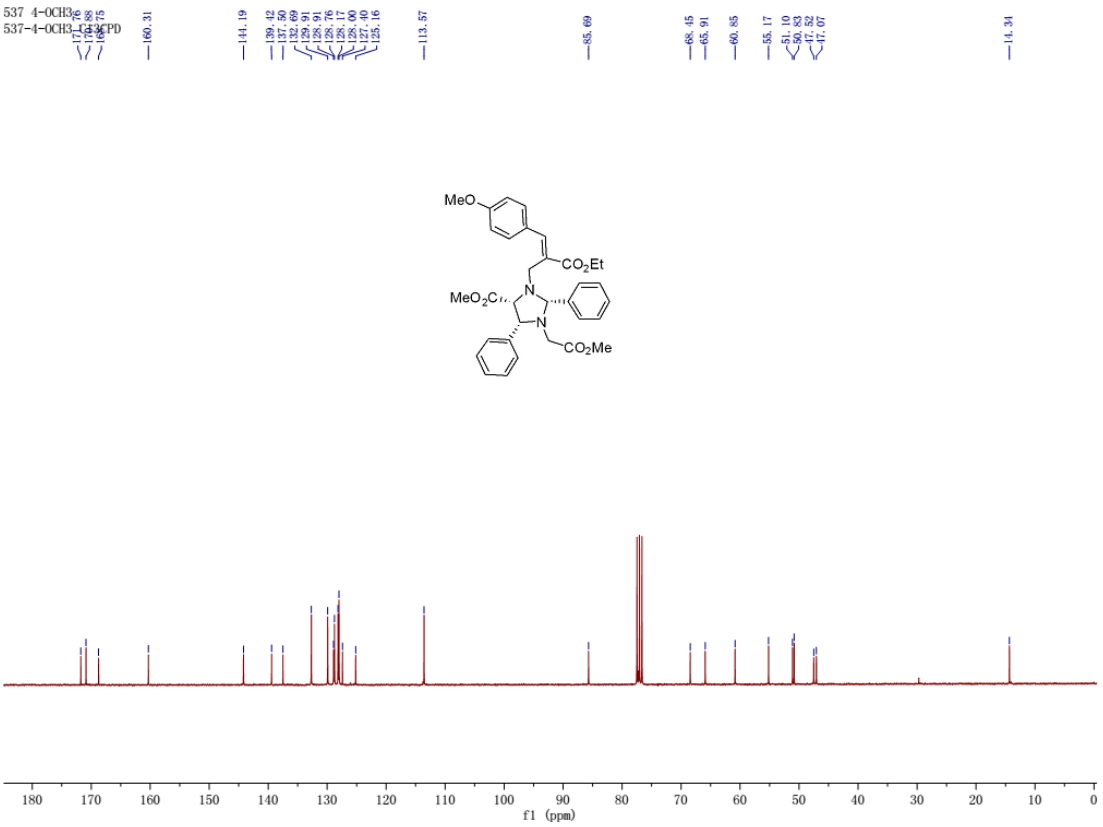
Compound 3f ^{1}H NMR



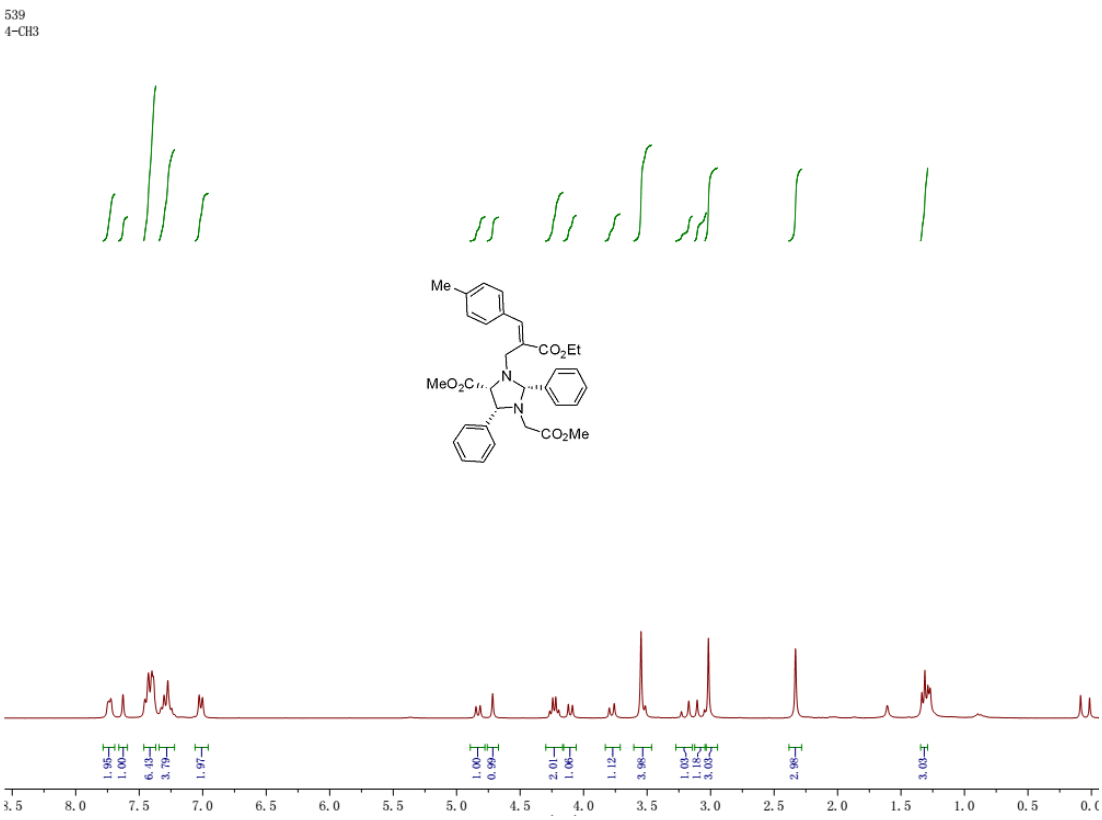
Compound 3f ^{13}C NMR



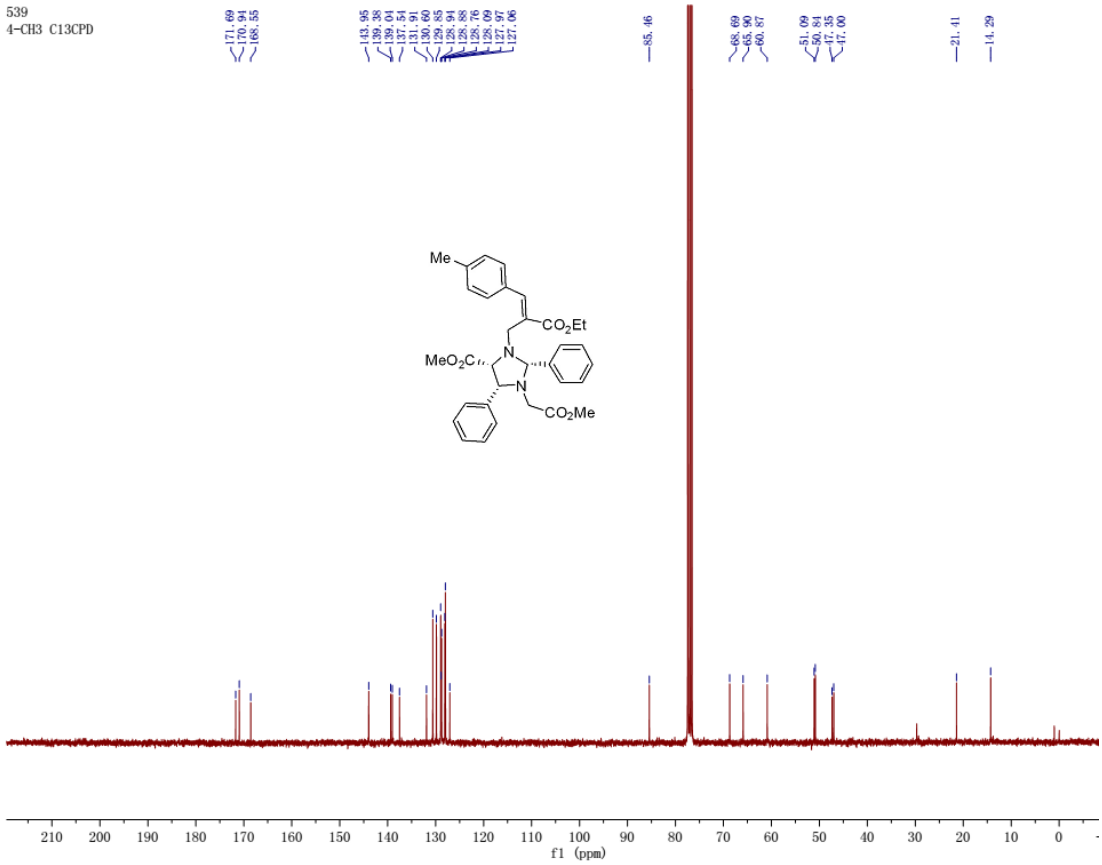
Compound 3g ^{1}H NMR



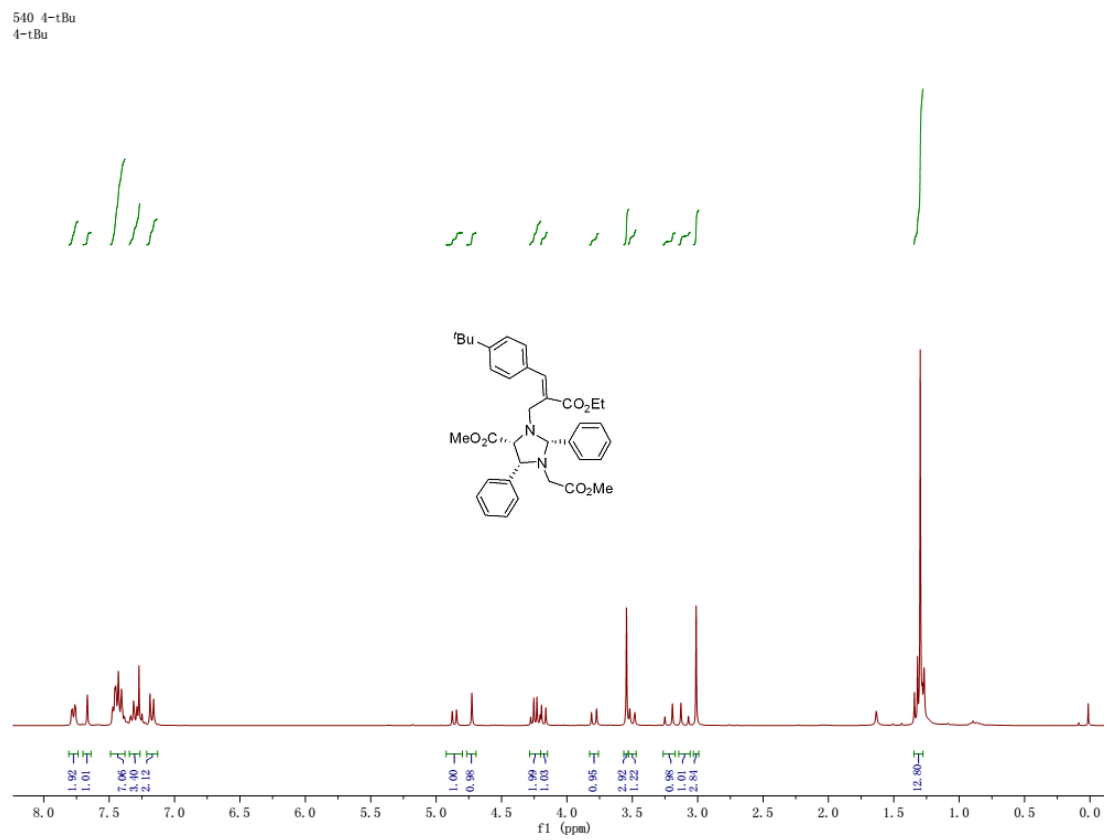
Compound 3g ^{13}C NMR



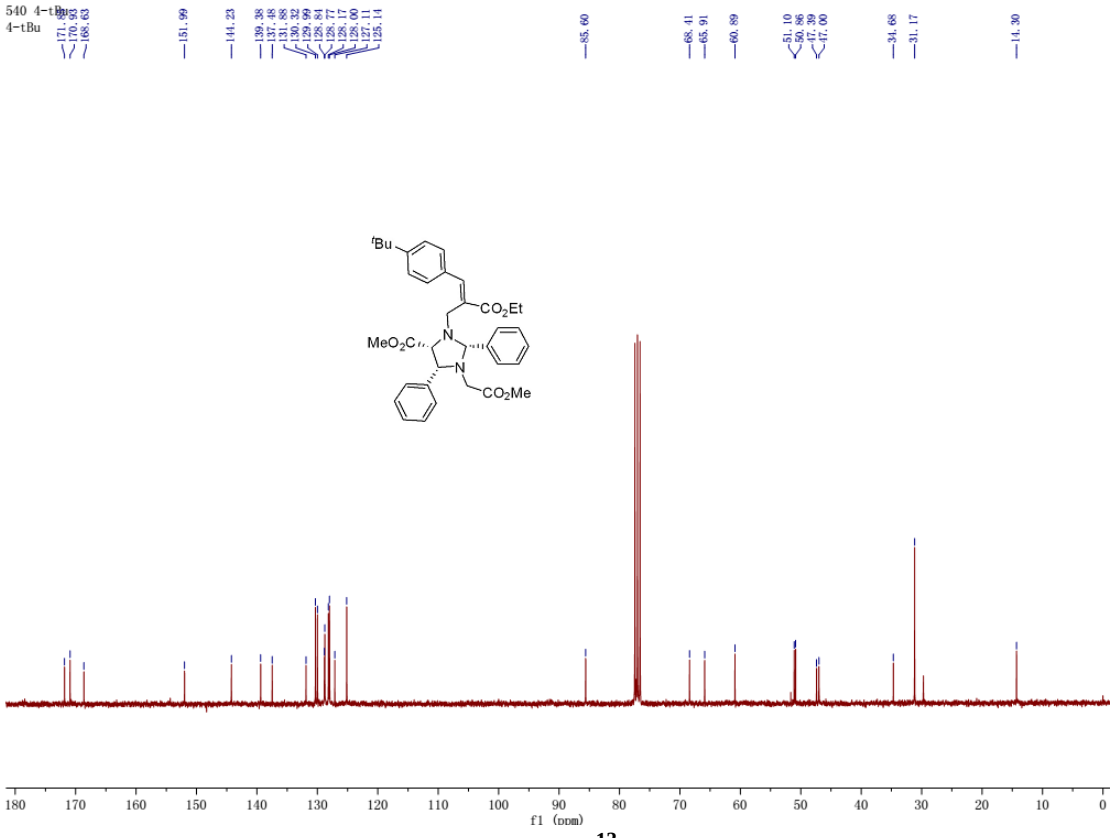
Compound 3h ^{1}H NMR



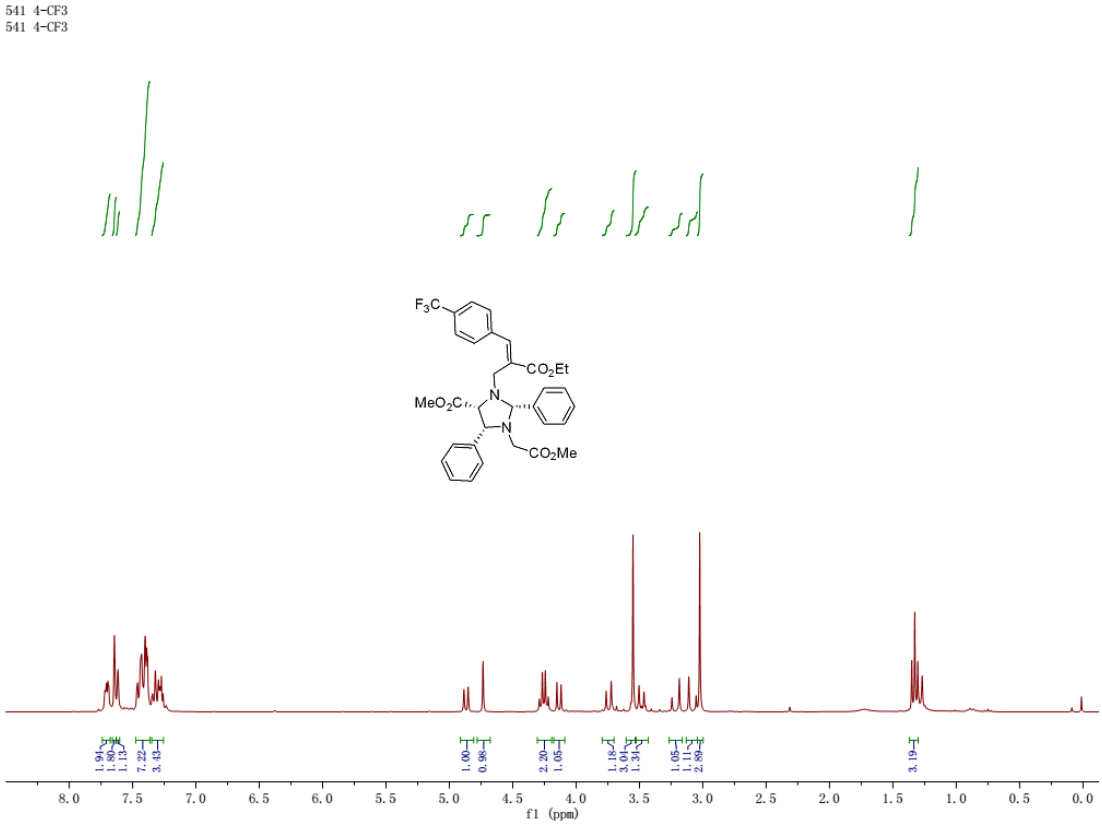
Compound 3h ^{13}C NMR



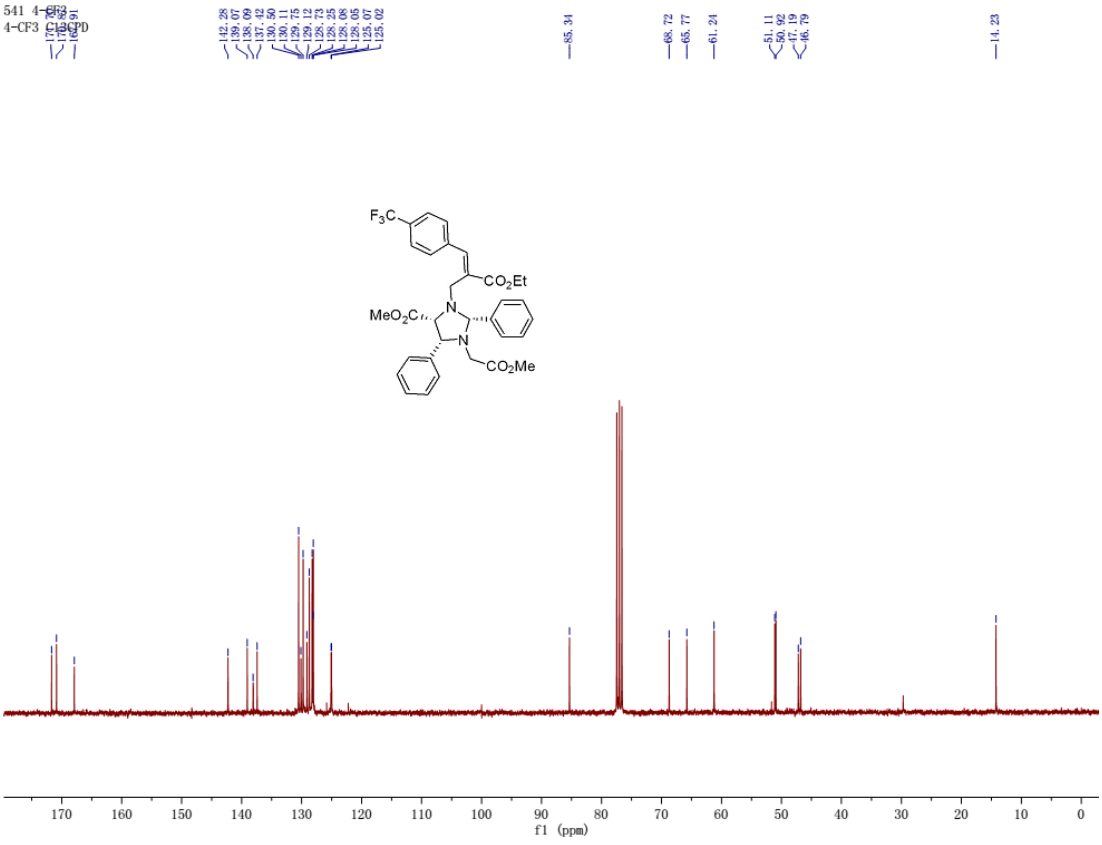
Compound 3i ^{1}H NMR



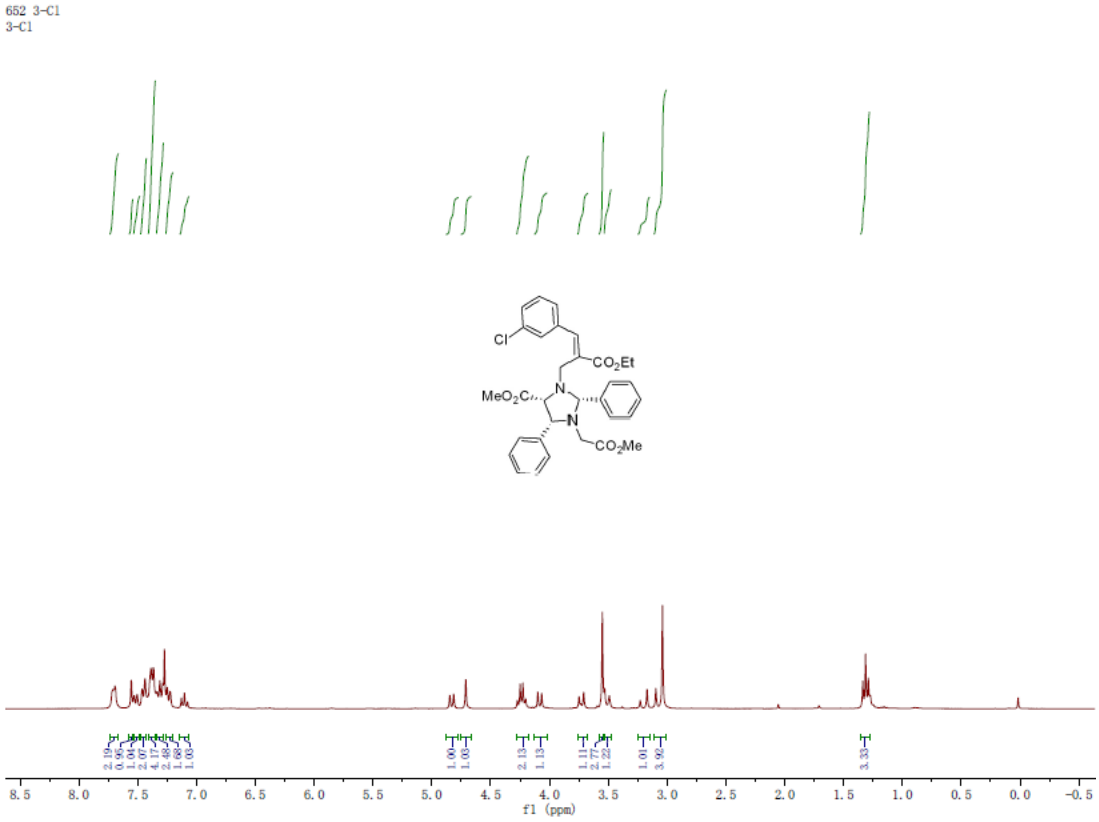
Compound 3i ^{13}C NMR



Compound 3j ^{1}H NMR



Compound 3j ^{13}C NMR



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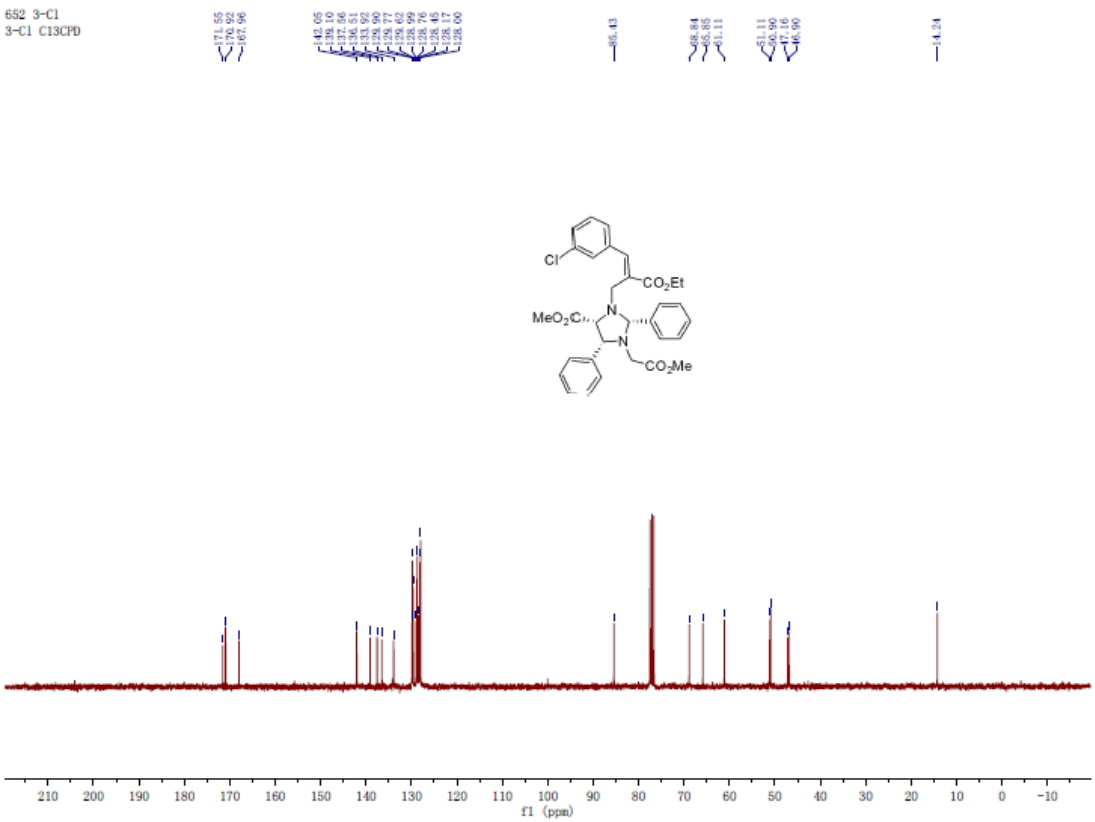
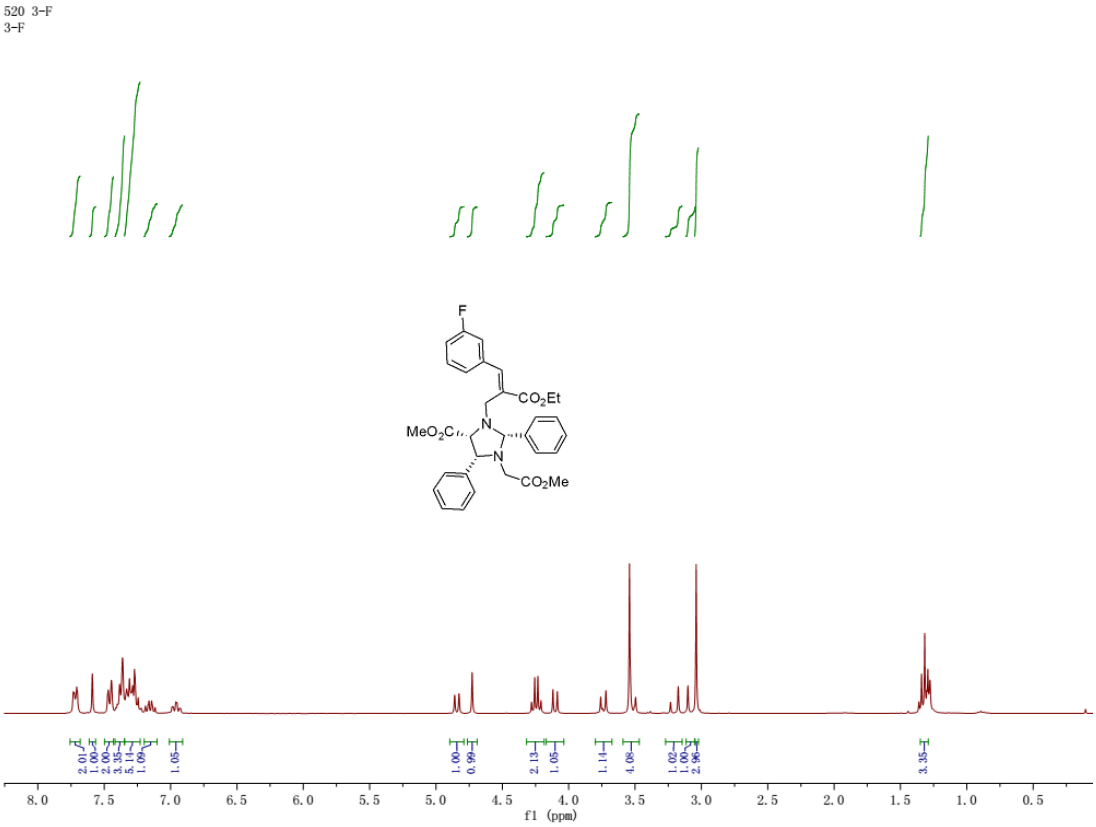


Compound 3k ^{13}C NMR



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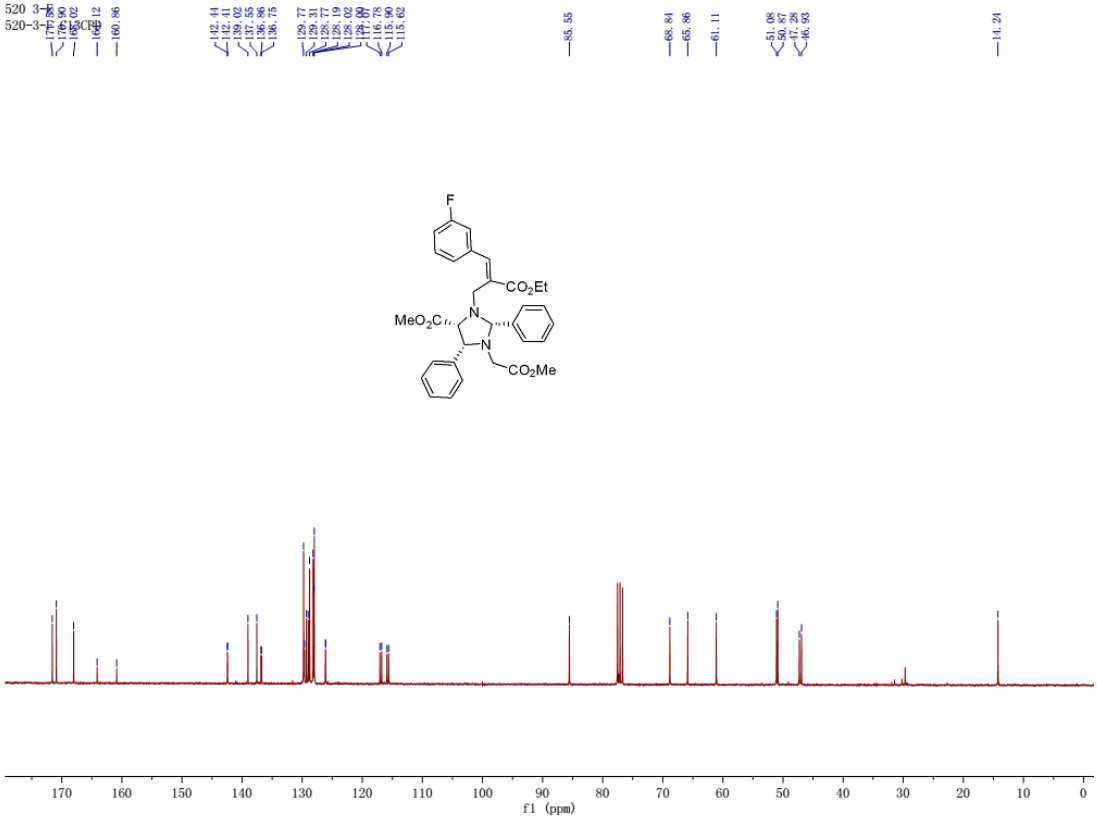
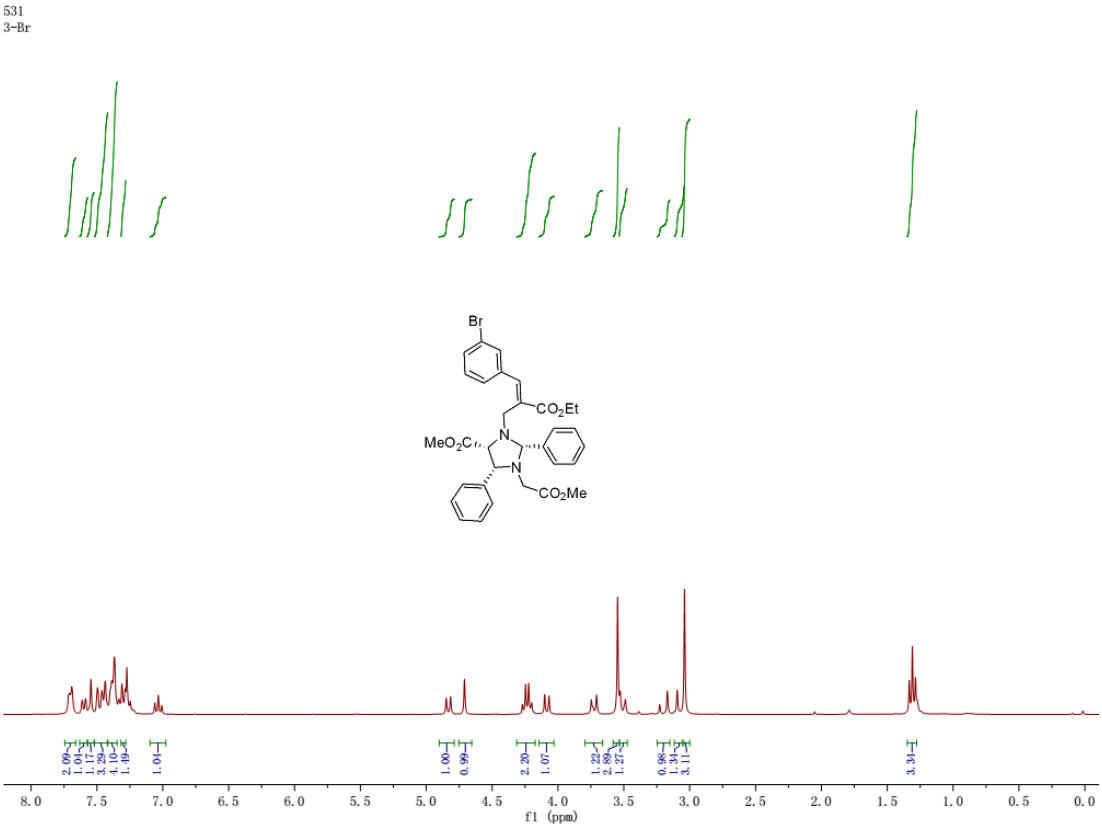
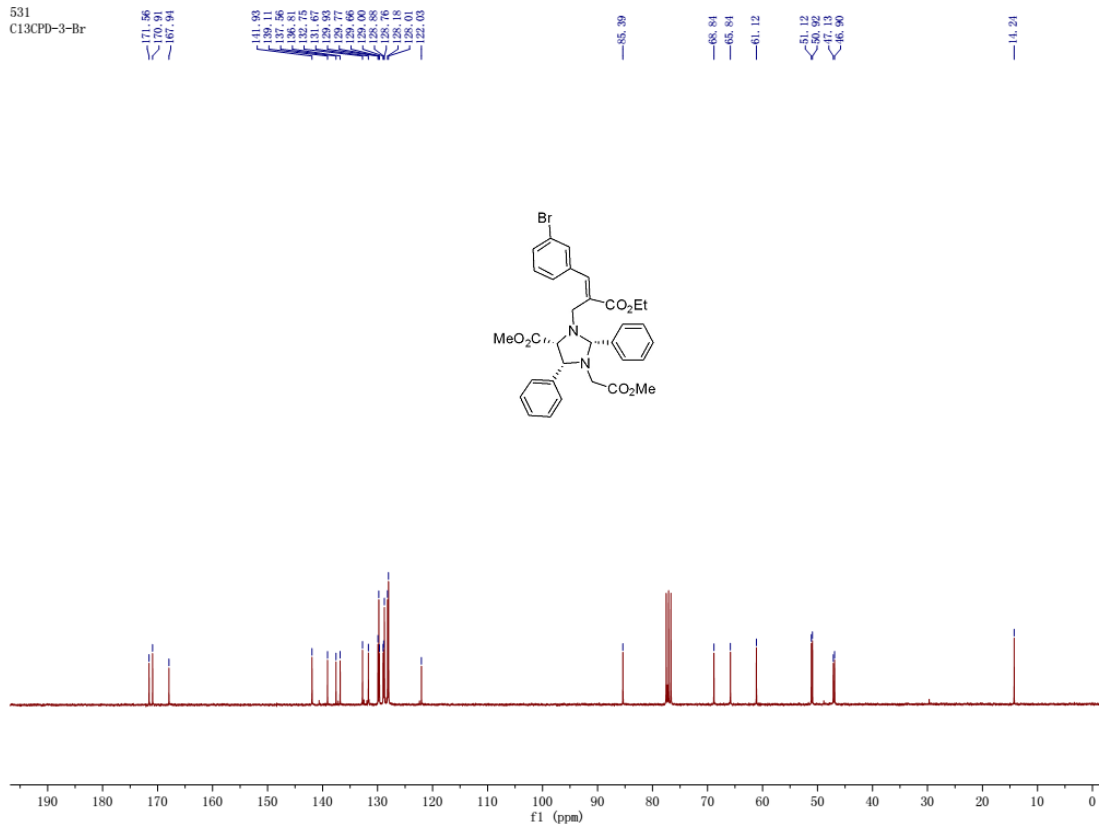


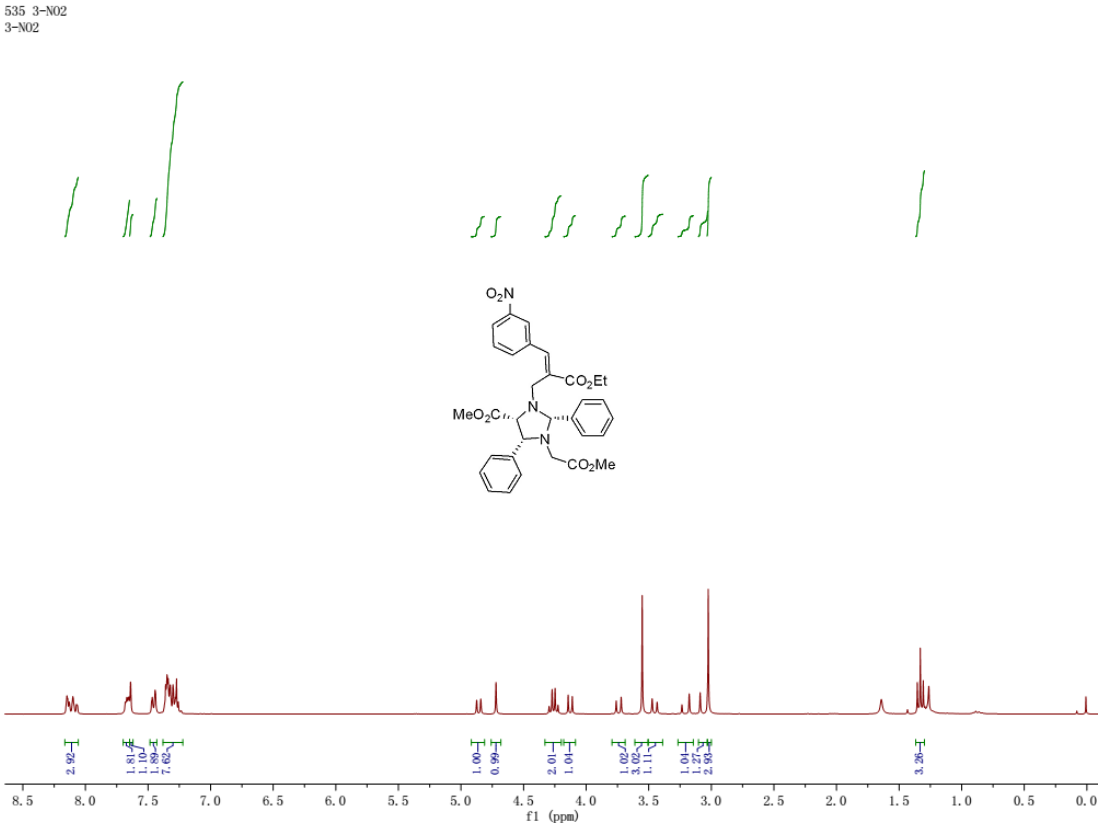
Compound 3l ^{13}C NMR



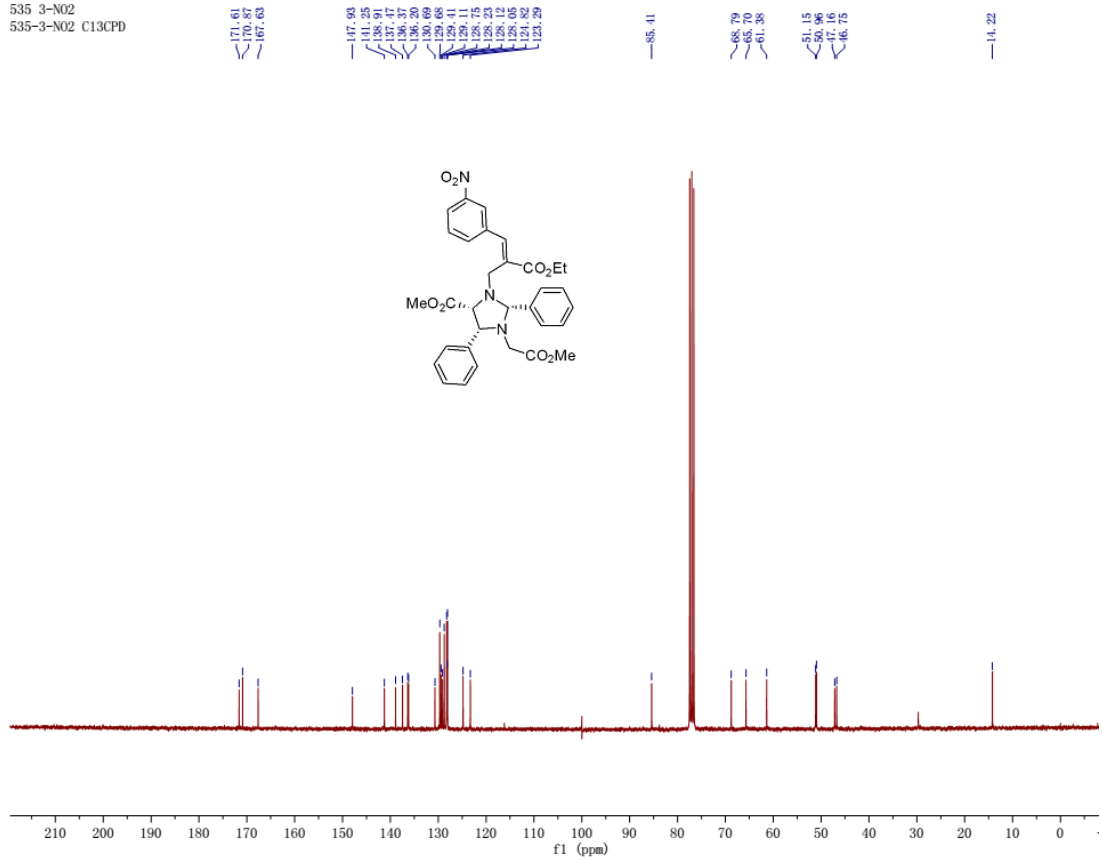
Compound 3m ^{1}H NMR



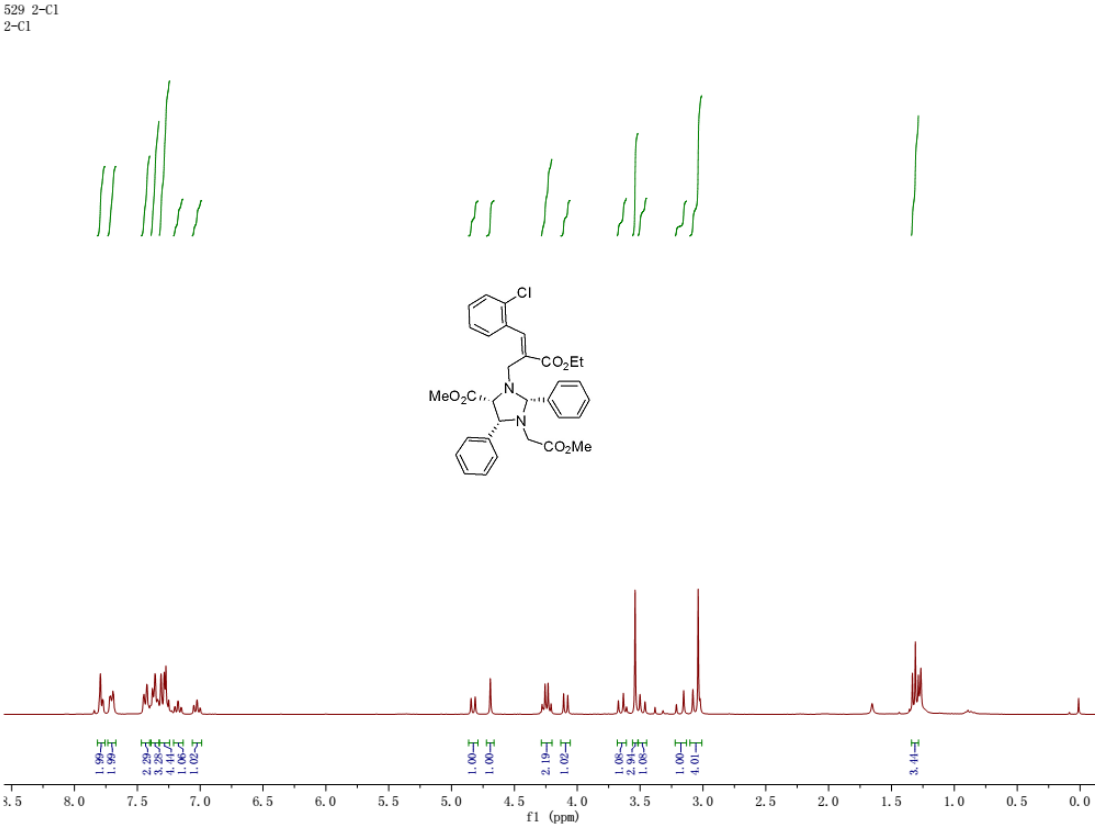
Compound 3m ^{13}C NMR



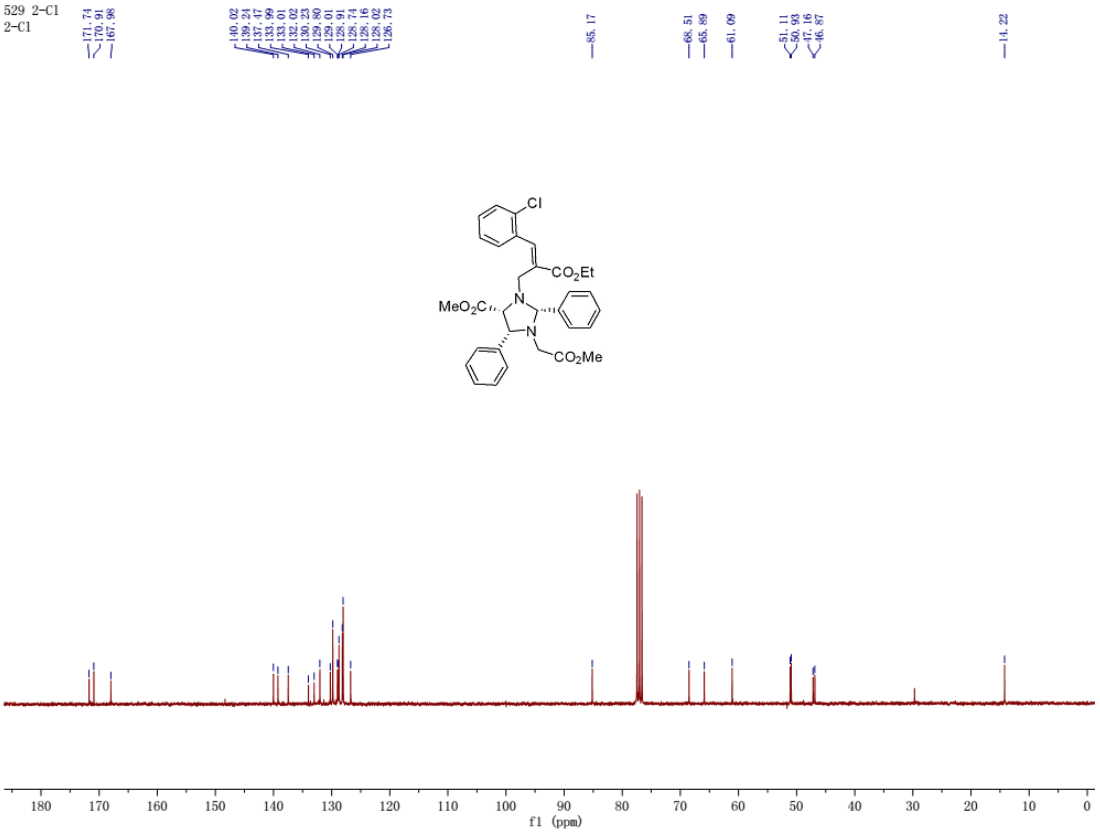
Compound 3n ^{1}H NMR



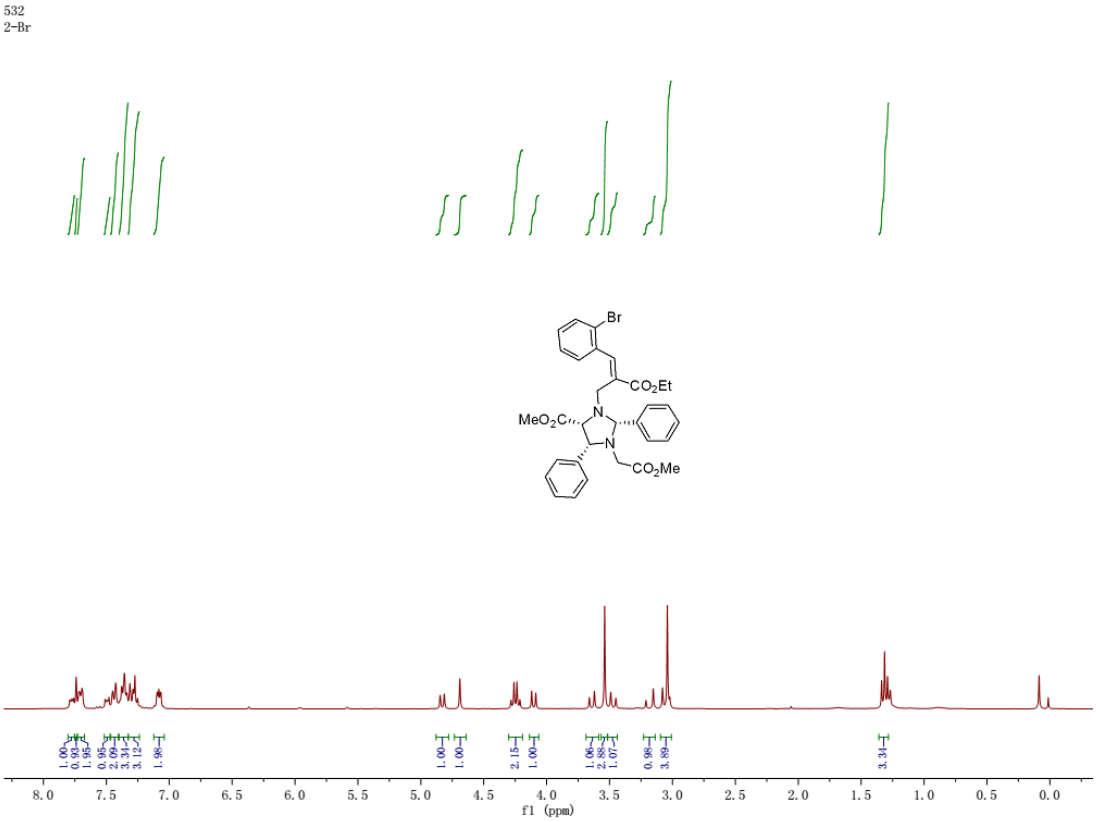
Compound 3n ^{13}C NMR



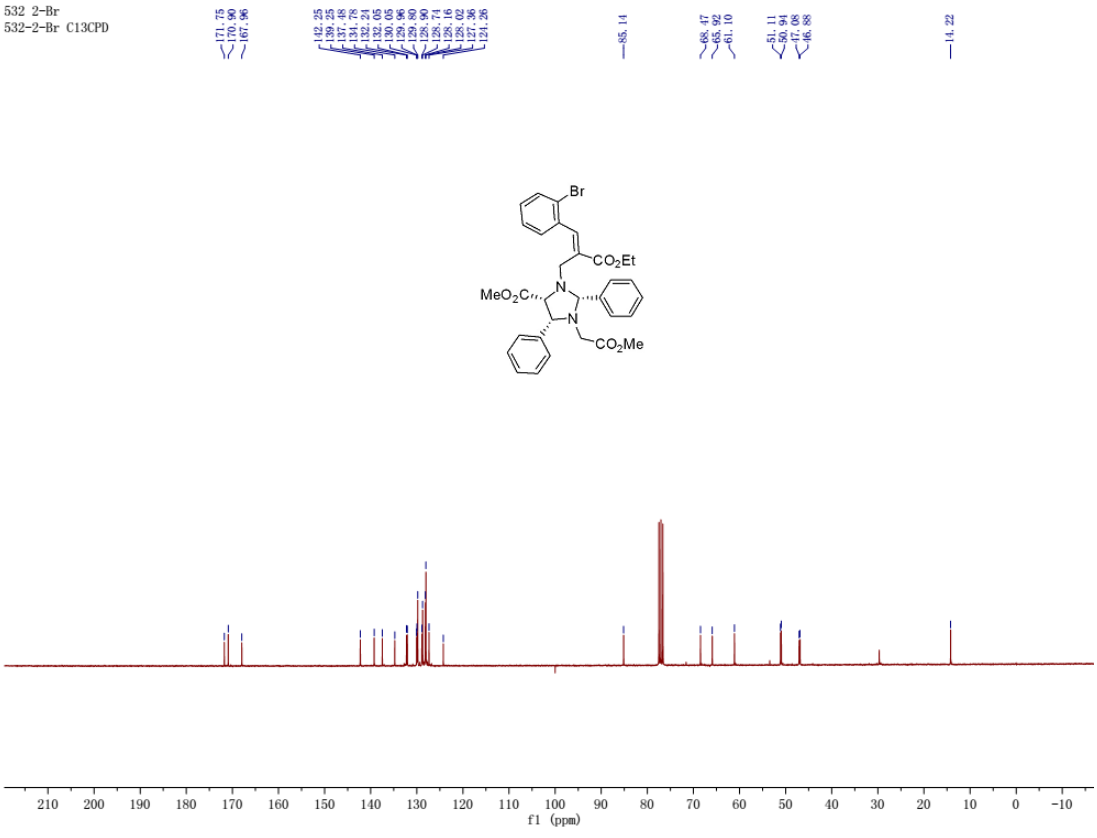
Compound 3o ^{1}H NMR



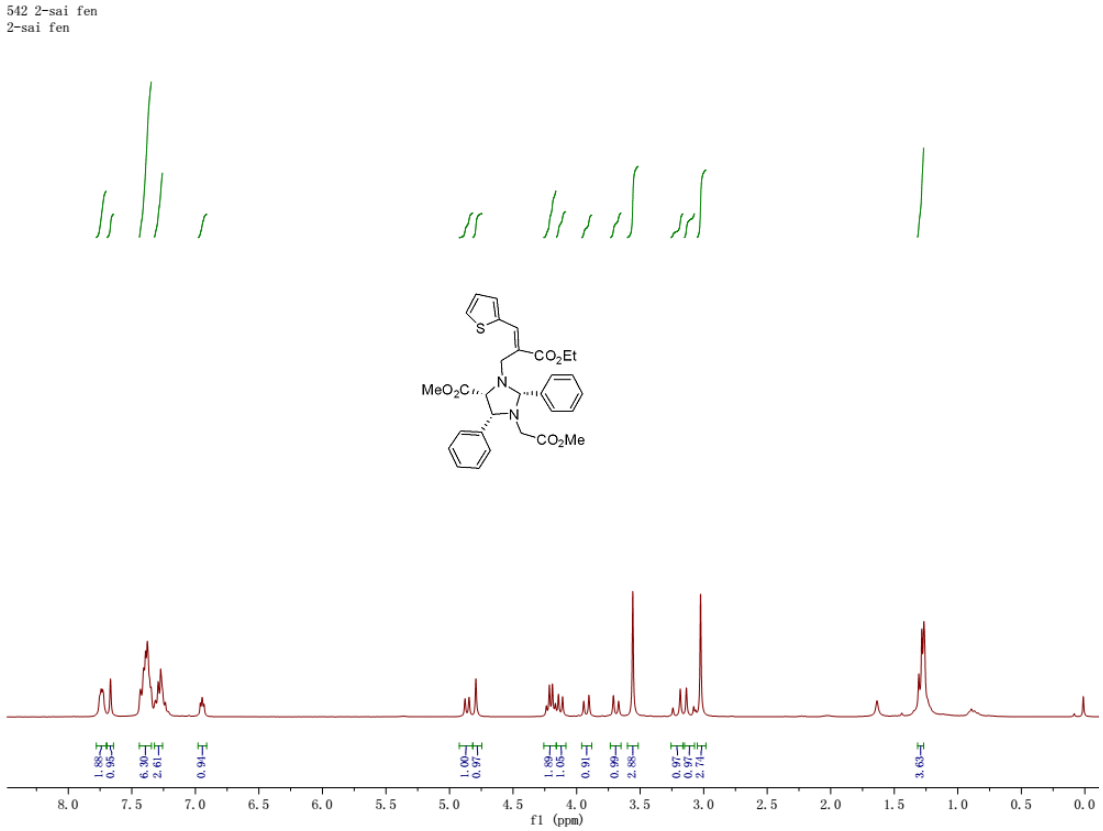
Compound 3o ^{13}C NMR



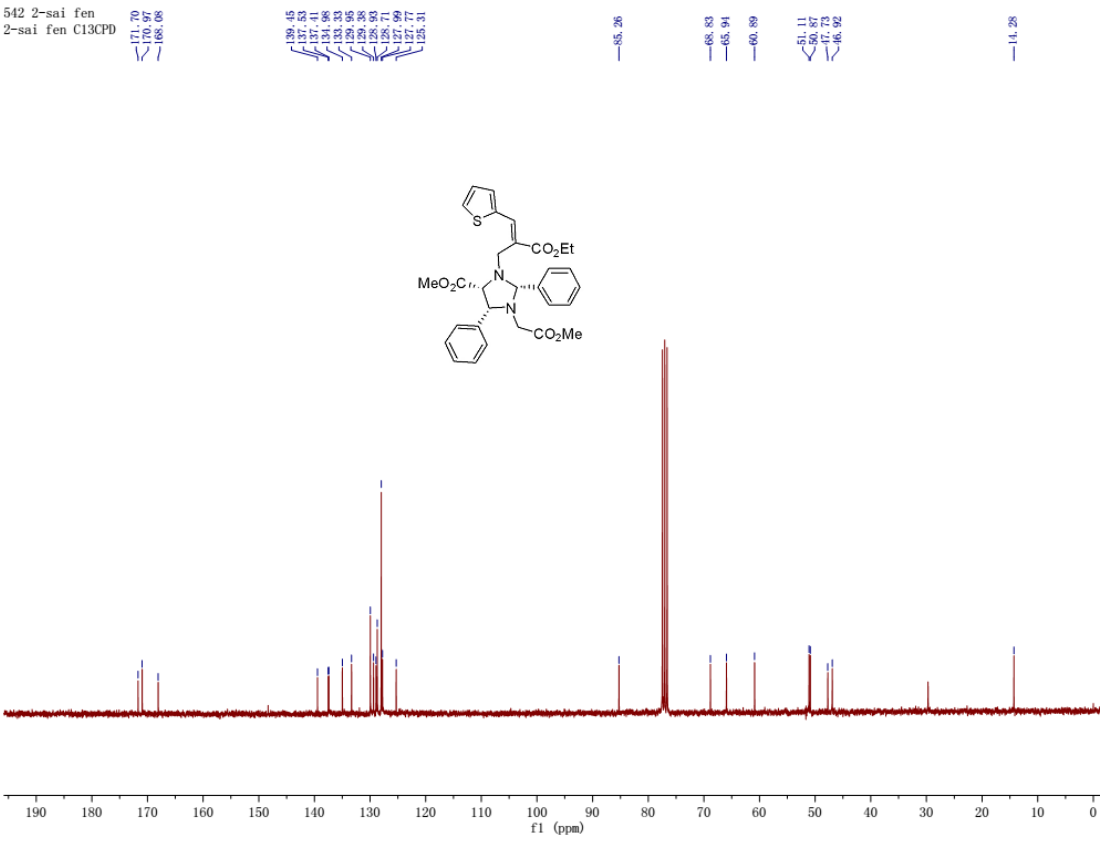
Compound 3p ^{1}H NMR



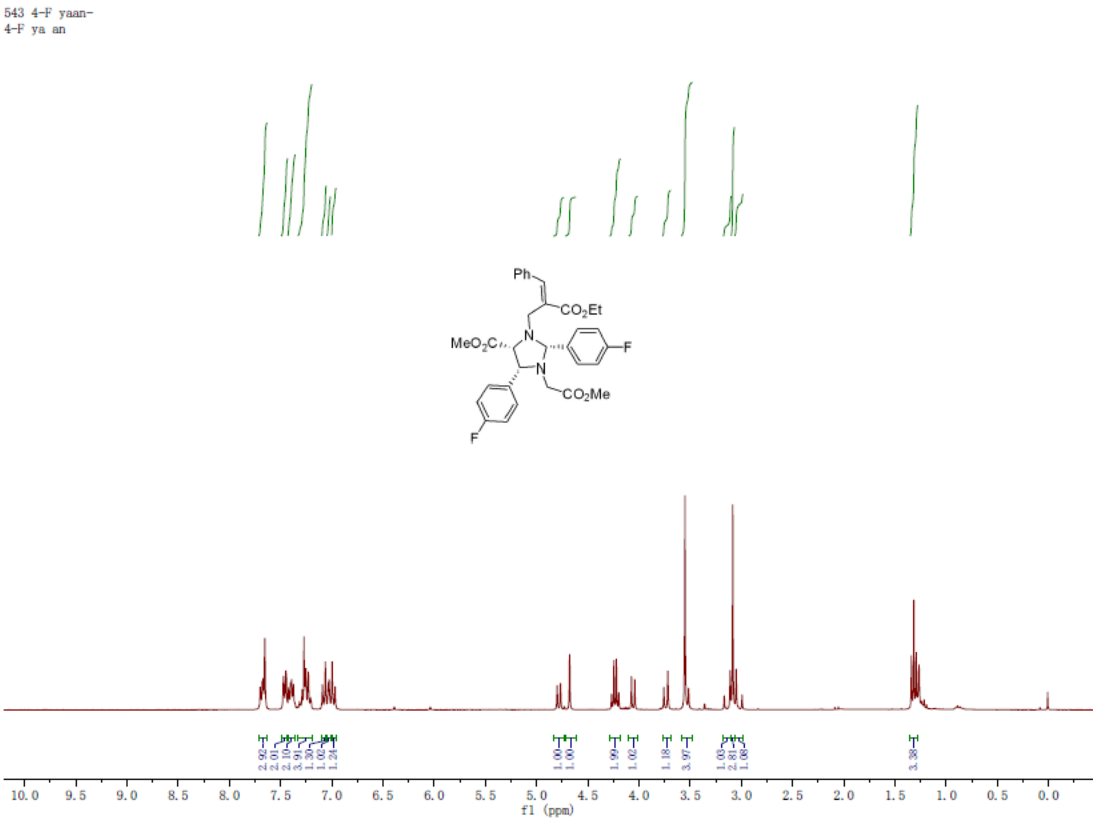
Compound 3p ^{13}C NMR



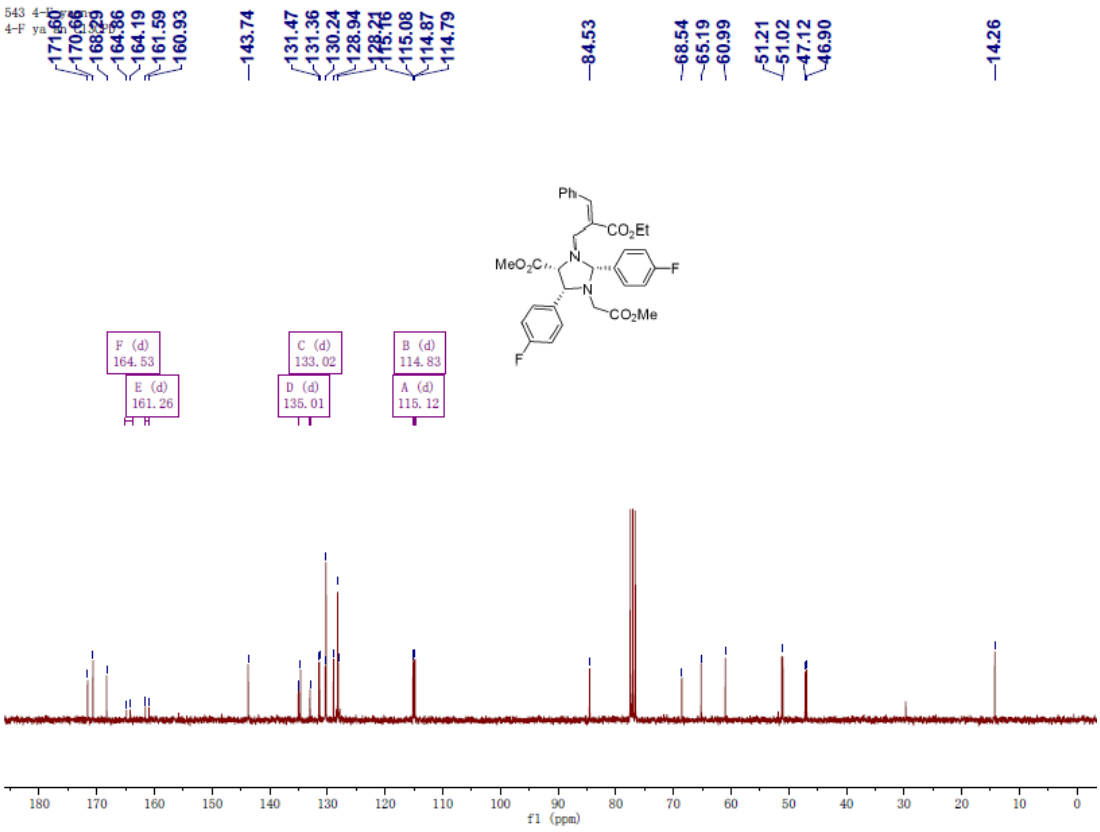
Compound 3q ^{1}H NMR



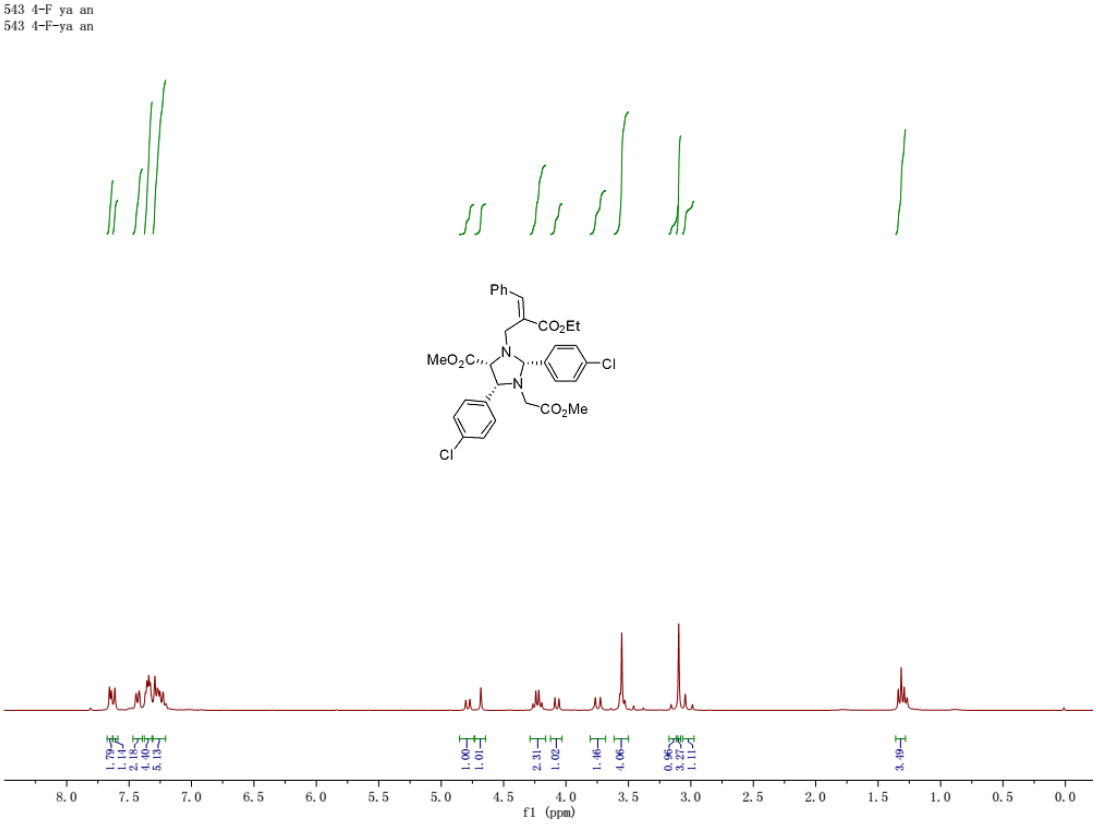
Compound 3q ^{13}C NMR



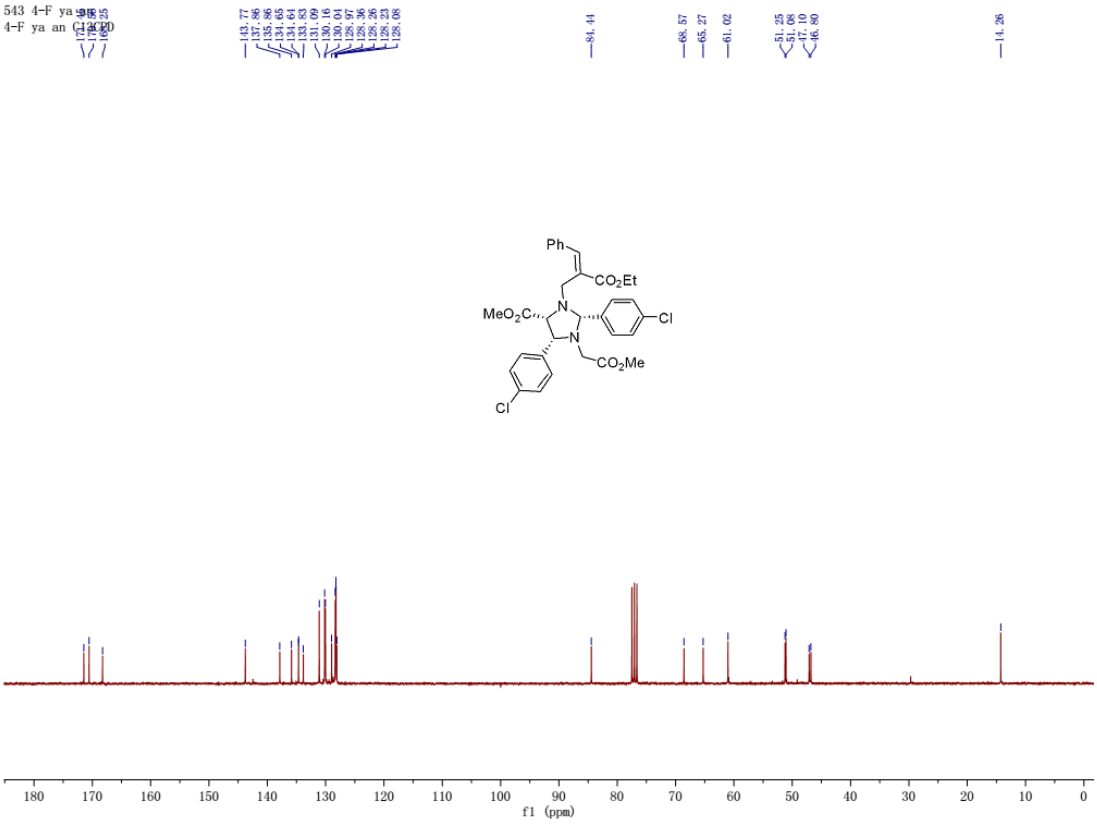
Compound 3r ^{1}H NMR



Compound 3r ^{13}C NMR



Compound 3s ^{1}H NMR



Compound 3s ^{13}C NMR

7. X-ray crystal structures.

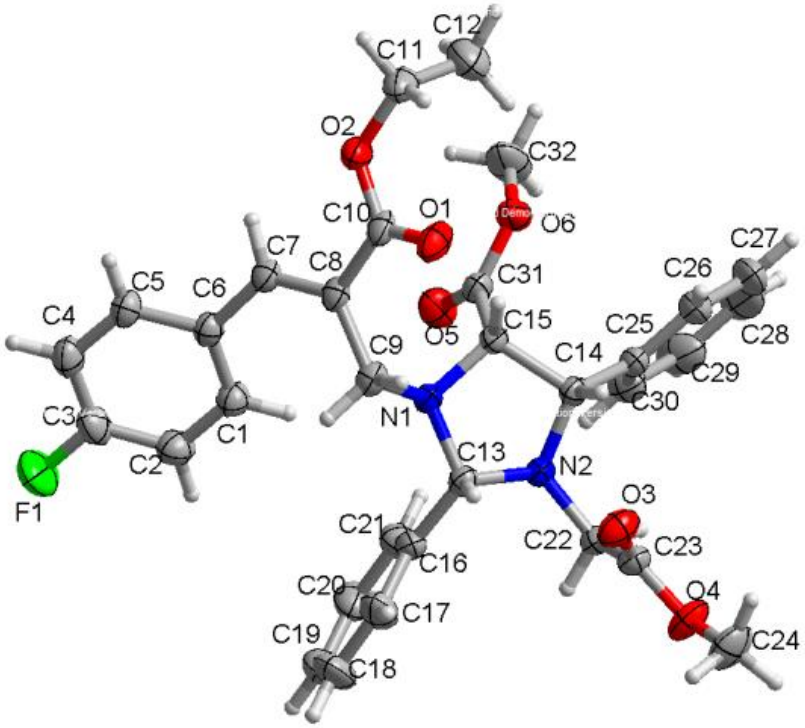


Table 1 Crystal data and structure refinement for 201909243.

Identification code	201909243
Empirical formula	$C_{32}H_{33}FN_2O_6$
Formula weight	560.60
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.31491(15)
b/Å	22.9483(3)
c/Å	13.02398(18)
α/°	90
β/°	101.4004(14)
γ/°	90
Volume/Å^3	3022.08(7)
Z	4
ρ_{calc}g/cm^3	1.232

μ/mm^{-1}	0.737
F(000)	1184.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.704 to 134.15
Index ranges	$-12 \leq h \leq 12$, $-27 \leq k \leq 27$, $-15 \leq l \leq 13$
Reflections collected	23672
Independent reflections	5396 [R_{int} = 0.0344, R_{sigma} = 0.0258]
Data/restraints/parameters	5396/24/349
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1388
Final R indexes [all data]	R_1 = 0.0676, wR_2 = 0.1541
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.20