Supporting Information

Regio- and Diastereoselective Construction of Conjugate Oxindole Derivatives Enabled by Delayed Acyl Transfer of Pyridinium Ylides

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1. General information

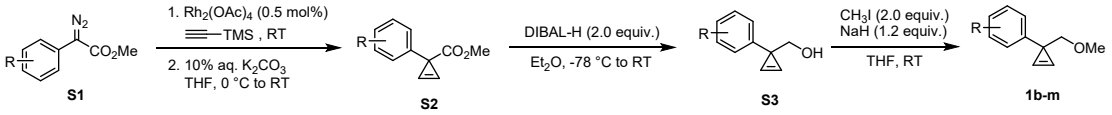
General: All ^{1}H NMR (400 MHz, 500 MHz) and ^{13}C NMR (100 MHz or 125 MHz) and ^{19}F NMR (376 MHz, 471 MHz) spectra were recorded on 400 MHz or 500 MHz Brucker spectrometers in $CDCl_3$; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectrometry (HRMS) data were collected on Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer. Low-resolution mass spectrometry (LRMS) data were collected on Waters SQD2 with Waters H-Class UPLC. Single crystal X-ray diffraction data (**4aa, 4ar, 6a, 8**) were recorded on Bruker-AXS SMART APEX II single crystal X-ray diffractometer. Yields for all compounds were isolated yields for all isomers.

2. Experimental procedures

2.1 General procedure for synthesis of cyclopropenes

Cyclopropenes **1a**, **1n-u** were known products and prepared according to the literature procedures[1].

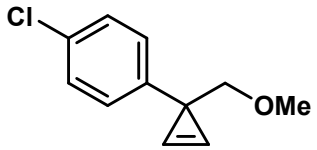
Cyclopropenes **1b-m** were new products and prepared using the follow procedures.



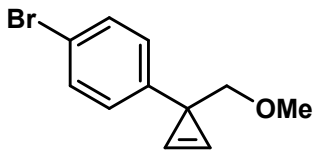
To a suspension of $Rh_2(OAc)_4$ (0.5 mol%) in TMS-acetylene (30 mL) stirred at room temperature, a solution of diazoacetate **S1** (10 mmol) in TMS-acetylene (10 mL) was added *via* syringe pump over 16 hrs. After the addition was complete, the mixture was stirred for additional 2 hrs, when TLC analysis showed completion of the reaction. Then, the most of TMS-acetylene was distilled off and the suspension was concentrated under reduced pressure. The residue was filtered through a short column of Silica gel, (eluent – EtOAc) and the eluate was concentrated and dissolved in THF (50 mL). To the obtained solution 10% aqueous K_2CO_3 (20 mL) was added dropwise at 0^oC. The mixture was warmed to room temperature and stirred overnight, when TLC analysis showed completion of the reaction. Two layers were separated; an organic layer was concentrated and combined back with aqueous phase. Ice-cold water was added, and the mixture was extracted with EtOAc. Combined organic phases were washed (brine), dried (Na_2SO_4), filtered, and concentrated in vacuum. The residue was purified by preparative column chromatography on silica gel, eluent Petroleum ether-EtOAc 10:1 to obtain ester **S2**.

To a stirred solution of ester **S2** (10 mmol) in dry ether (20 mL), DIBAL-H (1.5 M solution in hexanes, 13.5 mL, 2.0 equiv.) was added dropwise at -78°C. The mixture was stirred for 1 hr at -78°C, then warmed to room temperature and stirred for additional 1 hr, and then quenched with saturated NH_4Cl. Formed gel was dissolved in 2 N aqueous HCl, and extracted with EtOAc. Combined organic layers were washed with $NaHCO_3$ and brine, dried Na_2SO_4, filtered, and evaporated. The residue was purified by preparative column chromatography on silica gel, eluent Petroleum ether-EtOAc 5:1 to obtain alcohol **S3**.

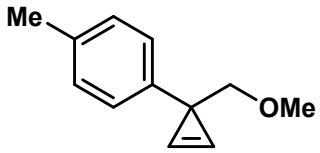
A solution of the alcohol **S3** in anhydrous THF was added to a stirring suspension of NaH (1.2 equiv.) in THF under argon. The mixture was stirred for 10 minutes or until hydrogen gas evolution had ceased. Iodomethane (2.0 equiv.) was added dropwise and the resulting mixture stirred at RT overnight. The mixture was diluted with EtOAc, washed with water and brine, then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative column chromatography on silica gel, eluent Petroleum ether-EtOAc 20:1 to afford the product **1** in quantitative yield.



1-chloro-4-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1b**)
Prepared following aforementioned methods to afford **1b** as pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 2H), 3.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 131.4, 128.2, 127.8, 112.82, 112.78, 80.0, 58.6, 26.4.
ChemDraw: calcd for $C_{11}H_{11}OCl$: 194.05; LRMS found: 195.02 [M+H]+.

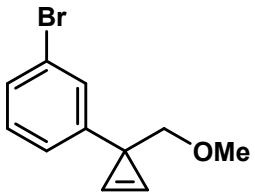


1-bromo-4-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1c**)
Prepared following aforementioned methods to afford **1c** as pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.27 (s, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.79 (s, 2H), 3.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 131.1, 128.3, 119.5, 112.8, 112.7, 80.0, 58.6, 26.5.
ChemDraw: calcd for $C_{11}H_{11}OBr$: 238.00; LRMS found: 239.01 [M+H]+.

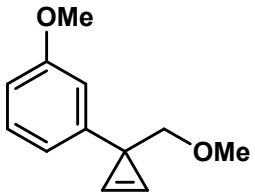


1-(1-(methoxymethyl)cycloprop-2-en-1-yl)-4-methylbenzene (**1d**)
Prepared following aforementioned methods to afford **1d** as pale-yellow oil.

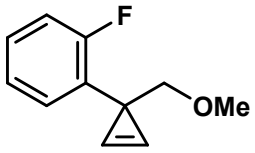
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.13 – 7.06 (m, 4H), 3.81 (s, 2H), 3.36 (s, 3H), 2.30 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 135.1, 128.8, 126.3, 113.12, 113.08, 80.0, 58.5, 26.5, 21.0.
ChemDraw: calcd for $C_{12}H_{14}O$: 174.10; LRMS found: 175.66 [M+H]+.



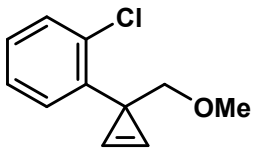
1-bromo-3-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1e**)
Prepared following aforementioned methods to afford **1e** as pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 1H), 7.30 – 7.27 (m, 2H), 7.21 – 7.08 (m, 3H), 3.78 (s, 2H), 3.37 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 129.7, 128.8, 125.1, 122.6, 112.60, 112.56, 79.8, 58.6, 26.6.
ChemDraw: calcd for $C_{11}H_{11}OBr$: 238.00; LRMS found: 239.12 [M+H]+.



1-methoxy-3-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1f**)
Prepared following aforementioned methods to afford **1f** as pale-yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.79 – 6.76 (m, 1H), 6.71 (dd, *J* = 8.1, 2.2 Hz, 1H), 3.82 (s, 2H), 3.79 (s, 3H), 3.38 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 148.5, 129.1, 118.9, 112.6, 112.5, 110.9, 79.9, 58.6, 55.3, 26.8.
ChemDraw: calcd for $C_{12}H_{14}O_2$: 190.10; LRMS found: 191.14 [M+H]+.



1-fluoro-2-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1g**)
Prepared following aforementioned methods to afford **1g** as pale-yellow oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.19 – 7.13 (m, 2H), 7.06 – 7.02 (m, 1H), 6.99 – 6.94 (m, 1H), 3.68 (s, 2H), 3.31 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.3 Hz), 132.8 (d, *J* = 15.4 Hz), 130.2 (d, *J* = 5.2 Hz), 128.0 (d, *J* = 8.2 Hz), 124.2 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 1.5 Hz), 115.7 (d, *J* = 22.5 Hz), 79.7 (d, *J* = 2.7 Hz), 58.7, 24.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.66.
ChemDraw: calcd for $C_{11}H_{11}OF$: 178.08; LRMS found: 179.79 [M+H]+.



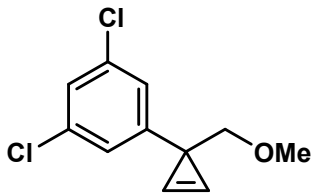
1-chloro-2-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1h**)

Prepared following aforementioned methods to afford **1h** as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.32 – 7.26 (m, 2H), 7.19 – 7.10 (m, 2H), 3.64 (s, 2H), 3.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.2, 130.8, 129.7, 127.9, 127.1, 116.7, 78.9, 58.8, 28.2.

ChemDraw: calcd for $C_{11}H_{11}OCl$: 194.05; LRMS found: 195.90 [M+H]+.



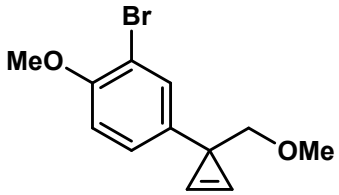
1,3-dichloro-5-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1i**)

Prepared following aforementioned methods to afford **1i** as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.08 – 7.05 (m, 1H), 3.76 (s, 2H), 3.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 132.2, 129.9, 129.5, 128.6, 126.0, 112.6, 112.5, 79.9, 58.6, 26.2.

ChemDraw: calcd for $C_{11}H_{10}OCl_2$: 228.01; LRMS found: 229.99 [M+H]+.



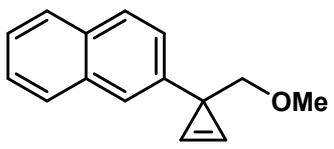
2-bromo-1-methoxy-4-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (**1j**)

Prepared following aforementioned methods to afford **1j** as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.29 (s, 1H), 7.15 (d, J = 8.5 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 2H), 3.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 140.6, 131.5, 126.5, 113.21, 113.17, 111.8, 111.6, 80.0, 58.6, 56.4, 26.0.

ChemDraw: calcd for $C_{12}H_{13}O_2Br$: 268.01; LRMS found: 269.04 [M+H]+.



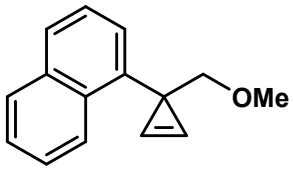
2-(1-(methoxymethyl)cycloprop-2-en-1-yl)naphthalene (**1k**)

Prepared following aforementioned methods to afford **1k** as pale-yellow oil.

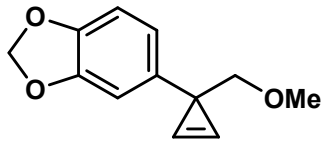
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.74 – 7.65 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.33 (m, 3H), 3.93 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 133.5, 132.0, 127.8, 127.6, 126.0, 125.3, 125.02, 124.97, 113.10,

113.07, 80.0, 58.6, 27.0.
ChemDraw: calcd for $C_{15}H_{14}O$: 210.10; LRMS found: 211.08 [M+H]+.



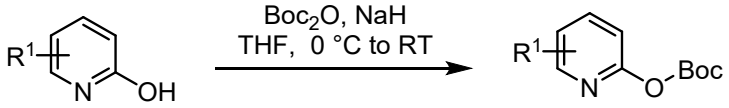
1-(1-(methoxymethyl)cycloprop-2-en-1-yl)naphthalene (**1l**)
Prepared following aforementioned methods to afford **1l** as pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 2H), 7.72 – 7.68 (m, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.41 – 7.37 (m, 2H), 3.73 (s, 2H), 3.28 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 134.2, 131.6, 129.0, 127.2, 126.0, 125.9, 125.6, 124.7, 117.0, 79.7, 58.8, 27.5.
ChemDraw: calcd for $C_{15}H_{14}O$: 210.10; LRMS found: 211.19 [M+H]+.



5-(1-(methoxymethyl)cycloprop-2-en-1-yl)benzo[*d*][1,3]dioxole (**1m**)
Prepared following aforementioned methods to afford **1m** as pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2H), 6.76 – 6.70 (m, 2H), 6.69 – 6.65 (m, 1H), 5.89 (s, 2H), 3.76 (s, 2H), 3.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 145.6, 141.0, 119.4, 113.40, 113.35, 107.9, 107.2, 100.9, 80.3, 58.5, 26.7.
ChemDraw: calcd for $C_{12}H_{12}O_3$: 204.08; LRMS found: 205.02 [M+H]+.

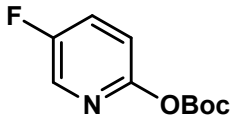
2.2 General procedure for synthesis of 2-oxypyridines

2-oxypyridines **2a-e**, **2h-j** were known products and prepared according to the literature procedures[2]. 2-oxypyridines **2f, 2g, 2k, 2l** were new products and prepared using the follow procedures.



To s suspension of 60% NaH (4.8 mmol) in THF (5 mL) was added dropwise a solution of 2-hydroxypyridine (4 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C, then

Boc_2O (4.4 mmol) in THF (2 mL) was added. After addition, the mixture was warmed to RT and stirred for 2-6 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum to give crude product; the crude was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:50-1:15, note: 3% Et_3N was added in the eluent) to give 2-BocO-pyridines.



tert-butyl (5-fluoropyridin-2-yl) carbonate (**2f**)

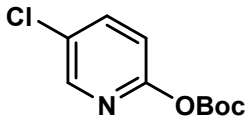
The compound was prepared *via* aforementioned method as white solid (752 mg, 88% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 3.0 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.11 (dd, *J* = 8.8, 3.6 Hz, 1H), 1.56 (s, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0 (d, *J* = 253.4 Hz), 153.6 (d, *J* = 2.1 Hz), 151.0, 135.9 (d, *J* = 26.6 Hz), 126.7 (d, *J* = 20.8 Hz), 116.8 (d, *J* = 5.2 Hz), 84.3, 27.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -130.73.

ChemDraw: calcd for $C_{10}H_{12}NO_3F$: 213.08; LRMS found: 214.09 [M+H]+.



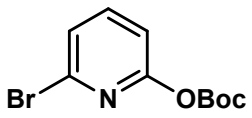
tert-butyl (5-chloropyridin-2-yl) carbonate (**2g**)

The compound was prepared *via* aforementioned method as white solid (780 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.4 Hz, 1H), 7.75 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 150.8, 147.1, 139.4, 129.8, 116.8, 84.6, 27.7.

ChemDraw: calcd for $C_{10}H_{12}NO_3Cl$: 229.05; LRMS found: 230.13 [M+H]+.



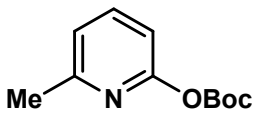
6-bromopyridin-2-yl *tert*-butyl carbonate (**2k**)

The compound was prepared *via* aforementioned method as white solid (983 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 150.5, 141.4, 139.5, 126.4, 114.7, 84.7, 27.7.

ChemDraw: calcd for $C_{10}H_{12}NO_3Br$: 273.00; LRMS found: 274.01 [M+H]+.



tert-butyl (6-methylpyridin-2-yl) carbonate (**2l**)

The compound was prepared *via* aforementioned method as white solid (761 mg, 91% yield).

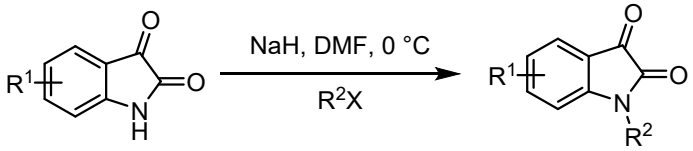
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 157.2, 151.4, 139.8, 121.5, 112.7, 83.9, 27.8, 24.1.

ChemDraw: calcd for $C_{11}H_{15}NO_3$: 209.11; LRMS found: 210.11 [M+H]+.

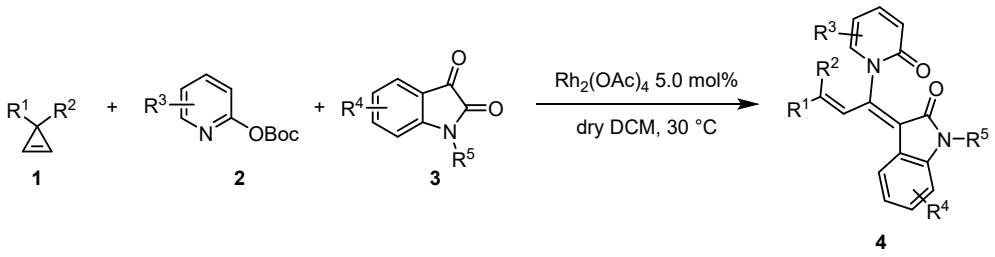
2.3 General procedure for synthesis of substituted isatins

All of the substituted isatins **3a-p** were known products and prepared according to the literature procedures[3].



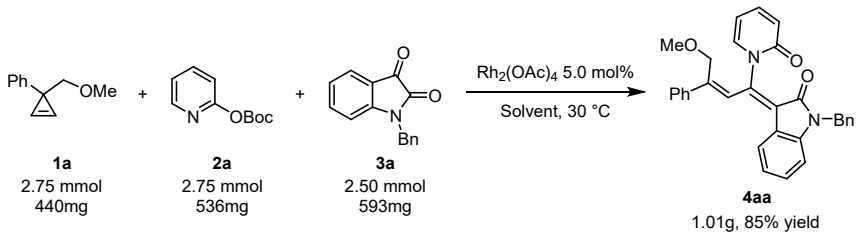
To a solution of substituted indoles (20 mmol, 1.0 equiv.) in DMF (40 mL) was added NaH (30 mmol, 1.5 equiv.) at 0 ºC and stirred 10 minutes, R substituted halogenated hydrocarbon (30 mmol, 1.5 equiv.) was dropped slowly and the reaction was stirred at 0 ºC until substituted indoles was consumed completely. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography.

2.4 General procedure for the three-component reaction



To an oven-dried test tube with a stirring bar were added substituted isatins (0.20 mmol, 1.0 equiv.), 2-BocO-pyridines (0.22 mmol, 1.1 equiv.), cyclopropenes (0.22 mmol, 1.1 equiv.) and $Rh_2(OAc)_4$ (4.4 mg, 5.0 mol%), and then the vessel capped by a septum for injection. The anhydrous CH_2Cl_2 (3.0 mL) was added, and the mixture was stirred at 30 ºC and monitored by TLC. Upon completion of the reaction, the mixture was concentrated to give a residue which was subjected to ^{1}H NMR spectroscopy analysis for the determination of diastereoselectivity (*dr* value). Carful purification the crude product by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1~3/1) afforded pure products.

2.5 General procedure for scale up



1a
2.75 mmol
440mg

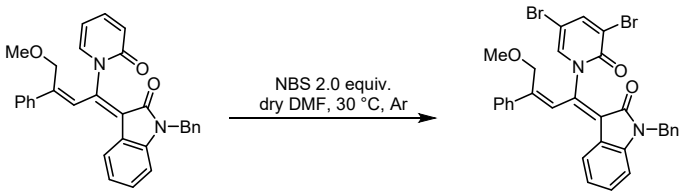
2a
2.75 mmol
536mg

3a
2.50 mmol
593mg

4aa
1.01g, 85% yield

To an oven-dried test tube with a stirring bar were added 1-benzylindoline-2,3-dione **3a** (2.50 mmol, 1.0 equiv.), *tert*-butyl pyridin-2-yl carbonate **2a** (2.75 mmol, 1.1 equiv.), (1-(methoxymethyl)cycloprop-2-en-1-yl)benzene **1a** (2.75 mmol, 1.1 equiv.) and $Rh_2(OAc)_4$ (55 mg, 5.0 mol%), and then the vessel capped by a septum for injection. The anhydrous CH_2Cl_2 (30.0 mL) was added, and the mixture was stirred at 30 °C and monitored by TLC. Upon completion of the reaction, the mixture was concentrated to give a residue which was subjected to ^1H NMR spectroscopy analysis for the determination of diastereoselectivity (*dr* value). Carful purification the crude product by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1~3/1) afforded 1.01g pure product **4aa** in 85% yield.

3. Product derivatizations



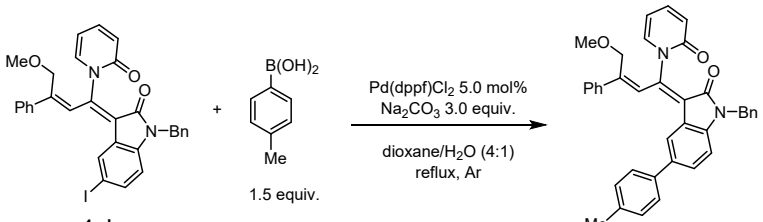
4aa

6a, 98%
(CCDC 2218836)

Synthesis of 6a: Following a modified procedure reported in the supporting information of Shimada[4]. To a 10-mL oven-dried vial with a magnetic stirring bar, **4aa** (47.4 mg, 0.10 mmol), NBS (26.7 mg, 0.20 mmol) and dry DMF (1.5 mL) were added under argon atmosphere. Then the reaction solution was stirred overnight at 30 ℃. After the completion of the reaction (monitored by TLC), the reaction mixture was treated with 10% $Na_2S_2O_3$ aq. (10 mL) and was extracted with AcOEt (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 10 mL) and brine (10 mL) and dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was chromatographed on silica gel (Petroleum ether/EtOAc = 10:1 to 5:1) to give 61.7 mg of pure product **6a** as red brown solid, 98% yield.

4aq **6b**, 90%

Synthesis of 6b: Following a modified procedure from Dess and Martin[5]. Dess-Martin reagent (DMP) (63.6 mg, 0.15 mmol) was added portionwise to a solution of the alcohol **4aq** (46.0 mg, 0.1 mmol) in dry DCM (2 mL) at 0 ºC. After being stirred at ambient temperature for 20 minutes, the reaction mixture was quenched with saturated $NaHCO_3$(aq) (10 mL) and washed with saturated $Na_2S_2O_3$(aq) (2 x 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (Petroleum ether/EtOAc = 10:1 to 2:1) to afford the aldehyde **6b** as red brown solid (41.2 mg, 90%).



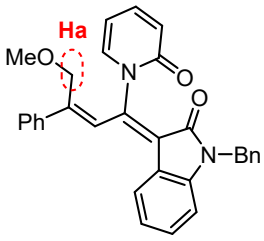
4cd
1.0 equiv.

1.5 equiv.

6c, 70%

Synthesis of 6c: Prepared by a Suzuki coupling following the literature procedure reported in the supporting information of Sun[2b]. To a 10-mL oven-dried Schlenk tube with a magnetic stirring bar, **4cd** (60.0 mg, 0.10 mmol), 4-tolyboronic acid (20.4 mg, 0.15 mmol), $Pd(dppf)Cl_2$ (3.6 mg, 0.005 mol), Na_2CO_3 (31.8 mg, 0.30 mmol), and a combined solvent (1,4-dioxane/H_2O = 4:1, 2.5 mL) were added in sequence at room temperature. The reaction mixture was stirred at 80 ºC for 10 hrs under argon atmosphere. When the reaction was completed (monitored by TLC), quenched with H_2O (15 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed successively with water and brine, dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel (Petroleum ether/EtOAc = 10:1 to 2:1) to give **6c** as red brown solid (39.5 mg, 70%).

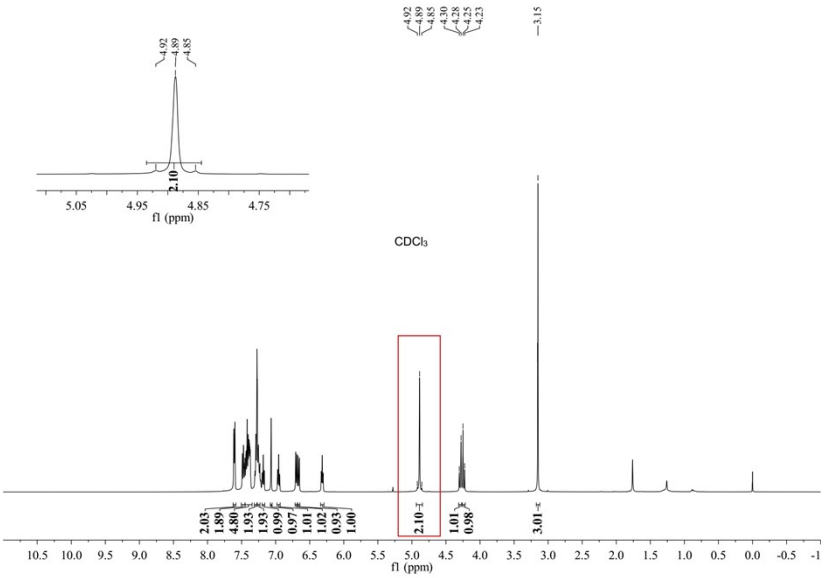
4. Explanation for the abnormal split of methylene at CH_2-O-CH_3 in most examples



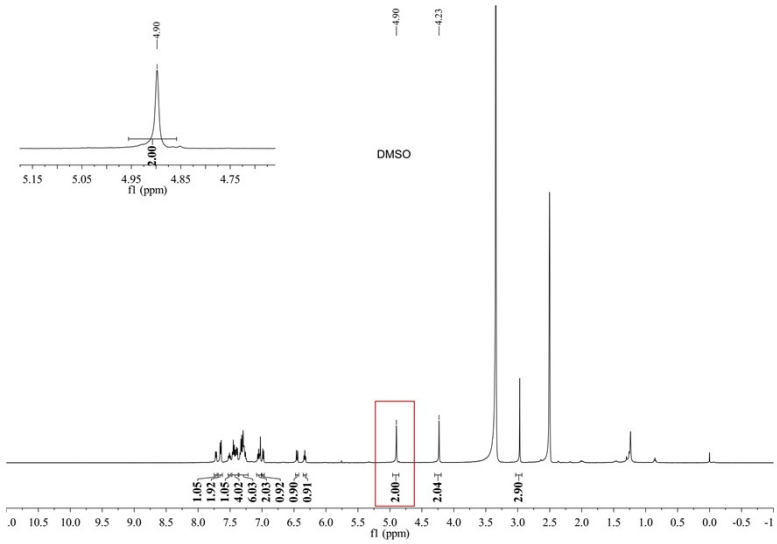
4aa

The abnormal split of **Ha** occurred due to the potential axis chirality of the desire products or the different polarity of deuterated solution. Here using **4aa** as an example and show the difference of Ha in different deuterated solution.

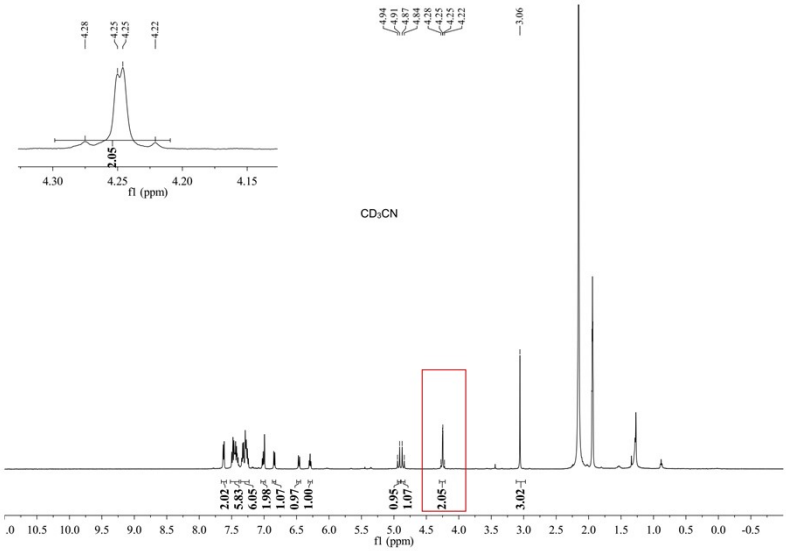
(1) ^{1}H NMR made in $CDCl_3$



(2) ^{1}H NMR made in DMSO



(3) ^{1}H NMR made in CD_3CN



5. General Procedure for the *in vitro* Anti-tumor Activity Study

Cell viability was measured by CCK-8 assay

Human cancer cell line HCT116 was obtained from Cell Cook. Cells were cultured in RPMI1640 medium containing 10% fetal bovine serum and 1% penicillin/streptomycin (Gibco) in a humidified incubator containing 5% CO_2 at 37 °C. Human cancer cell lines MCF-7 was obtained from Procell and cells were cultured in MEM medium containing 10% fetal bovine serum, 1% penicillin/streptomycin (Gibco) and 0.01 mg/mL insulin (Procell) in a humidified incubator containing 5% CO_2 at 37 °C. For cell viability, cells were seeded in 96-well plates at 5000 cells per well. After 24 hours, serially diluted compounds were added and cells were cultured for another 48 hours. Cell viability was measured using a Cell Counting Kit-8 (CCK-8) assay according to the manufacturer's instructions (Yeasen Biotechnology, China).

These representative products **4ac**, **4am**, **4bj**, **4cb**, **4cd**, **4ce**, **4cf**, **4ch**, **4cj**, and **4ck** on cell viability was evaluated *via* CCK8 assay in HCT116 (colon cancer) and MCF-7 (breast cancer) human cancer cell lines, and the *in vitro* anti-tumor activity results have been listed in **Table S1**.

Table S1. Anti-tumor Activity Study of Compounds **4ac**, **4am**, **4bj**, **4cb**, **4cd**, **4ce**, **4cf**, **4ch**, **4cj**, and **4ck** (Inhibitory rate at 20 μM)

Compound	Cancer cell line			
	HCT-116		MCF-7	
	Inhibition (%)	IC_{50} (μM)	Inhibition (%)	IC_{50} (μM)
4ac	92.37 ± 0.76	4.173 ± 0.3001	69.36 ± 1.37	--
4am	81.81 ± 0.97	--	54.27 ± 2.1	--
4bj	60.1 ± 5.23	--	1.85 ± 1.73	--
4cb	94.47 ± 0.42	7.664 ± 0.4152	78.75 ± 3.37	7.761 ± 0.7019
4cd	98.71 ± 0.13	1.546 ± 0.1361	76.83 ± 2.79	--
4ce	70.46 ± 3.89	18.45 ± 1.52	43.52 ± 5.84	--
4cf	99.03 ± 0.08	4.498 ± 0.2138	98.12 ± 0.26	4.789 ± 0.2491
4ch	81.58 ± 1.8	7.741 ± 0.4635	85.83 ± 2.1	9.343 ± 0.5133
4cj	98.85 ± 0.2	0.989 ± 0.0986	91.02 ± 0.1	9.797 ± 0.8555
4ck	97.35 ± 0.1	5.306 ± 0.7364	53.91 ± 2.89	--

6. References

[1] a) M. Rubina, M. Rubin and V. Gevorgyan, *J Am Chem Soc*. **2004**, *126*, 3688-3689; b) A. Edwards, M. Rubina and M. Rubin, *Chemistry*. **2018**, *24*, 1394-1403; c) C. Jiang, J. Wu, J. Han, K. Chen, Y. Qian, Z. Zhang and Y. Jiang, *Chem Commun (Camb)*. **2021**, *57*, 5710-5713; d) S. Nie, A. Lu, E. L. Kuker and V. M. Dong, *J Am Chem Soc*. **2021**, *143*, 6176-6184.

[2] a) G. Xu, P. Chen, P. Liu, S. Tang, X. Zhang and J. Sun, *Angew Chem Int Ed Engl*. **2019**, *58*, 1980-1984; b) H. L. Cui, G. Y. Xu, J. Zhu and J. T. Sun, *Organic Chemistry Frontiers*. **2022**, *9*, 1295-1299.

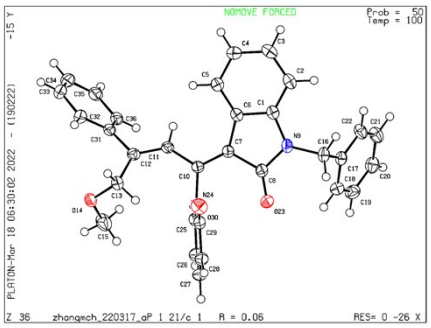
[3] a) R. H. Wang, Y. L. Li, H. J. He, Y. C. Xiao and F. E. Chen, *Chemistry*. **2021**, *27*, 4302-4306; b) Q. Chen, Y. Teng and F. Xu, *Org Lett*. **2021**, *23*, 4785-4790.

[4] T. Kamei, A. Ishibashi and T. Shimada, *Tetrahedron Letters*. **2014**, *55*, 4245-4247.

[5] D. B. Dess and J. C. Martin, *The Journal of Organic Chemistry*. **1983**, *48*, 4155-4156.

7. Single crystal X-ray diffraction data

Crystallographic Data for 4aa.



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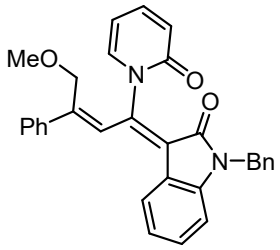

4aa
CCDC: 2218806

Datablock: zhangmch_220317_auto

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Bond precision:   C-C = 0.0032 A          Wavelength=1.54184

Cell:             a=10.8137(1)     b=19.1942(3)       c=11.7185(2)
                  alpha=90         beta=91.929(1)     gamma=90
Temperature:      100 K

                  Calculated                  Reported
Volume            2430.92(6)                  2430.92(6)
Space group       P 21/c                      P 1 21/c 1
Hall group        -P 2ybc                     -P 2ybc
Moiety formula    C31 H26 N2 O3               C31 H26 N2 O3
Sum formula       C31 H26 N2 O3               C31 H26 N2 O3
Mr                474.54                      474.54
Dx,g cm-3         1.297                       1.297
Z                 4                           4
Mu (mm-1)         0.668                       0.668
F000              1000.0                      1000.0
F000'             1002.93
h,k,lmax          13,24,14                    13,23,14
Nref              5030                        4808
Tmin,Tmax         0.777,0.818                 0.867,1.000
Tmin'             0.705

Correction method= # Reported T Limits: Tmin=0.867 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.956          Theta(max)= 75.319

R(reflections)= 0.0629( 4518)                wR2(reflections)=
                                             0.1466( 4808)
S = 1.147                 Npar= 326
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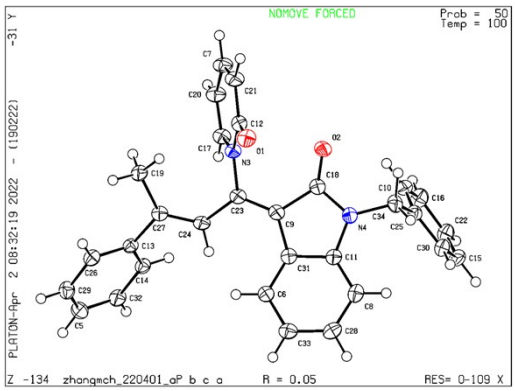
Crystallographic Data for 4ar.



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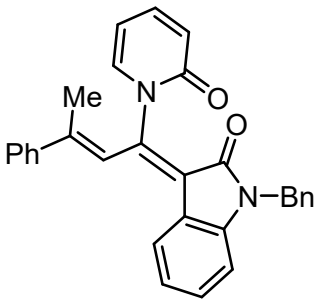


4ar
CCDC: 2218808

Datablock: zhangmch_220401_auto

Bond precision: C-C = 0.0026 A Wavelength=1.54184

Cell: a=19.0303(6) b=11.8859(2) c=20.2655(4)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	4583.90(19)	4583.9(2)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C30 H24 N2 O2	C30 H24 N2 O2
Sum formula	C30 H24 N2 O2	C30 H24 N2 O2
Mr	444.51	444.51
Dx,g cm-3	1.288	1.288
Z	8	8
Mu (mm-1)	0.640	0.640
F000	1872.0	1872.0
F000'	1877.33	
h,k,lmax	23,14,25	23,14,25
Nref	4761	4583
Tmin,Tmax	0.908,0.969	0.434,1.000
Tmin'	0.908	

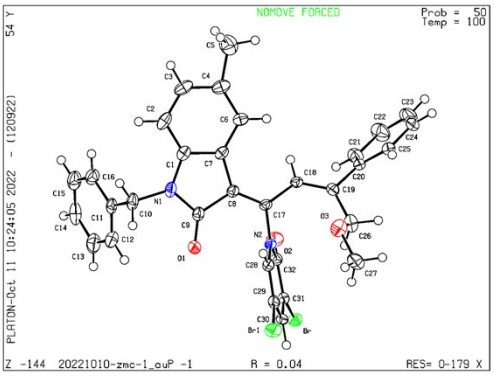
Correction method= # Reported T Limits: Tmin=0.434 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.963 Theta(max)= 75.700

R(reflections)= 0.0516(3768) wR2(reflections)= 0.1335(4583)

S = 1.046 Npar= 308

Crystallographic Data for 6a.



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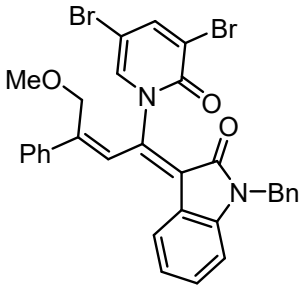
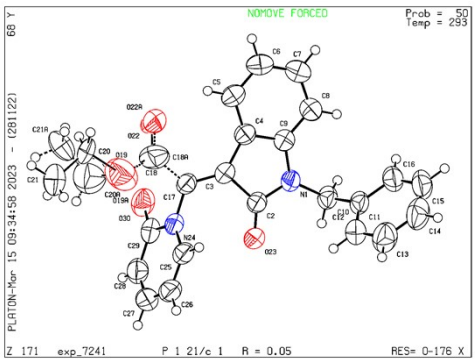


6a
CCDC: 2218836

Datablock: 20221010-zmc-1_auto

```
Bond precision:   C-C = 0.0056 A          Wavelength=1.54184

Cell:           a=8.4448(1)       b=12.1329(2)      c=13.4054(2)
                alpha=86.229(1)   beta=88.805(1)    gamma=71.450(2)
Temperature:    100 K

                Calculated                  Reported
Volume          1299.34(4)                  1299.34(4)
Space group     P -1                        P -1
Hall group      -P 1                        -P 1
Moiety formula  C32 H26 Br2 N2 O3           C32 H26 Br2 N2 O3
Sum formula     C32 H26 Br2 N2 O3           C32 H26 Br2 N2 O3
Mr              646.35                      646.37
Dx,g cm-3       1.652                       1.652
Z               2                           2
Mu (mm-1)       4.272                       4.272
F000            652.0                       652.0
F000'           650.79
h,k,lmax        10,15,16                    10,15,16
Nref            5391                        5119
Tmin,Tmax       0.629,0.808                 0.661,1.000
Tmin'           0.405

Correction method= # Reported T Limits: Tmin=0.661 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.950          Theta(max)= 75.345

R(reflections)= 0.0449( 5048)                wR2(reflections)=
                                             0.1275( 5119)
S = 1.059                 Npar= 354
```

Crystallographic Data for 8.



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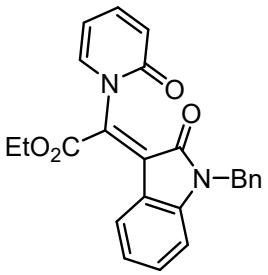


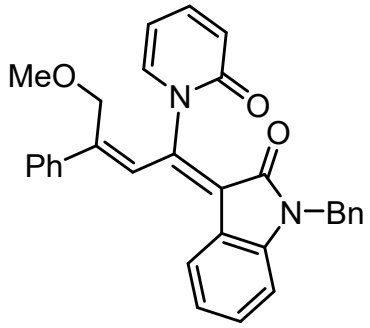
8

CCDC: 2248874

Datablock: exp_7241

```
Bond precision:   C-C = 0.0030 A          Wavelength=1.54184

Cell:             a=8.6150(3)     b=9.0762(3)         c=26.1585(8)
                  alpha=90        beta=91.231(3)      gamma=90
Temperature:      293 K

                  Calculated                  Reported
Volume            2044.90(12)                 2044.90(12)
Space group       P 21/c                      P 1 21/c 1
Hall group        -P 2ybc                     -P 2ybc
Moiety formula    C24 H20 N2 O4               C24 H20 N2 O4
Sum formula       C24 H20 N2 O4               C24 H20 N2 O4
Mr                400.42                      400.42
Dx,g cm-3         1.301                       1.301
Z                 4                           4
Mu (mm-1)         0.730                       0.730
F000              840.0                       840.0
F000'             842.64
h,k,lmax          10,10,31                    10,10,31
Nref              3645                        3644
Tmin,Tmax         0.916,0.964                 0.822,1.000
Tmin'             0.896

Correction method= # Reported T Limits: Tmin=0.822 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 67.043

R(reflections)= 0.0489( 3148)                wR2(reflections)=
                                             0.1518( 3644)
S = 1.039                  Npar= 319
```

8. Analytical data of products



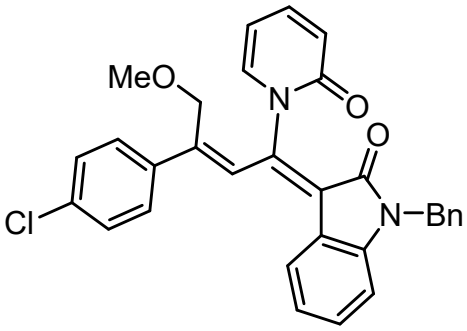
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-indolin-2-one

4aa: 90.0 mg, red brown solid, 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.50 – 7.37 (m, 6H), 7.31 – 7.22 (m, 5H), 7.20 – 7.16 (m, 1H), 7.07 (s, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.68 (dd, *J* = 17.9, 8.5 Hz, 2H), 6.31 (t, *J* = 6.7 Hz, 1H), 4.92 – 4.85 (m, 2H), 4.29 (d, *J* = 13.0 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.1, 146.8, 142.9, 142.2, 140.7, 139.8, 138.8, 135.8, 130.4, 129.1, 128.84, 128.82, 127.7, 127.4, 127.2, 125.3, 125.0, 124.4, 122.4, 122.0, 121.5, 109.3, 105.8, 69.6, 58.3, 43.6.

HRMS-ESI: calcd. for $C_{31}H_{27}N_2O_3$ $[M+H]^+$: 475.2016; found: 475.2028.



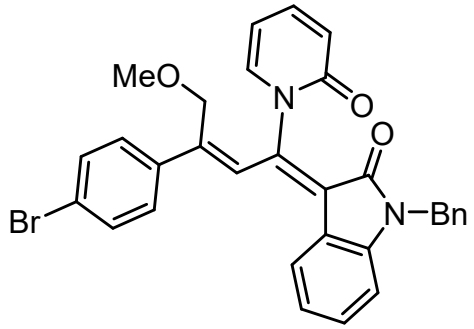
(*Z*)-1-benzyl-3-((*Z*)-3-(4-chlorophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ab: 95.6 mg, red brown solid, 94% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.48 – 7.35 (m, 5H), 7.31 – 7.24 (m, 5H), 7.22 – 7.18 (m, 1H), 7.03 (s, 1H), 6.99 – 6.94 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.33 (td, *J* = 6.8, 1.1 Hz, 1H), 4.93 – 4.83 (m, 2H), 4.26 (d, *J* = 12.6 Hz, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 3.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.1, 145.4, 143.0, 141.9, 140.8, 138.8, 138.3, 135.8, 135.1, 130.6, 129.0, 128.9, 128.6, 127.7, 127.5, 125.6, 125.0, 124.7, 122.5, 122.0, 121.4, 109.4, 105.9, 69.4, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1635.



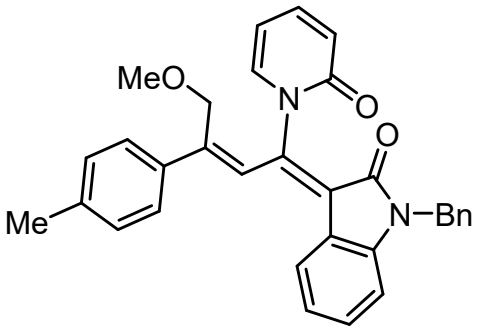
(*Z*)-1-benzyl-3-((*Z*)-3-(4-bromophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ac: 97.4 mg, red brown solid, 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 6.1 Hz, 1H), 7.31 – 7.23 (m, 5H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.33 (t, *J* = 6.6 Hz, 1H), 4.96 – 4.83 (m, 2H), 4.26 (d, *J* = 12.5 Hz, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 3.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.1, 145.5, 142.9, 141.9, 140.8, 138.8, 138.7, 135.8, 132.0, 130.6, 128.9, 128.8, 127.7, 127.4, 125.7, 124.9, 124.7, 123.4, 122.5, 122.0, 121.4, 109.4, 105.9, 69.4, 58.3, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Br$ $[M+H]^+$: 553.1121; found: 553.1117.



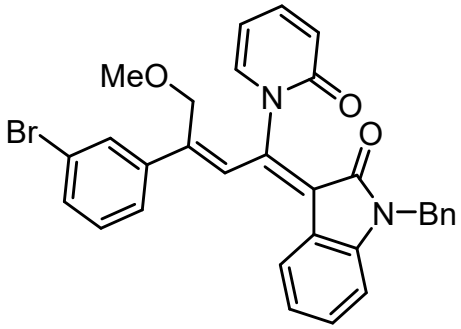
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-(p-tolyl)but-2-en-1-ylidene)indolin-2-one

4ad: 91.0 mg, red brown solid, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 4H), 7.39 – 7.35 (m, 1H), 7.30 – 7.21 (m, 7H), 7.19 – 7.15 (m, 1H), 7.05 (s, 1H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.2 Hz, 1H), 6.31 (td, *J* = 6.8, 1.1 Hz, 1H), 4.89 (s, 2H), 4.28 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.4 Hz, 1H), 3.14 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.2, 146.9, 142.8, 142.3, 140.6, 139.3, 138.8, 136.9, 135.9, 130.3, 129.6, 128.8, 127.7, 127.4, 127.1, 125.0, 124.5, 124.2, 122.4, 122.0, 121.6, 109.2, 105.8, 69.5, 58.3, 43.6, 21.4.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_3$ $[M+H]^+$: 489.2173; found: 489.2184.



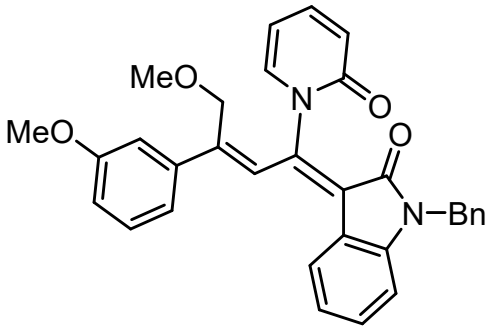
(*Z*)-1-benzyl-3-((*Z*)-3-(3-bromophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ae: 95.0 mg, red brown solid, 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.54 – 7.42 (m, 4H), 7.37 (d, *J* = 6.9 Hz, 1H), 7.31 – 7.18 (m, 7H), 7.02 (s, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.2 Hz, 1H), 6.33 (t, *J* = 6.7 Hz, 1H), 4.94 – 4.84 (m, 2H), 4.25 (d, *J* = 12.5 Hz, 1H), 4.18 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.0, 145.1, 143.0, 142.0, 141.7, 140.8, 138.9, 135.7, 132.0, 130.6, 130.3, 130.2, 128.9, 127.7, 127.4, 126.3, 125.9, 125.0, 124.8, 123.0, 122.5, 122.0, 121.4, 109.4, 105.9, 69.5, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Br$ $[M+H]^+$: 553.1121; found: 553.1138.



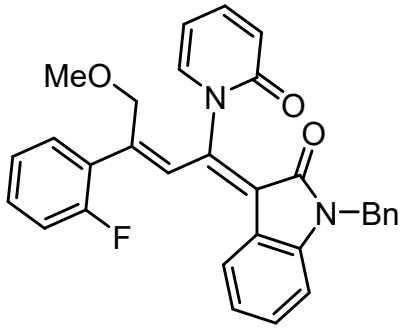
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-3-(3-methoxyphenyl)-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4af: 96.8 mg, red brown solid, 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.40 – 7.23 (m, 7H), 7.21 – 7.17 (m, 2H), 7.13 (s, 1H), 7.07 (s, 1H), 6.99 – 6.92 (m, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.32 (t, *J* = 6.7 Hz, 1H), 4.94 – 4.84 (m, 2H), 4.26 (d, *J* = 12.3 Hz, 1H), 4.21 (d, *J* = 12.3 Hz, 1H), 3.84 (s, 3H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.2, 159.9, 146.7, 142.9, 142.1, 141.4, 140.7, 138.9, 135.8, 130.4, 129.8, 128.9, 127.7, 127.4, 125.5, 125.1, 124.5, 122.5, 121.9, 121.5, 119.6, 114.6, 112.9, 109.3, 105.9, 69.7, 58.4, 55.5, 43.6.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_4$ $[M+H]^+$: 505.2122; found: 505.2119.



(*Z*)-1-benzyl-3-((*Z*)-3-(2-fluorophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

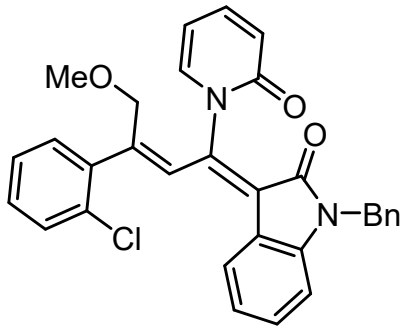
4ag: 58.1 mg, red brown solid, 59% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 – 7.17 (m, 7H), 7.16 – 7.09 (m, 1H), 7.02 – 6.95 (m, 2H), 6.73 – 6.64 (m, 2H), 6.33 (t, *J* = 6.7 Hz, 1H), 4.95 – 4.83 (m, 2H), 4.26 (d, *J* = 13.0 Hz, 1H), 4.19 (d, *J* = 13.0 Hz, 1H), 3.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.0, 160.2 (d, *J* = 248.5 Hz), 143.7 (d, *J* = 1.6 Hz), 142.9, 141.7, 140.8, 139.0, 135.8, 130.6 (d, *J* = 3.5 Hz), 130.5, 130.4 (d, *J* = 8.3 Hz), 128.9, 128.0 (d, *J* = 13.5 Hz), 127.7, 127.7 (d, *J* = 2.5 Hz), 127.4, 125.1, 124.6, 124.6, 122.5, 122.0, 121.3, 116.1 (d, *J* = 22.5 Hz), 109.3, 105.9, 70.3 (d, *J* = 3.3 Hz), 58.4, 43.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.38.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3F$ $[M+H]^+$: 493.1922; found: 493.1925.



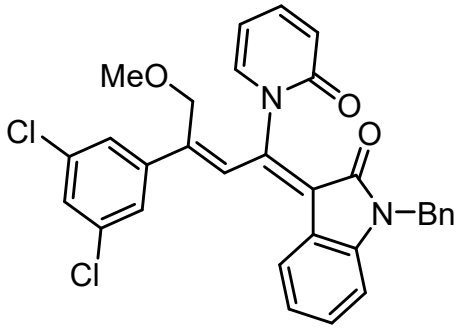
(*Z*)-1-benzyl-3-((*Z*)-3-(2-chlorophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ah: 27.4 mg, red brown solid, 37% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.32 – 7.27 (m, 5H), 7.26 – 7.17 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.72 – 6.66 (m, 2H), 6.34 (t, *J* = 6.7 Hz, 1H), 4.94 – 4.83 (m, 2H), 4.20 (d, *J* = 13.2 Hz, 1H), 4.14 (d, *J* = 13.2 Hz, 1H), 3.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.0, 147.0, 142.9, 141.7, 140.8, 139.8, 139.2, 135.8, 132.4, 131.1, 130.5, 129.9, 129.6, 128.9, 127.72, 127.70, 127.4, 127.1, 125.3, 124.4, 122.5, 121.9, 121.4, 109.3, 105.7, 70.6, 58.7, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1645.



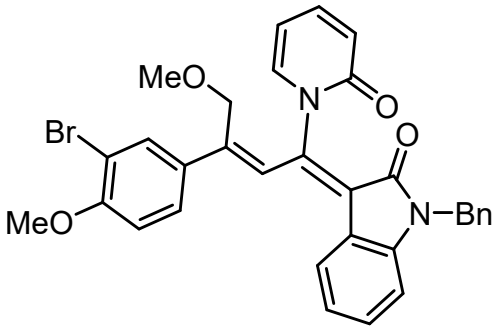
(*Z*)-1-benzyl-3-((*Z*)-3-(3,5-dichlorophenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ai: 93.2 mg, red brown solid, 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.7 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.32 – 7.19 (m, 6H), 7.02 (s, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.34 (t, *J* = 6.7 Hz, 1H), 4.97 – 4.83 (m, 2H), 4.24 (d, *J* = 12.5 Hz, 1H), 4.16 (d, *J* = 12.5 Hz, 1H), 3.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.0, 144.1, 143.0, 141.5, 140.9, 139.8, 138.9, 135.7, 133.2, 133.1, 130.8, 129.1, 128.9, 127.8, 127.4, 126.53, 126.50, 124.98, 124.95, 122.6, 122.1, 121.3, 109.5, 106.0, 69.3, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{25}N_2O_3Cl_2$ $[M+H]^+$: 543.1237; found: 543.1246.



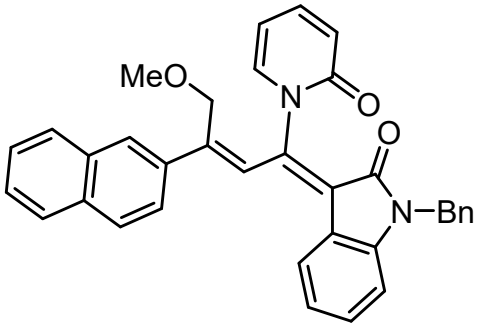
(*Z*)-1-benzyl-3-((*Z*)-3-(3-bromo-4-methoxyphenyl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4aj: 107.1 mg, red brown solid, 92% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.36 (d, *J* = 6.8 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.26 – 7.17 (m, 3H), 7.00 – 6.91 (m, 3H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.33 (t, *J* = 6.7 Hz, 1H), 4.93 – 4.84 (m, 2H), 4.24 (d, *J* = 12.5 Hz, 1H), 4.18 (d, *J* = 12.5 Hz, 1H), 3.92 (s, 3H), 3.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.1, 156.6, 145.0, 142.8, 141.9, 140.7, 138.8, 135.8, 133.4, 132.0, 130.4, 128.8, 127.67, 127.65, 127.4, 124.9, 124.6, 124.4, 122.4, 121.9, 121.5, 112.1, 111.9, 109.3, 106.0, 69.3, 58.3, 56.5, 43.6.

HRMS-ESI: calcd. for $C_{32}H_{28}N_2O_4Br$ $[M+H]^+$: 583.1227; found: 583.1230.



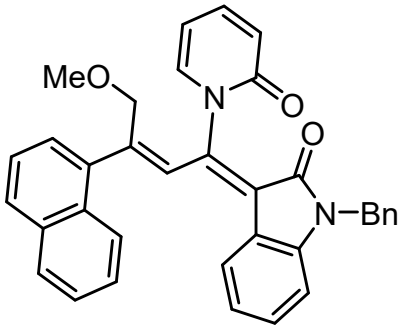
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-3-(naphthalen-2-yl)-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4ak: 82.8 mg, yellow solid, 79% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.90 – 7.83 (m, 3H), 7.72 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.44 – 7.40 (m, 1H), 7.32 – 7.25 (m, 5H), 7.21 – 7.16 (m, 2H), 6.93 (td, *J* = 7.7, 0.8 Hz, 1H), 6.73 – 6.66 (m, 2H), 6.34 (td, *J* = 6.8, 1.2 Hz, 1H), 4.95 – 4.84 (m, 2H), 4.39 (d, *J* = 12.5 Hz, 1H), 4.35 (d, *J* = 12.5 Hz, 1H), 3.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.2, 146.9, 142.9, 142.3, 140.8, 139.0, 137.3, 135.9, 133.6, 133.4, 130.4, 128.9, 128.7, 128.5, 127.8, 127.7, 127.5, 126.94, 126.89, 126.7, 125.9, 125.1, 124.7, 124.5, 122.5, 122.0, 121.6, 109.3, 105.9, 69.6, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{35}H_{29}N_2O_3$ $[M+H]^+$: 525.2173; found: 525.2178.



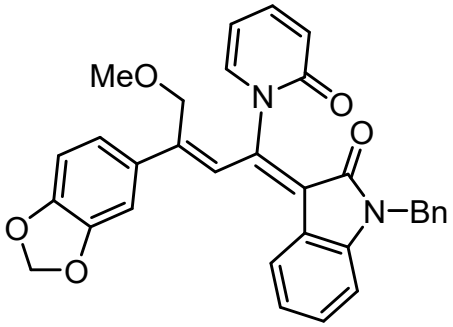
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-3-(naphthalen-1-yl)-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)indolin-2-one

4al: 38.8 mg, red brown solid, 37% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 17.4, 7.9 Hz, 2H), 7.59 – 7.48 (m, 7H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.00 (s, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 9.7 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.38 (t, *J* = 6.7 Hz, 1H), 4.95 – 4.81 (m, 2H), 4.16 (d, *J* = 12.4 Hz, 1H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 162.0, 147.4, 143.0, 142.8, 141.0, 140.3, 139.7, 135.8, 133.9, 131.4, 130.3, 128.9, 128.6, 127.9, 127.7, 127.5, 126.9, 126.31, 126.25, 125.7, 125.4, 125.3, 123.8, 122.5, 121.69, 121.66, 109.2, 105.4, 72.0, 58.7, 43.6.

HRMS-ESI: calcd. for $C_{35}H_{29}N_2O_3$ $[M+H]^+$: 525.2173; found: 525.2177.



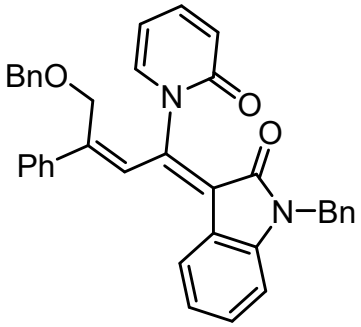
(*Z*)-3-((*Z*)-3-(benzo[d][1,3]dioxol-5-yl)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)but-2-en-1-ylidene)-1-benzylindolin-2-one

4am: 99.5 mg, red brown solid, 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.35 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.30 – 7.23 (m, 5H), 7.20 – 7.09 (m, 3H), 6.99 – 6.95 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.31 (td, *J* = 6.8, 1.0 Hz, 1H), 6.00 (s, 2H), 4.89 (s, 2H), 4.23 (d, *J* = 12.4 Hz, 1H), 4.17 (d, *J* = 12.3 Hz, 1H), 3.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.2, 148.6, 148.2, 146.4, 142.8, 142.2, 140.7, 138.8, 135.9, 134.0, 130.3, 128.8, 127.7, 127.4, 125.0, 124.2, 122.4, 122.0, 121.60, 121.56, 109.3, 108.6, 107.5, 105.9, 101.6, 69.6, 58.4, 43.6.

HRMS-ESI: calcd. for $C_{32}H_{27}N_2O_5$ $[M+H]^+$: 519.1914; found: 519.1916.



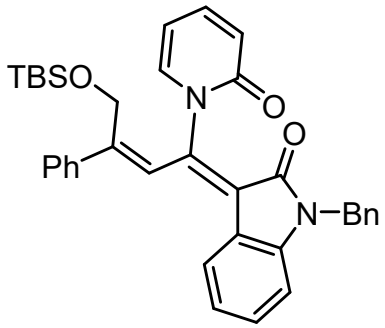
(*Z*)-1-benzyl-3-((*Z*)-4-(benzyloxy)-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4an: 101.2 mg, red brown solid, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.38 (m, 4H), 7.32 – 7.26 (m, 4H), 7.24 – 7.17 (m, 6H), 7.12 – 7.08 (m, 3H), 6.97 (td, *J* = 7.7, 0.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 9.2 Hz, 1H), 6.21 (td, *J* = 6.8, 1.2 Hz, 1H), 4.88 (s, 2H), 4.37 (s, 2H), 4.35 – 4.28 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.1, 146.6, 142.9, 142.3, 140.7, 139.7, 138.8, 137.7, 135.8, 130.4, 129.1, 128.9, 128.8, 128.4, 128.0, 127.9, 127.7, 127.4, 127.3, 125.5, 125.0, 124.3, 122.5, 121.9, 121.5, 109.3, 105.9, 72.6, 67.2, 43.6.

HRMS-ESI: calcd. for $C_{37}H_{31}N_2O_3$ $[M+H]^+$: 551.2329; found: 551.2344.



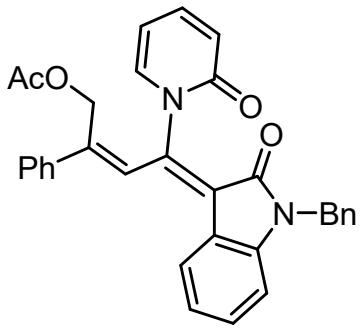
(*Z*)-1-benzyl-3-((*Z*)-4-((tert-butyldimethylsilyl)oxy)-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ao: 104.5 mg, red brown solid, 91% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.45 – 7.35 (m, 5H), 7.31 – 7.26 (m, 3H), 7.26 – 7.22 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.87 (s, 1H), 6.70 – 6.64 (m, 2H), 6.30 (t, *J* = 6.7 Hz, 1H), 4.94 – 4.84 (m, 2H), 4.58 (d, *J* = 13.3 Hz, 1H), 4.51 (d, *J* = 13.3 Hz, 1H), 0.70 (s, 9H), -0.11 (s, 3H), -0.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.1, 150.1, 142.8, 142.2, 140.6, 139.9, 138.3, 135.9, 130.3, 128.84, 128.80, 128.5, 127.68, 127.66, 127.4, 124.9, 124.1, 123.6, 122.4, 122.1, 121.5, 109.2, 106.1, 60.8, 43.6, 25.8, 18.2, -5.36, -5.41.

HRMS-ESI: calcd. for $C_{36}H_{39}N_2O_3Si$ $[M+H]^+$: 575.2724; found: 575.2746.



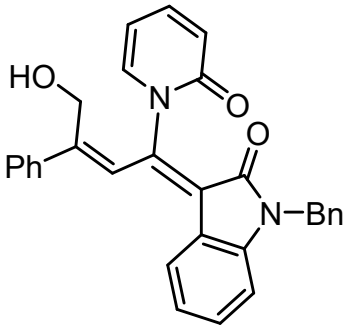
(*Z*)-4-((*Z*)-1-benzyl-2-oxoindolin-3-ylidene)-4-(2-oxopyridin-1(2*H*)-yl)-2-phenylbut-2-en-1-yl acetate

4ap: 94.4 mg, red brown solid, 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.47 – 7.40 (m, 6H), 7.33 – 7.26 (m, 4H), 7.25 – 7.17 (m, 2H), 7.13 (s, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 9.2 Hz, 1H), 6.32 (td, *J* = 6.8, 1.1 Hz, 1H), 4.99 – 4.83 (m, 4H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 164.6, 161.9, 143.6, 143.0, 141.6, 140.6, 138.8, 138.5, 135.7, 130.7, 129.3, 128.92, 128.87, 127.7, 127.4, 127.1, 126.7, 125.0, 124.9, 122.5, 122.2, 121.3, 109.4, 106.2, 61.4, 43.7, 20.8.

HRMS-ESI: calcd. for $C_{32}H_{26}N_2O_4$ $[M+H]^+$: 503.1965; found: 503.1973.



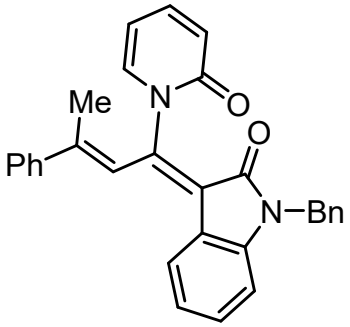
(*Z*)-1-benzyl-3-((*Z*)-4-hydroxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4aq: 16.6 mg, red brown solid, 38% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 6.5 Hz, 1H), 7.26 – 7.23 (m, 5H), 7.17 – 7.08 (m, 6H), 7.04 – 6.96 (m, 4H), 6.67 – 6.61 (m, 2H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.72 – 5.67 (m, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 4.77 (d, *J* = 15.7 Hz, 1H), 4.49 (d, *J* = 17.4 Hz, 1H), 4.36 (d, *J* = 17.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 161.8, 153.7, 143.7, 142.5, 140.7, 139.0, 137.3, 135.9, 130.0, 128.8, 128.4, 128.2, 127.7, 127.5, 125.3, 123.3, 122.6, 121.7, 121.2, 120.0, 109.0, 105.7, 67.2, 43.5.

HRMS-ESI: calcd. for $C_{30}H_{25}N_2O_4$ $[M+H]^+$: 461.1860; found: 461.1862.



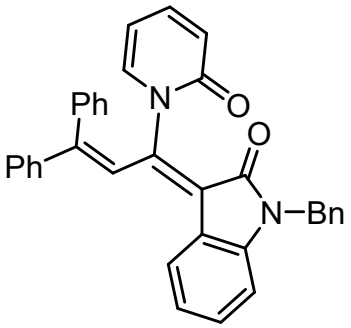
(*Z*)-1-benzyl-3-((*E*)-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ar: 58.6 mg, red brown solid, 66% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.36 (m, 4H), 7.32 – 7.26 (m, 5H), 7.25 – 7.16 (m, 2H), 7.01 – 6.95 (m, 2H), 6.72 – 6.66 (m, 2H), 6.32 (td, *J* = 6.9, 1.2 Hz, 1H), 4.93 (d, *J* = 15.8 Hz, 1H), 4.86 (d, *J* = 15.8 Hz, 1H), 2.11 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 162.4, 148.5, 142.9, 142.8, 142.5, 140.5, 137.4, 135.9, 130.1, 129.0, 128.82, 128.80, 127.6, 127.4, 126.6, 124.9, 123.7, 122.4, 122.34, 122.29, 121.5, 109.2, 106.6, 43.6, 17.7.

HRMS-ESI: calcd. for $C_{30}H_{25}N_2O_2$ $[M+H]^+$: 445.1911; found: 445.1913.



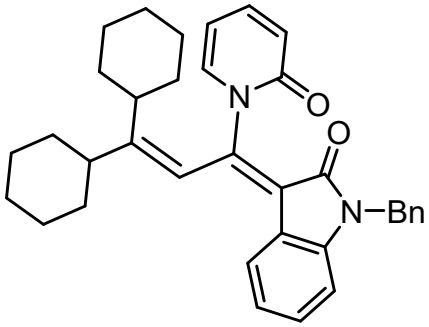
(*Z*)-1-benzyl-3-(1-(2-oxopyridin-1(2*H*)-yl)-3,3-diphenylallylidene)indolin-2-one

4as: 97.2 mg, red brown solid, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 5H), 7.33 – 7.27 (m, 4H), 7.26 – 7.18 (m, 6H), 7.09 – 6.98 (m, 4H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 (dd, *J* = 6.9, 1.6 Hz, 1H), 6.30 (d, *J* = 9.1 Hz, 1H), 5.67 (td, *J* = 6.8, 1.1 Hz, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.81 (d, *J* = 15.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 161.4, 151.5, 143.8, 142.7, 141.3, 140.0, 139.0, 138.8, 136.0, 130.1, 129.6, 129.4, 128.83, 128.77, 128.6, 128.53, 128.47, 127.7, 127.5, 124.8, 123.9, 123.3, 122.5, 122.2, 121.5, 109.2, 105.0, 43.6.

HRMS-ESI: calcd. for $C_{35}H_{26}N_2O_2$ $[M+H]^+$: 507.2067; found: 507.2076.



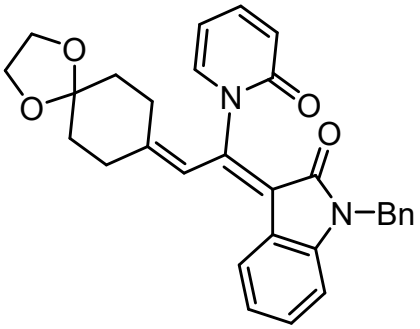
(*Z*)-1-benzyl-3-(3,3-dicyclohexyl-1-(2-oxopyridin-1(2*H*)-yl)allylidene)indolin-2-one

4at: 46.6 mg, yellow solid, 45% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.26 – 7.12 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.70 – 6.61 (m, 2H), 6.48 (s, 1H), 6.27 (t, *J* = 6.2 Hz, 1H), 4.92 – 4.83 (m, 2H), 2.43 – 2.36 (m, 1H), 2.18 – 2.12 (m, 1H), 1.85 – 1.72 (m, 6H), 1.66 – 1.54 (m, 4H), 1.45 – 1.31 (m, 6H), 1.13 – 0.99 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 165.1, 162.0, 144.3, 142.4, 140.2, 138.3, 136.0, 129.5, 128.8, 127.6, 127.4, 124.9, 122.4, 122.2, 122.1, 119.5, 109.1, 105.9, 43.5, 43.3, 40.9, 34.8, 34.6, 30.4, 30.2, 29.8, 27.0, 26.9, 26.21, 26.15, 26.0.

HRMS-ESI: calcd. for $C_{35}H_{39}N_2O_2$ $[M+H]^+$: 519.3006; found: 519.3004.



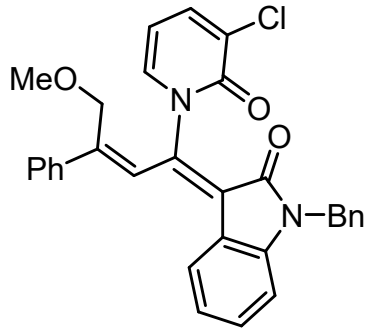
(*Z*)-1-benzyl-3-(1-(2-oxopyridin-1(2*H*)-yl)-2-(1,4-dioxaspiro[4.5]decan-8-ylidene)ethylidene)indolin-2-one

4au: 95.0 mg, red brown solid, 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.33 – 7.26 (m, 4H), 7.24 – 7.16 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.71 – 6.63 (m, 2H), 6.45 (s, 1H), 6.28 (t, *J* = 6.1 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.8 Hz, 1H), 3.99 – 3.92 (m, 4H), 2.61 – 2.53 (m, 2H), 2.31 – 2.25 (m, 2H), 1.89 – 1.83 (m, 2H), 1.66 – 1.64 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 162.1, 152.9, 142.7, 142.6, 140.4, 137.5, 136.0, 130.0, 128.8, 127.6, 127.4, 124.7, 123.2, 122.3, 122.2, 121.5, 119.0, 109.2, 108.0, 106.4, 64.6, 43.6, 36.1, 35.1, 34.8, 27.2.

HRMS-ESI: calcd. for $C_{30}H_{29}N_2O_4$ $[M+H]^+$: 481.2122; found: 481.2123.



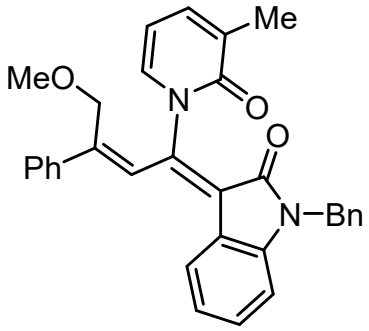
(*Z*)-1-benzyl-3-((*Z*)-1-(3-chloro-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ba: 95.5 mg, red brown solid, 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 3H), 7.51 – 7.48 (m, 1H), 7.46 – 7.34 (m, 5H), 7.33 – 7.27 (m, 4H), 7.23 – 7.18 (m, 1H), 7.02 (s, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.29 (t, *J* = 7.1 Hz, 1H), 4.93 – 4.83 (m, 2H), 4.28 (d, *J* = 12.5 Hz, 1H), 4.24 (d, *J* = 12.5 Hz, 1H), 3.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 158.3, 146.9, 143.0, 141.7, 139.7, 138.5, 137.7, 135.7, 130.6, 129.2, 128.88, 128.85, 127.7, 127.4, 127.2, 126.9, 125.0, 124.7, 124.5, 122.5, 121.3, 109.4, 105.2, 69.9, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1621.



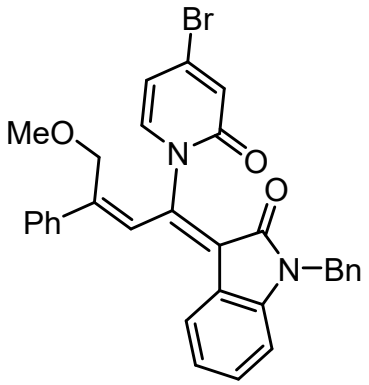
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(3-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bb: 78.1 mg, red brown solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.31 (d, *J* = 7.3 Hz, 4H), 7.26 – 7.16 (m, 3H), 7.07 (s, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.26 (td, *J* = 6.8, 1.5 Hz, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.85 (d, *J* = 15.7 Hz, 1H), 4.29 (d, *J* = 12.3 Hz, 1H), 4.23 (d, *J* = 12.3 Hz, 1H), 3.12 (d, *J* = 1.6 Hz, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.4, 146.2, 143.0, 142.8, 139.8, 137.7, 136.2, 135.9, 130.9, 130.3, 129.0, 128.84, 128.80, 127.7, 127.5, 127.2, 125.5, 124.9, 124.2, 122.4, 121.6, 109.2, 105.8, 69.5, 58.2, 43.7, 17.4.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_3$ $[M+H]^+$: 489.2173; found: 489.2171.



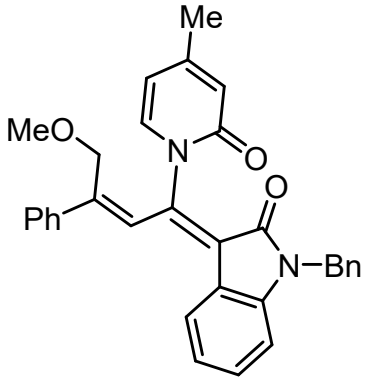
(*Z*)-1-benzyl-3-((*Z*)-1-(4-bromo-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bc: 40.8 mg, red brown solid, 37% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.48 – 7.39 (m, 4H), 7.33 – 7.27 (m, 4H), 7.26 – 7.17 (m, 3H), 7.01 (s, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.46 (dd, *J* = 7.4, 1.8 Hz, 1H), 4.94 – 4.84 (m, 2H), 4.27 (d, *J* = 12.4 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 160.7, 146.9, 142.9, 141.3, 139.8, 138.7, 137.0, 135.7, 130.6, 129.3, 128.9, 127.8, 127.4, 127.2, 125.1, 124.9, 124.5, 123.8, 122.6, 121.4, 110.2, 109.4, 70.0, 58.5, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Br$ $[M+H]^+$: 553.1121; found: 553.1133.



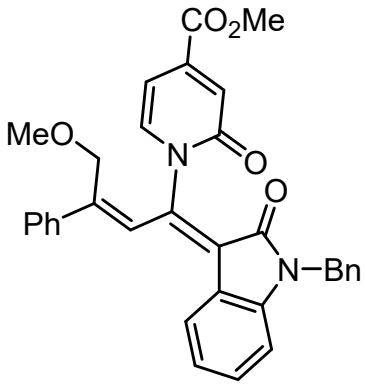
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bd: 42.9 mg, red brown solid, 44% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 3H), 7.27 – 7.21 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.46 (s, 1H), 6.17 (dd, *J* = 7.1, 0.9 Hz, 1H), 4.94 – 4.85 (m, 2H), 4.30 (d, *J* = 12.5 Hz, 1H), 4.24 (d, *J* = 12.5 Hz, 1H), 3.15 (d, *J* = 0.6 Hz, 3H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.0, 152.5, 146.6, 142.8, 142.3, 139.8, 137.6, 135.8, 130.2, 129.1, 128.83, 128.80, 127.7, 127.4, 127.2, 125.5, 125.0, 124.3, 122.4, 121.6, 120.1, 109.2, 108.5, 69.6, 58.2, 43.6, 21.7.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_3$ $[M+H]^+$: 489.2173; found: 489.2176.



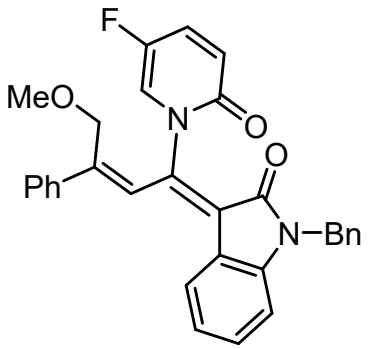
methyl 1-((*Z*)-1-((*Z*)-1-benzyl-2-oxoindolin-3-ylidene)-4-methoxy-3-phenylbut-2-en-1-yl)-2-oxo-1,2-dihydropyridine-4-carboxylate

4be: 96.8 mg, red brown solid, 91% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.50 – 7.38 (m, 5H), 7.33 – 7.26 (m, 5H), 7.25 – 7.17 (m, 2H), 7.04 (s, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.92 – 4.84 (m, 2H), 4.26 (d, *J* = 12.5 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.92 (s, 3H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 164.8, 161.9, 147.1, 143.0, 141.6, 141.4, 139.8, 139.3, 135.7, 130.6, 129.3, 128.9, 127.8, 127.5, 127.2, 125.1, 124.8, 124.5, 123.9, 122.6, 121.4, 109.4, 104.2, 69.9, 58.5, 53.0, 43.7.

HRMS-ESI: calcd. for $C_{33}H_{29}N_2O_5$ $[M+H]^+$: 533.2071; found: 533.2085.



(*Z*)-1-benzyl-3-((*Z*)-1-(5-fluoro-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

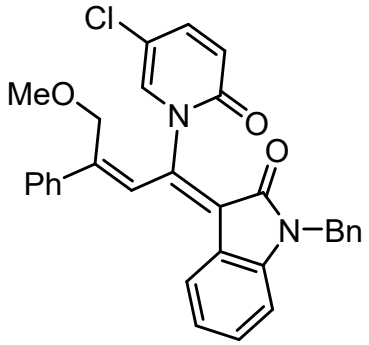
4bf: 85.6 mg, red brown solid, 87% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.50 – 7.38 (m, 6H), 7.34 – 7.29 (m, 3H), 7.27 – 7.17 (m, 3H), 7.00 (s, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.62 (dd, *J* = 10.1, 5.2 Hz, 1H), 4.93 – 4.86 (m, 2H), 4.30 (d, *J* = 12.3 Hz, 1H), 4.25 (d, *J* = 12.3 Hz, 1H), 3.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 160.4, 147.6 (d, *J* = 231.9 Hz), 147.2, 143.0, 141.1, 139.7, 135.76, 132.84 (d, *J* = 24.6 Hz), 130.6, 129.3, 128.9, 127.8, 127.4, 127.2, 125.0, 124.78, 124.75, 124.2 (d, *J* = 38.1 Hz), 122.5, 122.2 (d, *J* = 7.2 Hz), 121.3, 109.4, 69.9, 58.5, 43.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -149.85.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3F$ $[M+H]^+$: 493.1922; found: 493.1941.



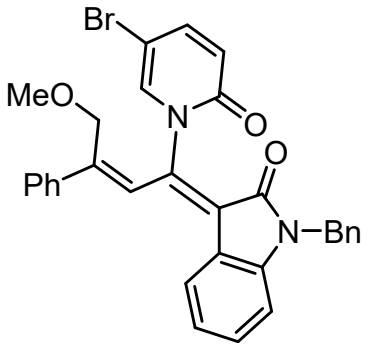
(*Z*)-1-benzyl-3-((*Z*)-1-(5-chloro-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bg: 84.3 mg, red brown solid, 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.49 – 7.42 (m, 4H), 7.42 – 7.37 (m, 3H), 7.32 – 7.28 (m, 3H), 7.25 – 7.17 (m, 2H), 7.00 (s, 1H), 6.96 (td, *J* = 7.7, 0.7 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.63 – 6.60 (m, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.87 (d, *J* = 15.7 Hz, 1H), 4.28 – 4.22 (m, 2H), 3.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 160.6, 147.1, 143.0, 141.6, 141.0, 139.8, 136.4, 135.7, 130.6, 129.3, 128.90, 128.88, 127.7, 127.4, 127.2, 125.1, 124.68, 124.66, 122.5, 122.4, 121.3, 112.3, 109.4, 70.0, 58.6, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1646.



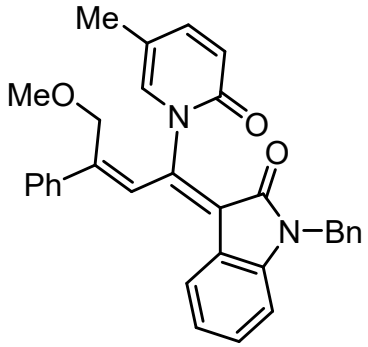
(*Z*)-1-benzyl-3-((*Z*)-1-(5-bromo-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bh: 100.6 mg, red brown solid, 91% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.52 – 7.51 (m, 1H), 7.47 – 7.39 (m, 5H), 7.32 – 7.28 (m, 3H), 7.27 – 7.17 (m, 3H), 7.00 (s, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 9.8 Hz, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 4.27 – 4.22 (m, 2H), 3.22 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 160.6, 147.1, 143.6, 143.0, 140.9, 139.8, 138.7, 135.7, 130.6, 129.2, 128.89, 128.86, 127.7, 127.4, 127.1, 125.0, 124.6, 122.7, 122.5, 121.3, 109.3, 97.9, 70.0, 58.7, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Br$ $[M+H]^+$: 553.1121; found: 553.1110.



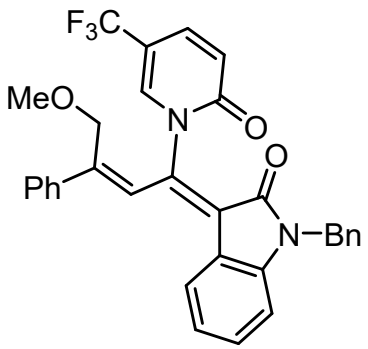
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(5-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4bi: 90.8 mg, red brown solid, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.51 – 7.41 (m, 3H), 7.41 – 7.35 (m, 2H), 7.33 – 7.28 (m, 3H), 7.26 – 7.14 (m, 3H), 7.12 (s, 1H), 7.05 (s, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 9.4 Hz, 1H), 4.89 (s, 2H), 4.29 (d, *J* = 12.3 Hz, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 3.14 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 161.6, 146.9, 143.5, 142.9, 141.8, 139.8, 135.9, 135.5, 130.3, 129.1, 128.8, 127.6, 127.4, 127.2, 125.4, 125.0, 124.6, 122.4, 121.5, 121.4, 114.9, 109.2, 69.4, 58.4, 43.6, 17.4.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_3$ $[M+H]^+$: 489.2173; found: 489.2183.



(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxo-5-(trifluoromethyl)pyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

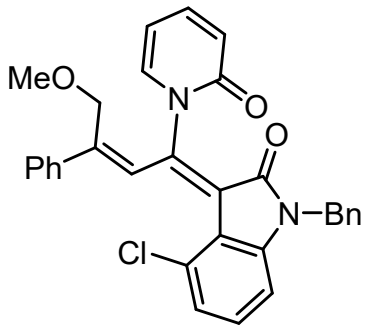
4bj: 105.1 mg, red brown solid, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.60 – 7.52 (m, 3H), 7.49 – 7.37 (m, 4H), 7.32 – 7.26 (m, 3H), 7.26 – 7.17 (m, 3H), 7.01 (s, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 8.3 Hz, 2H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.21 (s, 2H), 3.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 161.4, 147.1, 143.0, 141.1, 139.9, 139.4 (q, *J* = 5.5 Hz), 136.0 (q, *J* = 2.1 Hz), 135.6, 130.8, 129.3, 128.93, 128.88, 127.8, 127.4, 127.1, 125.1, 124.7, 124.4, 123.7 (q, *J* = 273.9 Hz), 122.6, 122.1, 121.2, 109.38 (q, *J* = 34.8 Hz), 109.42, 70.3, 58.6, 43.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.19.

HRMS-ESI: calcd. for $C_{32}H_{26}N_2O_3F_3$ $[M+H]^+$: 543.1890; found: 543.1915.



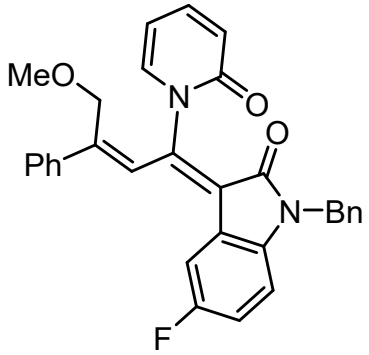
(*Z*)-1-benzyl-4-chloro-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ca: 91.4 mg, red brown solid, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.48 – 7.43 (m, 1H), 7.38 – 7.27 (m, 6H), 7.25 – 7.22 (m, 3H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.85 (s, 1H), 6.66 (d, *J* = 9.1 Hz, 1H), 6.60 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.30 (td, *J* = 6.9, 1.2 Hz, 1H), 4.93 (d, *J* = 15.8 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.3, 147.0, 144.3, 142.9, 140.6, 139.9, 138.9, 135.5, 131.0, 130.3, 129.1, 128.9, 128.6, 128.5, 127.8, 127.3, 127.0, 124.8, 124.7, 122.1, 120.1, 107.4, 105.9, 69.5, 58.5, 43.9.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1639.



(*Z*)-1-benzyl-5-fluoro-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

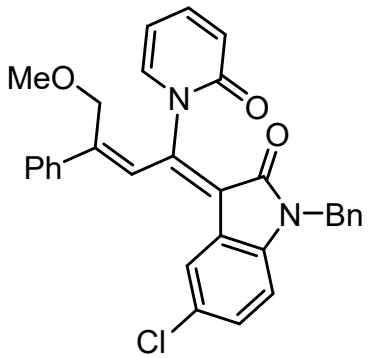
4cb: 91.5 mg, red brown solid, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.36 (m, 6H), 7.32 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 6.99 (s, 1H), 6.91 – 6.86 (m, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.62 – 6.58 (m, 1H), 6.32 (t, *J* = 6.6 Hz, 1H), 4.90 – 4.83 (m, 2H), 4.28 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.4 Hz, 1H), 3.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 162.0, 158.7 (d, *J* = 239.4 Hz), 147.7, 143.5, 140.7, 139.5, 138.78, 138.77, 138.7, 135.5, 129.3, 128.9, 127.7, 127.4, 127.1, 124.5, 123.84, 123.81, 122.4 (d, *J* = 8.9 Hz), 121.9, 116.5 (d, *J* = 24.0 Hz), 112.4 (d, *J* = 26.3 Hz), 109.7 (d, *J* = 8.2 Hz), 105.8, 69.7, 58.4, 43.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.47.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3F$ $[M+H]^+$: 493.1922; found: 493.1938.



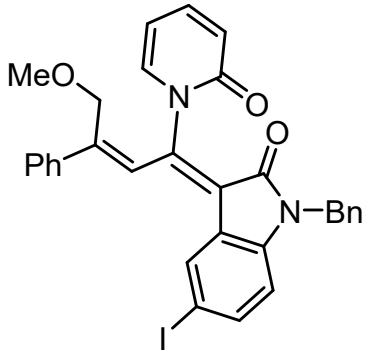
(*Z*)-1-benzyl-5-chloro-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4cc: 99.6 mg, red brown solid, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.47 – 7.34 (m, 6H), 7.31 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 7.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.99 (s, 1H), 6.67 – 6.59 (m, 2H), 6.31 (td, *J* = 6.8, 1.2 Hz, 1H), 4.87 (s, 2H), 4.28 (d, *J* = 12.4 Hz, 1H), 4.23 (d, *J* = 12.4 Hz, 1H), 3.16 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.0, 148.0, 143.6, 141.2, 140.7, 139.5, 138.5, 135.4, 129.9, 129.3, 128.9, 127.8, 127.7, 127.4, 127.2, 124.9, 124.5, 123.4, 122.9, 122.0, 110.1, 105.8, 69.8, 58.5, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1622.



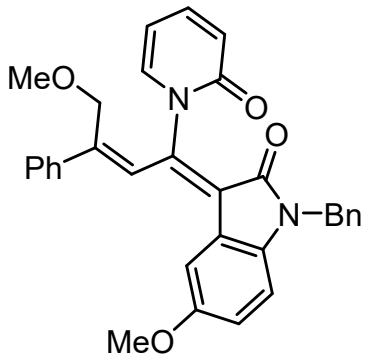
(*Z*)-1-benzyl-5-iodo-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4cd: 98.4 mg, red brown solid, 82% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.5 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.52 – 7.37 (m, 6H), 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 6.97 (s, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 6.32 (td, *J* = 6.8, 1.2 Hz, 1H), 4.91 – 4.82 (m, 2H), 4.28 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.4 Hz, 1H), 3.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 162.0, 148.0, 143.4, 142.3, 140.7, 139.6, 138.7, 138.4, 135.4, 133.5, 129.3, 129.0, 128.9, 127.9, 127.4, 127.1, 124.6, 123.8, 123.2, 122.0, 111.3, 106.0, 84.7, 69.9, 58.6, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3I$ $[M+H]^+$: 601.0983; found: 601.1001.



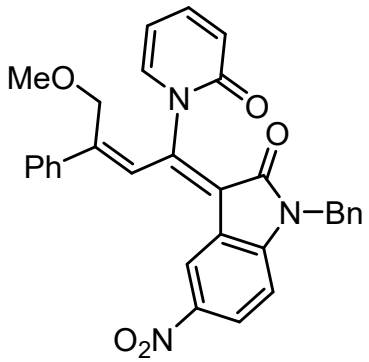
(*Z*)-1-benzyl-5-methoxy-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ce: 93.7 mg, red brown solid, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.34 (m, 6H), 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 7.13 (s, 1H), 7.03 (s, 1H), 6.75 – 6.71 (m, 1H), 6.67 (d, *J* = 9.2 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 6.32 (t, *J* = 6.7 Hz, 1H), 4.86 (s, 2H), 4.31 (d, *J* = 12.4 Hz, 1H), 4.26 (d, *J* = 12.3 Hz, 1H), 3.65 (s, 3H), 3.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 162.2, 155.5, 146.9, 142.4, 140.7, 139.7, 138.8, 136.8, 135.9, 129.1, 128.84, 128.82, 127.7, 127.4, 127.1, 125.1, 124.8, 122.3, 122.0, 115.2, 112.0, 109.6, 105.9, 69.7, 58.4, 55.7, 43.7.

HRMS-ESI: calcd. for $C_{32}H_{29}N_2O_4$ $[M+H]^+$: 505.2122; found: 505.2120.



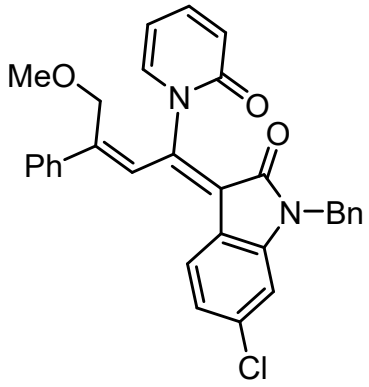
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-5-nitroindolin-2-one

4cf: 93.6 mg, yellow solid, 90% yield, 90:10 *dr*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.18 – 8.14 (m, 1H), 7.65 – 7.62 (m, 2H), 7.51 – 7.40 (m, 5H), 7.36 – 7.27 (m, 5H), 7.07 (s, 1H), 6.80 (dd, *J* = 8.7, 1.2 Hz, 1H), 6.68 (d, *J* = 9.3 Hz, 1H), 6.35 (t, *J* = 6.8 Hz, 1H), 4.99 – 4.92 (m, 2H), 4.30 (d, *J* = 12.4 Hz, 1H), 4.24 (d, *J* = 12.3 Hz, 1H), 3.17 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 161.9, 149.7, 147.4, 145.3, 143.2, 140.9, 139.5, 138.1, 134.8, 129.7, 129.14, 129.05, 128.2, 127.5, 127.1, 126.4, 124.2, 122.14, 122.07, 122.0, 120.3, 108.8, 106.2, 70.1, 58.7, 44.1.

HRMS-ESI: calcd. for $C_{31}H_{26}N_3O_5$ $[M+H]^+$: 520.1867; found: 520.1878.



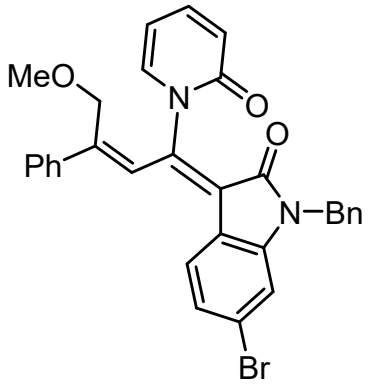
(*Z*)-1-benzyl-6-chloro-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4cg: 96.5 mg, red brown solid, 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.48 – 7.34 (m, 7H), 7.33 – 7.29 (m, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 6.99 (s, 1H), 6.94 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.66 (d, *J* = 9.2 Hz, 1H), 6.32 (td, *J* = 6.8, 1.2 Hz, 1H), 4.86 (s, 2H), 4.27 (d, *J* = 12.5 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.1, 147.4, 143.8, 142.7, 140.7, 139.7, 138.6, 136.2, 135.3, 129.3, 129.0, 128.9, 127.9, 127.4, 127.2, 125.7, 124.9, 123.4, 122.4, 122.0, 120.0, 109.8, 105.9, 69.7, 58.4, 43.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1639.



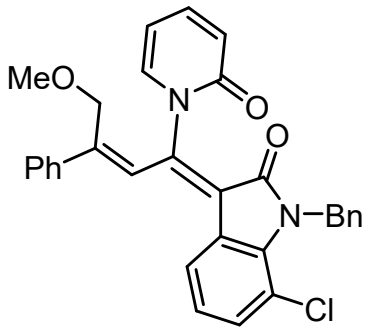
(*Z*)-1-benzyl-6-bromo-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ch: 102.7 mg, red brown solid, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.47 – 7.38 (m, 4H), 7.36 – 7.28 (m, 4H), 7.27 – 7.22 (m, 3H), 7.11 – 7.05 (m, 1H), 7.00 – 6.96 (m, 1H), 6.86 (s, 1H), 6.68 – 6.62 (m, 1H), 6.34 – 6.28 (m, 1H), 4.85 (s, 2H), 4.30 – 4.18 (m, 2H), 3.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 161.9, 147.3, 143.7, 142.7, 140.7, 139.6, 138.5, 135.2, 129.2, 128.9, 128.8, 127.8, 127.3, 127.1, 125.8, 125.3, 124.8, 124.2, 123.4, 121.9, 120.4, 112.4, 105.8, 69.6, 58.4, 43.6.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Br$ $[M+H]^+$: 553.1121; found: 553.1133.



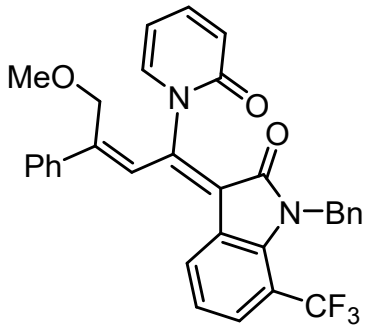
(*Z*)-1-benzyl-7-chloro-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4ci: 98.6 mg, red brown solid, 97% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.46 – 7.38 (m, 5H), 7.35 – 7.32 (m, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.14 (m, 4H), 7.02 (s, 1H), 6.89 (t, J = 7.9 Hz, 1H), 6.62 (d, J = 9.3 Hz, 1H), 6.28 (td, J = 6.8, 1.1 Hz, 1H), 5.39 – 5.29 (m, 2H), 4.27 (d, J = 12.6 Hz, 1H), 4.22 (d, J = 12.5 Hz, 1H), 3.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 161.9, 147.4, 143.4, 140.6, 139.5, 138.7, 138.6, 137.5, 132.5, 129.2, 128.8, 128.5, 127.2, 127.1, 126.4, 125.1, 124.4, 123.5, 123.1, 122.9, 121.9, 115.7, 105.8, 69.7, 58.3, 44.7.

HRMS-ESI: calcd. for $C_{31}H_{26}N_2O_3Cl$ $[M+H]^+$: 509.1626; found: 509.1628.



(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-7-(trifluoromethyl)indolin-2-one

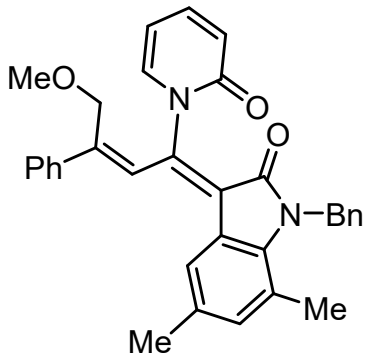
4cj: 75.9 mg, red brown solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.35 – 7.31 (m, 1H), 7.25 – 7.14 (m, 3H), 7.11 – 7.02 (m, 4H), 6.61 (d, *J* = 9.3 Hz, 1H), 6.28 (td, *J* = 6.8, 1.2 Hz, 1H), 5.25 – 5.14 (m, 2H), 4.28 (d, *J* = 13.0 Hz, 1H), 4.23 (d, *J* = 12.6 Hz, 1H), 3.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 161.9, 147.9, 143.9, 140.8, 140.6, 139.5, 138.6, 136.3, 129.5, 129.0, 128.5, 128.2, 128.1 (q, *J* = 6.3 Hz), 127.3, 126.8, 125.8 (q, *J* = 288.13 Hz), 125.6, 125.0, 124.7, 124.6 (q, *J* = 31.9 Hz), 122.0, 121.8, 121.7, 106.0, 69.9, 58.5, 45.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -55.06.

HRMS-ESI: calcd. for $C_{32}H_{26}N_2O_3F_3$ $[M+H]^+$: 543.1890; found: 543.1912.



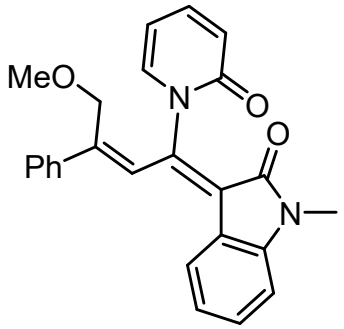
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-5,7-dimethylindolin-2-one

4ck: 93.4 mg, red brown solid, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.34 (m, 6H), 7.29 – 7.27 (m, 1H), 7.23 – 7.18 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.06 (s, 1H), 6.80 (s, 1H), 6.63 (d, *J* = 9.2 Hz, 1H), 6.28 (t, *J* = 6.7 Hz, 1H), 5.15 (s, 2H), 4.30 (d, *J* = 12.4 Hz, 1H), 4.25 (d, *J* = 12.4 Hz, 1H), 3.16 (s, 3H), 2.21 (d, *J* = 3.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 162.2, 146.4, 141.5, 140.6, 139.9, 138.9, 138.8, 137.8, 135.1, 131.7, 129.0, 128.9, 128.8, 127.2, 125.8, 125.6, 124.5, 123.9, 122.4, 122.0, 119.8, 105.9, 69.8, 58.4, 44.9, 21.1, 18.9.

HRMS-ESI: calcd. for $C_{33}H_{31}N_2O_3$ $[M+H]^+$: 503.2329; found: 503.2319.



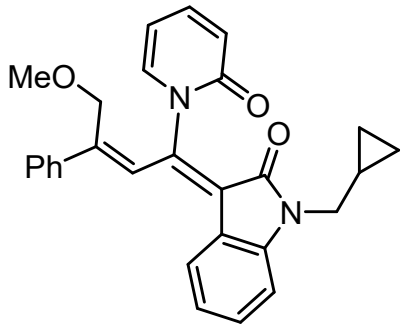
(*Z*)-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-1-methylindolin-2-one

4cl: 76.4 mg, red brown solid, 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.50 – 7.38 (m, 5H), 7.34 – 7.30 (m, 2H), 7.03 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.31 (t, *J* = 6.4 Hz, 1H), 4.29 (d, *J* = 12.4 Hz, 1H), 4.24 (d, *J* = 12.4 Hz, 1H), 3.18 (s, 3H), 3.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 162.2, 146.8, 143.7, 141.8, 140.7, 139.9, 138.6, 130.5, 129.1, 128.8, 127.2, 125.1, 124.9, 124.7, 122.4, 121.9, 121.3, 108.3, 105.9, 69.6, 58.4, 26.0.

HRMS-ESI: calcd. for $C_{25}H_{23}N_2O_3$ $[M+H]^+$: 399.1703; found: 399.1710.



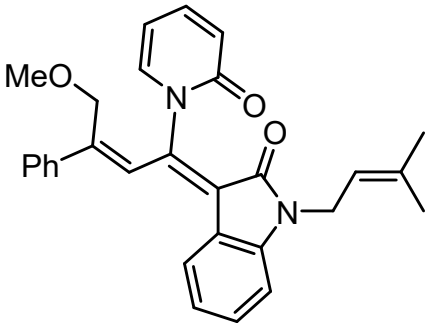
(*Z*)-1-(cyclopropylmethyl)-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4cm: 79.7 mg, red brown solid, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.26 (m, 3H), 7.05 (s, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 9.2 Hz, 1H), 6.29 (td, *J* = 6.8, 1.1 Hz, 1H), 4.28 (d, *J* = 12.5 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.56 (d, *J* = 6.9 Hz, 2H), 3.14 (s, 3H), 1.18 – 1.09 (m, 1H), 0.51 – 0.46 (m, 2H), 0.36 – 0.30 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.0, 146.4, 143.4, 141.9, 140.6, 139.9, 138.9, 130.3, 129.0, 128.8, 127.2, 125.3, 125.1, 124.6, 122.1, 121.9, 121.5, 108.6, 105.7, 69.6, 58.3, 44.2, 9.7, 4.1, 4.0.

HRMS-ESI: calcd. for $C_{28}H_{27}N_2O_3$ $[M+H]^+$: 439.2016; found: 439.2022.



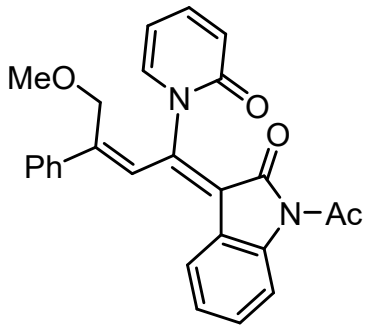
(*Z*)-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-1-(3-methylbut-2-en-1-yl)indolin-2-one

4cn: 75.9 mg, red brown solid, 84% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.49 – 7.42 (m, 3H), 7.42 – 7.37 (m, 2H), 7.34 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.03 (s, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 9.3 Hz, 1H), 6.33 – 6.28 (m, 1H), 5.12 (t, *J* = 6.5 Hz, 1H), 4.30 – 4.21 (m, 4H), 3.14 (s, 3H), 1.78 (s, 3H), 1.70 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 162.1, 146.5, 143.2, 141.9, 140.7, 139.9, 138.9, 136.4, 130.4, 129.1, 128.8, 127.2, 125.3, 125.0, 124.8, 122.2, 121.9, 121.5, 118.6, 108.9, 105.8, 69.6, 58.3, 37.9, 25.7, 18.3.

HRMS-ESI: calcd. for $C_{29}H_{29}N_2O_3$ $[M+H]^+$: 453.2173; found: 453.2176.



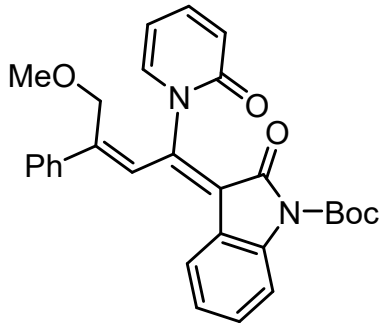
(*Z*)-1-acetyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4co: 80.9 mg, yellow solid, 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 3H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.99 (s, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.32 (t, *J* = 6.7 Hz, 1H), 4.26 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.5 Hz, 1H), 3.16 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 164.9, 162.0, 148.1, 142.8, 140.8, 139.8, 139.5, 138.3, 130.8, 129.4, 128.9, 127.2, 125.13, 125.11, 124.4, 123.3, 122.3, 122.0, 116.7, 106.1, 69.7, 58.5, 27.2.

HRMS-ESI: calcd. for $C_{26}H_{22}N_2O_4$ $[M+H]^+$: 427.1652; found: 427.1666.



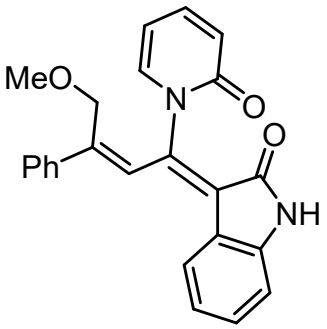
tert-butyl(*Z*)-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-2-oxoindoline-1-carboxylate

4cp: 80.3 mg, yellow solid, 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.29 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.62 (d, *J* = 9.2 Hz, 1H), 6.29 (t, *J* = 6.2 Hz, 1H), 4.25 (d, *J* = 12.4 Hz, 1H), 4.21 (d, *J* = 12.5 Hz, 1H), 3.14 (s, 3H), 1.61 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.0, 149.0, 147.2, 142.7, 140.7, 139.61, 139.55, 138.6, 130.6, 129.2, 128.8, 127.2, 125.3, 124.6, 124.3, 123.2, 122.0, 121.8, 115.1, 106.2, 84.6, 69.7, 58.4, 28.2.

HRMS-ESI: calcd. for $C_{29}H_{29}N_2O_5$ $[M+H]^+$: 485.2071; found: 485.2061.



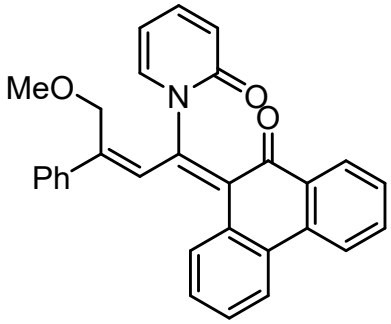
(*Z*)-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)indolin-2-one

4cq: 73.7 mg, red brown solid, 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.61 – 7.57 (m, 2H), 7.46 – 7.40 (m, 3H), 7.40 – 7.36 (m, 2H), 7.32 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.00 (s, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 9.3 Hz, 1H), 6.32 – 6.27 (m, 1H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.21 (d, *J* = 12.3 Hz, 1H), 3.13 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 162.3, 146.6, 141.6, 141.5, 140.8, 139.9, 138.8, 130.4, 129.1, 128.8, 127.2 125.23, 125.15, 125.0, 122.1, 121.9, 121.8, 110.2, 106.1, 69.5, 58.3.

HRMS-ESI: calcd. for $C_{24}H_{21}N_2O_3$ $[M+H]^+$: 385.1547; found: 385.1539.



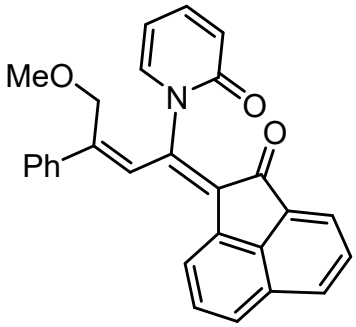
1-((*Z*)-4-methoxy-1-((*Z*)-10-oxophenanthren-9(10*H*)-ylidene)-3-phenylbut-2-en-1-yl)pyridin-2(1H)-one

4cr: 55.2 mg, red brown solid, 62% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 3H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.41 – 7.35 (m, 3H), 7.33 – 7.27 (m, 4H), 6.80 (s, 1H), 6.62 (d, *J* = 9.1 Hz, 1H), 6.30 (t, *J* = 6.7 Hz, 1H), 4.11 (d, *J* = 12.1 Hz, 1H), 4.06 (d, *J* = 12.0 Hz, 1H), 3.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.2, 162.3, 145.4, 140.9, 140.8, 140.7, 136.6, 134.8, 134.2, 131.9, 131.43, 131.39, 131.2, 130.0, 128.60, 128.56, 127.82, 127.82, 127.5, 127.0, 124.4, 123.1, 121.5, 104.3, 69.5, 58.5.

HRMS-ESI: calcd. for $C_{30}H_{24}NO_3$ $[M+H]^+$: 446.1751; found: 446.1752.



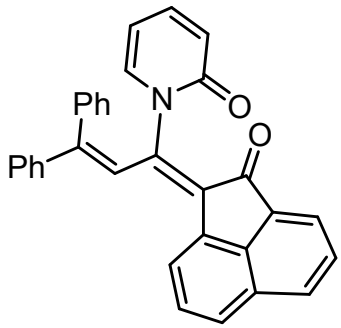
1-((*Z*)-4-methoxy-1-((*Z*)-2-oxoacenaphthylen-1(2*H*)-ylidene)-3-phenylbut-2-en-1-yl)pyridin-2(1*H*)-one

4cs: 51.1 mg, yellow solid, 61% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.76 – 7.68 (m, 2H), 7.66 – 7.59 (m, 3H), 7.55 – 7.46 (m, 2H), 7.45 – 7.39 (m, 3H), 7.16 (s, 1H), 6.70 (d, *J* = 9.2 Hz, 1H), 6.37 – 6.31 (m, 1H), 4.33 (d, *J* = 12.3 Hz, 1H), 4.28 (d, *J* = 12.3 Hz, 1H), 3.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 162.3, 146.7, 140.7, 140.1, 140.0, 139.8, 138.8, 133.0, 132.9, 131.5, 130.9, 130.5, 129.1, 128.8, 128.6, 128.3, 127.2, 126.6, 125.3, 122.4, 122.0, 105.8, 69.7, 58.4.

HRMS-ESI: calcd. for $C_{28}H_{22}NO_3$ $[M+H]^+$: 420.1594; found: 420.1595.



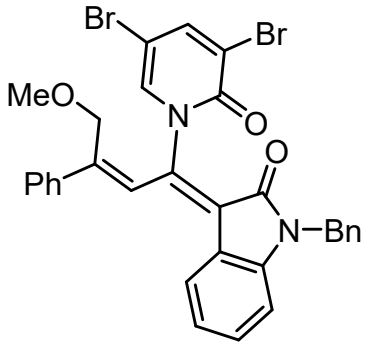
(*Z*)-1-(1-(2-oxoacenaphthylen-1(2*H*)-ylidene)-3,3-diphenylallyl)pyridin-2(1*H*)-one

4ct: 57.7 mg, yellow solid, 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.71 – 7.63 (m, 2H), 7.45 (s, 1H), 7.41 – 7.39 (m, 2H), 7.38 – 7.36 (m, 2H), 7.26 – 7.18 (m, 4H), 7.12 – 7.07 (m, 3H), 6.66 (d, *J* = 6.8 Hz, 1H), 6.33 (d, *J* = 9.3 Hz, 1H), 5.68 (t, *J* = 6.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 161.6, 151.3, 141.8, 141.5, 140.0, 139.5, 139.1, 138.9, 133.8, 133.2, 131.4, 130.6, 130.5, 129.6, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 126.4, 123.4, 122.2, 121.9, 121.4, 104.8.

HRMS-ESI: calcd. for $C_{32}H_{22}NO_2$ $[M+H]^+$: 452.1645; found: 452.1633.



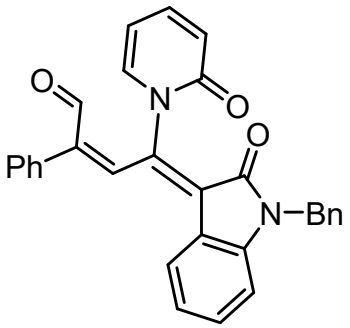
(*Z*)-1-benzyl-3-((*Z*)-1-(3,5-dibromo-2-oxopyridin-1(2*H*)-yl)-4-methoxy-3-phenylbut-2-en-1-ylidene)indolin-2-one

6a: 61.7 mg, red brown solid, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.3 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.55 – 7.53 (m, 1H), 7.49 – 7.45 (m, 1H), 7.43 – 7.39 (m, 3H), 7.33 – 7.28 (m, 3H), 7.26 – 7.18 (m, 3H), 6.98 – 6.93 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.88 (s, 2H), 4.24 (s, 2H), 3.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 156.9, 147.2, 144.7, 143.1, 140.8, 139.7, 138.3, 135.6, 130.8, 129.3, 128.9, 127.8, 127.4, 127.2, 125.1, 124.6, 124.10, 124.06, 122.6, 121.0, 117.6, 109.4, 96.7, 70.3, 58.7, 43.8.

HRMS-ESI: calcd. for $C_{31}H_{25}N_2O_3Br_2[M+H]^+$: 631.0226; found: 631.0222.



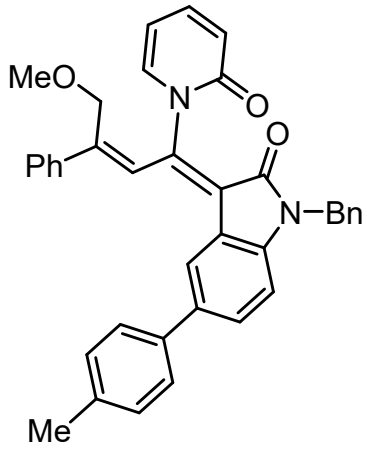
(*Z*)-4-((*Z*)-1-benzyl-2-oxoindolin-3-ylidene)-4-(2-oxopyridin-1(2*H*)-yl)-2-phenylbut-2-enal

6b: 41.2 mg, red brown solid, 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.87 – 7.81 (m, 1H), 7.69 – 7.62 (m, 1H), 7.36 – 7.27 (m, 4H), 7.26 – 7.20 (m, 5H), 7.14 – 7.06 (m, 2H), 7.05 – 7.00 (m, 2H), 6.79 – 6.75 (m, 1H), 6.72 – 6.66 (m, 1H), 6.35 – 6.28 (m, 1H), 5.79 – 5.70 (m, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 4.81 (d, *J* = 15.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 164.1, 161.4, 146.2, 143.6, 140.8, 140.4, 138.8, 135.4, 131.8, 131.8, 129.0, 128.93, 128.91, 128.4, 127.93, 127.88, 127.6, 127.5, 125.5, 123.0, 121.4, 121.1, 109.8, 105.7, 43.7.

HRMS-ESI: calcd. for $C_{30}H_{23}N_2O_3$ $[M+H]^+$: 459.1703; found: 459.1708.



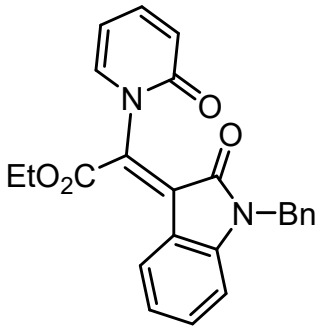
(*Z*)-1-benzyl-3-((*Z*)-4-methoxy-1-(2-oxopyridin-1(2*H*)-yl)-3-phenylbut-2-en-1-ylidene)-5-(p-tolyl)indolin-2-one

6c: 39.5 mg, red brown solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.63 – 7.59 (m, 2H), 7.50 – 7.37 (m, 7H), 7.34 – 7.29 (m, 6H), 7.16 – 7.12 (m, 3H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 9.3 Hz, 1H), 6.33 (t, *J* = 6.5 Hz, 1H), 4.92 (s, 2H), 4.32 (d, *J* = 12.4 Hz, 1H), 4.27 (d, *J* = 12.2 Hz, 1H), 3.15 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 162.2, 147.1, 142.4, 142.0, 140.7, 139.9, 138.6, 137.8, 137.1, 135.9, 135.6, 129.7, 129.1, 128.9, 128.8, 127.8, 127.5, 127.1, 126.8, 126.5, 125.4, 124.6, 123.7, 122.04, 122.02, 109.5, 106.0, 69.8, 58.5, 43.8, 21.2.

HRMS-ESI: calcd. for $C_{38}H_{33}N_2O_3$ $[M+H]^+$: 565.2486; found: 565.2490.



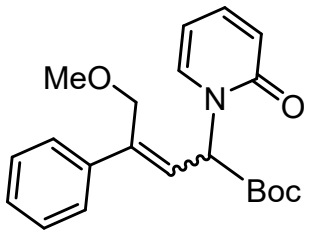
ethyl (*Z*)-2-(1-benzyl-2-oxoindolin-3-ylidene)-2-(2-oxopyridin-1(2*H*)-yl)acetate

8: 28.0 mg, red brown solid, 36% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 3H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 9.3 Hz, 1H), 6.31 (t, *J* = 6.7 Hz, 1H), 4.86 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 163.1, 162.5, 144.1, 141.4, 139.2, 135.31, 135.26, 132.5, 129.0, 128.1, 127.9, 127.5, 127.2, 122.7, 121.5, 119.2, 109.5, 106.4, 62.7, 43.9, 14.0.

HRMS-ESI: calcd. for $C_{24}H_{21}N_2O_4$ $[M+H]^+$: 401.1496; found: 401.1504.



***tert*-butyl (*Z*)-5-methoxy-2-(2-oxopyridin-1(2*H*)-yl)-4-phenylpent-3-enoate**

5a: 61.8 mg, light yellow solid, 87% yield.

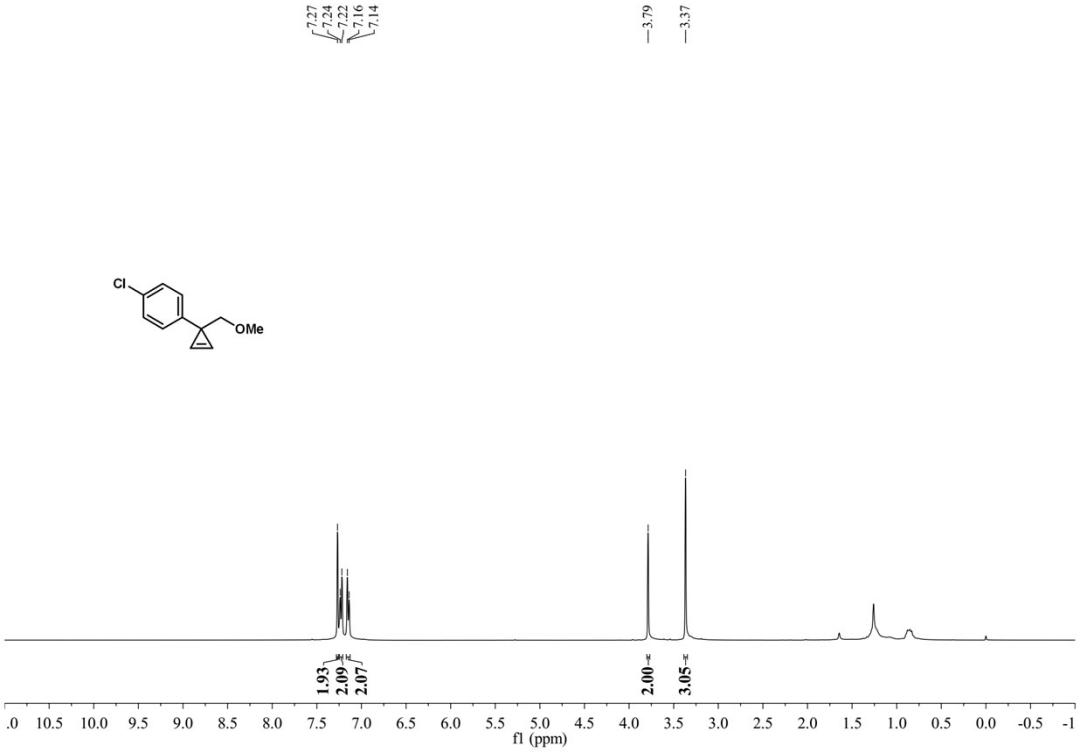
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 3H), 7.37 – 7.30 (m, 4H), 6.59 (d, *J* = 9.1 Hz, 1H), 6.35 (d, *J* = 9.1 Hz, 1H), 6.22 – 6.13 (m, 2H), 4.41 (s, 2H), 3.29 (s, 3H), 1.48 (s, 9H).

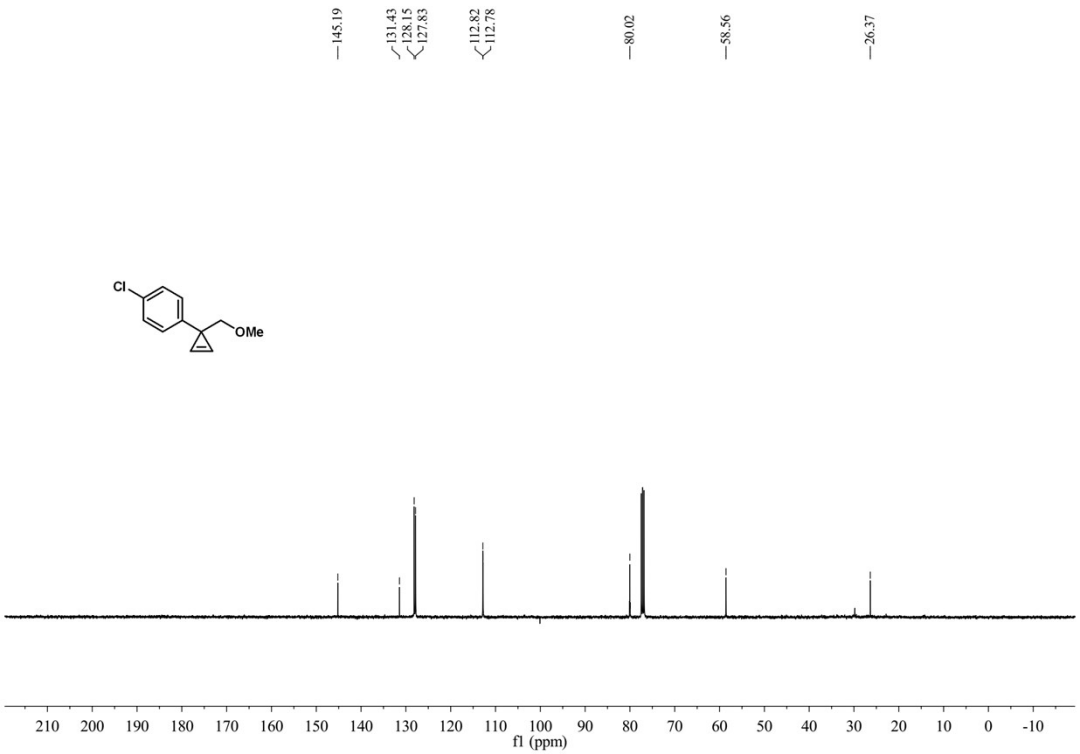
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 162.2, 144.9, 139.9, 139.7, 136.0, 128.6, 128.4, 126.8, 124.0, 120.8, 106.1, 83.2, 69.8, 58.2, 57.1, 28.1.

HRMS-ESI: calcd. for $C_{21}H_{26}NO_4$ $[M+H]^+$: 356.1856; found: 356.1860.

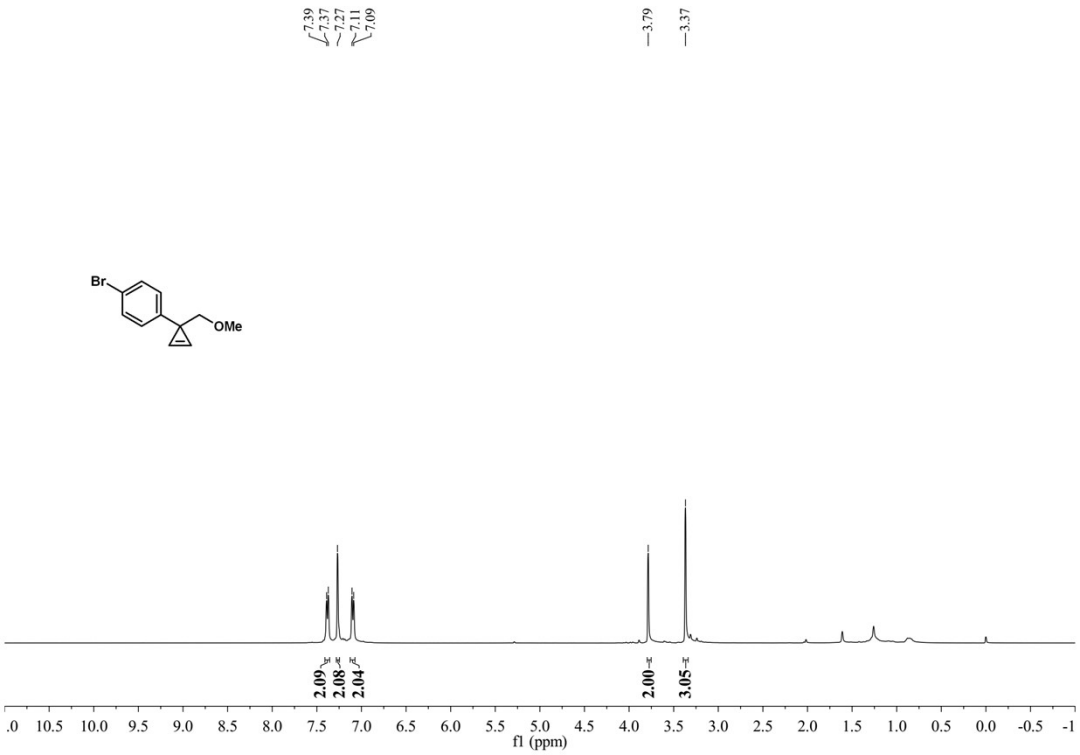
9. NMR spectra of new starting materials products

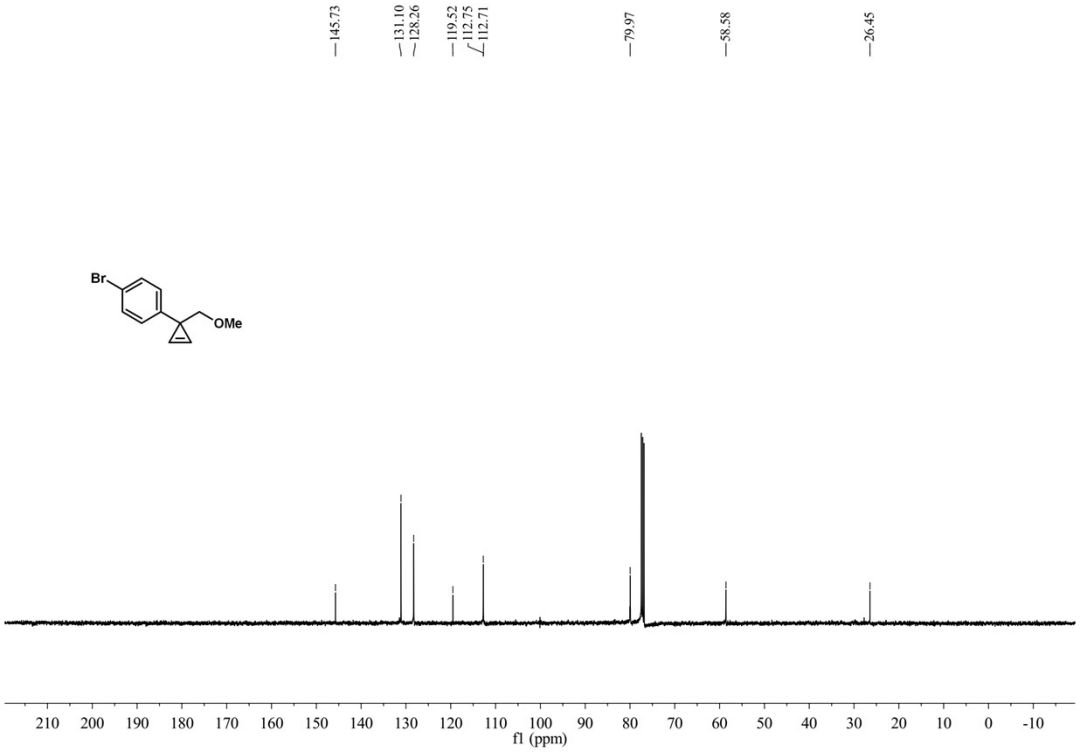
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1b



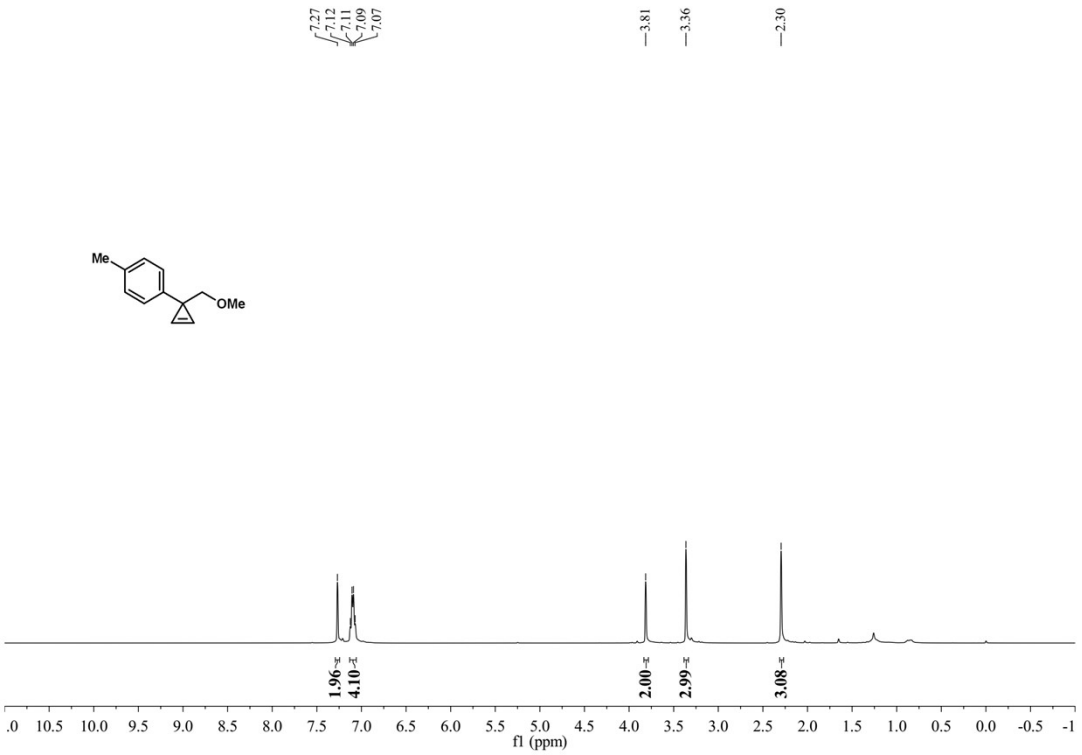


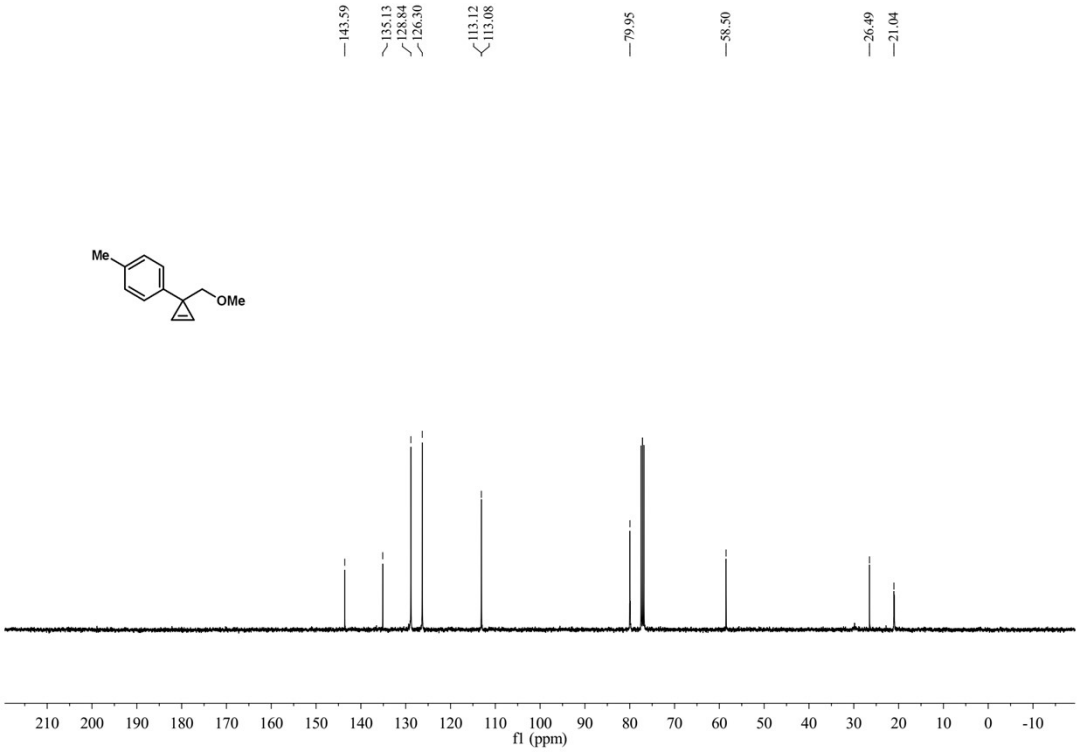
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1c



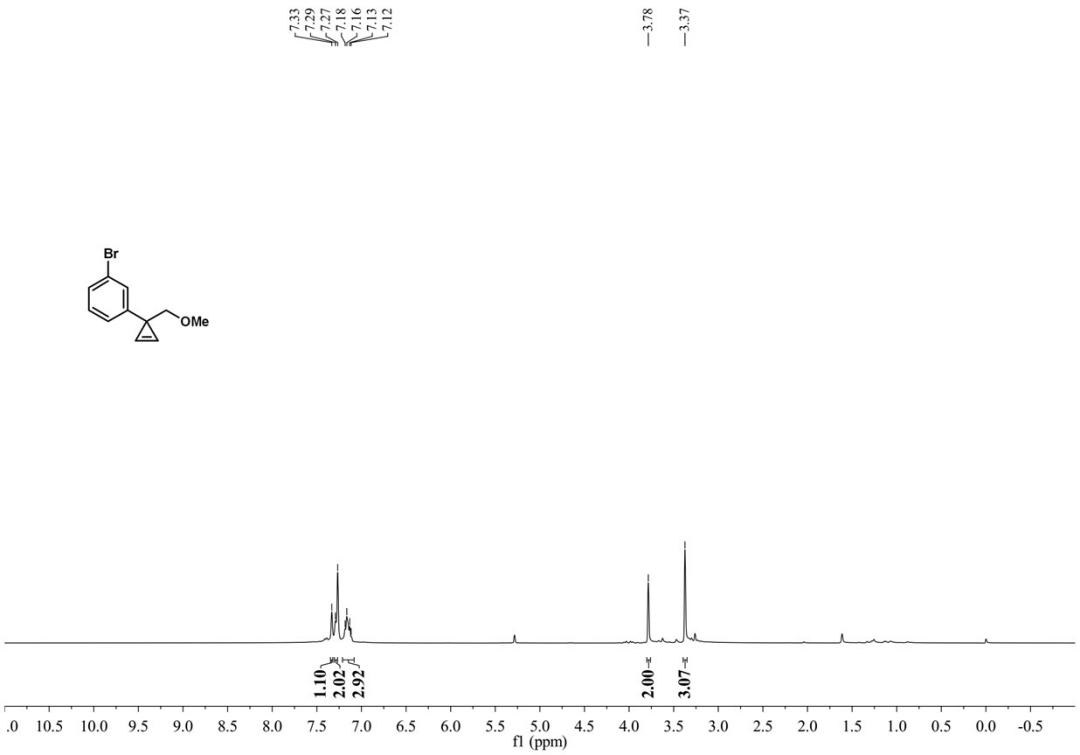


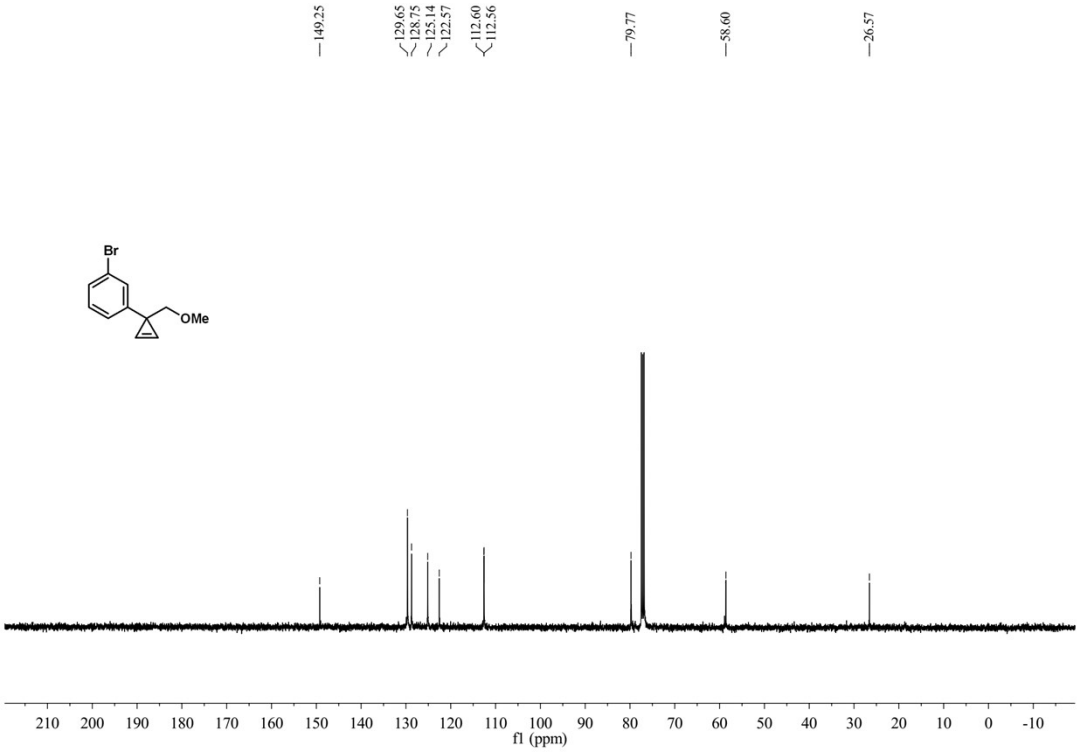
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1d



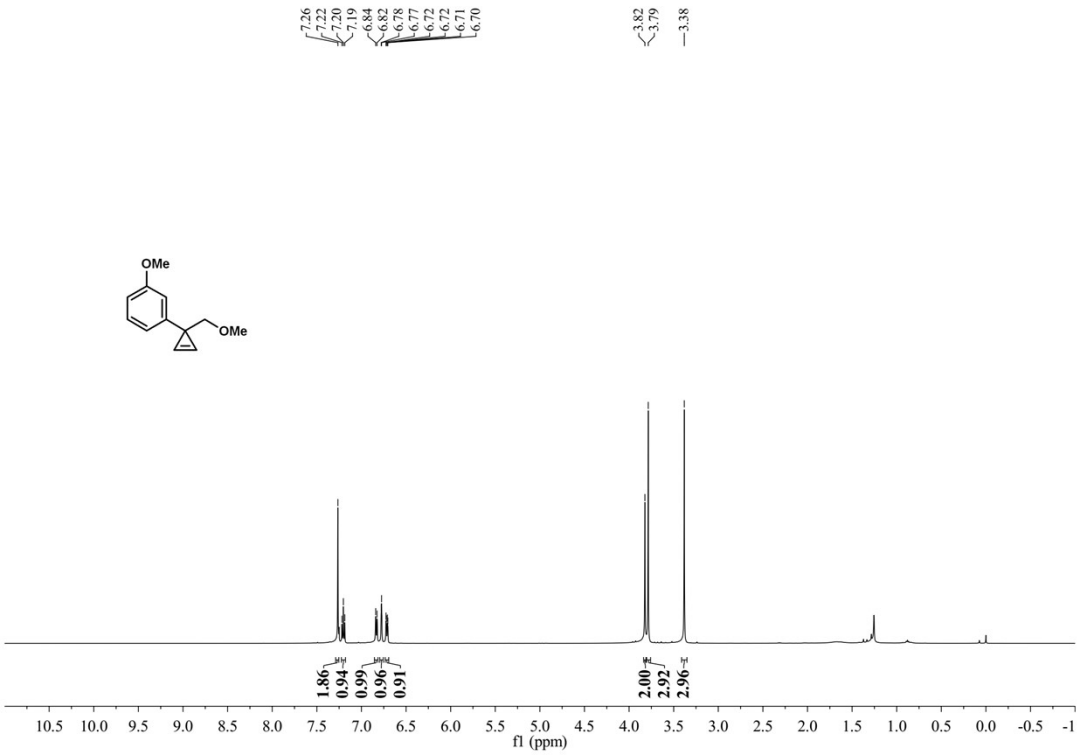


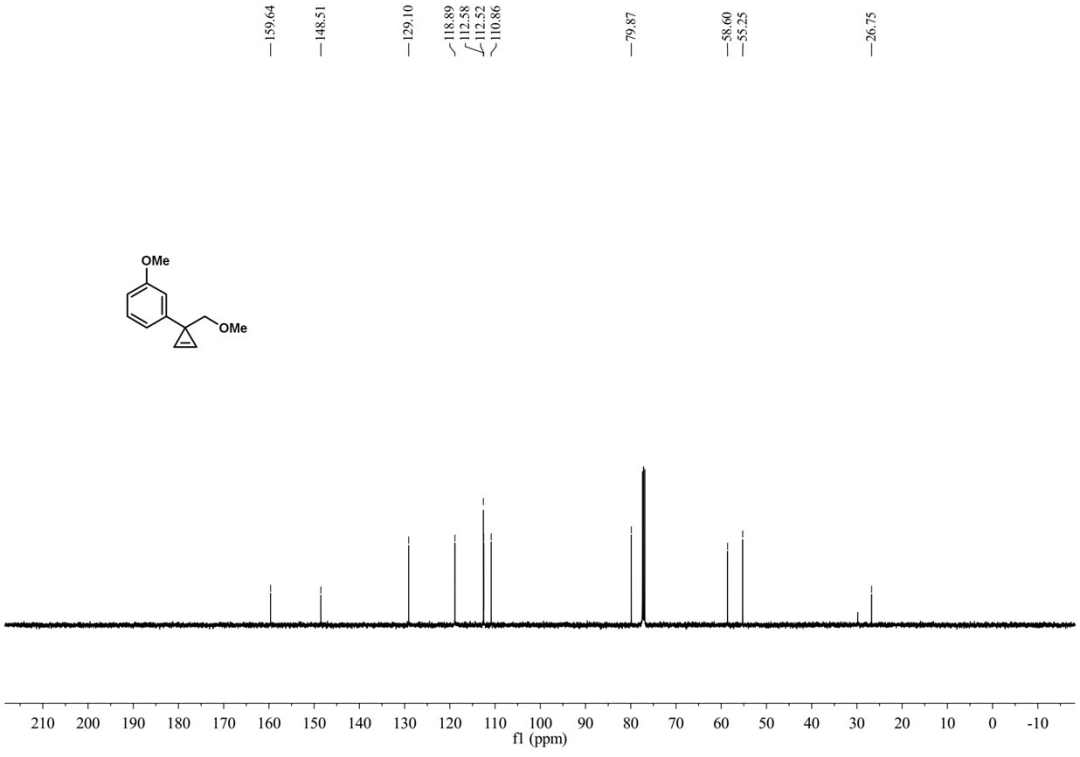
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1e



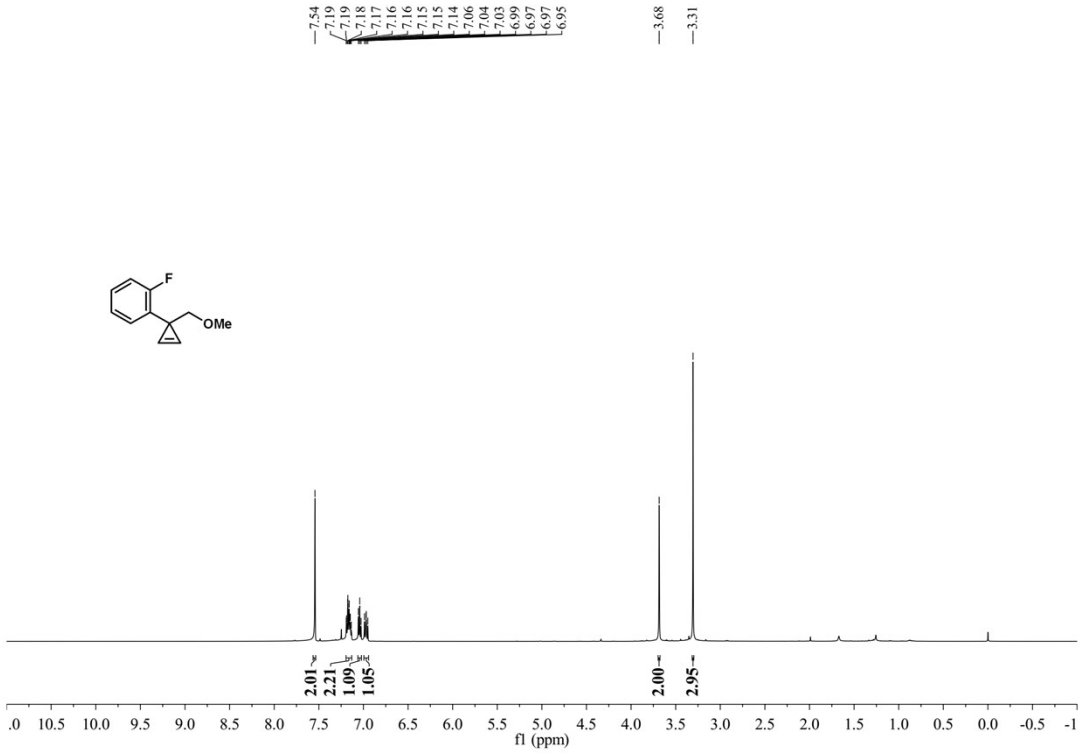


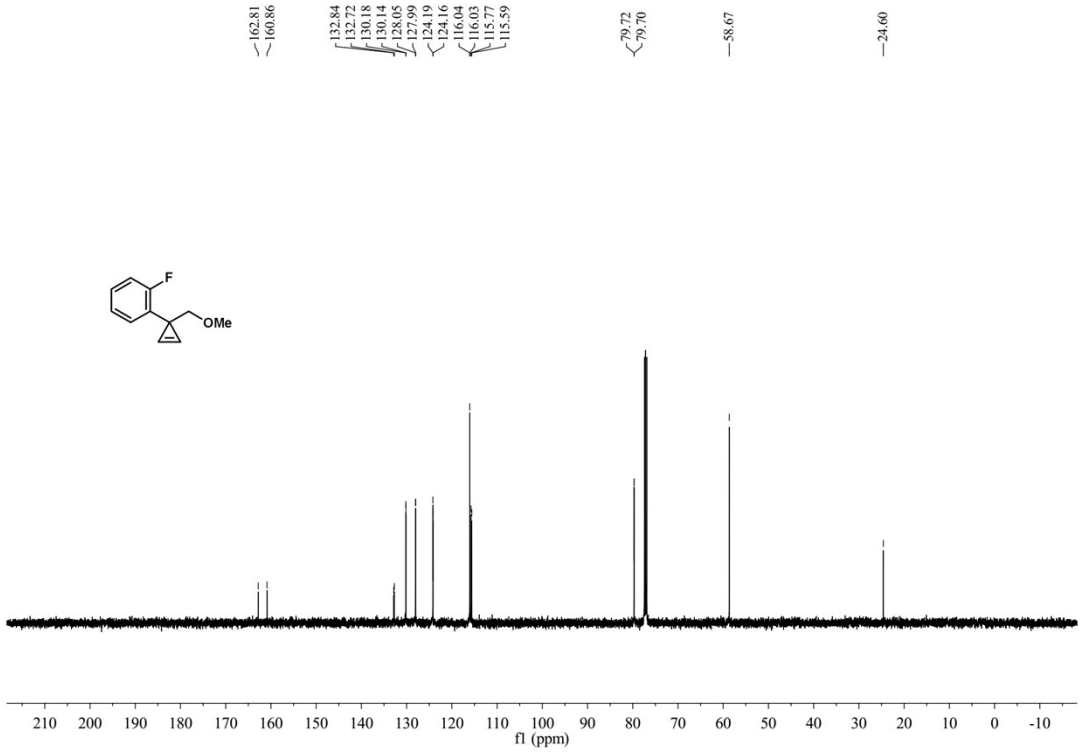
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1f



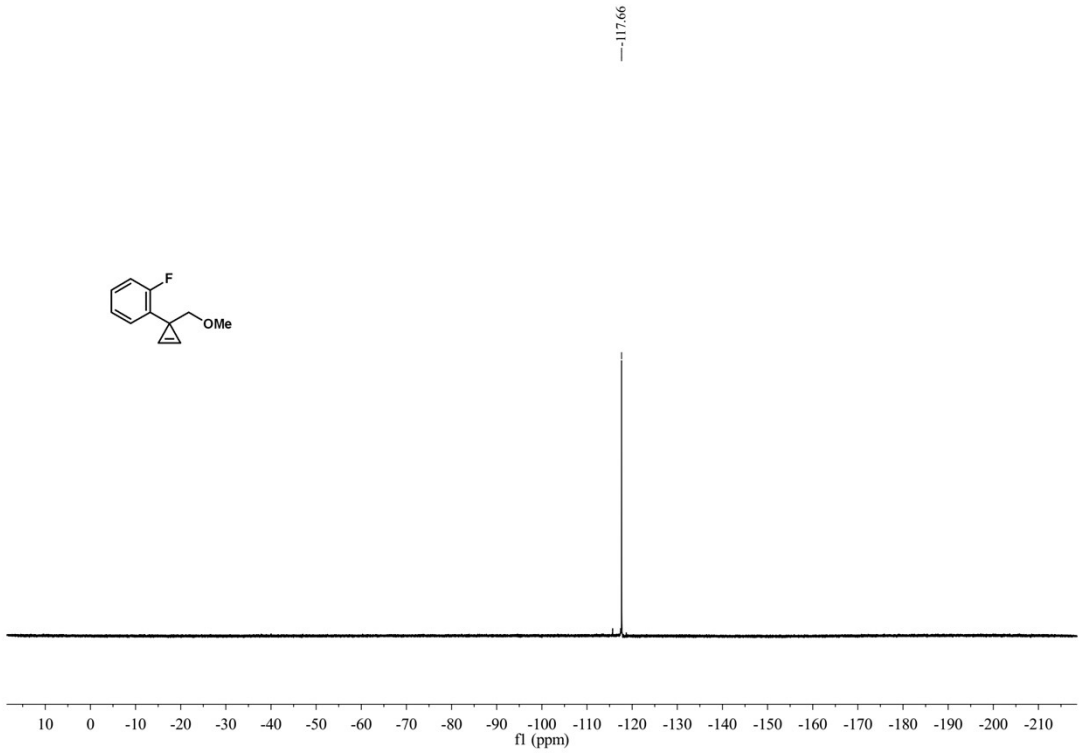


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 1g

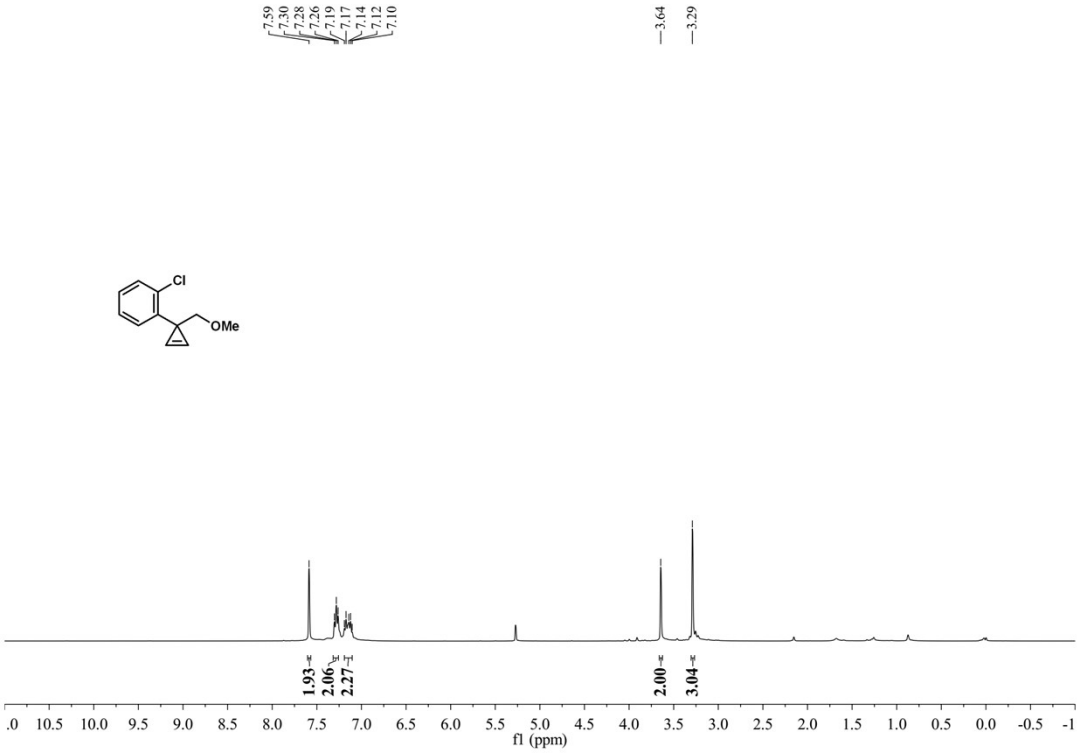


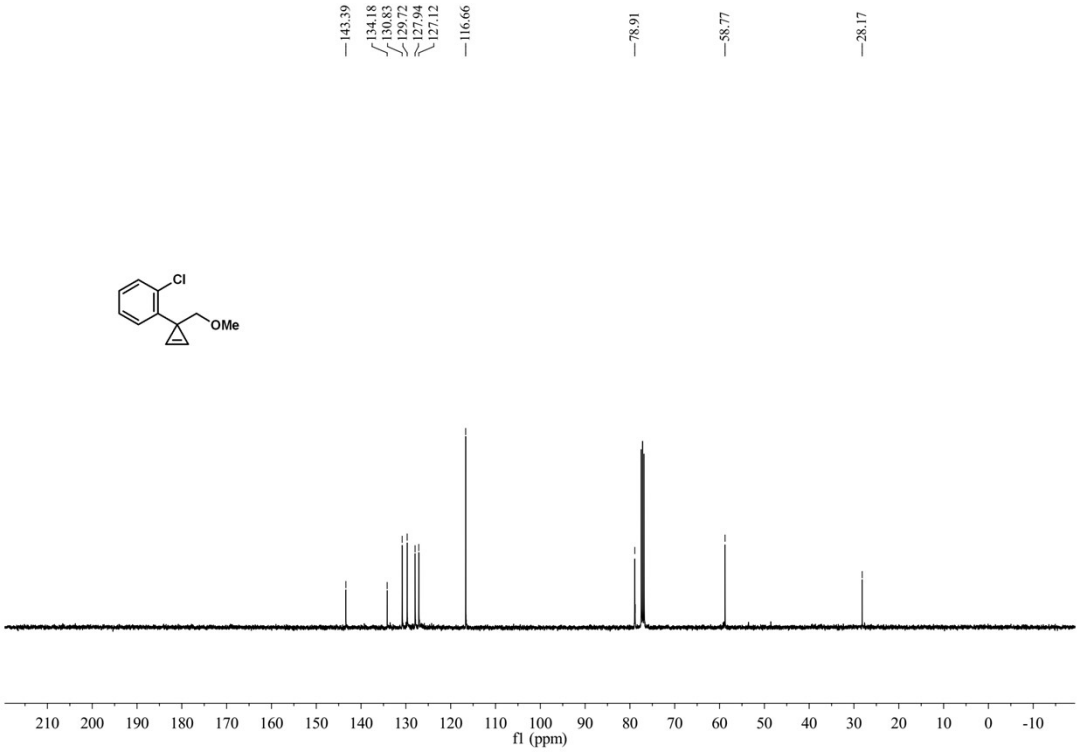


^{19}F NMR (376 MHz, $CDCl_3$) spectra for 1g

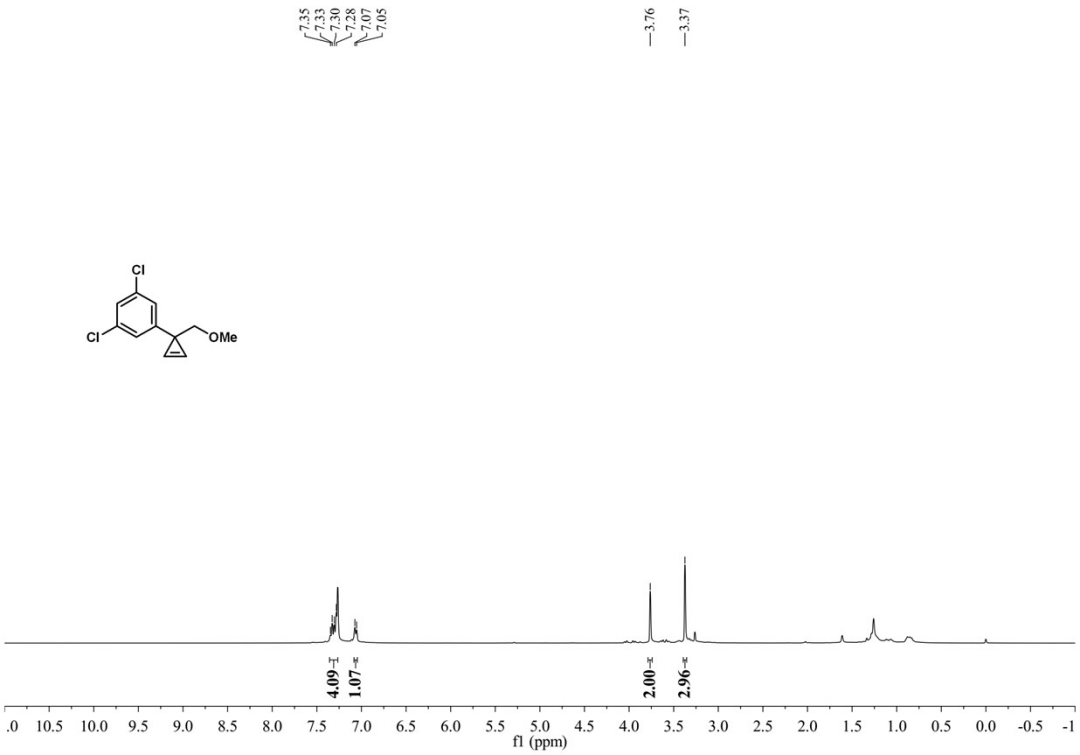


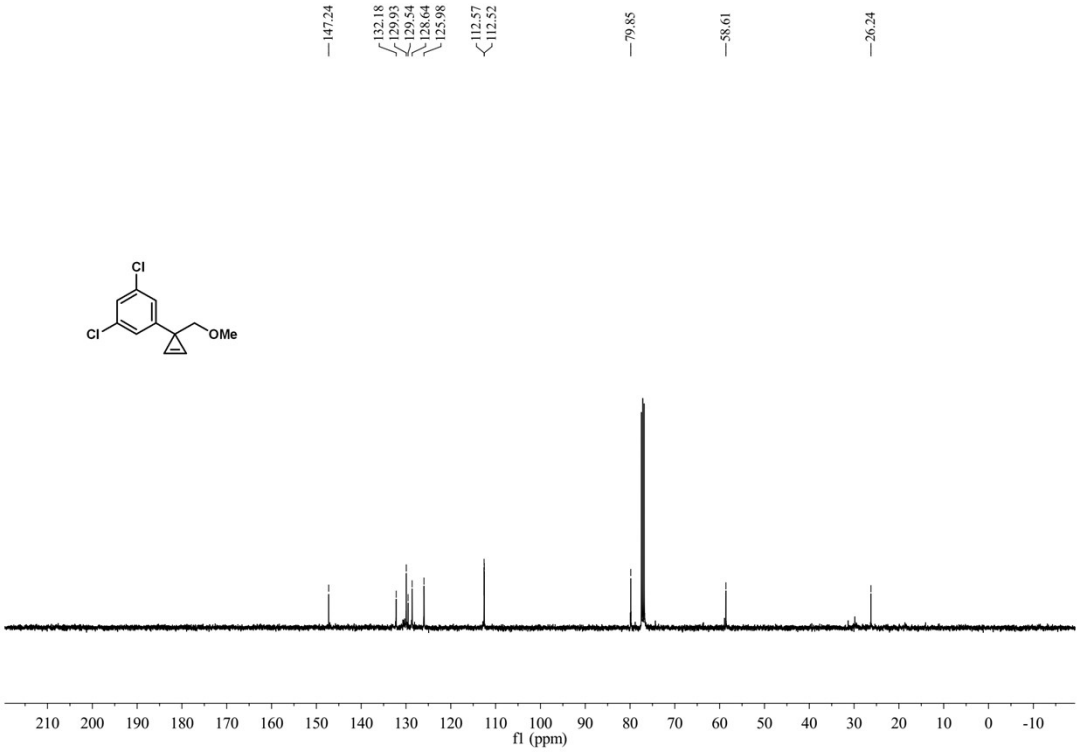
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1h



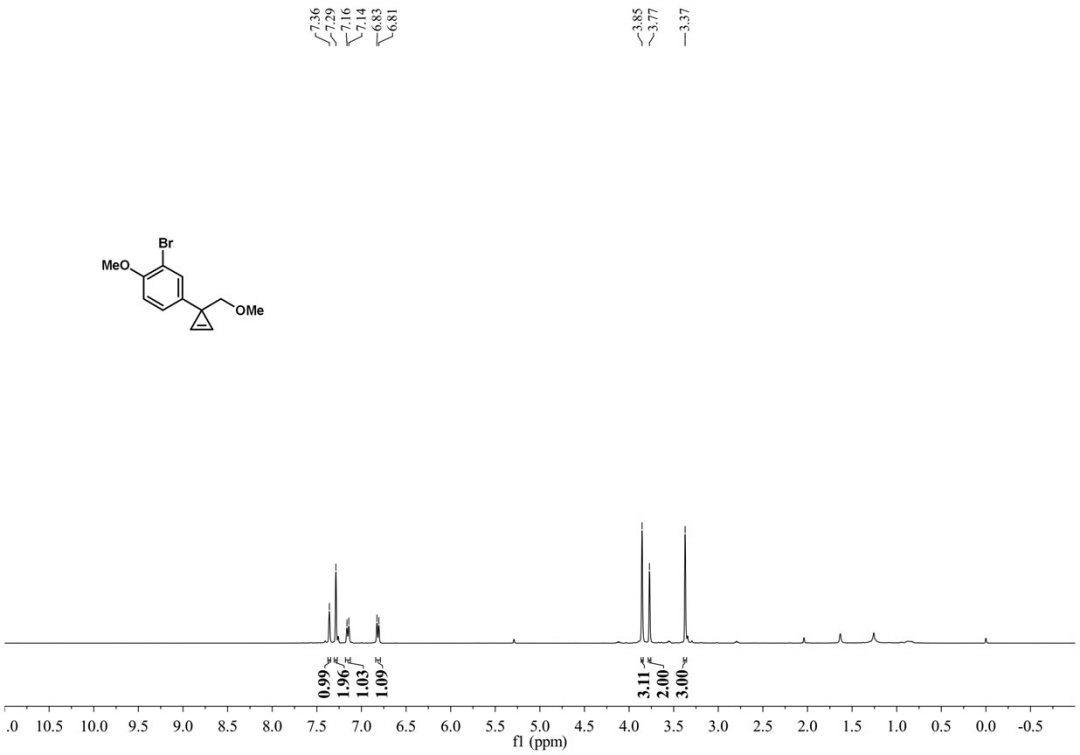


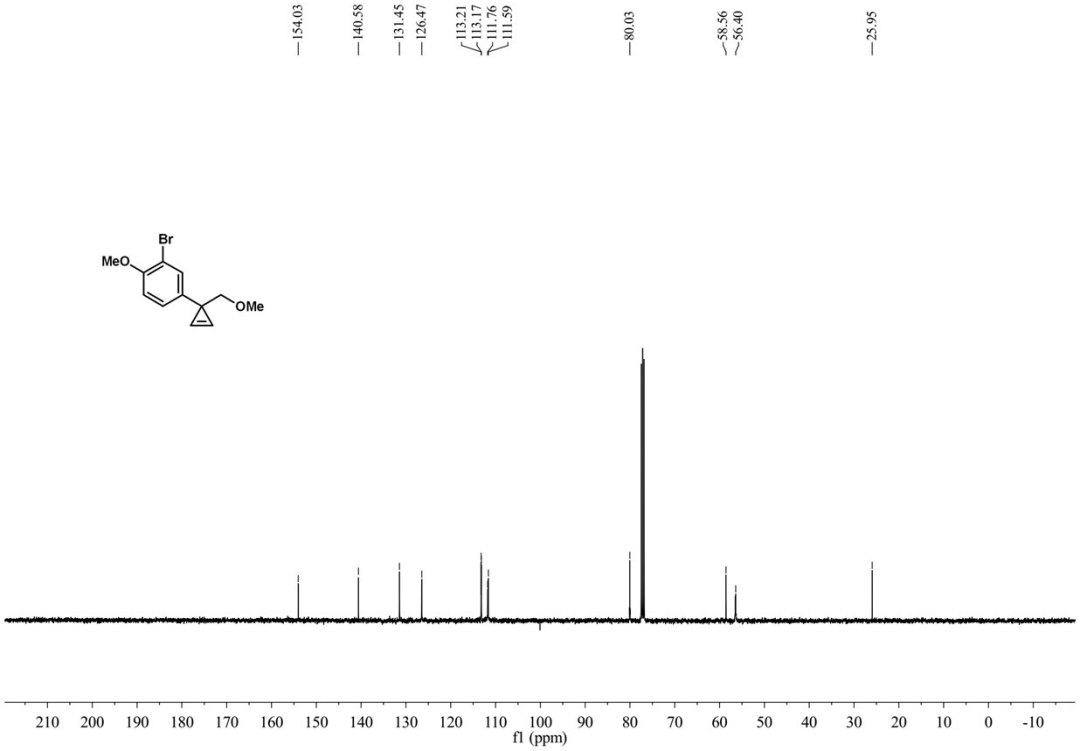
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1i



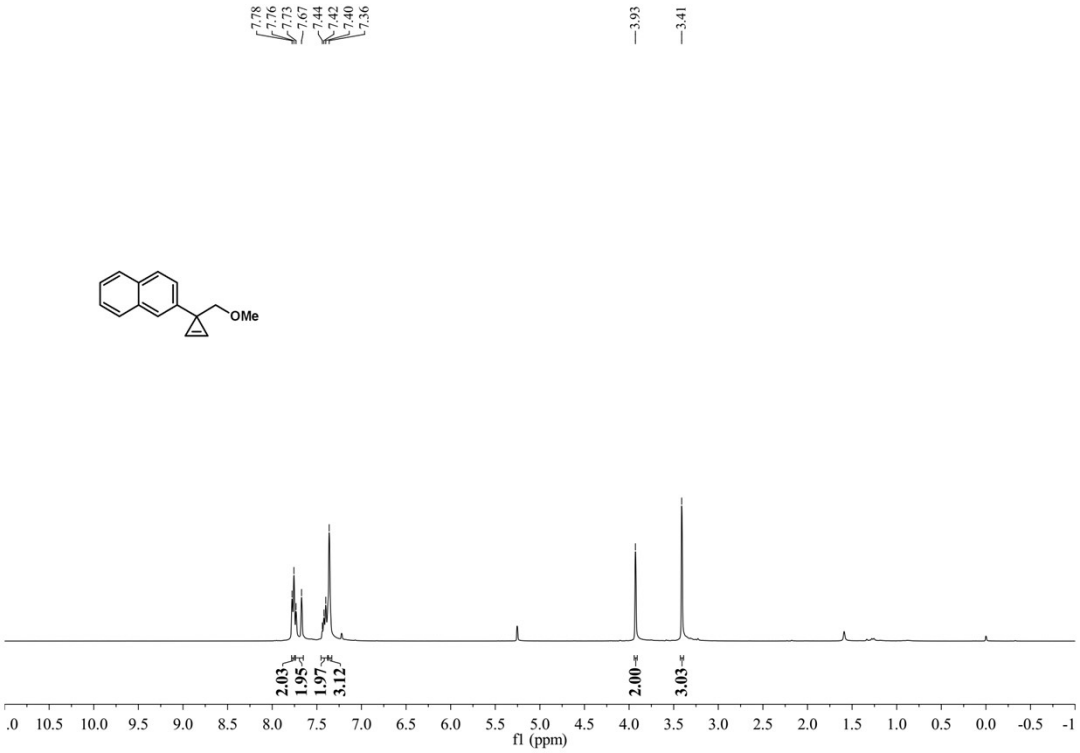


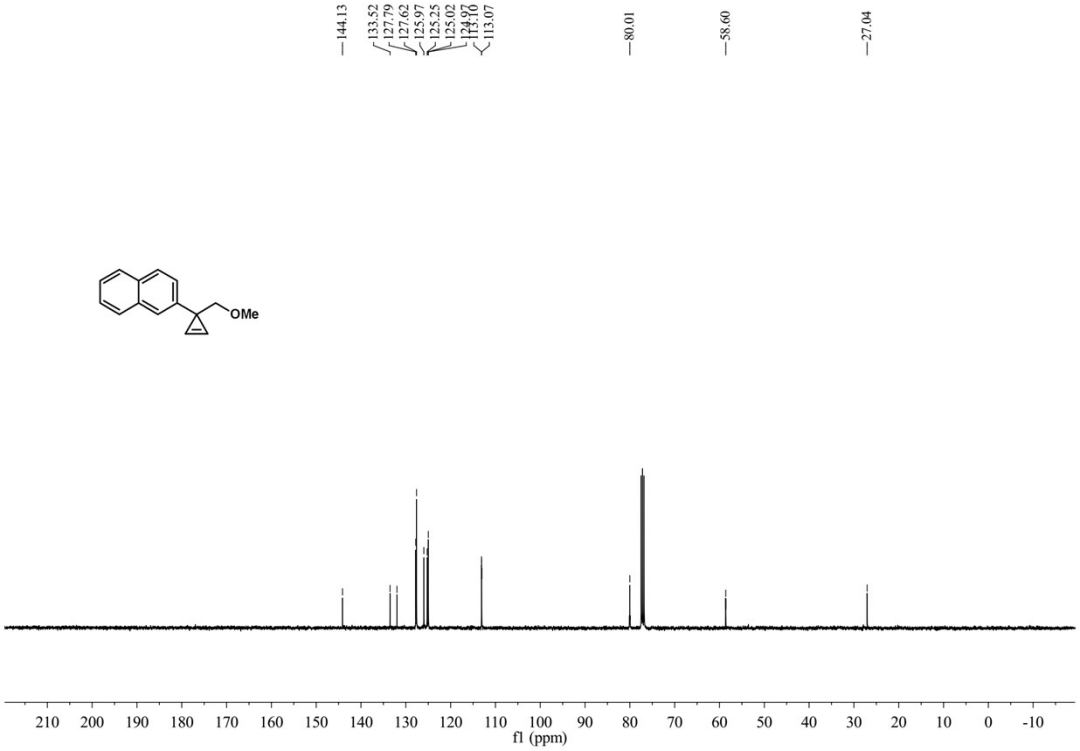
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1j



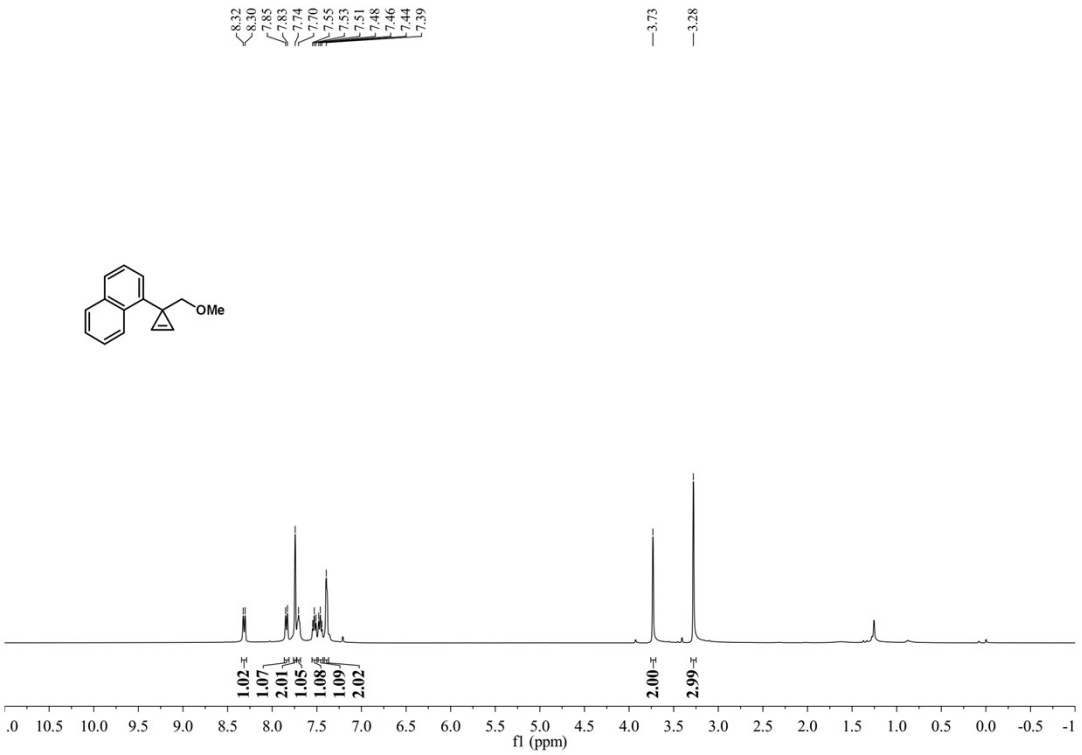


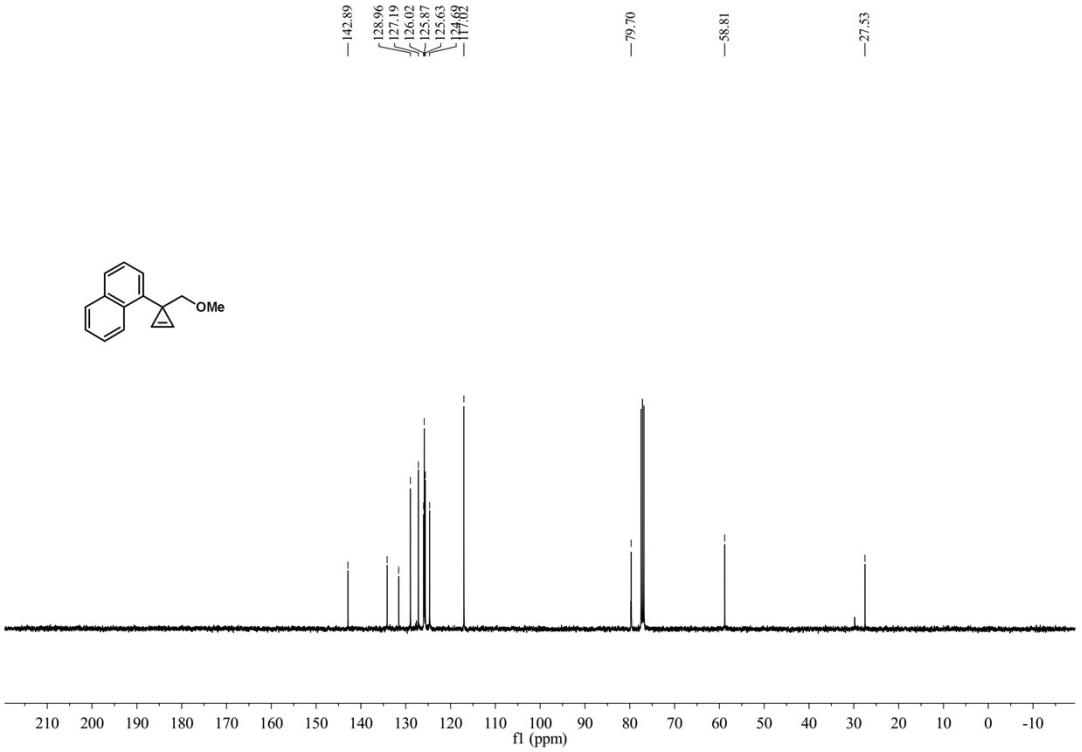
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1k



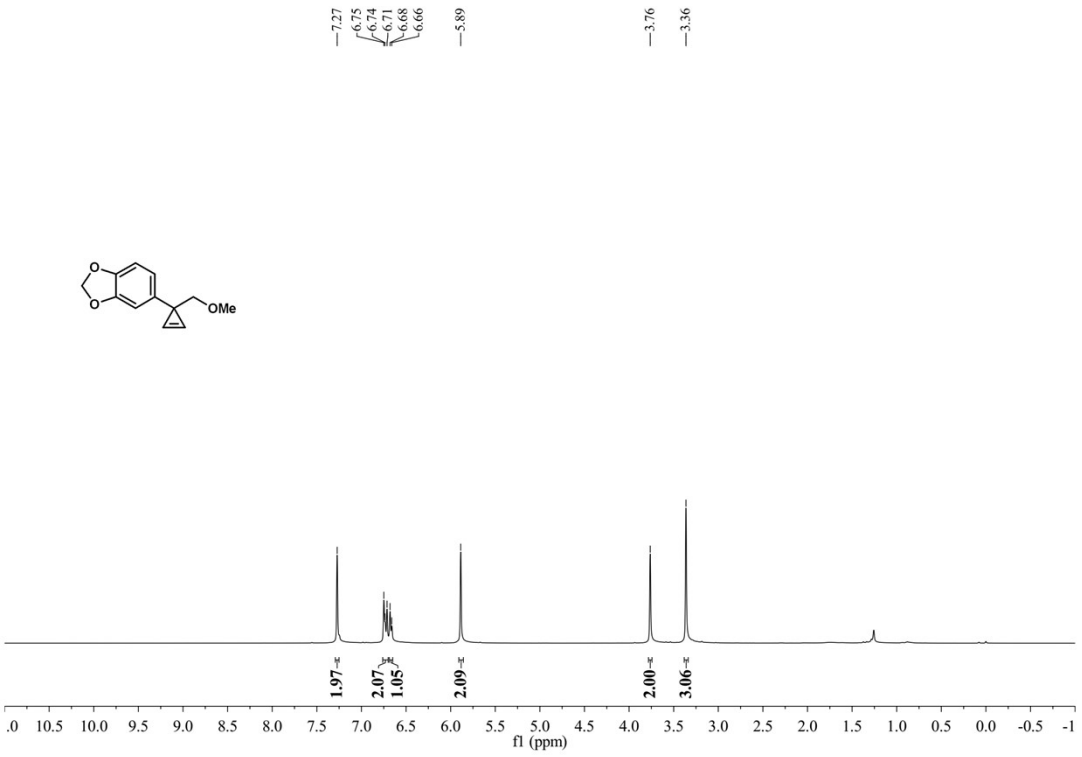


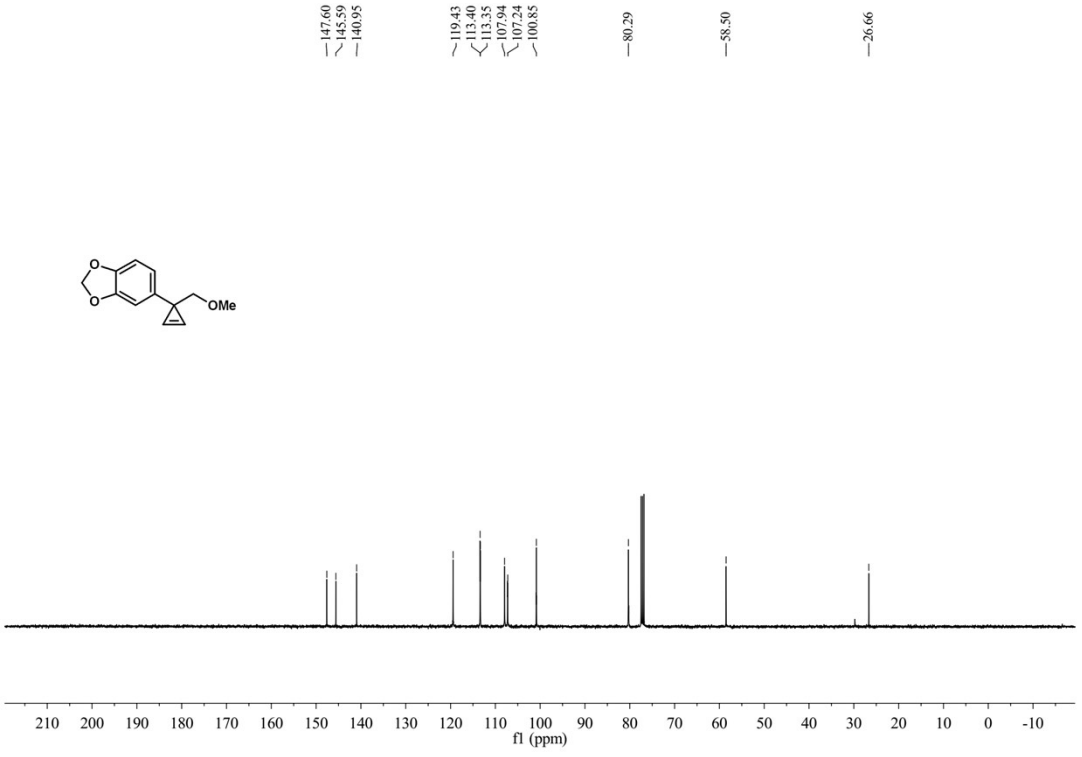
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1l



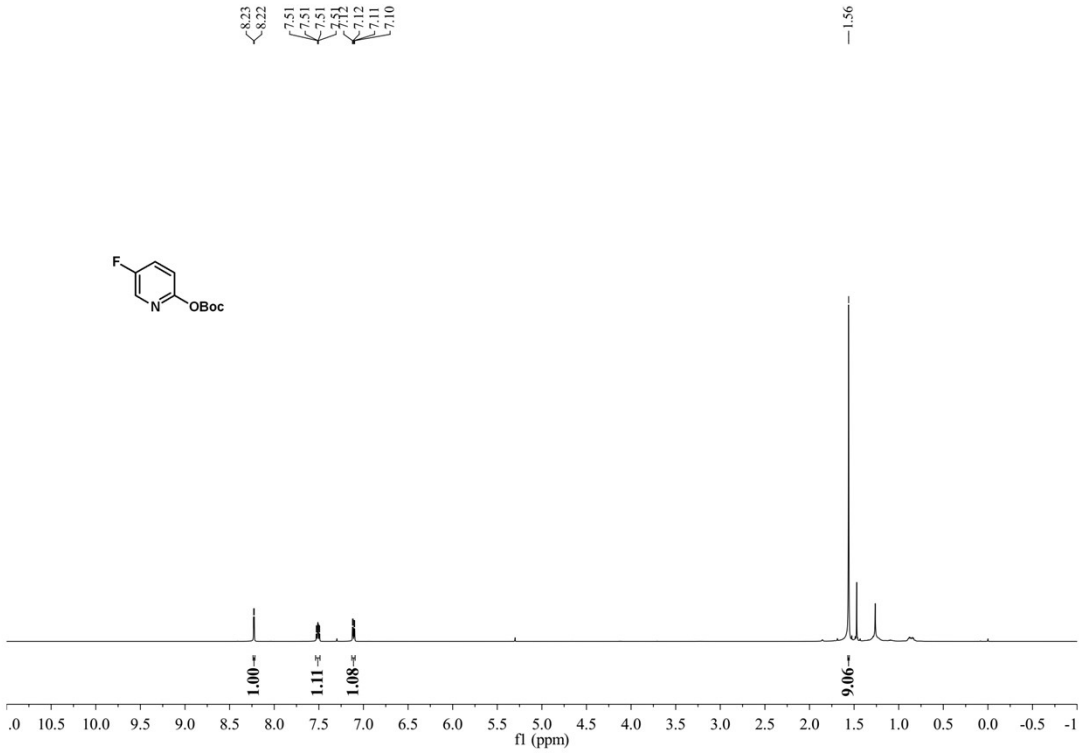


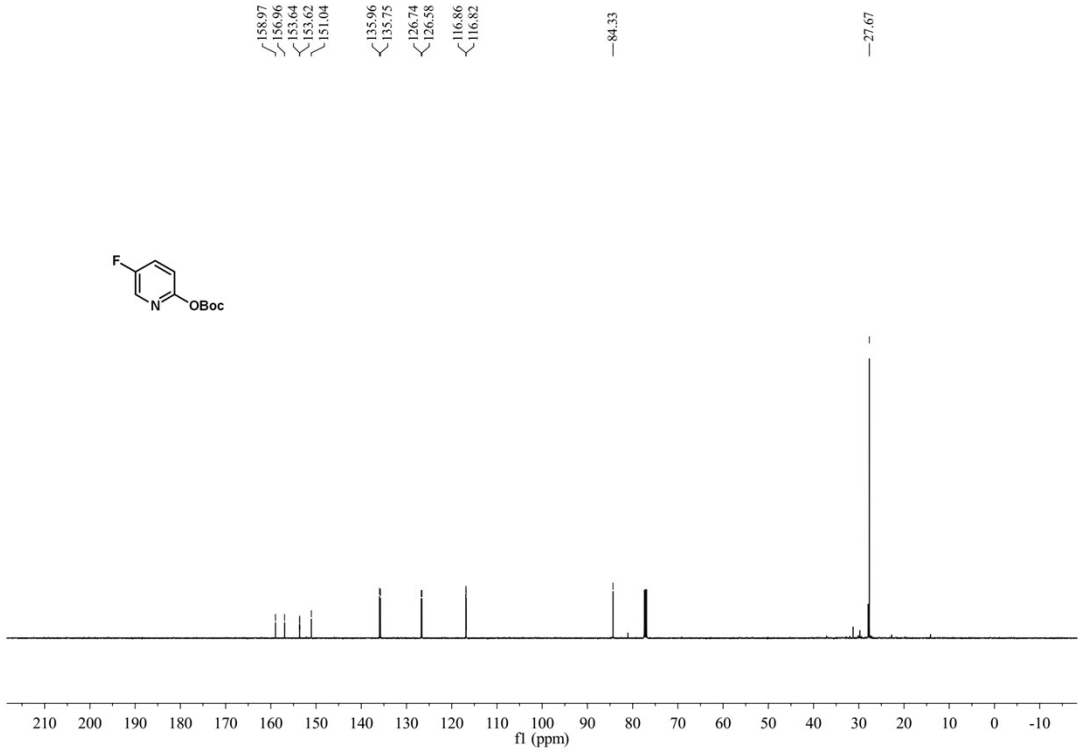
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 1m



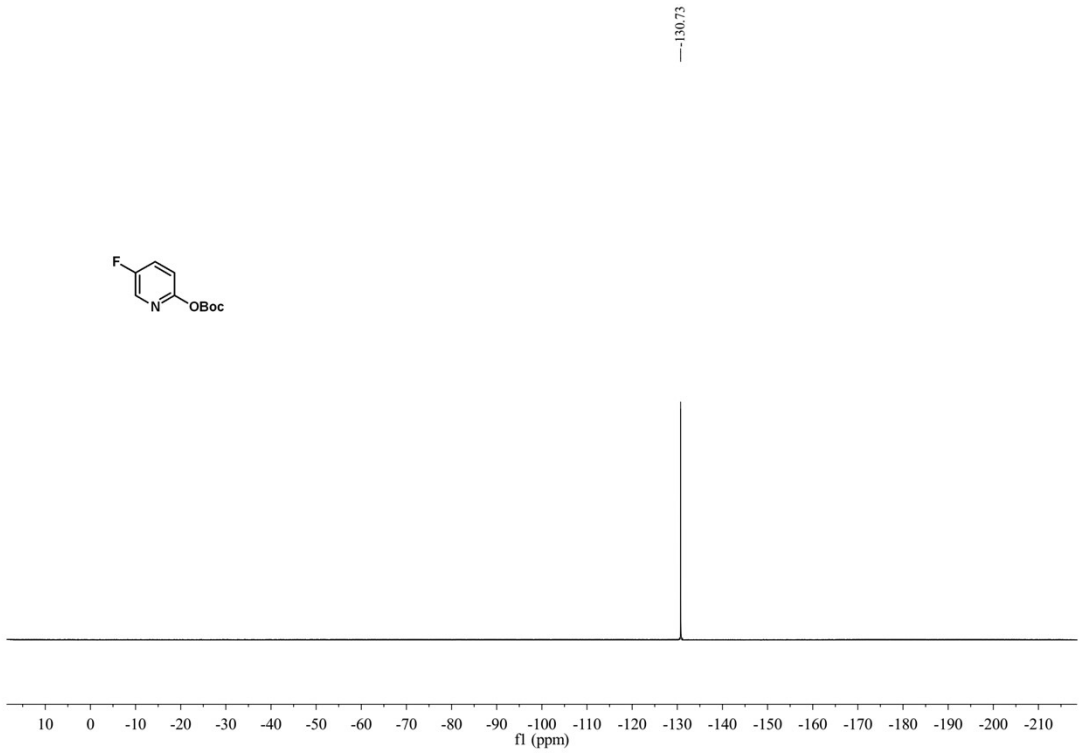


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 2f

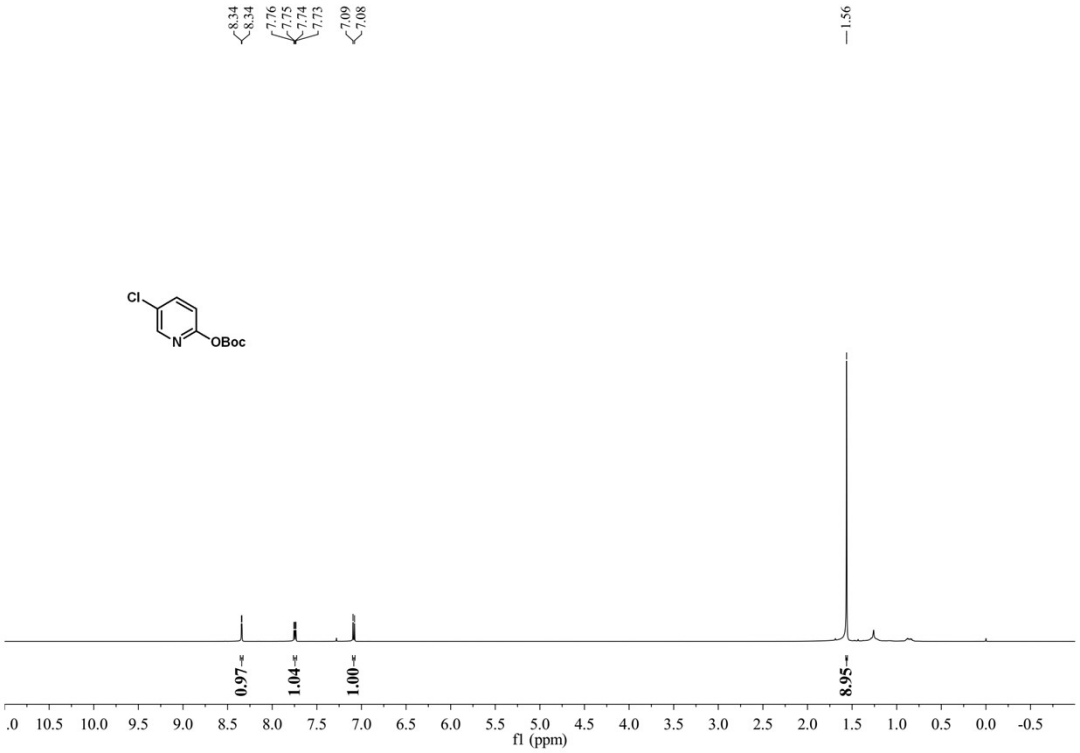


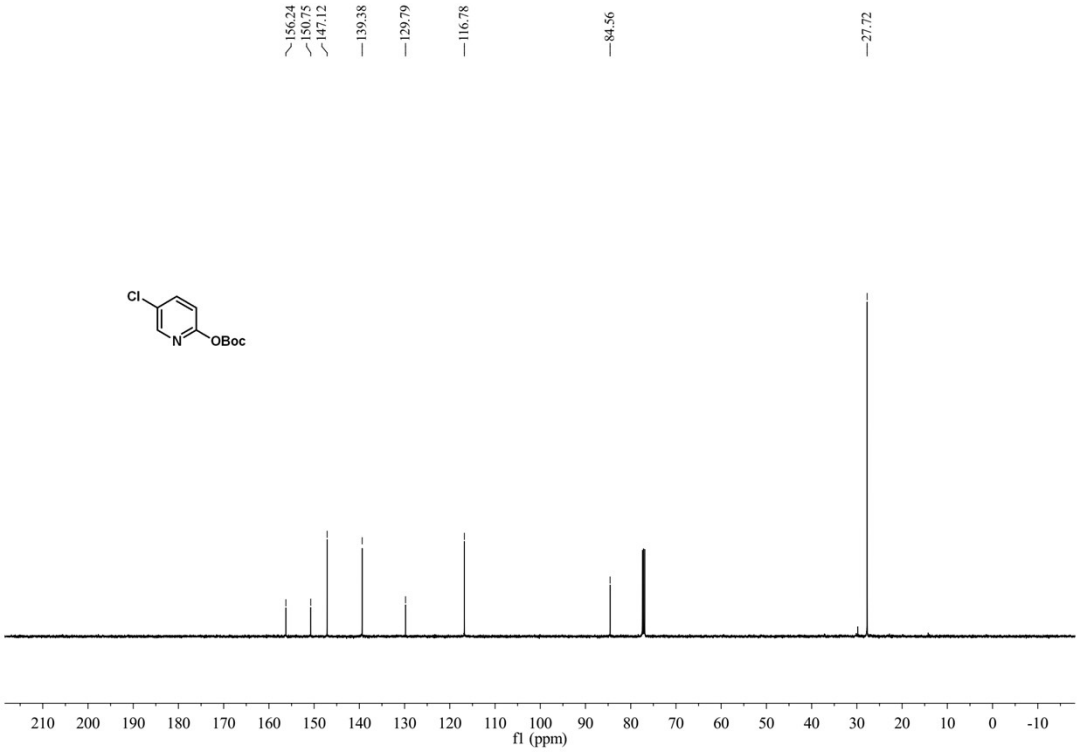


^{19}F NMR (376 MHz, $CDCl_3$) spectra for 2f

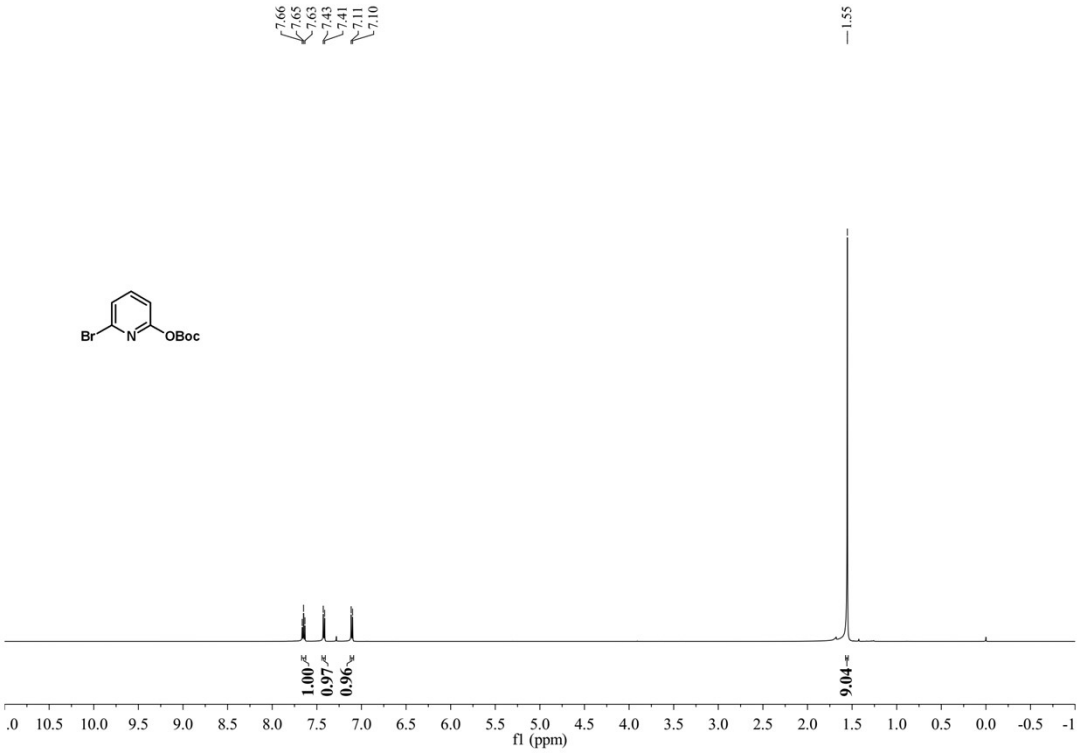


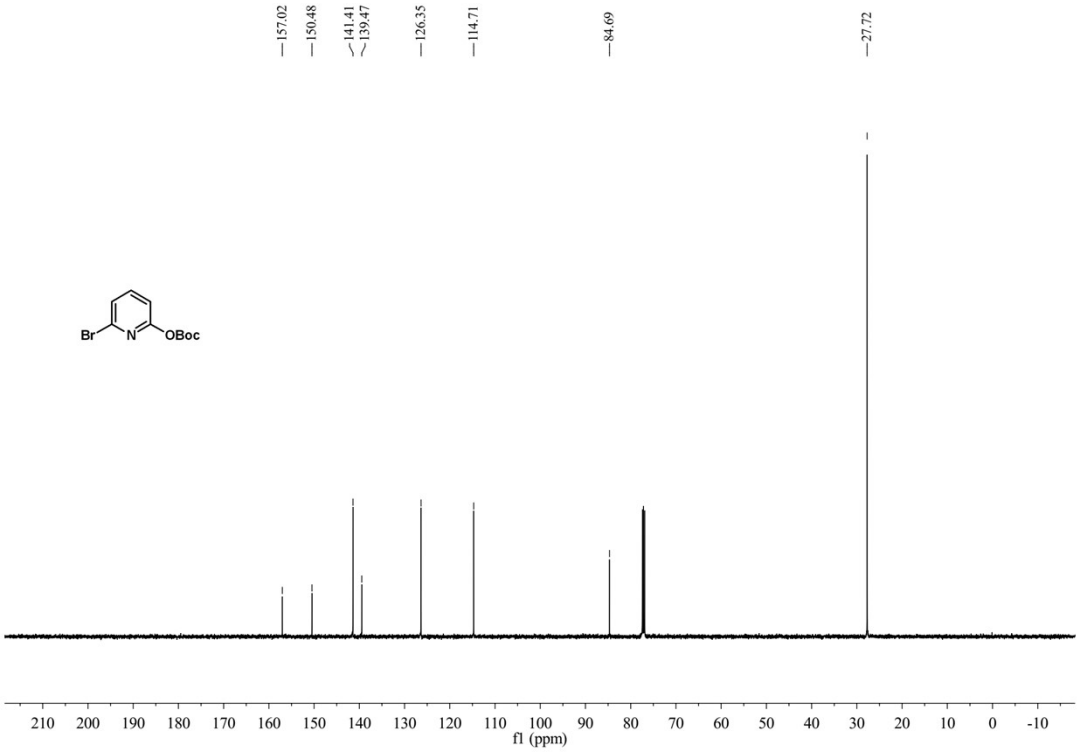
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 2g



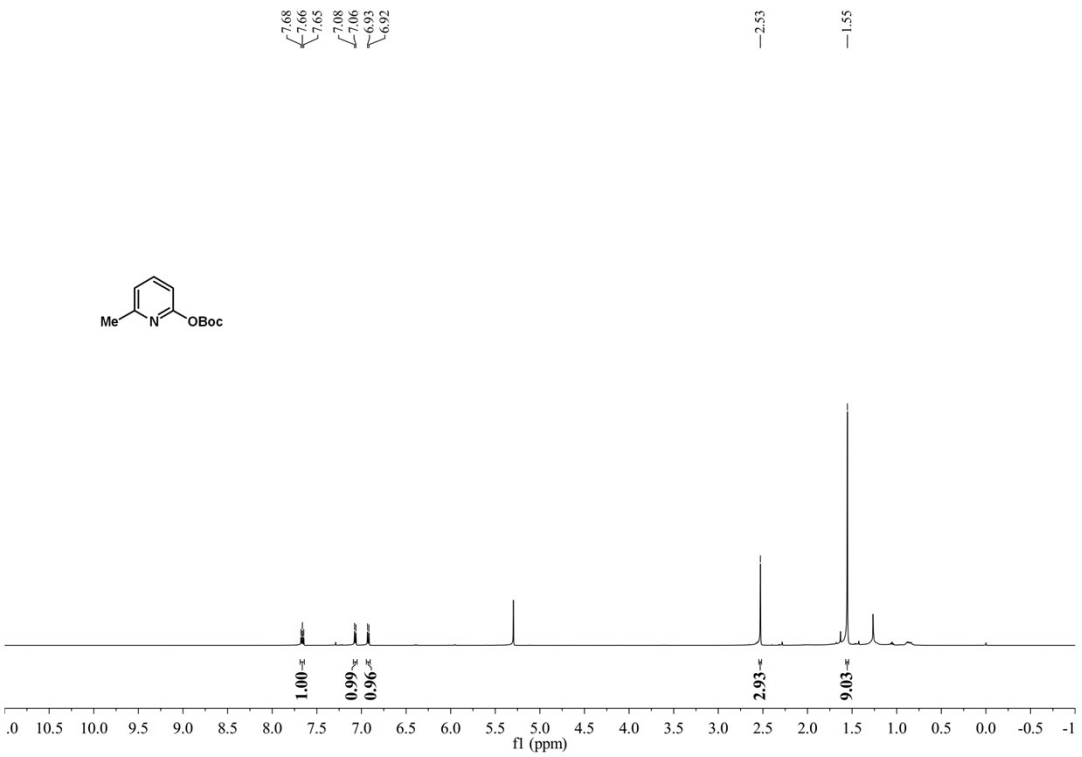


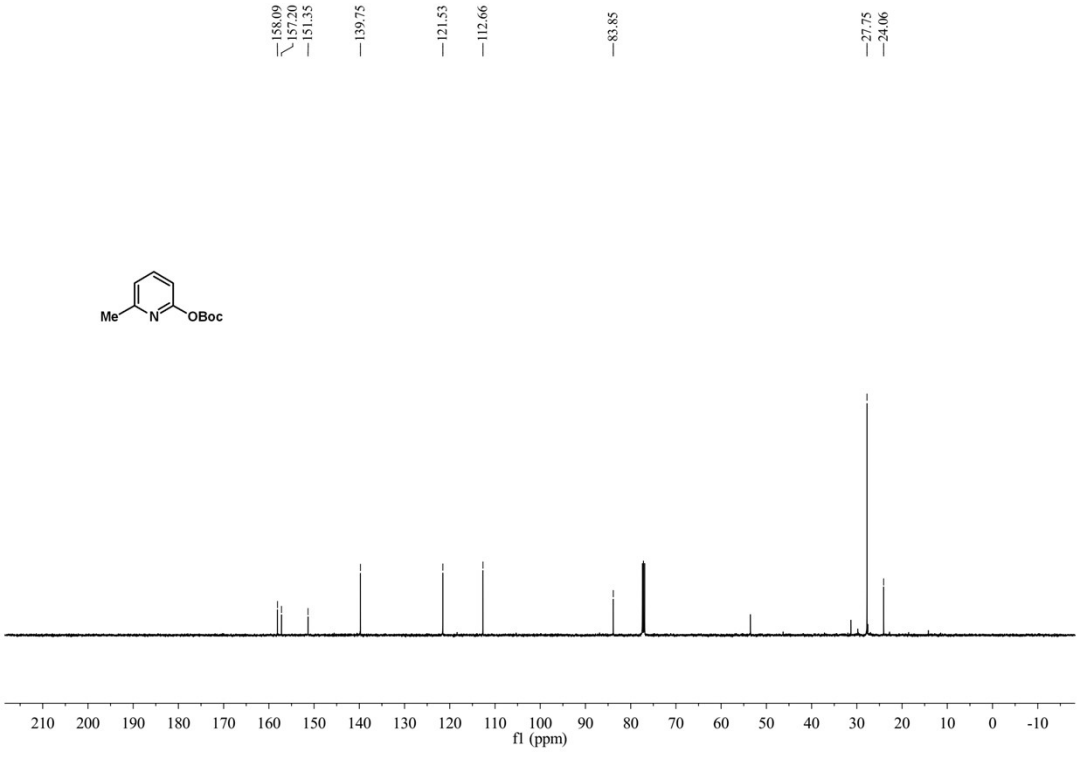
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 2k





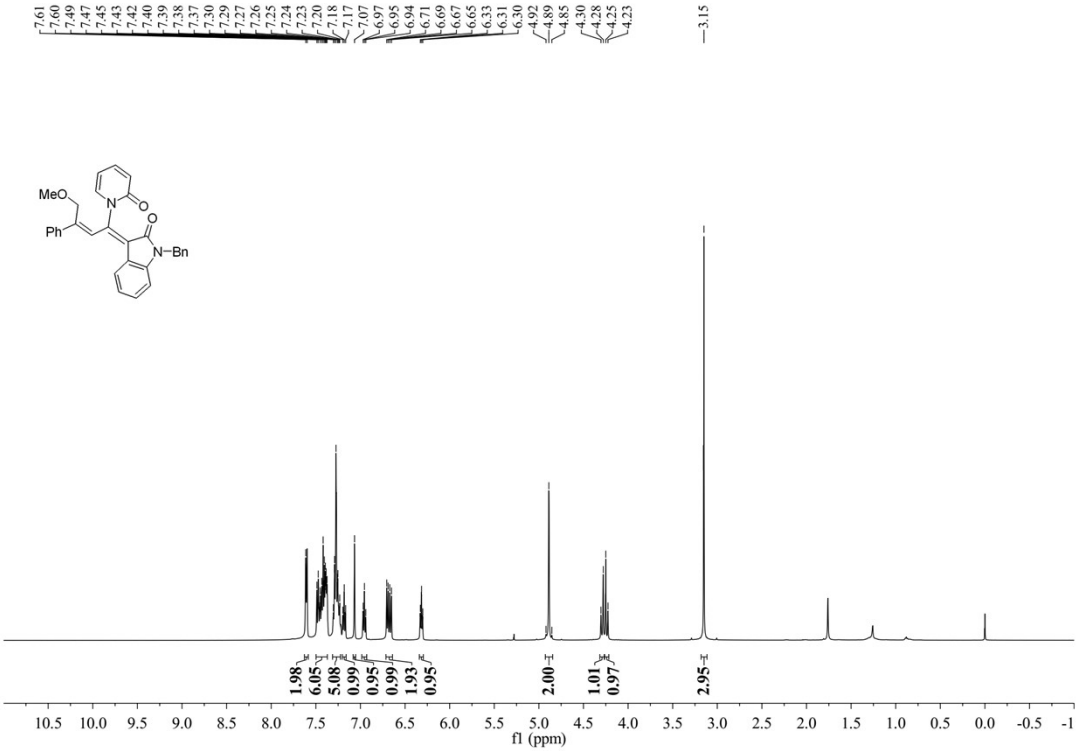
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 2l

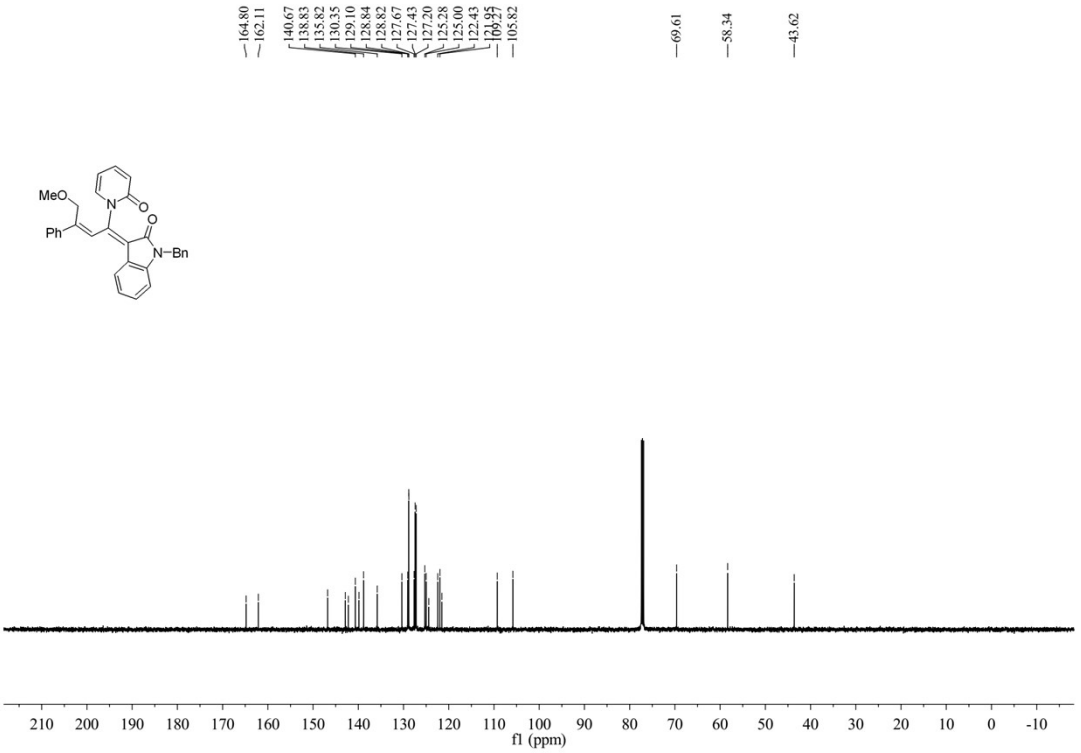




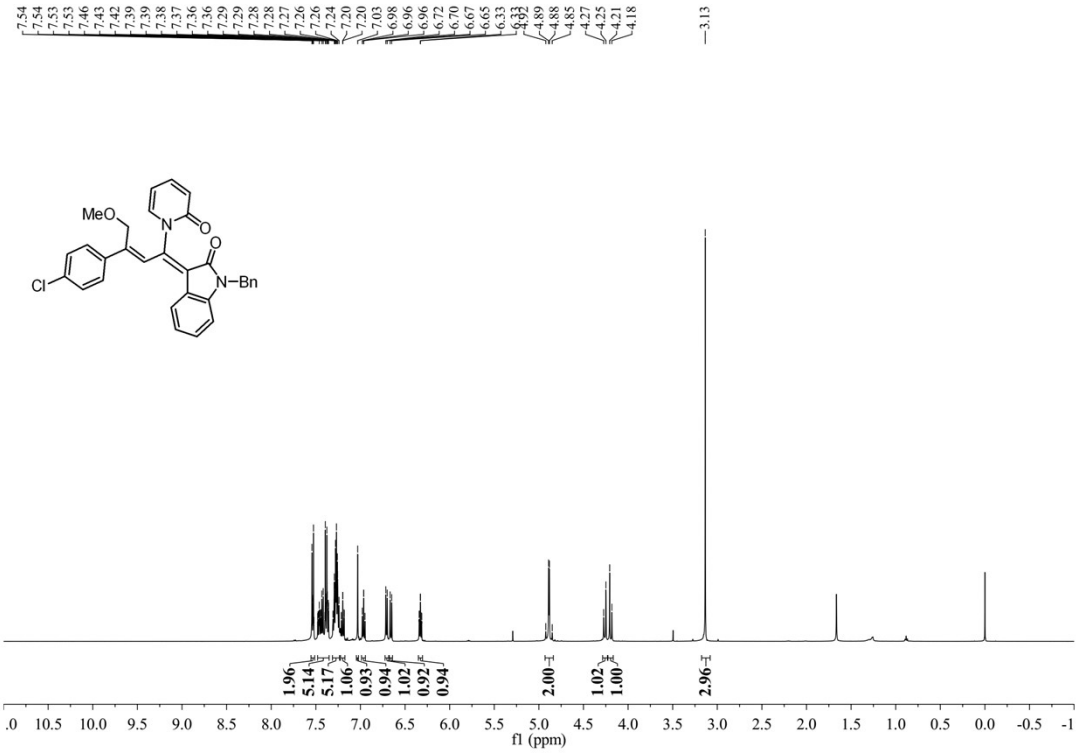
10.NMR spectra of products

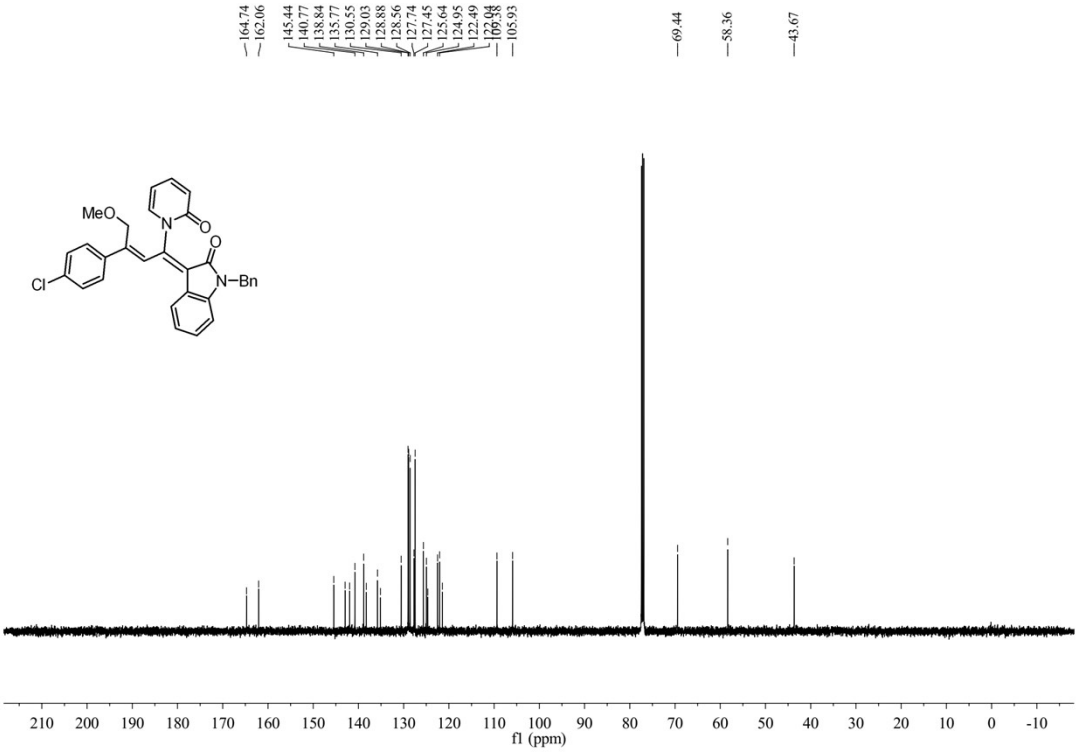
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4aa



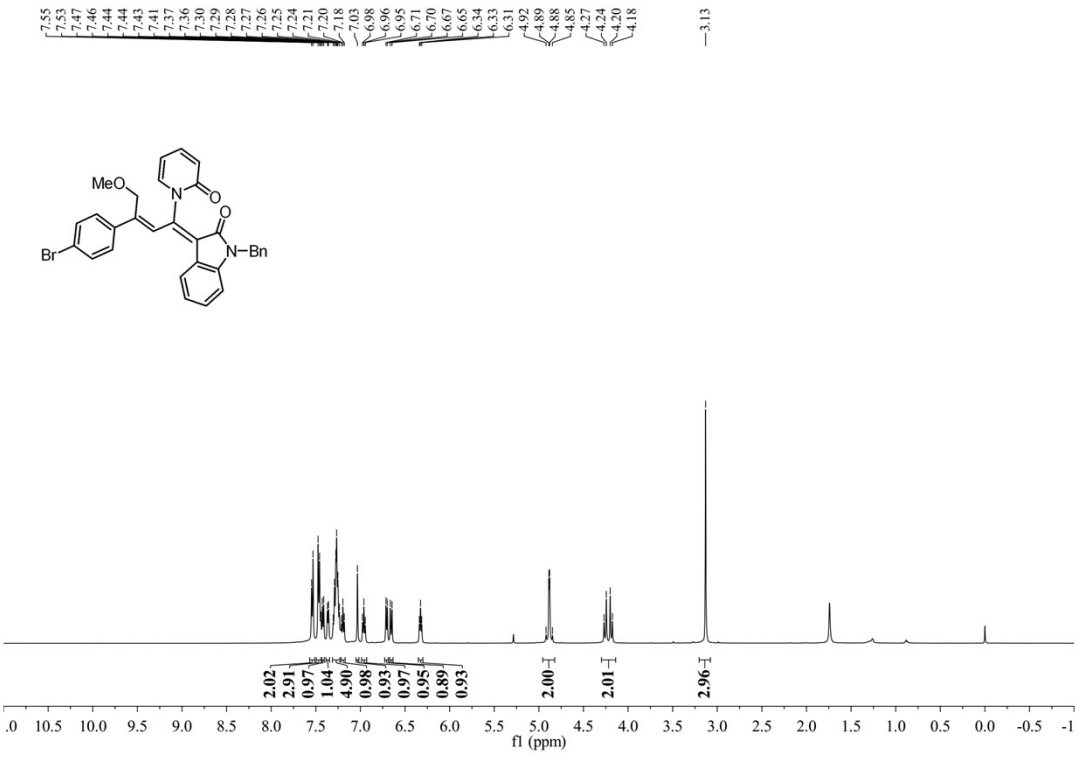


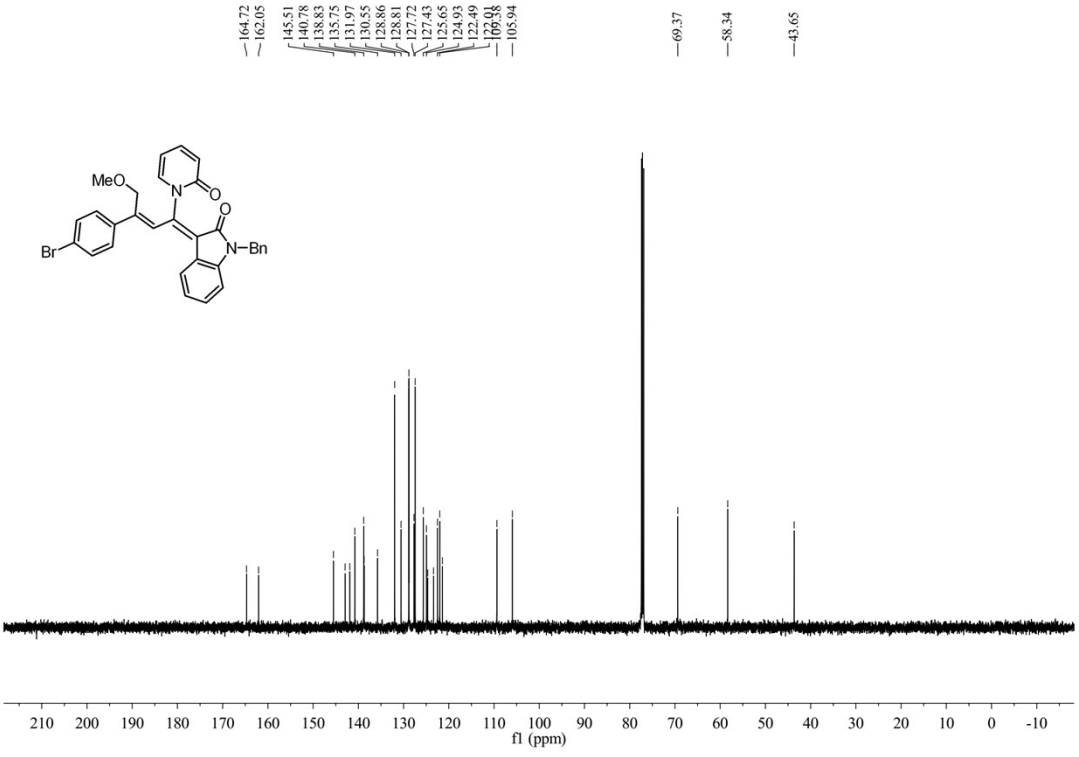
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ab



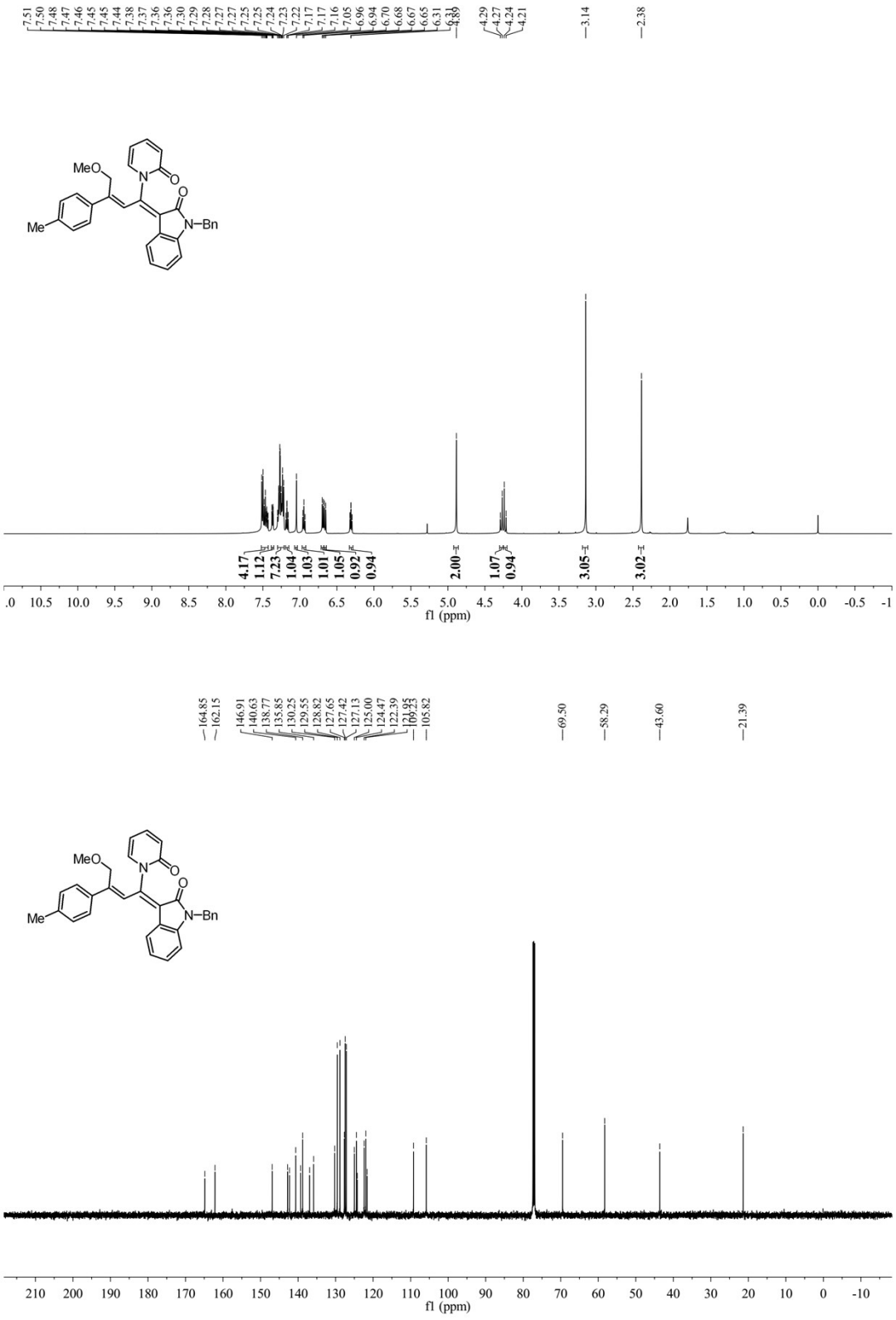


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ac

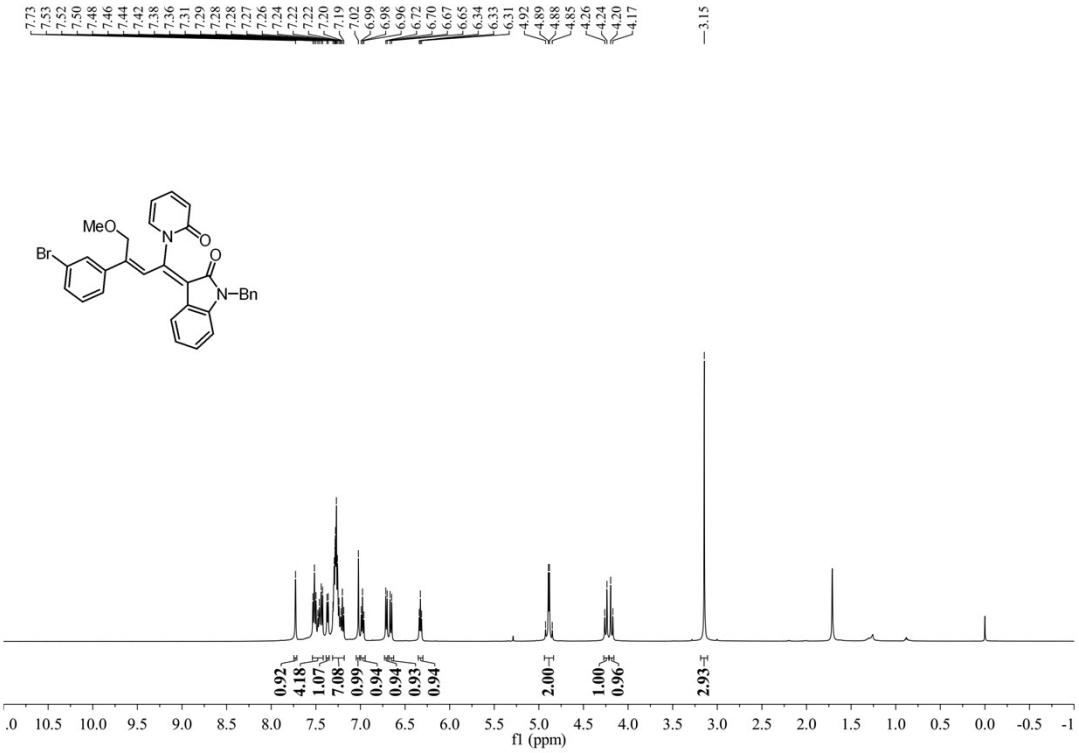


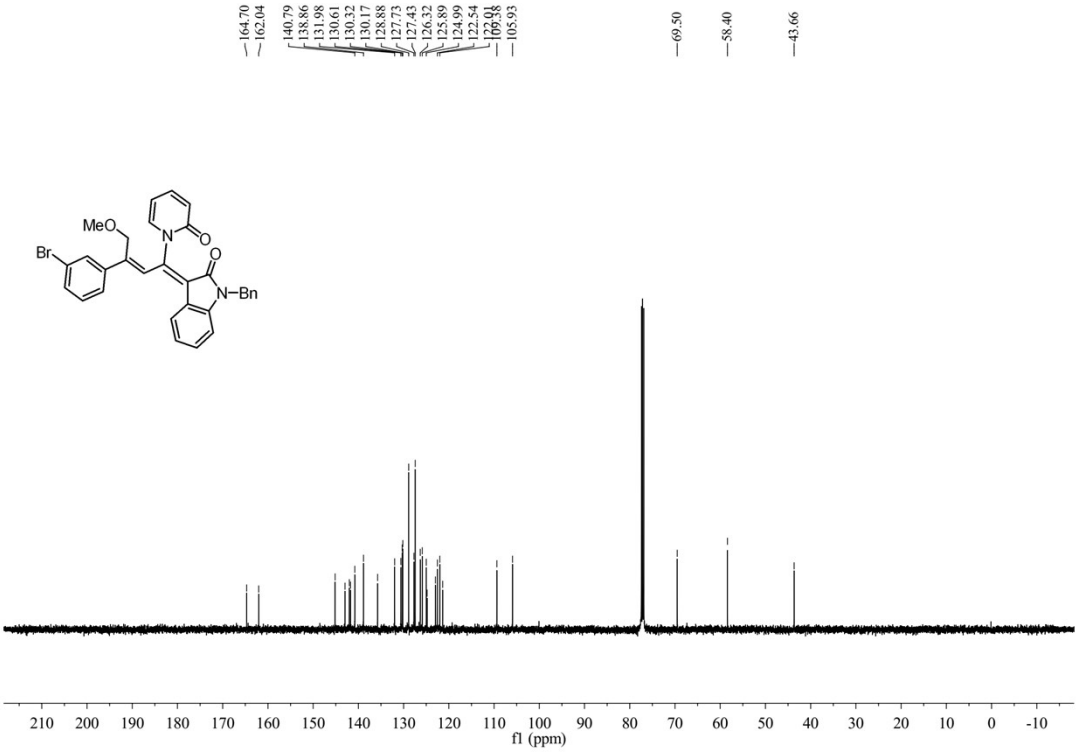


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ad

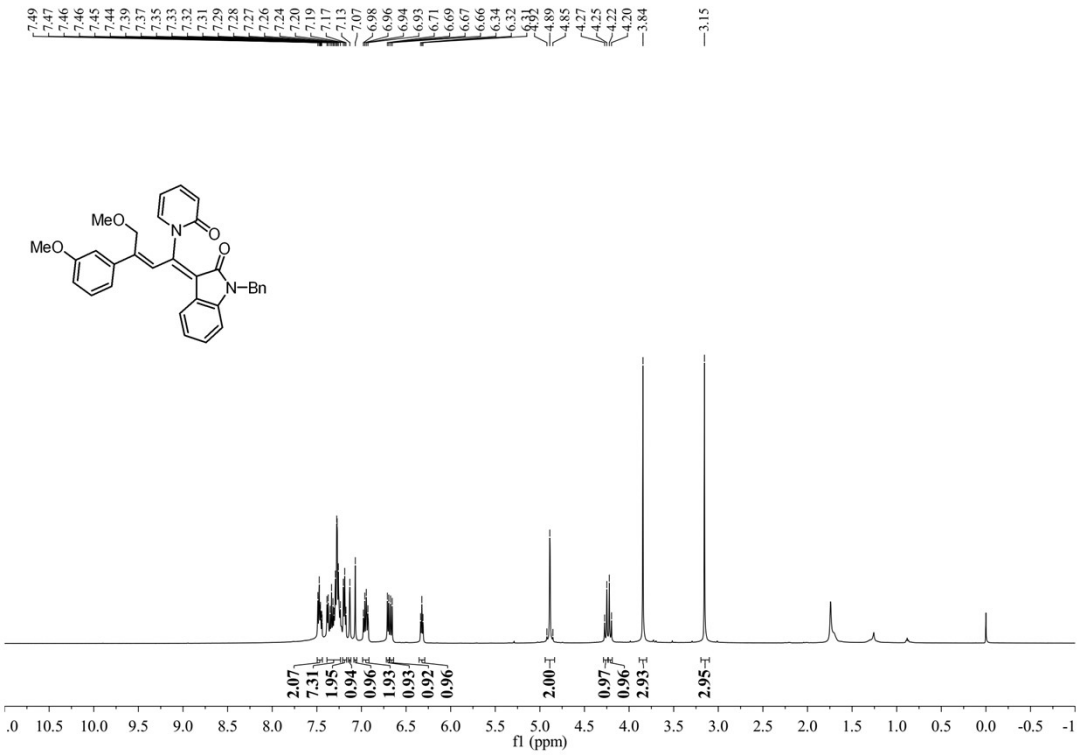


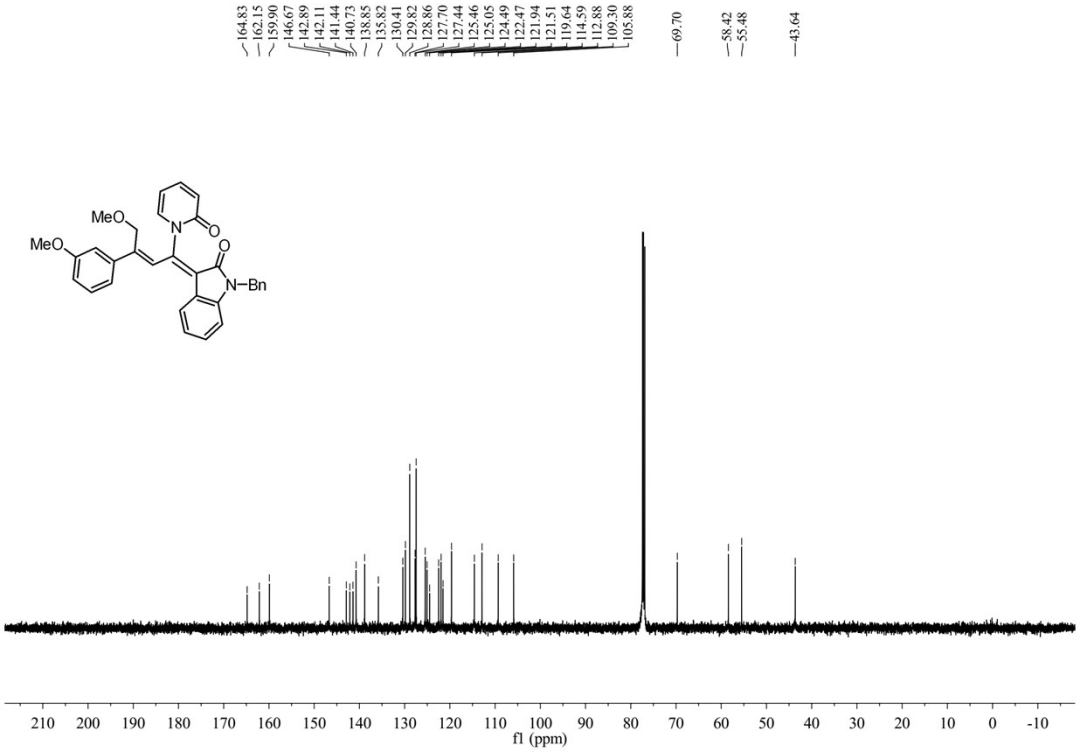
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ae



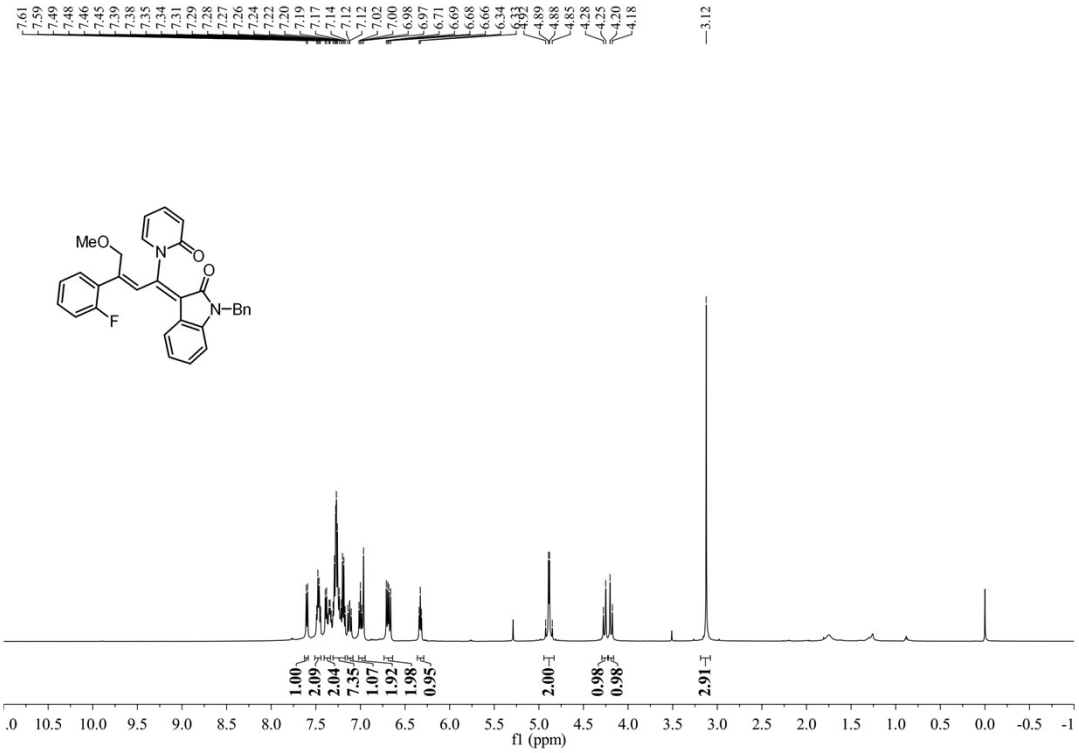


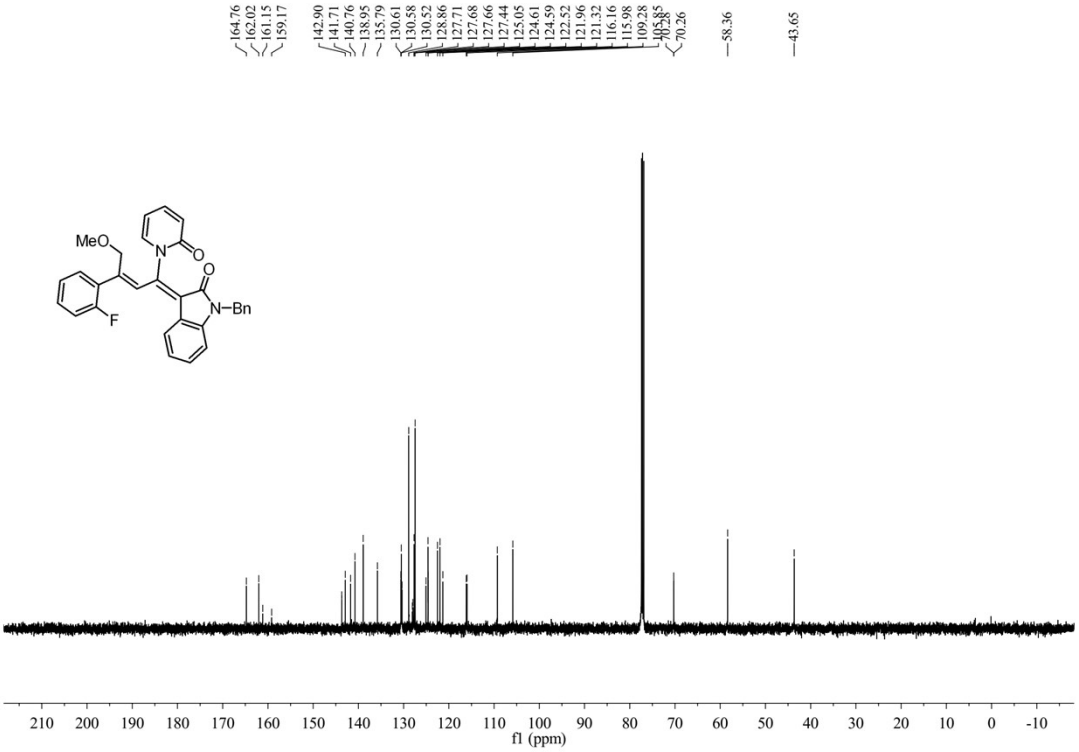
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4af



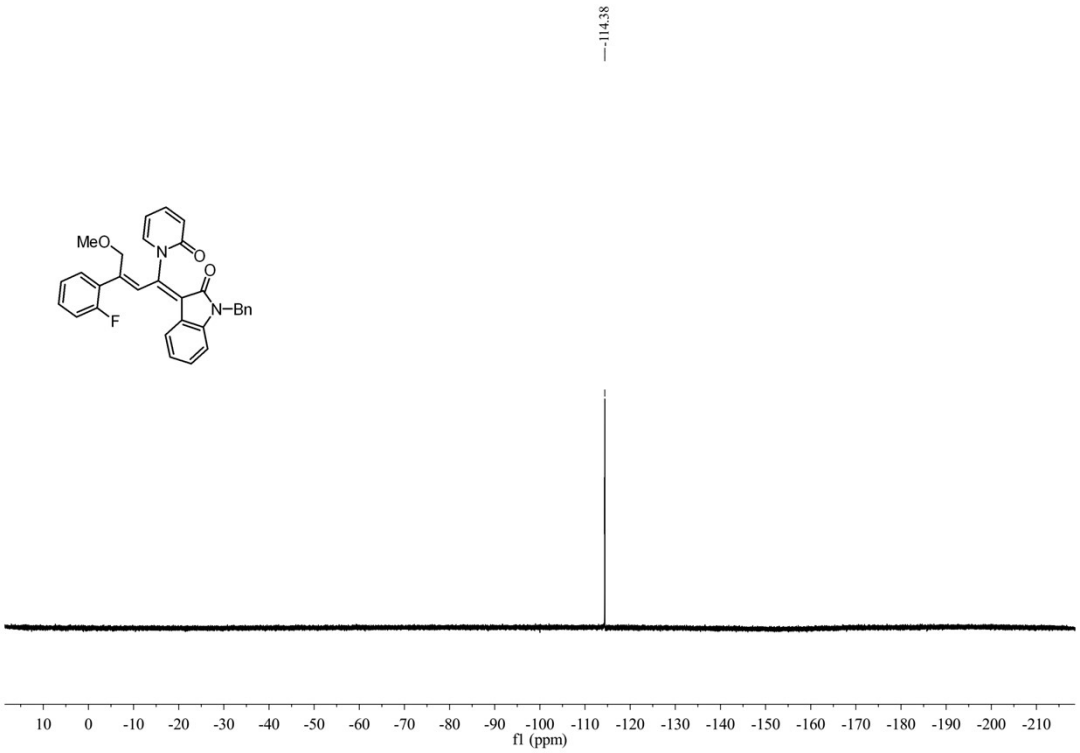


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ag

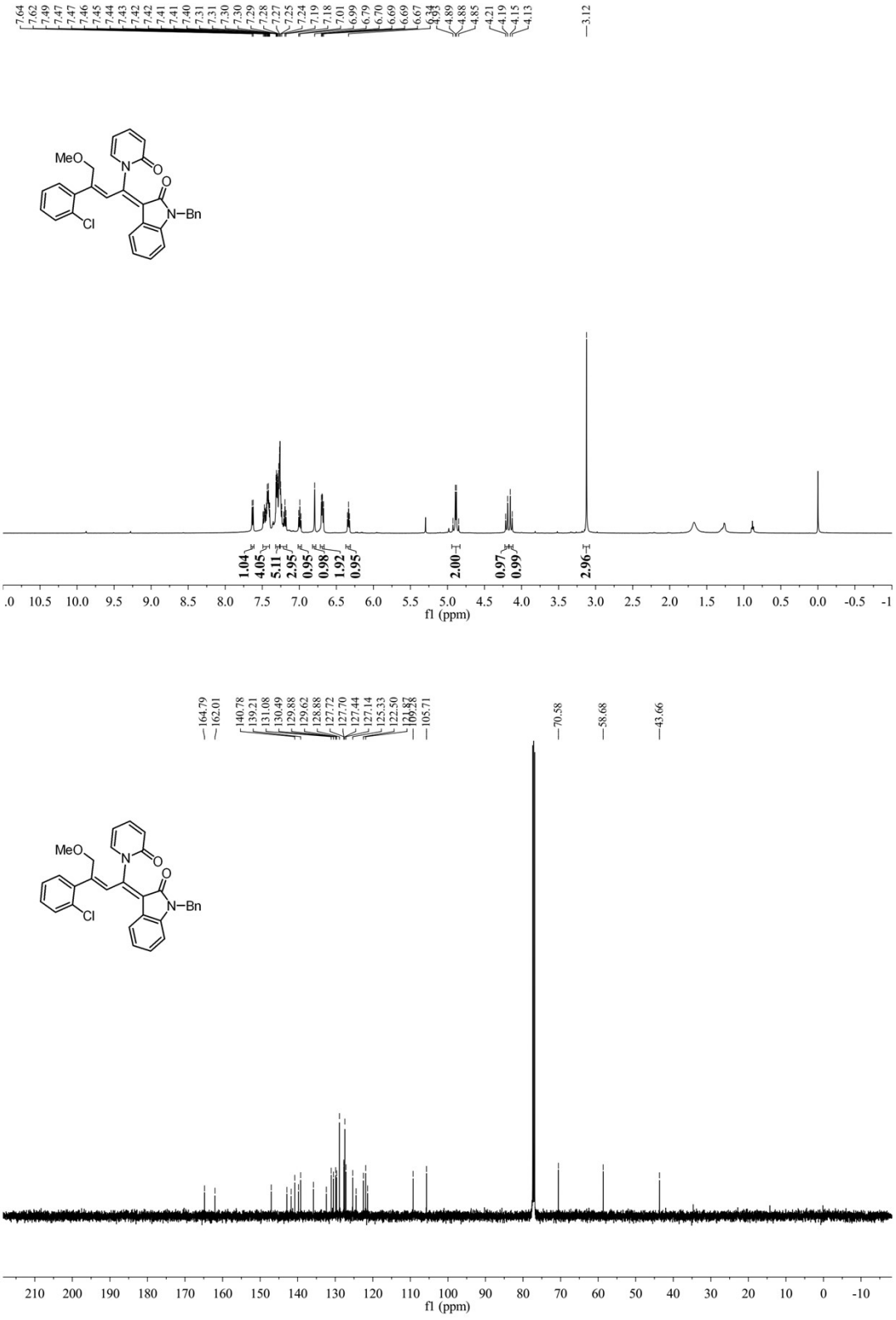




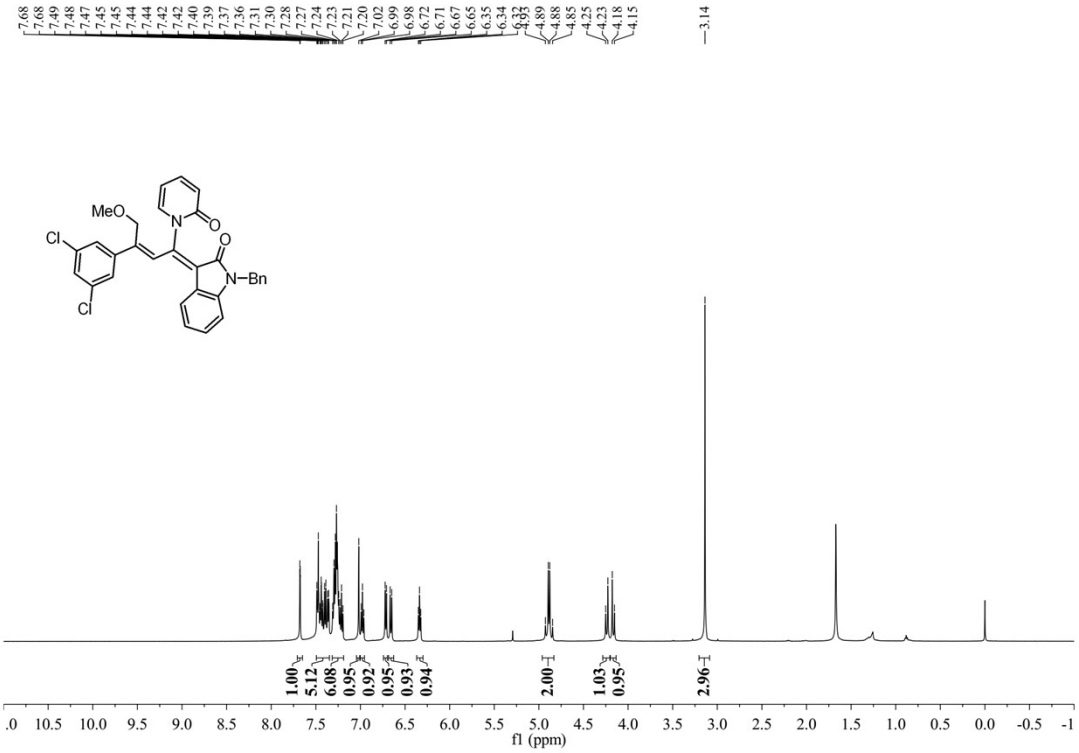
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4ag

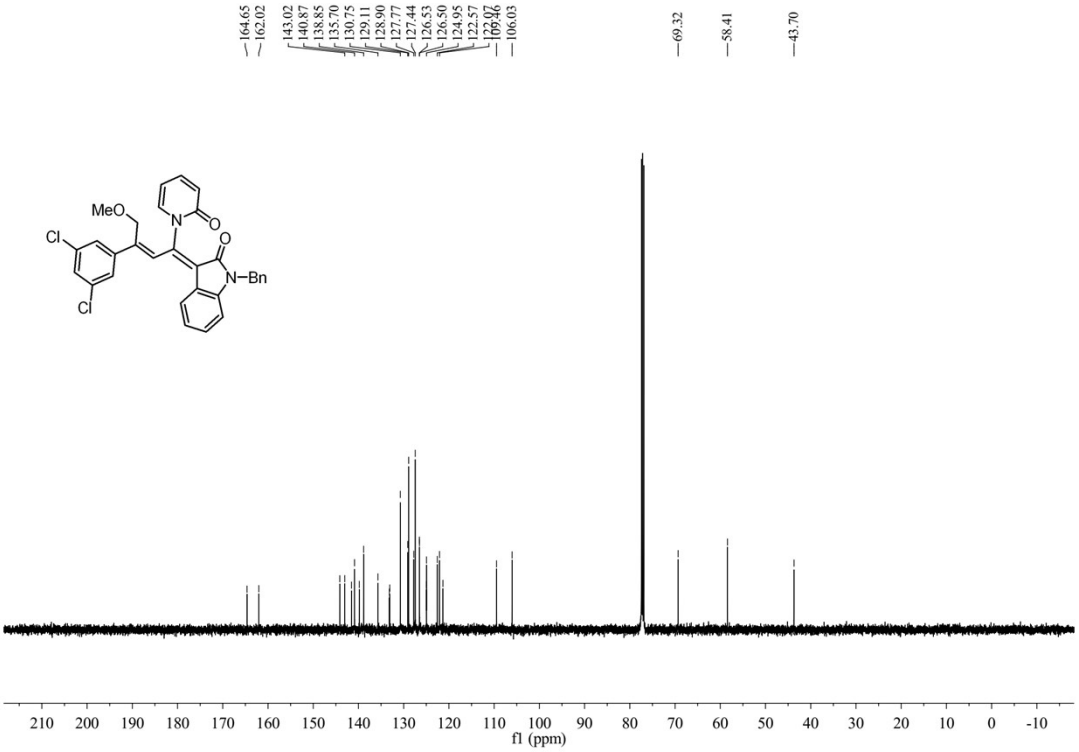


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ah

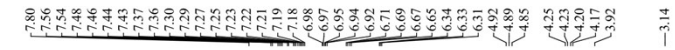


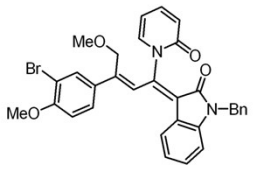
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ai

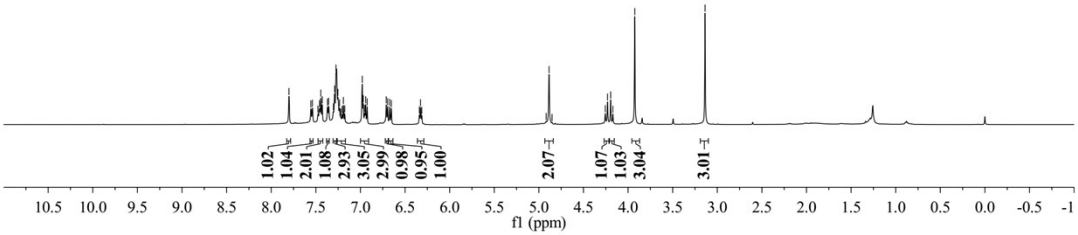


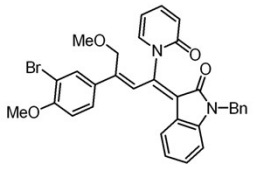


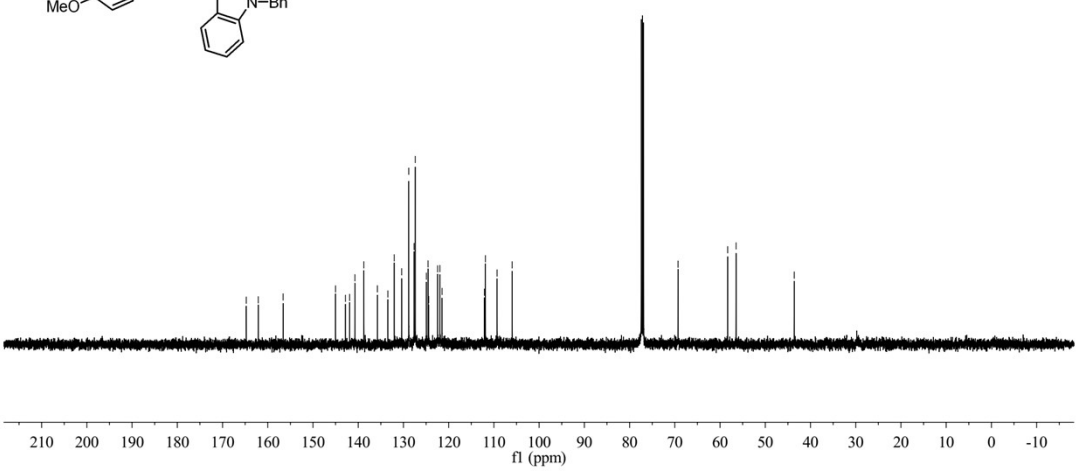
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4aj



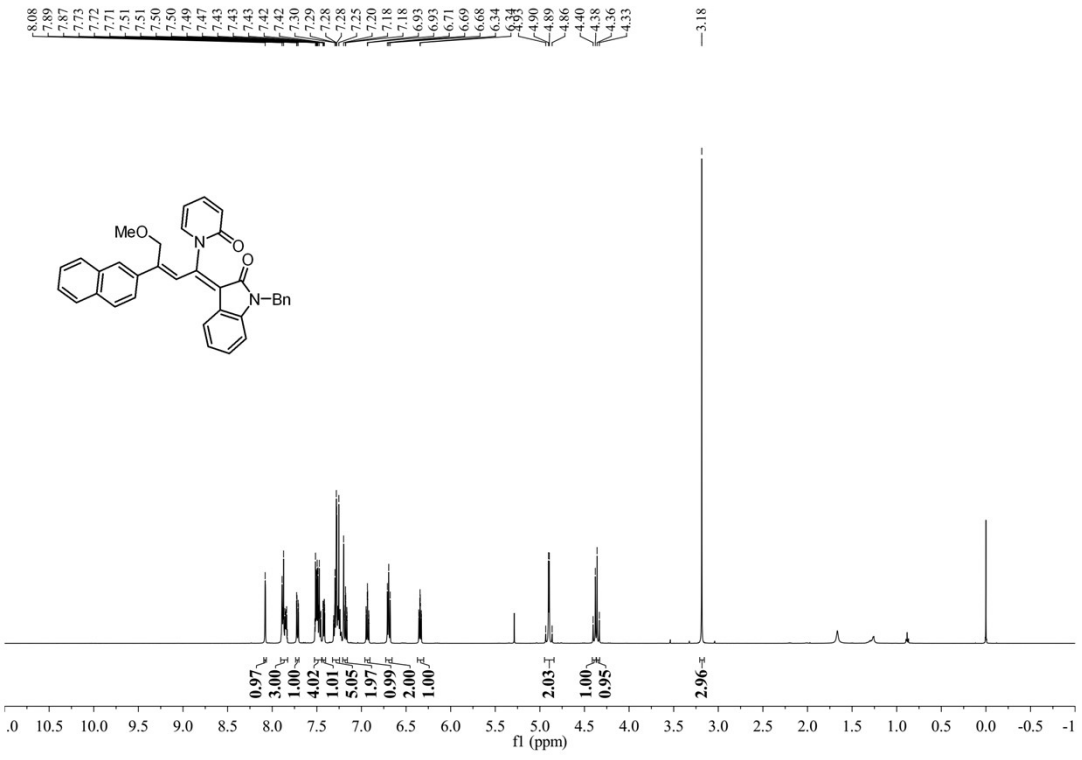


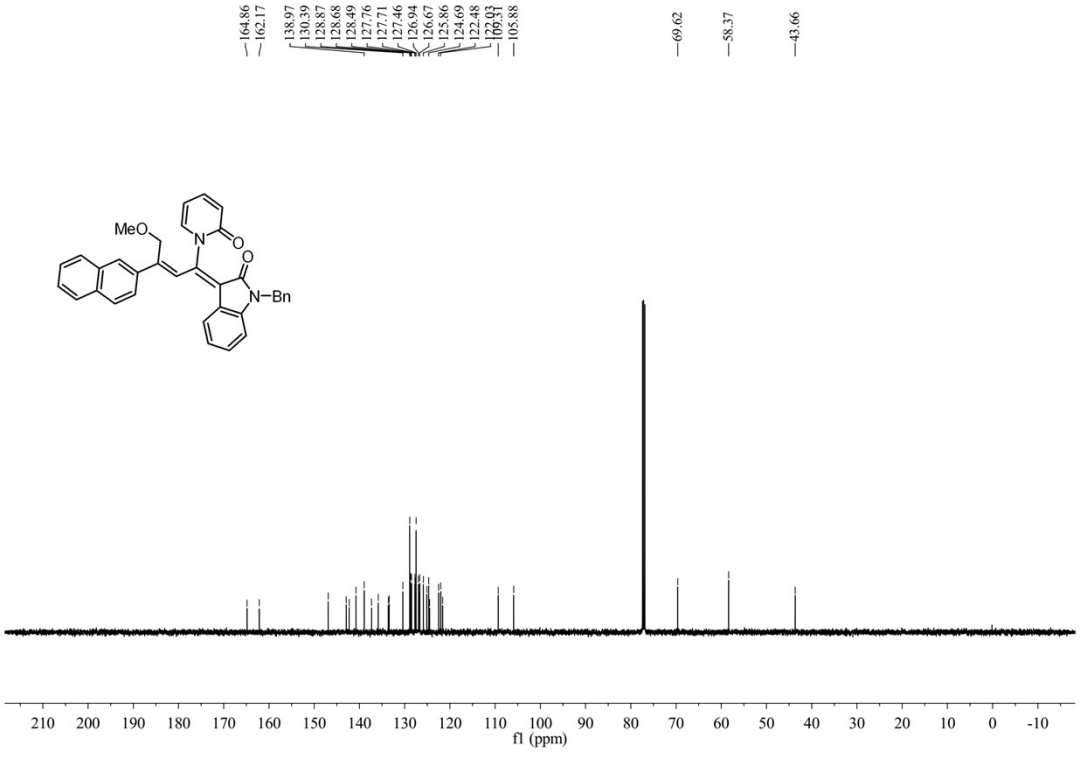




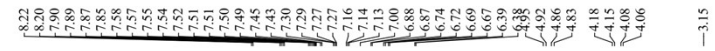


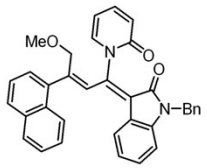
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ak

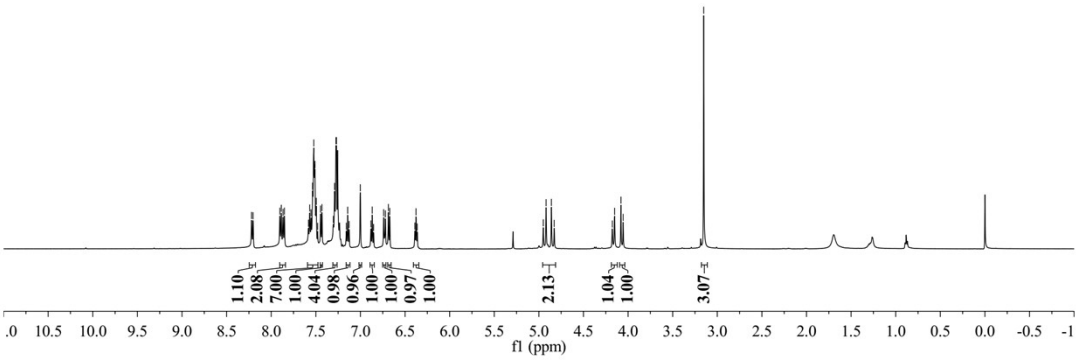


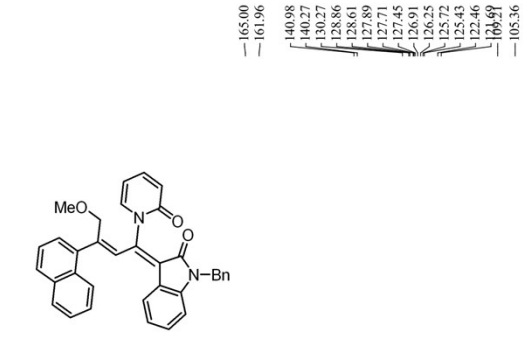


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4al

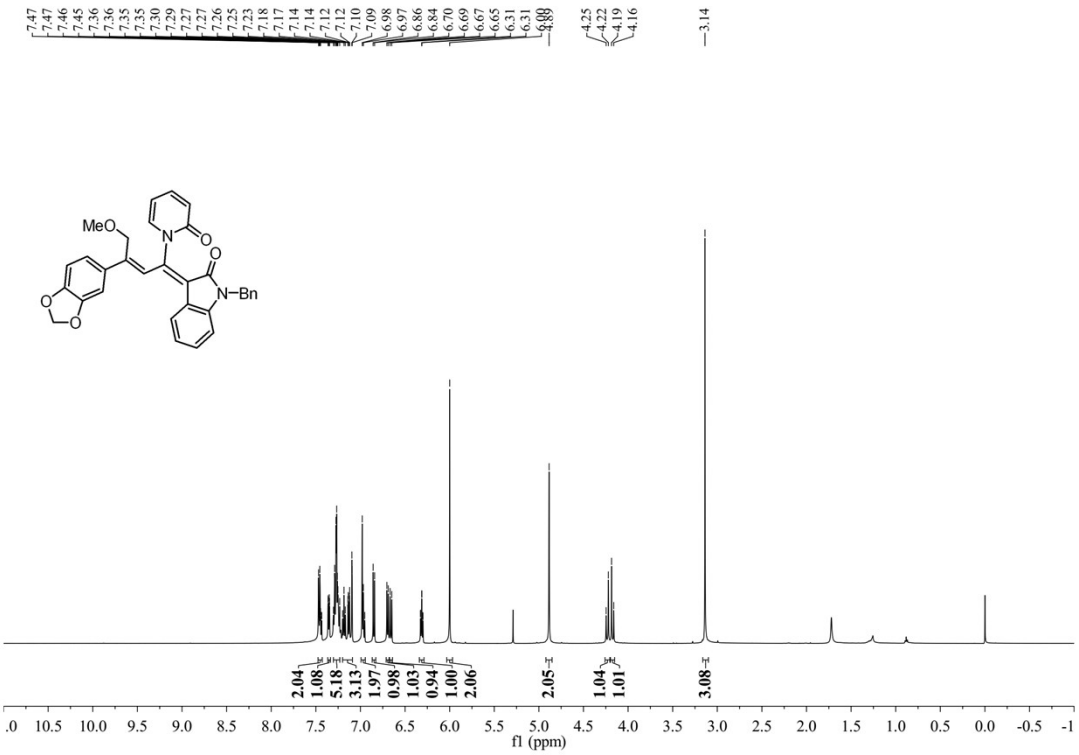


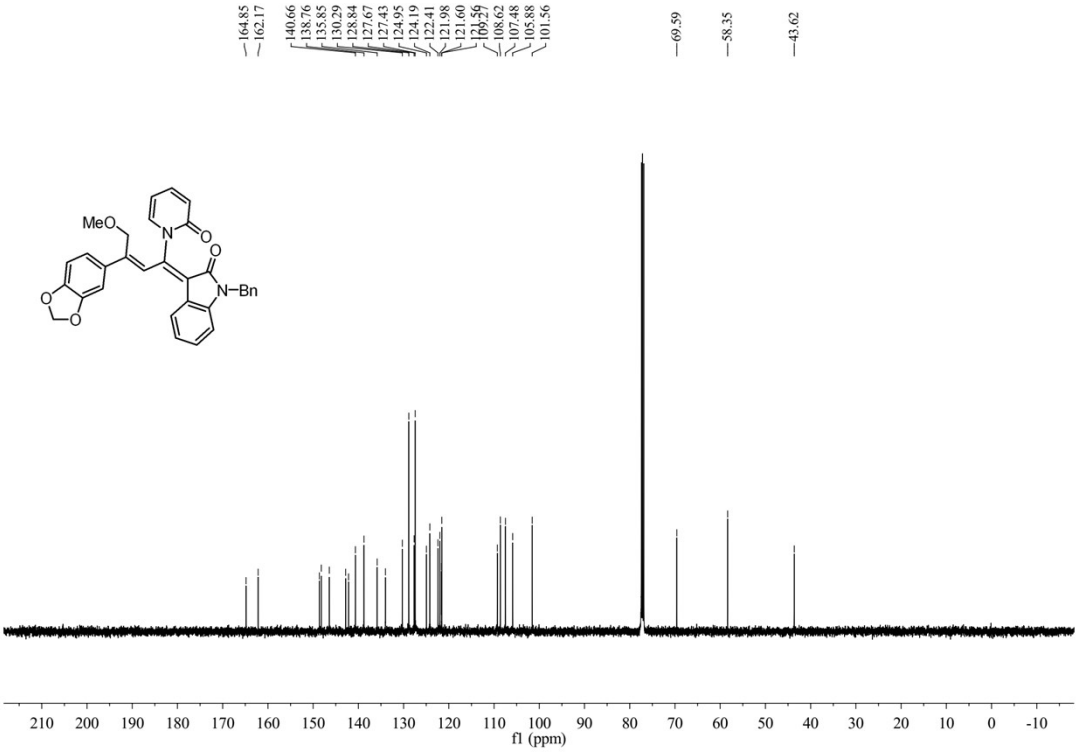




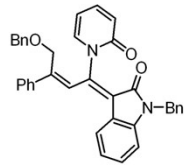


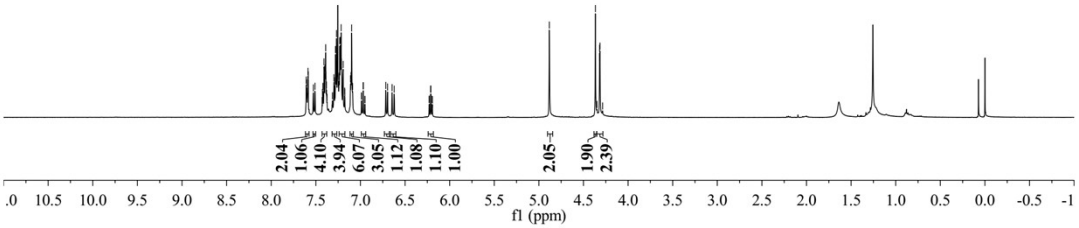
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4am

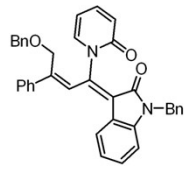


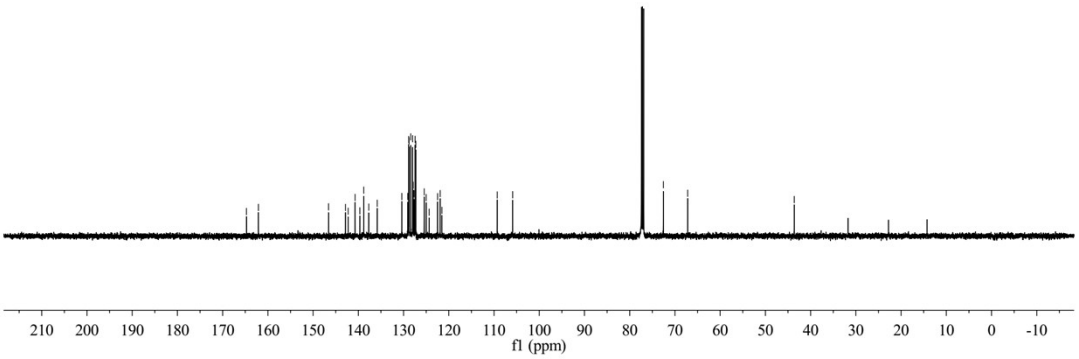


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4an

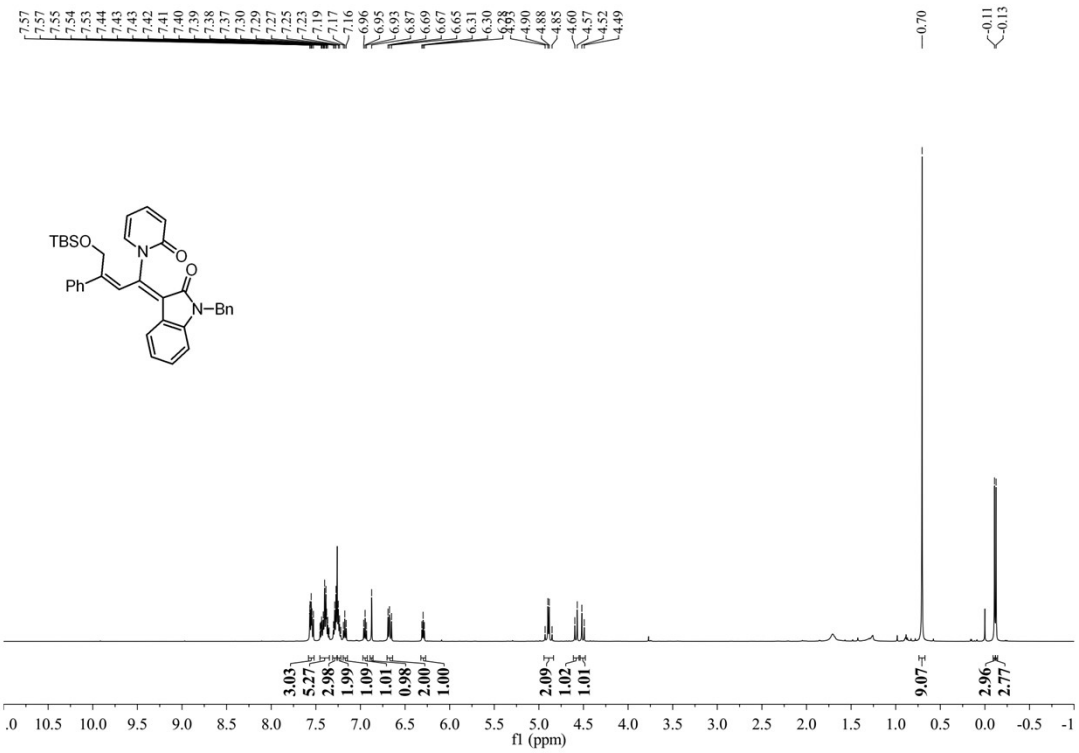


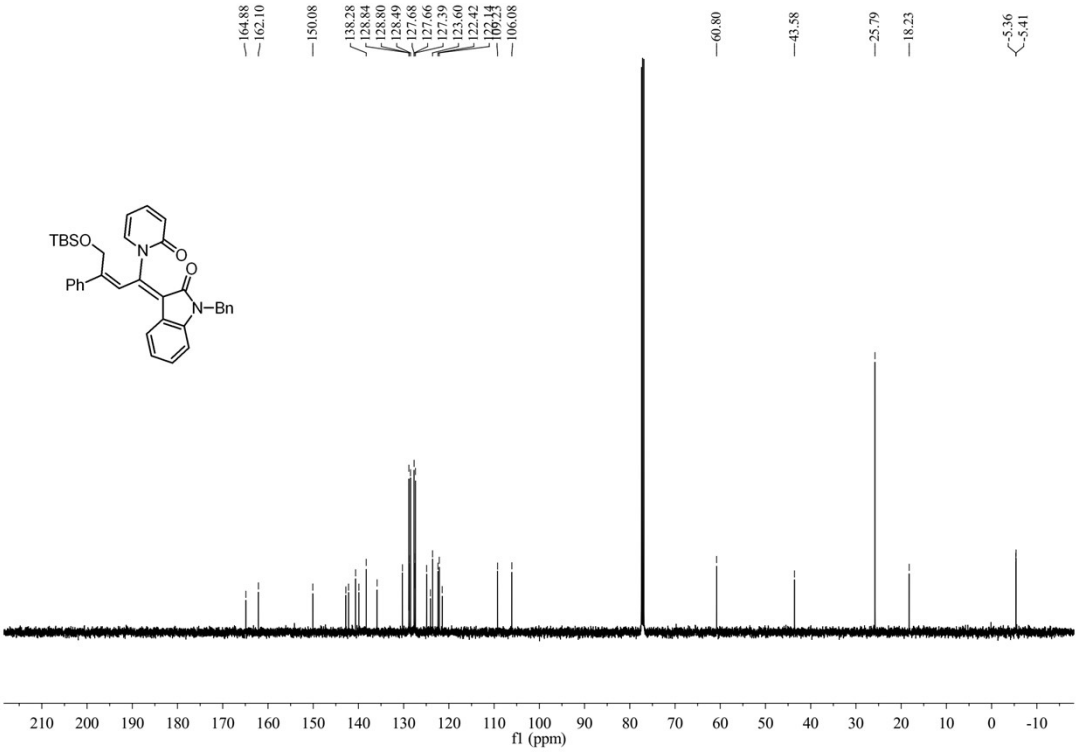




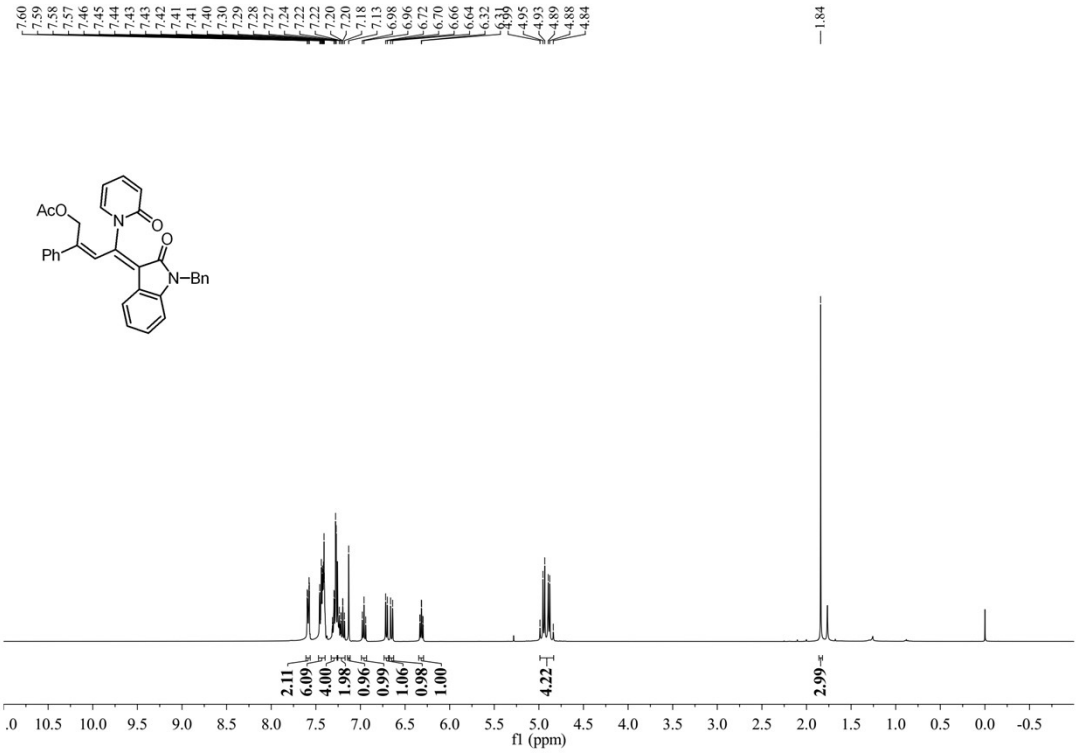


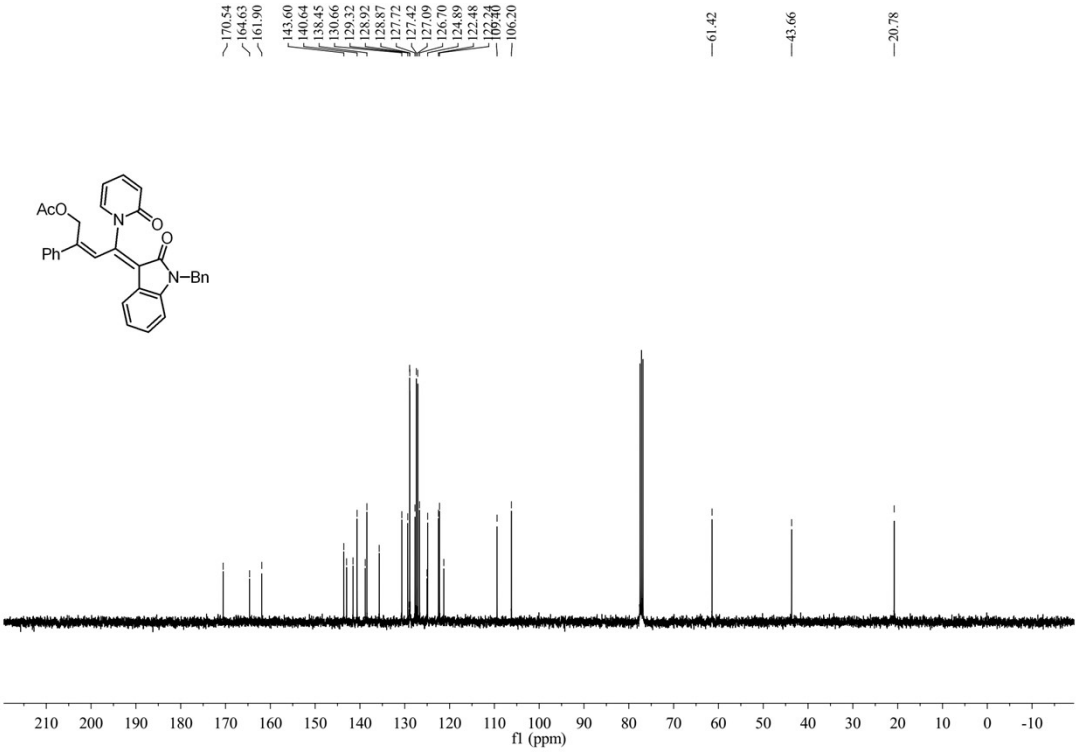
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ao



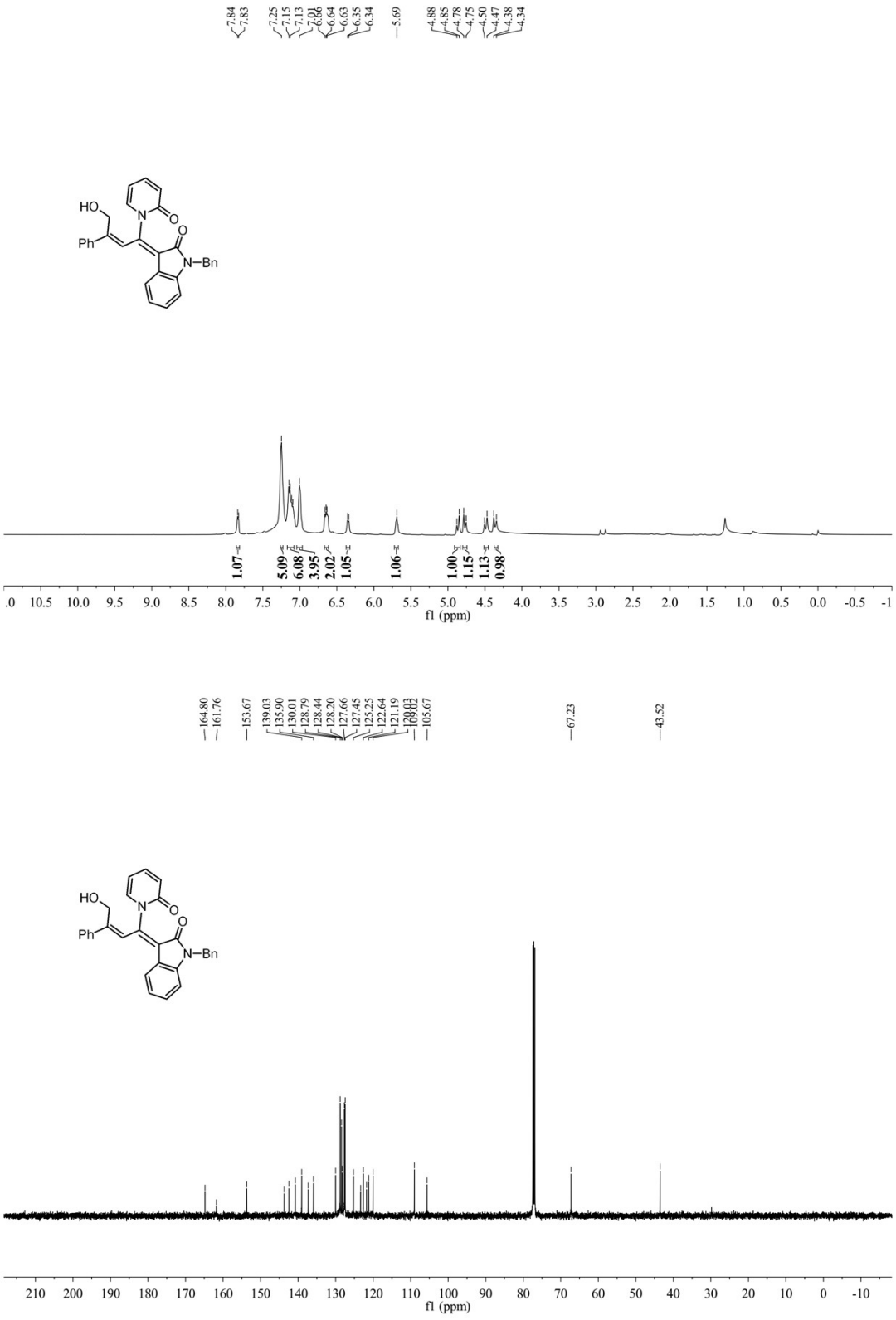


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ap

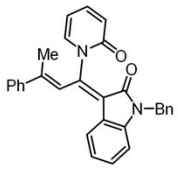


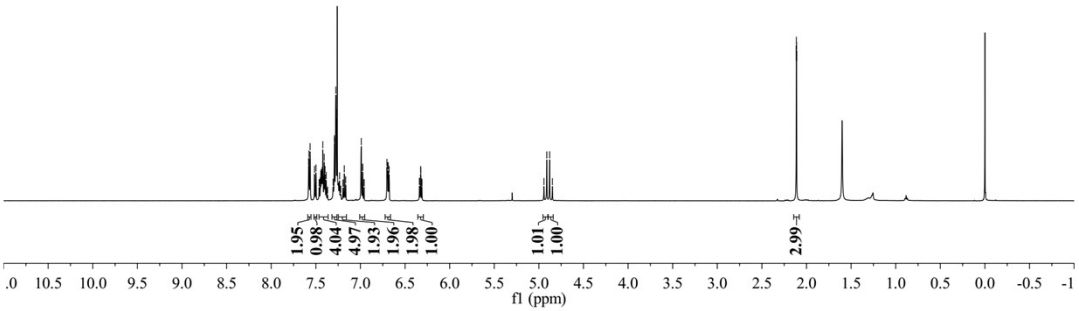


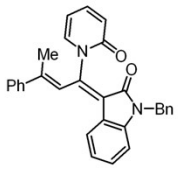
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4aq

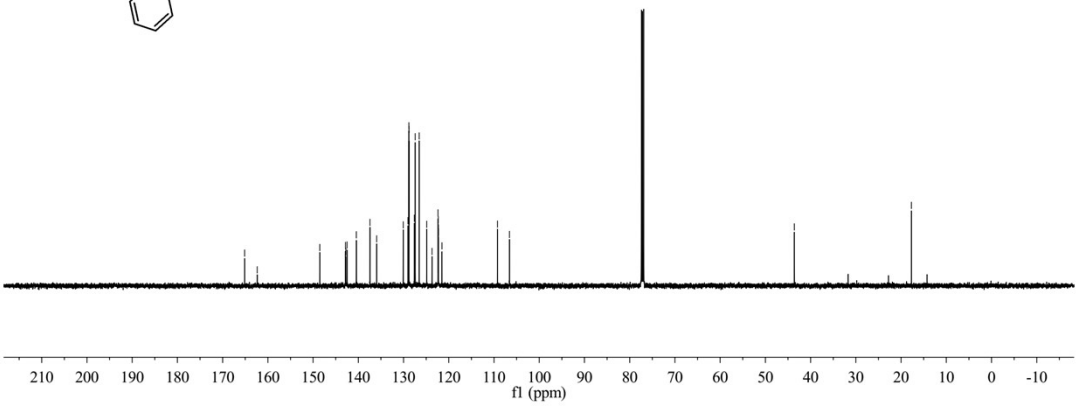


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ar

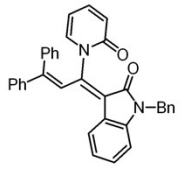


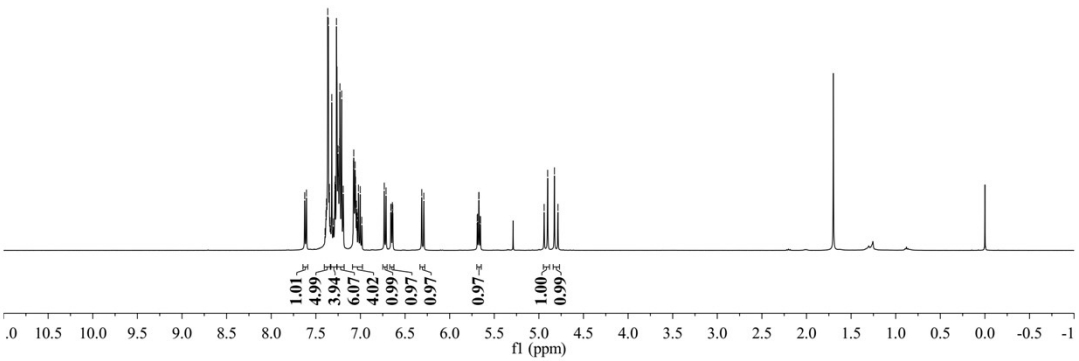


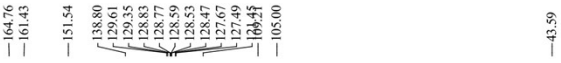


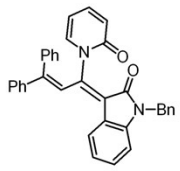


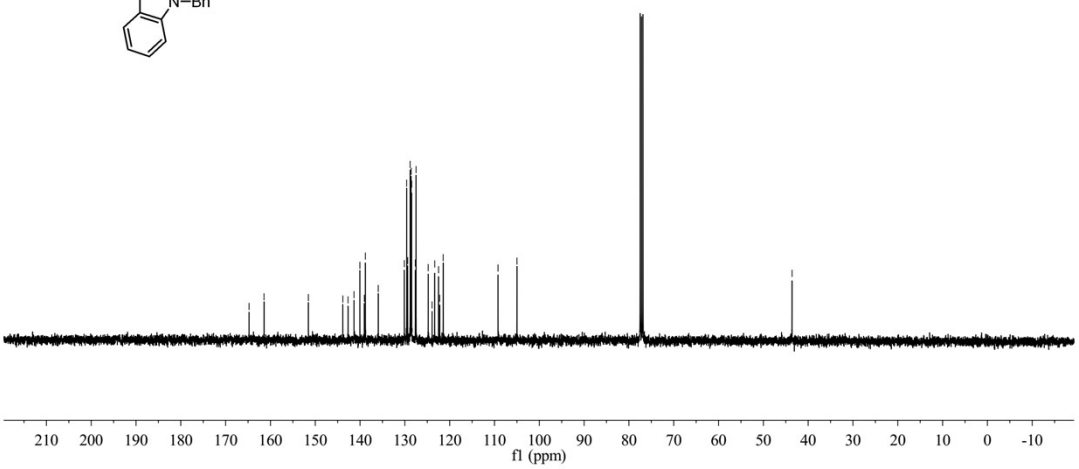
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4as



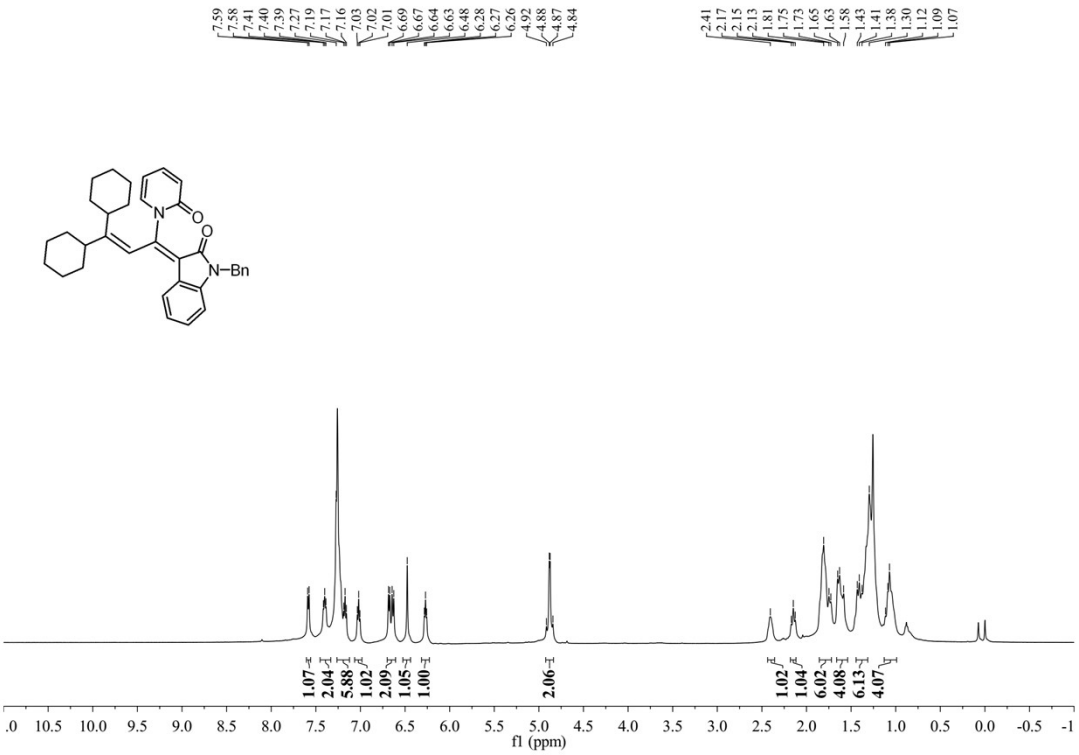


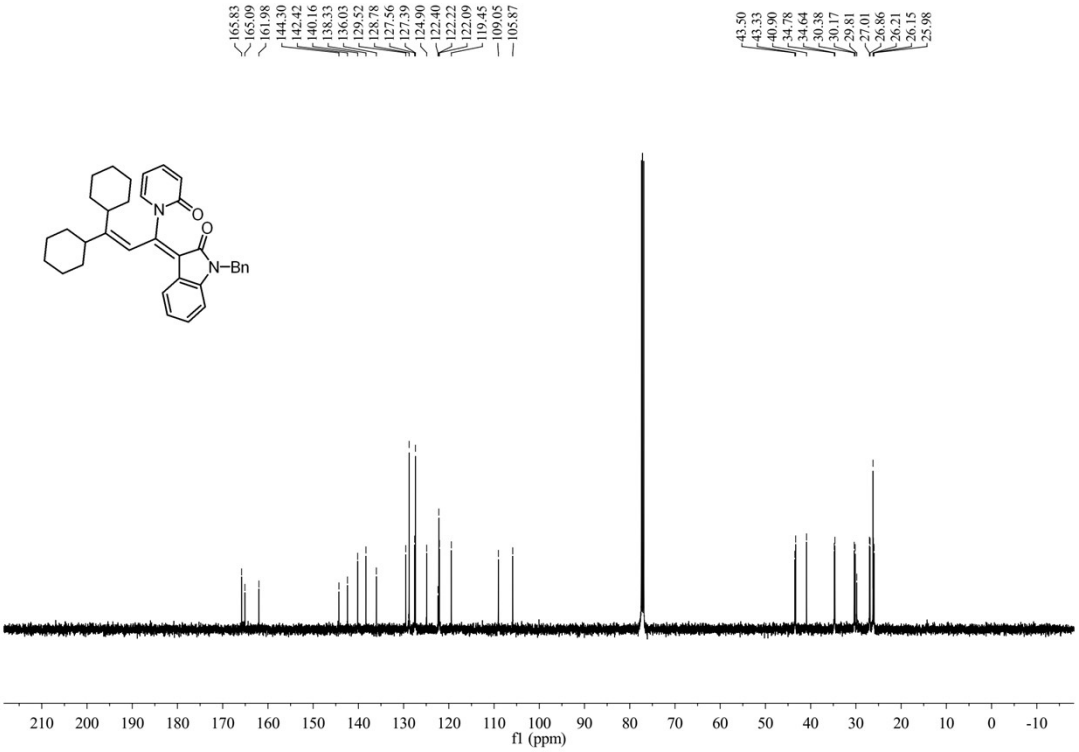




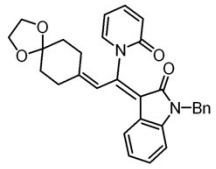


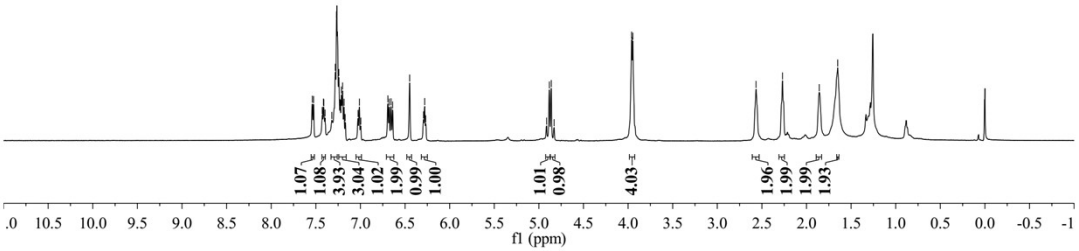
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4at

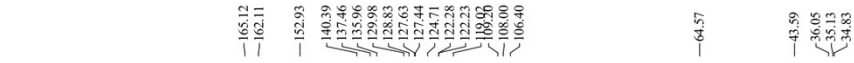


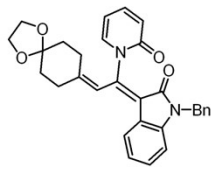


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4au

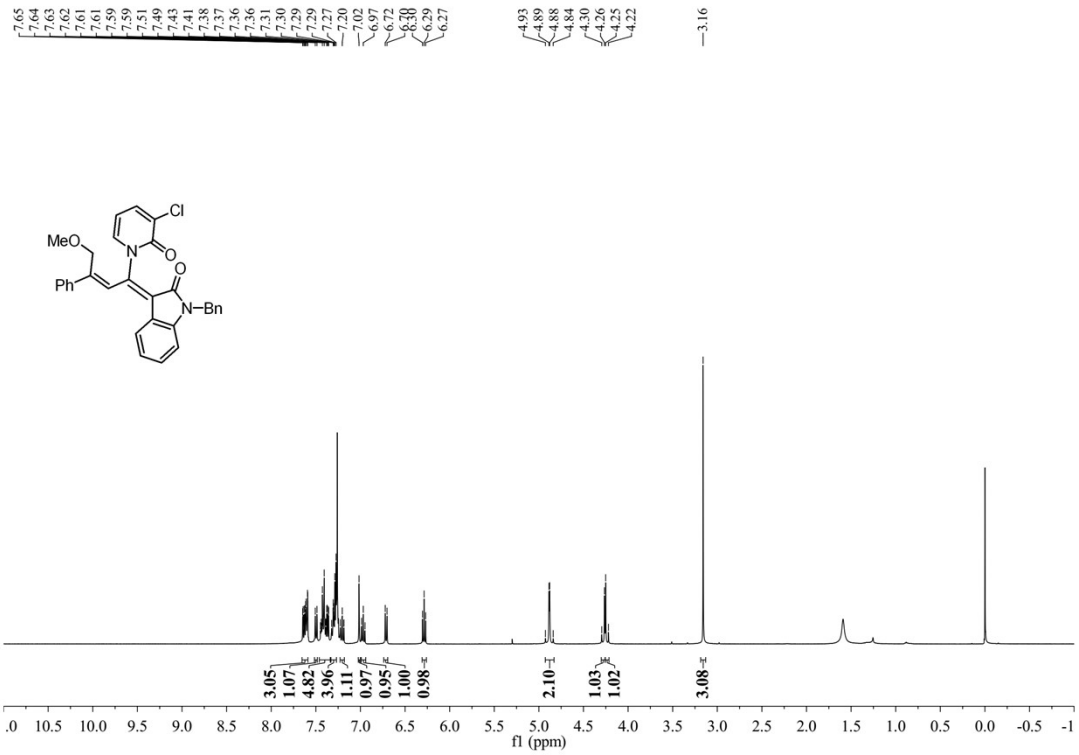


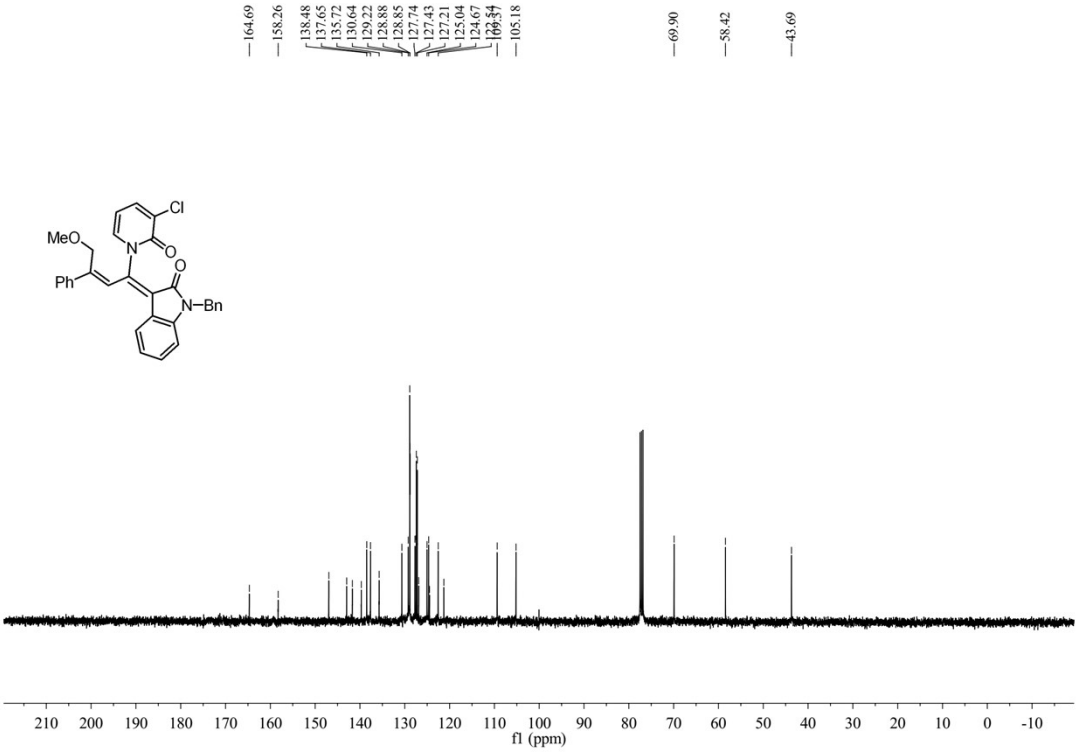




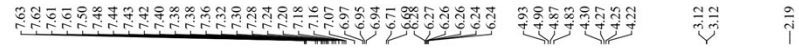


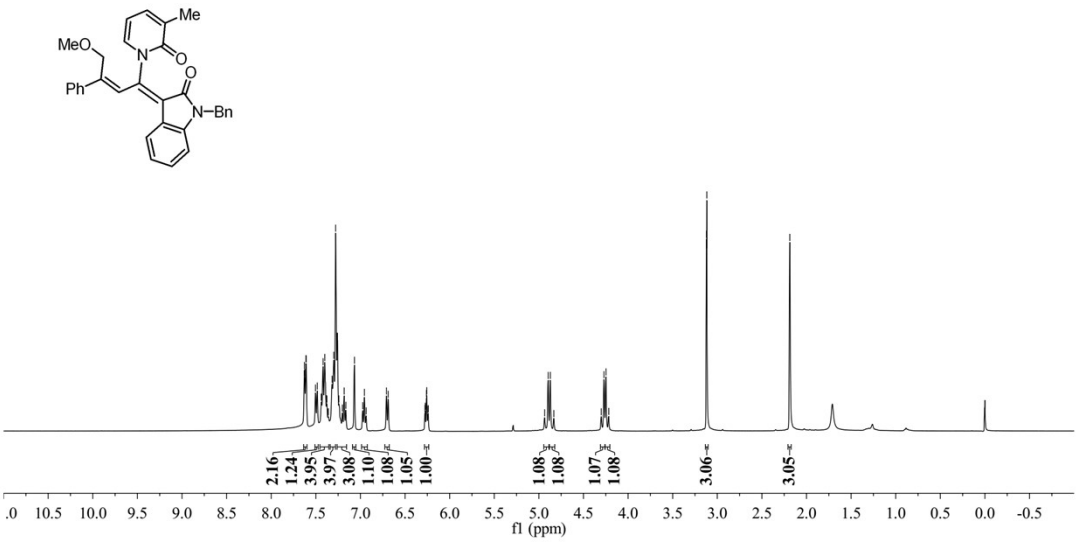
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ba

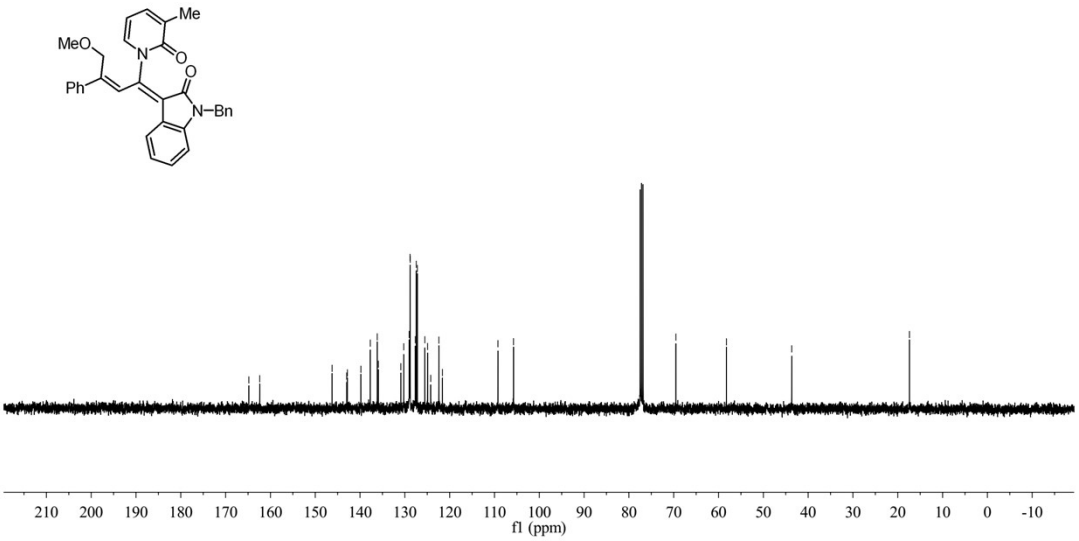




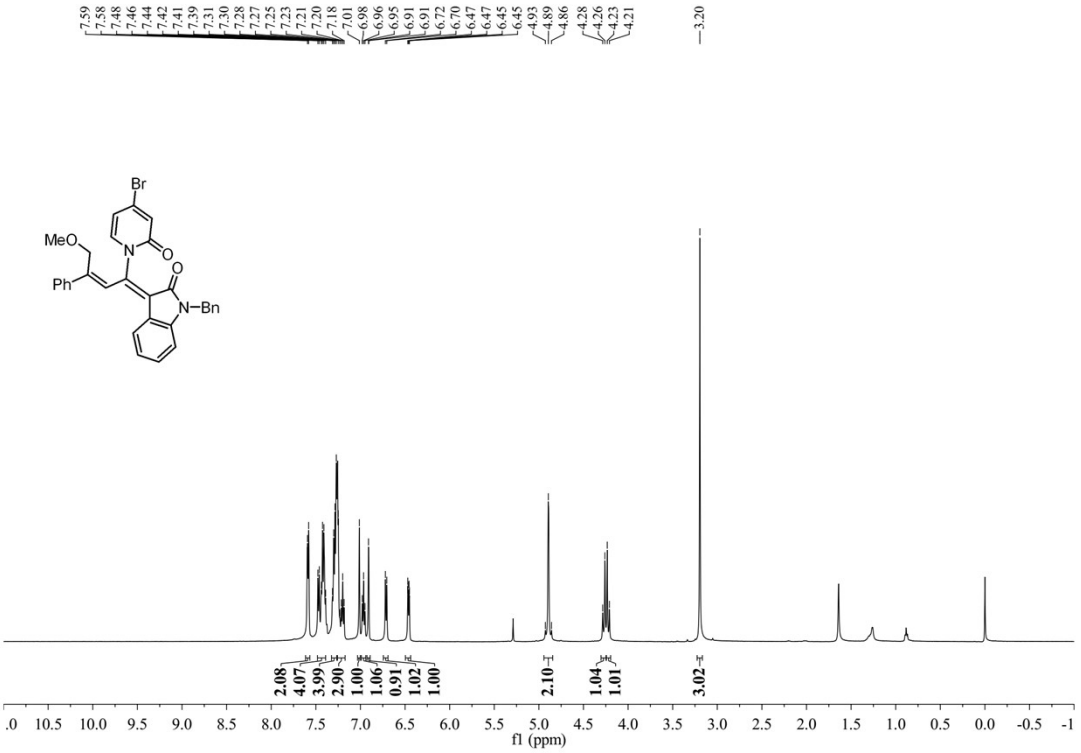
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4bb

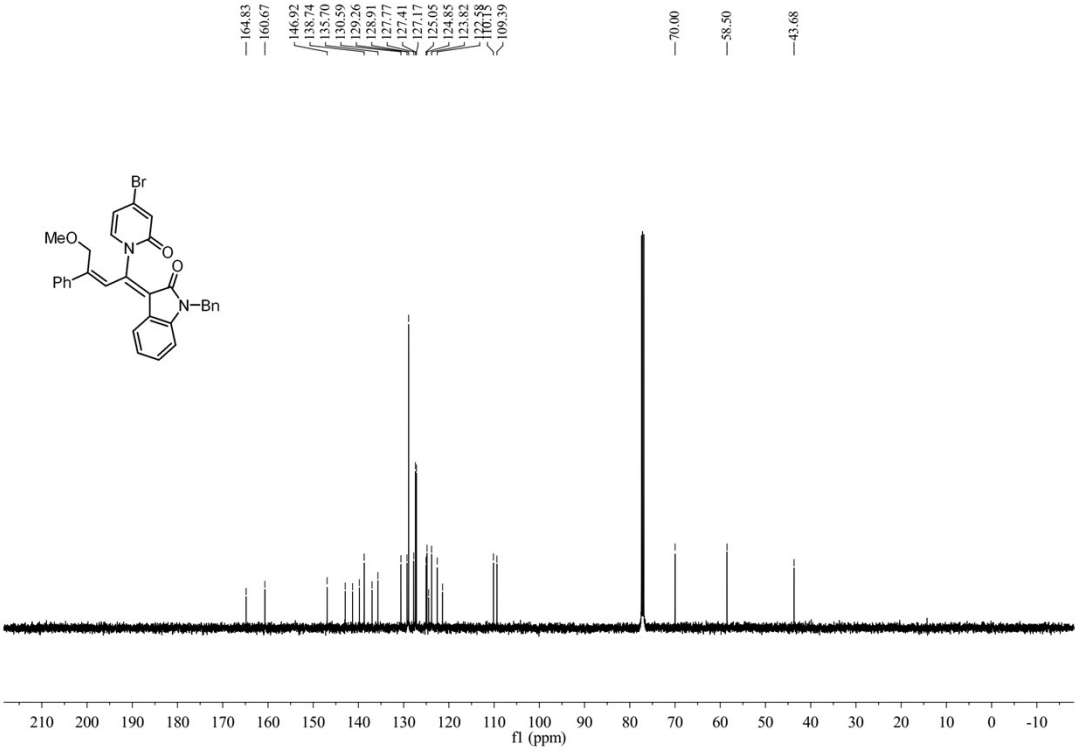




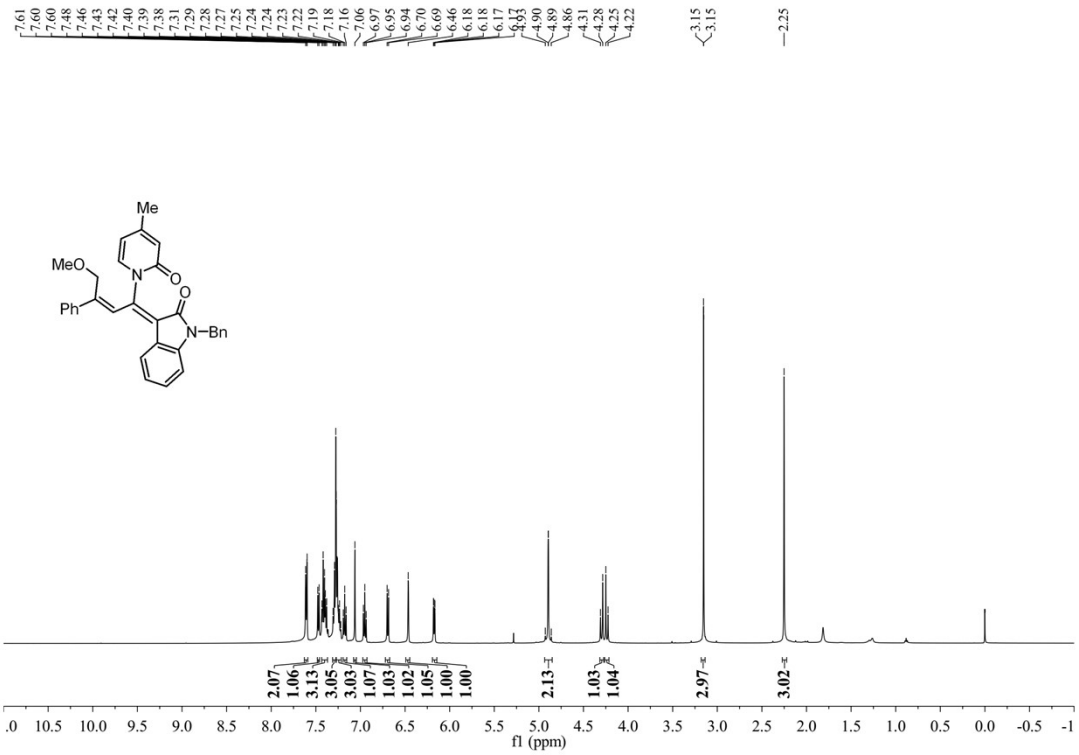


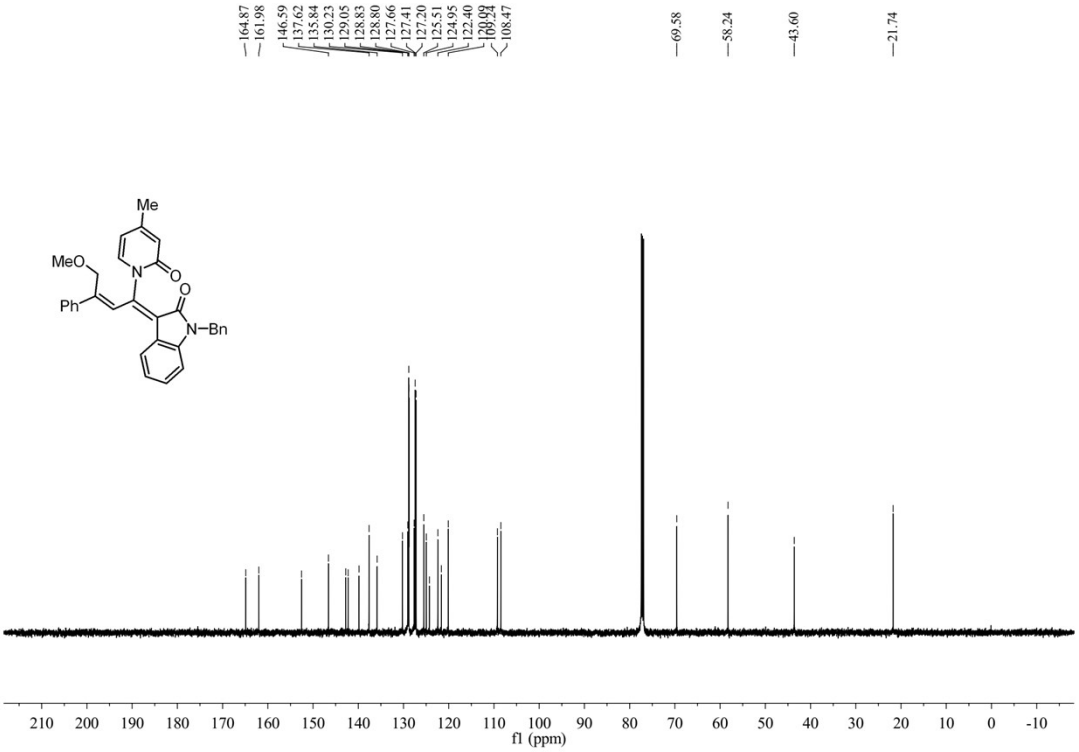
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bc



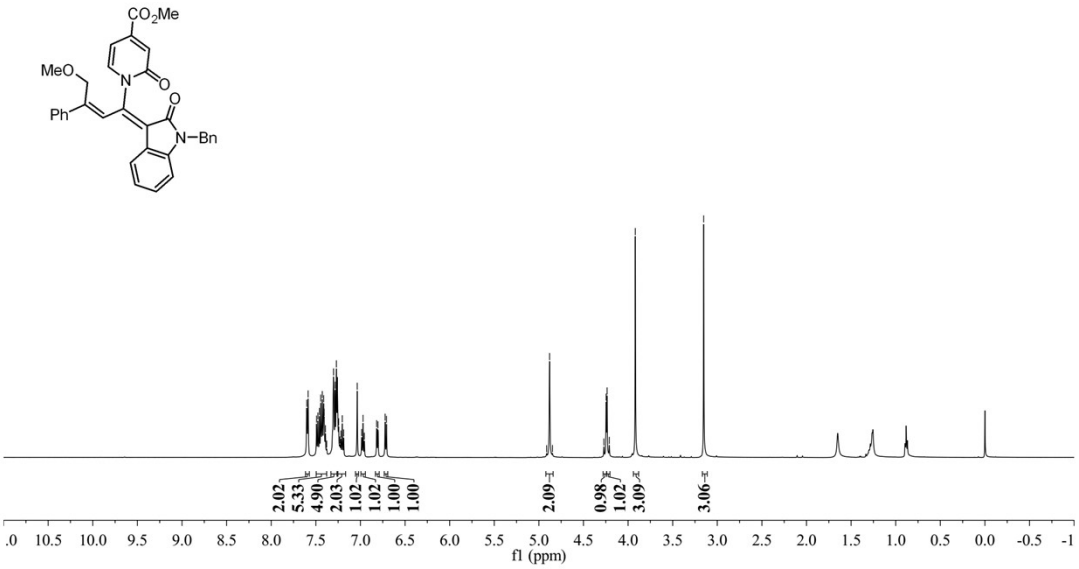


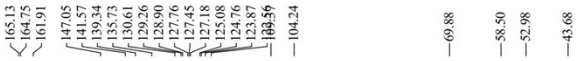
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bd

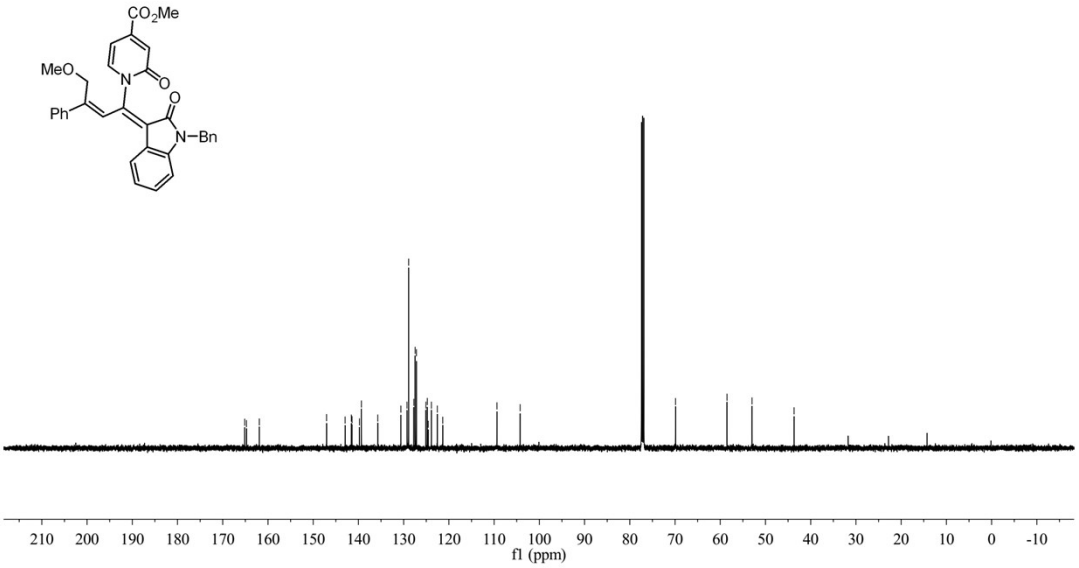




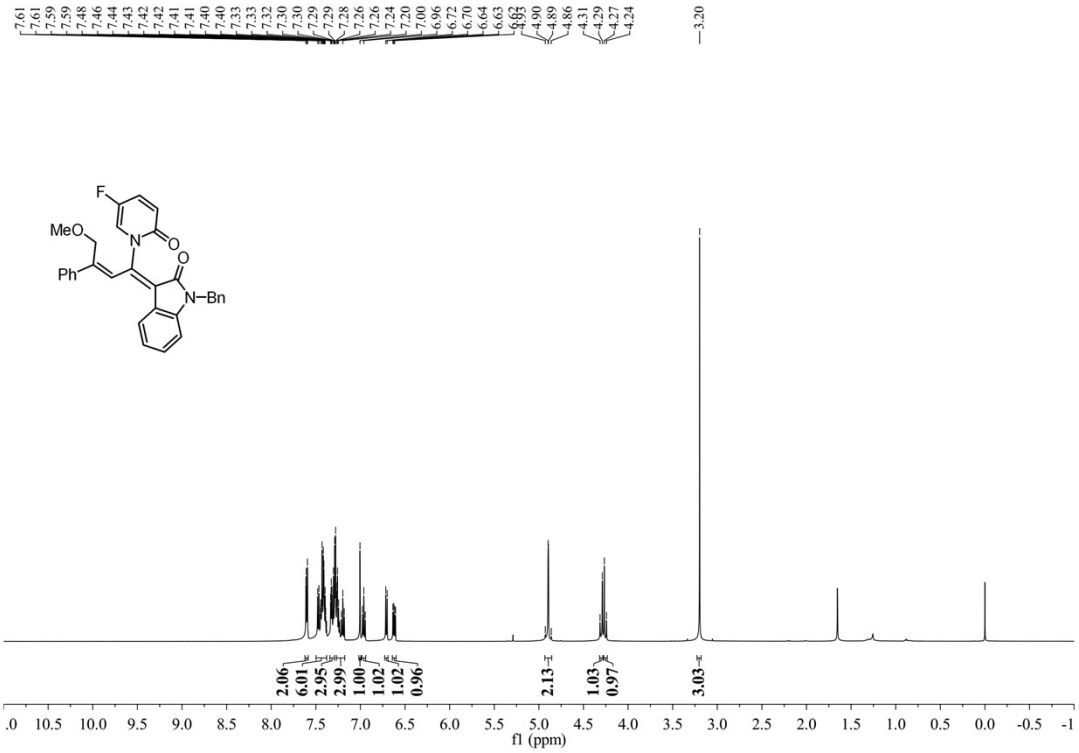
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4be

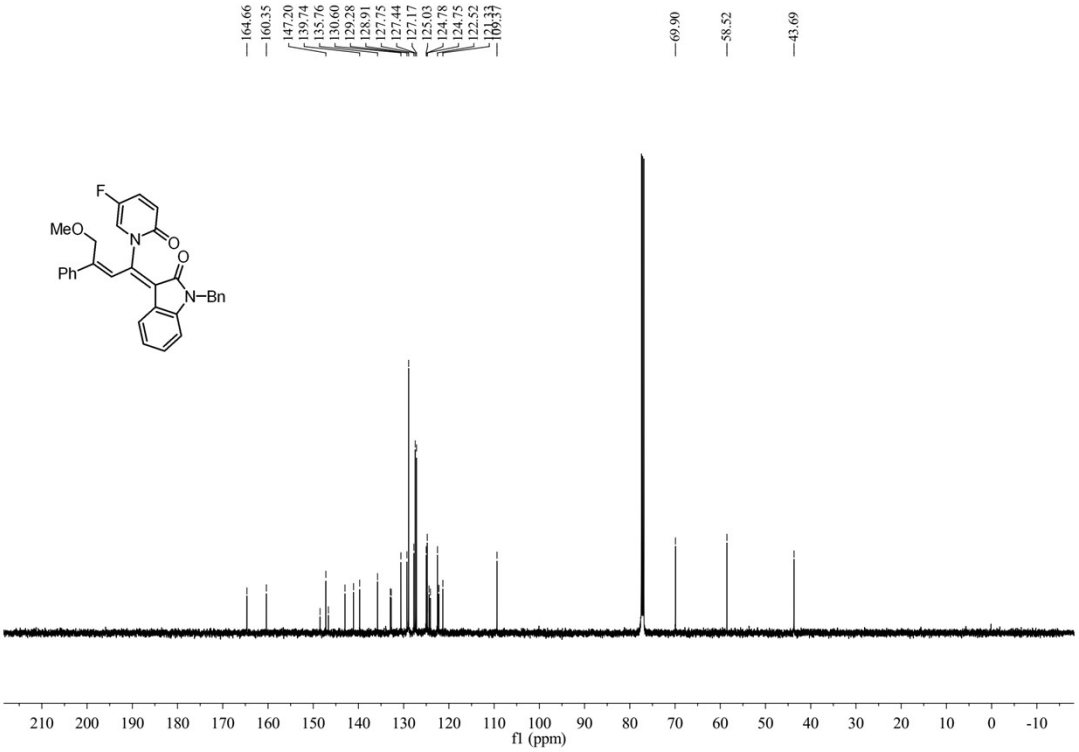




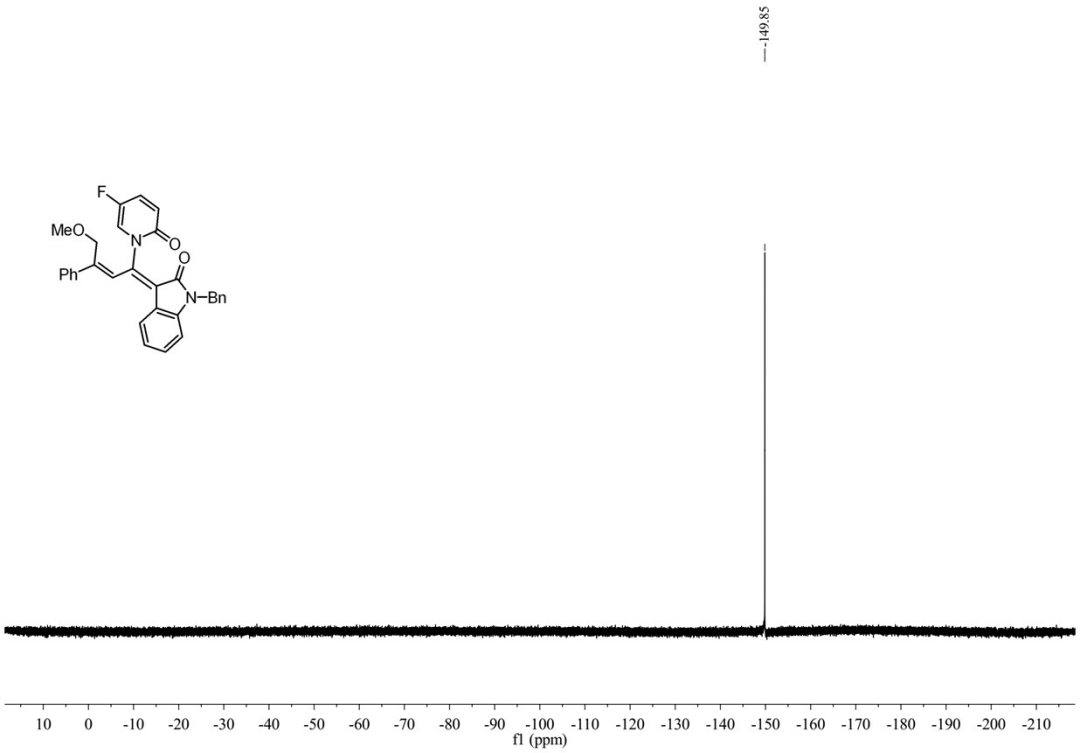


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bf

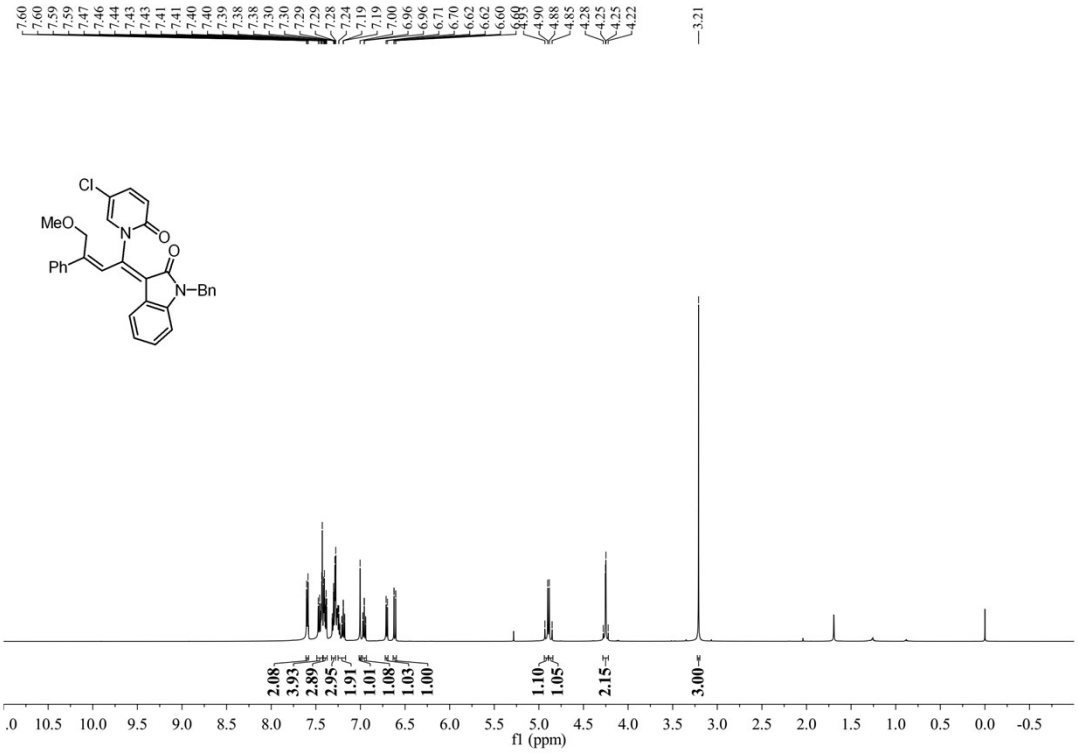


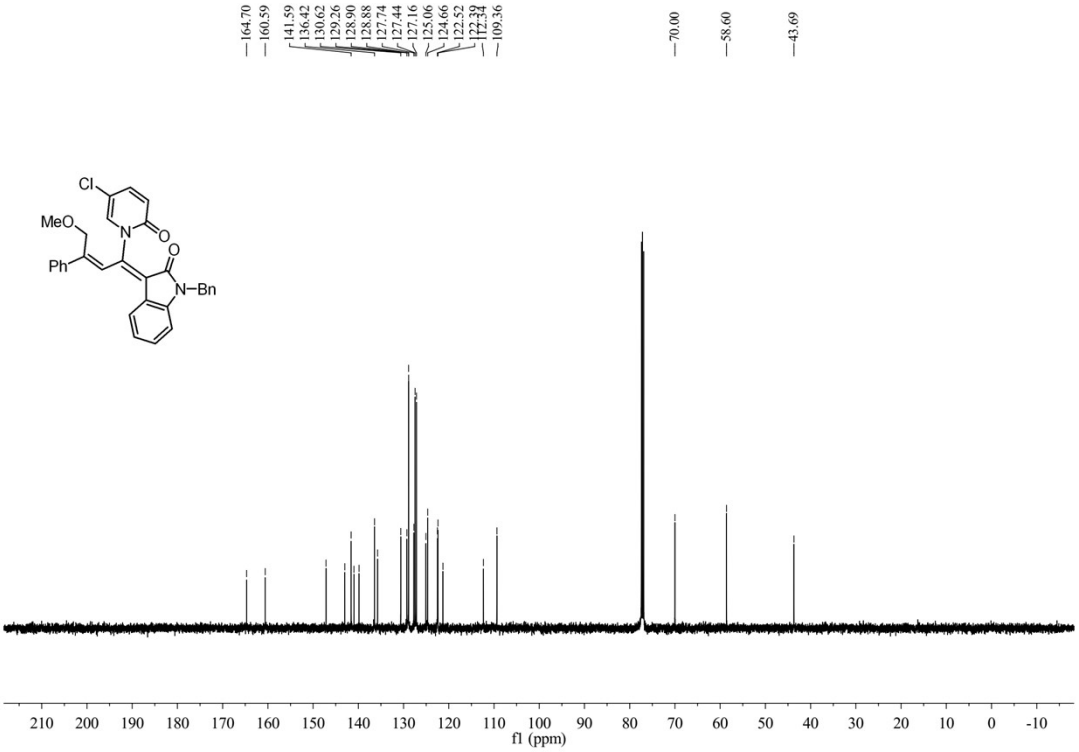


^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4bf

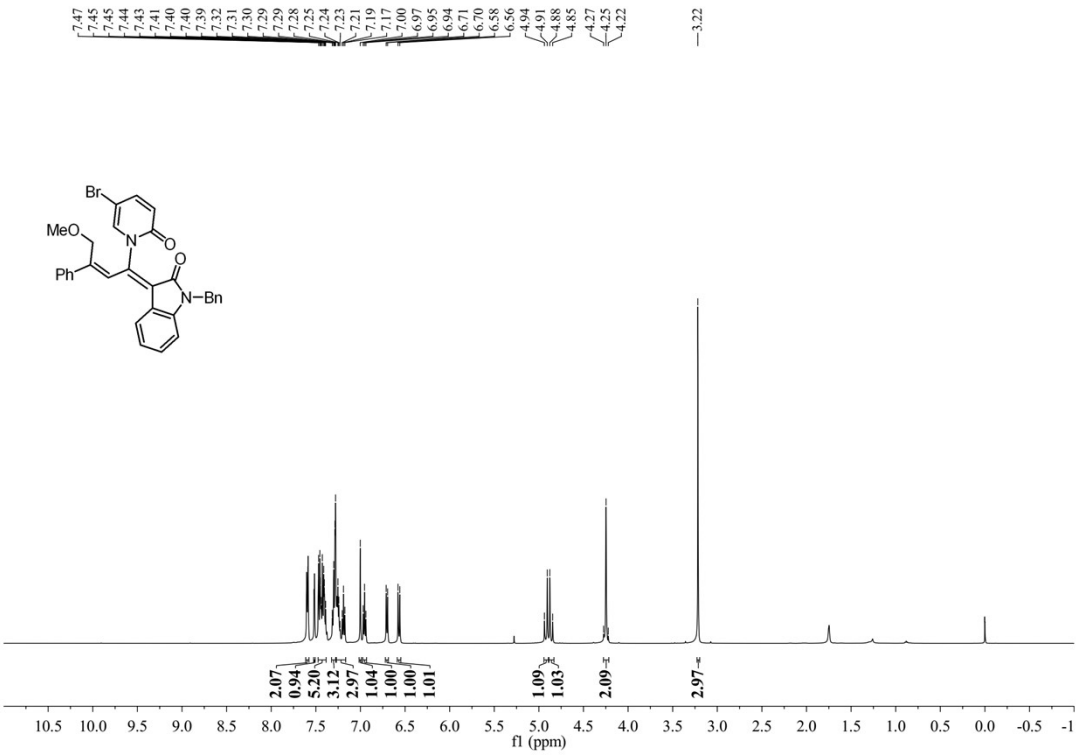


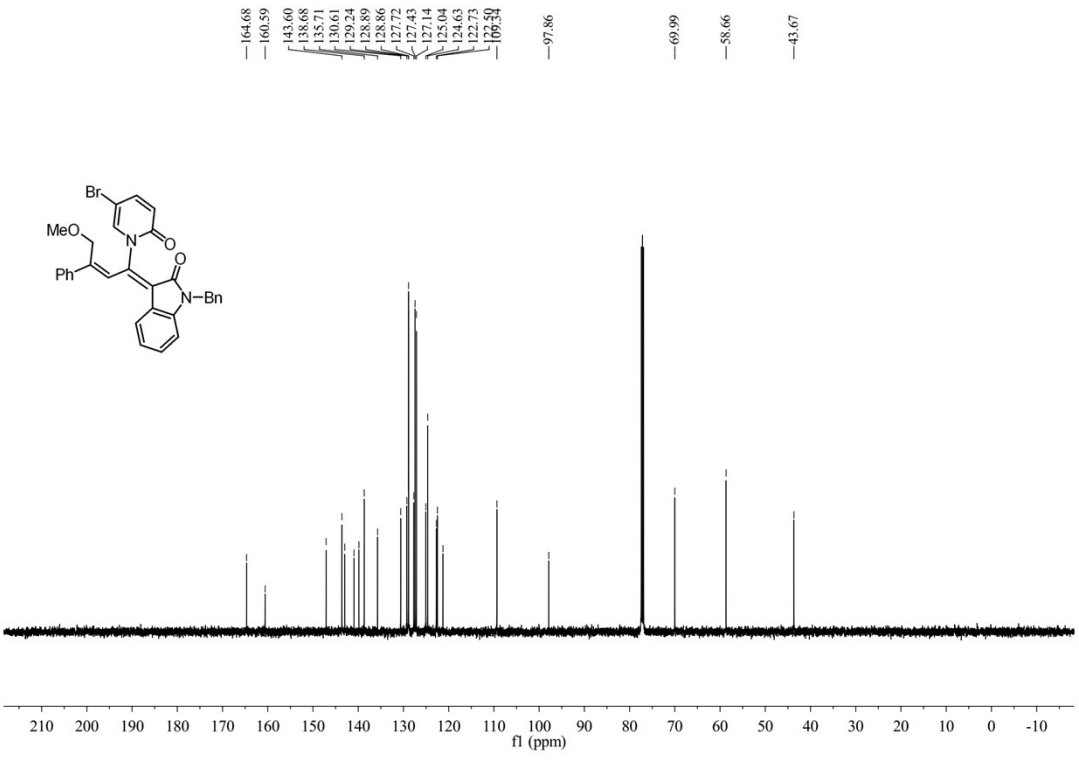
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bg



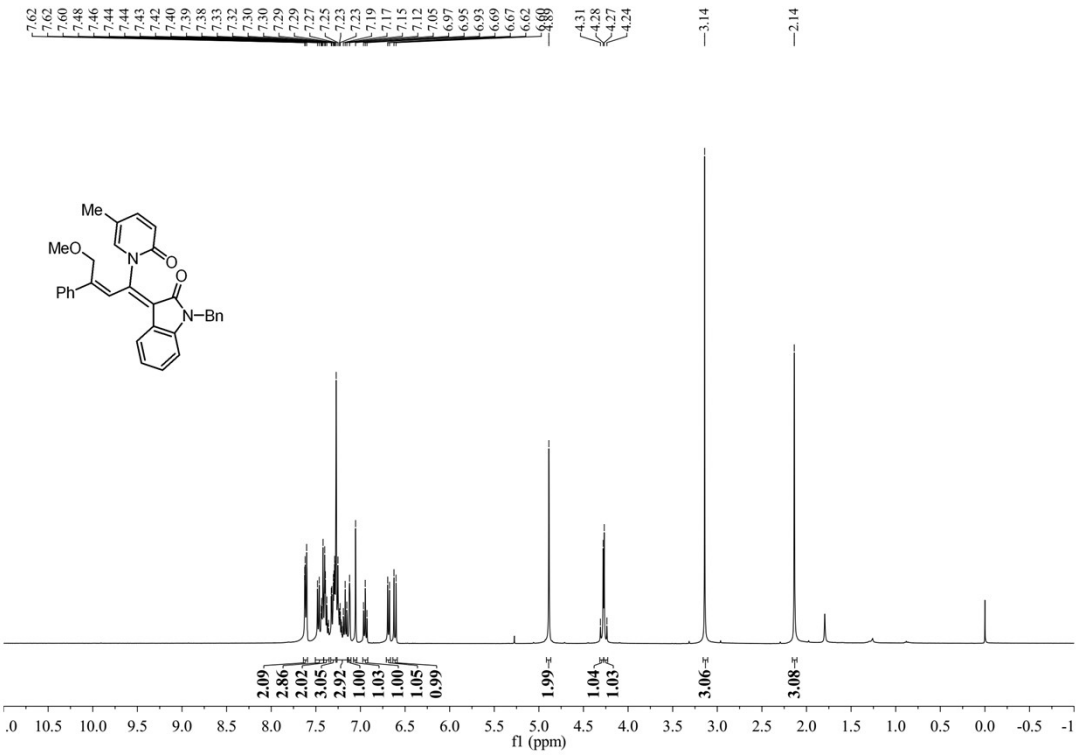


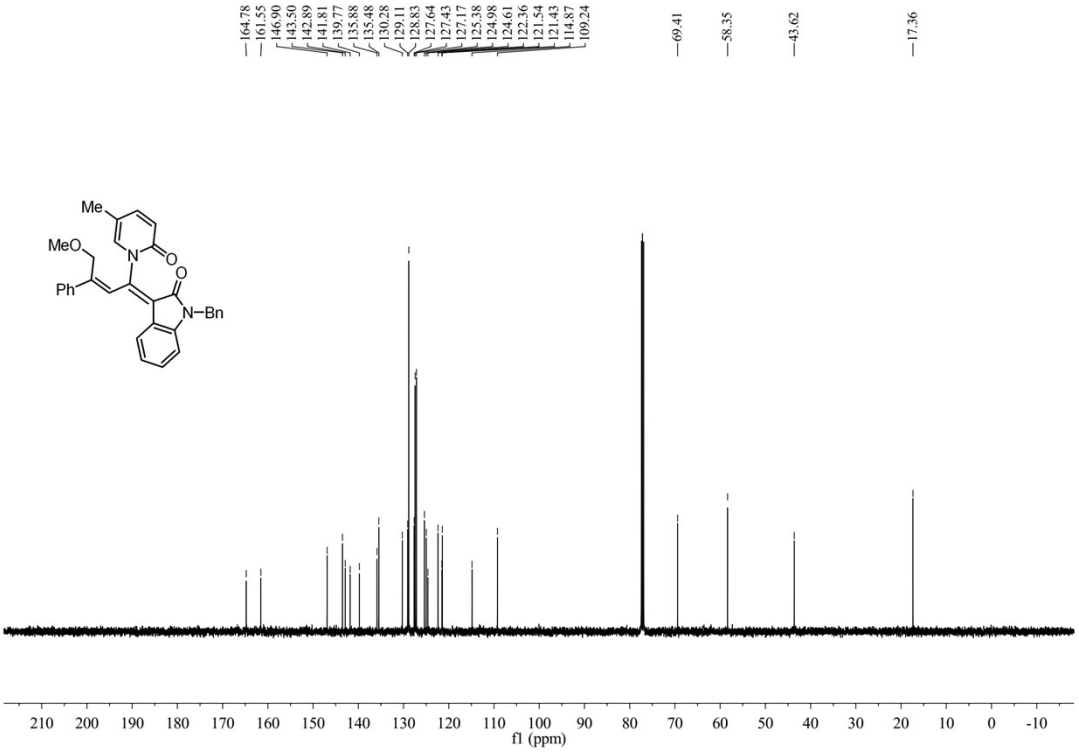
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bh



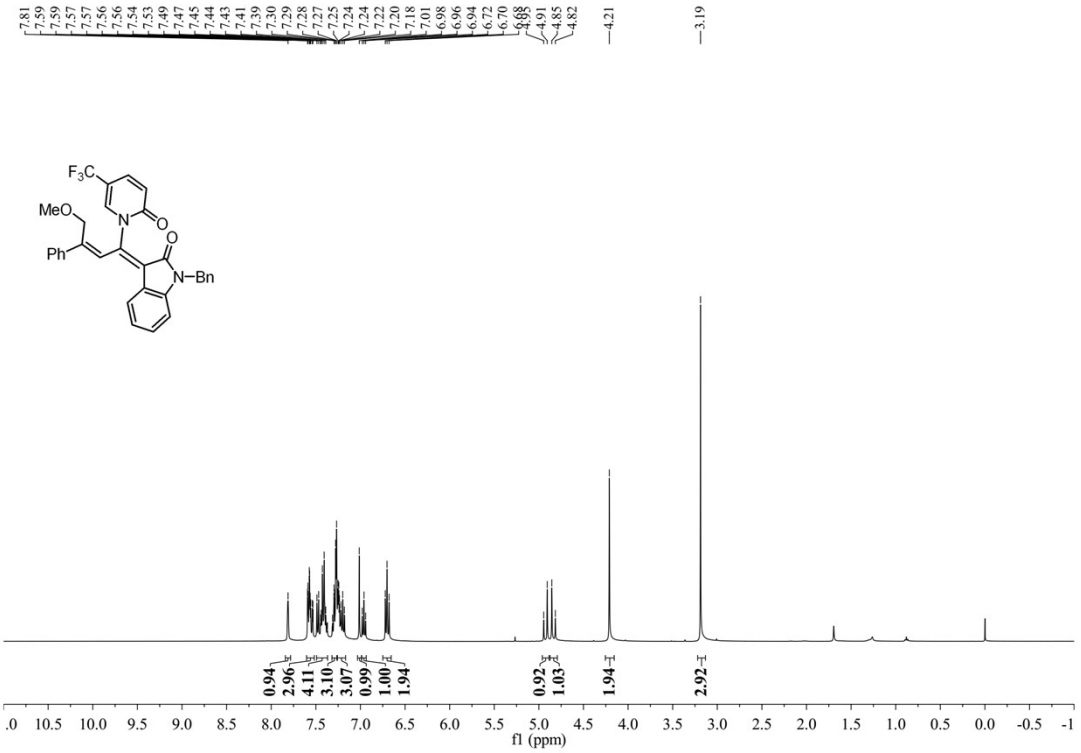


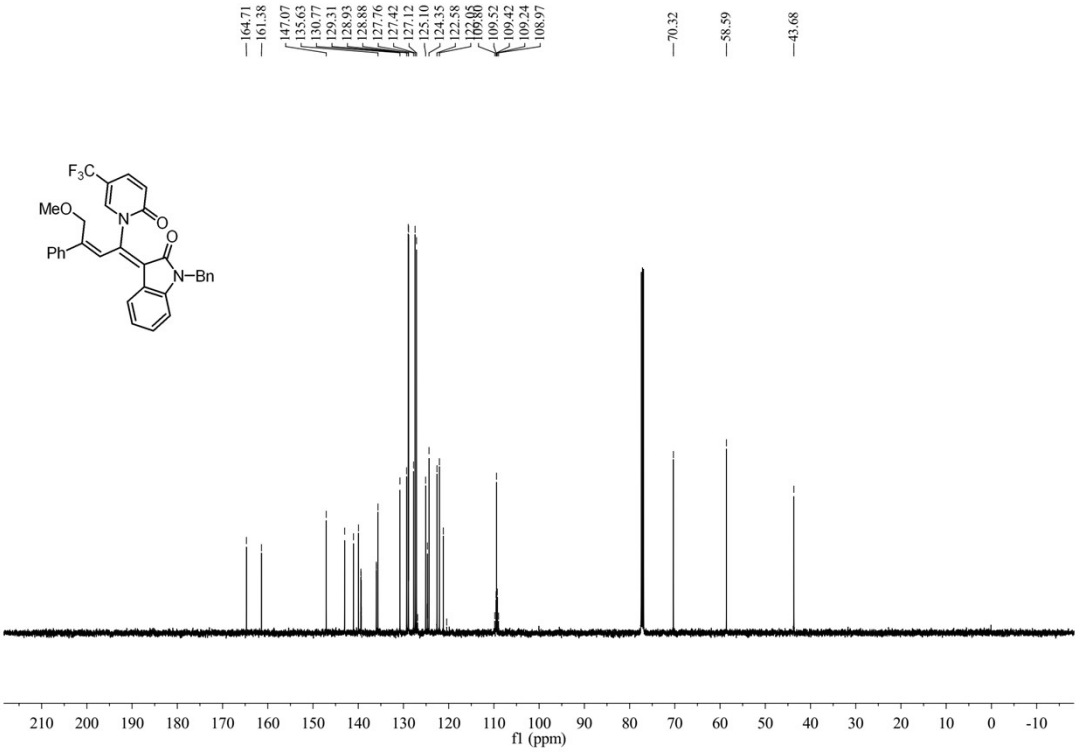
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bi



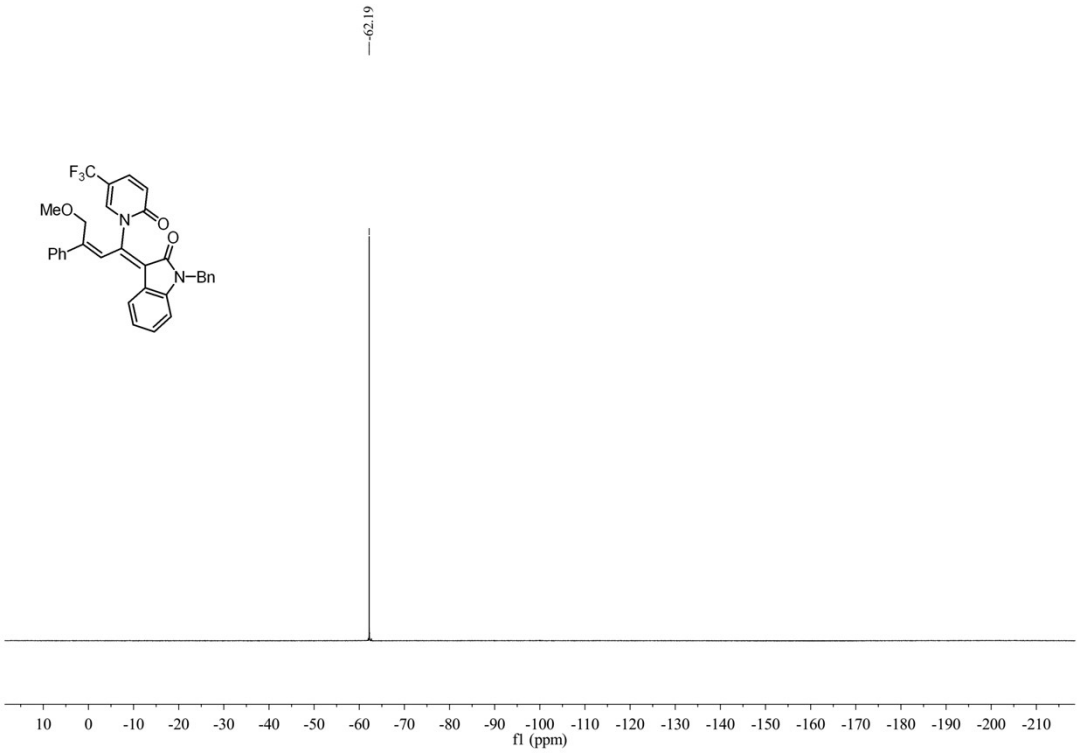


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4bj

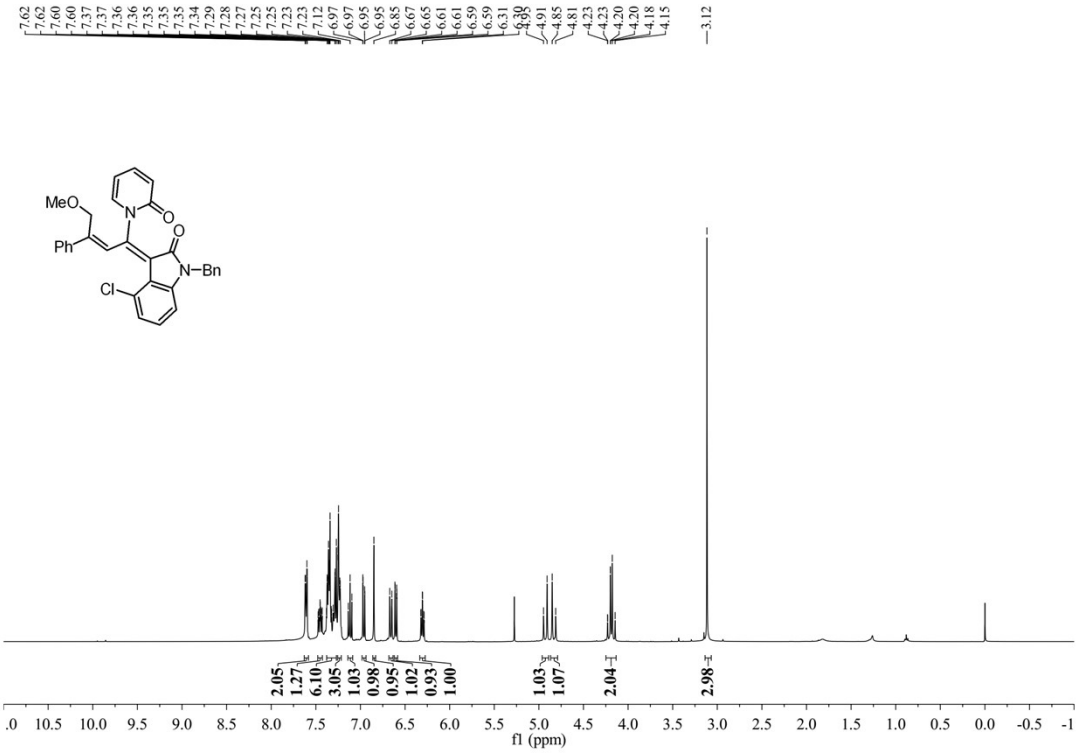


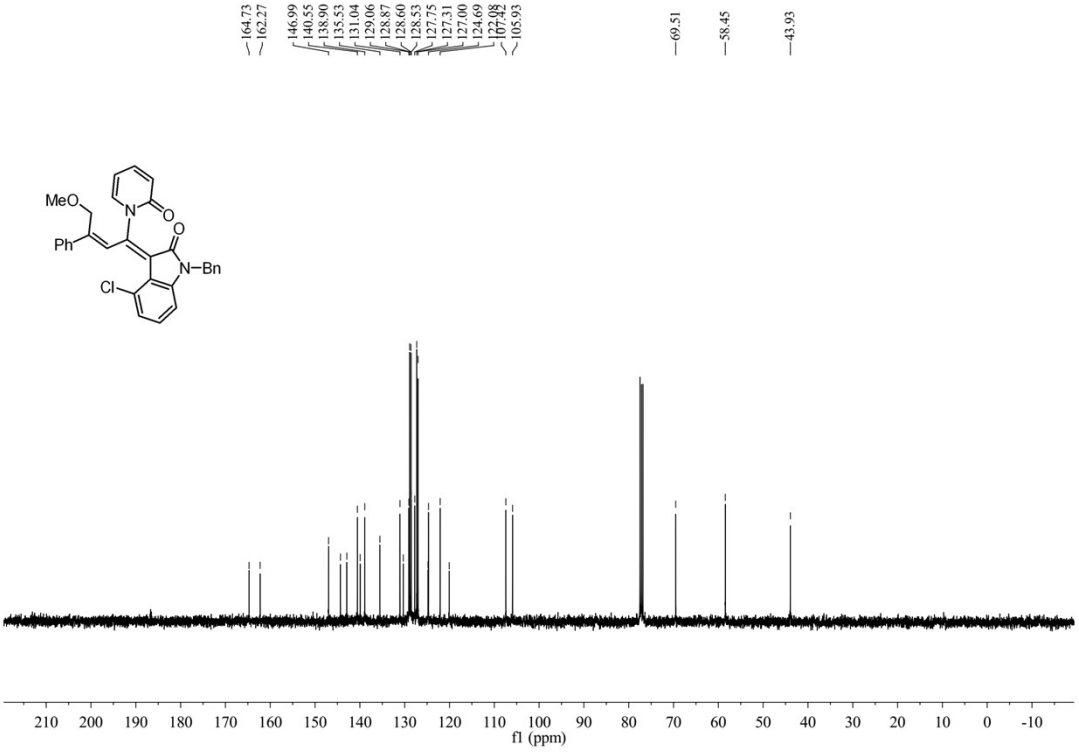


^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4bj

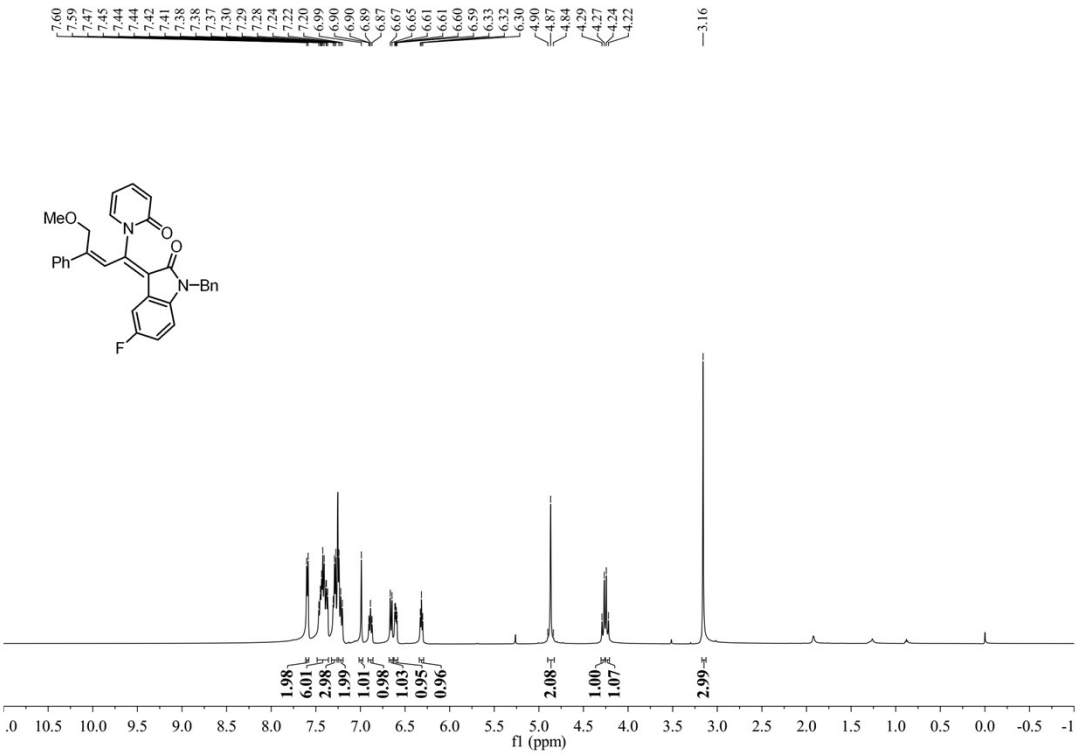


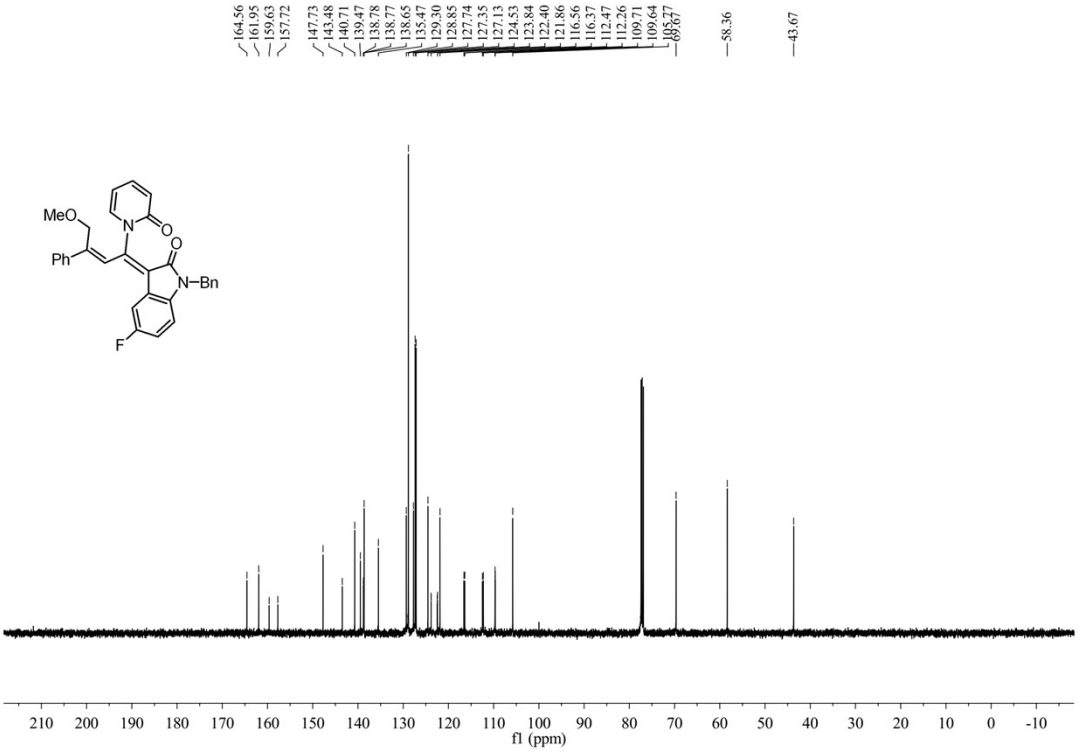
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ca



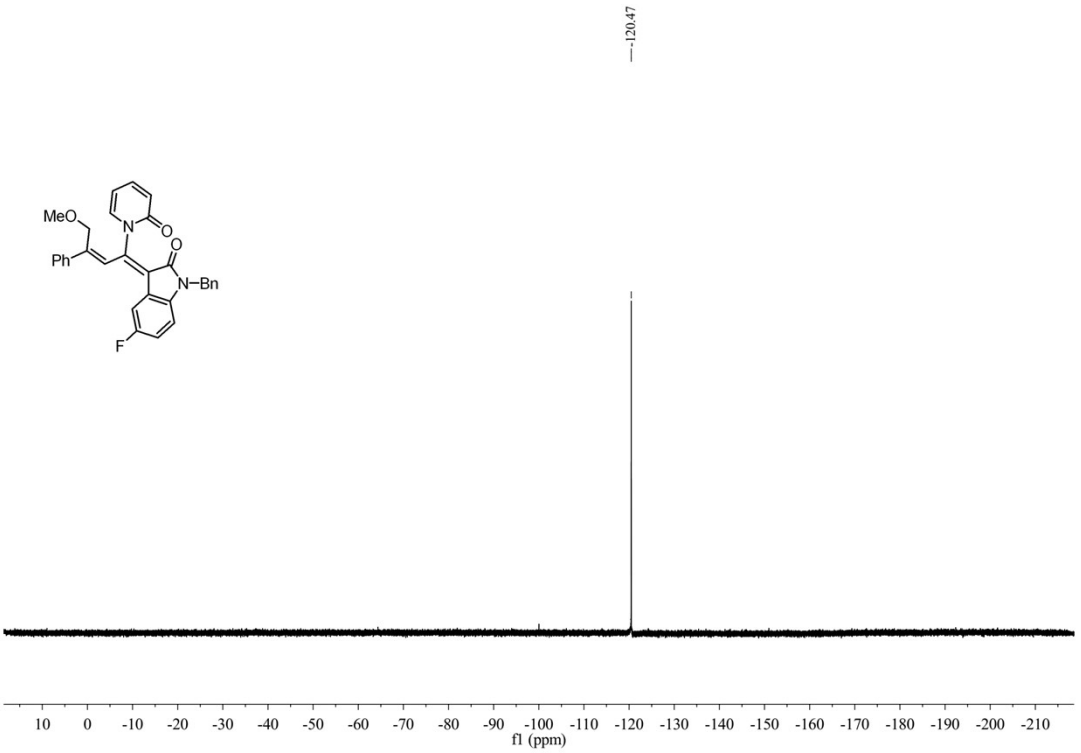


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cb

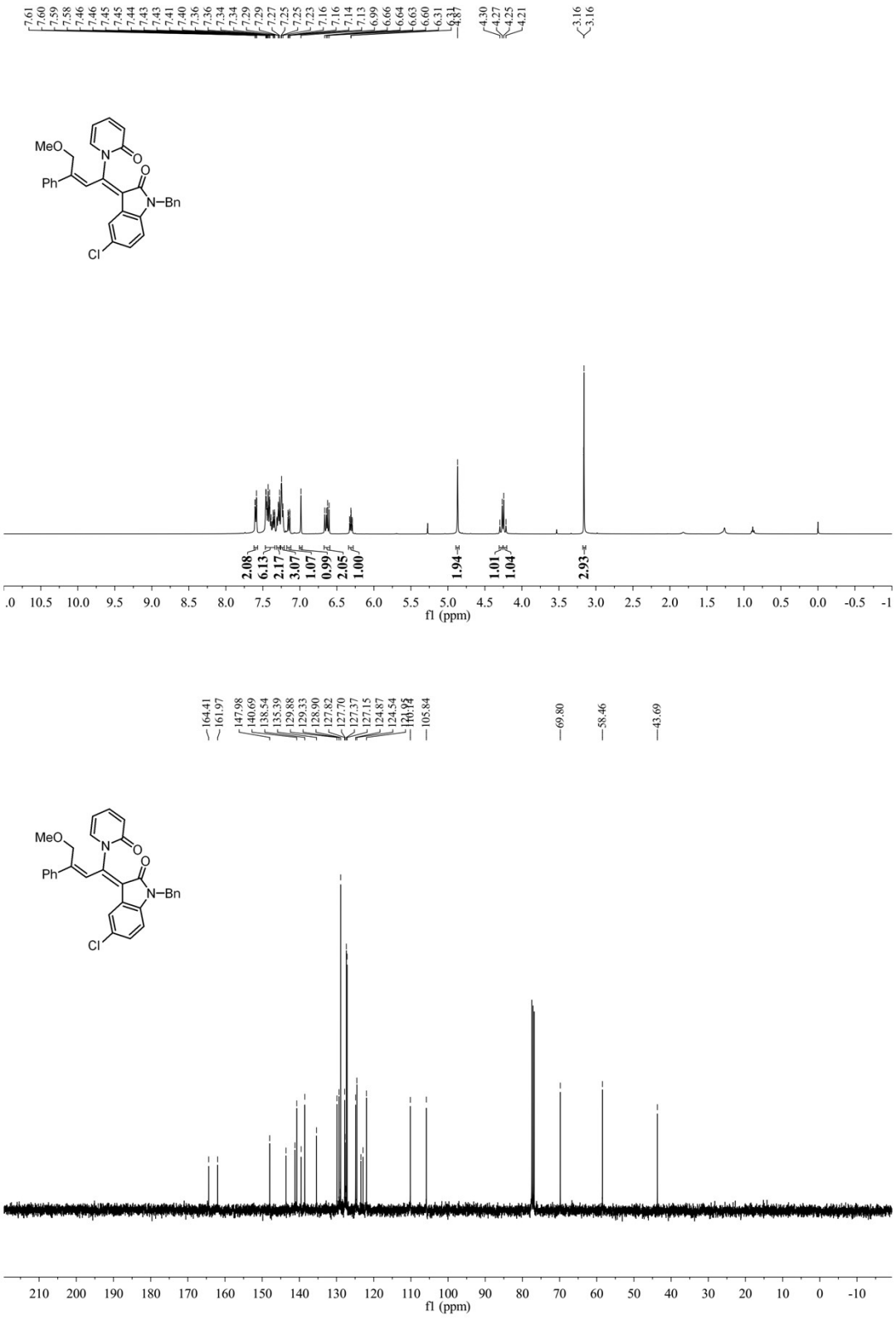




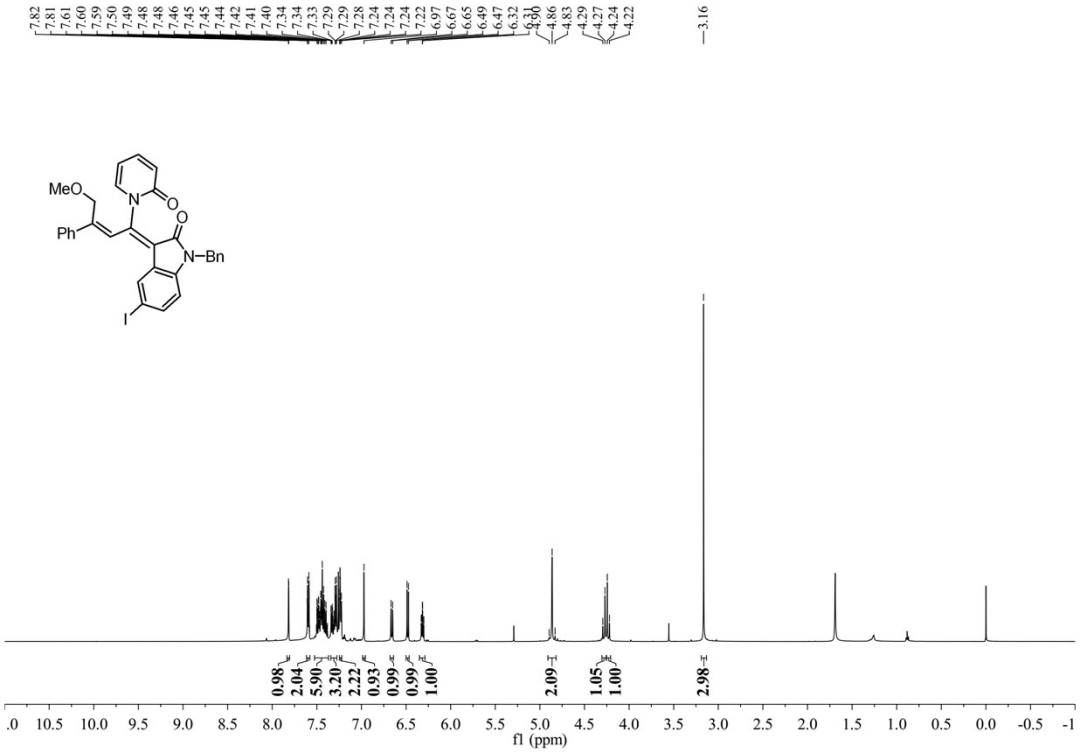
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4cb

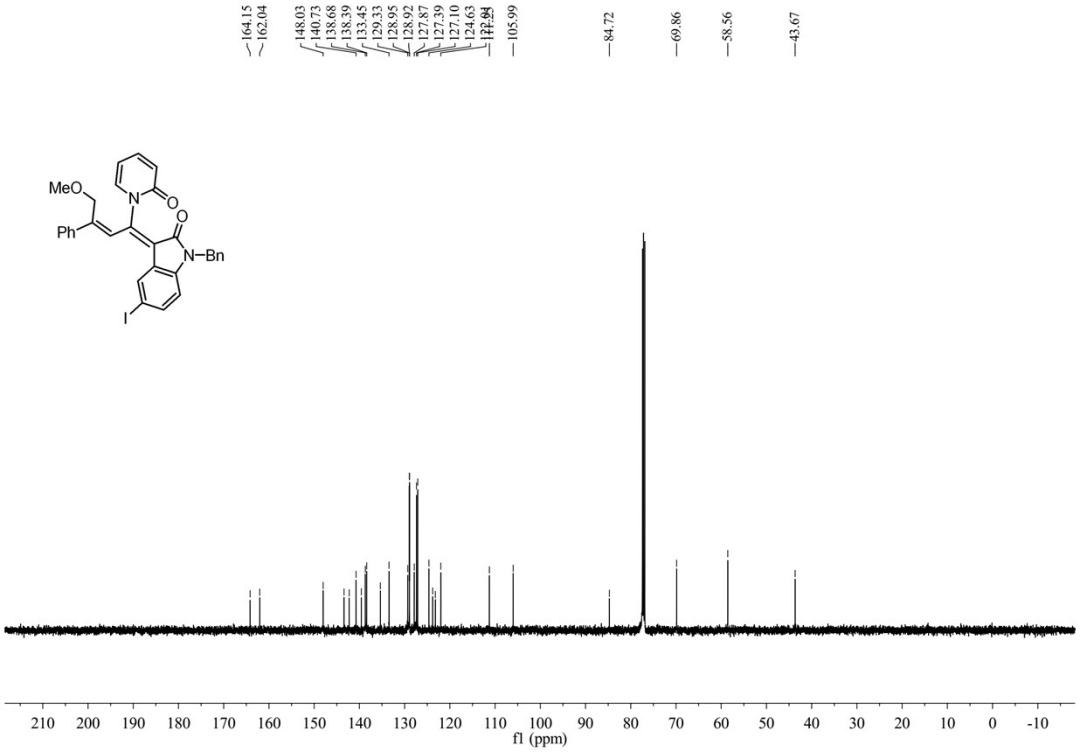


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4cc

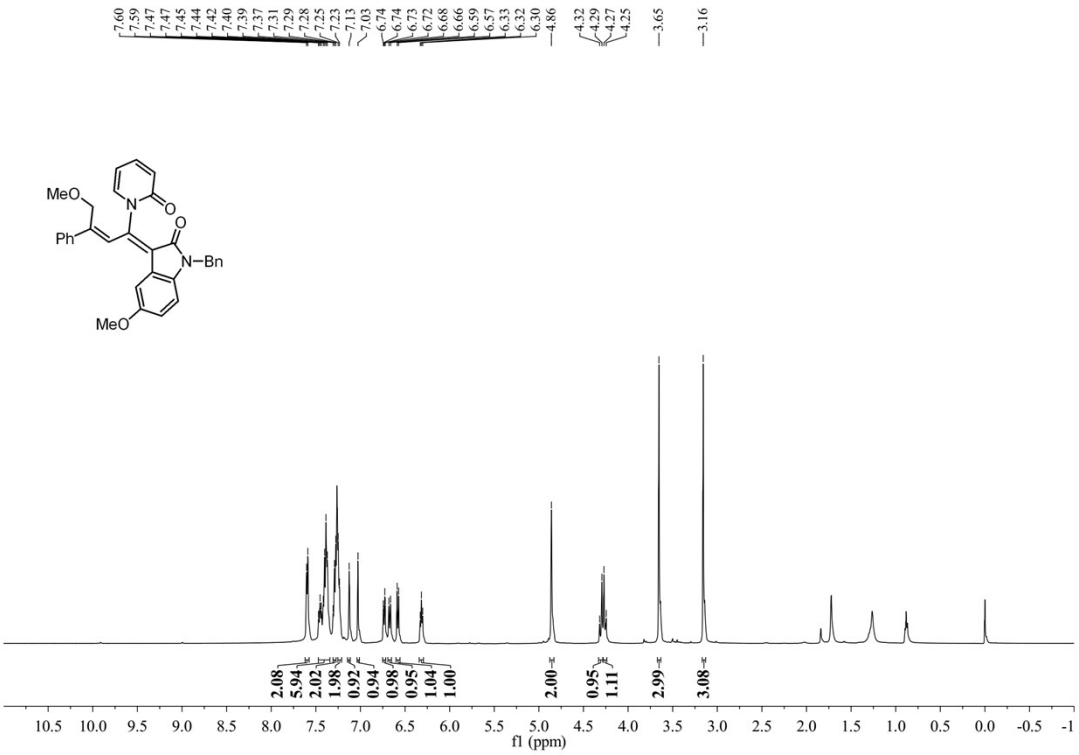


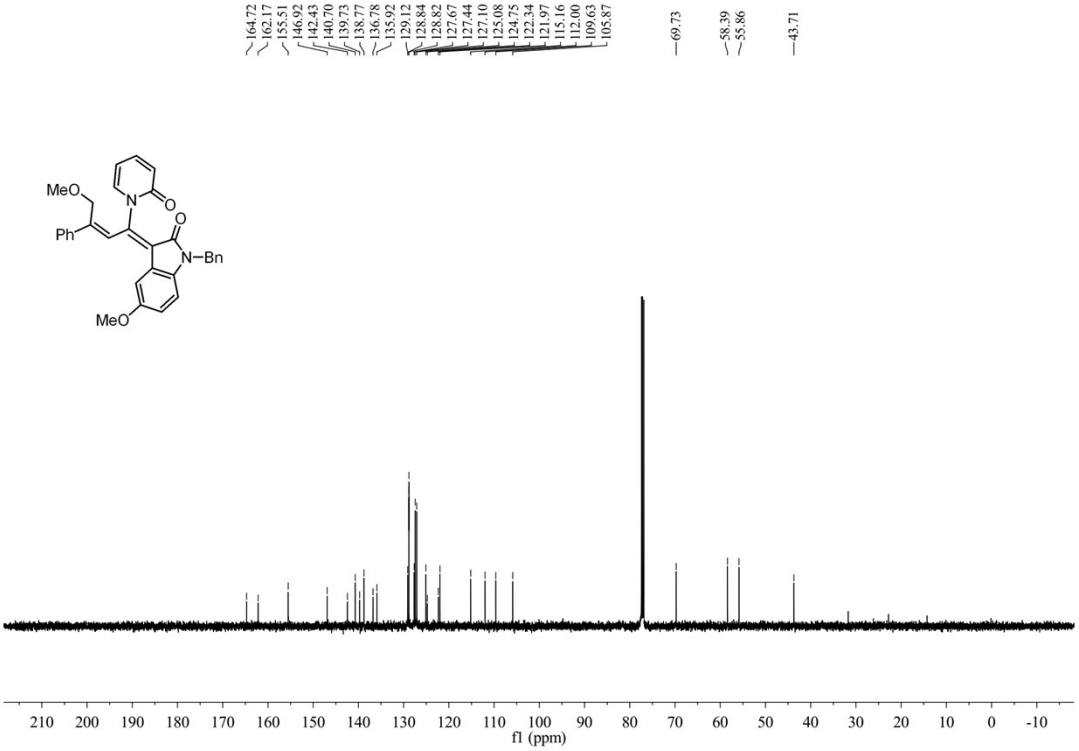
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cd



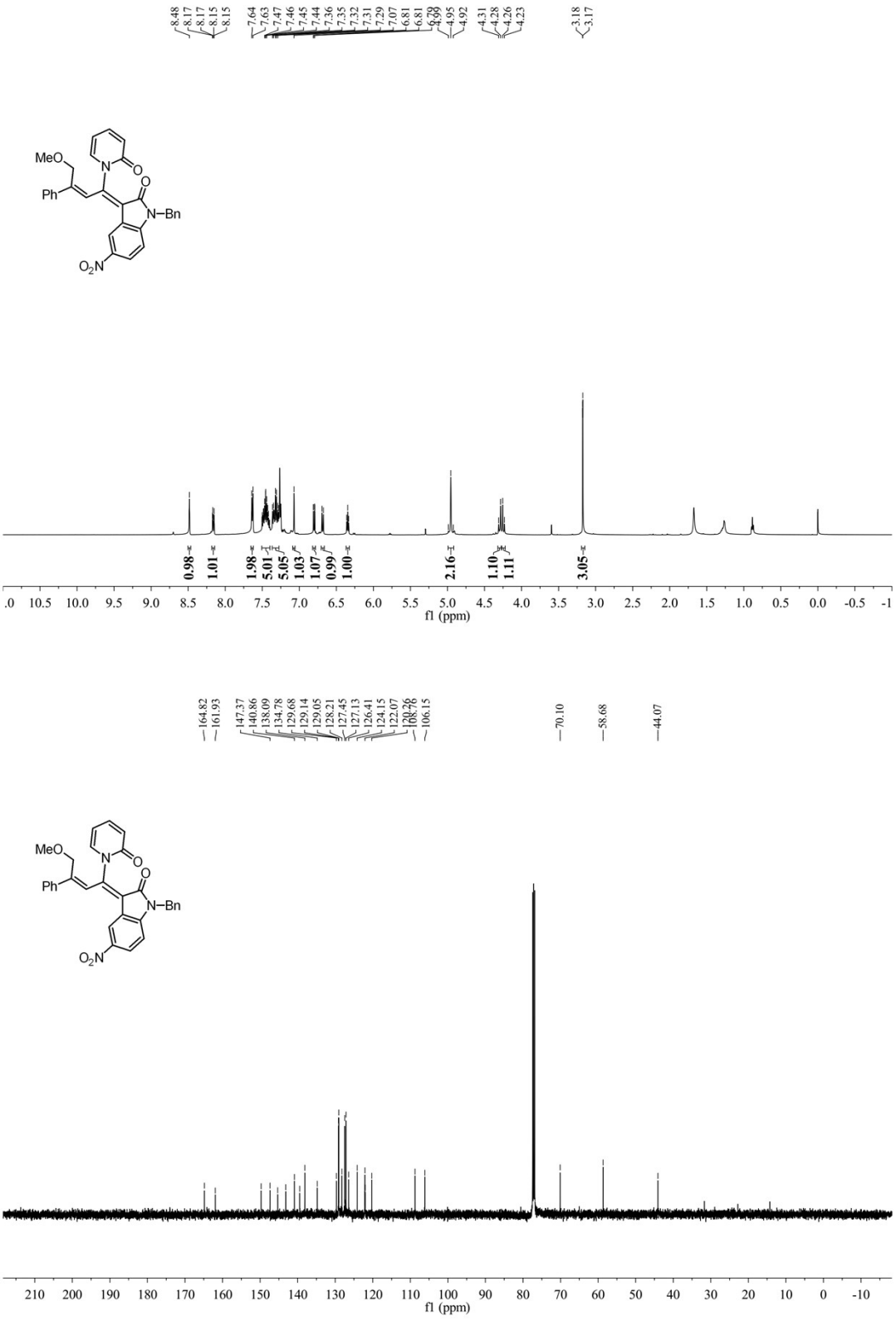


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ce

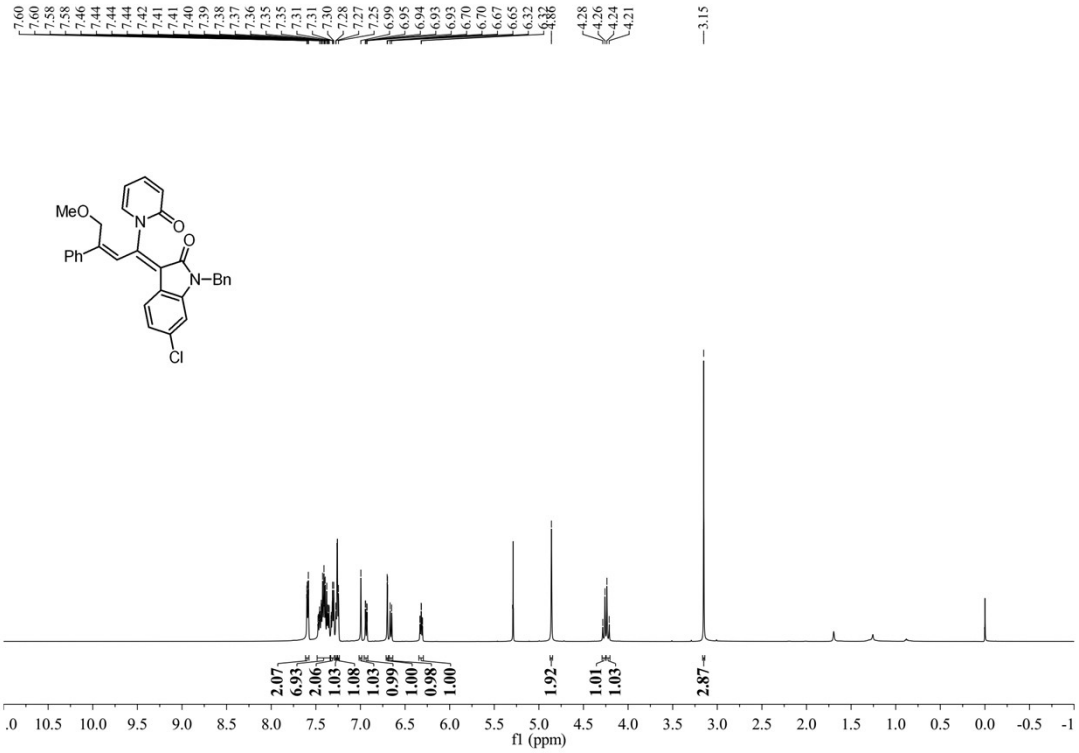


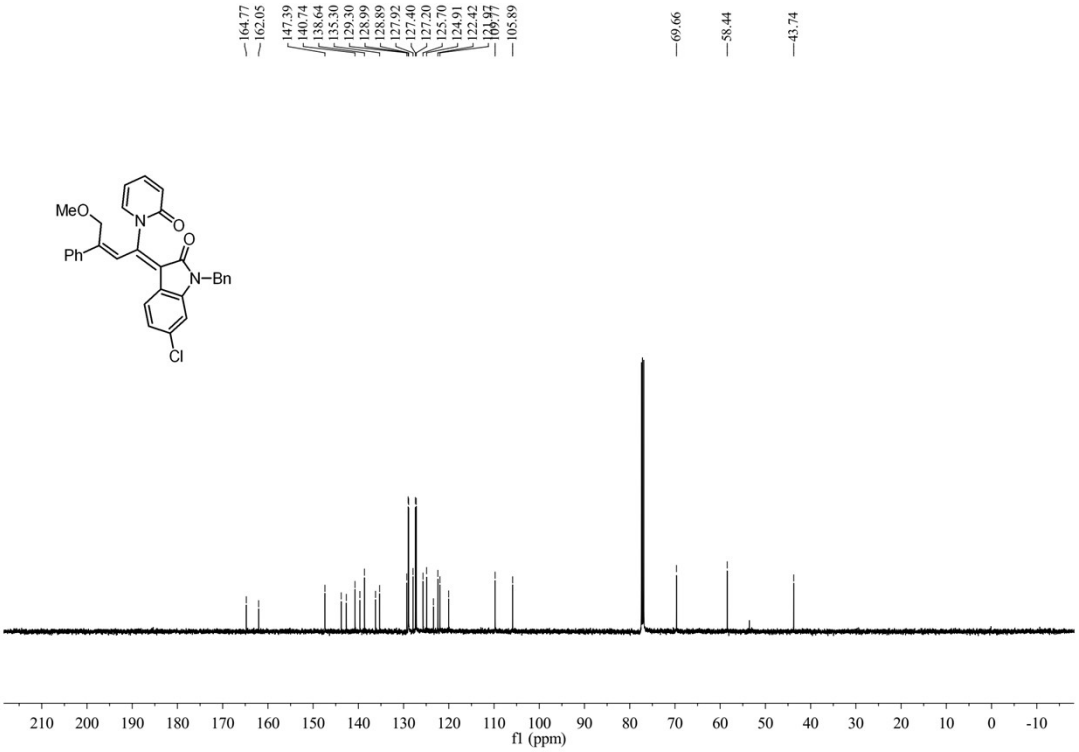


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cf

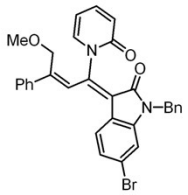


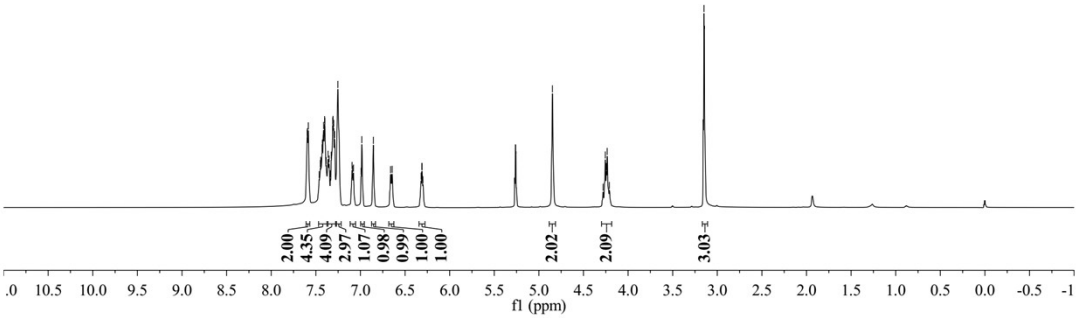
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cg

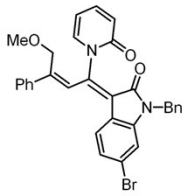


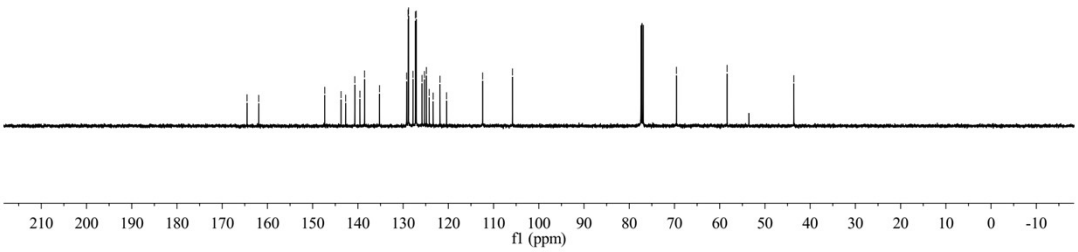


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ch

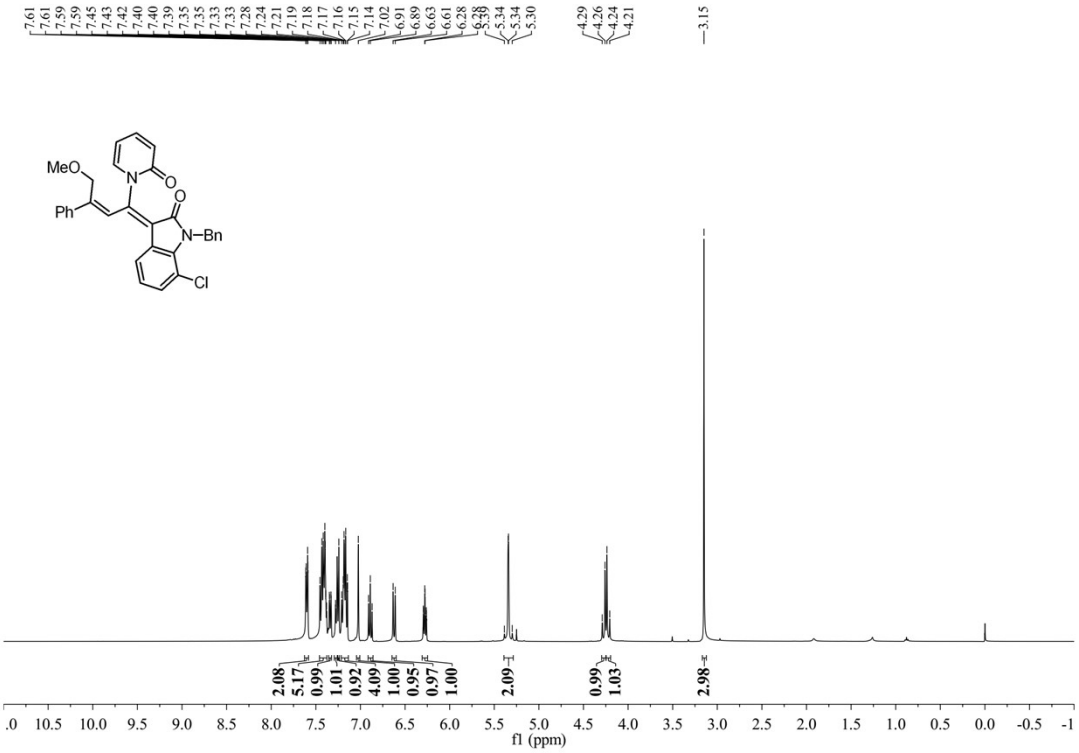


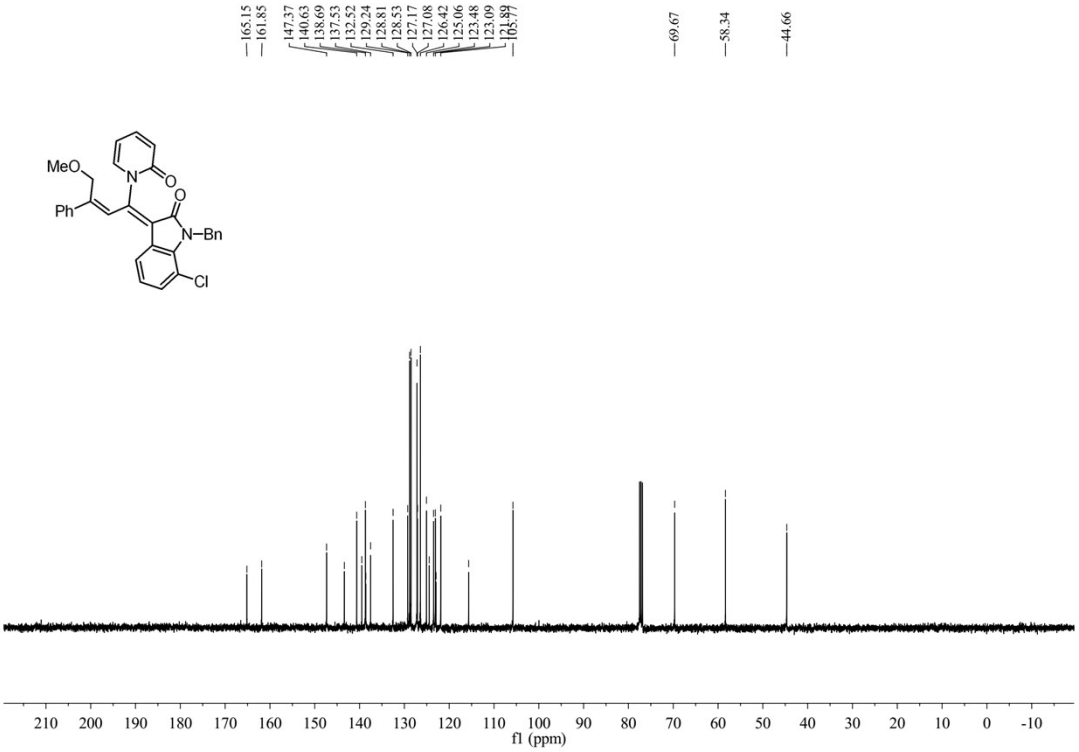




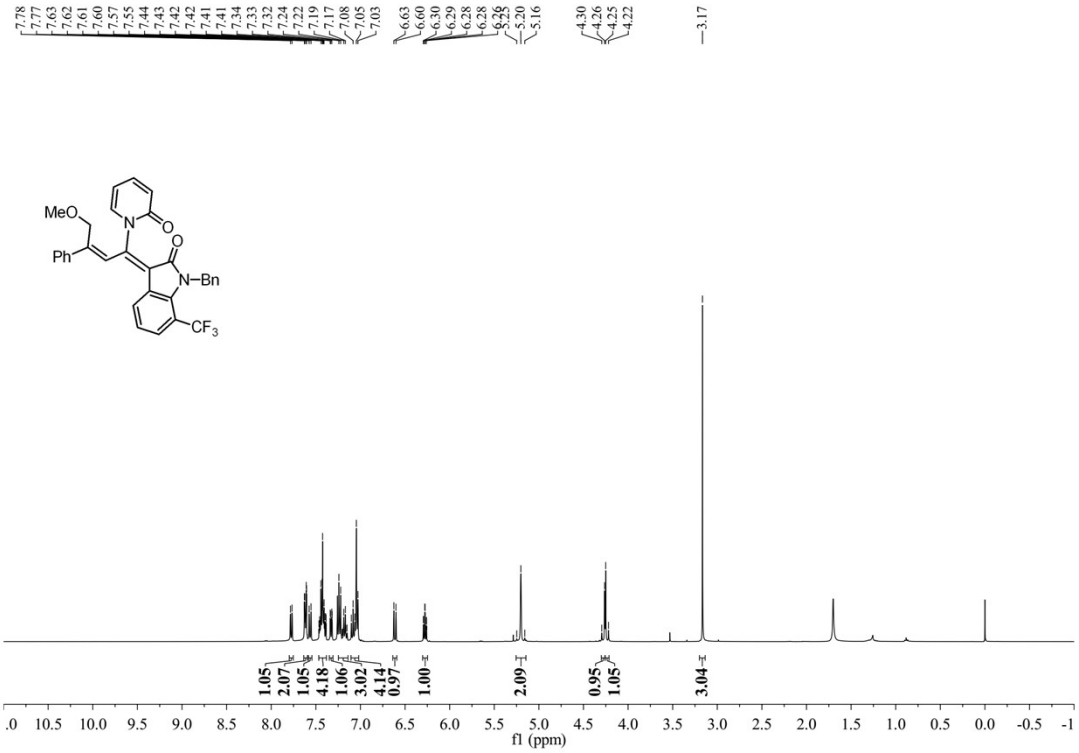


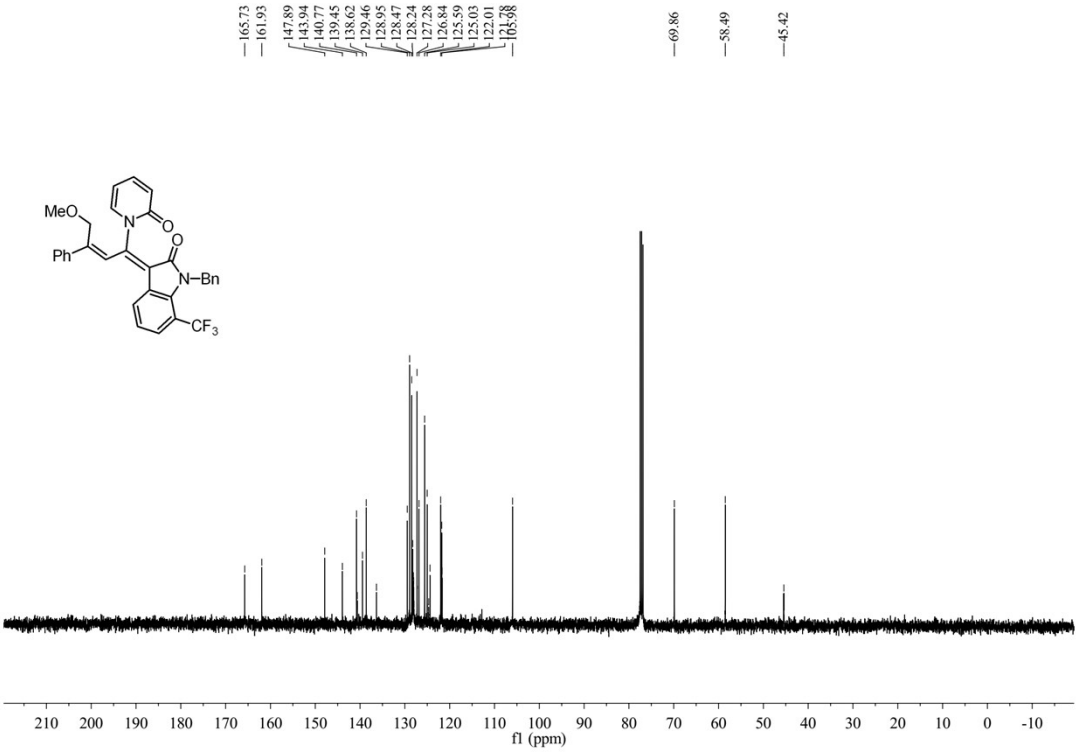
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4ci



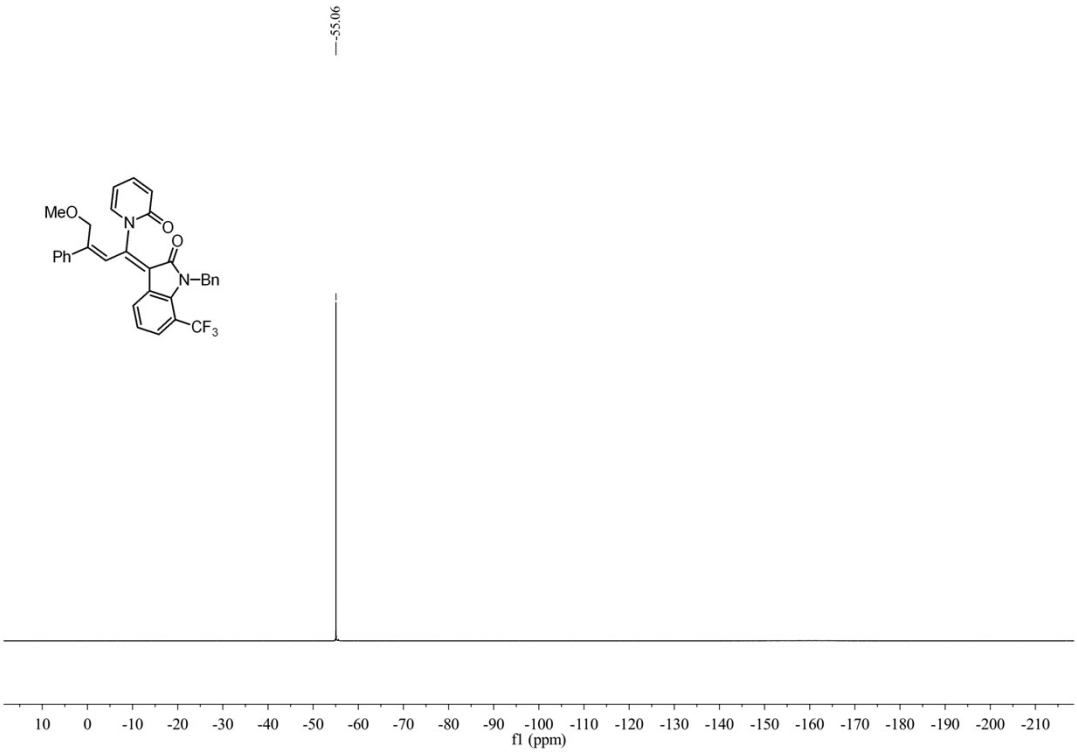


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4cj

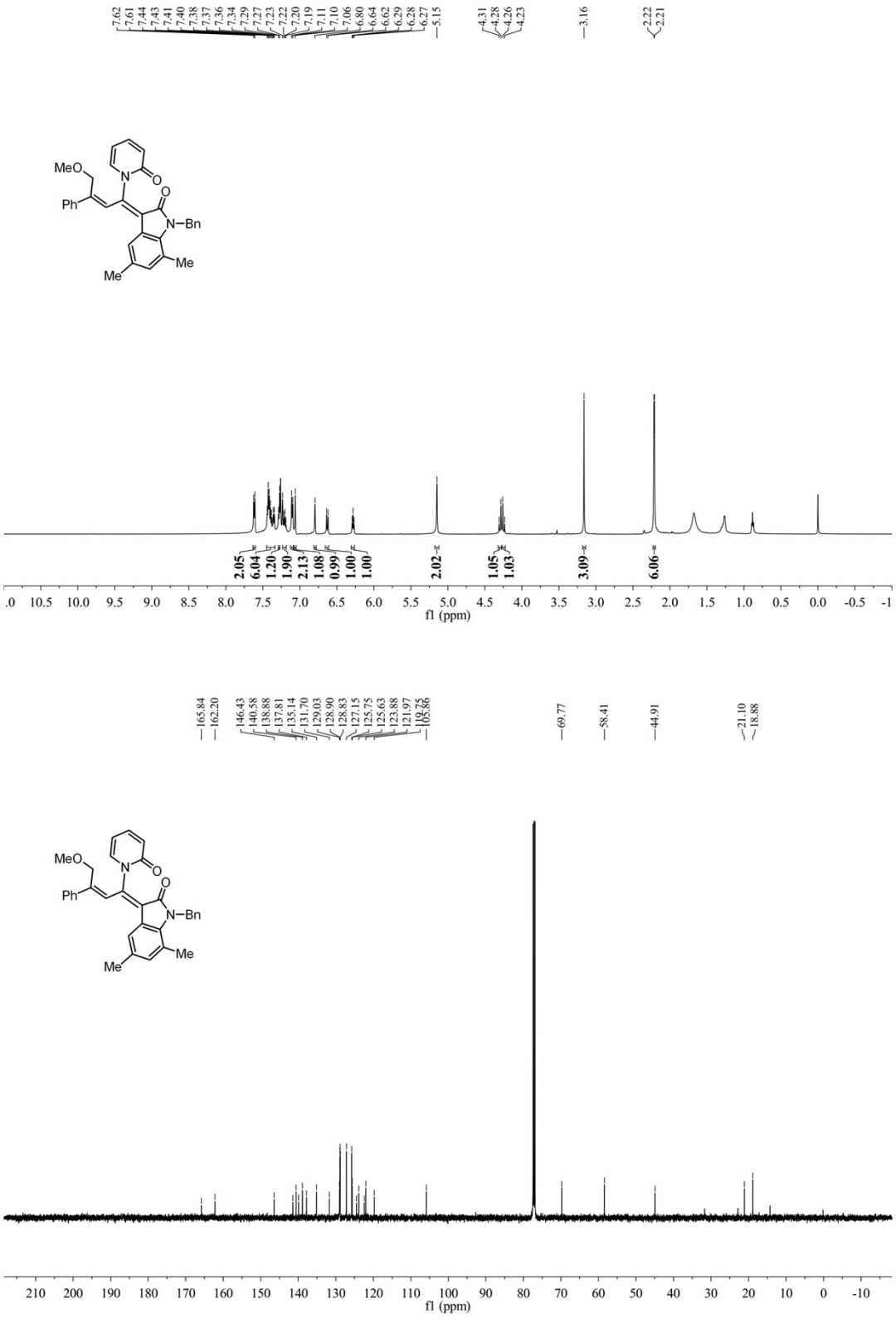




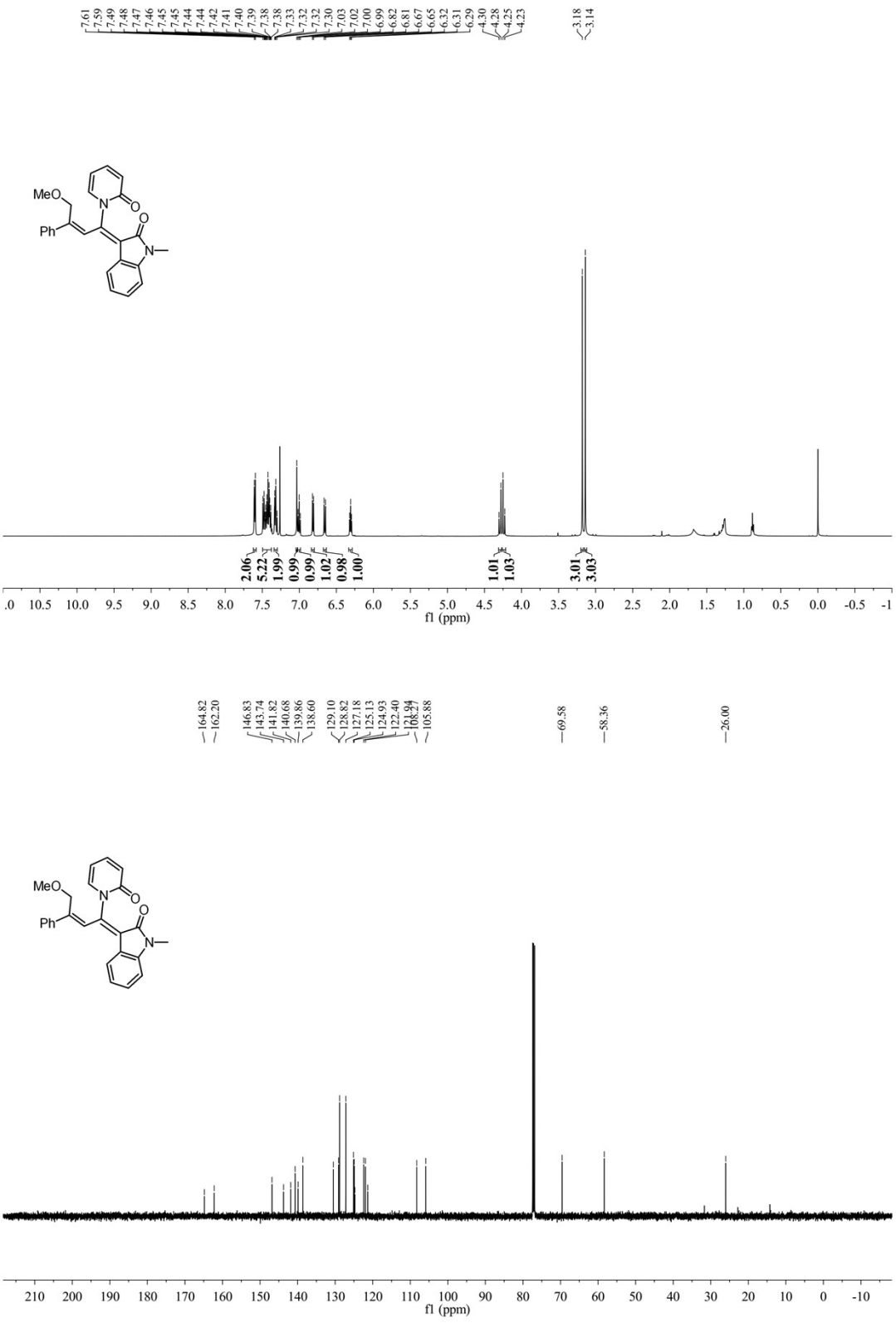
^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4cj



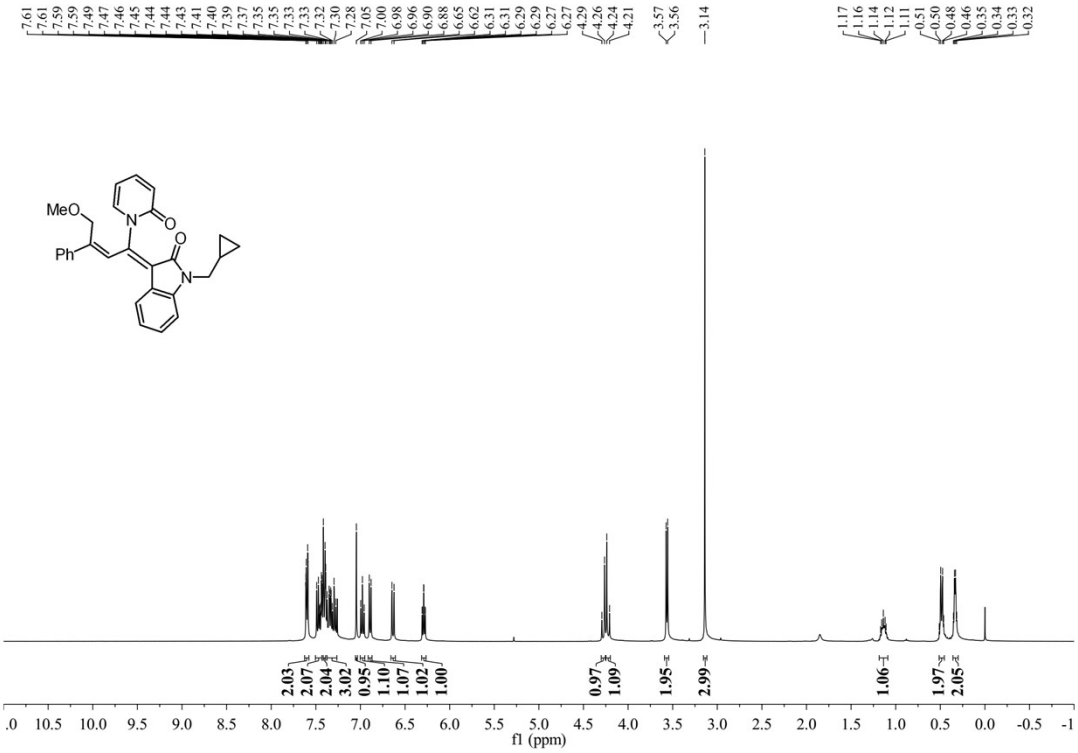
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ck

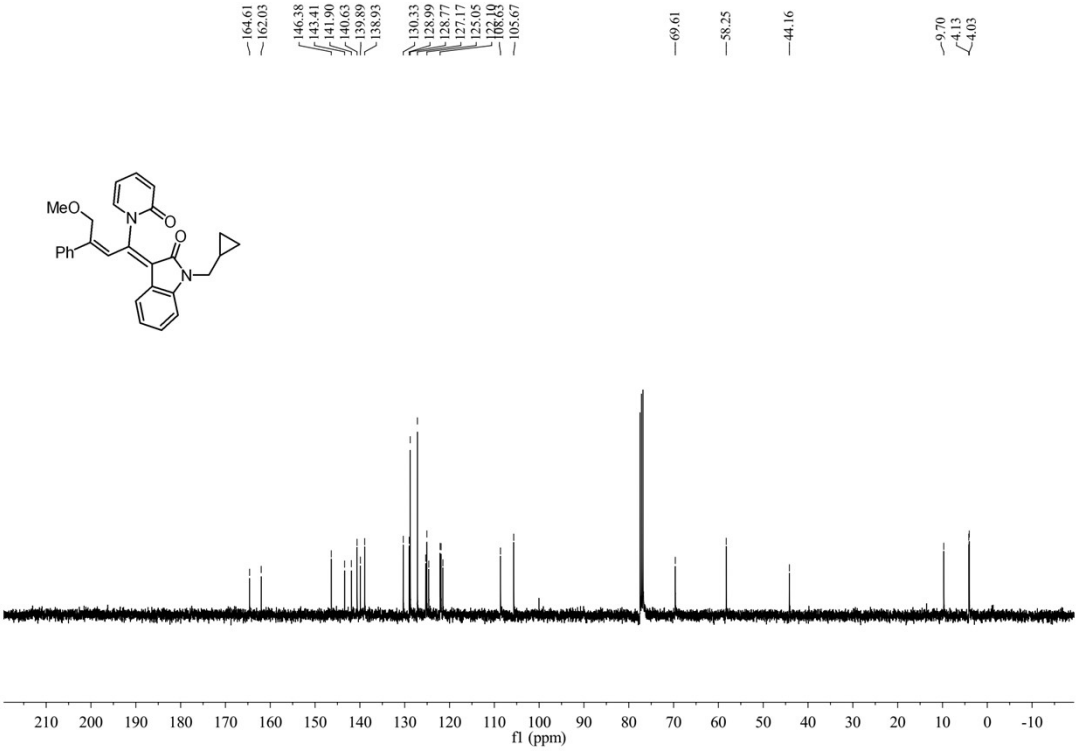


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cl

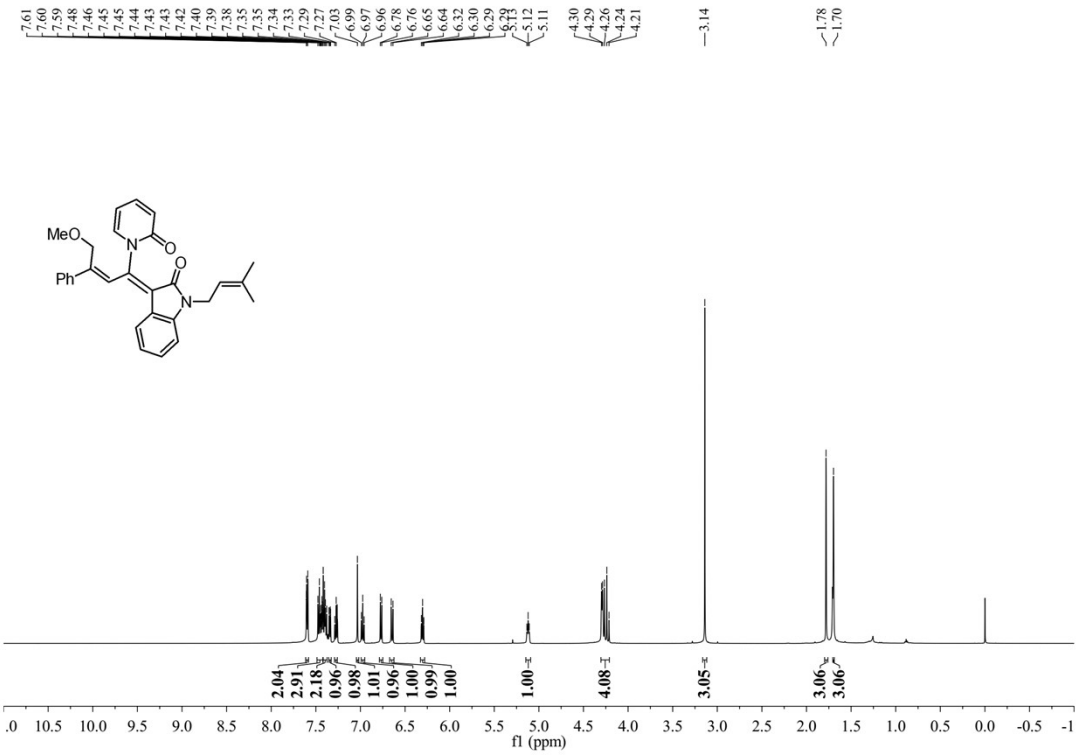


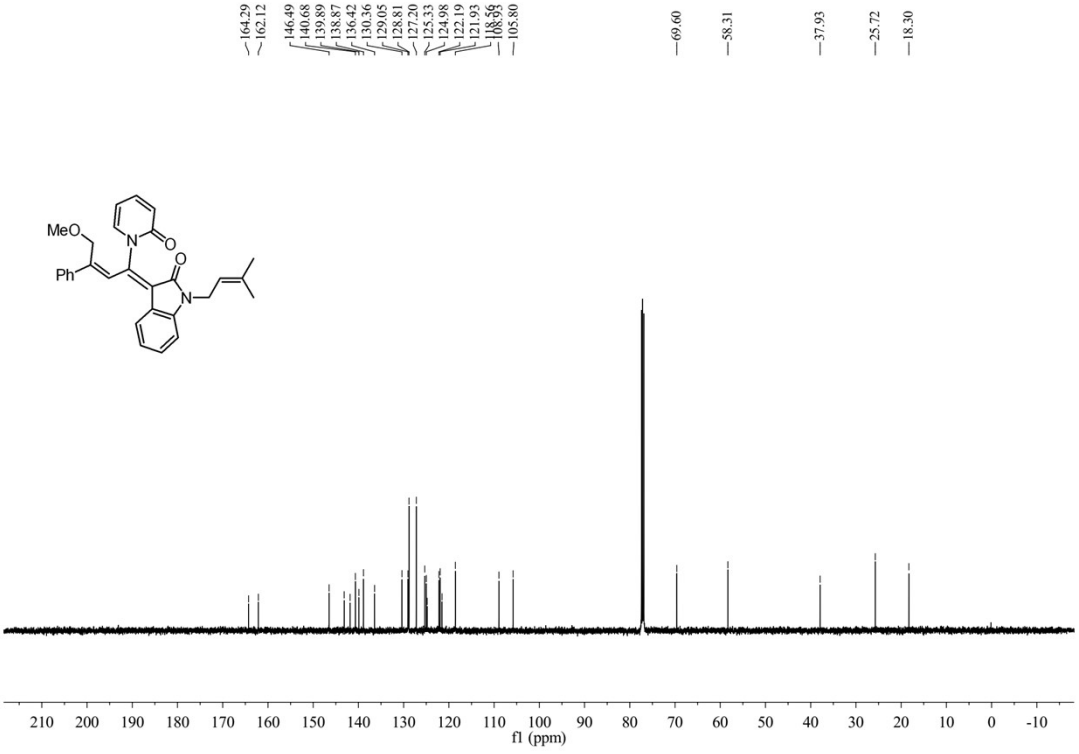
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4cm



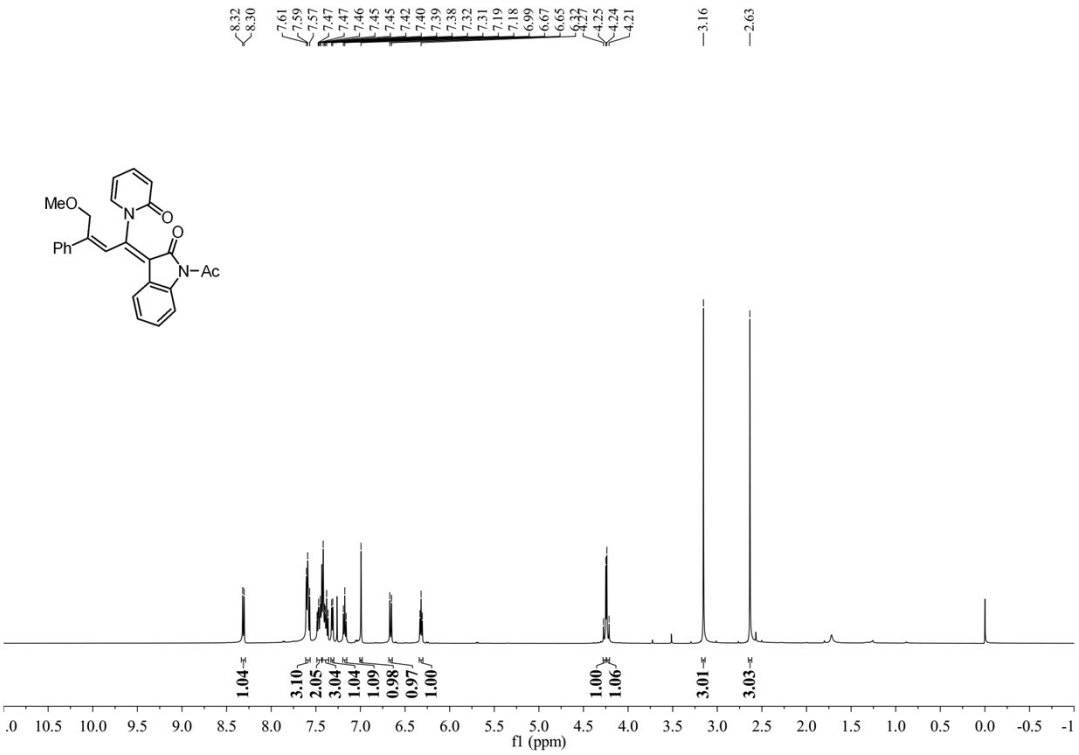


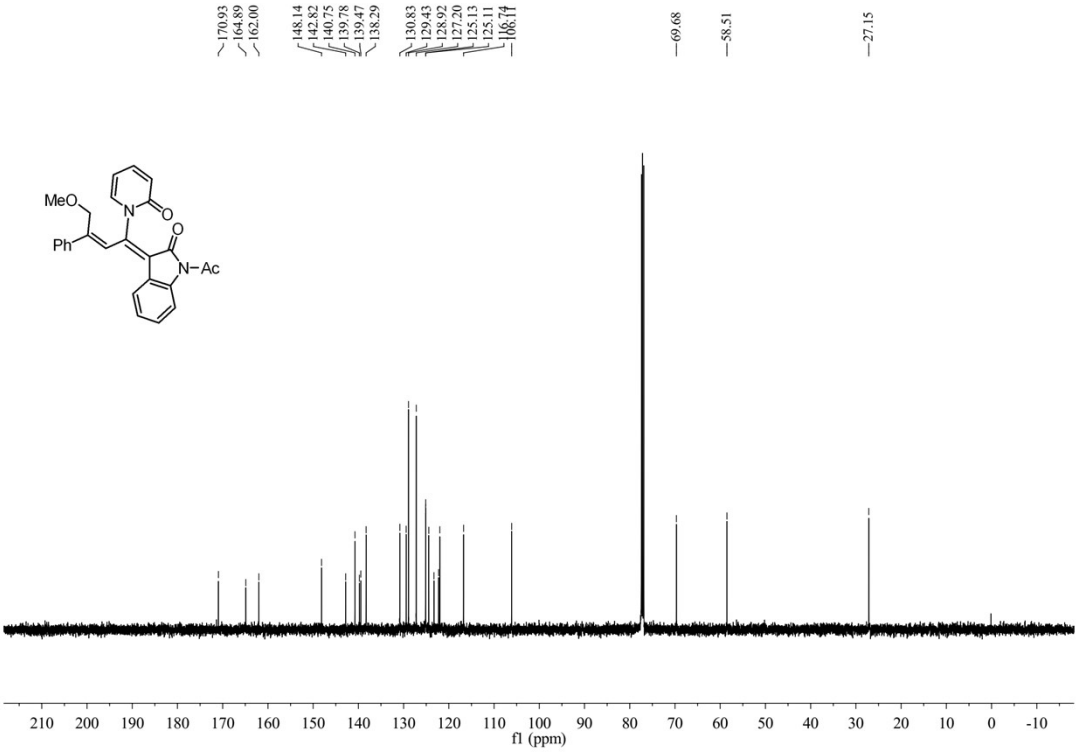
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cn



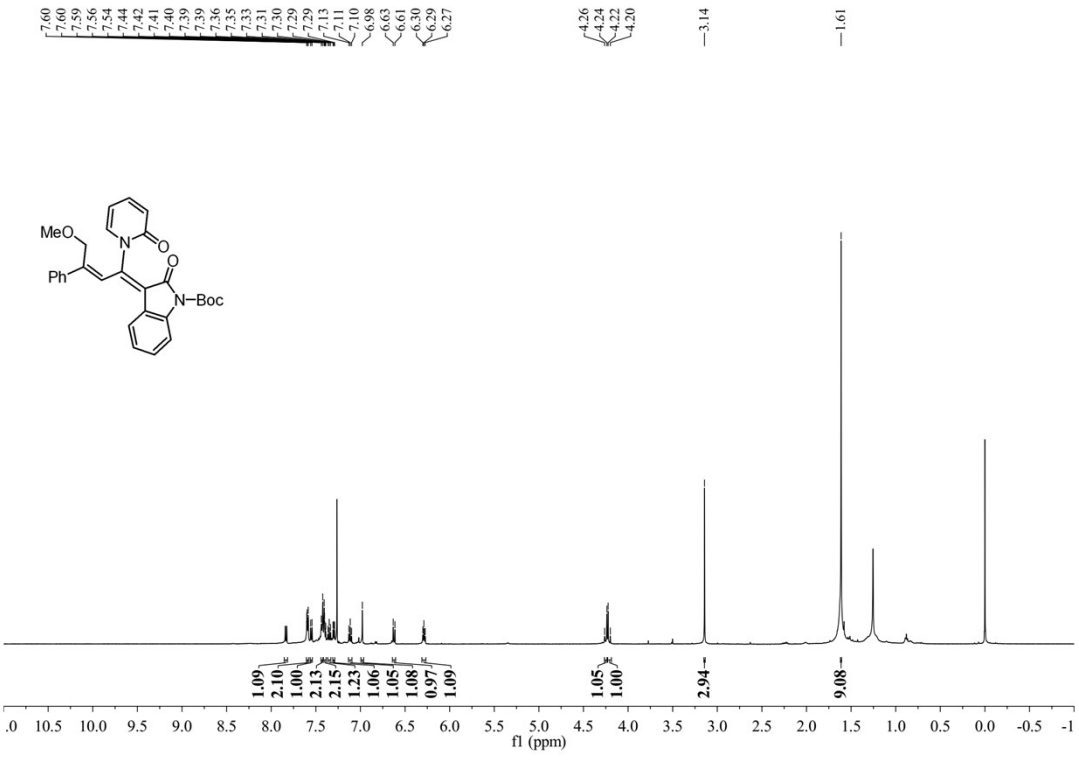


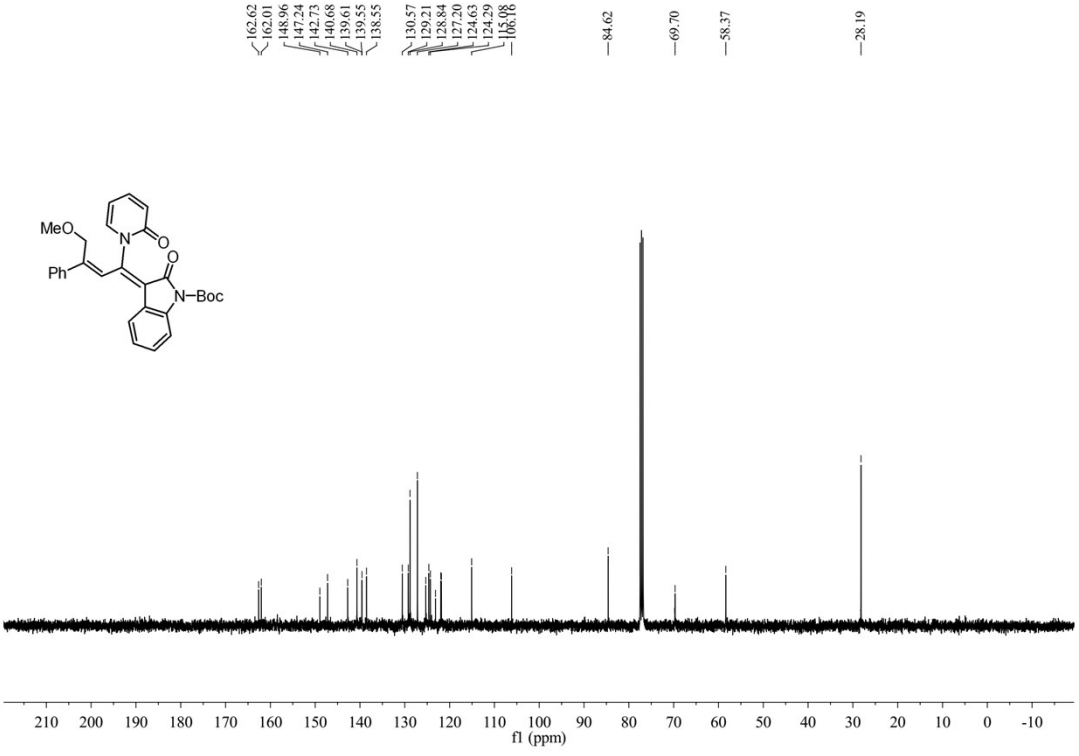
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4co



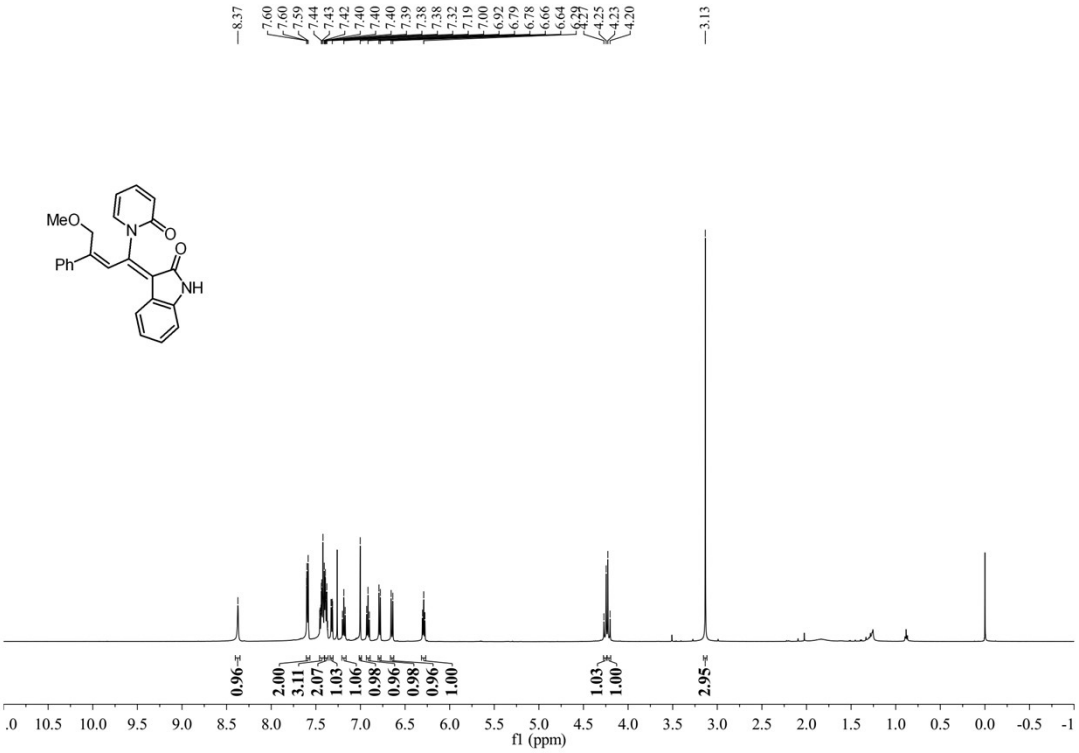


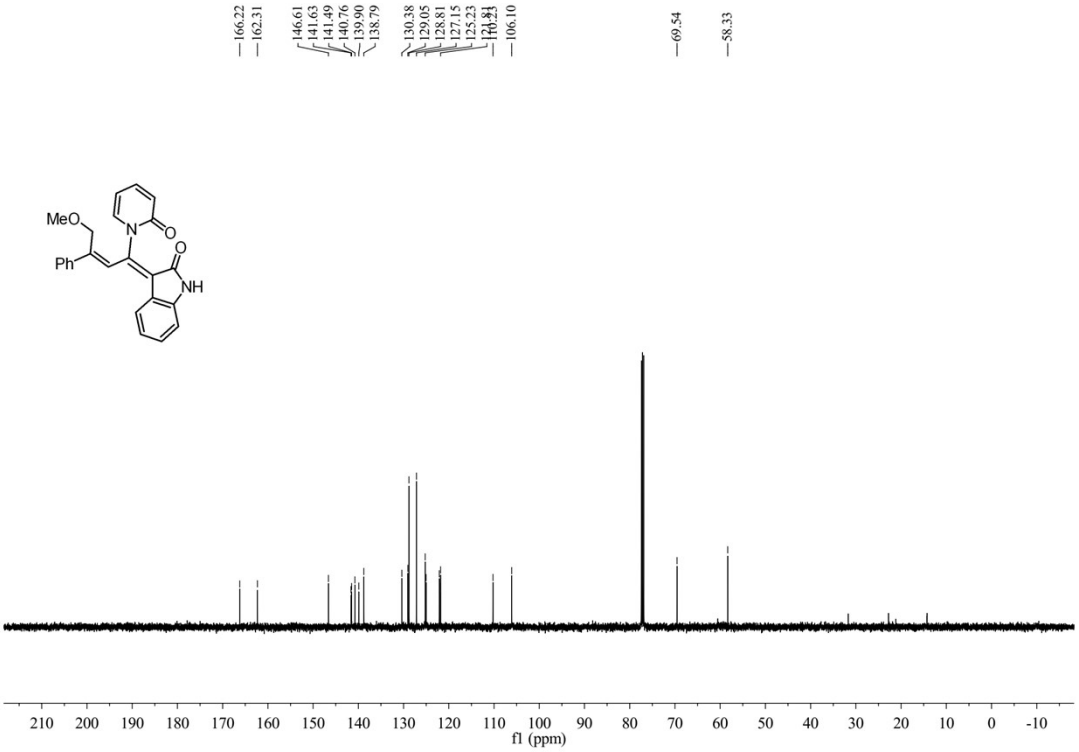
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4cp



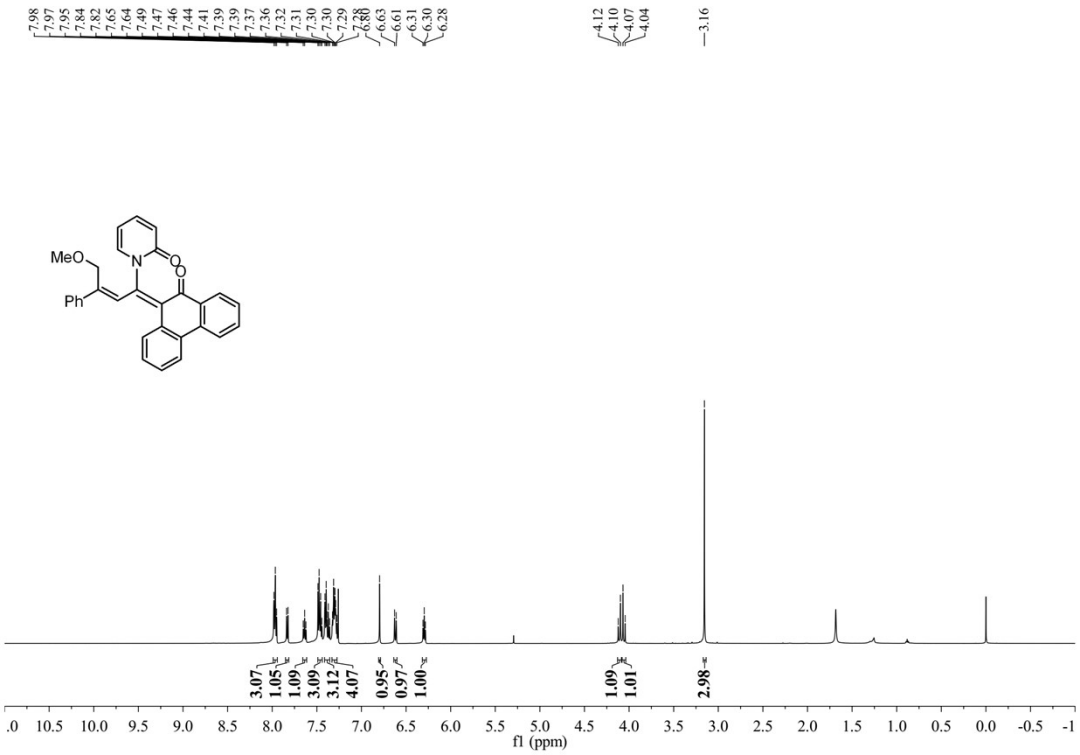


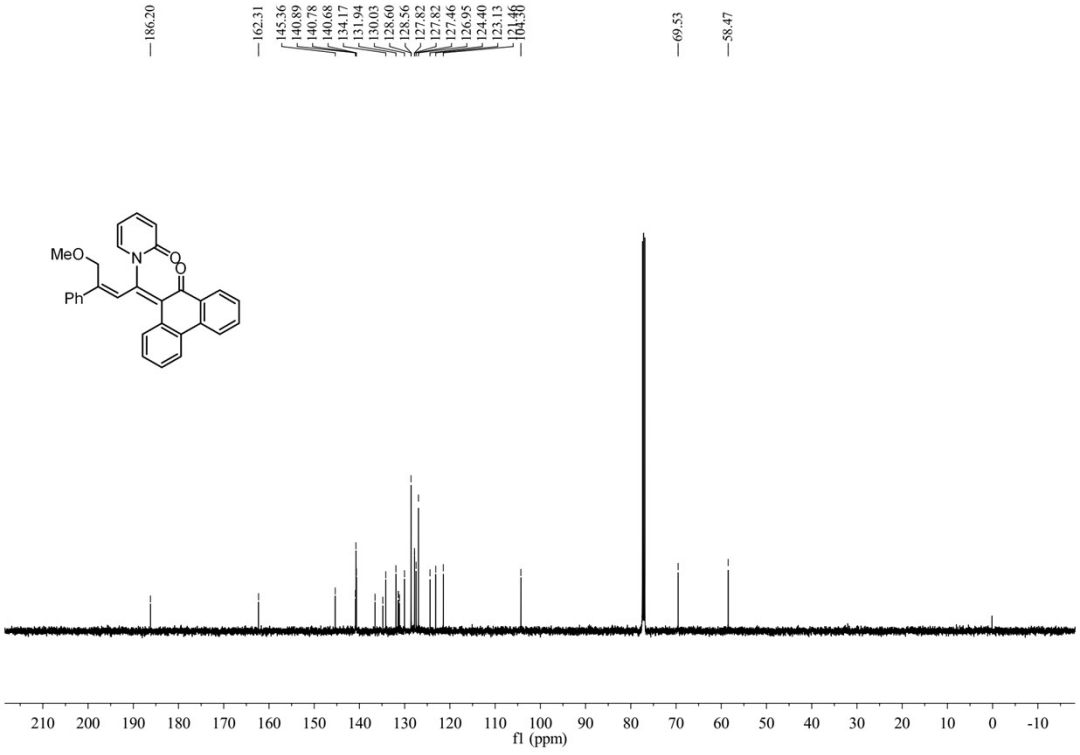
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cq



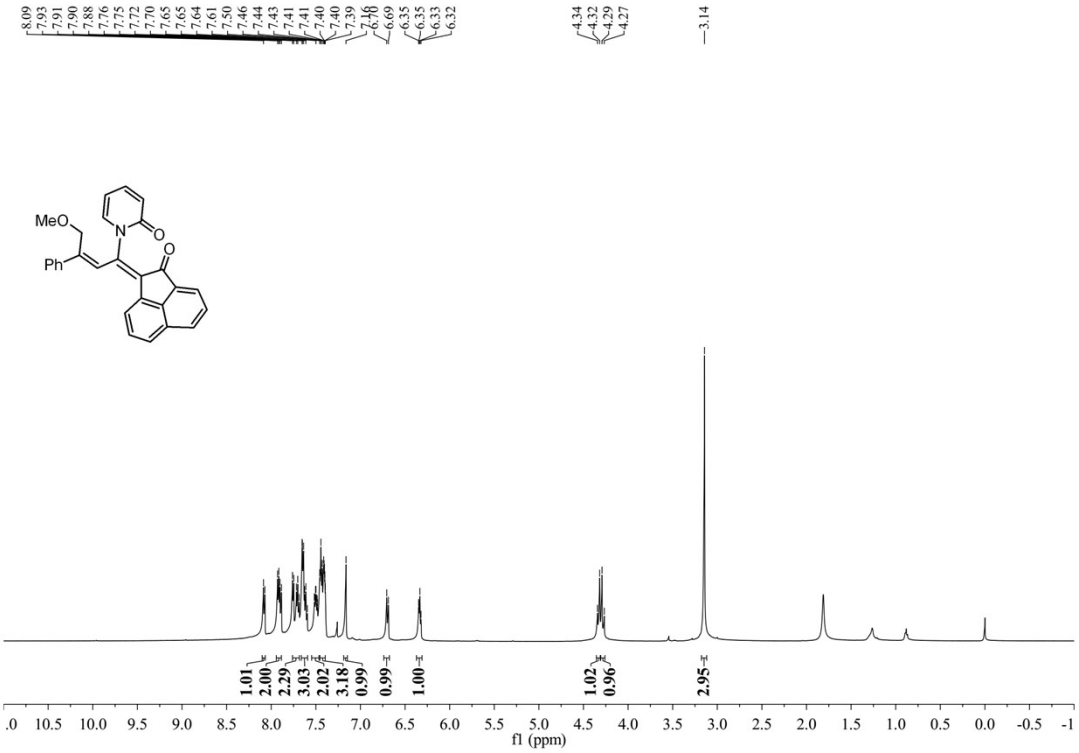


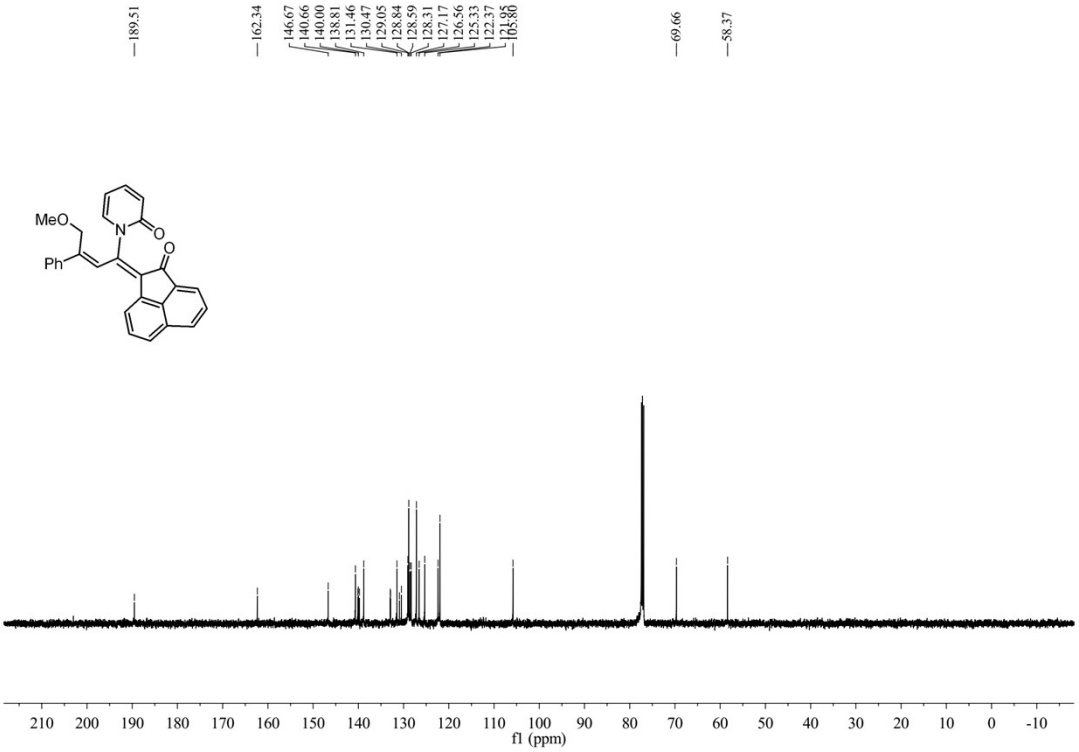
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cr



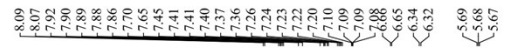


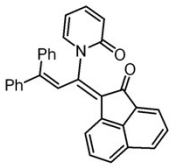
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4cs

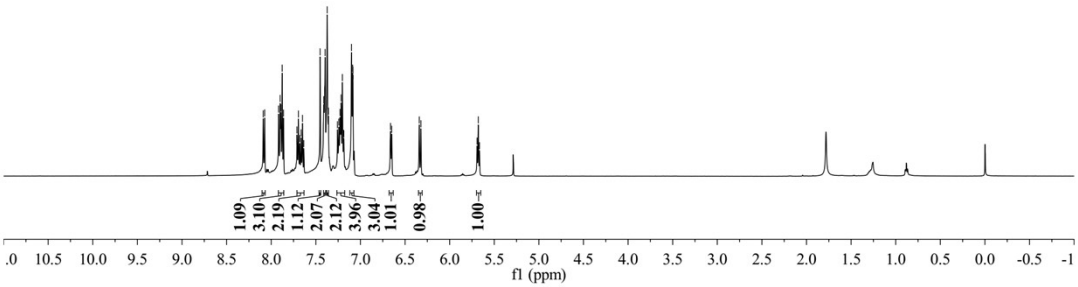


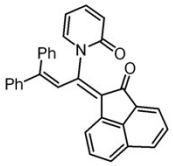


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 4ct

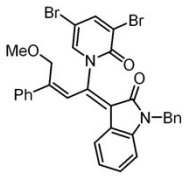


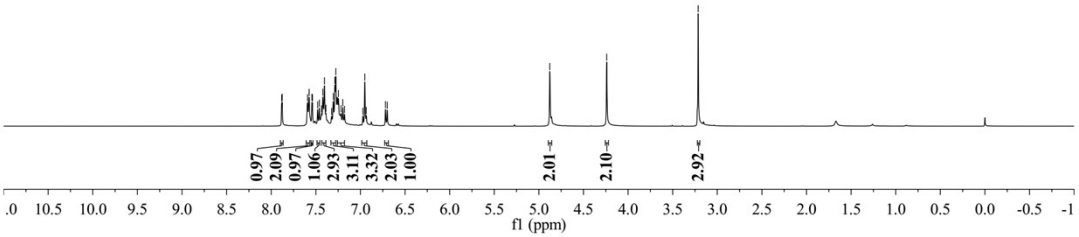


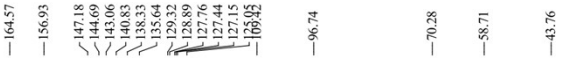


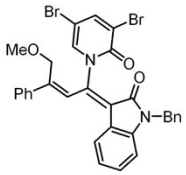


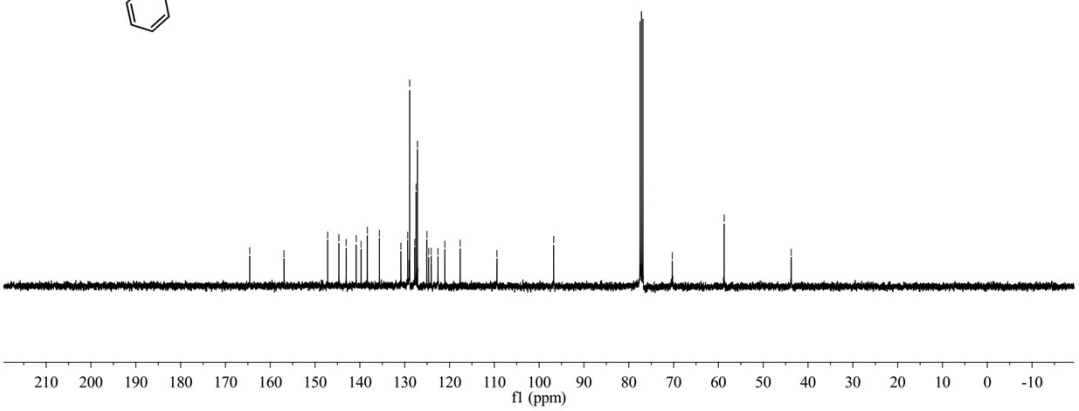
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 6a



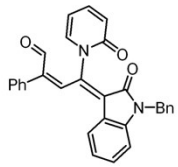


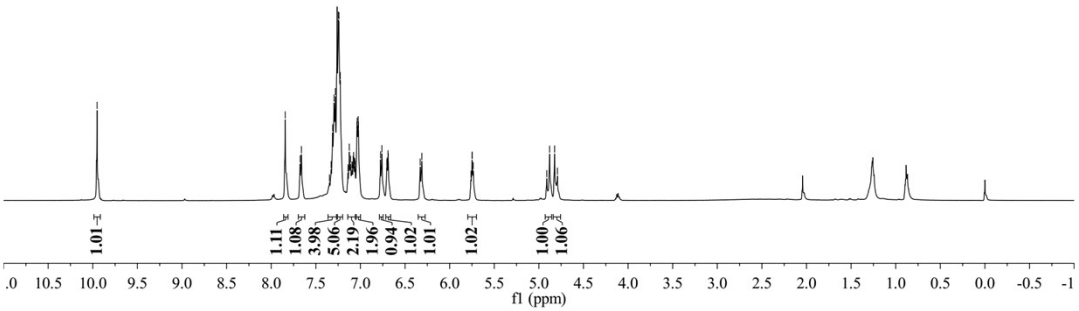


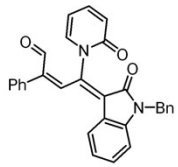


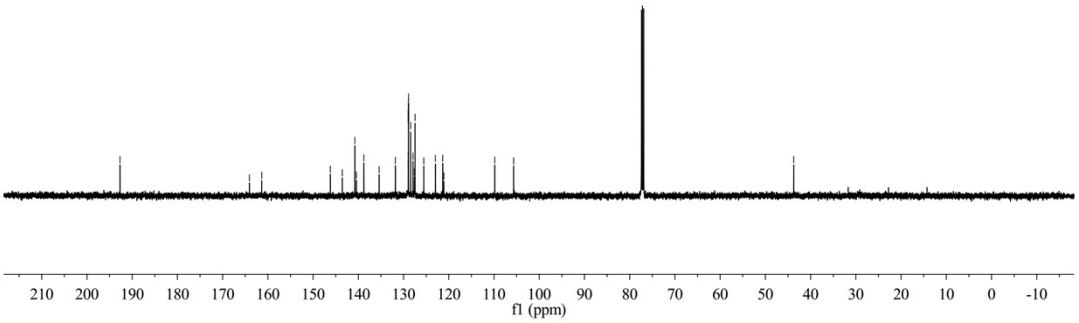


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 6b

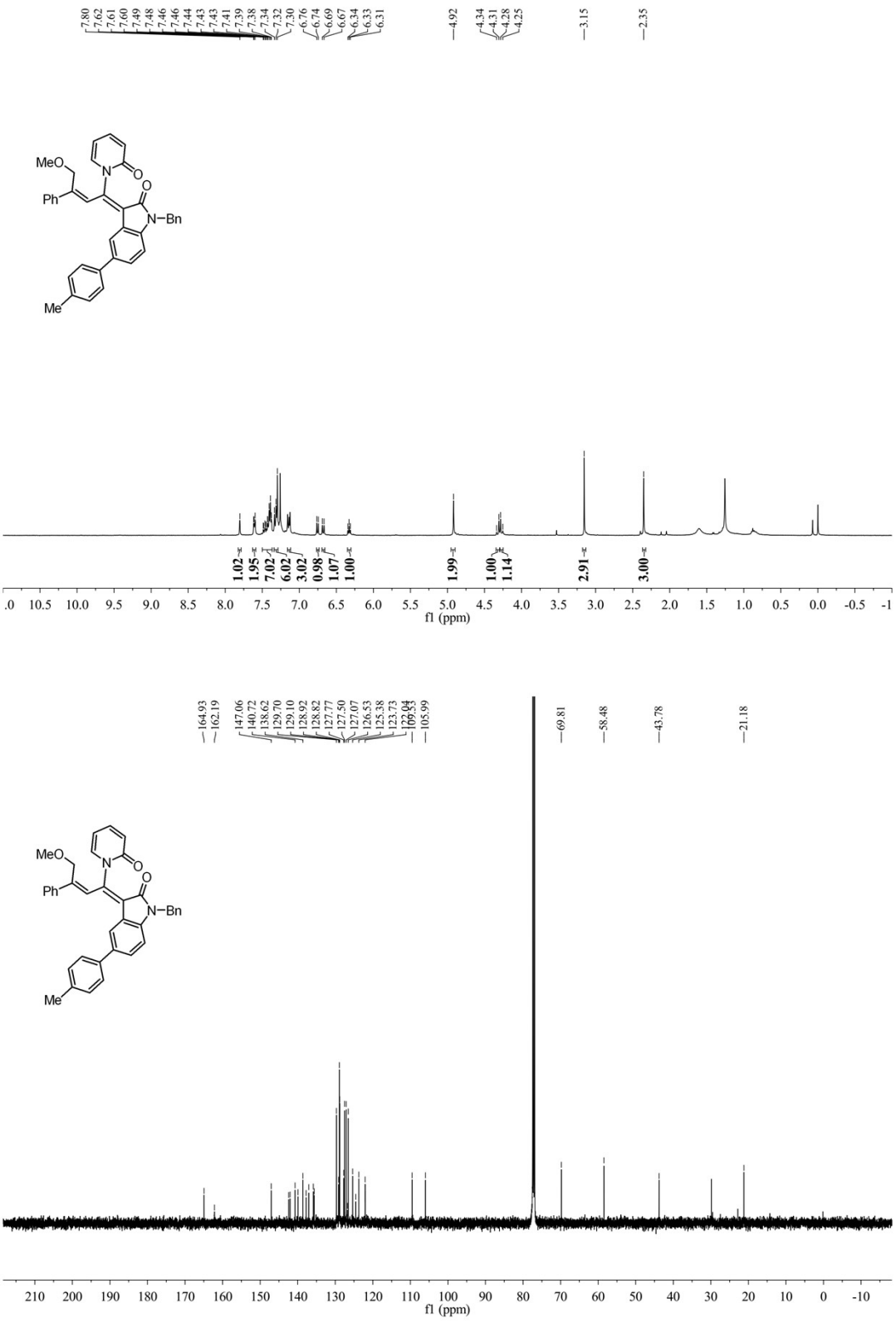




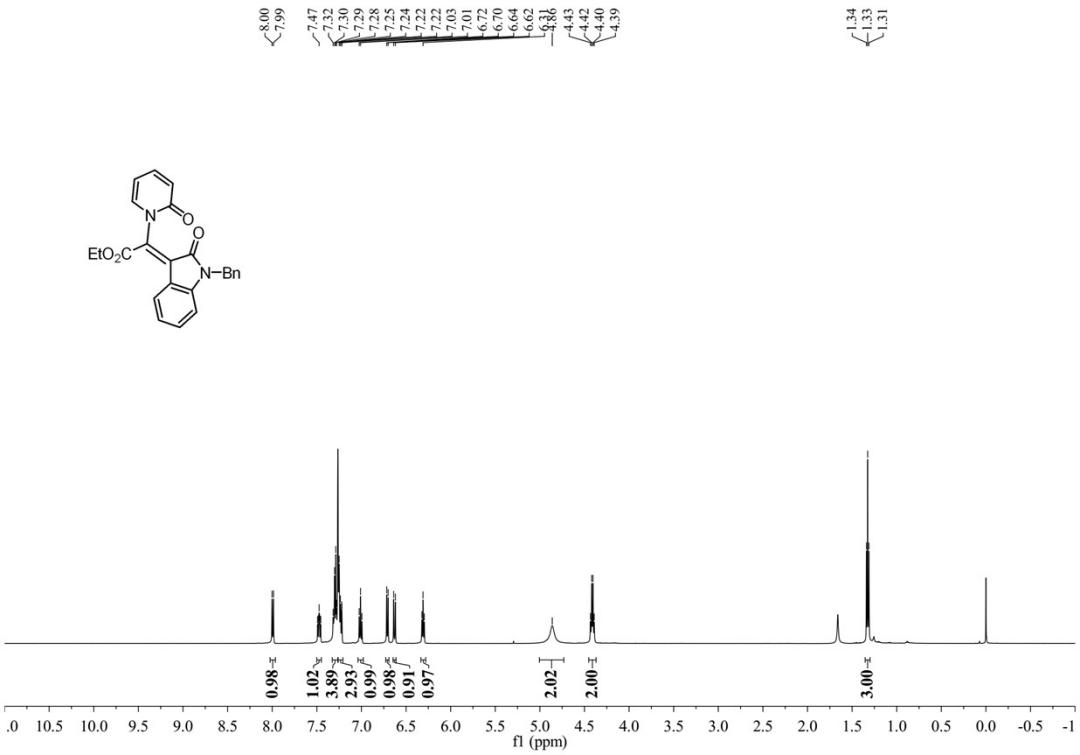


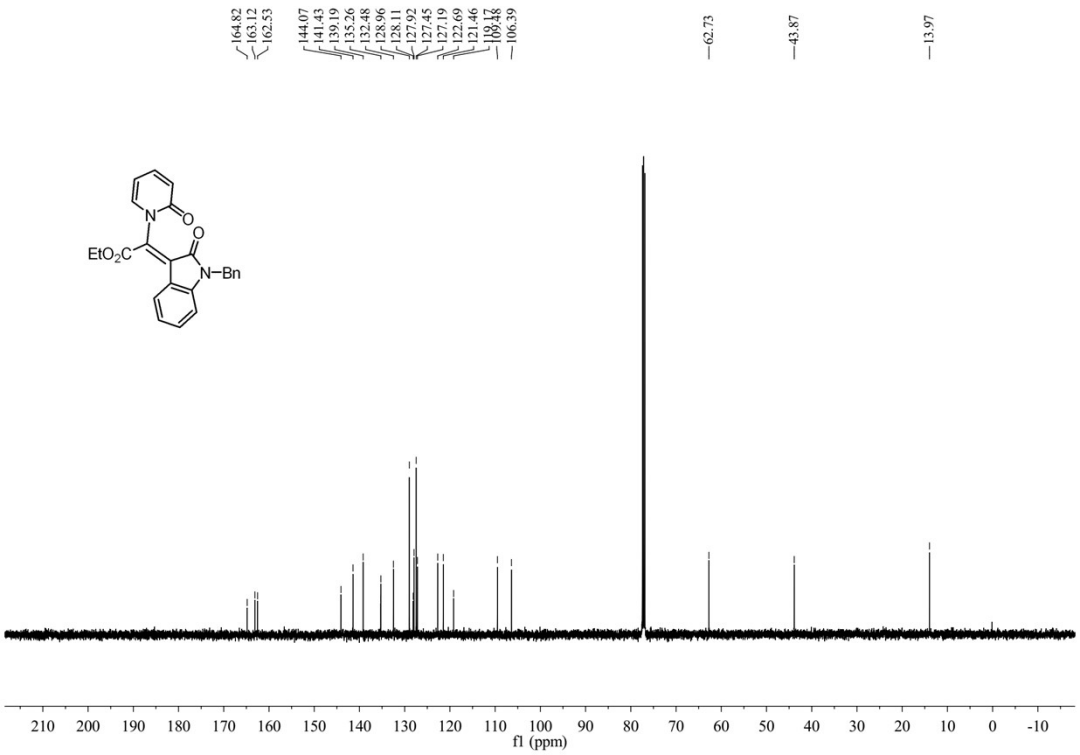


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 6c



^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 8





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 5a