Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

Palladium catalyzed direct allylation of azlactones with simple allylic alcohols in the absence of any activators†

Ruwei Cao,[ac] Jinlong Zhang,[a] Hui Zhou,[ac] Huameng Yang,[a] and Gaoxi Jiang[ab]

[a]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical and Physics, Chinese Academy of Sciences, Lanzhou, 730000, China, Fax: +86-512-62872775;

E-mail: cgxia@lzb.ac.cn, gxjiang2012@sinano.ac.cn

[b.]Graduate University of Chinese Academy of Sciences, Beijing, China.

[c.]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Contents

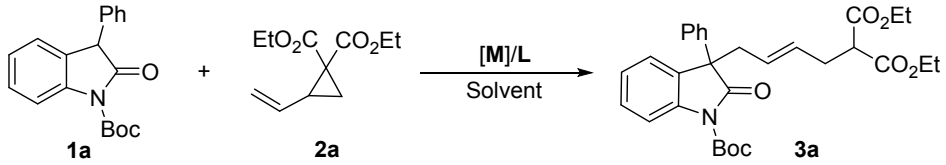
1. General experiment details and materials

Experimental: NMR spectra were recorded on BRUKER Avence III 400MHz spectrometers and Varian Mercury-300 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants(J) were reported in Hz. High resolution mass spectra (HRMS) were recorded on Bruker MicrOTOF-Q II mass instrument (ESI). The oxindoles with different substituent used here are known compounds, which were purchased from Alfa Aesar and Suzhou (China) Amatek Co. Ltd. The oxindole and vinyl cyclopropanes are both known compounds and synthesized according to the reported methods. $Pd(PPh_3)_4$ here were purchased and used as such. Moreover, commercially available reagents were used without additional purification. All non-aqueous manipulations and reactions were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under argon atmosphere. All reactions were monitored by TLC with silica gel-coated plates.

2. Optimization of the reaction conditions

Oxindole **1a** (31 mg, 0.1 mmol), transition metal catalysts, VCP **2a** (16 μL, 0.12 mmol), solvent (1.0 mL) were added to a 10 mL flame-dried schlenk tube, the reactions were monitored by TLC. When the reaction is over, the reaction mixture was diluted with CH_2Cl_2 (2.0 mL), filtered through diatomaceous earth to remove the metal salts and washed with CH_2Cl_2 (3.0 ml) for three times. All volatiles were removed by evaporation to give crude residue.

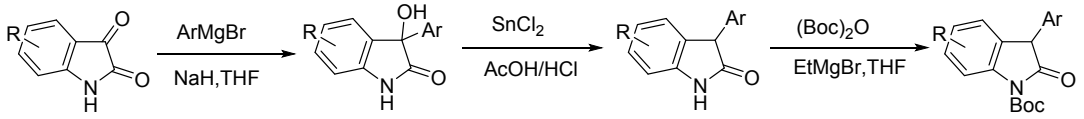
Table 1 Optimization of the reaction conditions for the allylation of oxindole **1a** with vinyl cyclopropane **2a**[a].



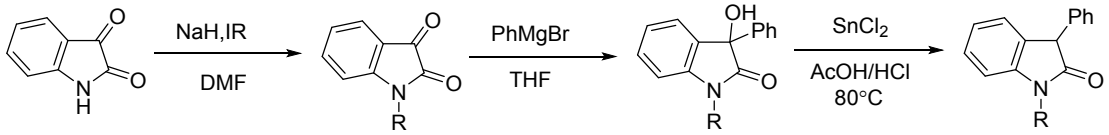
Entry	Cat. [mol%]	L [mol%]	Solvent	Yield (%)[b]	L/B[d]
1	$Fe(acac)_3$ [5]	PPh_3 [10]	Toluene	-	-
2	$Cu(OAc)_2$ [5]	-	Toluene	-	-
3	$Ni(AcAc)_2$ [5]	-	Toluene	-	-
4	$Sc(OTf)_3$ [5]	PPh_3 [10]	Toluene	-	
5	$Mn(OAc)_2$ [5]	PPh_3 [10]	Toluene	-	-
6	$Pd(PPh_3)_4$ [10]	-	Toluene	99	> 20:1
7	$Pd(PPh_3)_4$ [10]	-	THF	99	> 20:1
8	$Pd(PPh_3)_4$ [10]	-	Dioxane	91	> 20:1
9	$Pd(PPh_3)_4$ [10]	-	Hexane	-	-
10	$Pd(PPh_3)_4$ [10]	-	$PhNO_2$	-	-
11	$Pd(PPh_3)_4$ [10]	-	PhCl	-	-
12	$Pd(PPh_3)_4$ [5]	-	THF	99	> 20:1
13	$Pd(PPh_3)_4$ [2]	-	THF	97[c]	> 20:1
14	$Pd(PPh_3)_4$ [1]	-	THF	80	> 20:1

[a] Reaction conditions: oxindole **1a** (0.1 mmol), vinyl cyclopropane **2a** (0.12 mmol, 1.2 equiv.), catalyst and ligand in 1 mL of solvent at 25 °C for 3 h under nitrogen atmosphere. [b] Yield were determined by ^1H NMR analysis. [c] Isolated yield. [d] Determined by ^1H NMR analysis

3 General procedures for the synthesis of 1a-q.



The *N*-Boc substituted oxindoles used in this study were prepared according to the literature[1].



The *N*-alkyl substituted oxindoles used in this study were prepared by the following 3-step sequence according to the literature [2].

4 General procedure for the preparation of VCPs [3]

The corresponding C-H acidic compound (1 equiv) and 1,4-dibromobut-2-ene (1 equiv) are added to a round bottom flask with a stir bar under an atmosphere of nitrogen. To this is added tetrahydrofuran (0.2 M) and cesium carbonate (2.5 equiv). A condenser is added, and reaction mixture is then heated to 60 °C overnight. After cooling down to room temperature, the reaction mixture is filtered over celite and washed with diethyl ether. The organic phase is washed with saturated aqueous $NaHCO_3$, followed by water and brine. After filtration over Na_2SO_4, the solvent is removed under reduced pressure. The crude product is purified by means of silica gel chromotagraphy using petroleum ether and diethyl ether as the eluent. The yields are not optimized for the synthesis of vinyl cyclopropanes.

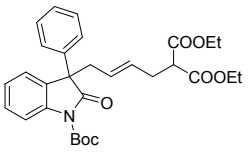
1 Xing-Li Zhu.; Jin-Hui Xu.; Xin-Yuan Liu.; and Bin Tan .*Org. Lett.* **2014**, *16*, 2192−2195.

2 Barry M. Trost, Jia Xie, *J. Am. Chem. Soc.* **2011**, *133*, 20611–20622.

3 Dieskau, Andre P.; Holzwarth, Michael S.; Plietker, Bernd *J. Am. Chem. Soc.* **2012**, *134*, 5048−5051.

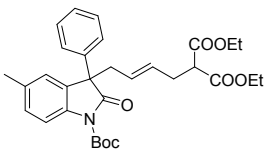
5. Experimental characterization data for products

diethyl-2-(4-(1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3a):



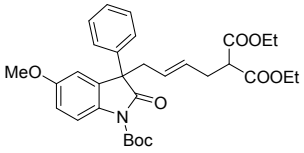
The title compound was prepared according to the general procedure as an oil liquid in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.17 (m, 8H), 5.41 (dd, *J* = 14.7, 7.5 Hz, 1H), 5.20 (dd, *J* = 14.9, 7.1 Hz, 1H), 4.23 – 3.98 (m, 4H), 3.17 (t, *J* = 7.5 Hz, 1H), 2.99 (t, *J* = 6.2 Hz, 2H), 2.52 – 2.36 (m, 2H), 1.62 (s, 9H), 1.21 (td, *J* = 7.1, 2.5 Hz,6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.17, 168.64, 168.63, 149.19, 139.78, 139.08, 128.55, 127.21, 124.29, 115.11, 84.25, 61.28, 56.66, 51.75, 51.57, 41.30, 31.53, 28.03, 14.02, 13.93; MS (EI) [M]+ Calcd. for $C_{30}H_{35}NO_7$: 521.2414, found for $C_{30}H_{35}NO_7$: 521.2424.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-5-methyl-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3b):



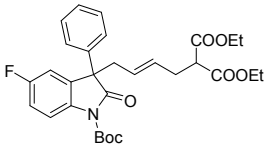
The title compound was prepared according to the general procedure as an oil liquid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.31 (m, *J* = 8.4, 7.2 Hz, 5H), 7.15 (d, *J* = 8.3, 1.1 Hz, 1H), 6.99 (s, 1H), 5.44 (m, *J* = 14.1, 7.0 Hz, 1H), 5.24 – 5.12 (m, 1H), 4.15 – 4.06 (m, 4H), 3.18 (t, *J* = 7.5 Hz, 1H), 3.08 – 2.91 (m, 2H), 2.50 – 2.34 (m, 5H), 1.61 (s, 9H), 1.21 (td, *J* = 7.1, 1.9 Hz, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.98, 168.73, 168.71, 142.91, 139.63, 135.93, 128.66, 127.34, 127.01, 122.48, 109.30, 61.31, 60.34, 56.46, 51.69, 40.67, 31.91, 29.34, 21.01, 14.19, 14.12, 14.06, 10.27; MS (EI) [M]+ Calcd for $C_{31}H_{37}O_7N$: 535.2570, found for $C_{31}H_{37}O_7N$ 535.2590.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-5-methoxy-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3c):



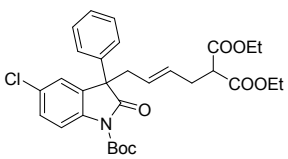
The title compound was prepared according to the general procedure as an oil liquid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 – 7.79 (m, 1H), 7.33 – 7.05 (m, 5H), 6.91 – 6.76 (m, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 5.51 – 5.32 (m, 1H), 5.50 – 5.37 (m, 1H), 4.16 – 4.05 (m, 4H), 3.81 (s, 3H), 3.17 (t, *J* = 7.5 Hz, 1H), 2.97 (m, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.60 (s, 9H), 1.23 – 1.07 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.23, 168.69, 168.67, 156.71, 149.25, 139.06, 133.18, 131.64, 131.15, 128.57, 127.57, 127.22, 126.37, 116.04, 113.26, 111.20, 84.09, 61.29, 57.02, 55.62, 51.74, 41.12, 31.54, 28.05, 14.17, 14.01; MS (EI) [M]+ Calcd for $C_{31}H_{37}NO_8$: 551.2519, found for $C_{31}H_{37}NO_8$: 551.2513.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-5-fluoro-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3d):



The title compound was prepared according to the general procedure as 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (q, *J* = 9.0, 4.6 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.04 (td, *J* = 2.7 Hz, 1H), 6.90 (dd, *J* = 7.9, 2.7 Hz, 1H), 5.41 (m, 1H), 5.21 – 5.13 (m, 1H), 4.15 – 4.05 (m, 4H), 3.16 (t, *J* = 7.5 Hz, 1H), 2.96 (m, *J* = 12.1, 7.3 Hz, 2H), 2.42 (m, *J* = 5.6 Hz, 2H), 1.59 (s, 9H), 1.19 (td, *J* = 7.1, 2.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.80, 168.64, 160.96, 158.53, 149.14, 138.43, 132.20, 128.72, 127.82, 127.08, 126.01, 121.03, 116.53, 115.15, 114.92, 112.66, 112.42, 84.54, 61.37, 61.35, 56.88, 51.69, 43.41, 41.14, 31.51, 28.02, 14.01; MS (EI) [M]+ Calcd. for $C_{30}H_{34}FNO_7$: 539.2319, found for $C_{30}H_{34}FNO_7$: 539.2339.

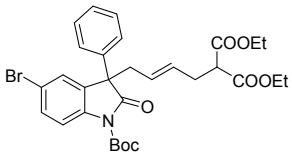
diethyl-2-(4-(1-(tert-butoxycarbonyl)-5-chloro-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3e):



The title compound was prepared according to the general procedure as an oil liquid in 93% yield. ^{1}H NMR (400 MHz, $cdcl_3$) δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.50 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.36 – 7.26 (m, 6H), 5.47 (m, *J* = 14.2, 7.0 Hz, 1H), 5.25 – 5.12 (m, 1H), 4.15 (m, *J* = 14.2, 7.1 Hz, 4H), 3.20 (t, *J* = 7.5 Hz, 1H), 3.07 – 2.92 (m, 2H), 2.47 (m, *J* = 7.3 Hz, 2H), 1.62 (s, 9H), 1.26 – 1.19 (td, 6H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 175.50, 168.66, 168.64, 149.02, 138.39, 138.34,

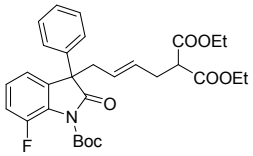
129.83, 127.86, 125.20, 116.44, 84.71, 61.39, 61.35, 56.81, 51.70, 43.41, 41.09, 31.52, 28.01, 14.03; MS (EI) [M]+ Calcd for $C_{30}H_{34}O_7NCl$: 555.2024, found for $C_{30}H_{34}O_7NCl$: 555.2054.

diethyl-2-(4-(5-bromo-1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3f):



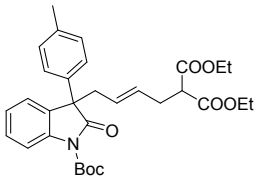
The title compound was prepared according to the general procedure as an oil liquid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.36 – 7.24 (m, 6H), 5.46 (m, *J* = 14.2, 7.0 Hz, 1H), 5.23 – 5.12 (m, 1H), 4.18 – 4.10 (m, 4H), 3.19 (t, *J* = 7.5 Hz, 1H), 3.06 – 2.90 (m, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 1.61 (s, 9H), 1.22 (td, *J* = 7.1, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.36, 168.65, 168.63, 148.99, 138.86, 138.40, 128.76, 125.86, 117.35, 116.84, 84.72, 61.38, 61.34, 56.77, 51.70, 41.07, 31.52, 28.01, 21.04, 14.18, 14.04; MS (EI) [M]+ Calcd for $C_{30}H_{34}BrNO_7$: 599.1519, found for $C_{30}H_{34}BrNO_7$: 9.1525.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-7-fluoro-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3g):



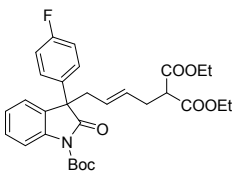
The title compound was prepared according to the general procedure as an oil liquid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 7.22 – 7.09 (m, 2H), 7.00 (dd, *J* = 7.3, 1.1 Hz, 1H), 5.41 – 5.48 (m, *J* = 14.7, 7.4 Hz, 1H), 5.24 – 5.15 (m, 1H), 4.20 – 4.09 (m, 4H), 3.21 (t, *J* = 7.6 Hz, 1H), 3.01 (m, *J* = 15.1, 6.9 Hz, 2H), 2.45 (m, *J* = 15.1, 7.5 Hz, 2H), 1.60 (s, 9H), 1.23 (td, *J* = 7.1, 2.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.70, 168.71, 168.66, 149.98, 147.48, 147.46, 138.40, 127.79, 126.70, 125.24, 120.91, 116.71, 116.51, 84.91 , 61.33, 57.52, 51.73, 41.24, 31.55, 27.66, 14.03; MS (EI) [M]+ Calcd for $C_{30}H_{34}FNO_7$: 539.2319, found for $C_{30}H_{34}FNO_7$: 539.2349.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-2-oxo-3-(p-tolyl)indolin-3-yl)but-2-en-1-yl)malonate (3h):



The title compound was prepared according to the general procedure as an oil liquid in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.19 (m, 2H), 7.19 – 7.08 (m, 5H), 7.08 (s, 1H), 5.48 – 5.29 (m, 1H), 5.46 – 5.35 (m, 1H), 4.34 – 3.90 (m, 4H),3.16 (m *J* = 7.4, 0.9 Hz, 1H), 2.95 (m,*J* = 6.4 Hz, 2H), 2.42 (d, *J* = 2.9 Hz, 2H), 2.28 (s, 4H), 1.60 (t, *J* = 3.0 Hz, 9H),1.27 – 1.07 (td, *J*=7.1, 2.5 Hz, 6H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 176.30, 168.65, 149.25, 139.77, 137.29, 136.14, 131.03, 126.55, 124.25, 115.08, 84.17, 61.28, 60.32, 56.36, 51.77, 41.24, 31.54, 28.02, 20.91, 14.17, 14.02; MS (EI) [M]+ Calcd for $C_{31}H_{37}NO_7$: 535.26, found.

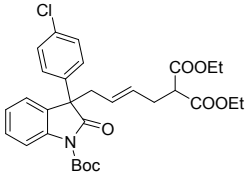
diethy-2-(4-(1-(tert-butoxycarbonyl)-3-(4-fluorophenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3i):



The title compound was prepared according to the general procedure as an oil liquid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.34 (td, 1H), 7.30 – 7.23 (m, 2H), 7.23 – 7.14 (m, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 5.39 (m, *J* = 14.7, 7.4 Hz, 1H), 5.16 (m, *J* = 15.0, 7.3 Hz, 1H), 4.10 (m, *J* = 9.2, 7.5, 1.6 Hz, 4H), 3.15 (t, *J* = 7.5 Hz, 1H), 2.98 – 2.87 (m,

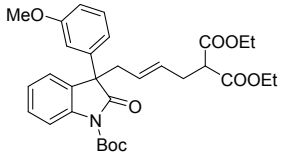
2H), 2.40 (td, *J* = 7.1, 3.1 Hz, 2H), 1.59 (s, 9H), 1.18 (td, *J* = 7.1, 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.09, 168.62, 163.36, 160.91, 149.11, 139.72, 131.07, 128.82, 124.37, 115.46, 115.25, 115.22, 84.41, 61.30, 56.05, 51.71, 41.56, 31.50, 28.01, 14.00; MS (EI) [M]+ Calcd for $C_{30}H_{34}FNO_7$: 539.2319, found for $C_{30}H_{34}FNO_7$: 539.2359.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-3-(4-chlorophenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3j):



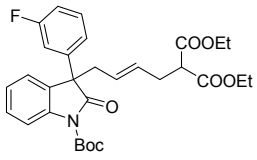
The title compound was prepared according to the general procedure as an oil liquid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 1H), 7.31 – 7.27 (m, 3H), 7.27 – 7.21 (m, 2H), 7.18 (m, *J* = 11.1, 5.7 Hz, 2H), 5.46 – 5.36 (m, 1H), 5.24 – 5.13 (m, 1H), 4.18 – 4.04 (m, 4H), 3.16 (t, *J* = 7.5 Hz, 1H), 3.02 – 2.90 (m, 2H), 2.47 – 2.36 (m, 2H), 1.58 (d, *J* = 16.6 Hz, 9H), 1.24 – 1.17 (td, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.09, 168.70, 149.21, 139.77, 139.04, 131.14, 130.26, 128.56, 128.41, 127.57, 127.24, 126.46, 125.26, 124.28, 115.12, 84.41,61.30, 56.05, 51.71, 41.56, 31.50, 28.01, 14.00; MS (EI) [M]+ Calcd for $C_{30}H_{34}ClNO_7$: 555.2024, found for $C_{30}H_{34}ClNO_7$: 555.2054.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-3-(3-methoxyphenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3k):



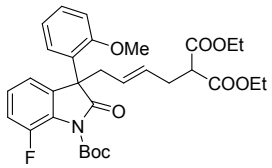
The title compound was prepared according to the general procedure as an oil liquid in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.20 (m, *J* = 11.4, 4.4 Hz, 2H), 6.99 (m, *J* = 7.5, 4.9, 0.9 Hz, 2H), 6.82 – 6.70 (m, 2H), 5.35 (m, *J* = 14.1, 6.9 Hz, 1H), 5.22 – 5.10 (m, 1H), 4.17 – 4.06 (m, 4H), 3.41 (s, 3H), 3.13 (t, *J* = 7.5 Hz, 1H), 2.90 (t, *J* = 6.7 Hz, 2H), 2.48 – 2.30 (m, 2H), 1.64 (s, *J* = 4.8 Hz, 9H), 1.20 (td, *J* = 7.1, 1.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.46, 168.74, 168.67, 156.67, 149.56, 140.05, 131.27, 127.07, 123.97, 120.84, 114.17, 112.23, 83.57, 61.27, 60.32, 55.62, 54.02, 51.84, 40.06, 31.60, 28.12, 21.00, 14.17, 14.02; MS (EI) [M]+ Calcd for $C_{31}H_{37}NO_8$: 551.2519, found for $C_{31}H_{37}NO_8$: 551.2525.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-3-(3-fluorophenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3l):



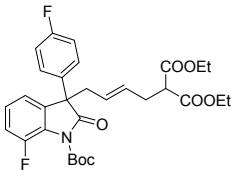
The title compound was prepared according to the general procedure as an oil liquid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.26 – 7.16 (m, 3H), 7.08 (ddd, *J* = 7.9, 1.6, 0.8 Hz, 1H), 7.01 (m, *J* = 10.6 Hz, 1H), 6.93 (m, *J* = 2.5, 0.8 Hz, 1H), 5.39 (m, 1H), 5.18 (m, 1H), 4.16 – 4.06 (m, 4H), 3.16 (t, *J* = 7.5 Hz, 1H), 2.94 (d, *J* = 7.2 Hz, 2H), 2.41 (m, *J* = 2.7 Hz, 2H), 1.60 (s, 9H), 1.22 – 1.16 (td, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.68, 168.62, 163.98, 161.54, 149.05, 141.53, 139.71, 131.49, 126.02, 124.43, 122.95, 115.24, 114.71, 114.65, 114.48, 114.45, 84.48, 61.31, 56.40, 51.69, 41.39, 31.50, 28.01, 14.01; MS (EI) [M]+ Calcd for $C_{30}H_{34}FNO_7$: 539.2319, found for $C_{30}H_{34}FNO_7$: 539.2303.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-7-fluoro-3-(2-methoxyphenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3m):



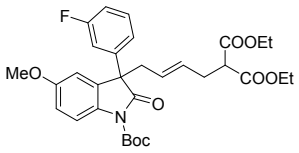
The title compound was prepared according to the general procedure as an oil liquid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.91 (m, 3H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.59 (m, *J* = 4.9, 3.3 Hz, 1H), 5.36 (m, *J* = 7.3 Hz, 1H), 5.19 (m, *J* = 7.5 Hz, 1H), 4.13 (m, *J* = 7.0, 4.2 Hz, 4H), 3.49 (s, 3H), 3.18 (t, *J* = 7.5 Hz, 1H), 2.92 (m, *J* = 14.2, 7.1 Hz, 2H), 2.43 (m, *J* = 26.1, 7.2 Hz, 2H), 1.62 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.94, 168.80, 168.71, 156.68, 149.75, 148.00, 147.27, 135.47, 127.10, 124.89, 120.81, 115.69, 111.90, 84.12, 61.31, 55.58, 51.81, 43.49, 43.47, 39.93, 31.64, 29.68, 27.80, 14.04; MS (EI) [M]+ Calcd for $C_{31}H_{36}FNO_8$: 569.2425, found for $C_{31}H_{36}FNO_8$: 569.2409.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-7-fluoro-3-(4-fluorophenyl)-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3n):



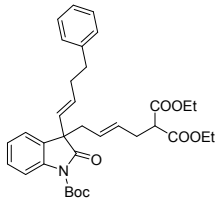
The title compound was prepared according to the general procedure as an oil liquid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.19 – 7.06 (m, 2H), 7.01 – 6.92 (m, 3H), 5.39 (m, 1H), 5.14 (m, *J* = 14.8, 7.5 Hz, 1H), 4.14 – 4.04 (m, 4H), 3.17 (t, *J* = 7.5 Hz, 1H), 2.93 (m, *J* = 12.9, 7.3 Hz, 2H), 2.42 (m, *J* = 7.4 Hz, 2H), 1.54 (s, *J* = 15.1 Hz, 9H), 1.20 (td, *J* = 7.1, 2.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.58, 168.63, 163.46, 161.00, 150.00, 147.50, 147.36, 134.09, 134.06, 133.42, 131.82, 128.93, 126.76, 125.68, 125.34, 120.90, 120.87, 116.90, 116.69, 115.63, 115.41, 85.06, 61.34, 60.36, 56.88, 51.67, 41.52, 31.51, 27.63, 27.52, 21.01, 14.16, 14.01; MS (EI) [M]+ Calcd for $C_{30}H_{33}F_2NO_7$: 557.2225, found for $C_{30}H_{33}F_2NO_7$: 557.2248.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-3-(3-fluorophenyl)-5-methoxy-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3o):



The title compound was prepared according to the general procedure as an oil liquid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.07 (ddd, *J* = 7.9, 1.5, 0.8 Hz, 1H), 7.00 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.96 – 6.85 (m, 2H), 6.72 (d, *J* = 2.6 Hz, 1H), 5.42 (s, 1H), 5.20 – 5.10 (m, 1H), 4.09 (m, *J* = 7.1, 6.4, 4.4, 1.9 Hz, 4H), 3.78 (s, 3H), 3.16 (t, *J* = 7.5 Hz, 1H), 2.92 (dd, *J* = 16.8, 7.1 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.59 (s, 9H), 1.21 – 1.16 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.70, 168.64, 161.54, 156.79, 149.11, 141.53, 141.46, 131.49, 130.01, 125.95, 122.97, 122.94, 116.18, 114.48, 114.46, 113.44, 111.20, 84.27, 61.30, 60.33, 56.79, 56.77, 55.61, 51.66, 41.17, 31.50, 29.65, 28.02, 21.00, 14.16, 14.00; MS (EI) [M]+ Calcd for $C_{31}H_{36}FNO_8$: 569.2425, found for $C_{31}H_{36}FNO_8$: 569.2451.

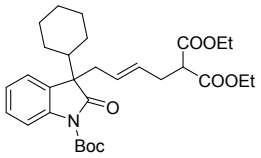
diethyl-2-(4-(1-(tert-butoxycarbonyl)-2-oxo-3-(4-phenylbutyl)indolin-3-yl)but-2-en-1-yl)malonate (3p):



The title compound was prepared according to the general procedure as a white solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.11 (m, 8H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.82 (m, *J* = 8.2 Hz, 1H), 5.38 (m, 1H), 5.29 – 5.18 (m, 1H), 4.12 (m, *J* = 7.1, 4.6, 2.6 Hz, 4H),

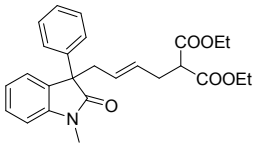
3.20 (t, *J* = 7.5 Hz, 1H), 2.66 (m, *J* = 10.4, 4.3 Hz, 2H), 2.55 (m, *J* = 13.5, 7.2 Hz, 2H), 2.44 (m, *J* = 3.1 Hz, 2H), 2.03 (s, 1H), 1.57 (s, 9H), 1.21 (td, *J* = 9.0, 6.0, 1.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.63, 168.74, 168.70, 149.02, 139.47, 137.00, 134.29, 130.71, 130.08, 128.83, 128.80, 128.35, 128.11, 127.28, 126.39, 126.18, 124.21, 123.28, 123.15, 114.93, 84.13, 61.32, 53.37, 51.84, 41.14, 40.37, 31.57, 27.99, 21.03, 14.18, 14.03; MS (EI) [M]+ Calcd for $C_{34}H_{41}NO_7$: 575.2883, found for $C_{34}H_{41}NO_7$: 575.2854.

diethyl-2-(4-(1-(tert-butoxycarbonyl)-3-cyclohexyl-2-oxoindolin-3-yl)but-2-en-1-yl)malonate (3q):



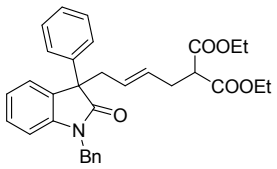
The title compound was prepared according to the general procedure as an oil liquid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.11 (m, *J* = 6.7, 0.9 Hz, 2H), 5.30 (m, *J* = 14.2, 6.9 Hz, 1H), 5.13 – 5.03 (m, 1H), 3.10 (t, *J* = 7.5 Hz, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 2.35 (dd, *J* = 12.7, 6.6 Hz, 2H), 1.87 – 1.74 (m, 1H), 1.73 – 1.48 (m, 14H), 1.21 – 0.78 (m, 11H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.14, 168.69, 168.65, 149.03, 139.90, 130.25, 127.66, 126.78, 123.89, 123.54, 114.50, 84.00, 61.22, 56.49, 51.88, 45.71, 38.20, 26.99, 26.06, 20.97, 13.99; MS (EI) [M]+ Calcd for $C_{30}H_{41}NO_7$: 527.2883, found for $C_{30}H_{41}NO_7$: 527.2866.

diethyl-2-(4-(1-methyl-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3r):



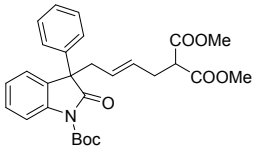
The title compound was prepared according to the general procedure as an oil liquid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 7H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.33 (dt, *J* = 14.1, 6.9 Hz, 1H), 5.13 – 5.03 (m, 1H), 4.05 (m, *J* = 8.5, 4.3 Hz, 4H), 3.14 (s, *J* = 2.7 Hz, 3H), 3.09 (s, *J* = 7.6 Hz, 1H), 2.88 (t, *J* = 14.4, 7.1 Hz, 2H), 2.39 – 2.29 (m, 2H), 1.15 (td, *J* = 7.1, 2.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.88, 168.74, 168.73, 143.76, 139.35, 128.48, 127.03, 126.99, 125.18, 122.39, 108.20, 61.32, 56.41, 51.86, 40.62, 31.54, 26.34, 14.04; MS (EI) [M]+ Calcd for $C_{26}H_{29}NO_5$: 435.2046, found for $C_{26}H_{29}NO_5$: 435.2058.

diethyl-2-(4-(1-benzyl-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3s):



The title compound was prepared according to the general procedure as a white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.26 (m, 6H), 7.26 – 7.17 (m, 4H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.51 – 5.41 (m, 1H), 5.25 – 5.15 (m, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.83 (d, *J* = 15.7 Hz, 1H), 4.17 – 4.08 (m, 4H), 3.16 (d, *J* = 7.6 Hz, 1H), 3.05 (m, *J* = 7.1 Hz, 2H), 2.50 – 2.33 (m, 2H), 1.23 (td, *J* = 12.4, 5.7, 3.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.35, 168.69, 168.66, 149.24, 131.02, 128.91, 128.53, 127.49, 127.23, 126.53, 125.59, 114.89, 84.07, 61.28, 61.26, 56.77, 51.80, 41.14, 29.66, 29.62, 28.05, 21.11, 14.09, 14.01; MS (EI) [M]+ Calcd for $C_{32}H_{33}NO_5$: 511.2359, found for $C_{32}H_{33}NO_5$: 511.2362.

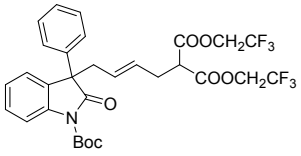
dimethyl-2-(4-(1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3u):



The title compound was prepared according to the general procedure as a white solid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J*

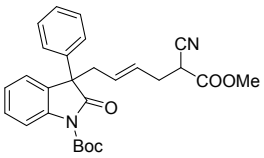
= 8.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.23 – 7.15 (m, 5H), 7.12 (m, *J* = 6.9, 1.0 Hz, 2H), 5.31 (m, 1H), 5.11 (m, *J* = 15.2, 7.2 Hz, 1H), 3.57 (d, *J* = 6.2 Hz, 6H), 3.13 (t, *J* = 7.5 Hz, 1H), 2.91 (m, *J* = 12.8, 7.1 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.54 (s, *J* = 5.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.20, 169.06, 169.04, 149.19, 139.78, 139.05, 130.95, 130.24, 128.57, 128.43, 127.59, 127.21, 126.64, 125.23, 124.31, 115.14, 84.33, 56.66, 52.47, 51.43, 41.25, 31.58, 29.67, 28.03, 21.04, 14.18; MS (EI) [M]+ Calcd for $C_{28}H_{31}NO_7$: 493.2101, found for $C_{28}H_{31}NO_7$: 493.2115.

bis(2,2,2-trifluoroethyl)-2-(4-(1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)but-2-en-1-yl)malonate (3v):



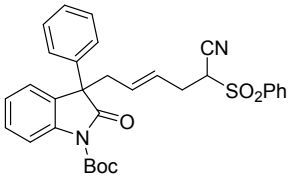
The title compound was prepared according to the general procedure as an oil liquid in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.11 (m, 8H), 5.33 (m, 1H), 5.20 – 5.08 (m, 1H), 4.43 – 4.28 (m, 4H), 3.33 (t, *J* = 7.4 Hz, 1H), 2.99 (m, *J* = 7.8 Hz, 1H), 2.87 (m, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.54 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.11, 166.23, 149.19, 139.83, 139.09, 130.18, 129.58, 128.62, 128.49, 127.89, 127.66, 127.13, 125.10, 124.38, 115.16, 84.44, 56.65, 50.71, 41.10, 31.24, 28.00; MS (EI) [M]+ Calcd for $C_{30}H_{29}F_6NO_7$: 629.1848, found for $C_{30}H_{29}F_6NO_7$: 629.1852.

tert-butyl-3-(5-cyano-6-methoxy-6-oxohex-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3w):



The title compound was prepared according to the general procedure as a white solid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.42 – 7.21 (m, 8H), 5.54 – 5.42 (m, 1H), 5.38 – 5.26 (m, 1H), 3.75 (t, *J* = 13.3 Hz, 3H), 3.30 (s, 1H), 3.10 (s, 1H), 3.05 – 2.93 (m, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.13, 176.09, 165.82, 165.74, 149.14, 139.79, 139.00, 138.97, 128.64, 127.68, 124.48, 124.43, 115.79, 115.76, 115.29, 84. 39, 56.60, 56.58, 53.46, 41.20, 37.40, 37.25, 32.50, 28.04, 21.03, 14.19; MS (EI) [M]+ Calcd for $C_{27}H_{28}N2O_5$: 460.1998, found for $C_{27}H_{28}N_2O_5$: 460.1992.

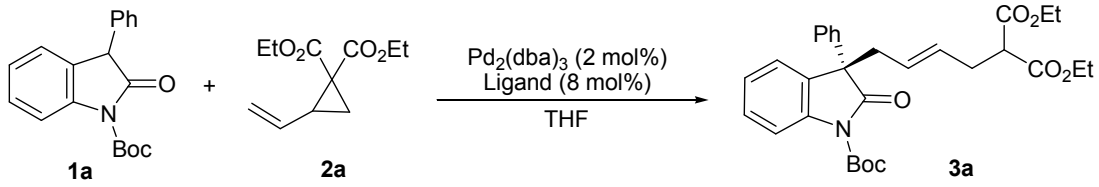
tert-butyl-3-(5-cyano-5-(phenylsulfonyl)pent-2-en-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3x):

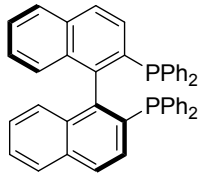


The title compound was prepared according to the general procedure as a white solid in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 3H), 7.75 (s, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.20 (m, 8H), 5.43 (m, *J* = 15.0, 7.5 Hz, 1H), 5.35 (m, *J* = 7.0 Hz, 1H), 3.68 (m, *J* = 24.0, 11.0, 4.1 Hz, 1H), 3.13 (td, *J* = 13.8, 7.6 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.73 (m, *J* = 8.7, 5.2 Hz, 1H), 2.38 (m, *J* = 11.8, 7.9 Hz, 1H), 1.58 (d, *J* = 9.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.11,176.06, 149.09, 149.04, 138.93, 135.38, 135.29, 128.68, 124.49, 115.36, 113.46, 113.41, 84.52, 57.22, 57.06, 56.66, 56.60, 41.22, 41.12, 29.75, 28.02, 21.05, 14.20; MS (EI) [M]+ Calcd for $C_{31}H_{30}N_2O_5S$: 542.1875, found for $C_{31}H_{30}N_2O_5S$: 542.1890.

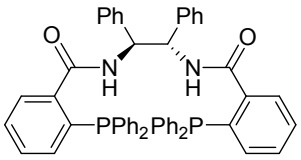
6 Asymmetric allyllation reaction:

The general procedure was followed: oxindole (30.9 mg, 0.10 mmol), catalyst $Pd_2(dba)_3$, ligands, and THF(1 mL). The product was isolated by column chromatography (hexanes/EA : 1/20) as white oil (50.5mg; 80% yield). HPLC analysis: [Daicel CHIRALPAK AD-H column; solvent system: 0.5% isopropanol/99.5% hexanes; 1.0 mL/min; retention times: 34.2 min (major), 41.5 min (minor)].

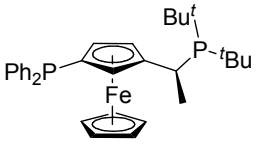




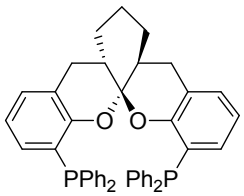
P-1
no reaction



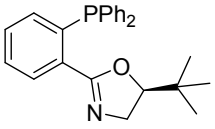
P-2
no reaction



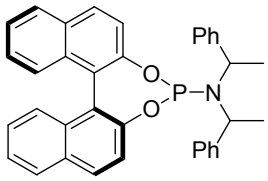
P-3
35%,[b] 7% ee[c]



P-4 (**SKP**)
99%, 25% ee
75%, 35% ee (at -25 °C)

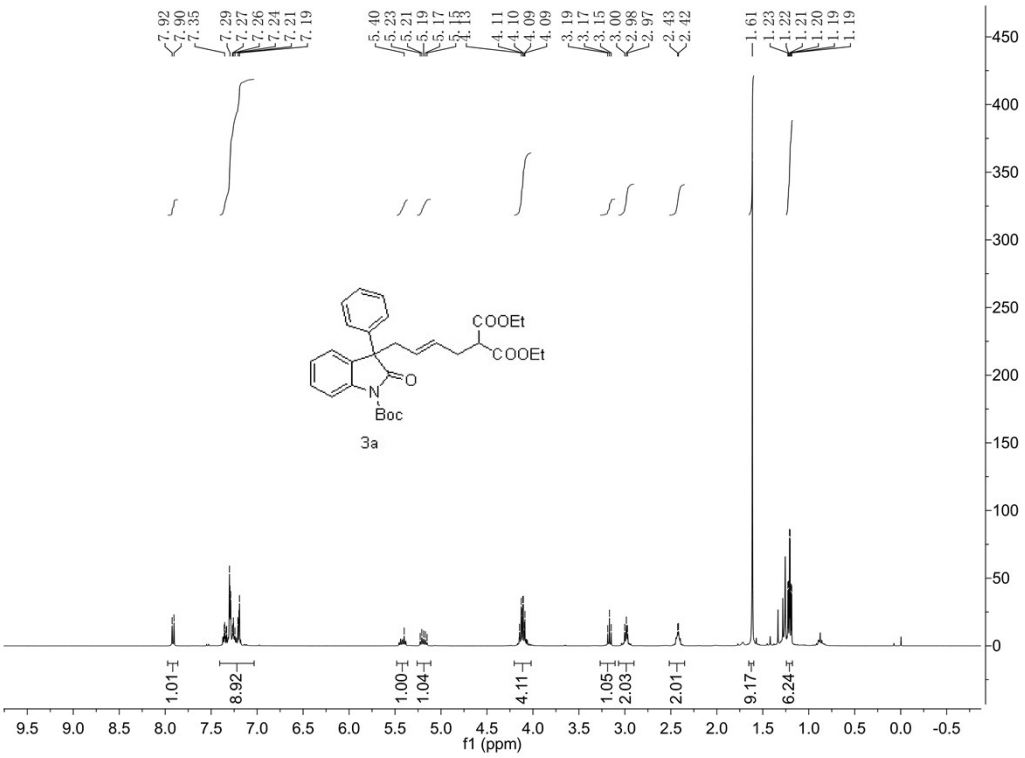


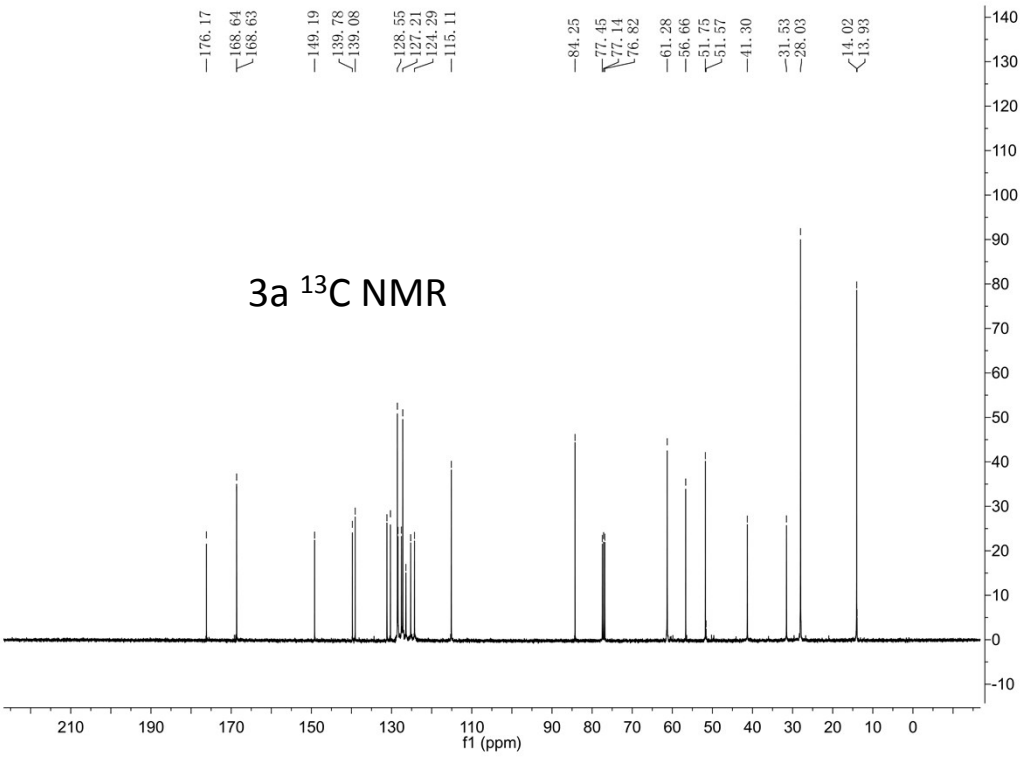
P-5
74%, 15% ee

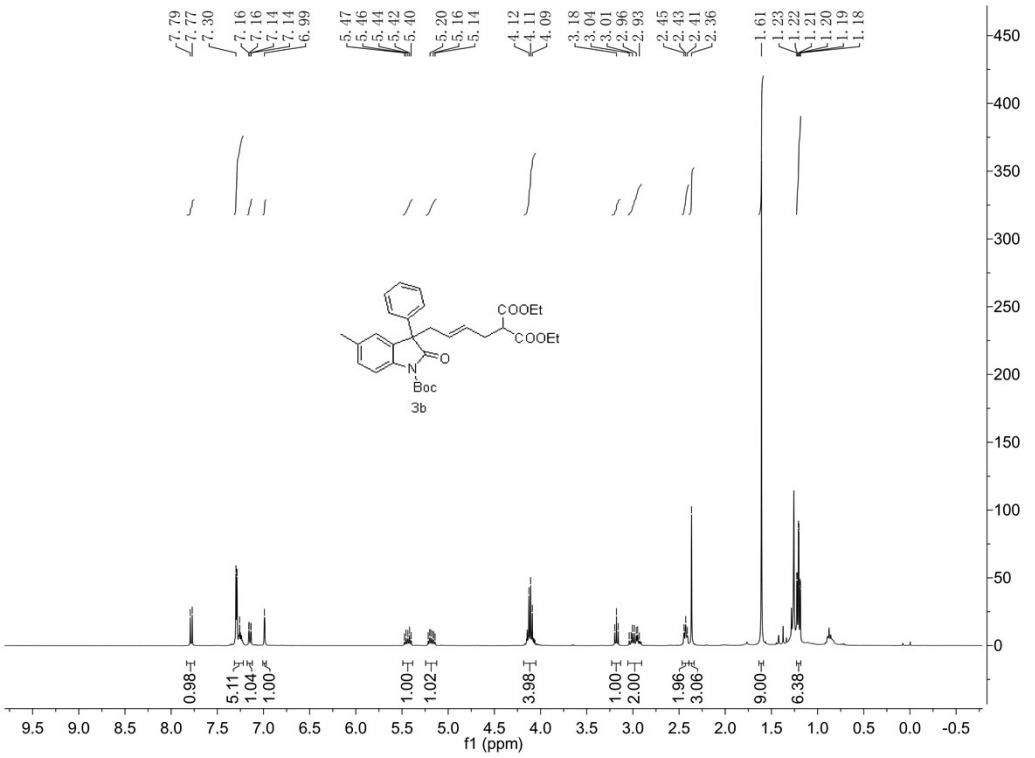


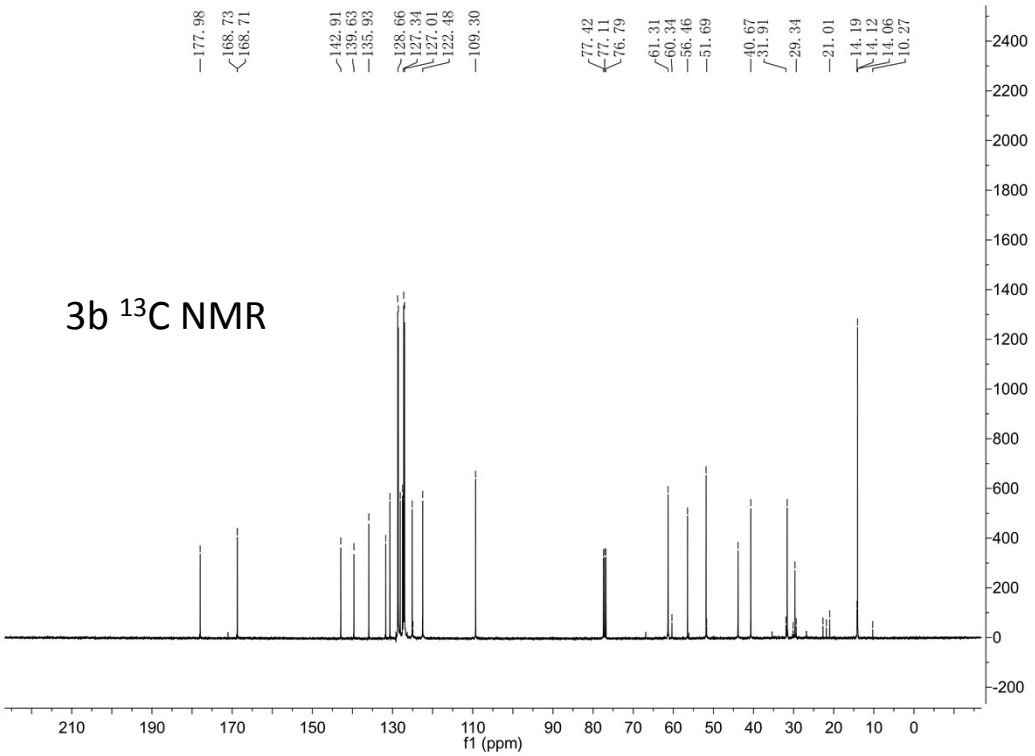
P-6
no reaction

7 ^{1}H and ^{13}C NMR spectras for all compounds

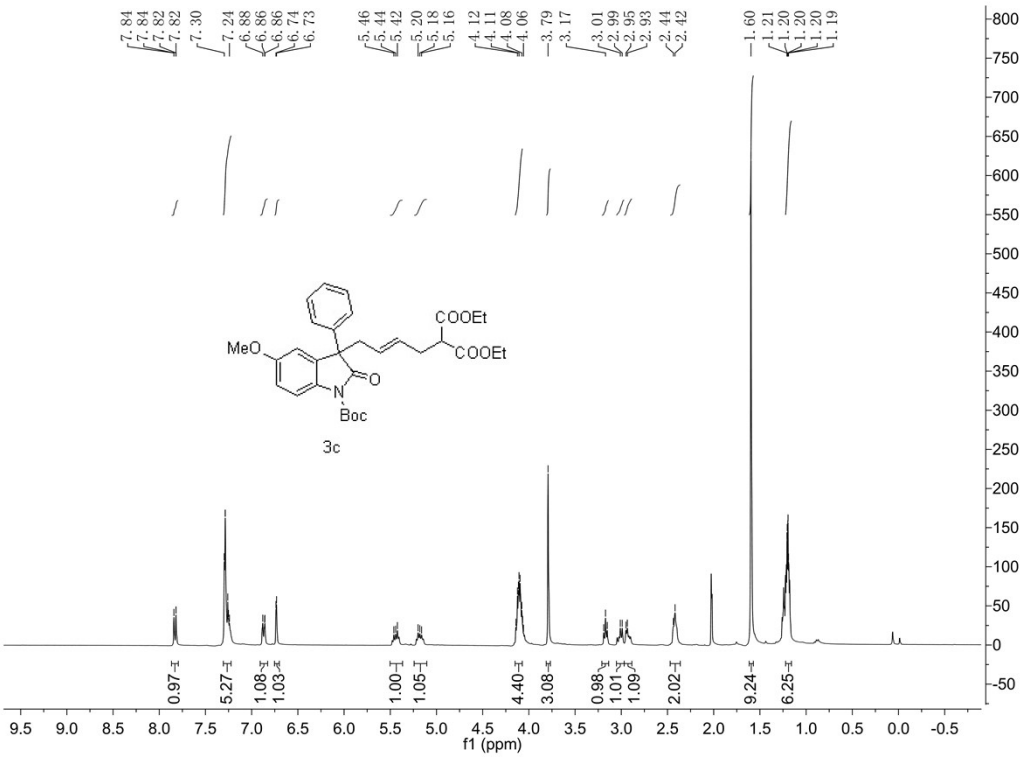


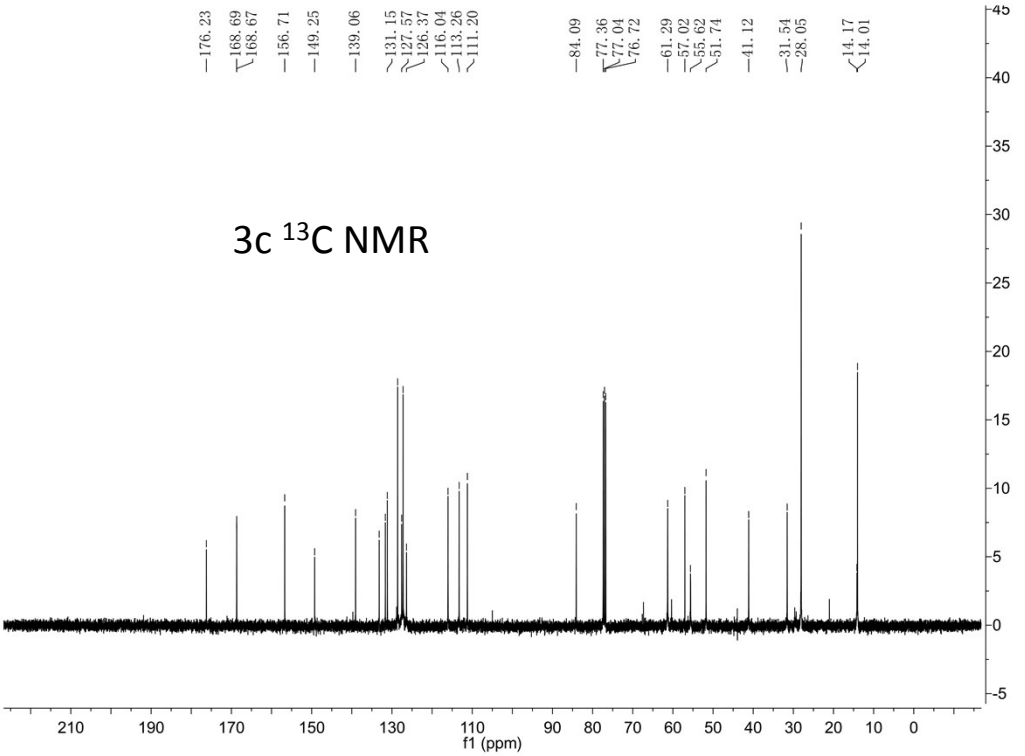


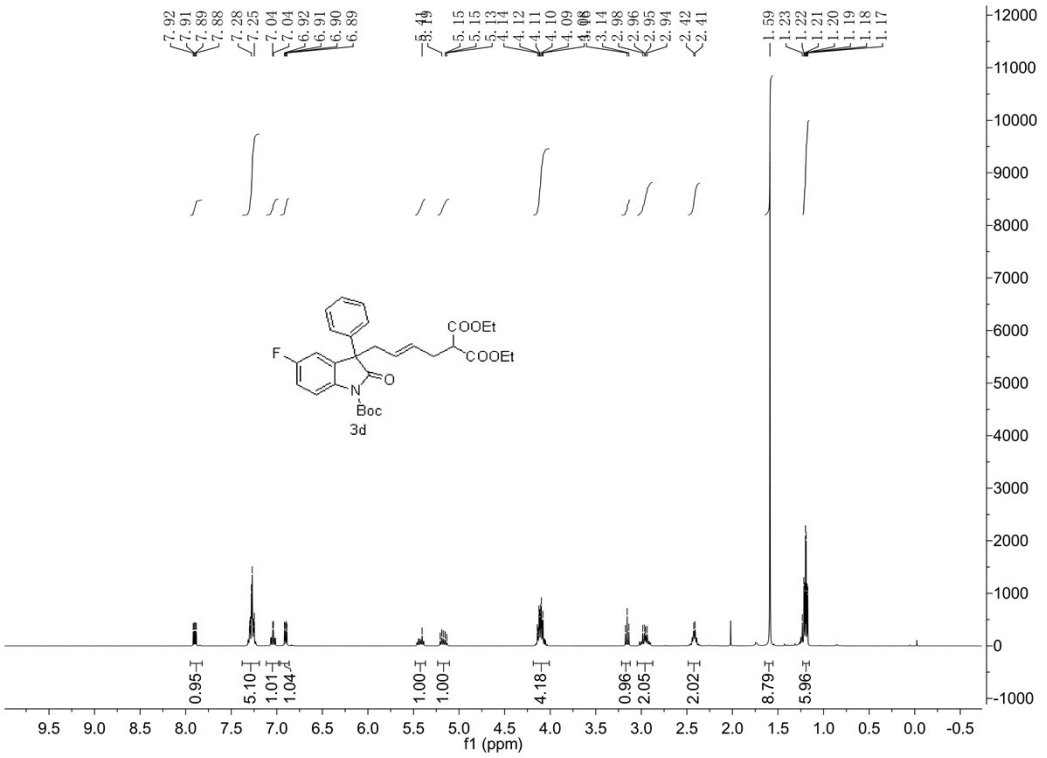

7.79
7.77
7.30
7.16
7.16
7.14
7.14
6.99
5.47
5.46
5.44
5.42
5.40
5.20
5.16
5.14
4.12
4.11
4.09
3.18
3.04
3.01
2.96
2.93
2.45
2.43
2.41
2.36
1.61
1.23
1.22
1.21
1.20
1.19
1.18
COOEt
COOEt
N
O
Boc
3b
0.98
5.11
1.04
1.00
1.00
1.02
3.98
1.00
2.00
1.96
3.06
9.00
6.38
f1 (ppm)

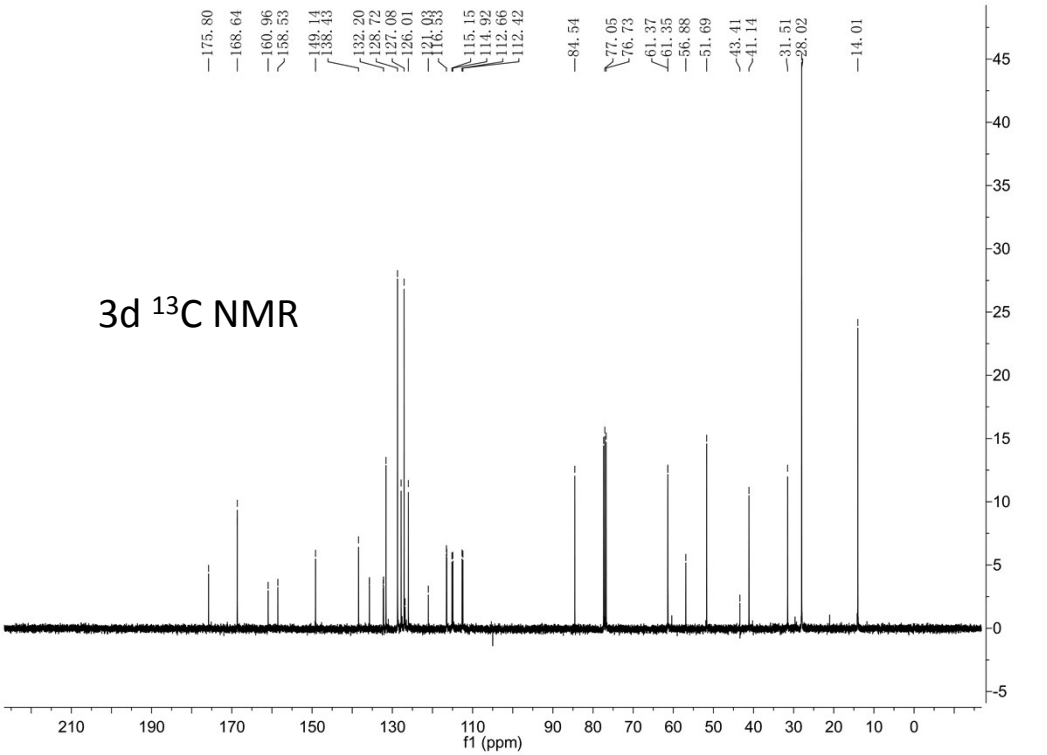

177.98
168.73
168.71
142.91
139.63
135.93
128.66
127.34
127.01
122.48
109.30
77.42
77.11
76.79
61.31
60.34
56.46
51.69
40.67
31.91
29.34
21.01
14.19
14.12
14.06
10.27
f1 (ppm)

3b ^{13}C NMR

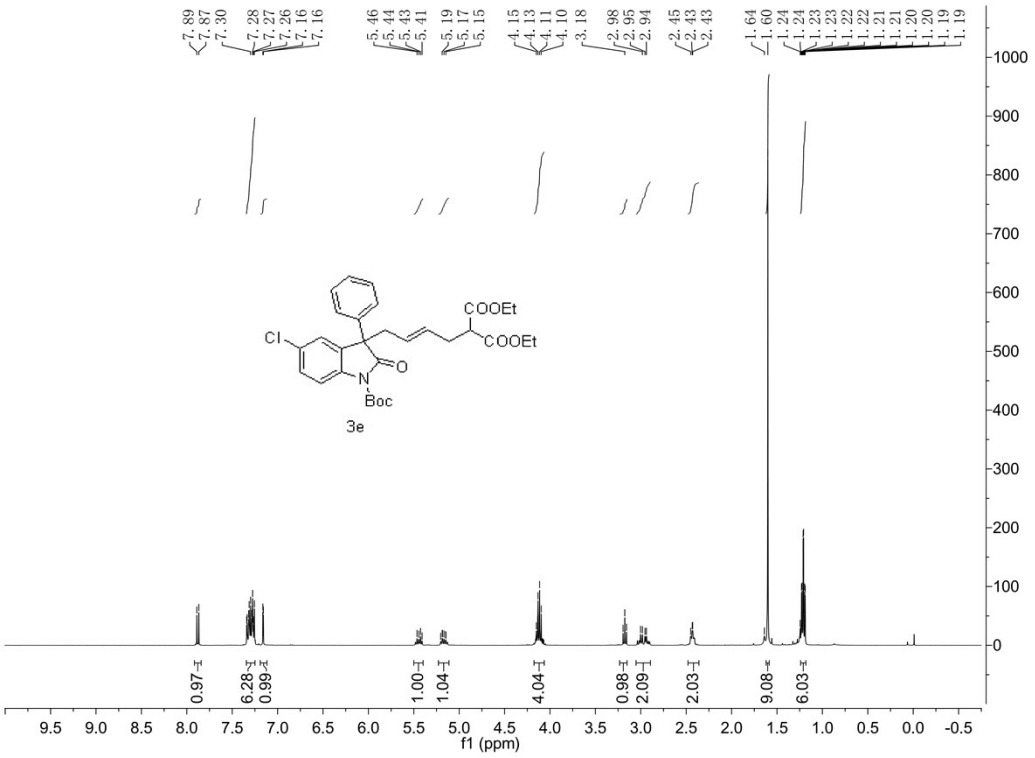

7.84
7.84
7.82
7.82
7.30
7.24
6.88
6.86
6.86
6.74
6.73
5.46
5.44
5.42
5.20
5.18
5.16
4.12
4.11
4.08
4.06
3.79
3.17
3.01
2.99
2.95
2.93
2.44
2.42
1.60
1.21
1.20
1.20
1.20
1.19
COOEt
COOEt
MeO
O
N
Boc
3c
0.97
5.27
1.08
1.03
1.00
1.05
4.40
3.08
0.98
1.01
1.09
2.02
9.24
6.25
f1 (ppm)

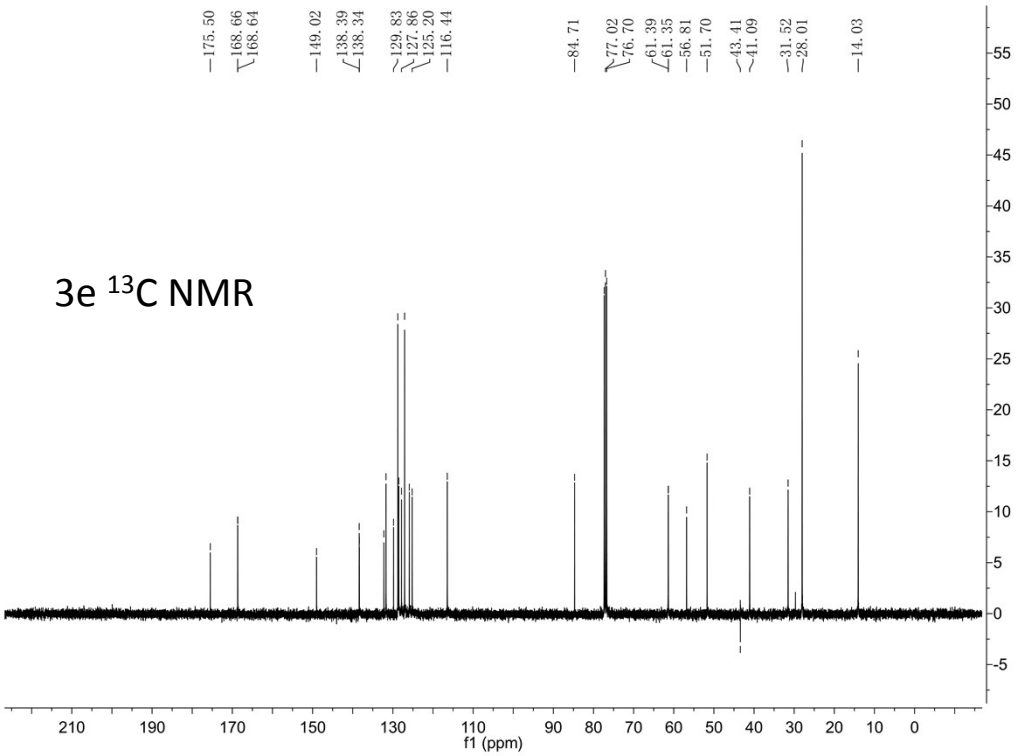

176.23
168.69
168.67
156.71
149.25
139.06
131.15
127.57
126.37
116.04
113.26
111.20
84.09
77.36
77.04
76.72
61.29
57.02
55.62
51.74
41.12
31.54
28.05
14.17
14.01
3c ^{13}C NMR
f1 (ppm)


7.92
7.91
7.89
7.88
7.28
7.25
7.04
7.04
6.92
6.91
6.90
6.89
5.15
5.15
5.13
4.14
4.12
4.11
4.10
4.09
3.14
2.98
2.96
2.95
2.94
2.42
2.41
1.59
1.23
1.22
1.21
1.20
1.19
1.18
1.17
COOEt
COOEt
F
O
N
Boc
3d
0.95
5.10
1.01
1.04
1.00
1.00
4.18
0.96
2.05
2.02
8.79
5.96
f1 (ppm)

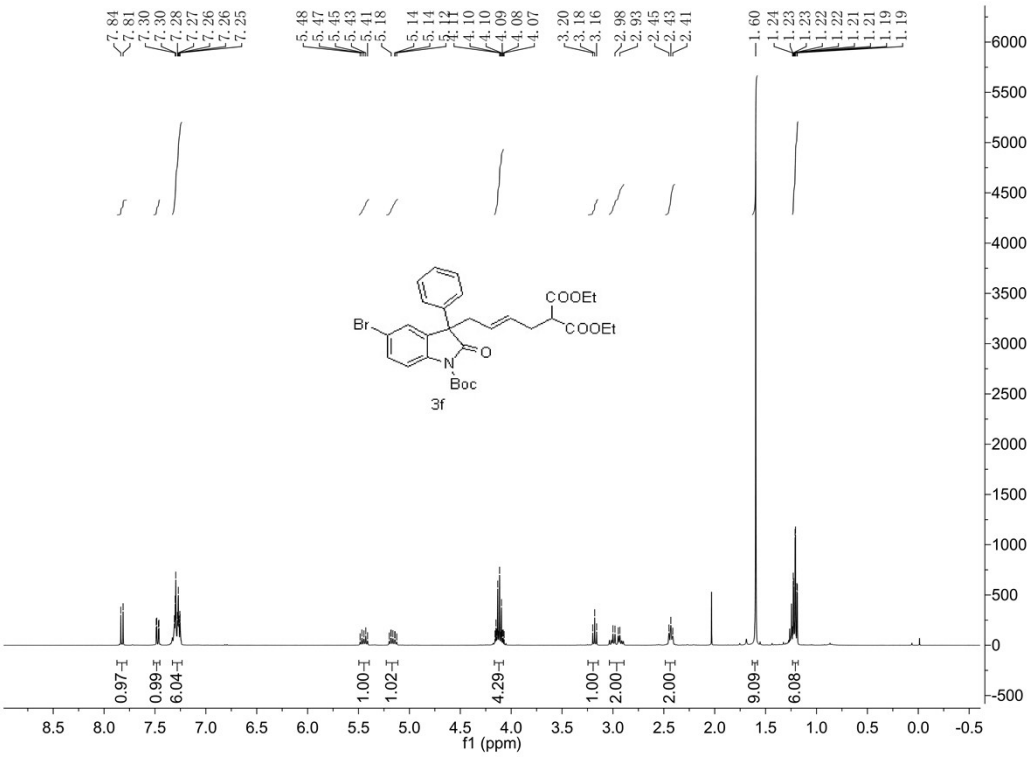

175.80
168.64
160.96
158.53
149.14
138.43
132.20
128.72
127.08
126.01
121.03
116.53
115.15
114.92
112.66
112.42
84.54
77.05
76.73
61.37
61.35
56.88
51.69
43.41
41.14
31.51
28.02
14.01
f1 (ppm)

3d ^{13}C NMR

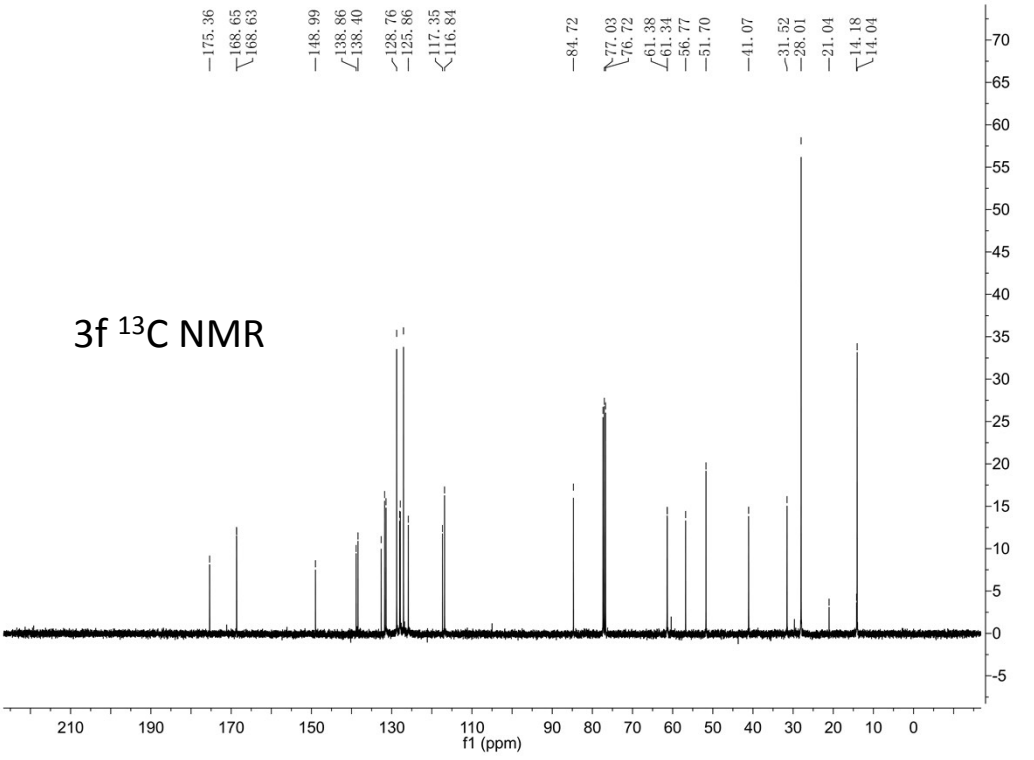

7.89
7.87
7.30
7.28
7.27
7.26
7.16
7.16
5.46
5.44
5.43
5.41
5.19
5.17
5.15
4.15
4.13
4.11
4.10
3.18
2.98
2.95
2.94
2.45
2.43
2.43
1.64
1.60
1.24
1.24
1.23
1.23
1.22
1.22
1.21
1.21
1.20
1.20
1.19
1.19
COOEt
COOEt
Cl
O
N
Boc
3e
0.97
6.28
0.99
1.00
1.04
4.04
0.98
2.09
2.03
9.08
6.03
f1 (ppm)

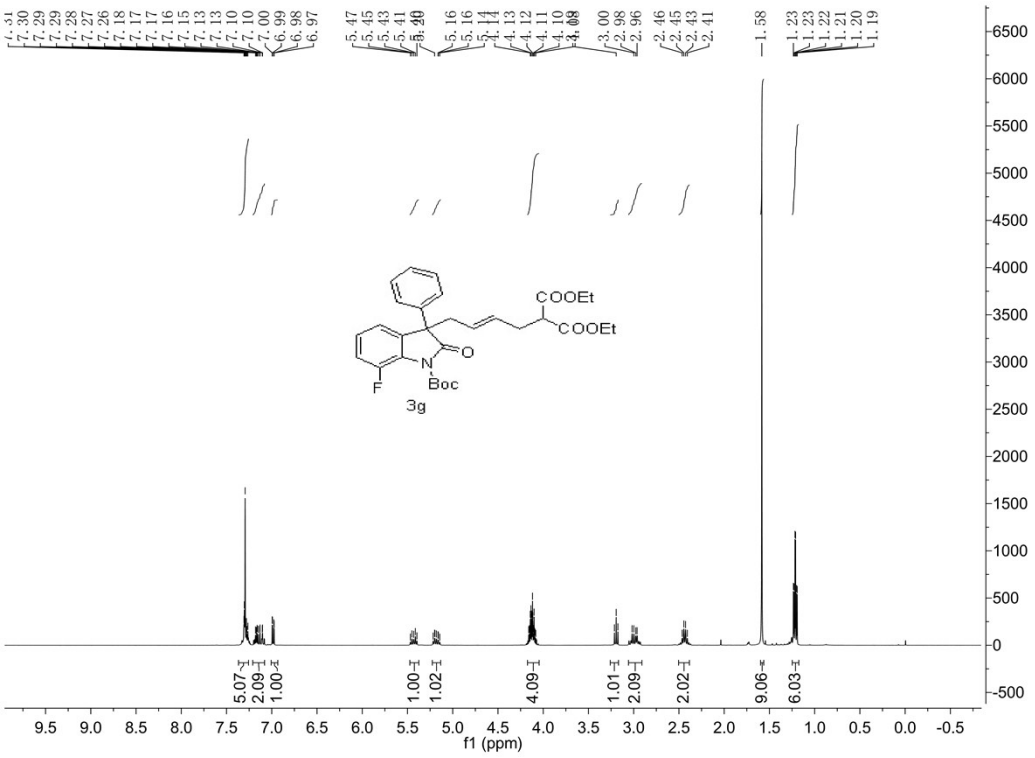

175.50
168.66
168.64
149.02
138.39
138.34
129.83
127.86
125.20
116.44
84.71
77.02
76.70
61.39
61.35
56.81
51.70
43.41
41.09
31.52
28.01
14.03
f1 (ppm)

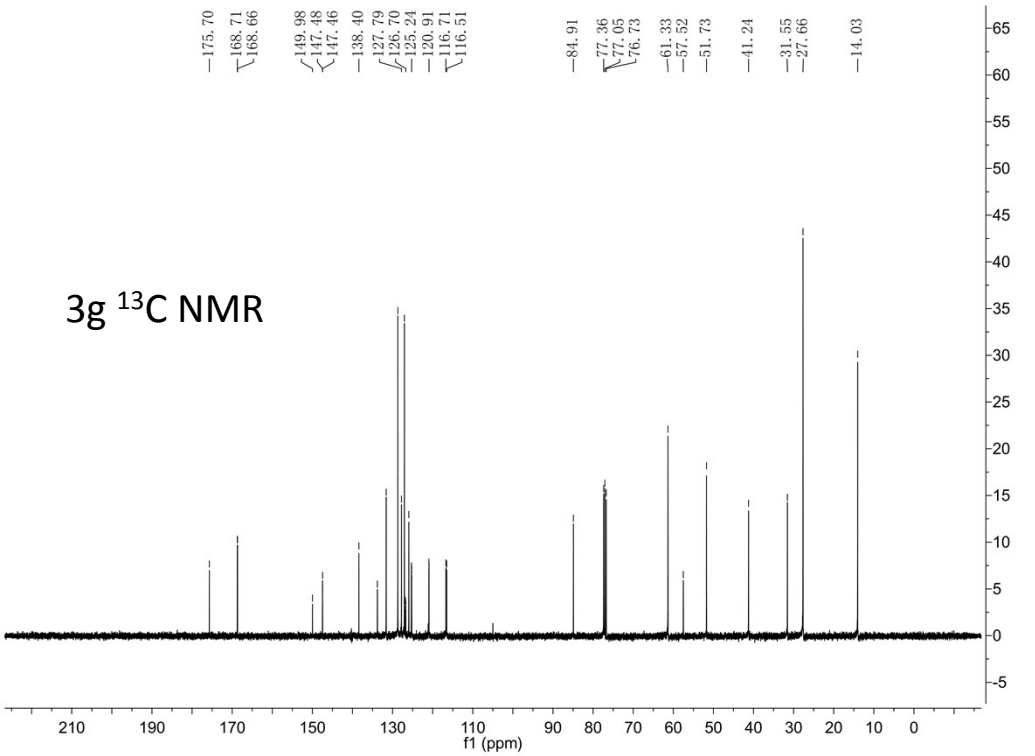
3e ^{13}C NMR

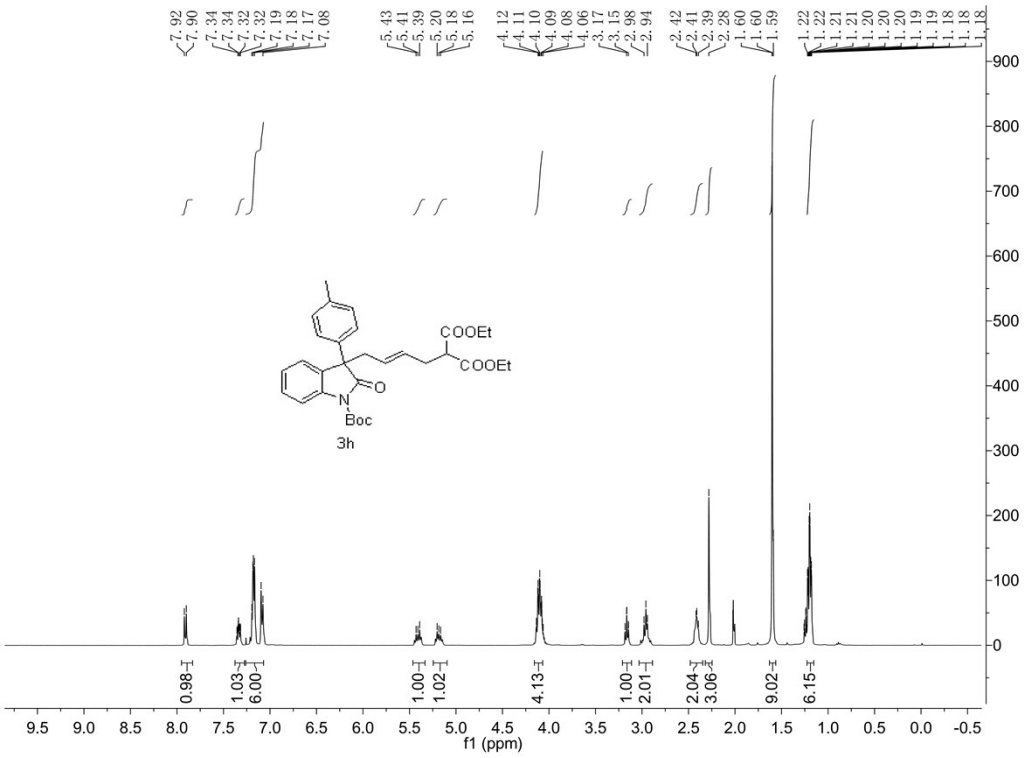

7.84
7.81
7.30
7.30
7.28
7.27
7.26
7.26
7.25
5.48
5.47
5.45
5.43
5.41
5.18
5.14
5.12
4.10
4.10
4.09
4.08
4.07
3.20
3.18
3.16
2.98
2.93
2.45
2.43
2.41
1.60
1.24
1.23
1.23
1.22
1.22
1.21
1.21
1.19
1.19
COOEt
COOEt
Br
O
N
Boc
3f
0.97
0.99
6.04
1.00
1.02
4.29
1.00
2.00
2.00
9.09
6.08
f1 (ppm)

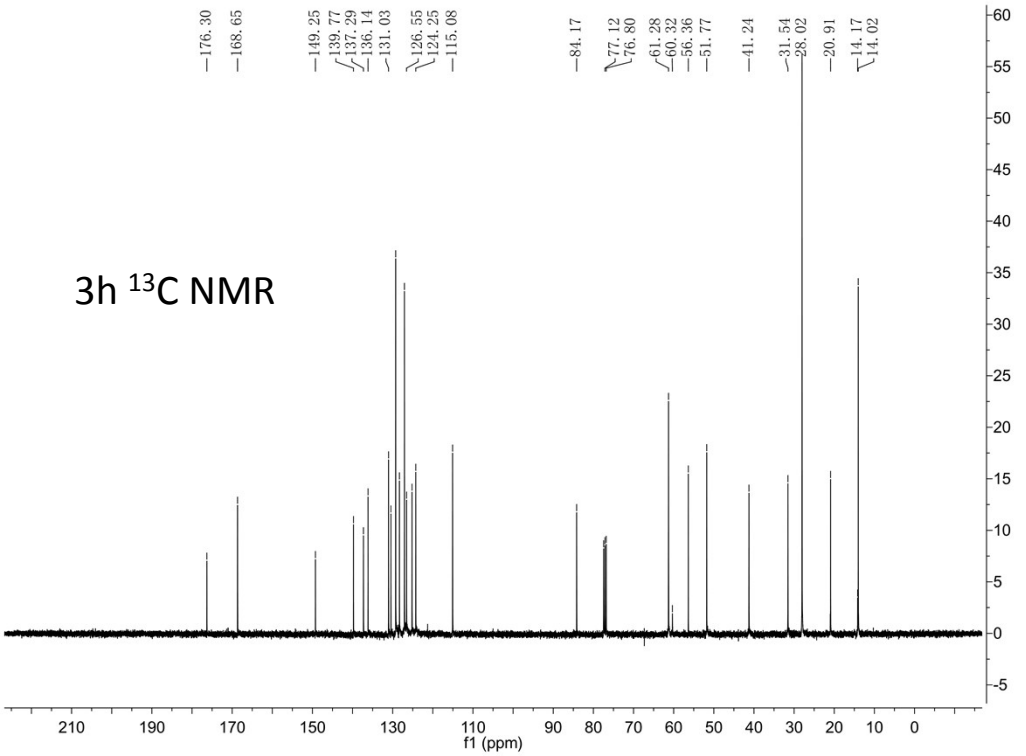
3f ^{13}C NMR


175.36
168.65
168.63
148.99
138.86
138.40
128.76
125.86
117.35
116.84
84.72
77.03
76.72
61.38
61.34
56.77
51.70
41.07
31.52
28.01
21.04
14.18
14.04
f1 (ppm)

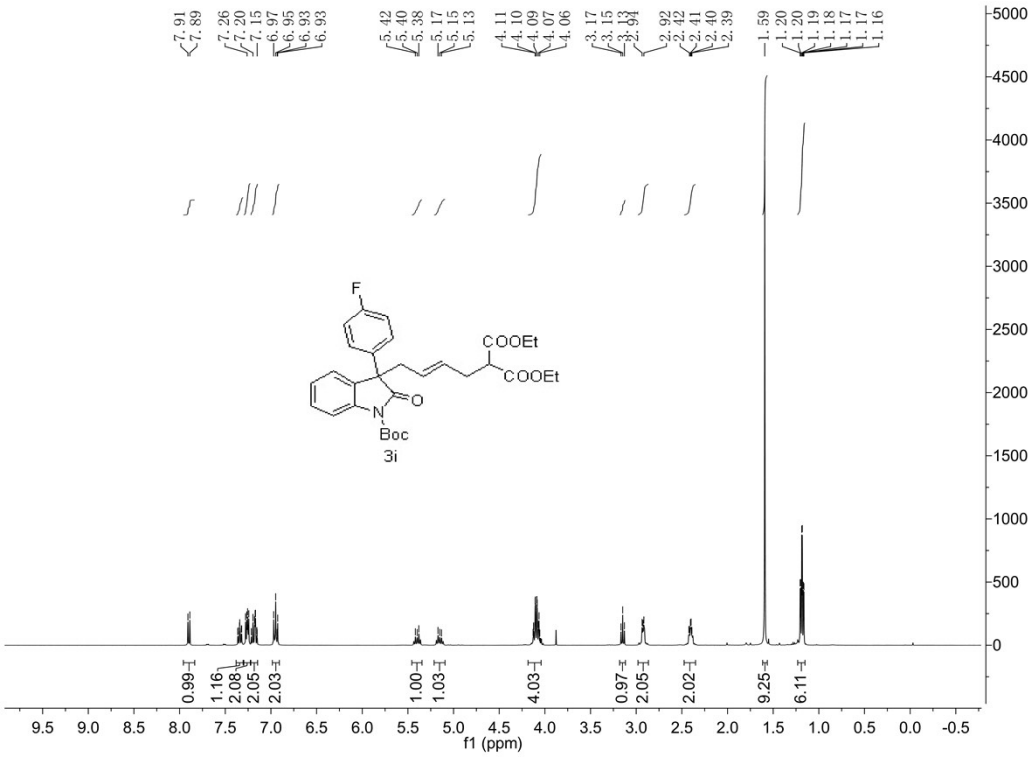

COOEt
COOEt
O
N
Boc
F
3g
f1 (ppm)

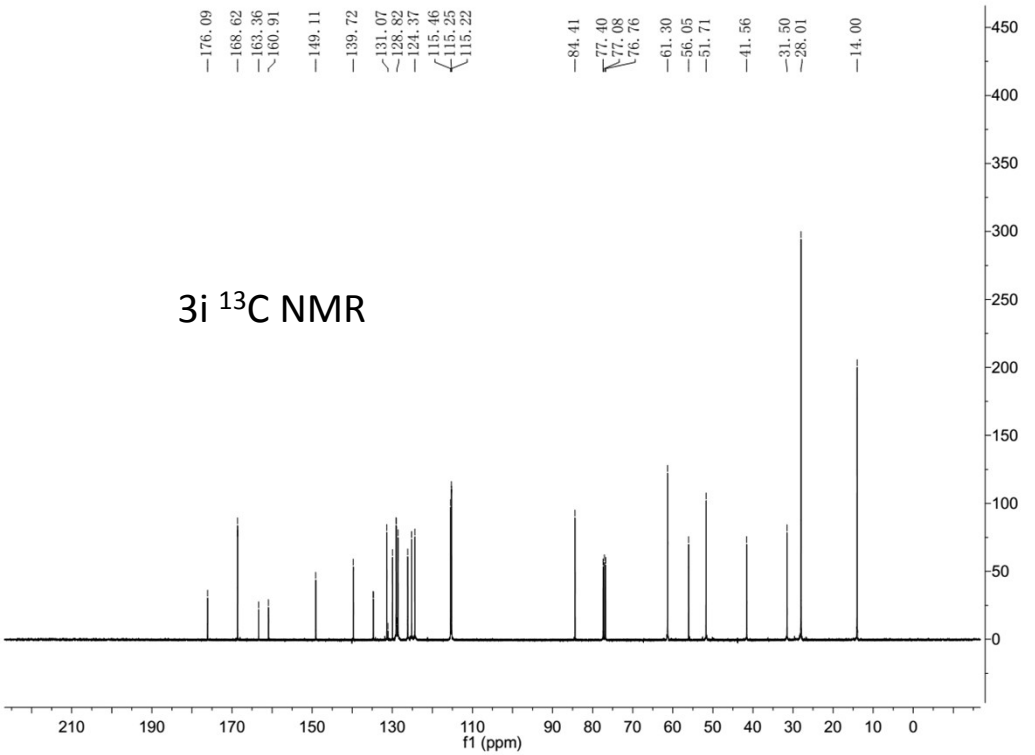

3g ^{13}C NMR
f1 (ppm)

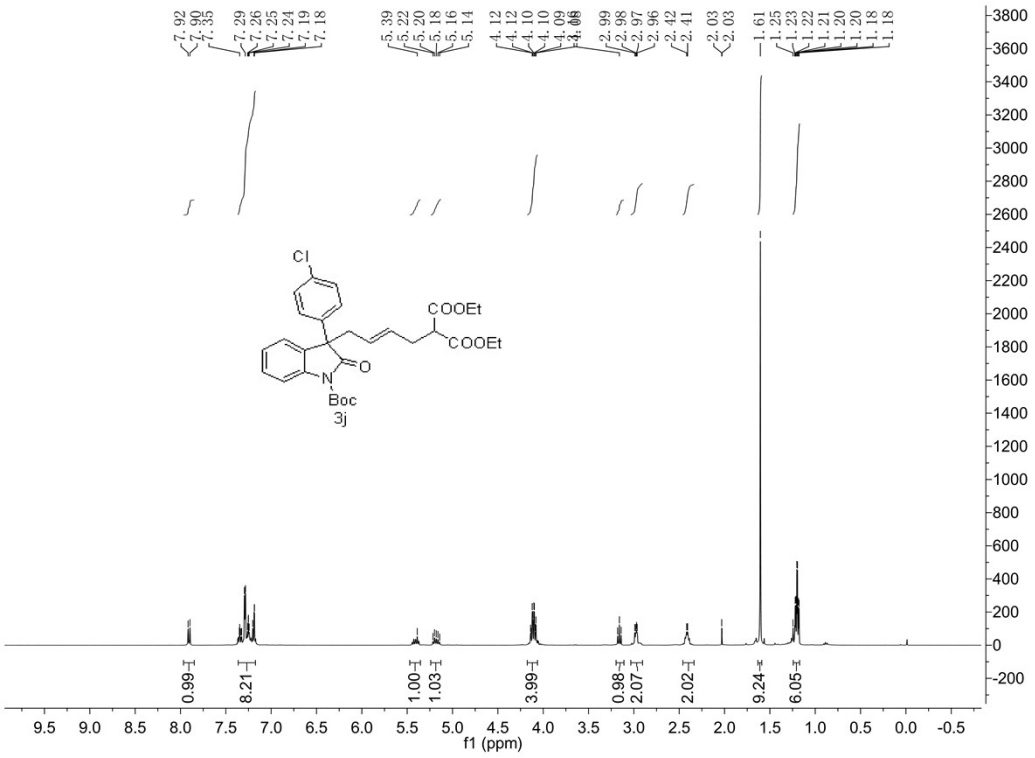

7.92
7.90
7.34
7.32
7.32
7.19
7.18
7.17
7.08
5.43
5.41
5.39
5.20
5.18
5.16
4.12
4.11
4.10
4.09
4.08
4.06
3.17
3.15
2.98
2.94
2.42
2.41
2.39
2.28
1.60
1.59
1.22
1.22
1.21
1.21
1.20
1.20
1.20
1.19
1.19
1.18
1.18
1.18
COOEt
COOEt
O
N
Boc
3h
0.98
1.03
6.00
1.00
1.02
4.13
1.00
2.01
2.04
3.06
9.02
6.15
f1 (ppm)


176.30
168.65
149.25
139.77
137.29
136.14
131.03
126.55
124.25
115.08
84.17
77.12
76.80
61.28
60.32
56.36
51.77
41.24
31.54
28.02
20.91
14.17
14.02
f1 (ppm)

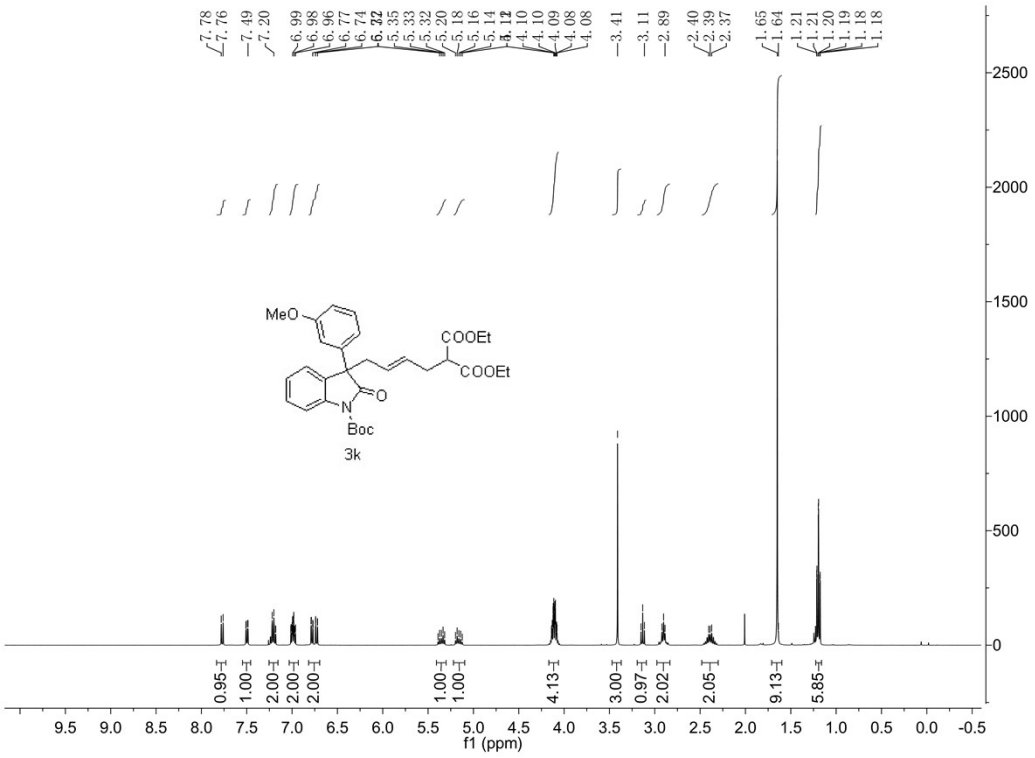
3h ^{13}C NMR

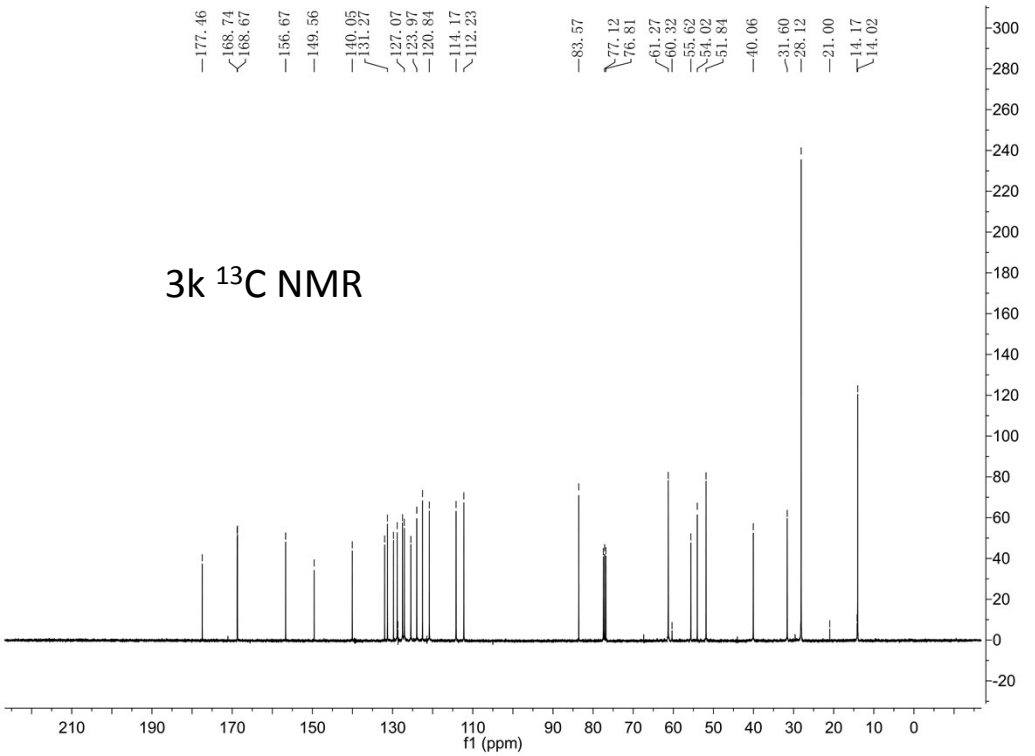

F
COOEt
COOEt
O
N
Boc
3i
f1 (ppm)

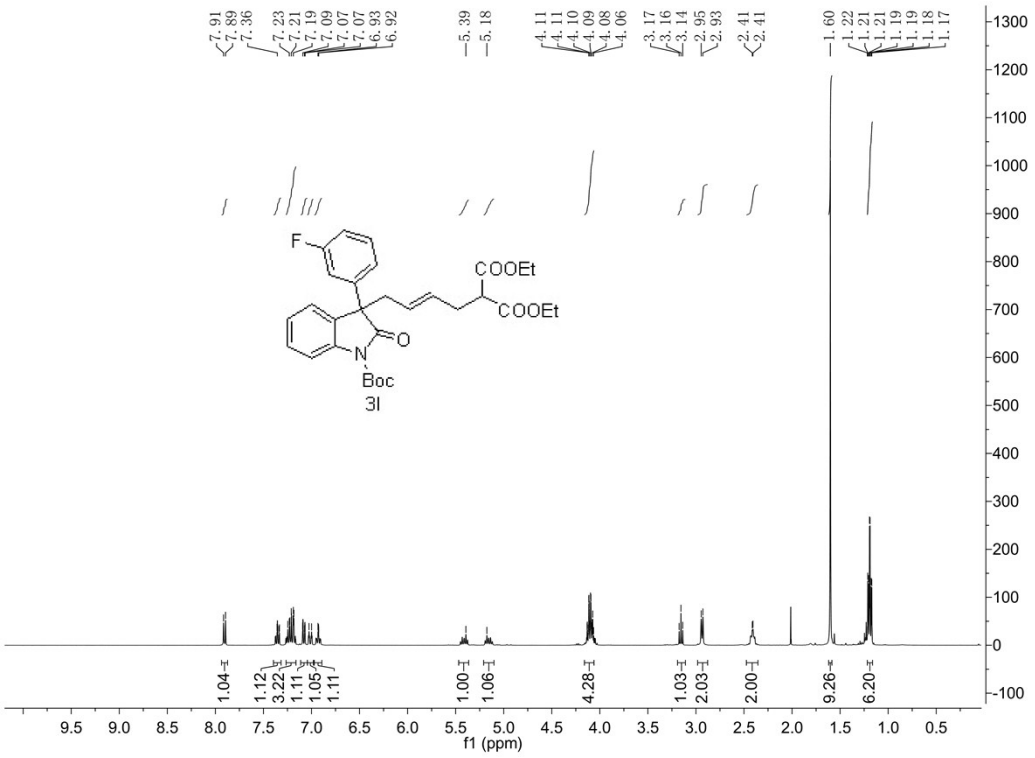

3i ^{13}C NMR
f1 (ppm)

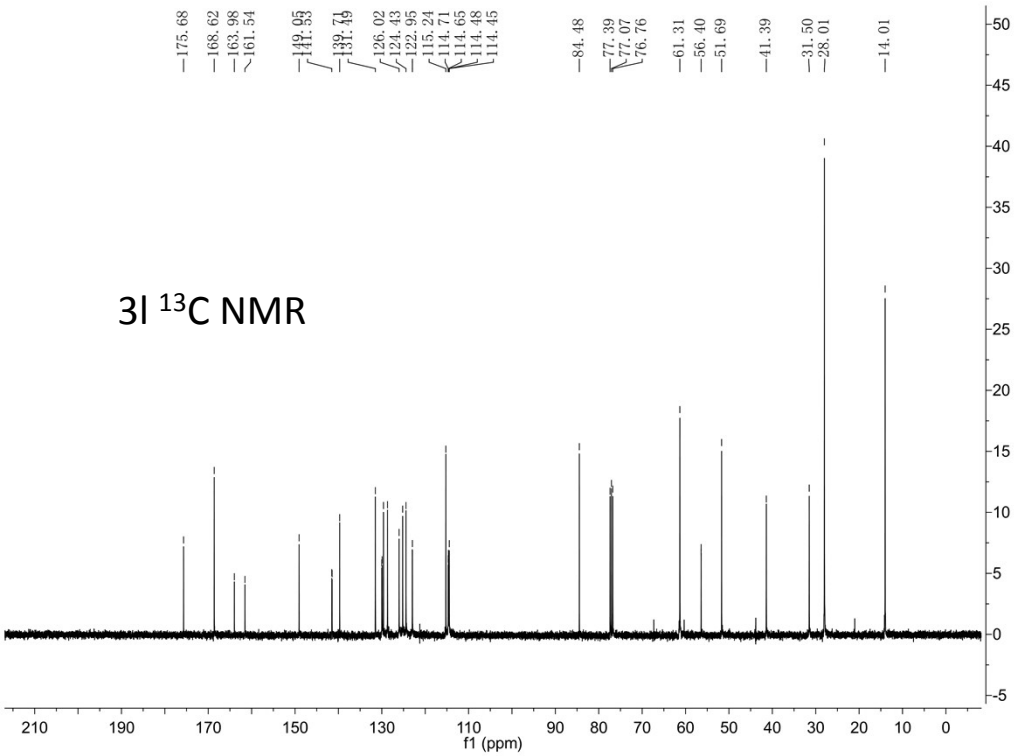


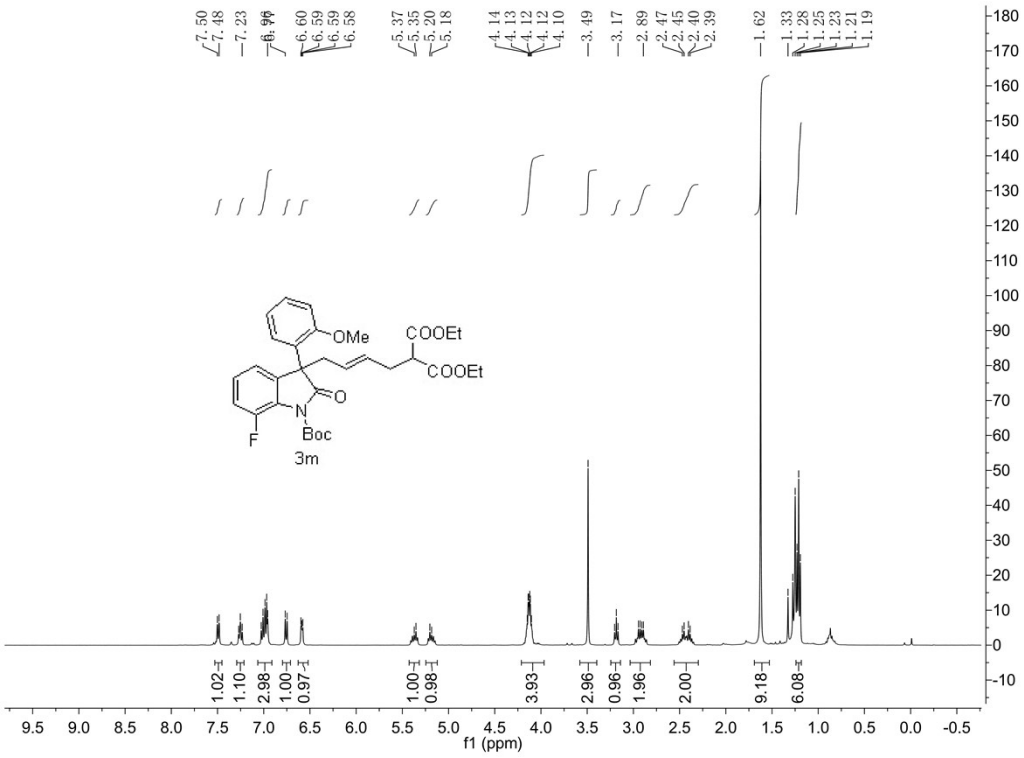
3j ^{13}C NMR

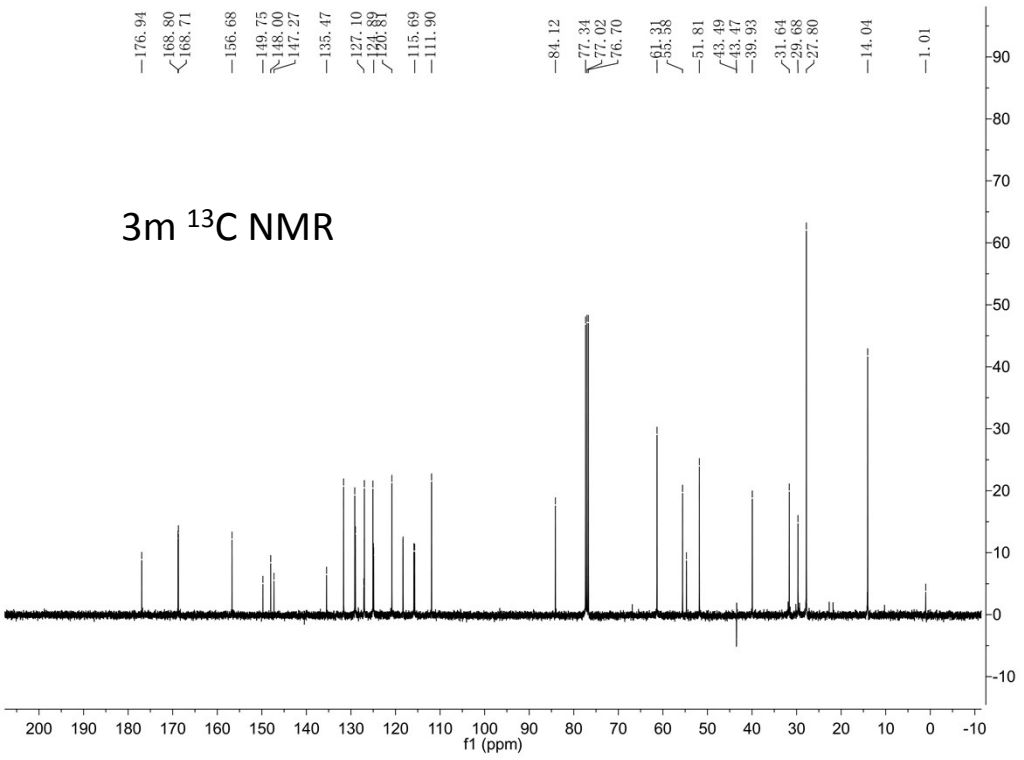

MeO
COOEt
COOEt
O
N
Boc
3k
f1 (ppm)

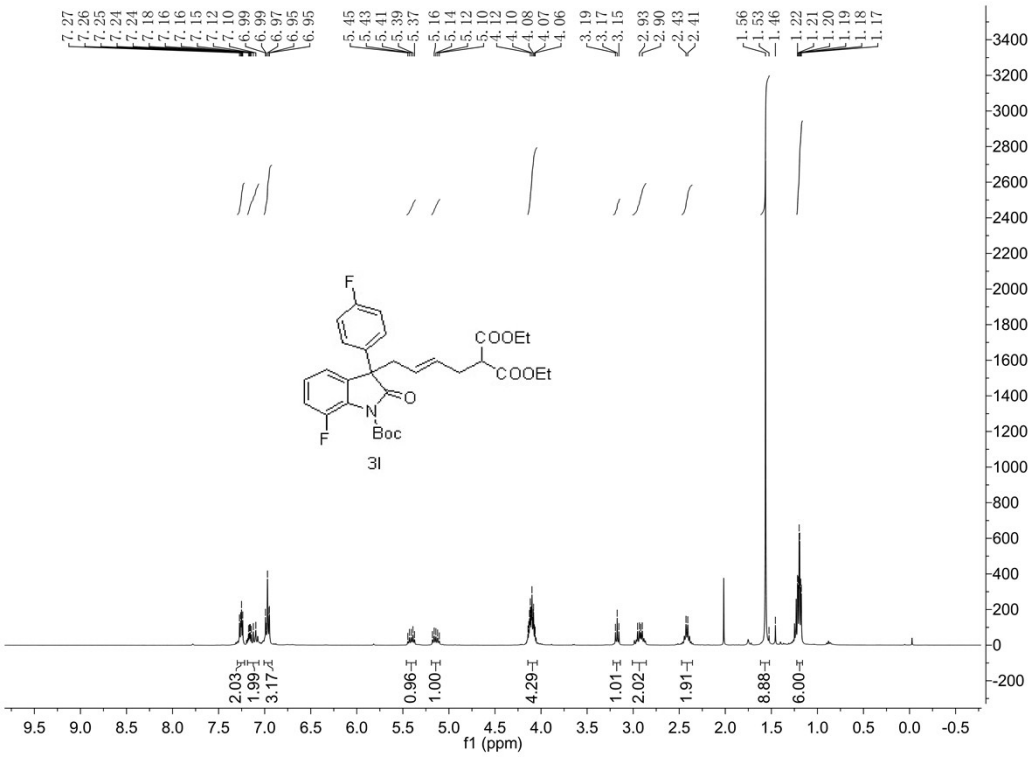

3k ^{13}C NMR
f1 (ppm)


F
COOEt
COOEt
O
N
Boc
3l
f1 (ppm)

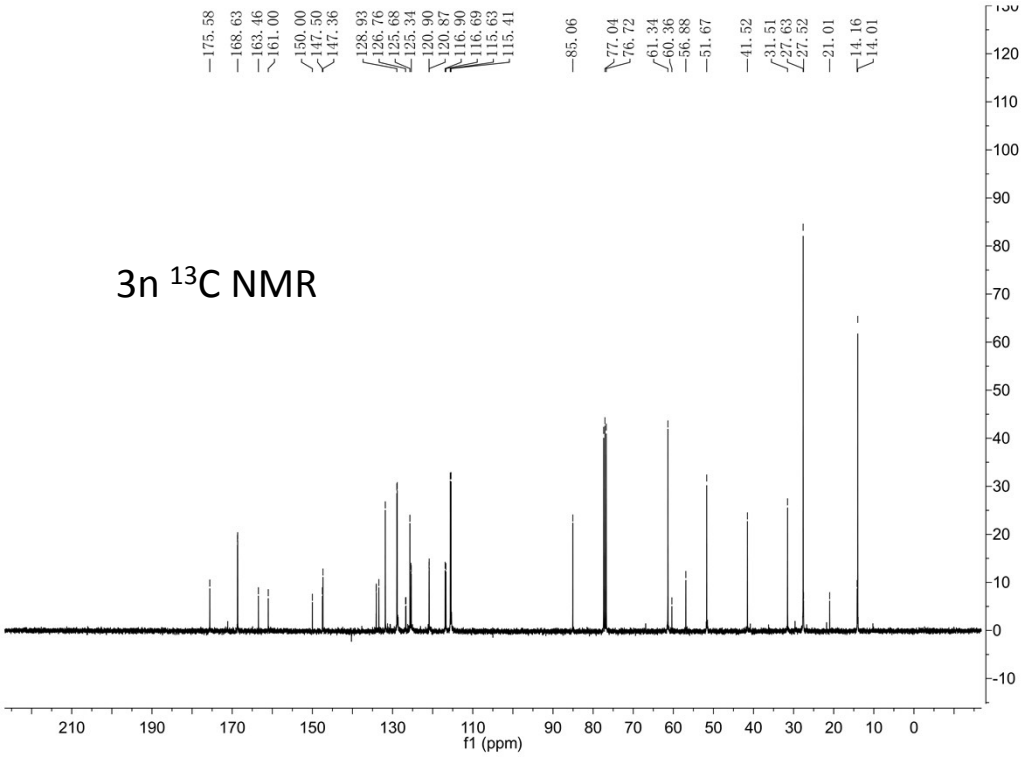

3l ^{13}C NMR
f1 (ppm)

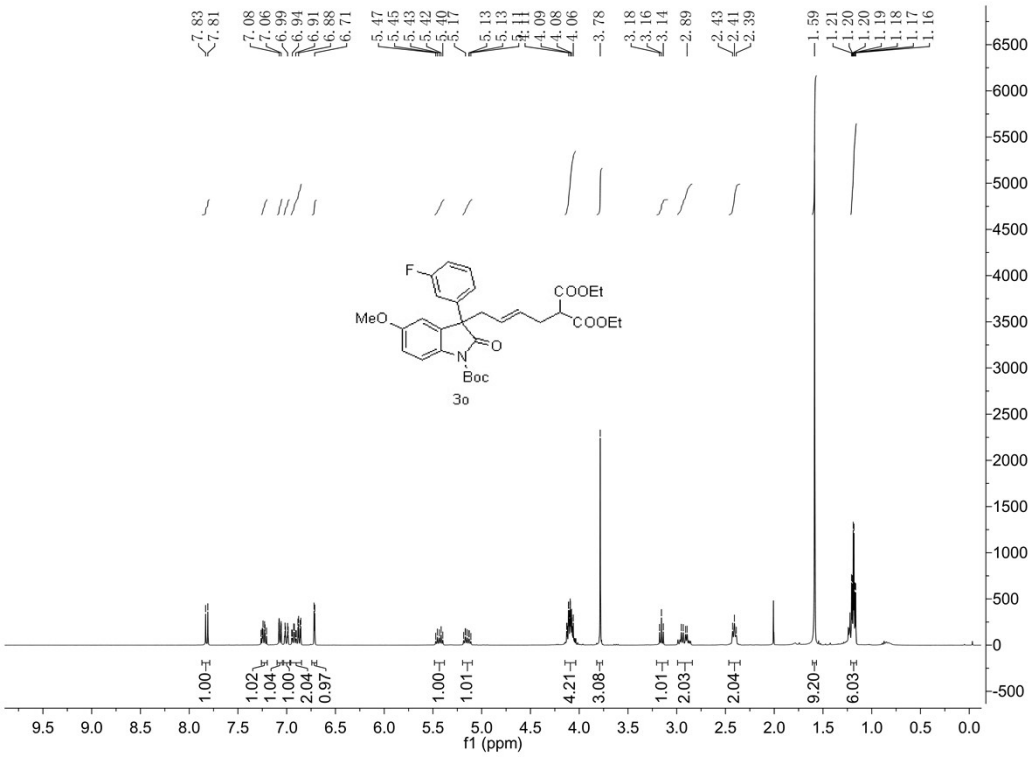

OMe
COOEt
COOEt
O
N
Boc
F
3m
f1 (ppm)

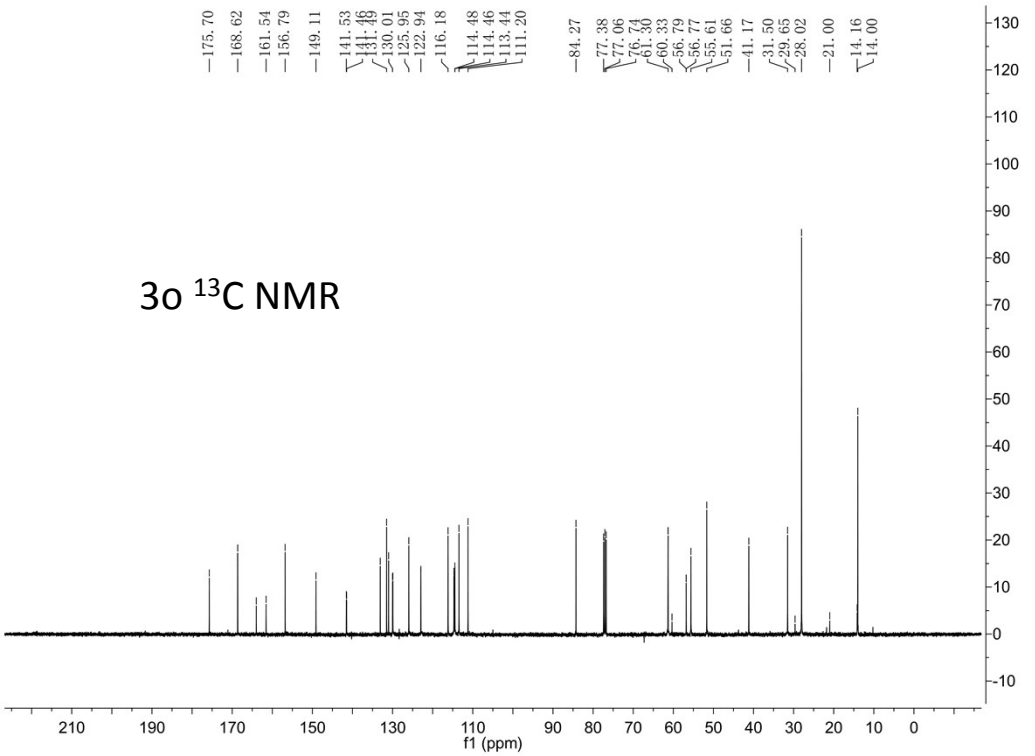

3m ^{13}C NMR
f1 (ppm)


7.27
7.26
7.25
7.24
7.24
7.18
7.16
7.16
7.15
7.12
7.10
6.99
6.99
6.97
6.95
6.95
5.45
5.43
5.41
5.39
5.37
5.16
5.14
5.12
5.10
4.12
4.10
4.08
4.07
4.06
3.19
3.17
3.15
2.93
2.90
2.43
2.41
1.56
1.53
1.46
1.22
1.21
1.20
1.19
1.18
1.17
F
COOEt
COOEt
O
N
Boc
F
3l
2.03
1.99
3.17
0.96
1.00
4.29
1.01
2.02
1.91
8.88
6.00
f1 (ppm)

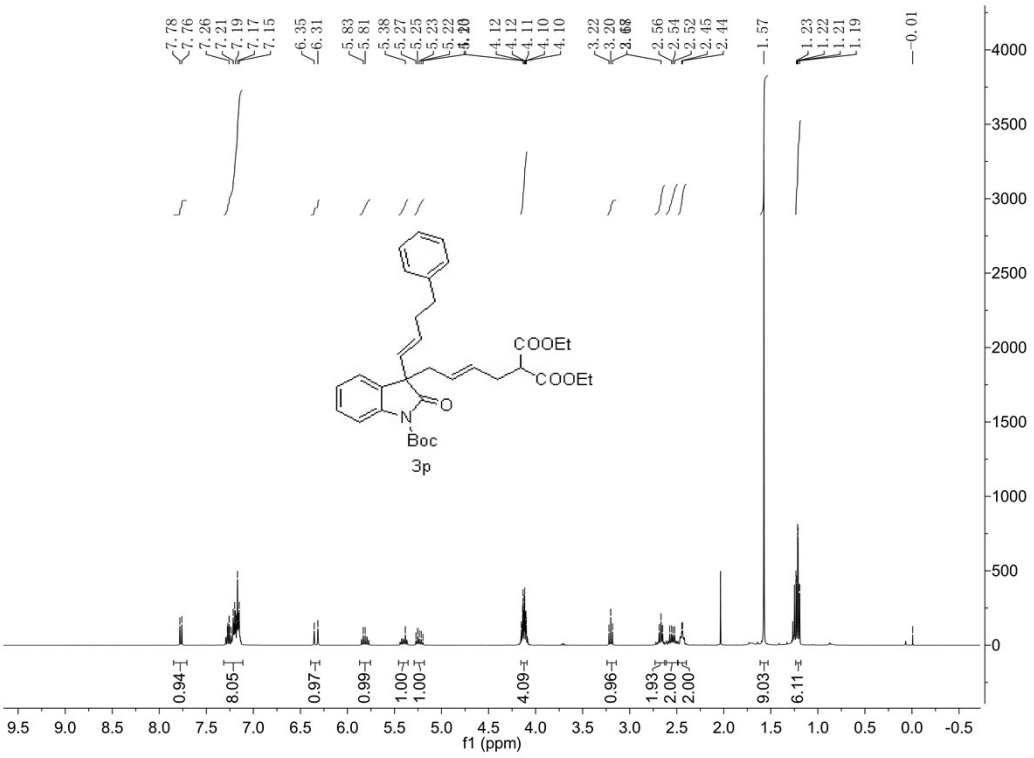
3n ^{13}C NMR


175.58
168.63
163.46
161.00
150.00
147.50
147.36
128.93
126.76
125.68
125.34
120.90
120.87
116.90
116.69
115.63
115.41
85.06
77.04
76.72
61.34
60.36
56.88
51.67
41.52
31.51
27.63
27.52
21.01
14.16
14.01
f1 (ppm)

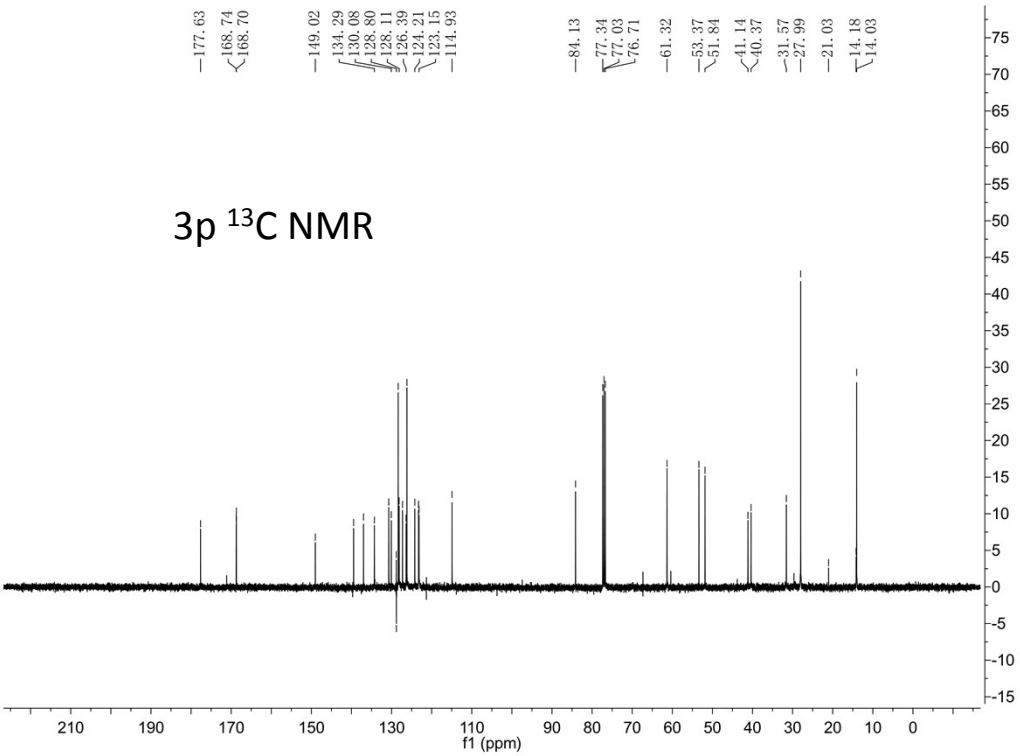

7.83
7.81
7.08
7.06
6.99
6.94
6.91
6.88
6.71
5.47
5.45
5.43
5.42
5.40
5.17
5.13
5.11
4.09
4.08
4.06
3.78
3.18
3.16
3.14
2.89
2.43
2.41
2.39
1.59
1.21
1.20
1.20
1.19
1.18
1.17
1.16
F
COOEt
COOEt
MeO
O
N
Boc
3o
1.00
1.02
1.04
1.00
2.04
0.97
1.00
1.01
4.21
3.08
1.01
2.03
2.04
9.20
6.03
f1 (ppm)

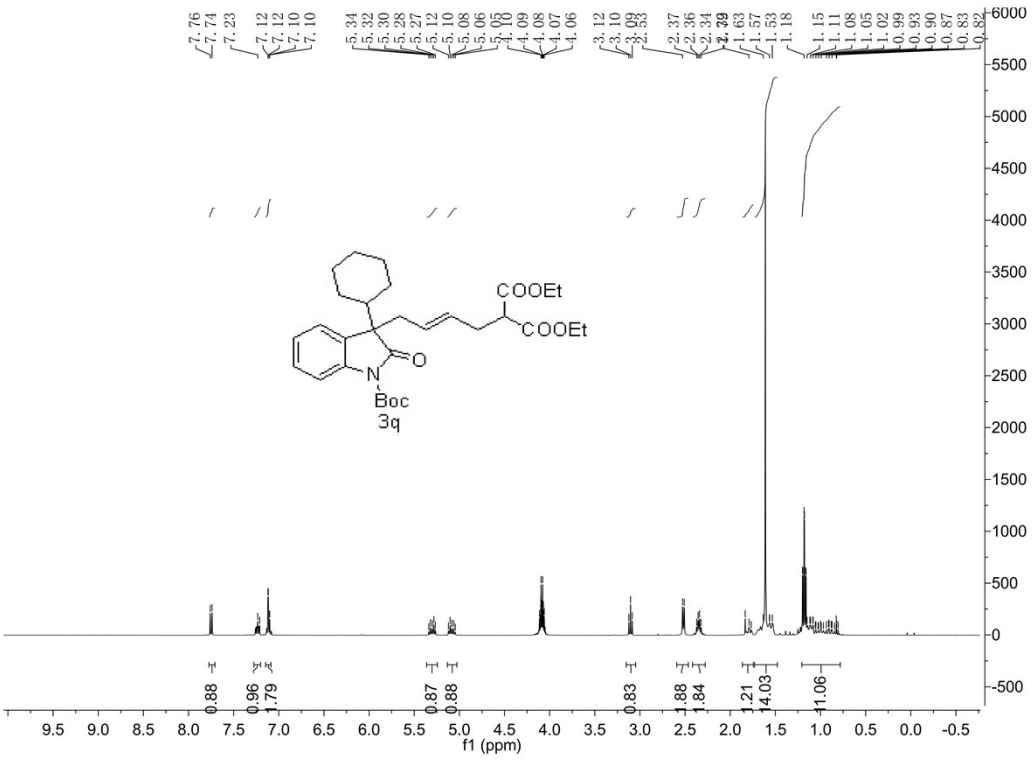

175.70
168.62
161.54
156.79
149.11
141.53
141.46
131.49
130.01
125.95
122.94
116.18
114.48
114.46
113.44
111.20
84.27
77.38
77.06
76.74
61.30
60.33
56.79
56.77
55.61
51.66
41.17
31.50
29.65
28.02
21.00
14.16
14.00
f1 (ppm)

3o ^{13}C NMR

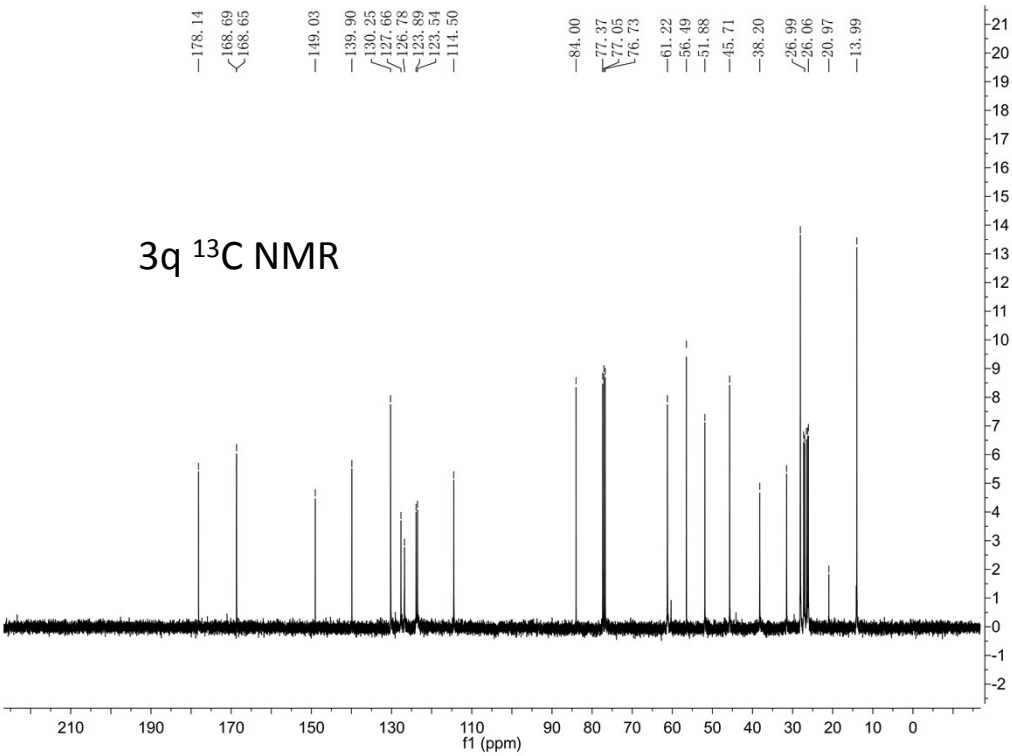


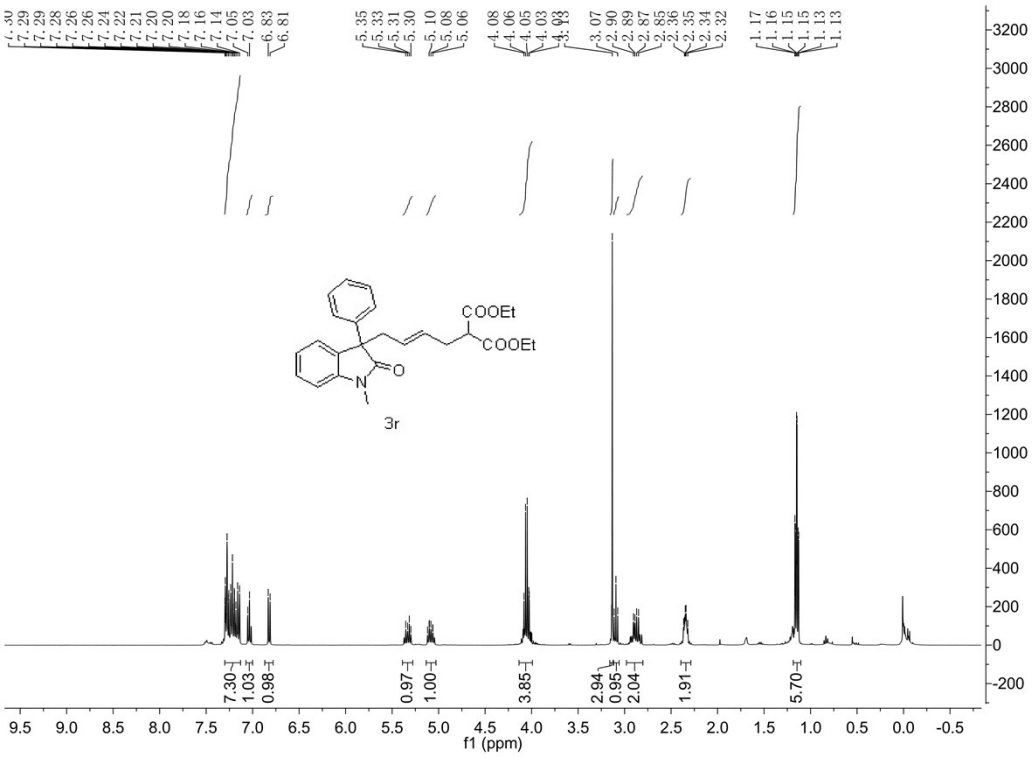
3p ^{13}C NMR

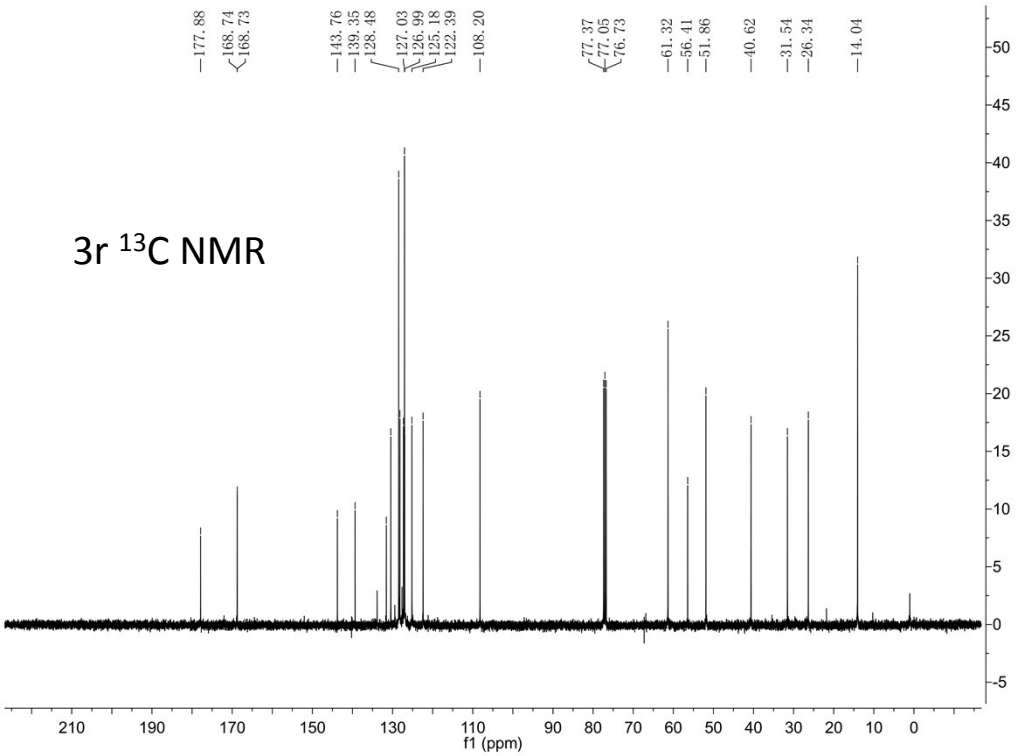


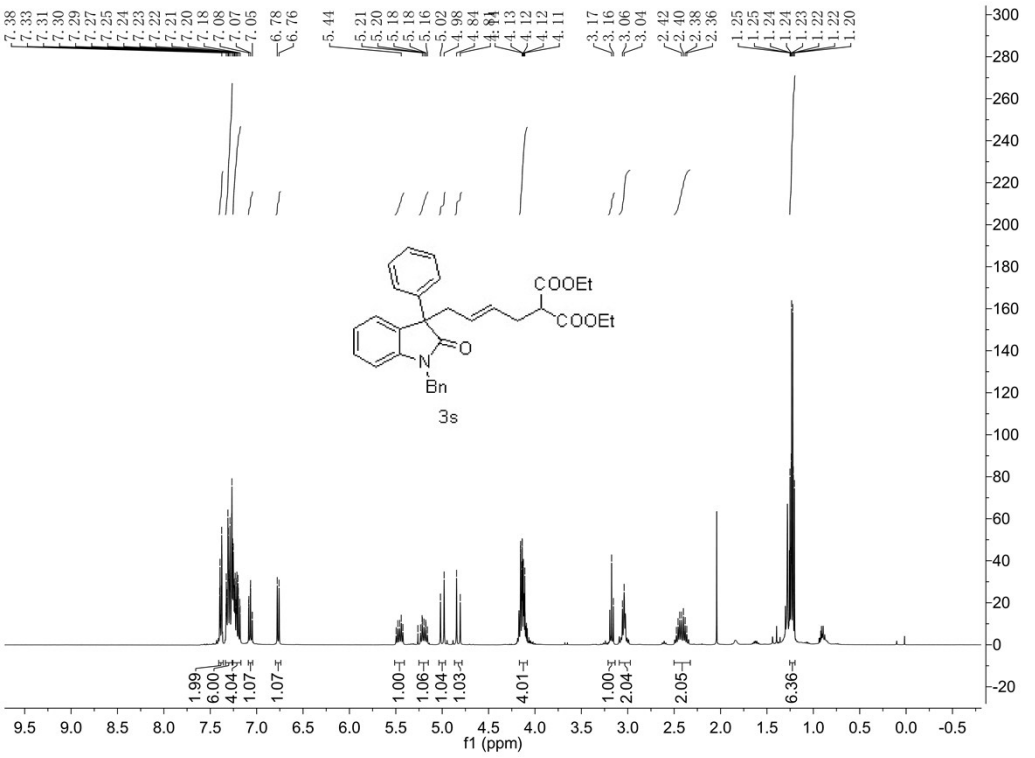


3q ^{13}C NMR

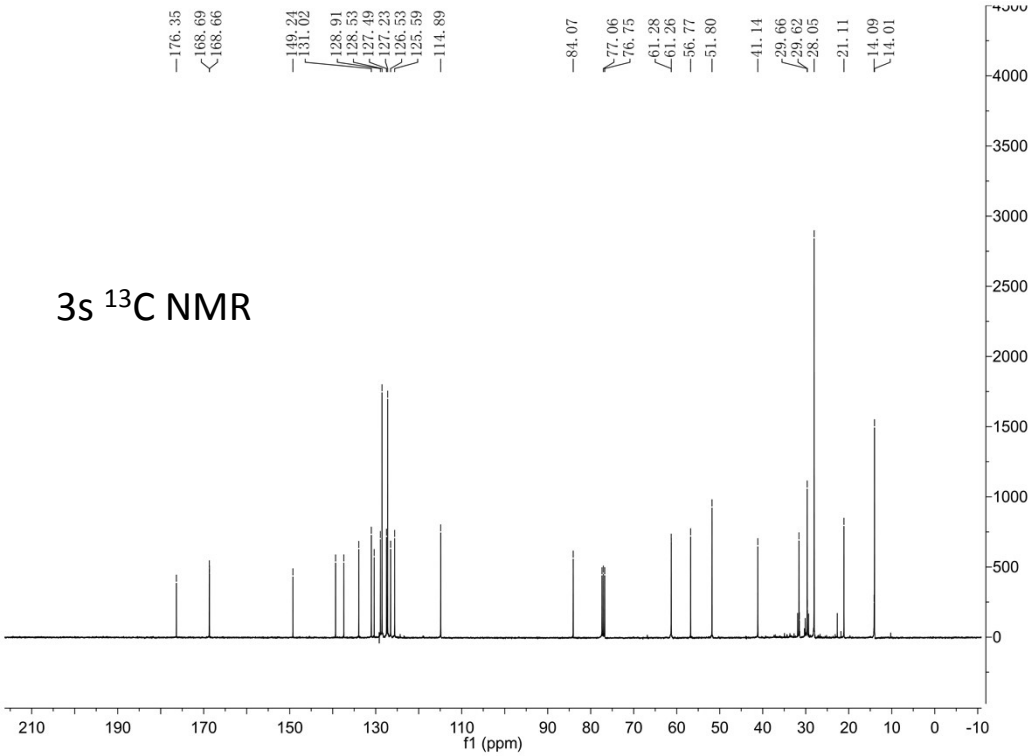


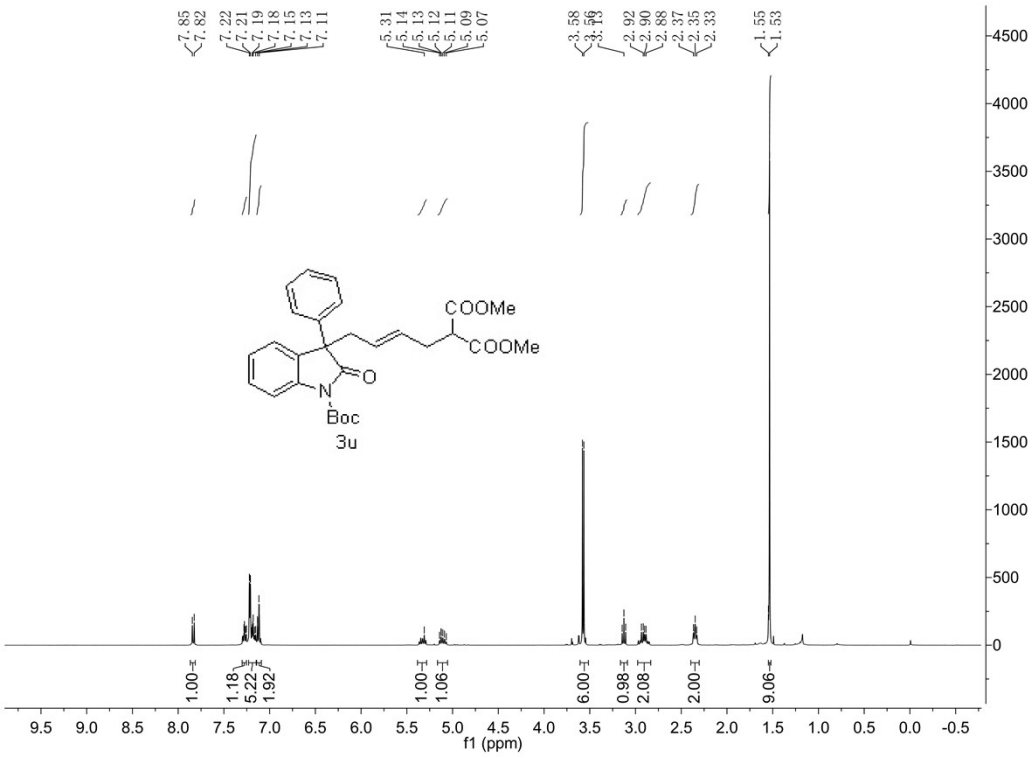

COOEt
COOEt
O
N
3r
7.30
1.03
0.98
0.97
1.00
3.85
2.94
0.95
2.04
1.91
5.70
f1 (ppm)


3r ^{13}C NMR
f1 (ppm)

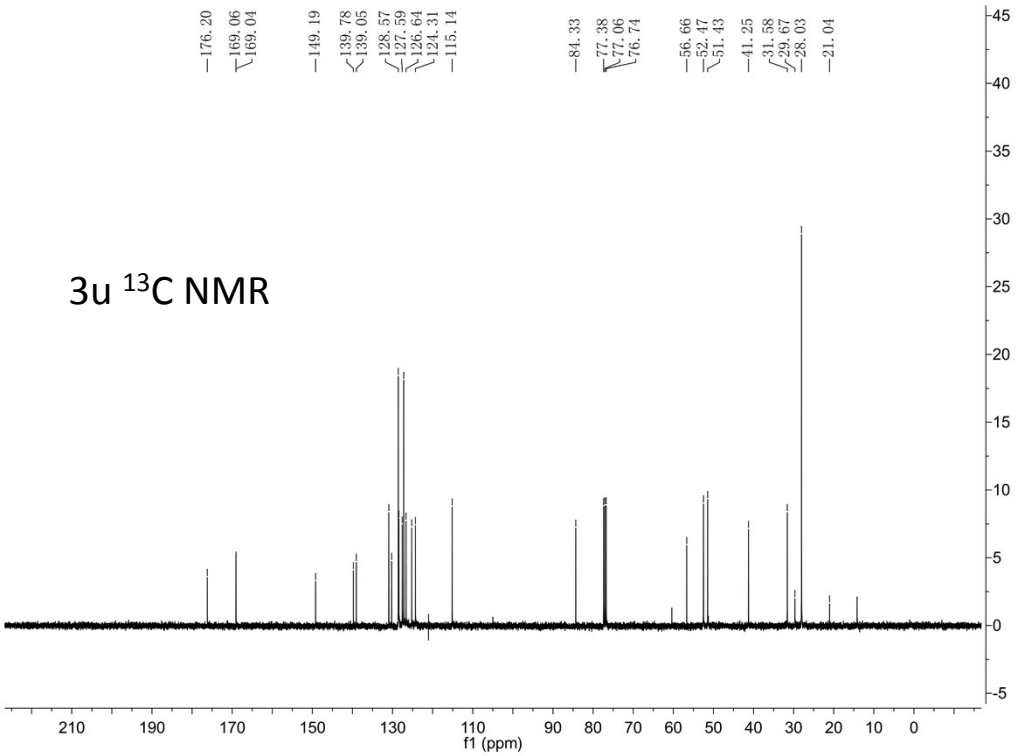


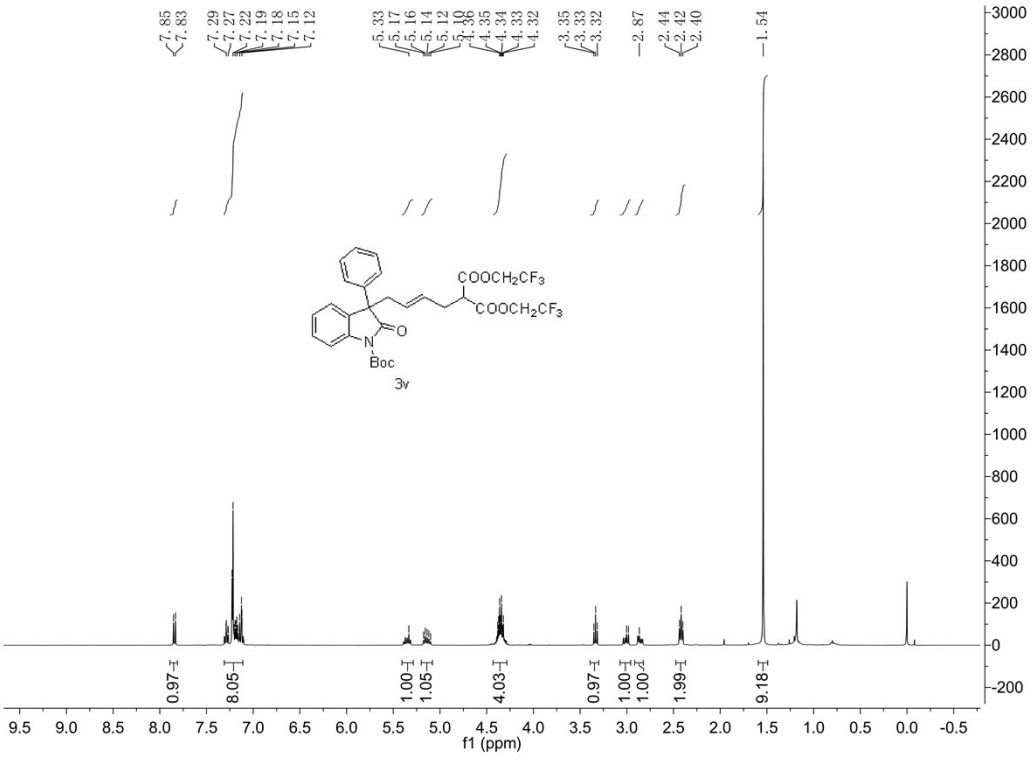
3s ^{13}C NMR

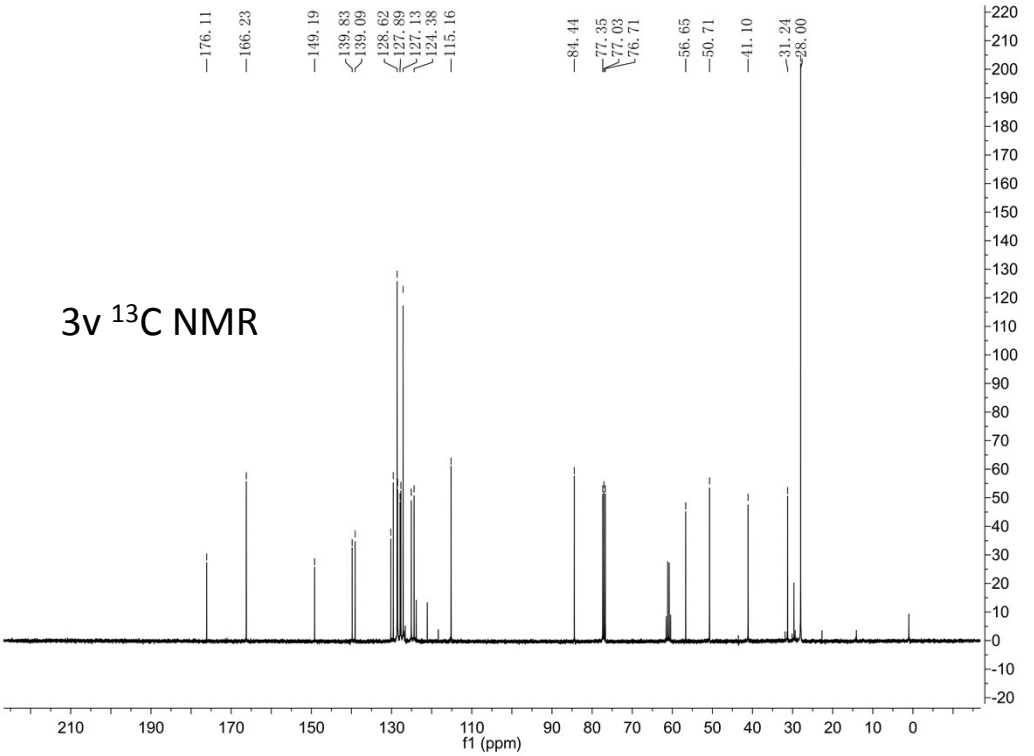



7.85
7.82
7.22
7.21
7.19
7.18
7.15
7.13
7.11
5.31
5.14
5.13
5.12
5.11
5.09
5.07
3.58
3.56
3.15
2.92
2.90
2.88
2.37
2.35
2.33
1.55
1.53
COOMe
COOMe
O
N
Boc
3u
1.00
1.18
5.22
1.92
1.00
1.06
6.00
0.98
2.08
2.00
9.06
f1 (ppm)

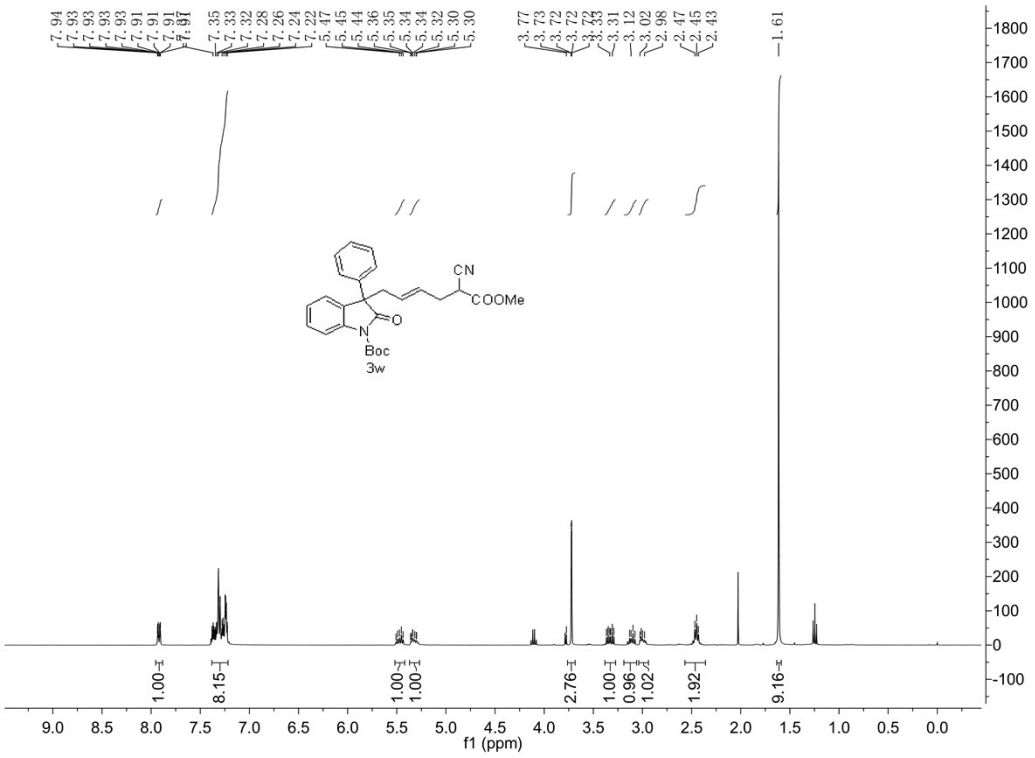
3u ^{13}C NMR

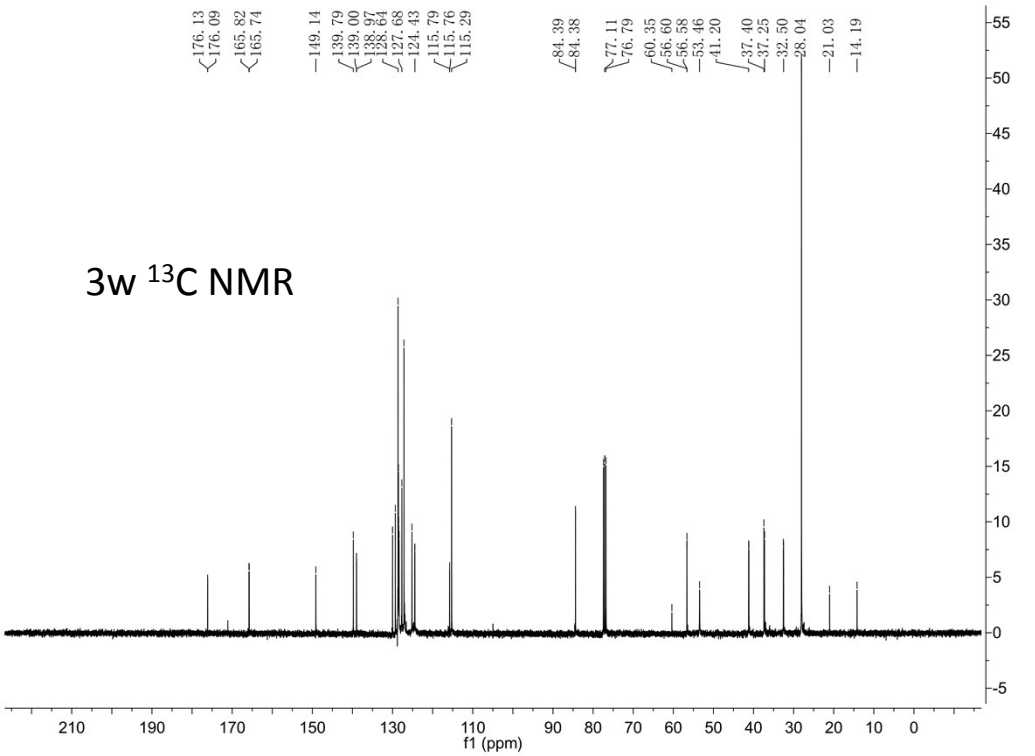

176.20
169.06
169.04
149.19
139.78
139.05
128.57
127.59
126.64
124.31
115.14
84.33
77.38
77.06
76.74
56.66
52.47
51.43
41.25
31.58
29.67
28.03
21.04
f1 (ppm)


7.85
7.83
7.29
7.27
7.22
7.19
7.18
7.15
7.12
5.33
5.17
5.16
5.14
5.12
5.10
4.35
4.34
4.33
4.32
3.35
3.33
3.32
2.87
2.44
2.42
2.40
1.54
COOCH2CF3
COOCH2CF3
O
N
Boc
3v
0.97
8.05
1.00
1.05
4.03
0.97
1.00
1.00
1.99
9.18
f1 (ppm)

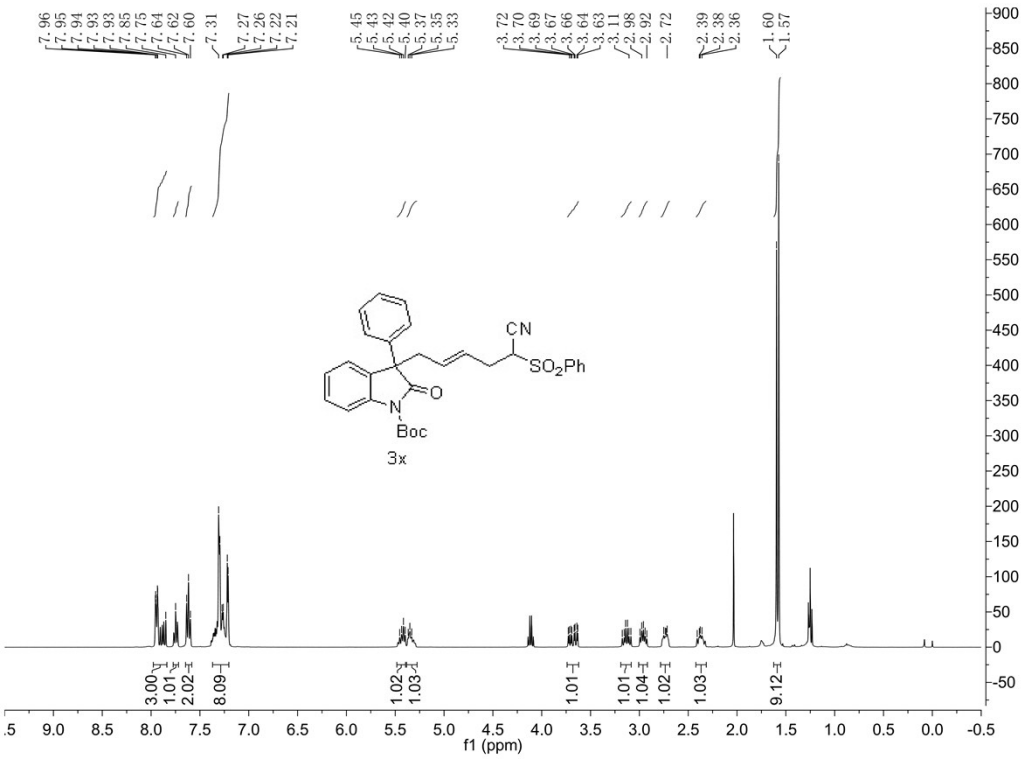

176.11
166.23
149.19
139.83
139.09
128.62
127.89
127.13
124.38
115.16
84.44
77.35
77.03
76.71
56.65
50.71
41.10
31.24
28.00
f1 (ppm)

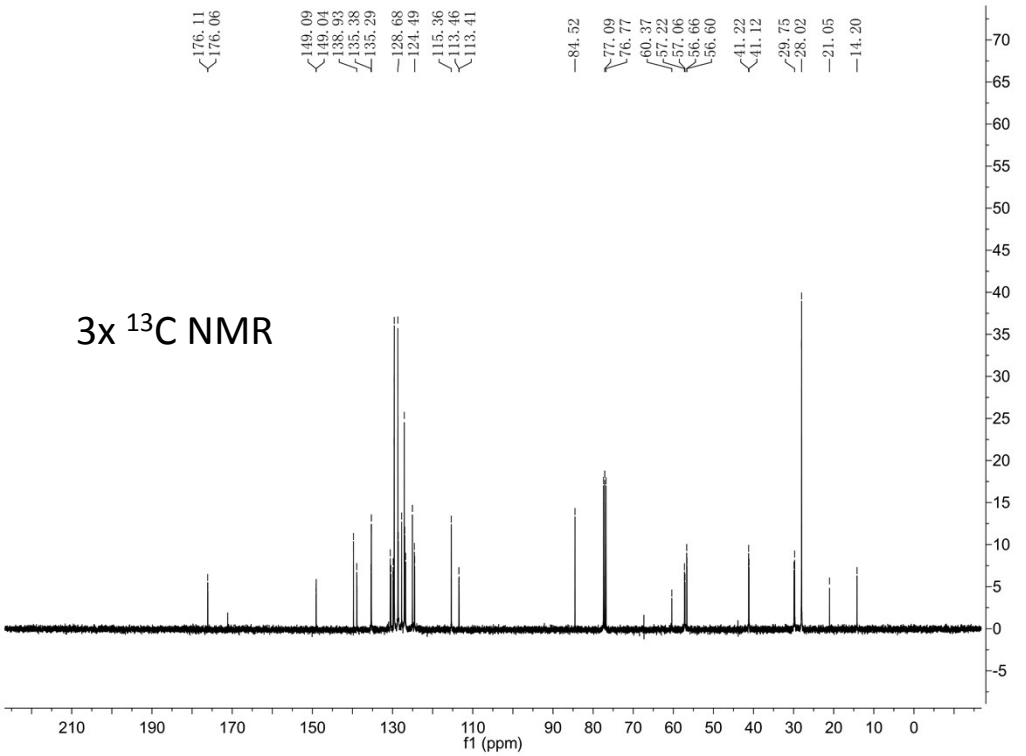
3v ^{13}C NMR


7.94
7.93
7.93
7.93
7.91
7.91
7.91
7.91
7.35
7.33
7.32
7.28
7.26
7.24
7.22
5.47
5.45
5.44
5.36
5.35
5.34
5.34
5.32
5.30
5.30
3.77
3.73
3.72
3.72
3.33
3.31
3.12
3.02
2.98
2.47
2.45
2.43
1.61
CN
COOMe
O
N
Boc
3w
1.00
8.15
1.00
1.00
2.76
1.00
0.96
1.02
1.92
9.16
f1 (ppm)

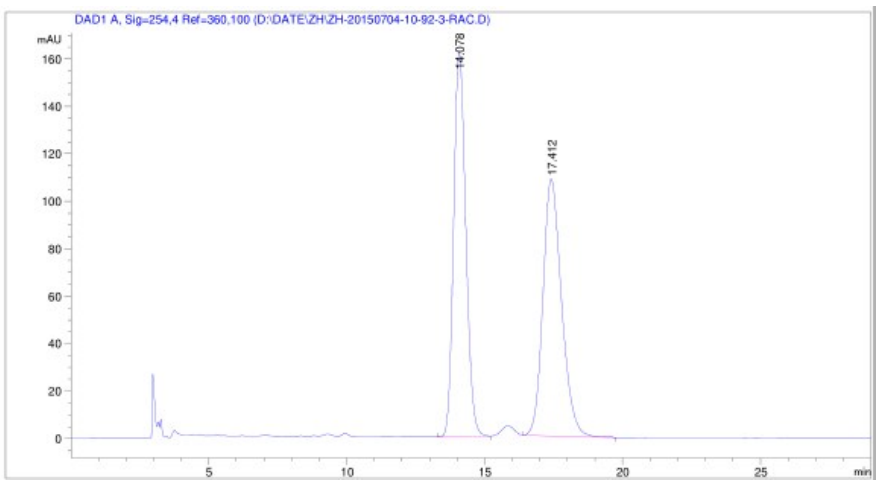

176.13
176.09
165.82
165.74
149.14
139.79
139.00
138.97
128.64
127.68
124.43
115.79
115.76
115.29
84.39
84.38
77.11
76.79
60.35
56.60
56.58
53.46
41.20
37.40
37.25
32.50
28.04
21.03
14.19
f1 (ppm)

3w ^{13}C NMR

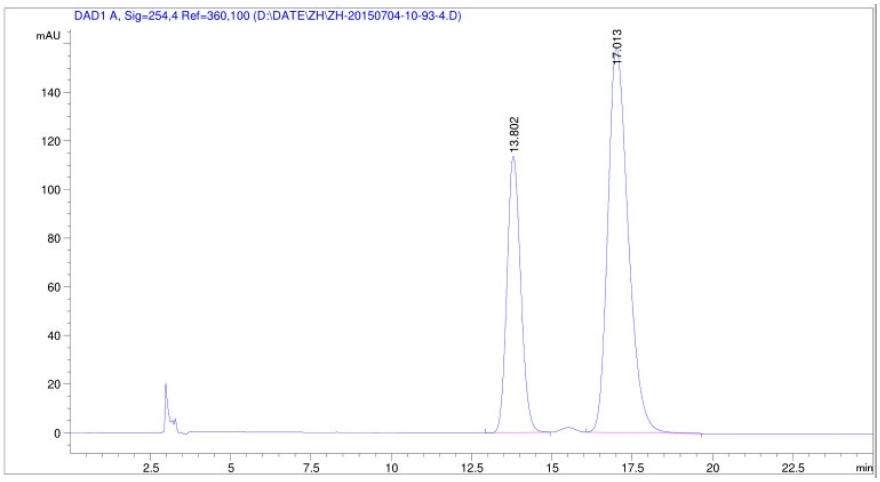

7.96
7.95
7.94
7.93
7.93
7.85
7.75
7.64
7.62
7.60
7.31
7.27
7.26
7.22
7.21
5.45
5.43
5.42
5.40
5.37
5.35
5.33
3.72
3.70
3.69
3.67
3.66
3.64
3.63
3.11
2.98
2.92
2.72
2.39
2.38
2.36
1.60
1.57
CN
SO2Ph
O
N
Boc
3x
3.00
1.01
2.02
8.09
1.02
1.03
1.01
1.01
1.04
1.02
1.03
9.12
f1 (ppm)


176.11
176.06
149.09
149.04
138.93
135.38
135.29
128.68
124.49
115.36
113.46
113.41
84.52
77.09
76.77
60.37
57.22
57.06
56.66
56.60
41.22
41.12
29.75
28.02
21.05
14.20
3x 13C NMR
f1 (ppm)

8 HPLC specture:



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.078	BB	0.4746	4952.92041	162.05212	49.3899
2	17.412	BB	0.7186	5075.29150	108.32153	50.6101



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.802	BB	0.4633	3385.19678	113.72012	32.6729
2	17.013	BB	0.6807	6975.66064	158.10435	67.3271