Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Highly Diastereoselective (5+1) Annulation of Allenoates and Pyrazolones Catalyzed by CH_3OK

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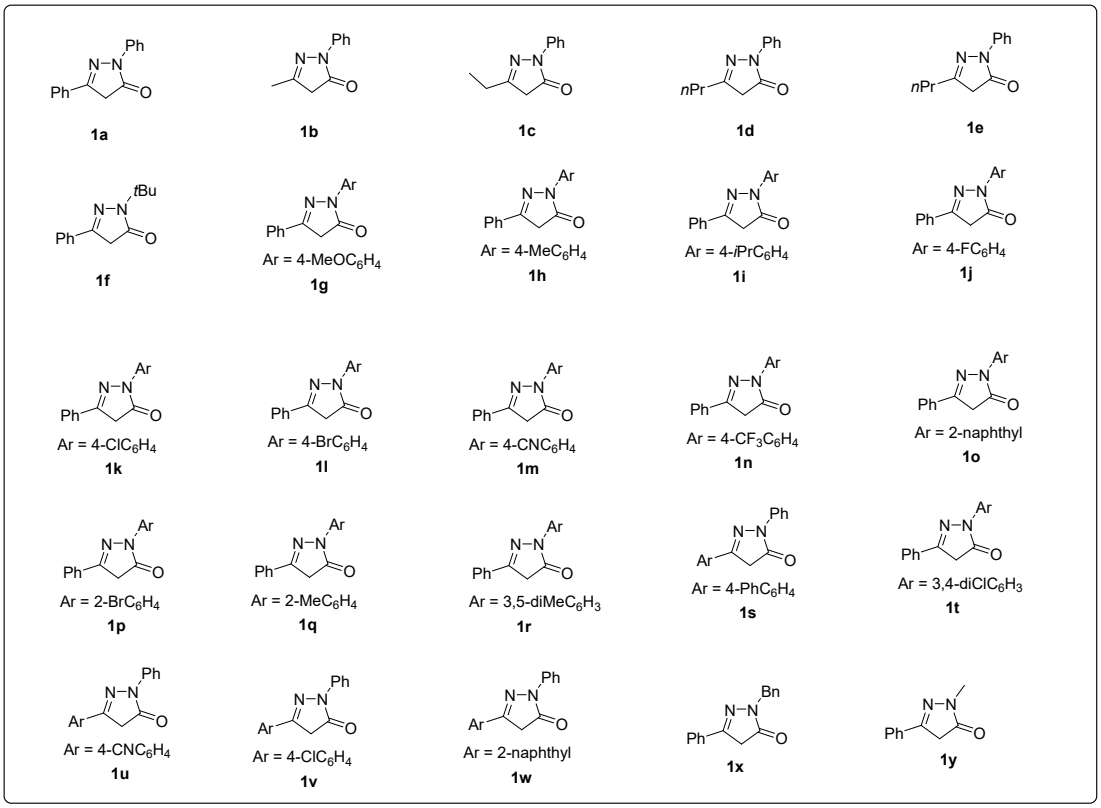
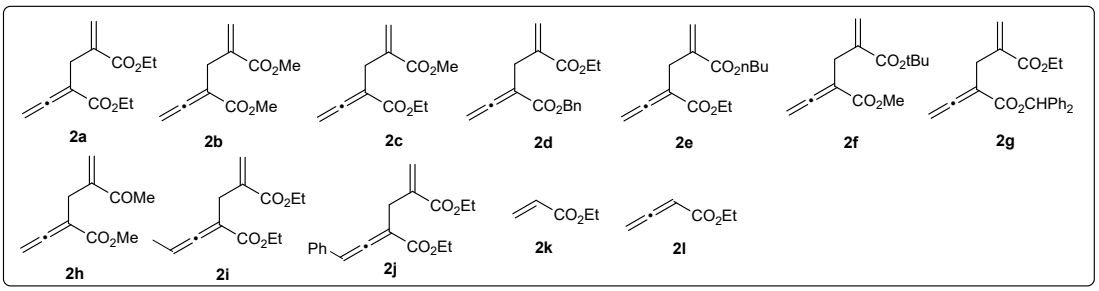
1. General Information

Commercial reagents and solvents were used as received without further purification, unless otherwise stated. Unless otherwise specified, reactions at 60 °C have been performed using the pre-heated water-bath or the pre-heated oil-bath maintained at 60 °C. Yields referred to isolated compounds through preparative TLC. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. And ^{19}F NMR were reported on a Bruker Avance (376 MHz) spectrometer. Chemical shifts for protons are reported in ppm and are referenced to the NMR solvent peak ($CDCl_3$: δ 7.26 ppm, D). Chemical shifts for carbons are reported in ppm and are referenced to the carbon resonances of the NMR solvent peak ($CDCl_3$: δ 77.06 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), brs (broad singlet) and m (multiplet). High resolution mass spectrometry (HRMS) obtained on Q Exactive Focus or Agilent 6520 Q-TOF LC/MS with ESI resource. Melting points were measured on a RY-I apparatus and reported uncorrected.

2. General Procedure of Starting Material

2.1. The substrates examined in this report.

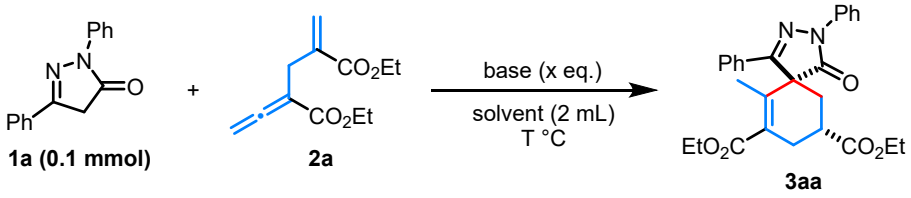




All pyrazolone substrates were prepared according to reported literature procedures.[1] The α-activated-allylic substituted allenoates were prepared following the synthetic method according to our reported literature procedures.[2]

3. Optimization of Reaction Conditions

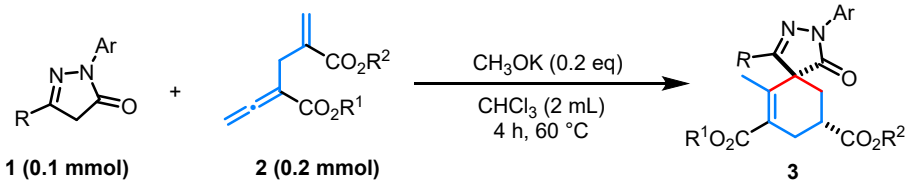
Table S1. Optimization of reaction conditions.[a]



entry	1a:2a	cat.	solvent	T/℃	time/h	yield/%[a]
1	1:2	CH_3OK (1.2 eq)	DCM	25	24	44
2	1:2	Cs_2CO_3 (1.2 eq)	DCM	25	24	-
3	1:2	tBuOK (1.2 eq)	DCM	25	24	20
4	1:2	DABCO (1.2 eq)	DCM	25	24	-
5	1:2	K_3PO_4-$3H_2O$ (1.2 eq)	DCM	25	24	30
6	1:2	CH_3OK (1.2 eq)	$CHCl_3$	25	24	50
7	1:2	CH_3OK (1.2 eq)	toluene	25	24	40
8	1:2	CH_3OK (1.2 eq)	Et_2O	25	24	30
9	1:2	CH_3OK (1.2 eq)	ClPh	25	24	43
10	1:2	CH_3OK (1.2 eq)	CH_3OPh	25	24	49
11	1:2	CH_3OK (0.2 eq)	$CHCl_3$	25	24	47
12	1:2	CH_3OK (0.2 eq)	$CHCl_3$	60	4	87
13	1:1	CH_3OK (0.2 eq)	$CHCl_3$	60	4	74
14	1.2:1	CH_3OK (0.2 eq)	$CHCl_3$	60	4	48
15	1:2	-	$CHCl_3$	60	24	-

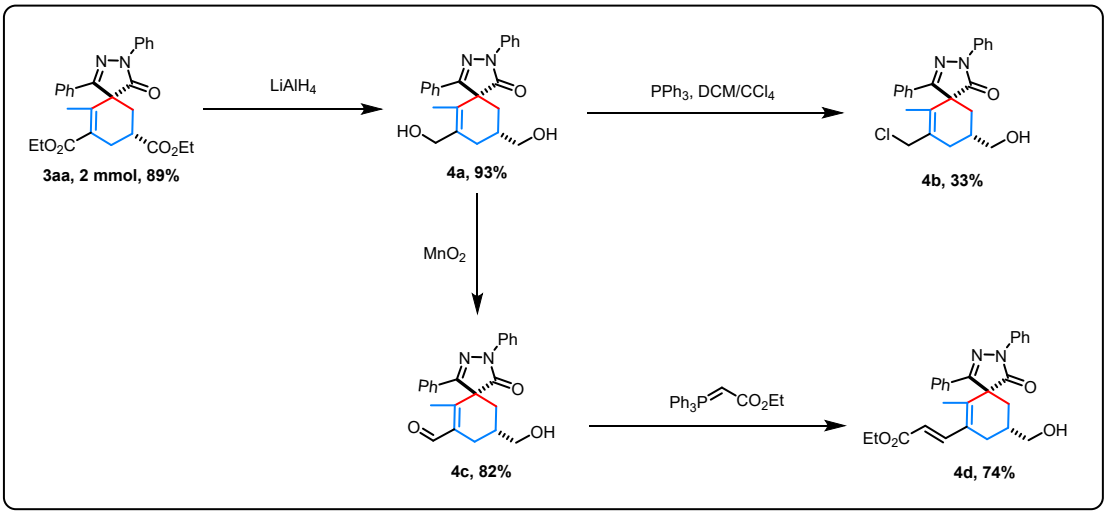
General reaction conditions: [a]**1a** (0.10 mmol), **2a** (0.2 mmol) and base (1.2 equiv.) in solvent (2 mL) at 25 °C. Dr values (>20:1) were determined by ^1H NMR analysis. Isolated yield.

General Procedure of new products



Under 60 °C heated by oil bath, to a solution of pyrazolone (0.1 mmol) and allenoate (0.2 mmol) in $CHCl_3$ (2 mL) was added CH_3OK (20 mol%). The resulting mixture was stirred for 4 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford desired products.

4. Scale-up Experiment and Transformations of the New Product 3aa.



Scale-up Experiment (3aa)

Under 60 °C heated by oil bath, to a solution of pyrazolone (2 mmol) and allenoate (4 mmol) in $CHCl_3$ (40 mL) was added CH_3OK (20 mol%). The resulting mixture was stirred for 4 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (20.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether: ethyl acetate = 5:1) to afford desired products (0.82 g, 89% yield).

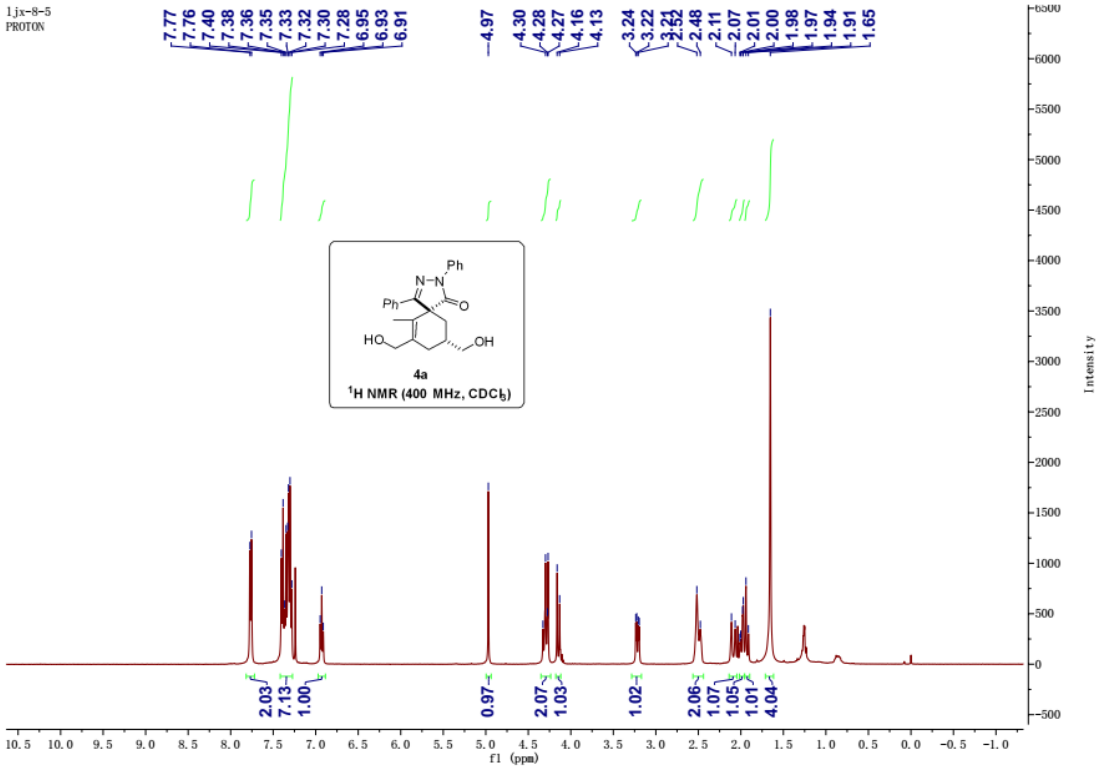
$LiAlH_4$ Reduction of 3aa

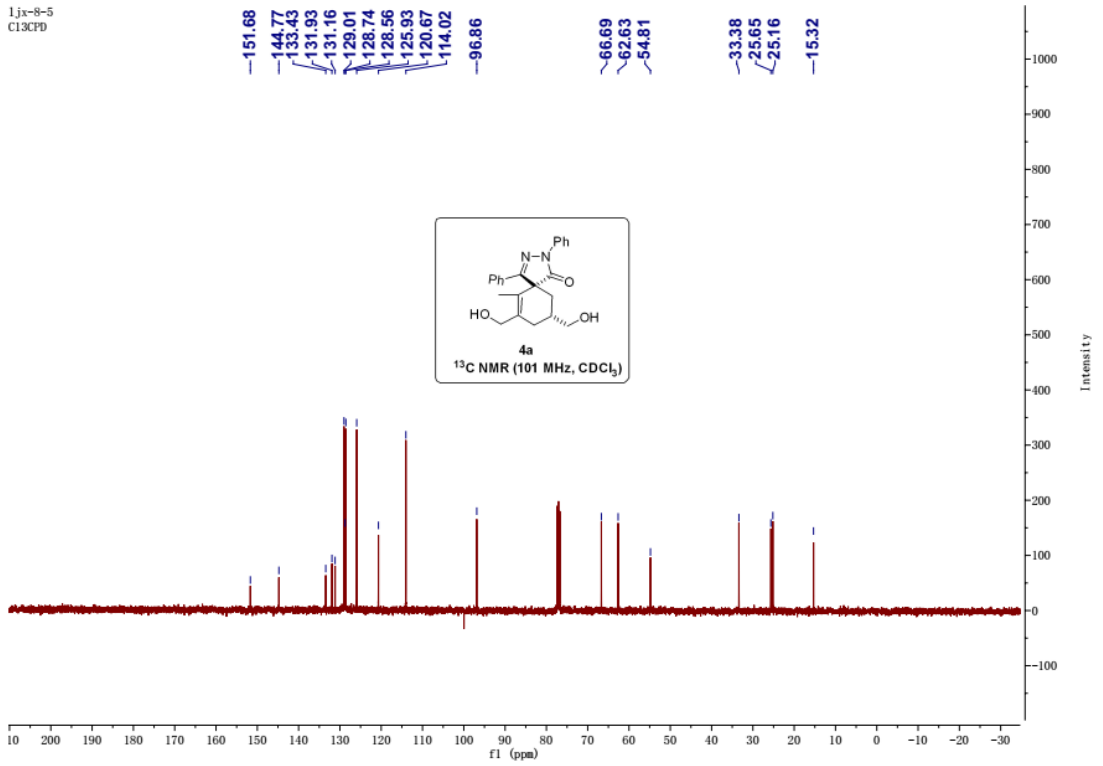
An oven-dried 25-mL round bottom flask with a stir bar was charged with of **3aa** (0.10 mmol, 1.0 equiv.), $LiAlH_4$ (0.25 mmol, 3.0 equiv.) in 4mL of anhydrous THF. Then the reaction mixture was stirred at room temperature for 10 mins under argon atmosphere. When the reaction was complete detected by TLC, the resulting reaction mixture was quenched by adding water (10 μL), 15% aqueous NaOH (20 μL), and water (10 μL) again. Then the suspension was filtered, washed with ethyl acetate, and the combined filtrates were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to afford the desired products **4a** (35.1 mg, 93% yield) as white solid (melting point 120-123°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.1 Hz, 2H), 7.34 (ddd, *J* = 19.0, 15.7, 8.2 Hz, 7H), 6.93 (t, *J* = 7.2 Hz, 1H), 4.97 (s, 1H), 4.29 (dd, *J* = 16.4, 7.6 Hz, 2H), 4.15 (d, *J* = 11.9 Hz, 1H), 3.22 (dd, *J* = 11.6, 4.6 Hz, 1H), 2.50 (d, *J* = 16.5 Hz, 2H), 2.09 (d, *J* = 17.4 Hz, 1H), 1.99 (dd, *J* = 12.5, 3.4 Hz, 1H), 1.93 (d, *J* = 11.2 Hz, 1H), 1.65 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.68, 144.77, 133.43, 131.93, 131.16, 129.01, 128.74, 128.56, 125.93, 120.67, 114.02, 96.86, 66.69, 62.63, 54.81, 33.38, 25.65, 25.16, 15.32.

HRMS (ESI): m/z calcd for $C_{23}H_{24}N_2O_3Na$ ($[M+Na]^+$): 399.1679; found: 399.1679.





Appel Reaction of 4a

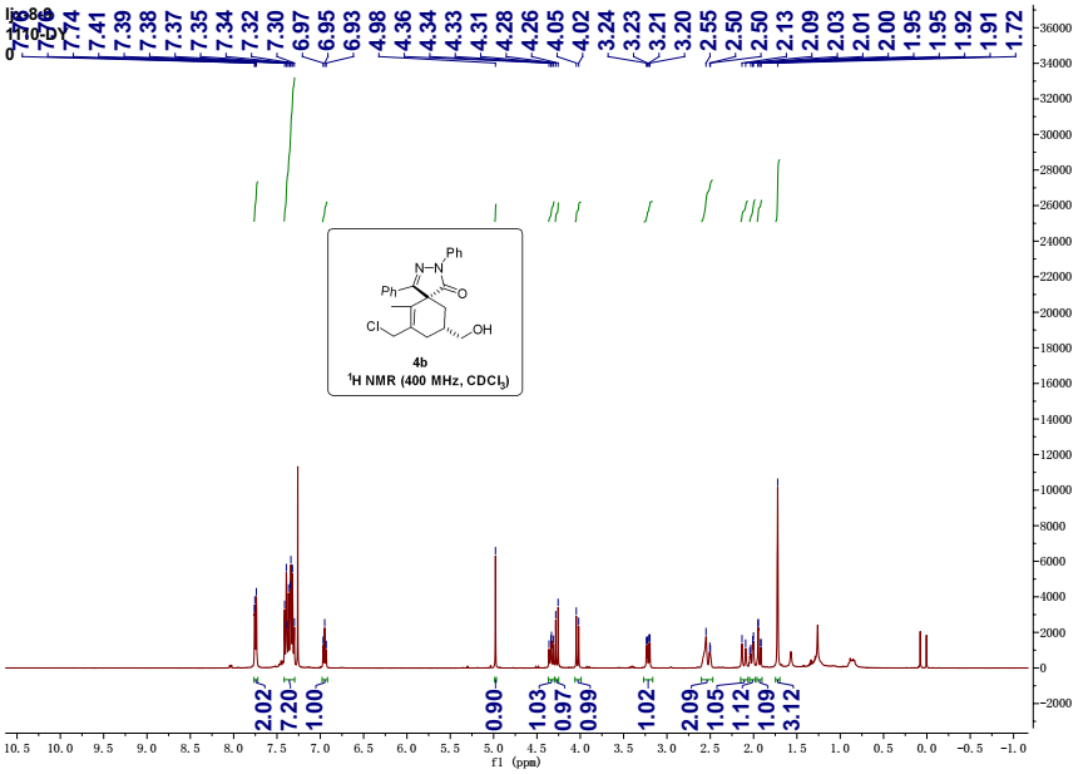
A solution of **4a** (0.1 mmol, 1.0 equiv.) and carbon tetrachloride (10.4 mmol, 104.0 equiv.) in anhydrous dichloromethane (6 mL) was stirred in an oven-dried 25-mL round bottom flask and cooled to 0 °C. Triphenyl phosphine (0.15 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at room

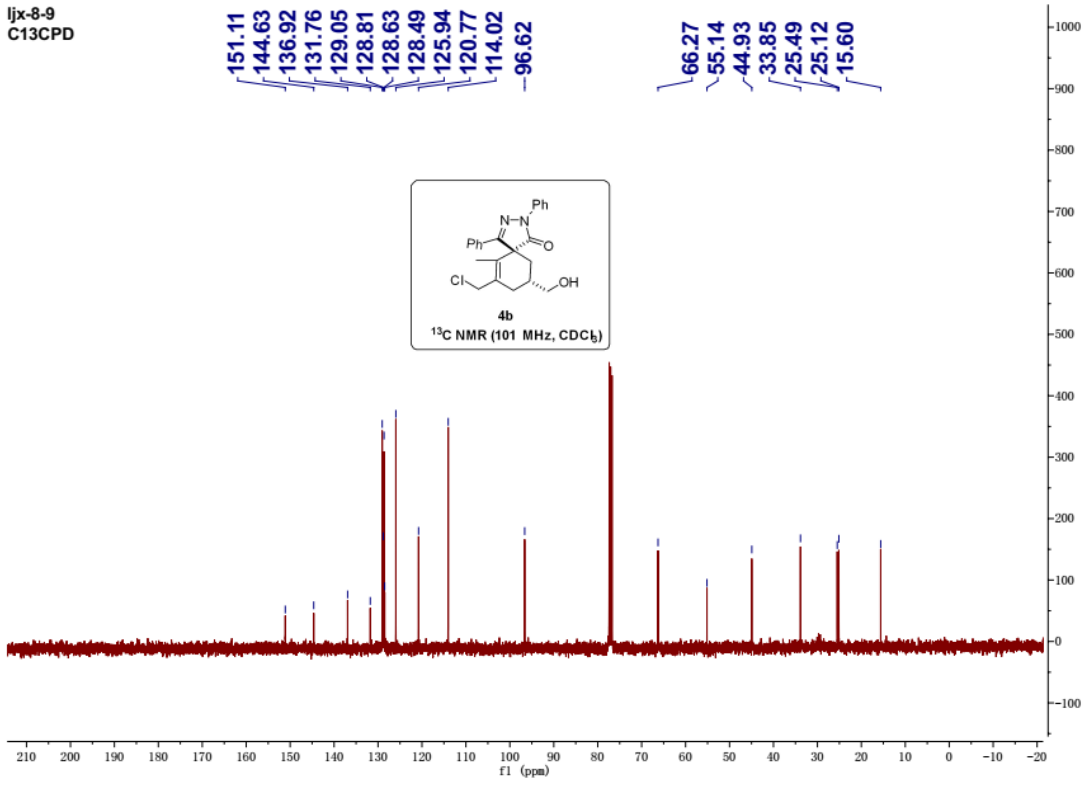
temperature for 12 h. When the reaction was complete detected by TLC, the resulting reaction mixture was directly purified by chromatography on a silica gel column (30 -120 mesh) using 4:1 petroleum ether-ethyl acetate solvent mixture as eluent to afford desired product **4b** (13 mg, 33% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.35 (ddd, *J* = 19.1, 13.5, 8.2 Hz, 7H), 6.94 (t, *J* = 7.2 Hz, 1H), 4.97 (s, 1H), 4.33 (dd, *J* = 11.6, 9.3 Hz, 1H), 4.26 (d, *J* = 10.9 Hz, 1H), 4.03 (d, *J* = 11.0 Hz, 1H), 3.21 (dd, *J* = 11.7, 5.0 Hz, 1H), 2.61 – 2.46 (m, 2H), 2.11 (d, *J* = 16.8 Hz, 1H), 2.02 (dd, *J* = 13.0, 3.8 Hz, 1H), 1.93 (dd, *J* = 12.3, 1.7 Hz, 1H), 1.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.11, 144.63, 136.92, 131.76, 129.05, 128.81, 128.63, 128.49, 125.94, 120.77, 114.02, 96.62, 66.27, 55.14, 44.93, 33.85, 25.49, 25.12, 15.60.

HRMS (ESI): m/z calcd for $C_{23}H_{24}ClN_2O$ ($[M\text{-}OH+2H]^+$): 379.1572; found: 379.1573.





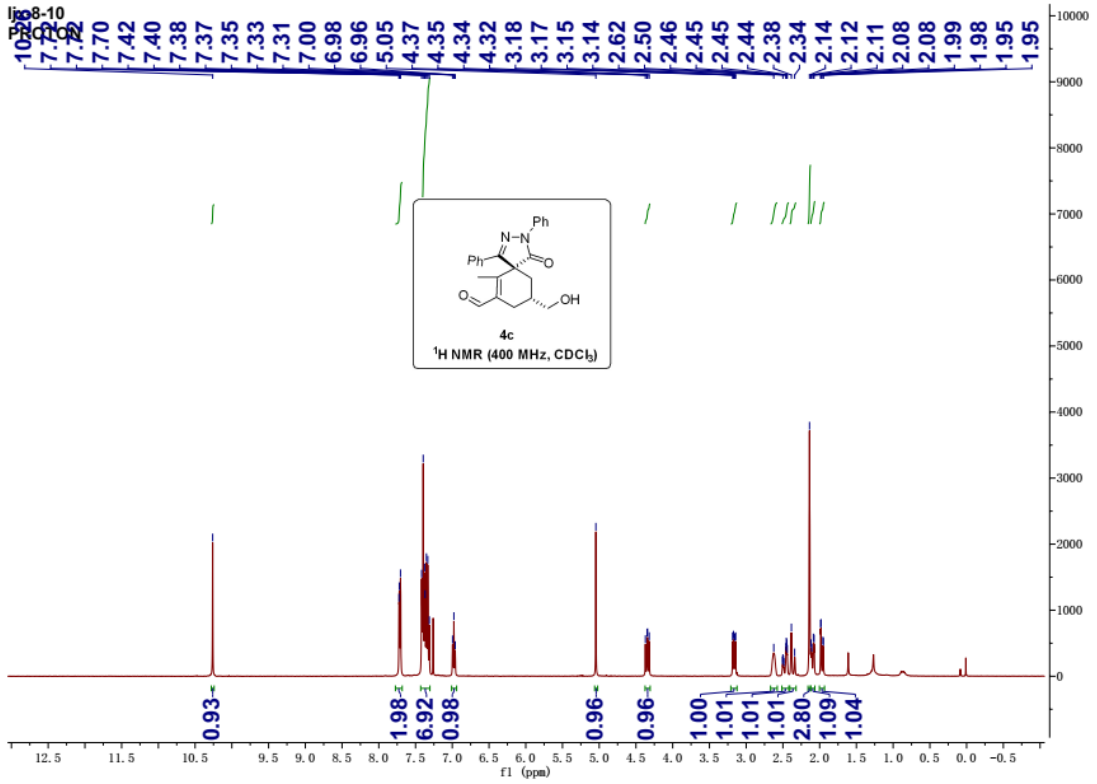
MnO_2 Oxidized of 4a

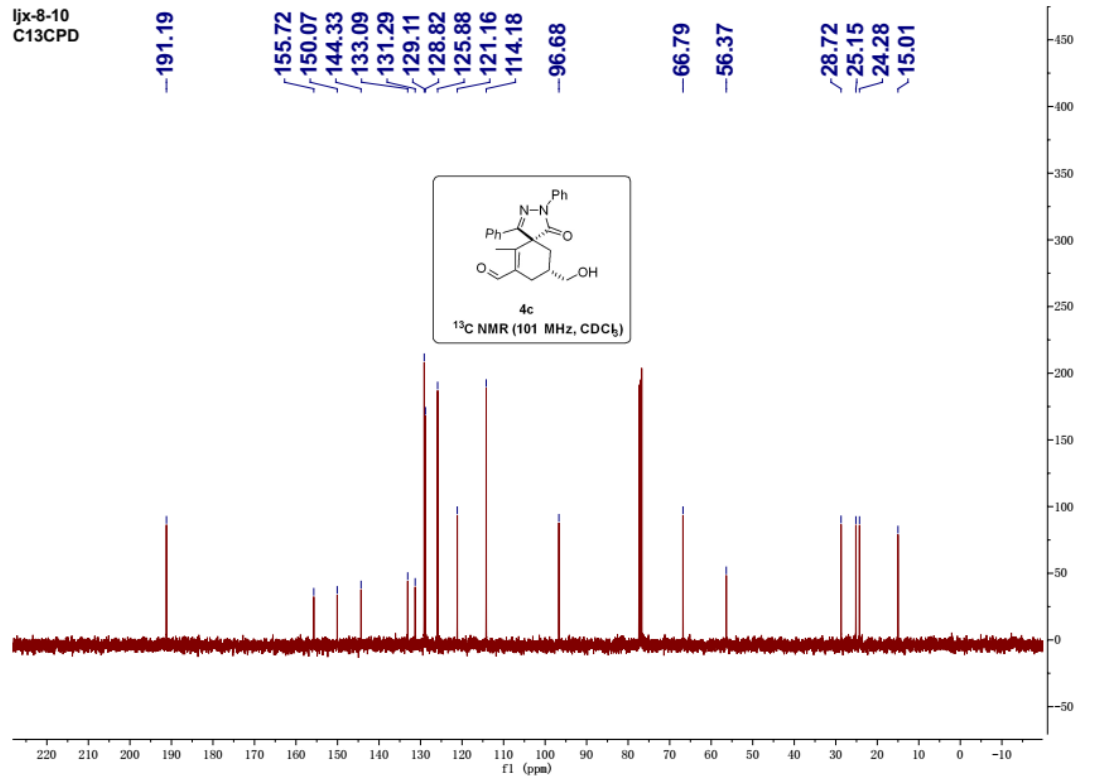
A mixture of **4a** (0.10 mmol, 1.0 equiv.), MnO_2 (2.1 mmol, 21.0 equiv.) was stirred in ethyl acetate (3.0 mL) was heated at 85°C for 3h in oil bath in a 10 mL pressure resistant reaction tube. When the reaction was complete detected by TLC, the reaction mixture was filtered through silica gel and the solid residue was washed with ethyl acetate and the solvent was removed under reduced pressure. Finally, the crude product was purified by chromatography on a silica gel column (30 -120 mesh) using 4:1 petroleum ether-ethyl acetate solvent mixture as eluent to afford **4c** (30.5 mg, 82% yield) as white solid (melted point 142-144°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.73 – 7.68 (m, 2H), 7.41 – 7.30 (m, 7H), 6.97 (t, *J* = 7.2 Hz, 1H), 5.04 (s, 1H), 4.34 (dd, *J* = 11.7, 9.0 Hz, 1H), 3.15 (dd, *J* = 11.8, 4.8 Hz, 1H), 2.61 (s, 1H), 2.46 (ddd, *J* = 18.6, 4.9, 2.3 Hz, 1H), 2.35 (d, *J* = 17.7 Hz, 1H), 2.13 (s, 3H), 2.09 (dd, *J* = 13.0, 4.0 Hz, 1H), 1.96 (dd, *J* = 12.5, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.19, 155.72, 150.07, 144.33, 133.09, 131.29, 129.11, 128.82, 125.88, 121.16, 114.18, 96.68, 66.79, 56.37, 28.72, 25.15, 24.28, 15.01.

HRMS (ESI): m/z calcd for $C_{23}H_{23}N_2O_3$ ($[M+H]^+$): 375.1703; found: 375.1702.





Wittig Reaction of 4c

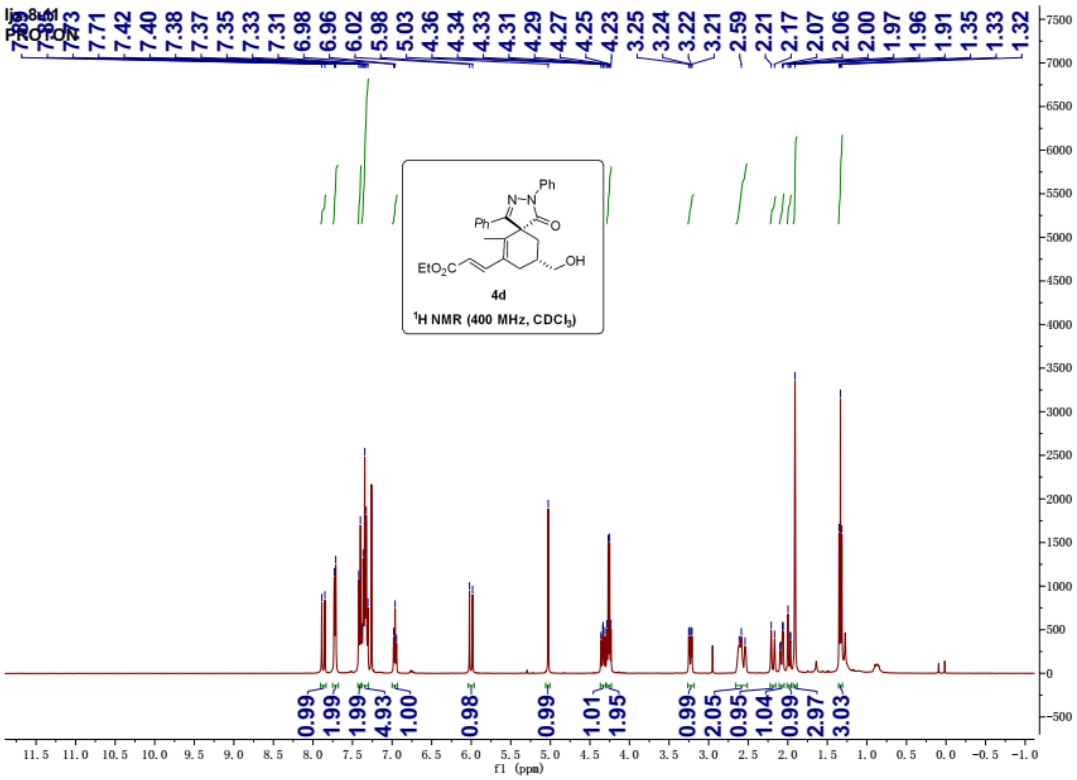
A solution of **4c** (0.082 mmol, 1.0 equiv.), wittig reagent (0.16 mmol, 2.0 equiv.) and 4Å MS (40 mg.) in anhydrous dichloromethane (2 mL) was stirred in an oven-dried 10-mL round bottom flask at 50 °C in oil bath for 24 h. When the reaction was complete detected by TLC, the resulting reaction mixture was

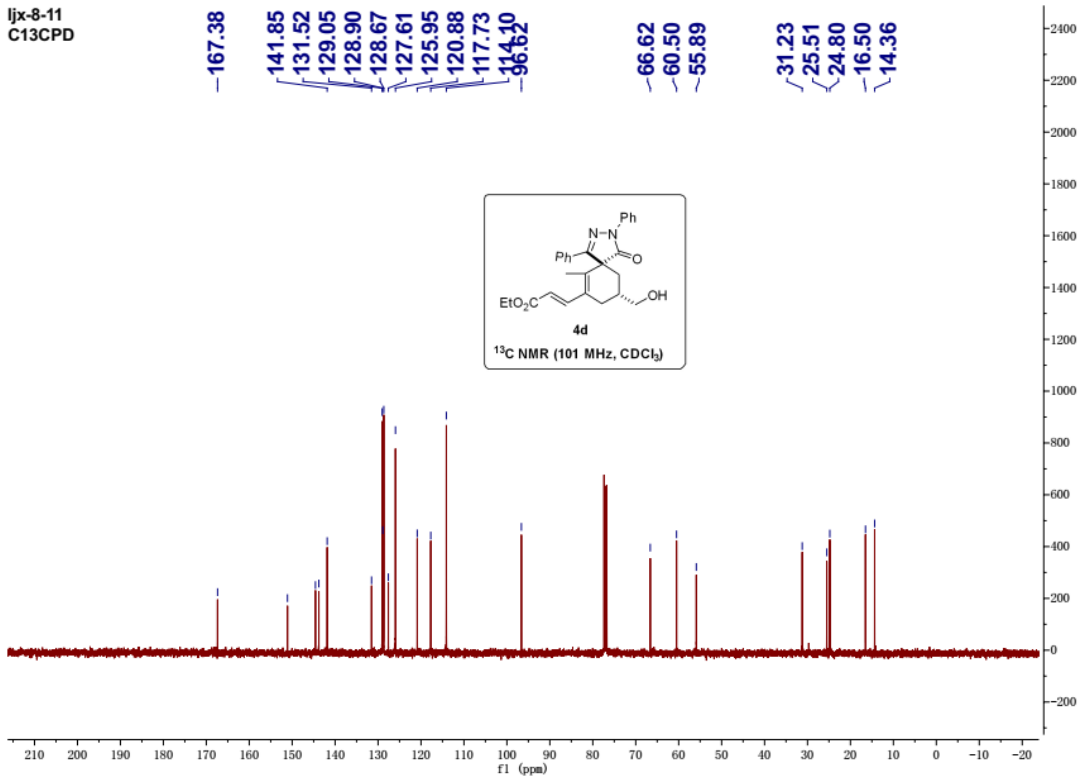
directly purified by chromatography on a silica gel column (30 -120 mesh) using 5:1 petroleum ether-ethyl acetate solvent mixture as eluent to afford desired product **4d** (33 mg, 74% yield) as white solid (melted point 129-131°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.8 Hz, 1H), 7.71 (d, *J* = 6.7 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 15.9, 8.2 Hz, 5H), 6.95 (t, *J* = 7.2 Hz, 1H), 5.99 (d, *J* = 15.7 Hz, 1H), 5.01 (s, 1H), 4.32 (dd, *J* = 11.6, 8.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.21 (dd, *J* = 11.7, 4.7 Hz, 1H), 2.64 – 2.50 (m, 2H), 2.17 (d, *J* = 17.1 Hz, 1H), 2.06 (dd, *J* = 12.4, 3.7 Hz, 1H), 2.00 – 1.94 (m, 1H), 1.89 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.38, 151.10, 144.58, 143.79, 141.85, 131.52, 129.05, 128.90, 128.67, 127.61, 125.95, 120.88, 117.73, 114.10, 96.62, 66.62, 60.50, 55.89, 31.23, 25.51, 24.80, 16.50, 14.36.

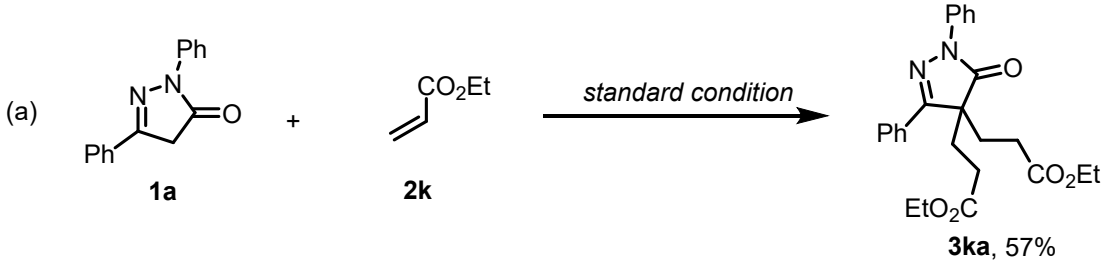
HRMS (ESI): m/z calcd for $C_{27}H_{29}N_2O_4$ ($[M+H]^+$): 445.2122; found: 445.2126.





5. Mechanism Investigation

Control experiment (a):

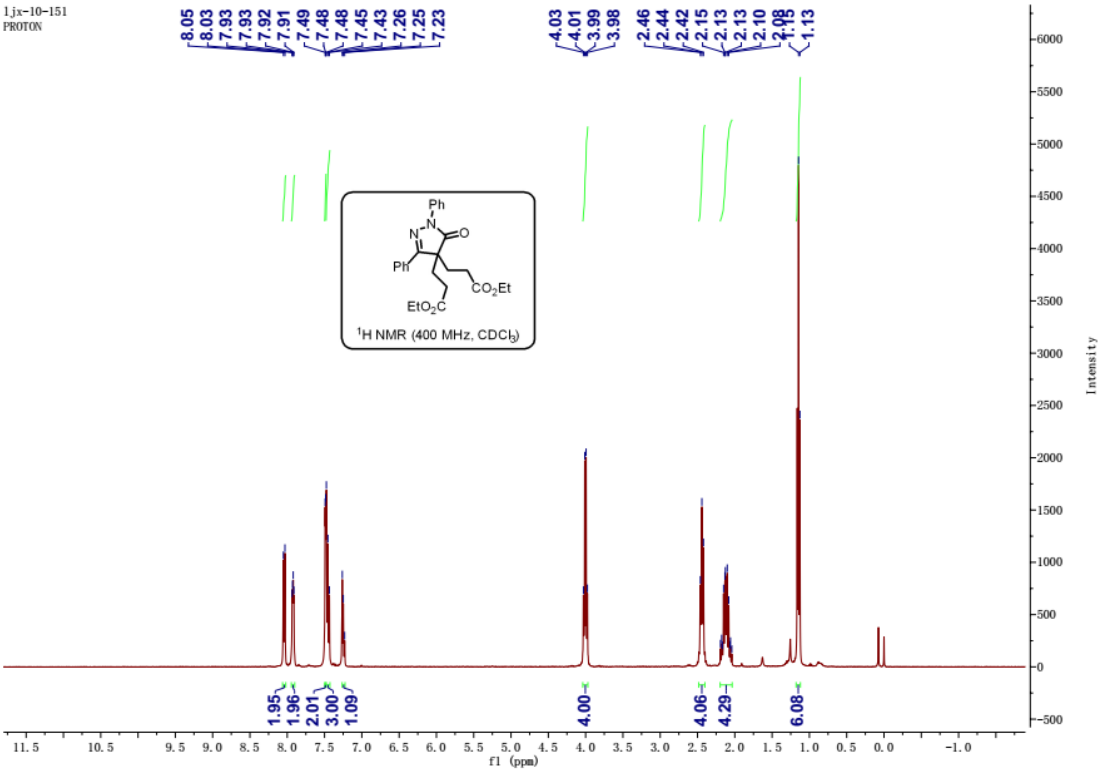


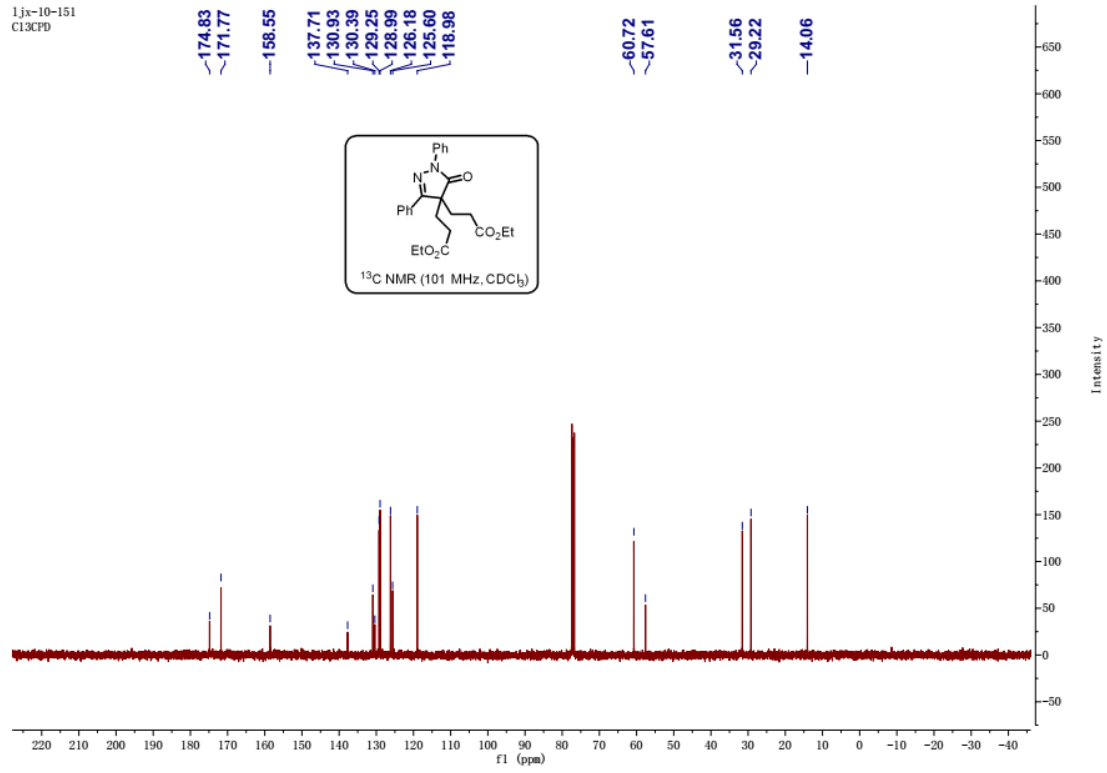
Under 60 °C heated by oil bath, to a solution of pyrazolone **1a** (0.1 mmol) and alkene **2k** (0.2 mmol) in $CHCl_3$ (2 mL) was added CH_3OK (20 mol%). The resulting mixture was stirred for 4 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford desired products (25 mg, 57% yield, yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.92 (dd, J = 6.5, 2.7 Hz, 2H), 7.49 (d, J = 2.5 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.26 – 7.23 (m, 1H), 4.00 (q, J = 7.1 Hz, 4H), 2.44 (t, J = 8.2 Hz, 4H), 2.20 – 2.04 (m, 4H), 1.14 (d, J = 7.1 Hz, 6H).

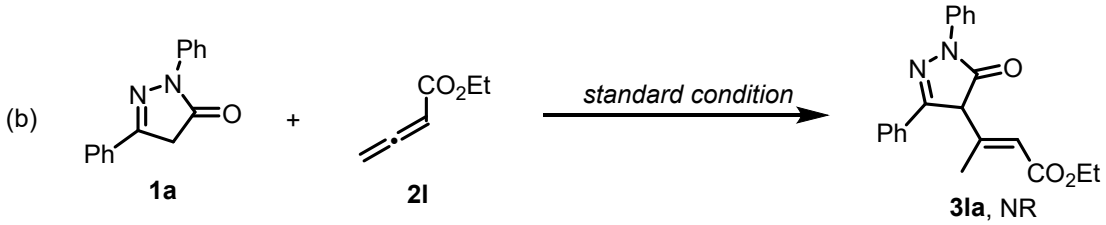
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 171.77, 158.55, 137.71, 130.93, 130.39, 129.25, 128.99, 126.18, 125.60, 118.98, 60.72, 57.61, 31.56, 29.22, 14.06.

HRMS (ESI): m/z calcd for $C_{25}H_{28}N_2O_5Na$ ($[M+Na]^+$): 459.1890; found: 459.1901.



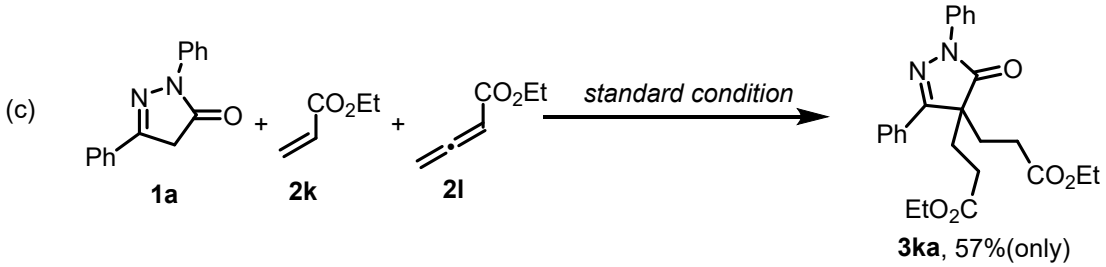


Control experiment (b):



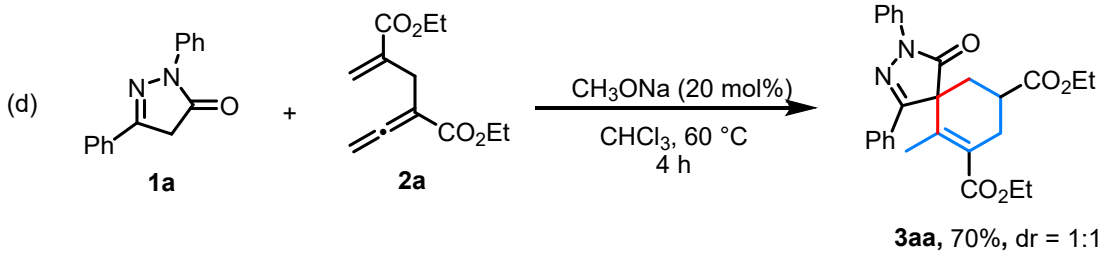
Under 60 °C heated by oil bath, to a solution of pyrazolone **1a** (0.1 mmol) and allene **2l** (0.2 mmol) in $CHCl_3$ (2 mL) was added CH_3OK (20 mol%). The resulting mixture was stirred for 4 hours but didn't find consumption of the starting materials **1a** monitored by TLC.

Control experiment (c):



Under 60 °C heated by oil bath, to a solution of pyrazolone **1a** (0.1 mmol), alkene **2k** (0.2 mmol) and allene **2l** (0.2 mmol) in $CHCl_3$ (2 mL) was added CH_3OK (20 mol%). The resulting mixture was stirred for 4 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford desired products (25 mg, 57% yield).

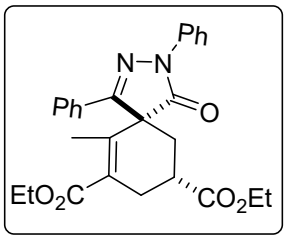
Control experiment (d):



Under 60 °C heated by oil bath, to a solution of pyrazolone **1a** (0.1 mmol) and allenoate **2a** (0.2 mmol) in $CHCl_3$ (2 mL) was added CH_3ONa (20 mol%). The resulting mixture was stirred for 4 hours until the complete consumption of the starting materials monitored by TLC. After removal of $CHCl_3$, the residue was diluted with ethyl acetate (2.0 mL) and washed with brine. The volatile was removed under reduced pressure and the residue was purified by preparative TLC (petroleum ether: ethyl acetate = 5:1) to afford desired products (32 mg, 70% yield, dr = 1:1).

6. Characterization Data of New Substrates

diethyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3aa).



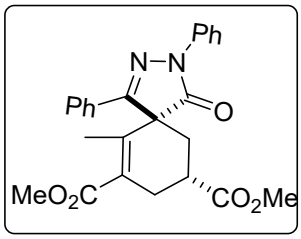
Yellow oil (40 mg, 87% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.51 – 7.42 (m, 5H), 7.23 (d, *J* = 7.4 Hz, 1H), 4.32 – 4.24 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.88 (dd, *J* = 14.3, 1.6 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.31 (dd, *J* = 13.8, 12.2 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.94 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.33, 173.15, 167.55, 160.74, 137.82, 136.43, 131.51, 130.75, 130.09, 129.05, 128.99, 127.44, 125.61, 119.03, 61.15, 60.97, 60.94, 35.13, 32.75, 28.58, 17.37, 14.27, 14.10.

HRMS (ESI): m/z calcd for $C_{27}H_{29}N_2O_5$ ($[M+H]^+$): 461.2071; found: 461.2069.

dimethyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ba).



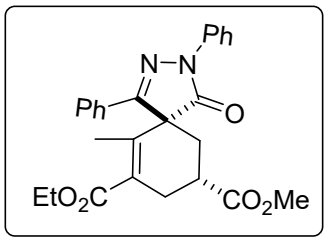
Yellow oil (39 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.50 – 7.42 (m, 5H), 7.23 (d, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.91 – 2.81 (m, 1H), 2.77 – 2.59 (m, 2H), 2.31 (dd, *J* = 13.8, 11.9 Hz, 1H), 2.23 – 2.16 (m, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.18, 173.51, 167.81, 160.58, 137.80, 137.29, 131.42, 130.79, 129.65, 129.06, 128.99, 127.40, 125.63, 61.09, 52.06, 51.90, 34.96, 32.64, 28.49, 17.47.

HRMS (ESI): m/z calcd for $C_{25}H_{25}N_2O_5$ ($[M+H]^+$): 433.1758; found: 433.1760.

7-ethyl 9-methyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ca).



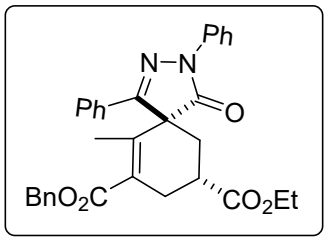
Yellow oil (39 mg, 87% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.72 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.49 – 7.42 (m, 5H), 7.23 (d, *J* = 7.4 Hz, 1H), 4.33 – 4.23 (m, 2H), 3.63 (s, 3H), 2.87 (dd, *J* = 14.0, 1.2 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.31 (dd, *J* = 13.9, 12.0 Hz, 1H), 2.23 – 2.14 (m, 1H), 1.94 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 173.59, 167.47, 160.66, 137.81, 136.56, 131.46, 130.76, 129.97, 129.05, 128.99, 127.42, 125.62, 119.04, 61.09, 60.94, 52.05, 34.98, 32.68, 28.49, 17.37, 14.27.

HRMS (ESI): m/z calcd for $C_{26}H_{27}N_2O_5$ ([M+H]$^+$): 447.1914; found: 447.1918.

7-benzyl 9-ethyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3da).



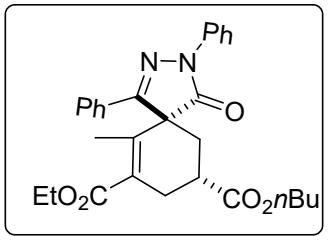
Yellow oil (43 mg, 82% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.48 – 7.35 (m, 10H), 7.70 – 7.18 (m, 13H), 7.23 (d, *J* = 7.2 Hz, 1H), 5.26 (s, 2H), 5.26 (s, 2H), 4.07 (dd, *J* = 14.0, 6.9 Hz, 2H), 2.90 (d, *J* = 16.7 Hz, 1H), 2.67 (dt, *J* = 22.4, 10.5 Hz, 2H), 2.32 (t, *J* = 13.0 Hz, 1H), 2.18 (d, *J* = 13.3 Hz, 1H), 1.94 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 173.06, 167.20, 160.64, 137.78, 137.40, 135.66, 131.44, 130.75, 129.69, 129.05, 128.98, 128.64, 128.35, 128.32, 127.41, 125.62, 119.02, 66.73, 61.19, 60.96, 35.11, 32.69, 28.52, 17.51, 14.07.

HRMS (ESI): m/z calcd for $C_{32}H_{31}N_2O_5$ ([M+H]$^+$): 523.2227; found: 523.2233.

9-butyl 7-ethyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ea).



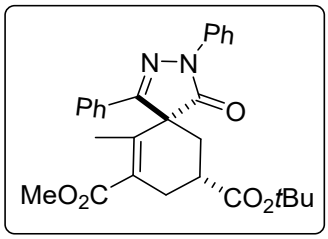
Yellow oil (44 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.72 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.46 (td, *J* = 7.9, 2.2 Hz, 5H), 7.23 (d, *J* = 7.4 Hz, 1H), 4.31 – 4.24 (m, 2H), 4.06 – 3.99 (m, 2H), 2.88 (dd, *J* = 14.3, 1.5 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.31 (dd, *J* = 13.8, 12.1 Hz, 1H), 2.22 – 2.14 (m, 1H), 1.94 (s, 3H), 1.54 (dt, *J* = 14.6, 6.8 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.30 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.30, 173.18, 167.54, 160.77, 137.82, 136.42, 131.50, 130.74, 130.11, 129.04, 128.98, 127.45, 125.61, 119.03, 64.86, 61.17, 60.93, 35.19, 32.73, 30.48, 28.57, 19.07, 17.67, 17.36, 14.26, 13.68.

HRMS (ESI): m/z calcd for $C_{29}H_{33}N_2O_5$ ([M+H]$^+$): 489.2384; found: 489.2386.

9-(tert-butyl) 7-methyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3fa).



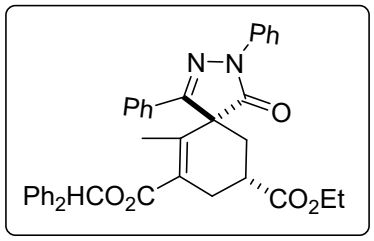
Yellow oil (45 mg, 95% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.72 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.46 (q, *J* = 8.0 Hz, 5H), 7.23 (d, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 2.90 – 2.80 (m, 1H), 2.67 – 2.56 (m, 1H), 2.55 – 2.45 (m, 1H), 2.25 (t, *J* = 13.3 Hz, 1H), 2.16 – 2.09 (m, 1H), 1.93 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.43, 172.35, 168.00, 160.88, 137.83, 136.94, 131.60, 130.71, 130.01, 129.01, 128.99, 127.48, 125.61, 119.04, 81.22, 61.39, 51.87, 36.12, 33.10, 28.80, 27.94, 17.43.

HRMS (ESI): m/z calcd for $C_{28}H_{30}N_2O_5Na$ ([M+Na]$^+$): 497.2047; found: 497.2050.

7-benzhydryl 9-ethyl 6-methyl-4-oxo-1,3-diphenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ga).



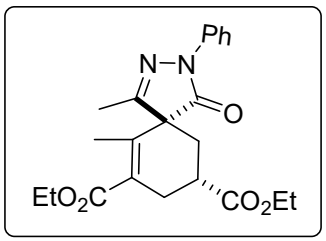
Yellow oil (isolated: 52 mg, 87% yield) (^{1}H NMR yield: 84% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.28 (m, 15H), 7.25 – 7.21 (m, 1H), 7.01 (s, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.94 (dd, *J* = 17.3, 4.3 Hz, 1H), 2.86 – 2.75 (m, 1H), 2.63 (dt, *J* = 10.1, 4.3 Hz, 1H), 2.34 (t, *J* = 13.1 Hz, 1H), 2.23 – 2.16 (m, 1H), 1.91 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19, 173.09, 166.38, 160.64, 140.13, 139.90, 137.78, 137.52, 131.47, 130.78, 129.66, 129.08, 129.00, 128.68, 128.64, 128.09, 127.44, 127.17, 127.12, 125.66, 119.05, 77.65, 61.21, 61.01, 35.12, 32.70, 28.47, 17.52, 14.09.

HRMS (ESI): m/z calcd for $C_{38}H_{34}N_2O_5Na$ ([M+H]$^+$): 621.2360; found: 621.2362.

diethyl 1,6-dimethyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ab).

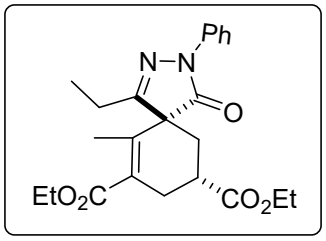


Yellow oil (20 mg, 50% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.44 – 7.37 (m, 2H), 7.24 – 7.18 (m, 1H), 4.24 (td, *J* = 7.1, 0.9 Hz, 2H), 4.17 (t, *J* = 7.1 Hz, 2H), 2.86 (ddd, *J* = 17.2, 3.1, 1.5 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.65 – 2.55 (m, 1H), 2.26 – 2.18 (m, 1H), 2.16 (s, 3H), 2.15 – 2.10 (m, 1H), 1.76 (dd, *J* = 2.2, 1.2 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

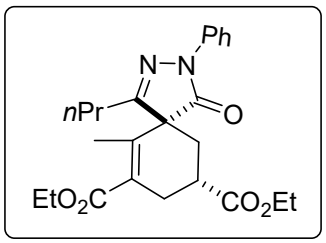
^{13}C NMR (101 MHz, $CDCl_3$)δ 174.09, 173.22, 167.42, 161.74, 137.75, 135.52, 130.27, 128.96, 125.40, 118.86, 61.61, 61.15, 60.89, 36.28, 31.91, 28.65, 16.38, 16.06, 14.25, 14.21.
HRMS (ESI): m/z calcd for $C_{22}H_{27}N_2O_5$ ($[M+H]^+$): 399.1914; found: 399.1918.

diethyl 1-ethyl-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ac).



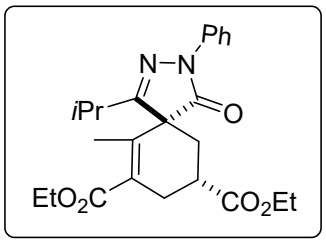
Yellow oil (19 mg, 46% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.45 – 7.38 (m, 2H), 7.23 – 7.18 (m, 1H), 4.26 – 4.15 (m, 4H), 2.89 – 2.81 (m, 1H), 2.81 – 2.72 (m, 1H), 2.64 – 2.47 (m, 2H), 2.37 (dq, *J* = 17.6, 7.3 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.12 (ddd, *J* = 13.8, 3.4, 1.8 Hz, 1H), 1.75 (dd, *J* = 2.2, 1.2 Hz, 3H), 1.34 – 1.25 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.25, 173.29, 167.46, 165.70, 137.94, 135.95, 130.03, 128.93, 125.31, 118.86, 61.73, 61.13, 60.87, 36.39, 32.04, 28.63, 23.47, 16.45, 14.25, 14.21, 9.69.
HRMS (ESI): m/z calcd for $C_{23}H_{29}N_2O_5$ ($[M+H]^+$): 413.2071; found: 413.2072.

diethyl 6-methyl-4-oxo-3-phenyl-1-propyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ad).



Yellow oil (25 mg, 59% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.26 – 4.15 (m, 4H), 2.90 – 2.82 (m, 1H), 2.81 – 2.71 (m, 1H), 2.59 (ddd, *J* = 17.1, 11.3, 2.5 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.29 (ddd, *J* = 17.1, 8.7, 6.6 Hz, 1H), 2.20 (t, *J* = 13.4 Hz, 1H), 2.12 (ddd, *J* = 13.8, 3.4, 1.7 Hz, 1H), 1.83 (dt, *J* = 23.2, 8.0 Hz, 2H), 1.75 (d, *J* = 0.9 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.16, 173.28, 167.44, 164.59, 137.91, 135.99, 130.00, 128.91, 125.29, 118.82, 61.78, 61.11, 60.84, 36.35, 32.04, 31.90, 28.62, 18.63, 16.49, 14.24, 14.20, 13.94.
HRMS (ESI): m/z calcd for $C_{24}H_{31}N_2O_5$ ($[M+H]^+$): 427.2227; found: 427.2228.

diethyl 1-isopropyl-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ae).



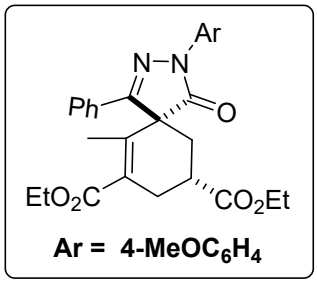
Yellow oil (25 mg, 59% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.44 – 7.38 (m, 2H), 7.23 – 7.17 (m, 1H), 4.26 – 4.15 (m, 4H), 2.91 – 2.56 (m, 4H), 2.24 – 2.11 (m, 2H), 1.76 (dd, *J* = 2.2, 1.2 Hz, 3H), 1.37 – 1.25 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.06, 173.33, 169.08, 167.45, 137.94, 136.36, 129.82, 128.92, 125.32, 118.89, 61.90, 61.13, 60.84, 36.31, 32.22, 29.58, 28.58, 21.45, 21.21, 16.88, 14.26, 14.21.

HRMS (ESI): m/z calcd for $C_{24}H_{31}N_2O_5$ ($[M+H]^+$): 427.2227; found: 427.2230.

diethyl 3-(4-methoxyphenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ag).



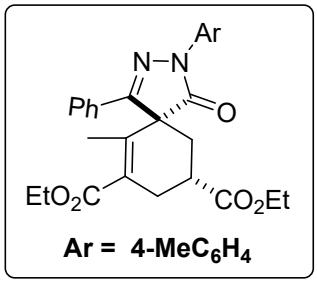
Yellow oil (38 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.71 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.00 – 6.94 (m, 2H), 4.33 – 4.23 (m, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.92 – 2.84 (m, 1H), 2.72 – 2.57 (m, 2H), 2.35 – 2.25 (m, 1H), 2.17 (dd, *J* = 14.8, 2.6 Hz, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.98, 173.19, 167.55, 160.60, 157.40, 136.58, 131.59, 131.15, 130.65, 129.99, 129.02, 127.40, 120.86, 114.11, 60.97, 60.95, 60.91, 55.54, 35.13, 32.70, 28.59, 17.34, 14.27, 14.09.

HRMS (ESI): m/z calcd for $C_{28}H_{31}N_2O_6$ ($[M+H]^+$): 491.2177; found: 491.2181.

diethyl 6-methyl-4-oxo-1-phenyl-3-(p-tolyl)-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ah).



Yellow oil (43 mg, 91% yield)

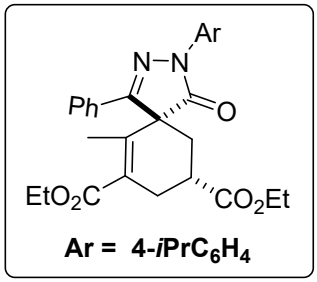
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.69 (m, 2H), 7.50 – 7.40 (m, 3H), 7.27

– 7.20 (m, 2H), 4.28 (tt, *J* = 7.1, 3.6 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 15.5 Hz, 1H), 2.73 – 2.55 (m, 2H), 2.37 (s, 3H), 2.35 – 2.26 (m, 1H), 2.21 – 2.13 (m, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.16, 173.18, 167.56, 160.60, 136.53, 135.41, 135.38, 131.60, 130.66, 130.02, 129.48, 129.02, 127.43, 119.10, 61.07, 60.94, 60.91, 35.16, 32.73, 28.59, 21.00, 17.32, 14.27, 14.09.

HRMS (ESI): m/z calcd for $C_{28}H_{31}N_2O_5$ ($[M+H]^+$): 475.2227; found: 475.2231.

diethyl 3-(4-isopropylphenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ai).



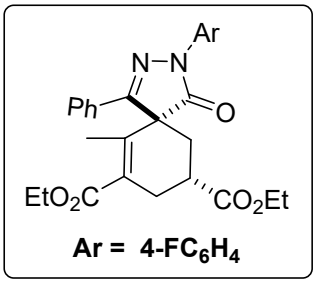
Yellow oil (39 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.28 (dd, *J* = 6.6 Hz, 2H), 4.08 (dd, *J* = 13.8, 6.8 Hz, 2H), 2.99 – 2.81 (m, 2H), 2.67 (dd, *J* = 27.6, 11.0 Hz, 2H), 2.30 (t, *J* = 12.8 Hz, 1H), 2.17 (d, *J* = 13.4 Hz, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 6.7 Hz, 6H), 1.19 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17, 173.18, 167.55, 160.59, 146.45, 136.57, 135.58, 131.58, 130.65, 129.98, 129.01, 127.42, 126.89, 119.22, 61.05, 60.94, 60.90, 35.13, 33.74, 32.72, 28.59, 24.02, 17.32, 14.26, 14.09.

HRMS (ESI): m/z calcd for $C_{30}H_{35}N_2O_5$ ($[M+H]^+$): 503.2540; found: 503.2543.

diethyl 3-(4-fluorophenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3aj).



Yellow oil (42 mg, 88% yield)

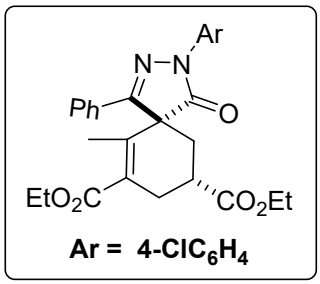
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.72 (d, *J* = 6.2 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.13 (t, *J* = 7.8 Hz, 2H), 4.29 (d, *J* = 6.5 Hz, 2H), 4.09 (d, *J* = 6.8 Hz, 2H), 2.88 (d, *J* = 15.1 Hz, 1H), 2.67 (dd, *J* = 29.1, 11.3 Hz, 2H), 2.30 (t, *J* = 12.6 Hz, 1H), 2.18 (d, *J* = 13.5 Hz, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 6.6 Hz, 3H), 1.19 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17, 173.10, 167.51, 161.41, 160.92, 158.98, 136.20, 133.95, 131.37, 130.84, 130.21, 129.07, 127.43, 120.82, 120.74, 115.81, 115.59, 61.07, 60.97, 35.08, 32.72, 28.56, 17.36, 14.26, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.30.

HRMS (ESI): m/z calcd for $C_{27}H_{28}FN_2O_5$ ([M+H]$^+$): 479.1977; found: 479.1981.

diethyl 3-(4-fluorophenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ak).



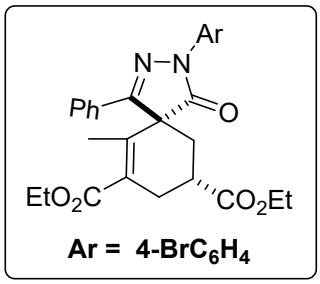
Yellow oil (47 mg, 95% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 6.8 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.40 (d, *J* = 8.9 Hz, 2H), 4.29 (dd, *J* = 13.5, 6.4 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 15.5 Hz, 1H), 2.74 – 2.56 (m, 2H), 1.92 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.28, 173.05, 167.48, 161.03, 136.37, 136.07, 131.27, 130.91, 130.70, 130.27, 129.08, 129.01, 127.43, 120.07, 61.12, 60.98, 35.06, 32.70, 28.53, 17.37, 14.26, 14.08.

HRMS (ESI): m/z calcd for $C_{27}H_{28}ClN_2O_5$ ([M+H]$^+$): 495.1681; found: 495.1685.

diethyl 3-(4-bromophenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3al).



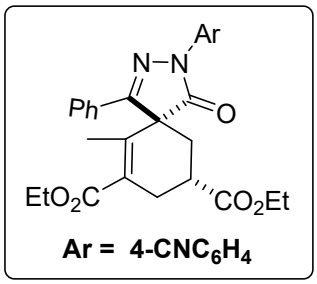
Yellow oil (50 mg, 93% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.72 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.57 – 7.53 (m, 2H), 7.50 – 7.43 (m, 3H), 4.32 – 4.25 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.84 (m, 1H), 2.65 (dtd, *J* = 15.4, 10.7, 3.4 Hz, 2H), 2.35 – 2.25 (m, 1H), 2.22 – 2.14 (m, 1H), 1.92 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.30, 173.04, 167.48, 161.05, 136.87, 136.04, 131.97, 131.26, 130.93, 130.29, 129.09, 127.44, 120.36, 118.48, 61.14, 60.98, 35.06, 32.70, 28.53, 17.37, 14.26, 14.09.

HRMS (ESI): m/z calcd for $C_{27}H_{28}BrN_2O_5$ ([M+H]$^+$): 539.1176; found: 539.1179.

diethyl 3-(4-cyanophenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3am).



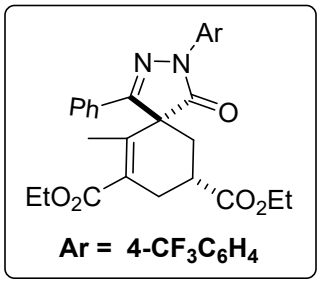
Yellow oil (42 mg, 87% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.77 – 7.70 (m, 4H), 7.55 – 7.44 (m, 3H), 4.34 – 4.25 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.88 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.76 – 2.56 (m, 2H), 2.31 (dd, *J* = 13.8, 11.9 Hz, 1H), 2.20 (dd, *J* = 13.9, 2.3 Hz, 1H), 1.92 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 174.79, 172.88, 167.39, 161.72, 141.17, 135.44, 133.20, 131.24, 130.91, 130.65, 129.17, 127.50, 118.71, 118.61, 108.42, 61.25, 61.05, 35.01, 32.74, 28.46, 17.41, 14.25, 14.08.

HRMS (ESI): m/z calcd for $C_{28}H_{28}N_3O_5$ ($[M+H]^+$): 486.2023; found: 486.2028.

diethyl 6-methyl-4-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3an).



Yellow oil (49.5 mg, 94% yield)

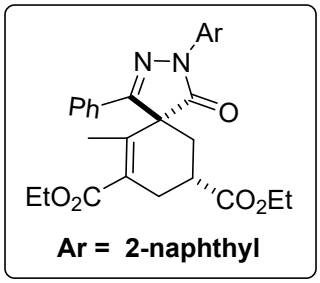
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.76 – 7.68 (m, 4H), 7.54 – 7.44 (m, 3H), 4.33 – 4.26 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.85 (m, 1H), 2.76 – 2.58 (m, 2H), 2.36 – 2.28 (m, 1H), 2.23 – 2.17 (m, 1H), 1.93 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) [1] δ 174.69, 173.00, 167.47, 161.39, 140.53, 135.80, 131.14, 131.09, 130.48, 129.15, 127.50, 127.32, 127.00, 126.26, 126.22, 125.41, 122.71, 61.24, 61.04, 35.07, 32.74, 28.52, 17.39, 14.26, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18.

HRMS (ESI): m/z calcd for $C_{28}H_{28}F_3N_2O_5$ ($[M+H]^+$): 529.1945; found: 529.1946.

diethyl 6-methyl-3-(naphthalen-2-yl)-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ao).



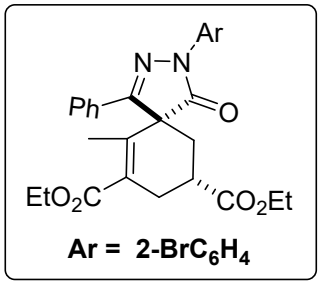
Yellow oil (45.6 mg, 89% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.24 – 8.16 (m, 1H), 7.93 – 7.82 (m, 3H), 7.77 (d, *J* = 6.2 Hz, 2H), 7.48 (dq, *J* = 13.2, 6.7 Hz, 5H), 4.29 (dd, *J* = 13.4, 6.4 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.90 (d, *J* = 15.5 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.36 (t, *J* = 12.8 Hz, 1H), 2.24 (d, *J* = 13.9 Hz, 1H), 1.97 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.54, 173.14, 167.55, 160.89, 136.36, 135.34, 133.44, 131.48, 131.26, 130.80, 130.16, 129.08, 128.86, 128.08, 127.65, 127.48, 126.64, 125.64, 118.41, 116.36, 61.21, 60.97, 60.95, 35.15, 32.76, 28.58, 17.40, 14.27, 14.09.

HRMS (ESI): m/z calcd for $C_{31}H_{31}N_2O_5$ ($[M+H]^+$): 511.2227; found: 511.2233.

diethyl 3-(2-bromophenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ap).



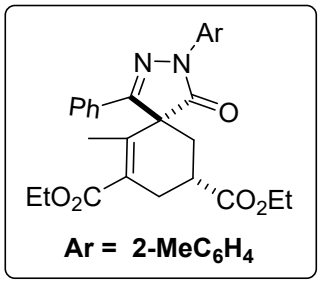
Yellow oil (50 mg, 93% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (ddd, *J* = 14.3, 8.1, 1.3 Hz, 3H), 7.49 – 7.39 (m, 5H), 7.30 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H), 4.33 – 4.25 (m, 2H), 4.13 – 4.05 (m, 2H), 2.87 (dd, *J* = 12.3, 10.5 Hz, 1H), 2.72 – 2.55 (m, 2H), 2.39 – 2.29 (m, 1H), 2.28 – 2.21 (m, 1H), 2.08 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.59, 173.19, 167.53, 160.89, 136.42, 135.78, 133.86, 131.59, 130.66, 130.45, 130.23, 129.28, 129.01, 128.29, 127.40, 121.73, 60.98, 60.92, 59.80, 35.16, 32.77, 28.67, 17.75, 14.27, 14.11.

HRMS (ESI): m/z calcd for $C_{27}H_{28}BrN_2O_5$ ($[M+H]^+$): 539.1176; found: 539.1172.

diethyl 6-methyl-4-oxo-1-phenyl-3-(o-tolyl)-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3aq).



Yellow oil (42 mg, 89% yield)

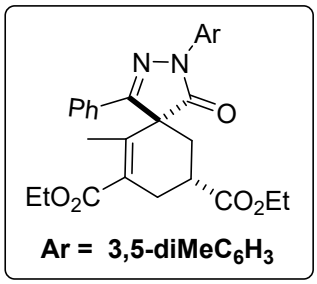
^{1}H NMR (400 MHz, $CDCl_3$)δ 7.69 (d, *J* = 6.6 Hz, 2H), 7.43 (dd, *J* = 15.3, 7.7 Hz, 3H), 7.39 – 7.35 (m, 1H), 7.34 – 7.27 (m, 3H), 4.29 (qd, *J* = 7.0, 2.3 Hz, 2H), 4.14 – 4.04 (m, 2H), 2.90 (d, *J* = 12.7 Hz, 1H), 2.73 – 2.59 (m, 2H), 2.32 (d, *J* = 19.7 Hz, 4H), 2.20 (d, *J* = 13.8 Hz, 1H), 2.04 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.79, 173.23, 167.51, 160.83, 136.61, 135.47, 135.09, 131.68, 131.30,

130.57, 130.04, 129.00, 128.83, 127.30, 126.68, 126.58, 60.99, 60.91, 59.88, 35.13, 32.91, 28.67, 18.58, 17.58, 14.27, 14.10.

HRMS (ESI): m/z calcd for $C_{28}H_{31}N_2O_5$ ($[M+H]^+$): 475.2227; found: 475.2230.

diethyl 3-(3,5-dimethylphenyl)-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ar).



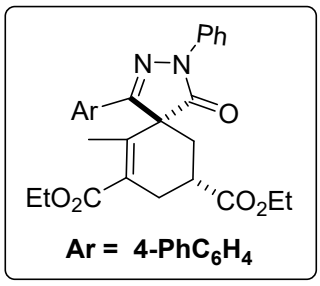
White solid (melting point 140-143°C) (44 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.5 Hz, 2H), 7.64 (s, 2H), 7.45 (d, *J* = 7.2 Hz, 3H), 6.89 (s, 1H), 4.28 (dd, *J* = 12.7, 6.3 Hz, 2H), 4.08 (dd, *J* = 14.0, 7.0 Hz, 2H), 2.87 (d, *J* = 15.4 Hz, 1H), 2.72 – 2.57 (m, 2H), 2.37 (s, 6H), 2.33 – 2.26 (m, 1H), 2.16 (d, *J* = 13.8 Hz, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 173.19, 167.58, 160.64, 138.76, 137.63, 136.51, 131.59, 130.68, 130.02, 129.03, 127.46, 127.43, 116.94, 61.12, 60.95, 60.92, 35.16, 32.72, 28.60, 21.53, 17.31, 14.28, 14.09.

HRMS (ESI): m/z calcd for $C_{29}H_{33}N_2O_5$ ($[M+H]^+$): 489.2384; found: 489.2385.

diethyl 1-([1,1'-biphenyl]-4-yl)-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3as).



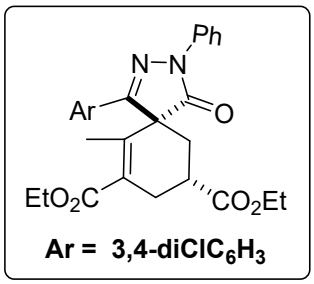
Yellow oil (42 mg, 78% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.50 – 7.43 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.21 (m, 1H), 4.29 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.92 (q, *J* = 9.9 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.39 – 2.30 (m, 1H), 2.26 – 2.19 (m, 1H), 1.95 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.37, 173.15, 167.59, 160.39, 143.42, 139.87, 137.86, 136.49, 130.31, 130.12, 129.00, 128.06, 127.83, 127.64, 127.08, 125.64, 119.07, 61.11, 61.00, 60.96, 35.23, 32.88, 28.61, 17.42, 14.29, 14.11.

HRMS (ESI): m/z calcd for $C_{33}H_{33}N_2O_5$ ($[M+H]^+$): 537.2384; found: 537.2388.

diethyl 1-(3,4-dichlorophenyl)-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3at).



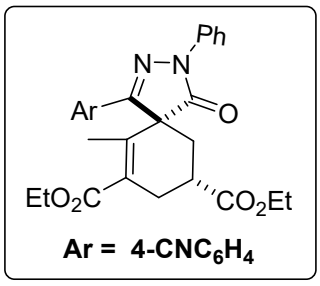
Yellow oil (47 mg, 89% yield)

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.52 (dd, *J* = 8.1, 5.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 4.29 (q, *J* = 7.0 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.88 (dd, *J* = 17.7, 5.0 Hz, 1H), 2.72 (ddd, *J* = 17.7, 10.6, 2.3 Hz, 1H), 2.60 (ddd, *J* = 15.7, 9.7, 4.5 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.17 (dd, *J* = 14.0, 2.3 Hz, 1H), 1.88 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.02, 172.80, 167.38, 158.25, 137.56, 135.27, 135.13, 133.68, 131.33, 131.05, 130.78, 129.21, 129.06, 126.14, 125.91, 119.07, 61.14, 61.07, 60.73, 35.23, 32.82, 28.42, 17.28, 14.25, 14.11.

HRMS (ESI): m/z calcd for $C_{27}H_{27}Cl_2N_2O_5$ ($[M+H]^+$): 529.1292; found: 529.1290.

diethyl 1-(4-cyanophenyl)-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3au).



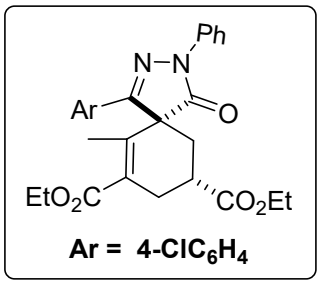
Yellow oil (16 mg, 33% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 4.30 (tt, *J* = 7.2, 3.6 Hz, 2H), 4.13 – 4.08 (m, 2H), 2.89 (dd, *J* = 17.9, 5.0 Hz, 1H), 2.73 (ddd, *J* = 17.9, 10.5, 2.3 Hz, 1H), 2.56 (ddd, *J* = 15.7, 11.3, 4.5 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.17 (dd, *J* = 14.0, 2.3 Hz, 1H), 1.89 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.09, 172.74, 167.38, 158.56, 137.50, 135.55, 135.45, 132.82, 130.81, 129.12, 127.79, 126.09, 119.12, 118.09, 114.19, 61.19, 61.15, 60.71, 35.33, 32.81, 28.49, 17.33, 14.27, 14.11.

HRMS (ESI): m/z calcd for $C_{28}H_{28}N_3O_5$ ($[M+H]^+$): 486.2023; found: 486.2025.

diethyl 1-(4-chlorophenyl)-6-methyl-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3av).



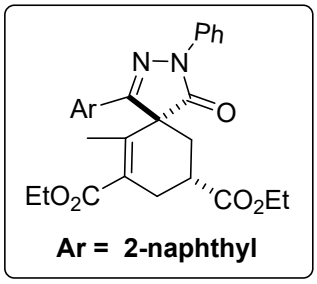
Yellow oil (28 mg, 57% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.44 (dd, *J* = 12.4, 6.3 Hz, 4H), 7.28 – 7.21 (m, 1H), 4.29 (tt, *J* = 7.1, 3.6 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.92 – 2.83 (m, 1H), 2.75 – 2.65 (m, 1H), 2.60 (ddd, *J* = 15.7, 9.6, 4.3 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.16 (dd, *J* = 13.9, 2.1 Hz, 1H), 1.90 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.17, 172.97, 167.48, 159.56, 137.71, 136.97, 135.95, 130.42, 129.96, 129.39, 129.02, 128.64, 125.76, 119.05, 61.07, 61.02, 60.95, 35.20, 32.83, 28.52, 17.32, 14.27, 14.11.

HRMS (ESI): m/z calcd for $C_{27}H_{28}ClN_2O_5$ ($[M+H]^+$): 495.1681; found: 495.1682.

diethyl 6-methyl-1-(naphthalen-2-yl)-4-oxo-3-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3aw).



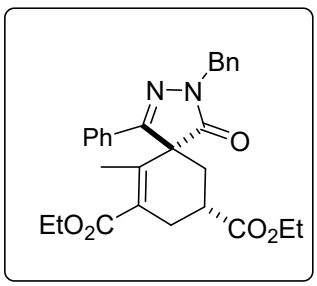
Yellow oil (13 mg, 25% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.92 (s, 2H), 7.90 – 7.85 (m, 2H), 7.60 – 7.53 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.23 (m, 1H), 4.37 – 4.28 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.80 – 2.66 (m, 2H), 2.40 – 2.32 (m, 1H), 2.26 (d, *J* = 14.0 Hz, 1H), 1.97 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.42, 173.09, 167.76, 160.60, 137.90, 136.05, 134.20, 132.92, 130.37, 129.05, 129.00, 128.96, 128.94, 127.85, 127.68, 127.62, 126.95, 125.70, 124.15, 119.15, 61.12, 61.02, 35.18, 33.07, 28.55, 17.49, 14.34, 14.10.

HRMS (ESI): m/z calcd for $C_{31}H_{31}N_2O_5$ ($[M+H]^+$): 511.2227; found: 511.2229.

diethyl 3-benzyl-6-methyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ax).



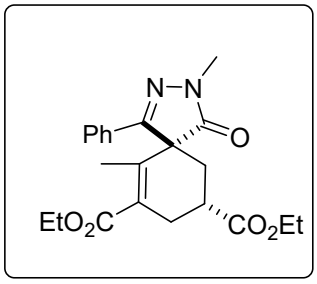
Yellow oil (31.1 mg, 66% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 2H), 7.42 – 7.29 (m, 8H), 4.97 (q, *J* = 15.0 Hz, 2H), 4.25 (tt, *J* = 16.2, 8.0 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.84 (d, *J* = 15.5 Hz, 1H), 2.69 – 2.51 (m, 2H), 2.21 (t, *J* = 12.9 Hz, 1H), 2.04 (d, *J* = 12.4 Hz, 1H), 1.79 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.69, 173.27, 167.52, 160.44, 136.82, 136.31, 131.72, 130.36, 129.69, 128.89, 128.69, 128.22, 127.83, 127.21, 60.91, 60.85, 59.57, 48.51, 35.05, 32.32, 28.58, 17.22, 14.26, 14.08.

HRMS (ESI): m/z calcd for $C_{28}H_{31}N_2O_5$ ($[M+Na]^+$): 497.2047; found: 497.2047.

diethyl 3,6-dimethyl-4-oxo-1-phenyl-2,3-diazaspiro[4.5]deca-1,6-diene-7,9-dicarboxylate (3ay).



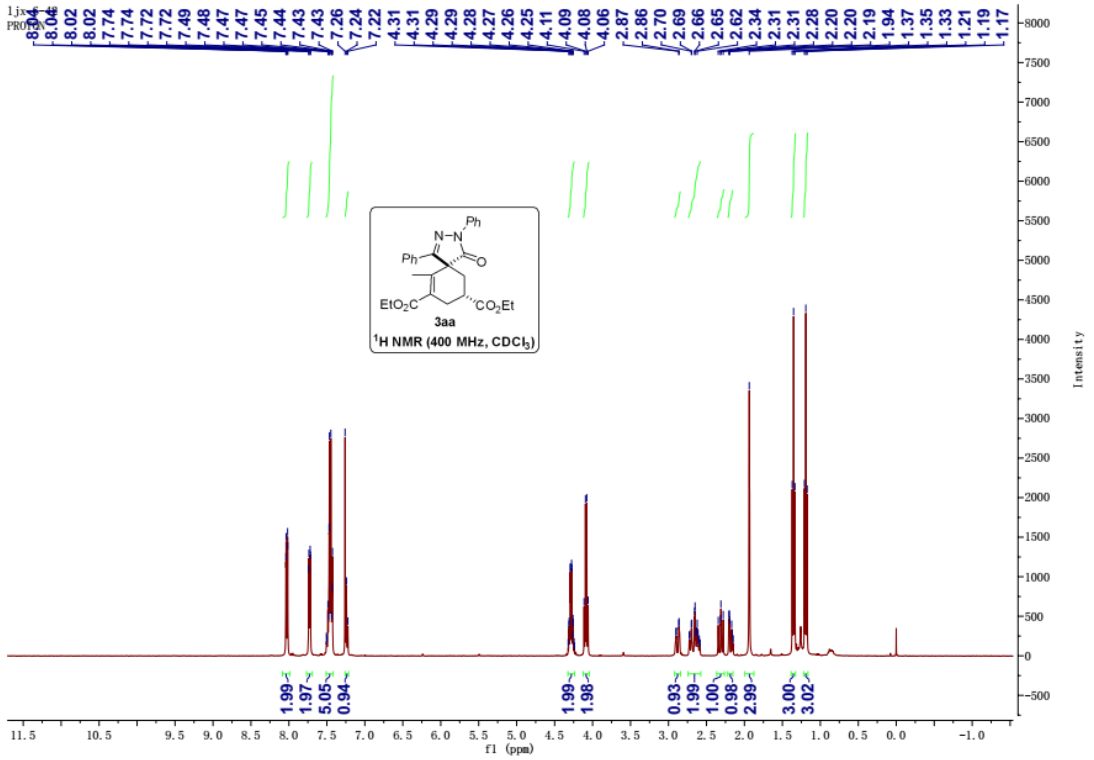
Yellow oil (20 mg, 50% yield)

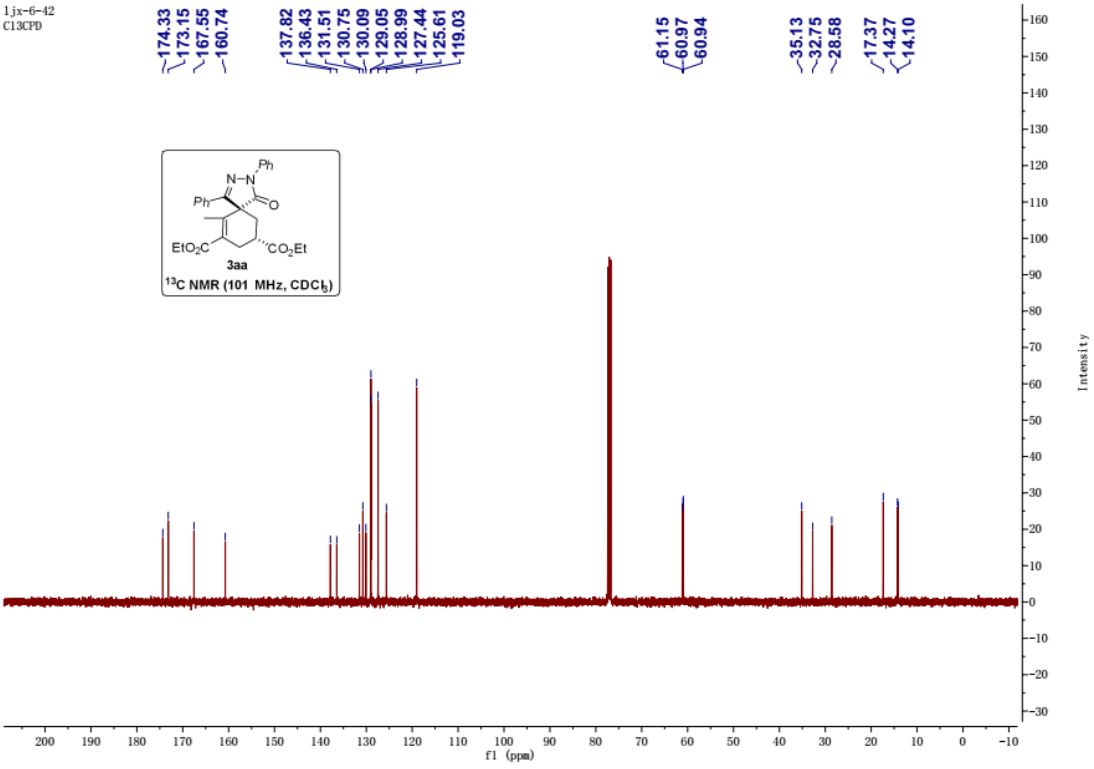
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.37 (m, 3H), 4.27 (dd, *J* = 13.6, 6.6 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 2.85 (d, *J* = 14.4 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.17 (t, *J* = 12.9 Hz, 1H), 2.03 (d, *J* = 13.0 Hz, 1H), 1.86 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

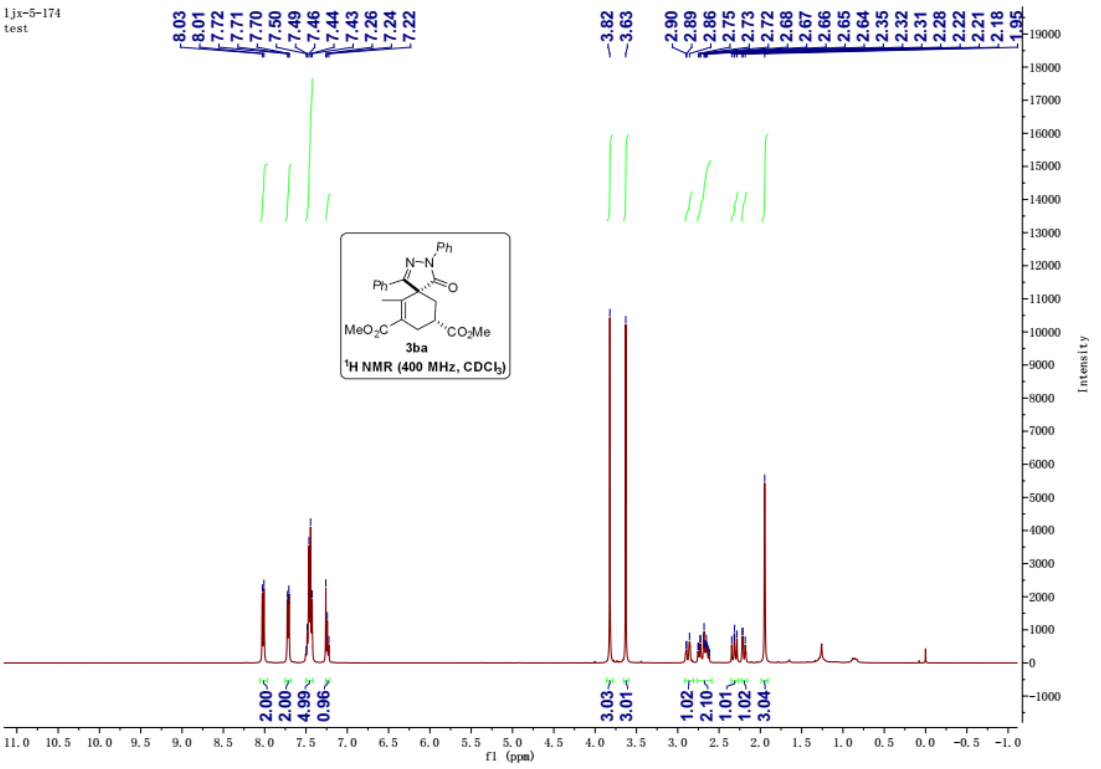
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.83, 173.27, 167.55, 160.40, 136.69, 131.77, 130.42, 129.79, 129.00, 127.16, 60.91, 60.87, 59.63, 35.08, 32.47, 31.78, 28.64, 17.25, 14.27, 14.10.

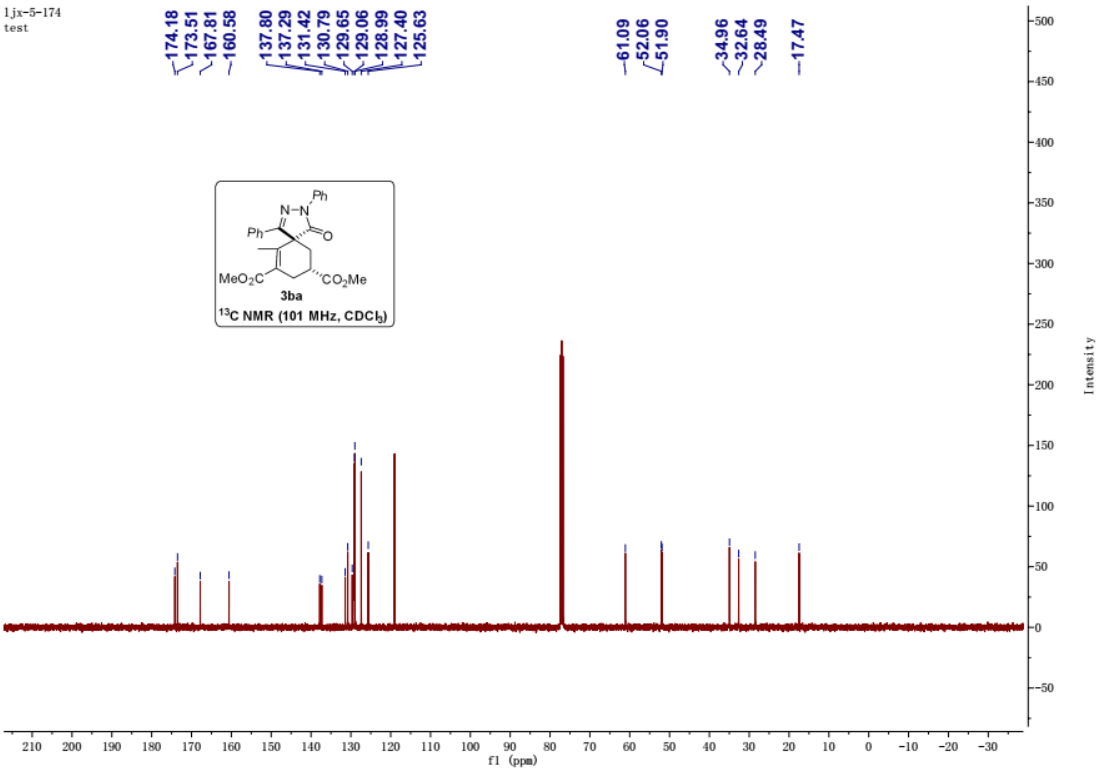
HRMS (ESI): m/z calcd for $C_{22}H_{27}N_2O_5$ ($[M+Na]^+$): 421.1734; found: 421.1734.

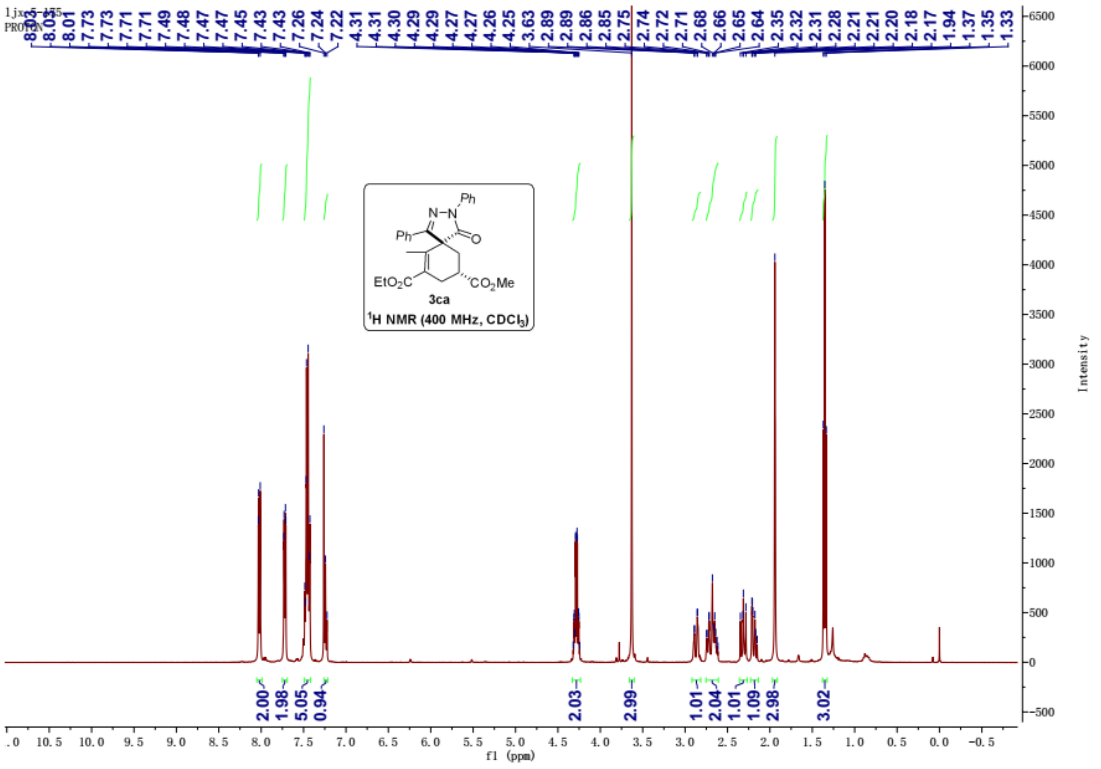
7. Spectra

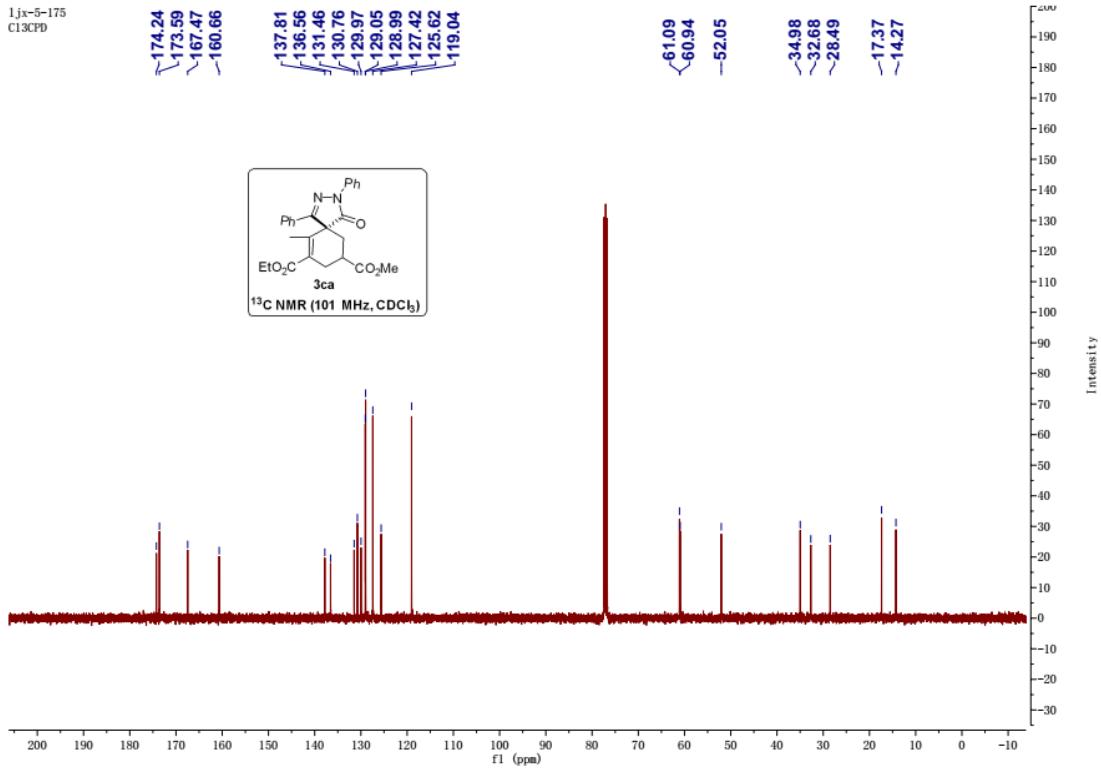

3aa
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

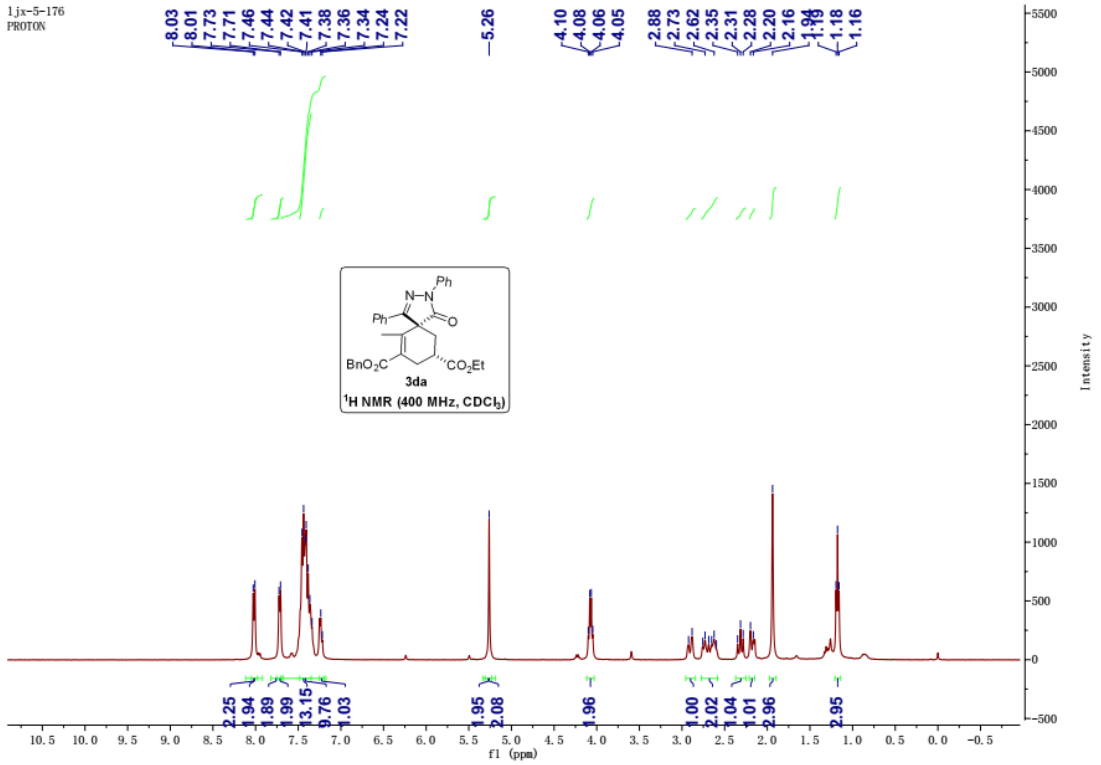

3aa
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

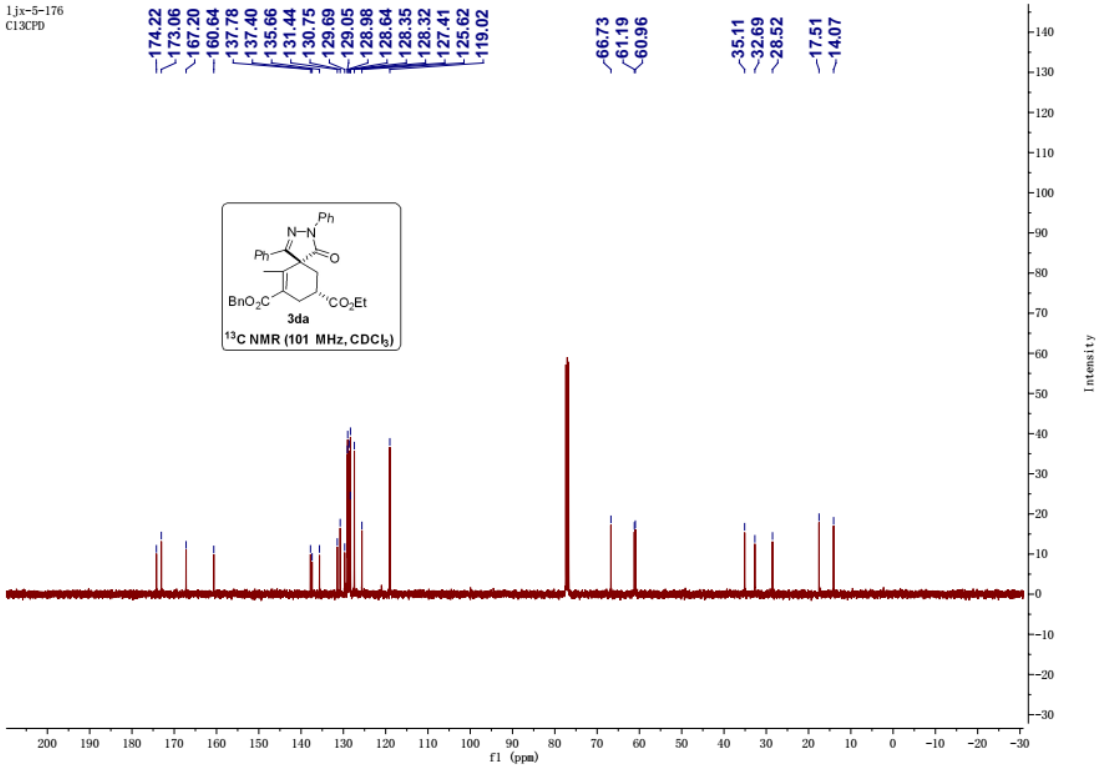

ljx-5-174
test
8.03
8.01
7.72
7.71
7.70
7.50
7.49
7.46
7.44
7.43
7.26
7.24
7.22
3.82
3.63
2.90
2.89
2.86
2.75
2.73
2.72
2.68
2.67
2.66
2.65
2.64
2.35
2.32
2.31
2.28
2.22
2.21
2.18
1.95
Ph
N–N
Ph
O
MeO2C
CO2Me
3ba
1H NMR (400 MHz, CDCl3)
2.00
2.00
4.99
0.96
3.03
3.01
1.02
2.10
1.01
1.02
3.04
f1 (ppm)
Intensity

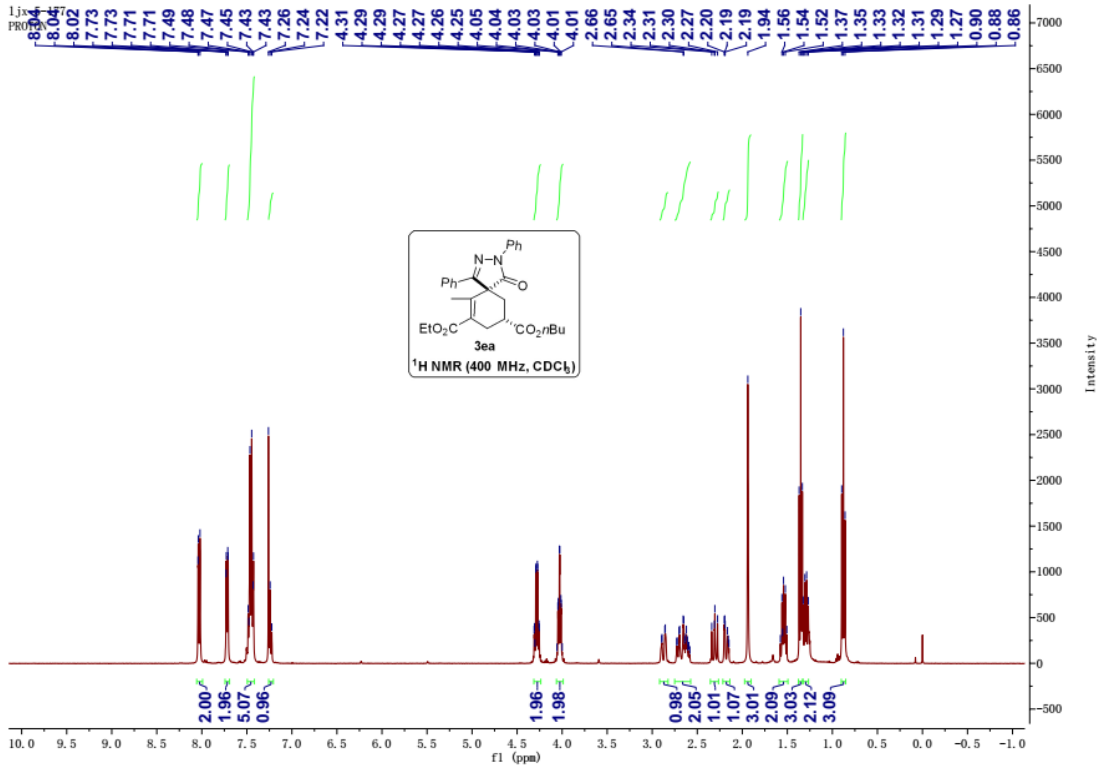

ljx-5-174
test
174.18
173.51
167.81
160.58
137.80
137.29
131.42
130.79
129.65
129.06
128.99
127.40
125.63
61.09
52.06
51.90
34.96
32.64
28.49
17.47
Ph
N–N
Ph
O
MeO2C
CO2Me
3ba
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

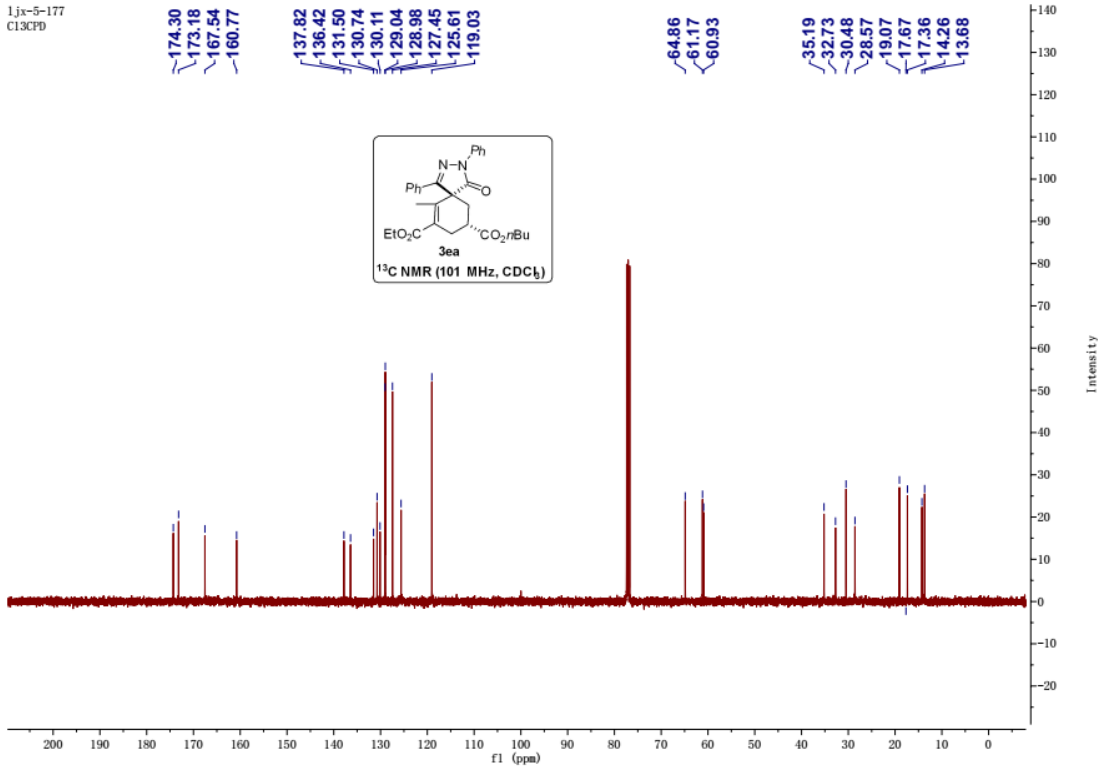

3ca
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

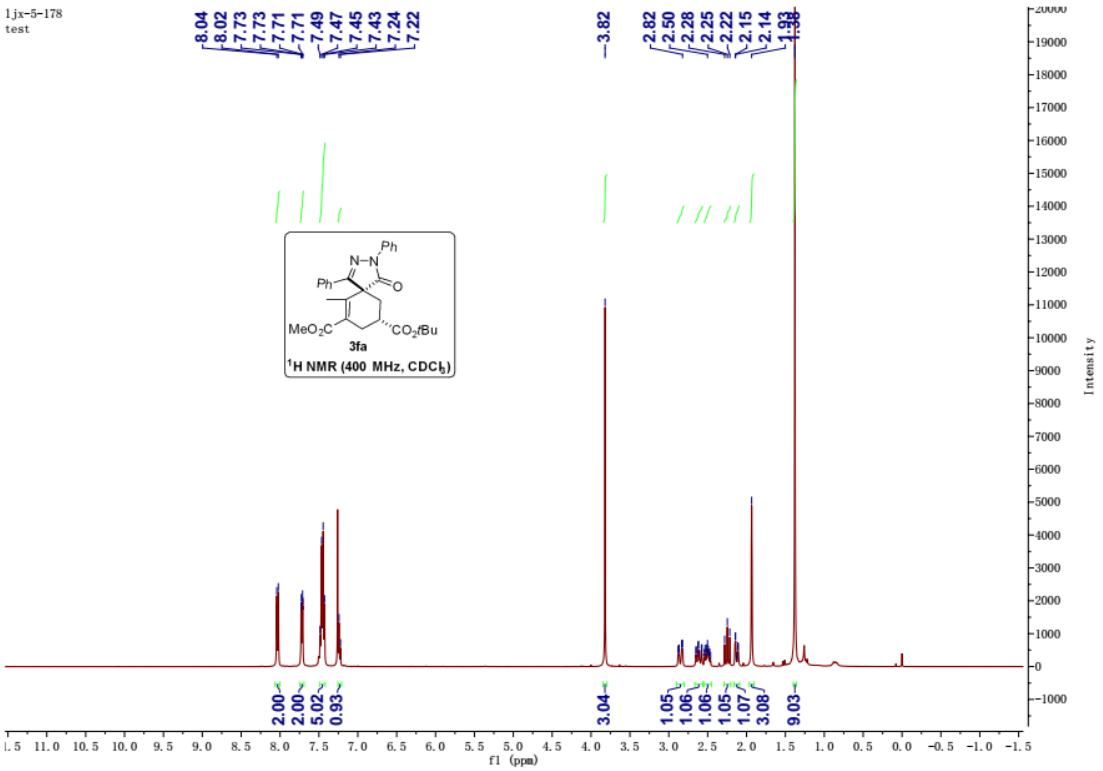

3ca
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

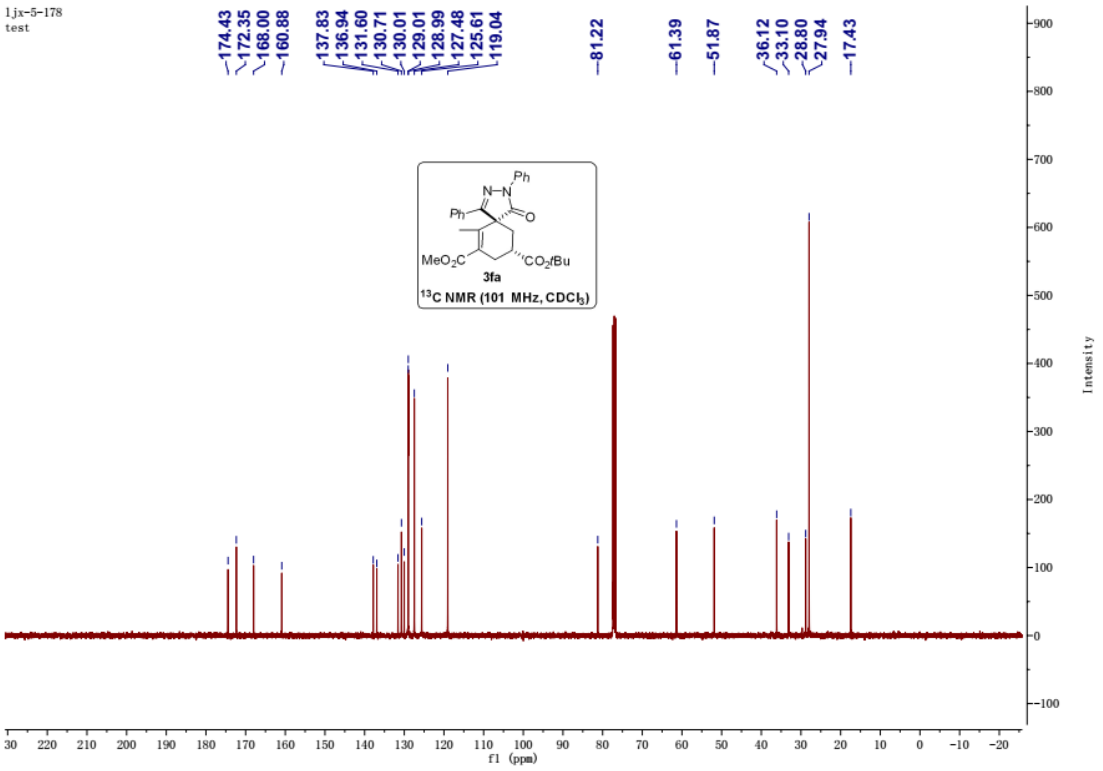

ljx-5-176
PROTON
3da
^{1}H NMR (400 MHz, CDCl$_3$)
Intensity
f1 (ppm)

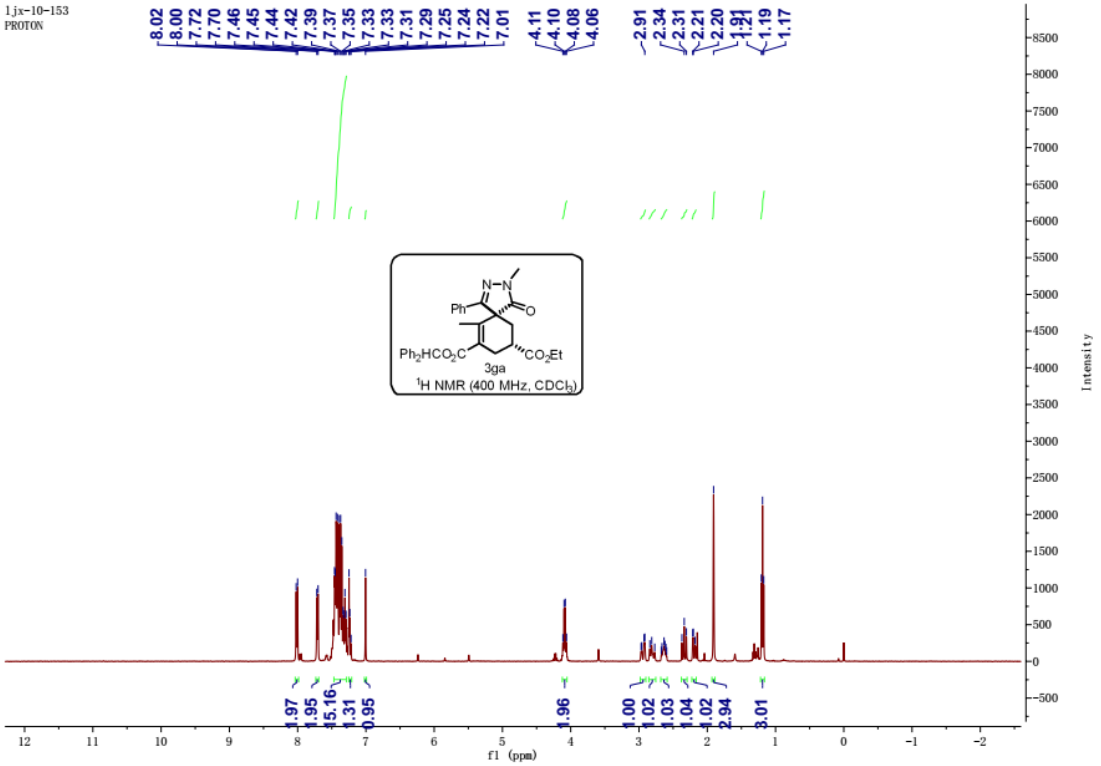

ljx-5-176
C13CPD
3da
^{13}C NMR (101 MHz, CDCl$_3$)
Intensity
f1 (ppm)

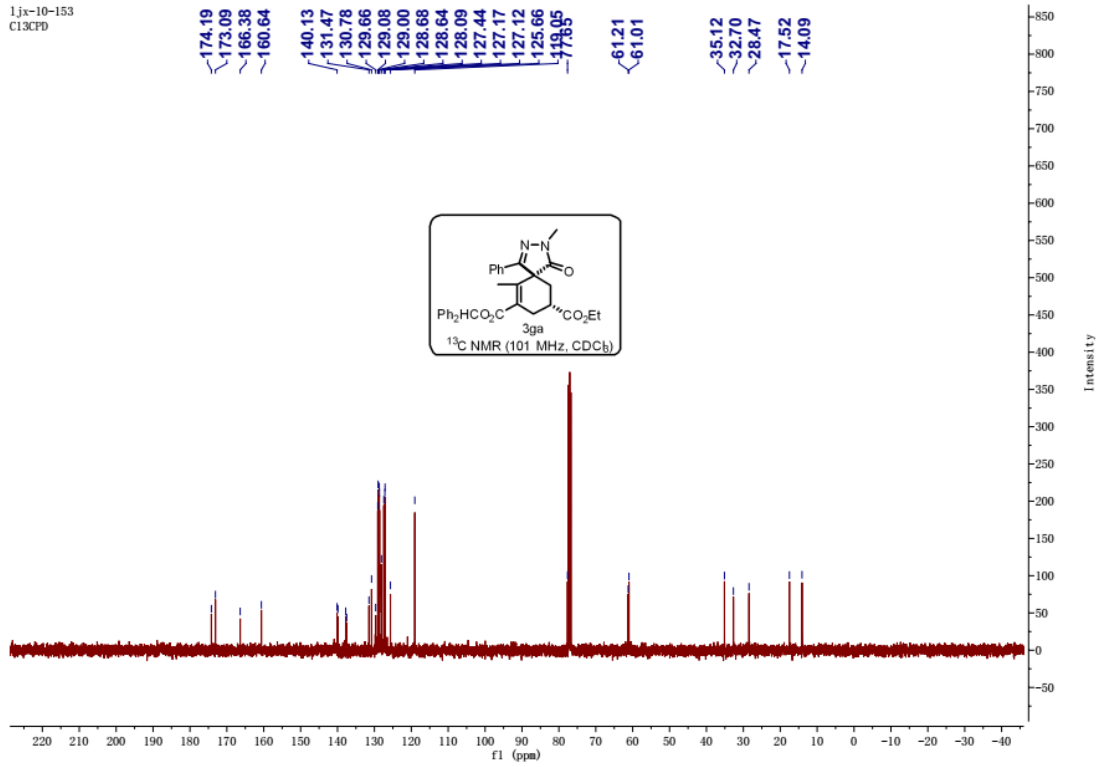

3ea
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

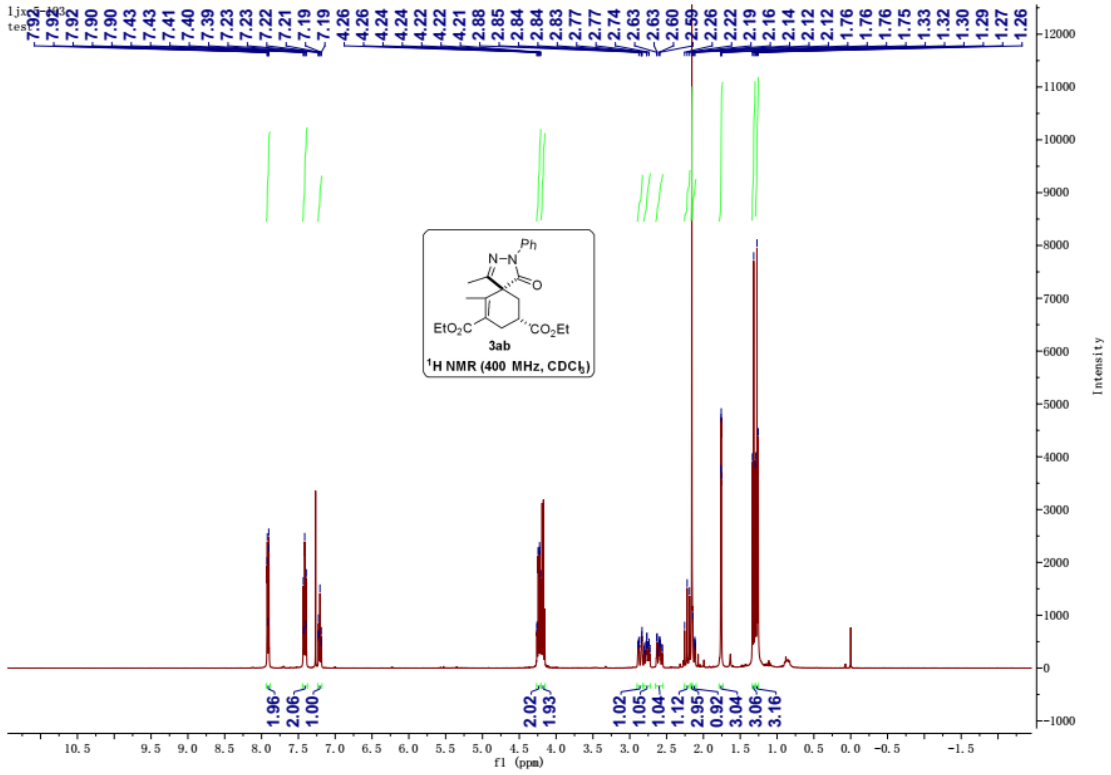

3ea
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

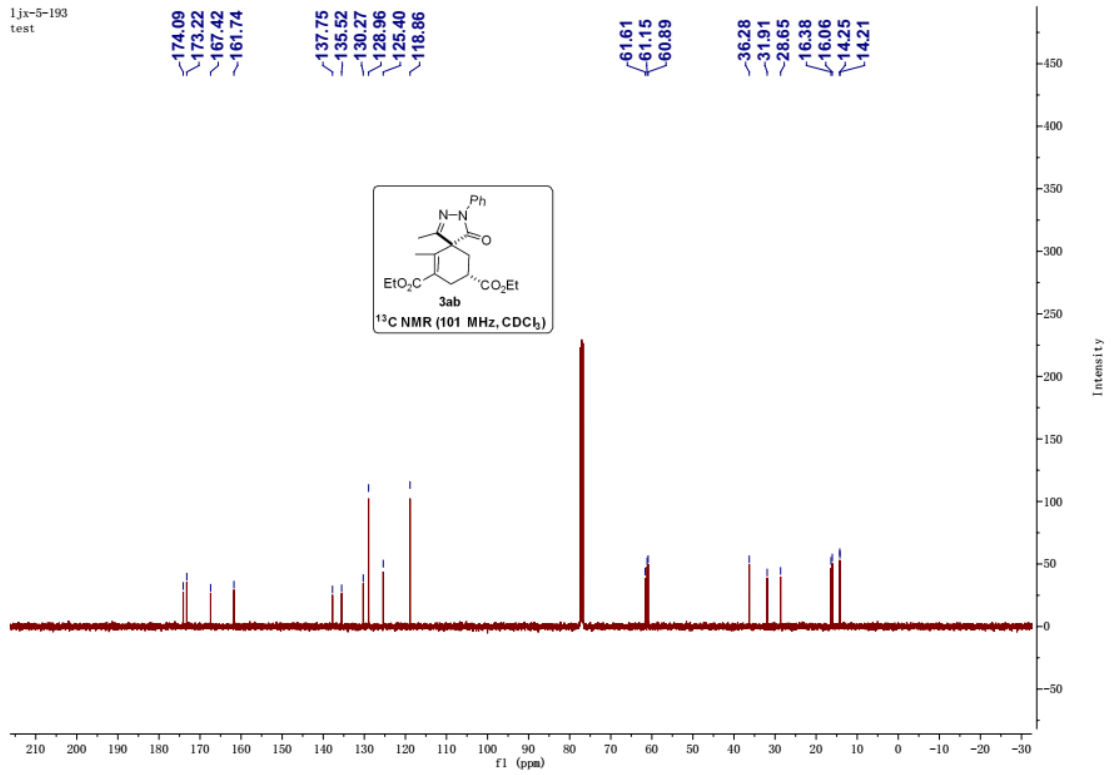

ljx-5-178
test
8.04
8.02
7.73
7.71
7.49
7.47
7.45
7.43
7.24
7.22
3.82
2.82
2.50
2.28
2.25
2.22
2.15
2.14
1.93
1.88
Ph
N–N
Ph
O
MeO2C
CO2tBu
3fa
1H NMR (400 MHz, CDCl3)
2.00
2.00
5.02
0.93
3.04
1.05
1.06
1.06
1.05
1.07
3.08
9.03
f1 (ppm)
Intensity

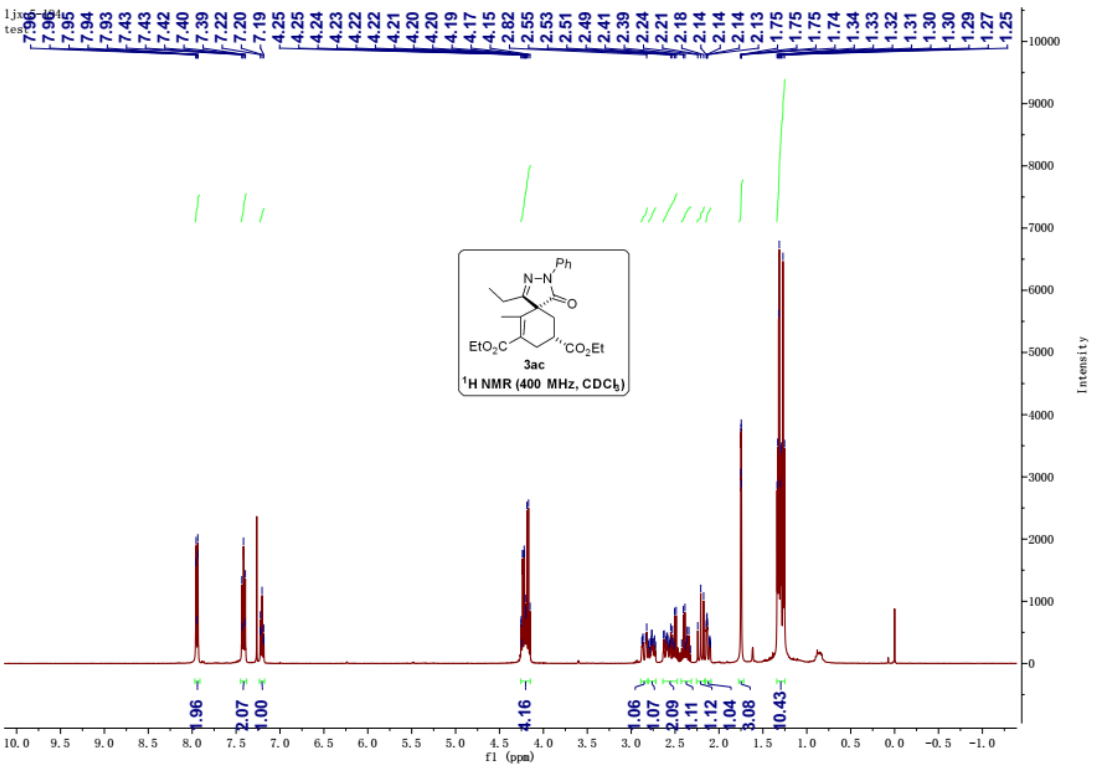

ljx-5-178
test
174.43
172.35
168.00
160.88
137.83
136.94
131.60
130.71
130.01
129.01
128.99
127.48
125.61
119.04
81.22
61.39
51.87
36.12
33.10
28.80
27.94
17.43
Ph
N–N
Ph
O
MeO2C
CO2tBu
3fa
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

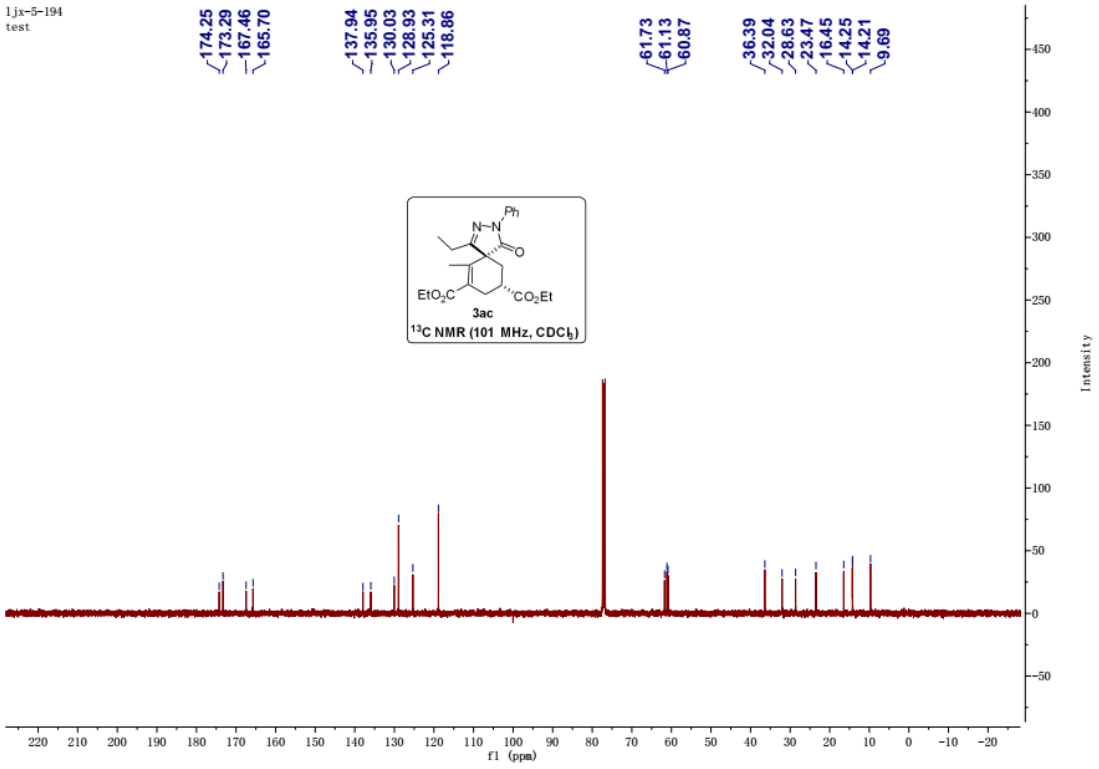

ljx-10-153
PROTON
8.02
8.00
7.72
7.70
7.46
7.45
7.44
7.42
7.39
7.37
7.35
7.33
7.33
7.31
7.29
7.25
7.24
7.22
7.01
4.11
4.10
4.08
4.06
2.91
2.34
2.31
2.21
2.20
1.91
1.21
1.19
1.17
Ph
Ph2HCO2C
CO2Et
3ga
1H NMR (400 MHz, CDCl3)
Intensity
1.97
1.95
15.16
1.31
0.95
1.96
1.00
1.02
1.03
1.04
1.02
2.94
3.01
f1 (ppm)

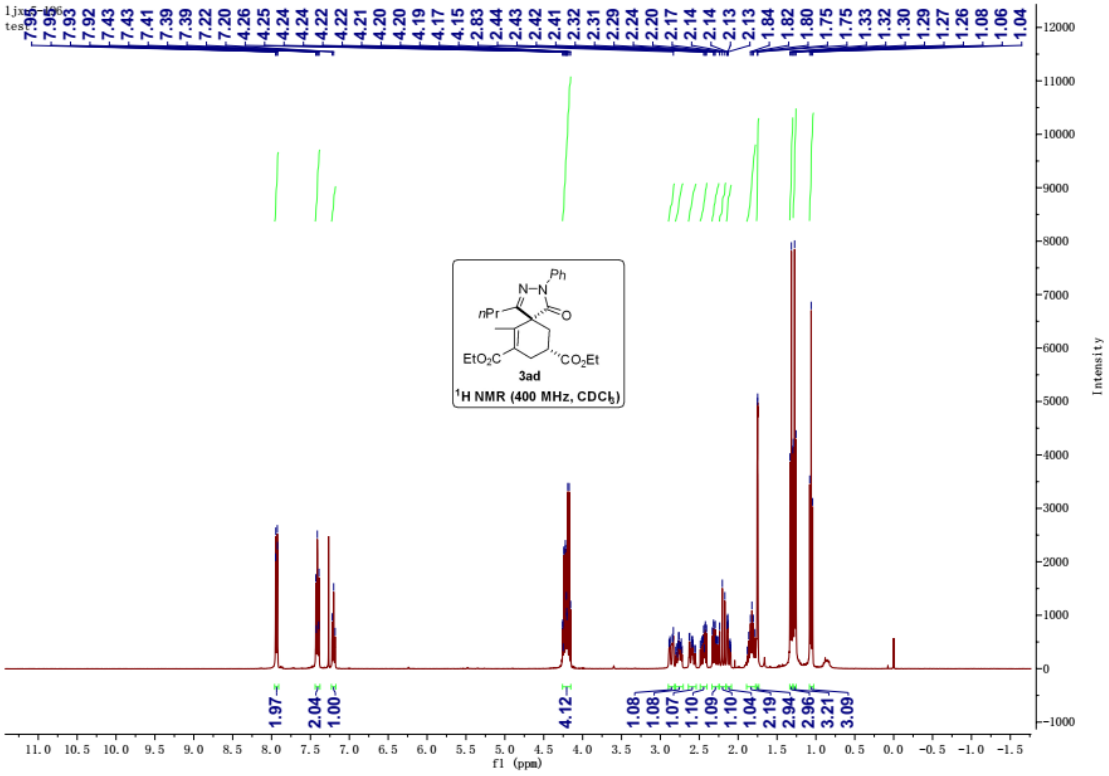

ljx-10-153
C13CPD
174.19
173.09
166.38
160.64
140.13
131.47
130.78
129.66
129.08
129.00
128.68
128.64
128.09
127.44
127.17
127.12
125.66
77.53
61.21
61.01
35.12
32.70
28.47
17.52
14.09
Ph
Ph2HCO2C
CO2Et
3ga
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

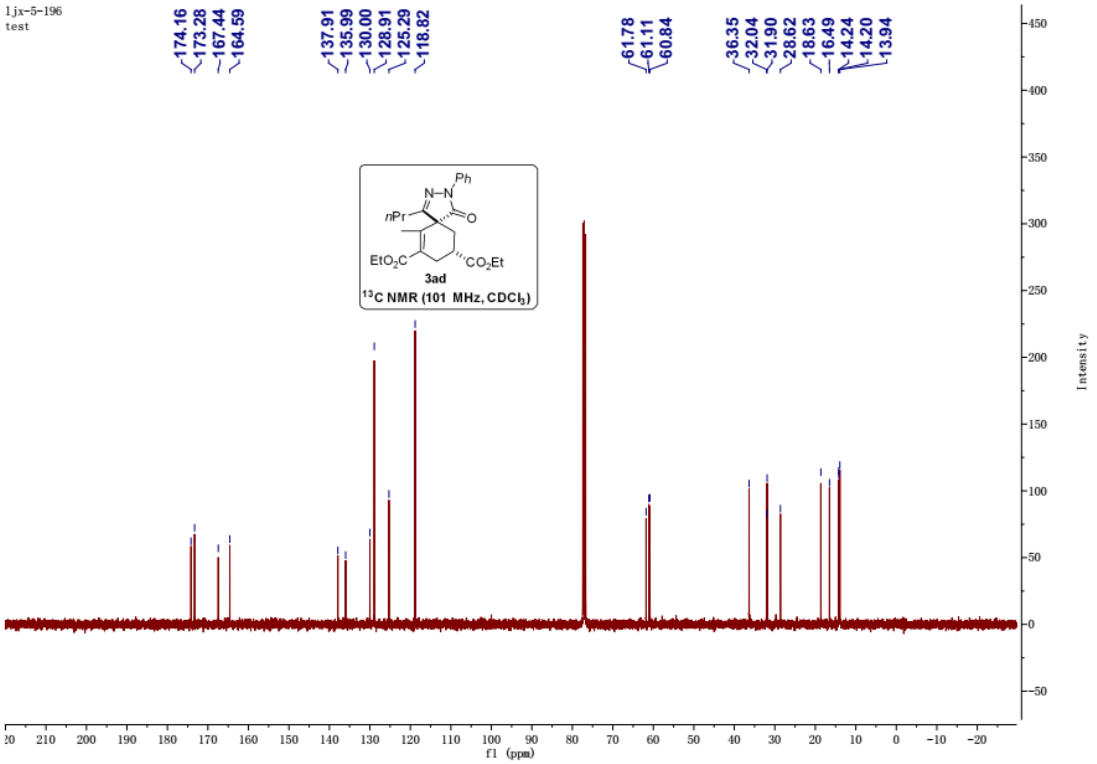

3ab
^{1}H NMR (400 MHz, CDCl$_3$)
Intensity
f1 (ppm)

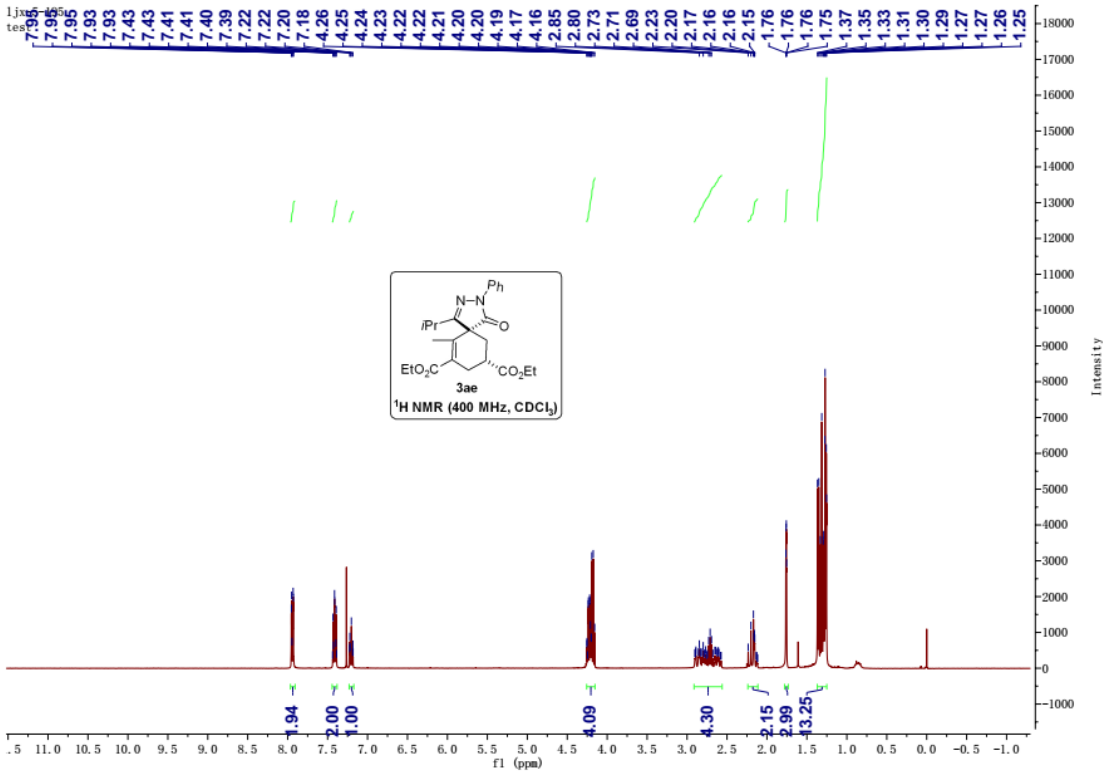

3ab
^{13}C NMR (101 MHz, CDCl$_3$)
Intensity
f1 (ppm)

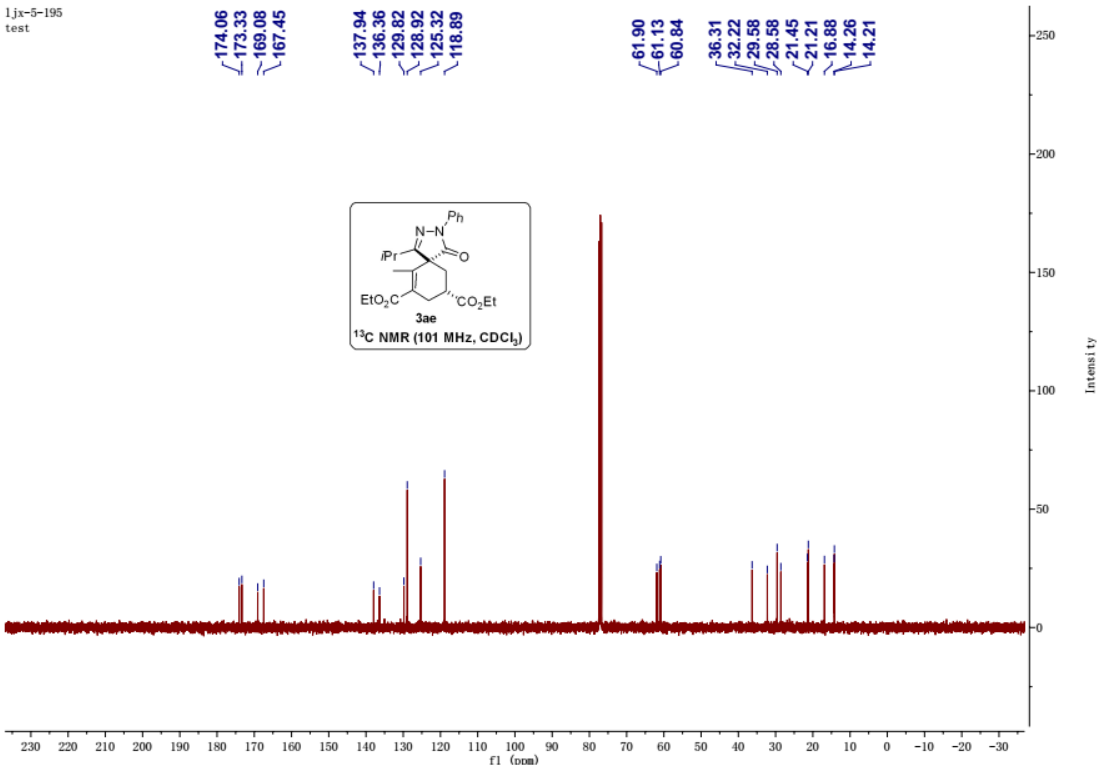

7.96
7.95
7.94
7.93
7.43
7.42
7.40
7.39
7.22
7.20
7.19
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.17
4.15
2.82
2.55
2.53
2.51
2.49
2.41
2.39
2.24
2.21
2.18
2.14
2.14
2.13
1.75
1.75
1.74
1.34
1.33
1.32
1.31
1.30
1.30
1.29
1.27
1.25
Ph
N
N
O
EtO2C
CO2Et
3ac
1H NMR (400 MHz, CDCl3)
Intensity
1.96
2.07
1.00
4.16
1.06
4.07
2.09
1.11
1.12
1.04
3.08
10.43
f1 (ppm)

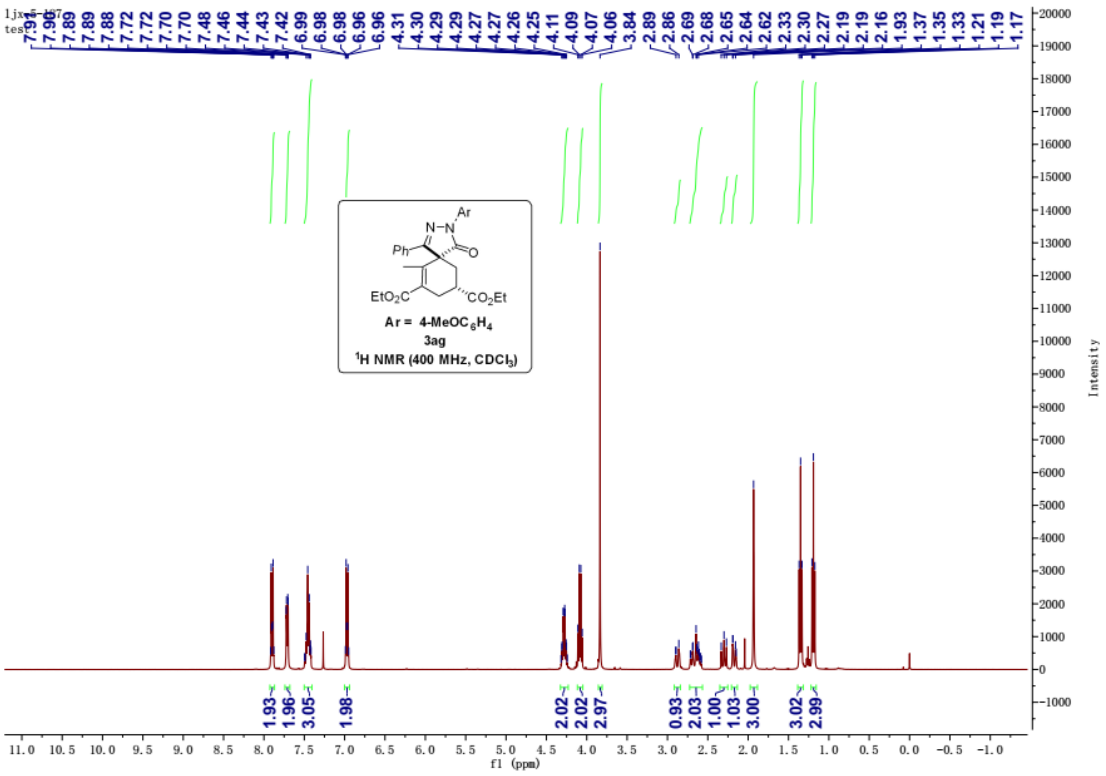

ljx-5-194
test
174.25
173.29
167.46
165.70
137.94
135.95
130.03
128.93
125.31
118.86
61.73
61.13
60.87
36.39
32.04
28.63
23.47
16.45
14.25
14.21
9.69
Ph
N
N
O
EtO2C
CO2Et
3ac
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

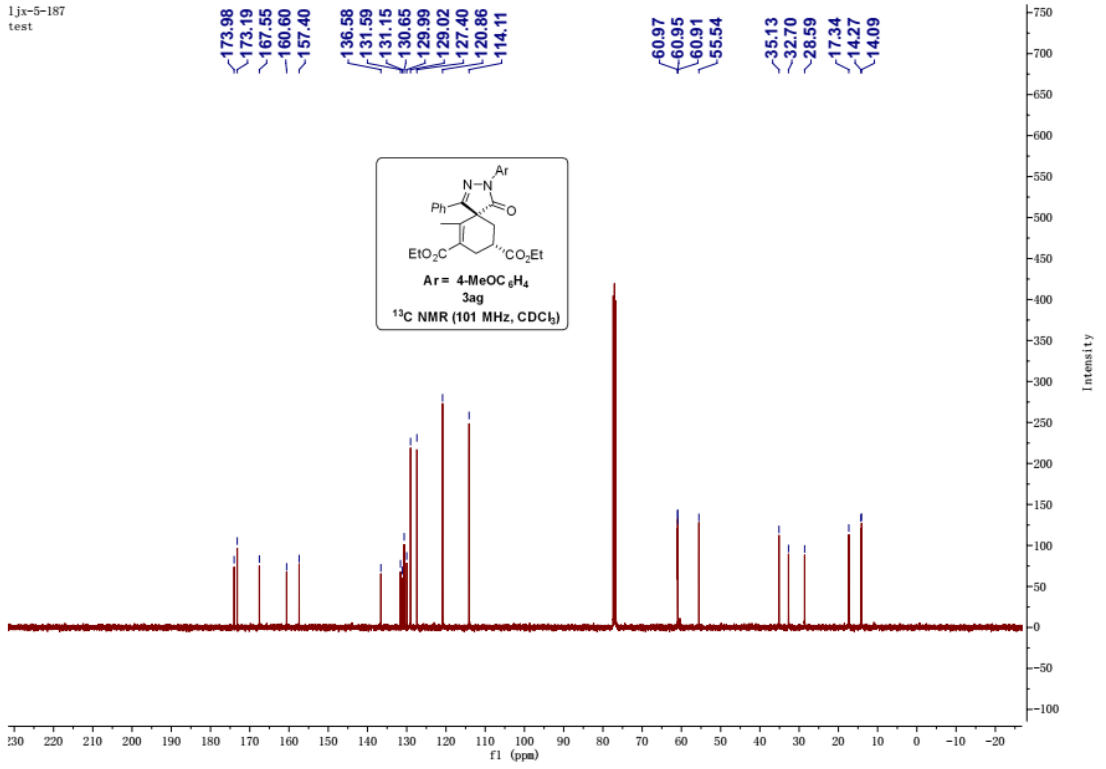

3ad
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)
Intensity

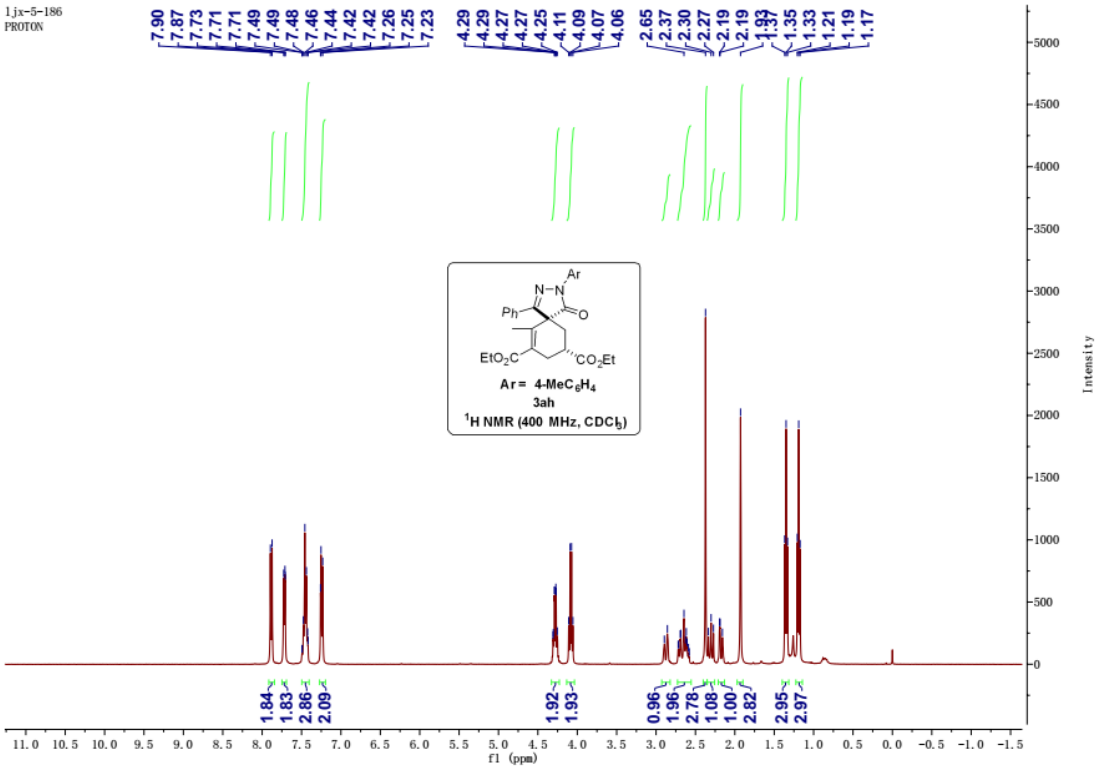

3ad
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)
Intensity

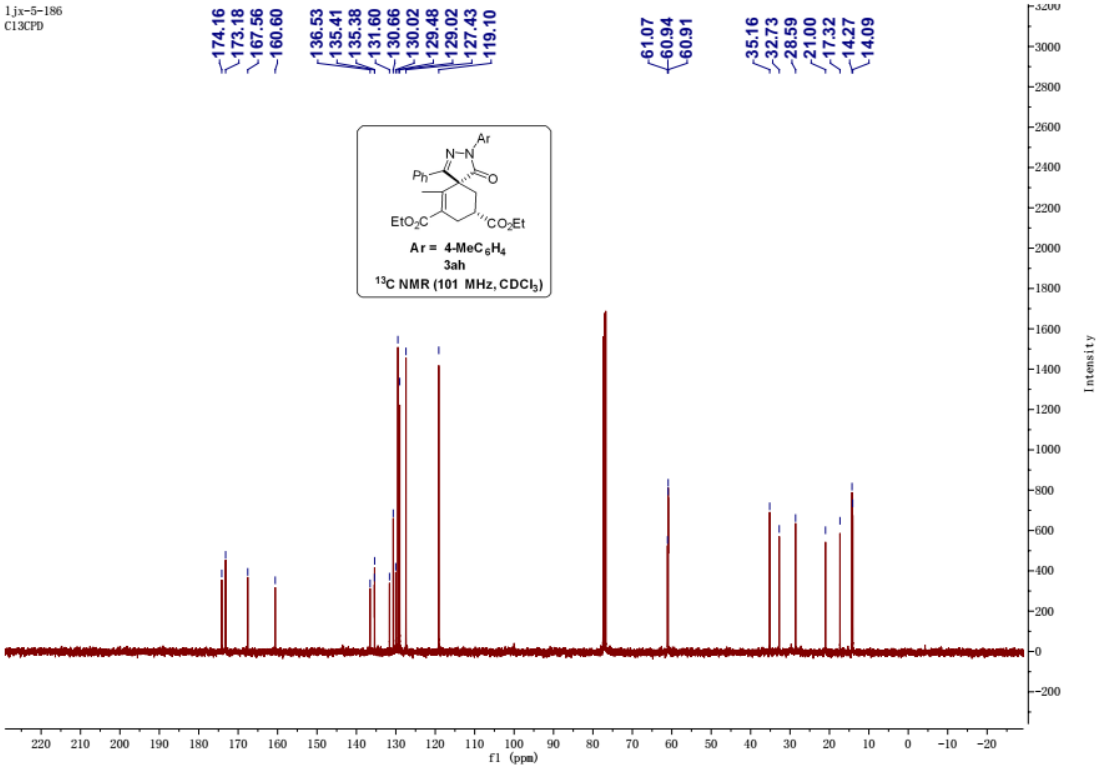

3ae
^{1}H NMR (400 MHz, CDCl$_3$)
Intensity
f1 (ppm)

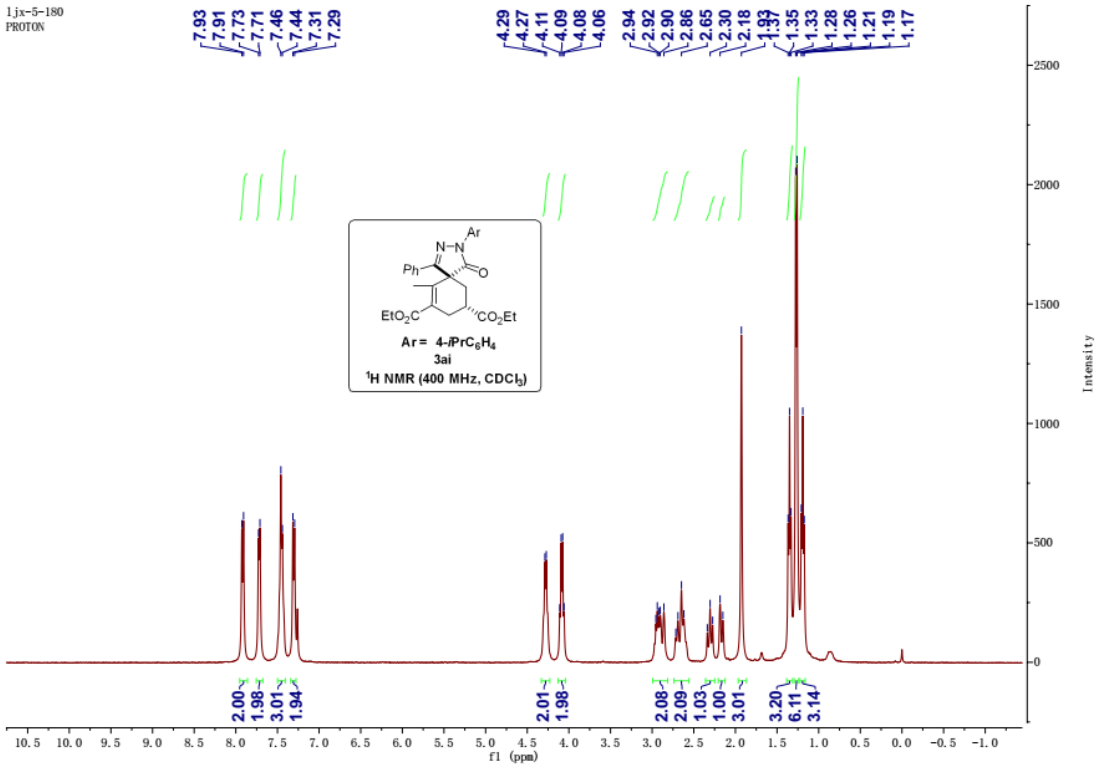

1jx-5-195
test
3ae
^{13}C NMR (101 MHz, CDCl$_3$)
Intensity
f1 (ppm)

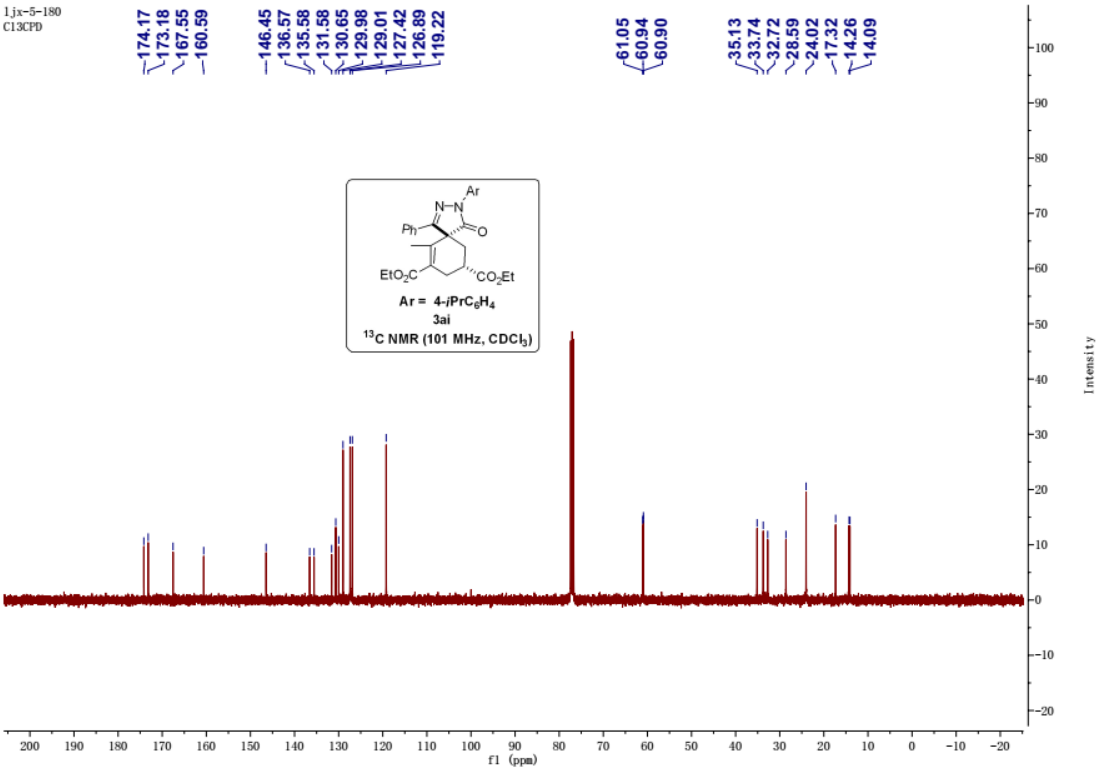

Ar = 4-MeOC6H4
3ag
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

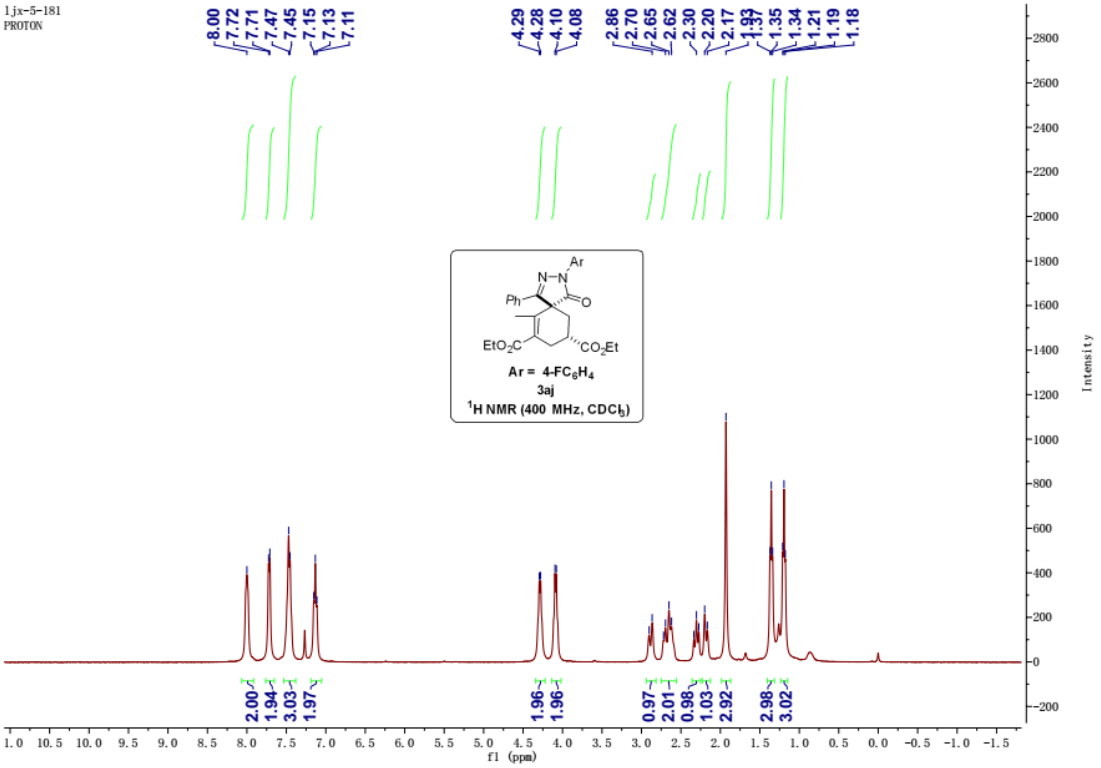

ljx-5-187
test
Ar = 4-MeOC6H4
3ag
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

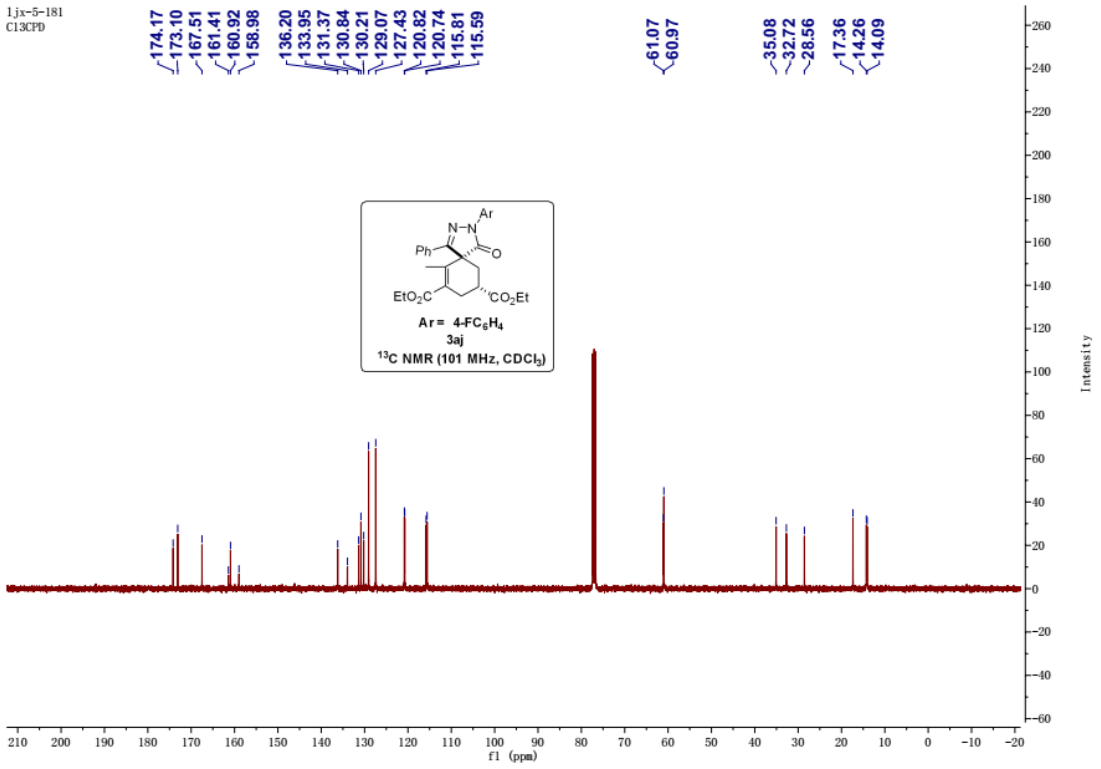

ljx-5-186
PROTON
Ar= 4-MeC6H4
3ah
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

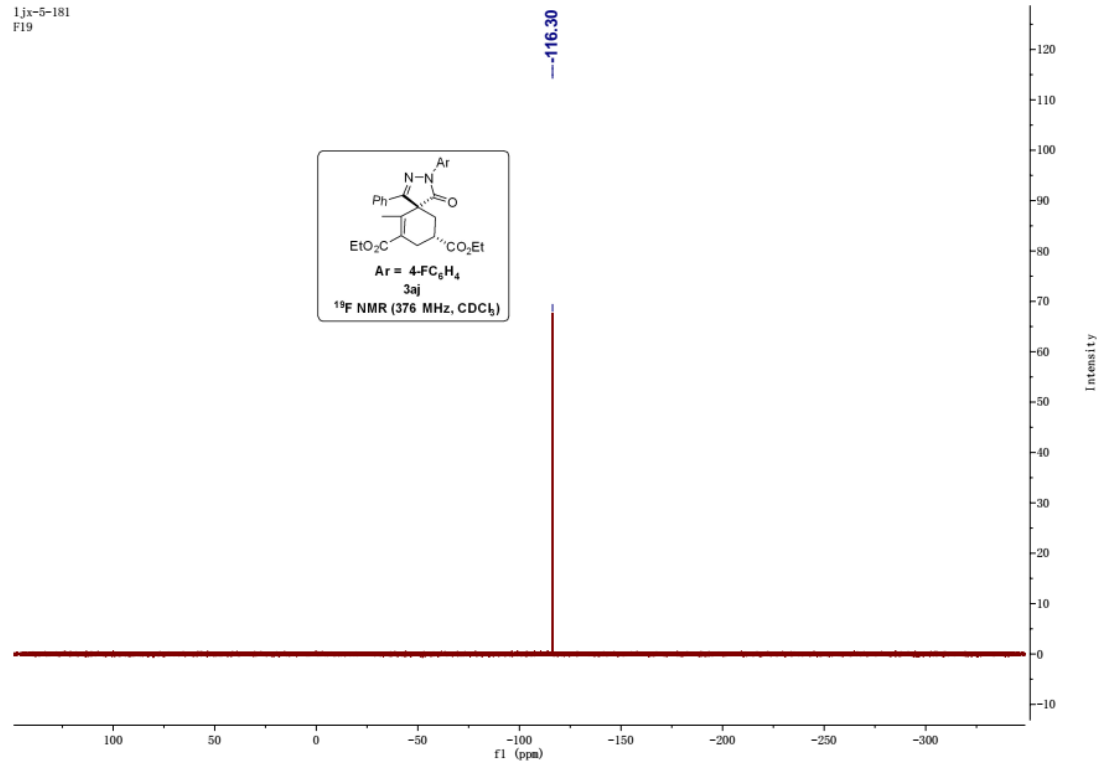

ljx-5-186
C13CPD
Ar= 4-MeC6H4
3ah
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

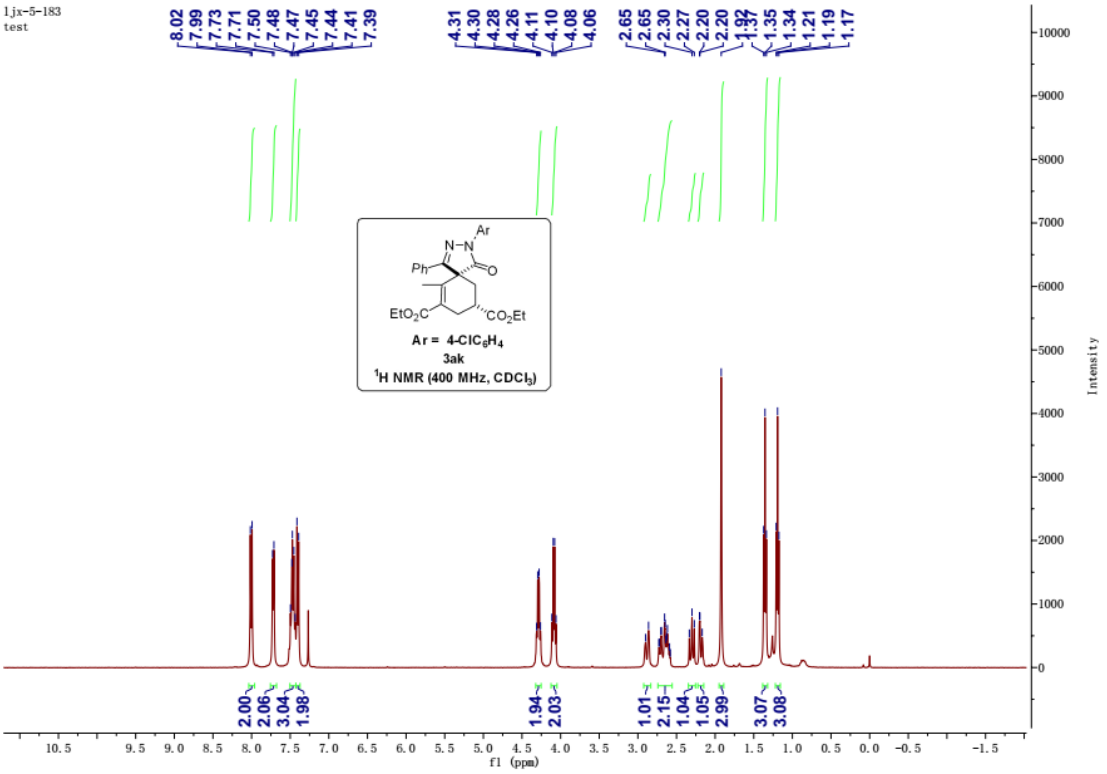

ljx-5-180
PROTON
Ar = 4-iPrC6H4
3ai
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

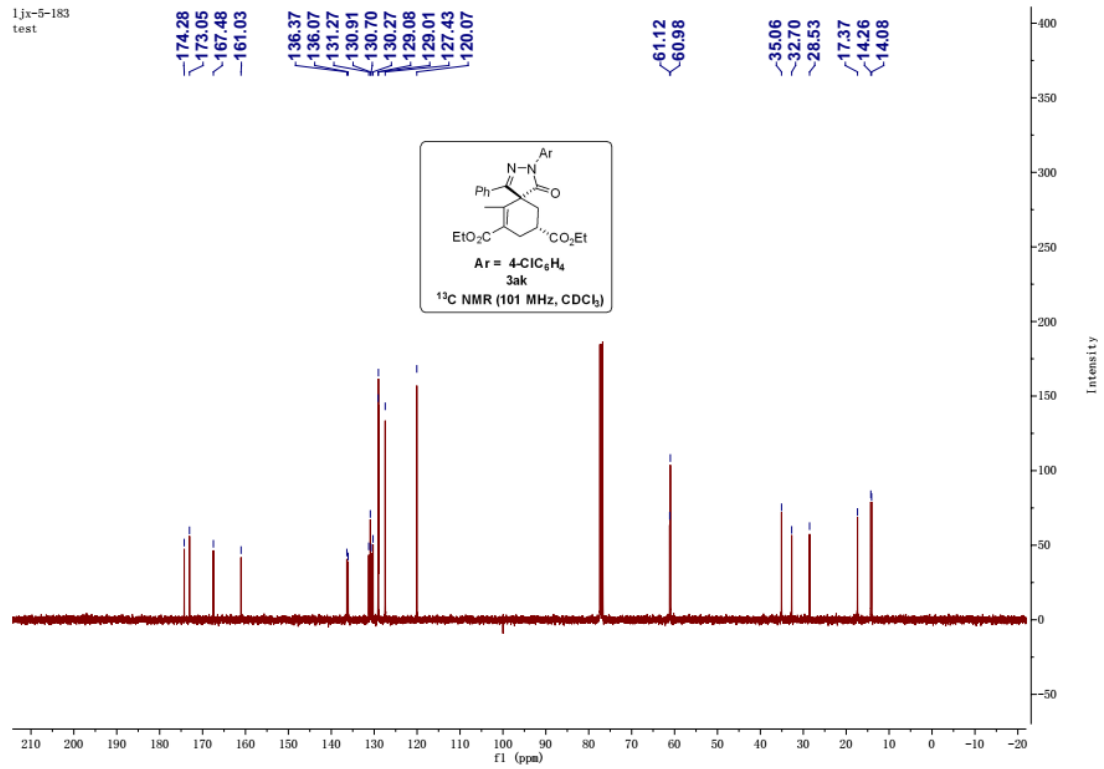

ljx-5-180
C13CPD
Ar = 4-iPrC6H4
3ai
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

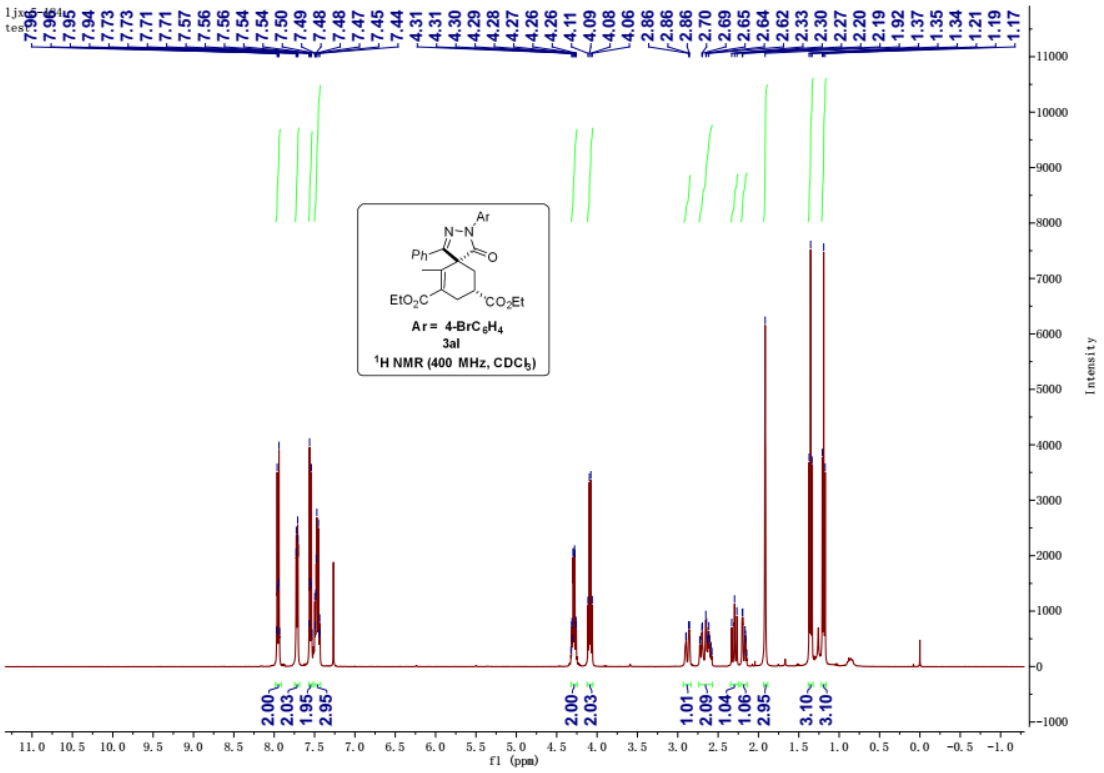

ljx-5-181
PROTON
8.00
7.72
7.71
7.47
7.45
7.15
7.13
7.11
4.29
4.28
4.10
4.08
2.86
2.70
2.65
2.62
2.30
2.20
2.17
1.37
1.35
1.34
1.21
1.19
1.18
Ar
Ph
EtO2C
CO2Et
Ar = 4-FC6H4
3aj
1H NMR (400 MHz, CDCl3)
2.00
1.94
3.03
1.97
1.96
1.96
0.97
2.01
0.98
1.03
2.92
2.98
3.02
f1 (ppm)
Intensity

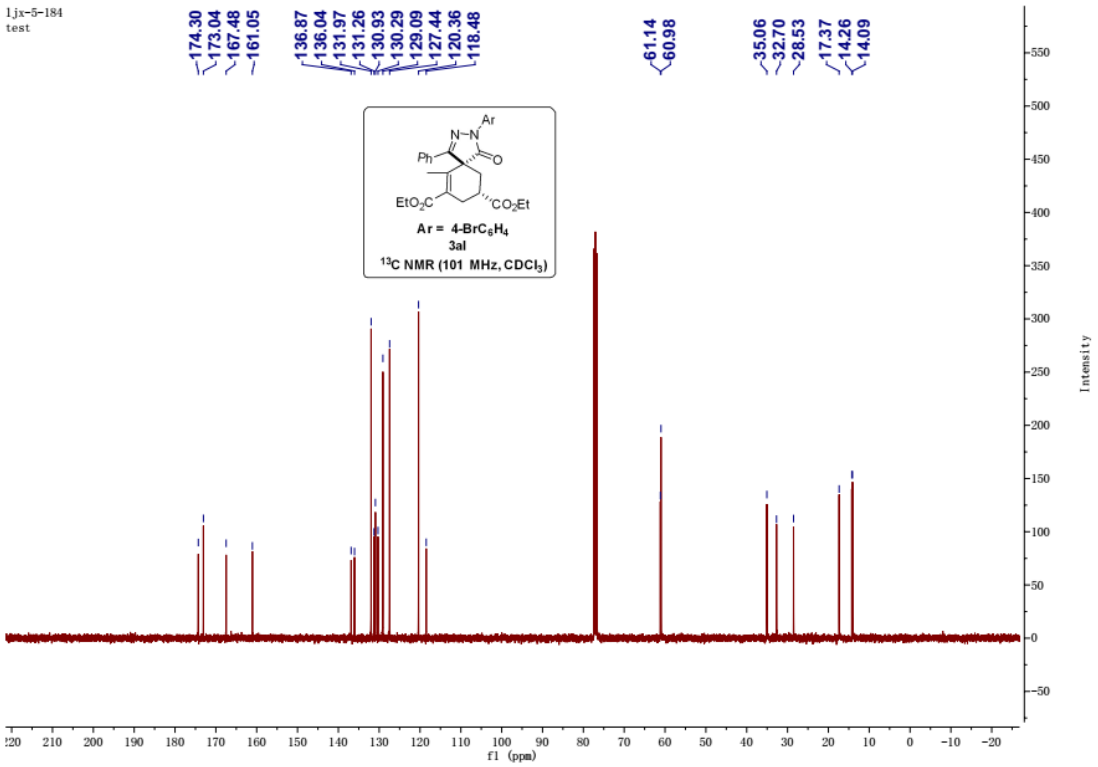

ljx-5-181
C13CPD
174.17
173.10
167.51
161.41
160.92
158.98
136.20
133.95
131.37
130.84
130.21
129.07
127.43
120.82
120.74
115.81
115.59
61.07
60.97
35.08
32.72
28.56
17.36
14.26
14.09
Ar
Ph
EtO2C
CO2Et
Ar = 4-FC6H4
3aj
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

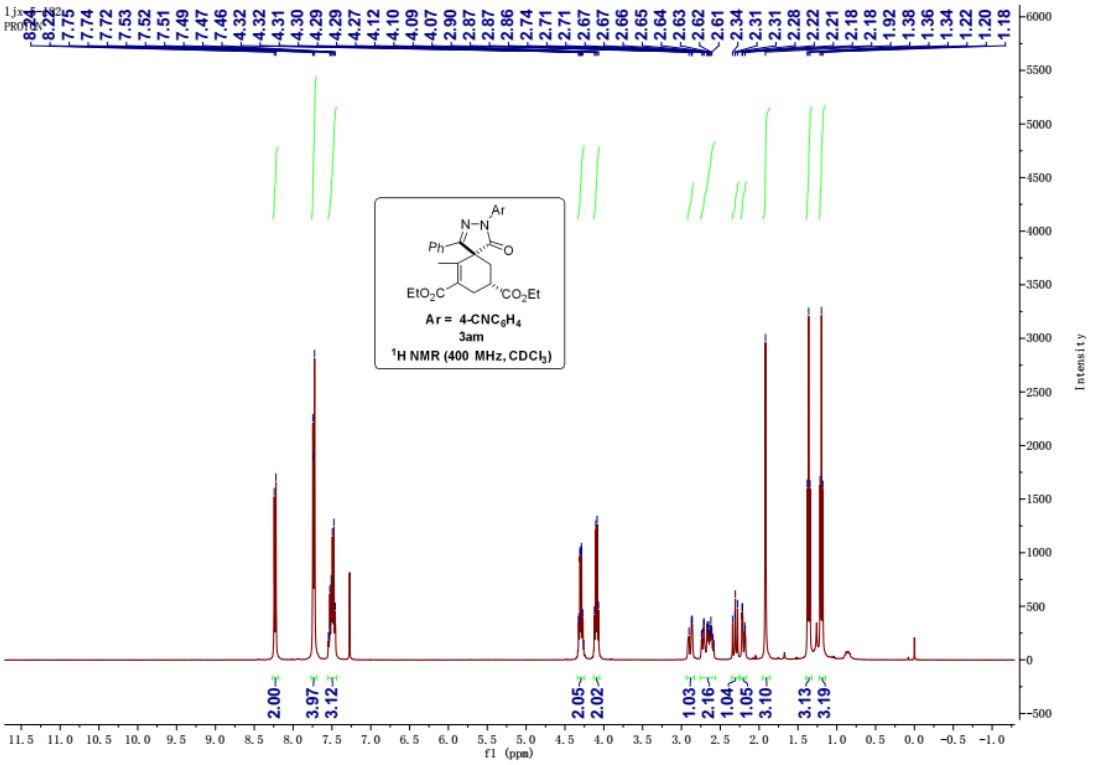

ljx-5-181
F19
-116.30
Ar = 4-FC6H4
3aj
19F NMR (376 MHz, CDCl3)
Intensity
f1 (ppm)

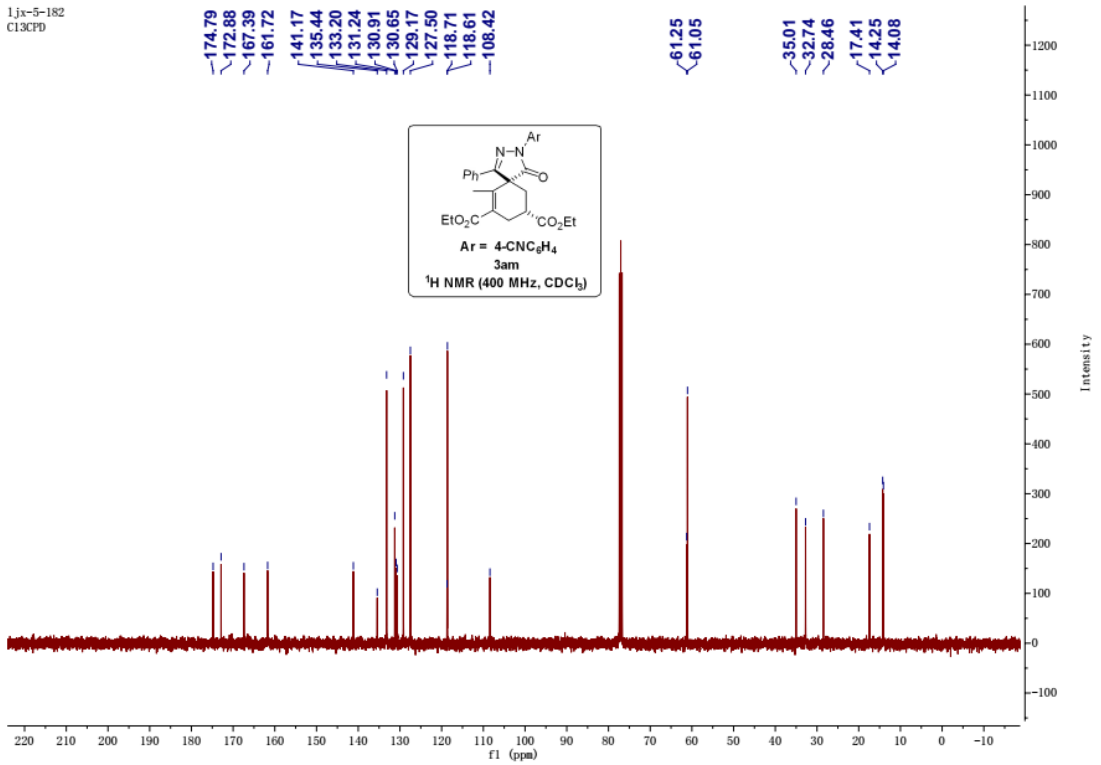

ljx-5-183
test
8.02 7.99 7.73 7.71 7.50 7.48 7.47 7.45 7.44 7.41 7.39
4.31 4.30 4.28 4.26 4.11 4.10 4.08 4.06
2.65 2.65 2.30 2.27 2.20 2.20
1.35 1.34 1.21 1.19 1.17
Ar = 4-ClC6H4
3ak
1H NMR (400 MHz, CDCl3)
2.00 2.06 3.04 1.98 1.94 2.03 1.01 2.15 1.04 1.05 2.99 3.07 3.08
Intensity
f1 (ppm)

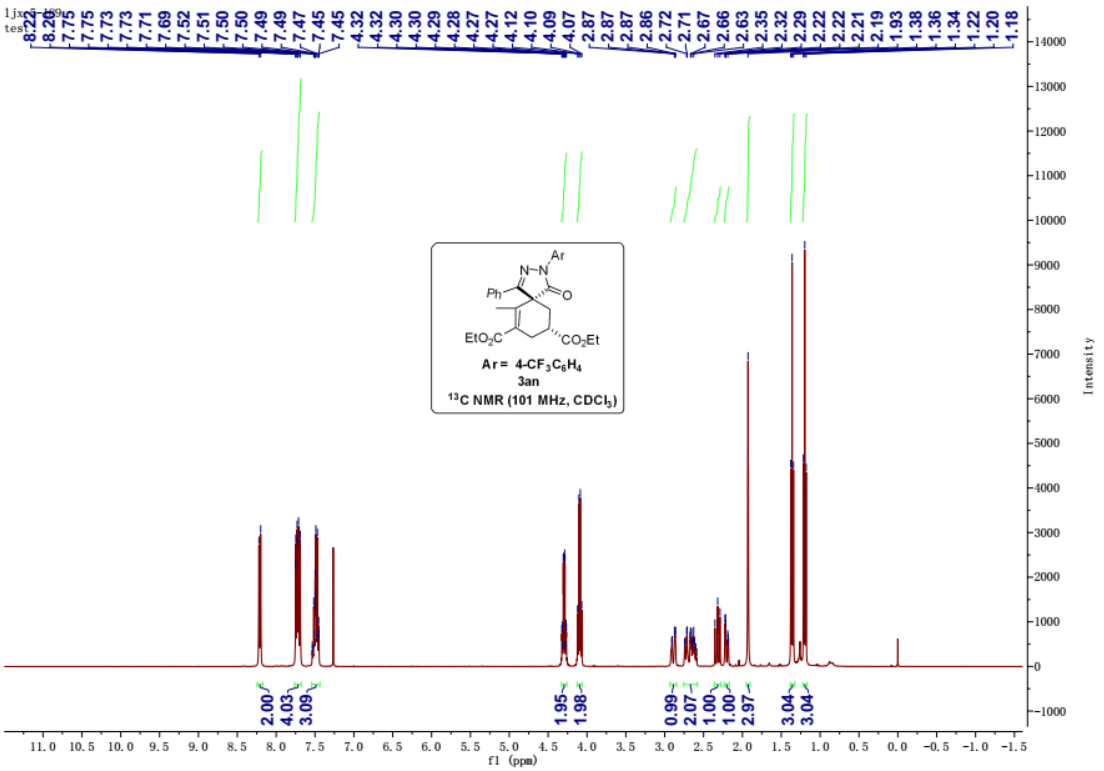

ljx-5-183
test
174.28
173.05
167.48
161.03
136.37
136.07
131.27
130.91
130.70
130.27
129.08
129.01
127.43
120.07
61.12
60.98
35.06
32.70
28.53
17.37
14.26
14.08
Ar = 4-ClC6H4
3ak
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

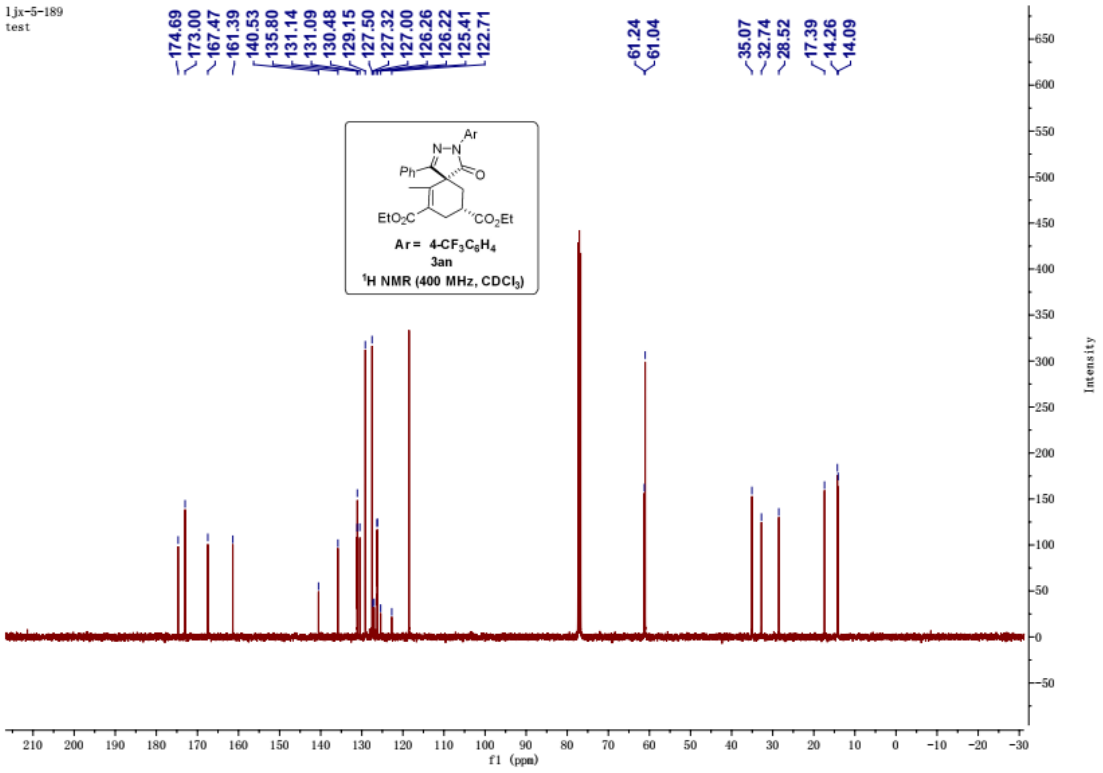

7.96
7.95
7.94
7.73
7.71
7.57
7.56
7.54
7.50
7.49
7.48
7.47
7.45
7.44
4.31
4.30
4.29
4.28
4.27
4.26
4.11
4.09
4.08
4.06
2.86
2.70
2.69
2.65
2.64
2.62
2.33
2.30
2.27
2.20
2.19
1.92
1.37
1.35
1.34
1.21
1.19
1.17
2.00
2.03
1.95
2.95
2.00
2.03
1.01
2.09
1.04
1.06
2.95
3.10
3.10
Ar = 4-BrC6H4
3al
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

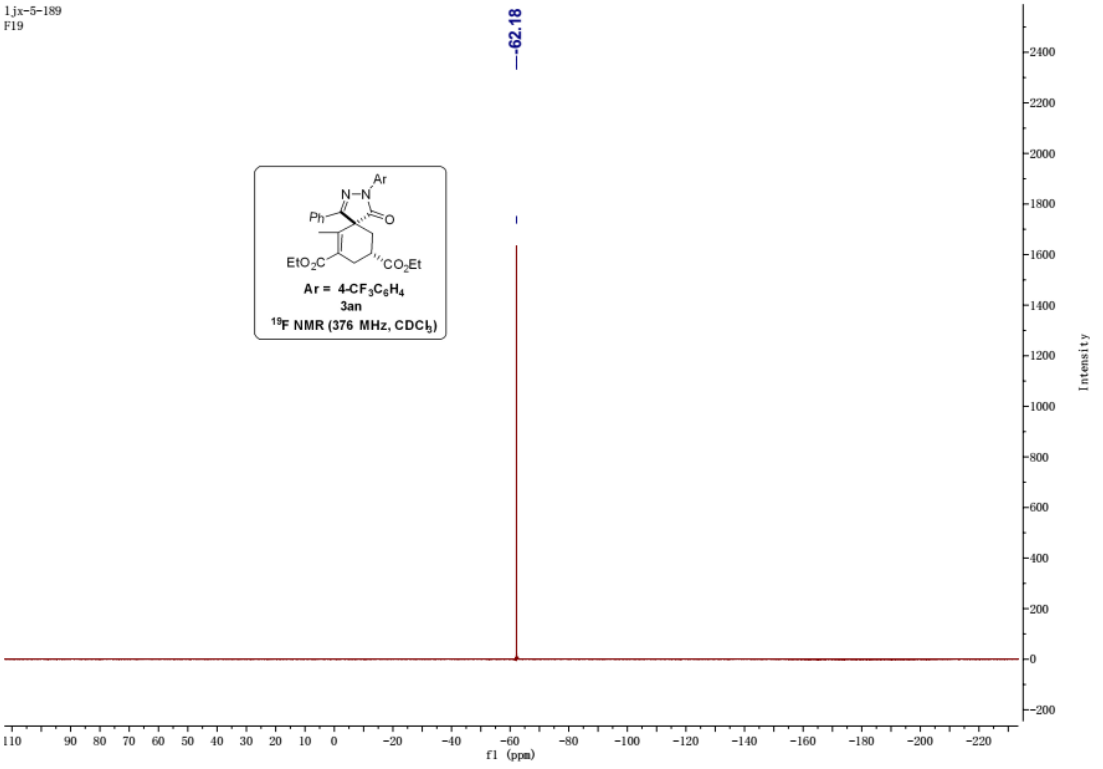

ljx-5-184
test
174.30
173.04
167.48
161.05
136.87
136.04
131.97
131.26
130.93
130.29
129.09
127.44
120.36
118.48
61.14
60.98
35.06
32.70
28.53
17.37
14.26
14.09
Ar = 4-BrC6H4
3al
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

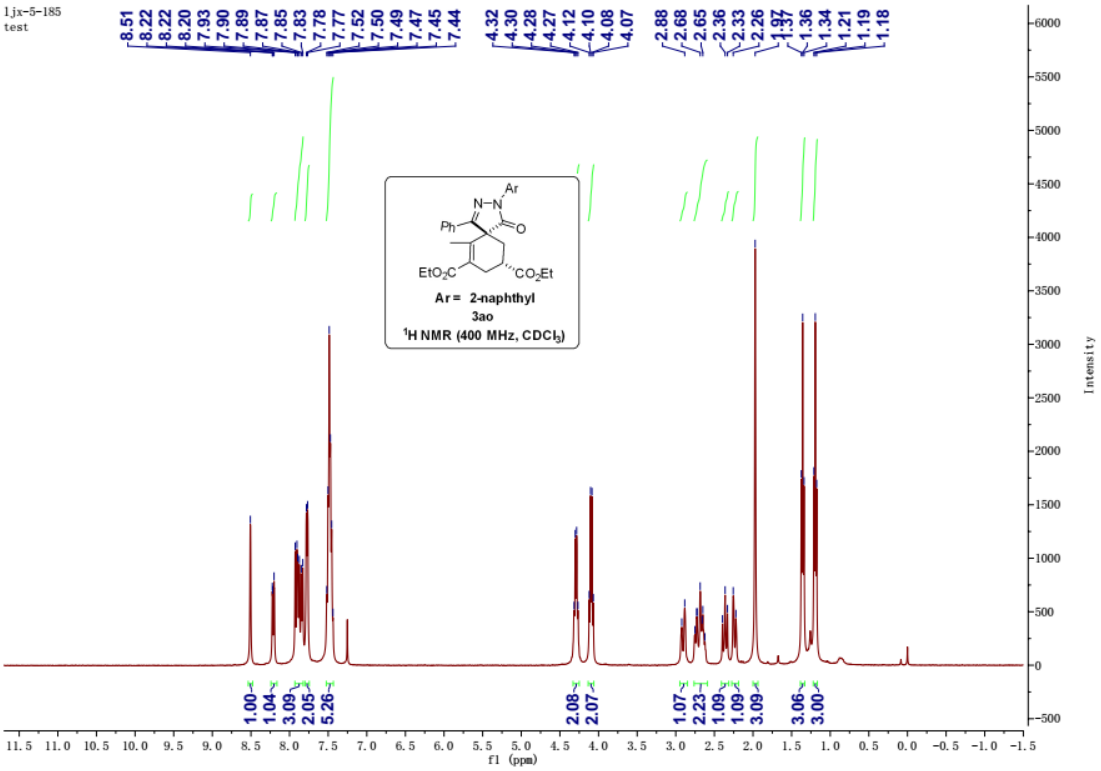

8.24
8.23
7.75
7.74
7.72
7.53
7.52
7.51
7.49
7.47
7.46
4.32
4.31
4.30
4.29
4.29
4.27
4.12
4.10
4.09
4.07
2.90
2.87
2.87
2.86
2.74
2.71
2.71
2.67
2.67
2.66
2.65
2.64
2.63
2.62
2.61
2.34
2.31
2.31
2.28
2.22
2.21
2.18
2.18
1.92
1.38
1.36
1.34
1.22
1.20
1.18
2.00
3.97
3.12
2.05
2.02
1.03
2.16
1.04
1.05
3.10
3.13
3.19
Ar = 4-CNC6H4
3am
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

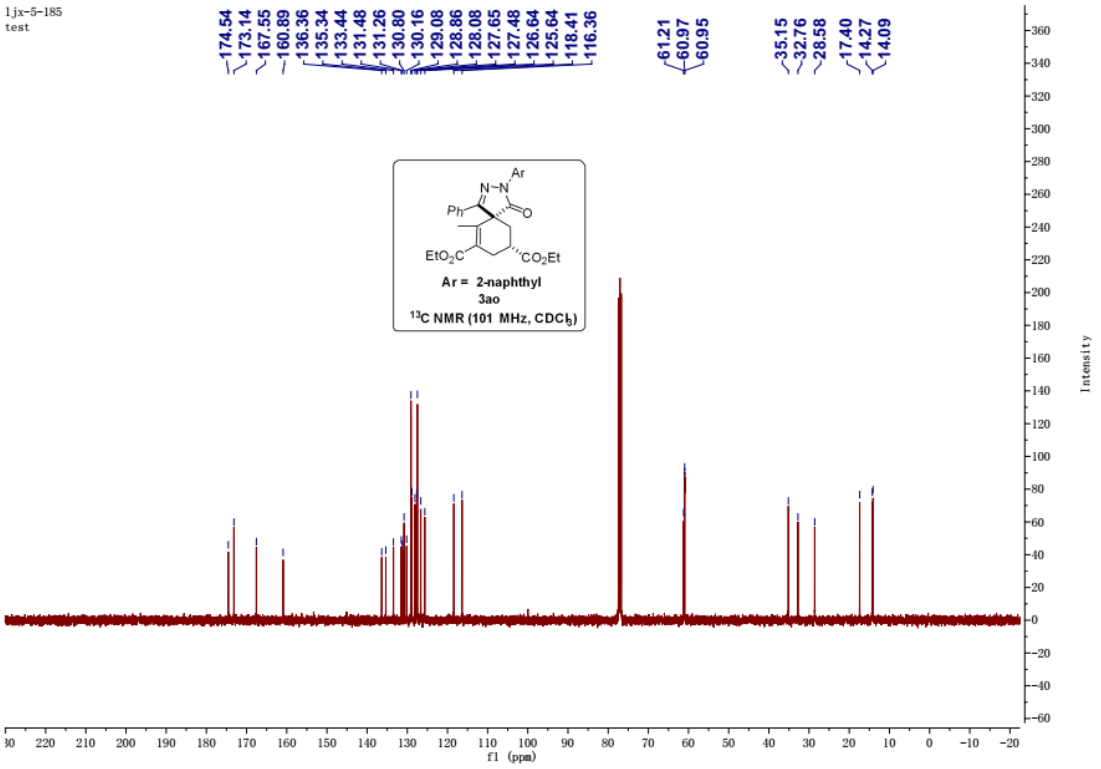

ljx-5-182
C13CPD
174.79
172.88
167.39
161.72
141.17
135.44
133.20
131.24
130.91
130.65
129.17
127.50
118.71
118.61
108.42
61.25
61.05
35.01
32.74
28.46
17.41
14.25
14.08
Ar
N-N
Ph
O
EtO2C
CO2Et
Ar = 4-CNC6H4
3am
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

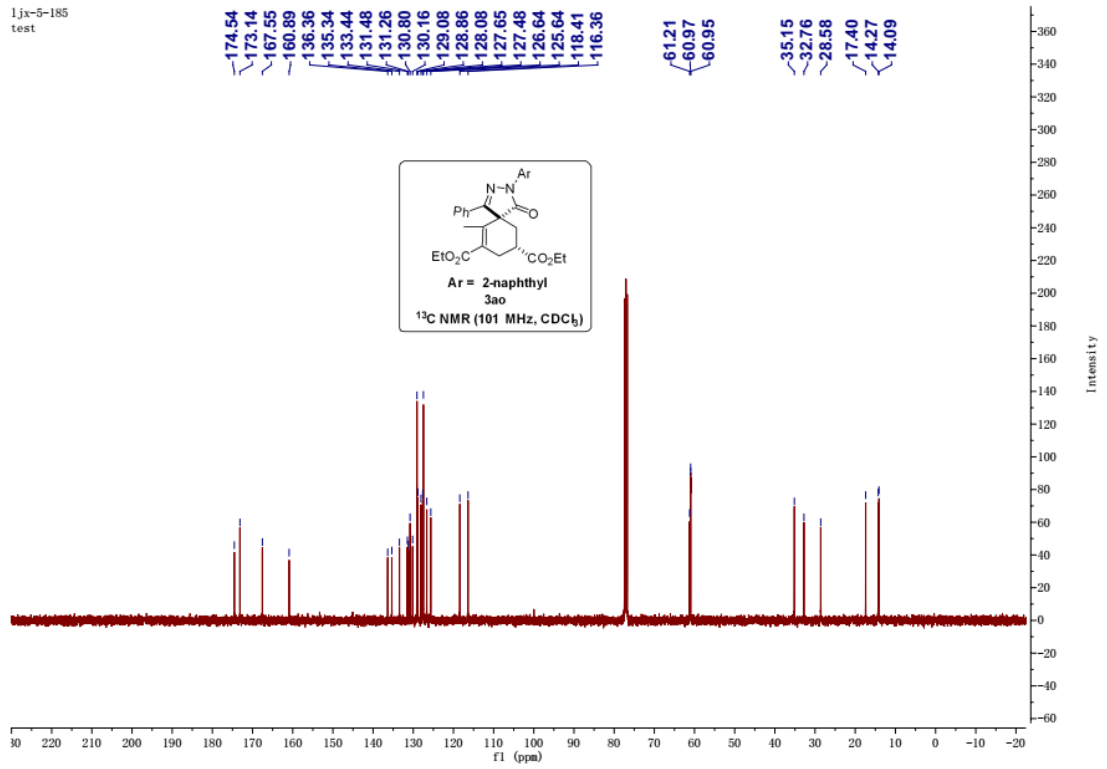

8.22
8.20
7.75
7.75
7.73
7.73
7.71
7.69
7.52
7.51
7.50
7.50
7.49
7.49
7.47
7.45
7.45
4.32
4.32
4.30
4.30
4.29
4.28
4.27
4.27
4.12
4.10
4.09
4.07
2.87
2.87
2.86
2.72
2.71
2.67
2.66
2.63
2.35
2.32
2.29
2.22
2.22
2.21
2.19
1.93
1.38
1.36
1.34
1.22
1.20
1.18
2.00
4.03
3.09
1.95
1.98
0.99
2.07
1.00
1.00
2.97
3.04
3.04
Ar
N-N
Ph
O
EtO2C
CO2Et
Ar = 4-CF3C6H4
3an
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

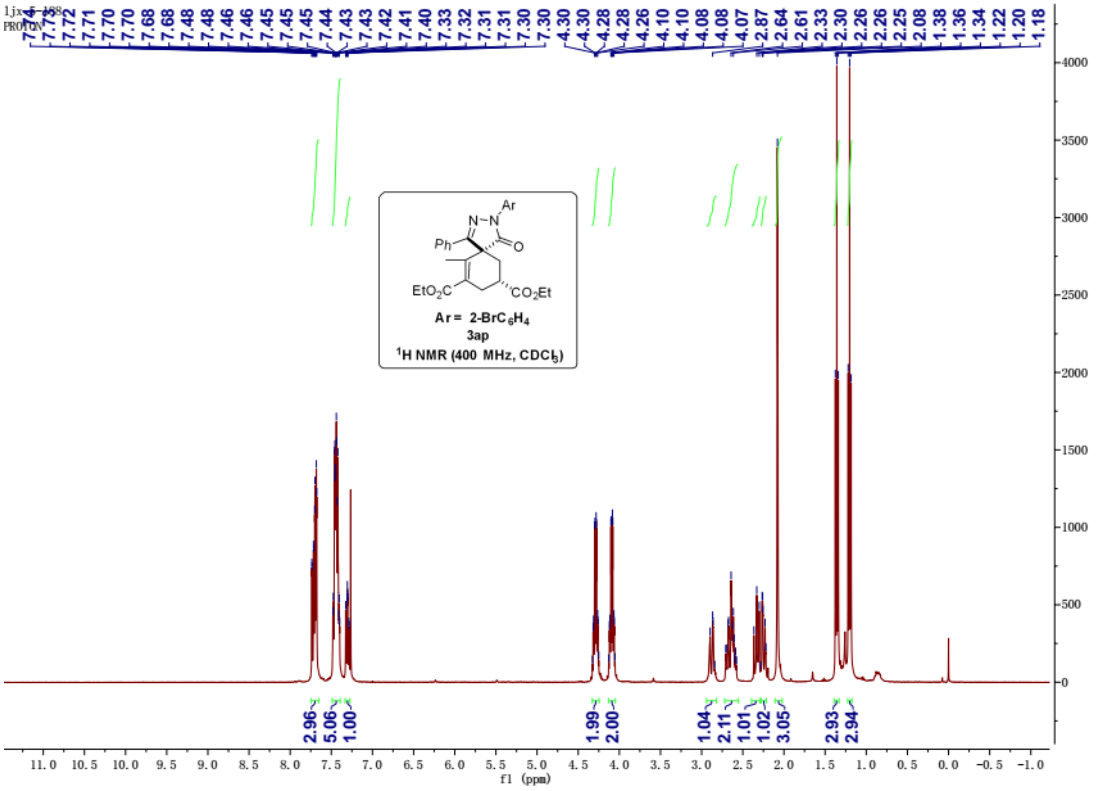

ljx-5-189
test
174.69
173.00
167.47
161.39
140.53
135.80
131.14
131.09
130.48
129.15
127.50
127.32
127.00
126.26
126.22
125.41
122.71
61.24
61.04
35.07
32.74
28.52
17.39
14.26
14.09
Ar = 4-CF3C6H4
3an
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity

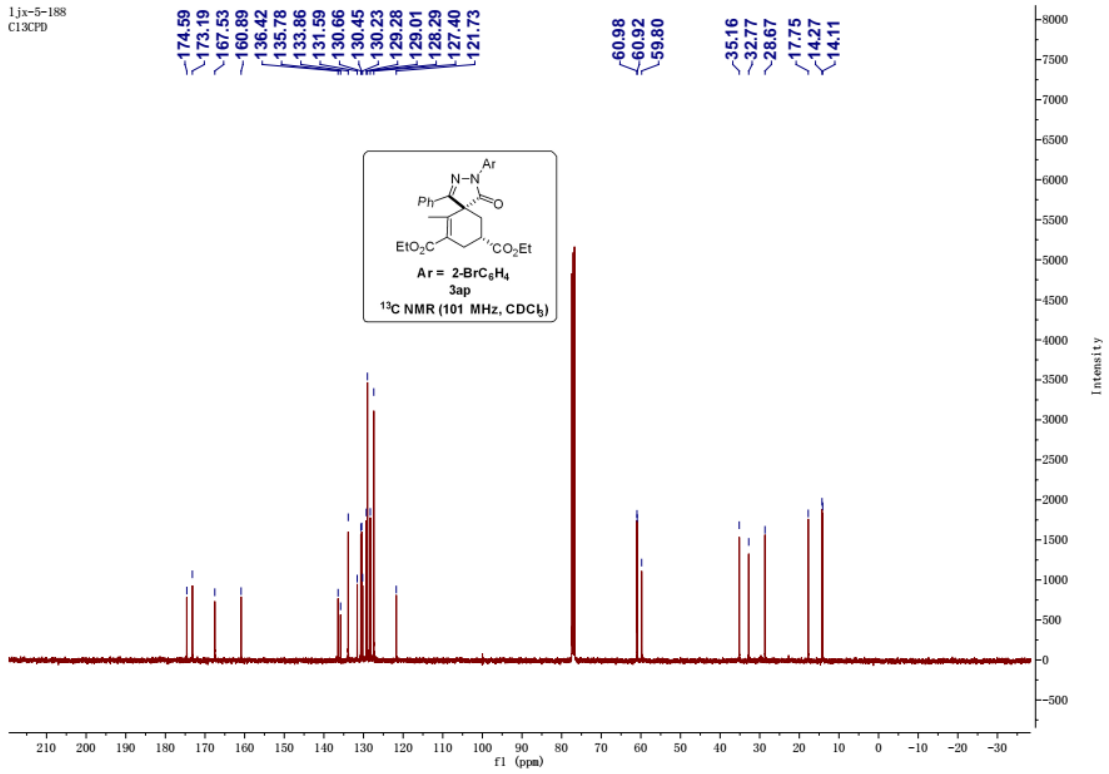

ljx-5-189
F19
-62.18
Ar = 4-CF3C6H4
3an
19F NMR (376 MHz, CDCl3)
f1 (ppm)
Intensity

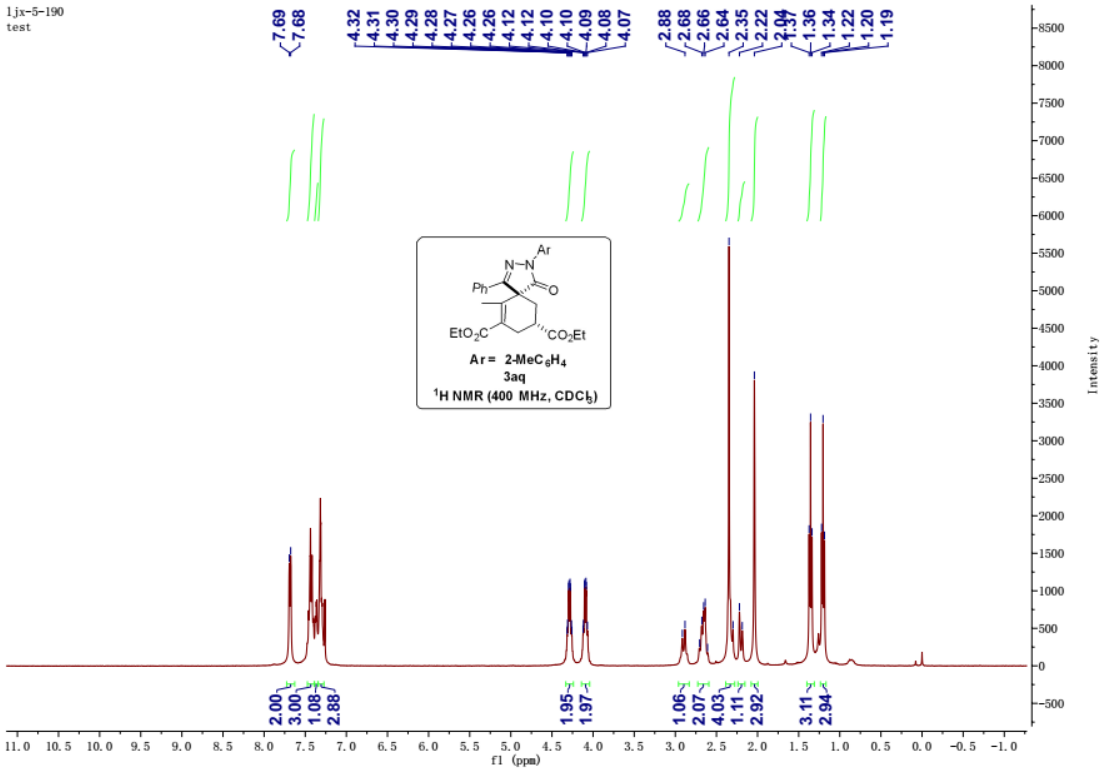

ljx-5-185
test
Ar = 2-naphthyl
3ao
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)

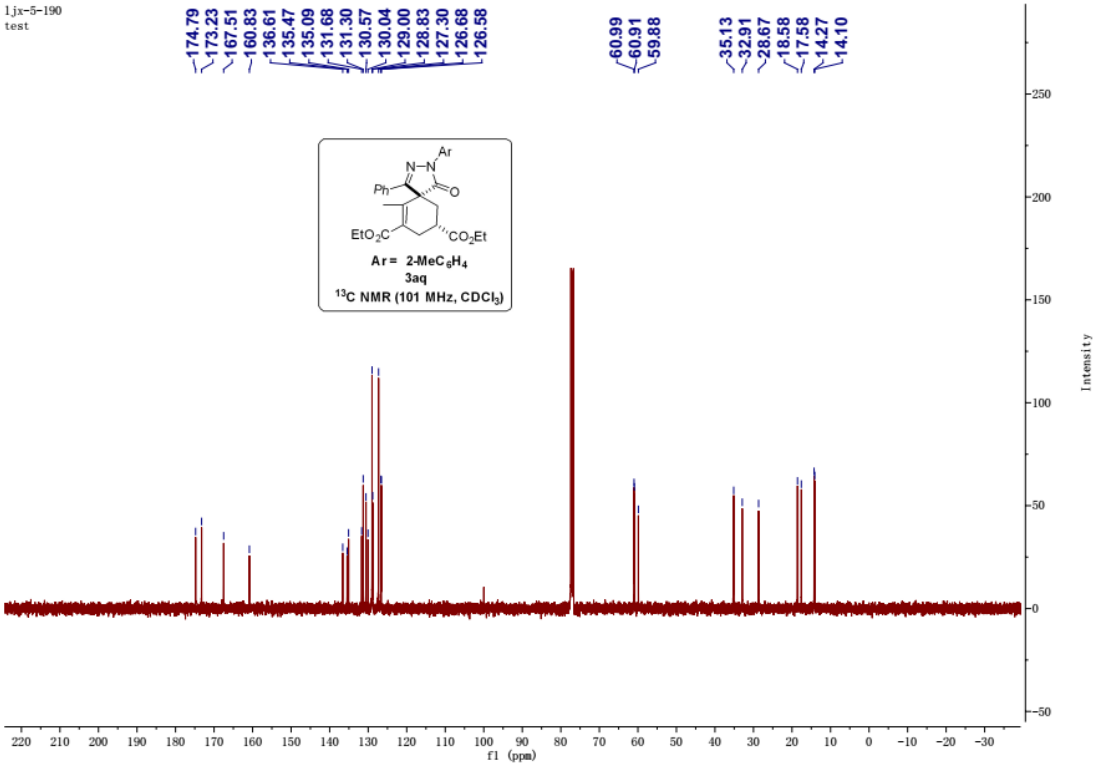

ljx-5-185
test
Ar = 2-naphthyl
3ao
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

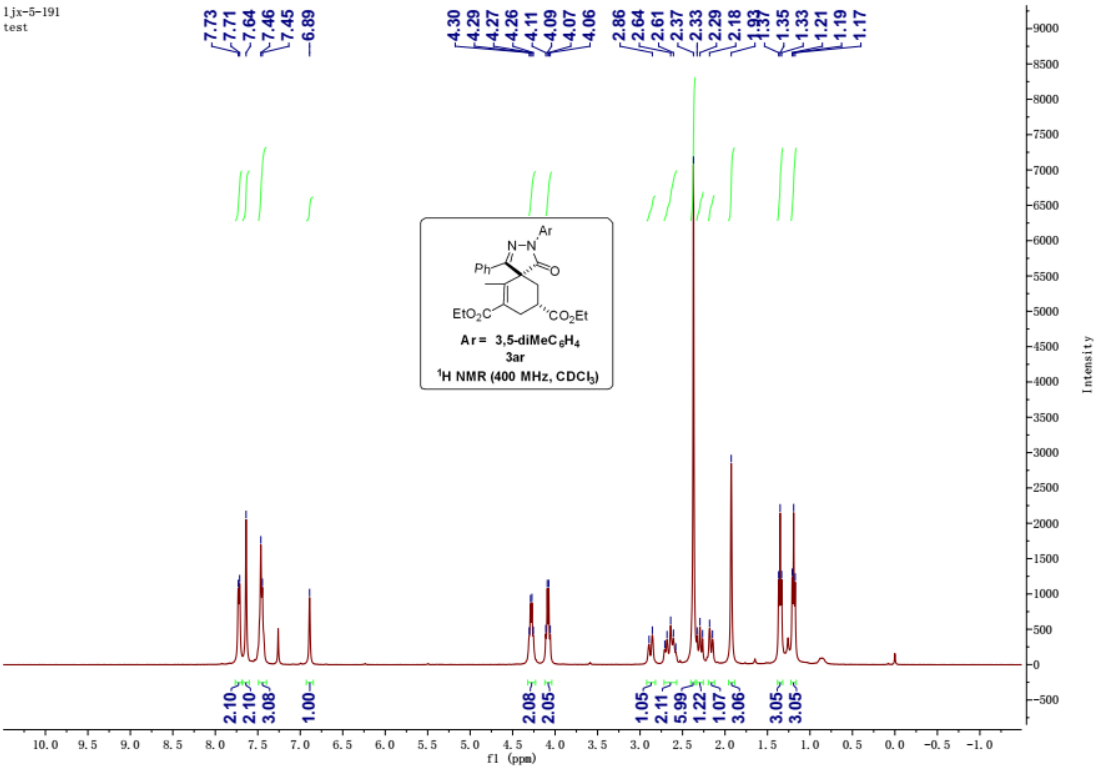

ljx-5-185
test
174.54
173.14
167.55
160.89
136.36
135.34
133.44
131.48
131.26
130.80
130.16
129.08
128.86
128.08
127.65
127.48
126.64
125.64
118.41
116.36
61.21
60.97
60.95
35.15
32.76
28.58
17.40
14.27
14.09
Ar = 2-naphthyl
3ao
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)

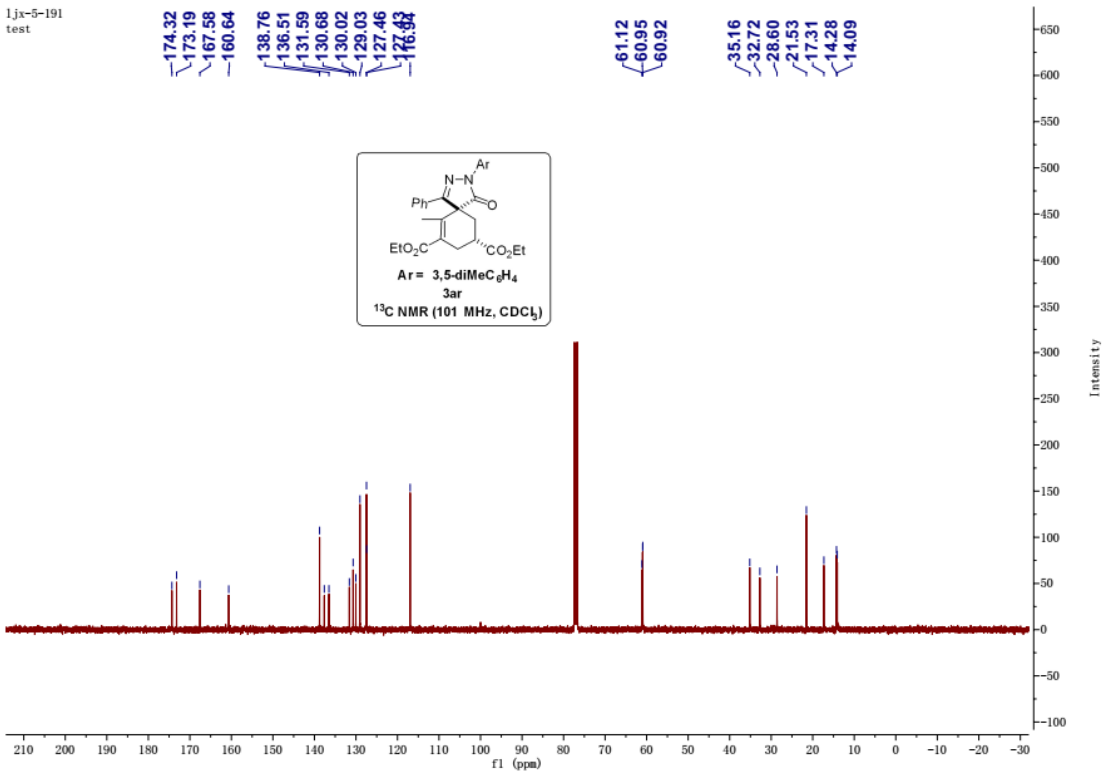

ljx-5-188
PROTON
Ar= 2-BrC6H4
3ap
1H NMR (400 MHz, CDCl3)
2.96
5.06
1.00
1.99
2.00
1.04
2.11
1.01
1.02
3.05
2.93
2.94
f1 (ppm)

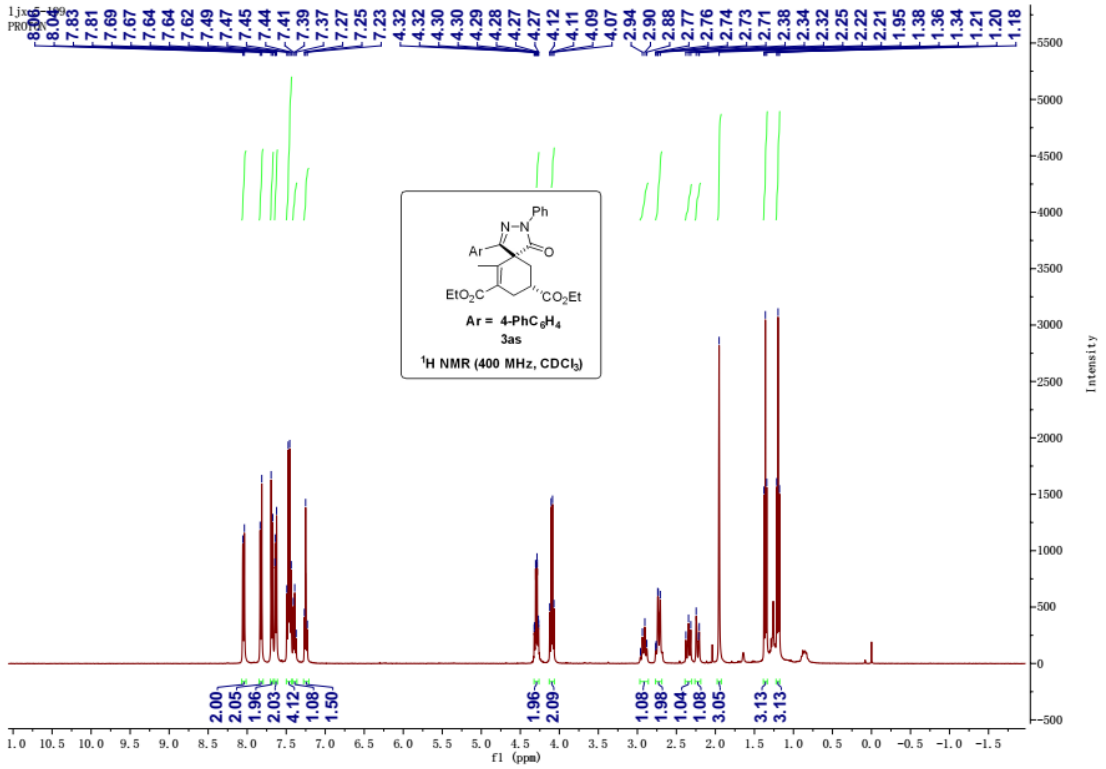

ljx-5-188
C13CPD
174.59
173.19
167.53
160.89
136.42
135.78
133.86
131.59
130.66
130.45
130.23
129.28
129.01
128.29
127.40
121.73
60.98
60.92
59.80
35.16
32.77
28.67
17.75
14.27
14.11
Ar = 2-BrC6H4
3ap
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity

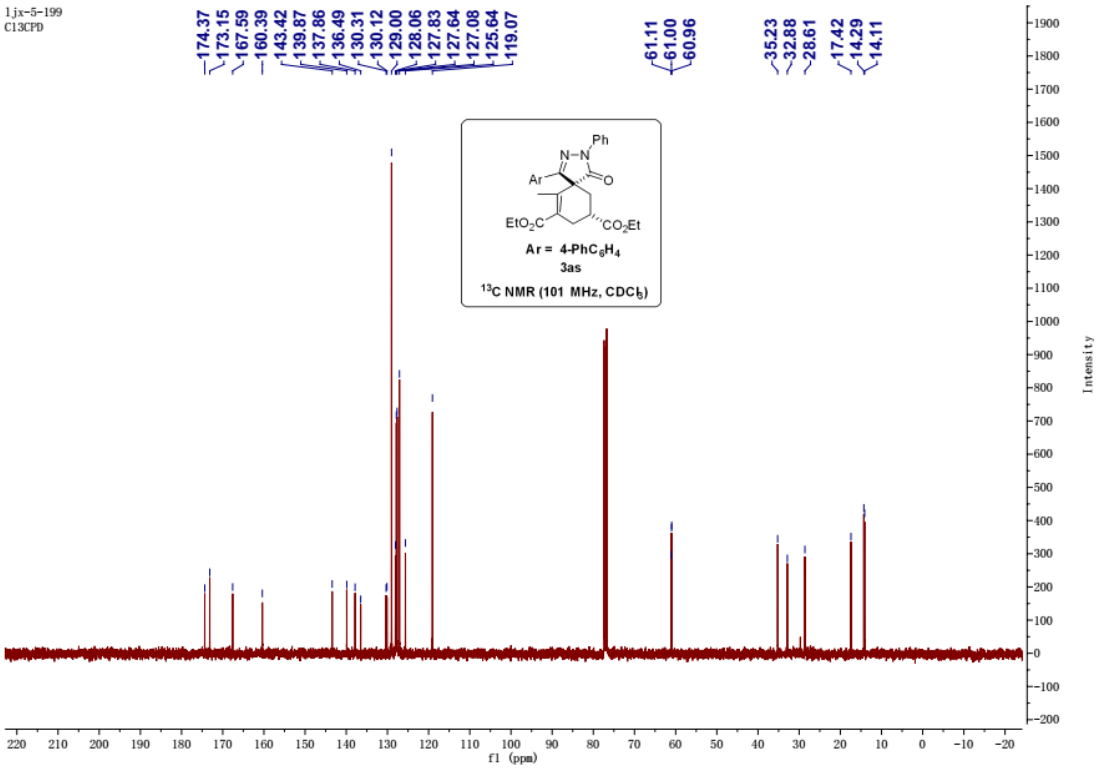

ljx-5-190
test
7.69
7.68
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.26
4.12
4.12
4.10
4.10
4.09
4.08
4.07
2.88
2.68
2.66
2.64
2.35
2.22
2.04
1.36
1.34
1.22
1.20
1.19
2.00
3.00
1.08
2.88
1.95
1.97
1.06
2.07
4.03
1.11
2.92
3.11
2.94
Ar = 2-MeC6H4
3aq
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity

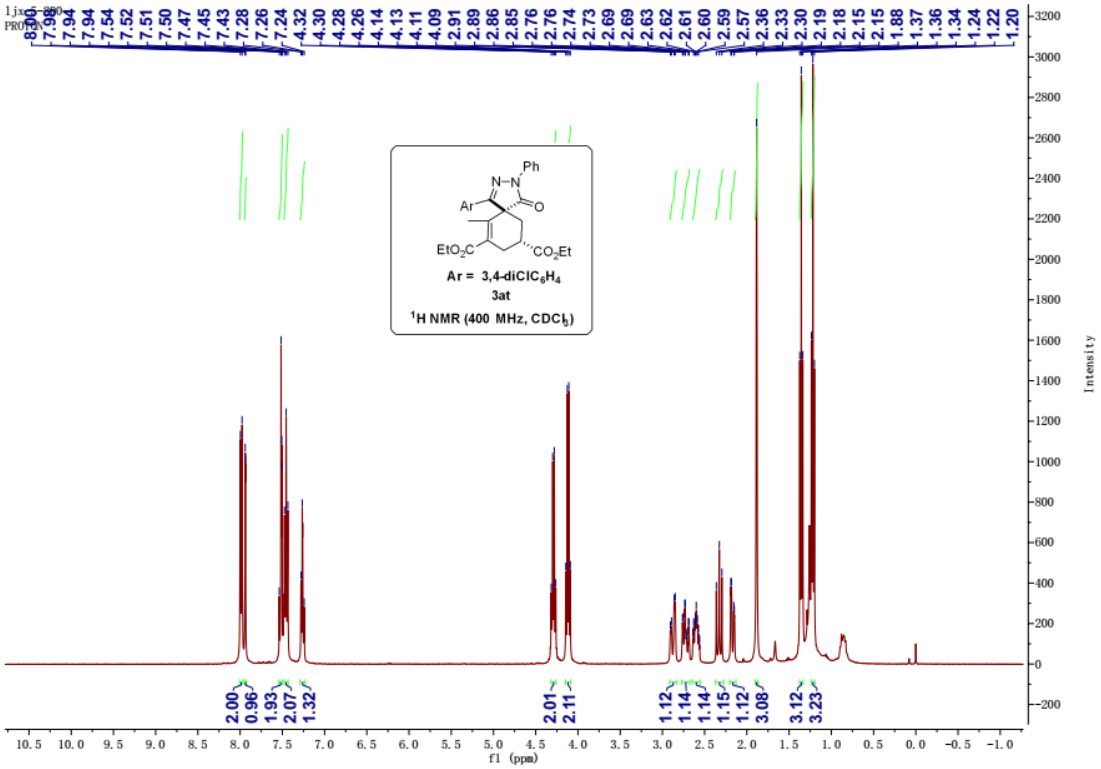

ljx-5-190
test
174.79
173.23
167.51
160.83
136.61
135.47
135.09
131.68
131.30
130.57
130.04
129.00
128.83
127.30
126.68
126.58
60.99
60.91
59.88
35.13
32.91
28.67
18.58
17.58
14.27
14.10
Ar= 2-MeC6H4
3aq
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)


ljx-5-191
test
7.73
7.71
7.64
7.46
7.45
6.89
4.30
4.29
4.27
4.26
4.11
4.09
4.07
4.06
2.86
2.64
2.61
2.37
2.33
2.29
2.18
1.93
1.37
1.35
1.33
1.21
1.19
1.17
2.10
2.10
3.08
1.00
2.08
2.05
1.05
2.11
5.99
1.22
1.07
3.06
3.05
3.05
Ar= 3,5-diMeC6H4
3ar
1H NMR (400 MHz, CDCl3)
Intensity
f1 (ppm)


ljx-5-191
test
174.32
173.19
167.58
160.64
138.76
136.51
131.59
130.68
130.02
129.03
127.46
127.43
116.94
61.12
60.95
60.92
35.16
32.72
28.60
21.53
17.31
14.28
14.09
Ar = 3,5-diMeC6H4
3ar
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


8.06
8.04
7.83
7.81
7.69
7.67
7.64
7.64
7.62
7.49
7.47
7.45
7.44
7.41
7.39
7.37
7.27
7.25
7.23
4.32
4.32
4.30
4.30
4.29
4.28
4.27
4.27
4.12
4.11
4.09
4.07
2.94
2.90
2.88
2.77
2.76
2.74
2.73
2.71
2.38
2.34
2.32
2.25
2.22
2.21
1.95
1.38
1.36
1.34
1.21
1.20
1.18
Ar = 4-PhC6H4
3as
1H NMR (400 MHz, CDCl3)
2.00
2.05
1.96
2.03
4.12
1.08
1.50
1.96
2.09
1.08
1.98
1.04
1.08
3.05
3.13
3.13
f1 (ppm)
Intensity


ljx-5-199
C13CPD
174.37
173.15
167.59
160.39
143.42
139.87
137.86
136.49
130.31
130.12
129.00
128.06
127.83
127.64
127.08
125.64
119.07
61.11
61.00
60.96
35.23
32.88
28.61
17.42
14.29
14.11
Ar = 4-PhC6H4
3as
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


ljx-5-200
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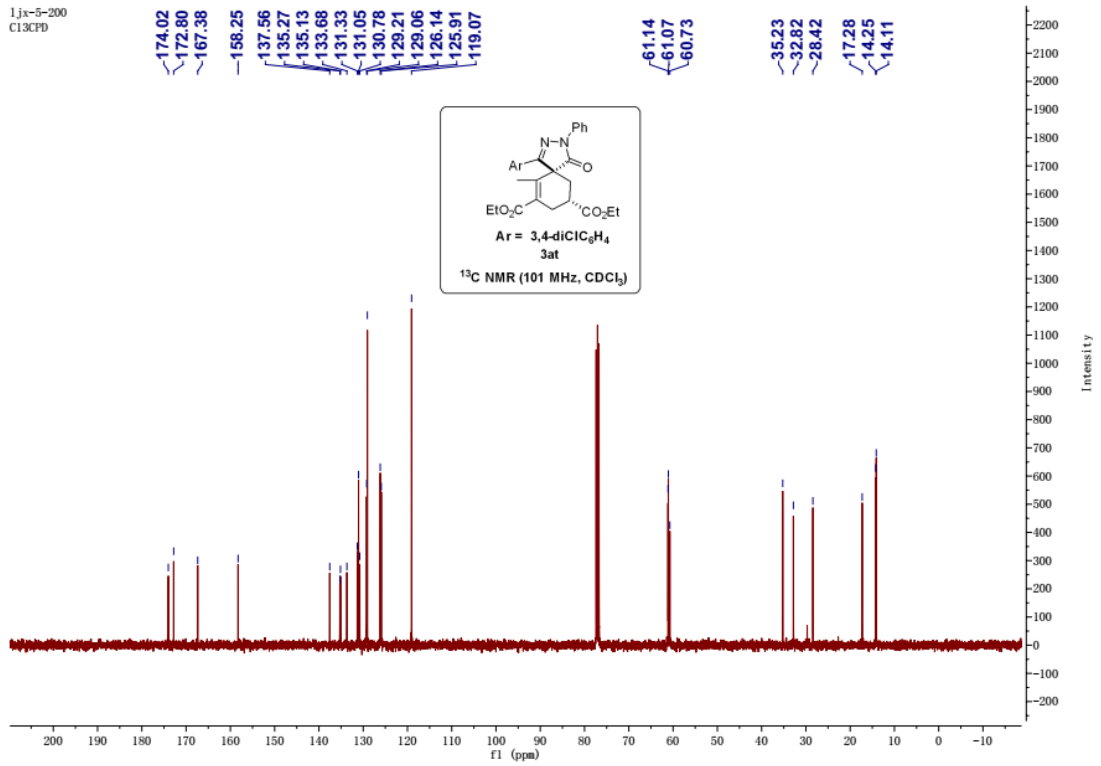
8.00
7.96
7.94
7.94
7.54
7.52
7.51
7.50
7.47
7.45
7.43
7.28
7.26
7.24
4.32
4.30
4.28
4.26
4.14
4.13
4.11
4.09
2.91
2.89
2.86
2.85
2.76
2.74
2.73
2.69
2.69
2.63
2.62
2.61
2.60
2.59
2.57
2.36
2.33
2.30
2.19
2.18
2.15
2.15
1.88
1.37
1.36
1.34
1.24
1.22
1.20
2.00
0.96
1.93
2.07
1.32
2.01
2.11
1.12
1.14
1.14
1.15
1.12
3.08
3.12
3.23
Ar = 3,4-diClC6H4
3at
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity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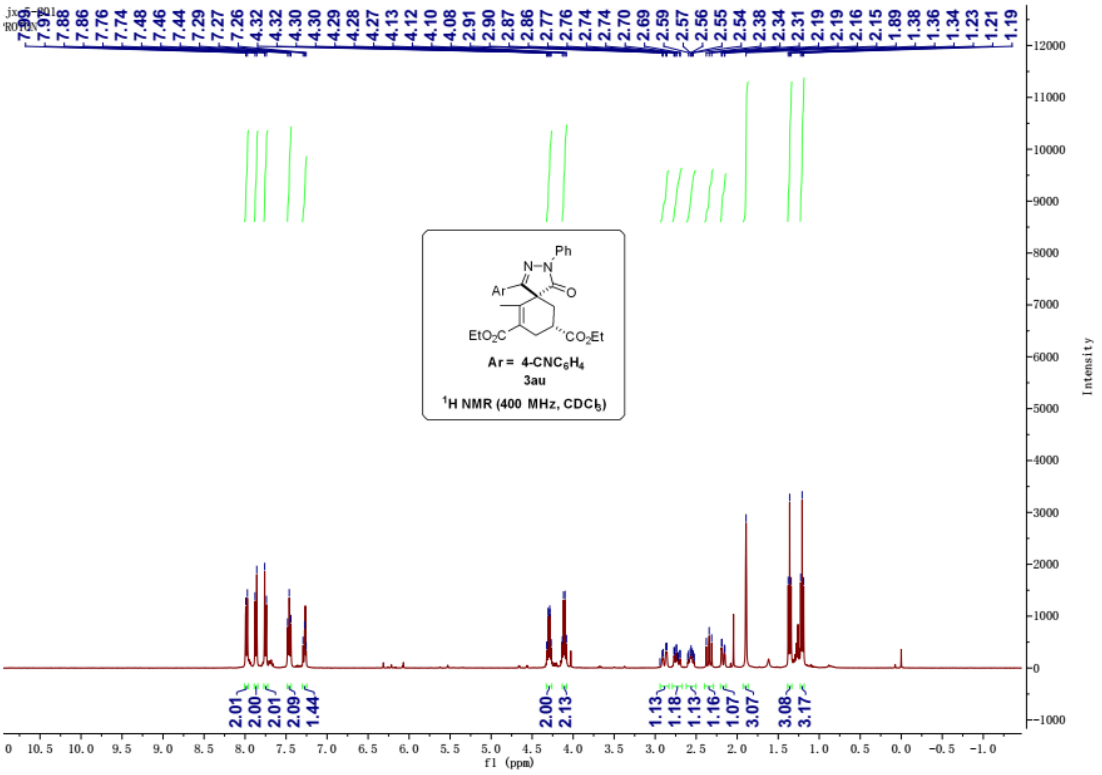
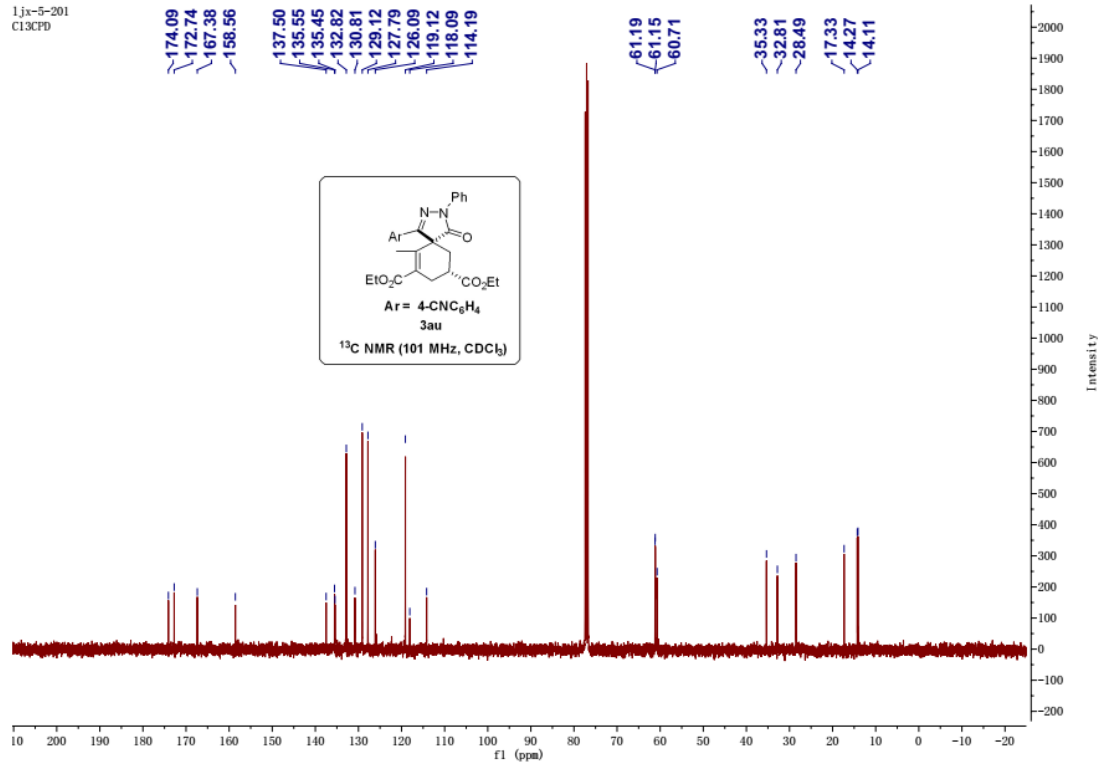
C13CPD
174.02
172.80
167.38
158.25
137.56
135.27
135.13
133.68
131.33
131.05
130.78
129.21
129.06
126.14
125.91
119.07
61.14
61.07
60.73
35.23
32.82
28.42
17.28
14.25
14.11
Ar = 3,4-diClC6H4
3at
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


7.93
7.91
7.88
7.86
7.76
7.74
7.48
7.46
7.44
7.29
7.27
7.26
4.32
4.32
4.30
4.30
4.29
4.28
4.27
4.13
4.12
4.10
4.08
2.91
2.90
2.87
2.86
2.77
2.76
2.74
2.74
2.70
2.69
2.59
2.57
2.56
2.55
2.54
2.38
2.34
2.31
2.19
2.19
2.16
2.15
1.89
1.38
1.36
1.34
1.23
1.21
1.19
Ar = 4-CNC6H4
3au
1H NMR (400 MHz, CDCl3)
2.01
2.00
2.01
2.09
1.44
2.00
2.13
1.13
1.18
1.13
1.16
1.07
3.07
3.08
3.17
f1 (ppm)
Intensity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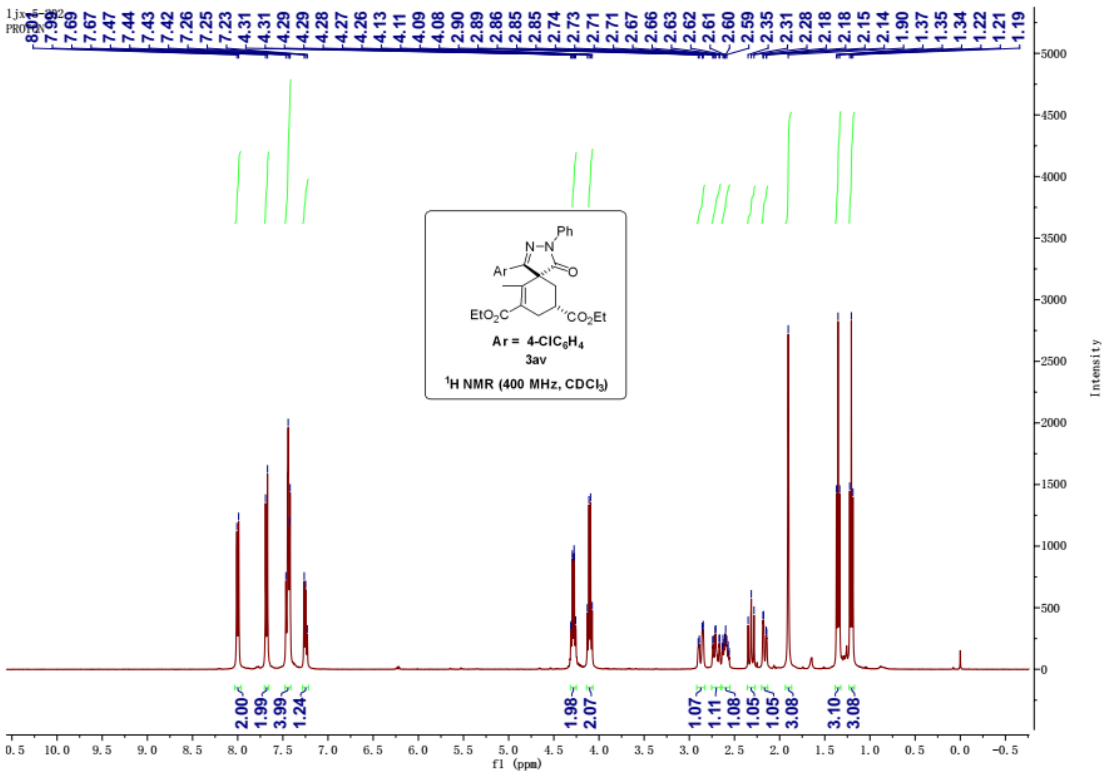
167.38
158.56
137.50
135.55
135.45
132.82
130.81
129.12
127.79
126.09
119.12
118.09
114.19
61.19
61.15
60.71
35.33
32.81
28.49
17.33
14.27
14.11
Ar = 4-CNC6H4
3au
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity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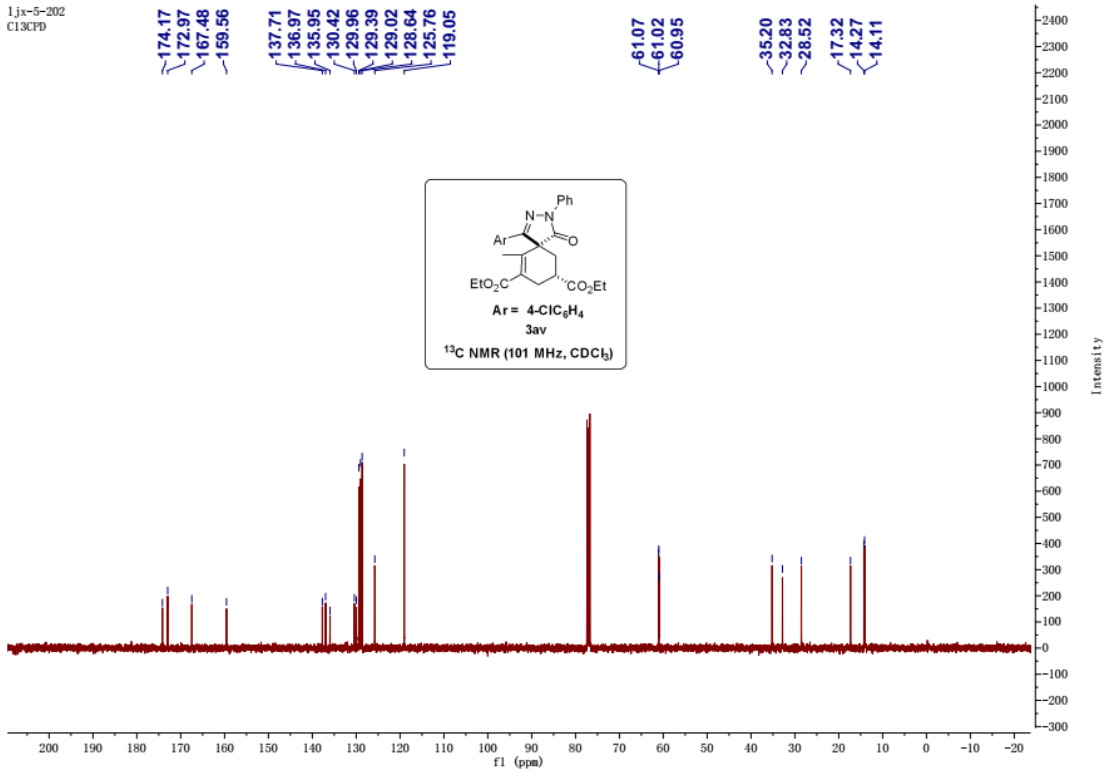
7.23
4.31
4.31
4.29
4.29
4.28
4.27
4.26
4.13
4.11
4.09
4.08
2.90
2.89
2.86
2.85
2.85
2.74
2.73
2.71
2.71
2.67
2.66
2.63
2.62
2.61
2.60
2.59
2.35
2.31
2.28
2.18
2.18
2.15
2.14
1.90
1.37
1.35
1.34
1.22
1.21
1.19
2.00
1.99
3.99
1.24
1.98
2.07
1.07
1.11
1.08
1.05
1.05
3.08
3.10
3.08
Ar = 4-ClC6H4
3av
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity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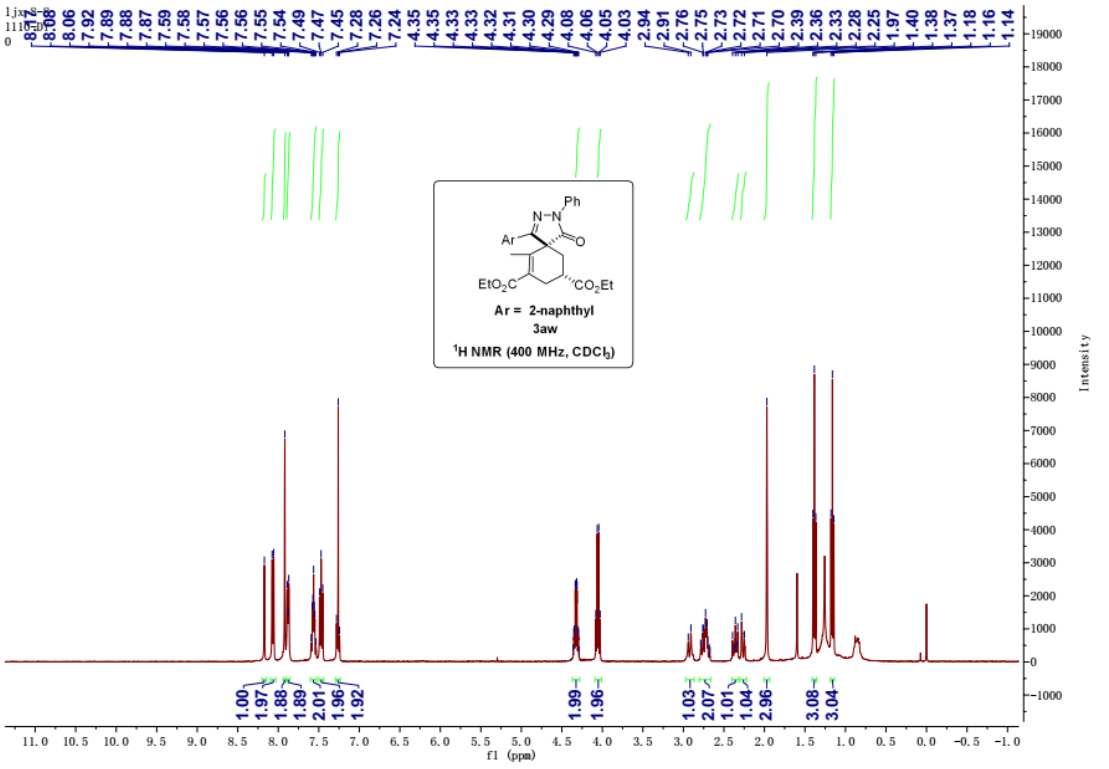
135.95
130.42
129.96
129.39
129.02
128.64
125.76
119.05
61.07
61.02
60.95
35.20
32.83
28.52
17.32
14.27
14.11
Ar = 4-ClC6H4
3av
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity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8.06
7.92
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7.88
7.87
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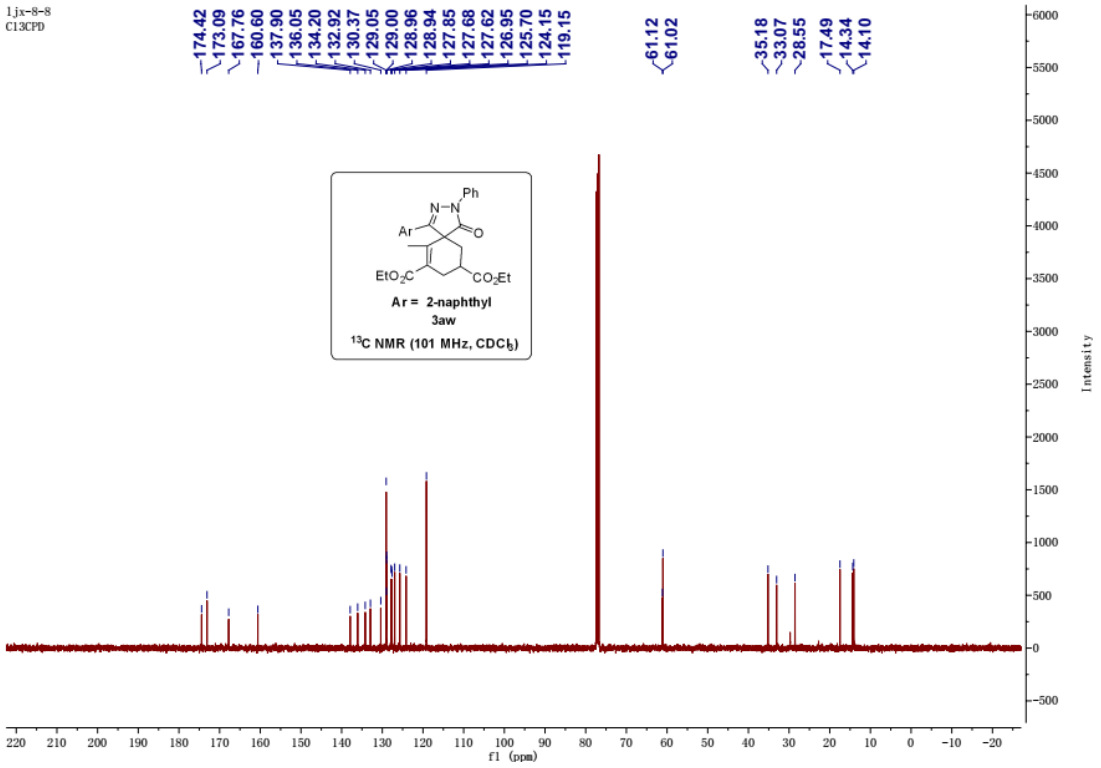
7.58
7.57
7.56
7.55
7.54
7.49
7.47
7.45
7.28
7.26
7.24
4.35
4.33
4.32
4.31
4.30
4.29
4.08
4.06
4.05
4.03
2.94
2.91
2.76
2.75
2.73
2.72
2.71
2.70
2.39
2.36
2.33
2.28
2.25
1.97
1.40
1.38
1.37
1.18
1.16
1.14
1.00
1.97
1.88
1.89
2.01
1.96
1.92
1.99
1.96
1.03
2.07
1.01
1.04
2.96
3.08
3.04
Ar = 2-naphthyl
3aw
1H NMR (400 MHz, CDCl3)
f1 (ppm)
Intensity


ljx-8-8
C13CPD
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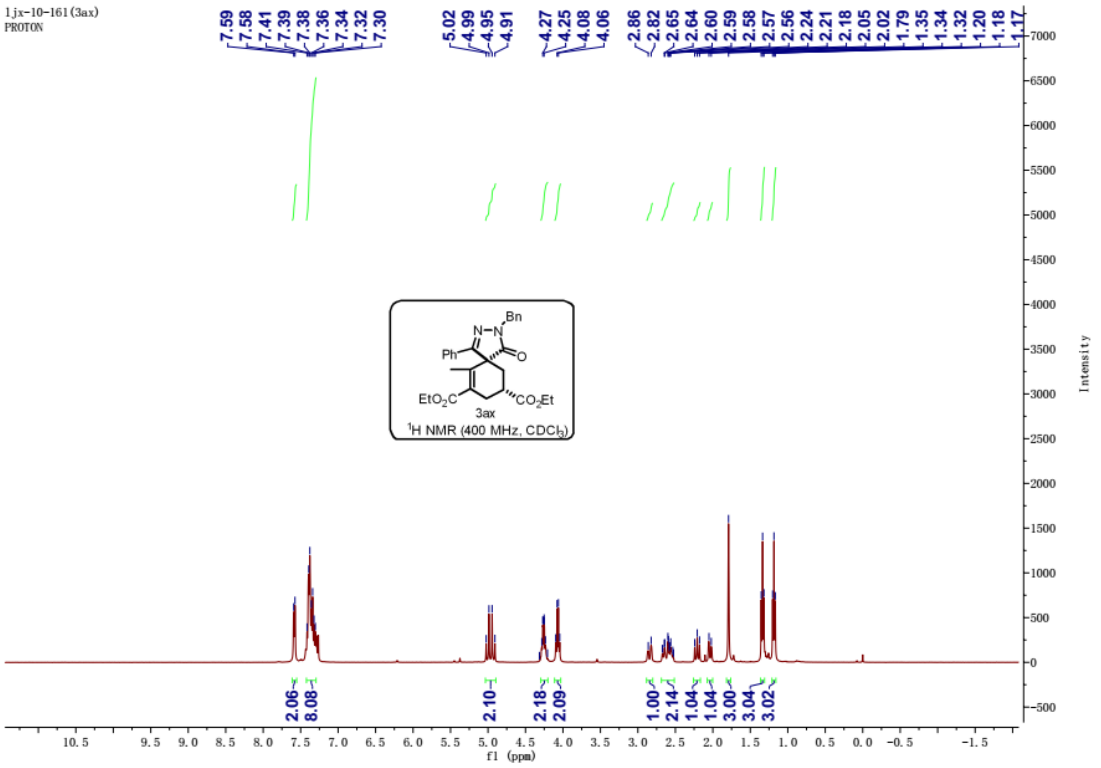
173.09
167.76
160.60
137.90
136.05
134.20
132.92
130.37
129.05
129.00
128.96
128.94
127.85
127.68
127.62
126.95
125.70
124.15
119.15
61.12
61.02
35.18
33.07
28.55
17.49
14.34
14.10
Ar = 2-naphthyl
3aw
13C NMR (101 MHz, CDCl3)
f1 (ppm)
Intensity


ljx-10-161(3ax)
PROTON
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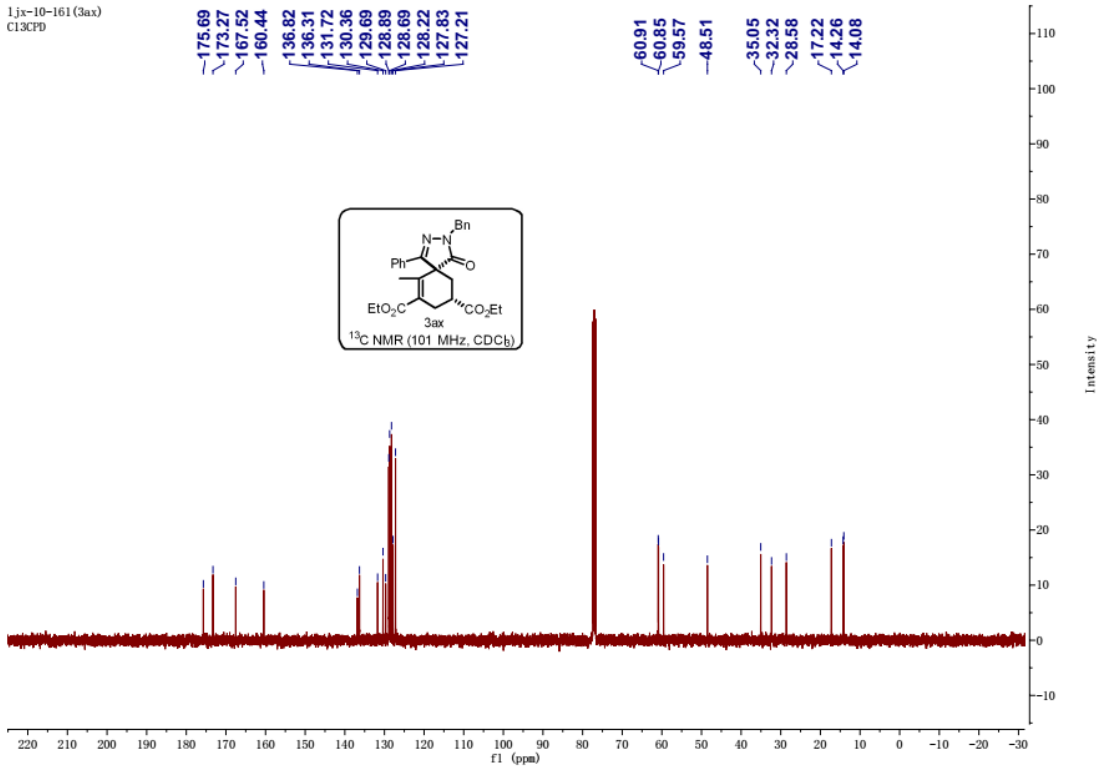
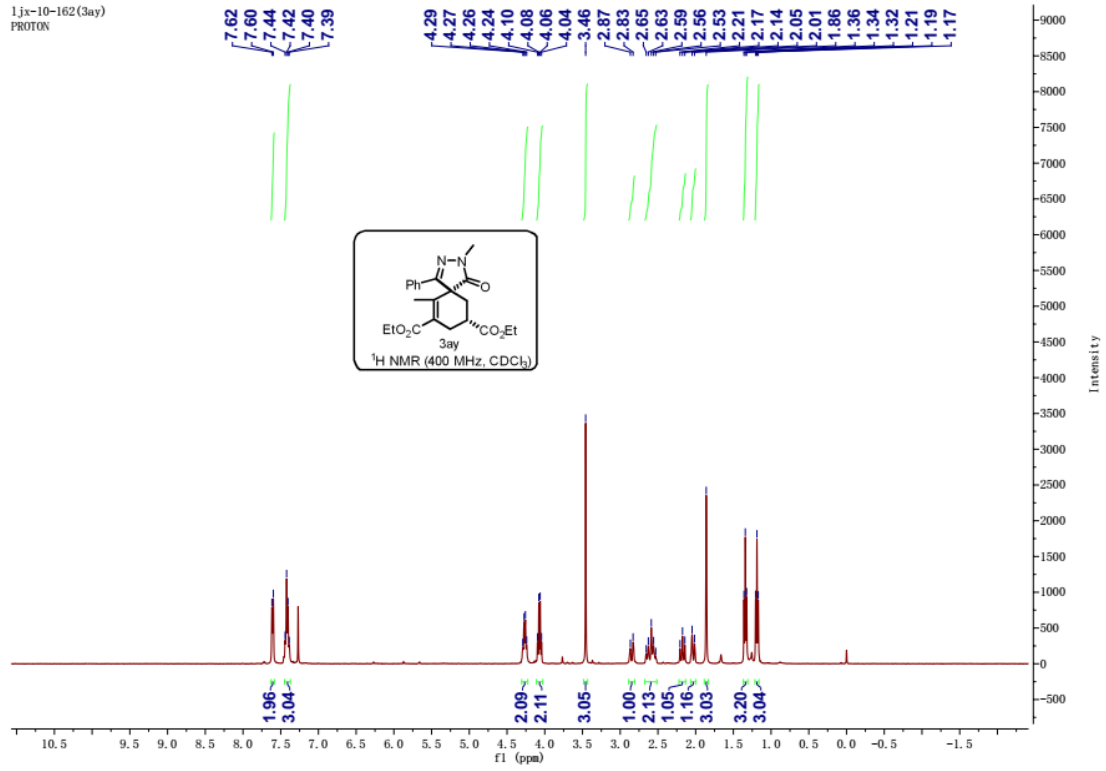
7.41
7.39
7.38
7.36
7.34
7.32
7.30
5.02
4.99
4.95
4.91
4.27
4.25
4.08
4.06
2.86
2.82
2.65
2.64
2.60
2.59
2.58
2.57
2.56
2.24
2.21
2.18
2.05
2.02
1.79
1.35
1.34
1.32
1.20
1.18
1.17
3ax
1H NMR (400 MHz, CDCl3)
2.06
8.08
2.10
2.18
2.09
1.00
2.14
1.04
1.04
3.00
3.04
3.02
f1 (ppm)
Intensity


1jx-10-161(3ax)
C13CPD
175.69
173.27
167.52
160.44
136.82
136.31
131.72
130.36
129.69
128.89
128.69
128.22
127.83
127.21
60.91
60.85
59.57
48.51
35.05
32.32
28.58
17.22
14.26
14.08
Bn
N
N
Ph
O
EtO2C
CO2Et
3ax
13C NMR (101 MHz, CDCl3)
Intensity
f1 (ppm)


1jx-10-162(3ay)
PROTON
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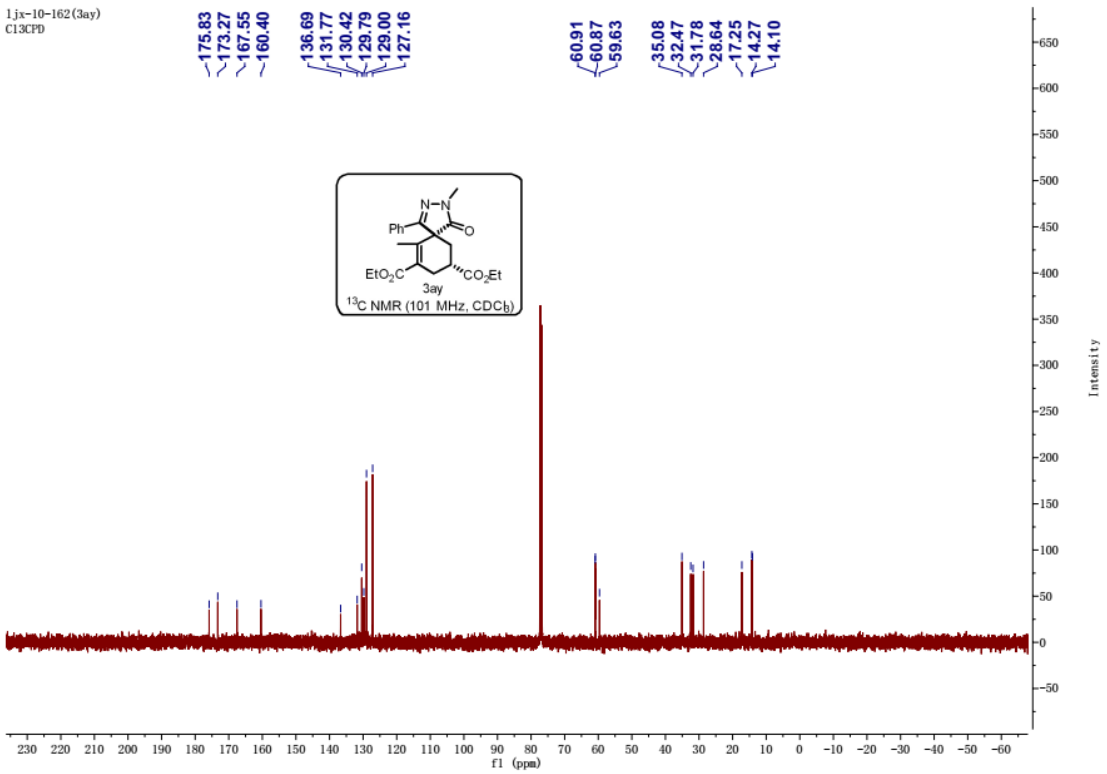
7.40
7.39
4.29
4.27
4.26
4.24
4.10
4.08
4.06
4.04
3.46
2.87
2.83
2.65
2.63
2.59
2.56
2.53
2.21
2.17
2.14
2.05
2.01
1.86
1.36
1.34
1.32
1.21
1.19
1.17
N
N
Ph
O
EtO2C
CO2Et
3ay
1H NMR (400 MHz, CDCl3)
1.96
3.04
2.09
2.11
3.05
1.00
2.13
1.05
1.16
3.03
3.20
3.04
Intensity
f1 (ppm)



8. X-Ray Crystallography Data of 3ar

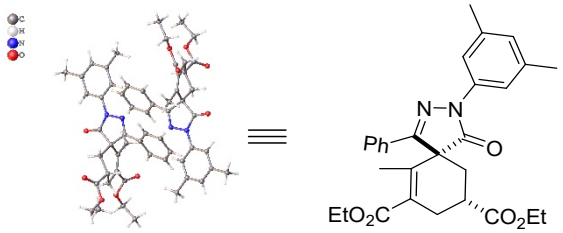


Figure S2. ORTEP diagram of **3ar**. (CCDC: 2208910) Thermal ellipsoids are shown at the 50% probability level. A colorless block crystal of **3ar** for X-ray diffraction was obtained by slowly volatilizing a solution of **3ar** in hexane/ ethyl acetate (5:1). The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer.

Table S2 Crystal data and structure refinement for 3ar.

Identification code	3ar
Empirical formula	$C_{29}H_{32}N_2O_5$
Formula weight	488.56
Temperature/K	113.15
Crystal system	triclinic
Space group	P-1
a/Å	11.4759(4)
b/Å	11.5363(3)
c/Å	19.7187(7)
α/°	85.779(3)
β/°	79.152(3)

γ/°	85.444(3)
Volume/Å^3	2551.20(15)
Z	4
ρ_{calc}g/cm^3	1.272
μ/mm^{-1}	0.087
F(000)	1040.0
Crystal size/mm^3	0.24 × 0.22 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.548 to 52.744
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected	27119
Independent reflections	10440 [R_{int} = 0.0364, R_{sigma} = 0.0420]
Data/restraints/parameters	10440/0/660
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1214
Final R indexes [all data]	R_1 =0.0651, wR_2 = 0.1343
Largest diff. peak/hole / e Å^{-3}	0.38/-0.24

9. References

[1] L. Li, L. Ma, X. Wang, J. Liu, *J. Heterocyclic Chem*. **2013**, *50*,164.

[2] J.-X. Lai, Y. Huang, *Chem. Commun*., **2023**, *59*, 13215.