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Supporting Information

Enantioselective [3 + 2] Annulation of Isatin-Derived MBH-Carbonates and 3-Nitroindoles Enabled by a Bifunctional DMAP-Thiourea

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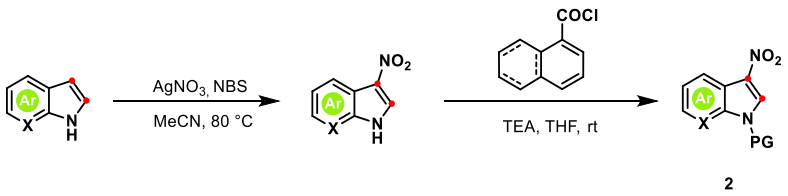
1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel (300-400 mesh). Chemical yields referred to pure isolated substances. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained using a Bruker 600 MHz spectrometer. Chemical shifts for ^{1}H, ^{13}C NMR spectra were reported in ppm from $CDCl_3$, DMSO-d_6 with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Optical rotations were measured on Rudolph Research Analytical AUTOPOL IV Automatic Polarimeter. Infrared spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer IRAffinity-1. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Enantiomeric ratio was determined by chiral HPLC analysis on Agilent 1260 Infinity II LC System. X-ray structure was determined on a Bruker D8 Venture X-ray Diffraction meter.

Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. All solvents were dried before use following the standard procedures. Unless otherwise noted, experiments involving moisture and/or air sensitive components were performed in nitrogen. Morita−Baylis−Hillman carbonates[1] and 3-nitro-1H-indoles **2a-h** were prepared according to the literature procedure[2]. Chiral DMAP-thiourea Catalyst **C2-C5** was prepared following the literature procedure.[3]

2. Substrate preparation

General Procedures for the Preparation of Substrates **2i, 2j, 2k, 2m, 2n 2p, 2s**.

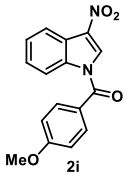


2

To a stirred mixture of MeCN (50 mL) and NBS (1.78 g, 10 mmol) at 80 °C was added $AgNO_3$ (1.70 g, 10 mmol). The substituted indole (10 mmol) was then added portionwise to the mixture. After 3 h, the mixture was filtered to remove AgBr. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 and washed with aqueous 4% $NaHCO_3$. The organic phase was separated, washed with brine, dried with Na_2SO_4 and concentrated. The residue was subjected to column chromatography over silica gel using petroleum ether (PE)/EtOAc (4:1, v/v) as eluent to give product.

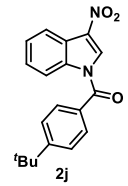
To a solution of above product (1.0 equiv) in THF (50 mL) was added TEA (1.0 mL, 7.5 mmol), followed by the dropwise addition of arylacyl chloride (6.0 mmol) under ice bath. Then the reaction was warmed to room temperature. After the reaction was completed (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (30 mL x 3). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was recrystallized from anhydrous ether to afford the desired product **2**.

(4-Methoxyphenyl)(3-nitro-1*H*-indol-1-yl)methanone (2i)



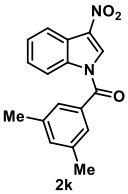
Yellow solid, 51% yield; Mp: 149−150 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.31 (ddd, *J* = 25.4, 6.2, 2.2 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.54−7.50 (m, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 3.94 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 167.6, 164.2, 135.4, 132.8, 132.5, 129.4, 127.0, 126.3, 124.0, 121.8, 120.8, 116.2, 114.7, 55.9; **IR** (KBr): 3138, 1701, 1602, 1504, 1276, 1190, 756, 646; **MS (EI)**: 296 (M^+), 135, 107, 92, 88, 77, 64, 50; **HRMS (EI)**: Exact mass calcd for $C_{16}H_{12}N_2O_4$ $[M]^+$: 296.0792, Found: 296.0801.

(4-(*tert*-Butyl)phenyl)(3-nitro-1*H*-indol-1-yl)methanone (2j)



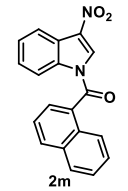
White solid, 36% yield; Mp: 154−155 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.42−8.37 (m, 1H), 8.36−8.29 (m, 2H), 7.73 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.64−7.58 (m, 2H), 7.57−7.49 (m, 2H), 1.40 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.3, 157.8, 135.3, 133.0, 129.9, 129.5, 129.2, 127.2, 126.5, 126.4, 121.8, 120.9, 116.5, 35.5, 31.2; **IR** (KBr): 3151, 2960, 1699, 1492, 1300, 1012, 777, 545; **MS (EI)**: 322 (M^+), 161 146, 131, 118, 91, 57, 41; **HRMS (EI)**: Exact mass calcd for $C_{19}H_{18}N_2O_3$ $[M]^+$: 322.1312, Found: 322.1315.

(3,5-Dimethylphenyl)(3-nitro-1*H*-indol-1-yl)methanone (2k)



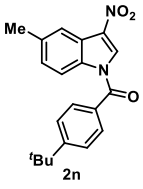
White solid, 14% yield; Mp: 178−179 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.41−8.35 (m, 1H), 8.35−8.31 (m, 1H), 8.30 (s, 1H), 7.57−7.49 (m, 2H), 7.35 (d, *J* = 13.4 Hz, 3H), 2.43 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.8, 139.3, 135.3, 135.3, 133.0, 132.2, 129.4, 127.3, 127.2, 126.4, 121.8, 120.8, 116.5, 21.4; **IR** (KBr): 3138, 1705, 1602, 1502, 1276, 1004, 825, 773; **MS (EI)**: 294 (M^+), 133, 105, 88, 78, 77, 63, 51; **HRMS (EI)**: Exact mass calcd for $C_{17}H_{14}N_2O_3$ $[M]^+$: 294.0999, Found: 294.1006.

Naphthalen-1-yl(3-nitro-1*H*-indol-1-yl)methanone (2m)



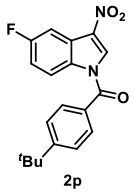
White solid, 23% yield; Mp: 152−153 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.61−8.50 (m, 1H), 8.37−8.28 (m, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.01−8.00 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.66−7.52 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.6, 135.1, 133.8, 133.5, 132.9, 130.3, 130.1, 129.1, 129.1, 128.5, 127.6, 127.6, 127.5, 126.8, 124.8, 124.4, 122.1, 121.0, 116.9; **IR** (KBr): 3157, 1712, 1552, 1475, 1298, 1138, 785, 516; **MS (EI)**: 316 (M^+), 155, 127, 103,101, 77, 63, 51; **HRMS (EI)**: Exact mass calcd for $C_{19}H_{12}N_2O_3$ $[M]^+$: 316.0842, Found: 316.0850.

(4-(*tert*-Butyl)phenyl)(5-methyl-3-nitro-1*H*-indol-1-yl)methanone (2n)



White solid, 42% yield; Mp: 149−150 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 8.11 (s, 1H), 7.72 (d, *J* = 10.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 1H), 2.55 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.3, 157.7, 136.6, 133.6, 132.8, 129.8, 129.4, 129.3, 128.6, 126.3, 122.0, 120.5, 116.1, 35.5, 31.2, 21.8; **IR** (KBr): 3138, 2964, 1701, 1550, 1292, 1193, 705, 594; **MS (EI)**: 336 (M^+), 161, 146, 118, 91, 89, 77, 57; **HRMS (EI)**: Exact mass calcd for $C_{20}H_{20}N_2O_3$ $[M]^+$: 336.1468, Found: 336.1473.

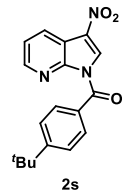
(4-(*tert*-Butyl)phenyl)(5-fluoro-3-nitro-1*H*-indol-1-yl)methanone (2p)



2p

White solid, 49% yield; Mp: 160−161 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.38−8.35 (m, 2H), 7.97−7.96 (m, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.26−7.23 (m, 1H), 1.41 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.0, 161.2 (d, *J* = 244.5 Hz, 1C) 158.0, 132.6, 131.6, 130.5, 129.9, 128.8, 126.4, 122.9 (d, *J* = 11.5 Hz, 1C), 118.0 (d, *J* = 9.6 Hz, 1C), 115.4 (d, *J* = 25.3 Hz, 1C), 106.8 (d, *J* = 26.7 Hz, 1C), 35.5, 31.2; **^{19}F NMR** (565 MHz, $CDCl_3$): δ −114.1; **IR** (KBr): 3151, 1699, 1606, 1300, 1219, 1012, 879, 705; **MS (EI)**: 340 (M^+), 161, 146, 118, 91, 78, 57, 41; **HRMS (EI)**: Exact mass calcd for $C_{19}H_{17}FN_2O_3$ $[M]^+$: 340.1218, Found: 340.1216.

(4-(*tert*-Butyl)phenyl)(3-nitro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)methanone (2s)



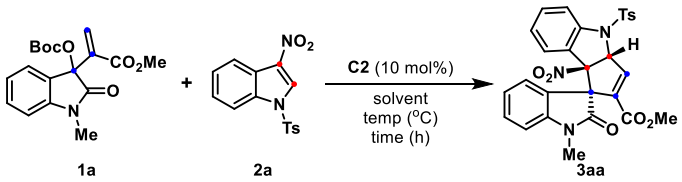
2s

White solid, 57% yield; Mp: 135−136 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.64 (d, *J* = 7.5 Hz, 1H), 8.60 (s, 1H), 8.51 (dd, *J* = 4.3, 2.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.49−7.41 (m, 1H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 166.5, 158.7, 147.1, 146.6, 131.0, 130.4, 129.9, 129.0, 128.8, 126.0, 121.5, 115.0, 35.1, 31.1; **IR** (KBr): 3138, 1699, 1544, 1398, 1004, 850, 773, 704; **MS (EI)**: 323 (M^+), 161, 146, 118, 105, 91, 63, 41; **HRMS (EI)**: Exact mass calcd for $C_{18}H_{17}N_3O_3$ $[M]^+$: 323.1264, Found: 323.1258.

3. Optimization conditions of enantioselective [3 + 2] annulations

We began our study with the reaction of isatin-derived MBH carbonate **1a** and 3-nitroindole **2a** in the presence of catalyst **C2** at room temperature in dioxane. To our delight, the desired product **3aa** was afforded in >20:1 dr, albeit with only 65% yield and 65% ee (Table S1, entry 1). Other solvents, including CH_2Cl_2, toluene, EtOAc, THF, acetone, CH_3CN, DCE, and $CHCl_3$, was subsequently screened (Table S1, entries 2−9). DCE turned out to be the best solvent, and up to 86% yield and 81% ee of product **3aa** was achieved (Table S1, entry 8). Lowering the reaction temperature to 0 °C resulted in an improvement of both yield and ee value (Table S1, entry 10), however, further lowering the temperature to −20 °C made the reaction very sluggish albeit in a slightly higher ee value (Table S1, entry 11). Pleasingly, with the aid of molecular sieve (4 Å) additives at 0 °C, the ee value was maintained in an equal level (Table S1, entry 12).

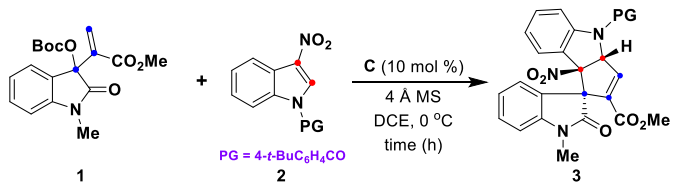
Table S1. Optimization of Reaction Conditions[a,b]

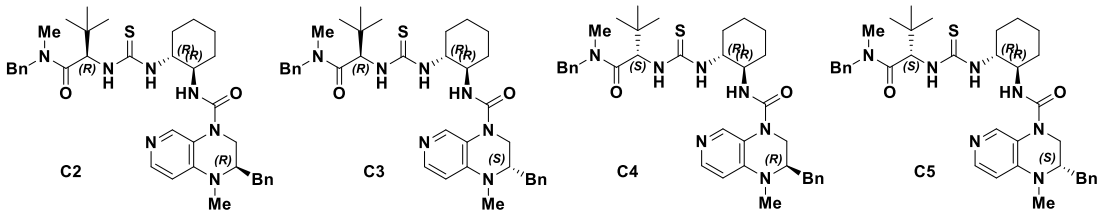


entry	solvent	temp (°C)	time (h)	yield (%)[c]	ee (%)[d]
1	dioxane	rt	48	65	65
2	CH_2Cl_2	rt	20	88	76
3	toluene	rt	20	62	69
4	EtOAc	rt	20	69	59
5	THF	rt	20	70	71
6	acetone	rt	20	74	69
7	CH_3CN	rt	20	77	40
8	DCE	rt	20	86	81
9	$CHCl_3$	rt	20	85	69
10	DCE	0	46	97	83
11	DCE	−20	108	88	85
12[e]	DCE	0	46	97	85

[a]Reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), cat. **C2** (10 mol%), and solvent (1.0 mL) under N_2 atmosphere. [b]All dr > 20:1. [c]Yield of isolated product. [d]Determined by HPLC analysis. [e]Molecular sieve (4 Å, 20 mg) was added. THF = tetrahydrofuran, DCE = 1,2-dichloroethane.

Table S2. Screening of Catalysts [a,b]

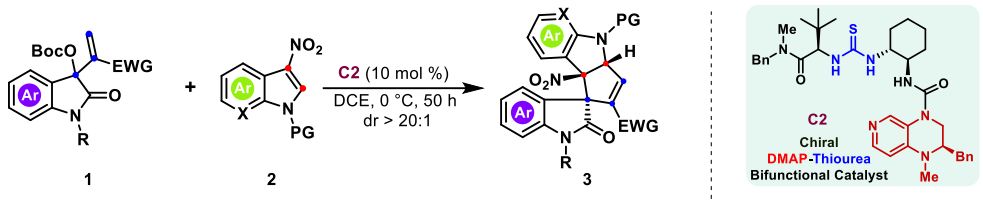




entry	C	time (h)	yield (%)[c]	ee (%)[d]
1	**C2**	**48**	**93**	**95**
2	C3	48	91	-22
3	C4	60	89	86
4	C5	60	80	62

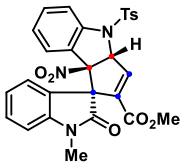
[a]Reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), cat. **C2** (10 mol%), molecular sieve (4 Å, 20 mg) and solvent (1.0 mL) under N_2 atmosphere. [b]All dr> 20:1. [c]Yield of isolated product. [d]Determined by HPLC analysis.

4. General procedure for enantioselective [3 + 2] annulations



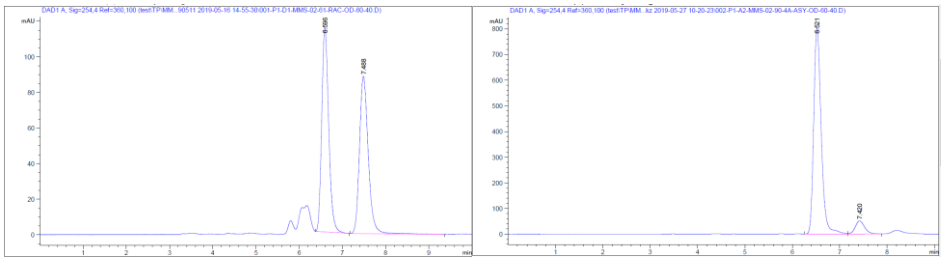
An oven-dried 10.0 mL vial was charged with DMAP-thiourea **C2** (0.02 mmol), Morita−Baylis−Hillman carbonate **1** (0.2 mmol), 3-nitro-1H-indole **2** (0.24 mmol), 4 Å molecular sieves (20 mg) and dry DCE (2.0 mL). Then the mixture was stirred at 0 °C for 50 h. After the reaction was completed (monitored by TLC, EtOAc / PE), the residue was purified by silica gel column chromatography (EtOAc / PE = 5:1 to 3:1, v/v) to give pure products **3**.

Methyl (1*S*,3a*R*,8b*R*)-1'-methyl-8b-nitro-2'-oxo-4-tosyl-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3aa)



3aa

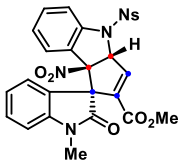
White solid, 97% yield; Mp: 258−261 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +40.5 (c = 1.0, $CHCl_3$) for 85% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.74−7.70 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.22−7.15 (m, 3H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 16.9, 7.6 Hz, 2H), 6.48 (d, *J* = 2.3 Hz, 1H), 3.58 (s, 3H), 3.36 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.3, 161.6, 145.2, 144.5, 141.2, 140.5, 136.9, 133.9, 133.0, 130.7, 130.1, 129.4, 127.5, 126.6, 124.0, 122.9, 122.8, 122.6, 115.4, 108.9, 104.4, 72.7, 63.8, 52.5, 27.2, 21.7; **IR** (KBr): 2924, 1720, 1612, 1556, 1238, 1170, 756, 667; **HRMS (ESI)**: Exact mass calcd for $C_{28}H_{23}N_3O_7S$ $[M+Na]^+$: 568.1149, Found: 568.1149; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 6.52 min (major), 7.42 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.596	BB	0.1706	1281.21704	114.87814	50.7434
2	7.488	MM R	0.2343	1243.67920	88.46529	49.2566

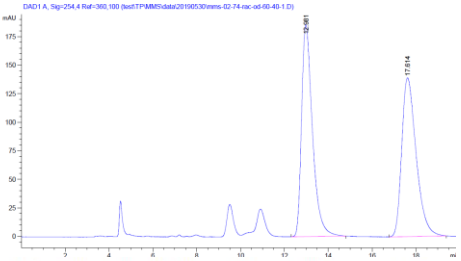
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.521	BV	0.1672	8800.73926	803.83887	92.6850
2	7.420	VB	0.2045	694.58447	50.48477	7.3150

Methyl (1*S*,3a*R*,8b*R*)-1'-methyl-8b-nitro-4-((4-nitrophenyl)sulfonyl)-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ac)

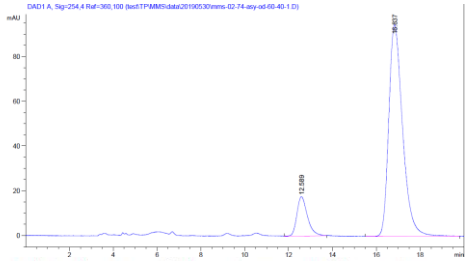


3ac

White solid, 40% yield; Mp: 158−160 °C; dr > 20:1; $[\alpha]^{25}_D$ = +74.8 (c = 1.0, $CHCl_3$) for 76% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.9 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.48−7.43 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.21−7.16 (m, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.91−6.90 (m, 2H), 6.47 (d, *J* = 2.3 Hz, 1H), 3.59 (s, 3H), 3.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.0, 161.4, 150.9, 144.5, 142.4, 140.2, 139.4, 137.6, 133.4, 130.9, 129.8, 128.8, 126.2, 124.9, 124.6, 123.3, 122.9, 122.4, 115.3, 109.1, 104.1, 72.8, 63.4, 52.6, 27.3; **IR** (KBr): 3103, 2953, 1716, 1610, 1556, 1375, 756, 732; **HRMS (ESI)**: Exact mass calcd for $C_{27}H_{20}N_4O_9S$ $[M+Na]^+$: 599.0843, Found: 599.0853; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 16.84 min (major), 12.59 min (minor).

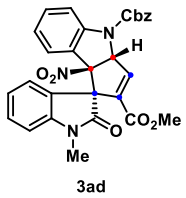


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.981	BV R	0.4630	6401.45117	185.55270	50.2020
2	17.614	VV R	0.5398	6349.93311	139.05060	49.7980



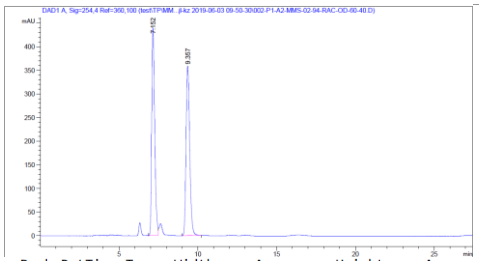
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.589	VV R	0.3792	560.33905	17.40245	12.1605
2	16.836	VV R	0.5074	4047.50415	94.26268	87.8395

4-Benzyl-2-methyl (1*S*,3a*R*,8b*R*)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2,4-dicarboxylate (3ad)

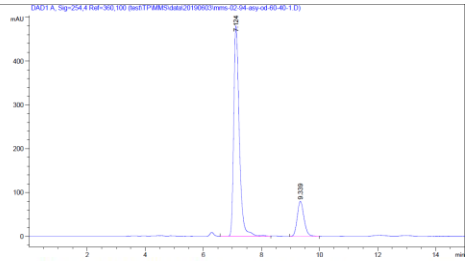


3ad

White solid, 97% yield; Mp: 217−219 °C; dr > 20:1; $[\alpha]^{20}_D$ = +164.4 (c = 0.7, $CHCl_3$) for 66% ee; due to the distinct presence of rotameric isomers, the ^{1}H NMR and ^{13}C NMR seemed complex, so we did not designate the data, but attached the spectrum behind; **IR** (KBr): 2953, 1740, 1610, 1558, 1481, 1338, 912, 754; **HRMS (ESI)**: Exact mass calcd for $C_{29}H_{23}N_3O_7$ $[M+Na]^+$: 548.1428, Found: 548.1433; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, 254 nm; Retention time: 7.12 min (major), 9.34 min (minor).



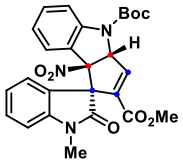
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.152	MM R	0.2171	5721.07764	439.11597	49.6754
2	9.357	BV R	0.2490	5795.83789	358.78265	50.3246



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.124	BB	0.1993	6306.02686	479.83893	83.0025
2	9.339	BB	0.2414	1291.36633	79.96312	16.9975

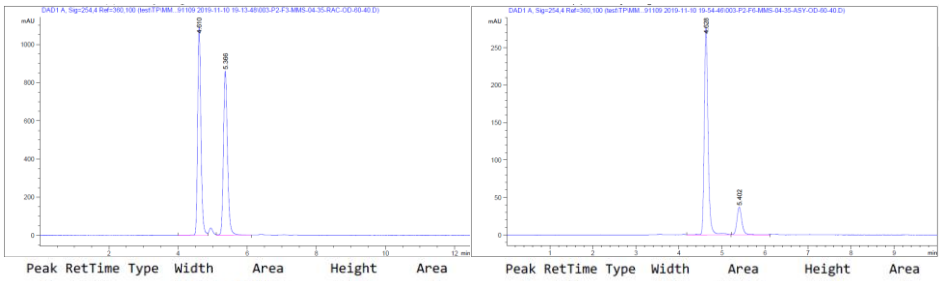
4-(*tert*-Butyl) 2-methyl (1*S*,3a*R*,8b*R*)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cycl

openta[*b*]indole-1,3'-indoline]-2,4-dicarboxylate (3ae)



3ae

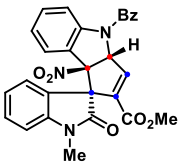
White solid, 81% yield; Mp: 221−222 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +101.0 (c = 1.0, $CHCl_3$) for 70% ee; due to the distinct presence of rotameric isomers, the ^1H NMR and ^{13}C NMR seemed complex, so we did not designate the data, but attached the spectrum behind; **IR** (KBr): 3161, 2976, 1718, 1647, 1552, 1377, 839, 754; **HRMS (ESI)**: Exact mass calcd for $C_{26}H_{25}N_3O_7$ $[M+Na]^+$: 514.1585, Found: 514.1587; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.63 min (major), (minor) 5.40 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.610	MM R	0.1105	7215.27100	1088.31616	50.6510
2	5.366	MM R	0.1362	7029.81104	859.97437	49.3490

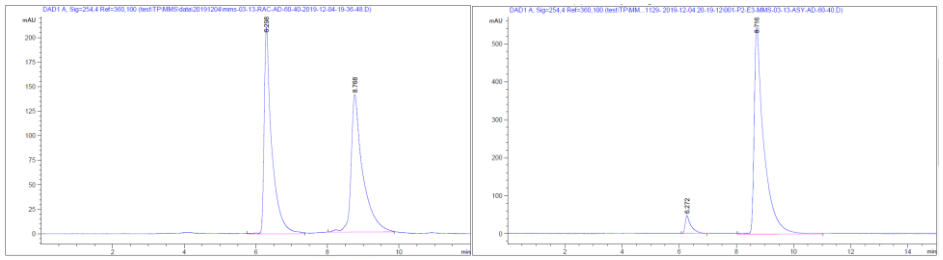
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.628	MM R	0.1023	1695.09961	276.17905	85.0873
2	5.402	MM R	0.1338	297.08798	36.99522	14.9127

Methyl (1*S*,3a*R*,8b*R*)-4-benzoyl-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3af)



3af

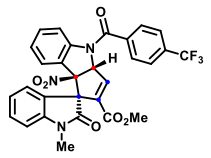
White solid, 97% yield; Mp: 134−136 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +143.6 (c = 1.0, $CHCl_3$) for 90% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.74−7.43 (m, 6H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.26−7.20 (s, br, 2H), 7.10−7.07 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 7.00−6.95 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.80 (s, 2H), 3.56 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.5, 161.6, 144.5, 141.7, 139.5, 137.7, 135.4, 132.2, 131.5, 130.7, 129.4, 129.3, 127.5, 126.5, 123.7, 122.9, 122.7, 115.9, 108.9, 103.2, 71.6, 63.8, 52.4, 27.2; **IR** (KBr): 2924, 1718, 1664, 1550, 1465, 1087, 860, 727; **HRMS (ESI)**: Exact mass calcd for $C_{28}H_{21}N_3O_6$ $[M+Na]^+$: 518.1323, Found: 518.1325; **HPLC**: Chiralpak AD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 8.72 min (major), 6.27 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.298	MM R	0.2449	3100.30396	210.96005	49.6204
2	8.768	MM R	0.3743	3147.73657	140.14383	50.3796

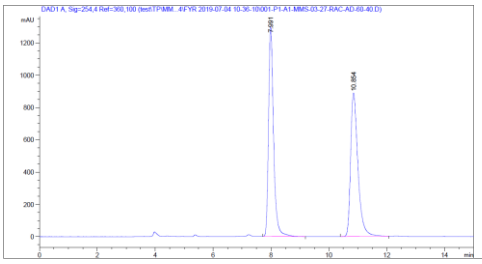
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.272	BV R	0.1977	682.95380	47.37153	5.0920
2	8.716	MM R	0.3901	1.27293e4	543.80426	94.9080

Methyl (1*S*,3a*R*,8b*R*)-1'-methyl-8b-nitro-2'-oxo-4-(4-(trifluoromethyl)benzoyl)-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ag)

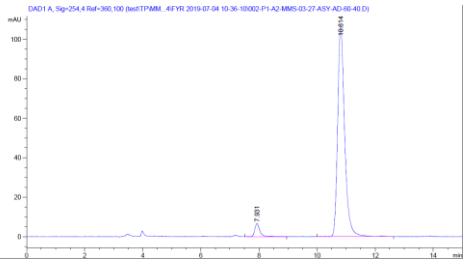


3ag

White solid, 95% yield; Mp: 210−211 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +114.17 (c = 1.0, $CHCl_3$) for 92% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.73 (s, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 2H), 7.13 (s, 2H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.80 (s, br, 1H), 3.57 (s, 3H), 3.39 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.3, 167.0, 161.5, 144.5, 141.3, 138.8, 138.0, 133.3 (q, *J* = 32.8 Hz, 1C), 132.4, 130.8, 129.6, 128.0, 126.4, 124.1, 123.6 (q, *J* = 264.9 Hz, 1C), 123.0, 122.7, 115.7, 112.4, 109.0, 103.1, 71.7, 63.9, 52.5, 27.3; **^{19}F NMR** (565 MHz, $CDCl_3$): δ -62.9; **IR** (KBr): 2956, 1718, 1653, 1477, 1377, 1064, 852, 750; **HRMS (ESI)**: Exact mass calcd for $C_{29}H_{20}F_3N_3O_6$ $[M+Na]^+$: 586.1196, Found: 586.1200; **HPLC**: Chiralpak AD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 10.81 min (major), 7.93 min (minor).

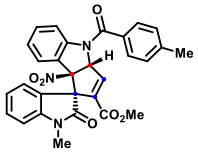


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.991	BV R	0.1802	1.55763e4	1296.58655	50.0585
2	10.854	BB	0.2641	1.55400e4	888.07910	49.9415



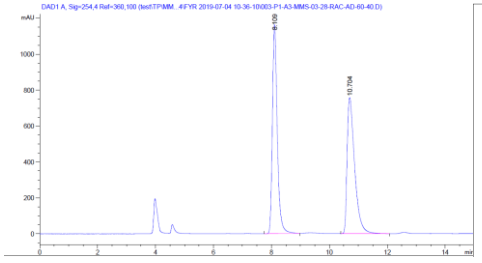
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.931	BB	0.1353	74.15450	6.56607	4.0701
2	10.814	BV R	0.2436	1747.76440	106.13998	95.9299

Methyl (1*S*,3a*R*,8b*R*)-1'-methyl-4-(4-methylbenzoyl)-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ah)

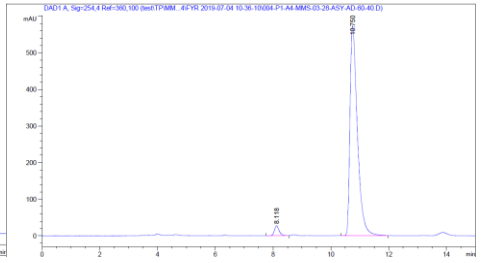


3ah

White solid, 95% yield; Mp: 230−231 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +153.1 (c = 1.0, $CHCl_3$) for 94% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.49 (s, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.27-7.20 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.7, 144.5, 142.0, 141.9, 139.7, 137.5, 132.5, 132.2, 130.6, 129.9, 129.4, 127.6, 126.5, 123.5, 122.9, 122.8, 122.7, 116.0, 108.9, 103.2, 71.7, 63.8, 52.4, 27.2, 21.8; **IR** (KBr): 3086, 2951, 1732, 1608, 1490, 1373, 752, 692; **HRMS (ESI)**: Exact mass calcd for $C_{29}H_{23}N_3O_6$ $[M+H]^+$: 510.1660, Found: 510.1662; **HPLC**: Chiralpak AD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 10.75 min (major), 8.12 min (minor).

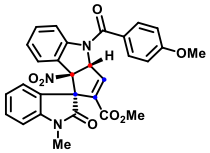


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.109	BB	0.1769	1.36153e4	1164.30481	49.9266
2	10.704	BV R	0.2684	1.36553e4	757.34302	50.0734



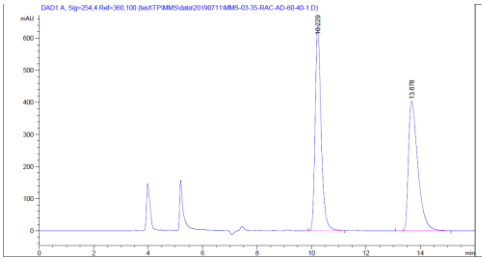
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.118	MM R	0.1916	311.22266	27.06552	2.9643
2	10.750	VB R	0.2605	1.01877e4	572.80731	97.0357

Methyl (1*S*,3a*R*,8b*R*)-4-(4-methoxybenzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ai)

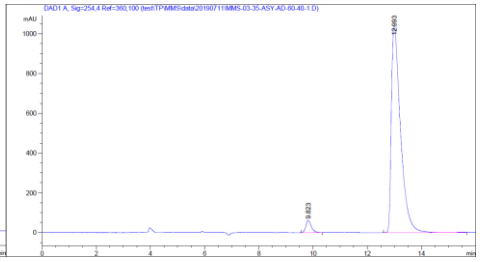


3ai

White solid, 97% yield; Mp: 188−189 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +130.4 (c = 1.0, $CHCl_3$) for 93% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26−7.22 (m, 2H), 7.17 (s, br, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.04−7.00 (m, 4H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.39 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.3, 162.2, 161.7, 144.5, 142.0, 139.8, 137.5, 132.1, 130.6, 129.8, 129.4, 127.3, 126.5, 123.3, 122.9, 122.8, 122.7, 115.9, 114.4, 108.9, 103.2, 71.8, 63.8, 55.6, 52.4, 27.2; **IR** (KBr): 2926, 1734, 1608, 1508, 1375, 840, 752, 418; **HRMS (ESI)**: Exact mass calcd for $C_{29}H_{23}N_3O_7$ [M+Na]$^+$: 548.1428, Found: 548.1443; **HPLC**: Chiralpak AD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 12.99 min (major), 9.82 min (minor).

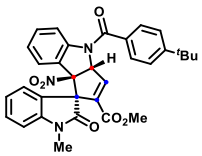


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.229	BV R	0.2310	9754.13770	639.20184	50.0951
2	13.678	VV R	0.3439	9717.11523	404.29648	49.9049



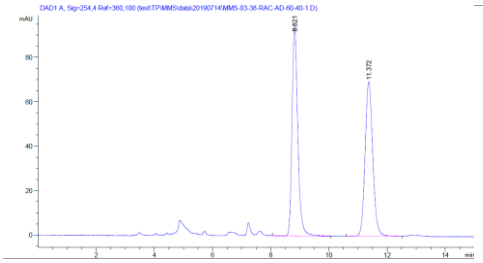
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.823	MM R	0.2381	870.52814	60.94473	3.4377
2	12.993	MM R	0.3921	2.44523e4	1039.50256	96.5623

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3aj)

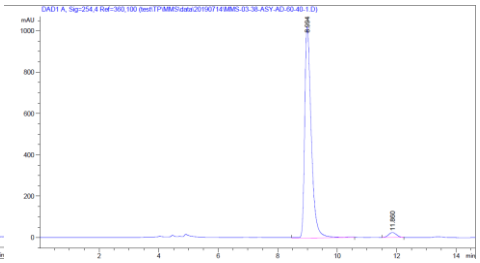


3aj

White solid, 93% yield; Mp: 121−123 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +191.7 (c = 1.0, $CHCl_3$) for 95% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 4H), 7.38−7.36 (m, 1H), 7.24−7.23 (m, 1H), 7.10−7.07 (m, 2H), 7.04−7.01 (m, 1H), 6.99−6.93 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.81 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 1.38 (s, 9H)c; **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.7, 155.1, 144.5, 141.9, 139.7, 137.5, 132.4, 132.2, 130.6, 129.4, 127.4, 126.5, 126.2, 123.5, 122.9, 122.8, 122.7, 116.3, 108.9, 103.3, 71.7, 63.8, 52.4, 35.2, 31.3, 27.2; **IR** (KBr): 2960, 1728, 1610, 1552, 1261, 1091, 846, 754; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{29}N_3O_6$ [M+Na]$^+$: 574.1949, Found: 574.1959; **HPLC:** Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 8.99 min (major), 11.86 min (minor).

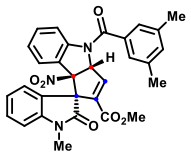


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.821	BV R	0.2002	1276.96924	94.45589	50.4213
2	11.372	VV R	0.2606	1255.63123	69.40676	49.5787



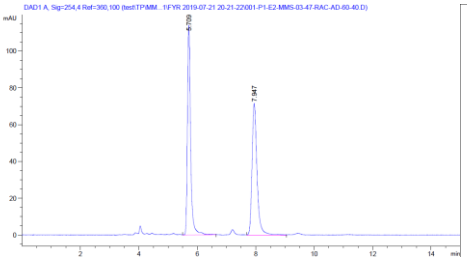
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.994	MM R	0.2554	1.56540e4	1021.40143	97.4028
2	11.860	MM R	0.2983	417.40707	23.32133	2.5972

Methyl (1*S*,3a*R*,8b*R*)-4-(3,5-dimethylbenzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ak)

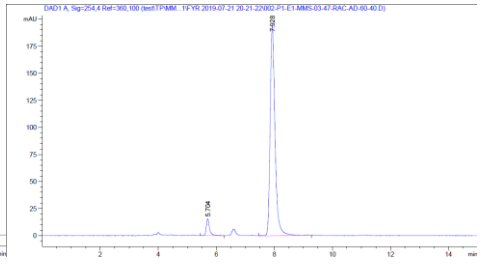


3ak

White solid, 92% yield; Mp: 195−197 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +89.4 (c = 1.0, $CHCl_3$) for 90% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.39−7.36 (m, 1H), 7.20−7.17 (m, 5H), 7.08−7.06 (m, 1H), 7.04−6.99 (m, 2H), 6.94 (d, *J* = 6.0 Hz, 1H), 6.82 (s, 2H), 3.57 (s, 3H), 3.40 (s, 3H), 2.38 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.9, 161.7, 144.4, 141.6, 139.6, 139.1, 137.4, 135.3, 133.0, 132.1, 130.6, 129.4, 126.5, 124.9, 123.5, 122.9, 122.7, 115.8, 108.9, 103.1, 71.4, 63.8, 52.4, 27.2, 21.4; **IR** (KBr): 2951, 1717, 1649, 1556, 1477, 1344, 858, 746; **HRMS (ESI)**: Exact mass **calcd for C30H25N3O6 [M+Na]+: 546.1636, Found: 546.1651; HPLC: Chiralpak AD-H (150 mm),** ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 7.93 min (major), 5.70 min (minor).

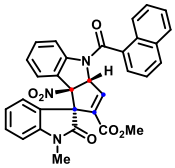


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.709	MM R	0.1263	864.15491	114.06258	50.2671
2	7.947	MM R	0.1988	854.97198	71.68508	49.7329



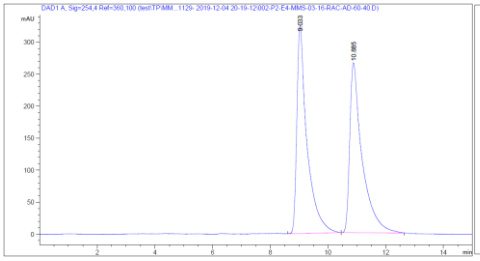
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.704	BB	0.1091	114.93204	15.48658	4.9231
2	7.928	BV R	0.1744	2219.63110	193.37520	95.0769

Methyl (1*S*,3a*R*,8b*R*)-4-(1-naphthoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3am)

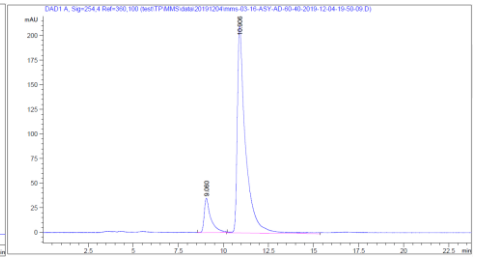


3am

White solid, 92% yield; Mp: 158−161 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +53.7 (c = 1.0, $CHCl_3$) for 77% ee; **^{1}H NMR** (600 MHz, DMSO-d_6, 100 °C): δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.81 (dd, *J* = 22.9, 7.6 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.60 (dt, *J* = 27.8, 7.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.26−7.23 (m, 1H), 7.18–7.01 (m, 4H), 6.97−6.95 (m, 1H), 6.74 (s, 2H), 3.50 (s, 3H), 3.29 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6, 100 °C): 171.3, 166.7, 160.6, 143.9, 140.8, 139.1, 136.4, 132.9, 132.8, 131.6, 130.0, 129.8, 128.44, 128.35, 128.2, 127.1, 126.4, 125.7, 125.1, 124.5, 123.5, 123.0, 122.8, 122.3, 121.9, 114.9, 108.4, 103.0, 70.6, 63.0, 51.6, 26.3; **IR** (KBr): 2961, 1716, 1647, 1550, 1428, 1228, 810, 744; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{23}N_3O_6$ $[M+Na]^+$: 568.1479, Found: 568.1491; **HPLC**: Chiralpak AD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 10.91 min (major), 9.06 min (minor).

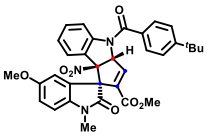


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.033	VV R	0.3409	7930.67188	324.77466	50.1664
2	10.885	VV R	0.3993	7878.05957	265.39502	49.8336



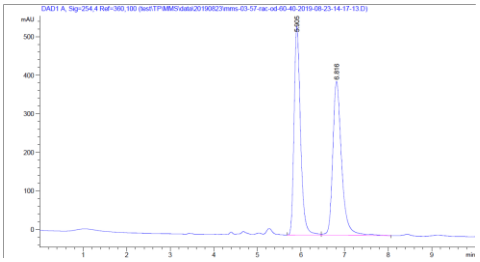
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.060	MM R	0.4163	870.43054	34.84621	11.4650
2	10.906	MM R	0.5340	6721.60596	209.77963	88.5350

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-5'-methoxy-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3bj)

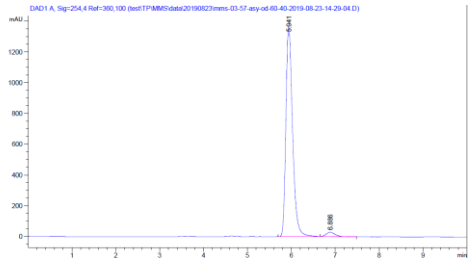


3bj

White solid, 94% yield; Mp: 228−229 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +101.3 (c = 1.0, $CHCl_3$) for 95% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 4H), 7.26−7.23 (m, 2H), 7.14−7.02 (m, 2H), 6.88−6.87 (m, 1H), 6.85−6.83 (m, 1H), 6.79 (s, 1H), 6.57 (s, 1H), 3.75 (s, 3H), 3.57 (s, 3H), 3.37 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.1, 168.7, 161.6, 155.9, 155.1, 141.8, 139.7, 137.9, 137.5, 132.4, 132.2, 129.4, 127.7, 127.4, 126.2, 123.5, 122.8, 116.0, 114.3, 110.6, 109.2, 103.3, 71.6, 64.2, 55.9, 52.4, 35.2, 31.3, 27.3; **IR** (KBr): 2960, 1726, 1664, 1496, 1428, 1375, 1099, 792; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_7$ [M+Na]$^+$: 604.2054, Found: 604.2054; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.94 min (major), 6.89 min (minor).

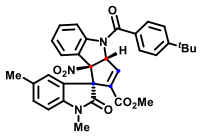


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.905	BV	0.1553	5560.54102	541.56433	49.7357
2	6.816	VB	0.2108	5619.64648	399.03342	50.2643



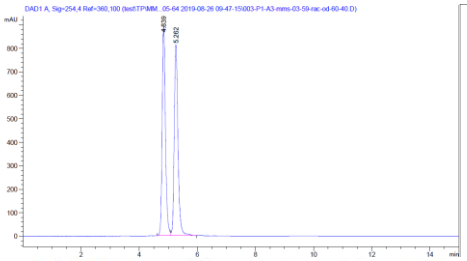
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.941	BV R	0.1626	1.44958e4	1367.98376	97.2573
2	6.886	VB E	0.1888	408.78815	28.68544	2.7427

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1',5'-dimethyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3cj)

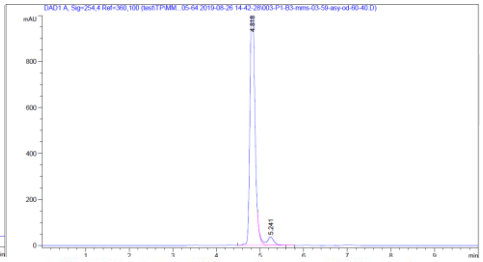


3cj

White solid, 78% yield; Mp: 113−115 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +102.2 (c = 1.0, $CHCl_3$) for 90% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.53 (s, 4H), 7.27 (s, 2H), 7.22−7.09 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.83−6.79 (m, 3H), 3.57 (s, 3H), 3.38 (s, 3H), 2.29 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.7, 155.2, 142.1, 139.6, 137.6, 132.5, 132.1, 131.0, 129.5, 127.5, 126.5, 126.2, 124.7, 124.2, 123.5, 123.0, 120.7, 115.9, 112.5, 108.6, 71.6, 63.9, 52.4, 35.2, 31.3, 27.3, 21.2; **IR** (KBr): 2953, 1728, 1662, 1575, 1477, 1099, 1086, 763; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_6$ [M+Na]$^+$: 588.2105, Found: 588.2108; **HPLC:** Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.82 min (major), 5.24 min (minor).

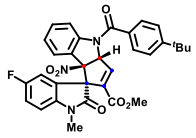


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.839	BV	0.1196	6994.42432	890.56030	49.1401
2	5.262	VV R	0.1364	7239.20801	812.52356	50.8599



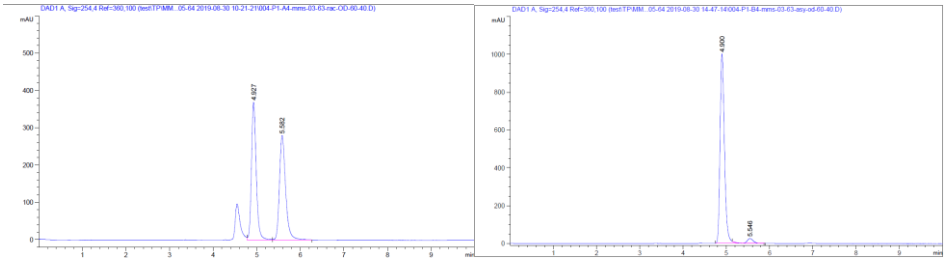
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.818	BV R	0.1143	8845.62598	1182.06836	95.2234
2	5.241	VV E	0.1709	443.71558	36.62048	4.7766

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-5'-fluoro-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[b]indole-1,3'-indoline]-2-carboxylate (3dj)



3dj

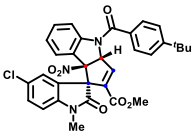
White solid, 88% yield; Mp: 147−150 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +96.7 (c = 1.0, $CHCl_3$) for 93% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56−7.54 (m, 5H), 7.26 (s, 2H), 7.10−7.07 (m, 3H), 6.88−6.85 (m, 1H), 6.78 (s, 1H), 6.75−6.74 (m, 1H), 3.58 (s, 3H), 3.38 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.2, 168.7, 161.6, 159.0 (d, *J* = 242.6 Hz, 1C), 155.2, 141.9, 140.6, 140.2, 137.2, 132.3, 129.2, 127.9 (d, *J* = 7.5 Hz, 1C), 127.4, 126.2, 123.6, 122.5, 117.0 (d, *J* = 22.5 Hz, 1C), 116.1, 111.2 (d, *J* = 25.5 Hz, 1C), 109.5 (d, *J* = 9.0 Hz, 1C), 103.2, 71.7, 64.1, 52.5, 35.2, 31.3, 27.4; **^{19}F NMR** (565 MHz, $CDCl_3$): δ -119.3; **IR** (KBr): 2956, 1720, 1651, 1548, 1375, 1109, 800, 756; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}FN_3O_6$ [M+Na]$^+$: 592.1854, Found: 592.1848; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.90 min (major), 5.55 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.927	VV	0.1147	2790.47412	369.15201	50.5274
2	5.582	VV R	0.1490	2732.21631	279.58188	49.4726

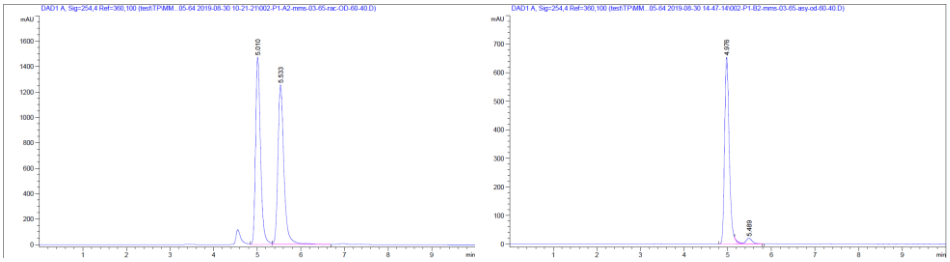
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.900	BV R	0.1080	7084.27197	1002.15887	96.3785
2	5.546	VV E	0.1513	266.19559	25.82393	3.6215

Methyl (1S,3aR,8bR)-4-(4-(tert-butyl)benzoyl)-5'-chloro-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4H-spiro[cyclopenta[b]indole-1,3'-indoline]-2-carboxylate (3ej)



3ej

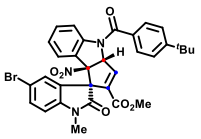
White solid, 99% yield; Mp: 147−149 °C; dr > 20:1; $[\alpha]^{20}_{D}$ = +106.53 (c = 1.0, $CHCl_3$) for 91% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (s, 5H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.26−7.23 (m, 2H), 7.10−7.07 (m, 2H), 6.95 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.79 (s, 1H), 3.58 (s, 3H), 3.38 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.0, 168.7, 161.6, 155.2, 143.1, 141.9, 140.2, 137.1, 132.4, 132.2, 130.6, 129.3, 128.2, 127.4, 126.2, 123.5, 123.2, 122.5, 116.1, 109.8, 103.2, 71.6, 63.8, 52.5, 35.2, 31.3, 27.4; **IR** (KBr): 2956, 1732, 1608, 1476, 1377, 1099, 810, 754; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}{}^{35}ClN_3O_6$ [M+H]$^+$: 586.1739, Found: 586.1741; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.98 min (major), 5.49 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.010	VV	0.1206	1.16336e4	1473.12158	49.1268
2	5.533	VV R	0.1469	1.20472e4	1255.35754	50.8732

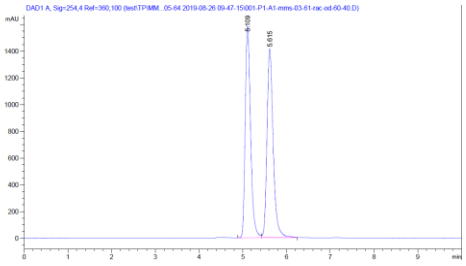
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.976	BV R	0.1140	4874.24756	653.61279	95.6516
2	5.489	VV E	0.1563	221.58681	20.31476	4.3484

Methyl (1*S*,3a*R*,8b*R*)-5'-bromo-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3fj)

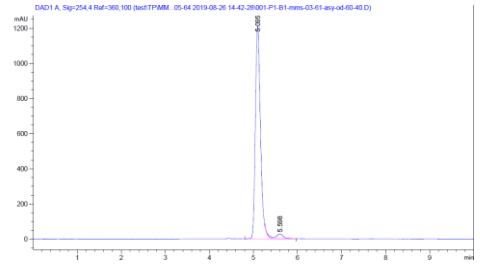


3fj

White solid, 85% yield; Mp: 134−136 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +143.5 (c = 1.0, $CHCl_3$) for 93% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54−7.53 (m, 5H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.36−7.20 (m, 2H), 7.14−6.98 (m, 3H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.79 (s, 1H), 3.58 (s, 3H), 3.38 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 171.9, 168.7, 161.5, 155.2, 143.6, 141.9, 140.1, 137.1, 133.5, 132.3, 132.2, 130.1, 129.2, 128.5, 127.4, 126.2, 125.8, 123.5, 122.5, 115.3, 110.3, 103.2, 71.6, 63.7, 52.5, 35.2, 31.3, 27.3; **IR** (KBr): 2956, 1732, 1608, 11479, 1234, 1097, 810, 750; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}{}^{79}BrN_3O_6$ $[M+Na]^+$: 652.1054, Found: 652.1060; **HPLC:** Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.10 min (major), 5.60 min (minor).

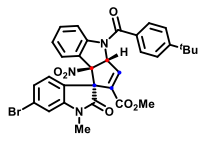


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.109	MM R	0.1414	1.34576e4	1585.92029	49.2264
2	5.615	MM R	0.1638	1.38806e4	1412.47827	50.7736



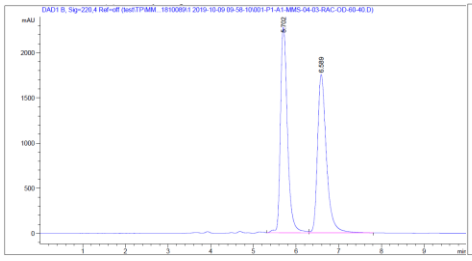
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.095	BV R	0.1227	9782.86328	1212.16626	96.4379
2	5.598	VB E	0.1831	361.35162	27.44358	3.5621

Methyl (1*S*,3a*R*,8b*R*)-6'-bromo-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3gj)

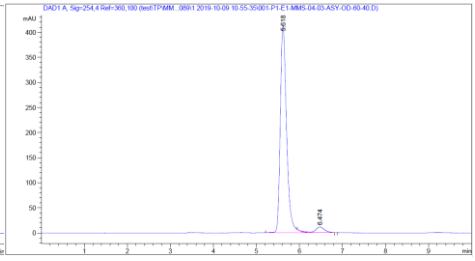


3gj

White solid, 80% yield; Mp: 250−251 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +94.9 (c = 1.0, $CHCl_3$) for 92% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53 (s, 5H), 7.26 (s, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.08 (s, 3H), 6.91−6.82 (m, 1H), 6.77 (s, 1H), 3.58 (s, 3H), 3.38 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.2, 168.7, 161.6, 155.2, 145.7, 141.9, 140.1, 137.1, 132.32, 132.25, 129.3, 127.4, 126.2, 125.7, 125.5, 124.5, 123.9, 123.6, 122.5, 116.0, 112.5, 103.1, 71.6, 63.6, 52.5, 35.2, 31.3, 27.3; **IR** (KBr): 2953, 1728, 1602, 1552, 1373, 977, 750, 509; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}{}^{79}BrN_3O_6$ $[M+Na]^+$: 652.1054, Found: 652.1043; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.62 min (major), 6.47 min (minor).

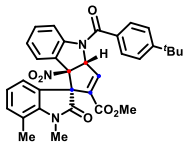


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.702	VV R	0.1427	2.58673e4	2275.17676	50.5019
2	6.589	VB	0.2077	2.53531e4	1753.43677	49.4981



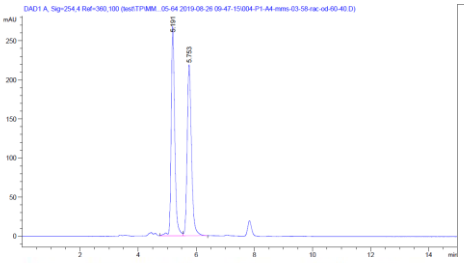
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.618	VV R	0.1528	4188.28711	413.04977	96.0469
2	6.474	VV E	0.1818	172.38066	11.31202	3.9531

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1',7'-dimethyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3hj)

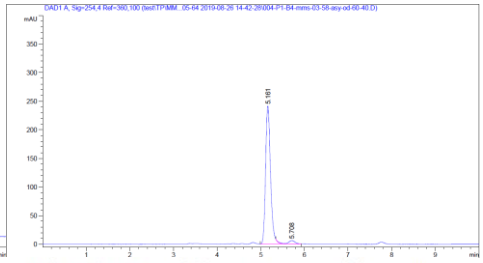


3hj

White solid, 96% yield; Mp: 226−228 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +84.0 (c = 1.0, $CHCl_3$) for 93% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 4H), 7.26−7.24 (m, 2H), 7.09 (d, *J* = 7.4 Hz, 3H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.78 (s, 2H), 3.66 (s, 3H), 3.58 (s, 3H), 2.63 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 173.2, 168.7, 161.7, 155.1, 142.3, 139.4, 137.8, 134.5, 132.4, 132.2, 129.4, 127.4, 127.0, 126.2, 125.6, 123.5, 122.9, 122.7, 120.6, 120.5, 116.7, 104.1, 71.6, 63.4, 52.4, 35.2, 31.4, 30.6, 19.3; **IR** (KBr): 2960, 1716, 1653, 1508, 1458, 1112, 848, 765; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_6$ $[M+Na]^+$: 588.2105, Found: 588.2108; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.16 min (major), 5.71 min (minor).

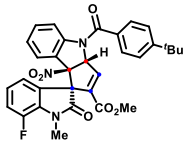


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.191	VV R	0.1288	2285.69214	267.70993	50.4149
2	5.753	VB	0.1573	2248.06763	218.91252	49.5851



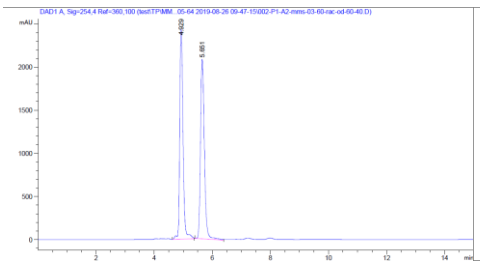
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.161	BV R	0.1206	1901.68970	240.92085	96.6711
2	5.708	VB E	0.1361	65.48445	5.76191	3.3289

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-7'-fluoro-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ij)

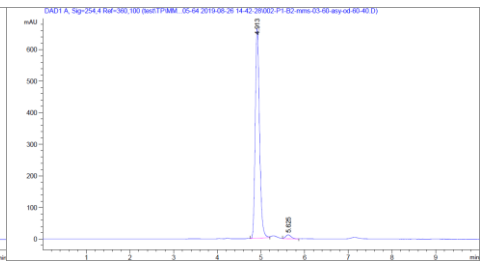


3ij

White solid, 86% yield; Mp: 259−260 °C; dr > 20:1; $[\alpha]^{20}_{D}$ = +87.5 (c = 1.0, $CHCl_3$) 95% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55−7.53 (m, 5H), 7.24 (s, 2H), 7.16−7.03 (m, 3H), 6.98−6.94 (m, 1H), 6.78 (s, 2H), 3.59 (d, *J* = 7.6 Hz, 6H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.1, 168.7, 161.6, 155.2, 147.8 (d, *J* = 245.2 Hz, 1C), 141.9, 140.0, 137.4, 132.3, 131.3 (d, *J* = 8.7 Hz, 1C), 130.2, 129.3, 127.4, 126.2, 125.6, 123.6, 123.5 (d, *J* = 6.5 Hz, 1C), 122.6, 118.7 (d, *J* = 19.6 Hz, 1C), 118.5 (d, *J* = 3.3 Hz, 1C), 116.2, 103.3, 71.6, 63.9, 52.5, 35.2, 31.3, 29.7 (d, *J* = 6.0 Hz, 1C); **^{19}F NMR** (565 MHz, $CDCl_3$): δ -135.1; **IR** (KBr): 2962, 1728, 1653, 1344, 1114, 1060, 833, 767; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}FN_3O_6$ $[M+Na]^+$: 592.1854, Found: 592.1861; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.91 min (major), 5.63 min (minor).

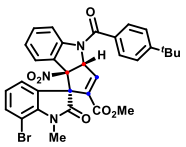


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.929	MV R	0.1202	1.92164e4	2430.93408	49.7776
2	5.651	MM R	0.1552	1.93881e4	2082.33911	50.2224



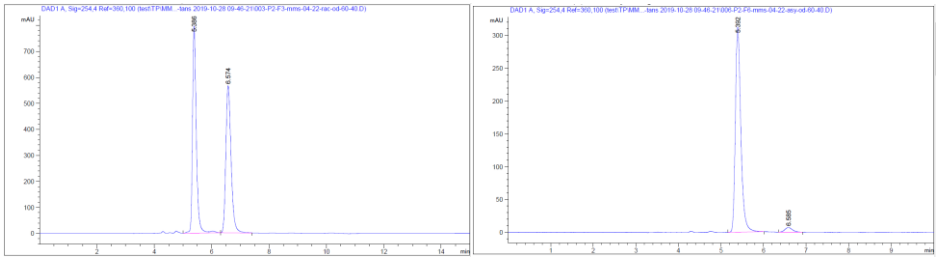
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.913	MM R	0.1135	4514.69922	662.67609	97.5632
2	5.625	MM R	0.1524	112.76258	12.32959	2.4368

Methyl (1*S*,3a*R*,8b*R*)-7'-bromo-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3jj)



3jj

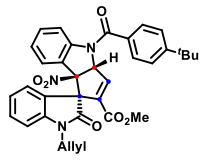
White solid, 93% yield; Mp: 118−120 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +108.0 (c = 1.0, $CHCl_3$) for 94% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53−7.48 (m, 5H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27−7.16 (m, 3H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89−6.85 (m, 2H), 6.78 (s, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 173.0, 168.7, 161.6, 157.6, 155.2, 142.0, 140.0, 137.4, 136.3, 132.3, 130.2, 129.5, 129.3, 127.5 , 126.2, 125.6, 123.9, 123.6, 122.6, 121.7, 116.3, 103.2, 71.6, 63.6, 52.6, 35.2, 31.3, 30.9; **IR** (KBr): 2954, 1732, 1604, 1479, 1294, 999, 759, 686; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}{}^{79}BrN_3O_6$ $[M+Na]^+$: 652.1054, Found: 652.1055; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.39 min (major), 6.59 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.386	BV R	0.1400	7371.61377	795.27454	50.8813
2	6.574	BV R	0.1928	7116.24902	565.72205	49.1187

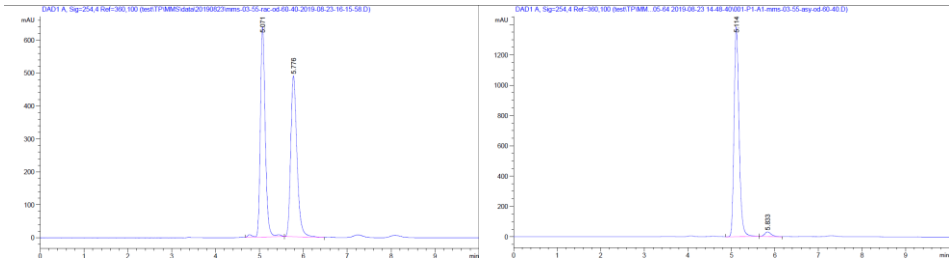
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.392	VV R	0.1365	2792.17725	311.80920	97.0448
2	6.585	VV R	0.1478	85.02822	6.92415	2.9552

Methyl (1*S*,3a*R*,8b*R*)-1'-allyl-4-(4-(*tert*-butyl)benzoyl)-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3kj)



3kj

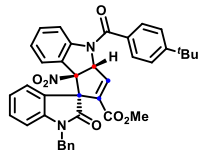
White solid, 92% yield; Mp: 188−190 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +131.3 (c = 1.0, $CHCl_3$) for 94% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57−7.54 (m, 5H), 7.34−7.32 (m, 2H), 7.26−7.23 (m, 2H), 7.09−7.06 (m, 2H), 7.03−7.00 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.81 (s, 1H), 6.02−5.96 (m, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 15.7 Hz, 1H), 4.36 (d, *J* = 14.7 Hz, 1H), 3.56 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.1, 168.7, 161.6, 155.1, 143.7, 141.9, 139.8, 137.5, 132.4, 132.2, 131.2, 130.5, 130.1, 129.4, 127.4, 126.4, 126.2, 125.5, 123.5, 122.8, 122.7, 117.6, 109.8, 103.4, 71.6, 63.8, 52.4, 43.0, 35.2, 31.3; **IR** (KBr): 2955, 2368, 1718, 1647, 1554, 1361, 810, 752; **HRMS (ESI)**: Exact mass calcd for $C_{34}H_{31}N_3O_6$ $[M+Na]^+$: 600.2105, Found: 600.2120; **HPLC:** Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.11 min (major), 5.83 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.071	VV R	0.1161	4954.54443	637.38873	50.5306
2	5.776	BB	0.1529	4850.49316	488.17291	49.4694

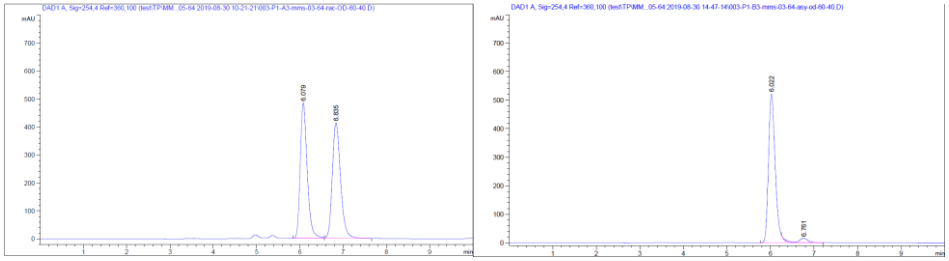
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.114	MM R	0.1327	1.10132e4	1383.69409	97.1301
2	5.833	MM R	0.1798	325.40161	30.15956	2.8699

Methyl (1*S*,3a*R*,8b*R*)-1'-benzyl-4-(4-(*tert*-butyl)benzoyl)-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3mj)



3mj

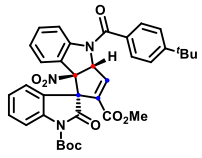
White solid, 95% yield; Mp: 189−191 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +62.7 (c = 1.0, $CHCl_3$) for 91% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54−7.51 (m, 7H), 7.42−7.39 (m, 2H), 7.34−7.31 (m, 1H), 7.26−7.24 (m, 3H), 7.24−7.23 (m, 1H), 7.03−6.99 (m, 3H), 6.81 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.28 (d, *J* = 16.0 Hz, 1H), 4.95 (d, *J* = 16.0 Hz, 1H), 3.53 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.7, 155.2, 143.8, 139.9, 137.5, 135.6, 132.4, 132.2, 130.6, 129.5, 129.0, 127.8, 127.5, 127.3, 126.4, 126.2, 123.6, 122.9, 122.8, 116.1, 110.0, 103.6, 71.6, 63.8, 52.4, 44.7, 35.2, 31.4; **IR** (KBr): 2963, 1716, 1556, 1377, 1222, 1014, 752, 696; **HRMS (ESI)**: Exact mass calcd for $C_{38}H_{33}N_3O_6$ [M+Na]$^+$: 650.2262, Found: 650.2278; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 6.02 min (major), 6.76 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.079	BV	0.1715	5416.93701	484.25214	49.8256
2	6.835	VV R	0.2006	5454.86182	412.87973	50.1744

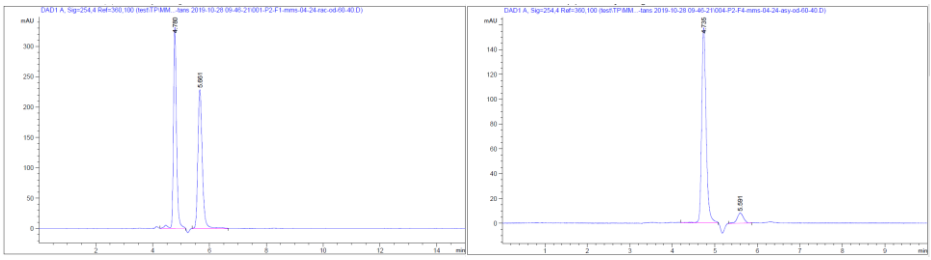
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.022	BV R	0.1654	5606.10889	521.68719	95.5621
2	6.761	VB E	0.2052	260.34900	15.52392	4.4379

1'-(*tert*-Butyl) 2-methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-1',2-dicarboxylate (3nj)



3nj

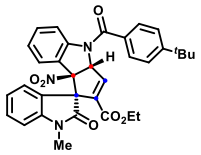
White solid, 88% yield; Mp: 158−160 °C; dr > 20:1; $[\alpha]^{20}_{D}$ = +63.2 (c = 1.0, $CHCl_3$) for 86% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 4H), 7.40 (td, *J* = 7.9, 1.3 Hz, 1H), 7.26−7.14 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.06−6.84 (m, 2H), 6.78 (s, 1H), 3.58 (s, 3H), 1.69 (s, 9H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 170.8, 168.7, 161.6, 155.3, 148.9, 142.4, 140.5, 140.1, 137.3, 132.3, 130.9, 129.4, 127.5, 126.2, 125.1, 124.7, 123.7, 122.9, 122.6, 115.6, 104.1, 84.9, 71.6, 64.9, 52.6, 35.3, 31.4, 28.3; **IR** (KBr): 2966, 2256, 1732, 1556, 1340, 1149, 842, 729; **HRMS (ESI)**: Exact mass calcd for $C_{36}H_{35}N_3O_8$ [M+Na]$^+$: 660.2316, Found: 660.2318; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.74 min (major), 5.59 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.780	MM R	0.1251	2488.30640	331.52731	50.4912
2	5.661	MM R	0.1778	2439.89478	228.70132	49.5088

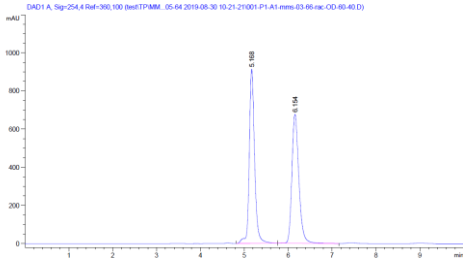
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.735	MM R	0.1196	1127.49841	157.15485	92.9306
2	5.591	MM R	0.1718	85.77029	8.32011	7.0694

Ethyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3pj)

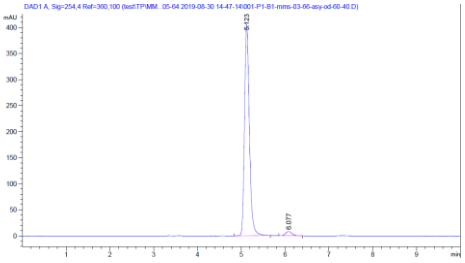


3pj

White solid, 98% yield; Mp: 196−197 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +135.4 (c = 1.0, $CHCl_3$) for 95% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.59−7.54 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26−7.24 (m, 3H), 7.10−7.07 (m, 1H), 7.03−6.98 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 3.99-3.95 (m, 2H), 3.39 (s, 3H), 1.39 (s, 9H), 1.08 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.1, 155.1, 144.4, 139.6, 137.8, 132.4, 132.1, 130.6, 129.3, 127.4, 126.6, 126.1, 123.4, 122.8, 122.7, 116.0, 108.7, 103.4, 71.6, 63.8, 61.5, 35.2, 31.3, 27.1, 13.9; **IR** (KBr): 2964, 1718, 1647, 1473, 1220, 893, 748, 542; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_6$ $[M+H]^+$: 566.2286, Found: 566.2294; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.12 min (major), 6.08 min (minor).

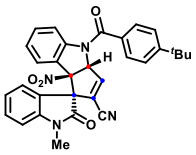


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.168	VB R	0.1263	7708.83057	912.64709	50.9300
2	6.154	VV R	0.1686	7427.29053	676.27496	49.0700



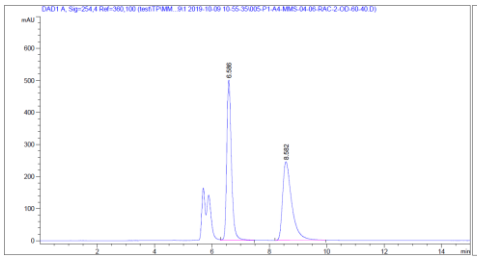
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.123	VV R	0.1177	3131.97144	405.26535	97.3651
2	6.077	BV R	0.1241	84.75721	8.19862	2.6349

(1*S*,3a*R*,8b*R*)-4-(4-(*tert*-Butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carbonitrile (3qj)

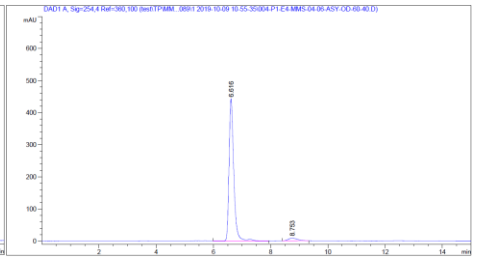


3qj

White solid, 85% yield; Mp: 209−211 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +105.3 (c = 1.0, $CHCl_3$) for 93% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53−7.51 (m, 5H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.26−7.24 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.77 (s, 1H), 3.36 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 170.4, 168.7, 155.5, 145.0, 143.9, 142.0, 132.4, 131.9, 131.7, 128.8, 127.5, 126.2, 124.0, 123.7, 123.5, 122.1, 120.7, 118.7, 115.8, 112.1, 109.5, 102.6, 72.2, 66.3, 35.3, 31.3, 27.3; **IR** (KBr): 2953, 1726, 1558, 1471, 1217, 756, 680, 561; **HRMS (ESI)**: Exact mass calcd for $C_{31}H_{26}N_4O_4$ $[M+Na]^+$: 541.1846, Found: 541.1846; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 6.62 min (major), 8.75 min (minor).

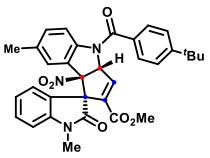


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.586	VV R	0.1730	5610.09717	499.53864	50.8491
2	8.582	BV R	0.3262	5422.72852	245.04048	49.1509



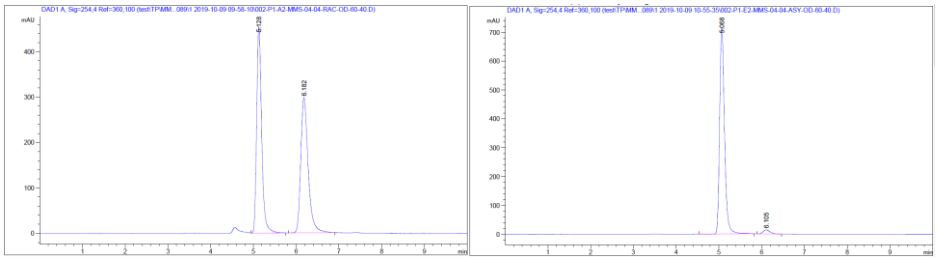
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.616	MM R	0.1919	5103.64258	443.34955	96.4946
2	8.753	BV R	0.2653	185.40294	8.26226	3.5054

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1',7-dimethyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3an)



3an

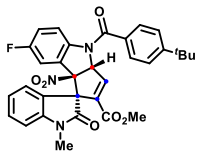
White solid, 88% yield; Mp: 197−199 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +104.4 (c = 1.0, $CHCl_3$) for 94% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.52 (s, 4H), 7.39−7.33 (m, 2H), 7.27 (s, 2H), 7.00−7.02 (m, 3H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.78 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 2.31 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.3, 168.4, 161.7, 154.9, 144.4, 139.8, 137.5, 133.3, 133.0, 132.4, 130.6, 130.1, 129.4, 127.4, 126.5, 126.1, 125.5, 122.8, 122.6, 115.9, 108.8, 103.3, 71.7, 63.7, 52.3, 35.2, 31.3, 27.2, 21.1; **IR** (KBr): 2954, 1728, 1532, 1489, 1238, 1114, 765, 540; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_6$ [M+Na]$^+$: 588.2105, Found: 588.2098; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.07 min (major), 6.11 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.128	VV R	0.1243	3691.88721	454.17642	50.8597
2	6.182	VV R	0.1830	3567.06982	297.28378	49.1403

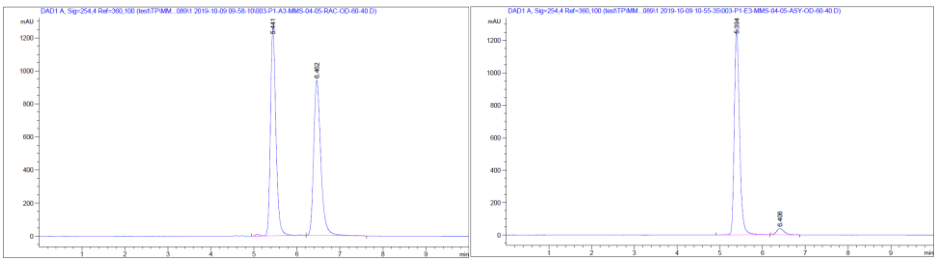
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.068	MM R	0.1317	5644.67920	714.57031	97.2220
2	6.105	BV R	0.1546	161.28787	14.13742	2.7780

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-7-fluoro-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ap)



3ap

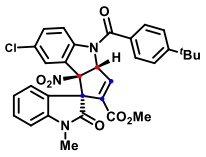
White solid, 96% yield; Mp: 264−265 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +125.8 (c = 1.0, $CHCl_3$) for 92% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55 (s, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29−7.26 (m, 1H), 7.02 (t, *J* = 7.0 Hz, 3H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.79 (s, 2H), 3.56 (s, 3H), 3.40 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.1, 168.4, 161.5, 158.5 (d, *J* = 244.1 Hz, 1C), 155.2, 144.4, 139.4, 137.6, 132.2, 130.8, 130.1, 127.3, 126.3, 126.0, 125.5, 124.2, 122.9, 122.7, 119.5 (d, *J* = 23.9 Hz, 1C), 116.2 (d, *J* = 25.8 Hz, 1C), 109.0, 102.9, 72.1, 63.8, 52.5, 35.2, 31.3, 27.2; **^{19}F NMR** (565 MHz, $CDCl_3$): δ -117.6; **IR** (KBr): 2956, 1732, 1558, 1340, 1234, 941, 846, 752; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}FN_3O_6$ [M+Na]$^+$: 592.1854, Found: 592.1843; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.39 min (major), 6.41 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.441	VV R	0.1350	1.11589e4	1252.88867	50.8655
2	6.462	BV R	0.1752	1.07792e4	939.97791	49.1345

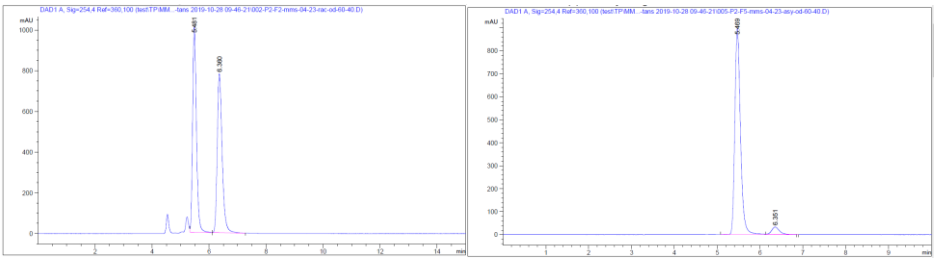
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.394	VV R	0.1297	1.07862e4	1274.92517	95.8880
2	6.406	BV R	0.1803	462.54358	37.79924	4.1120

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-7-chloro-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3aq)



3aq

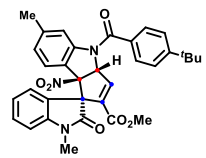
White solid, 92% yield; Mp: 152−154 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +80.2 (c = 1.0, $CHCl_3$) for 90% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54−7.53 (m, 5H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.27−7.21 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.99−6.93 (m, 2H), 6.78 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 1.38 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.1, 168.5, 161.5, 155.4, 144.4, 140.7, 139.3, 137.7, 132.3, 130.8, 129.2, 128.7, 128.3, 127.4, 126.2, 126.0, 125.4, 124.2, 122.9, 122.7, 109.0, 102.7, 72.0, 63.9, 52.4, 35.2, 31.3, 27.2; **IR** (KBr): 2956, 1724, 1653, 1473, 1371, 1114, 916, 732; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}{}^{35}ClN_3O_6$ $[M+Na]^+$: 608.1559, Found: 608.1556; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.47 min (major), 6.35 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.481	MM R	0.1546	9339.06641	1007.03912	49.9513
2	6.360	BV R	0.1834	9357.25879	780.46948	50.0487

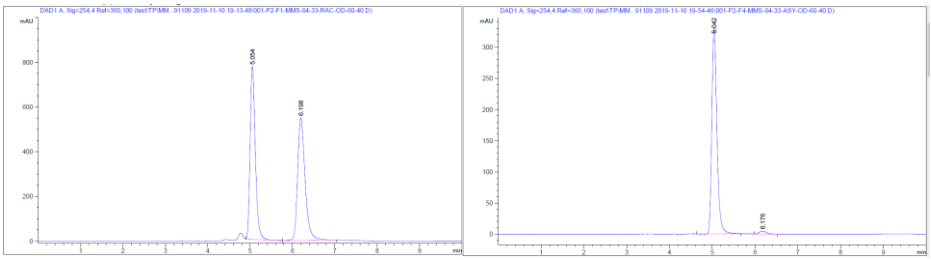
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.469	VV R	0.1406	8265.41406	895.04285	95.2308
2	6.351	VV E	0.1730	413.93549	32.30494	4.7692

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1',6-dimethyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3ar)



3ar

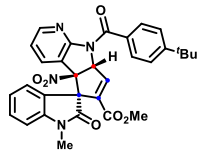
White solid, 85% yield; Mp: 240−241 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +108.6 (c = 1.0, $CHCl_3$) for 96% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55−7.54 (m, 4H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (s, br, 1H), 7.14 (s, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.91 (d, *J* = 12.0 Hz, 2H), 6.79 (s, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 2.17 (s, br, 3H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.7, 161.7, 155.0, 144.5, 143.0, 142.0, 139.8, 137.5, 132.6, 130.6, 128.9, 127.3, 126.6, 126.1, 124.7, 122.8, 122.7, 120.1, 116.8, 108.9, 103.7, 71.9, 63.6, 52.4, 35.2, 31.4, 27.2, 22.0; **IR** (KBr): 2958, 1732, 1610, 1496, 1261, 1111, 798, 732; **HRMS (ESI)**: Exact mass calcd for $C_{33}H_{31}N_3O_6$ $[M+Na]^+$: 588.2105, Found: 588.2099; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.04 min (major), 6.18 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.054	MM R	0.1427	6628.83887	774.20508	49.5953
2	6.198	BV R	0.1866	6737.01172	549.21967	50.4047

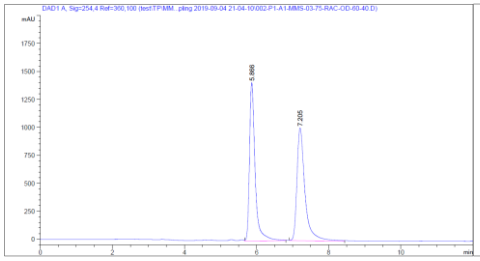
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.042	MM R	0.1382	2737.45361	330.08282	98.0238
2	6.176	BV R	0.1397	55.18769	4.70954	1.9762

Methyl (4b*R*,5*S*,7a*R*)-8-(4-(*tert*-butyl)benzoyl)-1'-methyl-4b-nitro-2'-oxo-4b,7a-dihydro-8*H*-spiro[cyclopenta[4,5]pyrrolo[2,3-*b*]pyridine-5,3'-indoline]-6-carboxylate (3as)

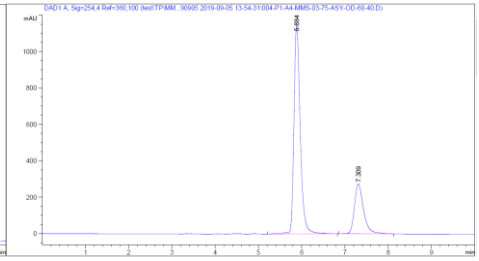


3as

White solid, 76% yield; Mp: 214−215 °C; dr > 20:1; $[\alpha]^{25}_{D}$ = +47.1 (c = 1.0, $CHCl_3$) for 48% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.60−7.54 (m, 2H), 7.44−7.42 (m, 2H), 7.41−7.38 (m, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.10−7.05 (m, 2H), 6.98 (dd, *J* = 7.9, 4.9 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 3.59 (s, 3H), 3.39 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.5, 168.8, 161.7, 155.3, 153.8, 151.6, 144.3, 139.9, 138.6, 137.8, 131.7, 130.8, 129.1, 126.1, 124.9, 123.2, 123.1, 118.7, 116.5, 109.0, 100.8, 70.0, 63.9, 52.5, 35.2, 31.3, 27.2; **IR** (KBr): 2926, 1718, 1647, 1508, 1255, 1174, 840, 752; **HRMS (ESI)**: Exact mass calcd for $C_{31}H_{28}N_4O_6$ $[M+Na]^+$: 575.1901, Found: 575.1915; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.88 min (major), 7.31 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.866	VV R	0.1818	1.54592e4	1417.45483	49.8018
2	7.205	VV R	0.2578	1.55822e4	1007.57404	50.1982



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.884	VV R	0.1528	1.15367e4	1144.52258	74.1809
2	7.309	VV R	0.2215	4015.40649	273.95163	25.8191

5. More studies on the reaction partners with isatin-derived MBH-carbonate

When we tried to expand the scope of 3-nitroindole **2**, we found that replacing the nitro group with ester and cyano-group or using 3-nitropyrrole led to no annulation product, which indicated that both nitro and indole were necessary to success of this annulation reaction (Fig. S1).

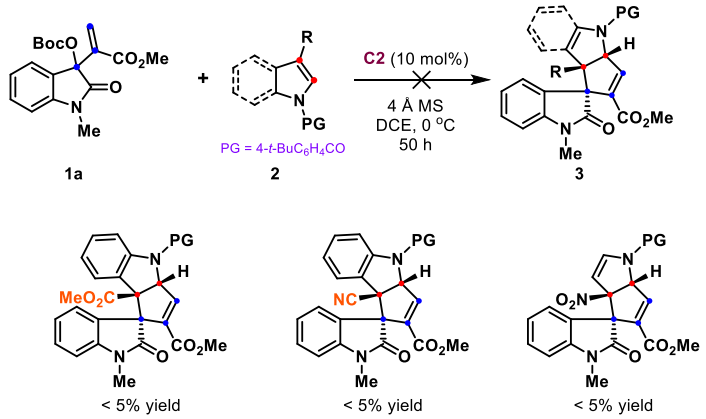
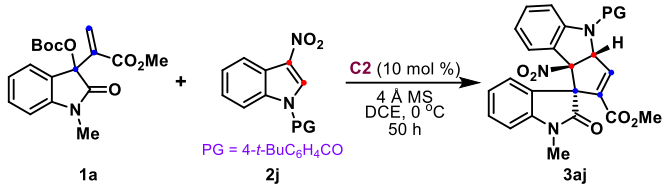


Figure S1. More Studies on Reaction Partners with Isatin-Derived MBH-Carbonates

6. Gram-scale experiment



1a
1.04 g
3.0 mmol

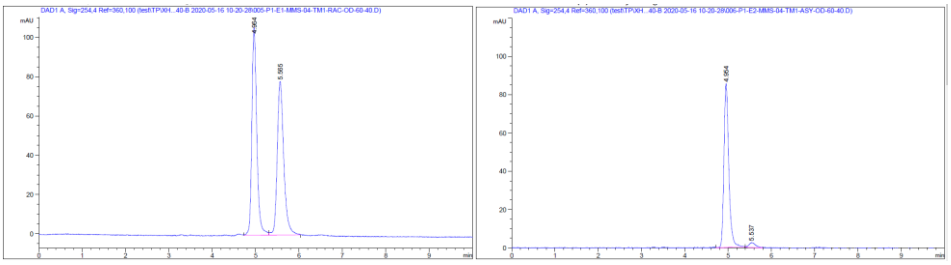
2j
1.06 g
3.3 mmol

3aj
1.39 g, dr > 20:1
84% yield, 92% ee
(after recrystallization, 99% ee)

According to general procedure, a dried Schlenk flask was charged with DMAP-thiourea **C2** (197 mg, 0.3 mmol, 0.1 equiv), MBH carbonate **1a** (1.04 g, 3.0 mmol, 1.0 equiv), 3-nitro-1H-indole **2j** (1.06 g, 3.3 mmol, 1.1 equiv) and 4 Å molecular sieves (300 mg) and dry DCE (20.0 mL). Then the mixture was stirred at 0 °C for 50 h. After the reaction was completed (monitored by TLC, EtOAc / petroleum ether (PE)), the residue was purified by silica gel column chromatography (EtOAc / PE = 4:1, v/v) to give pure products **3aj**.

Methyl (1*S*,3a*R*,8b*R*)-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-8b-nitro-2'-oxo-3a,8b-dihydro-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (3aj)

White solid, 1.39 g, 84% yield. $[\alpha]^{25}_{D}$ = +140.0 (c = 1.0, $CHCl_3$) for 92% ee. **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.95 min (major), 5.54 min (minor).

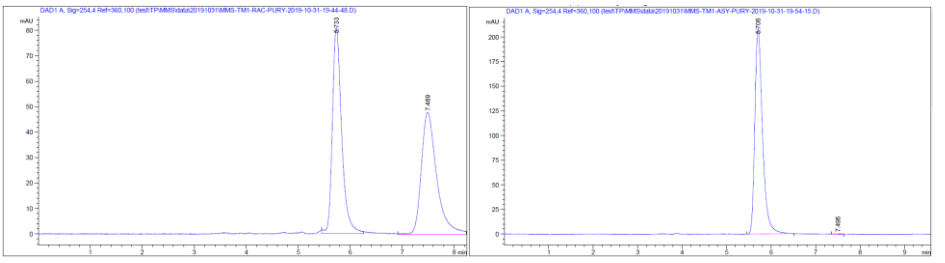


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.964	BV R	0.1173	835.52649	105.63882	50.7562
2	5.565	VV R	0.1474	810.63129	78.21315	49.2438

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.954	MM R	0.1301	667.96930	85.55009	96.1982
2	5.537	MM R	0.1749	26.39880	2.51597	3.8018

After a single recrystallization:

White solid, 50% yield. $[\alpha]^{25}_{D}$ = +171.2 (c = 1.0, $CHCl_3$) for 99% ee. **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.71 min (major), 7.50 min (minor).

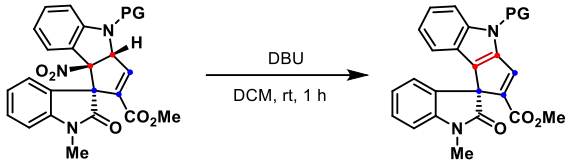


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.733	MM R	0.2062	1000.37817	80.84561	50.4260
2	7.489	MM R	0.3422	983.47461	47.90281	49.5740

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.706	BV R	0.1787	2506.81128	208.55397	99.6142
2	7.495	MM R	0.2166	9.70949	7.47225e-1	0.3858

7. Transformations of product

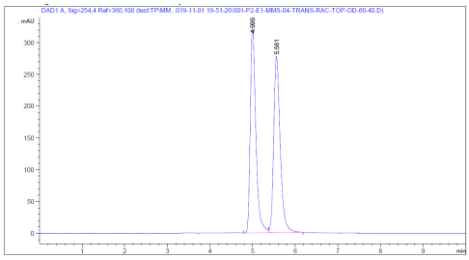
Methyl (*R*)-4-(4-(*tert*-butyl)benzoyl)-1'-methyl-2'-oxo-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (4aj)



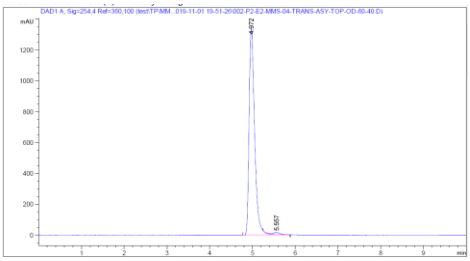
3aj
0.1 mmol
99% ee, dr > 20:1

4aj
(87% yield, 97% ee)

To a solution of **3aj** (55.1 mg, 0.1 mmol, 1 equiv) in CH_2Cl_2 (2.0 mL), DBU (30.4 mg, 0.2 mmol, 2 equiv) was added at room temperature. The solution was stirred for 1 h. After the reaction was completed, product **4aj** was obtained by flash chromatography on silica gel (petroleum ether / ethyl acetate = 5:1, v/v). White solid, 87% yield; Mp: 262−263 °C; $[\alpha]^{25}_D$ = -8.6 (c = 1.0, $CHCl_3$) for 97% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29−7.26 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.87−6.86 (m, 2H), 6.73 (d, *J* = 7.4 Hz, 1H), 3.55 (s, 3H), 3.43 (s, 3H), 1.42 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.4, 168.2, 162.5, 156.8, 145.3, 144.3, 141.5, 140.7, 137.2, 133.5, 131.8, 129.22, 129.17, 126.1, 125.8, 124.4, 124.1, 123.0, 122.9, 118.5, 117.2, 108.9, 59.9, 51.8, 35.4, 31.3, 27.5; **IR** (KBr): 2956, 1718, 1608, 1490, 1303, 1107, 831, 731; **HRMS (ESI)**: Exact mass calcd for $C_{32}H_{28}N_2O_4$ $[M+H]^+$: 505.2122, Found: 505.2114; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 4.97 min (major), 5.56 min (minor).

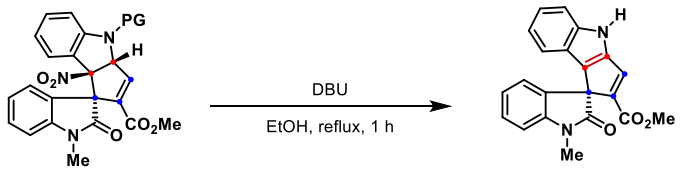


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.999	BV	0.1375	2921.53418	322.95316	49.9110
2	5.561	VV R	0.1607	2931.95020	277.70645	50.0890



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.972	BV R	0.1351	1.18862e4	1338.68604	98.4355
2	5.557	VV E	0.1710	188.90869	14.21684	1.5645

Methyl(*R*)-1'-methyl-2'-oxo-4*H*-spiro[cyclopenta[*b*]indole-1,3'-indoline]-2-carboxylate (5aj)

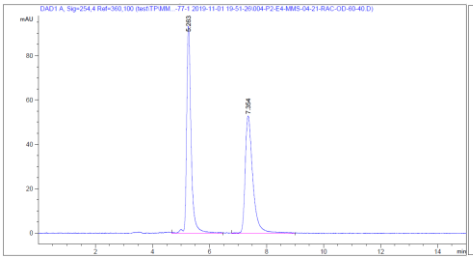


3aj
0.1 mmol
99% ee, dr > 20:1

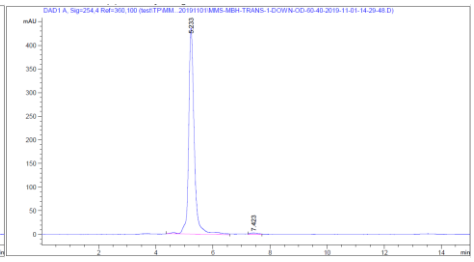
5aj
96% yield, 98% ee

To a solution of **3aj** (55.1 mg, 0.1 mmol, 1 equiv) in EtOH (2.0 mL), DBU (75 μL, 0.5 mmol, 5 equiv) was added at 80 °C. Then the resulting mixture was refluxed for 4 h. The reaction mixture was quenched and washed with NH_4Cl. Saturated NaCl solution was added to the

resulting solution and the organic layer was extracted with AcOEt three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 1:1, v/v) to afford compound **5aj** as a light yellow solid. Yellow solid, 96% yield; Mp: 262−263 ºC; $[\alpha]^{25}_D$ = -262.3 (c = 1.0, $CHCl_3$) for 98% ee; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.03 (s, 1H), 7.80−7.79 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.86−6.82 (m, 4H), 6.71 (d, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.50 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 175.2, 163.1, 145.2, 143.4, 141.7, 140.1, 136.5, 128.7, 127.5, 127.3, 123.2, 123.1, 123.0, 121.6, 120.6, 117.7, 112.8, 108.8, 59.8, 51.8, 27.5; **IR** (KBr): 2953, 1701, 1654, 1560, 1307, 1190, 746, 542; **HRMS (ESI)**: Exact mass calcd for $C_{21}H_{16}N_2O_3$ $[M+H]^+$: 345.1234, Found: 345.1235; **HPLC**: Chiralcel OD-H (150 mm), ^{i}PrOH/hexane = 40/60, 0.5 mL/min, detected at 254 nm; Retention time: 5.23 min (major), 7.42 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.263	MM R	0.1842	1033.81531	93.53074	50.7819
2	7.354	MM R	0.3151	1001.98077	52.99557	49.2181

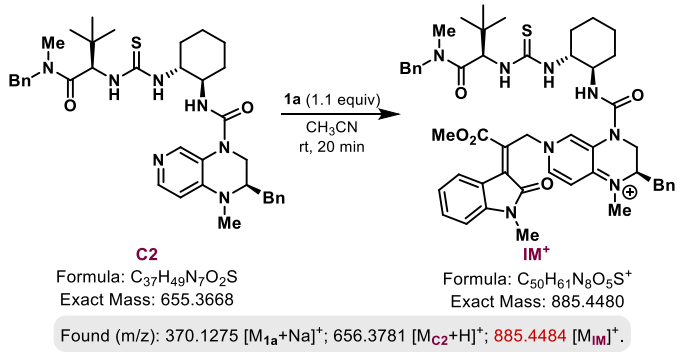


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.233	MM R	0.2255	5898.93848	435.99319	99.2052
2	7.423	MM R	0.2877	47.26087	2.73740	0.7948

8. Preliminary mechanistic study

1) ESI-HRMS experiment

To gain an insight regarding the role of the chiral DMAP-Thiourea **C2**, we performed ESI-HRMS experiment and captured a peak at m/z 885.4884, which corresponded to **IM**$^+$ generated from nucleophilic attack of catalyst **C2** to substrate **1a** (Fig. S2).



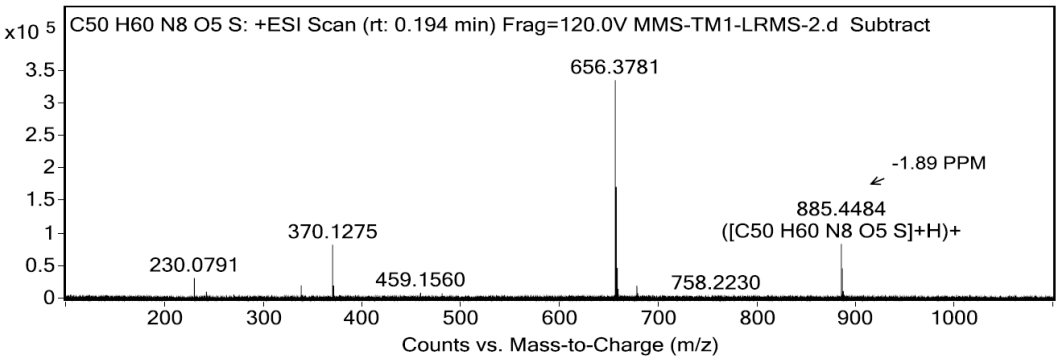


Figure S2. ESI-HRMS Experiment

2) NMR analysis

NMR analysis was straightforward to investigate the H-bonding interaction between **C2** and 3-nitroindole. In our previous report[3], the ^{1}H NMR spectrum of **C2** was recorded in acetone-d_6, where the double peak at 7.64 ppm (7.67 ppm as corresponding rotamer) was identified as N-H, although we cannot determined which one of the three (N)H atoms of **C2** this signal represented. When mixing **2j** with **C2** in a 1:1 ratio in the same solvent, this peak shifted to a higher field (overlapped with the signal from 7.48 to 7.19 ppm), suggesting the N-H of **C2** was interacted with substrate **2j** via H-bonding interaction (Fig. S3).

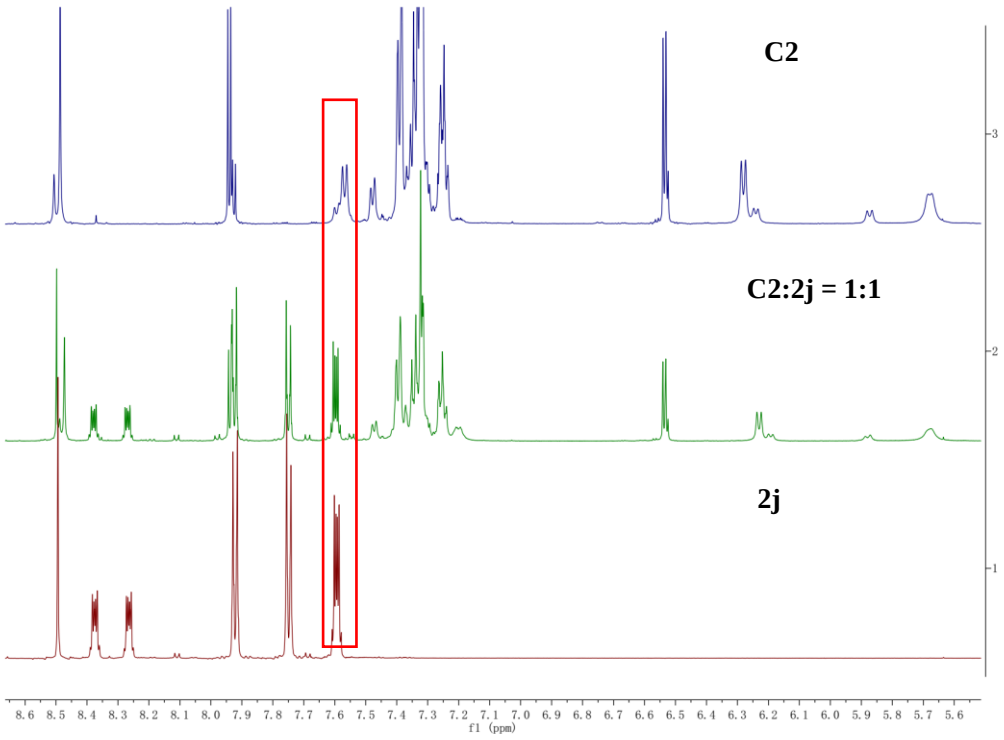


Figure S3. NMR Analysis

3) 3D model

The nucleophilic attack of substrate **1a** with catalyst **C2** could generate **IM**$^+$ (as shown in Fig. S2). After **IM**$^+$ was deprotonated by the leaving ^{t}BuO$^-$, zwitterionic ylide was thus obtained. Meanwhile, catalyst **C2** formed hydrogen bonds with **1a** because of the affinity of thiourea unit with the nitro group. In this way, two reactants were organized close to each other in the transition state. Then, the chiral diaminocyclohexane scaffold forced the ylide to attack the activated 3-nitroindole from the *Re*-face to afford the nitronate (Fig. S4a). Such transition state was shown as 3D model in Fig. S4b. (Gaussview 6.0 was used to draw the 3D structure diagram of the TS.)

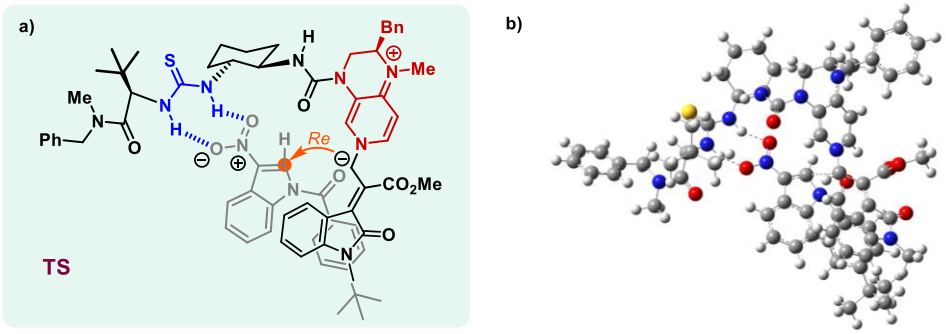


Figure S4. 3D Model for the Transition State of the [3 + 2] Reaction

9. *In vitro* PL inhibition assay

The inhibitory activities of our synthetic compounds against porcine pancreatic lipase (PL, type II, Lot.SLBN9099V; EC 3.1.1.3) were measured in a fluorescence-based assay using PL probe substrate 4-MUO (J&K chemical, China). In brief, the incubation mixture with a total volume of 200 μL contained lipase solution (10 μg/mL, final concentration), 0.1M McIlvane buffer (0.1M citrate-Na_2HPO_4, pH 7.4) and diverse inhibitors. After the reaction mixtures were incubated at 37 °C for 3 min, the enzyme reaction was initiated by adding of 4-MUO (10 μM, final concentration). Then, the fluorescence signal at 340 nm (excitation)/460 nm (emission) of the hydrolytic product (4-MU) was determined with a multi-mode microplate reader (SpectraMax iD3, Molecular Devices, Austria). The following formula was used to determine the residual activities of PL: the residual activity (%) = (the fluorescence intensity of 4-MU in the presence of inhibitor)/the fluorescence intensity of 4-MU in negative control (DMSO only) × 100%. All measurements were conducted in triplicates. The IC_{50} values were calculated by nonlinear regression using GraphPad Prism software (San Diego, CA, USA).

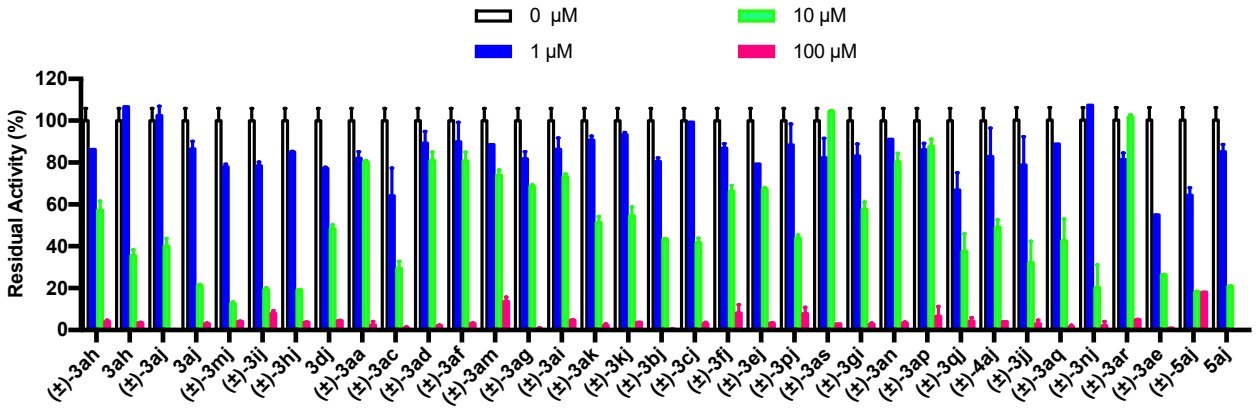


Figure S5. Residual Activity of [3 +2] Annulation Product

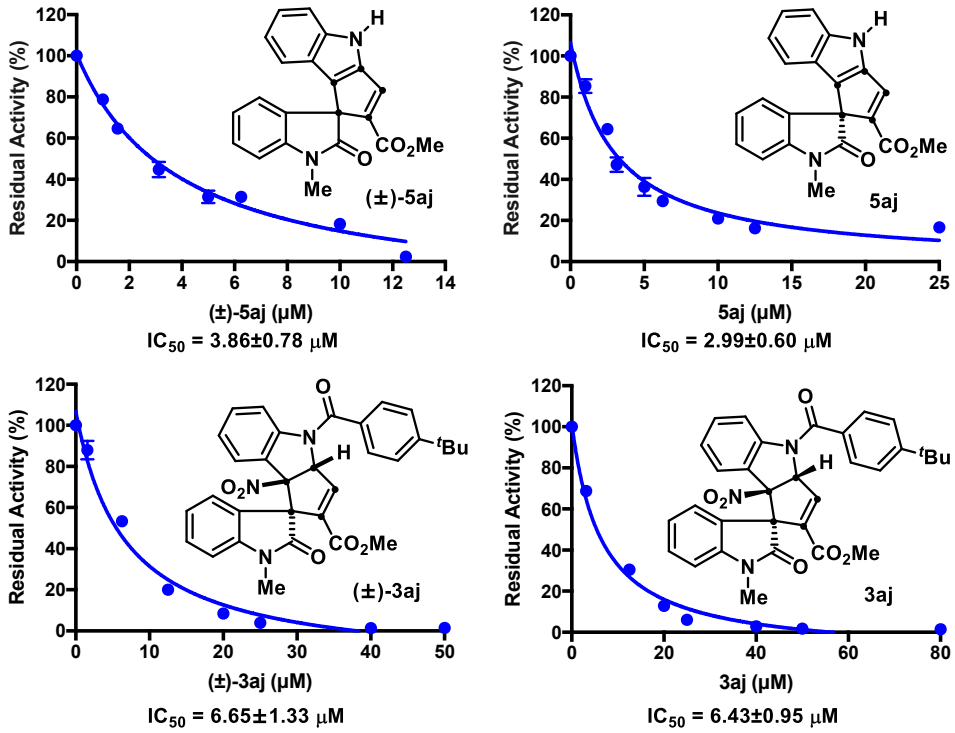


Figure S6. Inhibition Activities on PL

10. X-ray crystal data of compound 3ej (CCDC-1963946)

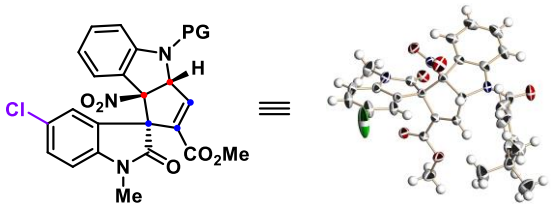
Sample preparation:

A solution of the substance (20.4 mg) is prepared using DCM (200 μL) and placed in test tube. A second solvent, *n*-hexane, is placed in a closed beaker, The test tube containing DCM is then placed in the beaker and the beaker is sealed. Slow diffusion of DCM into test tube and *n*-hexane out of test tube will cause crystals to form.

Crystal measurement for compounds **3ej**:

The frames were integrated with the Bruker SAINT software package using a narrow-f rame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 41842 reflections to a maximum θangle of 75.74º (0.80 Å resolution), of which 11973 were independent (average redundancy 3.495, completeness = 98.6%, R_{int} = 4.44%, R_{sig} = 4.53%) and 11149 (93.12%) were greater than 2σ(F2). The final cell constants of a = 10. 4684(19) Å, b = 12.280(2) Å, c = 45.879(8) Å, V = 5897.8(19) Å^3, are based upon the r efinement of the XYZ-centroids of 9381 reflections above 20 σ(I) with 7.452° < 2θ < 150. 3º .

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{66}H_{56}Cl_2N_6O_{10}$. The final anisotropic full-matrix least-squares refinement on F^2 with 767 variables converged at R_1 = 4.27%, for the observed data and wR_2 = 11.43% for all data. The goodness-of-fit was 1.023. The largest peak in the final difference electron density synthesis was 0.525 e$^-$/Å^3 and the largest hole was -0.702 e$^-$/Å^3 with an RMS deviation of 0.045 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.311 g/cm^3 and F(000), 2432 e$^-$.



3ej

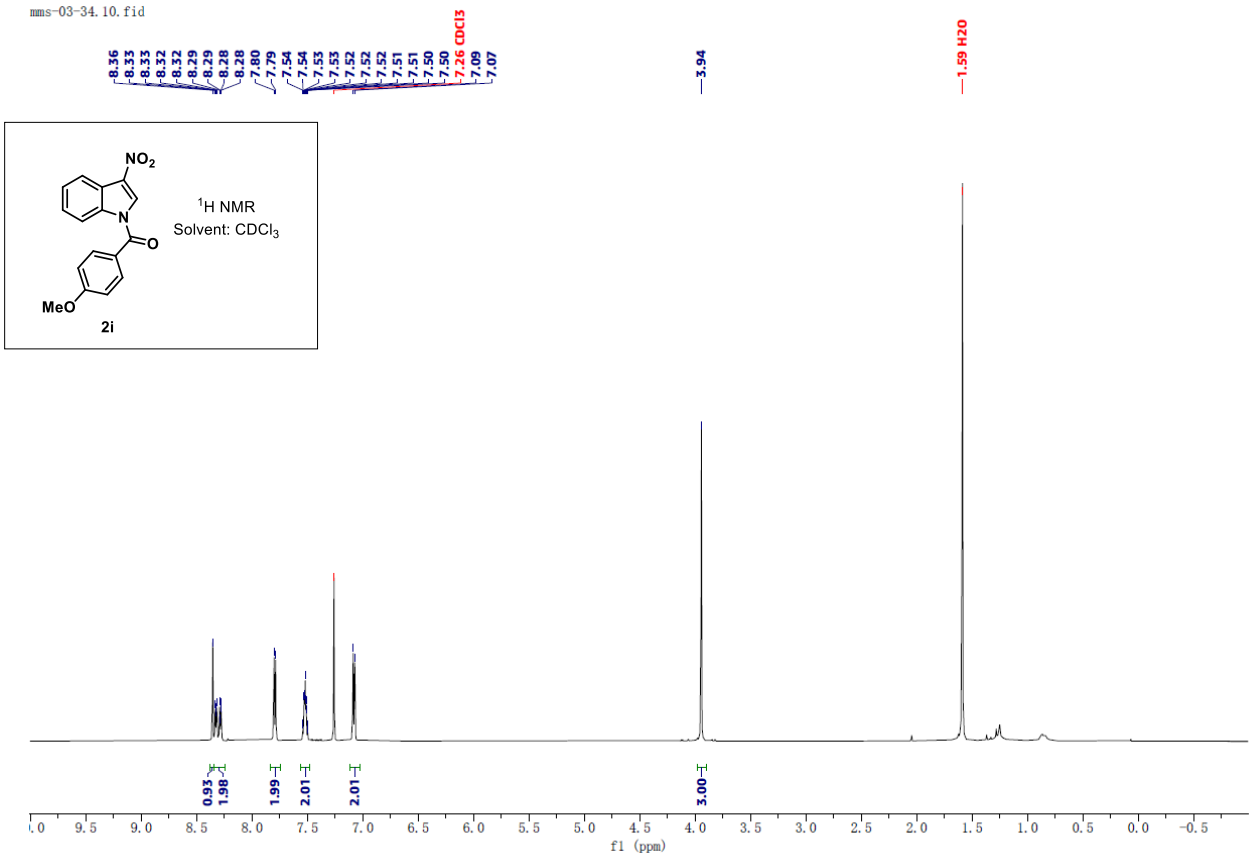
ORTEP of **3ej**
(CCDC 1963946)

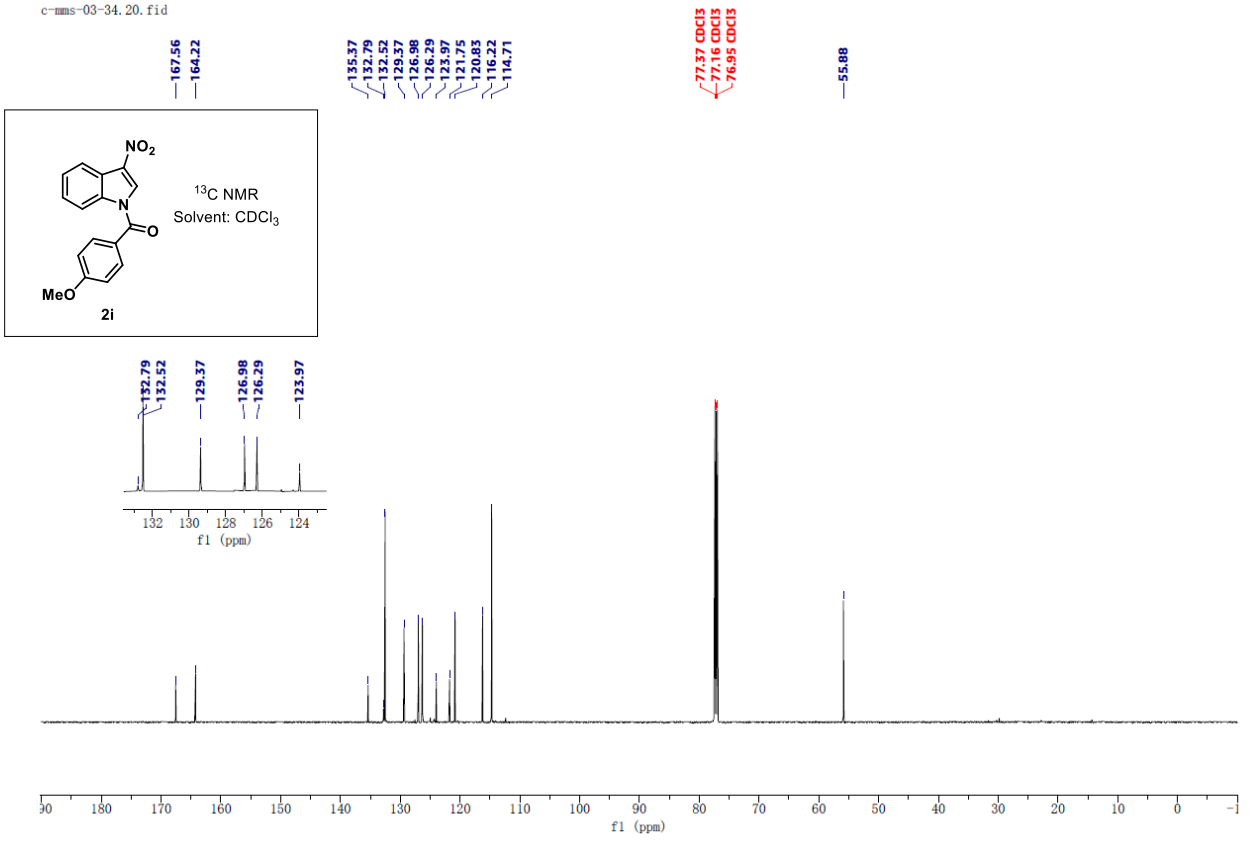
Table 1. Sample and crystal data for 3ej.

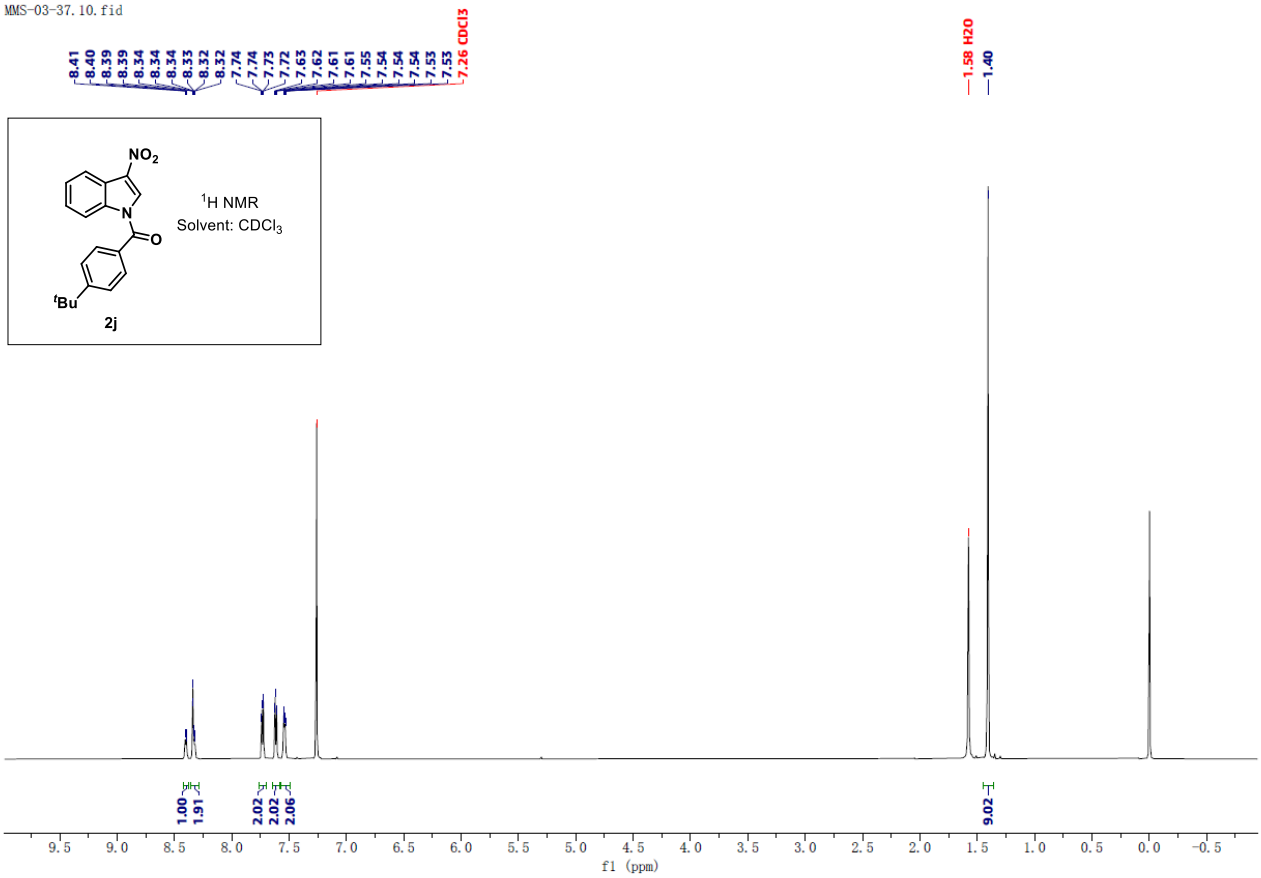
Identification code	20191030MMS0365	
Chemical formula	$C_{66}H_{56}Cl_2N_6O_{10}$	
Formula weight	1164.06 g/mol	
Temperature	262(2) K	
Wavelength	1.54178 Å	
Crystal size	0.030 x 0.100 x 0.180 mm	
Crystal habit	Clear light colourless block	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.4684(19) Å	α = 90 °
	b = 12.280(2) Å	β = 90 °
	c = 45.879(8) Å	γ = 90 °
Volume	5897.8(19) $Å^3$	
Z	4	
Density (calculated)	1.311 g/cm^3	
Absorption coefficient	1.528 mm^{-1}	
F(000)	2432	
Diffractometer	d8 venture	
Theta range for data collection	1.93 to 75.74 °	
Index ranges	-13<=h<=12,	-15<=k<=15,
	-56<=l<=57	
Reflections collected	41842	
Independent reflections	11973 [*R*(int) = 0.0444]	
Coverage of independent reflections	98.6%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9560 and 0.7710	
Structure solution technique	direct methods	

Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11973 / 0 / 767	
Goodness-of-fit on F^2	1.023	
Δ/σ_{max}	0.027	
Final R indices	11149 data; I>2σ(I)	R_1 = 0.0427, wR_2 = 0.1105
	all data	R_1 = 0.0459, wR_2 = 0.1143
Weighting scheme	$w=1/[\sigma^2 (F_o^2)+(0.0543P)^2+2.0265P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.034(6)	
Largest diff. peak and hole	0.525 and -0.702 eÅ^{-3}	
R.M.S. deviation from mean	0.045 eÅ^{-3}	

11. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR data



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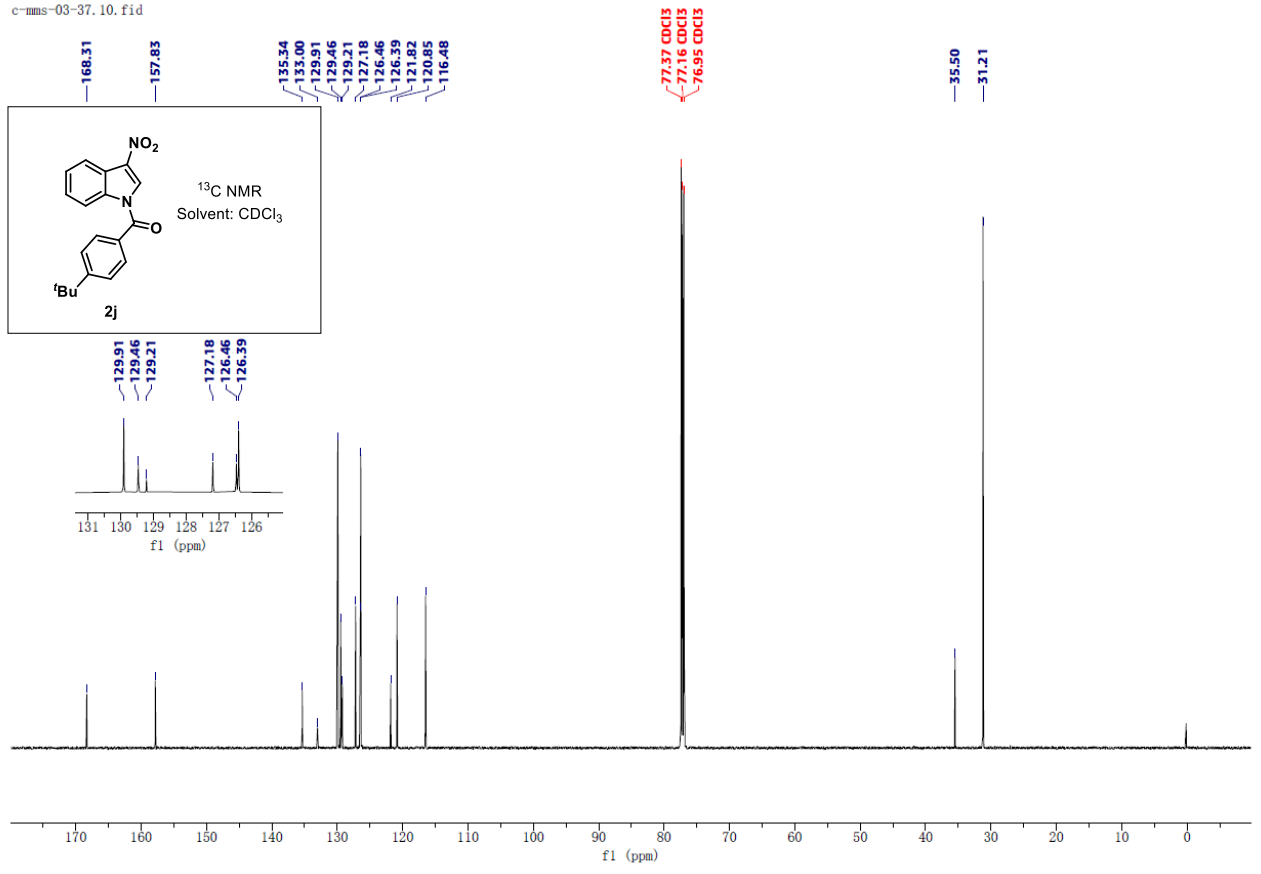
7.61
7.61
7.55
7.54
7.54
7.54
7.53
7.26 CDCl3
1.58 H2O
1.40
NO2
N
O
tBu
2j
1H NMR
Solvent: CDCl3
1.00
1.91
2.02
2.02
2.06
9.02
f1 (ppm)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116.48
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77.16 CDCl3
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35.50
31.21
NO2
N
O
tBu
2j
13C NMR
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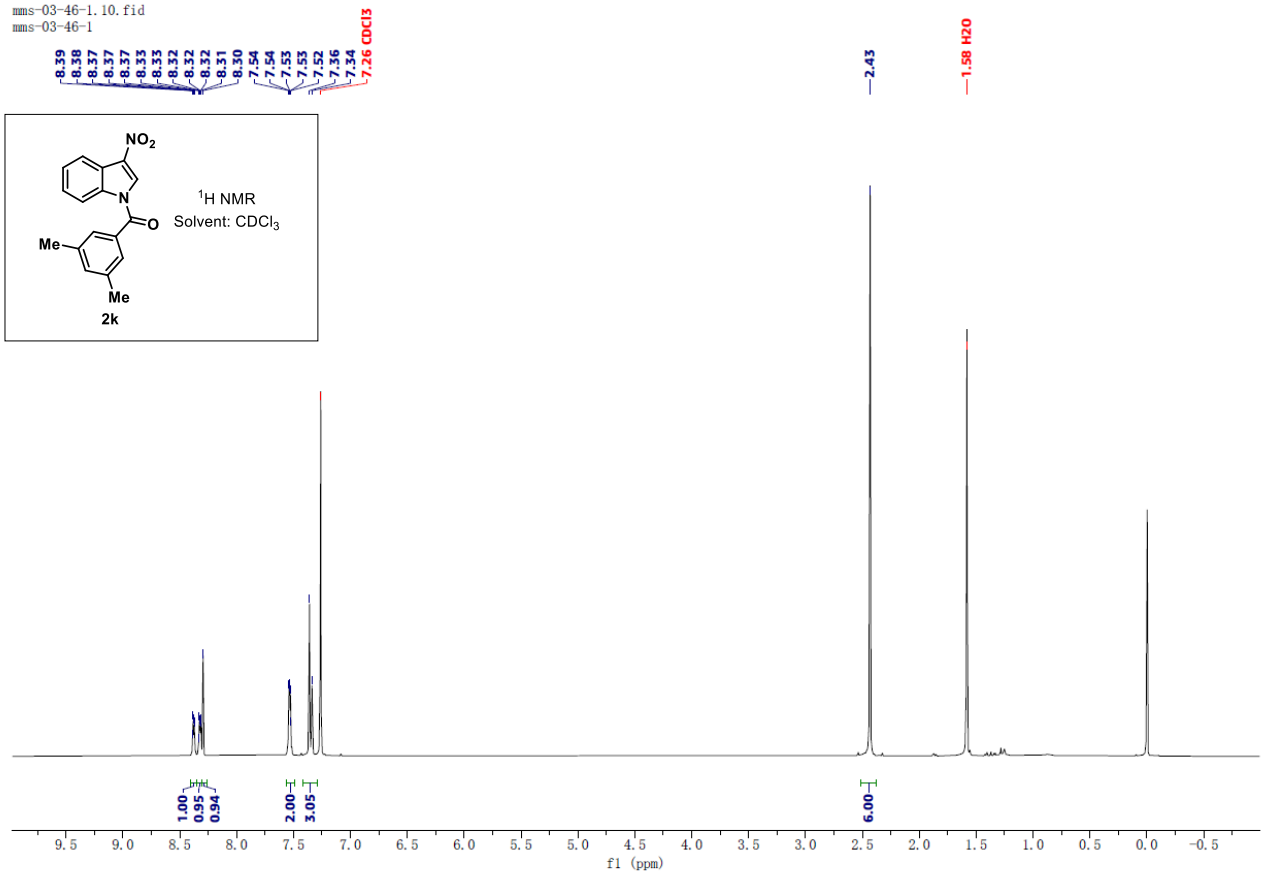
129.91
129.46
129.21
127.18
126.46
126.39
f1 (ppm)
f1 (ppm)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7.26 CDCl3
2.43
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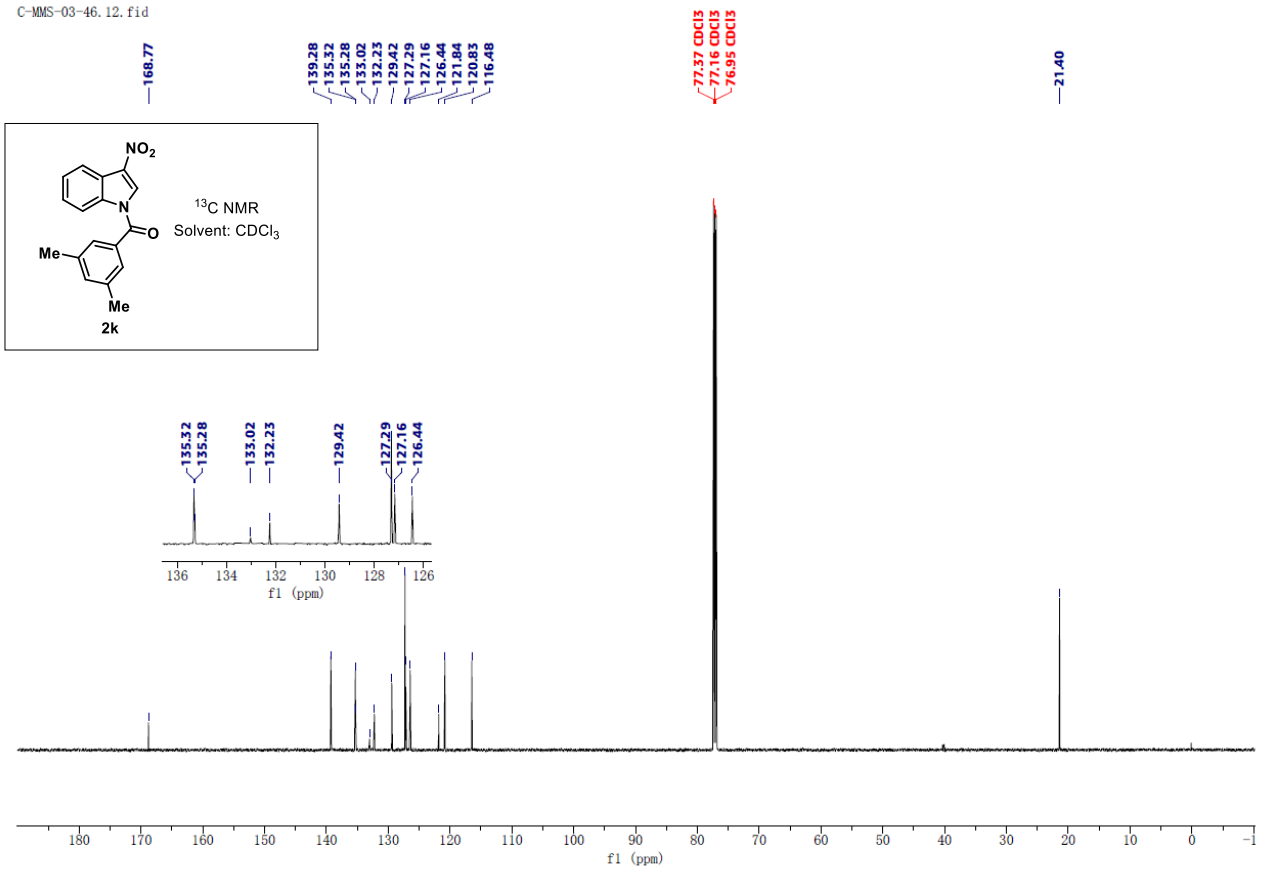
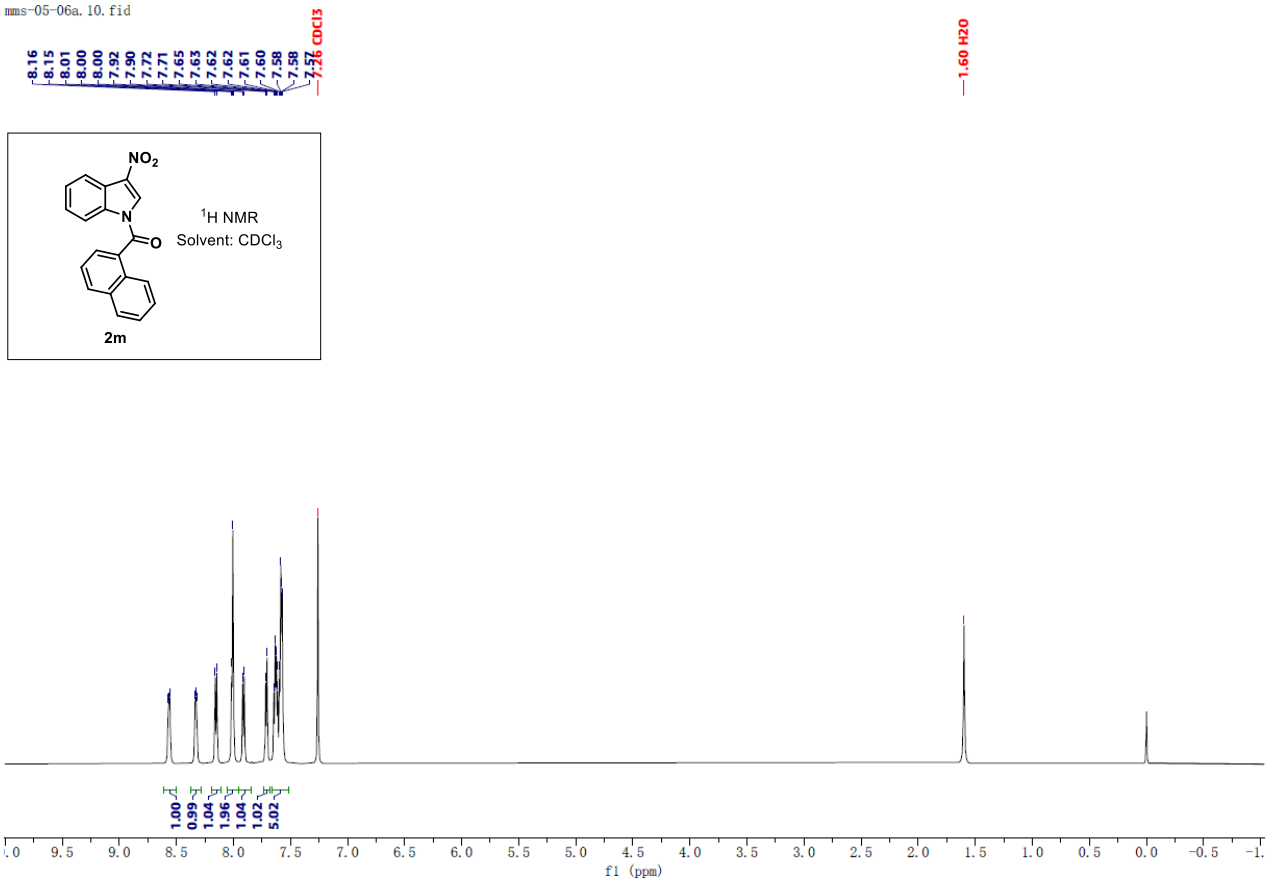
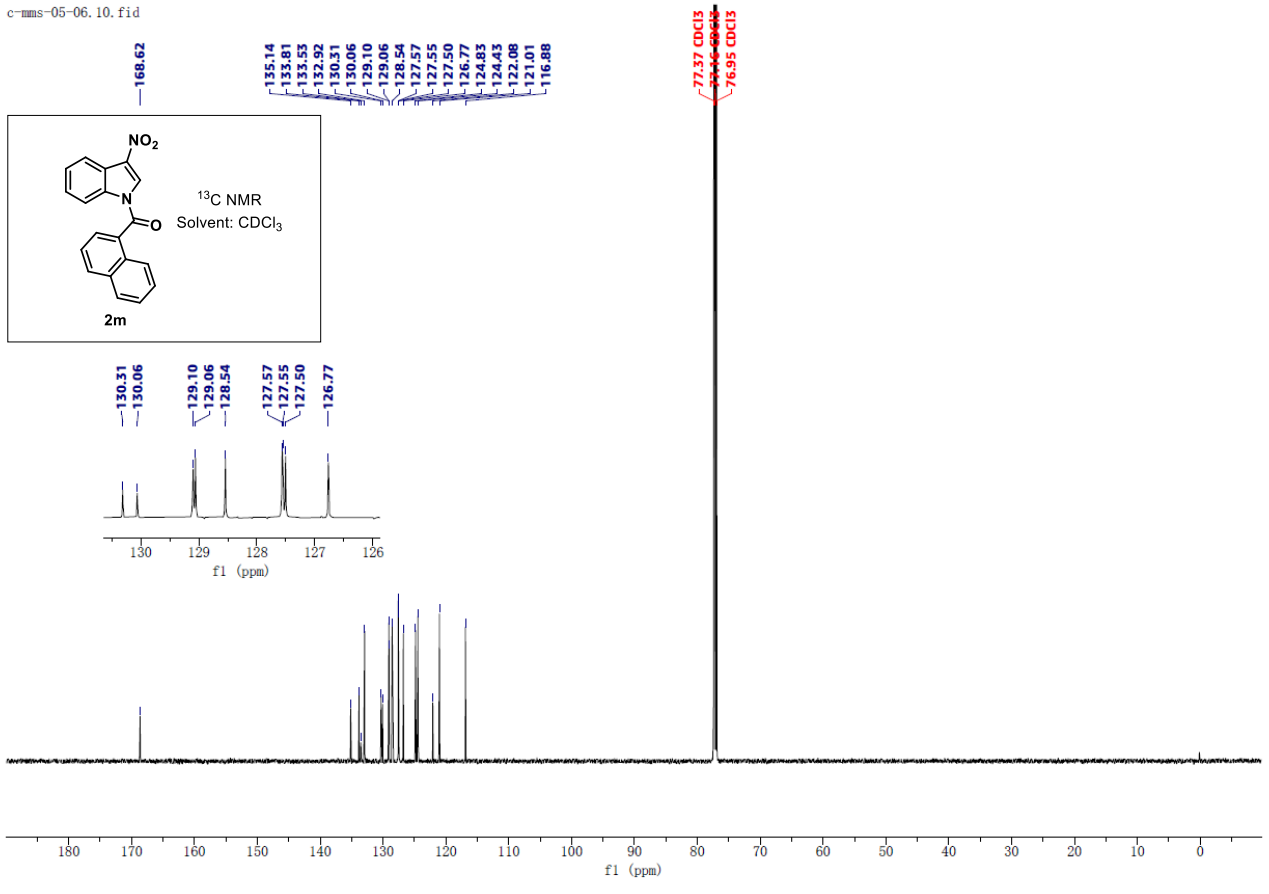
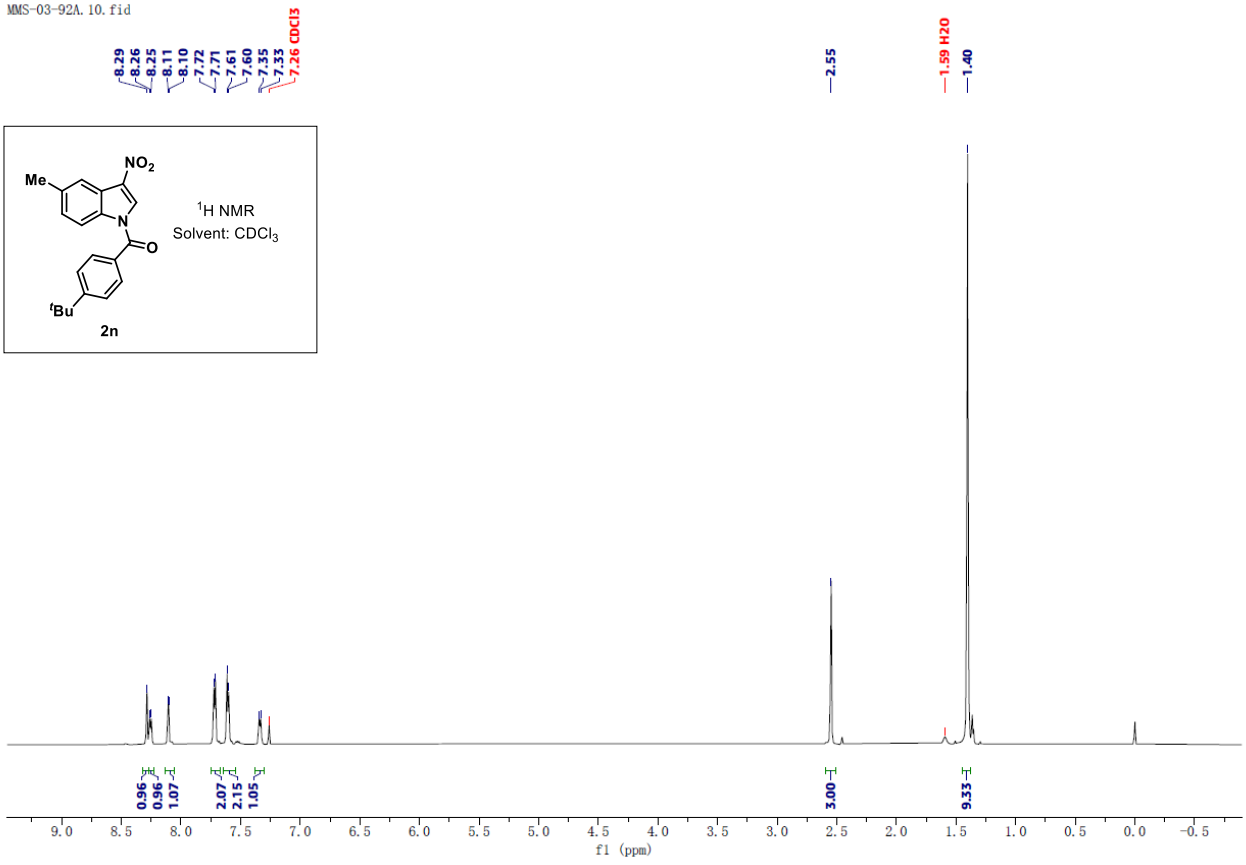
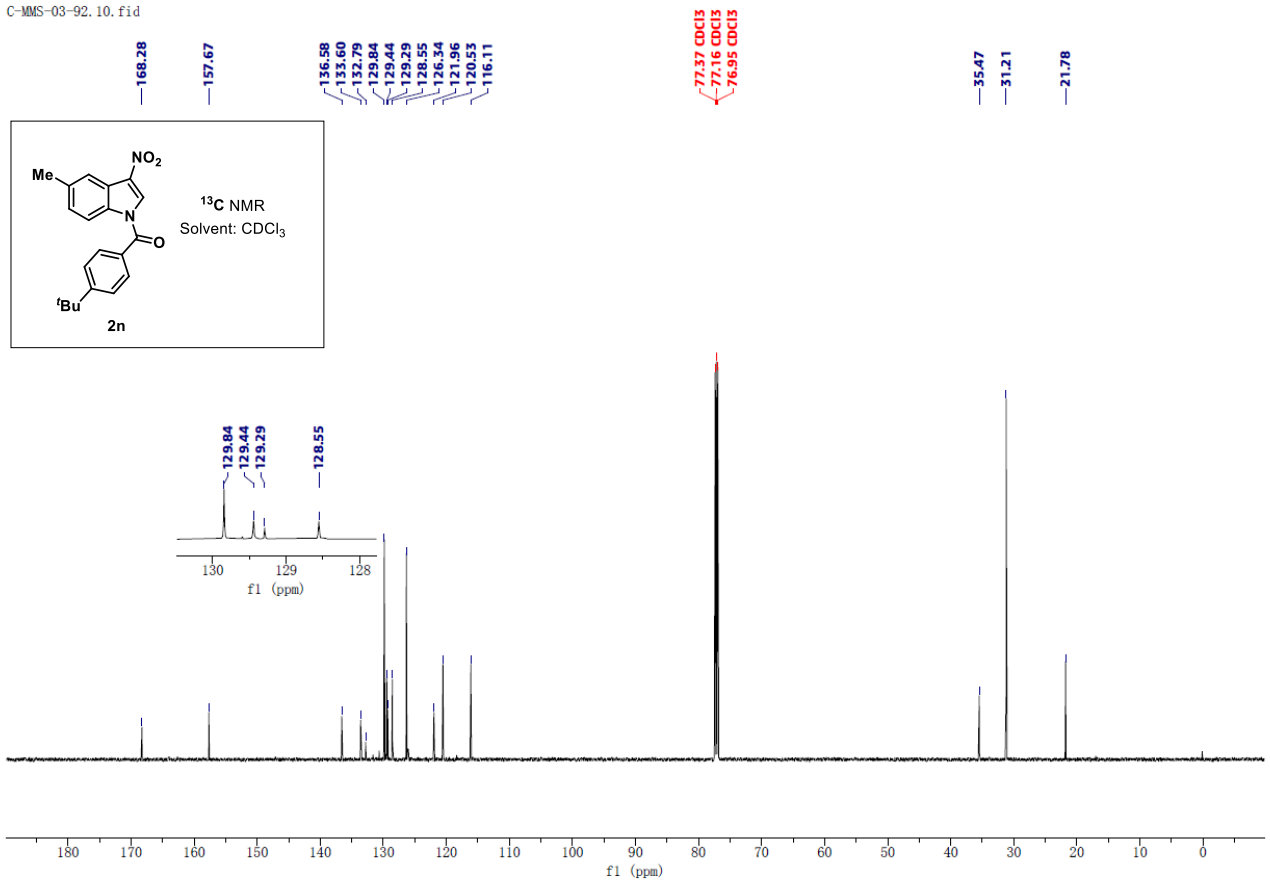
NO2
N
O
Me
Me
2k
1H NMR
Solvent: CDCl3
1.00
0.95
0.94
2.00
3.05
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


C-MMS-03-46.12.fid
168.77
139.28
135.32
135.28
133.02
132.23
129.42
127.29
127.16
126.44
121.84
120.83
116.48
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
21.40
NO2
N
O
Me
Me
2k
13C NMR
Solvent: CDCl3
135.32
135.28
133.02
132.23
129.42
127.29
127.16
126.44
136 134 132 130 128 126
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


mms-05-06a.10.fid
8.16
8.15
8.01
8.00
8.00
7.92
7.90
7.72
7.71
7.65
7.63
7.62
7.62
7.61
7.60
7.58
7.57
7.26 CDCl3
1.60 H2O
NO2
N
O
1H NMR
Solvent: CDCl3
2m
1.00
0.99
1.04
1.96
1.04
1.02
5.02
f1 (ppm)


c-mms-05-06.10.fid
168.62
135.14
133.81
133.53
132.92
130.31
130.06
129.10
129.06
128.54
127.57
127.55
127.50
126.77
124.83
124.43
122.08
121.01
116.88
77.37 CDCl3
76.95 CDCl3
NO2
N
O
13C NMR
Solvent: CDCl3
2m
f1 (ppm)


MMS-03-92A.10.fid
8.29
8.26
8.25
8.11
8.10
7.72
7.71
7.61
7.60
7.35
7.33
7.26 CDCl3
2.55
1.59 H2O
1.40
Me
NO2
N
O
tBu
2n
1H NMR
Solvent: CDCl3
0.96
0.96
1.07
2.07
2.15
1.05
3.00
9.33
f1 (ppm)


C-MMS-03-92.10.fid
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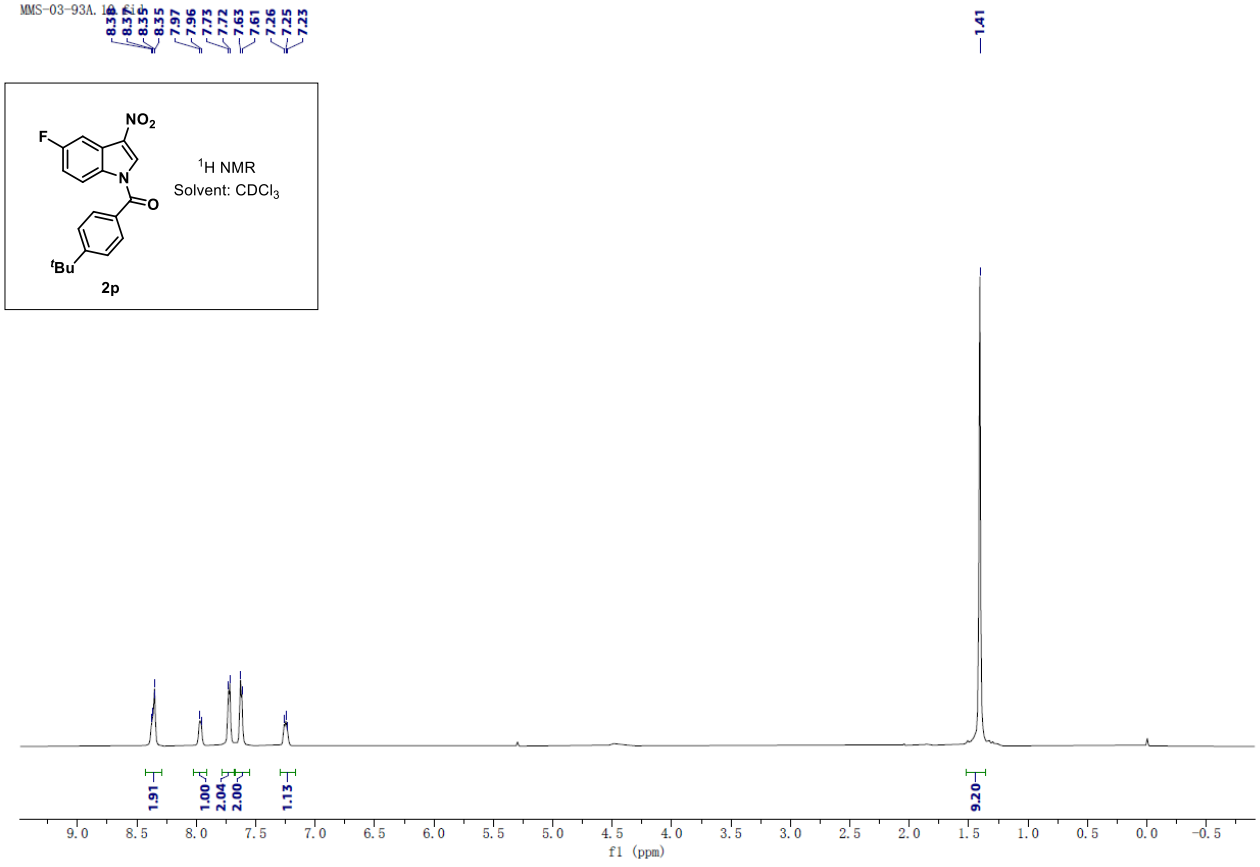
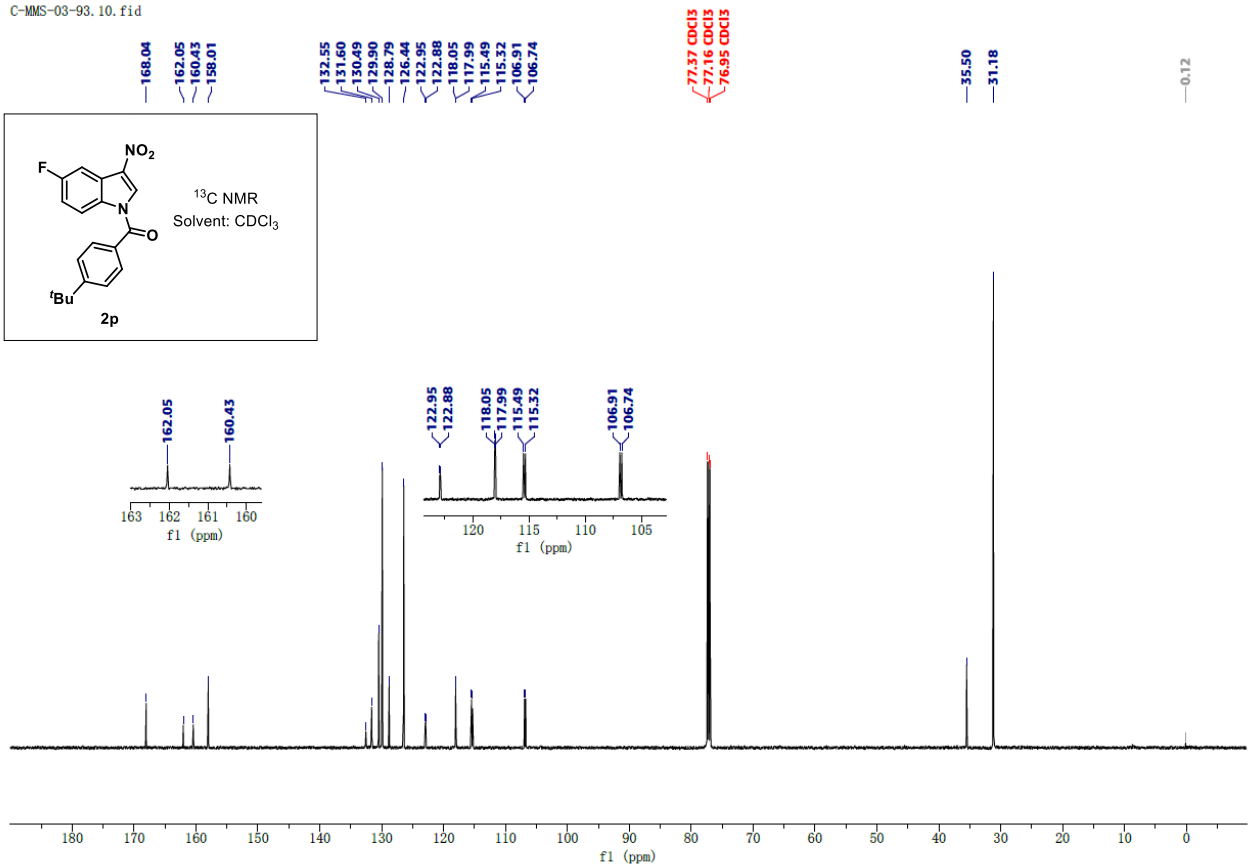
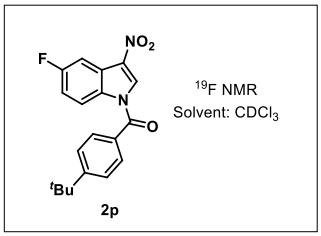
157.67
136.58
133.60
132.79
129.84
129.44
129.29
128.55
126.34
121.96
120.53
116.11
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
35.47
31.21
21.78
Me
NO2
N
O
tBu
2n
13C NMR
Solvent: CDCl3
129.84
129.44
129.29
128.55
f1 (ppm)


8.38
8.37
8.35
8.35
7.97
7.96
7.73
7.72
7.63
7.61
7.26
7.25
7.23
1.41
NO2
F
N
O
tBu
2p
1H NMR
Solvent: CDCl3
1.91
1.00
2.04
2.00
1.13
9.20
f1 (ppm)

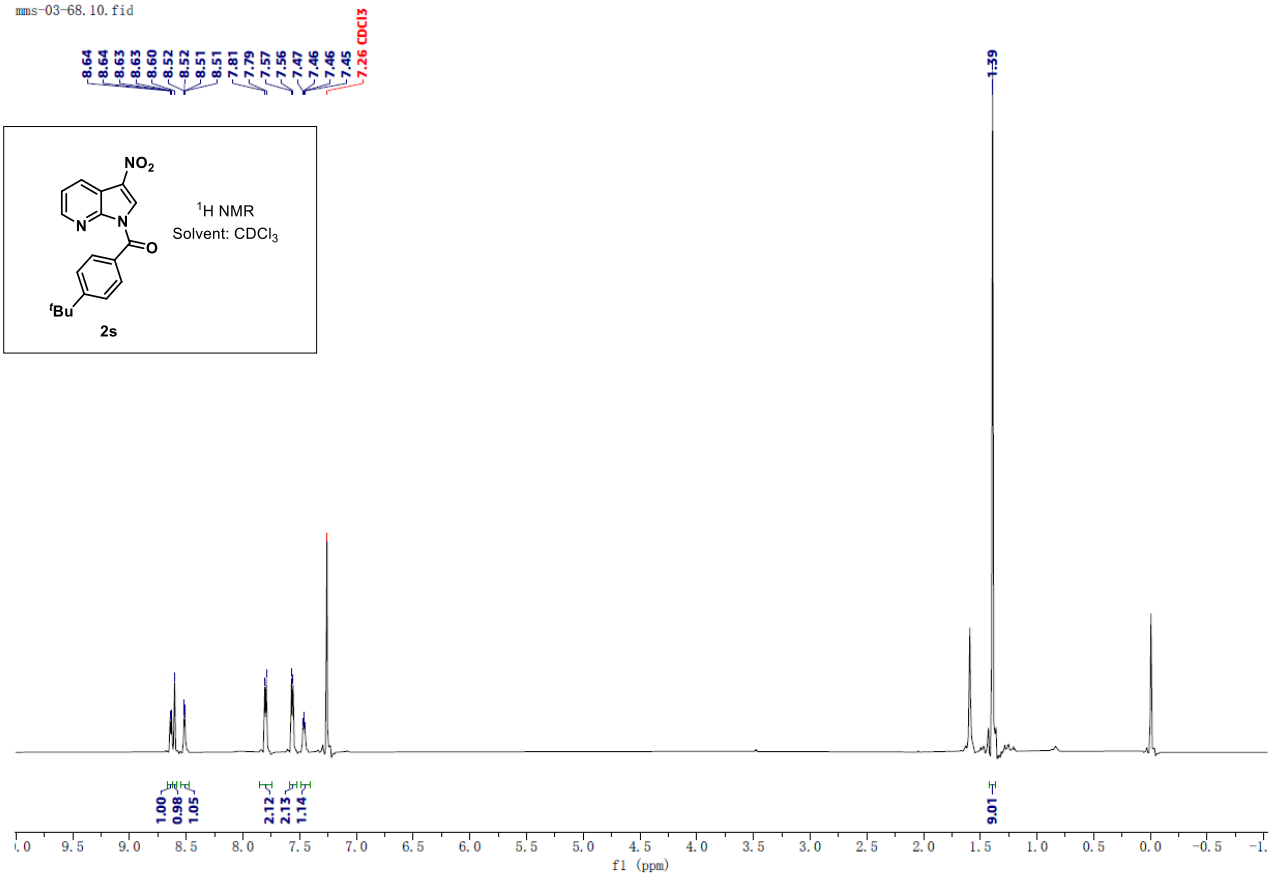

C-MMS-03-93.10.fid
168.04
162.05
160.43
158.01
132.55
131.60
130.49
129.90
128.79
126.44
122.95
122.88
118.05
117.99
115.49
115.32
106.91
106.74
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
35.50
31.18
0.12
NO2
F
N
O
tBu
2p
13C NMR
Solvent: CDCl3
f1 (ppm)

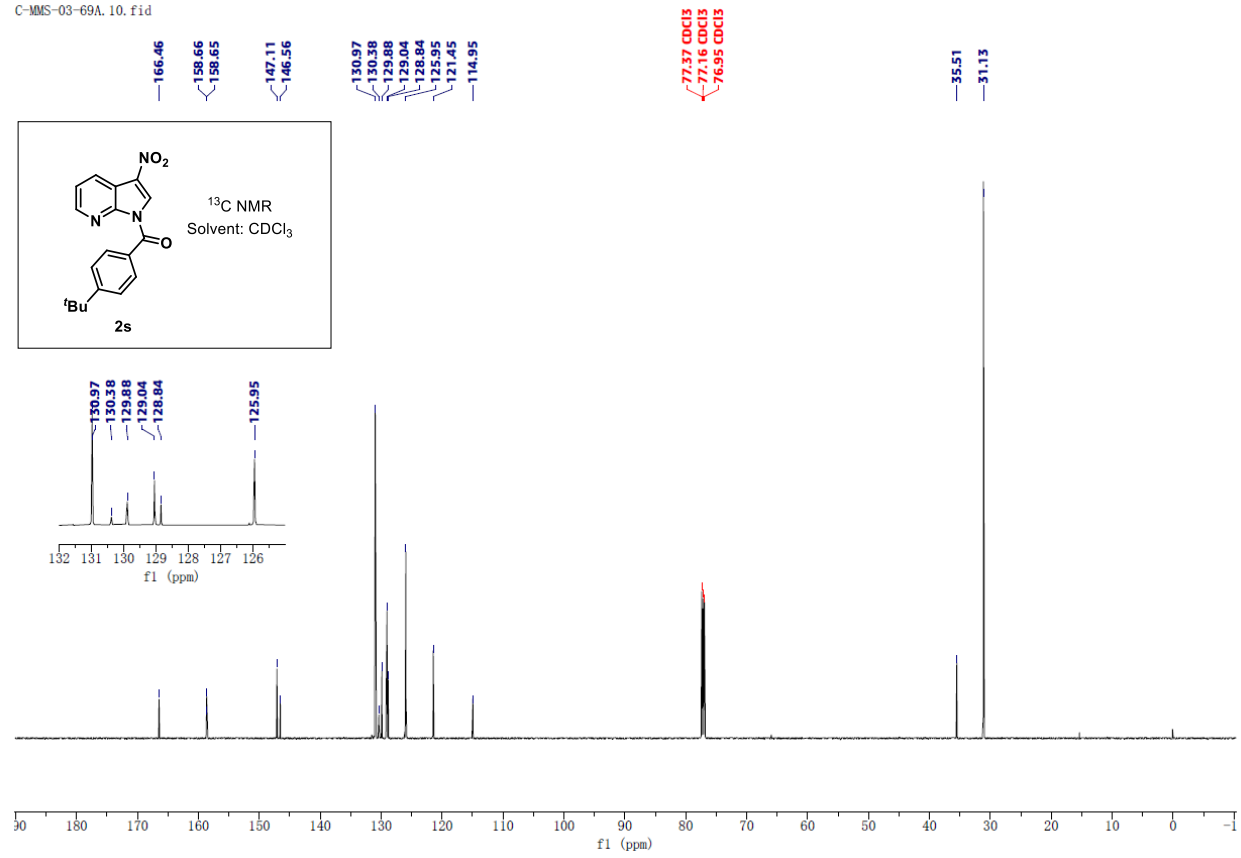
F-MMS-03-93.12.fid

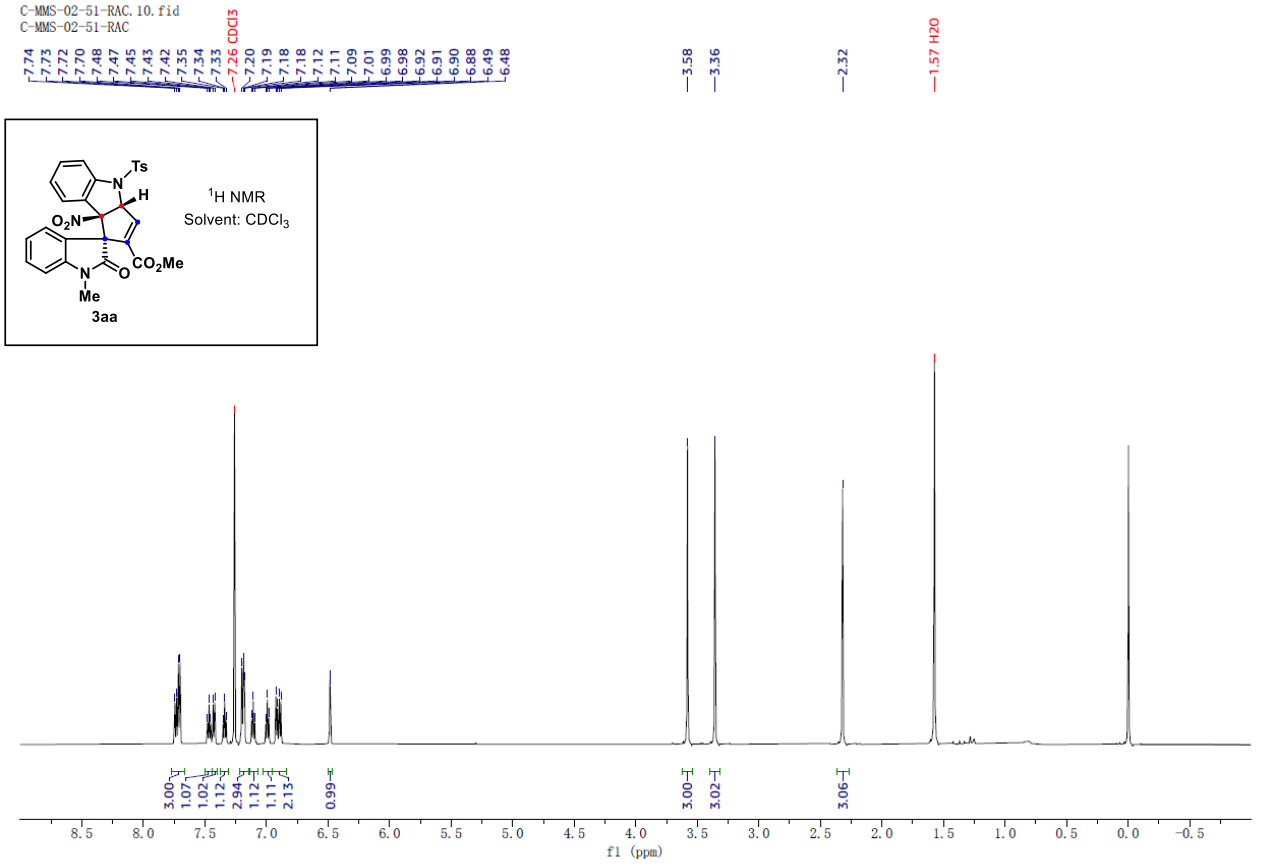


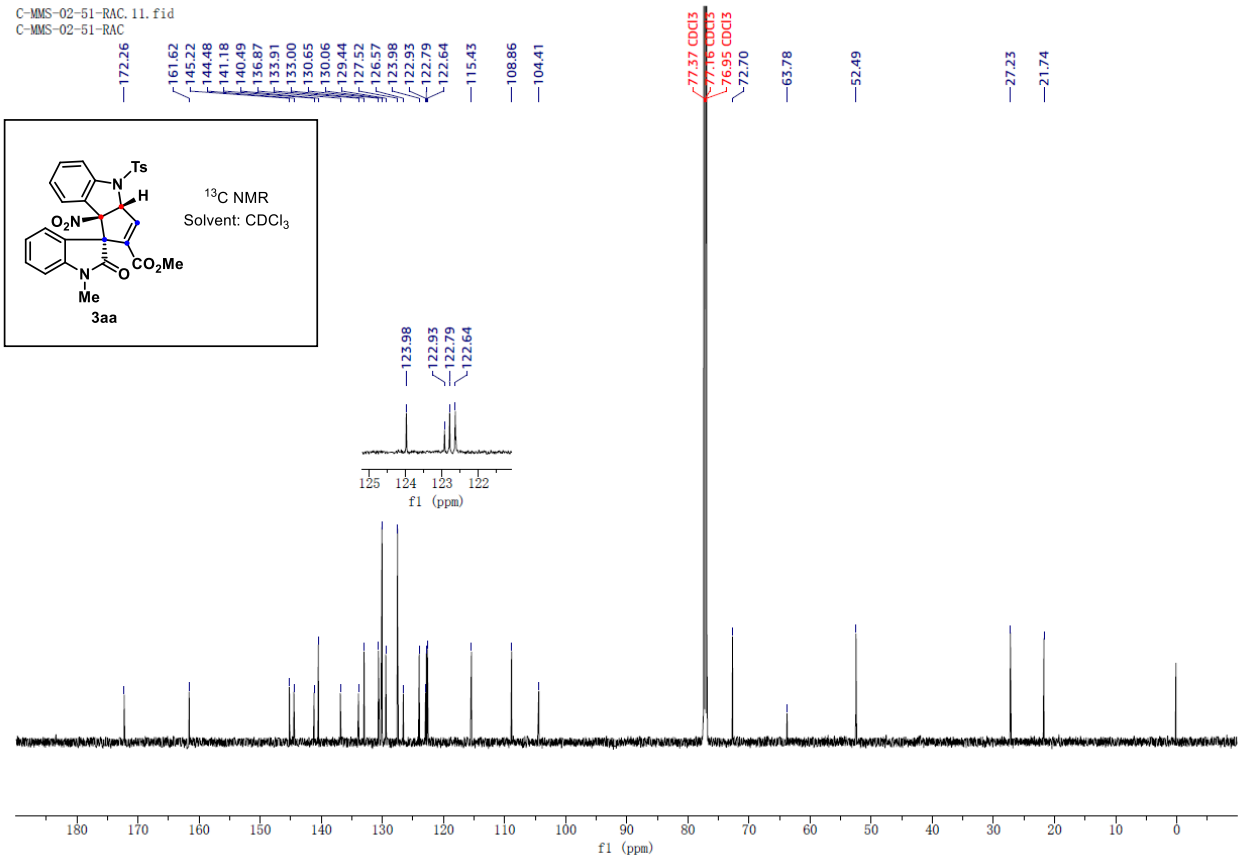
^{19}F NMR
Solvent: $CDCl_3$

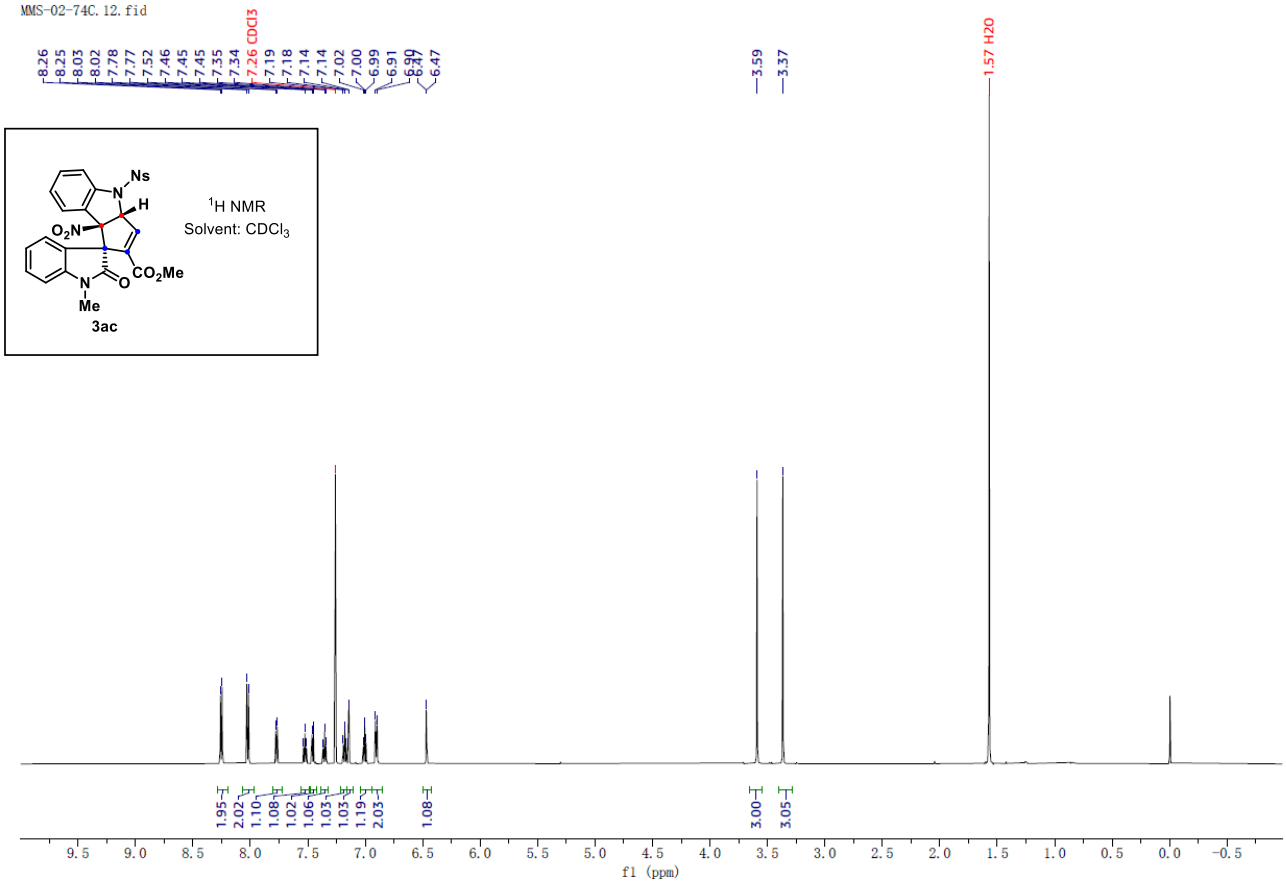
2p

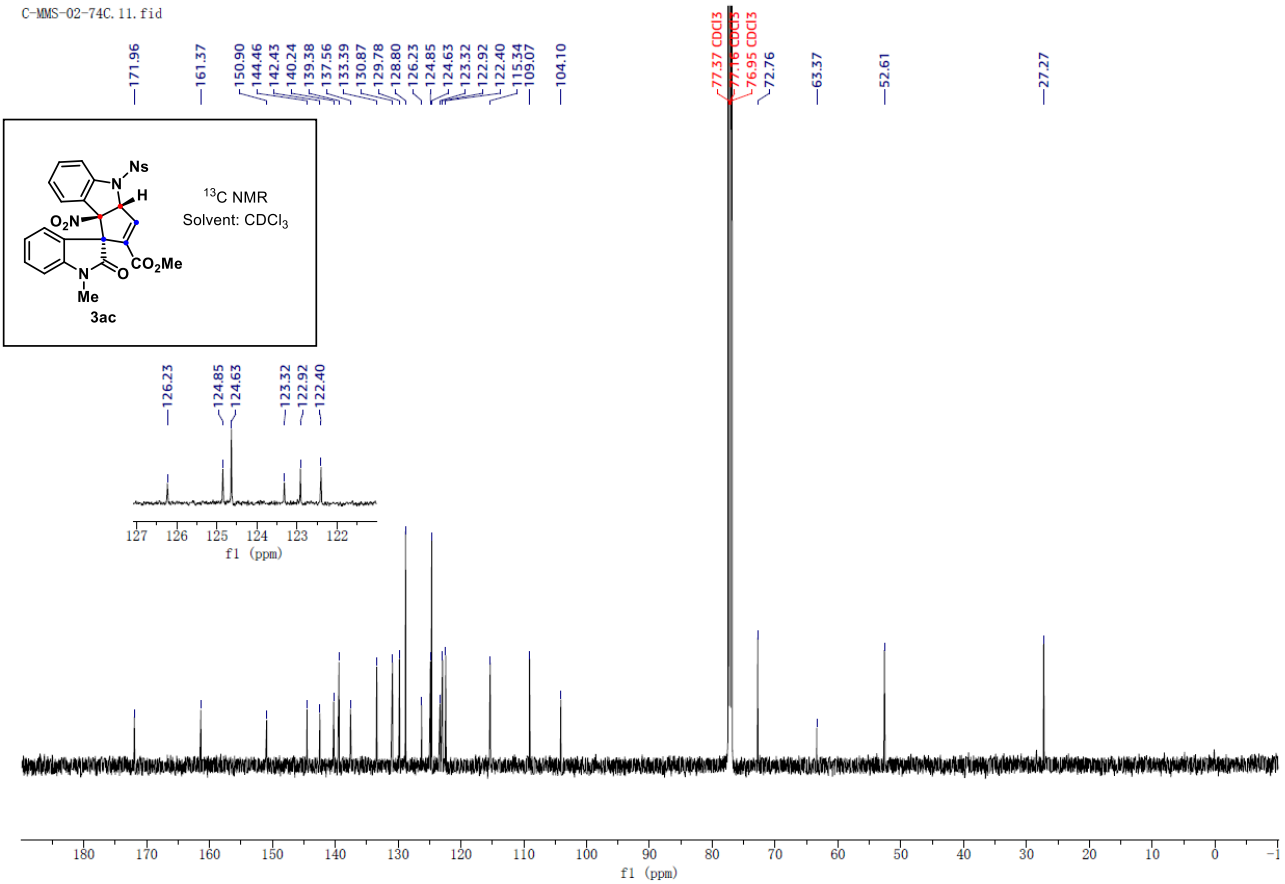

mms-03-68.10.fid
8.64
8.64
8.63
8.63
8.60
8.52
8.52
8.51
8.51
7.81
7.79
7.57
7.56
7.47
7.46
7.46
7.45
7.26 CDCl3
1.39
NO2
N
N
O
tBu
2s
1H NMR
Solvent: CDCl3
1.00
0.98
1.05
2.12
2.13
1.14
9.01
f1 (ppm)

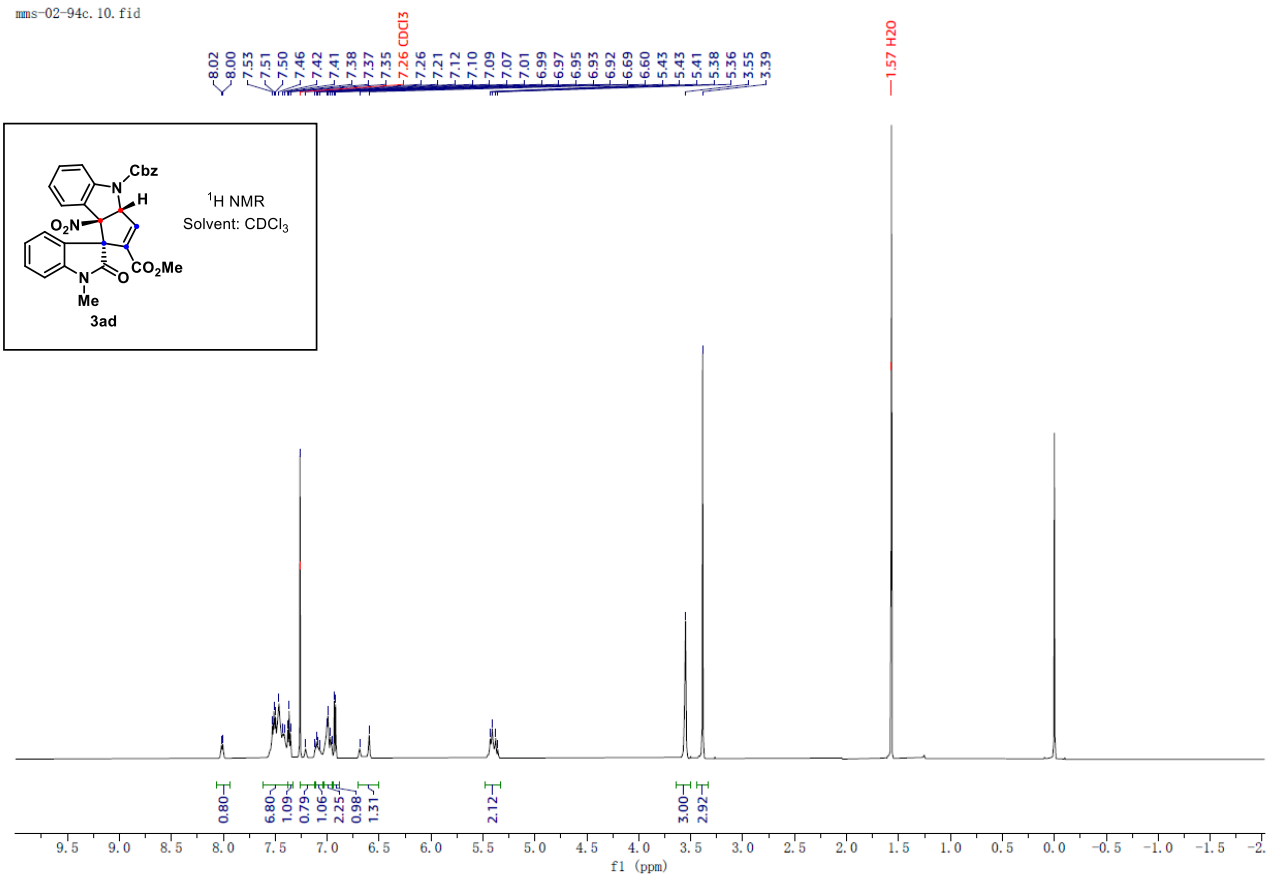

C-MMS-03-69A.10.fid
166.46
158.66
158.65
147.11
146.56
130.97
130.38
129.88
129.04
128.84
125.95
121.45
114.95
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
35.51
31.13
NO2
N
N
O
tBu
2s
13C NMR
Solvent: CDCl3
130.97
130.38
129.88
129.04
128.84
125.95
f1 (ppm)
f1 (ppm)

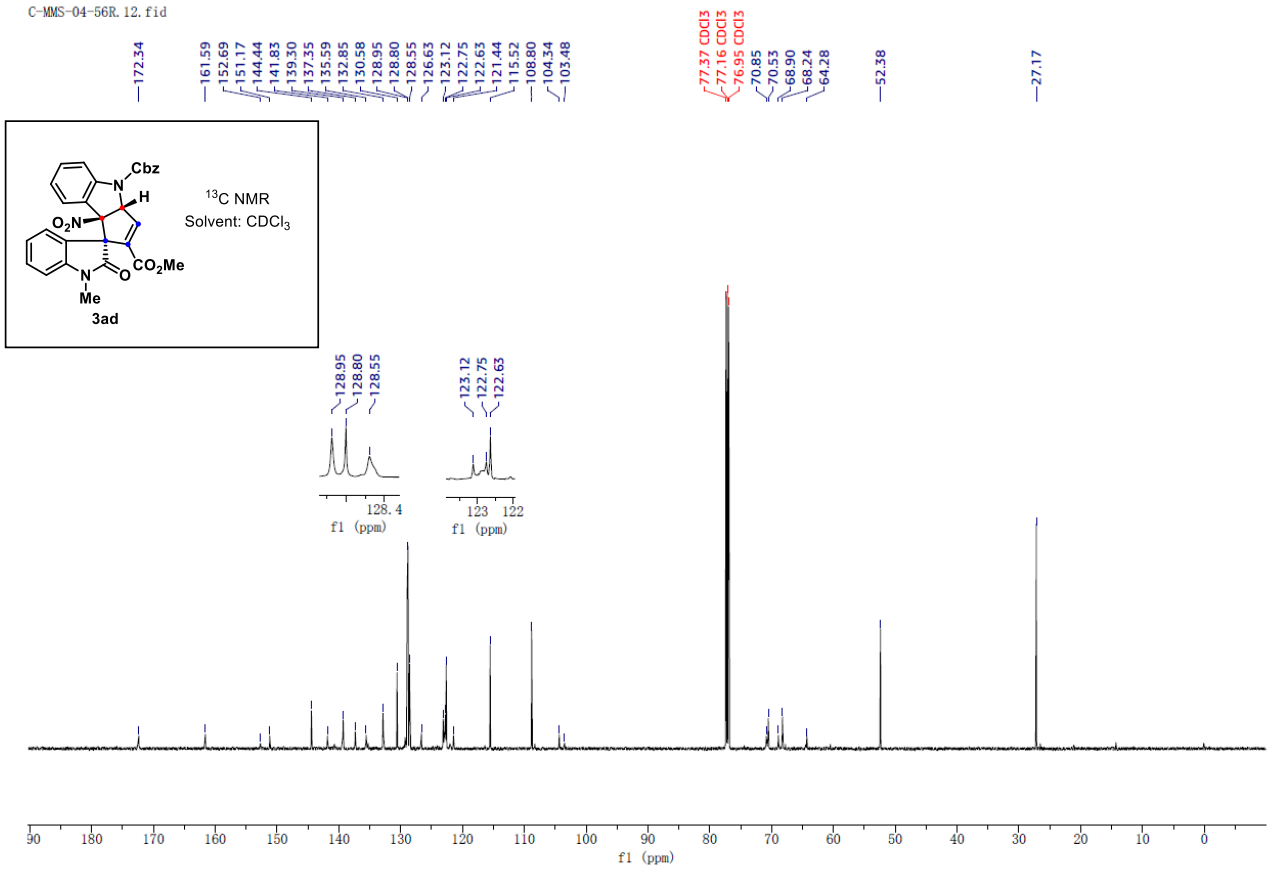

C-MMS-02-51-RAC.10.fid
C-MMS-02-51-RAC
7.74
7.73
7.72
7.70
7.48
7.47
7.45
7.43
7.42
7.35
7.34
7.33
7.26 CDCl3
7.20
7.19
7.18
7.18
7.12
7.11
7.09
7.01
6.99
6.98
6.92
6.91
6.90
6.88
6.49
6.48
3.58
3.36
2.32
1.57 H2O
Ts
H
O2N
CO2Me
N
O
Me
3aa
1H NMR
Solvent: CDCl3
3.00
1.07
1.02
1.12
2.94
1.12
1.11
2.13
0.99
3.00
3.02
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

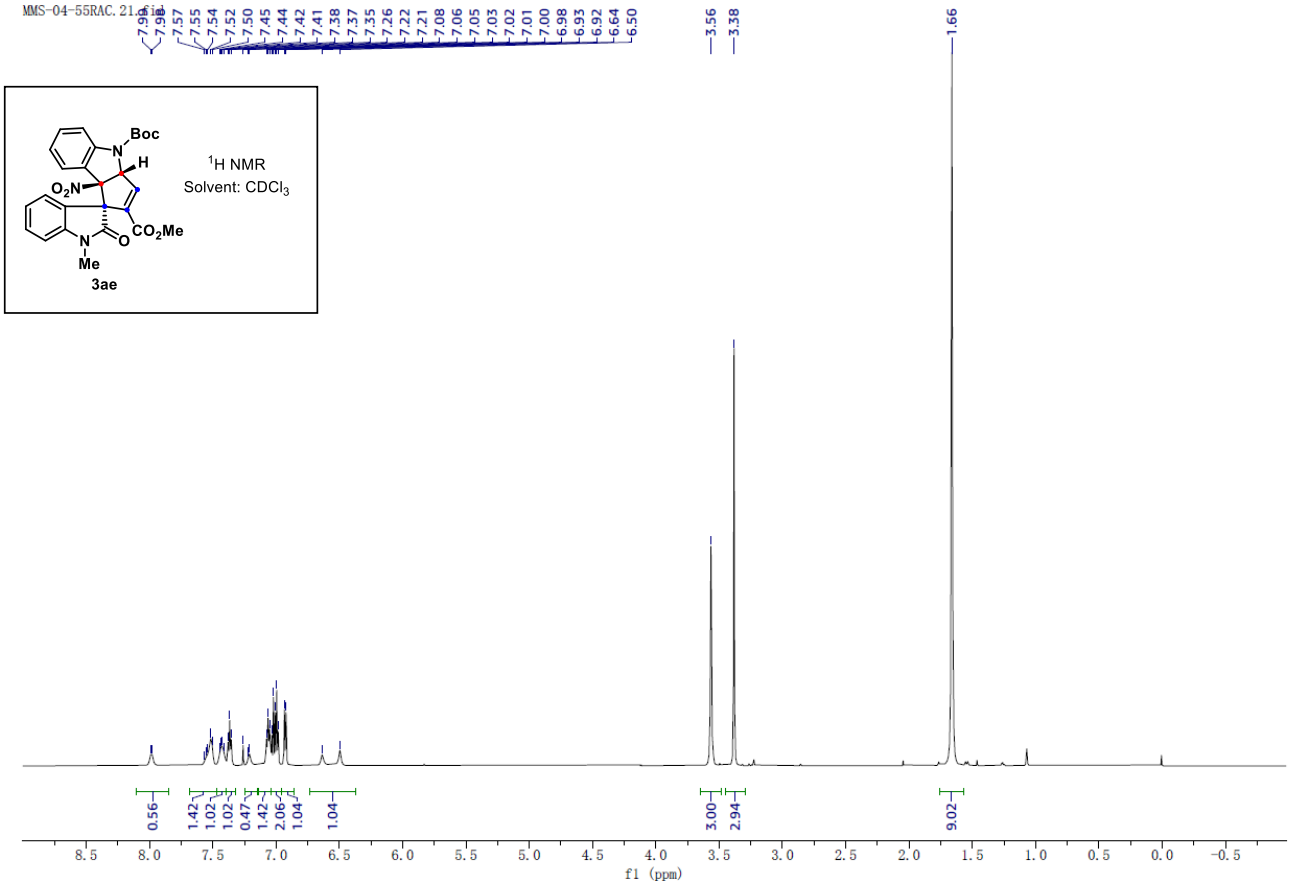

C-MMS-02-51-RAC.11.fid
C-MMS-02-51-RAC
172.26
161.62
145.22
144.48
141.18
140.49
136.87
133.91
133.00
130.65
130.06
129.44
127.52
126.57
123.98
122.93
122.79
122.64
115.43
108.86
104.41
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.70
63.78
52.49
27.23
21.74
Ts
H
O2N
CO2Me
N
O
Me
3aa
13C NMR
Solvent: CDCl3
123.98
122.93
122.79
122.64
125
124
123
122
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

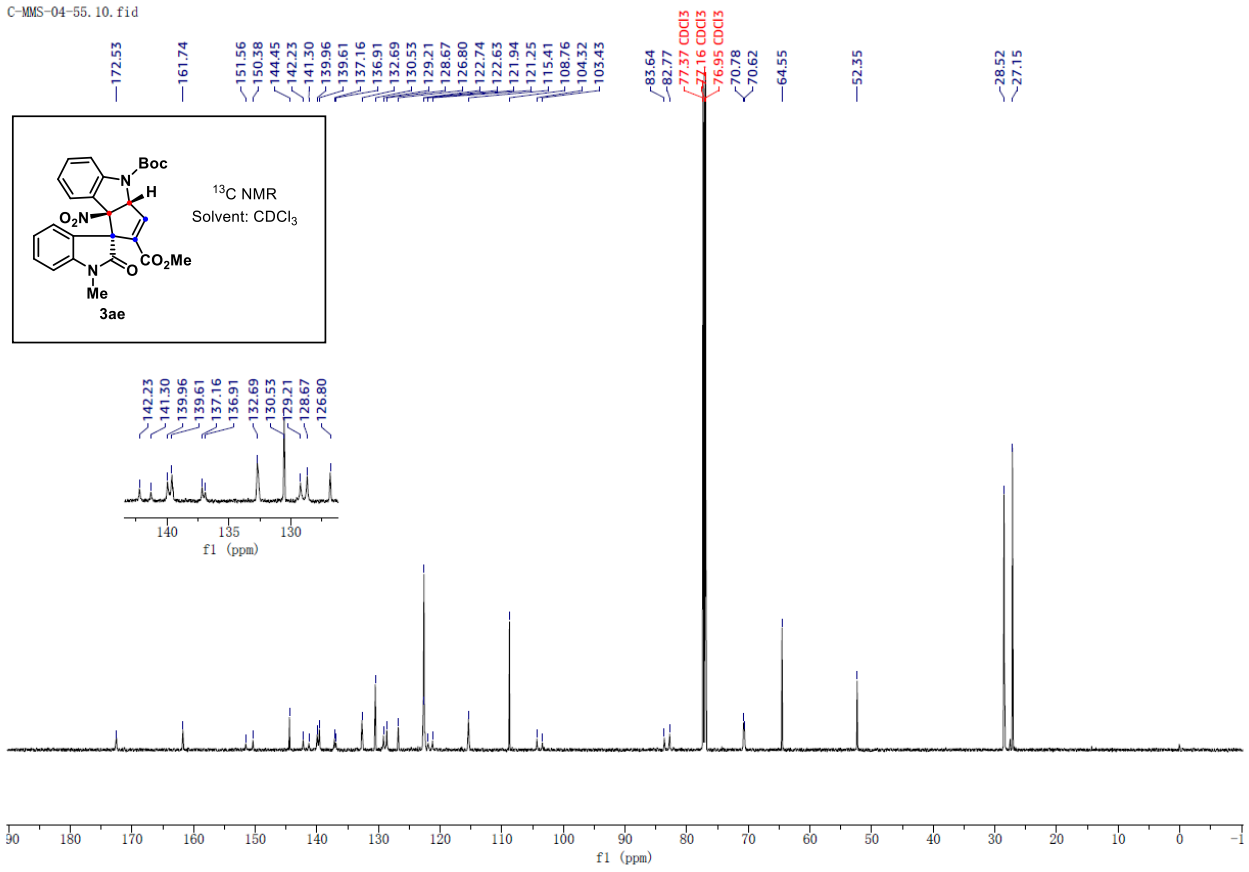

MMS-02-74C.12.fid
8.26
8.25
8.03
8.02
7.78
7.77
7.52
7.46
7.45
7.45
7.35
7.34
7.26 CDCl3
7.19
7.18
7.14
7.14
7.02
7.00
6.99
6.91
6.90
6.47
6.47
3.59
3.37
1.57 H2O
Ns
N
H
O2N
CO2Me
N
O
Me
3ac
1H NMR
Solvent: CDCl3
1.95
2.02
1.10
1.08
1.02
1.06
1.03
1.03
1.19
2.03
1.08
3.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

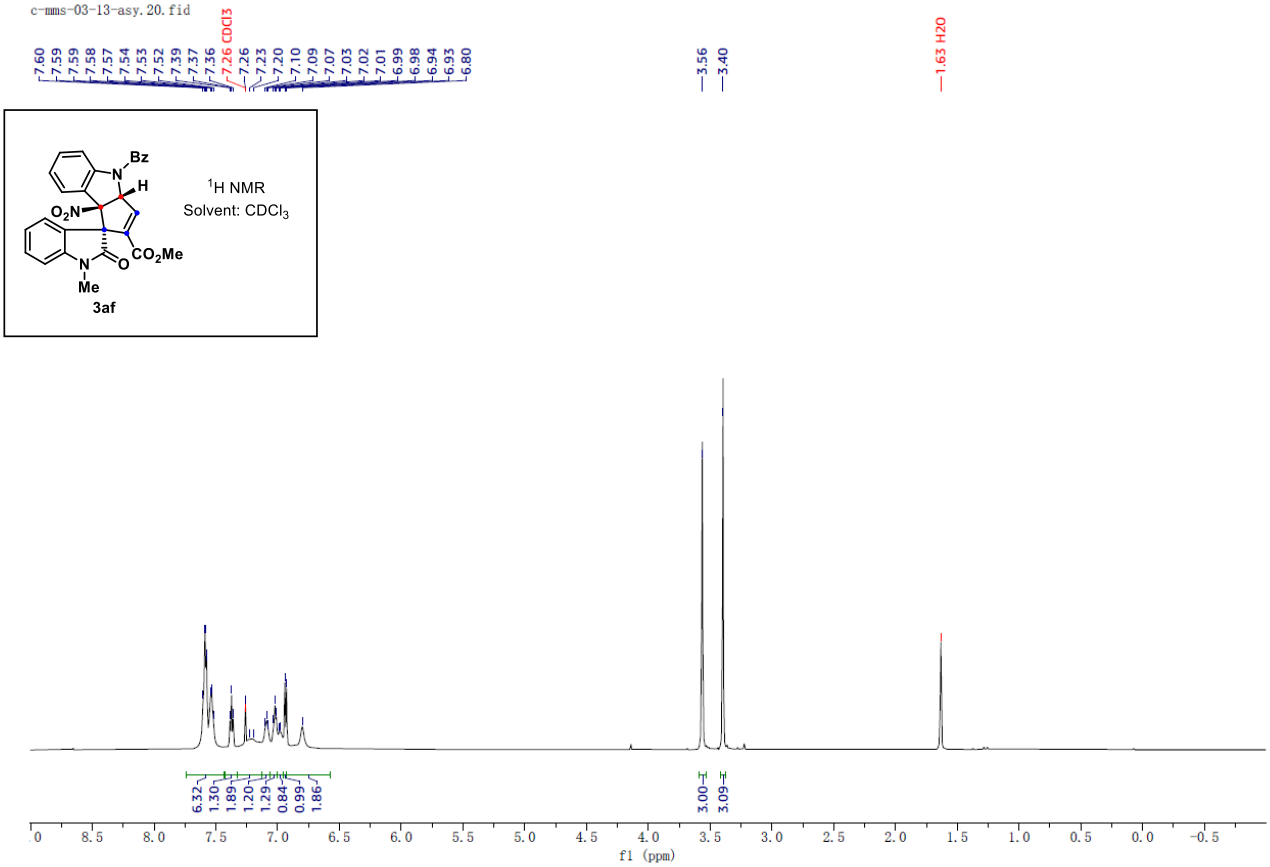

C-MMS-02-74C.11.fid
171.96
161.37
150.90
144.46
142.43
140.24
139.38
137.56
133.39
130.87
129.78
128.80
126.23
124.85
124.63
123.32
122.92
122.40
115.34
109.07
104.10
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.76
63.37
52.61
27.27
Ns
N
H
O2N
CO2Me
N
O
Me
3ac
13C NMR
Solvent: CDCl3
126.23
124.85
124.63
123.32
122.92
122.40
127 126 125 124 123 122
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

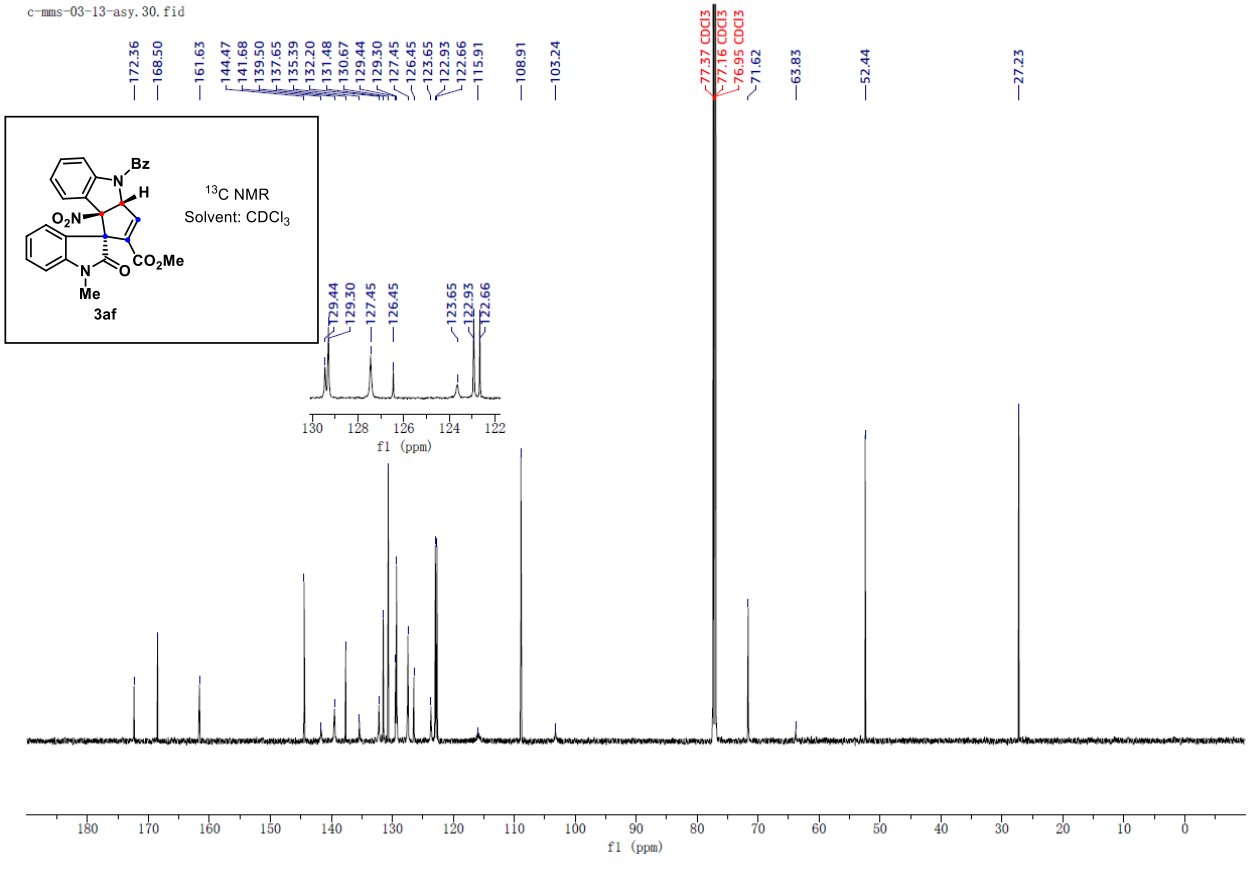

mms-02-94c.10.fid
8.02
8.00
7.53
7.51
7.50
7.46
7.42
7.41
7.38
7.37
7.35
7.26 CDCl3
7.26
7.21
7.12
7.10
7.09
7.07
7.01
6.99
6.97
6.95
6.93
6.92
6.69
6.60
5.43
5.43
5.41
5.38
5.36
3.55
3.39
1.57 H2O
Cbz
N
H
O2N
CO2Me
O
N
Me
3ad
1H NMR
Solvent: CDCl3
0.80
6.80
1.09
0.79
1.06
2.25
0.98
1.31
2.12
3.00
2.92
f1 (ppm)

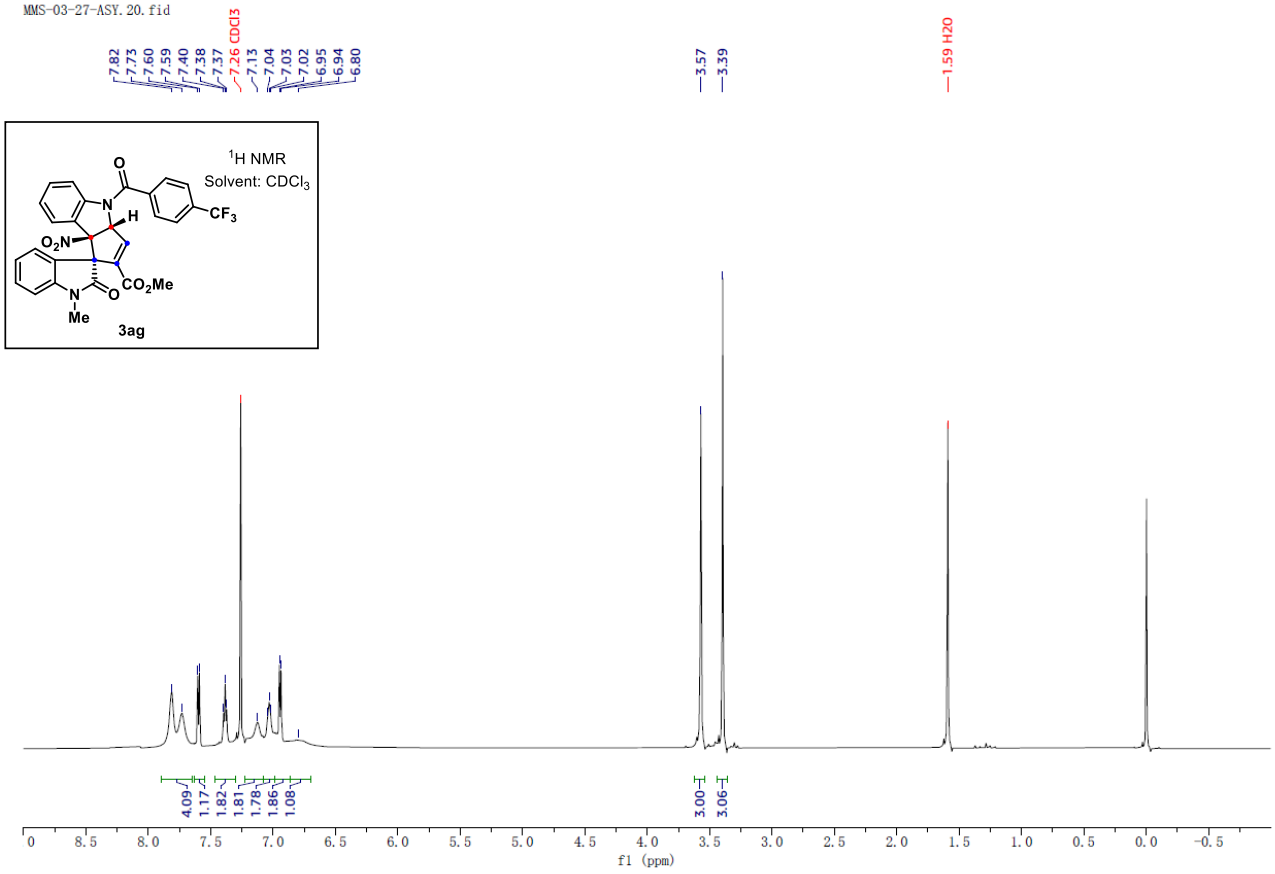

C-MMS-04-56R.12.fid
172.34
161.59
152.69
151.17
144.44
141.83
139.30
137.35
135.59
132.85
130.58
128.95
128.80
128.55
126.63
123.12
122.75
122.63
121.44
115.52
108.80
104.34
103.48
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
70.85
70.53
68.90
68.24
64.28
52.38
27.17
Cbz
N
H
O2N
CO2Me
O
N
Me
3ad
13C NMR
Solvent: CDCl3
128.95
128.80
128.55
123.12
122.75
122.63
128.4
f1 (ppm)
123
122
f1 (ppm)
f1 (ppm)

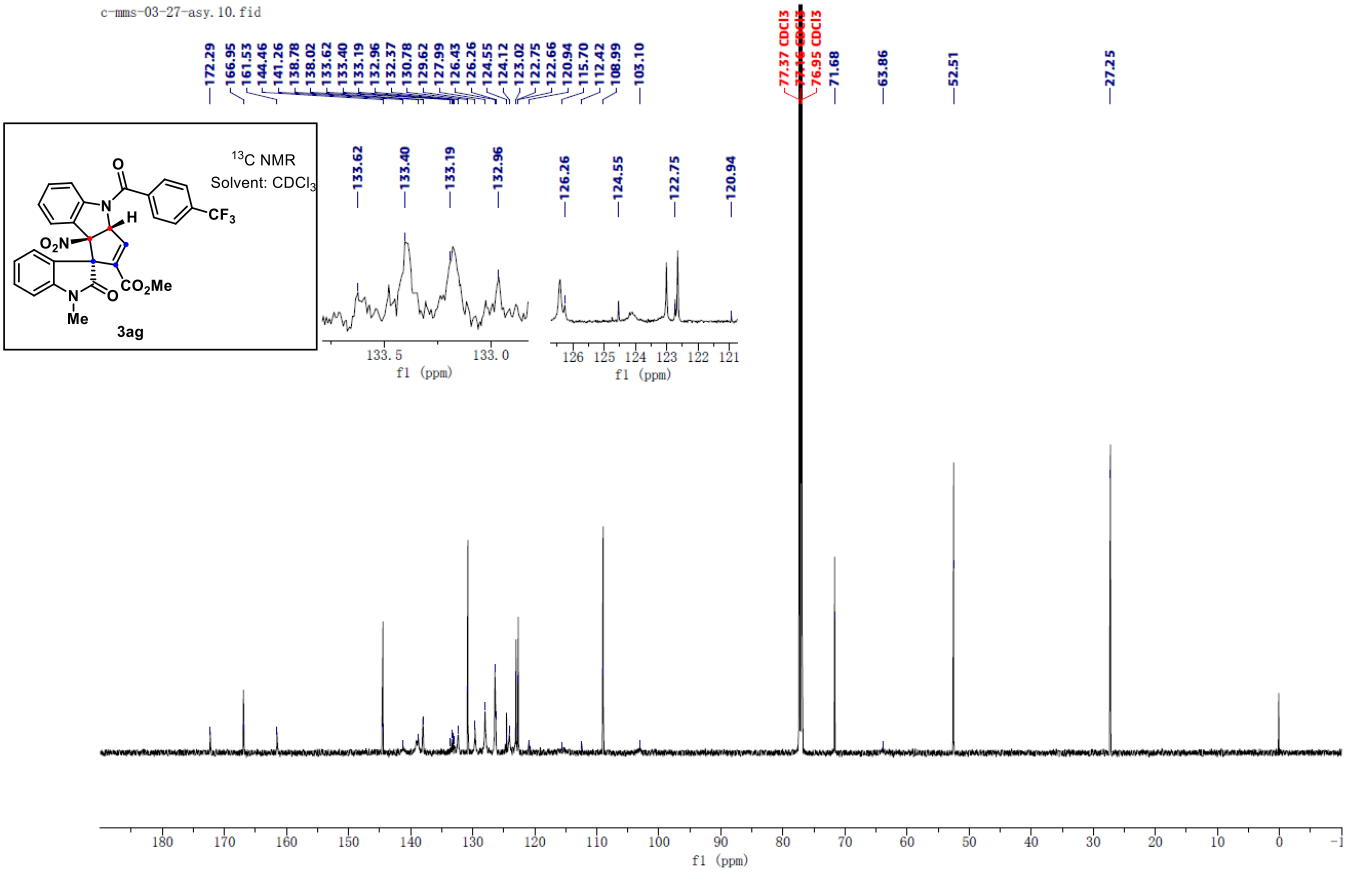

MMS-04-55RAC.21.fid
Boc
H
O2N
CO2Me
O
N
Me
3ae
1H NMR
Solvent: CDCl3
f1 (ppm)


C-MMS-04-55.10.fid
Boc
H
O2N
CO2Me
O
N
Me
3ae
13C NMR
Solvent: CDCl3
f1 (ppm)


c-mms-03-13-asy.20.fid
7.60
7.59
7.59
7.58
7.57
7.54
7.53
7.52
7.39
7.37
7.36
7.26 CDCl3
7.26
7.23
7.20
7.10
7.09
7.07
7.03
7.02
7.01
6.99
6.98
6.94
6.93
6.80
3.56
3.40
1.63 H2O
Bz
N
H
O2N
CO2Me
N
O
Me
3af
1H NMR
Solvent: CDCl3
6.32
1.30
1.89
1.20
1.29
0.84
0.99
1.86
3.00
3.09
f1 (ppm)

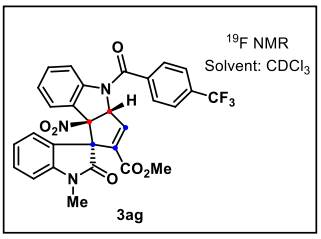

c-mms-03-13-asy.30.fid
172.36
168.50
161.63
144.47
141.68
139.50
137.65
135.39
132.20
131.48
130.67
129.44
129.30
127.45
126.45
123.65
122.93
122.66
115.91
108.91
103.24
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.62
63.83
52.44
27.23
Bz
N
H
O2N
CO2Me
N
O
Me
3af
13C NMR
Solvent: CDCl3
f1 (ppm)
f1 (ppm)


MMS-03-27-ASY.20.fid
7.82
7.73
7.60
7.59
7.40
7.38
7.37
7.26 CDCl3
7.13
7.04
7.03
7.02
6.95
6.94
6.80
3.57
3.39
1.59 H2O
1H NMR
Solvent: CDCl3
3ag
4.09
1.17
1.82
1.81
1.78
1.86
1.08
3.00
3.06
f1 (ppm)

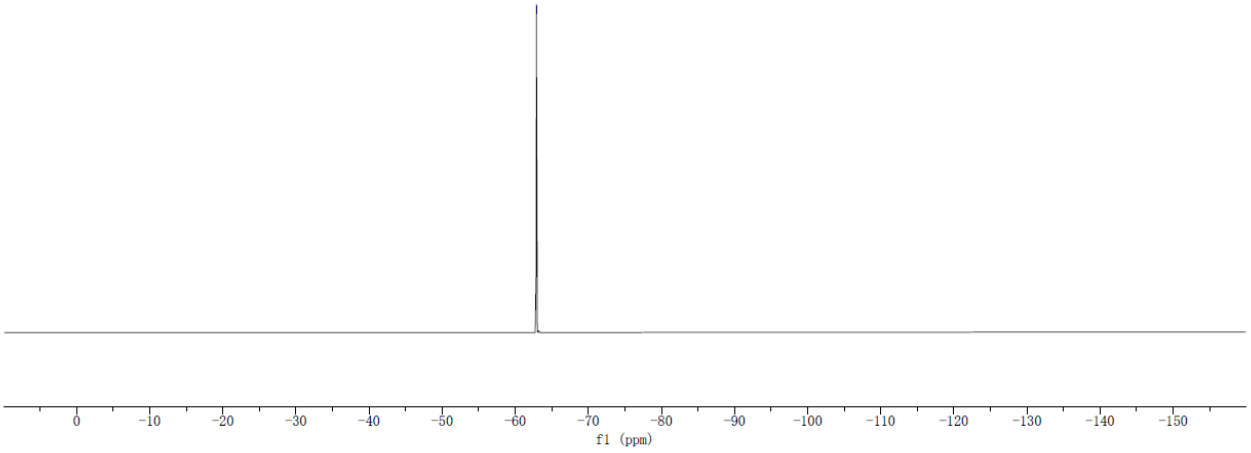

c-mms-03-27-asy.10.fid
172.29
166.95
161.53
144.46
141.26
138.78
138.02
133.62
133.40
133.19
132.96
132.37
130.78
129.62
127.99
126.43
126.26
124.55
124.12
123.02
122.75
122.66
120.94
115.70
112.42
108.99
103.10
77.37 CDCl3
76.95 CDCl3
71.68
63.86
52.51
27.25
13C NMR
Solvent: CDCl3
3ag
133.62
133.40
133.19
132.96
126.26
124.55
122.75
120.94
f1 (ppm)

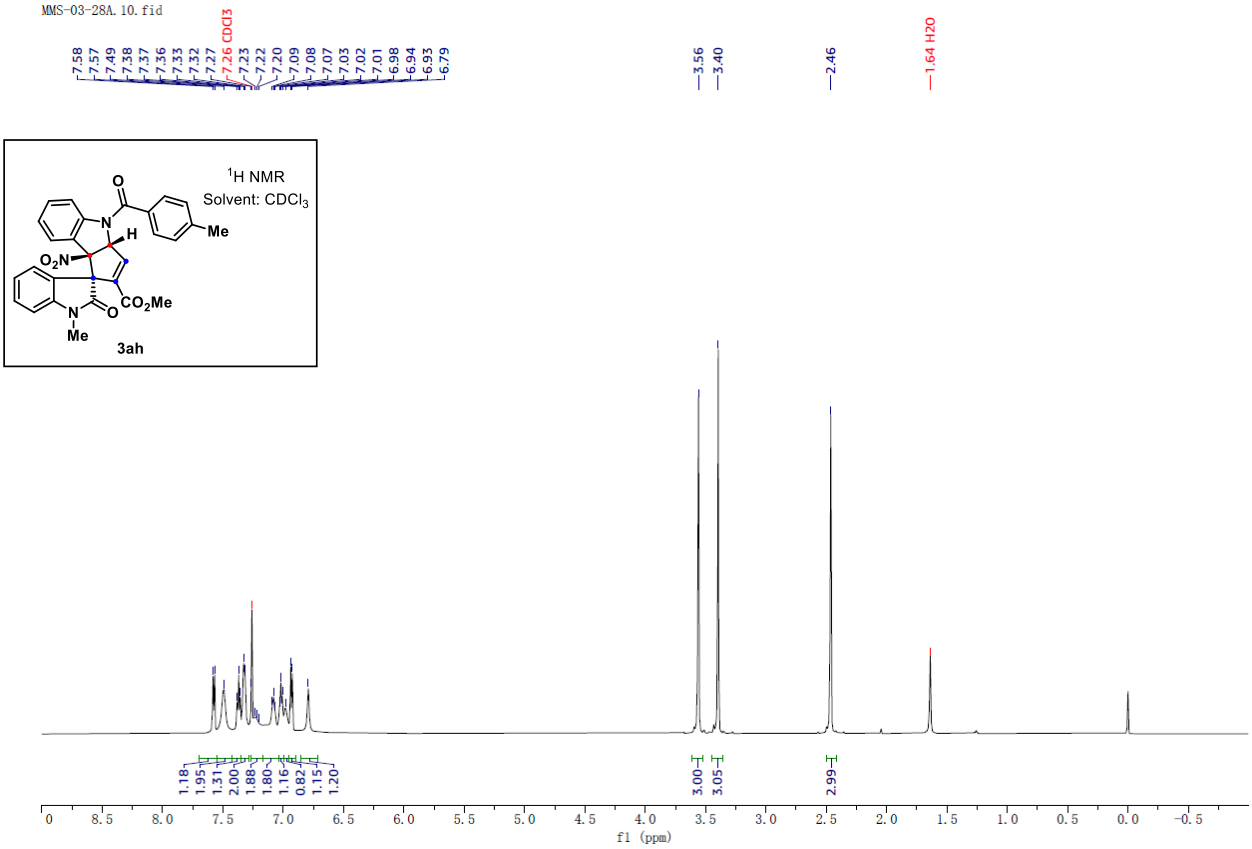
F-MMS-03-27A.12.fid

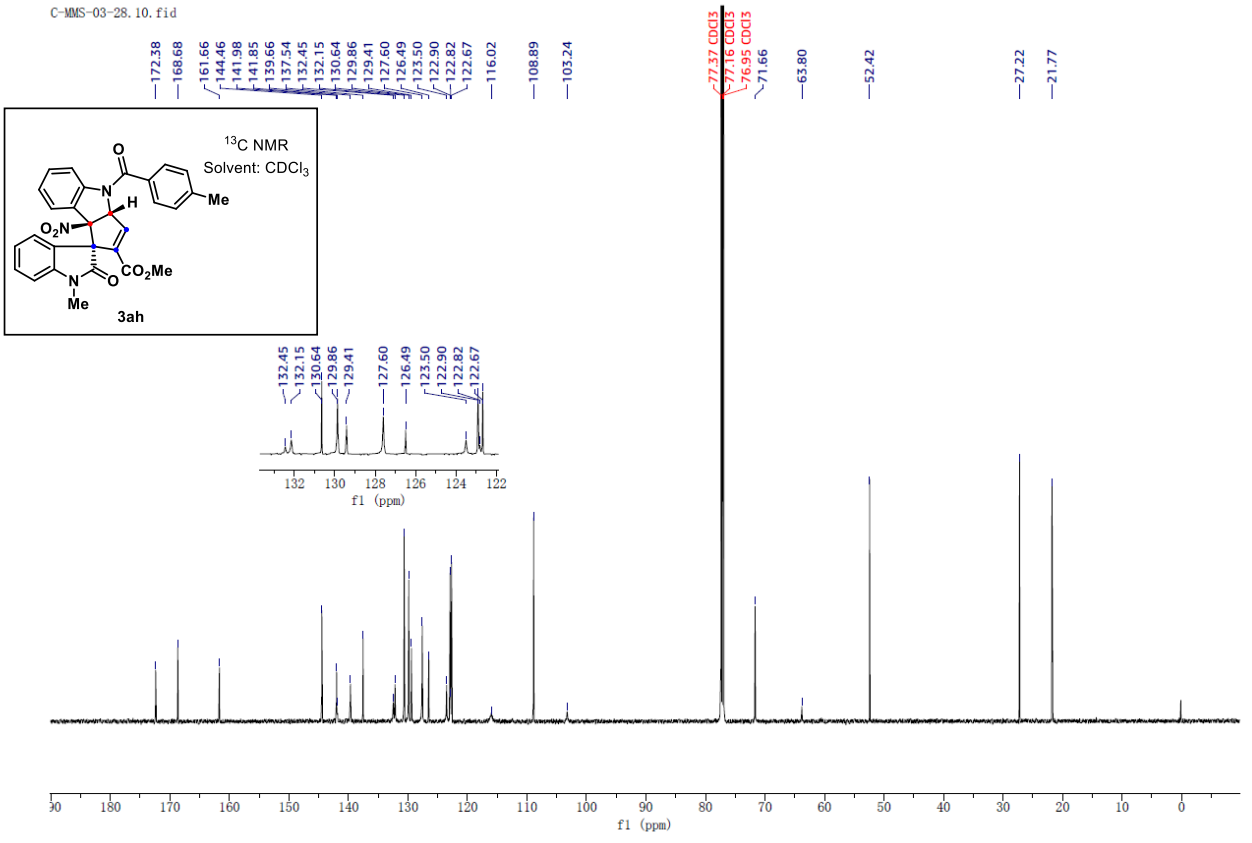
-62.89



3ag




MMS-03-28A.10.fid
7.58
7.57
7.49
7.38
7.37
7.36
7.33
7.32
7.27
7.26 CDCl3
7.23
7.22
7.20
7.09
7.08
7.07
7.03
7.02
7.01
6.98
6.94
6.93
6.79
3.56
3.40
2.46
1.64 H2O
1H NMR
Solvent: CDCl3
3ah
1.18
1.95
1.31
2.00
1.88
1.80
1.16
0.82
1.15
1.20
3.00
3.05
2.99
f1 (ppm)


C-MMS-03-28.10.fid
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168.68
161.66
144.46
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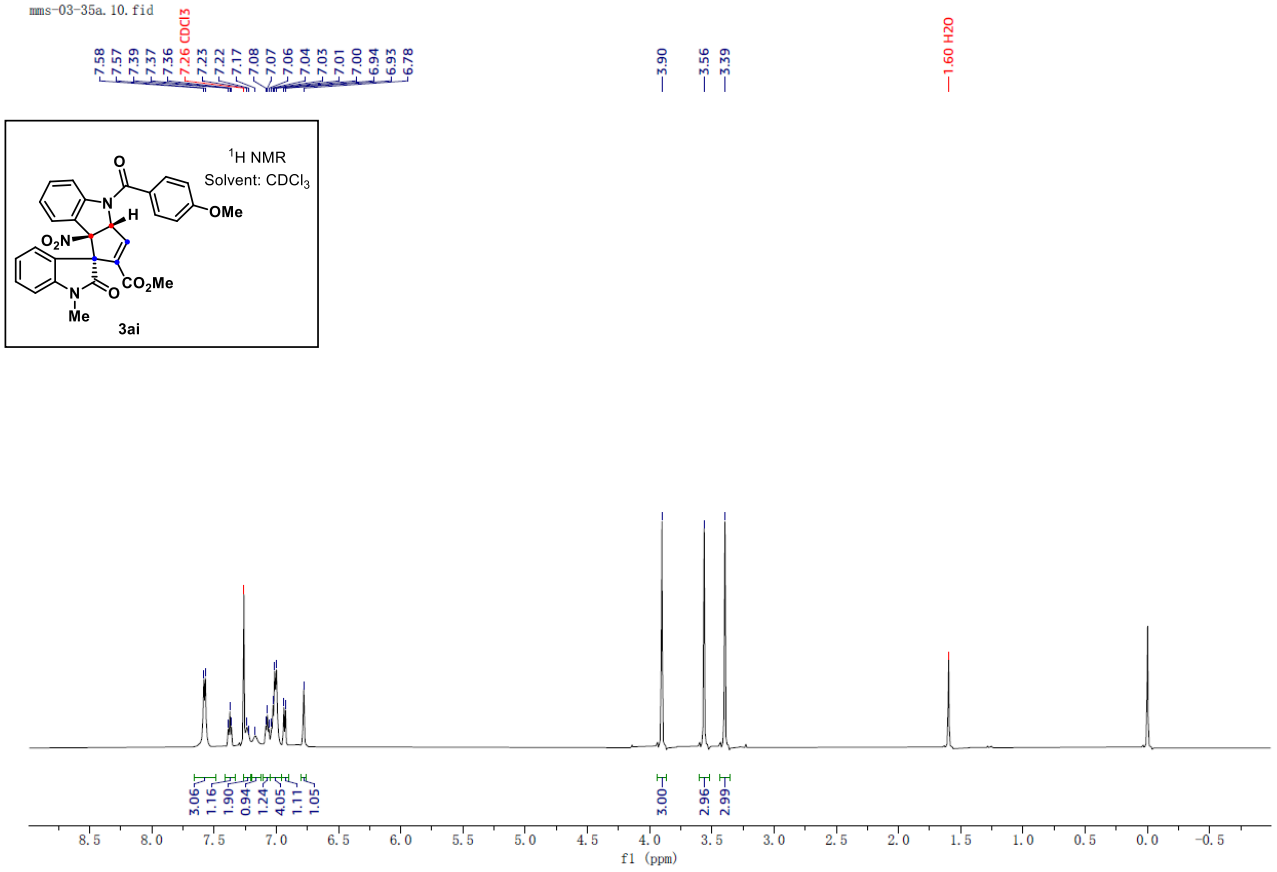
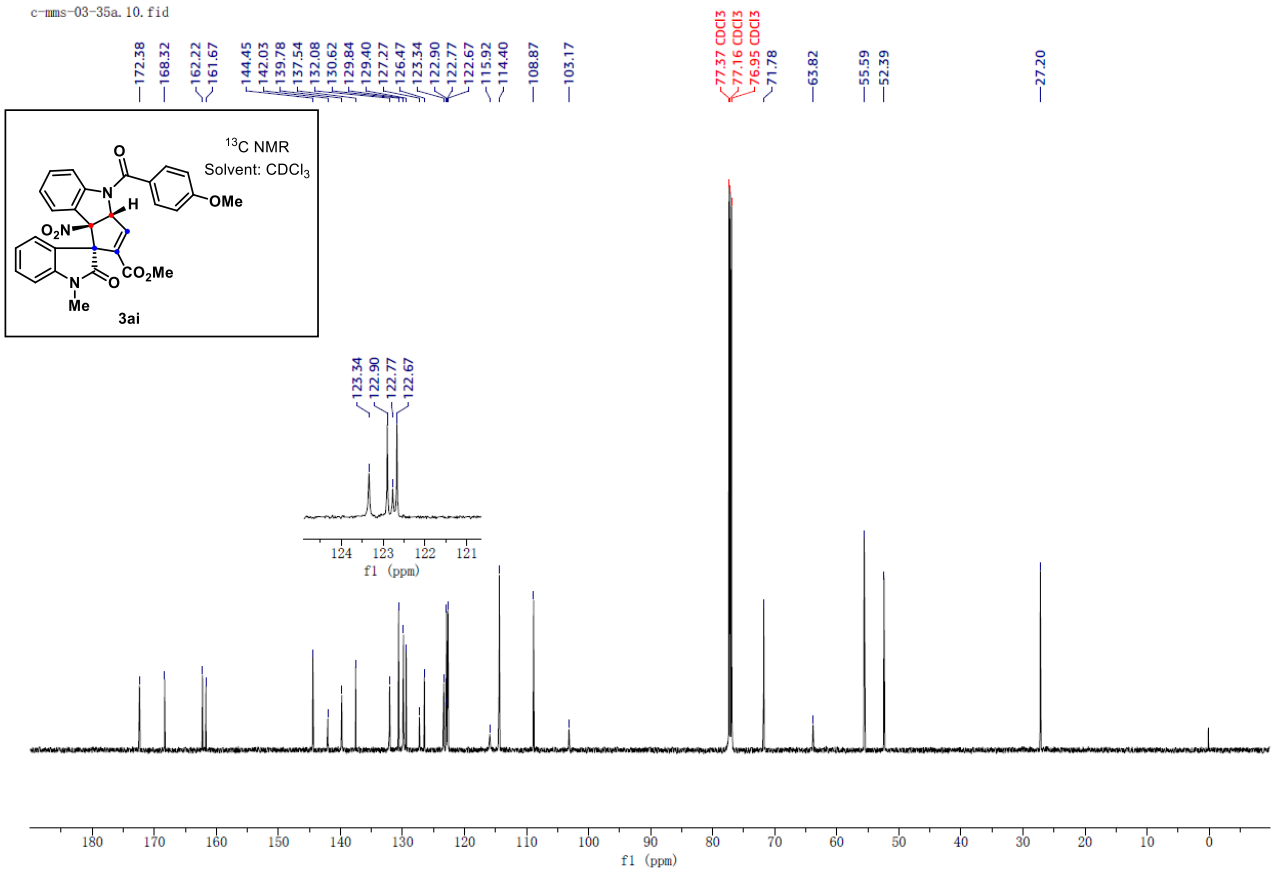
139.66
137.54
132.45
132.15
130.64
129.86
129.41
127.60
126.49
123.50
122.90
122.82
122.67
116.02
108.89
103.24
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.66
63.80
52.42
27.22
21.77
13C NMR
Solvent: CDCl3
3ah
f1 (ppm)
f1 (ppm)


mms-03-35a.10.fid
7.58
7.57
7.39
7.37
7.36
7.26 CDCl3
7.23
7.22
7.17
7.08
7.07
7.06
7.04
7.03
7.01
7.00
6.94
6.93
6.78
3.90
3.56
3.39
1.60 H2O
1H NMR
Solvent: CDCl3
OMe
O2N
H
CO2Me
N
Me
O
3ai
3.06
1.16
1.90
0.94
1.24
4.05
1.11
1.05
3.00
2.96
2.99
f1 (ppm)


c-mms-03-35a.10.fid
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161.67
144.45
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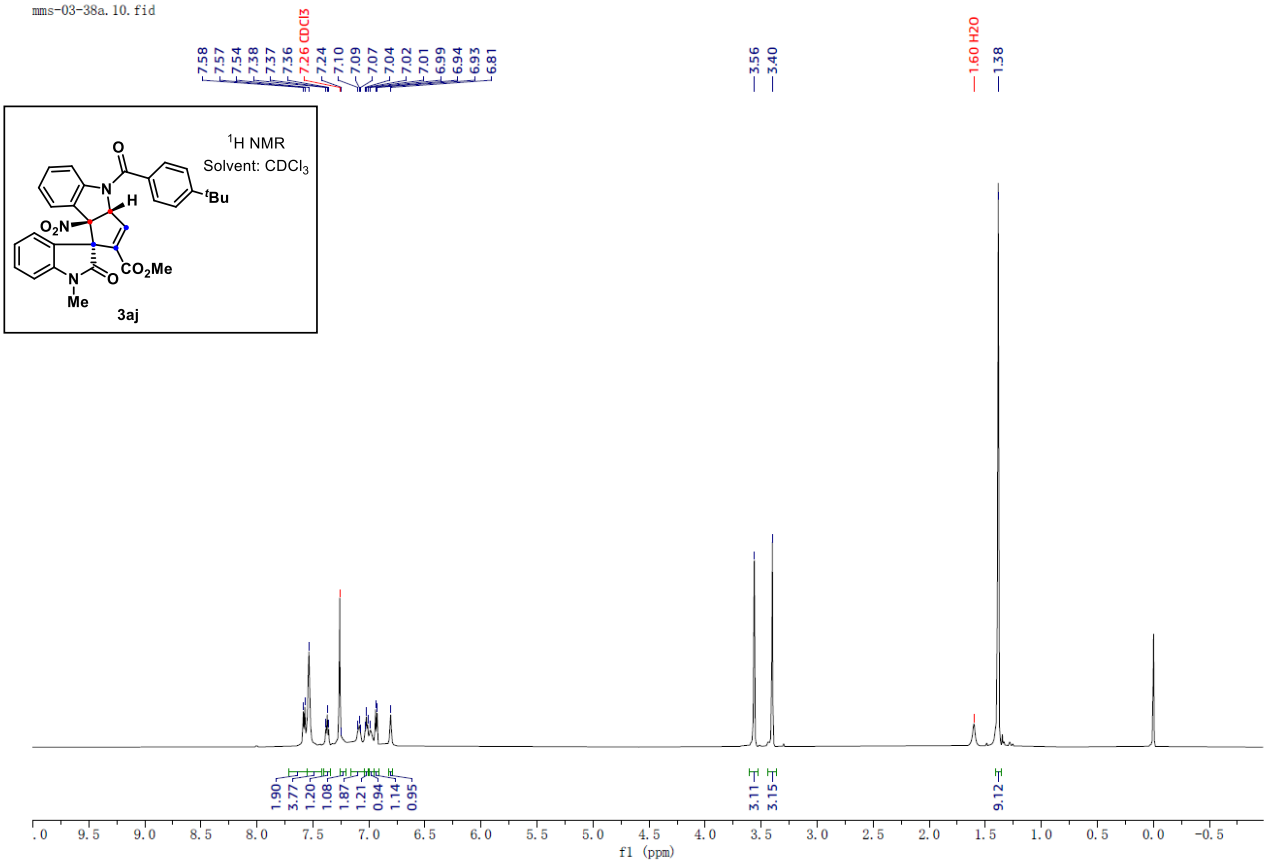
137.54
132.08
130.62
129.84
129.40
127.27
126.47
123.34
122.90
122.77
122.67
115.92
114.40
108.87
103.17
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.78
63.82
55.59
52.39
27.20
13C NMR
Solvent: CDCl3
OMe
O2N
H
CO2Me
N
Me
O
3ai
123.34
122.90
122.77
122.67
f1 (ppm)
f1 (ppm)


mms-03-38a.10.fid
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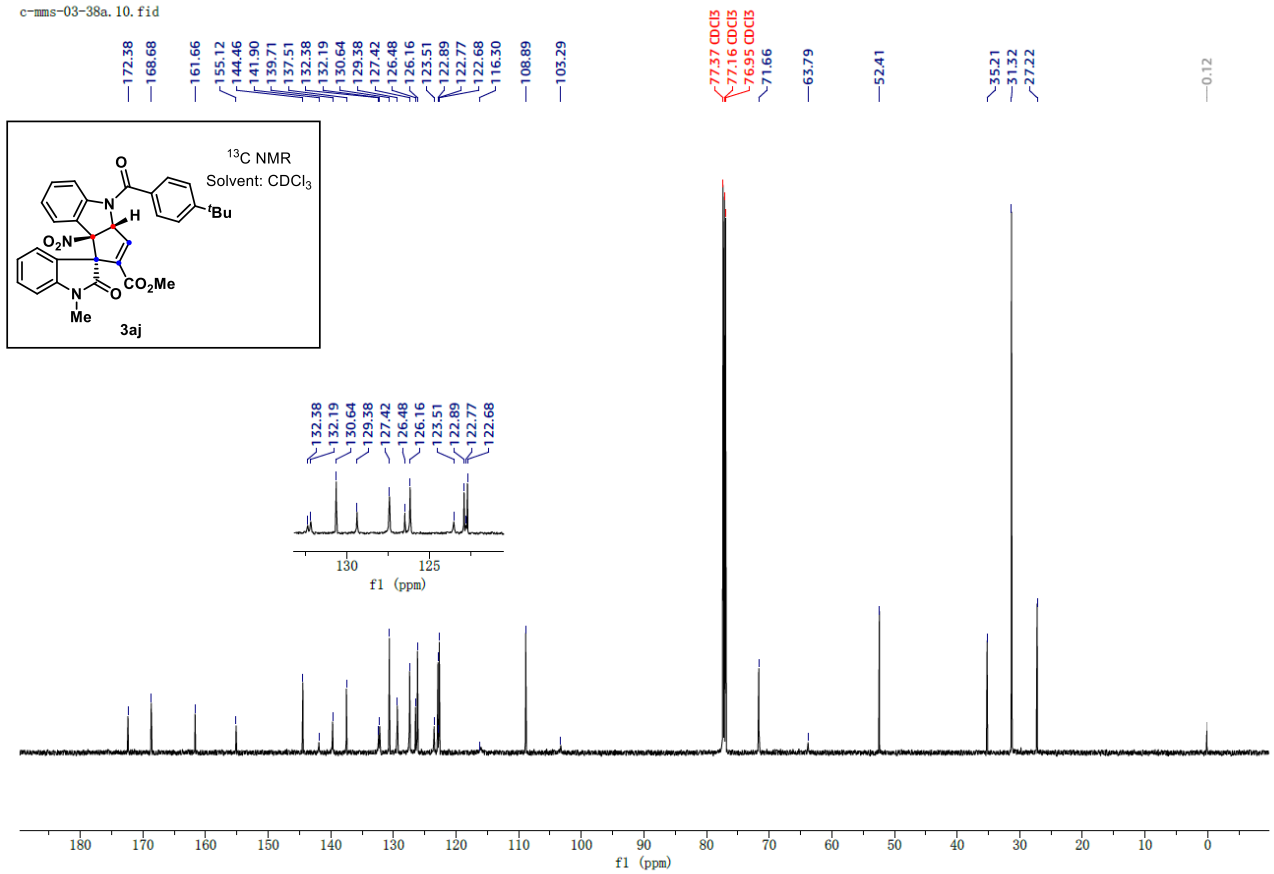
7.57
7.54
7.38
7.37
7.36
7.26 CDCl3
7.24
7.10
7.09
7.07
7.04
7.02
7.01
6.99
6.94
6.93
6.81
3.56
3.40
1.60 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Me
3aj
1.90
3.77
1.20
1.08
1.87
1.21
0.94
1.14
0.95
3.11
3.15
9.12
f1 (ppm)


c-mms-03-38a.10.fid
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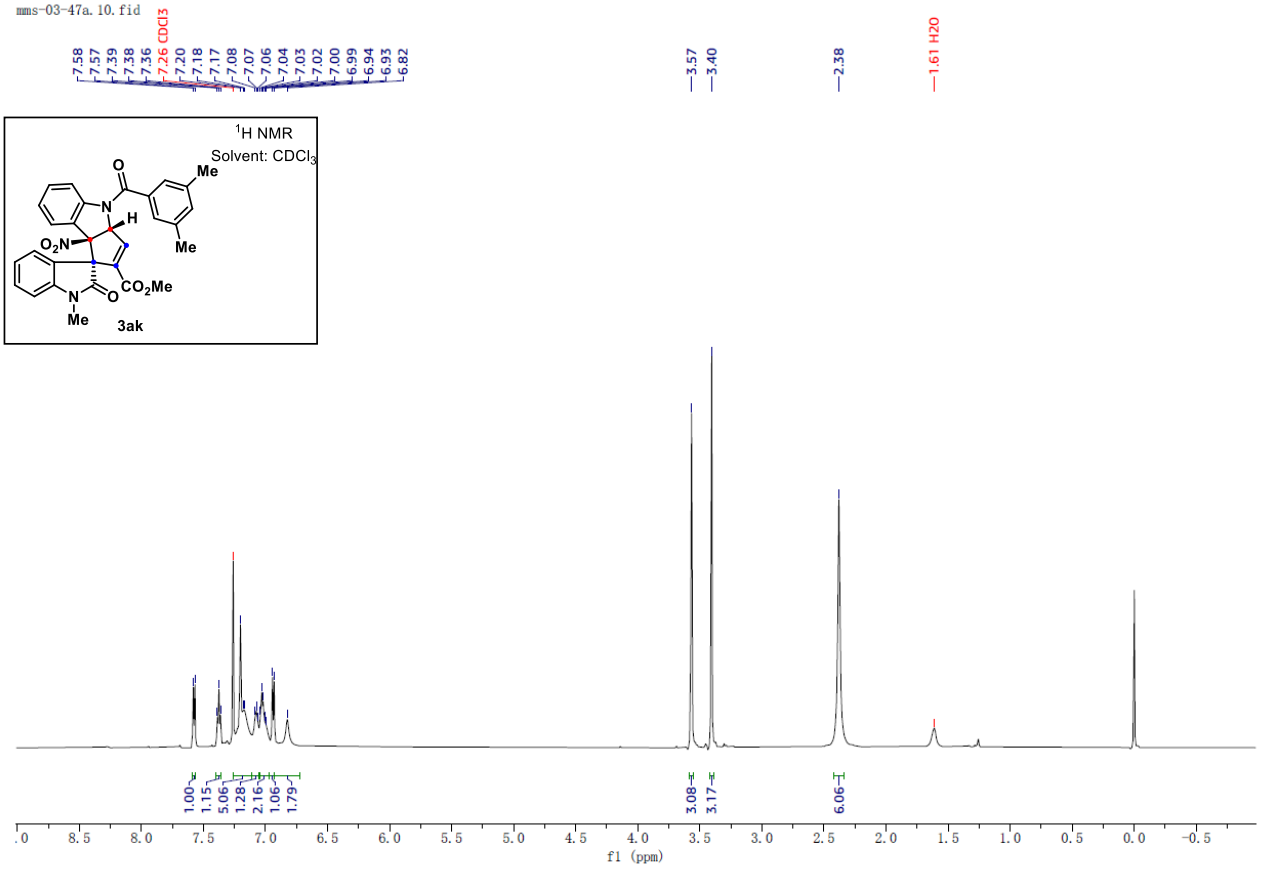
139.71
137.51
132.38
132.19
130.64
129.38
127.42
126.48
126.16
123.51
122.89
122.77
122.68
116.30
108.89
105.29
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.66
63.79
52.41
35.21
31.32
27.22
0.12
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Me
3aj
f1 (ppm)
f1 (ppm)


mms-03-47a.10.fid
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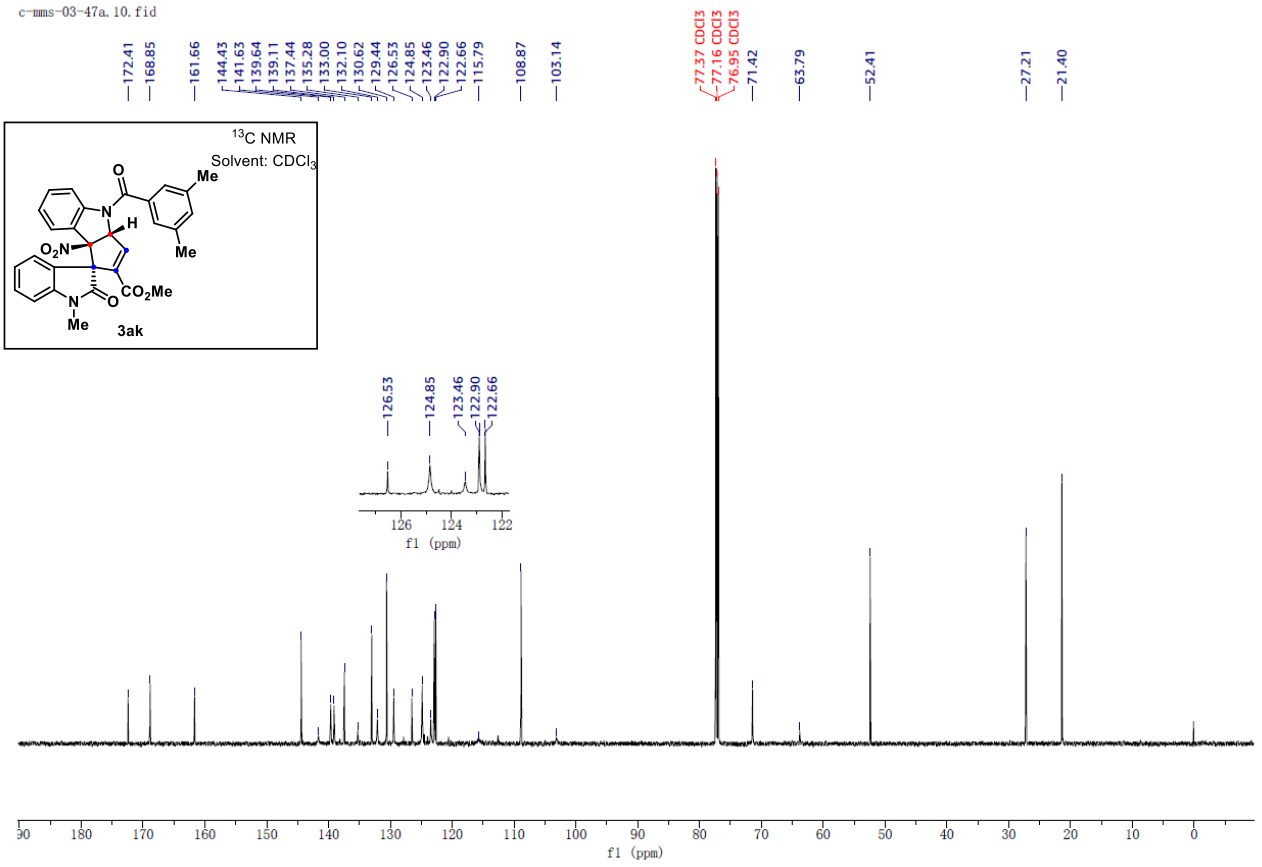
7.57
7.39
7.38
7.36
7.26 CDCl3
7.20
7.18
7.17
7.08
7.07
7.06
7.04
7.03
7.02
7.00
6.99
6.94
6.93
6.82
3.57
3.40
2.38
1.61 H2O
1H NMR
Solvent: CDCl3
3ak
1.00
1.15
5.06
1.28
2.16
1.06
1.79
3.08
3.17
6.06
f1 (ppm)


c-mms-03-47a.10.fid
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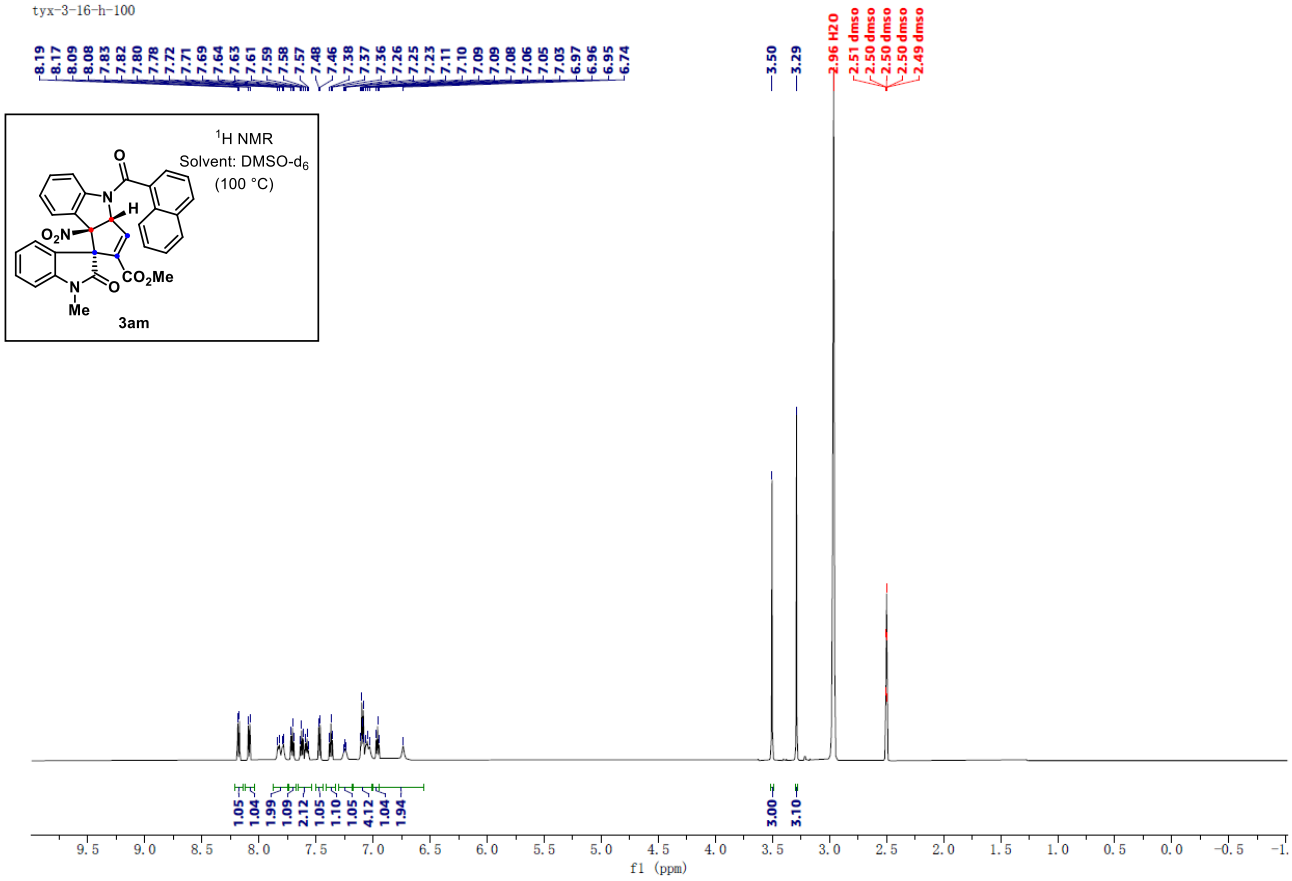
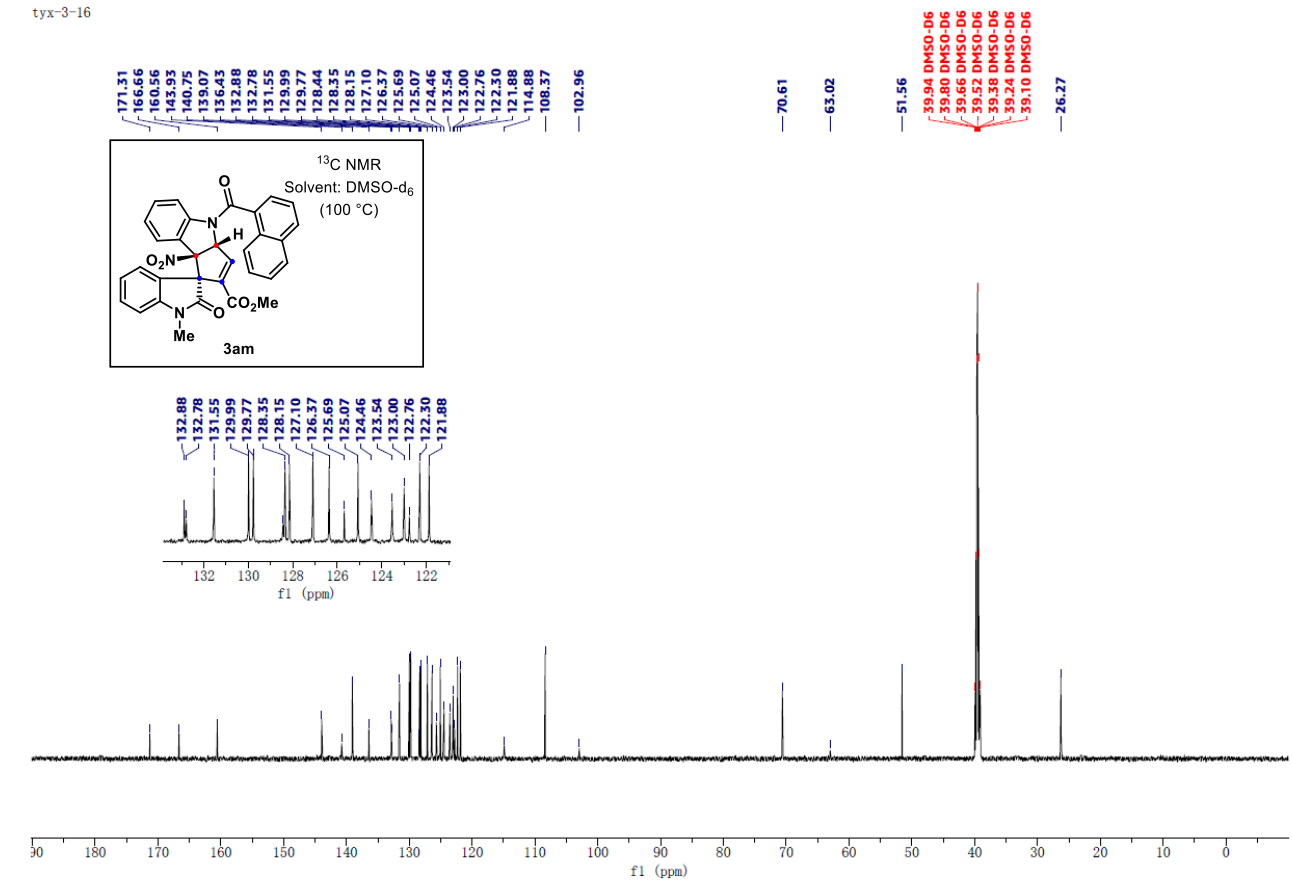
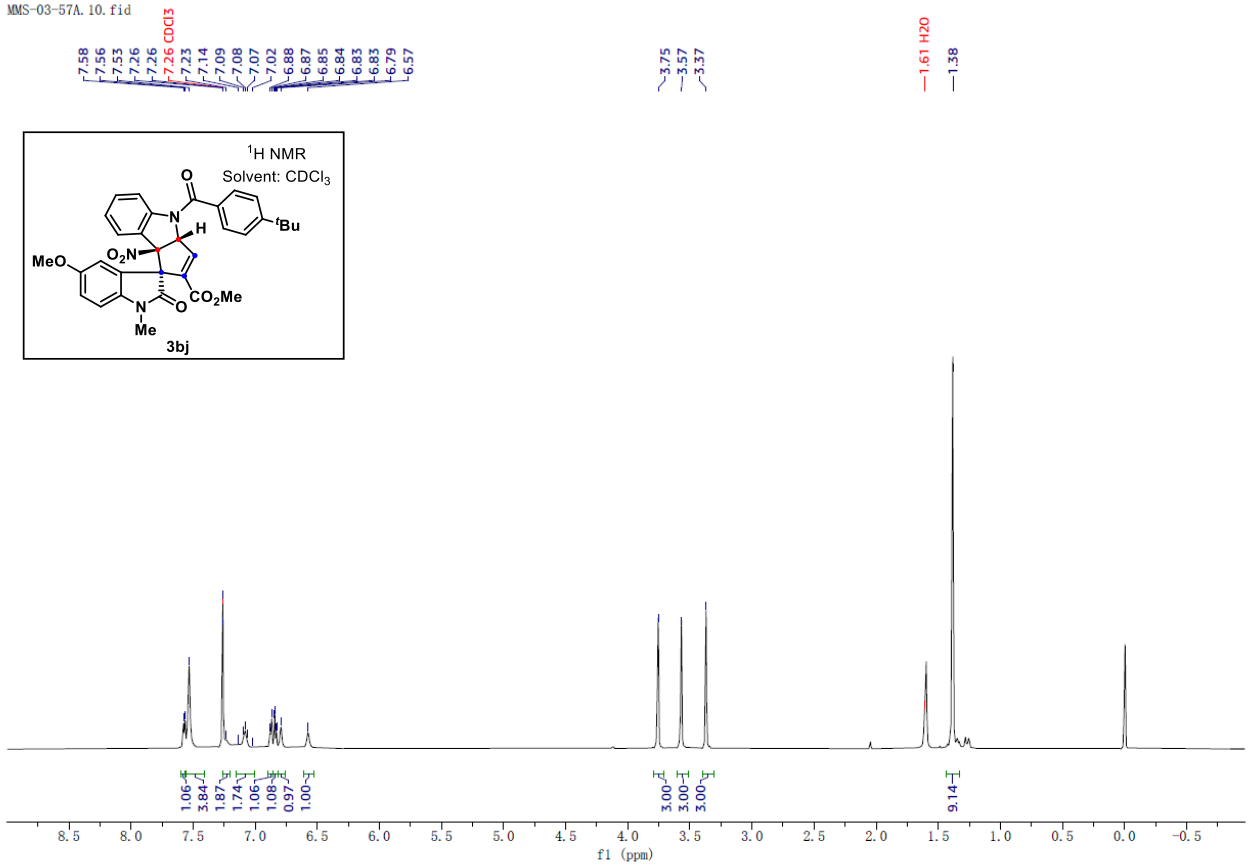
168.85
161.66
144.43
141.63
139.64
139.11
137.44
135.28
133.00
132.10
130.62
129.44
126.53
124.85
123.46
122.90
122.66
115.79
108.87
103.14
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.42
63.79
52.41
27.21
21.40
13C NMR
Solvent: CDCl3
3ak
f1 (ppm)


tyx-3-16-h-100
^{1}H NMR
Solvent: DMSO-d$_6$
(100 °C)
3am
f1 (ppm)


tyx-3-16
^{13}C NMR
Solvent: DMSO-d$_6$
(100 °C)
3am
f1 (ppm)


MMS-03-57A.10.fid
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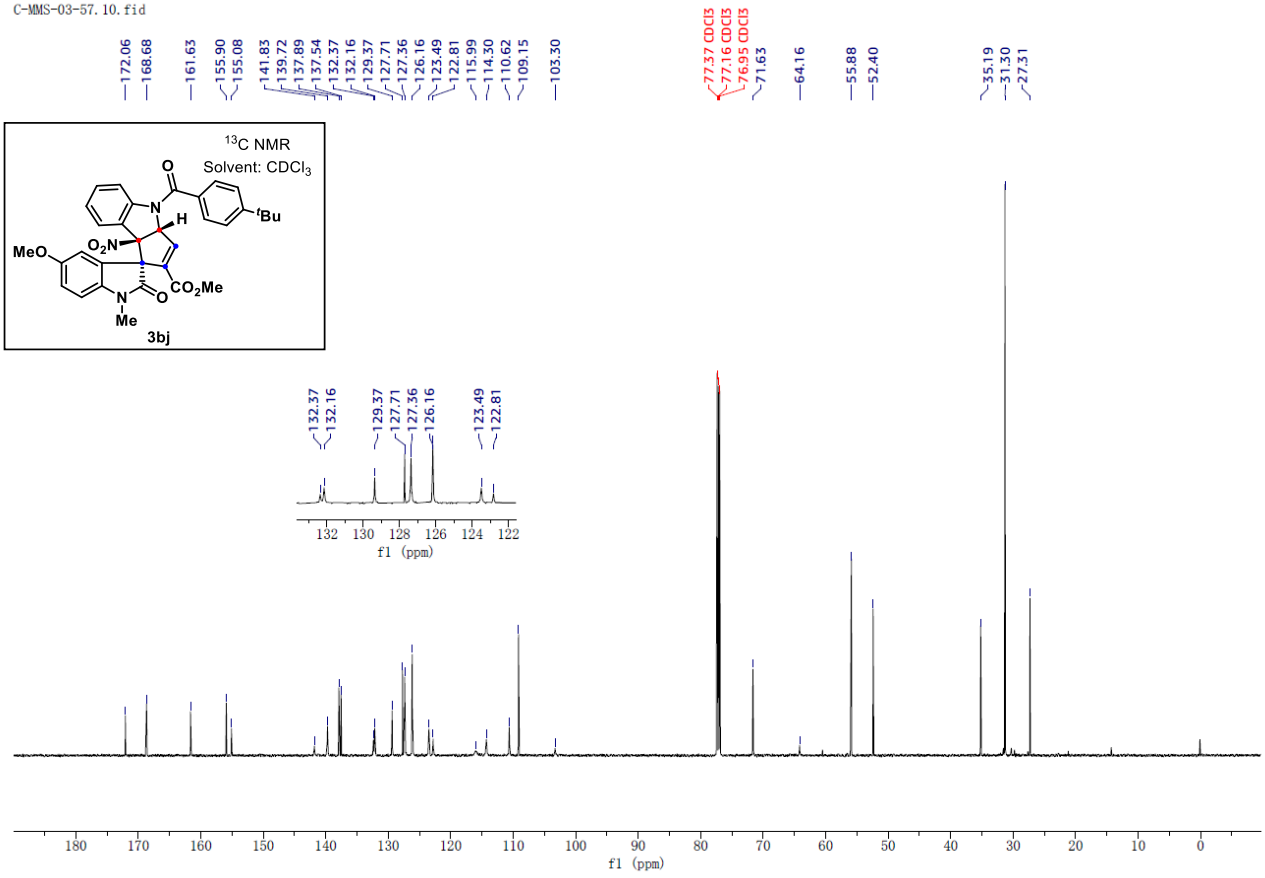
7.56
7.53
7.26
7.26
7.26 CDCl3
7.23
7.14
7.09
7.08
7.07
7.02
6.88
6.87
6.85
6.84
6.83
6.83
6.79
6.57
3.75
3.57
3.37
1.61 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
MeO
O2N
CO2Me
Me
3bj
1.06
3.84
1.87
1.74
1.06
1.08
0.97
1.00
3.00
3.00
3.00
9.14
f1 (ppm)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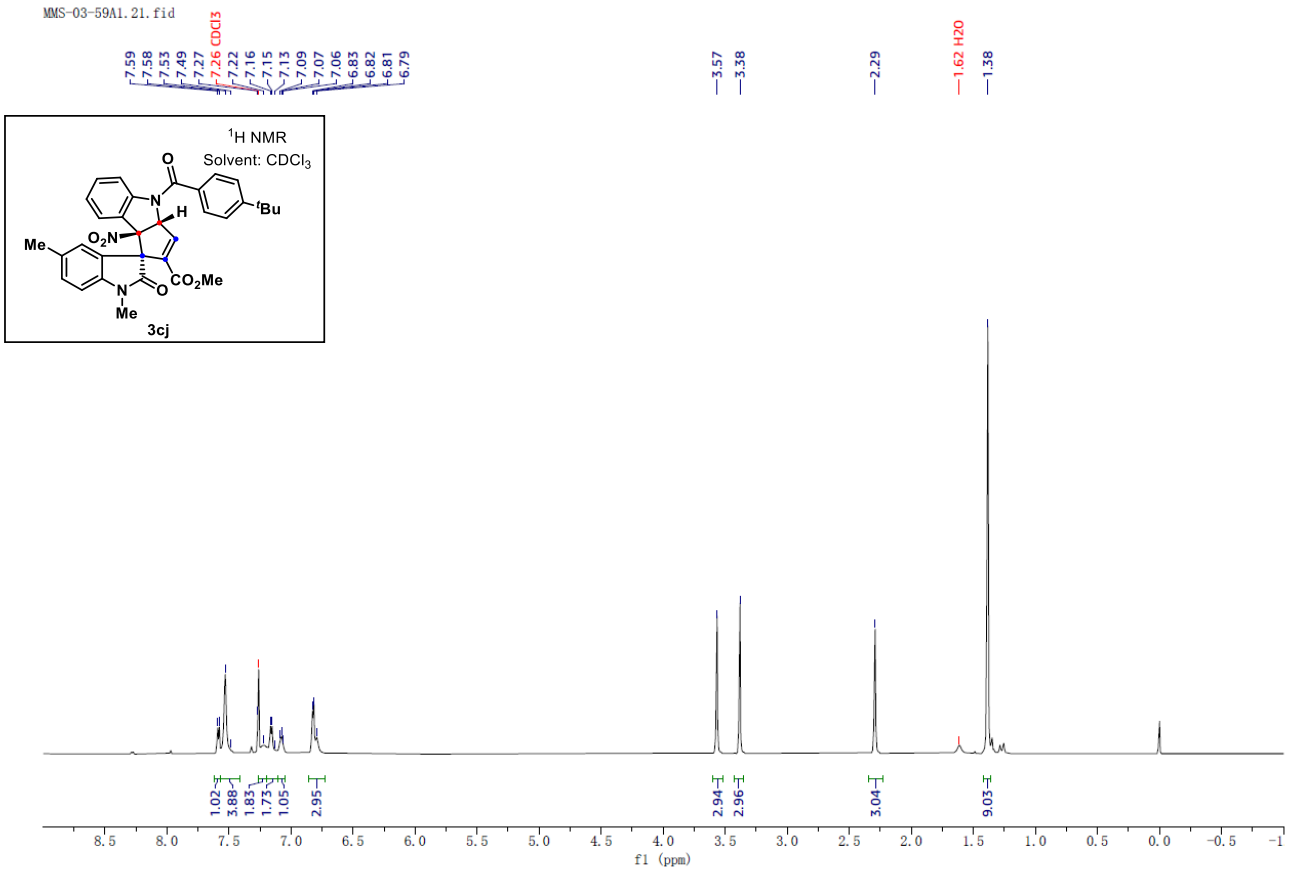
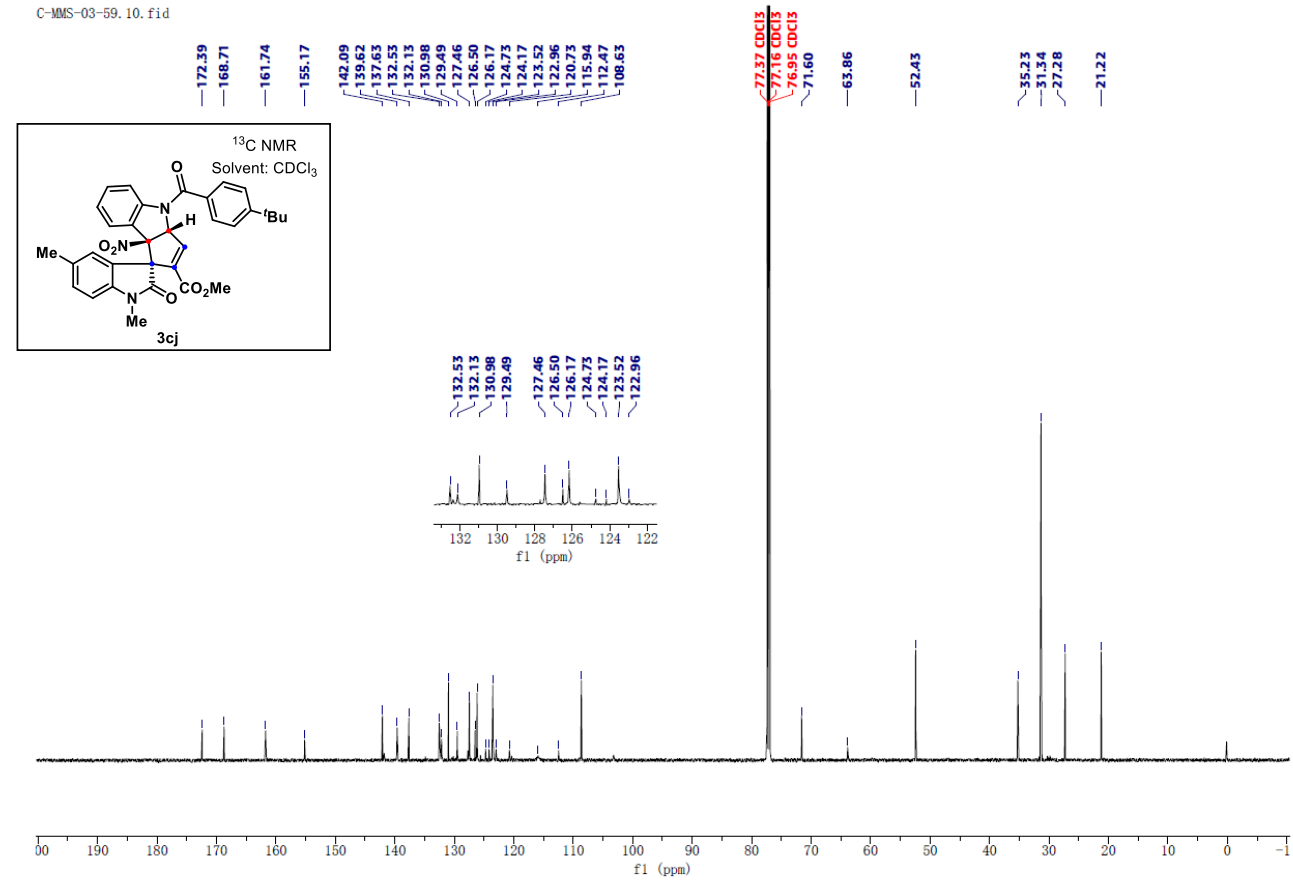
168.68
161.63
155.90
155.08
141.83
139.72
137.89
137.54
132.37
132.16
129.37
127.71
127.36
126.16
123.49
122.81
115.99
114.30
110.62
109.15
103.30
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.63
64.16
55.88
52.40
35.19
31.30
27.31
13C NMR
Solvent: CDCl3
tBu
MeO
O2N
CO2Me
Me
3bj
132.37
132.16
129.37
127.71
127.36
126.16
123.49
122.81
f1 (ppm)
f1 (ppm)


MMS-03-59A1.21.fid
7.59
7.58
7.53
7.49
7.27
7.26 CDCl3
7.22
7.16
7.15
7.13
7.09
7.07
7.06
6.83
6.82
6.81
6.79
3.57
3.38
2.29
1.62 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
Me
CO2Me
Me
3cj
1.02
3.88
1.83
1.73
1.05
2.95
2.94
2.96
3.04
9.03
f1 (ppm)


C-MMS-03-59.10.fid
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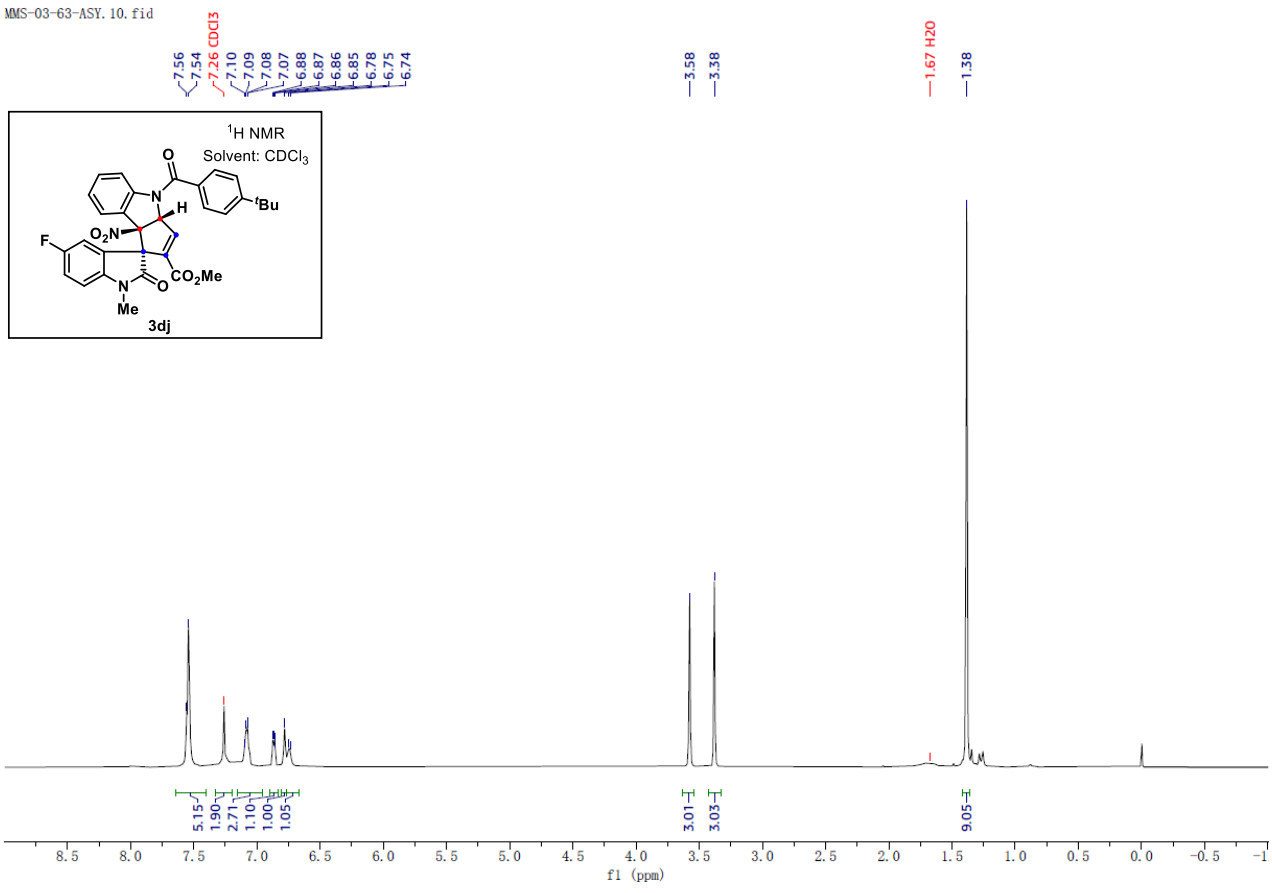
161.74
155.17
142.09
139.62
137.63
132.53
132.13
130.98
129.49
127.46
126.50
126.17
124.73
124.17
123.52
122.96
120.73
115.94
112.47
108.63
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.60
63.86
52.43
35.23
31.34
27.28
21.22
13C NMR
Solvent: CDCl3
tBu
Me
CO2Me
Me
3cj
f1 (ppm)
f1 (ppm)


MMS-03-63-ASY.10.fid
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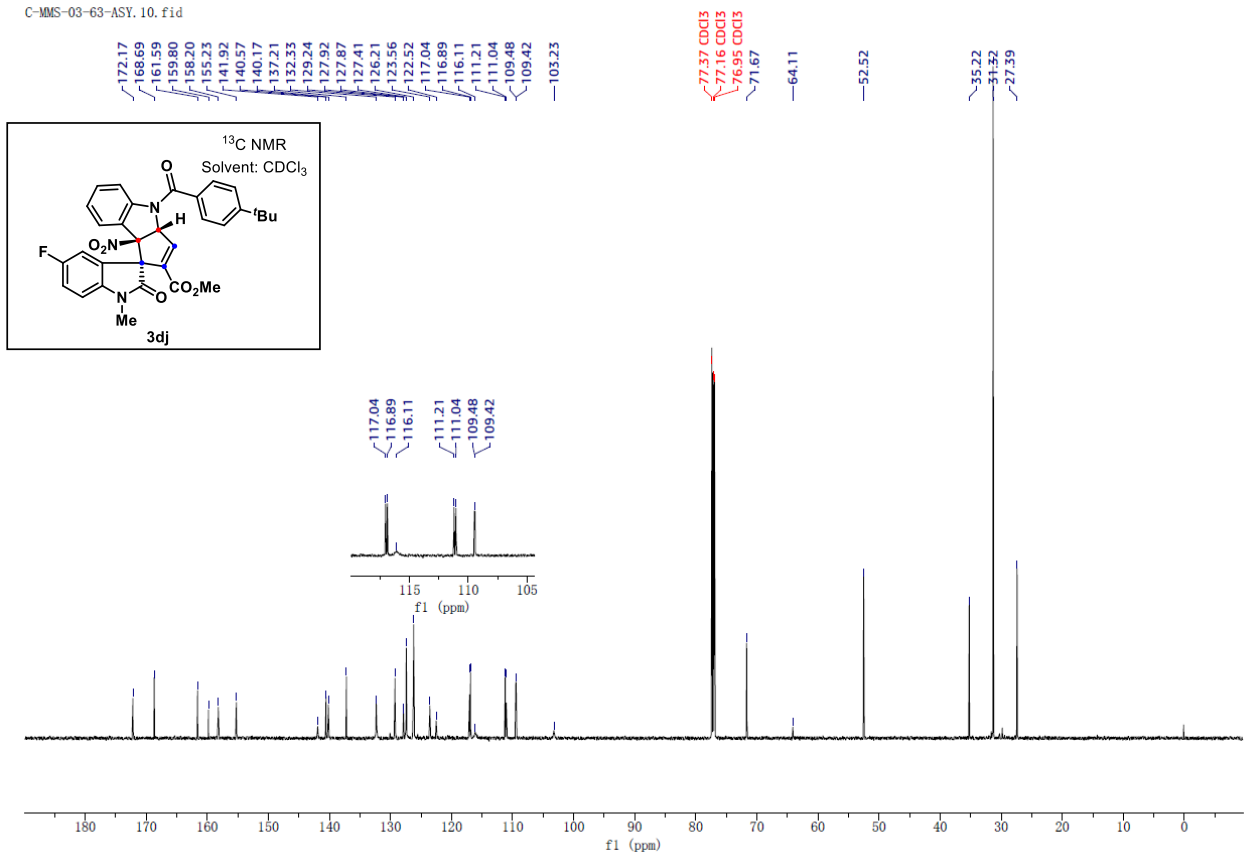
7.54
7.26 CDCl3
7.10
7.09
7.08
7.07
6.88
6.87
6.86
6.85
6.78
6.75
6.74
3.58
3.38
1.67 H2O
1.38
1H NMR
Solvent: CDCl3
3dj
5.15
1.90
2.71
1.10
1.00
1.05
3.01
3.03
9.05
f1 (ppm)


C-MMS-03-63-ASY.10.fid
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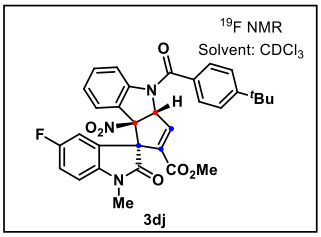
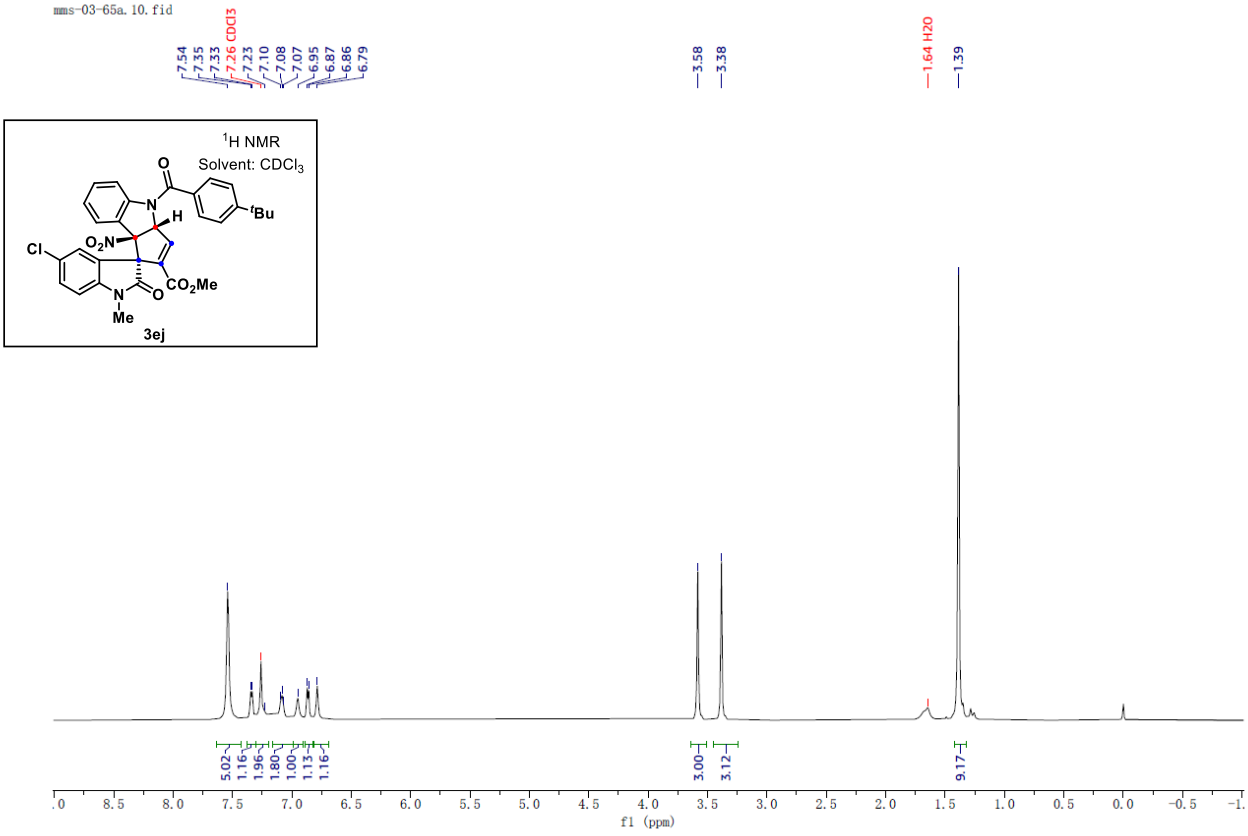
168.69
161.59
159.80
158.20
155.23
141.92
140.57
140.17
137.21
132.33
129.24
127.92
127.87
127.41
126.21
123.56
122.52
117.04
116.89
116.11
111.21
111.04
109.48
109.42
103.23
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.67
64.11
52.52
35.22
31.32
27.39
13C NMR
Solvent: CDCl3
3dj
f1 (ppm)
f1 (ppm)

MMS-03-63-ASY.11.fid

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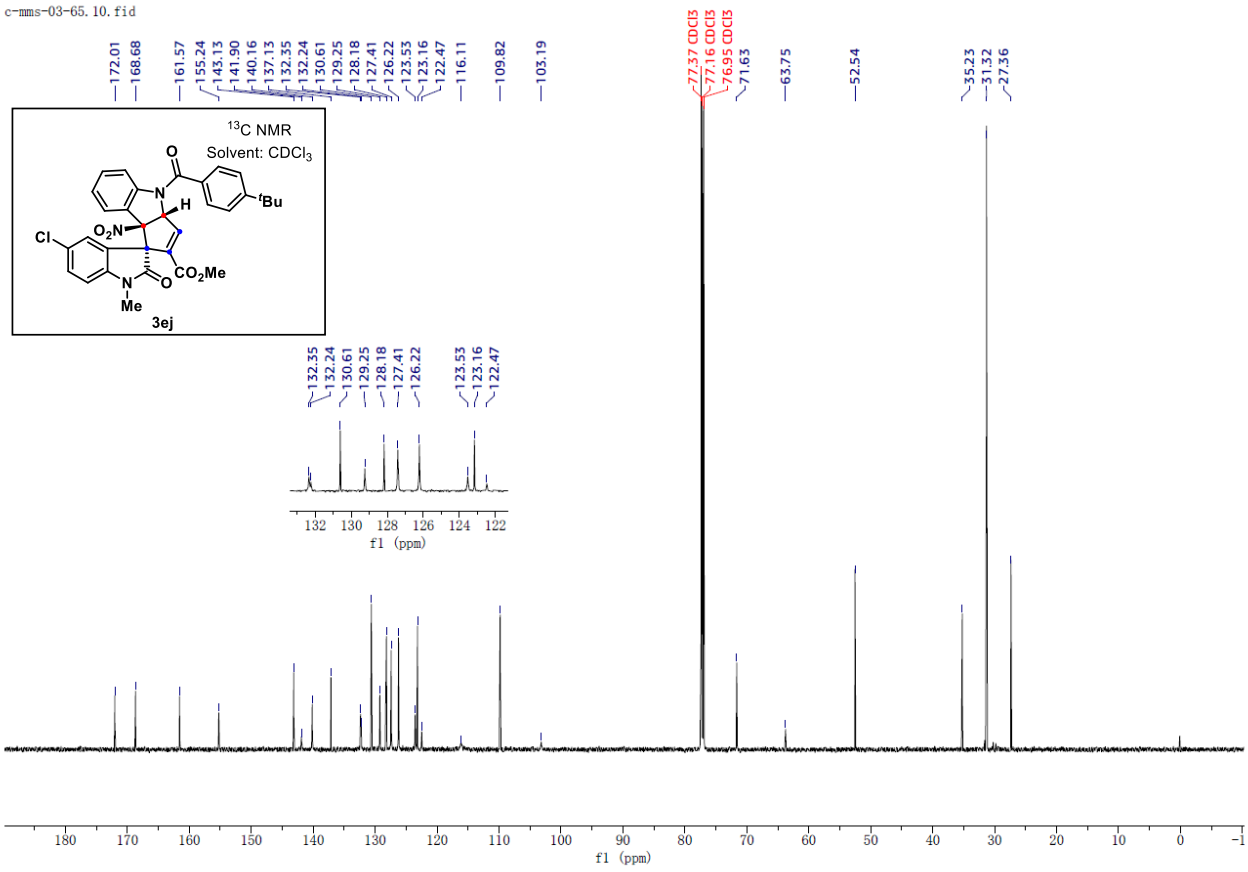
7.35
7.33
7.26 CDCl3
7.23
7.10
7.08
7.07
6.95
6.87
6.86
6.79
3.58
3.38
1.64 H2O
1.39
1H NMR
Solvent: CDCl3
tBu
O2N
Cl
CO2Me
Me
3ej
5.02
1.16
1.96
1.80
1.00
1.13
1.16
3.00
3.12
9.17
f1 (ppm)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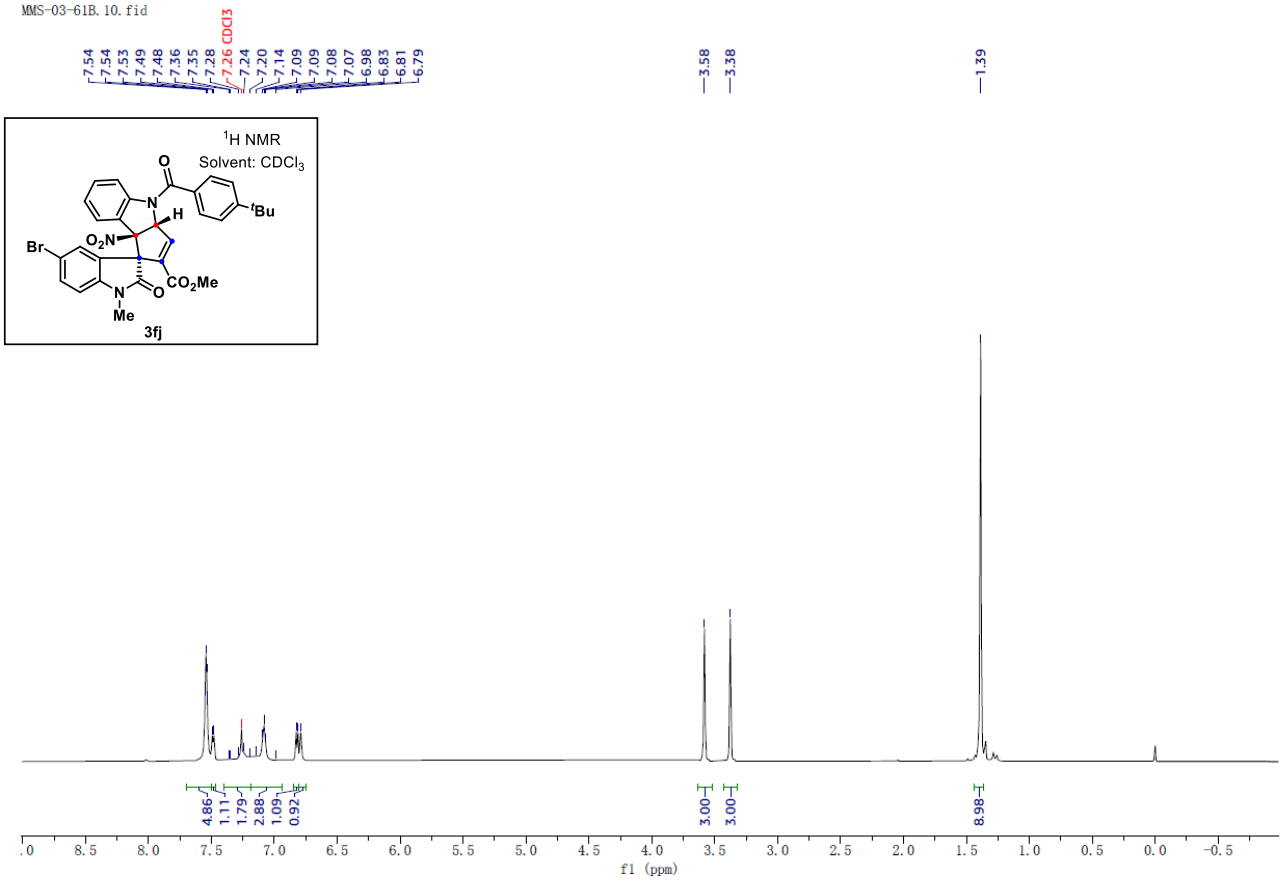
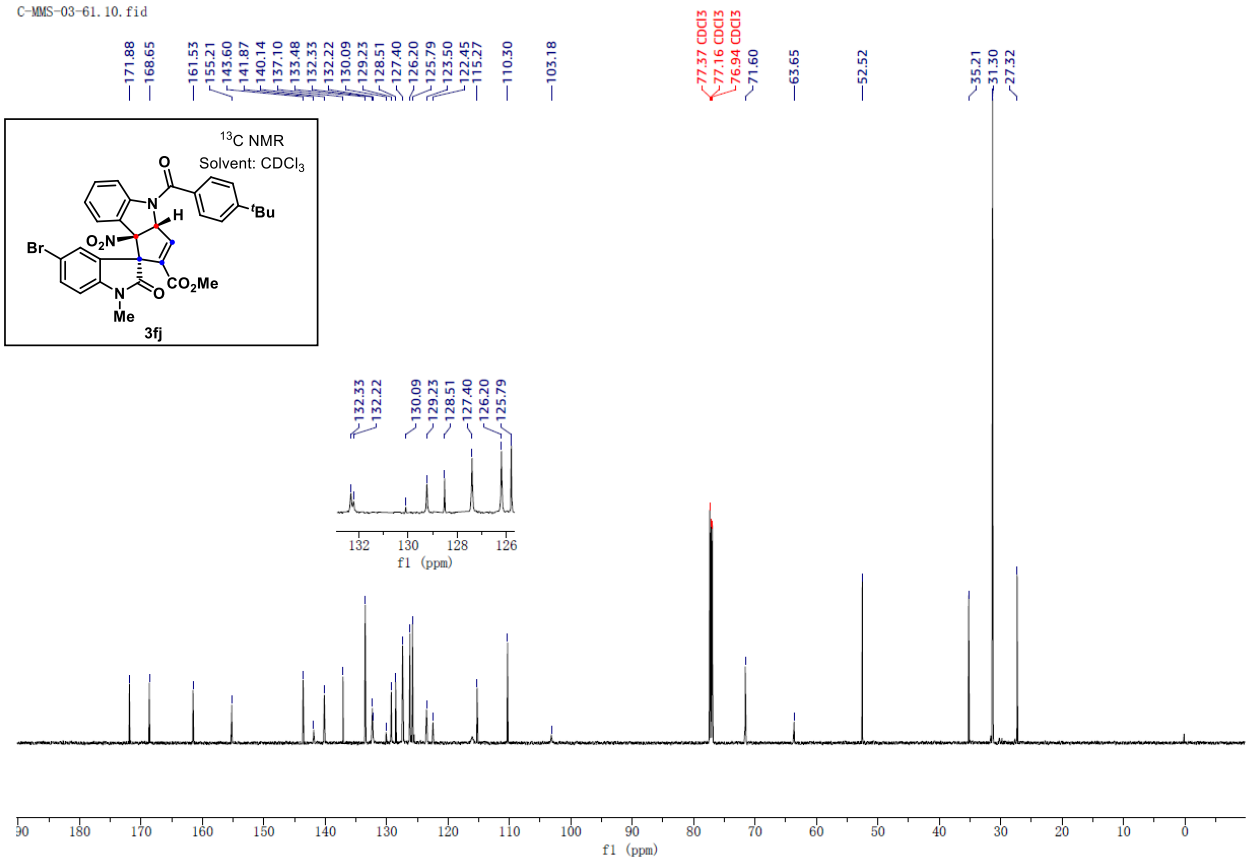
132.35
132.24
130.61
129.25
128.18
127.41
126.22
123.53
123.16
122.47
116.11
109.82
103.19
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.63
63.75
52.54
35.23
31.32
27.36
13C NMR
Solvent: CDCl3
tBu
O2N
Cl
CO2Me
Me
3ej
f1 (ppm)


MMS-03-61B.10.fid
7.54
7.54
7.53
7.49
7.48
7.36
7.35
7.28
7.26 CDCl3
7.24
7.20
7.14
7.09
7.09
7.08
7.07
6.98
6.83
6.81
6.79
3.58
3.38
1.39
1H NMR
Solvent: CDCl3
3fj
4.86
1.11
1.79
2.88
1.09
0.92
3.00
3.00
8.98
f1 (ppm)


C-MMS-03-61.10.fid
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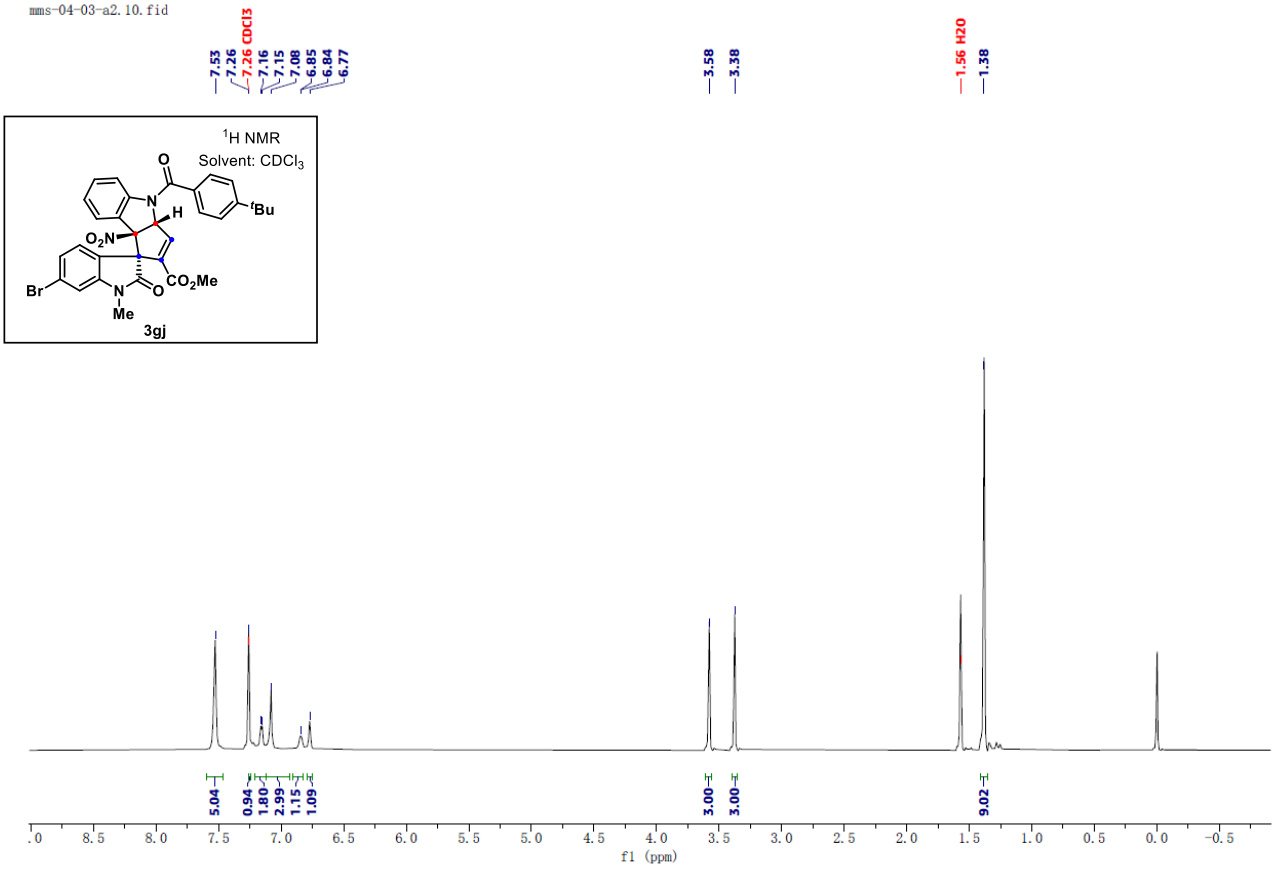
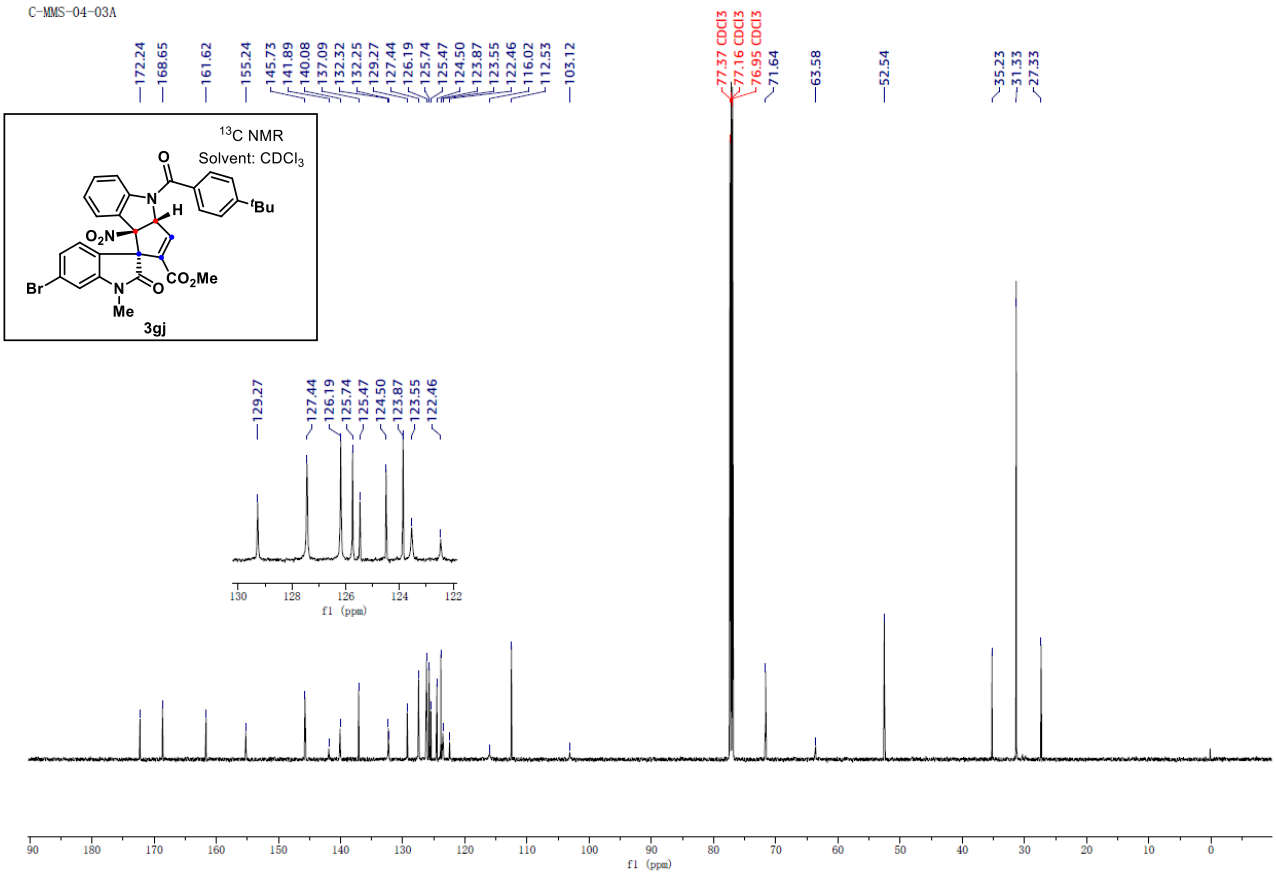
155.21
143.60
141.87
140.14
137.10
133.48
132.33
132.22
130.09
129.23
128.51
127.40
126.20
125.79
123.50
122.45
115.27
110.30
103.18
77.37 CDCl3
77.16 CDCl3
76.94 CDCl3
71.60
63.65
52.52
35.21
31.30
27.32
13C NMR
Solvent: CDCl3
3fj
f1 (ppm)


mms-04-03-a2.10.fid
7.53
7.26
7.26 CDCl3
7.16
7.15
7.08
6.85
6.84
6.77
3.58
3.38
1.56 H2O
1.38
1H NMR
Solvent: CDCl3
3gj
5.04
0.94
1.80
2.99
1.15
1.09
3.00
3.00
9.02
f1 (ppm)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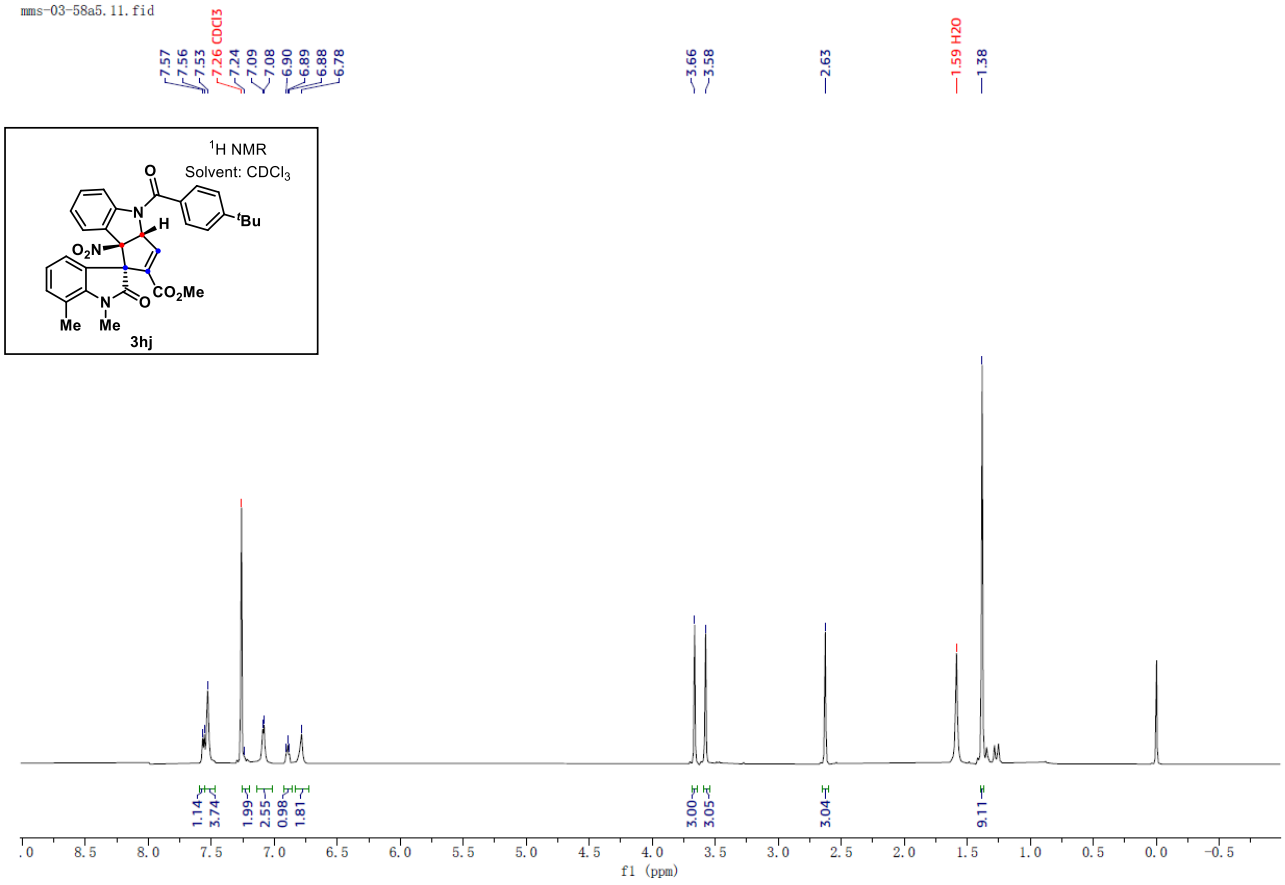
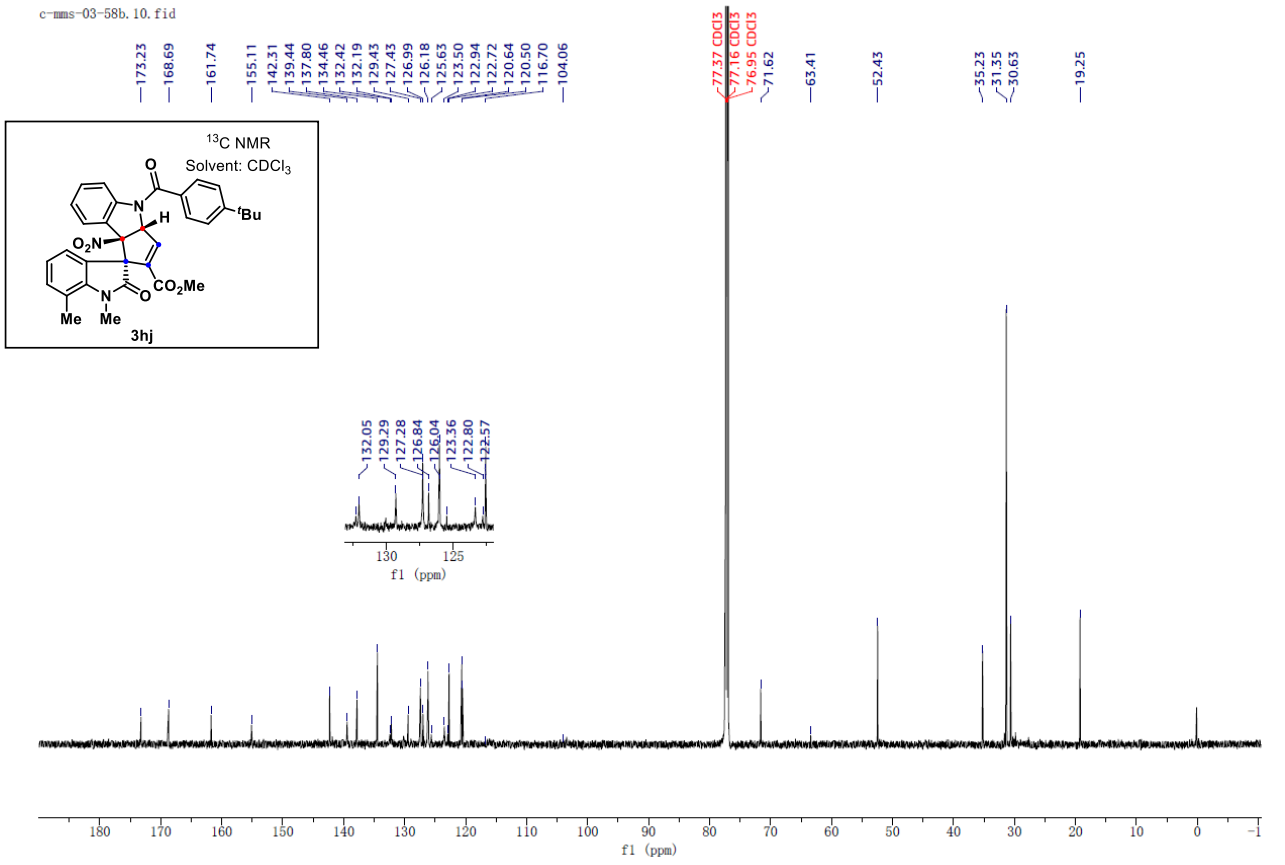
137.09
132.32
132.25
129.27
127.44
126.19
125.74
125.47
124.50
123.87
123.55
122.46
116.02
112.53
103.12
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.64
63.58
52.54
35.23
31.33
27.33
13C NMR
Solvent: CDCl3
3gj
f1 (ppm)
f1 (ppm)


mms-03-58a5.11.fid
7.57
7.56
7.53
7.26 CDCl3
7.24
7.09
7.08
6.90
6.89
6.88
6.78
3.66
3.58
2.63
1.59 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Me
Me
3hj
1.14
3.74
1.99
2.55
0.98
1.81
3.00
3.05
3.04
9.11
f1 (ppm)


c-mms-03-58b.10.fid
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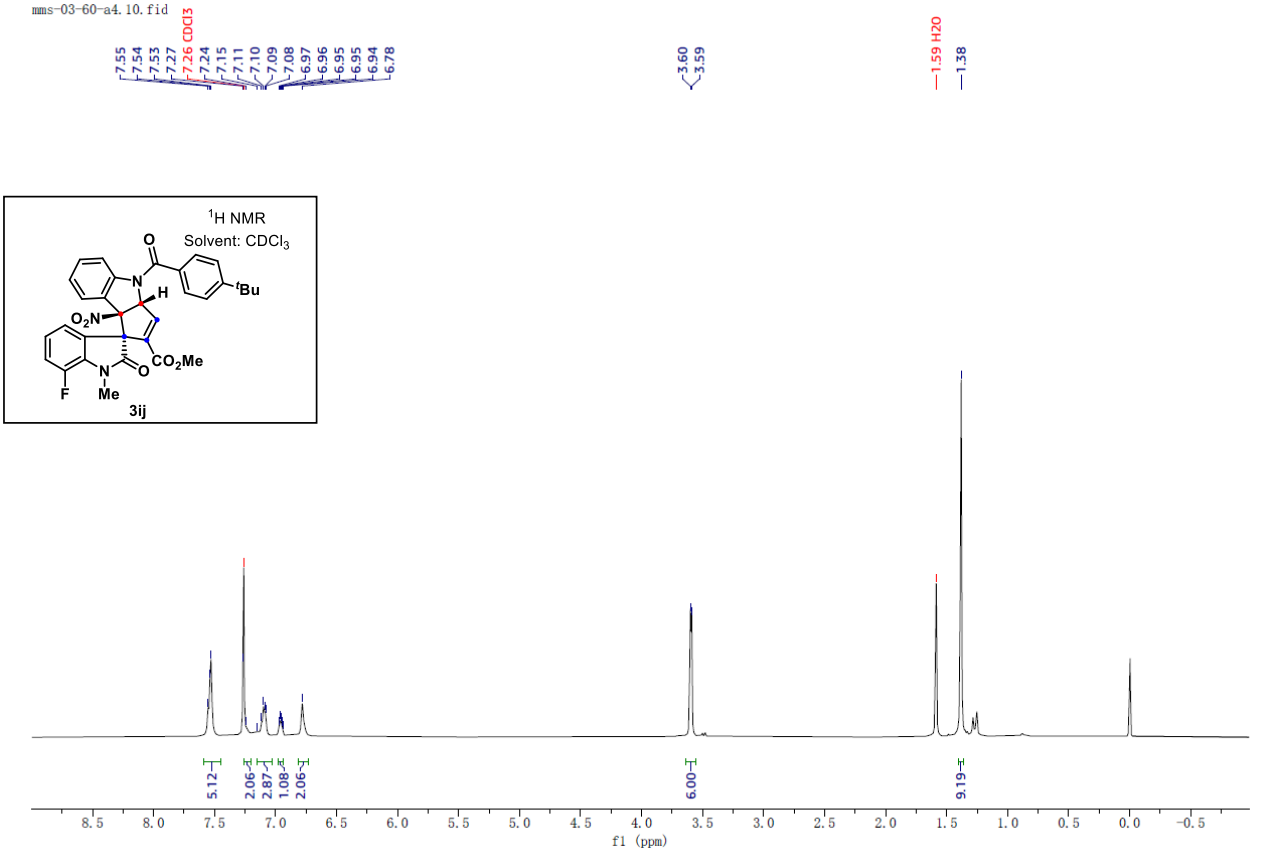
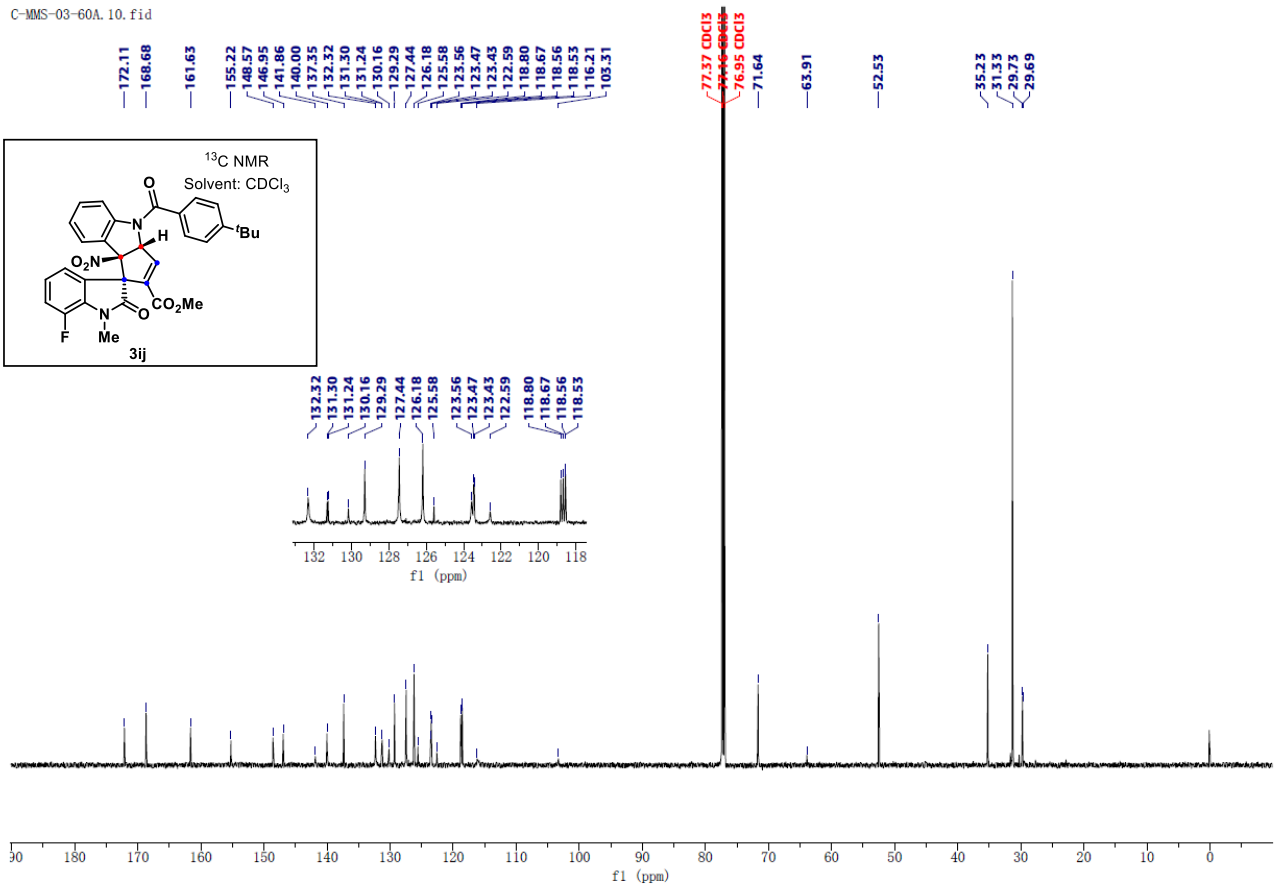
161.74
155.11
142.31
139.44
137.80
134.46
132.42
132.19
129.43
127.43
126.99
126.18
125.63
123.50
122.94
122.72
120.64
120.50
116.70
104.06
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.62
63.41
52.43
35.23
31.35
30.63
19.25
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Me
Me
3hj
132.05
129.29
127.28
126.84
126.04
123.36
122.80
122.57
f1 (ppm)


mms-03-60-a4.10.fid
7.55
7.54
7.53
7.27
7.26 CDCl3
7.24
7.15
7.11
7.10
7.09
7.08
6.97
6.96
6.95
6.95
6.94
6.78
3.60
3.59
1.59 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
F
Me
3ij
5.12
2.06
2.87
1.08
2.06
6.00
9.19
f1 (ppm)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161.63
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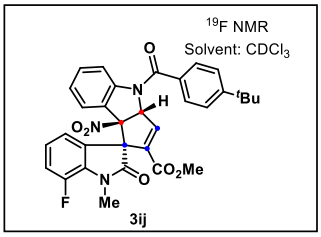
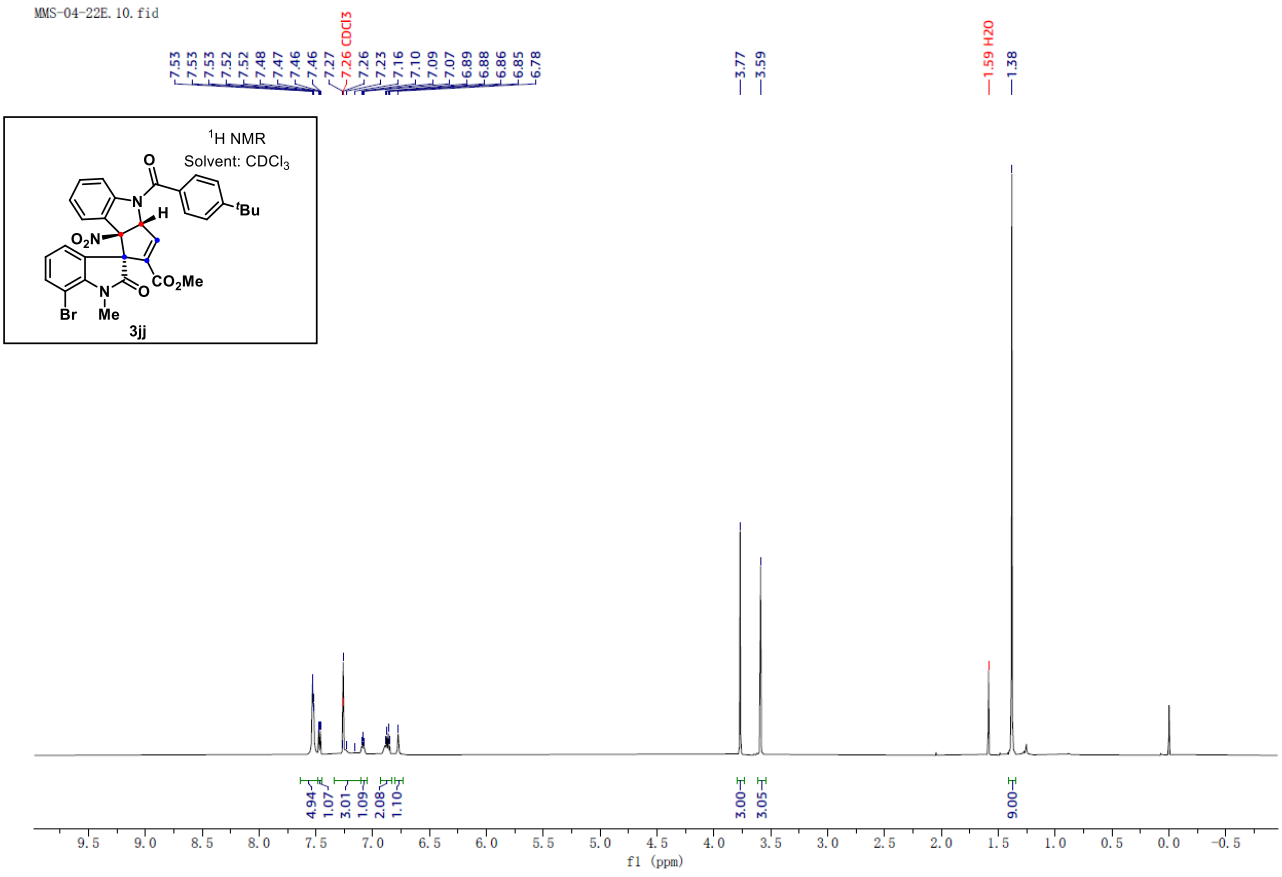
140.00
137.35
132.32
131.30
131.24
130.16
129.29
127.44
126.18
125.58
123.56
123.47
123.43
122.59
118.80
118.67
118.56
118.53
116.21
103.31
77.37 CDCl3
76.95 CDCl3
71.64
63.91
52.53
35.23
31.33
29.73
29.69
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
F
Me
3ij
f1 (ppm)
f1 (ppm)

MMS-03-60-A2.22.fid

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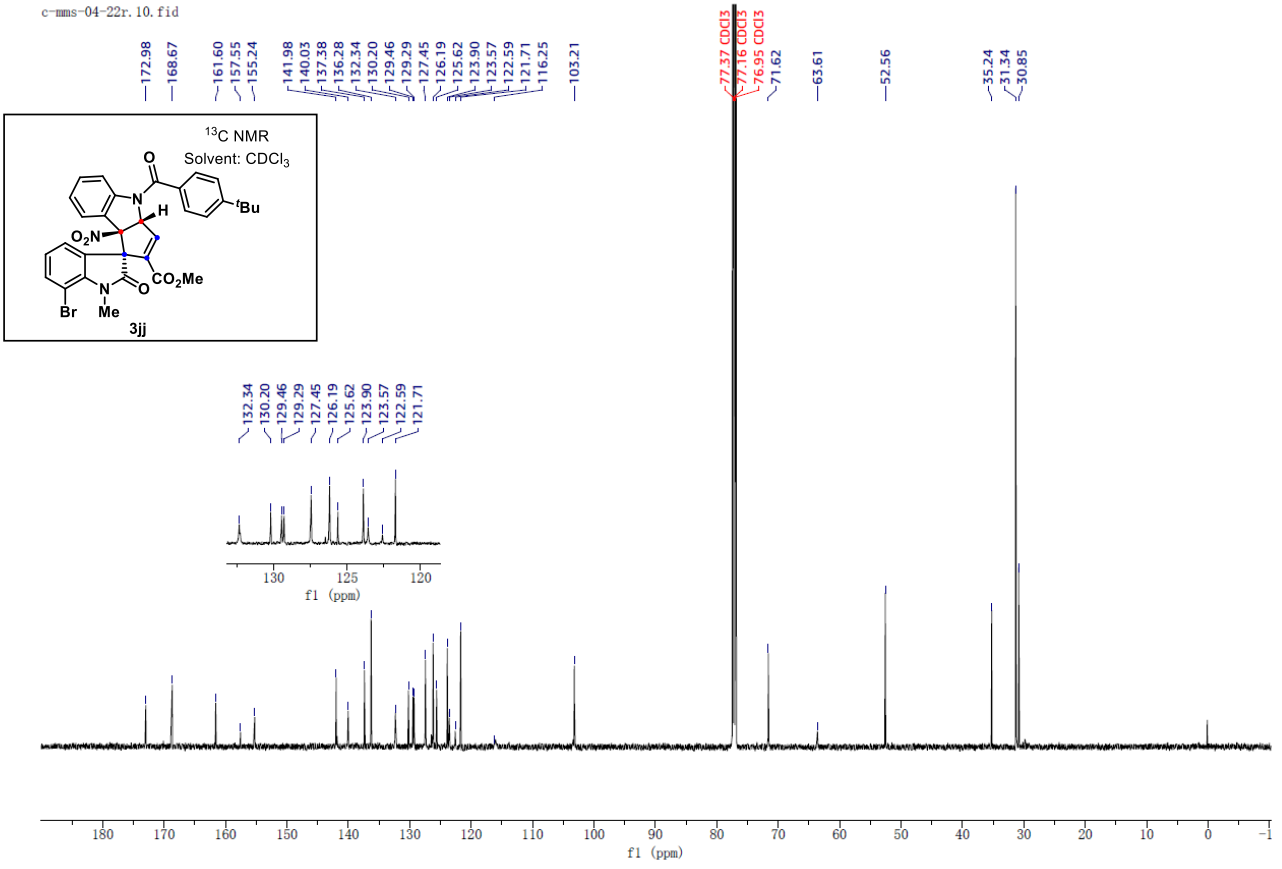
1H NMR
Solvent: CDCl3
3jj
f1 (ppm)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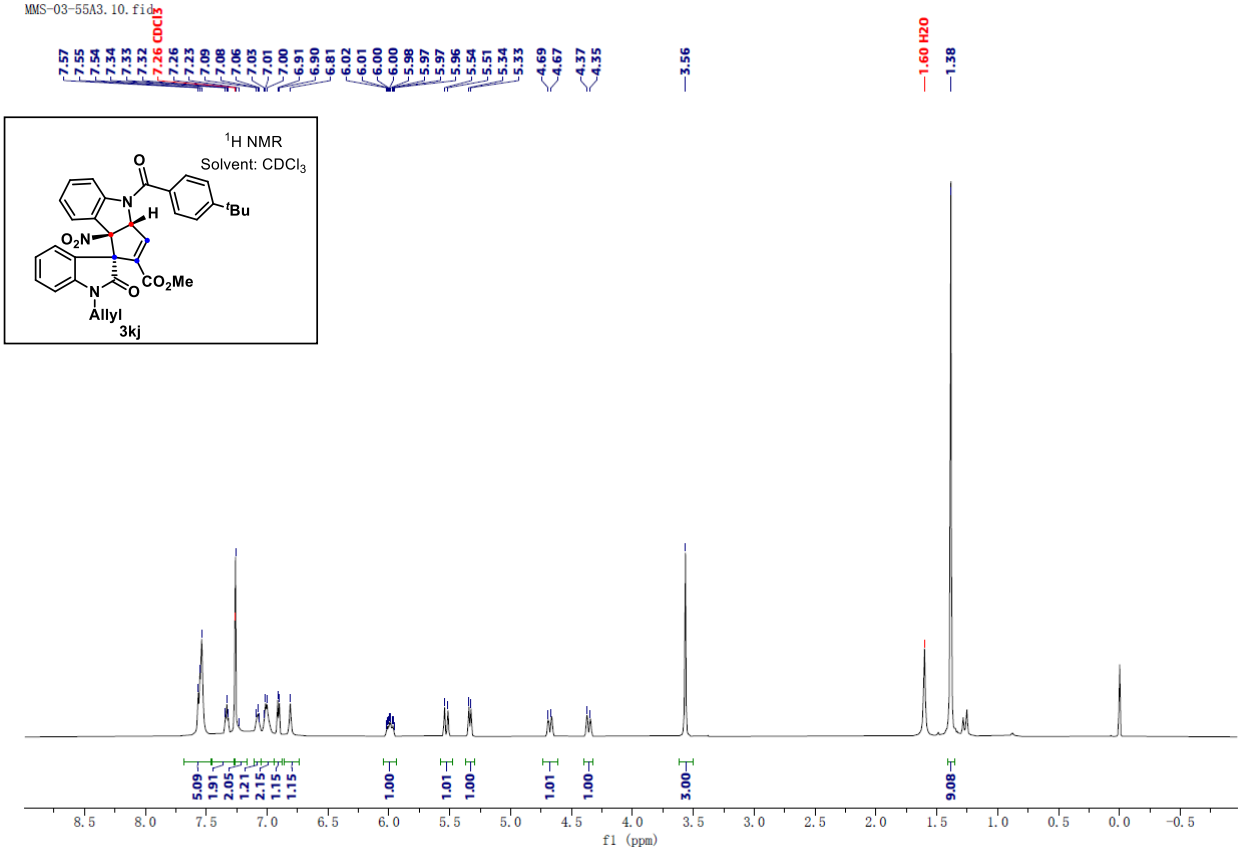
13C NMR
Solvent: CDCl3
3jj
f1 (ppm)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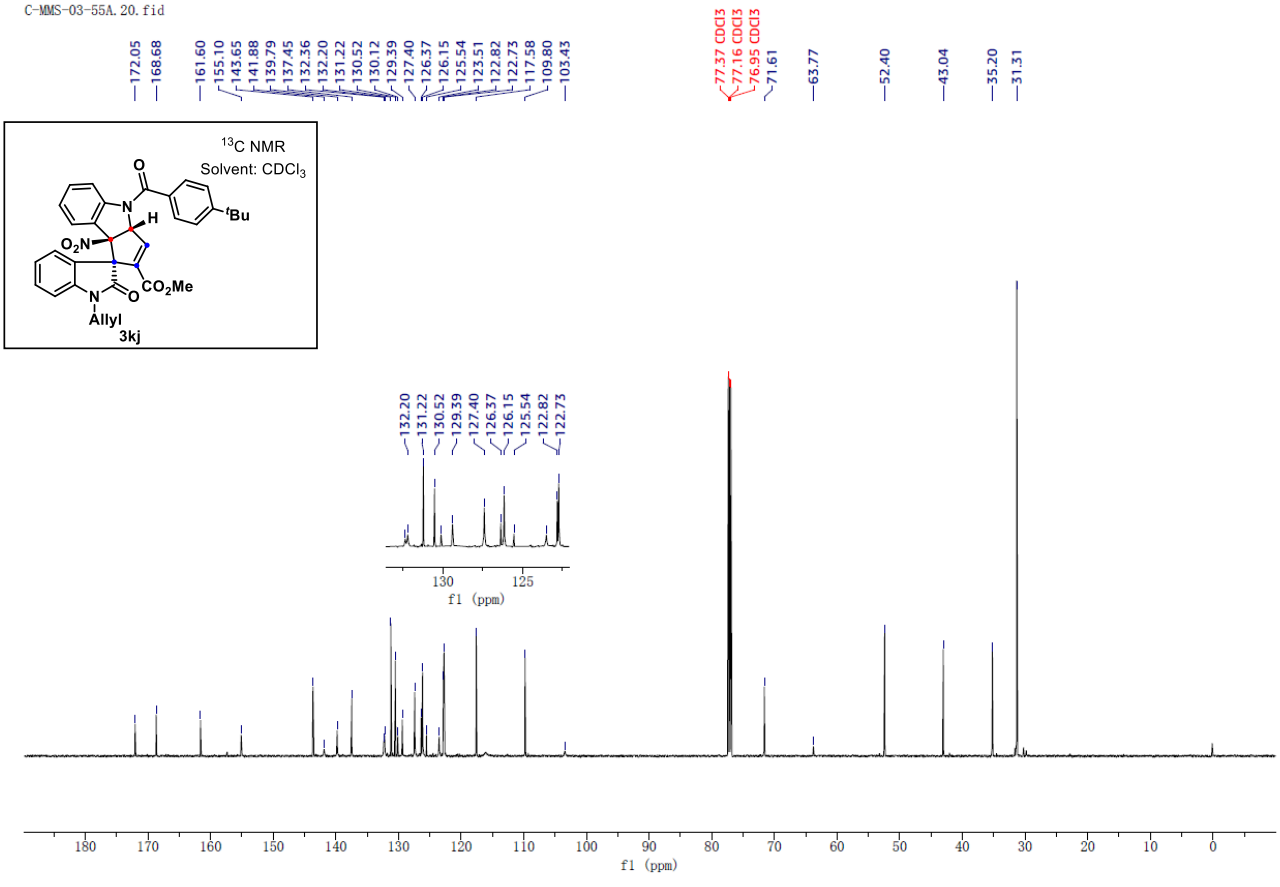
7.55
7.54
7.34
7.33
7.32
7.26 CDCl3
7.26
7.23
7.09
7.08
7.06
7.03
7.01
7.00
6.91
6.90
6.81
6.02
6.01
6.00
6.00
5.98
5.97
5.97
5.96
5.54
5.51
5.34
5.33
4.69
4.67
4.37
4.35
3.56
1.60 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Allyl
3kj
5.09
1.91
2.05
1.21
2.15
1.15
1.15
1.00
1.01
1.00
1.01
1.00
3.00
9.08
f1 (ppm)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139.79
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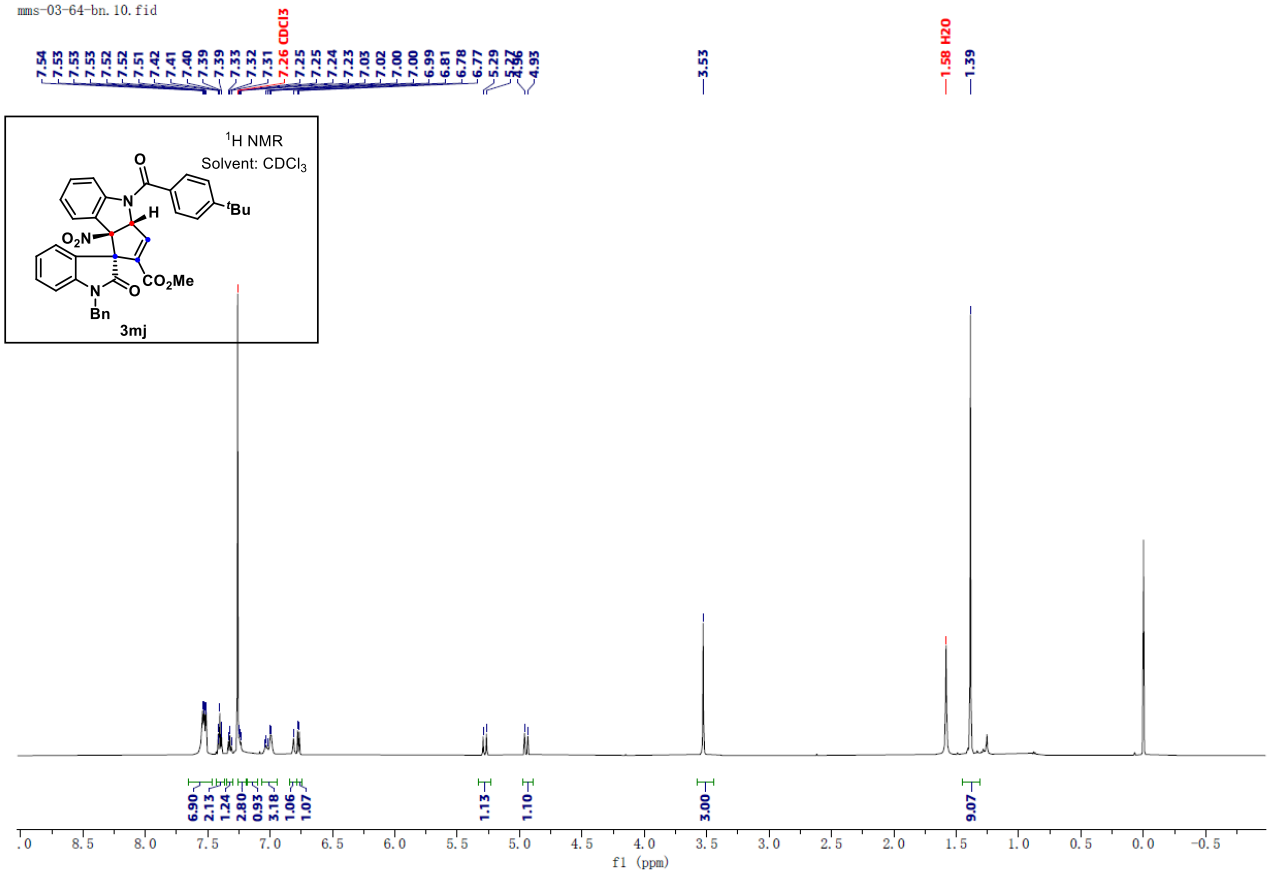
132.36
132.20
131.22
130.52
130.12
129.39
127.40
126.37
126.15
125.54
123.51
122.82
122.73
117.58
109.80
103.43
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.61
63.77
52.40
43.04
35.20
31.31
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Allyl
3kj
132.20
131.22
130.52
129.39
127.40
126.37
126.15
125.54
122.82
122.73
130
125
f1 (ppm)
f1 (ppm)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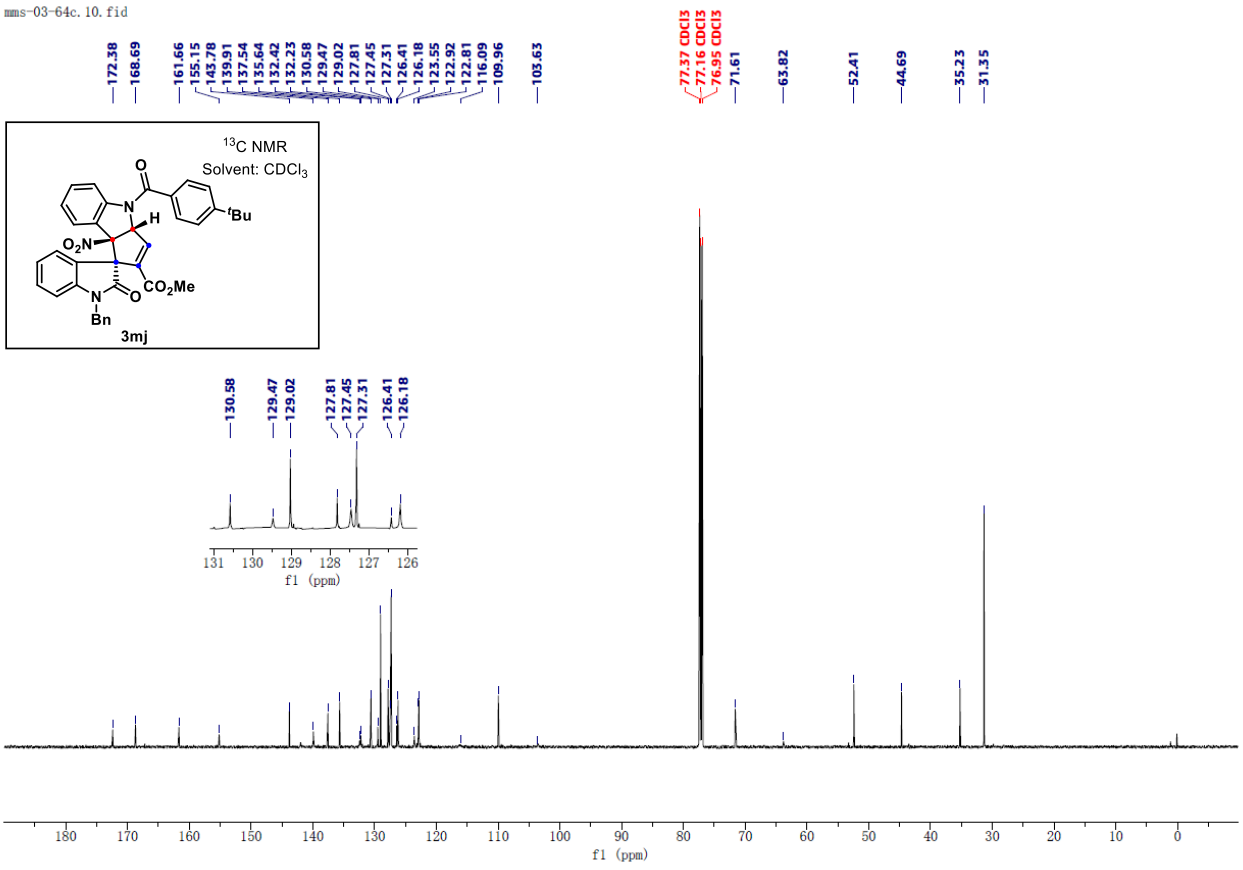
3.53
1.58 H2O
1.39
1H NMR
Solvent: CDCl3
3mj
6.90 2.13 1.24 2.80 0.93 3.18 1.06 1.07 1.13 1.10 3.00 9.07
f1 (ppm)


mms-03-64c.10.fid
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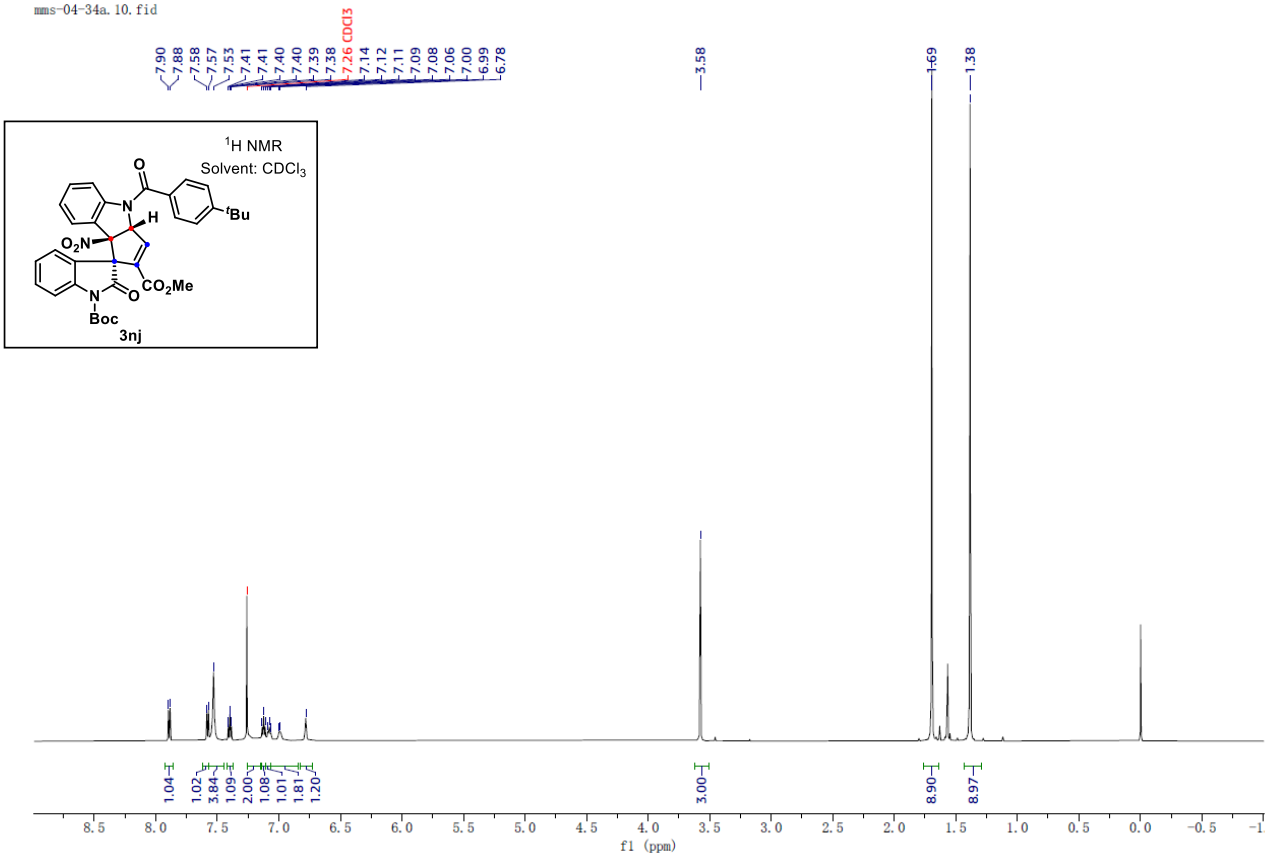
77.37 CDCl3 77.16 CDCl3 76.95 CDCl3 71.61 63.82 52.41 44.69 35.23 31.35
13C NMR
Solvent: CDCl3
3mj
130.58 129.47 129.02 127.81 127.45 127.31 126.41 126.18
f1 (ppm)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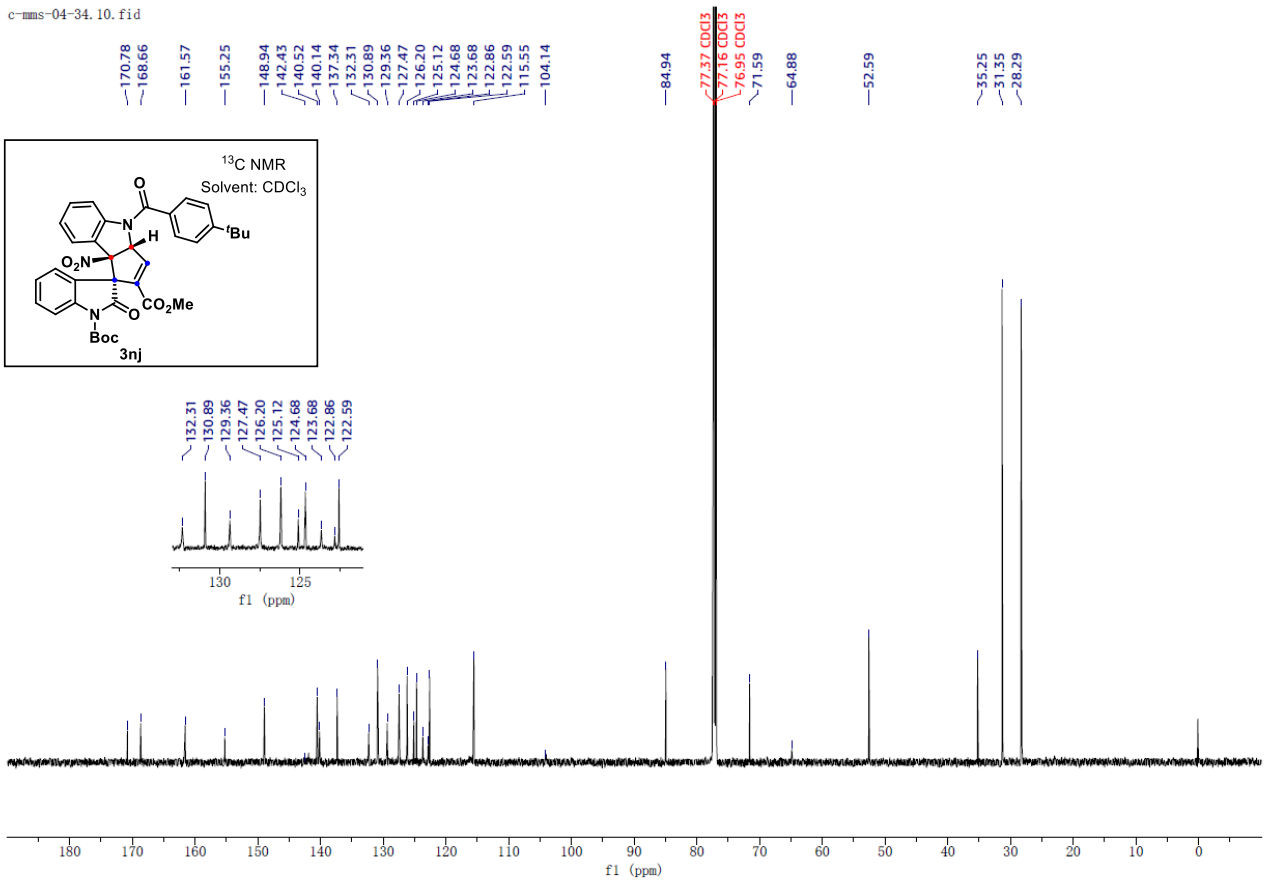
7.88
7.58
7.57
7.53
7.41
7.41
7.40
7.40
7.39
7.38
7.26 CDCl3
7.14
7.12
7.11
7.09
7.08
7.06
7.00
6.99
6.78
3.58
1.69
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Boc
3nj
1.04
1.02
3.84
1.09
2.00
1.08
1.01
1.81
1.20
3.00
8.90
8.97
f1 (ppm)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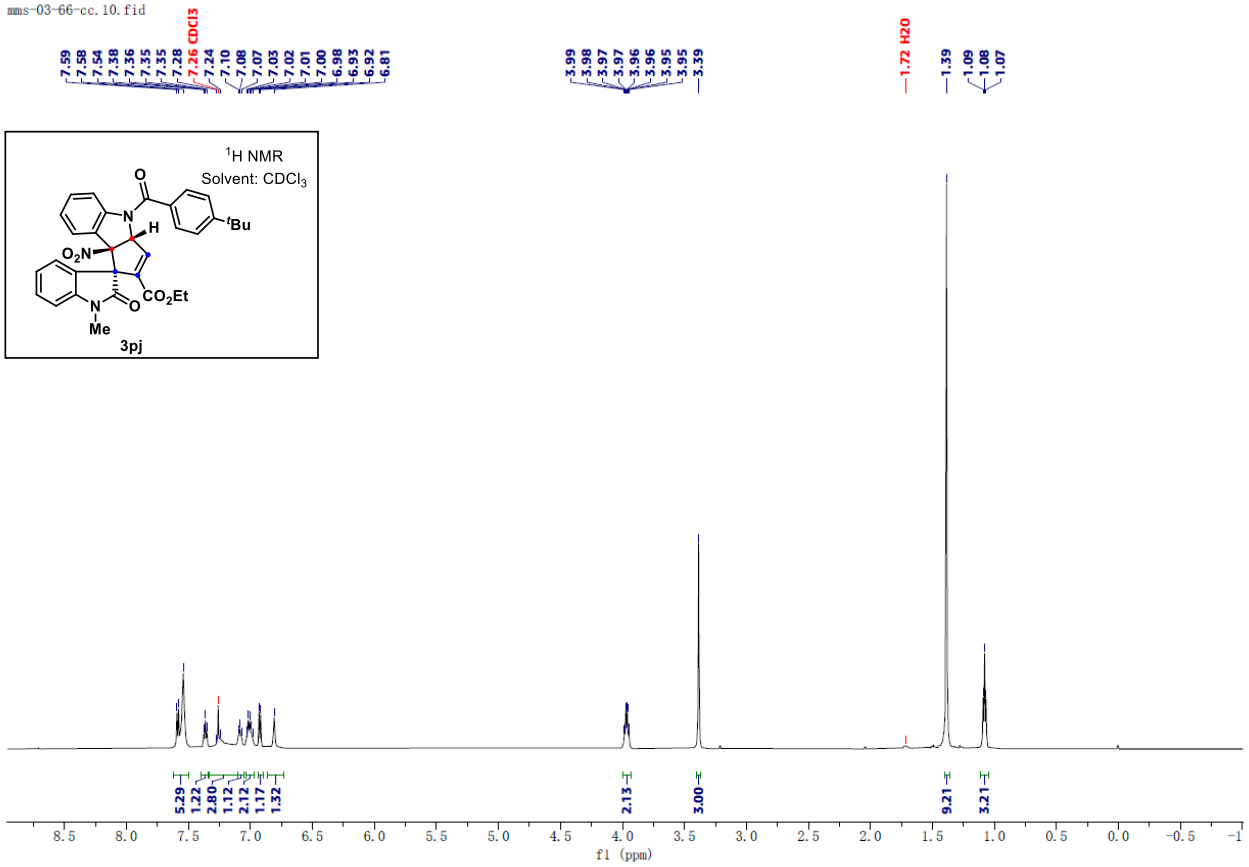
142.43
140.52
140.14
137.34
132.31
130.89
129.36
127.47
126.20
125.12
124.68
123.68
122.86
122.59
115.55
104.14
84.94
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.59
64.88
52.59
35.25
31.35
28.29
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
Boc
3nj
f1 (ppm)
f1 (ppm)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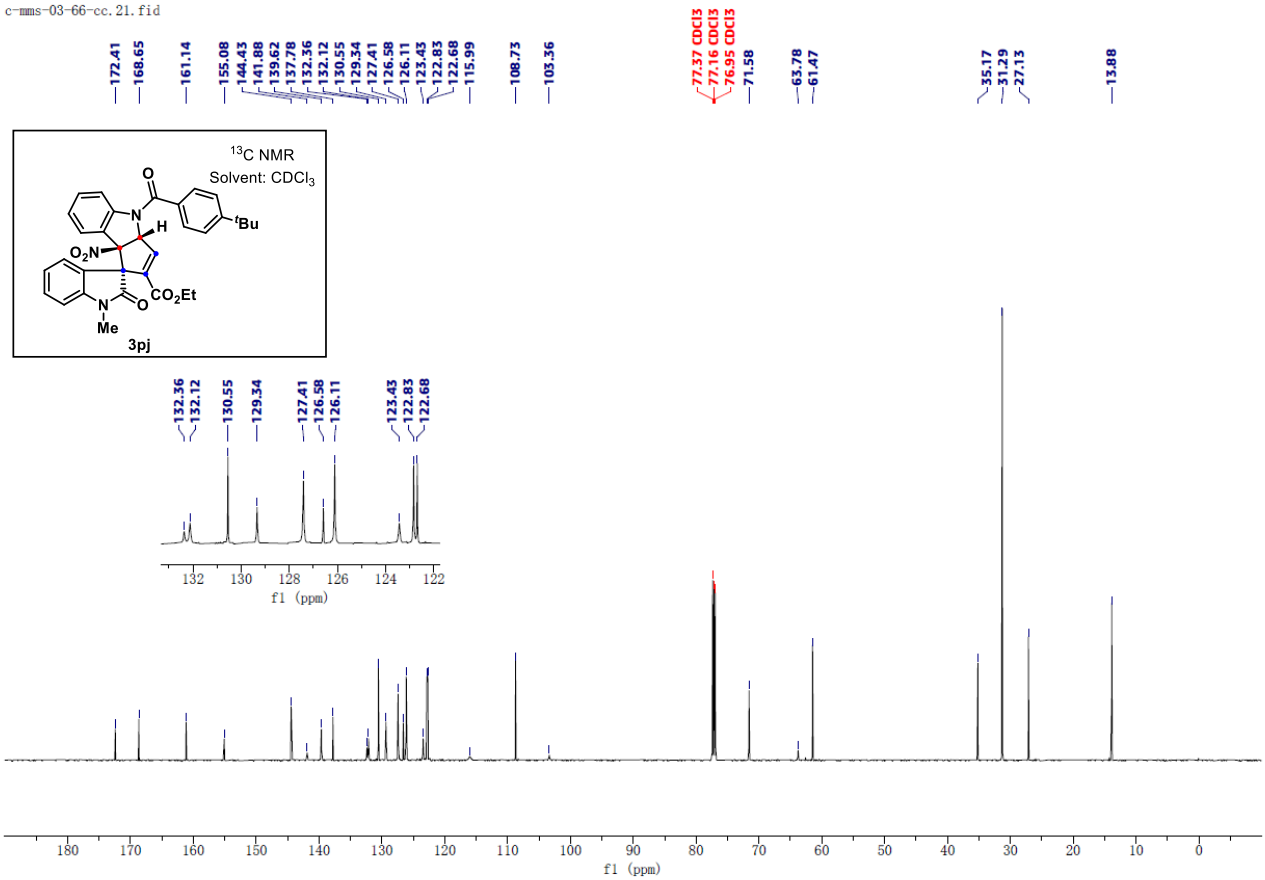
7.58
7.54
7.38
7.36
7.35
7.35
7.28
7.26 CDCl3
7.24
7.10
7.08
7.07
7.03
7.02
7.01
7.00
6.98
6.93
6.92
6.81
3.99
3.98
3.97
3.97
3.96
3.96
3.95
3.95
3.39
1.72 H2O
1.39
1.09
1.08
1.07
1H NMR
Solvent: CDCl3
3pj
5.29
1.22
2.80
1.12
2.12
1.17
1.32
2.13
3.00
9.21
3.21
f1 (ppm)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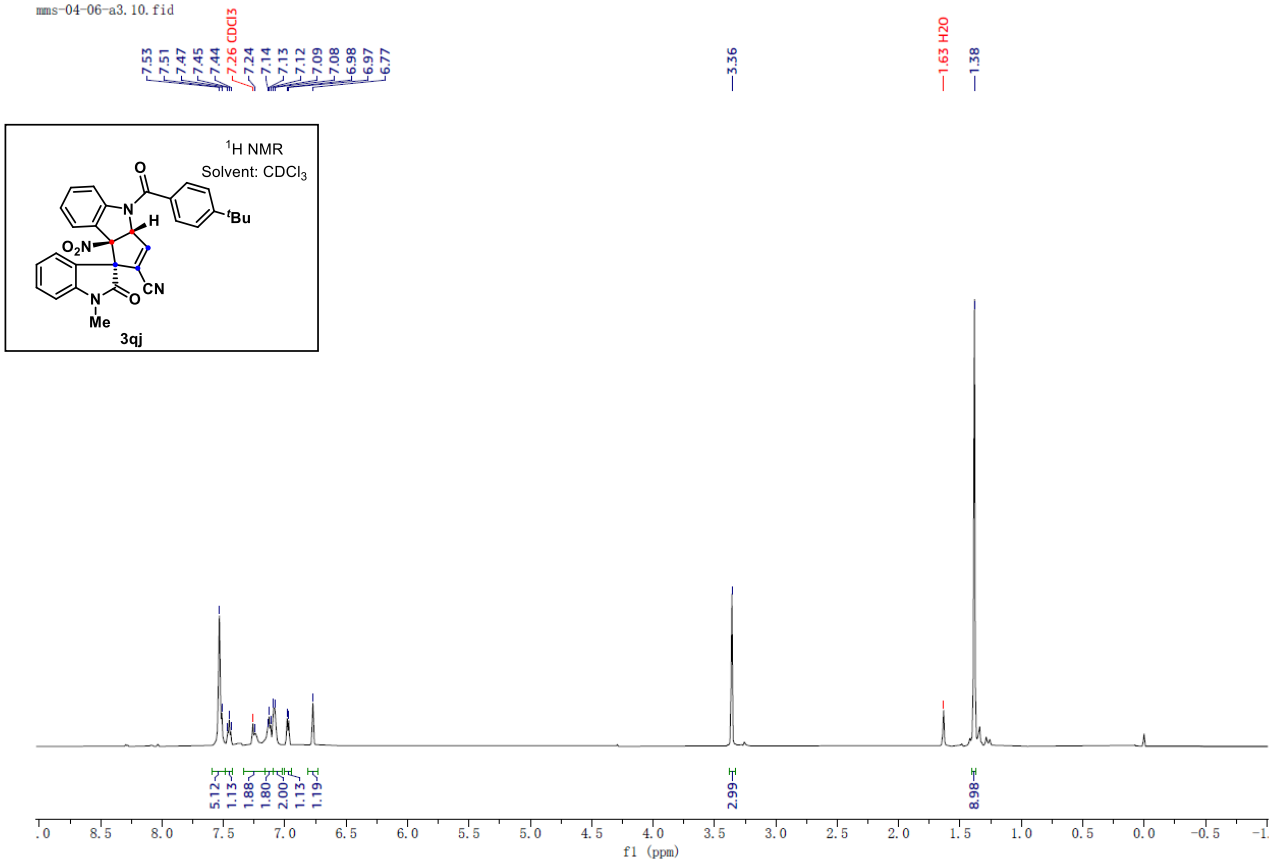
155.08
144.43
141.88
139.62
137.78
132.36
132.12
130.55
129.34
127.41
126.58
126.11
123.43
122.83
122.68
115.99
108.73
103.36
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.58
63.78
61.47
35.17
31.29
27.13
13.88
13C NMR
Solvent: CDCl3
3pj
f1 (ppm)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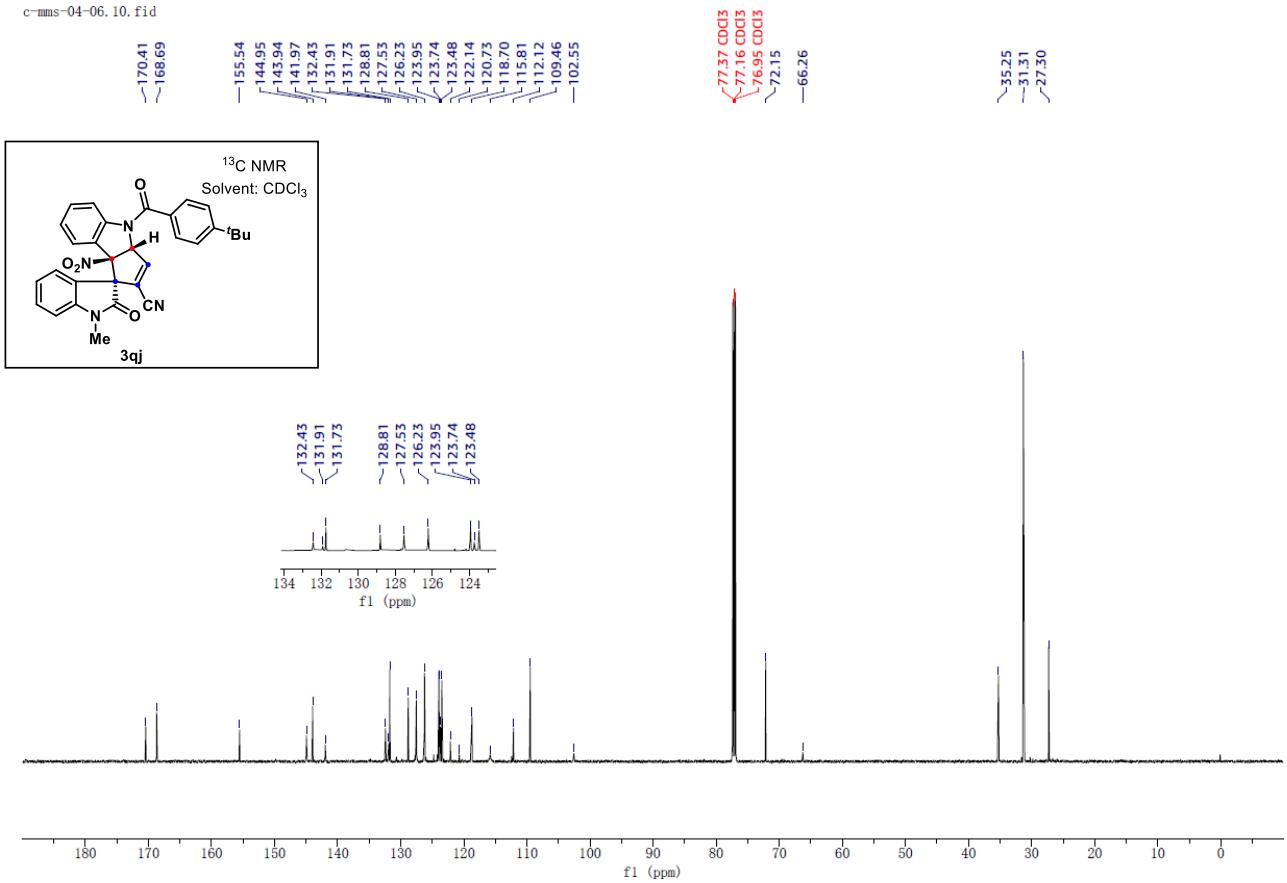
7.51
7.47
7.45
7.44
7.26 CDCl3
7.24
7.14
7.13
7.12
7.09
7.08
6.98
6.97
6.77
3.36
1.63 H2O
1.38
1H NMR
Solvent: CDCl3
tBu
O2N
CN
Me
3qj
5.12
1.13
1.88
1.80
2.00
1.13
1.19
2.99
8.98
f1 (ppm)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155.54
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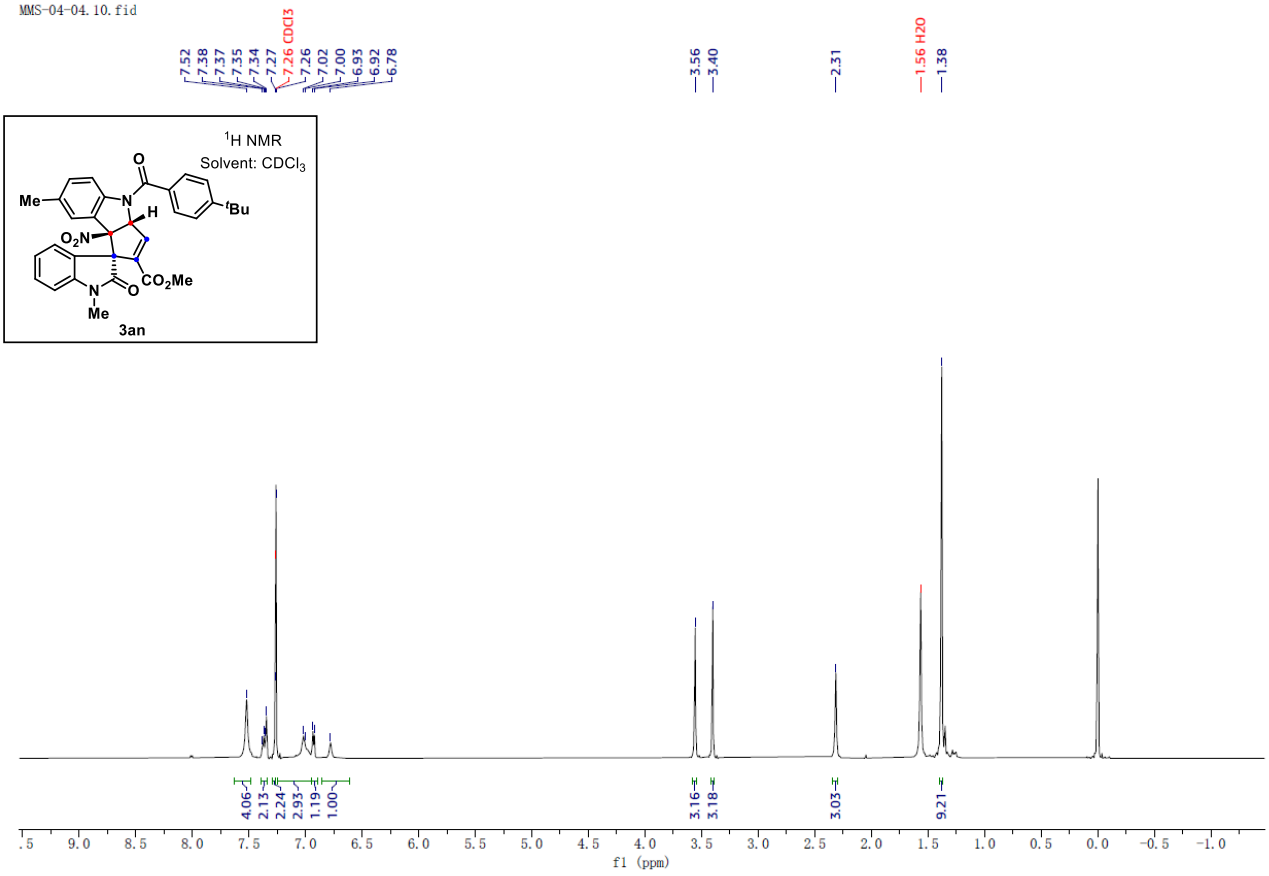
141.97
132.43
131.91
131.73
128.81
127.53
126.23
123.95
123.74
123.48
122.14
120.73
118.70
115.81
112.12
109.46
102.55
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.15
66.26
35.25
31.31
27.30
13C NMR
Solvent: CDCl3
tBu
O2N
CN
Me
3qj
f1 (ppm)
f1 (ppm)


MMS-04-04.10.fid
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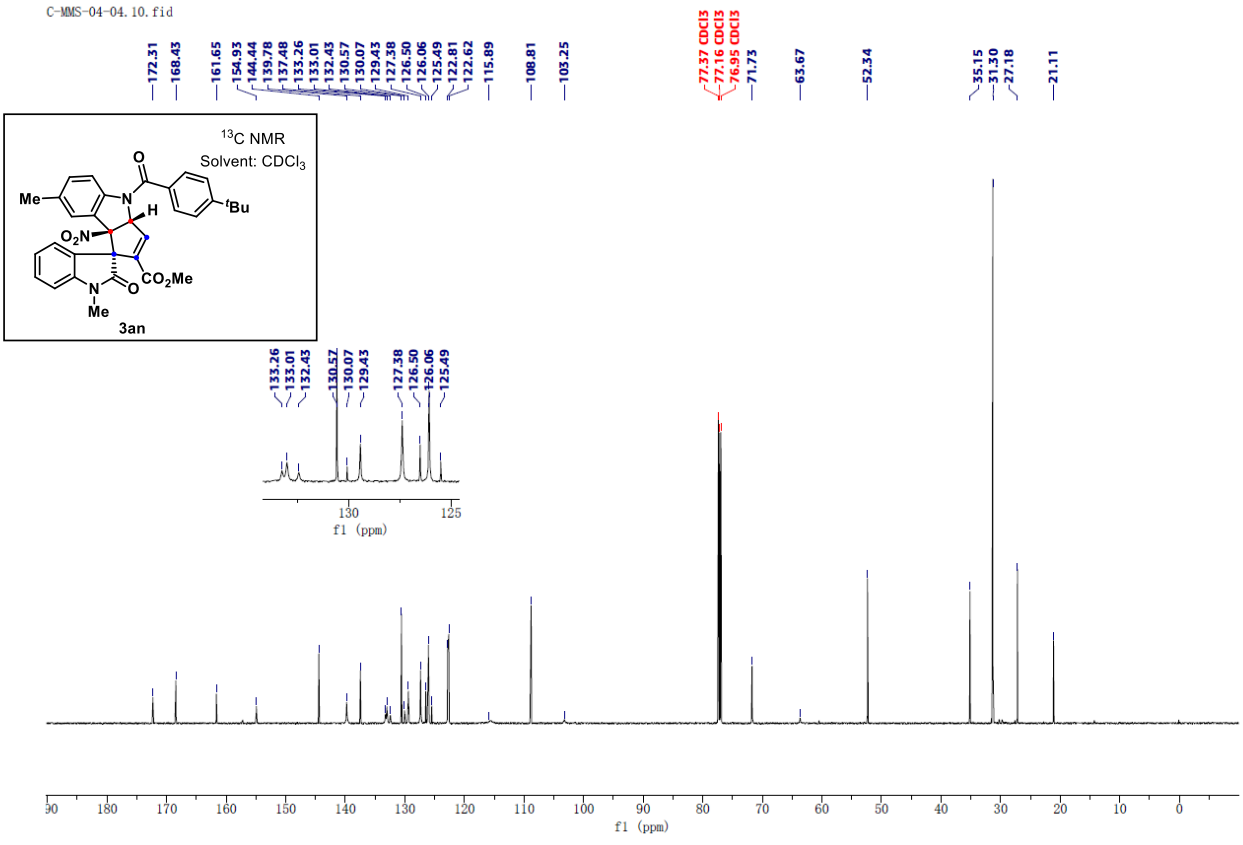
7.38
7.37
7.35
7.34
7.27
7.26 CDCl3
7.26
7.02
7.00
6.93
6.92
6.78
3.56
3.40
2.31
1.56 H2O
1.38
1H NMR
Solvent: CDCl3
Me
O2N
H
tBu
CO2Me
N
Me
3an
4.06
2.13
2.24
2.93
1.19
1.00
3.16
3.18
3.03
9.21
f1 (ppm)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133.26
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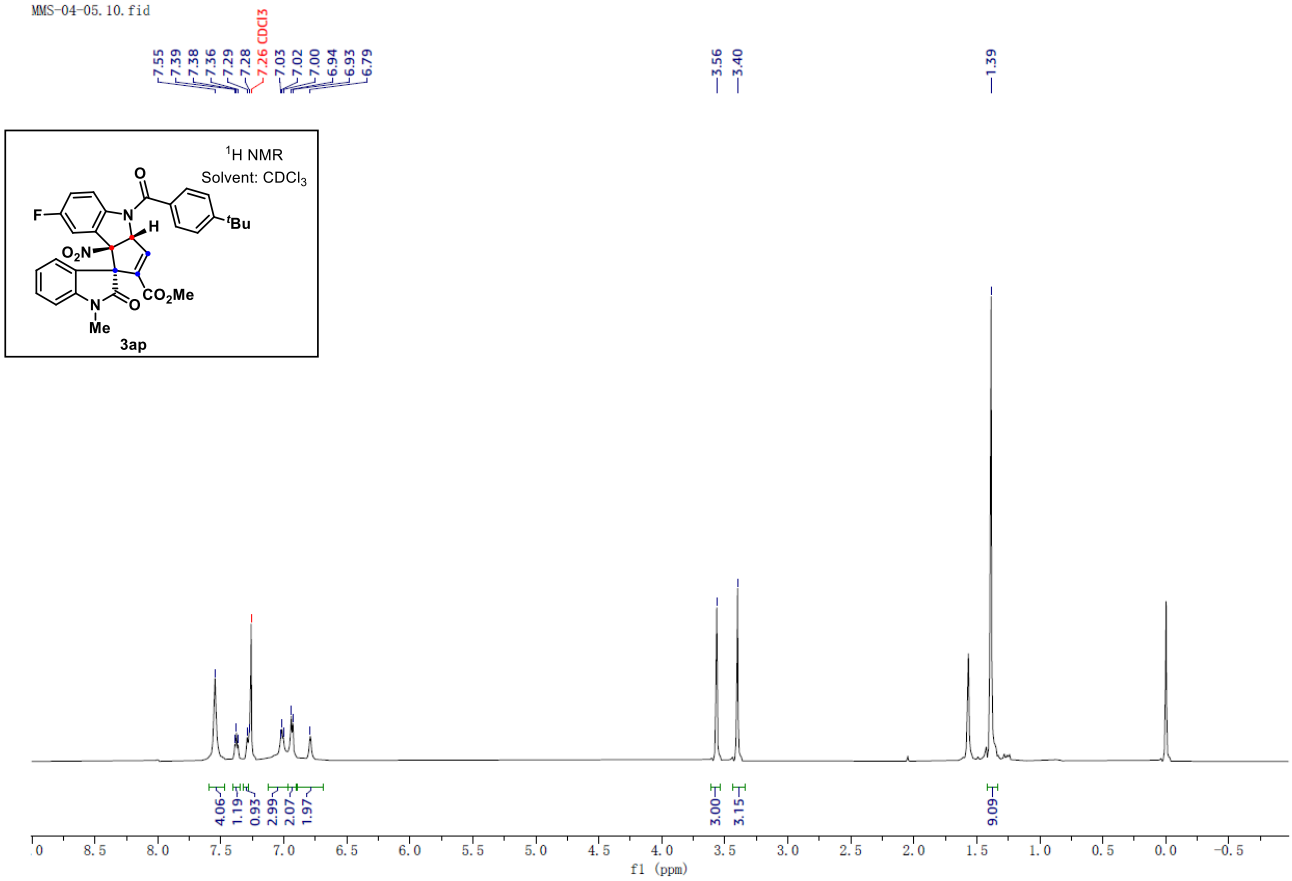
132.43
130.57
130.07
129.43
127.38
126.50
126.06
125.49
122.81
122.62
115.89
108.81
103.25
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.73
63.67
52.34
35.15
31.30
27.18
21.11
13C NMR
Solvent: CDCl3
Me
O2N
H
tBu
CO2Me
N
Me
3an
f1 (ppm)
f1 (ppm)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7.39
7.38
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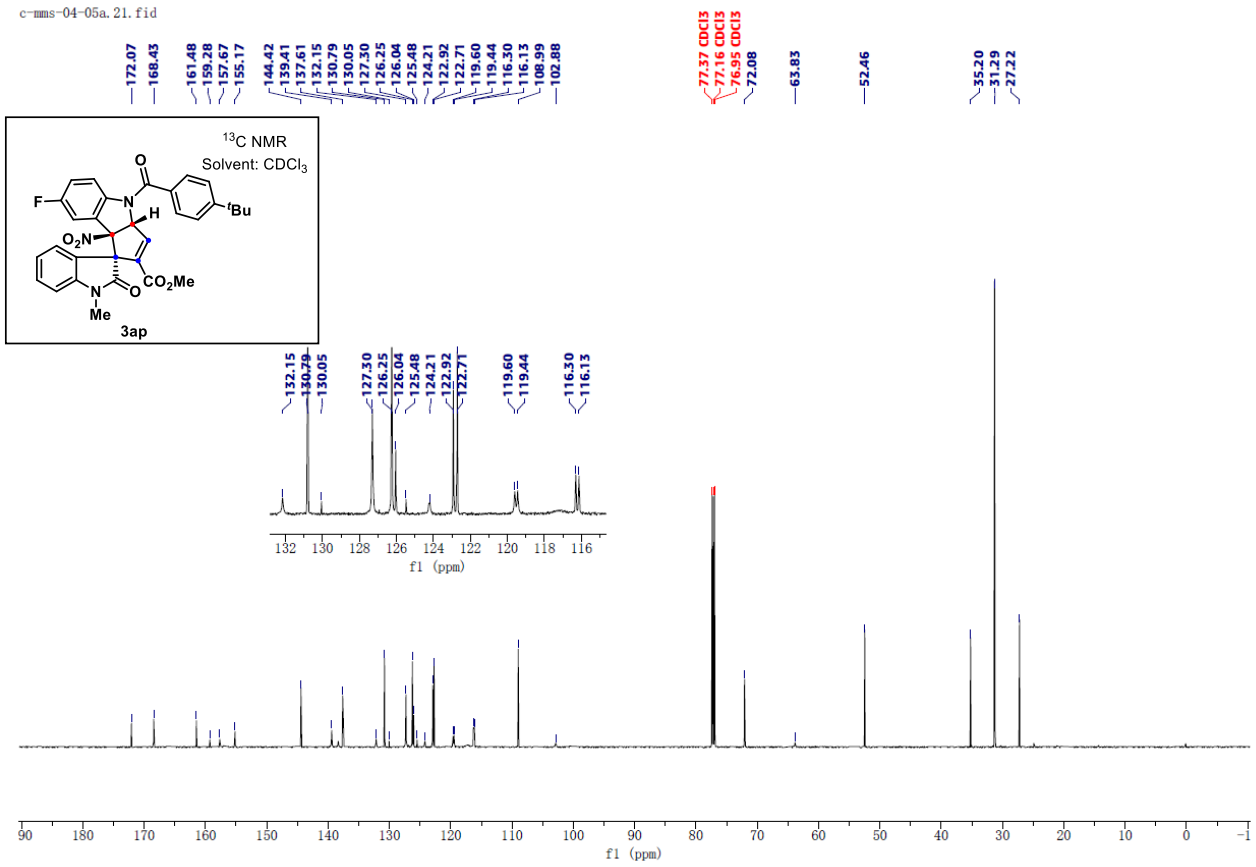
7.29
7.28
7.26 CDCl3
7.03
7.02
7.00
6.94
6.93
6.79
3.56
3.40
1.39
1H NMR
Solvent: CDCl3
F
O
N
H
tBu
O2N
CO2Me
N
O
Me
3ap
4.06
1.19
0.93
2.99
2.07
1.97
3.00
3.15
9.09
f1 (ppm)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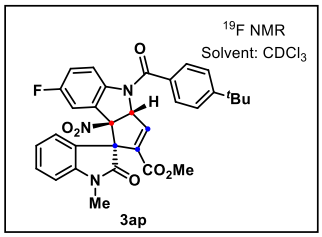
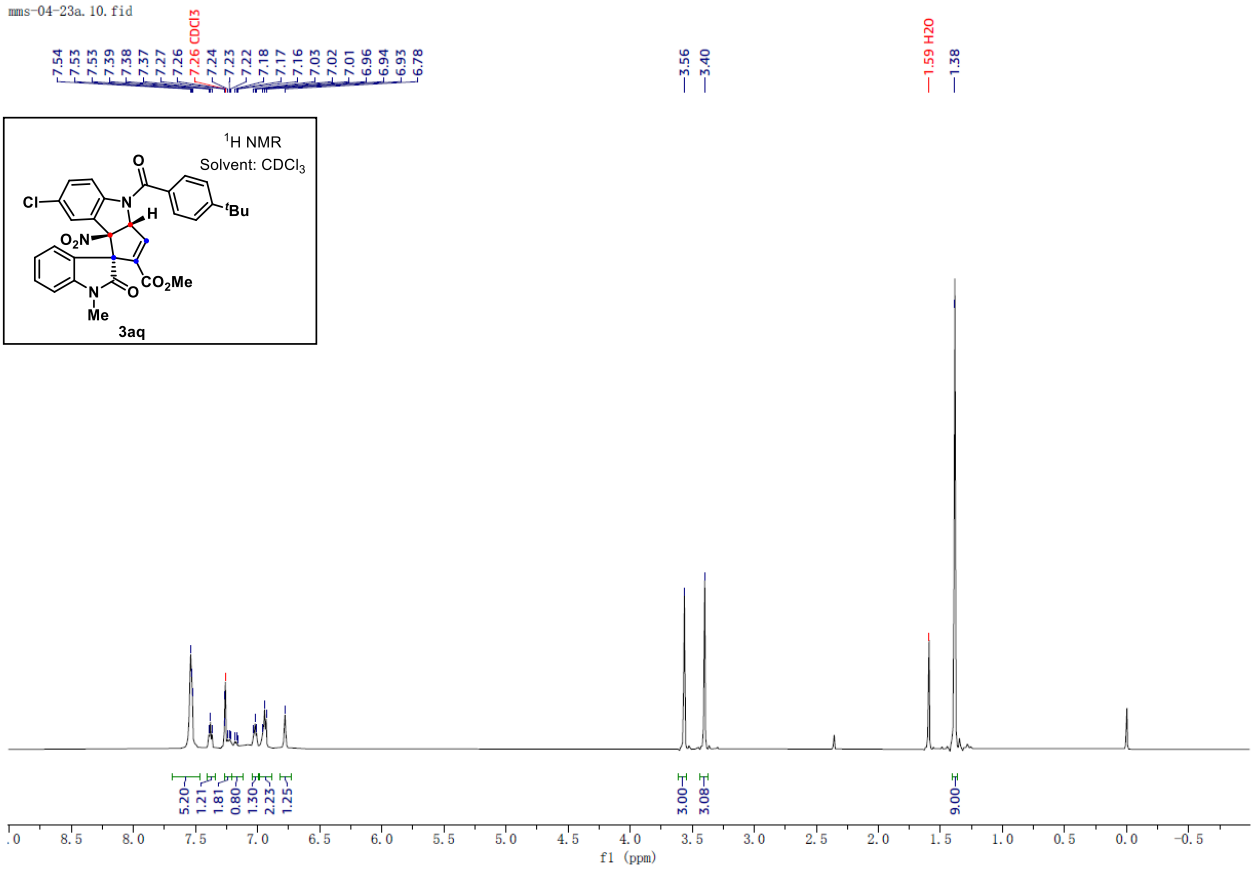
159.28
157.67
155.17
144.42
139.41
137.61
132.15
130.79
130.05
127.30
126.25
126.04
125.48
124.21
122.92
122.71
119.60
119.44
116.30
116.13
108.99
102.88
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.08
63.83
52.46
35.20
31.29
27.22
13C NMR
Solvent: CDCl3
F
O
N
H
tBu
O2N
CO2Me
N
O
Me
3ap
f1 (ppm)
f1 (ppm)

f-mms-04-05.12.fid

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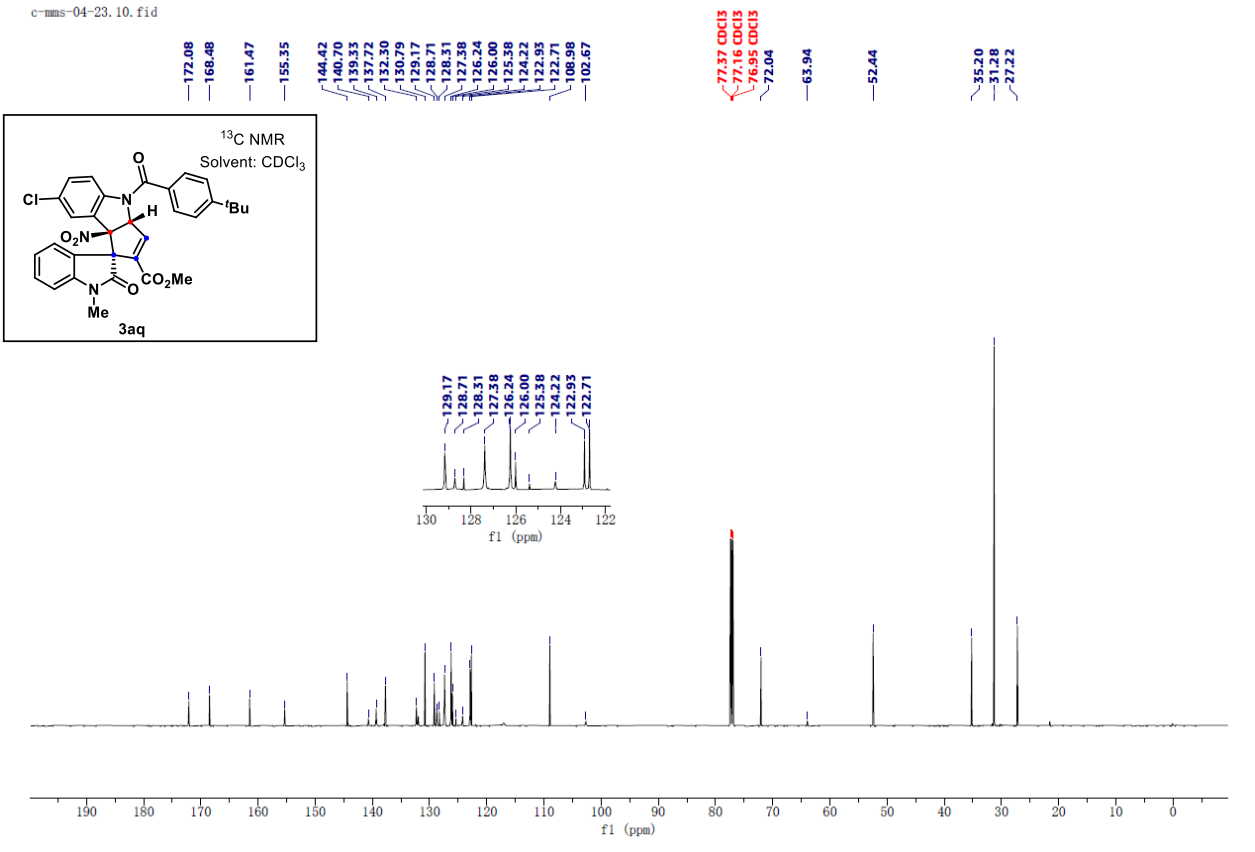
7.53
7.39
7.38
7.37
7.27
7.26
7.26 CDCl3
7.24
7.23
7.22
7.18
7.17
7.16
7.03
7.02
7.01
6.96
6.94
6.93
6.78
3.56
3.40
1.59 H2O
1.38
1H NMR
Solvent: CDCl3
Cl
O
N
H
tBu
O2N
CO2Me
N
Me
O
3aq
5.20
1.21
1.81
0.80
1.30
2.23
1.25
3.00
3.08
9.00
f1 (ppm)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144.42
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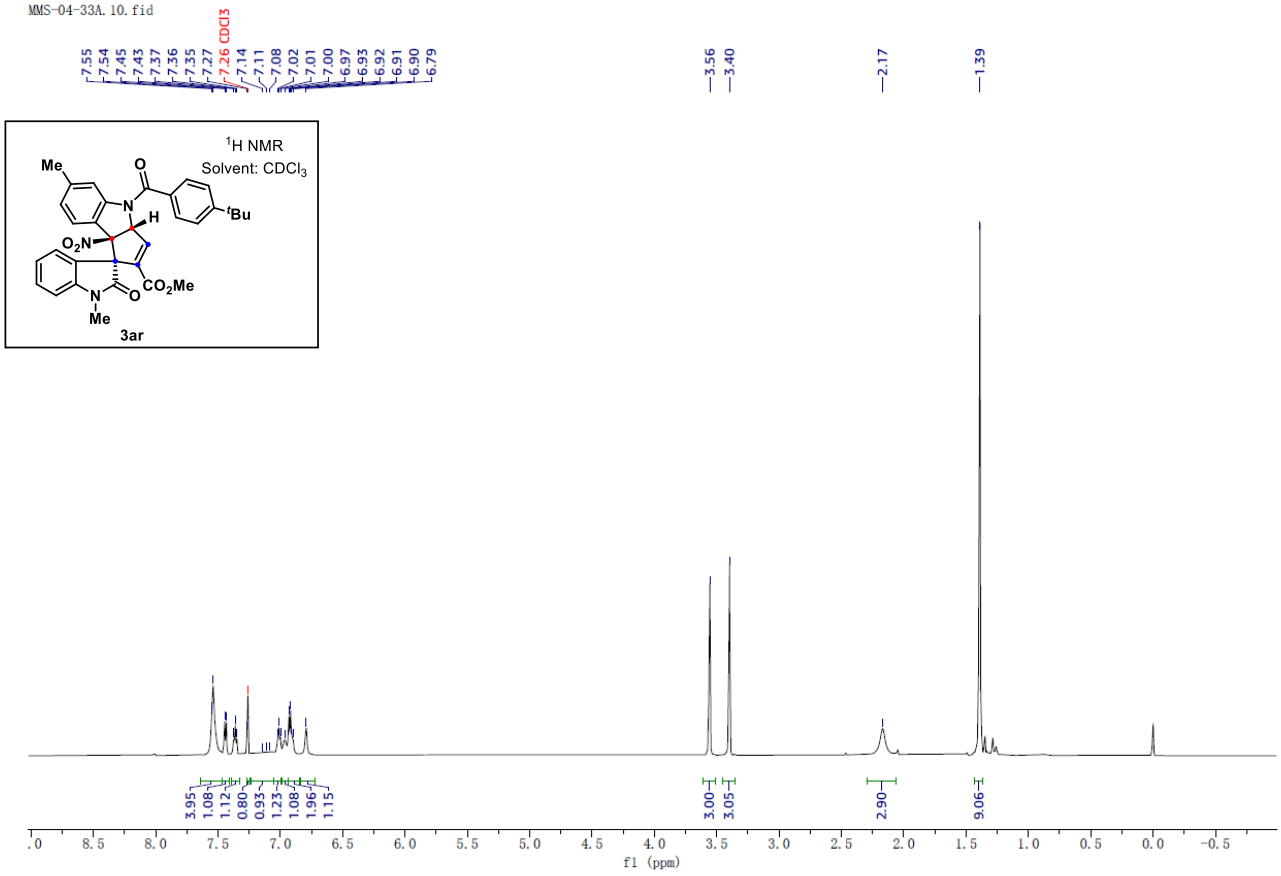
135.33
137.72
132.30
130.79
129.17
128.71
128.31
127.38
126.24
126.00
125.38
124.22
122.93
122.71
108.98
102.67
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.04
63.94
52.44
35.20
31.28
27.22
13C NMR
Solvent: CDCl3
Cl
O
N
H
tBu
O2N
CO2Me
N
Me
O
3aq
129.17
128.71
128.31
127.38
126.24
126.00
125.38
124.22
122.93
122.71
f1 (ppm)


MMS-04-33A.10.fid
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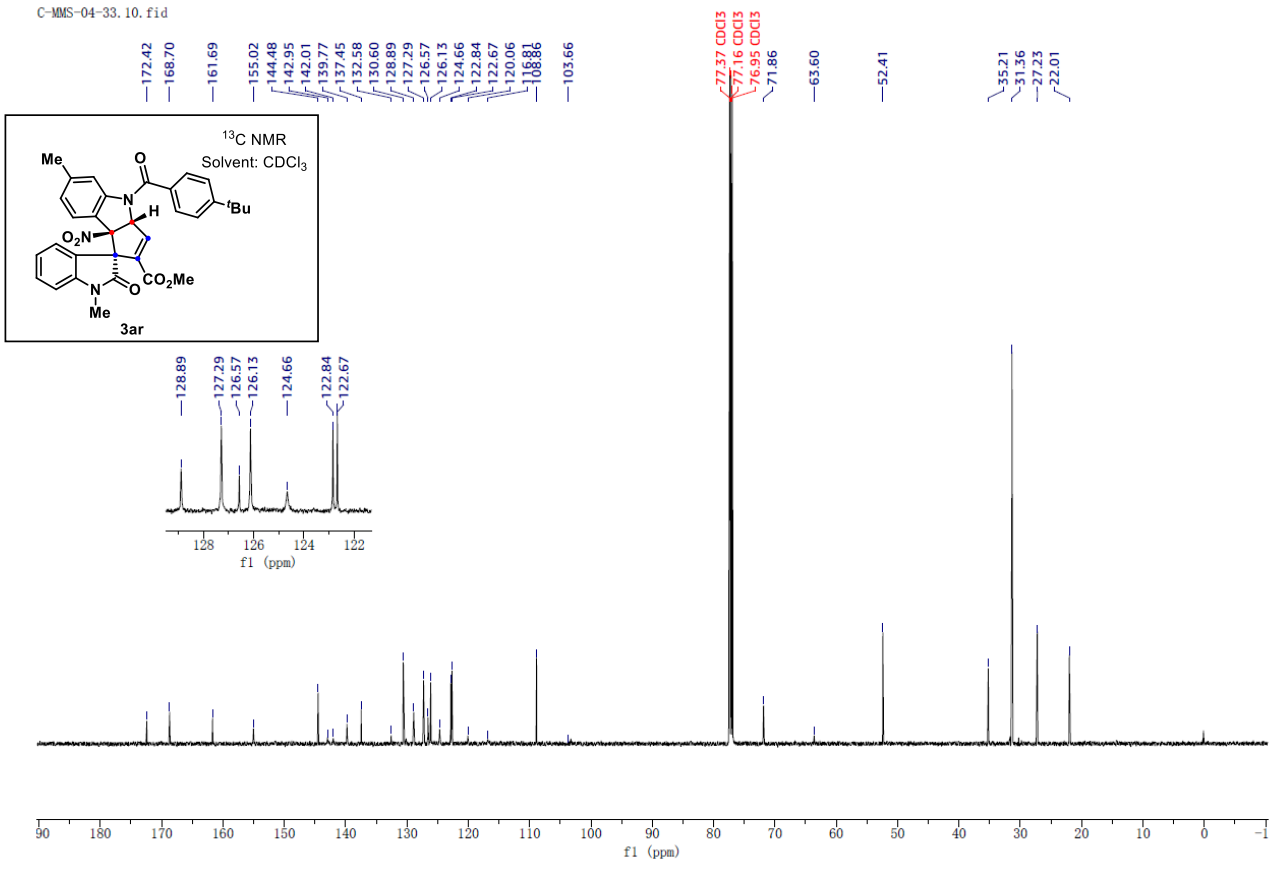
7.45
7.43
7.37
7.36
7.35
7.27
7.26 CDCl3
7.14
7.11
7.08
7.02
7.01
7.00
6.97
6.93
6.92
6.91
6.90
6.79
3.56
3.40
2.17
1.39
1H NMR
Solvent: CDCl3
Me
O
N
H
tBu
O2N
CO2Me
N
Me
O
3ar
3.95
1.08
1.12
0.80
0.93
1.23
1.08
1.96
1.15
3.00
3.05
2.90
9.06
f1 (ppm)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130.60
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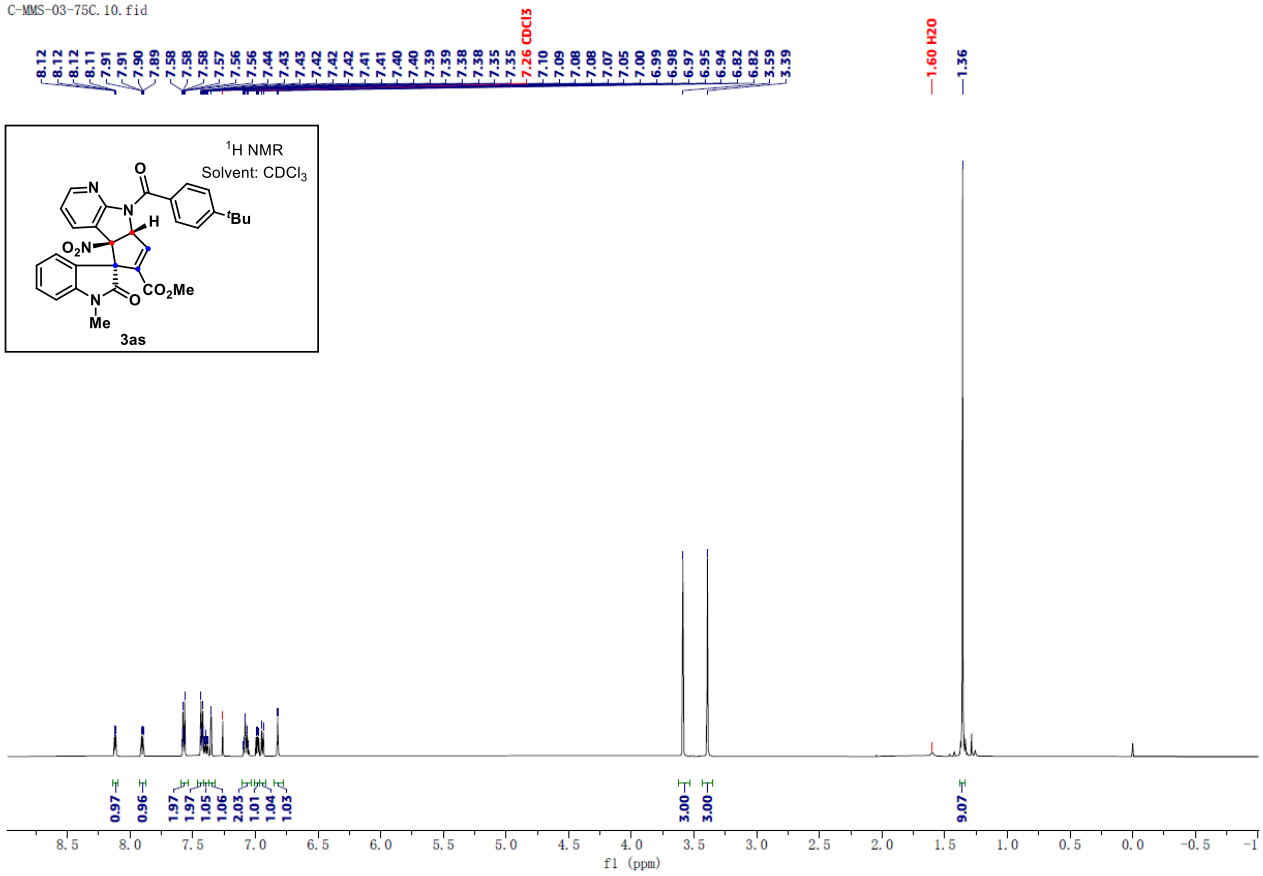
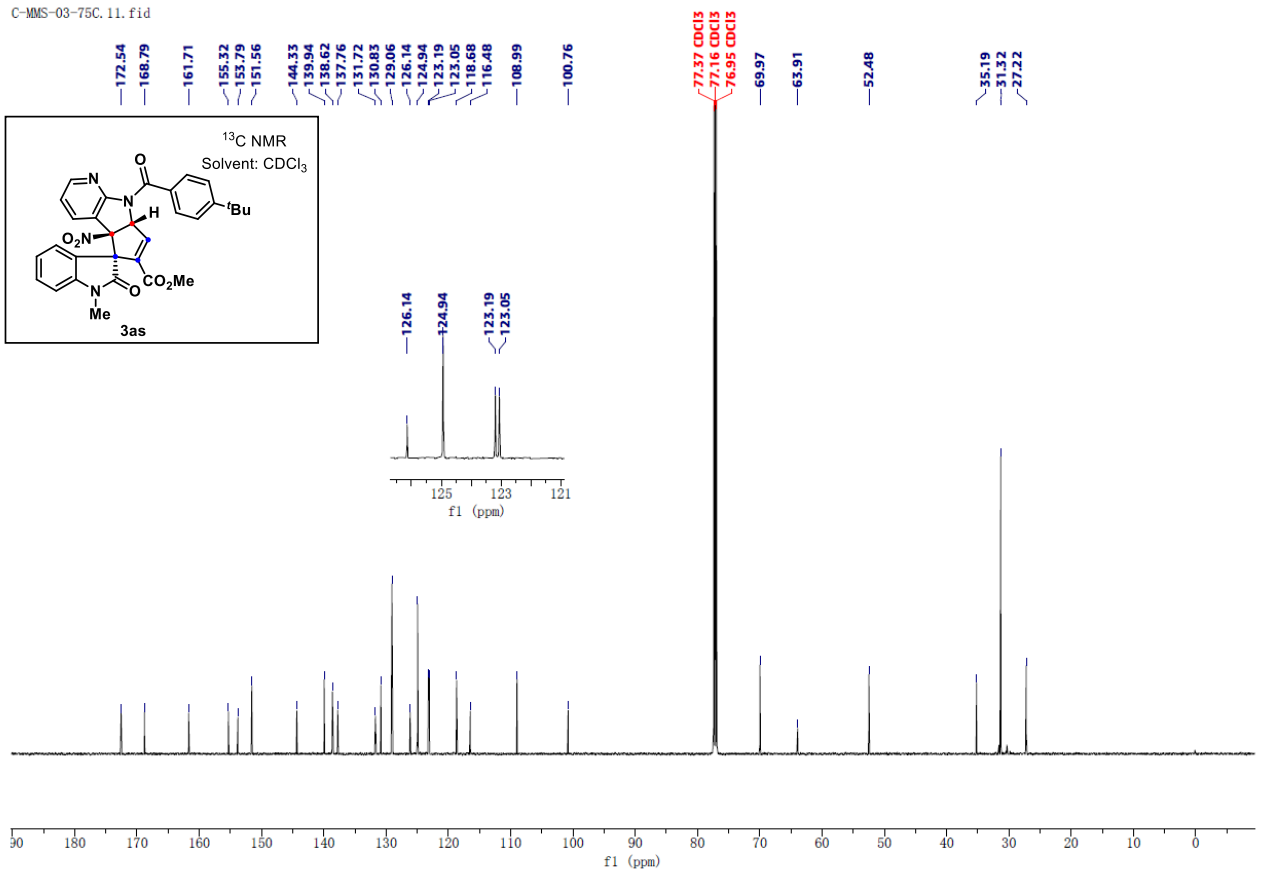
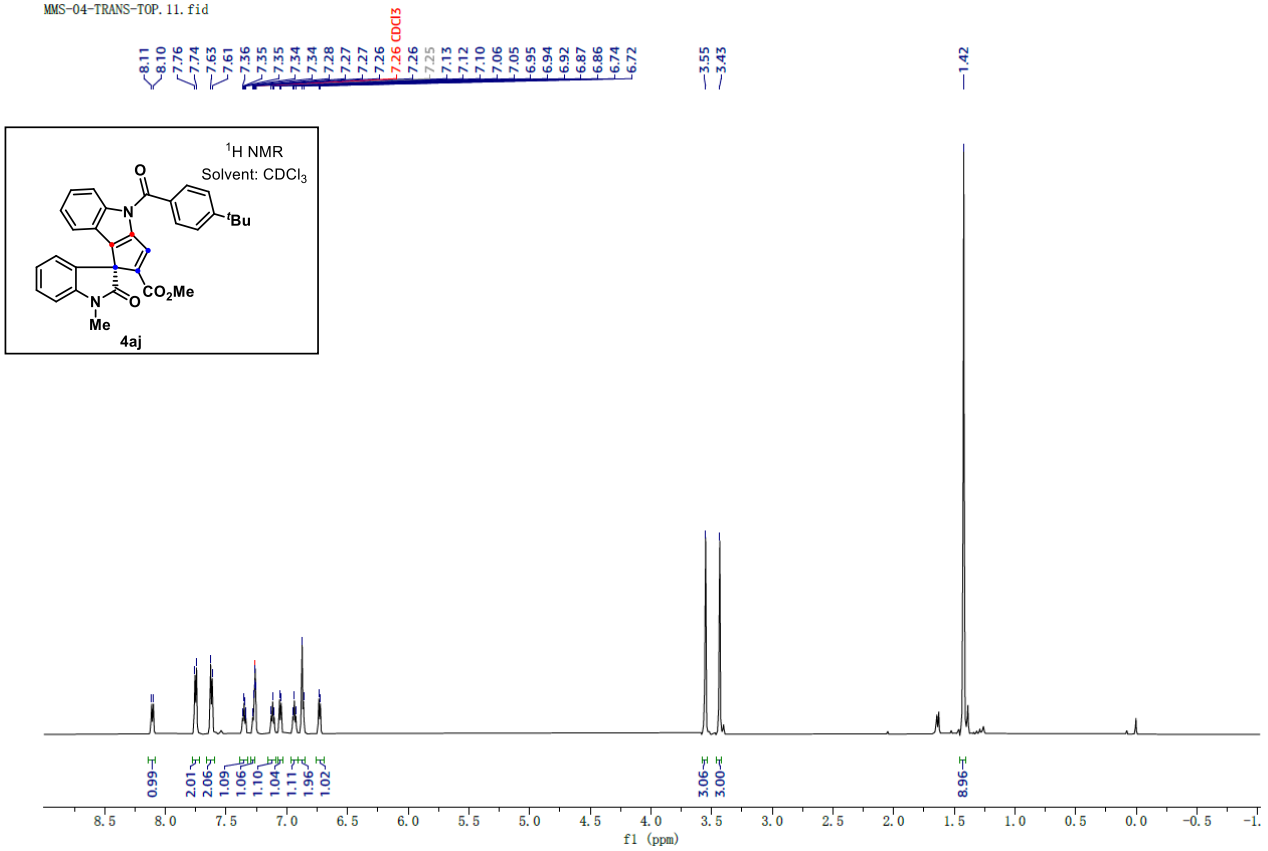
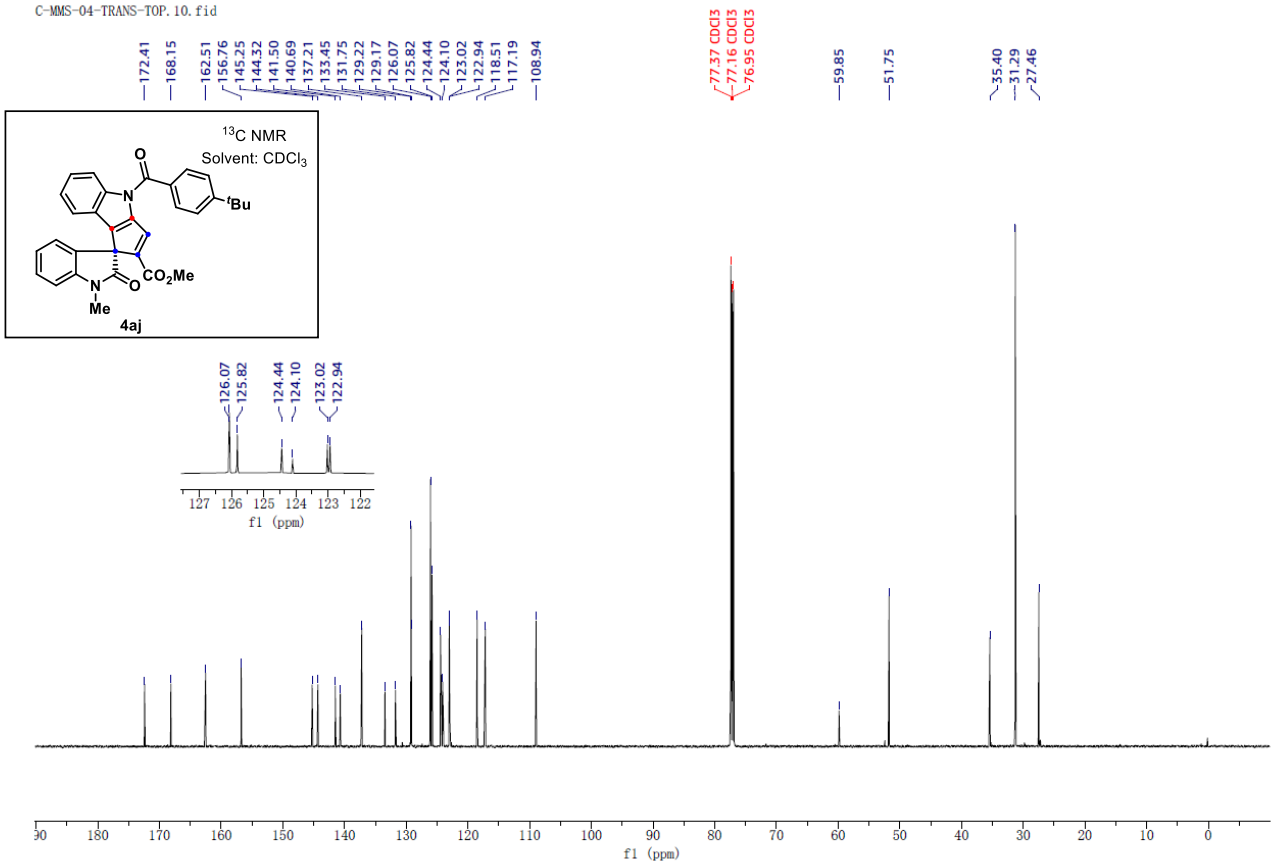
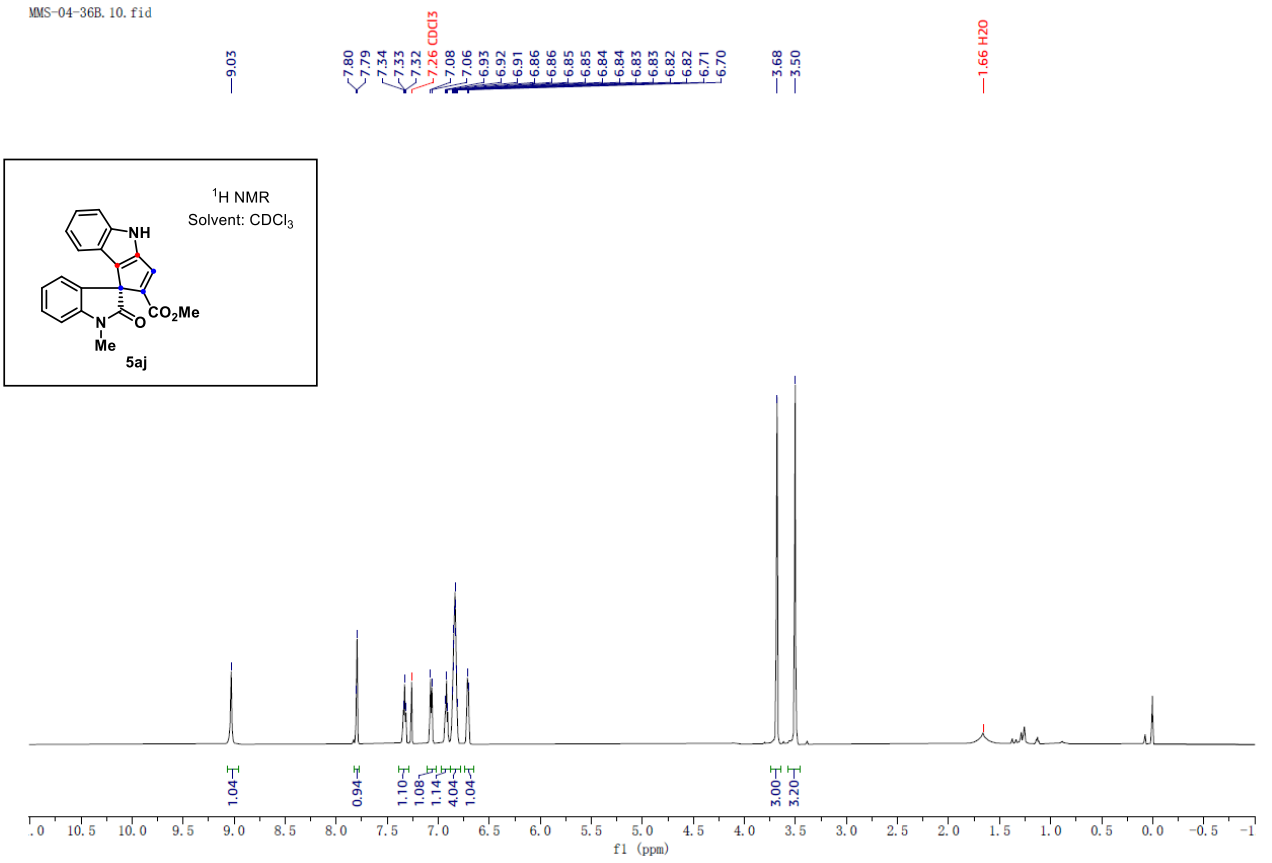
127.29
126.57
126.13
124.66
122.84
122.67
120.06
116.81
108.86
103.66
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.86
63.60
52.41
35.21
31.36
27.23
22.01
13C NMR
Solvent: CDCl3
Me
O
N
H
tBu
O2N
CO2Me
N
Me
O
3ar
128.89
127.29
126.57
126.13
124.66
122.84
122.67
f1 (ppm)
f1 (ppm)

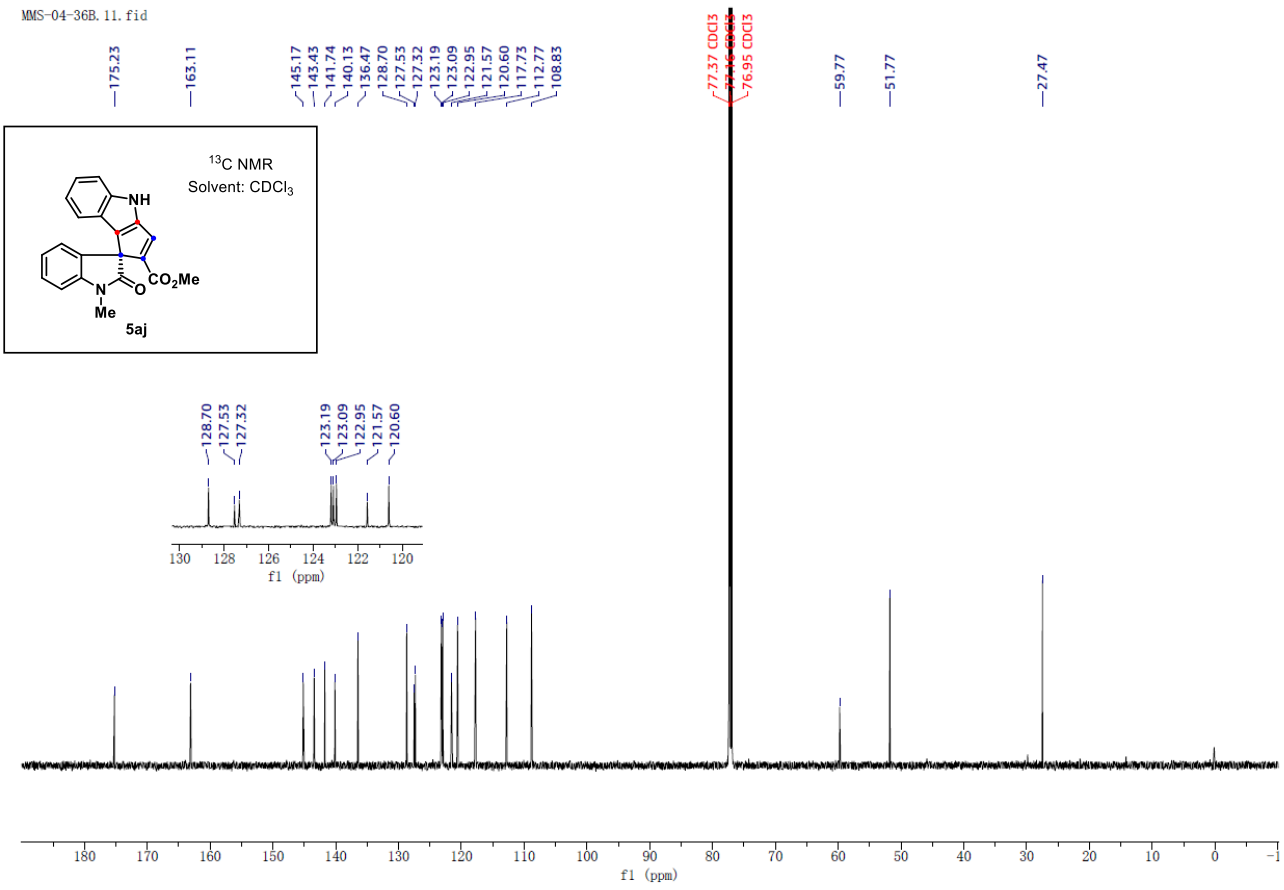

C-MMS-03-75C.10.fid
8.12 8.12 8.12 8.11 7.91 7.91 7.90 7.89 7.58 7.58 7.58 7.57 7.56 7.56 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.35 7.35 7.26 CDCl3 7.10 7.09 7.08 7.08 7.07 7.05 7.00 6.99 6.98 6.97 6.95 6.94 6.82 6.82 3.59 3.39
1.60 H2O
1.36
1H NMR
Solvent: CDCl3
tBu
O2N
CO2Me
N
Me
3as
0.97 0.96 1.97 1.97 1.05 1.06 2.03 1.01 1.04 1.03 3.00 3.00 9.07
f1 (ppm)


C-MMS-03-75C.11.fid
172.54 168.79 161.71 155.32 153.79 151.56 144.33 139.94 138.62 137.76 131.72 130.83 129.06 126.14 124.94 123.19 123.05 118.68 116.48 108.99 100.76
77.37 CDCl3 77.16 CDCl3 76.95 CDCl3
69.97 63.91 52.48 35.19 31.32 27.22
126.14 124.94 123.19 123.05
13C NMR
Solvent: CDCl3
tBu
O2N
CO2Me
N
Me
3as
f1 (ppm)


MMS-04-TRANS-TOP.11.fid
^{1}H NMR
Solvent: CDCl$_3$
4aj
f1 (ppm)


C-MMS-04-TRANS-TOP.10.fid
^{13}C NMR
Solvent: CDCl$_3$
4aj
f1 (ppm)


MMS-04-36B.10.fid
9.03
7.80
7.79
7.34
7.33
7.32
7.26 CDCl3
7.08
7.06
6.93
6.92
6.91
6.86
6.86
6.85
6.85
6.84
6.84
6.83
6.83
6.82
6.82
6.71
6.70
3.68
3.50
1.66 H2O
1H NMR
Solvent: CDCl3
NH
CO2Me
N
O
Me
5aj
1.04
0.94
1.10
1.08
1.14
4.04
1.04
3.00
3.20
f1 (ppm)


MMS-04-36B.11.fid
175.23
163.11
145.17
143.43
141.74
140.13
136.47
128.70
127.53
127.32
123.19
123.09
122.95
121.57
120.60
117.73
112.77
108.83
77.37 CDCl3
77.16
76.95 CDCl3
59.77
51.77
27.47
13C NMR
Solvent: CDCl3
NH
CO2Me
N
O
Me
5aj
f1 (ppm)

12.References

[1] (a) Y. M. Chung, Y. J. Im and J. N. Kim, *B. Kor. Chem. Soc.*, 2002, **23**, 1651−1654. (b) K. K. Wang, P. Wang, Q. Ouyang, W. Du and Y. C. Chen, *Chem. Commun.*, 2016, **52**, 11104−11107. (c) X. Fan, H. Yang and M. Shi, *Adv. Synth. Catal*., 2017, **359**, 49−57.

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