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SUPPORTING INFORMATION

Asymmetric Decarboxylative [3+2] Cycloaddition for the Diastereo- and Enantioselective Synthesis of Spiro[2.4]heptanes via Cyclopropanation

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# Can Gao and Ting Zhang contributed equally to this work.

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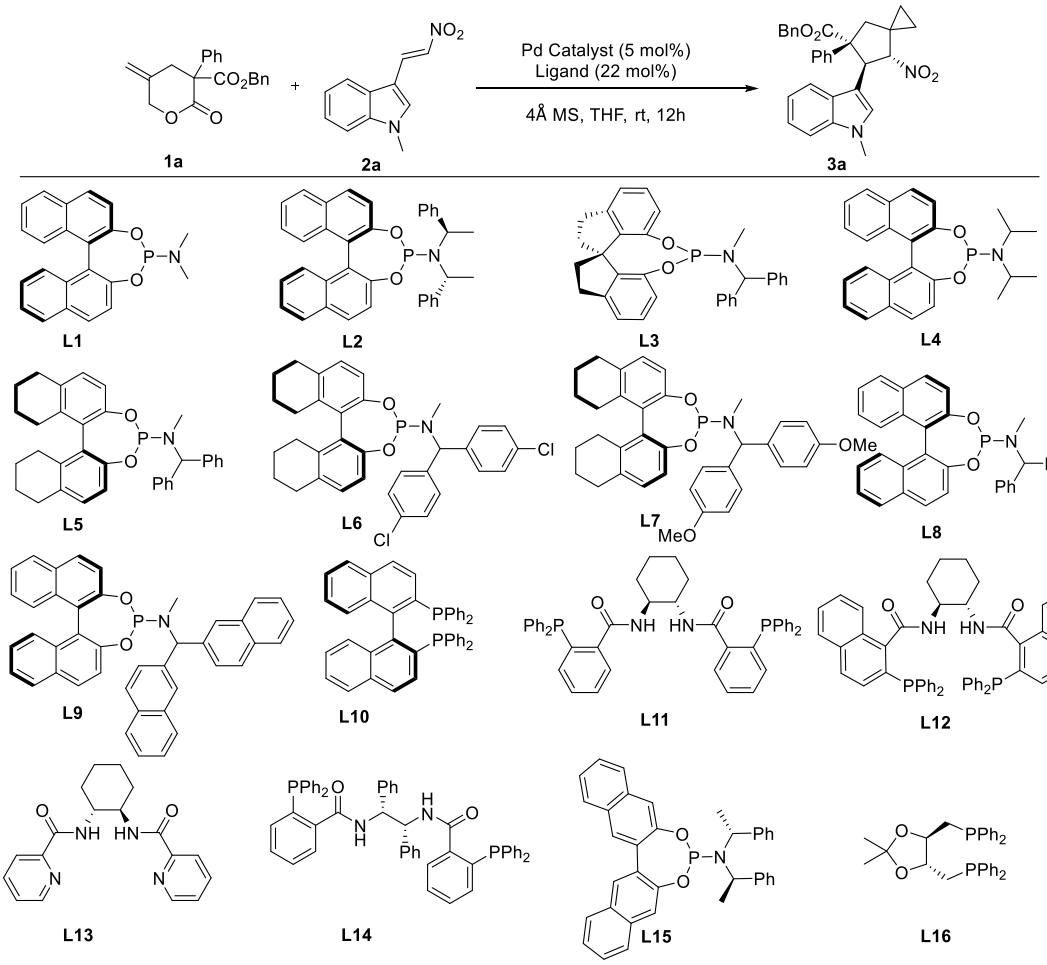
1.General Information

Unless otherwise noted, all the reactions for the preparation of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under nitrogen atmosphere. The solvents were purified by distillation from calcium hydride unless otherwise noted. All other commercial reagents were used without further purification unless otherwise indicated. ^{1}H NMR, ^{13}C NMR and ^{31}P spectra were recorded on Bruker 400 MHz spectrometer (ADVNCE III) using chloroform-*d* ($CDCl_3$) as the internal standard. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.1) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. The enantiomeric excesses (e.e.) was determined by HPLC analysis on LC-20AD/T LPGE KIT using Daicel CHIRALPAK® column IA-U, IC-U. *X*-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Cu radiation (λ = 1.54184 Å). If not specially mentioned, flash column chromatography was performed using 200-300 silica gel purchased from Yaitai Chemicals (China). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method. Optical rotations were recorded on an AUTOPOL II digital polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/100 mL solvent). The γ-methylidene-δ-valerolactones[1] and indolyl nitroolefins[2-3] were prepared according to the reported procedure.

2. Reaction Optimization

Table S1. Investigation of ligands. [a]



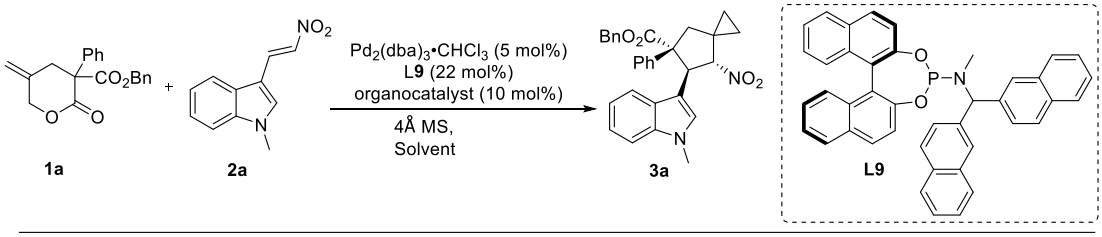
Entry	Catalyst	L	Yield[b]	dr[c]	ee[d]
1	$Pd_2(dba)_3{\cdot}CHCl_3$	**L1**	42%	1:1	62%
2	$Pd_2(dba)_3{\cdot}CHCl_3$	**L2**	25%	1:1	37%
3	$Pd_2(dba)_3{\cdot}CHCl_3$	**L3**	40%	1:1	66%
4	$Pd_2(dba)_3{\cdot}CHCl_3$	**L4**	32%	1:1	40%
5	$Pd_2(dba)_3{\cdot}CHCl_3$	**L5**	35%	1:1	-57%
6	$Pd_2(dba)_3{\cdot}CHCl_3$	**L6**	52%	1:1	-68%
7	$Pd_2(dba)_3{\cdot}CHCl_3$	**L7**	0	--	--
8	$Pd_2(dba)_3{\cdot}CHCl_3$	**L8**	43%	1:1	69%
9	$Pd_2(dba)_3{\cdot}CHCl_3$	**L9**	64%	1:1	85%
10	$Pd_2(dba)_3{\cdot}CHCl_3$	**L10**	0	--	--
11	$Pd_2(dba)_3{\cdot}CHCl_3$	**L11**	36%	10:1	45%
12	$Pd_2(dba)_3{\cdot}CHCl_3$	**L12**	0	--	--
13	$Pd_2(dba)_3{\cdot}CHCl_3$	**L13**	0	--	--
14	$Pd_2(dba)_3{\cdot}CHCl_3$	**L14**	0	--	--

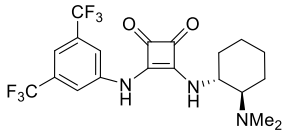
15	$Pd_2(dba)_3{\cdot}CHCl_3$	**L15**	0	--	--
16	$Pd_2(dba)_3{\cdot}CHCl_3$	**L16**	0	--	--
17	$Pd(PPh_3)_4$	\	50%	1:1	0

[a] Reaction conditions: 5 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$, 22 mol% of Ligand, 0.12 mmol of **1a**, 0.1 mmol of **2a** and 4Å MS in THF (1 mL) at room temperature. [b] Isolated yield of **3a**. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis.

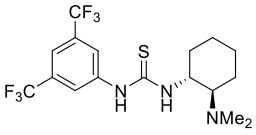
After optimization, **L9** was selected for the next investigation.

Table S2. Investigation of organocatalysts, solvents and temperature.[a]

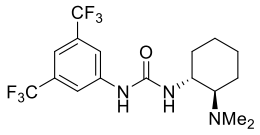




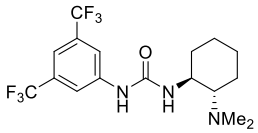
OC1



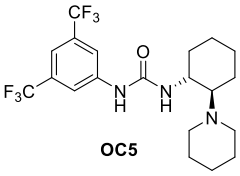
OC2



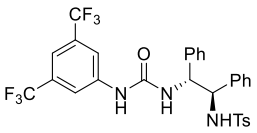
OC3



OC4



OC5



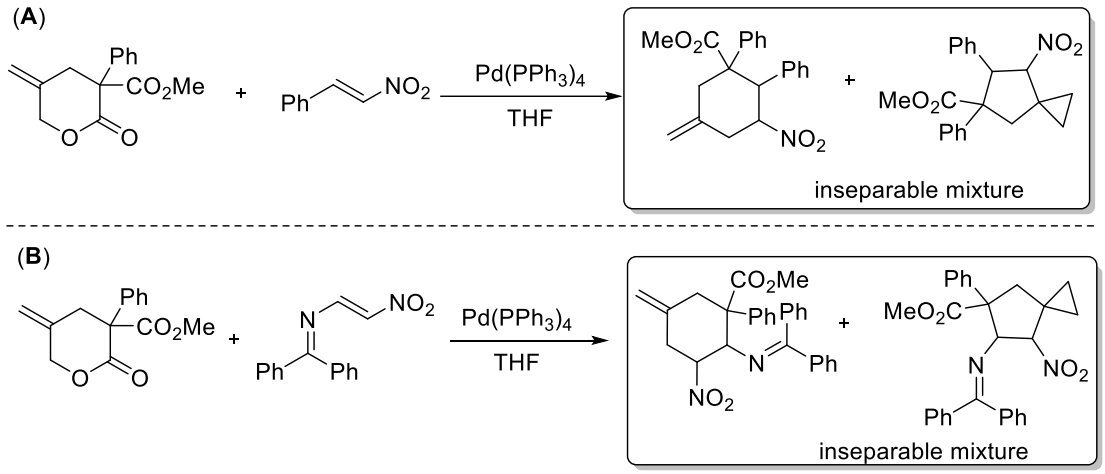
OC6

Entry	OC	Solvent	Temperature	Yield[b]	dr[c]	ee[d]
1	**OC1**	THF	rt	42%	1:1	83%
2	**OC2**	THF	rt	31	1:1	72%
3	**OC3**	THF	rt	63%	3:1	85%
4	**OC4**	THF	rt	50%	2:1	85%
5	**OC5**	THF	rt	64%	5:1	85%
6	**OC6**	THF	rt	0	--	--
7	**OC5**	Toluene	rt	53%	2:1	75%
8	**OC5**	DMF	rt	49%	2:1	76%
9	**OC5**	Xylene	rt	52%	2:1	82%
10	**OC5**	Anisole	rt	50%	2:1	82%
11	**OC5**	THF	0°C	64%	4:1	87%
12	**OC5**	THF	-10°C	73%	6:1	94%

[a] Reaction conditions: 5 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$, 22 mol% of **L9**, 0.12 mmol of **1a**, 0.1 mmol of **2a** and 4Å MS in THF (1 mL) at room temperature. [b] Isolated yield of **3a**. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis.

After optimization, the best reaction condition was with **OC6** and THF at -10 ºC, which was used for next exploration.

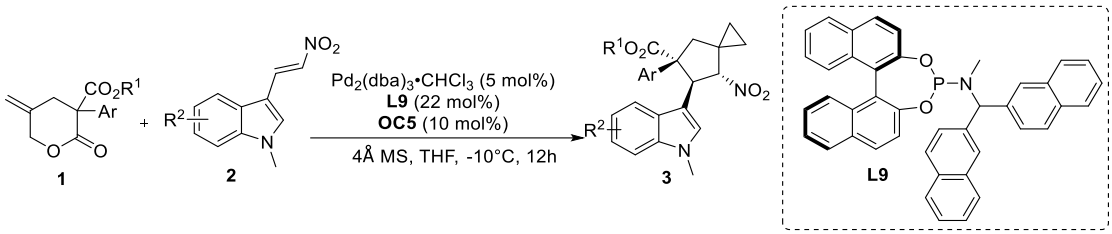
Table S3. Investigation of nitroolefins [a]



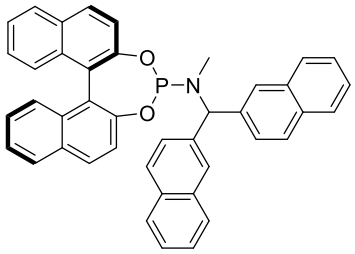
[a] Reaction conditions: *γ*-methylidene-*δ*-valerolactones (0.048 mmol), nitroolefins (0.04 mmol) and 5 mol% of $Pd(PPh_3)_4$ in 0.4 mL THF at room temperature.

Besides indolyl nitroolefins and 2-nitrobenzofuran, other nitroolefins were also screened for this asymmetric cycloaddition. When (E)-(2-nitrovinyl)benzene (Table S3, **A**) and (E)-N-(2-nitrovinyl)-1,1-diphenylmethanimine (Table S3, **B**) were submitted to the standard reaction conditions, A mixture of both [4+2] and [3+2] cycloaddition adducts were generated which could not be separated and purified by silica gel chromatography. Therefore, indolyl nitroolefins and 2-nitrobenzofuran were used in this asymmetric [3+2] cycloaddition reaction.

3. Representative procedure and data for the synthesis of L9 and 3



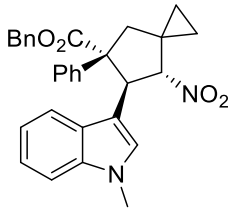
To a dried tube was added *γ*-methylidene-*δ*-valerolactone **1** (0.12 mmol, 1.2 equiv.), indole nitroolefins **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5.2 mg, 5 mol%), **L9** (0.022 mmol, 13.4 mg, 22 mol%), **OC5** (0.01 mmol, 4.4 mg, 10 mol%) followed with the addition of 4Å molecule sieve and 1 mL of THF under nitrogen atmosphere. The reaction mixture was stirred at -10 °C for 12 h and directly purified by silica gel chromatography (hexane/ethyl acetate = 20:1-5:1) to yield the products.



N-(di(naphthalen-2-yl) methyl)-N-methyldinaphtho[2,1-d:1',2'f][1,3,2] dioxaphosphepin-4-amine (L9)

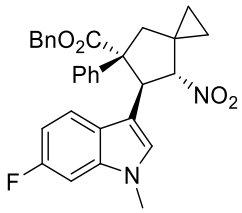
L9 was synthesized according to the literature reported by Fletcher.[4] White solid, m.p. = 161-162 ºC ; $[\alpha]_D^{20.0}$= - 6.6 (0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.25 (d, *J* = 4.0 Hz, 3H), 6.31 (d, *J* = 10.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 7.17-7.23 (m, 2H), 7.28 - 7.34 (m, 2H), 7.38 (dd, *J* = 8.4, 5.8 Hz, 2H), 7.43 -7.52 (m, 5H), 7.55 - 7.64 (m, 3H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.81-7.85 (m, 6H), 7.92 (dt, *J* = 16.5, 8.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 65.5, 65.9, 121.8, 122.2, 122.5, 124.0, 124.1, 124.6, 124.9, 126.1, 126.2, 126.3, 126.4, 126.8, 127.0, 127.1, 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 130.0, 130.4, 130.7, 131.5, 132.6, 132.8, 132.9, 133.3, 133.4, 137.4, 137.5, 137.7, 137.8, 149.5, 150.1, 150.2 ppm; ^{31}P NMR (160 MHz, $CDCl_3$)

δ 148.7 ppm; HRMS (ESI) m/z calcd. for $C_{42}H_{31}NO_2P$ $[M+H]^+$: 612.2087, found: 612.2084.



Benzyl (5R,6S,7R)-6-(1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4]heptane-5-carboxylate (3a)

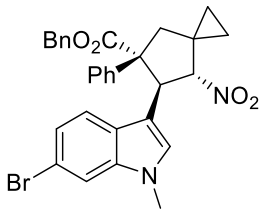
Colorless oil, 35mg, 73% yield; dr = 6 : 1, 94% ee; $[\alpha]_D^{20.0}$= - 5.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 13.3 min, t (minor) = 14.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73-0.81 (m, 1H), 0.85-0.93 (m, 1H), 1.07-1.14 (m, 1H), 1.15-1.21 (m, 1H), 2.63 (d, *J* = 13.8 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H), 3.55 (s, 3H), 5.00-5.04 (m, 2H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.36 (d, *J* = 10 Hz, 1H), 6.11 (s, 1H), 6.96 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.19 (m, 6H), 7.20 (dt, *J* = 9.3, 3.3 Hz, 2H), 7.28 (dd, *J* = 5.9, 2.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 14.4, 17.6, 23.2, 32.7, 44.5, 50.2, 60.9, 67.0, 97.5, 108.9, 109.00, 119.2, 119.8, 121.4, 127.0, 127.4, 127.8, 128.1, 128.2, 128.5, 128.6, 128.8, 135.7, 136.5, 138.9, 174.2 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{29}N_2O_4$ $[M+H]^+$: 481.2122, found: 481.2121.



Benzyl(5R,6S,7R)-6-(6-fluoro-1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4] heptane -5-carboxylate (3b)

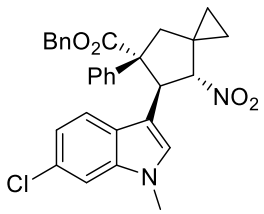
Colorless oil, 27 mg, 54% yield; dr = 2 : 1, 88% ee; $[\alpha]_D^{20.0}$= - 1.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 15.2 min, t (minor) = 18.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 0.72 – 0.79 (m, 1H), 0.83 – 0.89 (m, 1H), 1.09-1.13 (m, 1H), 1.16-1.20 (m, 1H), 2.61 (d, J = 13.8 Hz, 1H), 2.91 (d, J = 13.8 Hz, 1H), 3.49 (s, 3H), 4.96-5.03 (m, 2H), 5.18 (d, J = 12.4 Hz, 1H), 5.29 (d, J = 8.0 Hz, 1H), 6.08 (s, 1H), 6.49 – 6.59 (m, 1H), 6.70 (td, J = 9.2, 2.4 Hz, 1H), 6.78 – 6.84 (m, 1H), 7.02 (dd, J = 7.2, 1.8 Hz, 2H), 7.12 – 7.18 (m, 5H), 7.25 – 7.30 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.6, 23.1, 32.8, 44.5, 50.2, 60.7, 67.0, 95.3 (d, J = 26.0 Hz), 97.3, 108.0 (d, J = 24.2 Hz), 109.2, 120.7 (d, J = 10.0 Hz), 126.9, 127.5, 127.9, 128.2, 128.3 (d, J = 2.3 Hz), 128.4, 128.5, 128.6, 135.7, 136.5 (d, J = 11.9 Hz), 138.8, 159.7(d, J = 236.3 Hz), 174.1 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{28}FN_2O_4$ $[M+H]^+$: 499.2028, found: 499.2023.



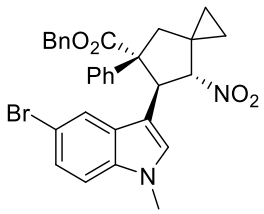
Benzyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4] heptane-5-carboxylate (3c)

Colorless oil, 36 mg, 65% yield; dr = 5 : 1, 94% ee; $[\alpha]_D^{20.0}$= - 18.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 22.0 min, t (minor) = 25.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74-0.79 (m, 1H), 0.85-0.89 (m, 1H), 1.07-1.14 (m, 1H), 1.17-1.22 (m, 1H), 2.61 (d, J = 13.8 Hz, 1H), 2.91 (d, J = 13.8 Hz, 1H), 3.51 (s, 3H), 4.97-5.03 (m, 2H), 5.17 (d, J = 12.4 Hz, 1H), 5.28 (d, J = 10.4 Hz, 1H), 6.07 (s, 1H), 7.00-7.04 (t, J = 8.4 Hz, 3H), 7.07-7.09 (d, J = 8.6 Hz, 1H), 7.14 – 7.19 (m, 4H), 7.23 (d, J = 7.4 Hz, 1H), 7.27-7.28 (m, 2H), 7.33-7.34 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 17.5, 23.1, 32.8, 44.5, 50.1, 60.6, 67.1, 97.1, 109.3, 112.1, 115.2, 121.1, 122.5, 126.7, 126.9, 127.5, 127.9, 128.2, 128.3, 128.5, 129.5, 135.6, 137.3, 138.8, 174.1 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{28}BrN_2O_4$ $[M+H]^+$: 559.1227, found: 559.1224.



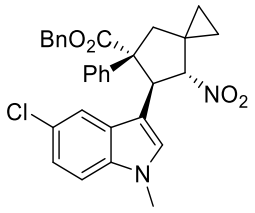
Benzyl(5R,6S,7R)-6-(6-chloro-1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4] heptane-5-carboxylate (3d)

Colorless oil, 35 mg, 68% yield; dr = 5 : 1, 93% ee; $[\alpha]_D^{20.0}$= - 22.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 15.2 min, t (minor) = 17.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.73-0.79 (m, 1H), 0.85-0.90 (m, 1H), 1.09-1.14 (m, 1H), 1.16-1.22 (m, 1H), 2.61 (d, *J* = 13.8 Hz, 1H), 2.90 (d, *J* = 13.8 Hz, 1H), 3.49 (s, 3H), 4.96-5.04 (m, 2H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 6.09 (s, 1H), 6.88-6.91 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 7.13 – 7.17 (m, 5H), 7.24-7.29 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.5, 17.5, 23.1, 32.8, 44.5, 50.1, 60.6, 67.1, 97.1, 109.1, 109.2, 120.0, 120.8, 126.4, 126.9, 127.5, 127.9, 128.2, 128.3, 128.4, 128.5, 129.5, 135.6, 136.9, 138.8, 174.1 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{28}ClN_2O_4$ $[M+H]^+$: 515.1732, found: 515.1736.



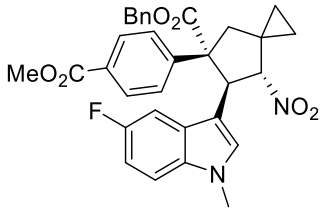
Benzyl(5R,6S,7R)-6-(5-bromo-1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4] heptane-5-carboxylate (3e)

Colorless oil, 41mg, 73% yield; dr = 4 : 1, 91% ee; $[\alpha]_D^{20.0}$= - 2.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 16.8 min, t (minor) = 16.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.74-0.79 (m, 1H), 0.85-0.91 (m, 1H), 1.13-1.23 (m, 2H), 2.60 (d, *J* = 13.8 Hz, 1H), 2.89 (d, *J* = 13.8 Hz, 1H), 3.54 (s, 3H), 5.03 (dd, *J* = 14.6, 11.4 Hz, 2H), 5.19 (d, *J* = 14.0 Hz, 1H), 5.22 (d, *J* = 8.8 Hz, 1H), 6.26 (s, 1H), 7.00 – 7.08 (m, 5H), 7.15 – 7.20 (m, 5H), 7.26-7.29 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.5, 17.7, 23.1, 32.9, 44.5, 50.5, 60.5, 67.0, 96.7, 108.5, 110.5, 112.8, 122.4, 124.3, 126.9, 127.7, 128.0, 128.2, 128.3, 128.5, 129.2, 130.4, 135.2, 135.6, 138.7, 174.1 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{28}BrN_2O_4$ $[M+H]^+$: 559.1227, found: 559.1231.



Benzyl(5R,6S,7R)-6-(5-chloro-1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4] heptane-5-carboxylate (3f)

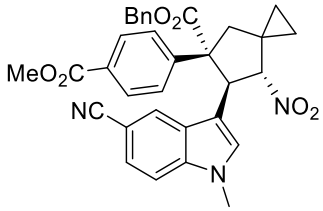
Colorless oil, 37 mg, 72% yield; dr = 3 : 1, 91% ee; $[\alpha]_D^{20.0}$= - 1.9 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IB-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 11.6 min, t (minor) = 10.3 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.74-0.80 (m, 1H), 0.87-0.91 (m, 1H), 1.13-1.24 (m, 2H), 2.61 (d, *J* = 13.8 Hz, 1H), 2.90 (d, *J* = 13.8 Hz, 1H), 3.55 (s, 3H), 5.03 (dd, *J* = 13.8, 11.4 Hz, 2H), 5.19 (d, *J* = 12.3 Hz, 1H), 5.23 (d, *J* = 10.6 Hz, 1H), 6.26 (s, 1H), 6.96 (s, 1H), 7.01-7.06 (m, 4H), 7.15-7.19 (m, 4H), 7.27-7.31 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.5, 17.7, 23.1, 32.9, 44.5, 50.4, 60.6, 67.0, 96.8, 108.5, 110.1, 119.3, 121.8, 125.2, 126.9, 127.7, 128.0, 128.2, 128.3, 128.4, 128.5, 130.5, 135.0, 135.7, 138.8, 174.1 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{28}ClN_2O_4$ $[M+H]^+$: 515.1732, found: 515.1737.



Benzyl(5R,6S,7R)-6-(5-fluoro-1-methyl-1H-indol-3-yl)-5-(4-(methoxycarbonyl) phenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3g)

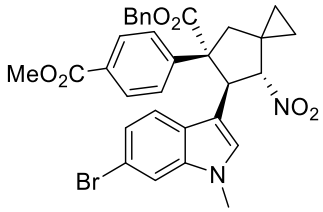
Colorless oil, 35 mg, 63% yield; dr = 4 : 1, 92% ee; $[\alpha]_D^{20.0}$= - 45.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 16.2 min, t (minor) = 13.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.75-0.81 (m, 1H), 0.86-0.93 (m, 1H), 1.10-1.16 (m, 1H), 1.17-1.22 (m, 1H), 2.62 (d, *J* = 13.8 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H), 3.54 (s, 3H), 3.90 (s, 3H), 4.93 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 10.0

Hz, 1H), 6.20 (s, 1H), 6.87 (td, *J* = 9.0, 2.5 Hz, 1H), 6.94 (dd, J = 10.2, 2.4 Hz, 1H), 7.08 (dd, *J* = 8.5, 5.7 Hz, 3H), 7.15 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.27 (dd, *J* = 6.3, 3.0 Hz, 3H), 7.81 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.6, 23.1, 33.1, 44.3, 50.2, 52.3, 61.0, 67.4, 96.9, 104.6 (d, *J* = 24.0 Hz), 108.7 (d, *J* = 4.8 Hz), 109.8 (d, *J* = 9.8 Hz), 110.2 (d, *J* = 26.2 Hz), 127.9 (d, *J* = 9.9 Hz), 128.3, 128.4, 128.5, 128.6, 129.0, 129.2, 130.1, 133.2, 135.3, 143.9, 157.8 (d, *J* = 233.0 Hz), 166.7, 173.5 ppm; HRMS (ESI) m/z calcd. for $C_{32}H_{30}FN_2O_6$ $[M+H]^+$: 557.2082, found: 557.2080.



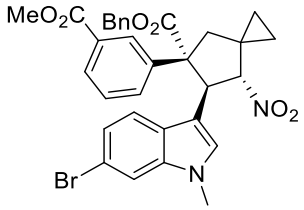
Benzyl(5R,6S,7R)-6-(5-cyano-1-methyl-1H-indol-3-yl)-5-(4-(methoxycarbonyl) phenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3h)

Colorless oil, 38 mg, 67% yield; dr = 4 : 1, 86% ee; $[\alpha]_D^{20.0}$= - 51.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 80/20, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 17.1 min, t (minor) = 13.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78-0.83 (m, 1H), 0.86-0.93 (m, 1H), 1.14-1.24 (m, 2H), 2.62 (d, *J* = 14.0 Hz, 1H), 2.92 (d, *J* = 14.0 Hz, 1H), 3.59 (s, 3H), 3.93 (s, 3H), 4.95 (d, *J* = 10.8 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 6.33 (s, 1H), 7.06 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.15 (dd, *J* = 6.0, 3.0 Hz, 2H), 7.21 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.26-7.30 (m, 3H), 7.34 (dt, *J* = 8.6, 1.4 Hz, 1H), 7.47 (s, 1H), 7.78 – 7.89 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 17.6, 23.0, 33.0, 44.3, 50.0, 52.3, 60.7, 67.4, 96.5, 102.7, 109.8, 110.1, 120.6, 124.6, 125.5, 127.2, 128.3, 128.4, 128.5, 128.6, 129.3, 129.6, 131.0, 135.2, 138.0, 143.6, 166.5, 173.3 ppm; HRMS (ESI) m/z calcd. for $C_{33}H_{30}N_3O_6$ $[M+H]^+$: 564.2129, found: 564.2126.



Benzyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-5-(4-(methoxycarbonyl) phenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3i)

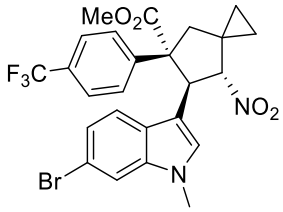
Colorless oil, 39 mg, 63% yield; dr = 6 : 1, 92% ee; $[\alpha]_D^{20.0}$= - 69.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 80/20, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 16.9 min, t (minor) = 15.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.75-0.80 (m, 1H), 0.85-0.93 (m, 1H), 1.10-1.14 (m, 1H), 1.16-1.21 (m, 1H), 2.62 (d, *J* = 14.0 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 3.50 (s, 3H), 3.91 (s, 3H), 4.92 (d, *J* = 10.0 Hz, 1H), 5.02 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.36 (d, *J* = 10.0 Hz, 1H), 6.10 (s, 1H), 7.04 -7.10 (m, 3H), 7.12 – 7.16 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.25 – 7.28 (m, 3H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.79 – 7.84 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.2, 17.5, 23.1, 32.9, 44.3, 49.9, 52.3, 61.0, 67.4, 97.1, 109.2, 112.3, 115.5, 121.0, 122.7, 126.5, 128.2, 128.5, 128.5, 128.6, 129.0, 129.1, 129.2, 135.3, 137.4, 143.8, 166.7, 173.5 ppm; HRMS (ESI) m/z calcd. for $C_{32}H_{30}BrN_2O_6$ $[M+H]^+$: 617.1282, found: 617.1287.



Benzyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-5-(3-(methoxycarbonyl) phenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3j)

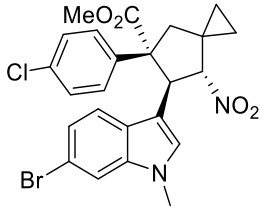
Colorless oil, 41mg, 67% yield; dr = 6 : 1, 85% ee; $[\alpha]_D^{20.0}$= - 75.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 16.1 min, t (minor) = 19.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.76-0.82 (m, 1H), 0.86-0.94 (m, 1H), 1.13-1.19 (m, 1H), 1.26-1.32 (m, 1H), 2.63 (d, *J* = 14.0 Hz, 1H), 2.98 (d, *J* = 14.0 Hz, 1H), 3.51 (s, 3H), 3.87 (s, 3H), 4.93 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.36 (d, *J* = 10.0 Hz, 1H), 6.17 (s, 1H), 6.87 – 6.92 (m, 1H), 7.00 – 7.07 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.16 (m, 2H), 7.24 – 7.29 (m, 3H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.88 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.97 (d, *J* = 2.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.0, 17.9, 23.3,

32.8, 44.2, 50.3, 52.2, 52.3, 60.9, 97.1, 109.2, 112.2, 115.4, 121.0, 122.6, 126.4, 127.7, 128.2, 128.4, 128.5, 128.7, 128.9, 129.4, 129.9, 133.7, 135.4, 137.4, 138.9, 166.8, 173.6 ppm; HRMS (ESI) m/z calcd. for $C_{32}H_{30}BrN_2O_6$ $[M+H]^+$: 617.1282, found: 617.1281.



Methyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-7-nitro-5-(4-(trifluoro methyl)phenyl)spiro[2.4]heptane-5-carboxylate (3k)

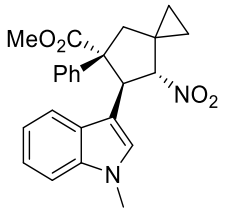
Colorless oil, 41 mg, 75% yield; dr = 5 : 1, 88% ee; $[\alpha]_D^{20.0}$= - 39.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 14.2 min, t (minor) = 13.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79-0.85 (m, 1H), 0.91-0.97 (m, 1H), 1.10-1.24 (m, 2H), 2.61 (d, J = 14.0 Hz, 1H), 3.00 (d, J = 14.0 Hz, 1H), 3.54 (s, 3H), 3.67 (s, 3H), 4.92 (d, J = 10.0 Hz, 1H), 5.36 (d, J = 10.0 Hz, 1H), 6.17 (s, 1H), 7.06 -7.18 (m, 4H), 7.35 (d, J = 1.8 Hz, 1H), 7.38 – 7.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.8, 23.1, 32.8, 44.4, 50.2, 52.9, 60.9, 96.8, 108.9, 112.4, 115.6, 120.9, 122.8, 124.0 (q, J = 270.6 Hz), 124.8 (q, J = 3.7 Hz), 126.4, 128.8, 129.2, 129.9 (q, J = 32.5 Hz), 137.4, 142.8, 174.2 ppm; HRMS (ESI) m/z calcd. for $C_{25}H_{23}BrF_3N_2O_4$ $[M+H]^+$: 551.0788, found: 551.0783.



Methyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-5-(4-chlorophenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3l)

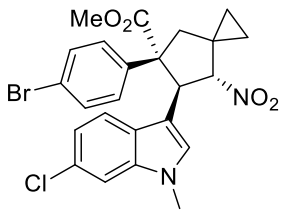
Colorless oil, 26 mg, 51% yield; dr = 4 : 1, 80% ee; $[\alpha]_D^{20.0}$= - 3.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 9.3 min, t (minor) = 10.8 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.82 (m, 1H), 0.89-0.93 (m, 1H), 1.09-1.14 (m, 1H), 1.16-1.21 (m, 1H), 2.56 (d,

J = 14.0 Hz, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 3.56 (s, 3H), 3.65 (s, 3H), 4.91 (d, *J* = 10.0 Hz, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 6.18 (s, 1H), 6.90 -6.97 (m, 2H), 7.14 (td, *J* = 8.6, 1.8 Hz, 3H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.6, 23.0, 32.9, 44.5, 50.0, 52.8, 60.4, 96.9, 109.2, 112.3, 115.5, 121.0, 122.7, 126.6, 128.1, 129.2, 129.8, 133.7, 137.2, 137.4, 174.4 ppm; HRMS (ESI) m/z calcd. for $C_{24}H_{23}BrClN_2O_4$ $[M+H]^+$: 517.0524, found: 517.0528.



Methyl(5R,6S,7R)-6-(1-methyl-1H-indol-3-yl)-7-nitro-5-phenylspiro[2.4]heptane-5-carboxylate (3m)

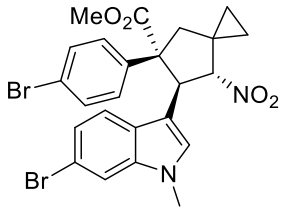
White solid, m.p. = 55 - 57 ºC; 23 mg, 57% yield; dr = 12 : 1, 87% ee; $[\alpha]_D^{20.0}$= - 4.8 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IB-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 8.5 min, t (minor) = 8.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77-0.82 (m, 1H), 0.89-0.95 (m, 1H), 1.09-1.16 (m, 1H), 1.18-1.23 (m, 1H), 2.63 (d, *J* = 13.8 Hz, 1H), 2.98 (d, *J* = 13.8 Hz, 1H), 3.56 (s, 3H), 3.66 (s, 3H), 5.01 (d, *J* = 10.0 Hz, 1H), 5.39 (d, *J* = 10.0 Hz, 1H), 6.10 (s, 1H), 6.98 -7.07 (m, 3H), 7.11-7.24 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.6, 23.0, 32.9, 44.5, 50.0, 52.8, 60.4, 96.9, 109.2, 112.3, 115.5, 121.0, 122.7, 126.6, 128.0, 129.2, 129.8, 133.6, 137.2, 137.4, 174.4 ppm; HRMS (ESI) m/z calcd. for $C_{24}H_{25}N_2O_4$ $[M+H]^+$: 405.1809, found: 405.1811.



Methyl(5R,6S,7R)-5-(4-bromophenyl)-6-(6-chloro-1-methyl-1H-indol-3-yl)-7-nitrospiro[2.4]heptane-5-carboxylate (3n)

Colorless oil, 27 mg, 52% yield; dr = 5 : 1, 87% ee; $[\alpha]_D^{20.0}$= - 3.1 (0.1, CH_2Cl_2); [Daicel

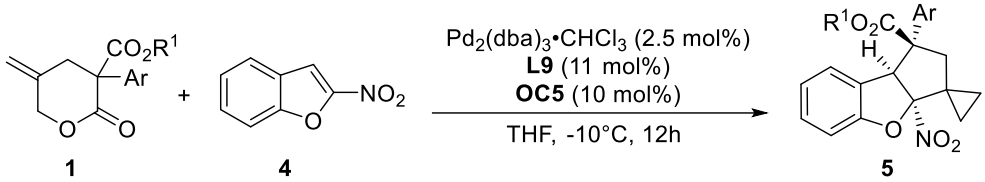
CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 9.5 min, t (minor) = 10.9 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.81 (m, 1H), 0.88-0.93 (m, 1H), 1.09-1.14 (m, 1H), 1.16-1.21 (m, 1H), 2.55 (d, J = 14.0 Hz, 1H), 2.95 (d, J = 14.0 Hz, 1H), 3.57 (s, 3H), 3.65 (s, 3H), 4.91 (d, J = 10.0 Hz, 1H), 5.31 (d, J = 10.0 Hz, 1H), 6.21 (s, 1H), 6.87 (dd, J = 8.9, 2.5 Hz, 2H), 7.00 (dd, J = 8.6, 1.9 Hz, 1H), 7.17 – 7.25 (m, 2H), 7.27 – 7.33 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.7, 23.0, 32.9, 44.4, 50.0, 52.8, 60.5, 96.9, 109.1, 109.3, 120.2, 120.7, 121.8, 126.2, 127.9, 129.3, 130.2, 131.0, 137.0, 137.7, 174.4 ppm; HRMS (ESI) m/z calcd. for $C_{24}H_{23}BrClN_2O_4$ $[M+H]^+$: 517.0524, found: 517.0525.



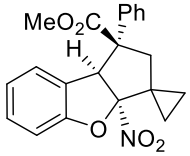
Methyl(5R,6S,7R)-6-(6-bromo-1-methyl-1H-indol-3-yl)-5-(4-bromophenyl)-7-nitrospiro[2.4]heptane-5-carboxylate (3o)

Colorless oil, 29mg, 52% yield; dr = 4 : 1, 87% ee; $[\alpha]_D^{20.0}$ = - 37.1 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 9.6 min, t (minor) = 11.2 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70-0.76 (m, 1H), 0.83-0.88 (m, 1H), 1.02-1.08 (m, 1H), 1.10-1.15 (m, 1H), 2.49 (d, J = 13.8 Hz, 1H), 2.90 (d, J = 13.8 Hz, 1H), 3.51 (s, 3H), 3.59 (s, 3H), 4.85 (d, J = 10.0 Hz, 1H), 5.26 (d, J = 10.0 Hz, 1H), 6.12 (s, 1H), 6.81 (d, J = 8.6 Hz, 2H), 7.08 (dd, J = 8.6, 1.7 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.20 – 7.26 (m, 2H) 7.30 (d, J = 1.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 17.6, 23.0, 32.9, 44.5, 50.0, 52.8, 60.5, 97.0, 109.2, 112.4, 115.6, 121.0, 121.8, 122.8, 126.6, 129.2, 130.2, 131.0, 137.4, 137.8, 174.4 ppm; HRMS (ESI) m/z calcd. for $C_{24}H_{23}Br_2N_2O_4$ $[M+H]^+$: 561.0019, found: 561.0019.

4. Representative procedure and data for the synthesis of 5

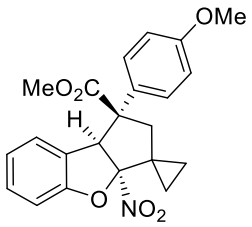


To a dried tube was added *γ*-methylidene-*δ*-valerolactone **1** (0.24 mmol, 1.2 equiv.), 2-nitrobenzofuran **4** (0.2 mmol, 1.0 equiv.), $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5.2 mg, 2.5 mol%), **L9** (0.022 mmol, 13.4 mg, 11 mol%), **OC5** (0.02 mmol, 8.8 mg, 10 mol%) followed with 1 mL of THF under nitrogen atmosphere. The reaction mixture was stirred at -10 °C for 12 h and directly purified by silica gel chromatography (hexane/ethyl acetate = 30:1-5:1) to yield the products.



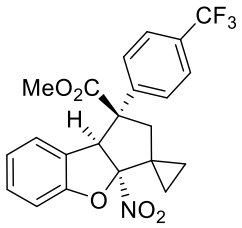
Methyl(1S,3aS)-3a-nitro-1-phenyl-1,2,3a,8b-tetrahydrospiro[cyclopenta[b] benzofuran-3,1'-cyclopropane]-1-carboxylate (5a)

White solid, m.p. = 49 - 51 ºC; 62 mg, 85% yield; dr = 7 : 1, 97% ee; $[\alpha]_D^{20.0}$= - 58.0 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U (0.46 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 10.9 min, t (minor) = 12.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.70-0.82 (m, 2H), 0.97 (dt, *J* = 9.3, 6.1 Hz, 1H), 1.48 (dt, *J* = 11.2, 6.2 Hz, 1H), 2.72 (d, *J* = 13.0 Hz, 1H), 2.99 (d, *J* = 13.0 Hz, 1H), 3.30 (s, 3H), 5.19 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.33 (m, 2H), 7.36 (t, *J* = 13.0 Hz, 1H), 7.42 – 7.51 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 11.1, 15.0, 29.8, 47.6, 52.0, 62.5, 62.6, 110.6, 122.7, 124.7, 126.0, 126.6, 126.9, 127.8, 129.0, 129.9, 141.4, 159.3, 172.7 ppm; HRMS (ESI) m/z calcd. for $C_{21}H_{20}NO_5$ $[M+H]^+$: 366.1336, found: 366.1337.



Methyl(1S,3aS)-1-(4-methoxyphenyl)-3a-nitro-1,2,3a,8b-tetrahydrospiro[cyclo penta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5b)

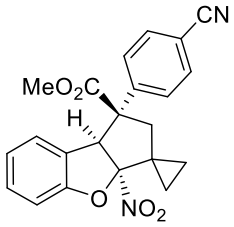
Colorless oil, 40 mg, 51% yield; dr = 5 : 1, 84% ee; $[\alpha]_D^{20.0}$= - 84.6 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.3 cm × 10 cm), *n*-hexane/2-propanol = 97/3, v = 0.3 mL·min^{-1}, λ = 254 nm, t (major) = 8.2 min, t (minor) = 11.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68-0.81 (m, 2H), 0.91 - 0.98 (m, 1H), 1.40 -1.50 (m, 1H), 2.69 (d, J = 13.0 Hz, 1H), 2.95 (d, J = 13.0 Hz, 1H), 3.31 (s, 3H), 3.85 (s, 3H), 5.14 (s, 1H), 6.94 - 6.99 (m, 2H), 7.03 (d, J = 7.8 Hz, 2H), 7.24 - 7.32 (m, 2H), 7.37 - 7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 14.7, 29.8, 47.5, 51.9, 55.4, 61.9, 62.9, 110.6, 114.3, 122.6, 124.8, 125.9, 126.9, 127.7, 129.8, 133.4, 159.0, 159.3, 172.8 ppm; HRMS (ESI) m/z calcd. for $C_{22}H_{22}NO_6$ $[M+H]^+$: 396.1442, found: 396.1447.



Methyl(1S,3aS)-3a-nitro-1-(4-(trifluoromethyl)phenyl)-1,2,3a,8b-tetrahydrospiro [cyclopenta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5c)

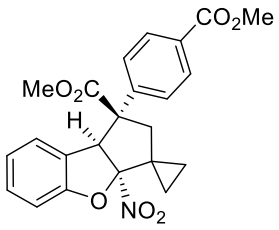
Colorless oil, 54 mg, 63% yield; dr = 4 : 1, 87% ee; $[\alpha]_D^{20.0}$= - 101.5 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U (0.46 cm × 25 cm), n-hexane/2-propanol = 95/5, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 8.4 min, t (minor) = 7.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69-0.81 (m, 2H), 0.91 - 0.98 (m, 1H), 1.40 -1.50 (m, 1H), 2.77 (d, J = 13.0 Hz, 1H), 2.92 (d, J = 13.0 Hz, 1H), 3.31 (s, 3H), 5.21 (s, 1H), 7.05 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 14.7, 29.8, 47.4, 52.2, 62.3, 62.6, 110.8, 122.8, 125.3 (q, J = 240.1 Hz), 125.8, 126.0 (q, J = 3.8 Hz), 127.2, 127.7, 129.0, 130.1 (q, J = 32.6

Hz), 130.2, 145.4, 159.2, 171.9 ppm; HRMS (ESI) m/z calcd. for $C_{22}H_{19}F_3NO_5$ $[M+H]^+$: 434.1210, found: 434.1208.



Methyl(1S,3aS)-1-(4-cyanophenyl)-3a-nitro-1,2,3a,8b-tetrahydrospiro[cyclopenta [b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5d)

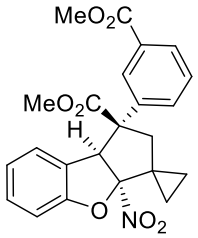
Colorless oil, 43mg, 55% yield; dr = 3 : 1, 80% ee; $[\alpha]_D^{20.0}$= - 100.4 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.46 cm × 25 cm), n-hexane/2-propanol = 83/17, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 29.3 min, t (minor) = 24.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70-0.82 (m, 2H), 1.00 (dt, *J* = 13.1, 6.4 Hz, 1H), 1.45 -1.55 (m, 1H), 2.79 (d, *J* = 13.0 Hz, 1H), 2.89 (d, *J* = 13.0 Hz, 1H), 3.33 (s, 3H), 5.22 (s, 1H), 7.04 - 7.08 (m, 2H), 7.28 - 7.39 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 14.6, 29.8, 47.2, 52.3, 62.0, 62.7, 110.8, 111.9, 118.3, 122.8, 123.8, 125.7, 126.4, 127.6, 130.2, 132.7, 146.7, 159.1, 171.5 ppm; HRMS (ESI) m/z calcd. for $C_{22}H_{19}N_2O_5$ $[M+H]^+$: 391.1288, found: 391.1288.



Methyl(1S,3aS)-1-(4-(methoxycarbonyl)phenyl)-3a-nitro-1,2,3a,8b-tetrahydro spiro[cyclopenta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5e)

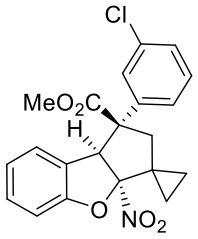
Colorless oil, 65mg, 77% yield; dr = 5 : 1, 83% ee; $[\alpha]_D^{20.0}$= - 67.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U(0.46 cm × 25 cm), n-hexane/2-propanol = 93/7, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 16.5 min, t (minor) = 19.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70-0.80 (m, 2H), 0.94 - 1.02 (m, 1H), 1.44 - 1.52 (m, 1H), 2.76 (d, *J* = 13.0 Hz, 1H), 2.93 (d, *J* = 13.0 Hz, 1H), 3.30 (s, 3H), 3.94 (s, 3H), 5.23 (s, 1H), 7.04 (q, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 8,12 (d, *J* = 8.1 Hz, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 14.7, 29.8, 47.3, 52.1, 52.3, 62.2, 62.6, 110.7, 122.7, 124.2, 125.8, 126.6, 126.7, 127.3, 130.0, 130.2, 146.3, 159.1, 166.5, 172.0 ppm; HRMS (ESI) m/z calcd. for $C_{23}H_{22}NO_7$ $[M+H]^+$: 424.1391, found: 424.1392.



Methyl(1S,3aS)-1-(3-(methoxycarbonyl)phenyl)-3a-nitro-1,2,3a,8b-tetrahydro spiro[cyclopenta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5f)

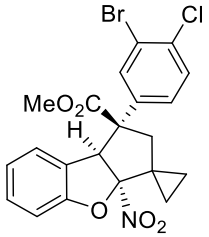
Colorless oil, 70 mg, 83% yield; dr = 3 : 1, 71% ee; $[\alpha]_D^{20.0}$= - 120.7 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IB-U(0.46 cm × 25 cm), n-hexane/2-propanol = 85/15, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 11.4 min, t (minor) = 22.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73-0.87 (m, 2H), 1.01 (dt, *J* = 9.5, 6.4 Hz, 1H), 1.51 (dt, *J* = 11.7, 6.3 Hz, 1H), 2.77 (d, *J* = 13.0 Hz, 1H), 2.99 (d, *J* = 13.0 Hz, 1H), 3.28 (s, 3H), 3.96 (s, 3H), 5.23 (s, 1H), 7.05 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.38 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.21 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 15.2, 29.9, 47.4, 52.1, 52.4, 62.5, 62.6, 110.7, 122.8, 124.3, 125.9, 126.7, 127.9, 129.0, 129.1, 130.0, 130.9, 131.2, 142.0, 159.2, 166.7, 172.2 ppm; HRMS (ESI) m/z calcd. for $C_{23}H_{22}NO_7$ $[M+H]^+$: 424.1391, found: 424.1387.



Methyl(1S,3aS)-1-(3-chlorophenyl)-3a-nitro-1,2,3a,8b-tetrahydrospiro[cyclo penta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5g)

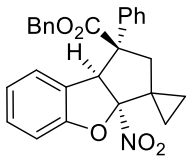
Colorless oil, 60 mg, 75% yield; dr = 5 : 1, 90% ee; $[\alpha]_D^{20.0}$= - 96 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.46 cm × 25 cm), n-hexane/2-propanol = 97/3, v = 1 mL·min-1, λ = 254 nm, t (major) = 10.8 min, t (minor) = 7.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 0.69-0.85 (m, 2H), 0.96-1.01 (m, 1H), 1.49 (dt, J = 10.3, 6.3 Hz, 1H), 2.70 (d, J = 13.0 Hz, 1H), 2.95 (d, J = 13.0 Hz, 1H), 3.30 (s, 3H), 5.15 (s, 1H), 7.01 - 7.08 (m, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.34 - 7.41 (m, 3H), 7.47 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2, 15.0, 29.8, 47.4, 52.1, 62.4, 62.5, 110.7, 122.8, 124.3, 124.9, 125.9, 126.7, 127.1, 128.0, 130.1, 130.2, 135.0, 143.5, 159.3, 172.0 ppm; HRMS (ESI) m/z calcd. for $C_{21}H_{19}ClNO_5$ $[M+H]^+$: 400.0946, found: 400.0950.



Methyl(1S,3aS)-1-(3-bromo-4-chlorophenyl)-3a-nitro-1,2,3a,8b-tetrahydrospiro [cyclopenta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5h)

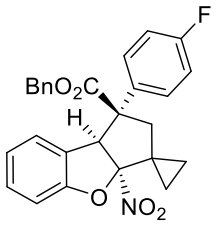
Colorless oil, 53 mg, 55% yield; dr = 4 : 1, 80% ee; $[\alpha]_D^{20.0}$= - 114.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.46 cm × 25 cm), n-hexane/2-propanol = 97/3, v = 1 mL·min-1, λ = 254 nm, t (major) = 11.7 min, t (minor) = 8.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64-0.75 (m, 2H), 0.87-0.92 (m, 1H), 1.40 (dt, J = 10.3, 6.3 Hz, 1H), 2.63 (d, J = 13.0 Hz, 1H), 2.81 (d, J = 13.0 Hz, 1H), 3.24 (s, 3H), 5.05 (s, 1H), 6.97 (t, J = 7.5 Hz, 2H), 7.22 (dd, J = 12.2, 4.4 Hz, 2H), 7.31 - 7.35 (m, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 2.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 14.8, 29.8, 47.2, 52.3, 61.9, 62.4, 110.8, 122.8, 123.1, 124.0, 125.7, 126.5, 126.9, 130.2, 130.7, 132.2, 134.1, 141.8, 159.2, 171.7 ppm; HRMS (ESI) m/z calcd. for $C_{21}H_{18}BrClNO_5$ $[M+H]^+$: 478.0051, found: 478.0054.



Benzyl(1S,3aS)-3a-nitro-1-phenyl-1,2,3a,8b-tetrahydrospiro[cyclopenta[b]benzo furan-3,1'-cyclopropane]-1-carboxylate (5i)

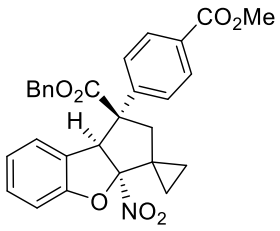
Colorless oil, 56 mg, 63% yield; dr > 20: 1, 71% ee; $[\alpha]_D^{20.0}$= - 112.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.3 cm x 10 cm), *n*-hexane/2-propanol = 98.8/1.2, v = 0.3 mL·min^{-1}, λ = 254 nm, t (major) = 9.2 min, t (minor) = 10.1 min]; ^{1}H NMR (400

MHz, $CDCl_3$) δ 0.59-0.79 (m, 3H), 1.28 (dt, J = 8.9, 4.8 Hz, 1H), 2.62 (d, J = 13.0 Hz, 1H), 2.98 (d, J = 13.0 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.72 (d, J = 12.2 Hz, 1H), 5.10 (s, 1H), 6.87 (d, J = 7.1 Hz, 3H), 6.91 (d, J = 8.2 Hz, 1H), 7.17 (dd, J = 9.1, 5.6 Hz, 5H), 7.29 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 15.3, 29.8, 47.5, 62.6, 62.8, 66.9, 110.6, 122.7, 124.7, 126.0, 126.7, 127.0, 127.8, 128.2, 128.3, 128.4, 128.9, 129.8, 135.1, 141.4, 159.4, 171.9 ppm; HRMS (ESI) m/z calcd. for $C_{27}H_{24}NO_5$ $[M+H]^+$: 442.1649, found: 442.1653.



Benzyl(1S,3aS)-1-(4-fluorophenyl)-3a-nitro-1,2,3a,8b-tetrahydrospiro[cyclopenta [b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5j)

Colorless oil, 62 mg, 67% yield; dr = 3 : 1, 91% ee; $[\alpha]_D^{20.0}$= - 109.3 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IC-U(0.46 cm × 25 cm), n-hexane/2-propanol = 97/3, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 10.1 min, t (minor) = 8.5 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67-0.82 (m, 3H), 1.32-1.37 (m, 1H), 2.69 (d, J = 13.0 Hz, 1H), 2.99 (d, J = 13.0 Hz, 1H), 4.66 (d, J = 12.2 Hz, 1H), 4.79 (d, J = 12.2 Hz, 1H), 5.13 (s, 1H), 6.93-7.01(m, 4H), 7.12 (t, J = 8.6 Hz, 2H), 7.24 (s, 1H), 7.27 - 7.36 (m, 4H), 7.46 (dd, J = 8.5, 5.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 15.0, 29.8, 47.5, 62.0, 62.9, 67.1, 110.7, 115.8 (d, J = 21.4 Hz), 122.8, 124.5, 125.8, 126.8, 128.4, 128.5, 128.5, 128.8 (d, J = 15.6 Hz), 129.9, 134.9, 137.3 (d, J = 3.3 Hz), 159.3, 162.2 (d, J = 245.8 Hz), 171.7 ppm; HRMS (ESI) m/z calcd. for $C_{27}H_{23}FNO_5$ $[M+H]^+$: 460.1555, found: 460.1554.

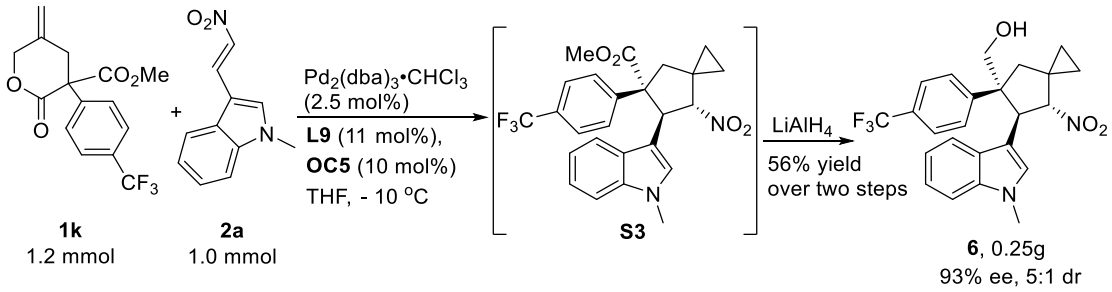


Benzyl(1S,3aS)-1-(4-(methoxycarbonyl)phenyl)-3a-nitro-1,2,3a,8b-tetrahydro spiro [cyclopenta[b]benzofuran-3,1'-cyclopropane]-1-carboxylate (5k)

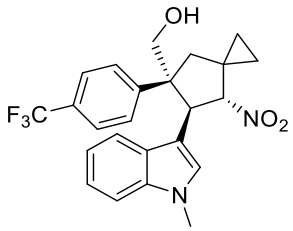
Colorless oil, 61 mg, 61% yield; dr = 5: 1, 89% ee; $[\alpha]_D^{20.0}$= - 151.2 (0.1, CH_2Cl_2); [Daicel CHIRALPAK® IA-U(0.46 cm × 25 cm), n-hexane/2-propanol = 90/10, v = 1 mL·min^{-1}, λ = 254 nm, t (major) = 17.5 min, t (minor) = 21.4 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61-0.86 (m, 3H), 1.36 (dt, *J* = 8.9, 4.8 Hz, 1H), 2.72 (d, *J* = 13.0 Hz, 1H), 2.98 (d, *J* = 13.0 Hz, 1H), 3.95 (s, 3H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.78(d, *J* = 12.2 Hz, 1H), 5.19 (s, 1H), 6.94 (d, *J* = 7.3 Hz, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 7.22-7.27 (m, 5H), 7.56 (d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 15.0, 29.8, 47.3, 52.3, 62.4, 62.6, 67.2, 110.7, 122.8, 124.2, 125.8, 126.7, 126.8, 128.4, 128.4, 128.5, 129.6, 130.0, 130.1, 134.7, 146.4, 159.3, 166.6, 171.3 ppm; HRMS (ESI) m/z calcd. for $C_{29}H_{26}NO_7$ $[M+H]^+$: 500.1704, found: 500.1700.

5. Large Scale Synthesis and Further Product Diversification

Synthesis of 6



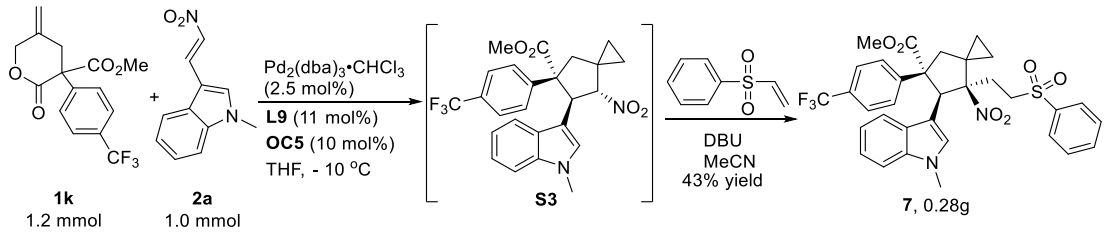
To a dried tube was added **1k** (1.2 mmol, 1.2 equiv.), indolyl nitroolefins **2a** (1 mmol, 1.0 equiv.), $Pd_2(dba)_3$·$CHCl_3$ (0.025 mmol, 26.4 mg, 2.5 mol%), **L9** (0.11 mmol, 67 mg, 11 mol%), **OC5** (0.1 mmol, 44 mg, 10 mol%) followed by the addition of 4Å molecule sieve and 5 mL of THF under nitrogen atmosphere. The reaction mixture was stirred at -10 °C for 12 h before $LiAlH_4$ (2 mmol, 76 mg) was added. The reaction mixture was stirred overnight and directly purified by silica gel chromatography (hexane/ethyl acetate = 5:1-3:1) to yield the product **6** as colorless oil.



((5R,6S,7R)-6-(1-methyl-1H-indol-3-yl)-7-nitro-5-(4-(trifluoromethyl)phenyl) spiro[2.4]heptan-5-yl)methanol (6)

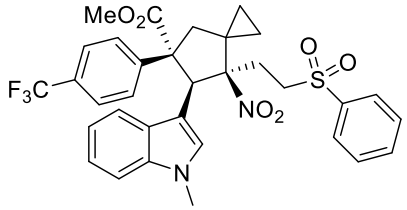
Colorless oil, 0.25g, 56% yield over two steps, dr = 5: 1, 93% ee, $[\alpha]_D^{20.0}$= - 83.4 (0.1, CH_2Cl_2)). [Daicel CHIRALPAK® IA-U (0.3 cm × 10 cm), n-hexane/2-propanol = 80/20, v = 0.3 mL·min^{-1}, λ = 254 nm, t (major) = 4.6 min, t (minor) = 5.3 min]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.81 (m, 1H), 0.89-0.95 (m, 1H), 1.09-1.15 (m, 1H), 1.18-1.23 (m, 1H), 2.43 (d, J = 13.8 Hz, 1H), 2.88 (d, J = 13.8 Hz, 1H), 3.60 (s, 3H), 4.05 (q, J = 10.9 Hz, 2H), 4.72 (d, J = 10.8 Hz, 1H), 4.98 (d, J = 10.8 Hz, 1H), 6.11 (s, 1H), 7.05 – 7.11 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.20-7.29 (m, 2H), 7.44 (dd, J = 12.6, 8.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 17.2, 23.3, 32.8, 43.6, 48.9, 55.8, 68.9, 96.3, 108.8, 109.5, 118.8, 119.6, 122.1,124.1 (q, J = 270.4 Hz), 124.7 (q, J = 3.7 Hz), 127.6, 127.9, 128.8, 129.3 (q, J = 32.1 Hz), 136.8, 144.6 ppm; HRMS (ESI) m/z calcd. for $C_{24}H_{24}F_3N_2O_3$ $[M+H]^+$: 445.1734, found: 445.1736.

Synthesis of 7



To a dried tube was added **1k** (1.2 mmol, 1.2 equiv.), indolyl nitroolefins **2a** (1 mmol, 1.0 equiv.), $Pd_2(dba)_3$·$CHCl_3$ (0.025 mmol, 26.4 mg, 2.5 mol%), **L9** (0.11 mmol, 67 mg, 11 mol%), **OC5** (0.1 mmol, 44 mg, 10 mol%) followed with the addition of 4Å molecule sieve and 5 mL of THF under nitrogen atmosphere. The reaction mixture was stirred at -10 °C for 12 h and directly purified by silica gel chromatography (hexane/ethyl acetate = 20:1-10:1) to yield the product **S3**. To a dried tube was added

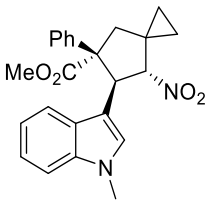
S3, phenyl vinyl sulfone (1.5 mmol, 252 mg, 1.5 equiv.) and 10 mL of CH_3CN under nitrogen atmosphere, the reaction mixture was stirred at 0 °C for 5 min before DBU (304 mg, 2 mmol, 2.0 equiv) was added. The reaction mixture was stirred overnight and purified directly by silica gel chromatography (hexane/ethyl acetate = 5:1-3:1) to yield the product **7** as colorless oil. (0.28 g, 44% yield).



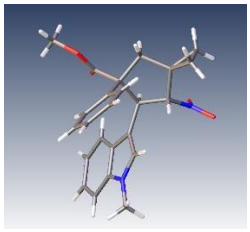
Methyl(5R,6S,7S)-6-(1-methyl-1H-indol-3-yl)-7-nitro-7-(2-(phenylsulfonyl)ethyl)-5-(4-(trifluoromethyl)phenyl)spiro[2.4]heptane-5-carboxylate (7)

Colorless oil, 0.28 g, 44% yield over two steps.^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75-0.81 (m, 2H), 0.86-0.93 (m, 1H), 0.95-0.99 (m, 1H), 2.30 (d, J = 13.2 Hz, 1H), 2.32-2.45 (m, 2H), 2.85 (td, J = 12.7, 5.1 Hz, 1H), 3.06 (ddd, J = 14.8, 11.5, 3.6 Hz, 1H), 3.37 (s, 3H), 3.69 (s, 3H), 3.89 (d, J = 13.2 Hz, 1H), 5.60 (s, 1H), 5.81 (s, 1H), 6.98 (d, J = 8.1 Hz, 2H), 7.15 - 7.21 (m, 1H), 7.25 (d, J = 8.8 Hz, 2H), 7.27 - 7.32 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.56 - 7.65 (m, 3H), 7.84 (d, J = 6.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.9, 15.5, 28.4, 30.5, 32.5, 43.6, 51.4, 53.2, 53.4, 62.0, 102.7, 107.6, 109.4, 117.9, 120.3, 122.0, 124.0 (q, J = 270.3 Hz), 124.2 (q, J = 3.9 Hz), 127.9, 128.1, 128.9, 129.0 (q, J = 32.3 Hz), 129.2, 129.8, 133.7, 135.4, 138.7, 143.4, 176.5 ppm; HRMS (ESI) m/z calcd. for $C_{33}H_{32}F_3N_2O_6S$ $[M+H]^+$: 641.1928, found: 641.1925.

6.X-ray Crystallography data of 3m and 5a



3m



CCDC 2124879

210325G

Table S4 Crystal data and structure refinement for 210325G.

Identification code	210325G
Empirical formula	$C_{48}H_{48}N_4O_8$
Formula weight	808.90
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.8261(3)
b/Å	13.6993(3)
c/Å	16.7931(4)
α/°	91.1649(17)
β/°	105.869(2)
γ/°	95.1952(18)
Volume/Å^3	2163.04(9)
Z	2
ρ_{calc}g/cm^3	1.242
μ/mm^{-1}	0.691
F(000)	856.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.478 to 134.12
Index ranges	-10 ≤ h ≤ 11, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	73249
Independent reflections	7715 [R_{int} = 0.0677, R_{sigma} = 0.0370]
Data/restraints/parameters	7715/0/546
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0620, wR_2 = 0.1753
Final R indexes [all data]	R_1 = 0.0733, wR_2 = 0.1843

Largest diff. peak/hole / e $Å^{-3}$ 0.45/-0.26

Table S5 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 210325G. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	5830(3)	4368.5(19)	9261.7(17)	109.0(8)
O3	10665(3)	8427(2)	11037.5(16)	125.5(10)
O6	7528(2)	4932.2(17)	8783.7(13)	94.2(7)
O7	10260(3)	7947(3)	9718.8(17)	137.6(12)
N1	6819(2)	4977.4(16)	9271.0(14)	68.1(5)
N3	4495(3)	7881.9(19)	8635.5(16)	88.7(7)
C2	7818(3)	4859(2)	11316.3(19)	83.2(8)
C5	7347(6)	8620(3)	7314(2)	115.1(15)
C11	3007(4)	8031(3)	8523(3)	119.3(14)
C13	5325(4)	8208(2)	8136.0(17)	83.7(9)
C15	9374(3)	6385(2)	10968.1(18)	77.4(7)
C19	7319(4)	7462(2)	11560(2)	87.6(9)
C21	6505(5)	8003(3)	11906(3)	117.3(14)
C23	11869(6)	9079(5)	10990(4)	175(3)
C25	5250(3)	7325(2)	9213.2(18)	78.0(7)
C26	7180(3)	5771.1(18)	9940.4(15)	62.1(6)
C28	8272(3)	5492(2)	10709.3(15)	64.1(6)
C32	7750(3)	6726.8(19)	9658.1(15)	66.1(6)
C33	7681(5)	8065(2)	8013.3(19)	97.6(11)
C34	6598(3)	7269.5(19)	9123.6(15)	70.2(7)
C35	8731(4)	4479(2)	10836(2)	85.7(8)
C36	7814(3)	7814(2)	10921.0(16)	69.5(7)
C37	9915(4)	7923(3)	10345(2)	91.0(9)
C39	7417(4)	8723(2)	10631(2)	97.3(10)
C41	4979(6)	8770(3)	7444(2)	113.6(14)
C42	8699(3)	7250(2)	10495.0(16)	69.2(7)
C43	6573(5)	9240(3)	10979(3)	121.2(14)
C44	6661(4)	7843.9(19)	8429.2(17)	79.5(8)
C45	6112(5)	8882(4)	11622(4)	127.7(16)
C47	6038(8)	8970(3)	7049(3)	133.9(19)

Table S6 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 210325G. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

O2	96.8(16)	103.3(16)	122.8(19)	-23.4(14)	39.3(14)	-33.0(14)
O3	109.1(18)	156(2)	103.0(17)	-40.8(16)	44.3(15)	-68.0(17)
O6	96.5(15)	104.9(16)	84.4(14)	-24.5(11)	38.4(12)	-8.8(12)
O7	126(2)	188(3)	94.2(17)	-14.4(18)	50.7(16)	-68(2)
N1	61.3(13)	72.0(13)	68.2(13)	-0.6(10)	16.0(10)	0.0(10)
N3	97.3(19)	79.5(16)	75.7(16)	-3.8(13)	0.3(14)	12.1(14)
C2	79.4(19)	98(2)	74.3(18)	18.2(15)	23.0(15)	12.0(16)
C5	195(5)	76(2)	74(2)	-2.1(17)	48(3)	-20(3)
C11	95(3)	110(3)	131(3)	-11(2)	-10(2)	31(2)
C13	124(3)	56.4(14)	56.0(15)	-8.7(12)	1.1(16)	5.9(16)
C15	60.1(15)	94(2)	73.5(17)	-2.8(14)	12.3(13)	3.9(14)
C19	92(2)	83.4(19)	95(2)	-5.9(16)	43.4(18)	-4.9(16)
C21	130(3)	106(3)	137(3)	-19(2)	80(3)	-4(2)
C23	141(4)	211(6)	160(4)	-58(4)	65(3)	-112(4)
C25	77.7(19)	78.9(18)	67.8(16)	1.2(13)	5.4(14)	4.5(14)
C26	60.6(14)	67.5(14)	57.8(13)	-0.8(11)	16.8(11)	4.7(11)
C28	57.6(14)	75.2(15)	59.1(14)	3.6(11)	14.4(11)	10.2(12)
C32	67.6(15)	71.3(15)	58.2(14)	-0.4(11)	19.0(12)	-3.7(12)
C33	156(3)	69.5(17)	68.1(18)	-10.8(14)	43(2)	-21.1(19)
C34	87.2(19)	64.0(15)	54.0(14)	-3.2(11)	14.6(13)	-4.3(13)
C35	86(2)	88(2)	86(2)	11.9(16)	21.5(16)	26.7(16)
C36	66.0(15)	74.1(16)	63.2(15)	-7.4(12)	15.1(12)	-8.5(12)
C37	84(2)	108(2)	80(2)	-9.9(17)	33.1(16)	-25.8(17)
C39	125(3)	73.4(19)	88(2)	-6.1(16)	22(2)	3.7(19)
C41	177(4)	74(2)	71(2)	-3.8(16)	1(2)	21(2)
C42	65.0(15)	77.3(16)	63.1(15)	-3.0(12)	19.0(12)	-6.7(12)
C43	139(4)	78(2)	137(4)	-19(2)	19(3)	21(2)
C44	116(2)	55.9(14)	59.7(15)	-12.9(12)	20.3(16)	-9.8(15)
C45	109(3)	109(3)	171(5)	-42(3)	53(3)	9(2)
C47	237(6)	76(2)	76(2)	9.9(18)	26(3)	6(3)

Table S7 Bond Lengths for 210325G.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	N1	1.219(3)	C19	C21	1.368(5)
O3	C23	1.438(5)	C19	C36	1.372(4)
O3	C37	1.333(4)	C21	C45	1.355(7)
O6	N1	1.215(3)	C25	C34	1.382(4)
O7	C37	1.191(4)	C26	C28	1.517(3)
N1	C26	1.495(3)	C26	C32	1.513(4)
N3	C11	1.455(5)	C28	C35	1.499(4)

N3	C13	1.375(4)	C32	C34	1.505(4)
N3	C25	1.346(4)	C32	C42	1.574(4)
C2	C28	1.485(4)	C33	C44	1.385(5)
C2	C35	1.480(4)	C34	C44	1.432(4)
C5	C33	1.391(5)	C36	C39	1.396(4)
C5	C47	1.375(7)	C36	C42	1.519(4)
C13	C41	1.388(5)	C37	C42	1.522(4)
C13	C44	1.411(5)	C39	C43	1.373(6)
C15	C28	1.529(4)	C41	C47	1.389(7)
C15	C42	1.539(4)	C43	C45	1.365(7)

Table S8 Bond Angles for 210325G.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C37	O3	C23	117.4(3)	C34	C32	C42	118.2(2)
O2	N1	C26	117.0(2)	C44	C33	C5	119.1(4)
O6	N1	O2	122.4(2)	C25	C34	C32	126.6(2)
O6	N1	C26	120.5(2)	C25	C34	C44	105.5(3)
C13	N3	C11	126.3(3)	C44	C34	C32	127.9(3)
C25	N3	C11	124.8(3)	C2	C35	C28	59.81(19)
C25	N3	C13	108.6(3)	C19	C36	C39	117.3(3)
C35	C2	C28	60.75(19)	C19	C36	C42	123.6(3)
C47	C5	C33	120.7(4)	C39	C36	C42	119.0(3)
N3	C13	C41	129.1(4)	O3	C37	C42	111.5(3)
N3	C13	C44	107.9(3)	O7	C37	O3	122.6(3)
C41	C13	C44	123.0(4)	O7	C37	C42	125.6(3)
C28	C15	C42	106.5(2)	C43	C39	C36	120.9(4)
C21	C19	C36	120.6(4)	C13	C41	C47	116.1(4)
C45	C21	C19	122.2(4)	C15	C42	C32	102.1(2)
N3	C25	C34	111.1(3)	C36	C42	C15	115.3(2)
N1	C26	C28	112.0(2)	C36	C42	C32	111.0(2)
N1	C26	C32	112.0(2)	C36	C42	C37	110.8(2)
C32	C26	C28	108.2(2)	C37	C42	C15	106.4(2)
C2	C28	C15	122.9(2)	C37	C42	C32	110.7(2)
C2	C28	C26	120.0(2)	C45	C43	C39	120.8(4)
C2	C28	C35	59.4(2)	C13	C44	C34	106.8(3)
C26	C28	C15	105.9(2)	C33	C44	C13	118.6(3)
C35	C28	C15	119.8(2)	C33	C44	C34	134.5(3)
C35	C28	C26	123.5(2)	C21	C45	C43	118.3(4)
C26	C32	C42	102.7(2)	C5	C47	C41	122.4(4)
C34	C32	C26	112.8(2)				

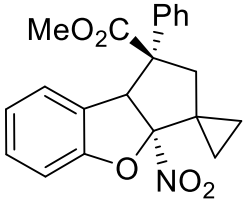
Table S9 Torsion Angles for 210325G.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	N1	C26	C28	90.5(3)	C25	C34	C44	C33	-178.3(3)
O2	N1	C26	C32	-147.8(3)	C26	C28	C35	C2	-107.8(3)
O3	C37	C42	C15	-74.4(4)	C26	C32	C34	C25	36.7(4)
O3	C37	C42	C32	175.3(3)	C26	C32	C34	C44	-144.3(3)
O3	C37	C42	C36	51.7(4)	C26	C32	C42	C15	38.0(3)
O6	N1	C26	C28	-86.7(3)	C26	C32	C42	C36	-85.5(3)
O6	N1	C26	C32	35.0(3)	C26	C32	C42	C37	151.0(3)
O7	C37	C42	C15	99.0(5)	C28	C15	C42	C32	-32.8(3)
O7	C37	C42	C32	-11.3(5)	C28	C15	C42	C36	87.7(3)
O7	C37	C42	C36	-134.9(4)	C28	C15	C42	C37	-149.0(2)
N1	C26	C28	C2	-81.5(3)	C28	C26	C32	C34	-158.3(2)
N1	C26	C28	C15	133.8(2)	C28	C26	C32	C42	-30.0(3)
N1	C26	C28	C35	-10.3(3)	C32	C26	C28	C2	154.6(2)
N1	C26	C32	C34	77.9(3)	C32	C26	C28	C15	9.9(3)
N1	C26	C32	C42	-153.8(2)	C32	C26	C28	C35	-134.1(3)
N3	C13	C41	C47	-178.6(3)	C32	C34	C44	C13	-179.7(2)
N3	C13	C44	C33	179.0(2)	C32	C34	C44	C33	2.5(5)
N3	C13	C44	C34	0.8(3)	C33	C5	C47	C41	-1.8(6)
N3	C25	C34	C32	179.2(2)	C34	C32	C42	C15	162.8(2)
N3	C25	C34	C44	0.0(3)	C34	C32	C42	C36	39.4(3)
C5	C33	C44	C13	-1.2(4)	C34	C32	C42	C37	-84.2(3)
C5	C33	C44	C34	176.4(3)	C35	C2	C28	C15	-107.8(3)
C11	N3	C13	C41	2.5(5)	C35	C2	C28	C26	113.6(3)
C11	N3	C13	C44	-175.7(3)	C36	C19	C21	C45	2.3(7)
C11	N3	C25	C34	175.5(3)	C36	C39	C43	C45	0.6(6)
C13	N3	C25	C34	0.5(3)	C39	C36	C42	C15	166.5(3)
C13	C41	C47	C5	1.2(6)	C39	C36	C42	C32	-78.0(3)
C15	C28	C35	C2	112.9(3)	C39	C36	C42	C37	45.5(4)
C19	C21	C45	C43	-1.2(7)	C39	C43	C45	C21	-0.2(7)
C19	C36	C39	C43	0.4(5)	C41	C13	C44	C33	0.7(4)
C19	C36	C42	C15	-16.5(4)	C41	C13	C44	C34	-177.5(3)
C19	C36	C42	C32	99.0(3)	C42	C15	C28	C2	-128.5(3)
C19	C36	C42	C37	-137.5(3)	C42	C15	C28	C26	15.0(3)
C21	C19	C36	C39	-1.7(5)	C42	C15	C28	C35	160.6(2)
C21	C19	C36	C42	-178.8(3)	C42	C32	C34	C25	-83.0(3)
C23	O3	C37	O7	5.1(7)	C42	C32	C34	C44	96.1(3)
C23	O3	C37	C42	178.7(4)	C42	C36	C39	C43	177.6(3)

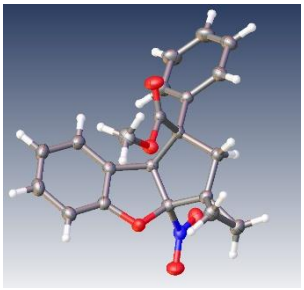
C25 N3	C13 C41 177.4(3)	C44 C13 C41 C47 -0.7(5)	
C25 N3	C13 C44 -0.8(3)	C47 C5	C33 C44 1.8(5)
C25 C34	C44 C13 -0.4(3)		

Table S10 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 210325G.

Atom	*x*	*y*	*z*	U(eq)
H2A	8245	5027	11901	100
H2B	6830	4587	11176	100
H5	8016	8756	7023	138
H11A	2416	7534	8140	179
H11B	2834	8666	8309	179
H11C	2792	7991	9046	179
H15A	10239	6267	10826	93
H15B	9604	6523	11561	93
H19	7540	6851	11759	105
H21	6211	7758	12351	141
H23A	11583	9500	10537	263
H23B	12598	8702	10903	263
H23C	12230	9469	11498	263
H25	4909	7018	9619	94
H26	6310	5882	10093	74
H32	8385	6568	9325	79
H33	8577	7845	8199	117
H35A	8301	3978	10402	103
H35B	9717	4418	11127	103
H39	7729	8982	10196	117
H41	4089	8999	7255	136
H43	6313	9842	10773	145
H45	5543	9233	11859	153
H47	5855	9355	6589	161



5a



CCDC 2143508

Table S11 Crystal data and structure refinement for 2143508.

Identification code	2143508
Empirical formula	$C_{21}H_{19}NO_5$
Formula weight	365.37
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.2248(3)
b/Å	10.9399(4)
c/Å	12.5947(5)
α/°	115.361(4)
β/°	100.031(3)
γ/°	95.232(3)
Volume/Å^3	870.27(6)
Z	2
ρ_{calc}g/cm^3	1.394
μ/mm^{-1}	0.826
F(000)	384.0
Crystal size/mm^3	0.07 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.996 to 134.118
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	22711
Independent reflections	3098 [R_{int} = 0.0645, R_{sigma} = 0.0345]
Data/restraints/parameters	3098/186/245
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0938

Final R indexes [all data] $R_1 = 0.0466$, $wR_2 = 0.0984$

Largest diff. peak/hole / e $Å^{-3}$ 0.20/-0.22

Table S12 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 220118F_auto. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	236.6(14)	2448.9(10)	6124.0(9)	26.6(2)
O2	-1083.9(15)	4304.1(11)	6413.7(11)	36.6(3)
O3	7221.4(15)	4569.5(11)	8667.1(10)	34.2(3)
O4	4279.7(14)	1768.3(10)	6180.5(9)	25.8(2)
O5	7536.3(15)	2446.2(12)	7734.7(11)	37.0(3)
N1	6616.3(17)	3370.1(13)	7921.4(11)	26.3(3)
C1	3473.7(19)	3415.1(14)	5579.8(13)	23.4(3)
C2	2284(2)	1504.8(15)	7899.5(14)	30.4(3)
C3	1189(2)	6744.3(15)	8969.5(14)	28.6(3)
C4	3864.1(19)	4131.4(14)	6938.4(13)	22.0(3)
C5	3129(3)	8388.9(17)	8209.7(17)	38.6(4)
C6	3735.2(19)	2068.3(15)	5215.6(13)	23.7(3)
C7	1207(2)	8150.0(16)	9492.3(15)	34.3(4)
C8	3346(2)	2876.8(14)	8137.1(13)	23.3(3)
C9	2739(2)	1542.8(17)	3161.4(14)	33.5(4)
C10	2467(2)	4155.1(14)	8575.4(13)	23.5(3)
C11	2823(2)	3831.8(16)	4711.3(14)	28.8(3)
C12	2161(2)	6140.2(14)	8063.2(13)	24.4(3)
C13	2449(2)	2879.7(17)	3493.6(15)	33.6(4)
C14	4475.5(19)	2983.9(14)	7254.1(13)	22.8(3)

C15	3108(2)	6981.3(16)	7681.4(15)	32.5(4)
C16	3395(2)	1102.5(16)	4021.0(14)	29.3(3)
C17	-1348(2)	1601.9(16)	5114.1(15)	34.5(4)
C18	241(2)	3801.7(14)	6638.8(13)	23.5(3)
C19	2188(2)	8976.1(16)	9117.4(16)	38.1(4)
C20	2153.7(19)	4595.0(14)	7547.2(13)	22.0(3)
C21	3964(2)	2250.9(16)	8969.4(14)	29.6(3)

Table S13 Anisotropic Displacement Parameters ($Å^2×10^3$) for 220118F_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22.4(5)	22.4(5)	28.3(6)	6.9(4)	2.7(4)	2.2(4)
O2	31.0(6)	32.8(6)	41.7(7)	15.6(5)	-1.0(5)	10.8(5)
O3	27.7(6)	36.7(6)	26.5(6)	6.7(5)	2.3(5)	-1.6(5)
O4	30.9(5)	23.2(5)	21.4(5)	8.4(4)	4.3(4)	8.4(4)
O5	28.1(6)	45.1(7)	41.2(7)	20.8(6)	7.5(5)	16.7(5)
N1	22.0(6)	34.2(7)	22.9(6)	13.1(6)	5.8(5)	5.3(5)
C1	20.3(6)	25.4(7)	24.3(7)	10.4(6)	6.9(5)	4.0(5)
C2	33.1(8)	25.2(7)	32.0(8)	14.4(6)	4.2(7)	0.8(6)
C3	27.9(7)	27.0(7)	28.5(8)	10.4(6)	6.6(6)	5.4(6)
C4	21.7(6)	21.6(7)	23.1(7)	10.2(6)	5.7(5)	4.1(5)
C5	44.3(9)	27.3(8)	50.7(10)	21.5(7)	15.9(8)	7.8(7)
C6	20.6(6)	27.1(7)	23.5(7)	11.5(6)	4.9(5)	5.0(5)
C7	35.6(8)	29.7(8)	33.0(9)	8.6(7)	9.3(7)	11.8(6)
C8	22.8(6)	23.2(7)	23.1(7)	10.7(6)	3.2(5)	3.4(5)
C9	33.9(8)	38.6(9)	22.7(8)	9.1(7)	6.4(6)	6.3(7)
C10	24.4(7)	23.6(7)	22.1(7)	9.4(6)	6.3(6)	4.9(5)

C11	30.1(8)	31.8(8)	29.3(8)	16.5(6)	9.9(6)	9.2(6)
C12	24.3(7)	23.1(7)	24.1(7)	9.9(6)	3.4(6)	5.3(5)
C13	35.5(8)	43.2(9)	26.5(8)	19.3(7)	7.4(6)	10.1(7)
C14	21.4(6)	22.0(7)	21.9(7)	7.9(5)	2.9(5)	4.2(5)
C15	37.8(8)	27.6(8)	36.9(9)	16.0(7)	14.6(7)	9.9(6)
C16	28.9(7)	28.6(7)	26.4(8)	8.4(6)	7.0(6)	7.0(6)
C17	27.5(8)	31.8(8)	29.7(9)	4.6(7)	0.3(7)	-1.1(6)
C18	25.7(7)	24.3(7)	22.2(7)	11.2(6)	7.9(6)	5.6(6)
C19	43.2(9)	22.7(8)	44.0(10)	11.2(7)	8.3(8)	10.1(7)
C20	22.3(7)	21.4(7)	22.1(7)	9.2(5)	6.3(5)	4.8(5)
C21	31.4(8)	30.5(8)	29.3(8)	16.9(6)	4.5(6)	4.7(6)

Table S14 Bond Lengths for 220118F_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C17	1.4412(18)	C4	C20	1.5759(18)
O1	C18	1.3368(17)	C5	C15	1.389(2)
O2	C18	1.1972(18)	C5	C19	1.379(2)
O3	N1	1.2213(16)	C6	C16	1.379(2)
O4	C6	1.3921(18)	C7	C19	1.381(2)
O4	C14	1.4056(17)	C8	C10	1.5120(19)
O5	N1	1.2215(16)	C8	C14	1.526(2)
N1	C14	1.5495(18)	C8	C21	1.508(2)
C1	C4	1.505(2)	C9	C13	1.386(2)
C1	C6	1.385(2)	C9	C16	1.392(2)
C1	C11	1.383(2)	C10	C20	1.553(2)
C2	C8	1.502(2)	C11	C13	1.395(2)
C2	C21	1.504(2)	C12	C15	1.387(2)
C3	C7	1.387(2)	C12	C20	1.5284(19)

C3	C12	1.397(2)	C18	C20	1.534(2)
C4	C14	1.548(2)			

Table S15 Bond Angles for 220118F_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	O1	C17	116.22(11)	C8	C10	C20	107.32(11)
C6	O4	C14	107.67(10)	C1	C11	C13	118.85(14)
O3	N1	O5	124.63(13)	C3	C12	C20	118.88(13)
O3	N1	C14	116.99(11)	C15	C12	C3	118.07(13)
O5	N1	C14	118.15(12)	C15	C12	C20	123.04(13)
C6	C1	C4	108.51(12)	C9	C13	C11	120.50(15)
C11	C1	C4	132.22(13)	O4	C14	N1	106.42(10)
C11	C1	C6	119.12(14)	O4	C14	C4	109.33(11)
C8	C2	C21	60.22(10)	O4	C14	C8	115.77(11)
C7	C3	C12	120.95(15)	C4	C14	N1	110.89(11)
C1	C4	C14	101.32(11)	C8	C14	N1	106.43(11)
C1	C4	C20	118.67(12)	C8	C14	C4	107.98(11)
C14	C4	C20	106.36(11)	C12	C15	C5	120.83(15)
C19	C5	C15	120.51(16)	C6	C16	C9	116.32(14)
C1	C6	O4	112.98(12)	O1	C18	C20	110.58(11)
C16	C6	O4	123.30(13)	O2	C18	O1	123.84(13)
C16	C6	C1	123.64(14)	O2	C18	C20	125.59(13)
C19	C7	C3	120.18(15)	C5	C19	C7	119.43(15)
C2	C8	C10	121.64(12)	C10	C20	C4	102.50(11)
C2	C8	C14	120.28(12)	C12	C20	C4	114.06(11)
C2	C8	C21	59.96(10)	C12	C20	C10	110.62(11)
C10	C8	C14	105.82(11)	C12	C20	C18	109.37(11)
C21	C8	C10	120.35(12)	C18	C20	C4	110.05(11)

C21	C8	C14	123.69(12)	C18	C20	C10	110.06(11)
C13	C9	C16	121.57(15)	C2	C21	C8	59.81(10)

Table S16 Torsion Angles for 220118F_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C18	C20	C4	50.57(15)	C7	C3	C12	C20	177.94(14)
O1	C18	C20	C10	-61.68(14)	C8	C10	C20	C4	-32.06(14)
O1	C18	C20	C12	176.60(11)	C8	C10	C20	C12	-154.04(11)
O2	C18	C20	C4	-129.75(15)	C8	C10	C20	C18	84.99(13)
O2	C18	C20	C10	118.00(16)	C10	C8	C14	O4	-136.47(12)
O2	C18	C20	C12	-3.7(2)	C10	C8	C14	N1	105.52(12)
O3	N1	C14	O4	158.55(12)	C10	C8	C14	C4	-13.58(15)
O3	N1	C14	C4	39.75(16)	C10	C8	C21	C2	111.32(15)
O3	N1	C14	C8	-77.44(15)	C11	C1	C4	C14	177.92(15)
O4	C6	C16	C9	175.89(13)	C11	C1	C4	C20	62.0(2)
O5	N1	C14	O4	-26.81(17)	C11	C1	C6	O4	-176.28(12)
O5	N1	C14	C4	-145.61(13)	C11	C1	C6	C16	0.5(2)
O5	N1	C14	C8	97.20(14)	C12	C3	C7	C19	0.2(2)
C1	C4	C14	O4	-4.25(14)	C13	C9	C16	C6	0.1(2)
C1	C4	C14	N1	112.77(12)	C14	O4	C6	C1	-2.52(15)
C1	C4	C14	C8	-130.99(11)	C14	O4	C6	C16	-179.33(13)
C1	C4	C20	C10	136.13(13)	C14	C4	C20	C10	22.95(13)
C1	C4	C20	C12	-104.26(14)	C14	C4	C20	C12	142.56(12)
C1	C4	C20	C18	19.07(17)	C14	C4	C20	C18	-94.11(13)
C1	C6	C16	C9	-0.6(2)	C14	C8	C10	C20	28.88(14)
C1	C11	C13	C9	-0.5(2)	C14	C8	C21	C2	-108.33(15)
C2	C8	C10	C20	-113.31(14)	C15	C5	C19	C7	-0.5(3)
C2	C8	C14	O4	6.35(19)	C15	C12	C20	C4	21.8(2)

C2	C8	C14	N1	-111.66(14)	C15	C12	C20	C10	136.75(15)
C2	C8	C14	C4	129.23(14)	C15	C12	C20	C18	-101.87(16)
C3	C7	C19	C5	0.8(3)	C16	C9	C13	C11	0.4(2)
C3	C12	C15	C5	1.7(2)	C17	O1	C18	O2	10.0(2)
C3	C12	C20	C4	-157.54(13)	C17	O1	C18	C20	-170.33(12)
C3	C12	C20	C10	-42.62(17)	C19	C5	C15	C12	-0.7(3)
C3	C12	C20	C18	78.76(16)	C20	C4	C14	O4	120.40(12)
C4	C1	C6	O4	-0.34(16)	C20	C4	C14	N1	-122.57(12)
C4	C1	C6	C16	176.45(13)	C20	C4	C14	C8	-6.33(14)
C4	C1	C11	C13	-174.77(14)	C20	C12	C15	C5	-177.67(15)
C6	O4	C14	N1	-115.56(12)	C21	C2	C8	C10	-109.23(15)
C6	O4	C14	C4	4.26(14)	C21	C2	C8	C14	113.85(15)
C6	O4	C14	C8	126.43(12)	C21	C8	C10	C20	175.39(12)
C6	C1	C4	C14	2.72(14)	C21	C8	C14	O4	78.44(17)
C6	C1	C4	C20	-113.19(14)	C21	C8	C14	N1	-39.56(17)
C6	C1	C11	C13	0.0(2)	C21	C8	C14	C4	-158.67(13)
C7	C3	C12	C15	-1.5(2)					

Table S17 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 220118F_auto.

Atom	*x*	*y*	*z*	U(eq)
H2A	2453.46	676.41	7204.95	36
H2B	990.81	1465.16	8058.65	36
H3	506.48	6184.62	9231.76	34
H4	4954.51	4926.59	7274.27	26
H5	3796.22	8951.75	7943.81	46
H7	542.4	8545.42	10109.88	41
H9	2484.11	911.64	2327.16	40

H10A	3331.74	4900.81	9317.53	28
H10B	1231.37	3957.79	8762.15	28
H11	2633.77	4750.46	4940.05	35
H13	1992.52	3149.99	2887.46	40
H15	3749.47	6589.55	7050.75	39
H16	3598.12	187.38	3797.09	35
H17A	-1317.93	1844.98	4452.6	52
H17B	-2552.14	1754.05	5364.06	52
H17C	-1252.03	630.57	4838.84	52
H19	2214.54	9940.43	9481.5	46
H21A	5164.88	1881.32	8930.33	36
H21B	3701.82	2670.29	9784.27	36

7.References

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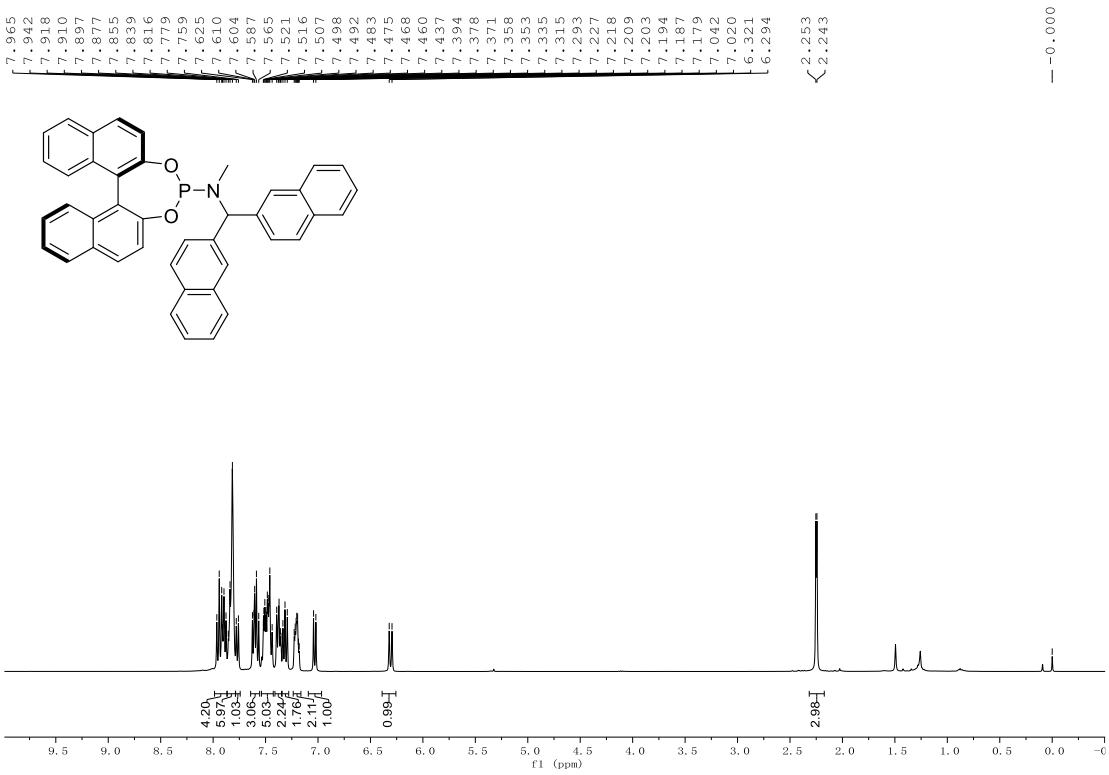
3. K. Sreenivas and F. A. Khan, 1,6-Conjugate addition of C-nucleophiles to p-quinone methide surrogate: Synthesis of diarylpropanes, *Tetrahedron*, 2019, **75**, 633–642.

4. R. Ardkhean, M. Mortimore, R. S. Paton, S. P. Fletcher, Formation of quaternary centres by copper catalysed asymmetric conjugate addition to β-substituted cyclopentenones with the aid of a quantitative structure–selectivity relationship, *Chem. Sci.* 2018, **9**, 2628-2632.

8. Spectra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7.604
7.587
7.565
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7.516
7.507
7.498
7.492
7.483
7.475
7.468
7.460
7.437
7.394
7.378
7.371
7.358
7.353
7.335
7.315
7.293
7.227
7.218
7.209
7.203
7.194
7.187
7.179
7.042
7.020
6.321
6.294
2.253
2.243
-0.000
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3.06
5.03
2.24
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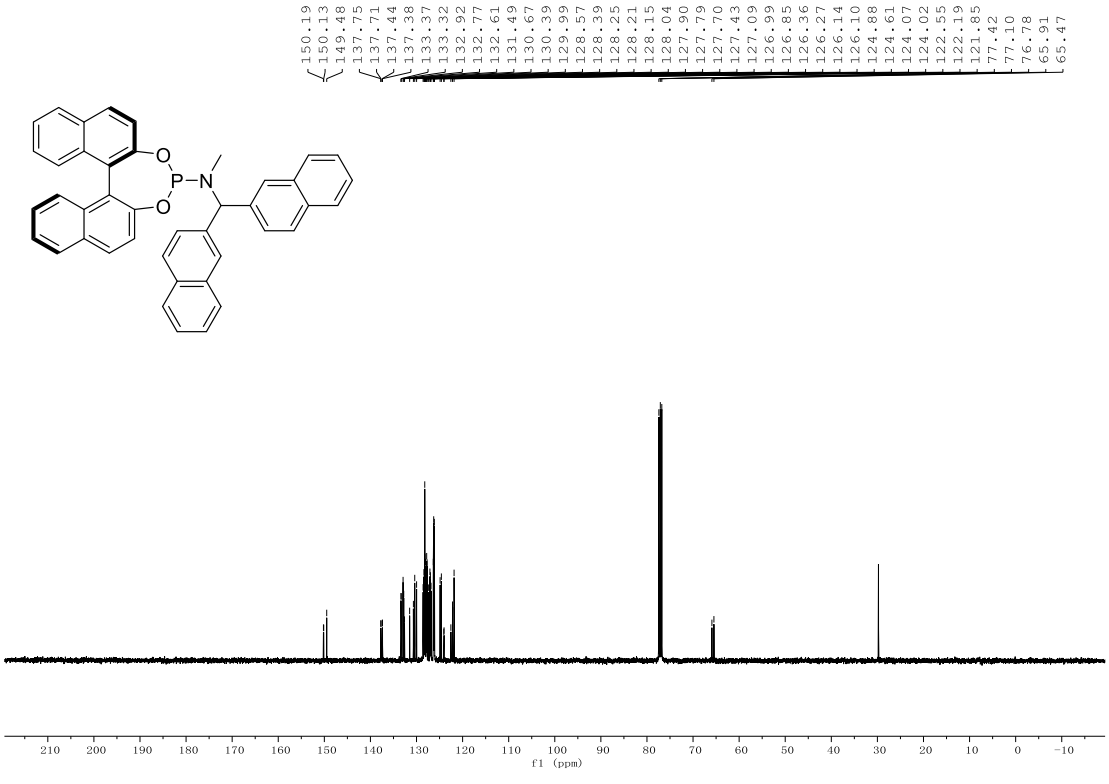
f1 (ppm)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129.99
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128.39
128.25
128.21
128.15
128.04
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127.70
127.43
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126.85
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124.61
124.07
124.02
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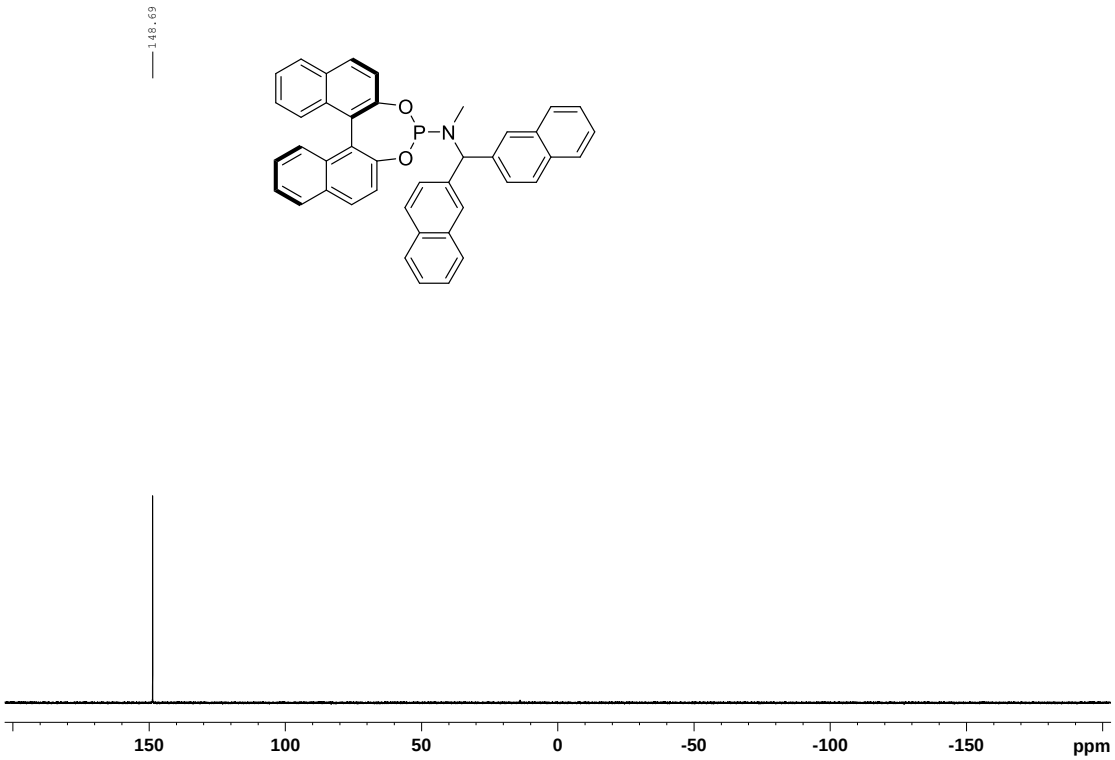
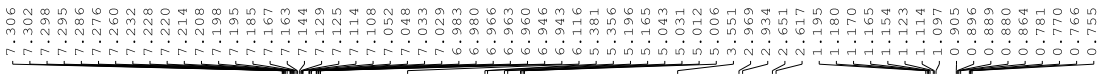
121.85
77.42
77.10
76.78
65.91
65.47
f1 (ppm)

^{31}P NMR spectrum of **L9**

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7.185
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6.960
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6.943
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5.031
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5.006
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2.651
2.617
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1.180
1.170
1.165
1.154
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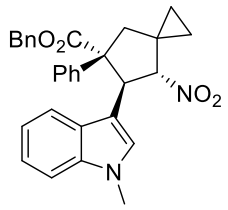
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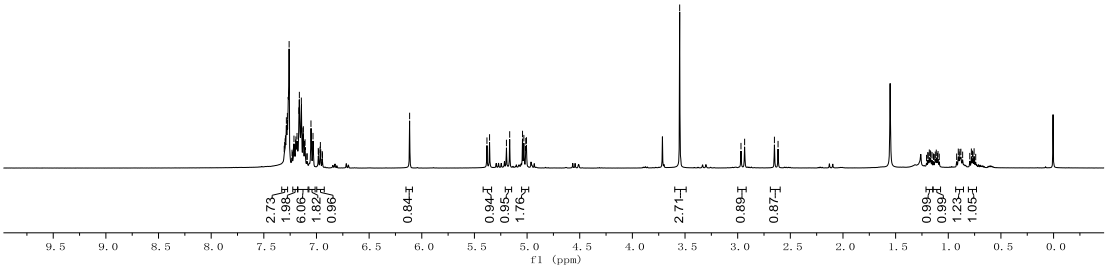
N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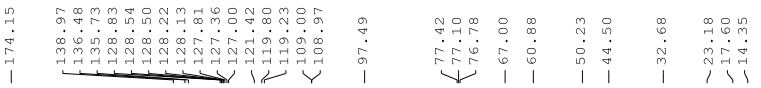
f1 (ppm)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128.22
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121.42
119.80
119.23
109.00
108.97
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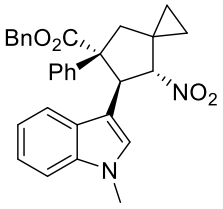
14.35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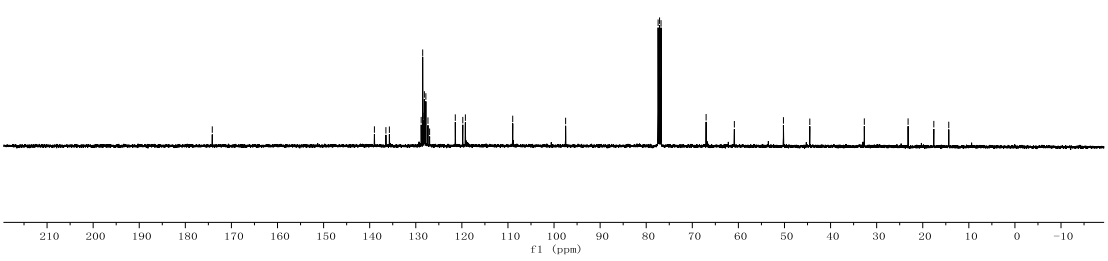
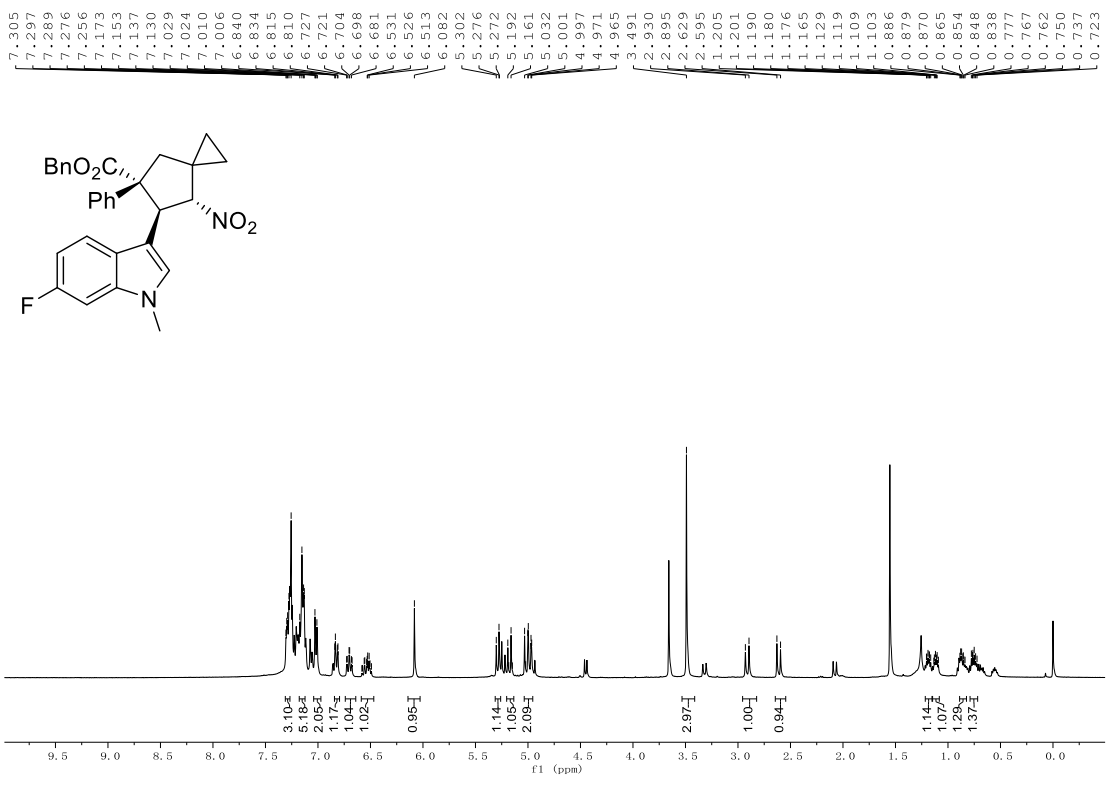
Ph
NO2
N


f1 (ppm)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6.810
6.727
6.721
6.704
6.698
6.681
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6.526
6.513
6.082
5.302
5.276
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5.161
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4.965
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2.629
2.595
1.205
1.201
1.190
1.180
1.176
1.165
1.129
1.119
1.109
1.103
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0.879
0.870
0.865
0.854
0.848
0.838
0.777
0.767
0.762
0.750
0.737
0.723
BnO2C
Ph
NO2
F
N
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5.18
2.05
1.17
1.04
1.02
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1.00
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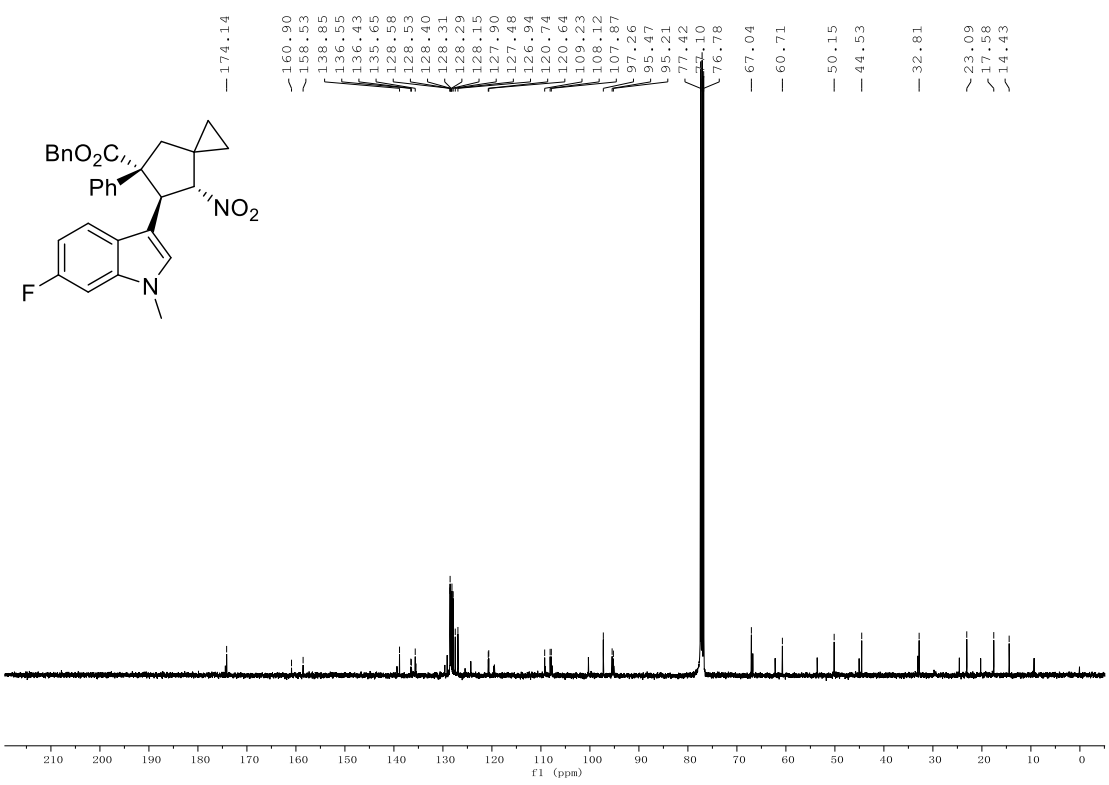
1.07
1.29
1.37
f1 (ppm)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109.23
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77.10
76.78
67.04
60.71
50.15
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14.43
BnO2C
Ph
NO2
F
N
f1 (ppm)


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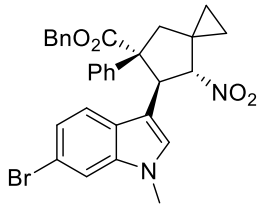
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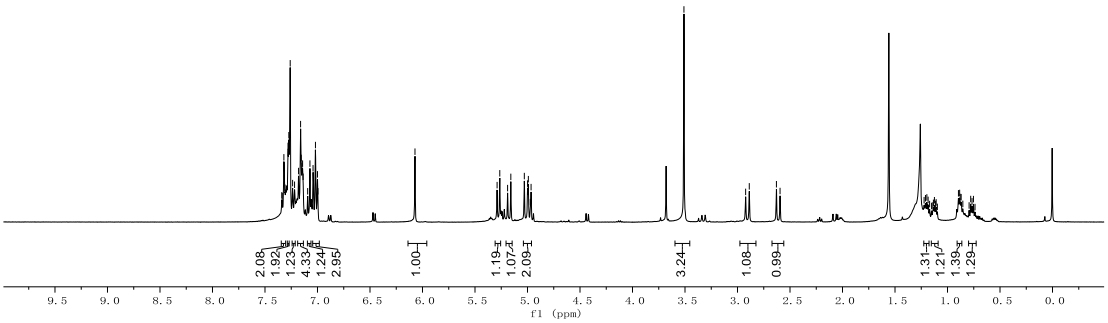
Ph
NO2
Br
N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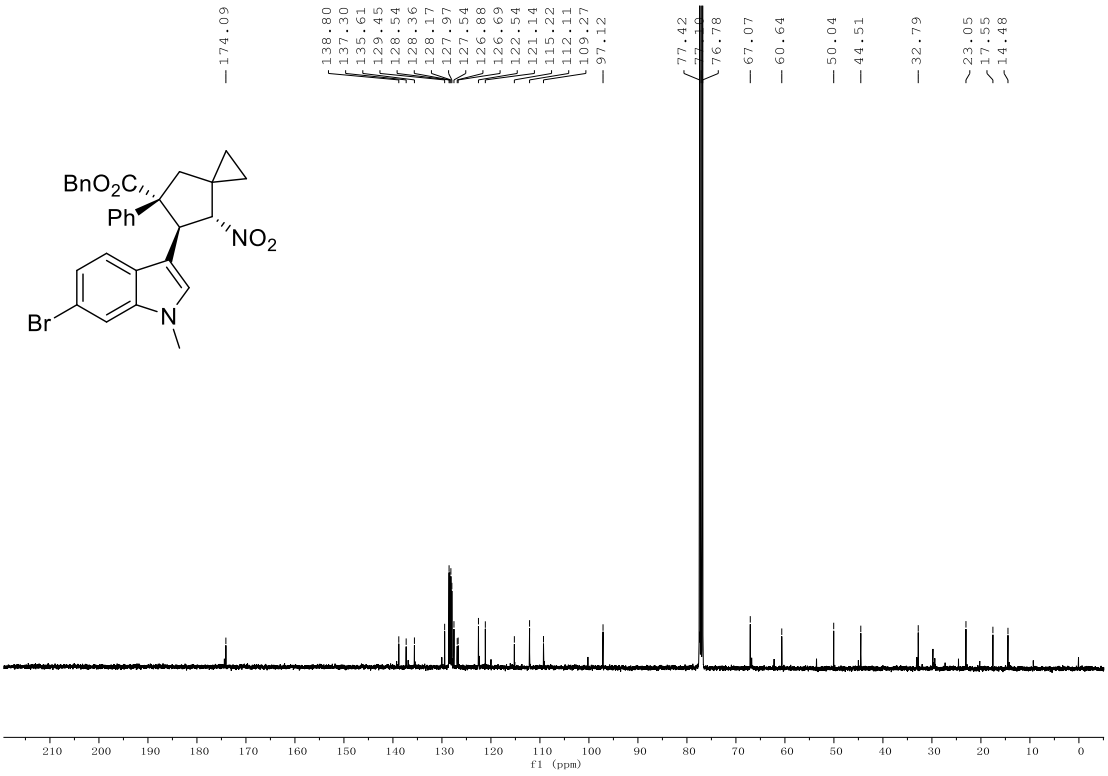
f1 (ppm)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109.27
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77.10
76.78
67.07
60.64
50.04
44.51
32.79
23.05
17.55
14.48
f1 (ppm)

BnO2C
Ph
NO2
Br
N


7.285
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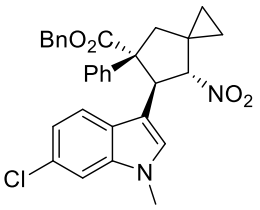
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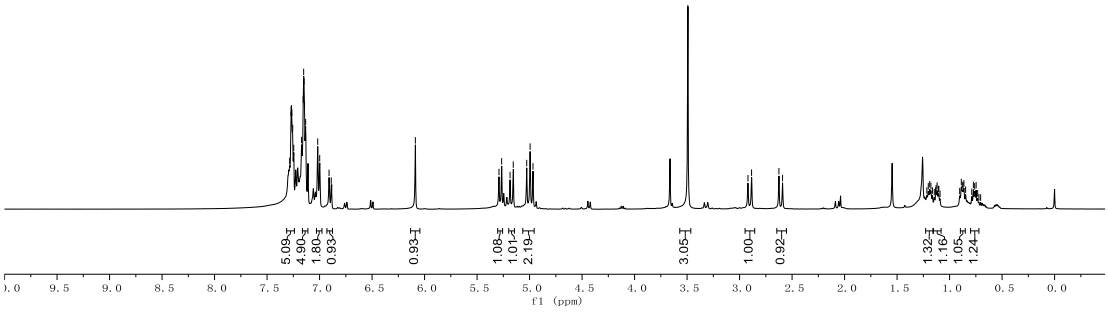
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f1 (ppm)


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109.08
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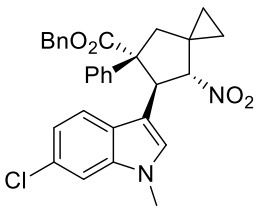
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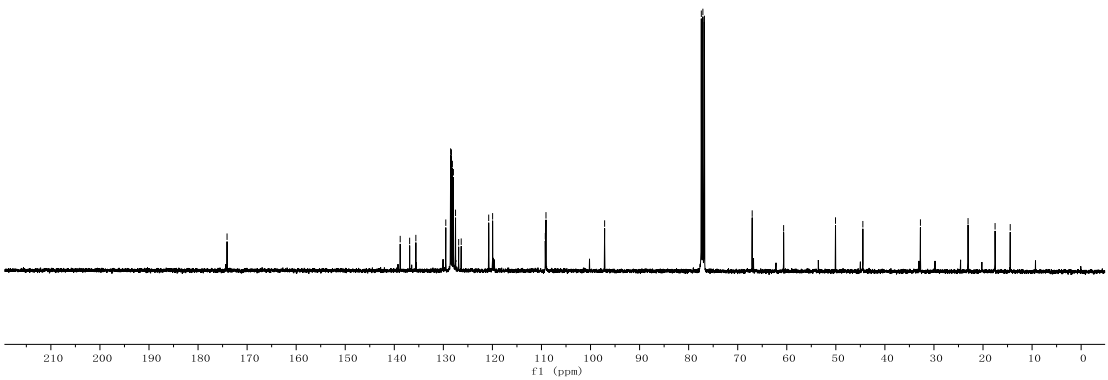
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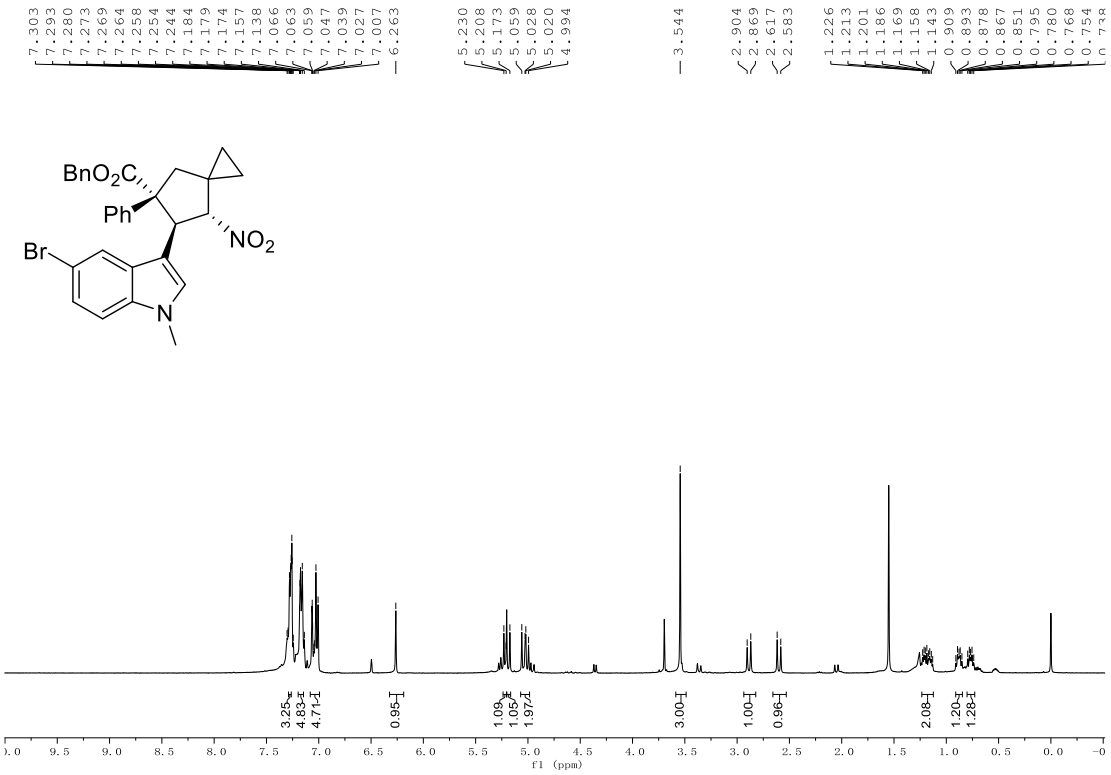
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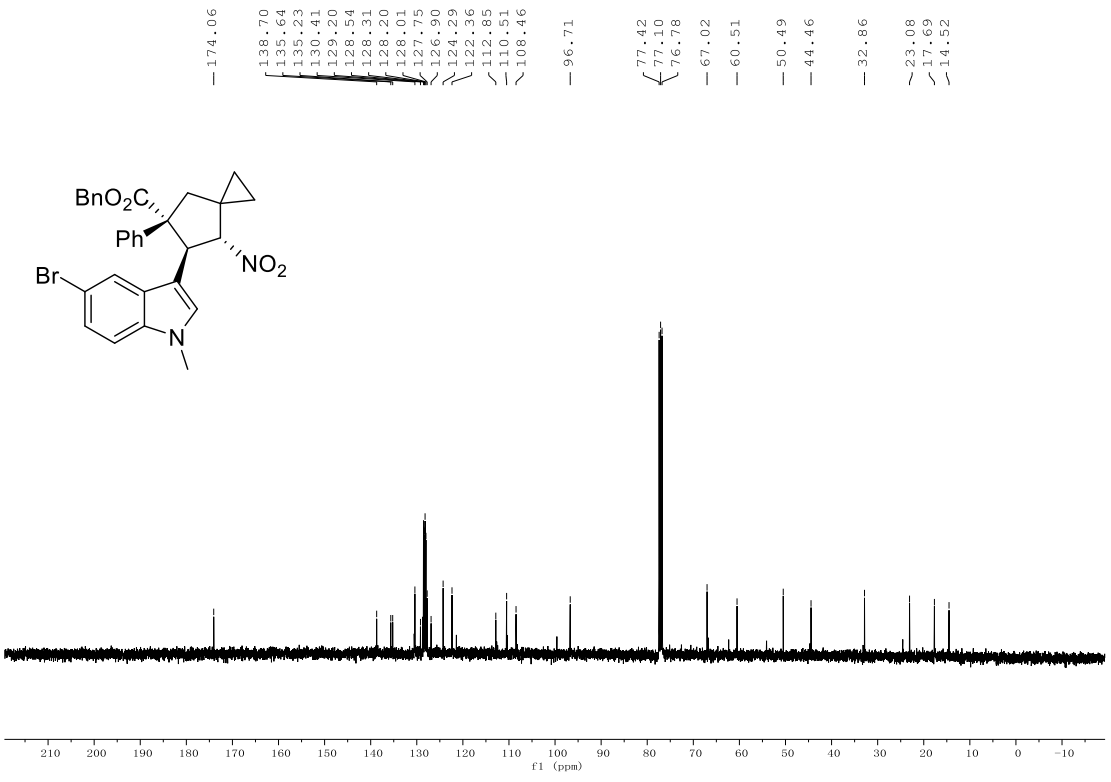
f1 (ppm)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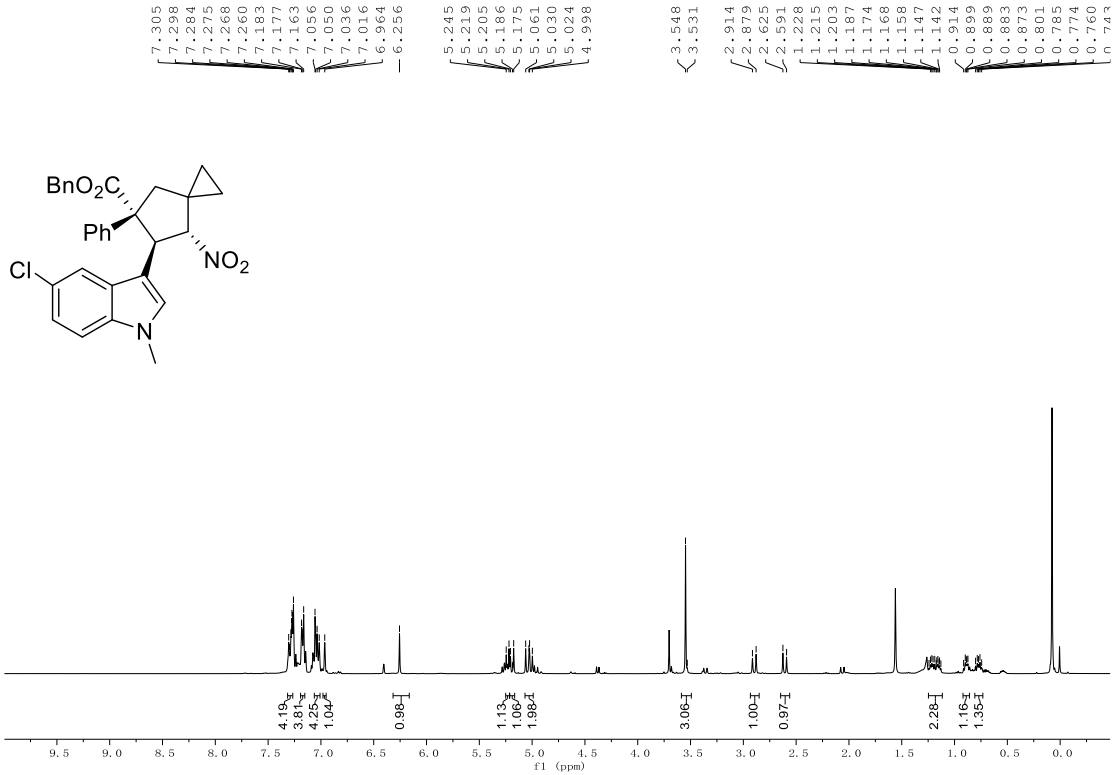
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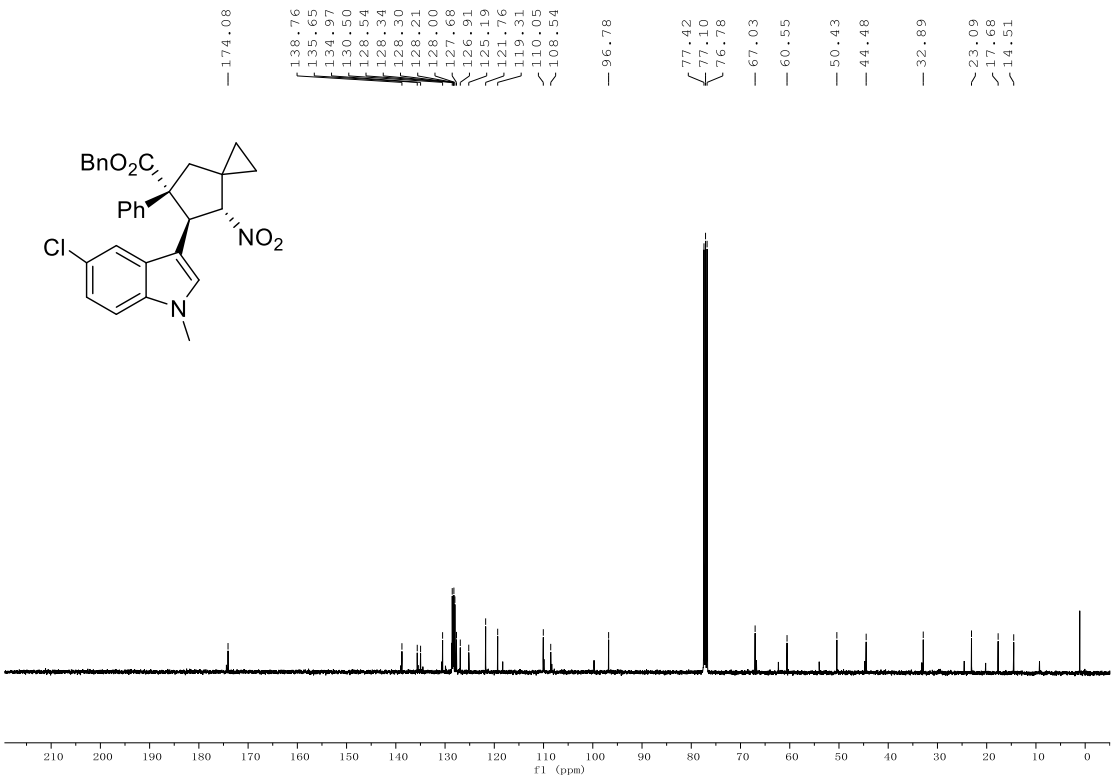
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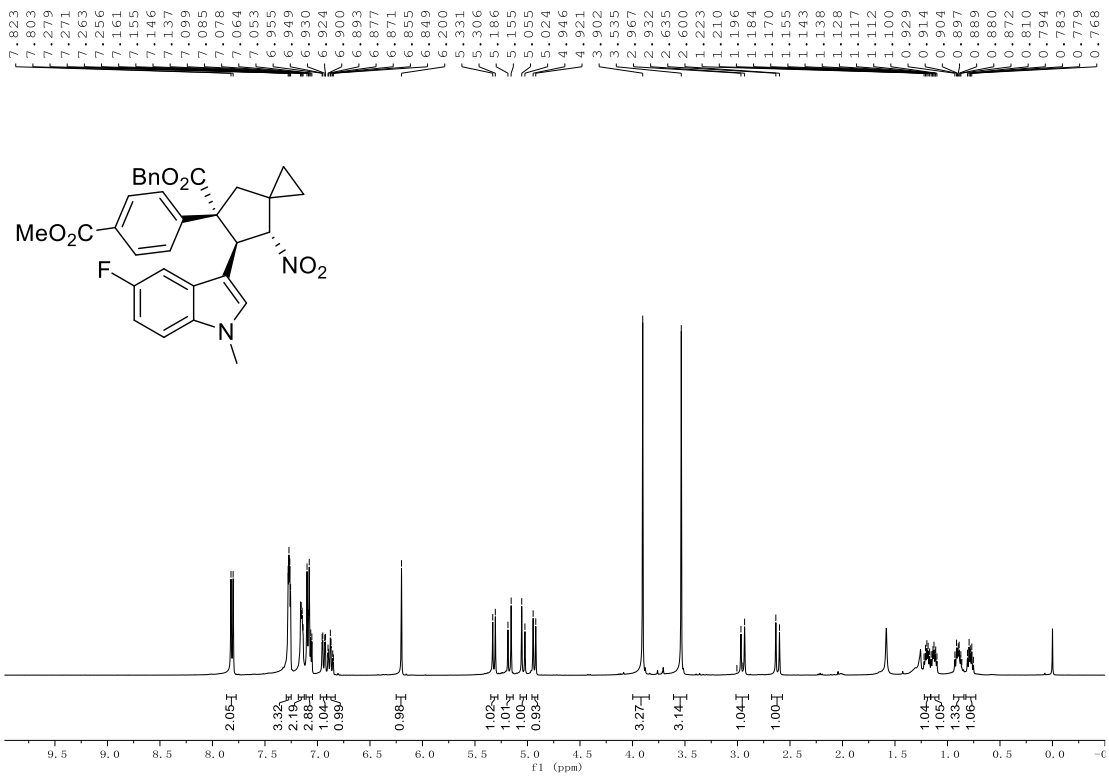
f1 (ppm)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0.779
0.768
BnO2C
MeO2C
NO2
F
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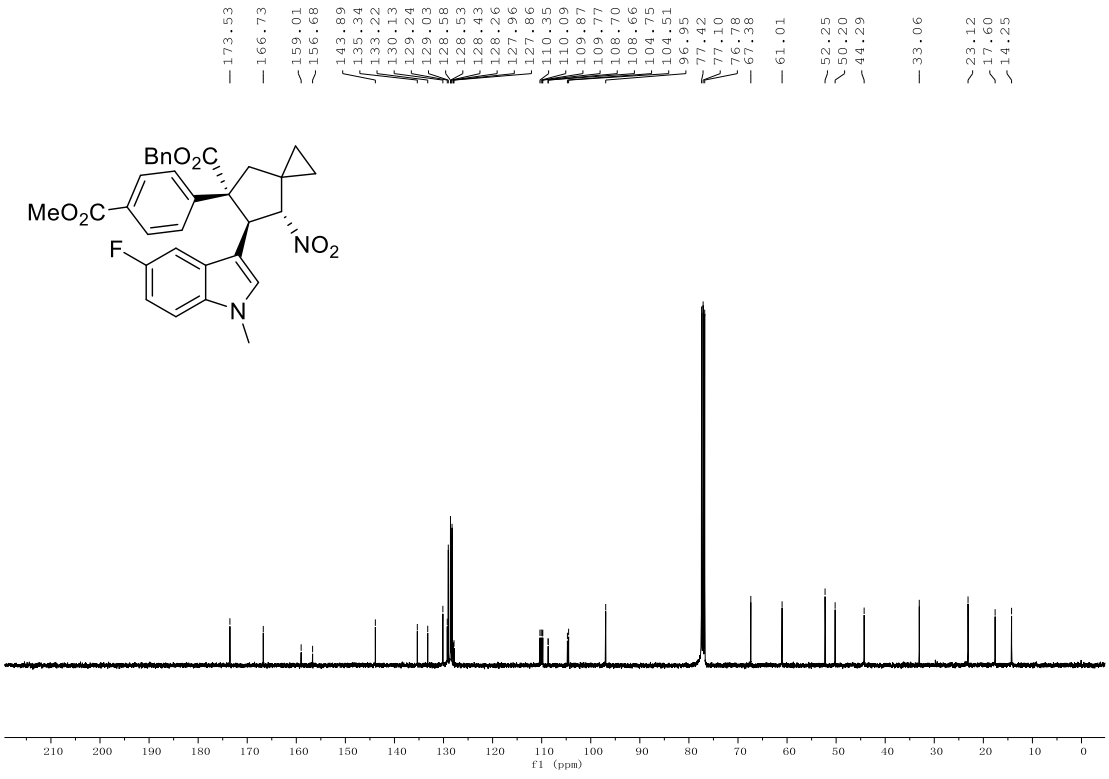
f1 (ppm)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128.26
127.96
127.86
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110.09
109.87
109.77
108.70
108.66
104.75
104.51
96.95
77.42
77.10
76.78
67.38
61.01
52.25
50.20
44.29
33.06
23.12
17.60
14.25
BnO2C
MeO2C
NO2
F
N
f1 (ppm)


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7.335
7.331
7.327
7.285
7.280
7.277
7.272
7.261
7.257
7.223
7.202
7.163
7.155
7.148
7.141
7.073
7.070
7.052
7.049
6.326
5.325
5.298
5.185
5.154
5.051
5.021
4.960
4.933
3.927
3.594
2.940
2.905
2.640
2.605
1.253
1.231
1.217
1.203
1.187
1.175
1.160
1.147
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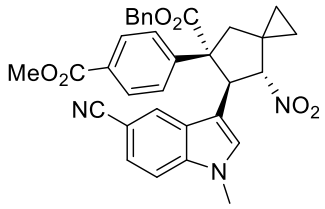
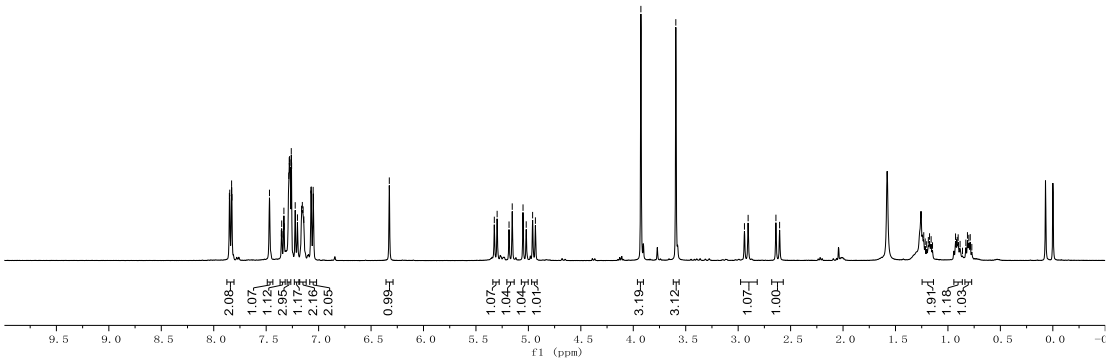
0.919
0.912
0.902
0.884
0.861
0.829
0.814
0.801
0.787
0.772


BnO2C
MeO2C
NC
NO2
N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1.07
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1.17
2.16
2.05
0.99
1.07
1.04
1.04
1.01
3.19
3.12
1.07
1.00
1.91
1.18
1.03
f1 (ppm)


173.34
166.51
143.60
137.98
135.17
131.04
129.60
129.25
128.61
128.50
128.38
128.28
127.23
125.55
124.58
120.57
110.14
109.83
102.68
96.50
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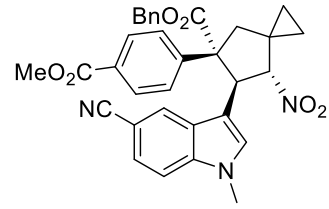
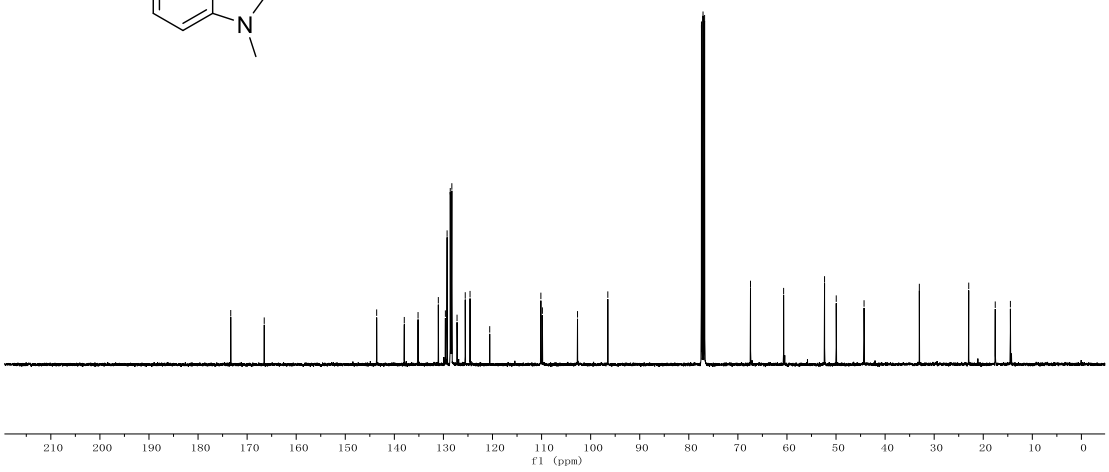
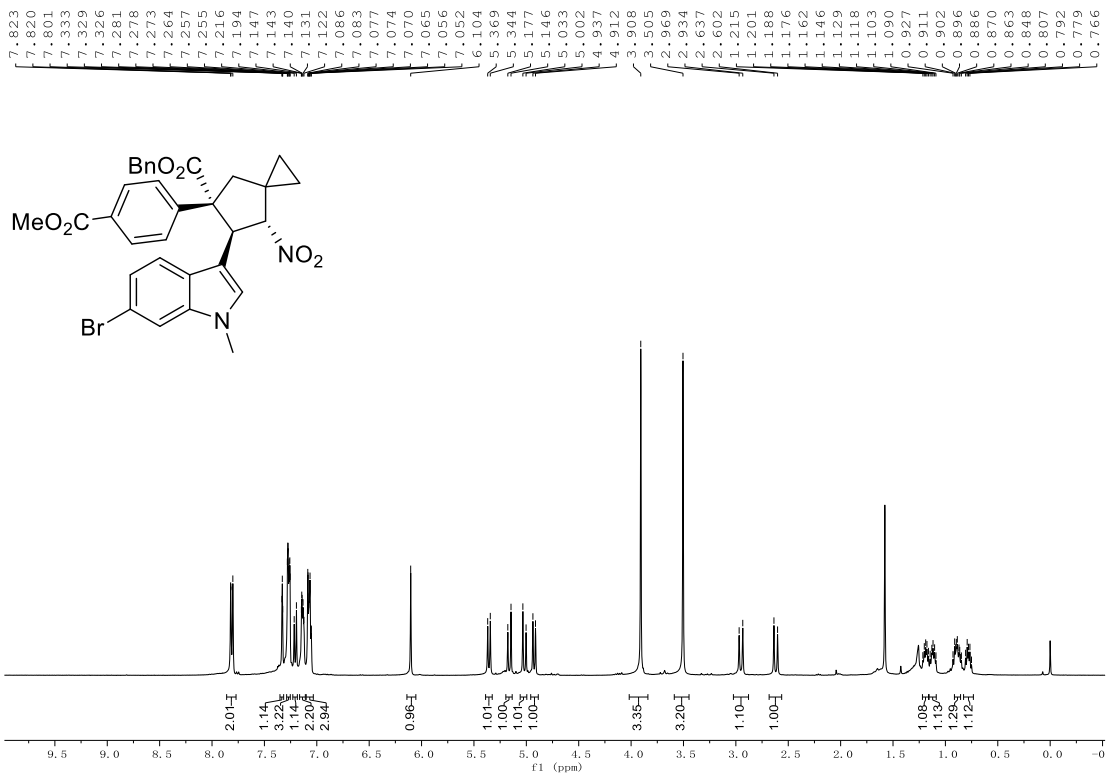
49.96
44.29
33.02
22.96
17.56
14.47


BnO2C
MeO2C
NC
NO2
N


f1 (ppm)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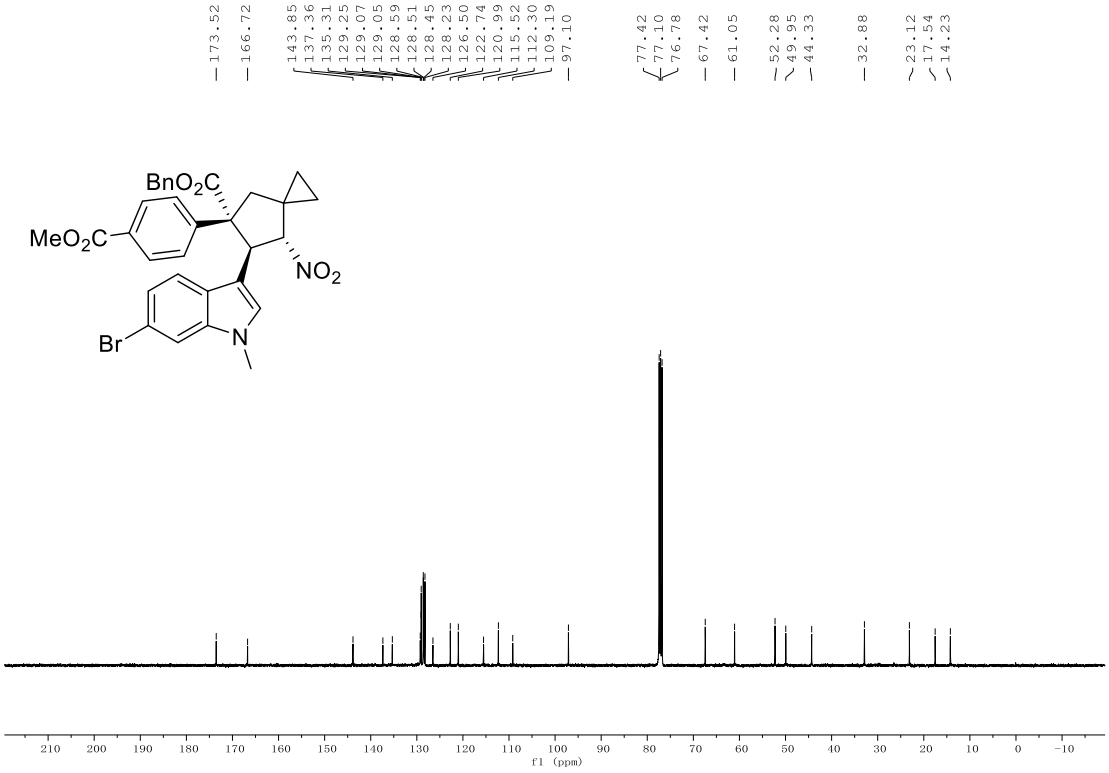
7.257
7.255
7.216
7.194
7.147
7.143
7.140
7.131
7.122
7.086
7.083
7.077
7.074
7.070
7.065
7.056
7.052
6.104
5.369
5.344
5.177
5.146
5.033
5.002
4.937
4.912
3.908
3.505
2.969
2.934
2.637
2.602
1.215
1.201
1.188
1.176
1.162
1.146
1.129
1.118
1.103
1.090
0.927
0.911
0.902
0.896
0.886
0.870
0.863
0.848
0.807
0.792
0.779
0.766
BnO2C
MeO2C
NO2
Br
N
2.01
1.14
3.22
1.14
2.20
2.94
0.96
1.01
1.00
1.01
1.00
3.35
3.20
1.10
1.00
1.08
1.13
1.29
1.12
f1 (ppm)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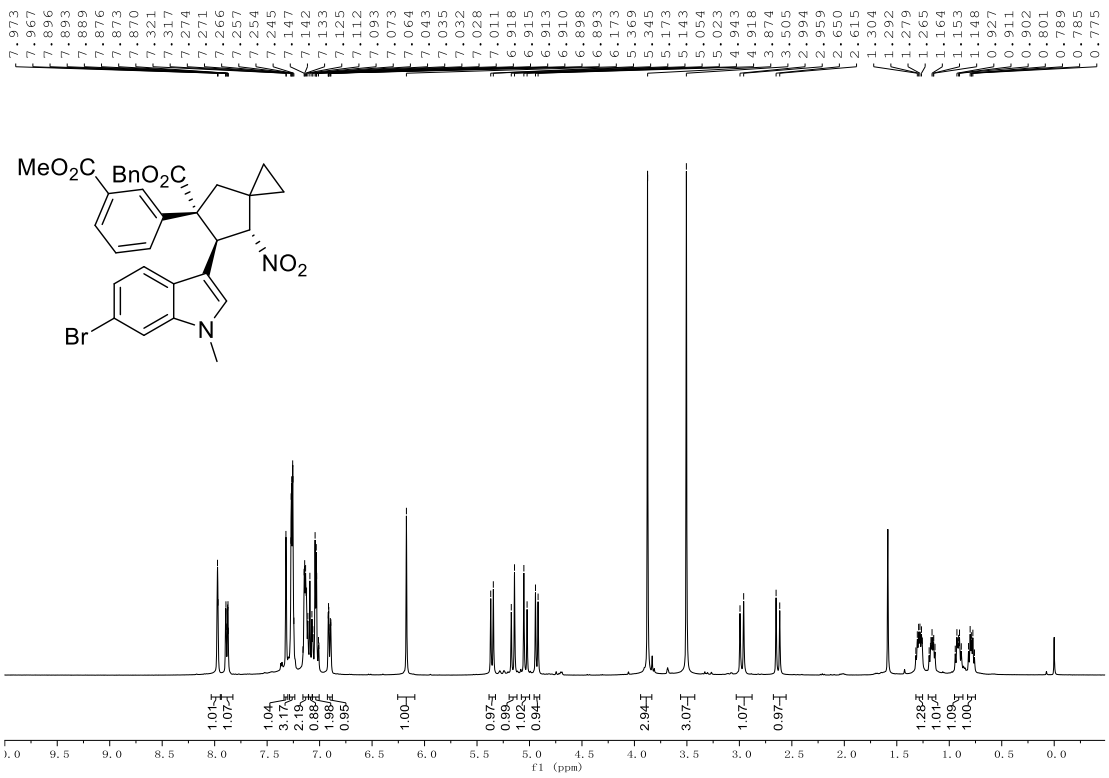
129.25
129.07
129.05
128.59
128.51
128.45
128.23
126.50
122.74
120.99
115.52
112.30
109.19
97.10
77.42
77.10
76.78
67.42
61.05
52.28
49.95
44.33
32.88
23.12
17.54
14.23
BnO2C
MeO2C
NO2
Br
N
f1 (ppm)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7.873
7.870
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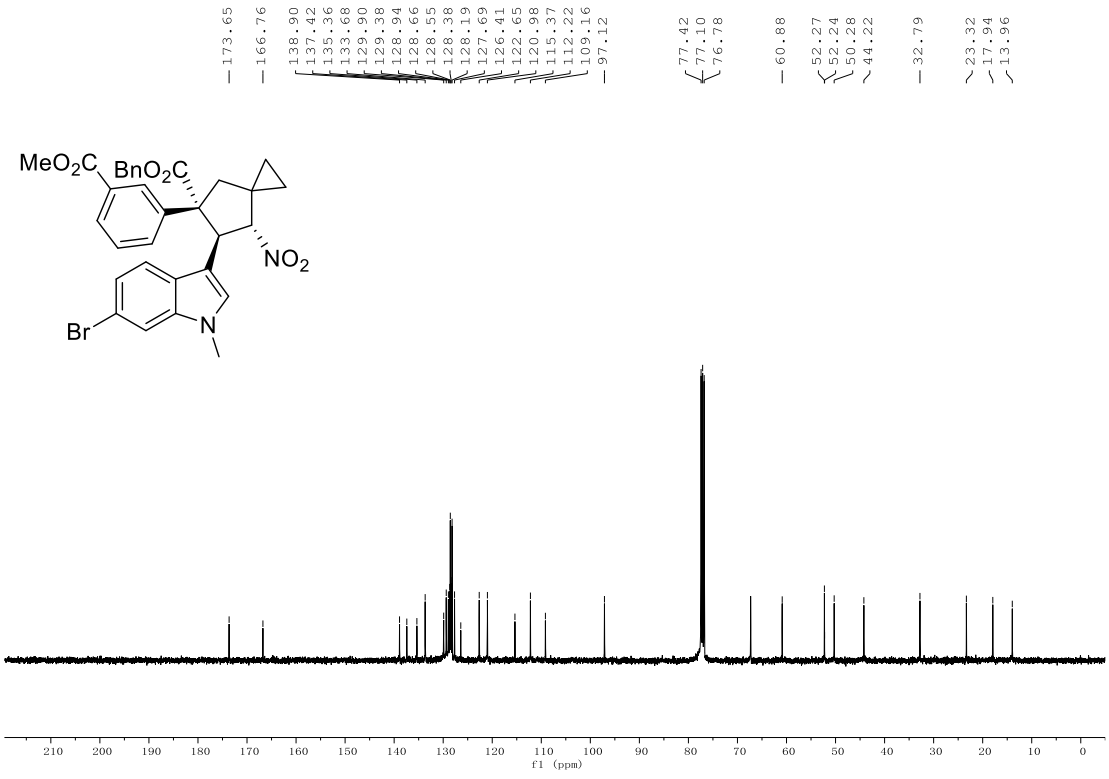
7.271
7.266
7.257
7.254
7.245
7.147
7.142
7.133
7.125
7.112
7.093
7.073
7.064
7.043
7.035
7.032
7.028
7.011
6.918
6.915
6.913
6.910
6.898
6.893
6.173
5.369
5.345
5.173
5.143
5.054
5.023
4.943
4.918
3.874
3.505
2.994
2.959
2.650
2.615
1.304
1.292
1.279
1.265
1.164
1.153
1.148
0.927
0.911
0.902
0.801
0.789
0.785
0.775
MeO2C
BnO2C
NO2
Br
N
1.01
1.07
1.04
3.17
2.19
0.88
1.98
0.95
1.00
0.97
0.99
1.02
0.94
2.94
3.07
1.07
0.97
1.28
1.01
1.09
1.00
f1 (ppm)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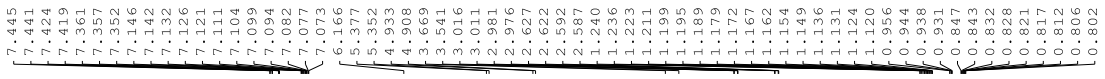
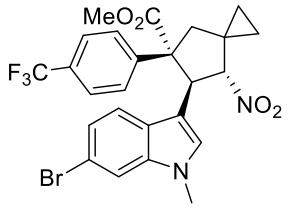
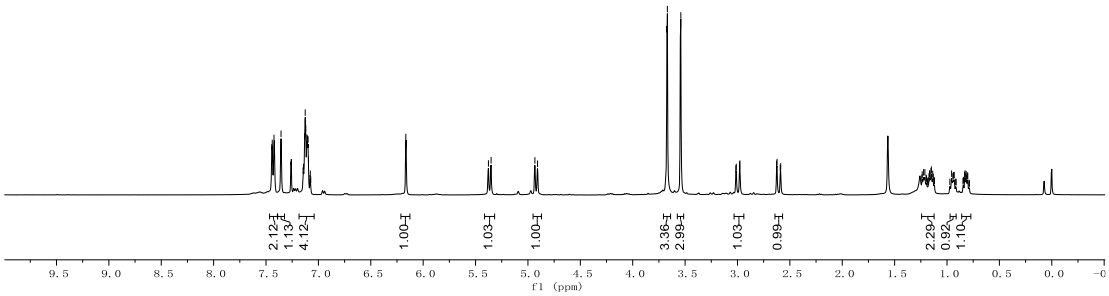
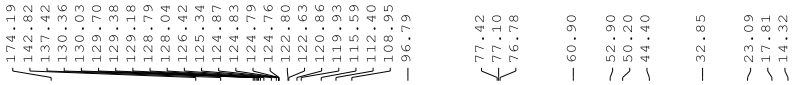
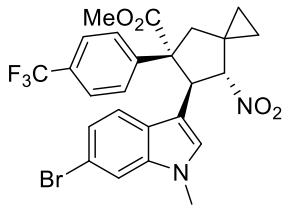
129.90
129.38
128.94
128.66
128.55
128.38
128.19
127.69
126.41
122.65
120.98
115.37
112.22
109.16
97.12
77.42
77.10
76.78
60.88
52.27
52.24
50.28
44.22
32.79
23.32
17.94
13.96
MeO2C
BnO2C
NO2
Br
N
f1 (ppm)



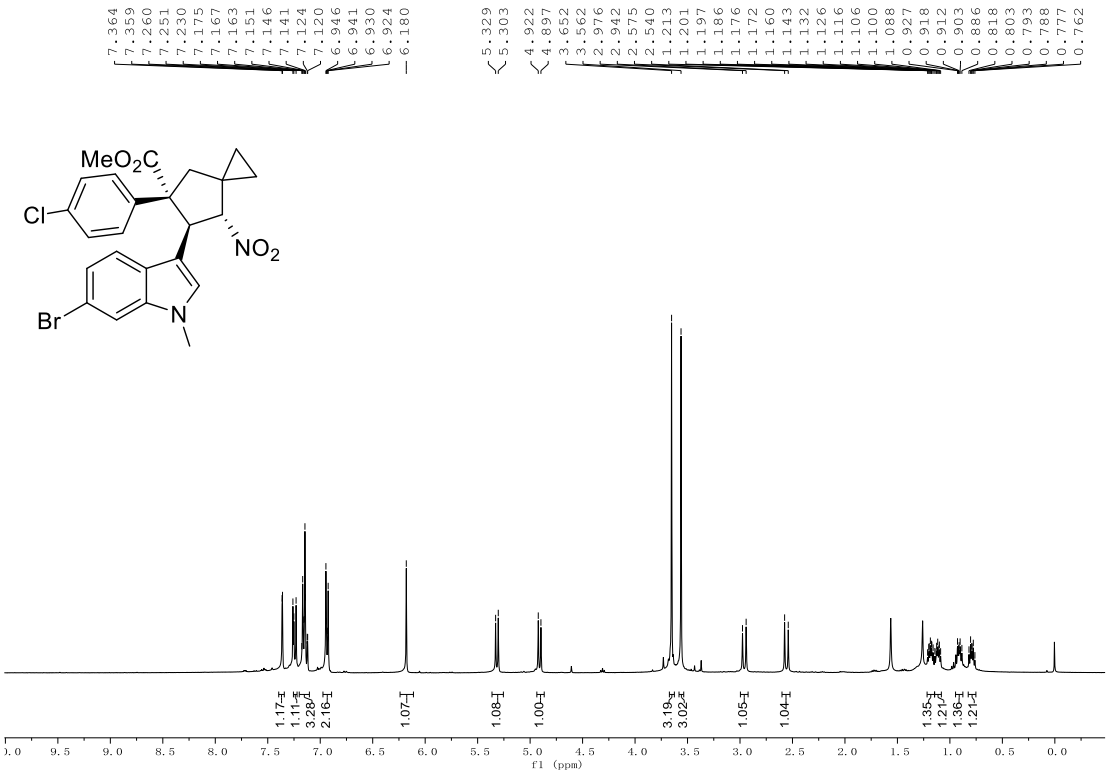

MeO2C
F3C
NO2
Br
N


2.12
1.13
4.12
1.00
1.03
1.00
3.36
2.99
1.03
0.99
2.29
0.92
1.10
f1 (ppm)




MeO2C
F3C
NO2
Br
N

f1 (ppm)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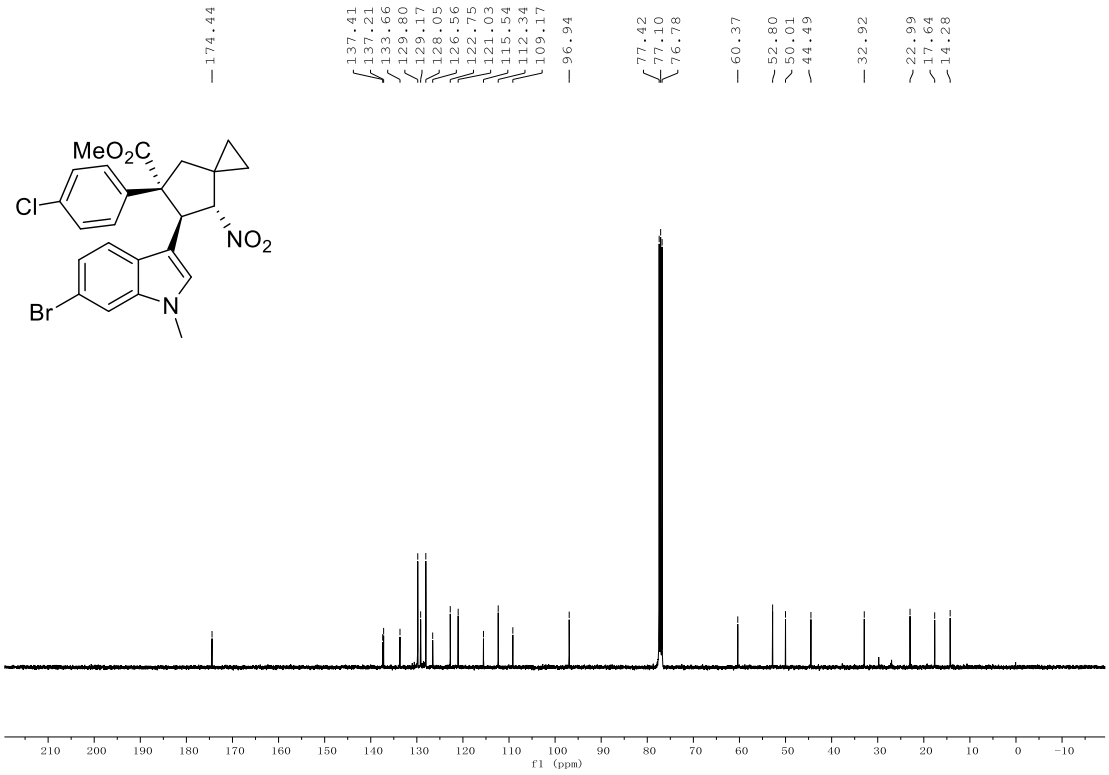
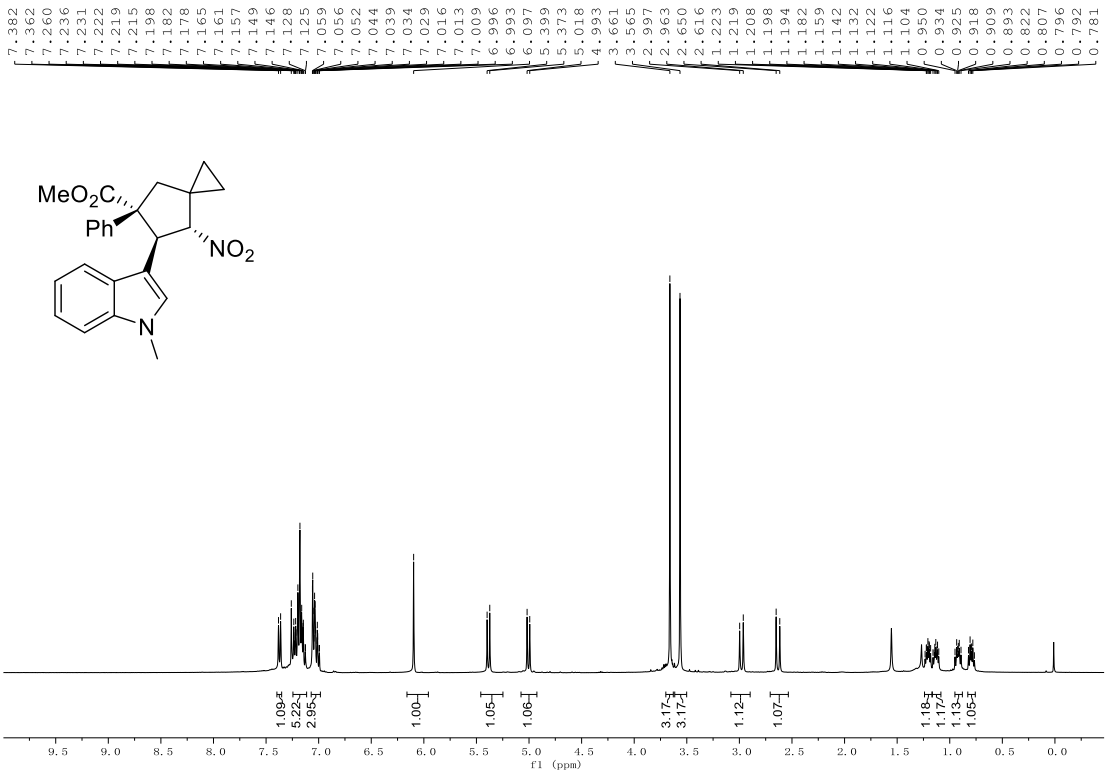
7.175
7.167
7.163
7.151
7.146
7.141
7.124
7.120
6.946
6.941
6.930
6.924
6.180
5.329
5.303
4.922
4.897
3.652
3.562
2.976
2.942
2.575
2.540
1.213
1.201
1.197
1.186
1.176
1.172
1.160
1.143
1.132
1.126
1.116
1.106
1.100
1.088
0.927
0.918
0.912
0.903
0.886
0.818
0.803
0.793
0.788
0.777
0.762
MeO2C
Cl
NO2
Br
N
1.17
1.11
3.28
2.16
1.07
1.08
1.00
3.19
3.02
1.05
1.04
1.35
1.21
1.36
1.21
f1 (ppm)


174.44
137.41
137.21
133.66
129.80
129.17
128.05
126.56
122.75
121.03
115.54
112.34
109.17
96.94
77.42
77.10
76.78
60.37
52.80
50.01
44.49
32.92
22.99
17.64
14.28
MeO2C
Cl
NO2
Br
N
f1 (ppm)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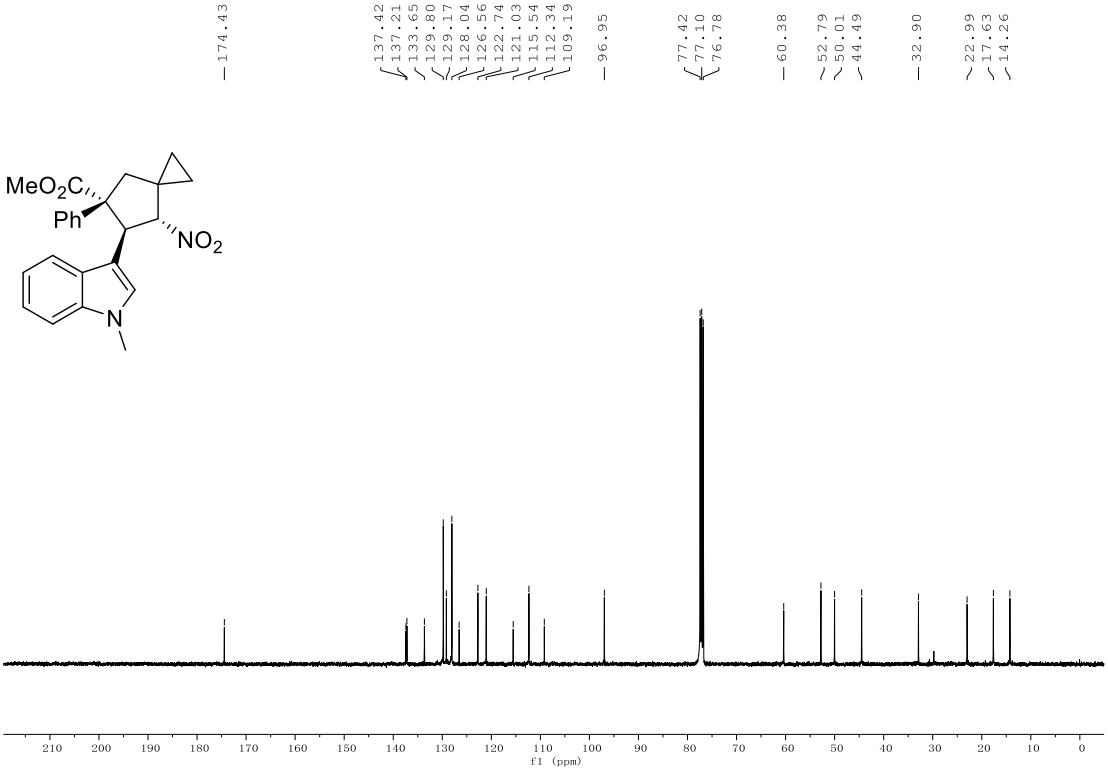
7.231
7.222
7.219
7.215
7.198
7.182
7.178
7.165
7.161
7.157
7.149
7.146
7.128
7.125
7.059
7.056
7.052
7.044
7.039
7.034
7.029
7.016
7.013
7.009
6.996
6.993
6.097
5.399
5.373
5.018
4.993
3.661
3.565
2.997
2.963
2.650
2.616
1.223
1.219
1.208
1.198
1.194
1.182
1.159
1.142
1.132
1.122
1.116
1.104
0.950
0.934
0.925
0.918
0.909
0.893
0.822
0.807
0.796
0.792
0.781
MeO2C
Ph
NO2
N
1.09
5.22
2.95
1.00
1.05
1.06
3.17
3.17
1.12
1.07
1.18
1.17
1.13
1.05
f1 (ppm)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129.80
129.17
128.04
126.56
122.74
121.03
115.54
112.34
109.19
96.95
77.42
77.10
76.78
60.38
52.79
50.01
44.49
32.90
22.99
17.63
14.26
MeO2C
Ph
NO2
N
f1 (ppm)


7.316
7.311
7.300
7.295
7.288
7.271
7.260
7.250
7.240
7.199
7.194
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7.007
7.001
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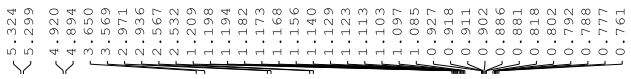
6.869
6.864
6.856
6.206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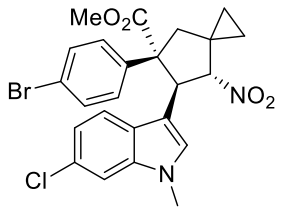
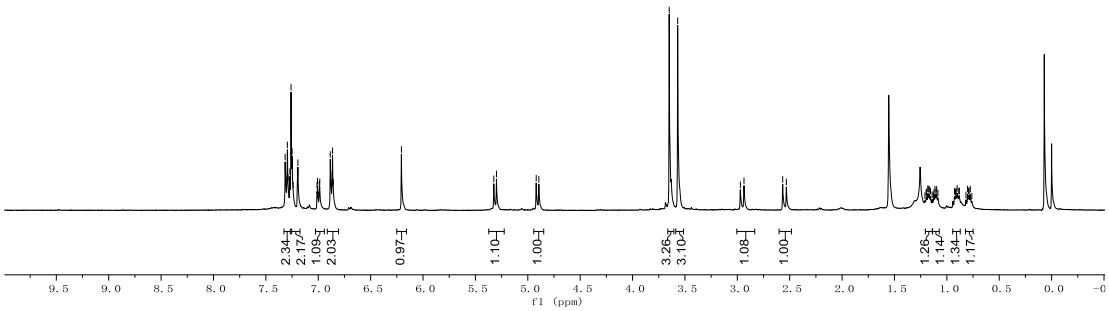
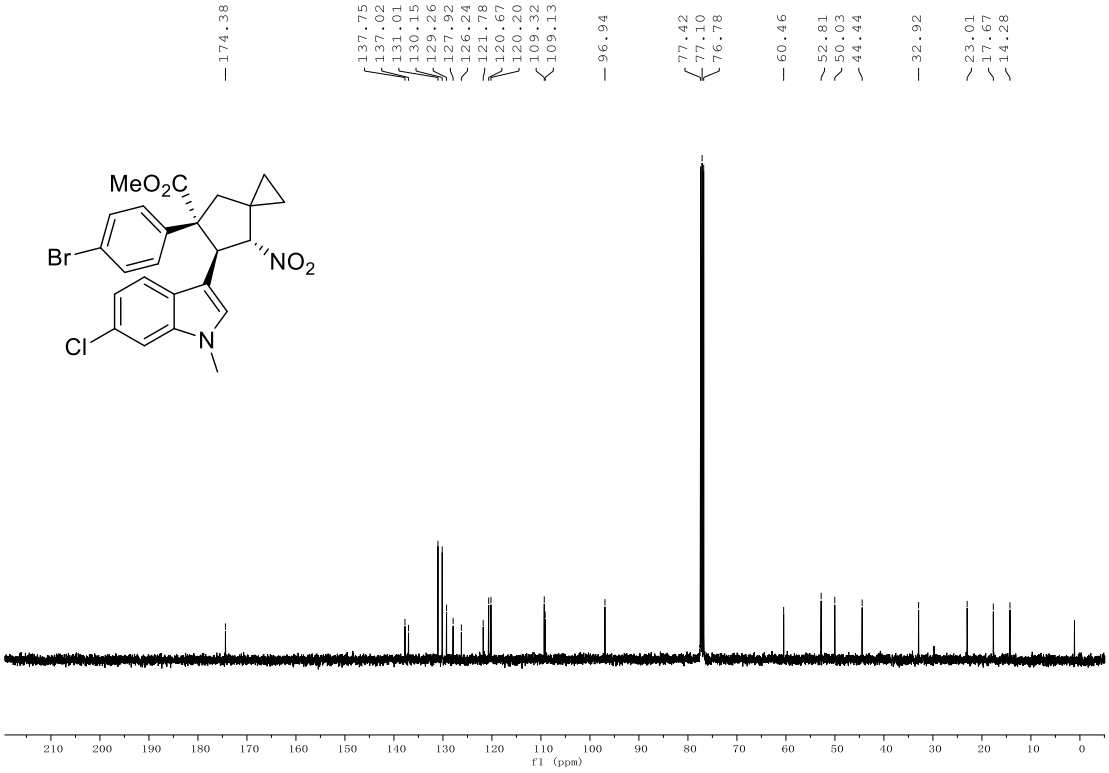
3.569
2.971
2.936
2.567
2.532
1.209
1.198
1.194
1.182
1.173
1.168
1.156
1.140
1.129
1.123
1.113
1.103
1.097
1.085
0.927
0.918
0.911
0.902
0.886
0.881
0.818
0.802
0.792
0.788
0.777
0.761


MeO2C
Br
NO2
Cl
N


2.34
2.17
1.09
2.03
0.97
1.10
1.00
3.26
3.10
1.08
1.00
1.26
1.14
1.34
1.17
f1 (ppm)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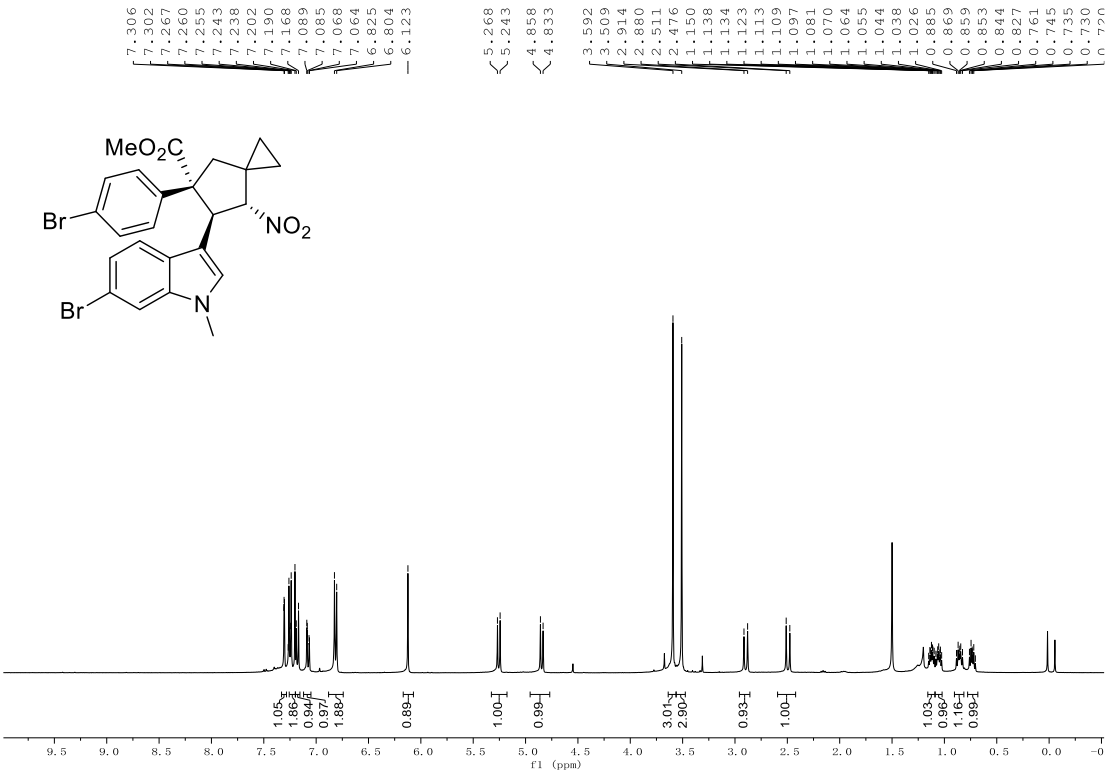
137.02
131.01
130.15
129.26
127.92
126.24
121.78
120.67
120.20
109.32
109.13
96.94
77.42
77.10
76.78
60.46
52.81
50.03
44.44
32.92
23.01
17.67
14.28
f1 (ppm)

MeO2C
Br
NO2
Cl
N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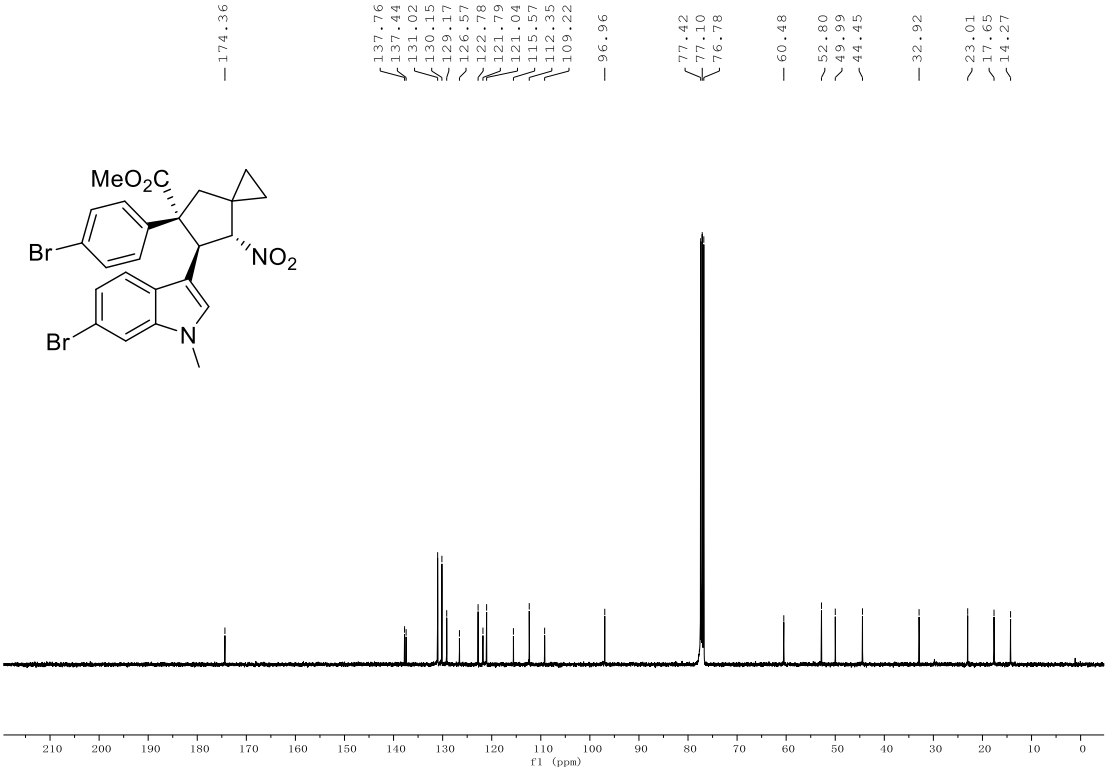
7.255
7.243
7.238
7.202
7.190
7.168
7.089
7.085
7.068
7.064
6.825
6.804
6.123
5.268
5.243
4.858
4.833
3.592
3.509
2.914
2.880
2.511
2.476
1.150
1.138
1.134
1.123
1.113
1.109
1.097
1.081
1.070
1.064
1.055
1.044
1.038
1.026
0.885
0.869
0.859
0.853
0.844
0.827
0.761
0.745
0.735
0.730
MeO2C
Br
NO2
Br
N
1.05
1.86
0.94
0.97
1.88
0.89
1.00
0.99
3.01
2.90
0.93
1.00
1.03
0.96
1.16
0.99
f1 (ppm)


174.36
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137.44
131.02
130.15
129.17
126.57
122.78
121.79
121.04
115.57
112.35
109.22
96.96
77.42
77.10
76.78
60.48
52.80
49.99
44.45
32.92
23.01
17.65
14.27
MeO2C
Br
NO2
Br
N
f1 (ppm)


7.506
7.500
7.482
7.466
7.448
7.429
7.390
7.386
7.382
7.367
7.351
7.347
7.317
7.300
7.285
7.261
5.194
3.296
3.001
2.969
2.736
2.703
1.511
1.495
1.482
1.469
1.453
1.002
0.986
0.979
0.971
0.962
0.947
0.820
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0.788
0.783
0.779
0.763
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0.737
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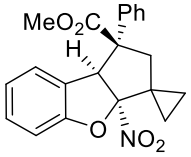
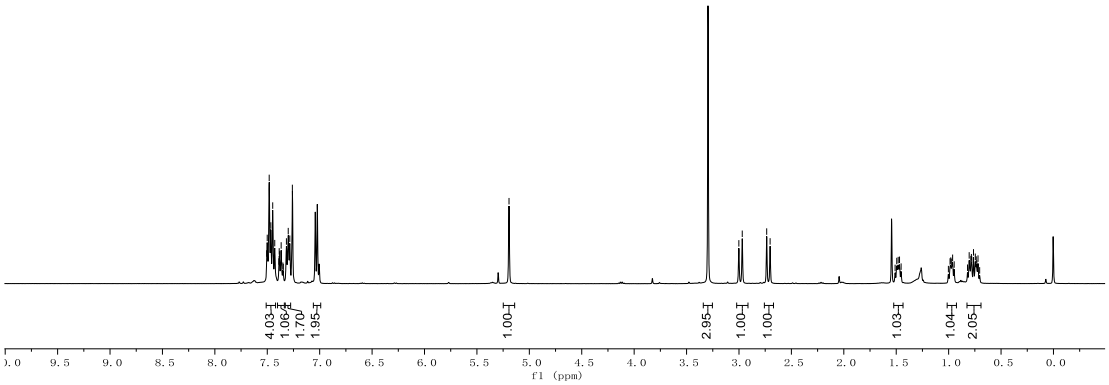
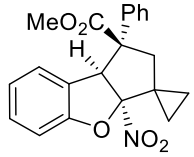
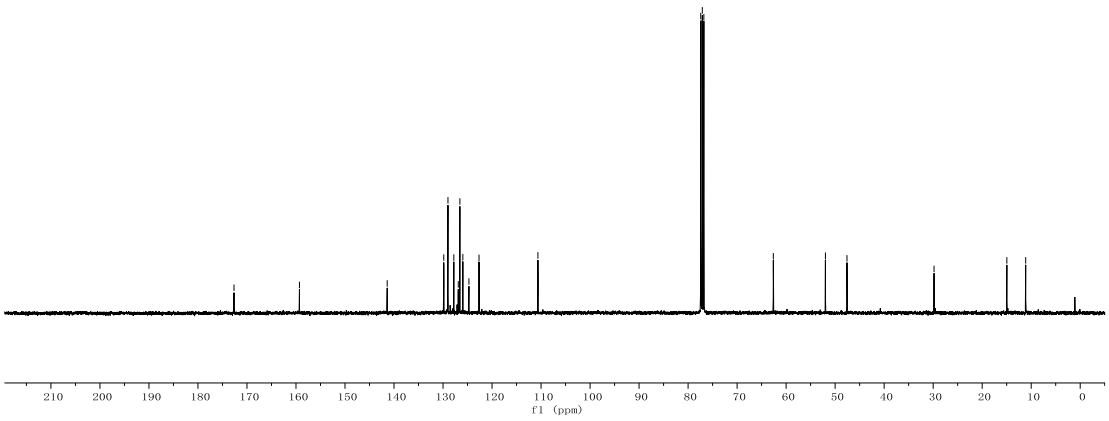
0.704


MeO2C
Ph
H
O
NO2


4.03
1.06
1.70
1.95
1.00
2.95
1.00
1.00
1.03
1.04
2.05
f1 (ppm)


172.65
159.29
141.39
129.85
128.99
127.80
126.89
126.56
125.96
124.71
122.66
110.64
77.42
77.10
76.78
62.61
62.58
51.98
47.58
29.82
14.97
11.12


MeO2C
Ph
H
O
NO2


f1 (ppm)


7.422
7.416
7.400
7.393
7.310
7.302
7.292
7.282
7.276
7.259
7.036
7.016
6.982
6.976
6.960
6.954
5.140
3.848
3.306
2.966
2.933
2.709
2.677
1.484
1.472
1.464
1.458
1.451
1.445
1.433
0.963
0.957
0.950
0.944
0.939
0.925
0.920
0.811
0.800
0.796
0.792
0.783
0.776
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0.751
0.745
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0.732
0.725
0.718
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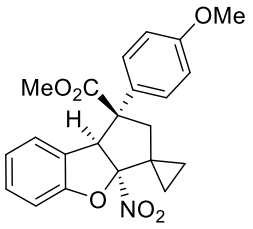
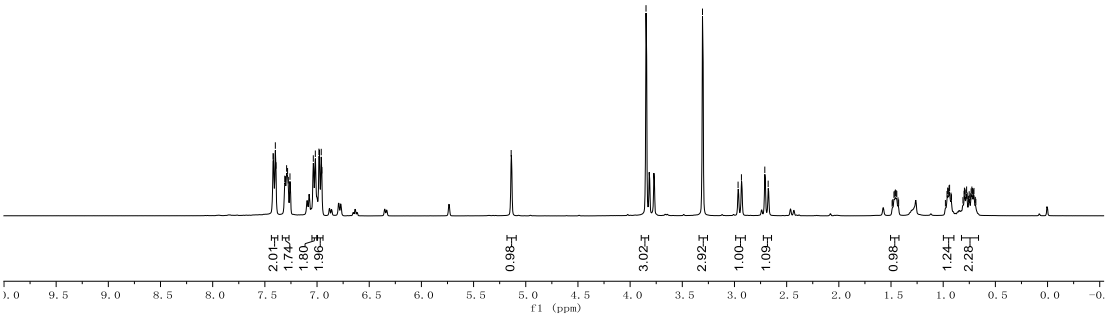
0.705
0.692


OMe
MeO2C
H
O
NO2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3.02
2.92
1.00
1.09
0.98
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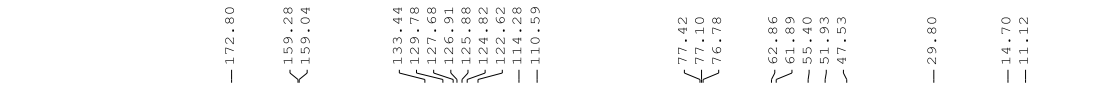
2.28
f1 (ppm)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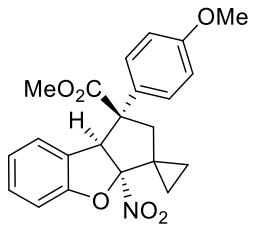
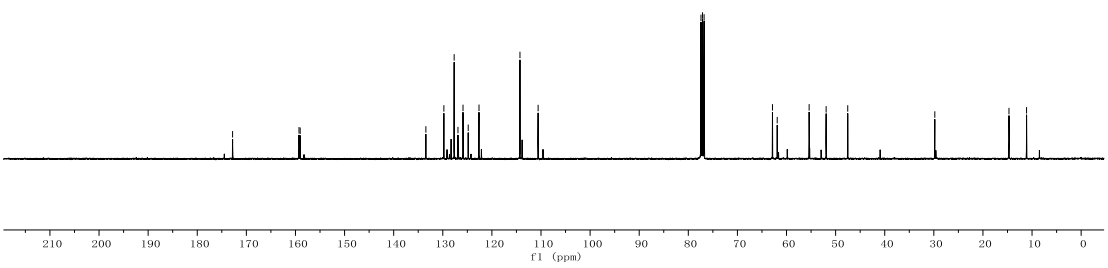
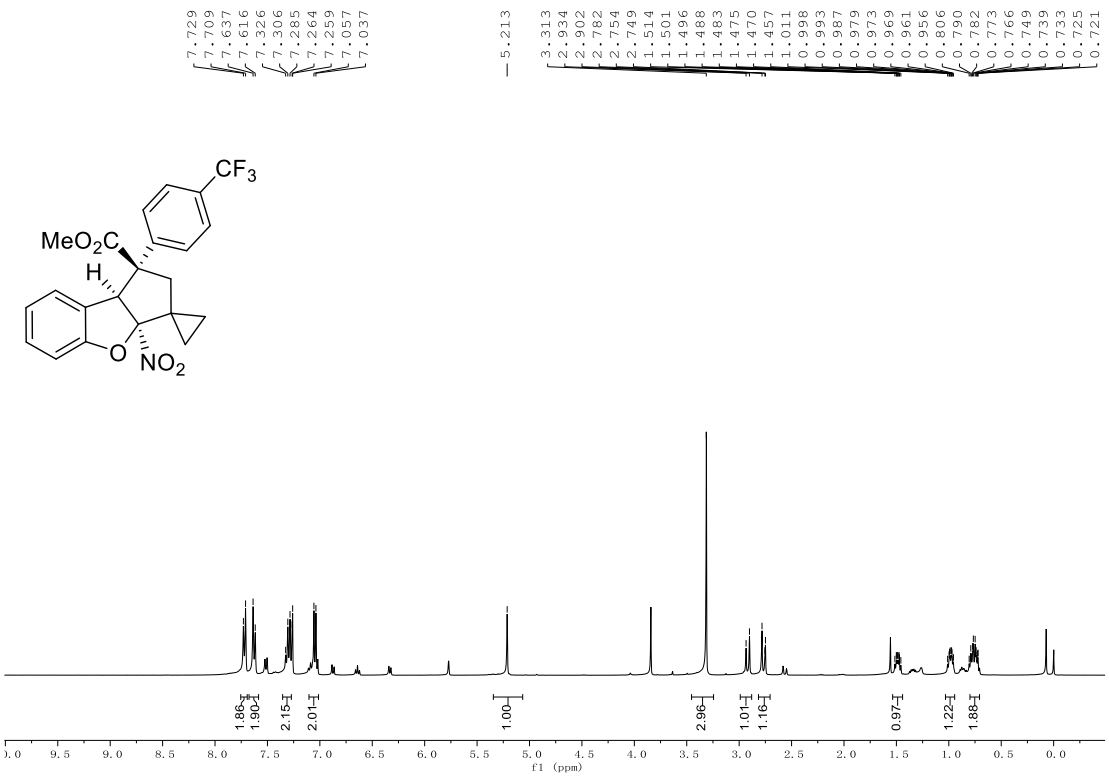
159.28
159.04
133.44
129.78
127.68
126.91
125.88
124.82
122.62
114.28
110.59
77.42
77.10
76.78
62.86
61.89
55.40
51.93
47.53
29.80
14.70
11.12


OMe
MeO2C
H
O
NO2


f1 (ppm)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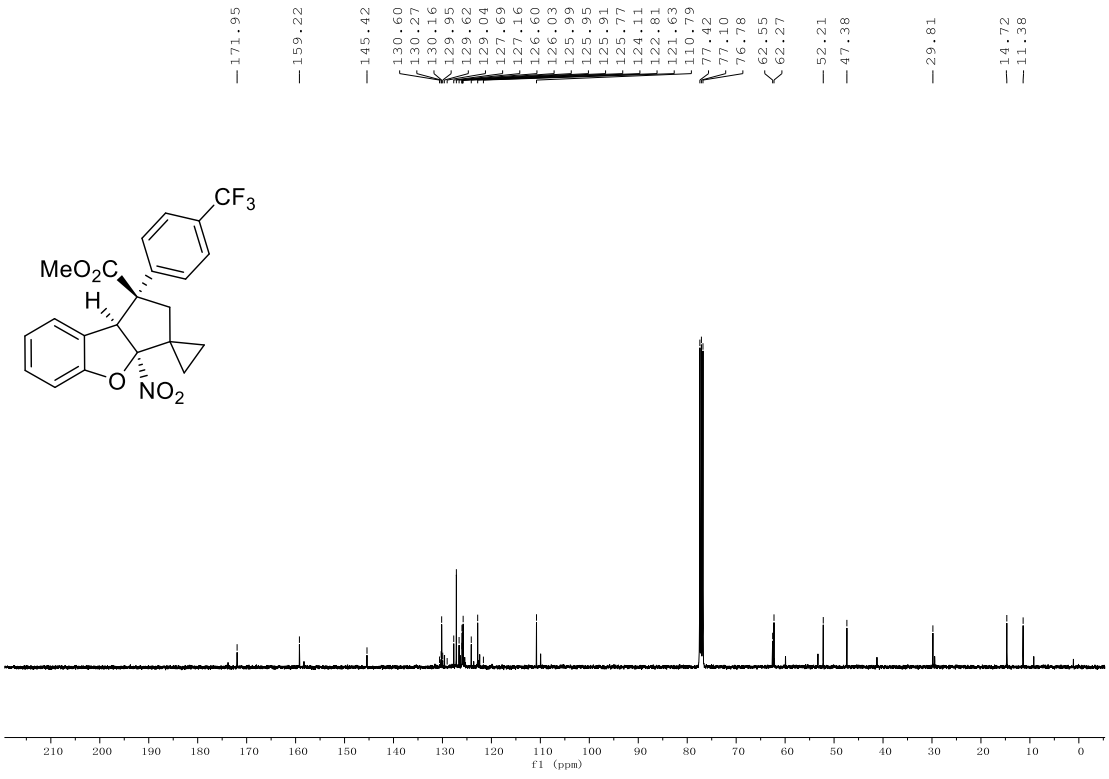
7.037
5.213
3.313
2.934
2.902
2.782
2.754
2.749
1.514
1.501
1.496
1.488
1.483
1.475
1.470
1.457
1.011
0.998
0.993
0.987
0.979
0.973
0.969
0.961
0.956
0.806
0.790
0.782
0.773
0.766
0.749
0.739
0.733
0.725
0.721
CF3
MeO2C
H
O
NO2
1.86
1.90
2.15
2.01
1.00
2.96
1.01
1.16
0.97
1.22
1.88
f1 (ppm)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145.42
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130.16
129.95
129.62
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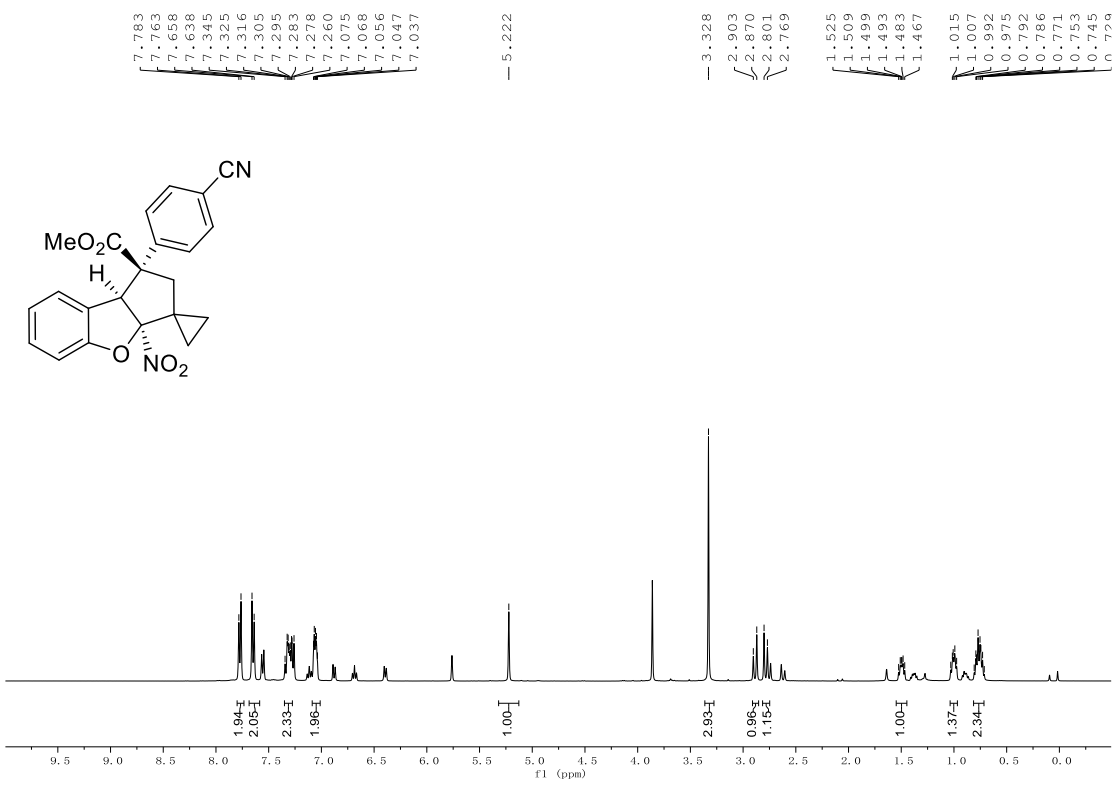
127.69
127.16
126.60
126.03
125.99
125.95
125.91
125.77
124.11
122.81
121.63
110.79
77.42
77.10
76.78
62.55
62.27
52.21
47.38
29.81
14.72
11.38
CF3
MeO2C
H
O
NO2
f1 (ppm)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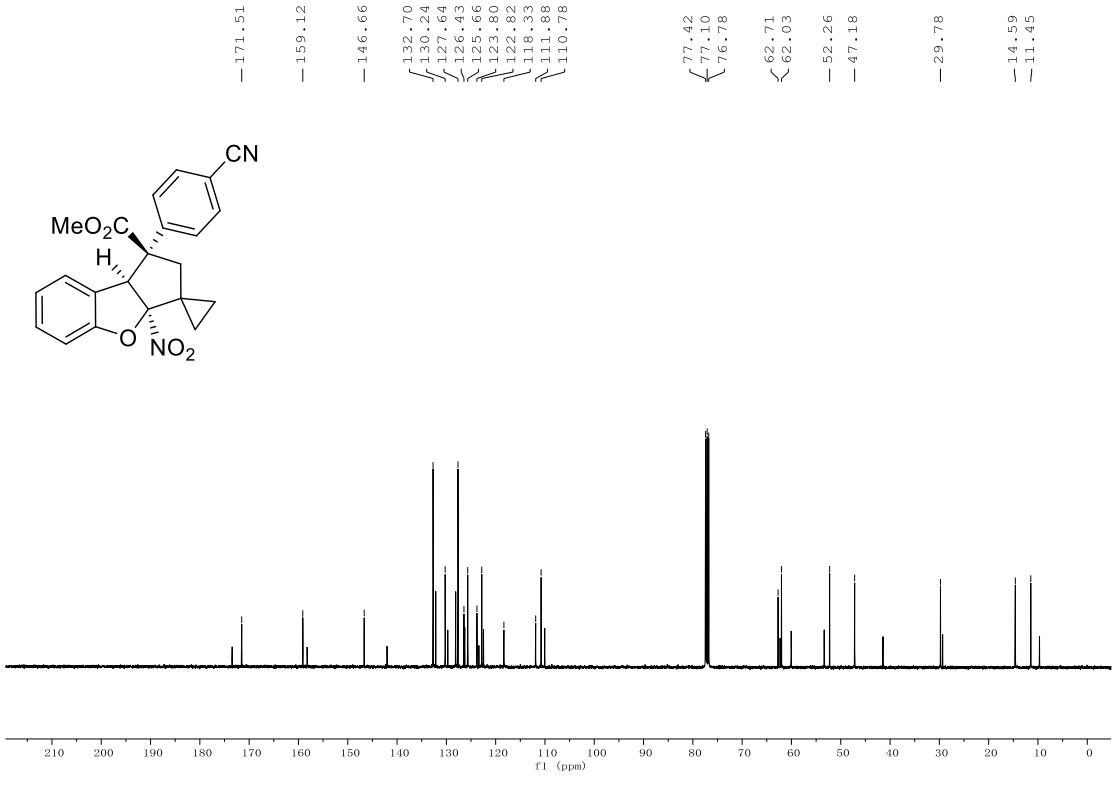
7.305
7.295
7.283
7.278
7.260
7.075
7.068
7.056
7.047
7.037
5.222
3.328
2.903
2.870
2.801
2.769
1.525
1.509
1.499
1.493
1.483
1.467
1.015
1.007
0.992
0.975
0.792
0.786
0.771
0.753
0.745
CN
MeO2C
H
O
NO2
1.94
2.05
2.33
1.96
1.00
2.93
0.96
1.15
1.00
1.37
2.34
f1 (ppm)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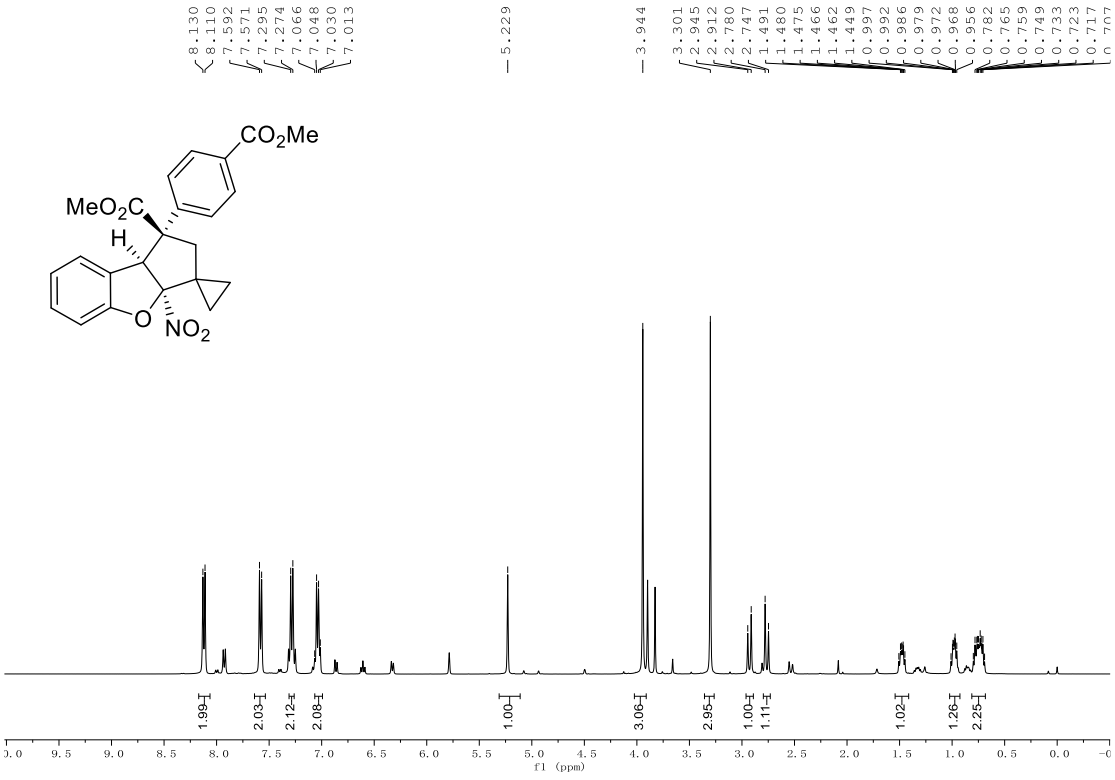
146.66
132.70
130.24
127.64
126.43
125.66
123.80
122.82
118.33
111.88
110.78
77.42
77.10
76.78
62.71
62.03
52.26
47.18
29.78
14.59
11.45
CN
MeO2C
H
O
NO2
f1 (ppm)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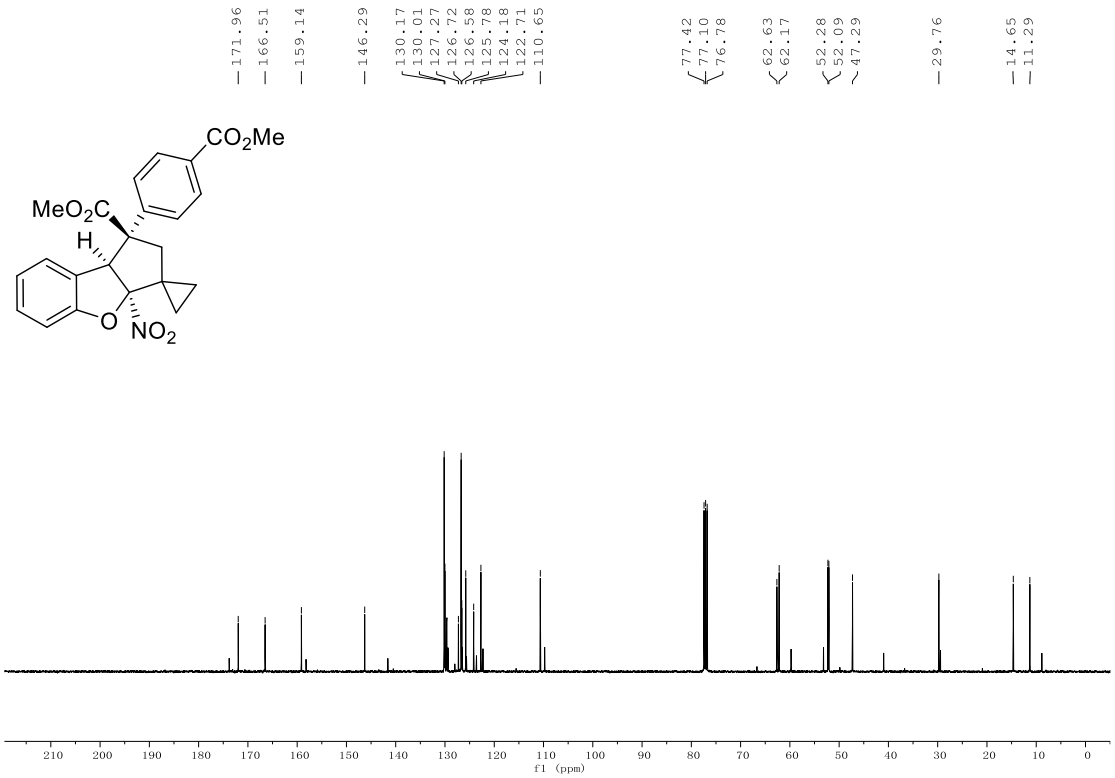
8.110
7.592
7.571
7.295
7.274
7.066
7.048
7.030
7.013
5.229
3.944
3.301
2.945
2.912
2.780
2.747
1.491
1.480
1.475
1.466
1.462
1.449
0.997
0.992
0.986
0.979
0.972
0.968
0.956
0.782
0.765
0.759
0.749
0.733
0.723
0.717
CO2Me
MeO2C
H
O
NO2
1.99
2.03
2.12
2.08
1.00
3.06
2.95
1.00
1.11
1.02
1.26
2.25
f1 (ppm)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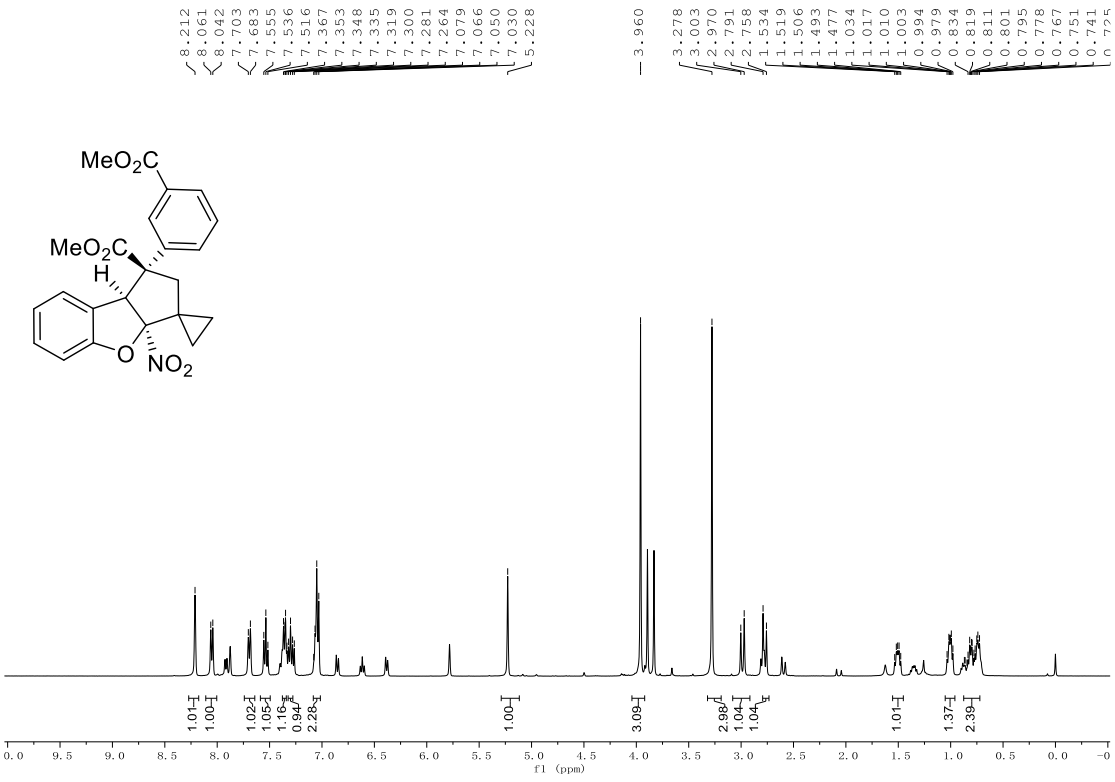
166.51
159.14
146.29
130.17
130.01
127.27
126.72
126.58
125.78
124.18
122.71
110.65
77.42
77.10
76.78
62.63
62.17
52.28
52.09
47.29
29.76
14.65
11.29
CO2Me
MeO2C
H
O
NO2
f1 (ppm)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7.536
7.516
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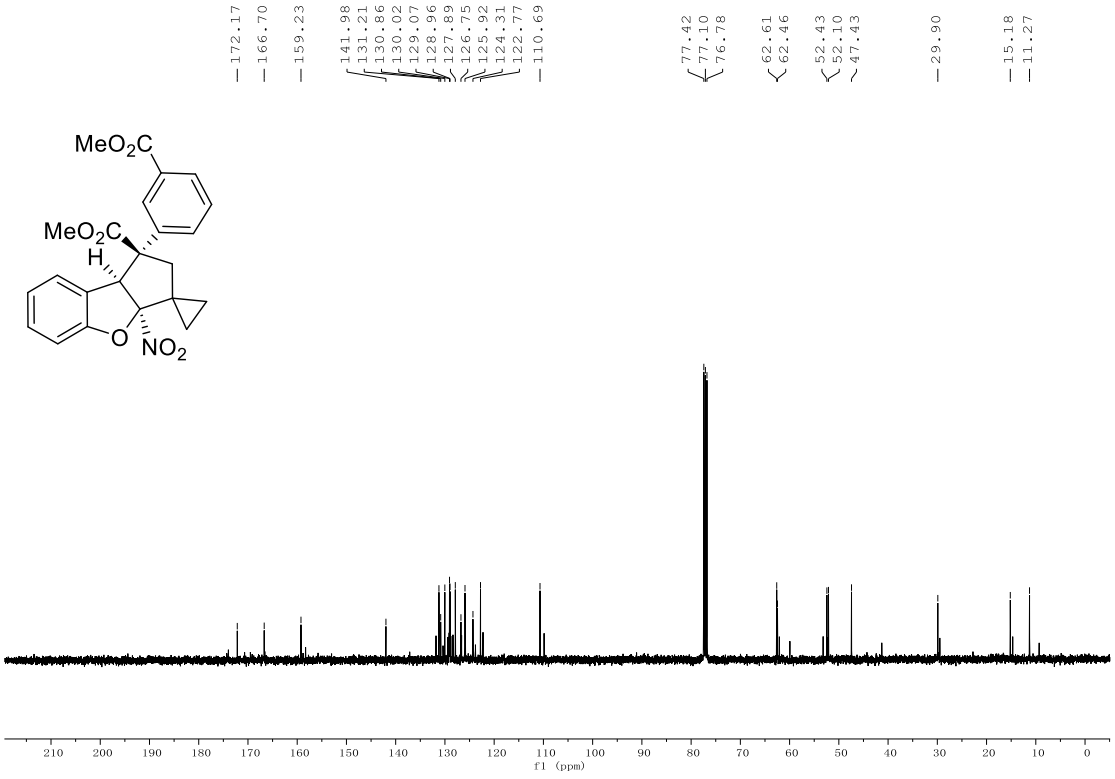
7.353
7.348
7.335
7.319
7.300
7.281
7.264
7.079
7.066
7.050
7.030
5.228
3.960
3.278
3.003
2.970
2.791
2.758
1.534
1.519
1.506
1.493
1.477
1.034
1.017
1.010
1.003
0.994
0.979
0.834
0.819
0.811
0.801
0.795
0.778
0.767
0.751
0.741
MeO2C
MeO2C
H
O
NO2
1.01
1.00
1.02
1.05
1.16
0.94
2.28
1.00
3.09
2.98
1.04
1.04
1.01
1.37
2.39
f1 (ppm)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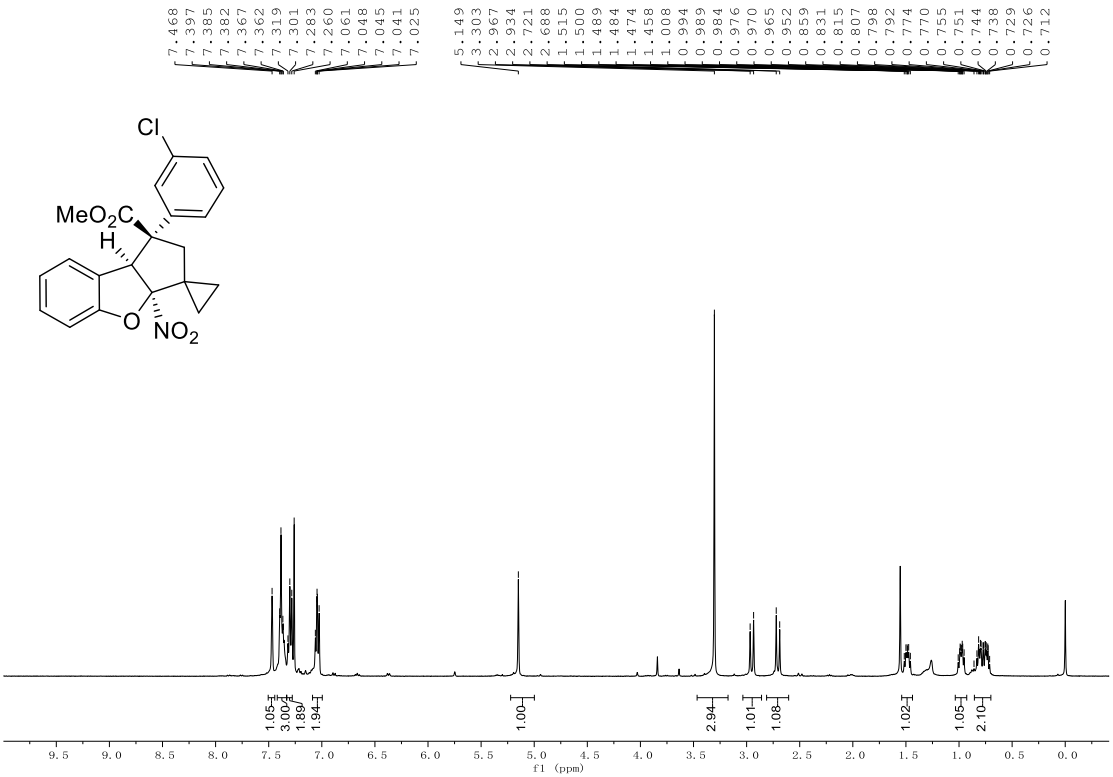
159.23
141.98
131.21
130.86
130.02
129.07
128.96
127.89
126.75
125.92
124.31
122.77
110.69
77.42
77.10
76.78
62.61
62.46
52.43
52.10
47.43
29.90
15.18
11.27
MeO2C
MeO2C
H
O
NO2
f1 (ppm)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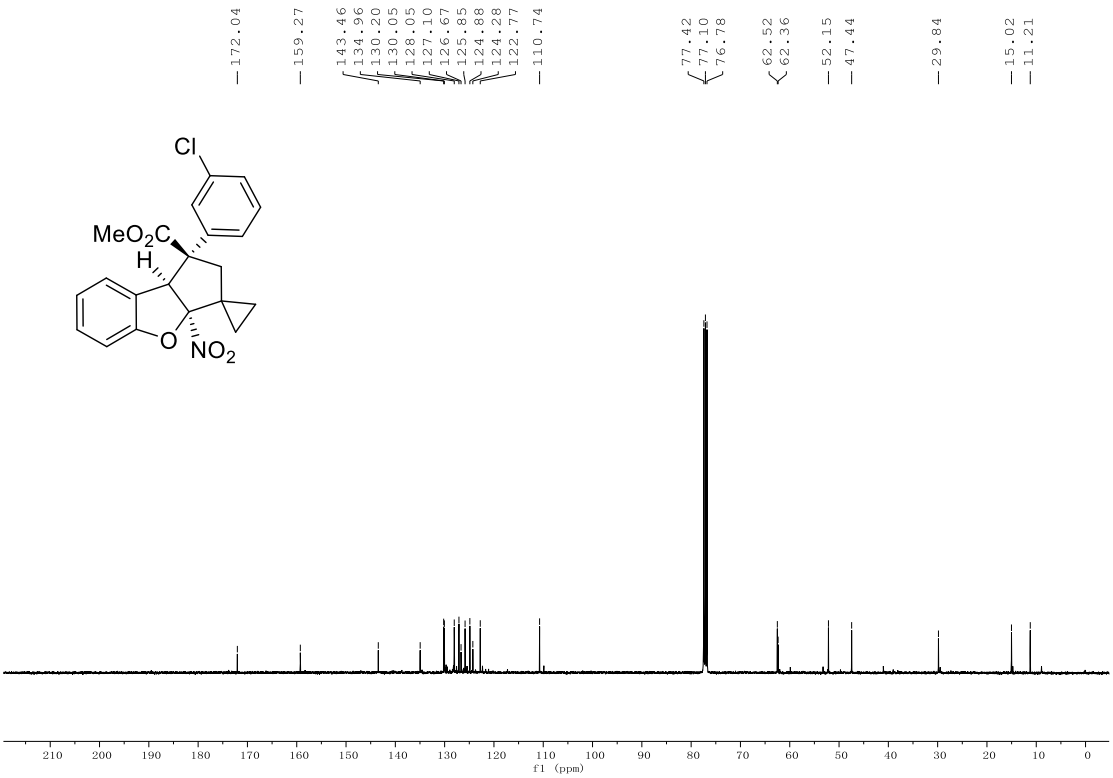
7.367
7.362
7.319
7.301
7.283
7.260
7.061
7.048
7.045
7.041
7.025
5.149
3.303
2.967
2.934
2.721
2.688
1.515
1.500
1.489
1.484
1.474
1.458
1.008
0.994
0.989
0.984
0.976
0.970
0.965
0.952
0.859
0.831
0.815
0.807
0.798
0.792
0.774
0.770
0.755
0.751
0.744
0.738
0.729
0.726
0.712
Cl
MeO2C
H
O
NO2
1.05
3.00
1.89
1.94
1.00
2.94
1.01
1.08
1.02
1.05
2.10
f1 (ppm)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130.05
128.05
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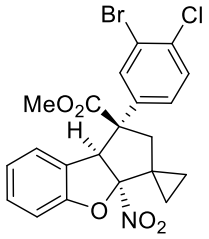
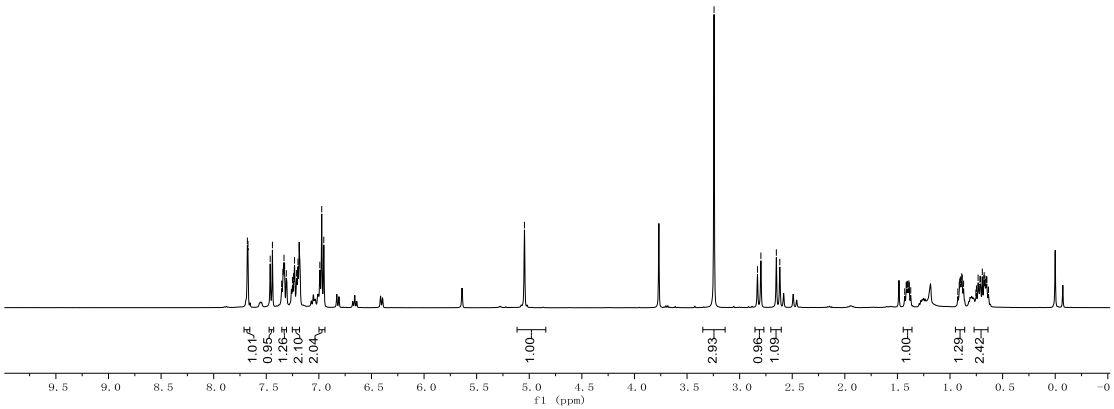
126.67
125.85
124.88
124.28
122.77
110.74
77.42
77.10
76.78
62.52
62.36
52.15
47.44
29.84
15.02
11.21
Cl
MeO2C
H
O
NO2
f1 (ppm)


7.680
7.674
7.463
7.441
7.354
7.342
7.336
7.331
7.326
7.310
7.251
7.240
7.231
7.212
7.199
6.991
6.973
6.953
5.046
3.243
2.831
2.798
2.651
2.618
1.431
1.417
1.413
1.404
1.399
1.391
1.387
1.374
0.926
0.912
0.908
0.902
0.894
0.889
0.884
0.871
0.754
0.749
0.733
0.726
0.716
0.710
0.693
0.679
0.675
0.668
0.660
0.653
0.649
0.634


Br
Cl
MeO2C
H
O
NO2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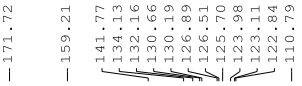
0.95
1.26
2.10
2.04
1.00
2.93
0.96
1.09
1.00
1.29
2.42
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.66
130.19
126.89
126.51
125.70
123.98
123.11
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77.42
77.10
76.78
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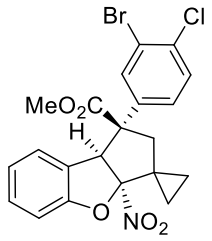
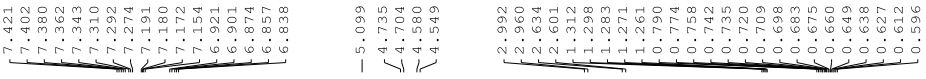
52.27
47.24
29.84
14.77
11.36


Br
Cl
MeO2C
H
O
NO2

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.310
7.292
7.274
7.191
7.180
7.172
7.154
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6.901
6.874
6.857
6.838
5.099
4.735
4.704
4.580
4.549
2.992
2.960
2.634
2.601
1.312
1.298
1.283
1.271
1.261
0.790
0.774
0.758
0.742
0.735
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0.709
0.698
0.683
0.675
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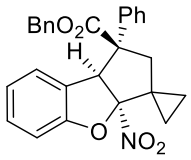
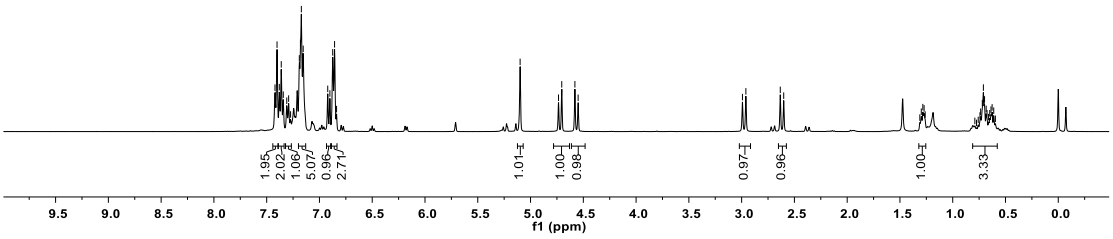
0.649
0.638
0.627
0.612
0.596


BnO2C
Ph
H
O
NO2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2.02
1.06
5.07
0.96
2.71
1.01
1.00
0.98
0.97
0.96
1.00
3.33
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
f1 (ppm)


171.94
159.36
141.43
135.07
129.78
128.94
128.41
128.31
128.28
127.79
126.96
126.69
125.99
124.72
122.71
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77.10
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62.57
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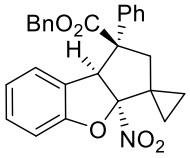
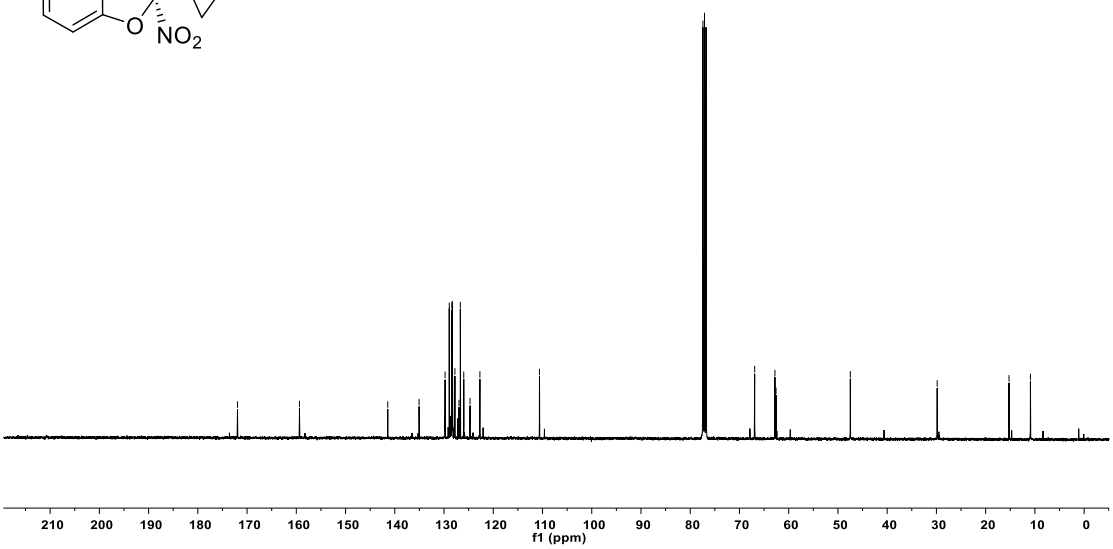
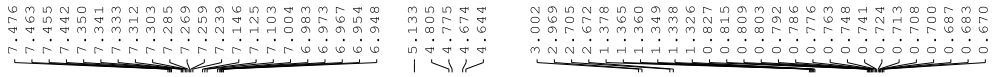
15.26
10.91


BnO2C
Ph
H
O
NO2


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.303
7.285
7.269
7.259
7.239
7.146
7.125
7.103
7.004
6.983
6.973
6.967
6.954
6.948
5.133
4.805
4.775
4.674
4.644
3.002
2.969
2.705
2.672
1.378
1.365
1.360
1.349
1.338
1.326
0.827
0.815
0.809
0.803
0.792
0.786
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0.741
0.724
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0.708
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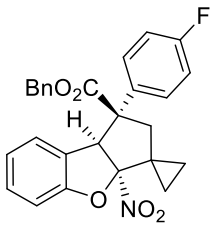
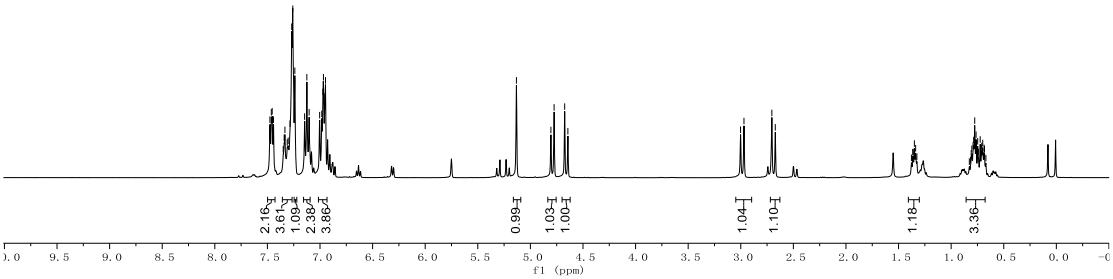
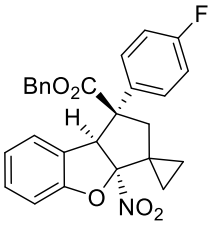
0.670


F
BnO2C
H
O
NO2


2.16
3.61
1.09
2.38
3.86
0.99
1.03
1.00
1.04
1.10
1.18
3.36
f1 (ppm)


171.73
163.40
160.94
159.32
137.37
137.33
134.90
129.92
128.84
128.68
128.50
128.47
128.42
126.84
125.83
124.46
122.78
115.90
115.68
110.68
77.42
77.10
76.78
67.10
62.87
62.00
47.50
29.83
15.02
11.04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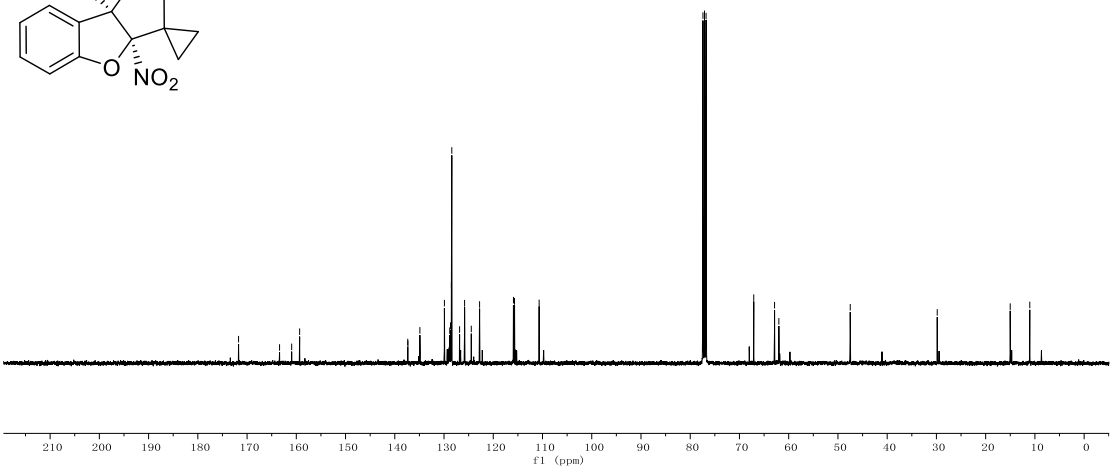
BnO2C
H
O
NO2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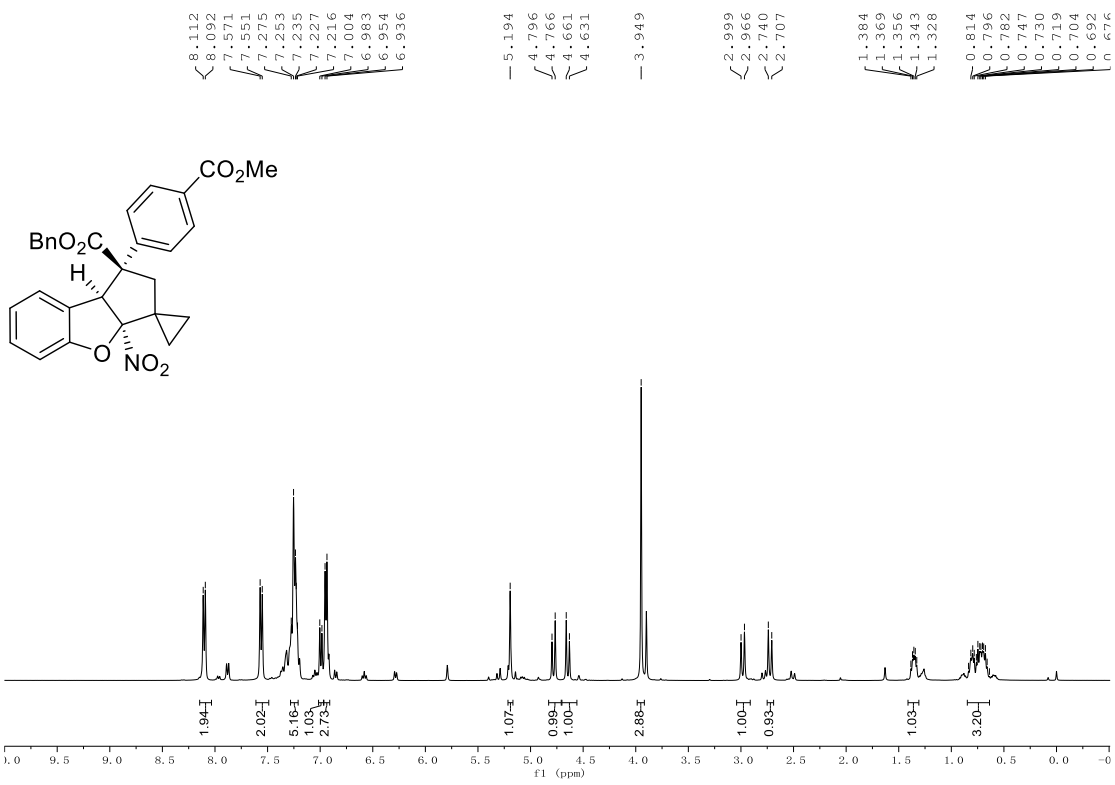
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1.356
1.343
1.328
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0.796
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0.730
0.719
0.704
0.692
CO2Me
BnO2C
H
O
NO2
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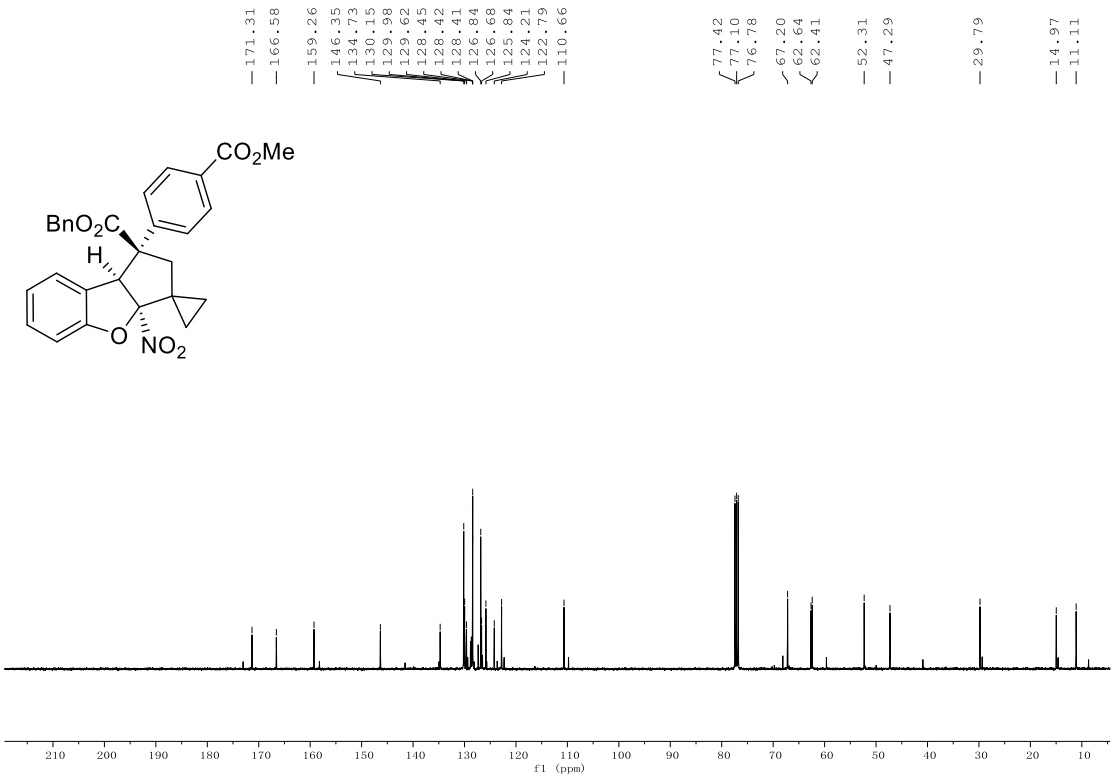
f1 (ppm)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CO2Me
BnO2C
H
O
NO2
f1 (ppm)


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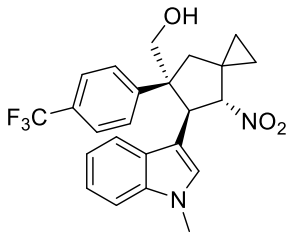
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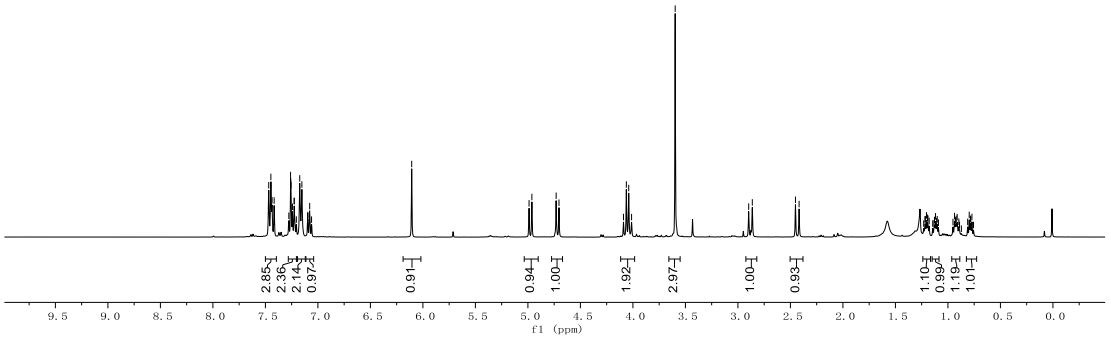
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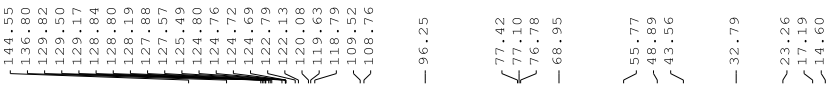
f1 (ppm)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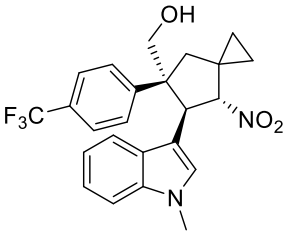
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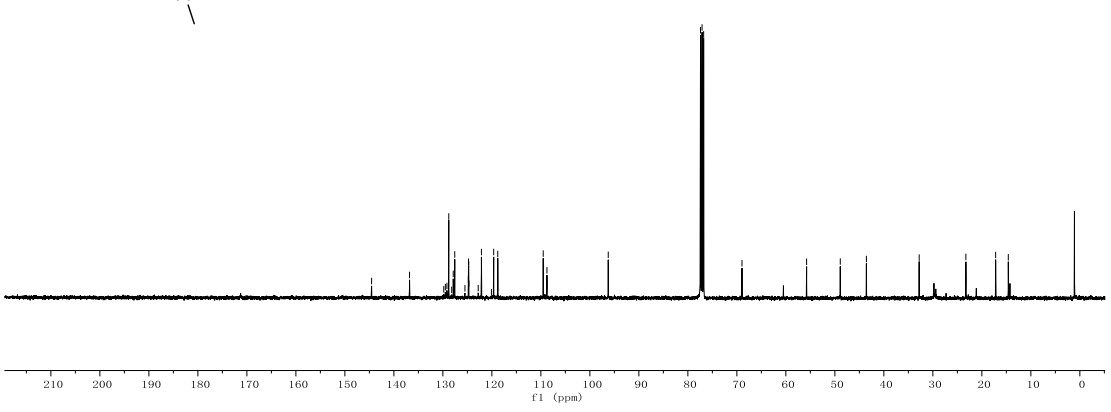
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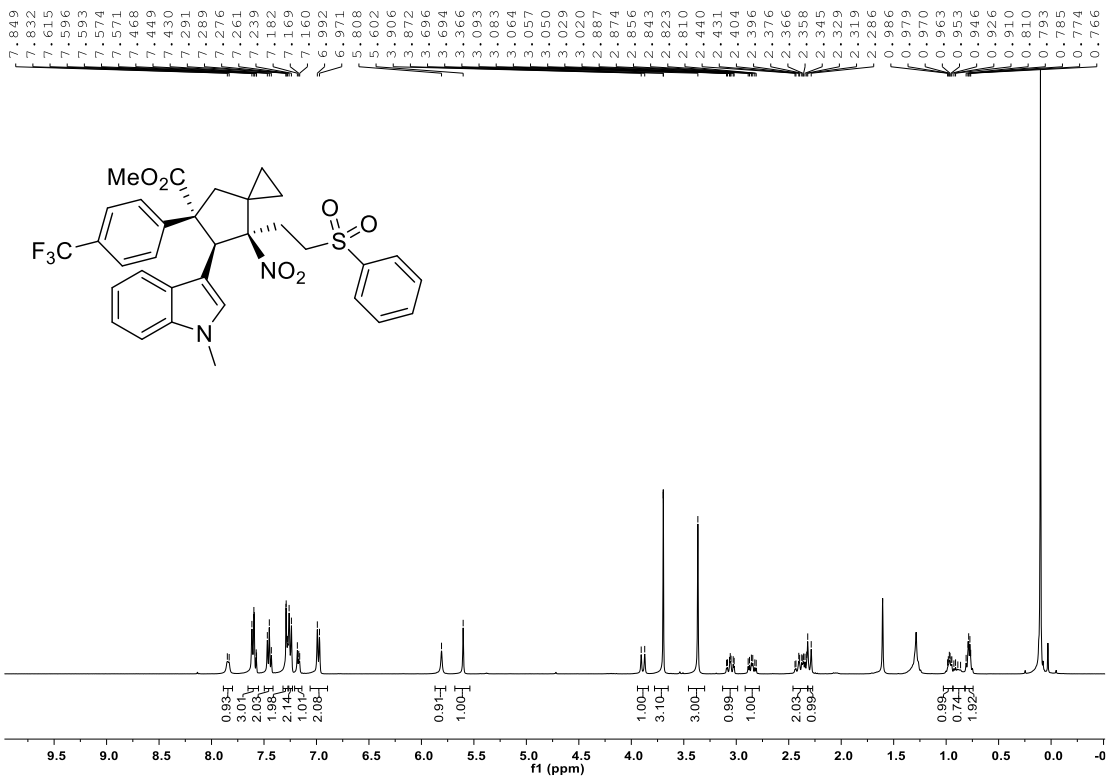
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5.602
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3.050
3.029
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0.774
0.766
MeO2C
F3C
NO2
O
S
N
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2.03
1.98
2.14
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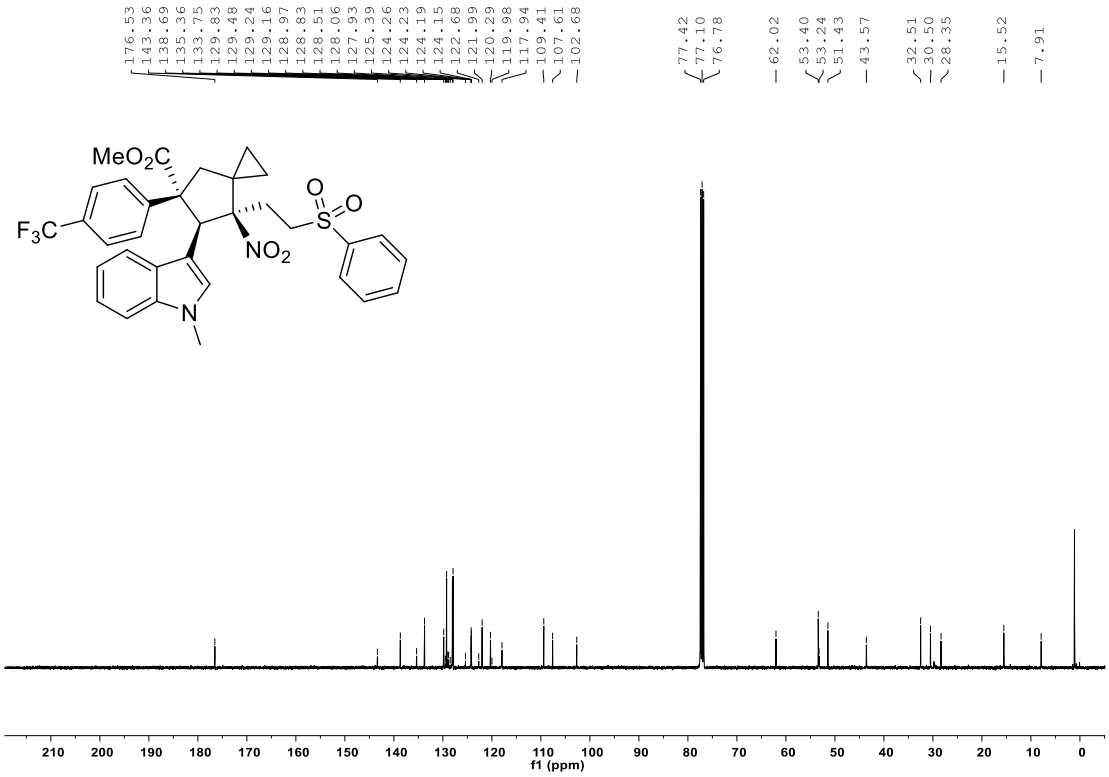
f1 (ppm)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102.68
77.42
77.10
76.78
62.02
53.40
53.24
51.43
43.57
32.51
30.50
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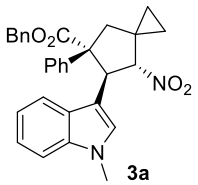
15.52
7.91
MeO2C
F3C
NO2
O
S
N
f1 (ppm)

9.HPLC Spectra



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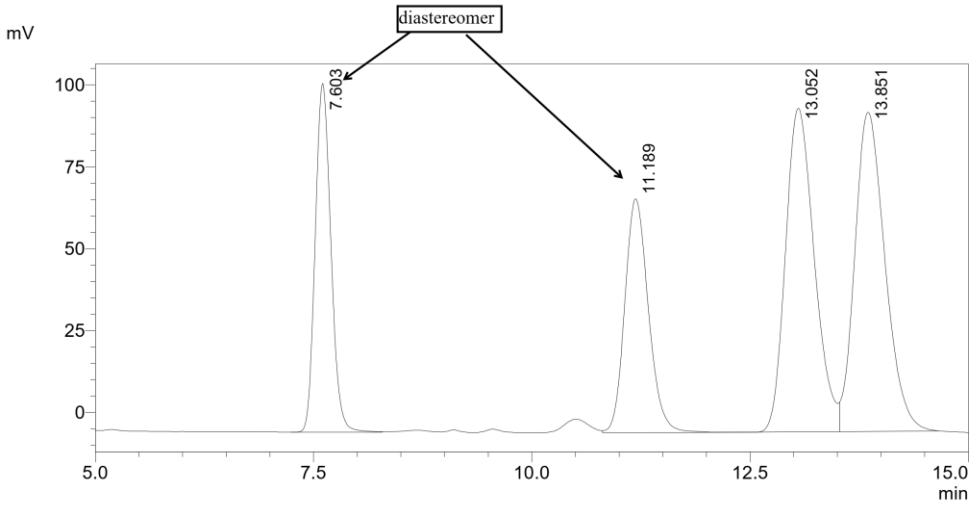
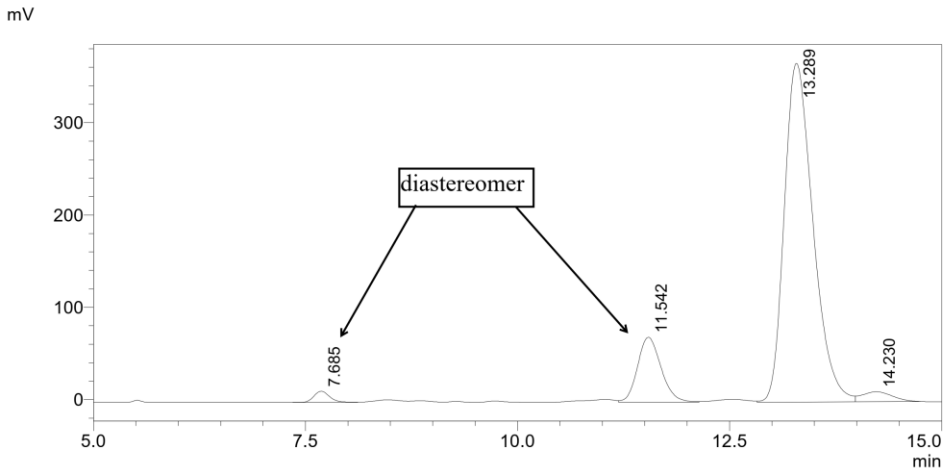
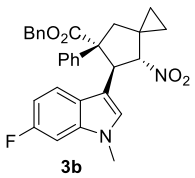


Peak#	Ret. Time	Area	Height	Area%
1	7.603	1333671	106443	18.278
2	11.189	1345295	71341	18.437
3	13.052	2273663	98785	31.161
4	13.851	2343985	97428	32.124
		7296614	373997	100.000



Peak#	Ret. Time	Area	Height	Area%
1	7.685	157581	12030	1.508
2	11.542	1364925	70467	13.064
3	13.289	8657418	366935	82.859
4	14.230	268455	10773	2.569
		10448379	460205	100.000



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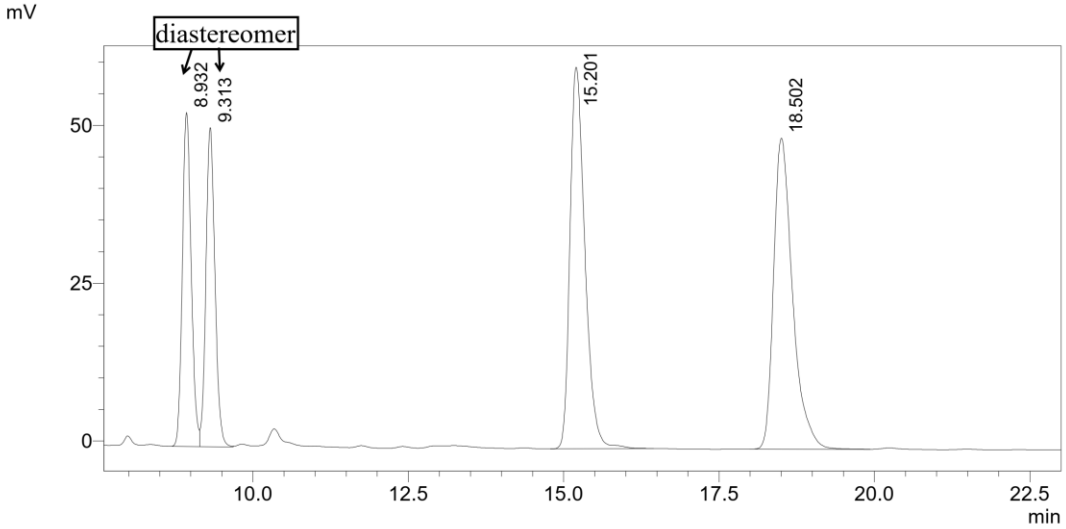
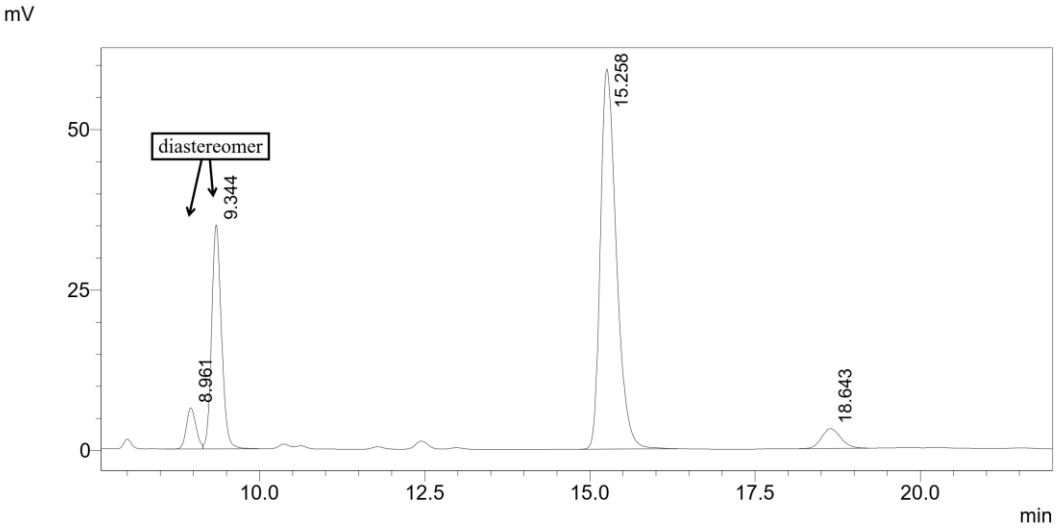
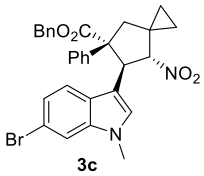


Peak#	Ret. Time	Area	Height	Area%
1	8.932	523484	52914	16.937
2	9.313	509840	50525	16.496
3	15.201	1012068	60461	32.745
4	18.502	1045330	49263	33.822
		3090721	213163	100.000



Peak#	Ret. Time	Area	Height	Area%
1	8.961	65063	6402	4.375
2	9.344	363567	34848	24.450
3	15.258	996213	59202	66.995
4	18.643	62162	3085	4.180
		1487005	103537	100.000



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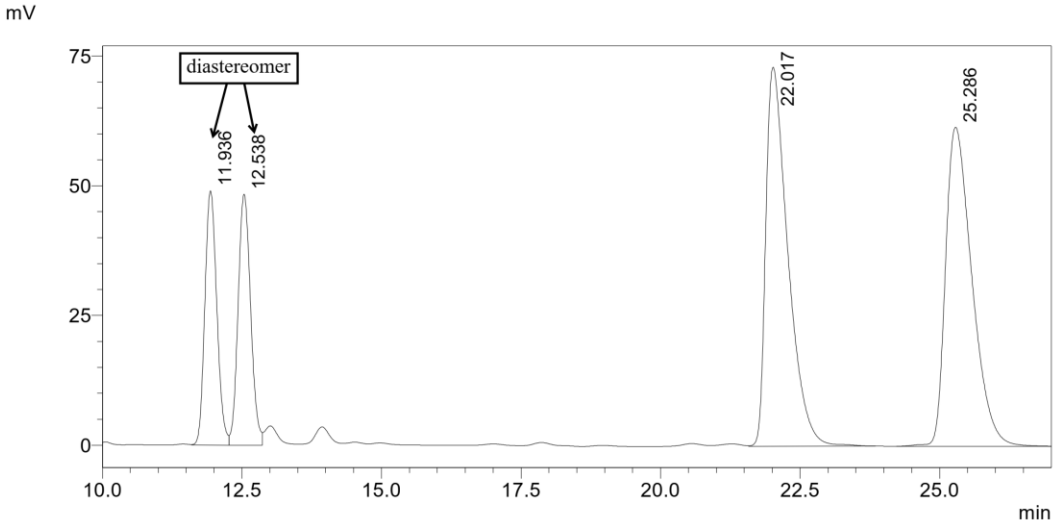
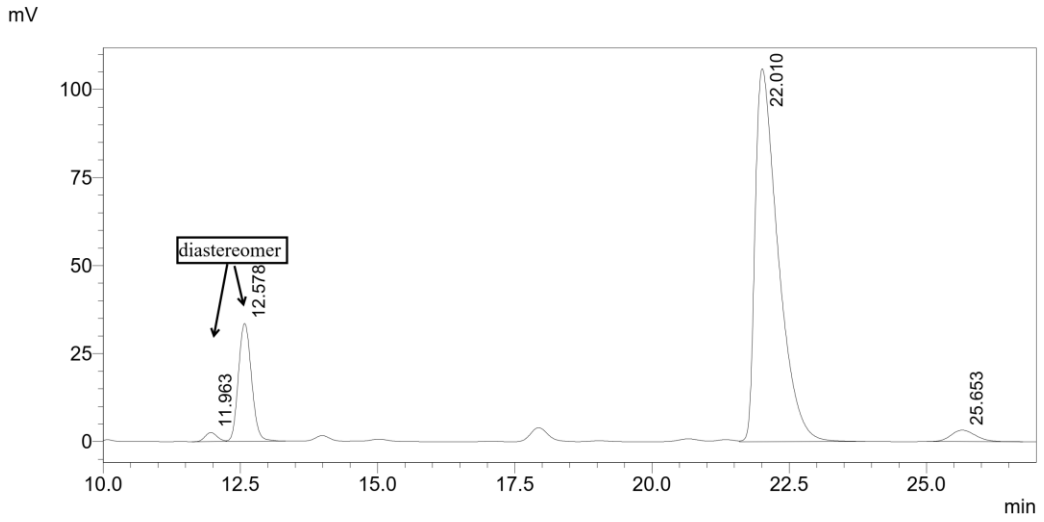
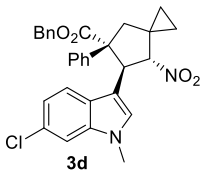
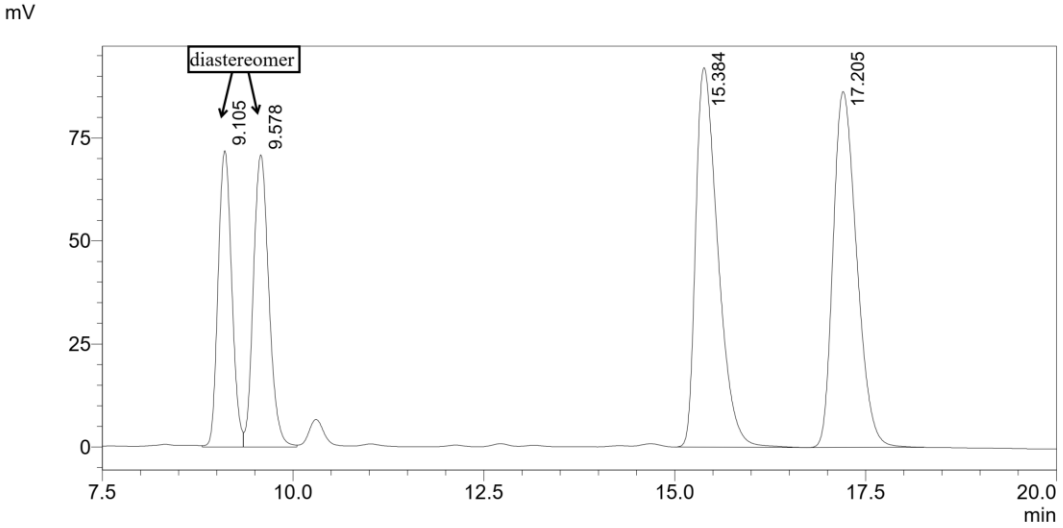


Peak#	Ret. Time	Area	Height	Area%
1	11.936	730478	48999	13.214
2	12.538	757742	48315	13.708
3	22.017	2015299	73089	36.457
4	25.286	2024407	61511	36.621
		5527925	231914	100.000

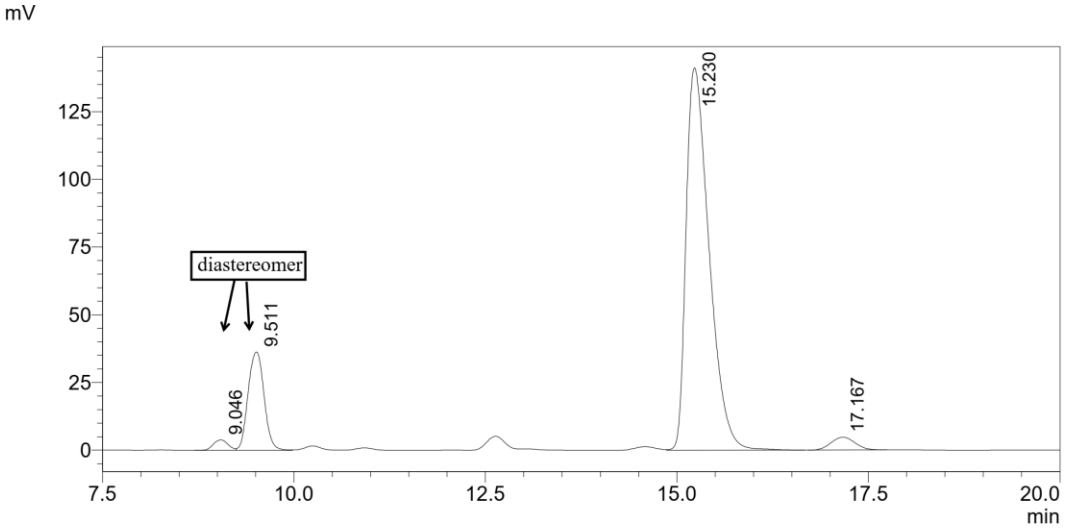


Peak#	Ret. Time	Area	Height	Area%
1	11.963	39663	2549	1.049
2	12.578	557074	33493	14.739
3	22.010	3080883	105919	81.512
4	25.653	102058	3269	2.700
		3779678	145230	100.000

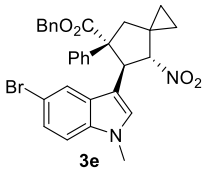




Peak#	Ret. Time	Area	Height	Area%
1	9.105	893168	71928	15.917
2	9.578	1000494	70917	17.830
3	15.384	1861671	92153	33.177
4	17.205	1856030	86391	33.076
		5611362	321389	100.000



Peak#	Ret. Time	Area	Height	Area%
1	9.046	51754	3825	1.424
2	9.511	527751	36305	14.522
3	15.230	2951954	141155	81.229
4	17.167	102634	4712	2.824
		3634092	185997	100.000



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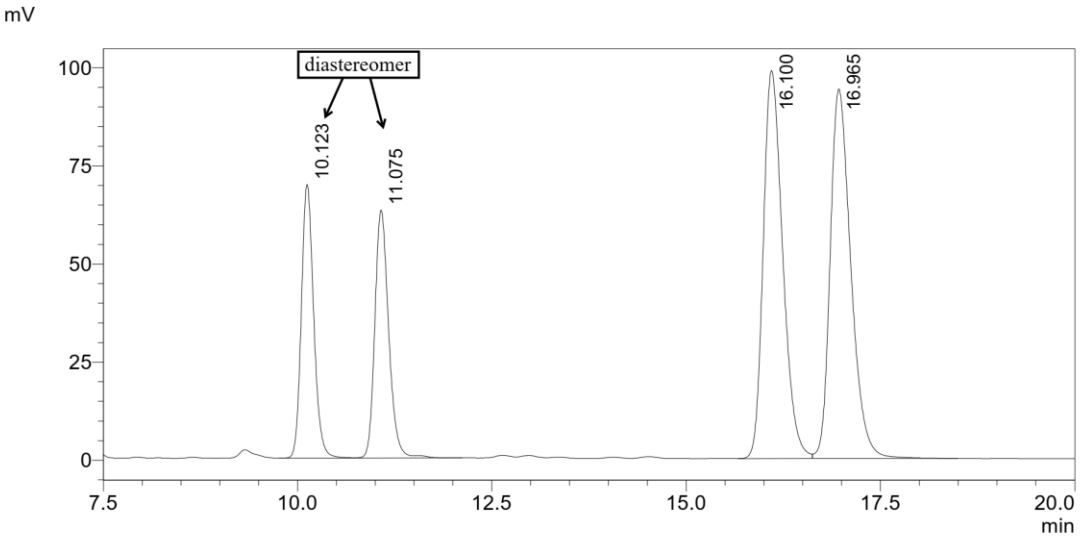
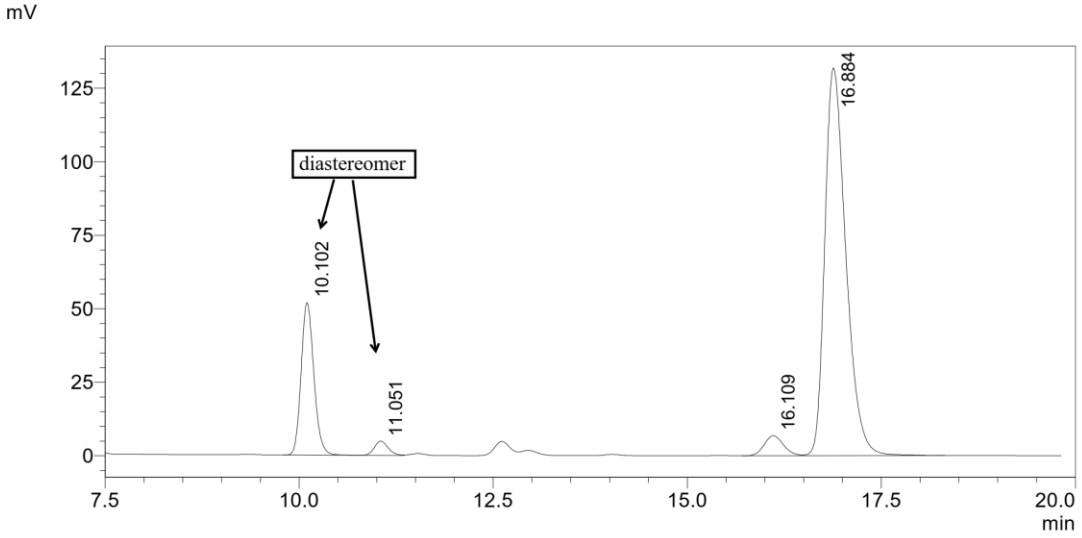
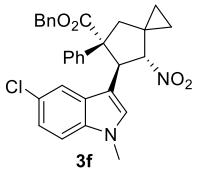


Peak#	Ret. Time	Area	Height	Area%
1	10.123	767874	69664	15.337
2	11.075	782685	63213	15.633
3	16.100	1715021	98850	34.254
4	16.965	1741186	94105	34.777
		5006767	325832	100.000



Peak#	Ret. Time	Area	Height	Area%
1	10.102	593561	51856	18.200
2	11.051	59850	4819	1.835
3	16.109	118772	6837	3.642
4	16.884	2489195	131897	76.323
		3261377	195408	100.000



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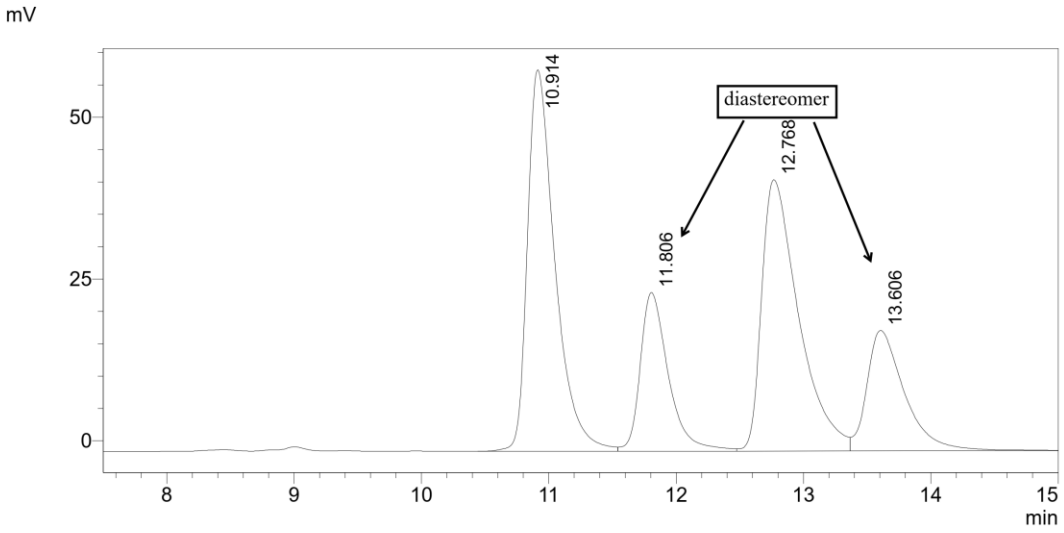
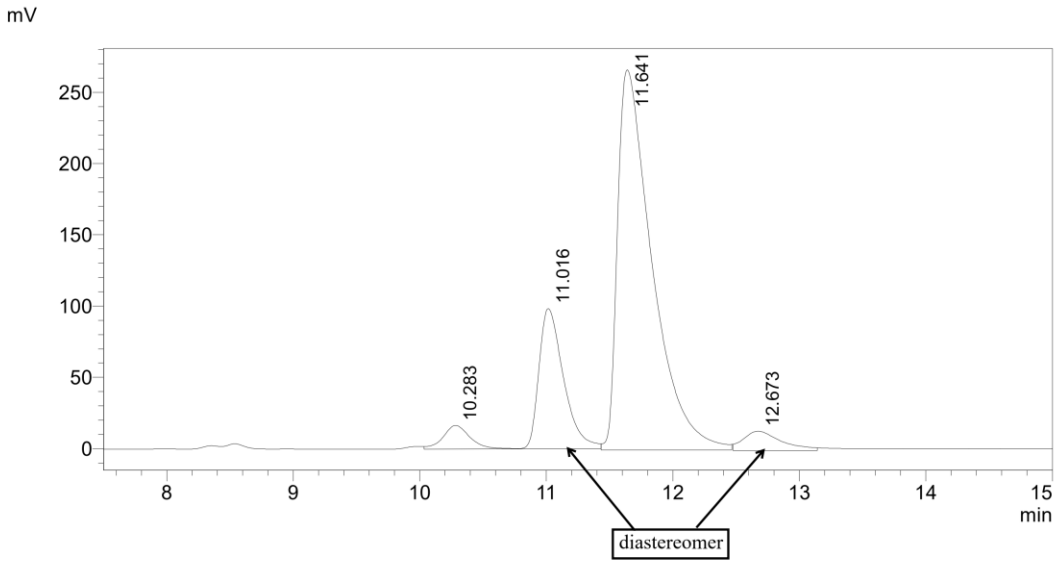
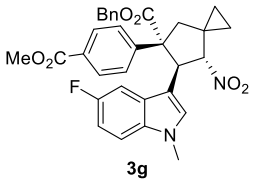


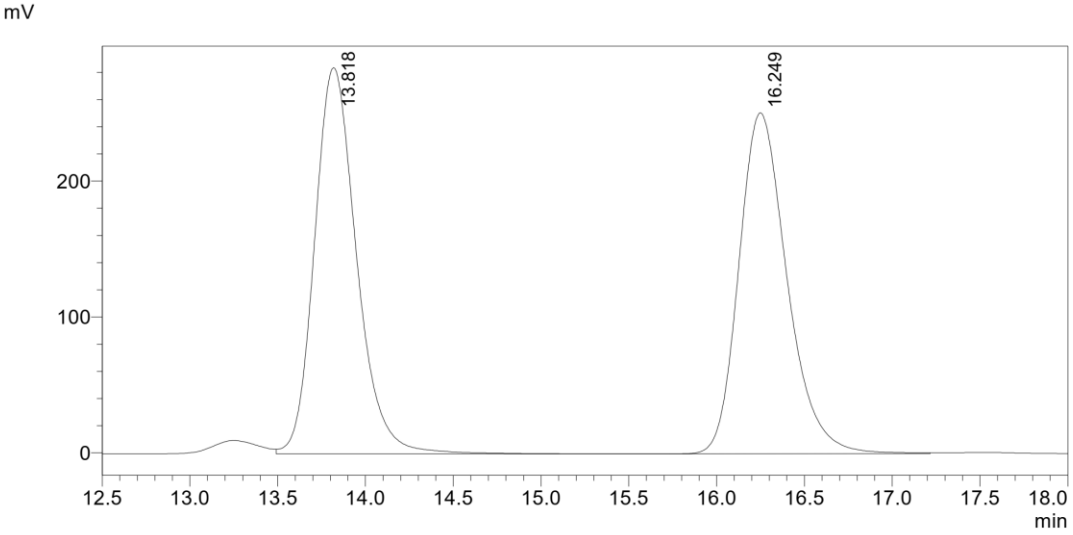
Peak#	Ret. Time	Area	Height	Area%
1	10.914	886511	58963	35.488
2	11.806	376496	24549	15.071
3	12.768	848653	41947	33.972
4	13.606	386426	18636	15.469
		2498086	144095	100.000



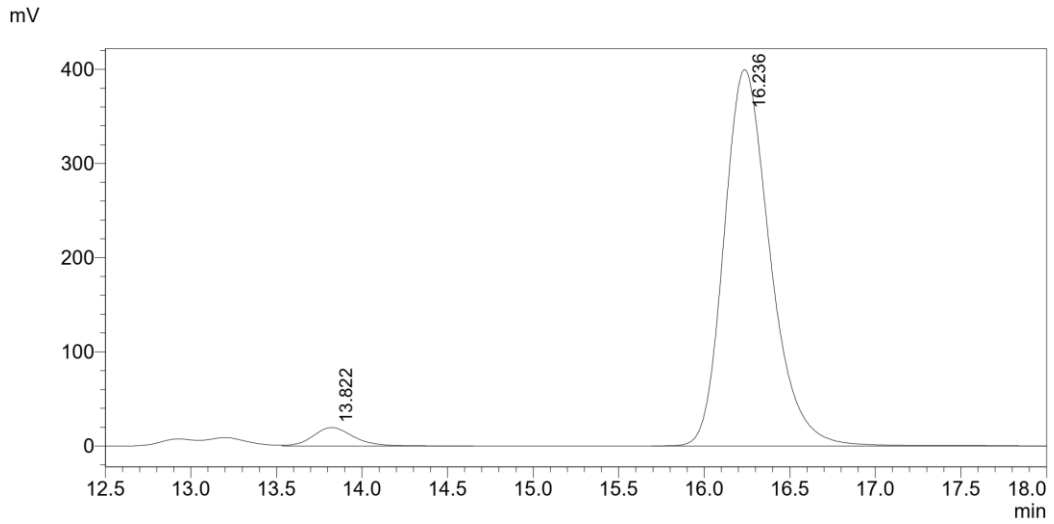
Peak#	Ret. Time	Area	Height	Area%
1	10.283	247795	16642	3.577
2	11.016	1330632	98521	19.209
3	11.641	5065326	266810	73.123
4	12.673	283356	13561	4.091
		6927109	395534	100.000



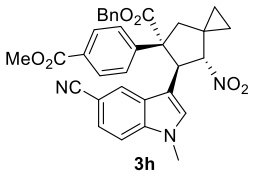
3g



Peak#	Ret. Time	Area	Height	Area%
1	13.818	4734791	284319	49.736
2	16.249	4785144	251003	50.264
		9519935	535323	100.000



Peak#	Ret. Time	Area	Height	Area%
1	13.822	322945	19620	4.130
2	16.236	7496354	399769	95.870
		7819298	419389	100.000



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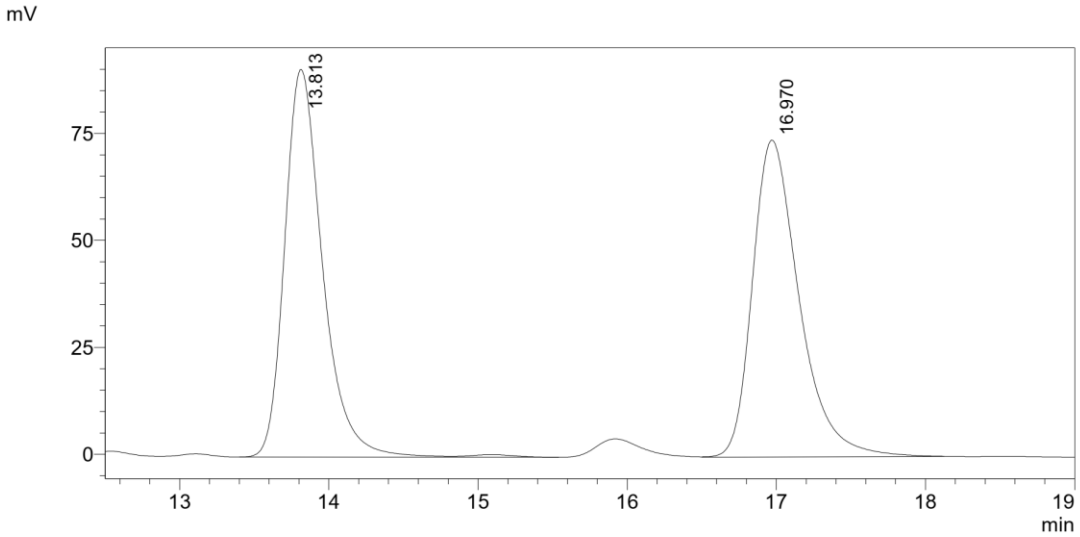
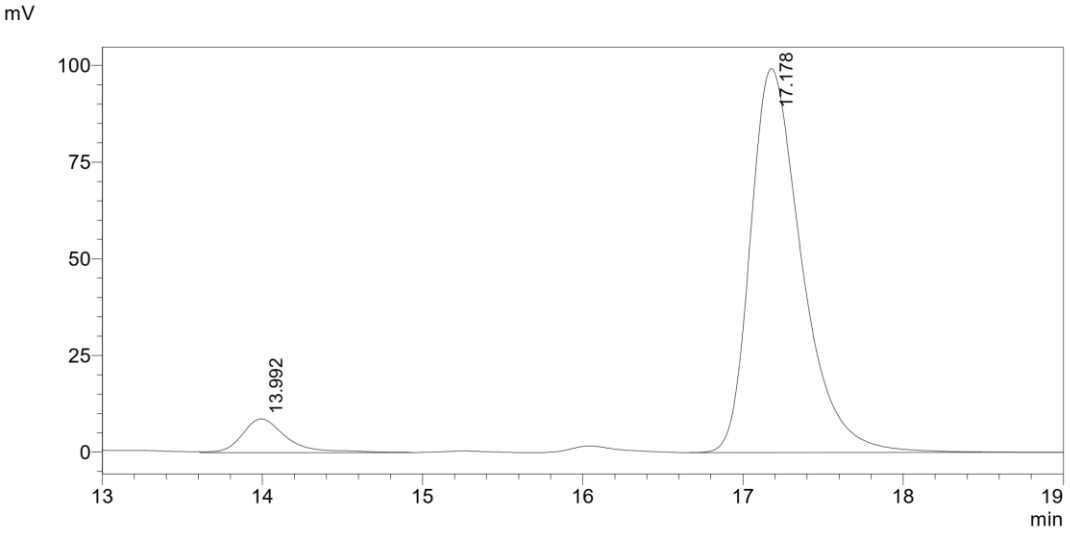
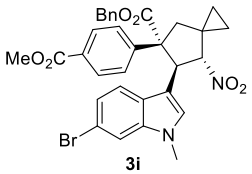


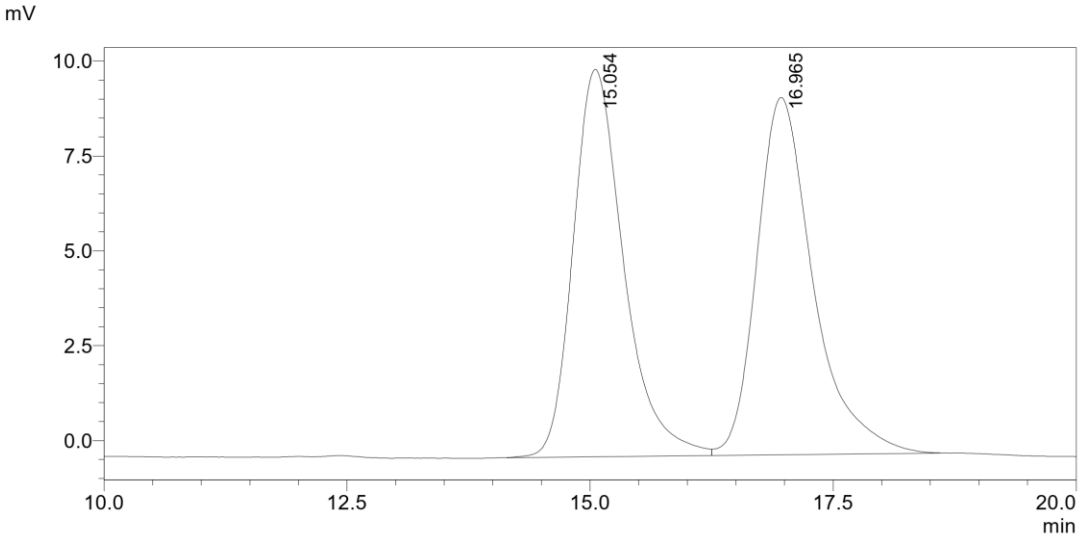
Peak#	Ret. Time	Area	Height	Area%
1	13.813	1608244	90616	49.940
2	16.970	1612092	74069	50.060
		3220335	164685	100.000



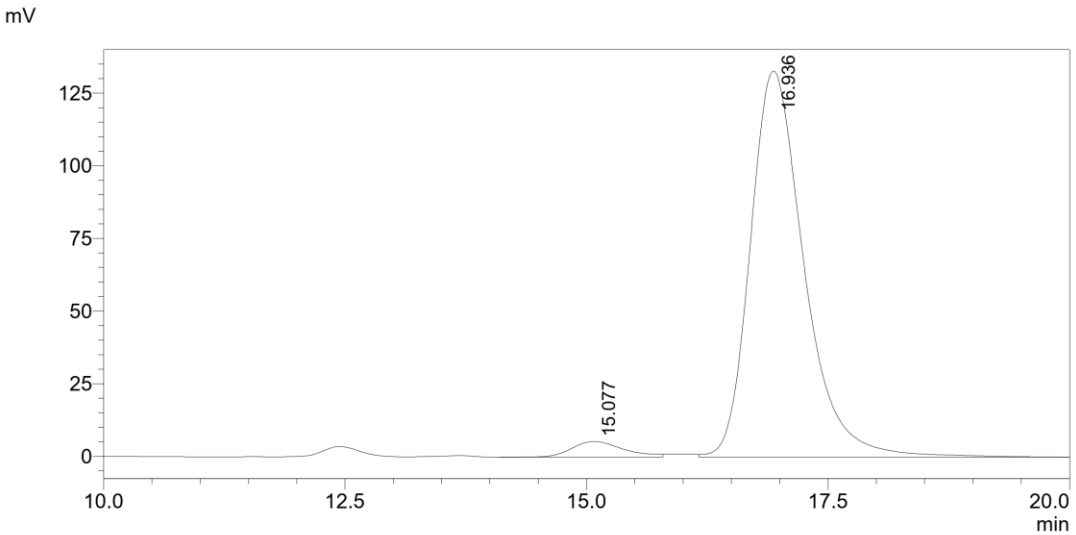
Peak#	Ret. Time	Area	Height	Area%
1	13.992	169587	8729	7.112
2	17.178	2215007	99310	92.888
		2384594	108039	100.000



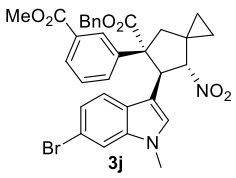
3i



Peak#	Ret. Time	Area	Height	Area%
1	15.054	368952	10211	49.287
2	16.965	379626	9420	50.713
		748577	19630	100.000



Peak#	Ret. Time	Area	Height	Area%
1	15.077	206099	5437	3.836
2	16.936	5166167	132853	96.164
		5372266	138290	100.000



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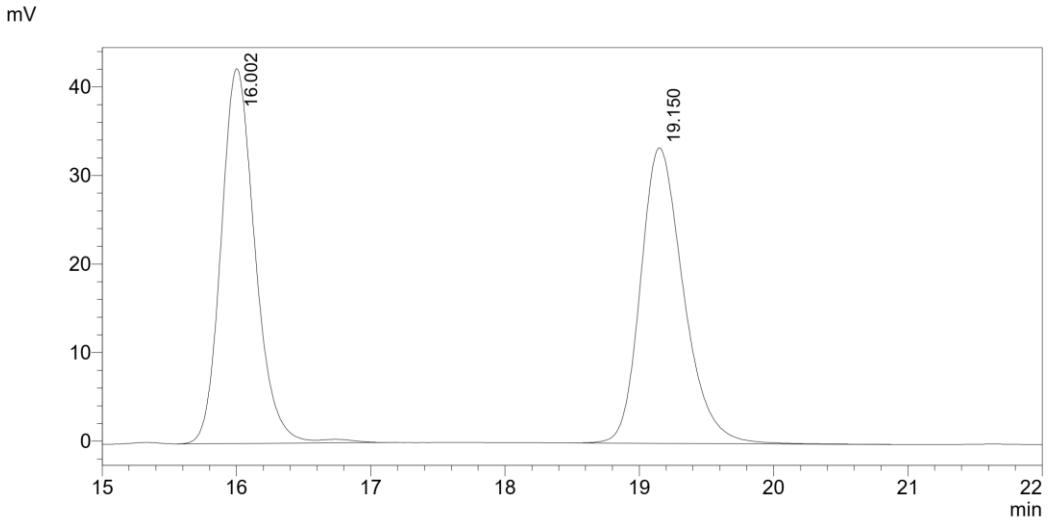
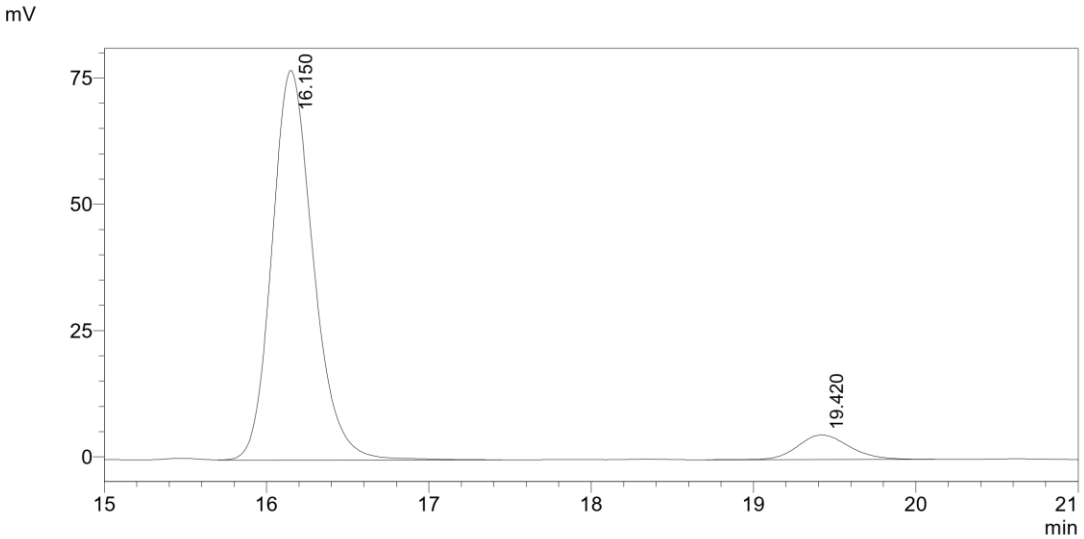
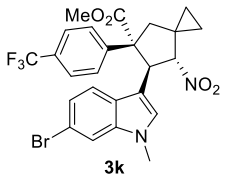


Peak#	Ret. Time	Area	Height	Area%
1	16.002	746503	42339	50.103
2	19.150	743436	33388	49.897
		1489939	75727	100.000



Peak#	Ret. Time	Area	Height	Area%
1	16.150	1364613	77162	92.652
2	19.420	108231	4891	7.348
		1472844	82053	100.000



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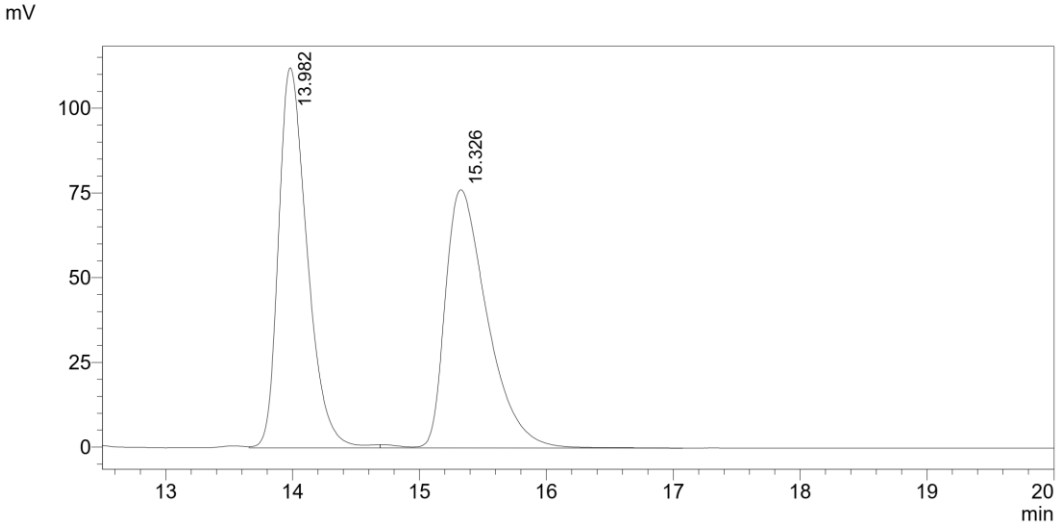
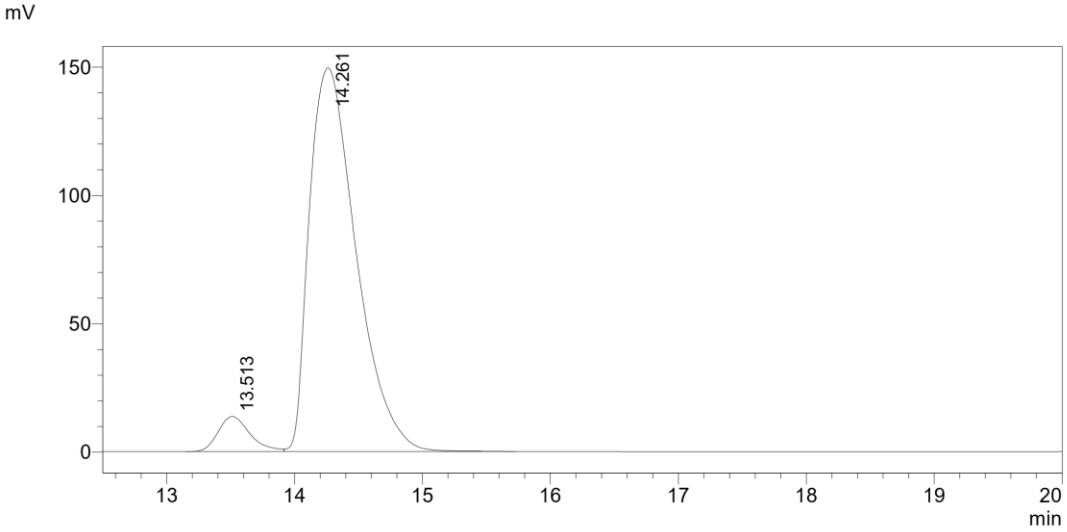
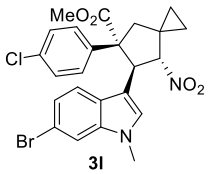


Peak#	Ret. Time	Area	Height	Area%
1	13.982	1764903	112250	50.086
2	15.326	1758847	76221	49.914
		3523750	188471	100.000



Peak#	Ret. Time	Area	Height	Area%
1	13.513	237461	13683	5.882
2	14.261	3799655	149462	94.118
		4037116	163145	100.000



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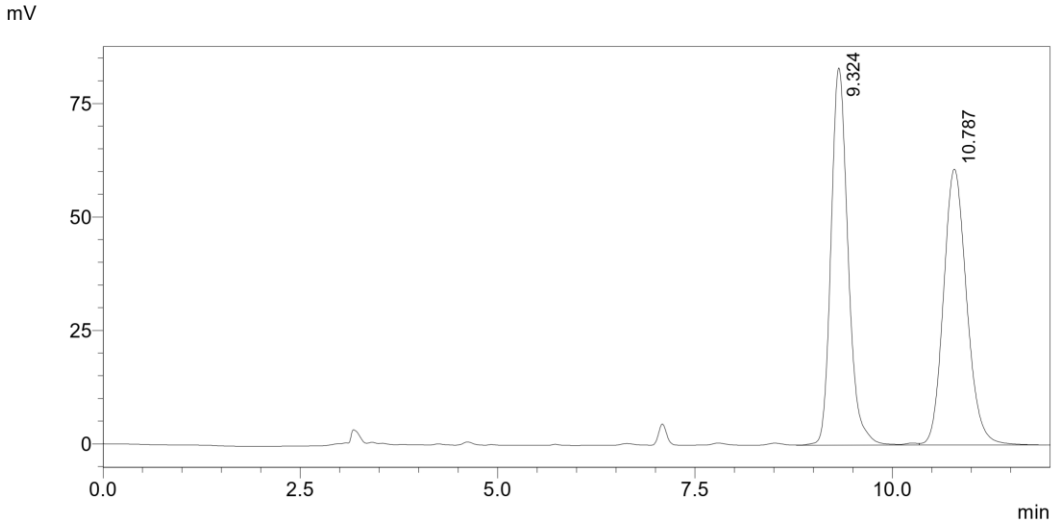
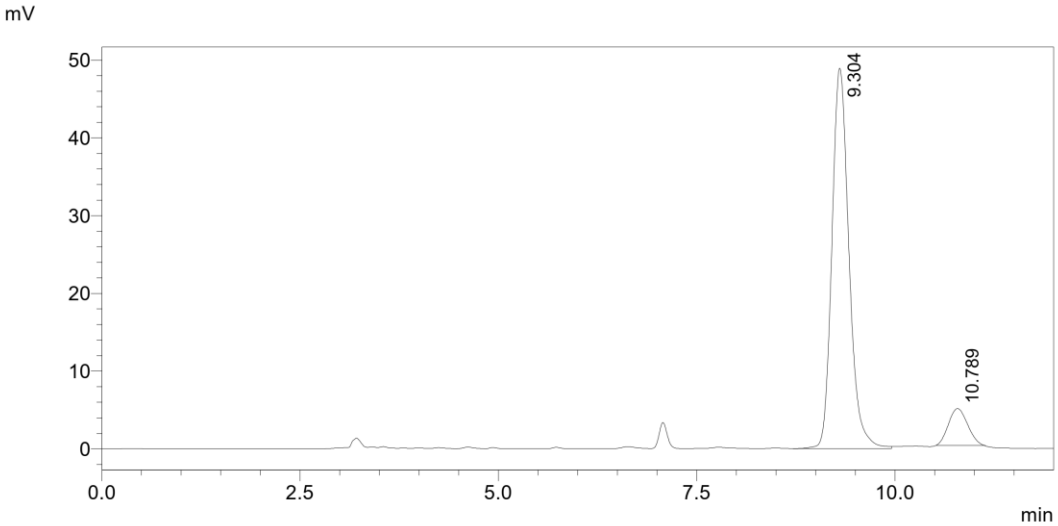
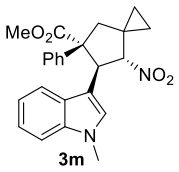
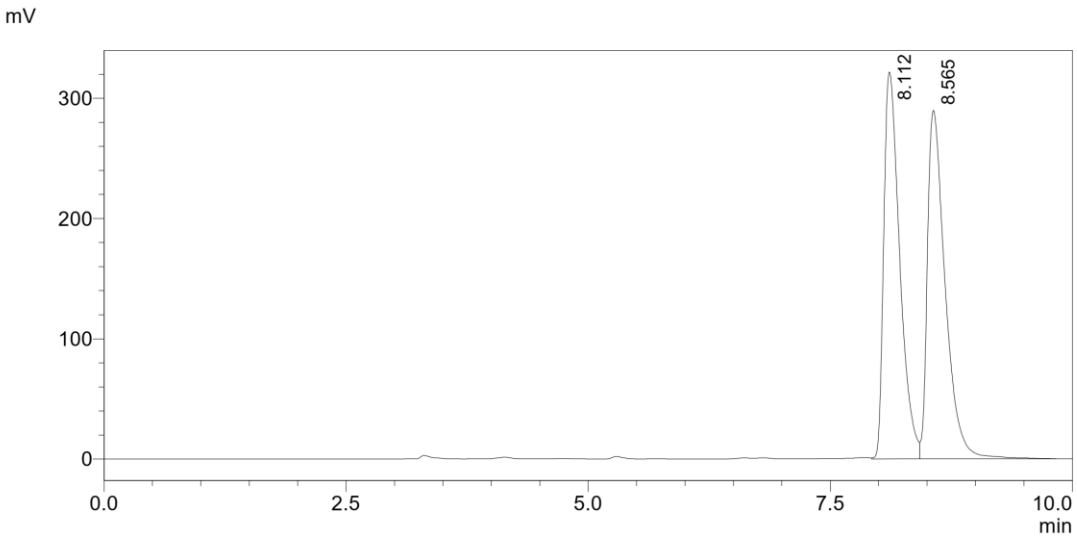


Peak#	Ret. Time	Area	Height	Area%
1	9.324	1252445	83164	50.139
2	10.787	1245484	60817	49.861
		2497929	143981	100.000

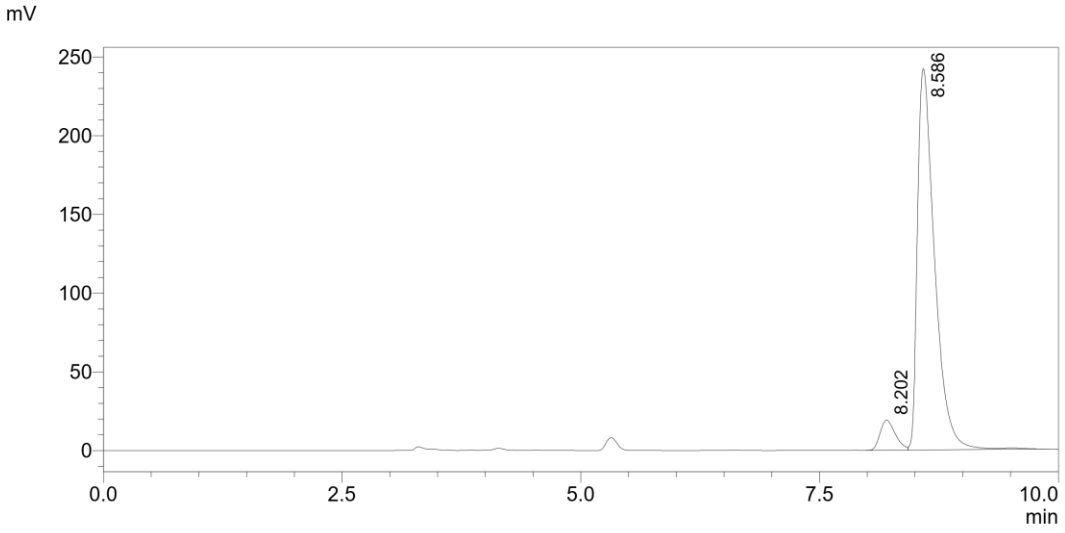


Peak#	Ret. Time	Area	Height	Area%
1	9.304	731458	48910	90.160
2	10.789	79827	4742	9.840
		811285	53652	100.000

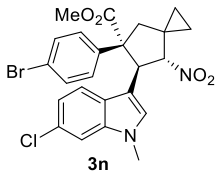




Peak#	Ret. Time	Area	Height	Area%
1	8.112	3697707	321664	49.961
2	8.565	3703492	289741	50.039
		7401199	611405	100.000



Peak#	Ret. Time	Area	Height	Area%
1	8.202	210115	19079	6.503
2	8.586	3020923	242048	93.497
		3231038	261126	100.000



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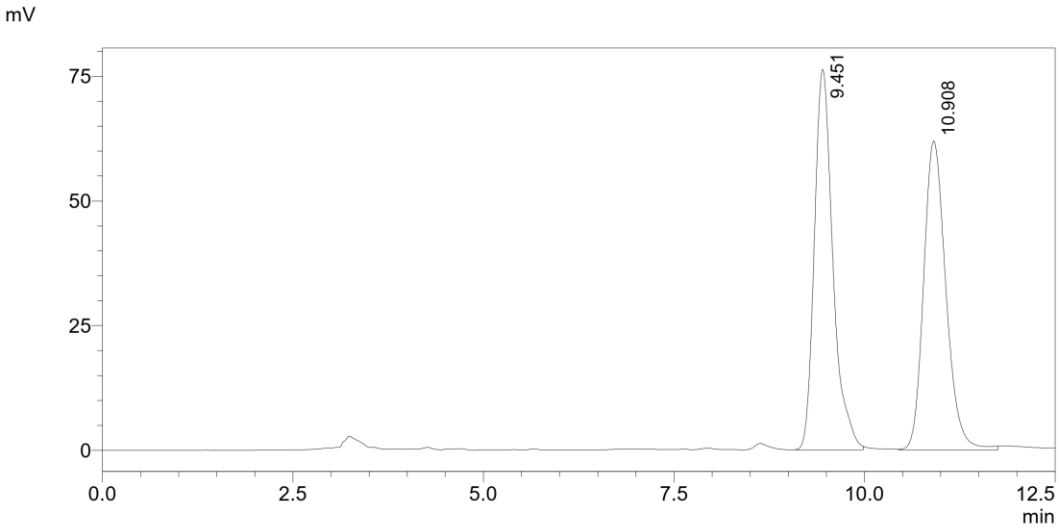
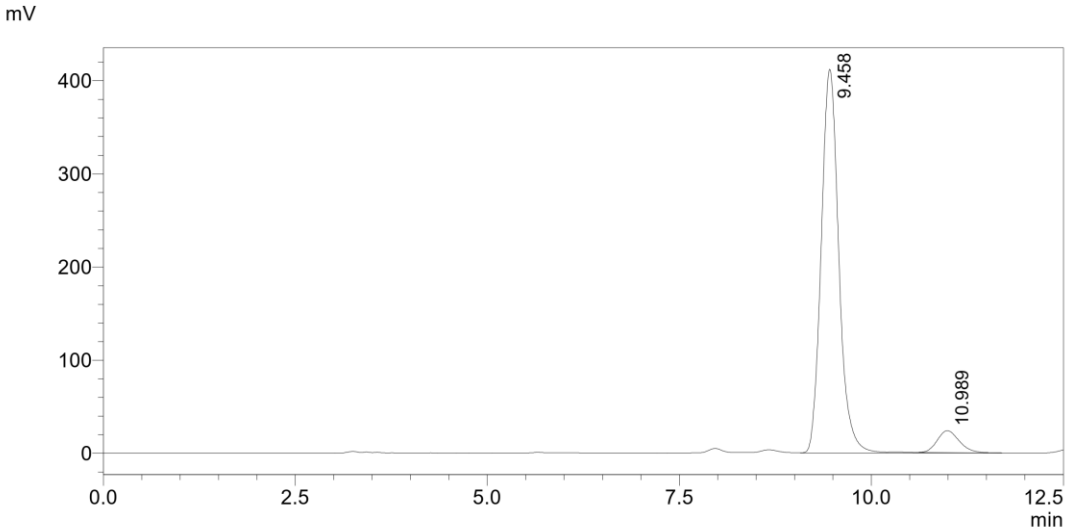
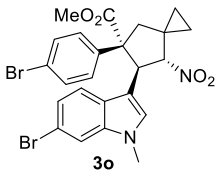


Peak#	Ret. Time	Area	Height	Area%
1	9.451	1295053	76393	50.555
2	10.908	1266635	62029	49.445
		2561688	138422	100.000



Peak#	Ret. Time	Area	Height	Area%
1	9.458	6596134	412217	93.362
2	10.989	468980	23509	6.638
		7065114	435726	100.000



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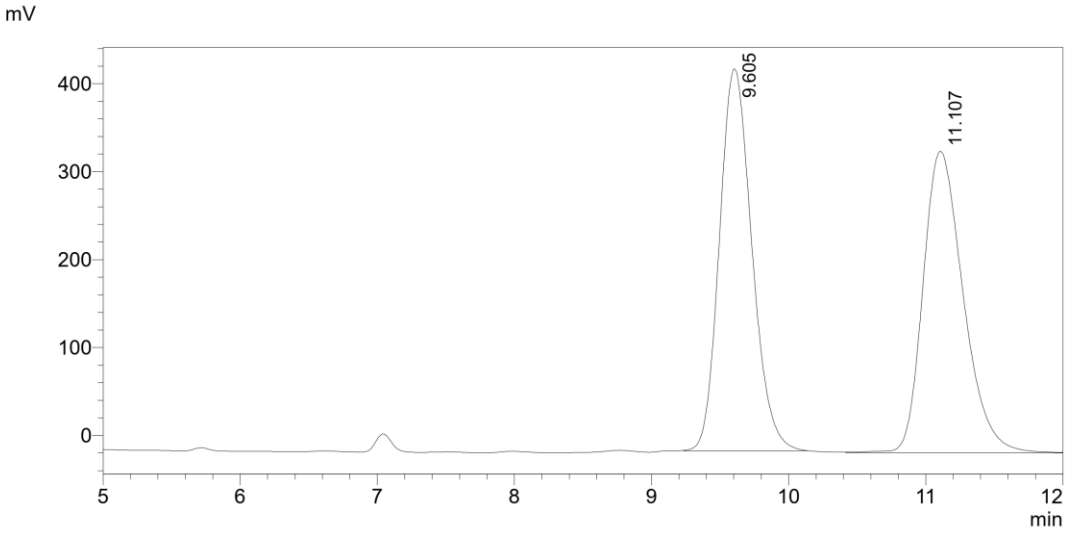
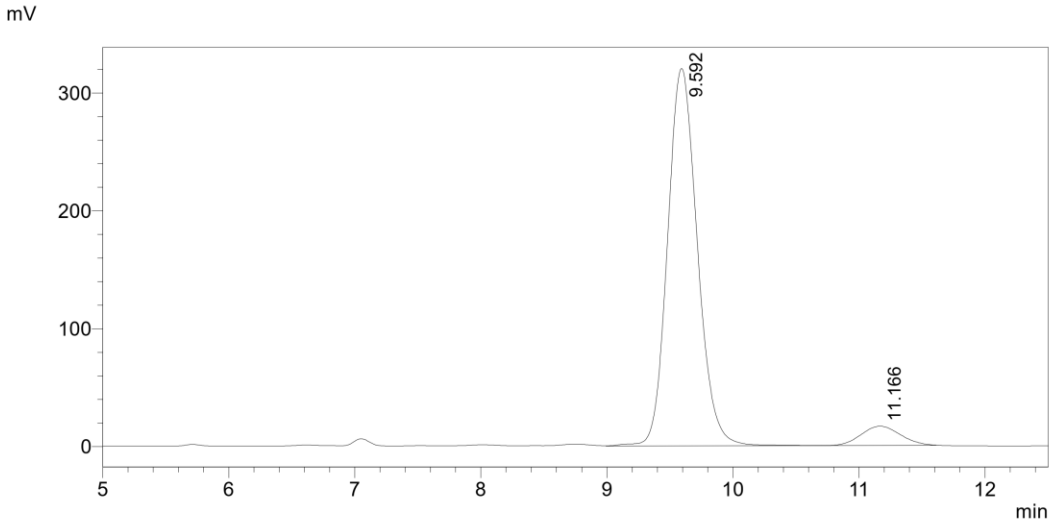
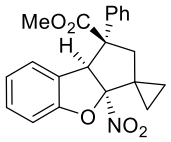


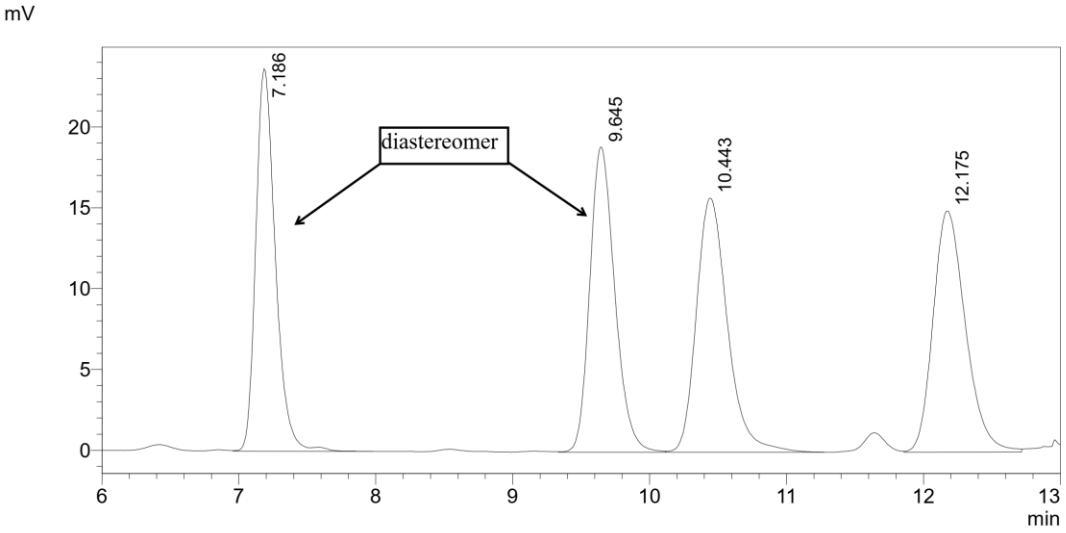
Peak#	Ret. Time	Area	Height	Area%
1	9.605	7139743	434248	50.483
2	11.107	7003232	343072	49.517
		14142975	777320	100.000



Peak#	Ret. Time	Area	Height	Area%
1	9.592	5261890	320306	93.693
2	11.166	354209	16303	6.307
		5616099	336609	100.000

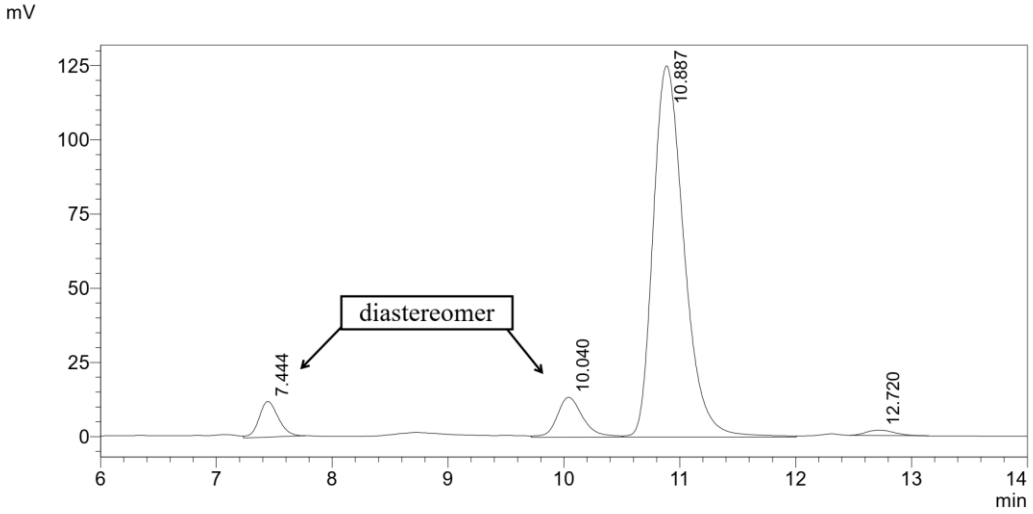


5a



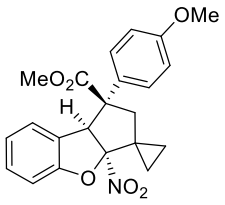
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.186	234721	23665	24.249
2	9.645	239885	18865	24.783
3	10.443	248203	15728	25.642
4	12.175	245141	14923	25.326
		967951	73181	100.000

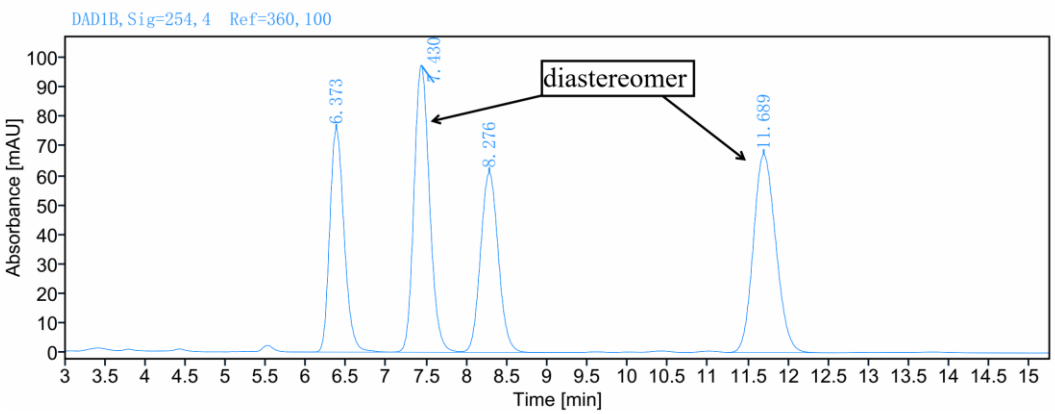


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.444	140207	12033	5.205
2	10.040	206954	13426	7.683
3	10.887	2314781	125004	85.939
4	12.720	31579	1870	1.172
		2693521	152332	100.000

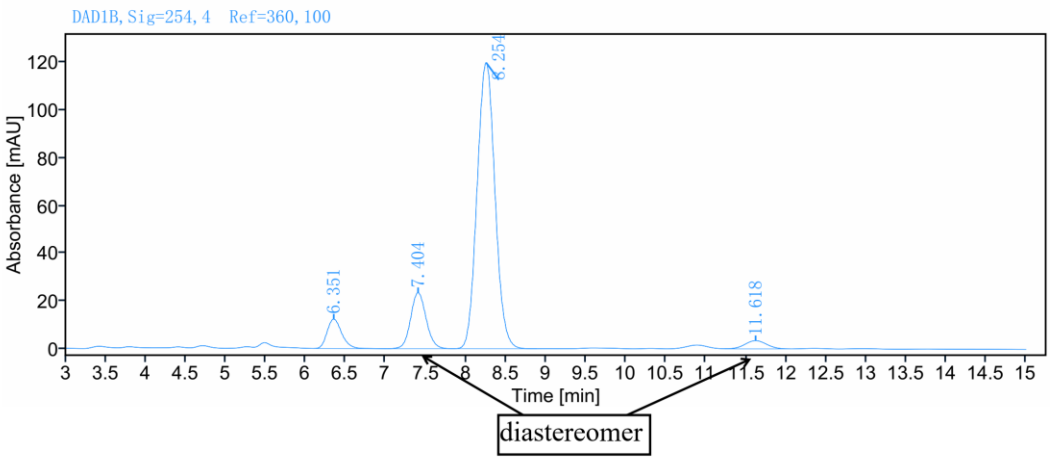


5b



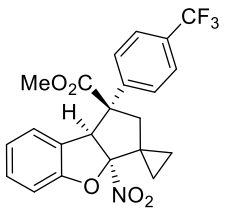
Signal: DAD1B, Sig=254, 4 Ref=360, 100

Rentention Time[min]	Area[mAU*min]	Height[mAU]	Relative Area[%]
6.373	946.12	75.77	20.99
7.430	1309.49	97.61	29.05
8.276	941.40	61.13	20.88
11.689	1311.19	67.43	29.08

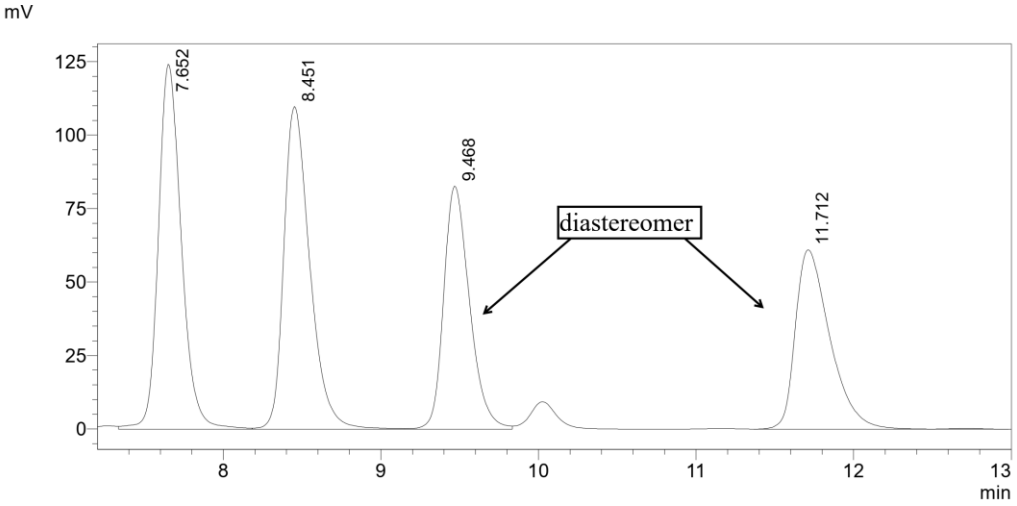


Signal: DAD1B, Sig=254, 4 Ref=360, 100

Rentention Time[min]	Area[mAU*min]	Height[mAU]	Relative Area[%]
6.351	157.16	12.33	6.55
7.404	315.36	23.50	13.14
8.254	1863.09	119.93	77.62
11.618	64.73	3.44	2.70

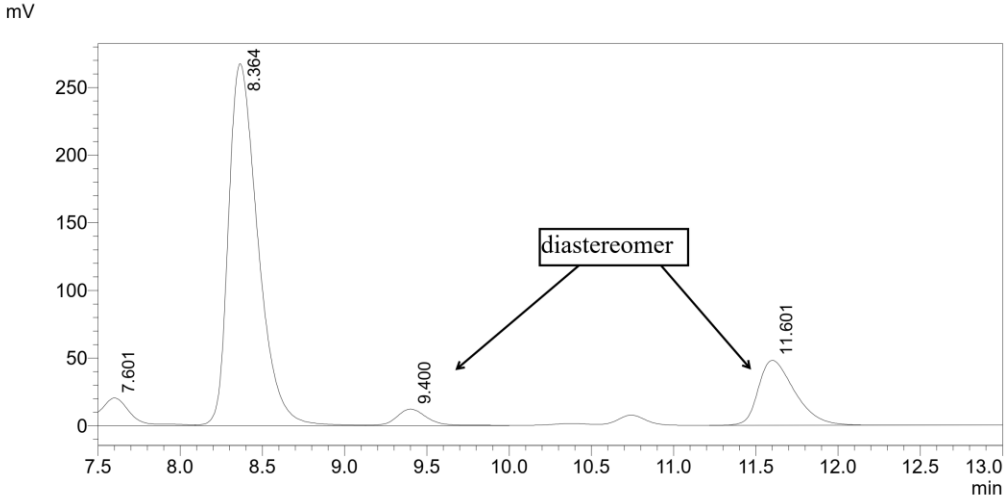


5c



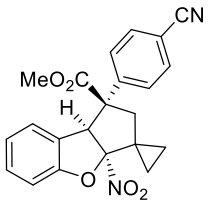
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.652	1259544	124184	28.631
2	8.451	1260909	109800	28.662
3	9.468	944772	82760	21.476
4	11.712	934017	61056	21.231
		4399242	377799	100.000

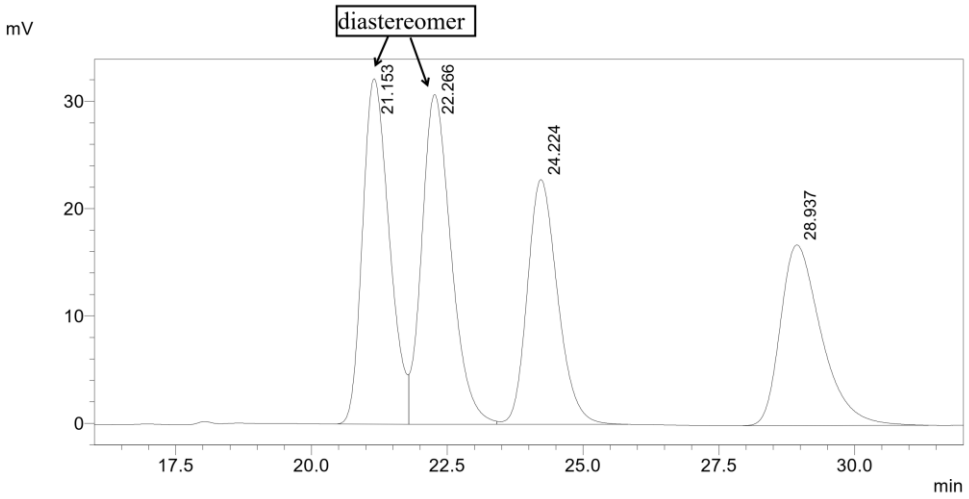


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.601	237697	20443	5.328
2	8.364	3328145	267508	74.605
3	9.400	155321	12187	3.482
4	11.601	739878	48082	16.585
		4461041	348220	100.000

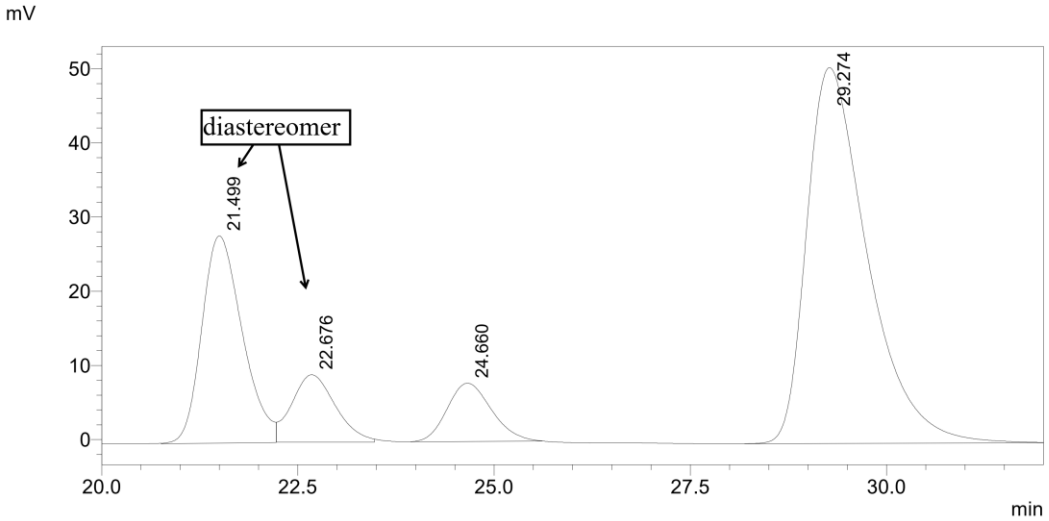


5d



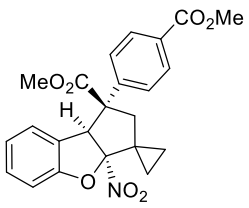
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	21.153	1105824	32185	27.449
2	22.266	1154072	30716	28.646
3	24.224	884995	22803	21.967
4	28.937	883828	16832	21.938
		4028718	102536	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	21.499	1002610	27935	22.825
2	22.676	352806	9104	8.032
3	24.660	308328	7858	7.019
4	29.274	2728942	50686	62.125
		4392686	95584	100.000



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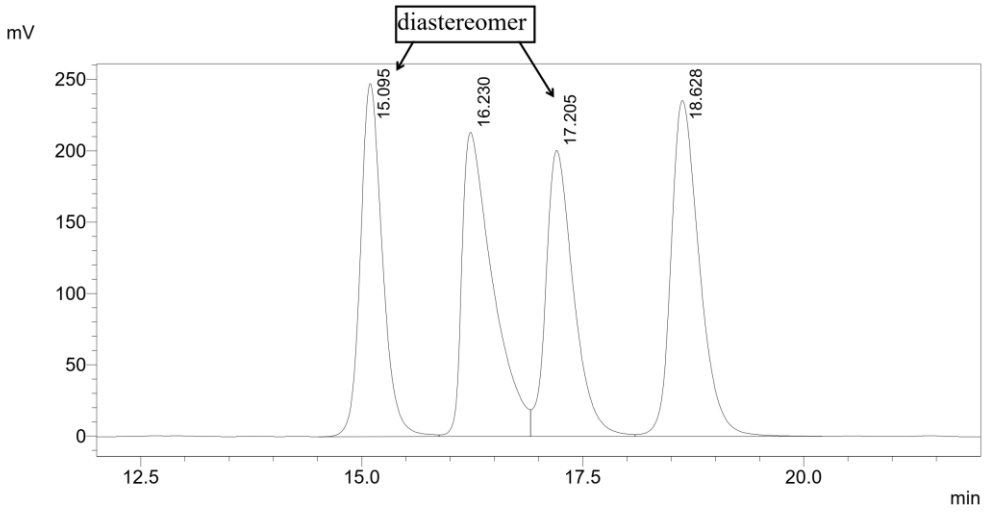
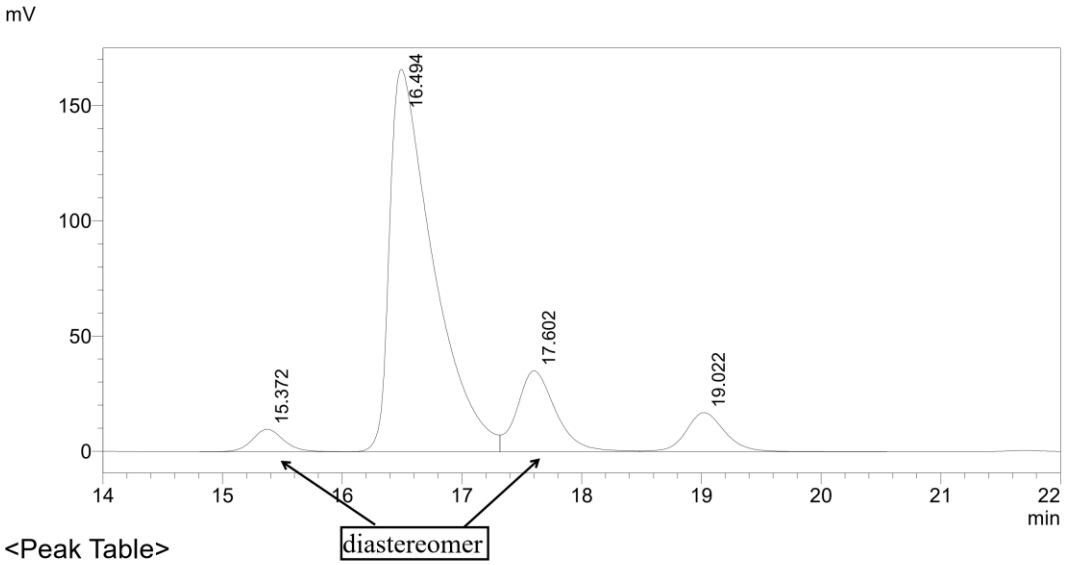


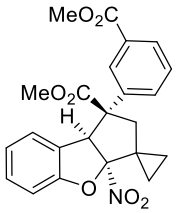
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	15.095	4271863	247502	22.379
2	16.230	5177778	213202	27.125
3	17.205	4371981	200615	22.903
4	18.628	5267128	235425	27.593
		19088750	896743	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	15.372	182513	9807	3.285
2	16.494	4192215	165902	75.464
3	17.602	791555	35136	14.249
4	19.022	389002	17009	7.002
		5555285	227854	100.000



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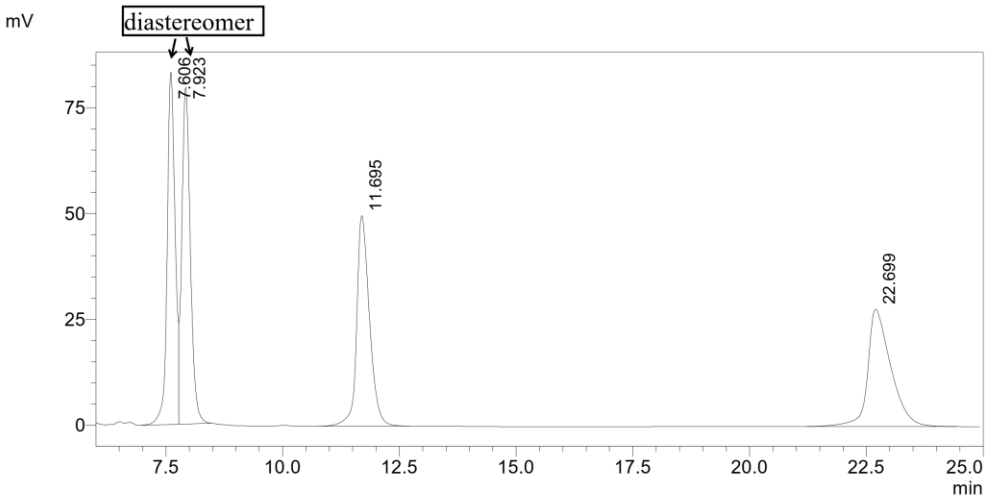
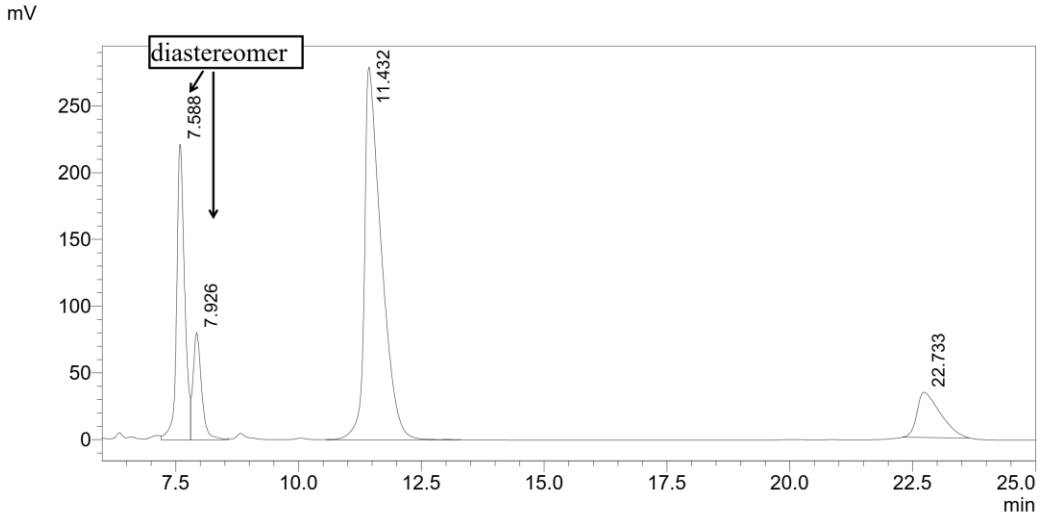


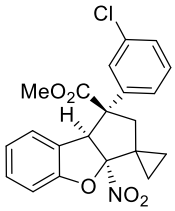
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.606	989146	83208	25.350
2	7.923	1013348	79486	25.971
3	11.695	948020	49690	24.296
4	22.699	951374	27688	24.382
		3901888	240072	100.000

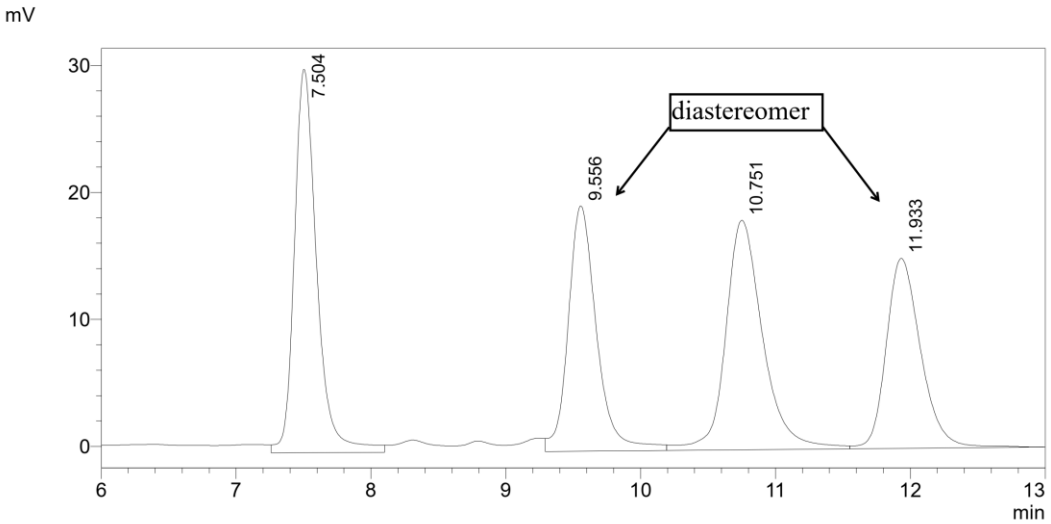


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.588	2495091	221431	22.107
2	7.926	980806	80430	8.690
3	11.432	6691557	279378	59.290
4	22.733	1118787	33891	9.913
		11286241	615131	100.000

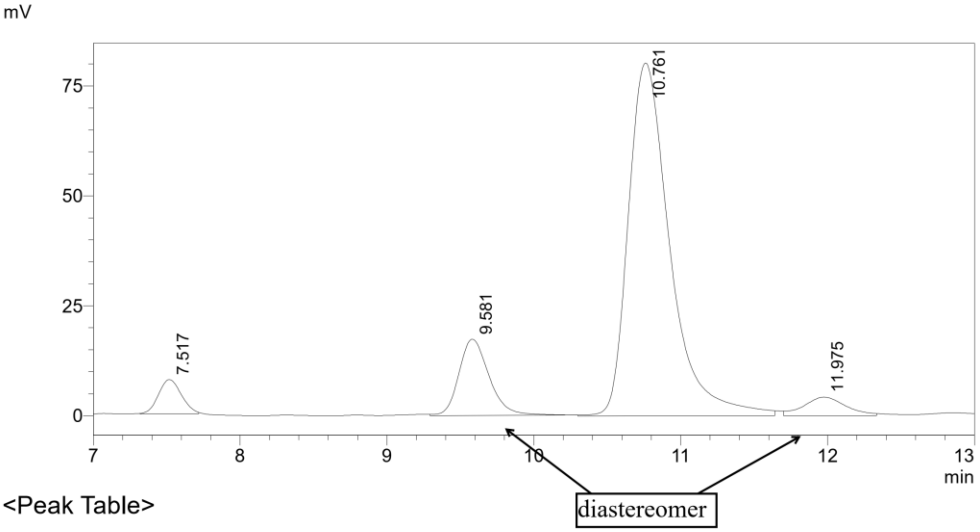


5g



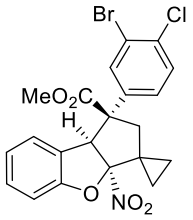
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.504	350517	30184	28.149
2	9.556	282561	19305	22.692
3	10.751	346352	18070	27.814
4	11.933	265793	14958	21.345
		1245222	82517	100.000

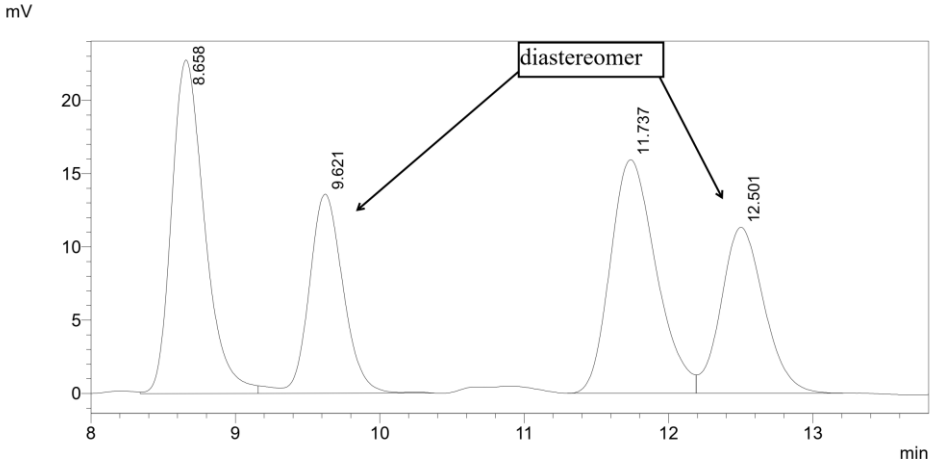


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.517	84378	7797	4.224
2	9.581	249483	17374	12.491
3	10.761	1579939	80304	79.101
4	11.975	83567	4201	4.184
		1997367	109676	100.000

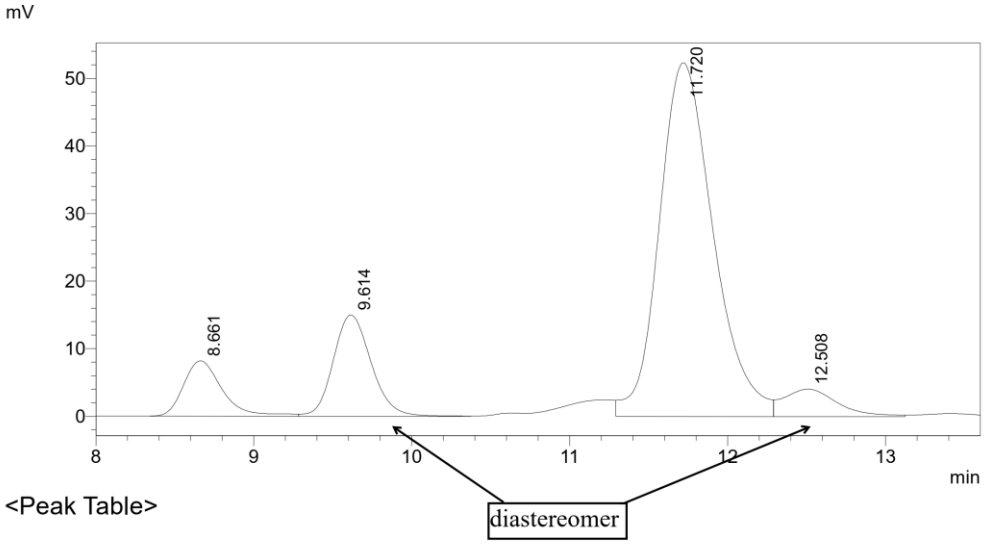


5h



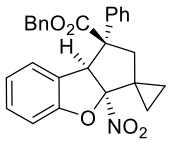
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.658	361744	22770	30.898
2	9.621	223465	13585	19.087
3	11.737	351464	15935	30.020
4	12.501	234092	11319	19.995
		1170765	63610	100.000

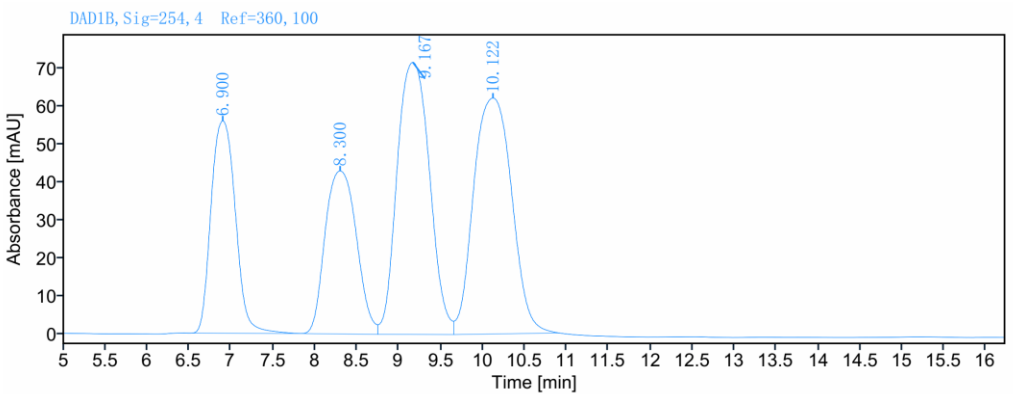


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.661	140030	8198	8.085
2	9.614	250195	14994	14.445
3	11.720	1245626	52349	71.916
4	12.508	96213	4070	5.555
		1732064	79612	100.000

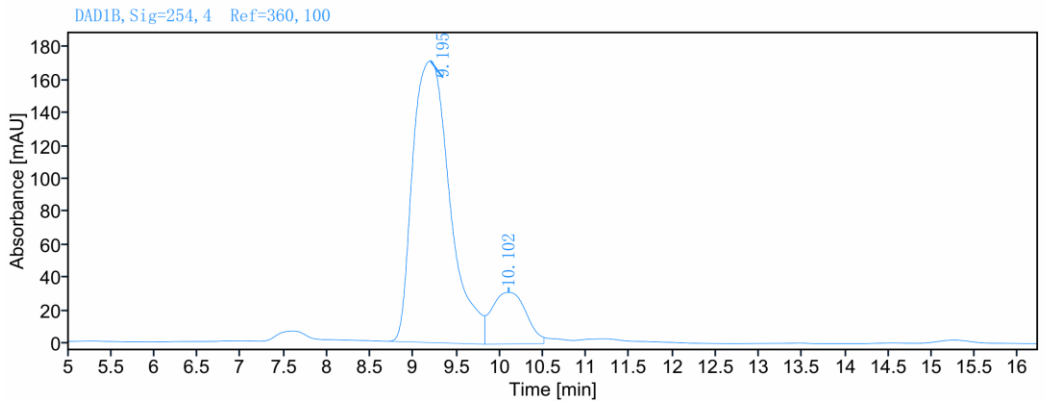


5i



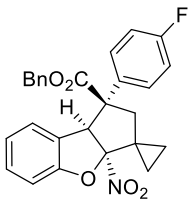
Signal: DAD1B, Sig=254, 4 Ref=360, 100

Rentention Time[min]	Area[mAU*min]	Height[mAU]	Relative Area[%]
6.900	1131.80	56.01	18.37
8.300	1119.51	43.00	18.17
9.167	1936.70	71.77	31.44
10.122	1971.88	62.23	32.01



Signal: DAD1B, Sig=254, 4 Ref=360, 100

Rentention Time[min]	Area[mAU*min]	Height[mAU]	Relative Area[%]
9.195	5137.48	171.08	85.51
10.102	870.50	31.31	14.49



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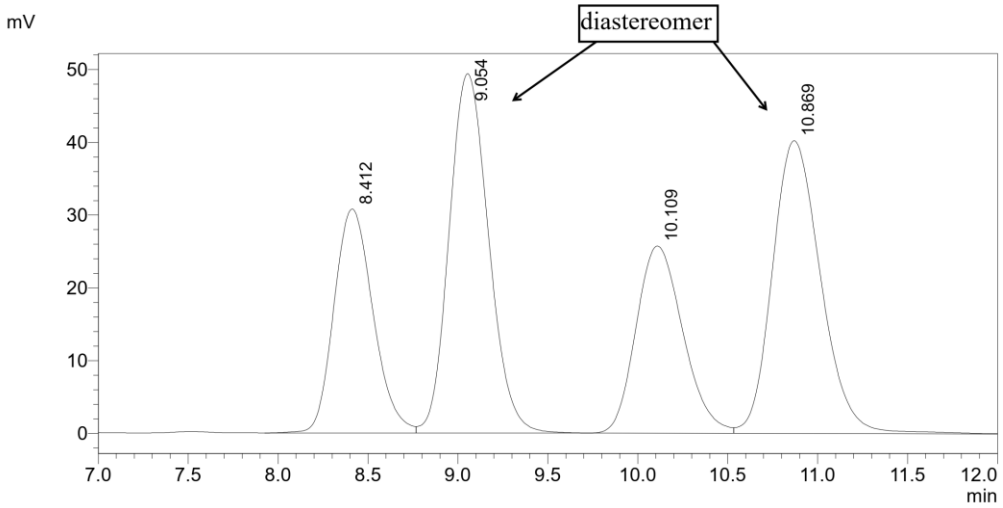
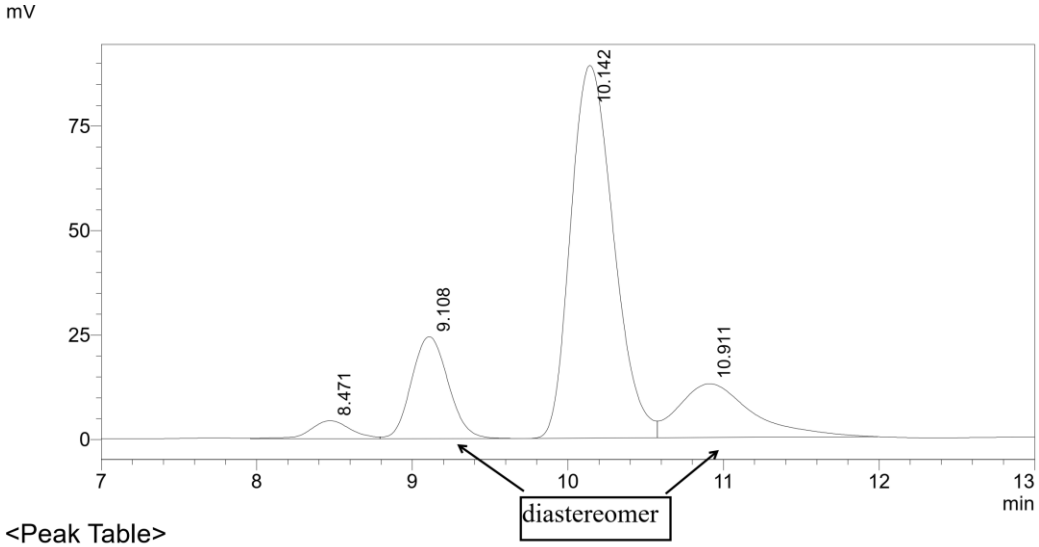


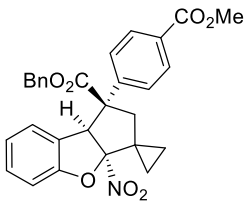
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.412	465936	30771	19.098
2	9.054	754377	49397	30.920
3	10.109	465994	25732	19.100
4	10.869	753428	40233	30.882
		2439736	146134	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	8.471	78098	4322	2.988
2	9.108	399977	24427	15.305
3	10.142	1711606	89242	65.492
4	10.911	423774	12876	16.215
		2613454	130867	100.000



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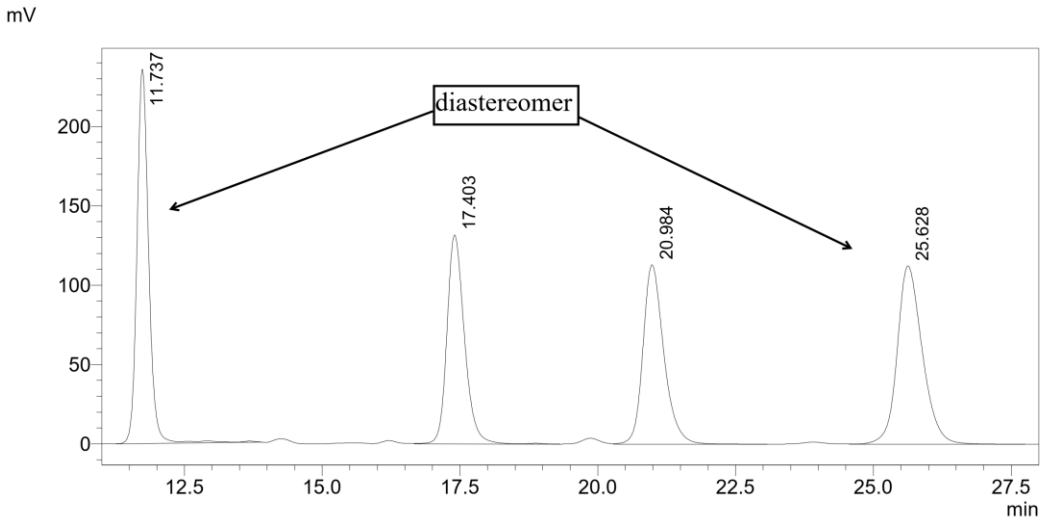
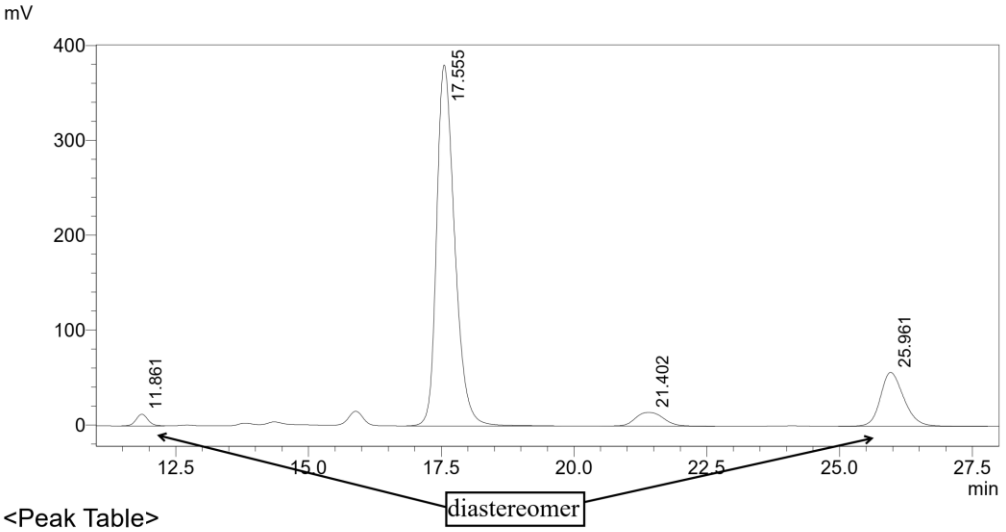


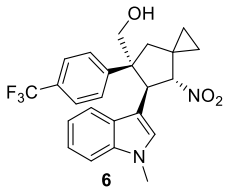
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	11.737	3492295	235850	26.925
2	17.403	2921583	131731	22.525
3	20.984	2986611	112956	23.026
4	25.628	3570166	112402	27.525
		12970655	592938	100.000

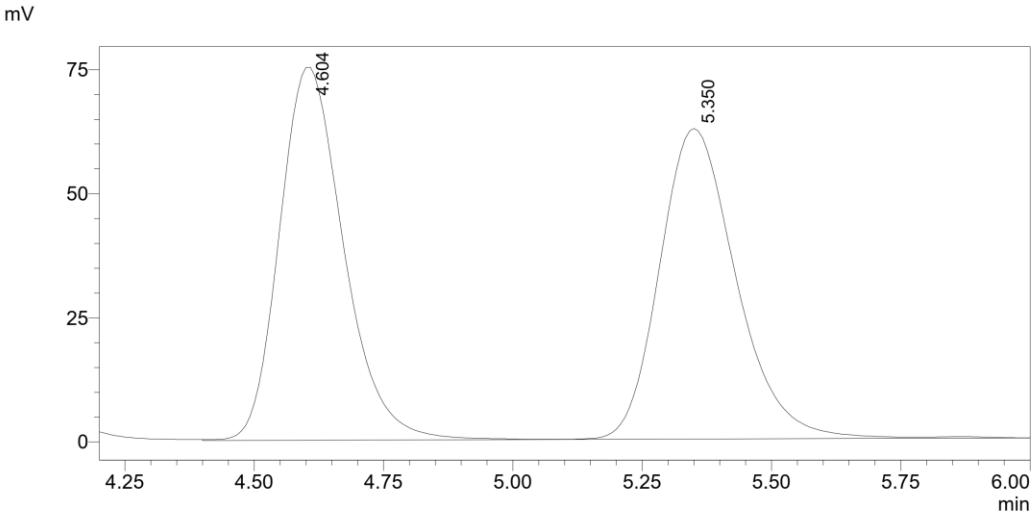


<Peak Table>

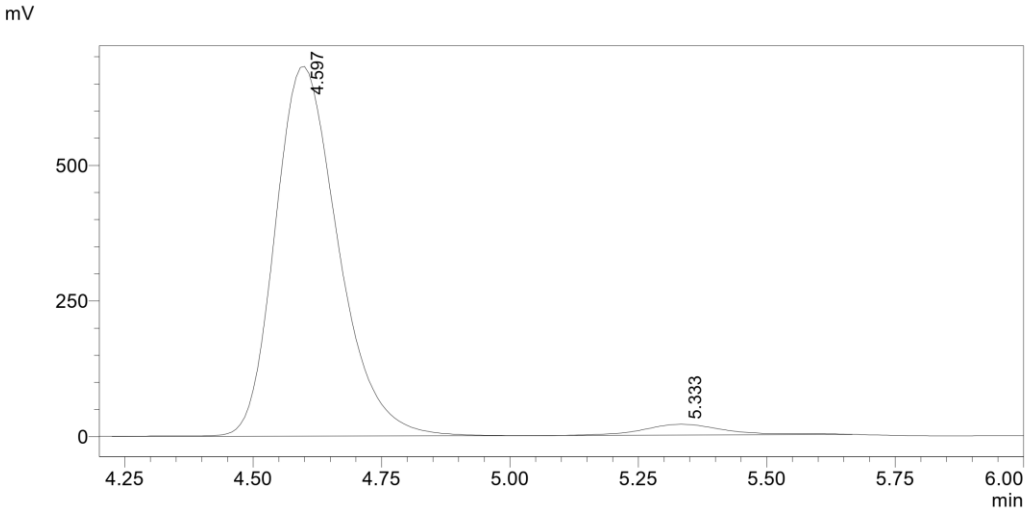
Peak#	Ret. Time	Area	Height	Area%
1	11.861	194503	12383	1.696
2	17.555	9001904	380379	78.476
3	21.402	527595	14394	4.599
4	25.961	1746931	56796	15.229
		11470932	463953	100.000



6



Peak#	Ret. Time	Area	Height	Area%
1	4.604	649487	75138	50.127
2	5.350	646195	62597	49.873
		1295682	137735	100.000



Peak#	Ret. Time	Area	Height	Area%
1	4.597	5831648	681413	96.308
2	5.333	223528	19971	3.692
		6055175	701383	100.000