Double Thiol-Chiral Brønsted Base Catalysis: Asymmetric Cross Rauhut–Currier Reaction and Sequential [4 + 2] Annulation for Assembly of Different Activated Olefins

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Supporting Information

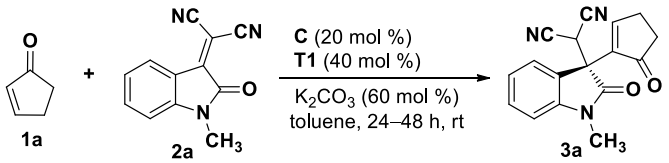
1. General methods

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 150 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. In each case, enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with the authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralcel OD-H Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak ID Column (250 × 4.6 mm) UV detection was monitored at 220 nm or 254 nm. Optical rotation was measured in $CHCl_3$ solution at 25 ℃ or 20 ℃. Column chromatography was performed on silica gel (200-300 mesh) eluting with EtOAc and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and EtOAc were distilled. THF was freshly distilled from sodium/benzophenone before use. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes. The substrates were synthesized according to the literature procedures.[1]

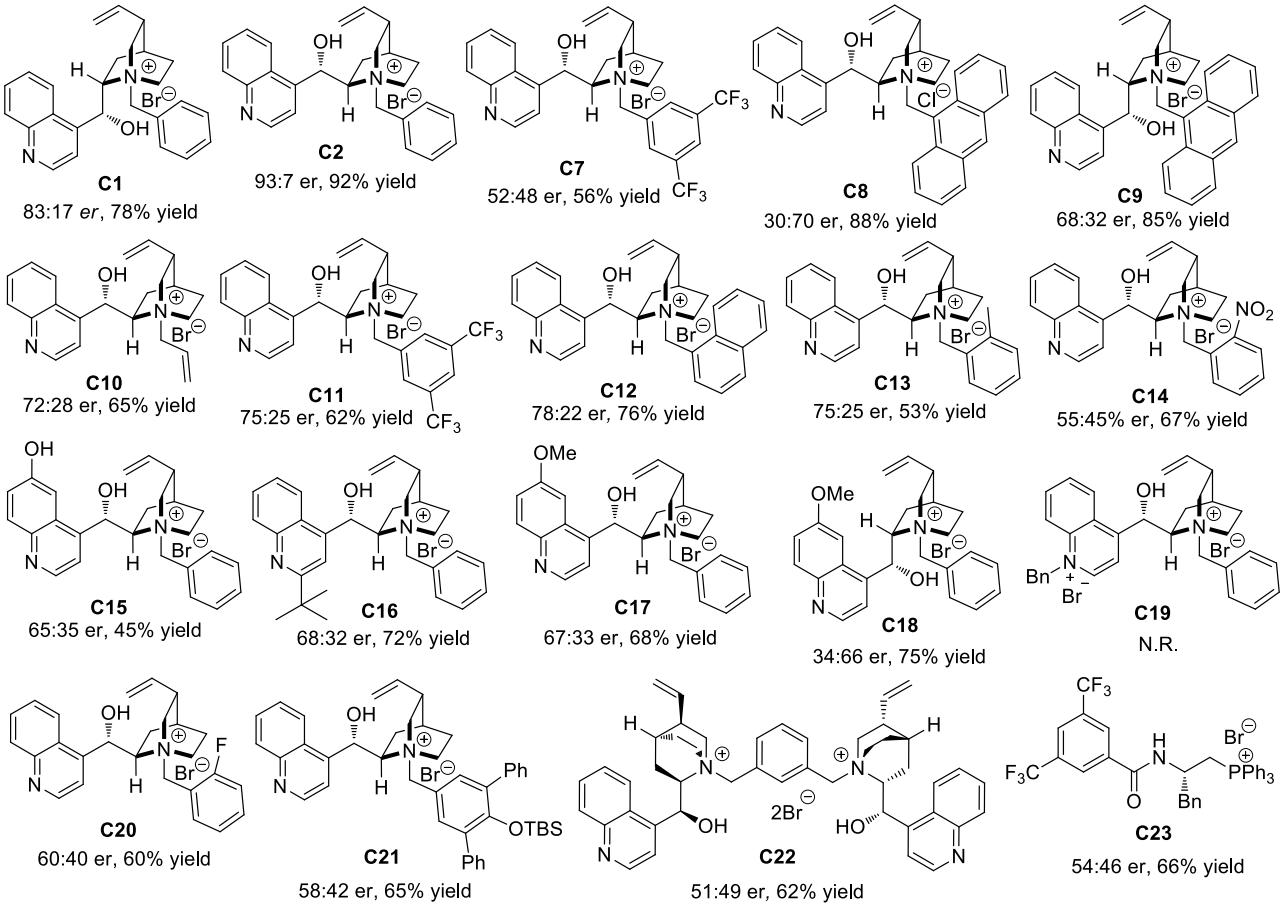
(1) (a) Peng, J.; Ran, G.-Y.; Du, W.; Chen, Y.-C. *Org. Lett.* **2015**, *17*, 4490–4493. (b) Shi, M.-L.; Zhan, G.; Zhou, S.-L.; Du, W.; Chen, Y.-C. *Org. Lett.* **2016**, *18*, 6480–6483.

2. More screening conditions for the cross RC reaction of enone 1a with isatin-derived alkylidene malononitrile 2a

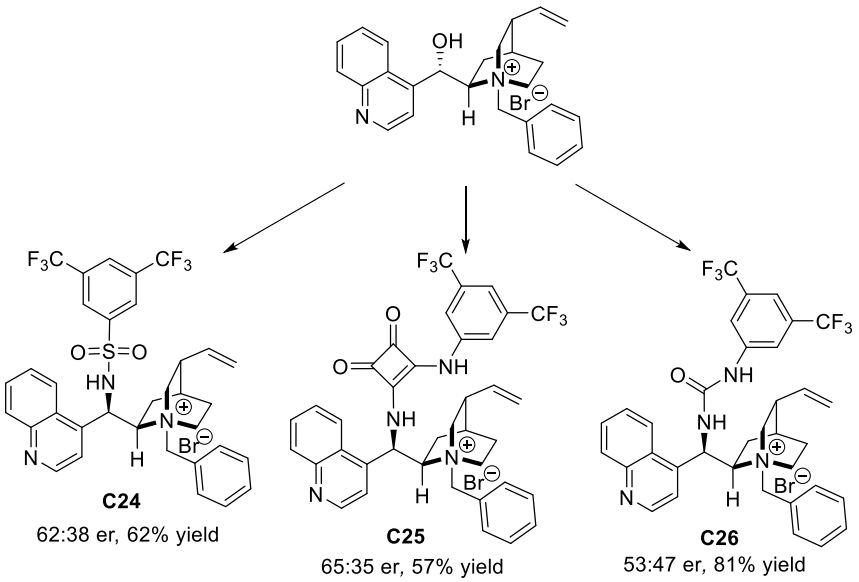
As noted in the text, the reaction was performed with 2-mercaptobenzoic acid **T1**, cinchonidine derived PTC and K_2CO_3 in toluene at 25 ^{o}C for 24 h to 48 h, giving the RC adduct with 83:17 er, 78% yield. Then an array of PTCs were investigated, and the cinchonine derived PTC **C2** gave the best enantioselectivity and reactivity (92% yield, 93:7 er).



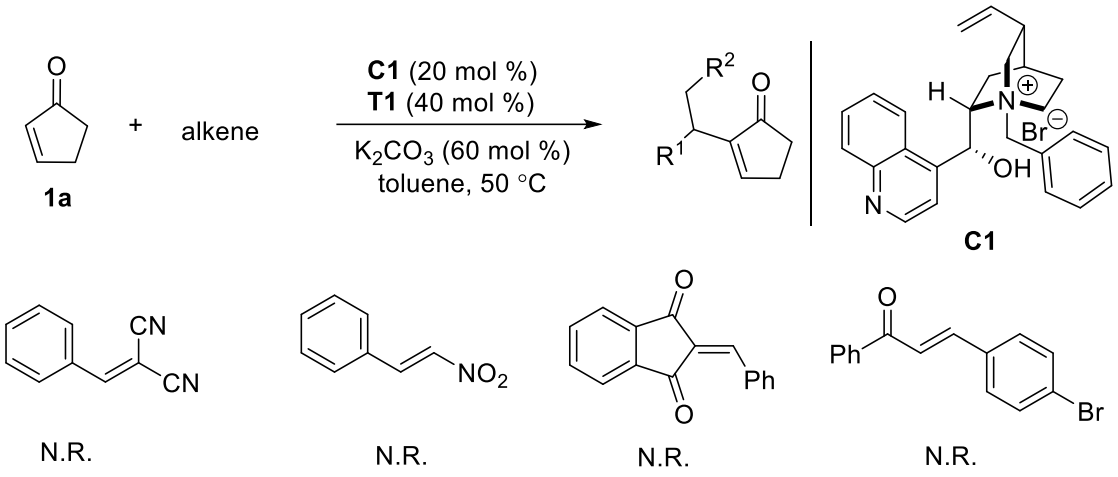
1a + 2a → 3a



After screening many parameters, we paid our attention to structural modifications of the catalysts. Some bifunctional PTCs were prepared and investigated.

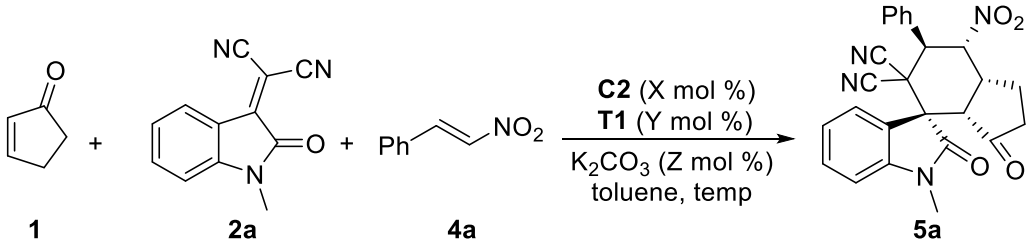


More screening studies on other electrophiles resulted in no success.



3. Screening conditions for the three-component domino [2 + 2 + 2] annulation and substrate scope

3.1 Screening conditions for the three-component domino [2 + 2 + 2] annulation[a]

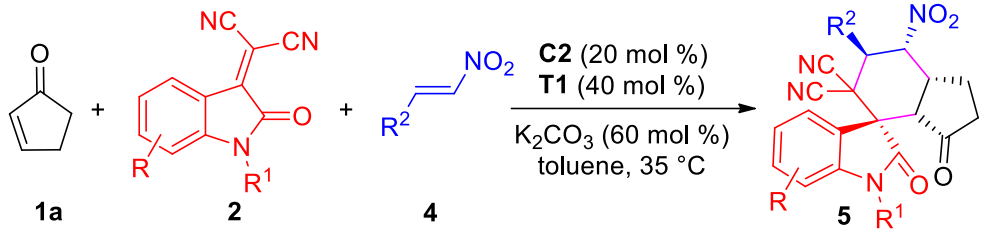


entry	**1**:**2a**:**4a**	X	Y	Z	time (h)	temp (℃)	yield (%)[b]	er[c]	dr[c]
1	2:1:1	20	40	60	18	50	62	86.5:13.5	3:1
2	2:1:1	20	40	60	30	35	73	87.5:12.5	3:1
3	1.5:1:1	20	40	60	48	35	/		
4	3:1:1	20	40	60	24	35	71	81:19	2:1
5	3:1:1	20	40	80	15	35	74	82.5:17.5	2:1
6	3:1:1	20	40	120	10	35	68	82:18	1.8:1
7	3:1:1	20	40	80	48	25	71	84:16	3:1

[a]Unless noted otherwise, reactions were performed with 2-cyclopentenone **1a** (0.2 mmol), activated olefin **2a** (0.1 mmol), nitroolefin **4a** (0.1 mmol), PTC **C2**, thiol **T1** and K_2CO_3 in toluene (1.0 mL) for 10–48 h. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

It was found that chemoselective assembly of the three different activated alkenes could be conducted under the catalysis of thiol **T1** and PTC **C2**. However, the reaction would quickly become dark after the early addition of nitroolefin **4a**, which might probably result from its aggregation promoted by thiol addition. As summarized in the above table, the yield together with stereoselectivity generally decreased significantly compared to those in the sequential one-pot process, even under the optimized conditions.

3.2 Substrate scope of the three-component domino [2 + 2 + 2] annulation[a]

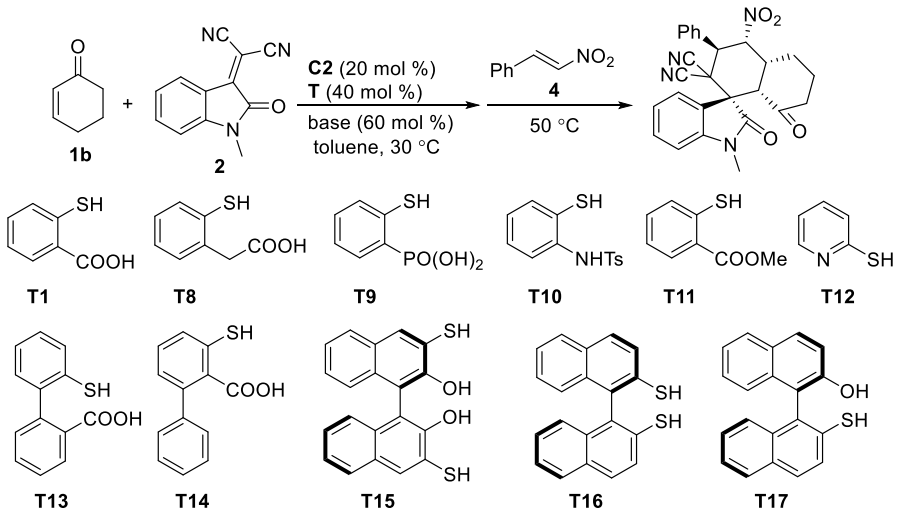


entry	R,R^1	R^2	yield (%)[b]	er[c]	dr[c]
1	H, Me	Ph	**5a**, 73	87.5:12.5	3:1
2	H, Bn	Ph	**5b**, 70	82:18	3.2:1
3	H, allyl	Ph	**5c**, 63	82:18	4.5:1
4	H, MOM	Ph	**5d**, 68	80.5:19.5	3.3:1
5	7-Me, Me	Ph	**5f**, 62	80:20	2.5:1
6	5-MeO, Me	Ph	**5g**, 71	78.5:21.5	2:1
7	5,7-Me$_2$, Me	Ph	**5h**, 72	85.5:14.5	4:1
8	5,7-Me$_2$, Me	2-BrC$_6$H$_4$	**5o,** 61	85:15	1:1
9	5,7-Me$_2$, Me	2-naphthyl	**5r,** 62	87.5:12.5	5:1
10	5,7-Me$_2$, Me	2-thienyl	**5s,** 59	86.5:13.5	3:1

[a]Unless noted otherwise, reactions were performed with 2-cyclopentenone **1a** (0.2 mmol), activated olefin **2** (0.1 mmol), nitroolefin **4** (0.1 mmol), PTC **C2** (20 mol %), thiol **T1** (40 mol %) and K_2CO_3 (60 mol %) in toluene (1.0 mL) at 35 ℃ for 24–48 h. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Some other activated olefins or nitroolefins were applied to the three-component reaction as well, and the corresponding products **5** were generally obtained with moderate yields and stereoselectivity. Therefore, better data were obtained by conducting the RC/[4 + 2] annulation in a sequential process.

4. More screening conditions for the cross RC reaction of 2-cyclohexenone with 2a and one-pot [4 + 2] annulation[a]

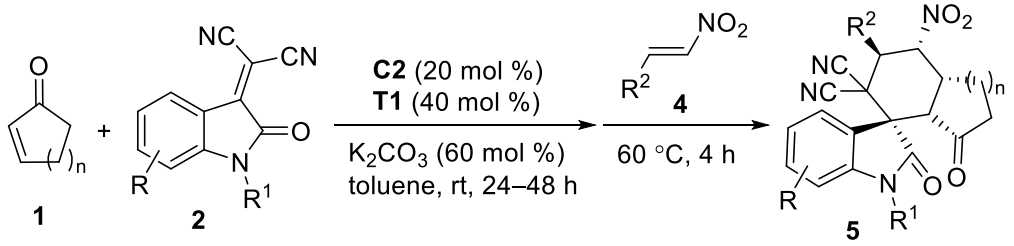


entry	**T**	base	yield (%)[b]	er (%)[c]
1	**T1**	K_2CO_3	75	64.5:35.5
2	**T8**	K_2CO_3	<10	/
3	**T9**	K_2CO_3	<10	/
4	**T10**	K_2CO_3	<10	/
5	**T11**	K_2CO_3	<10	/
6	**T12**	K_2CO_3	78	53:47
7	**T13**	K_2CO_3	<10	/
8	**T14**	K_2CO_3	73	60:40
9	**T15**	K_2CO_3	/	
10	**T16**	K_2CO_3	/	
11	**T17**	K_2CO_3	/	
12	**T1**	Na_2CO_3	/	
13	**T1**	Cs_2CO_3	46	59:41
14	**T1**	K_3PO_4	54	57.5:42.5

[a]Unless noted otherwise, reactions were performed with 2-cyclohexenone (0.8 mmol), activated alkene **2** (0.1 mmol), PTC **C2** (20 mol %), thiol **T** (40 mol %), base (60 mol %) in toluene (0.5 mL) at 30 ℃ for 48–72 h. After completion, nitroolefin **4** (0.1 mmol) was added, and stirred at 50 °C for 4 h. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase; dr >19:1.

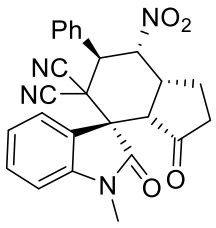
As outlined in the above table, we further screened a number of thiol compounds for the reaction of 2-cyclohexenone, but the results could not be further improved.

5. General procedure for the cross RC reactions of enones 1 with isatin-derived alkylidene malononitriles 2 and annulations



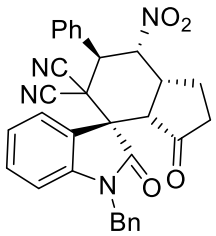
A mixture of cyclic enone **1** (0.2 mmol, 2.0 equiv), activated olefin **2** (0.1 mmol, 1.0 equiv), PTC **C2** (20 mol %), thiol **T1** (40 mol %) and K_2CO_3 (60 mol %) in toluene (1.0 mL) was stirred at room temperature for 24 h. After completion, nitroolefin **4** (0.1 mmol, 1.0 equiv) was added and the reaction was stirred at 60 ^oC for 4 h. Then the annulation product **5** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5).

Most racemates could be obtained by using triethylamine and thiol **T1** as the catalysts, but a few reactions failed. So two peaks of these enantiomers were assigned by HPLC analysis on a chiral stationary phase with the mixture of two enantiomers, which were produced by using quinine and quindine as the catalyst, respectively.

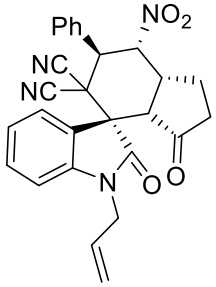


Synthesis of 5a: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile **2a** (20.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5a**: 38.7 mg, as a white solid, yield 88%; $[\alpha]_D^{20}$: +52.0 (*c* = 0.32 in $CHCl_3$); 93:7 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 8.08 min, t (minor) = 9.84 min; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J* = 8.4 Hz, 1H), 7.55–7.53 (m, 2H), 7.49 (t, *J* = 8.6 Hz, 1H), 7.45–7.43 (m, 3H), 7.27 (t, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 5.93 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.34 (d, *J* = 12.6 Hz, 1H), 3.55–3.52 (m, 1H), 3.34–3.28 (m, 1H), 3.26 (s, 3H), 2.95–2.90 (m, 1H), 2.50 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.33–2.26 (m, 1H), 1.82–1.77 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.3, 172.2, 143.4, 131.8,

131.3, 130.1, 129.5, 125.1, 124.5, 124.3, 111.6, 110.3, 109.4, 84.2, 53.1, 48.4, 48.3, 39.7, 38.4, 38.3, 27.0, 22.6; ESI-HRMS: calcd. for $C_{25}H_{20}N_4O_4$+Na^+ 463.1377, found 463.1375.

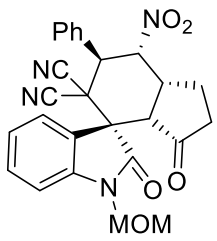


Synthesis of 5b: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1-benzyl-2-oxoindolin-3-ylidene)malononitrile (28.5 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5b**: 41.2 mg, as a white solid, yield 80%; $[\alpha]_D^{20}$: +38.5 (*c* = 0.26 in $CHCl_3$); 90.5:9.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.28 min, t (minor) = 8.62 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.71 (d, *J* = 7.2 Hz, 1H), 7.57–7.55 (m, 2H), 7.46–7.45 (m, 3H), 7.42–7.38 (m, 3H), 7.30–7.22 (m, 4H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.95 (dd, *J* = 13.2, 7.2 Hz, 1H), 5.41 (d, *J* = 12.6 Hz, 1H), 5.05 (d, *J* = 16.2 Hz, 1H), 4.88 (d, *J* = 16.2 Hz, 1H), 3.56–3.53 (m, 1H), 3.33 (d, *J* = 9.0 Hz, 1H), 2.95–2.93 (m, 1H), 2.45 (dd, *J* = 19.2, 8.4 Hz, 1H), 2.32–2.30 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.3, 172.4, 142.7, 134.0, 131.7, 131.2, 130.0, 129.5, 128.8, 127.9, 126.9, 125.0, 124.5, 124.3, 111.6, 110.5, 110.4, 84.1, 52.7, 48.8, 48.3, 44.8, 39.8, 38.5, 38.2, 22.5; ESI-HRMS: calcd. for $C_{31}H_{24}N_4O_4$+Na^+ 539.1690, found 539.1692.

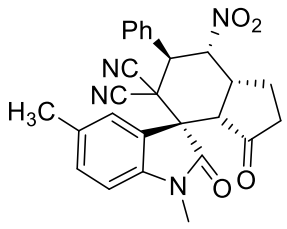


Synthesis of 5c: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1-allyl-2-oxoindolin-3-ylidene)malononitrile (20.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5c**: 40.1 mg, as a white solid, yield 86%; $[\alpha]_D^{20}$: +62.3 (*c* = 0.41 in $CHCl_3$); 90.5:9.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 5.98 min, t (minor) = 7.72 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.69 (d, *J* = 7.8 Hz, 1H), 7.56–7.53 (m, 2H), 7.47–7.42 (m, 4H), 7.26–7.25 (m, 1H),

7.17–7.15 (m, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.94 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.81–5.79 (m, 1H), 5.37–5.26 (m, 3H), 4.38–4.36 (m, 2H), 3.55–3.53 (m, 1H), 3.32–3.30 (m, 1H), 2.93–2.91 (m, 1H), 2.48 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.33–2.31 (m, 1H), 1.82–1.80 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.1, 172.0, 142.7, 131.8, 131.2, 130.1, 129.9, 129.5, 125.0, 124.5, 124.3, 118.6, 111.6, 110.4, 84.2, 52.7, 48.7, 48.3, 43.2, 39.8, 38.5, 38.2, 22.6; ESI-HRMS: calcd. for $C_{27}H_{22}N_4O_4$+Na^+ 489.1533, found 489.1532.

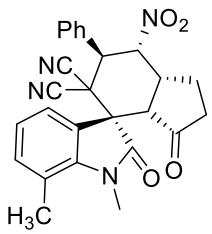


Synthesis of 5d: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1-(methoxymethyl)-2-oxoindolin-3-ylidene)malononitrile (23.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5d**: 38.5 mg, as a white solid, yield 82%; $[\alpha]_D^{20}$: +45.6 (*c* = 0.35 in $CHCl_3$); 89.5:10.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.16 min, t (minor) = 7.44 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 8.8 Hz, 1H), 7.55–7.53 (m, 2H), 7.49 (t, *J* = 8.8 Hz, 1H), 7.45–7.43 (m, 3H), 7.29 (t, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 5.95 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.29 (d, *J* = 12.6 Hz, 1H), 5.16 (dd, *J* = 20.4, 11.4 Hz, 2H), 3.56–3.54 (m, 1H), 3.36 (s, 3H), 3.34–3.32 (m, 1H), 2.90–2.88 (m, 1H), 2.47 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.35–2.33 (m, 1H), 1.82–1.80 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.3, 173.2, 142.0, 131.7, 131.5, 130.1, 129.5, 124.7, 124.5, 111.5, 110.9, 110.5, 84.2, 72.5, 56.8, 53.6, 48.8, 48.4, 39.9, 38.4, 38.4, 22.6; ESI-HRMS: calcd. for $C_{26}H_{22}N_4O_5$ + Na^+ 493.1482, found 493.1485.

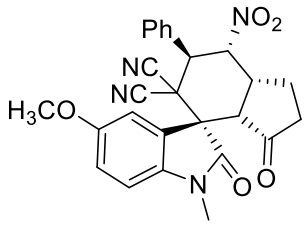


Synthesis of 5e: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5-dimethyl-2-oxoindolin-3-ylidene)malononitrile (22.3 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel

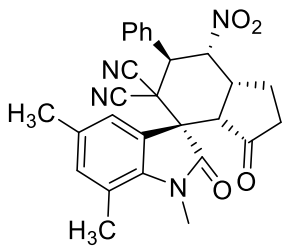
(EtOAc/petroleum ether = 1/8–1/5) gave product **5e**: 36.3 mg, as a white solid, yield 80%; $[\alpha]_D^{20}$: +73.4 (*c* = 0.52 in $CHCl_3$); 91:9 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.44 min, t (minor) = 8.13 min; ^1H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.56–7.53 (m, 2H), 7.47 (s, 1H), 7.45–7.42 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.93 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.36 (d, *J* = 12.0 Hz, 1H), 3.53–3.51 (m, 1H), 3.29 (d, *J* = 8.4 Hz, 1H), 3.23 (s, 3H), 2.94–2.92 (m, 1H), 2.50 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.41 (s, 3H), 2.31–2.29 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.3, 172.0, 141.0, 134.0, 131.9, 131.7, 130.6, 129.5, 125.2, 125.0, 111.6, 110.4, 109.1, 84.3, 53.1, 48.5, 48.4, 39.7, 38.5, 38.3, 27.0, 22.6, 21.4; ESI-HRMS: calcd. for $C_{26}H_{22}N_4O_4+Na^+$ 477.1533, found 477.1532.



Synthesis of 5f: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,7-dimethyl-2-oxoindolin-3-ylidene)malononitrile (22.3 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5f**: 38.6 mg, as a white solid, yield 85%; $[\alpha]_D^{20}$: +61.7 (*c* = 0.45 in $CHCl_3$); 92:8 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 8.04 min, t (minor) = 9.47 min; ^1H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.54–7.50 (m, 3H), 7.44–7.40 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.93 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.36 (d, *J* = 12.0 Hz, 1H), 3.54–3.49 (m, 4H), 3.29–3.26 (m, 1H), 2.95–2.93 (m, 1H), 2.59 (s, 3H), 2.50 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.31–2.28 (m, 1H), 1.81–1.78 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.4, 172.9, 141.2, 135.2, 131.8, 130.0, 129.5, 125.6, 124.0, 122.3, 121.0, 111.6, 110.5, 84.2, 52.6, 48.7, 48.5, 39.8, 38.5, 38.3, 30.5, 22.6, 19.1; ESI-HRMS: calcd. for $C_{26}H_{22}N_4O_4+Na^+$ 477.1533, found 477.1534.

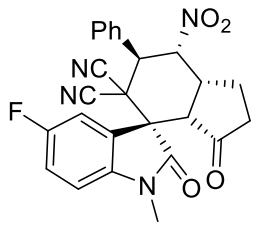


Synthesis of 5g: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile (23.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5g**: 38.5 mg, as a white solid, yield 82%; $[\alpha]_D^{20}$: +87.2 (*c* = 0.48 in $CHCl_3$); 96:4 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 11.23 min, t (minor) = 12.74 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.55–7.53 (m, 2H), 7.47–7.43 (m, 3H), 7.28 (s, 1H), 7.00 (t, *J* = 6.6 Hz, 1H), 6.86 (d, *J* = 6.6 Hz, 1H), 5.93 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.37 (d, *J* = 12.6 Hz, 1H), 3.84 (s, 3H), 3.57–3.55 (m, 1H), 3.29–3.27 (m, 1H), 3.24 (s, 3H), 2.95–2.93 (m, 1H), 2.52 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.32–2.30 (m, 1H), 1.83–1.80 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.2, 171.7, 156.9, 136.6, 131.8, 130.0, 129.5, 126.2, 115.5, 111.9, 111.5, 110.3, 109.9, 84.2, 55.8, 53.3, 48.5, 48.4, 39.7, 38.4, 38.3, 27.1, 22.6; ESI-HRMS: calcd. for $C_{26}H_{22}N_4O_5$ + Na^+ 493.1482, found 493.1485.

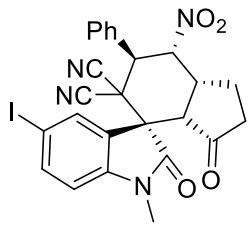


Synthesis of 5h: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5h**: 38.8 mg, as a white solid, yield 83%; $[\alpha]_D^{20}$: +72.8 (*c* = 0.36 in $CHCl_3$); 95.5:4.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.04 min, t (minor) = 8.03 min; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.56–7.53 (m, 2H), 7.45–7.42 (m, 3H), 7.30 (s, 1H), 7.00 (s, 1H), 5.92 (dd, *J* = 12.4, 7.6 Hz, 1H), 5.37 (d, *J* = 12.4 Hz, 1H), 3.55–3.48 (m, 4H), 3.27–3.24 (m, 1H), 2.94–2.92 (m, 1H), 2.59 (s, 3H), 2.50–2.48 (m, 1H), 2.35 (s, 3H), 2.33-2.23 (m, 1H), 1.80–1.77 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.4, 172.8, 138.8, 135.7, 133.6, 131.9, 130.0, 129.4, 125.6, 122.9, 120.6, 111.5, 110.5, 84.3, 52.6, 48.8, 48.5, 39.8, 38.4, 38.3, 30.3, 22.6, 21.1, 18.9; ESI-

HRMS: calcd. for $C_{27}H_{24}N_4O_4$+Na^+ 491.1690, found 491.1692.

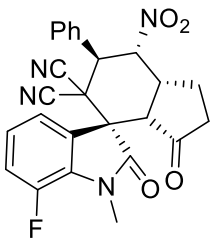


Synthesis of 5i: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (22.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5i**: 39.4 mg, as a white solid, yield 86%; $[\alpha]_D^{20}$: +31.5 (*c* = 0.27 in $CHCl_3$); 83:17 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 7.81 min, t (minor) = 8.34 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.55–7.51 (m, 2H), 7.46–7.43 (m, 4H), 7.20 (t, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.92 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.35 (d, *J* = 12.6 Hz, 1H), 3.55–3.53 (m, 1H), 3.25–3.23 (m, 4H), 2.94–2.92 (m, 1H), 2.50 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.33–2.31 (m, 1H), 1.82–1.80 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.1, 171.9, 159.8 (d, $^1J_{FC}$ = 240.7 Hz), 139.5, 131.7 (d, $^3J_{FC}$ = 7.8 Hz), 130.2, 129.6, 129.5, 126.7, 126.6, 118.0 (d, $^2J_{FC}$ = 23.4 Hz), 113.1 (d, $^3J_{FC}$ = 7.8 Hz), 111.5, 110.3, 110.2, 84.1, 53.3, 48.5, 48.2, 39.7, 38.4, 38.3, 27.2, 22.7; ESI-HRMS: calcd. for $C_{25}H_{19}FN_4O_4$ + Na^+ 481.1283, found 481.1285.

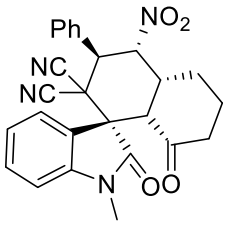


Synthesis of 5j: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(5-iodo-1-methyl-2-oxoindolin-3-ylidene)malononitrile (33.5 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5j**: 50.9 mg, as a white solid, yield 90%; $[\alpha]_D^{20}$: +39.3 (*c* = 0.34 in $CHCl_3$); 88:12 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 12.11 min, t (minor) = 9.03 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.94 (s, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.55–7.51 (m, 2H), 7.46–7.43 (m, 3H), 6.73 (d, *J* = 7.2 Hz, 1H), 5.90 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 3.55–3.53 (m, 1H), 3.31–3.23

(m, 4H), 2.89–2.87 (m, 1H), 2.50 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.33–2.31 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.1, 171.7, 140.2, 133.3, 131.6, 130.2, 129.6, 127.4, 111.3, 110.6, 84.1, 48.3, 39.8, 38.4, 38.3, 29.7, 27.0, 22.8; ESI-HRMS: calcd. for $C_{25}H_{19}IN_4O_4$+Na^+ 589.0343, found 589.0346.

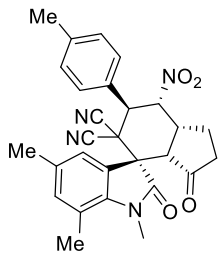


Synthesis of 5k: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)malononitrile (22.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5k**: 39.8 mg, as a white solid, yield 87%; $[\alpha]_D^{20}$: +43.6 (*c* = 0.31 in $CHCl_3$); 89:11 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.36 min, t (minor) = 7.50 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.55–7.53 (m, 2H), 7.49–7.43 (m, 4H), 7.24–7.20 (m, 2H), 5.92 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 3.53–3.51 (m, 1H), 3.46 (s, 3H), 3.29–3.27 (m, 1H), 2.93–2.91 (m, 1H), 2.52 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.31–2.29 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.2, 171.9, 147.8 (d, $^1J_{FC}$ = 244.8 Hz), 131.6, 130.4 (d, $^2J_{FC}$ = 9.1 Hz), 130.2, 129.5, 127.8 (d, $^3J_{FC}$ = 2.9 Hz), 124.9, 124.8, 120.3 (d, $^3J_{FC}$ = 3.4 Hz), 119.4 (d, $^2J_{FC}$ = 18.9 Hz), 111.4, 110.2, 84.1, 53.3, 48.5, 48.3, 39.7, 38.3, 38.3, 29.6, 22.7; ESI-HRMS: calcd. for $C_{25}H_{19}FN_4O_4$+Na^+ 481.1283, found 481.1286.

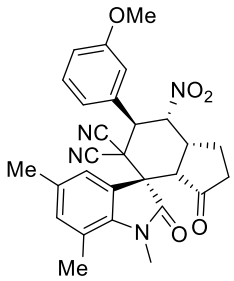


Synthesis of 5l: 2-Cyclohexenone **1b** (19.2 mg, 0.2 mmol), 2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile **2a** (20.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-β-nitrostyrene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5l**: 19.0 mg, as a white solid, yield 42%; $[\alpha]_D^{20}$: +25.4 (*c* = 0.22 in $CHCl_3$); 68:32 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ

= 254 nm]: t (major) = 9.68 min, t (minor) = 16.5 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 7.8 Hz, 1H), 7.53–7.51 (m, 2H), 7.47–7.42 (m, 4H), 7.27 (t, J = 8.6 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 5.68 (dd, J = 12.6, 7.2 Hz, 1H), 5.45 (d, J = 12.0 Hz, 1H), 3.53–3.51 (m, 1H), 3.32 (s, 3H), 3.25–3.23 (m, 1H), 3.04–3.02 (m, 1H), 2.29–2.18 (m, 3H), 1.65–1.63 (m, 1H), 1.35–1.32 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.5, 172.5, 142.4, 132.2, 131.3, 129.9, 129.4, 125.8, 124.2, 123.3, 111.5, 110.7, 109.3, 85.3, 53.3, 52.9, 49.0, 40.7, 40.4, 38.9, 27.1, 24.0, 20.7; ESI-HRMS: calcd. for $C_{26}H_{22}N_4O_4$+Na^+ 477.1533, found 477.1532.

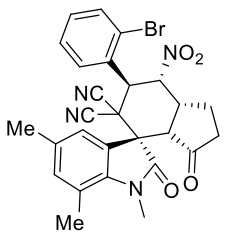


Synthesis of 5m: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-1-methyl-4-(2-nitrovinyl)benzene (16.3 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5m**: 39.8 mg, as a white solid, yield 82%; $[\alpha]_D^{20}$: +83.7 (c = 0.35 in $CHCl_3$); 93:7 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.57 min, t (minor) = 9.30 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.41 (d, J = 11.4 Hz, 2H), 7.30 (s, 1H), 7.23 (d, J = 11.4 Hz, 1H), 7.0 (s, 1H), 5.90 (dd, J = 12.0, 7.2 Hz, 1H), 5.32 (d, J = 12.0 Hz, 1H), 3.53–3.45 (m, 4H), 3.25–3.23 (m, 1H), 2.95–2.93 (m, 1H), 2.54–2.46 (m, 4H), 2.35–2.25 (m, 7H), 1.77–1.75 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.5, 172.8, 140.0, 138.8, 135.7, 133.6, 130.1, 128.8, 125.7, 123.0, 120.6, 111.6, 110.6, 84.4, 52.6, 48.9, 48.5, 39.5, 38.5, 38.3, 30.4, 22.6, 21.2, 21.1, 18.9; ESI-HRMS: calcd. for $C_{28}H_{26}N_4O_4$+Na^+ 505.1846, found 505.1848.

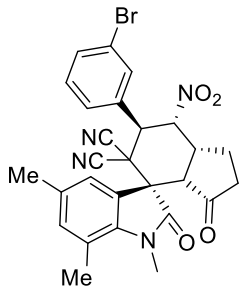


Synthesis of 5n: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-1-methoxy-3-(2-nitrovinyl)benzene (17.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica

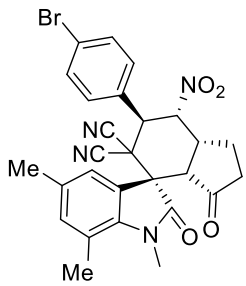
gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5n**: 40.8 mg, as a white solid, yield 82%; $[\alpha]_D^{20}$: +76.2 (*c* = 0.28 in $CHCl_3$); 94:6 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.16 min, t (minor) = 20.20 min; ^1H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.37–7.30 (m, 2H), 7.16–7.13 (m, 1H), 7.05–7.03 (m, 2H), 6.97–6.95 (m, 1H), 5.90 (dd, *J* = 11.4, 7.2 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.55–3.50 (m, 4H), 3.27–3.25 (m, 1H), 2.96–2.94 (m, 1H), 2.58 (s, 3H), 2.55 (dd, *J* = 18.6, 8.4 Hz, 1H), 2.39 (s, 3H), 2.32–2.30 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.5, 172.8, 140.1, 138.8, 135.8, 133.4, 130.5, 125.7, 123.0, 120.6, 115.6, 84.4, 55.3, 52.7, 48.6, 39.8, 38.5, 38.3, 30.4, 22.6, 21.1, 18.9; ESI-HRMS: calcd. for $C_{28}H_{26}N_4O_5+Na^+$ 521.1795, found 521.1796.



Synthesis of 5o: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-1-bromo-2-(2-nitrovinyl)benzene (22.7 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5o**: 40.9 mg, as a white solid, yield 75%; $[\alpha]_D^{20}$: +85.3 (*c* = 0.42 in $CHCl_3$); 92.5:7.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.15 min, t (minor) = 8.19 min; ^1H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.74 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 7.32–7.29 (m, 2H), 7.03 (s, 1H), 6.28 (d, *J* = 7.2 Hz, 1H), 5.88 (dd, *J* = 12.6, 7.2 Hz, 1H), 3.59–3.54 (m, 1H), 3.52 (s, 3H), 3.30–3.28 (m, 1H), 3.06–3.04 (m, 1H), 2.61–2.51 (m, 4H), 2.37–2.30 (m, 4H), 1.84–1.82 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 212.6, 172.3, 139.0, 135.8, 134.7, 133.5, 131.8, 131.1, 128.3, 127.9, 126.8, 125.5, 122.9, 120.6, 111.6, 109.8, 84.9, 52.8, 48.4, 47.9, 38.6, 38.3, 37.6, 30.4, 22.7, 21.1, 18.9; ESI-HRMS: calcd. for $C_{27}H_{23}Br^{79}N_4O_4+Na^+$ 569.0795, found 569.0798, calcd. for $C_{27}H_{23}Br^{81}N_4O_4 + Na^+$ 571.0774, found 571.0776.

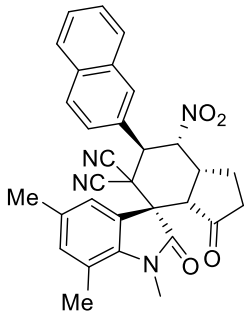


Synthesis of 5p: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-1-bromo-3-(2-nitrovinyl)benzene (22.7 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5p**: 41.5 mg, as a white solid, yield 76%; $[\alpha]_D^{20}$: +70.0 (*c* = 0.34 in $CHCl_3$); 94:6 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 5.60 min, t (minor) = 8.60 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.69 (s, 1H), 7.59–7.57 (m, 1H), 7.52–7.50 (m, 1H), 7.35–7.33 (m, 2H), 7.04 (s, 1H), 5.86 (dd, *J* = 12.6, 7.2 Hz, 1H), 5.39 (d, *J* = 12.6 Hz, 1H), 3.56–3.53 (m, 4H), 3.27–3.25 (m, 1H), 2.93–2.91 (m, 1H), 2.58 (s, 3H), 2.52 (dd, *J* = 19.2, 9.0 Hz, 1H), 2.40–2.38 (s, 3H), 2.37–2.27 (m, 1H), 1.81–1.79 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.2, 172.7, 138.6, 135.9, 134.3, 133.7, 133.3, 130.9, 125.5, 123.5, 122.9, 120.7, 111.3, 110.3, 84.2, 52.5, 48.5, 48.5, 39.4, 38.4, 38.3, 30.4, 22.6, 21.1, 18.9; ESI-HRMS: calcd. for $C_{27}H_{23}Br^{79}N_4O_4$+$Na^+$ 569.0795, found 569.0796, calcd. for $C_{27}H_{23}Br^{81}N_4O_4$+$Na^+$ 571.0774, found 571.0773.

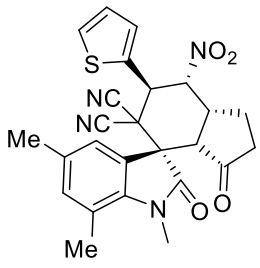


Synthesis of 5q: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-1-bromo-4-(2-nitrovinyl)benzene (22.7 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5q**: 42.6 mg, as a white solid, yield 78%; $[\alpha]_D^{20}$: +75.8 (*c* = 0.37 in $CHCl_3$); 93.5:6.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 15.87 min, t (minor) = 17.88 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (s, 1H), 7.01 (s, 1H), 5.85 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.36 (d, *J* = 12.0 Hz, 1H), 3.56–3.45 (m, 4H), 3.25–3.23 (m, 1H), 2.93–2.91 (m, 1H), 2.59–2.46 (m, 4H), 2.35–2.23 (m, 4H),

1.80–1.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.2, 172.7, 138.7, 135.8, 133.7, 132.7, 131.0, 125.5, 124.4, 122.9, 120.7, 111.4, 110.4, 84.2, 52.5, 48.5, 48.4, 39.4, 38.3, 38.2, 30.3, 22.5, 21.1, 18.9; ESI-HRMS: calcd. for $C_{27}H_{23}Br^{79}N_4O_4$+$Na^+$ 569.0795, found 569.0797, calcd. for $C_{27}H_{23}Br^{81}N_4O_4$+$Na^+$ 571.0774, found 571.0775.

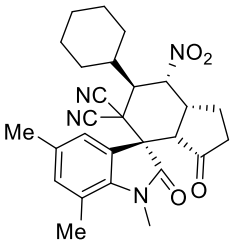


Synthesis of 5r: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-2-(2-nitrovinyl)naphthalene (19.9 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5r**: 36.7 mg, as a white solid, yield 71%; $[\alpha]_D^{20}$: +68.5 (*c* = 0.29 in $CHCl_3$); 94:6 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 8.00 min, t (minor) = 17.7 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 1H), 7.92–7.90 (m, 2H), 7.87–7.85 (m, 1H), 7.64–7.62 (m, 1H), 7.56–7.54 (m, 2H), 7.35 (s, 1H), 7.03 (s, 1H), 6.08 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.58 (d, *J* = 12.0 Hz, 1H), 3.58–3.56 (m, 1H), 3.53 (s, 3H), 3.33–3.31 (m, 1H), 3.03–3.01 (m, 1H), 2.56–2.51 (m, 4H), 2.38–2.30 (m, 4H), 1.83–1.81 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.4, 172.9, 138.9, 135.8, 133.8, 133.7, 133.2, 129.5, 128.4, 127.7, 127.2, 126.8, 125.7, 123.0, 120.7, 111.7, 110.6, 84.6, 52.8, 48.8, 48.6, 39.9, 38.6, 38.4, 30.4, 22.7, 21.1, 18.9; ESI-HRMS: calcd. for $C_{31}H_{26}N_4O_4$+Na^+ 541.1846, found 541.1845.

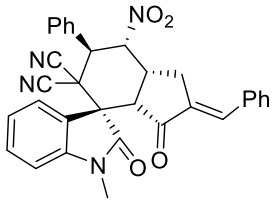


Synthesis of 5s: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-2-(2-nitrovinyl)thiophene (15.5 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5s**: 35.1 mg, as a white solid, yield 74%; $[\alpha]_D^{20}$: +72.2 (*c* = 0.31 in $CHCl_3$); 92:8 er, determined by HPLC analysis [Daicel Chiralpak AD-H,

n-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.20 min, t (minor) = 8.33 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.39–7.35 (m, 2H), 7.31 (s, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 5.77 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.67 (d, *J* = 12.0 Hz, 1H), 3.56–3.44 (m, 4H), 3.26–3.24 (m, 1H), 2.90 (s, 1H), 2.54–2.44 (m, 4H), 2.35–2.22 (m, 4H), 1.78–1.76 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.2, 172.7, 138.8, 135.8, 133.8, 133.7, 128.7, 127.5, 127.4, 125.6, 122.9, 120.7, 111.7, 110.6, 86.1, 52.6, 49.4, 48.4, 38.5, 38.2, 36.6, 30.4, 22.7, 21.1, 18.9; ESI-HRMS: calcd. for $C_{25}H_{22}N_4O_4S+Na^+$ 497.1254, found 497.1255.

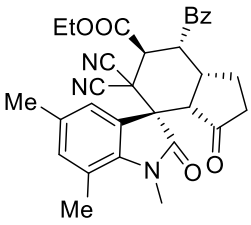


Synthesis of 5t: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-(2-nitrovinyl)cyclohexane (15.5 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **5t**: 34.1 mg, as a white solid, yield 72%; $[\alpha]_D^{20}$: +83.4 (*c* = 0.43 in $CHCl_3$); 92.5:7.5 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 4.70 min, t (minor) = 5.94 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.27 (s, 1H), 7.01 (s, 1H), 5.40 (dd, *J* = 11.4, 6.6 Hz, 1H), 4.01 (d, *J* = 11.4 Hz, 1H), 3.44 (s, 3H), 3.31–3.29 (m, 1H), 3.09–3.07 (m, 1H), 2.81–2.79 (m, 1H), 2.59 (s, 3H), 2.43–2.35 (m, 4H), 2.23–2.21 (m, 1H), 1.99–1.92 (m, 2H), 1.83–1.55 (m, 6H), 1.31–1.14 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.5, 172.5, 139.0, 135.7, 133.5, 125.8, 122.8, 120.5, 112.2, 111.8, 83.9, 52.2, 48.3, 47.3, 41.8, 38.4, 38.0, 33.0, 30.3, 28.6, 26.9, 25.7, 23.0, 21.1, 19.0; ESI-HRMS: calcd. for $C_{27}H_{30}N_4O_4+Na^+$ 497.2159, found 497.2158.

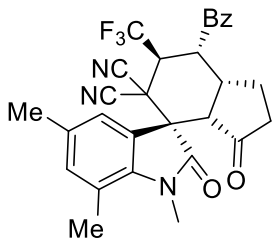


Synthesis of 7: (*E*)-5-benzylidenecyclopent-2-en-1-one **6** (20.4 mg, 0.12 mmol), 2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile **2a** (20.9 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were dissolved in distilled toluene (1.0 mL). The mixture was stirred at 25 °C for 12 h. Then (*E*)-(2-nitrovinyl)benzene **4a** (14.9 mg, 0.1 mmol) was added and the reaction was moved to 50 °C for 4 h. After completion, purification

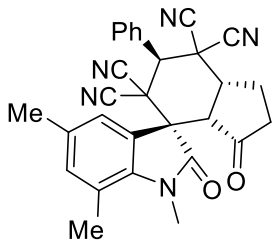
by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **7**: 48.6 mg, as a white solid, yield 92%; $[\alpha]_D^{20}$: +25.6 (*c* = 0.27 in $CHCl_3$); 72:28 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 7.42 min, t (minor) = 8.78 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.78 (d, *J* = 8.4 Hz, 1H), 7.60–7.58 (m, 2H), 7.53–7.39 (m, 10H), 7.31 (t, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 5.98 (dd, *J* = 12.0, 7.2 Hz, 1H), 5.60 (d, *J* = 12.0 Hz, 1H), 3.84–3.82 (m, 1H), 3.55–3.53 (m, 1H), 3.45–3.43 (m, 1H), 3.19 (s, 3H), 2.80 (dd, *J* = 19.2, 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 199.6, 171.5, 143.4, 136.9, 134.2, 132.8, 131.8, 131.4, 131.1, 130.6, 130.2, 129.6, 129.0, 124.8, 124.6, 124.4, 111.7, 110.6, 109.4, 84.0, 53.2, 49.1, 48.2, 39.9, 36.5, 29.6, 27.0; ESI-HRMS: calcd. for $C_{32}H_{24}N_4O_4$+Na^+ 551.1690, found 551.1693.



Synthesis of 8: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then ethyl (*E*)-4-oxo-4-phenylbut-2-enoate (20.4 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **8**: 40.8 mg, as a white solid, yield 78%; $[\alpha]_D^{20}$: +88.5 (*c* = 0.46 in $CHCl_3$); 94:6 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 8.55 min, t (minor) = 13.81 min; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 8.06 (d, *J* = 8.4 Hz, 2H), 7.68–7.66 (m, 1H), 7.56 (t, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.02 (s, 1H), 4.89–4.87 (m, 1H), 4.70–4.68 (m, 1H), 4.29–4.27 (m, 2H), 3.46 (s, 3H), 3.11–3.09 (m, 2H), 2.60–2.51 (m, 4H), 2.37 (s, 3H), 2.31–2.29 (m, 1H), 2.04–2.02 (m, 1H), 1.45–1.43 (m, 1H), 1.27 (t, *J* = 12 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *δ* (ppm) 213.9, 197.6, 172.7, 169.1, 139.0, 135.6, 135.5, 133.9, 133.4, 129.1, 128.2, 126.1, 123.1, 120.4, 111.3, 110.9, 62.6, 52.3, 48.2, 44.5, 44.1, 40.1, 38.6, 36.7, 30.3, 23.0, 21.1, 18.9, 13.9; ESI-HRMS: calcd. for $C_{31}H_{29}N_3O_5$+Na^+ 546.1999, found 546.1998.



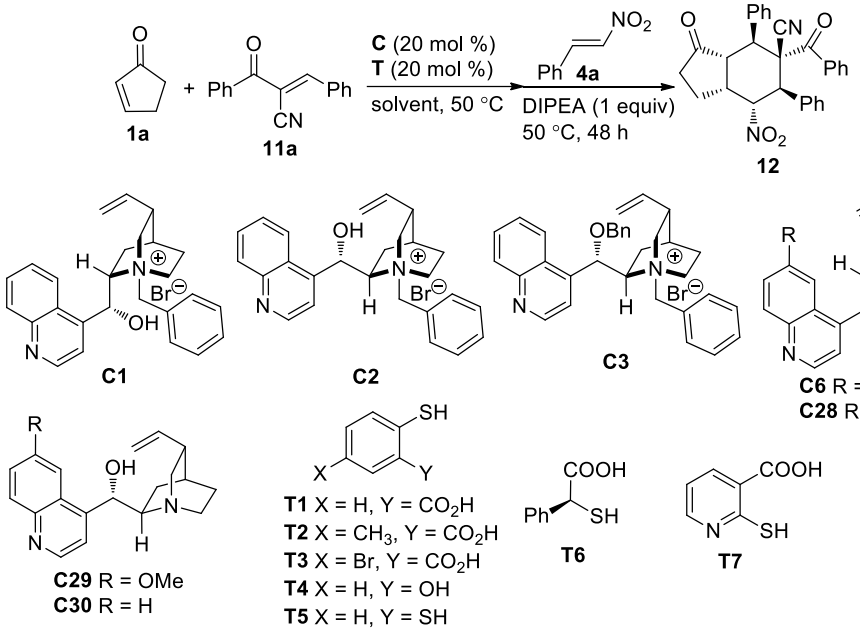
Synthesis of 9: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (20.0 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **9**: 31.6 mg, as a white solid, yield 61%; $[\alpha]_D^{20}$: +81.2 (*c* = 0.38 in $CHCl_3$); 93:7 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.06 min, t (minor) = 7.46 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 8.4 Hz, 2H), 7.70–7.68 (m, 1H), 7.58 (t, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.04 (s, 1H), 5.23–5.21 (m, 1H), 4.61–4.59 (m, 1H), 3.47 (s, 3H), 3.16–3.14 (m, 1H), 3.05–3.03 (m, 1H), 2.67–2.65 (m, 1H), 2.56 (s, 3H), 2.38 (s, 3H), 2.31–2.29 (m, 1H), 2.07–2.05 (m, 1H), 1.46–1.44 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 212.7, 194.3, 172.3, 139.2, 135.9, 135.2, 134.3, 133.6, 129.3, 129.2, 128.6, 124.5 (q, J_{CF} = 279.2 Hz), 122.9, 111.5, 110.5, 53.4, 52.1, 47.8, 41.7 (q, J_{CF} = 28.6 Hz), 38.2, 35.9, 30.3, 29.7, 24.3, 21.1, 19.0 ; ESI-HRMS: calcd. for $C_{29}H_{24}F_3N_3O_3$+Na^+ 542.1662, found 542.1665.



Synthesis of 10: 2-Cyclopentenone **1a** (16.4 mg, 0.2 mmol), 2-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)malononitrile (23.7 mg, 0.1 mmol), PTC **C2** (9.3 mg, 0.02 mmol), 2-mercaptobenzoic acid **T1** (6.2 mg, 0.04 mmol) and K_2CO_3 (8.3 mg, 0.06 mmol) were stirred in distilled toluene (1.0 mL) at rt for 24 h. Then 2-benzylidenemalononitrile (15.4 mg, 0.1 mmol) was added and the reaction was stirred at 60 °C for 4 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8–1/5) gave product **10**: 30.7 mg, as a white solid, yield 65%; $[\alpha]_D^{20}$: +93.4 (*c* = 0.52 in $CHCl_3$); 94:6 er, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 5.35 min, t (minor) = 6.45 min; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91–7.88 (m, 2H), 7.58–7.55 (m, 3H), 7.33 (s, 1H), 7.03 (s, 1H), 4.75 (s, 1H), 3.96–3.94 (m, 1H), 3.52 (s, 3H), 3.19 (d, *J* = 18, 1H), 2.60–2.54 (m, 5H), 2.37–2.29 (m, 4H), 2.19–2.17 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 205.2, 172.5, 135.7, 133.5, 131.3, 130.2, 129.9, 129.8, 123.5, 123.2, 120.8, 112.2, 111.9, 110.8, 110.3, 51.3, 49.9, 47.2,

46.3, 42.0, 41.9, 35.6, 30.3, 22.7, 20.9, 19.0; ESI-HRMS: calcd. for $C_{29}H_{23}N_5O_2$+Na^+ 496.1744, found 496.1745.

6. More screening conditions for the cross RC reaction of enone 1a with α-cyano chalcone 11a and annulation[a]

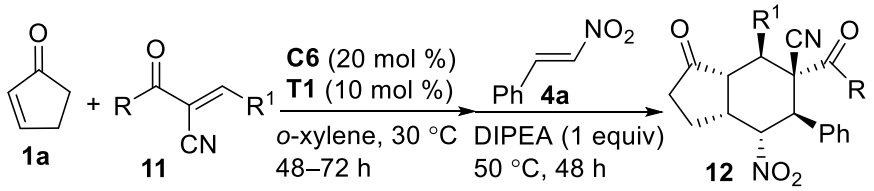


entry	C	T	solvent	yield (%)[b]	er (%)[c]
1[d]	**C1**	**T1**	toluene	47	55.5:44.5
2[d]	**C2**	**T1**	toluene	45	58:42
3[d]	**C3**	**T1**	toluene	41	57:43
4	**C6**	**T1**	toluene	52	85.5:14.5
5	**C28**	**T1**	toluene	36	62.5:37.5
6	**C29**	**T1**	toluene	42	63:36
7	**C30**	**T1**	toluene	47	54.5:45.5
8	**C6**	**T1**	*o*-xylene	79	89:11
9	**C6**	**T1**	*m*-xylene	80	88:12
10	**C6**	**T1**	$PhCF_3$	69	83.5:16.5
11	**C6**	**T1**	mesitylene	75	88:12
12	**C6**	**T1**	$CHCl_3$	62	78.5:21.5
13	**C6**	**T2**	*o*-xylene	72	85.5:14.5
14	**C6**	**T3**	*o*-xylene	74	84.5:15.5

15	**C6**	**T4**	*o*-xylene	64	74:26
16	**C6**	**T5**	*o*-xylene	42	57:43
17	**C6**	**T6**	*o*-xylene	<10	/
18[e]	**C6**	**T7**	*o*-xylene	51	51.5:48.5
19[d]	**C6**	**T1**	*o*-xylene	80	90.5:9.5
20[f,g]	**C6**	**T1**	*o*-xylene	82	91.5:8.5
21[f,g,h]	**C6**	**T1**	*o*-xylene	82	91.5:8.5
22[f,g,h,i]	**C6**	**T1**	*o*-xylene	77	89:11

[a]Unless noted otherwise, reactions were performed with 2-cyclopentenone **1a** (8.6 mg, 0.1 mmol), **11a** (11.7 mg, 0.05 mmol), **C** (6.4 mg, 20 mol %), and thiol **T** (3.1 mg, 20 mol %) in solvent (0.5 mL) at 50 ℃ for 48–72 h. After completion, the intermediate was obtained by flash chromatography on silica gel. After that, the activated alkene **4a** (1.0 equiv), DIPEA (1.0 equiv) and *o*-xylene (0.5 mL) was added and the reaction was stirred at 50 °C for 48 h. [b]Isolated yield for two steps. [c]Determined by HPLC analysis on a chiral stationary phase; dr >19:1. [d]Thiol **T** (6.4 mg, 40 mol %) and K_2CO_3 (8.3 mg, 60 mol %) were added. [e]Dr = 4:1. [f]At 30 ℃ for 72 h. [g]With 10 mol % **T1**. [h]At a 0.1 mmol scale. [i]The reaction was performed in one-pot.

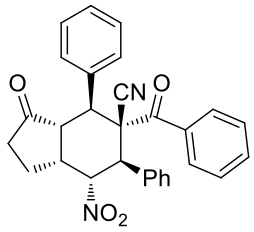
7. General procedure for the cross RC reactions of enone 1a with α-cyano chalcones 11 and annulations



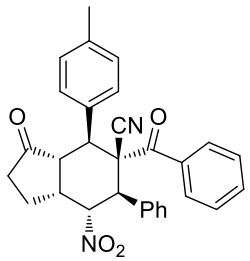
A solution of 2-cyclopentenone **1a** (0.2 mmol, 2.0 equiv), α-cyano chalcone **11** (0.1 mmol, 1.0 equiv), quinine **C6** (20 mol %), thiol **T1** (10 mol %) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48–72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). Then, the activated alkene **4a** (0.1 mmol, 1.0 equiv), *N*,*N*-Diisopropylenthylamine (DIPEA, 0.1 mmol, 1.0 equiv) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h (monitored by TLC). After completion, the product **12** was obtained by flash chromatography on silica gel (EtOAc/petroleum

ether = 1/9–1/7).

The racemates could not be obtained by using DABCO as the catalyst. So two peaks of these enantiomers were assigned by HPLC analysis on a chiral stationary phase with the mixture of two enantiomers, which were produced by using quinine and cinchonine as the catalyst, respectively.

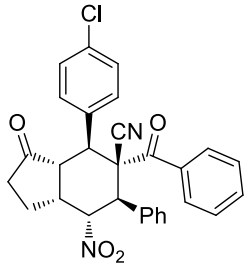


Synthesis of 12a: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-phenylacrylonitrile **11a** (23.3 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) was added and the reaction were stirred at 50 ºC for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12a**: 39.0 mg, as a white solid, yield 84%; $[\alpha]_D^{25}$ = +58.8 (*c* = 0.32 in $CHCl_3$); 91.5:8.5 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 13.77 min, t (major) = 26.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.43–7.42 (m, 2H), 7.33–7.26 (m, 8H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.97–6.94 (m, 2H), 6.31 (d, *J* = 7.6 Hz, 2H), 5.92 (dd, *J* = 12.8, 5.6 Hz, 1H), 4.45 (d, *J* = 8.8 Hz, 1H), 3.75–3.72 (m, 1H), 3.45–3.37 (m, 2H), 2.69–2.51 (m, 2H), 2.41–2.32 (m, 1H), 2.03–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.6, 196.4, 137.0, 133.2, 132.7, 132.1, 129.3, 129.2, 129.0, 128.9, 127.5, 126.6, 118.0, 85.4, 62.0, 49.5, 47.4, 46.9, 39.5, 36.4, 21.1; ESI-HRMS: calcd. for $C_{29}H_{24}N_2O_4$+Na^+ 487.1628, found 487.1630.

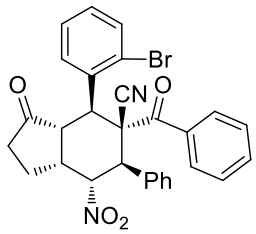


Synthesis of 12b: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(*p*-tolyl)acrylonitrile (24.7 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 ºC for 48 h. After completion,

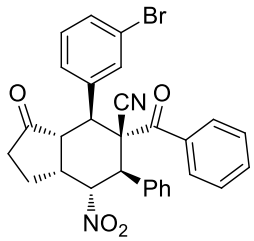
purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12b**: 37.3 mg, as a white solid, yield 78%; $[\alpha]_D^{25}$ = +90.0 (*c* = 0.24 in $CHCl_3$); 90.5:9.5 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 14.23 min, t (major) = 40.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.42–7.41 (m, 2H), 7.31–7.18 (m, 6H), 7.10–7.08 (m, 2H), 6.98–6.94 (m, 2H), 6.33 (d, *J* = 8.0 Hz, 2H), 5.92 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 3.72–3.69 (m, 1H), 3.42–3.34 (m, 2H), 2.68–2.50 (m, 2H), 2.39–2.30 (m, 1H), 2.26 (s, 3H), 2.01–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.6, 196.4, 138.7, 137.0, 132.7, 132.0, 130.1, 129.6, 129.3, 129.2, 127.5, 126.6, 118.1, 85.5, 62.1, 49.6, 47.4, 46.5, 39.6, 36.3, 21.1, 21.0; ESI-HRMS: calcd. for $C_{30}H_{26}N_2O_4$+Na^+ 501.1785, found 501.1786.



Synthesis of 12c: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(4-chlorophenyl)acrylonitrile (26.7 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 ºC for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12c**: 38.8 mg, as a white solid, yield 78%; $[\alpha]_D^{25}$ = +72.8 (*c* = 0.5 in $CHCl_3$); 90:10 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 13.39 min, t (major) = 39.98 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.42–7.40 (m, 2H), 7.33–7.23 (m, 8H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 2H), 5.91 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 3.74–3.71 (m, 1H), 3.45–3.32 (m, 2H), 2.69–2.48 (m, 2H), 2.42–2.32 (m, 1H), 2.03–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.5, 196.0, 136.7, 135.0, 132.6, 132.5, 131.8, 131.0, 129.4, 129.1, 129.0, 127.7, 127.7, 126.8, 117.9, 85.3, 61.7, 49.4, 47.4, 46.2, 39.5, 36.4, 21.1; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{35}ClN_2O_4$+$Na^+$ 521.1239, found 521.1240, $C_{29}H_{23}{}^{37}ClN_2O_4$+$Na^+$ 523.1215, found 523.1217.

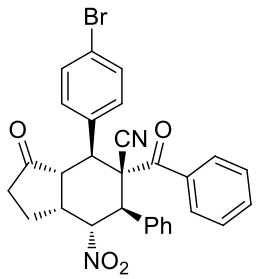


Synthesis of 12d: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(2-bromophenyl)acrylonitrile (31.0 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12d**: 40.1 mg, as a white solid, yield 74%; $[\alpha]_D^{25}$ = +105.7 (*c* = 0.14 in $CHCl_3$); 92:8 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 26.49 min, t (major) = 33.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.89–7.85 (m, 1H), 7.55–7.47 (m, 3H), 7.36–7.29 (m, 3H), 7.25–7.20 (m, 2H), 7.13–7.09 (m, 1H), 7.02–6.98 (m, 2H), 6.43 (d, *J* = 7.6 Hz, 2H), 5.95 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.59 (dd, *J* = 26.0, 13.2 Hz, 2H), 3.43–3.35 (m, 1H), 3.14 (dd, *J* = 13.2 Hz, *J* = 6.4 Hz, 1H), 2.86–2.79 (m, 1H), 2.72–2.60 (m, 1H), 2.41–2.31 (m, 1H), 2.07–2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.4, 194.6, 136.9, 133.5, 133.4, 132.6, 132.2, 130.2, 129.4, 129.1, 129.0, 128.1, 127.7, 126.6, 118.7, 85.4, 60.4, 51.6, 48.0, 44.2, 39.8, 36.5, 21.4; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{79}BrN_2O_4$+$Na^+$ 565.0733, found 565.0737, $C_{29}H_{23}{}^{81}BrN_2O_4$+$Na^+$ 567.0713, found 567.0723.

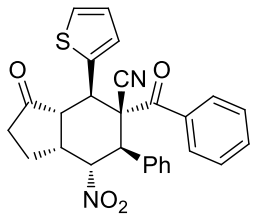


Synthesis of 12e: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(3-bromophenyl)acrylonitrile (31.0 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12e**: 43.9 mg, as a white solid, yield 81%; $[\alpha]_D^{25}$ = +85.0 (*c* = 0.28 in $CHCl_3$); 90:10 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 14.70 min, t (major) = 28.45 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ*

(ppm) 7.43–7.23 (m, 9H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 7.6 Hz, 2H), 5.91 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 3.70–3.66 (m, 1H), 3.45–3.32 (m, 2H), 2.67 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.58–2.47 (m, 1H), 2.42–2.33 (m, 1H), 2.04–2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 211.3, 195.9, 136.7, 133.5, 132.5, 132.1, 130.3, 129.4, 129.0, 127.7, 126.9, 122.8, 117.8, 85.2, 61.7, 49.2, 47.4, 46.4, 39.5, 36.5, 21.1; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{79}BrN_2O_4$+$Na^+$ 565.0733, found 565.0733, $C_{29}H_{23}{}^{81}BrN_2O_4$+$Na^+$ 567.0713, found 567.0718.

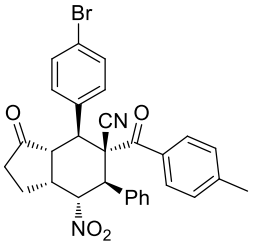


Synthesis of 12f: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(4-bromophenyl)acrylonitrile (31.0 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12f**: 42.8 mg, as a white solid, yield 79%; $[\alpha]_D^{25}$ = +92.0 (*c* = 0.15 in $CHCl_3$); 96.5:3.5 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 13.98 min, t (major) = 49.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43–7.41 (m, 4H), 7.33–7.21 (m, 6H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 8.0 Hz, 2H), 5.91 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.40 (d, *J* = 12.4 Hz, 1H), 3.72–3.69 (m, 1H), 3.45–3.32 (m, 2H), 2.69–2.48 (m, 2H), 2.42–2.33 (m, 1H), 2.04–1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 211.5, 196.0, 136.7, 132.5, 132.3, 132.1, 131.3, 129.4, 129.4, 129.0, 127.7, 126.8, 123.2, 117.9, 85.2, 61.6, 49.3, 47.4, 46.3, 39.5, 36.5, 21.1; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{79}BrN_2O_4$+$Na^+$ 565.0733, found 565.0731, $C_{29}H_{23}{}^{81}BrN_2O_4$+$Na^+$ 567.0713, found 567.0717.

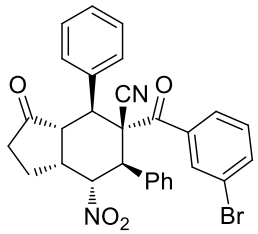


Synthesis of 12g: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-benzoyl-3-(thiophen-2-yl)acrylonitrile (23.9 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–

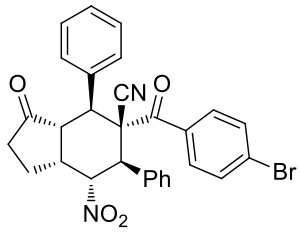
1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12g**: 37.1 mg, as a white solid, yield 79%; $[\alpha]_D^{25}$ = +35.2 (*c* = 0.75 in $CHCl_3$); 91.5:8.5 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 18.02 min, t (major) = 53.62 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.42–7.40 (m, 2H), 7.31–7.21 (m, 5H), 7.06–7.01 (m, 3H), 6.91 (dd, *J* = 5.2 Hz, *J* = 3.6 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 2H), 5.90 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.40 (d, *J* = 12.4 Hz, 1H), 4.01 (d, *J* = 13.2 Hz, 1H), 3.41–3.27 (m, 2H), 2.72–2.65 (m, 1H), 2.57–2.46 (m, 1H), 2.41–2.33 (m, 1H), 2.02–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 210.9, 196.3, 136.9, 135.5, 132.6, 132.4, 129.4, 129.3, 128.5, 127.7, 127.0, 126.8, 126.3, 117.9, 85.2, 62.5, 51.4, 47.2, 42.7, 39.7, 36.3, 21.0; ESI-HRMS: calcd. for $C_{27}H_{22}N_2O_4S+Na^+$ 493.1192, found 493.1188.



Synthesis of 12h: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-3-(4-bromophenyl)-2-(4-methylbenzoyl)acrylonitrile (32.5 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12h**: 45.6 mg, as a white solid, yield 82%; $[\alpha]_D^{25}$ = +85.0 (*c* = 0.24 in $CHCl_3$); 96:4 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 13.56 min, t (major) = 46.91 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.42–7.39 (m, 4H), 7.31–7.20 (m, 5H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 8.0 Hz, 2H), 5.91 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 3.72–3.69 (m, 1H), 3.44–3.31 (m, 2H), 2.68–2.48 (m, 2H), 2.42–2.32 (m, 1H), 2.19 (s, 3H), 2.03–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.6, 195.3, 143.7, 134.1, 132.6, 132.3, 132.0, 131.2, 129.4, 129.3, 129.0, 128.5, 127.1, 123.1, 118.0, 85.2, 61.4, 49.3, 47.3, 46.1, 39.5, 36.5, 21.5, 21.1; ESI-HRMS: calcd. for $C_{30}H_{25}{}^{79}BrN_2O_4+Na^+$ 579.0890, found 579.0891, $C_{30}H_{25}{}^{81}BrN_2O_4+Na^+$ 581.0869, found 581.0873.

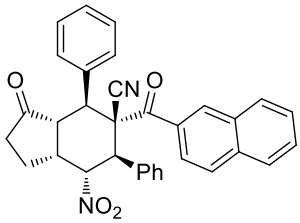


Synthesis of 12i: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-(3-bromobenzoyl)-3-phenylacrylonitrile (31.0 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12i**: 45.0 mg, as a white solid, yield 83%; 17:1 dr, $[\alpha]_D^{25}$ = +55.5 (*c* = 0.22 in $CHCl_3$); 95:5 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 27.17 min, t (major) = 54.73 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.41–7.33 (m, 11H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 6.09 (d, *J* = 7.6 Hz, 1H), 5.90 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 3.71–3.68 (m, 1H), 3.43 –3.37 (m, 2H), 2.66 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.60–2.49 (m, 1H), 2.42–2.32 (m, 1H), 2.04–1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.4, 195.5, 138.5, 134.9, 134.9, 133.0, 132.5, 129.5, 129.3, 129.2, 129.1, 124.6, 124.6, 121.8, 117.7, 85.3, 62.5, 49.4, 47.3, 46.9, 39.5, 36.4, 21.1; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{79}BrN_2O_4$+$Na^+$ 565.0733, found 565.0734, $C_{29}H_{23}{}^{81}BrN_2O_4$+$Na^+$ 567.0713, found 567.0707.



Synthesis of 12j: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-(4-bromobenzoyl)-3-phenylacrylonitrile (31.0 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12j**: 43.9 mg, as a white solid, yield 81%; $[\alpha]_D^{25}$ = +56.0 (*c* = 0.2 in $CHCl_3$); 91:9 er, determined by HPLC analysis [Daicel chiralcel OD-H, *n*-hexane/*i*-

PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 15.55 min, t (major) = 37.73 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.41–7.30 (m, 10H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.16 (d, *J* = 8.4 Hz, 2H), 5.91 (dd, *J* = 12.8, 5.6 Hz, 1H), 4.20 (d, *J* = 12.4 Hz, 1H), 3.72–3.69 (m, 1H), 3.43–3.37 (m, 2H), 2.69–2.49 (m, 2H), 2.41–2.32 (m, 1H), 2.03–1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.4, 195.6, 135.6, 133.0, 132.6, 131.0, 129.4, 129.1, 129.0, 128.1, 127.5, 117.9, 85.3, 62.1, 49.4, 47.3, 46.8, 39.5, 36.4, 21.1; ESI-HRMS: calcd. for $C_{29}H_{23}{}^{79}BrN_2O_4$+$Na^+$ 565.0733, found 565.0731, $C_{29}H_{23}{}^{81}BrN_2O_4$+$Na^+$ 567.0713, found 567.0717.



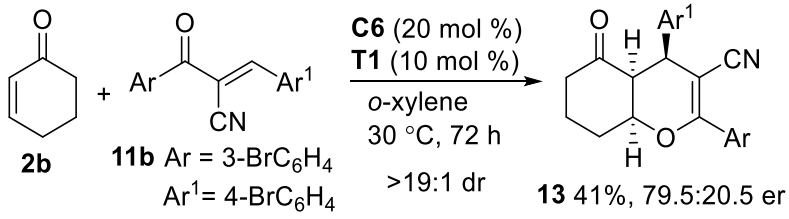
Synthesis of 12k: A solution of 2-cyclopentenone **1a** (16.4 mg, 0.2 mmol), (*E*)-2-(2-naphthoyl)-3-phenylacrylonitrile (28.3 mg, 0.1 mmol), quinine **C6** (6.4 mg, 0.02 mmol), thiol **T1** (1.5 mg, 0.01 mmol) in *o*-xylene (1.0 mL) was stirred at 30 ℃ for 48 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12–1/9). After that, the activated alkene **4a** (14.9 mg, 0.1 mmol), DIPEA (12.9 mg, 0.1 mmol) and *o*-xylene (1.0 mL) were added and the reaction was stirred at 50 ºC for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/9–1/7) gave product **12k**: 41.6 mg, as a white solid, yield 81%; $[\alpha]_D^{25}$ = +64.0 (*c* = 0.5 in $CHCl_3$); 90:10 er, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 12.31 min, t (major) = 21.15 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.63–7.61 (m, 2H), 7.47–7.36 (m, 7H), 7.34–7.25 (m, 5H), 6.72 (s, 1H), 6.46 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.95 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.51 (d, *J* = 12.8 Hz, 1H), 3.78 (d, *J* = 12.8 Hz, 1H), 3.49–3.39 (m, 2H), 2.72–2.54 (m, 2H), 2.43–2.33 (m, 1H), 2.05–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 211.6, 196.2, 134.5, 134.3, 133.3, 132.9, 131.2, 129.4, 129.3, 129.0, 128.5, 128.4, 127.6, 127.4, 126.7, 122.5, 118.1, 85.4, 62.3, 49.5, 47.4, 46.9, 39.6, 36.4, 21.1; ESI-HRMS: calcd. for $C_{33}H_{26}N_2O_4$+Na^+ 537.1785, found 537.1786.

8. Reaction at a 1.0 mmol scale

A solution of 2-cyclopentenone **1a** (164 mg, 2.0 mmol), (*E*)-2-benzoyl-3-(4-bromophenyl) acrylonitrile (310 mg, 1.0 mmol), quinine **C6** (64 mg, 0.2 mmol), thiol **T1** (15 mg, 0.1 mmol) in *o*-xylene (10.0 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. After completion, the intermediate was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10).

Then the activated alkene **4a** (149 mg, 1.0 mmol), *N*,*N*-diisopropylenthylamine (DIPEA, 129 mg, 1.0 mmol) and *o*-xylene (10.0 mL) were added and the reaction was stirred at 50 ºC for 48 h (monitored by TLC). After completion, the product **12f** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/8): 406 mg, as a white solid, yield 75%, 94.5:5.5 er.

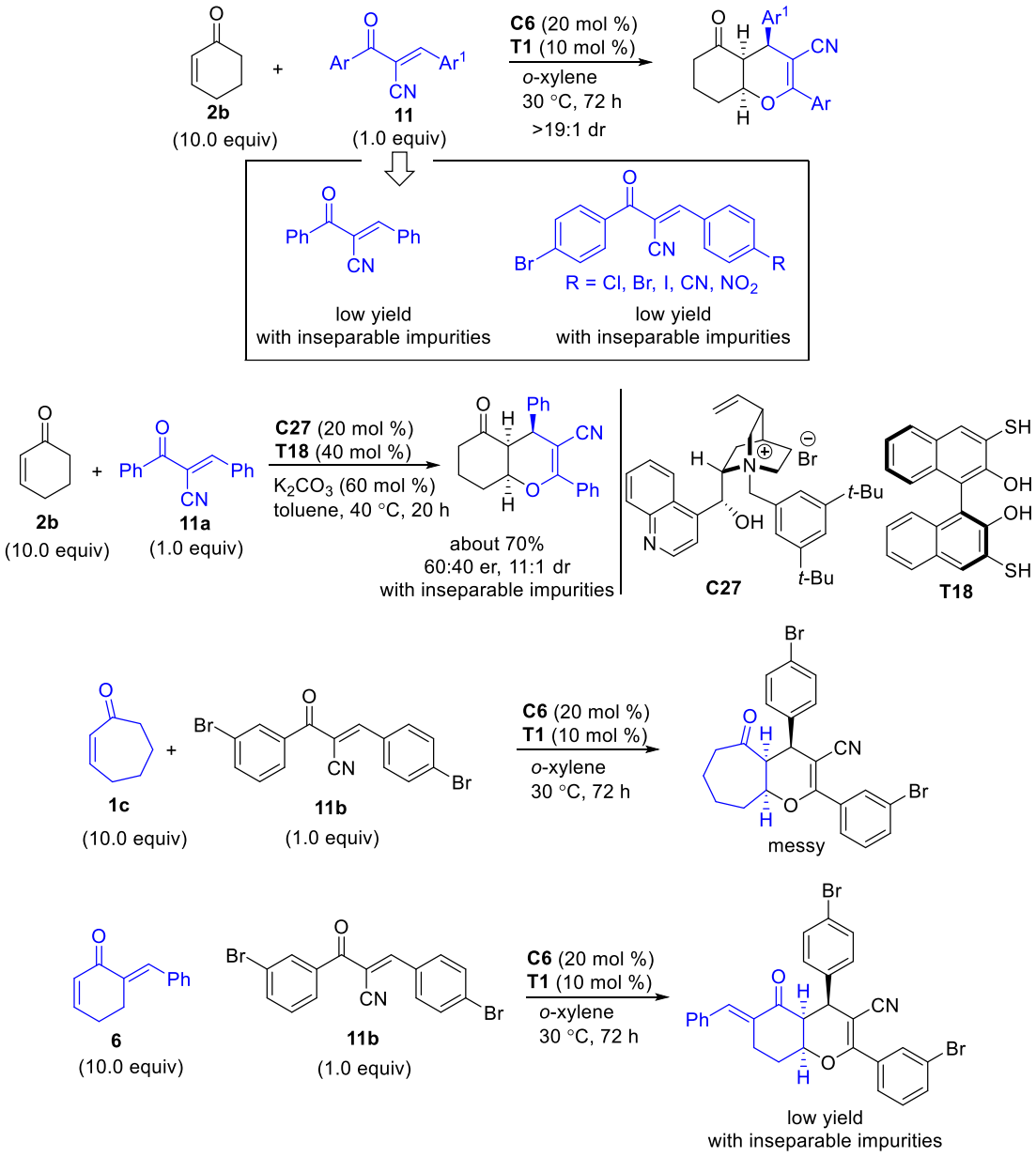
9. Procedure for the cross RC reaction-initiated [4 + 2] annulation



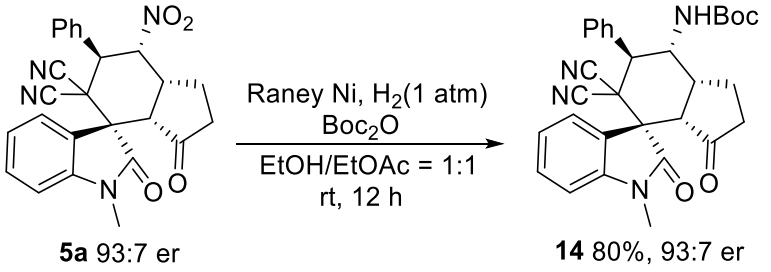
A solution of 2-cyclohexenone **2b** (1.0 mmol, 10.0 equiv), α-cyanochalcone **11b** (0.1 mmol, 1.0 equiv), quinine **C6** (20 mol %), thiol **T1** (10 mol %) in *o*-xylene (0.4 mL) was stirred at 30 ℃ for 72 h. The reaction was monitored by TLC. The product **13** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether): 20.8 mg, as a white solid, yield 41%; $[\alpha]_D^{25}$ = +84.0 (*c* = 0.3 in $CHCl_3$); 79.5:20.5 er, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 8.85 min, t (major) = 20.00 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.83 (m, 1H), 7.81–7.78 (m, 1H), 7.62–7.59 (m, 1H), 7.53–7.50 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.15–7.12 (m, 2H), 4.59 (d, *J* = 2.8 Hz, 1H), 4.48 (s, 1H), 2.73 (d, *J* = 3.2 Hz, 1H), 2.56–2.52 (m, 1H), 2.44–2.36 (m, 2H), 2.07–2.03 (m, 2H), 1.95–1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.2, 164.0, 140.4, 134.3, 134.0, 132.3, 130.9, 129.9, 129.7, 127.0, 122.4, 121.8, 118.9, 85.0, 74.4, 54.3, 40.7, 37.6, 29.2, 21.6; ESI-HRMS: calcd. for $C_{22}H_{17}{}^{79}BrNO_2$+$Na^+$ 507.9518, found 507.9516. $C_{22}H_{17}{}^{81}BrNO_2$+$Na^+$ 509.9498, found 509.9503.

10. More attempts for the cross RC reaction-initiated [4 + 2] annulations

The [4 + 2] annulation reactions between 2-cyclohexenone **2b** and α-cyano chalcone derivatives **11** generally proceeded not well, and excess **2b** (10.0 equiv) was required for better conversions. For simple α-cyano chalcone **11a**, the desired product could not be isolated due to the low yield and some inseparable impurities. Similar phenomena were observed for some other α-cyano chalcone derivatives **11** with electron-withdrawing groups on the phenyl ring. We have made efforts to optimize the reaction conditions by employing **11a** as the substrate, and a better yield with a low er value was obtained under the catalysis of **C27** and **T18**. In addition, cyclohept-2-enone **1c** and α′-benzylidene 2-cyclopentenone **6** were also applied to the [4 + 2] annulation, but the reaction were not satisfactory.

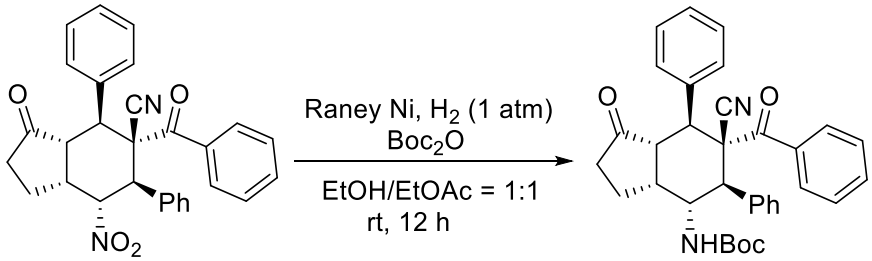


11. Synthetic transfomations of the annulation products 5a and 12a



A solution of **5a** (0.1 mmol, 44.0 mg, 93:7 er), Boc_2O (0.15 mmol, 32.7 mg) in the solvent of EtOH (0.5 mL) and EtOAc (0.5 mL) was combined with Raney Ni (W2; 50.0 mg, wet weight). The mixture was stirred at room temperature under hydrogen (1 atm) for 12 h. The mixture was filtered through a bed of celite and concentrated under reduced pressure. The residue was purified by flash

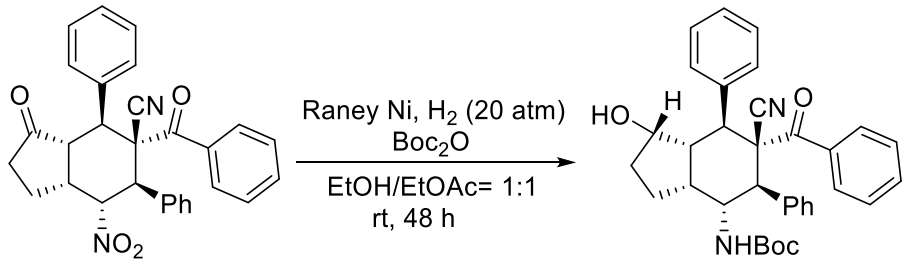
chromatography (EtOAc/petroleum ether = 1:5) to gived compound **14**: 40.8 mg, as a white solid, yield 80%; $[\alpha]_D^{25}$ = +66.2 (*c* = 0.65 in $CHCl_3$); 93:7 er, determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 8.04 min, t (major) = 9.17 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H), 7.56–7.50 (m, 2H), 7.49–7.35 (m, 4H), 7.28–7.22 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 5.14–5.09 (m, 1H), 4.74 (brs, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 3.40–3.26 (m, 1H), 3.22 (d, *J* = 9.3 Hz, 1H), 3.18 (s, 3H), 2.67–2.56 (m, 1H), 2.45–2.38 (m, 1H), 2.31–2.21 (m, 1H), 2.11–2.04 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 214.8, 173.1, 155.1, 143.3, 133.2, 130.9, 129.7, 129.4, 129.0, 126.2, 124.7, 124.2, 112.1, 111.5, 109.2, 80.1, 53.3, 49.3, 49.1, 48.3, 42.8, 39.4, 38.5, 28.2, 26.9, 22.4; ESI-HRMS: calcd. for $C_{30}H_{30}N_4O_4$+Na^+ 533.2159, found 533.2158.



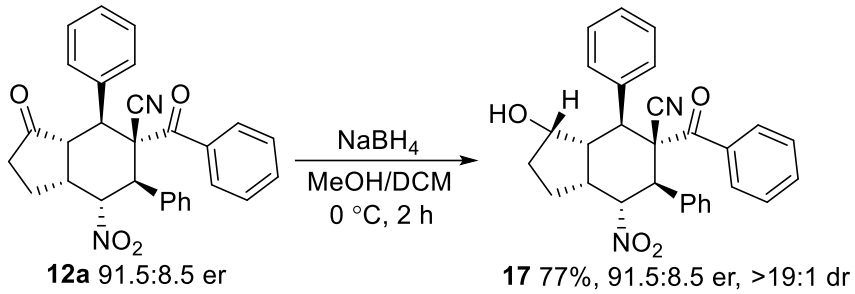
12a 91.5:8.5 er

15 87%, 91.5:8.5 er

A solution of **12a** (0.1 mmol, 46.4 mg, 91.5:8.5 er), Boc_2O (0.15 mmol, 32.7 mg) in the solvent of EtOH (0.5 mL) and EtOAc (0.5 mL) was combined with Raney Ni (W2; 50.0 mg, wet weight). The mixture was stirred at room temperature under hydrogen (1 atm) for 12 h. The mixture was filtered through a bed of celite and condensed under reduced pressure. The residue was purified by flash chromatography (EtOAc/petroleum ether = 1:5) to gived compound **15**: 46.4 mg, as a white solid, yield 87%; $[\alpha]_D^{25}$ = +37.1 (*c* = 0.75 in $CHCl_3$); 91.5:8.5 er, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 8.95 min, t (major) = 10.13 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47–7.20 (m, 10H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.9 Hz, 2H), 6.31–6.22 (m, 2H), 5.04 (brs, 1H), 4.32 (d, *J* = 8.5 Hz, 1H), 3.69 (d, *J* = 12.7 Hz, 1H), 3.62 (d, *J* = 13.3 Hz, 1H), 3.31 (dd, *J* = 13.3, 6.5 Hz, 1H), 3.17–3.14 (m, 1H), 2.63–2.51 (m, 1H), 2.41–2.13 (m, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.9, 198.0, 155.0, 137.5, 134.4, 134.3, 131.8, 129.9, 128.9, 128.8, 128.6, 127.4, 126.6, 118.3, 80.0, 63.6, 50.5, 49.8, 46.9, 40.3, 36.6, 28.2, 20.3; ESI-HRMS: calcd. for $C_{34}H_{34}N_2O_4$+Na^+ 557.2411, found 557.2409.

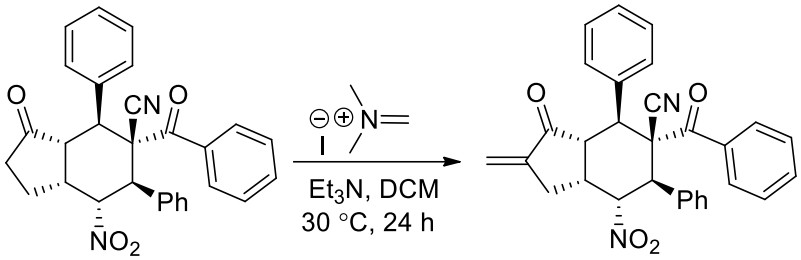


A solution of **12a** (0.1 mmol, 46.4 mg, 91.5:8.5 er), Boc_2O (0.15 mmol, 32.7 mg) in the solvent of EtOH (0.5 mL) and EtOAc (0.5 mL) was combined with Raney Ni (W2; 50.0 mg, wet weight). The mixture was stirred at room temperature under hydrogen (20 atm) for 48 h. The mixture was filtered through a bed of celite and condensed under reduced pressure. The residue was purified by flash chromatography (EtOAc/petroleum ether = 1:4) to gived compound **16**: 44.0 mg, as a white solid, yield 82%; $[\alpha]_D^{25}$ = –12.6 (*c* = 0.35 in $CHCl_3$); 91.5:8.5 er, >19:1 dr, determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 8.67 min, t (minor) = 12.18 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51–7.00 (m, 11H), 6.85 (t, *J* = 7.7 Hz, 2H), 6.18 (d, *J* = 7.8 Hz, 2H), 4.81 (brs, 1H), 4.37–4.33 (m, 2H), 3.69–3.60 (m, 2H), 3.17–3.02 (m, 1H), 2.96–2.82 (m, 1H), 2.10–2.07 (m, 1H), 2.00–1.85 (m, 1H), 1.81–1.72 (m, 2H), 1.22 (s, 9H), 0.67 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.9, 155.1, 138.2, 137.9, 135.1, 130.0, 129.1, 128.8, 128.3, 128.1, 127.3, 126.6, 119.0, 79.5, 76.0, 64.4, 50.9, 49.7, 47.1, 44.5, 40.0, 28.2, 20.9; ESI-HRMS: calcd. for $C_{34}H_{37}N_2O_4+H^+$ 537.2748, found 537.2750.



To a solution of **12a** (0.1 mmol, 46.4 mg, 91.5:8.5 er) in the solvent of MeOH (0.5 mL) and DCM (0.5 mL) was added $NaBH_4$ (0.15 mmol, 5.7 mg) at 0 ℃. After 2 h, the mixture was quenched with saturated NH_4Cl solution. The phases were separated and the aqueous phase was extracted with DCM (2 × 5 mL). The combined organic phases were washed with brine (10 mL) before being dried (Na_2SO_4) and concentrated in vacuum. The residue was purified by flash chromatography (EtOAc/petroleum ether = 1:6) to gived compound **17**: 35.9 mg, as a white solid, yield 77%; $[\alpha]_D^{25}$ = –26.7 (*c* = 0.15 in $CHCl_3$); 91.5:8.5 er, >19:1 dr, determined by HPLC analysis [Daicel chiralpak AD-

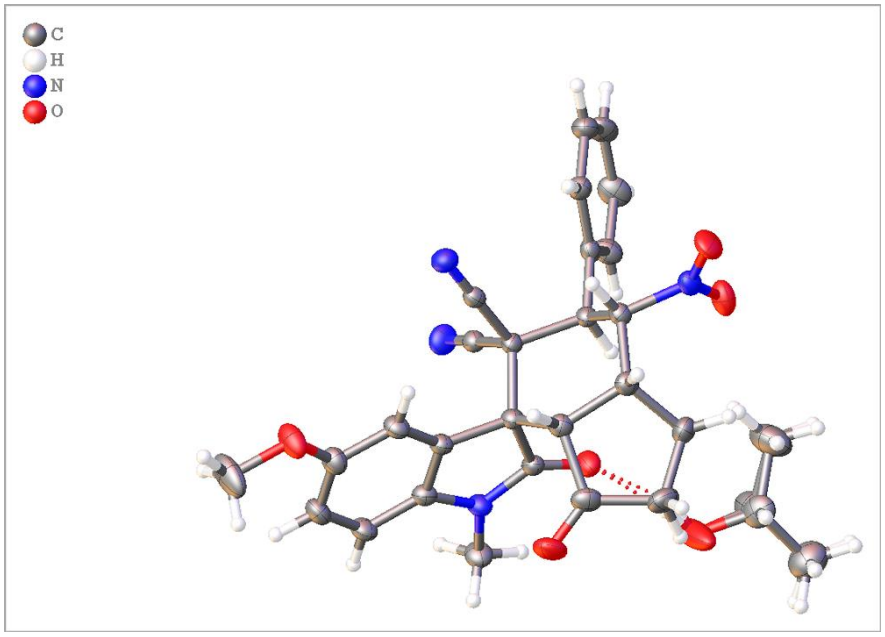
H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (major) = 6.88 min, t (minor) = 10.74 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.38–7.14 (m, 10H), 7.13–7.08 (m, 1H), 6.86 (t, *J* = 7.9 Hz, 2H), 6.19 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.72 (dd, *J* = 12.6, 5.8 Hz, 1H), 4.48–4.42 (m, 1H), 4.31 (d, *J* = 12.6 Hz, 1H), 3.79 (d, *J* = 12.6 Hz, 1H), 3.30–3.23 (m, 1H), 3.10–3.02 (m, 1H), 2.33–2.22 (m, 1H), 2.19–2.10 (m, 1H), 1.88–1.79 (m, 1H), 1.60–1.51 (m, 1H), 0.64 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (ppm) 197.6, 137.5, 137.6, 133.5, 132.3, 129.7, 128.8, 127.8, 127.0, 119.0, 86.4, 76.1, 63.4, 47.4, 47.4, 44.8, 40.8, 30.6, 21.6; ESI-HRMS: calcd. for $C_{29}H_{26}N_2O_4$+Na^+ 489.1785, found 489.1786.

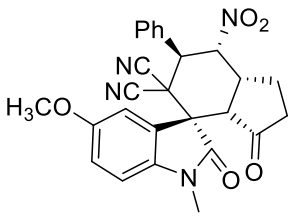


12a 91.5:8.5 er **18** 86%, 91.5:8.5 er

To a solution of **12a** (0.1 mmol, 46.4 mg, 91.5:8.5 er) in dry DCM (1.0 mL) was added Et_3N (0.2 mmol, 20.2 mg) at room temperature. The mixture was stirred for 15 min and Eschensomer′s salt (0.2 mmol, 37 mg) was added, and then continuously stirred for 24 h at 30 ℃. The mixture was quenched with saturated NH_4Cl solution. The phases were separated and the aqueous phase was extracted with DCM (2 × 5 mL). The combined organic phases were washed with brine (10 mL) before being dried (Na_2SO_4) and concentrated in vacuum. The residue was purified by flash chromatography (EtOAc/petroleum ether = 1:12) to gived compound **18**: 41.1 mg, as a white solid, yield 86%; $[\alpha]_D^{25}$ = +46.8 (*c* = 0.8 in MeOH); 91.5:8.5 er, determined by HPLC analysis [Daicel chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL min^{-1}, λ = 254 nm]: t (minor) = 12.32 min, t (major) = 14.68 min]; ^{1}H NMR (400 MHz, CD_3OD): *δ* (ppm) 7.47–7.46 (m, 3H), 7.35–7.20 (m, 8H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.30 (d, *J* = 7.6 Hz, 2H), 6.09–6.04 (m, 2H), 5.61 (s, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.61 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.49–3.45 (m, 1H), 3.40–3.32 (m, 1H), 2.62 (dd, *J* = 16.4, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): *δ* (ppm) 200.8, 196.2, 142.0, 137.3, 134.0, 133.4, 131.7, 128.8, 128.7, 128.4, 128.3, 127.1, 126.5, 120.3, 117.8, 85.2, 62.1, 53.4, 49.7, 36.8, 27.5; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_4$+Na^+ 499.1628, found 499.1624.

12. Crystal data and structure refinement for enantiopure 5g and 12f

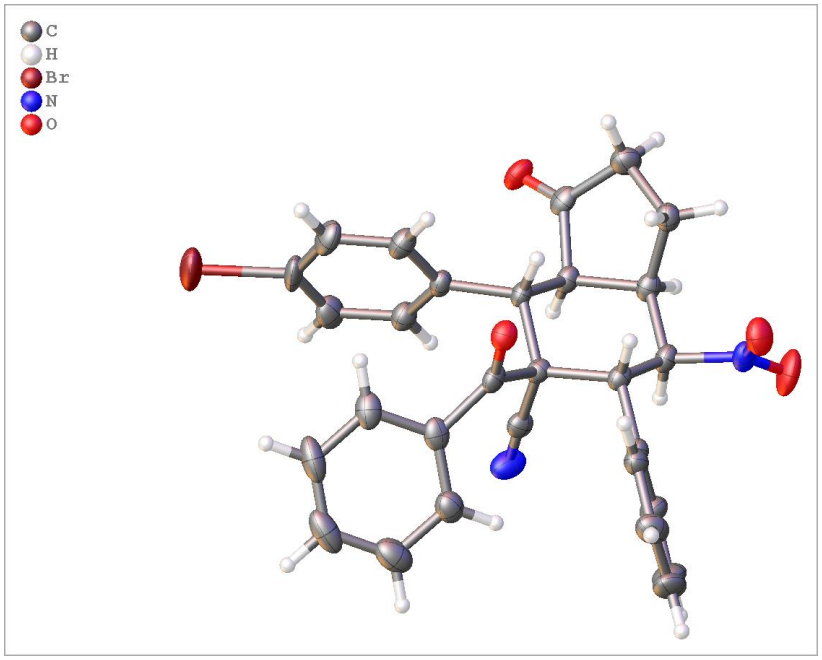


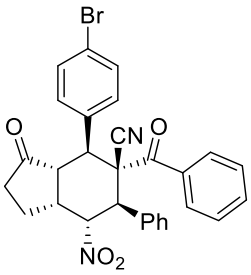


5g

Identification code	**5g** (CCDC 1877057)
Empirical formula	$C_{29}H_{30}N_4O_6$
Formula weight	530.57
Temperature/K	136
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.25485(18)
b/Å	9.9771(2)
c/Å	29.5378(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2727.40(9)
Z	4
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.754
F(000)	1120.0
Crystal size/mm^3	0.5 × 0.4 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.356 to 134.152
Index ranges	$-10 \le h \le 11$, $-11 \le k \le 11$, $-25 \le l \le 35$
Reflections collected	14563
Independent reflections	4852 [R_{int} = 0.0372, R_{sigma} = 0.0337]
Data/restraints/parameters	4852/0/364

Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.1159
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1190
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.25
Flack parameter	0.09(10)





12f

Identification code	**12f** (CCDC 1877058)
Empirical formula	$C_{29}H_{23}BrN_2O_4$
Formula weight	543.40
Temperature/K	142
Crystal system	orthorhombic
Space group	P212121
a/Å	7.6578(2)
b/Å	11.9171(4)
c/Å	27.6310(7)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2521.56(13)
Z	4
ρcalcg/cm^3	1.431
μ/mm^{-1}	2.536
F(000)	1112.0
Crystal size/mm^3	0.65 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.802 to 145.462
Index ranges	-5 ≤ h ≤ 9, -13 ≤ k ≤ 14, -34 ≤ l ≤ 22
Reflections collected	11266
Independent reflections	4854 [R_{int} = 0.0326, R_{sigma} = 0.0371]

Data/restraints/parameters	4854/0/325
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1472
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1501
Largest diff. peak/hole / e $Å^{-3}$	1.23/-0.96
Flack parameter	-0.005(12)

13. DFT calculations of the key intermediates for the asymmetric cross Rauhut–Currier reaction and proposed catalytic mechanism

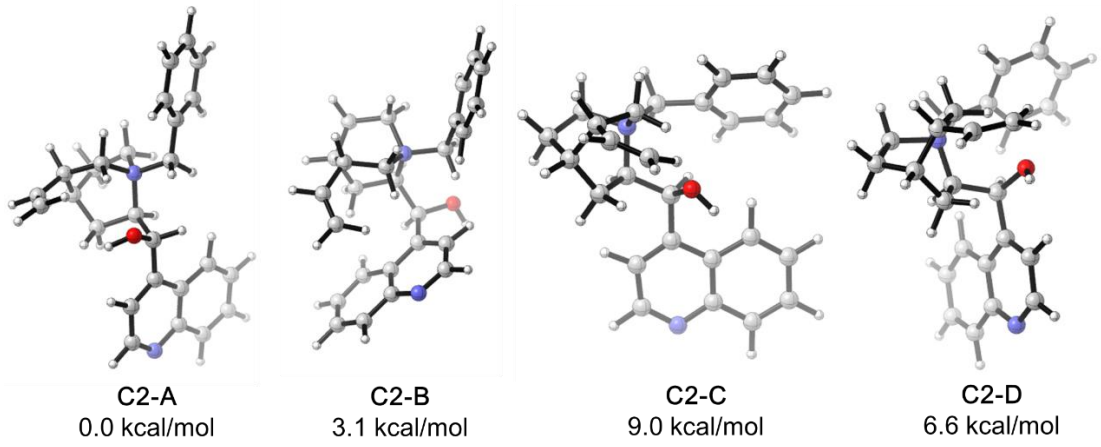
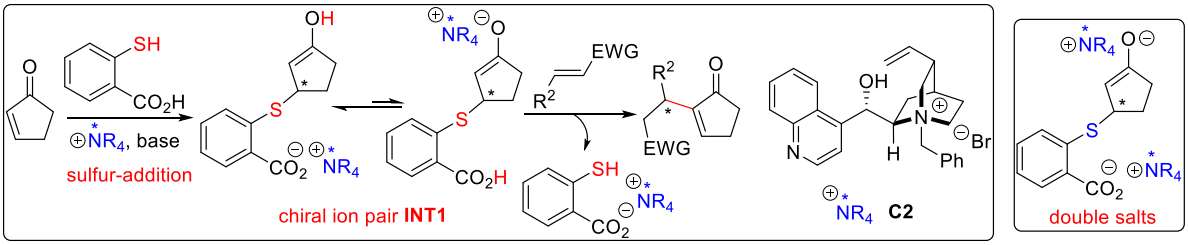


Figure S1. The conformations and energies of PTC C2.

The conformations and energies of chiral PTC **C2** were calculated as outlined Figure S1. The structure as **C2-A** with the lowest energy was selected as the most favorable conformation for the following calculations.



We have investigated the possible double salts after the early sulfur addition to enone **1a**. However, we could not identify any stable intermediate assembled from enone **1a**, thiol **T1** and two equivalent of ammonium cation of **C2**. Therefore, it suggests that the double salt might be unstable and not be generated in the catalytic process. In contrast, we could successfully identify the complexes assembled from one equivalent of enone **1a**, thiol **T1** and PTC **C2**. As shown in the following Figure S2, the carboxylic anion might be better to combine with cation center of **C2**, because the energy of **INT1-*R*-A** is 8.9 kcal/mol higher that of **INR1-*R*-B**. We also tried different complex conformations, while their energies are higher than that of **INR1-*R*-B**. To explain the stereoselectivity, the pose employing the lowest energy of *S*-configuration (sulfide moiety) was calculated as **INT1-*S*-*B***, whose energy was 2.0 kcal/mol lower than **INT1-*R*-B**, suggesting that the **C2**-catalyzed sulfur addition of **T1** to enone **1a** prefers to produce *S*-intermediate, which might be the key species for the subsequent stereoselective RC reaction. In addition, the enolate anion-complexed one **INT1-*S*-*A*** also has a higher

energy than that of the carboxylic anion-related **INT1-*S*-*B***. *Nevertheless, **INT1-S-A** might be the more reliable active intermediate involved in the key RC reaction*.

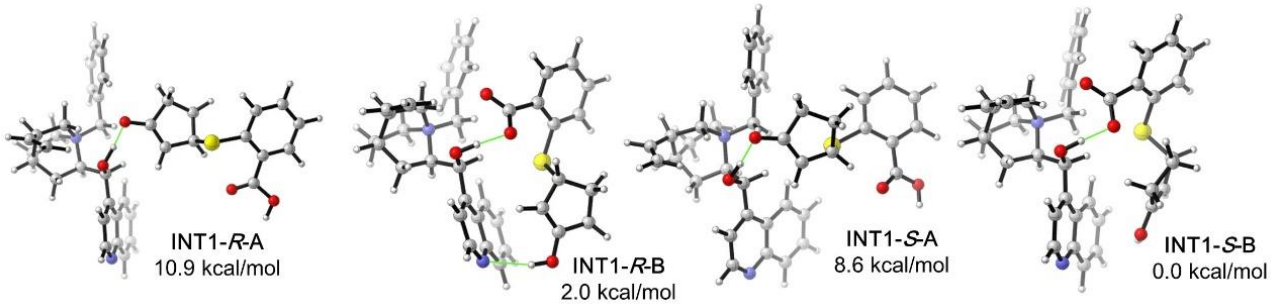
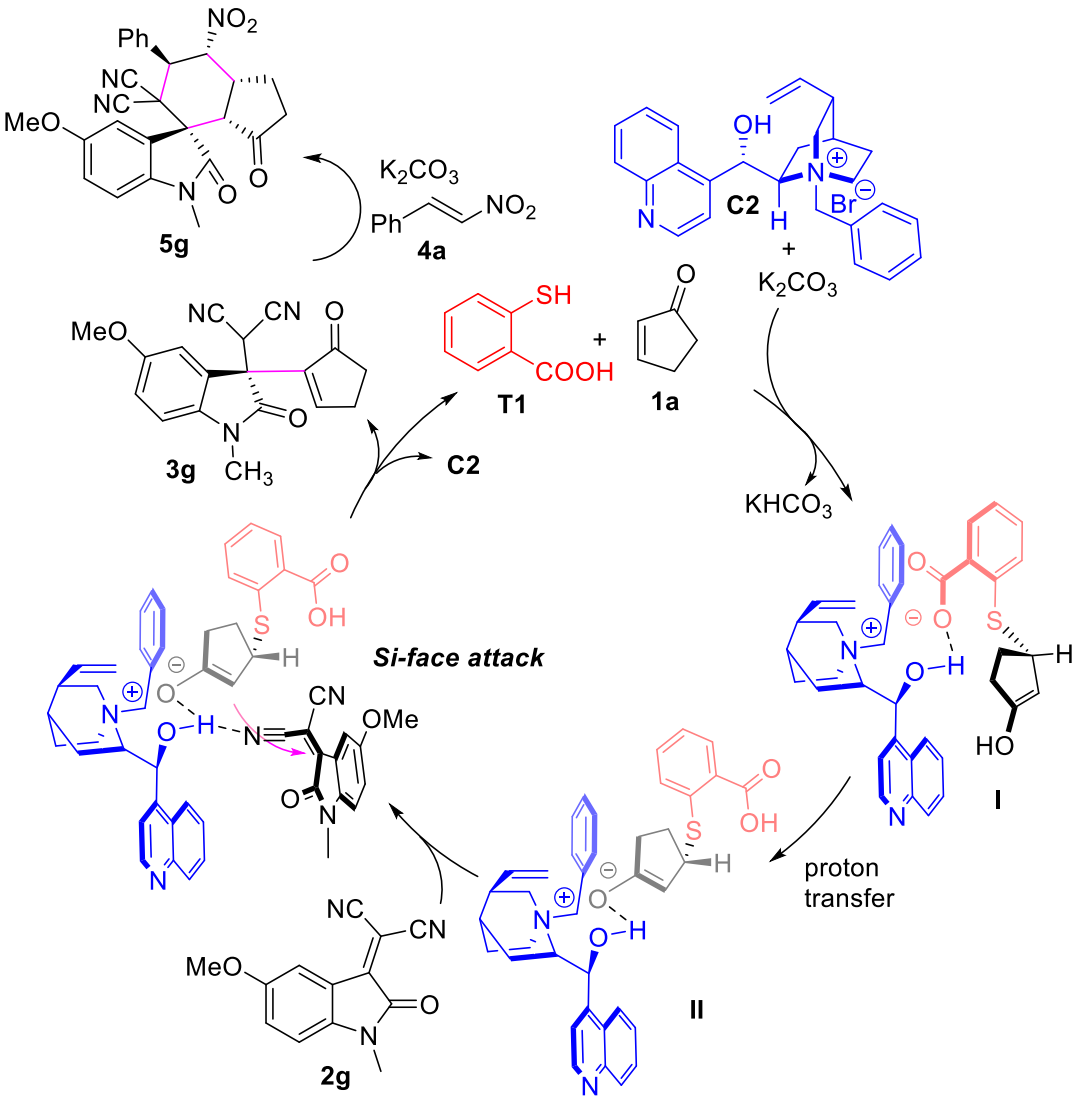


Figure S2. The structures and energies of the key ion pair INT1.

Since the subsequent addition of the chiral intermediate **INT1-*S*-A** to activated alkene **2** would generate the complicated intermediate with three stereogenic centers, and there are a lot of conformation possibilities for the ion pairs in the PTC-based reaction, we were unable to successfully conduct the DFT calculation studies on the following catalytic process [in fact, in comparison with well-established Lewis base catalysis (covalent bonding catalysis), there are very few examples involving DFT calculations of PTC catalysis; for a relatively simple asymmetric alkylation reaction, see: Petrova, G. P.; Li, H.-B.; Maruoka, K.; Morokuma, K. *J. Phys. Chem. B* **2014**, *118*, 5154]. As a result, based on the preliminary DFT calculations, a possible catalytic mechanism was proposed. As outlined in the following scheme, in the presence of PTC **C2** and K_2CO_3, **T1** attacks enone **1a** from *Si*-face, generating carboxylate ion pair intermediate **I**. After proton transfer, the more reactive enolate ion pair intermediated **II** is formed, followed by another *Si*-face attack to acceptor **2g**. Then **3g** is afforded after elimination of thiol **T1**, and then undergoes diastereoselective Michael addition and annulation with nitroolefin **4a** to give final product **5g**, with the assistance of bases.



Proposed mechanism for the double activation catalysis

Computational method:

All calculations were carried out with the GAUSSIAN 09 packages.[2] The M06-2X functional, together with a basis set 6-31G(d), were used for optimizing the geometry of all the minima and transition states. All the optimized structures were confirmed by frequency calculations to minima states using the same level of theory. To take solvent effects into account, solution-phase single-point calculations were performed on the gas-phase geometries.[3] The solution-phase single point energy were done using M06-2X method with a basis set 6-311++G(2d,p). Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using SMD model and UAKS radii.[4] Toluene was used as the solvent. Solution-phase single-point energies corrected by the gas-phase Gibbs free energy corrections were used to describe all the reaction energetics. All of these energies correspond

to the reference state of 1 mol/L, 298 K. All energetics reported throughout the text are in kcal/mol. Structures were generated using GaussView5.0.8 and CYLview.

(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Gaussian, Inc.: Wallingford, CT, USA, 2009.
(3) Um, J. M.; DiRocco, D. A.; Noey, E. L.; Rovis, T.; Houk, K. N. *J. Am. Chem. Soc.* **2011,***133*, 11249–11254.
(4) (a) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**,*113*, 6378–6396. (b) Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2011**,*115*, 14556–14562.

Computational data:

C2-A

Zero-point correction= 0.507703 (Hartree/Particle)
Thermal correction to Energy= 0.531230
Thermal correction to Enthalpy= 0.532174
Thermal correction to Gibbs Free Energy= 0.454412
E(sov) = -1192.63956251 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.402282	1.218742	-1.885185
2	6	0	0.918140	0.210332	-1.047973
3	6	0	0.269875	0.254091	0.356339

4	7	0	-1.266854	0.152375	0.346896
5	6	0	-1.690912	-0.199375	1.756048
6	6	0	-1.094652	0.809697	2.755348
7	6	0	-1.927513	1.468122	-0.008969
8	6	0	-1.566714	2.560010	1.018434
9	6	0	-1.105292	3.858716	0.399399
10	6	0	-1.077396	4.199654	-0.889478
11	6	0	-0.505484	1.994415	1.984307
12	6	0	0.681217	1.499931	1.162062
13	6	0	2.427916	0.242901	-0.875919
14	6	0	3.116462	-0.899646	-0.360822
15	6	0	2.504211	-2.156562	-0.096952
16	6	0	3.237168	-3.206617	0.401069
17	6	0	4.619743	-3.057821	0.665649
18	6	0	5.245113	-1.865654	0.402371
19	6	0	4.515513	-0.767882	-0.124491
20	7	0	5.210331	0.374380	-0.393398
21	6	0	4.555030	1.380219	-0.911008
22	6	0	3.158668	1.365007	-1.169574
23	6	0	-3.161275	-1.309987	-0.567901
24	6	0	-3.584748	-2.360123	0.253764
25	6	0	-4.925222	-2.734643	0.286333
26	6	0	-5.853715	-2.068042	-0.512410
27	6	0	-5.437362	-1.037105	-1.353053
28	6	0	-4.095579	-0.664537	-1.384511
29	6	0	-1.705964	-0.929084	-0.633516
30	1	0	0.695737	2.095846	-1.588588
31	1	0	0.660441	-0.724224	-1.553164
32	1	0	0.577552	-0.648822	0.894430
33	1	0	-2.782427	-0.191226	1.754554
34	1	0	-1.356737	-1.223339	1.943568
35	1	0	-0.313029	0.333780	3.355736
36	1	0	-1.875840	1.142949	3.444235
37	1	0	-3.000273	1.268867	-0.021785
38	1	0	-1.598324	1.699976	-1.019623
39	1	0	-2.460824	2.789964	1.614776
40	1	0	-0.780420	4.597645	1.133355
41	1	0	-0.738934	5.187243	-1.186635
42	1	0	-1.412581	3.550702	-1.695321
43	1	0	-0.186358	2.776490	2.679518
44	1	0	1.529971	1.237906	1.800439
45	1	0	1.026531	2.301669	0.499133
46	1	0	1.452788	-2.315617	-0.324194
47	1	0	2.757241	-4.164219	0.579174
48	1	0	5.183975	-3.896693	1.060912

49	1	0	6.307420	-1.721938	0.572910
50	1	0	5.131844	2.273461	-1.141156
51	1	0	2.710081	2.250517	-1.610831
52	1	0	-2.861715	-2.902897	0.859823
53	1	0	-5.241807	-3.555082	0.922603
54	1	0	-6.897811	-2.364611	-0.493553
55	1	0	-6.153032	-0.533695	-1.995449
56	1	0	-3.770209	0.119254	-2.066085
57	1	0	-1.072176	-1.795126	-0.414794
58	1	0	-1.457043	-0.542099	-1.624287

C2-B

Zero-point correction= 0.507985 (Hartree/Particle)
Thermal correction to Energy= 0.531384
Thermal correction to Enthalpy= 0.532328
Thermal correction to Gibbs Free Energy= 0.455409
E(sov) = -1192.63566738 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.029794	0.550276	-2.968068
2	6	0	0.792373	-0.108816	-2.024001
3	6	0	-0.065588	-1.219149	-1.357275
4	7	0	-1.253686	-0.827260	-0.460577
5	6	0	-2.164799	-2.037618	-0.381114
6	6	0	-1.362808	-3.298567	-0.030008
7	6	0	-0.763456	-0.513105	0.936453
8	6	0	-0.263828	-1.789544	1.635965
9	6	0	0.962421	-1.571516	2.488960
10	6	0	1.656485	-0.447420	2.664639
11	6	0	-0.018666	-2.859687	0.549398
12	6	0	0.805915	-2.209102	-0.559345
13	6	0	1.538352	0.874732	-1.123836
14	6	0	2.831139	0.586194	-0.577518
15	6	0	3.619643	-0.554584	-0.903184
16	6	0	4.843294	-0.759651	-0.316344
17	6	0	5.352285	0.158145	0.635374
18	6	0	4.638787	1.285942	0.946944
19	6	0	3.381821	1.538025	0.334982
20	7	0	2.764652	2.709907	0.654429
21	6	0	1.639921	2.990626	0.046069

22	6	0	0.993275	2.110613	-0.855998
23	6	0	-3.293327	0.714035	-0.293329
24	6	0	-4.530322	0.157511	-0.634590
25	6	0	-5.687988	0.541589	0.037670
26	6	0	-5.621320	1.496799	1.051326
27	6	0	-4.398116	2.078023	1.381009
28	6	0	-3.242449	1.691943	0.706631
29	6	0	-2.041380	0.342881	-1.044452
30	1	0	0.525498	1.062376	-3.576018
31	1	0	1.539405	-0.711029	-2.560990
32	1	0	-0.549402	-1.724335	-2.201151
33	1	0	-2.910707	-1.795971	0.378790
34	1	0	-2.671418	-2.115609	-1.346415
35	1	0	-1.206151	-3.919413	-0.918304
36	1	0	-1.929285	-3.896364	0.689669
37	1	0	-1.597877	-0.061744	1.473669
38	1	0	0.020595	0.234031	0.813508
39	1	0	-1.058791	-2.163989	2.296773
40	1	0	1.291028	-2.470141	3.011711
41	1	0	2.531257	-0.437379	3.307349
42	1	0	1.399797	0.505737	2.207754
43	1	0	0.519291	-3.711637	0.974677
44	1	0	1.208221	-2.954998	-1.252937
45	1	0	1.651158	-1.692394	-0.098709
46	1	0	3.269901	-1.273335	-1.637675
47	1	0	5.432087	-1.629151	-0.591941
48	1	0	6.318263	-0.024177	1.095735
49	1	0	5.010169	2.028825	1.645785
50	1	0	1.188245	3.954558	0.272965
51	1	0	0.075104	2.434941	-1.334391
52	1	0	-4.596089	-0.567266	-1.443579
53	1	0	-6.642992	0.105716	-0.238837
54	1	0	-6.524345	1.800164	1.571946
55	1	0	-4.344380	2.839567	2.152819
56	1	0	-2.293321	2.168438	0.948552
57	1	0	-2.254188	0.064975	-2.079113
58	1	0	-1.349488	1.179072	-1.060614

C2-C

Zero-point correction=	0.508352 (Hartree/Particle)
Thermal correction to Energy=	0.531877
Thermal correction to Enthalpy=	0.532821
Thermal correction to Gibbs Free Energy=	0.455801

E(sov) = -1192.62657014 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.033908	0.071354	1.097454
2	6	0	0.302095	-0.362925	-0.227589
3	6	0	-0.954469	-1.078632	-0.728614
4	7	0	-2.157021	-0.129099	-0.928651
5	6	0	-3.136495	-0.871164	-1.827401
6	6	0	-3.392892	-2.290580	-1.299946
7	6	0	-2.866946	0.137097	0.385045
8	6	0	-3.548243	-1.139758	0.910179
9	6	0	-3.461227	-1.307280	2.408191
10	6	0	-2.566708	-0.769161	3.236180
11	6	0	-2.940075	-2.343962	0.161540
12	6	0	-1.417700	-2.229050	0.190526
13	6	0	1.579596	-1.184086	-0.318750
14	6	0	2.800245	-0.527881	0.051859
15	6	0	2.891196	0.847195	0.413167
16	6	0	4.098930	1.398862	0.770130
17	6	0	5.276222	0.613842	0.785570
18	6	0	5.225360	-0.706408	0.416389
19	6	0	3.996386	-1.301452	0.031083
20	7	0	4.030353	-2.606242	-0.365865
21	6	0	2.910346	-3.152059	-0.757259
22	6	0	1.656325	-2.483398	-0.750753
23	6	0	-1.167020	2.323149	-0.926060
24	6	0	-1.819749	3.069877	0.061524
25	6	0	-1.197677	4.168451	0.648586
26	6	0	0.072445	4.562543	0.232733
27	6	0	0.709976	3.862465	-0.789089
28	6	0	0.091402	2.754544	-1.362758
29	6	0	-1.836514	1.177901	-1.659011
30	1	0	0.862315	0.167755	1.592251
31	1	0	0.471809	0.512641	-0.860067
32	1	0	-0.745841	-1.435401	-1.745103
33	1	0	-4.047421	-0.266868	-1.830563
34	1	0	-2.713996	-0.862214	-2.835511
35	1	0	-2.845856	-3.029825	-1.894186
36	1	0	-4.458112	-2.519875	-1.395008
37	1	0	-3.610864	0.907787	0.173500
38	1	0	-2.115624	0.537788	1.061161
39	1	0	-4.614381	-1.096731	0.649427
40	1	0	-4.211969	-1.982328	2.817729

41	1	0	-2.596797	-0.998358	4.296712
42	1	0	-1.774071	-0.101183	2.908961
43	1	0	-3.259403	-3.278209	0.631545
44	1	0	-0.975503	-3.166552	-0.151246
45	1	0	-1.061852	-2.045924	1.208922
46	1	0	2.011836	1.487533	0.385373
47	1	0	4.150493	2.450160	1.037930
48	1	0	6.219452	1.064559	1.077909
49	1	0	6.110957	-1.333539	0.396789
50	1	0	2.960646	-4.186757	-1.090339
51	1	0	0.787423	-3.036494	-1.087255
52	1	0	-2.828447	2.821782	0.374192
53	1	0	-1.717304	4.727848	1.420100
54	1	0	0.550836	5.425390	0.685572
55	1	0	1.684183	4.180186	-1.148471
56	1	0	0.595749	2.229141	-2.172261
57	1	0	-2.808305	1.512810	-2.035310
58	1	0	-1.233388	0.882647	-2.523616

C2-D

Zero-point correction= 0.507686 (Hartree/Particle)
Thermal correction to Energy= 0.531191
Thermal correction to Enthalpy= 0.532135
Thermal correction to Gibbs Free Energy= 0.454731
E(sov) = -1192.62935513 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.641701	-0.203164	1.581305
2	6	0	-0.296269	-0.263271	0.535310
3	6	0	0.024273	0.751789	-0.582502
4	7	0	1.407695	0.577115	-1.233243
5	6	0	1.386105	1.397274	-2.513204
6	6	0	0.957993	2.846671	-2.232155
7	6	0	2.513120	1.134590	-0.365498
8	6	0	2.327769	2.649214	-0.139288
9	6	0	2.469818	3.077874	1.302476
10	6	0	2.762039	2.329927	2.367004
11	6	0	0.964103	3.077689	-0.720550
12	6	0	-0.123252	2.209278	-0.099399
13	6	0	-1.740576	-0.052604	0.960614
14	6	0	-2.806751	-0.452471	0.094640
15	6	0	-2.627645	-1.158487	-1.127621

16	6	0	-3.704397	-1.502715	-1.908815
17	6	0	-5.019081	-1.158385	-1.512496
18	6	0	-5.228415	-0.494694	-0.330497
19	6	0	-4.135117	-0.136447	0.501496
20	7	0	-4.422413	0.494001	1.675959
21	6	0	-3.425081	0.799239	2.464220
22	6	0	-2.062959	0.548268	2.150044
23	6	0	2.194358	-1.867981	-0.645815
24	6	0	3.498175	-1.822596	-0.138355
25	6	0	3.951725	-2.800241	0.741809
26	6	0	3.118787	-3.857790	1.102910
27	6	0	1.840089	-3.946665	0.558523
28	6	0	1.387004	-2.960928	-0.313709
29	6	0	1.709143	-0.863939	-1.666516
30	1	0	0.516434	0.603333	2.106196
31	1	0	-0.206929	-1.275855	0.147098
32	1	0	-0.666574	0.565941	-1.411729
33	1	0	2.401429	1.343244	-2.914118
34	1	0	0.715268	0.883918	-3.206998
35	1	0	-0.042484	3.034590	-2.633473
36	1	0	1.645389	3.531871	-2.736390
37	1	0	3.443798	0.928219	-0.898867
38	1	0	2.495639	0.553885	0.552600
39	1	0	3.103009	3.183369	-0.706749
40	1	0	2.325474	4.148902	1.450599
41	1	0	2.852425	2.788581	3.346769
42	1	0	2.951925	1.259974	2.323640
43	1	0	0.783184	4.133242	-0.497434
44	1	0	-1.121130	2.566387	-0.370340
45	1	0	-0.056020	2.268290	0.992536
46	1	0	-1.633055	-1.463934	-1.444595
47	1	0	-3.548776	-2.052817	-2.832075
48	1	0	-5.859692	-1.435119	-2.140771
49	1	0	-6.223625	-0.231234	0.013589
50	1	0	-3.676425	1.281581	3.406610
51	1	0	-1.310304	0.835053	2.879345
52	1	0	4.183517	-1.037079	-0.443409
53	1	0	4.963774	-2.745237	1.130419
54	1	0	3.475060	-4.622453	1.785964
55	1	0	1.197196	-4.785724	0.804674
56	1	0	0.396803	-3.062230	-0.755344
57	1	0	2.466063	-0.751956	-2.448775
58	1	0	0.788291	-1.214819	-2.144189

INT1-*R*-A

Zero-point correction= 0.718649 (Hartree/Particle)
Thermal correction to Energy= 0.757193
Thermal correction to Enthalpy= 0.758137
Thermal correction to Gibbs Free Energy= 0.644645
E(sov) = -2280.52368238 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.701189	-0.134783	-0.581587
2	6	0	-6.453435	0.166773	-0.025738
3	6	0	-5.721666	-0.828510	0.653182
4	6	0	-6.285896	-2.106587	0.747871
5	6	0	-7.520522	-2.403594	0.180509
6	6	0	-8.232208	-1.414895	-0.491762
7	1	0	-8.250731	0.651218	-1.088018
8	1	0	-5.730893	-2.870003	1.284416
9	1	0	-7.926693	-3.407046	0.268106
10	1	0	-9.197350	-1.634479	-0.937168
11	16	0	-4.168585	-0.549373	1.489658
12	6	0	-5.941983	1.559230	-0.193989
13	8	0	-4.790899	1.898873	-0.305787
14	6	0	-2.945954	-0.591257	0.070155
15	6	0	-2.795582	-2.010111	-0.505528
16	6	0	-1.593836	-0.301747	0.630850
17	1	0	-3.322995	0.139168	-0.646804
18	6	0	-1.683032	-2.649188	0.333920
19	1	0	-2.457925	-1.913405	-1.544801
20	1	0	-3.733367	-2.573983	-0.511374
21	6	0	-0.882642	-1.447630	0.817970
22	1	0	-1.294436	0.680431	0.982626
23	1	0	-2.080660	-3.189395	1.203012
24	1	0	-1.061878	-3.352903	-0.232739
25	8	0	0.315290	-1.613364	1.318940
26	8	0	1.379731	0.563378	1.764584
27	6	0	1.590415	1.039658	0.481519
28	6	0	3.035867	0.728050	-0.009915
29	7	0	3.329635	-0.765443	-0.242906
30	6	0	4.608467	-0.853056	-1.037295
31	6	0	5.709519	0.001880	-0.389418
32	6	0	3.544418	-1.470310	1.080384
33	6	0	4.854412	-0.986439	1.734207
34	6	0	4.764340	-0.832238	3.234175

35	6	0	3.684121	-0.503200	3.938556
36	6	0	5.282352	0.329412	1.043416
37	6	0	4.080504	1.269361	0.982447
38	6	0	1.445494	2.555070	0.433547
39	6	0	1.369257	3.274481	-0.798663
40	6	0	1.297170	2.659235	-2.077989
41	6	0	1.233513	3.414627	-3.222055
42	6	0	1.238648	4.827147	-3.149500
43	6	0	1.282200	5.451113	-1.929998
44	6	0	1.336465	4.695861	-0.729861
45	7	0	1.346748	5.386802	0.446232
46	6	0	1.365605	4.684917	1.552062
47	6	0	1.417169	3.269911	1.602246
48	6	0	2.407820	-2.849604	-1.391209
49	6	0	3.037609	-3.228667	-2.579603
50	6	0	3.188615	-4.574750	-2.898258
51	6	0	2.701488	-5.552096	-2.033100
52	6	0	2.052402	-5.181359	-0.857657
53	6	0	1.898499	-3.835185	-0.537369
54	6	0	2.191572	-1.404654	-1.026836
55	1	0	0.845458	-0.354945	1.671937
56	1	0	0.853428	0.614947	-0.217236
57	1	0	3.179156	1.168652	-1.003138
58	1	0	4.870892	-1.912672	-1.070614
59	1	0	4.372587	-0.527703	-2.054040
60	1	0	5.860639	0.926364	-0.955979
61	1	0	6.652384	-0.552559	-0.404881
62	1	0	3.585671	-2.537416	0.860060
63	1	0	2.658145	-1.269691	1.676194
64	1	0	5.637281	-1.728471	1.526915
65	1	0	5.712124	-0.969944	3.753387
66	1	0	3.751270	-0.387114	5.015970
67	1	0	2.713172	-0.318194	3.484791
68	1	0	6.105505	0.791294	1.596194
69	1	0	4.382244	2.270963	0.662667
70	1	0	3.617891	1.355852	1.970344
71	1	0	1.252352	1.576001	-2.151087
72	1	0	1.162087	2.926838	-4.189421
73	1	0	1.190833	5.412324	-4.062561
74	1	0	1.265950	6.531832	-1.833550
75	1	0	1.352008	5.250860	2.482289
76	1	0	1.431268	2.743128	2.549464
77	1	0	3.398971	-2.468014	-3.268688
78	1	0	3.676643	-4.860362	-3.824922
79	1	0	2.816053	-6.602387	-2.283137

80	1	0	1.653077	-5.940550	-0.192548
81	1	0	1.364894	-3.520272	0.360063
82	1	0	2.068684	-0.777007	-1.916412
83	1	0	1.316872	-1.339352	-0.375906
84	8	0	-6.950027	2.461771	-0.245942
85	1	0	-6.520687	3.321975	-0.393678

INT1-*S*-B

Zero-point correction= 0.720418 (Hartree/Particle)
Thermal correction to Energy= 0.758590
Thermal correction to Enthalpy= 0.759534
Thermal correction to Gibbs Free Energy= 0.649767
E(sov) = -2280.54312107 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	0.146078	-3.017546	1.213301
3	6	0	-0.876935	-3.198953	0.265589
4	6	0	-1.096323	-4.472556	-0.269202
5	6	0	-0.328700	-5.560575	0.135252
6	6	0	0.690189	-5.378709	1.066236
7	1	0	1.738263	-3.944003	2.291601
8	1	0	-1.873409	-4.597139	-1.017548
9	1	0	-0.519723	-6.543761	-0.284693
10	1	0	1.300807	-6.220409	1.379688
11	16	0	-1.840827	-1.830890	-0.373343
12	6	0	0.475881	-1.669273	1.831064
13	8	0	1.682468	-1.323377	1.811328
14	6	0	-3.146399	-1.676915	0.950783
15	6	0	-4.351843	-2.596439	0.673711
16	6	0	-3.749793	-0.306615	0.896578
17	1	0	-2.614649	-1.886634	1.879759
18	6	0	-5.318680	-1.734600	-0.157181
19	1	0	-4.821283	-2.834649	1.635037
20	1	0	-4.069546	-3.535786	0.191412
21	6	0	-4.933867	-0.341165	0.268943
22	1	0	-3.248376	0.570776	1.285796
23	1	0	-5.158616	-1.850997	-1.236755
24	1	0	-6.373253	-1.944845	0.045514
25	8	0	-5.788290	0.659427	-0.030166

26	8	0	0.331170	1.378699	1.861097
27	6	0	0.026221	1.402624	0.504836
28	6	0	1.149987	2.148687	-0.248449
29	7	0	2.437644	1.322966	-0.449883
30	6	0	3.316500	2.081266	-1.411932
31	6	0	3.530538	3.528985	-0.937632
32	6	0	3.174049	1.167277	0.863203
33	6	0	3.686058	2.535808	1.348703
34	6	0	3.496699	2.765477	2.827951
35	6	0	2.862406	1.985412	3.698812
36	6	0	3.026909	3.646222	0.500999
37	6	0	1.513819	3.451823	0.494181
38	6	0	-1.307305	2.099190	0.241477
39	6	0	-2.025567	1.917606	-0.978845
40	6	0	-1.534242	1.182499	-2.089588
41	6	0	-2.301468	0.998900	-3.211104
42	6	0	-3.608085	1.535197	-3.281669
43	6	0	-4.122064	2.233630	-2.221149
44	6	0	-3.346789	2.438530	-1.051009
45	7	0	-3.942521	3.093672	-0.009929
46	6	0	-3.225975	3.288367	1.073434
47	6	0	-1.904271	2.816230	1.247198
48	6	0	3.287539	-0.886850	-1.434160
49	6	0	3.851117	-0.788655	-2.710209
50	6	0	4.915593	-1.605261	-3.076098
51	6	0	5.416307	-2.538392	-2.170092
52	6	0	4.840946	-2.660735	-0.908209
53	6	0	3.774664	-1.844508	-0.537763
54	6	0	2.102673	-0.046562	-1.030279
55	1	0	0.013254	0.474955	2.211526
56	1	0	-0.104901	0.382719	0.118339
57	1	0	0.823156	2.355851	-1.274058
58	1	0	4.252793	1.523573	-1.464893
59	1	0	2.832527	2.029402	-2.391398
60	1	0	2.986221	4.226403	-1.582263
61	1	0	4.593520	3.778329	-1.005583
62	1	0	3.995693	0.475165	0.668938
63	1	0	2.467757	0.682700	1.536378
64	1	0	4.767076	2.593456	1.150440
65	1	0	3.951655	3.690278	3.185537
66	1	0	2.806624	2.277012	4.743240
67	1	0	2.375900	1.051845	3.431703
68	1	0	3.281902	4.626581	0.915733
69	1	0	1.016693	4.292329	0.000752
70	1	0	1.147178	3.382127	1.521024

71	1	0	-0.557667	0.715727	-2.031896
72	1	0	-1.913761	0.417425	-4.041661
73	1	0	-4.207708	1.373572	-4.171912
74	1	0	-5.130682	2.633656	-2.230263
75	1	0	-3.719987	3.813274	1.889165
76	1	0	-1.395444	2.932254	2.197366
77	1	0	3.445580	-0.080127	-3.429628
78	1	0	5.345316	-1.522067	-4.069457
79	1	0	6.244693	-3.179405	-2.455802
80	1	0	5.213871	-3.404011	-0.210595
81	1	0	3.286449	-1.950928	0.431270
82	1	0	1.455846	0.155381	-1.889730
83	1	0	1.551214	-0.572773	-0.251778
84	8	0	-0.479882	-0.996846	2.301471
85	1	0	-5.384978	1.516444	0.202901

INT1-*R*-A

Zero-point correction= 0.719391 (Hartree/Particle)
Thermal correction to Energy= 0.757813
Thermal correction to Enthalpy= 0.758758
Thermal correction to Gibbs Free Energy= 0.648548
E(sov) = -2280.54501531 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.785533	2.287987	-1.927502
2	6	0	2.554484	2.029567	-1.317723
3	6	0	2.177526	2.787888	-0.198157
4	6	0	3.020673	3.806851	0.259566
5	6	0	4.214976	4.090606	-0.392254
6	6	0	4.602406	3.321828	-1.488235
7	1	0	4.083071	1.662501	-2.763868
8	1	0	2.732694	4.367926	1.144258
9	1	0	4.850894	4.894082	-0.032775
10	1	0	5.543786	3.522509	-1.991195
11	16	0	0.686735	2.438447	0.731489
12	6	0	1.717556	0.898685	-1.897914
13	8	0	2.287450	-0.208618	-2.015567
14	6	0	-0.420470	3.841361	0.220499
15	6	0	-0.721414	3.871334	-1.290624
16	6	0	-1.765345	3.604273	0.844286
17	1	0	0.077312	4.752905	0.564445

18	6	0	-2.015720	3.063942	-1.453397
19	1	0	0.094702	3.475513	-1.895679
20	1	0	-0.902898	4.916103	-1.567553
21	6	0	-2.626894	3.162256	-0.083896
22	1	0	-1.965282	3.698214	1.906775
23	1	0	-2.683366	3.456779	-2.226218
24	1	0	-1.804097	2.014470	-1.697852
25	8	0	-3.912454	2.779652	0.052512
26	8	0	-0.749566	-1.026741	-1.974249
27	6	0	-1.178394	-0.830878	-0.665707
28	6	0	-0.844051	-2.084075	0.186519
29	7	0	0.642964	-2.257595	0.540160
30	6	0	0.728394	-3.298507	1.624647
31	6	0	-0.027846	-4.572128	1.209129
32	6	0	1.420467	-2.743612	-0.663165
33	6	0	0.990430	-4.170478	-1.036542
34	6	0	0.861858	-4.378692	-2.525689
35	6	0	1.014982	-3.470106	-3.485673
36	6	0	-0.321556	-4.495978	-0.290904
37	6	0	-1.319539	-3.364883	-0.528476
38	6	0	-2.692407	-0.660159	-0.584844
39	6	0	-3.336542	-0.165399	0.589781
40	6	0	-2.638654	0.339095	1.719676
41	6	0	-3.320268	0.842779	2.801272
42	6	0	-4.736269	0.857936	2.812757
43	6	0	-5.437972	0.383905	1.731765
44	6	0	-4.759222	-0.124189	0.594209
45	7	0	-5.521108	-0.524349	-0.462750
46	6	0	-4.887567	-0.927601	-1.535908
47	6	0	-3.477676	-1.011993	-1.650819
48	6	0	2.591963	-0.994841	1.623844
49	6	0	2.769327	-1.221548	2.992197
50	6	0	4.044070	-1.230762	3.547097
51	6	0	5.153340	-0.996226	2.737135
52	6	0	4.981877	-0.743840	1.378951
53	6	0	3.706717	-0.738017	0.818116
54	6	0	1.210743	-0.935509	1.025818
55	1	0	-0.247761	-0.183384	-2.246520
56	1	0	-0.715337	0.072845	-0.243263
57	1	0	-1.322049	-1.978015	1.167558
58	1	0	1.792924	-3.480379	1.784305
59	1	0	0.319831	-2.848211	2.533617
60	1	0	-0.964786	-4.659711	1.768445
61	1	0	0.581932	-5.448162	1.448430
62	1	0	2.475748	-2.692311	-0.389301

63	1	0	1.236526	-2.007118	-1.442388
64	1	0	1.749313	-4.878726	-0.671077
65	1	0	0.615970	-5.404361	-2.804268
66	1	0	0.892466	-3.758341	-4.525367
67	1	0	1.265809	-2.428629	-3.300500
68	1	0	-0.727661	-5.446508	-0.650391
69	1	0	-2.311966	-3.631922	-0.153845
70	1	0	-1.396726	-3.158924	-1.599799
71	1	0	-1.553290	0.391998	1.704164
72	1	0	-2.770006	1.246665	3.645958
73	1	0	-5.262714	1.253511	3.676268
74	1	0	-6.522480	0.396276	1.697321
75	1	0	-5.508842	-1.222533	-2.380145
76	1	0	-3.010434	-1.348229	-2.569887
77	1	0	1.902615	-1.373815	3.632405
78	1	0	4.170976	-1.404961	4.611044
79	1	0	6.149226	-0.993862	3.169875
80	1	0	5.842012	-0.534091	0.750936
81	1	0	3.558892	-0.519631	-0.240228
82	1	0	0.486949	-0.552446	1.752516
83	1	0	1.215861	-0.285692	0.153837
84	8	0	0.525109	1.166855	-2.207761
85	1	0	-4.131974	2.701710	0.995793

INT1-*S*-B

Zero-point correction= 0.718072 (Hartree/Particle)
Thermal correction to Energy= 0.756800
Thermal correction to Enthalpy= 0.757745
Thermal correction to Gibbs Free Energy= 0.643008
E(sov) = -2280.52572036 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.527930	0.057991	-0.600615
2	6	0	5.278326	-0.414885	-0.184622
3	6	0	4.153626	0.433627	-0.226602
4	6	0	4.334028	1.743501	-0.689149
5	6	0	5.580827	2.208797	-1.091861
6	6	0	6.685811	1.363952	-1.045460
7	1	0	7.377972	-0.614665	-0.569344
8	1	0	3.465758	2.395442	-0.723897
9	1	0	5.687958	3.231787	-1.440461

10	1	0	7.663727	1.716822	-1.356805
11	16	0	2.483165	-0.054879	0.171024
12	6	0	5.192539	-1.822303	0.303248
13	8	0	4.413706	-2.258389	1.113106
14	6	0	2.386466	-0.073115	2.068136
15	6	0	2.693972	1.318051	2.635161
16	6	0	0.947222	-0.269832	2.383784
17	1	0	3.076561	-0.857784	2.376024
18	6	0	1.356860	2.056717	2.533305
19	1	0	3.523316	1.821899	2.128797
20	1	0	2.969041	1.187139	3.688285
21	6	0	0.321209	0.934620	2.561580
22	1	0	0.457848	-1.237972	2.363704
23	1	0	1.180051	2.779770	3.336047
24	1	0	1.281499	2.600428	1.580653
25	8	0	-0.941674	1.223691	2.644650
26	8	0	-2.463582	-0.571405	1.811711
27	6	0	-1.846787	-1.006225	0.644330
28	6	0	-2.527654	-0.412702	-0.617976
29	7	0	-2.367385	1.111665	-0.762744
30	6	0	-2.727557	1.469558	-2.180319
31	6	0	-4.080726	0.847676	-2.564250
32	6	0	-3.323044	1.825524	0.169198
33	6	0	-4.778098	1.613758	-0.293610
34	6	0	-5.753808	1.424003	0.843738
35	6	0	-5.498803	0.872627	2.028260
36	6	0	-4.799453	0.422618	-1.280157
37	6	0	-4.029377	-0.740066	-0.659259
38	6	0	-1.935423	-2.518129	0.502751
39	6	0	-1.121029	-3.233106	-0.426753
40	6	0	-0.076625	-2.637154	-1.184155
41	6	0	0.671803	-3.385723	-2.057219
42	6	0	0.410204	-4.765803	-2.225236
43	6	0	-0.576226	-5.373961	-1.492712
44	6	0	-1.354107	-4.630144	-0.567920
45	7	0	-2.291814	-5.305967	0.157026
46	6	0	-2.977539	-4.619337	1.037814
47	6	0	-2.839460	-3.225635	1.251622
48	6	0	-0.621290	2.965884	-0.700300
49	6	0	-0.157558	3.432440	-1.932909
50	6	0	0.146189	4.779560	-2.107423
51	6	0	-0.003392	5.668723	-1.045561
52	6	0	-0.440261	5.206946	0.194132
53	6	0	-0.741855	3.859543	0.370292
54	6	0	-0.928979	1.511295	-0.466649

55	1	0	-1.816521	0.113537	2.279773
56	1	0	-0.784016	-0.734048	0.643452
57	1	0	-2.016826	-0.805295	-1.505224
58	1	0	-2.745117	2.560722	-2.223753
59	1	0	-1.909907	1.116910	-2.814491
60	1	0	-3.932714	-0.020552	-3.214401
61	1	0	-4.669593	1.581323	-3.122580
62	1	0	-3.053292	2.881492	0.141884
63	1	0	-3.116163	1.430495	1.161967
64	1	0	-5.094664	2.503804	-0.854145
65	1	0	-6.770686	1.743514	0.618383
66	1	0	-6.294192	0.756946	2.758127
67	1	0	-4.516398	0.501158	2.311708
68	1	0	-5.832645	0.133635	-1.493511
69	1	0	-4.173452	-1.659335	-1.234154
70	1	0	-4.382555	-0.924857	0.360162
71	1	0	0.175565	-1.590548	-1.036095
72	1	0	1.484788	-2.917565	-2.603445
73	1	0	1.008672	-5.345381	-2.921445
74	1	0	-0.788327	-6.434786	-1.578544
75	1	0	-3.705541	-5.178882	1.623781
76	1	0	-3.434362	-2.712342	1.998983
77	1	0	-0.016128	2.734552	-2.755462
78	1	0	0.509382	5.132782	-3.067447
79	1	0	0.237104	6.718806	-1.180689
80	1	0	-0.531272	5.893402	1.029934
81	1	0	-1.037798	3.470652	1.345000
82	1	0	-0.300096	0.860197	-1.082143
83	1	0	-0.781165	1.285819	0.589319
84	8	0	6.138528	-2.610265	-0.259821
85	1	0	6.024336	-3.485657	0.148736

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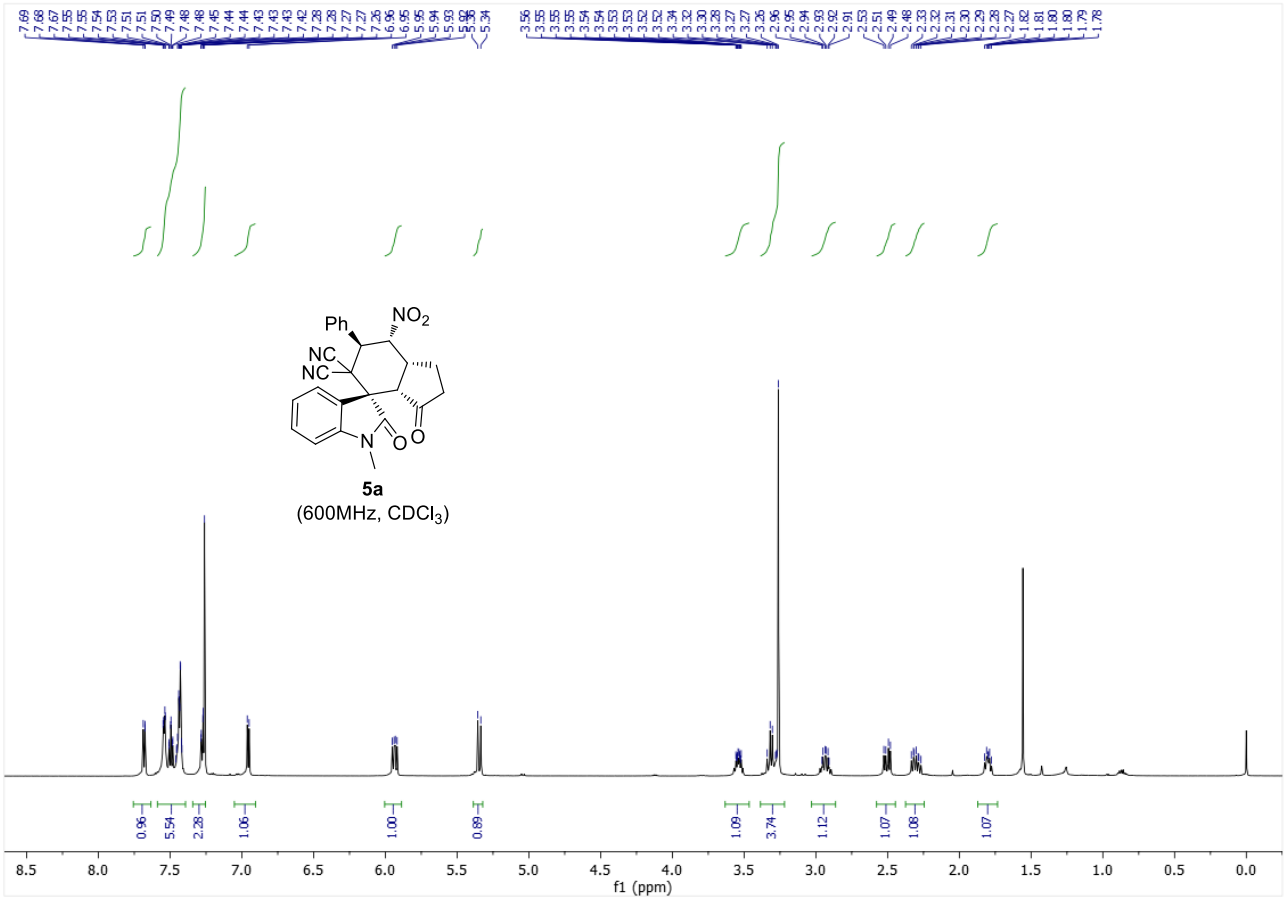
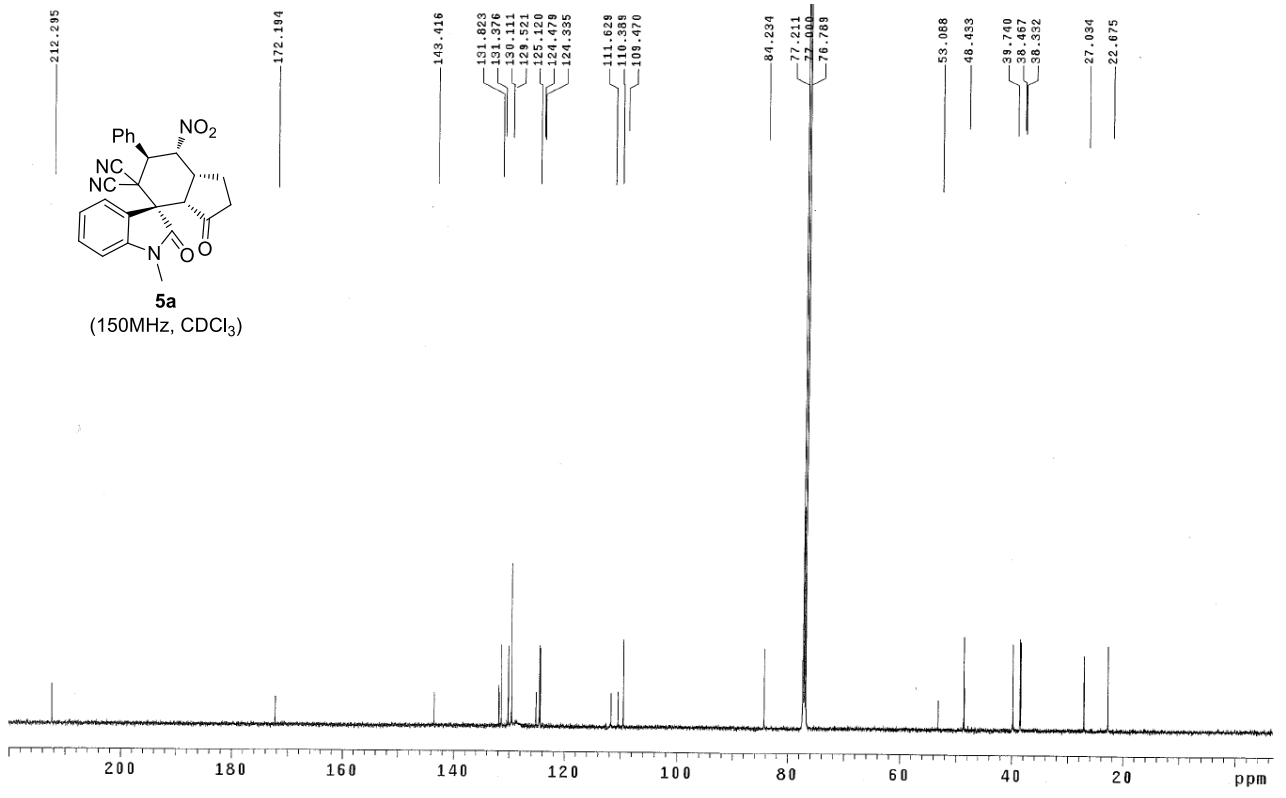
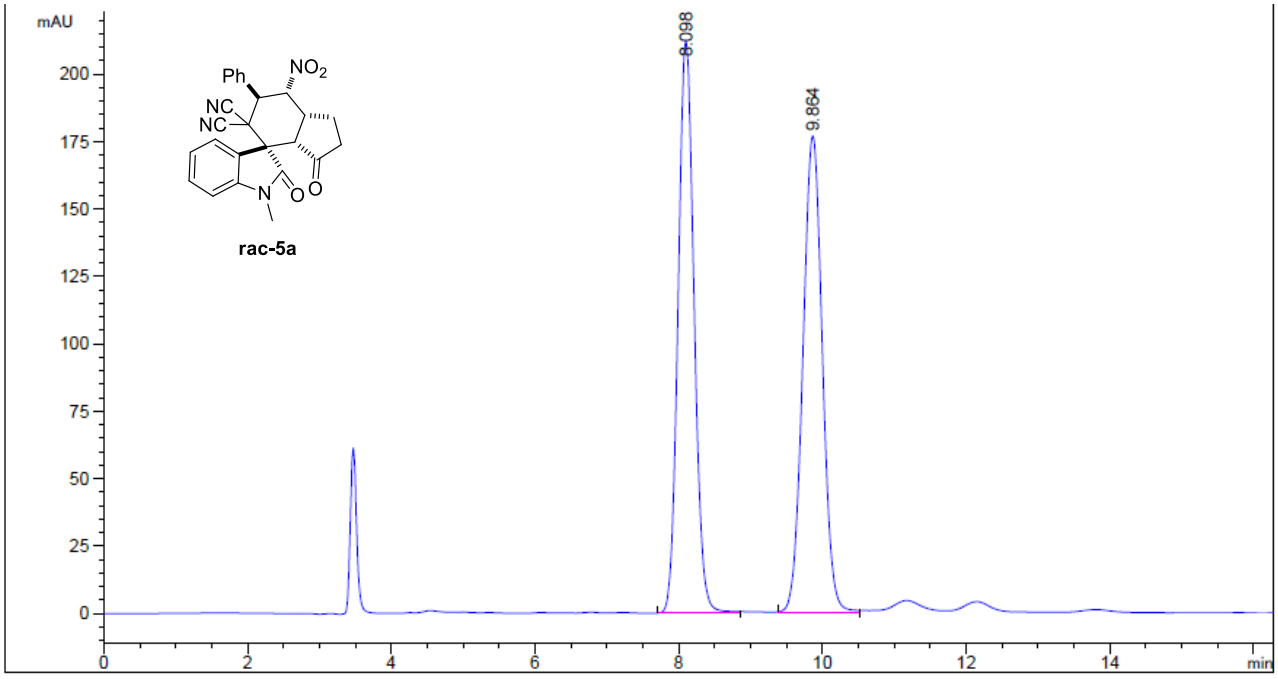
14. NMR spectra and HPLC chromatograms







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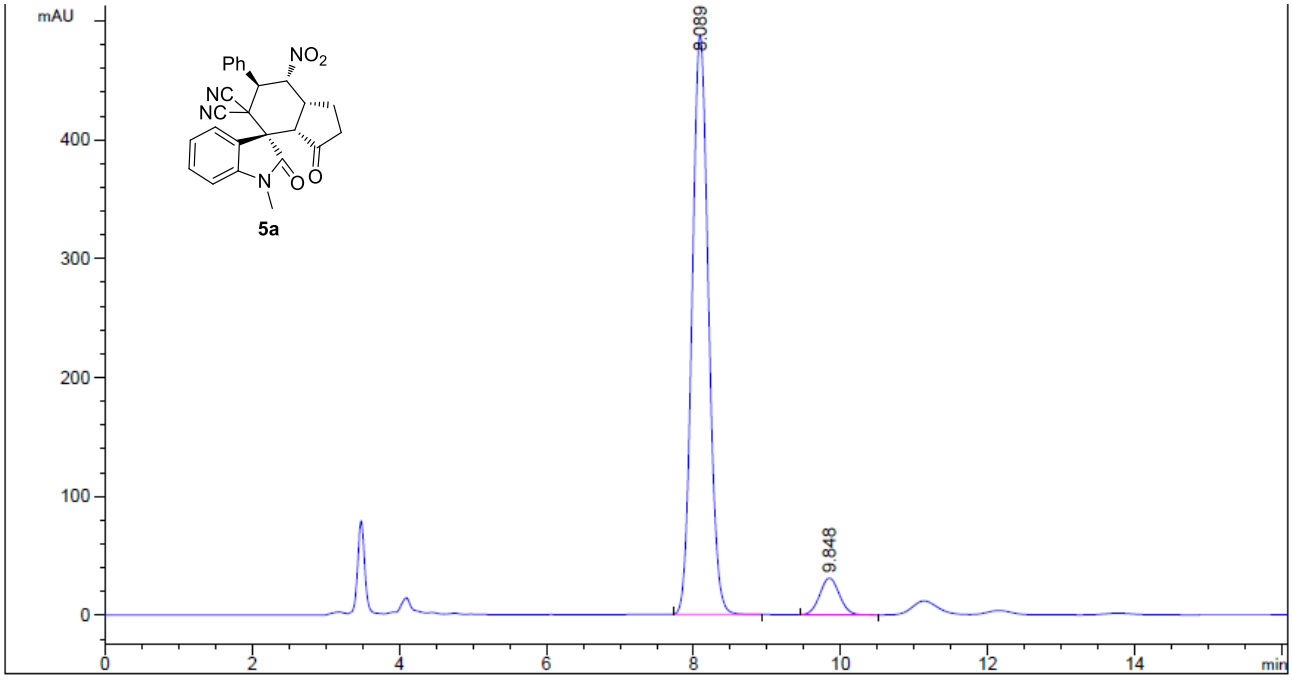

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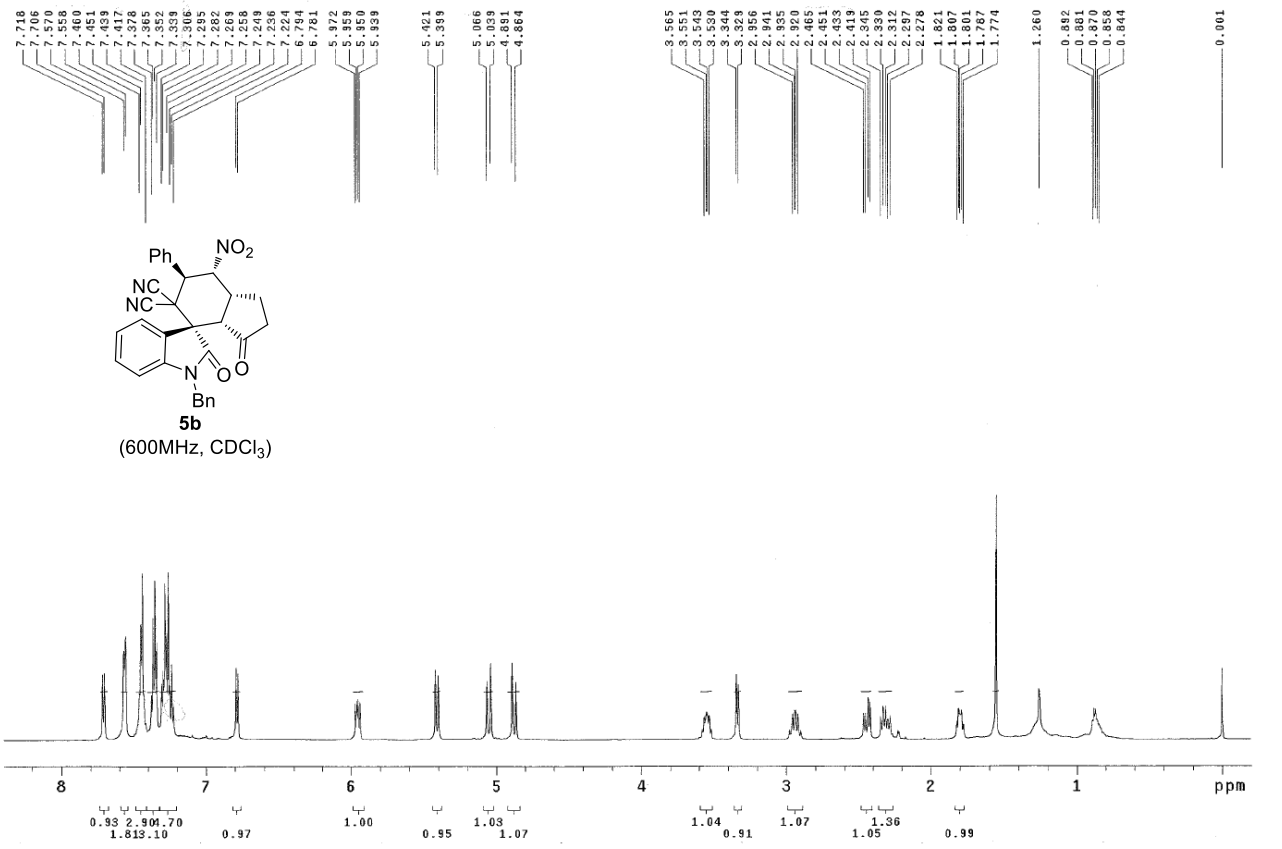
2	9.848	BB	0.2914	569.46741		30.80433		7.0585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Ph
NO2
NC
NC
O
N
O
Bn
5b
(600MHz, CDCl3)
8
7
6
5
4
3
2
1
ppm
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1.81
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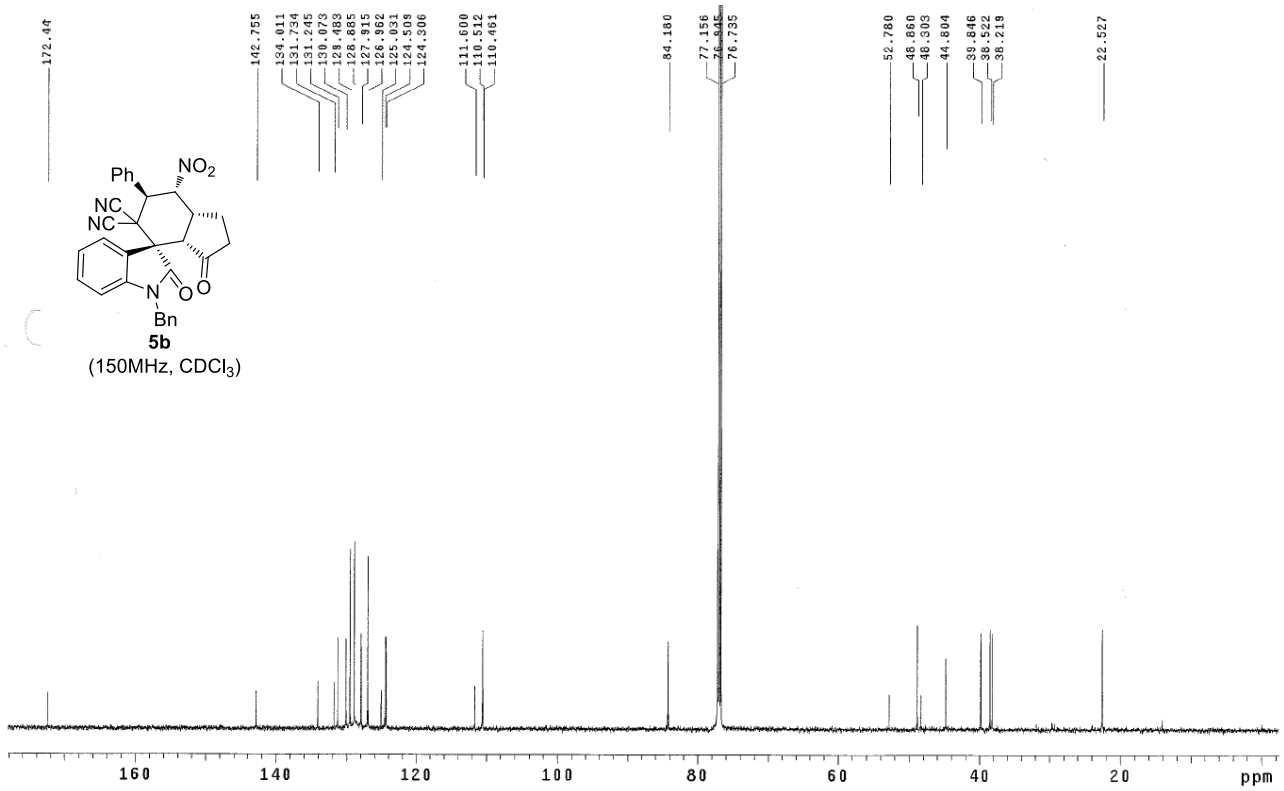
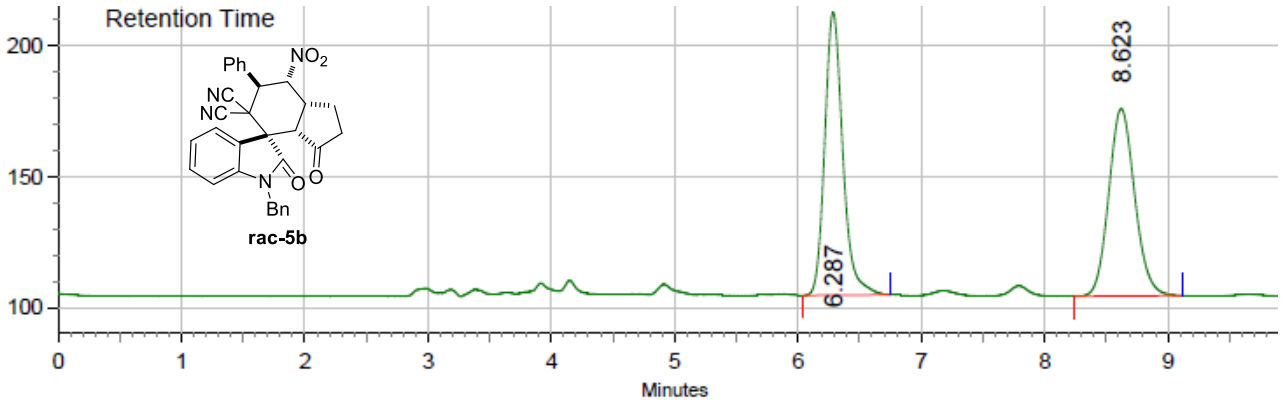
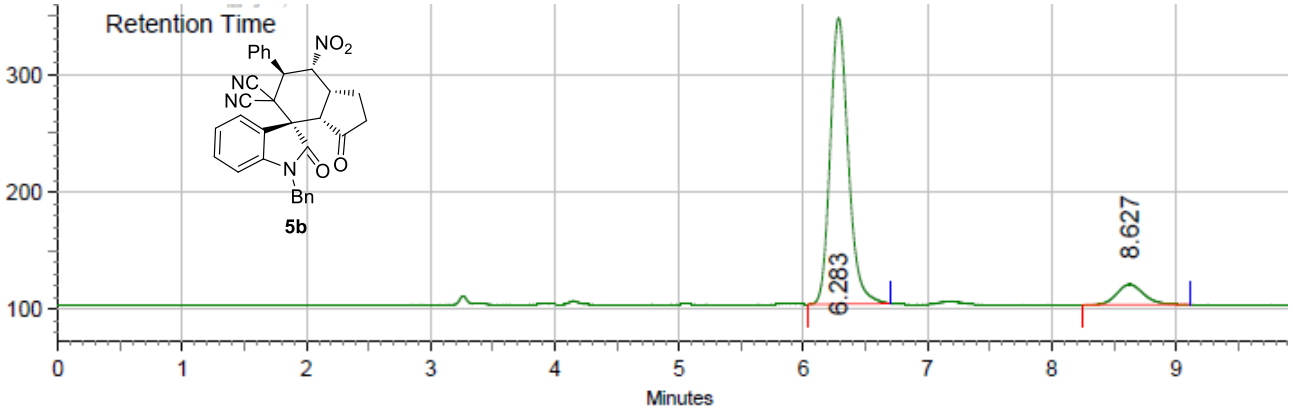
0.99

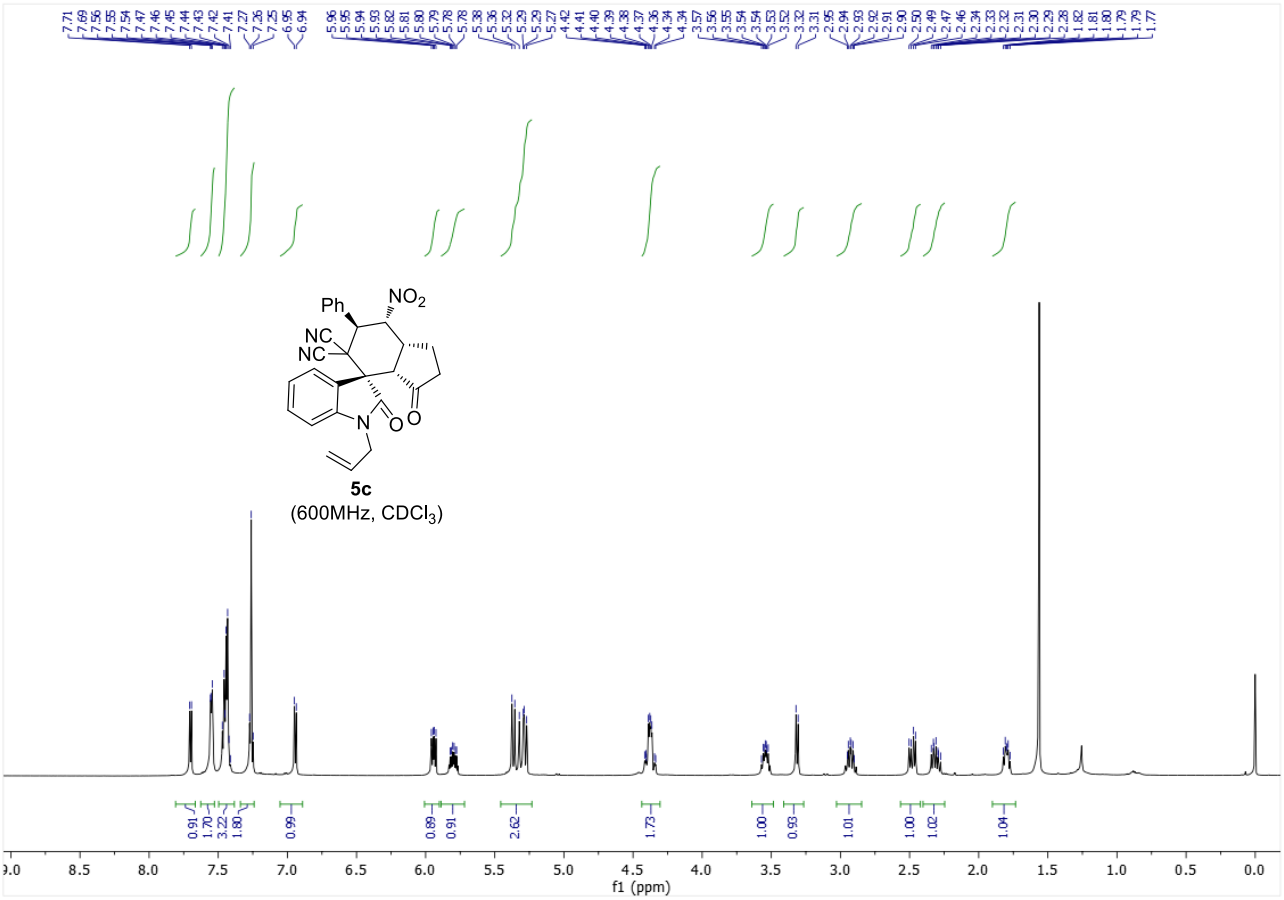

172.44
142.755
134.011
131.734
131.245
130.073
129.483
128.885
127.915
126.962
125.031
124.509
124.306
111.600
110.512
110.461
84.180
77.156
76.735
52.780
48.660
48.303
44.804
39.846
38.522
38.219
22.527
Ph
NO2
NC
NC
O
N
O
Bn
5b
(150MHz, CDCl3)
160
140
120
100
80
60
40
20
ppm

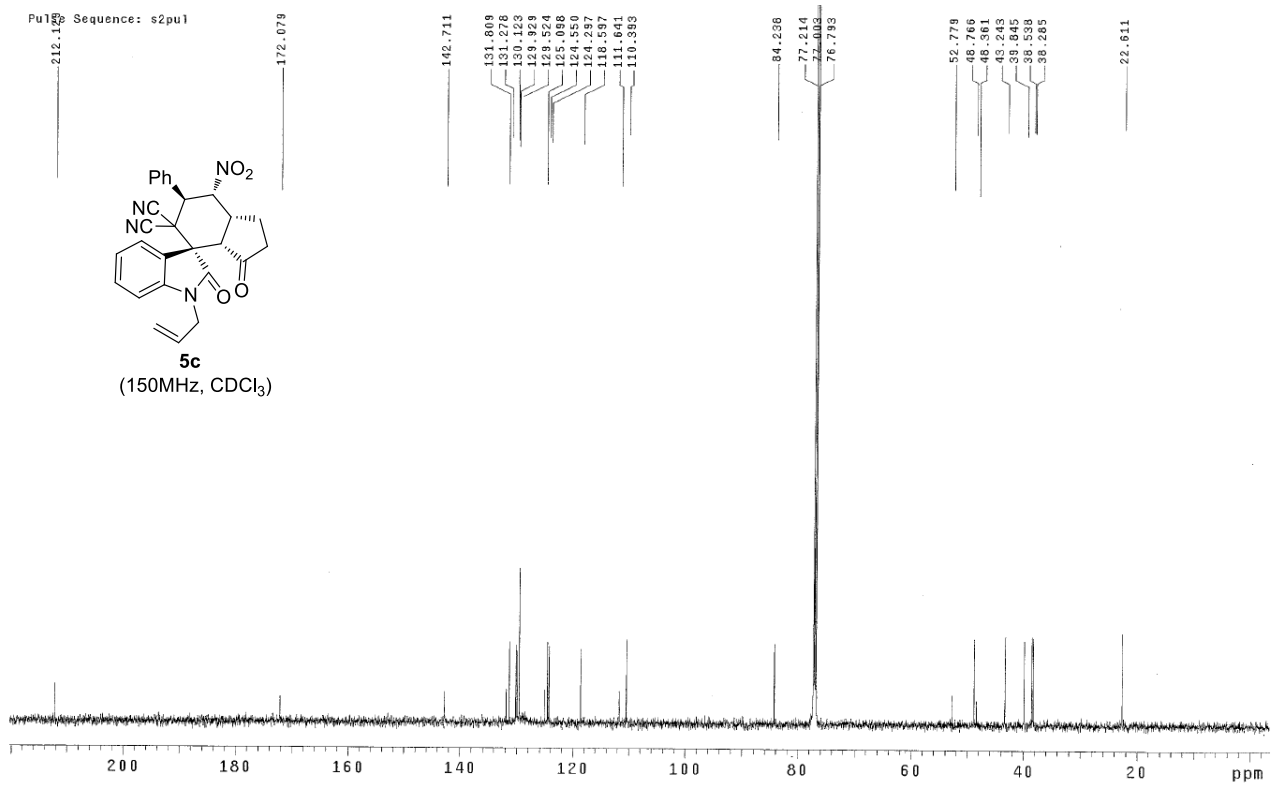


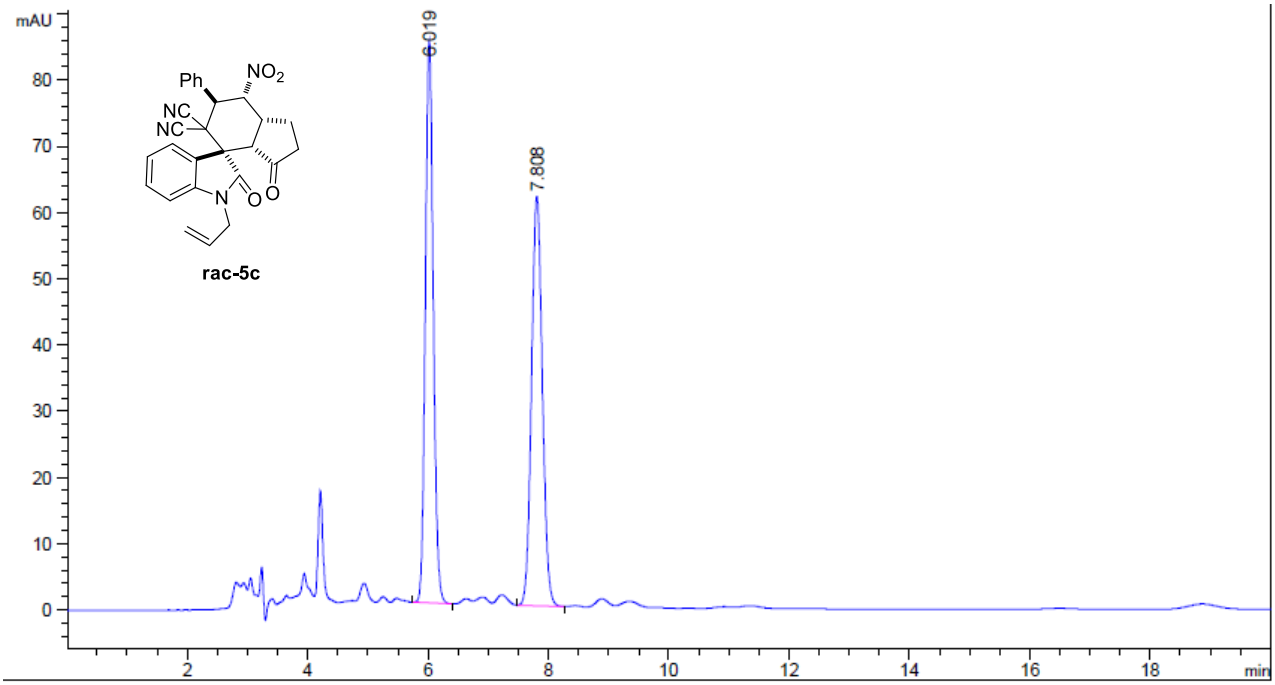
Peak	RT (min)	Height	% Height	Area	% Area
1	6.287	1809114	60.18	18437039	51.25
2	8.623	1197170	39.82	17536246	48.75



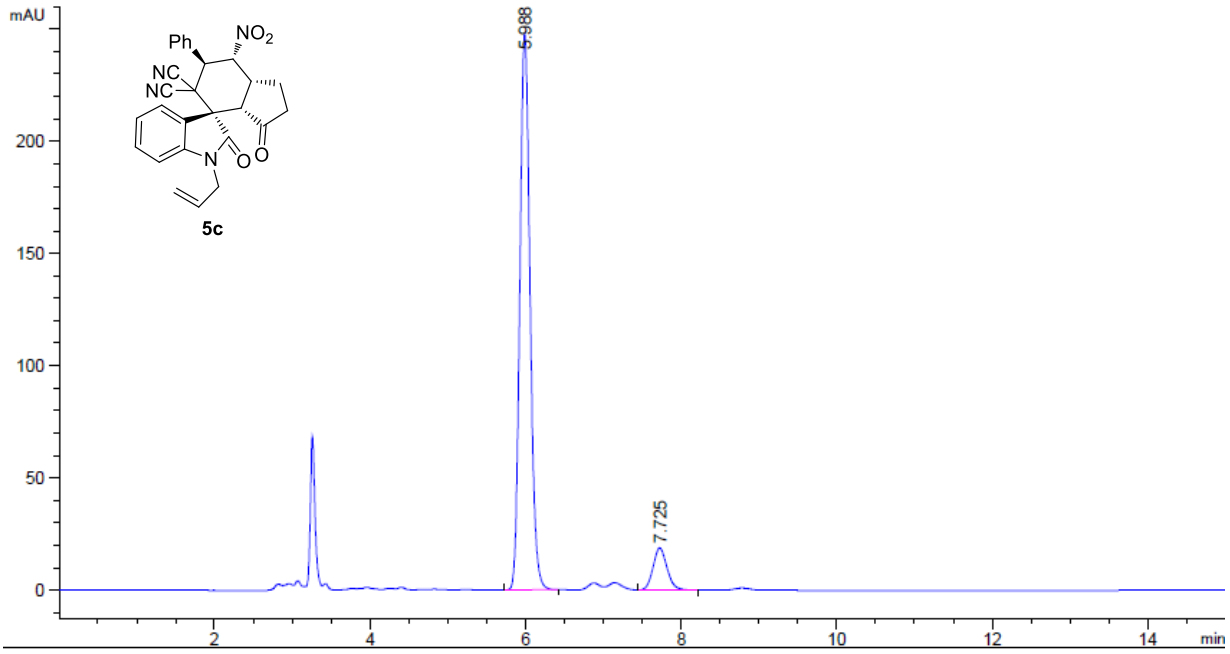
Peak	RT (min)	Height	% Height	Area	% Area
1	6.283	4083472	93.42	41391473	90.52
2	8.627	287437	6.58	4332692	9.48


Ph
NO2
NC
NC
O
O
N
5c
(600MHz, CDCl3)
f1 (ppm)

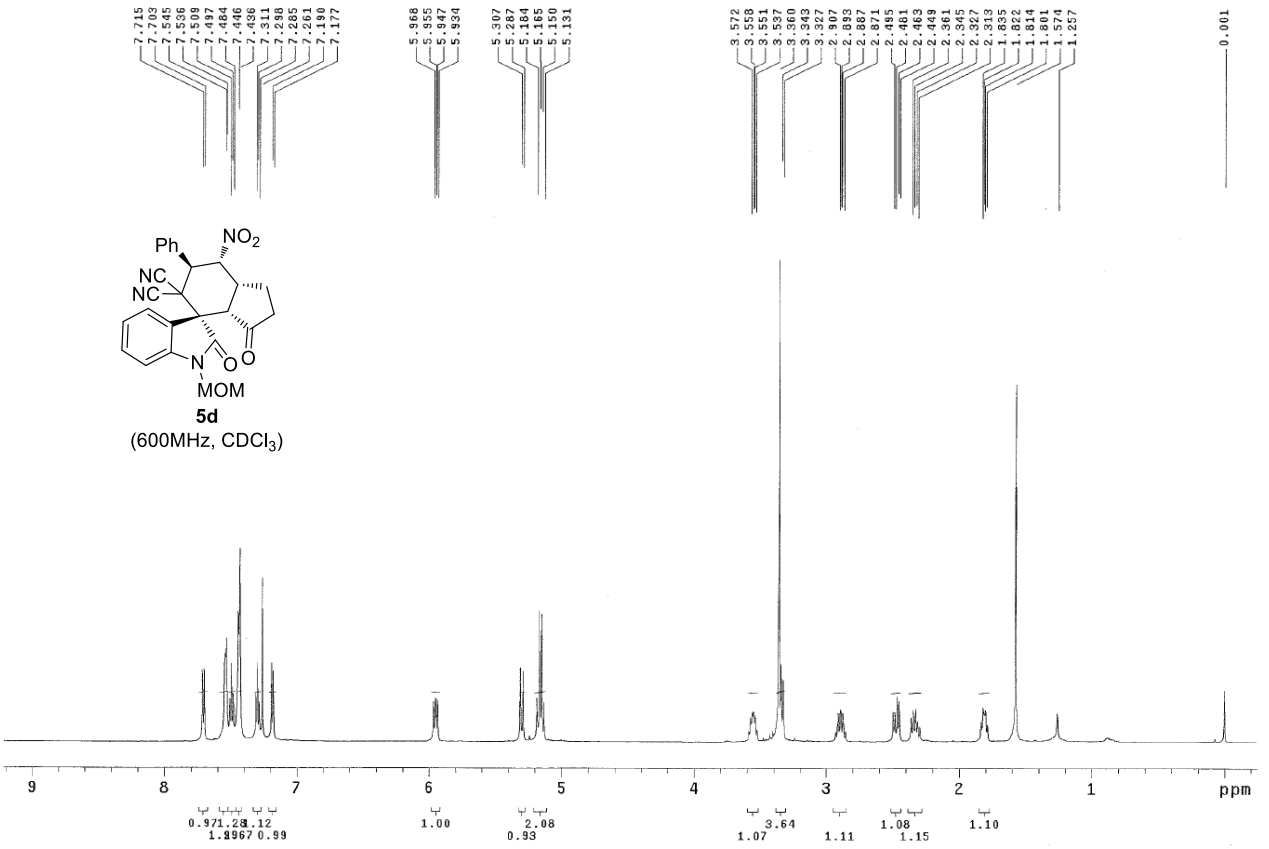

Ph
NO2
NC
NC
O
O
N
5c
(150MHz, CDCl3)
ppm



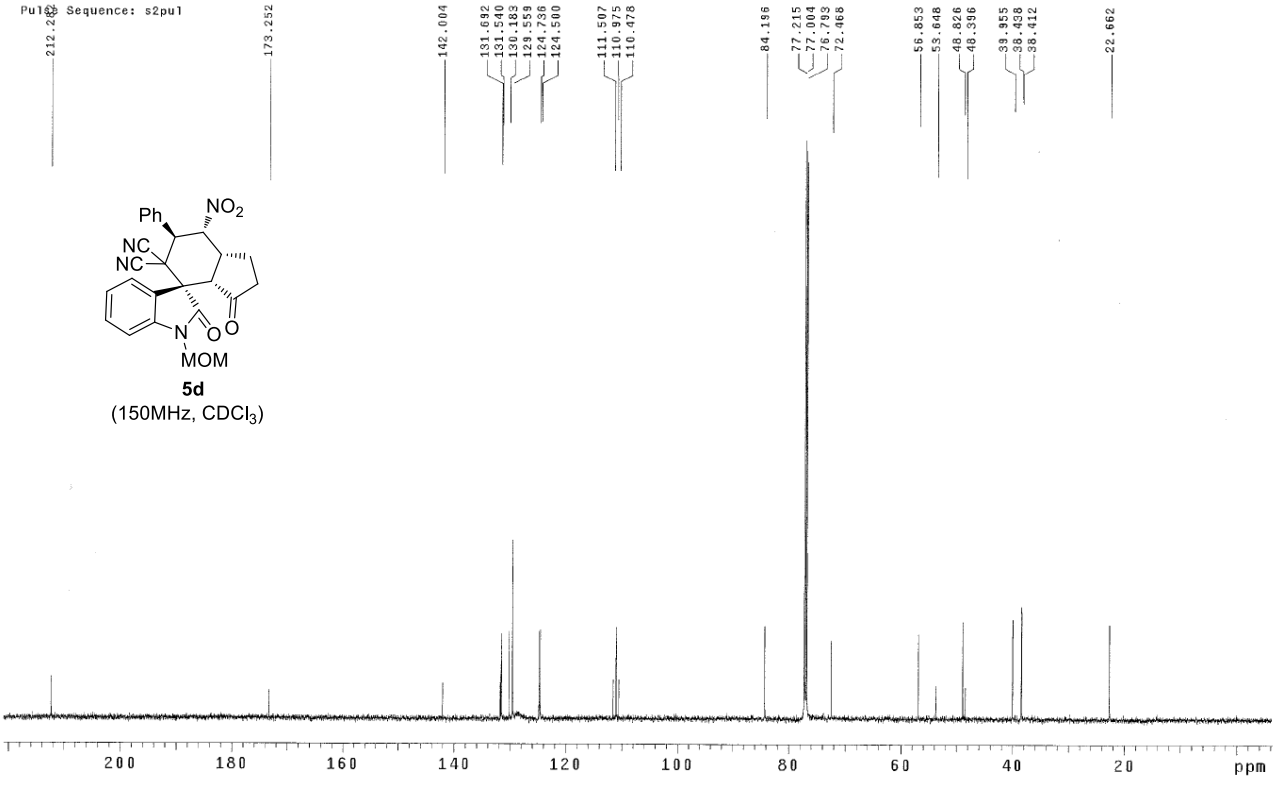
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.019	BB	0.1420	779.92871	85.01702	50.2002
2	7.808	BB	0.1949	773.70929	61.88151	49.7998



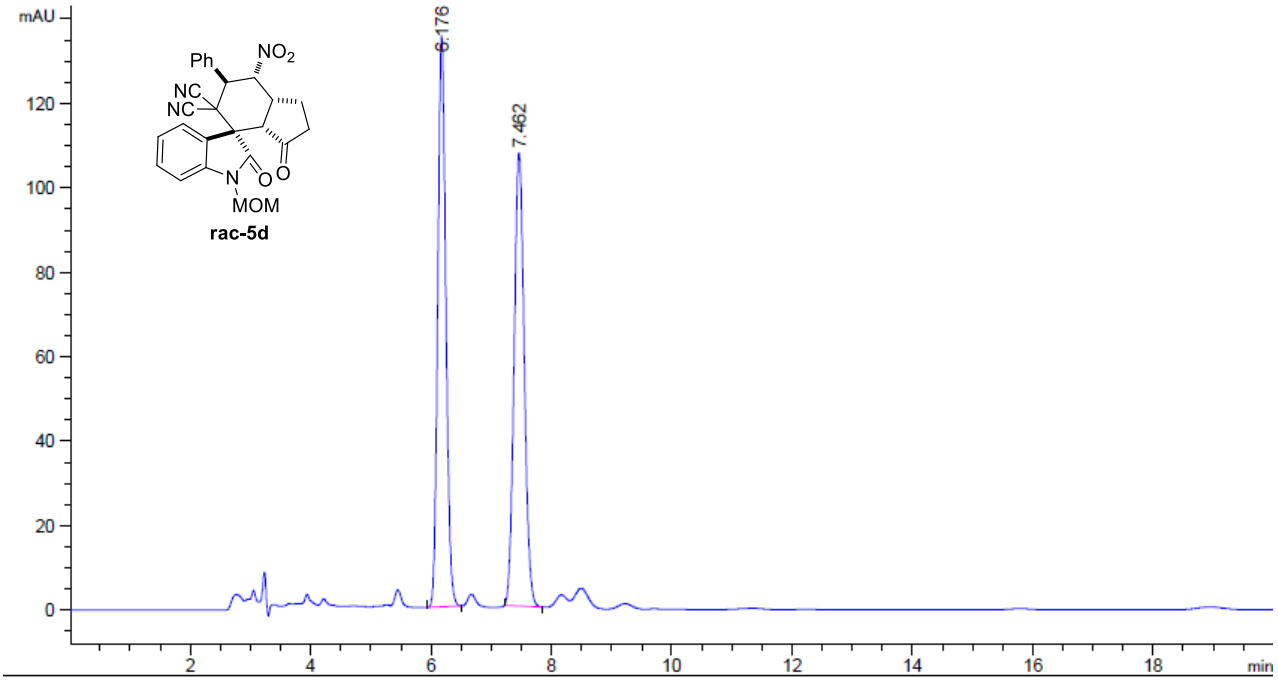
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.988	BB	0.1399	2248.15601	247.78429	90.5249
2	7.725	VB	0.1933	235.31224	18.76380	9.4751



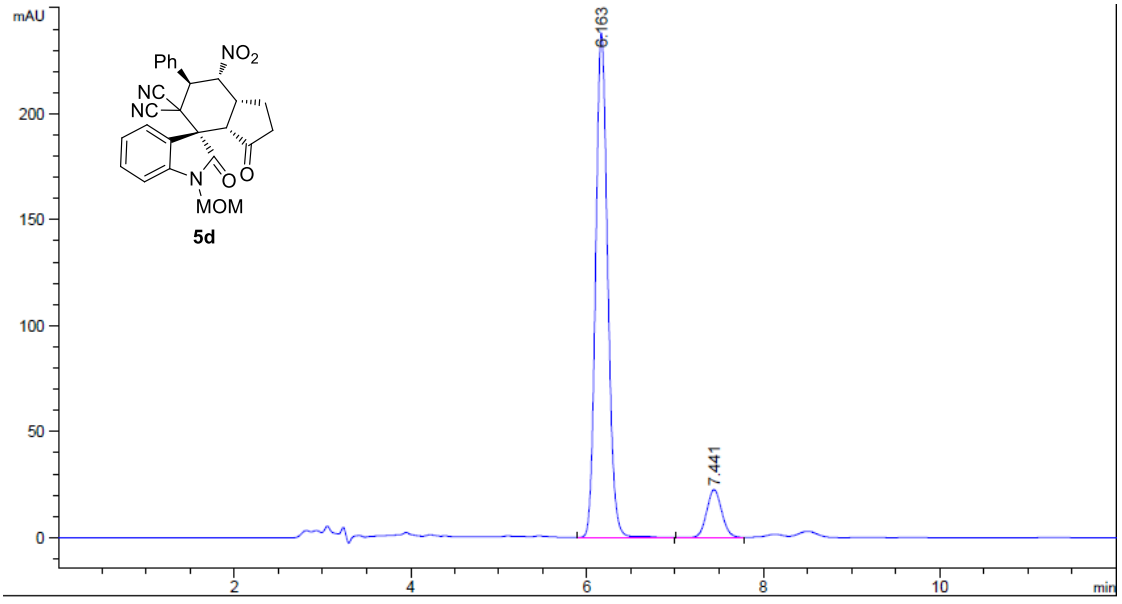
5d
(600MHz, $CDCl_3$)



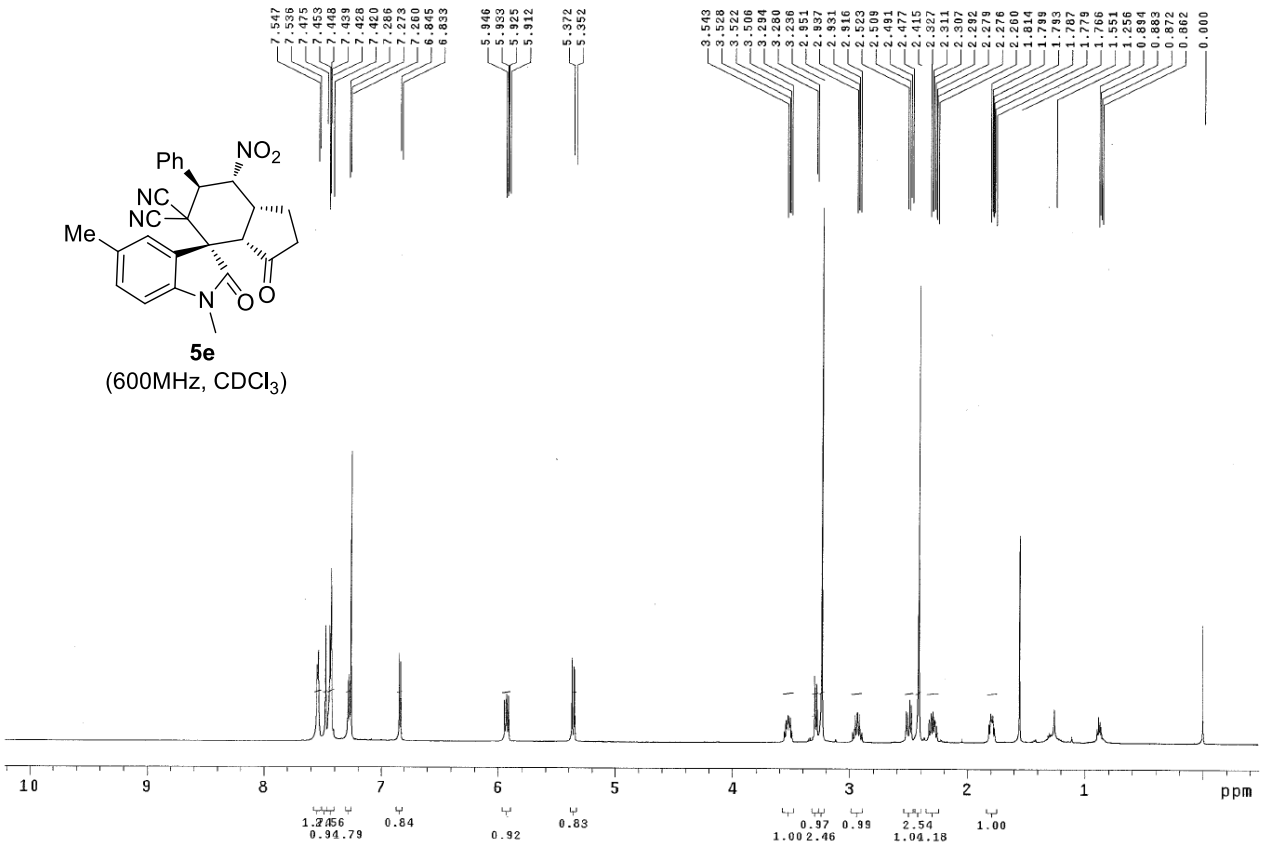
5d
(150MHz, $CDCl_3$)

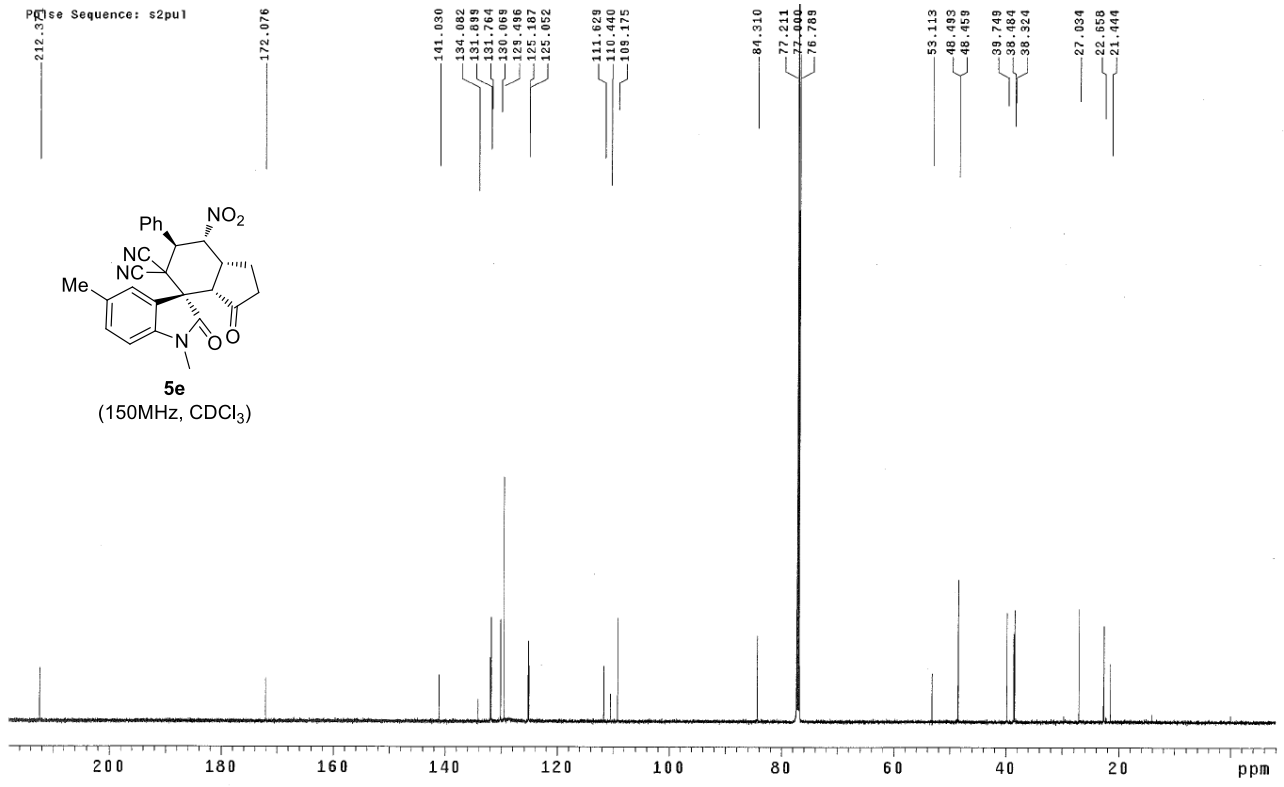


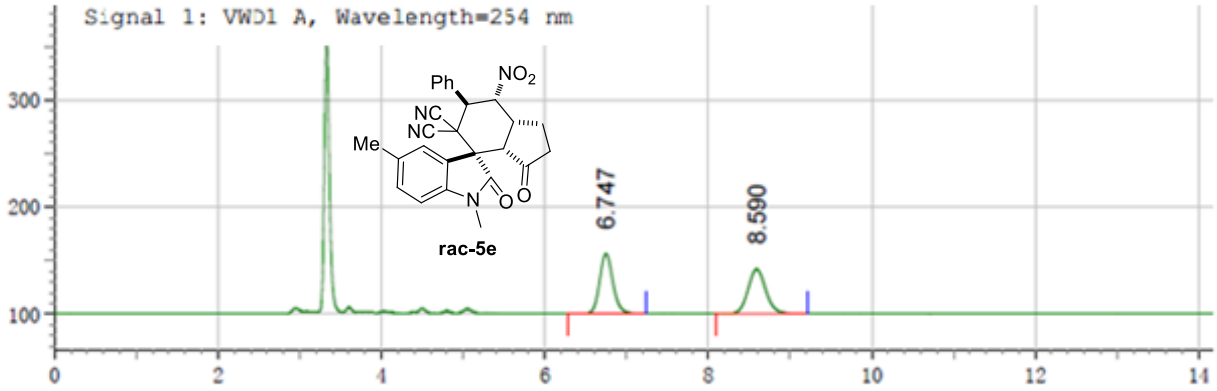
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.176	BB	0.1450	1264.97888	135.37314	50.1139
2	7.462	BB	0.1828	1259.22888	107.40987	49.8861



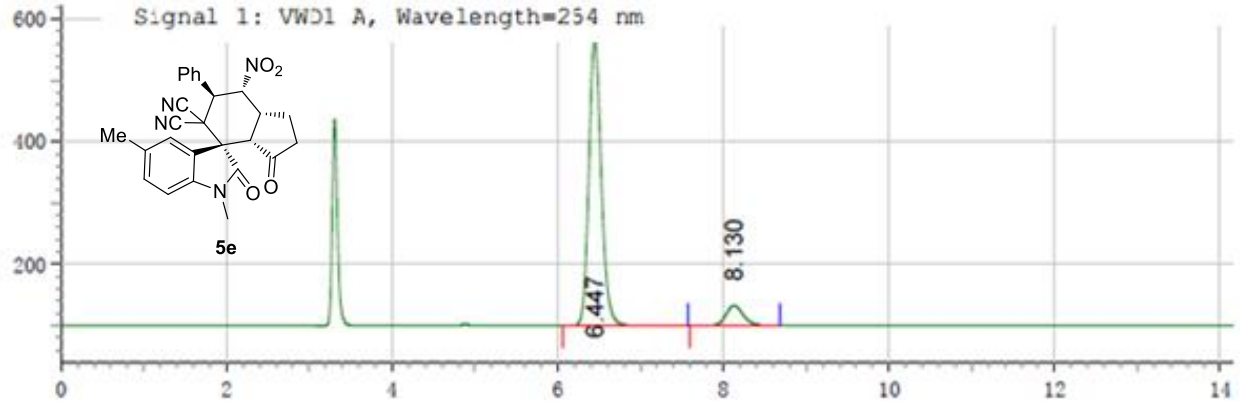
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.163	BV R	0.1464	2251.74829	237.85497	89.5125
2	7.441	BB	0.1831	263.82001	22.44286	10.4875


Ph
NO2
NC
NC
Me
N
O
O
5e
(600MHz, CDCl3)
ppm

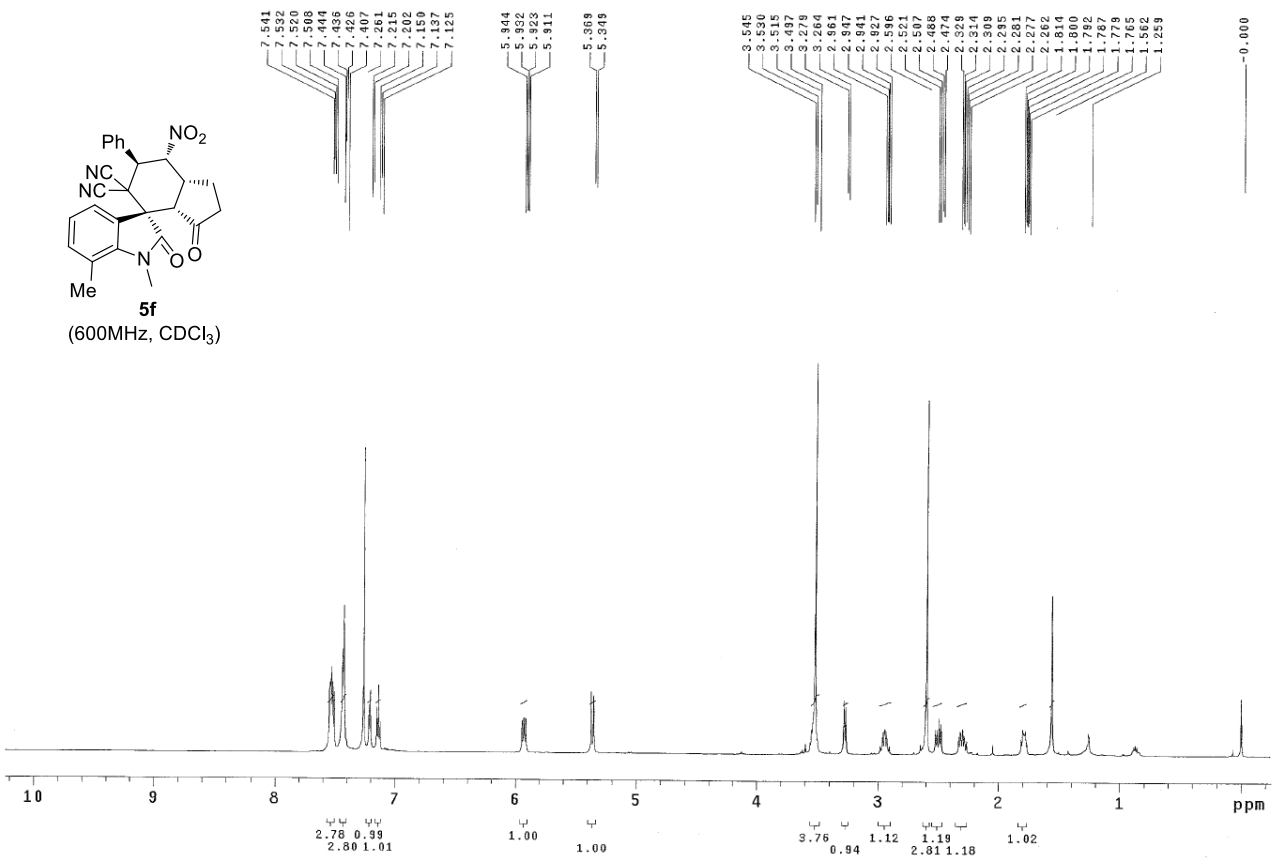

Pulse Sequence: s2pul
Ph
NO2
NC
NC
Me
N
O
O
5e
(150MHz, CDCl3)
ppm

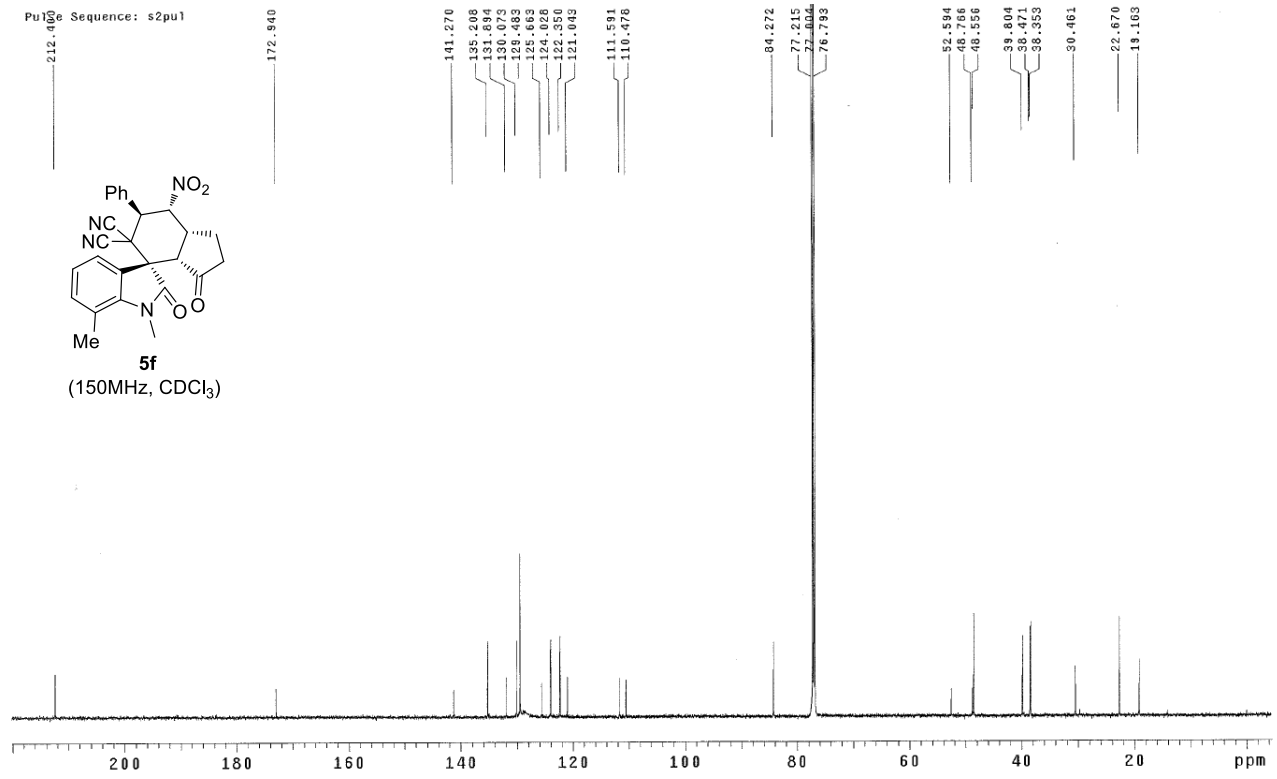


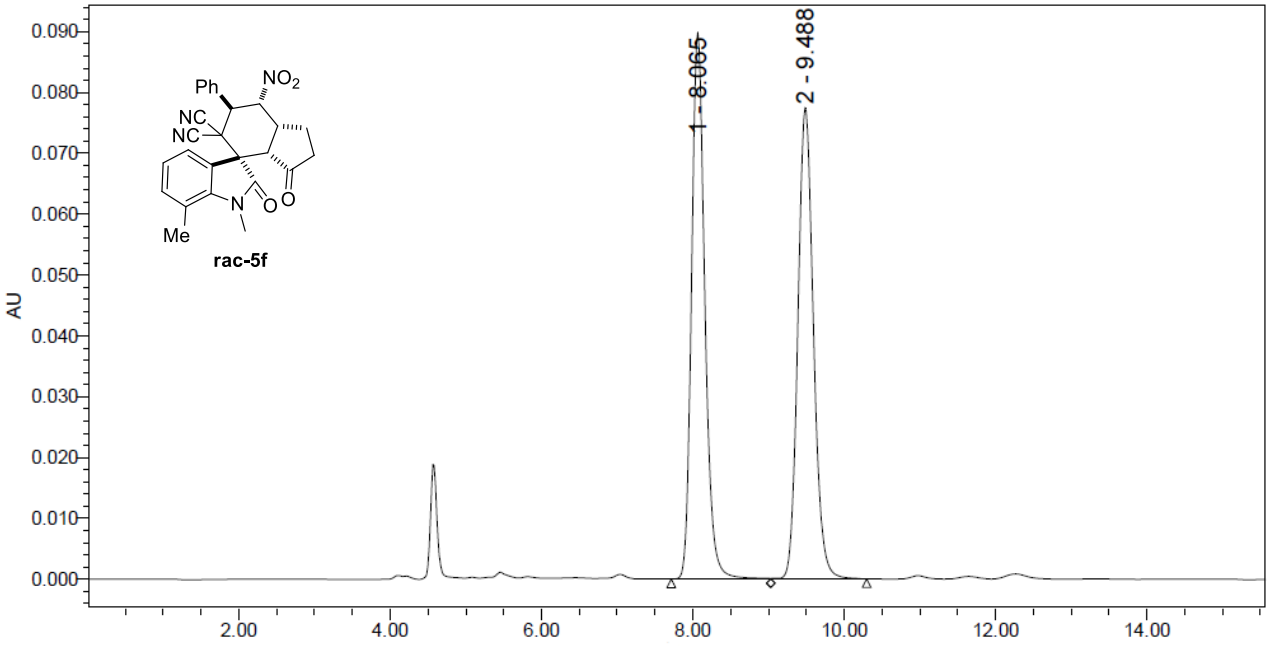
Peak	RT (min)	Height	% Height	Area	% Area
1	6.747	939051	57.45	10599081	50.29
2	8.590	695641	42.55	10476522	49.71



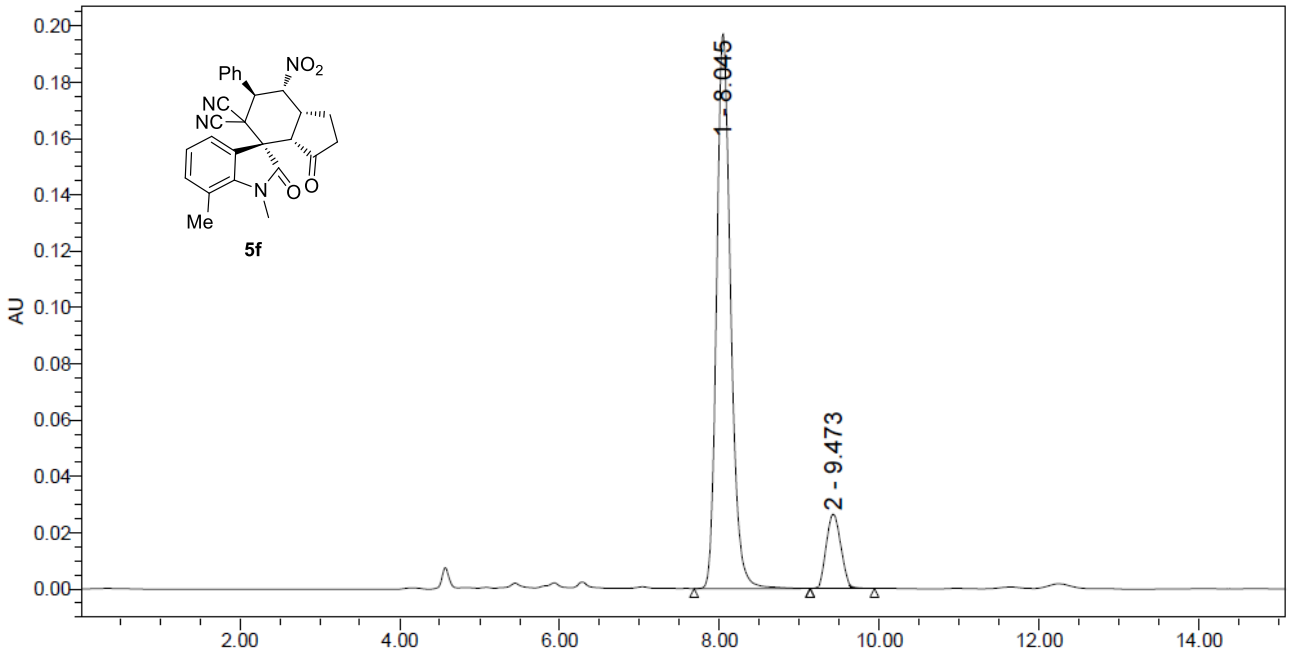
Peak	RT (min)	Height	% Height	Area	% Area
1	6.447	7820298	93.40	81609694	90.95
2	8.130	552262	6.60	8122373	9.05


Ph
NO2
NC
NC
O
O
N
Me
5f
(600MHz, CDCl3)
7.541
7.532
7.520
7.508
7.444
7.436
7.426
7.407
7.261
7.215
7.202
7.159
7.137
7.125
5.944
5.932
5.923
5.911
5.369
5.349
3.545
3.530
3.515
3.497
3.279
3.264
2.961
2.947
2.941
2.927
2.596
2.521
2.507
2.488
2.474
2.329
2.314
2.309
2.295
2.281
2.277
2.262
1.814
1.800
1.782
1.787
1.779
1.765
1.562
1.259
0.000
ppm
2.78
0.99
2.80
1.01
1.00
1.00
3.76
0.94
1.12
1.19
2.81
1.18
1.02

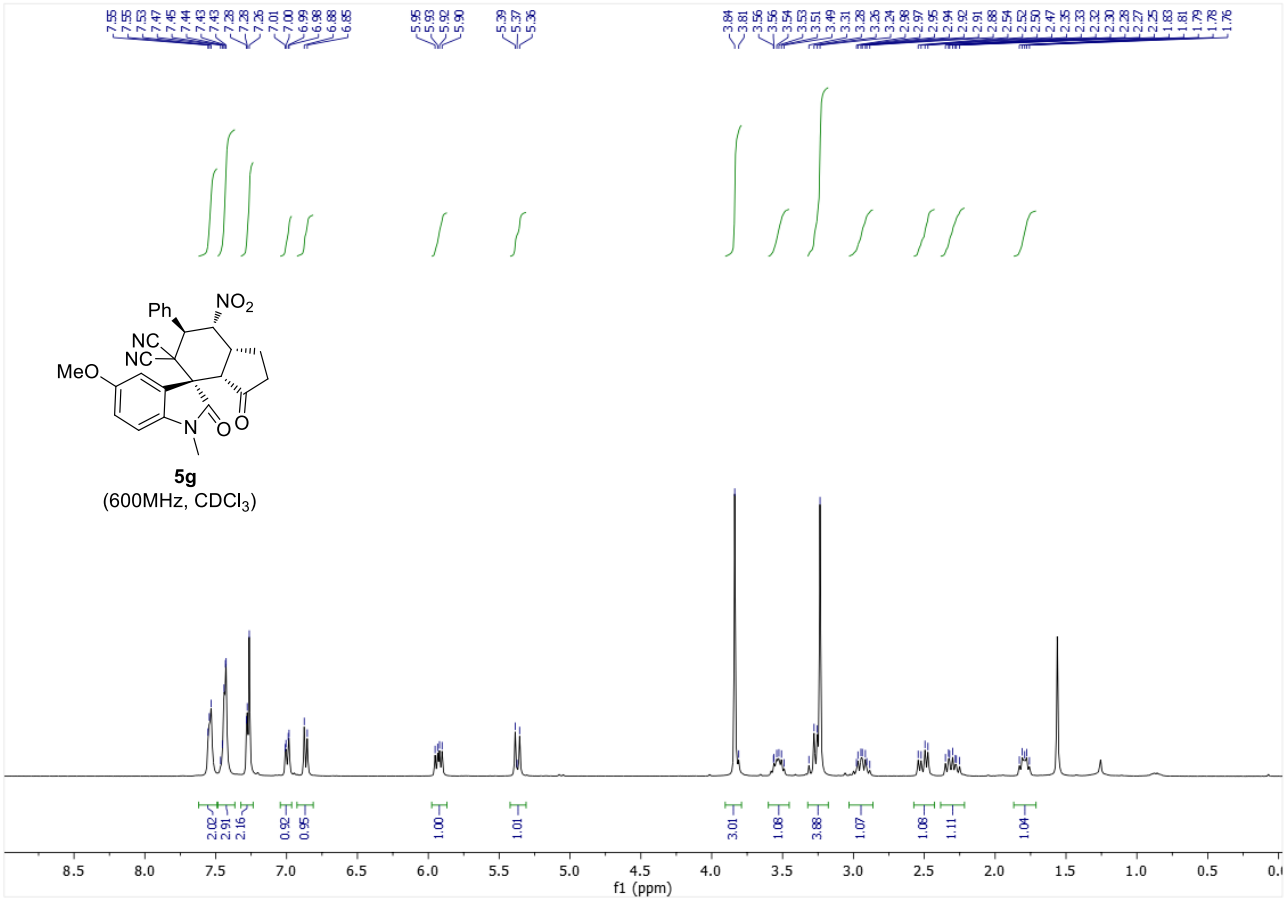

Pulse Sequence: s2pul
212.405
172.940
141.270
135.208
131.894
130.073
129.483
125.663
124.028
122.350
121.043
111.591
110.476
84.272
77.215
77.004
76.793
52.594
48.766
48.556
39.804
38.471
38.353
30.461
22.670
19.163
Ph
NO2
NC
NC
O
O
N
Me
5f
(150MHz, CDCl3)
ppm

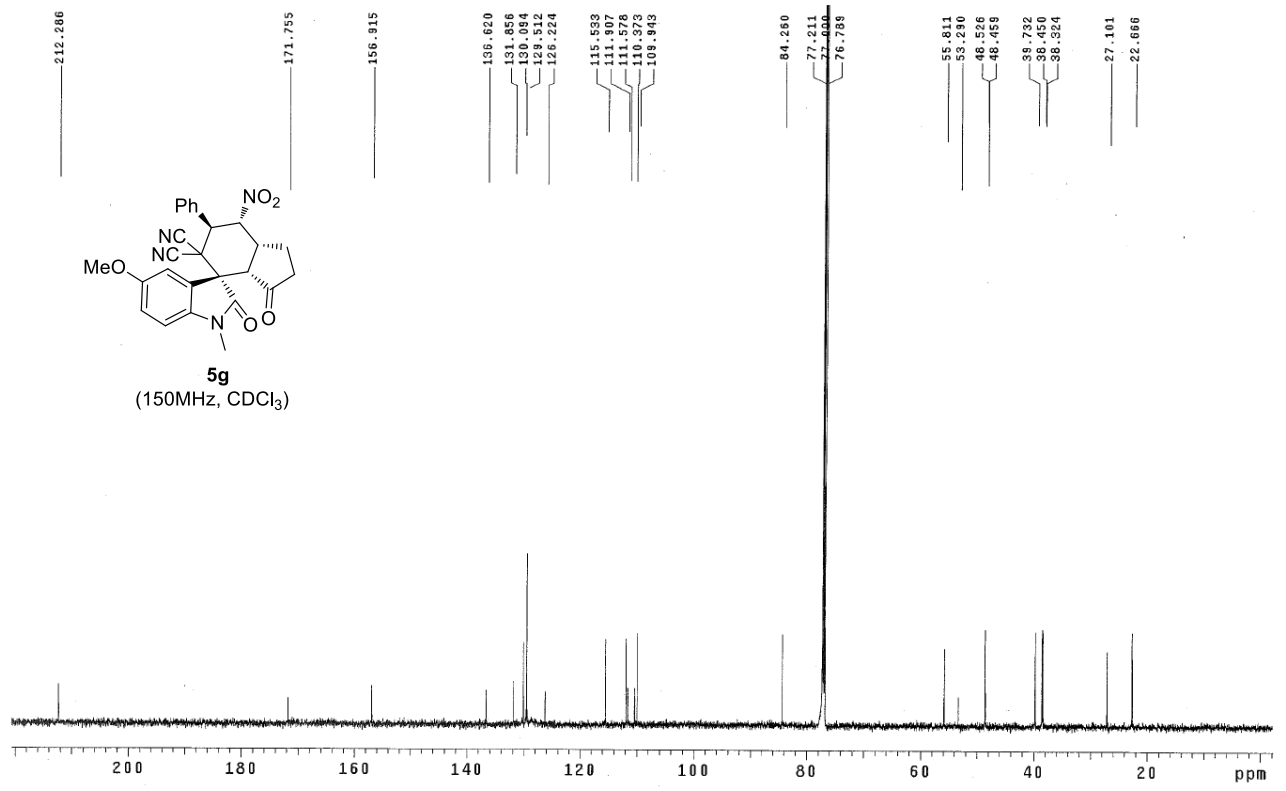


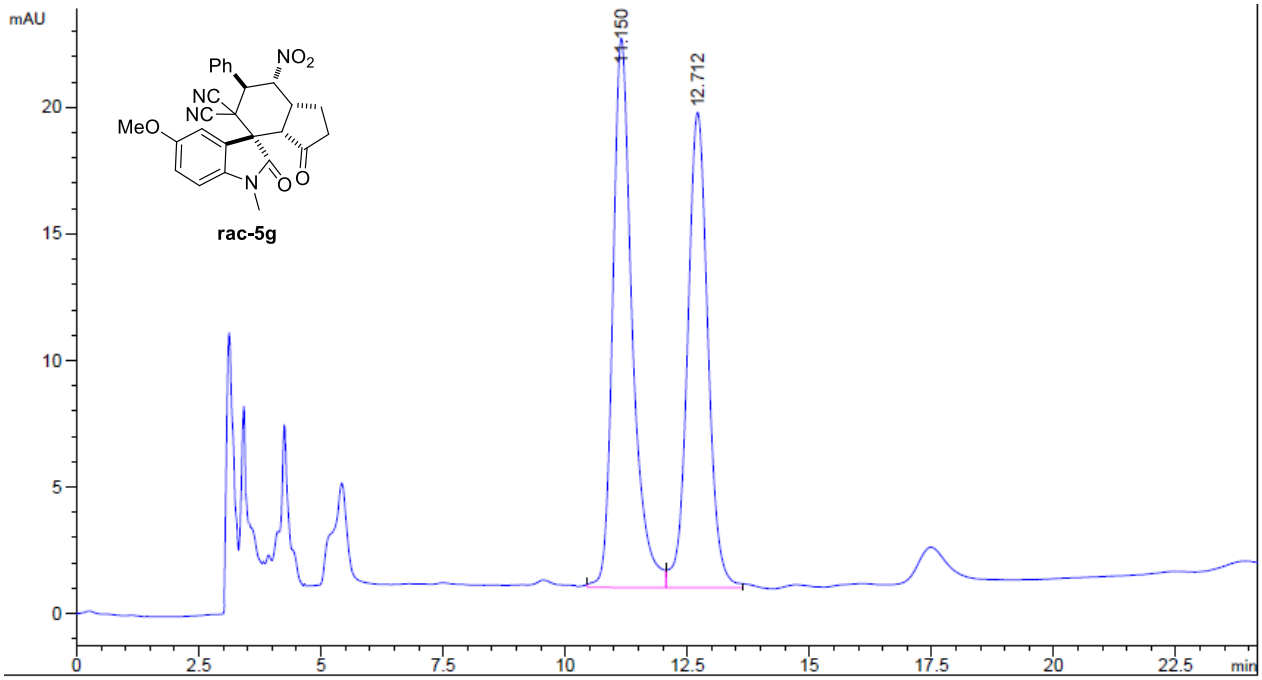
Peak	RT (min)	Height	% Height	Area	% Area
1	8.065	89818	53.68	1094525	49.69
2	9.488	77502	46.32	1108114	50.31



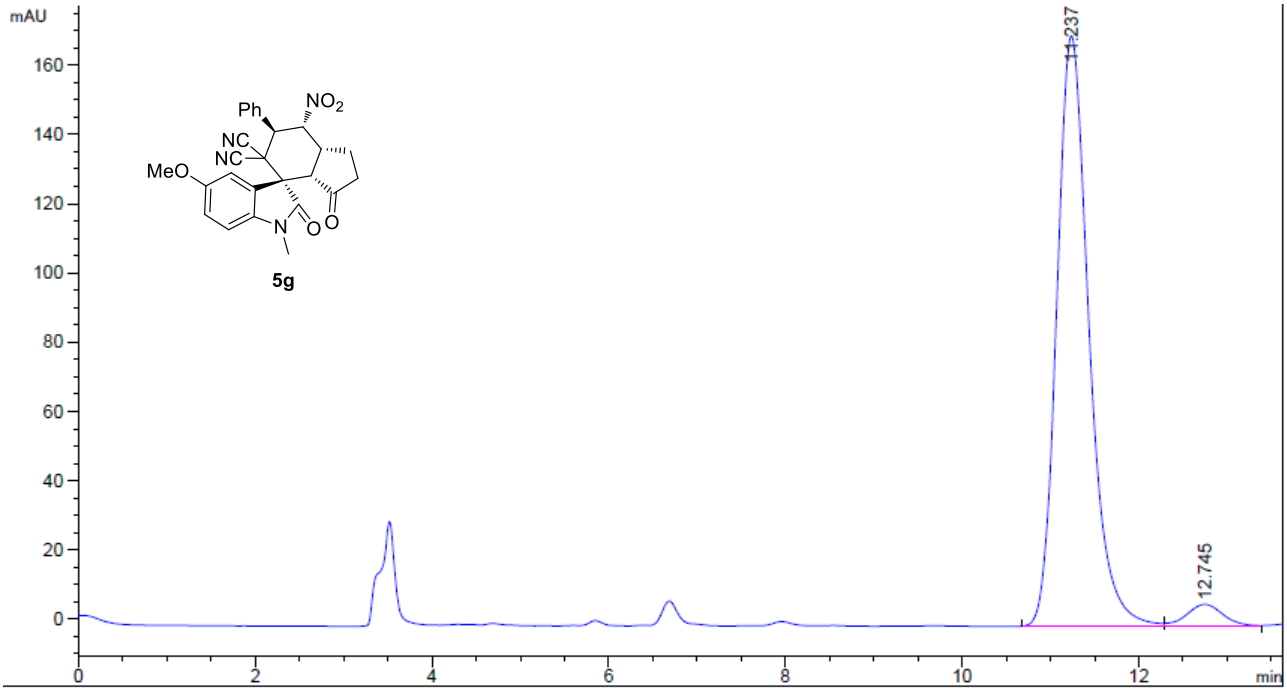
Peak	RT (min)	Height	% Height	Area	% Area
1	8.045	197523	86.94	2518839	92.02
2	9.473	29683	13.06	331093	7.98


Ph
NO2
NC
NC
MeO
N
O
O
5g
(600MHz, CDCl3)
f1 (ppm)

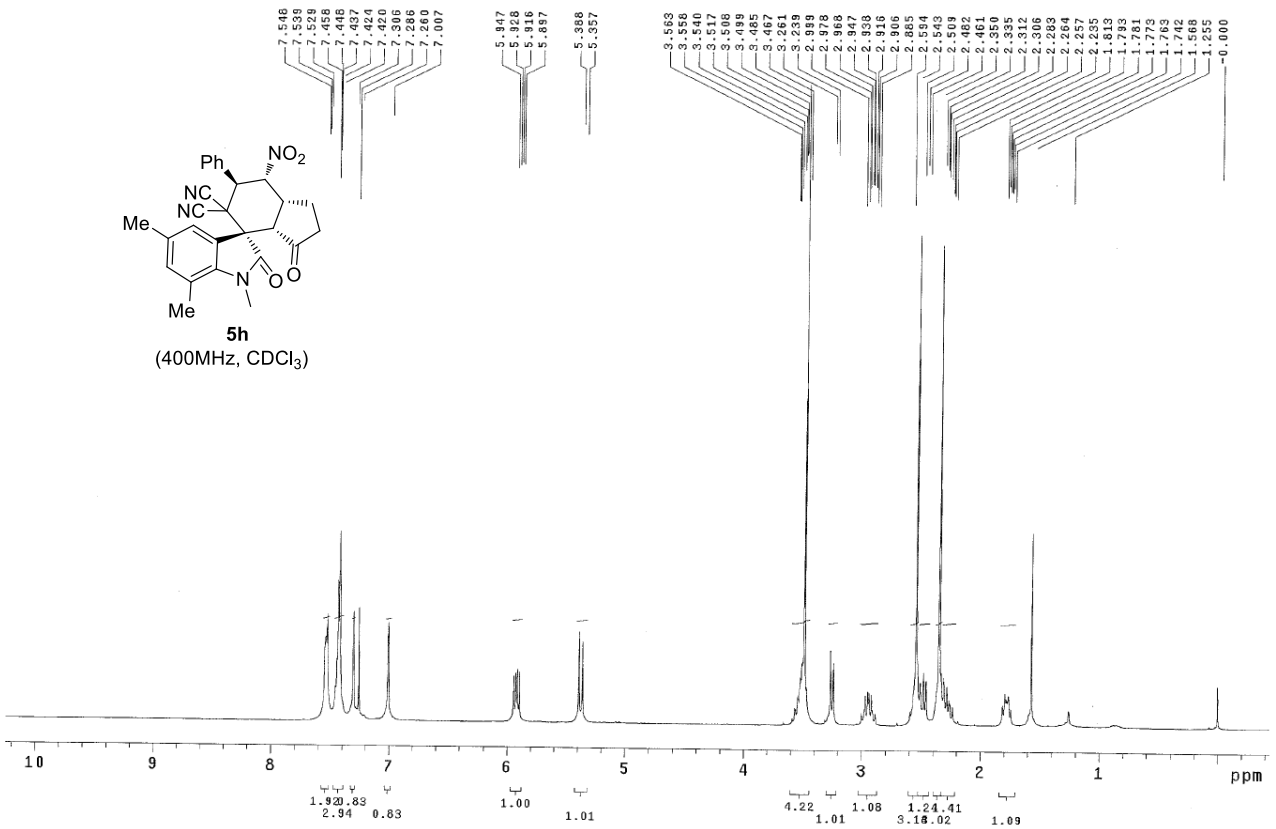

Ph
NO2
NC
NC
MeO
N
O
O
5g
(150MHz, CDCl3)
ppm

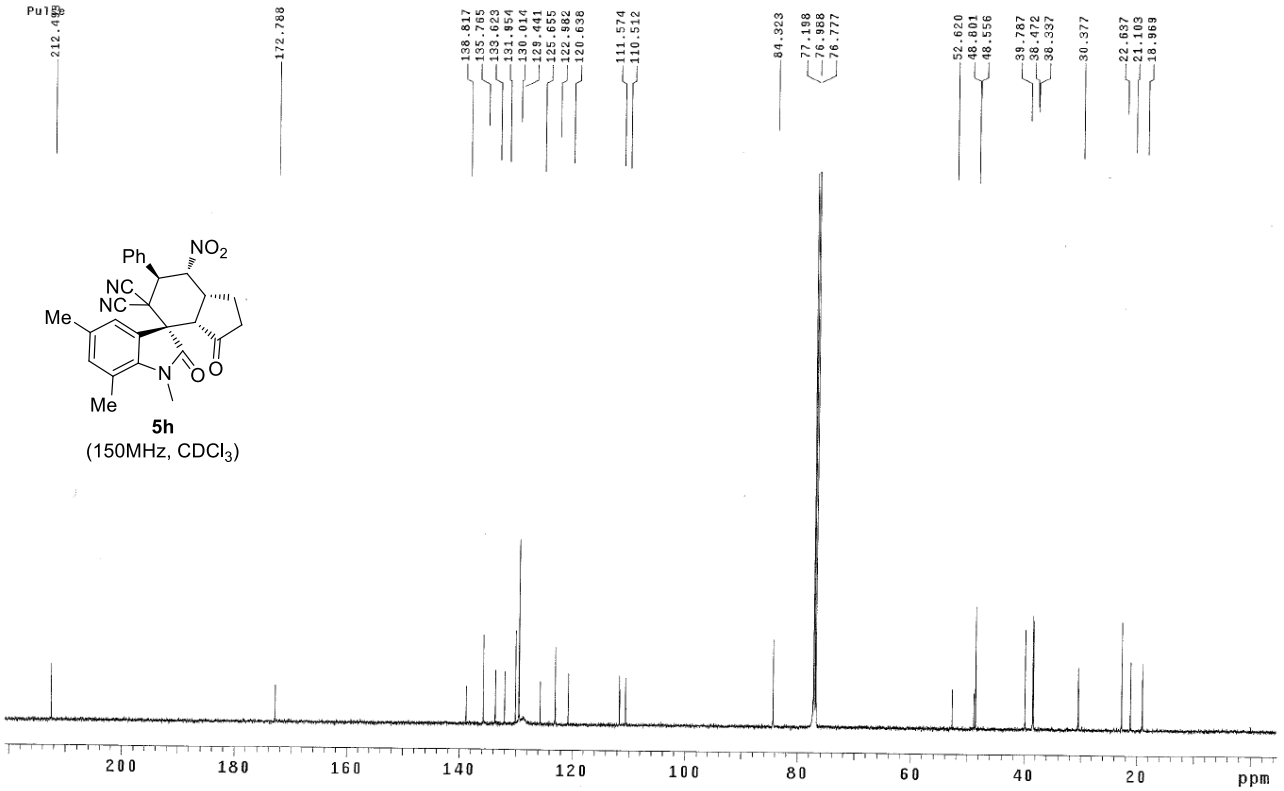


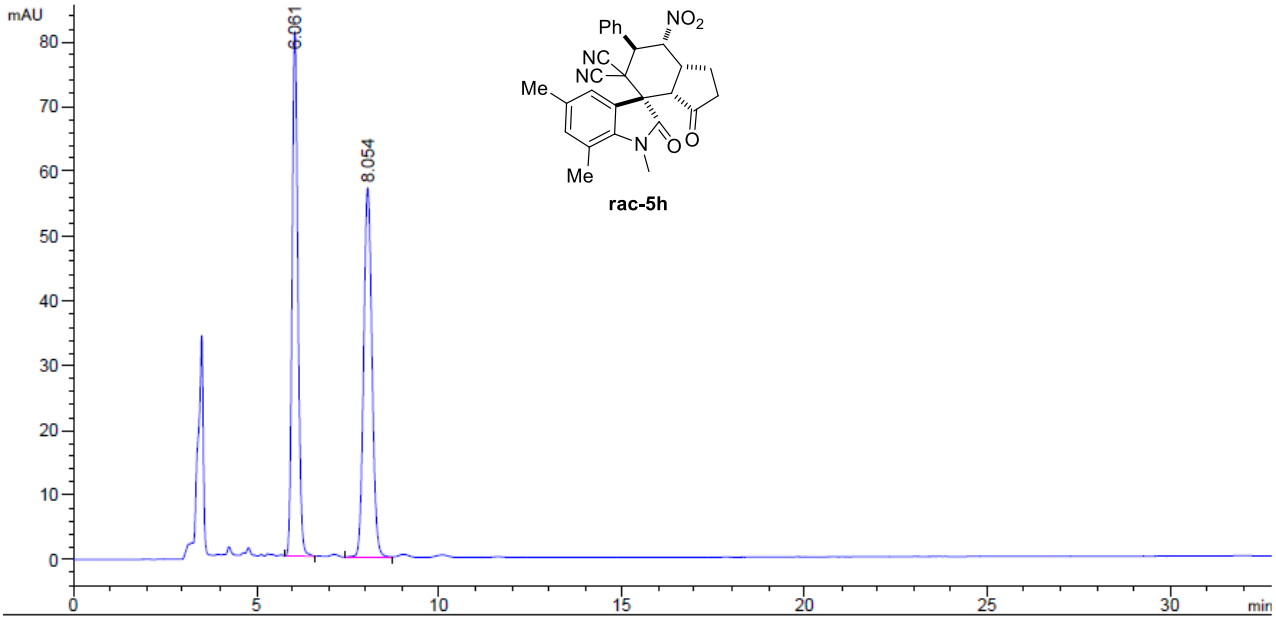
Peak	RT (min)	Height	% Height	Area	% Area
1	11.150	21.68	58.84	600.22	52.55
2	12.712	18.77	41.16	541.93	47.45



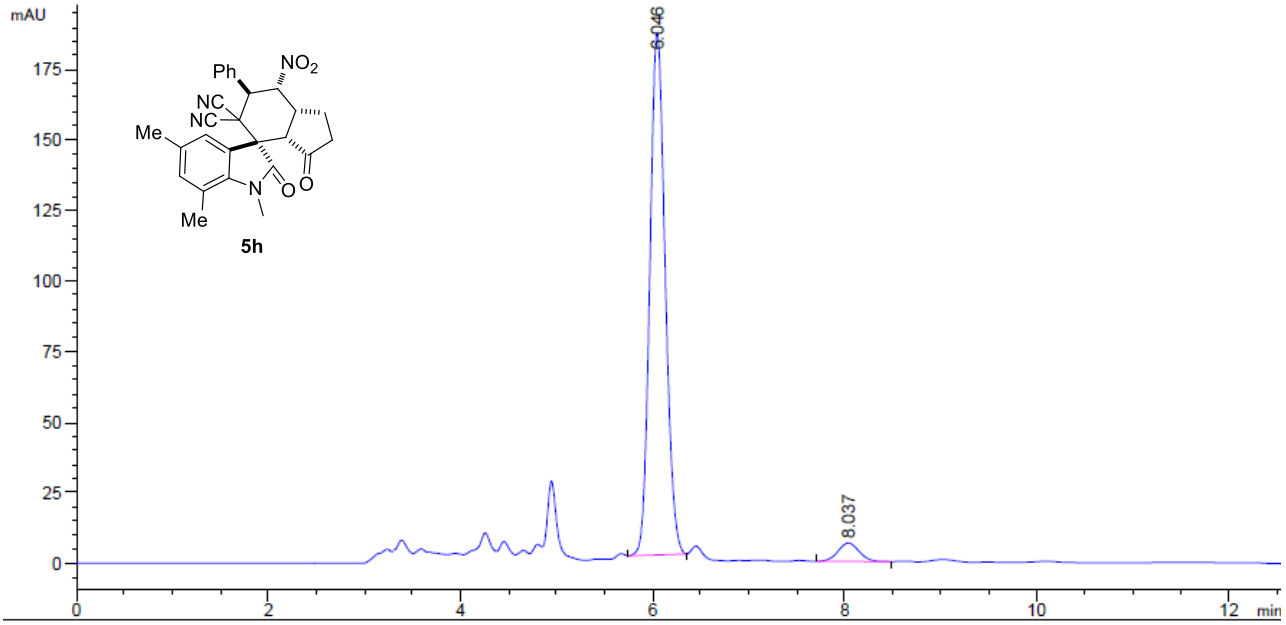
Peak	RT (min)	Height	% Height	Area	% Area
1	11.237	170.34	96.55	4303.2	95.97
2	12.745	6.30	3.45	180.6	4.03


Ph
NO2
NC
NC
Me
N
O
O
Me
5h
(400MHz, CDCl3)
ppm

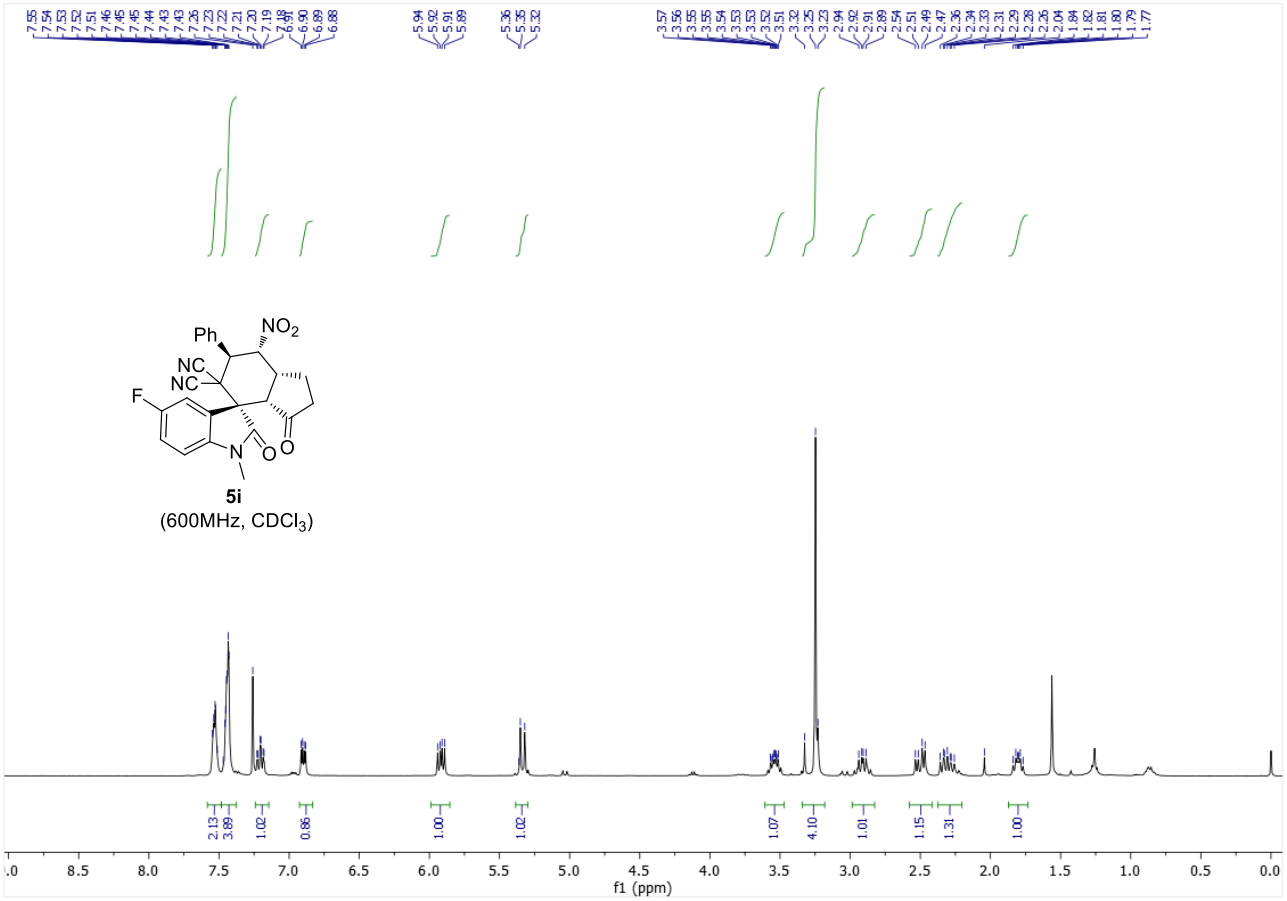

Ph
NO2
NC
NC
Me
N
O
O
Me
5h
(150MHz, CDCl3)
ppm



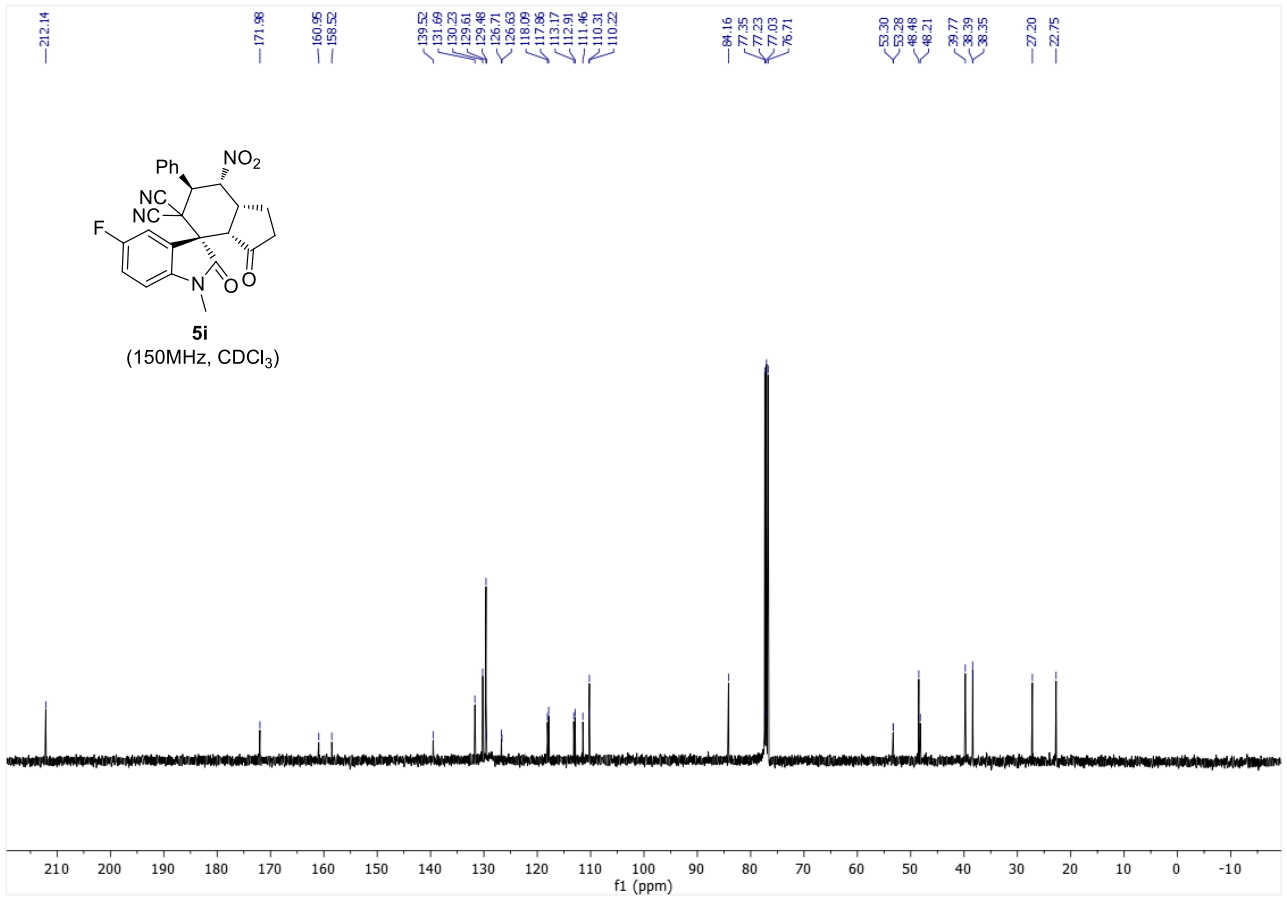
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.061	BB	0.1720	900.97498	80.97964	49.9825
2	8.054	BB	0.2456	901.60455	57.02062	50.0175



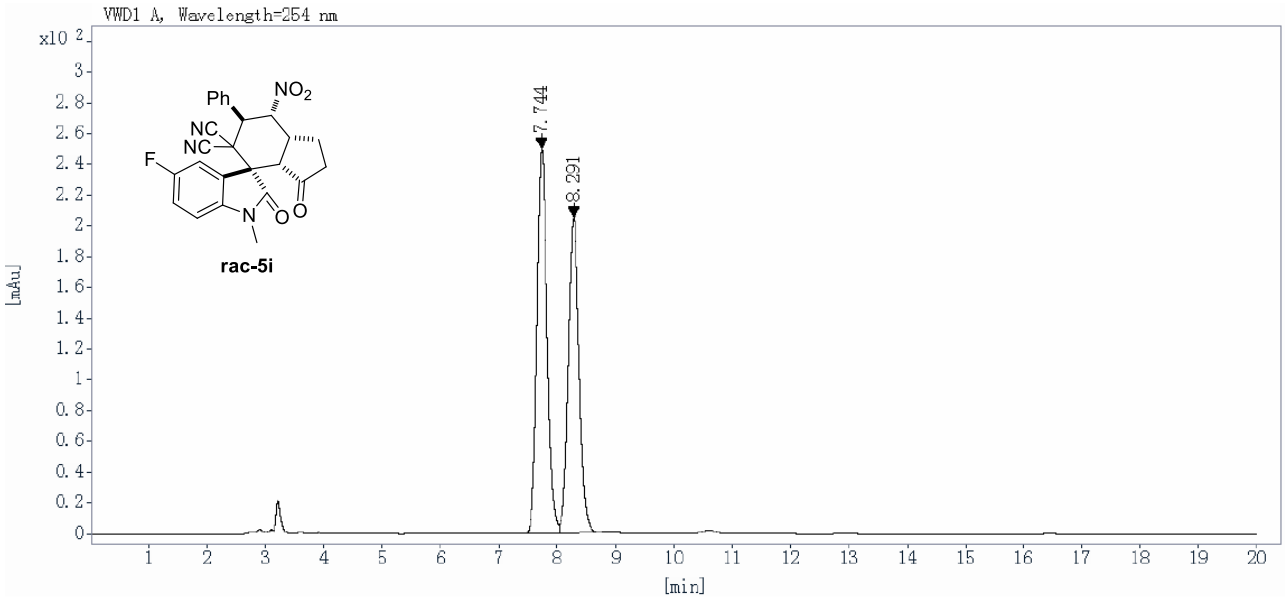
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.046	BBA	0.1715	2052.27954	185.25319	95.3367
2	8.037	BV	0.2400	100.38623	6.49527	4.6633



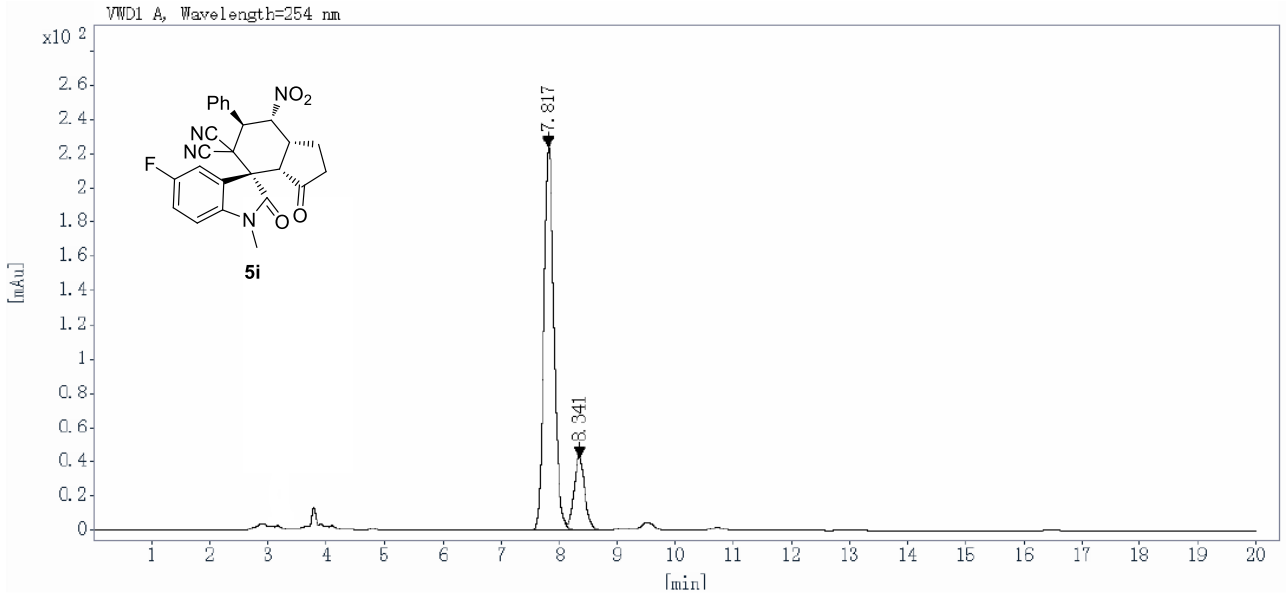
5i
(600MHz, $CDCl_3$)



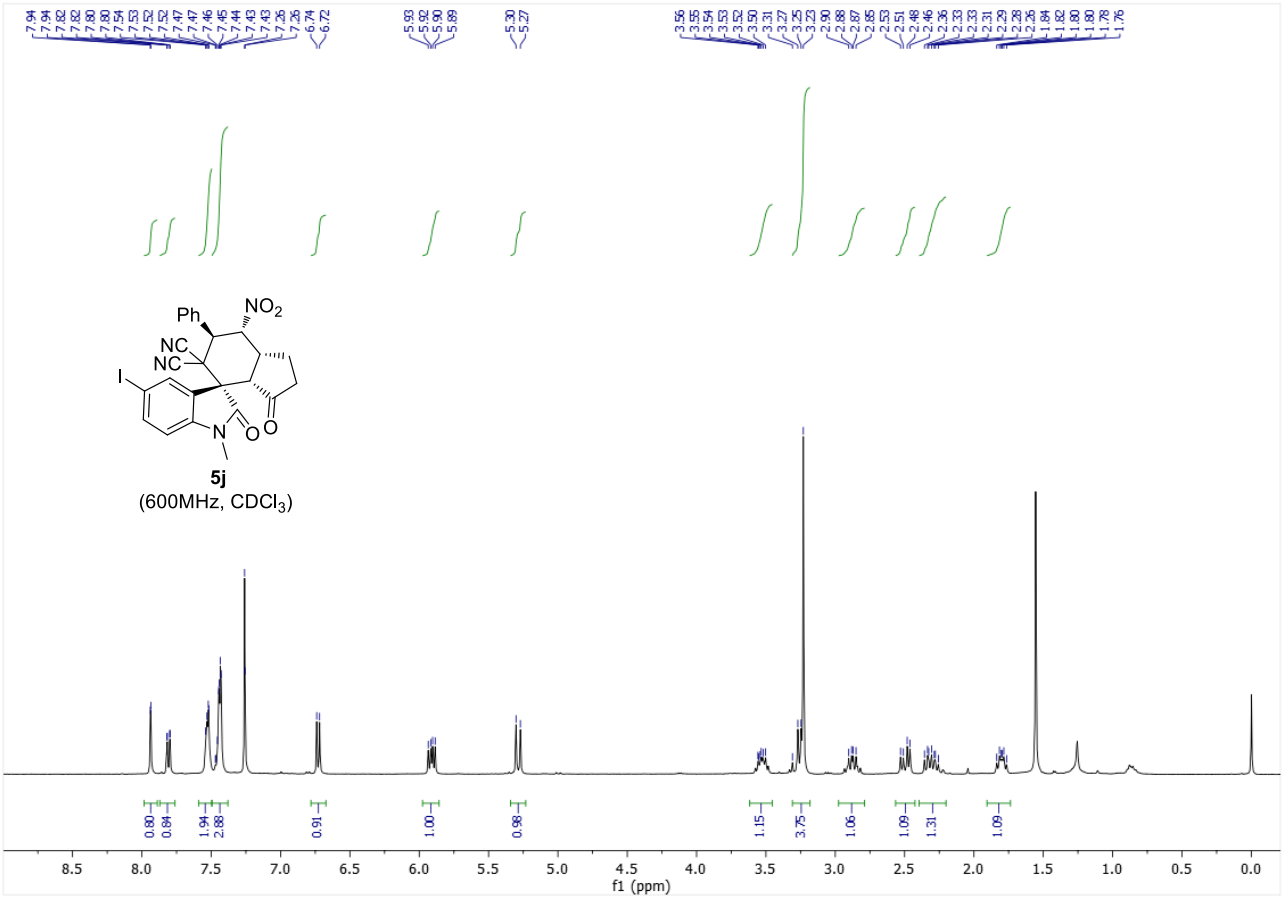
5i
(150MHz, $CDCl_3$)

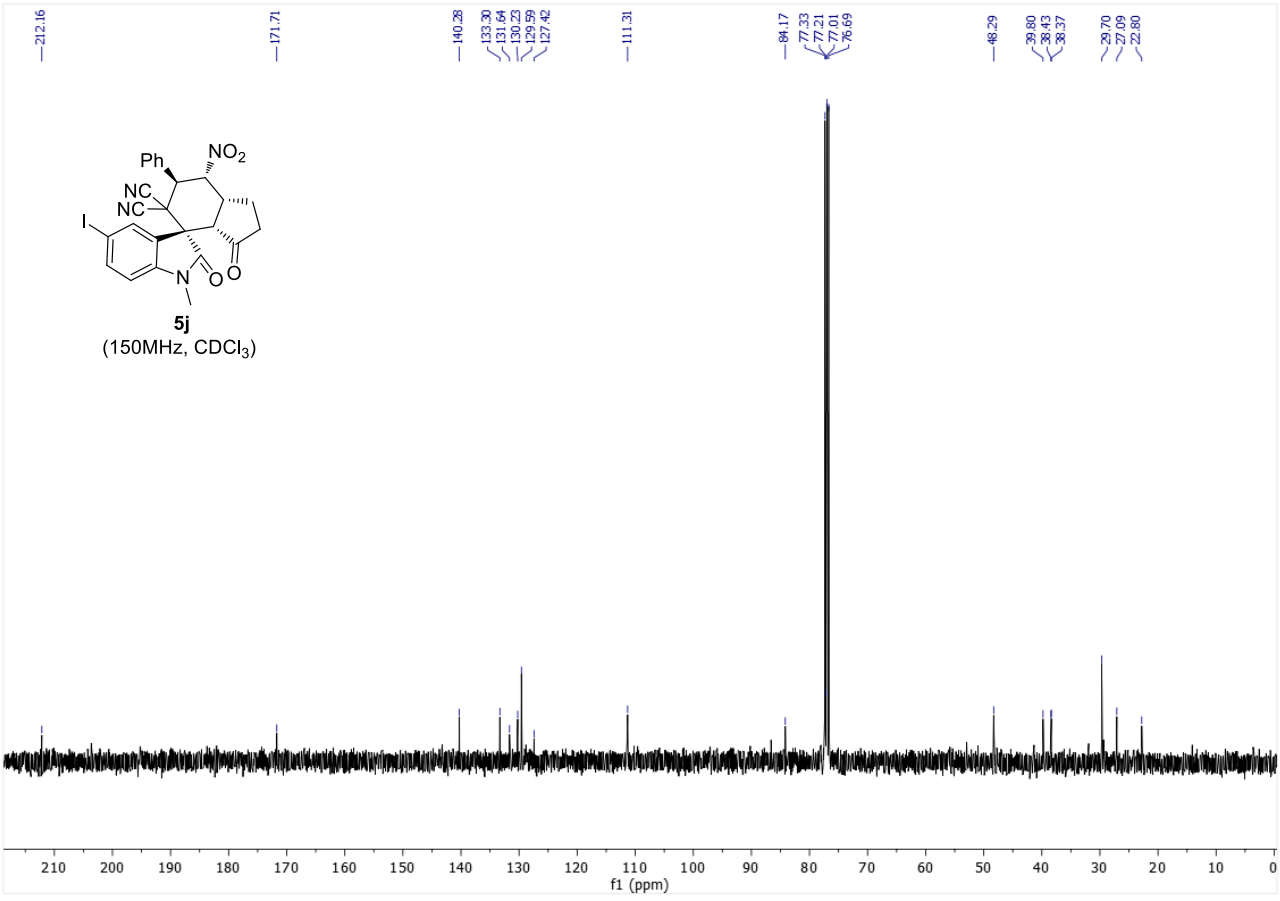


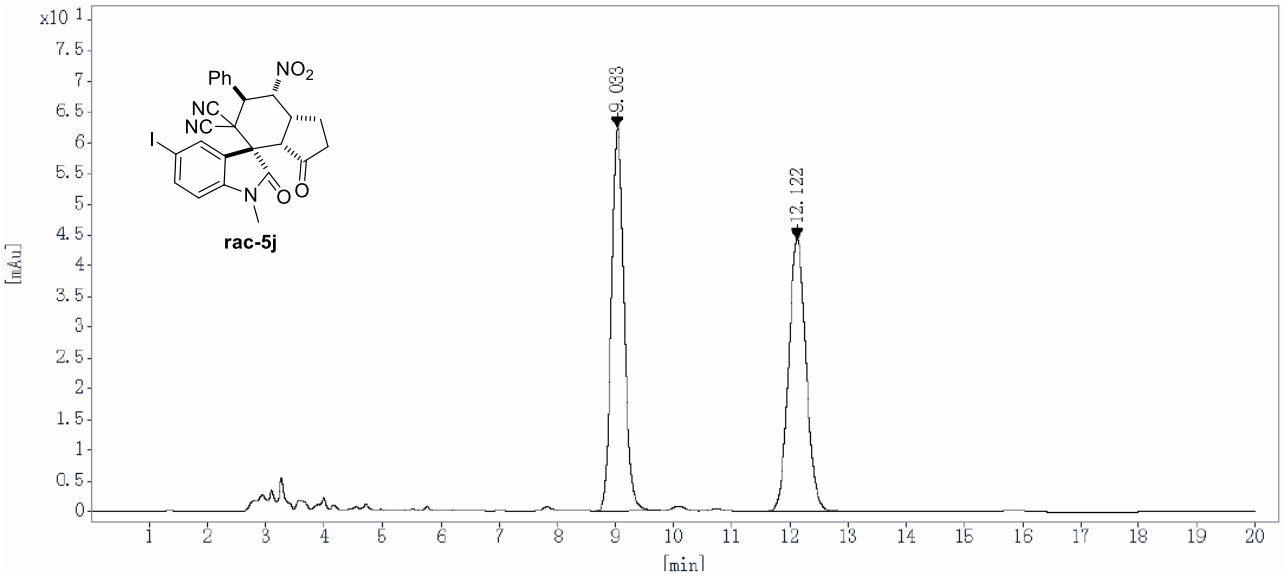
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.744	BV	0.19	249.9336	3032.8333	53.2981
8.291	VB	0.20	204.9978	2657.4839	46.7019



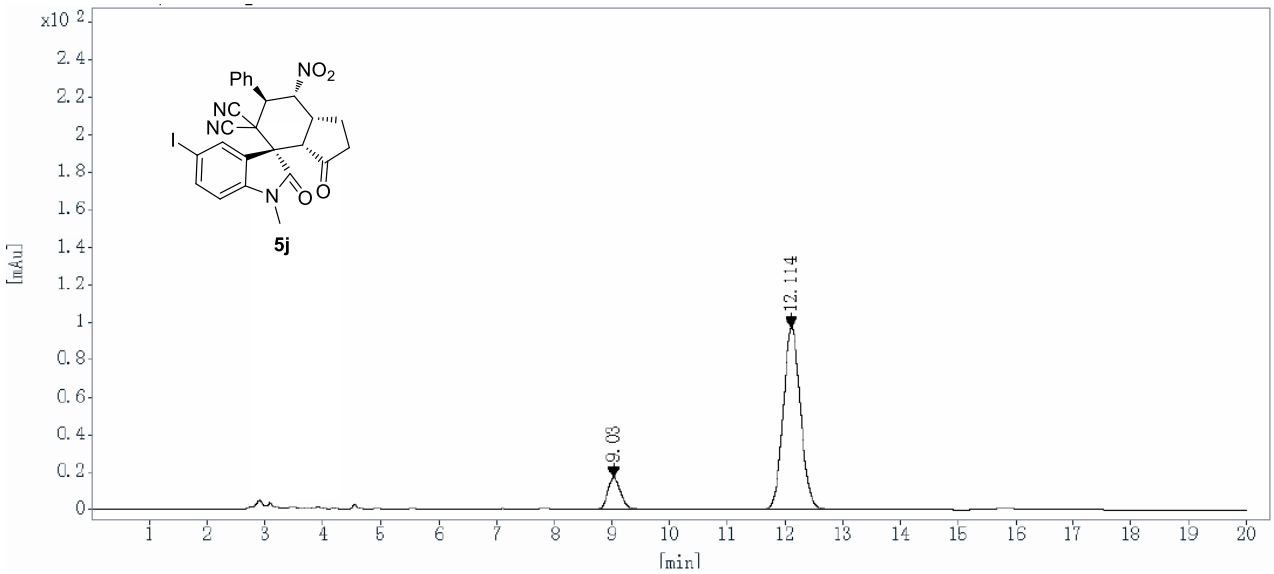
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.817	BV R	0.19	224.0534	2728.4934	83.0500
8.341	VB E	0.20	42.7743	556.8672	16.9500


Ph
NO2
NC
NC
I
O
N
O
5j
(600MHz, CDCl3)
f1 (ppm)

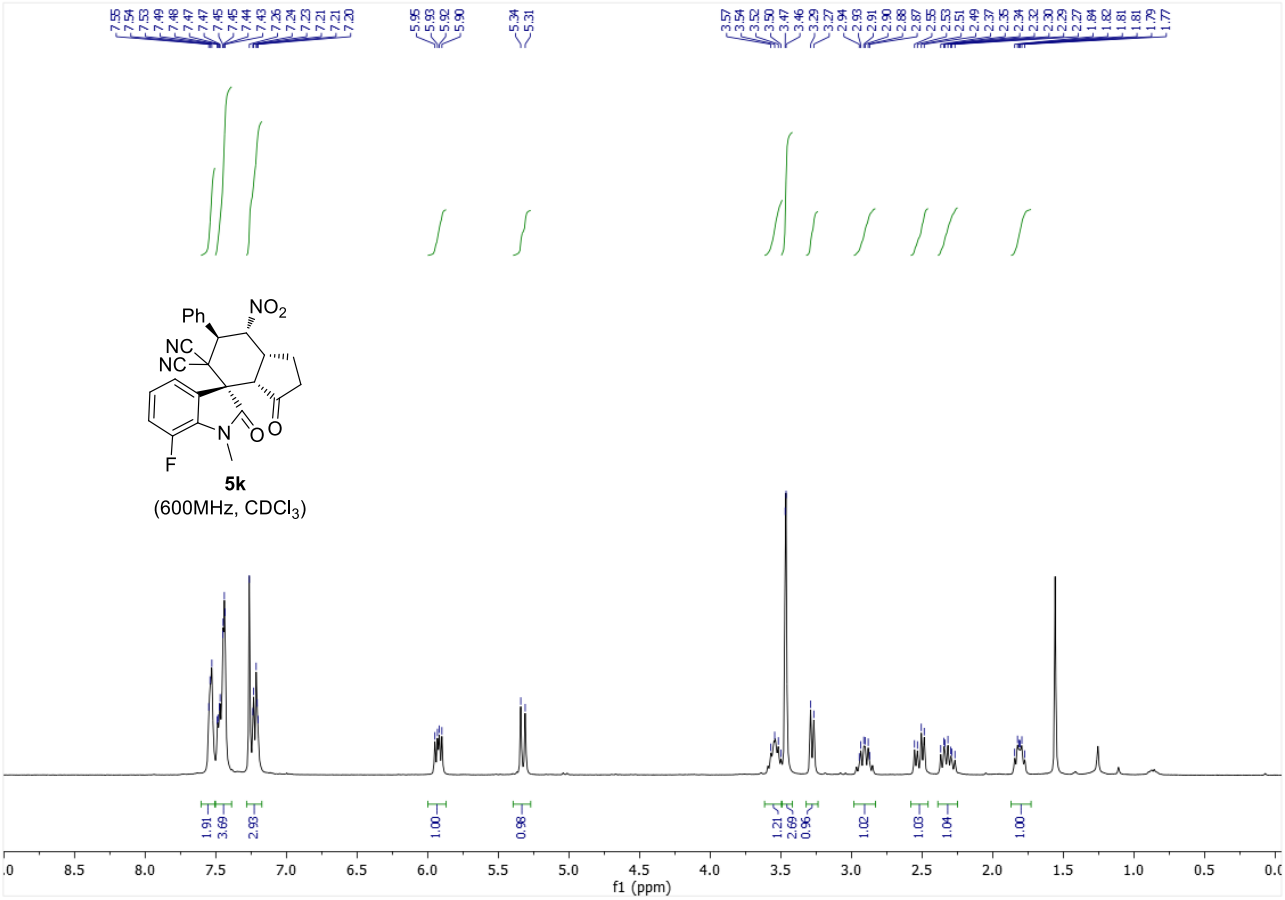

Ph
NO2
NC
NC
I
O
N
O
5j
(150MHz, CDCl3)
f1 (ppm)

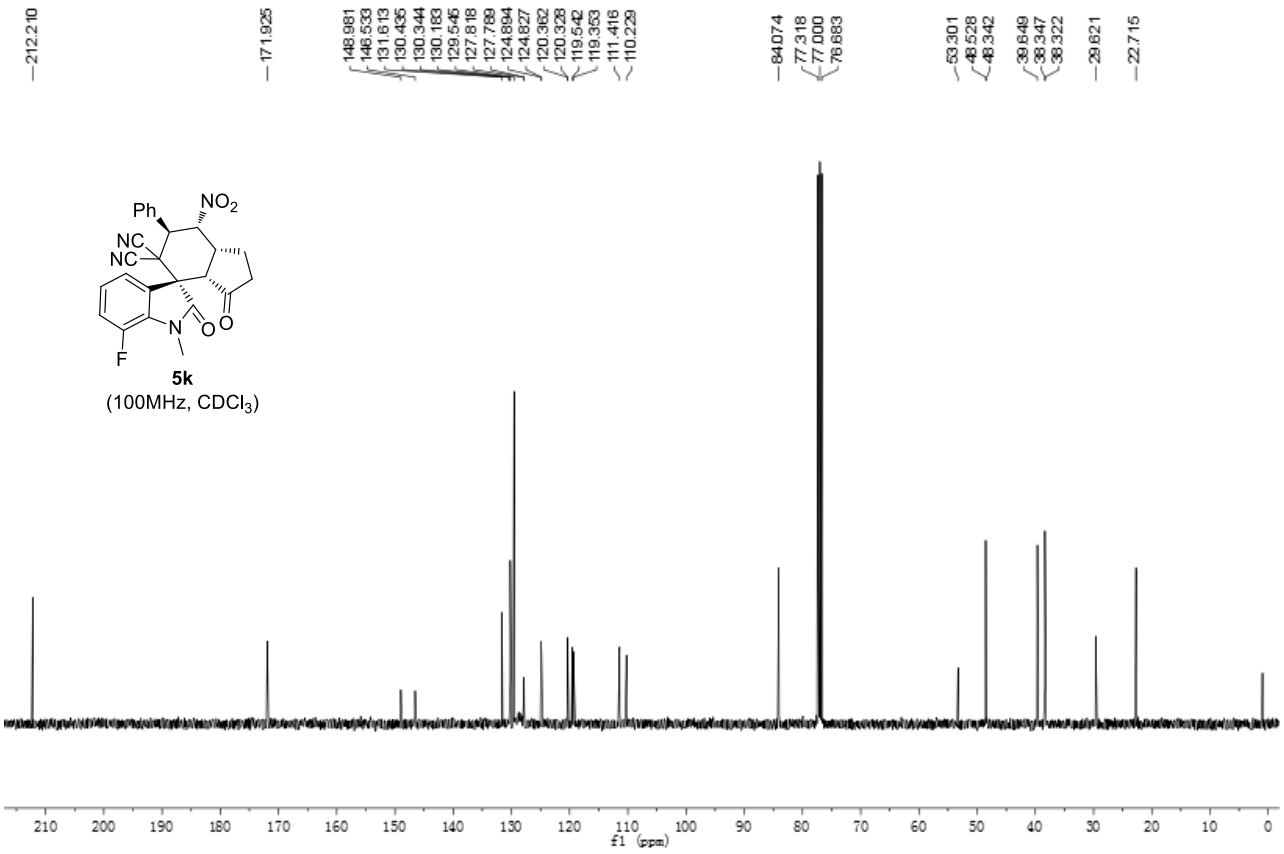


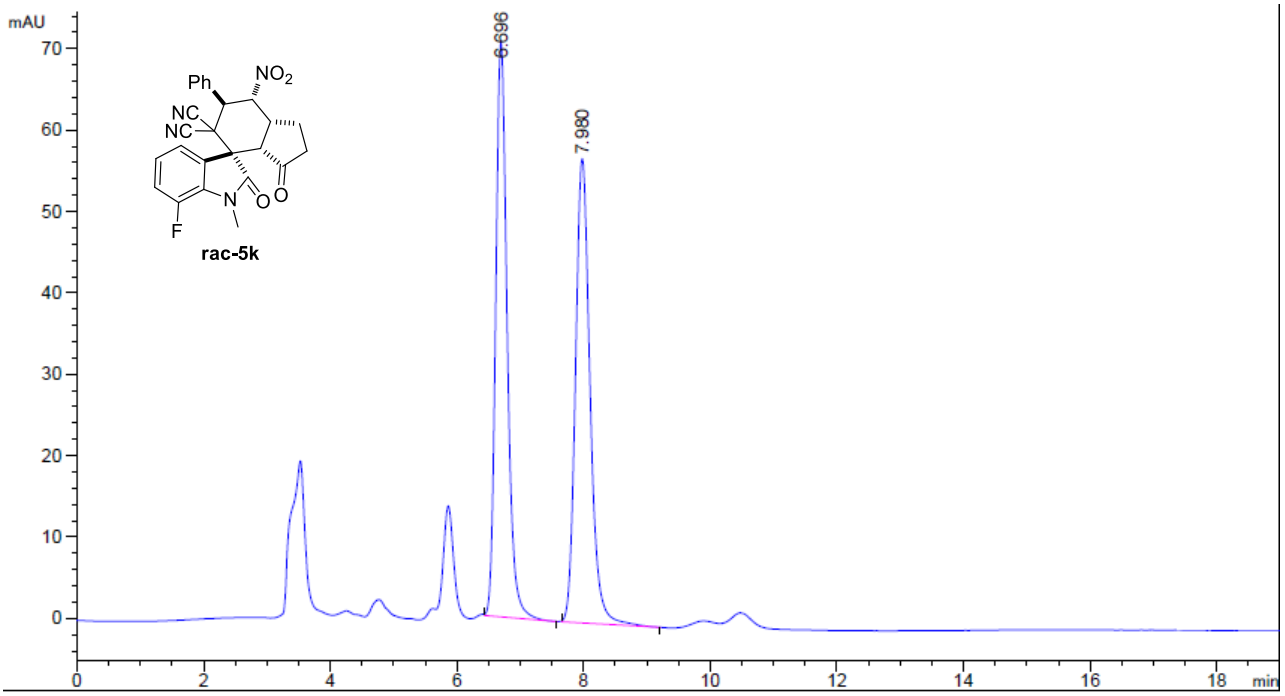
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.033	BB	0.23	62.2731	936.2390	50.2052
12.122	BB	0.33	44.3350	928.5851	49.7948



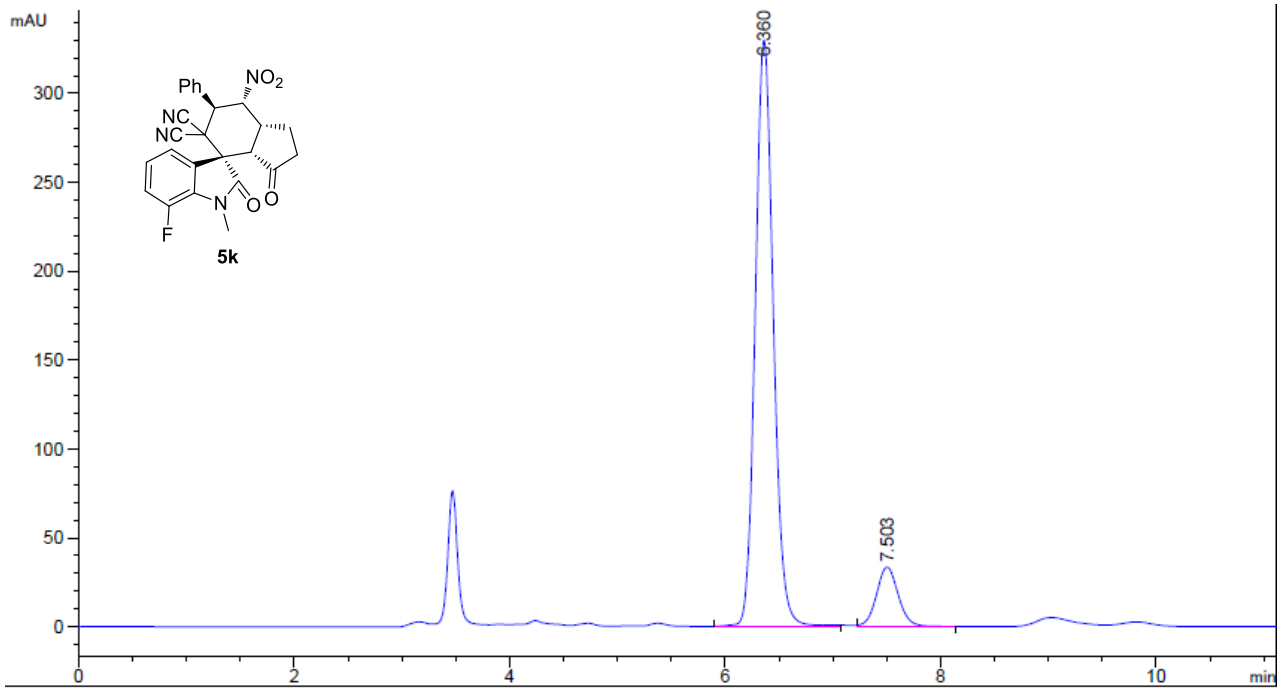
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.030	BBA	0.24	17.1948	273.0152	11.7910
12.114	BB	0.33	97.0805	2042.4358	88.2090


Ph
NO2
NC
NC
O
N
O
F
5k
(600MHz, CDCl3)
f1 (ppm)

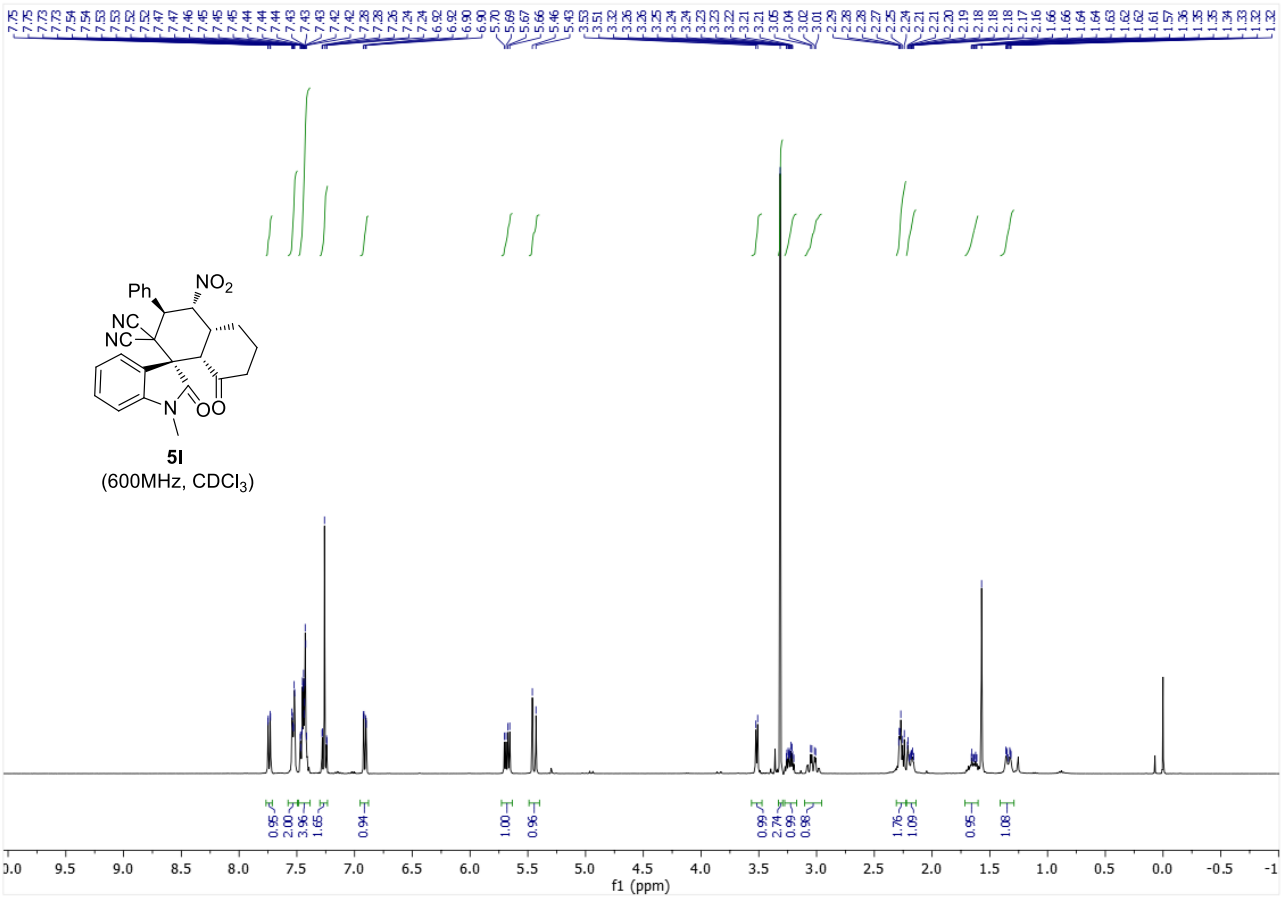

Ph
NO2
NC
NC
O
N
O
F
5k
(100MHz, CDCl3)
f1 (ppm)

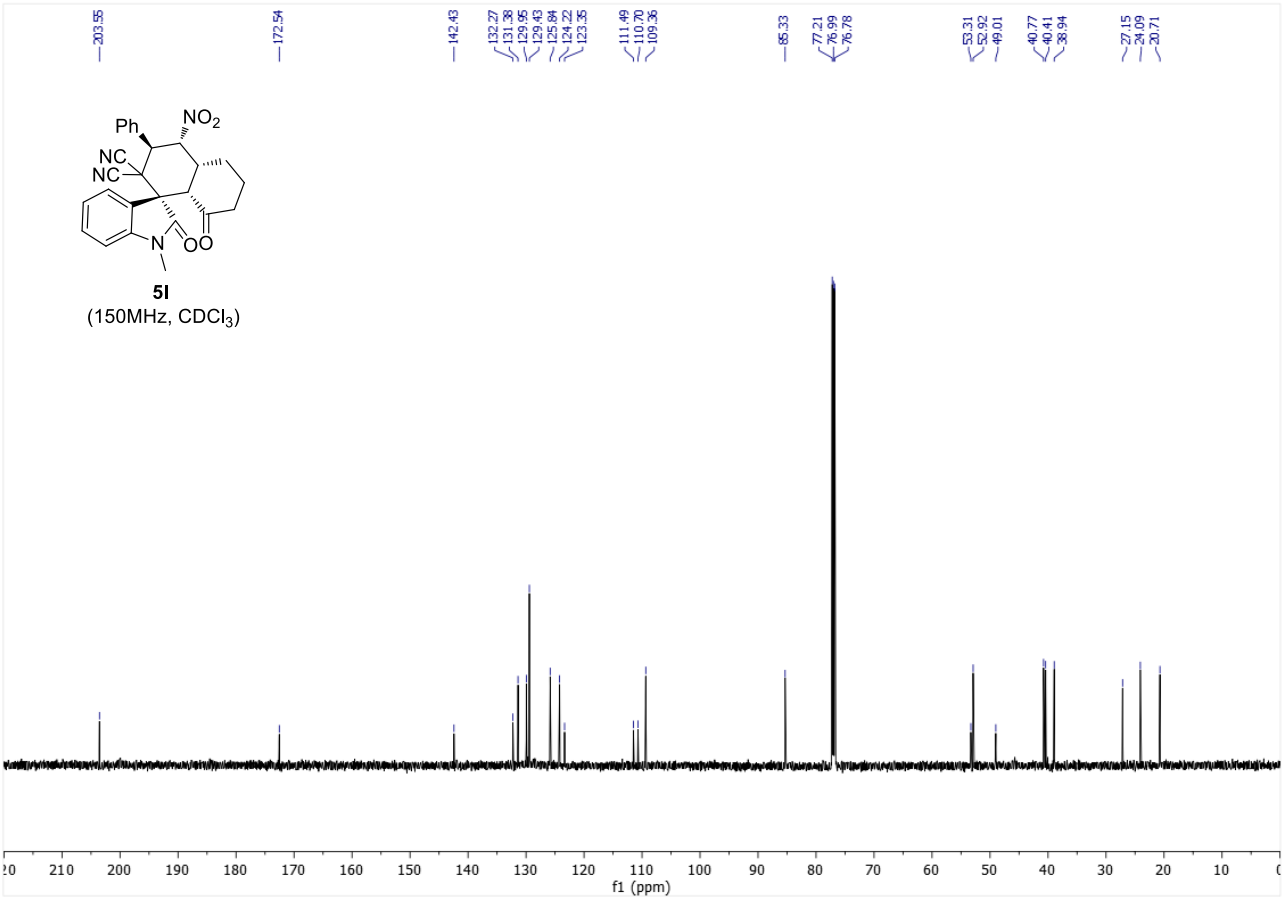


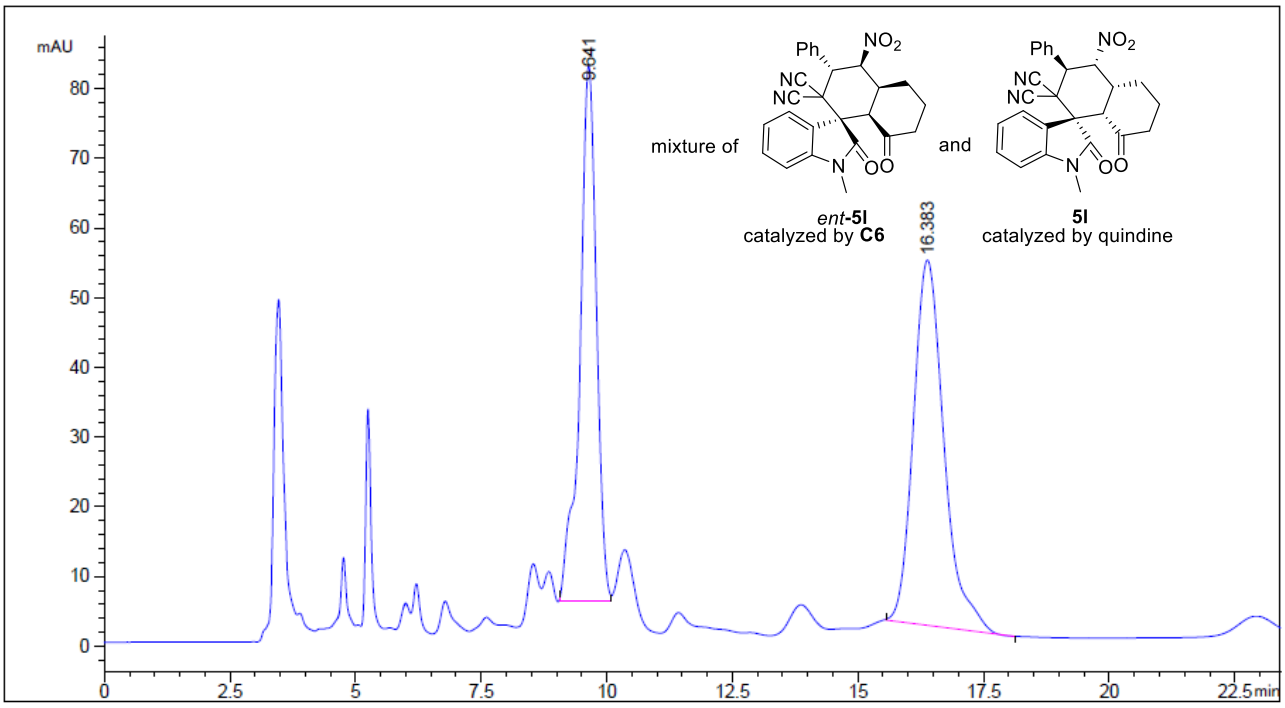
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.696	BB	0.1937	888.07391		70.40771	49.4315
2	7.980	BB	0.2443	908.49933		56.95322	50.5685



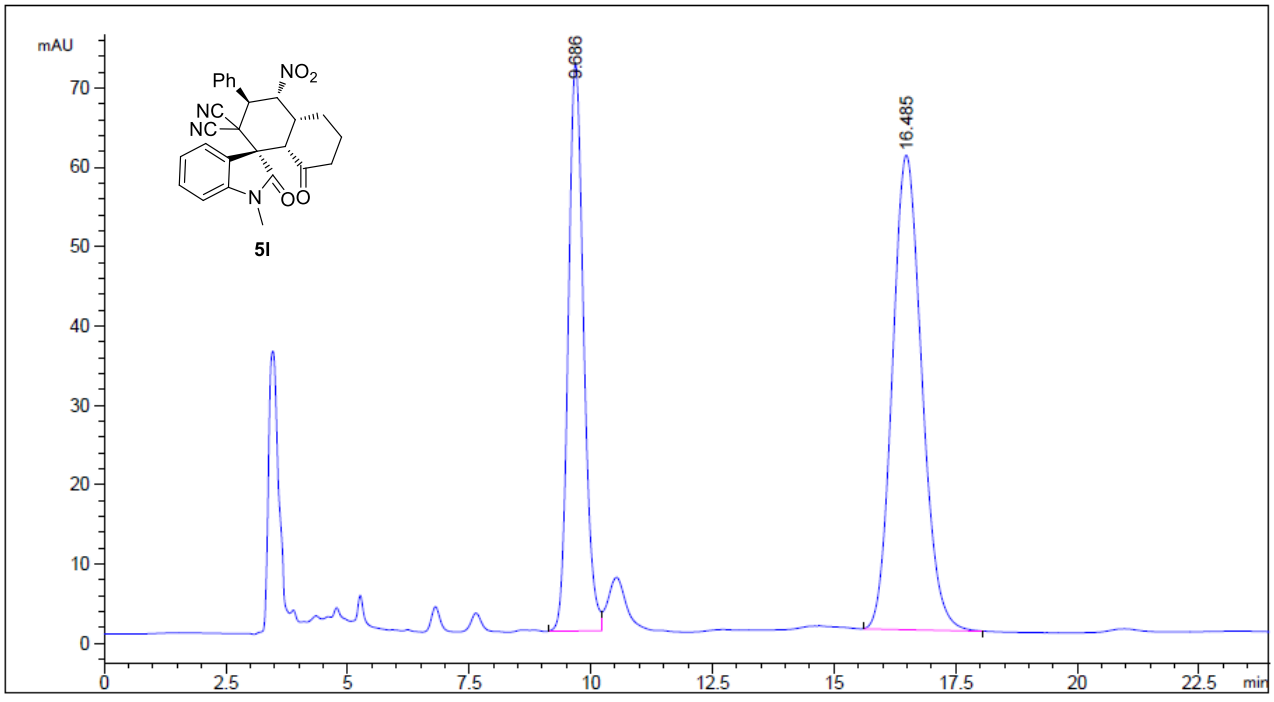
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.360	BB	0.1828	3841.84229		328.96249	89.1134
2	7.503	BB	0.2167	469.34079		33.33318	10.8866


Ph
NO2
NC
NC
N
O
O
5l
(600MHz, CDCl3)
f1 (ppm)

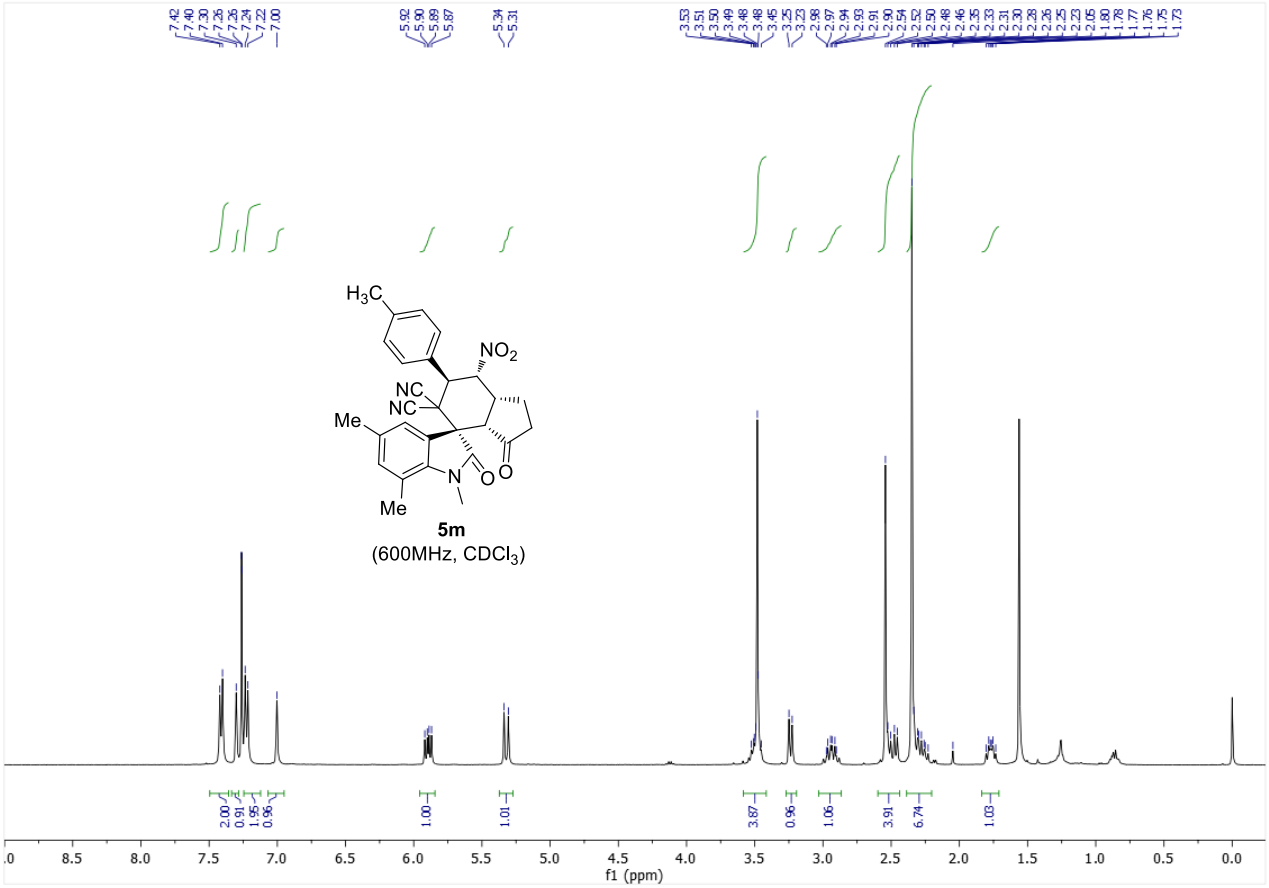

Ph
NO2
NC
NC
N
O
O
5l
(150MHz, CDCl3)
f1 (ppm)

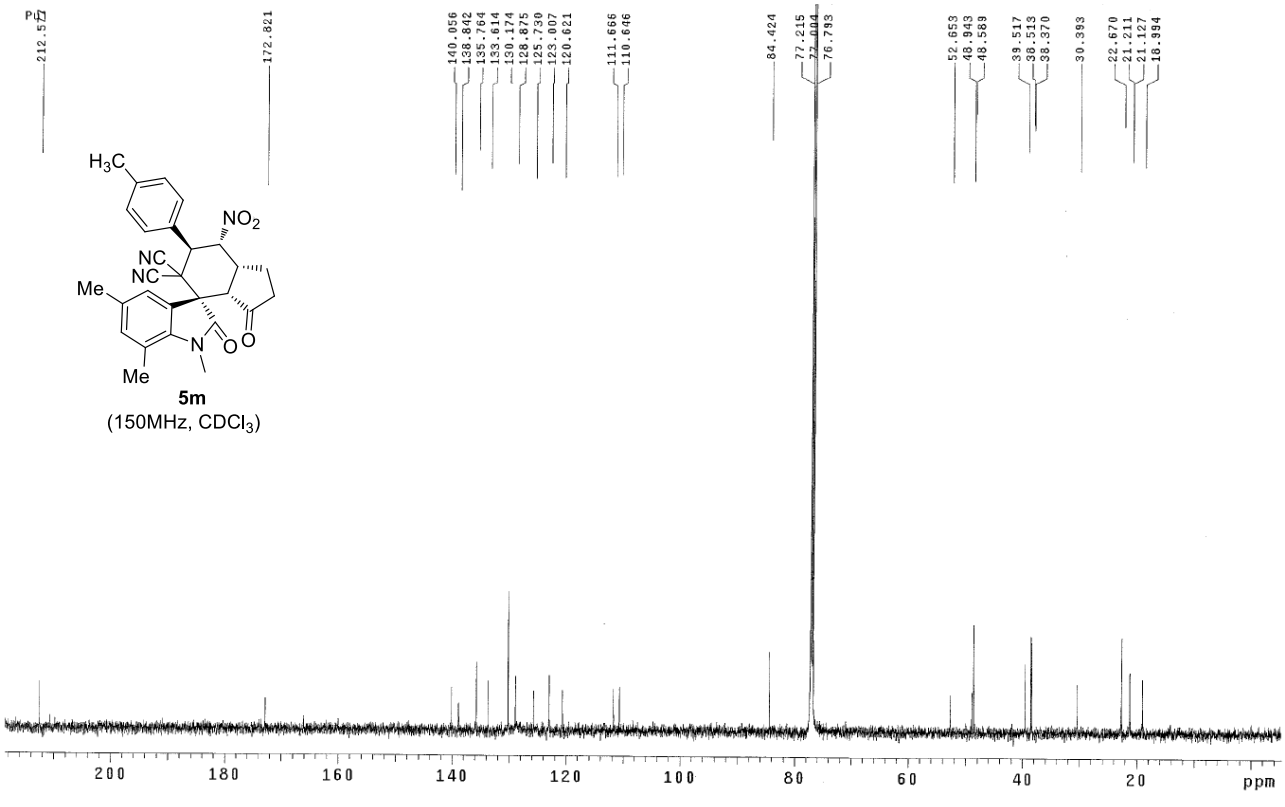


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.641	BV	0.3496	1767.90662	76.94705	44.3741
2	16.383	BB	0.6505	2216.18555	52.41575	55.6259



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.686	BV	0.3385	1572.94592	71.42467	31.5121
2	16.485	BB	0.6530	2511.34131	59.79663	68.4879


7.42
7.40
7.30
7.26
7.24
7.22
7.00
5.92
5.90
5.89
5.87
5.34
5.31
3.53
3.51
3.50
3.49
3.48
3.48
3.45
3.25
3.23
2.98
2.97
2.94
2.93
2.91
2.90
2.54
2.52
2.50
2.48
2.46
2.35
2.33
2.31
2.30
2.28
2.26
2.25
2.23
2.05
1.80
1.78
1.77
1.76
1.75
1.73
H3C
NO2
NC
NC
Me
N
O
O
Me
5m
(600MHz, CDCl3)
2.00
0.91
1.95
0.96
1.00
1.01
3.87
0.96
1.06
3.91
6.74
1.03
f1 (ppm)


212.572
172.821
140.056
138.842
135.764
133.614
130.174
128.875
125.730
123.007
120.621
111.666
110.646
84.424
77.215
77.004
76.793
52.653
48.943
48.583
39.517
38.513
38.370
30.393
22.670
21.211
21.127
18.984
H3C
NO2
NC
NC
Me
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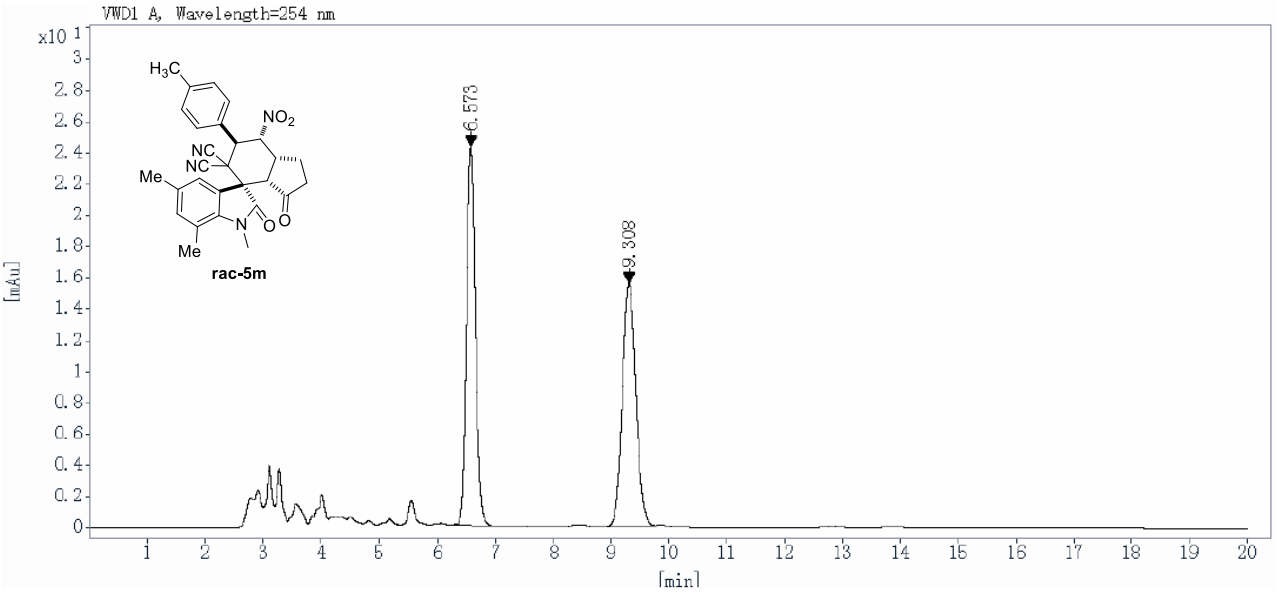
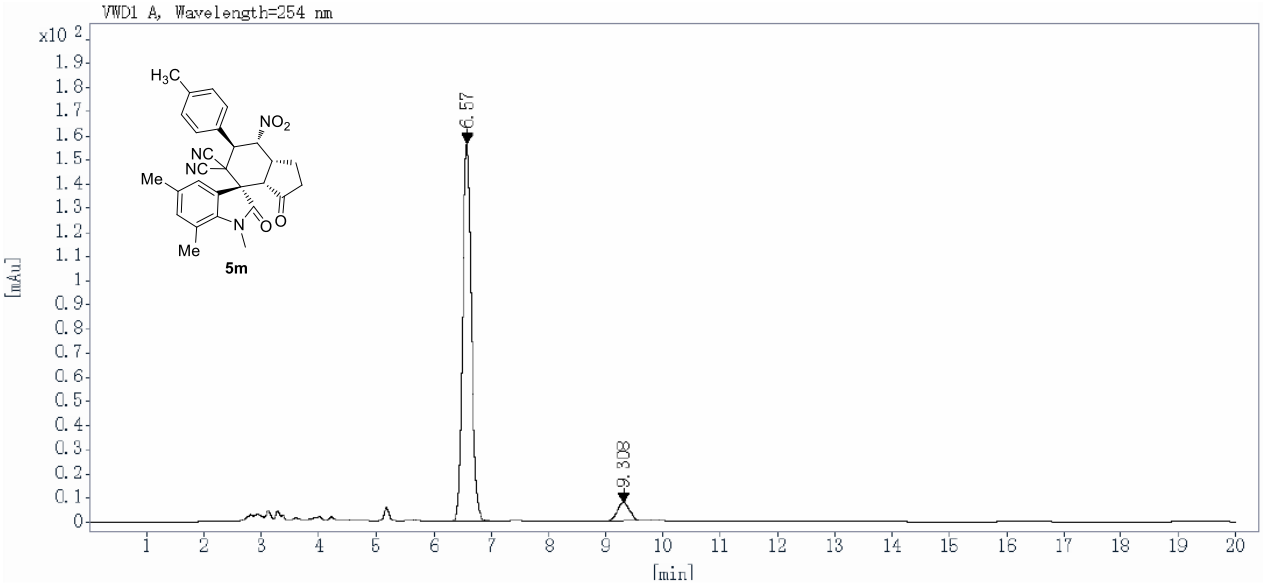
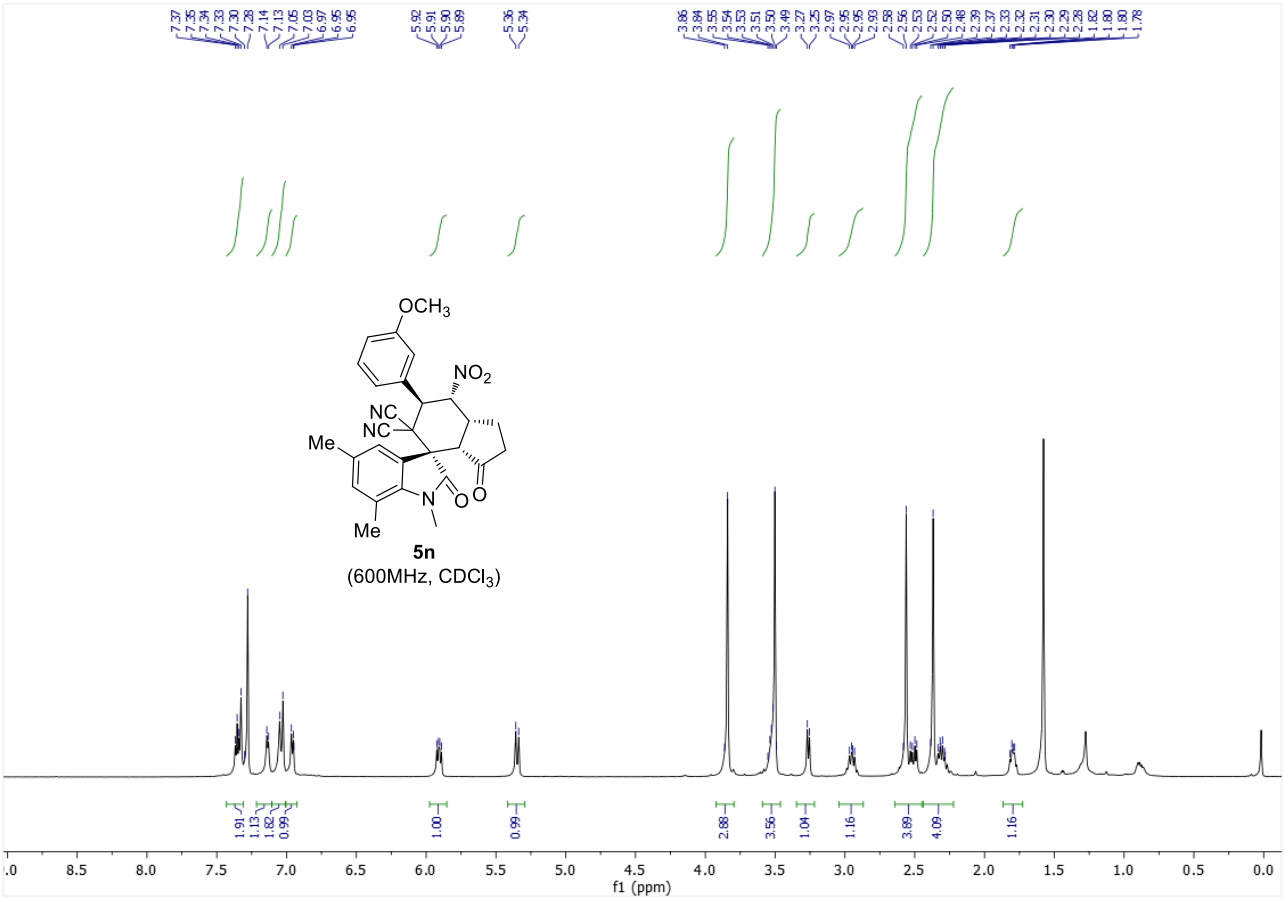
O
O
Me
5m
(150MHz, CDCl3)
ppm

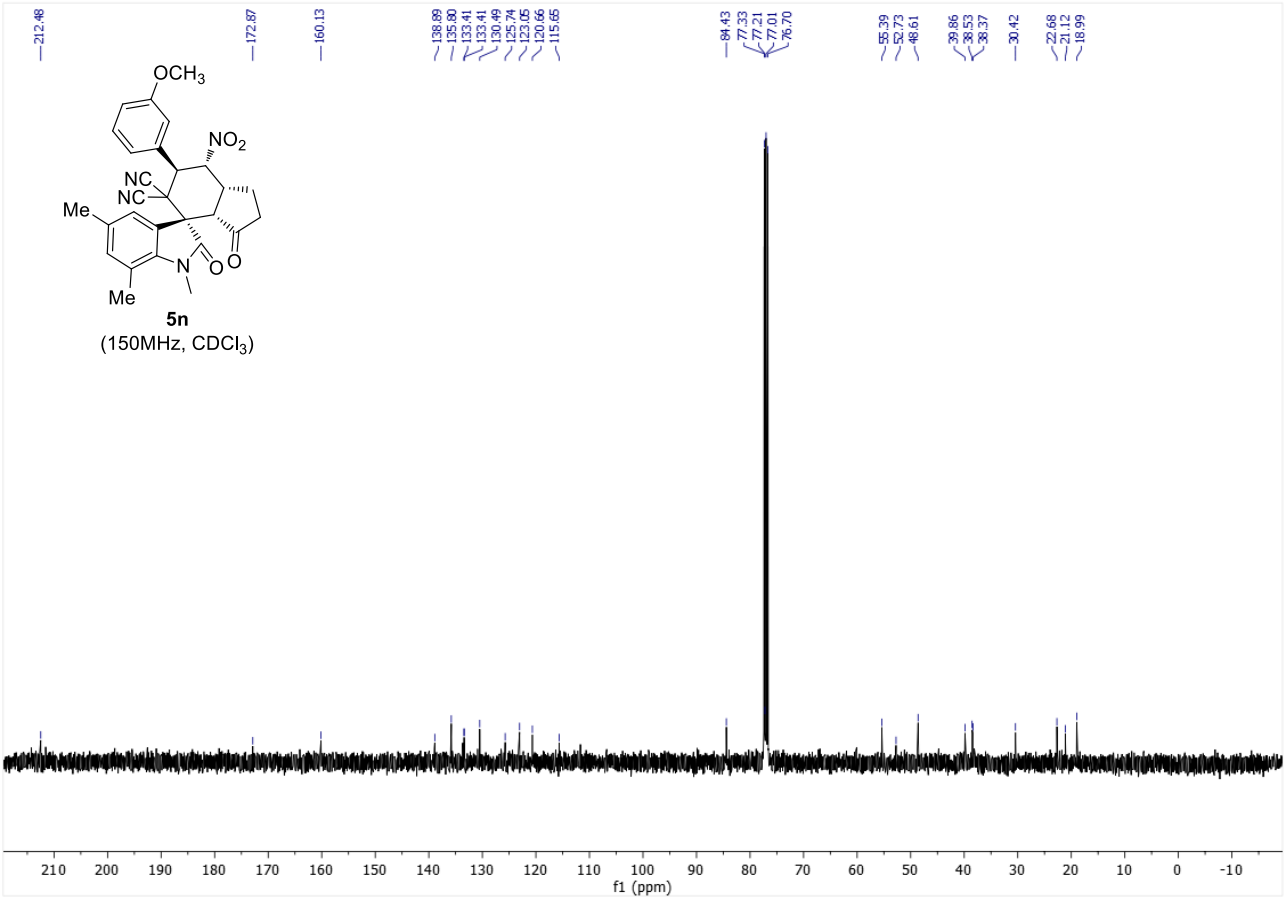


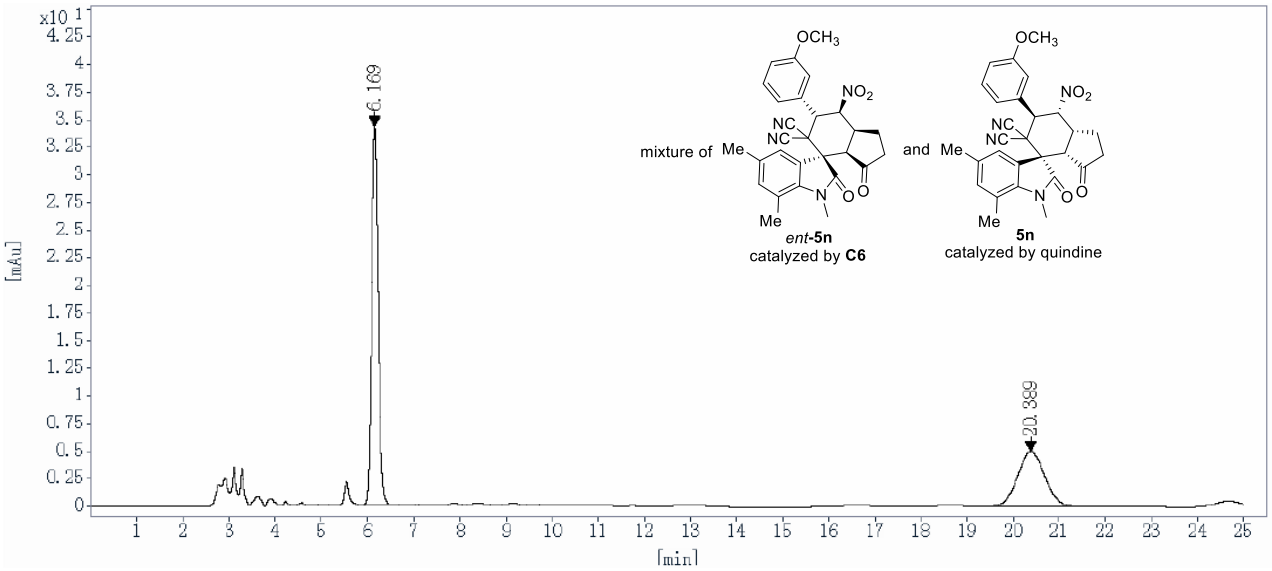
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.573	BB	0.16	24.2341	255.2037	50.1757
9.308	BB	0.25	15.5648	253.4164	49.8243



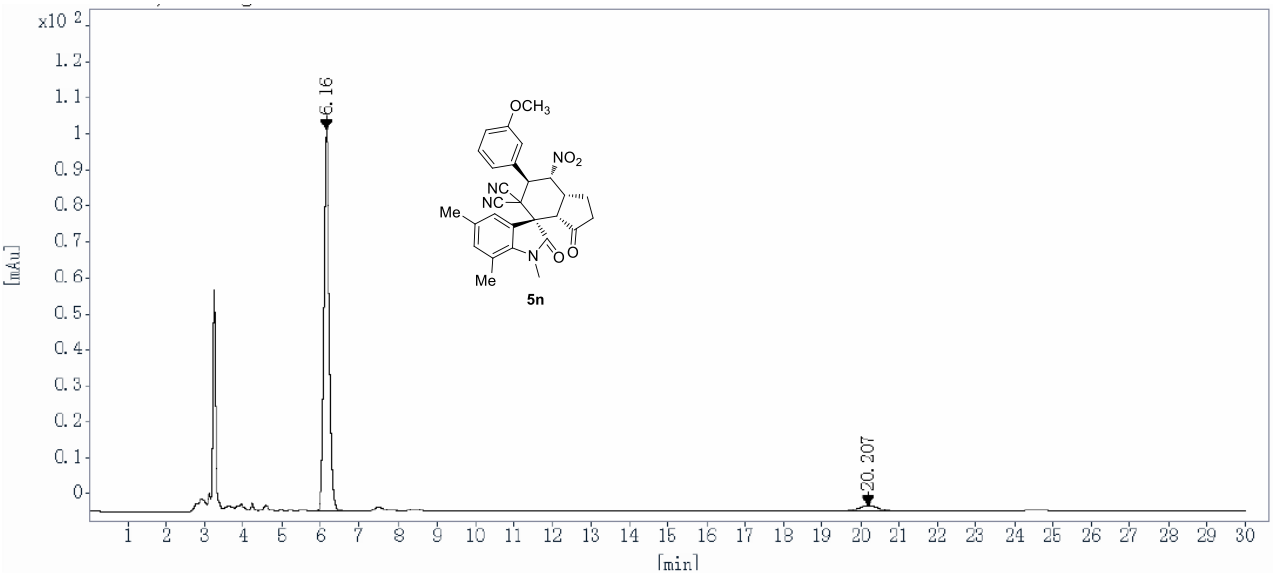
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.570	BB	0.16	156.4582	1636.0673	93.1627
9.308	BB	0.25	7.6018	120.0720	6.8373


OCH3
NO2
NC
NC
Me
N
O
O
Me
5n
(600MHz, CDCl3)
f1 (ppm)

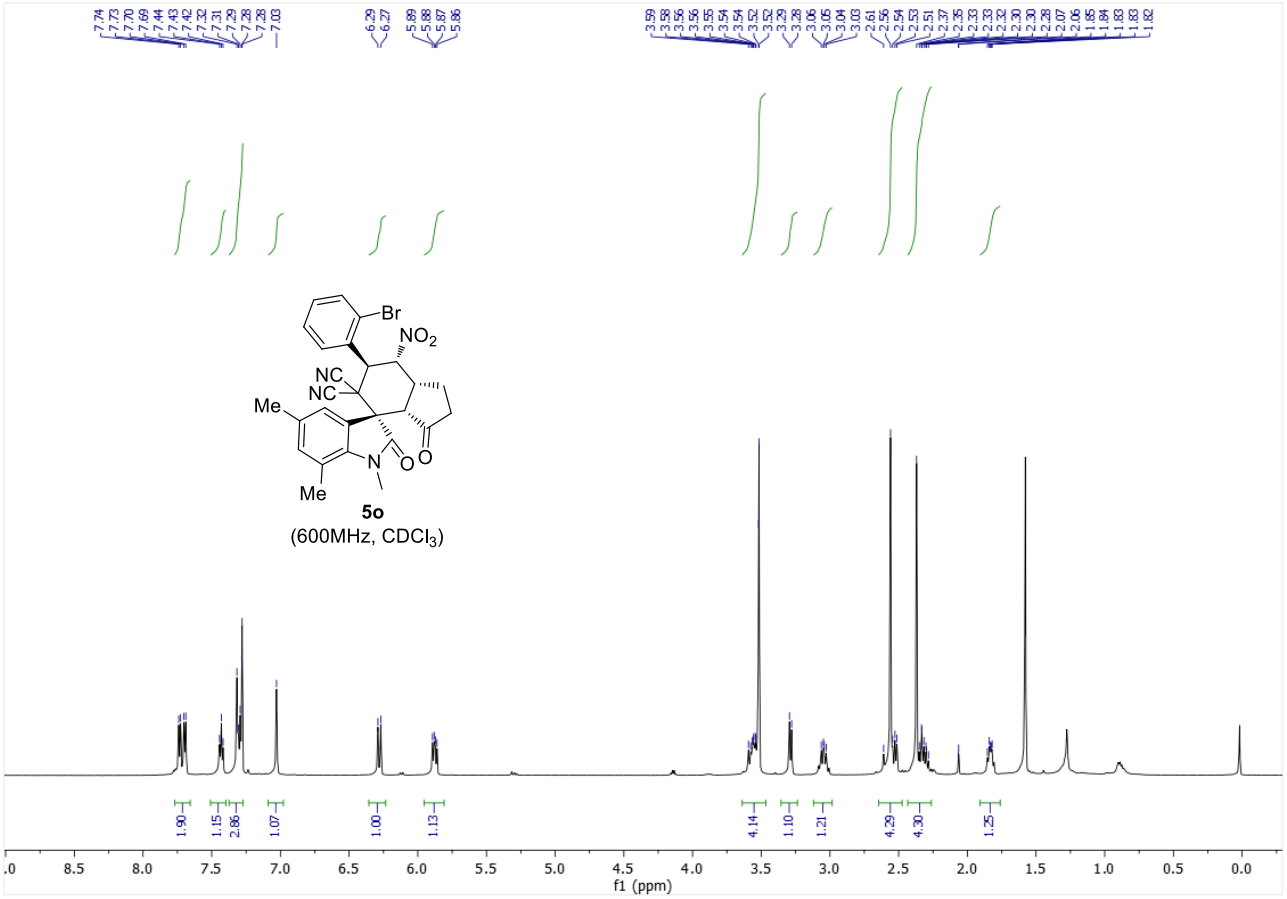

OCH3
NO2
NC
NC
Me
N
O
O
Me
5n
(150MHz, CDCl3)
f1 (ppm)

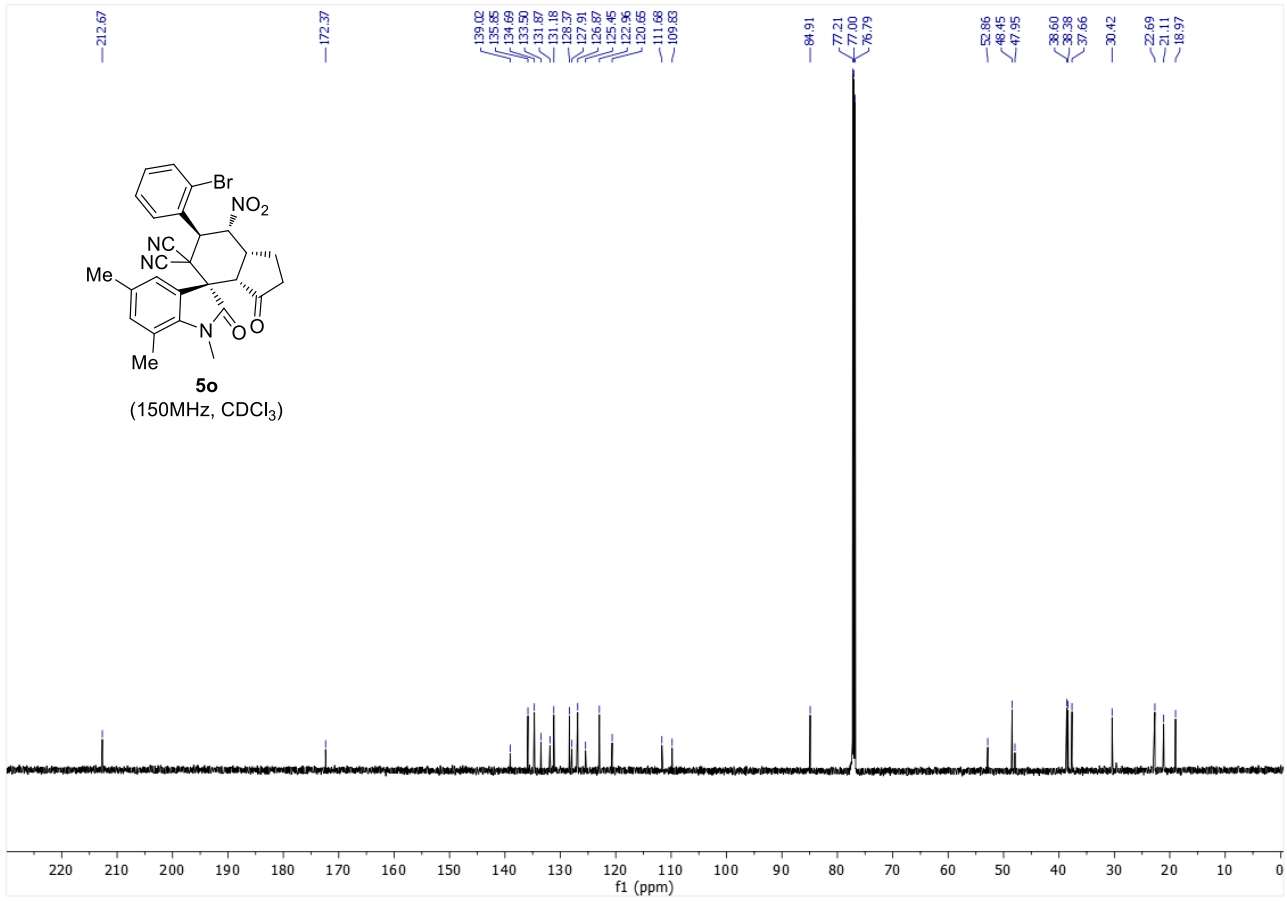


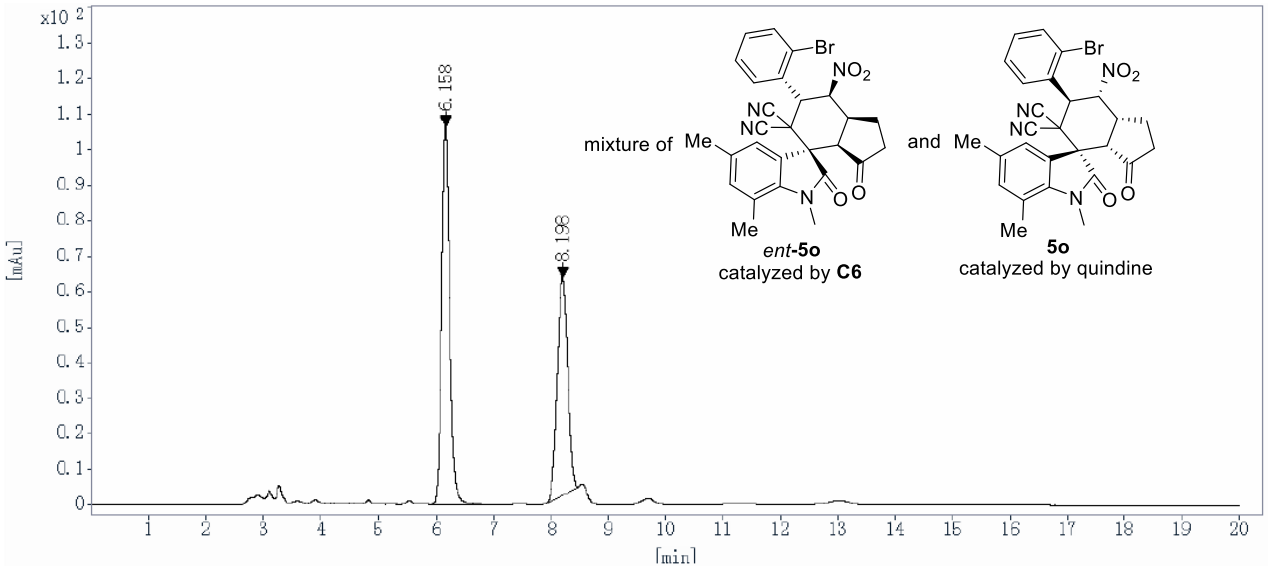
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.169	BB	0.15	34.2513	333.1806	62.2233
20.389	BB	0.62	4.9460	202.2790	37.7767



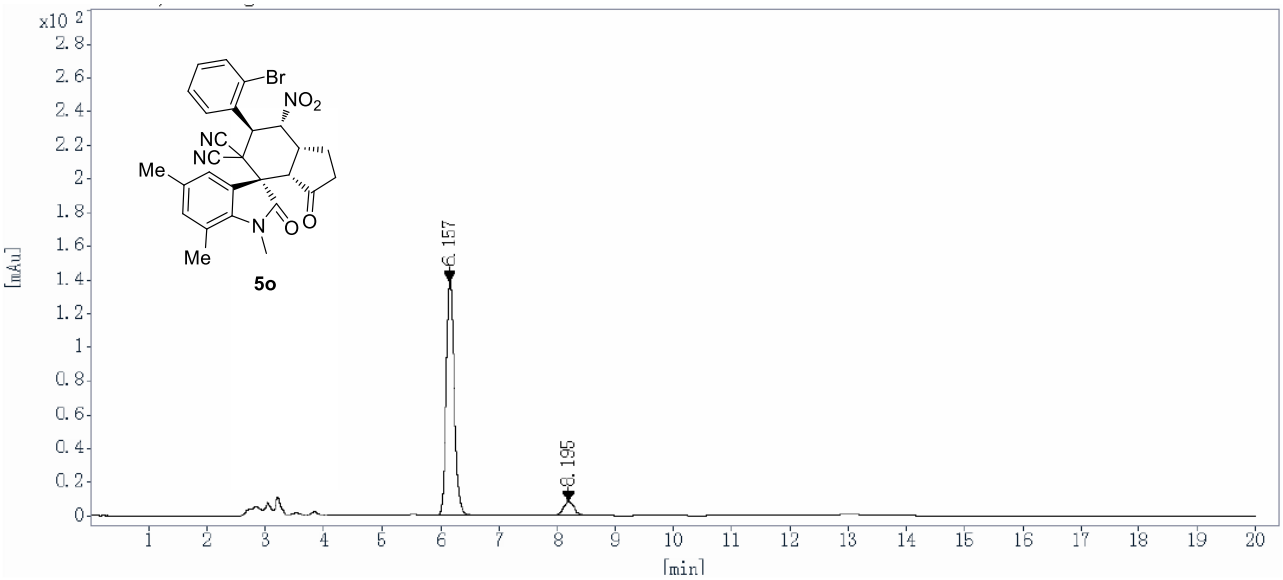
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.160	BB	0.15	105.7407	1029.4650	94.0840
20.207	BB	0.58	1.6240	64.7330	5.9160


Br
NO2
NC
NC
Me
N
O
O
Me
5o
(600MHz, CDCl3)
f1 (ppm)

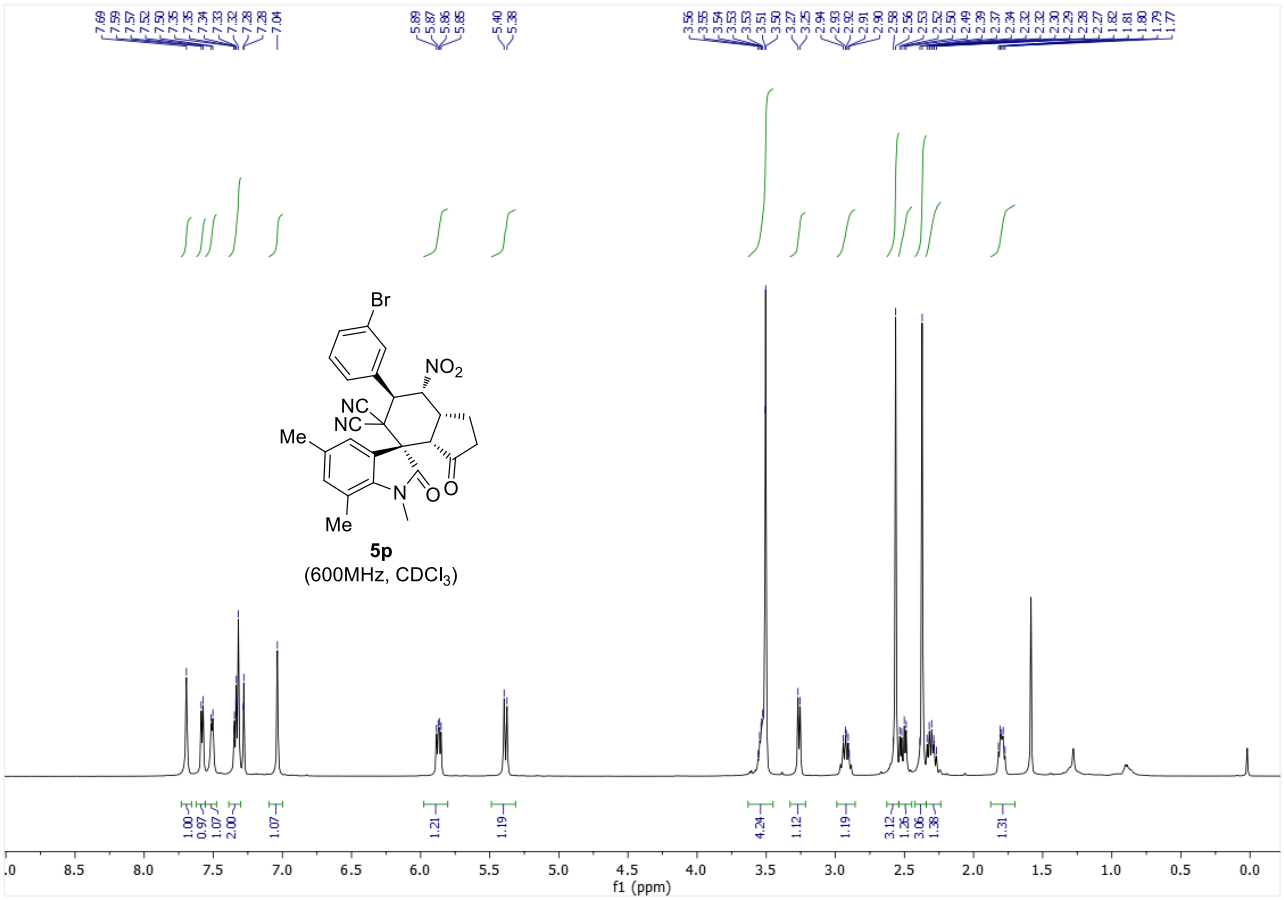

Br
NO2
NC
NC
Me
N
O
O
Me
5o
(150MHz, CDCl3)
f1 (ppm)

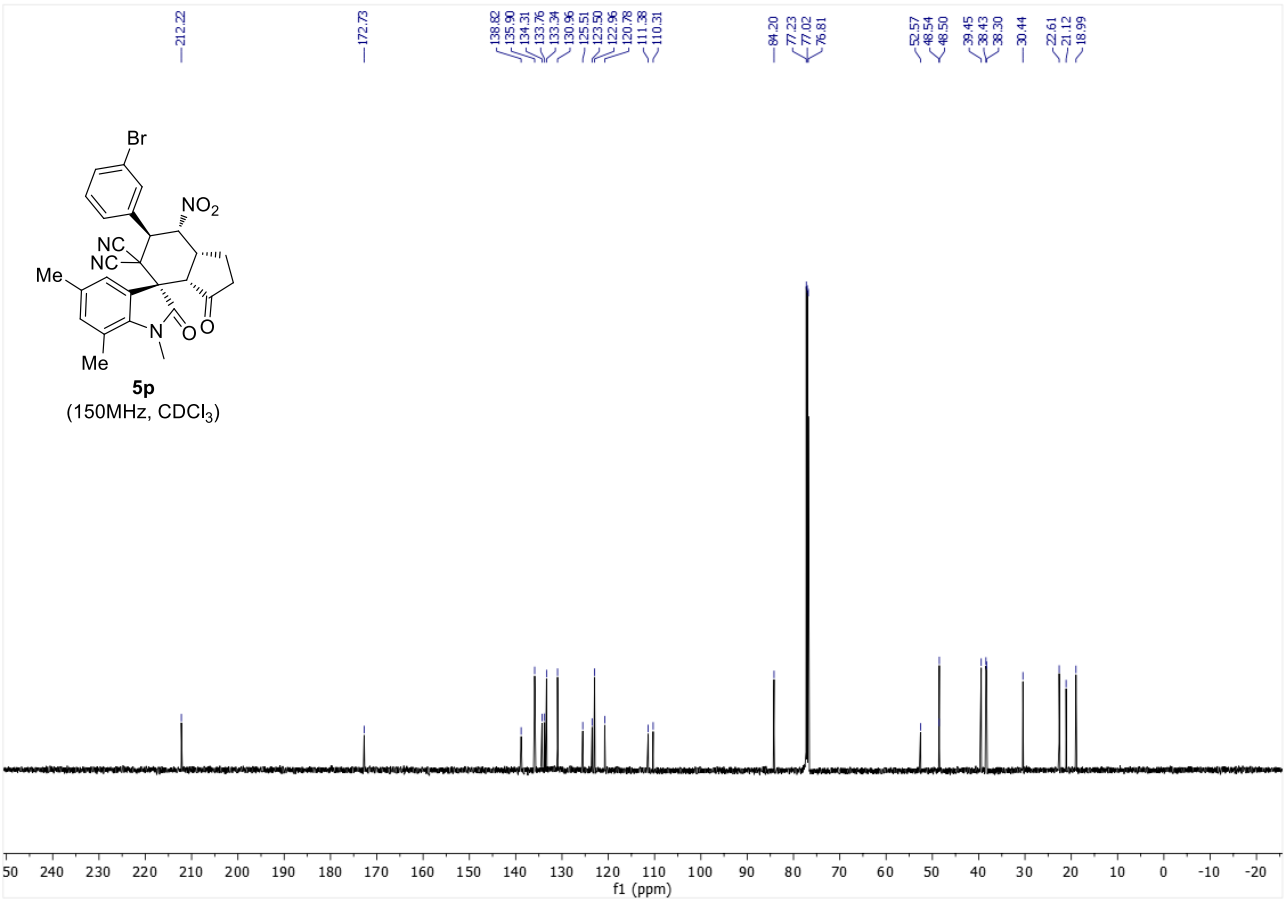


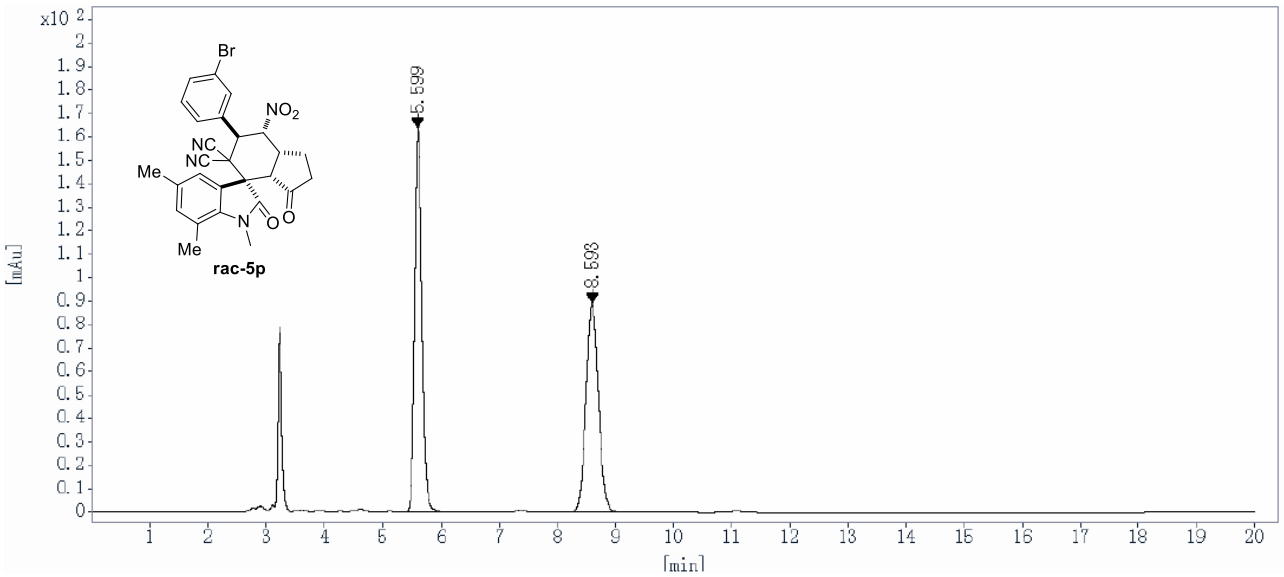
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.158	VB	0.15	106.4596	1023.8345	56.8231
8.198	BB	0.20	61.4051	777.9598	43.1769



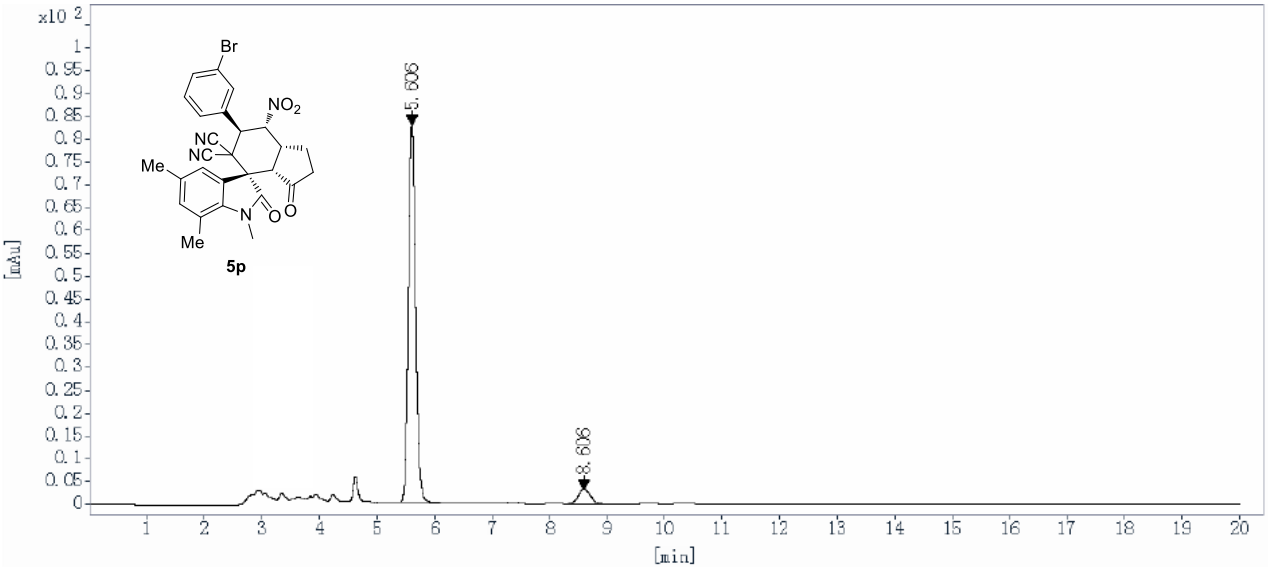
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.157	BB	0.15	139.4192	1330.5614	92.5702
8.195	BBA	0.20	8.1840	106.7920	7.4298


Br
NO2
NC
NC
Me
N
O
O
Me
5p
(600MHz, CDCl3)
f1 (ppm)

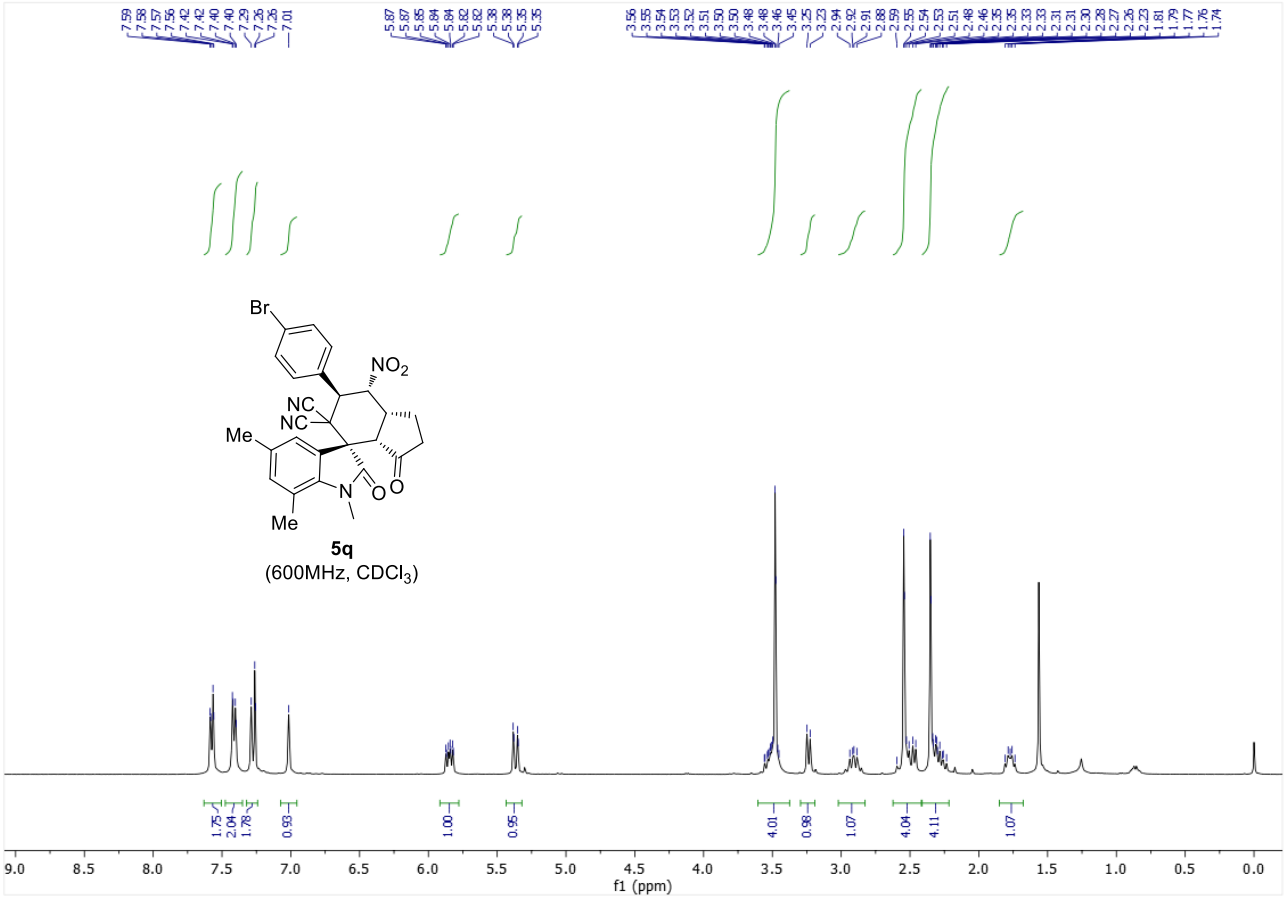

Br
NO2
NC
NC
Me
N
O
O
Me
5p
(150MHz, CDCl3)
f1 (ppm)

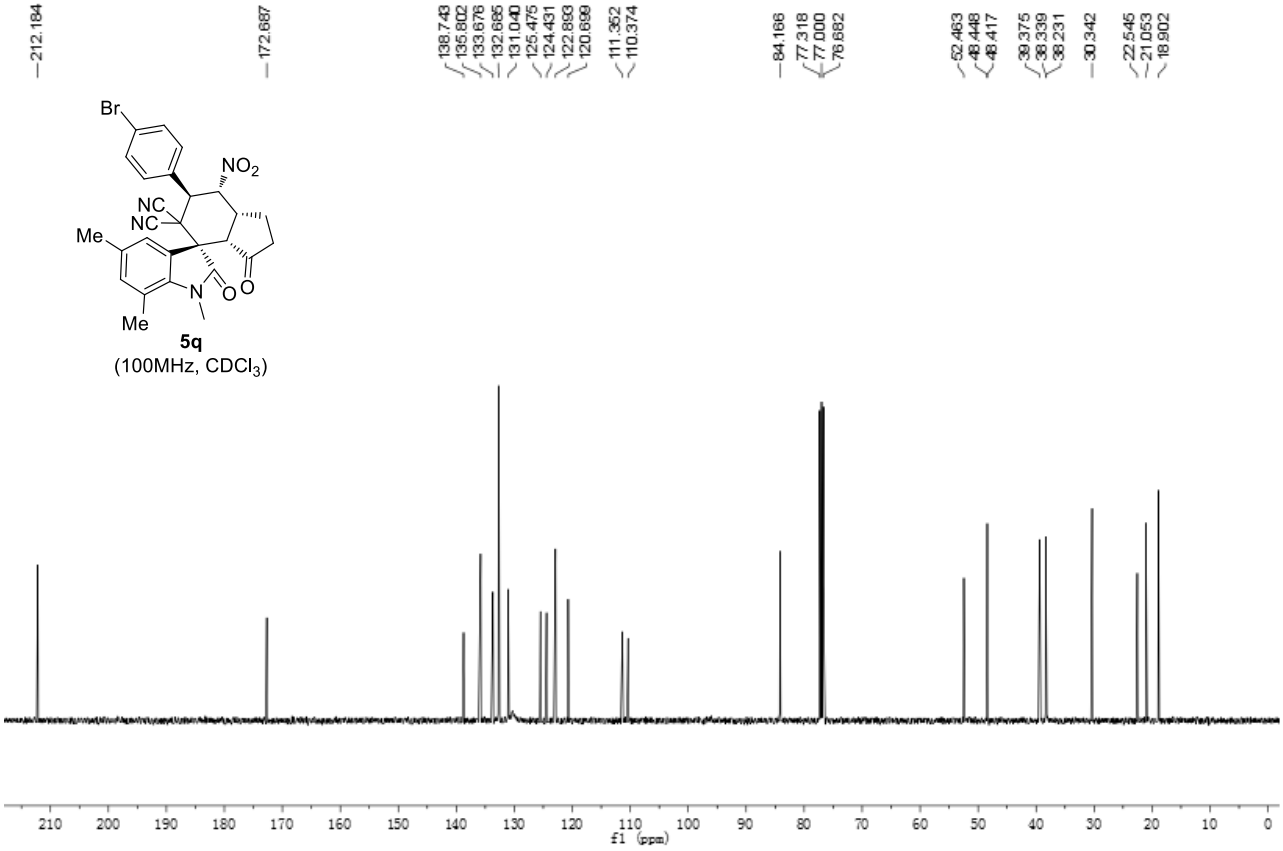


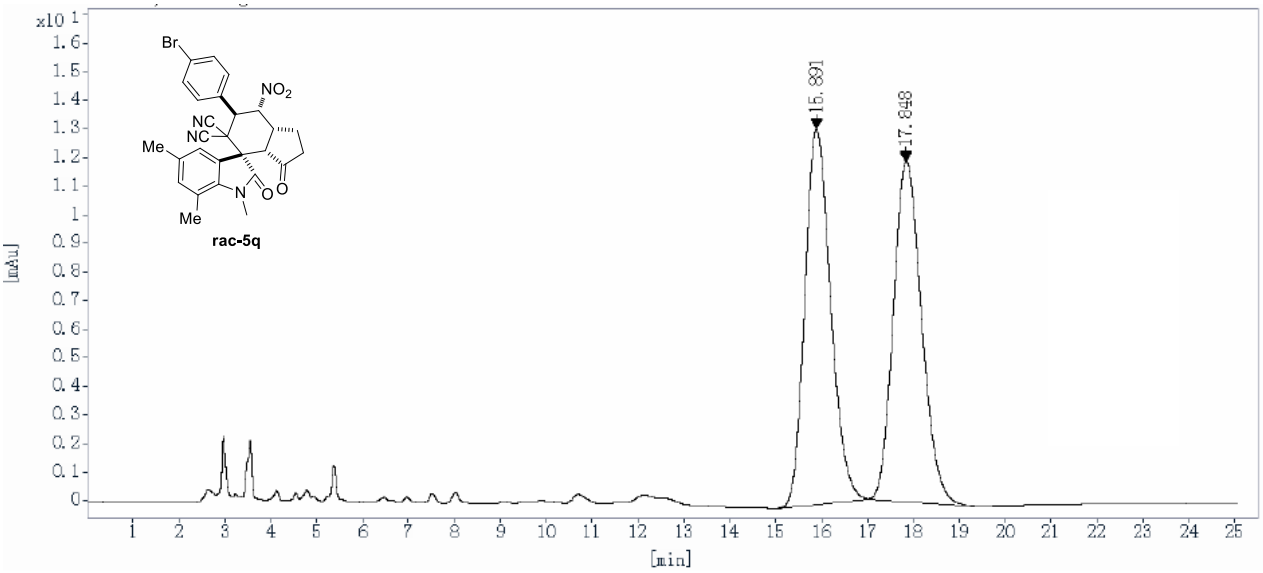
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
5.599	BB	0.13	163.3382	1419.0177	51.7719
8.593	BB	0.23	88.9735	1321.8844	48.2281



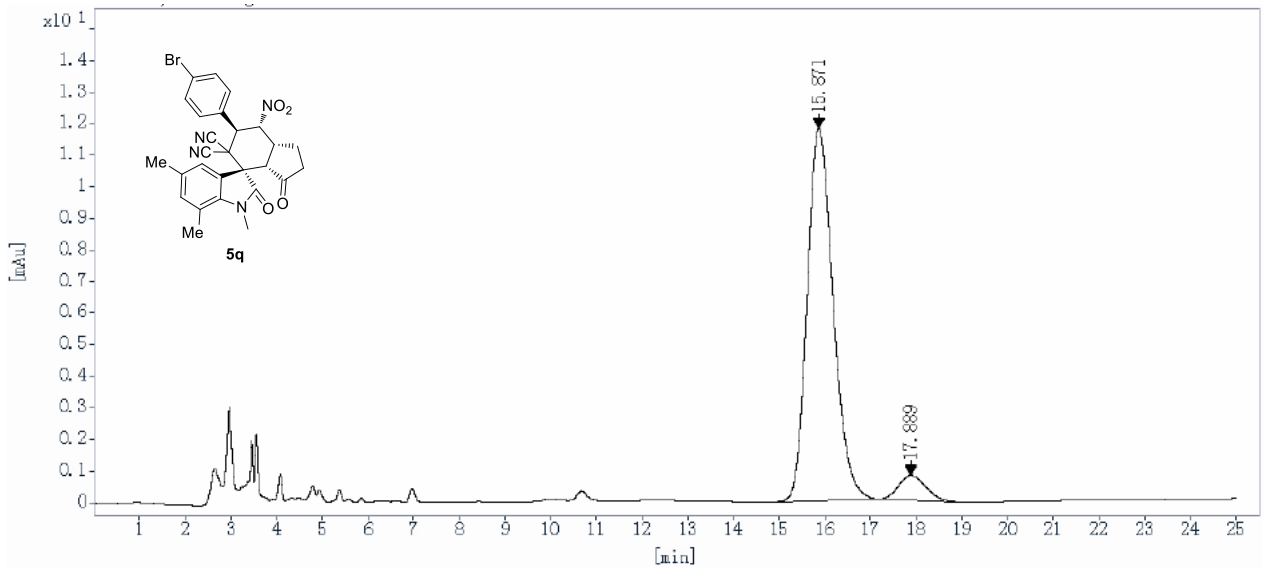
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
5.606	BB	0.13	82.6674	716.1127	93.8489
8.606	BB	0.23	3.1776	46.9359	6.1511


Br
NO2
NC
NC
Me
N
O
O
Me
5q
(600MHz, CDCl3)
f1 (ppm)

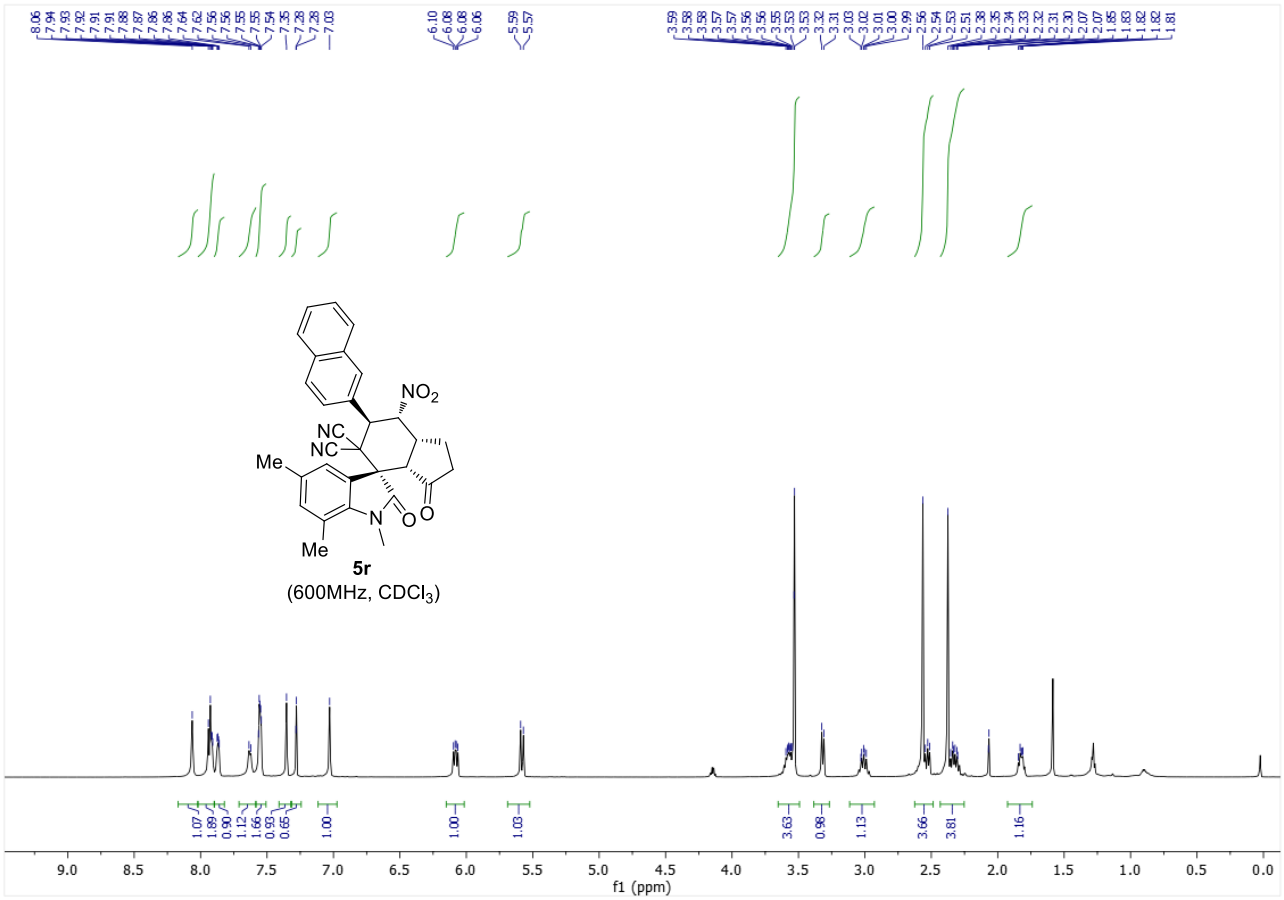

Br
NO2
NC
NC
Me
N
O
O
Me
5q
(100MHz, CDCl3)
f1 (ppm)

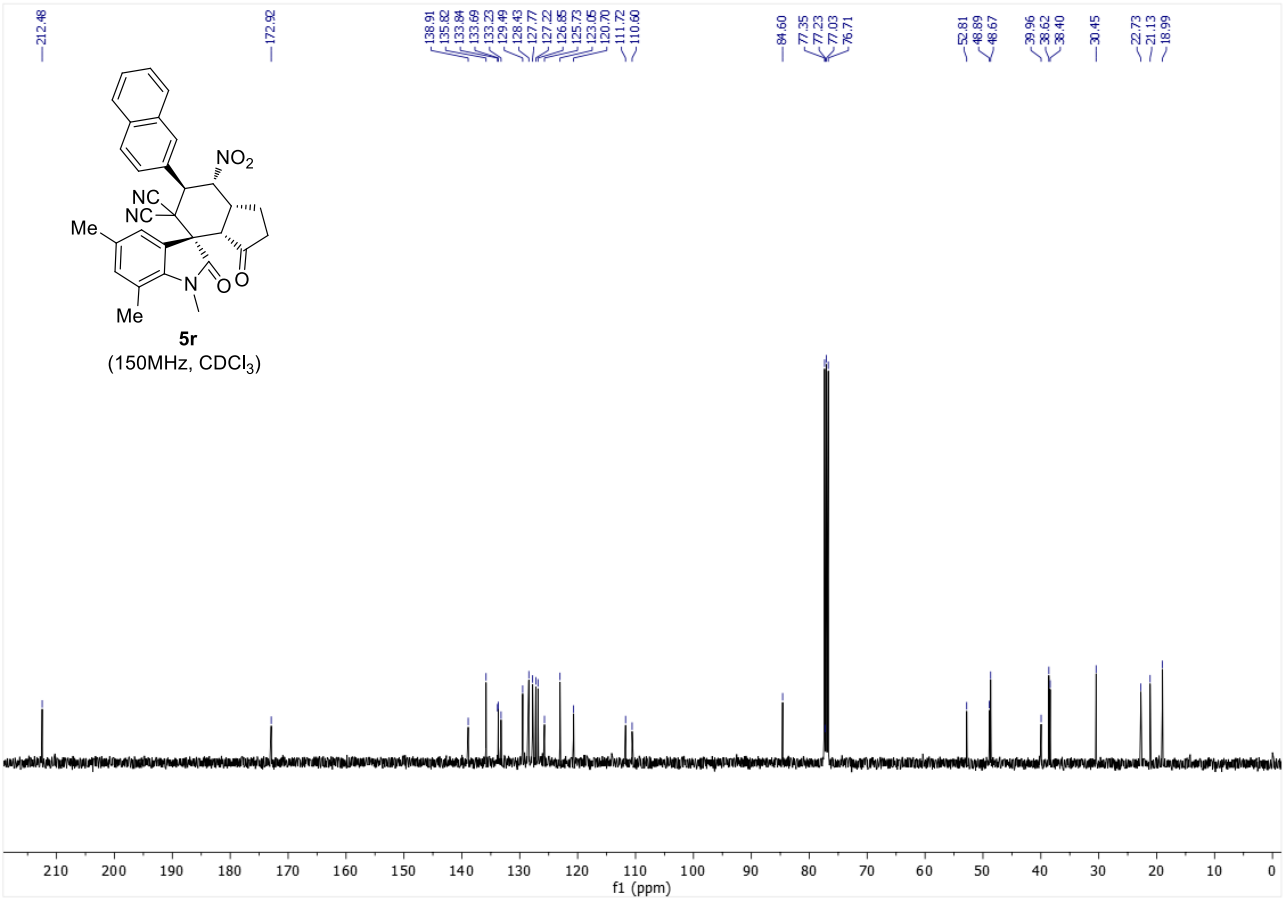


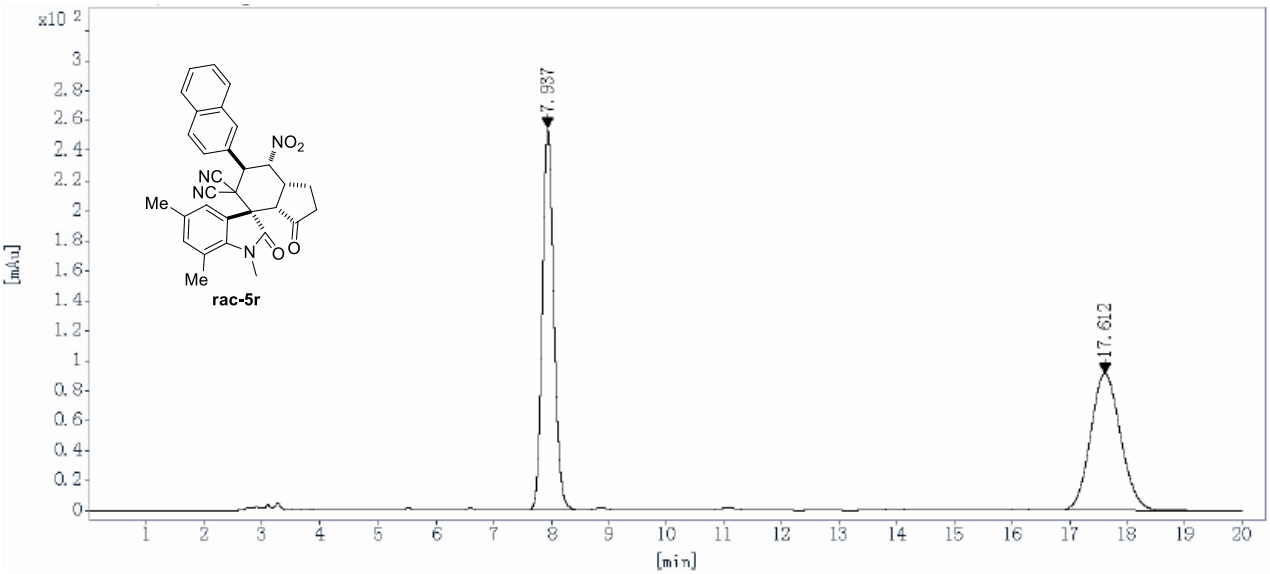
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.891	BB	0.60	13.1100	510.7031	50.1822
17.848	BB	0.66	11.8919	506.9955	49.8178



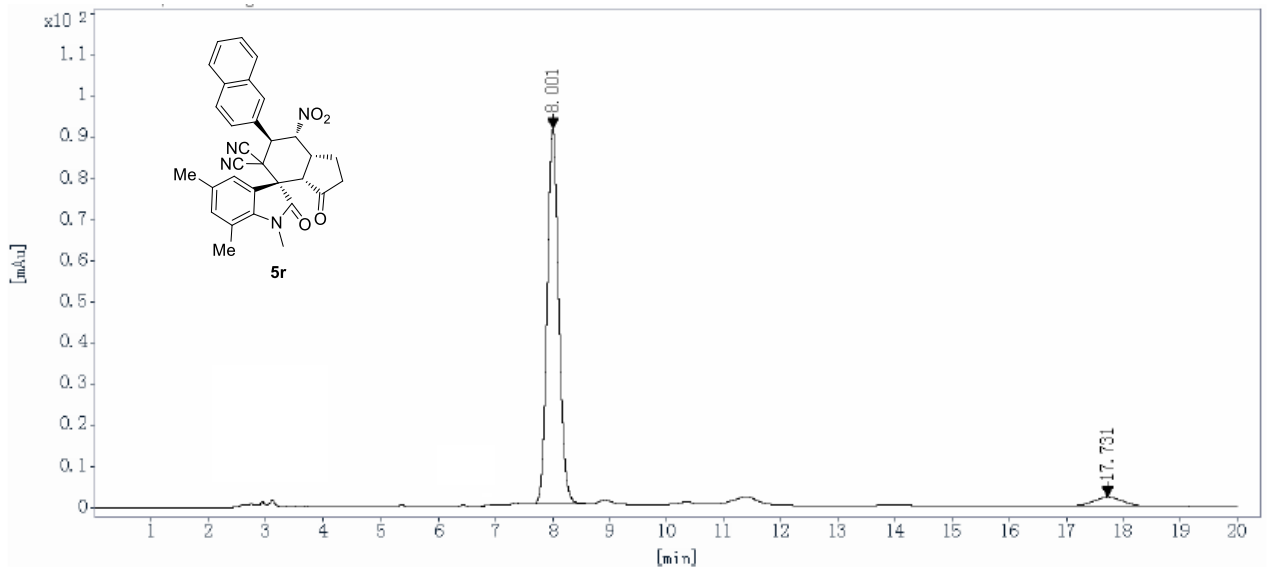
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.871	BB	0.60	11.7712	463.4202	93.5805
17.889	BB	0.50	0.7778	31.7898	6.4195


NO2
NC
NC
Me
N
O
O
Me
5r
(600MHz, CDCl3)
f1 (ppm)

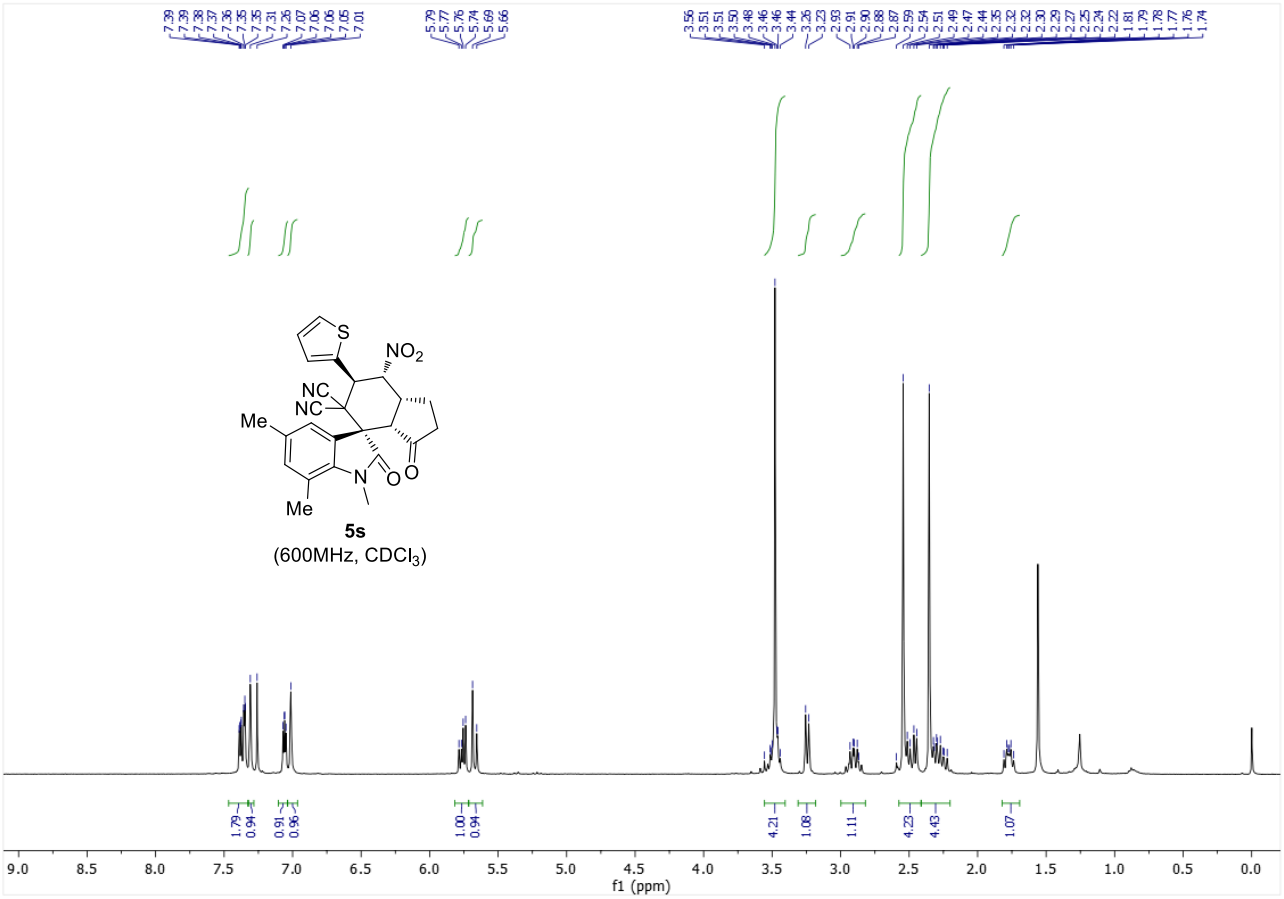

NO2
NC
NC
Me
N
O
O
Me
5r
(150MHz, CDCl3)
f1 (ppm)

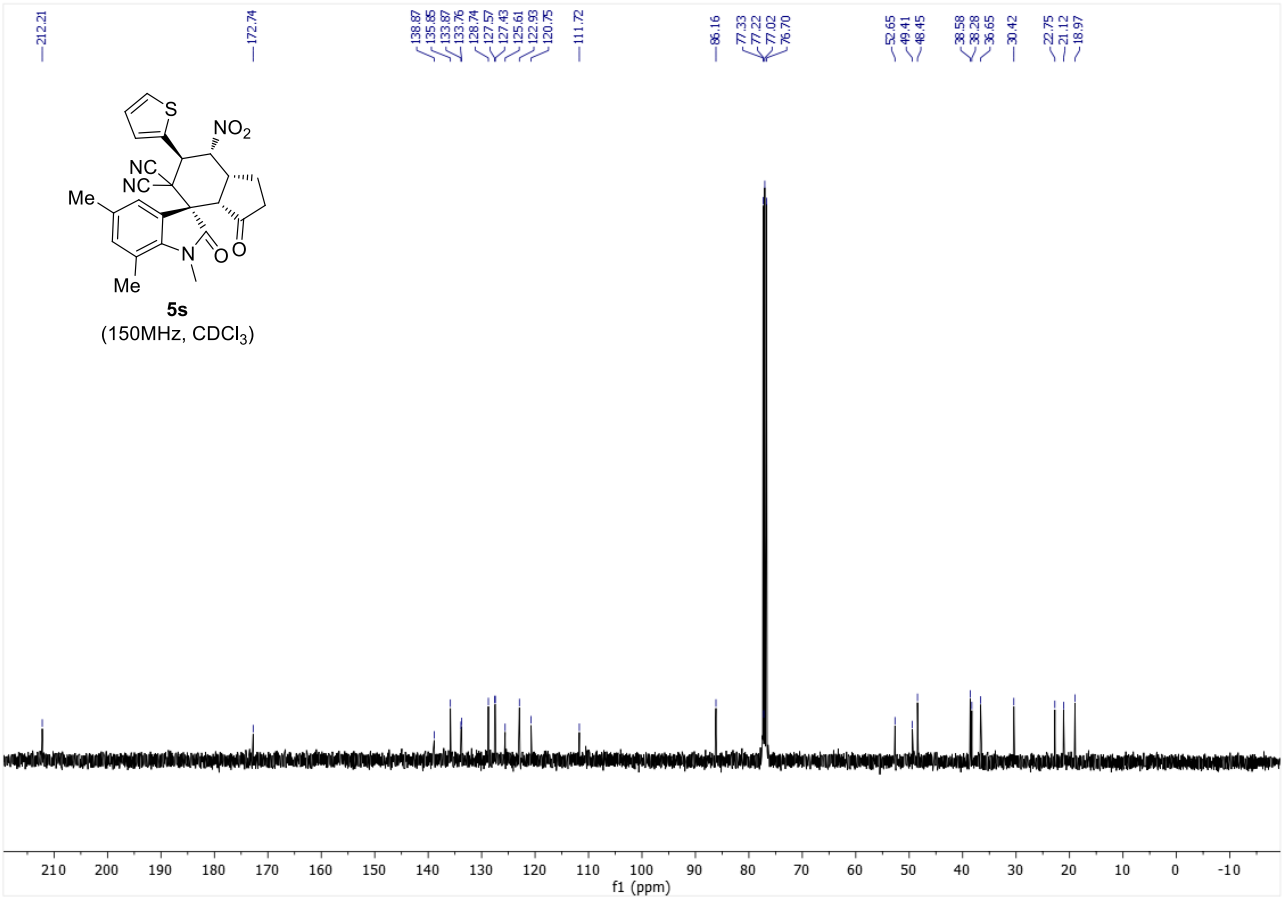


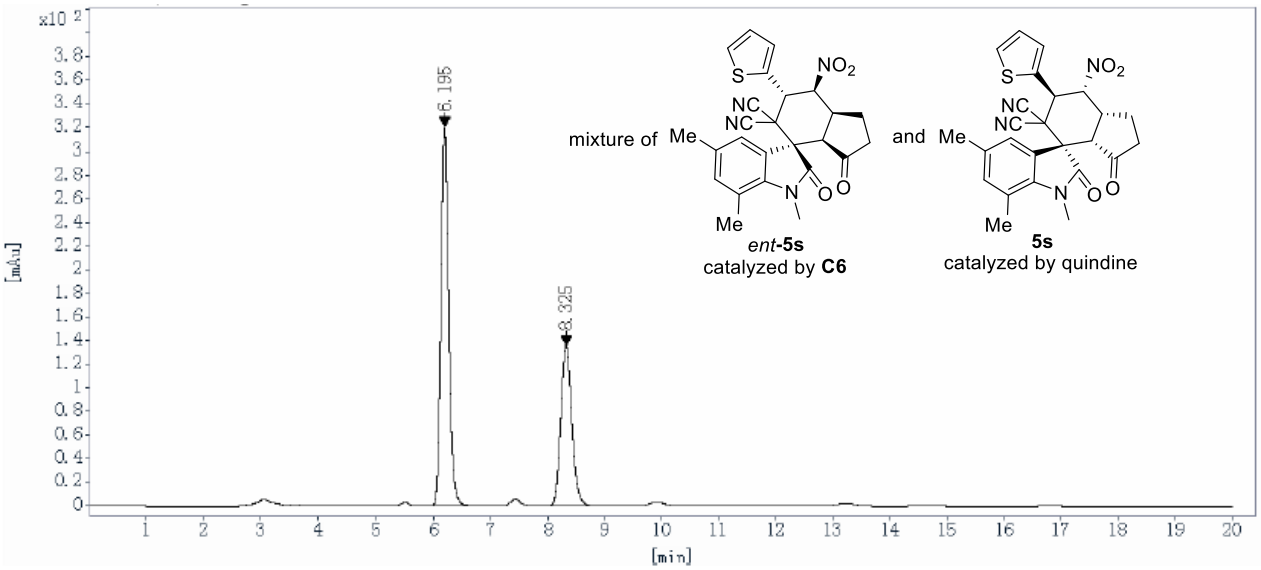
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.937	BB	0.22	254.2308	3553.9900	51.6617
17.612	BBA	0.57	91.3677	3325.3596	48.3383



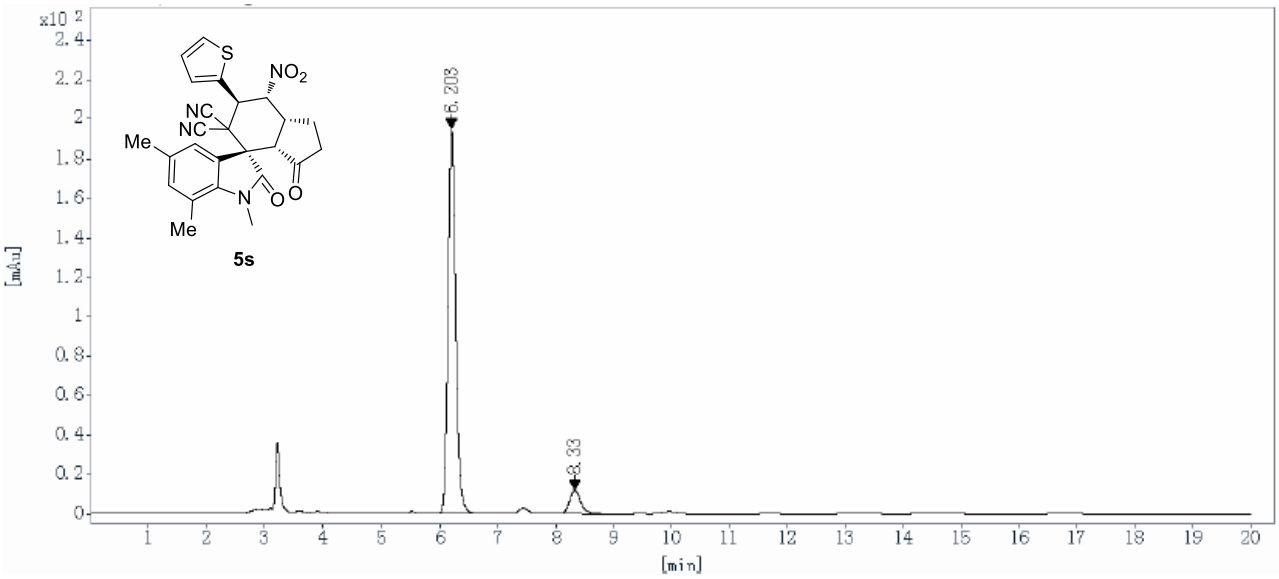
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.001	BB	0.22	91.0733	1299.8302	94.2841
17.731	BB	0.54	2.1994	78.8008	5.7159


S
NO2
NC
NC
Me
N
O
O
Me
5s
(600MHz, CDCl3)
f1 (ppm)

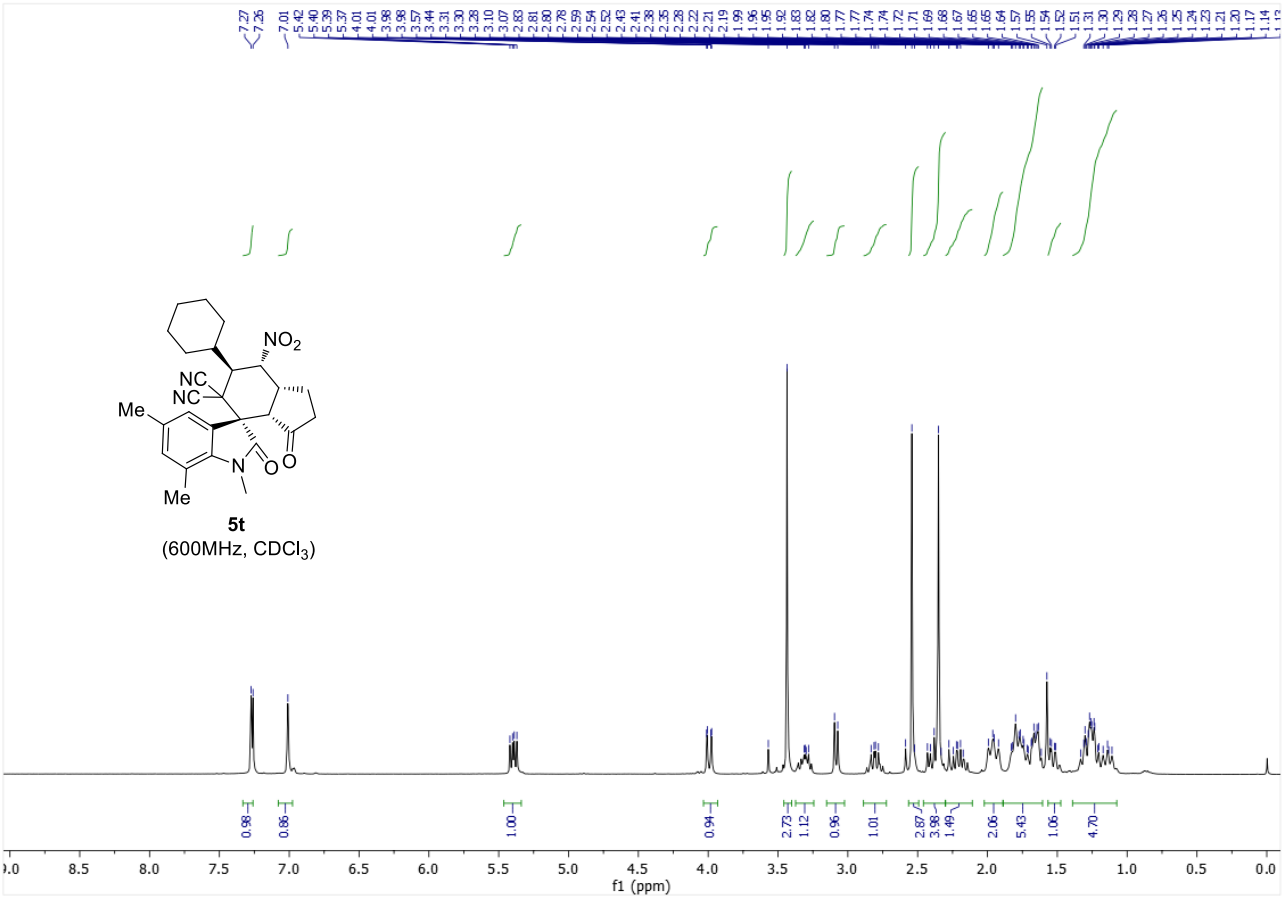

S
NO2
NC
NC
Me
N
O
O
Me
5s
(150MHz, CDCl3)
f1 (ppm)

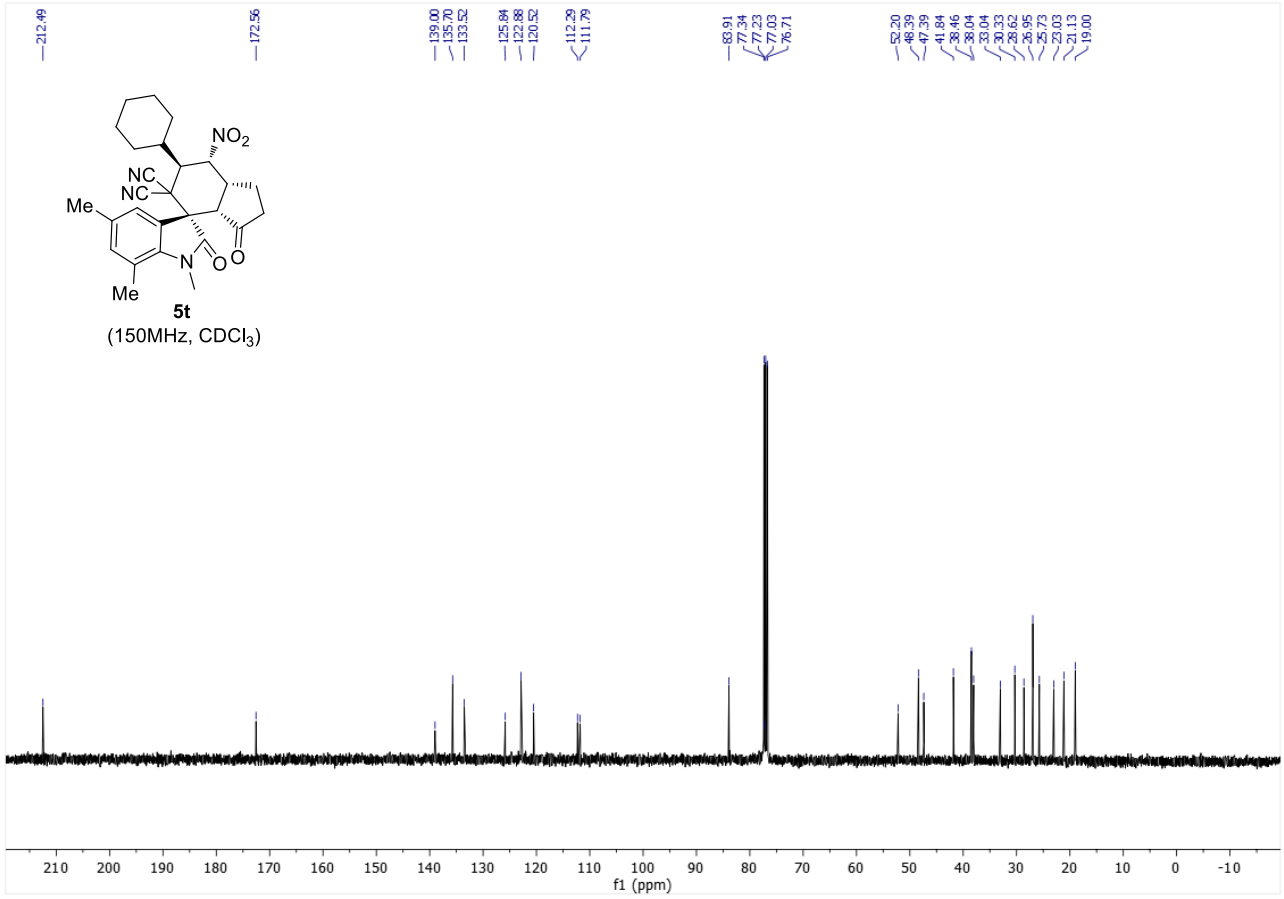


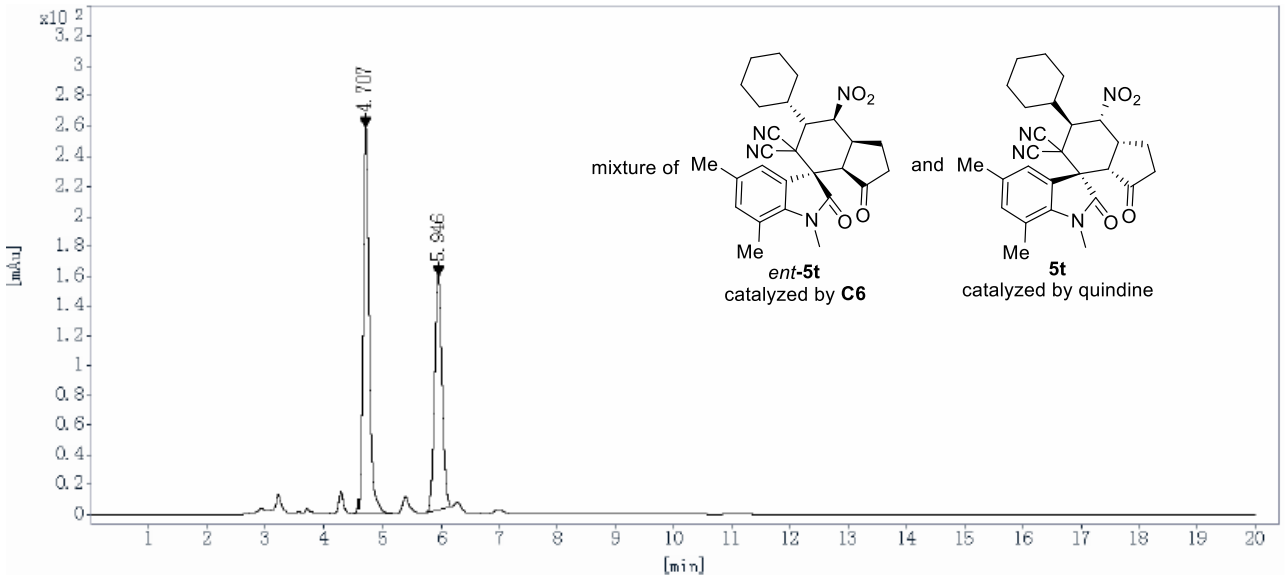
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.195	BB	0.15	319.6223	3068.2593	62.6669
8.325	BB	0.21	135.8993	1827.8781	37.3331



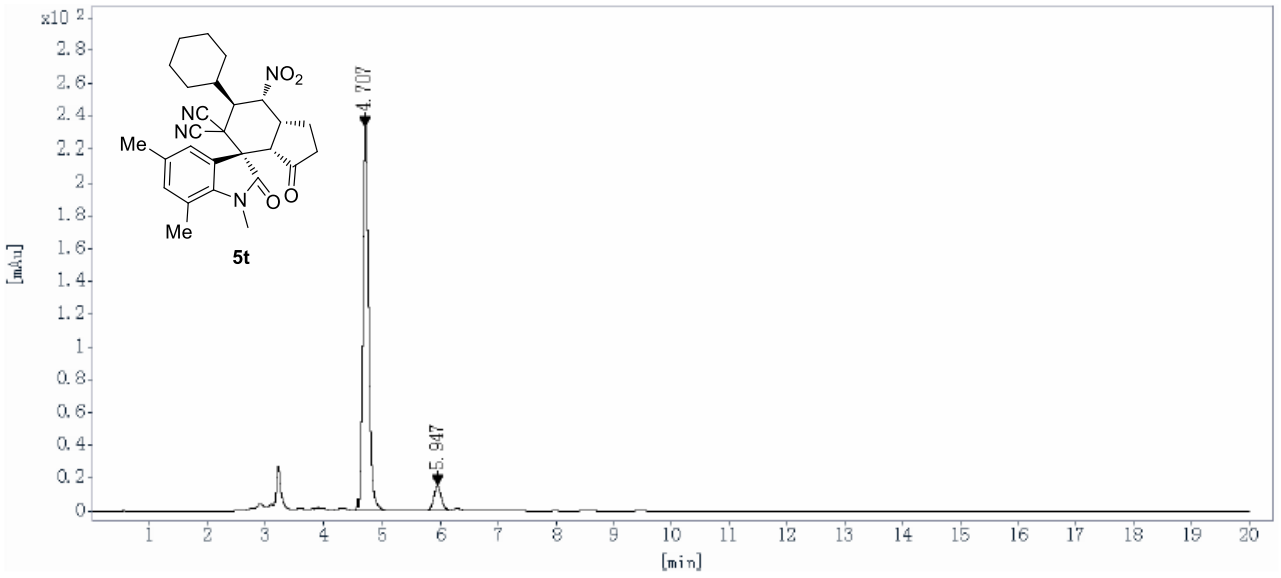
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.203	BBA	0.14	194.7155	1813.7520	92.0495
8.330	BB	0.21	11.6859	156.6579	7.9505


NO2
NC
NC
Me
N
O
O
Me
5t
(600MHz, CDCl3)
f1 (ppm)

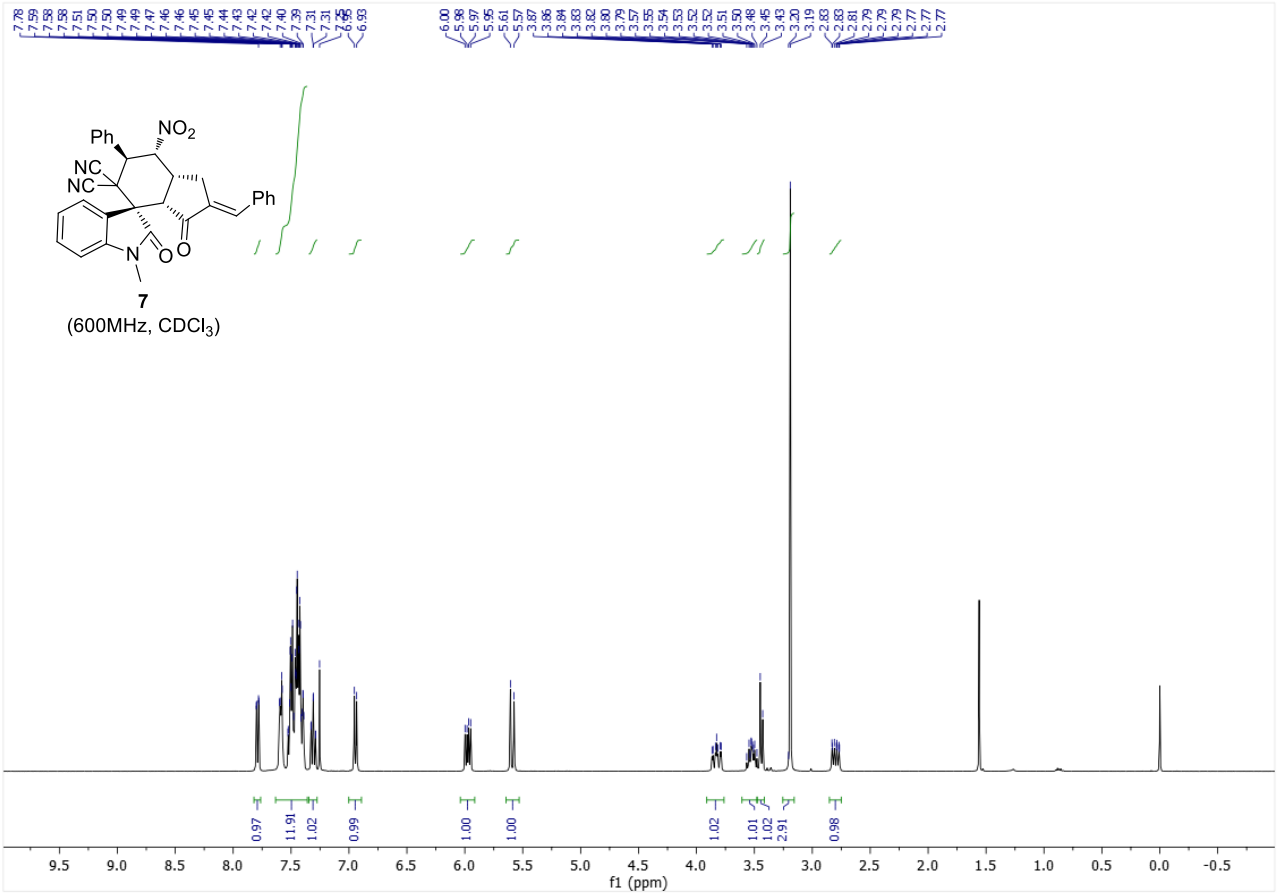

NO2
NC
NC
Me
N
O
O
Me
5t
(150MHz, CDCl3)
f1 (ppm)

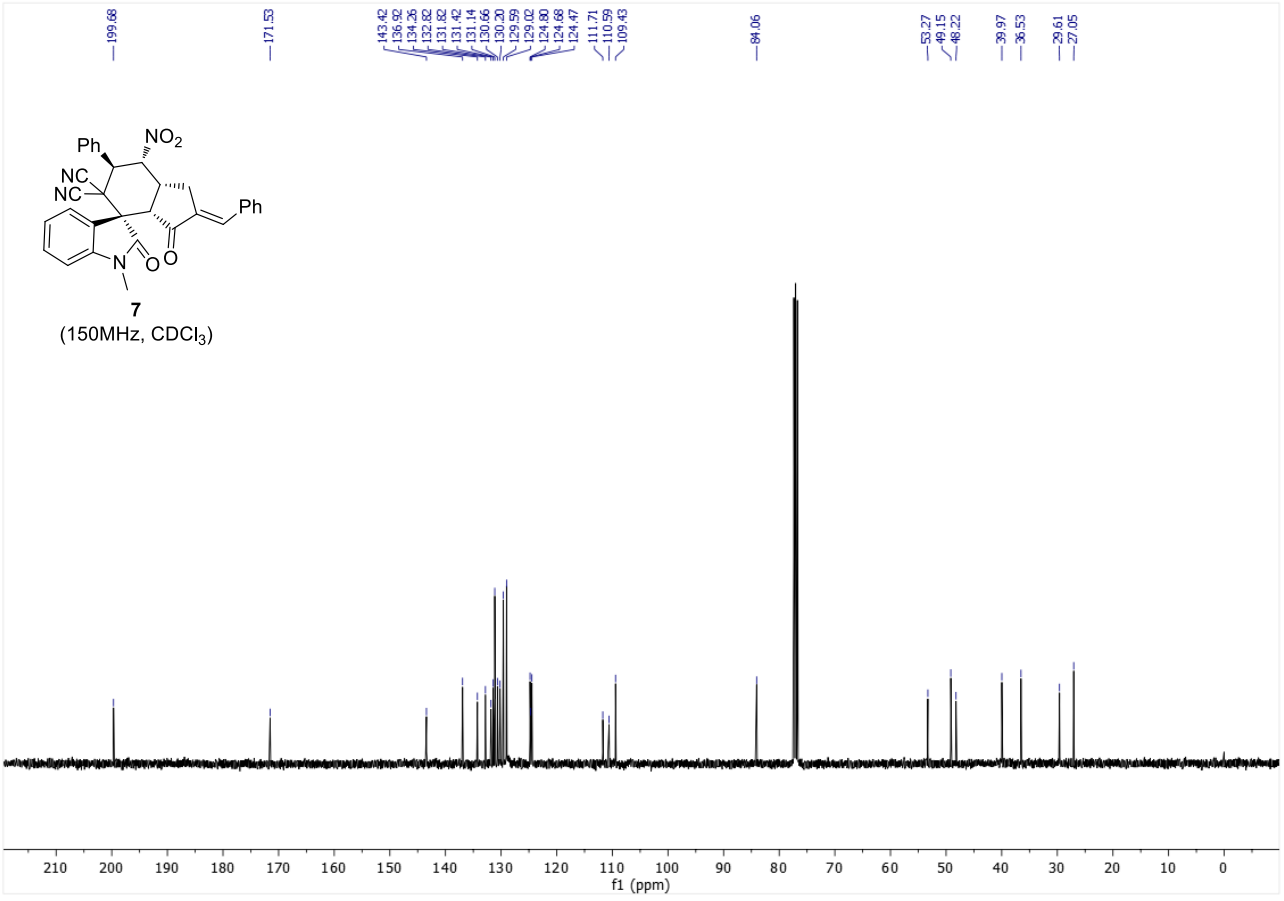


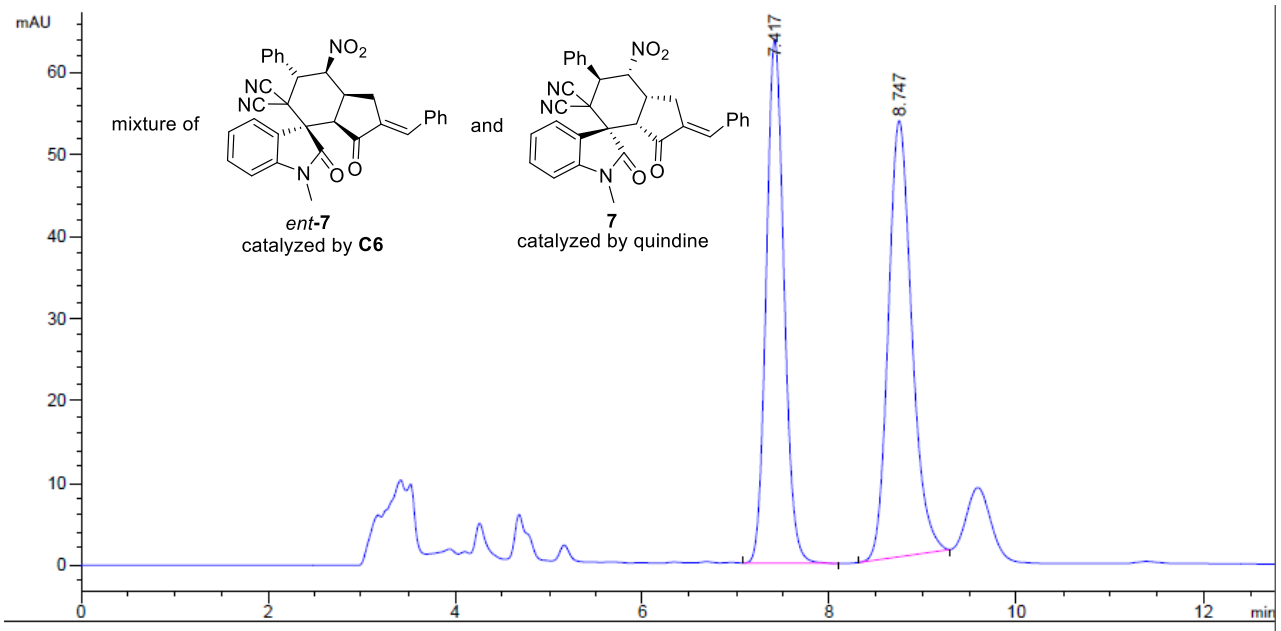
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
4.707	BB	0.11	257.7388	1850.9292	56.9245
5.946	BB	0.14	156.9358	1400.6216	43.0755



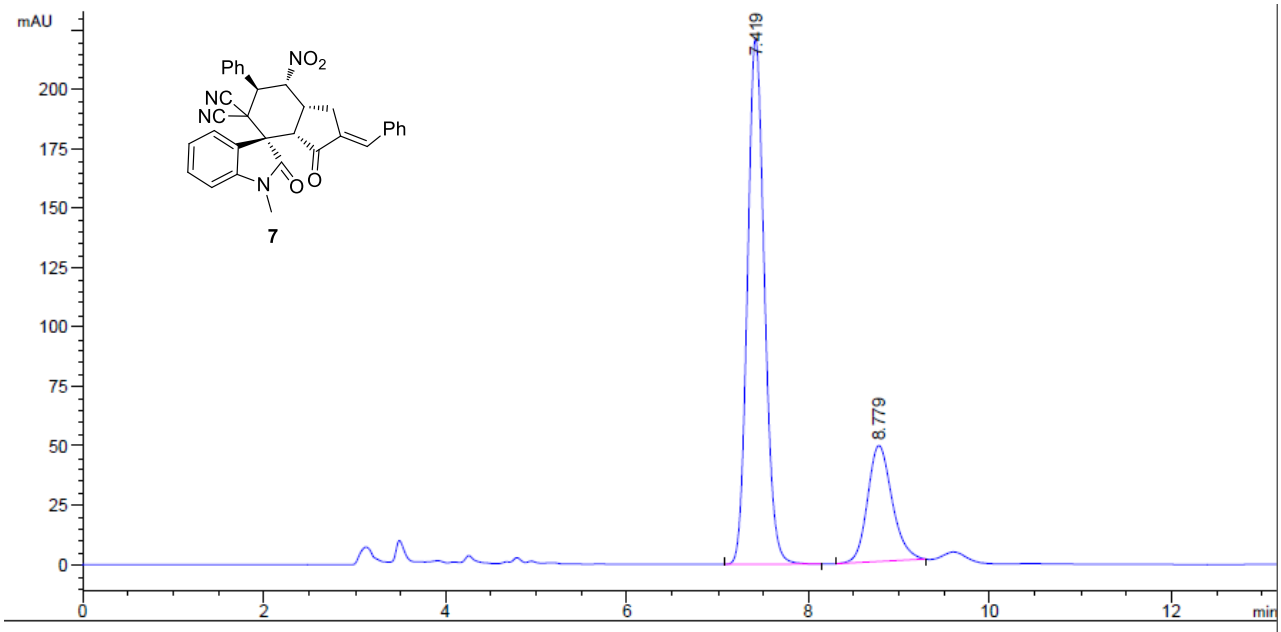
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
4.707	BB	0.11	232.7814	1625.1051	92.5136
5.947	BB	0.14	14.8609	131.5076	7.4864


Ph
NO2
NC
NC
Ph
O
N
O
7
(600MHz, CDCl3)
f1 (ppm)

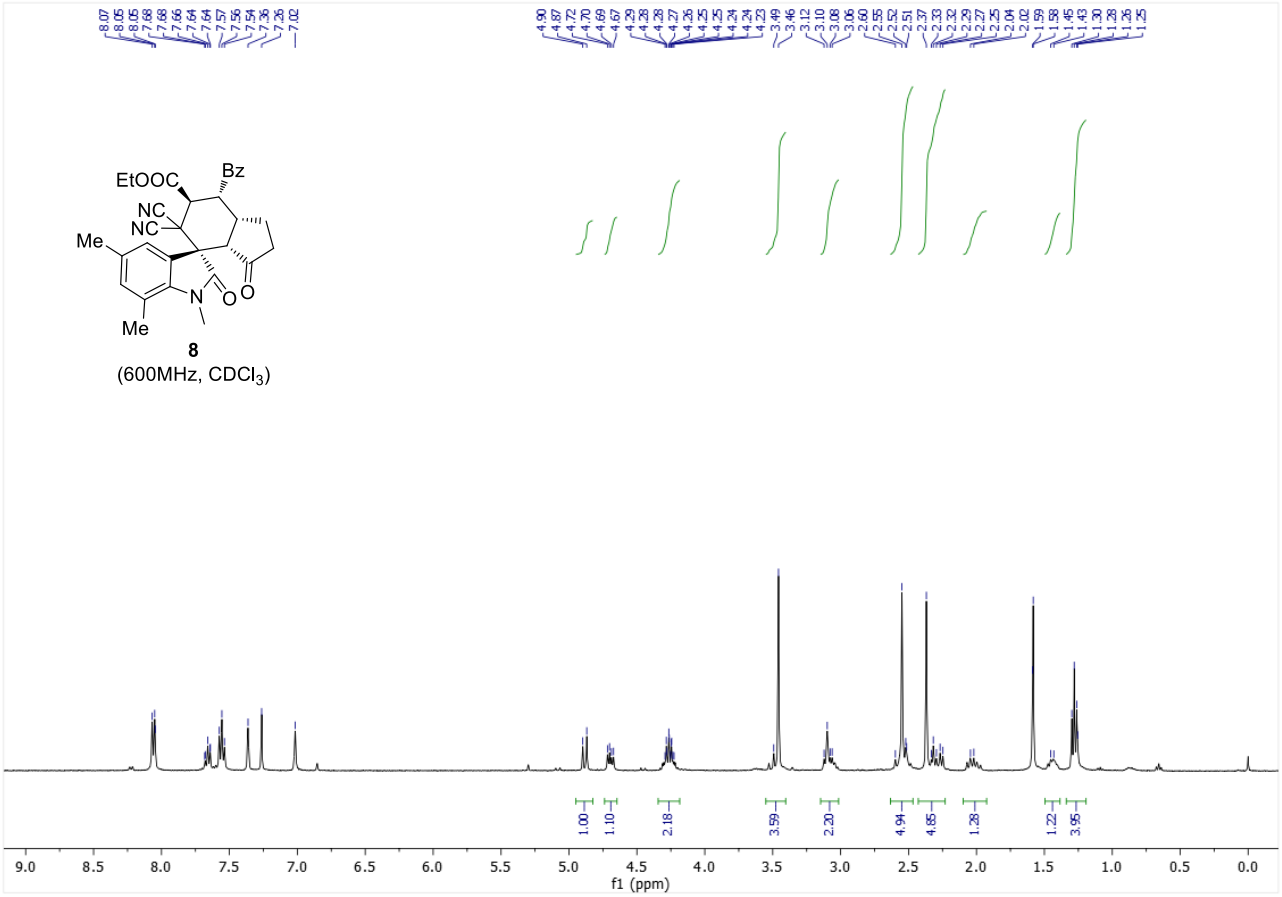

Ph
NO2
NC
NC
Ph
O
N
O
7
(150MHz, CDCl3)
f1 (ppm)

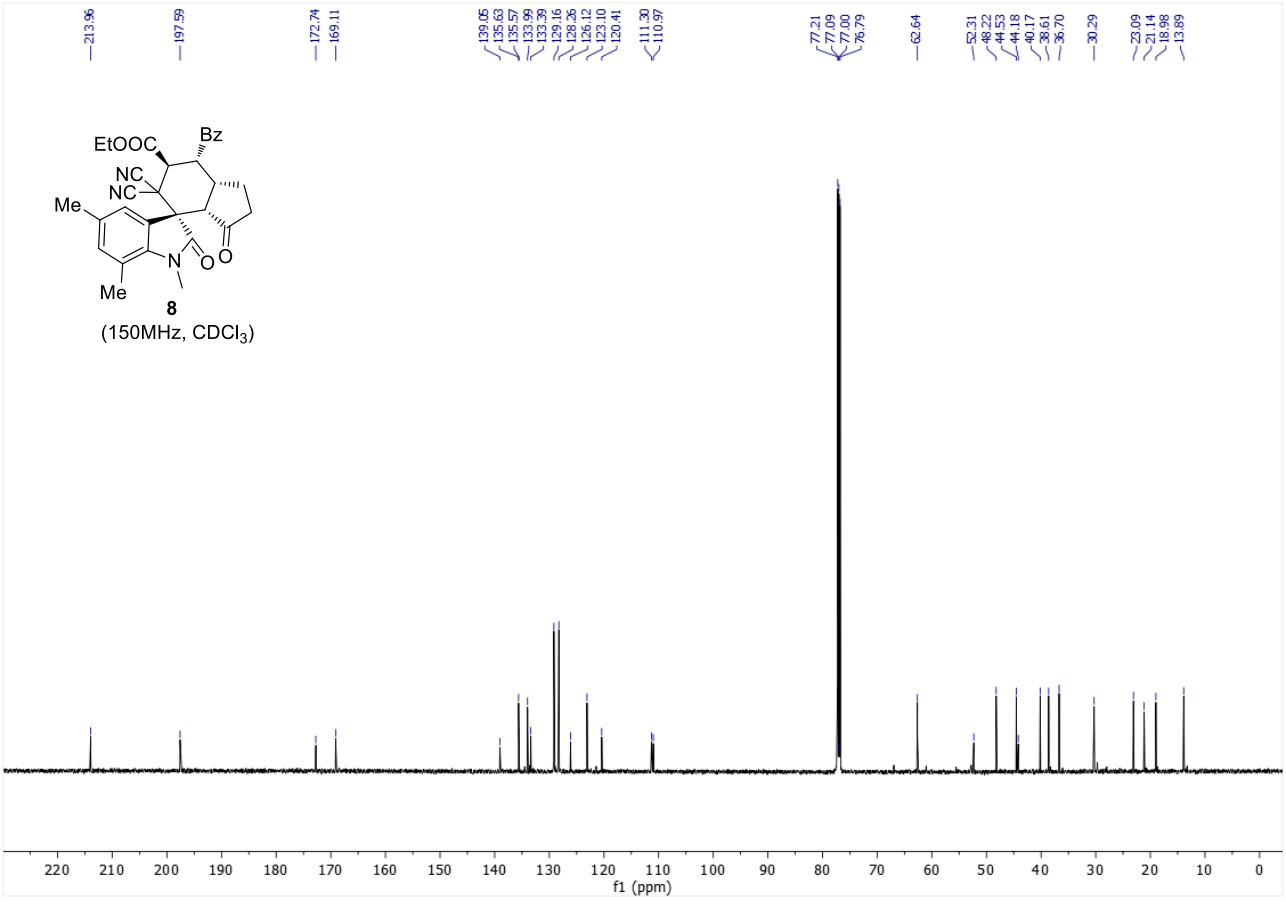


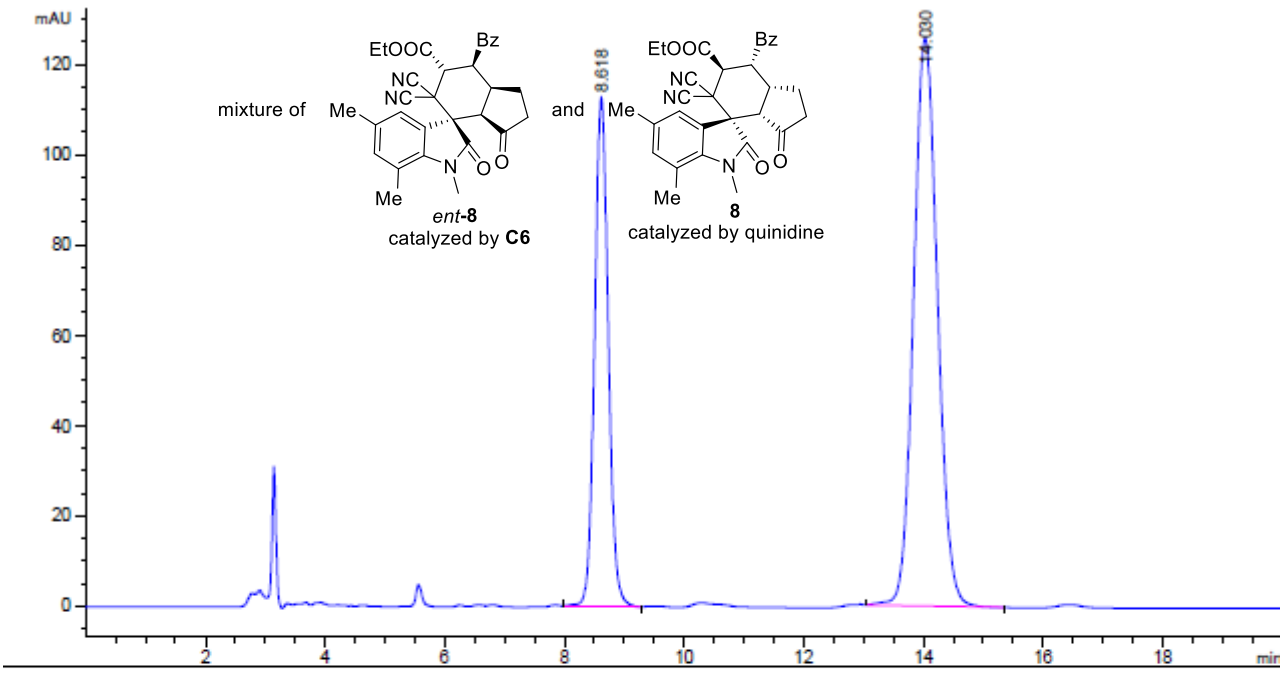
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.417	BB	0.2053	844.43127	63.82675	47.7028
2	8.747	BBA	0.2688	925.76221	53.13710	52.2972



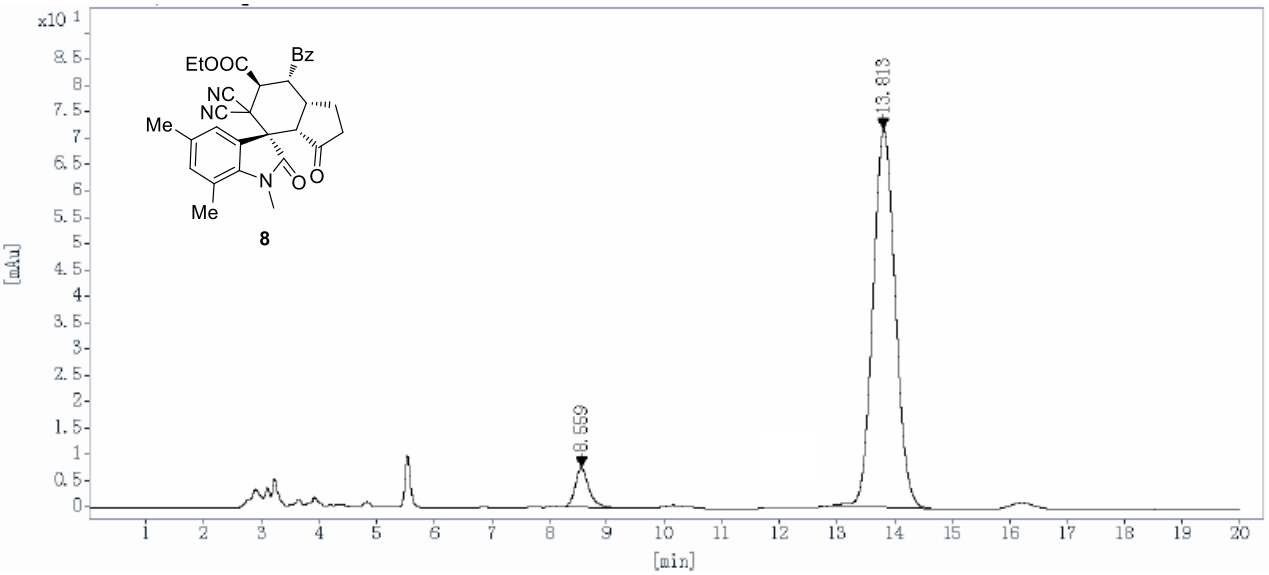
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.419	BB	0.2012	2878.10229	221.30852	71.8646
2	8.779	BBA	0.2888	915.63477	48.78722	28.1354


EtOOC
Bz
NC
NC
Me
N
O
O
Me
8
(600MHz, CDCl3)
f1 (ppm)

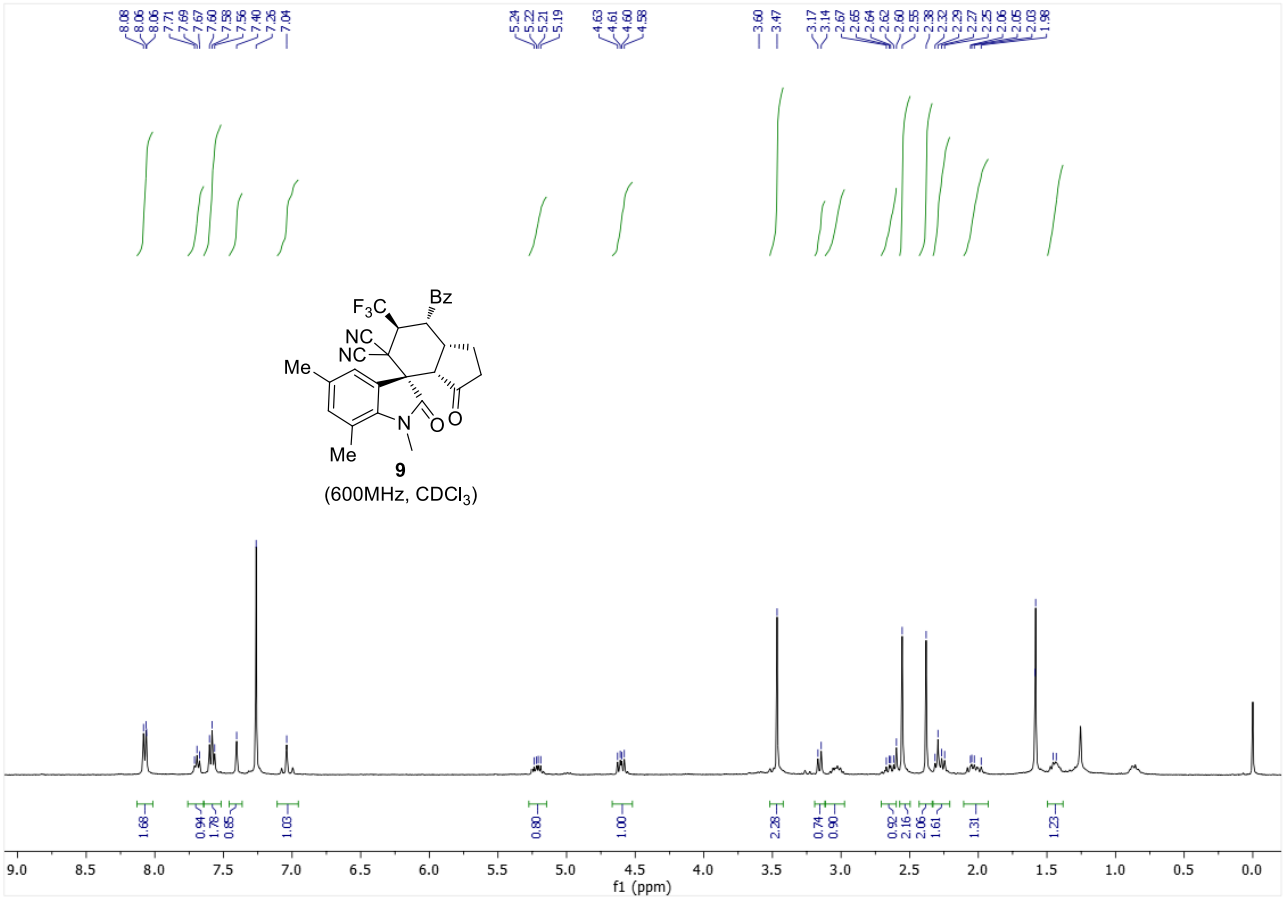

EtOOC
Bz
NC
NC
Me
N
O
O
Me
8
(150MHz, CDCl3)
f1 (ppm)

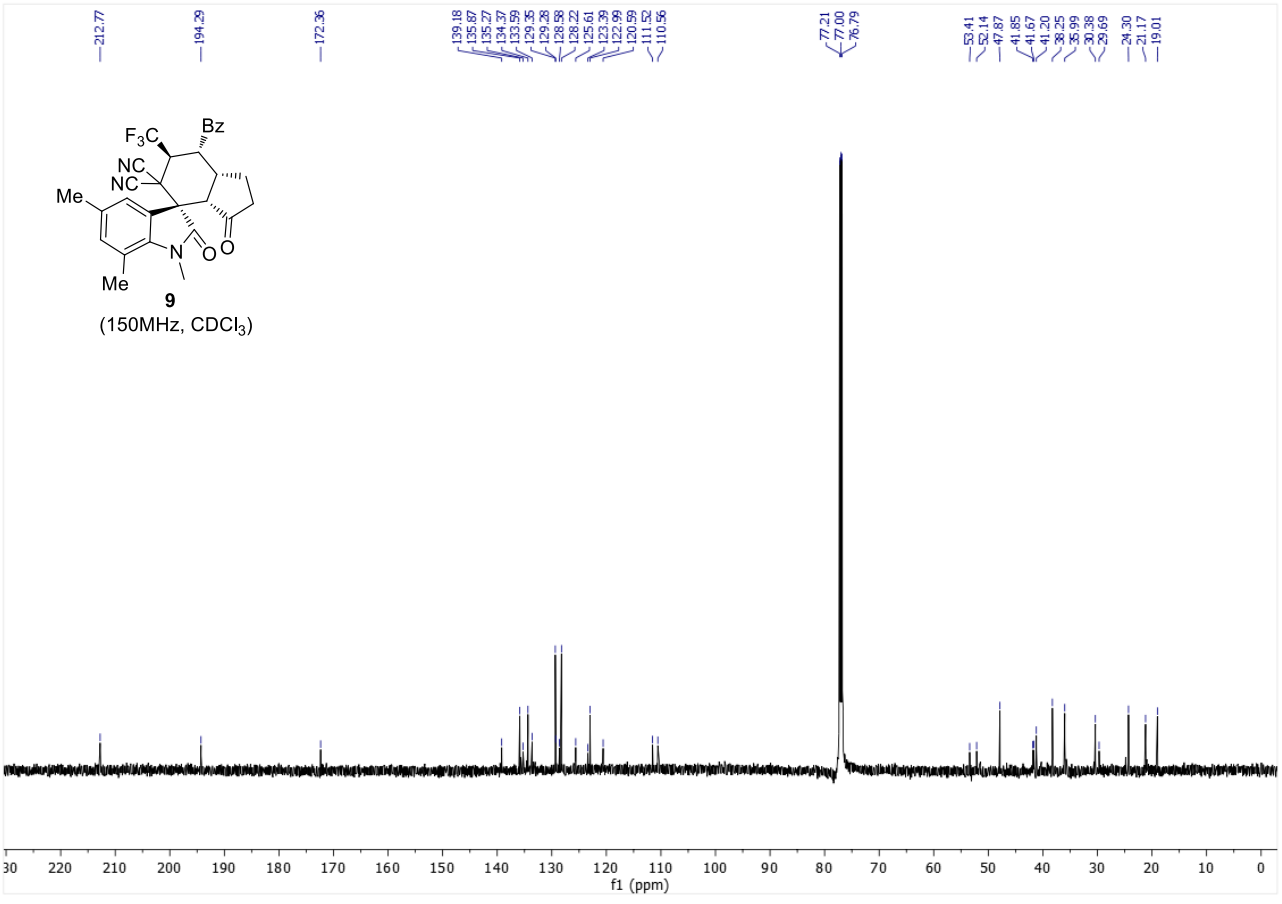


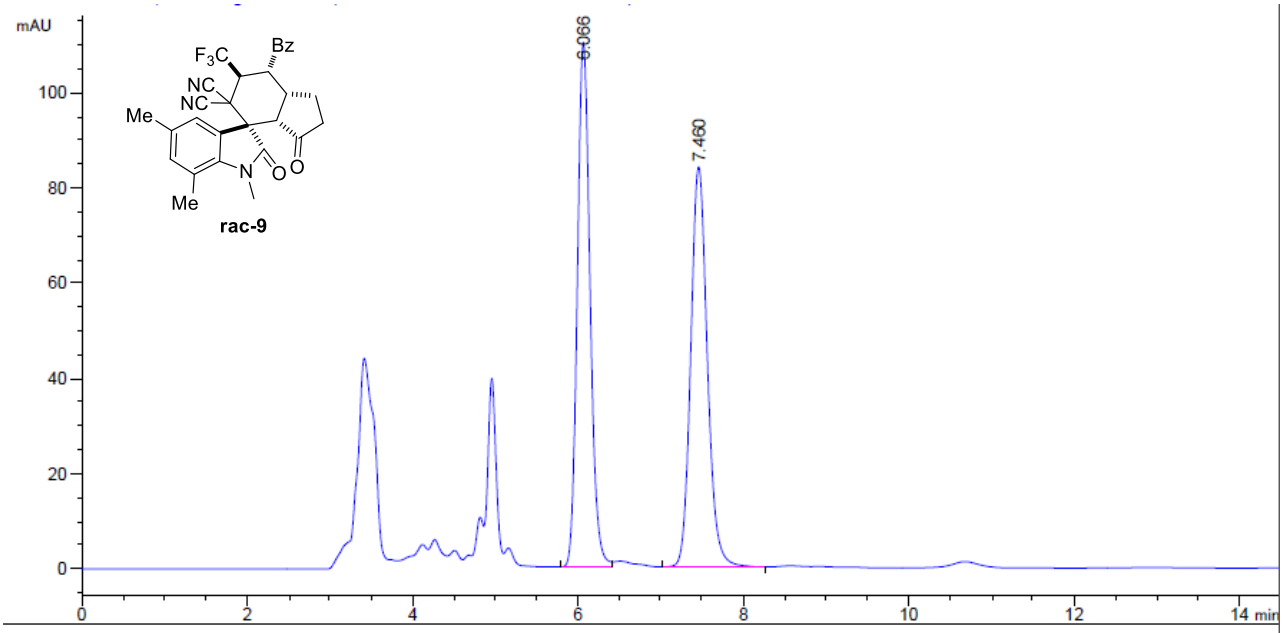
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.618	BB	0.2455	112.76895	1792.55115	33.8867
14.030	BB	0.4322	125.86776	3497.28491	66.1133



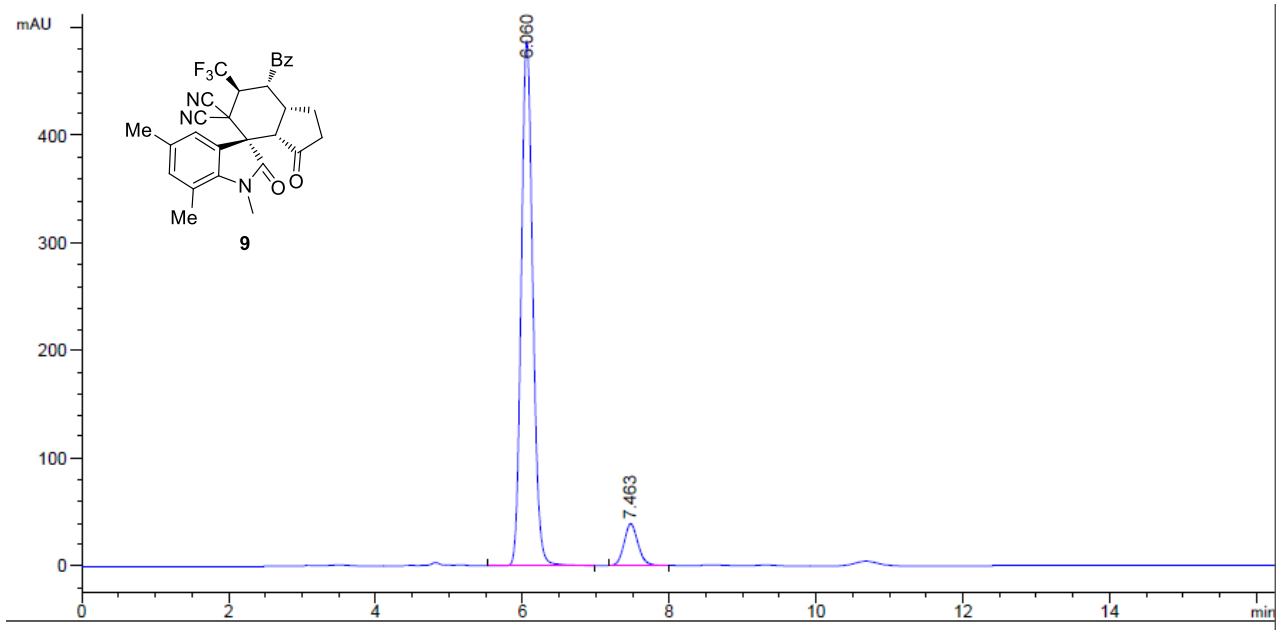
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.559	BB	0.25	7.5587	123.9443	6.0385
13.813	BB	0.42	71.6338	1928.6392	93.9615


8.08
8.06
8.06
8.06
7.71
7.69
7.67
7.60
7.58
7.55
7.40
7.26
7.04
5.24
5.22
5.21
5.19
4.63
4.61
4.60
4.58
3.60
3.47
3.17
3.14
2.67
2.65
2.64
2.62
2.60
2.55
2.38
2.32
2.29
2.27
2.25
2.06
2.05
2.03
1.98
F3C
Bz
NC
NC
Me
N
O
O
Me
9
(600MHz, CDCl3)
1.68
0.94
1.78
0.85
1.03
0.80
1.00
2.28
0.74
0.90
0.92
2.16
2.06
1.61
1.31
1.23
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)

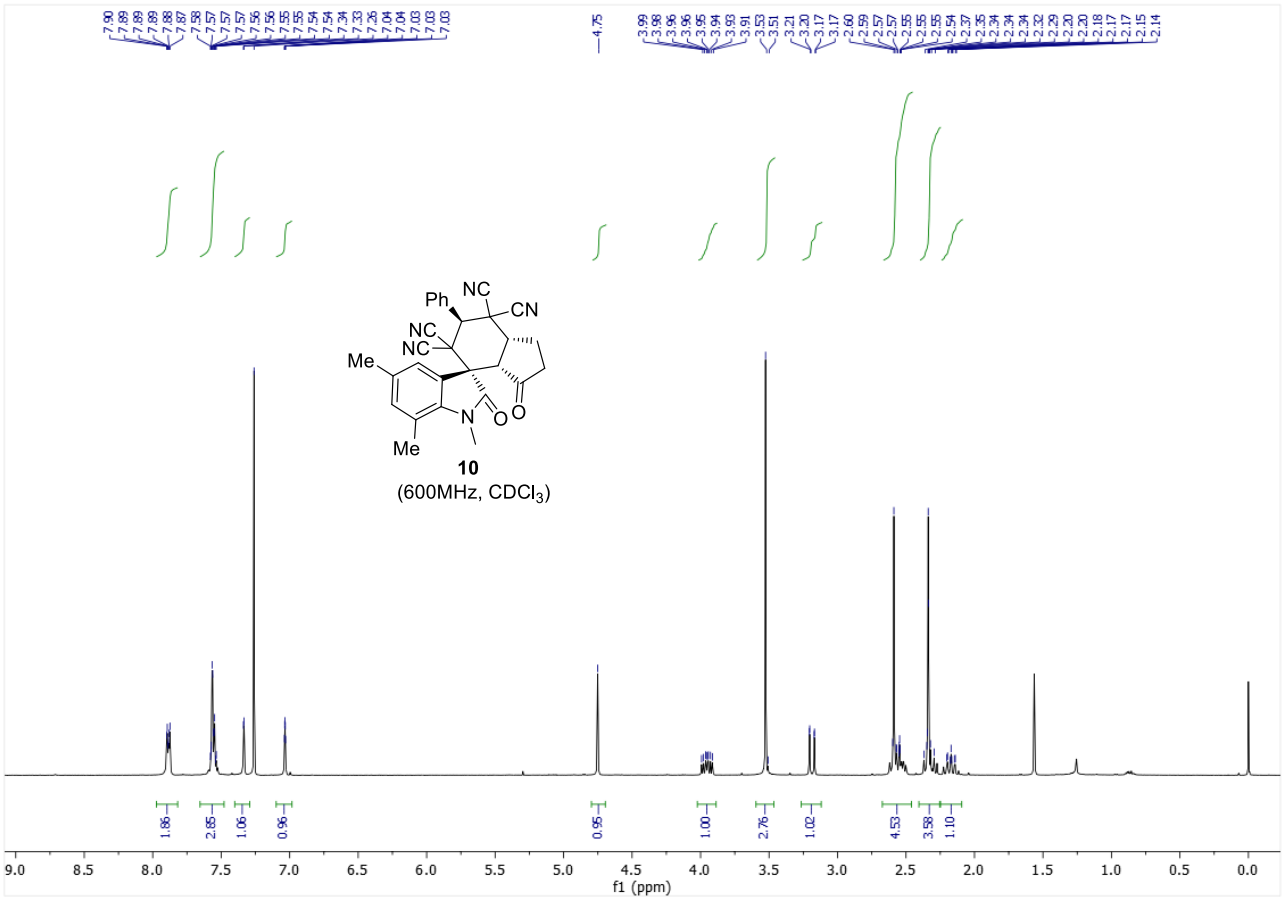

212.77
194.29
172.36
139.18
135.87
135.27
134.37
133.59
129.35
129.28
128.88
128.22
125.61
123.39
122.99
120.59
111.52
110.56
77.21
77.00
76.79
53.41
52.14
47.87
41.85
41.67
41.20
38.25
35.99
30.38
29.69
24.30
21.17
19.01
F3C
Bz
NC
NC
Me
N
O
O
Me
9
(150MHz, CDCl3)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

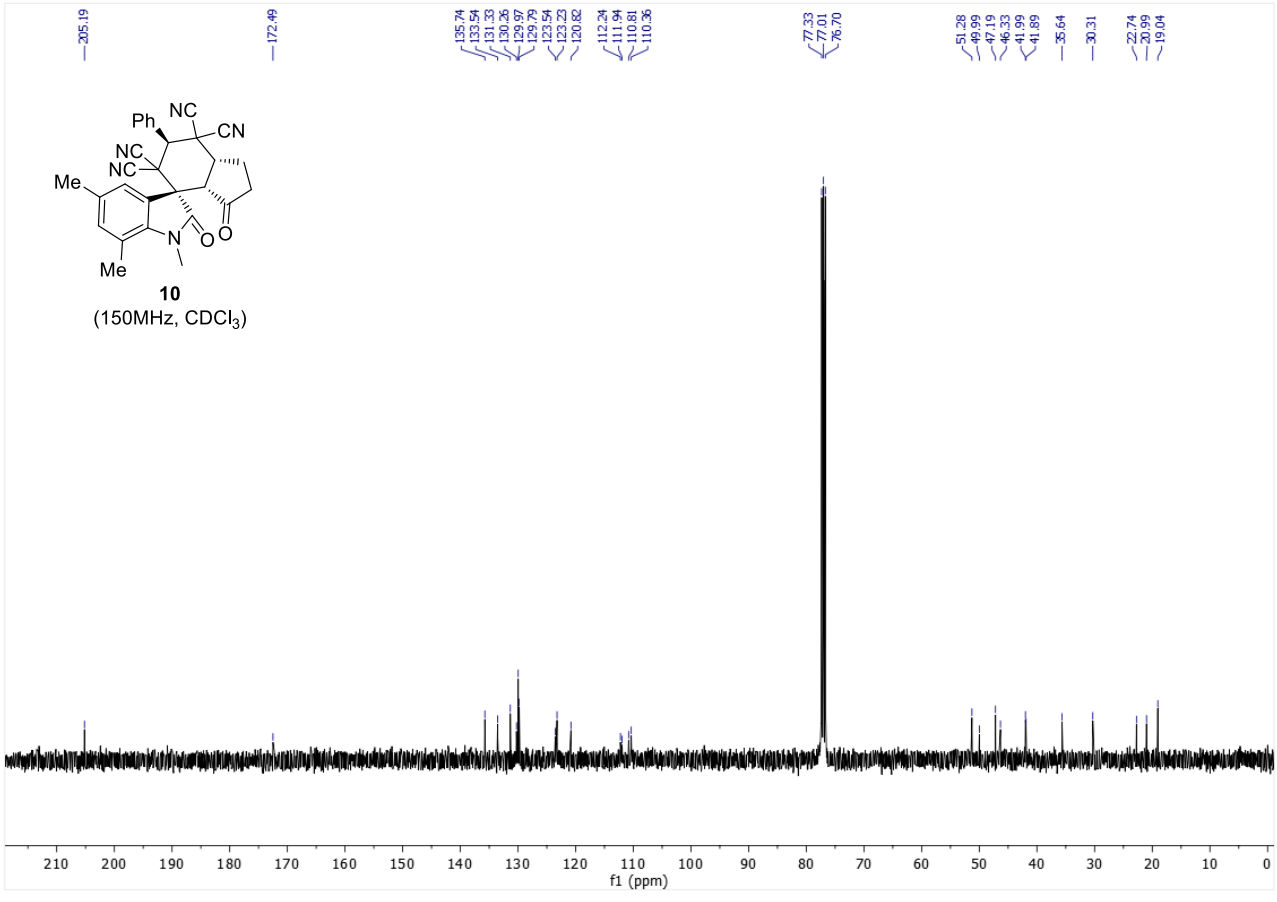


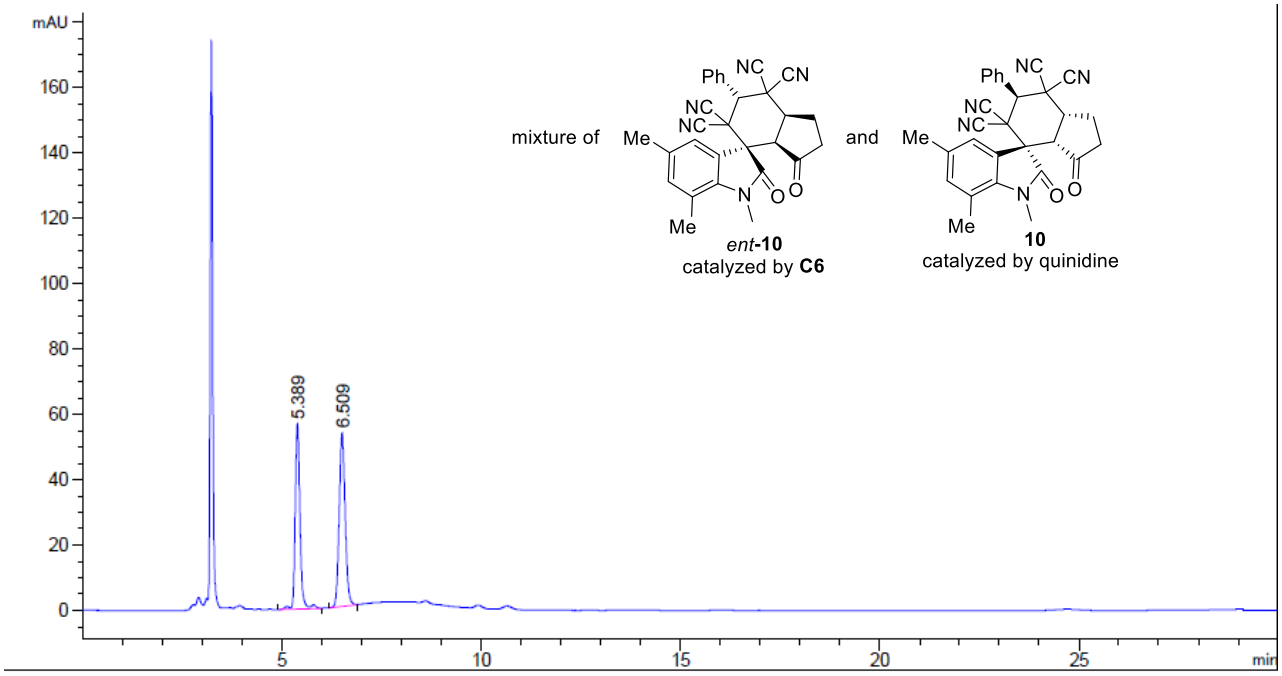
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.066	BV	0.1655	1176.99670	110.06493	50.1993
2	7.460	BB	0.2147	1167.65051	83.93517	49.8007



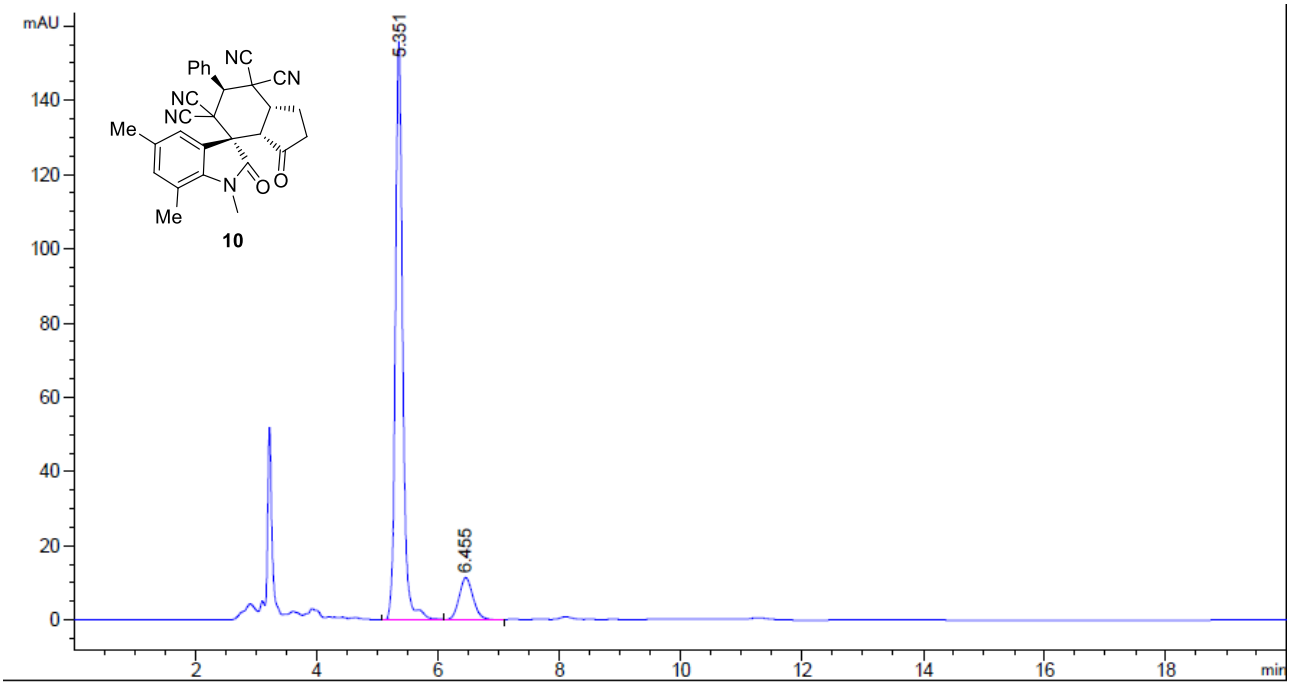
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.060	BB	0.1679	5320.36865	488.07773	93.4912
2	7.463	BB	0.2411	368.40515	56.27847	6.5088


Ph
NC
CN
NC
NC
Me
N
O
O
Me
10
(600MHz, CDCl3)
f1 (ppm)

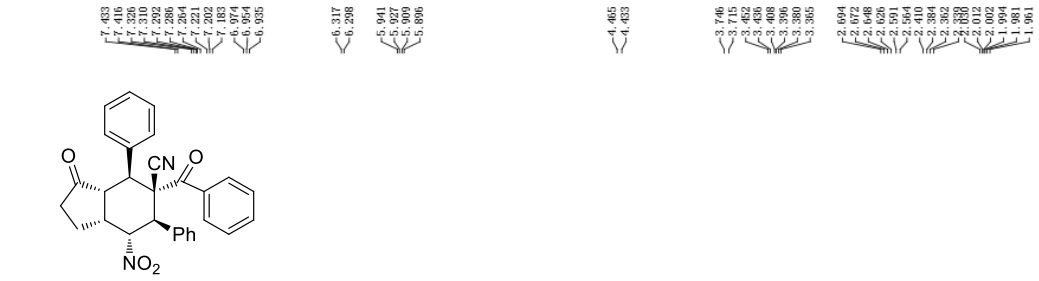

Ph
NC
CN
NC
NC
Me
N
O
O
Me
10
(150MHz, CDCl3)
f1 (ppm)



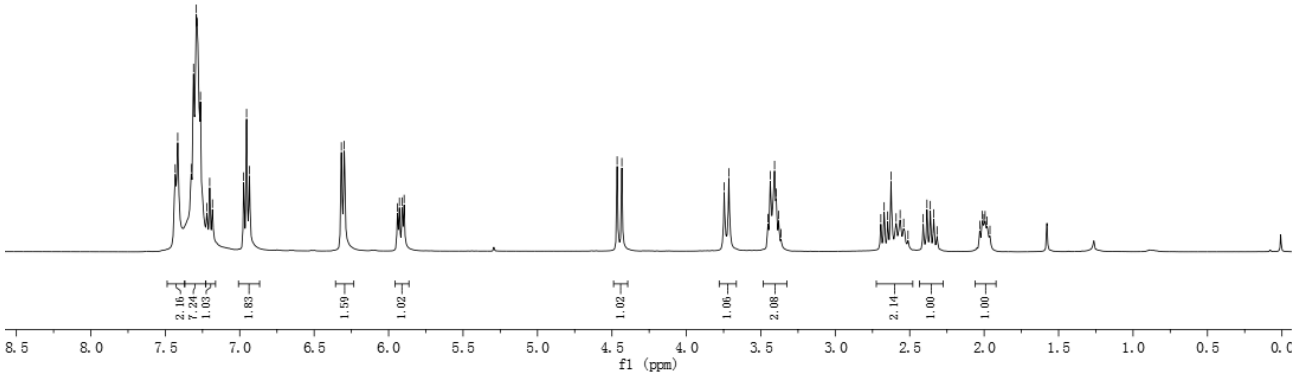
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.389	VV R	0.1286	478.44125	56.59073	46.4262
2	6.509	BB	0.1606	552.10089	52.96700	53.5738

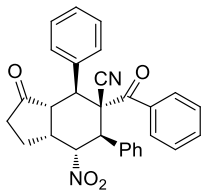


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.351	VV R	0.1240	1334.30347	155.62289	94.4163
2	6.455	BB	0.1609	78.94641	16.62692	5.5837

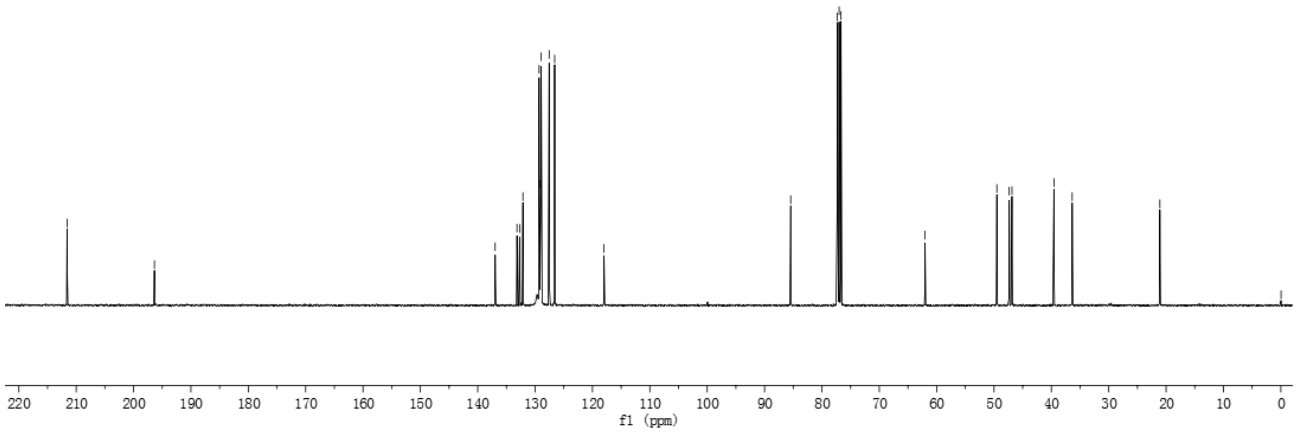


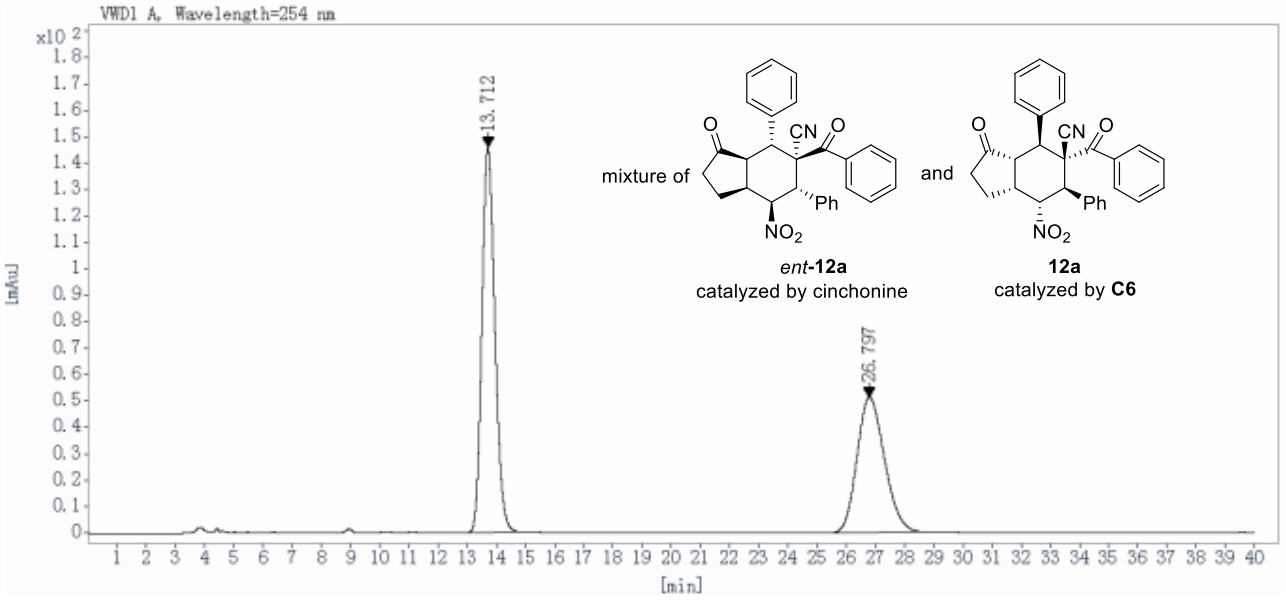
12a
(400MHz, $CDCl_3$)



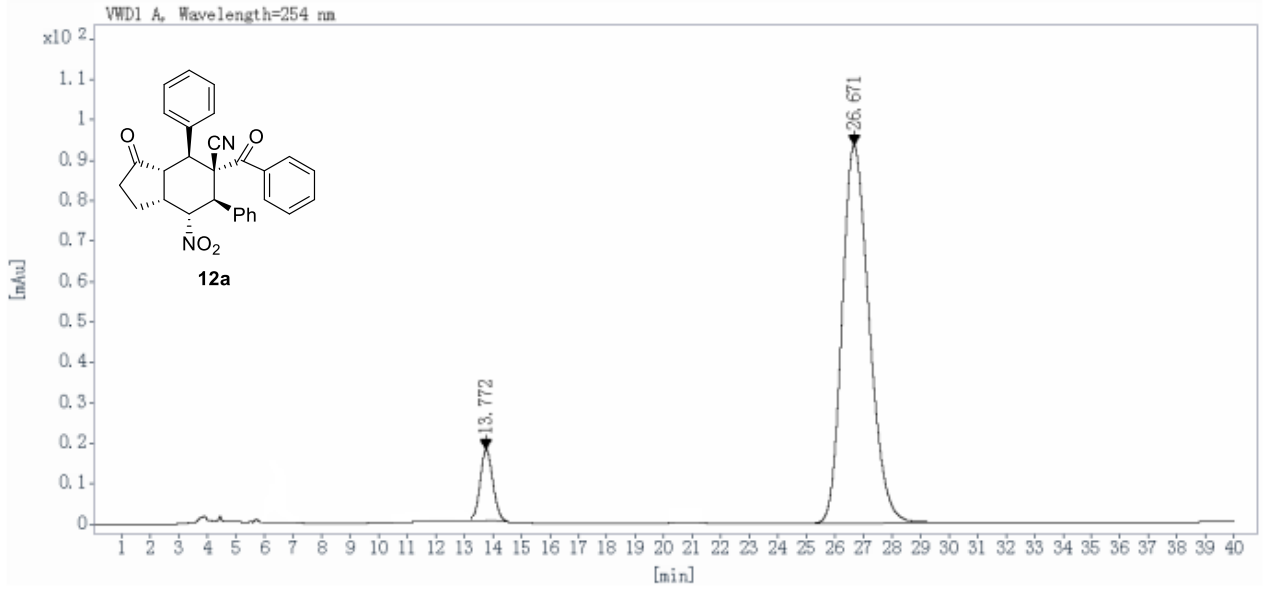


12a
(100MHz, $CDCl_3$)

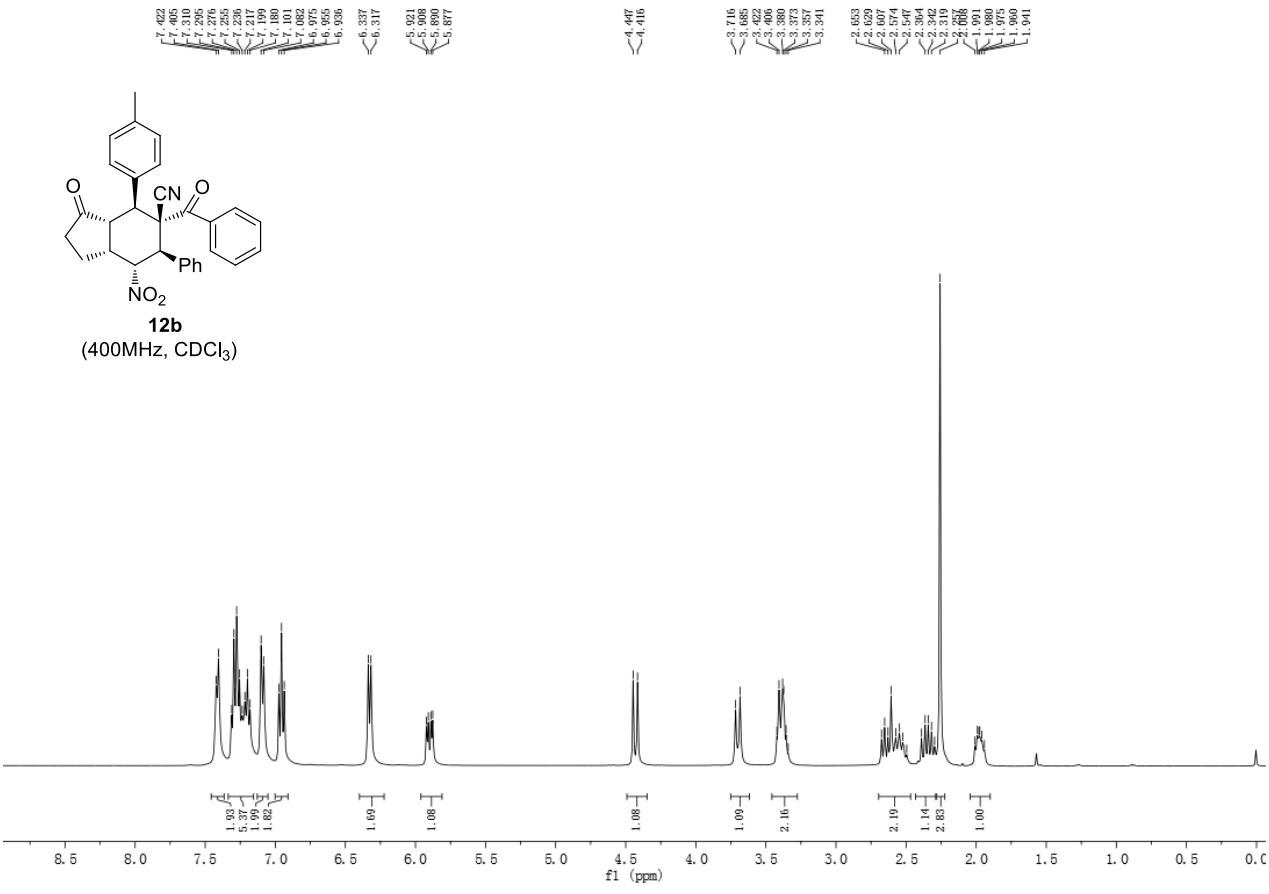




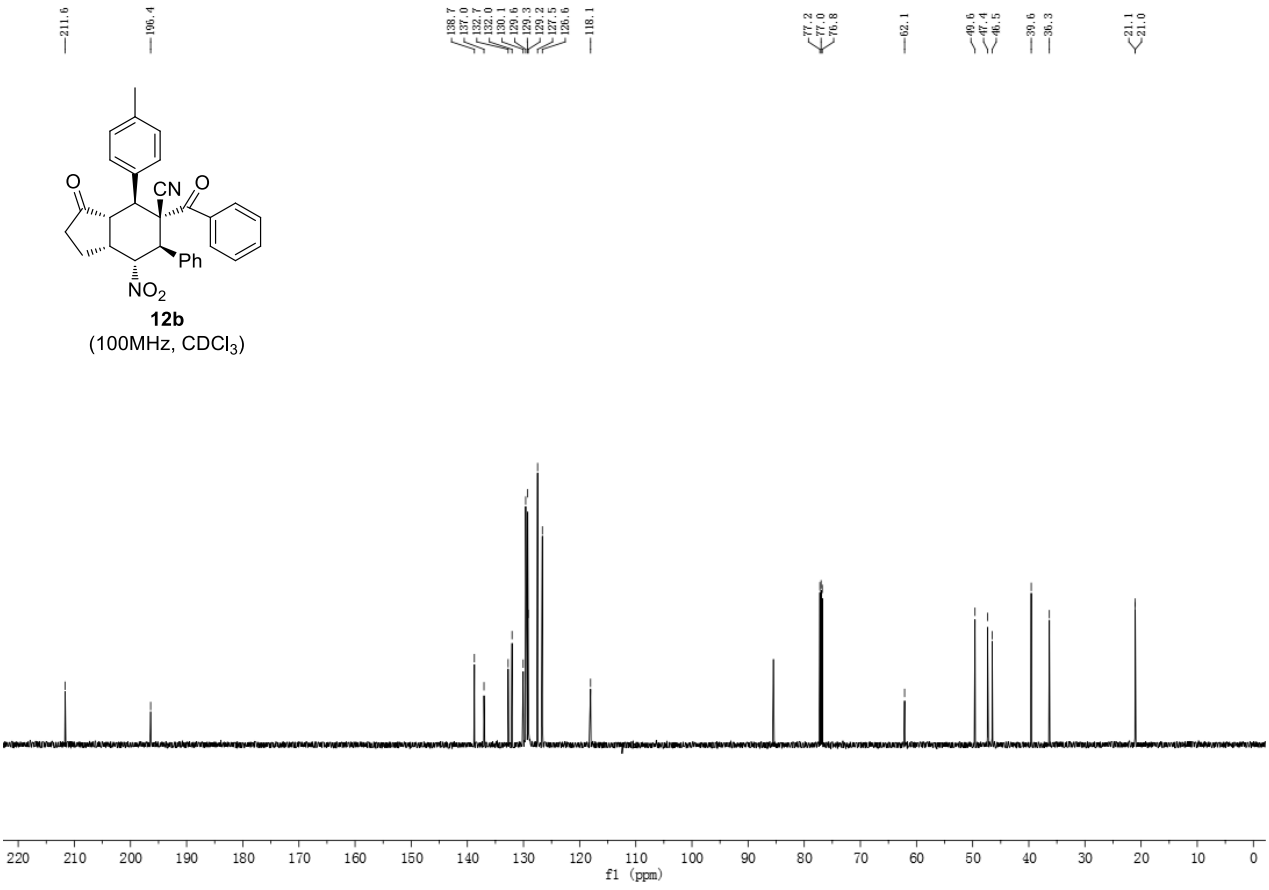
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.712	BB	0.48	145.7370	4502.7183	57.1926
26.797	BB	1.01	51.2258	3370.1804	42.8074
			Totals:	7872.8987	100.0000



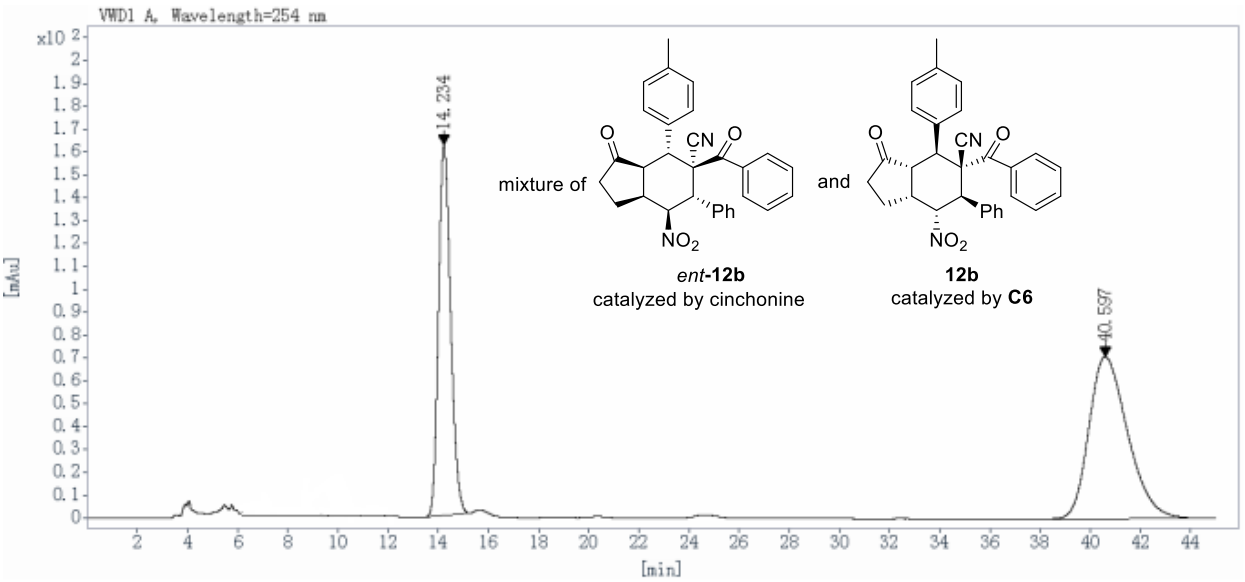
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.772	BB	0.48	17.4750	539.6851	8.0380
26.671	BB	1.02	93.4017	6174.4922	91.9620
			Totals:	6714.1772	100.0000



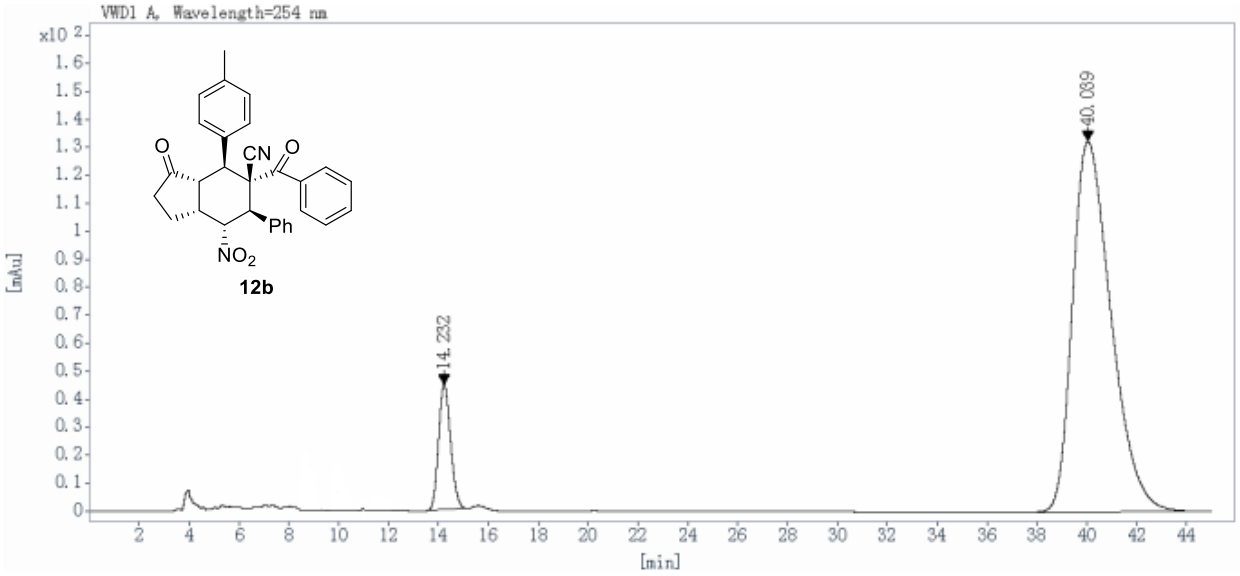
12b
(400MHz, $CDCl_3$)



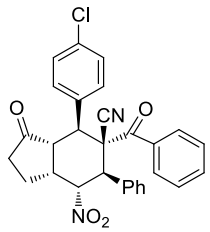
12b
(100MHz, $CDCl_3$)



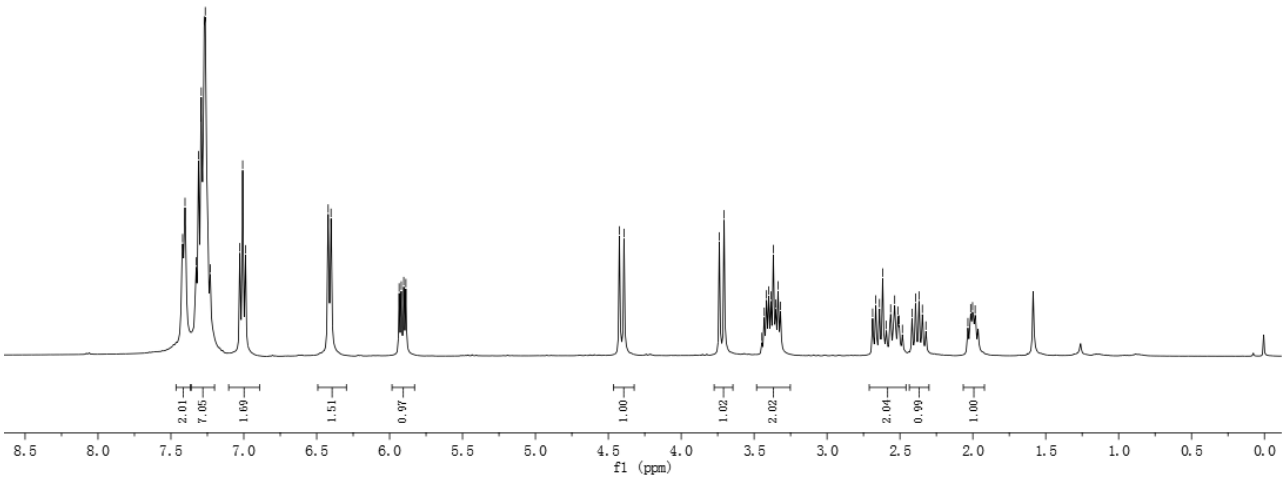
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.234	BB	0.52	161.8310	5458.3267	41.7577
40.597	BBA	1.64	70.7844	7613.1099	58.2423
			Totals:	13071.4365	100.0000

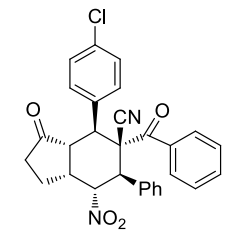


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.232	BBA	0.52	44.5588	1479.1577	9.4187
40.039	BBA	1.64	132.3924	14225.2979	90.5813
			Totals:	15704.4556	100.0000

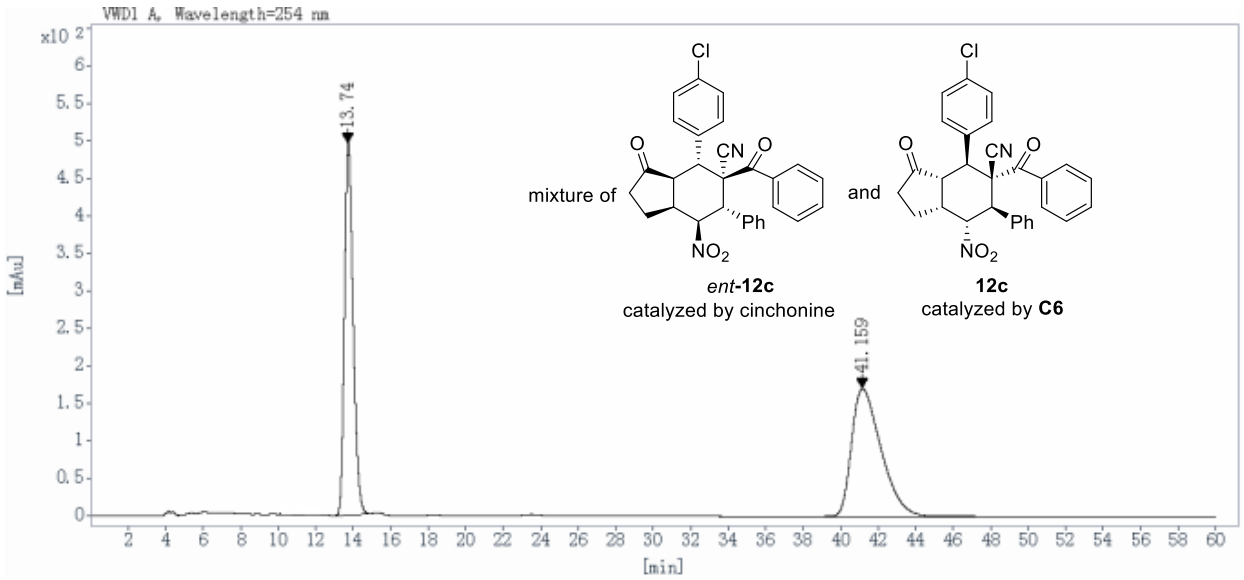


12c
(400MHz, $CDCl_3$)

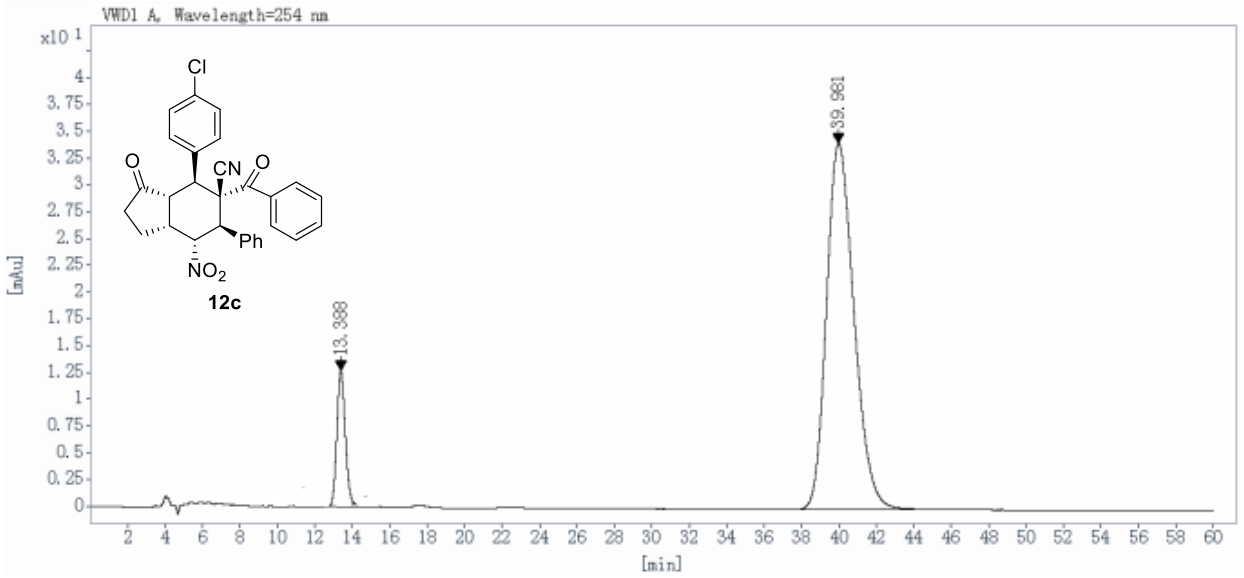




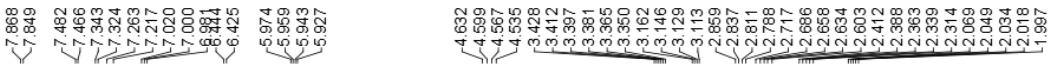
12c
(100MHz, $CDCl_3$)

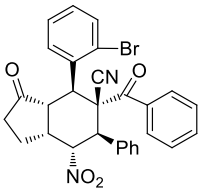


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.740	BB	0.50	495.3008	15924.6426	46.0731
41.159	BB	1.67	170.3046	18639.2207	53.9269
			Totals:	34563.8633	100.0000

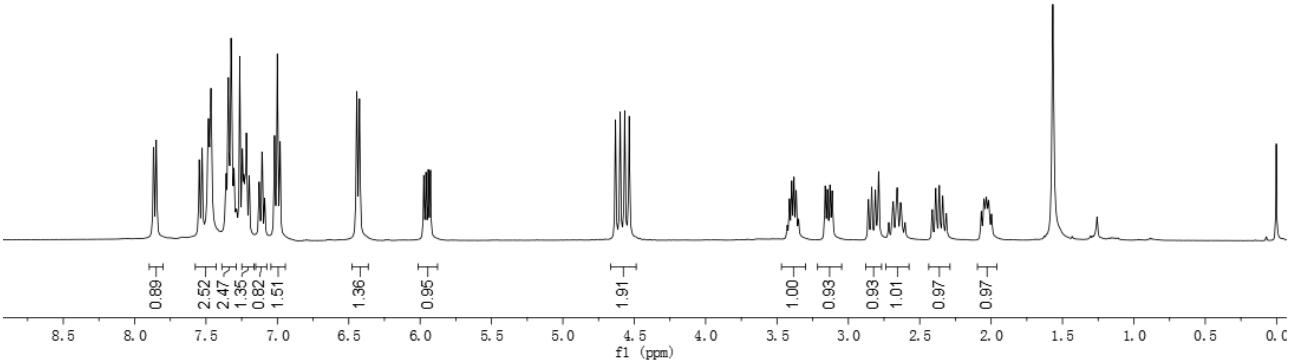


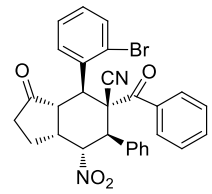
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.388	BB	0.48	12.5945	386.5583	9.9662
39.981	BB	1.57	34.1107	3492.1396	90.0338
			Totals:	3878.6979	100.0000



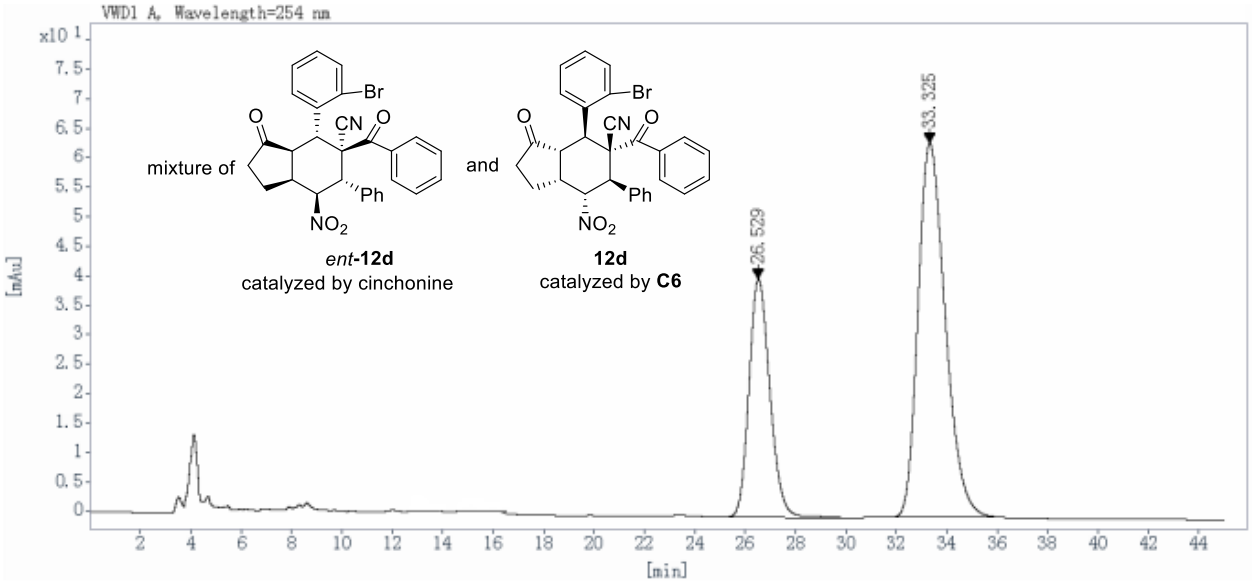


12d
(400MHz, $CDCl_3$)

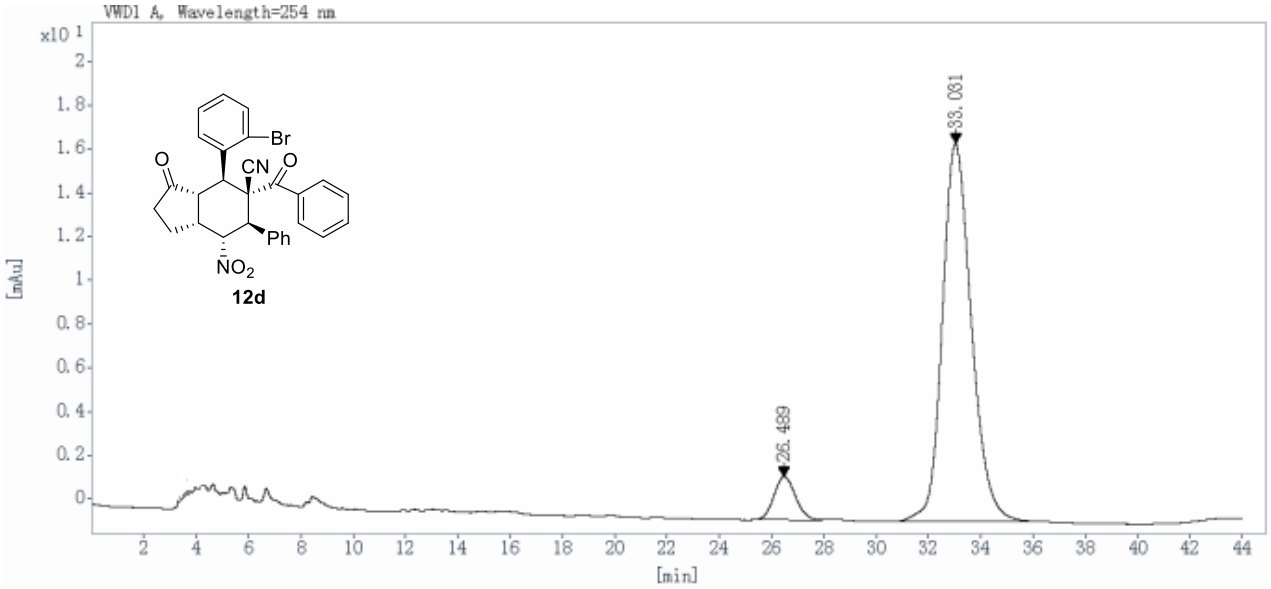




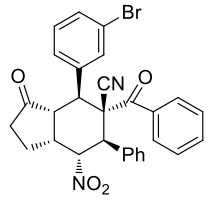
12d
(100MHz, $CDCl_3$)



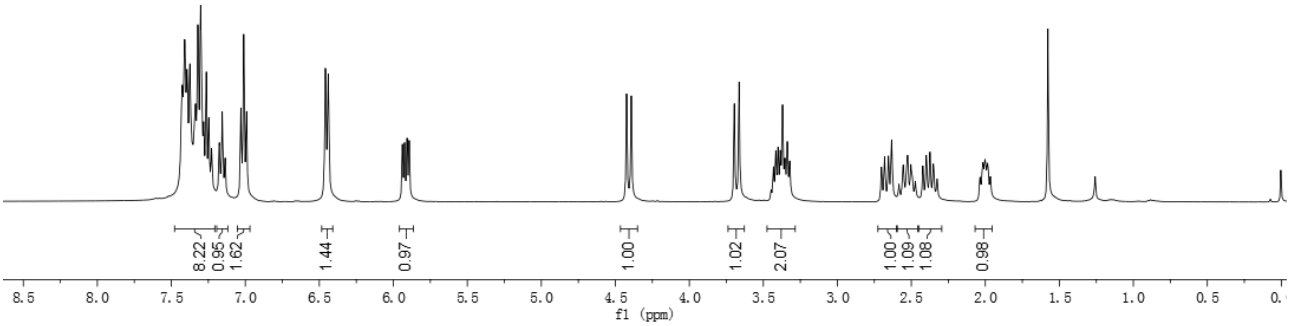
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
26.529	BB	0.88	40.3576	2322.3757	32.8290
33.325	BBA	1.13	63.3756	4751.7910	67.1710
			Totals:	7074.1667	100.0000

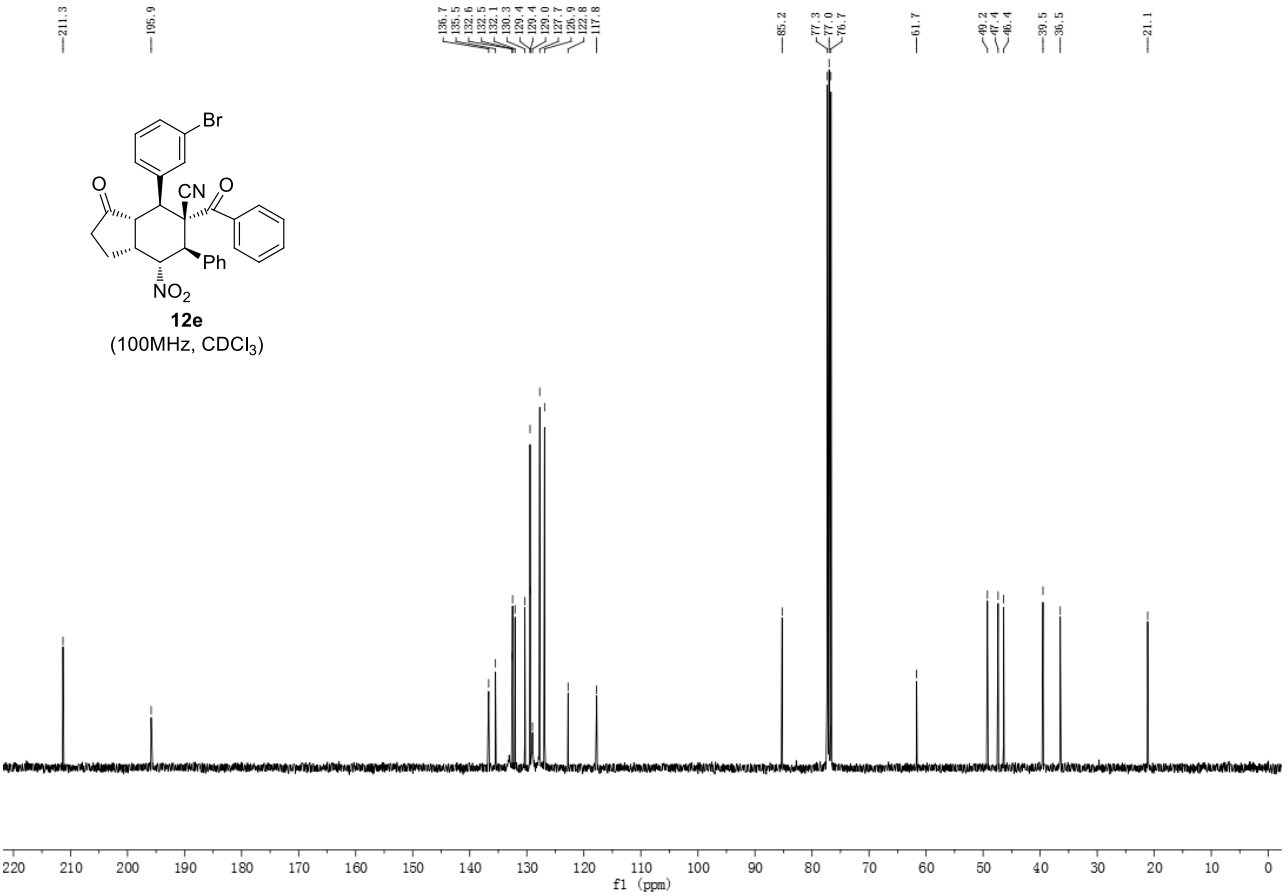


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
26.489	BB	0.78	1.9720	112.1931	7.7414
33.031	BB	1.17	17.2605	1337.0769	92.2586
			Totals:	1449.2701	100.0000

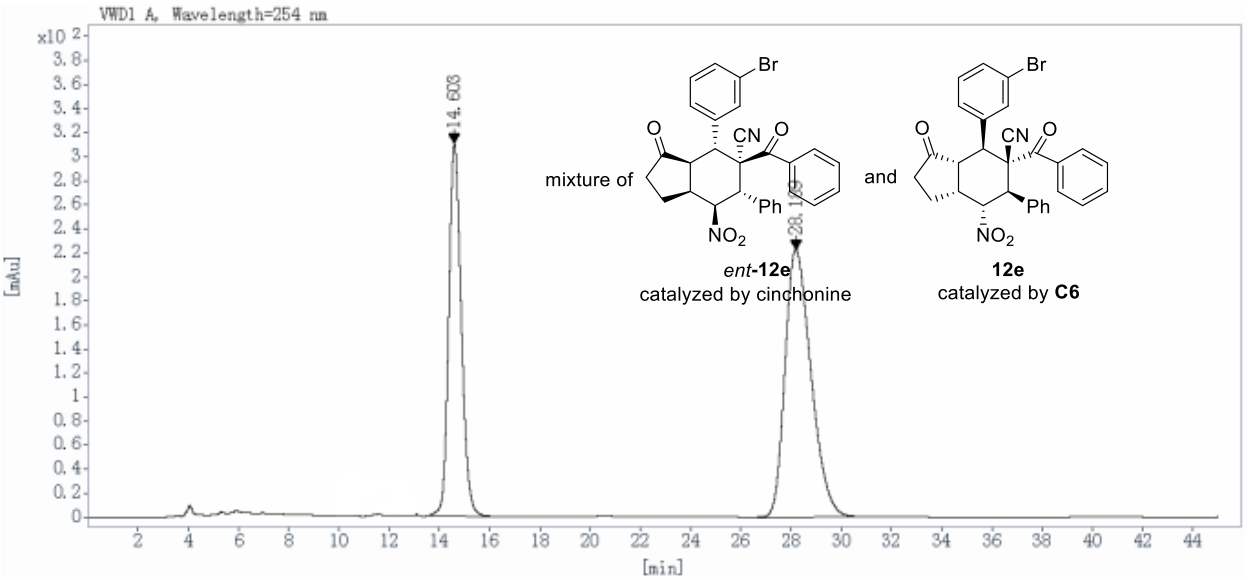


12e
(400MHz, $CDCl_3$)

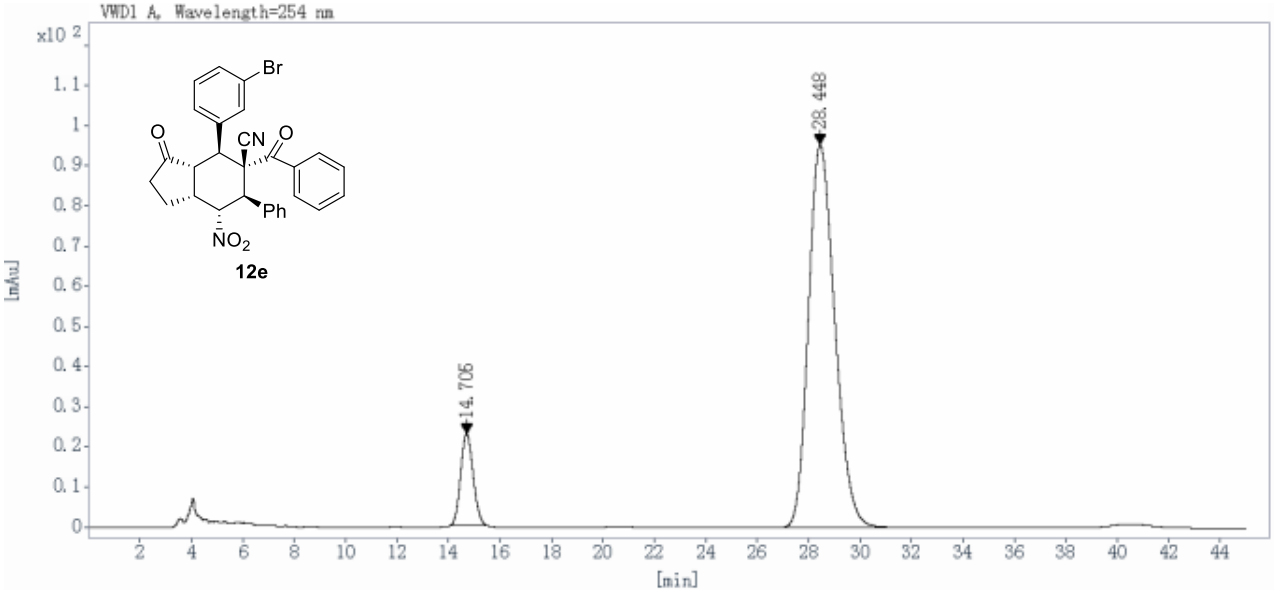




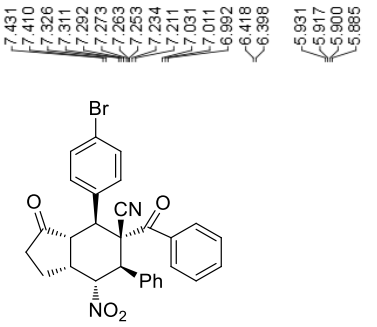
12e
(100MHz, $CDCl_3$)



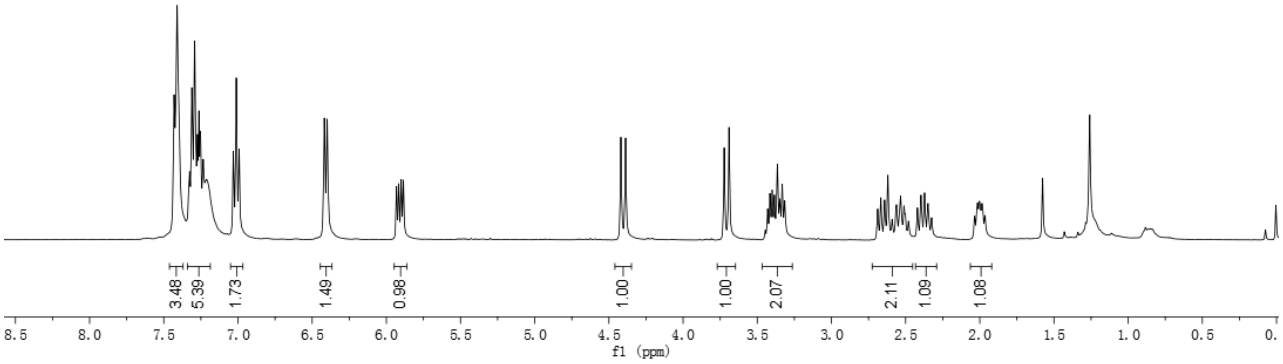
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.603	BB	0.53	309.4417	10716.9961	40.0750
28.189	BB	1.11	222.6176	16025.3486	59.9250
			Totals:	26742.3447	100.0000

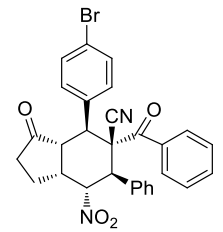


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.705	BBA	0.53	22.8103	768.6624	10.1246
28.448	BB	1.11	95.3737	6823.3579	89.8754
			Totals:	7592.0203	100.0000

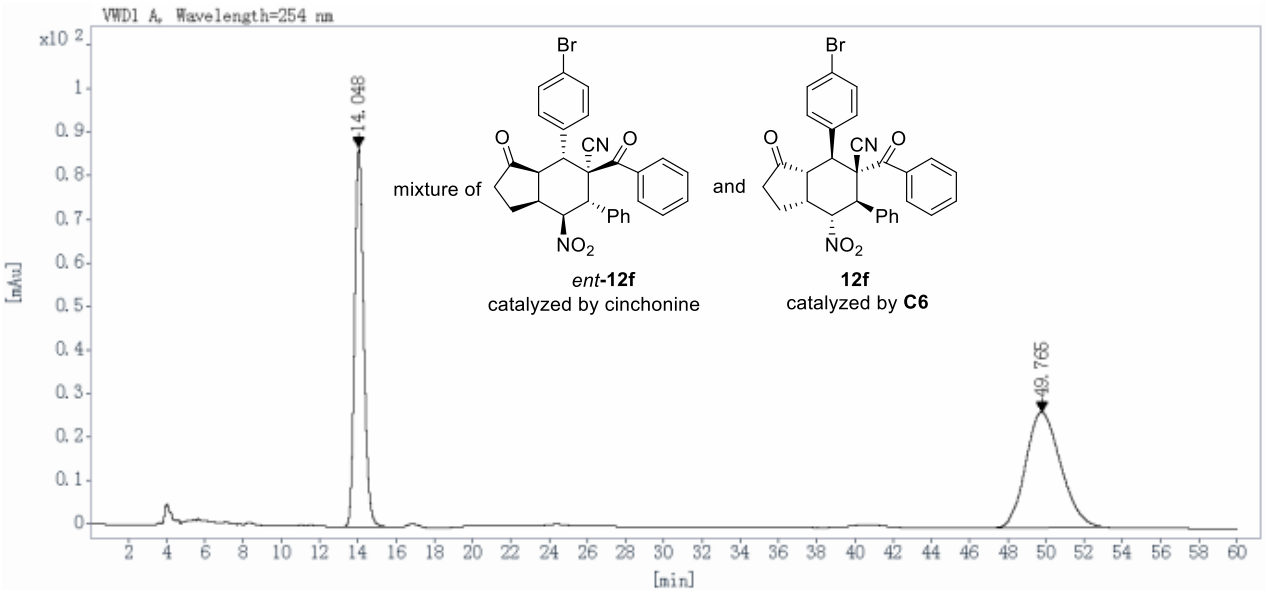


12f
(400MHz, $CDCl_3$)

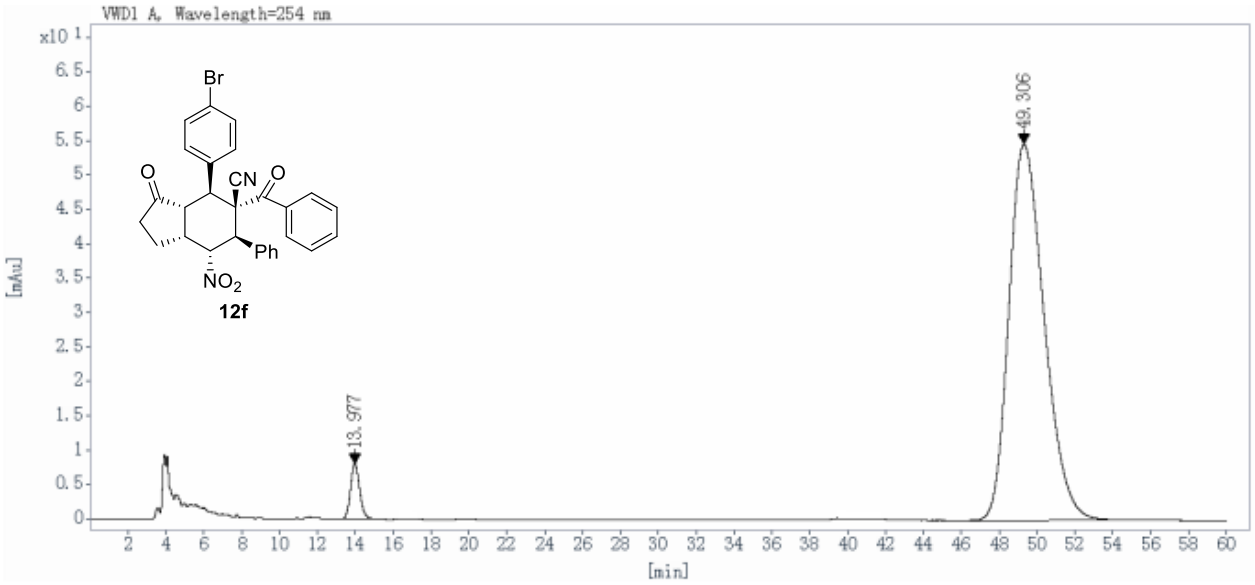




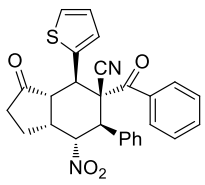
12f
(100MHz, $CDCl_3$)



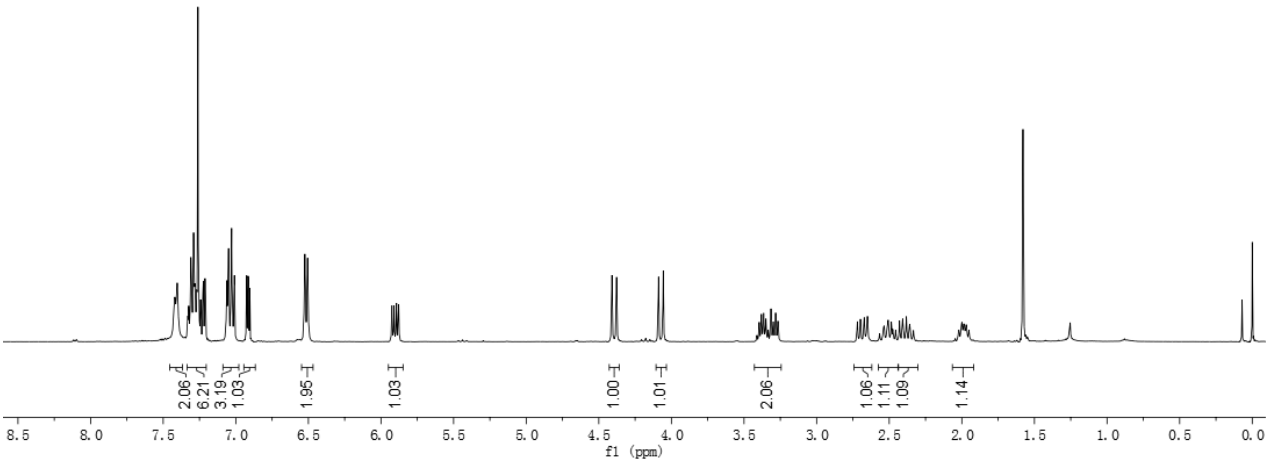
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.048	BB	0.51	87.0748	2878.2803	46.1540
49.765	BB	1.82	26.4309	3357.9717	53.8460
			Totals:	6236.2520	100.0000

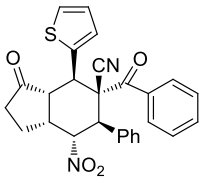


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.977	BBA	0.52	8.0256	270.7563	3.6868
49.306	BB	1.90	54.6272	7073.1079	96.3132
			Totals:	7343.8642	100.0000

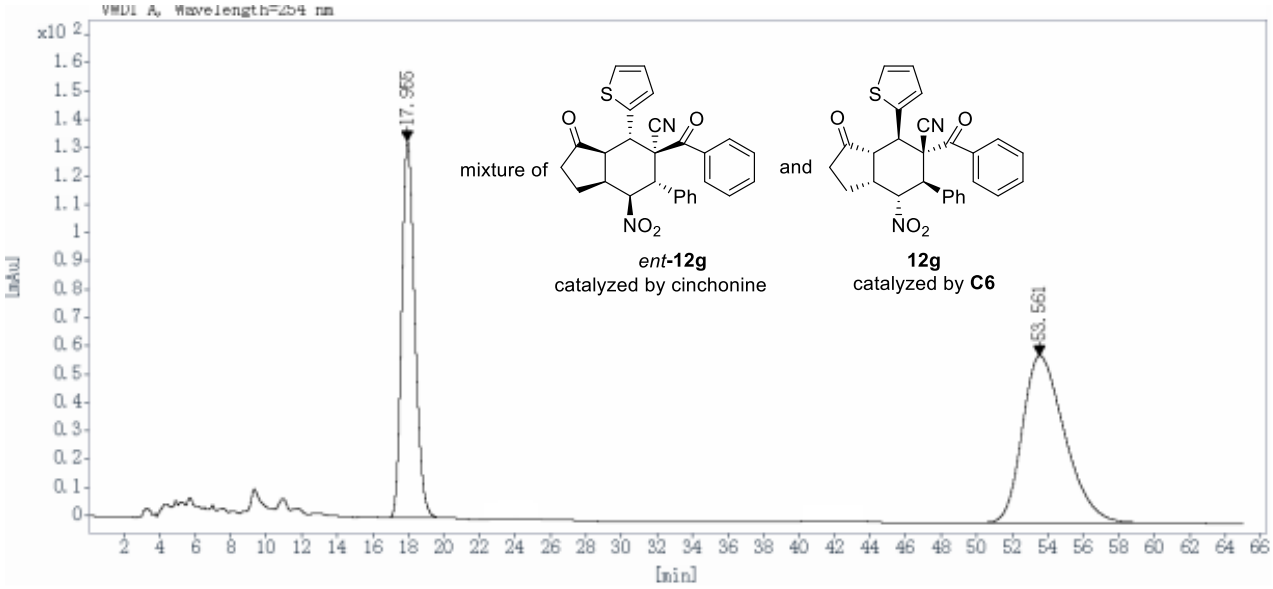


12g
(400MHz, $CDCl_3$)

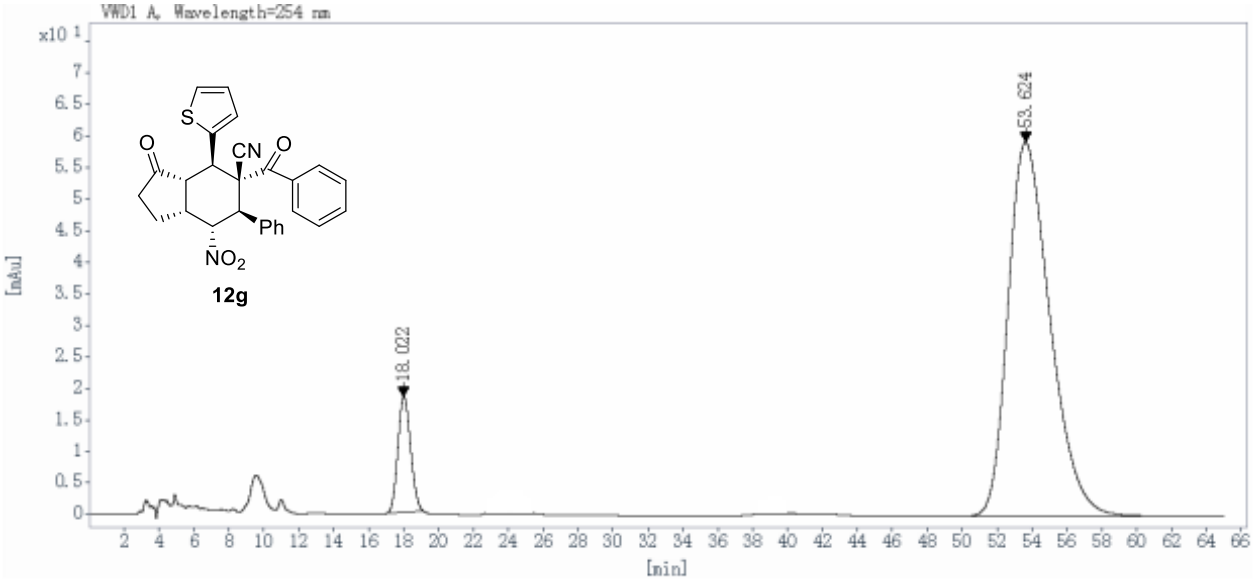




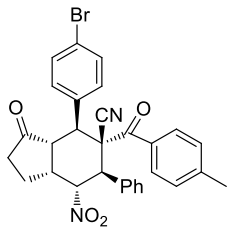
12g
(100MHz, $CDCl_3$)



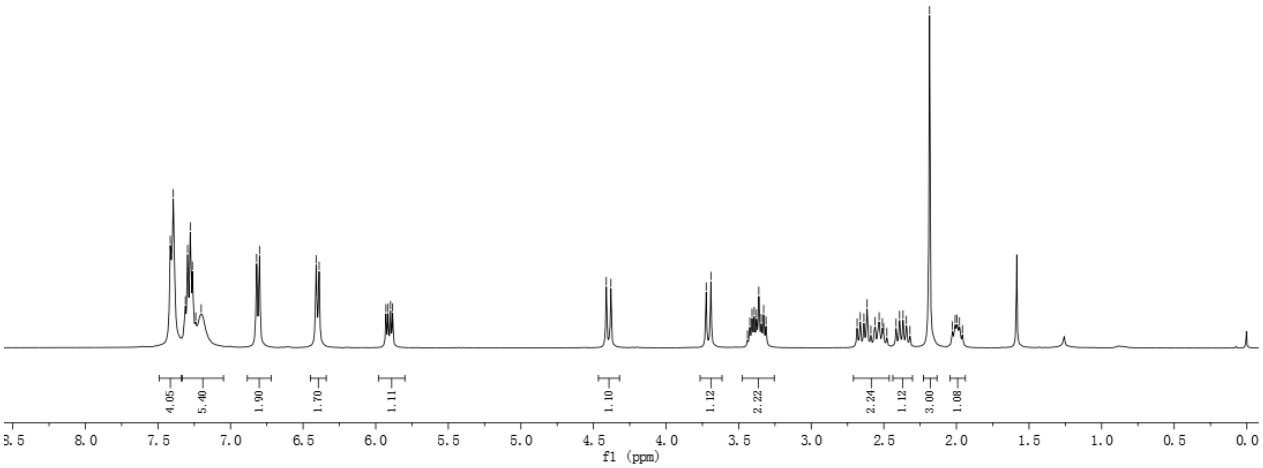
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
17.955	BB	0.79	133.0663	6816.8457	40.9767
53.561	BB	2.45	59.0161	9819.0713	59.0233
			Totals:	16635.9170	100.0000

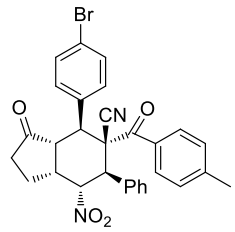


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
18.022	BBA	0.78	18.3559	926.4836	8.5706
53.624	BB	2.44	59.1773	9883.5273	91.4294
			Totals:	10810.0110	100.0000

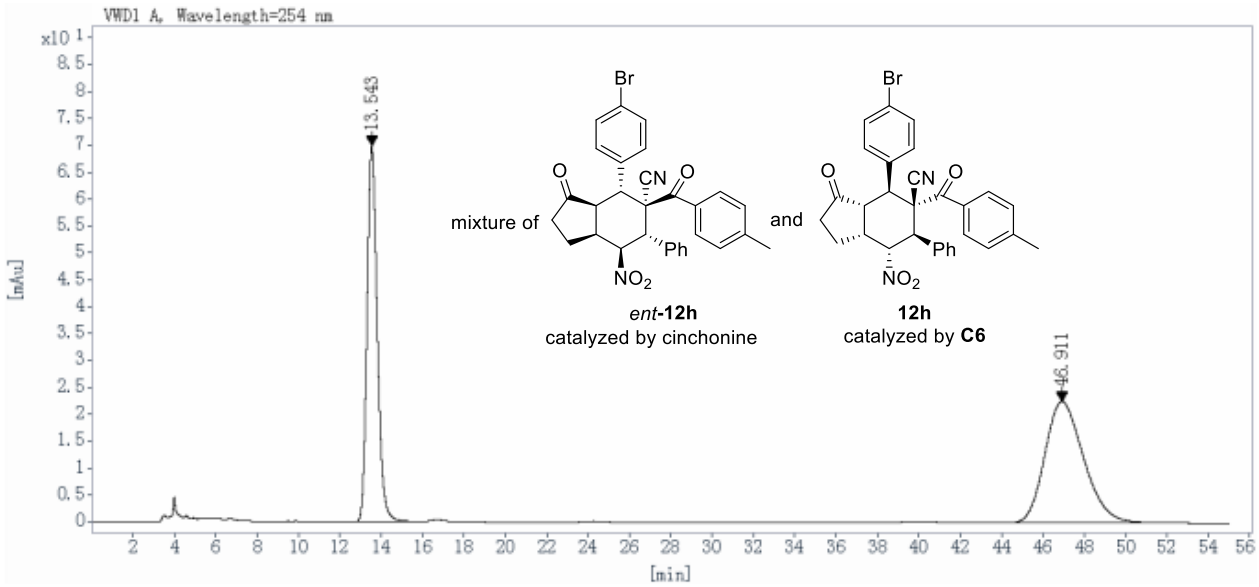


12h
(400MHz, $CDCl_3$)

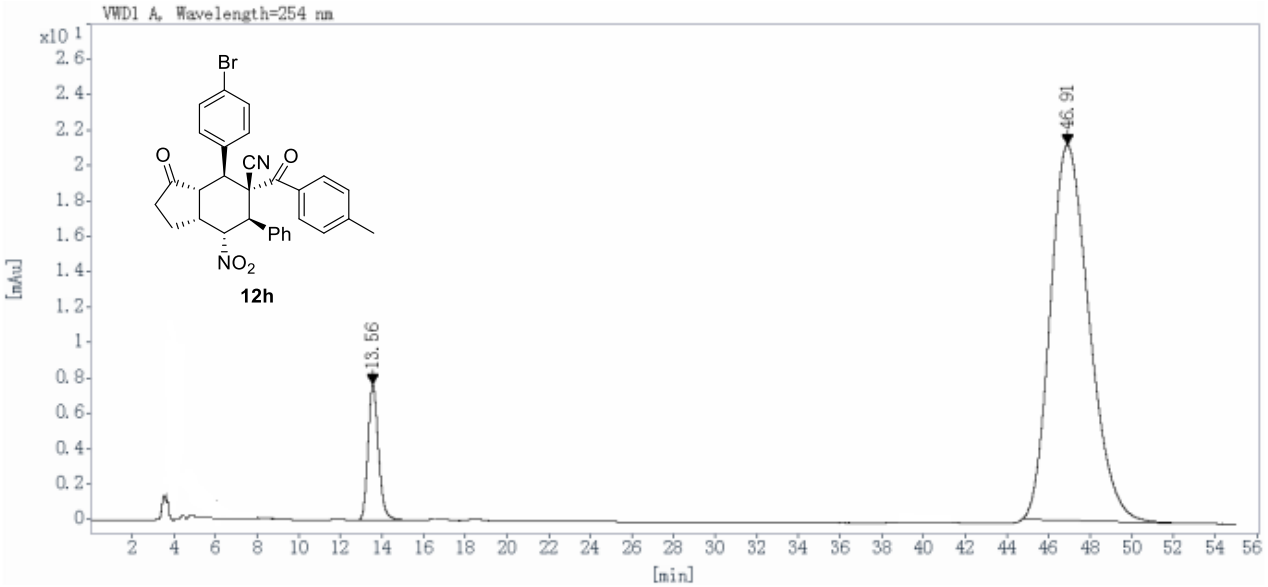




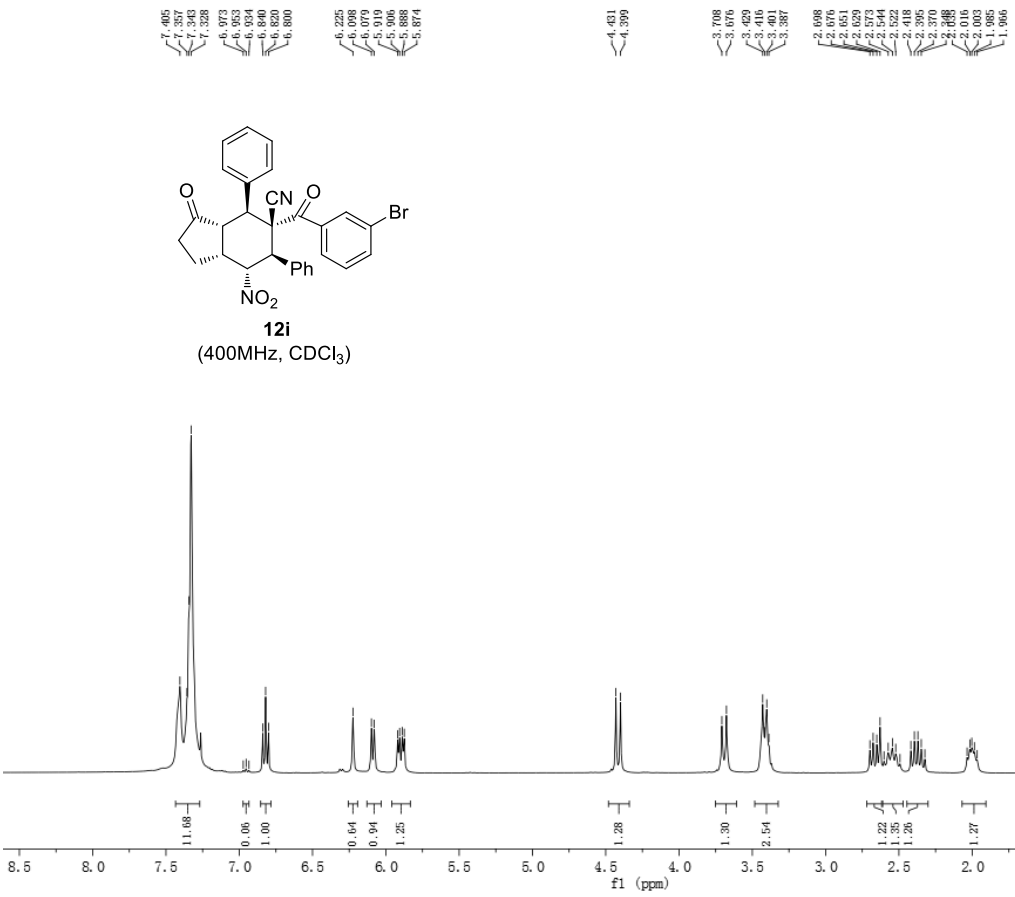
12h
(100MHz, $CDCl_3$)



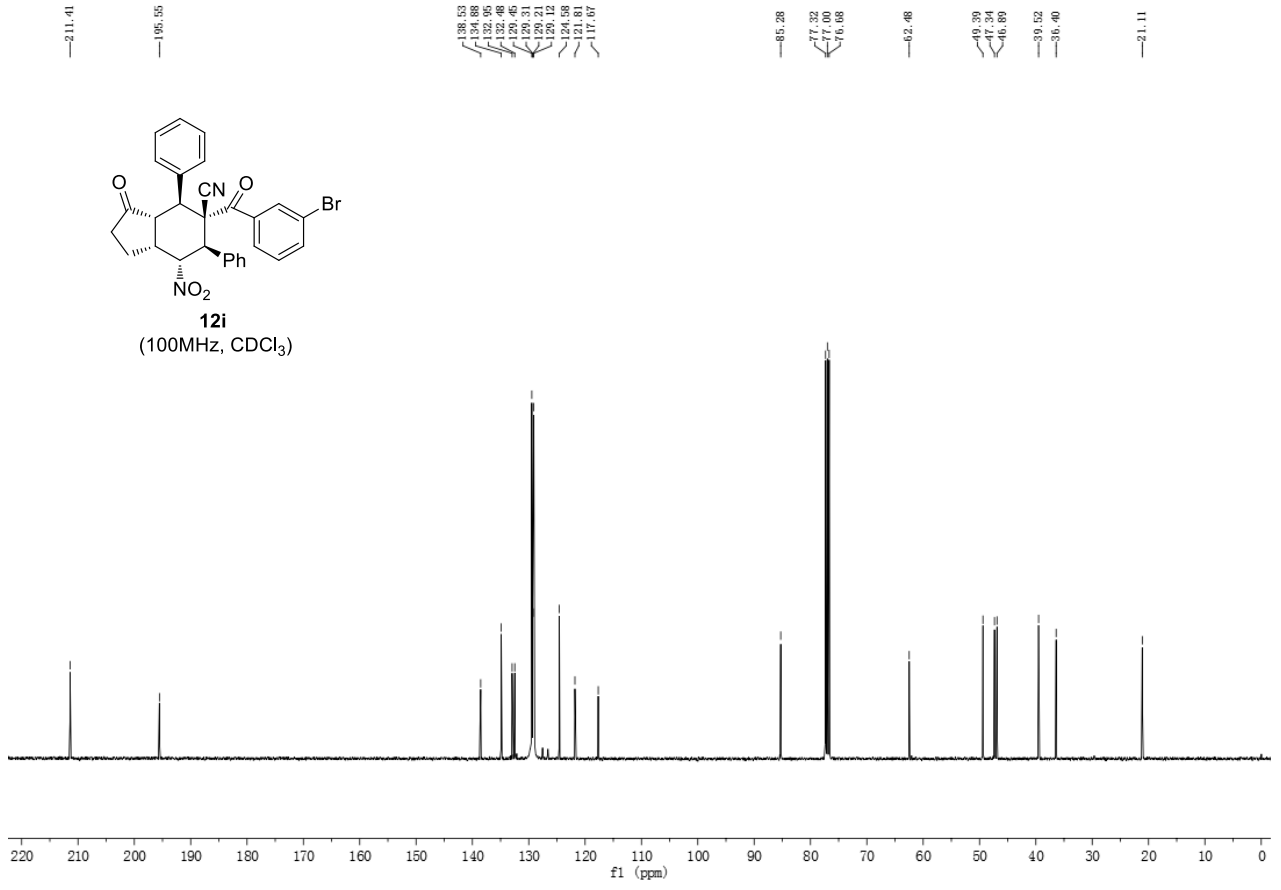
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.543	BB	0.53	69.7607	2395.4045	45.0591
46.911	BB	1.81	22.4417	2920.7400	54.9409
			Totals:	5316.1445	100.0000



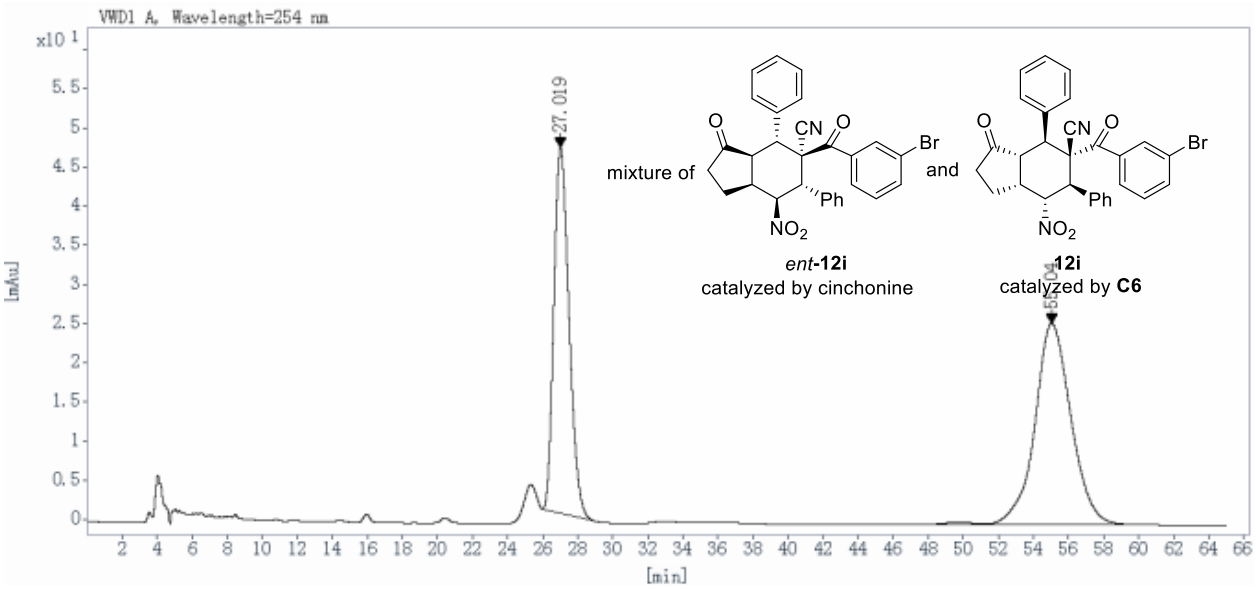
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.560	BB	0.54	7.6879	269.0080	8.9206
46.910	BB	1.79	21.1874	2746.5793	91.0794
			Totals:	3015.5874	100.0000



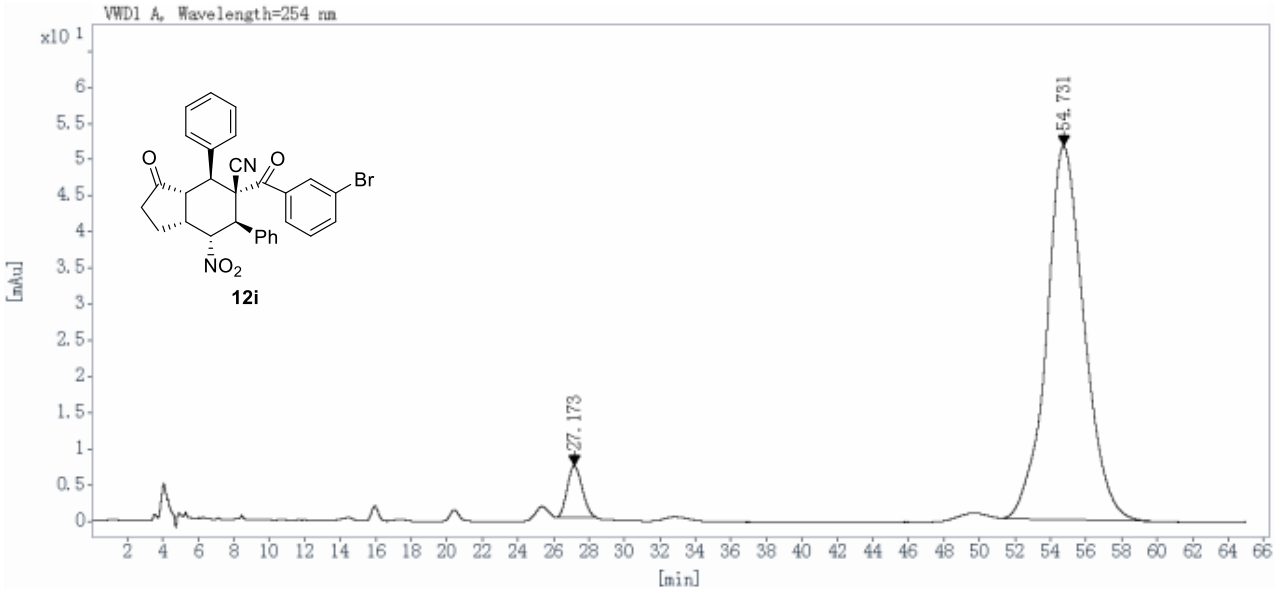
12i
(400MHz, $CDCl_3$)



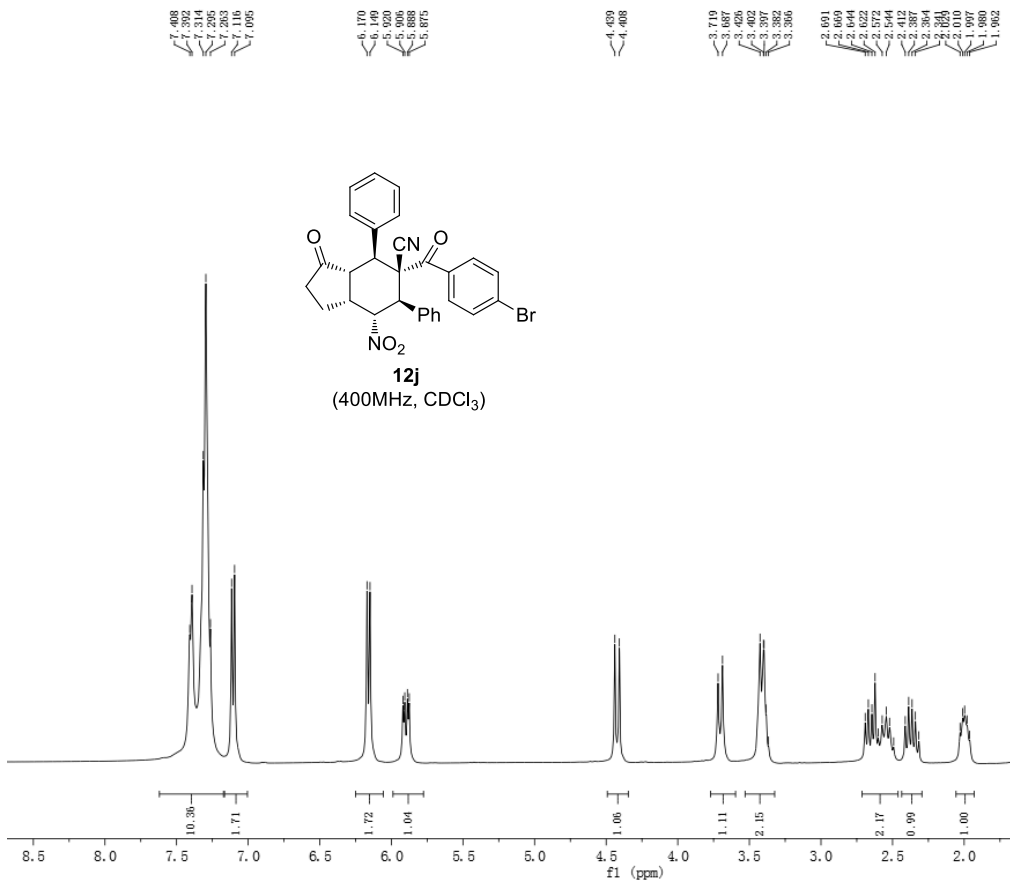
12i
(100MHz, $CDCl_3$)



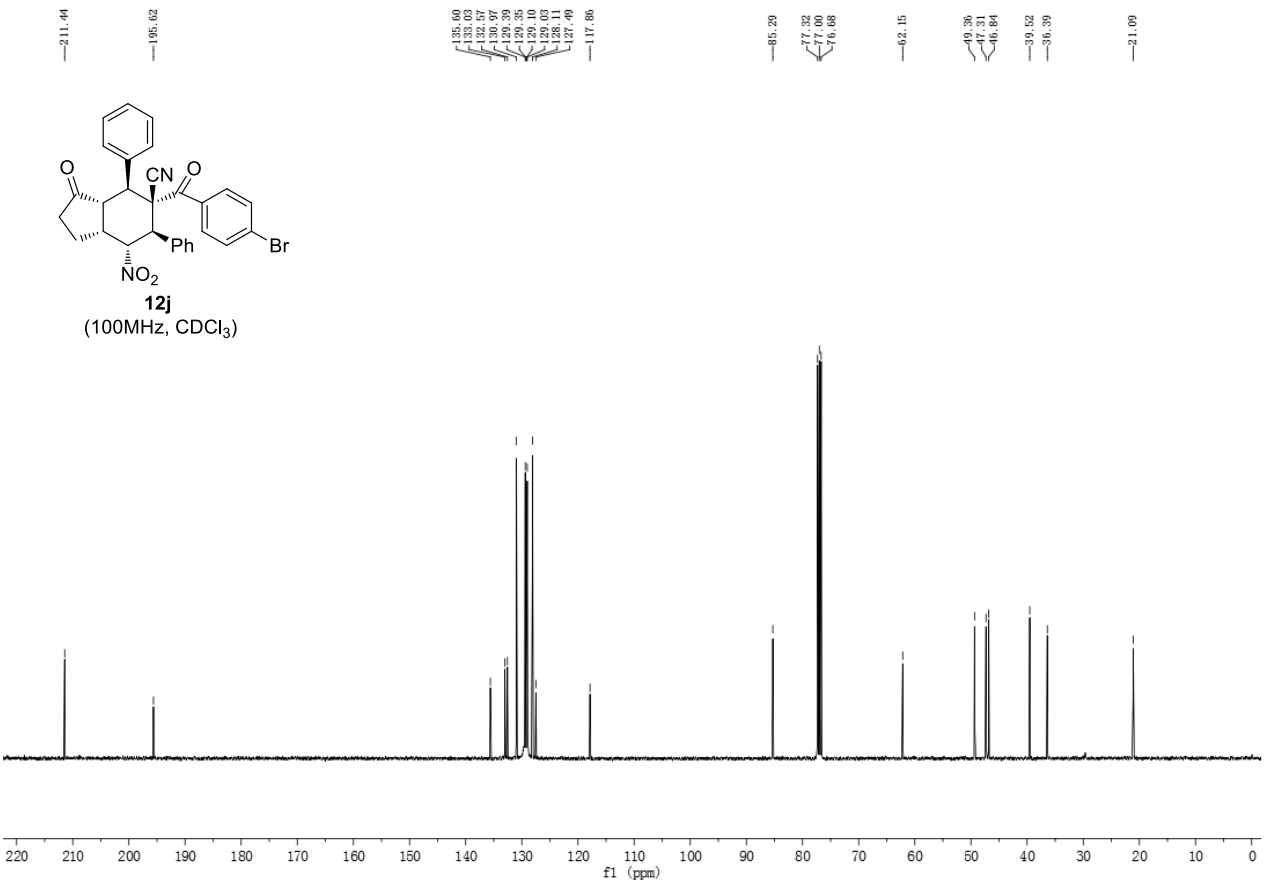
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
27.019	BB	0.93	46.6330	2809.3738	42.8499
55.040	VV R	2.14	25.7241	3746.9434	57.1501
			Totals:	6556.3171	100.0000



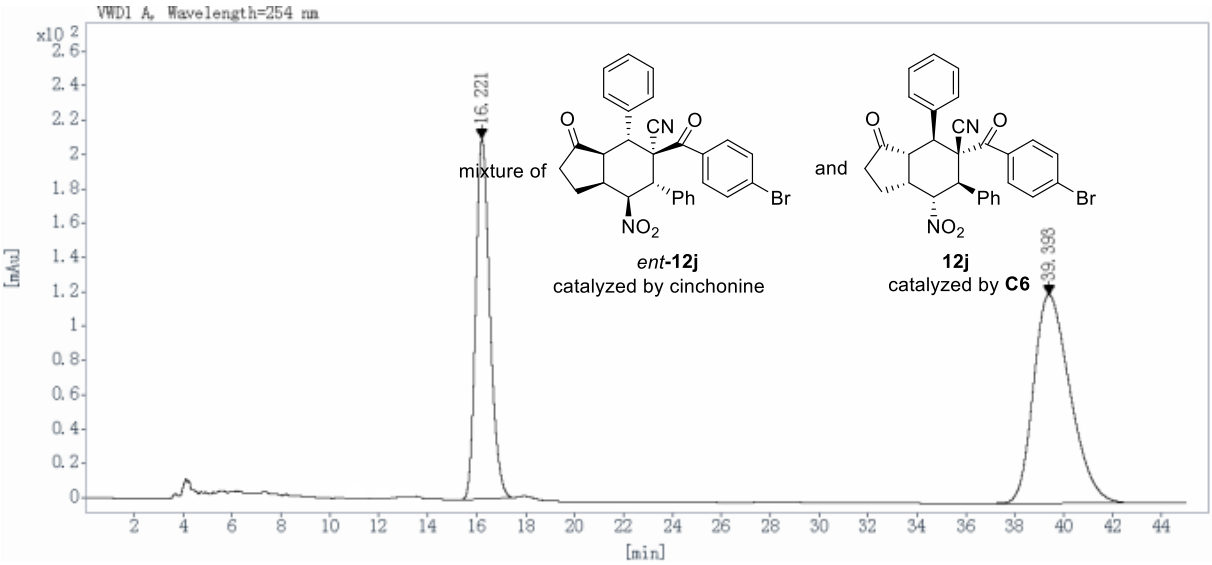
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
27.173	BBA	0.91	7.0865	413.7141	5.1486
54.731	BB	2.17	51.6717	7621.7832	94.8514
			Totals:	8035.4973	100.0000



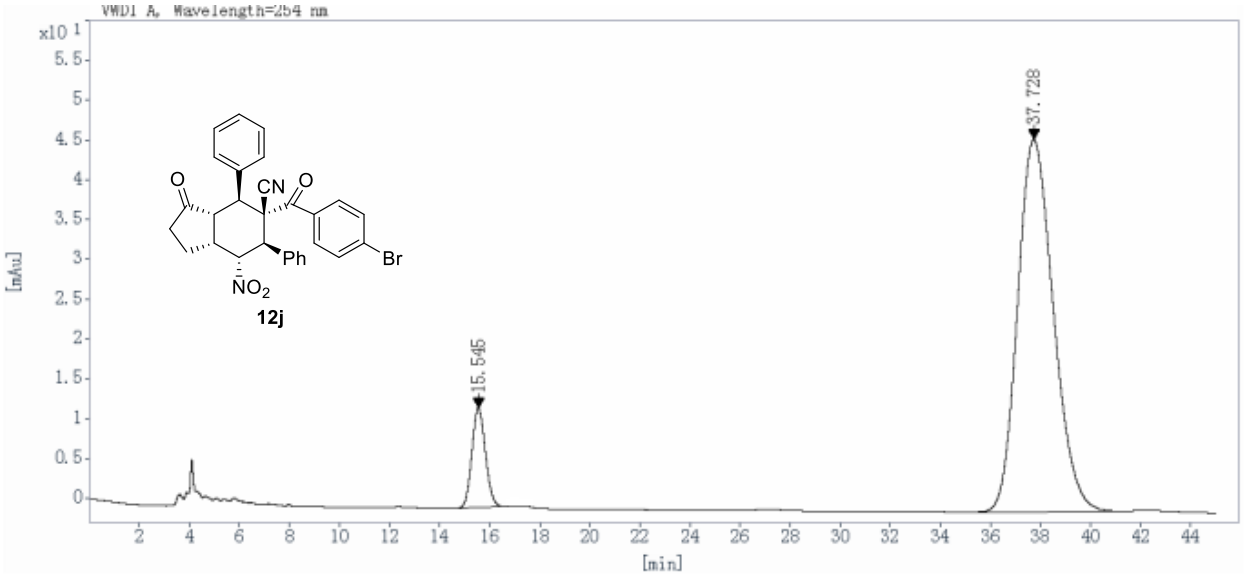
12j
(400MHz, $CDCl_3$)



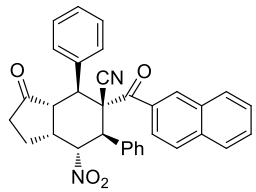
12j
(100MHz, $CDCl_3$)



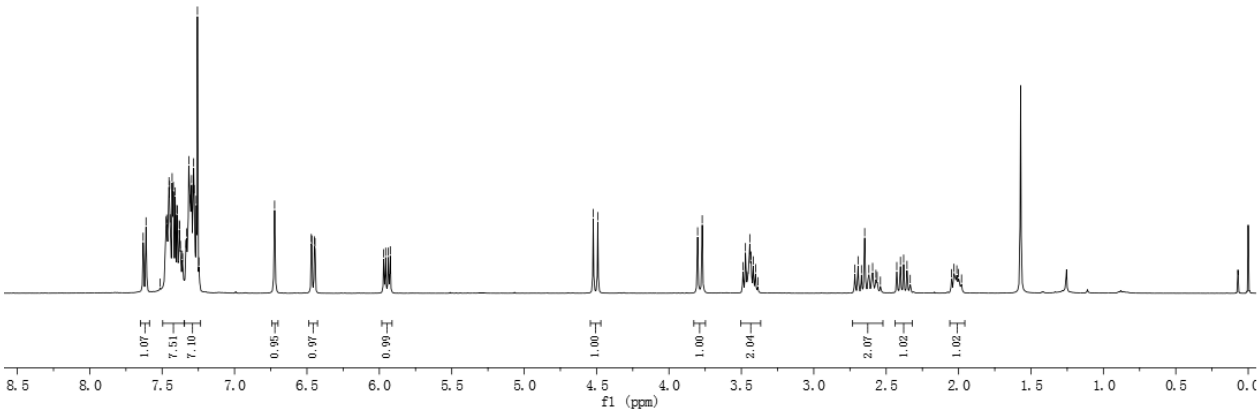
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
16.221	BB	0.62	209.6729	8408.2002	40.0232
39.393	BB	1.59	121.4745	12600.0928	59.9768
			Totals:	21008.2930	100.0000

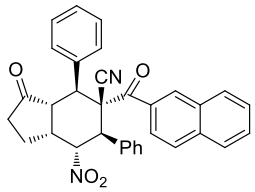


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
15.545	BB	0.58	12.5185	468.5338	9.1841
37.728	BB	1.53	46.6987	4633.0532	90.8159
			Totals:	5101.5871	100.0000

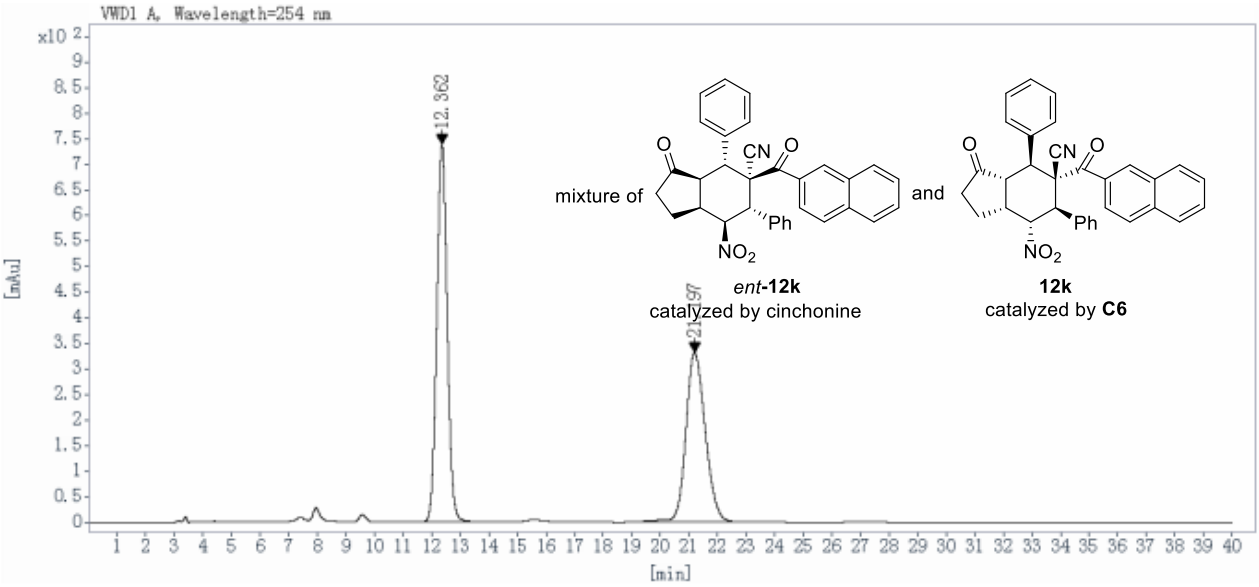


12k
(400MHz, $CDCl_3$)

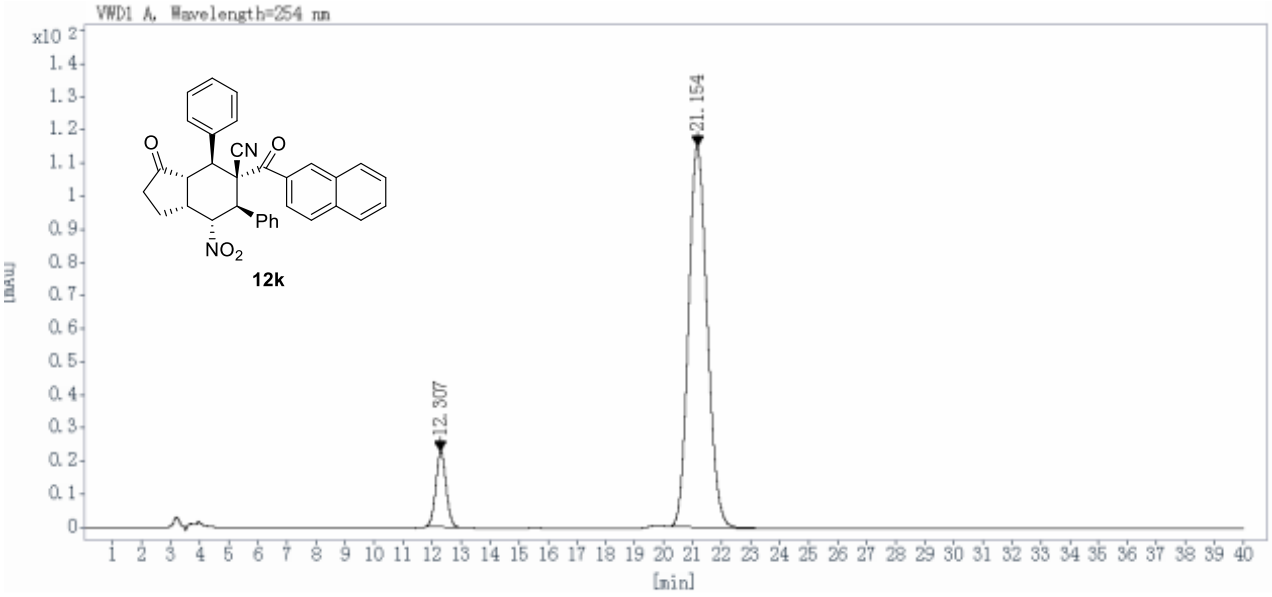




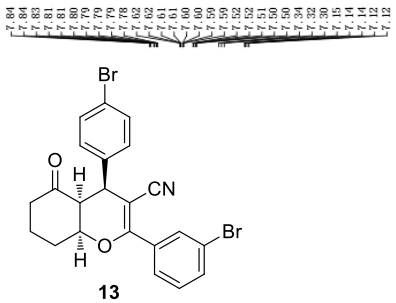
12k
(100MHz, $CDCl_3$)



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.362	BB	0.40	737.8484	18788.9141	54.6366
21.197	BB	0.73	330.5725	15599.9814	45.3634
			Totals:	34388.8955	100.0000

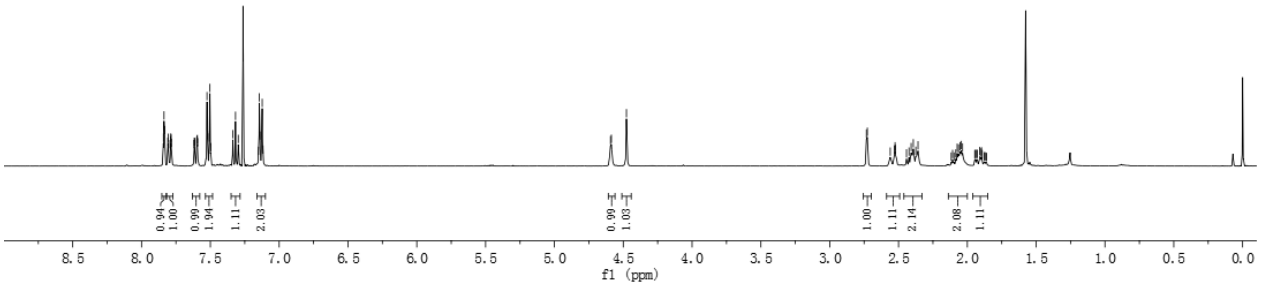


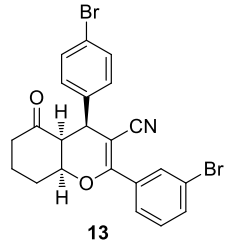
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.307	BBA	0.38	22.7717	565.5047	9.8843
21.154	BB	0.70	114.8843	5155.7139	90.1157
			Totals:	5721.2186	100.0000



13

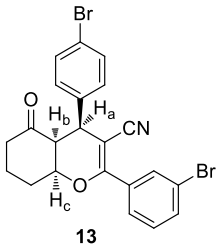
(400MHz, $CDCl_3$)





13

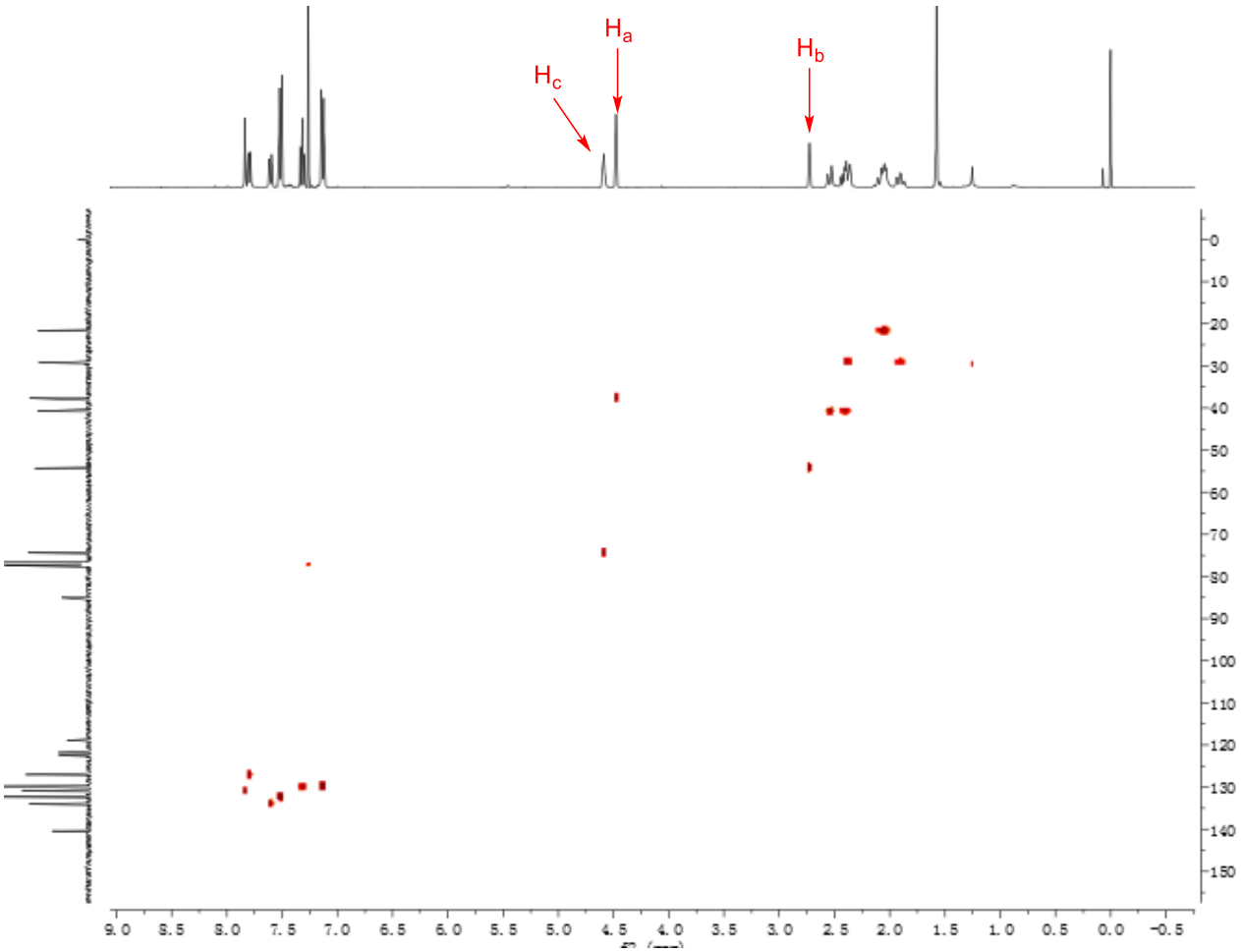
(100MHz, $CDCl_3$)

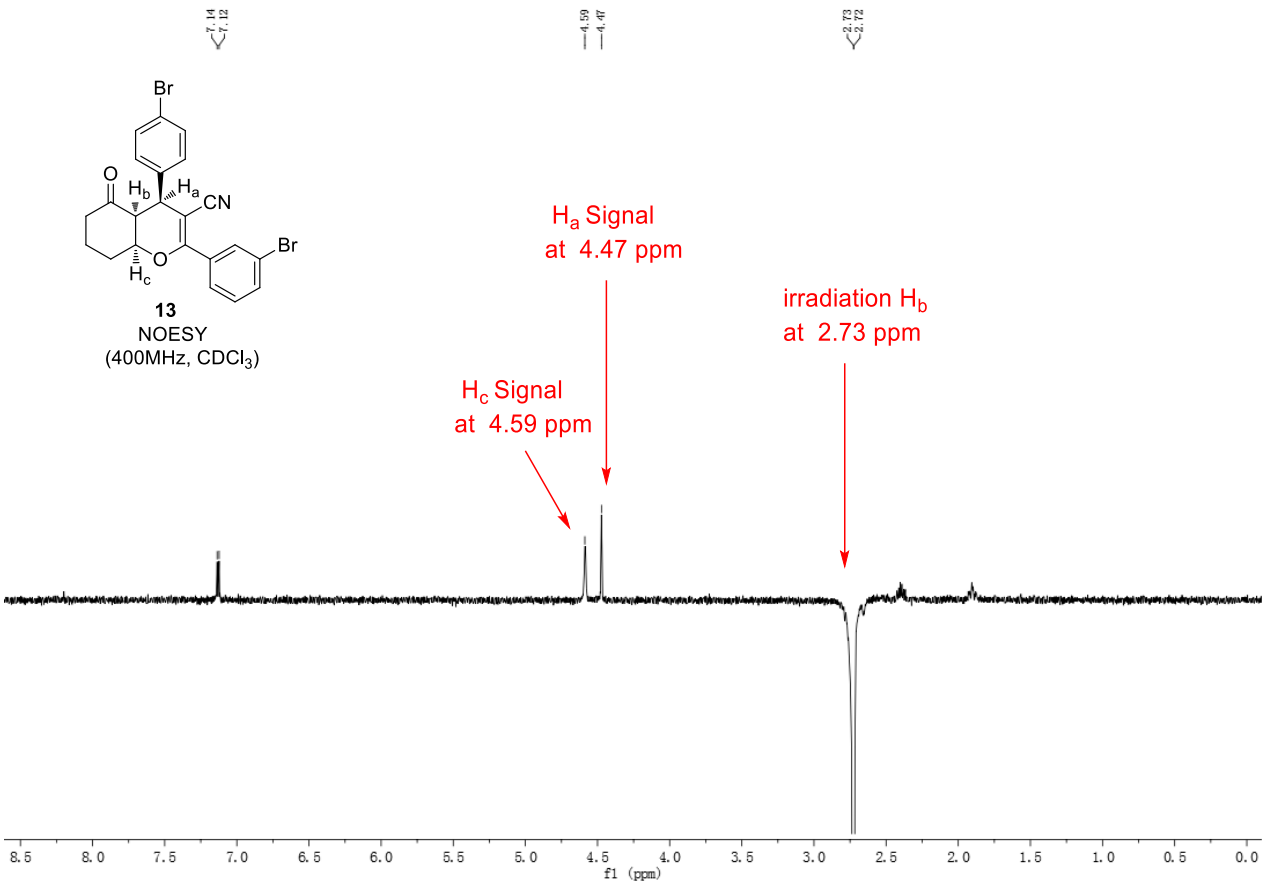


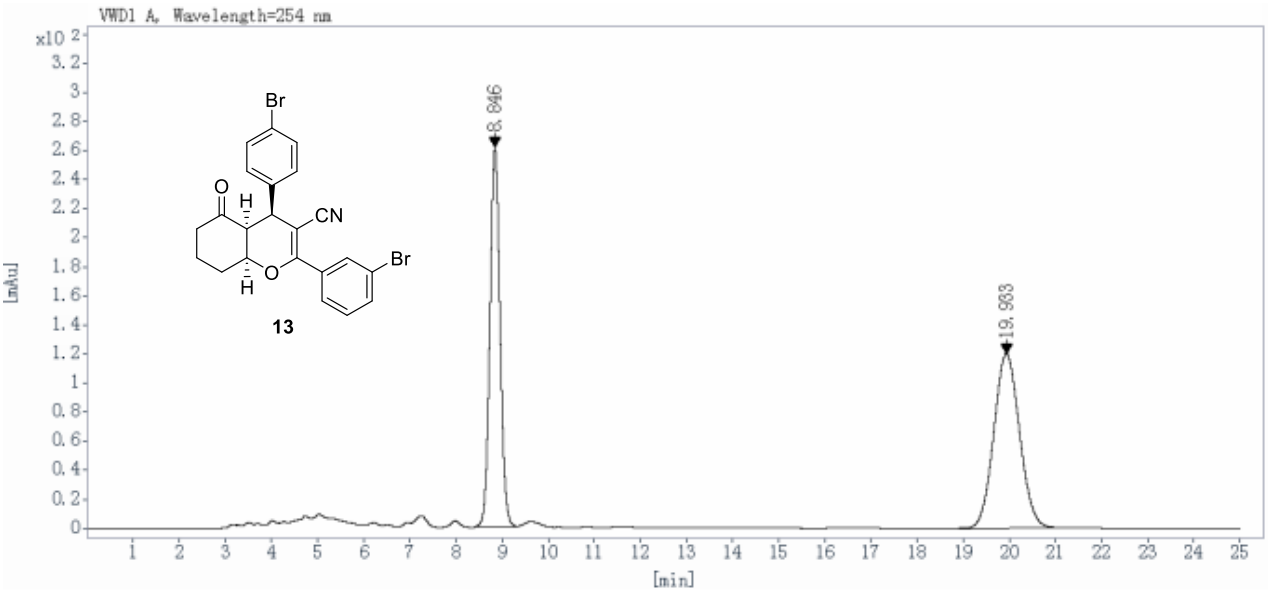
13

^{1}H NMR (400MHz, $CDCl_3$)

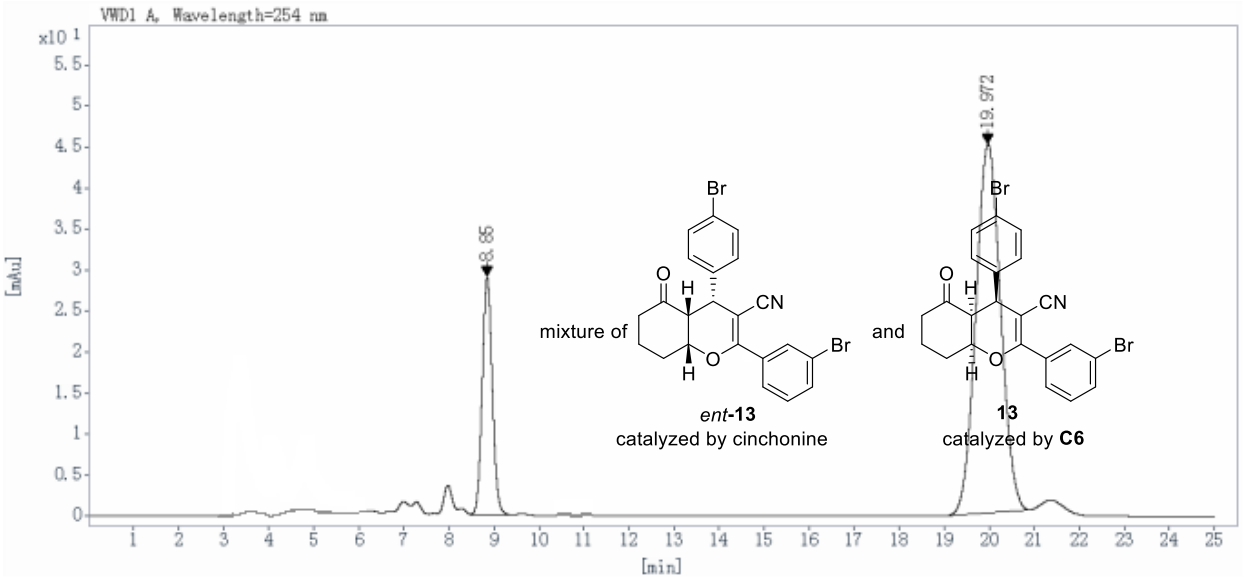
^{13}C NMR (100MHz, $CDCl_3$)



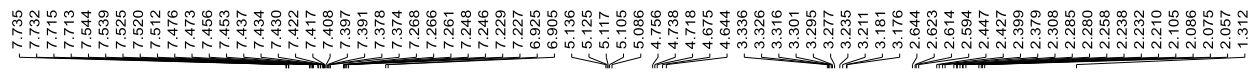

7.14
7.12
4.59
4.47
2.73
2.72
Br
O
H_b
H_a
CN
Br
O
H_c
13
NOESY
(400MHz, $CDCl_3$)
H_a Signal
at 4.47 ppm
irradiation H_b
at 2.73 ppm
H_c Signal
at 4.59 ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

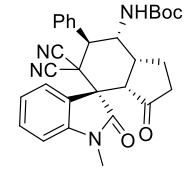


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.846	BB	0.24	260.5586	3960.1890	46.0579
19.933	BB	0.60	119.8027	4638.1021	53.9421
			Totals:	8598.2910	100.0000

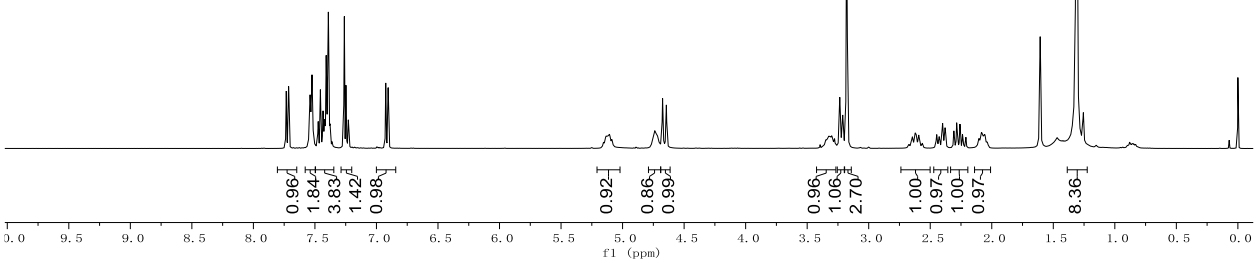


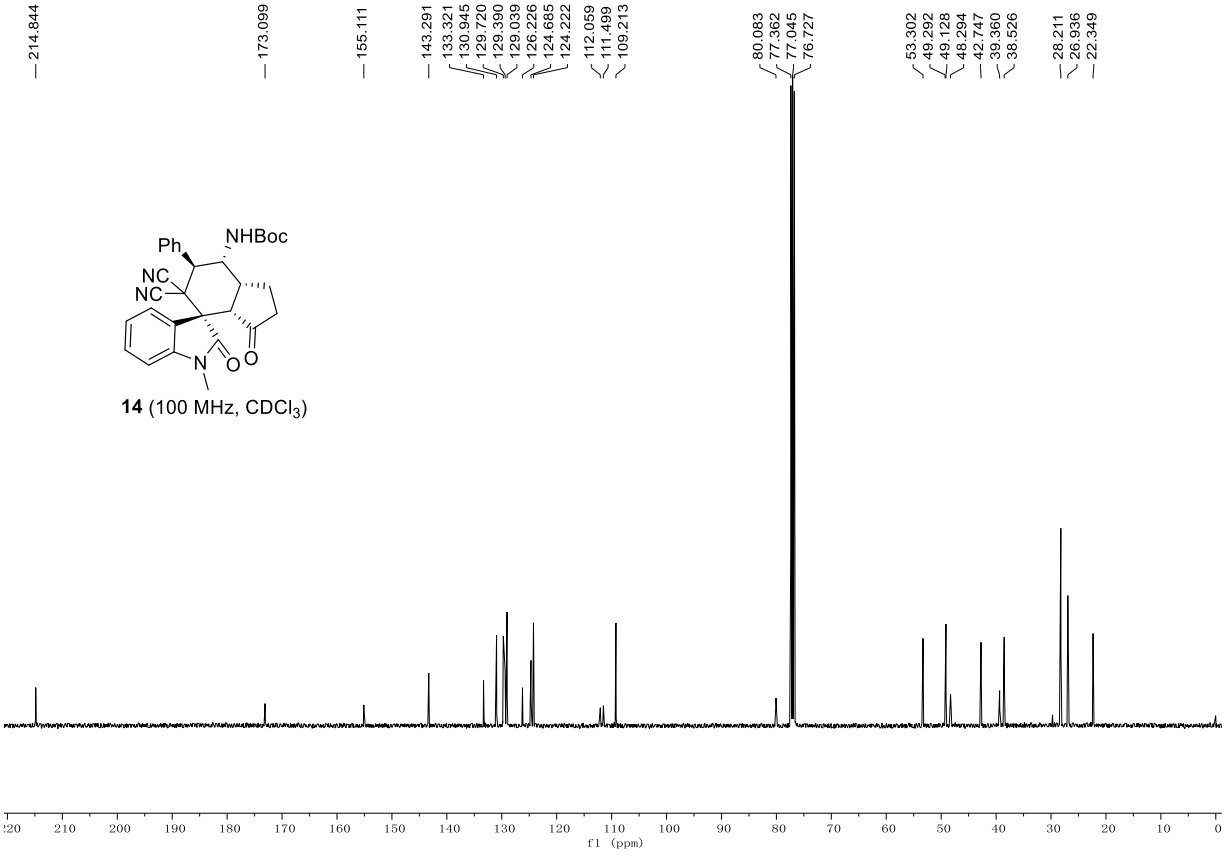
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.850	BB	0.24	28.9652	448.3345	20.6686
19.972	BB	0.60	44.9013	1720.8241	79.3314
			Totals:	2169.1586	100.0000



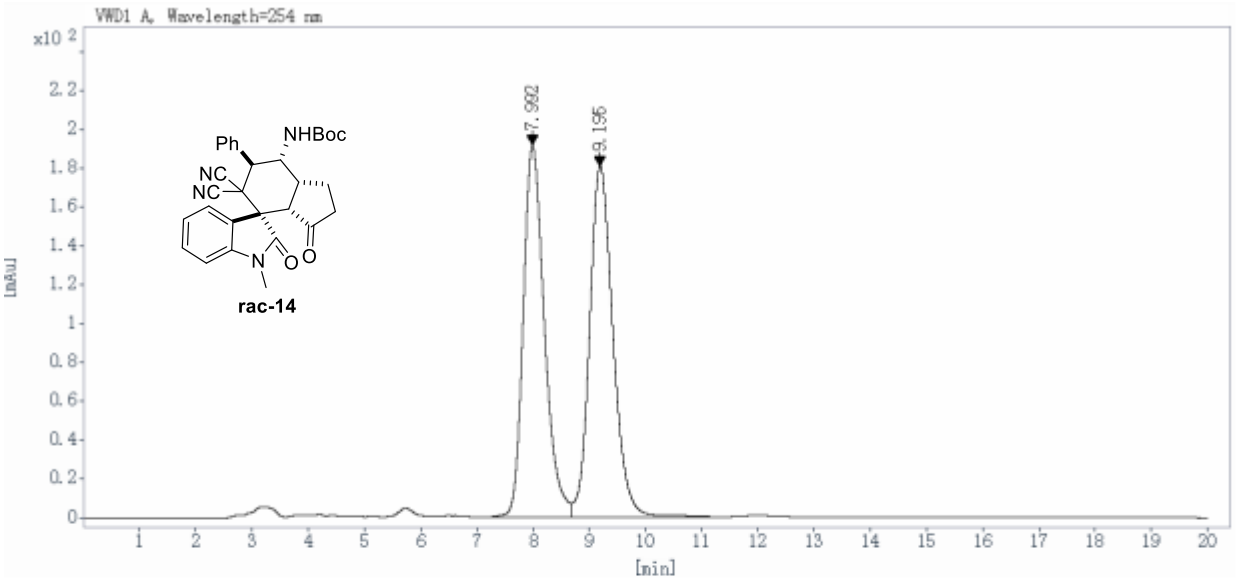


14 (400 MHz, $CDCl_3$)

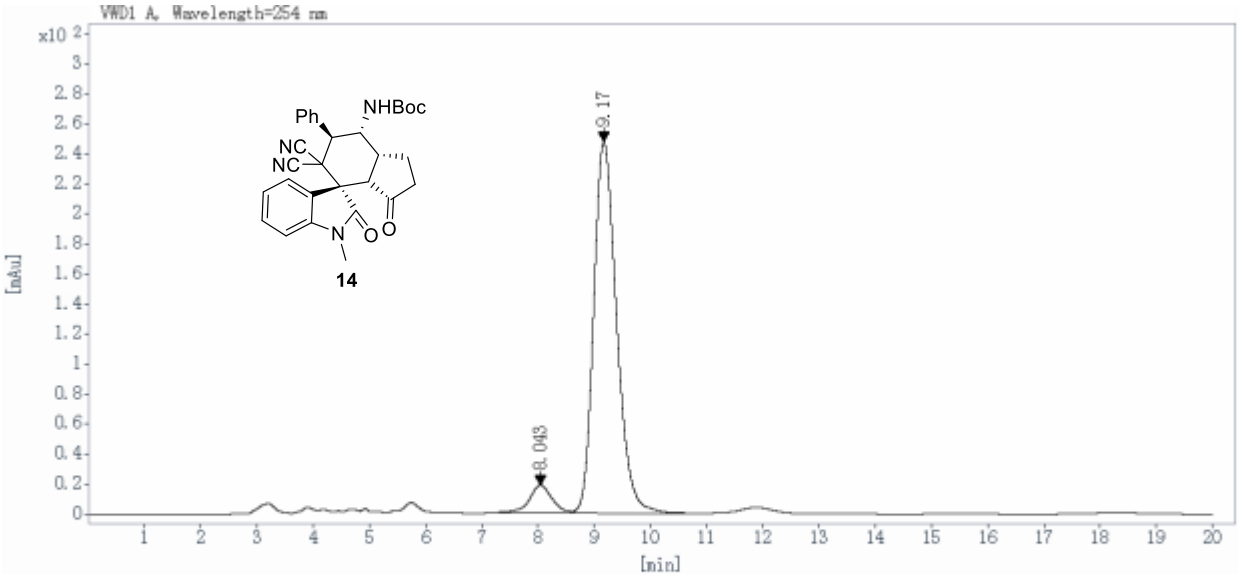




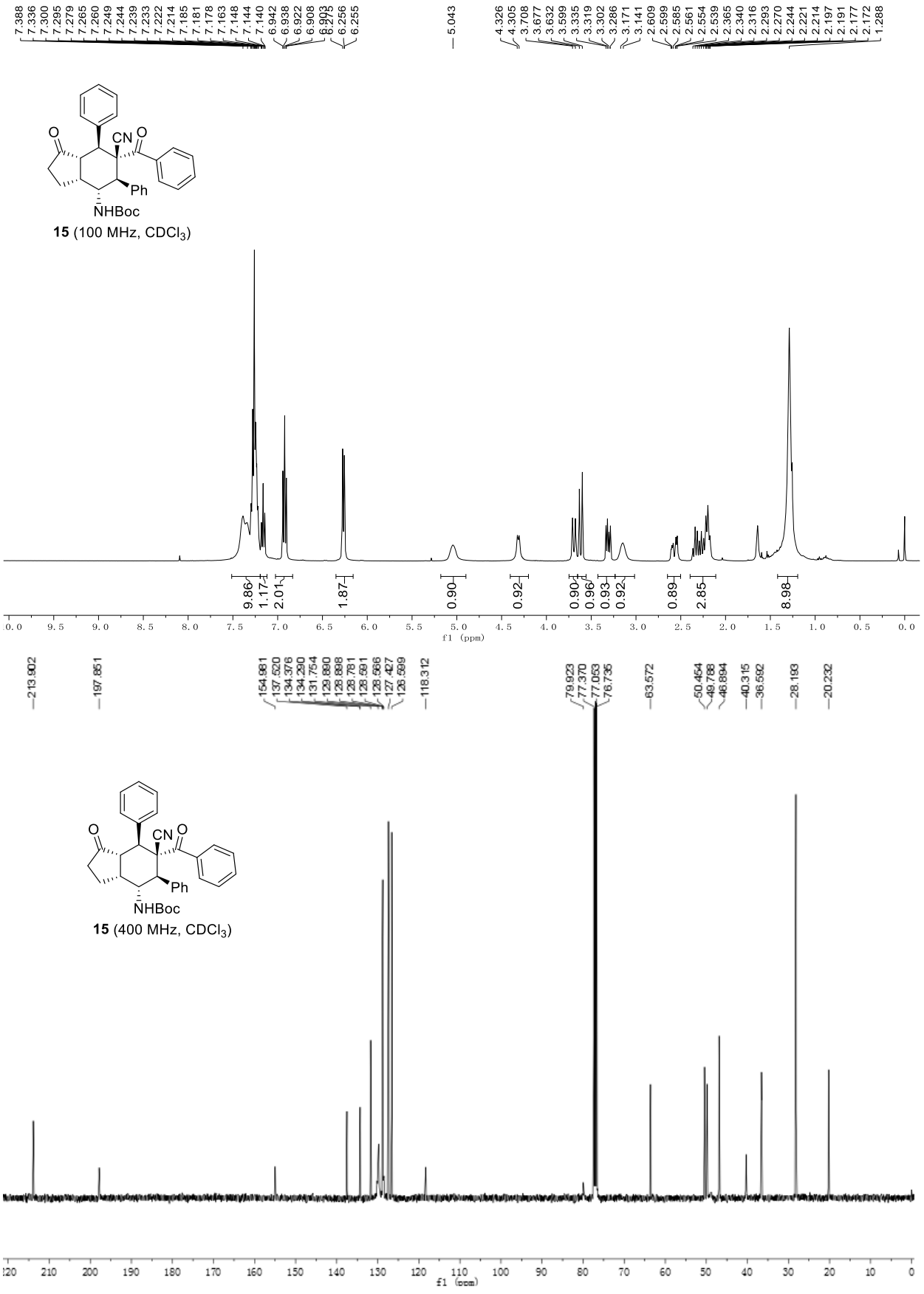
14 (100 MHz, $CDCl_3$)

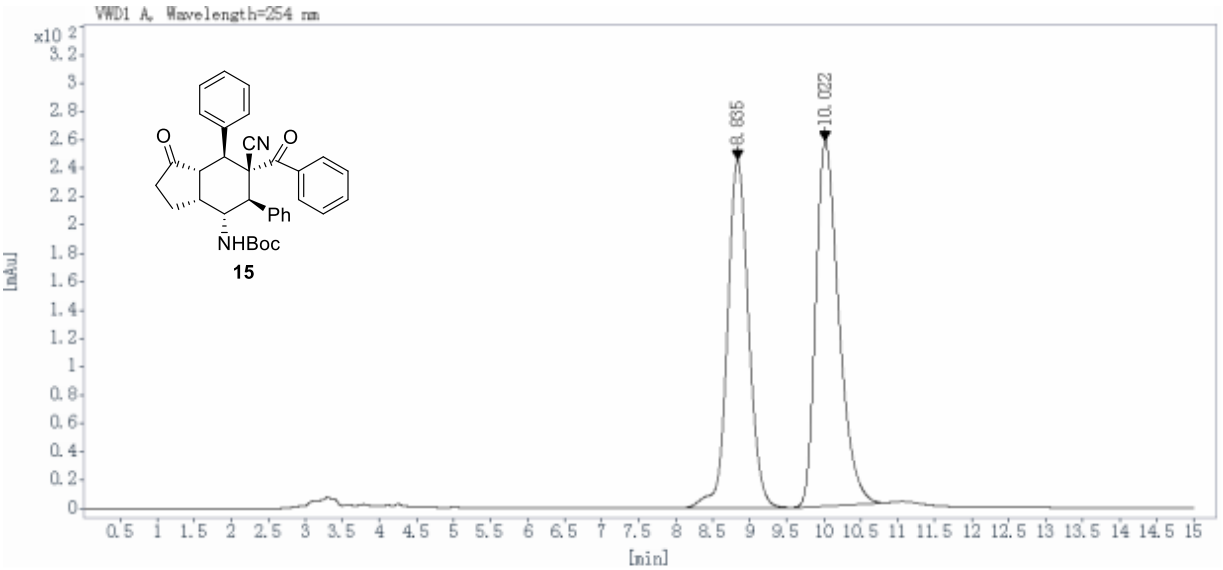


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
7.992	BV	0.40	191.4076	5003.5518	48.9300
9.195	VB	0.44	180.8650	5222.3867	51.0700
			Totals:	10225.9385	100.0000

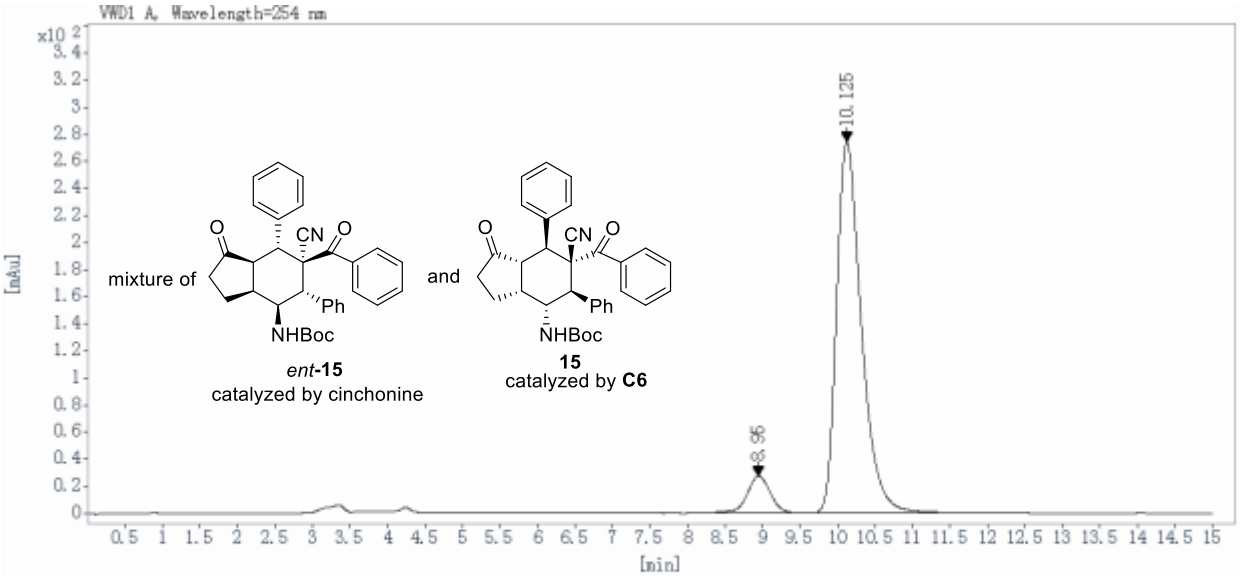


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.043	VV E	0.42	18.4417	518.0374	6.8868
9.170	VB R	0.44	247.1892	7004.0942	93.1132
			Totals:	7522.1316	100.0000

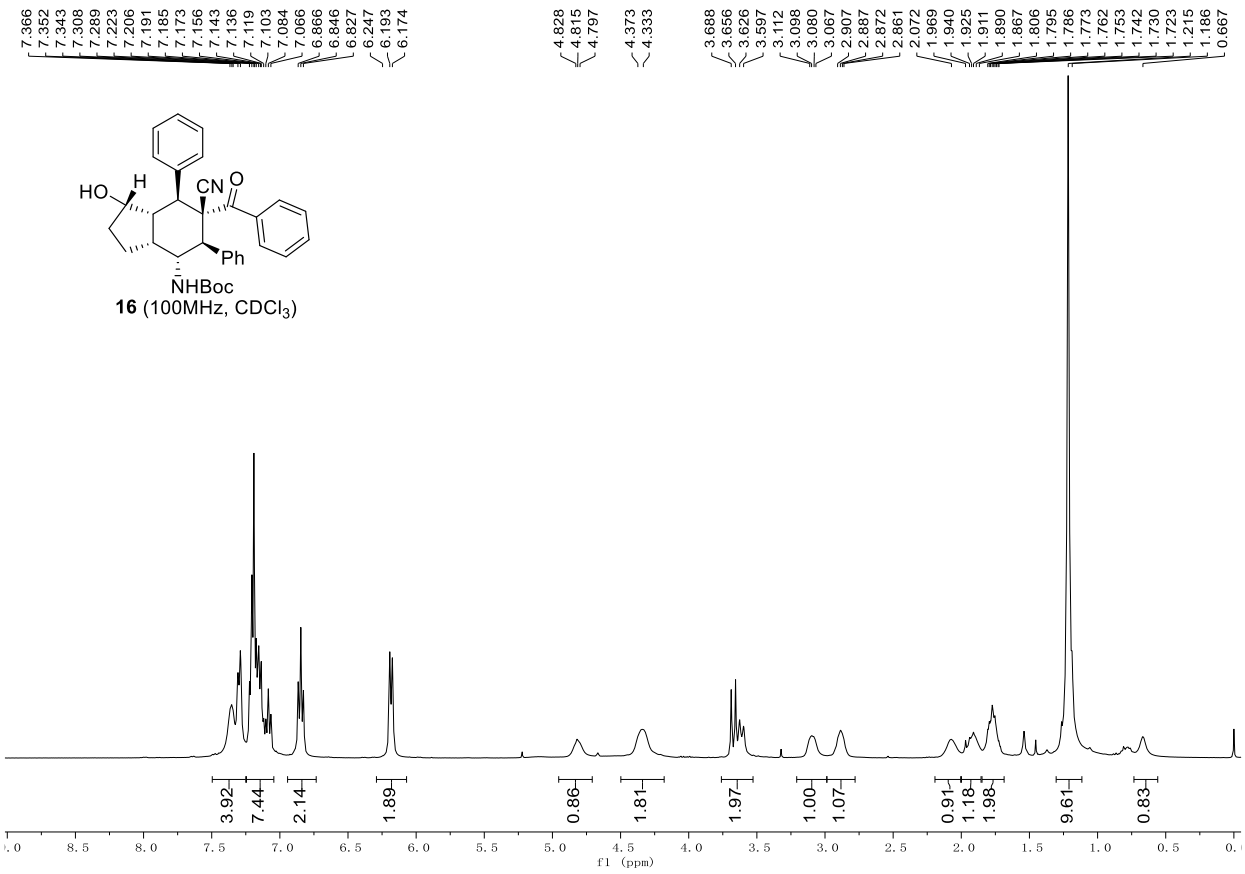

7.388
7.336
7.300
7.295
7.279
7.265
7.260
7.249
7.244
7.239
7.233
7.222
7.214
7.185
7.181
7.178
7.163
7.148
7.144
7.140
6.942
6.938
6.922
6.908
6.903
6.275
6.256
6.255
5.043
4.326
4.305
3.708
3.677
3.632
3.599
3.335
3.319
3.302
3.286
3.171
3.141
2.609
2.599
2.585
2.561
2.554
2.539
2.365
2.340
2.316
2.293
2.270
2.244
2.221
2.214
2.197
2.191
2.177
2.172
1.288
O
CN
O
Ph
NHBoc
15 (100 MHz, CDCl3)
9.86
1.17
2.01
1.87
0.90
0.92
0.90
0.96
0.93
0.92
0.89
2.85
8.98
f1 (ppm)
213.902
197.851
154.961
137.520
134.376
134.290
131.754
129.880
128.898
128.781
128.591
128.566
127.427
126.599
118.312
79.923
77.370
77.053
76.736
63.572
50.454
49.788
46.894
40.315
36.592
28.193
20.232
O
CN
O
Ph
NHBoc
15 (400 MHz, CDCl3)
f1 (ppm)



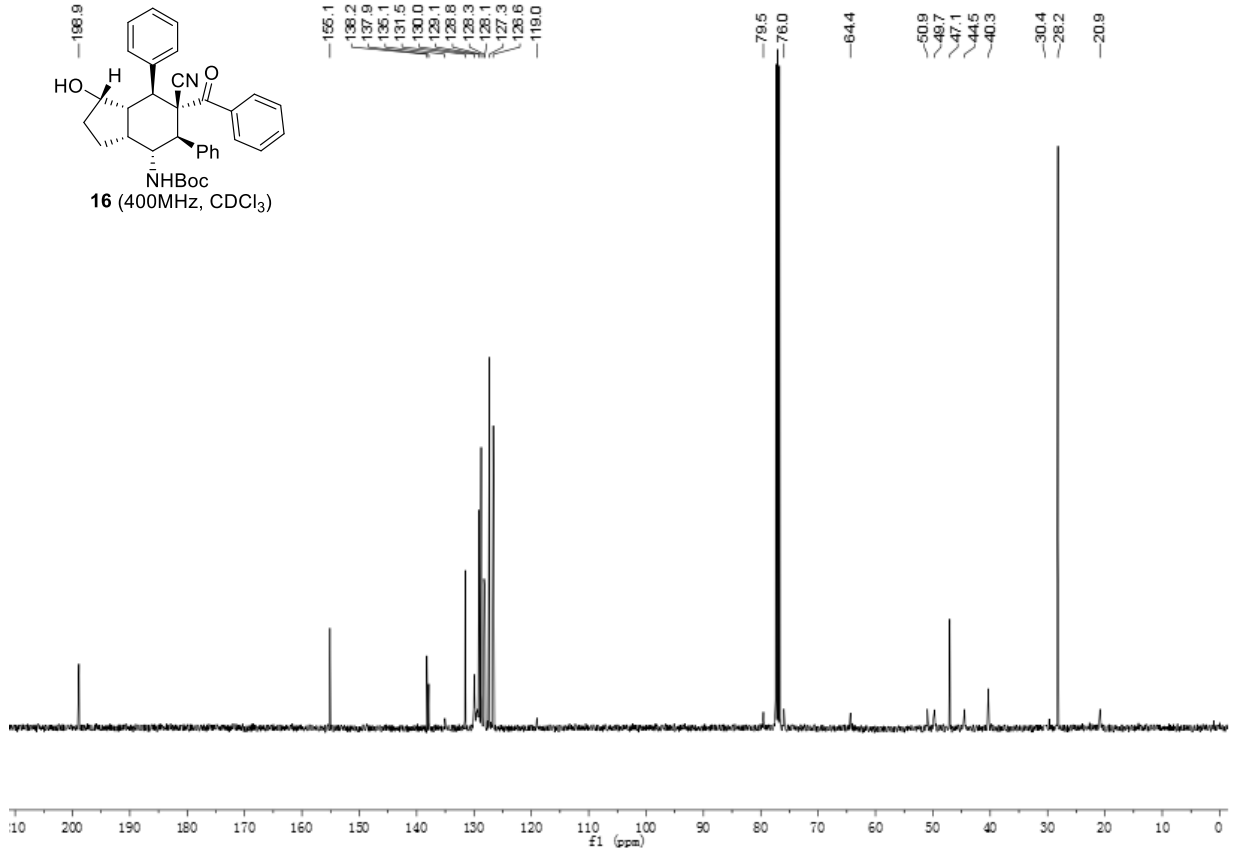
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.835	BB	0.31	244.9575	4879.1611	46.5816
10.022	BB	0.33	257.0048	5595.2871	53.4184
			Totals:	10474.4482	100.0000



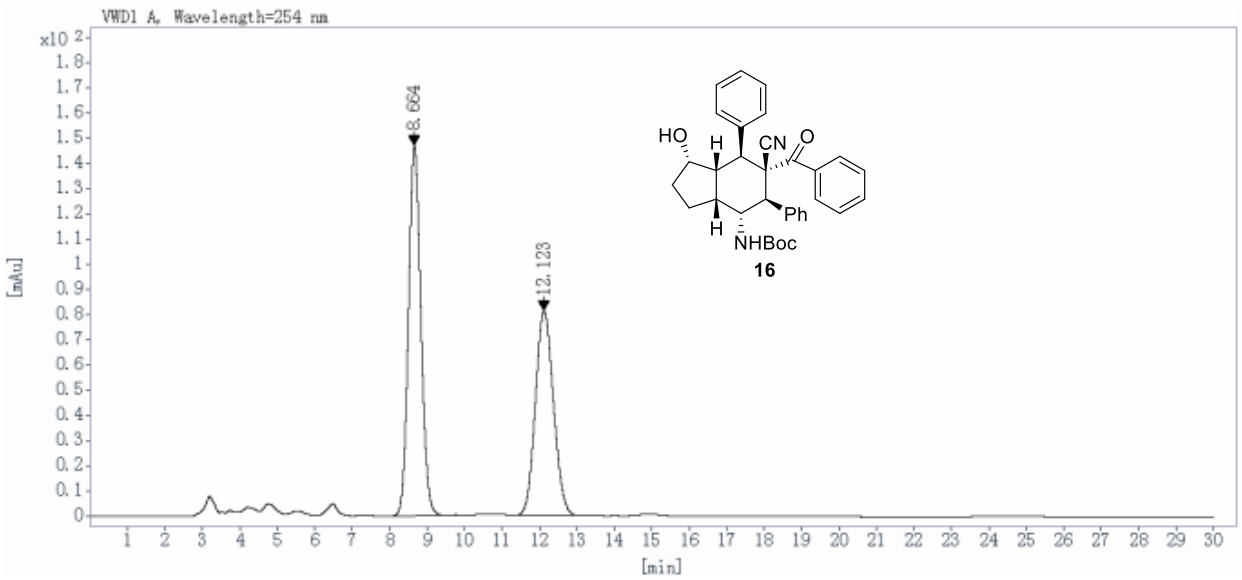
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.950	BB	0.33	27.2439	587.9487	8.5186
10.125	BB	0.35	273.8868	6313.9658	91.4814
			Totals:	6901.9145	100.0000



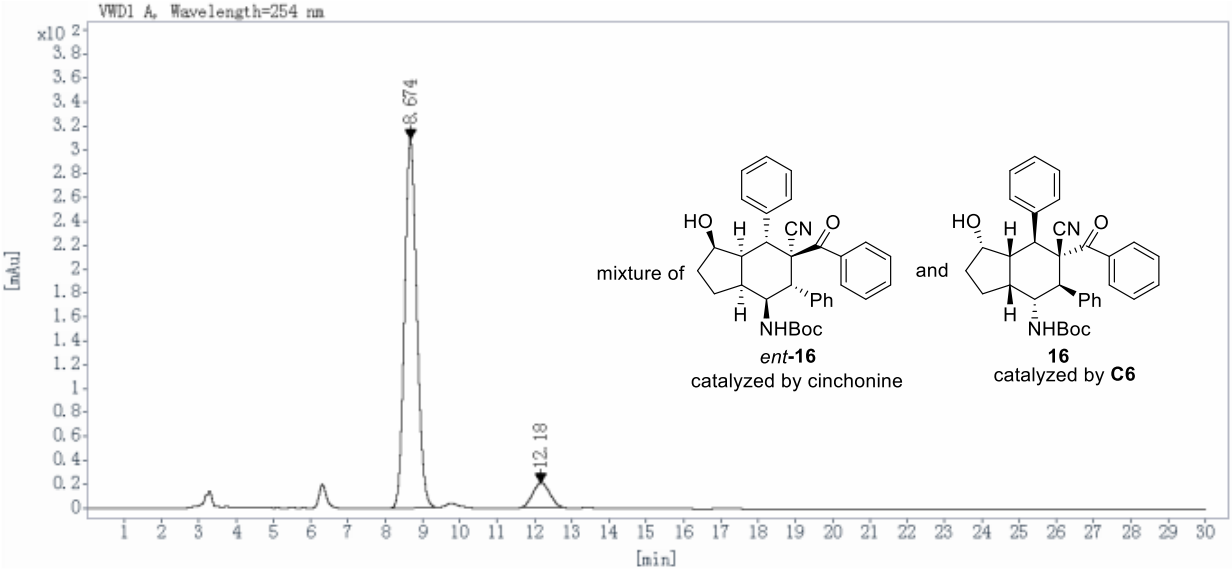
16 (100MHz, $CDCl_3$)



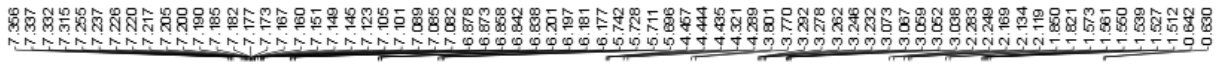
16 (400MHz, $CDCl_3$)

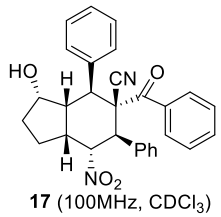


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.664	BB	0.36	146.8844	3369.2568	55.3245
12.123	BB	0.52	81.1911	2720.7334	44.6755
			Totals:	6089.9902	100.0000

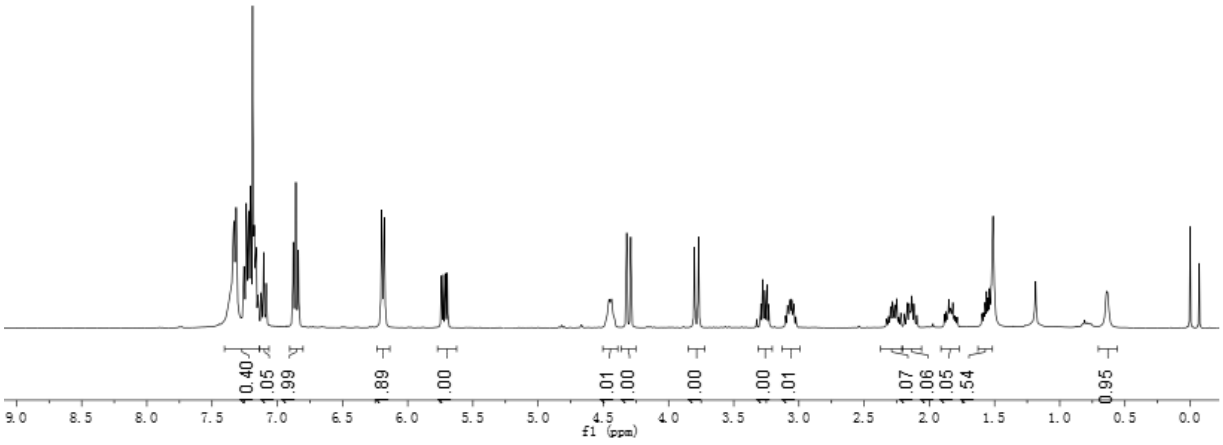


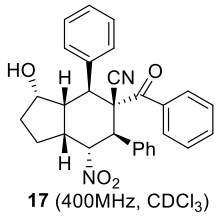
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.674	BB	0.35	308.3178	7006.1206	91.4741
12.180	BBA	0.50	20.6211	653.0064	8.5259
			Totals:	7659.1270	100.0000



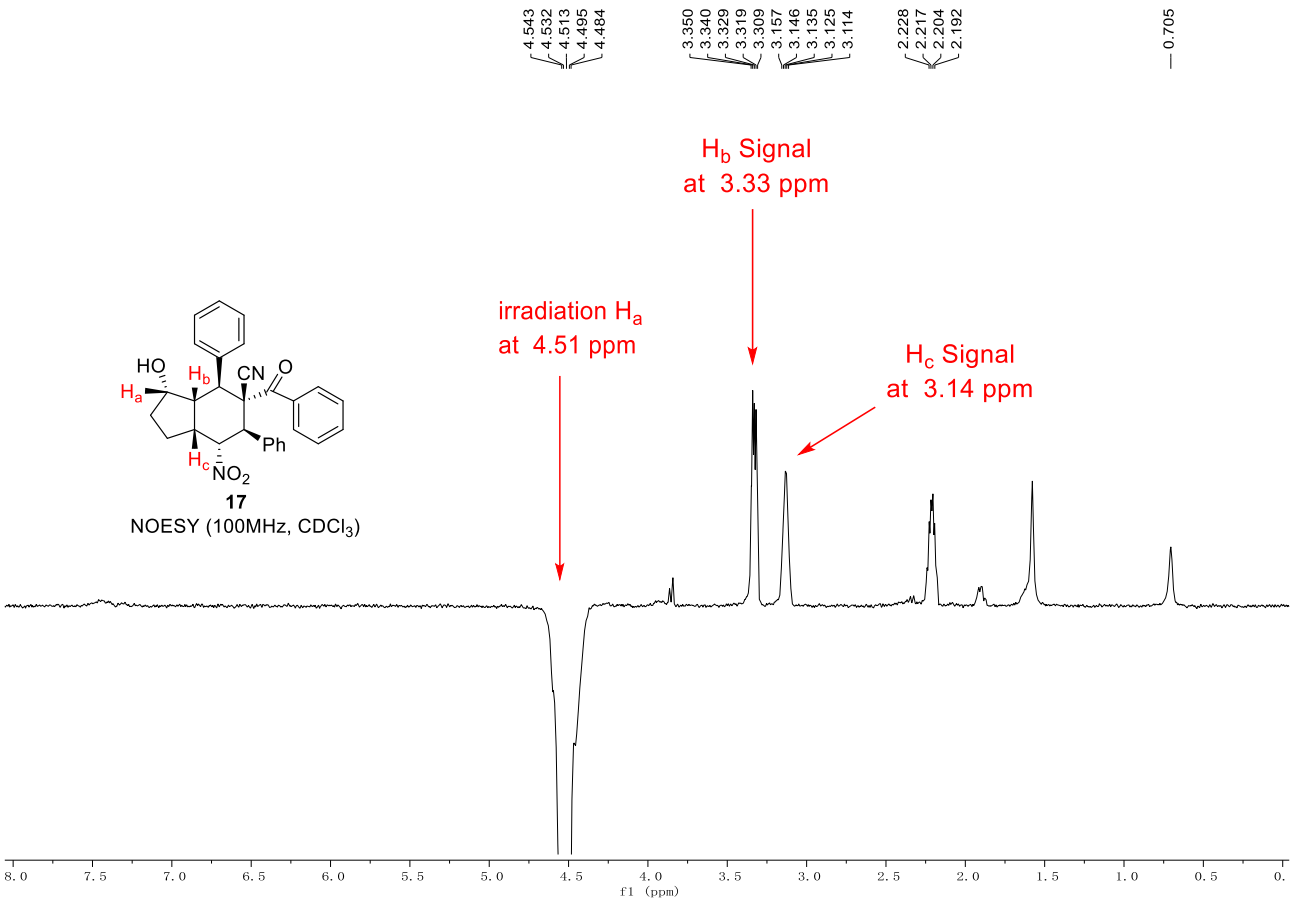


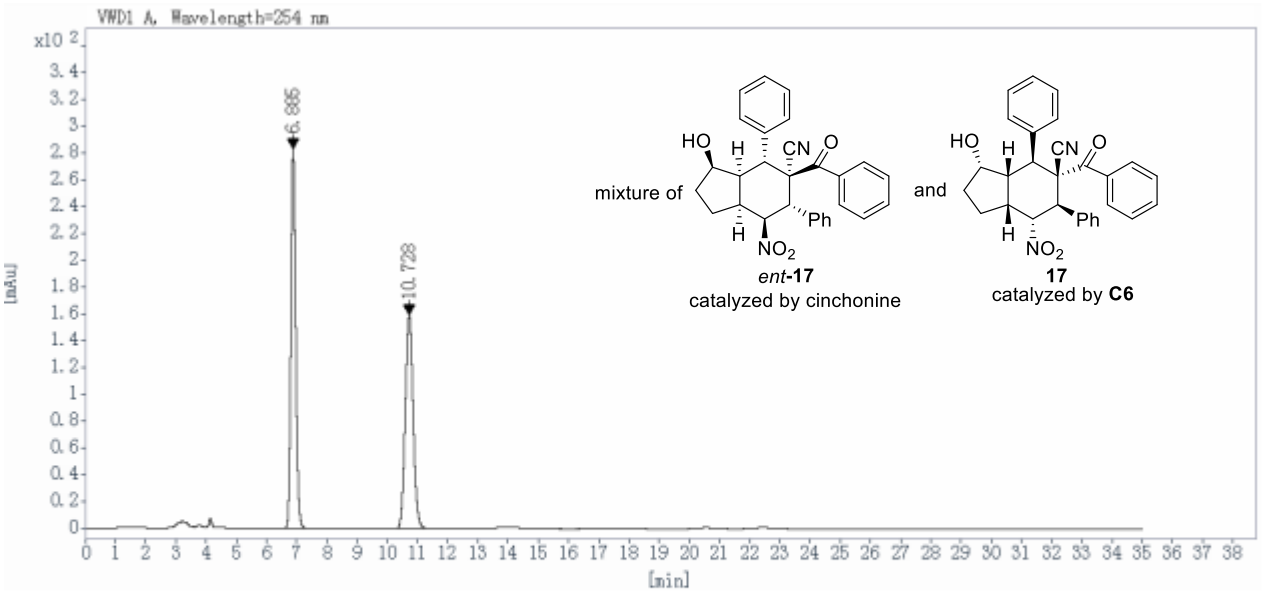
17 (100MHz, $CDCl_3$)



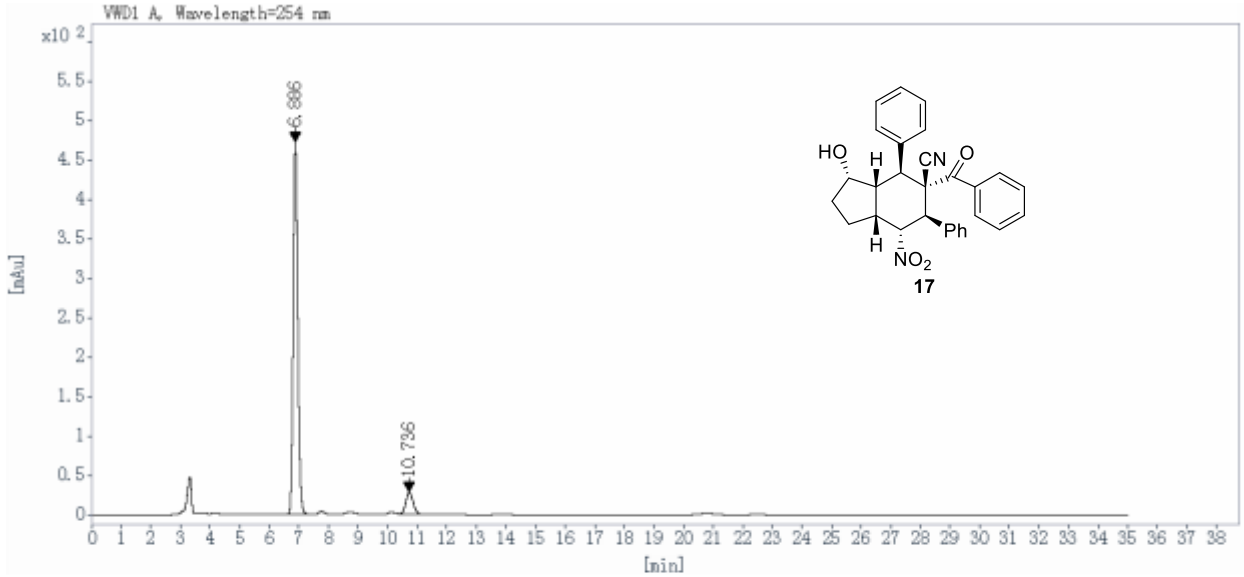


17 (400MHz, $CDCl_3$)

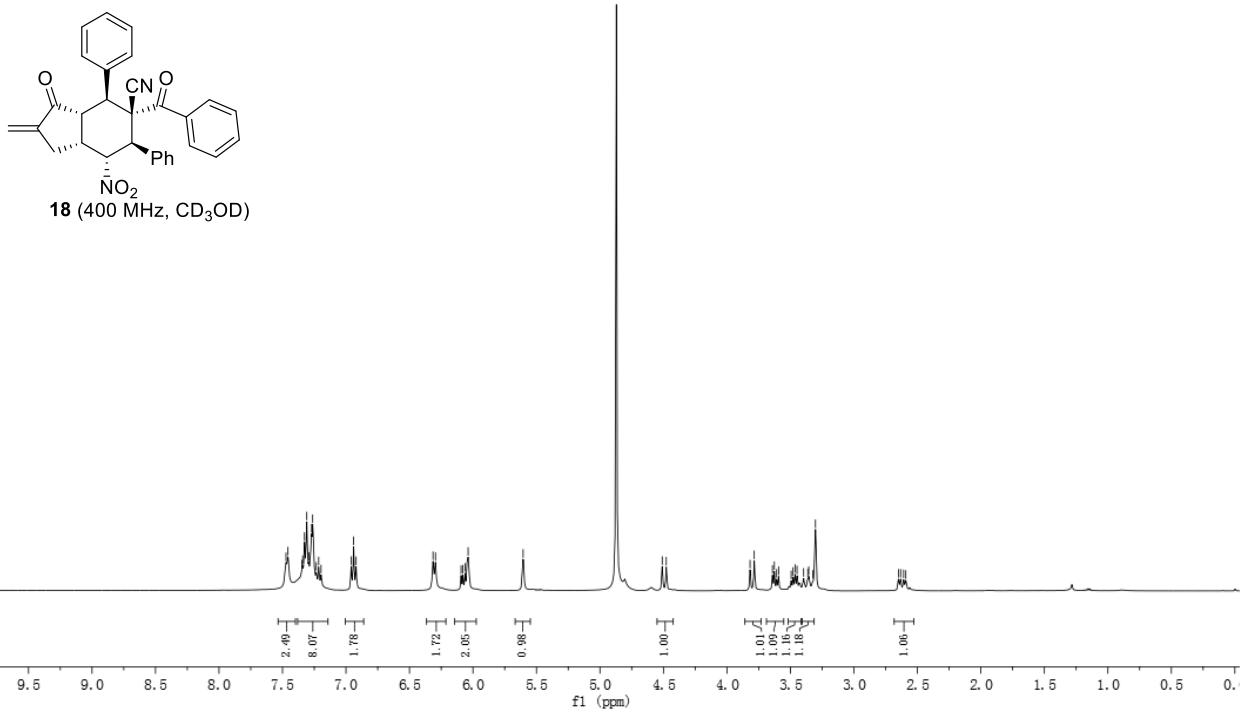

4.543
4.532
4.513
4.495
4.484
3.350
3.340
3.329
3.319
3.309
3.157
3.146
3.135
3.125
3.114
2.228
2.217
2.204
2.192
0.705
H$_b$ Signal
at 3.33 ppm
irradiation H$_a$
at 4.51 ppm
H$_c$ Signal
at 3.14 ppm
HO
H$_a$
H$_b$
CN
O
Ph
H$_c$
NO$_2$
17
NOESY (100MHz, CDCl$_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



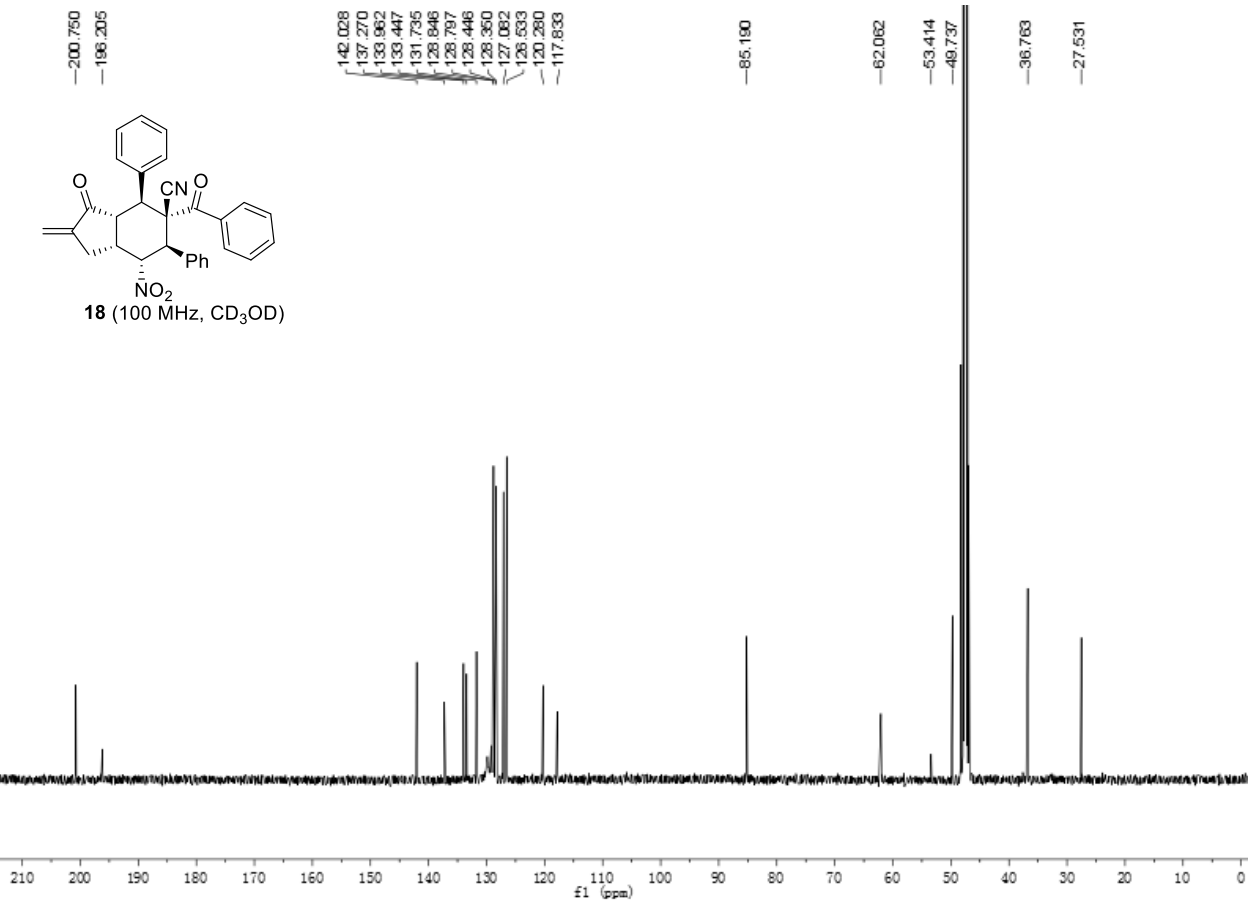
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.885	BB	0.17	282.8138	3109.9202	51.8464
10.728	VB R	0.28	159.7134	2888.4150	48.1536
			Totals:	5998.3352	100.0000



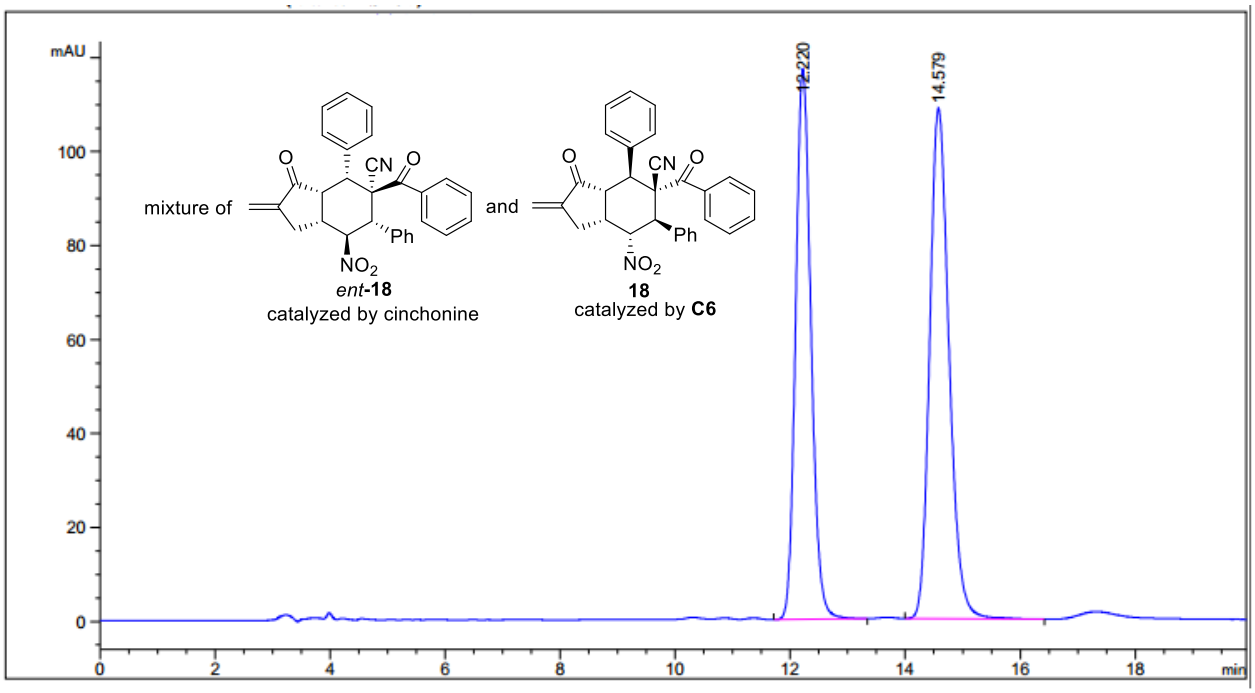
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.886	VB R	0.17	471.7472	5078.5771	91.3756
10.736	BB	0.27	27.4894	479.3391	8.6244
			Totals:	5557.9163	100.0000



18 (400 MHz, CD_3OD)

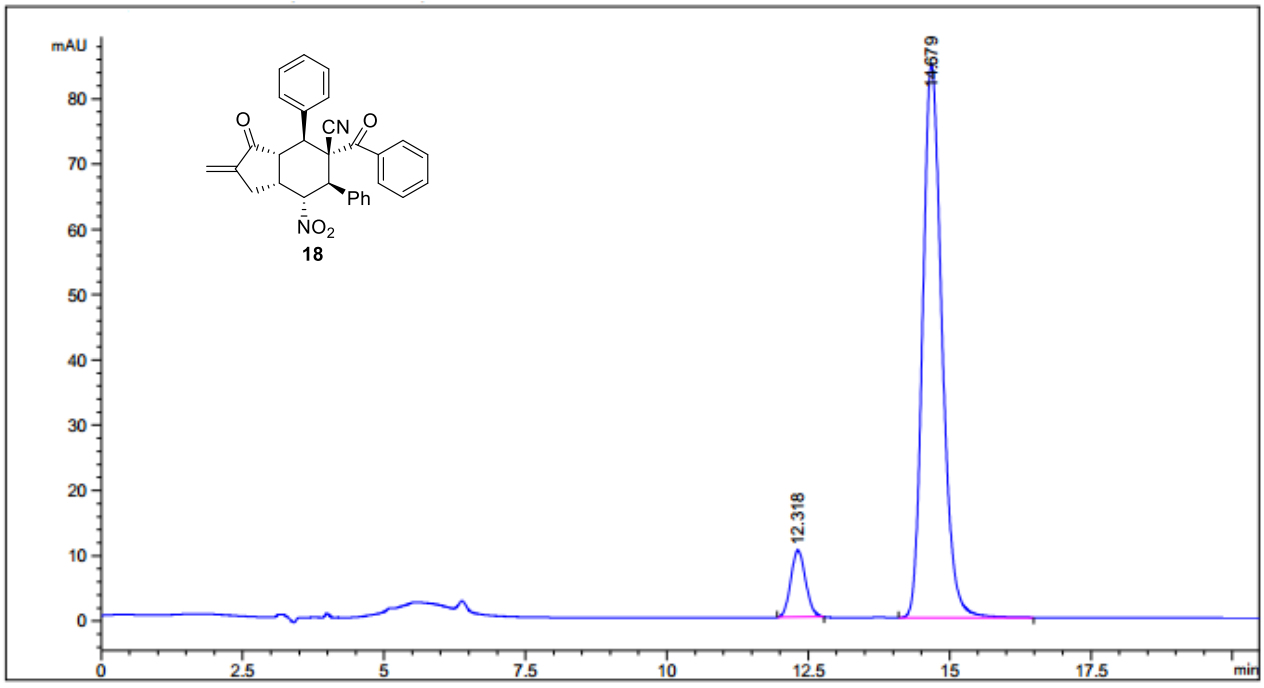


18 (100 MHz, CD_3OD)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.220	BB	0.2875	2170.83350	117.15895	46.0619
2	14.579	BB	0.3617	2542.03101	108.69978	53.9381



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.318	BBA	0.2843	187.05031	10.24533	8.5558
2	14.679	BB	0.3625	1999.19824	84.77782	91.4442