Substrate-Controlled Switchable Asymmetric Annulations to Access Polyheterocyclic Skeletons

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Supplementary Information

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1. General methods

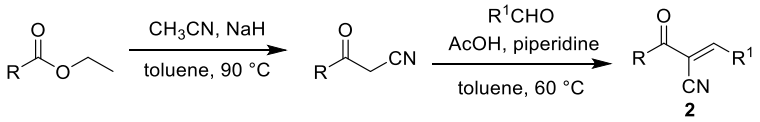
NMR data were obtained for ^{1}H at 400 MHz MHz or 600 MHz, and for ^{13}C at 100 MHz or 150 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. In each case, enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak OD-H Column (250 × 4.6 mm), Chiralpak IA Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm) or Chiralpak IC Column (250 × 4.6 mm). UV detection was monitored at 220 nm or 254 nm. Optical rotation was measured in $CHCl_3$ solution at 20 ℃. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate were distilled. THF was freshly distilled from sodium/benzophenone. Unless otherwise noted, 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. Morita-Baylis-Hillman carbonates were prepared according to the literature procedures.[1] Cinchona-derived catalysts β-isocupreidine **C1** (β-ICD), α-isocupreine **C2** (α-IC), **C3** and **C4** were prepared according to the literature procedures.[2]

(1) (*a*) Y. M. Chung, Y. J. Im and J. N. Kim, *Bull. Korean Chem. Soc.*, 2002, **23**, 1651; (*b*) K. Selvakumar, K. A. P. Lingam and R. V. L. Varma, *RSC Adv.*, 2014, **4**, 36538.

(2) (*a*) Y. Iwabuchi, M. Nakatani, N. Yokoyama and S. Hatakeyama, *J. Am. Chem. Soc.*, 1999, **121**, 10219; (*b*) H. Waldmann, V. Khedkar, H. Dückert, M. Schürmann, I. M. Oppel and K. Kumar, *Angew. Chem., Int. Ed.*, 2008, **47**, 6869; (*c*) Y. Nakamoto, F. Urabe, K. Takahashi, J. Ishihara and S. Hatakeyama, *Chem. Eur. J.*, 2013, **19**, 12653.

2. Preparation of α-cyano-α,β-unsaturated ketones

α-Cyano-α,β-unsaturated ketones were prepared according to the literature procedures.[3]



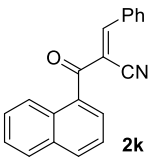
A dry and nitrogen-flushed 150 mL three-neck flask equipped with a magnetic stirring bar was charged with a solution of sodium hydride (60%) (1.5 equiv) and ester (64 mmol) in dry toluene (100 mL). The reaction mixture was stirred at 90 ℃, and acetonitrile (8.0 mL) was added dropwise in 1 h. Then, the mixture was stirred at 90 ℃ for 6 h. Saturated NH_4Cl (10 mL) and water (70 mL) were added at 0 ℃ to quench the

reaction. The suspension was extracted with ethyl acetate (3×100 mL). The solvent was evaporated and the crude mixture was recrystallized to obtain the 3-oxo-3-propanenitrile as a yellow solid.

A dry 50 mL round flask equipped with a magnetic stirring bar was charged with a solution of 3-oxo-3-propanenitrile (6.0 mmol), aldehyde (6.0 mmol), piperidine (0.2 equiv) and acetic acid (0.2 equiv) in toluene (20 mL). The mixture was heated at 60 ℃ for 12 h. After cooling to room temperature, the mixture was washed with water (10 mL) and the aqueous phase was extracted with ethyl acetate (3×10 mL). The solvent was evaporated and the crude mixture was subjected to column chromatography (PE/EA=10:1) to obtain the corresponding α-cyano-α,β-unsaturated ketone **2**.

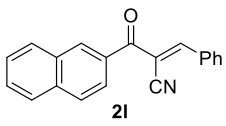
(3) (*a*) P. K. Amancha, Y.-C. Lai, I.-C. Chen, H.-J. Liu and J.-L. Zhu, *Tetrahedron*, 2010, **66**, 871; (*b*) W. Liu, J. Zhou, C. Zheng, X. Chen, H. Xiao, Y. Yang, Y. Guo and G. Zhao, *Tetrahedron*, 2011, **67**, 1768.

A few new substates **2**:



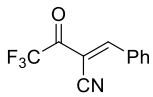
2k

(*E*)-2-(1-Naphthoyl)-3-phenylacrylonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.14 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.02–7.99 (m, 3H), 7.95–7.93 (m, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.60–7.54 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 156.0, 133.74, 133.70, 133.6, 132.5, 131.5, 131.2, 130.4, 129.3, 128.6, 127.9, 127.6, 126.8, 124.9, 124.2, 116.3, 112.4 ppm; ESI-HRMS: calcd. for $C_{20}H_{13}NO+Na^+$ 306.0889, found 306.0892.



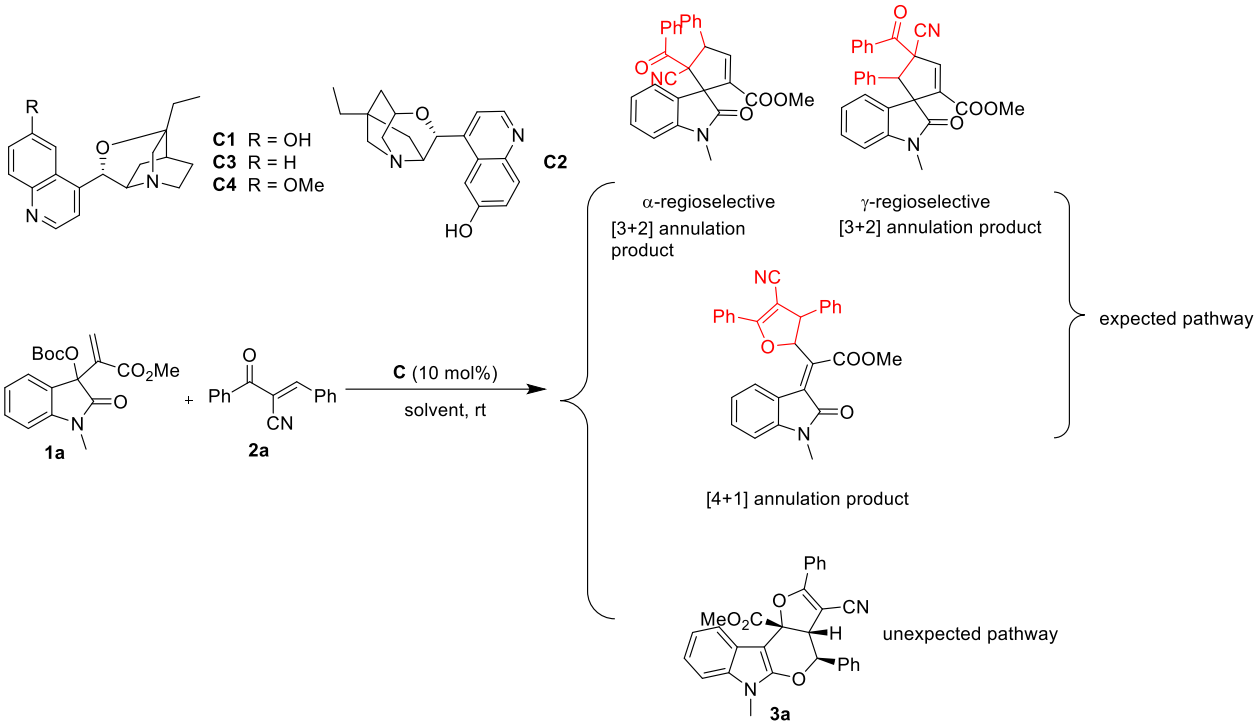
2l

(*E*)-2-(2-Naphthoyl)-3-phenylacrylonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.11 (s, 1H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.99–7.90 (m, 4H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 155.4, 135.6, 133.3, 133.0, 132.2, 131.9, 131.2, 131.1,129.6, 129.3, 128.9, 128.7, 127.9, 127.1, 124.8, 116.9, 110.3 ppm; ESI-HRMS: calcd. for $C_{20}H_{13}NO+Na^+$ 306.0889, found 306.0890.



(*E*)-2-Benzylidene-4,4,4-trifluoro-3-oxobutanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8 (q, *J* = 73.7Hz), 159.2 (d, *J* = 0.9 Hz), 135.5, 132.4, 130.9, 129.7, 115.8 (q, *J* = 289.7 Hz), 113.8, 103.5 ppm; ESI-HRMS: calcd. for $C_{11}H_6F_3NO+Na^+$ 248.0294, found 248.0296.

3. Screening conditions of asymmetric domino annulation[a]



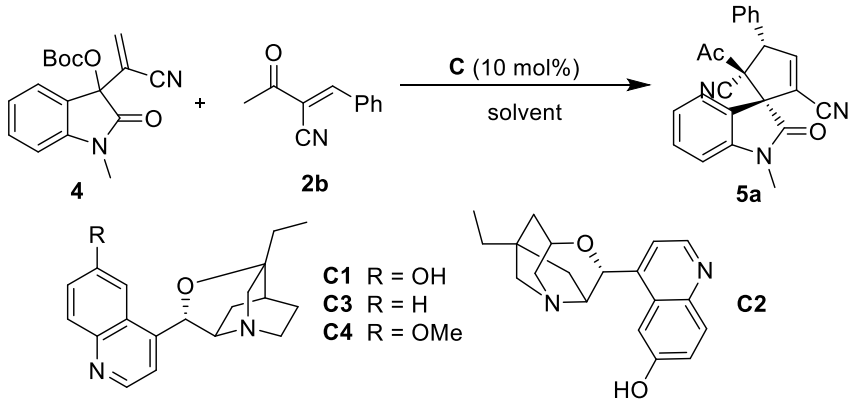
entry	catalyst	solvent	*t* (h)	yield/%[b]	ee/%[c]
1	DABCO	CH_2Cl_2	12	95	–
2	Ph_3P	CH_2Cl_2	24	NR[d]	–
3	nBu_3P	CH_2Cl_2	24	NR[d]	–
4	**C1**	CH_2Cl_2	12	87	99
5	**C2**	CH_2Cl_2	24	80	−98[e]
6	**C3**	CH_2Cl_2	12	92	70
7	**C4**	CH_2Cl_2	12	85	73
8	**C1**	DCE	12	91	95
9	**C1**	$CHCl_3$	12	89	86
10	**C1**	toluene	12	92	93
11	**C1**	THF	12	<5	–
12	**C1**	CH_3CN	12	76	91
13	**C1**	Et_2O	12	70	94
14	**C1**	EtOAc	12	92	95
15[f]	**C1**	CH_2Cl_2	18	85	84

16[g]	**C1**	CH_2Cl_2	30	78	77

[a] Unless noted otherwise, reactions were performed with α-cyano-α,β-unsaturated ketones **2a** (0.1 mmol) and MBH carbonate **1a** (0.1 mmol), catalyst **C** (10 mol%) in solvent (1.0 mL) at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase; d.r. >19:1 by ^{1}H NMR analysis. [d] No reaction. [e] Performed at 0 ℃. [f] With 5 mol% of **C1**. [g] With 2 mol% of **C1**.

The initial reaction of MBH carbonate **1a** and α-cyano-α,β-unsaturated ketones **2a** proceeded efficiently at room temperature in the presence of DABCO (10 mol%). An unusual [2+1] domino annulation-rearrangement product **3a** was cleanly obtained in a high yield after 12 h (entry 1). The reaction exhibited exclusive diastereoselectivity, and the common [3+2] or [4+1] annulation product was not observed. Ph_3P and nBu$_3$P showed much lower catalytic activity (entries 2 and 3). Consequently, we investigated the asymmetric domino reaction under the catalysis of chiral tertiary amines. β-isocupreidine **C1** (β-ICD, 10 mol%) was found to be highly efficient in the reaction of MBH carbonate **1a** and α-cyano-α,β-unsaturated ketone **2a** in CH_2Cl_2 at ambient temperature, affording the desired domino product **3a** in a high yield with enantiomerical purity (entry 4). α-Isocupreine **C2** (α-IC) also showed high catalytic activity and opposite enantioselectivity to that of β-ICD (entry 5). Chiral amines **C3** and **C4** without a free OH group delivered moderate enantioselectivity (entries 6 and 7). CH_2Cl_2 was the optimal solvent after further investigation (entries 8−14). The reaction still proceeded well with 5 mol% and 2 mol% of **C1**, albeit with the decreased enantioselectivity (entries 15 and 16).

4. Screening conditions of asymmetric [3+2] annulation[a]



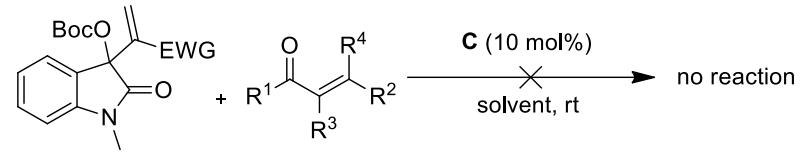
entry	catalyst	solvent	*t* (h)	*T* (℃)	yield/%[b]	ee/%[c]
1	DABCO	CH_2Cl_2	12	0	95	−
2	DMAP	CH_2Cl_2	12	0	94	−
3	Ph_3P	CH_2Cl_2	24	rt	NR[d]	−

4	$^{n}Bu_3P$	CH_2Cl_2	24	rt	NR[d]	–
5	**C1**	CH_2Cl_2	12	0	95	66
6	**C2**	CH_2Cl_2	12	0	94	30
7	**C1**	CH_2Cl_2	24	−20	92	75
8	**C2**	CH_2Cl_2	24	−20	91	37
9	**C3**	CH_2Cl_2	24	−20	92	86
10	**C4**	CH_2Cl_2	24	−20	90	85
11	**C3**	$CHCl_3$	24	−20	87	63
12	**C3**	**DCE**	**24**	**−20**	**93**	**92**
13	**C3**	CH_3CN	24	−20	91	90
14	**C3**	THF	24	−20	91	92
15	**C3**	dioxane/CH_2Cl_2 (5:1)	24	−20	88	90
16	**C3**	toluene	24	−20	71	83
17	**C3**	EtOAc	24	−20	89	89
18	**C3**	Et_2O	24	−20	NR[d]	–
19	**C3**	DCE	36	−30	92	91
20	**C3**	THF	36	−30	91	92

[a] Unless noted otherwise, reactions were performed with α-cyano-α,β-unsaturated ketones **2b** (0.1 mmol) and MBH carbonate **4** (0.1 mmol), catalyst **C** (10 mol%) in solvent (1.0 mL). [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase; d.r. >19:1 by ^{1}H NMR analysis. [d] No reaction.

To explore the catalytic asymmetric version of [3+2] annulation between α-cyano-α,β-unsaturated ketone **2b** and MBH carbonate **4** from isatin and acrylonitrile, more conditions were screened. In the model reaction in CH_2Cl_2 at 0 ℃ catalyzed by DABCO and DMAP, the reaction could smoothly afford the desired [3+2] product **5a** with excellent α-regioselective and diastereoselectivity (entries 1 and 2). Unfortunately, when phosphine catalysts was used, no reaction took place (entries 3 and 4). When **C1** or **C2** was used, the reaction could smoothly afford the desired [3+2] product **5a** while the enantioselectivity was low to moderate (entries 5−8). Chiral amines **C3** and **C4** without a free OH group delivered better enantioselectivity (entries 9 and 10). To further enhance the stereoselectivity, we continued optimizing a number of reaction parameters. Solvent screening revealed that DCE was the best solvent (entries 11−18). Lowering the reaction temperature did not offer further improvement (entries 19 and 20).

5. Exploration of other α,β-unsaturated ketones



EWG = COOMe or CN

R^1 = Ph, R^3 = CN, R^4 = H, R^2 = CF_3, Et, *c*Hex, or 2-styryl

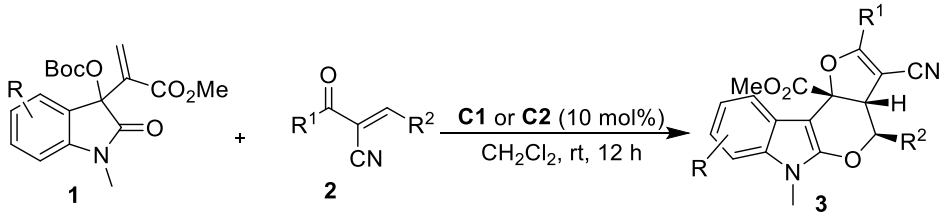
R^1 = Ph, R^2 = Ph, R^4 = H, R^3 = H, NO_2 or COOEt

R^1 = Ph, R^2 = Ph, R^3 = CN, R^4 = Me

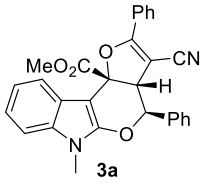
R^1 = CF_3, R^2 = Ph, R^3 = CN, R^4 = H

More α,β-unsaturated ketones with different substitutions at α or β site were tested in the domino annulation reaction and [3+2] annulation reaction. Nevertheless, The reaction hardly proceeded when R^2 is an alkyl group, 2-styryl group or CF_3. Notably, the cyano group at the α-position of enone **2a** was essential for the reaction. When it was replaced by H, NO_2 or CO_2Me, basically no reaction took place. Moreover, the tertrasubstituted alkene (R^4 = Me) failed to give the corresponding products, probably because of the crowded structures. When R^1 is a CF_3 group, unfortunately, no reaction was observed.

6. General procedure for asymmetric domino annulations

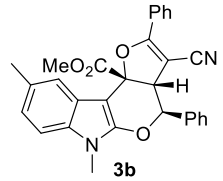


The Morita-Baylis-Hillman (MBH) carbonate **1** (0.1 mmol), α-cyano-α,β-unsaturated ketones **2** (0.1 mmol), and catalyst **C1** or **C2** (3.1 mg, 0.01 mmol) were dissolved in CH_2Cl_2 (1.0 mL). Then the solution was stirred at rt or 0 ℃. After completion, the mixture was directly purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 to 5:1) to afford the product **3**.

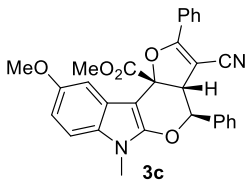


3a, 40.2 mg, 87% yield, white solid; $[\alpha]_D^{20}$ = −165.9 (*c* = 1.20 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.37 min, t (minor) = 6.81 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 7.2 Hz, 2H), 7.67–7.63 (m, 3H), 7.58–7.56 (m, 3H), 7.54–7.47 (m, 3H), 7.26–7.22 (m, 3H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.07 (d, *J* = 10.8 Hz, 1H), 3.80 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.0, 169.8, 152.1, 135.3, 132.7, 132.1, 130.2, 129.0, 128.7, 128.4, 127.8, 127.5, 124.0, 121.1, 121.0, 117.7, 115.8, 108.8, 86.2, 83.6, 83.1, 79.7, 53.3, 51.1, 27.7; ESI-HRMS: calcd. for $C_{29}H_{22}N_2O_4$+Na^+ 485.1472, found 485.1477.

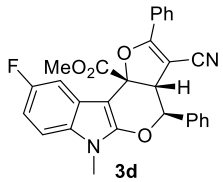
Enantiomer of **3a**, 37.0 mg, 80% yield, white solid; $[\alpha]_D^{20}$ = +165.0 (*c* = 1.20 in $CHCl_3$); −98% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.91 min, t (major) = 7.73 min



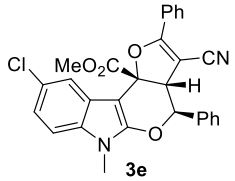
3b, 45.2 mg, 95% yield, white solid; $[\alpha]_D^{20}$= −89.6 (*c* = 0.24 in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.12 min, t (minor) = 9.24 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.14 (d, *J* = 7.2 Hz, 2H), 7.64–7.62 (m, 2H), 7.57–7.56 (m, 3H), 7.54–7.48 (m, 3H), 7.43 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.80 (s, 3H), 3.59 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.0, 169.9, 152.0, 135.4, 132.1, 130.9, 130.4, 130.1, 129.0, 128.7, 128.4, 127.8, 127.5, 124.1, 122.2, 117.7, 115.8, 108.5, 86.3, 83.1, 83.0, 79.7, 53.2, 51.1, 27.7, 21.6; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_4$+Na^+ 499.1628, found 499.1631.



3c, 44.3 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −285.9 (*c* = 1.00 in $CHCl_3$); > 99% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.83 min, t (minor) = 7.07 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.10 (d, *J* = 6.8 Hz, 2H), 7.62–7.61 (m, 2H), 7.56–7.54 (m, 3H), 7.53–7.46 (m, 3H), 7.15–7.13 (m, 2H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.0, 169.9, 155.2, 152.4, 135.3, 132.1, 130.2, 129.0, 128.7, 128.4, 127.8, 127.6, 127.5, 124.7, 115.8, 109.5, 109.3, 101.5, 86.3, 83.5, 83.0, 79.8, 56.0, 53.3, 51.1, 27.8; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_5$+Na^+ 515.1577, found 515.1578.

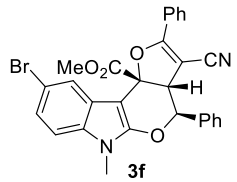


3d, 43.2 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −267.0 (*c* = 0.90 in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.40 min, t (minor) = 6.34 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.10 (d, *J* = 7.2 Hz, 2H), 7.60 (s, 2H), 7.56–7.54 (m, 3H), 7.53–7.47 (m, 3H), 7.32 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.15 (dd, *J* = 8.8, 4.4 Hz, 1H), 6.96–6.91 (m, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.06 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 170.8, 169.8, 158.8 (d, *J* = 234.2 Hz), 153.0, 135.1, 132.2, 130.3, 129.1 (d, *J* = 3.0 Hz), 128.8, 128.4, 127.8, 127.4, 124.6 (d, *J* = 10.7 Hz), 115.7, 109.5 (d, *J* = 9.7 Hz), 108.6 (d, *J* = 25.5 Hz), 103.7 (d, *J* =25.2 Hz), 85.9, 84.0 (d, *J* = 4.0 Hz), 83.2, 79.8, 53.4, 51.0, 27.9; ESI-HRMS: calcd. for $C_{29}H_{21}FN_2O_4$+Na^+ 503.1378, found 503.1377.



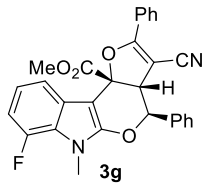
3e, 45.1 mg, 91% yield, white solid; $[\alpha]_D^{20}$ = −186.7 (*c* = 0.36 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 6.07 min, t (minor) = 7.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.10 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 3.6 Hz, 3H), 7.56–7.55 (m, 3H), 7.54–7.47 (m, 3H), 7.18–7.13 (m, 2H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 170.8, 169.8, 152.8, 135.0, 132.3, 131.1, 130.3, 129.1, 128.8, 128.4,

127.8, 127.4, 126.8, 125.1, 121.2, 117.4, 115.7, 109.9, 85.8, 83.7, 83.3, 79.7, 53.4, 51.1, 27.9; ESI-HRMS: calcd. for $C_{29}H_{21}ClN_2O_4$+Na^+ 519.1082, found 519.1086.

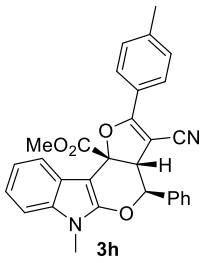


3f, 48.6 mg, 90% yield, white solid; $[\alpha]_D^{20}$= −105.7 (*c* = 1.00 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.61 min, t (minor) = 7.09 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 1.2 Hz, 1H), 7.60 (d, *J* = 2.8 Hz, 2H), 7.56–7.54 (m, 3H), 7.52– 7.47 (m, 3H), 7.30 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.05 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 169.8, 152.7, 135.0, 132.3, 131.4, 130.3, 129.1, 128.8, 128.4, 127.9, 127.3, 125.7, 123.8, 120.4, 115.7, 114.4, 110.3, 85.7, 83.6, 83.3, 79.7, 53.5, 51.0, 27.9; ESI-HRMS: calcd. for $C_{29}H_{21}BrN_2O_4$+Na^+ 563.0577(^{79}Br) and 565.0556(^{81}Br), found 563.0582, 565.0562.

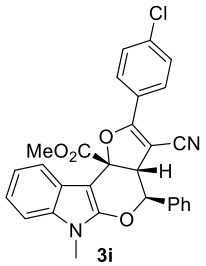
Enantiomer of **3f**, 48.6 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = +104.2 (*c* = 1.00 in $CHCl_3$); −97% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.62 min, t (major) = 7.09 min.



3g, 42.2 mg, 88% yield, white solid; $[\alpha]_D^{20}$ = −221.8 (*c* = 1.20 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 8.86 min, t (minor) = 7.81 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 7.6 Hz, 2H), 7.62−7.61 (m, 2H), 7.57–7.55 (m, 3H), 7.54–7.47 (m, 3H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.10−7.05 (m, 1H), 6.89 (dd, *J* = 12.4, 8.4 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 169.9, 152.0 (dd, *J* = 315.9 Hz, 125.5 Hz), 135.1, 133.38 (d, *J* = 3.2 Hz), 132.2, 131.1, 130.3, 129.3 (d, *J* = 1.4 Hz), 129.0, 128.7, 128.4, 127.8, 127.4, 121.3 (d, *J* = 6.9 Hz), 115.7, 113.5 (d, *J* = 3.3 Hz), 107.4 (d, *J* = 17.8 Hz), 85.9 (s), 84.6 (s), 83.3 (s), 79.7 (s), 53.4 (s), 51.1 (s), 30.4 (d, *J* = 5.3 Hz); ESI-HRMS: calcd. for $C_{29}H_{21}FN_2O_4$+Na^+ 503.1378, found 503.1380.

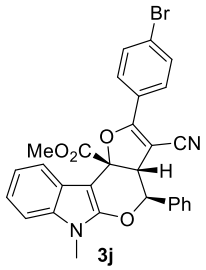


3h, 43.8 mg, 92% yield, white solid; $[\alpha]_D^{20}$ = −57.0 (*c* = 0.80 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 11.29 min, t (minor) = 10.20 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 8.0 Hz, 2H), 7.63−7.59 (m, 3H), 7.54−7.53 (m, 3H), 7.26–7.18 (m, 5H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.01 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.1, 170.0, 152.1, 142.9, 135.4, 132.7, 130.1, 129.4, 129.0, 128.4, 127.8, 124.8, 124.0, 121.0, 120.9, 117.7, 116.1, 108.8, 86.0, 83.6, 83.2, 78.7, 53.3, 51.0, 27.7, 21.7; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_4$+Na^+ 499.1628, found 499.1626.



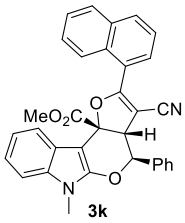
3i, 47.1 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = −241.8 (*c* = 1.25 in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.92 min, t (minor) = 13.02 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, *J* = 8.4 Hz, 2H), 7.61–7.59 (m, 3H), 7.54–7.53 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.25–7.17 (m, 3H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 168.7, 152.1, 138.3, 135.2, 132.7, 130.3, 129.1, 129.0, 128.4, 125.9, 123.9, 121.12, 121.06, 117.6, 115.6, 108.9, 86.4, 83.4, 83.0, 80.2, 53.4, 51.1, 27.7; ESI-HRMS: calcd. for $C_{29}H_{21}ClN_2O_4$+Na^+ 519.1082, found 519.1088.

Enantiomer of **3i**, 46.1 mg, 93% yield, white solid; $[\alpha]_D^{20}$ = +242.0 (*c* = 1.25 in $CHCl_3$); −90% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 8.56 min, t (major) = 13.57 min.



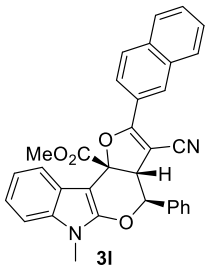
3j, 49.2 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = −133.4 (*c* = 1.00 in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.52 min, t (minor) = 15.63 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 8.4 Hz, 2H), 7.61–7.59 (m, 5H), 7.55–7.54 (m, 3H), 7.24 (s, 1H), 7.21–7.19 (m, 2H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 168.8, 152.1, 135.2, 132.7, 132.1, 130.3, 129.2, 129.1, 128.4, 126.9, 126.4, 124.0, 121.2, 121.1, 117.7, 115.6, 108.9, 86.5, 83.4, 83.0, 80.4, 53.4, 51.2, 27.8; ESI-HRMS: calcd. for $C_{29}H_{21}BrN_2O_4$+H^+ 541.0757 (^{79}Br) and 543.0737 (^{81}Br), found 541.0759, 543.0746.

Enantiomer of **3j**, 49.7 mg, 96% yield, white solid; $[\alpha]_D^{20}$ = +134.0 (*c* = 1.00 in $CHCl_3$); −92% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.99 min, t (major) = 16.28 min.



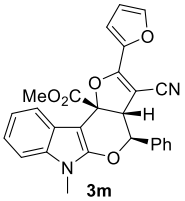
3k, 49.2 mg, 96% yield, white solid; $[\alpha]_D^{20}$ = −371.3 (*c* = 1.20 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 9.92 min, t (minor) = 16.87 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63 (d, *J* = 9.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 6.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.68−7.64 (m, 3H), 7.61–7.50 (m, 6H), 7.24–7.14 (m, 3H), 5.11 (d, *J* = 10.8 Hz, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 3.84 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.0, 171.0, 152.0, 135.3, 133.6, 132.7, 132.5, 130.6, 130.3, 129.3, 129.1, 128.5, 128.4, 127.4, 126.5, 125.6, 124.9, 124.8, 124.0, 121.1, 121.0, 118.0, 115.1, 108.8, 87.3, 84.2, 83.7, 83.6, 53.4, 50.7, 27.7; ESI-HRMS: calcd. for $C_{33}H_{24}N_2O_4$+H^+ 513.1809, found 513.1812.

Enantiomer of **3k**, 49.2 mg, 96% yield, white solid; $[\alpha]_D^{20}$ = +371.0 (*c* = 1.20 in $CHCl_3$); −97% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 9.76 min, t (major) = 16.47 min.

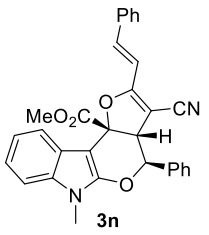


3l, 48.6 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = −279.3 (*c* = 0.80 in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.38 min, t (minor) = 16.57 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.61 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.70–7.68 (m, 1H), 7.64−7.63 (m, 2H), 7.59–7.52 (m, 5H), 7.25−7.22 (m, 3H), 5.01 (d, *J* = 10.8 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 3.78 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.1, 169.8, 152.2, 135.4, 134.9, 132.8, 132.6, 130.2, 129.3, 129.1, 128.9, 128.53, 128.47, 128.2, 127.7, 126.9, 124.9, 124.1, 123.6, 121.1, 121.0, 117.8, 116.0, 108.9, 86.2, 83.6, 83.2, 80.1, 53.3, 51.3, 27.8; ESI-HRMS: calcd. for $C_{33}H_{24}N_2O_4$+H^+ 513.1809, found 513.1808.

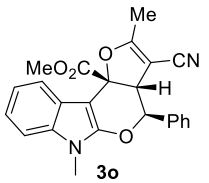
Enantiomer of **3l**, 48.6 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = +280.2 (*c* = 0.80 in $CHCl_3$); −85% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 14.52 min, t (major) = 15.60 min



3m, 40.7 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −253.5 (*c* = 1.00 in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.00 min, t (minor) = 10.62 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.62–7.58 (m, 4H), 7.53–7.52 (m, 3H), 7.24−7.22 (m, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 5.6, 3.2 Hz, 2H), 6.55 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 4.01 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 170.7, 160.4, 152.1, 146.1, 143.3, 135.2, 132.7, 130.2, 129.0, 128.4, 124.0, 121.12, 121.05, 117.8, 115.8, 114.9, 112.1, 108.8, 87.0, 83.4, 83.1, 78.3, 53.3, 50.6, 27.8; ESI-HRMS: calcd. for $C_{27}H_{20}N_2O_5$+Na^+ 475.1264, found 475.1270.

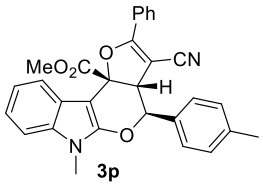


3n, 44.9 mg, 92% yield, yellow solid; $[\alpha]_D^{20}$ = −177.8 (*c* = 0.90 in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 18.89 min, t (minor) = 10.36 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.65–7.63 (m, 1H), 7.58 (d, *J* = 2.4 Hz, 2H), 7.55–7.51 (m, 6H), 7.41−7.37 (m, 3H), 7.23–7.20 (m, 3H), 6.84 (d, *J* = 16.0 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* (ppm) 171.0, 169.7, 152.1, 139.7, 135.3, 134.7, 132.7, 130.2, 130.1, 129.0, 128.9, 128.4, 128.0, 124.0, 121.11, 121.05, 117.8, 115.0, 112.9, 108.9, 86.5, 83.7, 83.1, 83.0, 53.3, 50.5, 27.8; ESI-HRMS: calcd. for $C_{31}H_{24}N_2O_4$+Na^+ 511.1628, found 511.1631.



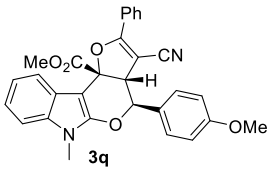
3o, 36.0 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −156.5 (*c* = 0.60 in $CHCl_3$); 83% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.17 min, t (minor) = 6.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.55–7.51 (m, 6H), 7.24–7.14 (m, 3H), 4.81 (d, *J* = 10.8 Hz, 1H), 3.88 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 174.3, 171.0, 152.0, 135.3,

132.7, 130.2, 129.0, 128.4, 123.8, 121.1, 121.0, 117.7, 114.9, 108.8, 87.1, 83.6, 83.4, 83.0, 53.3, 50.1, 27.7, 14.5; ESI-HRMS: calcd. for $C_{24}H_{20}N_2O_4$+Na^+ 423.1315, found 423.1318.

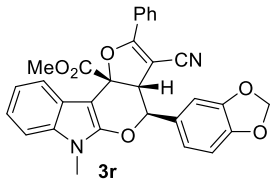


3p, 43.3 mg, 91% yield, white solid; $[\alpha]_D^{20}$ = −258.6 (*c* = 1.60 in $CHCl_3$); 87% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.59 min, t (minor) = 6.46 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.09 (d, *J* = 7.2 Hz, 2H), 7.62–7.60 (m, 1H), 7.50–7.44 (m, 5H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.24–7.18 (m, 3H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.1, 169.9, 152.2, 140.2, 132.7, 132.3, 132.1, 129.7, 128.7, 128.4, 127.8, 127.6, 124.0, 121.0, 120.9, 117.7, 115.9, 108.8, 86.2, 83.5, 83.0, 79.9, 53.3, 50.9, 27.7, 21.4; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_4$+Na^+ 499.1628, found 499.1629.

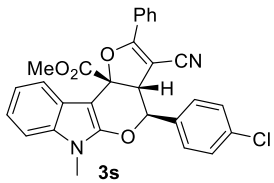
Enantiomer of **3p**, 42.8 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = +260.2 (*c* = 1.80 in $CHCl_3$); −90% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.64 min, t (major) = 6.53 min.



3q, 46.2 mg, 94% yield, white solid; $[\alpha]_D^{20}$ = −201.1 (*c* = 1.40 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 7.01 min, t (minor) = 8.03 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.09 (d, *J* = 7.2 Hz, 2H), 7.62–7.60 (m, 1H), 7.54−7.47 (m, 5H), 7.24−7.20 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 10.8 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.2, 169.8, 161.0, 152.3, 132.7, 132.1, 129.8, 128.7, 127.8, 127.6, 127.3, 124.1, 121.0, 120.9, 117.7, 115.9, 114.4, 108.8, 86.3, 83.5, 82.8, 79.9, 55.3, 53.3, 51.0, 27.7; ESI-HRMS: calcd. for $C_{30}H_{24}N_2O_5$+Na^+ 515.1577, found 515.1579.



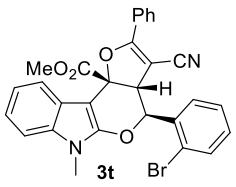
3r, 45.5 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −146.9 (*c* = 0.80 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.20 min, t (minor) = 12.32 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.09 (d, *J* = 7.2 Hz, 2H), 7.62–7.60 (m, 1H), 7.54–7.45 (m, 3H), 7.24–7.17 (m, 3H), 7.09–7.04 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H), 4.86 (d, *J* = 11.2 Hz, 1H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 171.1, 169.9, 152.1, 149.1, 148.3, 132.7, 132.2, 128.9, 128.7, 127.8, 127.5, 124.0, 122.9, 121.1, 121.0, 117.7, 115.9, 108.9, 108.6, 108.1, 101.5, 86.2, 83.5, 83.0, 79.8, 53.3, 51.1, 27.8; ESI-HRMS: calcd. for $C_{30}H_{22}N_2O_4$+Na^+ 529.1370, found 529.1370.



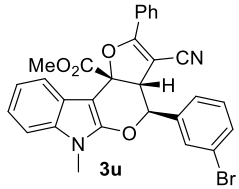
3s, 46.1 mg, 93% yield, white solid; $[\alpha]_D^{20}$ = −171.8 (*c* = 1.10 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 6.27 min, t (minor) = 7.38 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.09 (d, *J* = 7.6 Hz, 2H), 7.63–7.61 (m, 1H), 7.55–7.45 (m,

7H), 7.24–7.19 (m, 3H), 4.93 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 170.1, 151.8, 136.1, 133.9, 132.7, 132.3, 129.7, 129.3, 128.7, 127.8, 127.4, 123.9, 121.2, 121.1, 117.8, 115.9, 108.9, 86.2, 83.6, 82.4, 79.4, 53.4, 50.9, 27.7; ESI-HRMS: calcd. for $C_{29}H_{21}ClN_2O_4$+Na^+ 519.1082, found 519.1085.

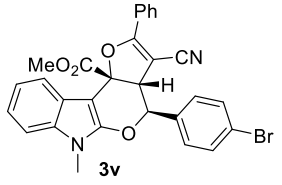
Enantiomer of **3s**, 45.6 mg, 92% yield, white solid; $[\alpha]_D^{20}$ = +170.6 (*c* = 1.10 in $CHCl_3$); −92% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 6.28 min, t (major) = 7.31 min.



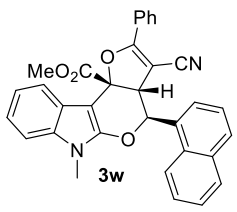
3t, 51.8 mg, 96% yield, white solid; $[\alpha]_D^{20}$ = −117.1 (*c* = 1.00 in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 20.86 min, t (minor) = 17.44 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 6.8 Hz, 2H), 7.76–7.73 (m, 2H), 7.64–7.62 (m, 1H), 7.54–7.46 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26–7.19 (m, 3H), 5.68 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.78 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.0, 170.3, 152.0, 135.1, 133.4, 132.7, 132.2, 131.3, 129.5, 128.7, 128.2, 128.0, 127.5, 124.7, 123.9, 121.2, 121.1, 117.8, 115.8, 108.9, 86.2, 83.7, 80.5, 79.2, 53.4, 51.5, 27.8; ESI-HRMS: calcd. for $C_{29}H_{21}BrN_2O_4$+H^+ 541.0757 (^{79}Br), 543.0737 (^{81}Br), found 541.0760, 543.0748.



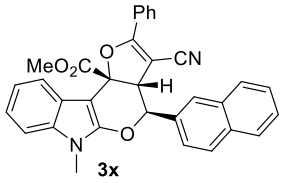
3u, 50.2 mg, 93% yield, white solid; $[\alpha]_D^{20}$ = −161.3 (*c* = 1.00 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 9.61 min, t (minor) = 15.56 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 7.6 Hz, 2H), 7.78 (s, 1H), 7.67−7.61 (m, 2H), 7.53–7.46 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.25–7.20 (m, 2H), 4.92 (d, *J* = 10.8 Hz, 1H), 3.98 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 170.1, 151.7, 137.6, 133.3, 132.7, 132.3, 131.2, 130.5, 128.8, 127.9, 127.4, 127.1, 123.9, 123.1, 121.18, 121.15, 117.8, 115.8, 108.9, 86.1, 83.6, 82.3, 79.3, 53.4, 51.1, 27.8; ESI-HRMS: calcd. for $C_{29}H_{21}BrN_2O_4$+H^+ 541.0757 found 541.0757.



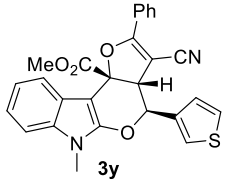
3v, 49.6 mg, 92% yield, white solid; $[\alpha]_D^{20}$ = −158.9 (*c* = 1.35 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 5.61 min, t (minor) = 6.60 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 4.8 Hz, 1H), 7.52−7.45 (m, 5H), 7.25−7.19 (m, 3H), 4.92 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 170.1, 151.8, 134.4, 132.7, 132.3, 132.2, 130.0, 128.8, 127.8, 127.4, 124.4, 123.9, 121.2, 121.1, 117.8, 115.9, 108.9, 86.2, 83.6, 82.4, 79.3, 53.4, 50.9, 27.8; ESI-HRMS: calcd. for $C_{29}H_{21}BrN_2O_4$+H^+ 541.0757, found 541.0760.



3w, 49.1 mg, 96% yield, white solid; $[\alpha]_D^{20}$ = −156.0 (*c* = 1.25 in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak AD, n-hexane/i-PrOH =90/10, 1.0 mL/min, λ = 254 nm, t (major) = 19.51 min, t (minor) = 17.41 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 3H), 7.99–7.97 (m, 1H), 7.83 (d, *J* = 6.4 Hz, 1H), 7.67–7.61 (m, 2H), 7.57–7.55 (m, 2H), 7.50–7.43 (m, 3H), 7.26−7,21 (m, 3H), 5.71 (d, *J* = 9.6 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.1, 169.9, 152.1, 134.2, 132.8, 132.2, 131.5, 130.9, 130.7, 129.4, 128.7, 127.9, 127.5, 126.8, 126.0, 125.2, 124.1, 123.2, 121.2, 121.1, 117.7, 115.7, 108.9, 86.4, 83.7, 80.2, 53.4, 50.4, 27.8; ESI-HRMS: calcd. for $C_{33}H_{24}N_2O_4$+Na^+ 535.1628, found 535.1627.

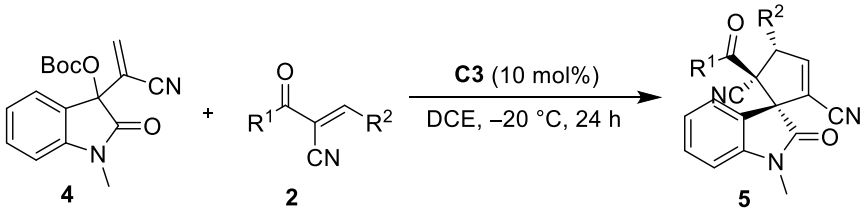


3x, 48.6 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = −167.9 (*c* = 0.90 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 6.84 min, t (minor) =22.18 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (d, *J* = 7.2 Hz, 2H), 8.07 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.98−7.93 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69−7.67 (m, 1H), 7.59–7.56 (m, 2H), 7.54–7.47 (m, 3H), 7.26–7.23 (m, 3H), 5.15 (d, *J* = 10.8 Hz, 1H), 4.20 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.1, 169.9, 152.1, 134.1, 133.1, 132.7, 132.5, 132.2, 129.1, 128.73, 128.71, 128.3, 128.0, 127.8, 127.5, 127.0, 126.7, 124.7, 124.0, 121.1, 121.0, 117.8, 115.8, 108.9, 86.2, 83.6, 83.3, 79.8, 53.3, 50.8, 27.8; ESI-HRMS: calcd. for $C_{33}H_{24}N_2O_4$+Na^+ 535.1628, found 535.1631.



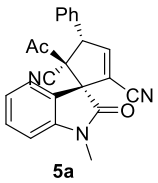
3y, 42.1 mg, 90% yield, yellow solid; $[\alpha]_D^{20}$ = −293.2 (*c* = 1.50 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 6.87 min, t (minor) = 9.02 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 7.2 Hz, 2H), 7.62−7.59 (m, 2H), 7.53−7.49 (m, 2H), 7.48−7.44 (m, 2H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.23−7.18 (m, 3H), 5.08 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 171.0, 169.7, 151.9, 136.2, 132.7, 132.2, 128.7, 127.8, 127.5, 126.6, 126.3, 124.0, 121.1, 121.0, 117.8, 115.8, 108.8, 86.1, 83.6, 79.8, 78.3, 53.3, 50.9, 27.8; ESI-HRMS: calcd. for $C_{27}H_{20}N_2O_4S$+Na^+ 491.1036, found 491.1045.

7. General procedure for asymmetric [3 + 2] annulations



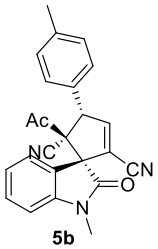
The Morita-Baylis-Hillman carbonate **4** (0.1 mmol), α-cyano-α,β-unsaturated ketone **2** (0.1 mmol), and catalyst **C3** (2.9 mg, 0.01 mmol) were dissolved in 1,2-dichloroethane (DCE, 1.0 mL). Then the solution was

stirred at −20 °C for 24 h. After completion, the mixture was directly purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 to 3:1) to afford the product **5**.



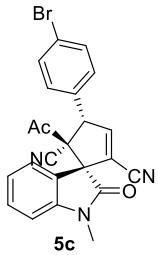
5a

5a, 34.1 mg, 93% yield, white solid; $[\alpha]_D^{20}$ = −261.3 (*c* = 1.10 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.92 min, t (minor) = 23.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.47–7.42 (m, 6H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.45 (d, *J* = 2.0 Hz, 1H), 3.37 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 195.6, 171.3, 151.7, 143.8, 135.2, 131.7, 129.6, 129.2, 129.0, 126.3, 123.9, 122.2, 115.2, 115.0, 112.3, 109.5, 67.3, 65.8, 55.4, 27.8, 27.3; ESI-HRMS: calcd. for $C_{23}H_{17}N_3O_2$+Na^+ 390.1213, found 390.1214.



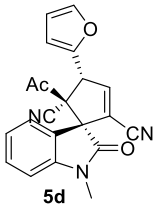
5b

5b, 35.1 mg, 92% yield, white solid; $[\alpha]_D^{20}$ = −189.4 (*c* = 1.25 in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak IE, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 32.49 min, t (minor) = 20.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.45 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.40 (d, *J* = 2.0 Hz, 1H), 3.37 (s, 3H), 2.36 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* (ppm) 195.6, 171.3, 151.9, 143.8, 139.0, 132.0, 131.6, 129.7, 129.3, 126.2, 123.8, 122.1, 115.1, 114.9, 112.3, 109.4, 67.3, 65.8, 55.1, 27.9, 27.3, 21.2; ESI HRMS: calcd. for $C_{24}H_{19}N_3O_2$+Na^+ 404.1369, found 404.1372.



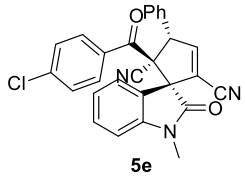
5c

5c, 42.3 mg, 95% yield, white solid; $[\alpha]_D^{20}$ = −248.3 (*c* = 1.40 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak IF, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 14.67 min, t (minor) = 40.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.38 (d, *J* = 2.0 Hz, 1H), 3.37 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* (ppm) 195.5, 171.2, 150.8, 143.8, 134.1, 132.1, 131.8, 131.2, 126.1, 123.9, 123.5, 121.8, 115.6, 114.9, 112.0, 109.5, 66.8, 65.8, 54.9, 27.9, 27.3; ESI HRMS: calcd. for $C_{23}H_{16}BrN_3O_2$+Na^+ 468.0318, found 468.0321.



5d

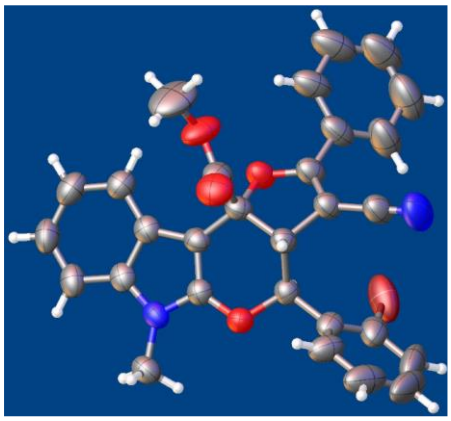
5d, 32.1 mg, 90% yield, white solid; $[\alpha]_D^{20}$ = −130.5 (*c* = 0.9 in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak IF, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.78 min, t (minor) = 28.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 7.49−7.45 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.47−6.44 (m, 2H), 4.43 (d, *J* = 1.6 Hz, 1H), 3.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* (ppm) 198.1, 172.3, 146.1, 144.9, 144.0, 132.2, 131.5, 125.0, 123.5, 123.2, 120.4, 117.0, 115.7, 111.9, 110.1, 109.6, 63.6, 62.5, 42.1, 30.5, 26.9; ESI HRMS: calcd. for $C_{21}H_{15}N_3O_3$+Na^+ 380.1006, found 380.1008.

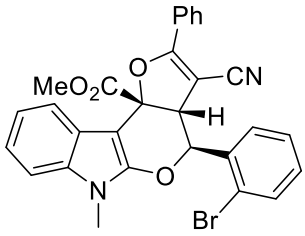


5e

5e, 43.1 mg, 93% yield, white solid; $[\alpha]_D^{20}$= −221.2 (*c* = 1.30 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak AD, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 25.36 min, t (minor) = 29.50 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56−7.52 (m, 4H), 7.45–7.38 (m, 3H), 7.23–7.19 (m, 1H), 7.16 (d, *J* = 8.4Hz, 2H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.04–6.99 (m, 2H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 1.6 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 186.6, 170.5, 150.9, 143.0, 140.6, 135.0, 132.4, 131.3, 129.9, 129.6, 129.1, 128.8, 128.3, 125.2, 123.5, 122.6, 115.9, 113.7, 112.2, 108.7, 66.4, 64.6, 55.8, 26.8; ESI HRMS: calcd. for $C_{28}H_{18}ClN_3O_2$+Na^+ 486.0980, found 486.0983.

8. Crystal data and structural refinement for enantiopure 3t and 5a

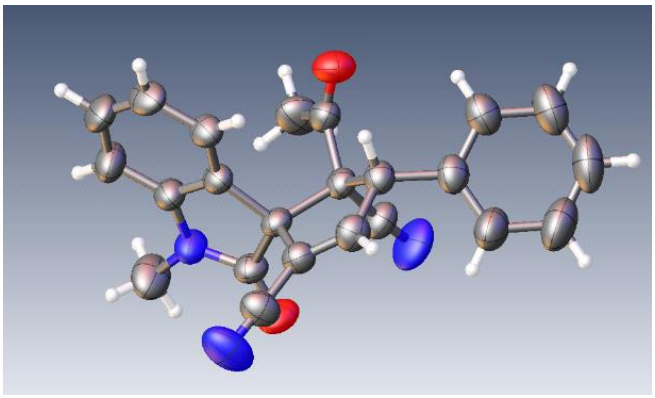


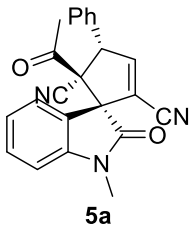


3t

Identification code	**3t**
Empirical formula	$C_{29}H_{21}BrN_2O_4$
Formula weight	541.39
Temperature/K	292.4(3)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.08473(14)
b/Å	16.7619(4)
c/Å	22.0850(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2622.68(10)

Z	4
ρ_{calc}g/cm^3	1.371
μ/mm^{-1}	2.438
F(000)	1104.0
Crystal size/mm^3	0.8 ×0.7 ×0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.556 to 144.988
Index ranges	-5 ≤ h ≤ 8, -19 ≤ k ≤ 20, -27 ≤ l ≤ 25
Reflections collected	14476
Independent reflections	5097 [R_{int} = 0.0440, R_{sigma} = 0.0321]
Data/restraints/parameters	5097/0/327
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0783, wR_2 = 0.2136
Final R indexes [all data]	R_1 = 0.0825, wR_2 = 0.2211
Largest diff. peak/hole / e Å^{-3}	0.82/-1.36
Flack parameter	-0.044(14)





5a

Identification code	**5a**
Empirical formula	$C_{23}H_{17}N_3O_2$
Formula weight	367.39
Temperature/K	292.6(5)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.06732(18)

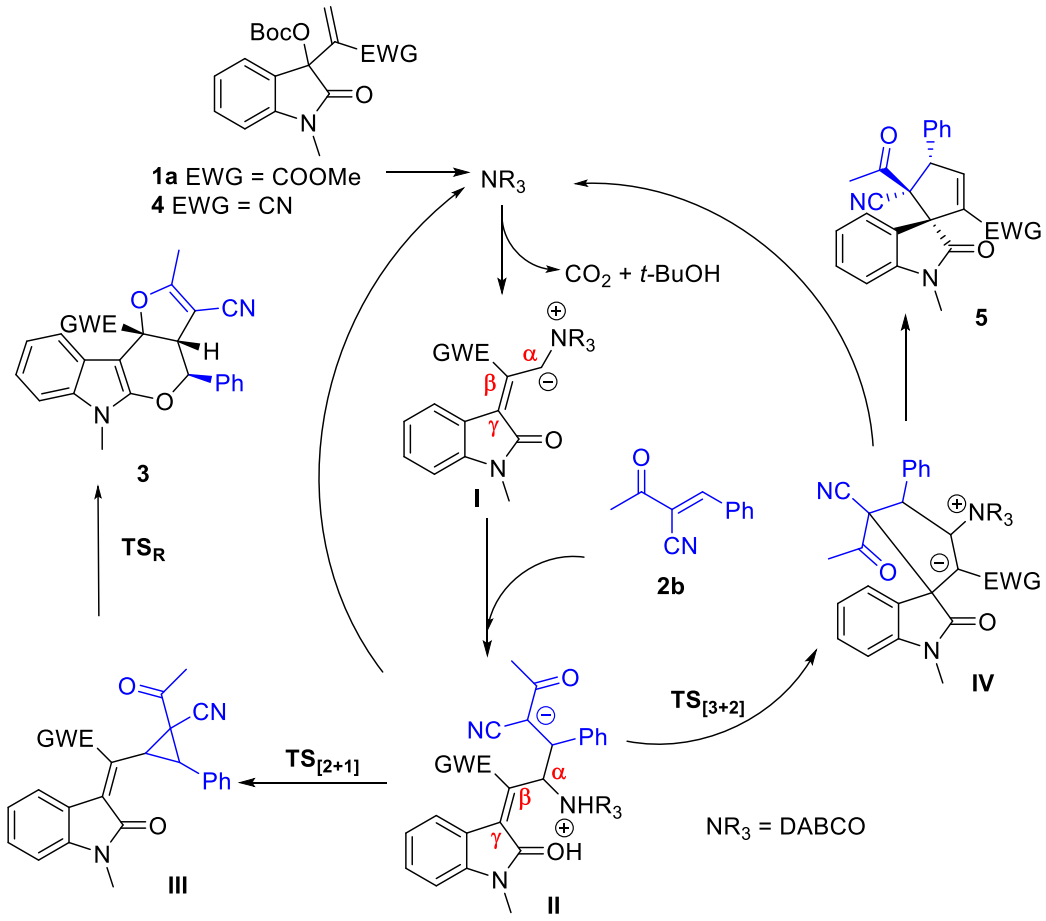
b/Å	10.59058(14)
c/Å	22.9703(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2449.06(7)
Z	4
ρ_{calc}g/cm^3	0.996
μ/mm^{-1}	0.524
F(000)	768.0
Crystal size/mm^3	0.7 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.196 to 145.212
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 8, -28 ≤ l ≤ 20
Reflections collected	13639
Independent reflections	4769 [R_{int} = 0.0309, R_{sigma} = 0.0272]
Data/restraints/parameters	4769/14/255
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1225
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1268
Largest diff. peak/hole / e Å^{-3}	0.14/-0.22
Flack parameter	-0.03(14)

9. DFT computational calculation studies

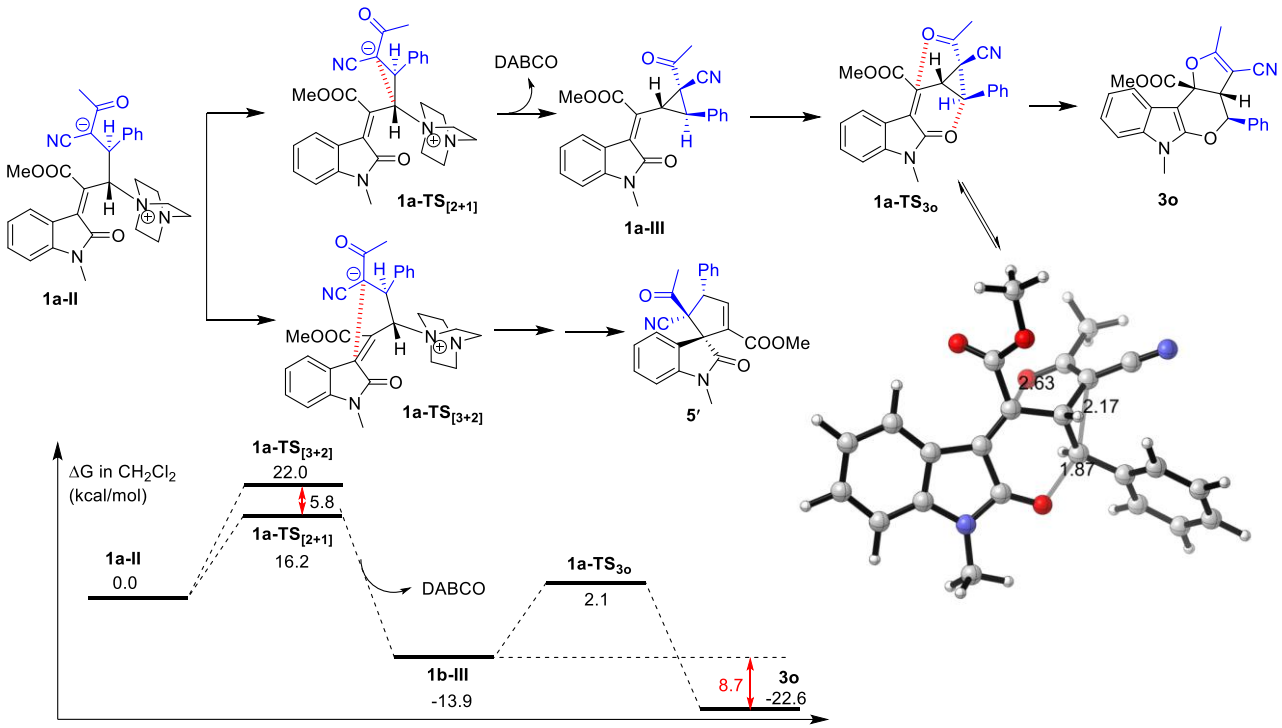
Computational method:

All calculations were carried out with the GAUSSIAN 09 packages.[4] The recently developed M06-2x functional,[5] together with the standard 6-31G(d) basis set, were used for optimizing the geometry of all the minima and transition states. All the optimized structures were confirmed by frequency calculations to be either minima or transition states using the same level of theory. For transition states, intrinsic reaction coordinate analysis (IRC) was done to verify that they connect

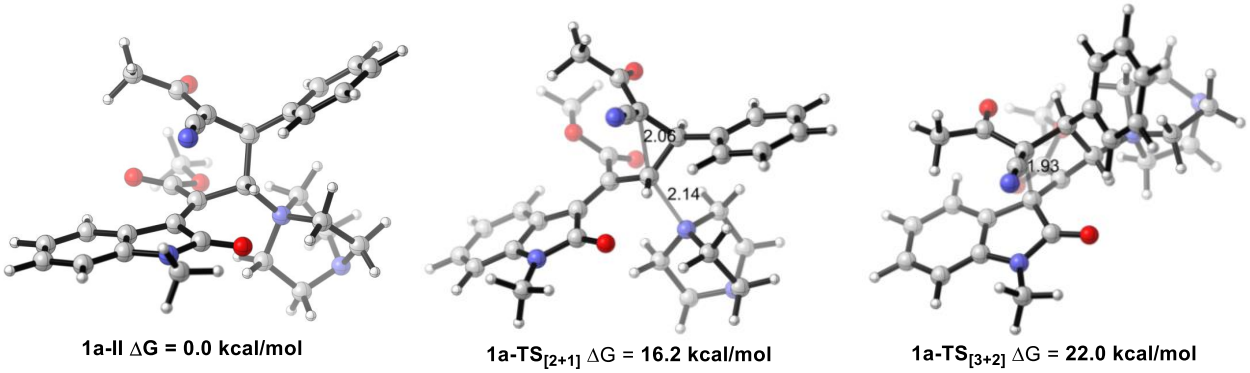
the right reactants.[6] To take solvent effects into account, solution-phase single-point calculations were performed on the gas-phase geometries.[7] The solution-phase single point energy calculations were done using M06-2x method at a larger basis set 6-311+G(2d,p). Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using SMD model and UAKS radii.[8] Dichloromethane 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, and the bond lengths are in angstroms (Å). Structures were generated using GaussView5.0.8 and CYLview.



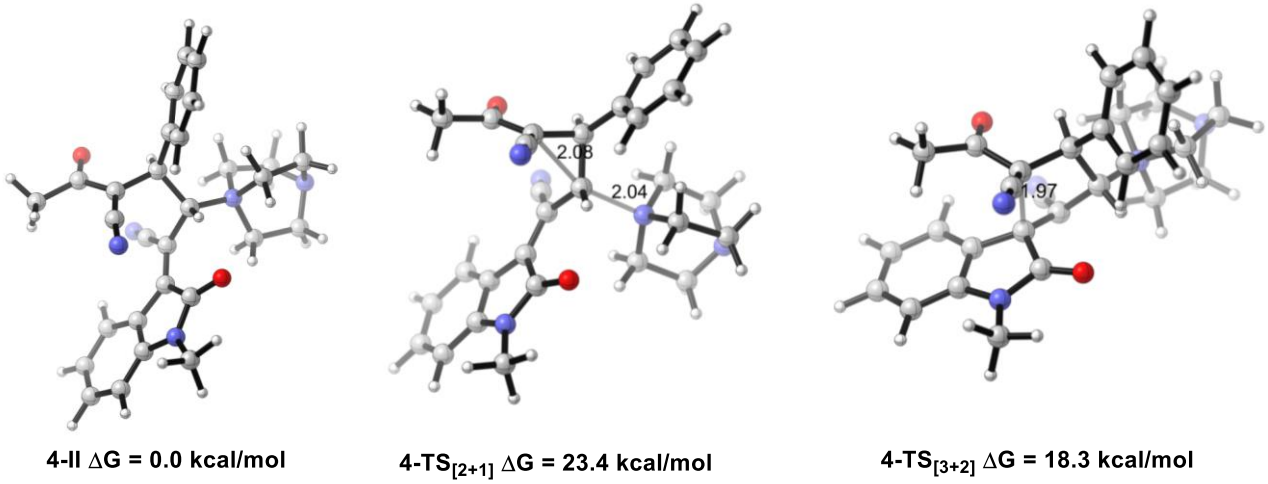
Scheme 1. Proposed catalytic cycles for domino reaction and [3+2] annulation.



Scheme 2. Computed potential energy surface of the formation of **3o** and **5'**.



Scheme 3. Key transition states and related energy for the reaction of **1a** and **2b**.

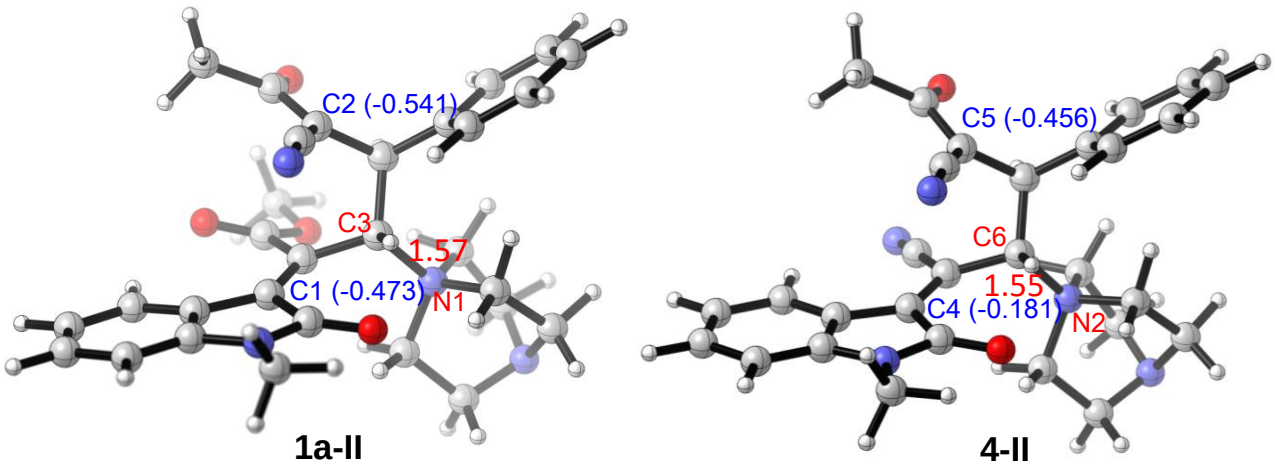


Scheme 4. Key transition states and related energy for the reaction of **4** and **2b**.

Density functional theory (DFT) computational calculations were performed to clarify the mechanism of the formation of dihydropyrano[2,3-*b*]indole architectures and the selectivity for different substrates. These geometries of intermediates and transition states (TSs) were optimized using M062X functional together with the standard 6-31G(d) basis set, and the energies were calculated at 6-311+G(2d,p) level (CH_2Cl_2 as solvent). As our previous calculation, [9] the ring-closure steps were considered as the decisive processes for formation of five-membered ring product by a sequential Michael addition via **TS$_{[3+2]}$** and three-membered ring intermediate by a S_N2 process via **TS$_{[2+1]}$** (Scheme 1). For the reaction of the substrates **1a** with an electron-withdrawing group COOMe, and alkene **2b** catalyzed by DABCO, the energy barrier of **1a-TS$_{[2+1]}$** was 5.8 kcal/mol lower than that of **1a-TS$_{[3+2]}$**, indicating that the [3+2] process was unfavorable (Schemes 2 and 3). Actually, [3+2] product **5'** wasn't found in our experiment. Due to the strong electron withdrawing ability of cyano and acetyl groups at the cyclopropane ring of **1a-III**, the lone pair electrons at O1 atom would attack the benzylic position and the ring would be opened. The O2 atom would accept the electron from the C-C bond breaking, and add to the double bond by Michael addition to generate product **3o**. The transition state **1a-TS$_{3o}$** for this rearrangement was calculated with energy barrier of 16.0 kcal/mol, suggesting a potentially concerted mechanism leading to the high diastereocontrol in the observed product **3o**. The energy difference of the intermediate **1a-III** and dihydropyrano[2,3-*b*]indole product **3o** was 8.7 kcal/mol, suggesting the **1a-III** may be converted directly to the thermodynamically stable product **3o** (Scheme 2).

In contrast, the reaction of **4** with a cyano group and alkene **2** produced [3+2] spiro compound **5a**. The calculated energy barrier of **4-TS$_{[2+1]}$** was 5.1 kcal/mol higher than **4-TS$_{[3+2]}$**, indicating that the [3+2] process was favorable and the theoretical result is consistent with the experimental data (Scheme 4).

To further analyze the selectivity, the natural population analysis (NPA) charge evaluation towards the reactants was conducted. The NPA charge values of **1a-II** and **4-II** showed that the eletrophilicity of C1 in **1a-II** was much weaker than that of C4 in **4-II** due to the higher negative charge, which suggested that a nucleophilic carbon anion would be easier to add to C4 atom. Moreover, the nucleophilicity of C2 is slightly stronger than that of C5. In addition, the distance of C3-N1 bond with value of 1.57 Å was a little longer than that of C6-N2 bond (1.55 Å), suggesting that DABCO in **1a-II** is easier to leave than that in **4-II** via a S_N2 reaction. Therefore, the introduction of a stronger electron-withdrawing group at C=C bond facilitated the Michael addition process, resulting in the completely switchable regioselectivity.



Scheme 5. Optimized structure of **1a-II** and **4-II.** The values in parentheses are corresponding NPA charge of certain atoms. The numbers in red were the distances between C-N bonds in Å.

(4) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Gaussian, Inc.: Wallingford, CT, USA, 2009.

(5) (a) Y. Zhao, N. E. Schultz and D. Truhlar, *J. Chem. Phys.*, 2005, **123**, 161103; (b) Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory. Comput.*, 2006, **2**, 364; (c) Y. Zhao and D. G. Truhlar, *J. Chem. Theory. Comput.*, 2006, **2**, 1009; (d) Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157; (e) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215; (f) Y. Zhao and D. G. Truhlar, *Chem. Phys. Lett.*, 2011, **502**, 1.

(6) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.

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(8) (a) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378; (b) R. F. Ribeiro, A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2011, **115**, 14556.

(9) G. Zhan, M.-L. Shi, Q. He, W.-J. Lin, Q. Ouyang, W. Du and Y.-C. Chen, *Angew. Chem., Int. Ed.*, 2016, **55**, 2147.

Computational data:

1a-II

Zero-point correction= 0.588938 (Hartree/Particle)

Thermal correction to Energy= 0.622199

Thermal correction to Enthalpy= 0.623143

Thermal correction to Gibbs Free Energy= 0.525358

SCF Done: E(SOV) = -1682.21857759 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.484287	-0.377648	0.913060
2	6	0	-6.058917	0.217630	-0.205069
3	6	0	-5.264926	0.886448	-1.136842
4	6	0	-3.901423	0.924964	-0.905625
5	6	0	-3.282134	0.305440	0.201978
6	6	0	-4.104004	-0.345421	1.121942
7	7	0	-2.954876	1.591590	-1.680324
8	6	0	-1.711208	1.474152	-1.136091
9	6	0	-1.828293	0.535606	0.051591
10	8	0	-0.733103	2.110031	-1.522350
11	6	0	-3.237779	2.332573	-2.884272
12	6	0	0.664804	0.205343	0.032788
13	6	0	-0.722680	0.016744	0.657317
14	6	0	-0.834986	-0.880146	1.848151
15	8	0	-1.771216	-1.579487	2.145353

16	8	0	0.258580	-0.783921	2.631905
17	6	0	0.290389	-1.711177	3.730743
18	6	0	0.234152	-2.110150	-0.494330
19	6	0	1.358069	-1.164290	-0.118728
20	1	0	-6.113283	-0.887717	1.635141
21	1	0	-7.132769	0.167167	-0.356482
22	1	0	-5.697980	1.360920	-2.011287
23	1	0	-3.684564	-0.831041	1.988733
24	1	0	-3.955149	3.135498	-2.684632
25	1	0	-3.643465	1.663068	-3.648678
26	1	0	-2.297633	2.758883	-3.233795
27	1	0	1.260586	-1.562653	4.205127
28	1	0	0.198249	-2.724946	3.341617
29	1	0	-0.517823	-1.483394	4.428682
30	1	0	0.487923	0.586285	-0.968864
31	6	0	2.513776	-1.175979	-1.104403
32	6	0	3.758683	-1.674258	-0.712570
33	6	0	2.353959	-0.741756	-2.427444
34	6	0	4.828122	-1.719117	-1.605349
35	1	0	3.879462	-2.054302	0.300091
36	6	0	3.421549	-0.782212	-3.318419
37	1	0	1.382864	-0.388383	-2.768645
38	6	0	4.664620	-1.265033	-2.909821
39	1	0	5.785705	-2.115247	-1.280362
40	1	0	3.279295	-0.444345	-4.340625
41	1	0	5.494806	-1.297683	-3.608654
42	1	0	1.712058	-1.539187	0.845143
43	6	0	-0.583290	-1.750642	-1.576841
44	7	0	-1.240867	-1.291431	-2.429242
45	6	0	0.016909	-3.262077	0.321912
46	8	0	0.724011	-3.511535	1.312011
47	6	0	-1.183728	-4.136263	0.021613
48	1	0	-2.011872	-3.788284	0.650238
49	1	0	-1.497745	-4.082938	-1.023169
50	1	0	-0.952883	-5.167441	0.296060

51	6	0	2.614832	0.826094	1.588383
52	1	0	2.146266	0.132866	2.282803
53	1	0	3.320957	0.284040	0.956419
54	6	0	2.228709	2.101912	-0.449943
55	1	0	2.721728	1.364880	-1.084893
56	1	0	1.428290	2.579867	-1.017588
57	6	0	0.683715	2.325230	1.418740
58	1	0	-0.149893	2.581184	0.765459
59	1	0	0.310330	1.792707	2.296315
60	7	0	2.966827	3.283518	1.603891
61	6	0	3.228734	3.102404	0.176240
62	1	0	3.150611	4.070064	-0.327126
63	1	0	4.257660	2.749041	0.060563
64	6	0	3.277122	2.033438	2.294223
65	1	0	4.361689	1.895789	2.321018
66	1	0	2.927014	2.120621	3.327238
67	6	0	1.543569	3.559998	1.781140
68	1	0	1.361418	3.848497	2.820236
69	1	0	1.278527	4.411580	1.147850
70	7	0	1.540212	1.341044	0.663712

1a-TS$_{[2+1]}$

Zero-point correction= 0.583783 (Hartree/Particle)

Thermal correction to Energy= 0.618064

Thermal correction to Enthalpy= 0.619008

Thermal correction to Gibbs Free Energy= 0.517083

SCF Done: E(SOV) = -1682.18453033 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-5.305115	0.831831	-1.113661
4	6	0	-3.931683	0.655859	-1.098265
5	6	0	-3.245641	0.090373	-0.003702
6	6	0	-3.978046	-0.260415	1.127684
7	7	0	-3.023785	1.024796	-2.090043
8	6	0	-1.728096	0.794809	-1.685334
9	6	0	-1.818081	0.083124	-0.356154
10	8	0	-0.742360	1.150802	-2.312690
11	6	0	-3.363630	1.695678	-3.321657
12	6	0	0.629484	-0.262552	-0.214563
13	6	0	-0.737368	-0.436620	0.285886
14	6	0	-0.904473	-1.096738	1.625378
15	8	0	-0.355689	-0.695269	2.625261
16	8	0	-1.737138	-2.130300	1.580162
17	6	0	-1.891109	-2.840753	2.814961
18	6	0	1.018972	-2.264058	-0.535005
19	6	0	1.758460	-1.145906	0.166904
20	1	0	-5.931107	-0.356418	2.014051
21	1	0	-7.096171	0.572023	0.042577
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23	1	0	-3.491775	-0.662973	2.007439
24	1	0	-3.868124	2.646469	-3.118308
25	1	0	-4.016455	1.064962	-3.932272
26	1	0	-2.431964	1.882378	-3.856494
27	1	0	-2.612421	-3.628916	2.605476
28	1	0	-2.265163	-2.168254	3.591444
29	1	0	-0.926041	-3.256747	3.105716
30	1	0	0.671767	0.123879	-1.227740
31	6	0	3.139166	-0.823316	-0.348715
32	6	0	4.236384	-1.021500	0.492776
33	6	0	3.366108	-0.383744	-1.657306
34	6	0	5.532144	-0.773128	0.048581
35	1	0	4.068633	-1.378939	1.506226
36	6	0	4.661800	-0.134784	-2.101807

37	1	0	2.535681	-0.243881	-2.344617
38	6	0	5.748087	-0.325029	-1.251319
39	1	0	6.371232	-0.933543	0.718796
40	1	0	4.820708	0.202896	-3.121356
41	1	0	6.756841	-0.131201	-1.602697
42	1	0	1.771674	-1.401879	1.229245
43	6	0	0.990563	-2.362811	-1.947564
44	7	0	0.945079	-2.440864	-3.107974
45	6	0	0.551803	-3.378665	0.280442
46	8	0	0.746847	-3.410129	1.493911
47	6	0	-0.210336	-4.486636	-0.413554
48	1	0	-1.182085	-4.098385	-0.739610
49	1	0	0.314305	-4.844995	-1.303380
50	1	0	-0.362504	-5.304152	0.291887
51	6	0	1.927356	1.525822	1.734249
52	1	0	1.412996	0.860109	2.432786
53	1	0	2.844291	1.037644	1.395898
54	6	0	1.765836	2.480899	-0.476284
55	1	0	2.617553	1.890360	-0.822602
56	1	0	1.077261	2.613971	-1.316091
57	6	0	-0.158479	2.430466	0.960411
58	1	0	-0.826499	2.484254	0.097263
59	1	0	-0.651463	1.846946	1.744076
60	7	0	1.695228	3.989913	1.502676
61	6	0	2.225571	3.833873	0.147286
62	1	0	1.884029	4.679579	-0.457931
63	1	0	3.317493	3.885406	0.203807
64	6	0	2.231488	2.923207	2.349579
65	1	0	3.310314	3.073937	2.456206
66	1	0	1.782669	3.023102	3.343014
67	6	0	0.241816	3.852250	1.453337
68	1	0	-0.161986	4.044750	2.452220
69	1	0	-0.151008	4.621905	0.781211
70	7	0	1.054120	1.693173	0.552055

1a-TS$_{[3+2]}$

Zero-point correction= 0.587688 (Hartree/Particle)

Thermal correction to Energy= 0.619996

Thermal correction to Enthalpy= 0.620940

Thermal correction to Gibbs Free Energy= 0.526303

SCF Done: E(SOV) = -1682.18450809 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.850283	-1.595725	-0.737669
2	6	0	-5.635707	-0.741464	0.031391
3	6	0	-5.049420	0.136840	0.943407
4	6	0	-3.667059	0.117849	1.048362
5	6	0	-2.852487	-0.730196	0.283304
6	6	0	-3.457551	-1.593682	-0.622843
7	7	0	-2.883425	0.910452	1.889564
8	6	0	-1.552699	0.682449	1.691719
9	6	0	-1.420788	-0.347287	0.550939
10	8	0	-0.668264	1.250076	2.320239
11	6	0	-3.390068	1.972597	2.725129
12	6	0	0.897255	-0.239085	0.438852
13	6	0	-0.257048	-1.204620	0.516819
14	6	0	-0.374301	-2.503681	-0.073562
15	8	0	-1.326931	-3.263425	-0.016940
16	8	0	0.779198	-2.945980	-0.716733
17	6	0	0.633936	-4.199948	-1.370197
18	6	0	-0.906872	0.861993	-0.858767
19	6	0	0.621041	0.699011	-0.811971
20	1	0	-5.321555	-2.274533	-1.441079
21	1	0	-6.716124	-0.755389	-0.075605
22	1	0	-5.649924	0.810364	1.546144
23	1	0	-2.857686	-2.255585	-1.232873

24	1	0	-4.098604	1.578153	3.459724
25	1	0	-3.881107	2.731578	2.107138
26	1	0	-2.537338	2.418031	3.237233
27	1	0	1.608685	-4.423821	-1.809444
28	1	0	-0.125396	-4.133203	-2.152841
29	1	0	0.342276	-4.980309	-0.664004
30	1	0	0.827309	0.407452	1.314954
31	6	0	1.391763	1.999919	-0.830212
32	6	0	2.260499	2.278832	-1.888525
33	6	0	1.292394	2.923387	0.219820
34	6	0	3.033051	3.439092	-1.896152
35	1	0	2.326688	1.579650	-2.720097
36	6	0	2.060269	4.083150	0.209852
37	1	0	0.615844	2.725237	1.049267
38	6	0	2.937857	4.342266	-0.842392
39	1	0	3.702217	3.637737	-2.728001
40	1	0	1.969979	4.791016	1.028149
41	1	0	3.536243	5.248052	-0.843856
42	1	0	0.872123	0.118040	-1.704364
43	6	0	-1.462407	2.167359	-0.596087
44	7	0	-1.982493	3.171729	-0.336923
45	6	0	-1.518983	0.193494	-2.056938
46	8	0	-0.981578	-0.793462	-2.529133
47	6	0	-2.807380	0.747456	-2.618729
48	1	0	-3.517862	1.005604	-1.828370
49	1	0	-2.586579	1.666831	-3.174160
50	1	0	-3.243511	0.009176	-3.292453
51	6	0	2.981880	-1.128171	-0.760241
52	1	0	2.258447	-1.689255	-1.345752
53	1	0	3.202738	-0.176865	-1.251136
54	6	0	3.226944	0.304725	1.171596
55	1	0	3.076090	1.232533	0.624946
56	1	0	2.871193	0.441619	2.196133
57	6	0	2.377668	-1.927324	1.525551
58	1	0	1.786763	-1.622323	2.391055

59	1	0	1.878452	-2.755039	1.033004
60	7	0	4.755335	-1.625287	0.897564
61	6	0	4.695275	-0.180438	1.104600
62	1	0	5.212372	0.074361	2.034020
63	1	0	5.226394	0.310680	0.283706
64	6	0	4.267411	-1.921621	-0.452755
65	1	0	5.041861	-1.668343	-1.182851
66	1	0	4.083032	-2.998533	-0.520025
67	6	0	3.851363	-2.250091	1.863086
68	1	0	4.002522	-3.333031	1.847008
69	1	0	4.120890	-1.893163	2.861827
70	7	0	2.339277	-0.760737	0.556765

1a-III

Zero-point correction= 0.396055 (Hartree/Particle)

Thermal correction to Energy= 0.422807

Thermal correction to Enthalpy= 0.423751

Thermal correction to Gibbs Free Energy= 0.338055

SCF Done: E(SOV) = -1336.89677306 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.352201	0.431873	-0.445307
2	6	0	-5.742944	-0.900215	-0.357565
3	6	0	-4.801407	-1.905029	-0.131457
4	6	0	-3.478168	-1.523633	0.009633
5	6	0	-3.050880	-0.179013	-0.064816
6	6	0	-4.012474	0.801250	-0.308851
7	7	0	-2.396817	-2.370395	0.239962
8	6	0	-1.226488	-1.658540	0.344695
9	6	0	-1.586723	-0.192295	0.136313

10	8	0	-0.143507	-2.145303	0.601425
11	6	0	-2.475489	-3.800977	0.407220
12	6	0	0.808013	0.374557	0.484334
13	6	0	-0.624289	0.753807	0.231350
14	6	0	-0.970523	2.210706	0.228496
15	8	0	-1.882868	2.727466	-0.364607
16	8	0	-0.129544	2.909304	1.014636
17	6	0	-0.379585	4.315574	1.040425
18	6	0	1.971541	1.231798	-0.016280
19	6	0	1.684787	-0.178660	-0.574864
20	1	0	-6.094944	1.200462	-0.630653
21	1	0	-6.789110	-1.166956	-0.472469
22	1	0	-5.093435	-2.948241	-0.069153
23	1	0	-3.726368	1.837373	-0.404644
24	1	0	-2.880330	-4.271366	-0.494467
25	1	0	-3.110582	-4.055508	1.262048
26	1	0	-1.461981	-4.162271	0.584493
27	1	0	0.355777	4.733334	1.726523
28	1	0	-1.393729	4.514575	1.392305
29	1	0	-0.262467	4.733807	0.036919
30	1	0	0.985505	-0.020117	1.482012
31	6	0	2.670515	-1.279338	-0.383671
32	6	0	3.419527	-1.687631	-1.490529
33	6	0	2.903339	-1.886677	0.851042
34	6	0	4.385406	-2.680742	-1.368246
35	1	0	3.242193	-1.219537	-2.455807
36	6	0	3.872263	-2.876655	0.975329
37	1	0	2.311257	-1.608292	1.716557
38	6	0	4.616588	-3.276451	-0.131418
39	1	0	4.957639	-2.986762	-2.238657
40	1	0	4.040672	-3.341431	1.941762
41	1	0	5.370846	-4.050593	-0.030009
42	1	0	1.271576	-0.090717	-1.578358
43	6	0	3.065639	1.390442	0.911955
44	7	0	3.938074	1.533766	1.658158

45	6	0	1.708277	2.377849	-0.957290
46	8	0	0.846002	2.272954	-1.803736
47	6	0	2.544583	3.619542	-0.792155
48	1	0	2.453727	3.995627	0.232471
49	1	0	3.602972	3.386345	-0.950491
50	1	0	2.215481	4.372048	-1.509037

1a-TS_{3o}

Zero-point correction= 0.395076 (Hartree/Particle)

Thermal correction to Energy= 0.421747

Thermal correction to Enthalpy= 0.422691

Thermal correction to Gibbs Free Energy= 0.337285

SCF Done: E(SOV) = -1336.87051491 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.354928	0.224223	0.015502
2	6	0	5.643277	-1.137919	0.011048
3	6	0	4.617190	-2.085465	-0.006018
4	6	0	3.320914	-1.607314	-0.026166
5	6	0	3.000429	-0.237407	-0.036013
6	6	0	4.037775	0.689033	-0.002166
7	7	0	2.135689	-2.371069	-0.026709
8	6	0	1.060422	-1.561405	-0.036473
9	6	0	1.530074	-0.154647	-0.082087
10	8	0	-0.118875	-1.986234	-0.027857
11	6	0	2.079389	-3.816524	0.016157
12	6	0	-0.846552	0.554101	-0.401534
13	6	0	0.628082	0.835208	-0.248789
14	6	0	1.047492	2.261277	-0.460136
15	8	0	1.964314	2.814307	0.091942

16	8	0	0.266805	2.835826	-1.378334
17	6	0	0.518983	4.223068	-1.608408
18	6	0	-1.767556	1.508535	0.327185
19	6	0	-1.337202	-0.620709	0.342224
20	1	0	6.167248	0.942885	0.043199
21	1	0	6.675505	-1.472482	0.029248
22	1	0	4.829135	-3.149754	-0.000628
23	1	0	3.824982	1.748757	0.029571
24	1	0	2.594988	-4.181976	0.908799
25	1	0	2.552399	-4.238223	-0.875168
26	1	0	1.030388	-4.110195	0.048943
27	1	0	-0.225712	4.539631	-2.335936
28	1	0	1.530034	4.364654	-1.996496
29	1	0	0.410222	4.778797	-0.674793
30	1	0	-1.081547	0.525854	-1.470527
31	6	0	-2.588898	-1.321304	0.005404
32	6	0	-3.075043	-2.265711	0.917551
33	6	0	-3.283299	-1.103775	-1.188669
34	6	0	-4.231753	-2.982448	0.642494
35	1	0	-2.533377	-2.435366	1.844514
36	6	0	-4.448548	-1.812930	-1.456498
37	1	0	-2.942140	-0.360450	-1.900975
38	6	0	-4.922216	-2.754192	-0.546516
39	1	0	-4.600786	-3.711172	1.357196
40	1	0	-4.990749	-1.621620	-2.376568
41	1	0	-5.833289	-3.304553	-0.760066
42	1	0	-1.064169	-0.594019	1.394737
43	6	0	-2.948745	1.918564	-0.324649
44	7	0	-3.914173	2.218572	-0.903325
45	6	0	-1.355005	1.965154	1.615018
46	8	0	-0.277517	1.589440	2.104843
47	6	0	-2.242675	2.921108	2.386647
48	1	0	-1.722781	3.879140	2.483535
49	1	0	-3.211305	3.084009	1.910710
50	1	0	-2.386242	2.525742	3.395545

3o

Zero-point correction= 0.399019 (Hartree/Particle)

Thermal correction to Energy= 0.424903

Thermal correction to Enthalpy= 0.425847

Thermal correction to Gibbs Free Energy= 0.341665

SCF Done: E(SOV) = -1336.91416730 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.159982	0.267202	0.541846
2	6	0	5.454255	-1.105070	0.509433
3	6	0	4.445677	-2.056166	0.413156
4	6	0	3.134802	-1.591970	0.349484
5	6	0	2.817304	-0.212557	0.390392
6	6	0	3.850674	0.724856	0.486200
7	7	0	1.949905	-2.309507	0.237617
8	6	0	0.927236	-1.406315	0.203838
9	6	0	1.384699	-0.120540	0.306941
10	8	0	-0.340090	-1.822438	0.067089
11	6	0	1.821975	-3.748741	0.192970
12	6	0	-0.962919	0.537288	-0.232595
13	6	0	0.469465	1.021325	0.104446
14	6	0	1.001775	1.963166	-0.992085
15	8	0	1.356460	3.097461	-0.807591
16	8	0	1.042926	1.339920	-2.173831
17	6	0	1.597253	2.115520	-3.238495
18	6	0	-1.752248	1.675949	0.381613
19	6	0	-1.279755	-0.805907	0.464867
20	1	0	5.973073	0.982278	0.617363
21	1	0	6.488204	-1.431120	0.560240

22	1	0	4.672131	-3.117925	0.384874
23	1	0	3.623840	1.786924	0.520193
24	1	0	2.279316	-4.196917	1.080109
25	1	0	2.305498	-4.150201	-0.702824
26	1	0	0.761039	-3.999019	0.171001
27	1	0	1.554514	1.480114	-4.121082
28	1	0	2.630036	2.382924	-3.004807
29	1	0	1.015073	3.027350	-3.386882
30	1	0	-1.095861	0.426623	-1.312681
31	6	0	-2.664245	-1.294323	0.139752
32	6	0	-3.713744	-1.052207	1.023909
33	6	0	-2.919210	-1.929864	-1.076958
34	6	0	-5.011849	-1.428879	0.692003
35	1	0	-3.516407	-0.552174	1.969078
36	6	0	-4.213968	-2.318949	-1.401686
37	1	0	-2.097105	-2.126863	-1.759269
38	6	0	-5.262782	-2.064426	-0.519795
39	1	0	-5.825244	-1.223955	1.380481
40	1	0	-4.406517	-2.816302	-2.347304
41	1	0	-6.274670	-2.359712	-0.779205
42	1	0	-1.165413	-0.656114	1.547722
43	6	0	-3.117088	1.991549	0.150421
44	7	0	-4.228378	2.267104	-0.034729
45	6	0	-0.949049	2.331666	1.249123
46	8	0	0.311148	1.849845	1.279514
47	6	0	-1.230904	3.477944	2.147514
48	1	0	-0.595102	4.320407	1.859282
49	1	0	-2.280644	3.768469	2.085067
50	1	0	-0.984022	3.210446	3.179199

4-II

Zero-point correction= 0.542143 (Hartree/Particle)

Thermal correction to Energy= 0.573473

Thermal correction to Enthalpy= 0.574417

Thermal correction to Gibbs Free Energy= 0.479184

SCF Done: E(SOV) = -1546.60593438 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.254327	0.387390	-1.488520
2	6	0	-5.988151	0.090362	-0.341768
3	6	0	-5.366437	-0.395631	0.811910
4	6	0	-3.995432	-0.575710	0.768521
5	6	0	-3.235628	-0.284247	-0.382204
6	6	0	-3.869781	0.208769	-1.517497
7	7	0	-3.159704	-1.048517	1.781313
8	6	0	-1.851157	-1.068744	1.371032
9	6	0	-1.840632	-0.527558	-0.032221
10	8	0	-0.920955	-1.543936	2.016844
11	6	0	-3.583614	-1.394871	3.115639
12	6	0	0.660048	-0.218972	-0.054413
13	6	0	-0.705892	-0.223247	-0.715465
14	6	0	0.160686	2.135169	-0.187963
15	6	0	1.301936	1.149155	-0.341459
16	1	0	-5.761488	0.767623	-2.368802
17	1	0	-7.063003	0.242331	-0.338643
18	1	0	-5.936137	-0.615976	1.708825
19	1	0	-3.305582	0.452132	-2.411362
20	1	0	-4.338807	-2.186803	3.085232
21	1	0	-3.994975	-0.515954	3.621769
22	1	0	-2.703811	-1.746592	3.655026
23	1	0	0.492773	-0.334468	1.016916
24	6	0	2.525627	1.470281	0.492462
25	6	0	3.744630	1.758934	-0.123441
26	6	0	2.451029	1.500827	1.891381

27	6	0	4.878617	2.043178	0.637479
28	1	0	3.793780	1.791452	-1.210270
29	6	0	3.581852	1.780233	2.650329
30	1	0	1.497355	1.319746	2.384020
31	6	0	4.801691	2.044611	2.026046
32	1	0	5.817467	2.272482	0.142208
33	1	0	3.510040	1.802749	3.733606
34	1	0	5.682058	2.266853	2.621162
35	1	0	1.564358	1.231939	-1.403170
36	6	0	-0.648012	2.056311	0.951352
37	7	0	-1.318021	1.826973	1.884347
38	6	0	0.002173	3.115543	-1.227912
39	8	0	0.751272	3.147563	-2.207324
40	6	0	-1.166617	4.080553	-1.141221
41	1	0	-1.945809	3.738781	-1.831225
42	1	0	-1.594230	4.149192	-0.138648
43	1	0	-0.836278	5.066006	-1.476387
44	6	0	2.309828	-1.257186	-1.684363
45	1	0	1.634195	-0.869997	-2.450836
46	1	0	3.057103	-0.495205	-1.454241
47	6	0	2.462899	-1.769420	0.709682
48	1	0	2.970803	-0.844866	0.981652
49	1	0	1.829210	-2.083006	1.544569
50	6	0	0.635112	-2.679414	-0.606231
51	1	0	-0.044718	-2.704939	0.247747
52	1	0	0.063701	-2.516490	-1.522281
53	7	0	2.932182	-3.546023	-0.952426
54	6	0	3.444833	-2.865490	0.236755
55	1	0	3.597962	-3.598288	1.033618
56	1	0	4.418355	-2.431023	-0.008966
57	6	0	2.955047	-2.609240	-2.075180
58	1	0	3.989910	-2.446098	-2.387807
59	1	0	2.422901	-3.067272	-2.913844
60	6	0	1.544748	-3.928079	-0.697632
61	1	0	1.197008	-4.581412	-1.502484

62	1	0	1.512283	-4.500336	0.233927
63	7	0	1.511575	-1.460490	-0.423205
64	6	0	-0.753280	0.133499	-2.104221
65	7	0	-0.734562	0.323256	-3.248989

4-TS$_{[2+1]}$

Zero-point correction= 0.538107 (Hartree/Particle)

Thermal correction to Energy= 0.570114

Thermal correction to Enthalpy= 0.571058

Thermal correction to Gibbs Free Energy= 0.472509

SCF Done: E(SOV) = -1546.56191510 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.303301	-0.266009	-1.748821
2	6	0	6.092780	0.010672	-0.634669
3	6	0	5.518917	0.273504	0.612511
4	6	0	4.138219	0.253075	0.694752
5	6	0	3.319401	-0.017548	-0.421263
6	6	0	3.910834	-0.287010	-1.652705
7	7	0	3.345343	0.482845	1.822161
8	6	0	2.007838	0.397073	1.511381
9	6	0	1.939748	0.014601	0.055436
10	8	0	1.093283	0.663829	2.275526
11	6	0	3.839013	0.846281	3.128884
12	6	0	-0.553527	-0.276796	0.045871
13	6	0	0.775315	-0.252528	-0.595554
14	6	0	-0.724989	-2.349727	0.018964
15	6	0	-1.584711	-1.209809	-0.486671
16	1	0	5.773650	-0.469369	-2.704745

17	1	0	7.173822	0.020957	-0.732074
18	1	0	6.132439	0.484130	1.482499
19	1	0	3.308606	-0.509695	-2.526220
20	1	0	4.403991	1.783011	3.081338
21	1	0	4.483208	0.056308	3.526715
22	1	0	2.973081	0.972937	3.779511
23	1	0	-0.526899	-0.151515	1.124090
24	6	0	-3.006754	-1.142964	0.012871
25	6	0	-4.047213	-1.235291	-0.915133
26	6	0	-3.325271	-1.041721	1.371669
27	6	0	-5.377164	-1.213563	-0.503882
28	1	0	-3.808247	-1.333343	-1.971721
29	6	0	-4.655023	-1.018621	1.783409
30	1	0	-2.536040	-0.993710	2.117499
31	6	0	-5.684673	-1.101641	0.848639
32	1	0	-6.170600	-1.289849	-1.241107
33	1	0	-4.884950	-0.944424	2.841880
34	1	0	-6.720016	-1.086752	1.174748
35	1	0	-1.554744	-1.272242	-1.579586
36	6	0	-0.695212	-2.685059	1.392773
37	7	0	-0.650817	-2.949679	2.526201
38	6	0	-0.060294	-3.211756	-0.951949
39	8	0	-0.146729	-3.010944	-2.157946
40	6	0	0.755708	-4.366600	-0.404370
41	1	0	1.552499	-3.993291	0.248098
42	1	0	0.132579	-5.032019	0.201010
43	1	0	1.187772	-4.917702	-1.239828
44	6	0	-1.972961	1.750178	-1.432450
45	1	0	-1.405538	1.348568	-2.278786
46	1	0	-2.841040	1.108267	-1.263636
47	6	0	-1.892635	2.079363	0.962725
48	1	0	-2.682395	1.343252	1.124723
49	1	0	-1.206859	2.045010	1.815390
50	6	0	0.029687	2.586402	-0.384921
51	1	0	0.685530	2.443568	0.477091

52	1	0	0.572847	2.297115	-1.289358
53	7	0	-1.958244	4.066708	-0.529722
54	6	0	-2.477673	3.500978	0.716110
55	1	0	-2.221558	4.175971	1.538370
56	1	0	-3.568952	3.464016	0.643352
57	6	0	-2.393273	3.233289	-1.651236
58	1	0	-3.480299	3.315089	-1.744826
59	1	0	-1.949213	3.636734	-2.566395
60	6	0	-0.498278	4.048581	-0.475063
61	1	0	-0.107883	4.545338	-1.368359
62	1	0	-0.182179	4.630754	0.395978
63	7	0	-1.118211	1.662858	-0.228063
64	6	0	0.799205	-0.333353	-2.034187
65	7	0	0.812368	-0.234757	-3.188435

4-TS$_{[3+2]}$

Zero-point correction= 0.541923 (Hartree/Particle)

Thermal correction to Energy= 0.571868

Thermal correction to Enthalpy= 0.572812

Thermal correction to Gibbs Free Energy= 0.482652

SCF Done: E(SOV) = -1546.58030766 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.602915	-2.045917	-1.031094
2	6	0	-5.509296	-1.299668	-0.283091
3	6	0	-5.076731	-0.380281	0.678783
4	6	0	-3.709931	-0.242135	0.854456
5	6	0	-2.783313	-0.974775	0.096286
6	6	0	-3.224344	-1.885009	-0.851605
7	7	0	-3.034619	0.588120	1.754942
8	6	0	-1.674598	0.455342	1.627736

9	6	0	-1.426112	-0.493646	0.459201
10	8	0	-0.849308	1.030420	2.318684
11	6	0	-3.660974	1.562579	2.616110
12	6	0	0.928680	-0.391596	0.473911
13	6	0	-0.256460	-1.306668	0.462537
14	6	0	-0.825955	0.877073	-0.820875
15	6	0	0.684411	0.674415	-0.688455
16	1	0	-4.967544	-2.755248	-1.766482
17	1	0	-6.574938	-1.432329	-0.443612
18	1	0	-5.783823	0.198404	1.264309
19	1	0	-2.514898	-2.445070	-1.452553
20	1	0	-4.329355	1.074266	3.332175
21	1	0	-4.225322	2.284464	2.017229
22	1	0	-2.864000	2.080985	3.149699
23	1	0	0.971718	0.161155	1.417769
24	6	0	1.484505	1.947806	-0.550132
25	6	0	2.345433	2.333678	-1.581601
26	6	0	1.426330	2.726958	0.611751
27	6	0	3.153987	3.460213	-1.453113
28	1	0	2.378672	1.743177	-2.495380
29	6	0	2.234623	3.852743	0.738552
30	1	0	0.736862	2.451795	1.408235
31	6	0	3.105374	4.218447	-0.286541
32	1	0	3.816317	3.746287	-2.264679
33	1	0	2.180439	4.451609	1.642642
34	1	0	3.734472	5.097068	-0.181283
35	1	0	0.965969	0.177302	-1.620418
36	6	0	-1.378320	2.156843	-0.463292
37	7	0	-1.890581	3.146718	-0.139465
38	6	0	-1.388584	0.297597	-2.077750
39	8	0	-0.808985	-0.625777	-2.625661
40	6	0	-2.699744	0.838159	-2.599173
41	1	0	-3.431485	0.960881	-1.794981
42	1	0	-2.534159	1.826389	-3.043130
43	1	0	-3.085166	0.154263	-3.356053

44	6	0	2.615309	-1.627806	-0.976557
45	1	0	1.725134	-2.086487	-1.408281
46	1	0	2.890845	-0.751385	-1.567857
47	6	0	3.409898	-0.178995	0.805992
48	1	0	3.316274	0.746484	0.241370
49	1	0	3.258370	0.042377	1.865803
50	6	0	2.291256	-2.247126	1.404363
51	1	0	1.886022	-1.845185	2.335297
52	1	0	1.614024	-3.009708	1.026743
53	7	0	4.546562	-2.343339	0.400892
54	6	0	4.749686	-0.902069	0.526228
55	1	0	5.454243	-0.703203	1.338578
56	1	0	5.199141	-0.533546	-0.400757
57	6	0	3.799019	-2.607820	-0.832209
58	1	0	4.466946	-2.506558	-1.692189
59	1	0	3.440599	-3.641141	-0.805248
60	6	0	3.734844	-2.780646	1.535860
61	1	0	3.717234	-3.873267	1.568186
62	1	0	4.212095	-2.427328	2.455095
63	7	0	2.281244	-1.103050	0.403315
64	6	0	-0.234652	-2.551781	-0.188086
65	7	0	-0.110735	-3.622605	-0.643050

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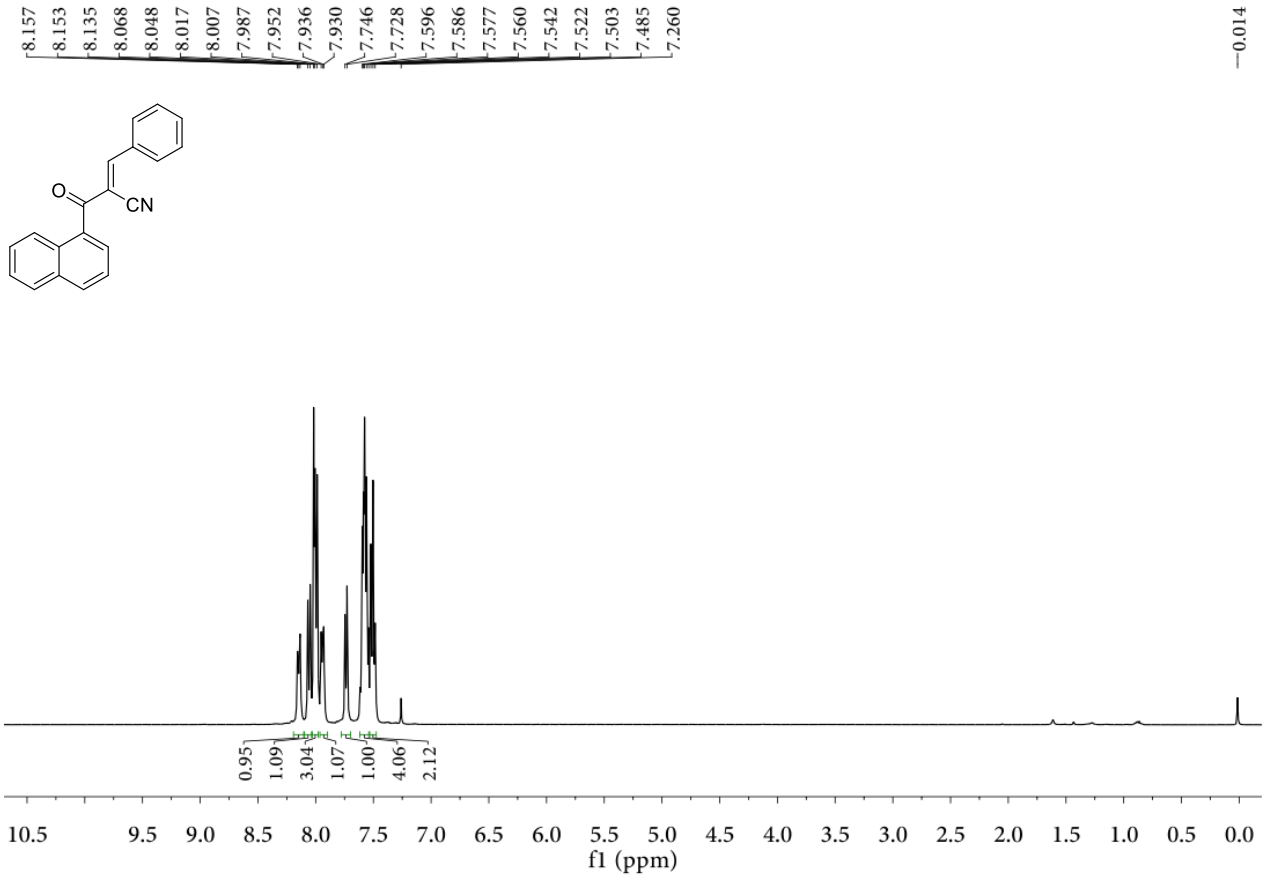
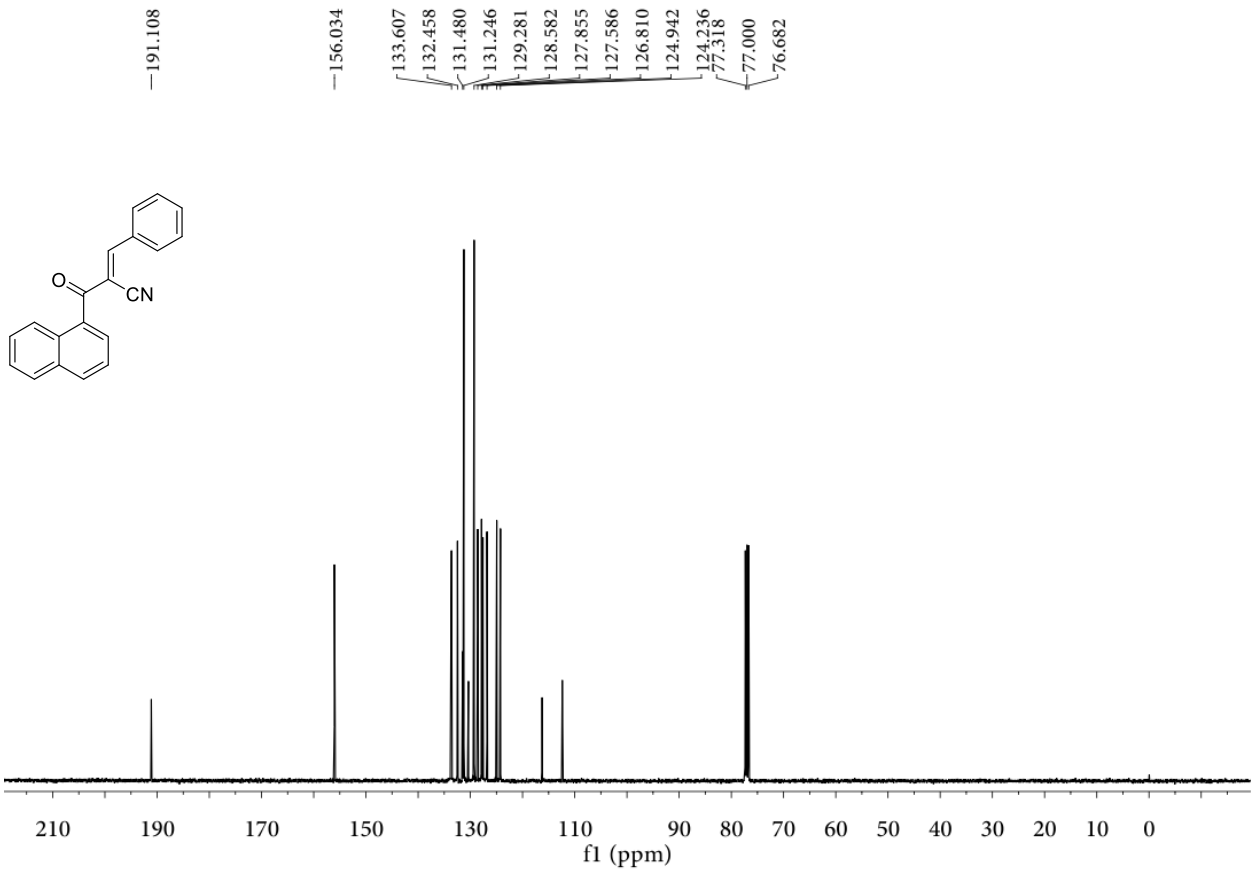
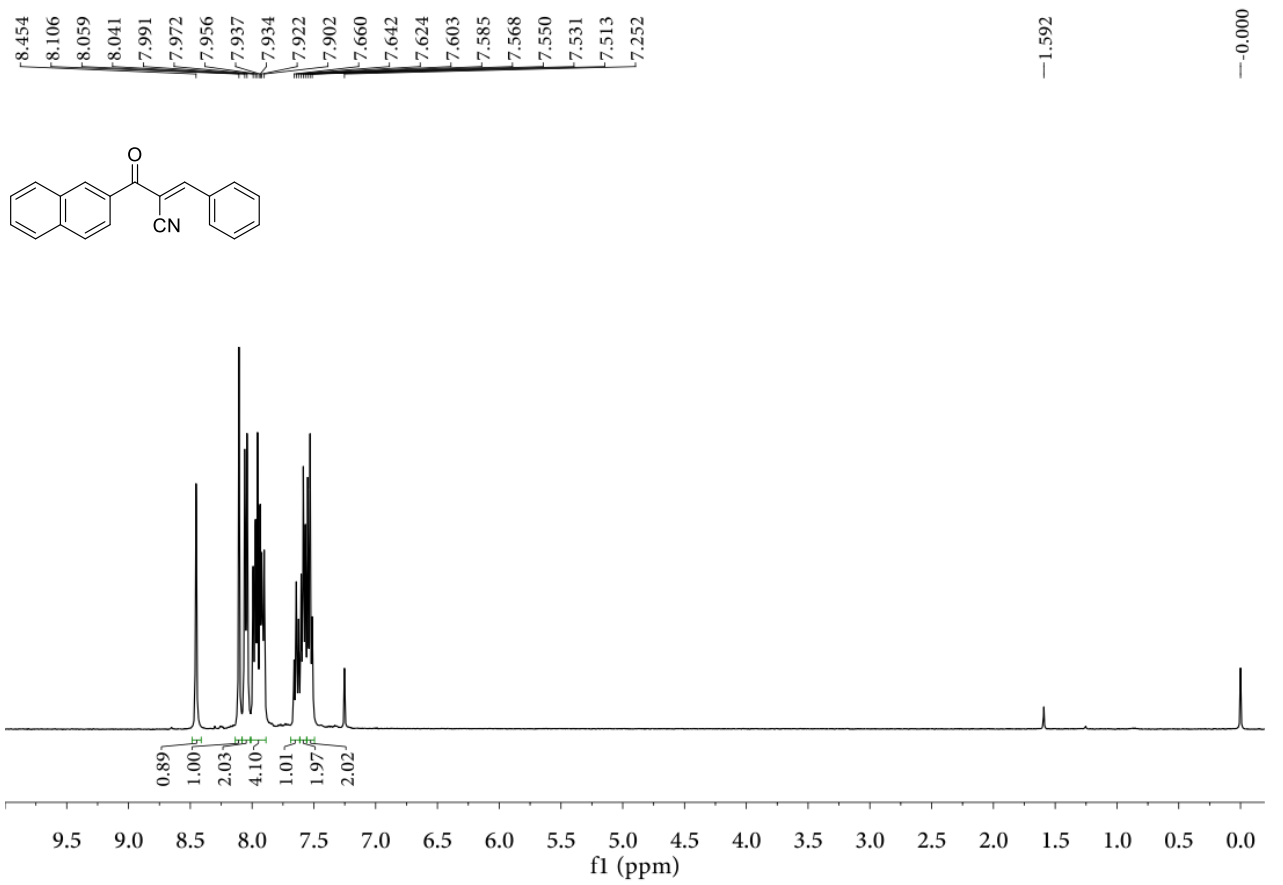
10. NMR spectra and HPLC chromatograms



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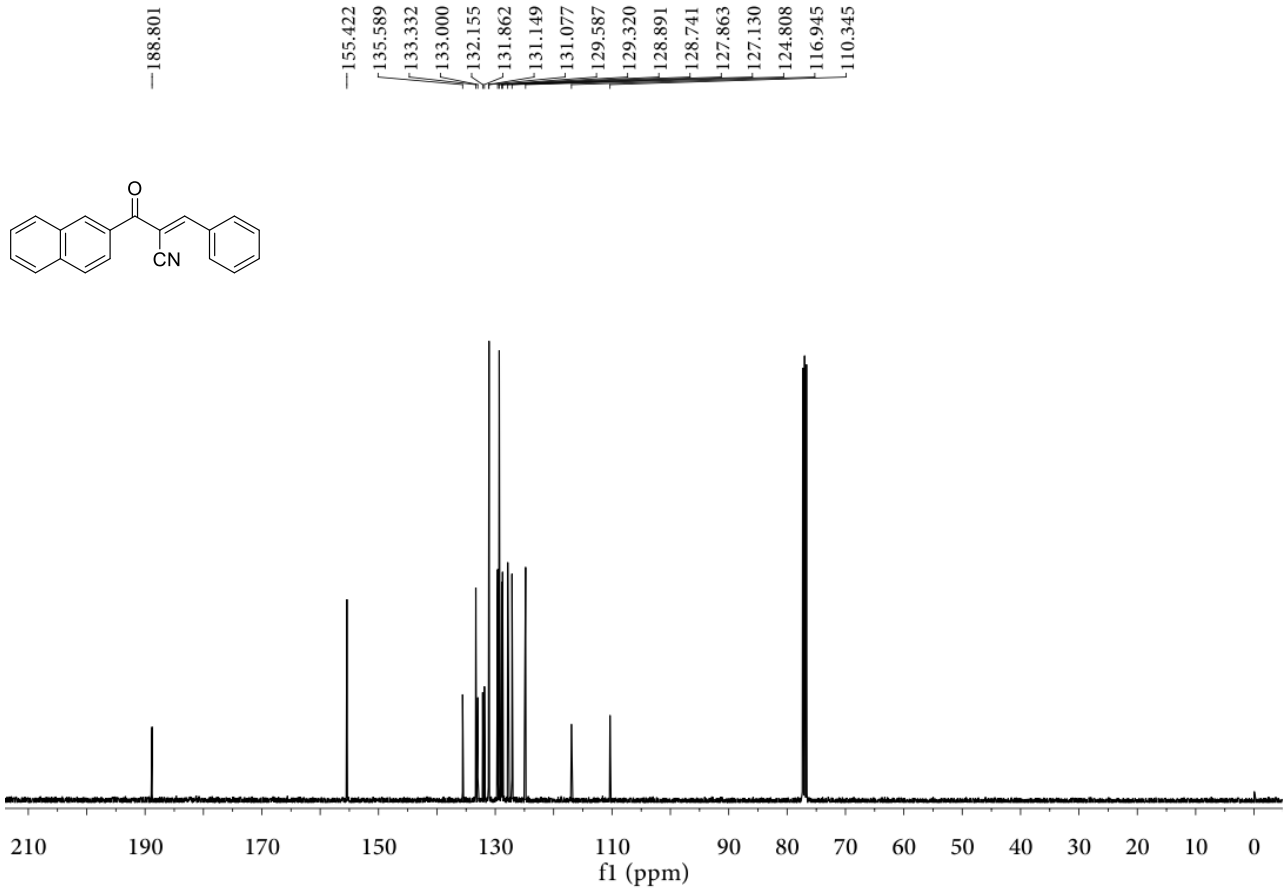
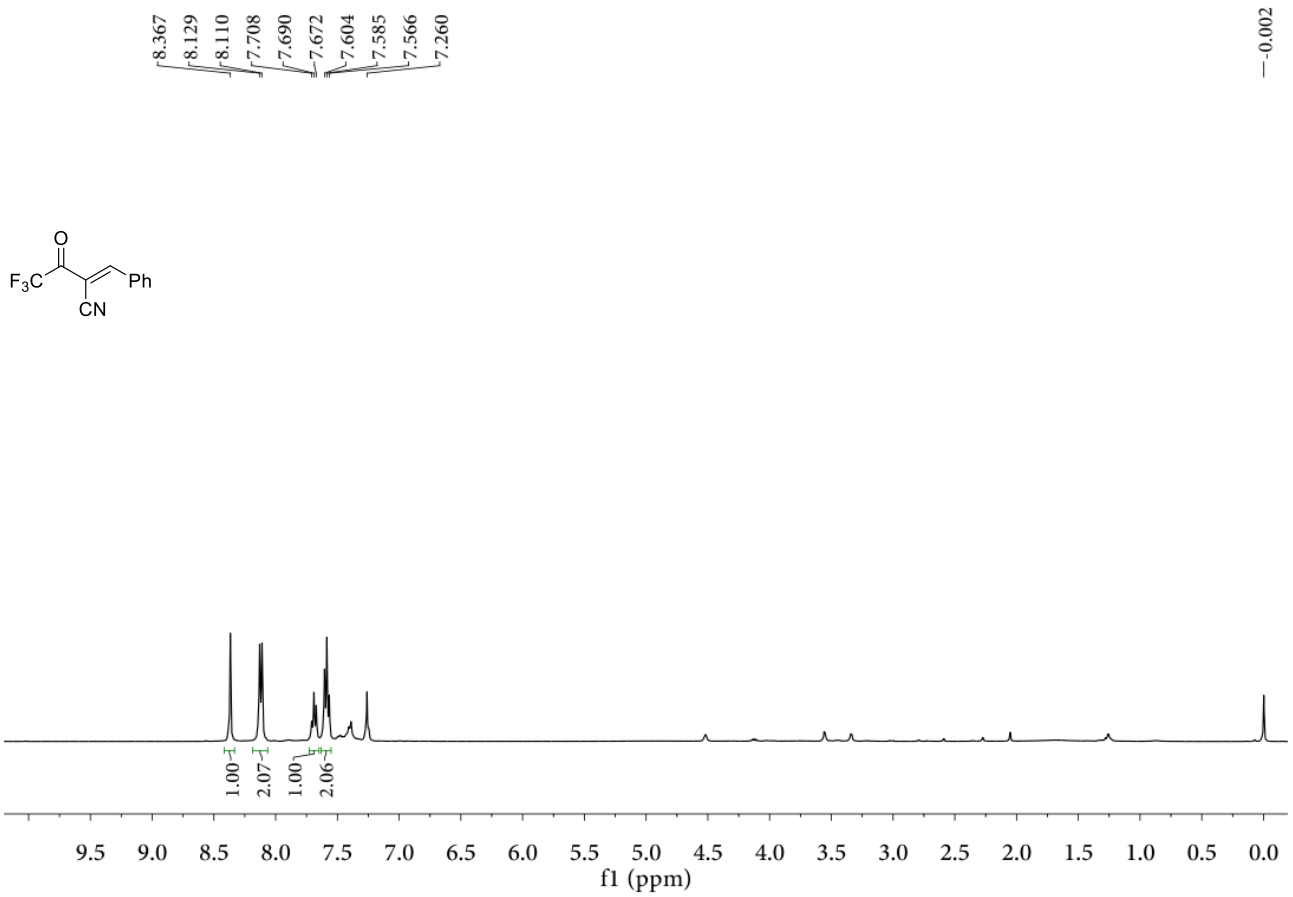
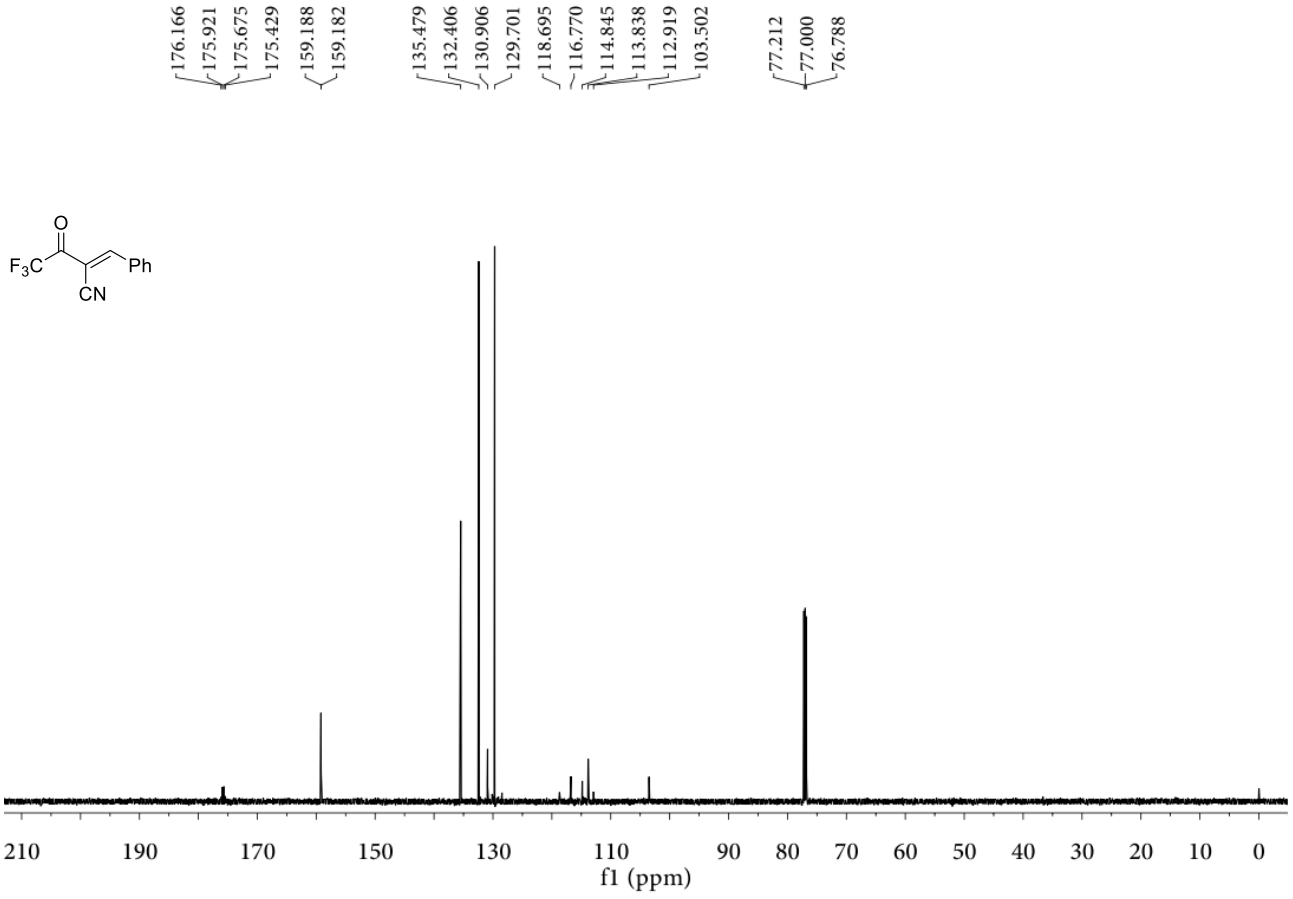
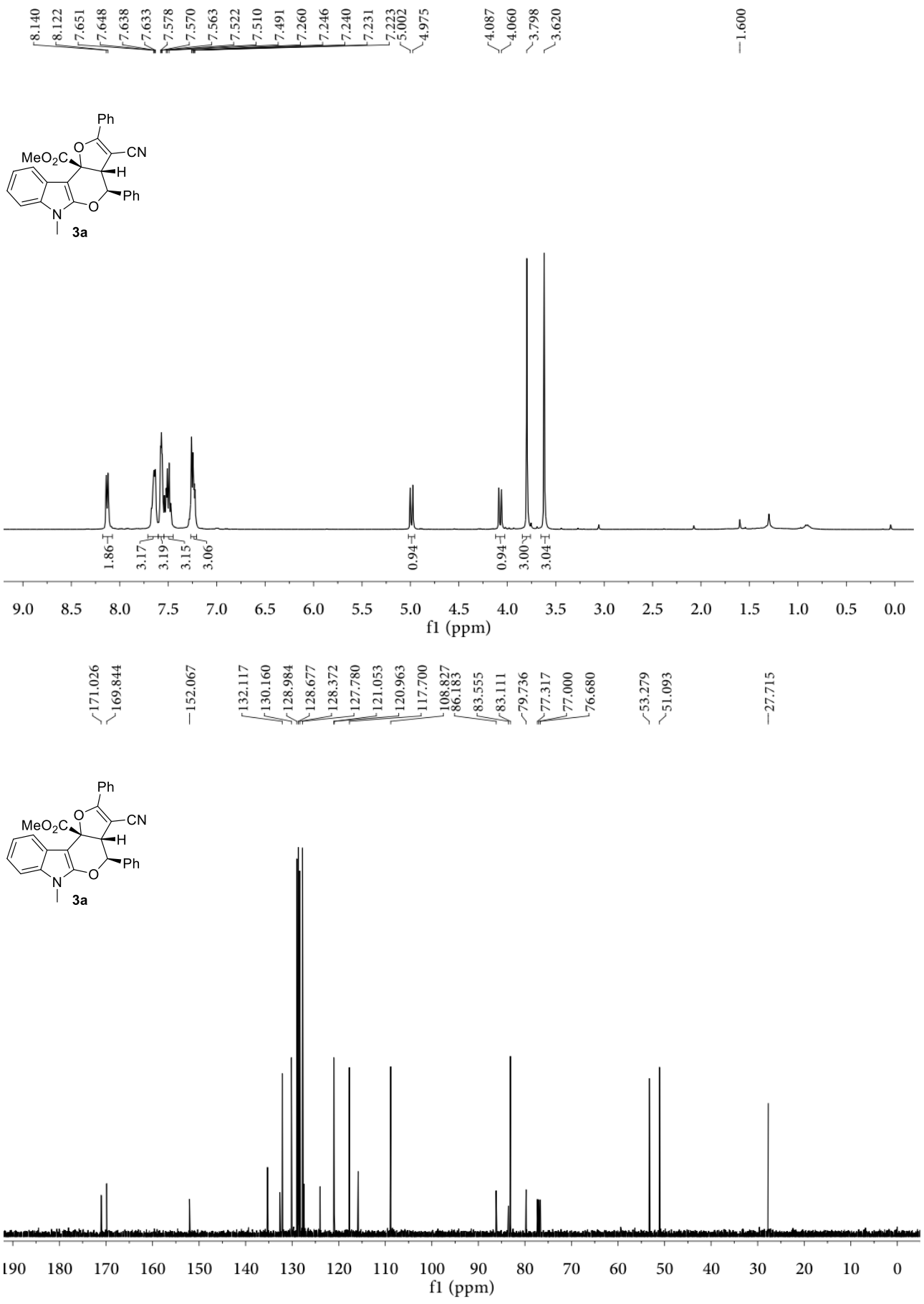
8.059
8.041
7.991
7.972
7.956
7.937
7.934
7.922
7.902
7.660
7.642
7.624
7.603
7.585
7.568
7.550
7.531
7.513
7.252
1.592
0.000
O
CN
0.89
1.00
2.03
4.10
1.01
1.97
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.801
155.422
135.589
133.332
133.000
132.155
131.862
131.149
131.077
129.587
129.320
128.891
128.741
127.863
127.130
124.808
116.945
110.345
O
CN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.367
8.129
8.110
7.708
7.690
7.672
7.604
7.585
7.566
7.260
-0.002
O
F3C
Ph
CN
1.00
2.07
1.00
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.166
175.921
175.675
175.429
159.188
159.182
135.479
132.406
130.906
129.701
118.695
116.770
114.845
113.838
112.919
103.502
77.212
77.000
76.788
O
F3C
Ph
CN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.140
8.122
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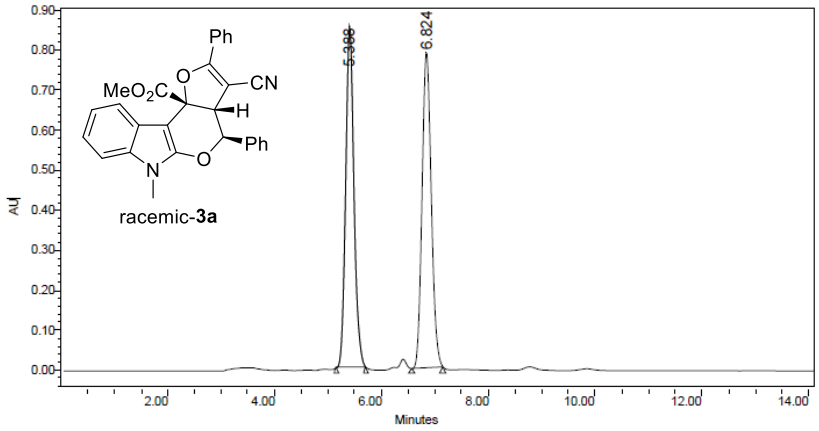
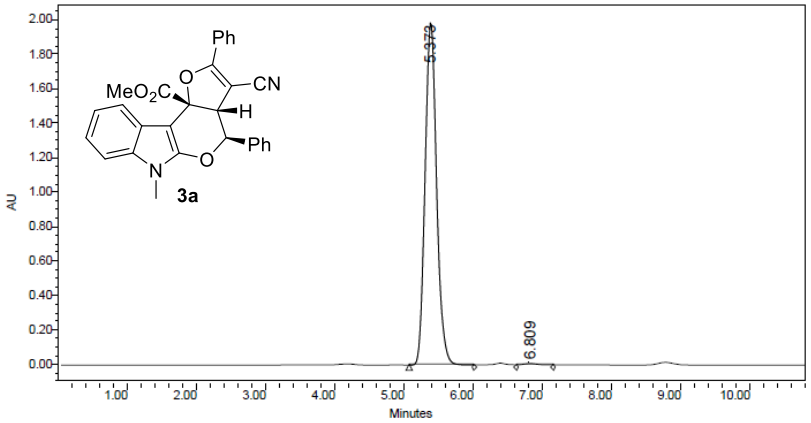
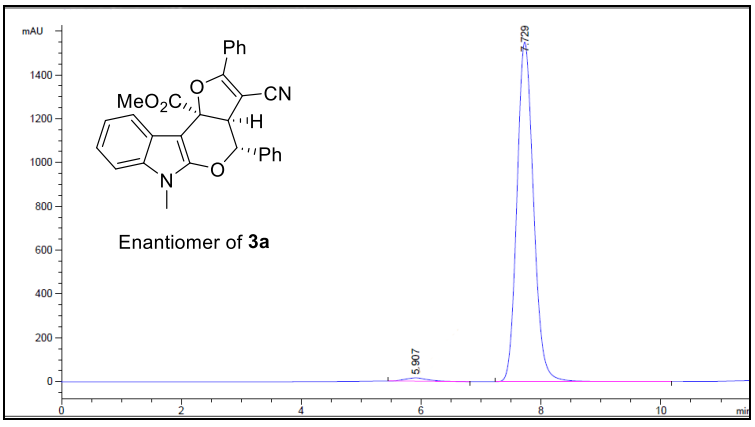
7.648
7.638
7.633
7.578
7.570
7.563
7.522
7.510
7.491
7.260
7.246
7.240
7.231
7.223
5.002
4.975
4.087
4.060
3.798
3.620
1.600
Ph
MeO2C
O
CN
H
Ph
O
N
3a
1.86
3.17
3.19
3.15
3.06
0.94
0.94
3.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
171.026
169.844
152.067
132.117
130.160
128.984
128.677
128.372
127.780
121.053
120.963
117.700
108.827
86.183
83.555
83.111
79.736
77.317
77.000
76.680
53.279
51.093
27.715
Ph
MeO2C
O
CN
H
Ph
O
N
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



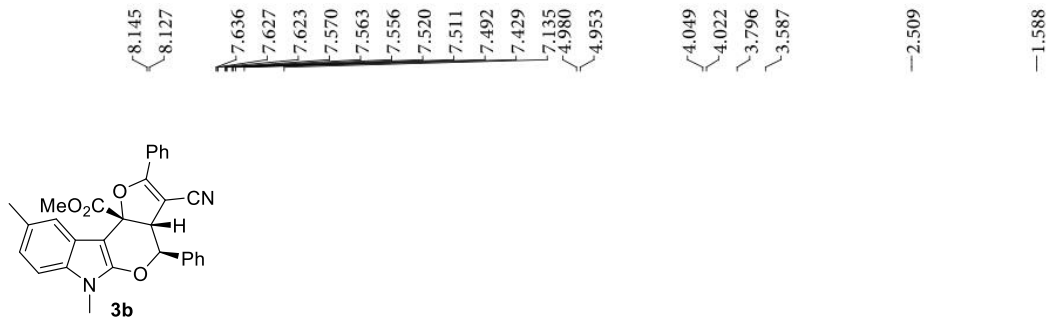
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	5.388	9152528	49.10	854109	51.90
2	6.824	9488979	50.90	791659	48.10



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	5.373	23091772	99.47	1991730	99.51
2	6.809	123363	0.53	9711	0.49

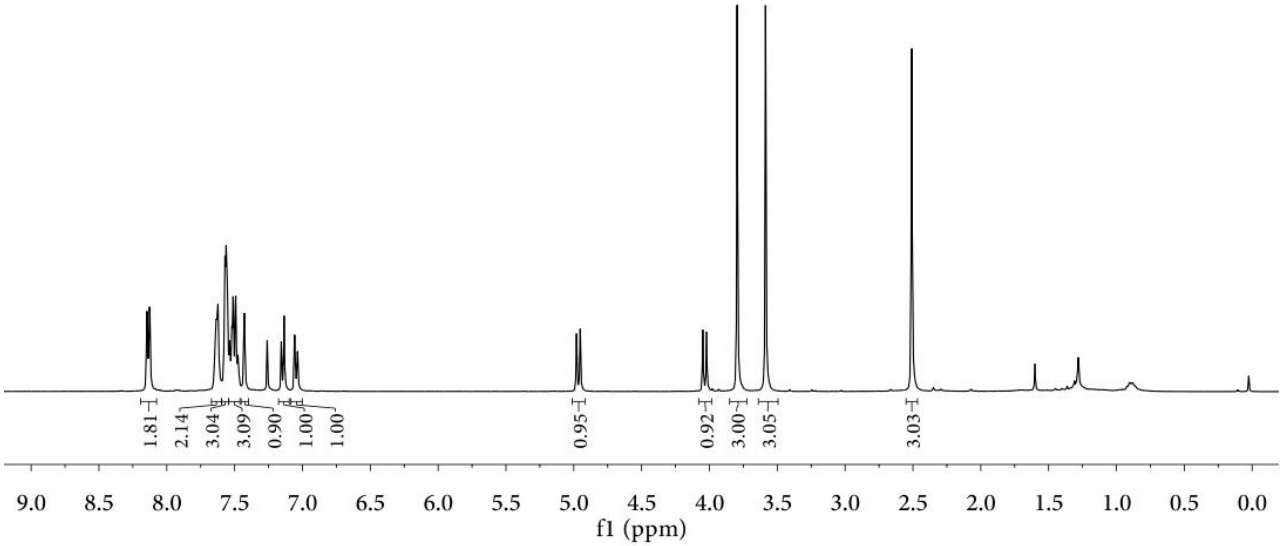


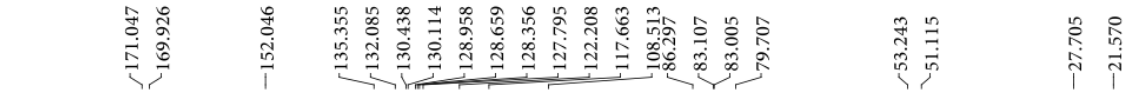
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.907	MM	0.4295	379.61414	14.73107	1.2591
2	7.729	BV	0.3001	2.97702e4	1547.93909	98.7409


8.145
8.127
7.636
7.627
7.623
7.570
7.563
7.556
7.520
7.511
7.492
7.429
7.135
4.980
4.953
4.049
4.022
3.796
3.587
2.509
1.588

Ph
MeO2C
O
CN
H
Ph
N
O

3b


1.81
2.14
3.04
3.09
0.90
1.00
1.00
0.95
0.92
3.00
3.05
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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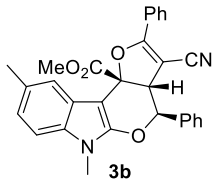
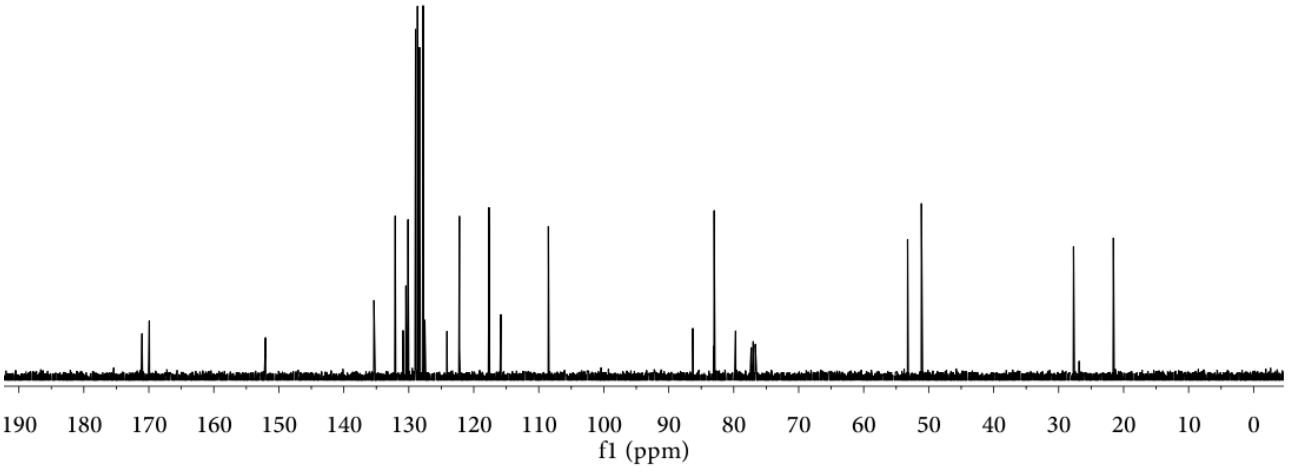
169.926
152.046
135.355
132.085
130.438
130.114
128.958
128.659
128.356
127.795
122.208
117.663
108.513
86.297
83.107
83.005
79.707
53.243
51.115
27.705
21.570


Ph
MeO2C
O
CN
H
Ph
N
O

3b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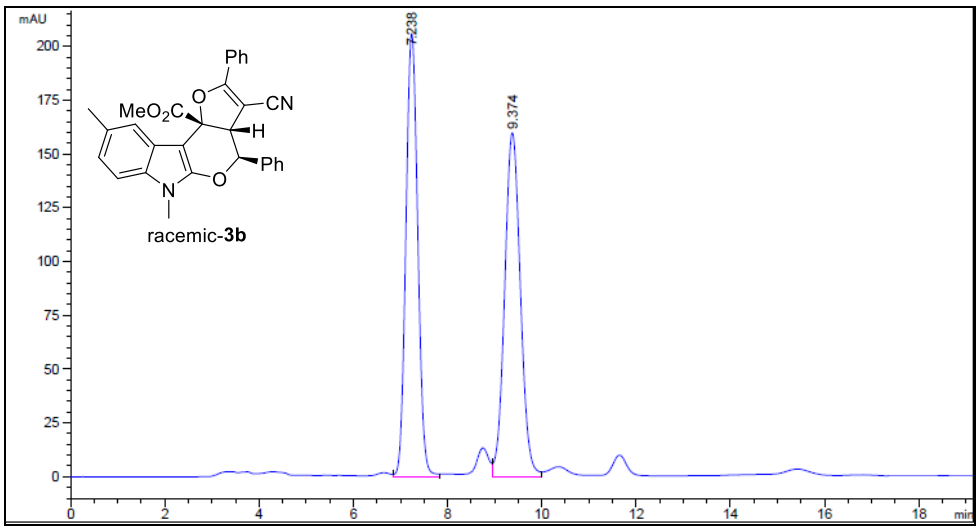
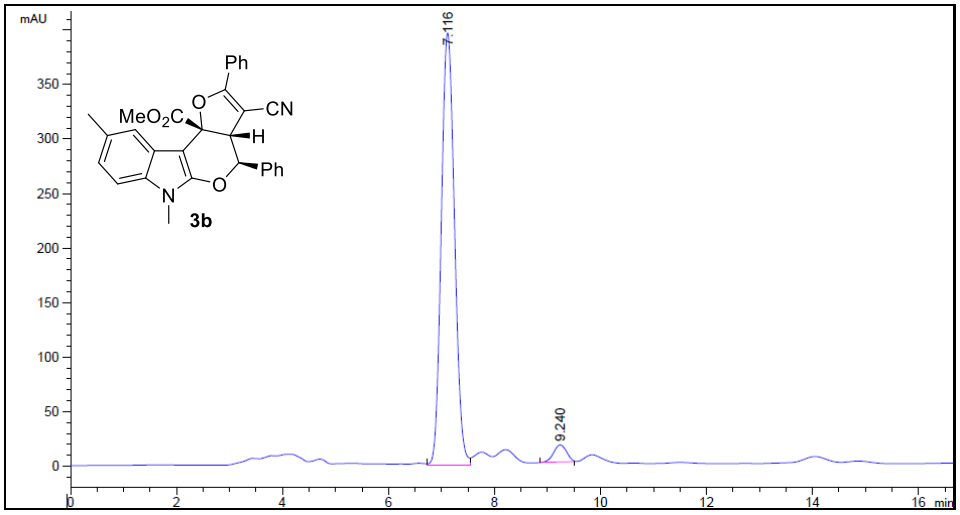
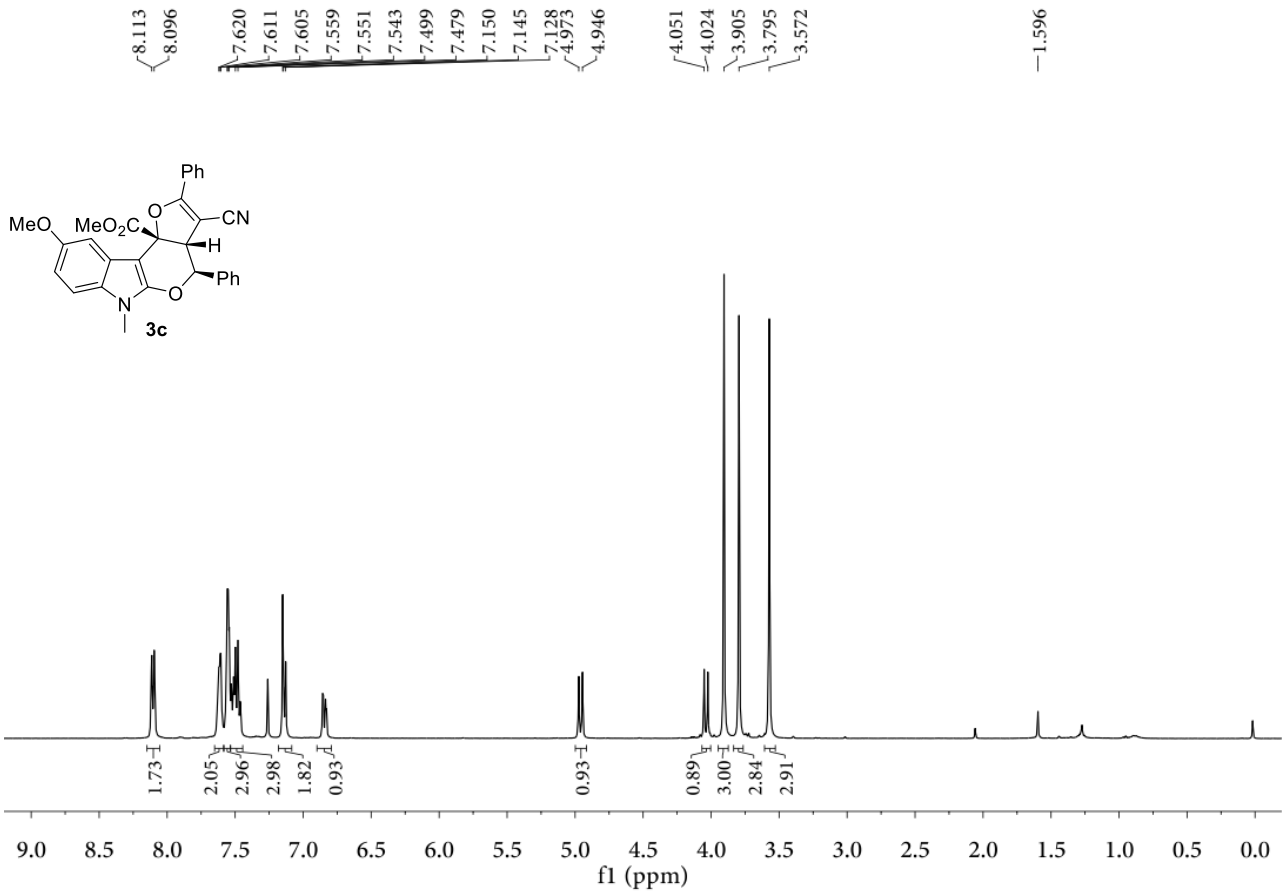
f1 (ppm)

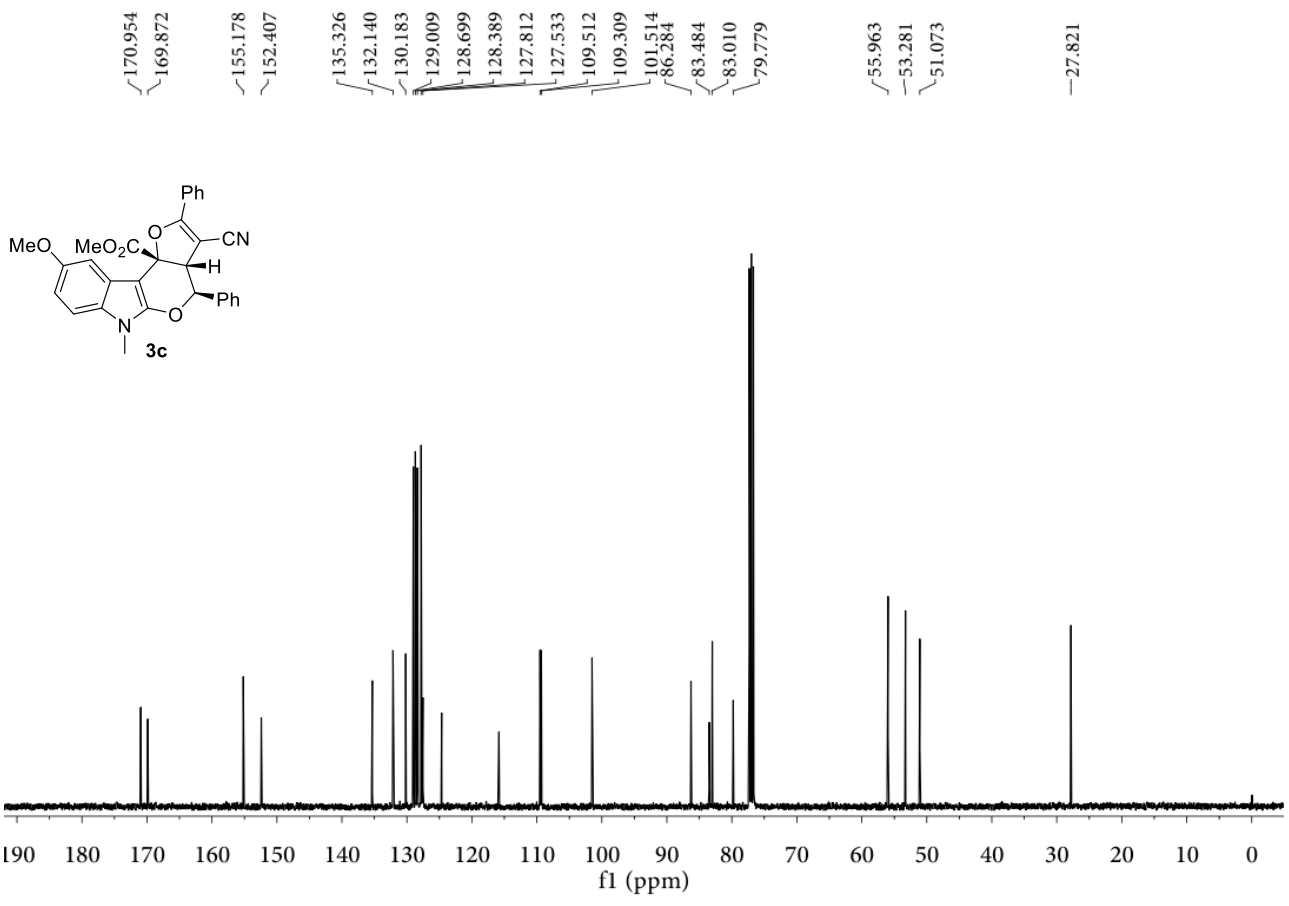


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.238	VV	0.2739	3595.11816	205.55402	49.2479
2	9.374	VV	0.3640	3704.92456	159.60110	50.7521



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.116	VV	0.2725	6881.36914	396.31644	96.2927
2	9.240	MM	0.2830	264.93204	15.60132	3.7073


8.113
8.096
7.620
7.611
7.605
7.559
7.551
7.543
7.499
7.479
7.150
7.145
7.128
4.973
4.946
4.051
4.024
3.905
3.795
3.572
1.596
Ph
MeO
MeO2C
O
CN
H
Ph
N
O
3c
1.73
2.05
2.96
2.98
1.82
0.93
0.93
0.89
3.00
2.84
2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.326
132.140
130.183
129.009
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128.389
127.812
127.533
109.512
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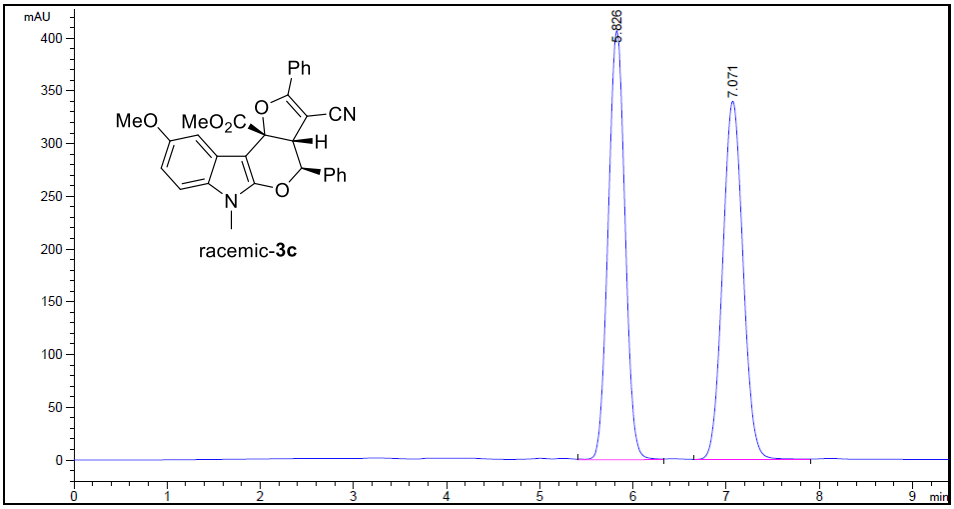
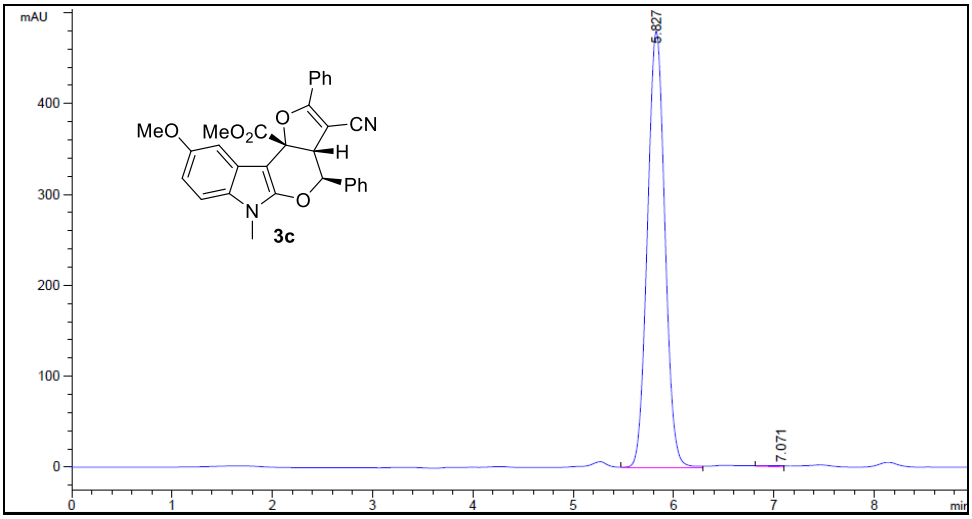
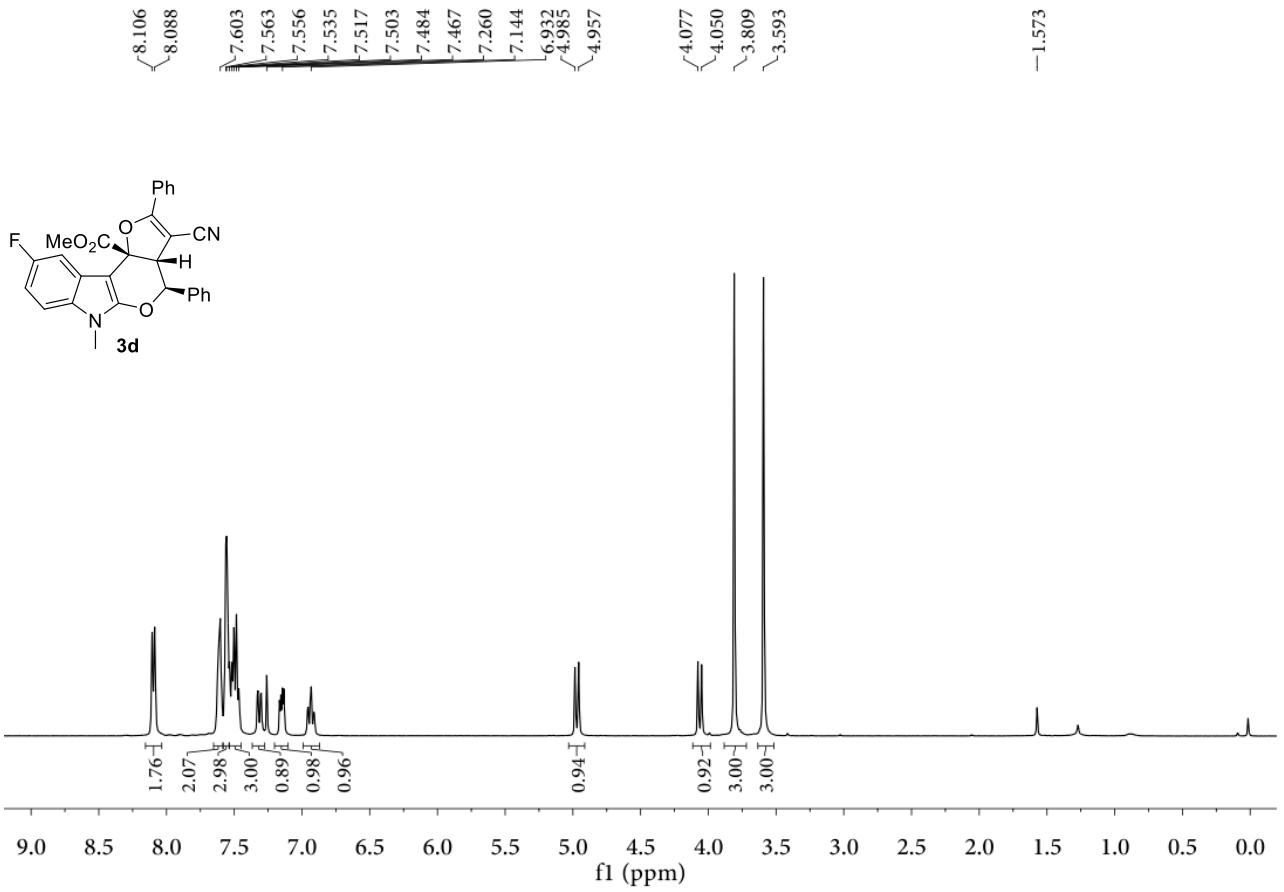
101.514
86.284
83.484
83.010
79.779
55.963
53.281
51.073
27.821
Ph
MeO
MeO2C
O
CN
H
Ph
N
O
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.826	VV	0.1998	5129.66553	406.00278	49.7448
2	7.071	VB	0.2422	5182.30322	339.35944	50.2552



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.827	VV	0.1885	5829.83594	479.25140	99.7147
2	7.071	MM	0.2319	16.67862	1.19846	0.2853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7.556
7.535
7.517
7.503
7.484
7.467
7.260
7.144
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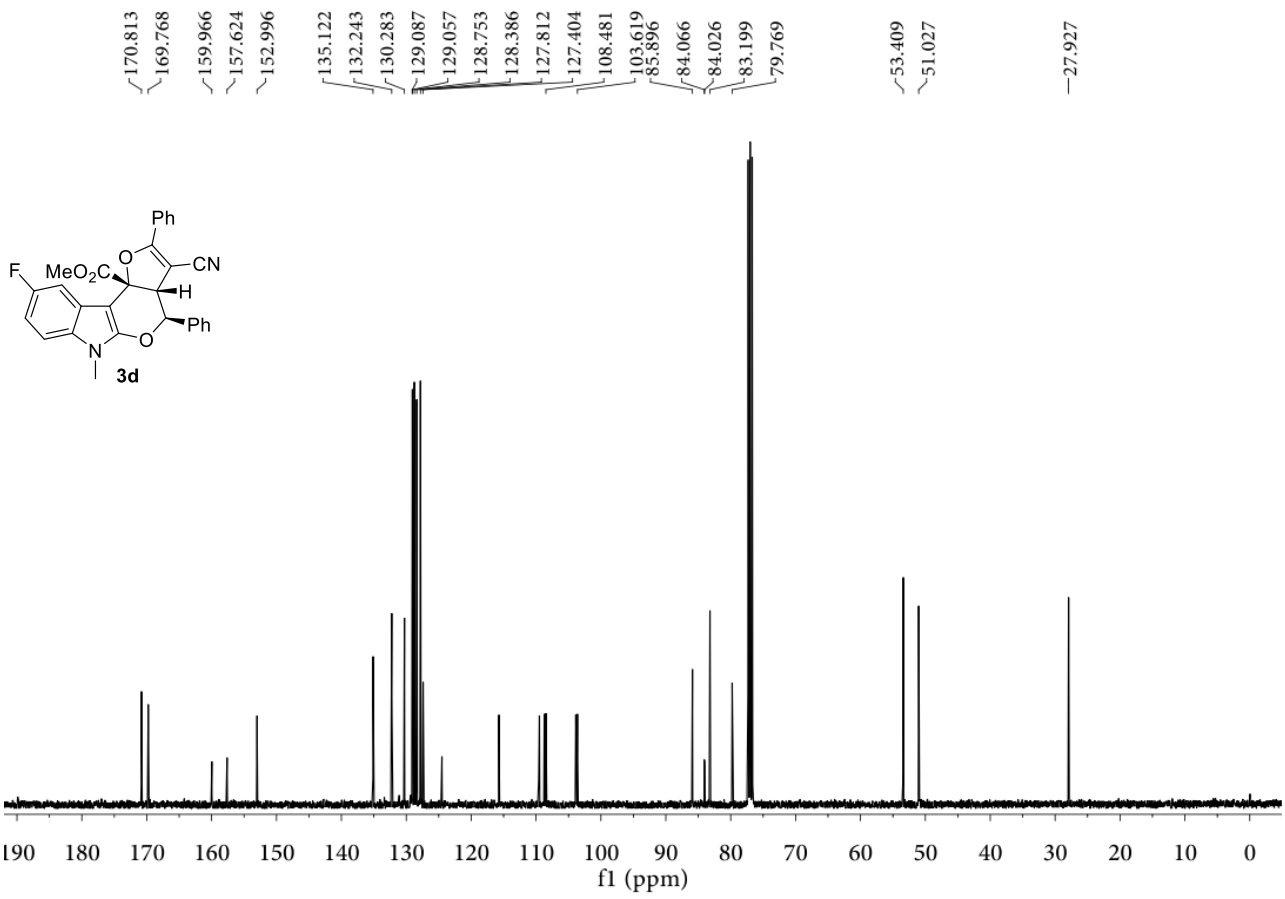
4.985
4.957
4.077
4.050
3.809
3.593
1.573
Ph
CN
F
MeO2C
O
H
Ph
N
O
3d
1.76
2.07
2.98
3.00
0.89
0.98
0.96
0.94
0.92
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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157.624
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130.283
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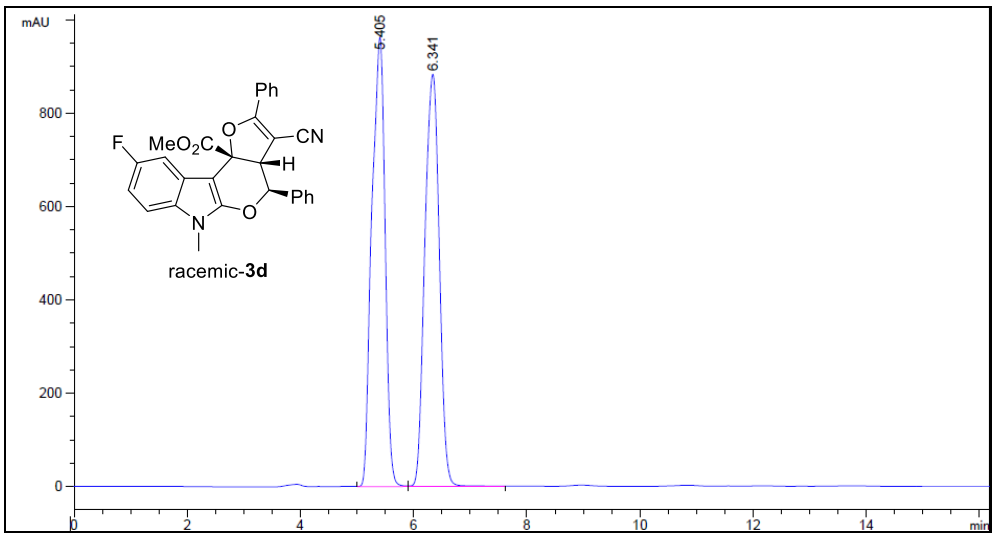
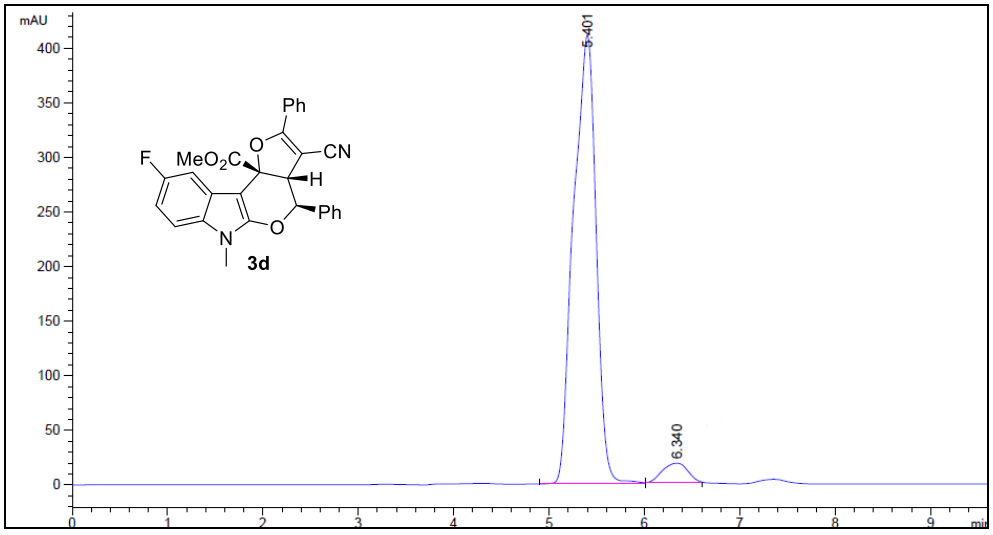
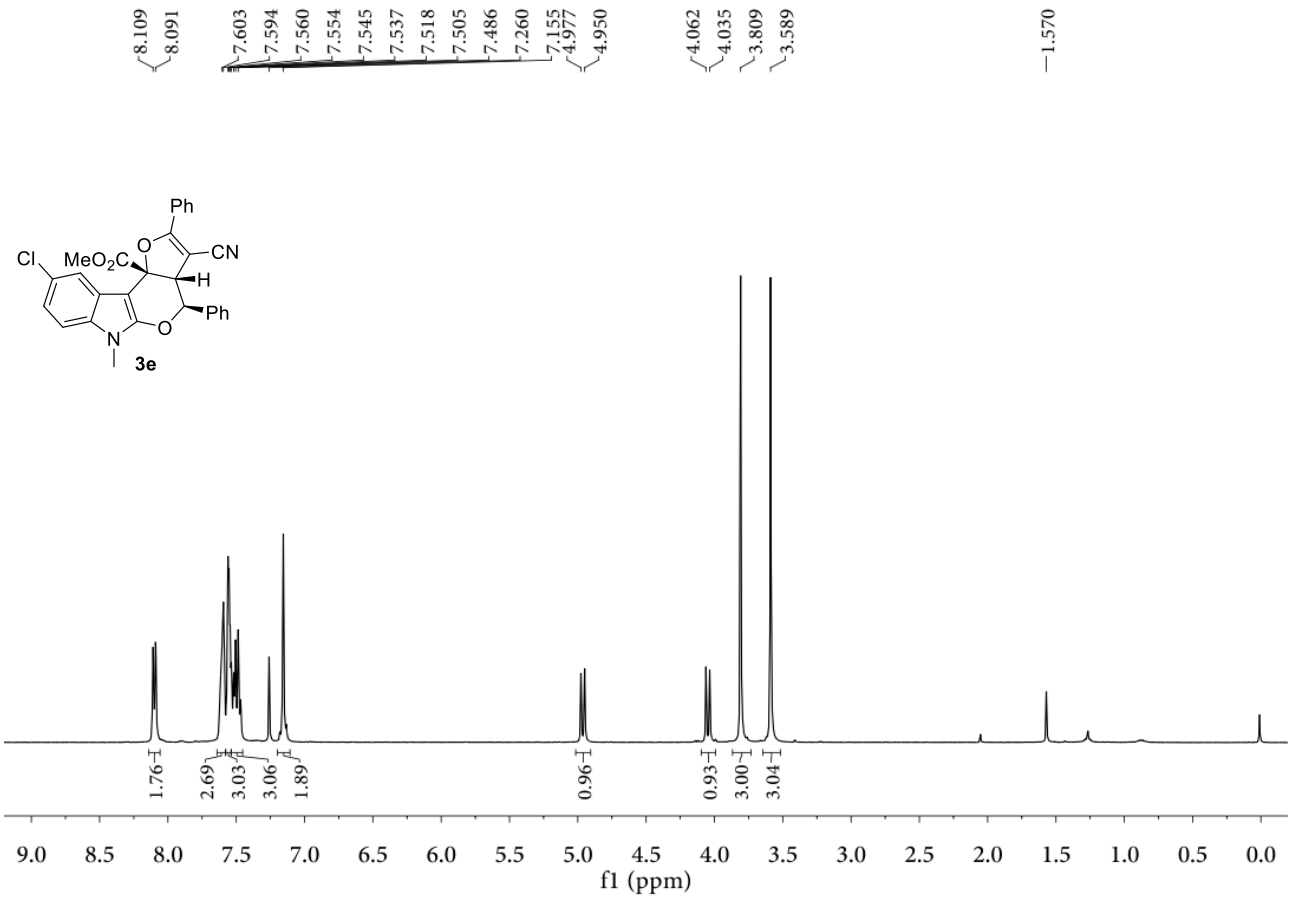
129.057
128.753
128.386
127.812
127.404
108.481
103.619
85.896
84.066
84.026
83.199
79.769
53.409
51.027
27.927
Ph
CN
F
MeO2C
O
H
Ph
N
O
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.405	VV	0.2306	1.56445e4	961.35602	49.8902
2	6.341	VB	0.2952	1.57134e4	882.20856	50.1098



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.401	MM	0.2737	6751.68506	411.19461	95.3871
2	6.340	MM	0.3041	326.51120	17.89628	4.6129


8.109
8.091
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7.594
7.560
7.554
7.545
7.537
7.518
7.505
7.486
7.260
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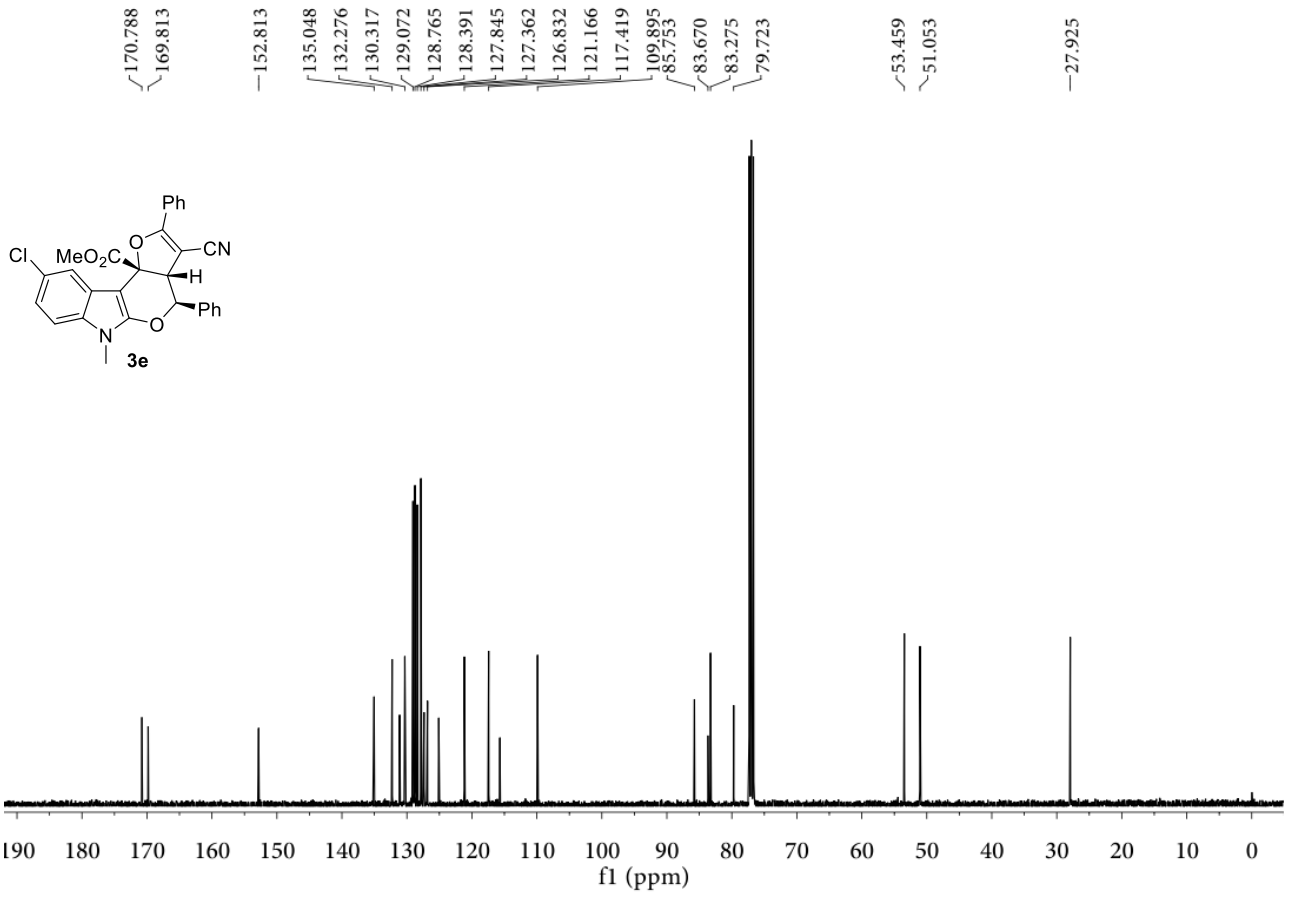
4.977
4.950
4.062
4.035
3.809
3.589
1.570
Ph
Cl
MeO2C
O
CN
H
Ph
O
N
3e
1.76
2.69
3.03
3.06
1.89
0.96
0.93
3.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.788
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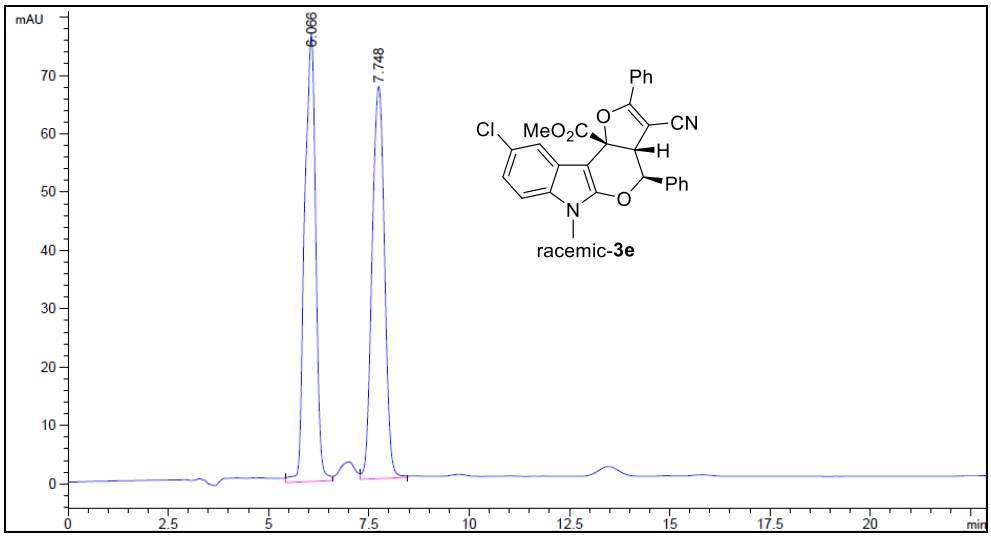
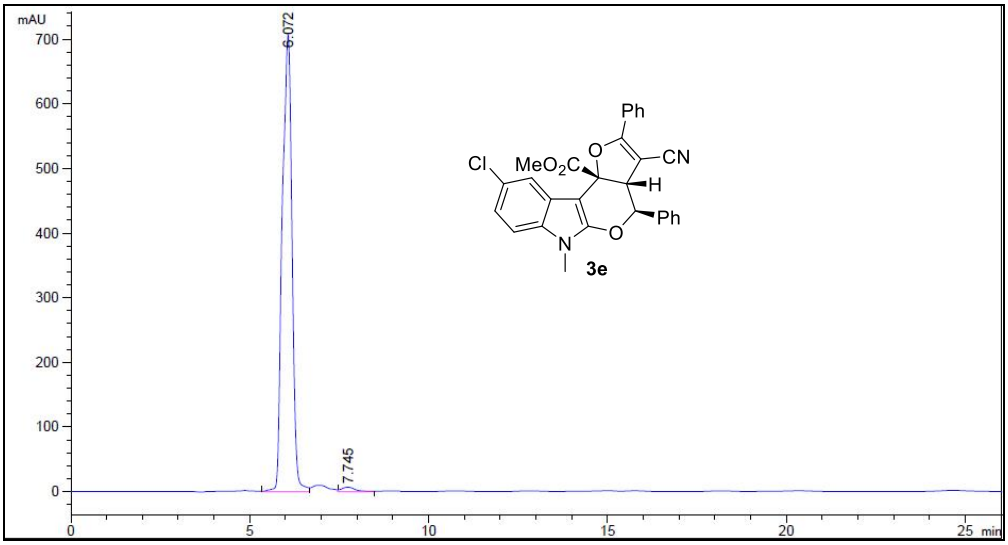
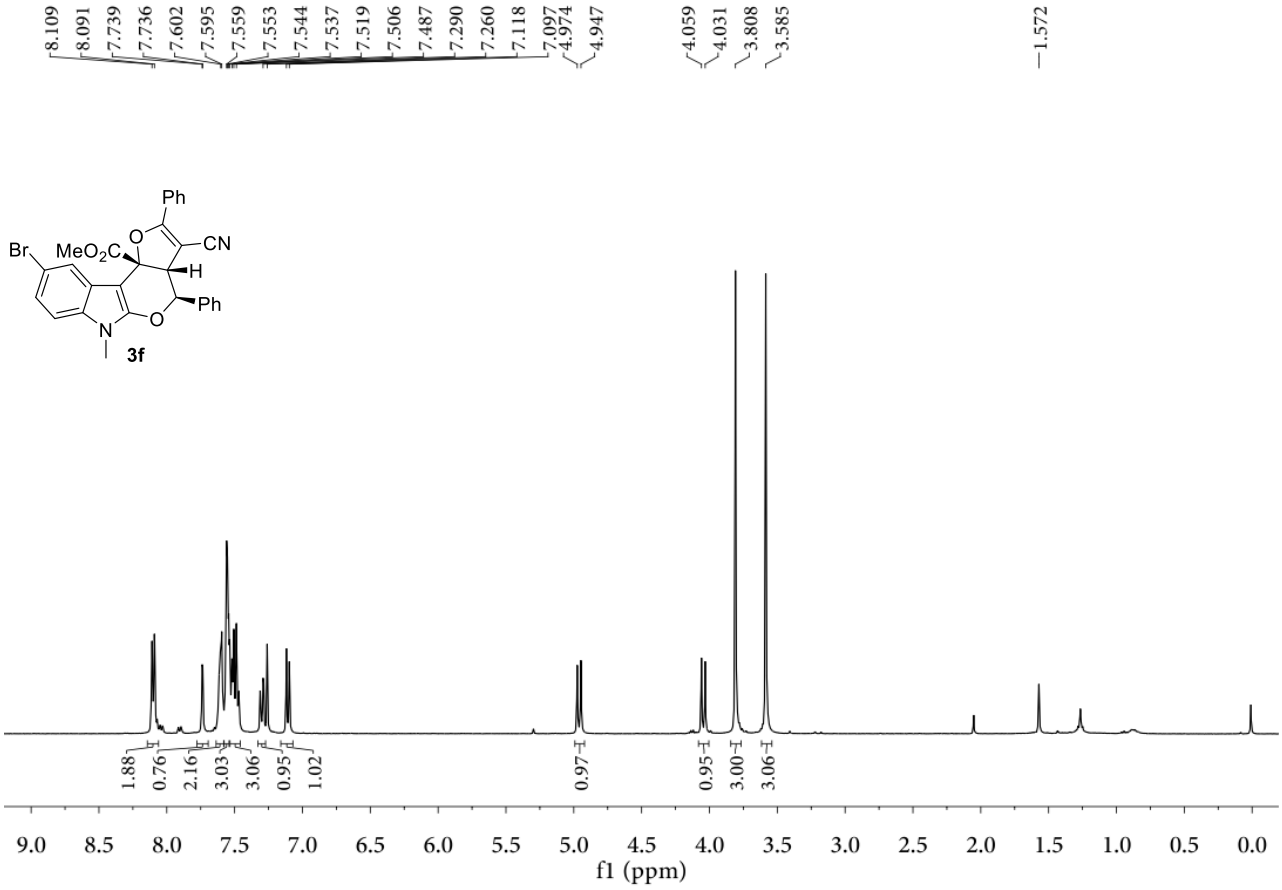
127.845
127.362
126.832
121.166
117.419
109.895
85.753
83.670
83.275
79.723
53.459
51.053
27.925
Ph
Cl
MeO2C
O
CN
H
Ph
O
N
3e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.066	BV	0.2769	1473.52661	76.57407	50.3588
2	7.748	VB	0.3452	1452.52710	67.24238	49.6412



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.072	VV	0.2677	1.33765e4	705.82098	98.6291
2	7.745	VB	0.4092	185.92235	6.86380	1.3709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7.519
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7.290
7.260
7.118
7.097
4.974
4.947
4.059
4.031
3.808
3.585
1.572
Ph
Br
MeO2C
O
CN
H
Ph
N
O
3f
1.88
0.76
2.16
3.03
3.06
0.95
1.02
0.97
0.95
3.00
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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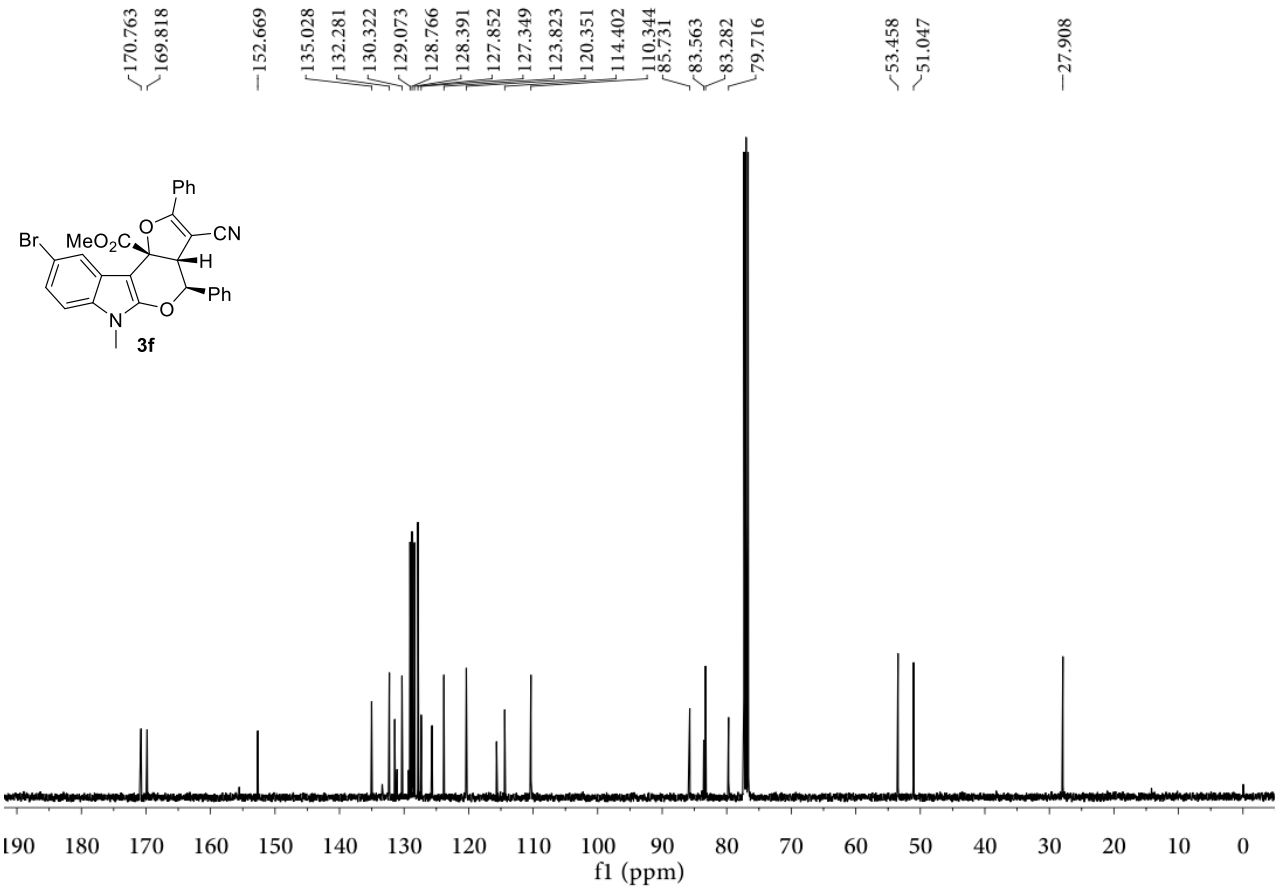
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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152.669
135.028
132.281
130.322
129.073
128.766
128.391
127.852
127.349
123.823
120.351
114.402
110.344
85.731
83.563
83.282
79.716
53.458
51.047
27.908
Ph
Br
MeO2C
O
CN
H
Ph
N
O
3f
190
180
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110
100
90
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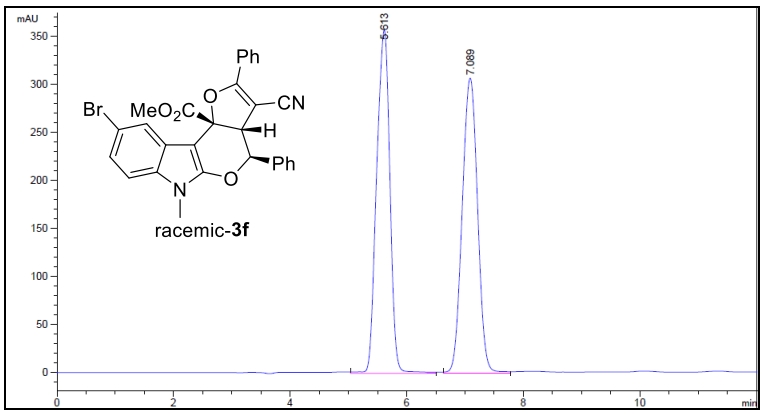
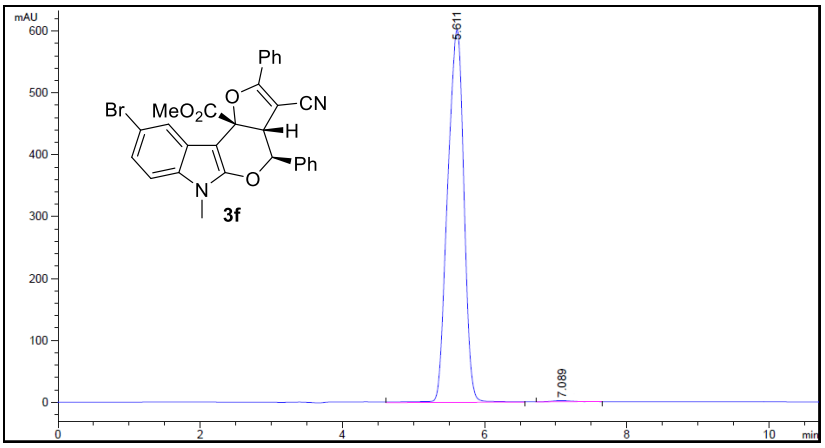
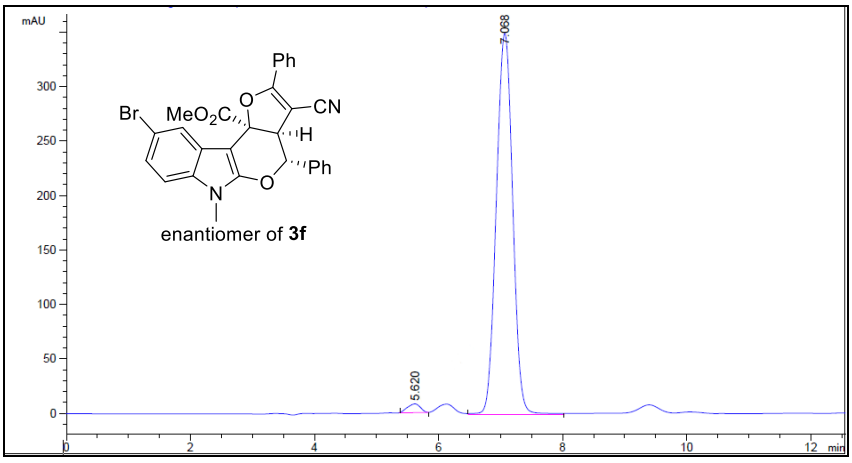
60
50
40
30
20
10
0
f1 (ppm)



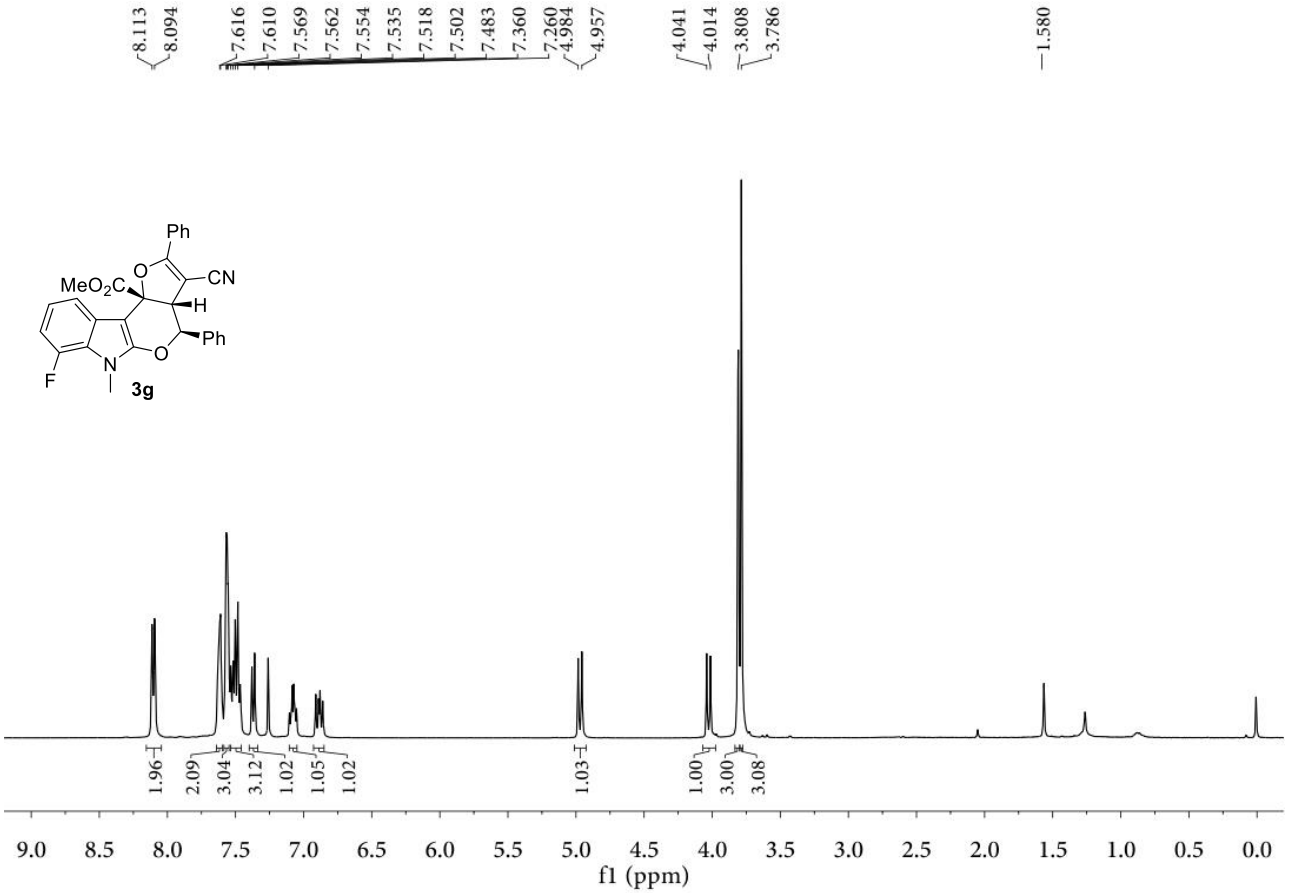
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.613	VB	0.2607	5655.35498	356.63089	50.1297
2	7.089	BV	0.2957	5626.10059	306.41946	49.8703

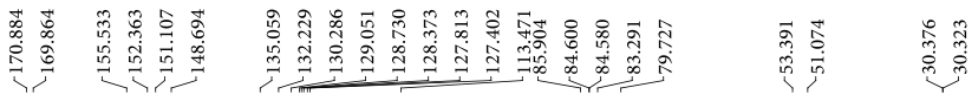


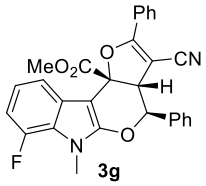
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.611	VB	0.2614	9592.30859	602.64075	99.6203
2	7.089	MM	0.3263	36.55666	1.86716	0.3797



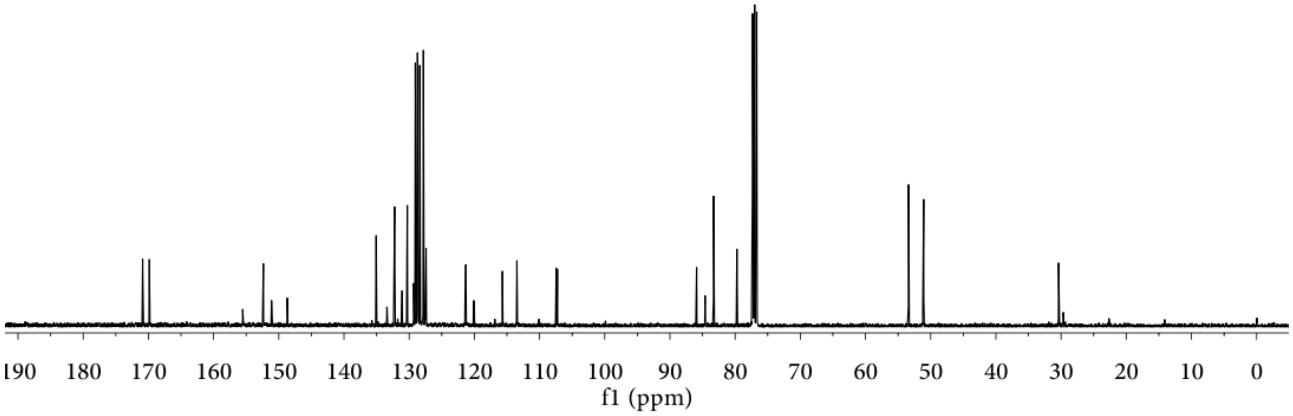
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.620	MM	0.2404	116.27843	8.06088	1.7762
2	7.068	VB	0.2960	6430.11084	349.73169	98.2238

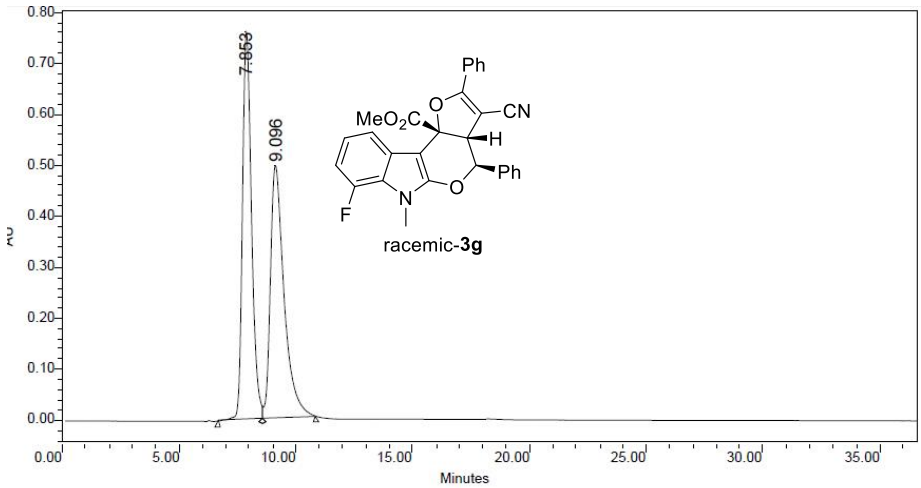




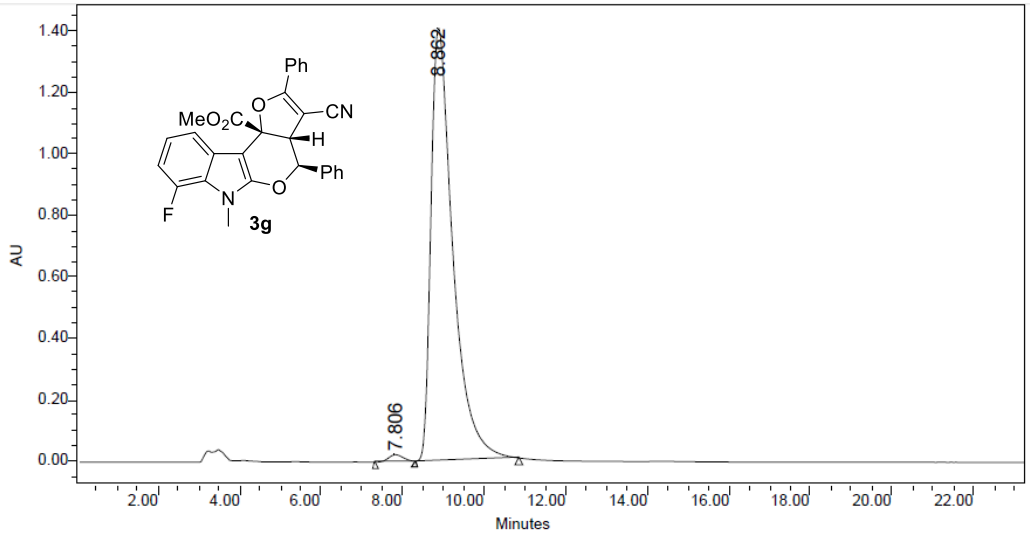


3g

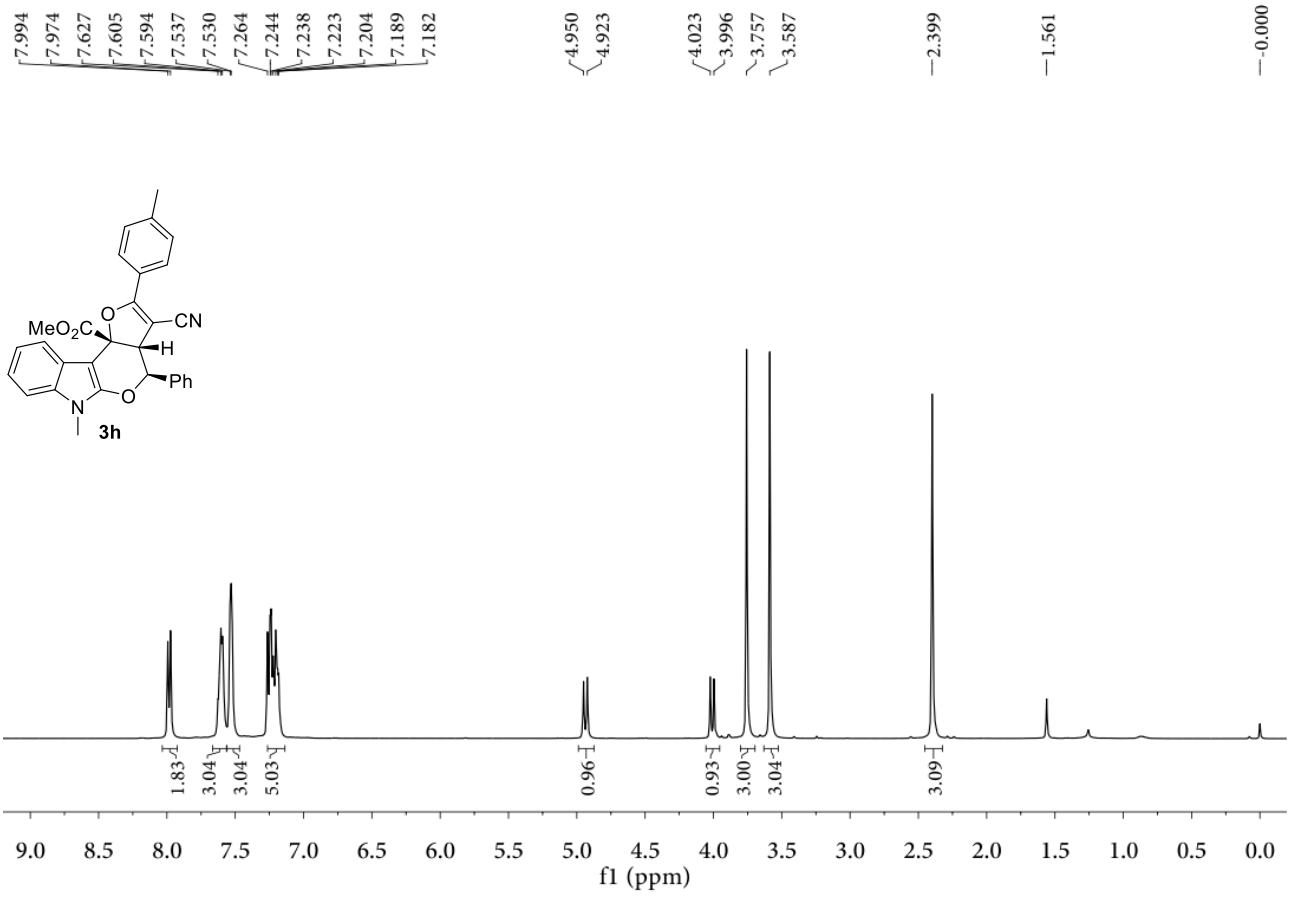


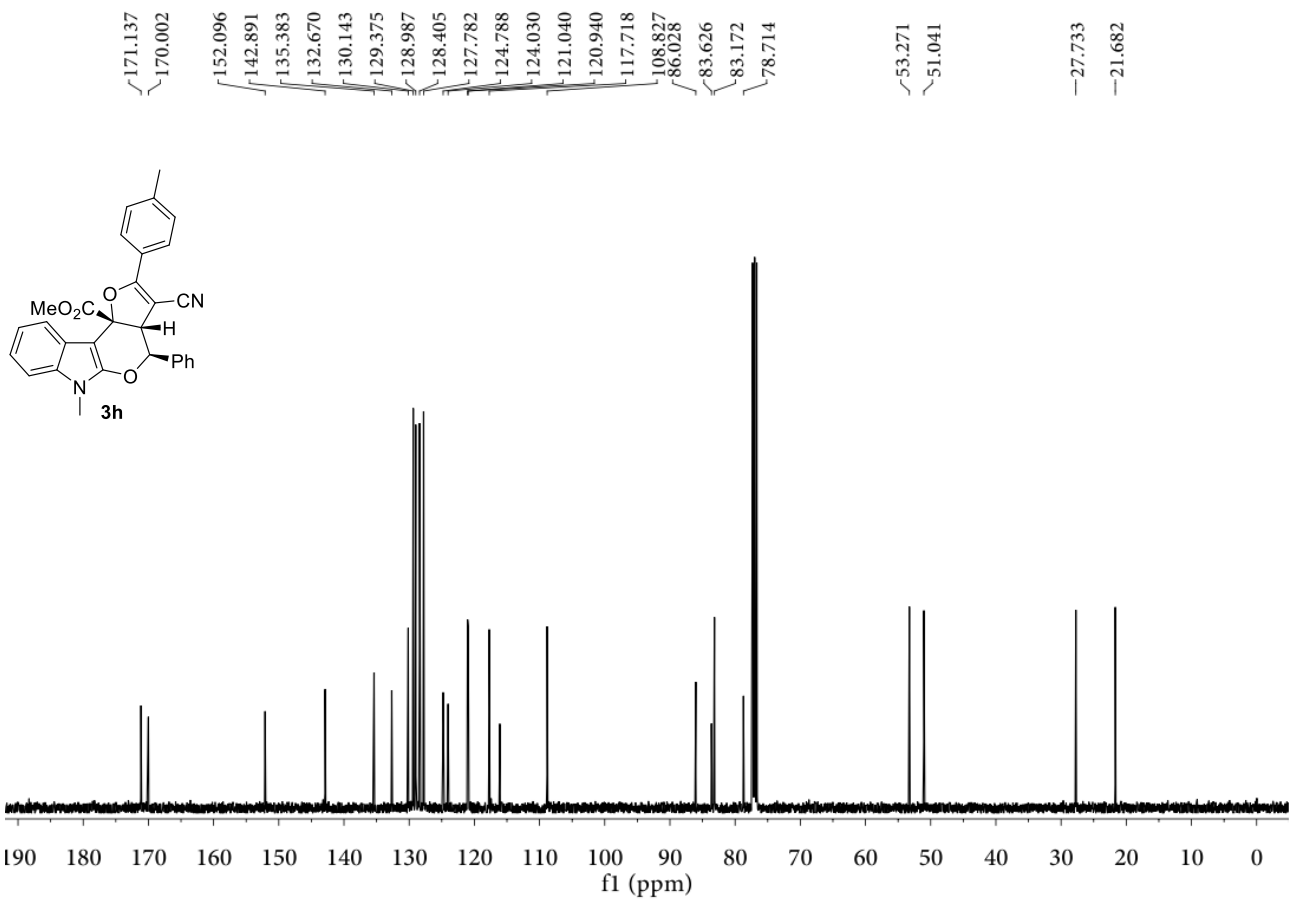


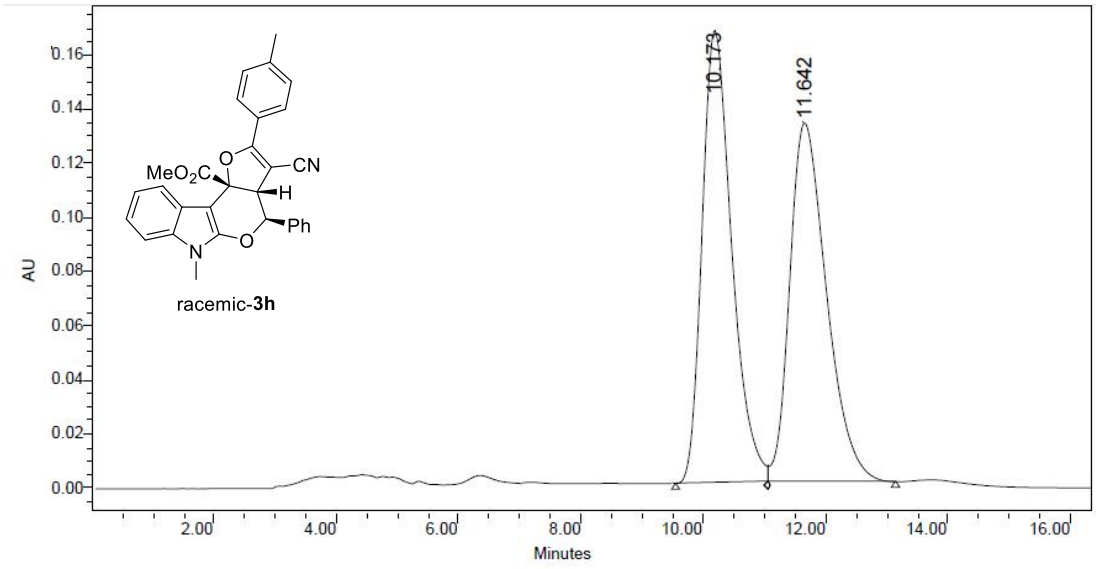
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.853	20599662	50.51	759964	60.53
2	9.096	20184215	49.49	495601	39.47



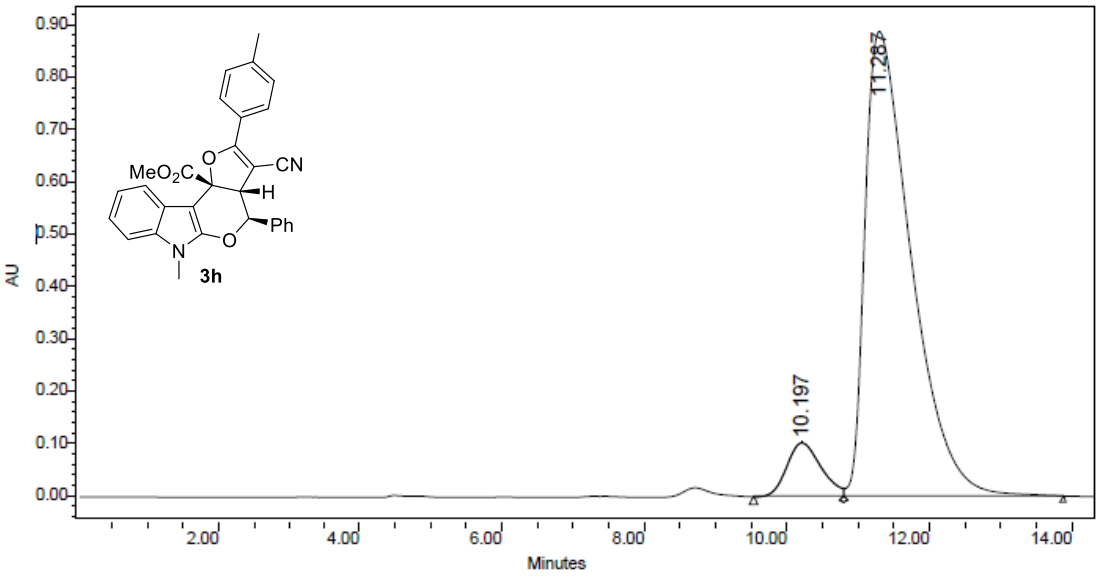
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.806	553687	1.04	22670	1.59
2	8.862	52506685	98.96	1405163	98.41



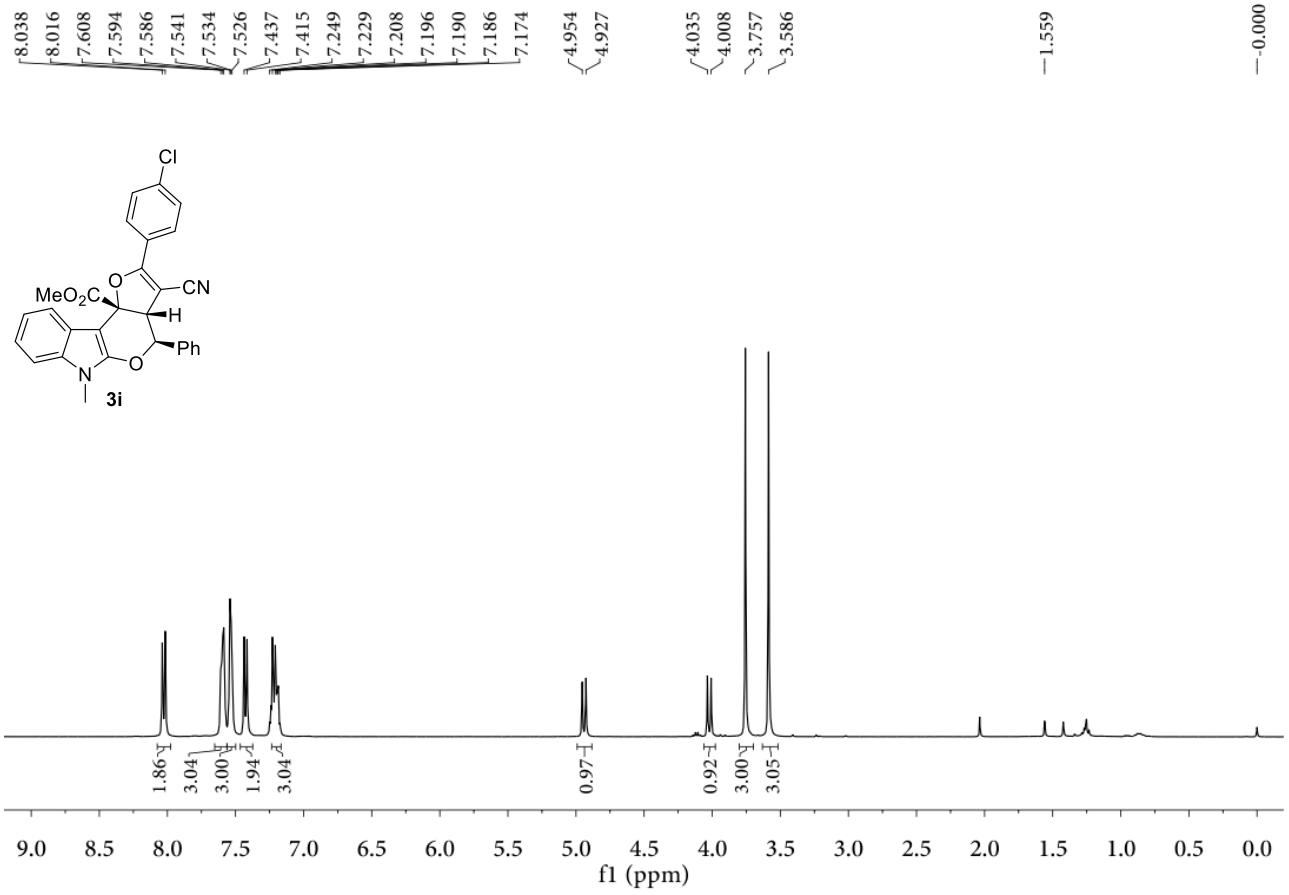


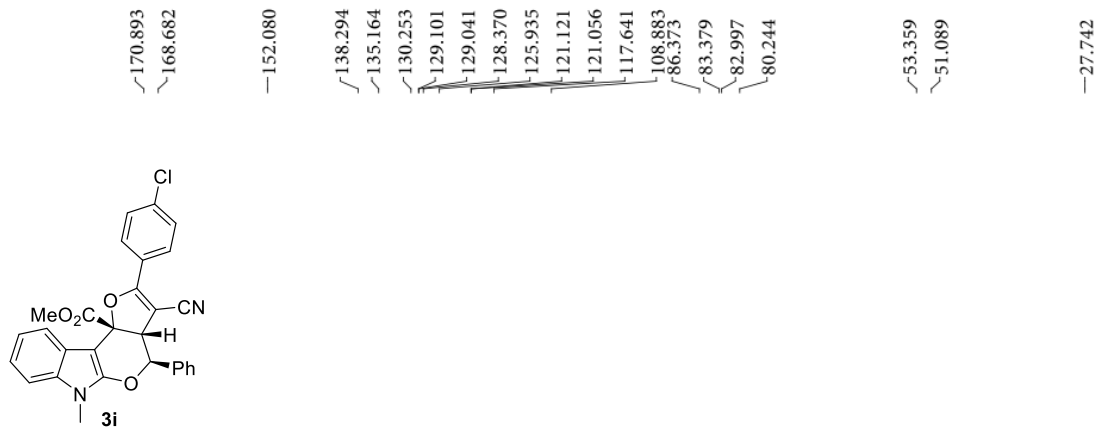


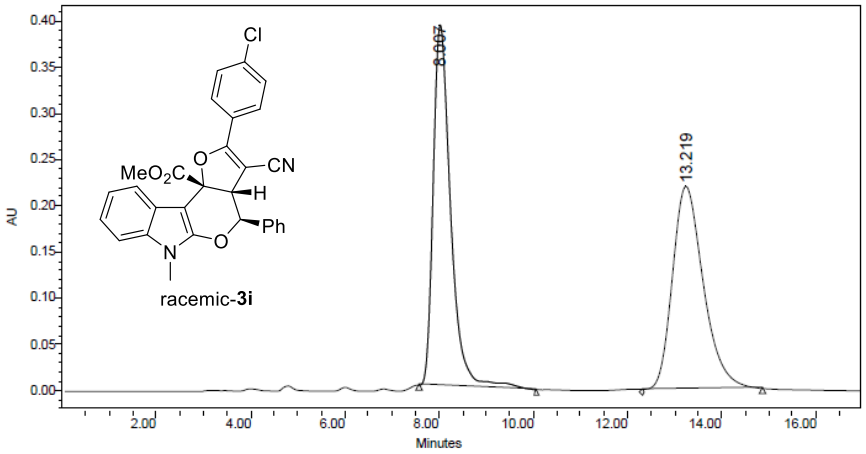
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.173	5656897	50.37	167289	55.72
2	11.642	5572814	49.63	132932	44.28



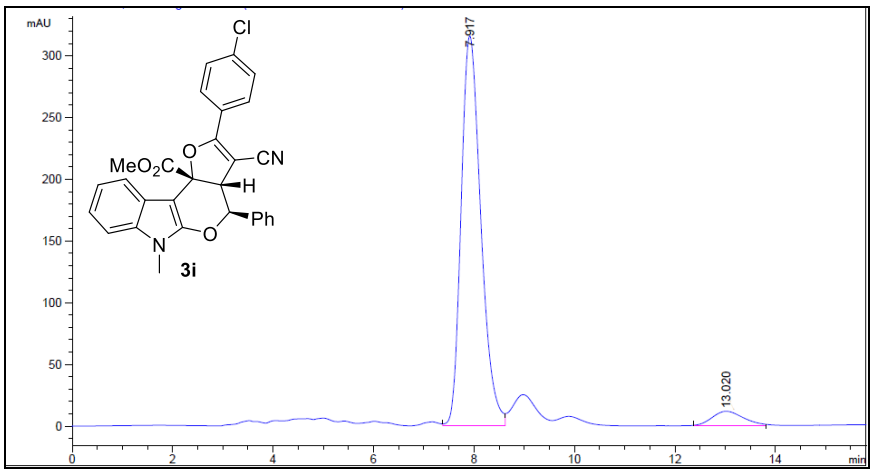
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.197	3457646	7.95	102559	10.36
2	11.287	40034148	92.05	887755	89.64



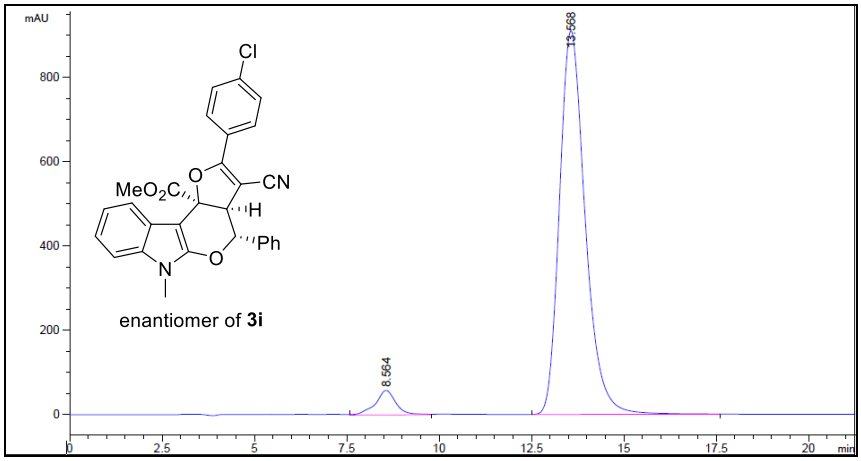




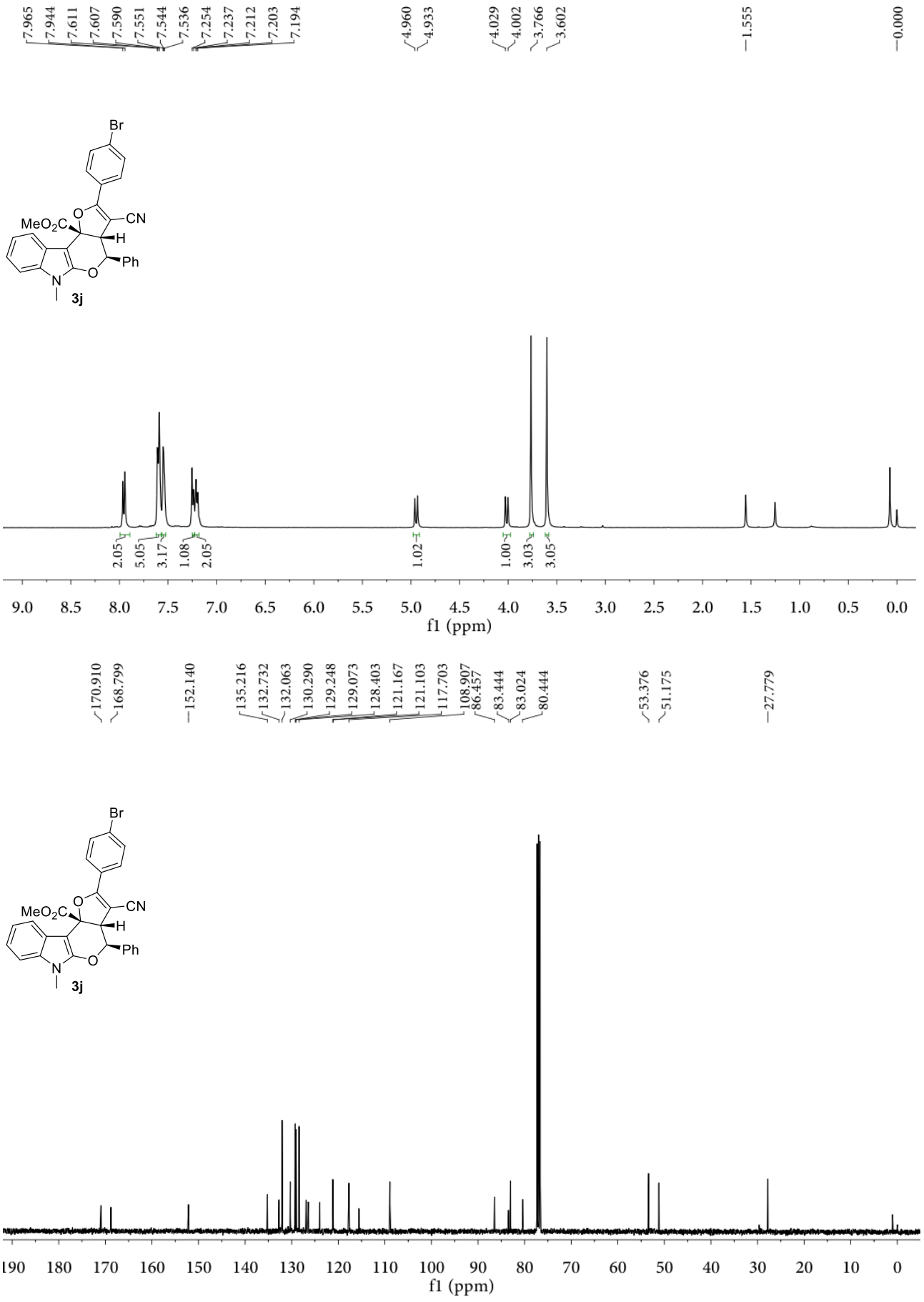
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	8.007	10100792	50.07	390974	64.00
2	13.219	10072979	49.93	219907	36.00



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.917	VV	0.4235	8620.59668	315.57886	94.8319
2	13.020	MM	0.6963	469.80179	11.24545	5.1681



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.564	VV	0.5666	2274.73853	58.20887	4.9143
2	13.568	BB	0.7451	4.40134e4	909.56244	95.0857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7.551
7.544
7.536
7.254
7.237
7.212
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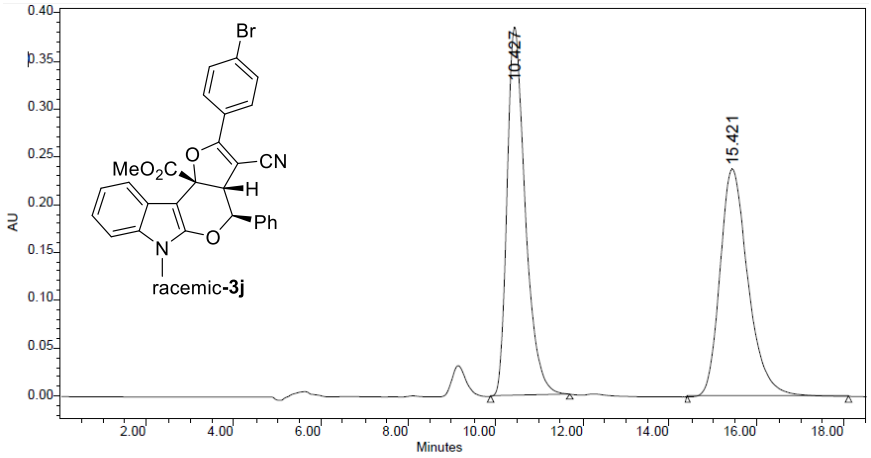
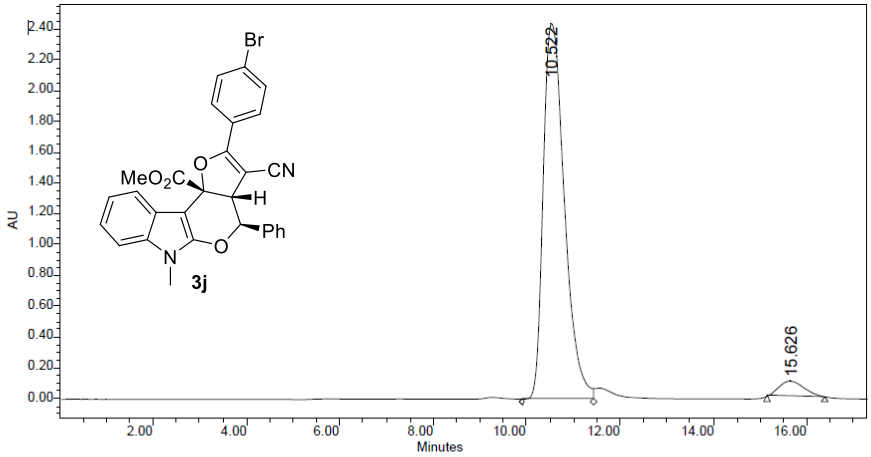
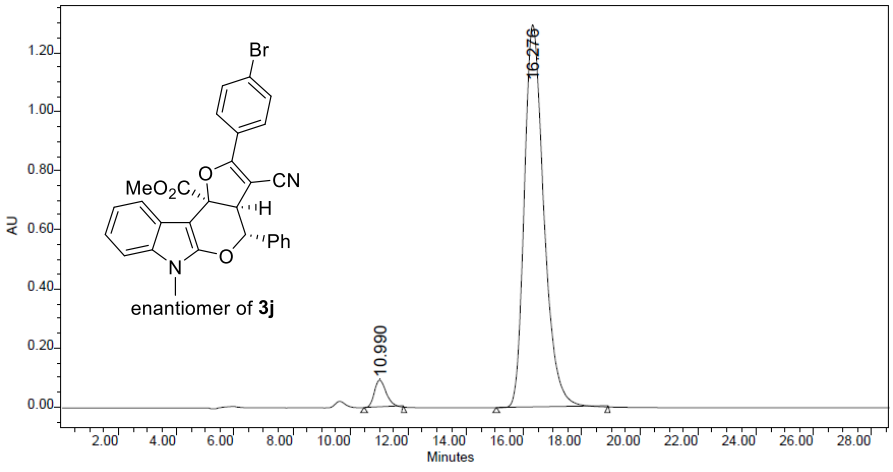
7.194
4.960
4.933
4.029
4.002
3.766
3.602
1.555
0.000
Br
MeO2C
O
CN
H
Ph
N
O
3j
2.05
5.05
3.17
1.08
2.05
1.02
1.00
3.03
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
170.910
168.799
152.140
135.216
132.732
132.063
130.290
129.248
129.073
128.403
121.167
121.103
117.703
108.907
86.457
83.444
83.024
80.444
53.376
51.175
27.779
Br
MeO2C
O
CN
H
Ph
N
O
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



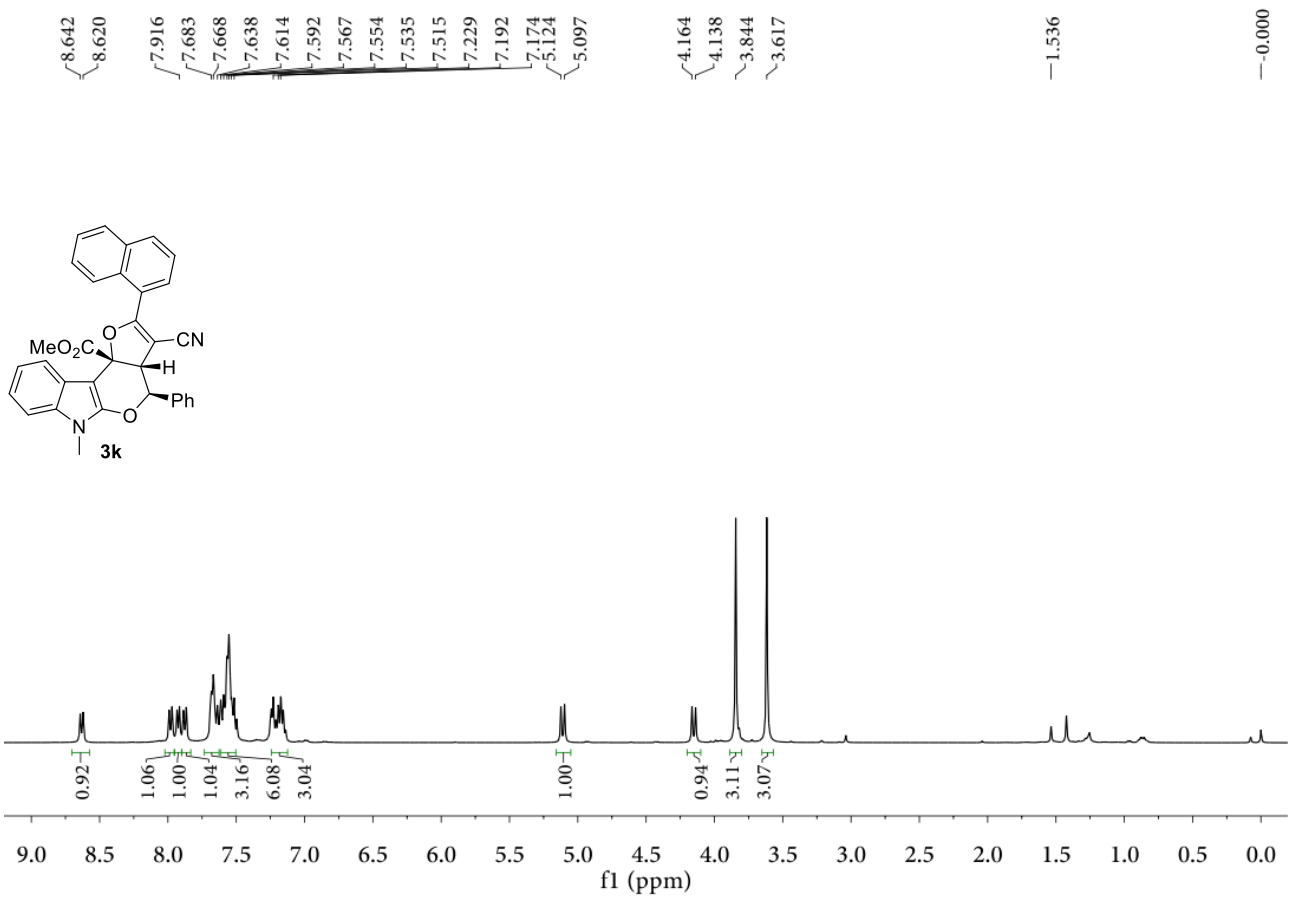
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.427	11194411	51.13	384931	61.82
2	15.421	10697603	48.87	237724	38.18



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.522	77046430	95.44	2441996	96.11
2	15.626	3684687	4.56	98818	3.89



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.990	2698376	4.25	92977	6.70
2	16.276	60827321	95.75	1294313	93.30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7.592
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7.515
7.229
7.192
7.174
5.124
5.097
4.164
4.138
3.844
3.617
1.536
0.000
MeO2C
CN
H
Ph
O
N
3k
0.92
1.06
1.00
1.04
3.16
6.08
3.04
1.00
0.94
3.11
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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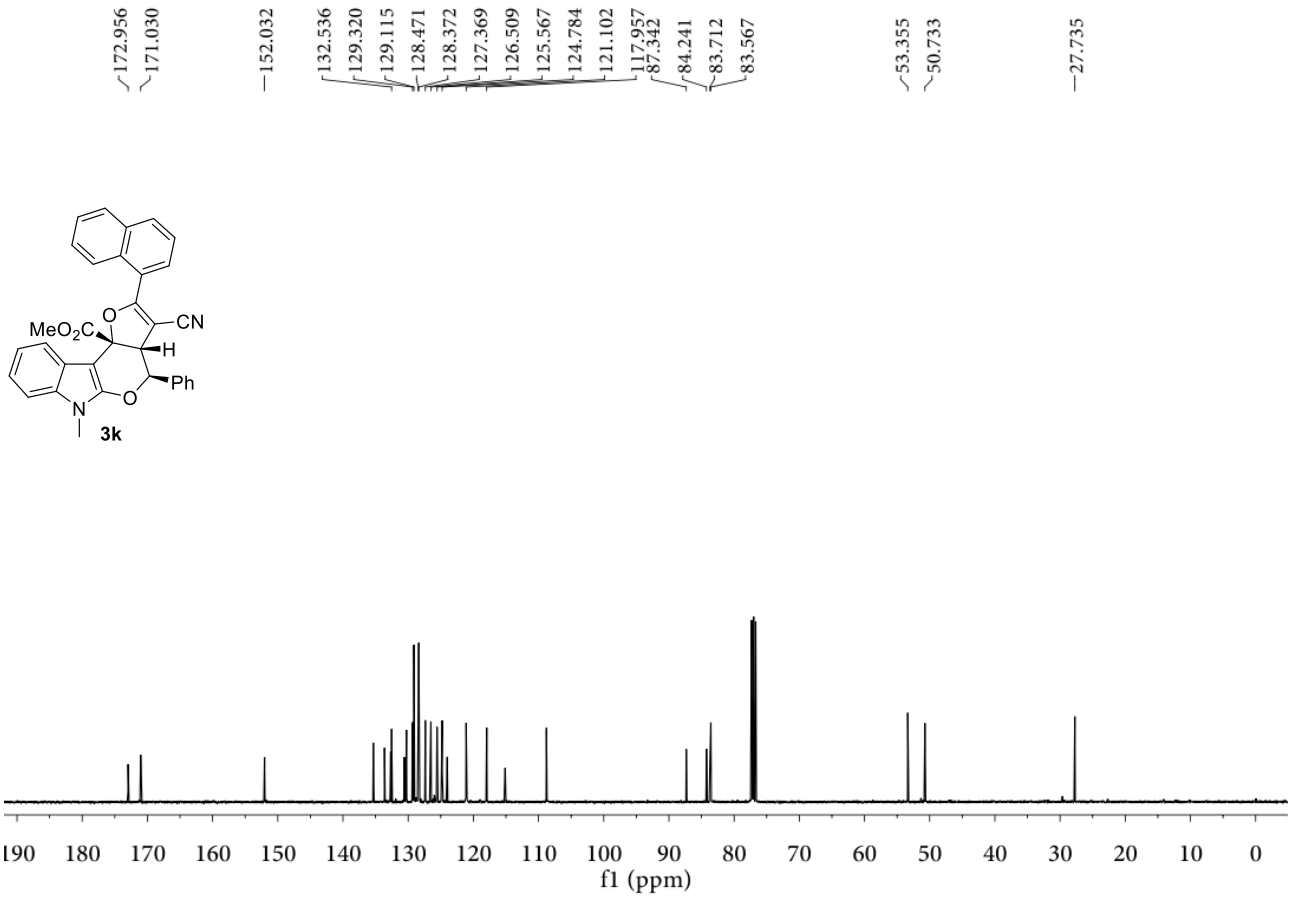
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.567
124.784
121.102
117.957
87.342
84.241
83.712
83.567
53.355
50.733
27.735
MeO2C
CN
H
Ph
O
N
3k
190
180
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160
150
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130
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110
100
90
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50
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30
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10
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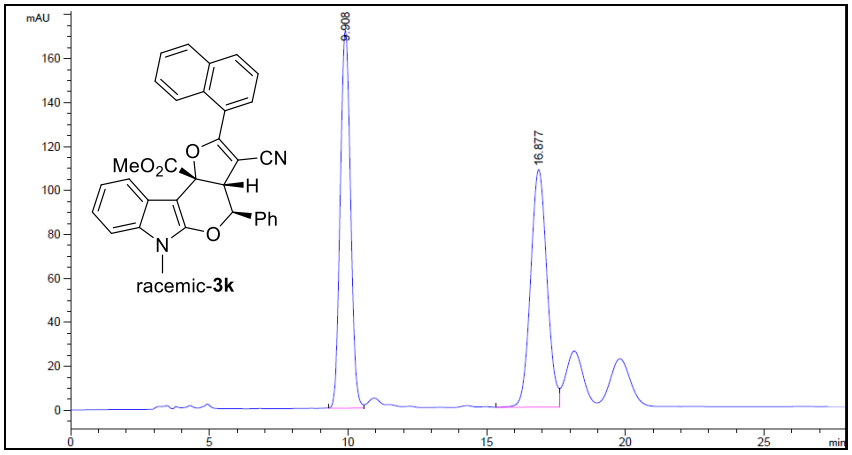
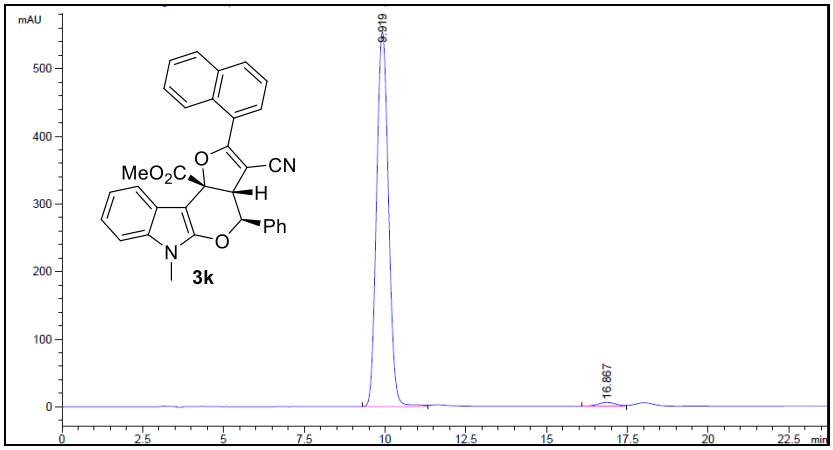
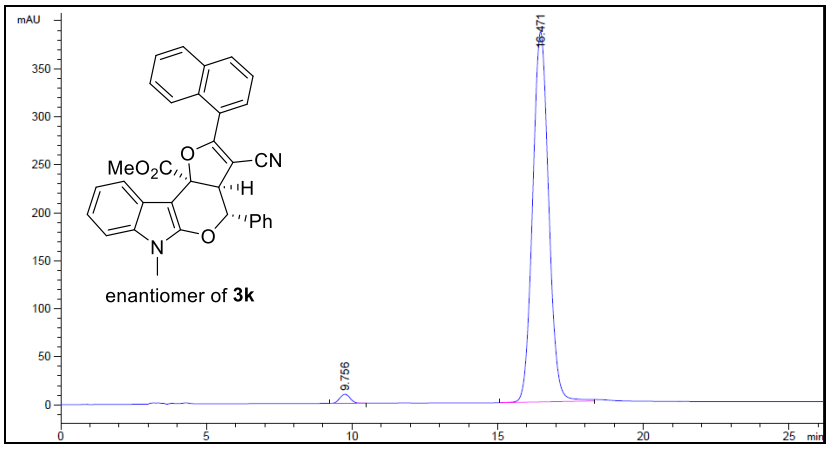
f1 (ppm)



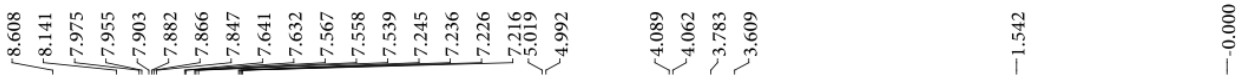
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.908	BV	0.4126	4446.44287	171.82504	50.0880
2	16.877	VV	0.6355	4430.82715	108.09156	49.9120

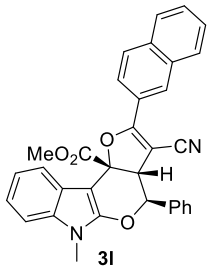


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.919	BV	0.4048	1.42302e4	553.54523	98.4561
2	16.867	BV	0.6180	223.15167	5.65088	1.5439



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.756	BB	0.3931	234.79292	9.50391	1.5654
2	16.471	BB	0.5984	1.47641e4	385.39102	98.4346





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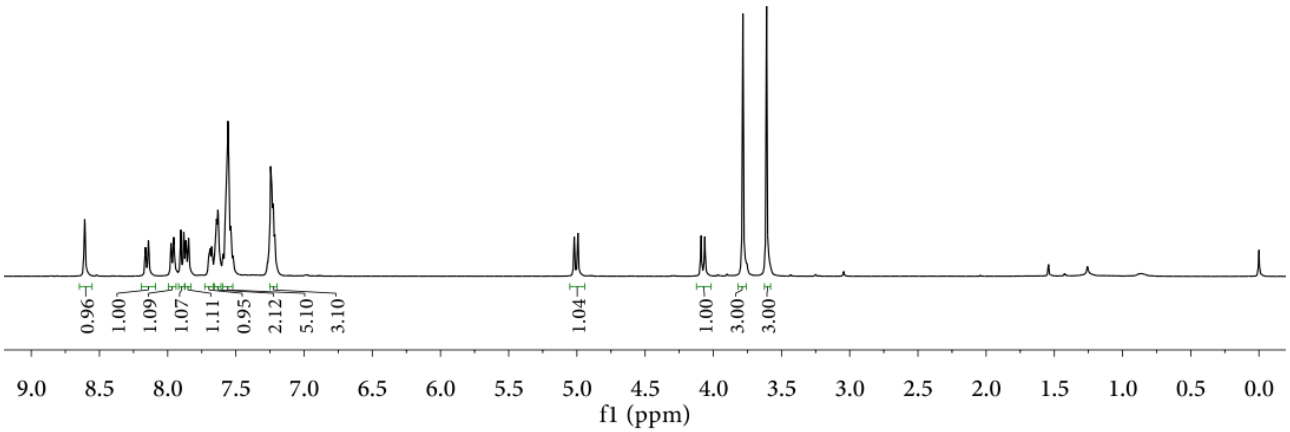
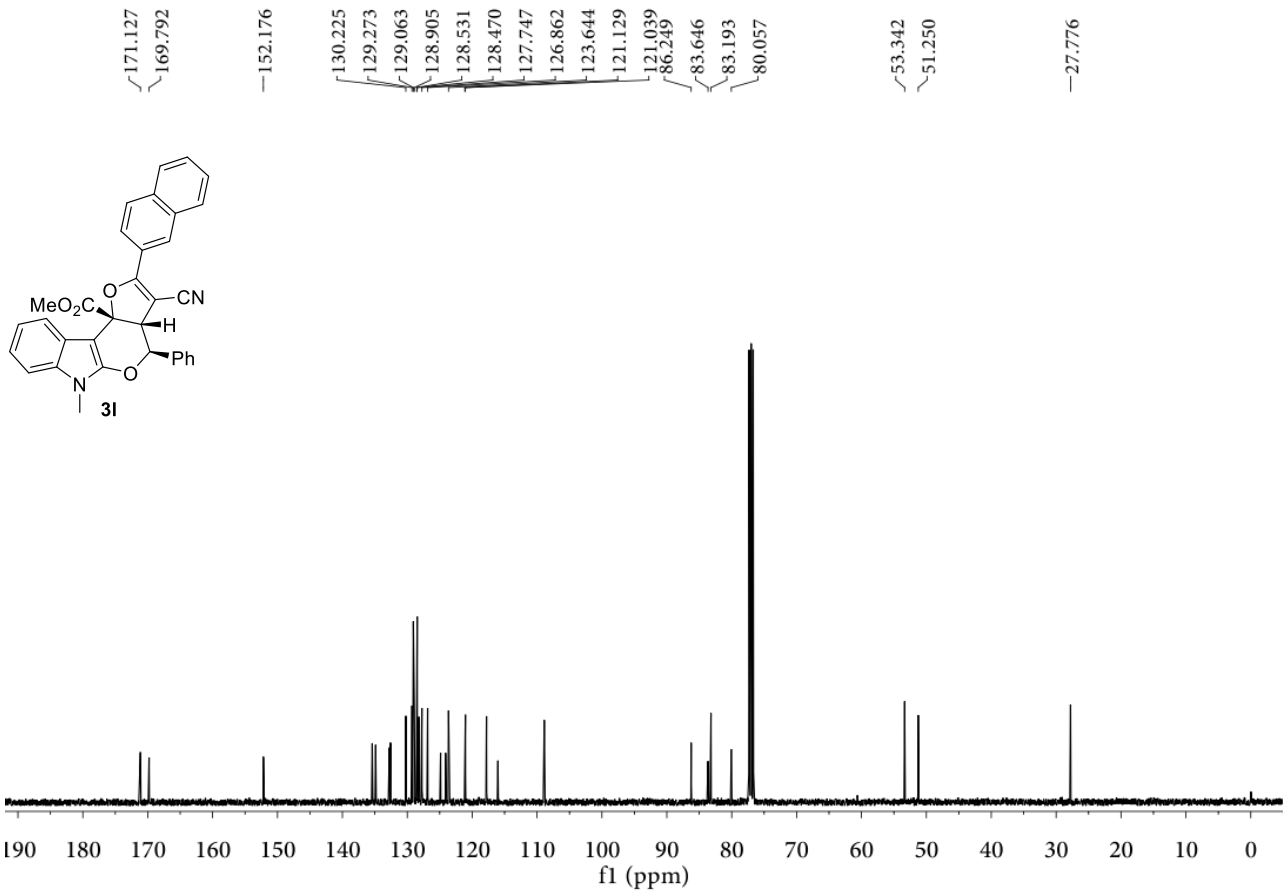
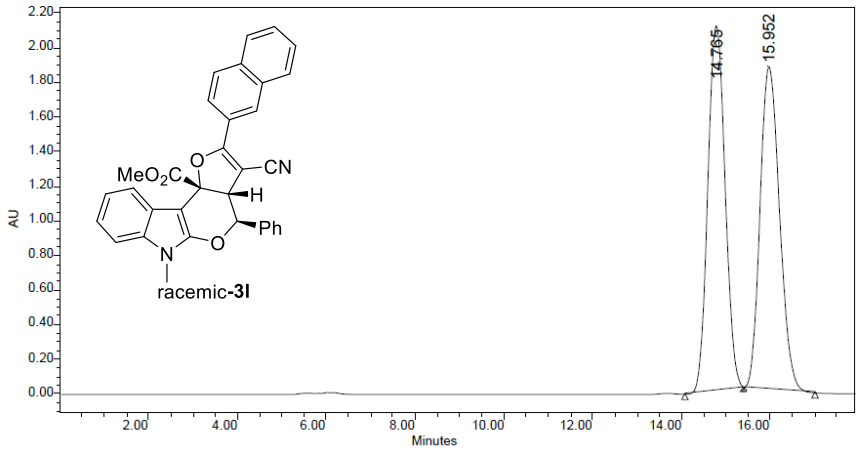
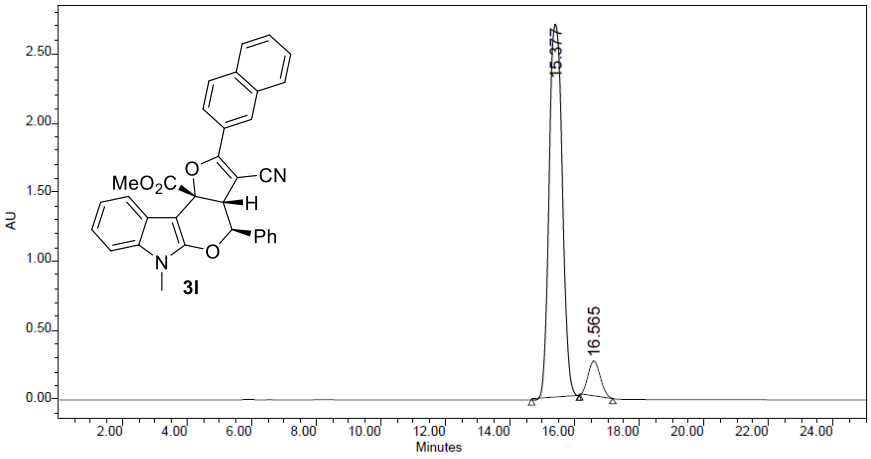


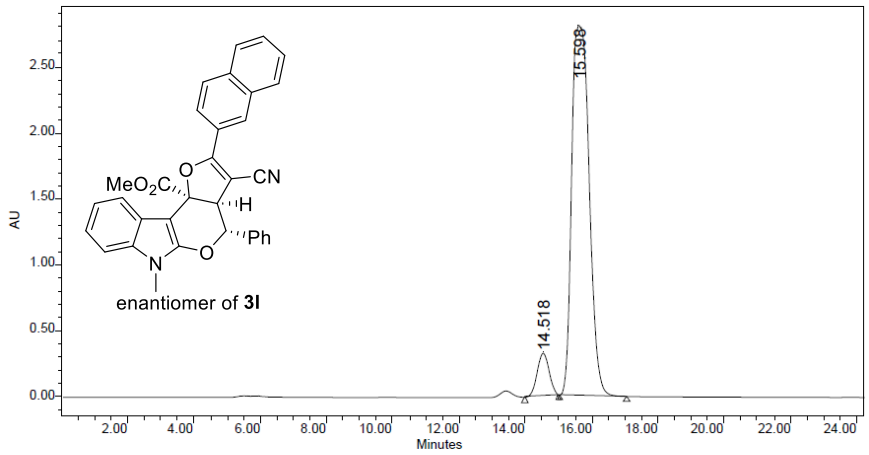




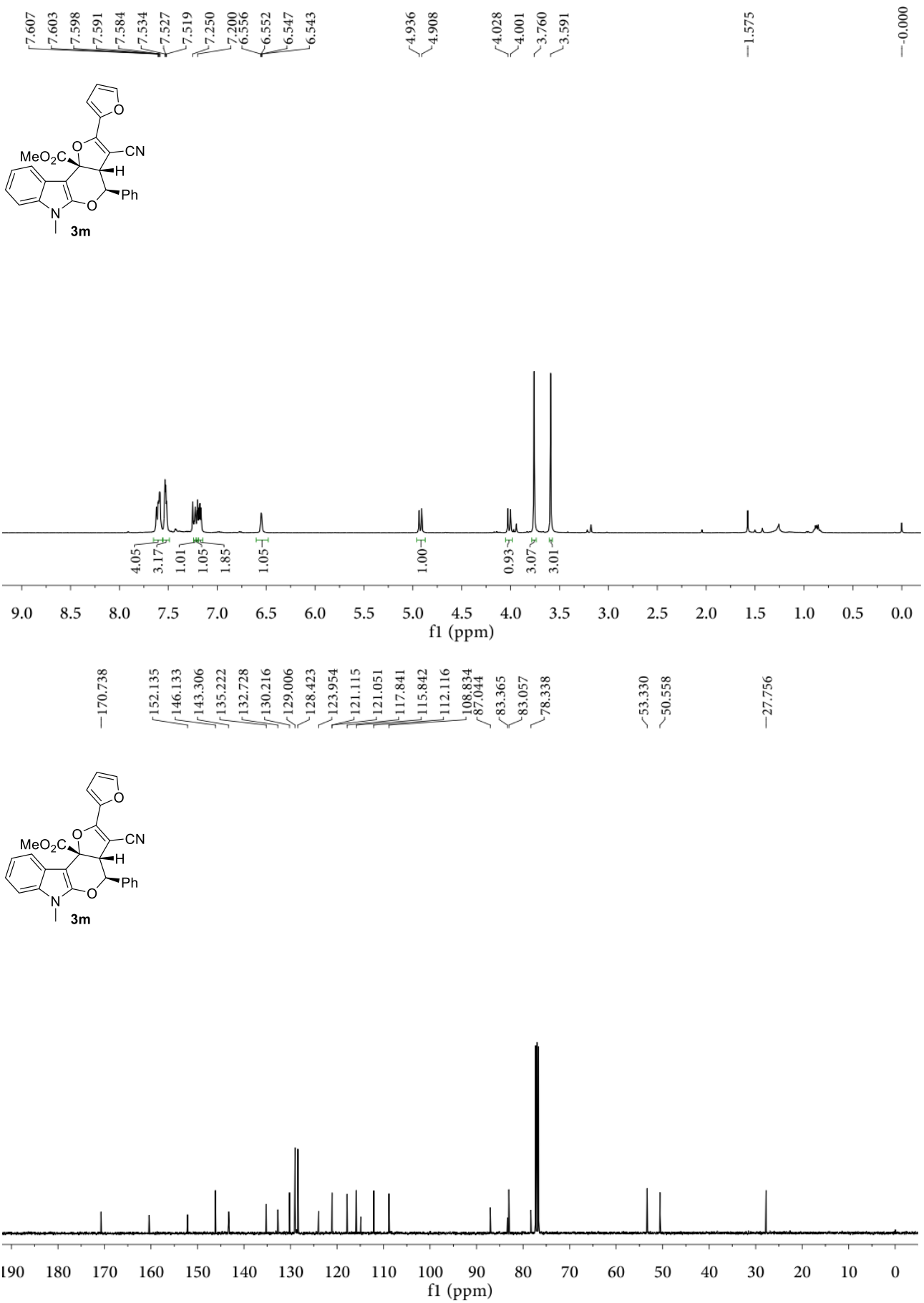
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	14.765	56920494	50.14	2106657	53.08
2	15.952	56610251	49.86	1862284	46.92



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.377	76796170	91.83	2699747	91.33
2	16.565	6829824	8.17	256288	8.67



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	14.518	8140656	7.34	324564	10.37
2	15.598	102705658	92.66	2805223	89.63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6.552
6.547
6.543
4.936
4.908
4.028
4.001
3.760
3.591
1.575
0.000
MeO2C
CN
H
Ph
N
3m
4.05
3.17
1.01
1.05
1.85
1.05
1.00
0.93
3.07
3.01
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)
170.738
152.135
146.133
143.306
135.222
132.728
130.216
129.006
128.423
123.954
121.115
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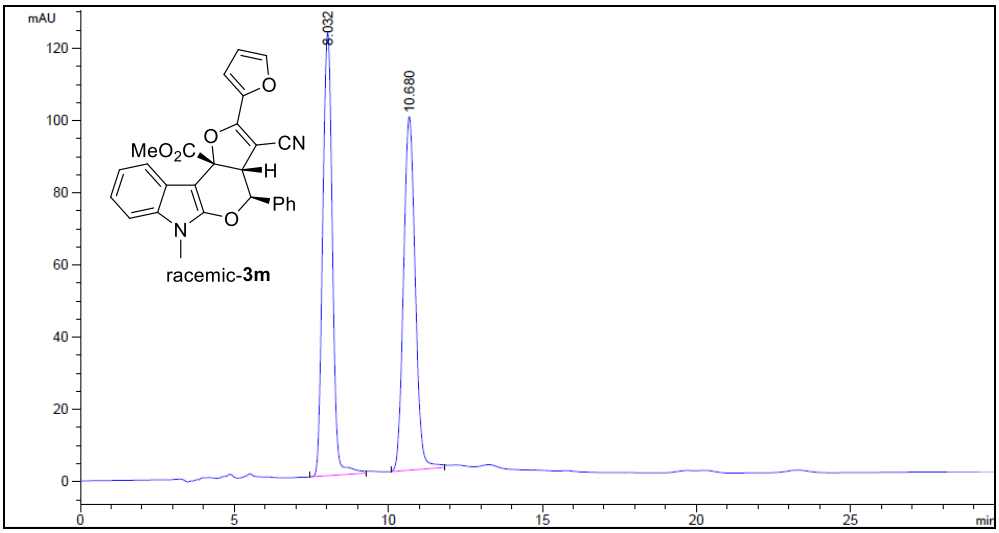
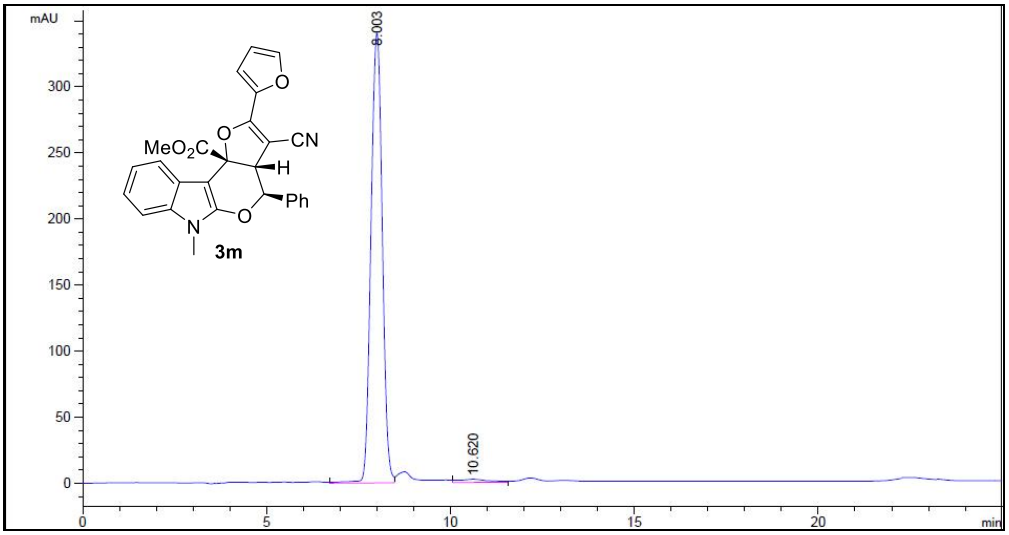
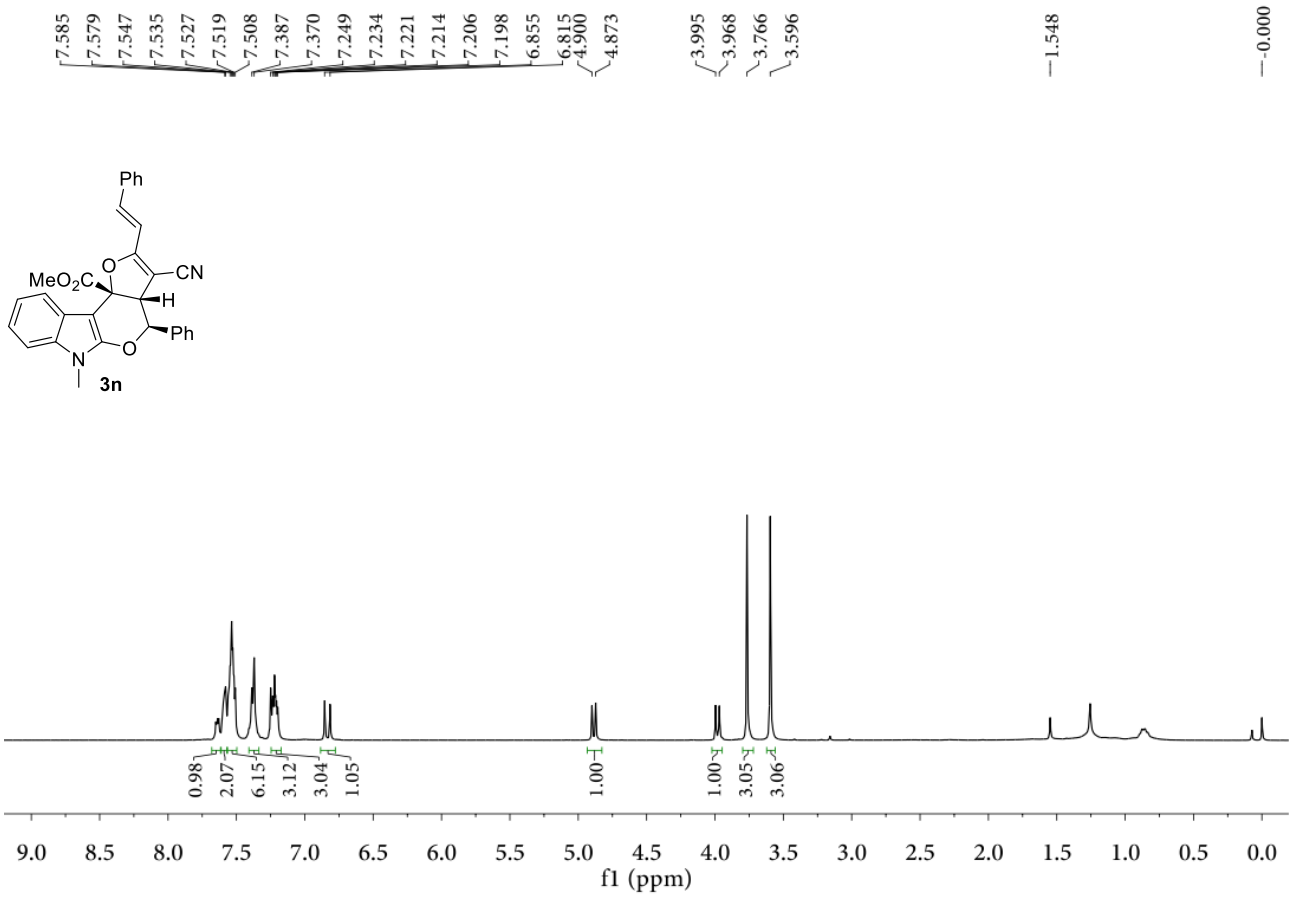
112.116
108.834
87.044
83.365
83.057
78.338
53.330
50.558
27.756
MeO2C
CN
H
Ph
N
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.032	BB	0.3490	2686.56372	122.50733	50.9305
2	10.680	BB	0.4134	2588.39429	97.84978	49.0695



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.003	VV	0.3488	7286.86328	340.29074	98.0862
2	10.620	BV	0.8027	142.17967	2.39699	1.9138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7.214
7.206
7.198
6.855
6.815
4.900
4.873
3.995
3.968
3.766
3.596
1.548
-0.000
Ph
MeO2C
O
CN
H
Ph
N
O
3n
0.98
2.07
6.15
3.12
3.04
1.05
1.00
1.00
3.05
3.06
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8.5
8.0
7.5
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6.5
6.0
5.5
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3.5
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2.5
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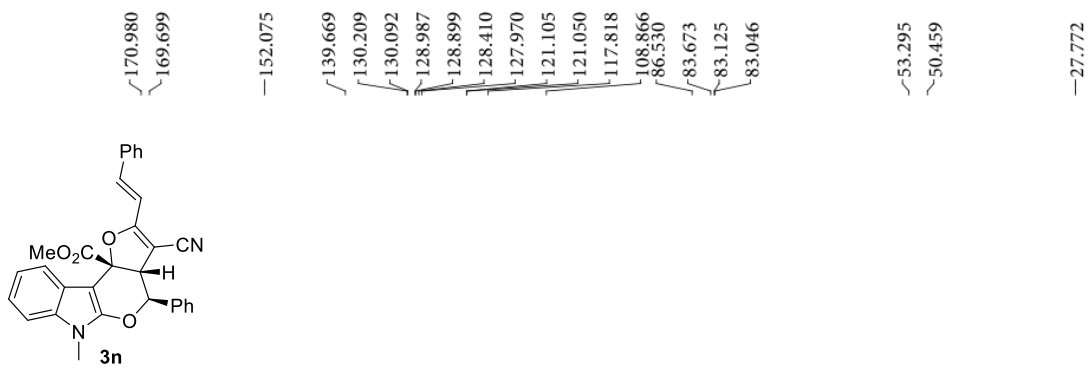
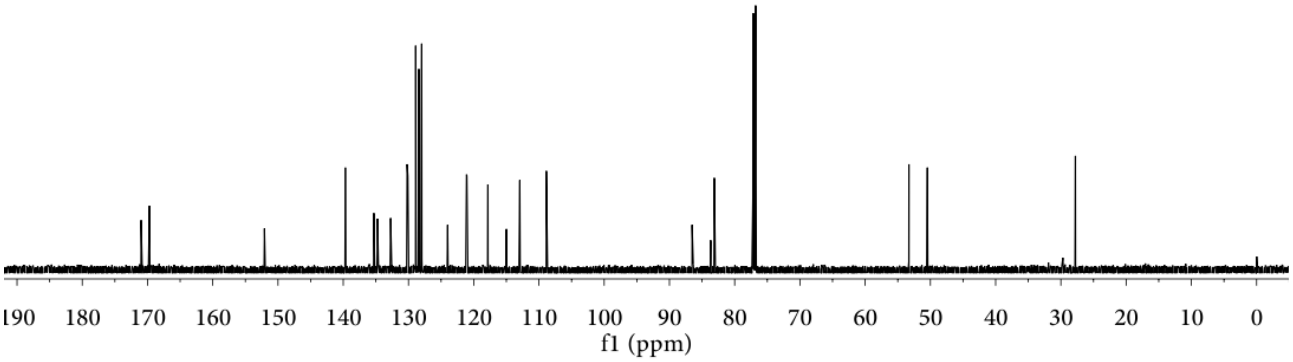
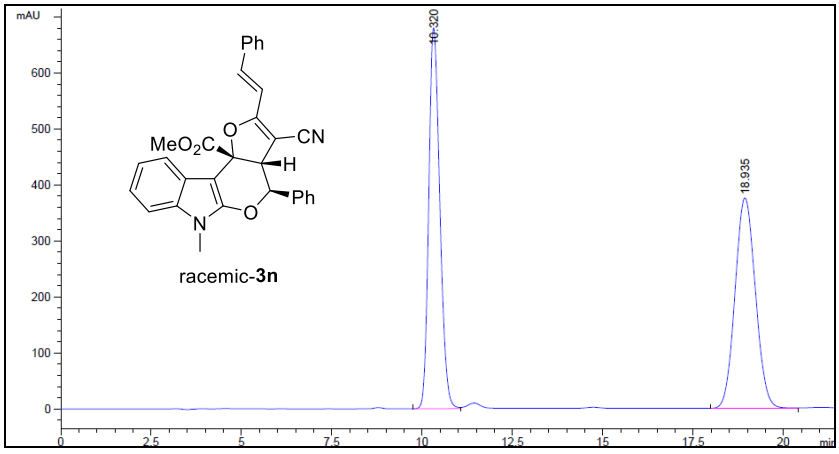
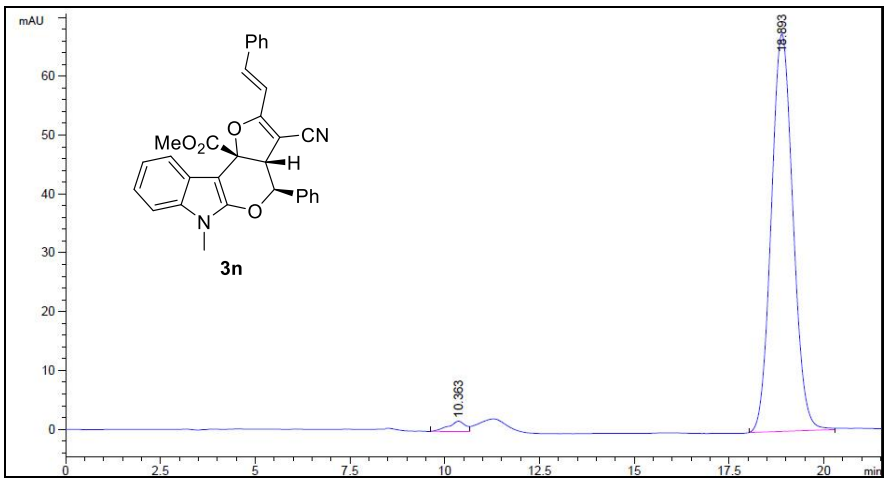
0.0
f1 (ppm)



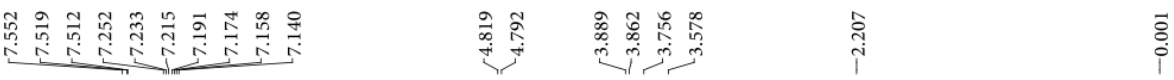


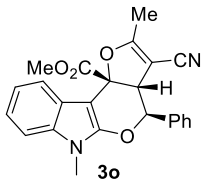


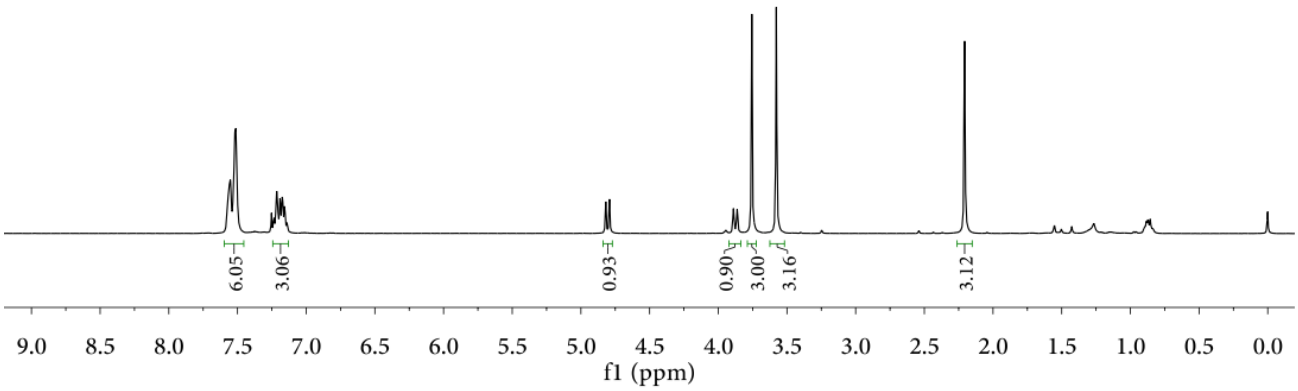
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.320	BV	0.3299	1.44656e4	679.46362	49.4866
2	18.935	BV	0.6156	1.47658e4	375.80792	50.5134



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.363	MM	0.5178	54.46294	1.75305	1.9861
2	18.893	BB	0.6216	2687.75293	67.52803	98.0139







174.333
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121.123
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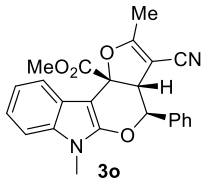
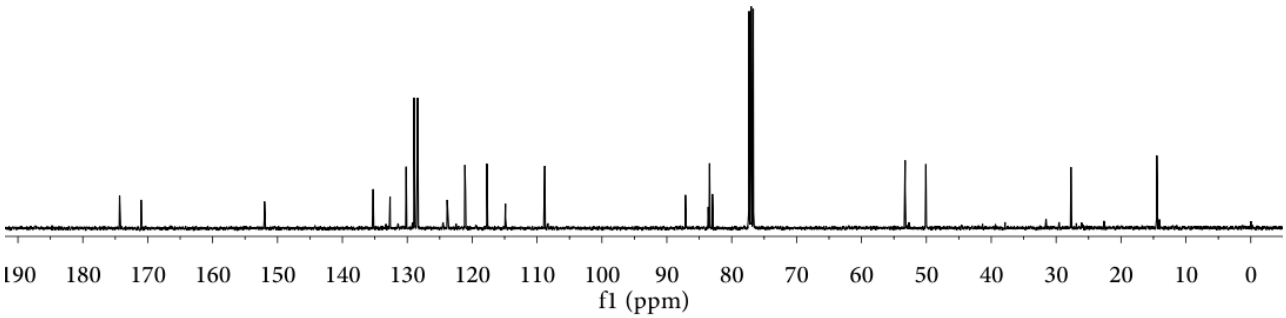
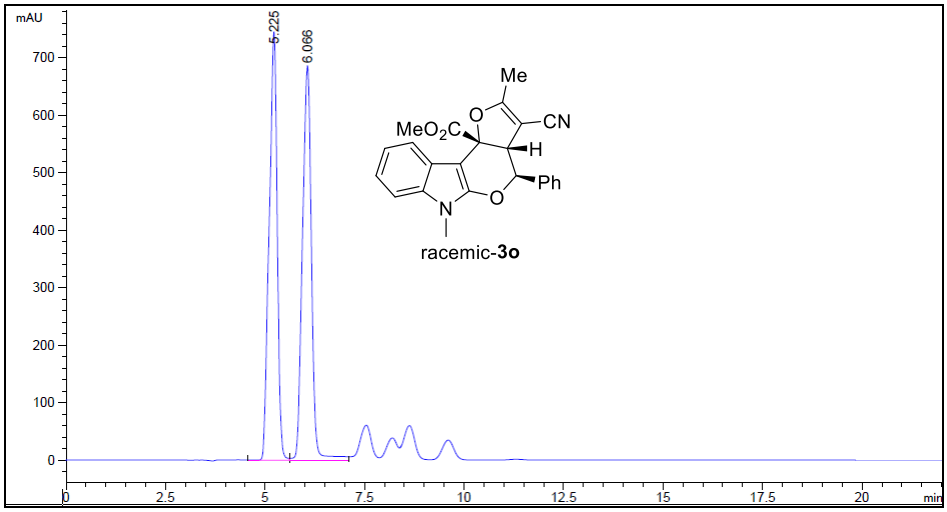
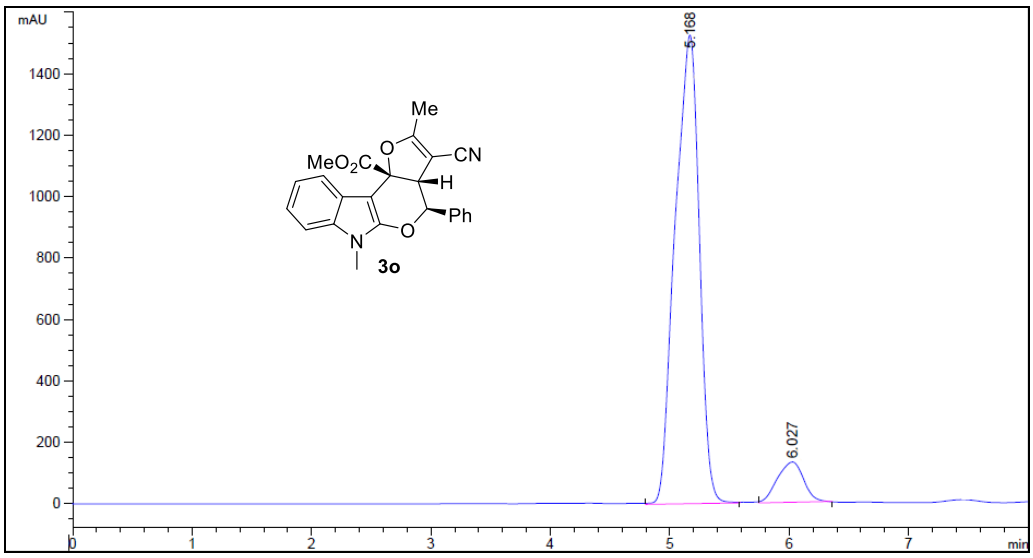


3o

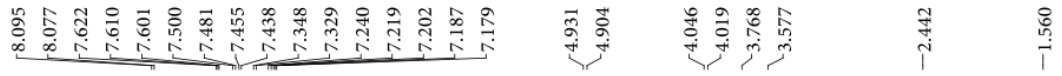


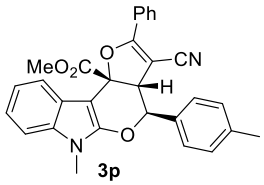


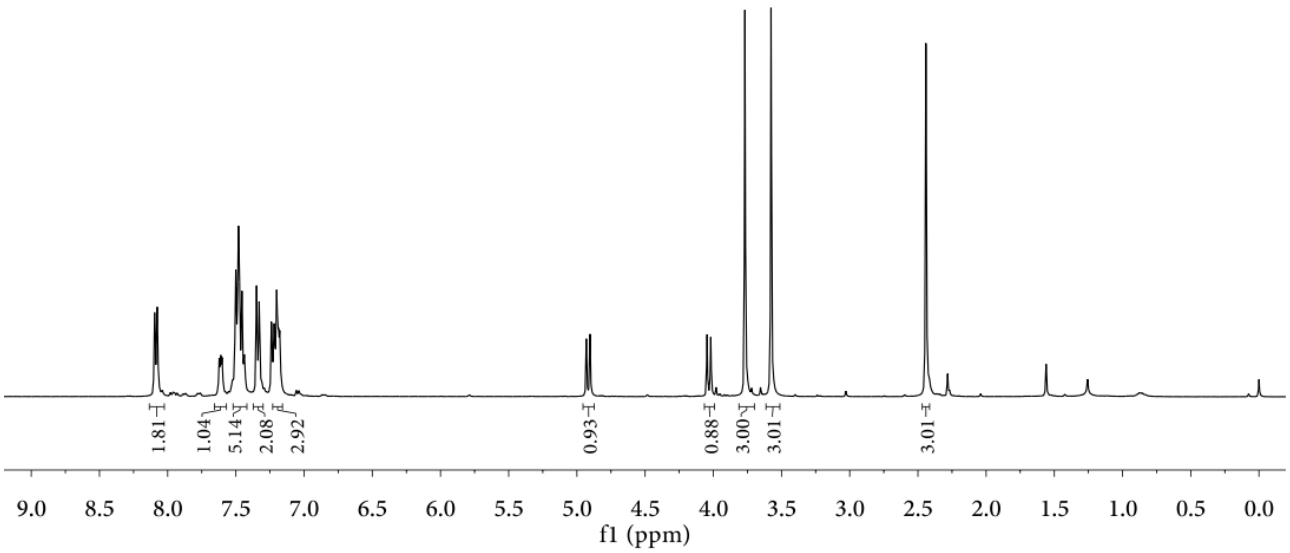
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.225	VV	0.2049	1.04660e4	744.15814	49.1123
2	6.066	VB	0.2604	1.08444e4	685.03015	50.8877

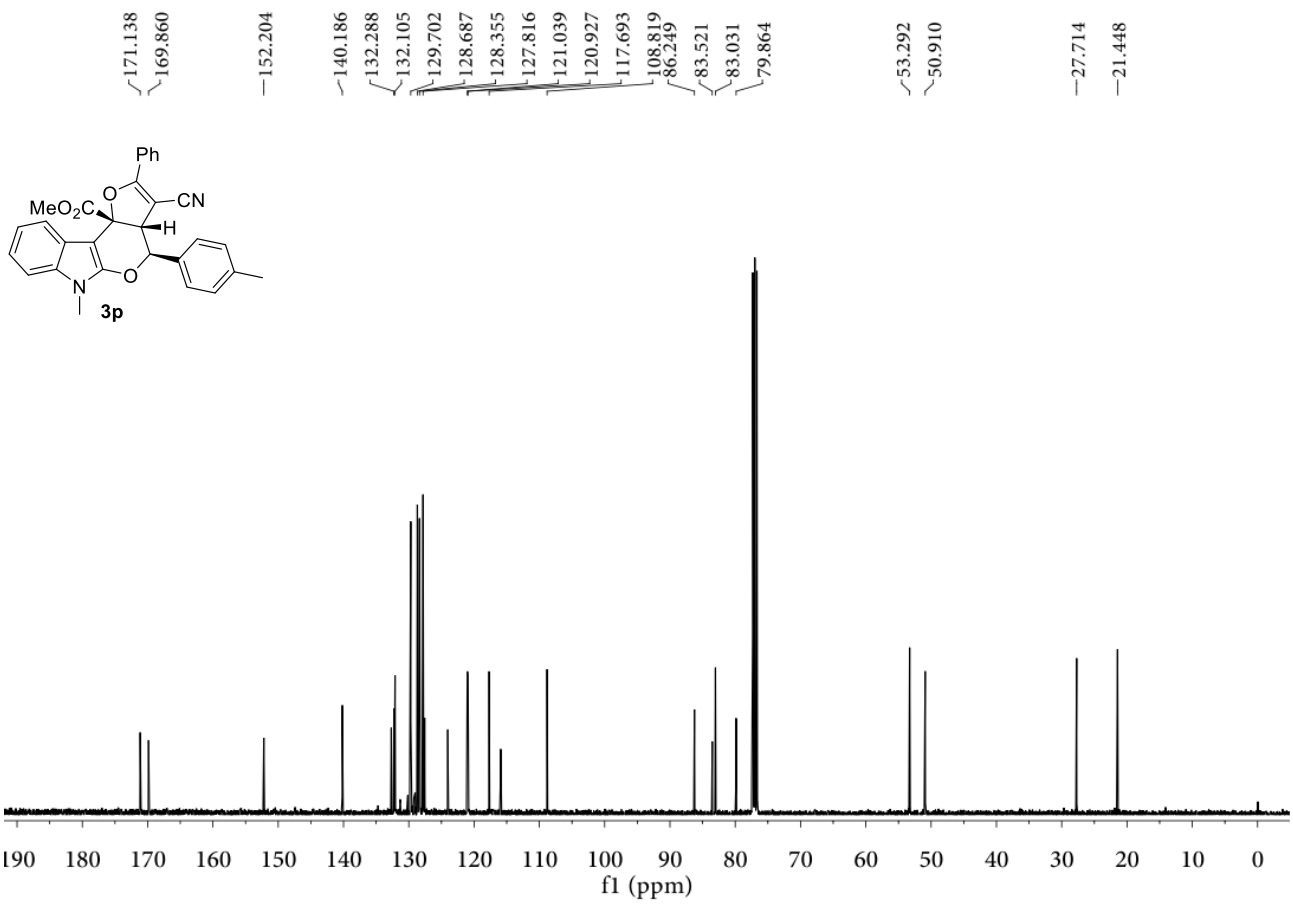


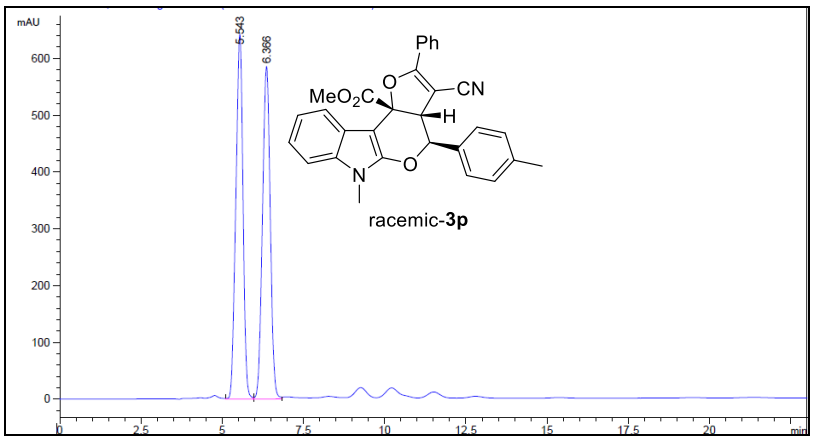
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.168	MM	0.2336	2.14363e4	1529.10999	91.4612
2	6.027	MM	0.2543	2001.27808	131.16069	8.5388



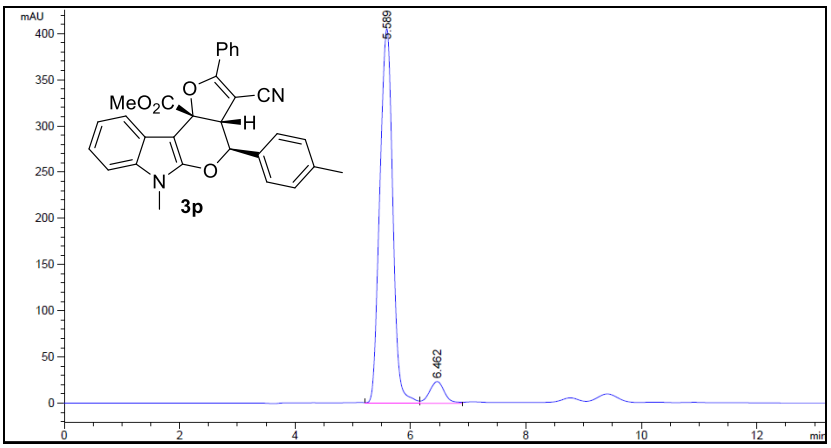




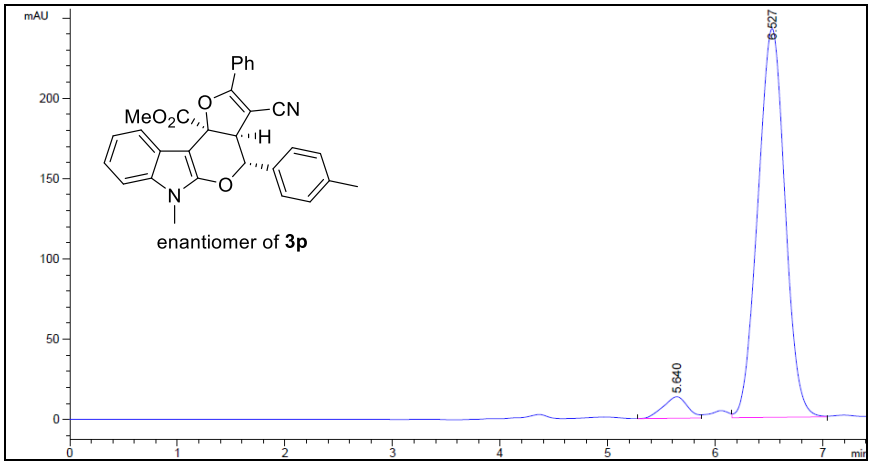




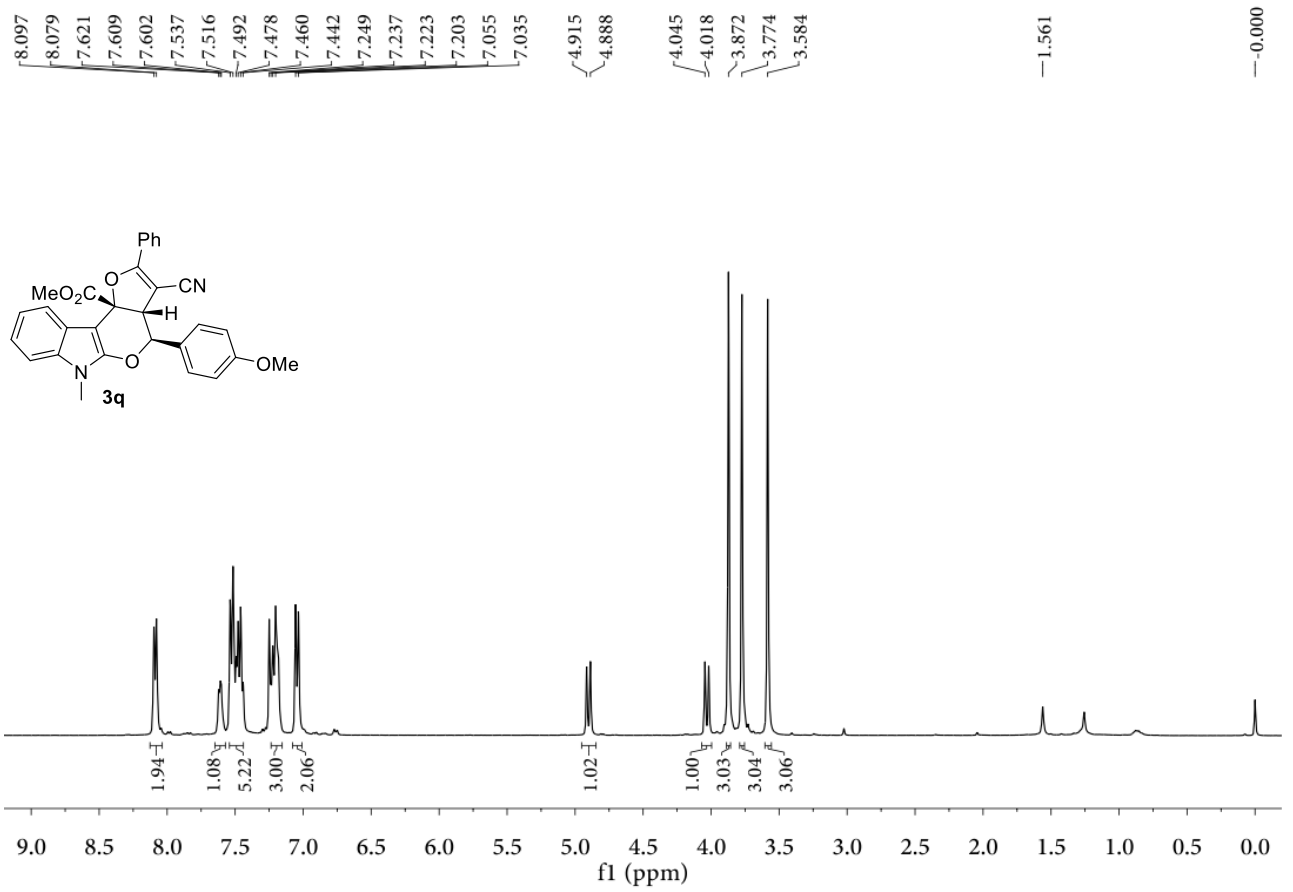
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.543	VV	0.2313	9835.90820	641.36163	50.2076
2	6.366	VV	0.2644	9754.56543	584.93188	49.7924



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.589	VV	0.2522	6330.13721	405.13907	93.6727
2	6.462	VV	0.2820	427.57843	23.51339	6.3273



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.640	VV	0.2364	210.49884	13.34438	4.7264
2	6.527	VV	0.2746	4243.21875	241.79958	95.2736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Ph
MeO2C
O
CN
H
N
O
OMe
3q
1.94
1.08
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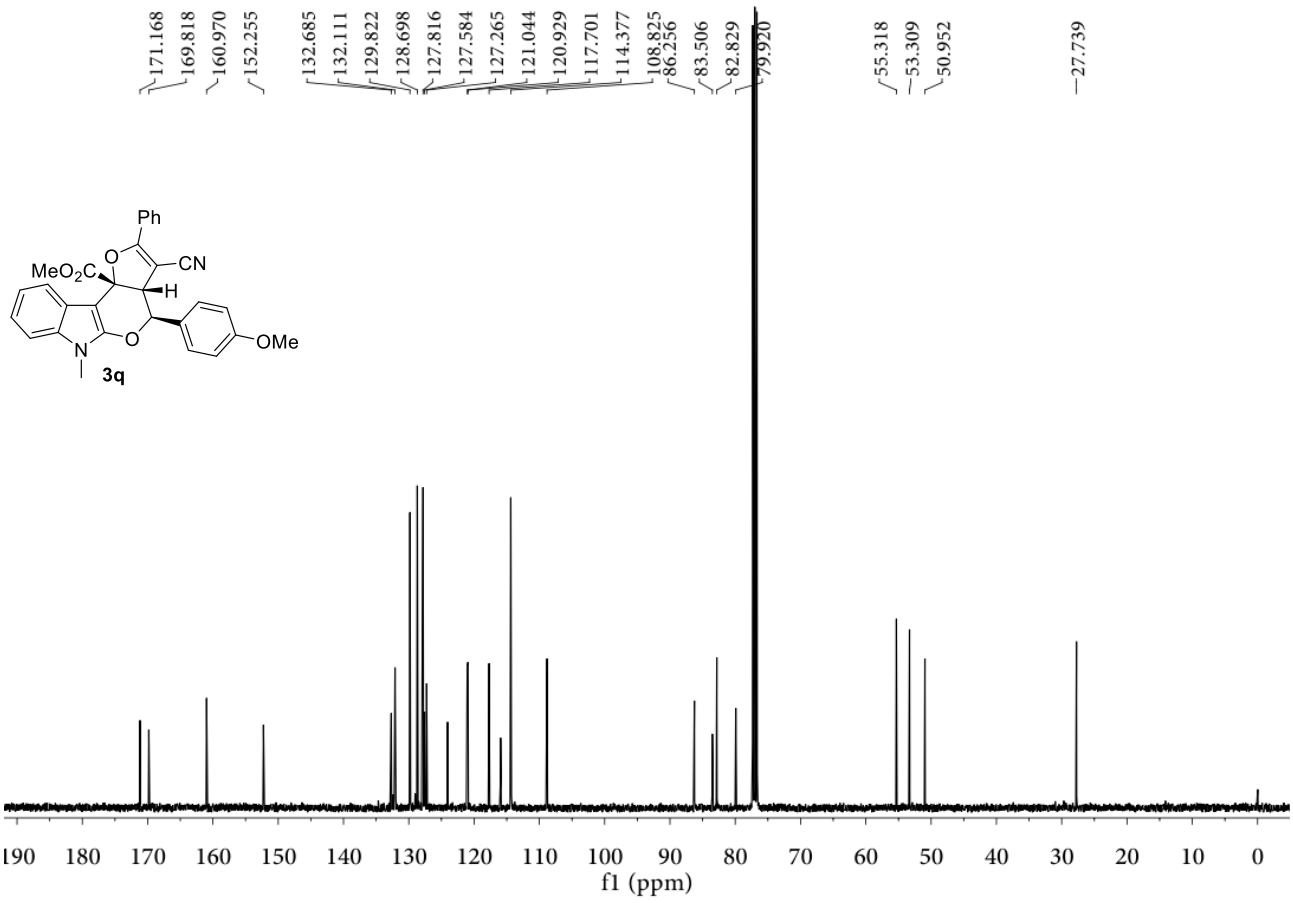
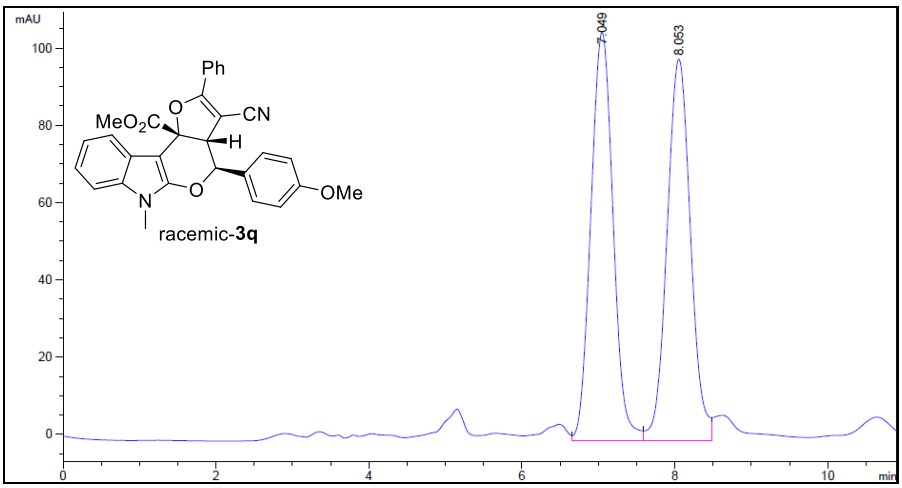
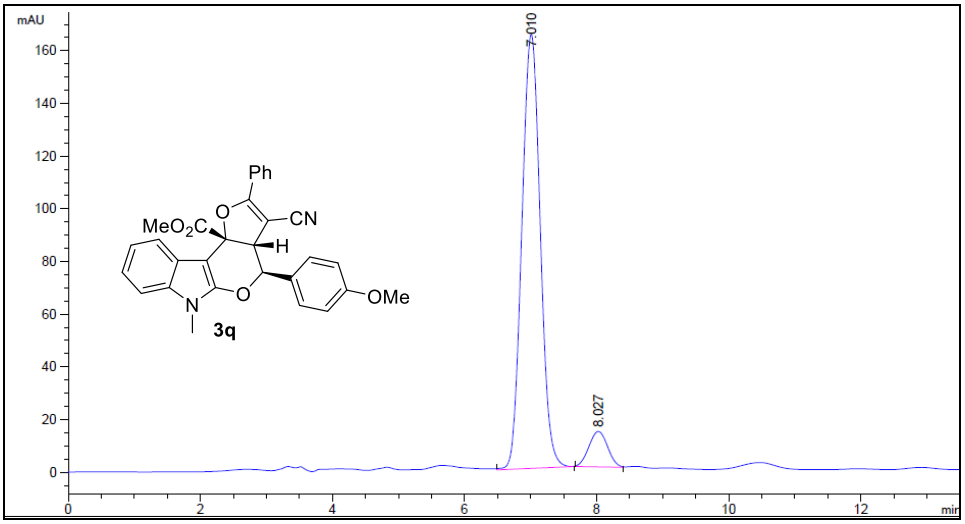
3.00
2.06
1.02
1.00
3.03
3.04
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

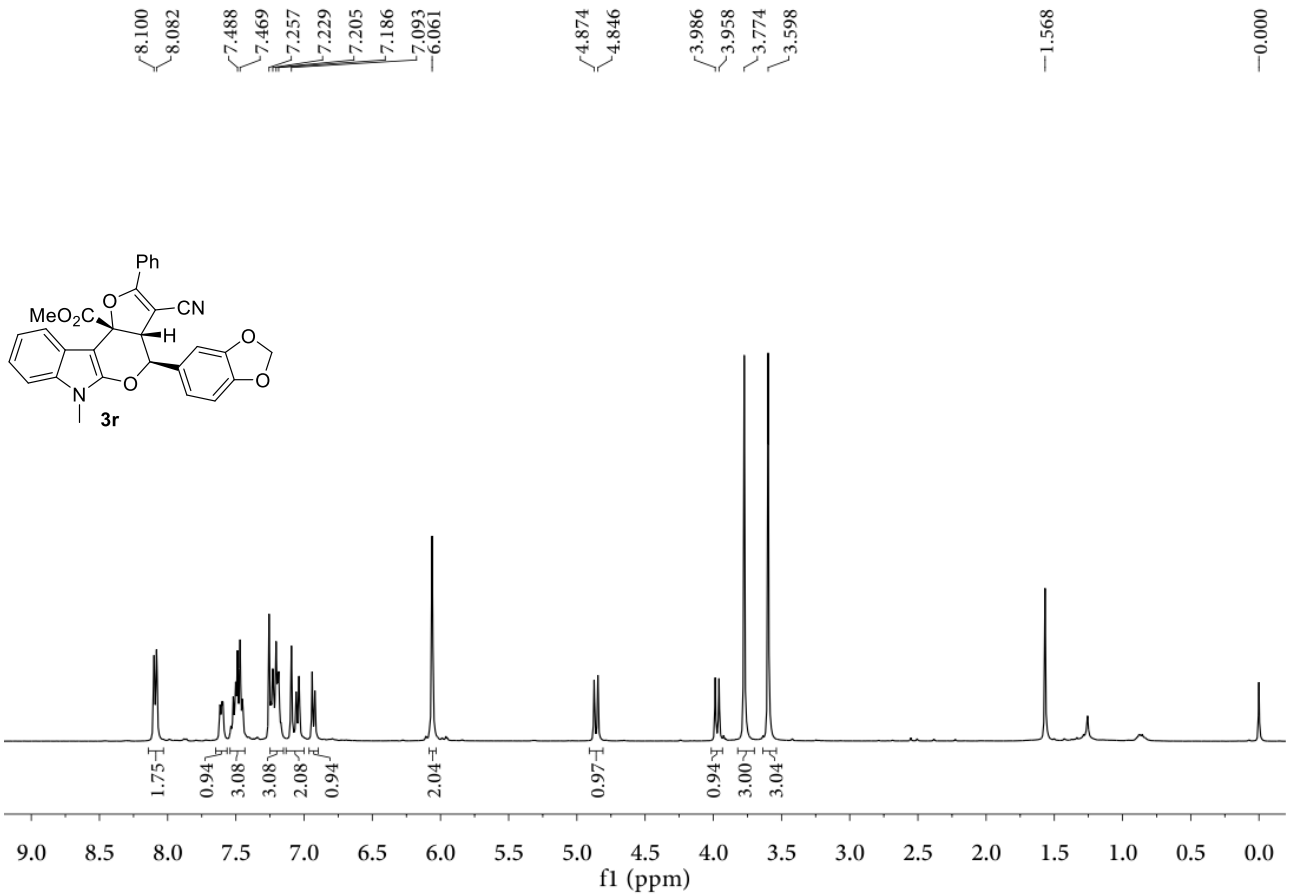

171.168
169.818
160.970
152.255
132.685
132.111
129.822
128.698
127.816
127.584
127.265
121.044
120.929
117.701
114.377
108.825
86.256
83.506
82.829
79.920
55.318
53.309
50.952
27.739
Ph
MeO2C
O
CN
H
N
O
OMe
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

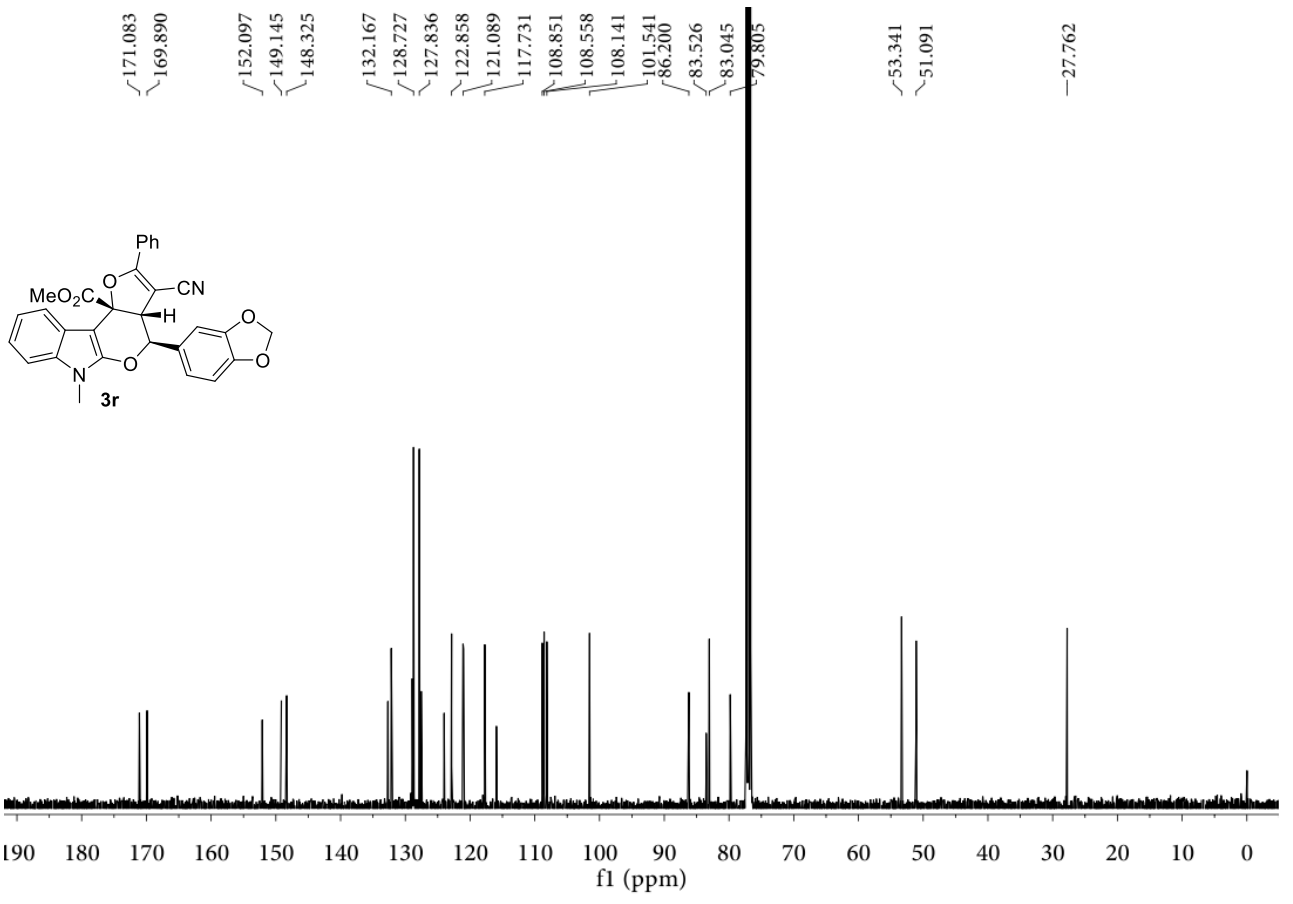


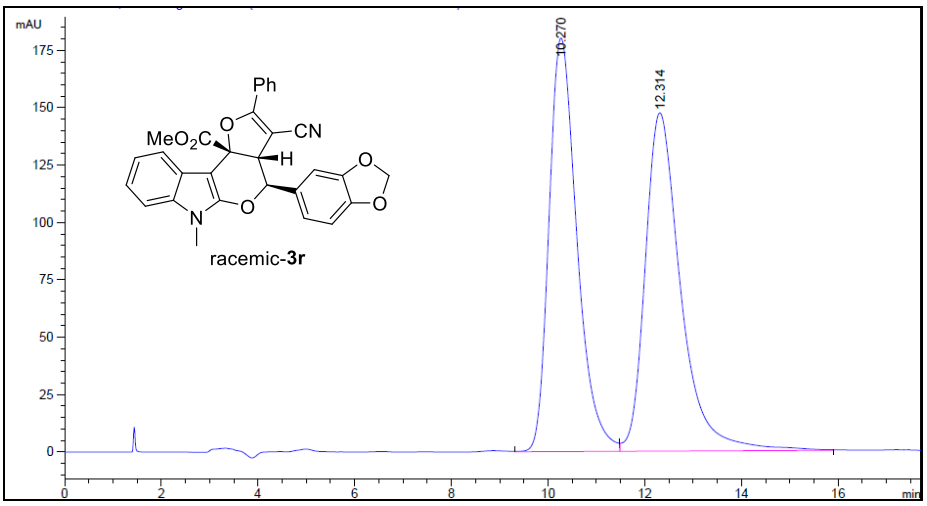
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.049	VV	0.3177	2138.81274	105.65670	50.3326
2	8.053	VV	0.3367	2110.54883	98.73692	49.6674



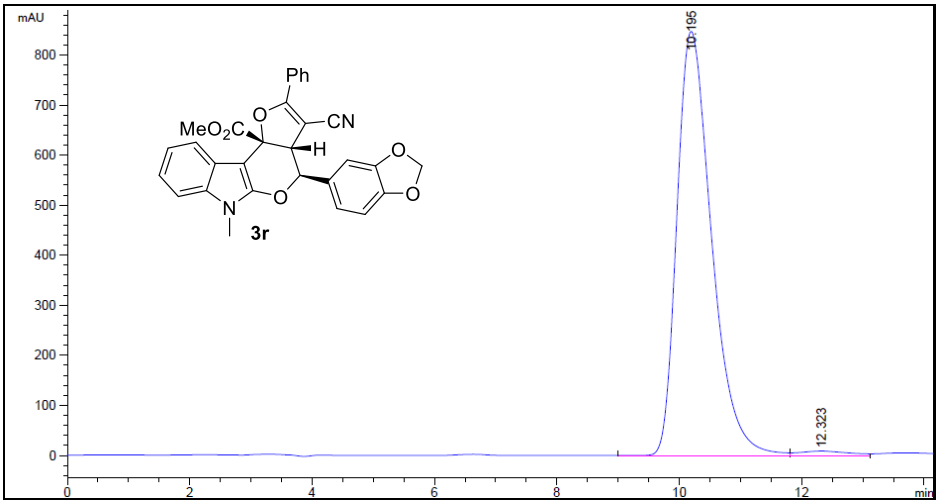
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.010	MM	0.3219	3186.64355	165.00511	92.3195
2	8.027	MM	0.3280	265.11169	13.47006	7.6805


8.100
8.082
7.488
7.469
7.257
7.229
7.205
7.186
7.093
6.061
4.874
4.846
3.986
3.958
3.774
3.598
1.568
0.000
Ph
MeO2C
CN
H
O
N
3r
1.75
0.94
3.08
3.08
2.08
0.94
2.04
0.97
0.94
3.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

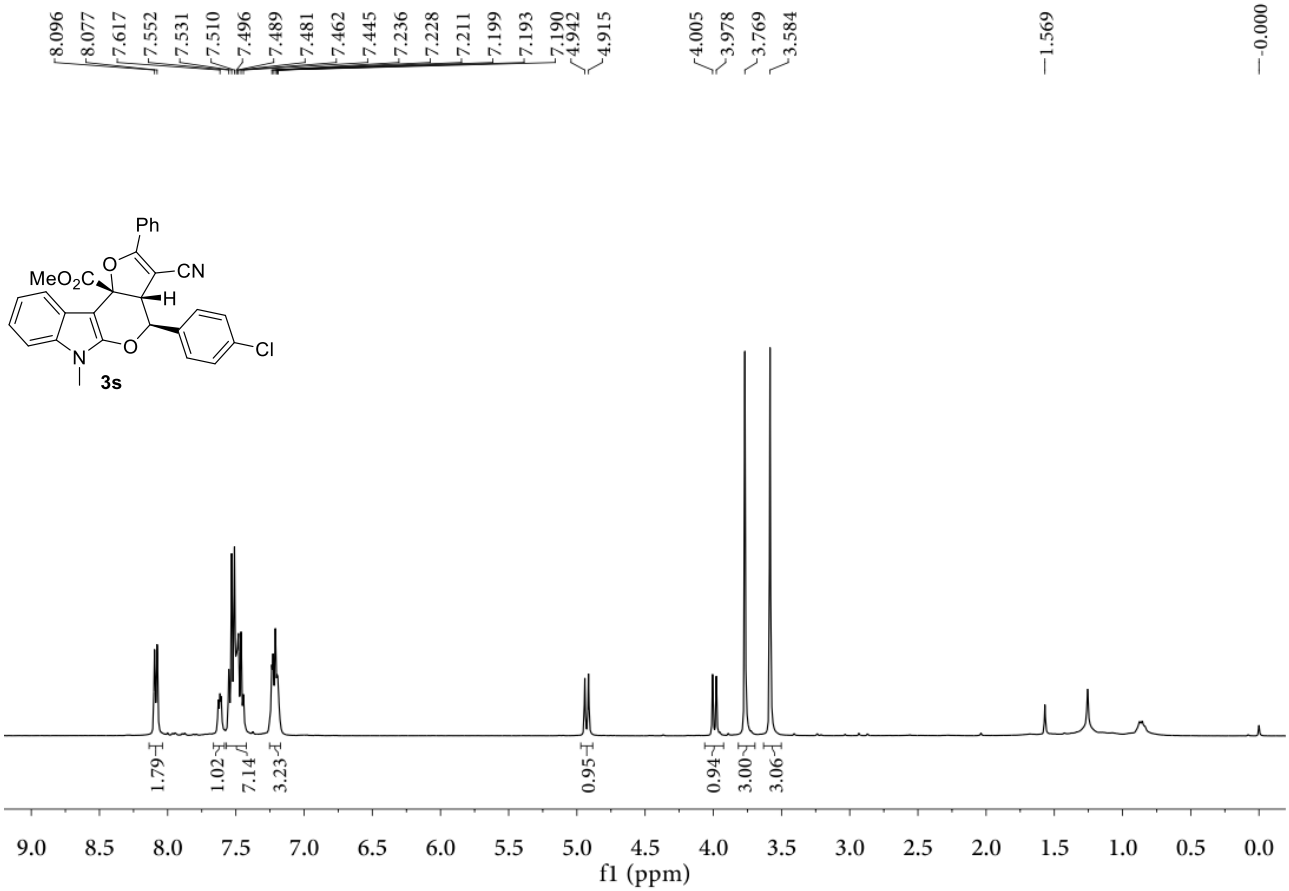

171.083
169.890
152.097
149.145
148.325
132.167
128.727
127.836
122.858
121.089
117.731
108.851
108.558
108.141
101.541
86.200
83.526
83.045
79.805
53.341
51.091
27.762
Ph
MeO2C
CN
H
O
N
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

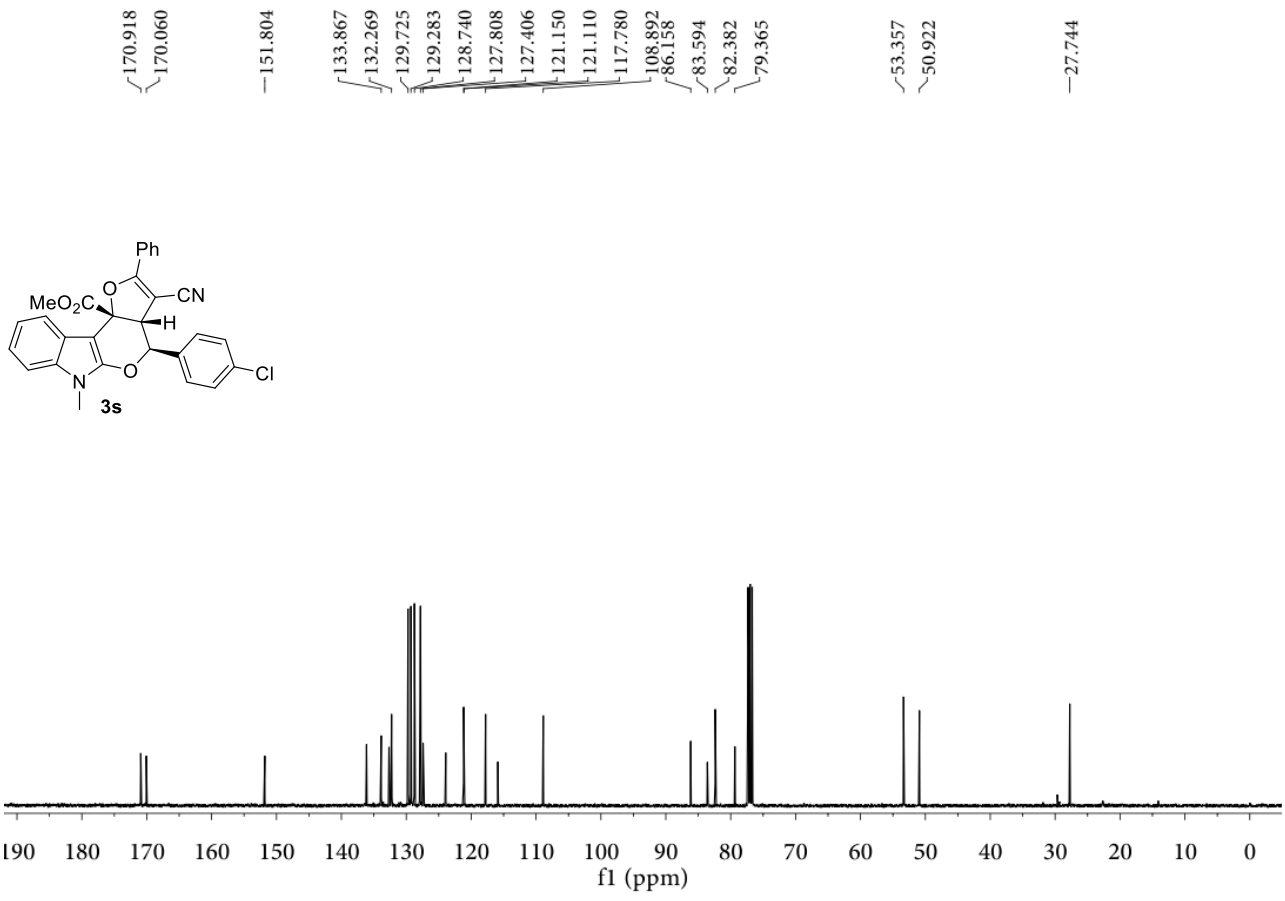


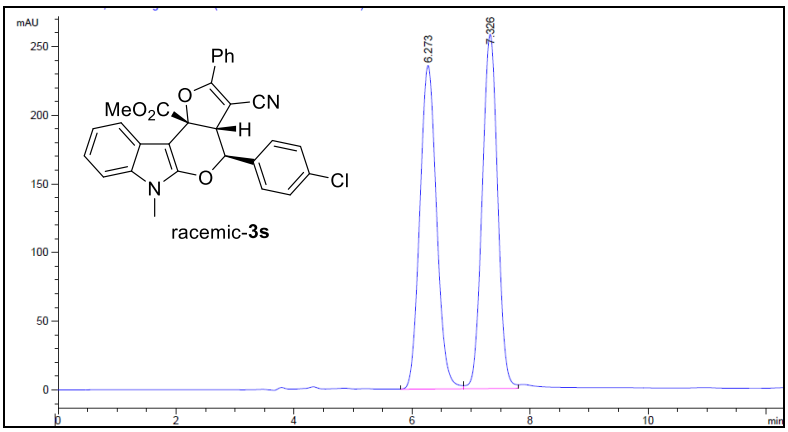
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.270	VV	0.6207	7245.58740	180.11516	48.9911
2	12.314	VB	0.7779	7544.01221	147.33261	51.0089



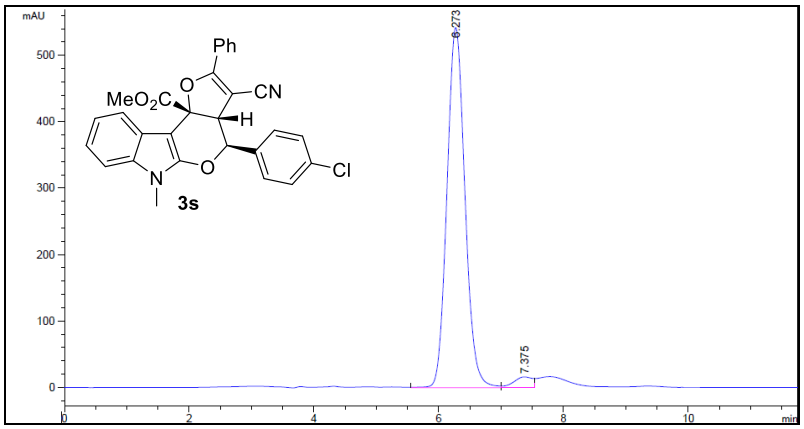
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.195	BV	0.6047	3.33298e4	846.93634	98.5213
2	12.323	VV	0.8172	500.24554	8.92203	1.4787


8.096
8.077
7.617
7.552
7.531
7.510
7.496
7.489
7.481
7.462
7.445
7.236
7.228
7.211
7.199
7.193
7.190
4.942
4.915
4.005
3.978
3.769
3.584
1.569
0.000
Ph
MeO2C
O
CN
H
N
O
Cl
3s
1.79
1.02
7.14
3.23
0.95
0.94
3.00
3.06
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)

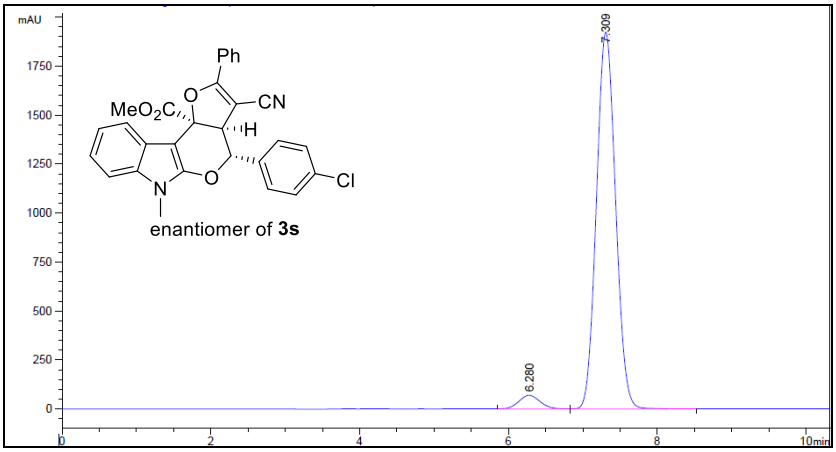

170.918
170.060
151.804
133.867
132.269
129.725
129.283
128.740
127.808
127.406
121.150
121.110
117.780
108.892
86.158
83.594
82.382
79.365
53.357
50.922
27.744
Ph
MeO2C
O
CN
H
N
O
Cl
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



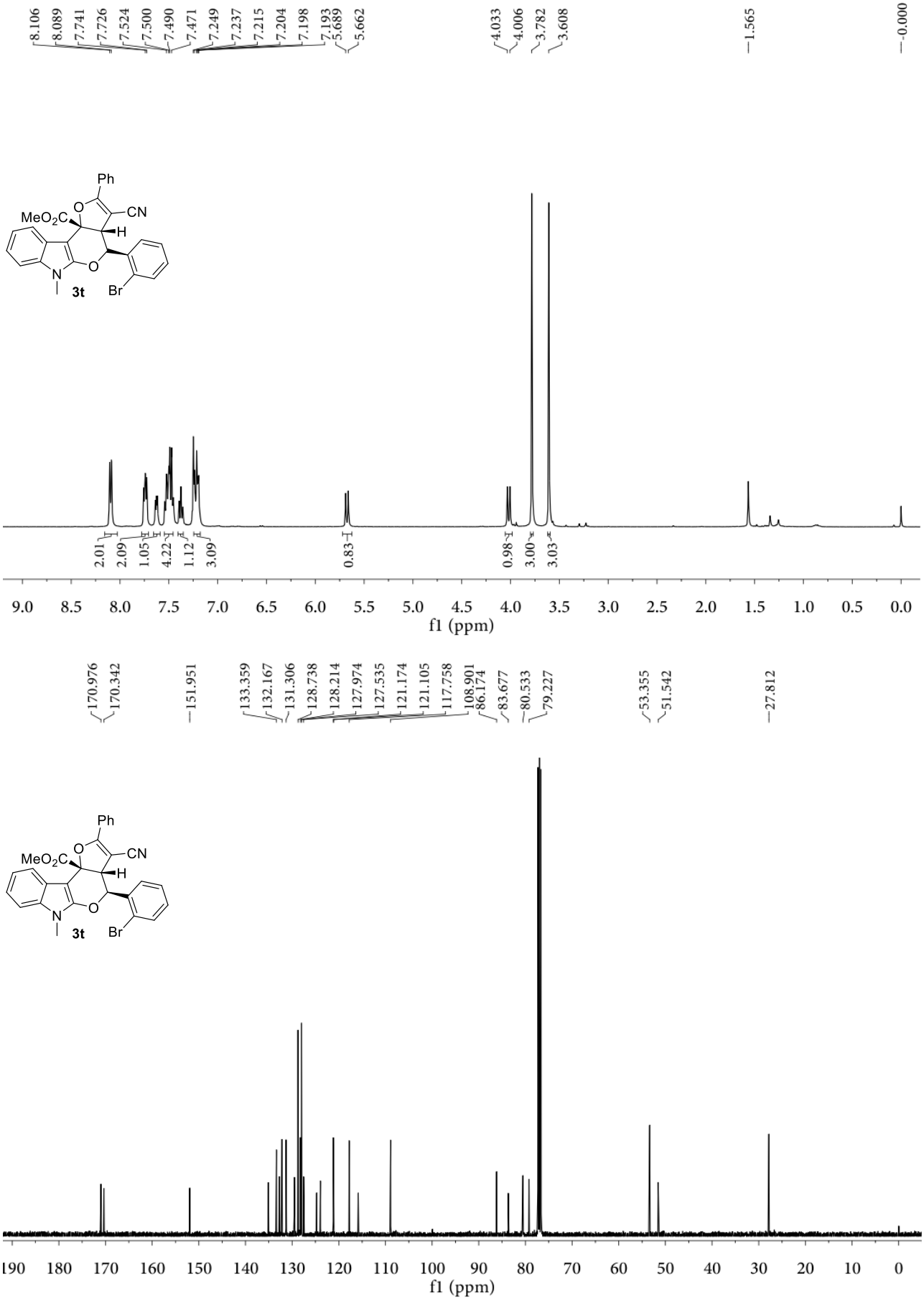
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.273	BV	0.3070	4667.60938	235.41473	49.8306
2	7.326	VV	0.2884	4699.35254	257.75470	50.1694

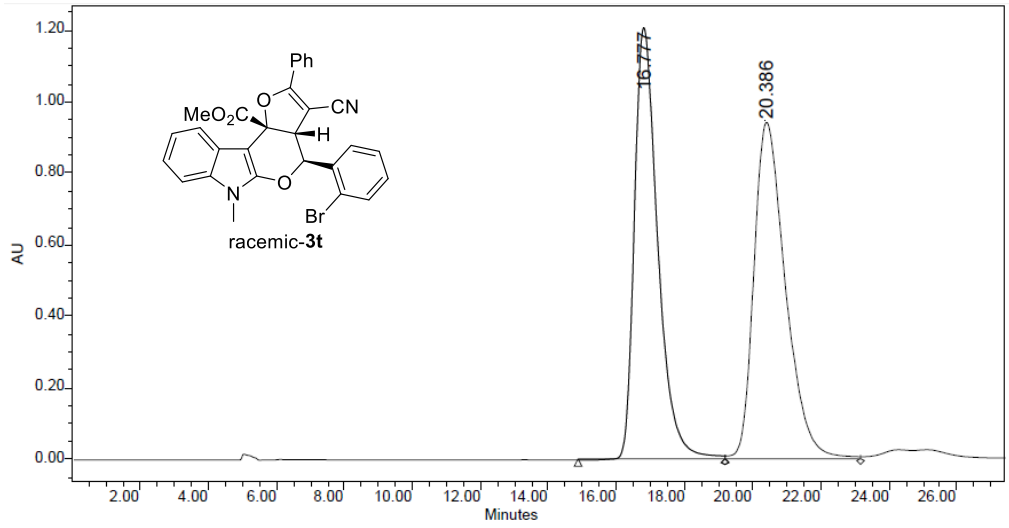


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.273	VV	0.3097	1.08659e4	541.83704	96.9622
2	7.375	VV	0.3144	340.43130	16.24006	3.0378

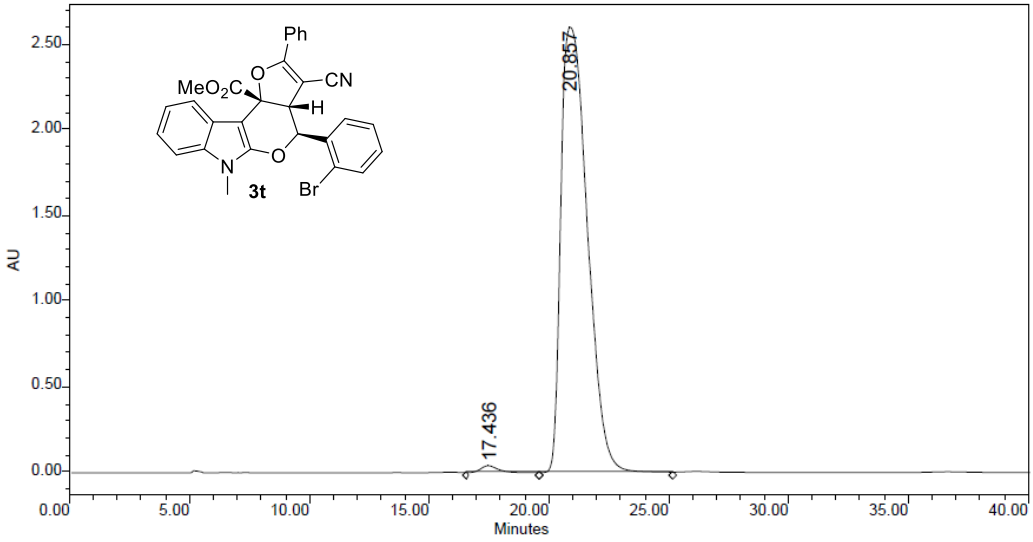


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.280	VV	0.3105	1406.95361	69.91431	3.9311
2	7.309	VB	0.2845	3.43837e4	1921.62354	96.0689

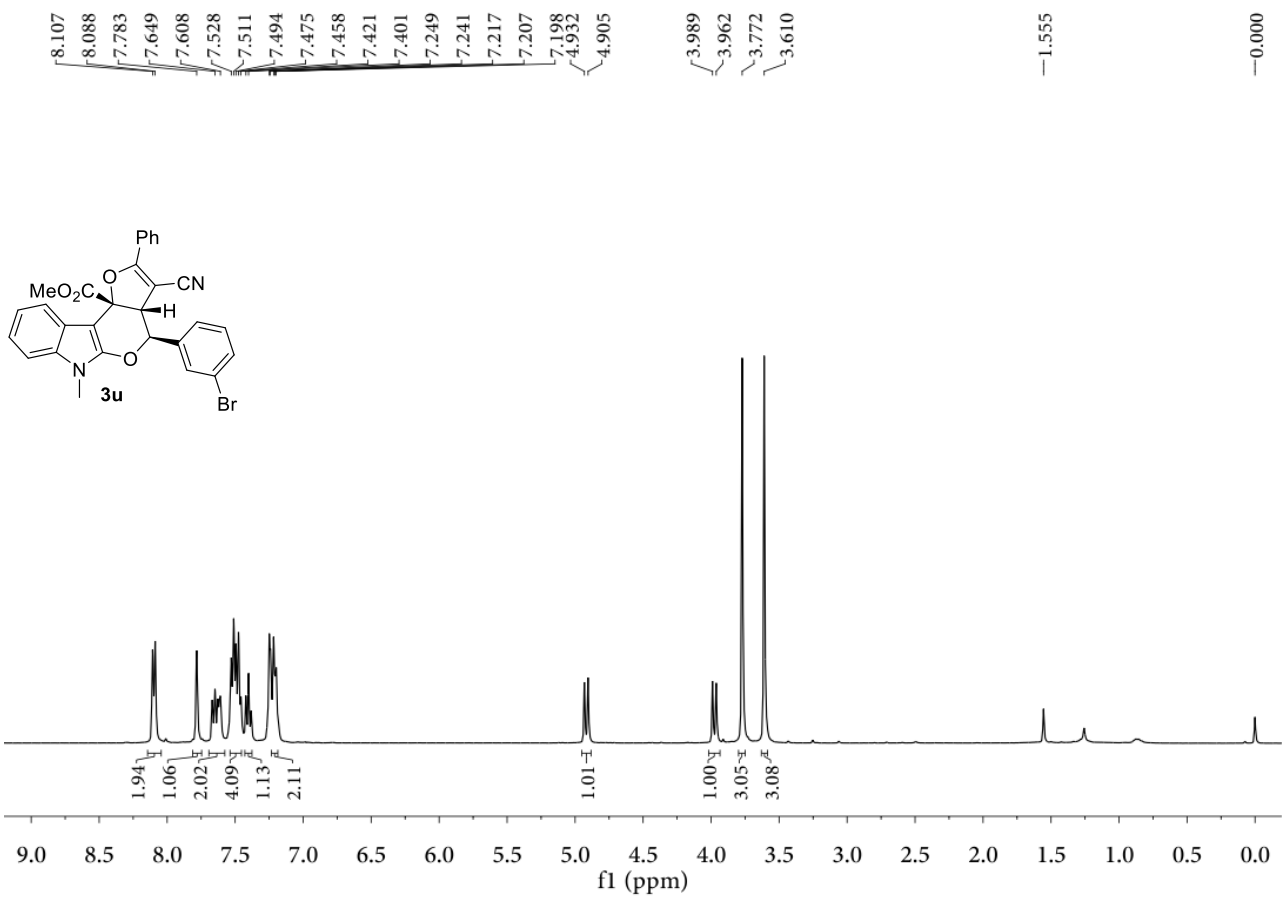

8.106
8.089
7.741
7.726
7.524
7.500
7.490
7.471
7.249
7.237
7.215
7.204
7.198
7.193
5.689
5.662
4.033
4.006
3.782
3.608
1.565
0.000
Ph
CN
MeO2C
H
O
N
Br
3t
2.01
2.09
1.05
4.22
1.12
3.09
0.83
0.98
3.00
3.03
f1 (ppm)
170.976
170.342
151.951
133.359
132.167
131.306
128.738
128.214
127.974
127.535
121.174
121.105
117.758
108.901
86.174
83.677
80.533
79.227
53.355
51.542
27.812
f1 (ppm)

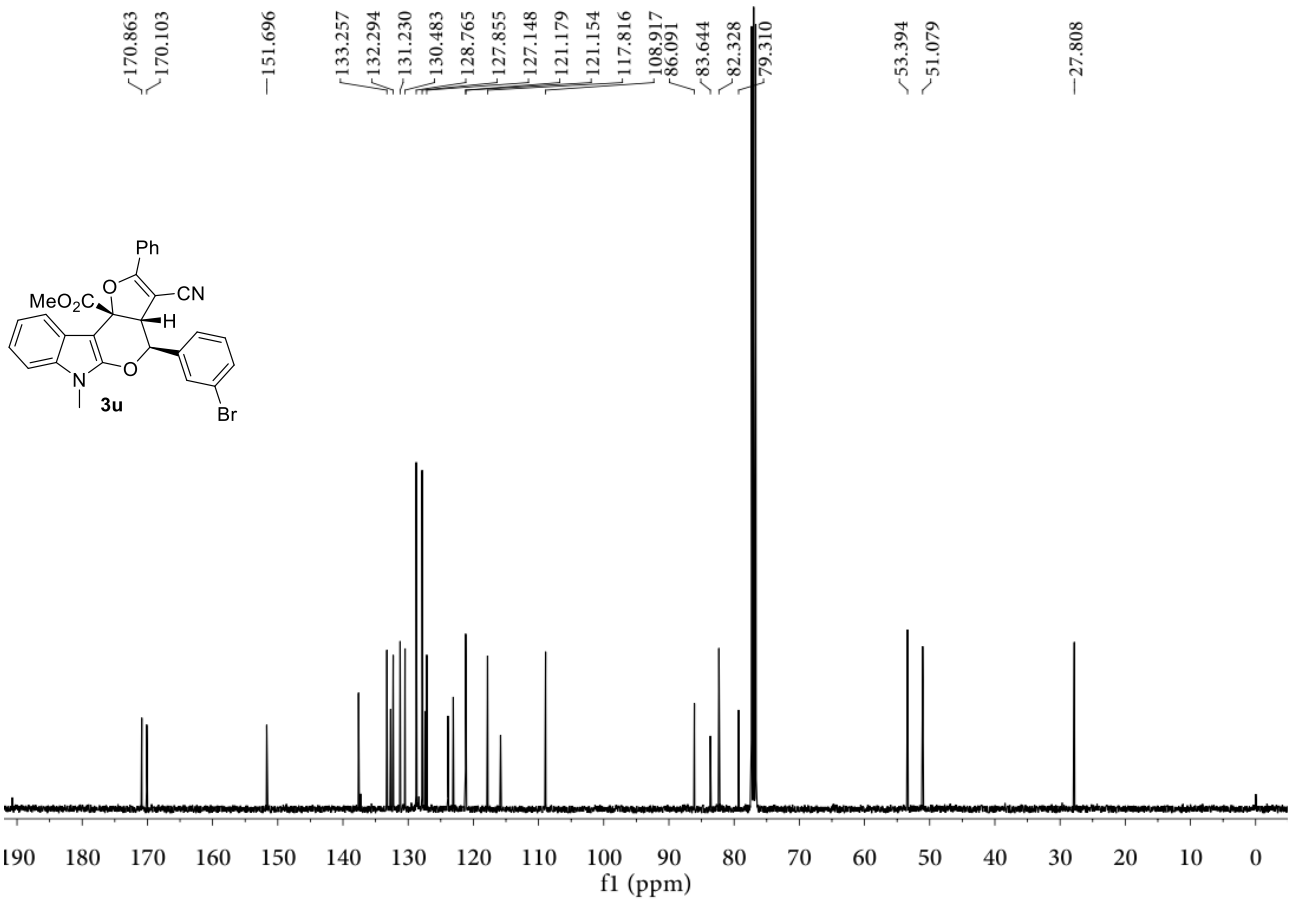


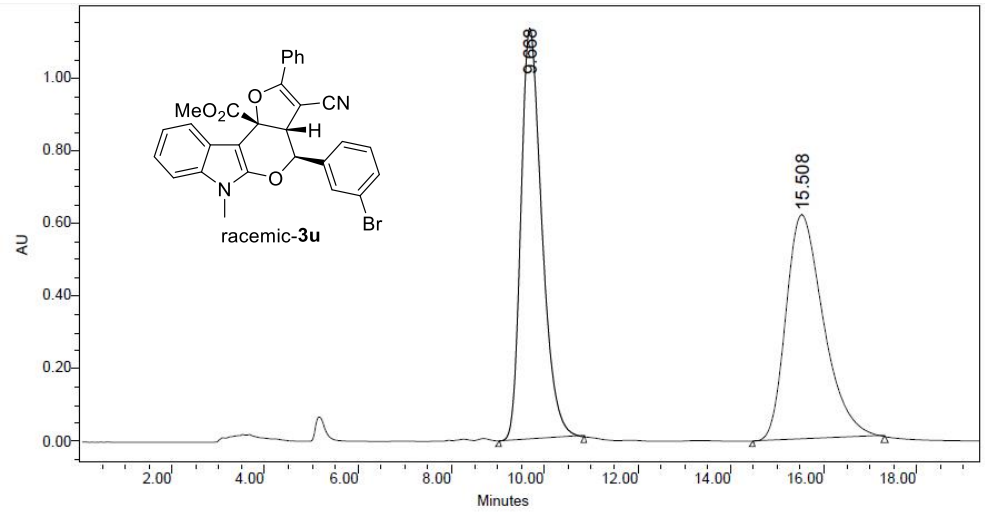
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	16.777	57881654	48.71	1208925	56.19
2	20.386	60954411	51.29	942448	43.81



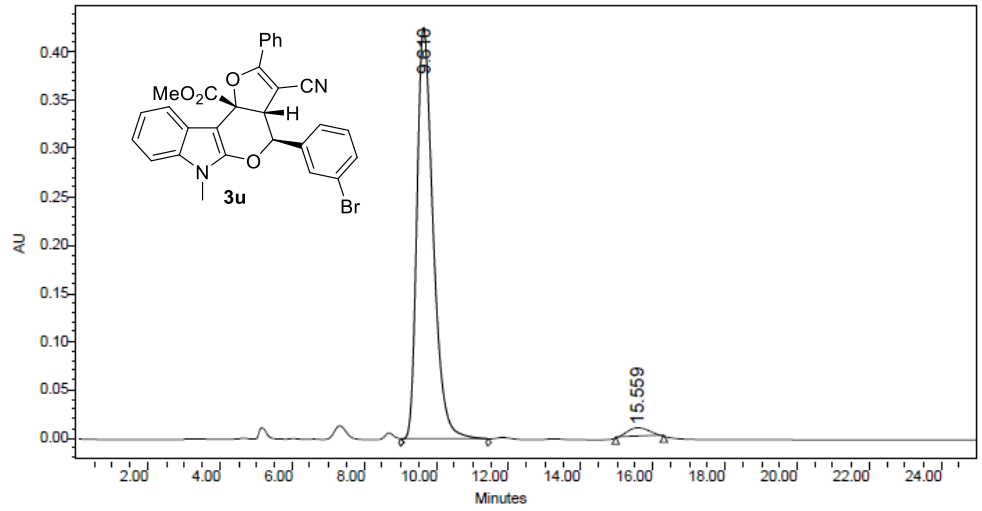
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	17.436	1998795	0.99	39772	1.50
2	20.857	200327687	99.01	2603961	98.50


8.107
8.088
7.783
7.649
7.608
7.528
7.511
7.494
7.475
7.458
7.421
7.401
7.249
7.241
7.217
7.207
7.198
4.932
4.905
3.989
3.962
3.772
3.610
1.555
0.000
Ph
MeO2C
O
CN
H
N
O
Br
3u
1.94
1.06
2.02
4.09
1.13
2.11
1.01
1.00
3.05
3.08
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)

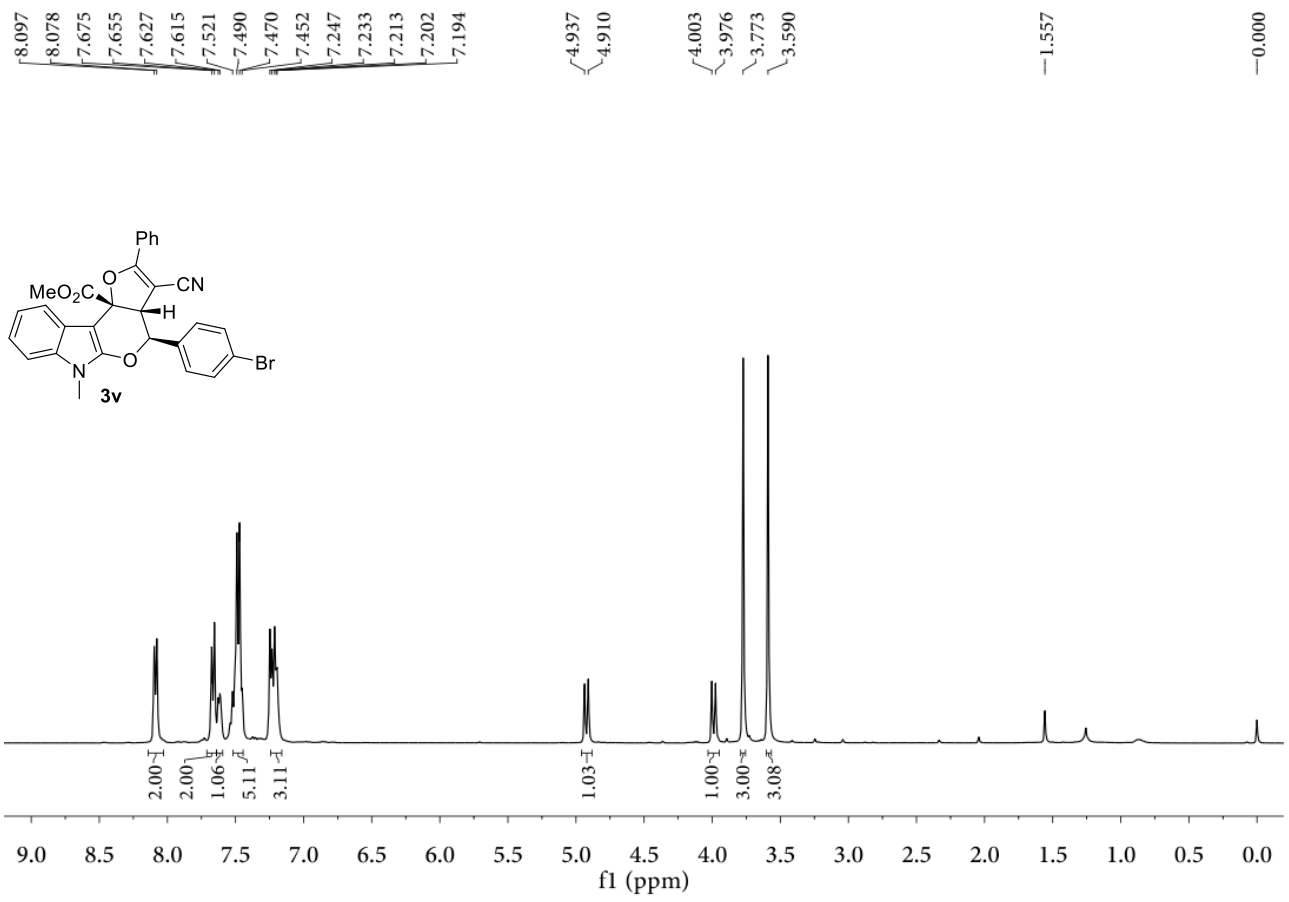

170.863
170.103
151.696
133.257
132.294
131.230
130.483
128.765
127.855
127.148
121.179
121.154
117.816
108.917
86.091
83.644
82.328
79.310
53.394
51.079
27.808
Ph
MeO2C
O
CN
H
N
O
Br
3u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

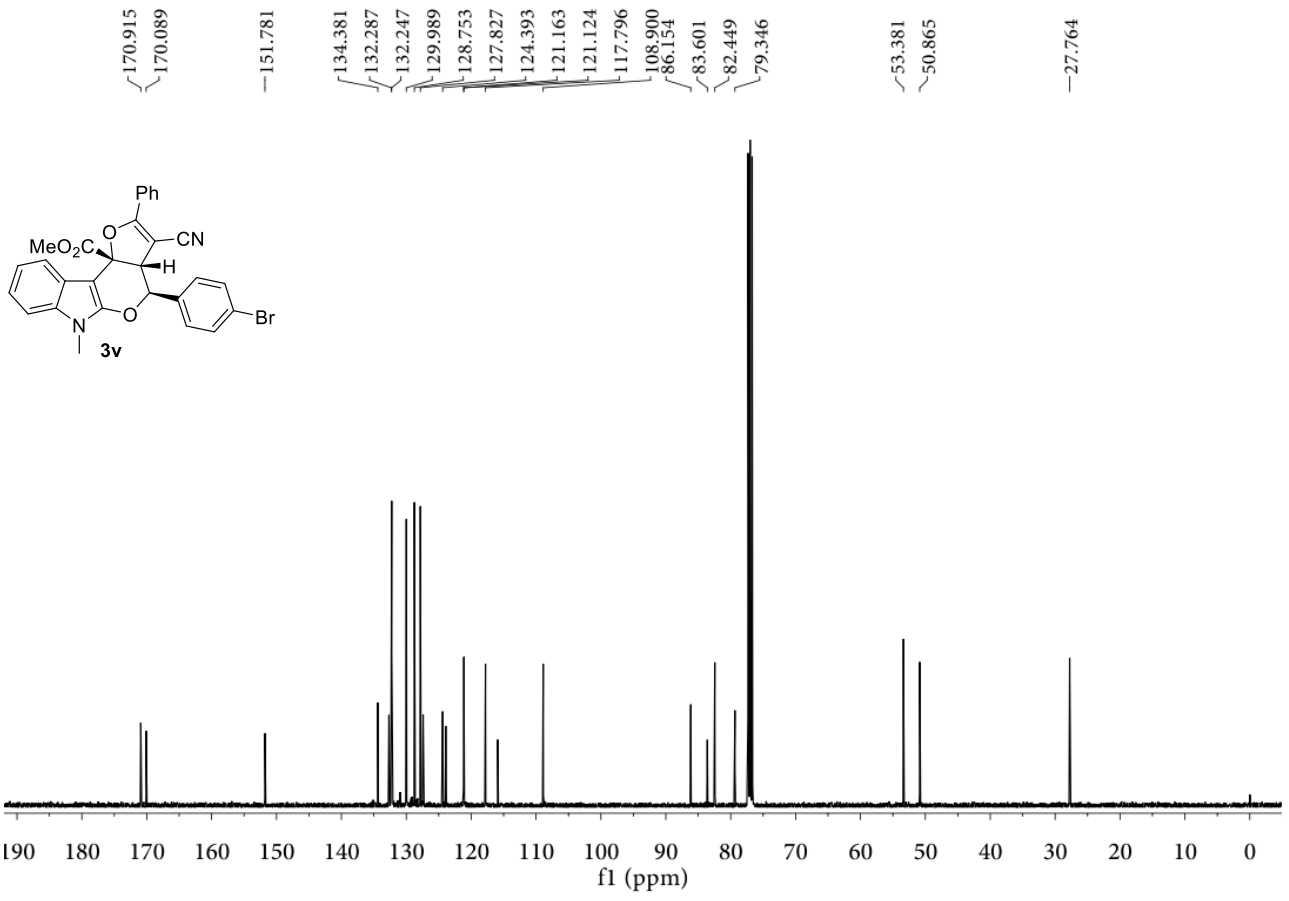


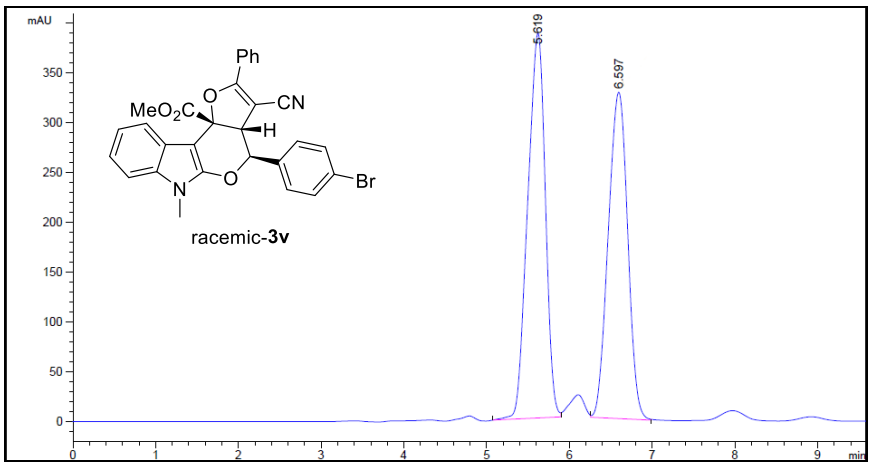
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.668	35418288	50.40	1131508	64.64
2	15.508	34859033	49.60	618860	35.36



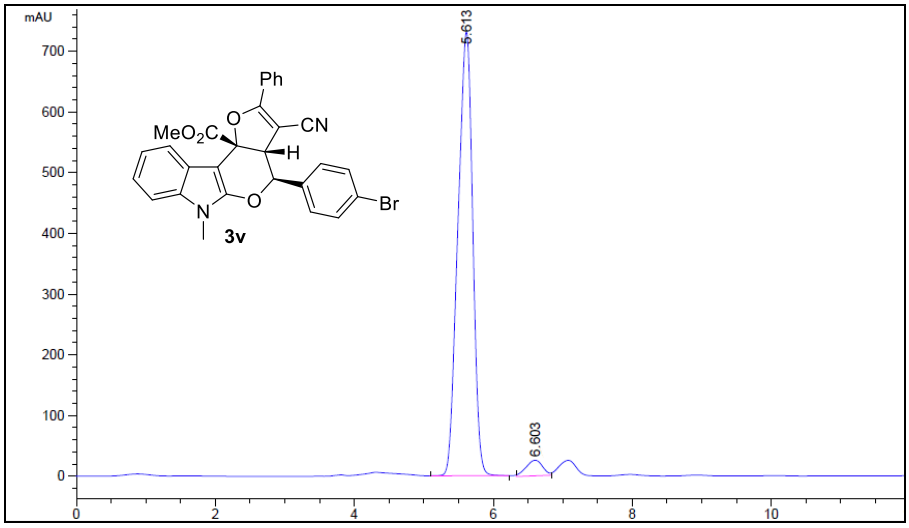
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.610	13387401	96.91	427175	97.77
2	15.559	426891	3.09	9744	2.23


8.097
8.078
7.675
7.655
7.627
7.615
7.521
7.490
7.470
7.452
7.247
7.233
7.213
7.202
7.194
4.937
4.910
4.003
3.976
3.773
3.590
1.557
0.000
Ph
MeO2C
O
CN
H
N
O
Br
3v
2.00
2.00
1.06
5.11
3.11
1.03
1.00
3.00
3.08
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)

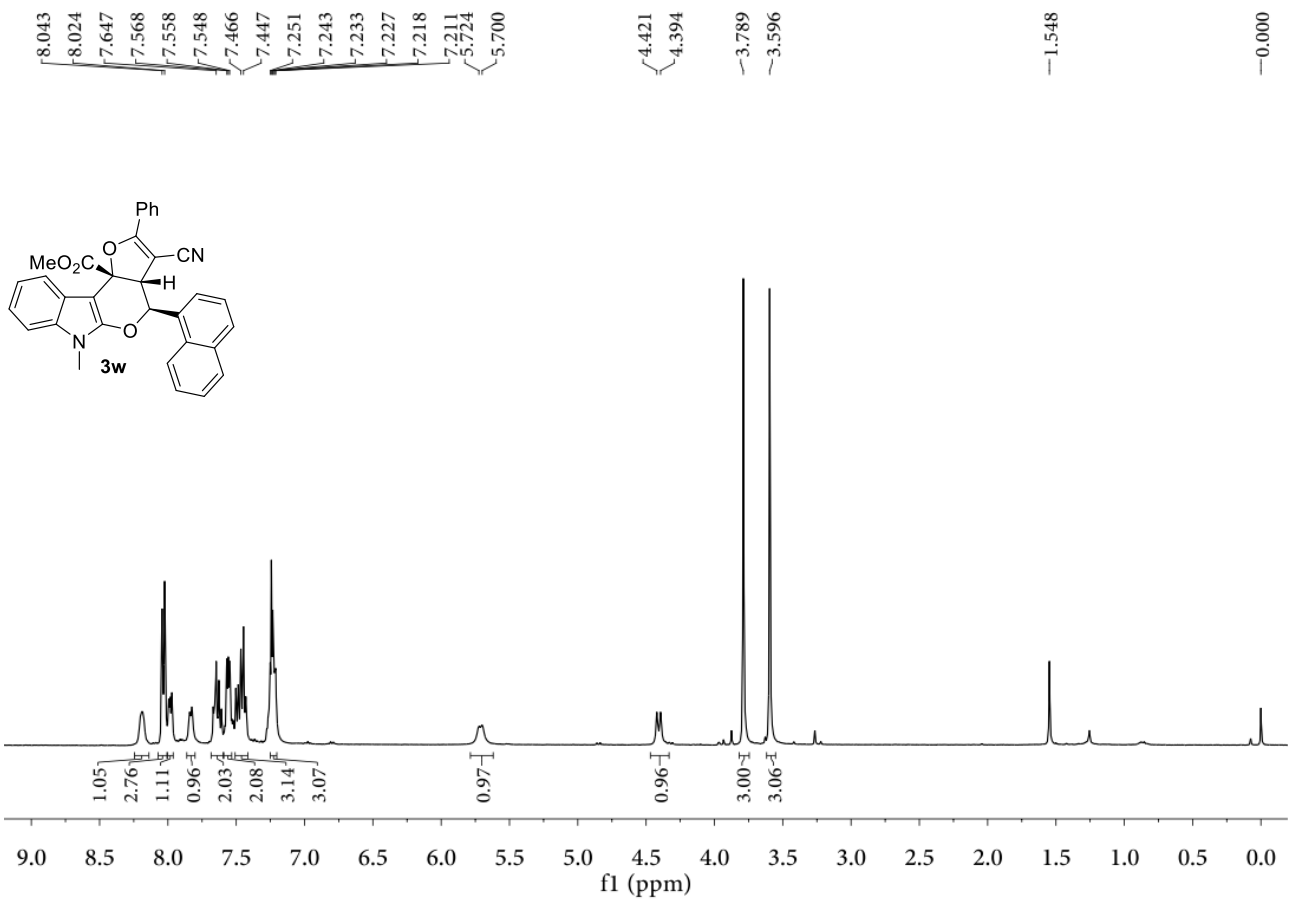

170.915
170.089
151.781
134.381
132.287
132.247
129.989
128.753
127.827
124.393
121.163
121.124
117.796
108.900
86.154
83.601
82.449
79.346
53.381
50.865
27.764
Ph
MeO2C
O
CN
H
N
O
Br
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

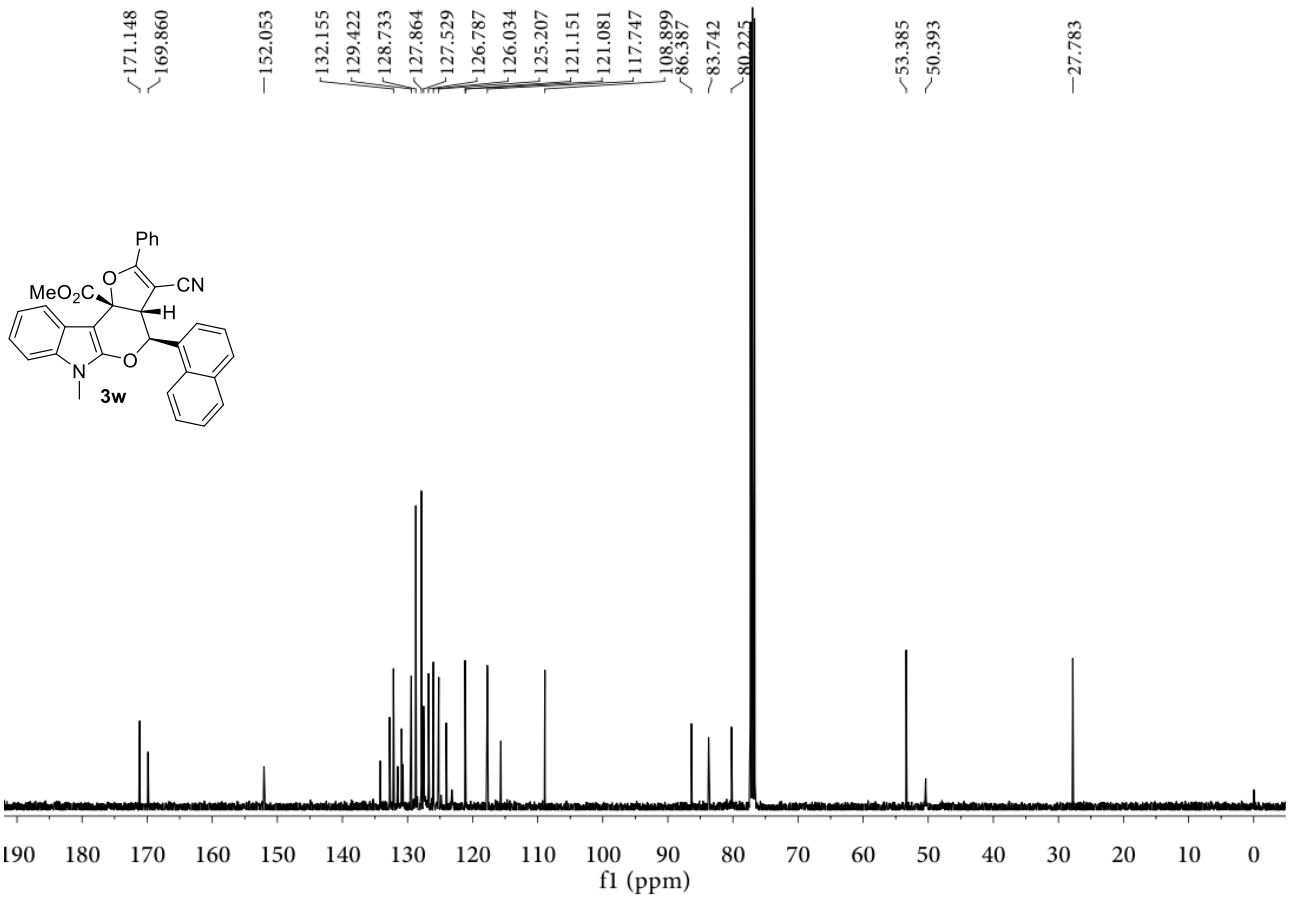


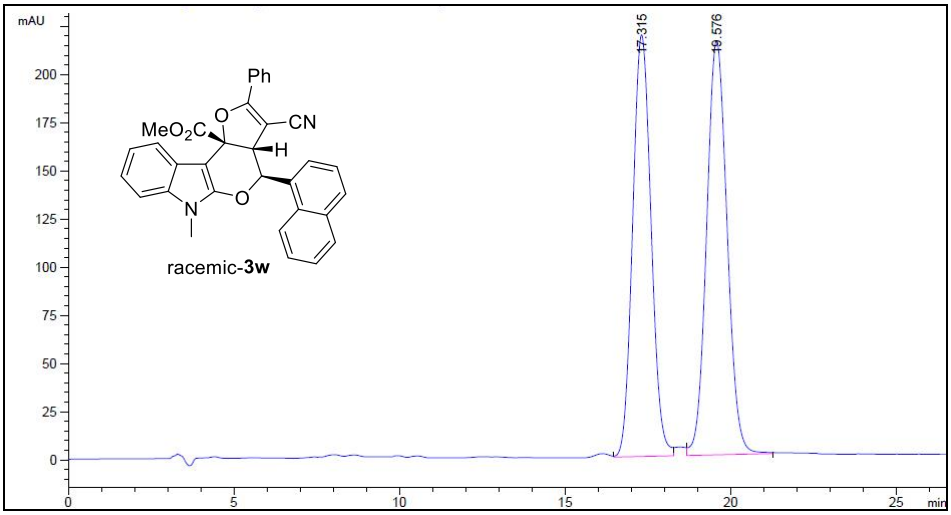
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.619	BV	0.2429	5717.28174	385.47632	51.6942
2	6.597	MM	0.2716	5342.52393	327.80688	48.3058



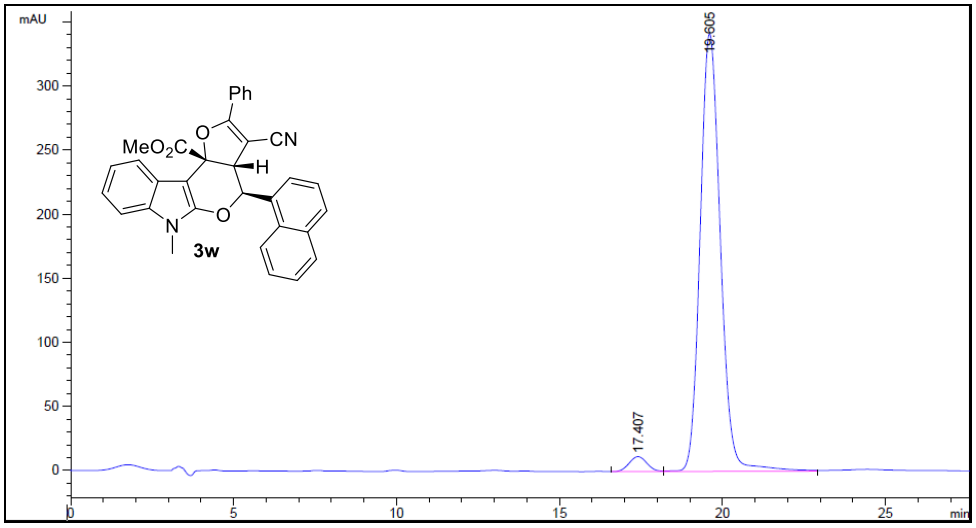
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.613	BBA	0.2485	1.08201e4	730.55878	96.1926
2	6.603	MM	0.2772	428.27133	25.74760	3.8074


8.043
8.024
7.647
7.568
7.558
7.548
7.466
7.447
7.251
7.243
7.233
7.227
7.218
7.211
5.724
5.700
4.421
4.394
3.789
3.596
1.548
0.000
Ph
MeO2C
O
CN
H
N
O
3w
1.05
2.76
1.11
0.96
2.03
2.08
3.14
3.07
0.97
0.96
3.00
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

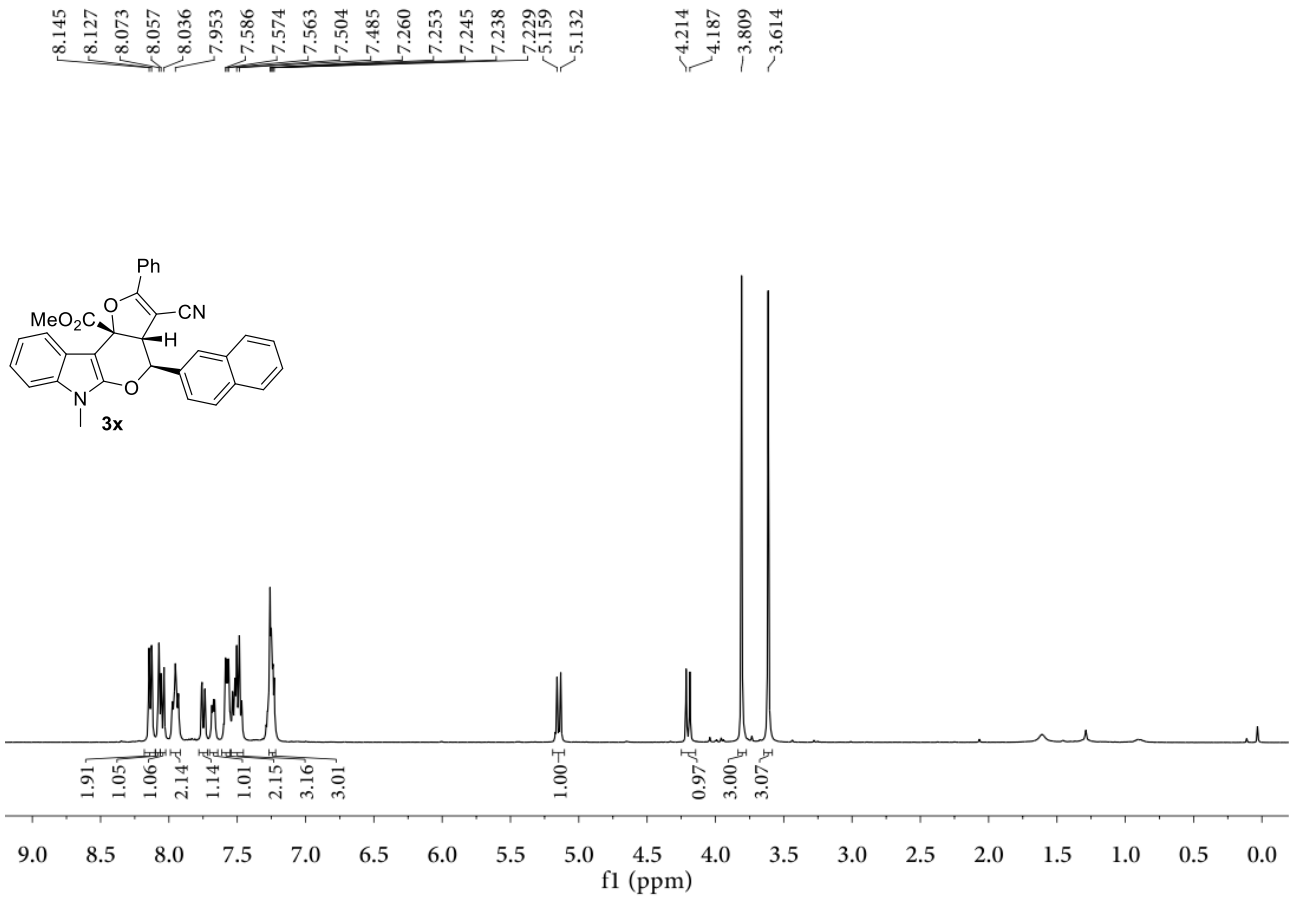

171.148
169.860
152.053
132.155
129.422
128.733
127.864
127.529
126.787
126.034
125.207
121.151
121.081
117.747
108.899
86.387
83.742
80.225
53.385
50.393
27.783
Ph
MeO2C
O
CN
H
N
O
3w
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

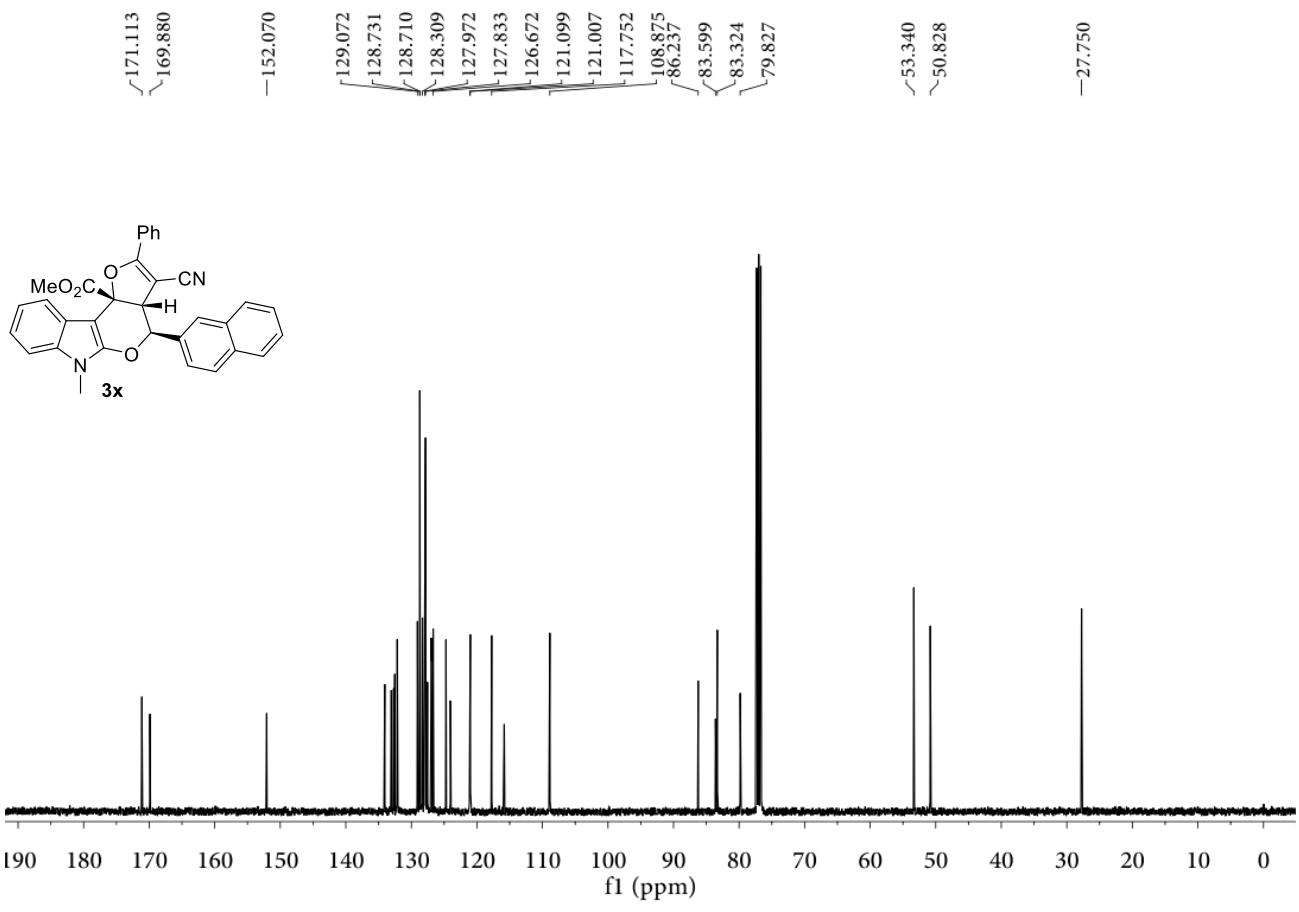


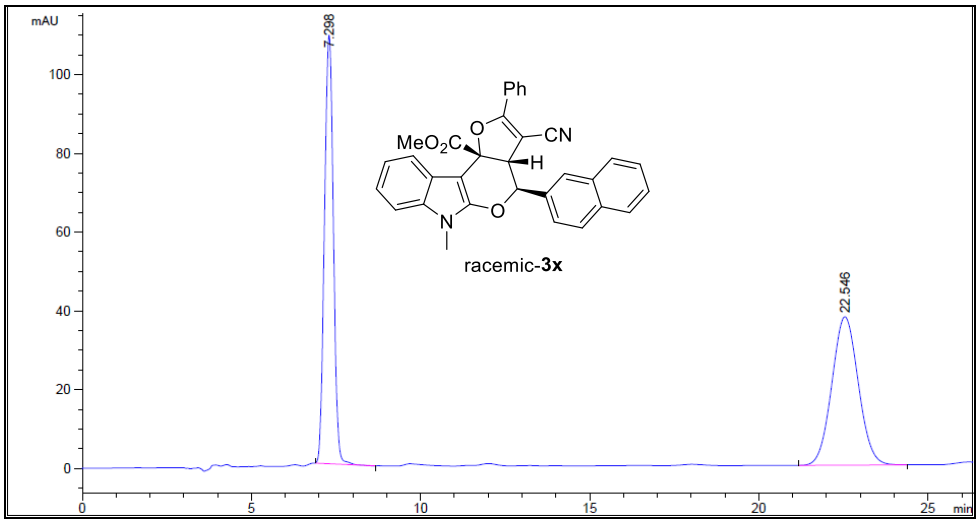
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.315	VV	0.6085	8463.36328	218.82716	47.7928
2	19.576	VB	0.6764	9245.08008	215.01561	52.2072



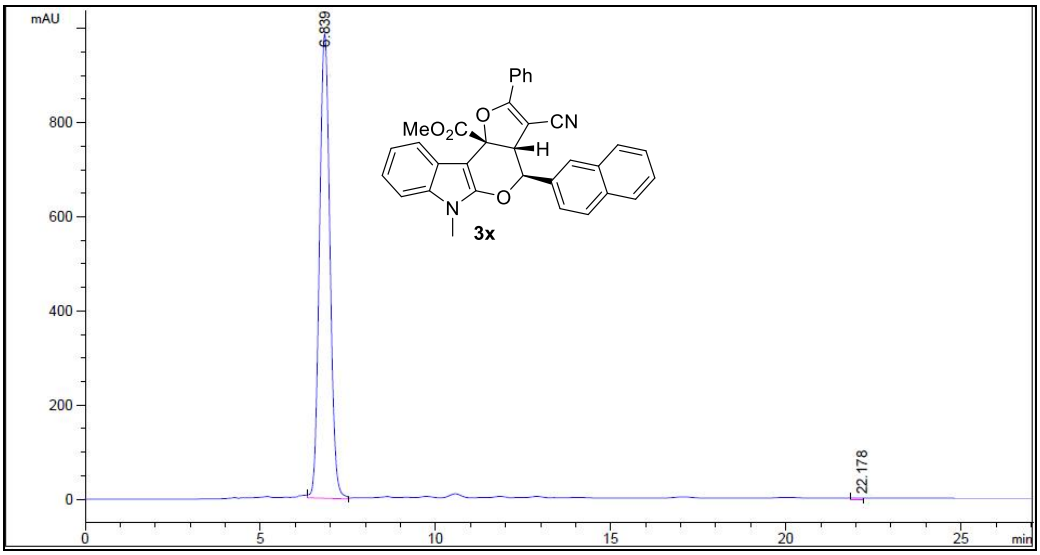
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.407	VV	0.6001	442.86618	11.66684	2.9182
2	19.605	VB	0.6721	1.47332e4	341.56509	97.0818


8.145
8.127
8.073
8.057
8.036
7.953
7.586
7.574
7.563
7.504
7.485
7.260
7.253
7.245
7.238
7.229
5.159
5.132
4.214
4.187
3.809
3.614
Ph
MeO2C
O
CN
H
N
O
3x
1.91
1.05
1.06
2.14
1.14
1.01
2.15
3.16
3.01
1.00
0.97
3.00
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

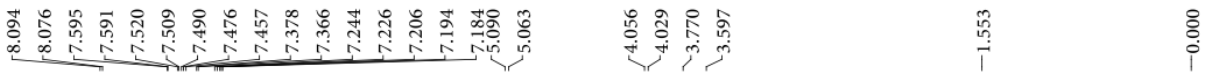

171.113
169.880
152.070
129.072
128.731
128.710
128.309
127.972
127.833
126.672
121.099
121.007
117.752
108.875
86.237
83.599
83.324
79.827
53.340
50.828
27.750
Ph
MeO2C
O
CN
H
N
O
3x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

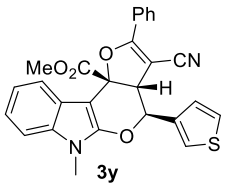


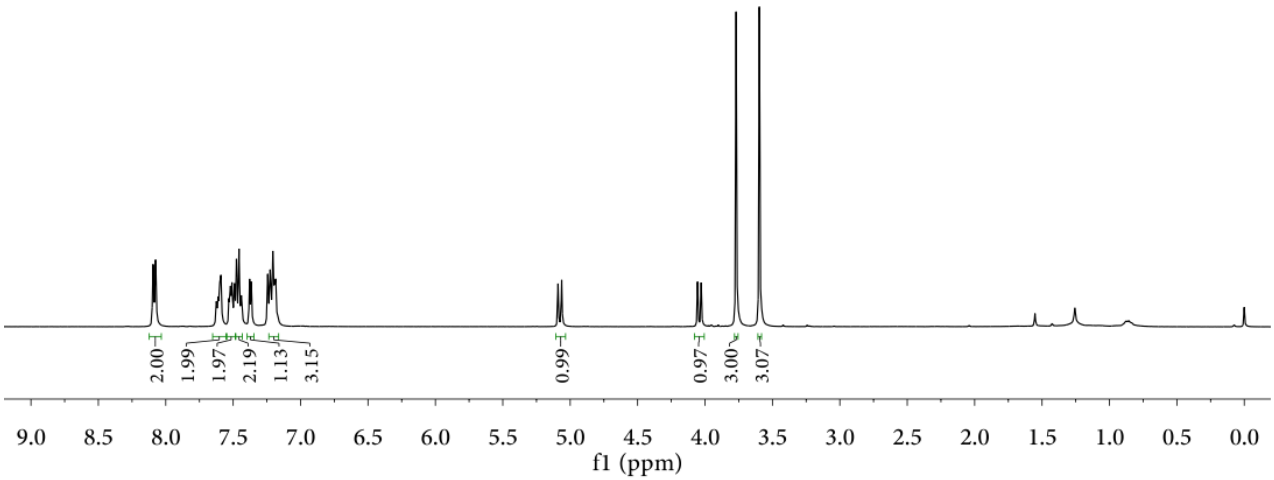
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.298	BB	0.2893	1991.24109	108.74486	49.2790
2	22.546	BB	0.8501	2049.50757	37.67701	50.7210

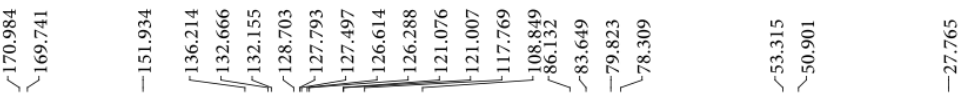


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.839	MM	0.3454	2.04596e4	987.21710	99.6623
2	22.178	MM	0.3646	69.32738	3.16894	0.3377


8.094
8.076
7.595
7.591
7.520
7.509
7.490
7.476
7.457
7.378
7.366
7.244
7.226
7.206
7.194
7.184
5.090
5.063
4.056
4.029
3.770
3.597
1.553
0.000


Ph
MeO2C
O
CN
H
N
O
S
3y


2.00
1.99
1.97
2.19
1.13
3.15
0.99
0.97
3.00
3.07
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)


170.984
169.741
151.934
136.214
132.666
132.155
128.703
127.793
127.497
126.614
126.288
121.076
121.007
117.769
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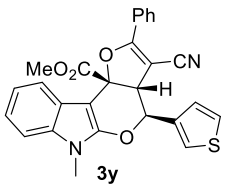
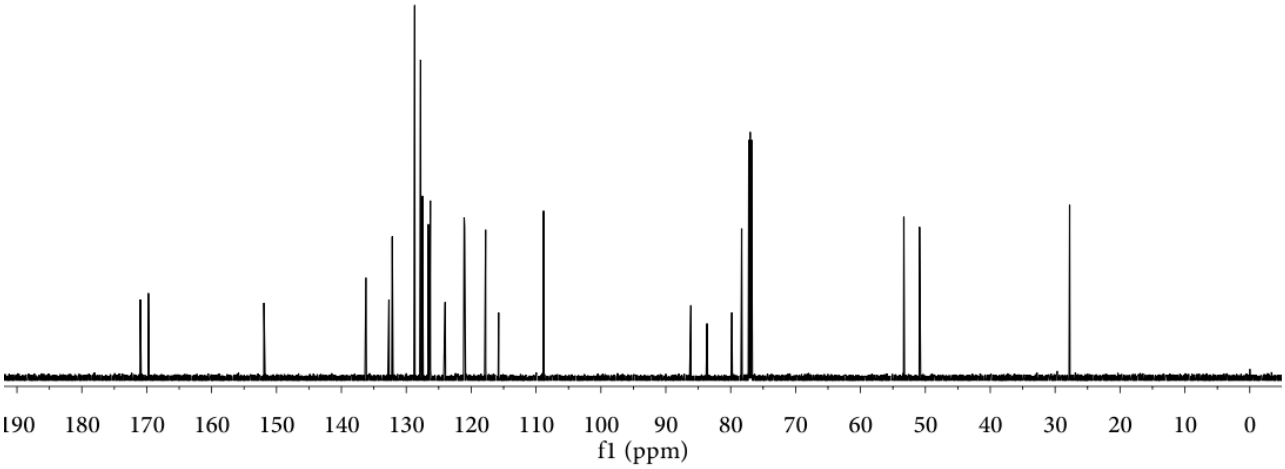
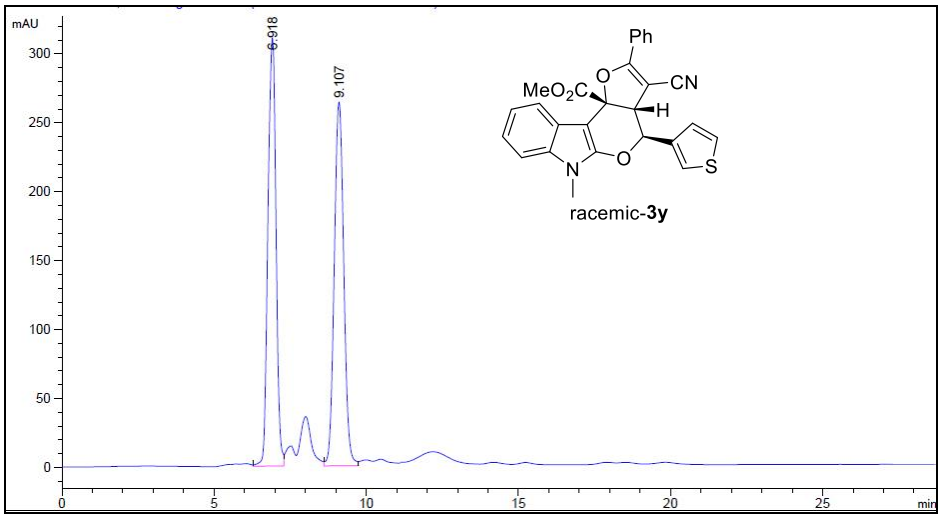
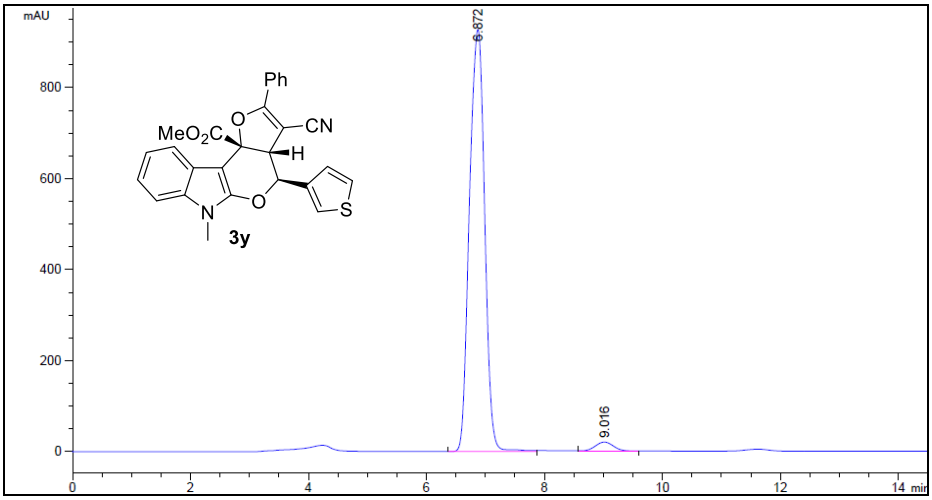
86.132
83.649
79.823
78.309
53.315
50.901
27.765


Ph
MeO2C
O
CN
H
N
O
S
3y

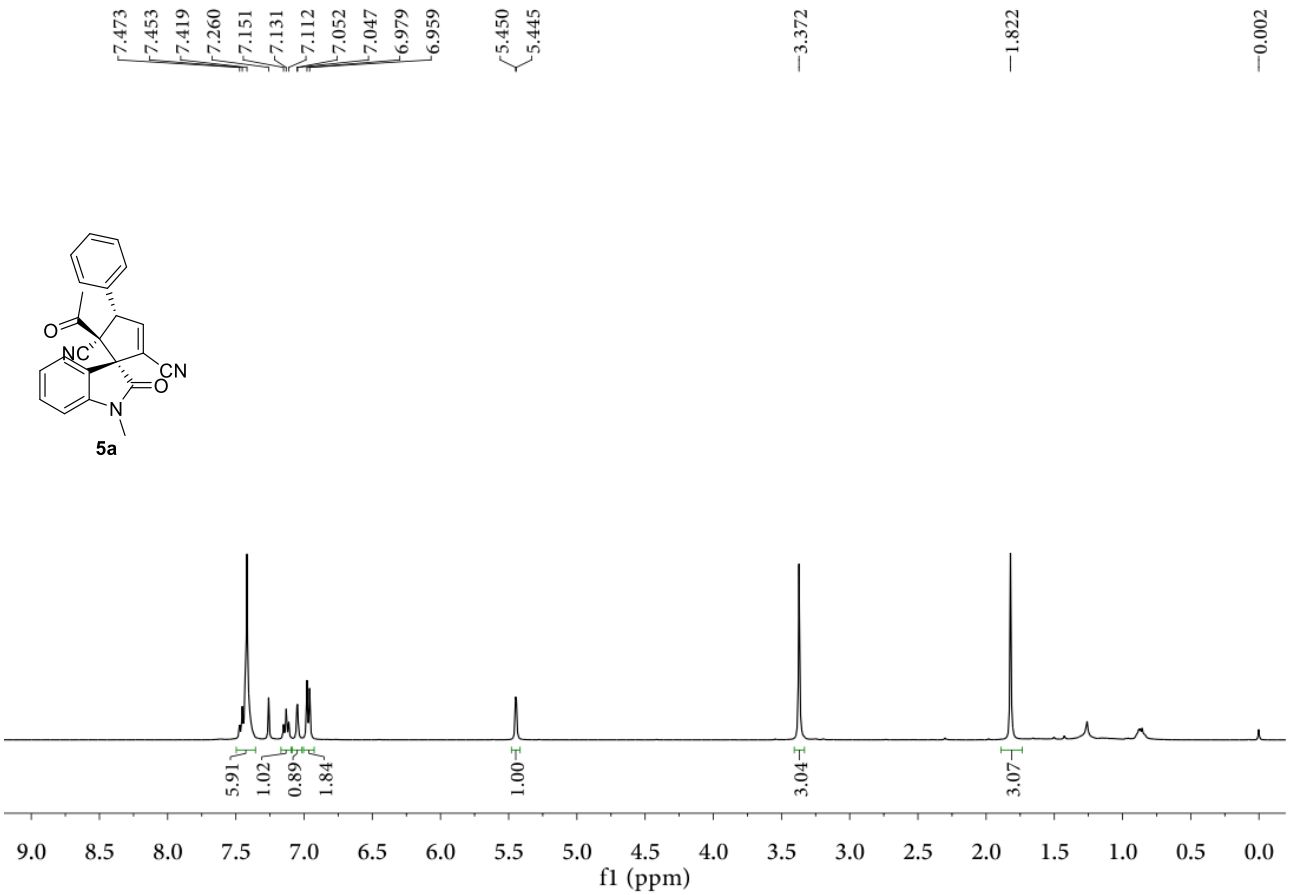

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

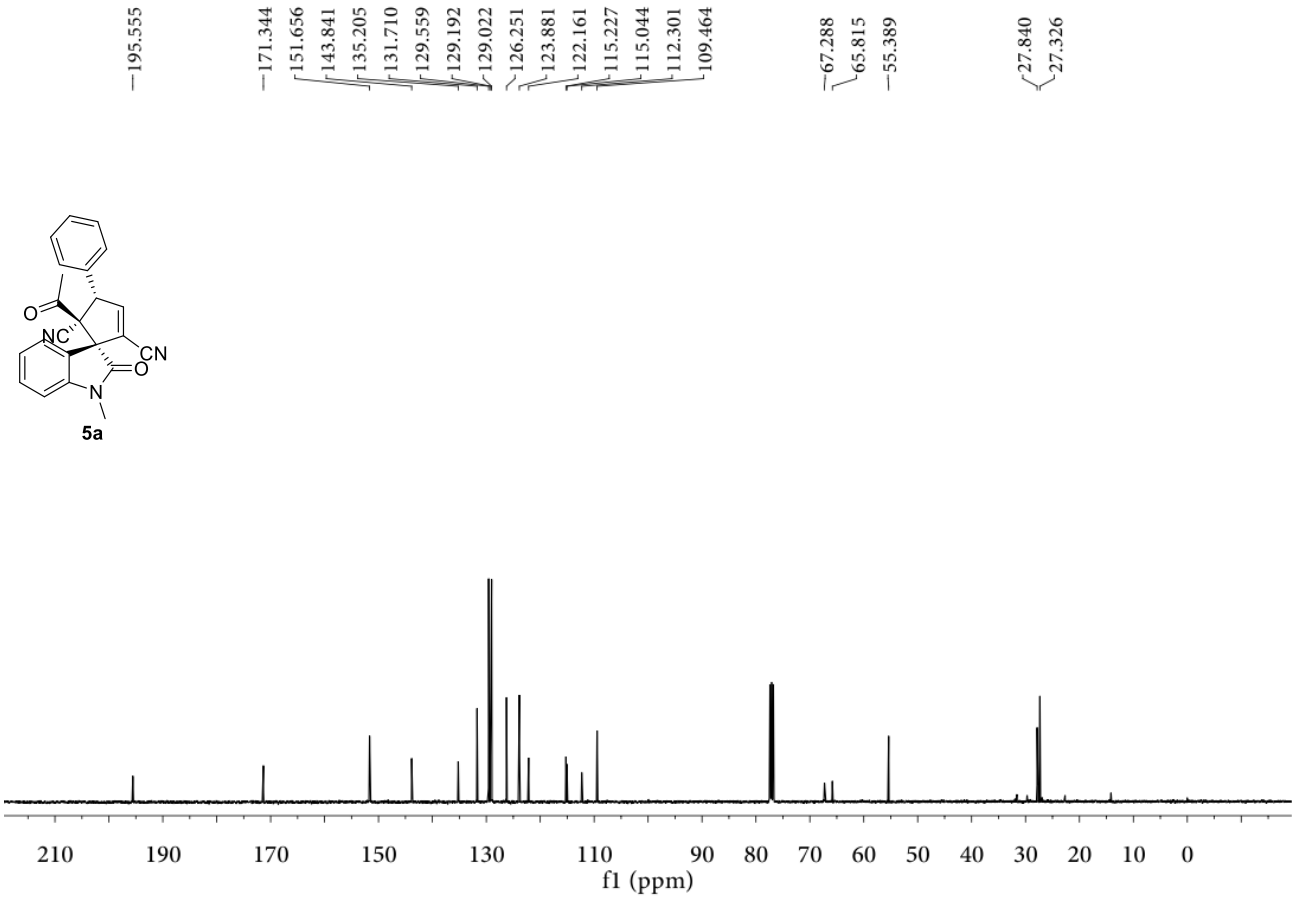


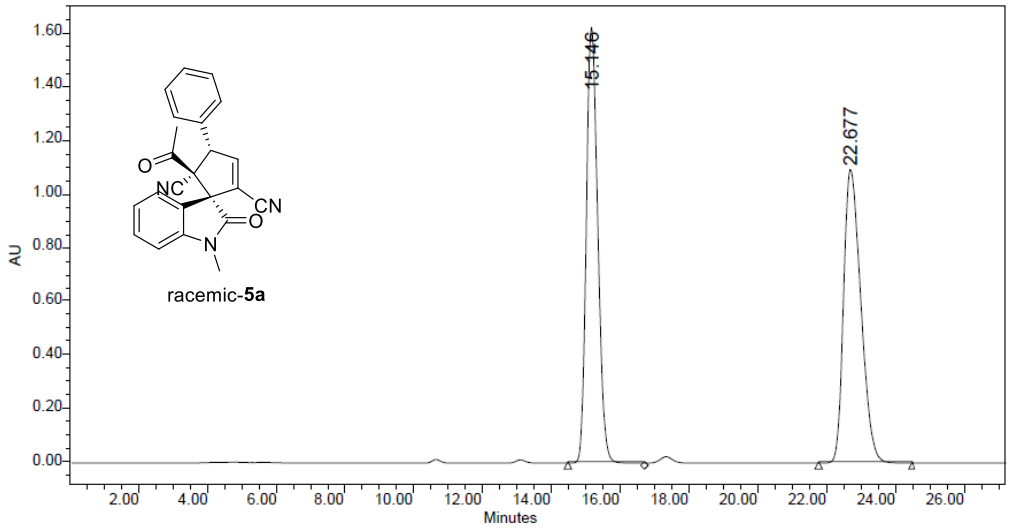
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.918	VV	0.2967	5725.08545	310.43542	49.8996
2	9.107	VV	0.3474	5748.12158	263.75644	50.1004



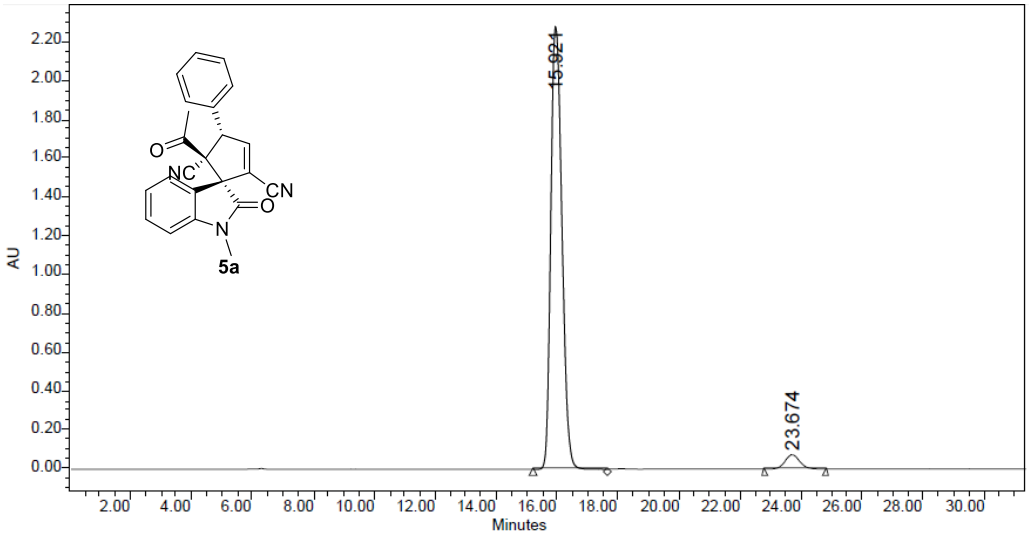
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.872	BB	0.2962	1.65987e4	927.19025	97.4987
2	9.016	MM	0.3576	425.83569	19.84614	2.5013


7.473
7.453
7.419
7.260
7.151
7.131
7.112
7.052
7.047
6.979
6.959
5.450
5.445
3.372
1.822
0.002
O
NC
CN
O
N
5a
5.91
1.02
0.89
1.84
1.00
3.04
3.07
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)

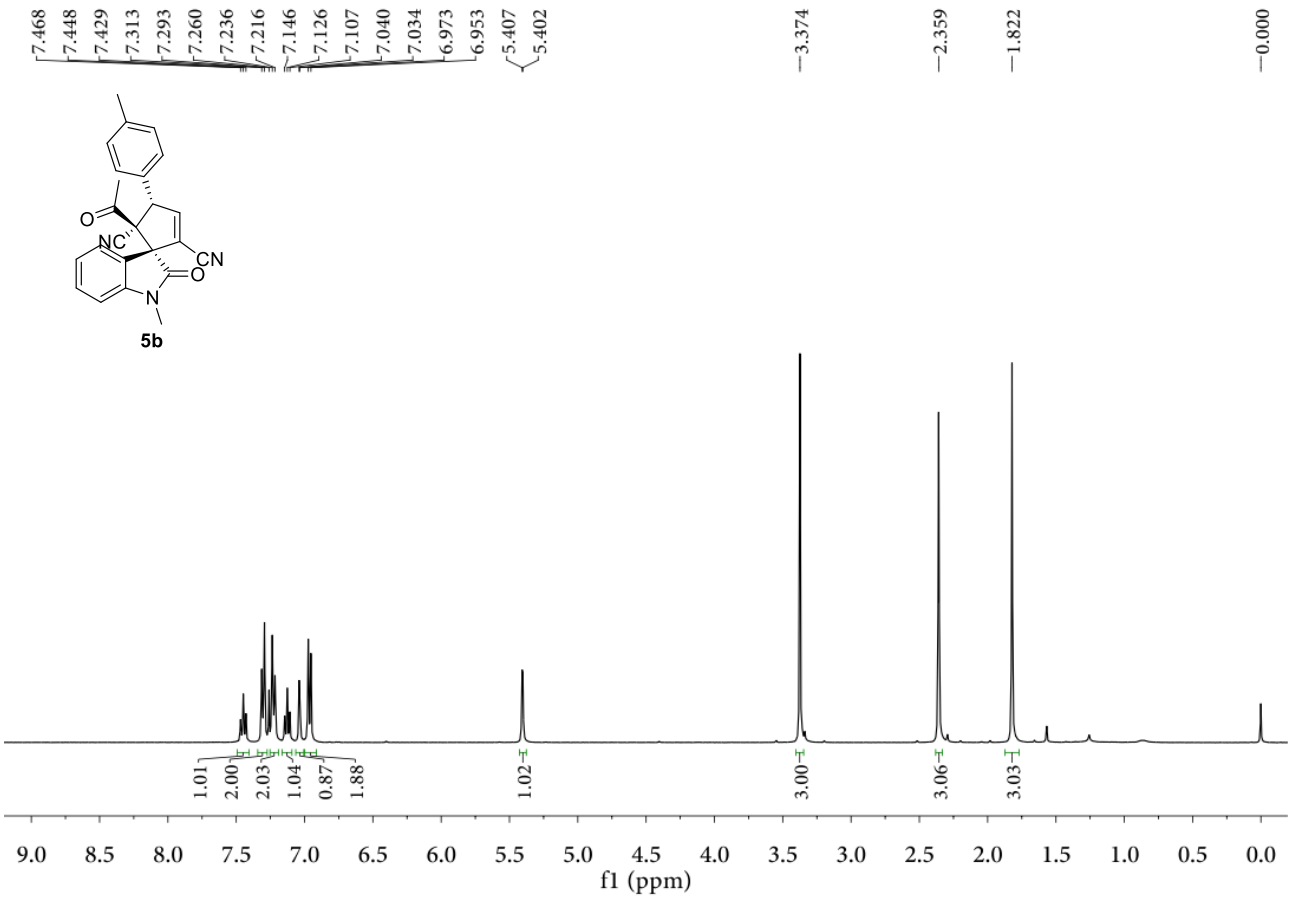

195.555
171.344
151.656
143.841
135.205
131.710
129.559
129.192
129.022
126.251
123.881
122.161
115.227
115.044
112.301
109.464
67.288
65.815
55.389
27.840
27.326
O
NC
CN
O
N
5a
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



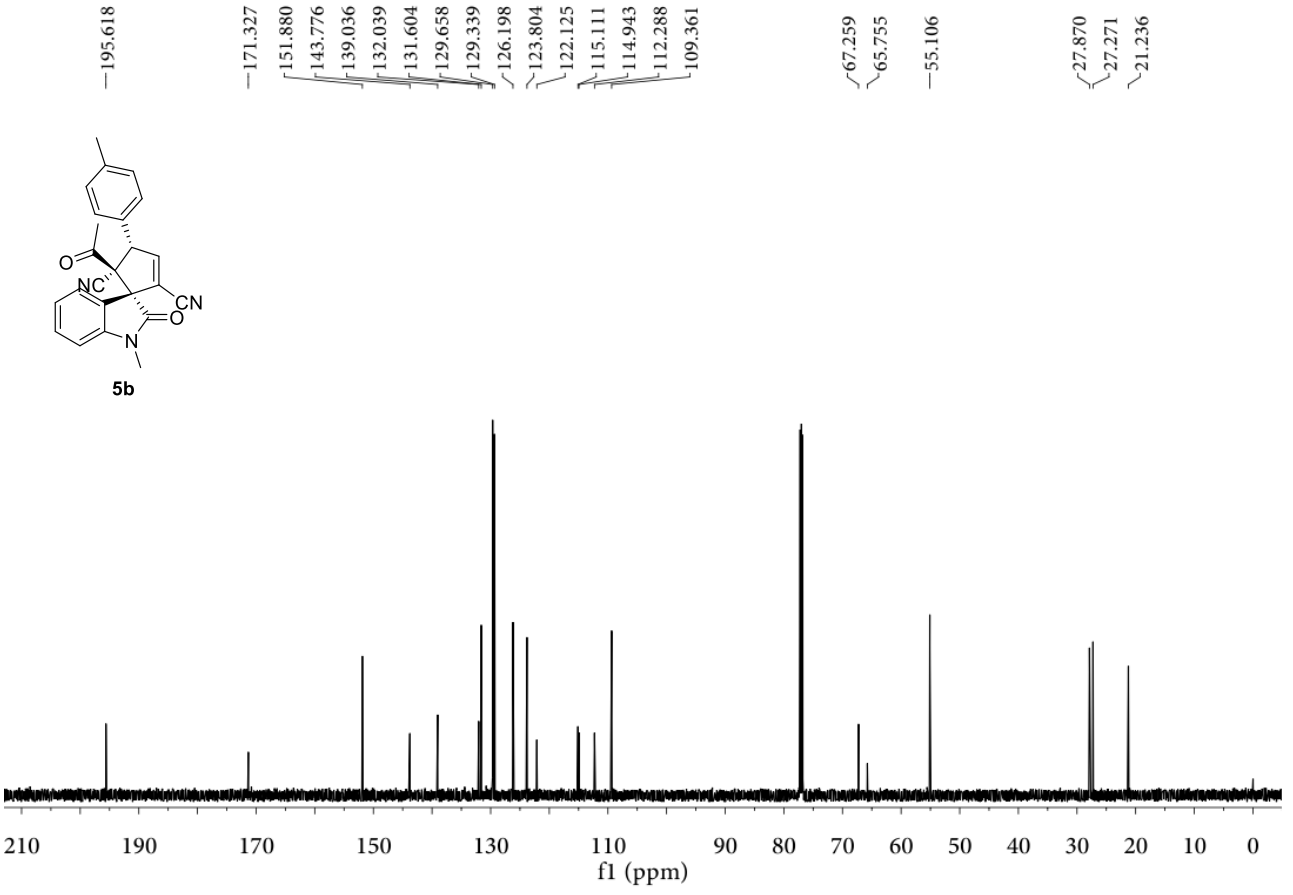
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.146	37458791	49.55	1621248	59.75
2	22.677	38141543	50.45	1091978	40.25



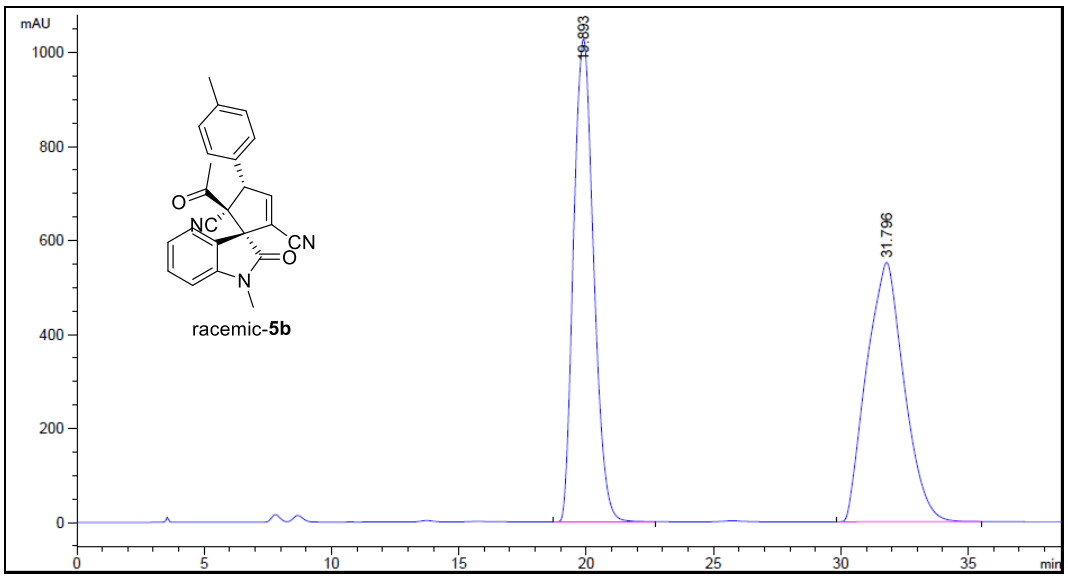
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.921	57615314	95.99	2278908	96.89
2	23.674	2405715	4.01	73072	3.11


7.468
7.448
7.429
7.313
7.293
7.260
7.236
7.216
7.146
7.126
7.107
7.040
7.034
6.973
6.953
5.407
5.402
3.374
2.359
1.822
0.000
O
NC
CN
O
N
1.01
2.00
2.03
1.04
0.87
1.88
1.02
3.00
3.06
3.03
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)

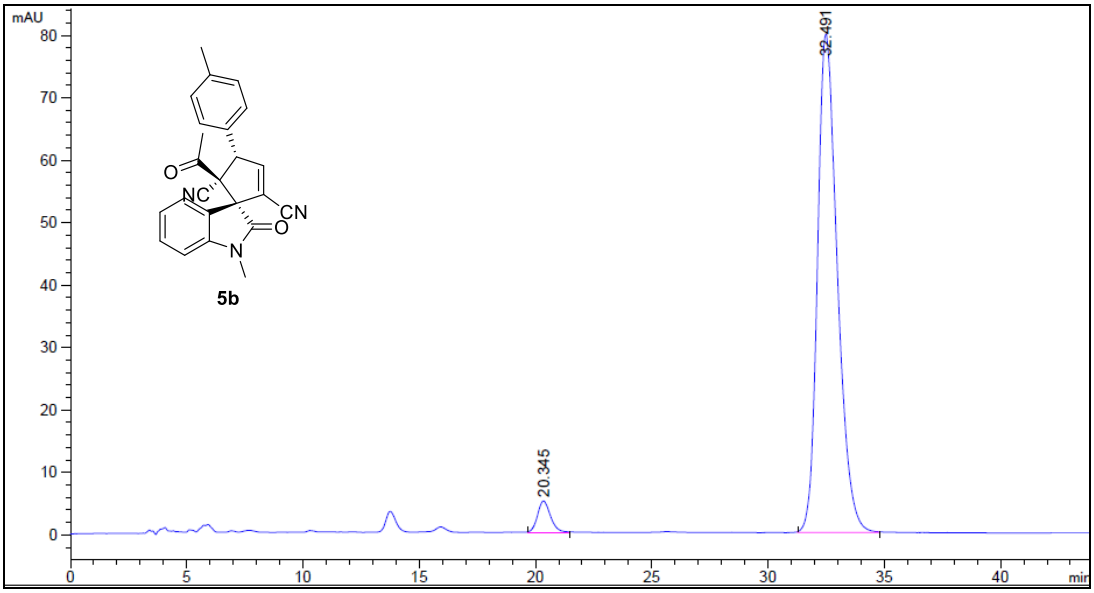
5b


195.618
171.327
151.880
143.776
139.036
132.039
131.604
129.658
129.339
126.198
123.804
122.125
115.111
114.943
112.288
109.361
67.259
65.755
55.106
27.870
27.271
21.236
O
NC
CN
O
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

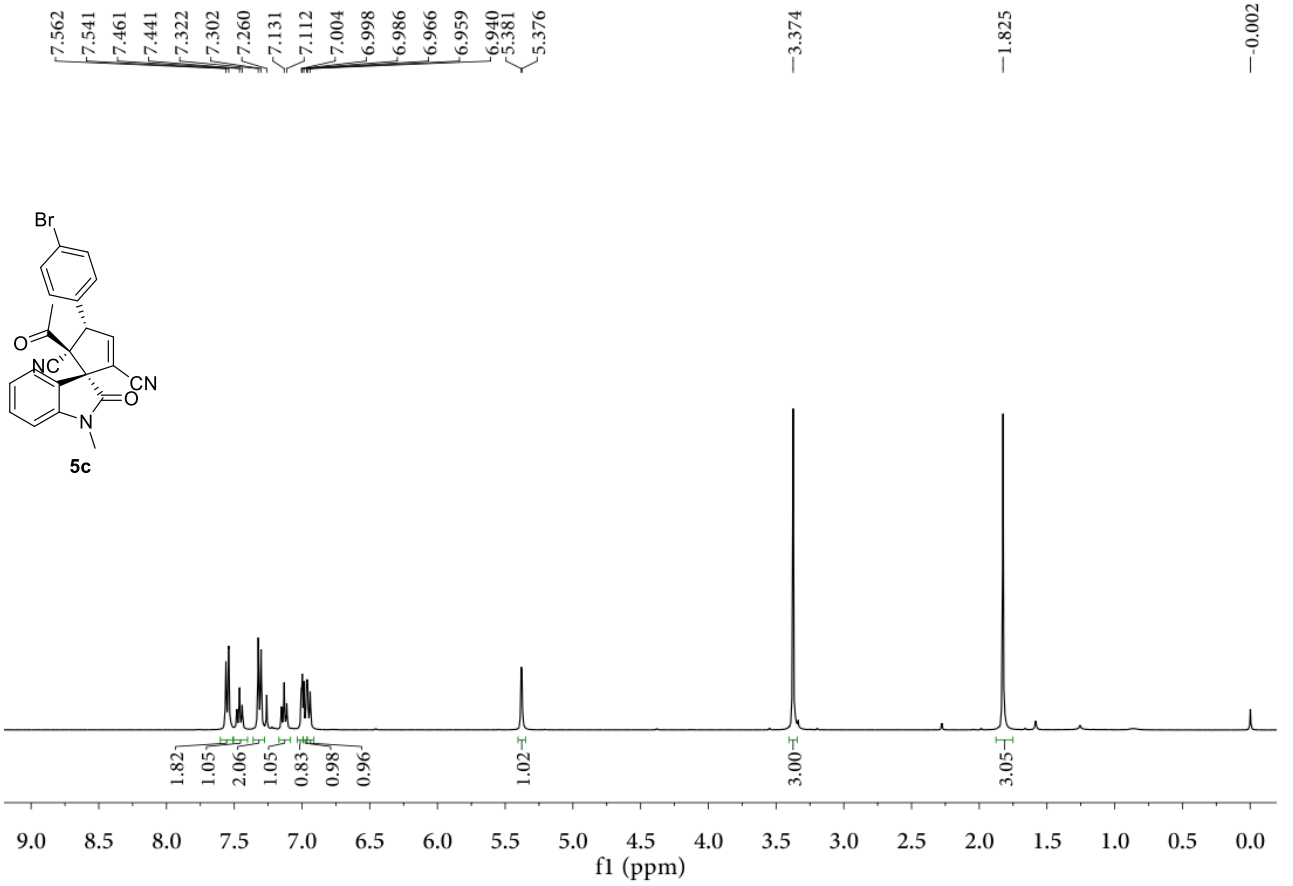
5b

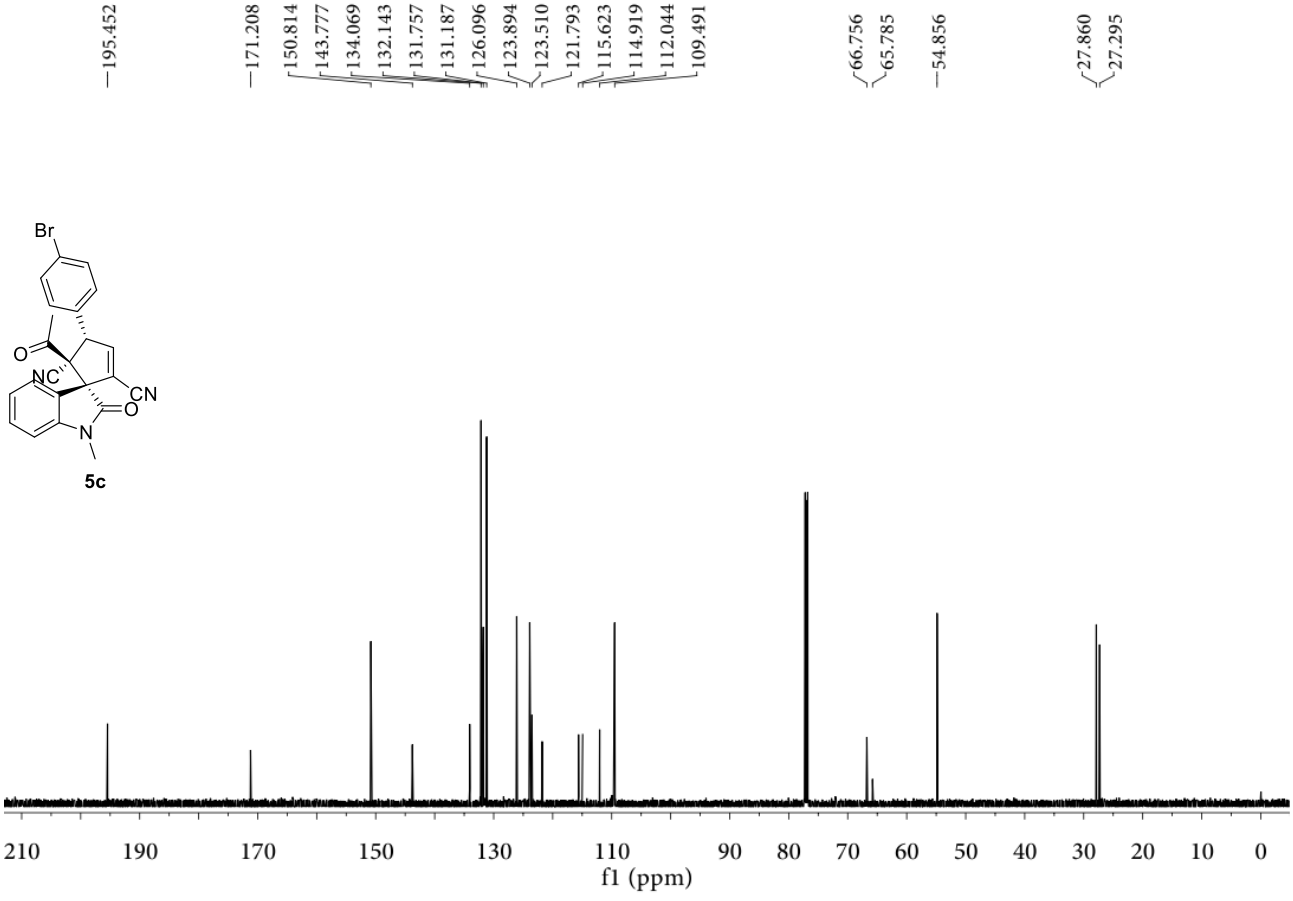


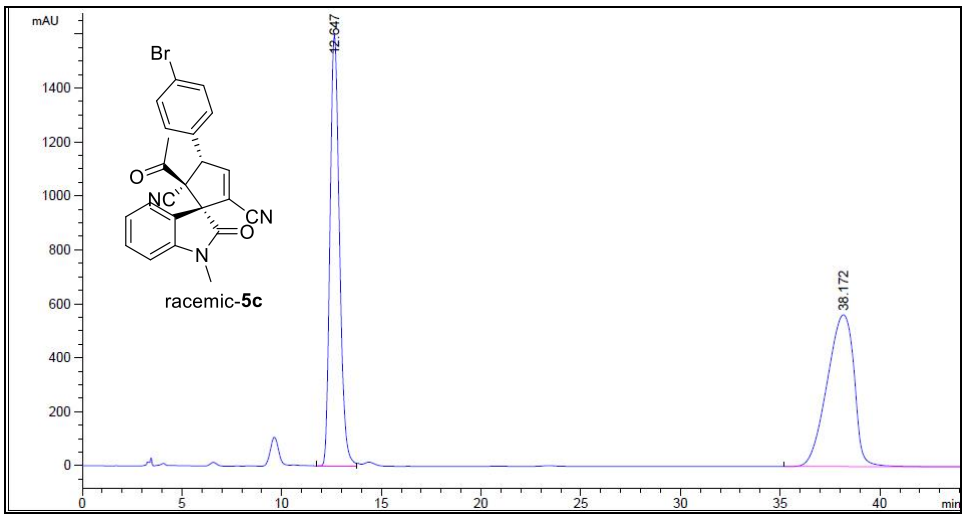
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.893	BB	0.8651	5.61622e4	1027.06824	49.9113
2	31.796	BB	1.6457	5.63618e4	551.91760	50.0887



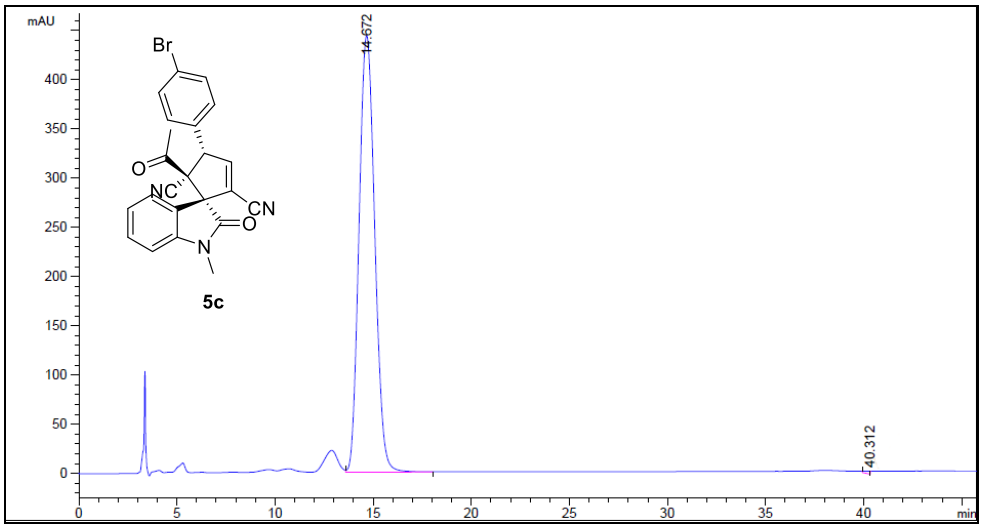
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.345	BB	0.5952	192.69928	5.00085	3.9105
2	32.491	BB	0.9073	4735.03369	79.85309	96.0895


7.562
7.541
7.461
7.441
7.322
7.302
7.260
7.131
7.112
7.004
6.998
6.986
6.966
6.959
6.940
5.381
5.376
3.374
1.825
0.002
Br
O
NC
CN
O
N
5c
1.82
1.05
2.06
1.05
0.83
0.98
0.96
1.02
3.00
3.05
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)

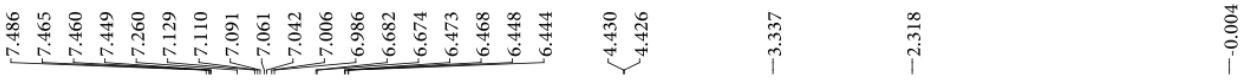

195.452
171.208
150.814
143.777
134.069
132.143
131.757
131.187
126.096
123.894
123.510
121.793
115.623
114.919
112.044
109.491
66.756
65.785
54.856
27.860
27.295
Br
O
NC
CN
O
N
5c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.647	VV	0.5132	5.27511e4	1598.29443	49.9267
2	38.172	BBA	1.5105	5.29060e4	562.64258	50.0733



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.672	VB	0.8764	2.46990e4	443.81152	99.7754
2	40.312	MM	0.3097	55.60847	2.99256	0.2246


7.486
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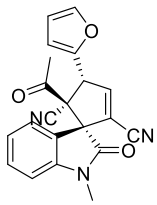
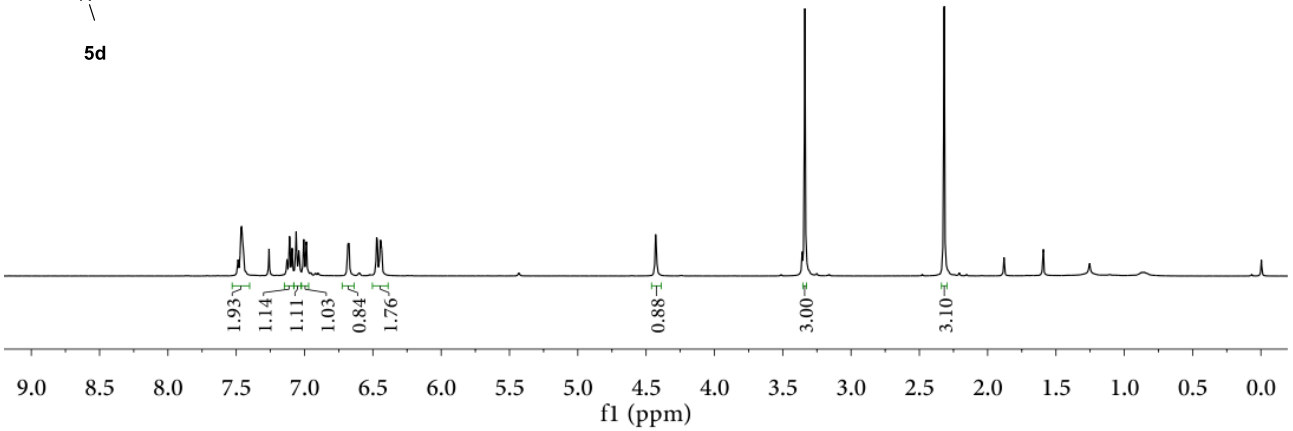
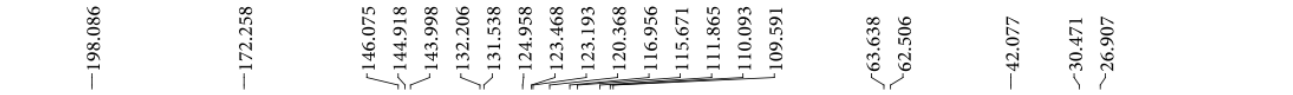
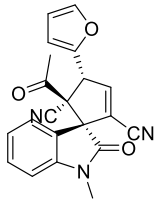
7.460
7.449
7.260
7.129
7.110
7.091
7.061
7.042
7.006
6.986
6.682
6.674
6.473
6.468
6.448
6.444
4.430
4.426
3.337
2.318
-0.004


O
O
NC
CN
O
N

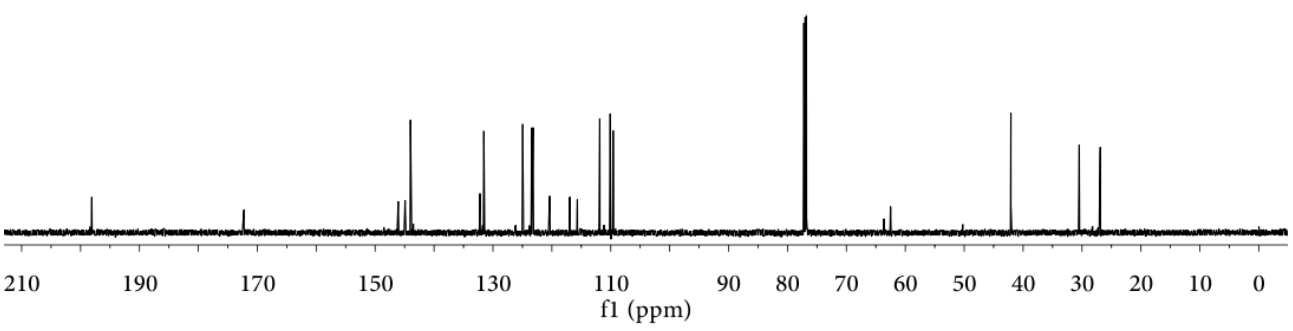
5d

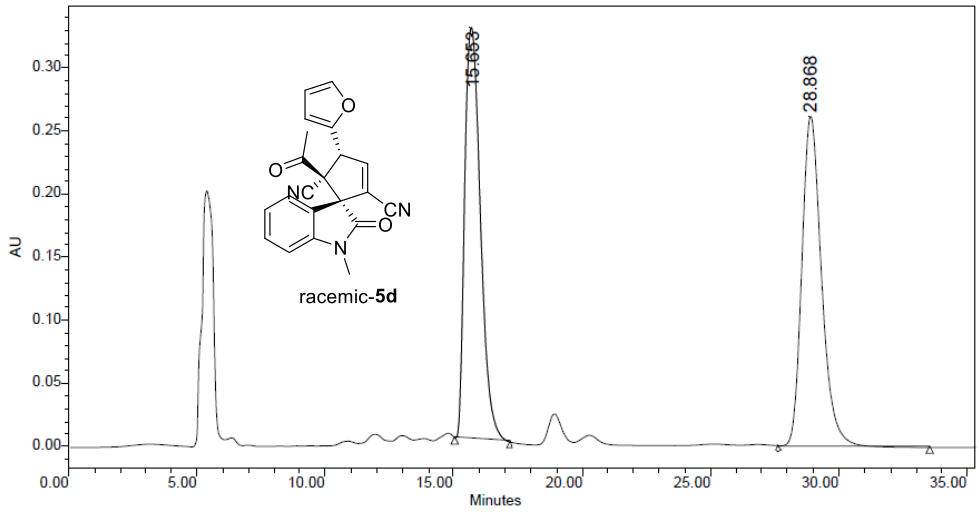

1.93
1.14
1.11
1.03
0.84
1.76
0.88
3.00
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.086
172.258
146.075
144.918
143.998
132.206
131.538
124.958
123.468
123.193
120.368
116.956
115.671
111.865
110.093
109.591
63.638
62.506
42.077
30.471
26.907

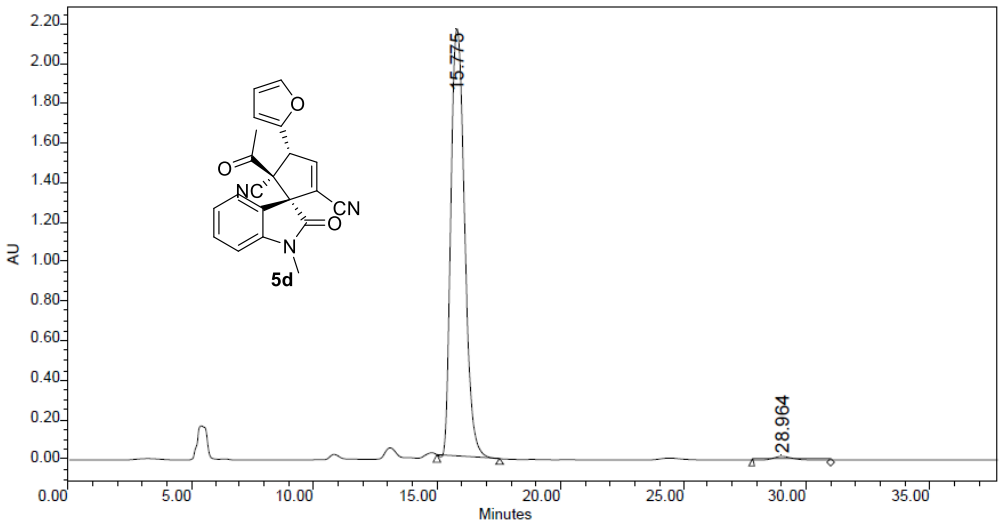

O
O
NC
CN
O
N

5d

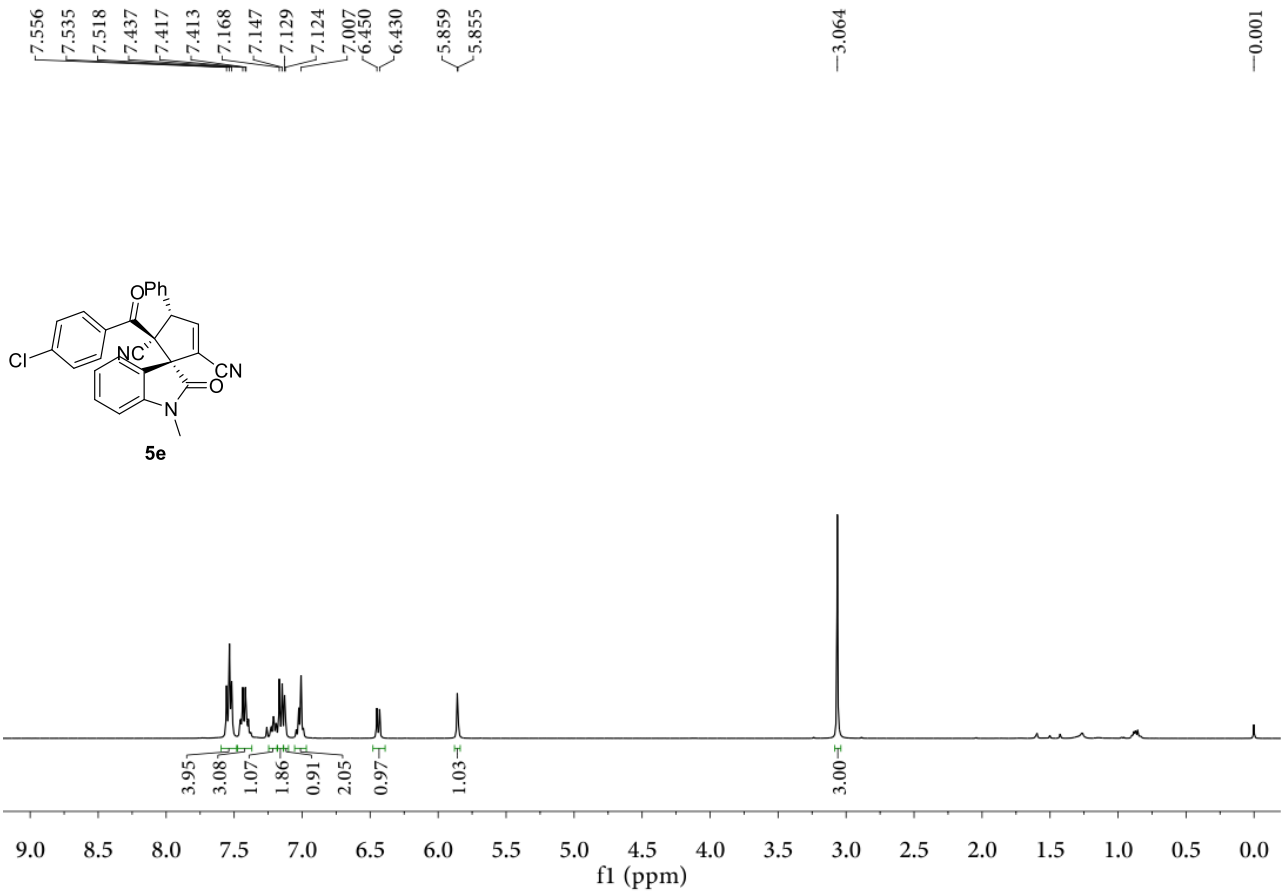

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

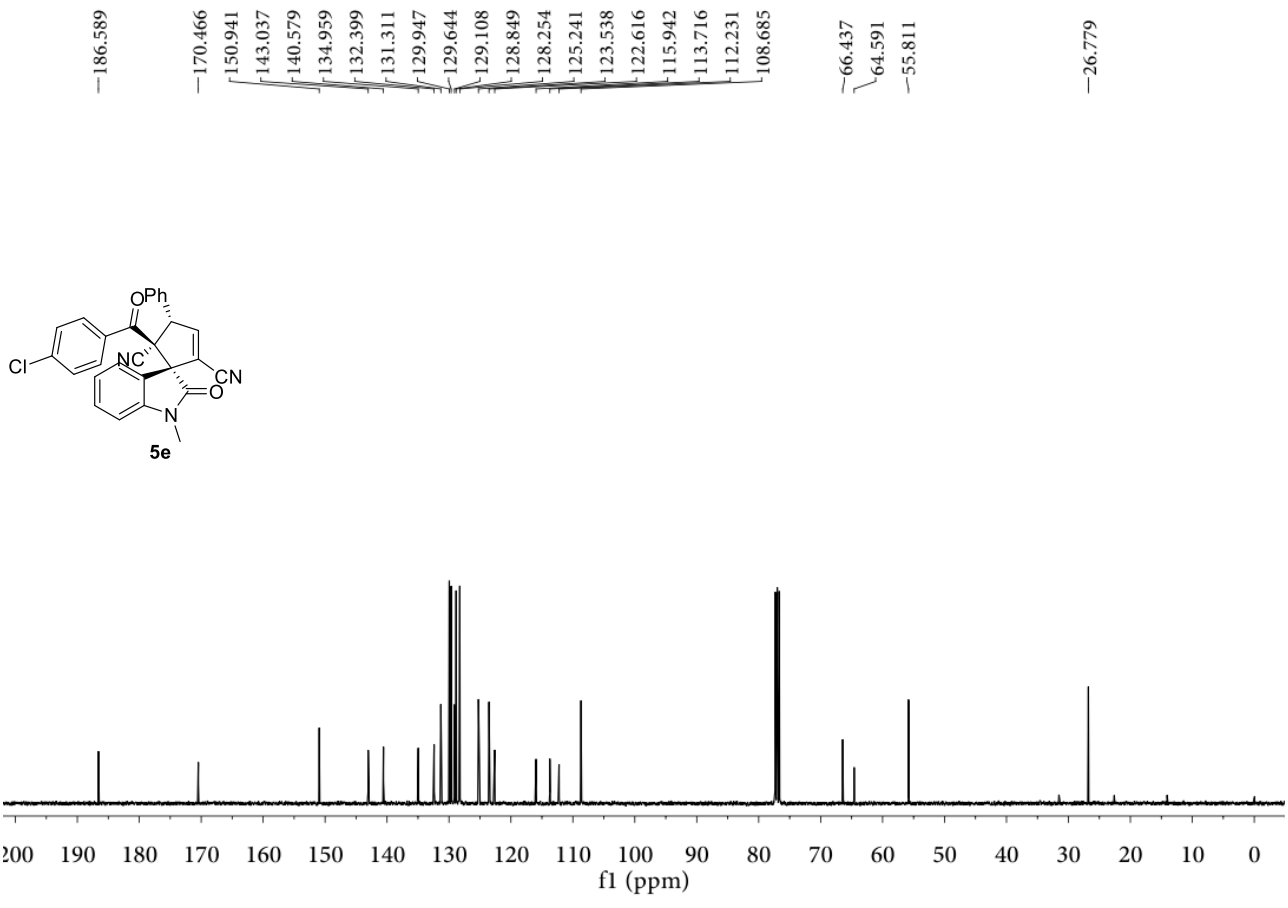


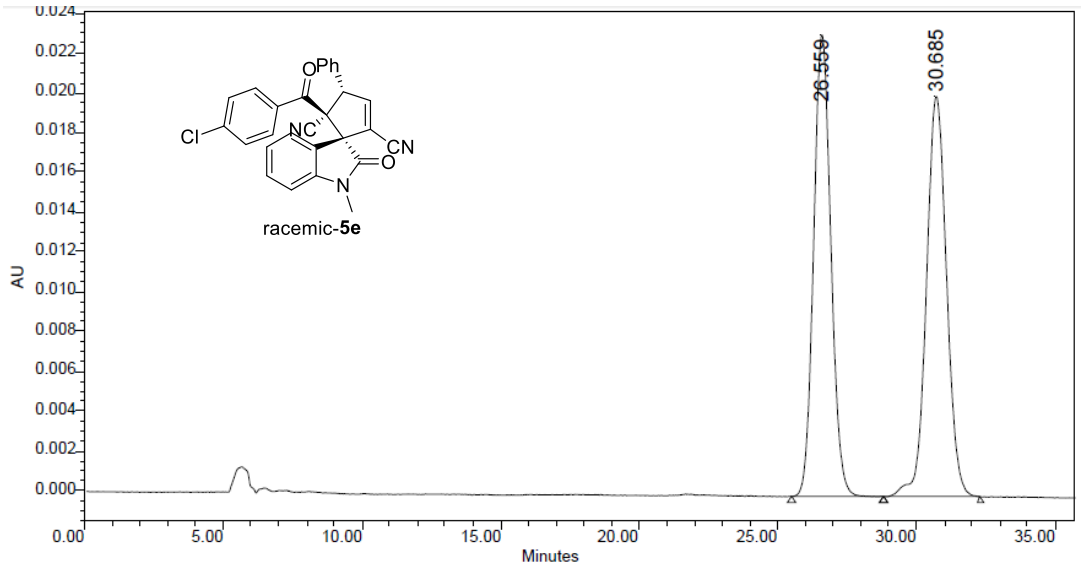
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.653	13912146	49.79	326373	55.48
2	28.868	14030817	50.21	261881	44.52



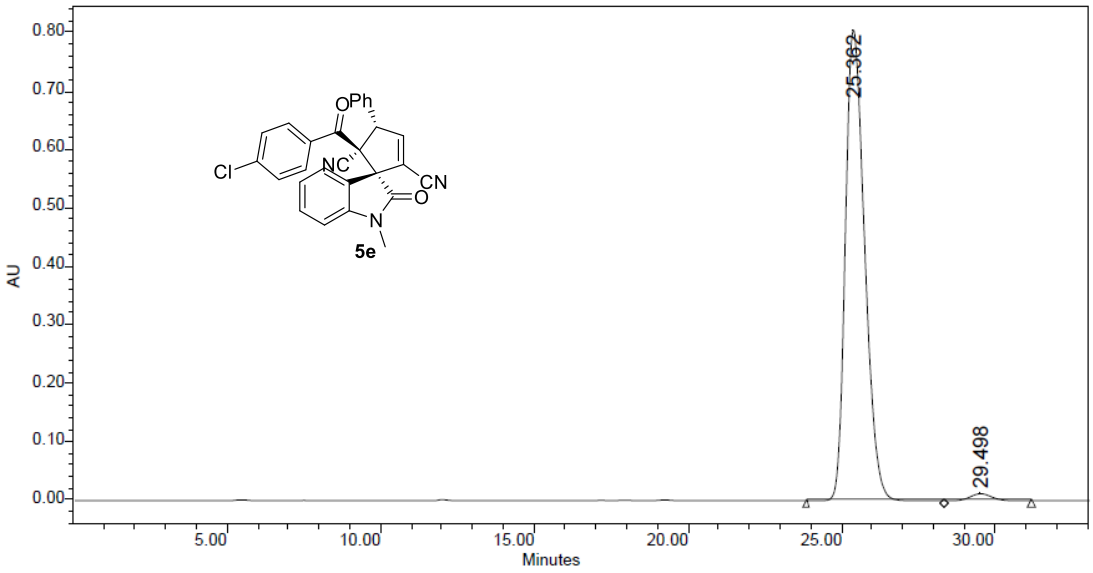
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	15.775	83857976	98.93	2163493	99.20
2	28.964	909019	1.07	17531	0.80


7.556
7.535
7.518
7.437
7.417
7.413
7.168
7.147
7.129
7.124
7.007
6.450
6.430
5.859
5.855
3.064
0.001
OPh
Cl
NC
CN
O
N
5e
3.95
3.08
1.07
1.86
0.91
2.05
0.97
1.03
3.00
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)


186.589
170.466
150.941
143.037
140.579
134.959
132.399
131.311
129.947
129.644
129.108
128.849
128.254
125.241
123.538
122.616
115.942
113.716
112.231
108.685
66.437
64.591
55.811
26.779
OPh
Cl
NC
CN
O
N
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	26.559	1004595	49.54	23201	53.55
2	30.685	1023208	50.46	20127	46.45



	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	25.362	35075499	98.35	805618	98.53
2	29.498	587081	1.65	12053	1.47