Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Organocatalytic Asymmetric Synthesis of Dihydrofuran-Spirooxindoles from Benzylidene Malononitriles and Dioxindoles

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Table of contents

1. General Information:

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR spectra were recorded on 400 MHz and 600 MHz spectrometer. ^{13}C NMR spectra were recorded on 100 MHz and 150 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (DMSO-d_6 δ 2.500), carbon (DMSO-d_6 δ 39.52). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants were reported in Hertz (Hz). Using ESI mode HRMS spectra were recorded. Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using a Daicel Chiralpak ID Column, Daicel Chiralpak IA Column, Daicel Chiralpak IC Column, Daicel Chiralpak IF Column and Phenomenex LUX C1 Column. For visualizing the products UV light and I_2 were used. Melting points were measured using BüCHI melting point B-540 apparatus. All melting points were measured in open glass capillary and values are uncorrected. DCM was distilled over CaH_2 under argon and stored over 4A° molecular sieves. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm).

2. General procedure for the synthesis of benzylidene malononitriles:

Benzylidene malononitriles were prepared according to reported procedure.[1]

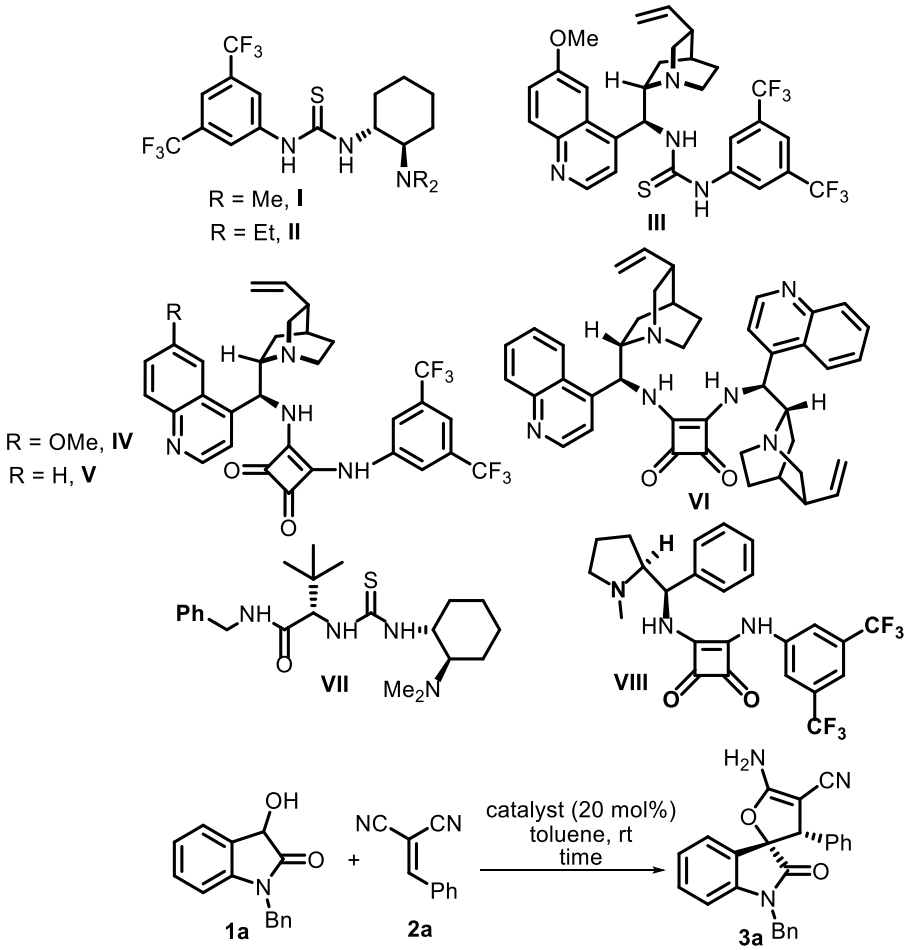
3. General procedure for the synthesis of dioxindoles:

Dioxindoles were prepared according to reported procedures.[2]

4. General procedure for the synthesis of catalyst:

The catalyst (**I, II, III, IV** and **V**) was prepared according to reported procedures.[3,4] The catalyst (**VI**) was prepared according to reported procedure. [5] The catalyst (**VII**) was prepared according to reported procedure. [6] The catalyst (**VIII**) was prepared according to reported procedure. [7]

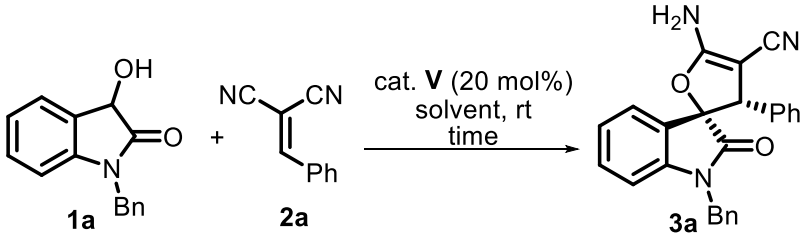
5. Catalyst optimization for Dihydrofuran-Spirooxindoles:



entry[a]	catalyst	time (h)	yield[b] (%)	dr[c]	ee[d]
1	**I**	2	78	1:1	95/54
2	**II**	2	72	1:1	94/54
3	**III**	2	70	1.5:1	64/66
3	**IV**	1	76	1.4:1	78/63
4	**V**	**1**	**80**	**1.7:1**	**95/86**
5	**VI**	3	62	1.4:1	43/39
6	**VII**	2	56	1:1	36/5
7	**VIII**	2.5	85	1.2:1	42/25

[a]Reaction condition: 0.05 mmol of **1a** and 0.06 mmol of **2a** in 0.2 mL toluene using 20 mol% catalyst. [b]Isolated yield after silica gel column chromatography. [c]Determined by ^{1}H NMR. [d]Determined by HPLC using stationary phase chiral column.

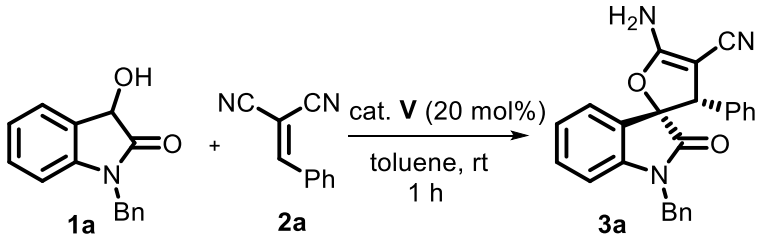
6. Solvent optimization for Dihydrofuran-Spirooxindoles:



entry[a]	solvent	time (h)	yield[b]	dr[c]	ee[d]
1	$PhCF_3$	3	71	1:1	88/47
2	*o*-xylene	3	73	1:1	88/50
3	Et_2O	2	78	1.3:1	94/80
4	CH_2Cl_2	2	79	1.3:1	95/70
5	$CHCl_3$	3	69	1.2:1	94/57

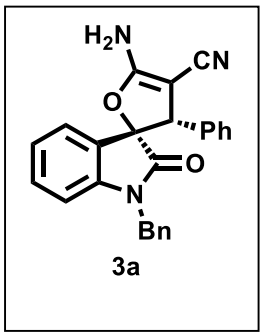
[a]Reaction condition: 0.05 mmol of **1a** and 0.06 mmol of **2a** in 0.2 mL solvent using 20 mol% catalyst **V**. [b]Isolated yield after silica gel column chromatography. [c]Determined by ^1H NMR. [d]Determined by HPLC.

7. General procedure for the synthesis of compound 3:



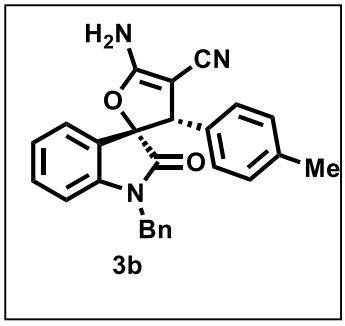
In an oven dried round bottom flask, **1** (11.96 mg, 0.05 mmol), **2** (9.25 mg, 0.06 mmol) and 20 mol% of catalyst (**V**) were taken. 0.2 mL of toluene was added to the reaction mixture and stirred at rt for 1 hour. Progress of the reaction was monitored by TLC. After the completion of reaction, solvent was concentrated and reaction mixture was directly purified by column chromatography on silica gel eluting with hexane/ethyl acetate (20 %) to afford desired product **3a-r**.

8. Characterisation of the products:



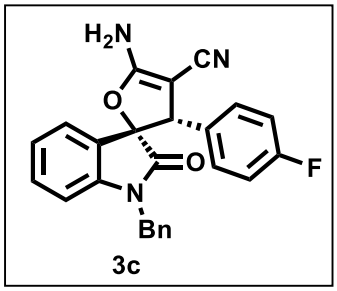
3a

3a (2*S*,3*S*)-5-amino-1'-benzyl-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow solid in 80% yield (15.7 mg) after column chromatography. M.P. = 197-198 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.81 (d, J = 7.3 Hz, 0.6H), 7.62 (s, 3H), 7.39 – 7.24 (m, 8H), 7.21 – 7.07 (m, 7H), 7.03 (t, J = 7.4 Hz, 3H), 6.84 (d, J = 7.9 Hz, 1H), 6.69 – 6.60 (m, 3H), 6.49 (d, J = 7.1 Hz, 1H), 5.03 (s, 0.6H), 4.92 (dd, J = 29.4, 15.6 Hz, 2H), 4.78 (d, J = 16.0 Hz, 0.6H), 4.73 (s, 1H), 4.32 (d, J = 16.0 Hz, 0.6H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.5, 170.8, 170.3, 168.1, 168.0, 142.9, 142.3, 137.0, 135.8, 135.1, 134.4, 131.2, 130.5, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.6, 127.6, 127.2, 12.13, 126.4, 125.9, 125.6, 125.1, 123.6, 123.3, 122.2, 118.9, 109.5, 109.4, 88.5, 87.3, 59.7, 56.2, 53.8, 51.9, 51.5, 42.8, 42.3. **HPLC Analysis:** 95% ee (t_{major} = 32.5 min, t_{minor} = 53.7 min) and 86% ee (t_{major} = 36.9 min, t_{minor} = 81.4 min); Daicel Chiralpak ID Column, n-Hexane/ i-PrOH = 80/20, flow rate 1.0 mL/min, 25 °C, λ = 220 nm. **FT-IR (thin film):** 3435, 2187, 1647, 1489, 1468, 1454, 1421, 1376, 1301, 1265, 1178, 1118, 1078, 1011, 735, 699 cm^{-1}; **ESI HRMS:** calcd. For $C_{25}H_{20}N_3O_2[M+H]^+$ 394.1550, found 394.1556.



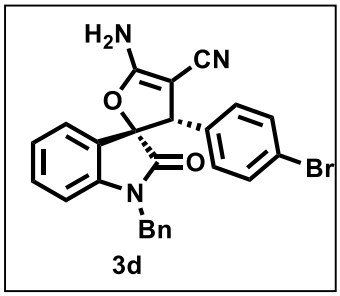
3b

3b (2*S*,3*S*)-5-amino-1'-benzyl-2'-oxo-3-(p-tolyl)-3H-spiro [furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow sticky solid in 89% yield (18.1 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.80 (d, *J* = 7.2 Hz, 0.7H), 7.60 (s, 3H), 7.33 (dt, *J* = 13.1, 7.1 Hz, 6H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.13 – 7.05 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.88 (m, 3H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.68 (dt, *J* = 12.7, 7.6 Hz, 2H), 6.51 (d, *J* = 7.4 Hz, 1H), 4.97 (s, 0.7H), 4.90 (dd, *J* = 18.0, 12.3 Hz, 2H), 4.80 (d, *J* = 16.0 Hz, 0.7H), 4.68 (s, 1H), 4.32 (d, *J* = 16.0 Hz, 0.7H), 2.30 (s, 2H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 174.0, 171.4, 168.5, 168.3, 143.3, 142.8, 137.6, 137.2, 136.2, 135.6, 134.4, 131.8, 131.6, 130.9, 129.2, 129.1, 129.0, 128.7, 128.0, 127.7, 127.6, 126.9, 126.4, 125.5, 124.2, 123.7, 122.7, 119.4, 110.0, 109.9, 89.0, 87.8, 56.5, 54.0, 52.6, 52.2, 43.3, 42.8, 21.2, 21.0. **HPLC Analysis**: 80% ee (t_{major} = 47.4 min, t_{minor} = 74.4 min) and 70% ee (t_{major} = 57.6 min, t_{minor} = 109.8 min); Daicel Chiralpak ID Column, n-Hexane/ i-PrOH = 75/15, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3449, 2923, 2187, 1660, 1468, 1077, 1019, 751, 704 cm^{-1}; **ESI HRMS**: calcd. For $C_{26}H_{22}N_3O_2[M+H]^+$ 408.1707, found 408.1716.



3c

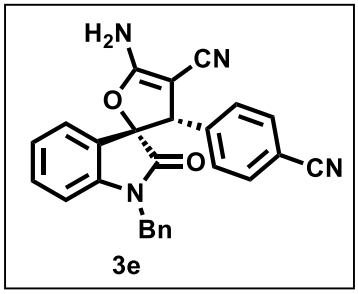
3c (2*S*,3*S*)-5-amino-1'-benzyl-3-(4-fluorophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow solid in 84% yield (17.3 mg) after column chromatography. M.P. = 186-187 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.81 (d, J = 7.3 Hz, 0.6H), 7.66 (s, 3H), 7.39 – 7.28 (m, 6H), 7.19 (t, J = 7.4 Hz, 1H), 7.11 (dd, J = 12.2, 7.4 Hz, 4H), 7.08 – 7.00 (m, 5H), 6.86 (d, J = 7.9 Hz, 1H), 6.71 (t, J = 7.3 Hz, 2H), 6.61 (d, J = 7.3 Hz, 1H), 6.55 (d, J = 7.3 Hz, 1H), 5.03 (s, 0.6H), 4.91 (dd, *J* = 21.8, 15.6 Hz, 2H), 4.79 (d, J = 16.1 Hz, 0.6H), 4.74 (s, 1H), 4.36 (d, J = 16.0 Hz, 0.6H). **^{13}C NMR (150 MHz, DMSO-d$_6$)** δ 173.5, 170.8, 168.1, 168.0, 162.3, 161.2, 160.6, 142.8, 142.4, 135.8, 135.2, 133.5, 131.3, 130.6, 130.3, 130.2, 128.7, 128.3, 127.6, 127.3, 126.5, 125.9, 123.5, 123.4, 122.3, 118.9, 115.2, 115.1, 115.0, 109.7, 109.5, 88.4, 87.2, 55.4, 52.9, 51.9, 51.6, 42.9, 42.4, 40.0. **HPLC Analysis**: 94% ee (t_{major} = 45.8 min, t_{minor} = 59.8 min) and 86% ee (t_{major} = 51.5 min, t_{minor} = 92.2 min); Daicel Chiralpak IA Column, n-Hexane/ i-PrOH = 93/7, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3433, 2924, 2193, 1718, 1655, 1490, 1344, 1172, 1078, 969, 736, 655, 557 cm^{-1}; **ESI HRMS**: calcd. For $C_{26}H_{18}FN_3O_2[M+H]^+$ 412.1456, found 412.1460.



3d

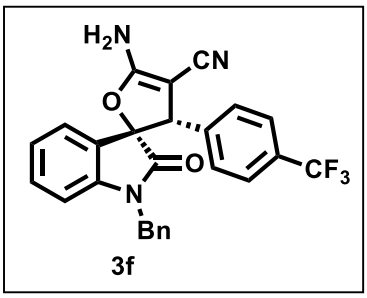
3d (2*S*,3*S*)-5-amino-1'-benzyl-3-(4-bromophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow solid in 78% yield (18.4 mg) after column chromatography. M.P. = 184-185 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** ^{1}H NMR (400 MHz, DMSO) δ 7.81 (d, *J* = 7.1 Hz, 0.6H), 7.69 (s, 3H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.29 (m, 6H), 7.19 (t, *J* = 6.2 Hz, 3H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.75 – 6.69 (m, 2H), 6.64 (d, *J* = 7.1 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 5.03 (s, 0.6H), 4.92 (dd, *J* = 21.4, 16.0 Hz, 2H), 4.83 (d, *J* = 16.0 Hz, 0.6H), 4.73 (s, 1H), 4.35 (d, *J* = 16.0 Hz, 0.6H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.3, 170.7, 168.1, 168.0, 142.8, 142.4, 136.7, 135.7, 135.2, 134.0, 131.3, 131.2, 131.1, 130.8, 130.7, 130.5, 128.7, 128.3, 127.6, 127.2, 127.0, 126.5, 125.9, 125.4, 125.2, 123.4, 122.3, 121.4, 120.7, 118.7, 109.7, 109.5, 88.2, 87.0, 55.5, 53.1, 51.6, 51.3, 42.9, 42.4, 40.1, 39.9, 39.7, 39.5, 39.3, 39.1, 38.8 **HPLC Analysis**: 88% ee (t_{major} = 54.9 min, t_{minor} = 81.5 min) and 94% ee (t_{major} = 70.2 min, t_{minor} = 121.9 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 90/10, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3430, 2924, 2853, 2188, 1731, 1663, 1486,

1373, 1178, 1062, 1011, 813, 727, 639, 514 cm^{-1}; **ESI HRMS**: calcd. For $C_{26}H_{18}BrN_3O_2[M+H]^+$ 472.0655, found 472.0654.



3e

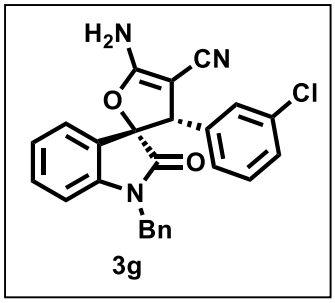
3e (2*S*,3*S*)-5-amino-1'-benzyl-3-(4-cyanophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a pale white sticky solid in 83% yield (17.4 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.75 (d, *J* = 7.0 Hz, 3H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.15 (dd, *J* = 16.2, 7.6 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 0.4H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 2H), 5.15 (s, 0.3H), 4.93 (s, 2H), 4.87 (s, 1H), 4.77 (d, *J* = 15.9 Hz, 0.3H), 4.38 (d, *J* = 15.9 Hz, 0.3H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.2, 170.5, 168.3, 143.3, 142.8, 142.4, 140.5, 135.7, 135.3, 132.2, 131.5, 130.8, 129.6, 129.4, 128.7, 128.3, 127.3, 126.6, 125.8, 125.3, 123.5, 123.0, 122.3, 118.6, 118.5, 110.9, 110.4, 109.8, 109.6, 88.0, 86.9, 55.8, 53.3, 51.2, 50.9, 42.9, 42.5. **HPLC Analysis**: 98% ee (t_{major} = 56.2 min, t_{minor} = 30.4 min) and 97% ee (t_{major} = 40.1 min, t_{minor} = 35.2 min); Phenomenex Chiralpak LUX C1 Column, n-Hexane/ i-PrOH = 80/20, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3465, 2078, 1640, 1467, 1377, 1179, 699, 475, 458 cm^{-1}; **ESI HRMS**: calcd. For $C_{26}H_{19}N_4O_2[M+H]^+$ 419.1503, found 419.1521.



3f

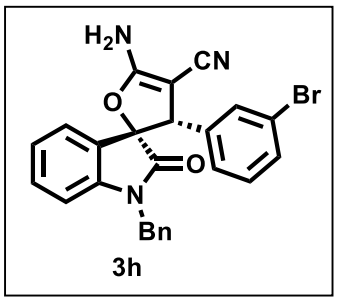
3f (2*S*,3*S*)-5-amino-1'-benzyl-2'-oxo-3-(4-(trifluoromethyl) phenyl) -3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a light yellow solid in 81% yield (18.7 mg) after column chromatography. M.P. = 186-187 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.84 (d, *J* = 6.9 Hz, 0.5H), 7.72 (d, *J* = 5.3 Hz, 3H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.31 (m, 5H), 7.30 – 7.13 (m, 6H), 7.13 – 7.06 (m, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 0.5H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.58 (dd, *J* = 13.7, 7.1 Hz, 2H), 5.16 (s, 0.5H), 4.92 (dd, *J* = 19.2, 16.0 Hz, 2H), 4.87 (s, 1H), 4.80 (d, *J* = 15.9 Hz, 0.5H), 4.36 (d, *J* = 16.0 Hz, 0.5H. **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.3, 170.5, 168.2, 168.1, 142.8, 142.4, 142.1, 139.6, 135.7, 135.2, 131.4, 130.7, 129.6, 129.2, 128.7, 128.2, 127.6, 127.2, 126.4, 125.8, 125.4, 125.1, 123.5, 123.2, 122.2, 118.7, 118.6, 109.7, 109.6, 88.0, 87.0, 55.6, 53.3, 51.6, 51.1, 42.9, 42.5 **HPLC Analysis**: 80% ee (t_{major} = 13.6 min, t_{minor} = 19.0 min) and 52% ee (t_{major} = 21.9 min, t_{minor} = 28.9 min); Daicel Chiralpak ID Column, n-Hexane/ i-PrOH = 80/20, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3448, 2925, 2854, 2188, 1718, 1655, 1488,

1469, 1325, 1273, 1169, 1067, 1016, 752, 699, 630 cm^{-1}; **ESI HRMS**: calcd. For $C_{26}H_{19}F_3N_3O_2[M+H]^+$ 462.1424, found 462.1429.



3g

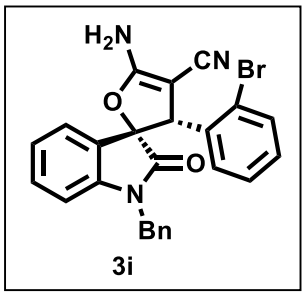
3g (2*S*,3*S*)-5-amino-1'-benzyl-3-(3-chlorophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a light yellow sticky solid in 81% yield (17.3 mg) after column chromatography. **^{1}H NMR (600 MHz, DMSO-d$_6$)** δ 7.80 (d, *J* = 7.3 Hz, 0.6H), 7.72 (s, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 4.6 Hz, 2H), 7.19 (dd, *J* = 14.2, 7.1 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.07 (s, 2H), 7.05 – 7.02 (m, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.73 (dd, *J* = 14.5, 7.5 Hz, 2H), 6.62 (d, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.3 Hz, 1H), 5.05 (s, 0.6H), 4.92 (dd, *J* = 39.9, 15.8 Hz, 2H), 4.82 (d, *J* = 15.9 Hz, 0.6H), 4.78 (s, 1H), 4.37 (d, *J* = 16.0 Hz, 0.6H). **^{13}C NMR (150 MHz, DMSO-d$_6$)** δ 173.3, 170.6, 168.2, 168.1, 142.7, 142.4, 139.9, 137.2, 135.7, 135.2, 133.0, 131.4, 130.7, 130.1, 128.7, 128.5, 128.3, 128.1, 127.7, 127.6, 127.4, 127.2, 127.1, 126.4, 125.8, 125.4, 125.2, 123.5, 123.3, 122.3, 118.8, 109.7, 109.6, 88.2, 87.1, 55.5, 53.1, 51.4, 51.1, 42.9, 42.4, 40.0. **HPLC Analysis**: 98% ee (t_{major} = 64.2 min, t_{minor} = 17.9 min) and 31% ee (t_{major} = 32.9 min, t_{minor} = 14.2 min); Daicel Chiralpak IC Column, n-Hexane/ i-PrOH = 80/20, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3435, 2925, 2854, 2188, 1650, 1488, 1433, 1376, 1263, 1178, 1118, 1078, 1011, 793, 734, 698, 552 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}ClN_3O_2[M+H]^+$ 428.1160, found 428.1163.



3h

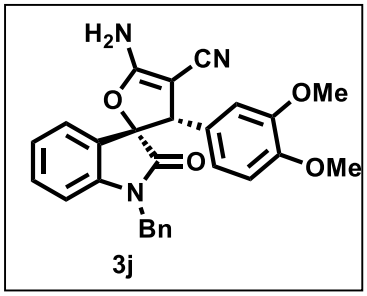
3h (2*S*,3*S*)-5-amino-1'-benzyl-3-(3-bromophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as an orange solid in 61% yield (14.4 mg) after column chromatography. M.P. = 183-184 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.79 (d, *J* = 7.2 Hz, 0.8H), 7.71 (s, 3H), 7.54 (d, *J* = 8.9 Hz, 0.8H), 7.34 (dd, *J* = 14.4, 7.2 Hz, 6H), 7.20 (d, *J* = 8.7 Hz, 3H), 7.18 – 7.12 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 6.4 Hz, 2H), 5.04 (s, 0.8H), 4.92 (dd, *J* = 30.6, 15.8 Hz, 2H), 4.82 (d, *J* = 16.0 Hz, 0.8H), 4.77 (s, 1H), 4.36 (d, *J* = 15.9 Hz, 0.8H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.3, 170.6, 168.2, 168.1, 142.8, 142.4, 140.1, 137.4, 135.7, 135.2,

131.4, 131.0, 130.7, 130.6, 130.4, 128.8, 128.5, 127.8, 127.6, 127.5, 127.2, 126.4, 125.8, 125.4, 123.3, 122.3, 121.6, 118.7, 109.7, 109.5, 88.2, 87.1, 55.4, 53.1, 51.5, 51.1, 42.9, 42.4. **HPLC Analysis**: 92% ee (t_{major} = 51.9 min, t_{minor} = 58.3 min) and 35% ee (t_{major} = 47.5 min, t_{minor} = 109.2 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 90/10, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm. **FT-IR (thin film):** 3433, 2923, 2853, 2187, 1729, 1665, 1486, 1426, 1372, 1178, 1121, 1078, 1011, 846, 727, 698, 590, 561 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}BrN_3O_2[M+H]^+$ 472.0655, found 472.0652.



3i

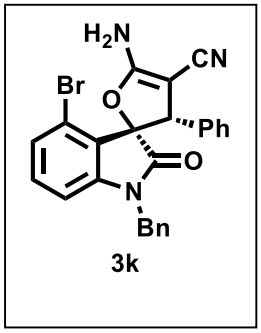
3i (2*S*,3*S*)-5-amino-1'-benzyl-3-(2-bromophenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a light yellow solid in 82% yield (19.4 mg) after column chromatography. M.P. = 189-191 ^{o}C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.73 (dd, *J* = 17.3, 8.9 Hz, 3H), 7.57 (d, *J* = 6.1 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.18 (dd, *J* = 9.9, 5.3 Hz, 3H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.79 (dd, *J* = 12.3, 6.0 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 7.4 Hz, 1H), 5.25 (s, 0.4H), 4.91 (s, 2H), 4.84 (s, 1H), 4.76 (d, *J* = 15.9 Hz, 0.4H), 4.47 (d, *J* = 15.9 Hz, 0.4H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.2, 170.3, 167.9, 167.9, 143.5, 142.6, 136.6, 135.6, 135.4, 134.7, 132.5, 131.1, 130.8, 130.0, 129.8, 128.6, 128.4, 127.9, 127.9, 127.7, 127.4, 127.3, 127.2, 126.8, 125.8, 125.1, 124.2, 123.4, 122.7, 122.1, 118.7, 109.6, 87.3, 86.1, 54.9, 52.5, 51.9, 50.9, 49.6, 43.0, 42.6 **HPLC Analysis**: 87% ee (t_{major} = 61.5 min, t_{minor} = 77.9 min) and 48% ee (t_{major} = 33.8 min, t_{minor} = 67.7 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 90/10, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm. **FT-IR (thin film):** 3445, 2924, 2853, 2187, 1729, 1659, 1486, 1426, 1372, 1262, 1178, 1121, 1062, 1011, 812, 727, 698, 640, 419 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}BrN_3O_2[M+H]^+$ 472.0655, found 472.0656.



3j

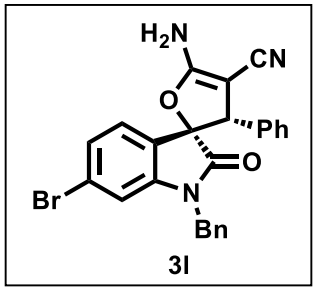
3j (2*S*,3*S*)-5-amino-1'-benzyl-3-(3,4-dimethoxyphenyl)-2'-oxo-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a light yellow sticky solid in 89% yield (20.2 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.79 (d, J = 6.9 Hz, 0.3H), 7.59 (s, 3H), 7.37 – 7.28 (m, 5H), 7.20 – 7.06 (m, 3H), 6.84 (d, J = 7.9 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.74 – 6.71 (m, 2H), 6.66 (dd, J = 8.0, 3.0 Hz, 1H), 6.52 (d, J = 6.5 Hz, 2H), 6.43 (d, J = 1.8 Hz, 1H), 5.00 (s,0. 3H), 4.95 (d, *J* = 3.7 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* =

10.9 Hz, 0.3H), 4.68 (s, 1H), 4.33 (d, J = 16.0 Hz, 0.3H), 3.73 (s, 1H), 3.65 (s, 3H), 3.46 (s, 3H), 3.45 (s, 1H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.7, 171.0, 170.3, 168.0, 167.8, 148.7, 148.3, 148.1, 143.0, 142.2, 135.8, 135.1, 131.1, 130.4, 129.2, 128.7, 128.2, 127.6, 127.2, 127.1, 126.3, 125.9, 125.7, 125.1, 123.9, 123.2, 122.3, 120.8, 120.2, 119.0, 112.1, 111.2, 109.5, 88.6, 87.5, 59.7, 56.1, 55.4, 55.3, 55.2, 55.2, 53.7, 52.1, 51.6, 42.8, 42.4. **HPLC Analysis**: 96% ee (t_{major} = 96.7 min, t_{minor} = 34.5 min) and 38% ee (t_{major} = 58.8 min, t_{minor} = 20.7 min); Daicel Chiralpak IC Column, n-Hexane/ i-PrOH = 70/30, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm. **FT-IR (thin film):** 3437, 2925, 2853, 2185, 1633, 1496, 1425, 1376, 1260, 1210, 1178, 1079, 800, 751, 699, 636, 551 cm^{-1}; **ESI HRMS**: calcd. For $C_{27}H_{24}N_3O_4[M+H]^+$ 454.1761, found 454.1760.



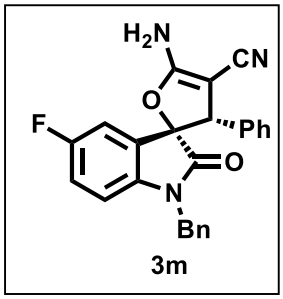
3k

3k (2S,3S)-5-amino-1'-benzyl-4'-bromo-2'-oxo-3-phenyl-3H-spiro [furan-2,3'-indoline]-4-carbonitrile was obtained as a creamy coloured solid in 93% yield (22.0 mg) after column chromatography. M.P. = 177-179 ^{o}C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.68 (d, *J* = 2.6 Hz, 3H), 7.38 (dd, *J* = 8.5, 3.9 Hz, 5H), 7.29 (t, *J* = 7.9 Hz, 3H), 7.18 – 7.11 (m, 3H), 7.06 – 7.00 (m, 7H), 6.95 (d, *J* = 7.2 Hz, 0.8H), 6.89 (d, *J* = 8.0 Hz, 0.8H), 6.73 (d, *J* = 7.5 Hz, 0.8H), 6.50 (d, *J* = 6.8 Hz, 2H), 5.23 (s, 0.8H), 4.96 (dd, *J* = 35.6, 15.6 Hz, 2H), 4.87 (s, 1H), 4.74 (d, *J* = 15.9 Hz, 0.8H), 4.29 (d, *J* = 16.0 Hz, 0.8H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 174.1, 170.2, 168.2, 167.8, 144.9, 144.1, 135.5, 135.4, 134.8, 134.4, 133.0, 132.0, 128.8, 128.7, 128.5, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.2, 127.1, 126.8, 126.5, 124.0, 123.8, 119.4, 119.2, 118.8, 118.6, 109.1, 108.9, 88.9, 88.7, 55.8, 53.2, 51.6, 51.4, 43.3, 42.6. **HPLC Analysis**: 97% ee (t_{major} = 42.8 min, t_{minor} = 48.0 min) and 77% ee (t_{major} = 39.3 min, t_{minor} = 55.2 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 85/15, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm. **FT-IR (thin film):** 3433, 2924, 2853, 2188, 1732, 1662, 1486, 1454, 1373, 1262, 1178, 1121, 1062, 810, 727, 698, 639, 514 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}BrN_3O_2[M+H]^+$ 472.0655, found 472.0655.



3l

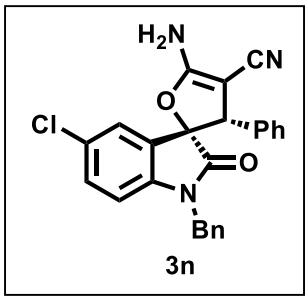
3l (2S,3S)-5-amino-1'-benzyl-6'-bromo-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow solid in 82% yield (19.4 mg) after column chromatography. M.P. = 176-178 °C. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.80 (d, *J* = 8.0 Hz, 0.6H), 7.66 (d, *J* = 5.4 Hz, 3H), 7.41 – 7.36 (m, 3H), 7.30 (dd, *J* = 18.3, 7.5 Hz, 5H), 7.24 – 7.10 (m, 7H), 7.04 (d, *J* = 7.4 Hz, 3H), 6.94 – 6.85 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 7.1 Hz, 1H), 5.04 (s, 0.6H), 4.94 (dd, *J* = 26.6, 15.8 Hz, 2H), 4.77 (d, *J* = 16.1 Hz, 0.6H), 4.73 (s, 1H), 4.37 (d, *J* = 16.0 Hz, 0.6H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.4, 170.7, 167.9, 167.8, 144.4, 143.9, 136.8, 135.5, 134.8, 134.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 127.2, 127.1, 126.4, 126.0, 124.9, 124.1, 123.5, 122.9, 118.7, 112.7, 112.4, 87.9, 86.7, 56.0, 53.7, 51.9, 51.4, 42.8, 42.3. **HPLC Analysis**: 97% ee (t_{major} = 31.8 min, t_{minor} = 35.0 min) and 71% ee (t_{major} = 42.6 min, t_{minor} = 58.4 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 85/15, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3436, 2925, 2854, 2187, 1663, 1486, 1454, 1427, 1372, 1262, 1178, 1121, 1062, 1011, 727, 698, 665, 443 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}BrN_3O_2[M+H]^+$ 472.0655, found 472.0656.



3m

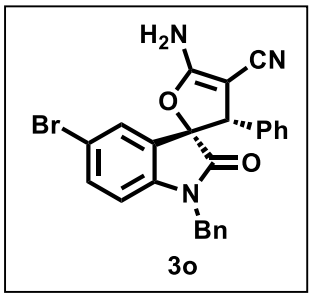
3m (2*S*,3*S*)-5-amino-1'-benzyl-5'-fluoro-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow sticky solid in 98% yield (20.2 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.84 (d, *J* = 8.0 Hz, 0.7H), 7.66 (d, *J* = 5.3 Hz, 3H), 7.32 (qd, *J* = 14.7, 7.4 Hz, 8H), 7.23 – 7.10 (m, 6H), 7.05 (t, *J* = 6.6 Hz, 4H), 6.97 (t, *J* = 9.0 Hz, 1H), 6.86 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.65 (dd, *J* = 8.6, 4.1 Hz, 0.7H), 6.44 (dd, *J* = 17.0, 7.7 Hz, 2H), 5.07 (s, 0.7H), 4.92 (dd, *J* = 27.2, 15.8 Hz, 2H), 4.79 (s, 0.7H), 4.74 (s, 1H), 4.31 (d, *J* = 16.0 Hz, 0.7H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.4, 170.7, 170.3, 168.0, 167.8, 159.9, 158.9, 157.5, 156.5, 139.1, 138.5, 136.8, 135.6, 134.9, 134.1, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.6, 127.2, 127.1, 126.4, 125.3, 125.2, 118.8, 117.7, 117.4, 117.0, 116.7, 113.8, 113.5, 113.2, 110.6, 88.4, 87.0, 59.7, 56.1, 53.8, 51.9, 51.4, 43.0, 42.4. **HPLC Analysis**: 98% ee (t_{major} = 29.5 min, t_{minor} = 34.7 min) and 25% ee (t_{major} = 37.6 min, t_{minor} = 55.8 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 85/15, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3433, 2922, 2853, 2193, 1718, 1670, 1455, 1424, 1343, 1276, 1172, 1119, 1078, 1029, 880, 797, 736,

699, 611, 556, 468 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}FN_3O_2[M+H]^+$ 412.1456, found 412.1460.



3n

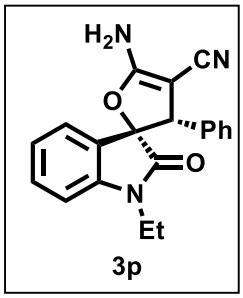
3n (2*S*,3*S*)-5-amino-1'-benzyl-5'-chloro-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow sticky solid in 71% yield (15.2 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.99 (d, *J* = 2.1 Hz, 0.8H), 7.66 (d, *J* = 9.7 Hz, 3H), 7.41 – 7.26 (m, 9H), 7.24 – 7.15 (m, 4H), 7.12 (dd, *J* = 14.5, 7.1 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 3H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 0.8H), 6.52 (d, *J* = 2.1 Hz, 0.8H), 6.46 (d, *J* = 7.1 Hz, 2H), 5.08 (s, 0.8H), 4.93 (dd, *J* = 26.8, 15.8 Hz, 2H), 4.77 (d, *J* = 16.1 Hz, 0.8H), 4.73 (s, 1H), 4.32 (d, *J* = 16.1 Hz, 0.8H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.1, 170.5, 167.9, 167.8, 141.7, 141.2, 136.9, 135.4, 134.8, 134.1, 131.0, 130.3, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.5, 127.4, 127.2, 127.2, 126.4, 125.9, 125.5, 125.4, 118.7, 111.1, 111.0, 88.1, 86.8, 59.7, 56.0, 53.7, 51.9, 51.4, 43.0, 42.4. **HPLC Analysis**: 71% ee (t_{major} = 30.4 min, t_{minor} = 33.1min) and 24% ee (t_{major} = 40.1 min, t_{minor} = 49.7 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 85/15, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3443, 2925, 2854, 2189, 1715, 1666, 1488, 1469, 1377, 1262, 1178, 1118, 1078, 1012, 794, 752, 698, 633, 552, 469 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}ClN_3O_2[M+H]^+$ 428.1160, found 428.1160.



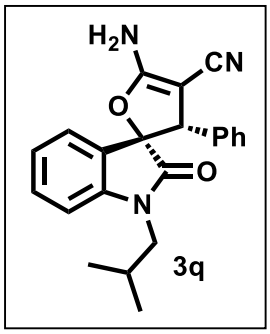
3o

3o (2*S*,3*S*)-5-amino-1'-benzyl-5'-bromo-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a yellow sticky solid in 89% yield (21.0 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 8.09 (d, *J* = 1.9 Hz, 0.7H), 7.66 (d, *J* = 11.1 Hz, 4H), 7.53 (d, *J* = 8.4 Hz, 0.7H), 7.39 – 7.27 (m, 9H), 7.23 (dd, *J* = 16.4, 9.1 Hz, 3H), 7.13 (dt, *J* = 14.3, 7.6 Hz, 3H), 7.04 (d, *J* = 6.9 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.64 – 6.59 (m, 2H), 6.45 (d, *J* = 7.2 Hz, 2H), 5.09 (s, 0.7H), 4.92 (dd, *J* = 26.4, 15.8 Hz, 2H), 4.77 (d, *J* = 16.1 Hz, 0.7H), 4.73 (s, 1H), 4.31 (d, *J* = 16.0 Hz, 0.7H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 173.0, 170.4, 167.9, 167.9, 142.1, 141.6, 136.9, 135.4, 134.7, 134.2, 133.9, 133.1, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.2, 127.2, 126.4, 125.6, 118.8, 118.7, 115.1, 114.0, 111.5, 111.4, 88.1, 86.8, 56.0, 53.7, 51.9, 51.4, 42.9, 42.4. **HPLC Analysis**: 75% ee (t_{major} = 31.1 min, t_{minor} = 33.8 min) and 23% ee (t_{major} =

40.6 min, t_{minor} = 50.1 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 85/15, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3434, 2923, 2853, 2187, 1729, 1664, 1486, 1426, 1372, 1262, 1178, 1121, 1062, 1011, 845, 813, 727, 639, 590, 561, 514, 458 cm^{-1}; **ESI HRMS**: calcd. For $C_{25}H_{19}BrN_3O_2[M+H]^+$ 472.0655, found 472.0654.

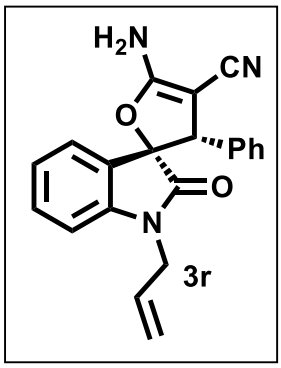


3p (2*S*,3*S*)-5-amino-1'-ethyl-2'-oxo-3-phenyl-3H-spiro [furan-2,3'-indoline]-4-carbonitrile was obtained as a light yellow sticky solid in 80% yield (13.3 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.75 (d, *J* = 7.1 Hz, 0.6H), 7.59 (d, *J* = 7.5 Hz, 3H), 7.42 (t, *J* = 7.3 Hz, 0.6H), 7.23 – 7.14 (m, 7H), 7.03 (d, *J* = 6.9 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.92 – 6.87 (m, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.0 Hz, 1H), 4.89 (s, 0.6H), 4.63 (s, 1H), 3.71 (tt, *J* = 14.1, 7.0 Hz, 2H), 3.41 – 3.36 (m, 0.6H), 3.16 (dd, *J* = 14.1, 7.1 Hz, 0.6H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.49 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 172.9, 170.3, 168.3, 168.0, 142.6, 142.3, 137.2, 134.5, 131.2, 130.5, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 126.0, 125.8, 124.8, 123.7, 123.0, 121.9, 119.0, 118.9, 108.9, 108.7, 88.6, 87.2, 56.7, 53.6, 51.4, 51.3, 34.3, 33.4, 12.2, 11.6. **HPLC Analysis**: 89% ee (t_{major} = 55.9 min, t_{minor} = 16.7 min) and 56% ee (t_{major} = 29.4 min, t_{minor} = 10.8 min); Daicel Chiralpak IC Column, n-Hexane/ i-PrOH = 70/30, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3442, 2979, 2189, 1714, 1666, 1489, 1469, 1422, 1374, 1269, 1208, 1160, 1103, 1029, 1010, 750, 700, 617, 554 cm^{-1}; **ESI HRMS**: calcd. For $C_{20}H_{18}N_3O_2[M+H]^+$ 332.1394, found 332.1398.



3q (2*S*,3*S*)-5-amino-1'-isobutyl-2'-oxo-3-phenyl-3H-spiro [furan-2,3'-indoline]-4-carbonitrile was obtained as a pale yellow sticky solid in 94% yield (16.9 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.76 (d, *J* = 7.1 Hz, 0.7H), 7.58 (d, *J* = 7.4 Hz, 3H), 7.41 (t, *J* = 7.3 Hz, 0.7H), 7.23 – 7.13 (m, 7H), 7.04 (d, *J* = 7.0 Hz, 2H), 7.00 – 6.93 (m, 3H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 4.94 (s, 0.7H), 4.62 (s, 1H), 3.54 (dd, *J* = 13.8, 7.3 Hz, 1H), 3.44 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.22 (dd, *J* = 13.8, 7.2 Hz, 0.7H), 2.97 (dd, *J* = 13.8, 7.4 Hz, 0.7H), 2.04 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.46 – 1.40 (m, 0.7H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.52 (d, *J* = 6.6 Hz, 2H), 0.35 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ

173.6, 170.9, 168.1, 168.0, 143.8, 143.1, 137.1, 134.6, 131.2, 130.5, 128.4, 128.2, 128.2, 128.0, 127.8, 127.6, 125.8, 125.8, 124.9, 123.5, 122.9, 121.9, 118.9, 109.3, 109.2, 88.3, 87.2, 56.2, 53.9, 51.7, 51.5, 46.7, 46.4, 26.5, 26.5, 19.8, 19.8, 19.7, 19.1. **HPLC Analysis**: 79% ee (t_{major} = 9.7 min, t_{minor} = 19.4 min) and 57% ee (t_{major} = 8.7 min, t_{minor} = 22.1 min); Daicel Chiralpak ID Column, n-Hexane/ i-PrOH = 70/30, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3448, 2961, 2927, 2188, 1718, 1655, 1488, 1468, 1421, 1376, 1268, 1201, 1145, 1108, 1031, 1012, 752, 699, 611, 537 cm^{-1}; **ESI HRMS**: calcd. For $C_{22}H_{22}N_3O_2[M+H]^+$ 360.1707, found 360.1709.

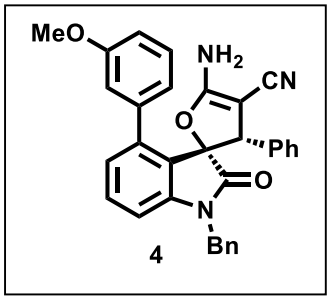


3r (2*S*,3*S*)-1'-allyl-5-amino-2'-oxo-3-phenyl-3H-spiro[furan -2,3'-indoline]-4-carbonitrile was obtained as a yellow sticky solid in 96% yield (16.5 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.78 (d, *J* = 6.9 Hz, 0.6H), 7.60 (s, 3H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 – 7.13 (m, 7H), 7.05 (d, *J* = 6.9 Hz, 2H), 6.94 (dd, *J* = 6.4, 2.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 0.6H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 6.9 Hz, 1H), 5.86 (ddt, *J* = 20.4, 10.2, 5.0 Hz, 1H), 5.28 – 5.21 (m, 0.6H), 5.16 (ddd, *J* = 18.5, 13.8, 1.2 Hz, 2H), 4.95 (s, 0.6H), 4.78 (d, *J* = 10.4 Hz, 0.6H), 4.65 (s, 1H), 4.42 – 4.25 (m, 3H), 4.07 – 4.01 (m, 0.6H), 3.77 (dd, *J* = 16.7, 5.4 Hz, 0.6H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 173.1, 170.5, 168.2, 168.0, 142.8, 142.4, 137.2, 134.5, 131.3, 131.1, 130.7, 130.4, 128.3, 128.2, 128.2, 128.0, 127.8, 127.6, 125.8, 125.7, 124.9, 123.5, 123.1, 122.1, 118.9, 118.9, 117.0, 116.2, 109.5, 109.3, 88.6, 87.2, 56.5, 53.6, 51.6, 51.5, 41.6, 41.0. **HPLC Analysis**: 80% ee (t_{major} = 11.0 min, t_{minor} = 21.8 min) and 53% ee (t_{major} = 10.0 min, t_{minor} = 23.6 min); Daicel Chiralpak ID Column, n-Hexane/ i-PrOH = 65/35, flow rate 1.0 mL/min, 25 °C, λ = 254 nm. **FT-IR (thin film):** 3433, 2924, 2186, 1637, 1488, 1468, 1422, 1381, 1278, 1182, 1134, 1009, 930, 725, 699, 611, 448 cm^{-1}; **ESI HRMS**: calcd. For $C_{21}H_{18}N_3O_2[M+H]^+$ 344.1394, found 344.1394.

General procedure for the preparation of compound 4:

In an oven dried round bottom flask, compound **3k** (47.2 mg, 0.1 mmol), phenylboronic acid (1.5 eq), palladium (II) acetate (0.05eq), tricyclohexylphosphine (0.06eq) and Na_2CO_3 (2eq) were taken, flushed with argon and then dry DMF (0.1 mL) was added. The reaction mixture was allowed to stir for 2 days under argon atmosphere. The solvent was evaporated under

reduced pressure. The obtained residue was purified by silica gel column chromatography using EtOAc-Hexane (10%) as eluent to afford the compound **4**.



4

4 (2*S*,3*S*)-5-amino-1'-benzyl-4'-(3-methoxyphenyl)-2'-oxo-3-phenyl-3H-spiro[furan-2,3'-indoline]-4-carbonitrile was obtained as a pale yellow sticky solid in 81% yield (20.2 mg) after column chromatography. **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 8.02 (s, 4H), 7.67 (s, 3H), 7.40 – 7.33 (m, 10H), 7.31 – 7.22 (m, 6H), 7.19 – 7.11 (m, 4H), 7.04 (t, *J* = 3.4 Hz, 6H), 6.95 (d, *J* = 7.0 Hz, 3H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.53 – 6.48 (m, 2H), 5.23 (s, 0.8H), 4.96 (dd, *J* = 35.3, 15.6 Hz, 2H), 4.86 (s, 1H), 4.74 (d, *J* = 16.0 Hz, 0.8H), 4.29 (d, *J* = 16.0 Hz, 0.8H), 3.74 (s, 6.6H). **^{13}C NMR (150 MHz, DMSO-d$_6$)** δ 174.1, 170.2, 168.2, 167.8, 158.5, 144.8, 144.1, 135.5, 135.3, 134.7, 134.4, 133.0, 132.0, 128.8, 128.7, 128.7, 128.4, 128.3, 128.1, 127.8, 127.8, 127.6, 127.4, 127.2, 127.0, 126.8, 126.5, 126.3, 125.2, 124.0, 123.8, 119.4, 119.1, 118.9, 118.7, 118.5, 115.7, 109.0, 108.9, 88.8, 88.7, 55.8, 54.8, 53.3, 51.6, 51.5, 43.3, 42.6. **HPLC Analysis**: 75% ee (t_{major} = 80.3 min, t_{minor} = 89.8 min) and 38% ee (t_{major} = 72.5 min, t_{minor} = 104.5 min); Daicel Chiralpak IF Column, n-Hexane/ i-PrOH = 90/10, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm. **FT-IR (thin film):** 3434, 2925, 2189, 1807, 1730, 1666, 1605, 1495, 1453, 1424, 1343, 1282, 1169, 1143, 1079, 1030, 863, 770, 700, 632, 580 cm^{-1}; **ESI HRMS**: calcd. For $C_{32}H_{26}N_3O_3[M+H]^+$ 500.1969, found 500.1977.

9. Single crystal X-ray diffraction analysis of 3i:

CCDC No.	1915125
Empirical formula	$C_{25}H_{18}BrN_3O_2$
Formula weight	472.32
Crystal habit, colour	block / colourless
Crystal size, mm^3	0.36×0.33×0.33
Temperature, T	296 K
Wavelength, λ (Å)	0.71073
Crystal system	Monoclinic
Space group	*'P 21/c'*
Unit cell dimensions	a = 9.925(4) Å
	b = 13.094(5) Å
	c = 16.855(6) Å
	α = 90°, β = 105.017°, γ = 90°
Volume, V ($Å^3$)	2115.8(14)
Z	4
Calculated density, $g \cdot cm^{-3}$	1.483
Absorption coefficient, μ (mm^{-1})	1.971
F(000)	960.0
θ range for data collection	1.996° to 25.000°
Limiting indices	$-11 \le h \le 11$, $-15 \le k \le 15$, $-20 \le l \le 20$
Reflection collected/unique	3733/ 2729
Refinement method	'SHELXL–2014/7 (Sheldrick, 2014)'
Data/restraints/parameters	3733/0/ 280
Goodness–of–fit on F^2	0.962
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0391, wR2 = 0.1219
R indices (all data)	R1 = 0.0637, wR2 = 0.1437

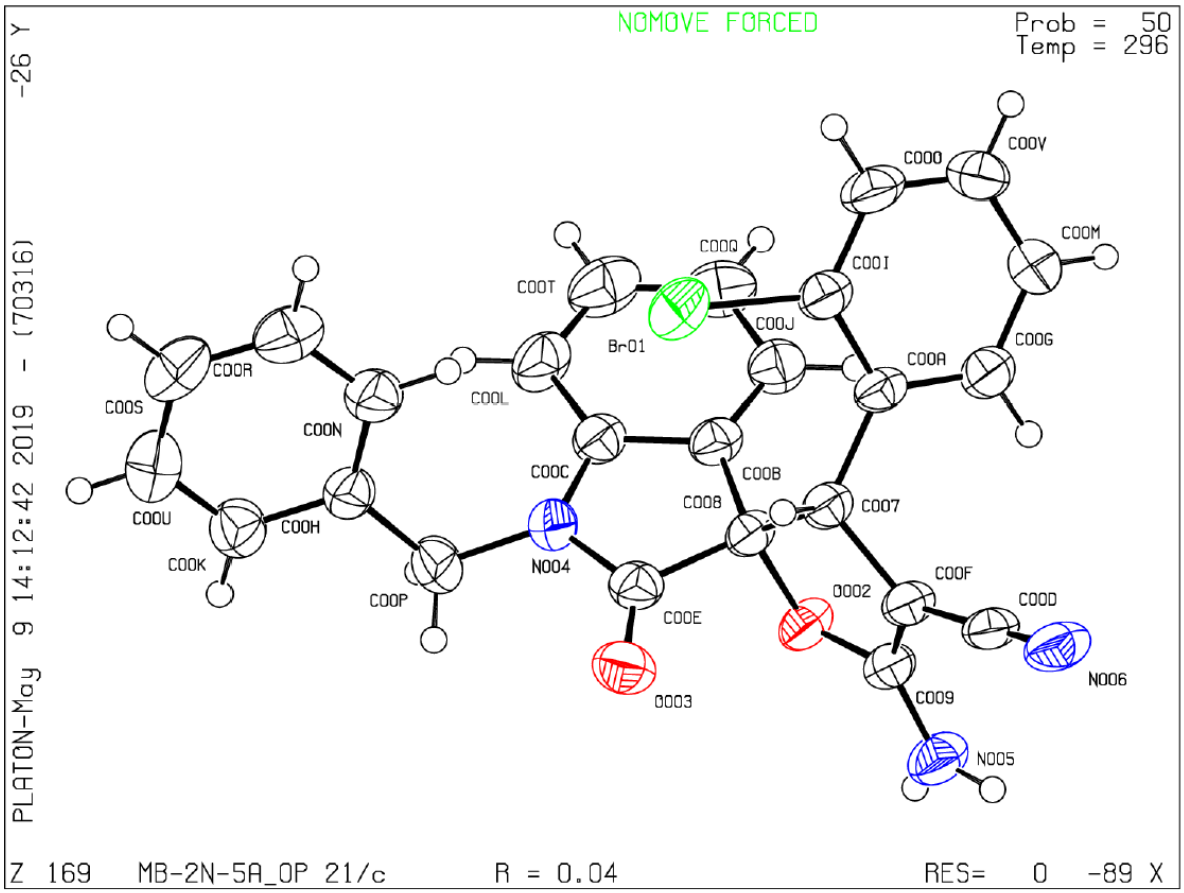
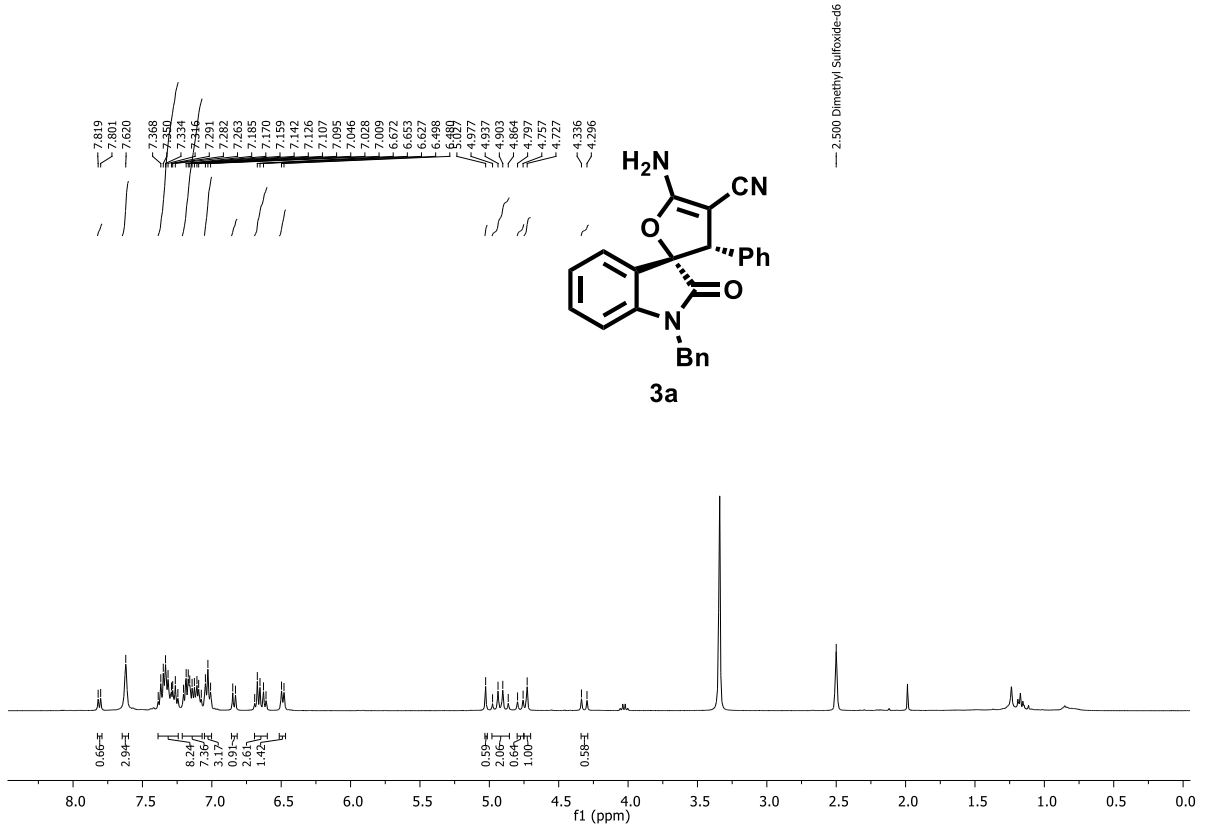
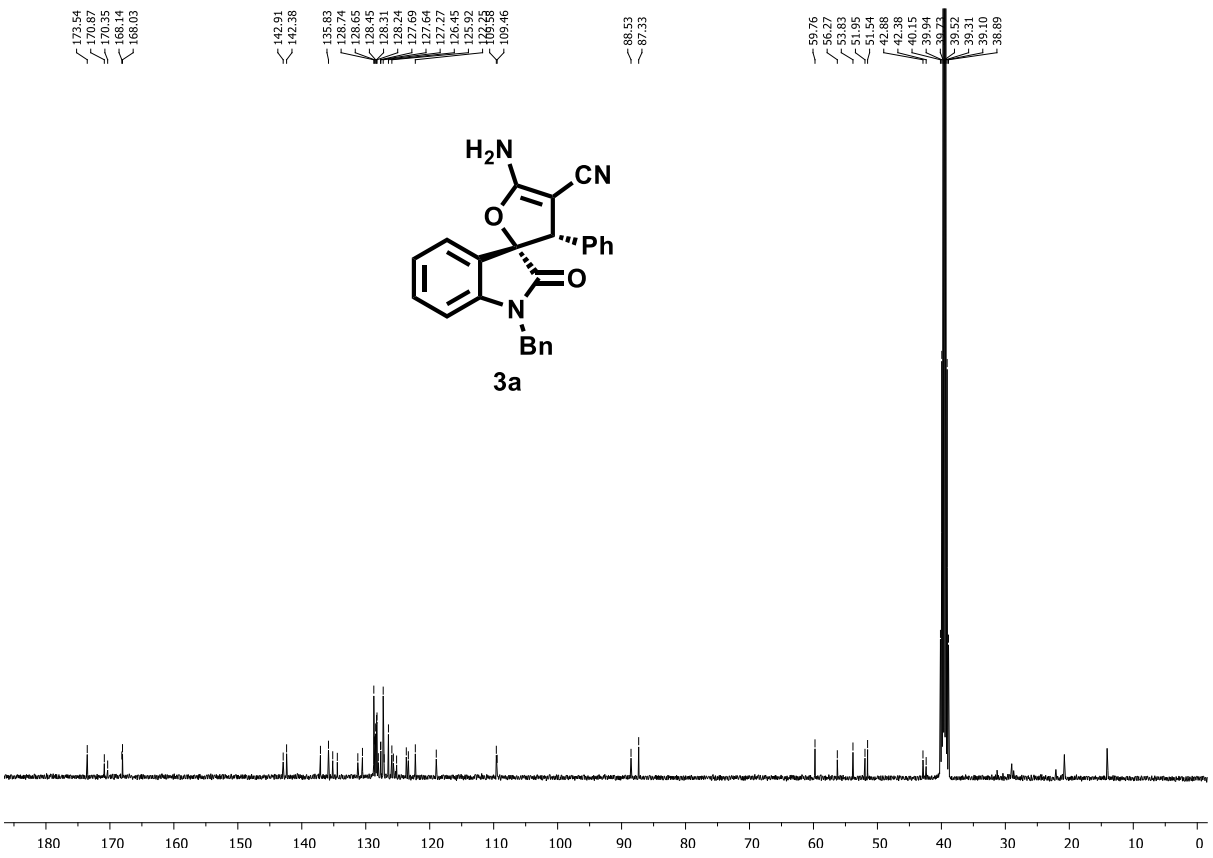
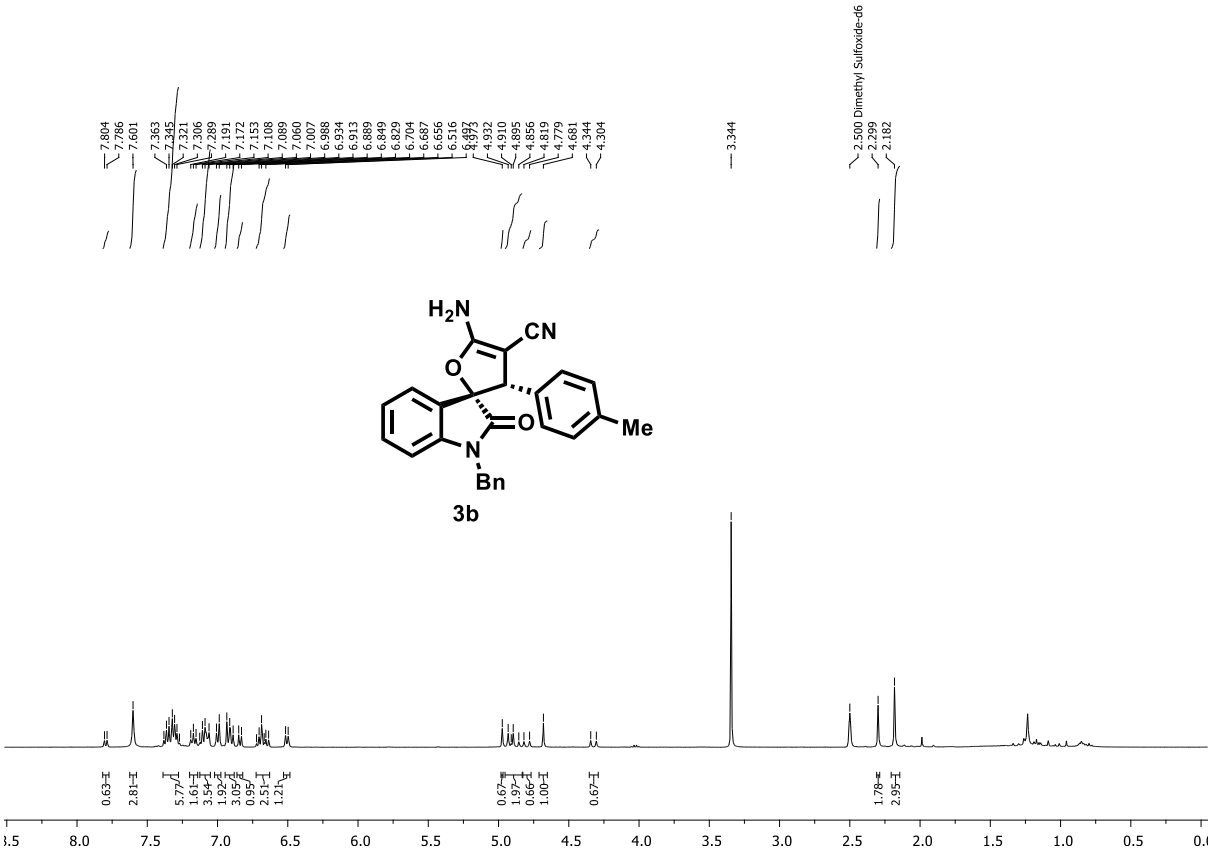


Fig. S1. Crystal structure of 3i

10. NMR spectra of the products:



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7.601
7.363
7.345
7.321
7.306
7.289
7.191
7.172
7.153
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7.089
7.060
7.007
6.988
6.934
6.913
6.889
6.849
6.829
6.704
6.687
6.656
6.516
6.497
4.973
4.932
4.910
4.895
4.856
4.819
4.779
4.681
4.344
4.304
3.344
2.500 Dimethyl Sulfoxide-d6
2.299
2.182
H2N
CN
O
O
N
Bn
Me
3b
0.63
2.81
5.77
1.61
3.54
1.92
3.05
0.95
2.51
1.21
0.67
1.97
0.66
1.00
0.67
1.78
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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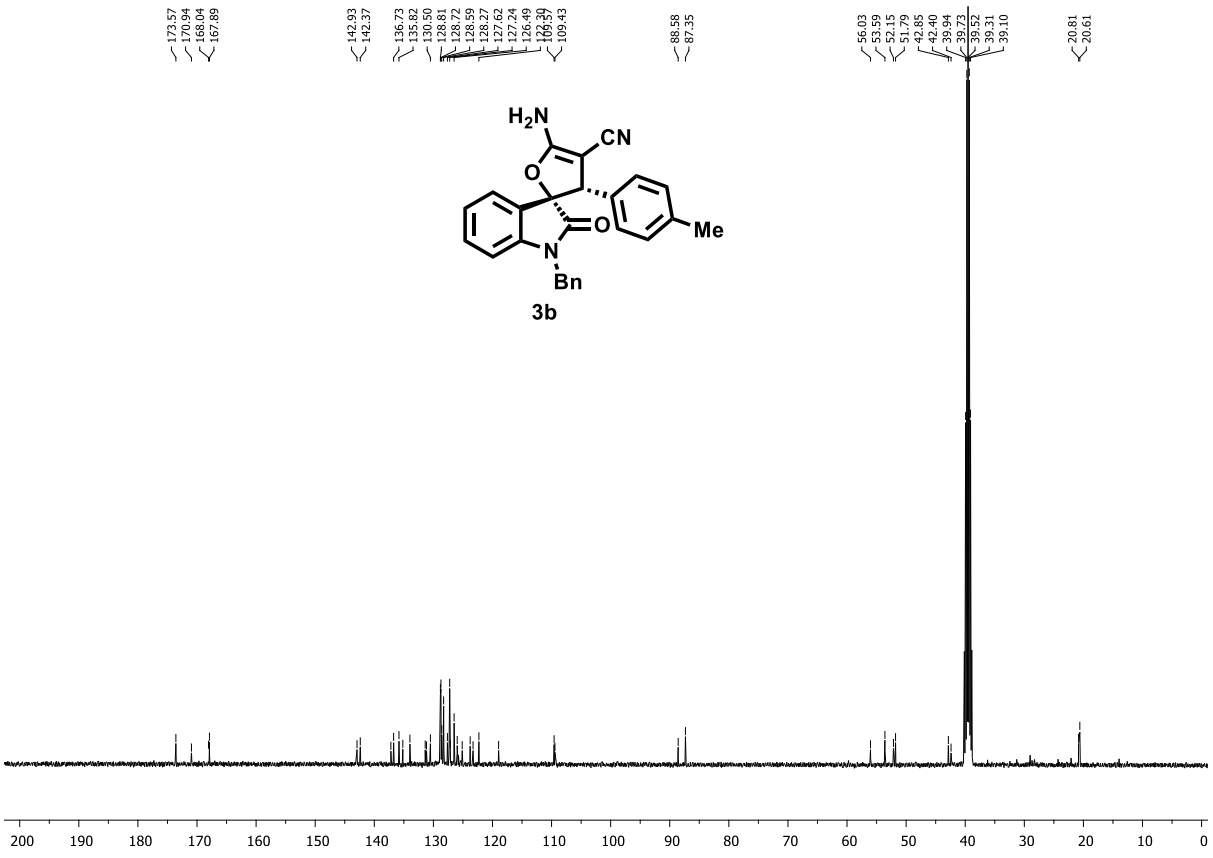
1.5
1.0
0.5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167.89
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142.37
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135.82
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127.62
127.24
126.49
109.50
109.43
88.58
87.35
56.03
53.59
52.15
51.79
42.85
42.40
39.94
39.73
39.52
39.31
39.10
20.81
20.61
H2N
CN
O
O
N
Bn
Me
3b
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140
130
120
110
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70
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50
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30
20
10
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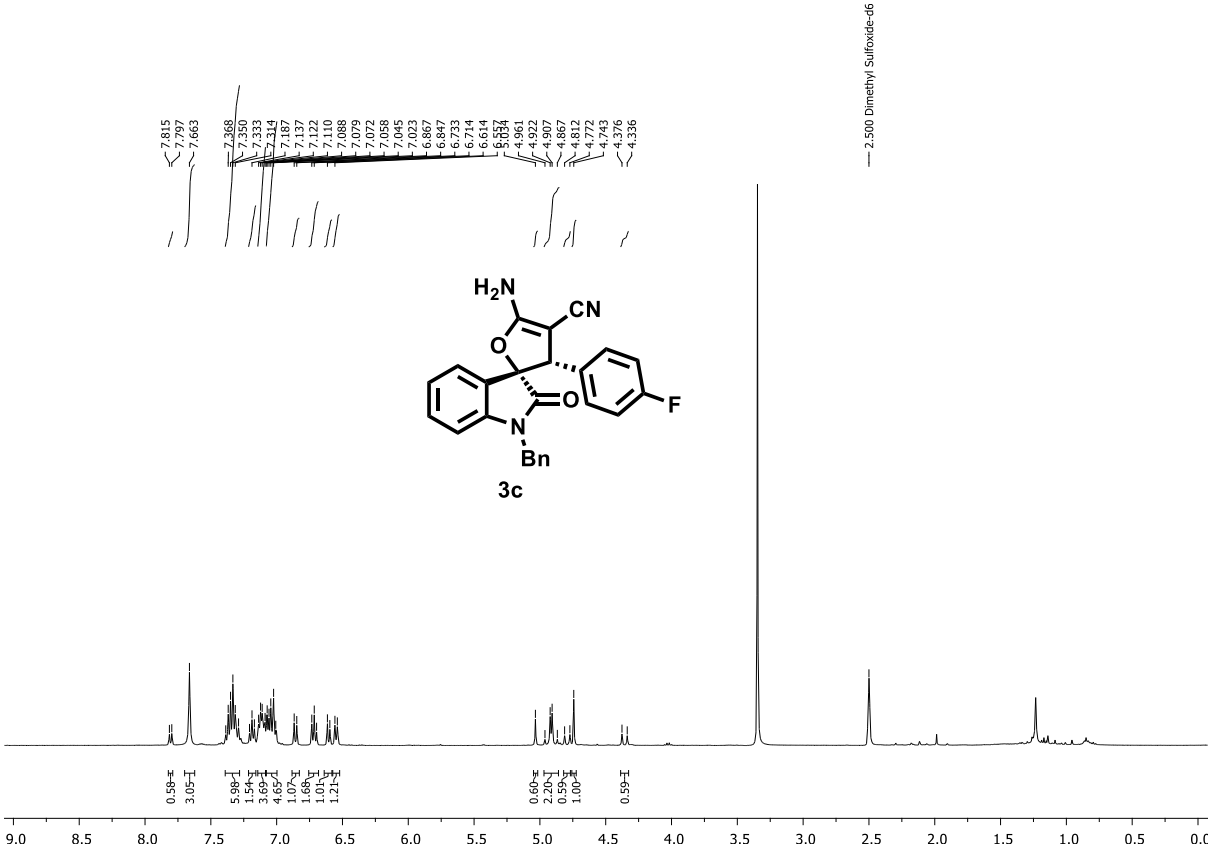
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7.314
7.187
7.137
7.122
7.110
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7.079
7.072
7.058
7.045
7.023
6.867
6.847
6.733
6.714
6.614
6.557
5.034
4.961
4.922
4.907
4.867
4.812
4.772
4.743
4.376
4.336
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
O
N
Bn
F
3c
0.59
3.05
5.98
1.54
3.69
4.65
1.07
1.68
1.01
1.21
0.60
2.20
0.59
1.00
0.59
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8.5
8.0
7.5
7.0
6.5
6.0
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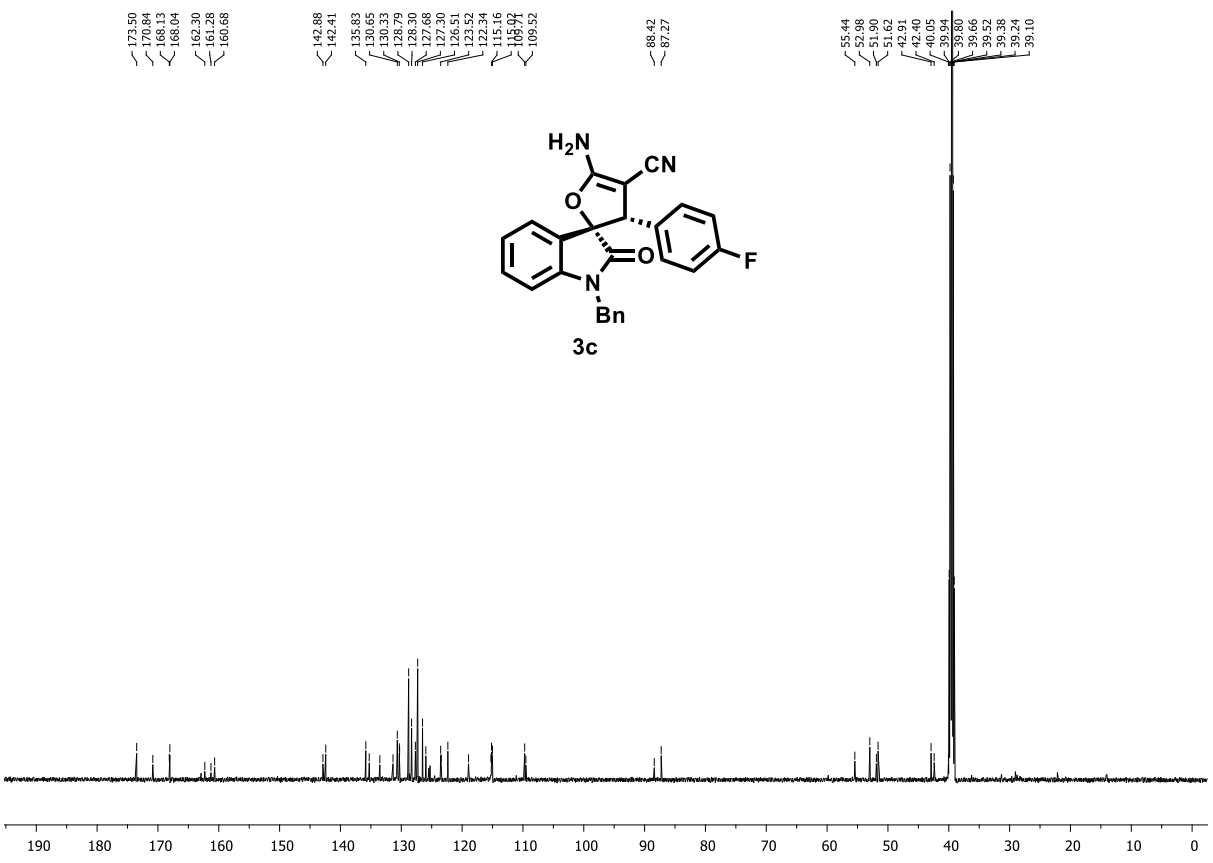
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168.04
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161.28
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130.65
130.33
128.79
128.30
127.68
127.30
126.51
123.52
122.34
115.16
115.02
109.71
109.52
88.42
87.27
55.44
52.98
51.90
51.62
42.91
42.40
40.05
39.94
39.80
39.66
39.52
39.38
39.24
39.10
H2N
CN
O
O
N
Bn
F
3c
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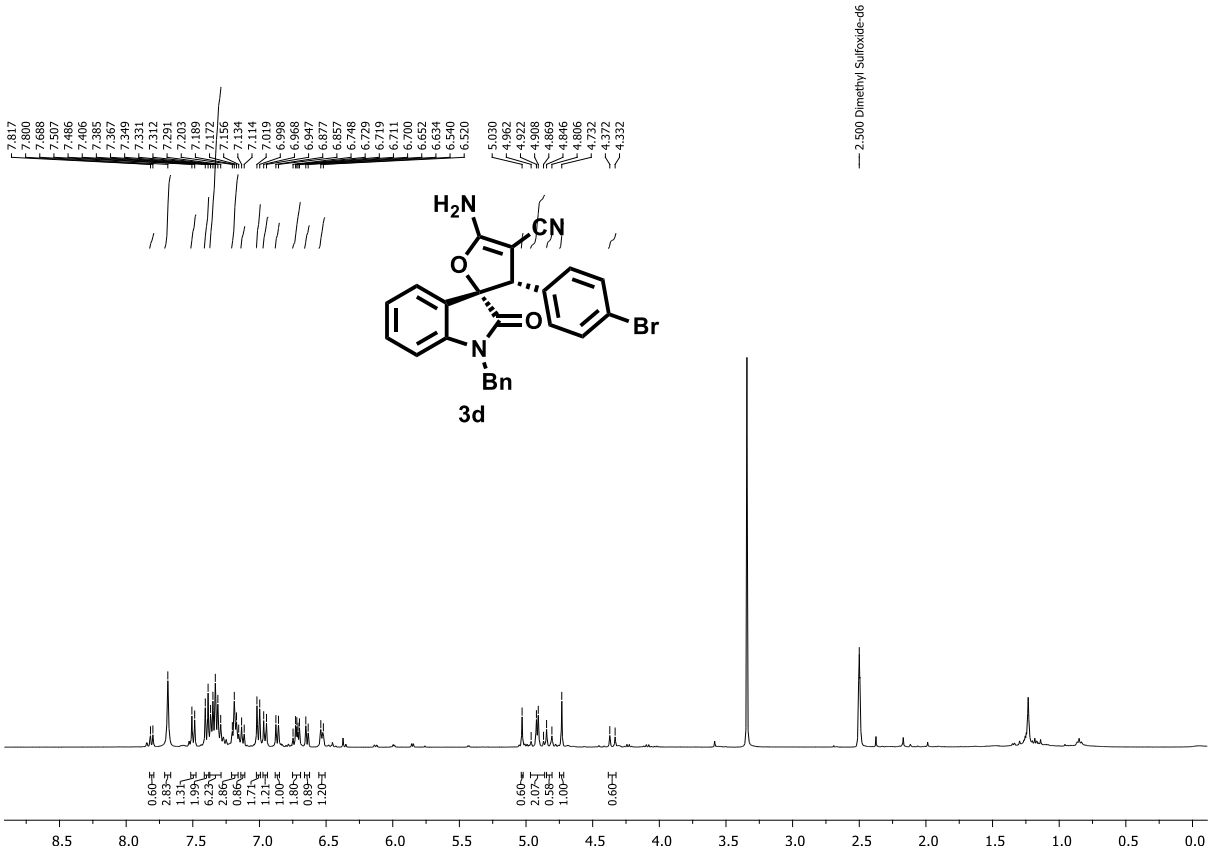
70
60
50
40
30
20
10
0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7.331
7.312
7.291
7.203
7.189
7.172
7.156
7.134
7.114
7.019
6.998
6.968
6.947
6.877
6.857
6.748
6.729
6.719
6.711
6.700
6.652
6.634
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4.922
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4.869
4.846
4.806
4.732
4.372
4.332
H2N
CN
O
O
Br
N
Bn
3d
0.60
2.83
1.31
1.99
6.23
2.86
0.86
1.71
1.21
1.00
1.80
0.89
1.20
0.60
2.07
0.58
1.00
0.60
8.5
8.0
7.5
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6.0
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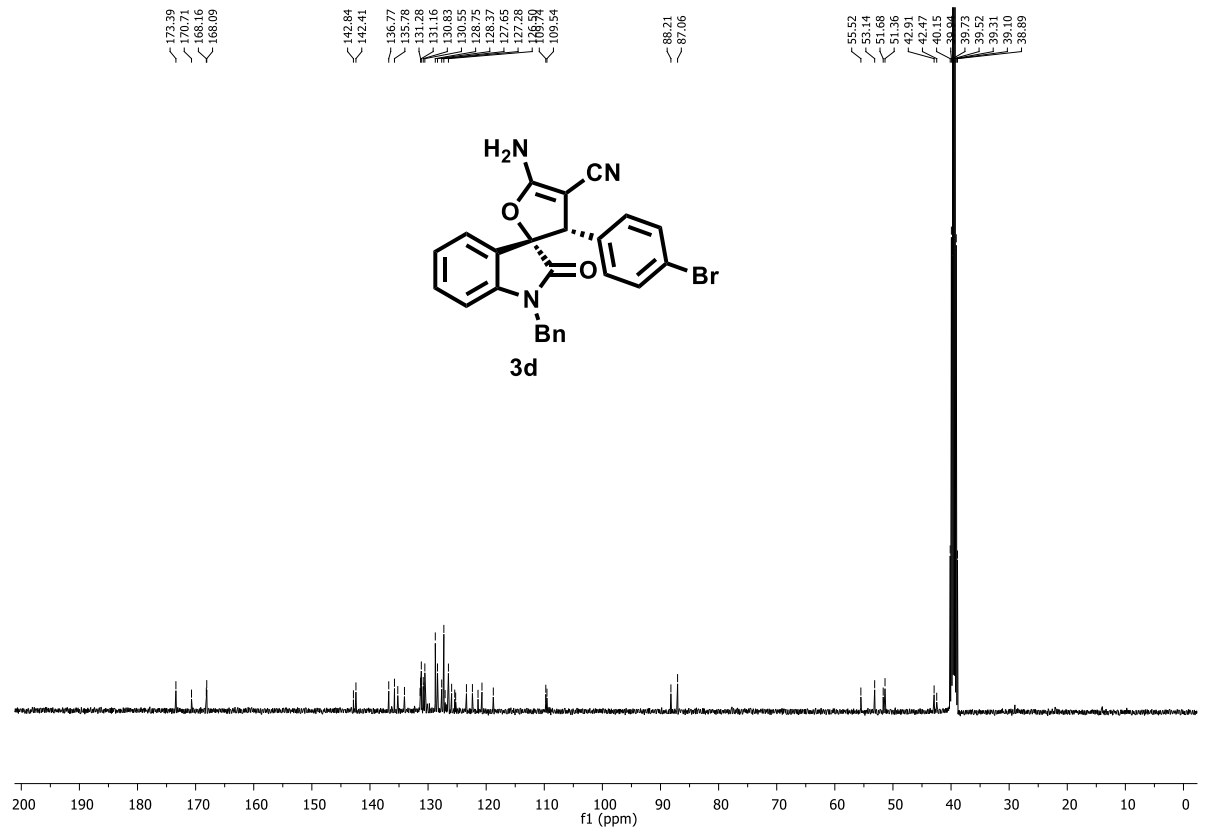
0.0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128.37
127.65
127.28
109.54
88.21
87.06
55.52
53.14
51.68
51.36
42.91
42.47
40.15
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
O
Br
N
Bn
3d
200
190
180
170
160
150
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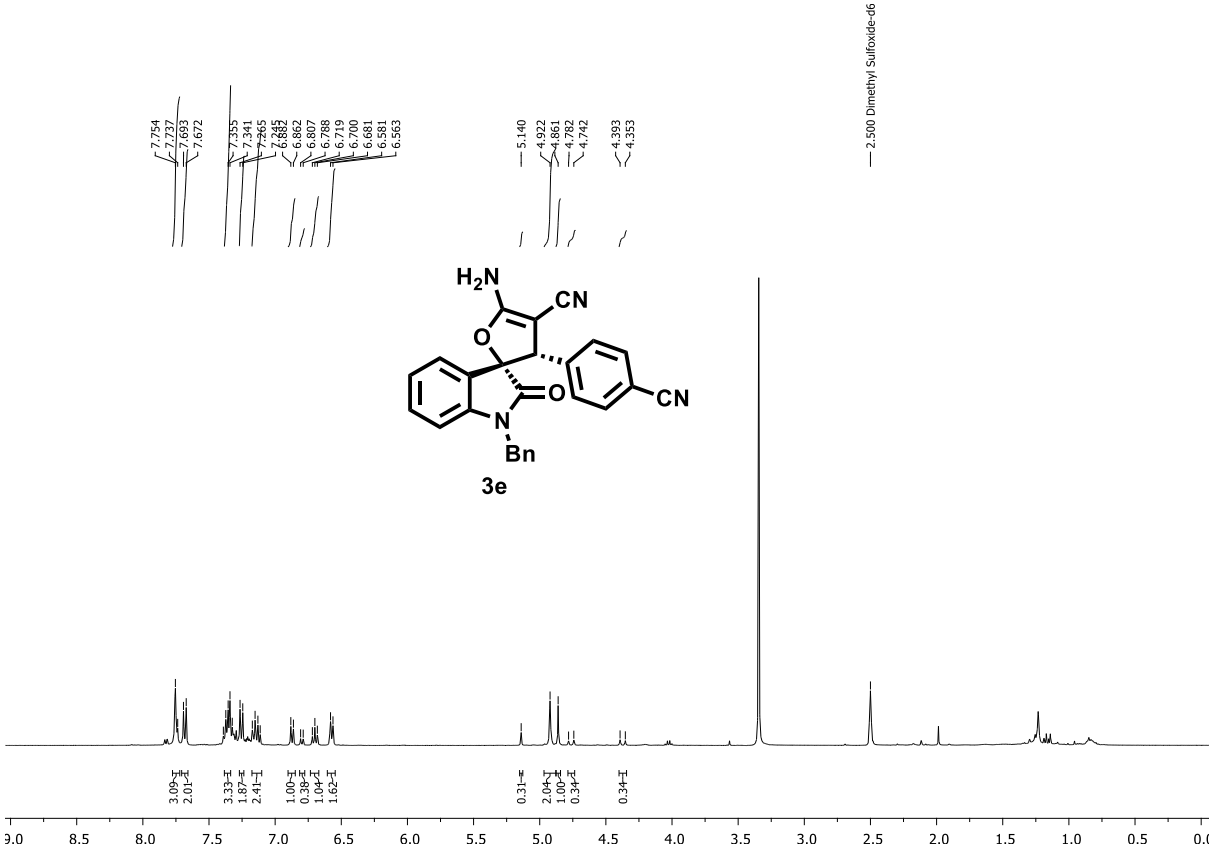
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.807
6.788
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6.681
6.581
6.563
5.140
4.922
4.861
4.782
4.742
4.393
4.353
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
O
CN
N
Bn
3e
3.09
2.01
3.33
1.87
2.41
1.00
0.38
1.04
1.62
0.31
2.04
1.00
0.34
0.34
9.0
8.5
8.0
7.5
7.0
6.5
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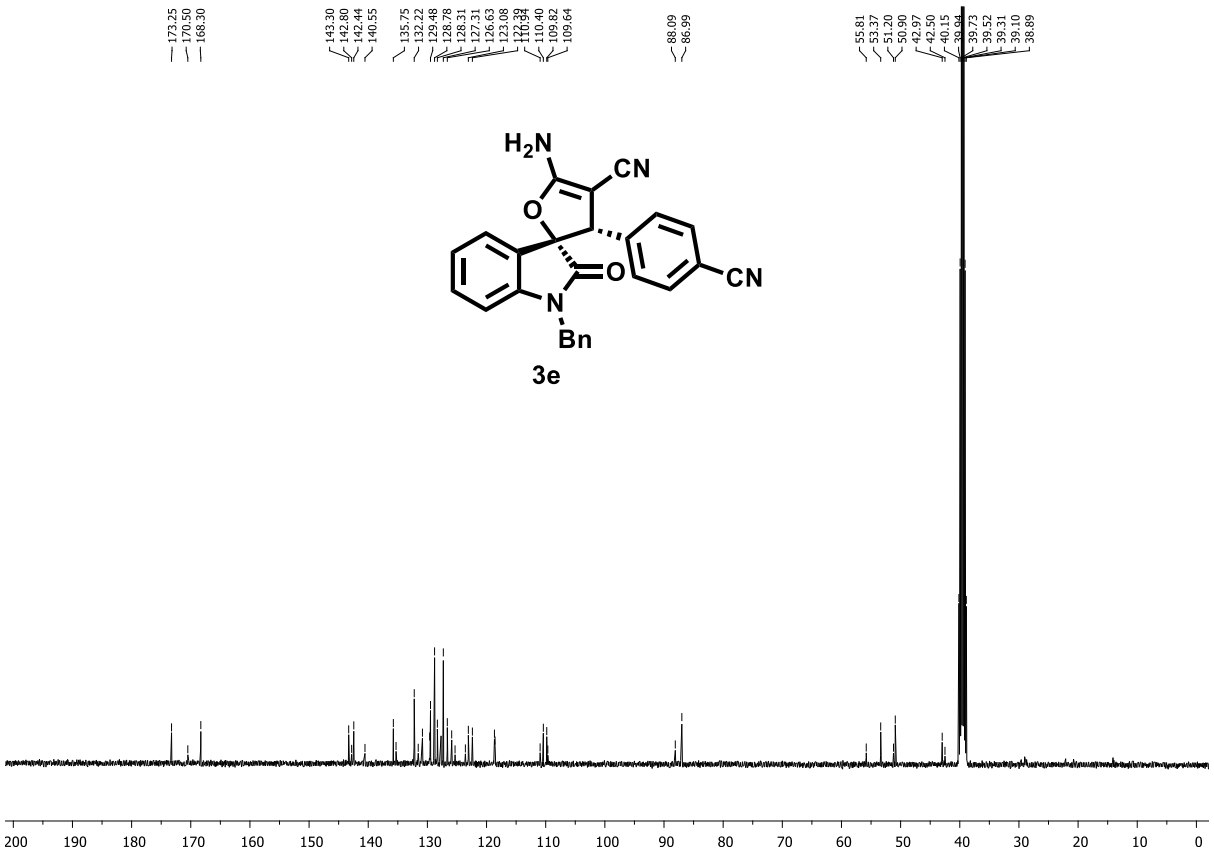
0.5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127.31
126.63
123.08
110.40
109.82
109.64
88.09
86.99
55.81
53.37
51.20
50.90
42.97
42.50
40.15
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
O
CN
N
Bn
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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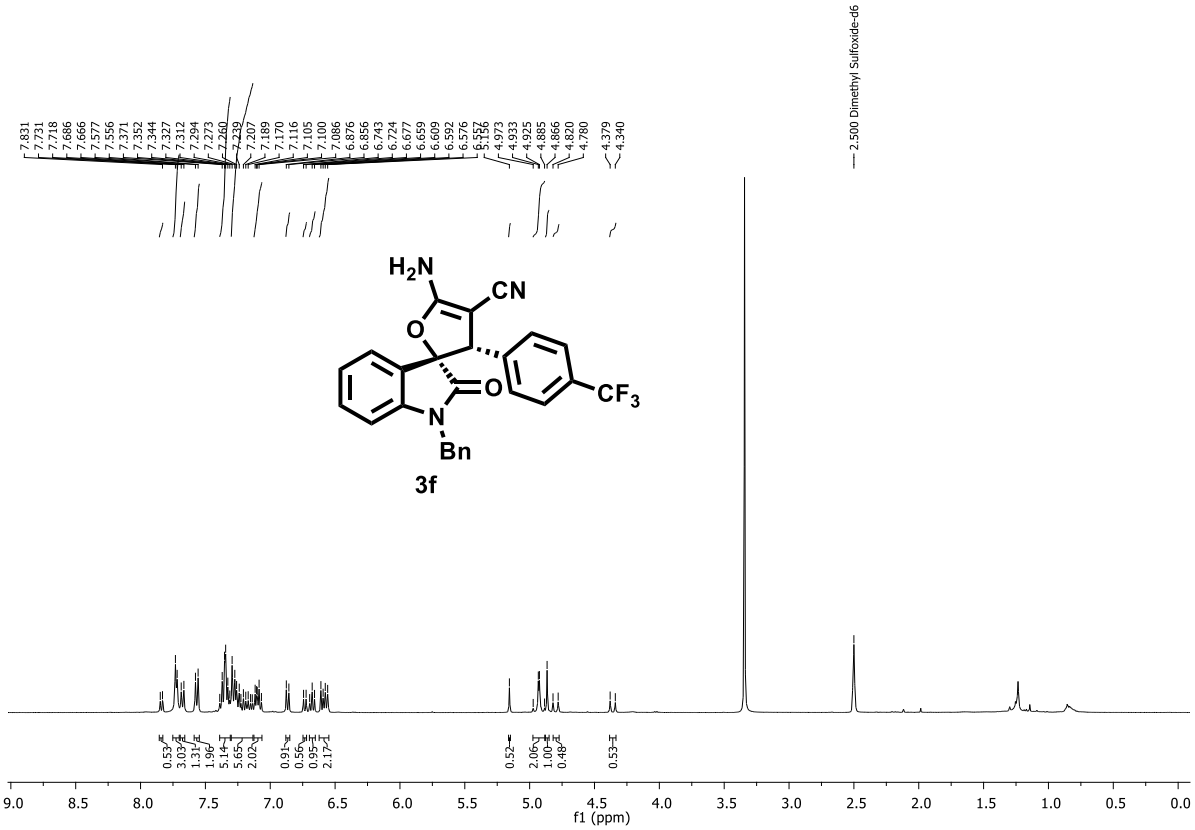
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7.666
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7.352
7.344
7.327
7.312
7.294
7.273
7.260
7.239
7.207
7.189
7.170
7.116
7.105
7.100
7.086
6.876
6.856
6.743
6.724
6.677
6.659
6.609
6.592
6.576
6.556
4.973
4.933
4.925
4.885
4.866
4.820
4.780
4.379
4.340
H2N
CN
O
O
N
Bn
CF3
3f
0.53
3.03
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1.96
5.14
5.65
2.02
0.91
0.56
0.95
2.17
0.52
2.06
1.00
0.48
0.53
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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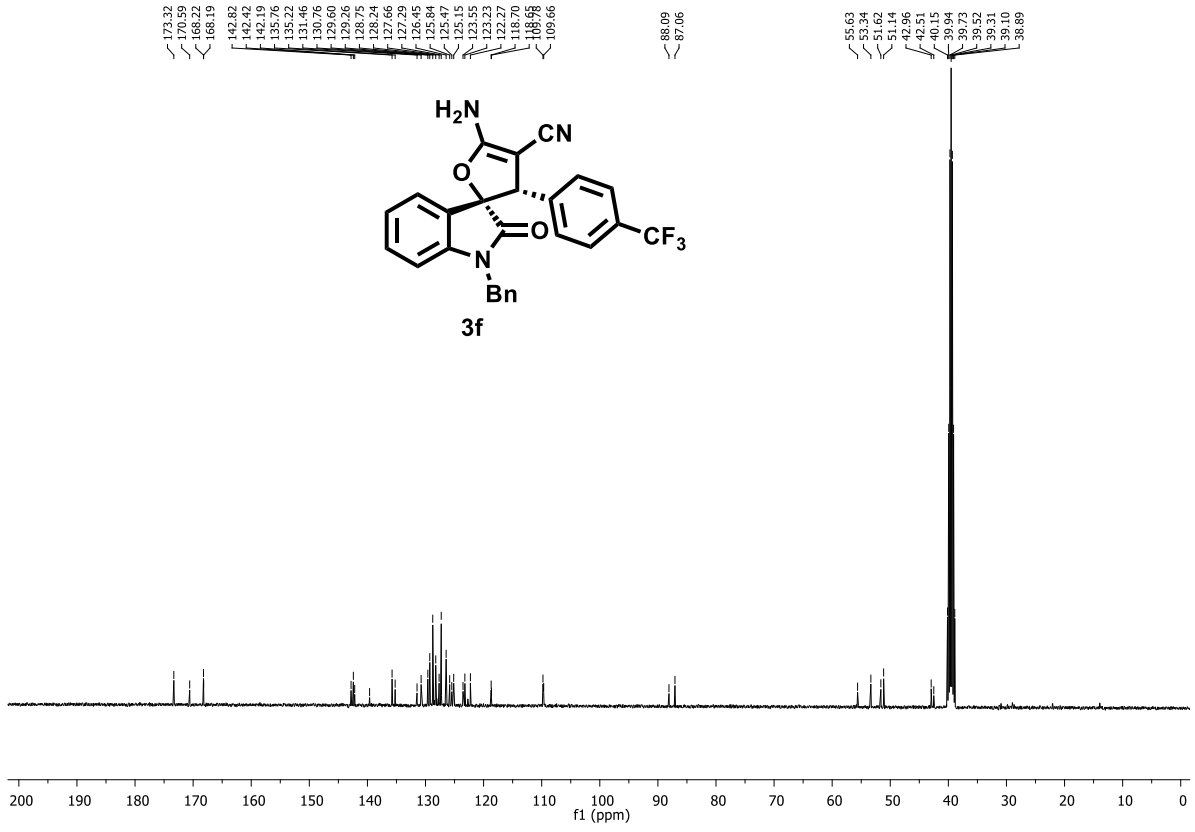
f1 (ppm)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142.19
135.76
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129.60
129.26
128.75
128.24
127.66
127.29
126.45
125.84
125.47
125.15
123.55
123.23
122.27
118.70
118.65
109.78
109.66
88.09
87.06
55.63
53.34
51.62
51.14
42.96
42.51
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
O
N
Bn
CF3
3f
200
190
180
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130
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50
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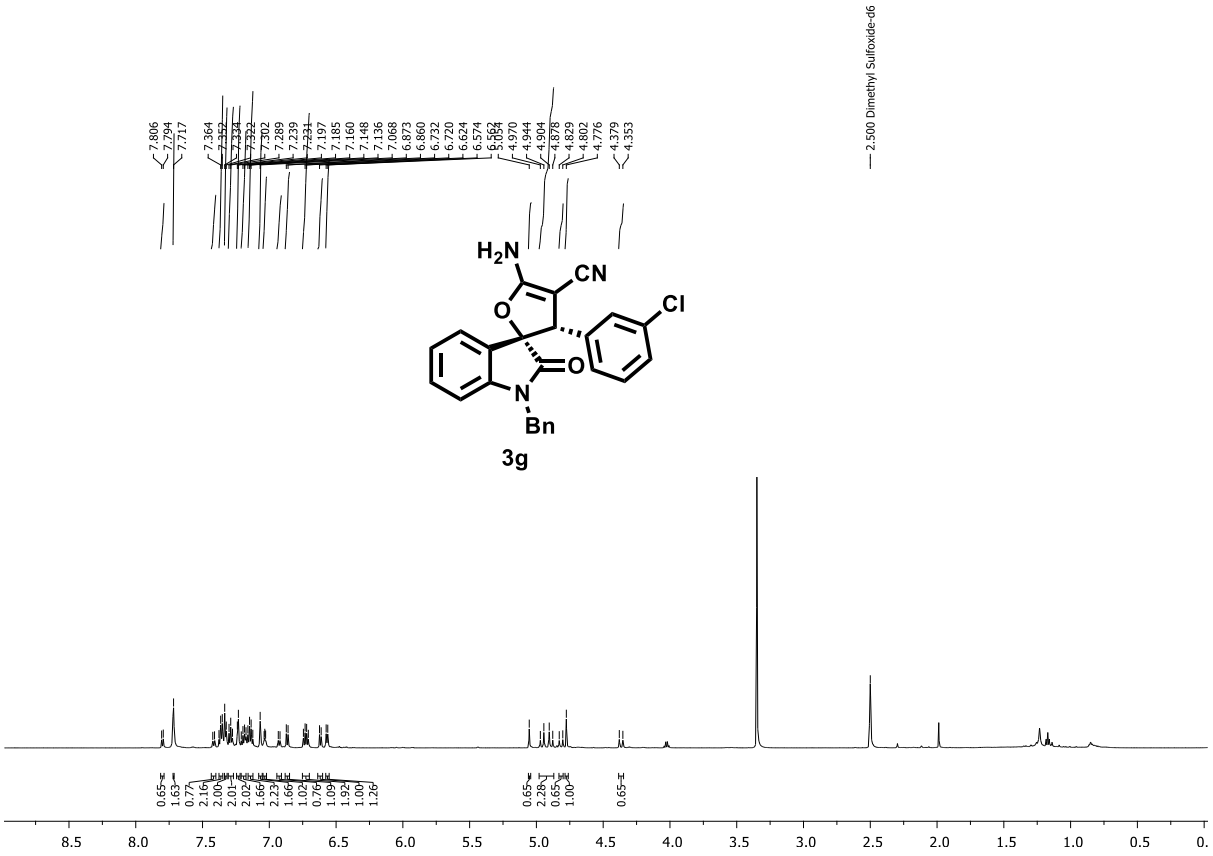
f1 (ppm)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7.231
7.197
7.185
7.160
7.148
7.136
7.068
6.873
6.860
6.732
6.720
6.624
6.574
6.562
5.054
4.970
4.944
4.904
4.878
4.829
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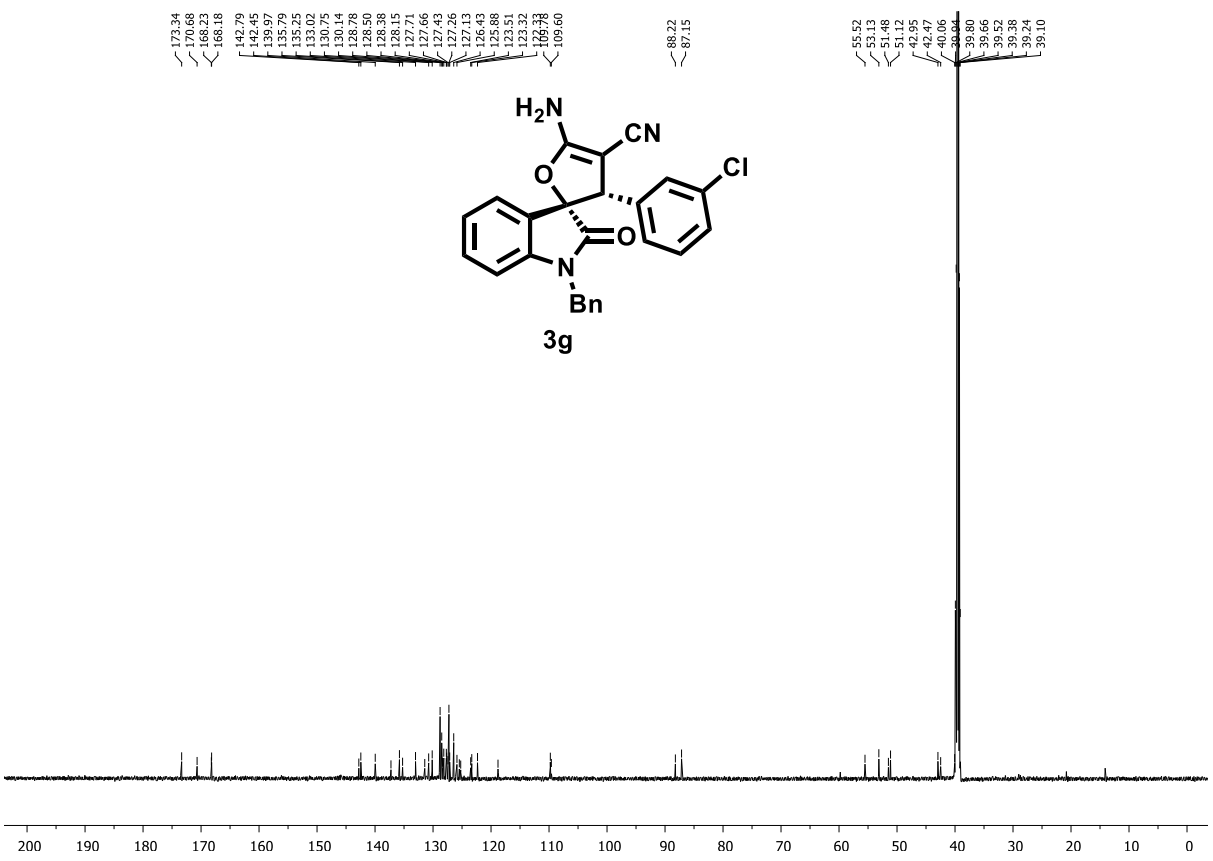
4.353
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
Cl
O
N
Bn
3g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130.14
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128.38
128.15
127.71
127.66
127.43
127.26
127.13
126.43
125.88
123.51
123.32
122.33
109.78
109.60
88.22
87.15
55.52
53.13
51.48
51.12
42.95
42.47
40.06
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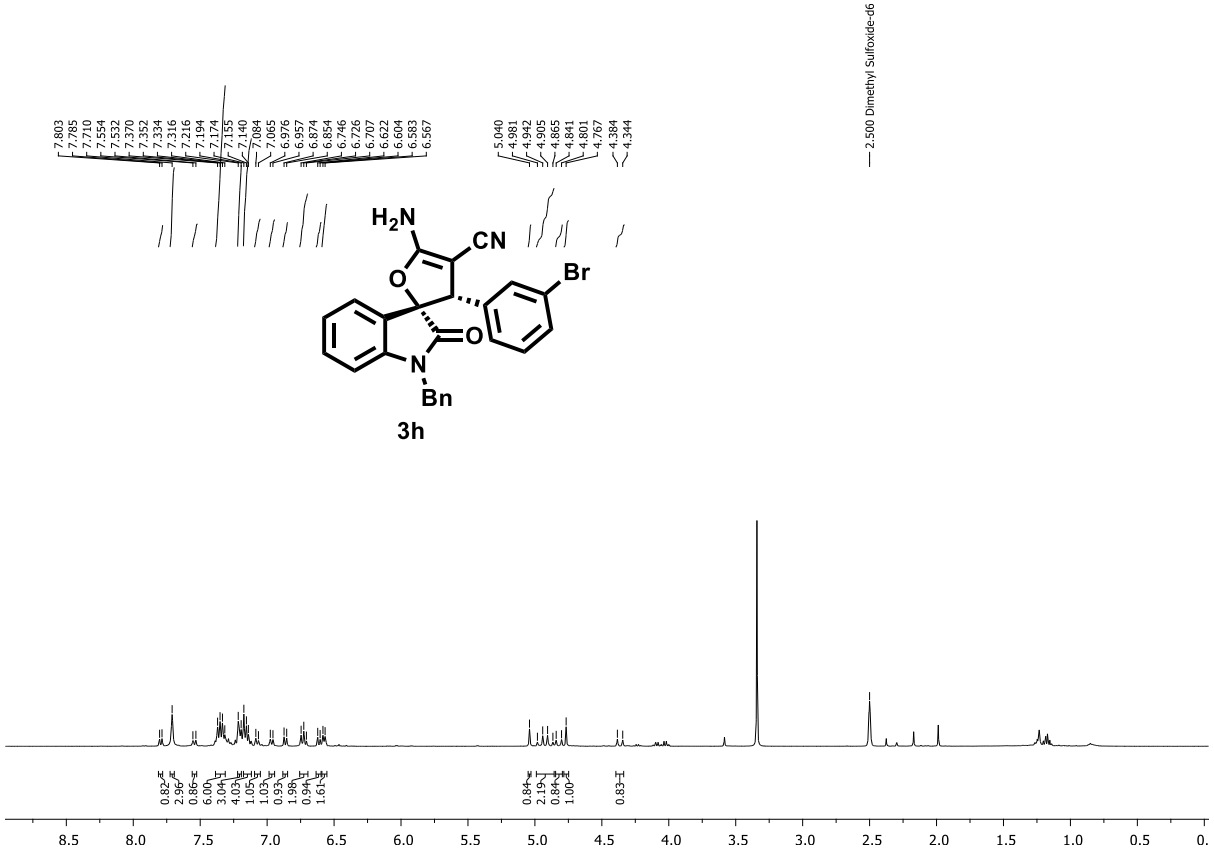
39.52
39.38
39.24
39.10
H2N
CN
O
Cl
O
N
Bn
3g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7.352
7.334
7.316
7.216
7.194
7.174
7.155
7.140
7.084
7.065
6.976
6.957
6.874
6.854
6.746
6.726
6.707
6.622
6.604
6.583
6.567
5.040
4.981
4.942
4.905
4.865
4.841
4.801
4.767
4.384
4.344
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
Br
O
N
Bn
3h
0.82
2.96
0.86
6.00
3.04
4.03
1.05
1.03
0.93
1.96
0.94
1.61
0.84
2.19
0.84
1.00
0.83
8.5
8.0
7.5
7.0
6.5
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4.5
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3.5
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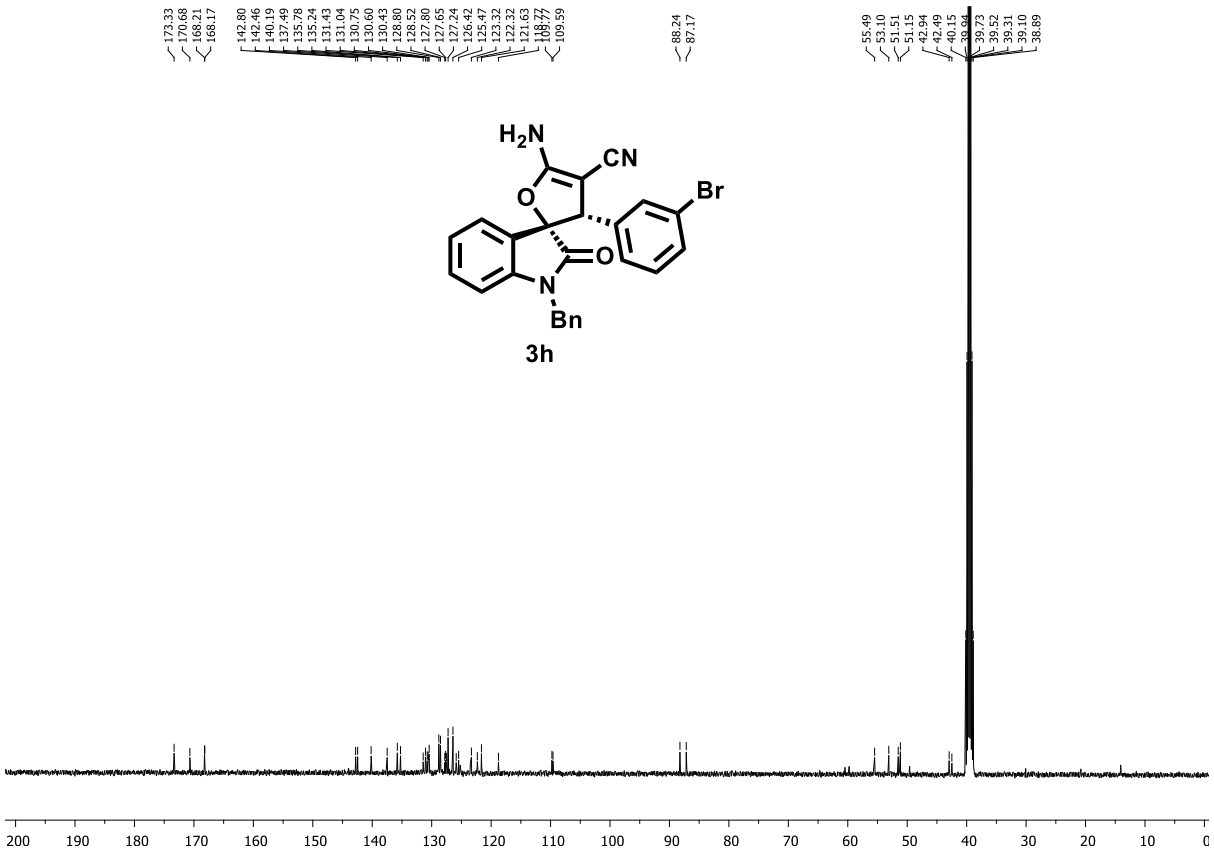
0.5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131.43
131.04
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130.43
128.80
128.52
127.80
127.65
127.24
126.42
125.47
123.32
122.32
121.63
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118.77
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88.24
87.17
55.49
53.10
51.51
51.15
42.94
42.49
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
Br
O
N
Bn
3h
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160
150
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130
120
110
100
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80
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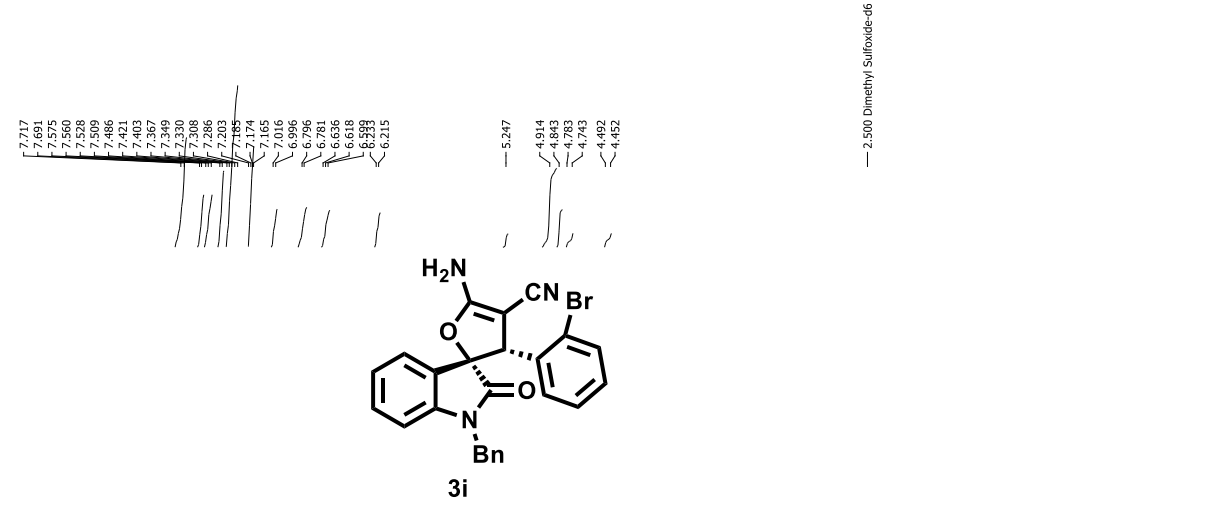
40
30
20
10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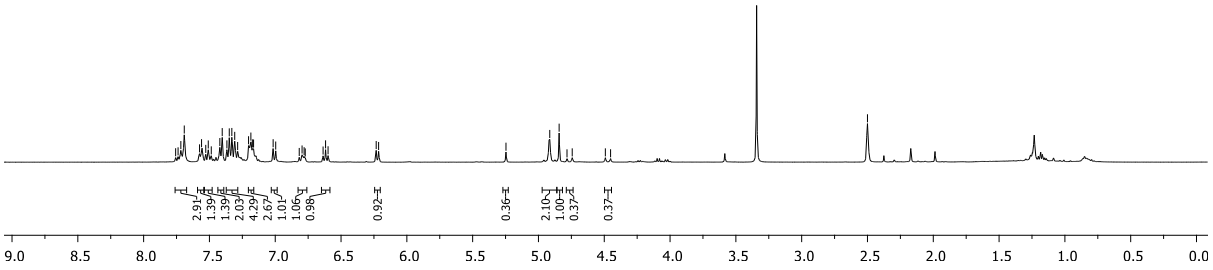
7.509
7.486
7.421
7.403
7.367
7.349
7.330
7.308
7.286
7.203
7.185
7.174
7.165
7.016
6.996
6.796
6.781
6.636
6.618
6.593
6.583
6.215
5.247
4.914
4.843
4.783
4.743
4.492
4.452
2.500 Dimethyl Sulfoxide-d6
H2N
CN
Br
O
O
N
Bn

3i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1.39
1.39
2.03
4.29
2.67
1.01
1.06
0.98
0.92
0.36
2.10
1.00
0.37
0.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
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2.0
1.5
1.0
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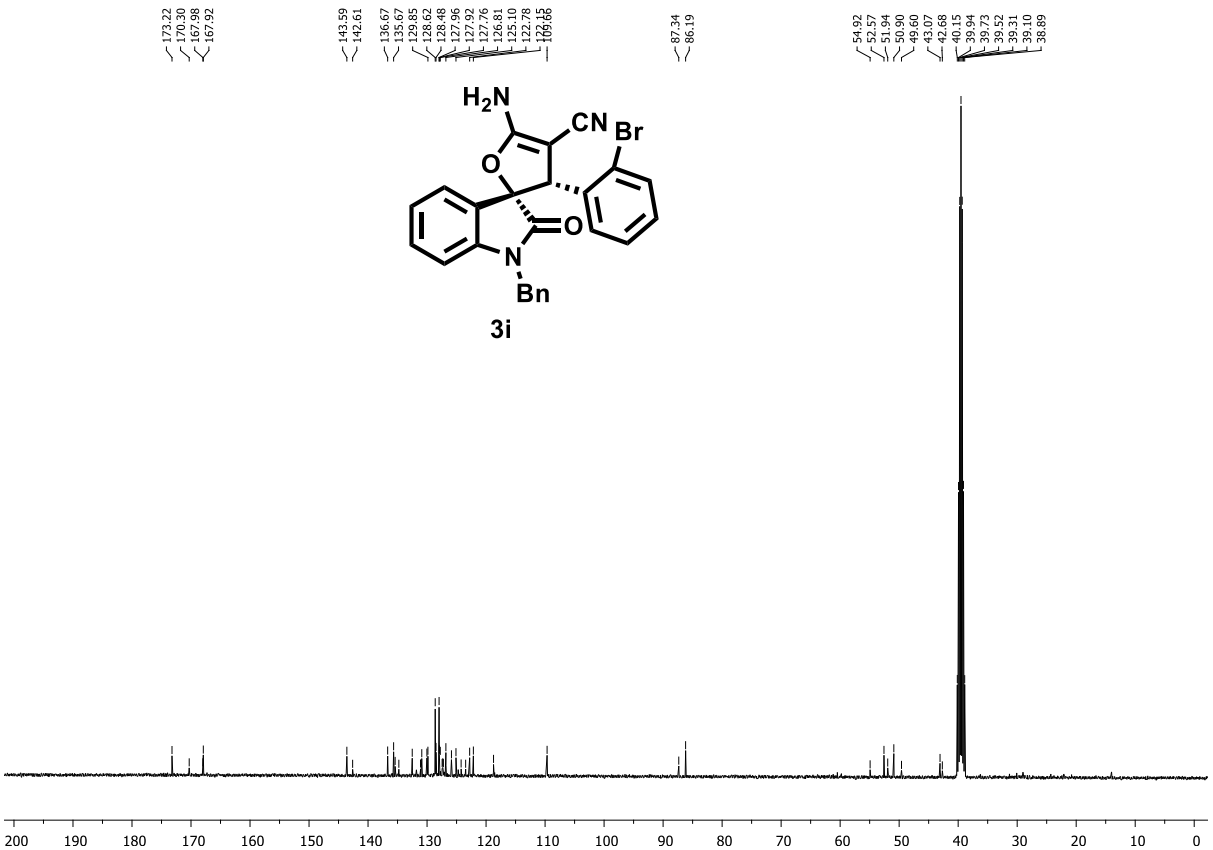
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142.61
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135.67
129.85
128.62
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127.96
127.92
127.76
126.81
125.10
122.78
122.15
109.65
87.34
86.19
54.92
52.57
51.94
50.90
49.60
43.07
42.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
Br
O
O
N
Bn
200
190
180
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140
130
120
110
100
90
80
70
60
50
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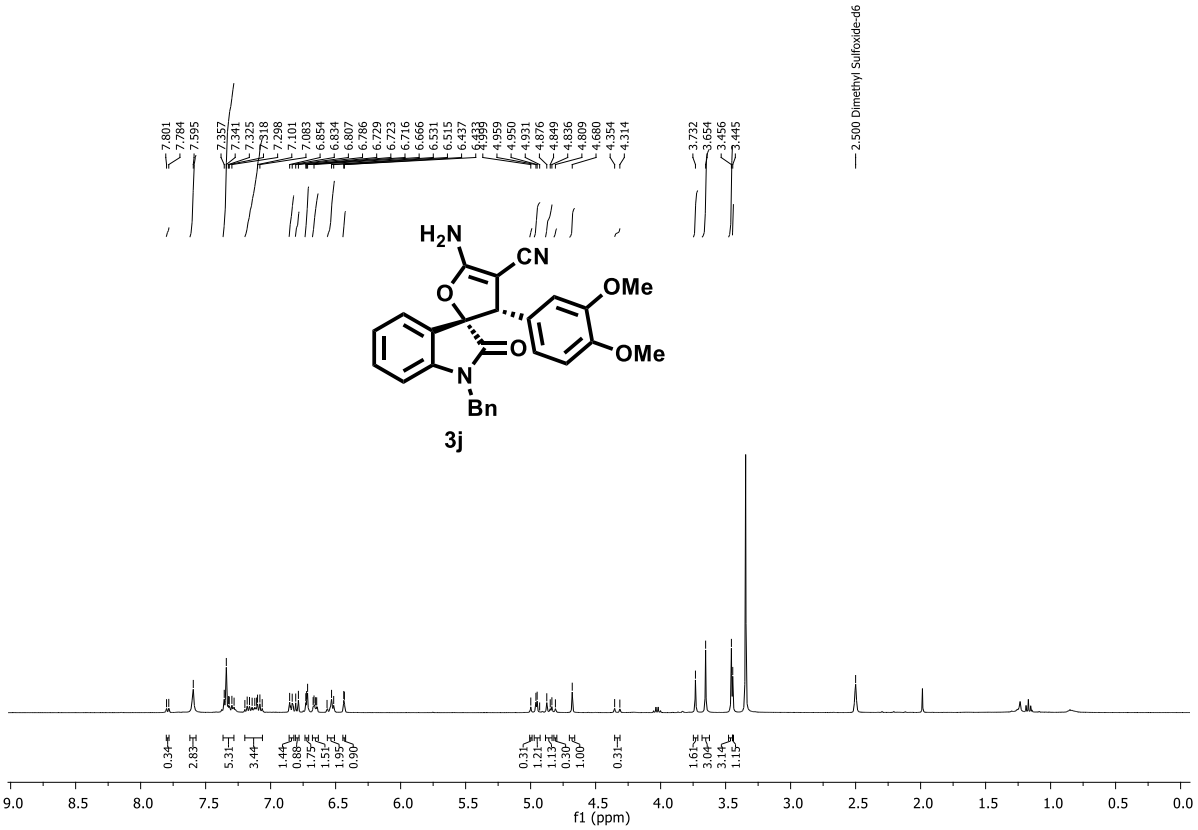
20
10
0

3i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7.595
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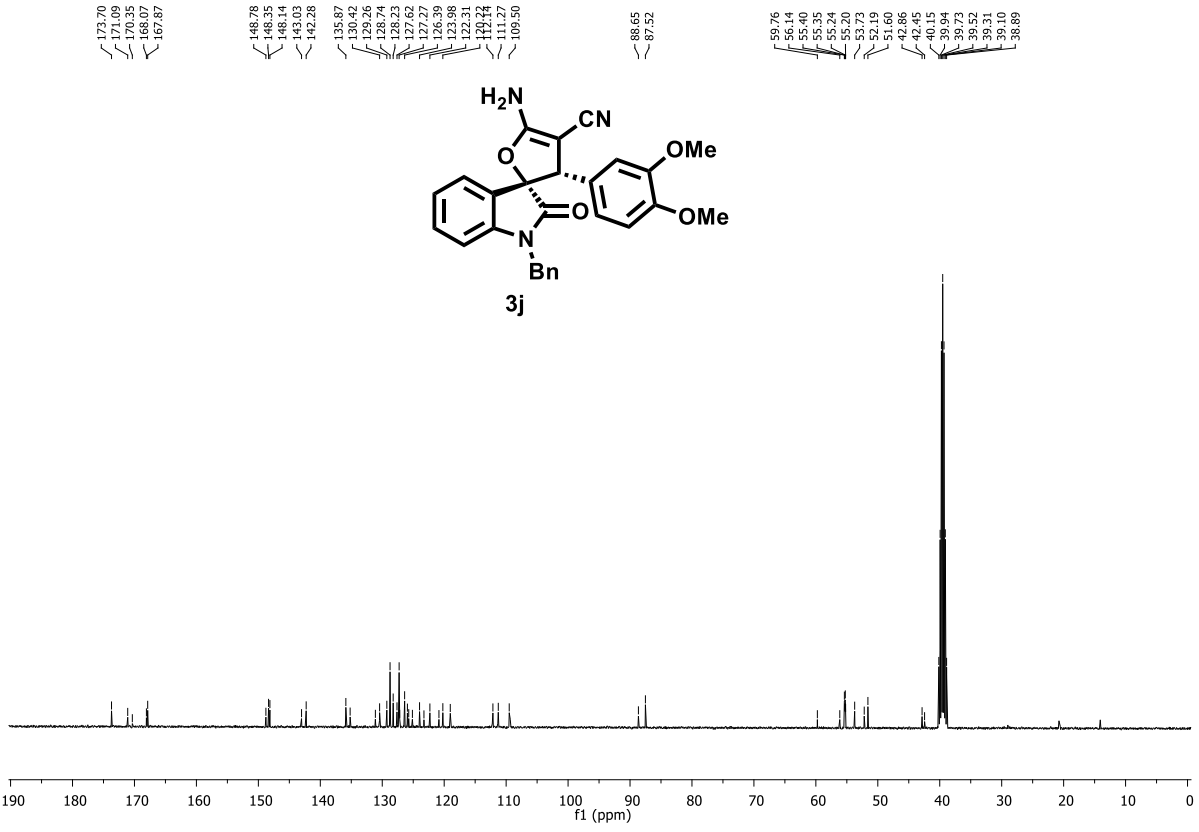
7.341
7.325
7.318
7.298
7.101
7.083
6.854
6.834
6.807
6.786
6.729
6.723
6.716
6.666
6.531
6.515
6.437
4.959
4.950
4.931
4.876
4.849
4.836
4.809
4.680
4.354
4.314
3.732
3.654
3.456
3.445
H2N
CN
O
OMe
OMe
O
N
Bn
3j
0.34
2.83
5.31
3.44
1.44
0.88
1.75
1.51
1.95
0.90
0.31
1.21
1.13
0.30
1.00
0.31
1.61
3.04
3.14
1.15
f1 (ppm)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148.78
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148.14
145.03
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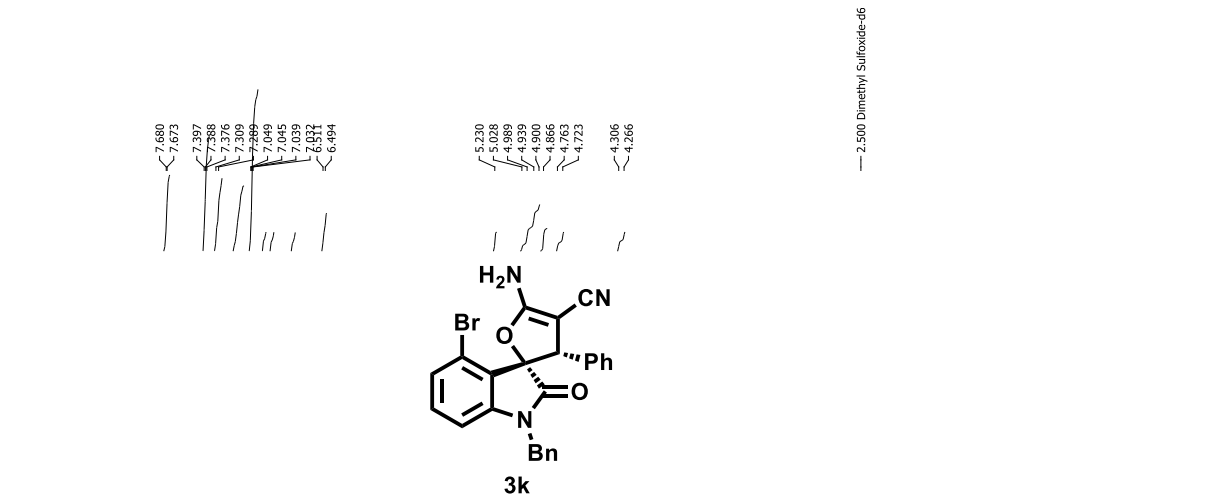
135.87
130.42
129.26
128.74
128.23
127.62
127.27
126.39
123.98
122.31
111.27
109.50
88.65
87.52
59.76
56.14
55.40
55.35
55.24
55.20
53.73
52.19
51.60
42.86
42.45
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
OMe
OMe
O
N
Bn
3j
f1 (ppm)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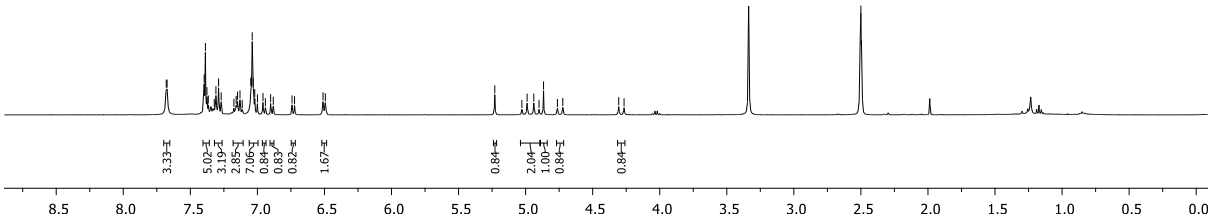
7.039
7.032
6.511
6.494
5.230
5.028
4.989
4.939
4.900
4.866
4.763
4.723
4.306
4.266
2.500 Dimethyl Sulfoxide-d6
H2N
CN
Br
O
Ph
O
N
Bn
3k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3.19
2.85
7.06
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0.83
0.82
1.67
0.84
2.04
1.00
0.84
0.84
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
1.5
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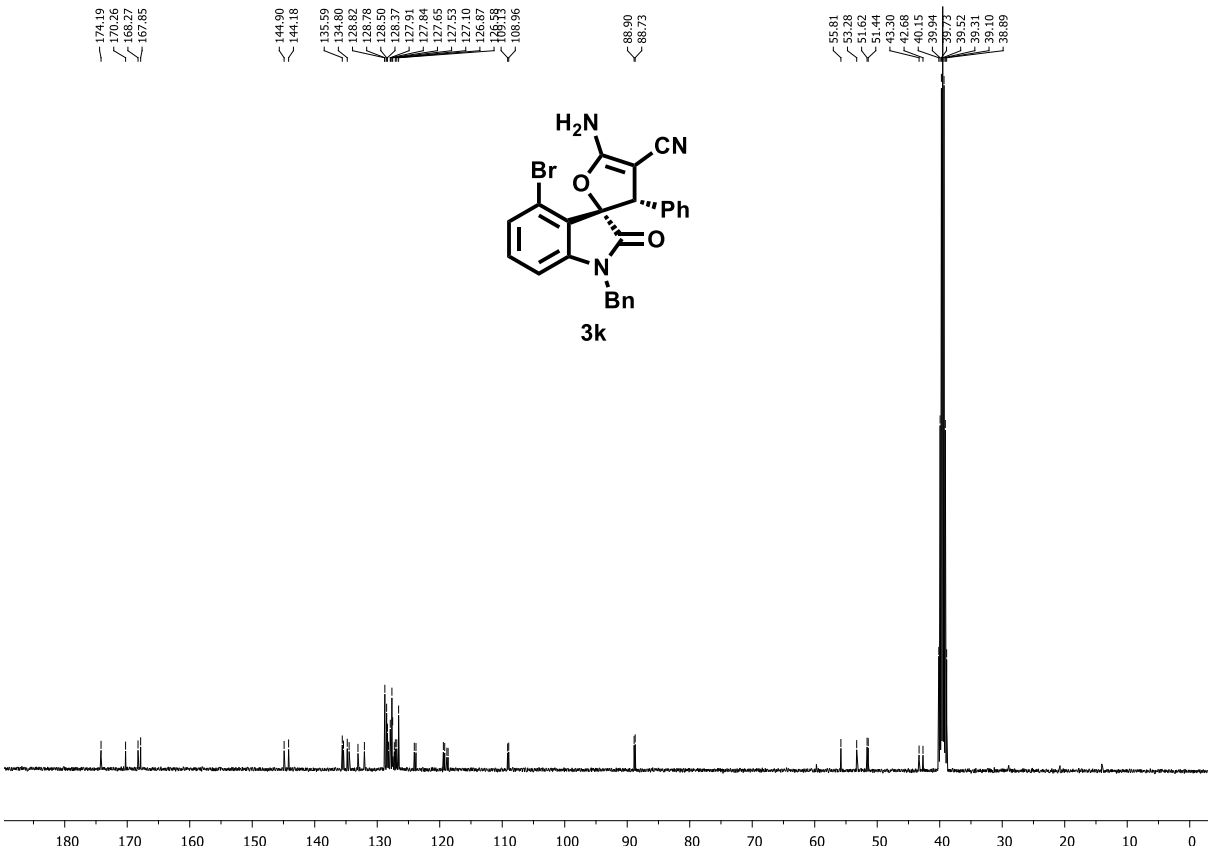
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109.13
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88.90
88.73
55.81
53.28
51.62
51.44
43.30
42.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
Br
O
Ph
O
N
Bn
3k
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150
140
130
120
110
100
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70
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50
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30
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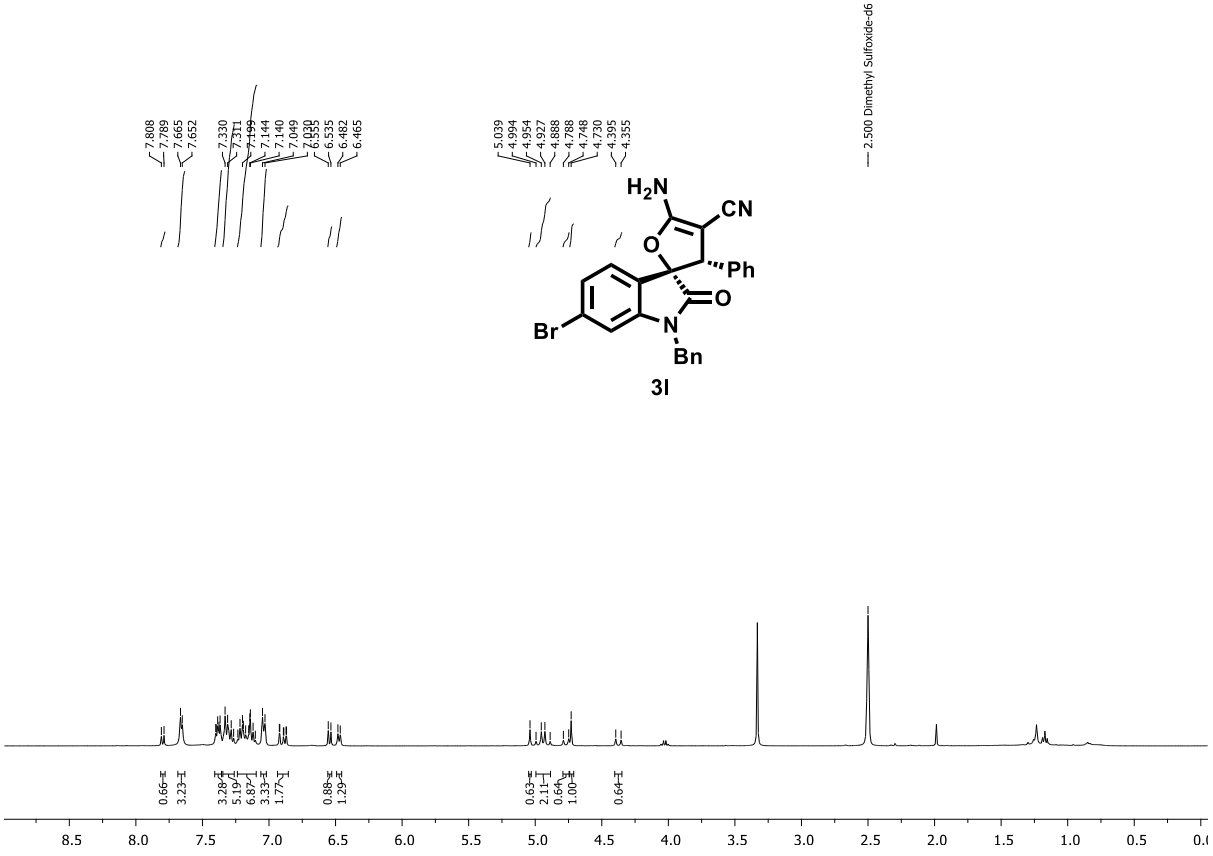
10
0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7.652
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7.311
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7.144
7.140
7.049
6.535
6.482
6.465
5.039
4.994
4.954
4.927
4.888
4.788
4.748
4.730
4.395
4.355
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
Ph
O
Br
N
Bn
0.66
3.23
3.28
5.19
6.87
3.33
1.77
0.88
1.29
0.63
2.11
0.64
1.00
0.64
8.5
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7.5
7.0
6.5
6.0
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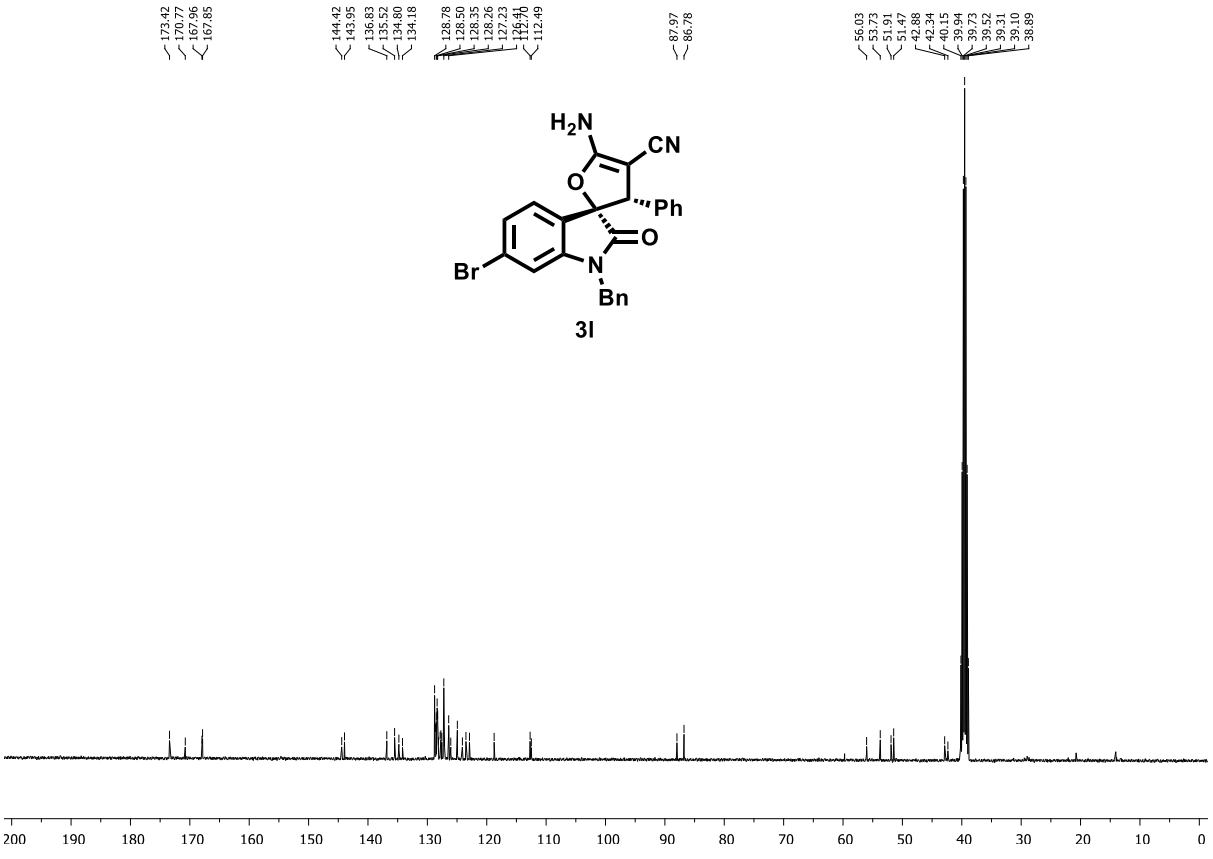
2.0
1.5
1.0
0.5

3l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86.78
56.03
53.73
51.91
51.47
42.88
42.34
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
Ph
O
Br
N
Bn
200
190
180
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120
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100
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80
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50
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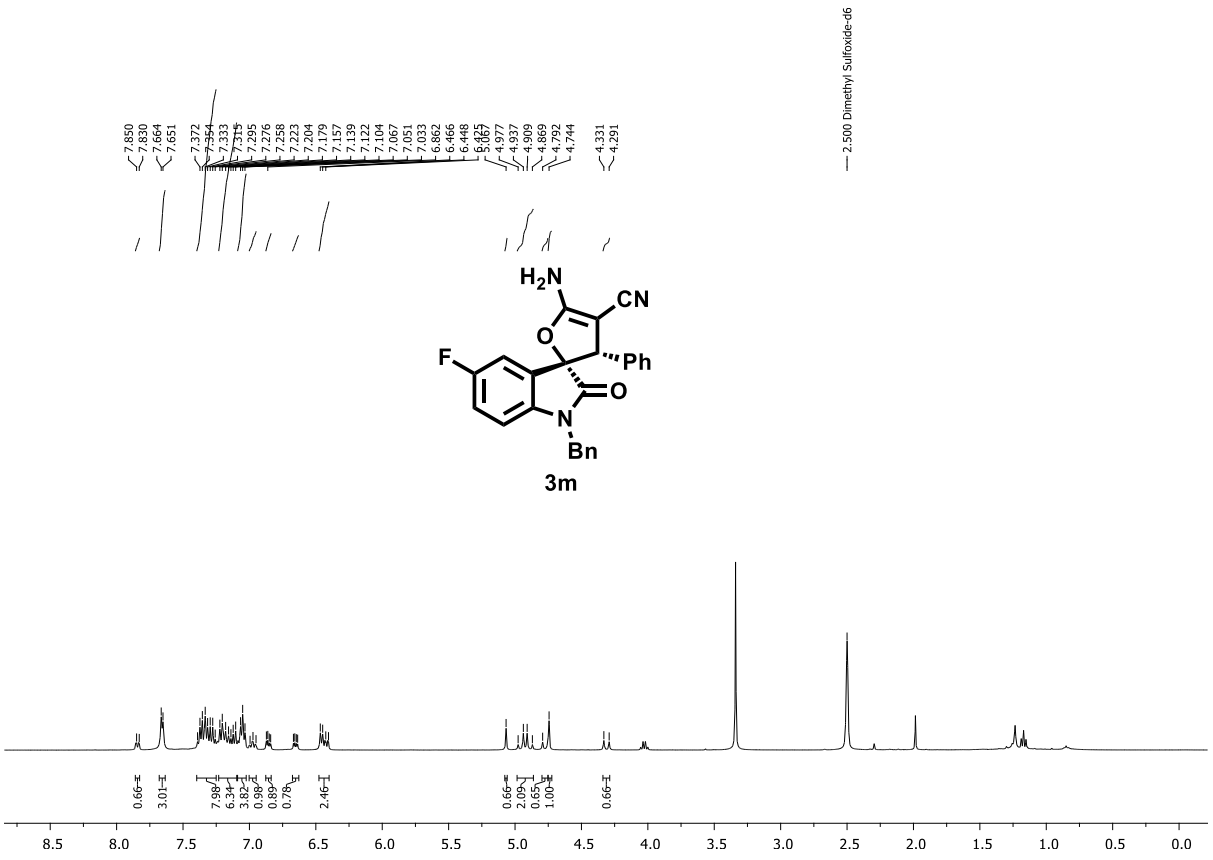
0

3l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7.315
7.295
7.276
7.258
7.223
7.204
7.179
7.157
7.139
7.122
7.104
7.067
7.051
7.033
6.862
6.466
6.448
6.425
5.067
4.977
4.937
4.909
4.869
4.792
4.744
4.331
4.291
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
F
Ph
O
N
Bn
3m
0.66
3.01
7.98
6.34
3.82
0.98
0.89
0.78
2.46
0.66
2.09
0.65
1.00
0.66
8.5
8.0
7.5
7.0
6.5
6.0
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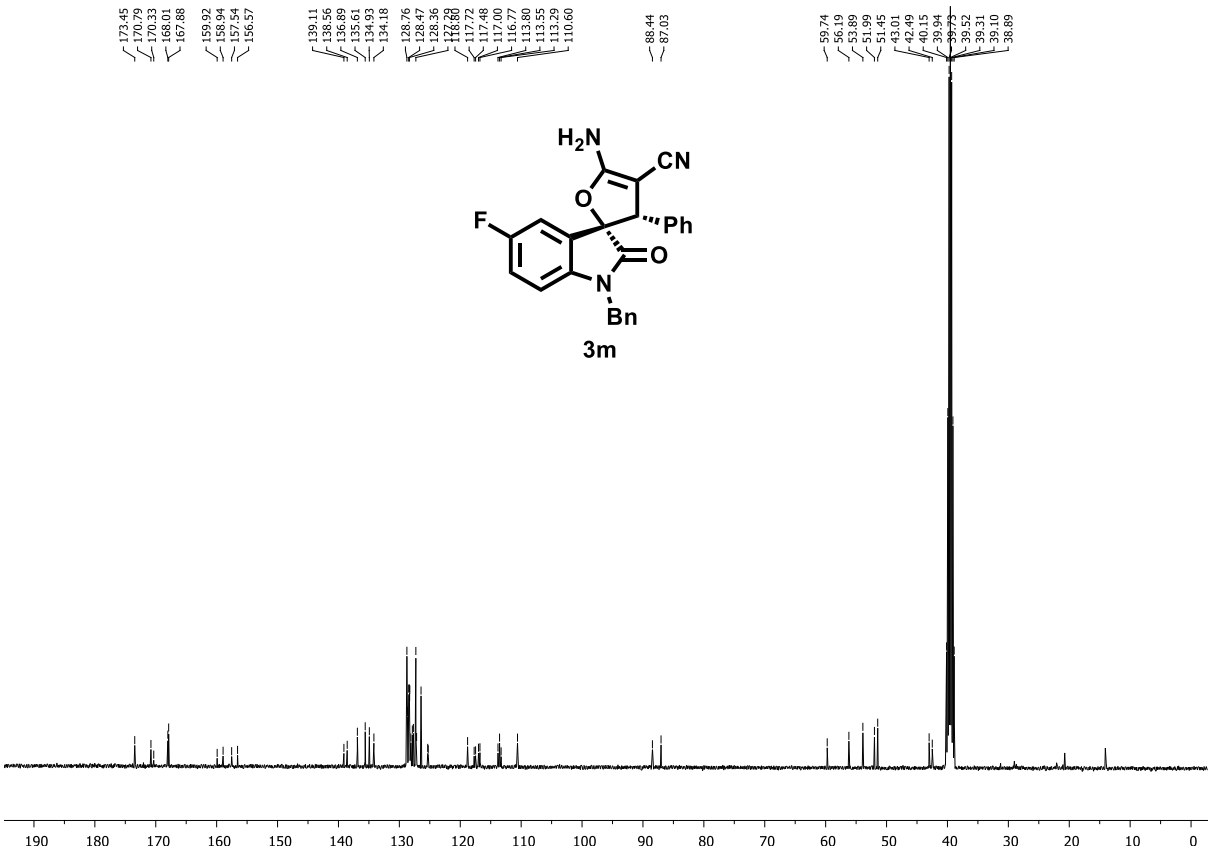
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136.89
135.61
134.93
134.18
128.76
128.47
128.36
117.72
117.48
117.00
116.77
113.80
113.55
113.29
110.60
88.44
87.03
59.74
56.19
53.89
51.99
51.45
43.01
42.49
40.15
39.94
39.73
39.52
39.31
39.10
38.89
H2N
CN
O
F
Ph
O
N
Bn
3m
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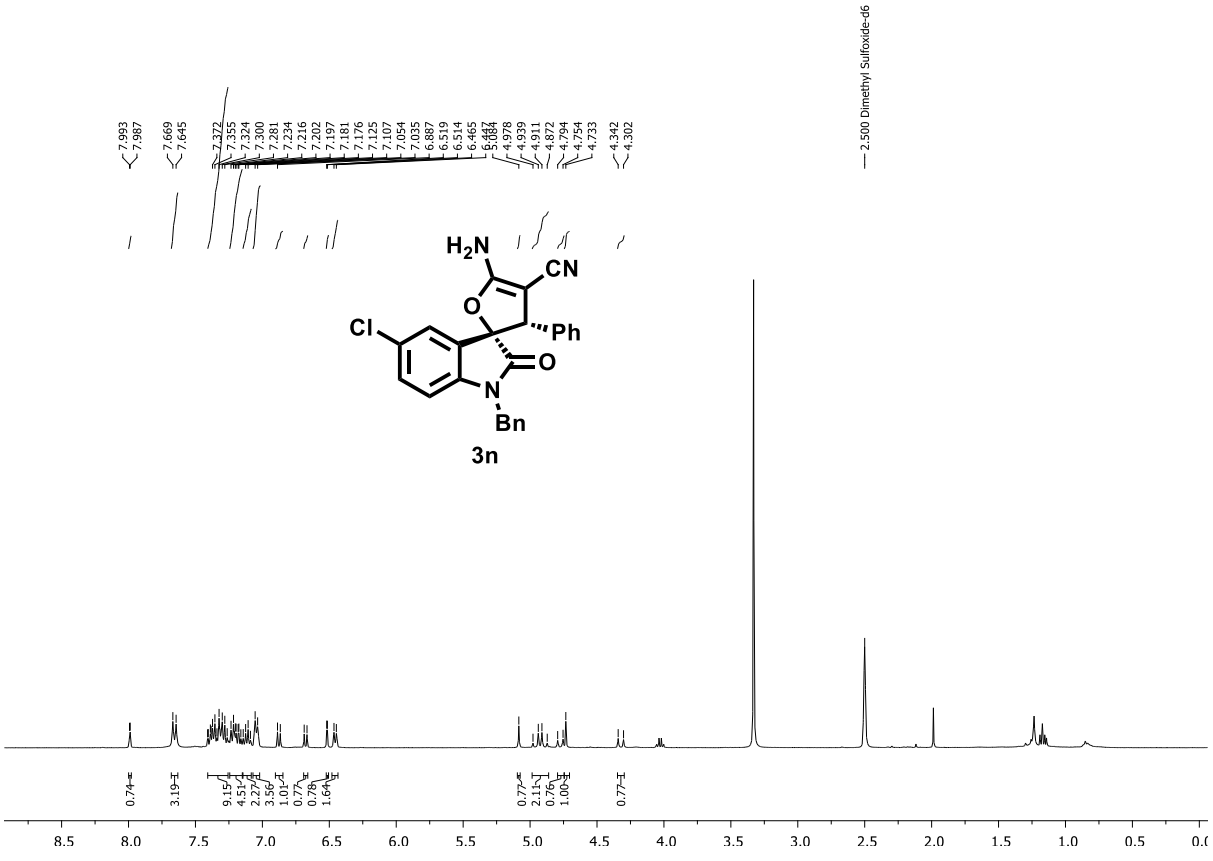
10
0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7.372
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7.324
7.300
7.281
7.234
7.216
7.202
7.197
7.181
7.176
7.125
7.107
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7.035
6.887
6.519
6.514
6.465
4.978
4.939
4.911
4.872
4.794
4.754
4.733
4.342
4.302
0.74
3.19
9.15
4.51
2.27
3.56
1.01
0.77
0.78
1.64
0.77
2.11
0.76
1.00
0.77
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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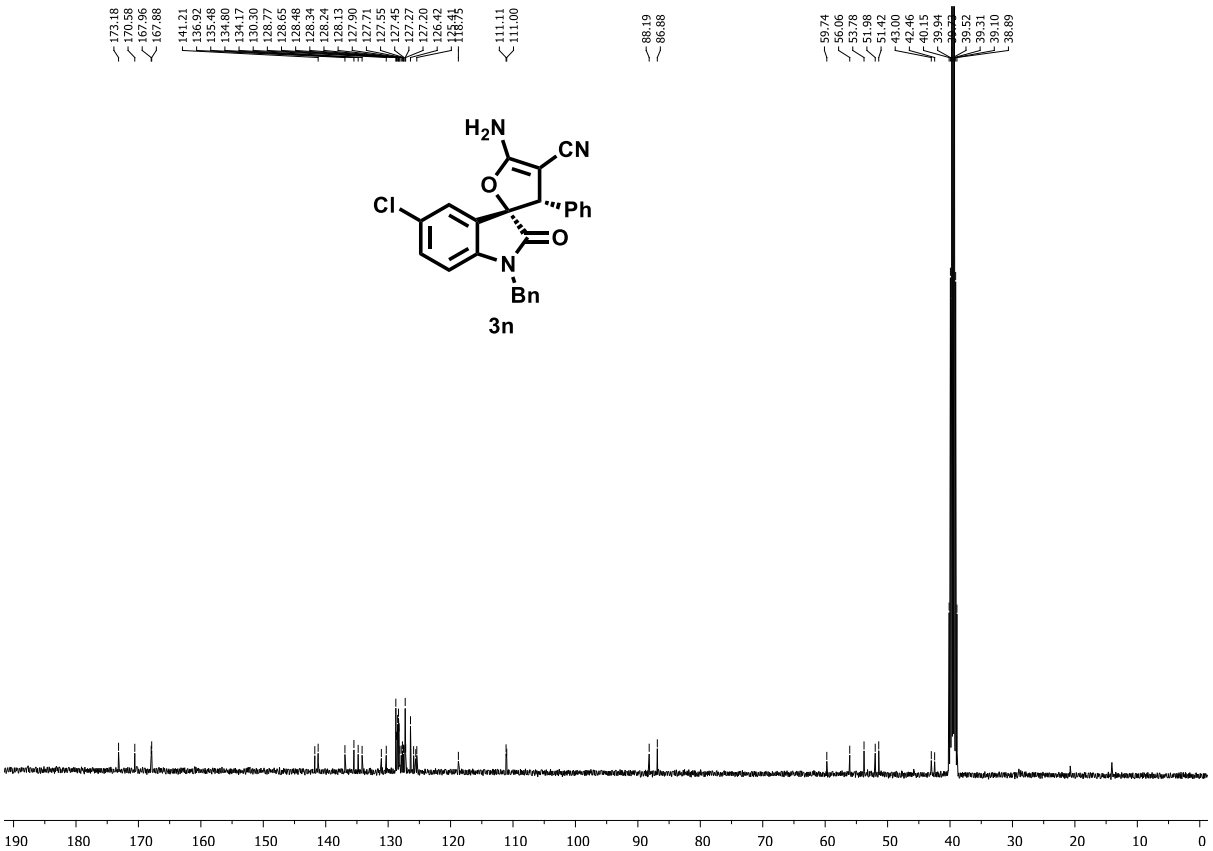
1.5
1.0
0.5
H2N
CN
O
Cl
Ph
O
N
Bn
3n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170.58
167.96
167.88
141.21
136.92
135.48
134.80
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128.65
128.48
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125.41
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38.89
190
180
170
160
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120
110
100
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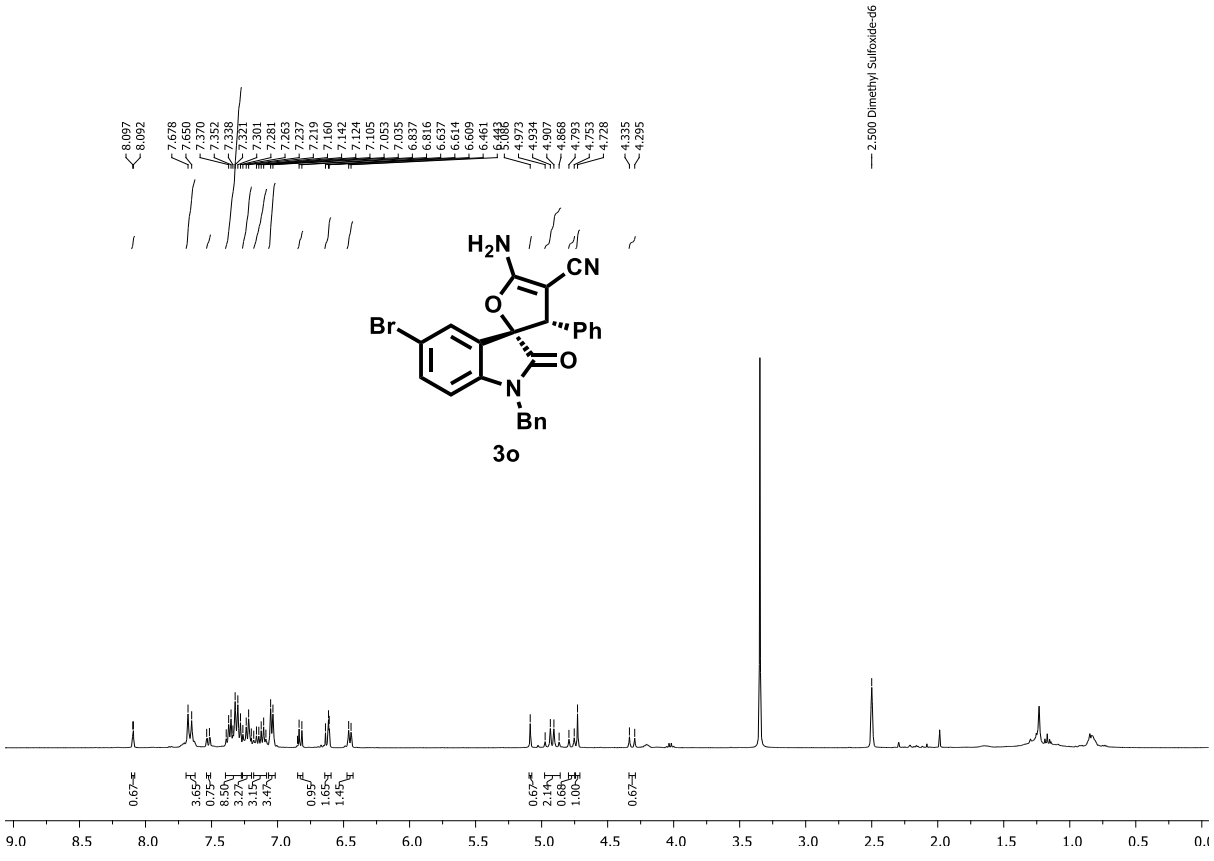
CN
O
Cl
Ph
O
N
Bn
3n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6.461
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CN
O
Br
Ph
O
N
Bn
3o
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0.75
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1.45
0.67
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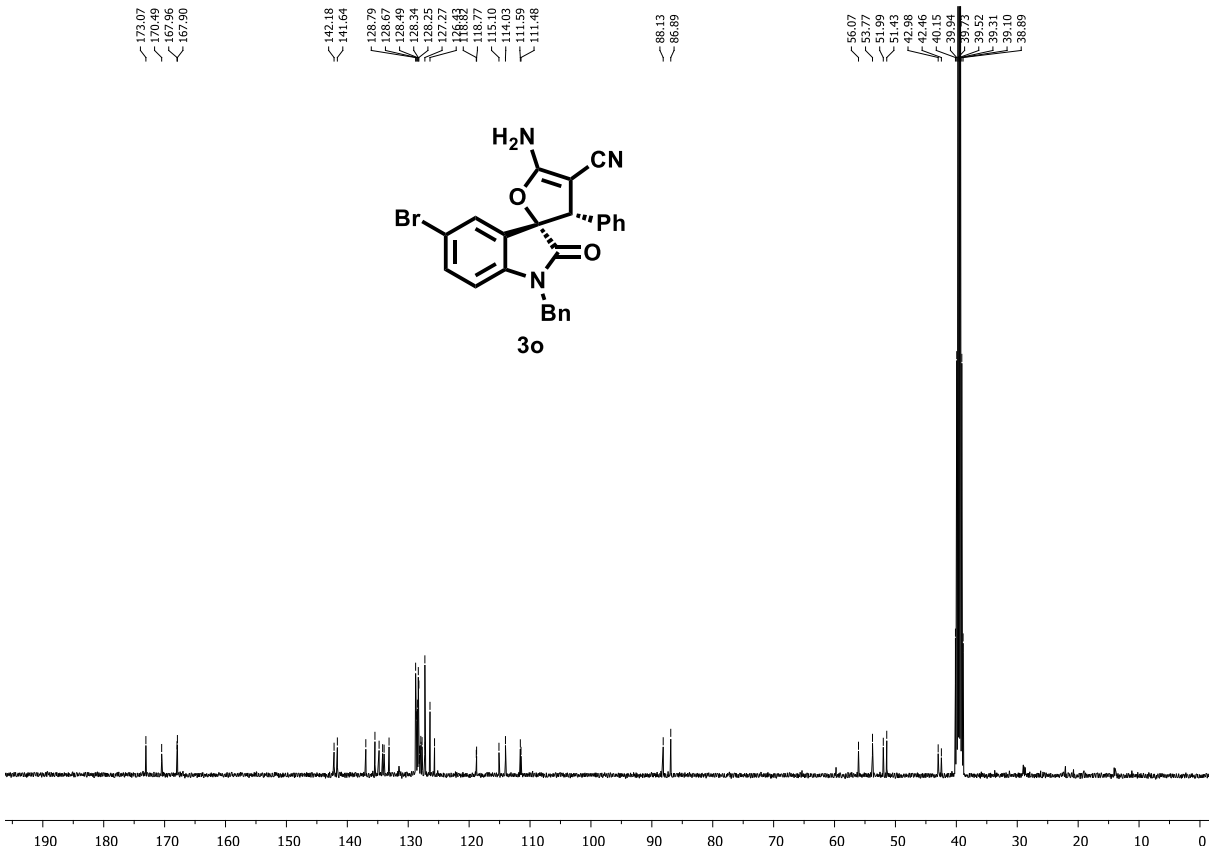
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114.03
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111.48
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86.89
56.07
53.77
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39.31
39.10
38.89
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CN
O
Br
Ph
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N
Bn
3o
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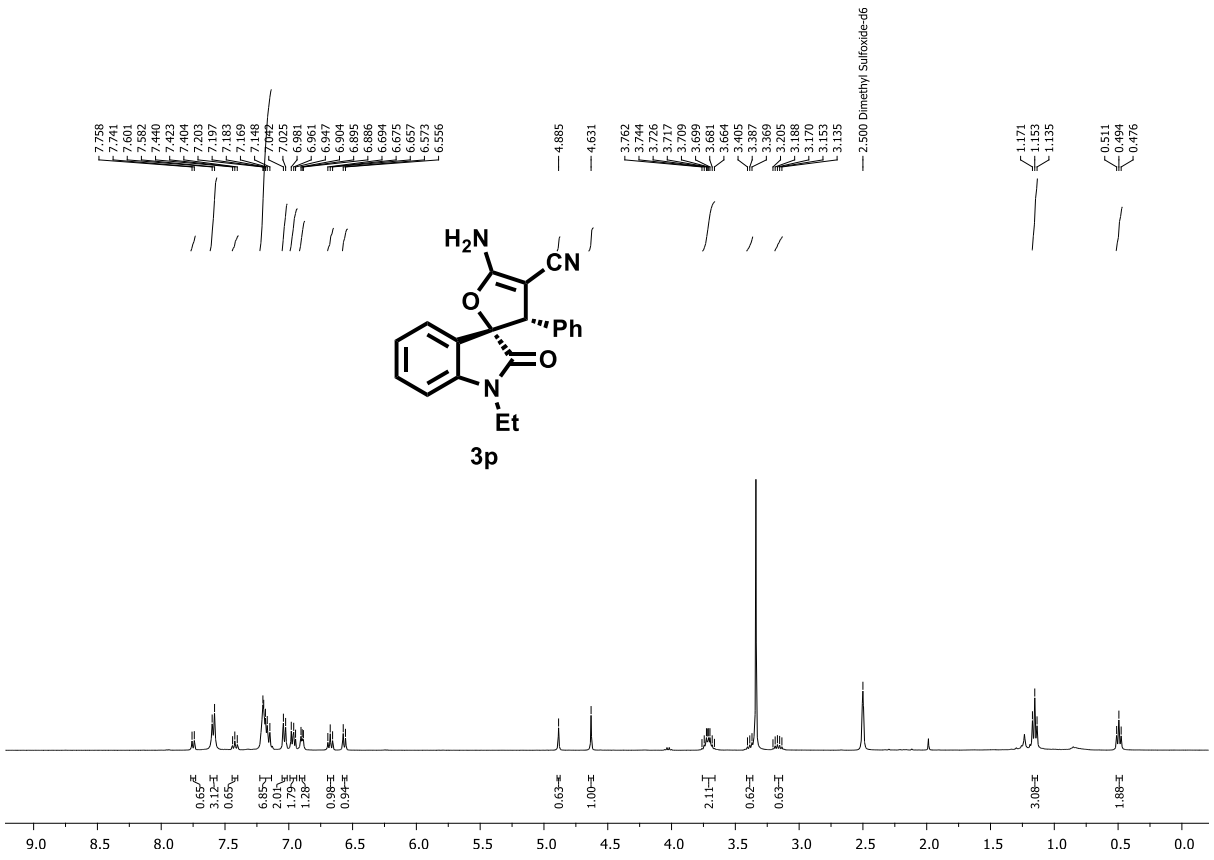
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7.025
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6.895
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6.573
6.556
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3.709
3.699
3.681
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3.405
3.387
3.369
3.205
3.188
3.170
3.153
3.135
2.500 Dimethyl Sulfoxide-d6
1.171
1.153
1.135
0.511
0.494
0.476
H2N
CN
O
Ph
O
N
Et
0.65
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0.65
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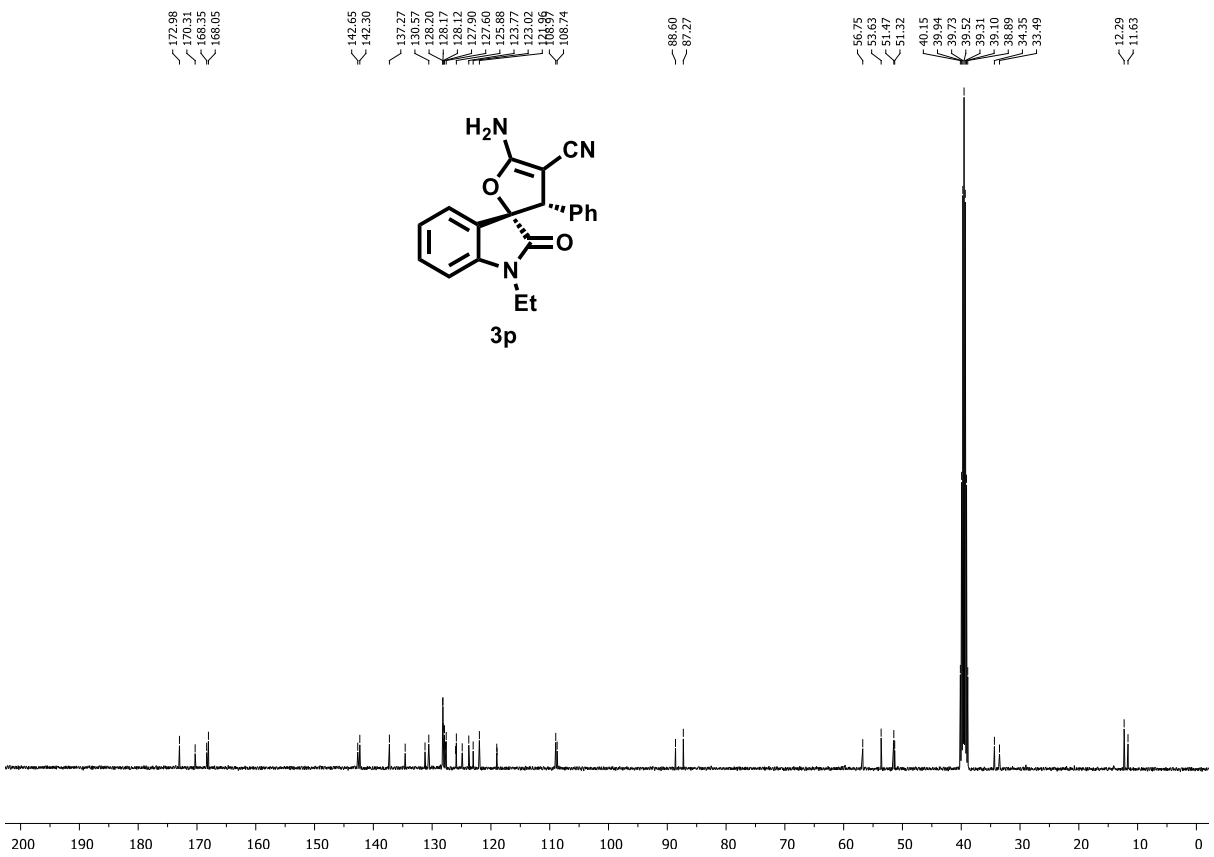
3p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127.60
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123.77
123.02
108.99
108.74
88.60
87.27
56.75
53.63
51.47
51.32
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.35
33.49
12.29
11.63
H2N
CN
O
Ph
O
N
Et
200
190
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100
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20
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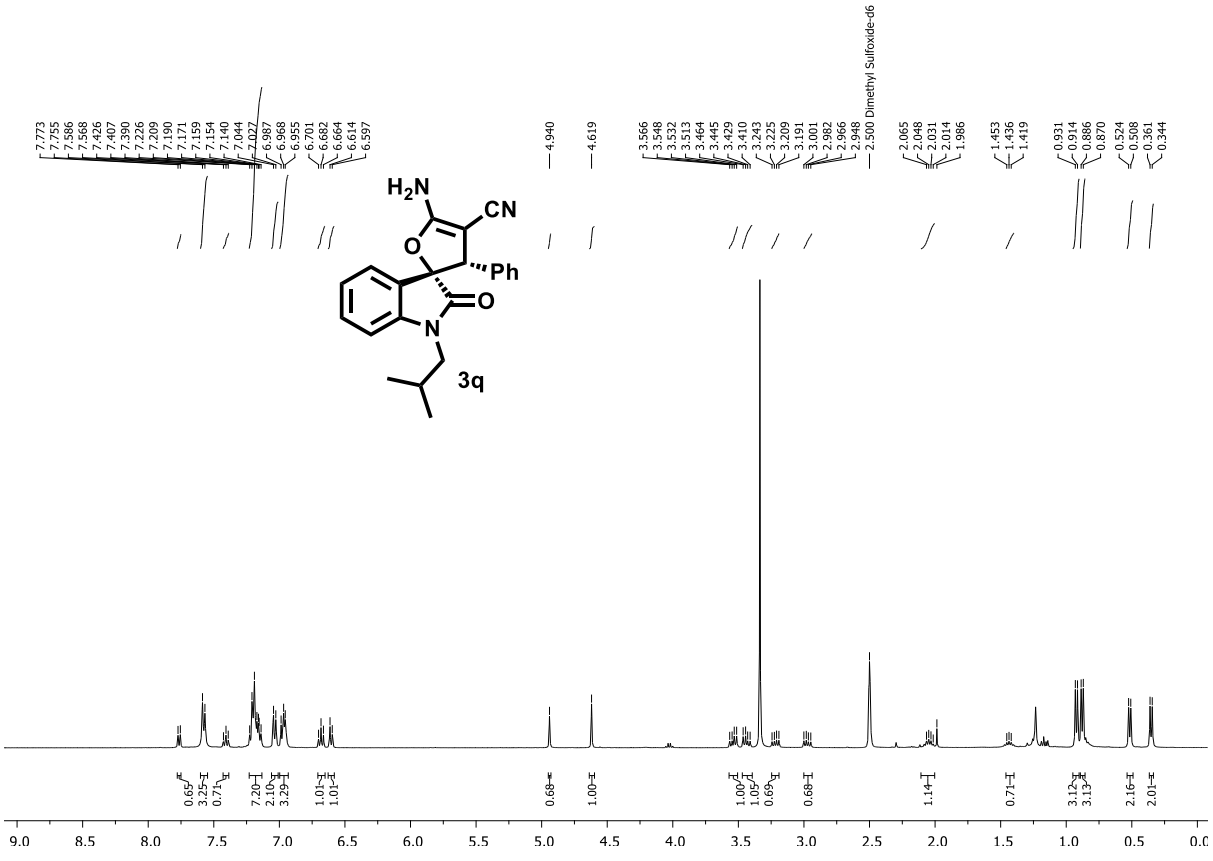
0

3p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6.597
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4.619
3.566
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3.513
3.464
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3.243
3.225
3.209
3.191
3.001
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2.500 Dimethyl Sulfoxide-d6
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2.048
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2.014
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1.436
1.419
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0.886
0.870
0.524
0.508
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0.344
H2N
CN
O
Ph
O
N
3q
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3.25
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3.29
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1.01
0.68
1.00
1.00
1.05
0.69
0.68
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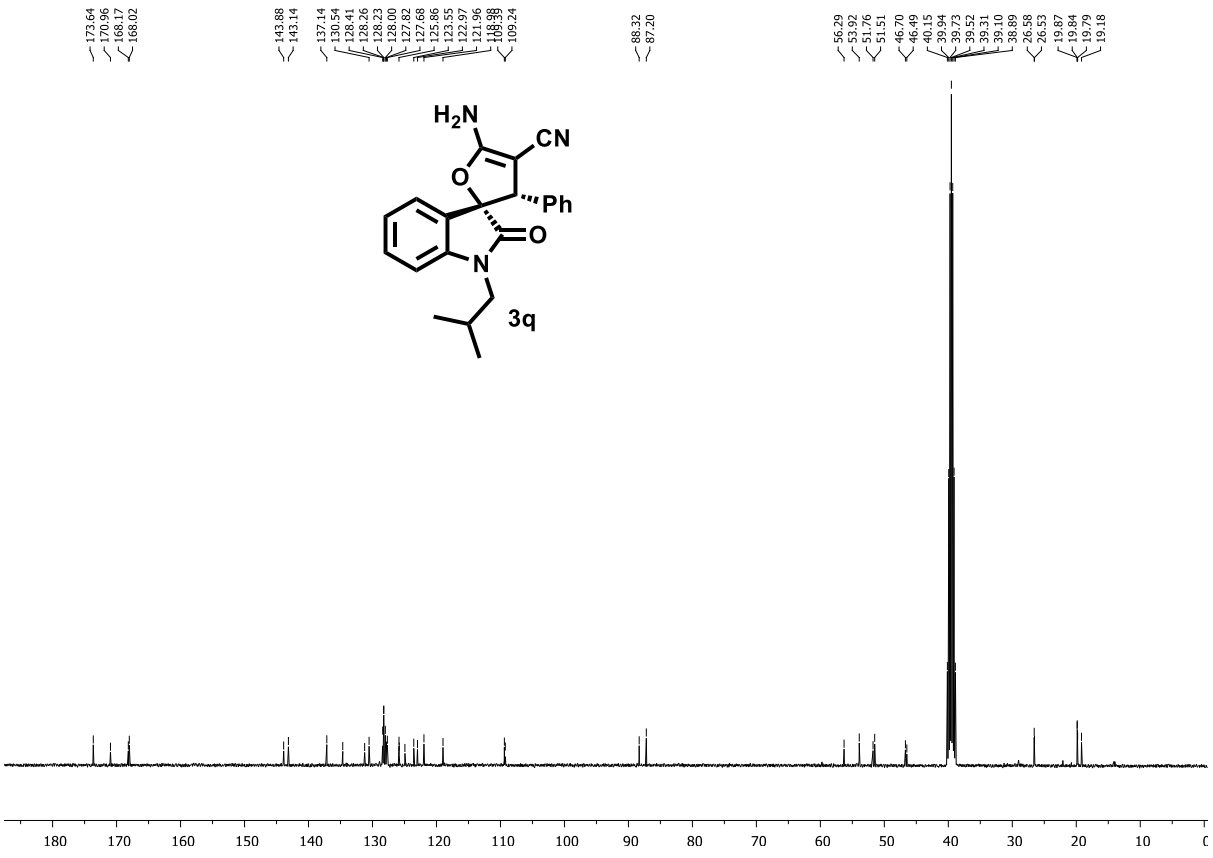
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121.96
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39.31
39.10
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19.84
19.79
19.18
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CN
O
Ph
O
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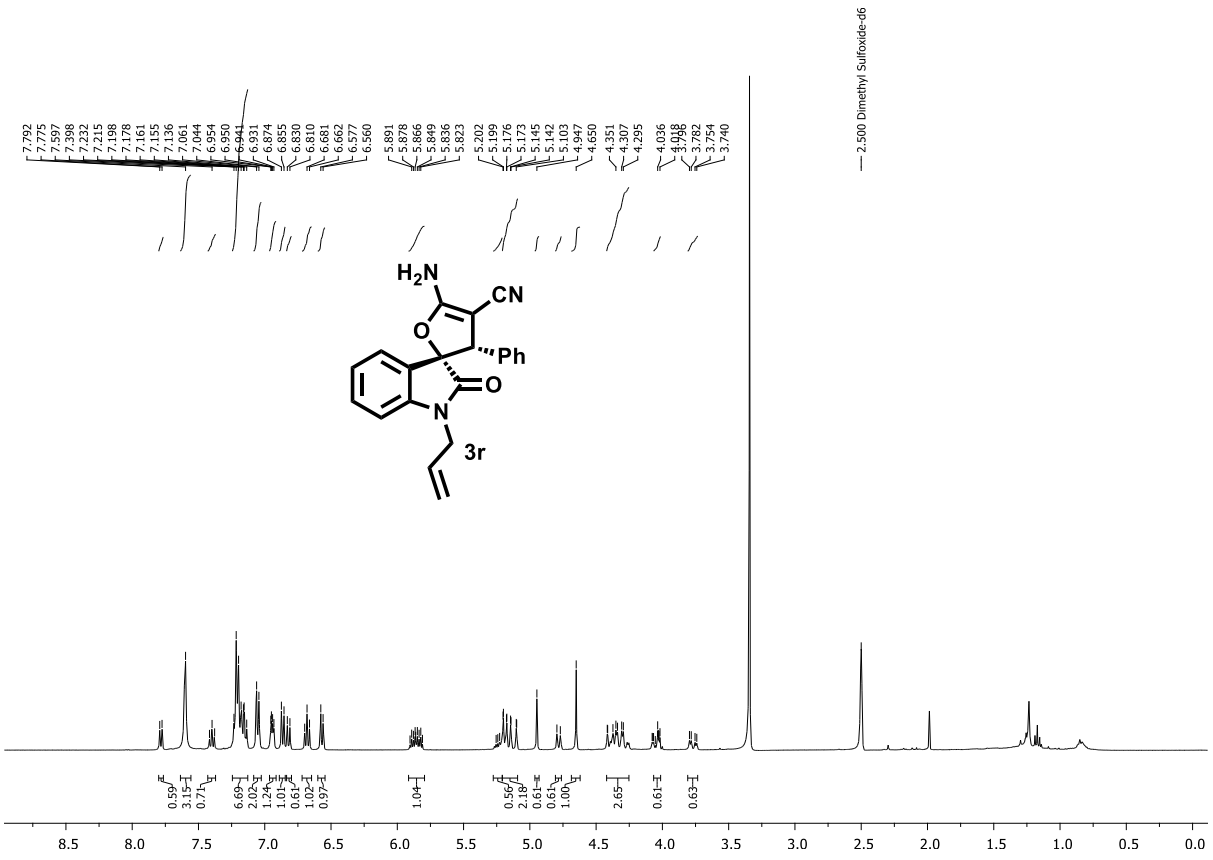
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4.351
4.307
4.295
4.036
4.018
3.998
3.782
3.754
3.740
2.500 Dimethyl Sulfoxide-d6
H2N
CN
O
Ph
O
N
3r
0.59
3.15
0.71
6.69
2.02
1.24
1.01
0.61
1.02
0.97
1.04
0.56
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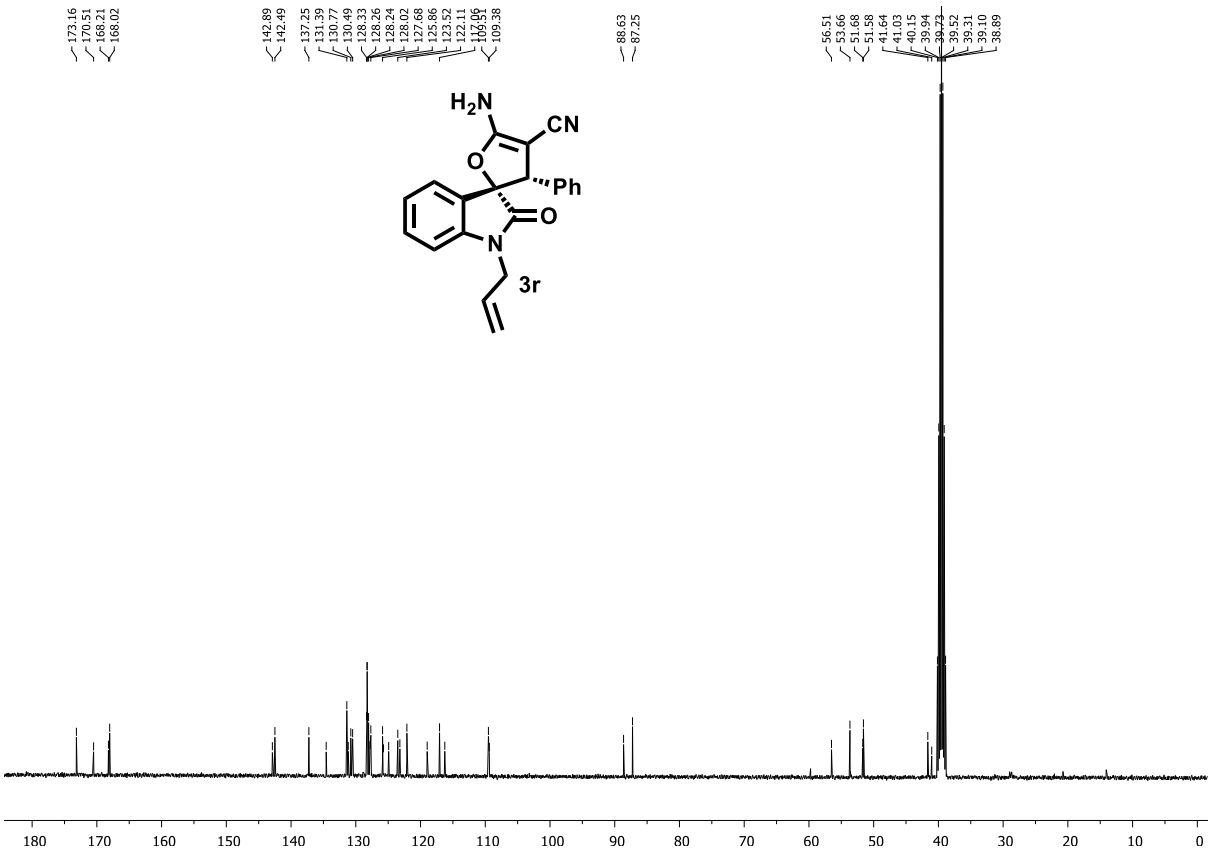
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128.24
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127.68
125.86
123.52
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87.25
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53.66
51.68
51.58
41.64
41.03
40.15
39.94
39.73
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39.31
39.10
38.89
H2N
CN
O
Ph
O
N
3r
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140
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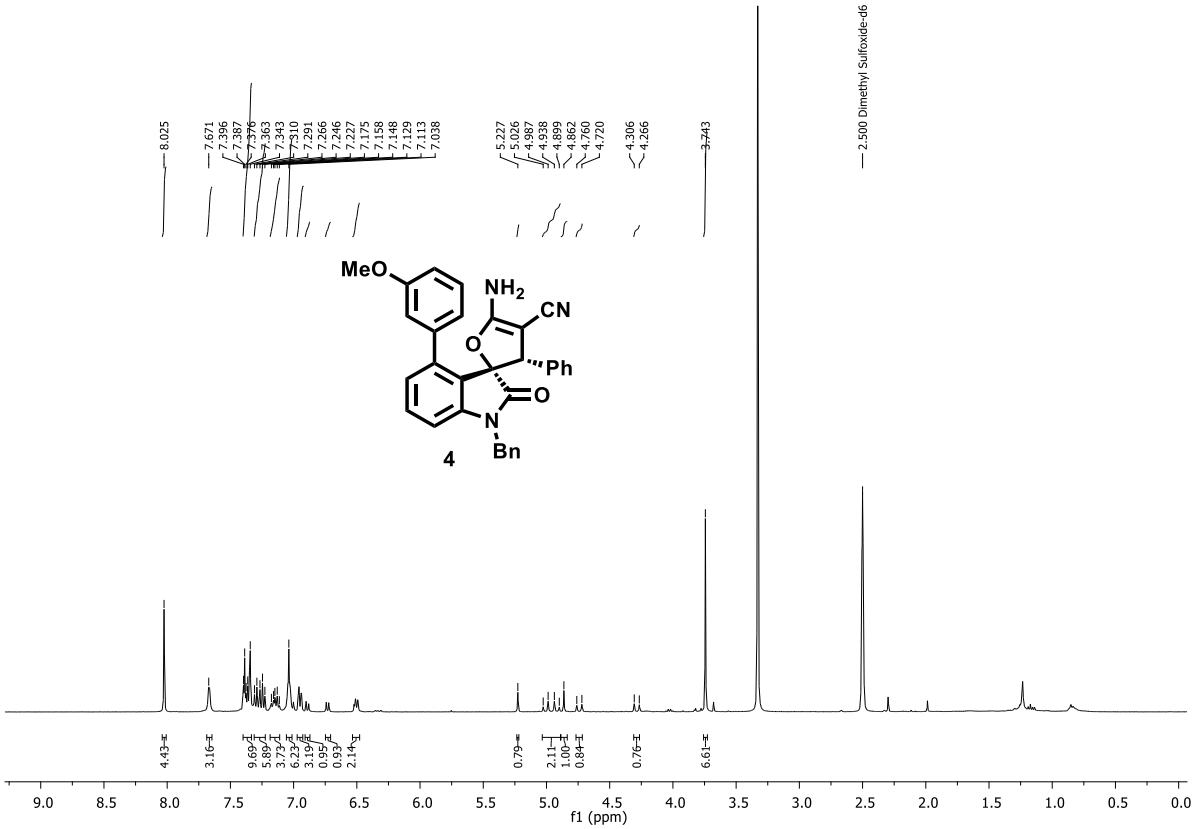
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5.227
5.026
4.987
4.938
4.899
4.862
4.760
4.720
4.306
4.266
3.343
2.500 Dimethyl Sulfoxide-d6
MeO
NH2
CN
O
Ph
O
N
Bn
4
4.43
3.16
9.69
5.89
3.73
6.23
3.19
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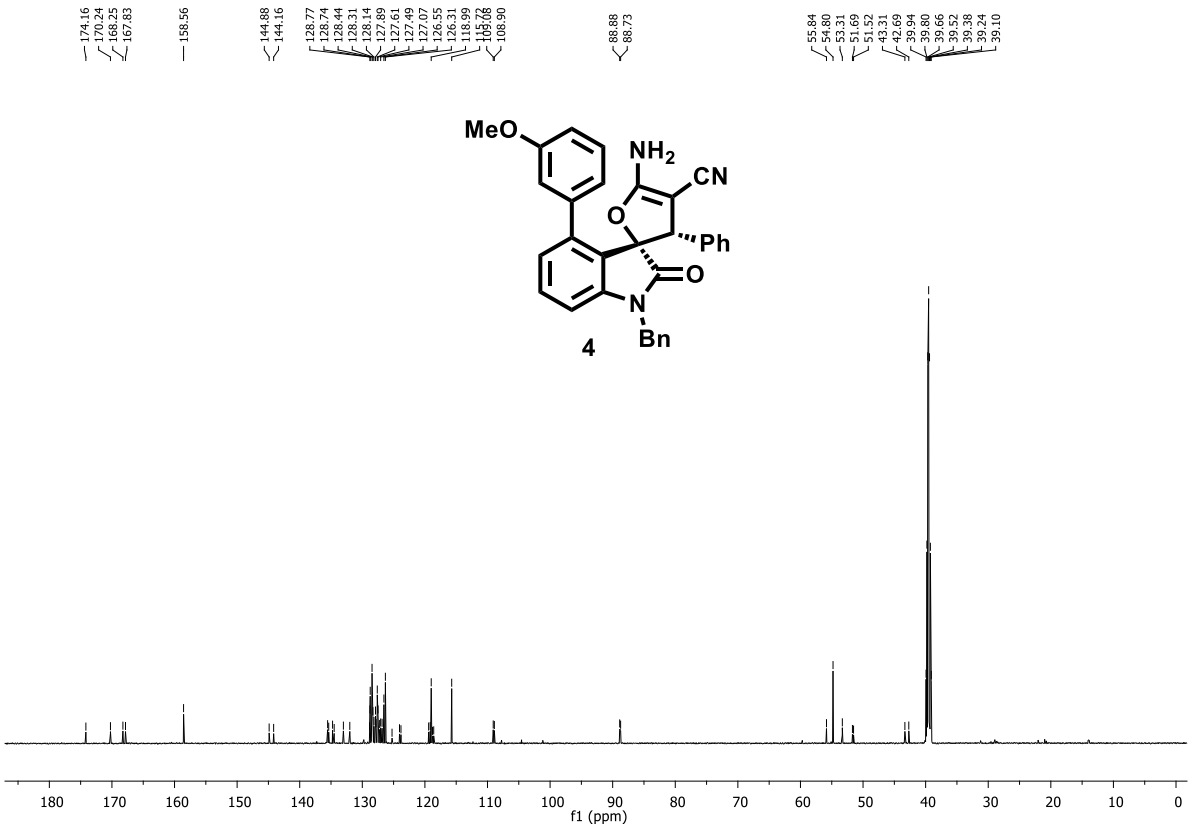
0.93
2.14
0.79
2.11
1.00
0.84
0.76
6.61
f1 (ppm)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127.07
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54.80
53.31
51.69
51.52
43.31
42.69
39.94
39.80
39.66
39.52
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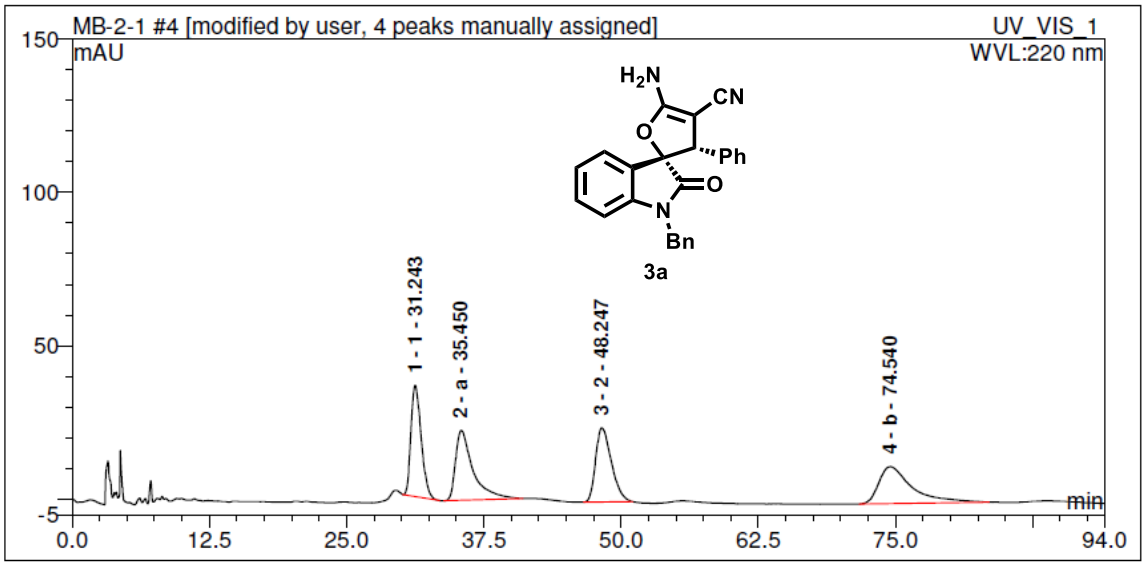
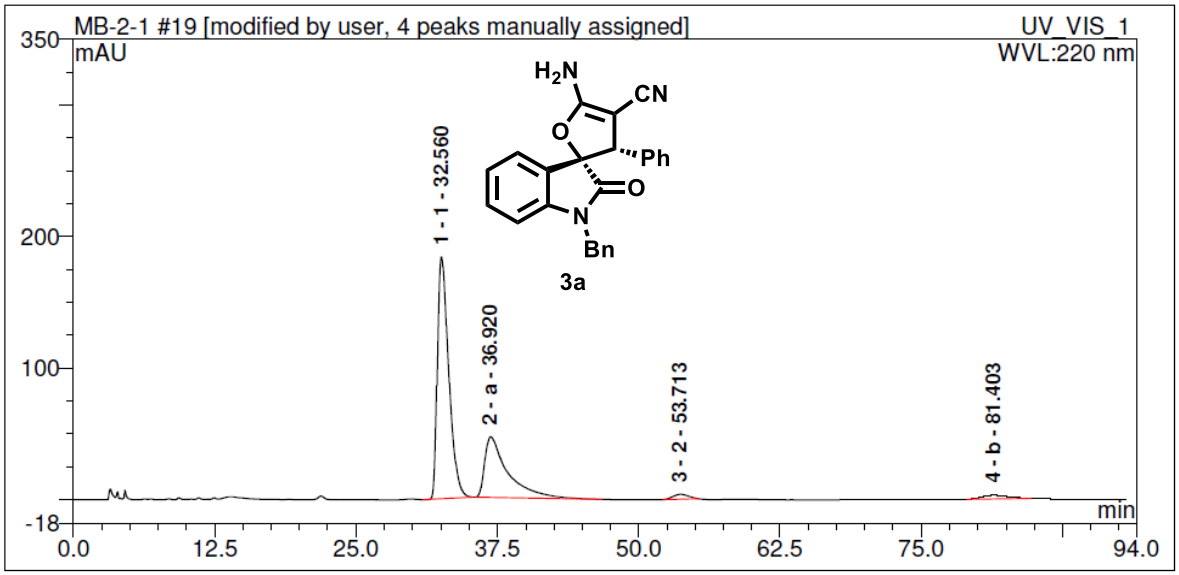
39.24
39.10
MeO
NH2
CN
O
Ph
O
N
Bn
4
f1 (ppm)

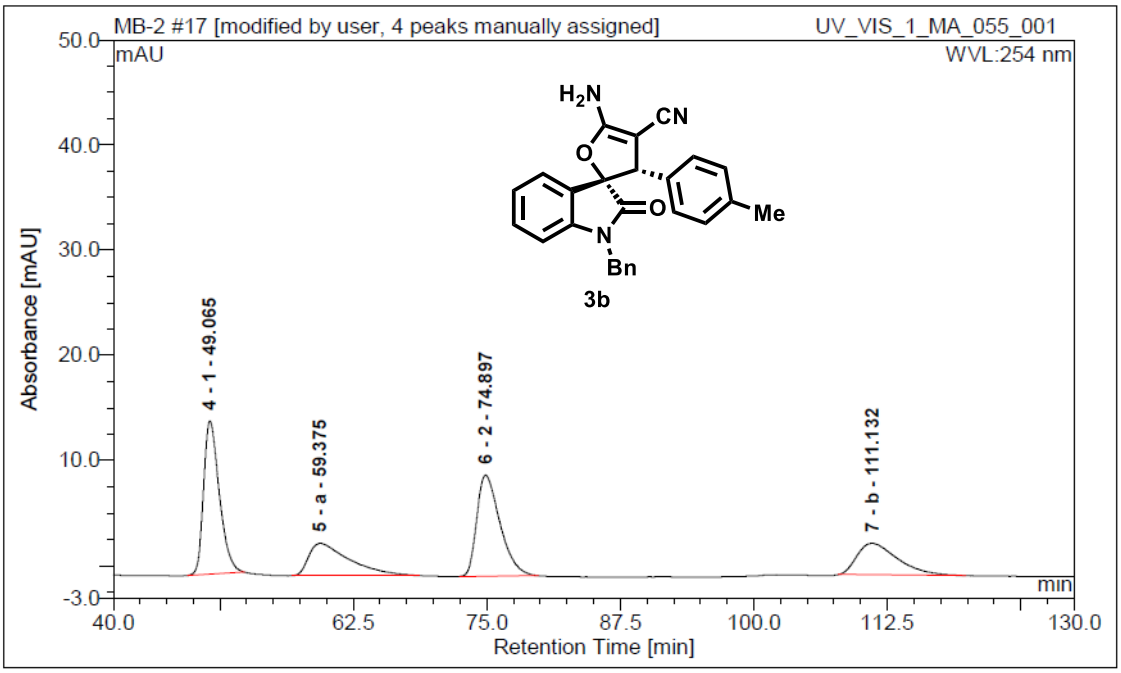
11. HPLC spectra of the products:



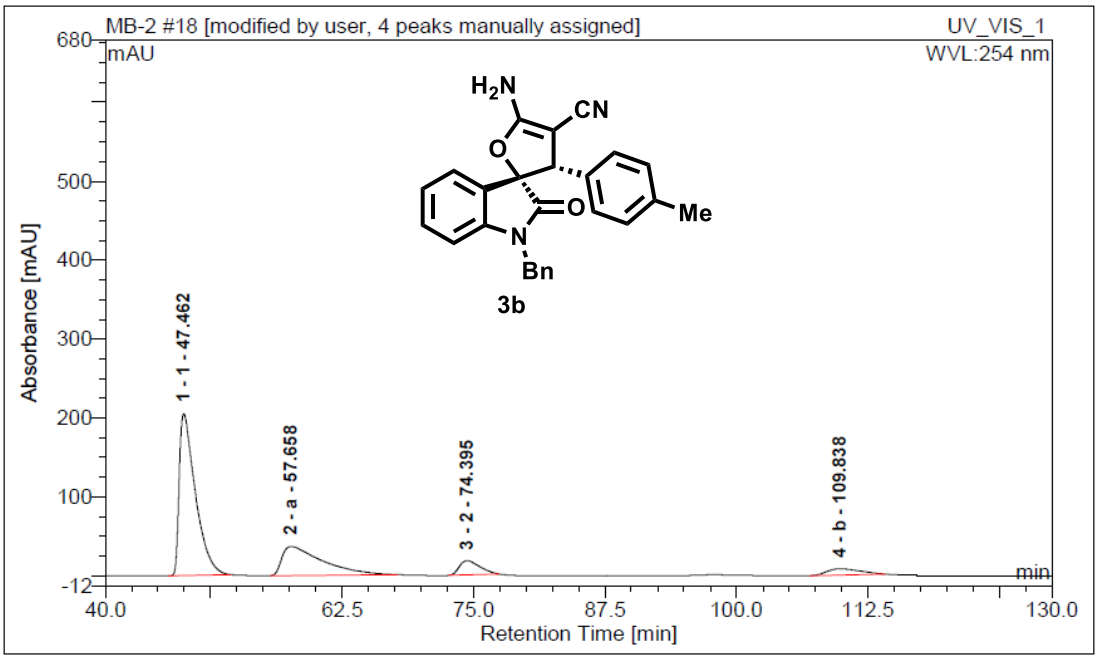
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	31.24	39.39308	24.066092	36.26502	n.a.
2	a	35.45	41.94765	25.62673197	22.6853	n.a.
3	2	48.25	40.30739	24.62465964	24.14593	n.a.
4	b	74.54	42.039	25.6825164	11.992	n.a.



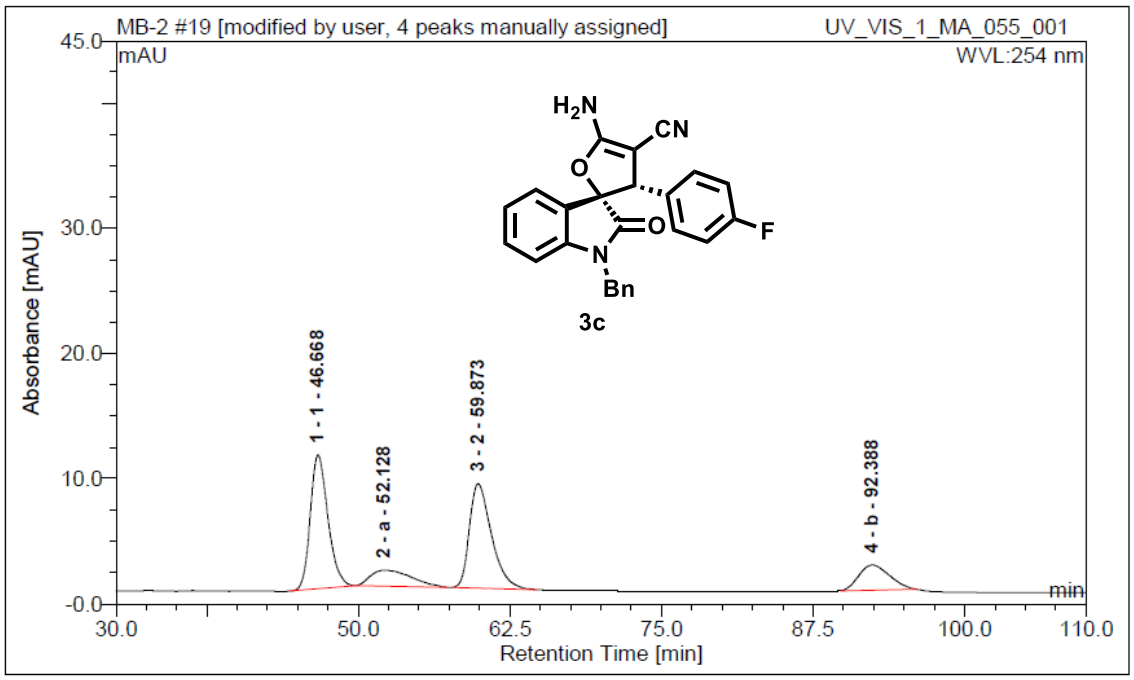
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	32.56	213.9057	63.59374561	183.7942	n.a.
2	a	36.92	108.8183	32.35146641	45.99431	n.a.
3	2	53.71	5.75005	1.709478435	3.61176	n.a.
4	b	81.40	7.889	2.345309546	2.744	n.a.



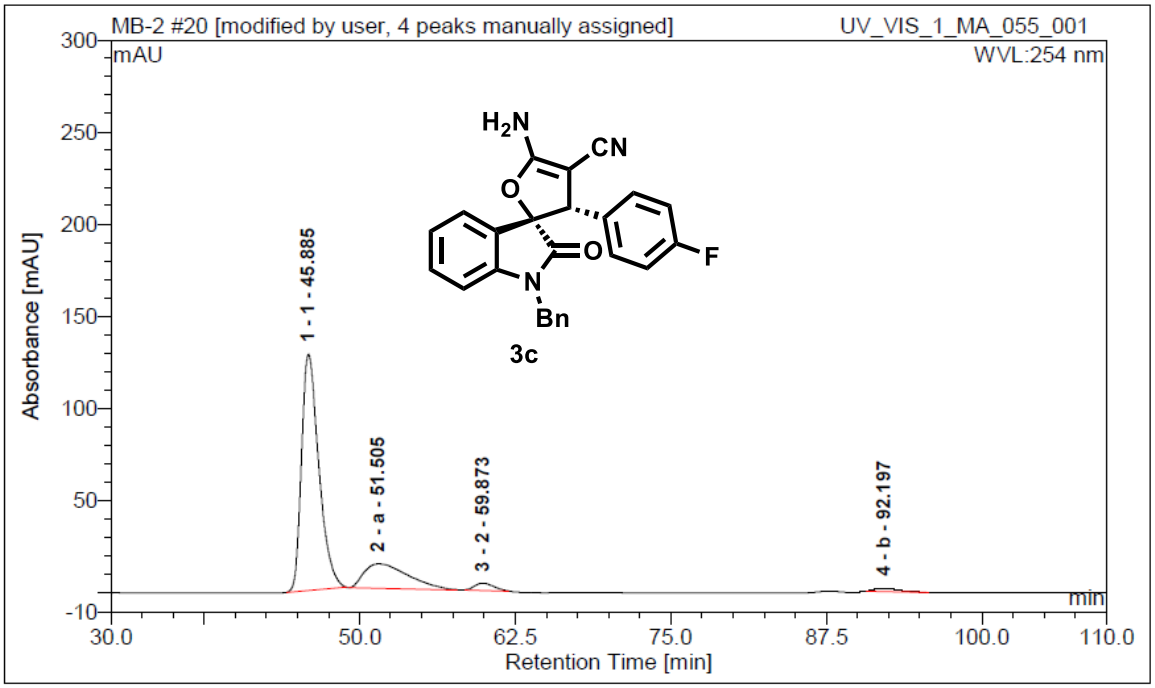
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
4	1	49.07	24.93703	32.8278039	14.56215	n.a.
5	a	59.38	13.50546	17.77896613	3.06555	n.a.
6	2	74.90	24.26384	31.94159378	9.61832	n.a.
7	b	111.13	13.257	17.45163619	2.994	n.a.



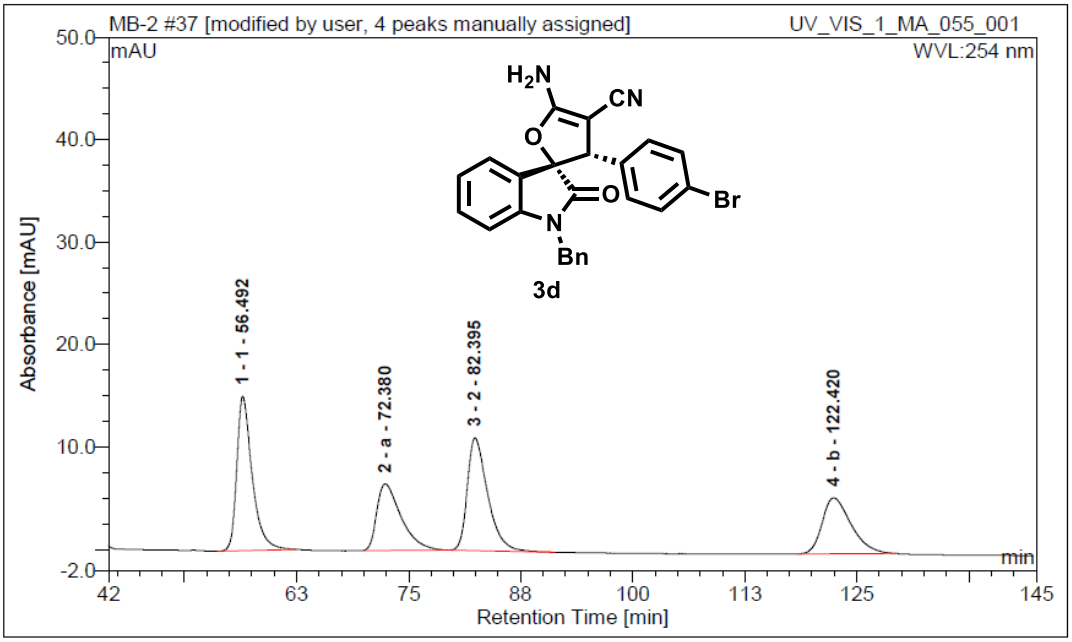
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	47.46	366.1008	61.07787578	204.9206	n.a.
2	a	57.66	163.736	27.31664178	36.56435	n.a.
3	2	74.40	40.63646	6.779521932	17.9036	n.a.
4	b	109.84	28.927	4.825960514	7.900	n.a.



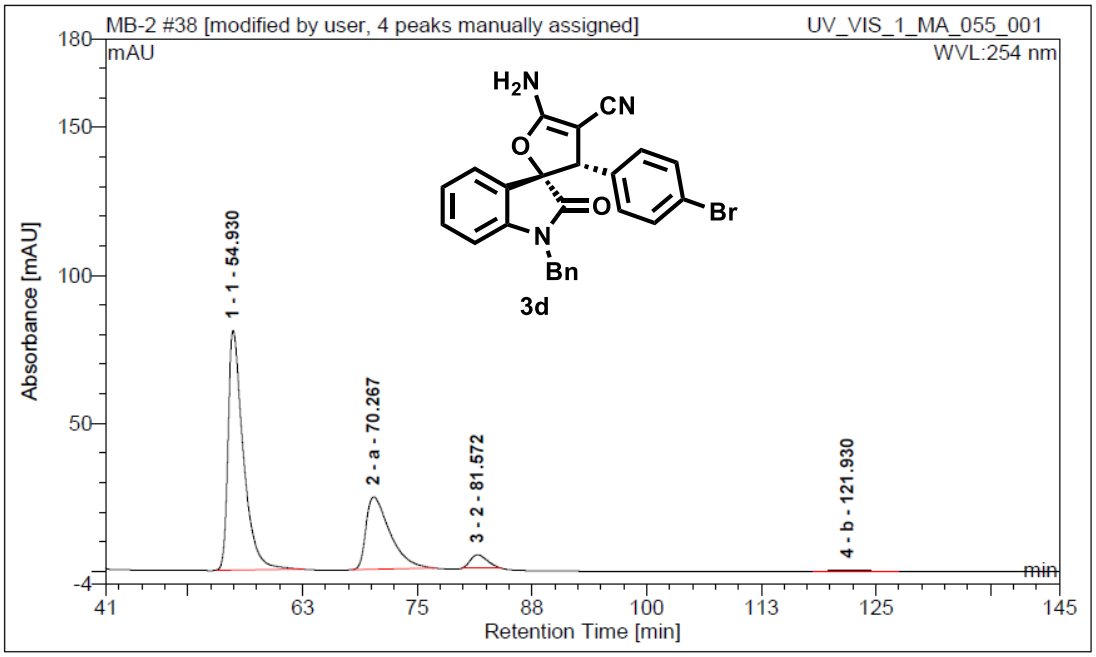
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	46.67	18.12158	38.7909577	10.70034	n.a.
2	a	52.13	4.955365	10.60743082	1.27109	n.a.
3	2	59.87	17.69035	37.86787774	8.3503	n.a.
4	b	92.39	5.949	12.73373374	2.009	n.a.



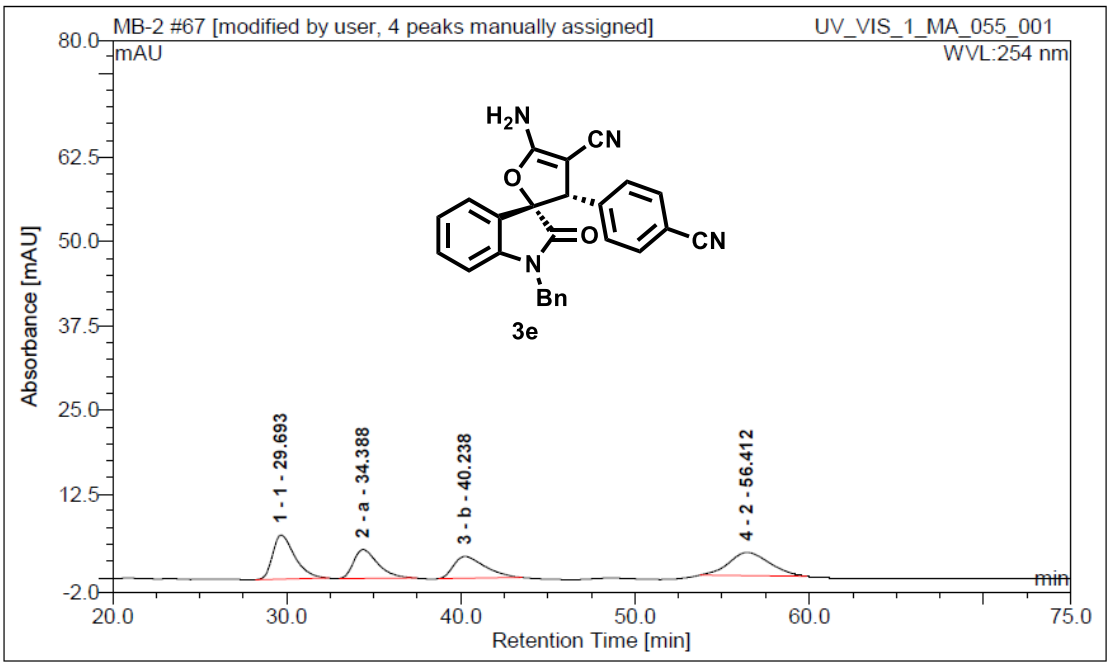
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	45.89	207.0448	75.97152112	128.065	n.a.
2	a	51.51	54.45341	19.98074297	13.31646	n.a.
3	2	59.87	6.783468	2.489077132	3.88085	n.a.
4	b	92.20	4.248	1.558658773	1.721	n.a.



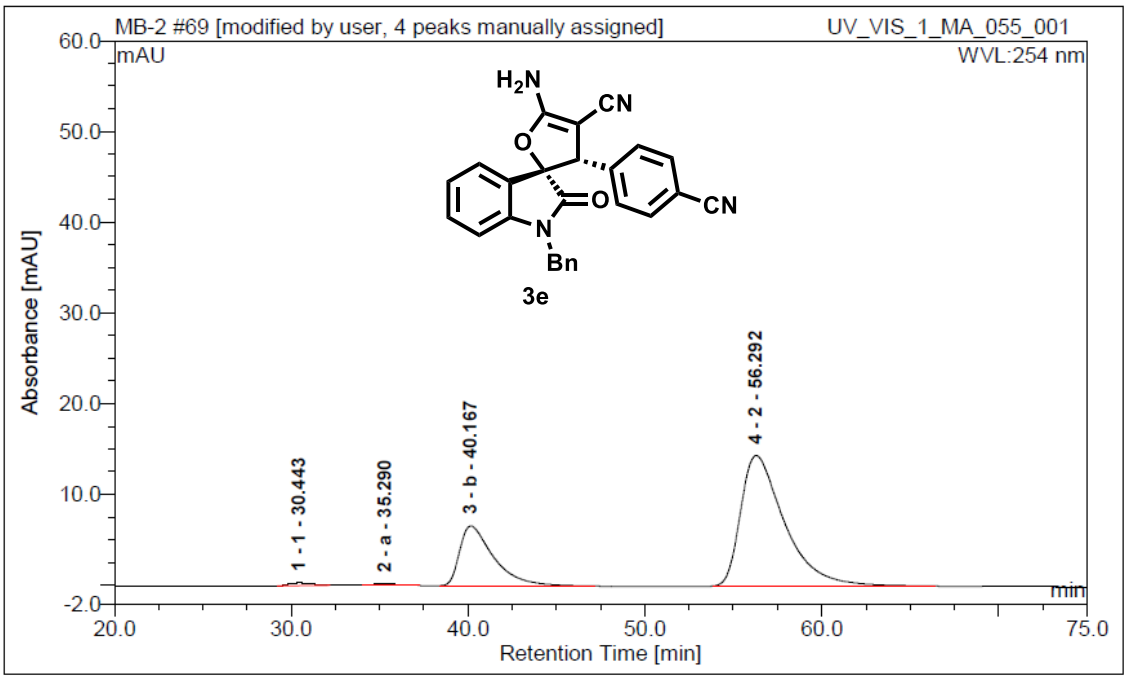
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	56.49	30.00862	30.00689215	15.05437	n.a.
2	a	72.38	20.34339	20.34222335	6.48294	n.a.
3	2	82.40	29.09083	29.08915978	11.02746	n.a.
4	b	122.42	20.563	20.56172473	5.477	n.a.



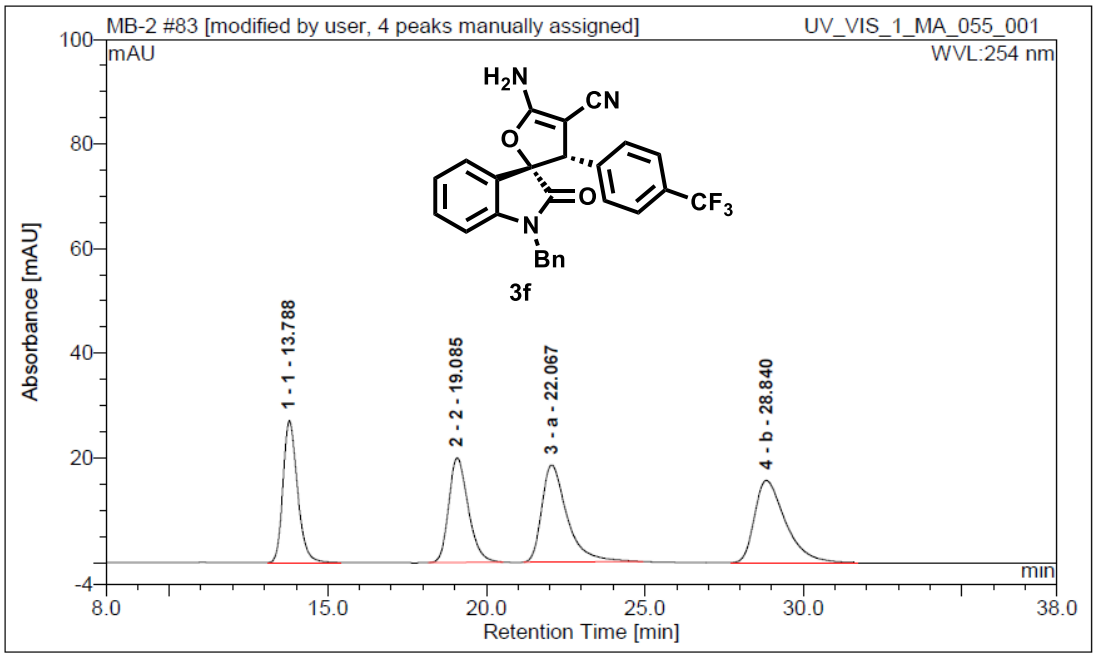
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	54.93	155.9019	64.4352431	80.86396	n.a.
2	a	70.27	74.23062	30.67997657	24.47022	n.a.
3	2	81.57	9.57992	3.959440626	4.47118	n.a.
4	b	121.93	2.239	0.9253397052	0.610	n.a.



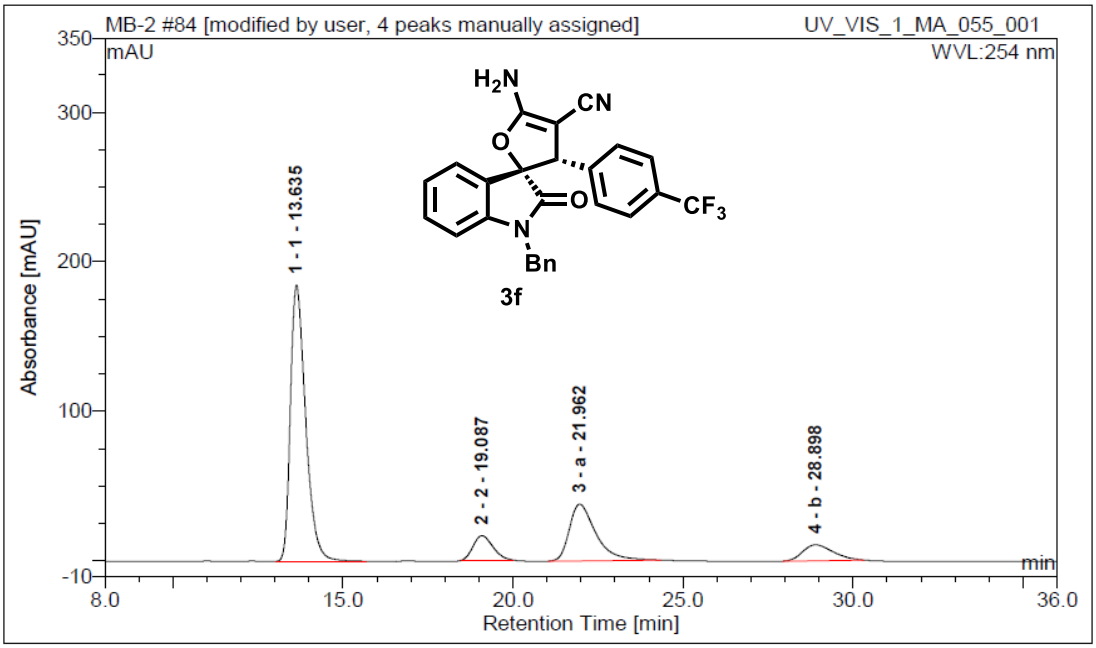
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	29.69	9.606211	29.61238918	6.53716	n.a.
2	a	34.39	6.911704	21.30622217	4.26136	n.a.
3	b	40.24	6.741885	20.78273385	3.22246	n.a.
4	2	56.41	9.180	28.2986548	3.400	n.a.



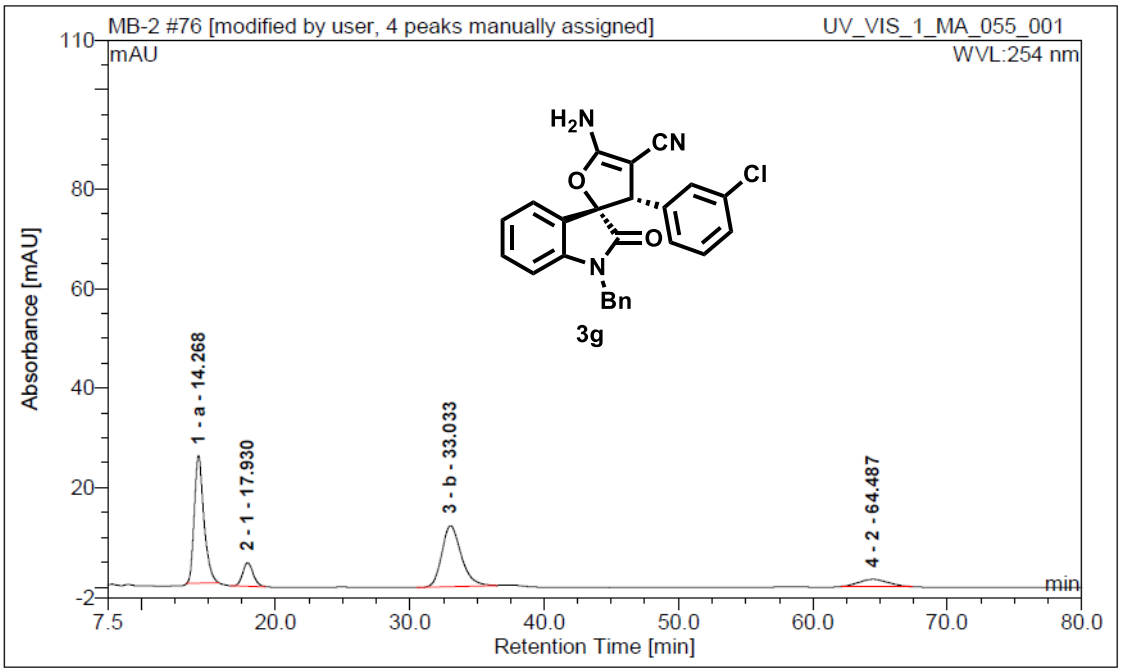
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	30.44	0.511471	0.8964484883	0.36321	n.a.
2	a	35.29	0.249705	0.4376545006	0.15031	n.a.
3	b	40.17	14.74173	25.83760928	6.5994	n.a.
4	2	56.29	41.552	72.82828773	14.395	n.a.



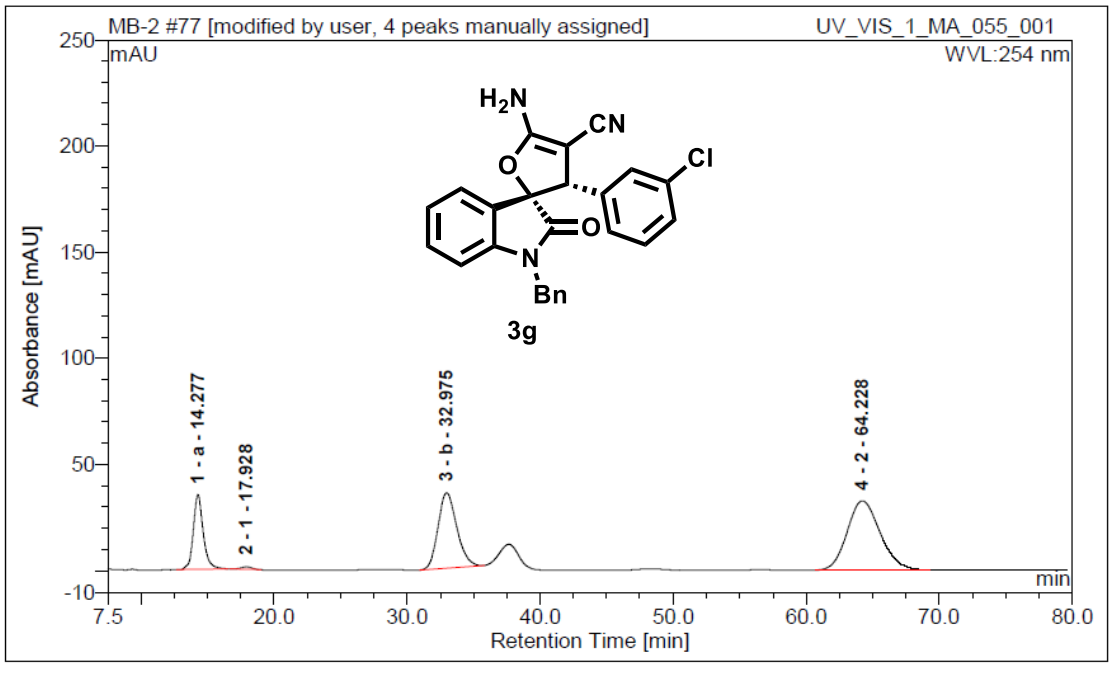
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.79	14.43704	22.73262168	27.09185	n.a.
2	2	19.09	14.21687	22.38593359	19.94326	n.a.
3	a	22.07	17.15804	27.01712064	18.52181	n.a.
4	b	28.84	17.696	27.86432409	15.700	n.a.



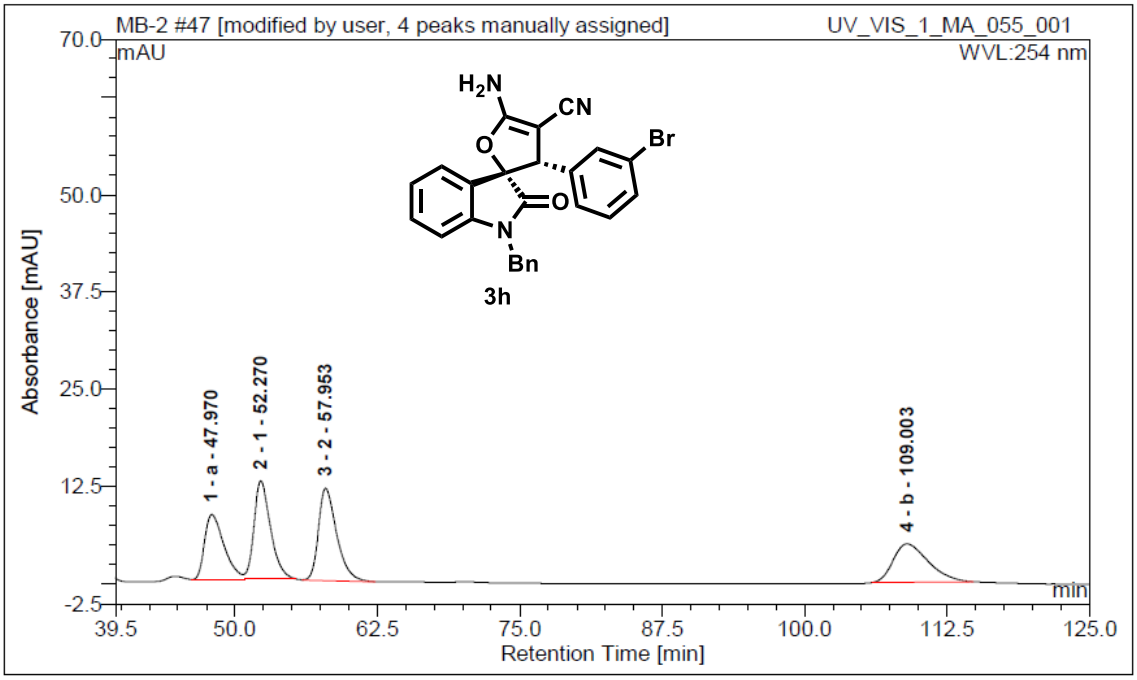
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.64	95.68589	63.08409409	184.7405	n.a.
2	2	19.09	10.88702	7.177631884	16.32807	n.a.
3	a	21.96	34.16793	22.52634272	37.84691	n.a.
4	b	28.90	10.939	7.211931304	10.567	n.a.



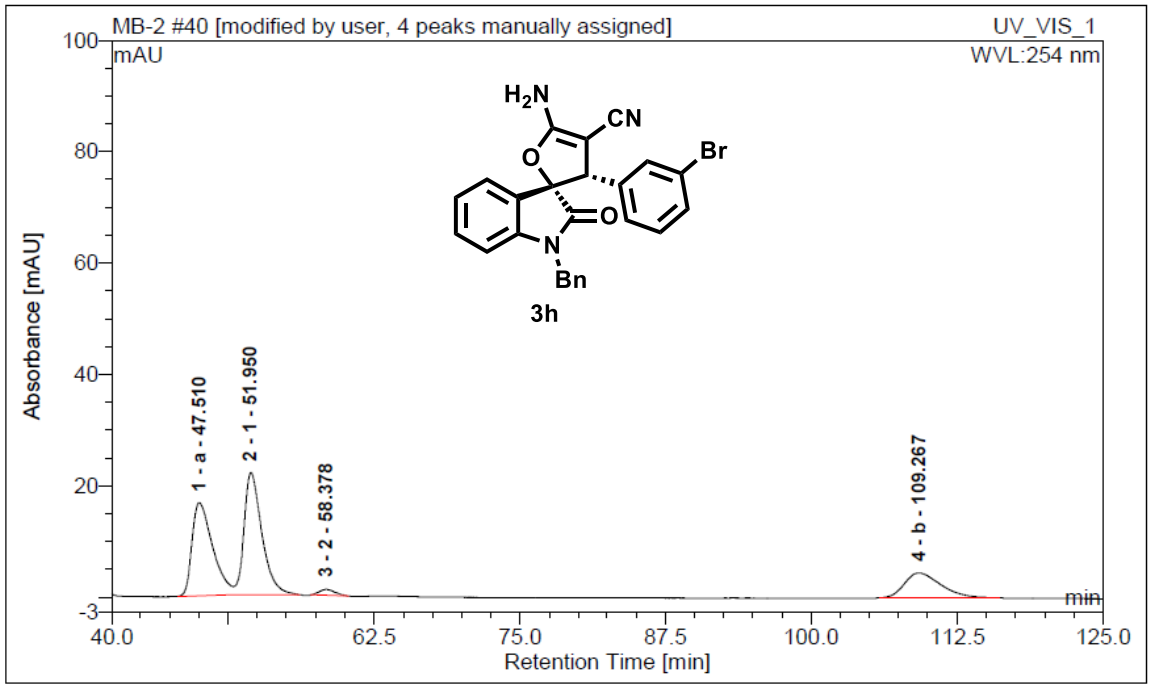
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.27	21.25974	42.82996015	25.64833	n.a.
2	1	17.93	4.217175	8.495939622	4.71558	n.a.
3	b	33.03	20.41649	41.13114544	12.24417	n.a.
4	2	64.49	3.744	7.542954783	1.445	n.a.



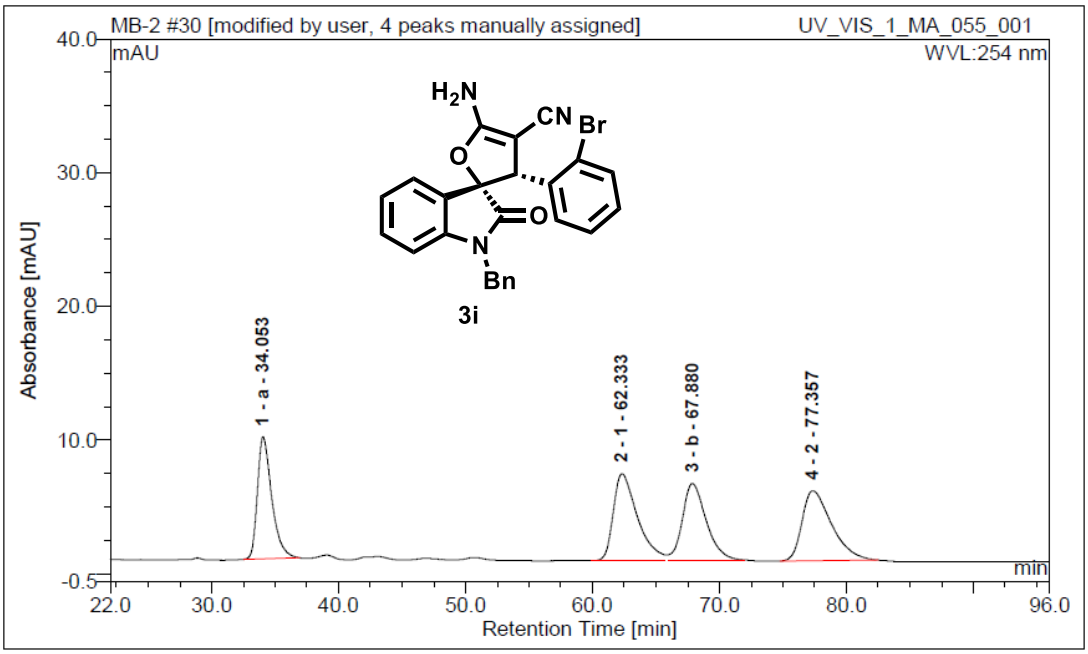
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.28	30.43323	16.64940537	35.13231	n.a.
2	1	17.93	1.143719	0.6257054697	1.23459	n.a.
3	b	32.98	57.7535	31.59577948	35.47512	n.a.
4	2	64.23	93.458	51.12910968	32.632	n.a.



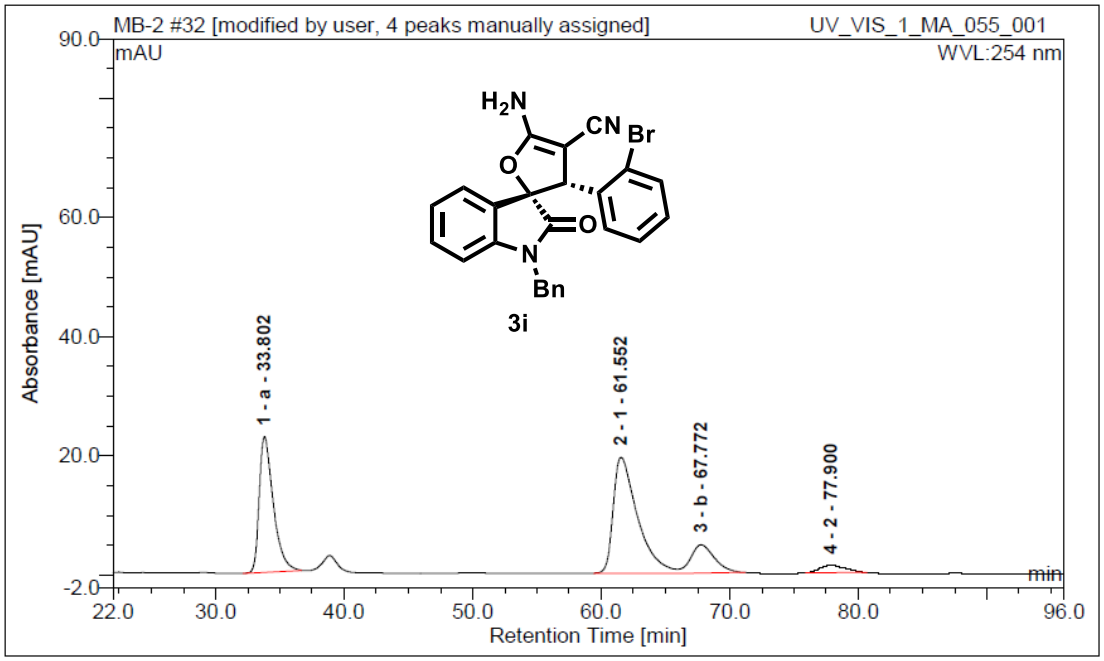
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	47.97	16.57396	21.41566521	8.36855	n.a.
2	1	52.27	21.16279	27.34501729	12.60861	n.a.
3	2	57.95	21.93533	28.34324473	11.84133	n.a.
4	b	109.00	17.720	22.89607277	4.929	n.a.



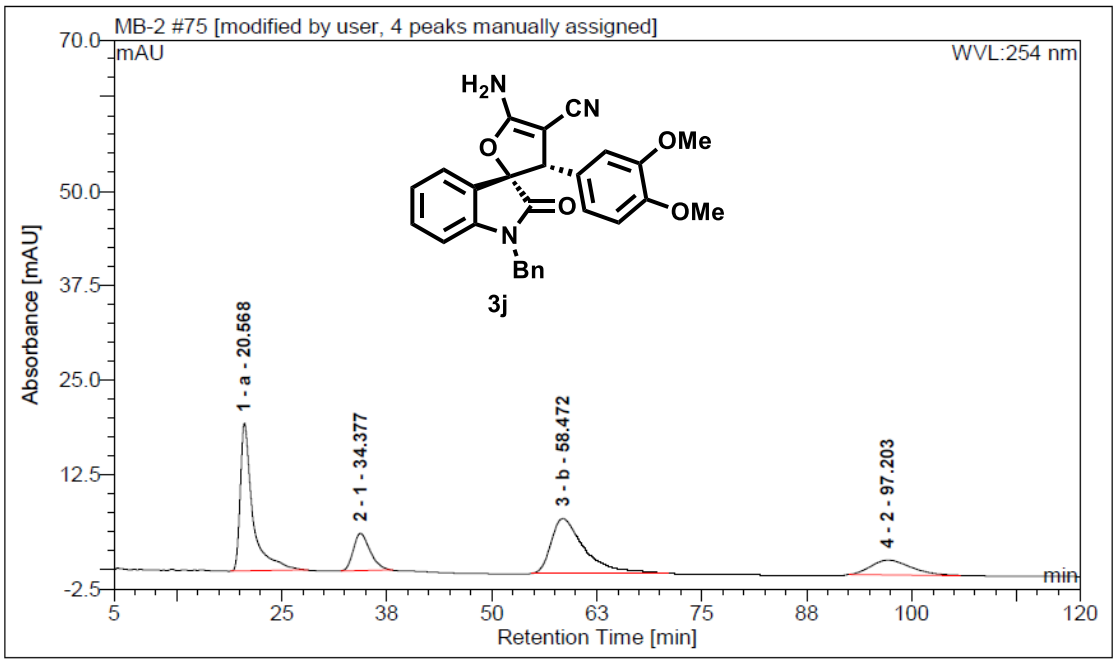
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	47.51	33.92215	37.19850379	16.68819	n.a.
2	1	51.95	39.28305	43.07718343	21.94652	n.a.
3	2	58.38	1.686225	1.849088368	1.05309	n.a.
4	b	109.27	16.301	17.87522441	4.474	n.a.



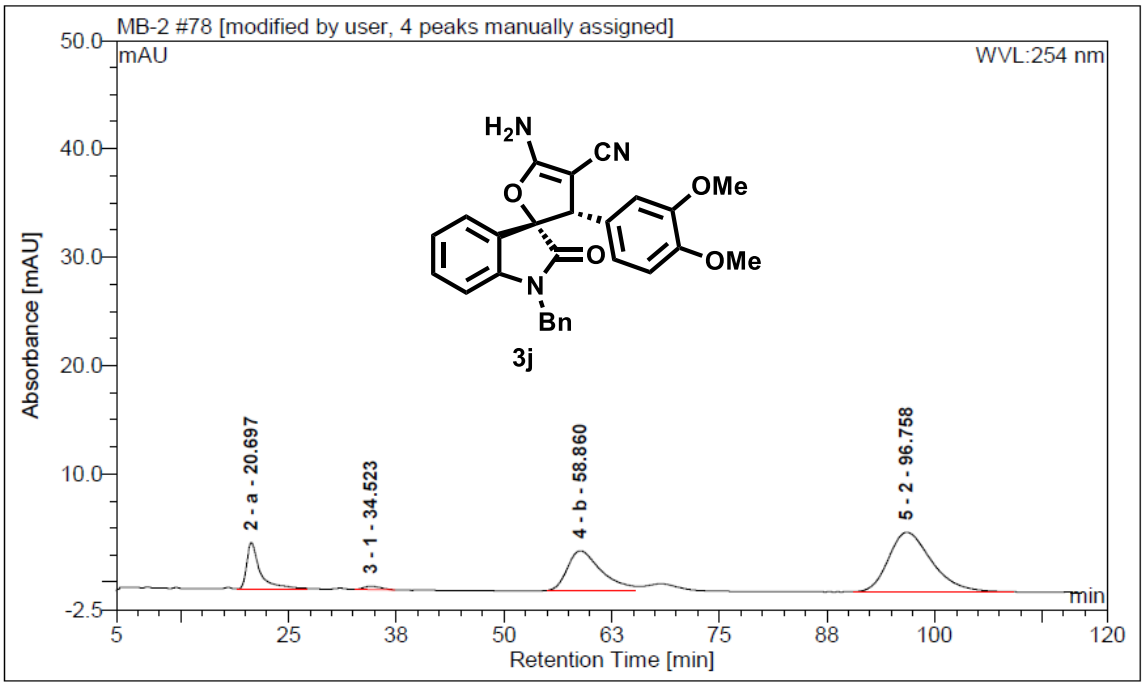
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	34.05	11.89449	22.59390873	9.10438	n.a.
2	1	62.33	14.26398	27.09481398	6.49805	n.a.
3	b	67.88	12.38031	23.51672512	5.72451	n.a.
4	2	77.36	14.106	26.79455216	5.232	n.a.



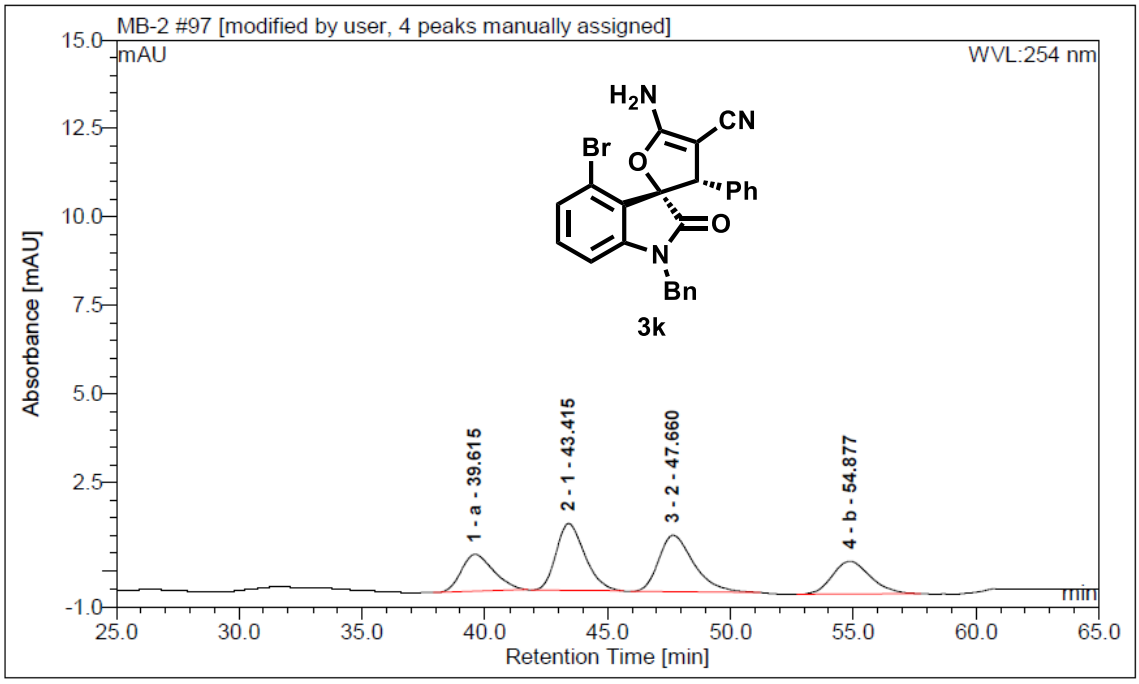
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	33.80	28.78973	34.0901207	22.73156	n.a.
2	1	61.55	42.67971	50.5373505	19.46881	n.a.
3	b	67.77	10.08736	11.94451407	4.722	n.a.
4	2	77.90	2.895	3.428014726	1.263	n.a.



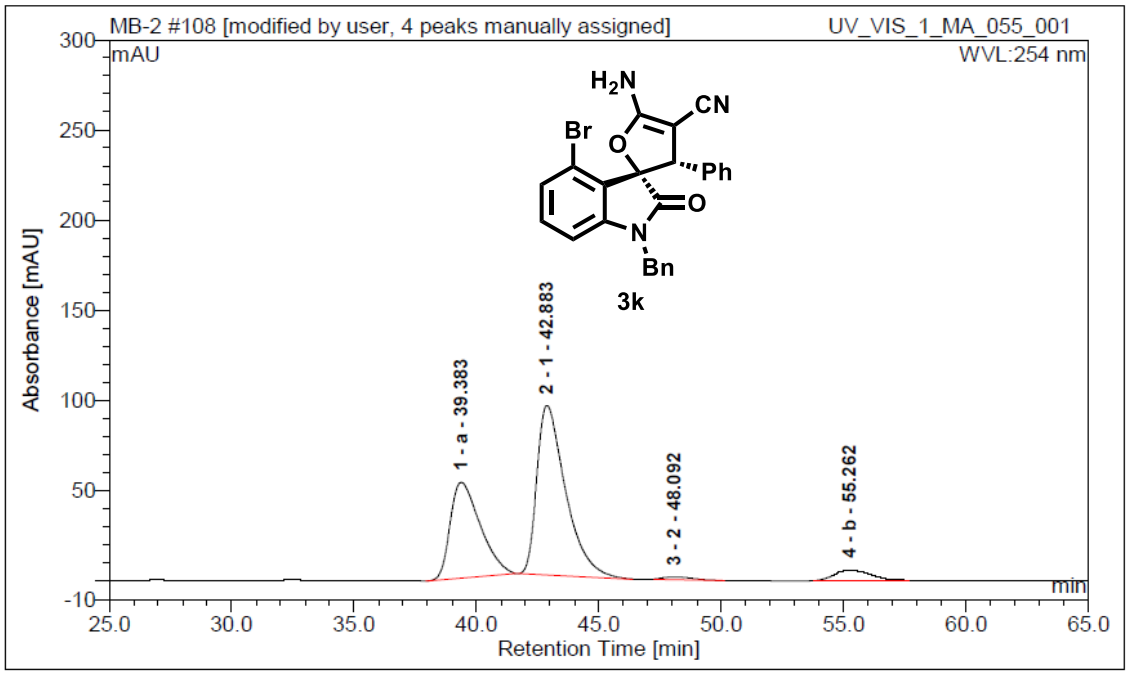
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	20.57	33.95214	38.00778712	19.54741	n.a.
2	1	34.38	11.42795	12.79303896	4.92311	n.a.
3	b	58.47	33.26096	37.2340435	7.24766	n.a.
4	2	97.20	10.688	11.96513042	1.934	n.a.



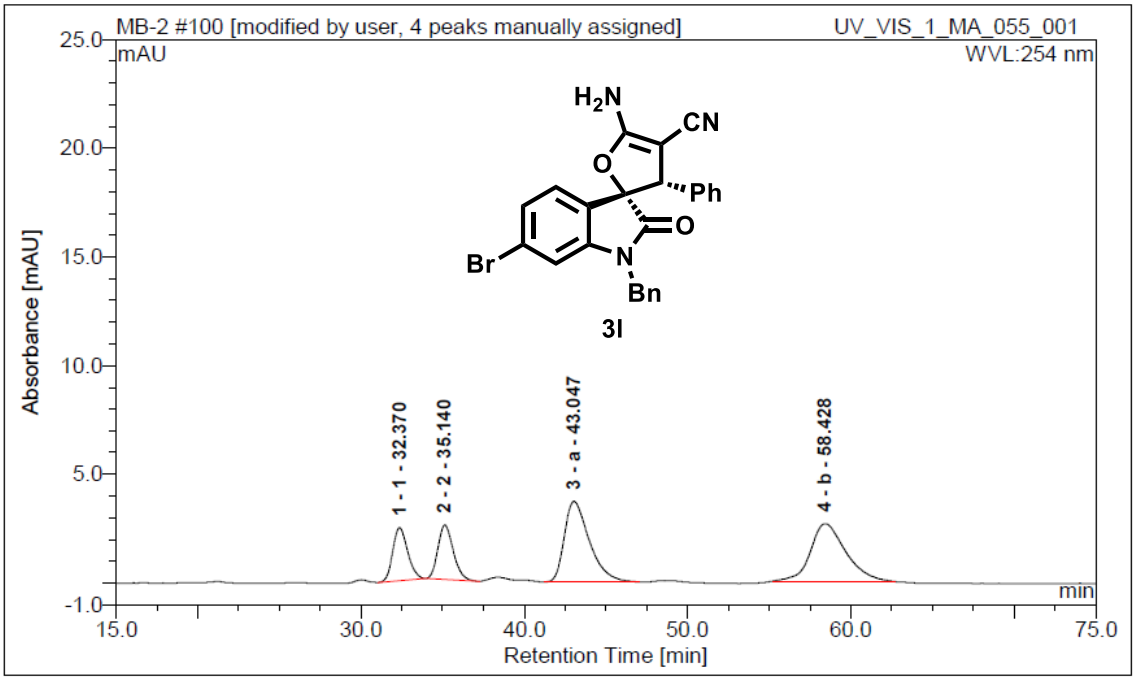
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
2	a	20.70	7.46012	13.190283	4.25526	n.a.
3	1	34.52	0.706817	1.249727116	0.31831	n.a.
4	b	58.86	16.48417	29.14575881	3.64285	n.a.
5	2	96.76	31.907	56.41423108	5.491	n.a.



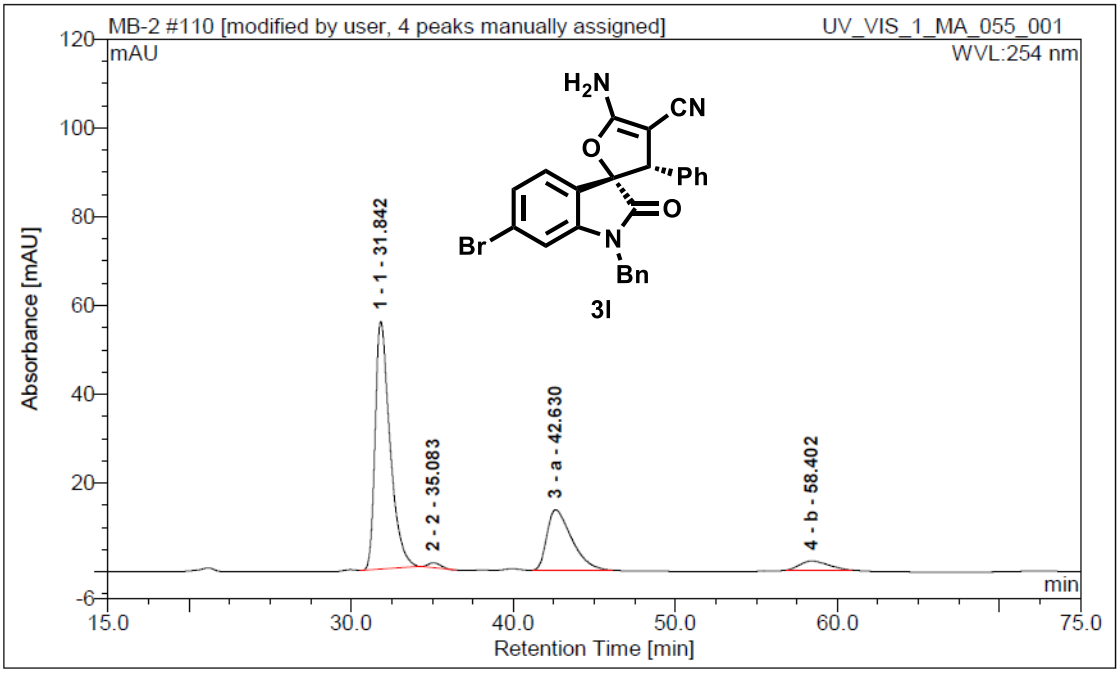
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	39.62	1.592117	18.82671372	1.04729	n.a.
2	1	43.42	2.552066	30.17807174	1.88588	n.a.
3	2	47.66	2.649134	31.32590117	1.59381	n.a.
4	b	54.88	1.663	19.66931337	0.926	n.a.



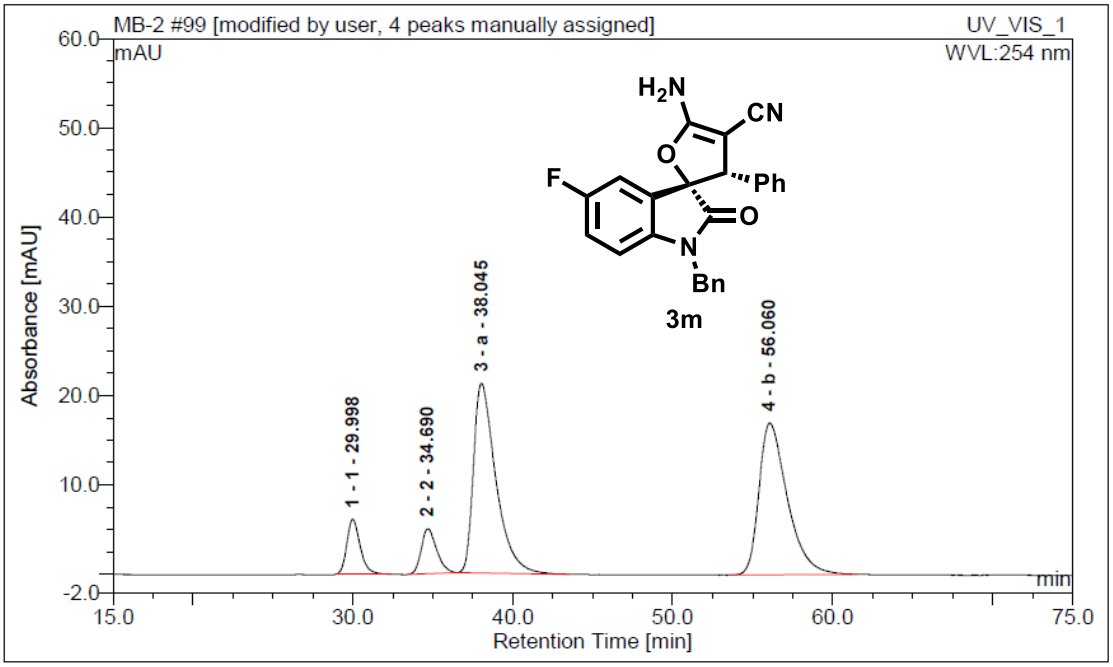
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	39.38	75.4387	34.97204118	53.01911	n.a.
2	1	42.88	128.4459	59.54521391	94.06553	n.a.
3	2	48.09	1.887378	0.8749550155	1.46013	n.a.
4	b	55.26	9.940	4.60778989	5.861	n.a.



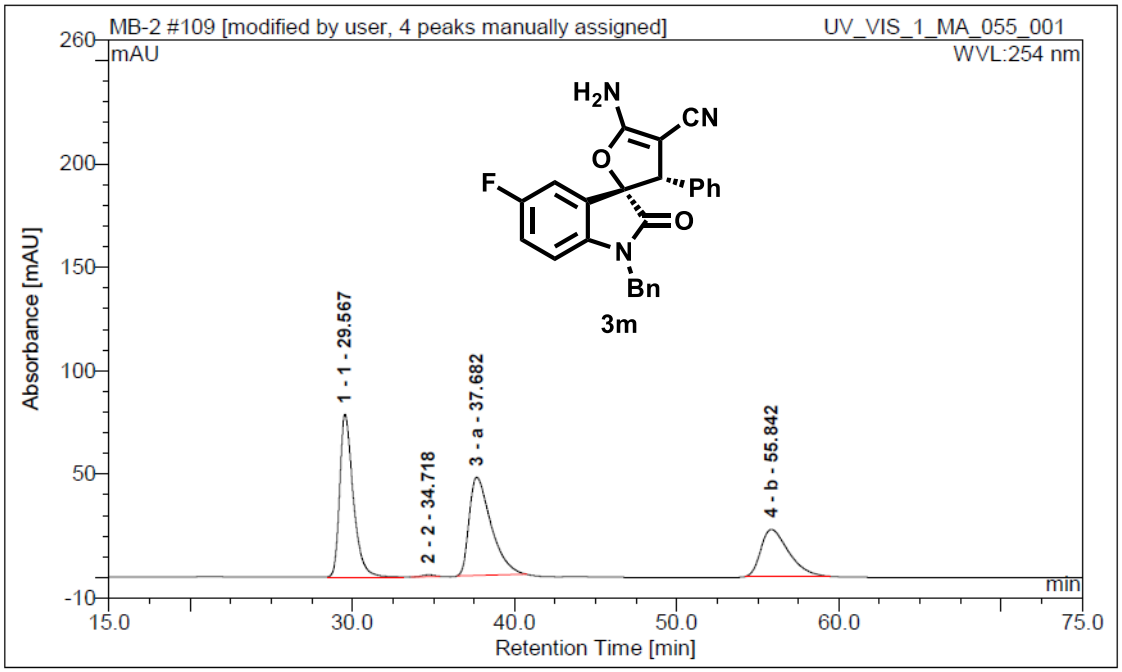
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	32.37	2.576905	13.84633484	2.44227	n.a.
2	2	35.14	2.737221	14.70775143	2.50332	n.a.
3	a	43.05	6.640807	35.68266343	3.71397	n.a.
4	b	58.43	6.656	35.76325029	2.649	n.a.



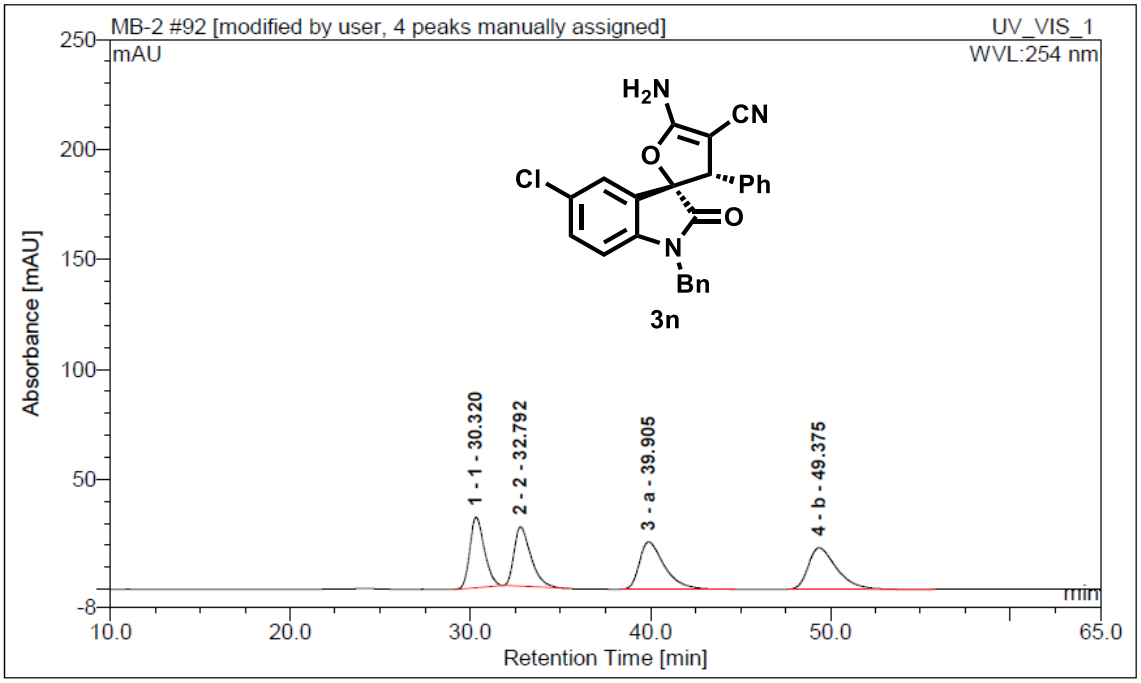
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	31.84	59.36276	66.9314379	55.7804	n.a.
2	2	35.08	1.04893	1.182667138	1.13971	n.a.
3	a	42.63	24.15728	27.23730141	13.6376	n.a.
4	b	58.40	4.123	4.648593552	2.033	n.a.



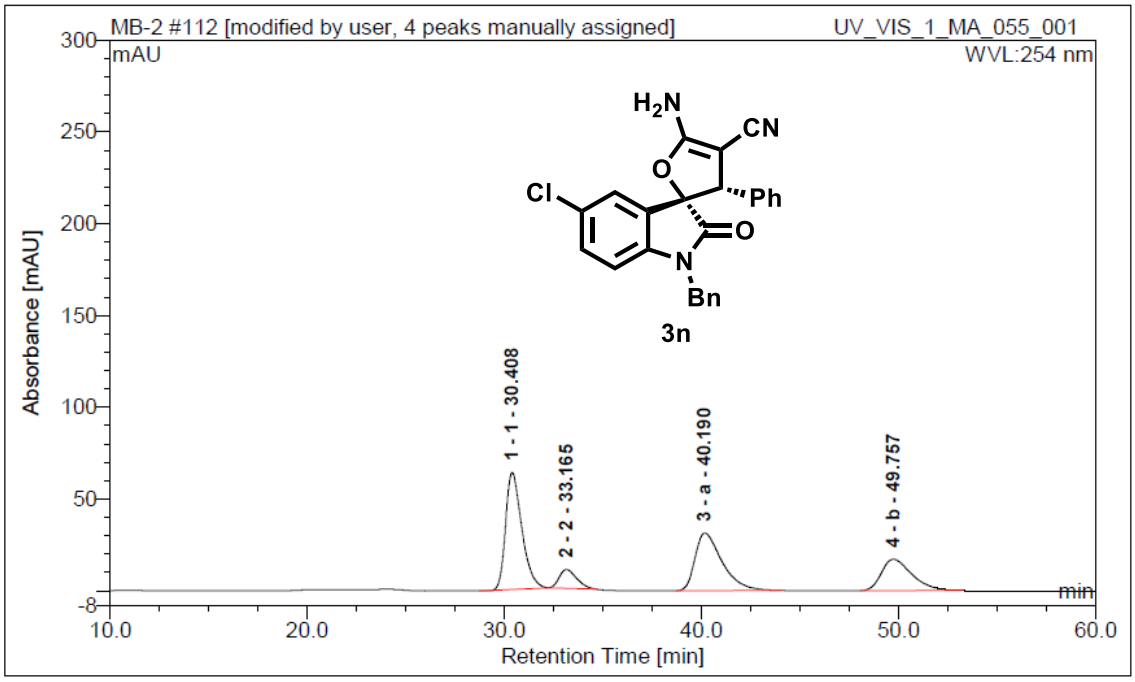
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	30.00	5.98692	7.385353719	6.16205	n.a.
2	2	34.69	5.607347	6.917118956	5.04784	n.a.
3	a	38.05	34.42154	42.46177493	21.20698	n.a.
4	b	56.06	35.049	43.23575239	17.009	n.a.



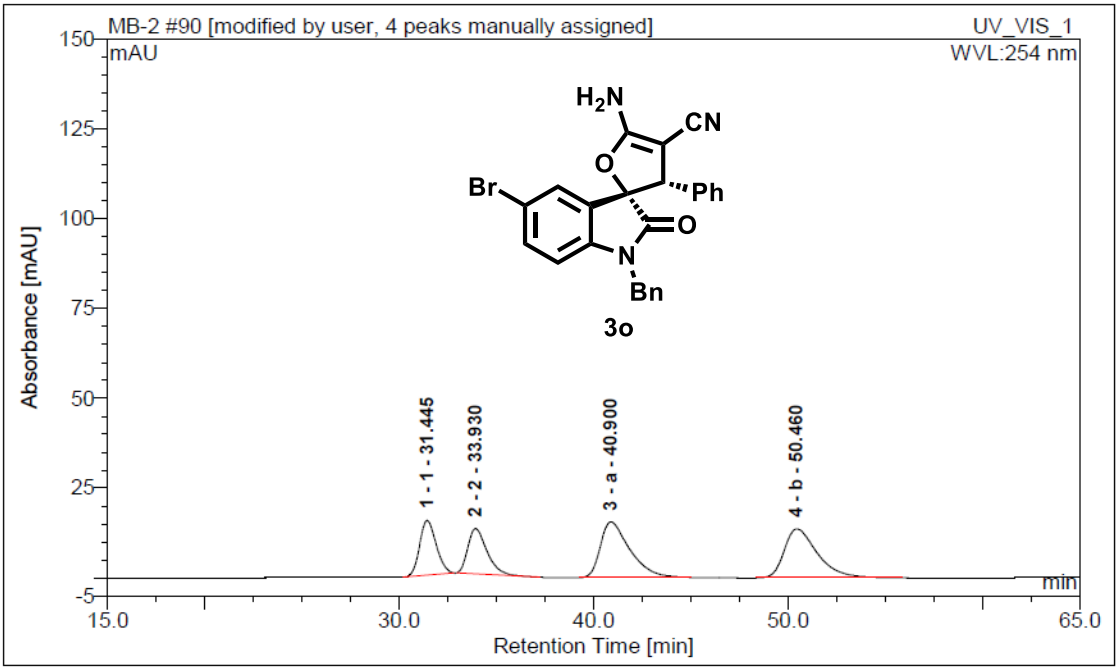
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	29.57	75.81412	38.62560223	78.64765	n.a.
2	2	34.72	0.673427	0.3430962587	0.79808	n.a.
3	a	37.68	74.55752	37.98539566	47.41441	n.a.
4	b	55.84	45.234	23.04590585	22.770	n.a.



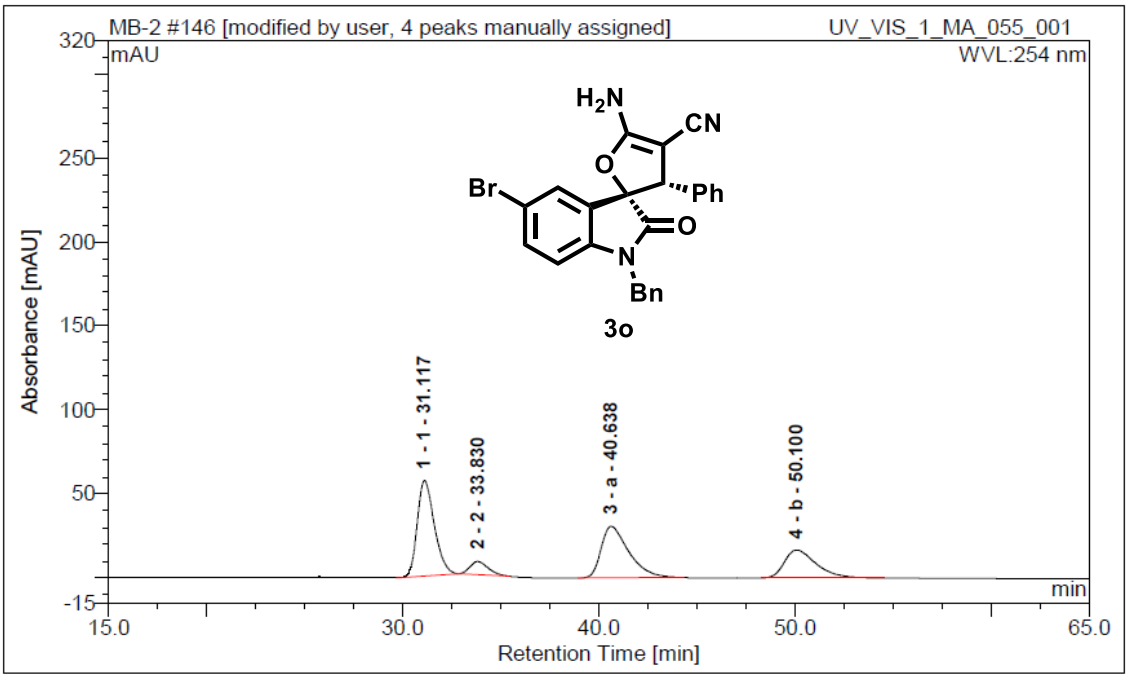
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	30.32	29.8195	23.2410647	31.95261	n.a.
2	2	32.79	29.0381	22.63204915	26.81922	n.a.
3	a	39.91	34.69326	27.03963422	21.53904	n.a.
4	b	49.38	34.754	27.08725192	18.838	n.a.



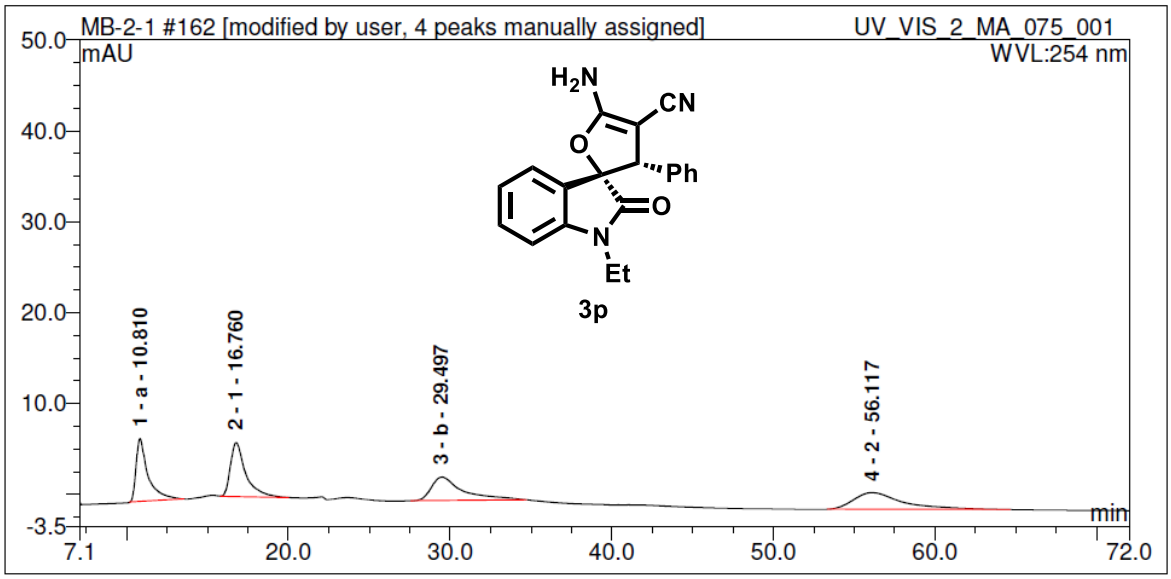
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	30.41	60.73274	39.96918874	63.7484	n.a.
2	2	33.17	10.38036	6.831479283	10.19343	n.a.
3	a	40.19	50.18736	33.02910468	31.4467	n.a.
4	b	49.76	30.648	20.17022729	17.056	n.a.



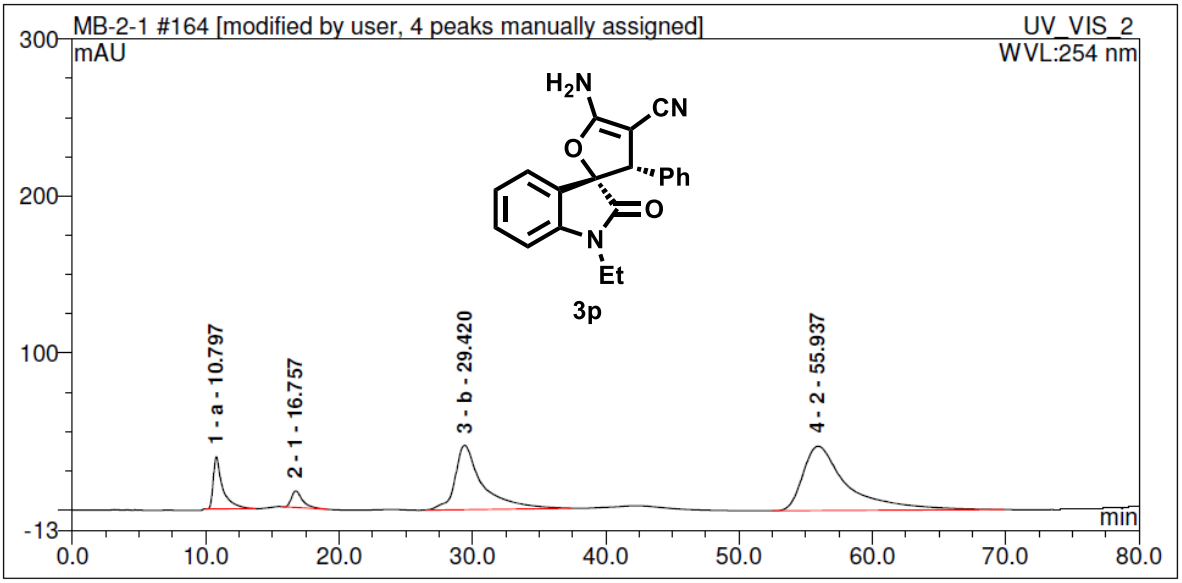
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	31.45	15.08619	18.0442489	15.28249	n.a.
2	2	33.93	14.35124	17.16518994	12.57074	n.a.
3	a	40.90	27.1704	32.49789291	15.49985	n.a.
4	b	50.46	26.999	32.29266826	13.635	n.a.



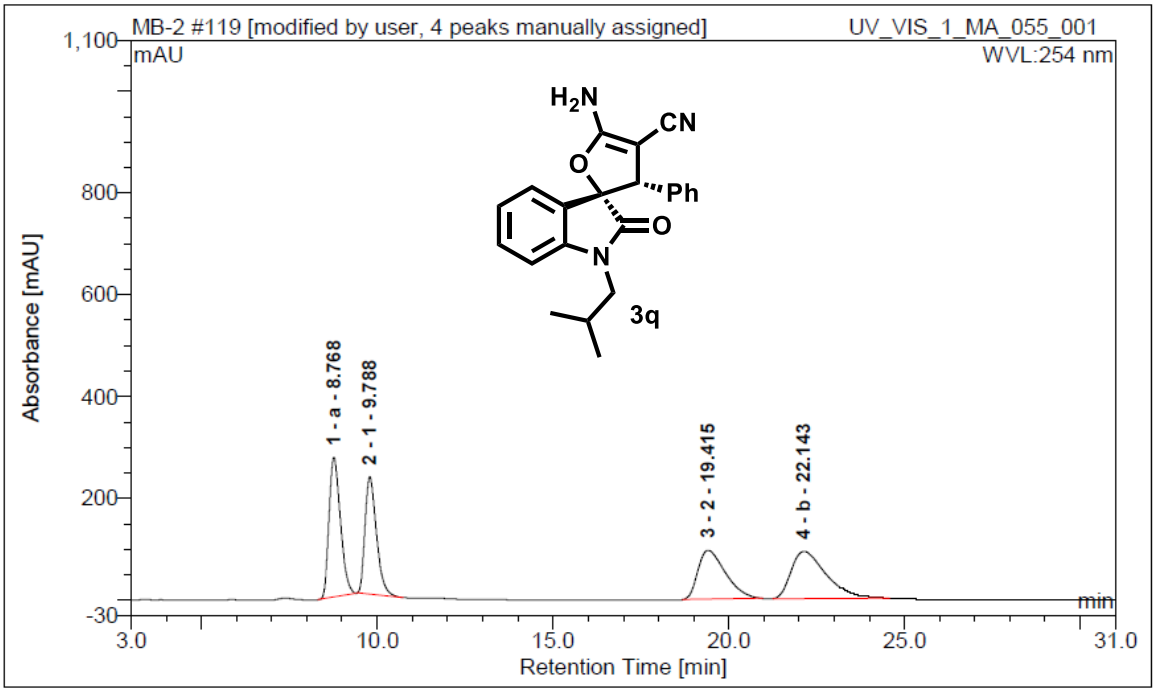
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	31.12	57.37818	38.94249898	56.88009	n.a.
2	2	33.83	8.31363	5.642449745	7.75497	n.a.
3	a	40.64	50.16874	34.04945638	30.58537	n.a.
4	b	50.10	31.480	21.3655949	16.632	n.a.



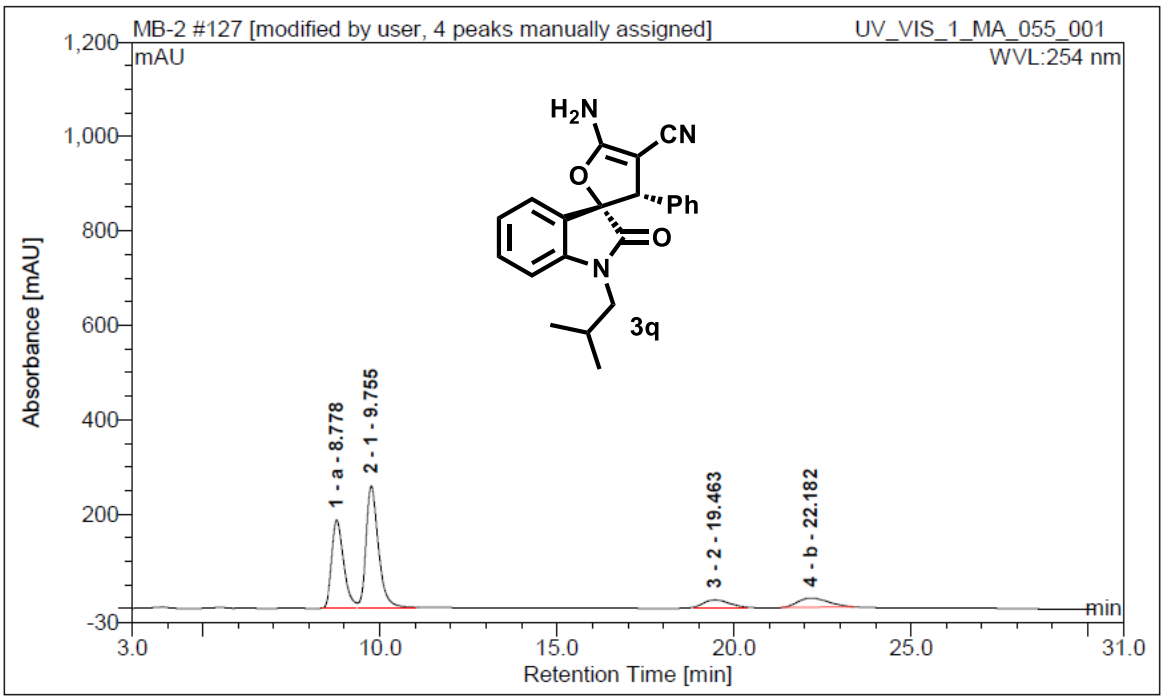
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.81	5.934526	23.98870964	6.89823	n.a.
2	1	16.76	6.493507	26.24823754	5.93399	n.a.
3	b	29.50	5.812909	23.49710648	2.56375	n.a.
4	2	56.12	6.498	26.26594634	1.839	n.a.



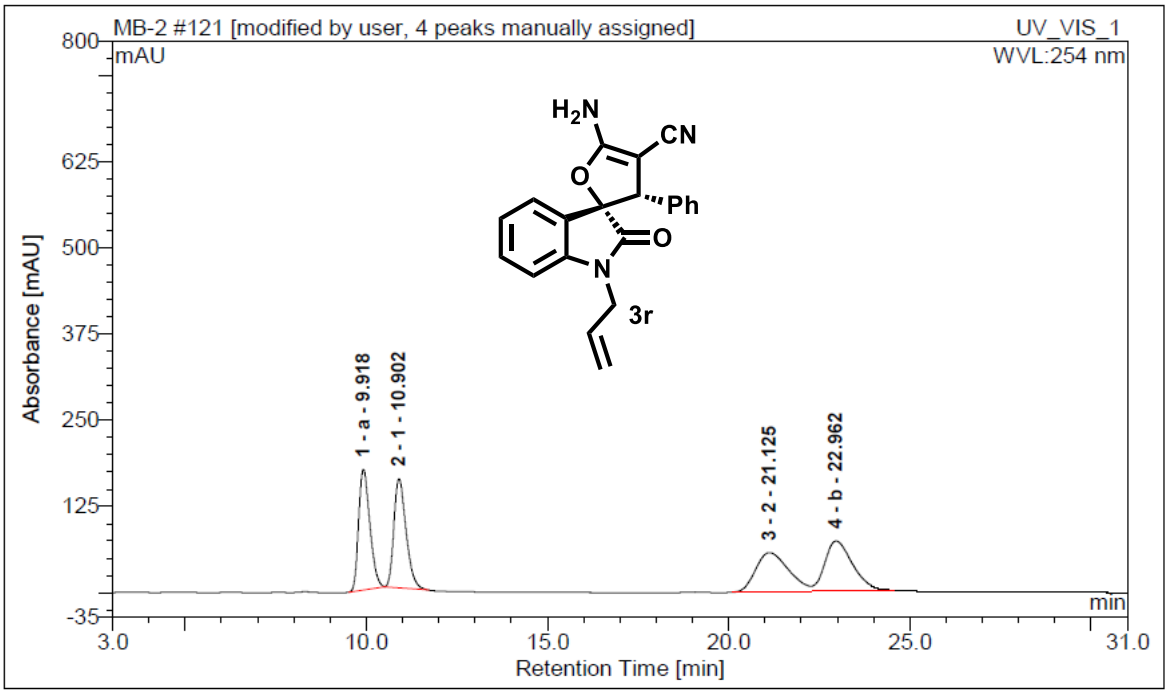
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.80	27.38627	9.285399067	33.21481	n.a.
2	1	16.76	10.28322	3.486555423	10.48825	n.a.
3	b	29.42	97.90333	33.19442108	40.9387	n.a.
4	2	55.94	159.366	54.03362443	41.085	n.a.



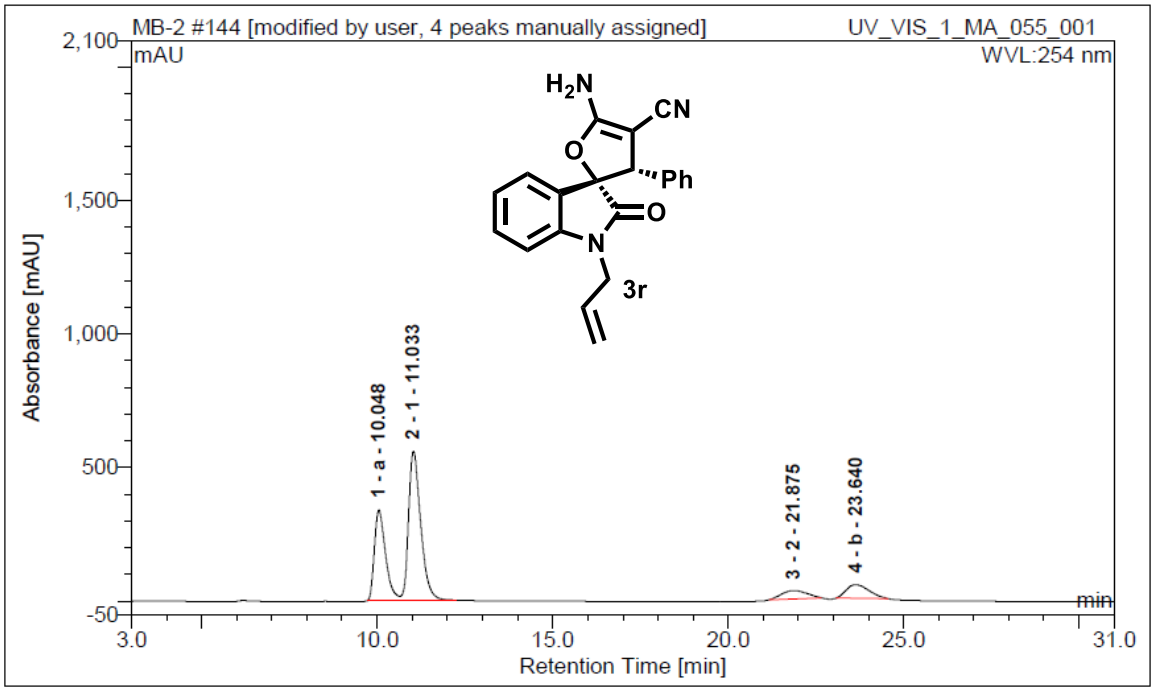
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	8.77	102.9829	26.72802078	274.0136	n.a.
2	1	9.79	87.2976	22.65709375	230.7515	n.a.
3	2	19.42	87.58357	22.7313138	96.16198	n.a.
4	b	22.14	107.435	27.88357168	92.679	n.a.



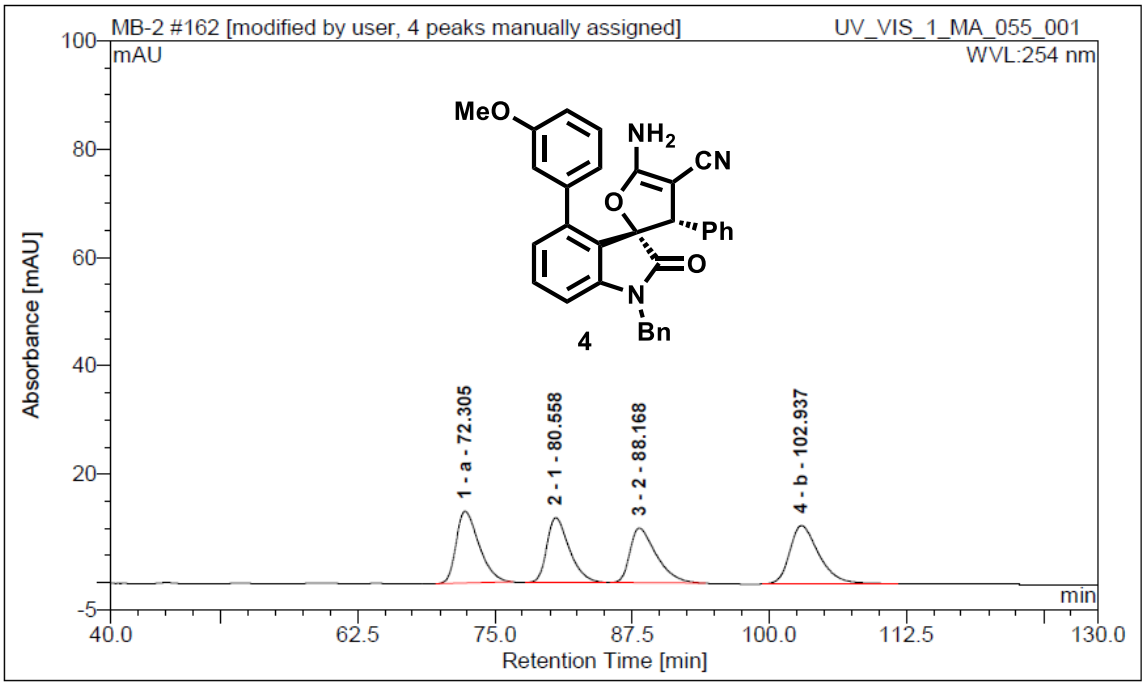
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	8.78	73.11059	35.11266856	187.2909	n.a.
2	1	9.76	103.0531	49.49307531	256.9695	n.a.
3	2	19.46	12.26204	5.889065203	15.60621	n.a.
4	b	22.18	19.791	9.505190924	19.767	n.a.



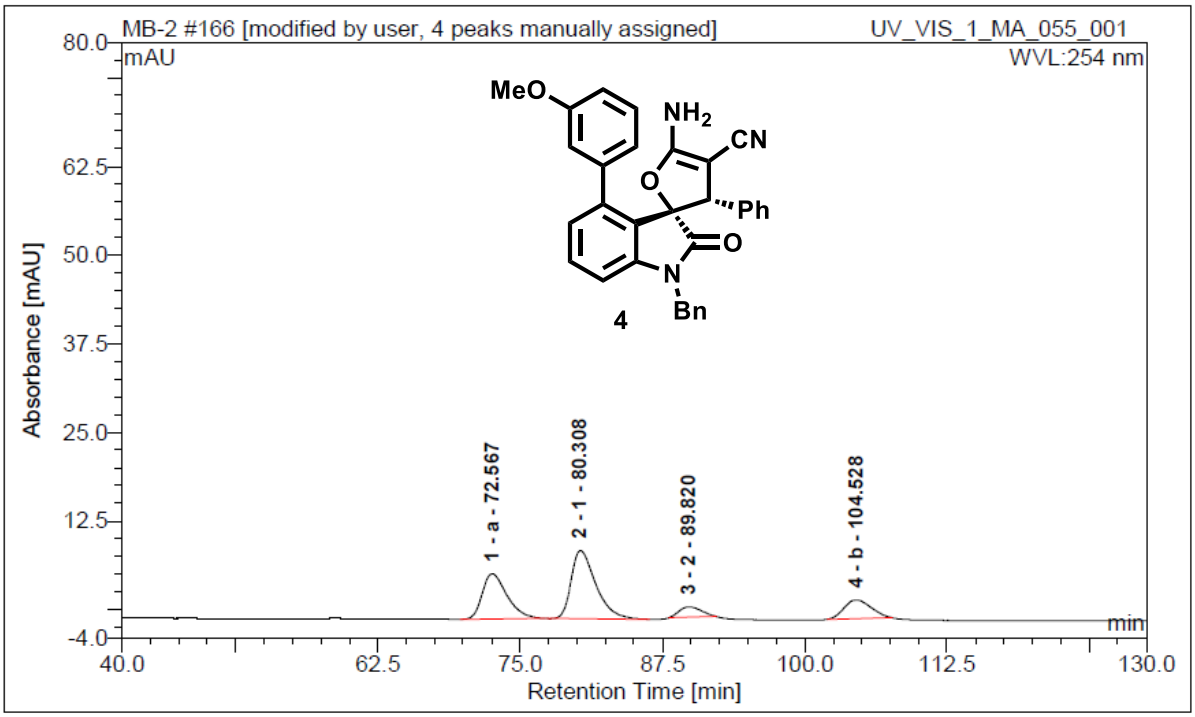
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	9.92	62.69203	25.1007768	174.9555	n.a.
2	1	10.90	61.85587	24.7659924	157.9427	n.a.
3	2	21.13	61.42924	24.59517651	57.47426	n.a.
4	b	22.96	63.784	25.53805429	72.067	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.05	123.9033	30.0424061	339.6024	n.a.
2	1	11.03	224.7231	54.4878297	557.3205	n.a.
3	2	21.88	25.6278	6.213883961	30.81872	n.a.
4	b	23.64	38.174	9.255880241	50.794	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	72.31	32.14397	26.27168845	13.25209	n.a.
2	1	80.56	28.58012	23.35891001	11.93825	n.a.
3	2	88.17	28.28625	23.11872247	10.09305	n.a.
4	b	102.94	33.342	27.25067907	10.738	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	72.57	16.11166	31.66369477	6.37993	n.a.
2	1	80.31	24.21518	47.58927105	9.65086	n.a.
3	2	89.82	3.30546	6.496107787	1.48544	n.a.
4	b	104.53	7.251	14.2509264	2.625	n.a.

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