Ni-catalyzed Enantioselective Reductive Arylcyanation/Cyclization of *N*-(2-iodo-aryl) Acrylamide

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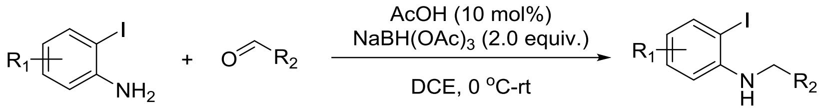
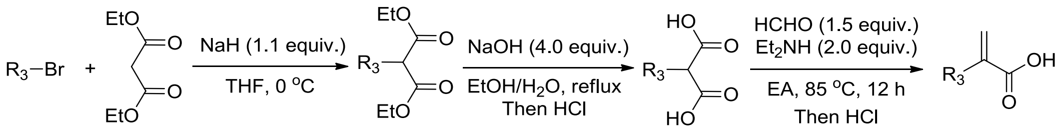
1. General information

All oxygen- and moisture-sensitive manipulations were carried out under an inert N_2 atmosphere using standard Schlenk techniques or glovebox. THF, DMA, toluene, dichloromethane were purified by passing through a neutral alumina column under argon atmosphere. The water is re-steamed under argon. MPMN were prepared according to the procedure reported in literature [S1] and the characterization data are consistent with the literature. All other chemicals and solvents were used as received. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR,^{32}P NMR spectra were recorded on Zhongke-Niujin 500, Bruker DRX500 and Varian 600 NMR spectrometers at ambient temperature with $CDCl_3$ as solvent. ^{13}C shifts were obtained with ^{1}H decoupling. Chemical shifts and coupling constants are listed in ppm and Hz, respectively. HRMS were recorded on a Bruker Daltonics maXis Impact + 1290 infinity mass spectrometer at the Center for Mass Spectrometry, East China Normal University. The absolute configuration was determined by single crystal X-ray diffraction analysis on Rigaku XtaLAB PRO MM003-DS dual system with a Cu micro-focus source. Optical rotation was determined using $CHCl_3$ and as the solvent on INESA WZZ-3. Enantiomeric ratios were determined by chiral HPLC (SHIMADZU LC-20) with ^{n}hexane and ^{i}PrOH as solvents. Optical rotation was recorded on a Perkin Elmer 341 polarimeter. High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF LC/MS spectrometer.

2. General experimental procedures of preparing *α,β*-saturated amides (1a-1y) and characterization data of substrates



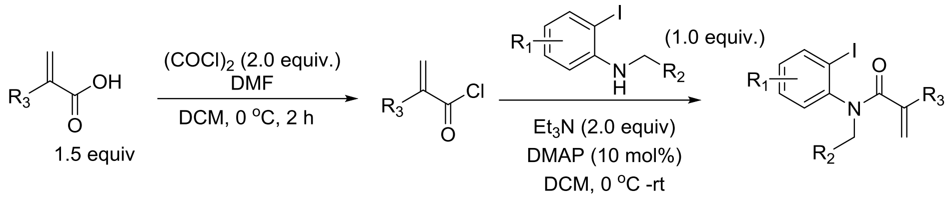
To a 100-mL round-bottom flask charged with 2-iodoaniline (20.0 mmol, 1.0 equiv.), aldehyde (24.0 mmol, 1.2 equiv) and dry 1,2-dichloroethane (30 mL) was added glacial acetic acid (120 μL, 2.0 mmol, 10 mol%) at room temperature. The reaction was stirred at this temperature for 1 h. Then $NaBH(OAc)_3$ (8.5 g, 40.0 mmol, 2.0 equiv.) was added protionwise at 0 °C. The mixture was allowed to stir at ambient temperature for 12 h. The resulting reaction mixture was cooled to 0 °C and the water (5 mL) was added. The mixture was diluted with ethyl acetate (15 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica using petroleum ether/ethyl acetate (20: 1, v/v) as the eluent to afford the corresponding amine.



The preparation of amine was adapted from literature procedures. [S2] To a 250-mL round-bottom flask was charged with diethyl malonate (40.0 mmol, 1.0 equiv.) and THF (100.0 mL). NaH (1.92 g, 48 mmol, 60% dispersion in mineral oil, 1.2 equiv.) was added at 0 °C. The reaction was stirred at this temperature for 1 h. Then alkyl bromide (44 mmol, 1.1 equiv.) was added carefully at 0 °C. The mixture was allowed to stir at rt for 12 h. After the reaction mixture was allowed to cool to 0 °C, saturated aq. NH_4Cl (2 mL) was then added. The reaction mixture was diluted with EA (50 mL x 3) and H_2O (50 mL). The combined ethereal solution was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude diester was used for the next step without further purification.

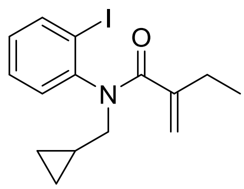
To the EtOH (80 mL) solution of the crude diester was slowly added aqueous NaOH (6.4 g, 160 mmol, 4.0 equiv.) and H_2O (30 mL). The solution was heated in an oil bath at 120 °C and stirred at this temperature for 5 h. The reaction mixture was cooled down to 0 °C, acidized with HCl (3.0 M) until pH=1, and extracted with diethyl ether (3 × 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the crude diacid was used for the next step without further purification.

To a 250-mL round-bottom flask was charged with crude diacid and ethyl acetate (100 mL). Then, Et_2NH (5.84 g, 80 mmol, 2.0 equiv.) and HCHO (5.14 g, 60 mmol, 35 wt% aq. solution, 1.5 equiv.) was added at 0 °C. The reaction was stirred at this temperature for 30 min. Then the solution was heated in an oil bath at 85 °C and stirred at this temperature for 12 h. The reaction mixture was cooled down to 0 °C, acidized with HCl (3.0 M) until pH=1, and extracted with diethyl ether (3 × 50 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using petroleum ether/ethyl acetate (5:1 → 1:1, v/v) as the eluent to afford the corresponding acrylic acid.

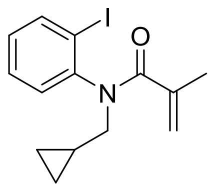


The procedure of preparing amide was adapted from literature procedures. [S3] To a 100-mL round-bottom flask was successively charged with acrylic acid (15.0 mmol, 1.5 equiv), a drop of DMF, dichloromethane (40.0 mL) and $(COCl)_2$ (3.8 g, 30 mmol, 2.0 equiv.) at 0 °C. The reaction was stirred at this temperature for 1 h. The excess of $(COCl)_2$ was removed under reduced pressure and the corresponding crude acryloyl chloride was afforded. To another 100-mL round-bottom flask was charged with the dichloromethane solution (30 mL) of amine (10.0 mmol, 1.0 equiv.) and Et_3N (2.0 g, 20.0 mmol, 2.0 equiv.). Afterwards, crude acryloyl chloride was added at 0 °C. The mixture was stirred at room temperature for 6 h. The reaction mixture was cooled down to 0 °C. Then saturated aqueous NH_4Cl (10 mL) was added. The reaction mixture was diluted with dichloromethane (50 mL x 3) and H_2O (50 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using petroleum ether/ethyl acetate (20:1 → 10:1, v/v) as the eluent to afford the corresponding amide. The obtained fractional ^{1}H count in ^{1}H NMR spectra of **1a-y** is due to the presence of rotatmer.

N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-methylenebutanamide (1a): White solid, 3.05 g, 86% yield. ratio of the rotamers 14:86 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 5.43-5.30 (m, 2H, minor), 5.10-4.95 (m, 2H, major),, 4.26 (dd, *J* = 13.2, 6.2 Hz, 1H, major), 3.70 (s, br, 1H, minor), 3.42 (s, br, 1H, minor), 3.01 (dd, *J* = 13.2, 7.2 Hz, 1H, major), 2.47 (s, br, 2H, minor), 2.31 – 2.16 (m, 2H, major), 1.21 (s, br, 4H, minor), 1.00 (t, *J* = 6.6 Hz, 4H, major), 0.47 – 0.39 (m, 2H), 0.21 (s, br, 1H), 0.02 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 146.2, 145.1, 140.0, 131.5, 129.1, 128.6, 115.7, 100.1, 52.6, 26.7, 11.9, 9.4, 4.6, 2.8. HRMS (ESI) calcd. for $C_{15}H_{18}INNaO$ ($[M+Na]^+$) 378.0325, found 378.0324.

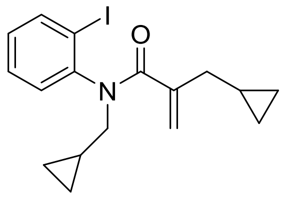


N-(cyclopropylmethyl)-N-(2-iodophenyl)methacrylamide (1b) (CAS: 2235399-21-8) [S4]: White solid, 2.97 g, 87% yield. ratio of the rotamers 10:90 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.34 - 5.29 (m, 2 H, minor), 5.03 - 4.96 (m, 2H, major), 4.16 (d, *J* = 7.2 Hz, 1H, major), 3.67 (s, br, 1H, minor), 3.40 (s, br, 1H, minor), 3.06-3.03 (m, 1H, major), 2.09 (s, br, 3H, minor), 1.84 (s, 3H, major), 1.01 (s, 1H), 0.48 – 0.35 (m, 2H), 0.17 (s, br, 1H), -0.01 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 145.2, 140.5, 140.0, 131.3, 129.1, 128.7, 118.4, 100.1,

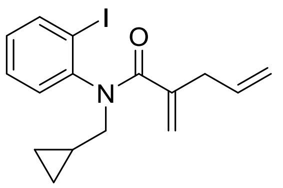


52.8, 20.7, 9.3, 4.6, 2.9. HRMS (ESI) calcd. for $C_{14}H_{16}INNaO$ ([M+Na]$^+$) 364.0169, found 364.0164.

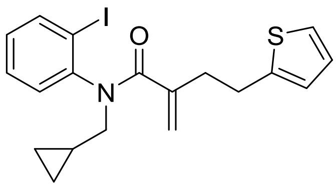
N'-bis(cyclopropylmethyl)-N-(2-iodophenyl)acrylamidec (1c): Colorless oil, 2.51 g, 66% yield. ratio of the rotamers 15:85 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.44 (s, br,2H, minor),5.12- 5.06 (m, 2H, major), 4.26 (dd, *J* = 13.8, 6.3 Hz, 1H, major), 3.71 (s, br, 1H, minor), 3.51 (s, br, 1H, minor), 2.99 (dd, *J* = 13.8, 7.5 Hz, 1H, major), 2.32 (s, 2H, minor), 2.20 -2.07 (m, 2H, major), 1.01 (s, 1H), 0.74 (s, 1H), 0.63 – 0.35 (m, 4H), 0.20 (s, 1H), 0.07 (s, 1H), 0.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 145.2, 144.4, 139.9, 131.6, 129.0, 128.5, 116.7, 100.1, 52.6, 38.6, 9.3, 8.8, 4.7, 4.54, 4.47, 2.8. HRMS (ESI) calcd. for $C_{17}H_{20}INNaO$ ([M+Na]$^+$) 404.0482, found 404.0480.



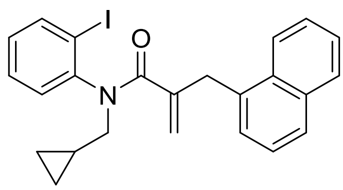
N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-methylenepent-4-enamide (1d): Colorless oil, 1.98 g, 54% yield. ratio of the rotamers 13:87 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.20 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 5.90 (s, br, 1H, minor), 5.77 – 5.57 (m, 1H, major), 5.51 – 5.25 (m, 4H, minor), 5.20 – 4.81 (m, 4H, major), 4.17 (dd, *J* = 13.2, 6.2 Hz, 1H, major), 3.63 (s, 1H, minor), 3.42 (s, 3H, minor), 3.25 – 2.74 (m, 3H, major), 0.97 (s, 1H), 0.41 - 0.35 (m, 2H), 0.15 (s, 1H), -0.03 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 144.9, 142.9, 139.9, 134.5, 131.4, 129.1, 128.6, 117.9, 117.3, 100.1, 52.7, 37.9, 9.3, 4.5, 2.8. HRMS (ESI) calcd. for $C_{16}H_{18}INNaO$ ([M+Na]$^+$) 390.0325, found 390.0317.



N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-methylene-4-(thiophen-2-yl)butanamide (1e): Faint yellow oil 2.66 g, 61% yield**.** ratio of the rotamers 11:89 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 4.8 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.81 (s, br 1H), 6.69 (s, br 1H), 5.40 – 5.26 (m, 1H, minor) 5.07- 4.93 (m, 2H, major), 4.16 (dd, *J* = 13.8, 6.2 Hz, 1H, major), 3.52 (s, 1H, minor), 3.30 (s, 1H, major), 3.09 (s, 3H, minor), 3.01 - 2.88 (m, 3H, major), 2.81 – 2.63 (m, 2H, minor), 2.52-2.42 (m, 2H, major), 0.93 (s, 1H), 0.36 – 0.32 (m, 2H), 0.12 (s, 1H), -0.08 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 144.9, 144.1, 143.4, 140.0, 131.5, 129.1, 128.7, 126.6, 124.3, 123.0, 117.9, 100.1, 52.7, 35.7, 28.3, 9.3, 4.6, 2.8. HRMS (ESI) calcd. for $C_{19}H_{20}INNaOS$ ([M+Na]$^+$) 460.0202, found 460.0198.

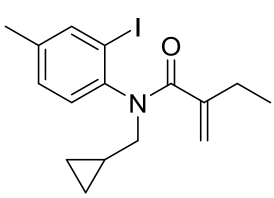


N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-(naphthalen-1-ylmethyl)acrylamide (1f): White solid, 3.69 g, 79% yield. ratio of the rotamers 7:93 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.65 (m, 4H), 7.45 – .32 (m, 4H), 6.90 – 6.79 (m, 2H), 6.29 (d, *J* = 7.8 Hz, 1H), 5.47 (s, 1H, minor), 5.19 (s, 1H, minor), 5.06 (s, 1H, major), 4.68 (s, 1H, major), 4.28 – 3.97 (m, 3H), 3.28 – 3.20 (m, 1H, minor),

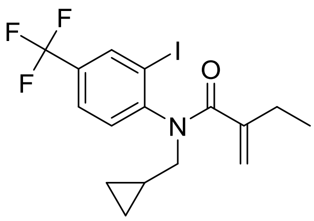


2.95 (dd, J = 13.8, 7.5 Hz, 1H, major), 0.88 – 0.86 (m, 1H), 0.35 – 0.31 (m, 2H), 0.18 – 0.17 (m, 1H), 0.07 – -0.08 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 144.6, 143.1, 139.8, 133.8, 133.7, 132.4, 131.5, 128.9, 128.5, 128.4, 128.3, 127.4, 125.8, 125.54, 125.49, 124.5, 118.0, 99.9, 52.6, 37.7, 9.2, 4.5, 2.8. HRMS (ESI) calcd. for $C_{24}HINNaO$ ($[M+Na]^+$) 490.0638, found 490.0639.

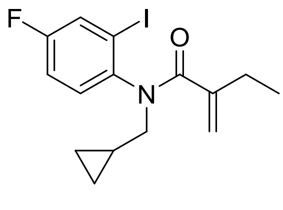
N-(cyclopropylmethyl)-N-(2-iodo-4-methylphenyl)-2-methylenebutanamide (1g): Faint yellow oil, 2.89 g, 78% yield**.** ratio of the rotamers 10:90 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.10 (s, br, 2H), 5.37 - 5.20 (m, 2H, minor) 5.08 - 4.92 (m, 2H, major), 4.21 (dd, J = 13.8, 6.5 Hz, 1H, major), 3.64 (s, 1H, minor), 3.37 (s, 1H, minor), 2.95 (dd, J = 13.2, 7.5 Hz, 1H, major), 2.31 (s, 3H), 2.22 – 2.18 (m, 2H), 0.99 – 0.96 (m, 4H), 0.43 – 0.37 (m, 2H), 0.18 (s, br, 1H), -0.01 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 146.3, 142.3, 140.3, 139.3, 130.9, 129.3, 115.4, 99.9, 52.6, 26.7, 20.4, 11.9, 9.3, 4.6, 2.8. HRMS (ESI) calcd. for $C_{16}H_{20}INNaO$ ($[M+Na]^+$) 392.0482, found 392.0482.



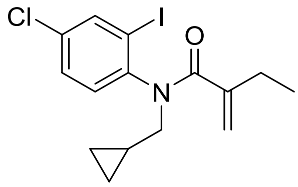
N-(cyclopropylmethyl)-N-(2-iodo-4-(trifluoromethyl)phenyl)-2-methylenebutanamide (1h): Colorless oil, 2.68 g, 62% yield. ratio of the rotamers 25:75 ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 5.42 – 5.30 (m, 1H, minor) 5.05– 5.00 (m, 2H, major), 4.26 (dd, J = 13.5, 6.1 Hz, 1H, major), 3.69 (s, br, 1H, minor), 3.42 (s, br, 1H, minor), 2.99 (dd, J = 13.5, 7.5 Hz, 1H, major), 2.45 – 2.40 (m, 2H, minor), 2.22 (q, J = 5.5 Hz, 2H, major), 1.28 – 1.12 (m, 1H), 1.00 (t, J = 6.0 Hz, 3H), 0.47 – 0.42 (m, 2H), 0.18 (s, br, 1H), -0.05 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 148.7, 145.9, 137.1, 131.5, 130.9 (q, J_{CF} = 33.15 Hz), 125.7, 122.6 (q, J_{CF} = 269.25 Hz), 116.5, 100.1, 52.6, 26.7, 11.8, 9.4, 4.7, 2.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.46. HRMS (ESI) calcd. for $C_{16}H_{17}F_3INNaO$ ($[M+Na]^+$) 446.0199, found 446.0198.



N-(cyclopropylmethyl)-N-(4-fluoro-2-iodophenyl)-2-methylenebutanamide (1i): White solid, 2.76 g, 74% yield. ratio of the rotamers 20:80 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.5, 2.5 Hz, 1H), 7.21 (dd, J = 8.5, 5.5 Hz, 1H), 7.08 – 7.04 (m, 1H), 5.38 – 5.29 (m, 1H, minor), 5.07 – 4.95 (m, 1H, major), 4.25 (dd, J = 14.0, 6.6 Hz, 1H, major), 3.66 (s, br, 1H, minor), 3.35 (s, br, 1H, minor), 2.92 (dd, J = 14.0, 7.8 Hz, 1H, major), 2.44 (s, br, 2H, minor), 2.26 – 2.15 (m, 2H, major), 1.28 – 1.16 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H), 0.46 – 0.41 (m, 2H), 0.20 – 0.17 (m, 1H), -0.01 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 160.7 (d, J_{CF} = 251.7 Hz), 146.1, 141.3, 131.9, 126.6 (d, J_{CF} = 24.3 Hz), 115.6, 115.6 (d, J_{CF} = 19.8 Hz), 99.9, 52.5, 26.6, 11.8, 9.2, 4.6, 2.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.37. HRMS (ESI) calcd. for $C_{15}H_{17}FINNaO$ ($[M+Na]^+$) 396.0231, found 396.0233.

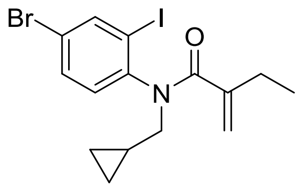


N-(4-chloro-2-iodophenyl)-N-(cyclopropylmethyl)-2-methylenebutanamide (1j):



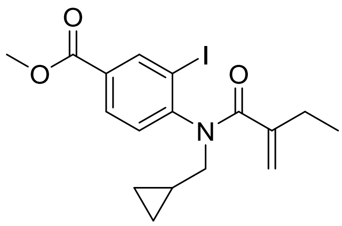
Colorless oil 3.15 g, 81% yield. ratio of the rotamers 15:85 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 5.37 – 5.30 (m, 2H, minor), 5.07 - 5.00 (m, 2H, major), 4.22 (d, *J* = 7.2 Hz, 1 H, major), 3.67 (s, br, 1H, minor), 3.36 (s, br, 1H, minor), 2.97 (s, br, 1H, major), 2.41 (s, br, 2H, minor), 2.20 (s, br, 2H, major), 1.17 – 0.99 (m, 4H), 0.46 – 0.42 (m, 2H), 0.18 (s, br, 1H), -0.01 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 146.0, 143.8, 139.2, 133.8, 131.8, 128.8, 115.9, 100.3, 52.5, 26.6, 11.8, 9.3, 4.6, 2.7. HRMS (ESI) calcd. for $C_{15}H_{17}{}^{35}ClINNaO$ ($[M+Na]^+$) 411.9936, found 411.9930; calcd. for $C_{15}H_{17}{}^{37}ClINNaO$ ($[M+Na]^+$) 419.9936, found 419.9930.

N-(4-bromo-2-iodophenyl)-N-(cyclopropylmethyl)-2-methylenebutanamide (1k):



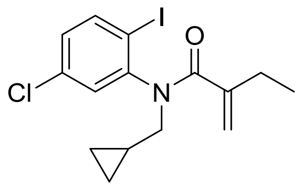
Faint yellow oil, 2.72 g, 63% yield**.** ratio of the rotamers 16:84 ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.46 (d, *J* = 6.6 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 5.37 – 5.29 (m, 2H, minor), 5.06–4.96 (m, 2H, major), 4.21 (s, br, 1H, major), 3.66 (s, br, 1H, minor), 3.37 (s, br, 1H, minor), 2.96 (s, br, 1H, major), 2.42 (s, br, 2H, minor), 2.20 (s, br, 2H, major), 1.17 – 0.99 (m, 4H), 0.42 (d, *J* = 7.2 Hz, 2H), 0.18 (s, br, 1H), -0.01 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 145.9, 144.3, 141.9, 132.2, 131.8, 121.7, 116.0, 100.8, 52.5, 26.6, 11.8, 9.3, 4.6, 2.7. HRMS (ESI) calcd. for $C_{15}H_{17}{}^{79}BrINNaO$ ($[M+Na]^+$) 455.9430, found 455.9426.

Methyl-4-(N-(cyclopropylmethyl)-2-methylene-butanamido)-3-iodobenzoate (1l):



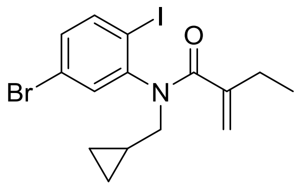
White solid, 3.26 g, 79% yield. ratio of the rotamers 14:86 ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.98 (d, *J* = 6.6 Hz, 1H), 7.28 (d, *J* = 6.6 Hz, 1H), 5.37 – 5.29 (m, 2H, minor), 5.05– 4.94 (m, 2H, major), 4.23 (s, br, 1H, major), 3.92 (s, 3H), 3.67 (s, br, 1H, minor), 3.42 (s, br, 1H, minor), 3.02 (s, br, 1H, major), 2.43 – 2.21 (m, 2H), 1.17 – 0.98 (m, 4H), 0.44 – 0.37 (m, 2H), 0.16 (s, br, 1H), -0.06 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 164.9, 149.4, 146.0, 141.2, 131.2, 130.6, 129.8, 116.3, 99.6, 52.6, 52.5, 26.6, 11.8, 9.3, 4.7, 2.8. HRMS (ESI) calcd. for $C_{17}H_{20}INNaO_3$ ($[M+Na]^+$) 436.0380, found 436.0368.

N-(5-chloro-2-iodophenyl)-N-(cyclopropylmethyl)-2-methylenebutanamide (1m):

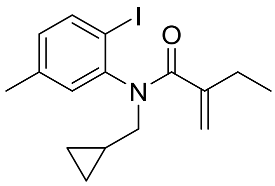


White solid, 3.00 g, 77% yield. ratio of the rotamers 18:82 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.22 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 5.38 -5.28 (m, 2H, minor) 5.04– 4.96 (m, 2H, major), 4.18 (s, br, 1H, major), 3.63 (s, br, 1H, minor), 3.39 (s, br, 1H, minor), 2.99 (s, br, 1H, major), 2.41 – 2.22 (m, 2H), 1.41 – 0.99 (m, 4H), 0.45 – 0.40 (m, 2H), 0.18 (s, br, 1H), -0.03 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 146.3, 145.9, 140.5, 134.4, 131.5, 129.2, 116.2, 97.4, 52.5, 26.7, 11.9, 9.3, 4.6, 2.8. HRMS (ESI) calcd. for $C_{15}H_{17}{}^{35}ClINNaO$ ($[M+Na]^+$) 411.9936, found 411.9926.

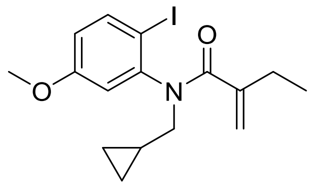
N-(5-bromo-2-iodophenyl)-N-(cyclopropylmethyl)-2-methylenebutanamide (1n): White solid, 2.68 g, 62% yield. ratio of the rotamers 20:80 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 5.40 – 5.30 (m, 2H, minor), 5.05– 4.98 (m, 2H, major), 4.21 (dd, *J* = 14.5, 6.5 Hz, 1H, major), 3.62 (s, br, 1H, minor), 3.40 (s, br, 1H, minor), 2.98 (dd, *J* = 14.0, 7.8 Hz, 0.1H, major), 2.44 (s, 2H, minor), 2.27 – 2.20 (m, 2H, major), 1.25 – 1.17 (m, 1H), 1.01 (t, *J* = 7.0 Hz, 3H), 0.48 – 0.42 (m, 2H), 0.19 (s, br, 1H), -0.01 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 146.6, 145.9, 140.9, 134.4, 132.2, 122.0, 116.3, 98.3, 52.6, 26.8, 11.9, 9.3, 4.6, 2.8. HRMS (ESI) calcd. for $C_{15}H_{17}{}^{79}BrINNaO$ ([M+Na]$^+$) 455.9430, found 455.9431.



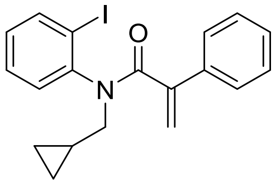
N-(cyclopropylmethyl)-N-(2-iodo-5-methylphenyl)-2-methylenebutanamide (1o): White solid, 3.21 g, 87% yield. ratio of the rotamers 17:83 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 1H), 7.11 – 7.04 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.40 – 5.27(m, 2H, minor), 5.07– 4.93 (m, 2H, major), 4.20 (dd, *J* = 14.0, 6.7 Hz, 1H, major), 3.61 (s, br, 1H, minor), 3.41 (s, br, 1H, minor), 2.99 (dd, *J* = 14.0, 7.6 Hz, 1H, major), 2.44 – 2.43 (m, 2H, minor), 2.30 (s, br, 3H), 2.26 – 2.15 (m, 2H, major), 1.25 – 0.97 (m, 4H), 0.45 – 0.37 (m, 2H), 0.21 – 0.19 (m, 1H), -0.01 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 146.2, 144.9, 139.5, 138.9, 132.3, 130.0, 115.6, 95.8, 52.6, 26.7, 20.8, 11.9, 9.4, 4.5, 2.8. HRMS (ESI) calcd. for $C_{16}H_{20}INNaO$ ([M+Na]$^+$) 392.0482, found 392.0475.



N-(cyclopropylmethyl)-N-(2-iodo-5methoxyphenyl)-2-methylenebutanamide (1p): Faint yellow oil, 3.12 g, 81% yield. ratio of the rotamers 13:87 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 6.80 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.40 – 5.26 (m, 2 H, minor), 5.09 – 4.94 (m, 2H, major), 4.21 – 4.19 (m, 1H, major), 3.77 (s, 3H), 3.65 (s, br, 1H, minor), 3.39 (s, br, 1H, minor), 3.00 – 2.97 (m, 1H, major), 2.43 – 2.39 (m, 2H, minor), 2.24 – 2.20 (m, 2H, major), 1.16 – 0.99 (m, 4H), 0.42 – 0.41 (m, 2H), 0.19 (s, br, 1H), 0.02 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 160.0, 146.1, 145.9, 134.0, 124.6, 117.8, 115.7, 115.0, 88.4, 55.5, 52.6, 26.8, 11.9, 9.4, 4.6. HRMS (ESI) calcd. for $C_{16}H_{20}INNaO_2$ ([M+Na]$^+$) 408.0431, found 408.0430.

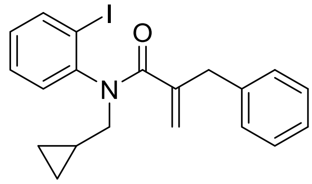


N-(cyclopropylmethyl)-N-(2-iodophenyl)-2phenylacrylamide (1q): Faint yellow oil 3.62 g, 90% yield. ratio of the rotamers 14:86 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H, minor), 7.75 (dd, *J* = 7.8, 1.1 Hz, 1H, major), 7.64 (d, *J* = 7.8 Hz, 1H, minor), 7.45 – 7.41 (m, 1H, major), 7.24 – 7.14 (m, 4H), 7.03 – 6.96 (m, 1H, minor), 7.00 – 6.97 (m, 1H), 6.79 – 6.78 (m, 1H), 5.84 (s, 1H, minor), 5.66 (s, 1 H, minor), 5.59 (s, 1H, major), 5.32 (s, 1H, major), 4.30 (dd, *J* = 13.8, 7.2 Hz, 1H, major), 3.57 (dd, *J* = 14.4, 6.6 Hz, 1H. minor), 3.30 (dd, *J* = 14.4, 6.6 Hz, 1H, minor), 3.02 (dd, *J* =

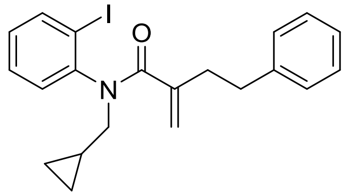


13.8, 7.2 Hz, 1H, major), 1.06 – 0.75 (m, 1H), 0.48 – 0.39 (m, 2H), 0.33 – 0.25 (m, 1H), 0.08 – 0.02 (m, 1H, major), -0.22 – -0.23 (m, 1H, minor). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 145.7, 143.6, 139.6, 137.0, 131.6, 129.0, 128.2, 128.0, 127.9, 125.9, 116.2, 100.3, 52.1, 9.4, 4.5, 2.9. HRMS (ESI) calcd. for $C_{19}H_{18}INNaO$ ([M+Na]$^+$) 426.0325, found 426.0320.

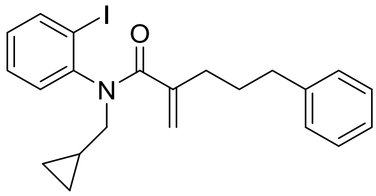
2-benzyl-N-(cyclopropylmethyl)-N-(2-iodophenyl)acrylamide (1r): White solid, 2.87 g, 69% yield. ratio of the rotamers 8:92 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.10 (d, *J* = 6.0 Hz, 3H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 7.2 Hz, 1H), 5.46 – 5.25 (m, 2H, minor), 5.01 - 4.82 (m, 2H, major), 4.24 (dd, *J* = 13.8, 6.5 Hz, 1H), 3.77 (d, *J* = 14.4 Hz, 1H), 3.40 (d, *J* = 15.0 Hz, 1H), 2.95 (dd, *J* = 13.8, 7.4 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 1H), 0.37 – 0.32 (m, 2H), 0.19 (s, br, 1H), -0.07 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 144.9, 143.9, 139.8, 138.0, 131.6, 129.7, 129.0, 128.6, 128.4, 126.5, 117.6, 99.9, 52.7, 40.8, 9.2, 4.5, 2.8. HRMS (ESI) calcd. for $C_{20}H_{20}INNaO$ ([M+Na]$^+$) 440.0482, found 440.0473.



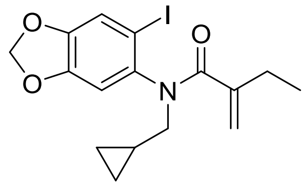
N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-methylene-4-phenylbutanamide (1s): Colorless oil, 3.19 g, 74% yield. ratio of the rotamers 13:87 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.34 – 19 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.52 – 5.21 (m, 2H, minor), 5.16 – 5.02 (m, 2H, major), 4.28 (dd, *J* = 13.8, 6.0, 1H, major), 3.64 (s, br, 1H, minor), 3.41 (s, br, 1H, minor), 3.04 (dd, *J* = 13.2, 7.2 Hz, 1H, major), 2.79 – 2.75 (m, 2H), 2.55 – 2.47 (m, 1.78H), 1.04 (s, br, 1H), 0.47 – 0.41 (m, 2H), 0.23 (s, br, 1H), 0.03 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 144.9, 144.1, 141.4, 140.0, 131.6, 129.1, 128.6, 128.3, 128.2, 125.8, 117.4, 100.2, 52.7, 35.4, 34.0, 9.3, 4.6, 2.8. HRMS (ESI) calcd. for $C_{21}H_{22}INNaO$ ([M+Na]$^+$) 454.0638, found 454.0633.



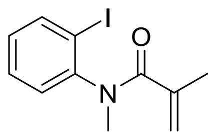
N-(cyclopropylmethyl)-N-(2-iodophenyl)-2-methylene-5-phenylpentanamide (1t): Colorless oil, 3.07g, 69% yield. ratio of the rotamers 13:87 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 3H), 7.21 – 7.17 (m, 3H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.46 – 5.45 (m, 2H, minor), 5.17 - 4.98 (m, 2H, major), 4.27 (dd, *J* = 13.8, 6.2 Hz, 1H, major), 3.69 (s, br, 1H, minor), 3.40 (s, br, 1H, minor), 3.01 (dd, *J* = 13.8, 7.5 Hz, 1H, major), 2.73 (s, br. 2H, minor), 2.66 – 2.60 (m, 2H, major), 2.49 (s, 2H, minor), 2.24 – 2.15 (m, 2H, major), 1.97 (s, br, 2H, minor), 1.84 – 1.74 (m, 2H, major), 1.02-0.91 (m, 1H), 0.45 – 0.42 (m, 2H), 0.22 (s, br, 1H), 0.02 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 144.8, 144.7, 142.0, 139.9, 131.6, 129.1, 128.5, 128.4, 128.2, 125.7, 116.9, 100.1, 52.6, 35.3, 33.3, 29.3, 9.3, 4.5, 2.7. HRMS (ESI) calcd. for $C_{22}H_{24}INNaO$ ([M+Na]$^+$) 468.0795, found 468.0791



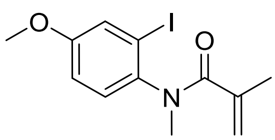
N-(cyclopropylmethyl)-N-(6-iodobenzo[d][1,3]dioxol-5-yl)-2-methylenebutenanamide (1u): Faint yellow oil, 2.95 g, 74% yield. ratio of the rotamers 15:85 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.76 (s, 1H), 6.03 (s, 2H), 5.37 - 5.30 (m, 1H, minor), 5.27 (s, br, 1H, minor), 5.11 (s, br, 1H, major), 4.98 (s, br, 1H, major), 4.20 – 4.18 (m, 1H, major), 4.17 – 4.02 (m, 1H, minor), 3.64 (s, br, 1H, minor), 3.34 (s, br, 1H, minor), 3,13 – 3.09 (m, 1H, minor), 2.96 – 2.92 (m, 1H, major), 2.43 – 2.23 (m, 2H), 1.16 – 1.00 (m, 4H), 0.46 – 0.43 (m, 2H), 0.21 (s, br, 1H), 0.07 (s, br, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.6, 148.3, 147.7, 146.2, 138.8, 118.1, 115.4, 111.5, 102.3, 88.9, 52.7, 26.7, 11.9, 9.4, 4.7, 2.9. HRMS (ESI) calcd. for $C_{16}H_{18}INNaO_3$ ([M+Na]$^+$) 422.0224, found 422.0223.



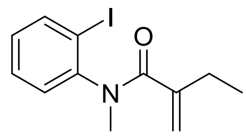
N-(2-iodophenyl)-N-methylmethacrylamide) (1v) (CAS: 154386-63-7) [S5]: White solid, 2.61 g, 87% yield. ratio of the rotamers 9:91 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 1H), 7.35 (s, br, 1H), 7.18 (s, br, 1H), 7.02 – 7.00 (m, 1H), 5.35 (s, br, 1H, minor), 5.05 – 4.98 (m, 2H, major), 3.23 (s, 3H), 2.09 (s, 3H, minor), 1.83 (s, 3H, major). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 146.9, 140.2, 140.1, 129.3, 129.2, 129.1, 119.0, 99.1, 36.8, 20.5. HRMS (ESI) calcd. for $C_{11}H_{12}INNaO$ ([M+Na]$^+$) 323.9856, found 323.9848.



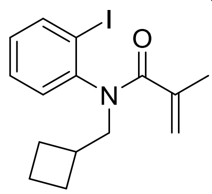
N-(2-iodo-4-methoxyphenyl)-N-methylmethacrylamide (1w) (CAS: 929610-36-6) [S6]: Faint yellow oil, 1.95 g, 59% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 1.80 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 6.89 – 6.86 (m, 1H), 5.33 – 4.99 (m, 2H), 3.80 (s, 3H), 3.26 – 3.21 (m, 3H), 1.97 (s, 0.35H), 1.82 (s, 2.58H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 158.8, 140.2, 139.6, 129.3, 124.6, 118.5, 115.0, 99.3, 55.6, 36.9, 20.6. HRMS (ESI) calcd. for $C_{12}H_{14}INNaO_2$ ([M+Na]$^+$) 353.9961, found 353.9956



N-(2-iodophenyl)-N-methyl-2-methylenebutanamide (1x): Faint yellow oil, 2.87 g, 91% yield. ratio of the rotamers 12:88 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 5.38 – 5.31 (m, 2 H, minor), 5.11– 4.96 (m, 2H, major), 3.30 – 3.22 (m, 3H), 2.46 (s, br, 1H, minor), 2.20– 2.19 (m, 2H, major), 1.19 – 0.96 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 146.7, 145.8, 140.0, 129.4, 129.2, 129.1, 116.2, 99.0, 36.7, 26.3, 11.8. HRMS (ESI) calcd. for $C_{12}H_{14}INNaO$ ([M+Na]$^+$) 338.0012, found 338.0011.

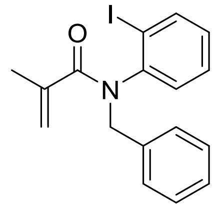


N-(cyclobutylmethyl)-N-(2-iodophenyl)methacrylamide (1y): White solid, 3.12 g, 88% yield. ratio of the rotamers 10:90 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 5.35 (s, br, 2H, minor), 4.98 – 4.93 (m, 2H, major), 4.31 (dd, J = 13.2, 7.8 Hz, 1H, major), 3.84 (s, br, 1H, minor), 3.62 (s, br, 1H,minor), 3.30 (dd, J = 13.2, 7.0 Hz, 1H, major), 2.57 – 2.50 (m, 1H), 2.10 – 1.75 (m, 8H), 1.59 – 1.55 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4,

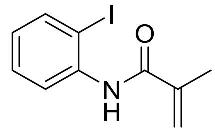


145.0, 140.5, 140.1, 130.9, 129.1, 128.7, 118.1, 99.9, 53.1, 33.9, 26.8, 26.3, 20.7, 18.4. HRMS (ESI) calcd. for $C_{15}H_{18}INNaO$ ($[M+Na]^+$) 378.0325, found 378.0318.

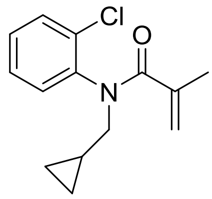
***N*-benzyl-N-(2-iodophenyl)methacrylamide (1z)** Yellow oil, 2.95 g, 76% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.25 (m, 3H), 7.23 – 7.17 (m, 2H), 7.14 (m, 1H), 6.96 (td, *J* = 7.5, 1.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 5.68 (d, *J* = 14.5 Hz, 1H), 5.01 (m, 2H), 4.11 (d, *J* = 14.5 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 144.4, 140.2, 140.1, 136.7, 131.3, 129.4, 129.2, 128.6, 128.3, 127.5, 118.7, 99.9, 51.7, 20.7.



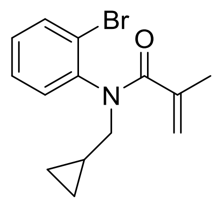
***N*-(2-iodophenyl)-2-methylenebutanamide (1aa)** White solid, 2.57 g, 90% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 1H), 7.96 (s, 1H), 7.79 – 7.76 (m, 1H), 7.37 – 7.33 (m, 1H), 6.87 – 6.83 (m, 1H), 5.97 (s, 1H), 5.53 – 5.52 (m, 1H), 2.12 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 140.3, 138.7, 138.1, 129.3, 125.9, 121.5, 121.0, 90.0, 18.69.



N-(2-chlorophenyl)-2-methylenebutanamide Colorless oil, 1.94 g, 78% yield, ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 4.8 Hz, 1H), 7.27 (s, 3H), 4.96 (d, *J* = 7.2 Hz, 2H), 4.00 (dd, *J* = 13.8, 6.6 Hz, 1H), 3.25 (dd, *J* = 13.2, 7.2 Hz, 1H), 1.83 (s, 3H), 1.68 – 1.66 (m, 1H), 0.99 (s, br, 1H), 0.43 – 0.38 (m, 2H), 0.12 (s, br, 1H), 0.03-0.02 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 140.5, 140.3, 132.9, 131.2, 130.3, 128.7, 127.2, 117.9, 52.5, 20.1, 9.3, 4.1 2.9. HRMS (EI) calcd. for $C_{14}H_{17}{}^{35}ClNO$ ($[M+H]^+$) 250.0993, found 250.0997; calcd. for $C_{14}H_{17}{}^{37}ClNO$ ($[M+H]^+$) 252.0964, found 252.0957.

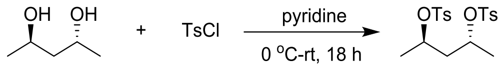


N-(2-bromophenyl)-2-methylenebutanamide Colorless oil, 2.37 g, 81% yield, ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.19 – 7.17 (m, 1H), 5.30 – 4.96 (m, 2H), 4.09 (dd, *J* = 13.2, 6.0 Hz, 0.89 H), 3.78 – 3.71 (m, 0.05H), 3.42 (s, br, 0.05H), 3.16 (dd, *J* = 13.2, 7.2 Hz, 0.90H), 1.84 (s, 3H), 1.00 (s, br, 1H), 0.44 – 0.38 (m, 2H), 0.14 (s, br, 1H), 0.04 – 0.01 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 142.0, 140.4, 133.6, 131.6, 129.0, 127.9, 123.6, 118.1, 52.5, 20.4, 9.3, 4.4, 2.9. HRMS (EI) calcd. for $C_{14}H_{17}{}^{79}BrNO$ ($[M+H]^+$) 294.0488, found 294.0487; calcd. for $C_{14}H_{17}{}^{81}BrNO$ ($[M+H]^+$) 296.0468, found 296.0468.



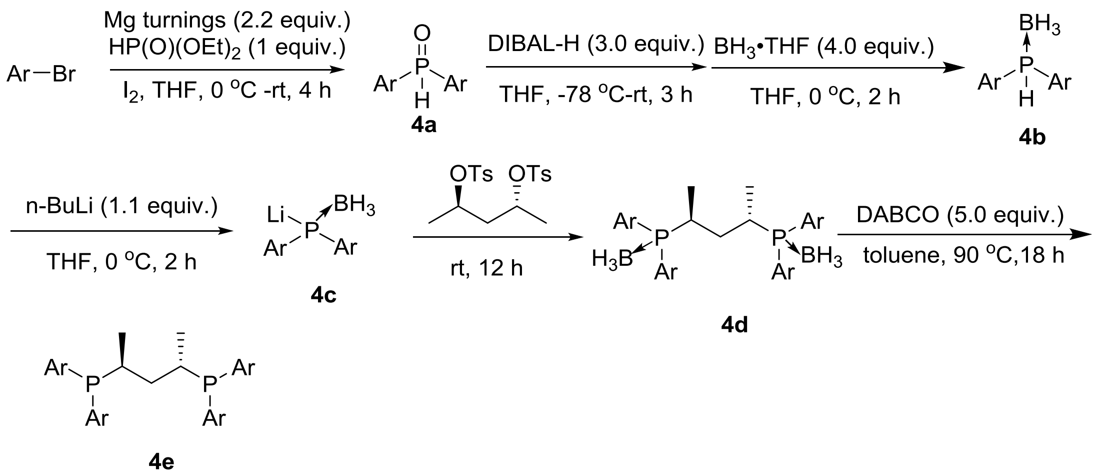
3. General procedures to prepare chiral bidentate phosphine ligand

3.1 General procedures of preparing the skeleton of chiral bidentate phosphine ligands



The procedure of preparing the chiral bidentate phosphine ligand skeleton was adapted from literature. [S7] To a 100-mL round-bottom flask was charged with (*2R,4R*)-pentane-2,4-diol (2.08 g, 20.0 mmol, 1.0 equiv.) and pyridine (50 mL). Afterwards, TsCl (15.20 g, 80 mmol, 4 equiv.) was added slowly at 0 °C. The reaction was stirred at room temperature for 18 h. Then HCl (2 M) was slowly added at 0 °C until the value of pH reached 1. The mixture was stirred at 0 °C for 30 min. Then, water (30 mL) was added for work-up. The reaction mixture was diluted with dichloromethane (50 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using the eluent of petroleum ether/dichloromethane (1:1, v/v) to afford (*2R,4R*)-pentane-2,4-diyl bis(4-methylbenzenesulfonate) (CAS:96243-67-3) as white solid (7.83 g, 95 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.4 Hz, 4H), 4.71 (m, 2H), 2.45 (s, 6H), 1.88 (t, *J* = 6.0 Hz, 2H), 1.23 (d, *J* = 6.0 Hz, 6H).

3.2 General procedures to prepare ligand

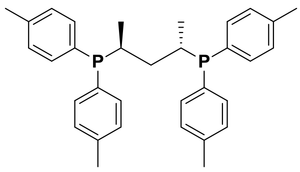


The procedure of preparing aryl phosphine oxide was adapted from the literature.[S8] To a 250-mL round-bottom flask charged with magnesium turnings (1.32 g, 55 mmol, 2.2 equiv.), a small I_2 bead and THF (40 mL) was added at room temperature. The mixture was then stirred at this temperature for 3 h. Then aryl bromide was added carefully at 0 °C. The mixture was allowed to stir at this temperature for 5 h. To the other 250-mL round-bottom flask equipped with reflux condenser was charged with diethyl phosphonate (3.45 g, 25 mmol, 1.0 equiv.). Then THF (15 mL) and the THF solution of aryl magnesium bromide was added at 0 °C. Subsequently, the solution was heated in an oil bath at 80 °C and stirred for 12 h. The reaction mixture was allowed to cool to 0 °C. H_2O (10 mL) and NaOH (30 mL, 3 M) was added. The reaction mixture was diluted with ethyl acetate (50 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica using petroleum ether/ ethyl acetate (5: 1 → 1:1, v/v) as the eluent to afford **4a**.

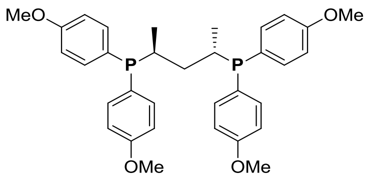
The procedure of preparing phosphine hydrogen **4b** was adapted from literature procedures.[S9] To a 250-mL round-bottom flask was charged with **4a** (15 mmol,1.0 equiv.), THF (25 mL). Then, the hexane solution of DIBAL-H (45 mL, 1.0 M, 45.0 mmol, 3.0 equiv.) was added -78 °C. The reaction was stirred at this temperature for 1 h and then warmed up to room temperature. After stirring for 3 h at room temperature, The THF solution of BH_3 (60 mL, 1.0 M, 60 mmol, 4.0 equiv.) was added slowly at 0 °C. The resulted mixture was allowed to stir at 0 °C for 2 h. The saturated aqueous potassium sodium tartrate tetrahydrate (15 mL) was added carefully at -78 °C and the resulted mixture was than stirred for 3 h. The reaction mixture was diluted with ethyl acetate (50 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using the mixture of petroleum ether/ethyl acetate (10: 1 → 5:1, v/v) as eluent to afford **4b**.

The procedure of preparing (*S,S*)-BDPP was adapted from the literature.[S10] To a 100-mL round-bottom flask was charged with **4b** (10.0 mmol, 4.0 equiv.) and THF (20 mL). The hexane solution of *n*-BuLi (4.4 mL, 2.5 M, 11.0 mmol, 1.1 equiv.) was added dropwise at 0 °C. The reaction was then stirred at room temperature for 1 h. Subsequently, THF solution (5 mL) of (*2R,4R*)-pentane-2,4-diyl bis(4-methylbenzenesulfonate) (1.03 g, 2.5 mmol, 1.0 equiv.) was added. The mixture was allowed to stir at room temperature for 12 h. Saturated aqueous NH_4Cl (5 mL) was added at 0 °C. The resulted mixture was diluted with ethyl acetate (20 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (1: 1, v/v) as the eluent to afford **4d**.

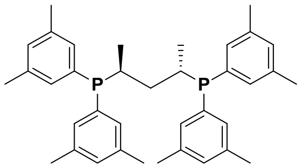
To a 25-mL round-bottom flask was charged with **4d** (1.5 mmol, 1.0 equiv.) and toluene (8 mL). Then, DABCO (840 mg, 7.5 mmol, 5.0 equiv.) was added. The reaction was stirred at 90 °C for 18 h. The reaction proceeding was monitored by ^{31}P NMR. After the full conversion of **4d**, then solution was removed to obtain the crude product was purified by flash column chromatography on silica gel using degassed toluene and the obtained product was recrystallized in methanol to afford **4e**.



((*2S,4S*)-pentane-2,4-diyl)bis(di-p-tolylphosphine) (CAS: 254454-75-6) ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 8H), 7.10 (t, *J* = 8.5 Hz, 8H), 2.45 – 2.43 (m, 2H), 2.32 (s, 6H), 2.31 (s, 6H), 1.38 – 1.33 (m, 2H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). ^{31}P NMR (203 MHz, $CDCl_3$) δ -2.78.

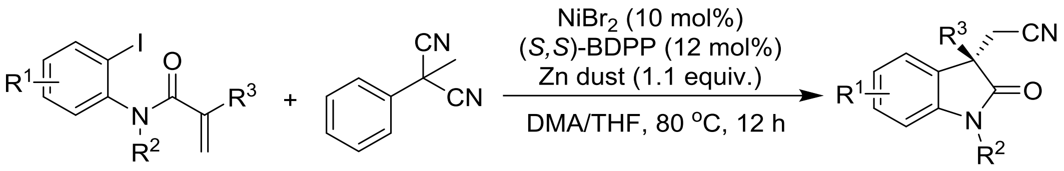


((2S,4S)-pentane-2,4-diyl)bis(bis(4-methoxyphenyl)phosphine) (CAS: 738594-25-7) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 8H), 6.84 (t, *J* = 7.8 Hz, 8H), 3.79 (s, 6H), 3.78 (s, 6H), 2.40 (s, br, 2H), 1.33 (s, br, 2H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.0 Hz, 3H). ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.58.



((2S,4S)-pentane-2,4-diyl)bis(bis(3,5-dimethylphenyl)phosphine) (CAS:551950-92-6) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 4H), 7.04 (s, 4H), 6.91 (s, 4H), 2.46 – 2.42 (m, 2H), 2.26 (s, 12H), 2.24 (s, 12H), 1.39 – 1.38 (m, 2H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 7.2 Hz, 3H). ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.85.

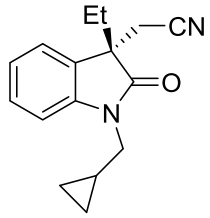
4. General experimental procedure for the Ni-catalyzed enantioselective arylcyanation, characterization data and HPLC charts of products

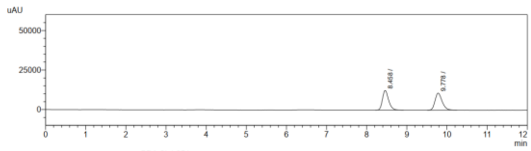


1 2

To a 25-mL oven-dried Schlenk tube was charged with amide 1 (0.1 mmol, 1.0 equiv.), MPMN (31.2 mg, 2.0 equiv.), $NiBr_2$ (2.2 mg, 10 mol%), (*S,S*)-BDPP (5.3 mg, 12 mol%) and zinc dust (7.2 mg, 1.1 equiv.) in the glove box under N_2 atmosphere. Then DMA (1 mL) and THF (1 mL) were added. The reaction was stirred at 80 ^{o}C for 12 h. After cooling to room temperature and concentrating the mixture, the residue was purified by column chromatography on silica gel using the mixture of petroleum ether/ethyl acetate (7:1 → 4:1, v/v) as the eluent to afford product **2**.

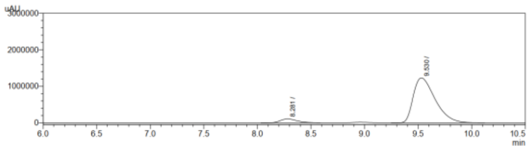
2-(1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetonitrile (2a): White solid (23.4 mg, 92% yield, 94:6 er). $[\alpha]_D^{25}$ = 24.500 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.63 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.61 (d, *J* = 16.8 Hz, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.23 – 1.16 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H), 0.56 – 0.51 (m, 2H), 0.41 – 0.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.9, 143.3, 129.1 (2C), 123.3, 123.0, 116.5, 108.9, 49.5, 44.4, 29.5, 25.8, 9.6, 8.3, 3.8. HRMS (ESI) calcd. for $C_{16}H_{18}N_2NaO$ ($[M+Na]^+$) 277.1311, found 277.1311. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 8.27 min. (minor), 9.53 min. (major).





PDA Ch1 254nm

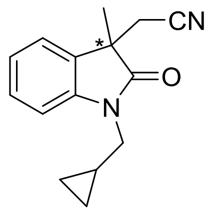
Peak#	Ret. Time	Height	Area	Area%
1	8.458	12388	130726	50.019
2	9.778	10699	130626	49.981
总计		23087	261352	100.000

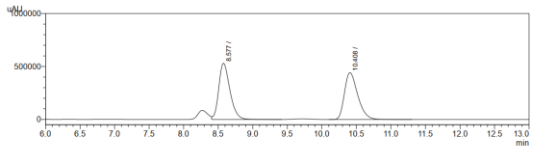


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	8.281	105603	1140614	6.149
2	9.530	1226704	17409022	93.851
总计		1332307	18549636	100.000

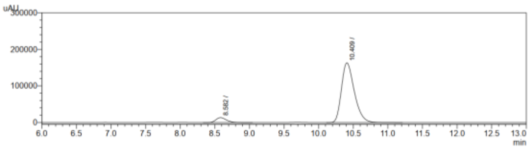
2-(1-(cyclopropylmethyl)-3-methyl-2-oxoindolin-3-yl)acetonitrile (2b): Colorless oil (20.9 mg, 74% yield, 93.5:6.5 er). $[\alpha]_D^{25}$ = 26.400 (*c* = 0.500, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.66 – 3.60 (m, 2H), 2.85 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.8 Hz, 1H), 1.53 (s, 3H), 1.23 – 1.12 (m, 1H), 0.55 – 0.52 (m, 2H), 0.41 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 142.3, 131.1, 129.1, 123.2, 123.0, 116.6, 109.1, 44.8, 44.5, 26.3, 22.2, 9.5, 3.8. HRMS (ESI) calcd. for $C_{15}H_{16}N_2NaO$ ($[M+Na]^+$) 263.1155, found 263.1150. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 8.58. min (minor), 10.41 min. (major).





PDA Ch1 254nm

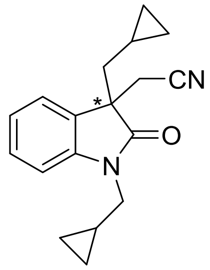
Peak#	Ret. Time	Height	Area	Area%
1	8.577	531638	5972027	50.365
2	10.408	442265	5885575	49.635
总计		973902	11857602	100.000



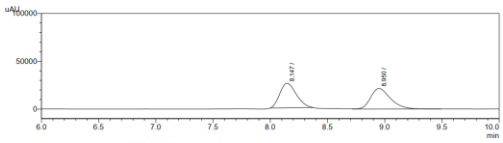
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	8.582	13551	143091	6.344
2	10.409	163416	2112359	93.656
总计		176967	2255450	100.000

2-(1,3-bis(cyclopropylmethyl)-2-oxoindolin-3-yl)acetonitrile (2c): Yellow oil (23.2 mg, 83% yield, 94.5:5.5 er). $[\alpha]_D^{25}$ = 16.370 (*c* = 0.450, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.69 – 3.58 (m, 2H), 2.85 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.8 Hz, 1H), 2.19 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.68 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.23 – 1.16 (m, 1H), 0.58 – 0.50 (m, 2H), 0.44 – 0.39 (m, 2H), 0.37 – 0.32 (m, 1H), 0.28 – 0.18 (m, 2H), 0.16 – 13 (m, 1H), -0.07 – -0.10 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 143.3, 129.7, 129.0, 123.5, 122.8, 116.6, 108.9, 49.2, 44.6, 40.9, 25.6, 9.5, 6.0, 4.2, 4.0, 3.8, 3.7. HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO$ ($[M+Na]^+$) 303.1468, found

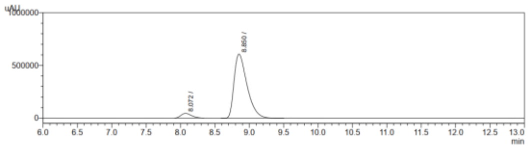


303.1466. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 8.07 min. (minor), 8.85 min. (major).



PDA Ch1 254nm

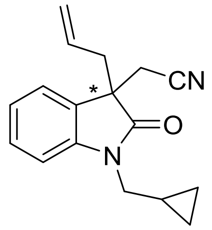
Peak#	Ret. Time	Height	Area	Area%
1	8.147	25790	257539	49.971
2	8.950	21534	257843	50.029
总计		47324	515382	100.000

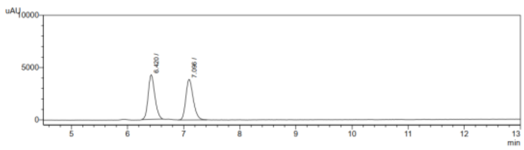


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	8.072	44569	469320	5.568
2	8.850	608096	7959345	94.432
总计		652664	8428665	100.000

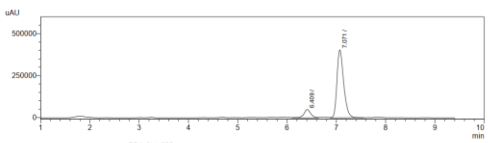
2-(3-allyl-1-(cyclopropylmethyl)-2-oxoindolin-3-yl)acetonitrile (2d): Yellow oil (21.2 mg, 80% yield, 89:11 er). $[\alpha]_D^{25}$ = 22.067 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 1H), 7.35 (td, *J* = 7.8, 1.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.44 – 5.37 (m, 1H), 5.10 – 5.06 (m, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.65 – 3.57 (m, 2H), 2.87 (d, *J* = 16.8 Hz, 1H), 2.73 – 2.62 (m, 3H), 1.20 – 1.13 (m, 1H), 0.56 – 0.48 (m, 2H), 0.41 – 0.35 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 143.0, 130.5, 129.2, 128.9, 123.6, 122.9, 120.2, 116.4, 109.0, 48.7, 44.4, 40.3, 25.1, 9.6, 3.9, 3.8. HRMS (ESI) calcd. for $C_{17}H_{18}N_2NaO$ ($[M+Na]^+$) 289.1311, found 289.1308. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 255 nm, t_R = 6.42 min. (minor), 7.10 min. (major).





PDA Ch1 255nm

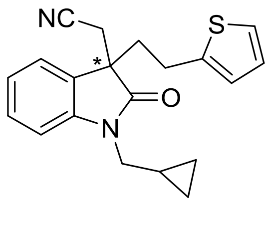
Peak#	Ret. Time	Height	Area	Area%
1	6.420	4265	35308	50.092
2	7.096	3866	35178	49.908
总计		8131	70486	100.000

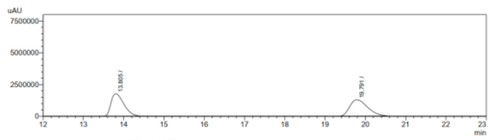


PDA Ch1 255nm

Peak#	Ret. Time	Height	Area	Area%
1	6.409	48892	469281	10.945
2	7.071	404073	3818360	89.055
总计		452965	4287641	100.000

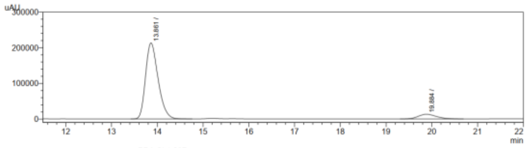
2-(1-(cyclopropylmethyl)-2-oxo-3-(2-(thiophen-2-yl)ethyl)indolin-3-yl)acetonitrile (2e): Yellow solid (25.5 mg, 76% yield, 92:8 er). $[\alpha]_D^{25}$ = 35.917 (*c* = 0.4, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 4.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.85 (dd, *J* = 4.8, 3.7 Hz, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 3.63 (d, *J* = 7.2 Hz, 2H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.64 (d, *J* = 16.8 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.44 – 2.30 (m, 3H), 1.23 – 1.17 (m, 1H), 0.57 – 0.52 (m, 2H), 0.44 – 0.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 143.1, 142.9, 129.4, 128.6, 126.7, 124.4, 123.41, 123.39, 123.2, 116.2, 109.2, 48.8, 44.6, 38.0, 26.1, 24.5, 9.7, 3.9. HRMS (ESI) calcd. for $C_{20}H_{20}N_2NaOS$ ($[M+Na]^+$) 359.1189, found 359.1183. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 237 nm, t_R = 19.88 min. (minor), 13.86 min. (major).





PDA Ch1 237nm

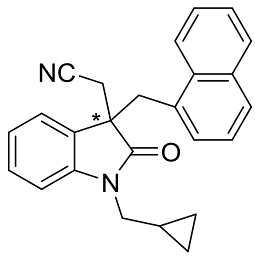
Peak#	Ret. Time	Height	Area	Area%
1	13.805	1772836	39431489	50.055
2	19.791	1289855	39345506	49.945
总计		3062691	78776994	100.000

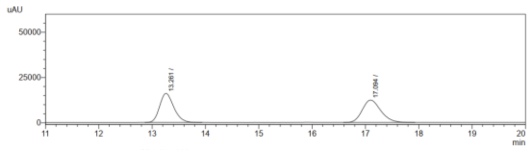


PDA Ch1 237nm

Peak#	Ret. Time	Height	Area	Area%
1	13.861	213390	4068037	91.795
2	19.884	13140	363641	8.205
总计		226529	4431678	100.000

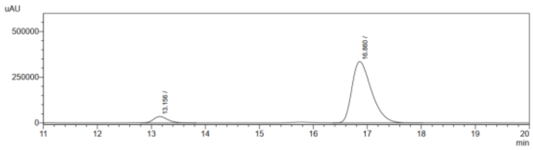
2-(1-(cyclopropylmethyl)-3-(naphthalen-1-ylmethyl)-2-oxoindolin-3-yl)acetonitrile (2f): Yellow solid (34.0 mg, 93% yield, 93:7 er). $[\alpha]_D^{25}$ = 47.778 (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.21 – 7.14 (m, 2H), 7.06 – 6.94 (m, 2H), 6.69 (d, J = 7.8 Hz, 1H), 3.79 – 3.72 (m, 2H), 3.40 (dd, J = 14.4, 7.2 Hz, 1H), 3.28 (dd, J = 14.4, 6.6 Hz, 1H), 3.05 (d, J = 16.8 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 0.73 – 0.64 (m, 1H), 0.33 – 0.22 (m, 1H), 0.12 – 0.08 (m, 2H), -0.02 – -0.05 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.5, 143.0, 133.6, 132.1, 130.6, 129.1, 128.6, 128.4, 128.3, 127.9, 125.6, 125.4, 124.6, 124.5, 124.2, 122.4, 116.7, 108.7, 50.2, 44.3, 37.4, 25.6, 9.1, 3.5, 3.4. HRMS (ESI) calcd. for $C_{25}H_{22}N_2NaO$ ($[M+Na]^+$) 389.1624, found 389.1623. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 263 nm, t_R = 13.16 min. (minor), 16.86 min. (major).





PDA Ch1 263nm

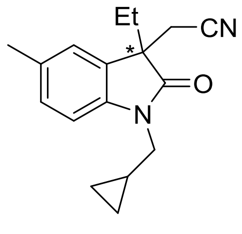
Peak#	Ret. Time	Height	Area	Area%
1	13.261	16027	295137	49.868
2	17.094	12340	296702	50.132
总计		28367	591839	100.000

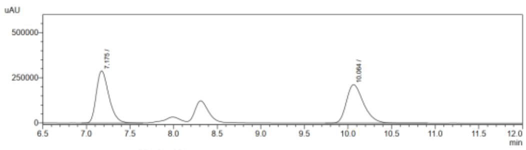


PDA Ch1 263nm

Peak#	Ret. Time	Height	Area	Area%
1	13.156	35016	641793	7.069
2	16.860	335373	8436986	92.931
总计		370389	9078779	100.000

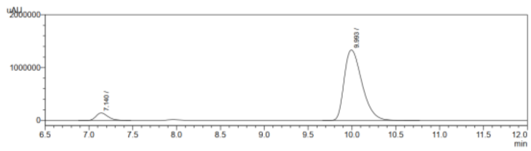
2-(1-(cyclopropylmethyl)-3-ethyl-5-methyl-2-oxoindolin-3-yl)acetonitrile (2g): Yellow oil (22.8 mg, 85% yield, 93.5:6.5 er). $[\alpha]_D^{25}$ = 18.667 (c = 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.14 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.60 (m, 2H), 2.82 (d, J = 16.8 Hz, 1H), 2.59 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H), 2.01 (q, J = 7.2 Hz, 2H), 1.21 – 1.12 (m, 1H), 0.62 (t, J = 7.2 Hz, 3H), 0.51 (m, 2H), 0.43 – 0.33 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 140.9, 132.6, 129.3, 129.1, 124.0, 116.6, 108.6, 49.5, 44.4, 29.5, 25.8, 21.1, 9.6, 8.3. HRMS (ESI) calcd. for $C_{17}H_{20}N_2NaO$ ($[M+Na]^+$) 291.1468, found 291.1462. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-Hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 7.14 min. (minor), 9.99 min. (major).





PDA Ch1 254nm

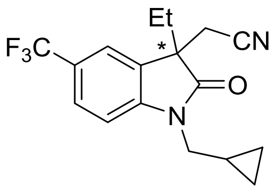
Peak#	Ret. Time	Height	Area	Area%
1	7.175	288878	2901377	50.002
2	10.064	212456	2901122	49.998
总计		501334	5802499	100.000

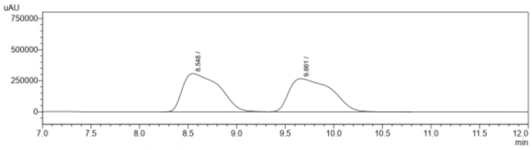


PDA Ch1 257nm

Peak#	Ret. Time	Height	Area	Area%
1	7.140	141464	1331503	6.610
2	9.993	1333055	18812982	93.390
总计		1474518	20144485	100.000

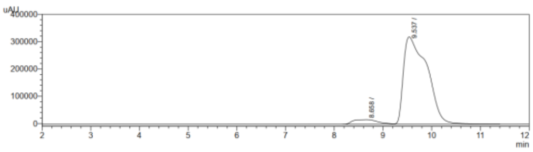
2-(1-(cyclopropylmethyl)-3-ethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetonitrile (2h) : Yellow oil (20.6 mg, 64% yield, 95:5 er). $[\alpha]_D^{25}$ = 17.333 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 3.66 (d, *J* = 7.2 Hz, 2H), 2.85 (d, *J* = 16.2 Hz, 1H), 2.69 (d, *J* = 16.2 Hz, 1H), 2.08 – 2.01 (m, 2H), 0.64 (t, *J* = 7.2 Hz, 3H), 0.57-0.54 (m, 2H), 0.43-0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 146.4, 129.7, 127.0 (q, J_{CF} = 3.7 Hz), 125.3 (q, J_{CF} = 33.0 Hz), 124.1 (q, J_{CF} = 270.0 Hz), 120.3 (q, J_{CF} = 4.1 Hz), 115.9, 108.8, 49.7, 44.7, 29.6, 25.6, 9.5, 8.3, 3.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.40. HRMS (ESI) calcd. for $C_{17}H_{17}F_3N_2NaO$ ($[M+Na]^+$) 345.1185, found 345.1181. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/*i*-PrOH = 97:3, flow rate = 1.0 mL/min., λ = 258 nm, t_R = 8.66 min. (minor), 9.54 min. (major).





PDA Ch1 258nm

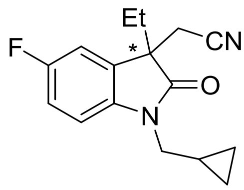
Peak#	Ret. Time	Height	Area	Area%
1	8.548	307117	8040636	50.112
2	9.661	266196	8004619	49.888
总计		573313	16045255	100.000

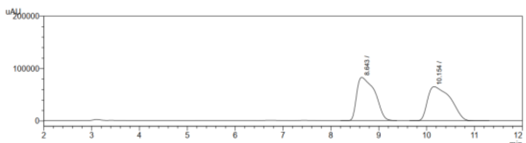


PDA Ch1 258nm

Peak#	Ret. Time	Height	Area	Area%
1	8.658	16554	580140	5.134
2	9.537	319581	10720189	94.866
总计		336136	11300330	100.000

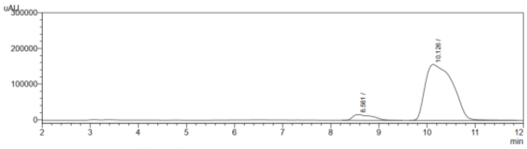
2-(1-(cyclopropylmethyl)-3-ethyl-5-fluoro-2-oxoindolin-3-yl)acetonitrile (2i): Yellow oil (21.5 mg, 79% yield, 93:7 er). $[\alpha]_D^{25}$ = 18.333 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.06 (td, *J* = 9.0, 3.0 Hz, 1H), 6.92 (dd, *J* = 8.4, 4.2Hz, 1H), 3.63 – 3.61 (m, 2H), 2.83 (d, *J* = 16.2 Hz, 1H), 2.63 (d, *J* = 16.2 Hz, 1H), 2.06 – 1.96 (m, 2H), 1.20-1.14 (m, 1H), 0.64 (t, *J* = 7.2 Hz, 3H), 0.55 – 0.52 (m, 2H), 0.40 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.5, 159.3 (d, J_{CF} = 240.3 Hz), 139.2, 130.6 (d, J_{CF} = 8.2 Hz), 116.2, 115.4 (d, J_{CF} = 23.4 Hz), 111.5 (d, J_{CF} = 24.8 Hz), 109.5 (d, J_{CF} =7.8 Hz), 50.0, 44.6, 29.5, 25.6, 9.5, 8.3, 3.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.49. HRMS (ESI) calcd. for $C_{16}H_{17}FN_2NaO$ ($[M+Na]^+$) 295.1217, found 295.1211. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 253 nm, t_R = 8.56 min. (minor), 10.12 min. (major).





PDA Ch1 253nm

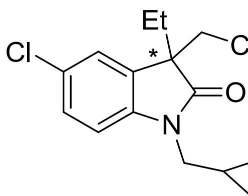
Peak#	Ret. Time	Height	Area	Area%
1	8.643	82336	2152123	50.065
2	10.154	64894	2146507	49.935
总计		147230	4298630	100.000



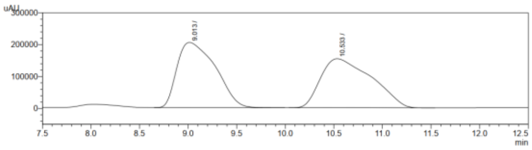
PDA Ch1 253nm

Peak#	Ret. Time	Height	Area	Area%
1	8.561	15960	450930	6.750
2	10.126	156195	6229984	93.250
总计		172156	6680914	100.000

2-(5-chloro-1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetonitrile (2j): Yellow oil (12.3 mg, 43% yield, 95.5:4.5 er). $[\alpha]_D^{25}$ = 24.600 (*c* = 0.1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.61 (dd, *J* = 7.2, 2.0 Hz, 2H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.64 (d, *J* = 16.8 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.17 – 1.13 (m, 1H), 0.64 (t, *J* = 7.2 Hz, 3H), 0.57 – 0.50 (m, 2H), 0.41 – 0.39 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 141.9,

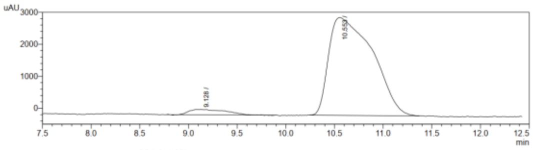


130.7, 129.1, 128.4, 123.8, 116.1, 109.9, 49.8, 44.6, 29.6, 25.6, 9.5, 8.3, 3.9. HRMS (ESI) calcd. for $C_{16}H_{17}{}^{35}ClN_2NaO$ ($[M+Na]^+$) 311.0922, found 311.0917. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 259 nm, t_R = 9.13 min. (minor), 10.55 min. (major).



PDA Ch1 259nm

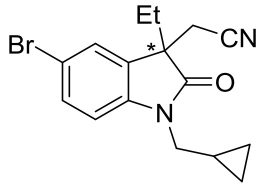
Peak#	Ret. Time	Height	Area	Area%
1	9.013	204600	5635876	50.060
2	10.533	153769	5622378	49.940
总计		358369	11258254	100.000

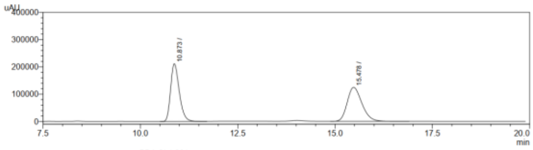


PDA Ch1 259nm

Peak#	Ret. Time	Height	Area	Area%
1	9.128	171	4331	4.319
2	10.553	3059	95929	95.681
总计		3231	100260	100.000

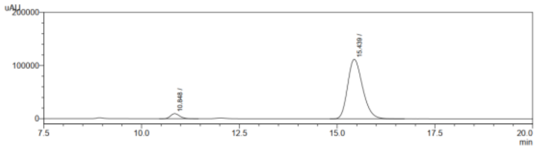
2-(5-bromo-1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetonitrile (2k): Yellow oil (17.6 mg, 53% yield, 95:5 er). $[\alpha]_D^{25}$ = 12.533 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 1.8 Hz, 1H), 7.49 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.61 (dd, *J* = 7.2, 2.1 Hz, 2H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.64 (d, *J* = 16.8 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.18 – 1.12 (m, 1H), 0.64 (t, *J* = 7.2 Hz, 3H), 0.55 – 0.52 (m, 2H), 0.39 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 142.4, 132.1, 131.1, 126.5, 116.1, 115.6, 110.4, 49.8, 44.6, 29.6, 25.6, 9.5, 8.3, 3.8. HRMS (ESI) calcd. for $C_{16}H_{17}{}^{79}BrN_2NaO$ ($[M+Na]^+$) 355.0416, found 355.0407. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OJ-3 column. *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 261 nm, t_R = 10.84 min. (minor), 15.44 min. (major).





PDA Ch1 261nm

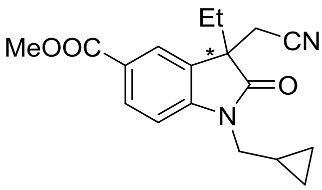
Peak#	Ret. Time	Height	Area	Area%
1	10.873	211623	3286028	50.155
2	15.478	124629	3265724	49.845
总计		336251	6551752	100.000

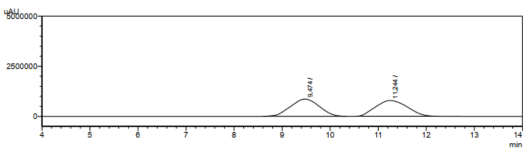


PDA Ch1 261nm

Peak#	Ret. Time	Height	Area	Area%
1	10.848	9601	157699	5.042
2	15.439	111866	2969755	94.958
总计		121467	3127454	100.000

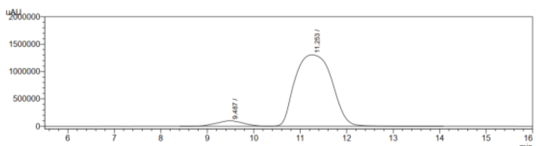
Methyl-3-(cyanomethyl)-1-(cyclopropylmethyl)-3-ethyl-2-oxoindoline-5-carboxylate (2l): Yellow solid (20.9 mg, 67% yield, 95:5 er). $[\alpha]_D^{25}$ = -23.333 (*c* = 0.15, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.03 (d, *J* = 1.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.67 (d, *J* = 6.6 Hz, 2H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.72 (d, *J* = 16.8 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.22 – 1.15 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H), 0.57 – 0.53 (m, 2H), 0.42 – 0.39 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.2, 166.5, 147.5, 131.8, 129.0, 125.0, 124.4, 115.9, 108.5, 52.2, 49.8, 44.7, 29.7, 25.6, 9.6, 8.3, 3.9. HRMS (ESI) calcd. for $C_{18}H_{20}N_2NaO_3$ ($[M+Na]^+$) 335.1366, found 335.1363. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 278 nm, t_R = 9.48 min. (minor), 11.25 min. (major).





PDA Ch1 278nm

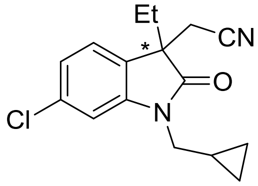
Peak#	Ret. Time	Height	Area	Area%
1	9.474	861884	35797361	49.956
2	11.244	783191	35859830	50.044
总计		1645075	71657191	100.000

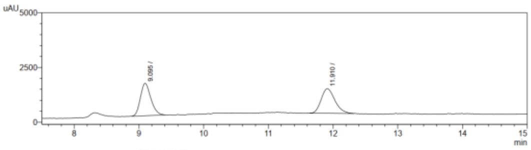


PDA Ch1 278nm

Peak#	Ret. Time	Height	Area	Area%
1	9.487	98450	3993774	5.238
2	11.253	1303272	72248496	94.762
总计		1401721	76242269	100.000

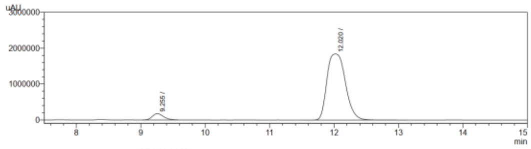
2-(6-chloro-1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetonitrile (2m): Yellow oil (23.3 mg, 81% yield, 94.5:5.5 er). $[\alpha]_D^{25}$ = 24.200 (*c* = 0.5, $CHCl_3$).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 3.60 (dd, *J* = 7.2, 1.9 Hz, 2H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.61 (d, *J* = 16.8 Hz, 1H), 2.01 (q, *J* = 7.2 Hz, 2H), 1.21 – 1.15 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H), 0.59 – 0.51 (m, 2H), 0.42 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 144.5, 135.0, 127.3, 124.3, 122.8, 116.2, 109.7, 49.3, 44.6, 29.4, 25.6, 9.5, 8.3, 3.9. HRMS (ESI) calcd. for $C_{16}H_{17}{}^{35}ClN_2NaO$ ($[M+Na]^+$) 311.0922, found 311.0925. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 257 nm, t_R = 9.26 min. (minor), 10.02 min. (major).





PDA Ch1 257nm

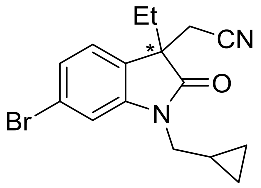
Peak#	Ret. Time	Height	Area	Area%
1	9.095	1482	16696	50.054
2	11.910	1130	16660	49.946
总计		2612	33355	100.000

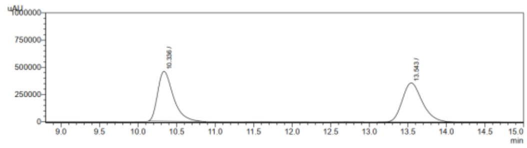


PDA Ch1 257nm

Peak#	Ret. Time	Height	Area	Area%
1	9.255	176703	2146481	5.537
2	12.020	1841026	36616241	94.463
总计		2017729	38762722	100.000

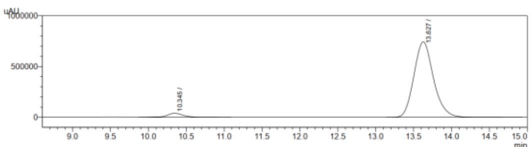
2-(6-bromo-1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetonitrile (2n): White solid (20.2 mg, 61% yield, 96:4 er). $[\alpha]_D^{25}$ = 18.833 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.14 (s, 1H), 3.60 (dd, *J* = 7.2, 1.2 Hz, 2H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.61 (d, *J* = 16.8 Hz, 1H), 2.01 (q, *J* = 7.2 Hz, 2H), 1.25 – 1.14 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H), 0.59 – 0.51 (m, 2H), 0.42 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 144.6, 127.9, 125.8, 124.6, 122.8, 116.2, 112.4, 49.4, 44.6, 29.4, 25.6, 9.6, 8.3, 3.9. HRMS (ESI) calcd. for $C_{16}H_{17}{}^{79}BrN_2NaO$ ($[M+Na]^+$) 355.0416, found 355.0415. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 258 nm, t_R = 10.34 min. (minor), 13.63 min. (major).





PDA Ch1 258nm

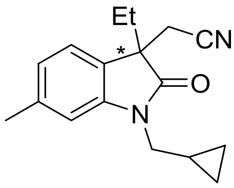
Peak#	Ret. Time	Height	Area	Area%
1	10.336	458667	6477998	49.830
2	13.543	359772	6522311	50.170
总计		818440	13000309	100.000



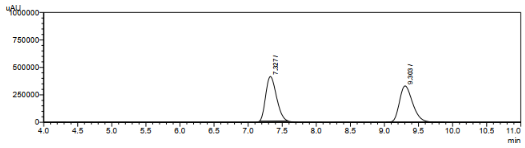
PDA Ch1 258nm

Peak#	Ret. Time	Height	Area	Area%
1	10.345	39063	572918	4.124
2	13.627	742895	13317996	95.876
总计		781958	13890914	100.000

2-(1-(cyclopropylmethyl)-3-ethyl-6-methyl-2-oxoindolin-3-yl)acetonitrile (2o): Yellow oil (22.2 mg, 83% yield, 93.5:6.5 er). $[\alpha]_D^{25}$ = 24.667 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.81 (s, 1H), 3.61 – 3.60 (m, 2H), 2.81 (d, *J* = 16.6 Hz, 1H), 2.58 (d, *J* = 16.6 Hz, 1H), 2.41 (s, 3H), 2.00 (q, *J* = 7.2 Hz, 2H), 1.23 – 1.17 (m, 1H), 0.62 (t, *J* = 7.2 Hz, 3H), 0.56 – 0.49 (m, 2H), 0.42 – 0.38 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 143.3, 139.3, 126.0, 123.5, 123.0, 116.6, 109.8, 49.3, 44.3, 29.4, 25.9, 21.9, 9.7, 8.3, 3.8. HRMS (ESI)

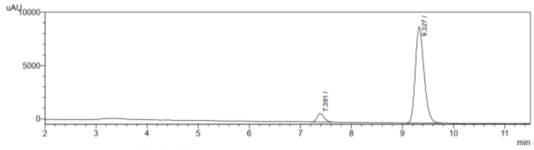


calcd. for $C_{17}H_{20}N_2NaO$ ([M+Na]$^+$) 291.1468, found 291.1472. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 257 nm, t_R = 7.39 min. (minor), 9.33 min. (major).



PDA Ch1 257nm

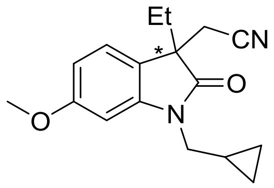
Peak#	Ret. Time	Height	Area	Area%
1	7.327	405734	4408010	49.804
2	9.303	330345	4442714	50.196
总计		736079	8850724	100.000

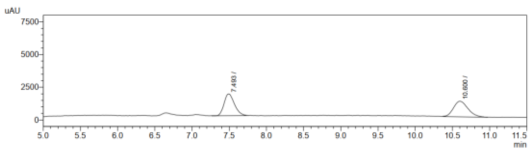


PDA Ch1 257nm

Peak#	Ret. Time	Height	Area	Area%
1	7.391	792	7440	6.486
2	9.327	9034	107271	93.514
总计		9826	114711	100.000

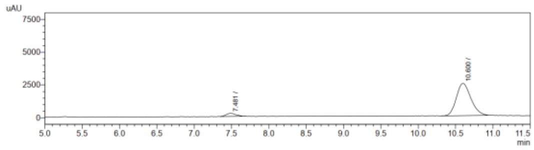
2-(1-(cyclopropylmethyl)-3-ethyl-5-methoxy-2-oxoindolin-3-yl)acetonitrile (2p): Yellow oil (25.0 mg, 88% yield, 94:6 er). $[\alpha]_D^{25}$ =18.444 (*c* = 0.15, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 3H), 3.60 (dd, *J* = 7.2, 3.6 Hz, 2H), 2.80 (d, *J* = 16.6 Hz, 1H), 2.58 (d, *J* = 16.6 Hz, 1H), 1.99 (q, *J* = 7.2 Hz, 2H), 1.21 – 1.15 (m, 1H), 0.62 (t, *J* = 7.8 Hz, 3H), 0.56 – 0.49 (m, 2H), 0.41 – 0.37 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.4, 160.7, 144.5, 124.0, 120.8, 116.7, 106.5, 97.1, 55.5, 49.1, 44.4, 29.5, 26.0, 9.6, 8.3, 3.8. HRMS (ESI) calcd. for $C_{17}H_{20}N_2NaO_2$ ([M+Na]$^+$) 307.1417, found 307.1415. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 7.48 min. (minor), 10.60 min. (major).





PDA Ch1 254nm

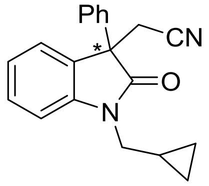
Peak#	Ret. Time	Height	Area	Area%
1	7.493	1671	16127	49.956
2	10.600	1197	16155	50.044
总计		2868	32282	100.000

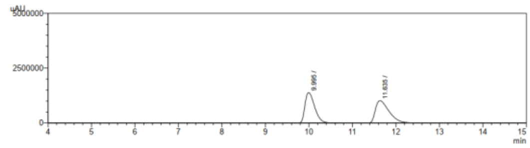


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	7.481	236	2183	6.162
2	10.600	2453	33243	93.838
总计		2689	35426	100.000

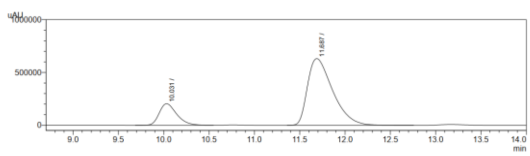
2-(1-(cyclopropylmethyl)-2-oxo-3-phenylindolin-3-yl)acetonitrile (2q): White solid (28.7 mg, 95% yield, 82:18 er). $[\alpha]_D^{25}$ = 36.467 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.36 – 7.29 (m, 5H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 3.67 – 3.59 (m, 2H), 3.37 (d, *J* = 16.8 Hz, 1H), 3.08 (d, *J* = 16.8 Hz, 1H), 1.22 – 1.16 (m, 1H), 0.56 – 0.48 (m, 2H), 0.42 – 0.32 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 143.2, 136.7, 129.7, 129.5, 129.0, 128.3, 126.6, 125.2, 123.1, 116.3, 109.4, 52.7, 44.7, 26.2, 9.5, 3.8, 3.7. HRMS (ESI) calcd. for $C_{20}H_{18}N_2NaO$ ([M+Na]$^+$) 325.1311, found 325.1313. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 10.03 min. (minor), 11.69 min. (major).





PDA Ch1 254nm

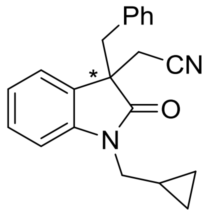
Peak#	Ret. Time	Height	Area	Area%
1	9.995	1384658	21258279	49.811
2	11.635	1008763	21419830	50.189
总计		2393421	42678109	100.000

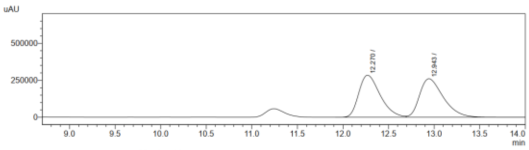


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	10.031	203478	2717636	18.257
2	11.687	631708	12167446	81.743
总计		835187	14885082	100.000

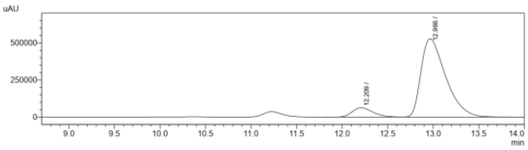
2-(3-benzyl-1-(cyclopropylmethyl)-2-oxoindolin-3-yl)acetonitrile (2r): Colorless oil (26.5 mg, 84% yield, 91:9 er). $[\alpha]_D^{25}$ = 19.556 (*c* = 0.3, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.14 – 7.12 (m, 1H), 7.08 – 7.03 (m, 3H), 6.85 – 6.84 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.45 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.33 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.28 (d, *J* = 14.4 Hz, 1H), 3.22 (d, *J* = 12.6 Hz, 1H), 2.97 (d, *J* = 16.8 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 0.84 – 0.78 (m, 1H), 0.39 – 0.31 (m, 2H), 0.24 – 0.17 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 143.0, 134.2, 129.9, 129.2, 128.5, 127.8, 126.9, 124.0, 122.6, 116.5, 108.9, 50.2, 44.4, 42.1, 25.6, 9.2, 3.8, 3.7. HRMS (ESI) calcd. for $C_{21}H_{20}N_2NaO$ ($[M+Na]^+$) 339.1468, found 339.1466. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 12.21 min. (minor), 12.97 min. (major).





PDA Ch1 254nm

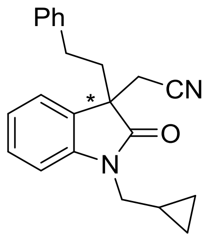
Peak#	Ret. Time	Height	Area	Area%
1	12.270	284669	4656419	49.542
2	12.943	260629	4742512	50.458
总计		545298	9398931	100.000

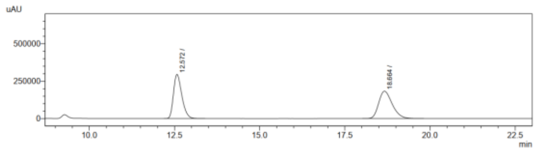


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	12.209	62880	998239	9.123
2	12.966	528015	9943915	90.877
总计		590895	10942153	100.000

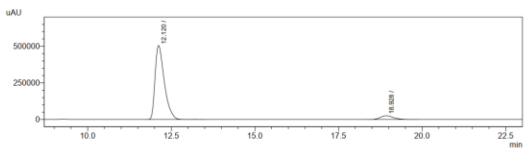
2-(1-(cyclopropylmethyl)-2-oxo-3-phenethylindolin-3-yl)acetonitrile (2s): Yellow solid (29.0 mg, 88% yield, 93:7 er). $[\alpha]_D^{25}$ = 19.000 (*c* = 0.1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.03 – 7.01 (m, 3H), 3.63 (d, *J* = 7.2 Hz, 2H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.62 (d, *J* = 16.8 Hz, 1H), 2.37 – 2.23 (m, 3H), 2.15 – 2.10 (m, 1H), 1.33 – 1.17 (m, 3H), 0.57 – 0.51 (m, 2H), 0.44 – 0.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 143.2, 140.4, 129.3, 128.9, 128.4, 128.2, 126.2, 123.4, 123.2, 116.4, 109.1, 48.9, 44.5, 38.1, 30.3, 26.1, 9.7, 3.9. HRMS (ESI) calcd. for $C_{22}H_{22}N_2NaO$ ($[M+Na]^+$) 353.1624, found 353.1633. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 12.12 min. (major), 18.93 min. (minor).





PDA Ch1 254nm

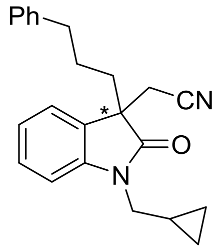
Peak#	Ret. Time	Height	Area	Area%
1	12.572	294639	5020371	49.912
2	18.664	182514	5038038	50.088
总计		477153	10058409	100.000

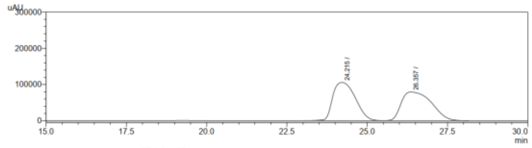


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	12.120	505529	9694153	93.159
2	18.928	26143	711870	6.841
总计		531672	10406023	100.000

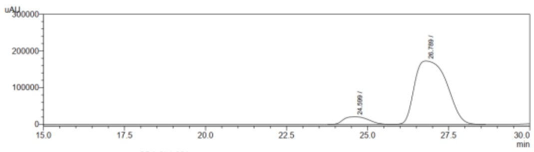
2-(1-(cyclopropylmethyl)-2-oxo-3-(3-phenylpropyl)indolin-3-yl)acetonitrile (2t): Yellow oil (31.3 mg, 91% yield, 92:8 er). $[\alpha]_D^{25}$ = 21.222 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.21 (t, *J* = 7.0 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.61 (dd, *J* = 7.0, 3.5 Hz, 2H), 2.81 (d, *J* = 16.5 Hz, 1H), 2.60 – 2.43 (m, 3H), 2.06 – 1.99 (m, 2H), 1.43 – 1.34 (m, 1H), 1.19 – 1.11 (m, 2H), 0.54 – 0.36 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 143.1, 141.3, 129.2, 129.1, 128.3, 128.2, 125.9, 123.3, 123.0, 116.4, 109.0, 48.9, 44.5, 35.8, 35.5, 26.1, 25.7, 9.6, 3.9, 3.8. HRMS (ESI) calcd. for $C_{23}H_{24}N_2NaO$ ($[M+Na]^+$) 367.1781, found 367.1779. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/i-PrOH = 98:2, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 24.60 min. (minor), 26.79 min. (major).





PDA Ch1 254nm

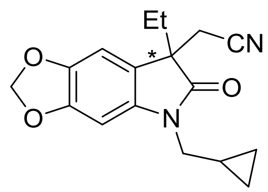
Peak#	Ret. Time	Height	Area	Area%
1	24.215	105297	5136787	49.956
2	26.357	78983	5145755	50.044
总计		184279	10282542	100.000

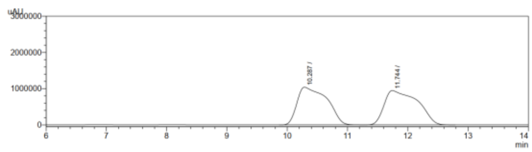


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	24.599	20687	1084815	8.321
2	26.789	172885	11951853	91.679
总计		193572	13036668	100.000

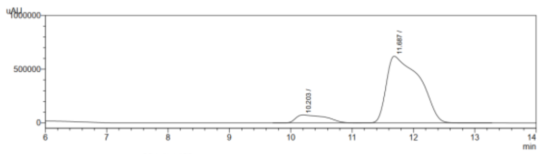
2-(5-(cyclopropylmethyl)-7-ethyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-7-yl)acetonitrile(2u): Yellow oil (17.0 mg, 57% yield, 90:10 er). $[\alpha]_D^{25}$ = 27.111 (*c* = 0.15, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.59 (s, 1H), 5.99 – 5.97 (m, 2H), 3.58 (dd, *J* = 7.2, 3.6 Hz, 2H), 2.78 (d, *J* = 16.8 Hz, 1H), 2.59 (d, *J* = 16.8 Hz, 1H), 2.01 – 1.91 (m, 2H), 1.17 – 1.12 (m, 1H), 0.63 (t, *J* = 7.8 Hz, 3H), 0.56 – 0.49 (m, 2H), 0.41 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 148.1, 143.6, 137.7, 120.6, 116.5, 104.8, 101.3, 92.8, 49.9, 44.5, 29.5, 26.0, 9.6, 8.3, 3.8. HRMS (ESI) calcd. for $C_{17}H_{18}N_2NaO_3$ ($[M+Na]^+$) 321.1210, found 321.1217. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 277 nm, t_R = 10.20 min. (minor), 11.69 min. (major).





PDA Ch1 277nm

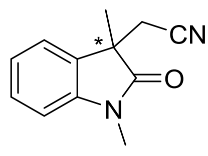
Peak#	Ret. Time	Height	Area	Area%
1	10.287	1040936	35775496	49.466
2	11.744	948256	36547577	50.534
总计		1989192	72323073	100.000



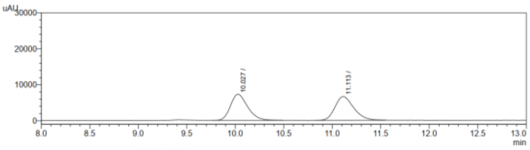
PDA Ch1 277nm

Peak#	Ret. Time	Height	Area	Area%
1	10.203	73701	2535354	9.816
2	11.687	620317	23292386	90.184
总计		694018	25827740	100.000

2-(1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2v) (CAS: 685089-46-7) [S11]: Yellow oil (8.6 mg, 43% yield, 94.5:5.5 er). $[\alpha]_D^{25}$ = 28.334 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.57 (d, *J* = 16.8 Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 142.7, 131.0, 129.2, 123.3, 123.1, 116.6, 108.7, 44.8, 26.5, 26.3, 22.1. HRMS (ESI) calcd. for $C_{12}H_{12}N_2NaO$ ($[M+Na]^+$) 223.0842, found 223.0846. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column.

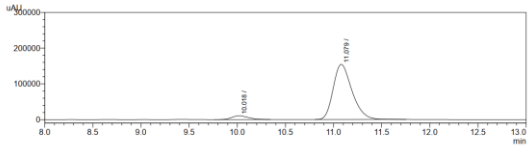


n-Hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 10.02 min. (minor), 11.08 min. (major).



PDA Ch1 254nm

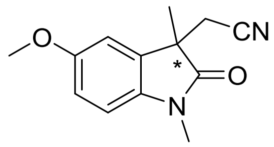
Peak#	Ret. Time	Height	Area	Area%
1	10.027	7255	88875	50.114
2	11.113	6591	88469	49.886
总计		13846	177343	100.000



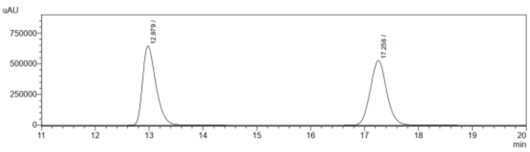
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	10.018	10422	125556	5.645
2	11.079	154233	2098494	94.355
总计		164655	2224050	100.000

2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (2w) (CAS: 131101-13-8) [S11]

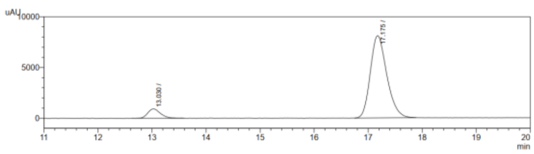


Colorless oil (9.7 mg, 42% yield, 92:8 er). $[\alpha]_D^{25}$ = 25.000 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H), 3.22 (s, 3H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.57 (d, *J* = 16.8 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 156.5, 136.0, 132.2, 116.6, 113.5, 110.5, 109.1, 55.9, 45.2, 26.6, 26.3, 22.2. HRMS (ESI) calcd. for $C_{13}H_{14}N_2NaO_2$ ($[M+Na]^+$) 253.0947, found 253.0941. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. n-hexane/i-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 13.03 min. (minor), 17.18 min. (major).



PDA Ch1 254nm

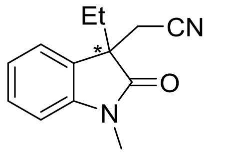
Peak#	Ret. Time	Height	Area	Area%
1	12.979	644881	11028596	49.956
2	17.256	526757	11048115	50.044
总计		1171638	22076711	100.000

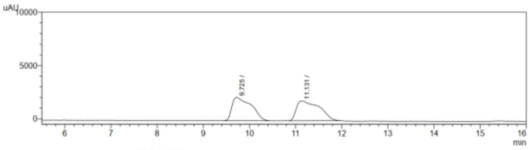


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	13.030	920	14932	7.995
2	17.175	8112	171829	92.005
总计		9032	186761	100.000

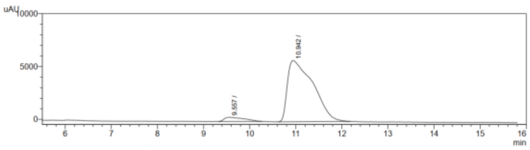
2-(3-ethyl-1-methyl-2-oxoindolin-3-yl)acetonitrile (2x): Yellow solid (13.9 mg, 65% yield, 95:5 er). $[\alpha]_D^{25}$ = 14.888 (*c* = 0.15, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2, Hz 1H), 7.36 (td, *J* = 7.8, 0.6 Hz 1H), 7.15 (td, *J* = 7.8, 0.6 Hz 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.85 (d, *J* = 16.8 Hz, 1H), 2.60 (d, *J* = 16.8 Hz, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 0.62 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 143.6, 129.2, 129.0, 123.2 (2C), 116.6, 108.5, 49.5, 29.4, 26.4, 25.6, 8.4. HRMS (ESI) calcd. for $C_{13}H_{14}N_2NaO$ ($[M+Na]^+$) 237.0998, found 237.0997. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 9.56 min. (minor), 10.94 min. (major).





PDA Ch1 254nm

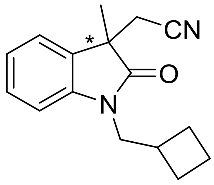
Peak#	Ret. Time	Height	Area	Area%
1	9.725	2183	63698	49.663
2	11.131	1862	64562	50.337
总计		4045	128260	100.000

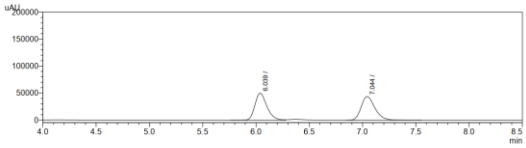


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	9.557	406	12387	5.241
2	10.942	5795	223939	94.759
总计		6201	236326	100.000

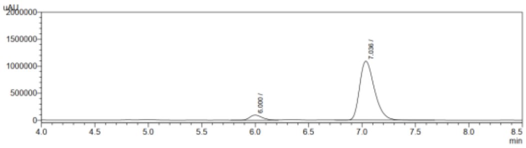
2-(1-(cyclobutylmethyl)-3-methyl-2-oxoindolin-3-yl)acetonitrile (2y): Yellow oil (20.3 mg, 80% yield, 93:7 er). $[\alpha]_D^{25}$ = 21.331 (*c* = 0.35, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.8, 0.6 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.81 – 3.71 (m, 2H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.57 (d, *J* = 16.8 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.91 – 1.81 (m, 4H), 1.51 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 142.4, 131.0, 129.0, 123.2, 123.0, 116.6, 109.1, 45.2, 44.8, 33.8, 26.4, 26.2, 26.1, 22.4, 18.2. HRMS (ESI) calcd. for $C_{16}H_{18}N_2NaO$ ($[M+Na]^+$) 277.1311, found 277.1307. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 6.00 min. (minor), 7.04 min. (major).





PDA Ch1 254nm

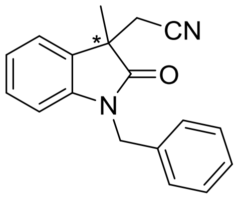
Peak#	Ret. Time	Height	Area	Area%
1	6.039	50081	391010	50.033
2	7.044	43770	390489	49.967
总计		93851	781499	100.000

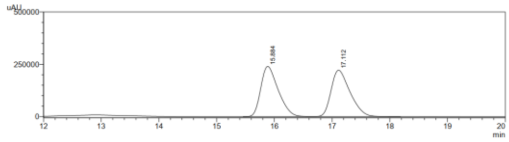


PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	6.000	95364	792019	7.013
2	7.036	1091526	10502139	92.987
总计		1186890	11294159	100.000

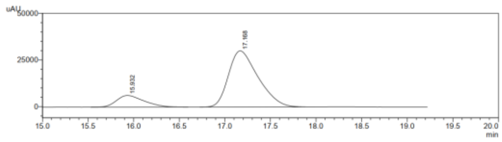
2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetonitrile (**2z**) Yellow oil (47.9 mg, 87% yield, 84:16 er). $[\alpha]_D^{25}$ = 18.667 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.21 (m, 6H), 7.08 - 7.07 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.93 (d, *J* = 3.0 Hz, 2H), 2.89 (d, *J* = 16.6 Hz, 1H), 2.64 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 141.7, 135.2, 130.8, 129.0, 128.8, 127.7, 127.1, 123.2, 123.0, 116.5, 109.6, 44.8, 43.8, 26.2, 22.4. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 15.93 min. (minor), 17.17 min. (major).





PDA Ch1 252nm

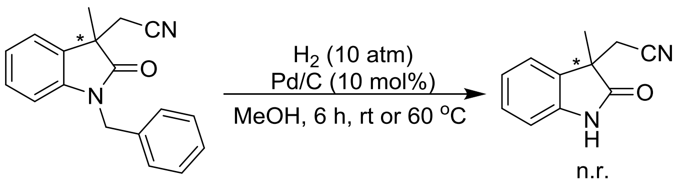
Peak#	Ret. Time	Height	Area	Area%
1	15.884	239961	5027236	49.954
2	17.112	221599	5036500	50.046
总计		461561	10063736	100.000



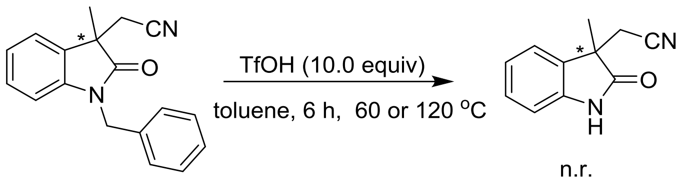
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	15.932	6195	129467	15.987
2	17.168	30045	680361	84.013
总计		36240	809828	100.000

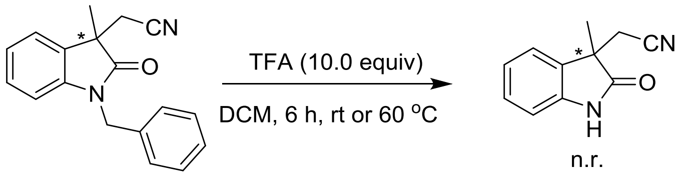
Removing the Bn group in **2z** has been attempted by the reported methods. All of them are failed. Detailed reaction conditions and reference of adopted methods see the picture below.



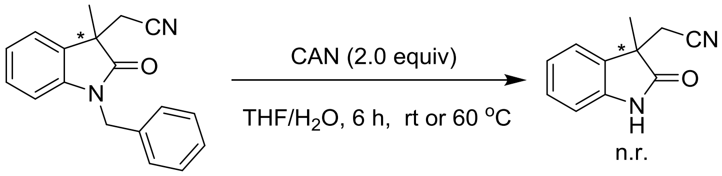
ref. *Angew. Chem. Int. Ed.* 2021, **60**, 7669



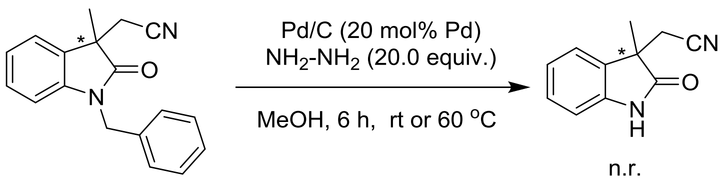
ref. Angew.Chem. Int. Ed. 2021, 60,14068

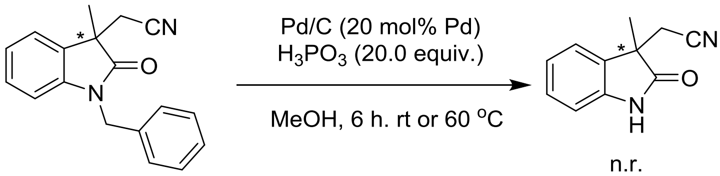


ref. ACS Catal. 2019, 9, 9285

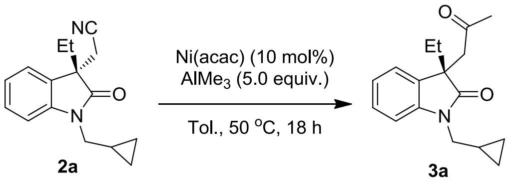


ref. Angew.Chem. Int. Ed. 2020, 59,2764

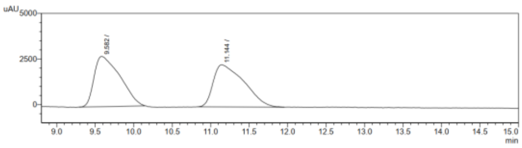




5. Experimental procedures for the derivatization of products

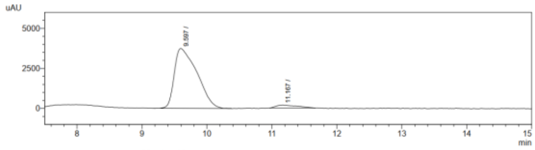


1-(cyclopropylmethyl)-3-ethyl-3-(2-oxopropyl)indolin-2-one: The procedure of preparing **3c** was adapted from the literature procedures.[S12] To a 25-mL flame-dried Schlenk tube was charged with **2a** (50 mg, 0.2 mmol, 1.0 equiv.), Ni(acac)$_2$ (5.2 mg, 0.02 mmol, 10 mol%) and toluene (2 mL). The toluene solution of $AlMe_3$ (100 μL, 1.0 mmol, 1.0 M, 5 equiv.) were added dropwise by syringe. The resulted mixture was stirred for 18 h at 50 ^oC. Saturated aqueous NH_4Cl (2 mL) was then added. The mixture was diluted with ethyl acetate (5 mL x 3). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using petroleum ether/ethyl acetate (6:1, v/v) as the eluent to afford **3a** as colorless oil (40.0 mg, 73% yield, 95.5:4.5 er)，$[\alpha]_D^{25}$ = -16.335 (*c* = 0.1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.65 (d, *J* = 6.6 Hz, 2H), 3.07 (d, *J* = 2.4 Hz, 2H), 1.97 (s, 3H), 1.85 – 1.76 (m, 2H), 1.23 – 1.19 (m, 1H), 0.58 (t, *J* = 7.2 Hz, 3H), 0.55 – 0.51 (m, 2H), 0.43 – 0.40 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.6, 179.5, 144.2, 131.4, 127.8, 122.3, 122.0, 108.4, 50.1, 49.9, 44.2, 31.4, 30.1, 9.6, 7.7, 3.9, 3.8. HRMS (ESI) calcd. for $C_{17}H_{21}NNaO_2$ ($[M+Na]^+$) 294.1465, found 294.1465. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak AD-3 column. *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 9.60 min. (major), 11.17 min. (minor).



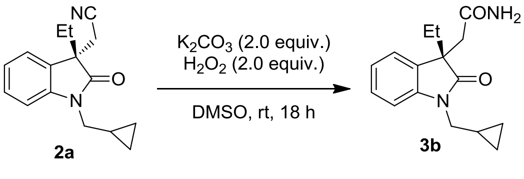
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	9.582	2756	64623	50.047
2	11.144	2306	64501	49.953
总计		5062	129124	100.000



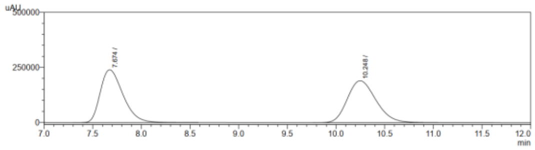
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	9.597	3736	90842	95.553
2	11.167	183	4228	4.447
总计		3919	95071	100.000



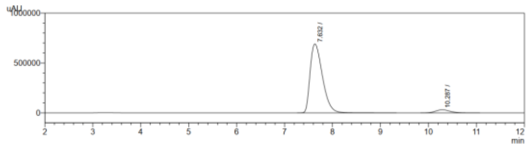
Preparation of (*S*)-2-(1-(cyclopropylmethyl)-3-ethyl-2-oxoindolin-3-yl)acetamide The procedure of preparing **3b** was adapted from literature procedures.[S13] To a 25-mL flame-dried Schlenk tube was successively charged with **2a** (50 mg, 0.2 mmol, 1.0 equiv.), K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.), DMSO (2 mL) and H_2O_2 (30 wt%, 0.3 mL, 2.5 mmol, 5 equiv.) were added. The resulting mixture was stirred for 18 h at room temperature. The reaction mixture was then diluted with ethyl acetate (15 mL) and water (15 mL) followed by separation and extraction. The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using the eluent of dichloromethane/MeOH (10:1, v/v) to afford **3b** as white solid

(51.7 mg, 95% yield, 95:5 er). $[\alpha]_D^{25}$ = - 19.667 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 5.47 (s, 1H), 3.66 – 3.58 (m, 2H), 2.80 (d, *J* = 15.0 Hz, 1H), 2.68 (d, *J* = 15.0 Hz, 1H), 2.02 – 1.96 (m, 1H), 1.90 – 1.84 (m, 1H), 1.21 – 1.15 (m, 1H), 0.59 (t, *J* = 7.2 Hz, 3H), 0.54 – 0.48 (m, 2H), 0.39 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.8, 171.4, 143.3, 131.0, 128.1, 123.1, 122.6, 108.5, 50.8, 44.2, 43.0, 30.6, 9.5, 8.1, 3.8, 3.7. HRMS (ESI) calcd. for $C_{16}H_{20}N_2NaO_2$ ($[M+Na]^+$) 295.1417, found 295.1419. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OD-3 column. *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min., λ = 254 nm, t_R = 7.63 min. (major), 10.29 min. (minor).



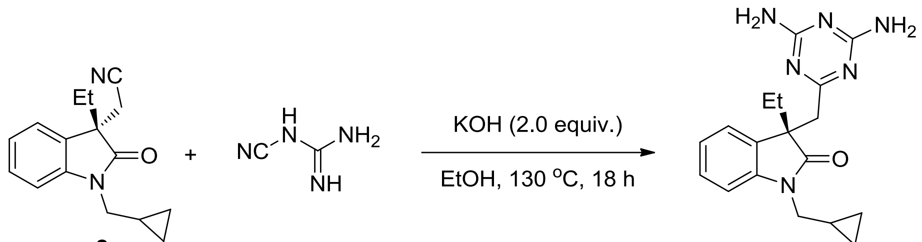
PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	7.674	239869	3890329	49.923
2	10.248	190286	3902406	50.077
总计		430155	7792735	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	7.632	690122	12328021	95.011
2	10.287	31267	647315	4.989
总计		721389	12975336	100.000

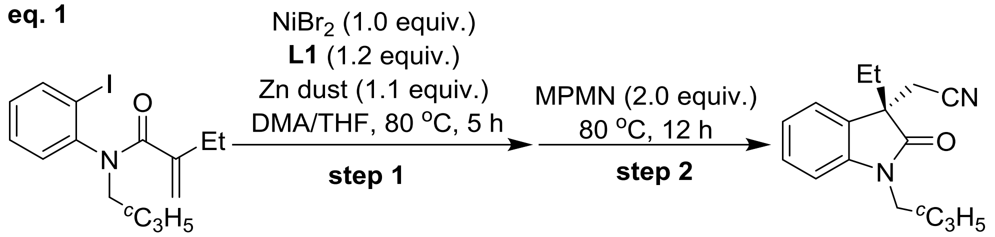


2a **3c**

Preparation of 1-(cyclopropylmethyl)-3-((4,6-diamino-1,3,5-triazin-2-yl)methyl)-3-ethylindol-in-2-one (3c): The procedure of preparing **3c** was adapted from literature procedures.[S14] To a 25-mL flame-dried Schlenk tube was charged with **2a** (50 mg, 0.2 mmol, 1.0 equiv.), 1-cyanoguanidine (20.1 mg, 0.24 mmol, 1.2 equiv.) and EtOH (5.0 mL).Then KOH (22.4 mg, 0.4 mmol, 2.0 equiv.) was added at 0 °C. After sealing the Schlenk tube with a cap, the reaction was heated to 130 °C and stirred for 18 h. The reaction mixture was diluted with ethyl acetate (15 mL x 3) and water (15 mL). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica using the eluent of dichloromethane/MeOH (10:1, v/v) to afford **3c** as white solid (50.7 mg, 75% yield). $[\alpha]_D^{25}$ = 18.333 (*c* = 0.2, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.21 (s, 4H), 3.62 (dd, *J* = 6.0, 2.4 Hz, 2H), 3.18 (d, *J* = 15.0 Hz, 1H), 2.94 (d, *J* = 15.6 Hz, 1H), 2.00 – 1.95 (m, 1H), 1.88 – 1.82 (m, 1H), 1.20 – 1.16 (m, 1H), 0.59 (t, *J* = 7.2 Hz, 3H), 0.54 – 0.46 (m, 2H), 0.44 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.6, 175.3, 166.5, 144.1, 131.1, 127.5, 123.1, 121.7, 107.7, 51.7, 44.5, 44.0, 31.9, 9.7, 8.1, 3.9, 3.8. HRMS (ESI) calcd. for $C_{18}H_{22}N_6NaO$ ($[M+Na]^+$) 361.1747, found 361.1749.

6. Procedure for the control experiments

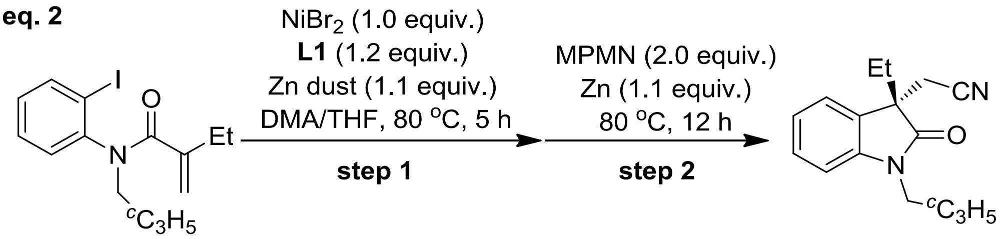
eq. 1



1a (1.0 equiv.) **2a**, trace

To a 25-mL flame-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (22.5 mg, 0.1 mmol, 1.0 equiv.), (*S,S*)-BDPP (53.0 mg, 1.2 equiv.), Zn dust (7.2 mg, 1.1 equiv.) under N_2 atmosphere in glove box. Then DMA (1 mL) and THF (1 mL) were added. The reaction was stirred at 80 °C for 5 h. Afterwards, MPMN (31.2 mg, 0.2 mmol, 2.0 equiv.) was added. The reaction was further stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted and analyzed by GC-MS and GC-FID.

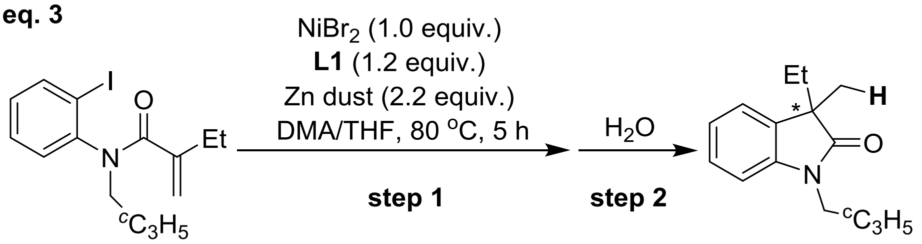
eq. 2



1a (1.0 equiv.) **2a**, 61%, 94:6 er

To a 25-mL oven-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (22.5 mg, 0.1 mmol, 1.0 equiv.), (*S,S*)-BDPP (53.0 mg, 1.2 equiv.), Zn dust (7.2 mg, 0.11 mmol, 1.1 equiv.) under N_2 atmosphere in glove box. Then, DMA (1 mL) and THF (1 mL) were added. The reaction was stirred at 80 °C for 5 h. Afterwards, MPMN (31.2 mg, 0.2 mmol, 2.0 equiv.) and Zn dust (7.2 mg, 0.11 mmol, 1.1 equiv.) was added. The reaction was further stirred at 80 °C for 12 h. After cooling to room temperature, the enantiomeric ratio and yield of **2a** was determined by HPLC.

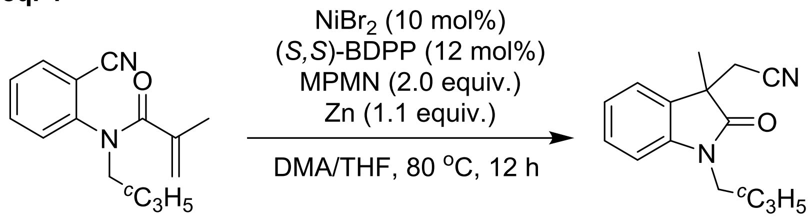
eq. 3



1a (1.0 equiv.) **2ab**, 89%, 92:8 er

To a 25-mL oven-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (22.5 mg, 0.1 mmol, 1.0 equiv.), (*S,S*)-BDPP (53.0 mg, 1.2 equiv.) and zinc dust (14.4 mg, 0.22 mmol, 2.2 equiv.) under N_2 atmosphere in glove box. Then DMA (1 mL) and THF (1 mL) were added. The reaction was stirred at 80 °C for 5 h. And then H_2O (1 mL) was added. The reaction was further stir at room temperature for 1 h. The enantiomeric ratio and yield of **2ab** was determined by HPLC.

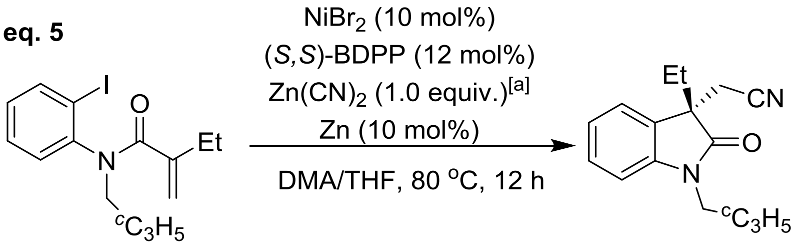
eq. 4



4 n.r.

To an oven-dried 25-mL Schlenk tube was charged with aryl nitrile **4** (0.1 mmol, 1.0 equiv.), MPMN (31.2 mg, 2.0 equiv.), $NiBr_2$ (2.2 mg, 10 mol%), (*S,S*)-BDPP (5.3 mg, 12 mol%) and zinc dust (7.2 mg, 1.1 equiv.) in the glove box under N_2 atmosphere. Then, DMA (1 mL) and THF (1 mL) were added. The reaction was stirred at 80 °C for 12 h. After cooling to room temperature, the conversion of **4** and product yield were determined by GC-FID, GC-MS and TLC.

eq. 5

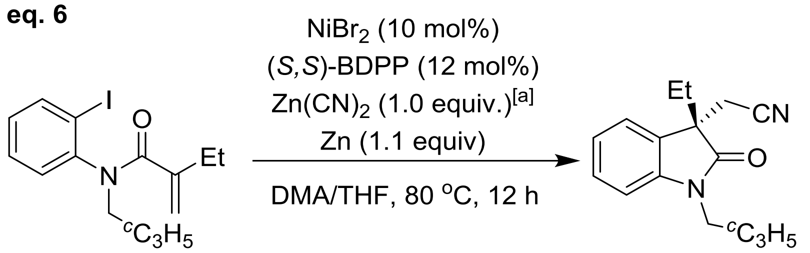


1a (1.0 equiv.) **2a**, 15%, 94.5:5.5 er

[a]The DMA/THF solution dissolving $Zn(CN)_2$ was fed into the reaction solution with programmable syringe pump in 5 h

To a 25-mL oven-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (2.3 mg, 0.01 mmol, 10 mol%), (*S,S*)-BDPP (5.3 mg, 12 mol%) and zinc dust (0.65 mg, 0.01 mmol, 10 mol%) under N_2 atmosphere in glove box. Then DMA (0.5 mL) and THF (0.5 mL) were added. The reaction was stirred at 80 °C for 12 h. With the beginning of stirring, the solution of DMA/THF (1 mL, v/v= 1:1) dissolving $Zn(CN)_2$ (11.7 mg, 1.0 equiv.) was fed into the reaction solution with programmable syringe pump in 5 hours. After reaction, the enantiomeric ratio and yield of **2a** was determined by GC-FID and HPLC.

eq. 6

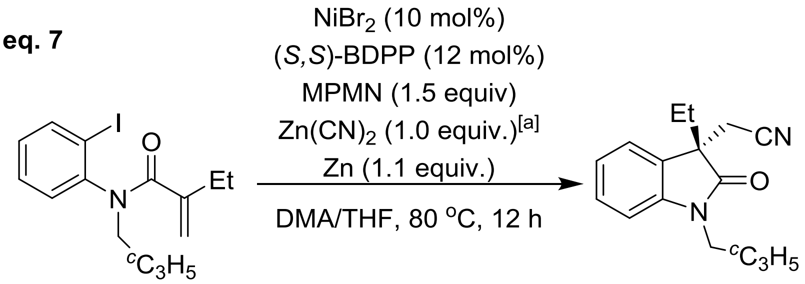


1a (1.0 equiv.) **2a**, 16%, 78.5:21.5 er

[a]The DMA/THF solution dissolving $Zn(CN)_2$ was fed into the reaction solution with programmable syringe pump in 5 h

To a 25-mL oven-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (2.3mg, 0.01 mmol, 10 mol%), (*S,S*)-BDPP (5.3 mg, 12 mol%) and zinc dust (7.2 mg, 0.1 mmol, 1.1 equiv.) under N_2 atmosphere in glove box. Then DMA (0.5 mL) and THF (0.5 mL) were added. The reaction was stirred at 80 °C for 12 h. With the beginning of stirring, the solution of DMA/THF (1 mL, v/v= 1:1) dissolving $Zn(CN)_2$ (11.7 mg, 1.0 equiv.) was fed into the reaction solution with programmable syringe pump in 5 hours. After reaction, the enantiomeric ratio and yield of **2a** was determined by GC-FID and HPLC.

eq. 7



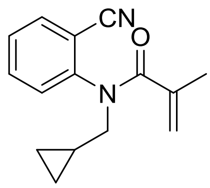
1a (1.0 equiv.) **2a**, 67%, 85:15 er

[a]The DMA/THF solution dissolving $Zn(CN)_2$ was fed into the reaction solution with programmable syringe pump in 5 h

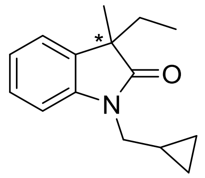
To a 25-mL oven-dried Schlenk tube was charged with **1a** (33.5 mg, 0.1 mmol, 1.0 equiv.), $NiBr_2$ (2.3mg, 0.01 mmol, 10 mol%), (*S,S*)-BDPP (5.3 mg, 12 mol%), zinc dust (7.2 mg, 0.1 mmol, 1.1 equiv.) and MPMN (23.4 mg, 0.15 mmol, 1.5 equiv.) under N_2 atmosphere in glove box. Then DMA (0.5 mL) and THF (0.5 mL) were added. The reaction was stirred at 80 °C for 12 h. With the beginning of stirring, the solution of DMA/THF (1 mL, v/v= 1:1) dissolving $Zn(CN)_2$ (11.7 mg, 1.0 equiv.) was fed into the reaction solution with programmable syringe pump in 5 hours. After reaction, the enantiomeric ratio and yield of **2a** was determined by GC-FID and HPLC.

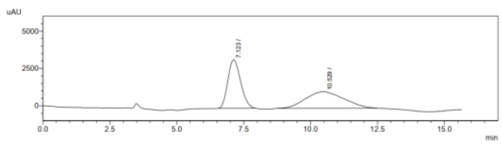
The preparation of aryl nitrile **4** followed the method described in section 2 of ESI using 2-aminobenzonitrile as the starting material.

N-(2-cyanophenyl)-N-(cyclopropylmethyl)methacrylamide (4) White solid, 1.66 g, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5, 1H), 7.64 (t, *J* = 7.5, 1H), 7.43 (t, *J* = 7.5, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 5.11-5.02 (m, 2H), 3.75 (d, *J* = 7.0 Hz, 2H), 1.92 (s, 3H), 1.06 – 1.00 (m, 1H), 0.50 - 0.42 (m, 2H), 0.07 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 145.9, 140.2, 133.5, 129.9, 127.8, 119.5, 116.5, 113.3, 54.2, 20.2, 9.5, 3.7. HRMS (EI) calcd. for $C_{15}H_{17}N_2O$ ($[M+H]^+$) 241.1335, found 241.1335.



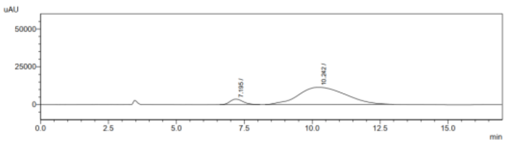
1-(cyclopropylmethyl)-3-ethyl-3-methylindolin-2-one (2ab) 89%, 92:8 er. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.65 – 3.56 (m, 2H), 1.98 – 1.92 (m, 1H), 1.80 – 1.74 (m, 1H), 1.35 (s, 3H), 1.21 – 1.17 (m, 1H), 0.59 (t, *J* = 7.2 Hz, 3H), 0.53 – 0.47 (m, 2H), 0.40 – 0.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.7, 143.1, 134.0, 127.5, 122.6, 122.1, 108.2, 48.4, 43.9, 31.6, 23.5, 9.7, 8.8, 3.8, 3.7. HRMS (ESI) calcd. for $C_{15}H_{19}NNaO$ ($[M+Na]^+$) 252.1359, found 252.1358. The enantiomeric ratio was determined by HPLC analysis on Daicel Chiralpak OB-H column. *n*-Hexane/*i*-PrOH = 99:1, flow rate = 1.0 mL/min., λ = 254nm, t_R = 7.20 min. (minor), 10.24 min. (major).





PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	7.123	3249	107997	49.729
2	10.529	1109	109173	50.271
总计		4359	217170	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	7.195	3630	120104	8.087
2	10.242	11330	1365043	91.913
总计		14960	1485148	100.000

7. Information of X-ray Crystallographic analysis

Method of cultivating single crystal of **2a**: To determine the absolute configuration of product **2a**, its single crystal was both cultivated in 5-mL glass vial by slow evaporation technique. **2a** (40 mg) was dissolved in the mixing solvent of dichloromethane/petroleum ether (0.2 mL/3 mL) at ambient temperature. Dichloromethane and petroleum ether spontaneously evaporates in open air at 25 °C. After several days, the crystal of **2a** emerged and was collected for x-ray diffraction analysis. The ellipsoid contour 50% probability levels were used for the images of the crystal structures. The crystal structures were determined by single crystal X-ray diffraction analysis on Rigaku XtaLAB PRO MM003-DS dual system at 293 K with a Cu micro-focus source. CCDC numbers of **2a** are 2083292.

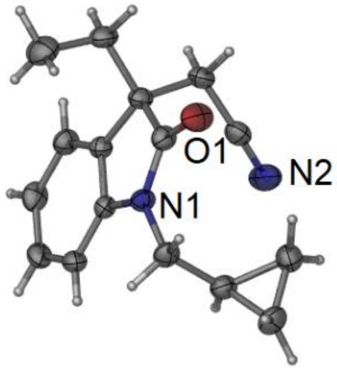


Figure S2 ORTEP diagram of 2a (the ellipsoid contour probability level is 50%)

Table S1 Crystal data and structure refinement for exp_1837.

Identification code	exp_1837
Empirical formula	$C_{16}H_{18}N_2O$
Formula weight	254.32
Temperature/K	169(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6715(2)
b/Å	9.0287(3)
c/Å	17.7211(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1387.43(7)
Z	4
ρ_{calc}g/cm^3	1.218
μ/mm^{-1}	0.605
F(000)	544.0
Crystal size/mm^3	0.42 × 0.32 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.982 to 134.03
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21
Reflections collected	27293
Independent reflections	2443 [R_{int} = 0.0500, R_{sigma} = 0.0154]
Data/restraints/parameters	2443/0/174
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0250, wR_2 = 0.0625

Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0626
Largest diff. peak/hole / e Å^{-3}	0.17/-0.10
Flack parameter	0.14(7)

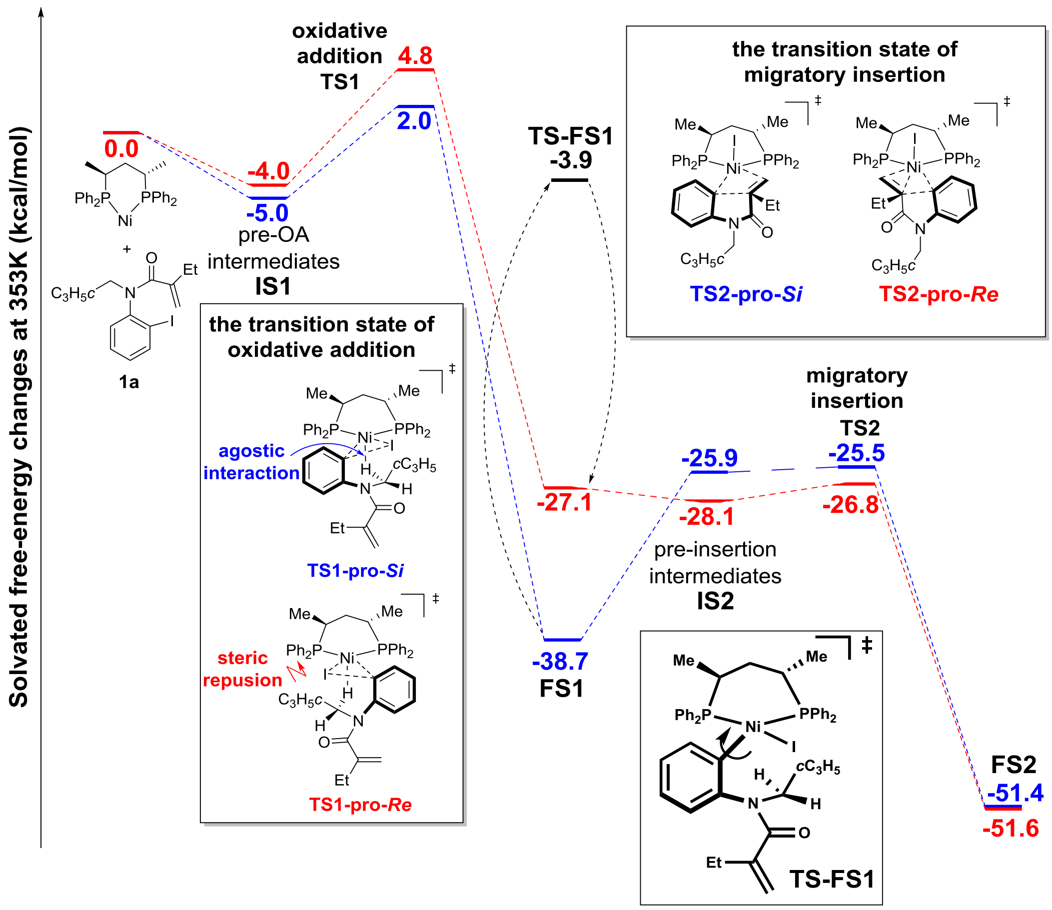
Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_1837. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7343.2(14)	6481.4(12)	3558.1(7)	42.8(3)
N1	5642.1(14)	4536.9(13)	3444.9(7)	27.3(3)
N2	6384.6(17)	3927(2)	5515.2(8)	45.5(4)
C1	7226.1(17)	2556.2(16)	3667.1(8)	25.7(3)
C11	8711.2(18)	4143.4(18)	4591.6(9)	32.7(4)
C12	7411.6(18)	4028.9(18)	5118.0(9)	32.7(3)
C6	5718.4(17)	2981.6(16)	3496.4(8)	25.2(3)
C2	7587.9(19)	1075.9(17)	3744.1(8)	31.6(3)
C7	7049.9(18)	5162.4(16)	3571.5(9)	29.3(3)
C13	4202.1(17)	5380.5(18)	3403.5(9)	32.0(4)
C8	8207.9(17)	3923.7(17)	3760.7(8)	27.5(3)
C14	3434.9(18)	5499.8(18)	4162.0(9)	32.8(4)
C5	4557.5(18)	1959.0(17)	3394.7(8)	31.2(3)
C9	9647.0(17)	3989.1(19)	3255.0(9)	34.8(4)
C15	3980(2)	6676.9(19)	4691.2(10)	39.0(4)
C4	4939.2(19)	467.5(18)	3474.2(9)	34.8(4)
C3	6430(2)	27.5(17)	3644.9(9)	35.9(4)
C16	2443(2)	6821(2)	4320.5(11)	43.3(4)
C10	9305(2)	3789(3)	2421.3(10)	49.9(5)

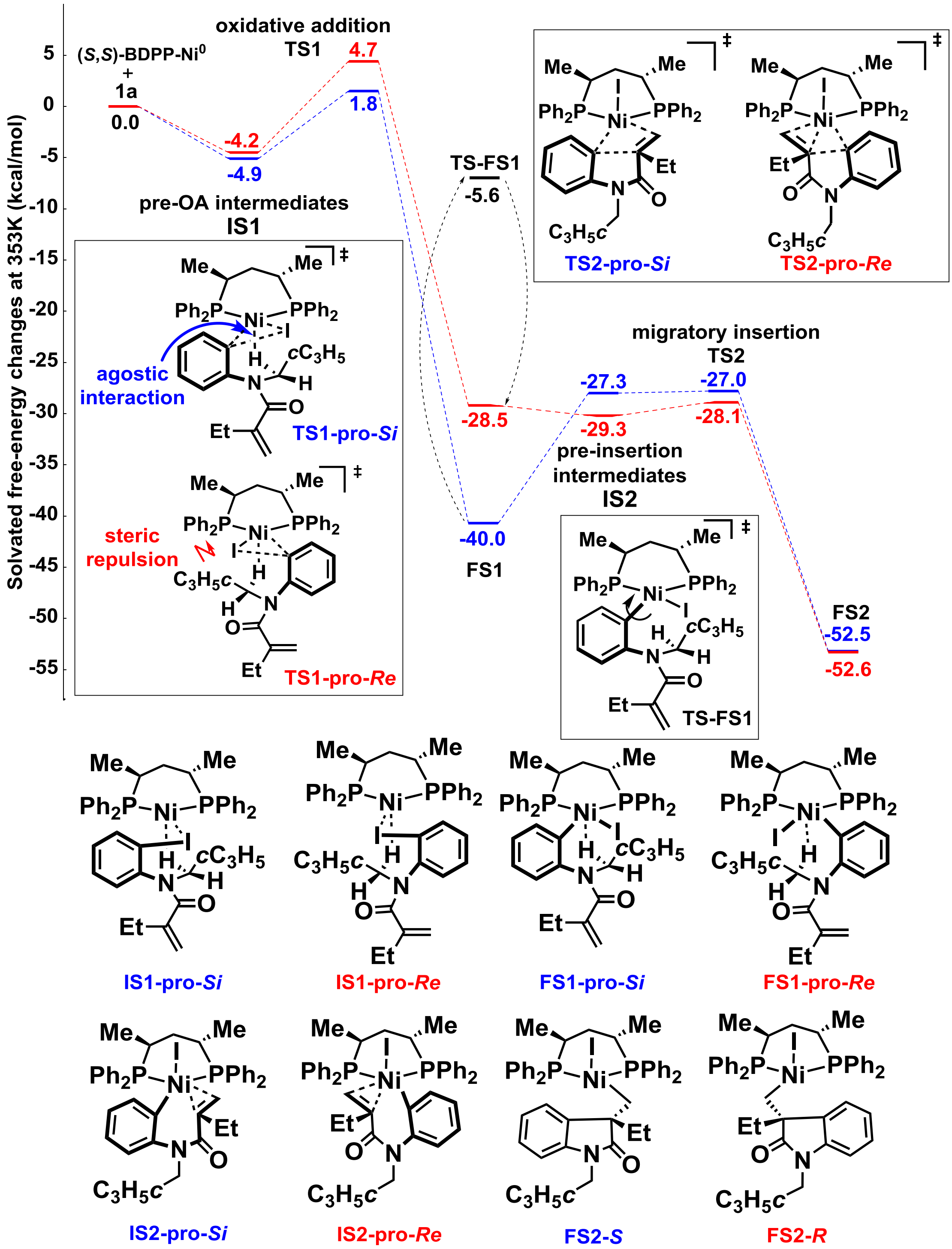
8. Computational methods and Cartesian coordinate of geometry-optimized structures

Considering the applicability of local meta-generalized gradient approximation (meta-GGA) functional M06L[S15] on homogeneous organometallic thermochemistry,[S16] the M06L functional in conjugation with the def2-SVP basis set[S17] was used for structure optimization. The corresponding frequency calculation using the same method was used to characterize the nature of the optimized structures; i.e. energy minimums without imaginary frequencies or transition states with only one imaginary frequency; and the imaginary model connects the initial and the final states. In addition, we used M06L in conjugation with the def2-TZVP basis set to calculate the single-point energies on the M06L/def2-SVP optimized geometries (M06L /def2-TZVP//M06L/def2-SVP). Furthermore, we also carried self-consistent reaction field (SCRF) single-point energies at the M06L/def2-TZVP level by using the SMD solvation model.[S18] *N*,*N*-Dimethylacetamide (DMA), tetrahydrofuran (THF) and the mixture of DMA/THF (1:1, v/v) were used as solvent to estimate the solvation influence (M06L-SCRF/def2-TZVP(SMD)//M06L/def2-SVP). The inputted genric parameter for the binary solvent symstem consisting of DMA/THF (1:1, v/v) using the SMD solvation model is set as follows: ε (ε: dielectric constant at 298 K) = 22.6034; $\varepsilon_{inf} \approx n^2$ (*n*: index of refraction at optical frequencies at 293 K) = 2.0209; α (Abraham's hydrogen bond acidity) = 0; β (Abraham's hydrogen bond basicity) =0.63; γ (γ: macroscopic surface tension at a liquid-air interface at 298 K) = 43.53; φ (φ: aromaticity) = 0; ψ (ψ: electronegative halogenicity) = 0.[S19] The thermal corrections to Gibbs free energy at 353 K calculated by Shermo[S20] were added to the total electronic energies from the single-point energy calculations, and we therefore used the corrected Gibbs free energy (ΔG) at 353 K (80 °C) for our energetic discussion and comparison. All other calculations were performed on the Gaussian 16 package.[S21] Structure of **TS1-pro-*Si*** and **TS1-pro-*Re*** are render by visualization software CYLview 1.0b.[S22]

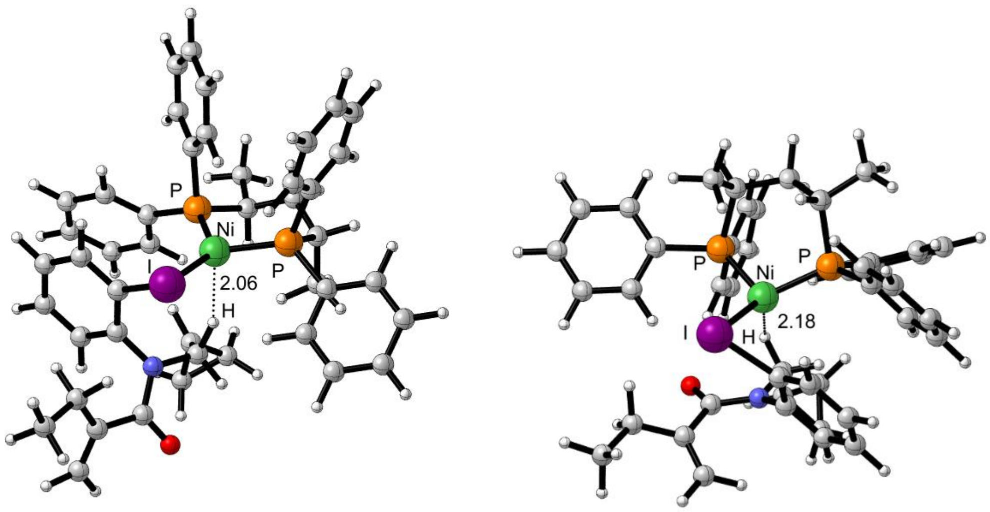
8.1 Potential energy surface in the solvation of DMA or binary solvent consisting of DMA and THF (1:1, v/v)



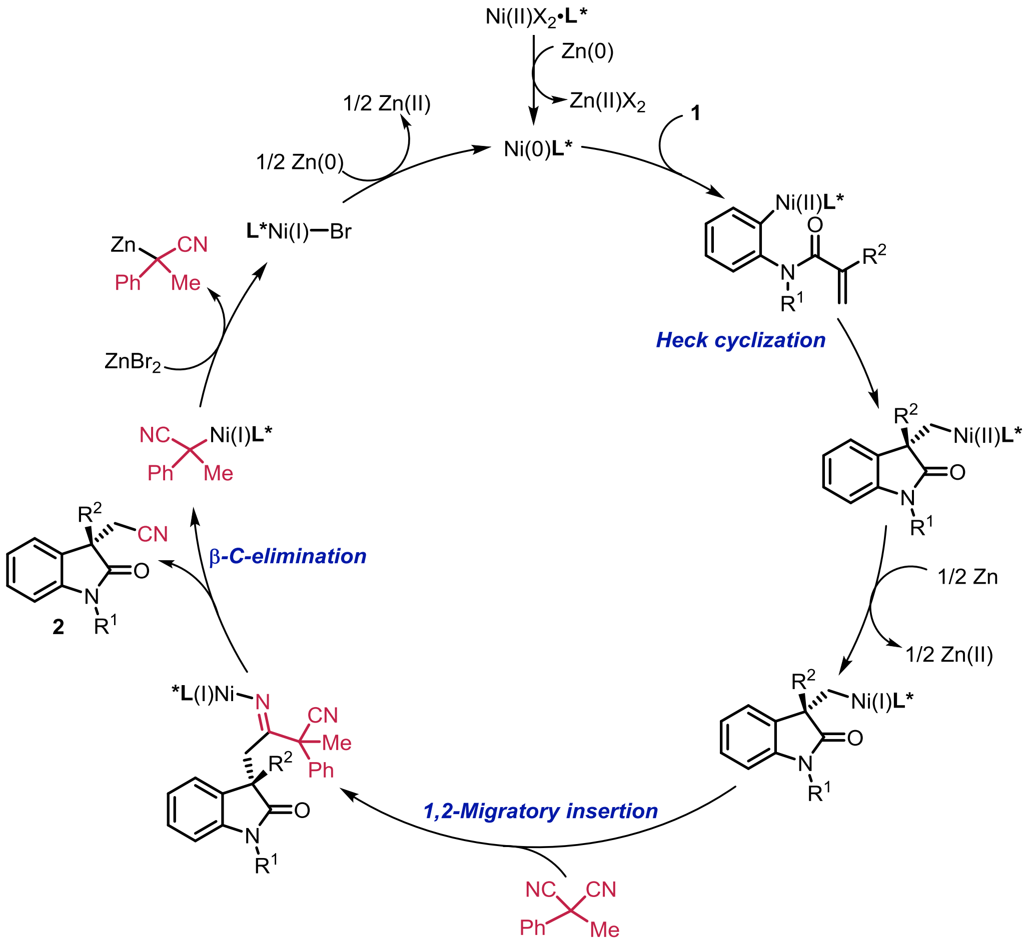
Scheme S1 Energetic profiles for oxidative addition and insertion steps of Mizoroki-Heck cyclization of **1a** catalyzed by Ni/(*S*,*S*)-BDPP in the solvation of THF at 353 K.



Scheme S2 Energetic profiles for oxidative addition and insertion steps of Mizoroki-Heck cyclization of **1a** catalyzed by Ni/(*S*,*S*)-BDPP in the solvation of binary solvent DMA/THF (1:1, v/v) at 353 K.

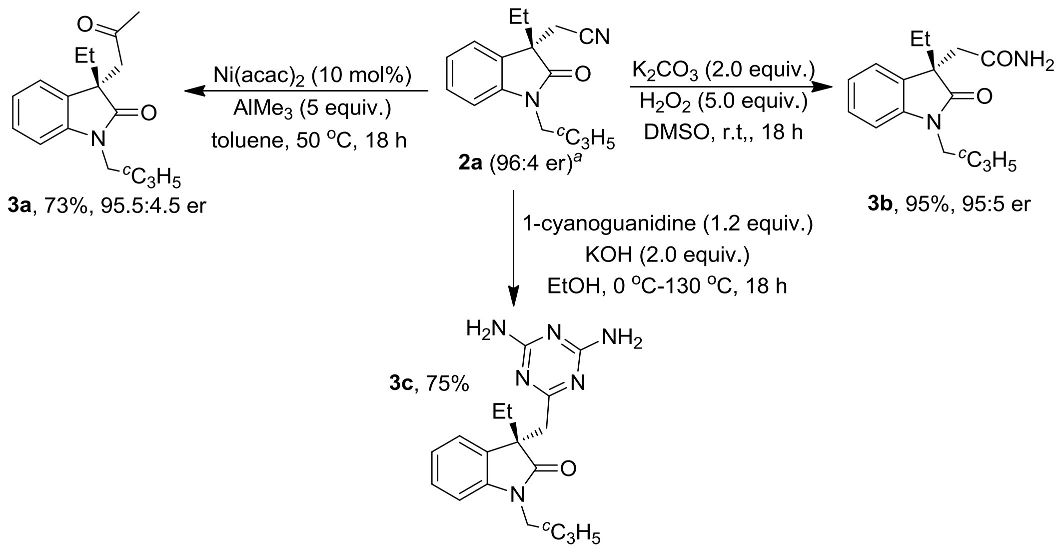


Scheme S3 Structure of **TS1-pro-*Si*** and **TS1-pro-*Re*** (Unit of distance: Å)



Scheme S4 Plausible mechanism based on the results of computation and control experiments.

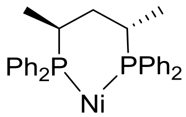
The practical application of Ni-catalyzed enantioselective reductive arylcyanation of alkenes was demonstrated by the product derivatization (Scheme S5). Exploiting the Ni-catalyzed 1,2-addition with trimethylaluminum, H2O2-promoted hydrolysis or the cyclization with 1-cyanoguanidine, the installed nitrile group can be respectively transformed to ketone, amide or 4,6-diamino-1,3,5-triazin-2-yl group in good yields. The established chiral centers are well preserved in all cases. These transformations exemplify the diversified utility of chiral nitrile product in the synthesis of chiral complex molecules.



Scheme S5 The transformation of product's nitrile group. [a]Recrystallized product **2a**.

8.2 Cartesian coordinate of geometry-optimized structures

Ni((*S*,*S*)-BDPP)



EE (DMA) = -3314.4576695 a.u.

EE (THF) = -3314.4596127 a.u.

EE (DMA/THF) = -3314.4596760 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.427411 a.u.

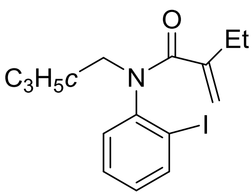
NImag = 0

0 1

P	-1.74305900	-0.41671500	-0.12502200
P	1.74905500	-0.40409800	-0.09238100
C	2.42799000	-0.08141500	2.66885500
C	1.35868800	-0.63996200	1.74253700
C	-0.01372000	-0.06487200	2.11804200
C	-1.28719800	-0.79293000	1.65880600
C	-1.19517700	-2.30001100	1.83995500
C	4.28361800	-0.75180900	-1.25072700
C	5.48159400	-1.41481800	-1.49980600
C	5.82606900	-2.54816100	-0.76084800
C	4.95642700	-3.00796400	0.22675100
C	3.75895200	-2.33954400	0.47834600
C	3.40128700	-1.19247700	-0.24866100
C	1.14485900	2.24873100	-0.60735300
C	1.32248000	3.63049200	-0.62384600
C	2.53282000	4.17852900	-0.20028500
C	3.55725200	3.33838000	0.23989200
C	3.37175800	1.95689300	0.26940600
C	2.15842300	1.39309500	-0.15190200
C	-3.41712600	-2.46901100	-0.99151500
C	-4.59662100	-3.20441800	-1.09529900
C	-5.75157500	-2.75720800	-0.45384100
C	-5.71961700	-1.57682900	0.29035100
C	-4.53613300	-0.84794400	0.39758500
C	-3.36839100	-1.28939800	-0.23897700
C	-2.46464700	2.10053000	1.09570600
C	-2.82704900	3.44694800	1.02598200
C	-3.04754800	4.05378700	-0.20849600
C	-2.90055900	3.30572500	-1.37841600
C	-2.52417100	1.96797600	-1.30621900
C	-2.30506800	1.33837600	-0.06991700

H	2.24980800	-0.39886900	3.70821800
H	3.44031900	-0.41178700	2.39508100
H	2.42611500	1.01913100	2.66357500
H	1.32242400	-1.73583100	1.87069900
H	-0.04795300	0.99920400	1.81718300
H	-0.04674100	-0.04397800	3.22298600
H	-2.11911800	-0.42719500	2.28982600
H	-0.80828000	-2.56264700	2.83719300
H	-2.17241200	-2.78880900	1.72394300
H	-0.51923400	-2.73922800	1.08639000
H	4.02588000	0.13195700	-1.84332600
H	6.15305700	-1.04386800	-2.27842200
H	6.76551800	-3.07028400	-0.95588400
H	5.21253400	-3.89454500	0.81247400
H	3.09621300	-2.72246800	1.25970000
H	0.20930900	1.79492100	-0.95231800
H	0.51348100	4.27577900	-0.97607800
H	2.68258900	5.26091400	-0.21721400
H	4.50886600	3.76398900	0.56863500
H	4.18078600	1.31047900	0.62262100
H	-2.50362200	-2.79975400	-1.49915900
H	-4.61747300	-4.12498500	-1.68397700
H	-6.68087900	-3.32570400	-0.53847200
H	-6.62505800	-1.22101100	0.78868200
H	-4.52160000	0.07985700	0.97931400
H	-2.30585000	1.64936700	2.07860800
H	-2.93939900	4.02419000	1.94715200
H	-3.33098100	5.10763000	-0.26064200
H	-3.07188400	3.77086200	-2.35242500
H	-2.38270300	1.39053100	-2.22646500
Ni	0.00180900	-0.82285000	-1.12226700

1a



EE (DMA) = -1010.4296228 a.u.

EE (THF) = -1010.4297659 a.u.

EE (DMA/THF) = -1010.4304120 a.u.

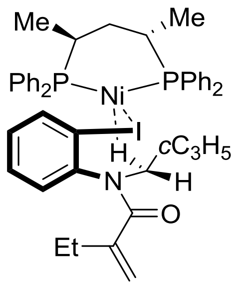
Thermal correction to Gibbs free energy at 353 K = 0.235322 a.u.

NImag = 0

0 1

C	-0.74625600	0.39671800	1.10252400
C	-3.10883600	-0.97972000	-0.81867400
C	0.87606200	-1.50145600	0.95016700
C	2.06795800	-0.61826500	1.16913300
C	3.27328000	-1.04378700	0.38106200
C	4.48524100	-0.15164200	0.50254400
C	2.08677900	0.35755100	2.08878100
C	-1.43339500	0.90833300	2.21367700
C	-1.85702700	2.23035300	2.26607600
C	-1.59069800	3.08224100	1.19510000
C	-0.91560600	2.59825200	0.07779300
C	-0.50728800	1.26274400	0.01933500
C	-1.52343700	-1.92148100	1.01453300
C	-2.11507100	-2.00558200	-0.36387600
C	-3.55408300	-2.37825600	-0.53234700
I	0.42803700	0.59255600	-1.75500300
N	-0.40233800	-0.97903600	1.10268000
O	1.03760000	-2.68197100	0.68419000
H	-3.39587600	-0.19515000	-0.11159700
H	-3.06900700	-0.64212000	-1.85672900
H	2.97506700	-1.14760100	-0.67619000
H	3.50935900	-2.07820700	0.68218700
H	5.30632000	-0.51294500	-0.13031000
H	4.86775800	-0.10957300	1.53294400
H	4.26261900	0.88104500	0.19301800
H	2.99452200	0.93184000	2.28840900
H	1.21629300	0.60948200	2.69563500
H	-1.61677200	0.23509100	3.05528500
H	-1.91147200	4.12569400	1.22108100
H	-0.71898400	3.26027100	-0.76747800
H	-2.29630900	-1.60682900	1.73526000
H	-1.14354500	-2.89981500	1.33470200
H	-1.41643100	-2.38283900	-1.11834100
H	-3.82816500	-3.02466700	-1.36813500
H	-4.14578900	-2.55426200	0.37031300
H	-2.38571900	2.59810900	3.14784300

IS1-pro-*Si*



EE (DMA) = -4324.9244673 a.u.

EE (THF) = -4324.9263797 a.u.

EE (DMA/THF) = -4324.9269478 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.691758 a.u.

NImag = 0

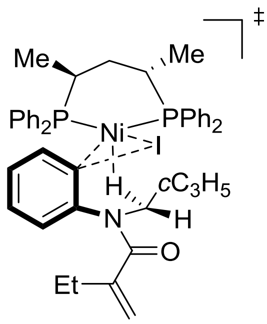
0 1

C	2.98518800	1.62395200	-2.59447700
C	4.14074500	2.38681000	-2.41445800
C	4.93870800	2.18521700	-1.28887700
C	4.57985000	1.22509200	-0.34625400
C	3.43450500	0.43717700	-0.52292600
C	2.63895300	0.65334000	-1.65881100
H	2.36035000	1.77930400	-3.47857200
H	4.41510700	3.13917400	-3.15830200
H	5.84140800	2.78179400	-1.13987300
H	5.18965900	1.06062100	0.54665300
C	3.93154000	-1.61522800	0.76116100
C	4.99231100	-2.01497300	-0.23321800
C	6.12026700	-2.51420000	0.29282100
C	2.09138700	-0.16125800	1.44169100
H	1.15347100	0.08435300	0.89807200
H	1.89845100	-1.05615400	2.04913400
N	3.10596400	-0.54392200	0.45323600
O	3.78428500	-2.24636600	1.79742500
C	4.72303600	-1.97396200	-1.71635000
H	3.64417500	-2.14589300	-1.87833000
H	4.89848400	-0.95852100	-2.10925300
Ni	-0.83921800	-0.09038900	-0.32425800
H	6.24550700	-2.57118200	1.37570100
C	2.50361100	0.98269200	2.32268300
C	2.01463000	1.02554700	3.73673900
C	3.45583100	0.73784400	3.45370200
H	2.58790900	1.95161100	1.81510900
H	1.39071100	0.19963300	4.08999000
H	1.74767500	1.99667200	4.16047900
H	4.19282900	1.51016900	3.68610600
H	3.80903100	-0.28656500	3.59535700

H	6.93667800	-2.88645600	-0.32888200
P	-2.18670100	-1.48659800	0.47366300
P	-1.31383400	1.77405800	0.56819500
C	-3.13143200	2.98012700	2.40097500
C	-2.33494100	1.70988800	2.14079000
C	-3.27187200	0.49471600	2.16736200
C	-2.64846900	-0.91082500	2.19739200
C	-1.42504100	-0.99251900	3.09717300
C	0.83725600	3.34618800	-0.12896900
C	1.91218400	4.20933100	0.05089400
C	2.14967700	4.77759800	1.30581200
C	1.29500000	4.48184000	2.36537600
C	0.20703600	3.62657600	2.17877000
C	-0.04051500	3.04469800	0.92802000
C	-3.35710400	1.84086600	-1.30817500
C	-4.28912100	2.41671600	-2.16829600
C	-4.31714500	3.80081800	-2.34005600
C	-3.41004700	4.60163900	-1.64509900
C	-2.48677800	4.02761700	-0.77179900
C	-2.45159700	2.63830600	-0.58892000
C	-0.15907300	-3.32282600	0.90327900
C	0.41253700	-4.54540900	1.24591500
C	-0.40857300	-5.64747300	1.48941100
C	-1.79502300	-5.51748500	1.39680800
C	-2.36642200	-4.28638200	1.07413900
C	-1.55139400	-3.17477300	0.82673500
C	-5.04565000	-1.81967200	0.32145300
C	-6.22970200	-1.98892200	-0.39760300
C	-6.19507800	-2.14951600	-1.78130700
C	-4.96793900	-2.13589000	-2.44700400
C	-3.78971900	-1.95046100	-1.73009300
C	-3.80678300	-1.79814500	-0.33399600
H	-3.56207900	2.97529600	3.41447900
H	-2.52769900	3.89346600	2.30130700
H	-3.96822900	3.07227100	1.69202500
H	-1.58149000	1.58376700	2.93996100
H	-3.98572700	0.57840600	1.32545300
H	-3.89729100	0.60144400	3.07254900
H	-3.40854800	-1.60989500	2.59062100
H	-1.61199600	-0.52094000	4.07473900
H	-1.11807500	-2.03082300	3.28369100
H	-0.56631600	-0.47618300	2.63379300
H	0.67308100	2.87550800	-1.10556400
H	2.57810900	4.42761400	-0.78786700

H	3.00060200	5.44634100	1.45516500
H	1.47397300	4.91915000	3.35128900
H	-0.44052600	3.40771900	3.03138200
H	-3.31295000	0.75307500	-1.19135300
H	-4.98780900	1.77540300	-2.71208500
H	-5.04155900	4.25633400	-3.01949300
H	-3.42485000	5.68621100	-1.77954500
H	-1.78795000	4.66784000	-0.22484400
H	0.47195700	-2.45183100	0.69169400
H	1.49945700	-4.63160100	1.31984200
H	0.03309400	-6.61256600	1.74926400
H	-2.43769200	-6.38225000	1.58065100
H	-3.45546400	-4.19108900	1.01123400
H	-5.10006600	-1.69977500	1.40677900
H	-7.18654500	-1.99592800	0.13026800
H	-7.12347900	-2.28025600	-2.34214300
H	-4.93075900	-2.25855400	-3.53217200
H	-2.82722400	-1.90202200	-2.25209500
I	0.87749300	-0.63135300	-1.98000200
C	5.53047800	-2.96033800	-2.53542700
H	5.21932200	-2.94078800	-3.58829400
H	6.60536500	-2.73070300	-2.51704000
H	5.40904900	-3.99012900	-2.16957900

TS1-pro-*Si*



EE (DMA) = -4324.9139401 a.u.

EE (THF) = -4324.9150945 a.u.

EE (DMA/THF) = -4324.9161876 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.691692 a.u.

NImag (298 K) = 1 (119.62*i* cm^{-1})

0 1

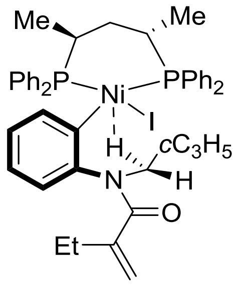
C	2.14518700	1.54110600	-2.18499200
C	3.11099200	2.50884200	-1.93511500
C	4.03970800	2.33322200	-0.90662900
C	3.99118900	1.17805300	-0.13275900
C	3.05490000	0.16904500	-0.38799300

C	2.09924000	0.38155800	-1.40073300
H	1.42115400	1.68285300	-2.99082700
H	3.13144400	3.41248000	-2.54904200
H	4.78690400	3.10120000	-0.69807000
H	4.69648000	1.02374100	0.68871600
C	4.19316800	-1.76171900	0.61760700
C	5.24602900	-1.75855900	-0.46103100
C	6.49954900	-2.00016200	-0.04942400
C	2.01259000	-1.04969200	1.44855700
H	1.01076500	-1.04947200	0.95207100
H	2.12155000	-2.01256200	1.96539200
N	3.04632500	-1.00186200	0.41147100
O	4.32177900	-2.45011800	1.61806200
C	4.86646200	-1.62408300	-1.91403500
H	3.87318300	-2.08597100	-2.05575100
H	4.71104700	-0.56310400	-2.17236500
Ni	-0.51140800	-0.11834800	-0.08592800
H	6.71149200	-2.13843000	1.01241500
C	2.08552400	0.10174700	2.40753600
C	1.75818200	-0.08849500	3.85550900
C	3.17055200	0.16859200	3.43719500
H	1.78885600	1.05650300	1.96088300
H	1.50142800	-1.09654500	4.19230700
H	1.20747900	0.70002700	4.37636200
H	3.60678400	1.14722600	3.65449700
H	3.87353400	-0.66699700	3.47858100
H	7.33645100	-2.07744900	-0.74580800
P	-2.15133200	-1.27860300	0.57079400
P	-0.86225100	1.87342200	0.55525100
C	-2.24951000	3.22210800	2.69055600
C	-1.76936000	1.85943200	2.21335000
C	-2.95832400	0.88665400	2.20443000
C	-2.69971100	-0.62687800	2.23397500
C	-1.67171900	-1.01973100	3.28310300
C	0.73862100	4.04666400	-0.27162300
C	1.74644600	4.99753400	-0.13264000
C	2.41660800	5.14430300	1.08127200
C	2.05280100	4.34000600	2.16215300
C	1.03093900	3.40349600	2.02732200
C	0.35330800	3.23185200	0.80624500
C	-2.72886000	1.87696600	-1.51355600
C	-3.71122700	2.39811100	-2.35433500
C	-4.06744900	3.74209500	-2.25655900
C	-3.43338200	4.55978200	-1.31938700

C	-2.45747700	4.03446400	-0.47444400
C	-2.09699000	2.67998300	-0.55393400
C	-0.75642900	-3.68598500	0.86707000
C	-0.59477300	-5.04017700	1.16029800
C	-1.70254100	-5.81308000	1.50399700
C	-2.97032900	-5.22934400	1.54991500
C	-3.12836100	-3.87613900	1.25876800
C	-2.01970300	-3.08646600	0.92176900
C	-4.94981500	-0.82826000	0.01099600
C	-6.04926300	-0.81706100	-0.84963200
C	-5.92089200	-1.26207800	-2.16302900
C	-4.68136700	-1.72101000	-2.61458100
C	-3.58459700	-1.71884400	-1.75904400
C	-3.69754200	-1.27671200	-0.42999300
H	-2.58498600	3.16775800	3.73808400
H	-1.47400500	3.99845200	2.63585500
H	-3.11067800	3.56836900	2.09934900
H	-1.00940100	1.48163300	2.92228900
H	-3.61564700	1.15071500	1.35496500
H	-3.55707300	1.11963000	3.10381200
H	-3.65766600	-1.11769200	2.48793900
H	-1.87202000	-0.52460300	4.24662200
H	-1.65872400	-2.10391600	3.46160100
H	-0.65730100	-0.72895300	2.96464800
H	0.23566000	3.93649600	-1.23733200
H	2.01691600	5.62537600	-0.98613100
H	3.21056600	5.88696600	1.18883900
H	2.55851100	4.45255500	3.12481500
H	0.74923600	2.80225800	2.89702100
H	-2.43339000	0.82487900	-1.58744400
H	-4.19367000	1.74928500	-3.08971100
H	-4.83415100	4.15740400	-2.91530200
H	-3.70175800	5.61670300	-1.24547700
H	-1.95933200	4.68923500	0.24607900
H	0.10572900	-3.07213000	0.58629900
H	0.39924500	-5.49175000	1.11650000
H	-1.58086000	-6.87483900	1.73157500
H	-3.84150500	-5.83521900	1.81172500
H	-4.12722400	-3.42782800	1.28720900
H	-5.08595000	-0.48379500	1.03895500
H	-7.01541100	-0.45956100	-0.48491800
H	-6.78274600	-1.25299400	-2.83427100
H	-4.56914400	-2.07805700	-3.64132900
H	-2.61128800	-2.06611900	-2.12414800

I	0.84401800	-1.22210200	-2.04762800
C	5.85677200	-2.22474400	-2.89054100
H	5.47318100	-2.17175600	-3.91807700
H	6.81872800	-1.69265900	-2.88299900
H	6.06440900	-3.28088500	-2.66527800

FS1-pro-*Si*



EE (DMA) = -4324.9808083 a.u.

EE (THF) = -4324.9797668 a.u.

EE (DMA/THF) = -4324.9825876 a.u.

Thermal correction to Gibbs free energy at 353K = 0.691437 a.u.

NImag = 0

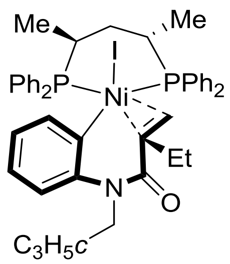
0 1

C	1.27054100	1.16113100	-2.29914200
C	2.40895600	1.59499900	-2.98297200
C	3.67124300	1.27774900	-2.48401100
C	3.77264800	0.46073200	-1.36117300
C	2.62679400	-0.05639100	-0.73755900
C	1.33900100	0.37244100	-1.14013900
H	0.29152600	1.45145100	-2.69399000
H	2.30374100	2.20049100	-3.88720100
H	4.57580000	1.65043000	-2.97113800
H	4.75350600	0.18389700	-0.96928000
C	3.62605200	-2.15805800	0.14339700
C	4.30377700	-2.43727800	-1.17466400
C	5.62924400	-2.63187100	-1.13458900
C	2.11435600	-0.90138800	1.53918600
H	1.15024100	-0.38579300	1.34310300
H	1.87937300	-1.90402300	1.92814500
N	2.79310700	-1.05569900	0.26254900
O	3.80567300	-2.90457500	1.09455800
C	3.46935100	-2.62250800	-2.40916400
H	2.81763100	-3.49803200	-2.23405400
H	2.75206200	-1.79357800	-2.51562300
Ni	-0.30610600	-0.05686700	-0.20062900
H	6.17872000	-2.54951500	-0.19422700
C	2.90989100	-0.12588700	2.55153500

C	2.51931200	-0.20300400	3.99523000
C	3.79505700	-0.83126700	3.52844900
H	3.26147700	0.84644200	2.18756200
H	1.69225100	-0.86834900	4.26307100
H	2.56749300	0.70621900	4.60050100
H	4.73696000	-0.35338100	3.80637100
H	3.84569300	-1.91914400	3.45519500
H	6.20604600	-2.88099200	-2.02768300
P	-2.29759600	-0.64645800	0.67949100
P	-0.28615200	2.01710300	0.60051900
C	-1.68072600	4.04660900	1.99769700
C	-1.48419800	2.53933000	1.95087700
C	-2.82268600	1.81070800	1.91534300
C	-2.76849700	0.30806200	2.20775700
C	-1.84611400	-0.05306000	3.36428800
C	2.32826900	3.02613600	0.34906300
C	3.54580000	3.51835700	0.81296900
C	3.74944900	3.72832100	2.17577900
C	2.72318900	3.43756000	3.07186200
C	1.50828400	2.93436400	2.61058900
C	1.28424100	2.72505400	1.24030500
C	-1.83402600	2.66669100	-1.58675200
C	-2.33847000	3.46288700	-2.61159900
C	-1.79692300	4.72791000	-2.83877500
C	-0.76178000	5.19345400	-2.02837200
C	-0.26854200	4.40412200	-0.98997200
C	-0.79805100	3.12840500	-0.76299000
C	-1.35298900	-3.00096700	1.81527100
C	-1.45348600	-4.27333000	2.36894300
C	-2.68432600	-4.93097200	2.38581300
C	-3.81132000	-4.30868600	1.85266800
C	-3.71453900	-3.02744200	1.30822500
C	-2.48436800	-2.36204600	1.28928500
C	-5.01657700	-0.03960000	0.04794800
C	-6.07669600	0.17390900	-0.83167400
C	-5.88272300	0.05213200	-2.20664100
C	-4.62081500	-0.28098500	-2.69579300
C	-3.55874800	-0.48783800	-1.81783200
C	-3.74056100	-0.37615500	-0.43089700
H	-2.22101300	4.33023900	2.91357100
H	-0.72874900	4.59681100	1.99348100
H	-2.27406900	4.40446800	1.14350100
H	-0.98383400	2.23214100	2.88061900
H	-3.33798700	2.00594100	0.95648500

H	-3.46418700	2.28550000	2.67918000
H	-3.78362100	-0.02403700	2.48177000
H	-2.02279500	0.60562900	4.22853400
H	-2.00552200	-1.08520300	3.70267500
H	-0.77921200	0.03394100	3.09479600
H	2.19122900	2.88247100	-0.72441800
H	4.33996100	3.73381700	0.09423100
H	4.70422300	4.11581500	2.53839700
H	2.86778700	3.59163300	4.14389300
H	0.74291800	2.69524500	3.35090600
H	-2.23266600	1.65932100	-1.43060500
H	-3.14696100	3.08522900	-3.24218200
H	-2.17884300	5.35087300	-3.65079700
H	-0.33427900	6.18365000	-2.20246700
H	0.53255800	4.78955300	-0.35404200
H	-0.38365300	-2.49472400	1.77167800
H	-0.56249900	-4.76006200	2.77140000
H	-2.76200400	-5.93573700	2.80760600
H	-4.77453600	-4.82425500	1.85335100
H	-4.60430400	-2.55356000	0.88406300
H	-5.20094900	0.06192800	1.12008800
H	-7.06091000	0.43647200	-0.43677600
H	-6.71463200	0.21875400	-2.89490100
H	-4.45547000	-0.37890600	-3.77125200
H	-2.56856900	-0.73928000	-2.21009900
I	-0.22772900	-2.26872200	-1.51794500
C	4.24351500	-2.80078500	-3.69527800
H	4.88726800	-3.69250200	-3.67525400
H	3.56198600	-2.91191500	-4.54900800
H	4.88963500	-1.93329000	-3.89989400

IS2-pro-*Si*



EE (DMA) = -4324.9718243 a.u.

EE (THF) = -4324.9704184 a.u.

EE (DMA/THF) = -4324.9734648 a.u.

Thermal correction to Gibbs free energy = 0.702573 a.u.

NImag = 0

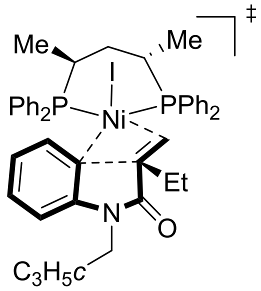
0 1

C	-1.88584400	-1.86027600	-1.84848500
C	-3.16759600	-2.26587900	-2.22773000
C	-4.24290600	-1.39374400	-2.09186400
C	-4.01029900	-0.08949200	-1.66543300
C	-2.71227000	0.32052400	-1.32797500
C	-1.63730200	-0.59899600	-1.30000700
H	-1.05844200	-2.56475900	-1.95969500
H	-3.31906400	-3.27961700	-2.60730600
H	-5.25526200	-1.70654400	-2.35766000
H	-4.83138800	0.63057200	-1.64656900
C	-1.18575900	2.16661100	-1.36367100
C	-0.28529000	1.20755700	-2.09118400
C	1.05033300	1.26775400	-1.72865400
C	-3.46887900	2.62427800	-0.66401300
H	-4.20043000	2.07095600	-0.05361900
H	-2.97750000	3.35705100	-0.00411900
N	-2.44399000	1.68256600	-1.09208700
O	-0.83446000	3.30086800	-1.06678800
C	-0.64404100	0.77759000	-3.49874300
H	-0.09512700	-0.15144200	-3.72549700
H	-1.71166200	0.53347500	-3.58917900
H	1.35314400	2.10675000	-1.09486200
Ni	0.18216800	-0.20572700	-0.52280300
H	1.81660700	0.82213700	-2.37076600
C	-4.15120200	3.34447700	-1.79675500
C	-4.73805800	4.70113600	-1.55741300
C	-3.51632100	4.55780800	-2.40614800
H	-4.70273300	2.69531400	-2.48556700
H	-4.61992100	5.13793600	-0.56208800
H	-5.68842600	4.94796400	-2.03476100
H	-3.61375900	4.70208100	-3.48416200
H	-2.55924600	4.88118700	-1.99221800
P	-0.57350100	-1.27837600	1.37826400
P	2.17562700	0.32876800	0.56707000
C	4.17602500	-0.52315300	2.43294400
C	2.85135200	-0.90875800	1.78958000
C	1.82704500	-1.19470600	2.88503100
C	0.66569100	-2.11075200	2.51255300
C	1.16915100	-3.47157400	2.05037400
C	3.96713900	2.05791300	-0.77781400
C	5.08103100	2.34788900	-1.56436100
C	5.91374400	1.32105300	-2.00511800
C	5.62777500	0.00320900	-1.65196700

C	4.51291000	-0.29022500	-0.86985200
C	3.66673800	0.73511900	-0.42168600
C	0.60017600	2.34976700	1.65751000
C	0.32227400	3.48418500	2.41798000
C	1.35179800	4.13530400	3.09208700
C	2.66150500	3.66155000	2.98610700
C	2.93949700	2.53316700	2.21926300
C	1.90376500	1.85012200	1.55882100
C	-1.41316100	-3.74120500	0.38282300
C	-2.28448300	-4.81112100	0.20537400
C	-3.55483600	-4.78568300	0.78078500
C	-3.94371700	-3.68572600	1.54128500
C	-3.06728400	-2.61737700	1.73563100
C	-1.79089600	-2.63411100	1.16025700
C	-1.08377800	0.02671800	3.89938900
C	-1.75468400	0.94639700	4.70676800
C	-2.80034100	1.70719800	4.19272200
C	-3.17955400	1.53227900	2.86139700
C	-2.50114600	0.62441000	2.05401600
C	-1.43530800	-0.14204700	2.55245600
H	4.60066900	-1.40082200	2.94315200
H	4.92838000	-0.16437300	1.71908500
H	4.03642400	0.25087500	3.20168300
H	2.99412300	-1.81129400	1.16748000
H	1.47538200	-0.23283000	3.29813500
H	2.36058300	-1.68207400	3.72029300
H	0.07207400	-2.28164200	3.42736800
H	1.99333500	-3.79013600	2.70725000
H	0.39272400	-4.24262800	2.11345400
H	1.55106000	-3.46205200	1.01766800
H	3.32920800	2.87870100	-0.43902300
H	5.29481200	3.38483000	-1.83315200
H	6.78570800	1.54797600	-2.62295600
H	6.27179400	-0.81035500	-1.99281300
H	4.29270200	-1.33020000	-0.62012100
H	-0.20491500	1.84139700	1.11803700
H	-0.70184900	3.86121200	2.46823100
H	1.14049800	5.02626300	3.68820000
H	3.47538500	4.18388600	3.49450500
H	3.97432300	2.19970900	2.10995300
H	-0.43523300	-3.75043300	-0.11007500
H	-1.97114500	-5.66325600	-0.40248000
H	-4.24230100	-5.62211800	0.63376900
H	-4.93686600	-3.65479100	1.99548800

H	-3.39041600	-1.77132300	2.34566000
H	-0.28285500	-0.55711900	4.35285600
H	-1.45362100	1.06122000	5.75060000
H	-3.32391000	2.42618000	4.82685400
H	-4.01233100	2.10654100	2.44778300
H	-2.81509000	0.48189300	1.01944800
I	1.74000100	-2.41752300	-1.76782000
C	-0.28630500	1.87941100	-4.48448900
H	0.79127000	2.09575900	-4.48380900
H	-0.56843600	1.59527900	-5.50727800
H	-0.80746600	2.81935200	-4.24608800

TS2-pro-*Si*



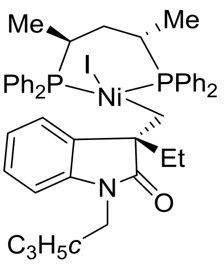
EE (DMA) = -4324.9704761 a.u.
EE (THF) = -4324.9689164 a.u.
EE (DMA/THF) = -4324.9720731 a.u.
Thermal correction to Gibbs free energy at 353 K = 0.701656 a.u.
NImag (298 K) = 1 (170.18*i* cm^{-1})
0 1

C	-1.76874400	-1.74984600	-1.97489100
C	-3.05035400	-2.23652100	-2.23890900
C	-4.17121400	-1.45937200	-1.95784700
C	-4.00213300	-0.15257600	-1.50565500
C	-2.71089400	0.33890800	-1.28401700
C	-1.57315000	-0.49460800	-1.38609800
H	-0.90224500	-2.38286300	-2.18646800
H	-3.16586300	-3.24649600	-2.63993900
H	-5.17695000	-1.84789700	-2.13309900
H	-4.86766800	0.50174600	-1.37829600
C	-1.21525600	2.15204200	-1.40537600
C	-0.36805400	1.09713700	-2.07818500
C	0.99801900	1.16732600	-1.72555300
C	-3.48710700	2.64966800	-0.65389700
H	-4.18035600	2.13211400	0.02848800
H	-2.97814800	3.43408700	-0.07134800
N	-2.46584300	1.69926100	-1.05942800

O	-0.83625600	3.29603000	-1.21015700
C	-0.69229700	0.79101100	-3.53618400
H	-0.17454600	-0.14431900	-3.80491600
H	-1.76830900	0.59916100	-3.66898600
H	1.30063800	2.07710900	-1.19630900
Ni	0.23348900	-0.20270600	-0.48777300
H	1.74923800	0.72784200	-2.39094400
C	-4.22862700	3.27367800	-1.80627300
C	-4.81443600	4.64249700	-1.64970300
C	-3.62862000	4.43716800	-2.53588200
H	-4.80338400	2.56811700	-2.41608400
H	-4.65769500	5.15751800	-0.69813100
H	-5.78563800	4.84696400	-2.10447200
H	-3.77119900	4.49557100	-3.61687400
H	-2.65754400	4.79657000	-2.18920900
P	-0.55679100	-1.31076900	1.38116900
P	2.15010100	0.37944400	0.59883700
C	4.16883000	-0.47447100	2.44214600
C	2.85102600	-0.87343700	1.79249500
C	1.83879000	-1.21480000	2.88489000
C	0.68735500	-2.14363100	2.50555400
C	1.19940300	-3.48899300	2.01122600
C	3.86507600	2.19468900	-0.72038100
C	4.95641900	2.54178000	-1.51495100
C	5.82327600	1.55590100	-1.98317600
C	5.59391400	0.22200200	-1.64983100
C	4.50216600	-0.12895900	-0.85847800
C	3.62313000	0.85515500	-0.38231000
C	0.50716700	2.34672900	1.69242000
C	0.19176700	3.46146100	2.46745300
C	1.19459600	4.12103800	3.17318900
C	2.51538500	3.67568100	3.08487300
C	2.83072100	2.56611600	2.30501300
C	1.82237900	1.87418400	1.61273400
C	-1.36915500	-3.71808600	0.25492500
C	-2.21963300	-4.79619300	0.03030100
C	-3.48087300	-4.83190300	0.62470900
C	-3.88204700	-3.78607900	1.45303600
C	-3.02538100	-2.71203100	1.69667600
C	-1.75814000	-2.66771000	1.10189800
C	-1.09462900	-0.05006500	3.91801100
C	-1.78291900	0.84373100	4.73977400
C	-2.84834000	1.58605600	4.23980200
C	-3.22911300	1.41784500	2.90811100

C	-2.53350800	0.53573200	2.08685500
C	-1.44704400	-0.21155900	2.57041400
H	4.61684100	-1.35436800	2.92781700
H	4.90936000	-0.07930000	1.73514200
H	4.01423900	0.27600300	3.23130600
H	3.01120700	-1.75516700	1.14454900
H	1.47308800	-0.27229300	3.32937200
H	2.39097200	-1.71427800	3.70067800
H	0.10486300	-2.33716900	3.42315000
H	2.01418500	-3.82853800	2.66922600
H	0.42105400	-4.26086100	2.03821400
H	1.59461900	-3.44739200	0.98409700
H	3.19680200	2.98254000	-0.36206300
H	5.12533800	3.59057800	-1.76939200
H	6.67746300	1.82733900	-2.60792900
H	6.26449000	-0.55957100	-2.01366200
H	4.32518500	-1.18129300	-0.62588300
H	-0.27649100	1.82943900	1.12928200
H	-0.84092700	3.81575600	2.50846400
H	0.95332100	4.99619600	3.78119400
H	3.30840500	4.20520000	3.61816100
H	3.87400000	2.25521400	2.20987500
H	-0.39585900	-3.67870000	-0.24738600
H	-1.89705700	-5.60584800	-0.62876700
H	-4.15207900	-5.67435000	0.44091800
H	-4.86820900	-3.80447700	1.92308600
H	-3.35446900	-1.91020300	2.36132600
H	-0.27837000	-0.62067000	4.36076500
H	-1.47994900	0.95253600	5.78370500
H	-3.38610700	2.28455700	4.88485600
H	-4.07806000	1.97659700	2.50597200
H	-2.85142200	0.39924300	1.05247600
I	1.85140800	-2.43193500	-1.77058800
C	-0.25083400	1.93442200	-4.43344600
H	0.83484900	2.09703500	-4.38495600
H	-0.50968100	1.72717100	-5.48049900
H	-0.73441400	2.88226900	-4.15331000

FS2-*S*



EE (DMA) = -4325.0103726 a.u.

EE (THF) = -4325.0096647 a.u.

EE (DMA/THF) = -4325.0121708 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.701112 a.u.

NImag = 0

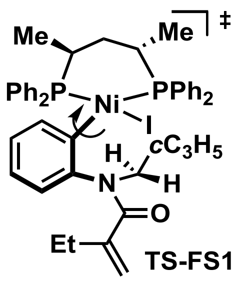
0 1

C	-1.28027000	1.34771800	-3.33558300
C	-2.29533500	2.31339700	-3.31788000
C	-2.20301200	3.42123800	-2.47443700
C	-1.10077400	3.59634000	-1.62928700
C	-0.10495300	2.62295400	-1.65677000
C	-0.18740800	1.50085500	-2.49578700
H	-1.35391100	0.47498700	-3.99012500
H	-3.16621700	2.19573800	-3.96659100
H	-3.00160300	4.16714300	-2.46974900
H	-1.02872800	4.46677900	-0.97171700
C	1.79644100	1.41506500	-1.22171800
C	1.08081600	0.69497000	-2.36423900
C	0.90986000	-0.79140200	-2.09549800
C	1.58877500	3.59984300	-0.05137700
H	0.79737600	3.92042600	0.64850700
H	2.38311800	3.13189500	0.55040900
N	1.07038500	2.55463000	-0.90597400
O	2.84952200	1.10608800	-0.69311900
C	1.93207600	0.93882100	-3.65254800
H	1.30268200	0.63545800	-4.50588900
H	2.07222300	2.03032200	-3.76271100
H	1.89975600	-1.23608100	-1.94037300
Ni	-0.28173600	-0.88038400	-0.53590200
H	0.46441100	-1.27999600	-2.97514400
C	2.15073600	4.76205500	-0.82620100
C	3.33874600	5.49924500	-0.29302100
C	3.48804000	4.60316200	-1.48125000
H	1.41061100	5.35706200	-1.37243500
H	3.76224900	5.16410800	0.65749800
H	3.38974700	6.57981300	-0.44061600
H	3.64496000	5.05782500	-2.46134200

H	4.00209200	3.64812700	-1.34187100
P	-1.77931200	-0.51403300	1.15441900
P	1.35017000	-1.46583900	0.79924400
C	1.58859500	-3.69286900	2.60560000
C	0.58211400	-2.83298200	1.85272900
C	-0.45926000	-2.30004400	2.84505800
C	-1.85711100	-1.95607800	2.31850300
C	-2.55380600	-3.16438200	1.71004100
C	4.00250000	-1.80367900	-0.14109800
C	4.98527300	-2.46305600	-0.88022100
C	4.69763100	-3.66697900	-1.51956300
C	3.41416600	-4.20863000	-1.42844600
C	2.43059100	-3.55248200	-0.69489700
C	2.71971500	-2.35211000	-0.02642600
C	1.74837900	0.91997700	2.17693300
C	2.31053500	1.76031900	3.13632100
C	3.33600400	1.29160300	3.95482900
C	3.80713600	-0.01283800	3.79815000
C	3.24014000	-0.85281300	2.84214900
C	2.18707000	-0.39965400	2.03117800
C	-3.75025300	0.59198300	-0.46250400
C	-5.03409800	1.02788800	-0.77954200
C	-6.10155000	0.73280500	0.06823000
C	-5.87708000	0.01702700	1.24368400
C	-4.58786600	-0.39935100	1.57388100
C	-3.51614100	-0.12481700	0.71686000
C	-1.40522800	0.85896300	3.67422000
C	-1.23962100	2.01937900	4.43283300
C	-1.20488100	3.26685400	3.81556800
C	-1.34166800	3.34890400	2.42832200
C	-1.49566100	2.19151200	1.67175100
C	-1.52600900	0.92747300	2.28157500
H	1.09251700	-4.59964700	2.98361200
H	2.43584200	-4.01708800	1.98701500
H	1.98855000	-3.16337300	3.48273500
H	0.07349700	-3.46384200	1.10173500
H	-0.01950200	-1.44517200	3.38920100
H	-0.59918100	-3.07894100	3.61527800
H	-2.45243000	-1.62222000	3.18749900
H	-2.60827700	-3.97782100	2.44966000
H	-3.57777200	-2.93552000	1.38563000
H	-2.03290800	-3.54459100	0.82069100
H	4.22610600	-0.84132800	0.32365100
H	5.98150100	-2.02220900	-0.96436000

H	5.46859900	-4.17870800	-2.10035500
H	3.17361100	-5.14204100	-1.94242500
H	1.41617200	-3.96379300	-0.66995400
H	0.96278100	1.28897100	1.51337700
H	1.94820000	2.78711700	3.23535100
H	3.78194700	1.94707600	4.70677200
H	4.62785300	-0.37731800	4.42053400
H	3.64032600	-1.86085700	2.70916700
H	-2.91514700	0.79604700	-1.13970300
H	-5.20052200	1.58873100	-1.70246400
H	-7.11174000	1.06210200	-0.18639200
H	-6.70882200	-0.21286700	1.91378500
H	-4.42520200	-0.93573600	2.51345800
H	-1.44188700	-0.09997000	4.19517400
H	-1.14230500	1.94240200	5.51838000
H	-1.08105700	4.17348300	4.41236200
H	-1.33663400	4.32343000	1.93185400
H	-1.60621500	2.26888500	0.58420300
I	-2.05381300	-2.13338800	-1.97000200
C	3.26767200	0.22925000	-3.70801400
H	3.15069700	-0.86280000	-3.75040900
H	3.82461500	0.53129500	-4.60595700
H	3.89084700	0.45733500	-2.83238700

TS-FS1



TS-FS1

EE (DMA) = -4324.9307875 a.u.

EE (THF) = -4324.9289622 a.u.

EE (DMA/THF) = -4324.9323860 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.696143 a.u.

NImag = 1 (9.07*i* cm^{-1})

0 1

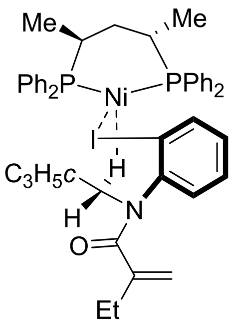
C	-1.38782500	2.53181300	0.52840800
C	-2.36799600	3.51332400	0.65879800
C	-3.69771100	3.18131300	0.44266300
C	-3.98935400	1.84235600	0.23528200
C	-2.99415600	0.85252300	0.15534400

C	-1.60195200	1.18075200	0.17227400
H	-0.38409500	2.89181900	0.73766200
H	-2.07286400	4.53455300	0.91650500
H	-4.49489000	3.92556200	0.50698700
H	-5.03003600	1.51163100	0.21912000
C	-3.40442800	-1.20074200	1.39006700
C	-2.78625200	-0.48715300	2.56376100
C	-3.53084000	0.36150800	3.28132600
C	-4.28474400	-1.04834500	-0.87574800
H	-3.79531600	-0.75318300	-1.81600500
H	-4.17686900	-2.13938600	-0.78530600
N	-3.51767500	-0.47663600	0.22833500
O	-3.79083200	-2.35532600	1.50022700
C	-1.37241900	-0.86021900	2.87807300
H	-1.33999600	-1.94589600	3.08459600
H	-0.78500100	-0.75607400	1.94259300
Ni	0.08458000	0.10409200	-0.32812700
H	-4.55781700	0.59872700	2.98998800
C	-5.75030500	-0.69096100	-0.89938000
C	-6.76100200	-1.74696200	-1.22952600
C	-6.66018900	-1.22093200	0.16663500
H	-5.98317100	0.30958000	-1.27909400
H	-6.39482100	-2.75918700	-1.42007800
H	-7.62511100	-1.46773200	-1.83637100
H	-7.45918300	-0.57535800	0.53901800
H	-6.21169700	-1.87145200	0.92114200
H	-3.15097000	0.85256600	4.18077600
P	2.07005200	-1.23540000	-0.32662700
P	1.31799100	1.92847400	-0.64014000
C	3.52006700	2.86973800	-2.23613300
C	2.90828200	1.64126700	-1.58279100
C	3.91534100	0.91041600	-0.68554500
C	3.81411000	-0.60779700	-0.74845300
C	4.33409600	-1.10839100	-2.09188500
C	0.39949500	4.50070300	-1.52580000
C	-0.33485300	5.30935500	-2.39147700
C	-1.03316200	4.74478200	-3.45765700
C	-0.99915900	3.36460300	-3.65432400
C	-0.27049600	2.55379500	-2.78830500
C	0.44275400	3.11600300	-1.72042000
C	1.62410900	2.10251600	2.08752200
C	2.10283300	2.58438500	3.30272400
C	2.87143800	3.74726900	3.33507600
C	3.15267400	4.42507400	2.14905200

C	2.67617000	3.94151800	0.93075800
C	1.90484200	2.76972800	0.88449700
C	1.86138300	-3.01789600	-2.46471700
C	2.11994800	-4.19753700	-3.15373500
C	2.73160400	-5.27018600	-2.50140300
C	3.09358200	-5.14805500	-1.16279200
C	2.84698200	-3.95842100	-0.47314600
C	2.22124700	-2.88542200	-1.11538300
C	3.10173900	-0.94452200	2.30762900
C	3.17702700	-1.26878100	3.66220900
C	2.35743300	-2.26387300	4.19141600
C	1.44419600	-2.91729100	3.36312300
C	1.35732600	-2.58698100	2.01381500
C	2.20274800	-1.61059000	1.46239800
H	4.33355100	2.55787200	-2.90883200
H	2.79954900	3.44299400	-2.83437600
H	3.97108100	3.54879800	-1.49908900
H	2.58483000	0.95900100	-2.39157900
H	3.83703800	1.27479800	0.35215600
H	4.93535800	1.19187300	-0.99870900
H	4.45720900	-1.04035300	0.03785300
H	5.29969400	-0.62594100	-2.30730900
H	4.49714000	-2.19200400	-2.11017000
H	3.66177200	-0.87107900	-2.93046400
H	0.90774300	4.95576800	-0.67219100
H	-0.37149100	6.38799600	-2.22199300
H	-1.61580600	5.37986000	-4.12867200
H	-1.55959600	2.91232300	-4.47536300
H	-0.28703000	1.46527500	-2.91776200
H	1.00755700	1.19505500	2.05532400
H	1.86837700	2.04771400	4.22544100
H	3.24836400	4.13035300	4.28614600
H	3.74942200	5.33994000	2.16980400
H	2.91296300	4.48960800	0.01685100
H	1.36866200	-2.18597700	-2.97562700
H	1.83188200	-4.28517600	-4.20366300
H	2.92464800	-6.20119400	-3.03942400
H	3.57619400	-5.98056400	-0.64554900
H	3.15480900	-3.87347500	0.57206700
H	3.76000700	-0.16381700	1.91756500
H	3.88716000	-0.74079200	4.30343900
H	2.42259900	-2.52377600	5.25042700
H	0.78572300	-3.68809000	3.77052400
H	0.62958500	-3.09637600	1.37261200

I	-1.07728400	-2.06401700	-1.03862900
C	-0.72289700	-0.06385800	3.98488800
H	-1.21188500	-0.22701200	4.95695500
H	0.33708600	-0.33377300	4.10088800
H	-0.77487900	1.01630800	3.77273300

IS1-pro-*Re*



EE (DMA) = -4324.9233627 a.u.

EE (THF) = -4324.9246458 a.u.

EE (DMA/THF) = -4324.9256450 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.691575 a.u.

NImag = 0

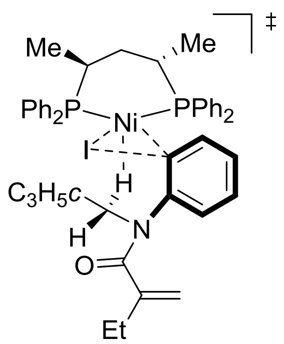
0 1

C	4.14292000	1.51545200	-0.60111400
C	5.22145100	1.18359600	0.21624200
C	5.00808100	0.89300500	1.56331300
C	3.72272000	0.95839600	2.09185500
C	2.62567000	1.30916100	1.29360500
C	2.85571900	1.56769000	-0.07103500
H	4.30424800	1.70571400	-1.66511500
H	6.22605300	1.13143200	-0.21042000
H	5.84658900	0.62348300	2.20916900
H	3.54367500	0.76040600	3.15220800
C	0.44171200	2.39310900	1.80941100
C	0.95692300	3.78567900	1.62018900
C	2.14511500	4.17958000	2.10249300
C	0.72859400	0.03185100	2.22663800
H	1.47475700	-0.74603900	2.00478900
H	-0.13617700	-0.15151400	1.53978200
N	1.32755900	1.32929300	1.87527600
O	-0.75928100	2.20652800	1.96625600
C	-0.04344900	4.71694900	0.99808100
H	-0.95307200	4.68732000	1.62161200
H	-0.37288900	4.27346500	0.04225700
H	2.82863900	3.49201600	2.60231100

Ni	-0.30773400	0.06369800	-0.52402600
H	2.47073400	5.22000900	2.03263000
C	0.27372400	-0.07060900	3.65340300
C	0.20285200	-1.41739000	4.30017700
C	1.24532600	-0.43719800	4.73415600
H	-0.51071100	0.64185100	3.92482900
H	0.53004400	-2.28078400	3.71435600
H	-0.63482800	-1.63168900	4.96766600
H	1.14624800	0.04428200	5.70930700
H	2.28007500	-0.64670700	4.44846800
P	-2.38569400	-0.09490500	-0.73808100
P	0.53836200	-1.82802200	-0.94078800
C	0.06632100	-3.81525100	-2.94980600
C	-0.40564600	-2.46008800	-2.44769700
C	-1.92217800	-2.48249700	-2.19254500
C	-2.71022700	-1.16301500	-2.23749100
C	-2.43930400	-0.36354000	-3.50434100
C	3.30486600	-2.14627300	-0.51125100
C	4.64975300	-2.03336500	-0.85048100
C	5.02293100	-1.66840200	-2.14537300
C	4.03220600	-1.41122600	-3.09267400
C	2.68514300	-1.52961800	-2.75409200
C	2.29222800	-1.91589000	-1.46059500
C	-0.58305500	-3.17596300	1.21665000
C	-0.81076500	-4.24254600	2.08677600
C	-0.05533700	-5.40758700	1.97228000
C	0.92420200	-5.50212500	0.98116600
C	1.13963400	-4.44184200	0.10365200
C	0.38513500	-3.26144400	0.20673400
C	-2.95230100	2.62478700	-0.93919500
C	-3.74240500	3.75797000	-1.13019300
C	-5.09985800	3.61699000	-1.41374000
C	-5.66583900	2.34235900	-1.49384200
C	-4.87549300	1.21298500	-1.29201400
C	-3.50628400	1.34437100	-1.02334000
C	-4.10187400	-2.06668300	0.48887500
C	-4.66708500	-2.67843300	1.60964500
C	-4.43957700	-2.16020100	2.88292700
C	-3.64343500	-1.02203700	3.03146900
C	-3.07013900	-0.41695800	1.91663400
C	-3.29265700	-0.93162100	0.62704000
H	-0.39367400	-4.05475800	-3.92143200
H	1.15710900	-3.85726700	-3.08403300
H	-0.21471900	-4.62032500	-2.25373000

H	-0.19318800	-1.70472600	-3.22507800
H	-2.11778900	-3.01127000	-1.24047900
H	-2.36203900	-3.13502200	-2.96868100
H	-3.78277600	-1.43238400	-2.23637400
H	-1.43582700	0.09249400	-3.48873400
H	-2.50223400	-1.00306100	-4.39866400
H	-3.15946700	0.45666900	-3.63070000
H	3.03347000	-2.42422900	0.51278400
H	5.41447300	-2.22461400	-0.09286500
H	6.07888400	-1.58058000	-2.41240400
H	4.30879900	-1.12079000	-4.10967200
H	1.92711500	-1.31805700	-3.51470700
H	-1.16180900	-2.25233100	1.31909300
H	-1.57351800	-4.15032600	2.86463900
H	-0.22365200	-6.24232300	2.65717000
H	1.52166400	-6.41264100	0.88798400
H	1.90598300	-4.53144600	-0.67184300
H	-1.88594700	2.70610100	-0.70052700
H	-3.29724500	4.75381700	-1.05327600
H	-5.72344300	4.50142100	-1.56581300
H	-6.73202000	2.23094900	-1.70726600
H	-5.33190900	0.21802900	-1.33549000
H	-4.29690600	-2.49332900	-0.49896900
H	-5.28975300	-3.56788900	1.48363900
H	-4.88186300	-2.64153400	3.75862500
H	-3.46166700	-0.60517300	4.02568400
H	-2.42686500	0.46312500	2.03838900
I	1.16412200	1.89241500	-1.37997300
C	0.42466900	6.13605400	0.78333900
H	-0.35515200	6.74002200	0.30091500
H	0.67964700	6.63478700	1.73001500
H	1.31641500	6.17943100	0.13972300

TS1-pro-*Re*



EE (DMA) = -4324.9122790 a.u.

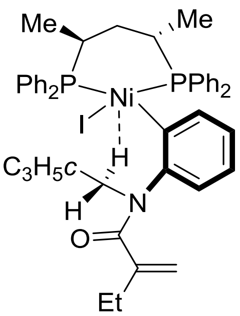
EE (THF) = -4324.9138300 a.u.
EE (DMA/THF) = -4324.9146082 a.u.
Thermal correction to Gibbs free energy at 353 K = 0.694801 a.u.
NImag = 1 (121.92i cm^{-1})
0 1

C	-1.90538000	-3.36598900	-0.45236900
C	-2.87217600	-3.84252200	0.42571000
C	-2.75247800	-3.60898300	1.79588500
C	-1.65519000	-2.89789000	2.27148500
C	-0.65748000	-2.42371100	1.41228900
C	-0.80728100	-2.63637200	0.02596300
H	-2.00862900	-3.55242000	-1.52342200
H	-3.72500900	-4.39709500	0.02825400
H	-3.50559100	-3.98282200	2.49236900
H	-1.53583400	-2.69998200	3.34046600
C	1.73319200	-1.87494600	1.89078400
C	2.21801100	-3.27395900	1.66526500
C	1.56072900	-4.34537100	2.13327400
C	-0.00409400	-0.25349900	2.36572800
H	-1.09014300	-0.16137800	2.21171900
H	0.48328700	0.45419400	1.65509600
N	0.37802900	-1.61562500	1.95859400
O	2.54484600	-0.97225200	2.06793800
C	3.57247800	-3.34233300	1.02027800
H	4.26957300	-2.77222100	1.65774800
H	3.53592100	-2.75429400	0.08650700
H	0.60553500	-4.26424800	2.65258900
Ni	0.00788200	0.02996000	-0.42960700
H	1.97133000	-5.35254100	2.03041500
C	0.35053400	0.10577300	3.77906500
C	-0.42475000	1.18845900	4.46044800
C	-0.58249300	-0.23129200	4.90264100
H	1.42074300	0.06158400	3.99891500
H	-1.25328800	1.64373200	3.91059500
H	0.11517800	1.88720400	5.10303800
H	-0.15554100	-0.53687400	5.86020400
H	-1.52372000	-0.73164600	4.65800000
P	1.41389200	1.55879200	-0.89103000
P	-1.92558500	0.76253000	-0.83044300
C	-3.11273800	2.46574900	-2.81373400
C	-1.80681400	1.80586600	-2.40022500
C	-0.69844300	2.86121000	-2.28495600
C	0.76865800	2.42385800	-2.41944800
C	0.99300200	1.54806900	-3.64488100

C	-4.23451700	-0.73777500	-0.18736100
C	-5.23274100	-1.67519700	-0.43797500
C	-5.35542100	-2.25628400	-1.70081100
C	-4.45660400	-1.89748100	-2.70559000
C	-3.46194100	-0.95363600	-2.45572200
C	-3.34455800	-0.33748700	-1.19773000
C	-1.78534200	2.61445300	1.24042900
C	-2.23263600	3.61856100	2.09940800
C	-3.57138900	4.00416100	2.08055000
C	-4.45614700	3.38518100	1.19507500
C	-4.00357700	2.39322500	0.32775000
C	-2.65750600	1.99246300	0.33608200
C	3.78941900	0.09890900	-0.86595900
C	5.13348500	-0.16714400	-1.12898500
C	5.88863100	0.73610200	-1.87392400
C	5.29894100	1.91286900	-2.34143400
C	3.96040700	2.18204900	-2.06609300
C	3.18628600	1.27186500	-1.33209900
C	1.31981900	4.26142600	0.12184500
C	1.45042900	5.19689000	1.14999200
C	1.91844600	4.80604700	2.40274200
C	2.26850200	3.47134100	2.61953700
C	2.13333100	2.53547900	1.59831600
C	1.64787500	2.91537600	0.33398200
H	-3.02388500	2.90425000	-3.82008400
H	-3.95539600	1.75984900	-2.83772000
H	-3.38236900	3.28524000	-2.13043800
H	-1.52113600	1.07890700	-3.18030500
H	-0.84818400	3.43053500	-1.34907000
H	-0.87863000	3.59645600	-3.09029200
H	1.35784400	3.35002700	-2.55203100
H	0.57467500	0.53870100	-3.50119500
H	0.51161400	1.98358100	-4.53454900
H	2.05993300	1.42203900	-3.87364900
H	-4.14306600	-0.30909400	0.81583500
H	-5.91715700	-1.96103400	0.36548900
H	-6.14113000	-2.98929600	-1.89866900
H	-4.53367700	-2.35101900	-3.69726600
H	-2.76653200	-0.69053800	-3.25932100
H	-0.73646600	2.30108100	1.25931200
H	-1.52811200	4.09148100	2.78893200
H	-3.92909400	4.78470000	2.75649500
H	-5.50771700	3.68266200	1.17588800
H	-4.70744200	1.92394300	-0.36544800

H	3.19001200	-0.59438300	-0.26952000
H	5.59132700	-1.08332100	-0.74619300
H	6.94040300	0.52983100	-2.08674300
H	5.89080100	2.62959800	-2.91648600
H	3.51871600	3.11890100	-2.42102600
H	0.95520400	4.59994100	-0.85121700
H	1.18287600	6.24063200	0.96620600
H	2.01642400	5.53957700	3.20667200
H	2.64813100	3.15355600	3.59429500
H	2.40581500	1.48909700	1.78127800
I	0.78282400	-2.28734600	-1.40359900
C	4.09768000	-4.72972700	0.73989100
H	5.07436600	-4.68877200	0.23992700
H	4.23099200	-5.31634100	1.66065100
H	3.41814700	-5.29665500	0.08522100

FS1-pro-*Re*



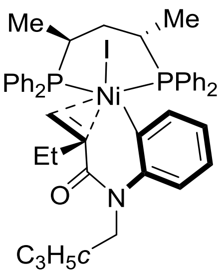
EE (DMA) = -4324.9696522 a.u.
EE (THF) = -4324.9684551 a.u.
EE (DMA/THF) = -4324.9713740 a.u.
Thermal correction to Gibbs free energy = 0.698630 a.u.
NImag = 0
0 1

C	-1.39390800	-2.97559900	-1.11528600
C	-2.15383000	-4.06228400	-0.69318200
C	-2.37045900	-4.27972900	0.67011900
C	-1.76367600	-3.43635900	1.59430100
C	-0.94337200	-2.38653600	1.16259200
C	-0.81197900	-2.08204200	-0.20292500
H	-1.25206300	-2.81331600	-2.18859700
H	-2.59509500	-4.73527900	-1.43375600
H	-2.99166900	-5.11190600	1.00992700
H	-1.88816300	-3.59858700	2.66951800
C	1.08625100	-1.58312900	2.34875600
C	1.85901900	-2.86021900	2.24211800
C	1.31228000	-4.06093500	2.48039200

C	-0.91756600	-0.25538900	2.38370900
H	-1.92861100	-0.31602800	1.95217600
H	-0.38037800	0.52791100	1.81679400
N	-0.27816800	-1.55080500	2.13345800
O	1.67777800	-0.55970700	2.69980900
C	3.33205600	-2.66073800	2.02260700
H	3.70553300	-2.02750600	2.84571900
H	3.46226300	-2.03912200	1.12163100
H	0.25614800	-4.18806400	2.70806400
Ni	0.09395100	-0.42351100	-0.59873700
H	1.91891600	-4.96933500	2.47429300
C	-1.02223700	0.12874500	3.83052400
C	-2.22316500	0.90306900	4.28113700
C	-2.06065400	-0.52820500	4.68399900
H	-0.06800200	0.36684500	4.30881100
H	-2.98586000	1.14059400	3.53293400
H	-2.09124000	1.68240900	5.03522500
H	-1.81435100	-0.75916300	5.72224100
H	-2.70916000	-1.26973300	4.20828200
P	1.40535600	1.45917400	-0.84333000
P	-1.83997800	0.63383500	-0.97266300
C	-2.95866300	2.35064100	-2.94524500
C	-1.66353900	1.66536300	-2.53353800
C	-0.54288700	2.70500700	-2.43753000
C	0.91326700	2.21783900	-2.46263600
C	1.17879600	1.25961800	-3.61663200
C	-3.93426400	-1.09211500	-0.33671900
C	-4.89890700	-2.06086700	-0.58959900
C	-5.13993000	-2.48412400	-1.89698600
C	-4.40451900	-1.93570100	-2.94495900
C	-3.43521400	-0.96540800	-2.69040100
C	-3.19574200	-0.52194100	-1.38471000
C	-1.96430900	2.62712500	1.01375800
C	-2.57905100	3.59538900	1.80702000
C	-3.95944700	3.76797000	1.75135600
C	-4.71740600	2.97218200	0.89112600
C	-4.10051700	2.01443000	0.08967800
C	-2.70846300	1.82520400	0.14071400
C	3.83616600	0.59532600	0.15299000
C	5.22116100	0.48864900	0.22307700
C	6.01994500	1.07110500	-0.76219800
C	5.42533100	1.77521700	-1.80635200
C	4.03589400	1.89436000	-1.87261100
C	3.23019700	1.29344500	-0.90116100

C	1.24363200	4.20155900	-0.01075800
C	1.22986800	5.20516000	0.95824700
C	1.33959600	4.87930900	2.30895800
C	1.47568700	3.54292600	2.68595600
C	1.48658200	2.53687000	1.72212400
C	1.35475800	2.85532800	0.36028800
H	-2.85834300	2.77368600	-3.95621300
H	-3.82102300	1.67025200	-2.95799000
H	-3.20245400	3.18277200	-2.26828300
H	-1.38903500	0.92687200	-3.30622800
H	-0.72768500	3.34822600	-1.55794700
H	-0.66706800	3.37786700	-3.30452200
H	1.54365100	3.11405200	-2.60299300
H	0.64455100	0.30634600	-3.48946100
H	0.86038500	1.70833500	-4.57036100
H	2.24015800	0.99296100	-3.70509000
H	-3.74548100	-0.78055200	0.69588300
H	-5.45507900	-2.49867300	0.24237400
H	-5.89510000	-3.24773900	-2.09686300
H	-4.57978600	-2.26675700	-3.97118400
H	-2.85701500	-0.56432200	-3.52701300
H	-0.88634900	2.49261800	1.08511900
H	-1.96910000	4.20105400	2.48158200
H	-4.44773200	4.51754800	2.37850700
H	-5.80114500	3.10054900	0.83775100
H	-4.71313900	1.41284500	-0.58555900
H	3.21453400	0.12718800	0.92406300
H	5.67696700	-0.06401800	1.04849500
H	7.10739200	0.97820300	-0.71390200
H	6.04384700	2.24072800	-2.57734600
H	3.59443600	2.46404900	-2.69433100
H	1.16593600	4.48835700	-1.06238100
H	1.13617700	6.24962700	0.65132700
H	1.32620000	5.66720900	3.06589300
H	1.57274700	3.27441400	3.74082300
H	1.58293800	1.49259400	2.04040900
I	1.93813200	-1.94975700	-1.49176700
C	4.15401000	-3.92024400	1.89045300
H	5.20912700	-3.68138800	1.70021300
H	4.12105200	-4.53977300	2.79932300
H	3.80508800	-4.54289700	1.05270000

IS2-pro-*Re*



EE (DMA) = -4324.9721114 a.u.

EE (THF) = -4324.9708415 a.u.

EE (DMA/THF) = -4324.9735845 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.699465 a.u.

NImag = 0

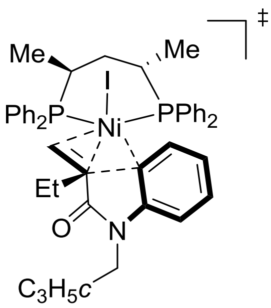
0 1

C	2.06938000	-1.77640600	-1.63358500
C	3.42018000	-2.01055000	-1.89030400
C	4.34705800	-0.97929800	-1.74237900
C	3.90061400	0.30384200	-1.44241200
C	2.53268400	0.54108400	-1.24672900
C	1.60706900	-0.52181800	-1.22292800
H	1.35817000	-2.60409400	-1.71852200
H	3.74799300	-3.01358300	-2.17533100
H	5.41204500	-1.15806800	-1.90936300
H	4.59761400	1.14398600	-1.44200200
C	0.79610700	2.06570700	-1.83546800
C	0.13676700	0.83885000	-2.40787200
C	-1.22526200	0.69208900	-2.16310700
C	2.75248000	3.01955300	-0.77196500
H	3.51750800	2.67153300	-0.06025200
H	2.02785600	3.62602300	-0.20256900
N	2.02499400	1.85526300	-1.25852900
O	0.28928200	3.18024100	-1.90175700
C	0.70608100	0.24625200	-3.68307400
H	0.37453000	-0.80275400	-3.75359400
H	1.80532300	0.22296200	-3.66056900
H	-1.78733800	1.54556000	-1.77946400
Ni	-0.29545100	-0.28297900	-0.60111900
H	-1.79908700	-0.02025000	-2.76388700
C	3.36050300	3.87675800	-1.85153100
C	4.33913700	4.94273700	-1.47403300
C	4.79673100	3.75349800	-2.25649400
H	2.64870500	4.13930100	-2.64006800
H	4.64270100	5.00561500	-0.42519900
H	4.27453900	5.91280200	-1.97059300
H	5.05514500	3.88189100	-3.30967000

H	5.42623700	3.02548900	-1.73777100
P	-2.19013900	0.40692400	0.59640800
P	0.53401000	-1.17703400	1.32559000
C	-0.15657900	-2.90097800	3.53812000
C	-0.72339200	-2.07956200	2.38676100
C	-1.78412500	-1.12780300	2.93805500
C	-2.86615700	-0.65686000	1.97298800
C	-3.73566400	-1.80632000	1.48323100
C	3.21108600	-2.06507900	1.43928100
C	4.21803600	-3.01862300	1.30227700
C	3.90272100	-4.32461100	0.93208800
C	2.57298700	-4.67471600	0.69557700
C	1.56287500	-3.72652200	0.83225200
C	1.87417900	-2.41168100	1.21083900
C	1.24066700	1.44537600	1.97268300
C	1.74851700	2.46709000	2.77498600
C	2.27394300	2.16917200	4.02979100
C	2.31504300	0.84415500	4.46819400
C	1.81796800	-0.17647100	3.66197400
C	1.25224000	0.11640000	2.40948200
C	-4.15667500	-0.15402600	-1.31639800
C	-5.35769600	0.04388300	-1.99209200
C	-6.15555500	1.15057500	-1.70079900
C	-5.74794900	2.05661600	-0.72407900
C	-4.54721400	1.86163100	-0.04067600
C	-3.73922700	0.75427600	-0.33252000
C	-2.05190100	2.23326800	2.82040400
C	-1.75698700	3.47463500	3.38652000
C	-1.30595100	4.52455800	2.59068900
C	-1.16222700	4.32800600	1.21640700
C	-1.45368200	3.08973100	0.65309800
C	-1.89324200	2.01675600	1.44441000
H	-0.92883800	-3.59876300	3.89523700
H	0.72348000	-3.49867700	3.27165500
H	0.10698200	-2.26499300	4.39566300
H	-1.18705500	-2.76234300	1.64906400
H	-1.27597400	-0.27550700	3.42261400
H	-2.30112900	-1.65076100	3.76190300
H	-3.52391100	0.03883300	2.52444600
H	-4.02868300	-2.43196700	2.33996700
H	-4.65945900	-1.44853600	1.01151400
H	-3.22238000	-2.45065700	0.75284600
H	3.47779900	-1.03754400	1.69916700
H	5.25817000	-2.73199300	1.47528700

H	4.69410800	-5.07001200	0.82241500
H	2.31679900	-5.69348900	0.39592800
H	0.52630700	-4.00193100	0.61310800
H	0.82318400	1.67198400	0.98761900
H	1.72586700	3.49928900	2.41682600
H	2.66600100	2.96732100	4.66467300
H	2.74858900	0.60221700	5.44142500
H	1.89967500	-1.21253500	3.99790200
H	-3.53586600	-1.02953800	-1.54441600
H	-5.66900700	-0.67449000	-2.75398600
H	-7.09521400	1.30731300	-2.23581400
H	-6.36601100	2.92623900	-0.48866600
H	-4.24377700	2.58262700	0.72267800
H	-2.41195600	1.44172700	3.47888600
H	-1.88370200	3.61616900	4.46247000
H	-1.07249600	5.49349900	3.03855500
H	-0.81650400	5.13675500	0.56757100
H	-1.32166000	2.97412400	-0.42414600
I	-1.42270900	-2.93733600	-1.48034500
C	0.22906500	1.04687400	-4.88504200
H	0.66871300	0.65544800	-5.81238900
H	-0.86398400	1.00935000	-4.99213000
H	0.51105800	2.10726000	-4.80530300

TS2-pro-*Re*



EE (DMA) = -4324.9708849 a.u.

EE (THF) = -4324.9697345 a.u.

EE (DMA/THF) = -4324.9725057 a.u.

Thermal correction to Gibbs free energy at 353 K = 0.700337 a.u.

NImag = 1 (145.73*i* cm^{-1})

0 1

C	1.98136700	-1.75203400	-1.72388700
C	3.33284000	-2.03881800	-1.90896500
C	4.29676600	-1.05824400	-1.67305900
C	3.89650600	0.23516900	-1.35141900
C	2.53244900	0.52822700	-1.22867200

C	1.55658400	-0.48775300	-1.29522800
H	1.23877700	-2.54248800	-1.87391000
H	3.63222400	-3.04727000	-2.20547900
H	5.35988700	-1.28517300	-1.78399900
H	4.63081000	1.03953500	-1.27825100
C	0.83707700	2.05267700	-1.83329700
C	0.19824300	0.79633800	-2.37323200
C	-1.18474400	0.67031300	-2.13489000
C	2.79854400	3.00871100	-0.76450600
H	3.55406700	2.66021200	-0.04296100
H	2.07862400	3.63146300	-0.20674300
N	2.05854100	1.85010900	-1.24060700
O	0.32865300	3.16207200	-1.93409100
C	0.72421300	0.28022300	-3.70599000
H	0.38776400	-0.76282900	-3.82219300
H	1.82463100	0.25400000	-3.71456600
H	-1.73154100	1.56082300	-1.81474700
Ni	-0.33732400	-0.28192300	-0.58320100
H	-1.75726000	-0.02459000	-2.75773800
C	3.42449400	3.83989400	-1.85326800
C	4.45245000	4.86490600	-1.49362200
C	4.84802100	3.65514500	-2.27844500
H	2.71267200	4.12779300	-2.63297700
H	4.77357600	4.91877500	-0.44957700
H	4.42120400	5.83510300	-1.99310000
H	5.09517200	3.76995300	-3.33583100
H	5.45328500	2.90136500	-1.76811100
P	-2.17526700	0.44732500	0.60983200
P	0.51515000	-1.20061100	1.32389700
C	-0.19329500	-2.93432000	3.52204100
C	-0.74940500	-2.08836000	2.38435500
C	-1.78516000	-1.11354400	2.94565800
C	-2.86125900	-0.60765300	1.98979700
C	-3.76271500	-1.73112600	1.49766100
C	3.18049400	-2.13039600	1.40345600
C	4.17220300	-3.09630900	1.24083400
C	3.83590400	-4.38733500	0.83910800
C	2.50030300	-4.70980800	0.59534000
C	1.50559300	-3.74935900	0.75658200
C	1.83777100	-2.44943100	1.16903000
C	1.28382700	1.39929600	1.98734200
C	1.82445600	2.40390100	2.78993900
C	2.35685900	2.08573600	4.03684900
C	2.37102100	0.75728900	4.46665100

C	1.84147200	-0.24623100	3.65949800
C	1.26952600	0.06704500	2.41482200
C	-4.15180100	-0.05488000	-1.30893600
C	-5.35243900	0.17072700	-1.97680400
C	-6.13477500	1.28243700	-1.66322100
C	-5.71257800	2.16569700	-0.67183200
C	-4.51250400	1.94259400	0.00384200
C	-3.71973400	0.83046000	-0.31073600
C	-1.97041300	2.26698800	2.83316000
C	-1.64454500	3.50266300	3.39495800
C	-1.18767200	4.54472800	2.59217800
C	-1.06948900	4.34685100	1.21538700
C	-1.39222600	3.11459600	0.65616100
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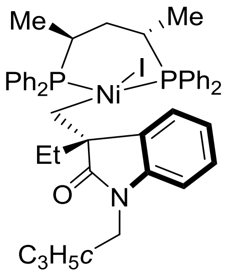
FS2-*R*



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Thermal correction to Gibbs free energy at 353 K = 0.699395 a.u.

NImag = 0

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[S19] The average value of the sum of each parameter respectively for DMA and THF. ε_{DMA} = 37.781; n_{DMA} = 1.438; ε_{inf} (DMA) = 2.0678; α_{DMA} = 0; β_{DMA} = 0.48; γ_{DMA} = 47.62; φ_{DMA} = 0; ψ_{DMA} = 0. ε_{THF} = 7.4257; n_{THF} = 1.405; ε_{inf} (THF) = 1.974; α_{THF} = 0; β_{THF} = 0.78; γ_{THF} = 39.44; φ_{THF} = 0; ψ_{THF} = 0.

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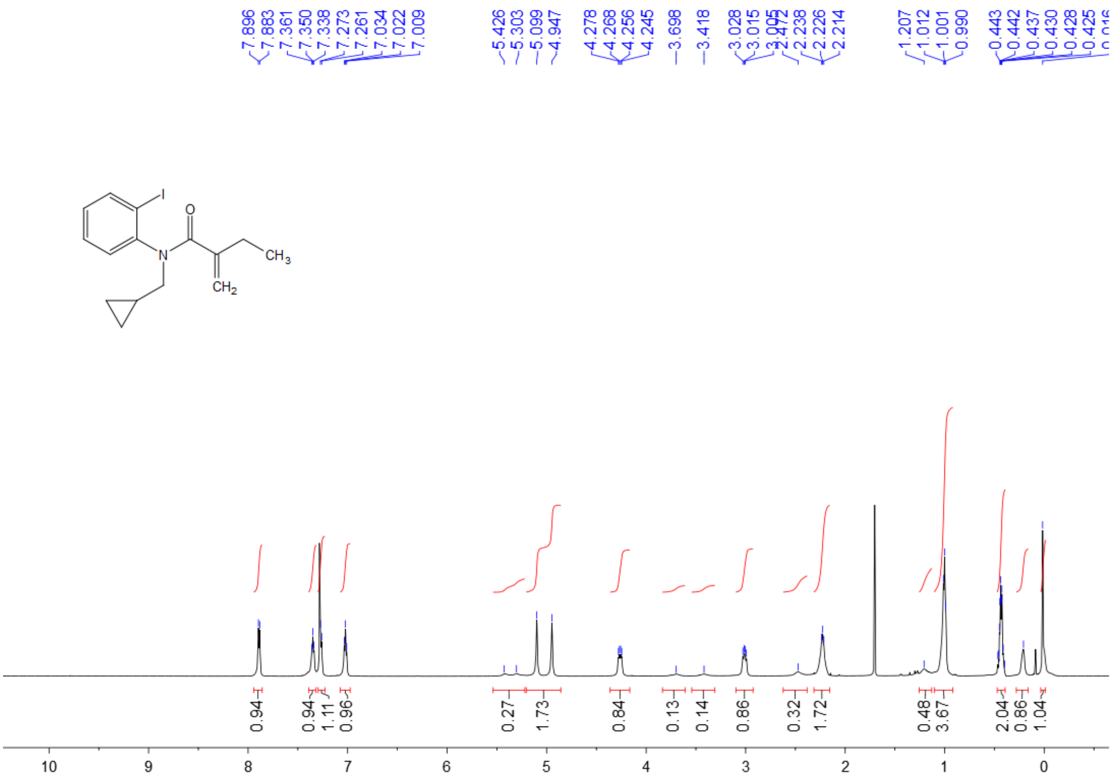
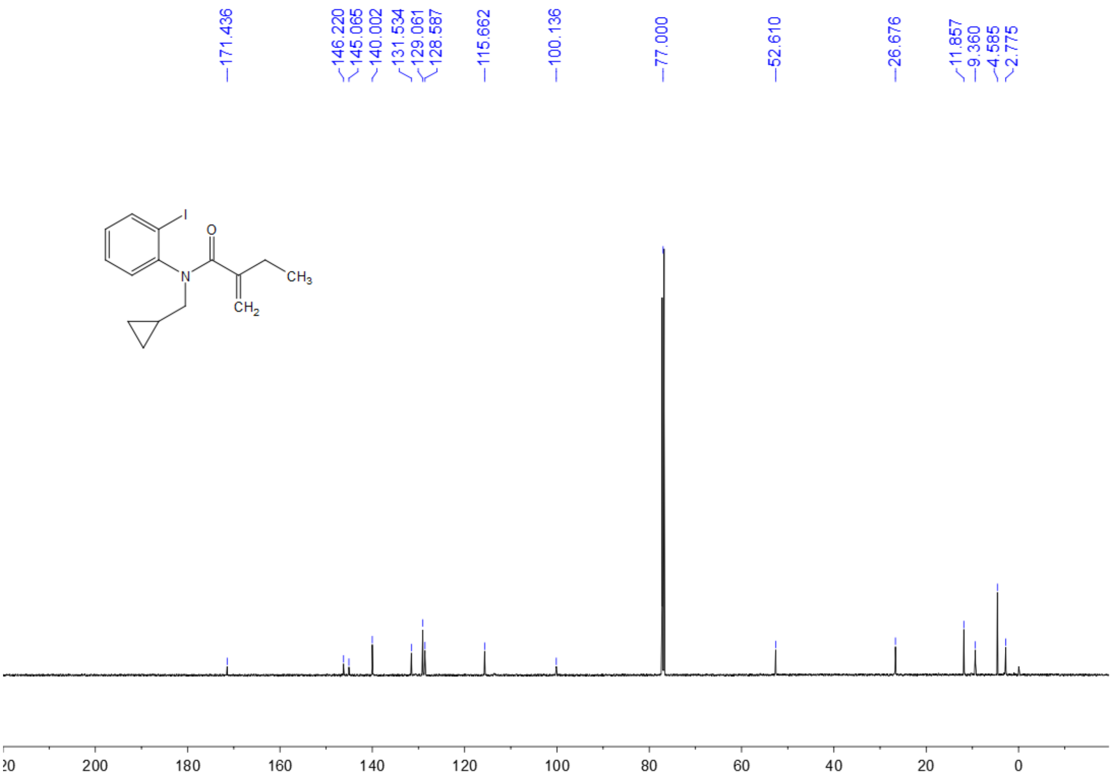
10. NMR spectra copies of compounds

^{1}H NMR spectra of **1a**



^{13}C NMR spectra of **1a**



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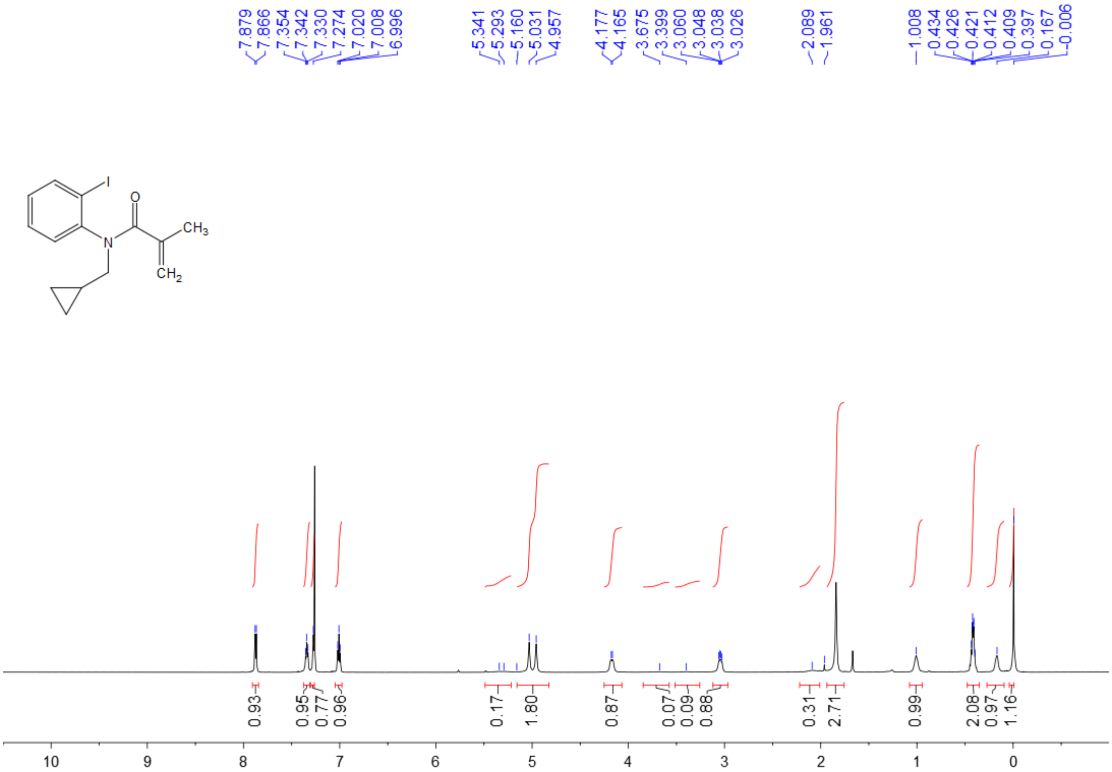

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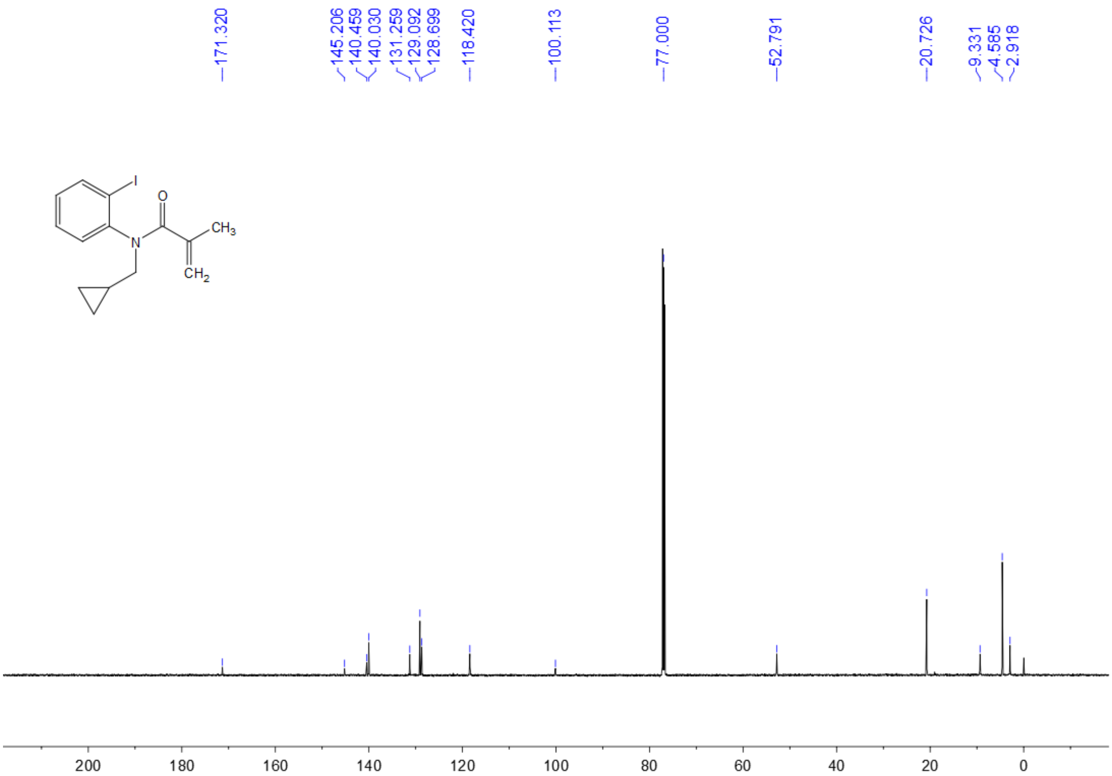

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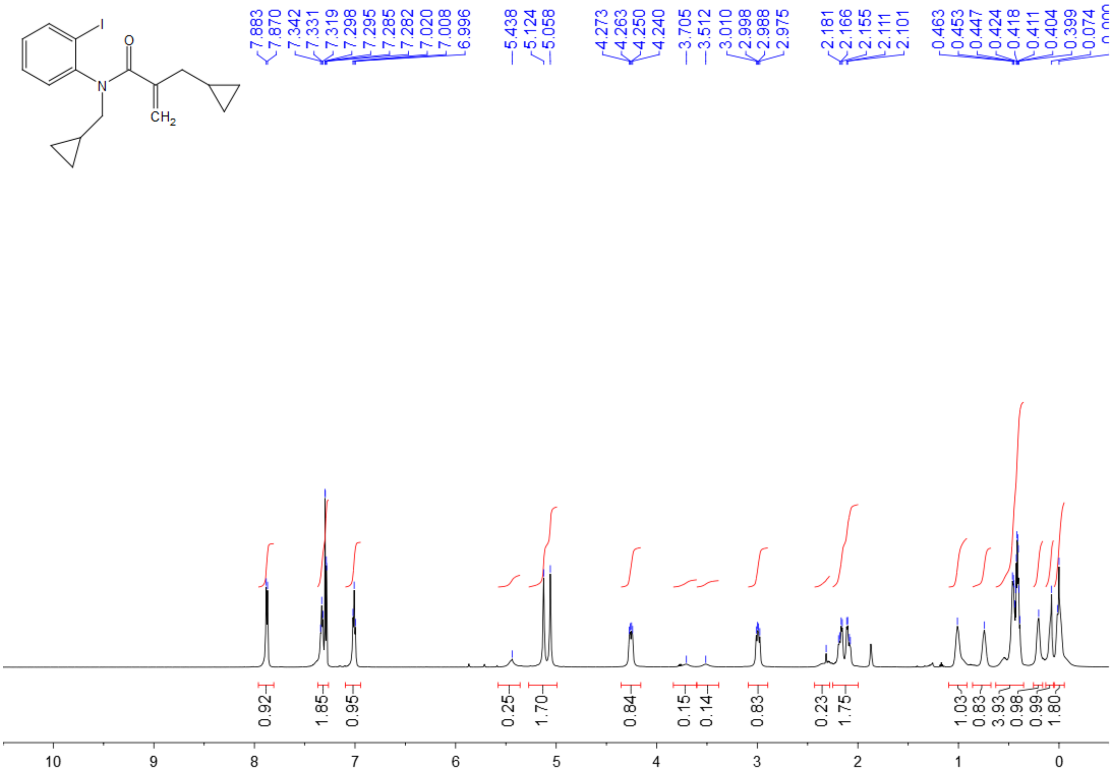

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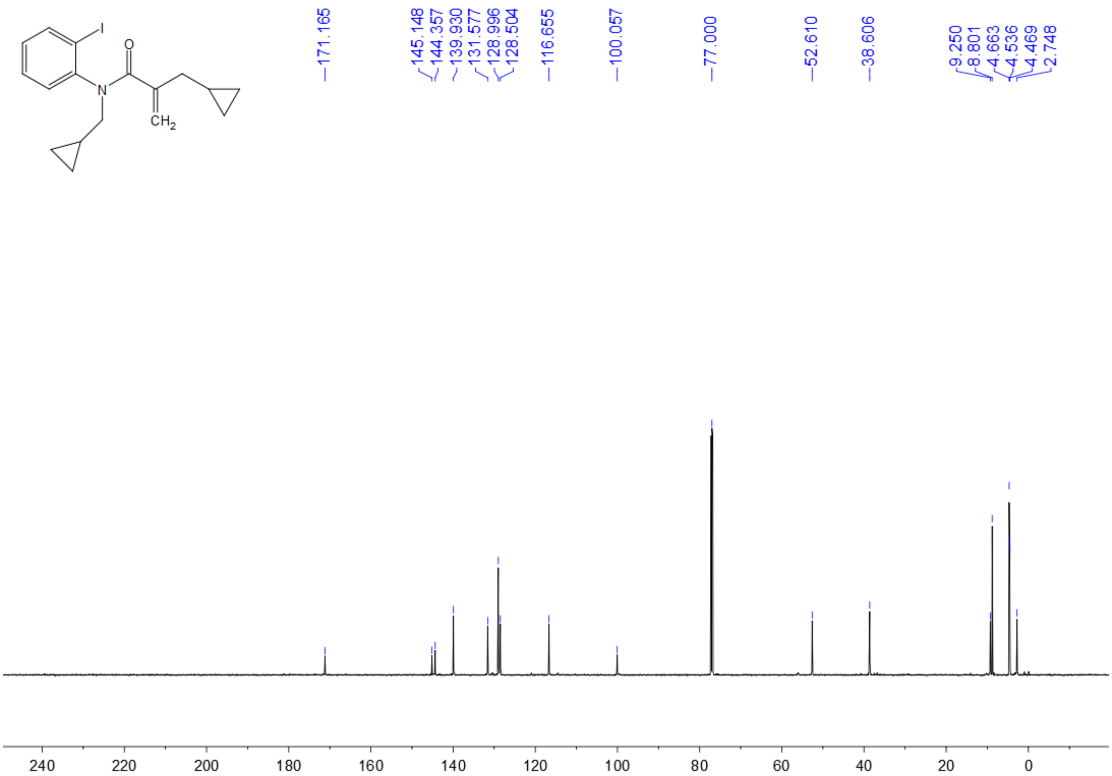

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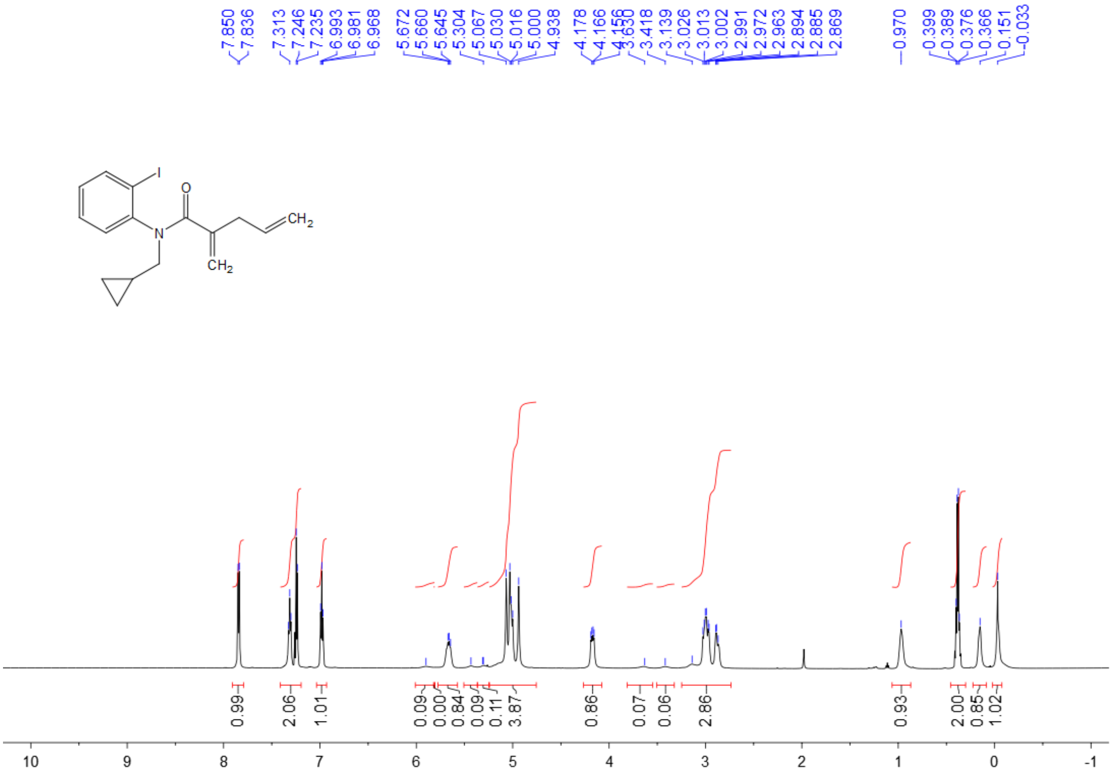

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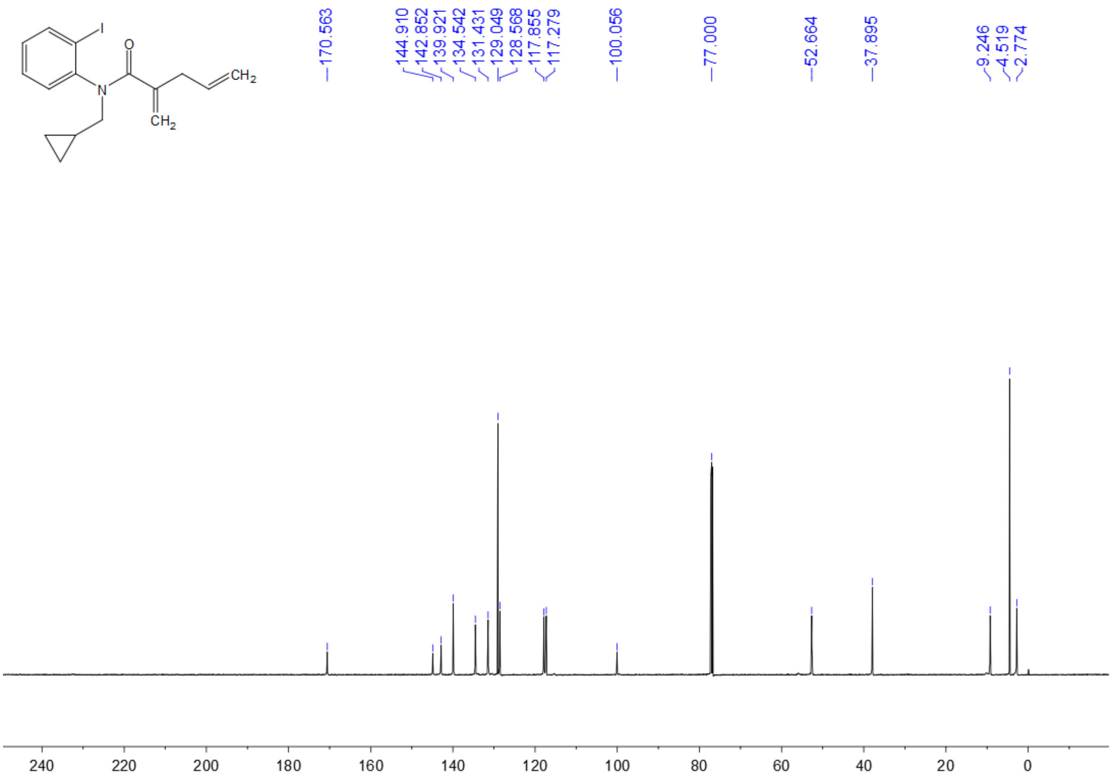

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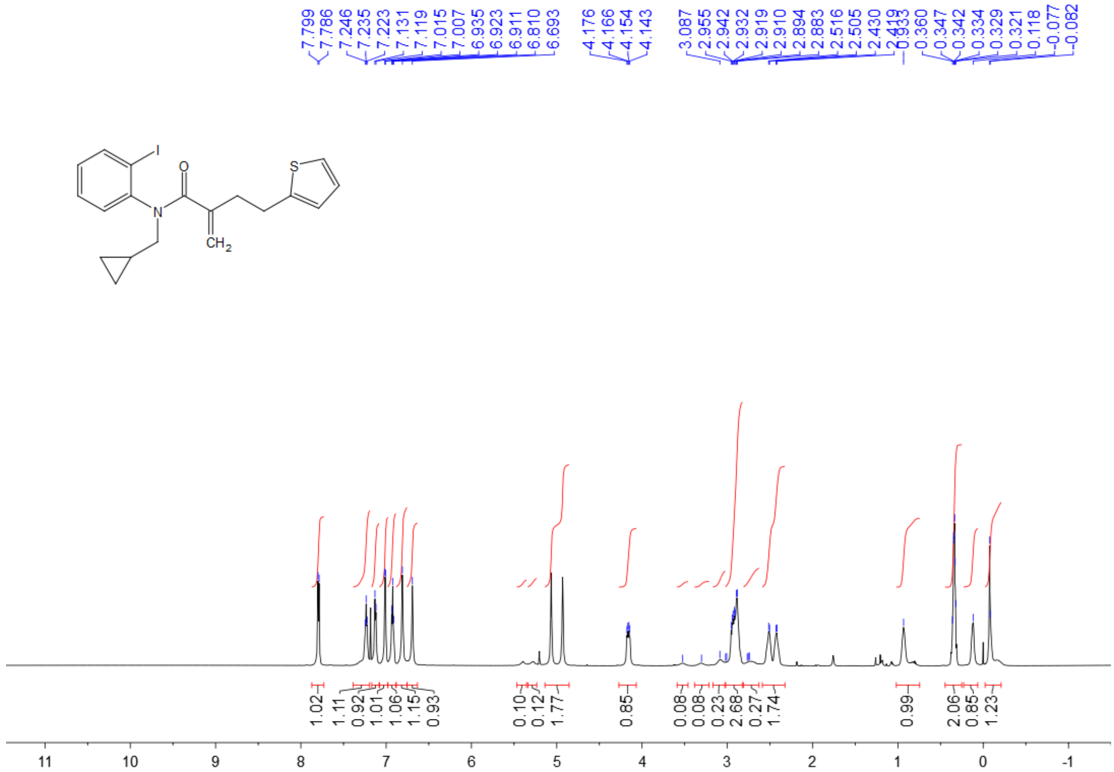

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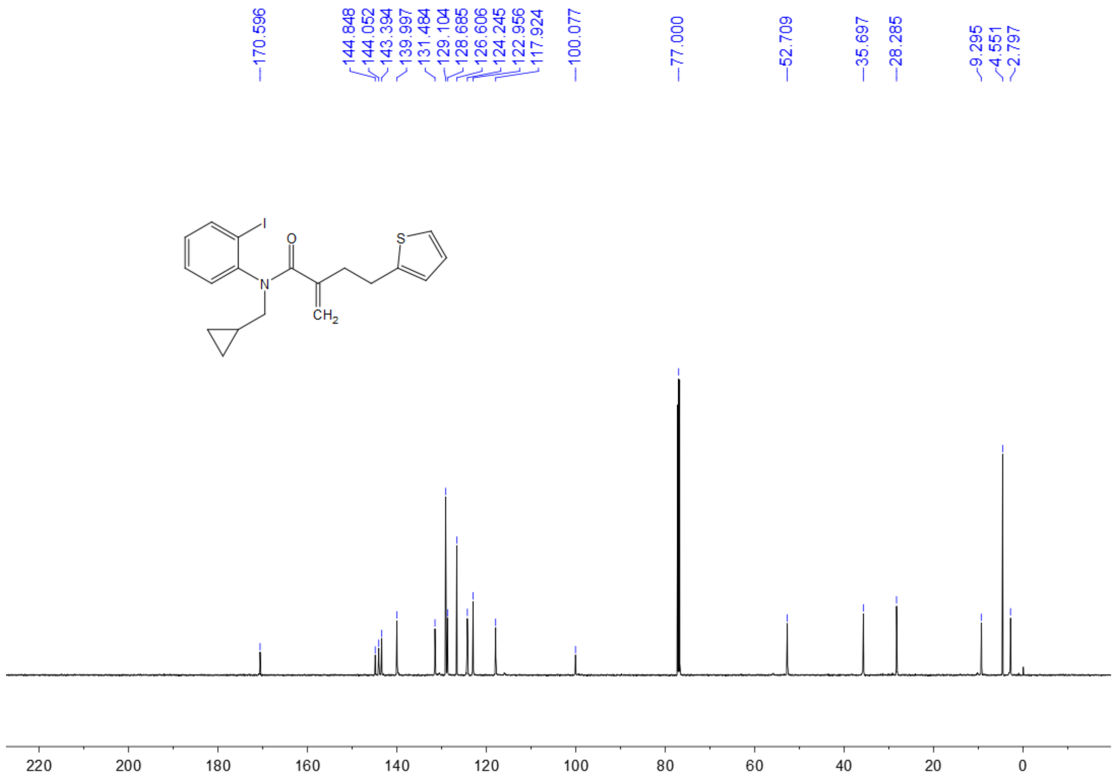

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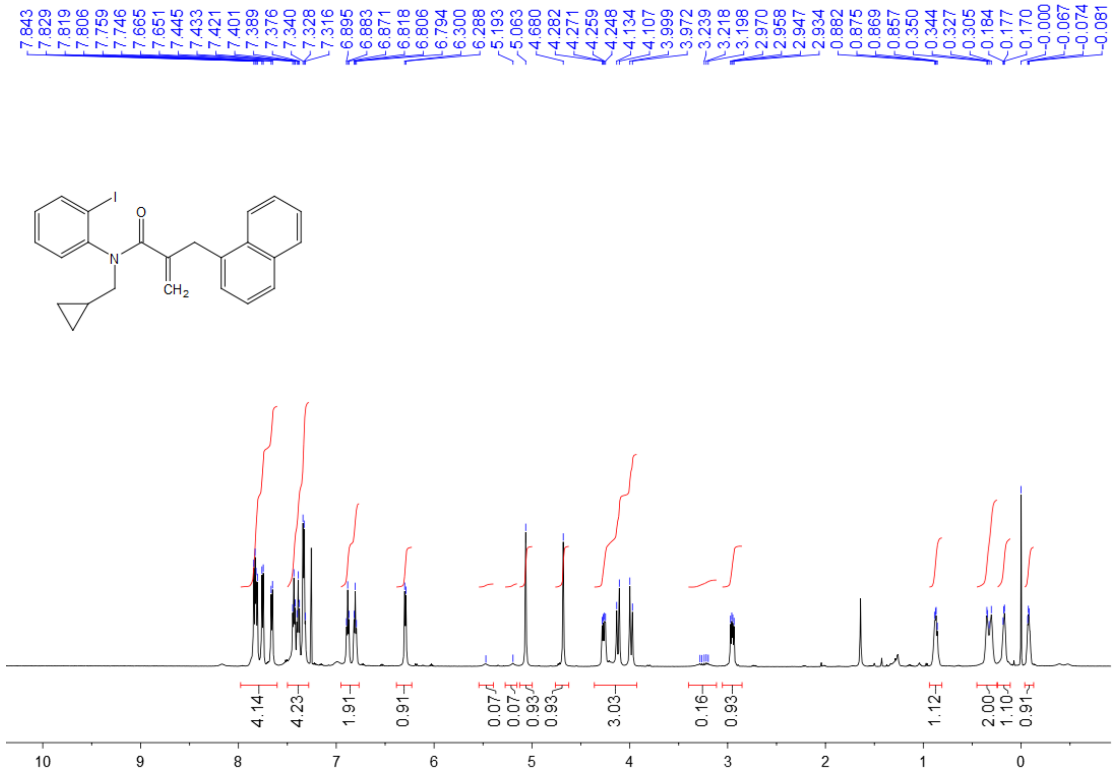

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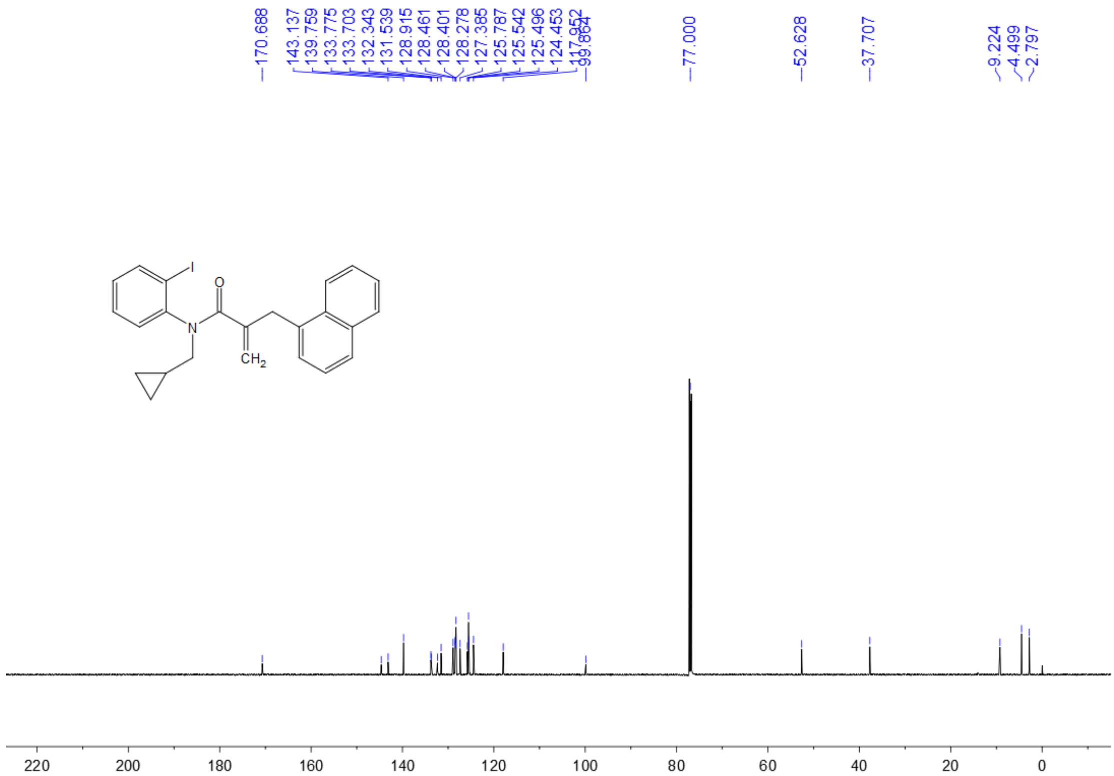

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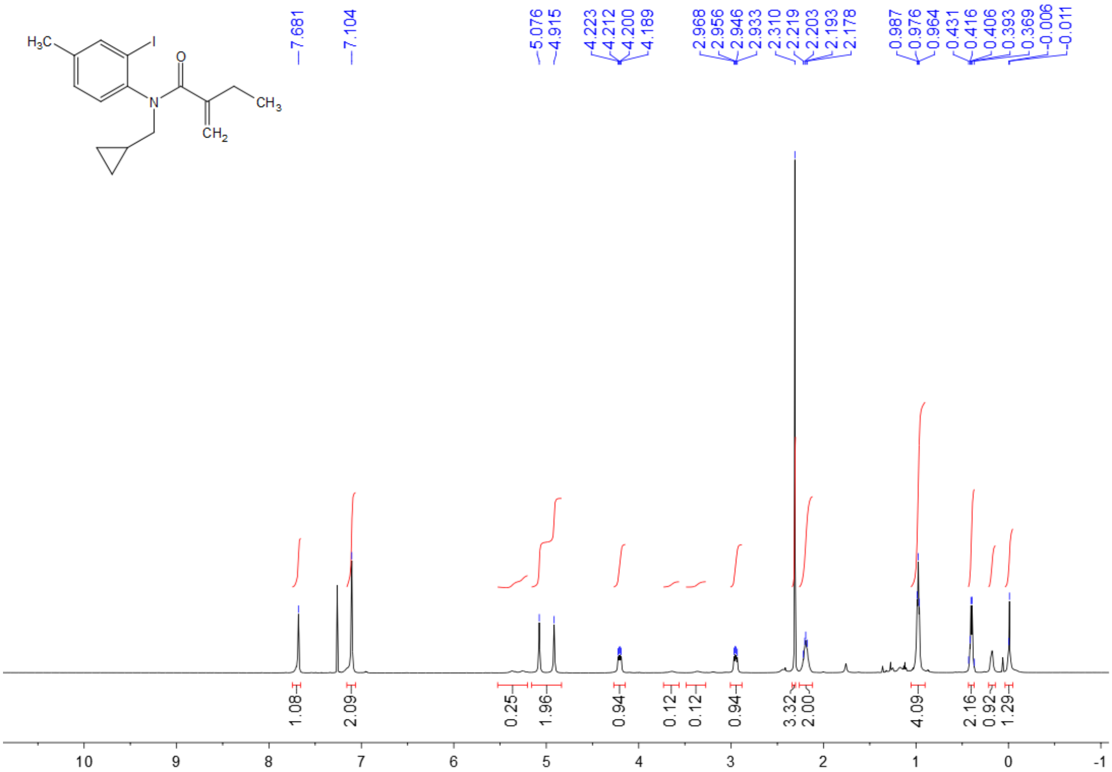

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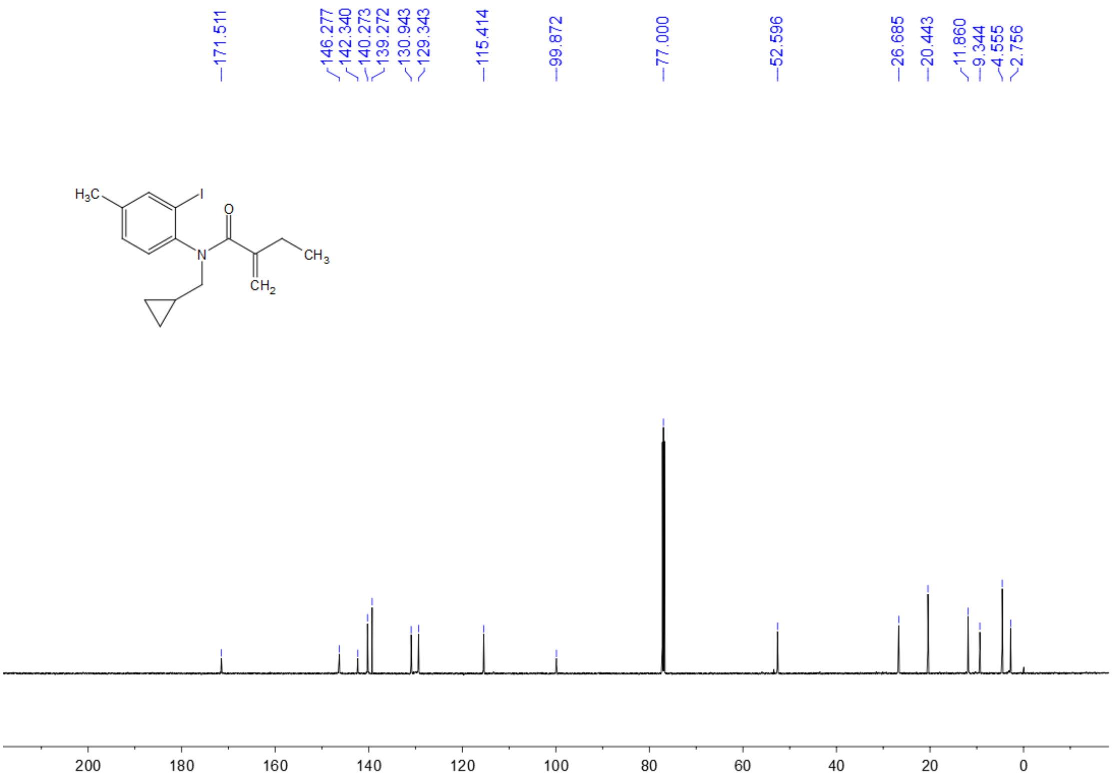

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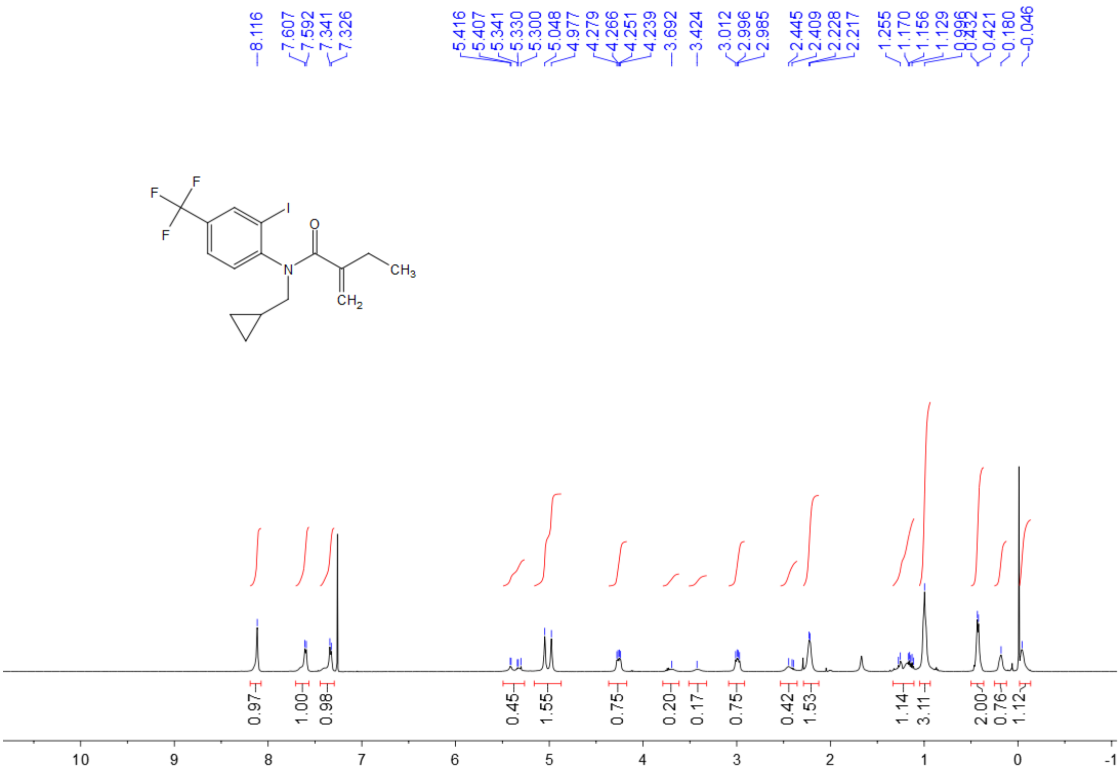

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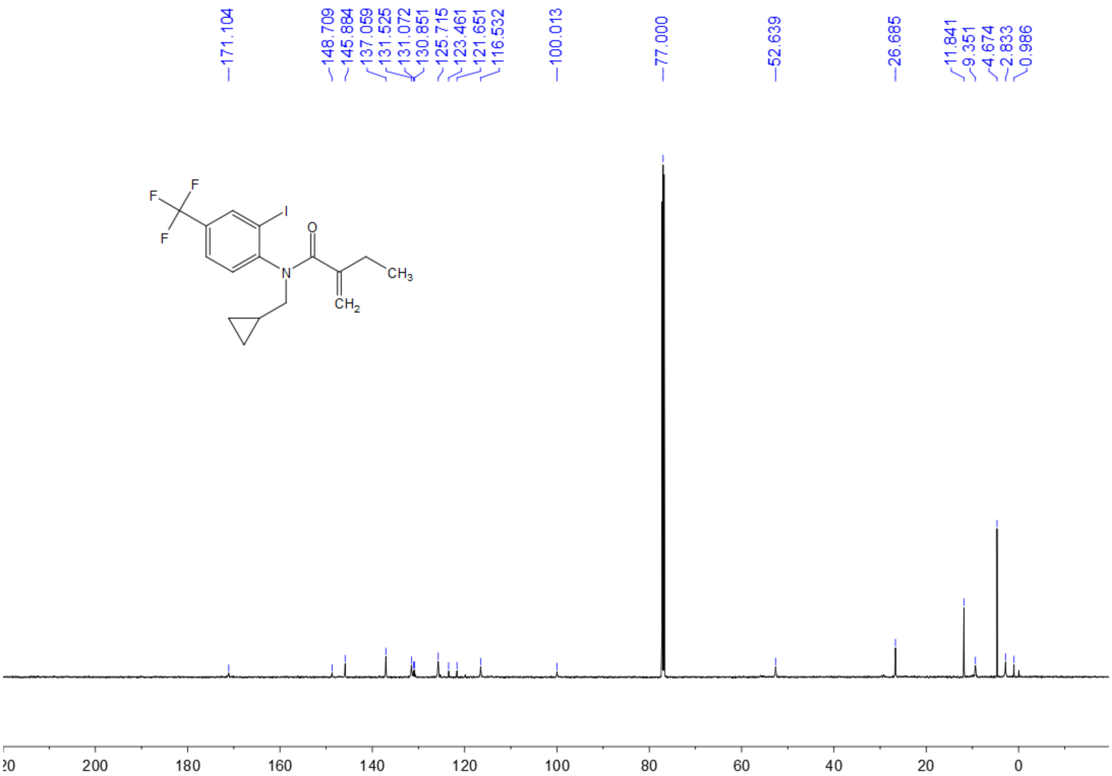
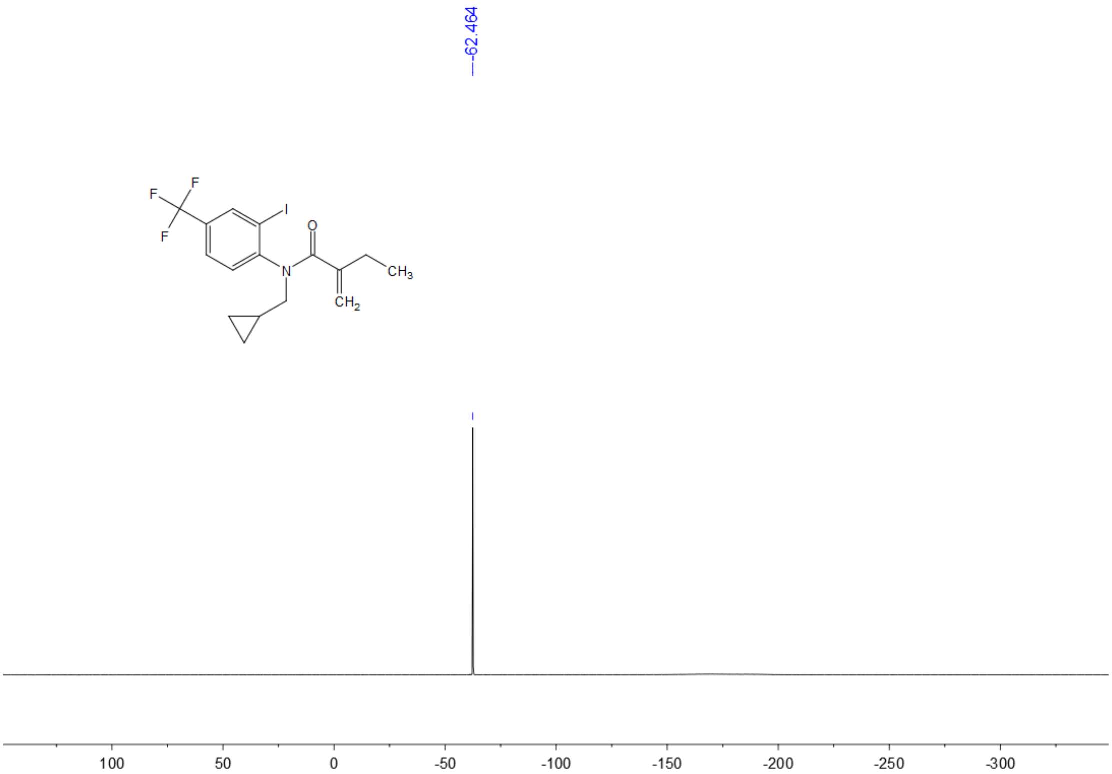


[19]F NMR spectra of **1h**



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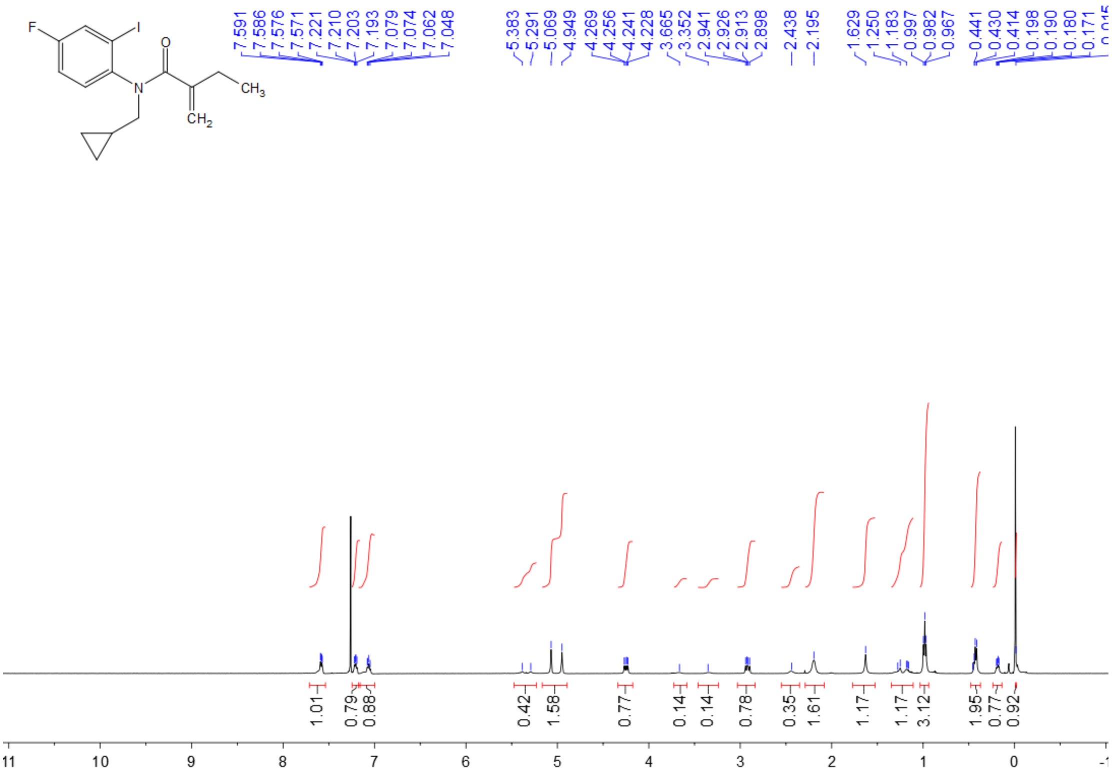

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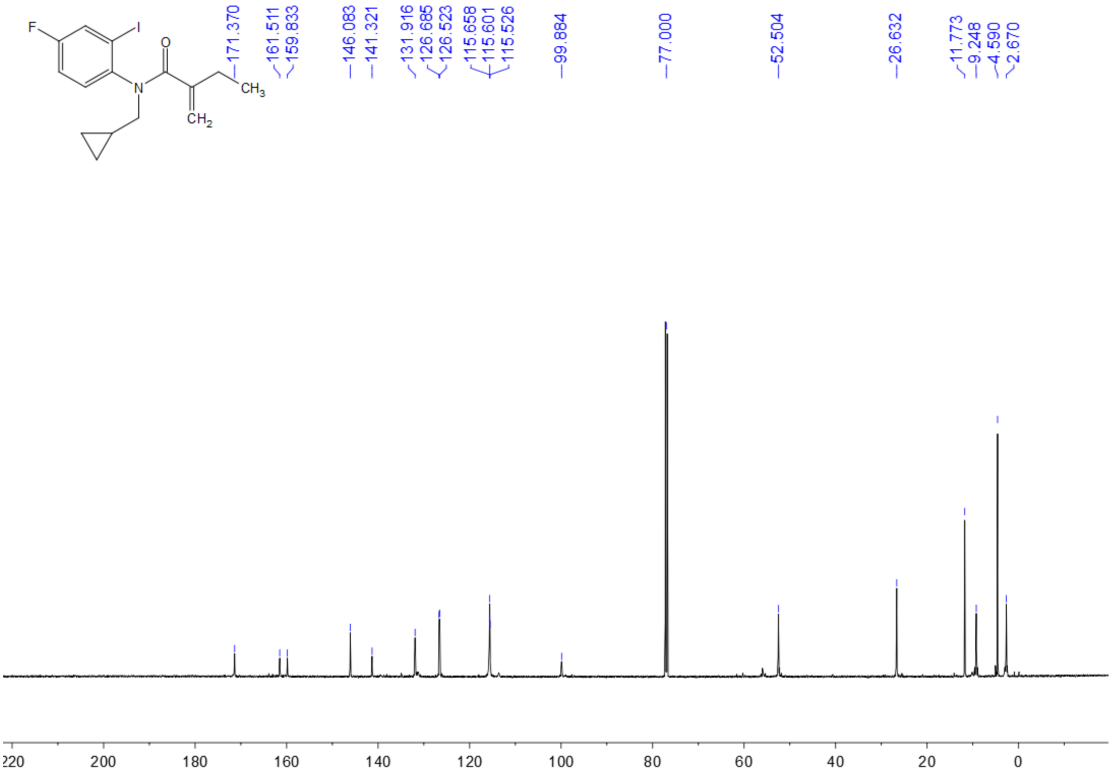

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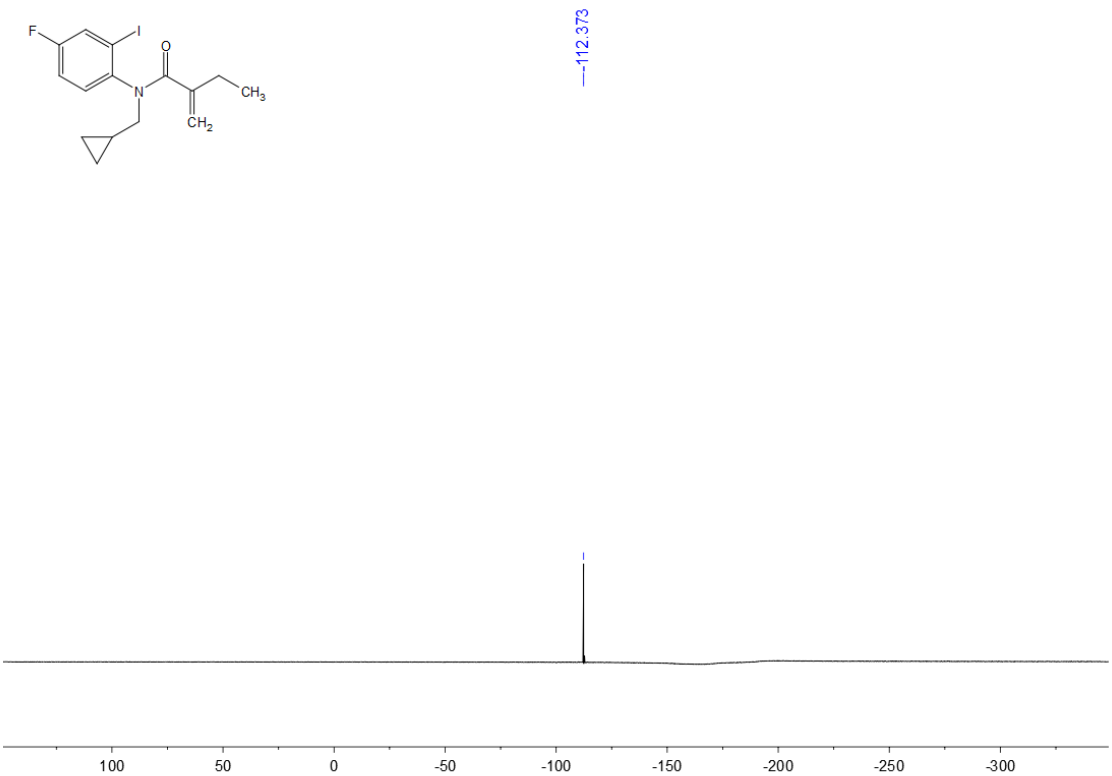

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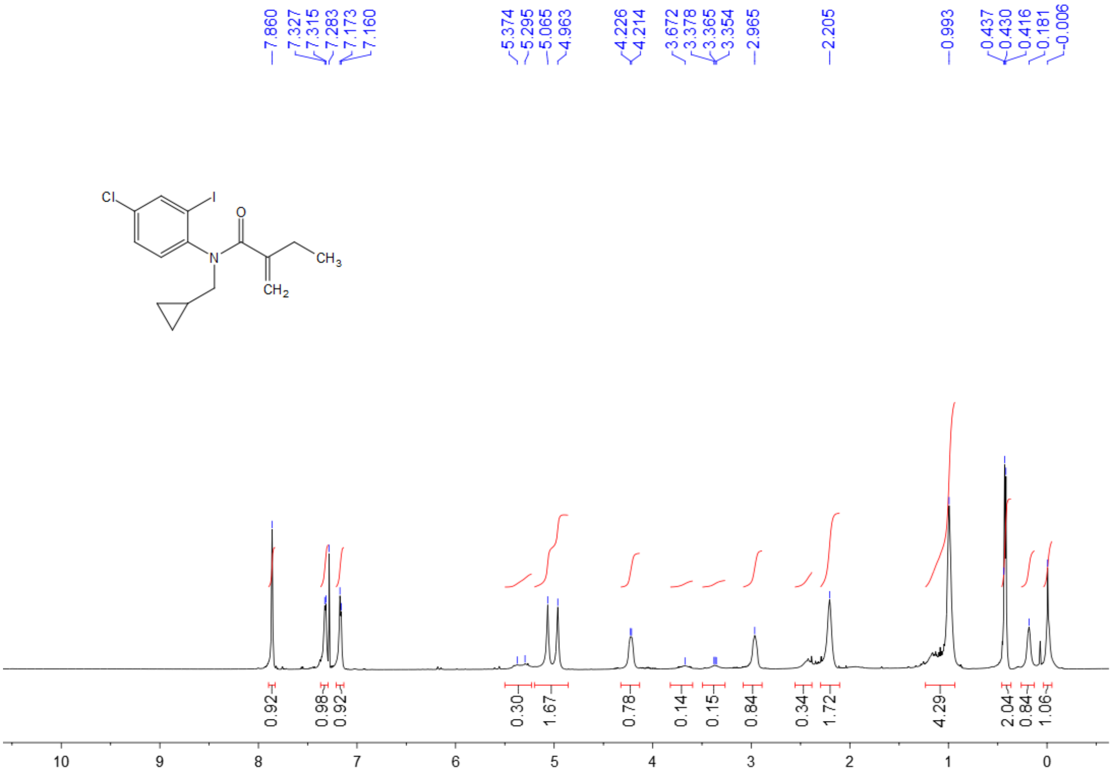

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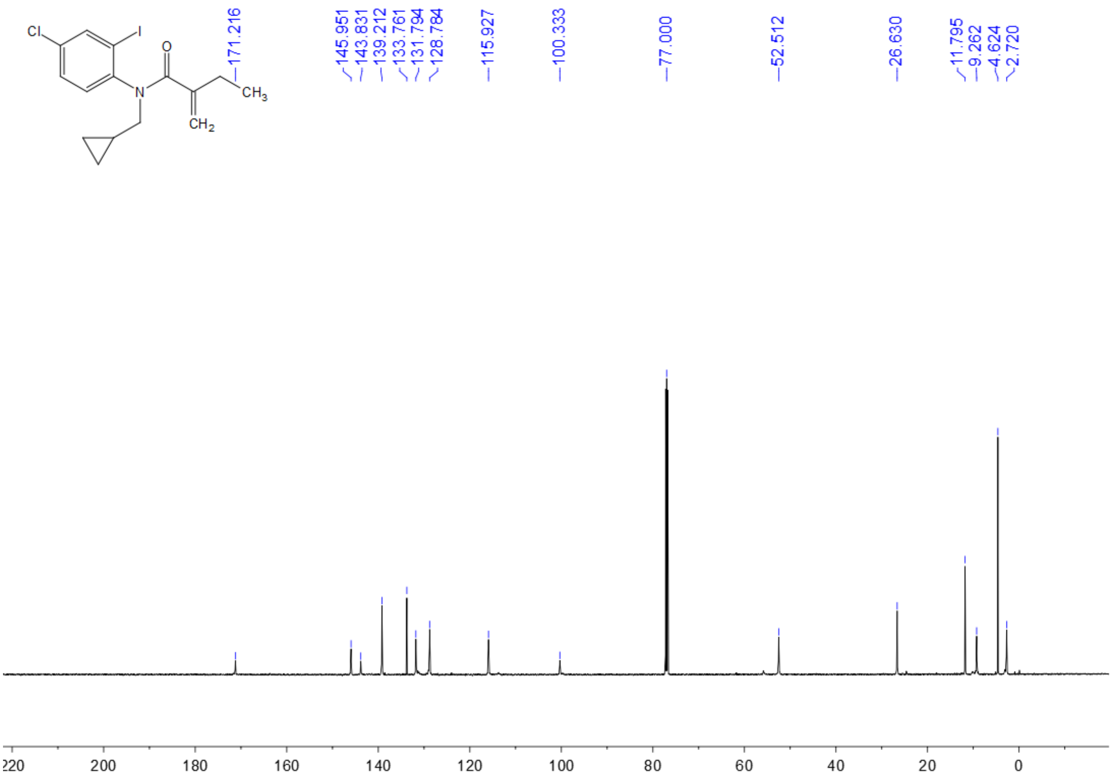

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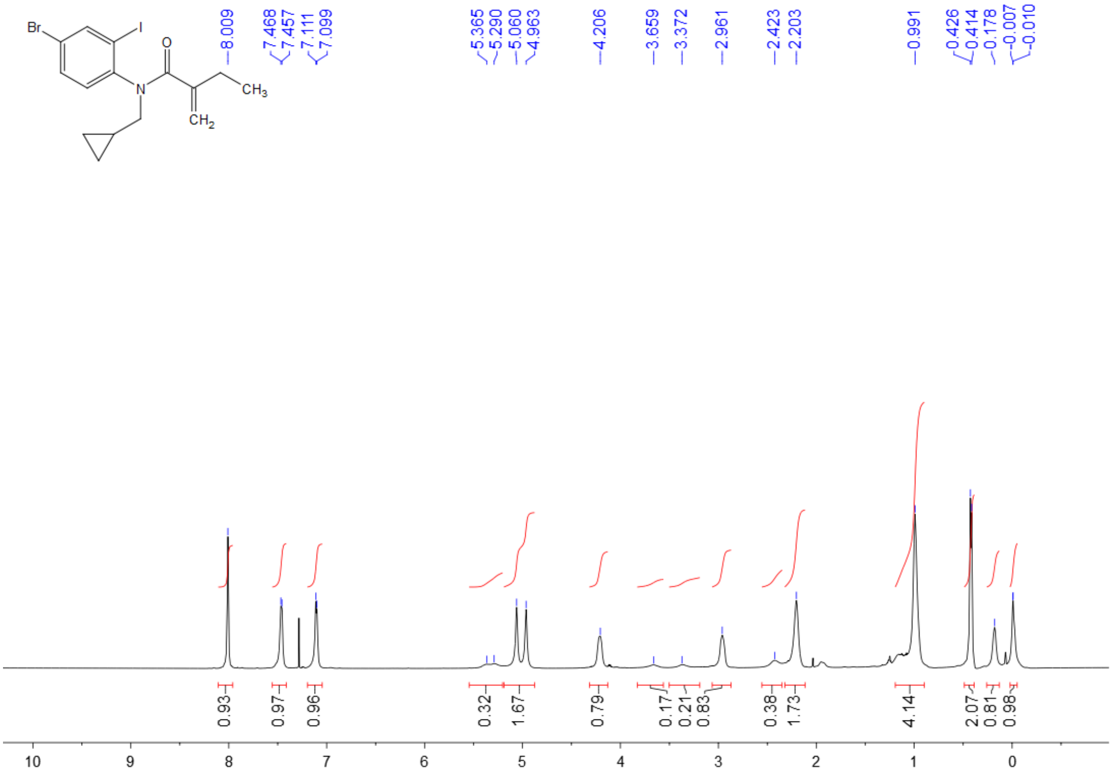

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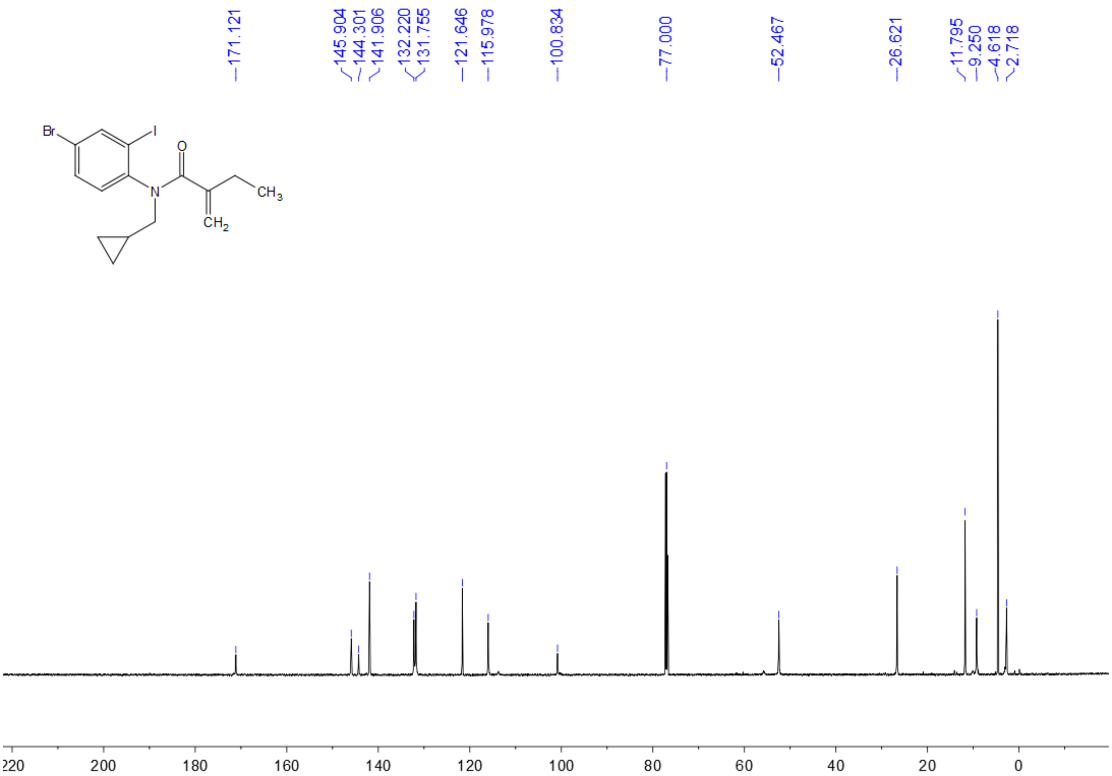

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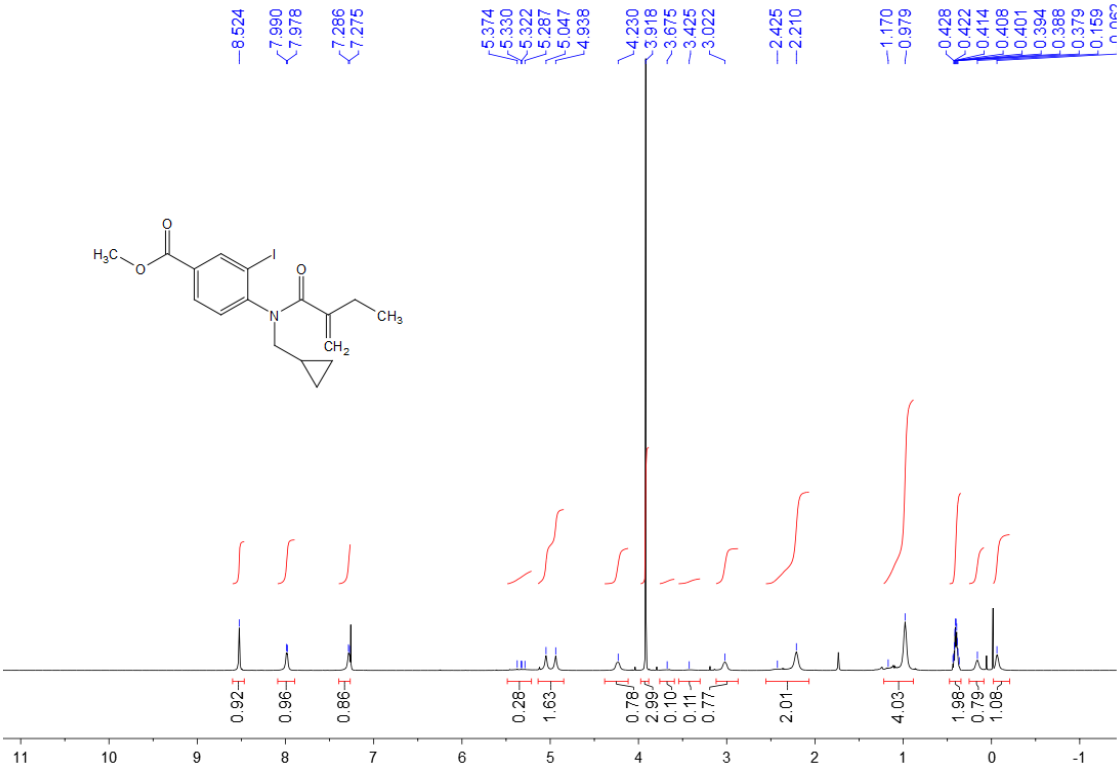

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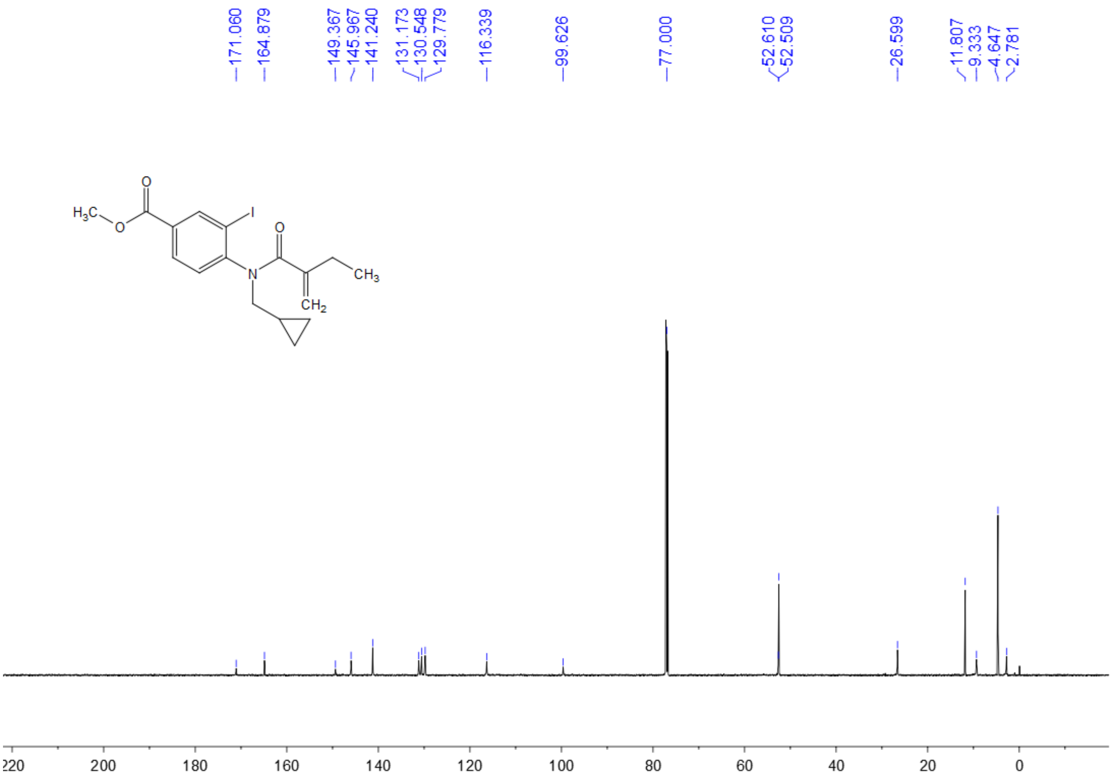

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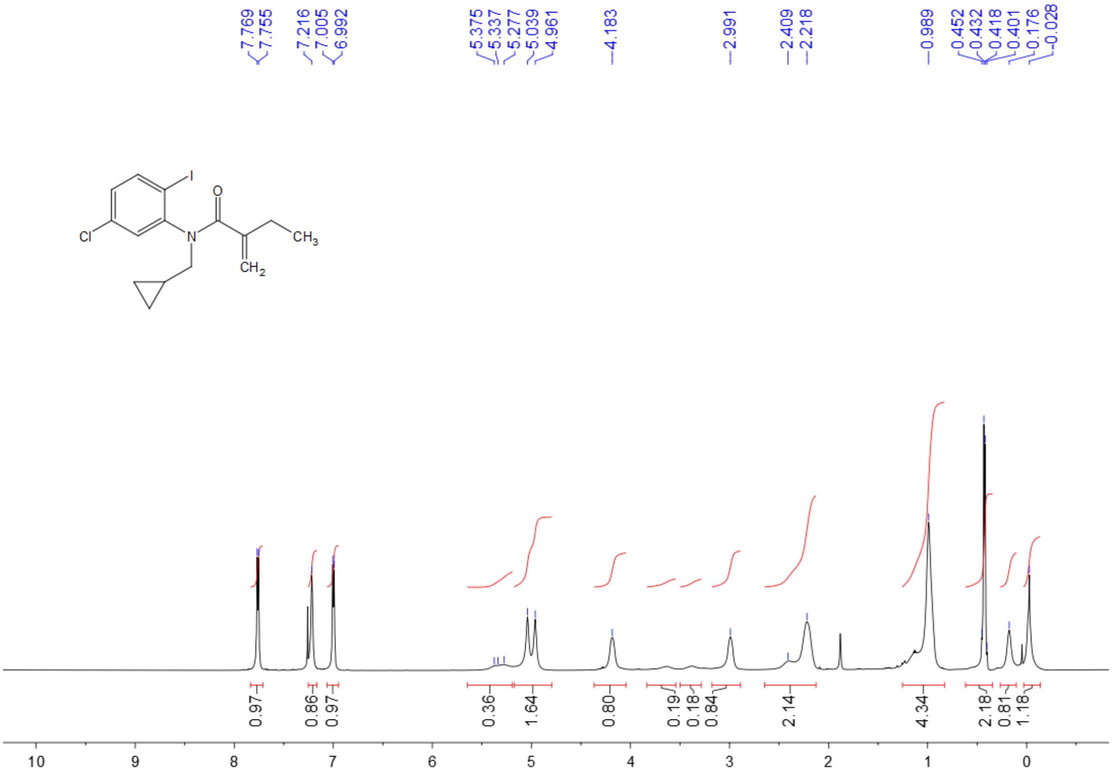

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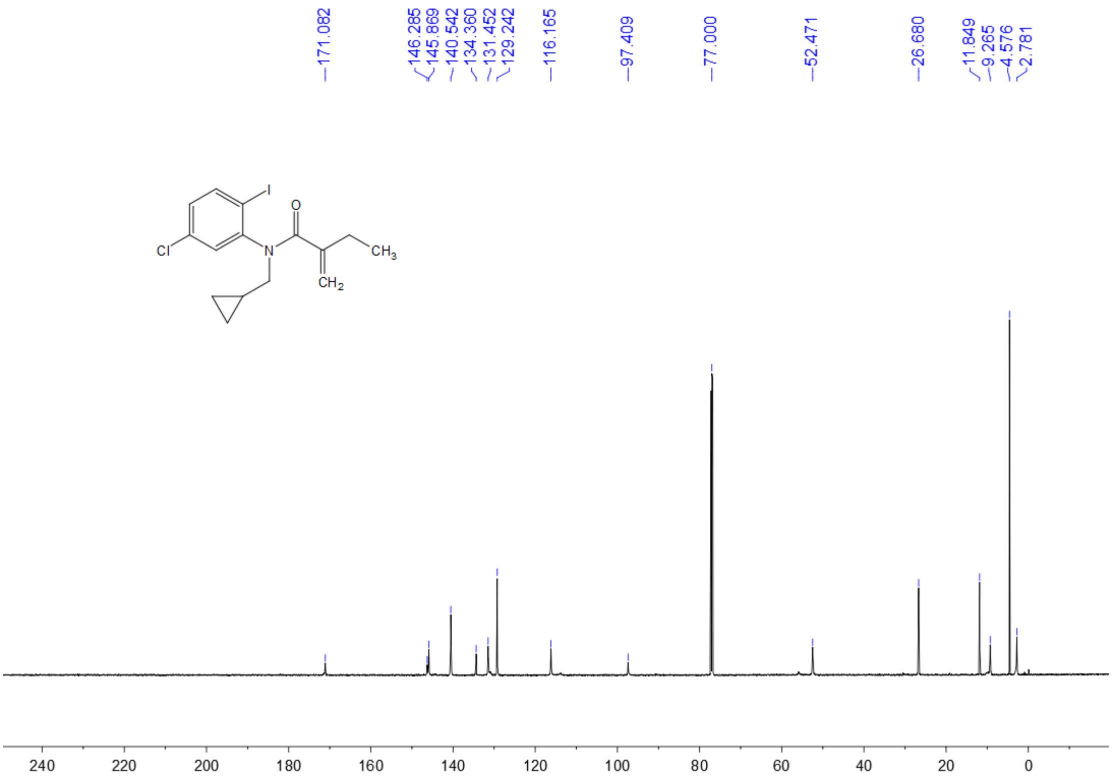
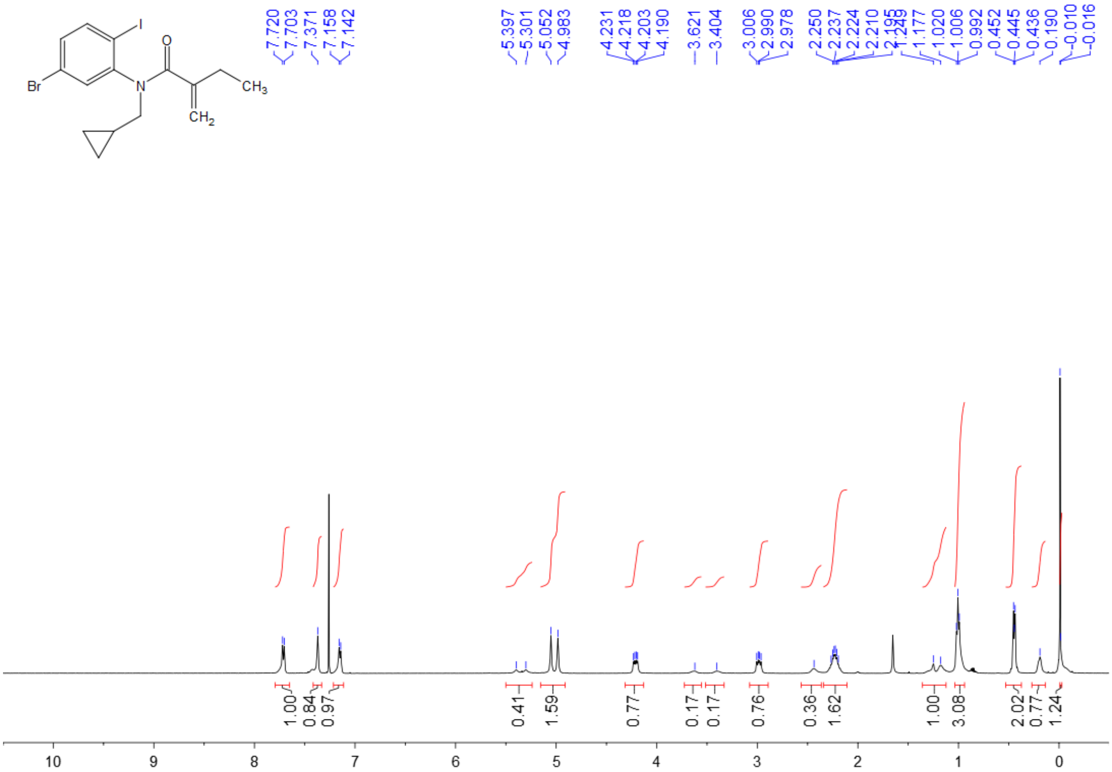
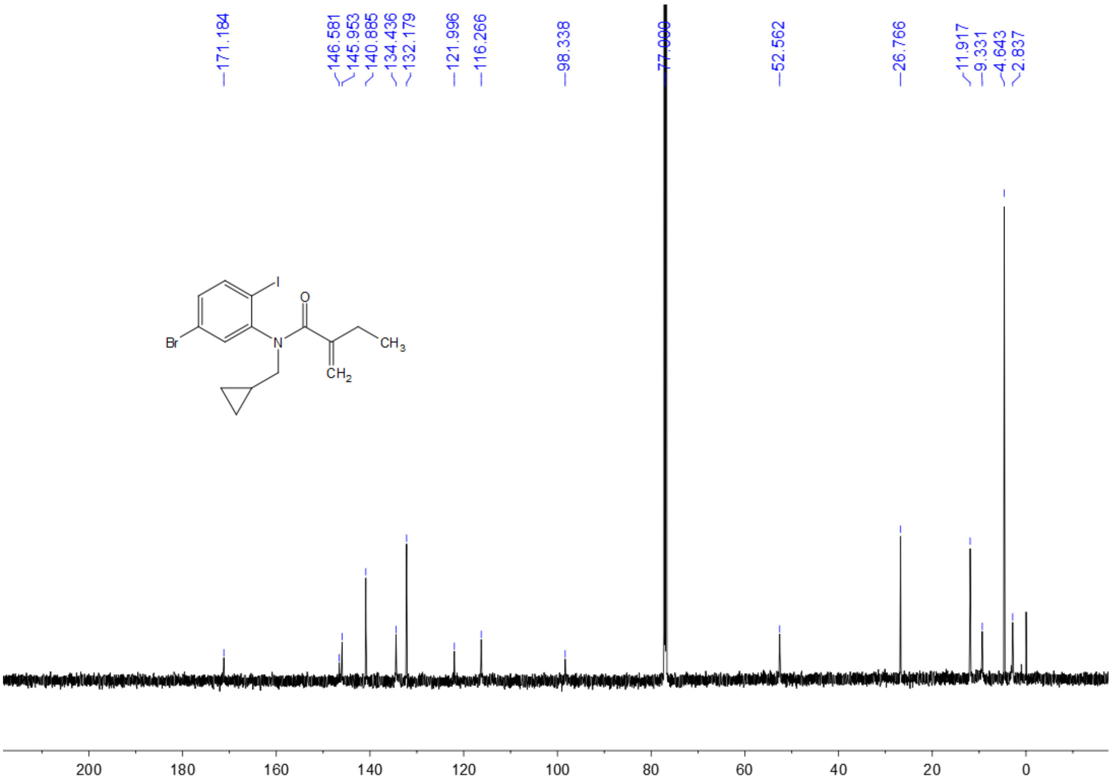


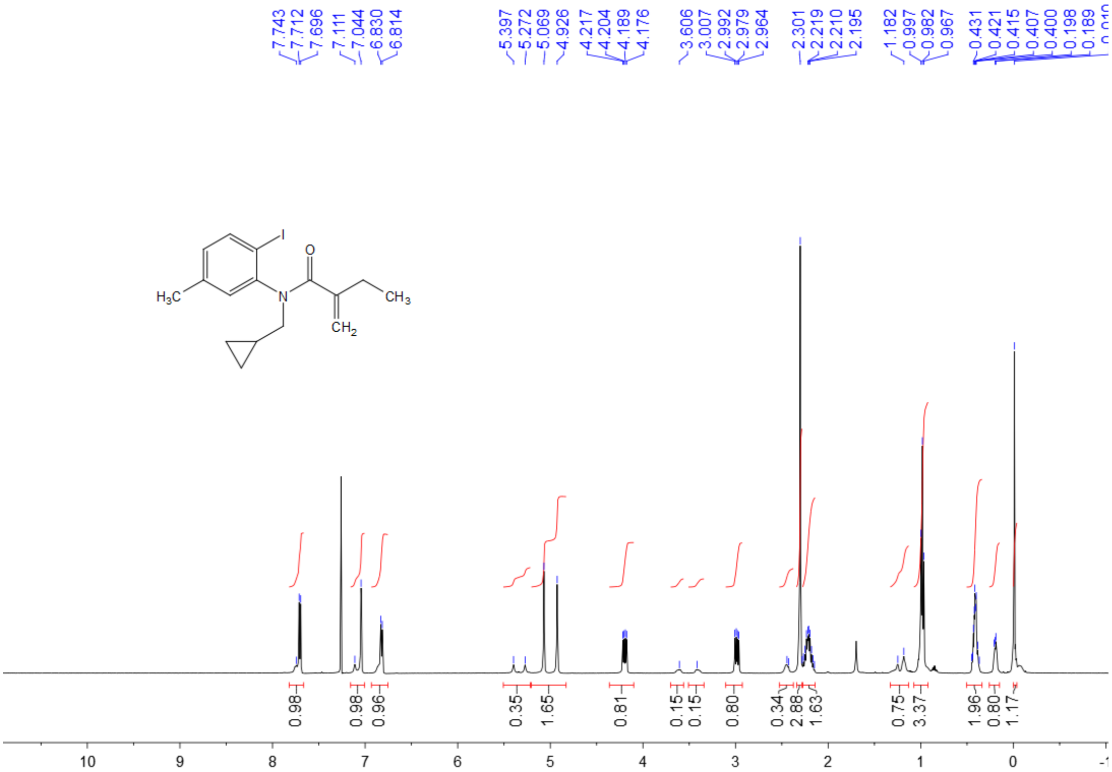
[1]H NMR spectra of **1n**



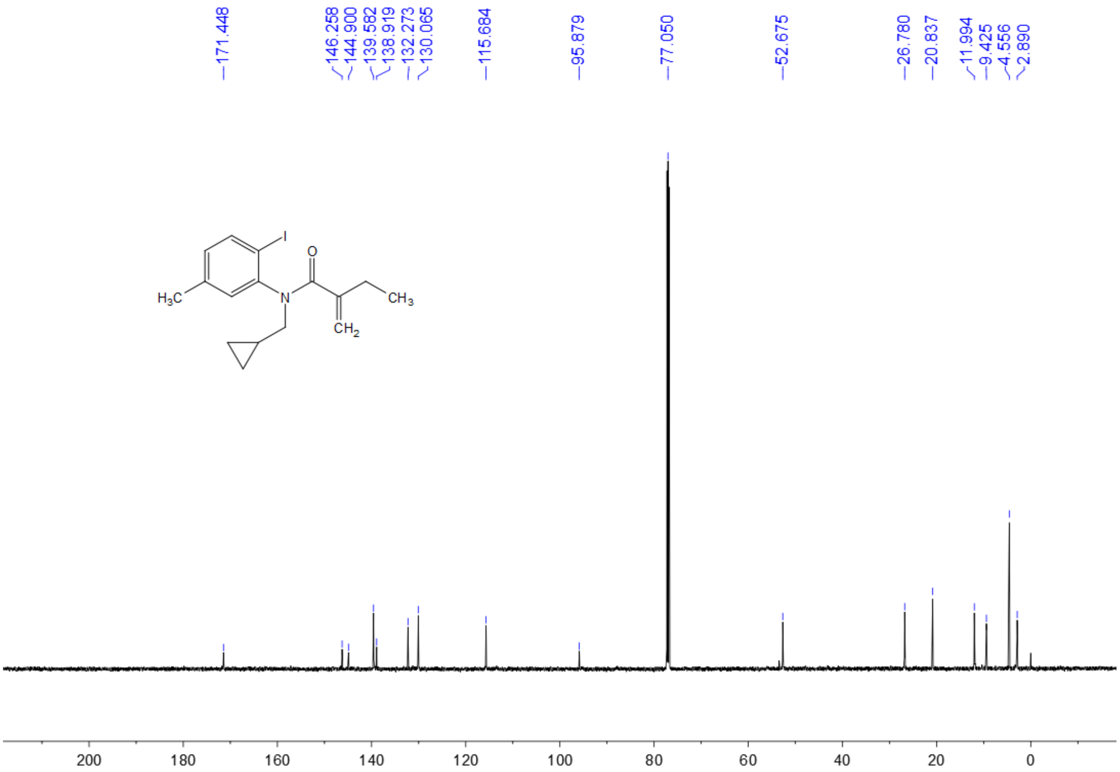
[13]C NMR spectra of **1n**



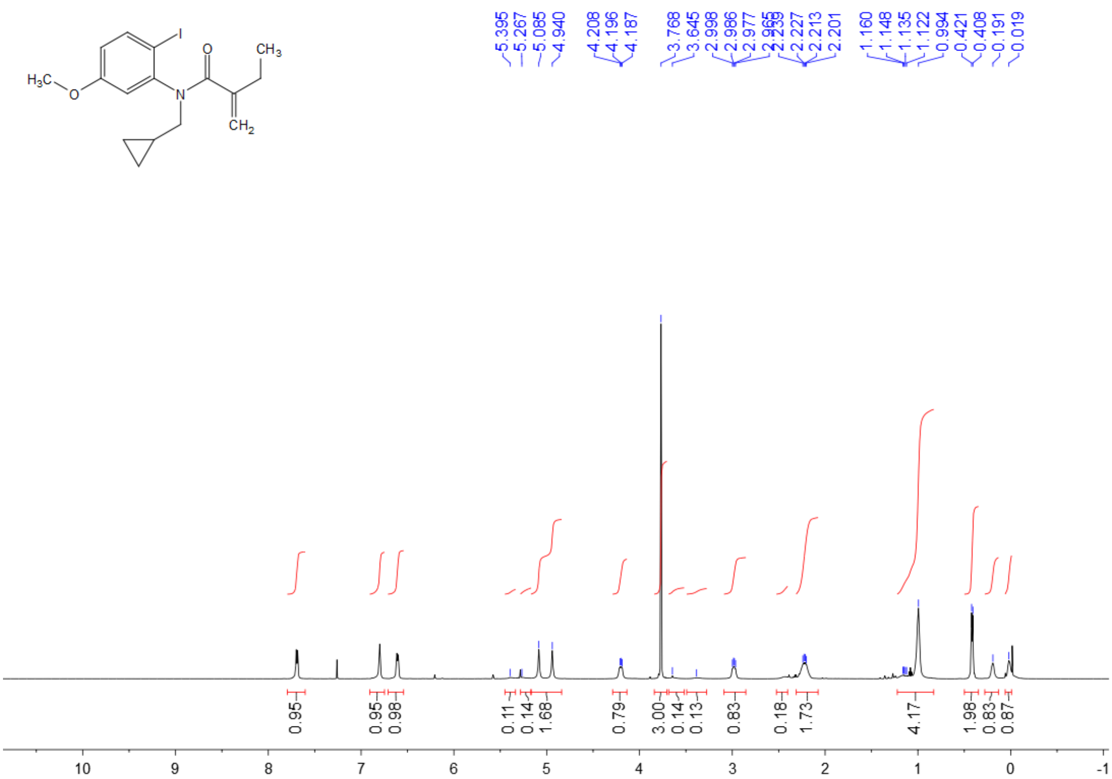
^{1}H NMR spectra of **1o**



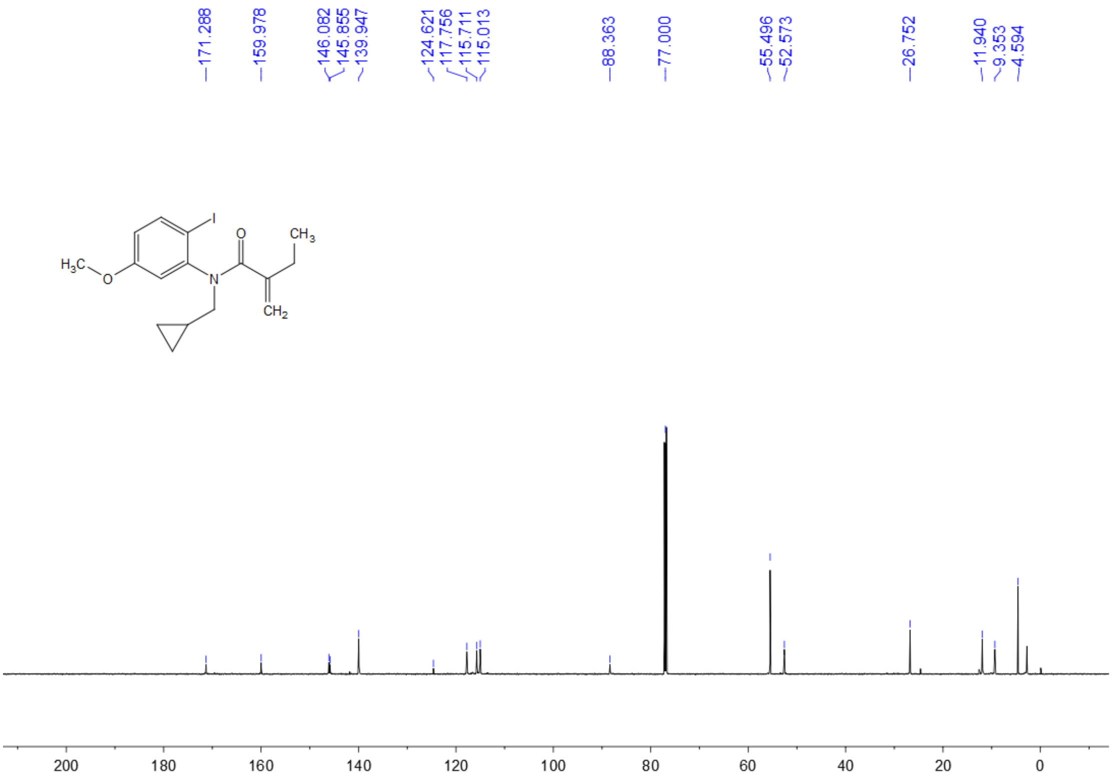
^{13}C NMR spectra of **1o**



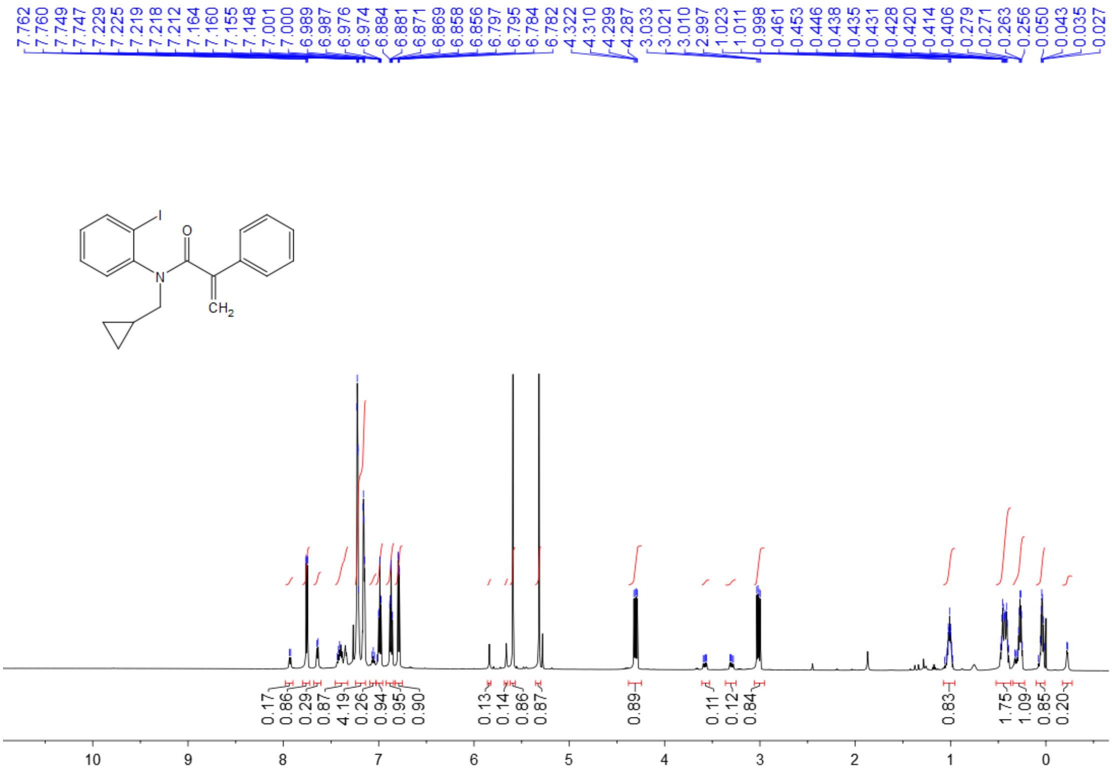
^{1}H NMR spectra of **1p**



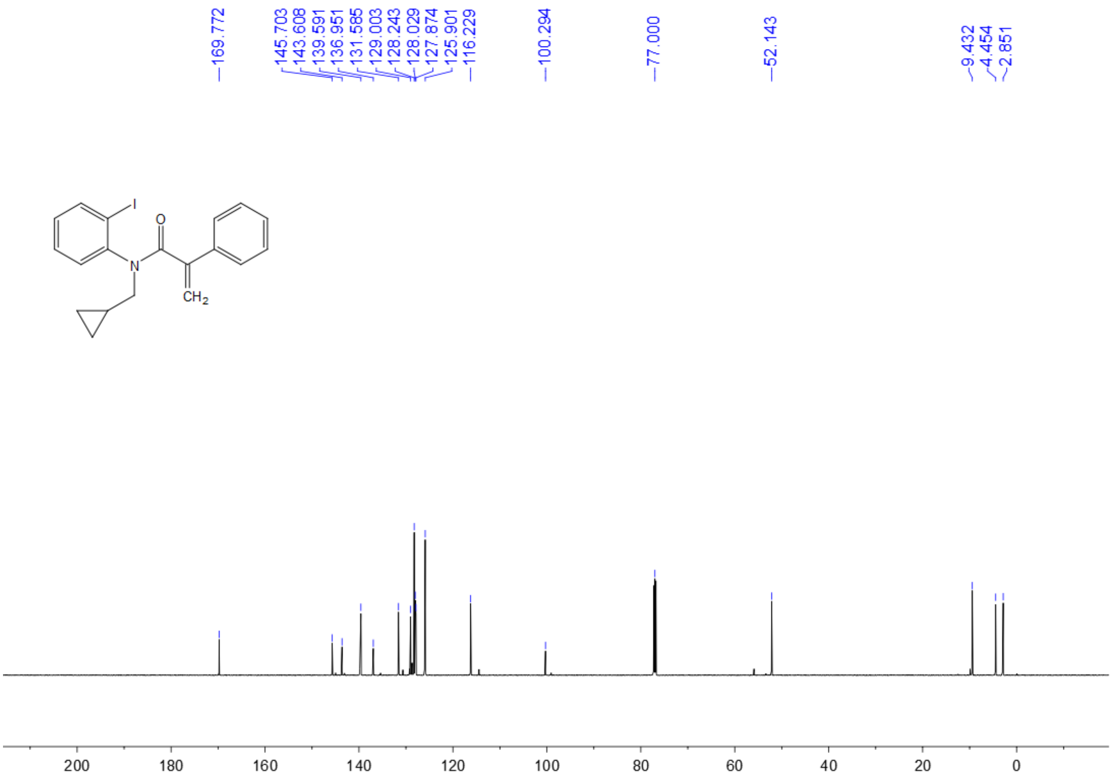
^{13}C NMR spectra of **1p**



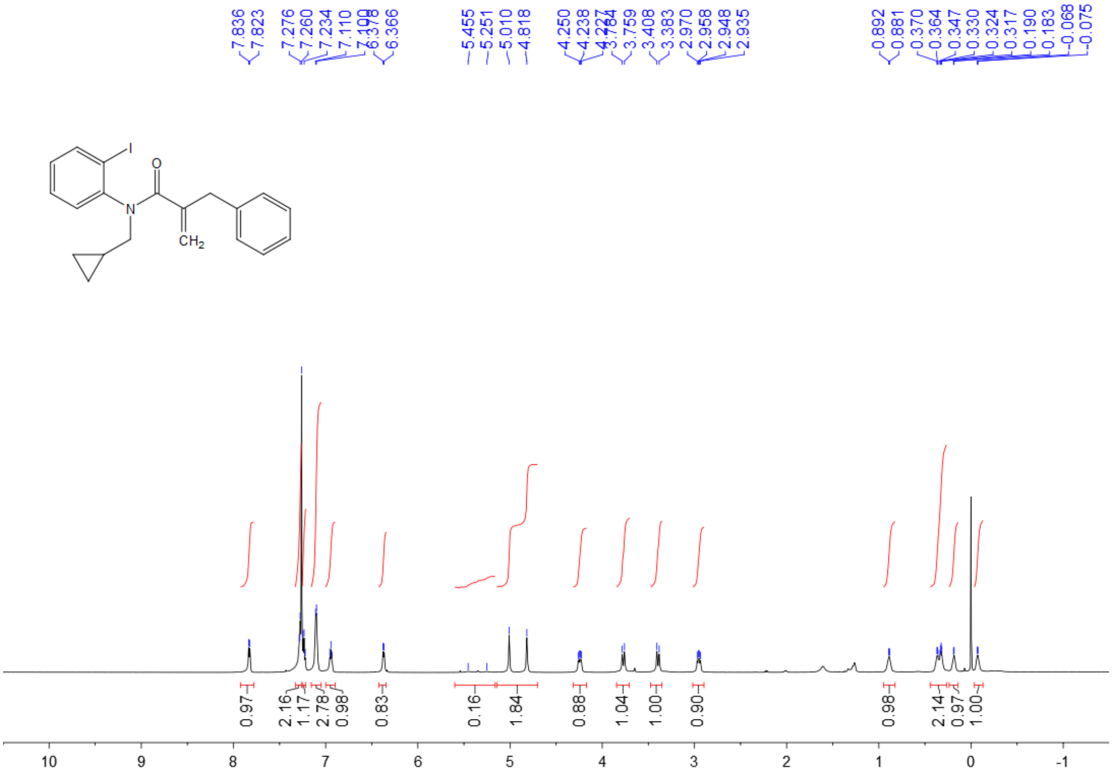
^{1}H NMR spectra of **1q**



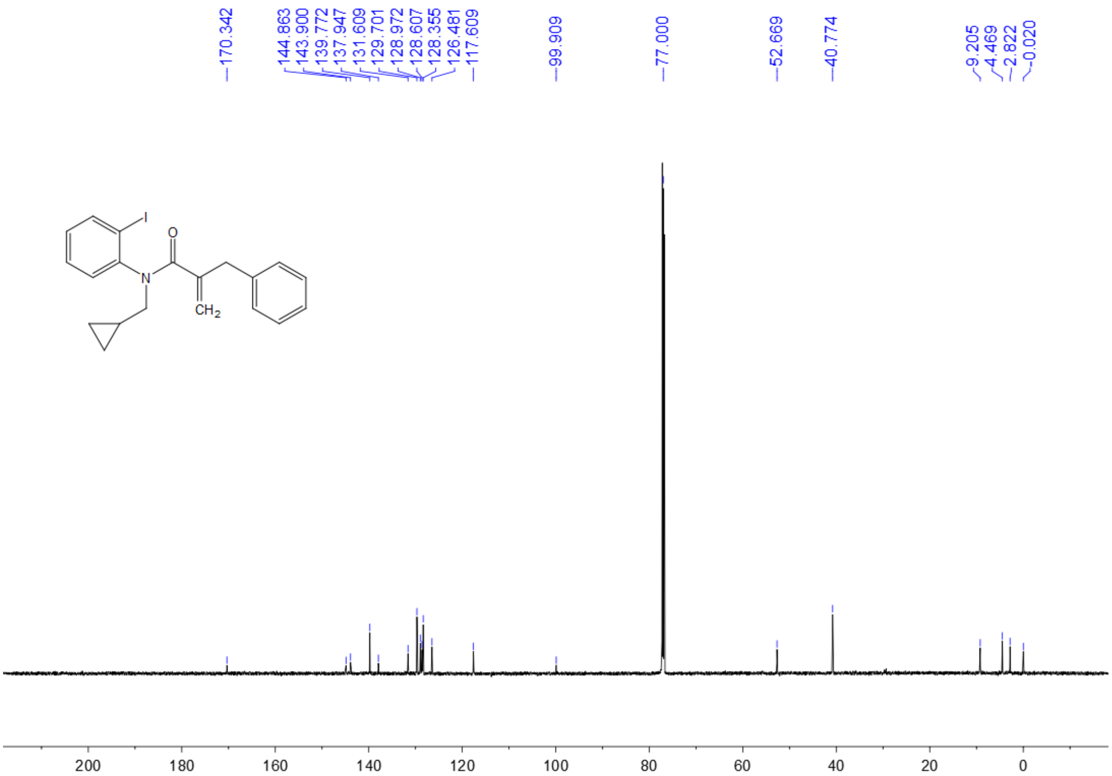
^{13}C NMR spectra of **1q**



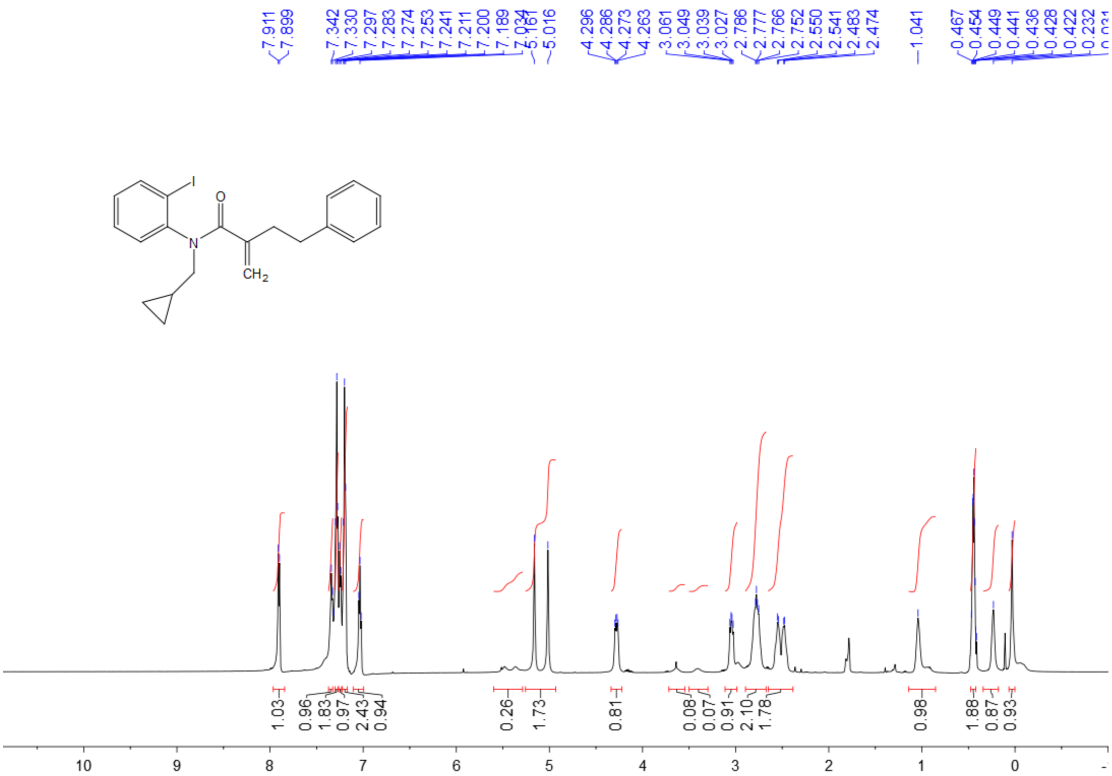
^1H NMR spectra of **1r**



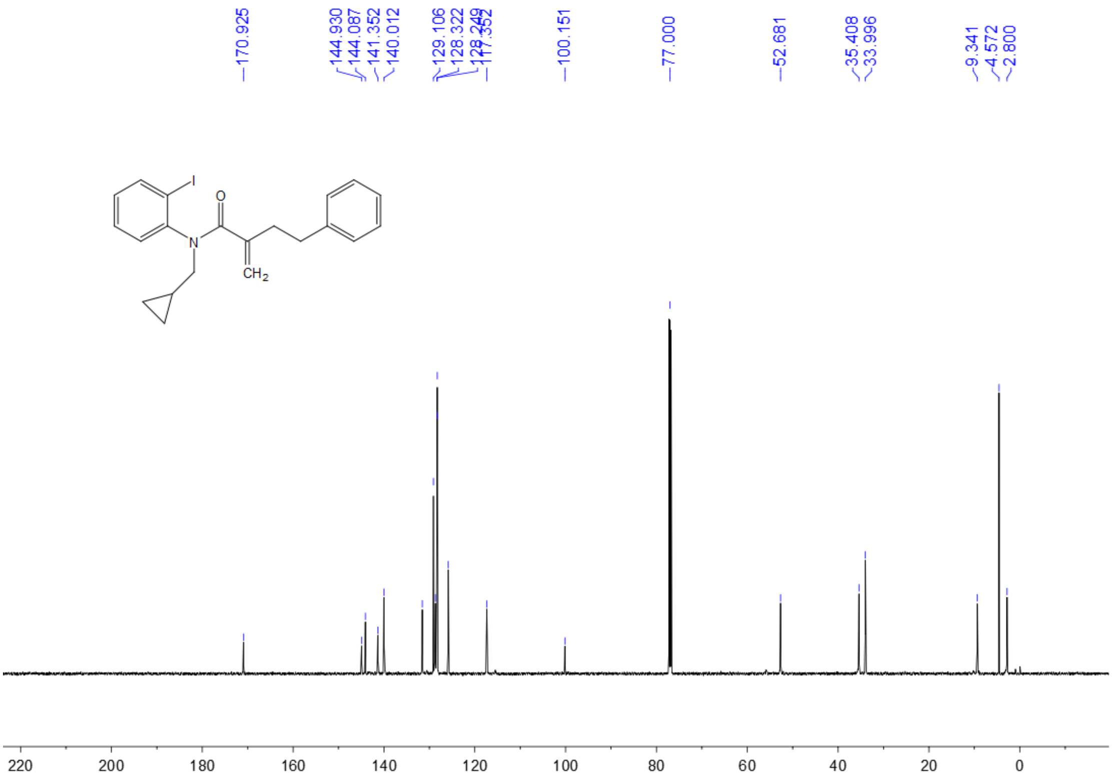
^{13}C NMR spectra of **1r**



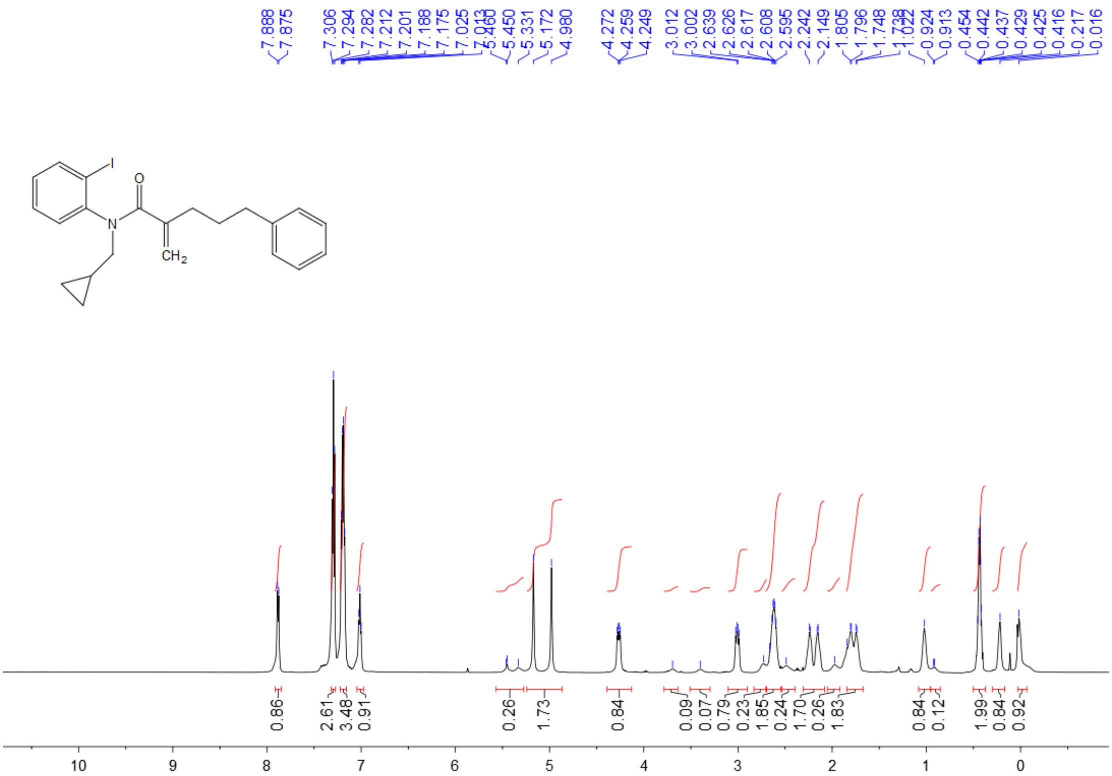
[1]H NMR spectra of **1s**



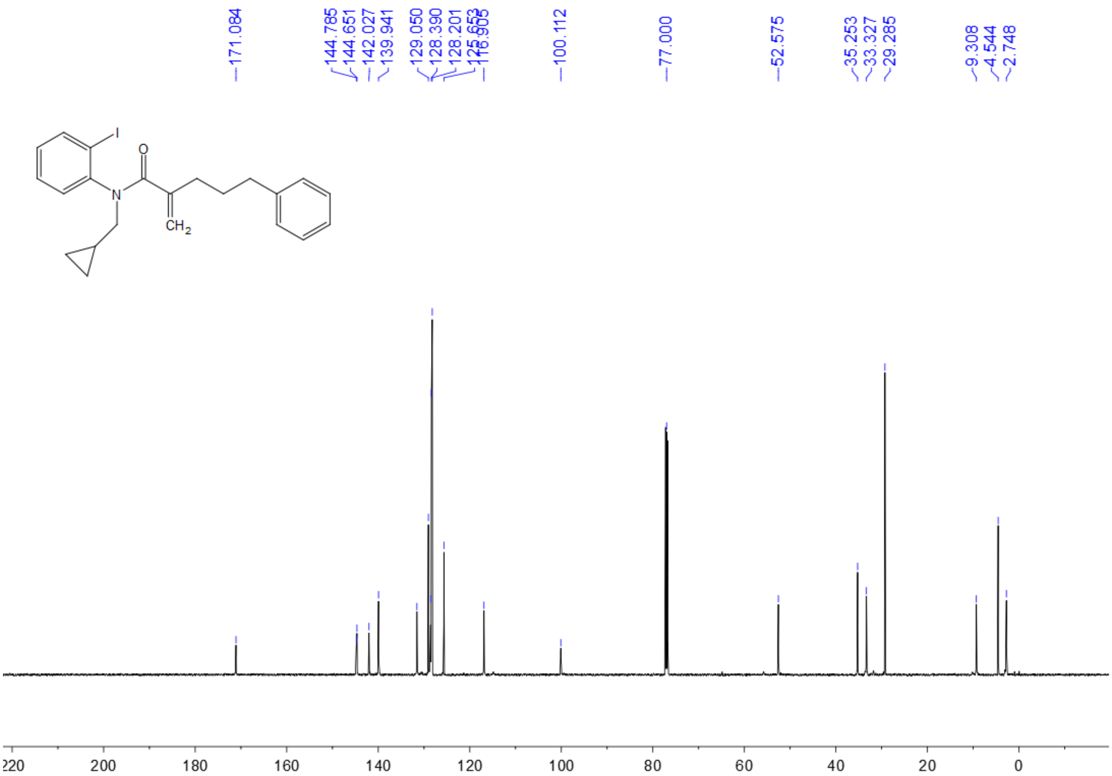
[13]C NMR spectra of **1s**



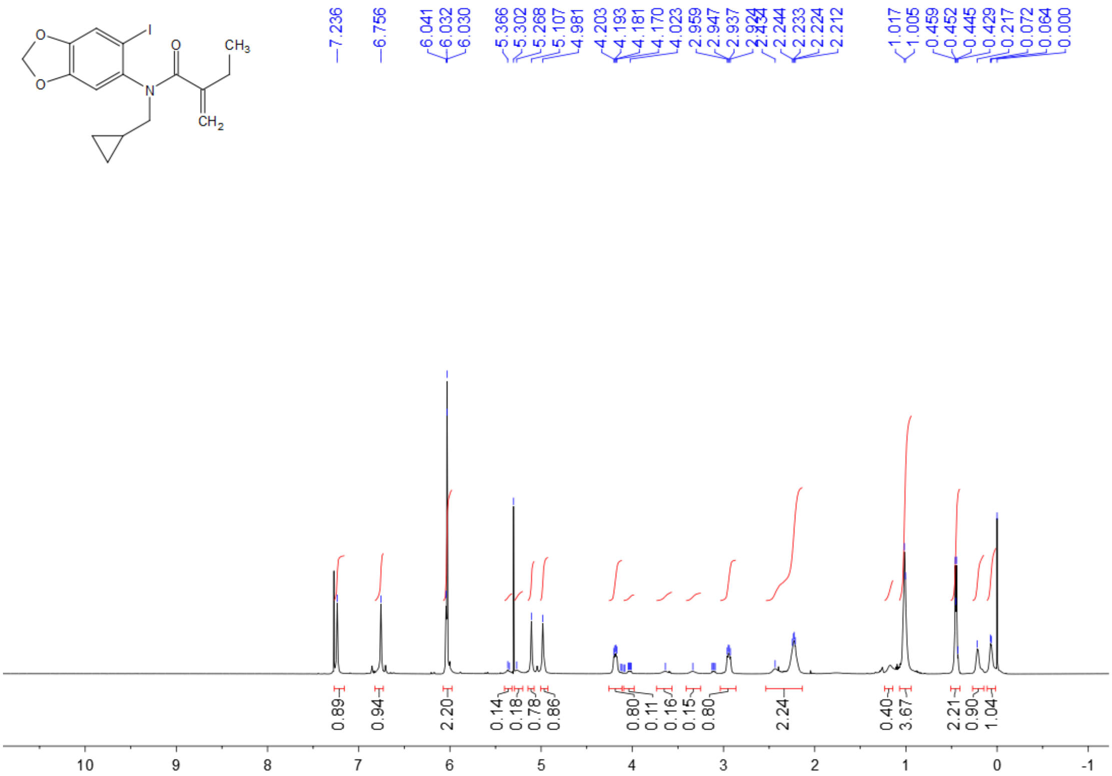
[1]H NMR spectra of **1t**



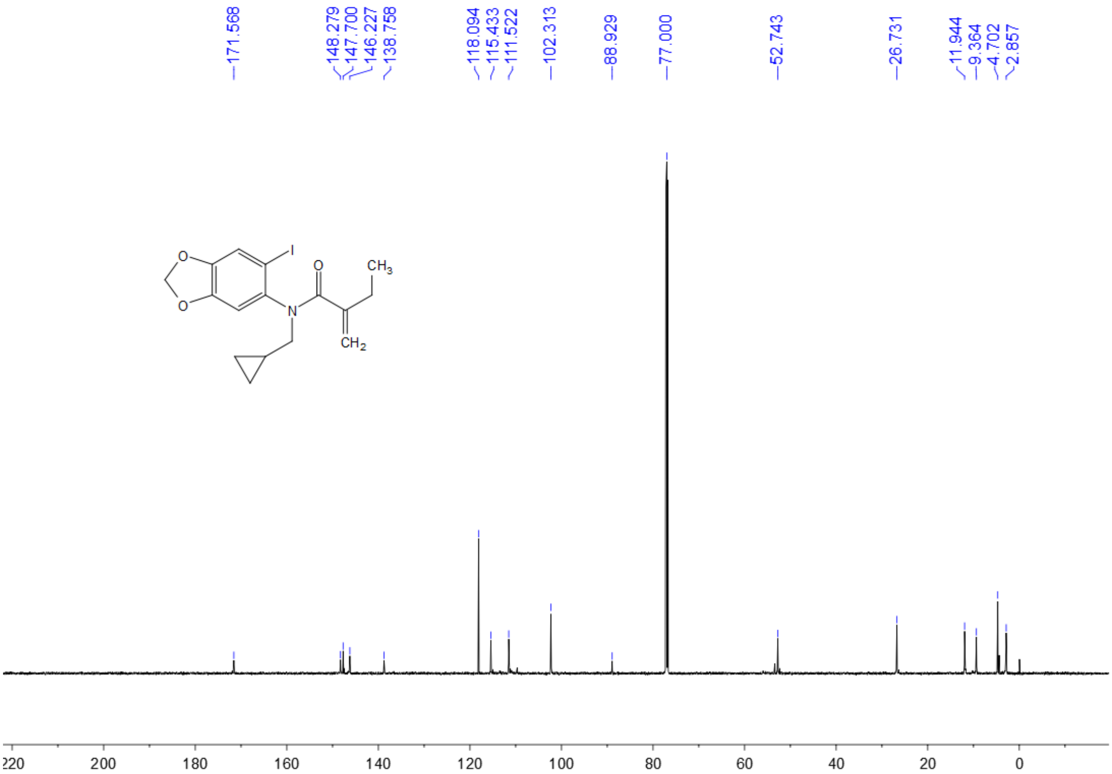
[13]C NMR spectra of **1t**



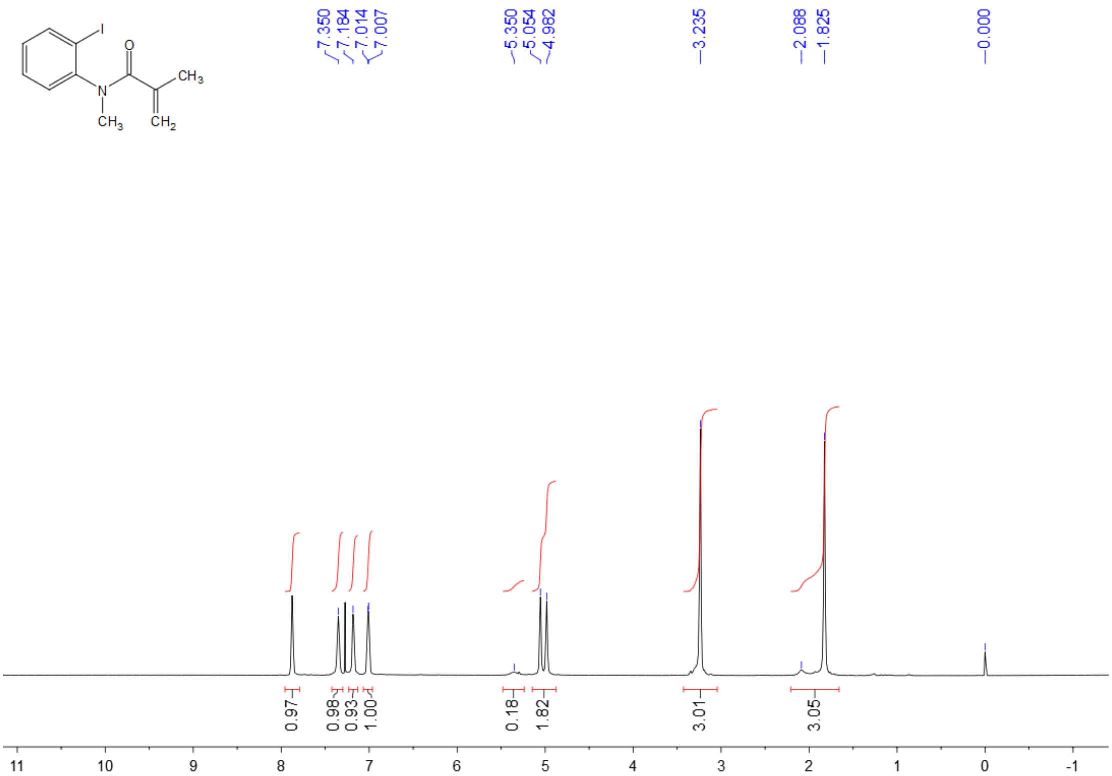
^{1}H NMR spectra of **1u**



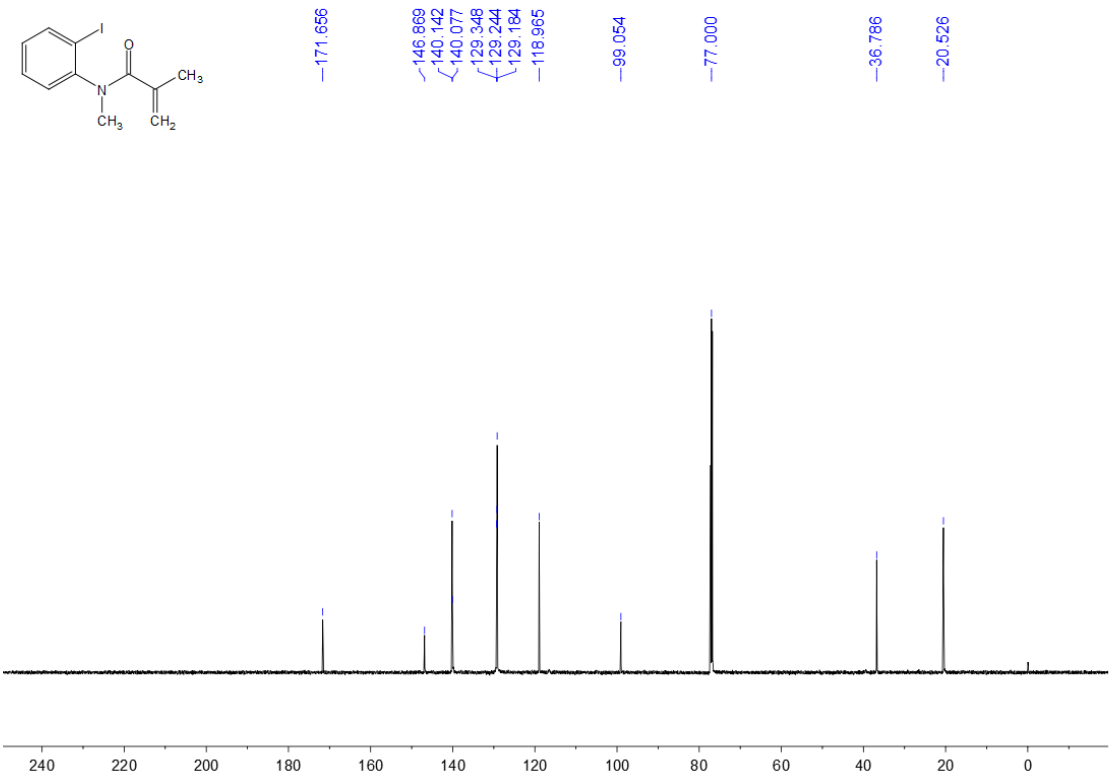
^{13}C NMR spectra of **1u**



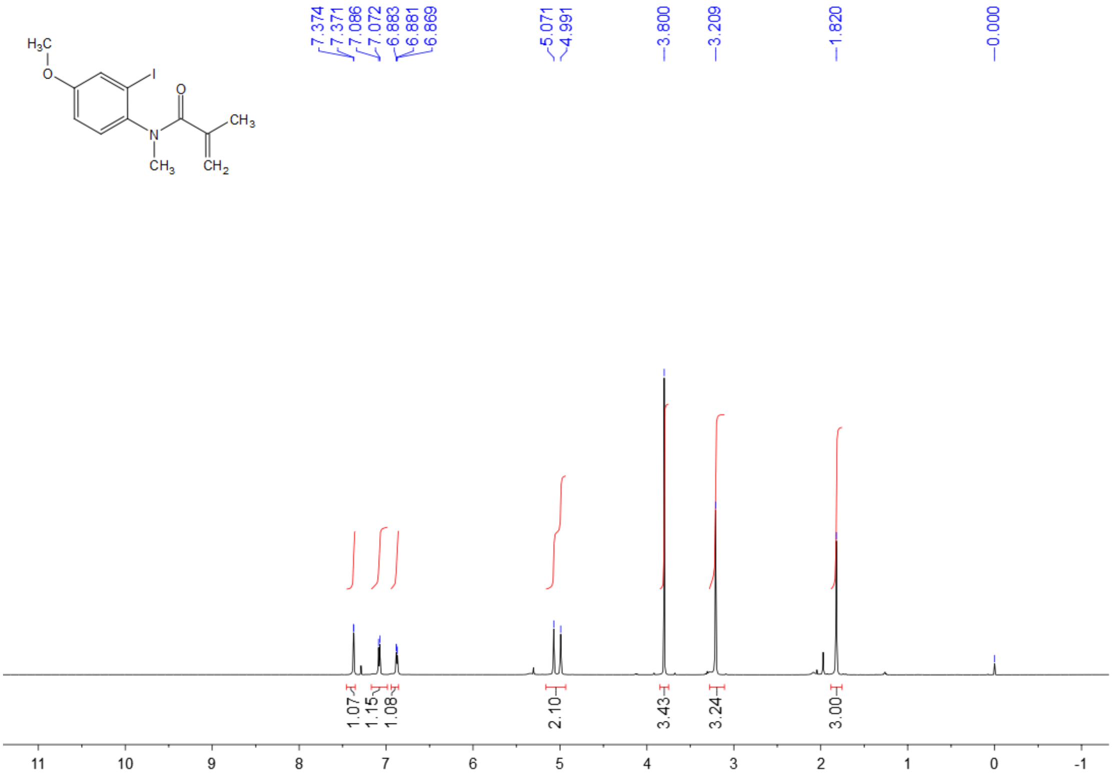
[1]H NMR spectra of **1v**



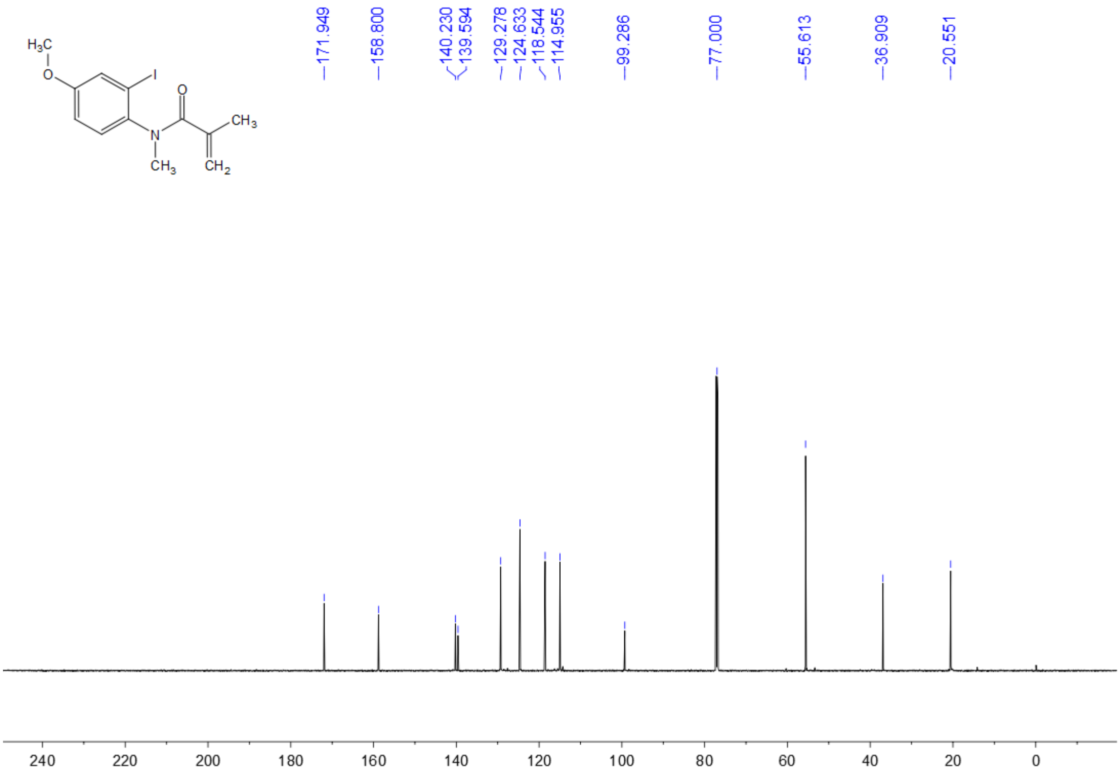
[13]C NMR spectra of **1v**



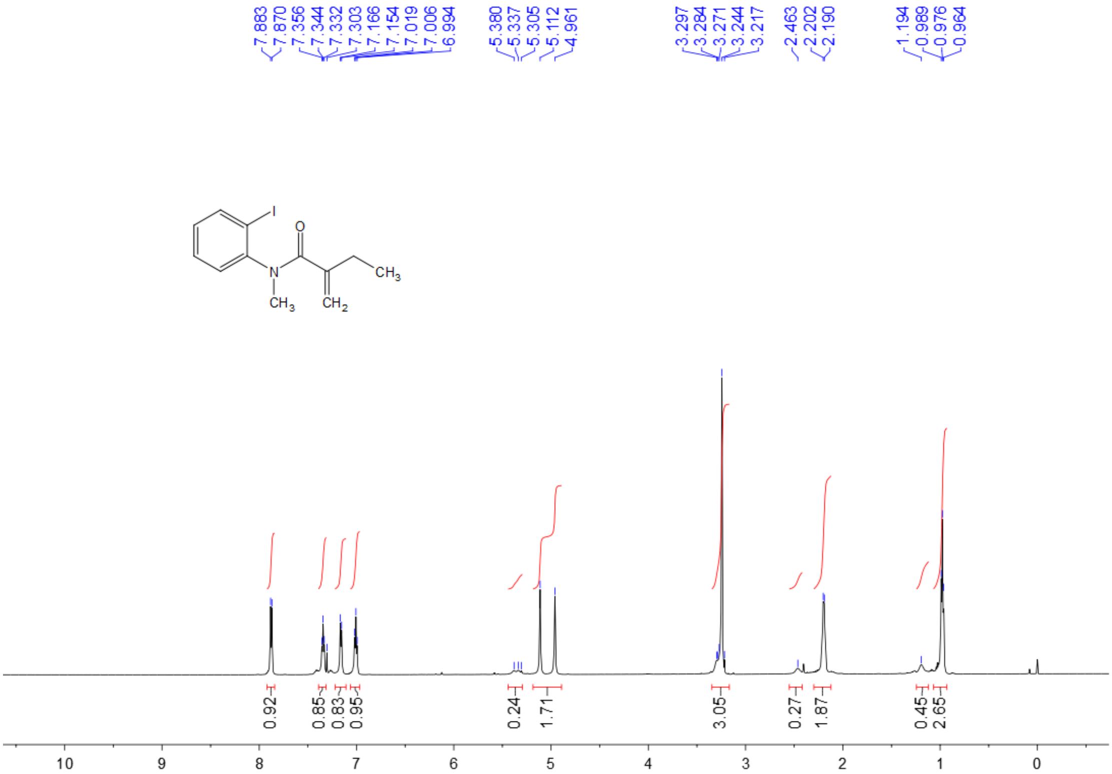
[1]H NMR spectra of **1w**



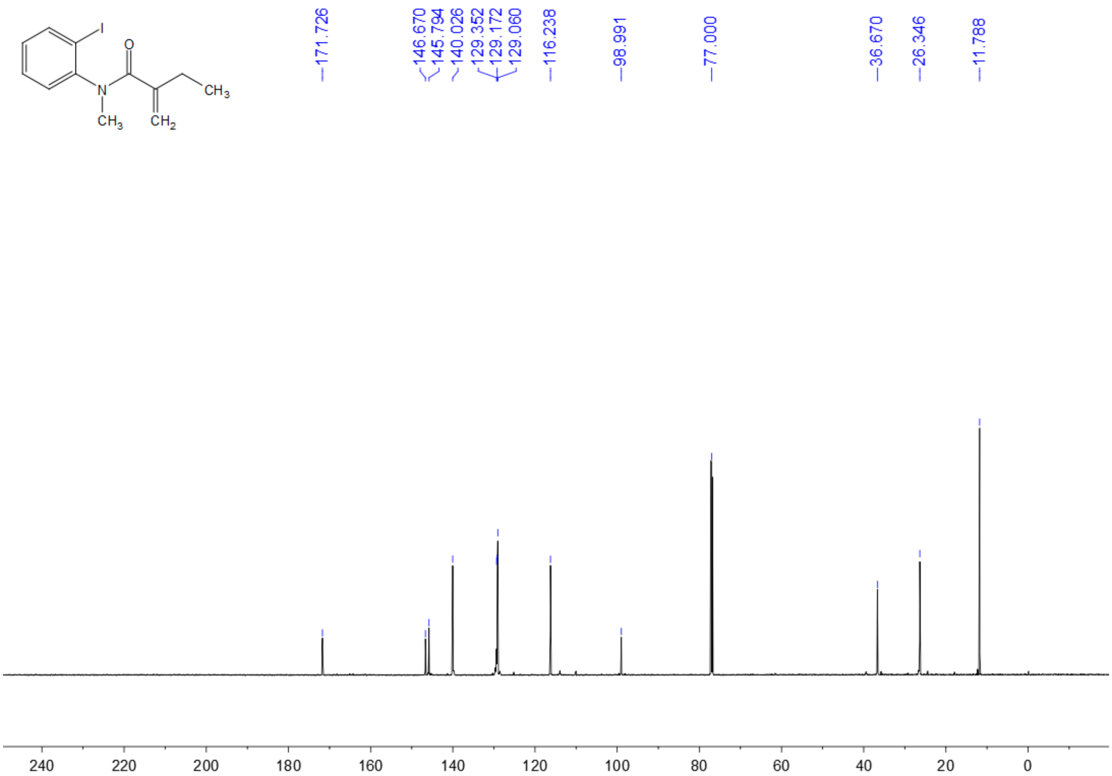
[13]C NMR spectra of **1w**



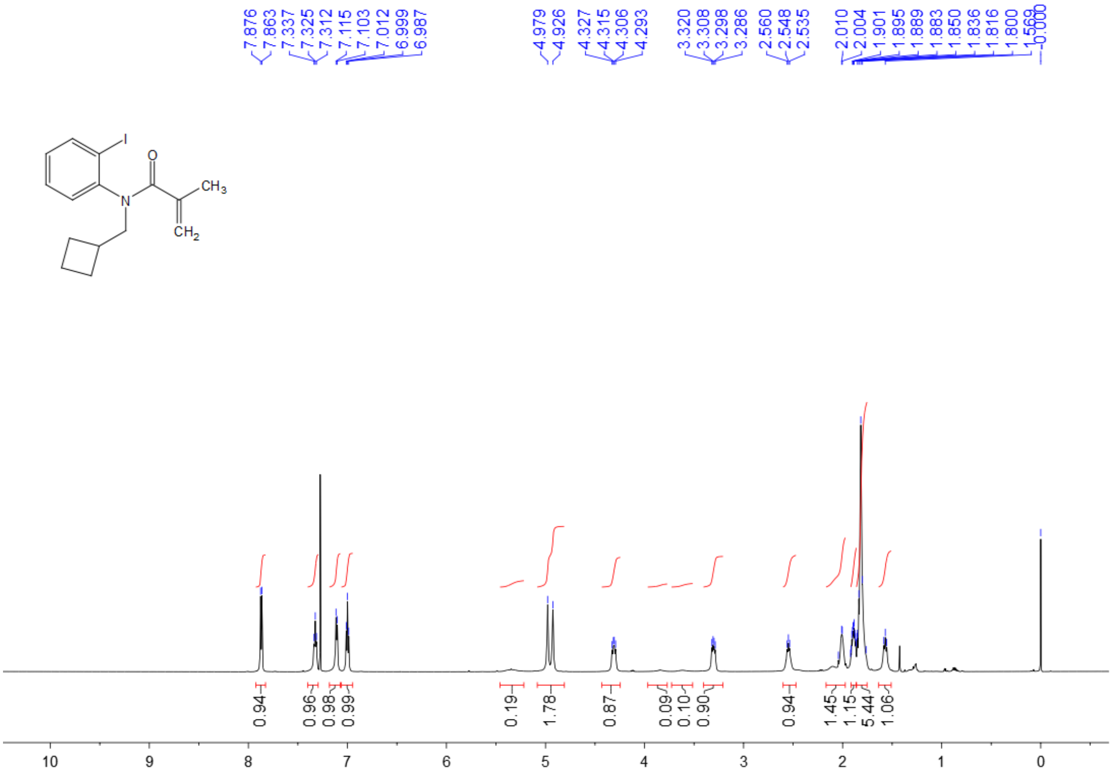
^{1}H NMR spectra of **1x**



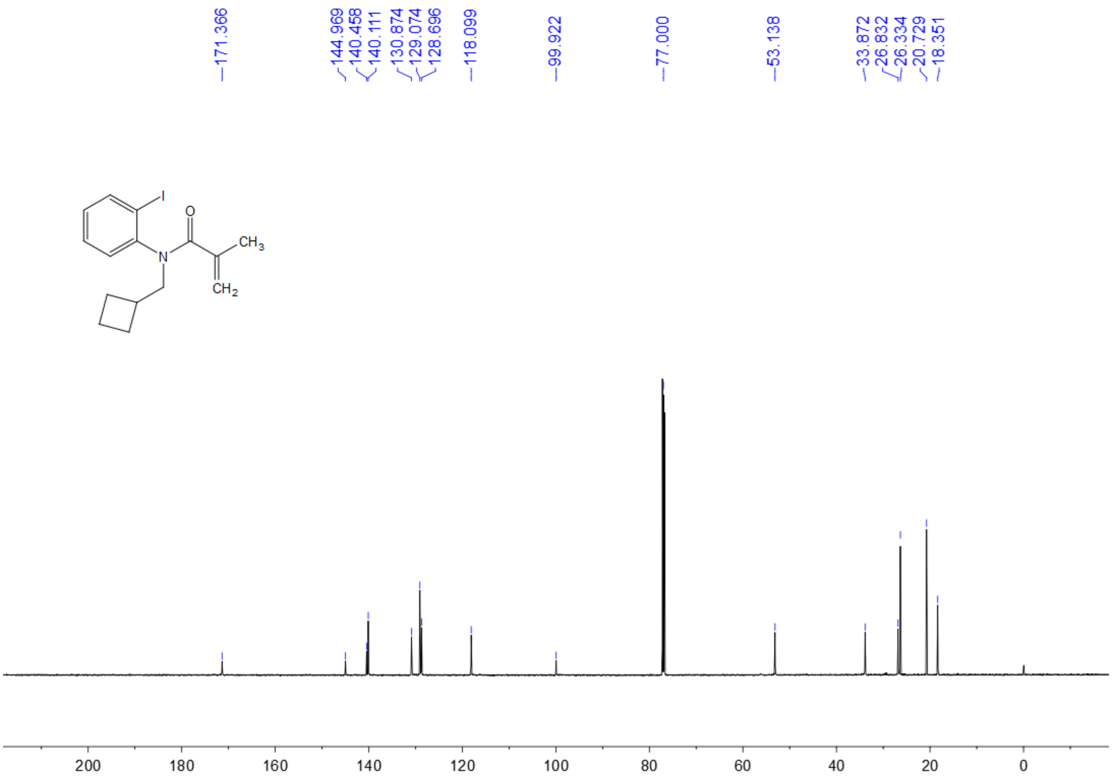
^{13}C NMR spectra of **1x**



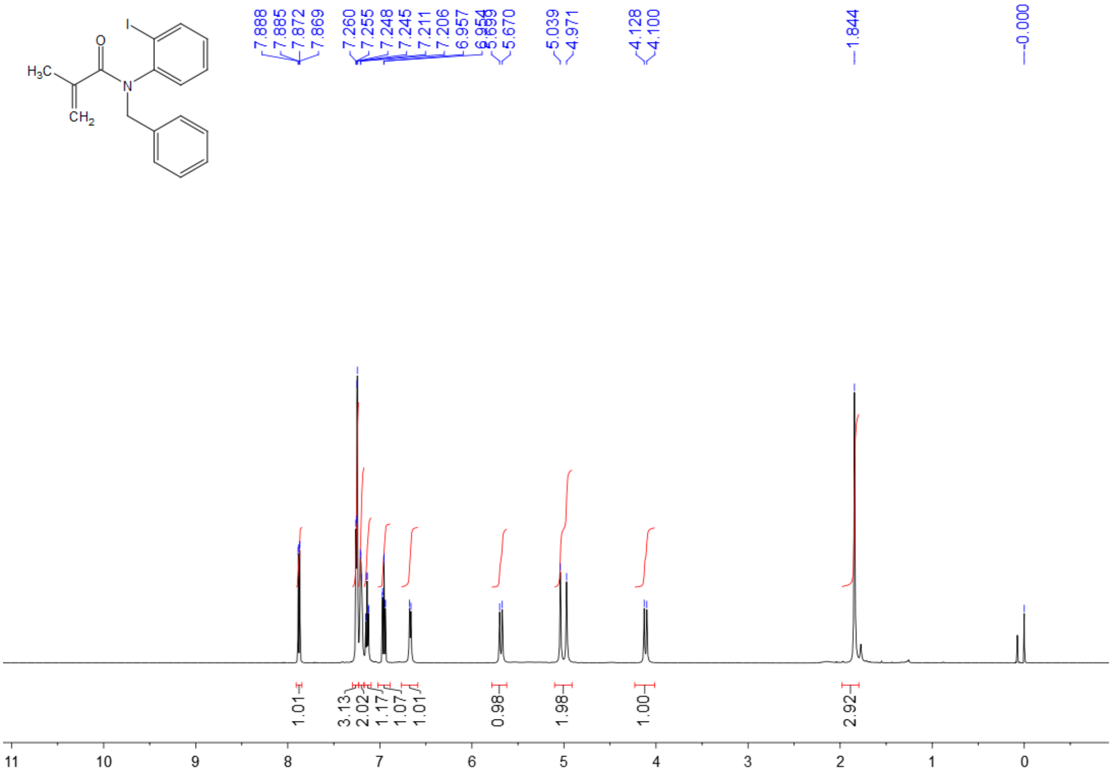
^{1}H NMR spectra of **1y**



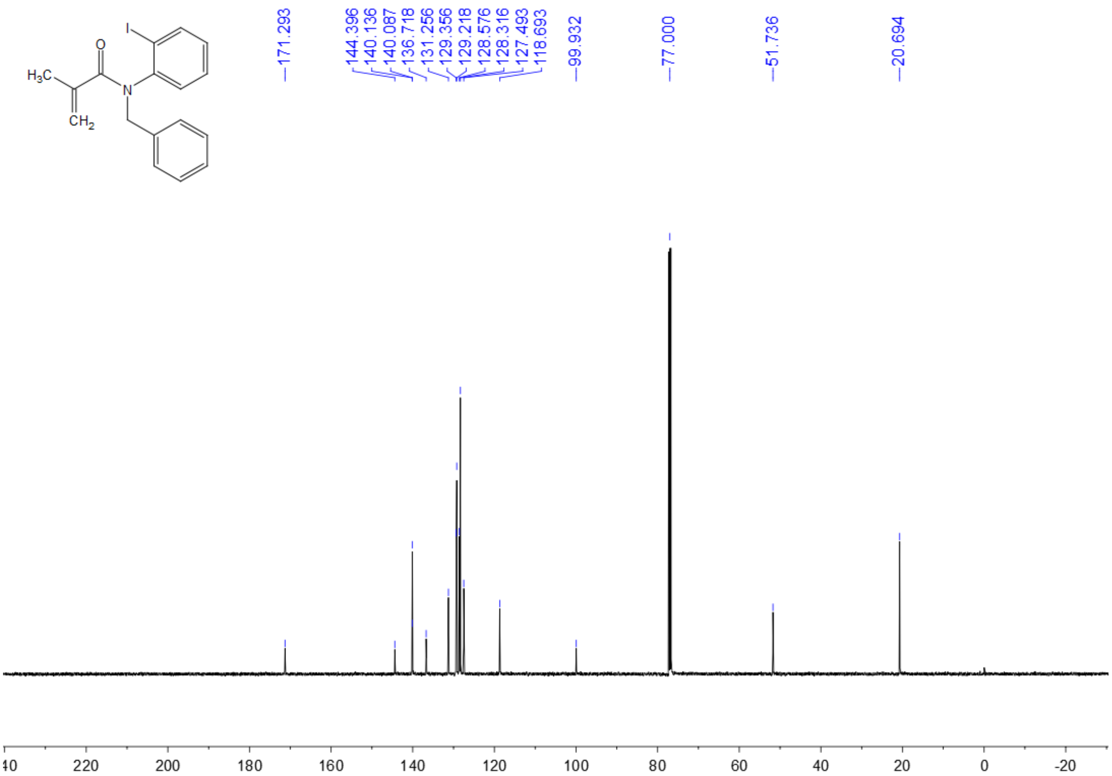
^{13}C NMR spectra of **1y**

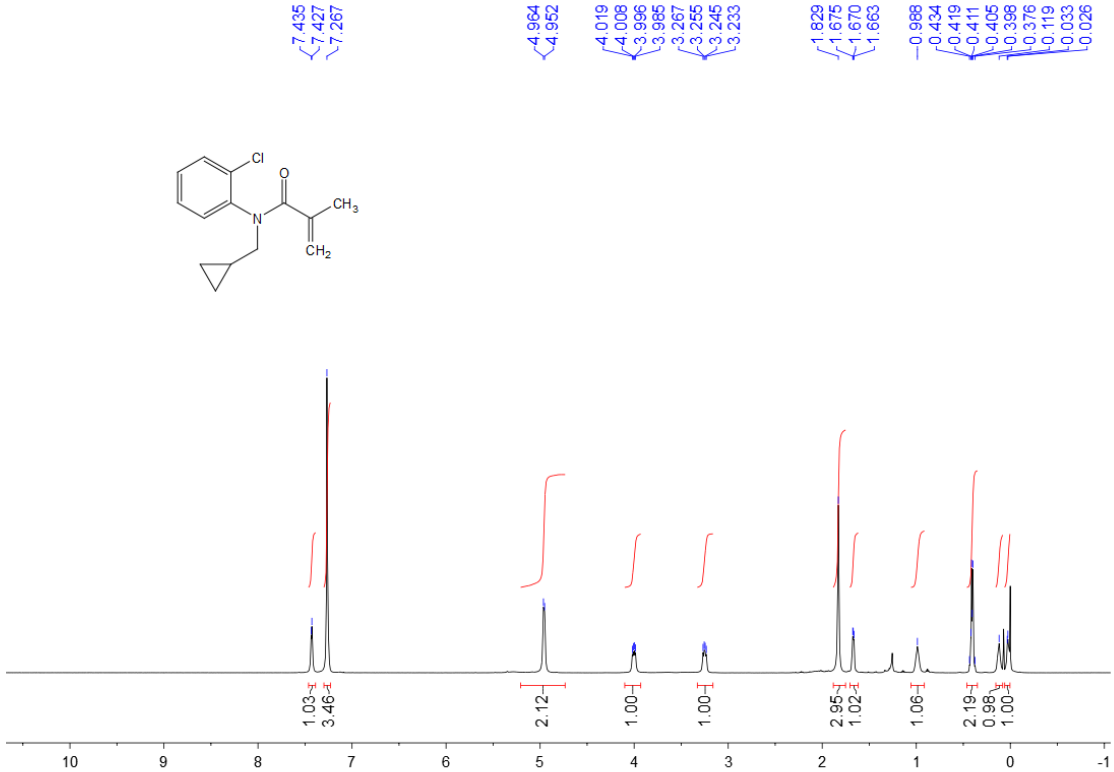


^{1}H NMR spectra of **1z**



^{13}C NMR spectra of **1z**

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3.233
1.829
1.675
1.670
1.663
0.988
0.434
0.419
0.411
0.405
0.398
0.376
0.119
0.033
0.026
Cl
O
N
CH3
CH2
1.03
3.46
2.12
1.00
1.00
2.95
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0.98
1.00
10
9
8
7
6
5
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3
2
1
0
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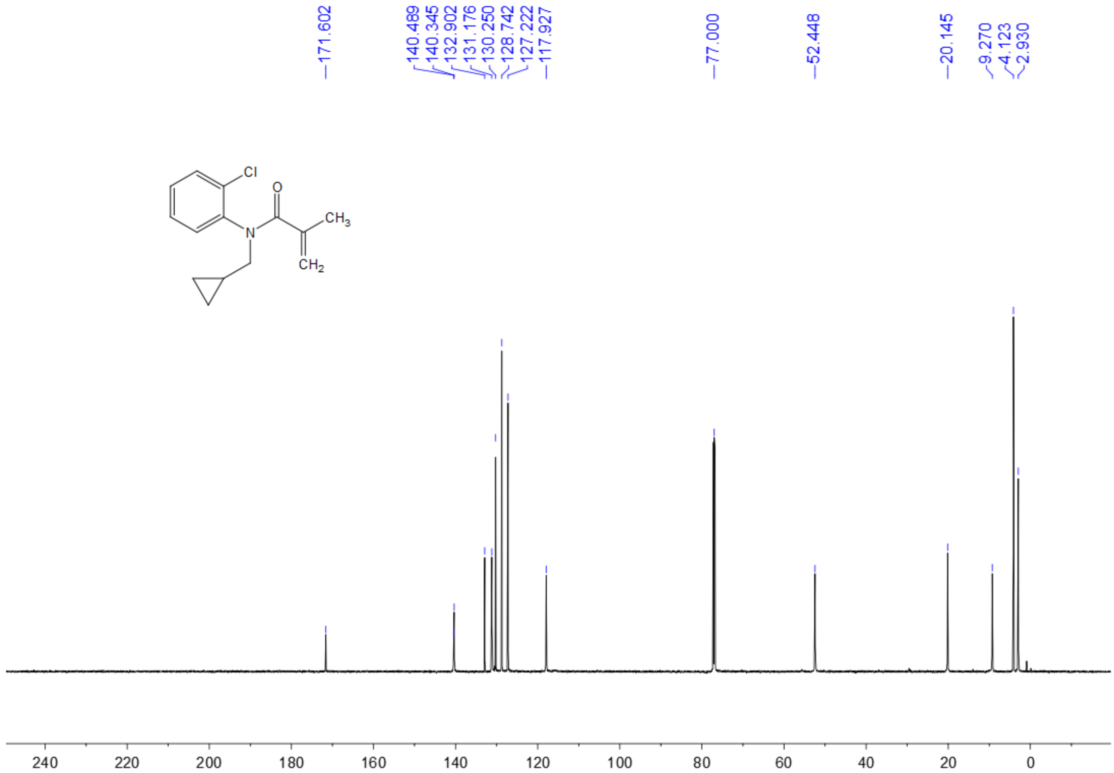
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4.123
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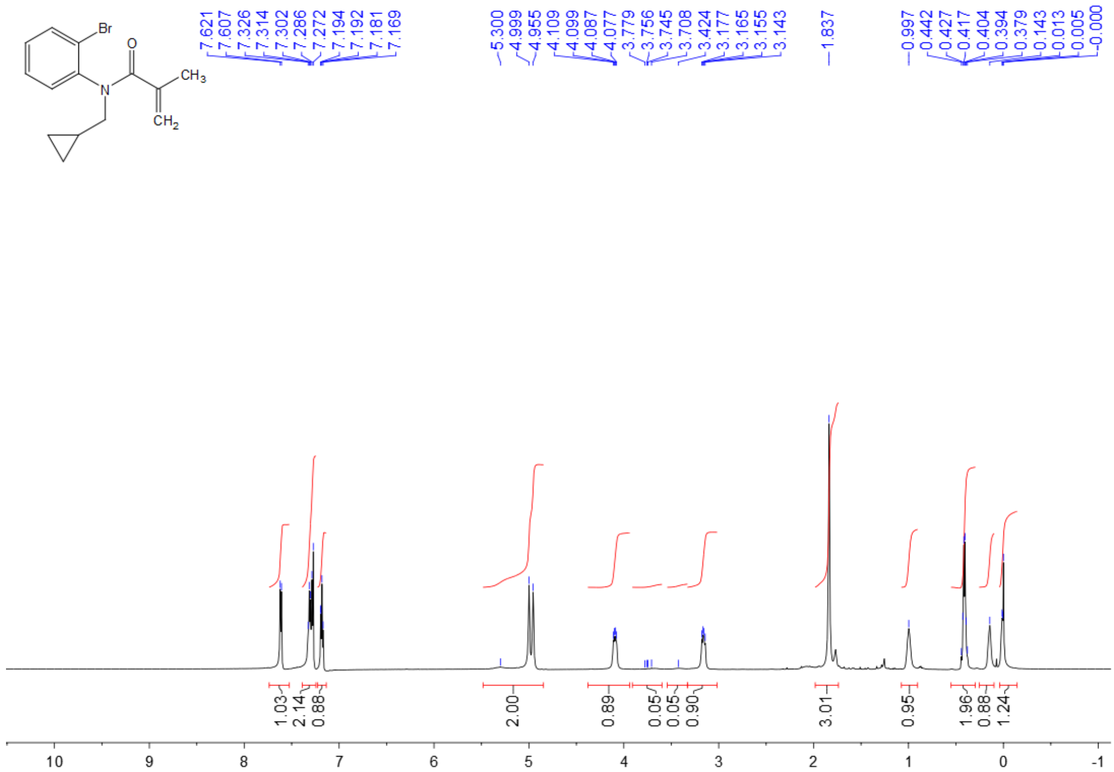
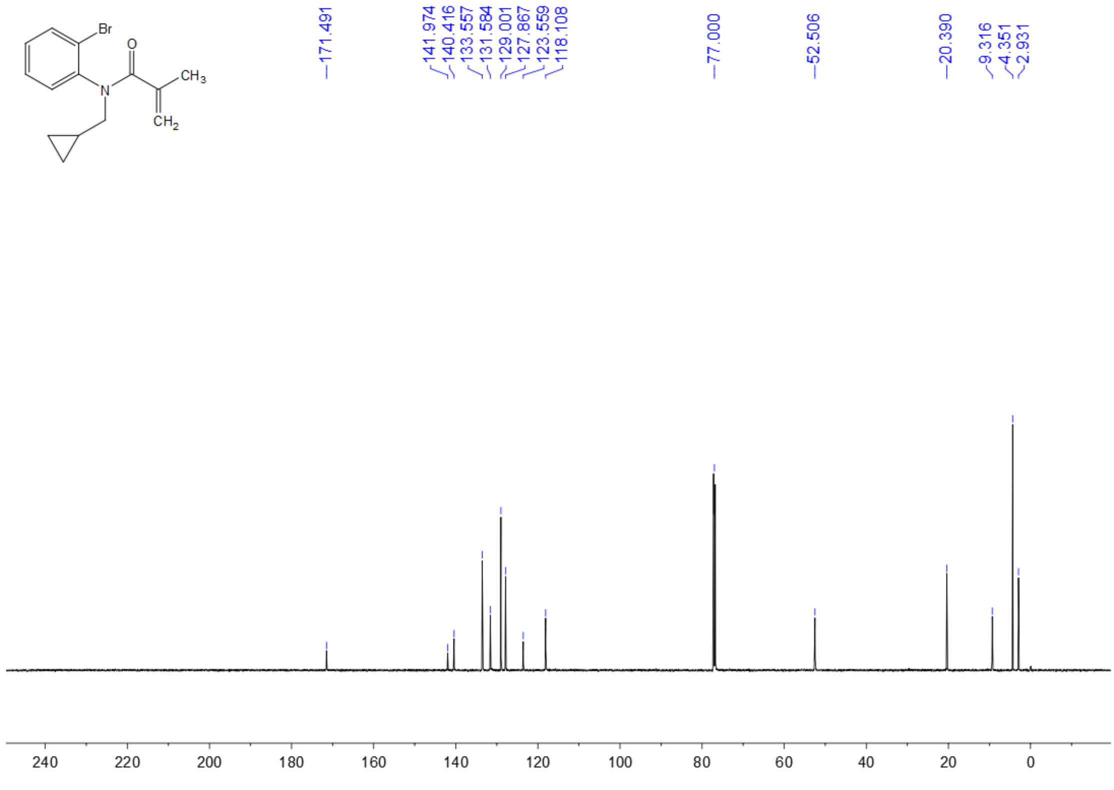
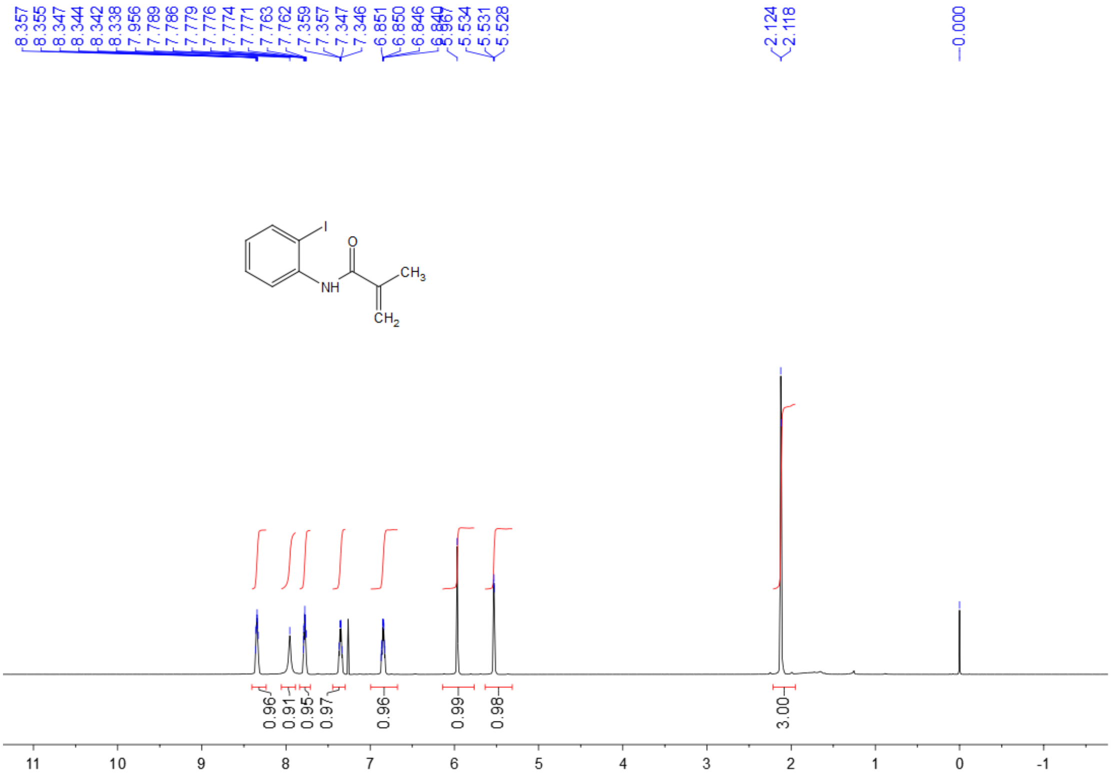
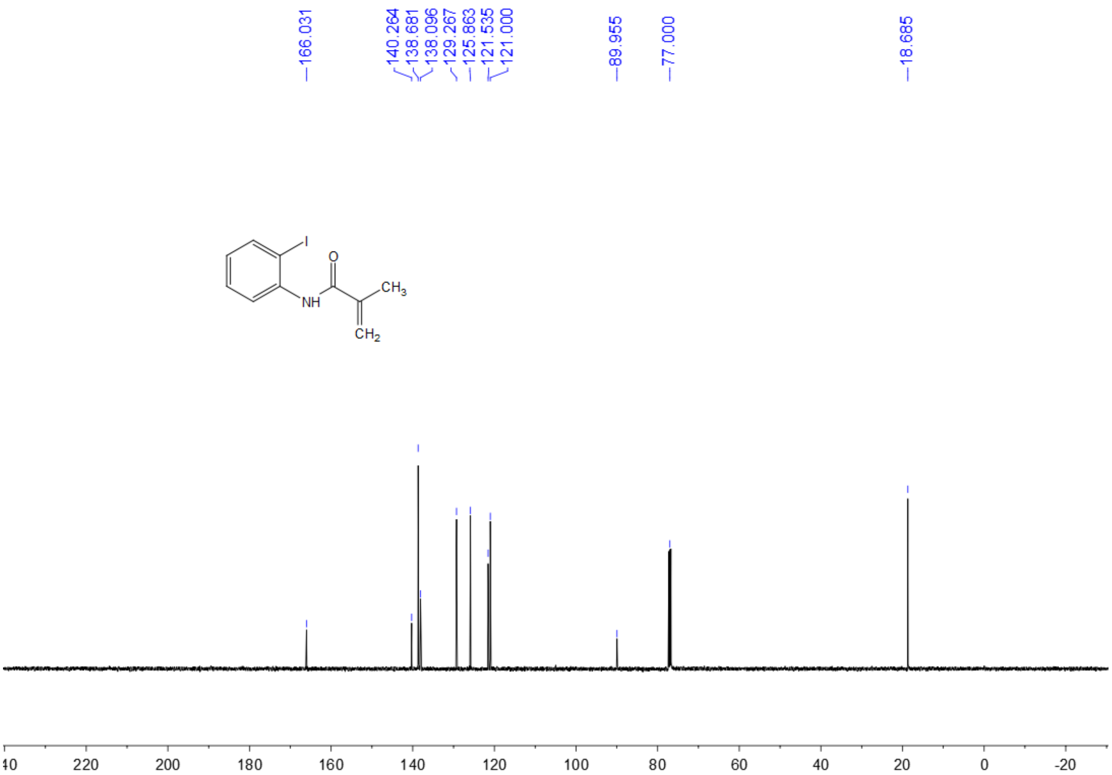




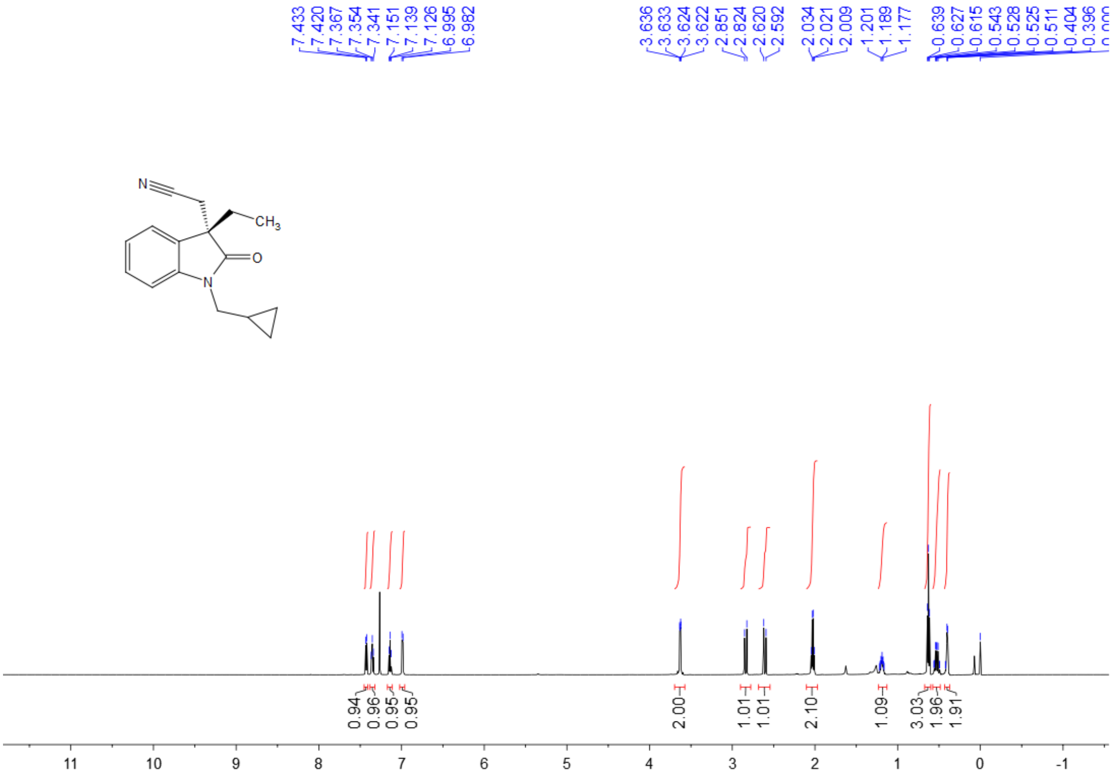
[1]H NMR spectra of **1aa**



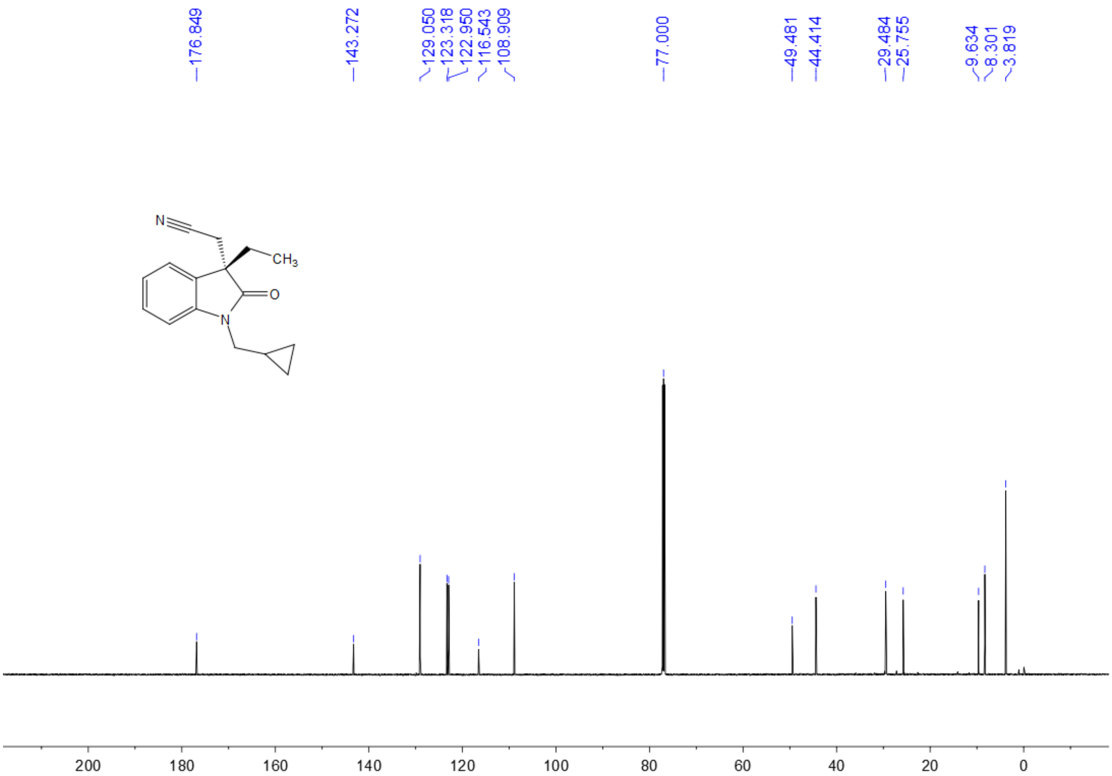
[13]C NMR spectra of **1aa**



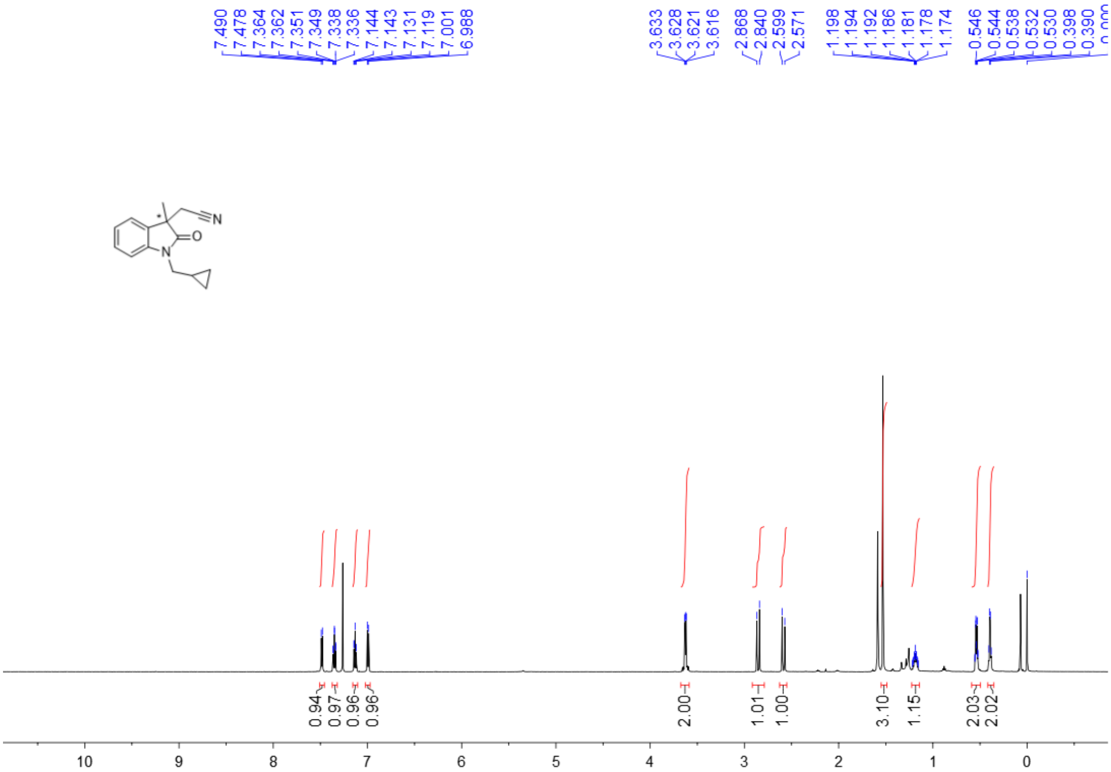
1H NMR spectra of **2a**



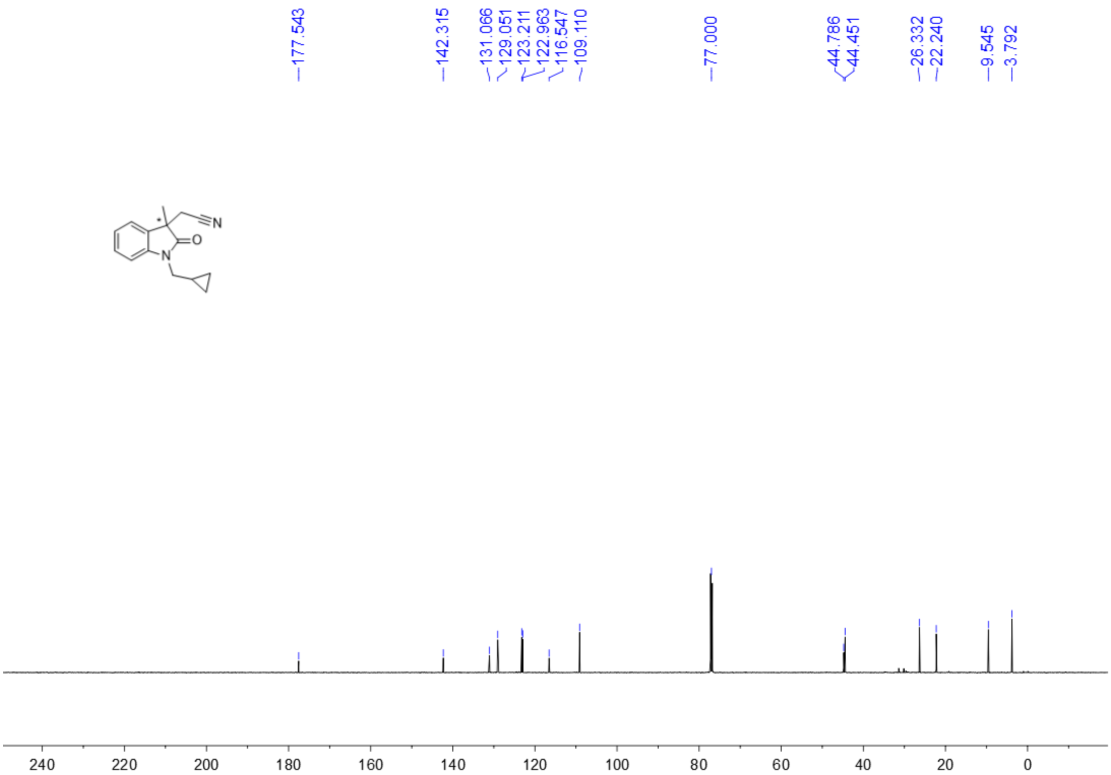
^{13}C NMR spectra of ***2a***



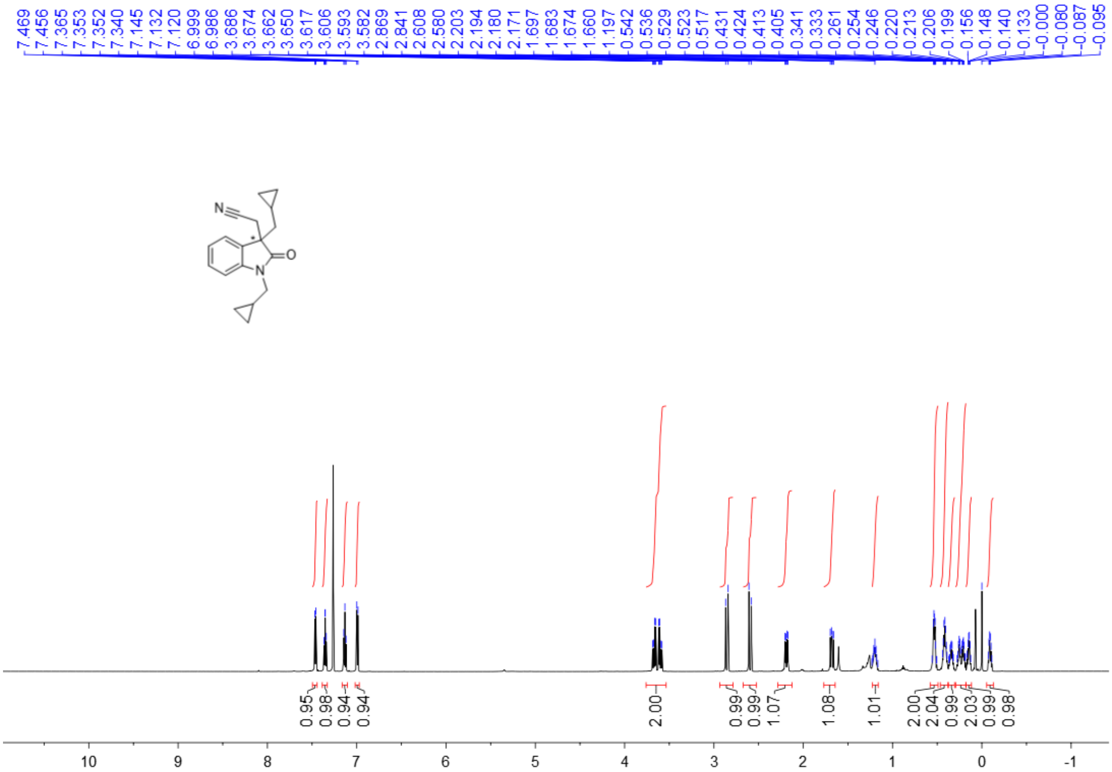
1H NMR spectra of ***2b***



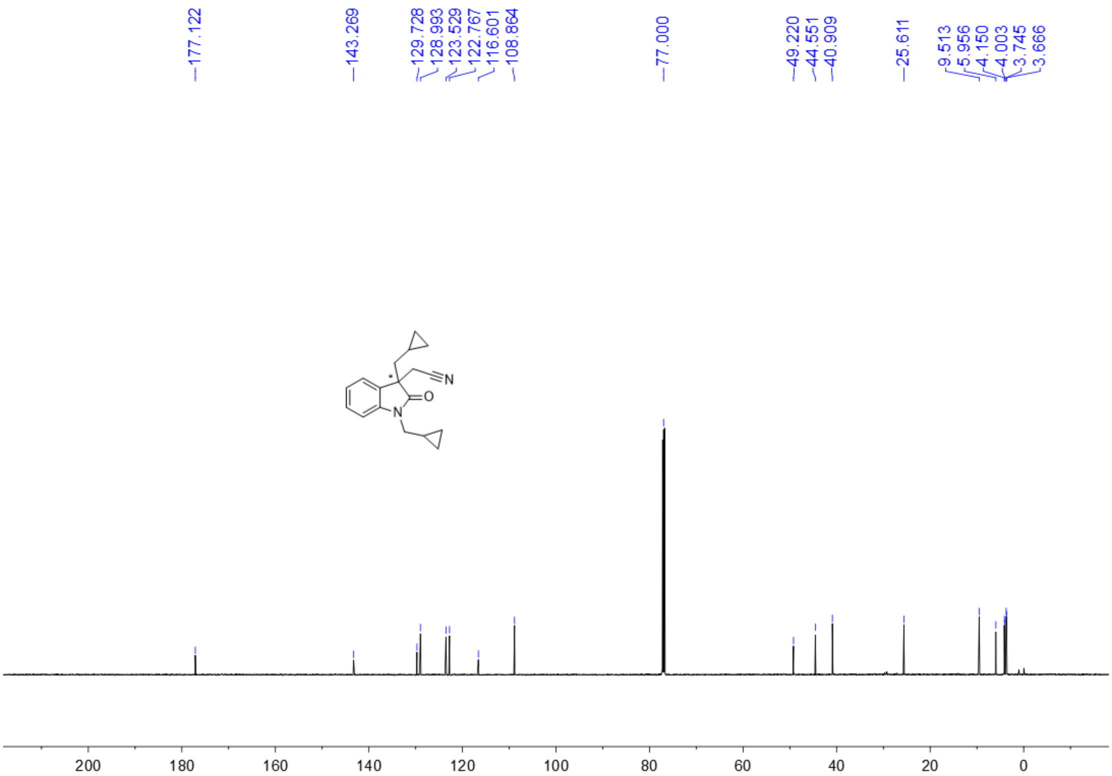
^{13}C NMR spectra of ***2b***



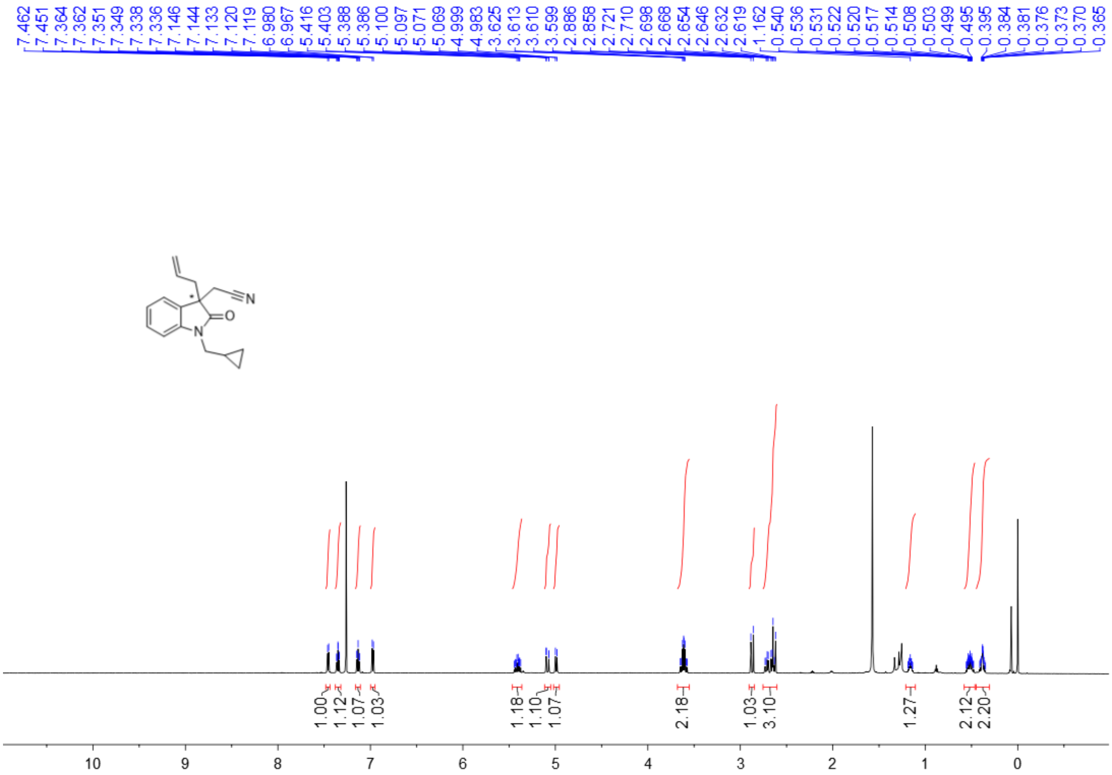
1H NMR spectra of ***2c***



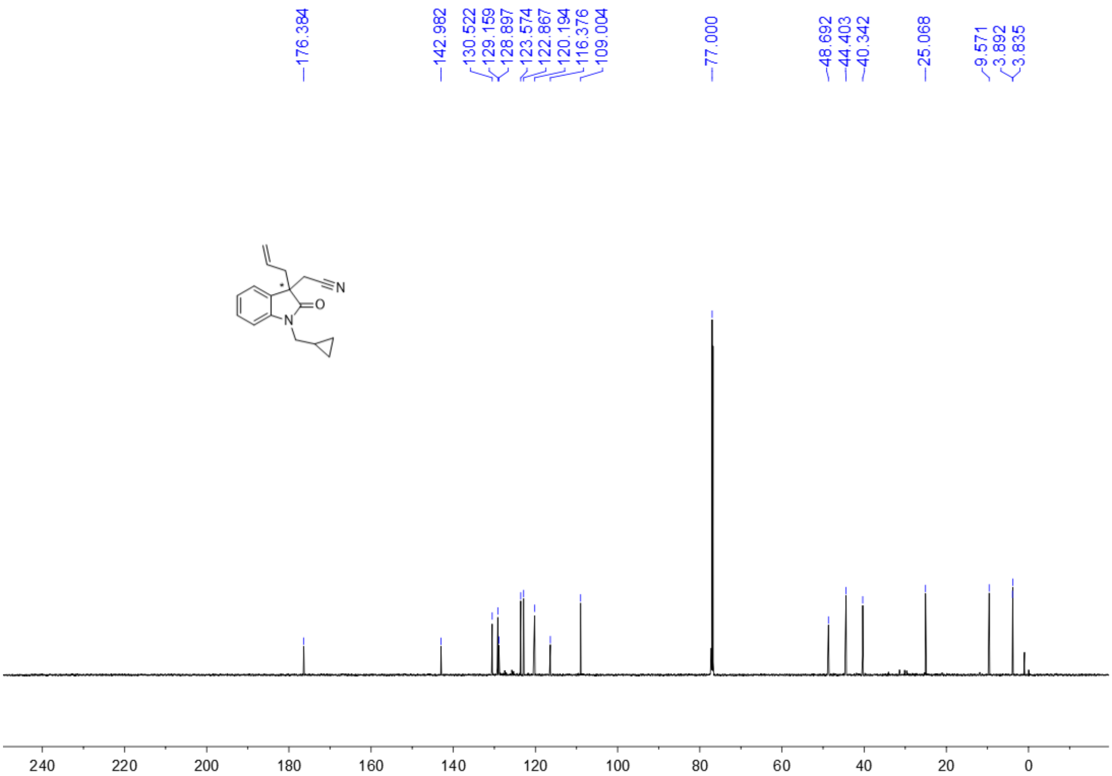
^{13}C NMR spectra of ***2c***



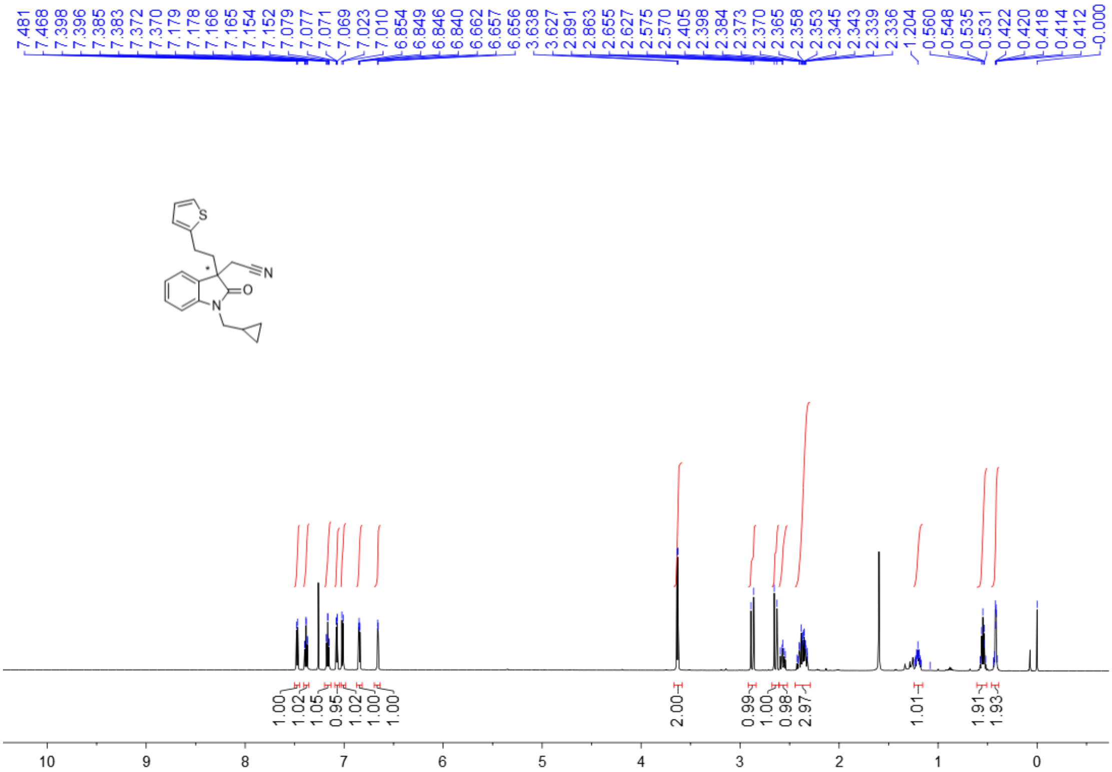
1H NMR spectra of ***2d***



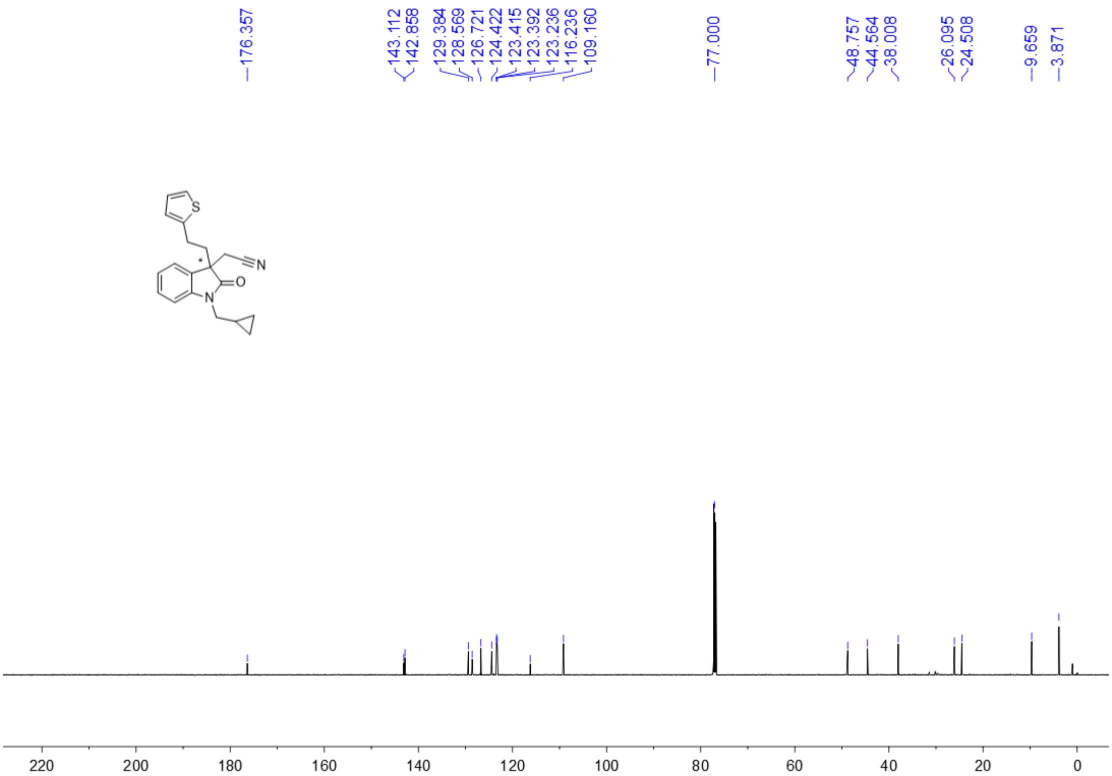
[13]C NMR spectra of ***2d***



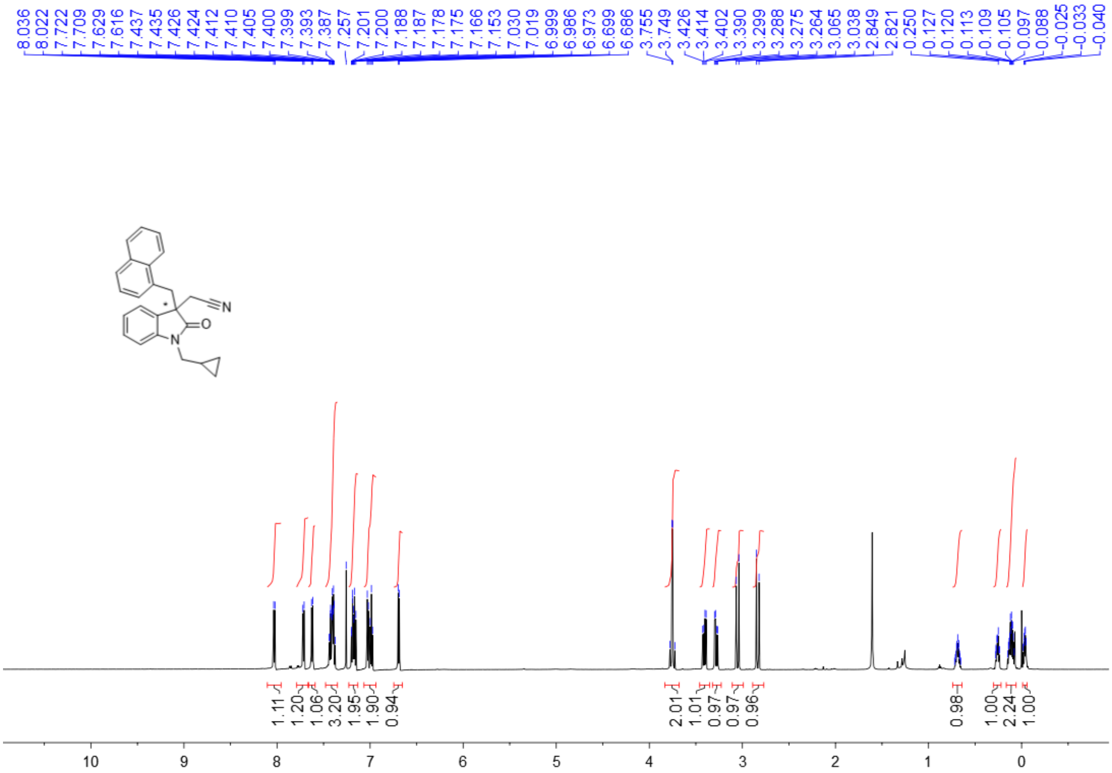
1H NMR spectra of ***2e***



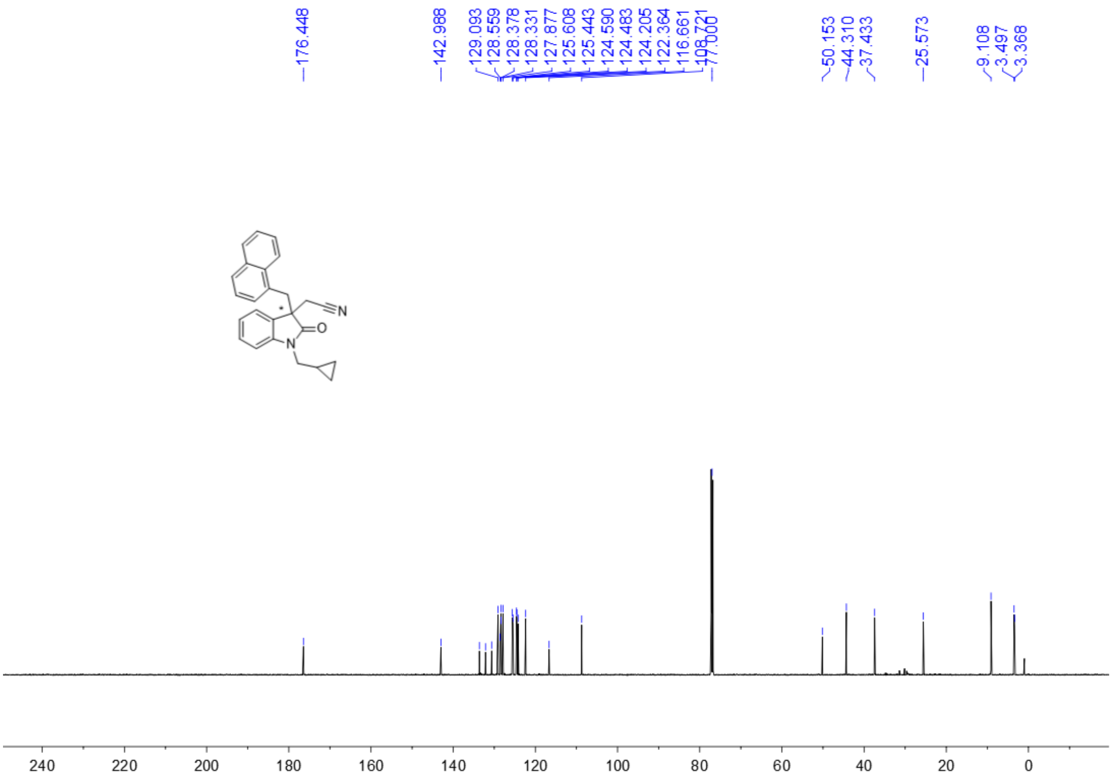
^{13}C NMR spectra of ***2e***



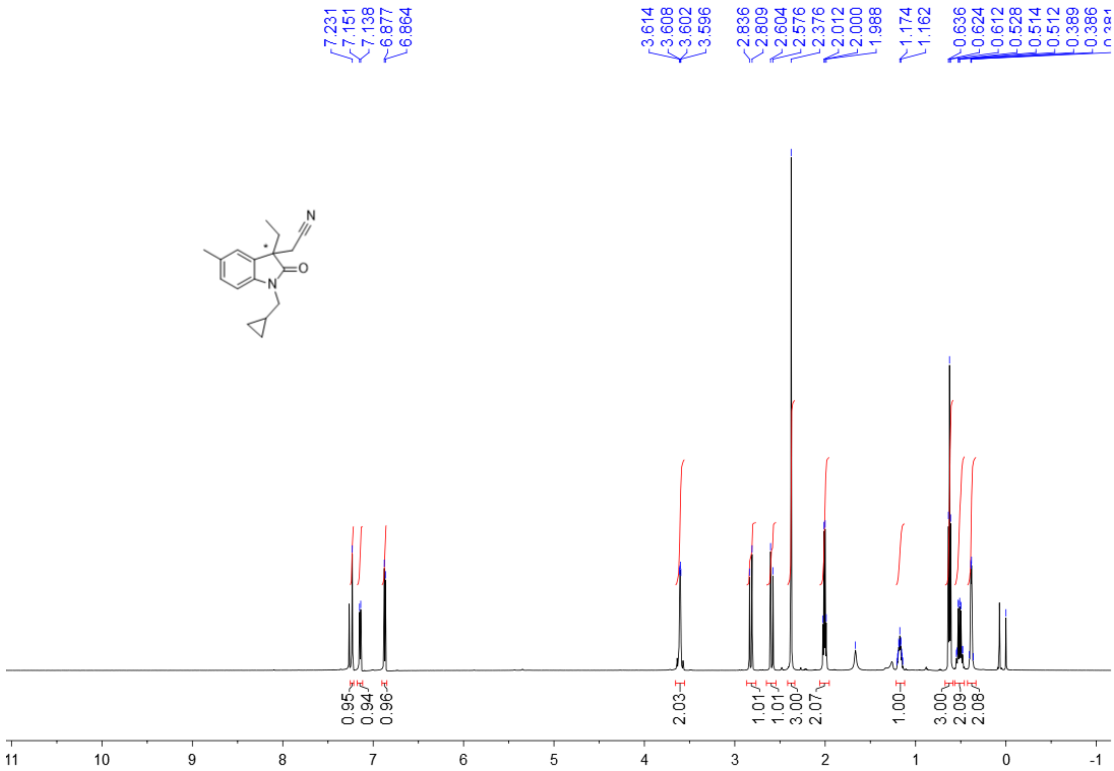
1H NMR spectra of ***2f***



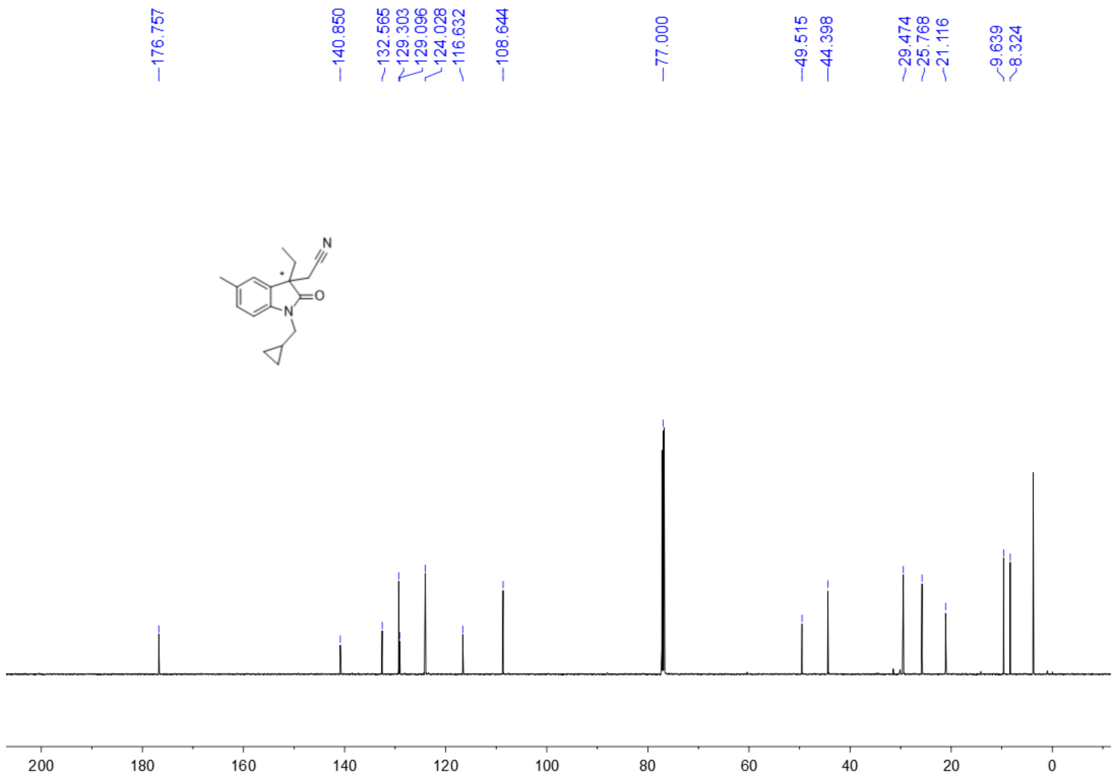
^{13}C NMR spectra of ***2f***



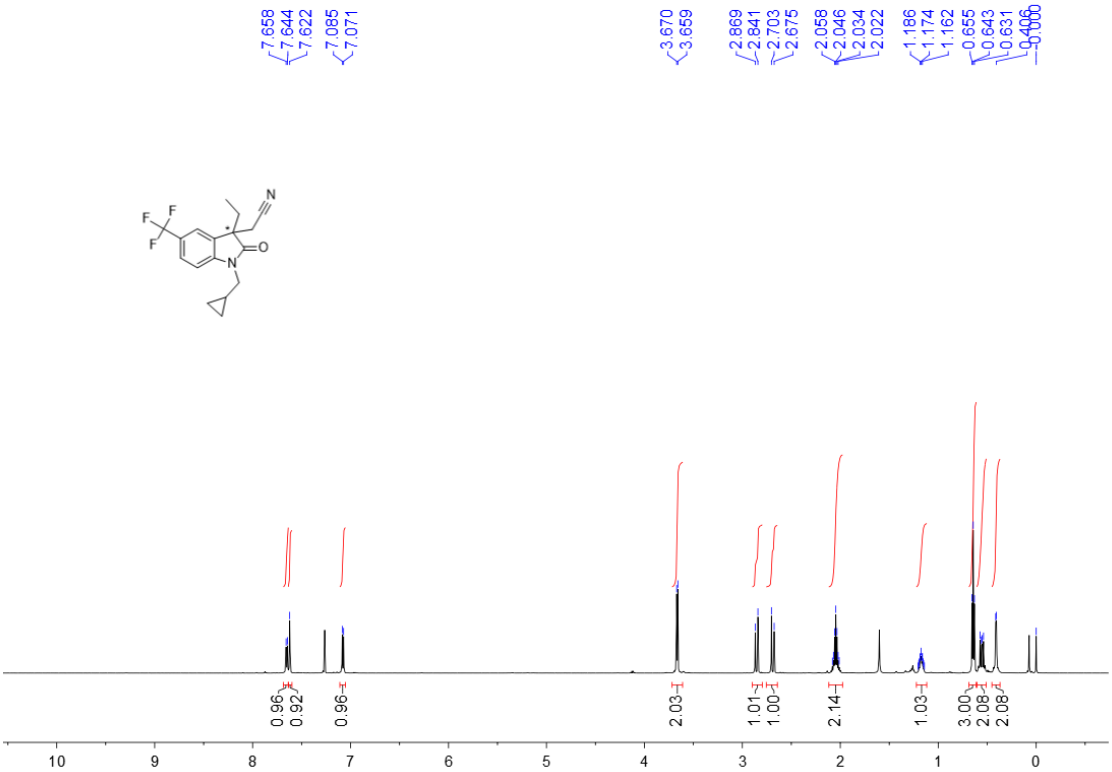
1H NMR spectra of ***2g***



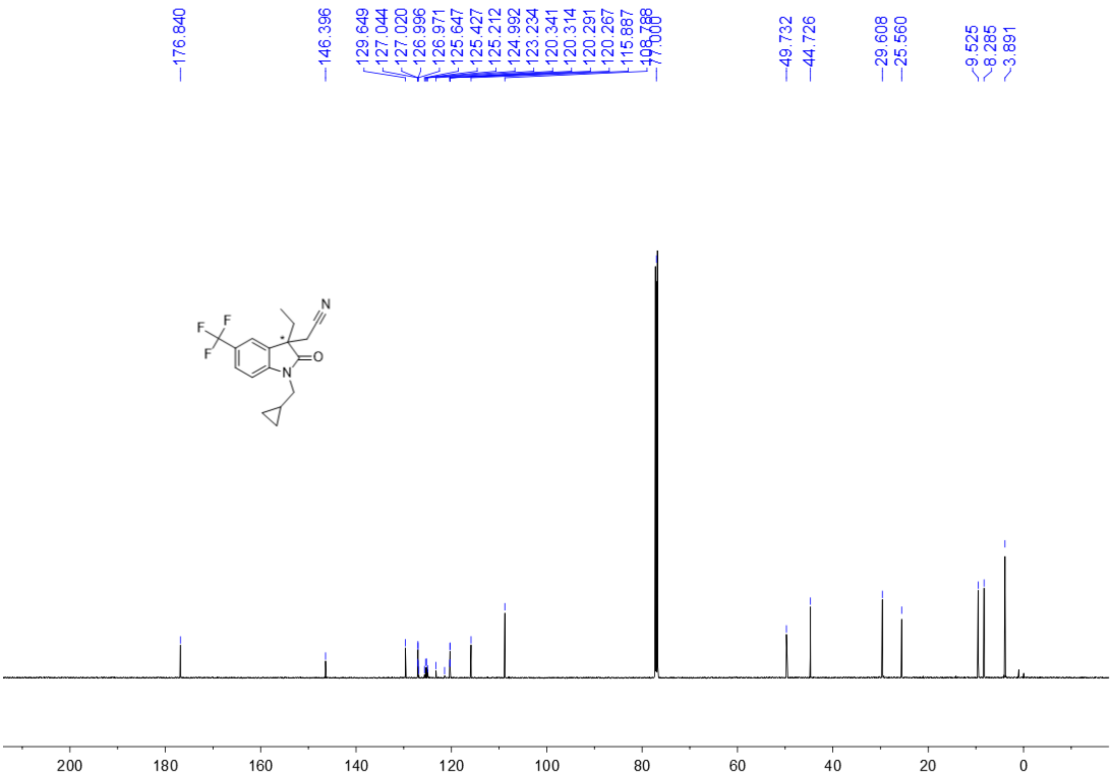
^{13}C NMR spectra of ***2g***



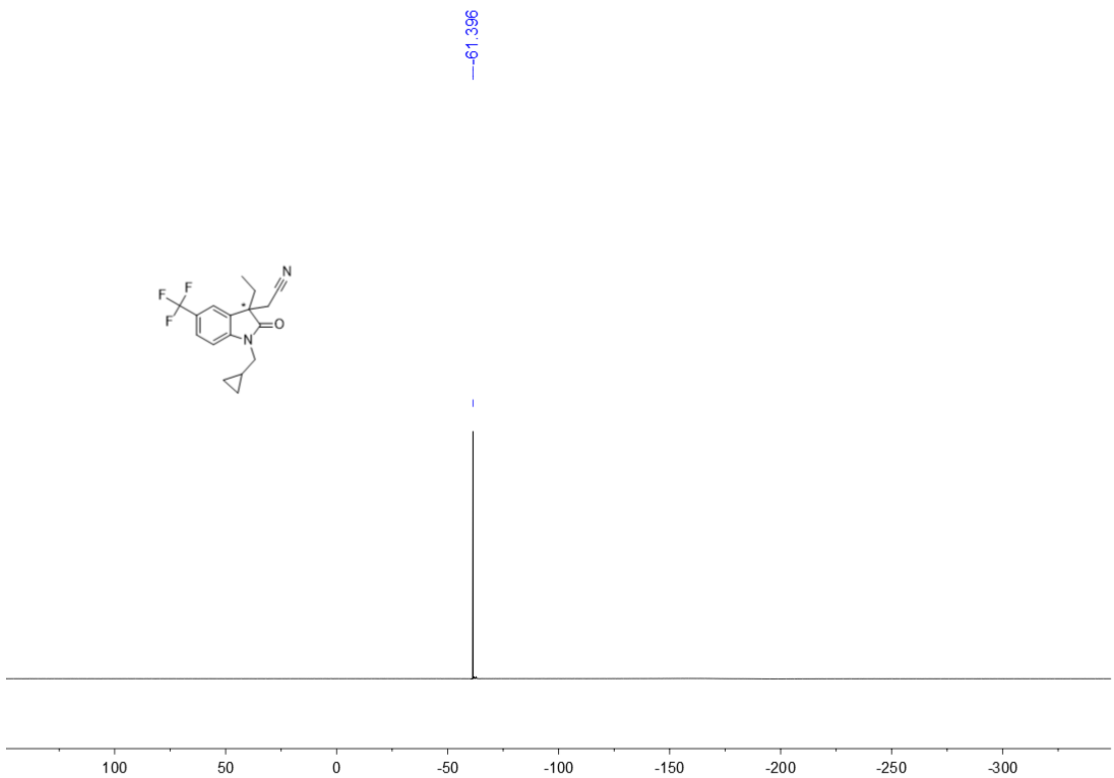
1H NMR spectra of ***2h***



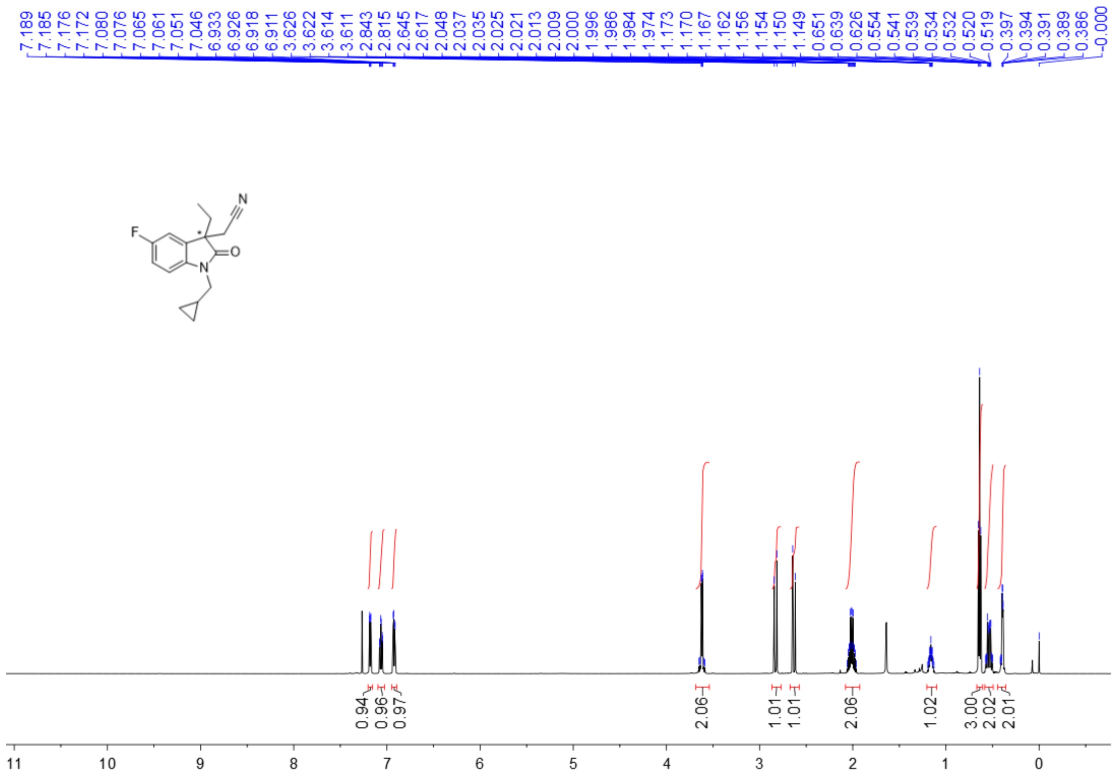
^{13}C NMR spectra of ***2h***



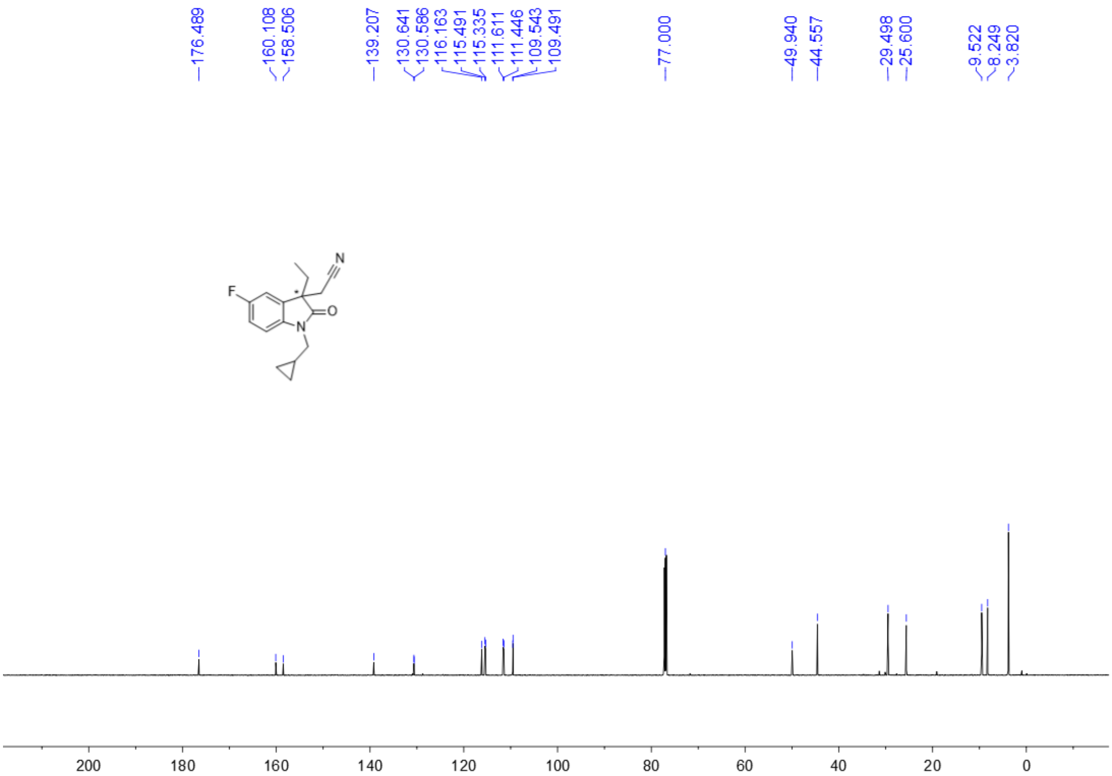
^{19}F NMR spectra of Compound 2h



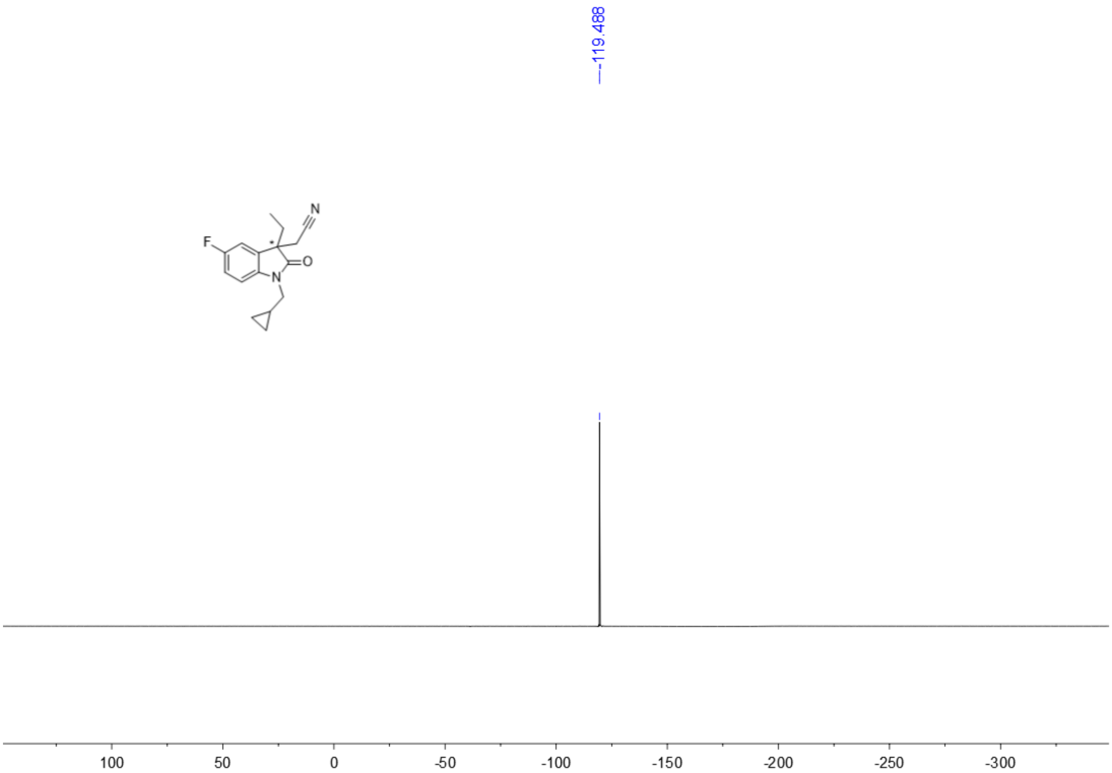
1H NMR spectra of ***2i***



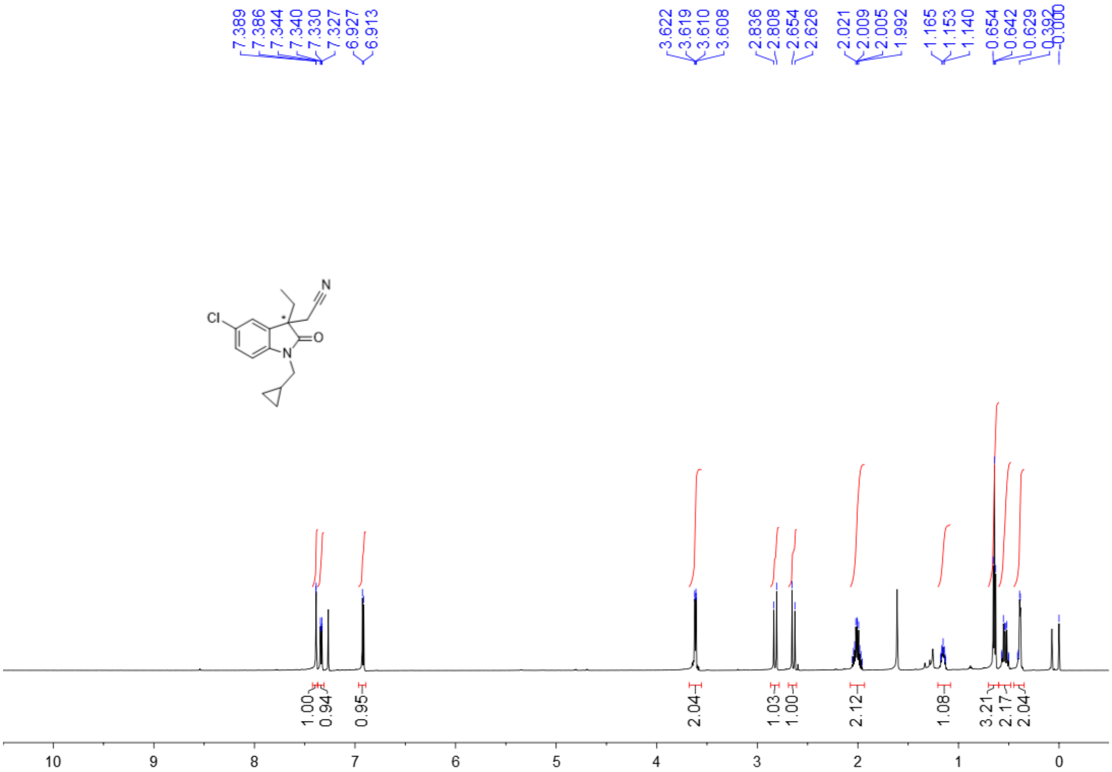
^{13}C NMR spectra of ***2i***



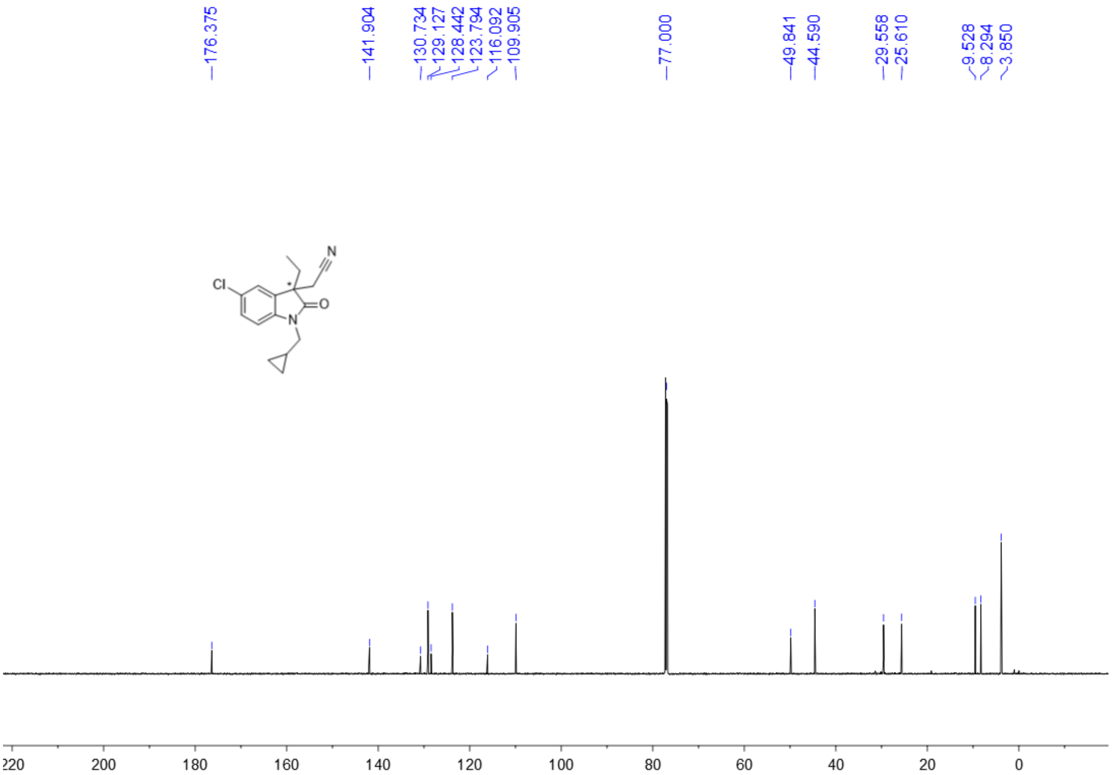
^{19}F NMR spectra of Compound 2i



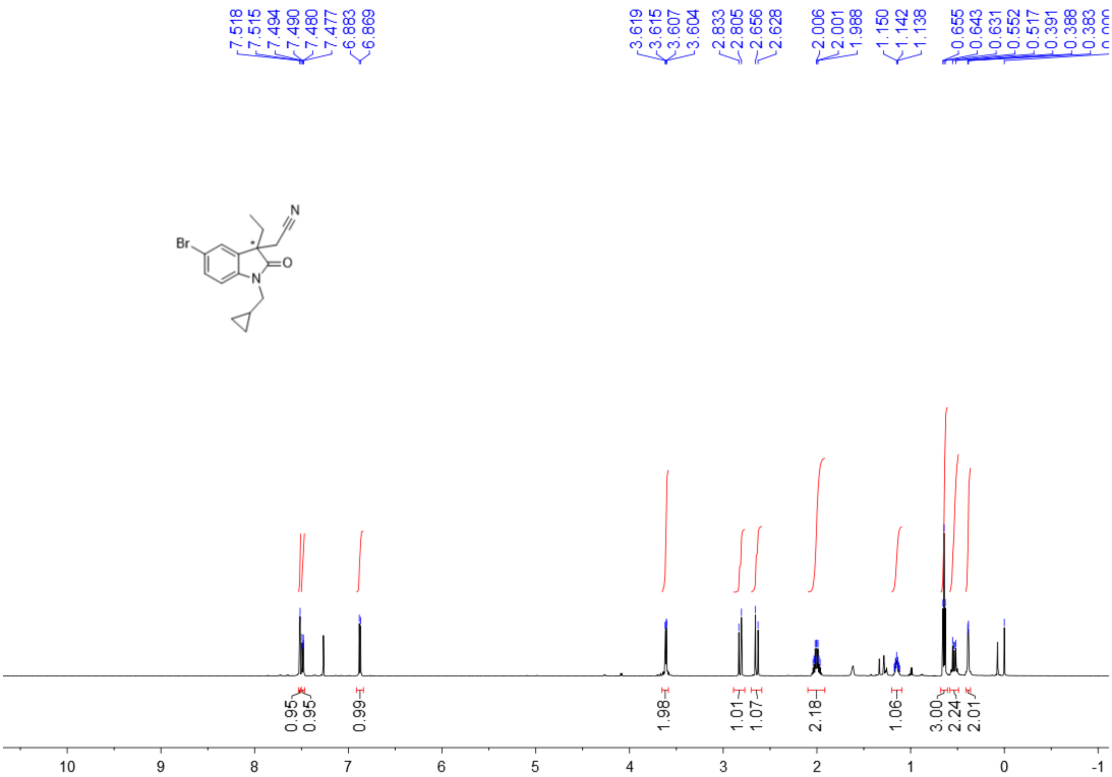
1H NMR spectra of ***2j***



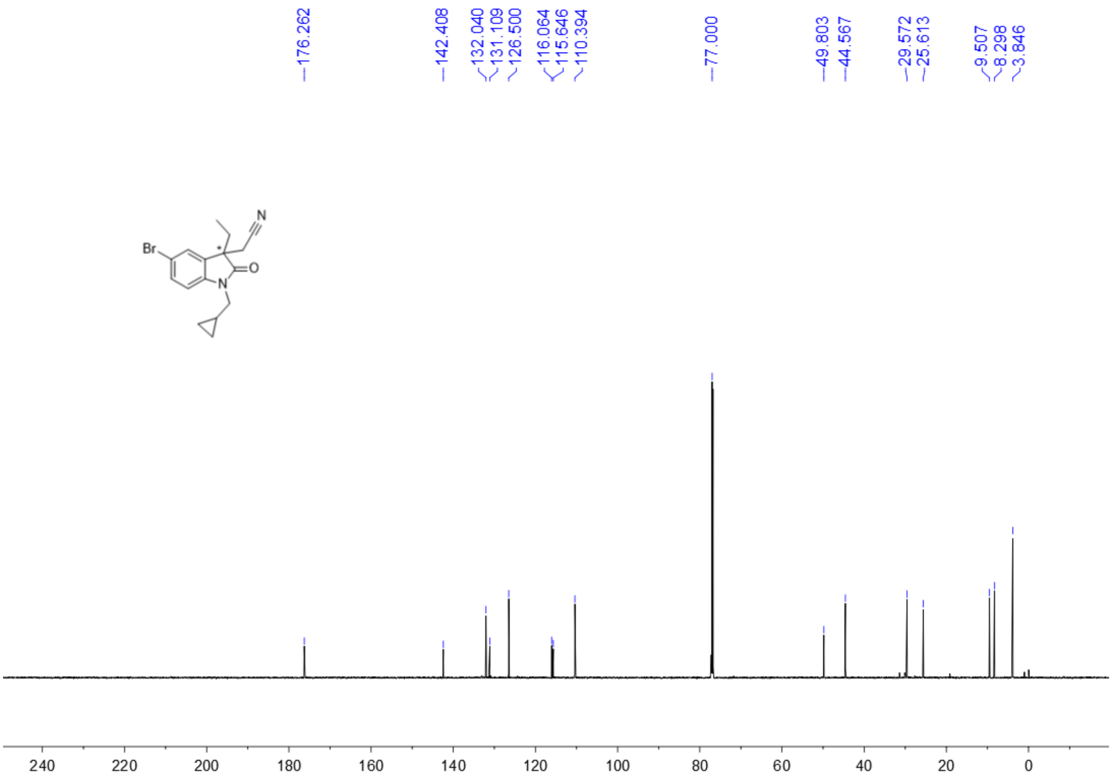
^{13}C NMR spectra of ***2j***



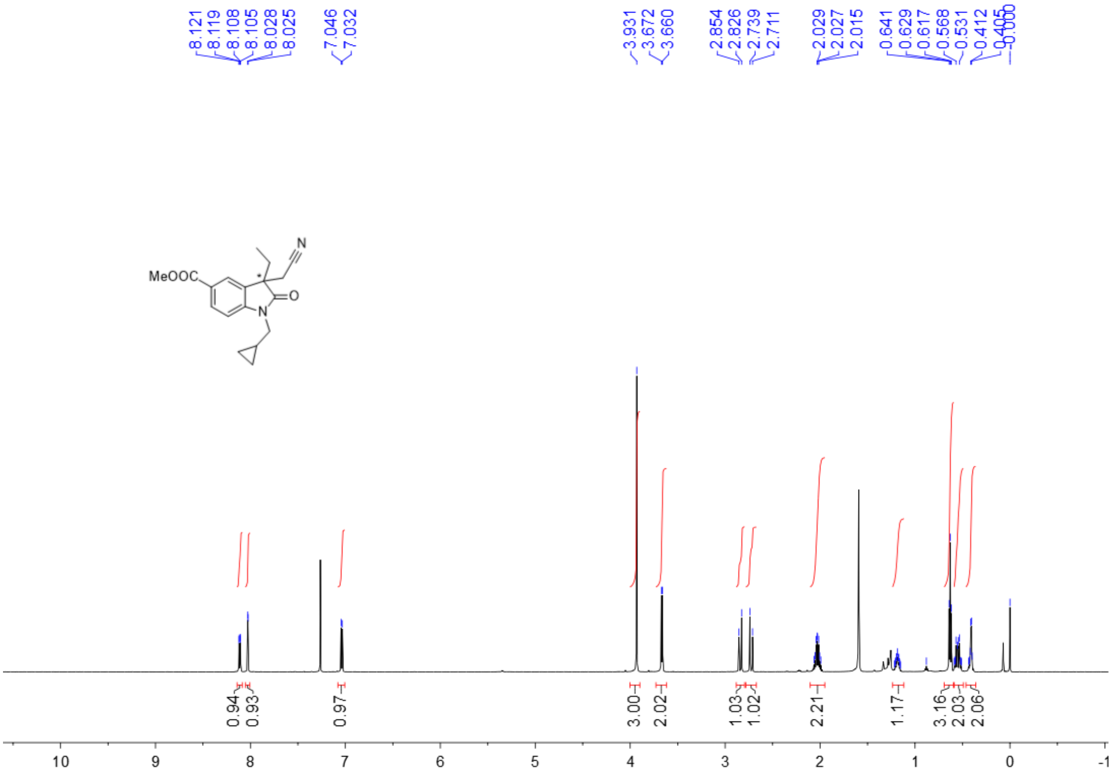
1H NMR spectra of ***2k***



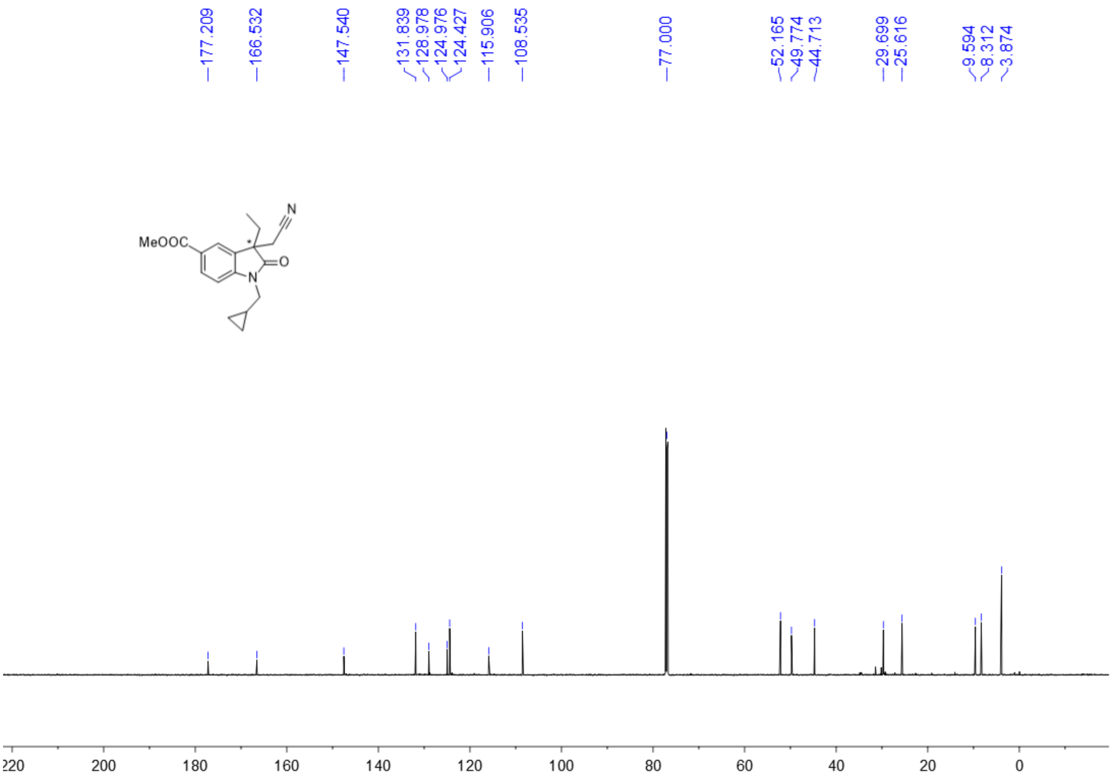
^{13}C NMR spectra of ***2k***



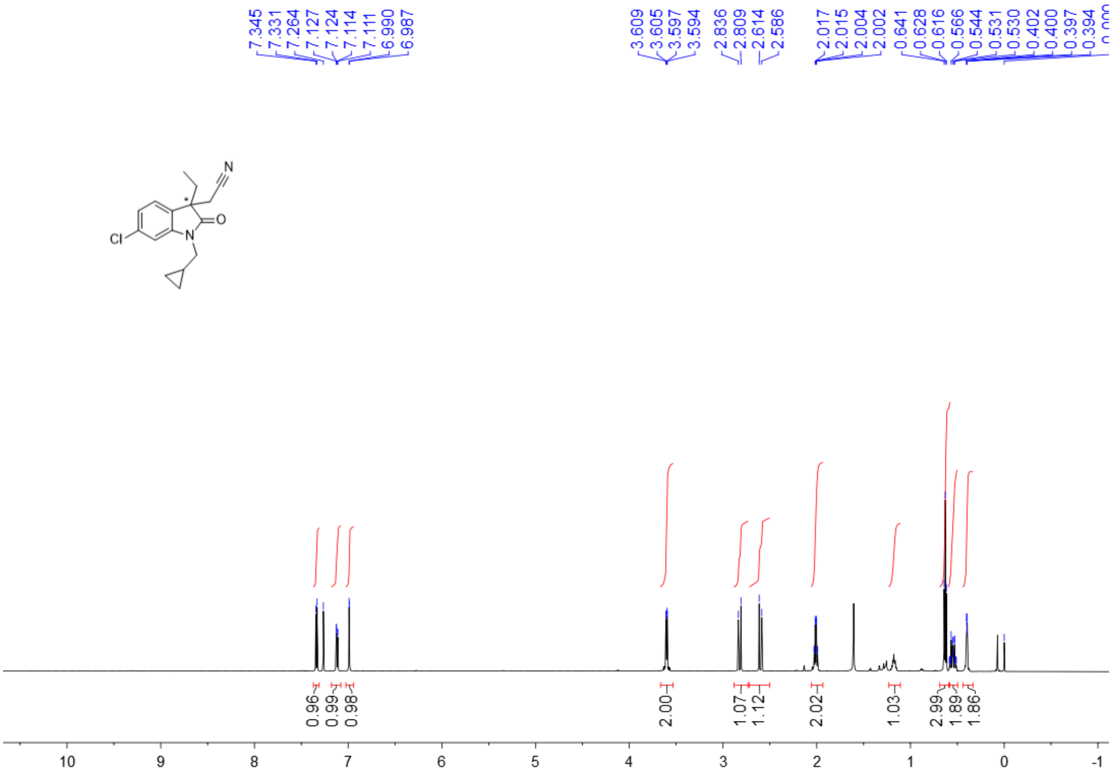
1H NMR spectra of ***2l***



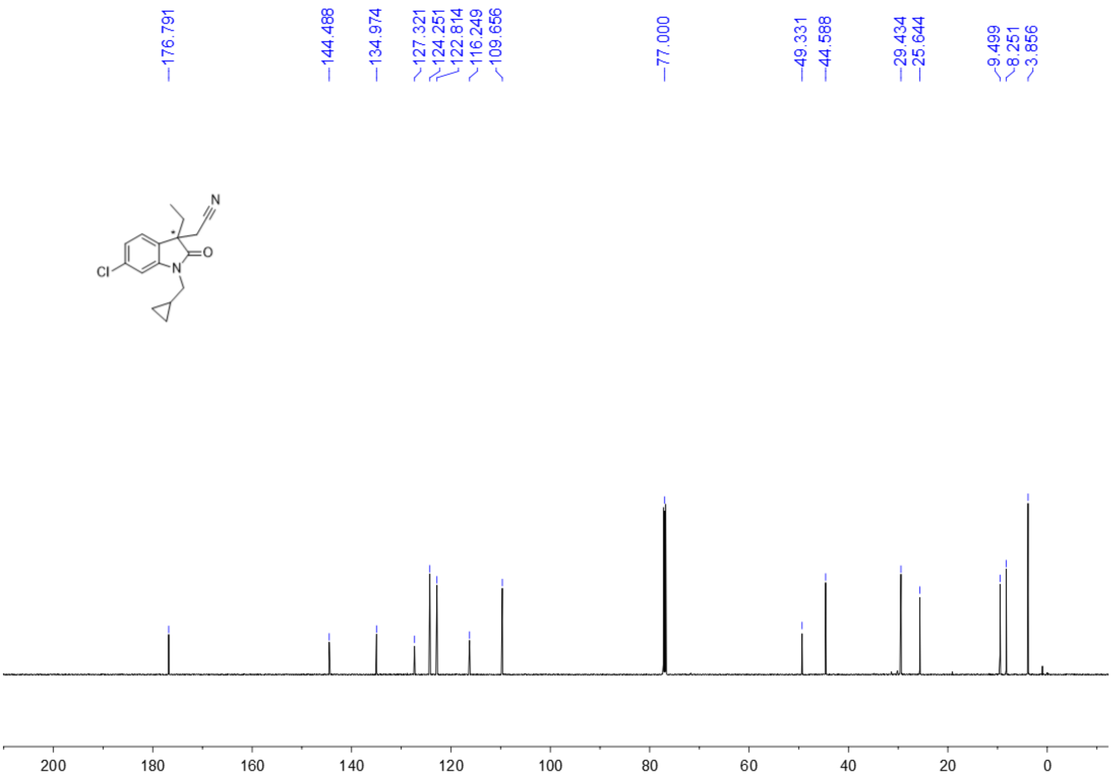
^{13}C NMR spectra of ***2l***



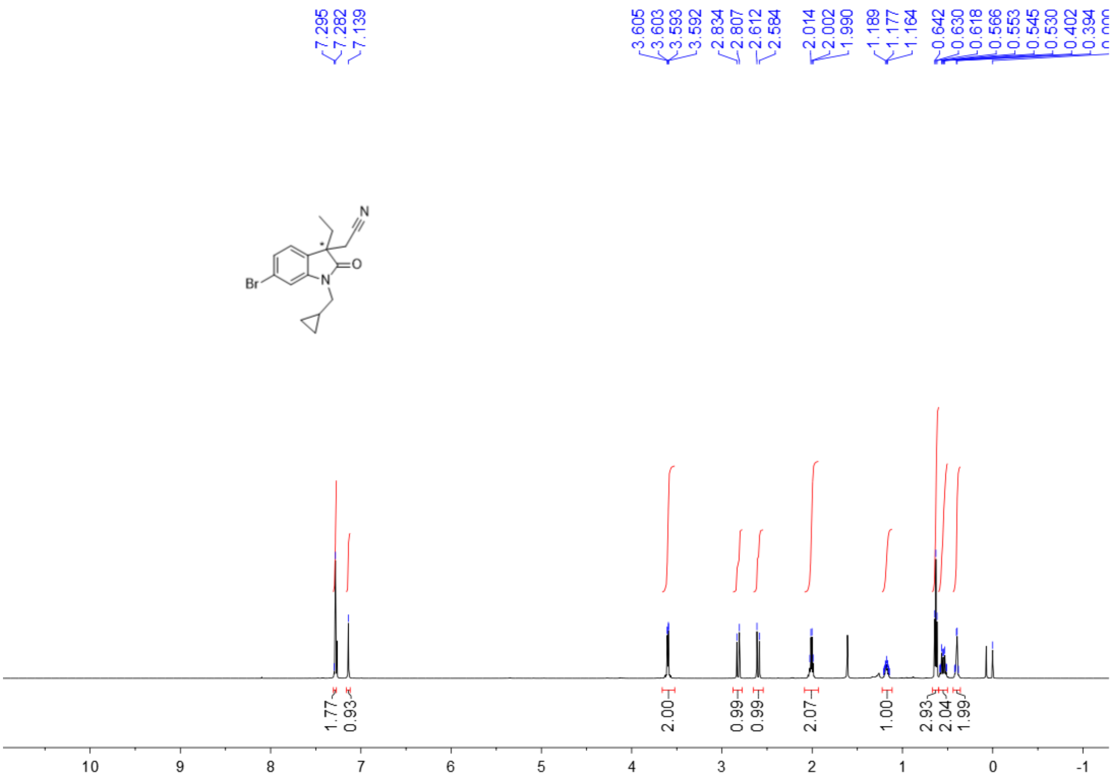
1H NMR spectra of ***2m***



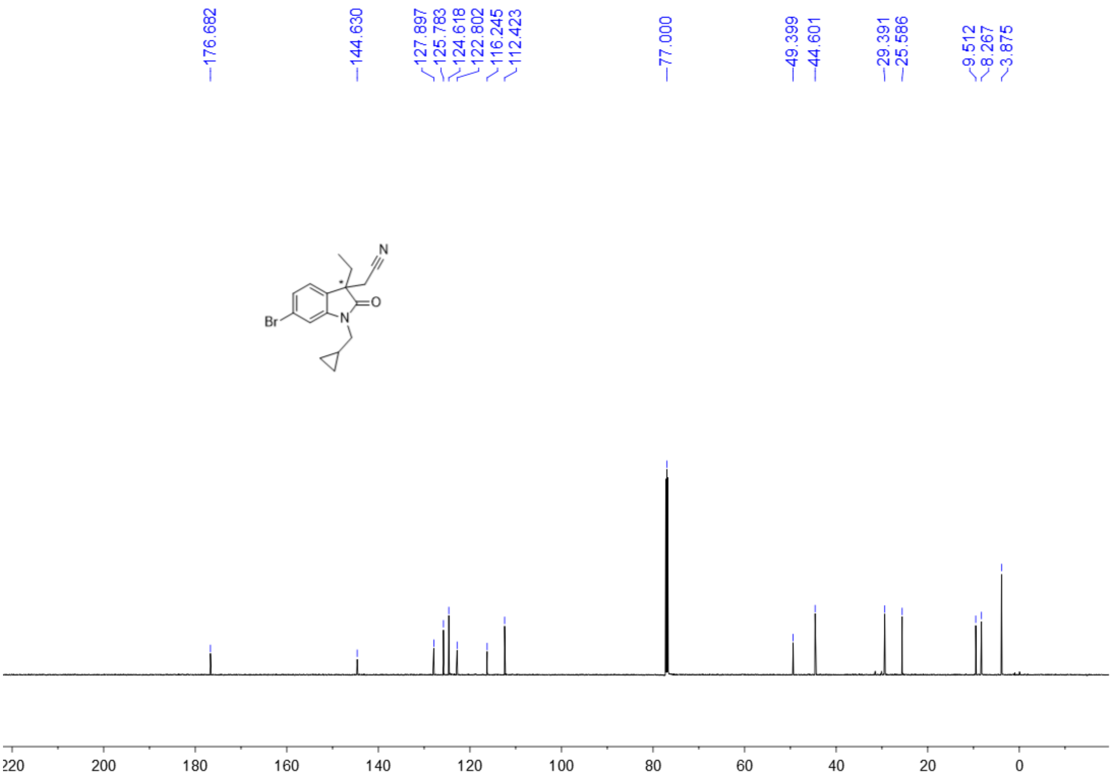
^{13}C NMR spectra of ***2m***



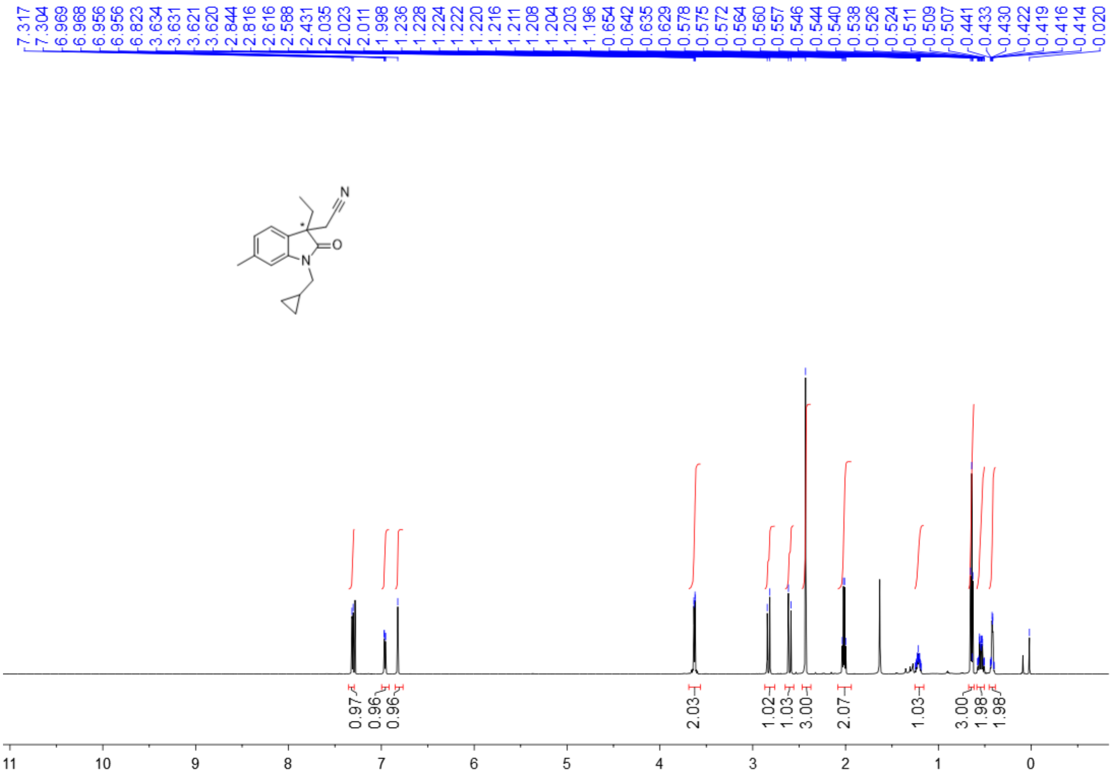
1H NMR spectra of ***2n***



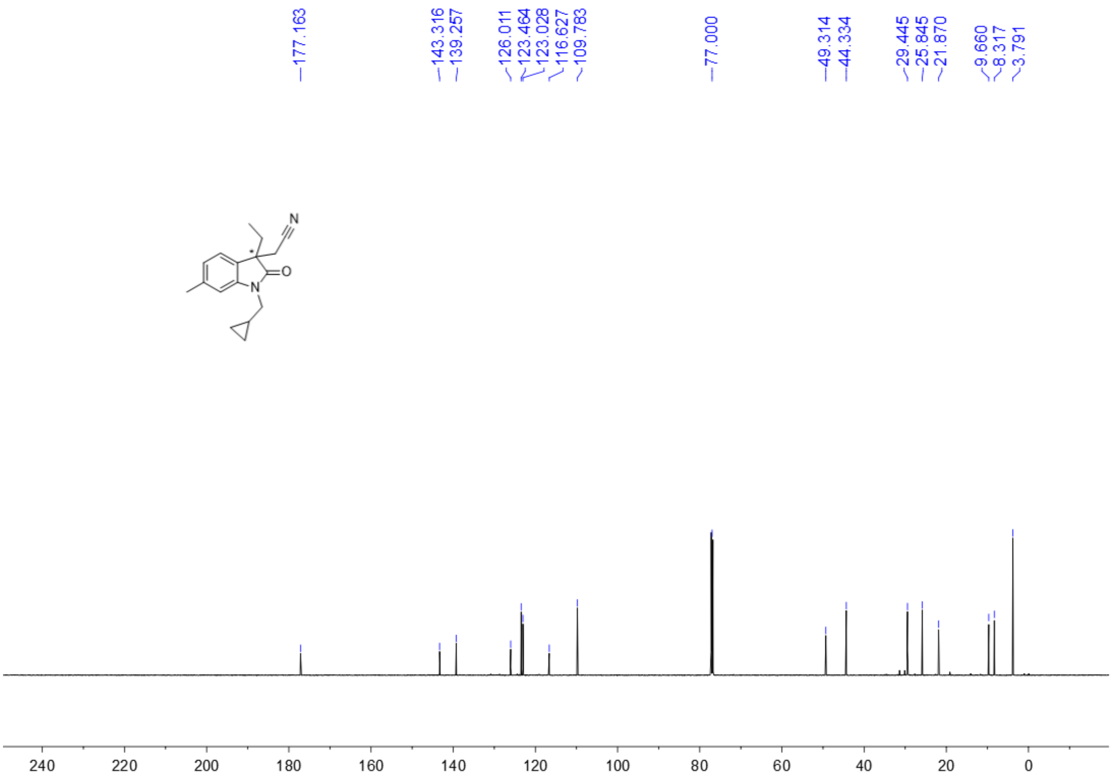
13C NMR spectra of ***2n***



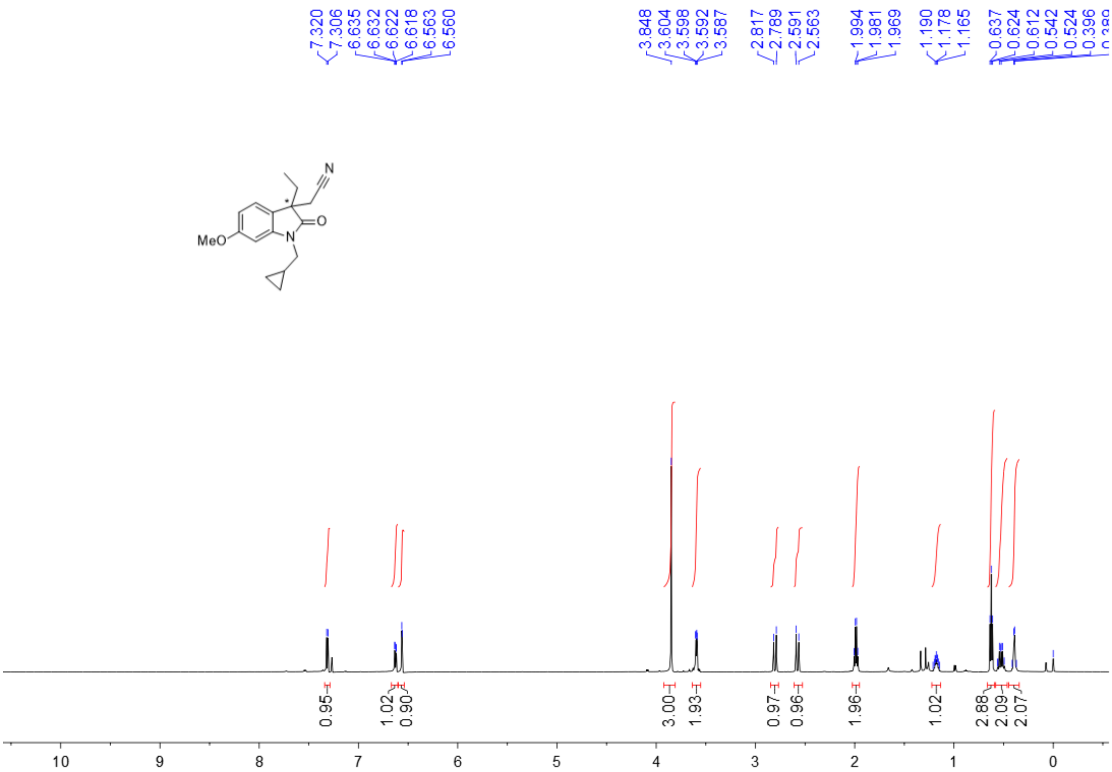
1H NMR spectra of ***2o***



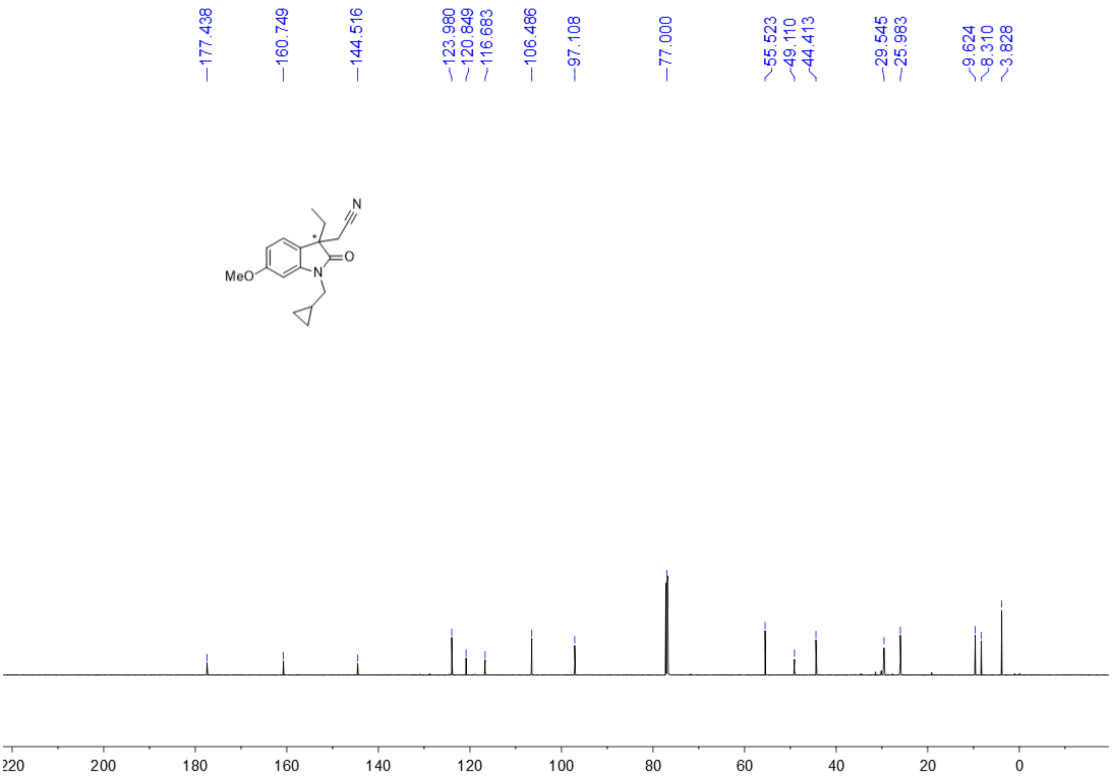
^{13}C NMR spectra of ***2o***



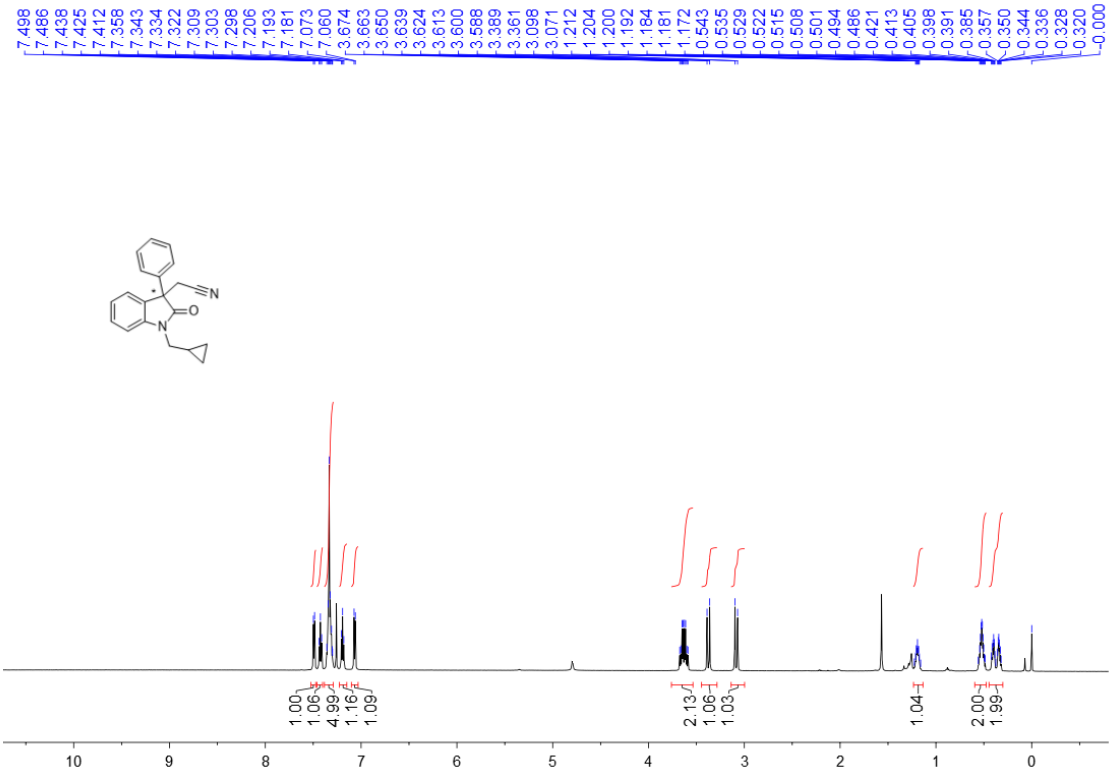
1H NMR spectra of ***2p***



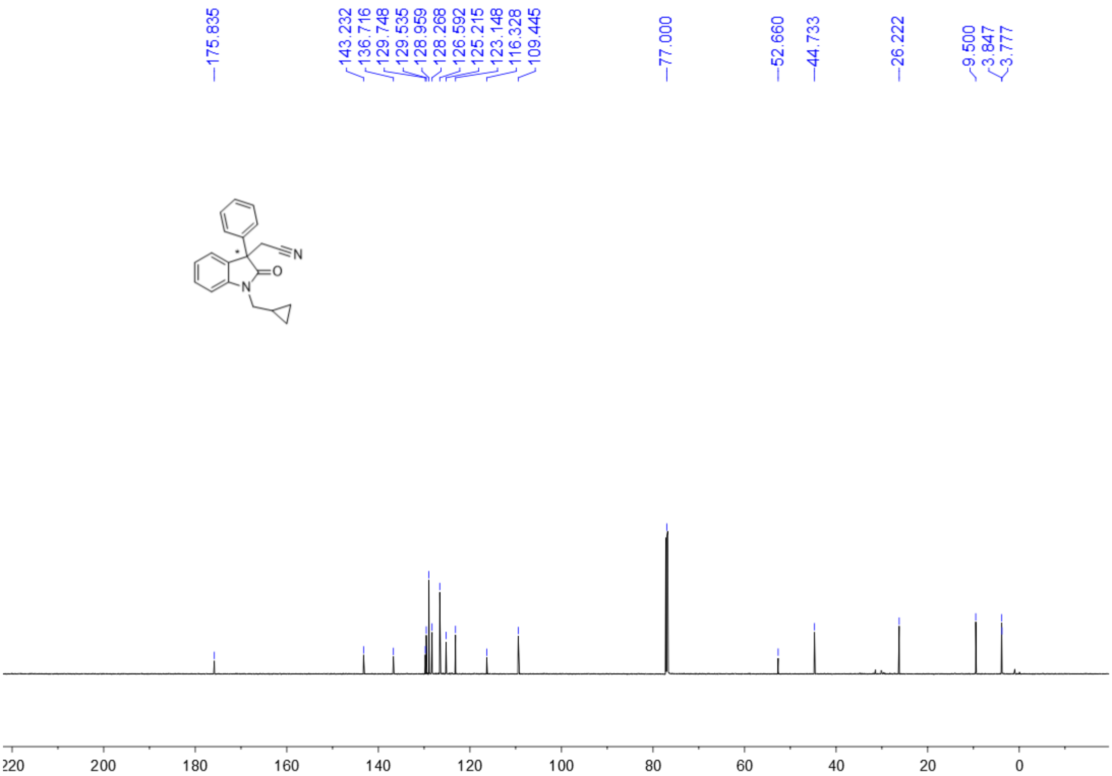
^{13}C NMR spectra of ***2p***



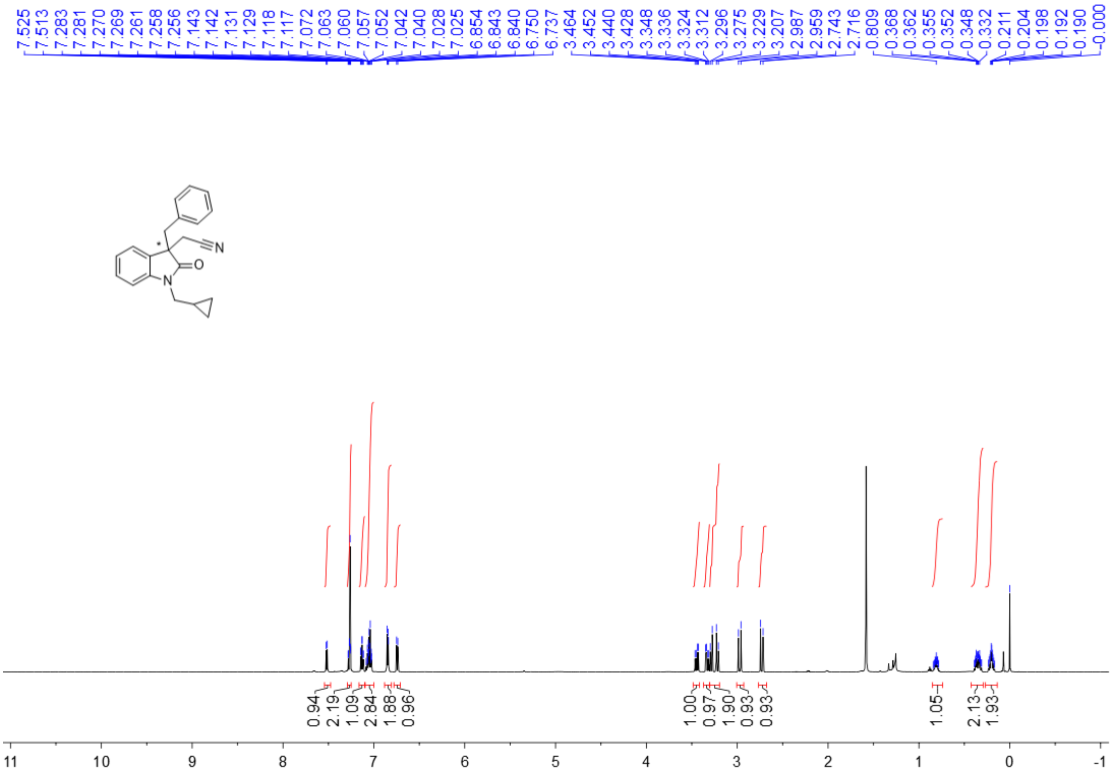
1H NMR spectra of ***2q***



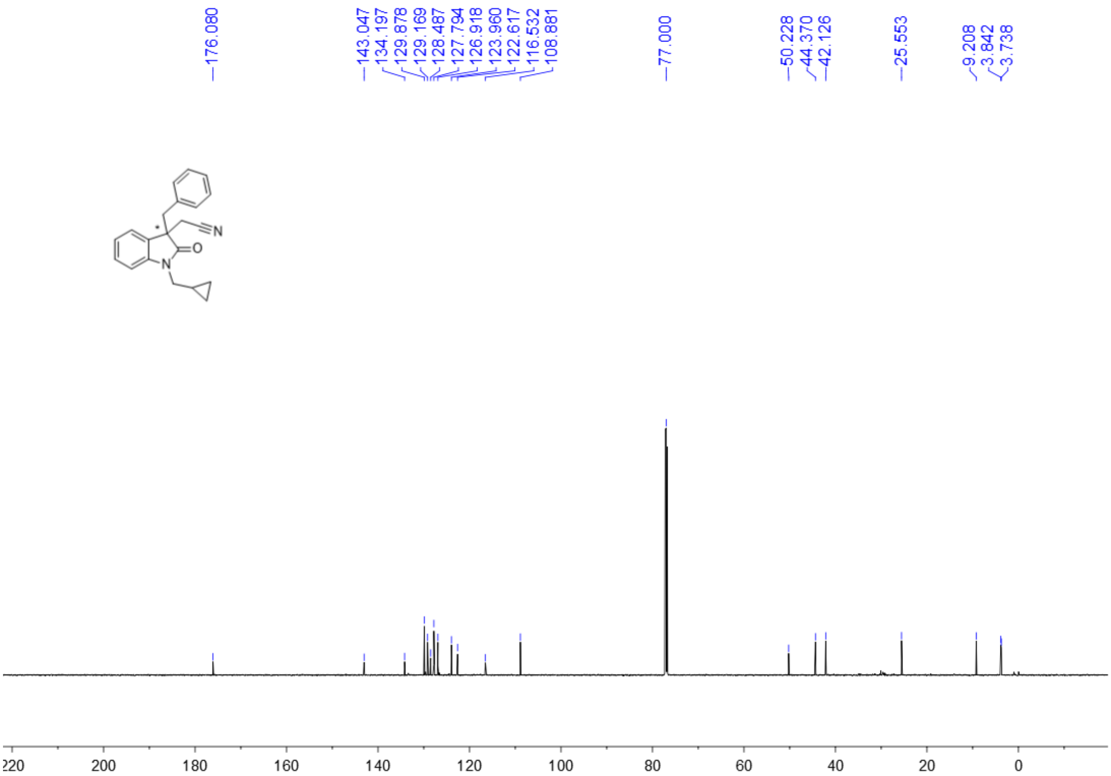
^{13}C NMR spectra of ***2q***



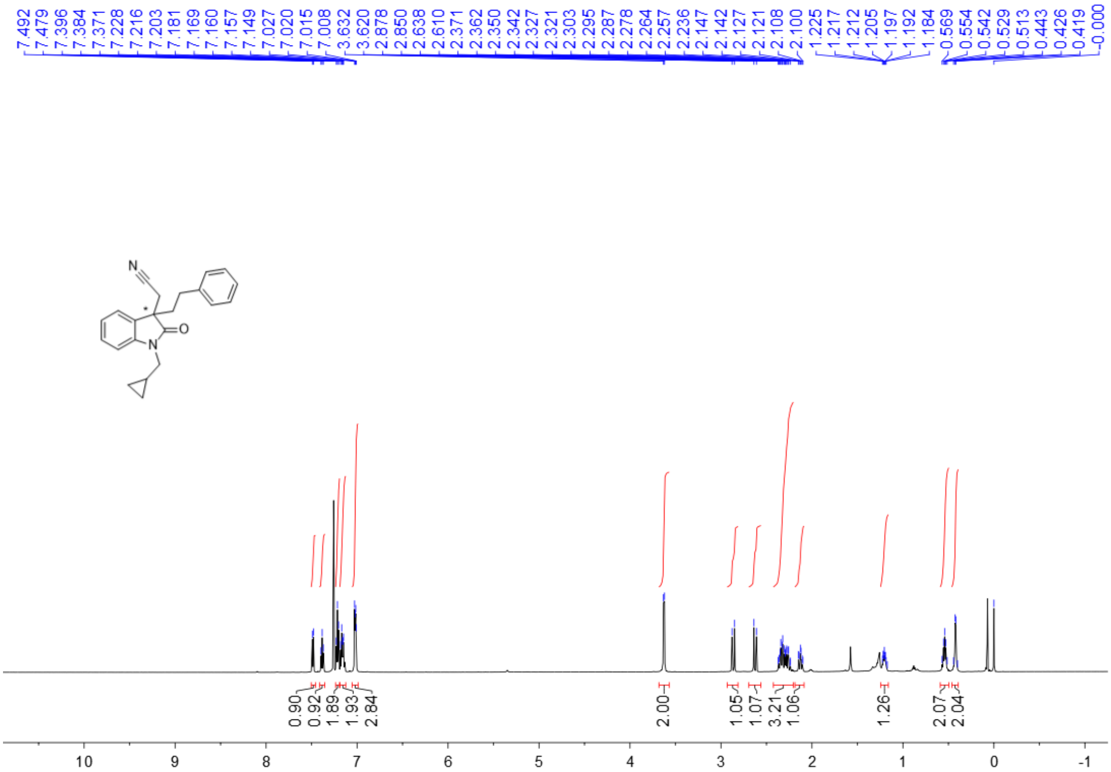
1H NMR spectra of ***2r***



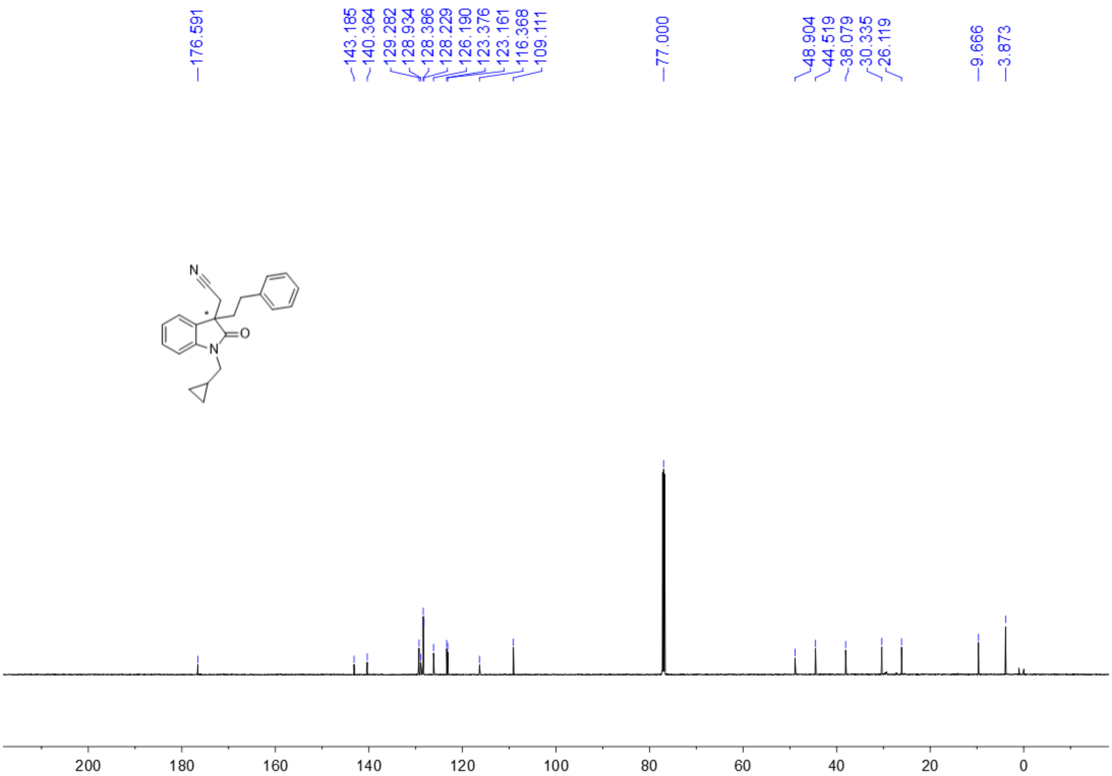
^{13}C NMR spectra of ***2r***



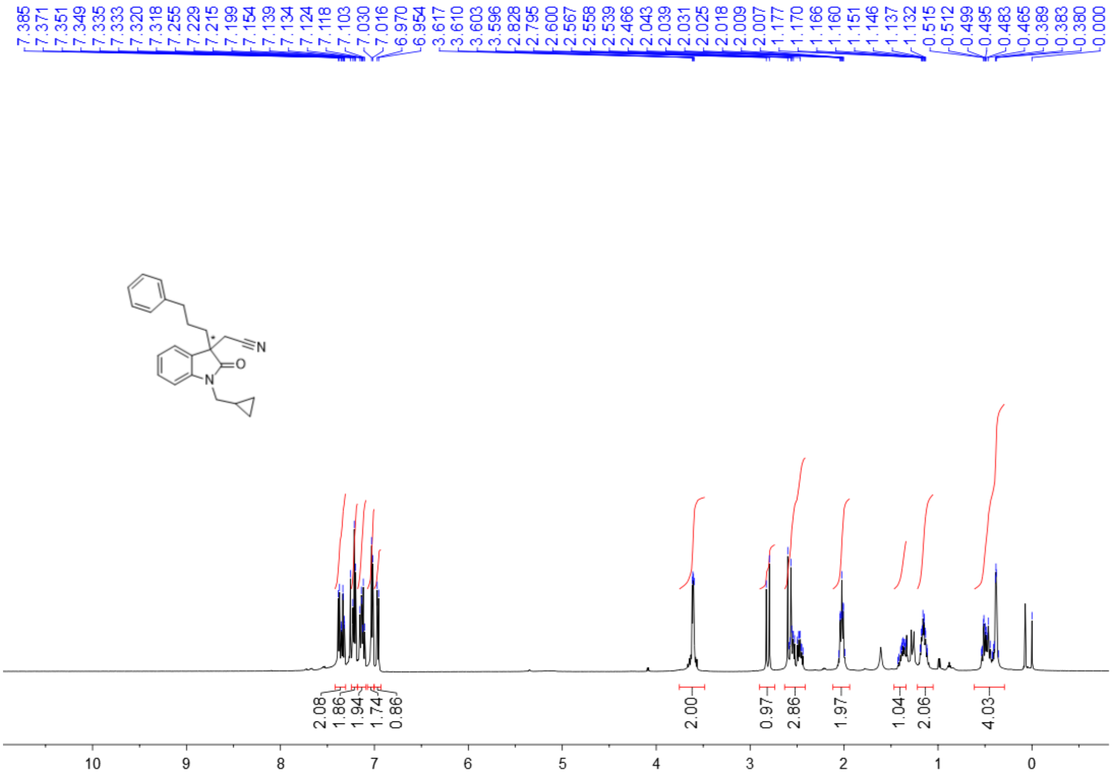
1H NMR spectra of ***2s***



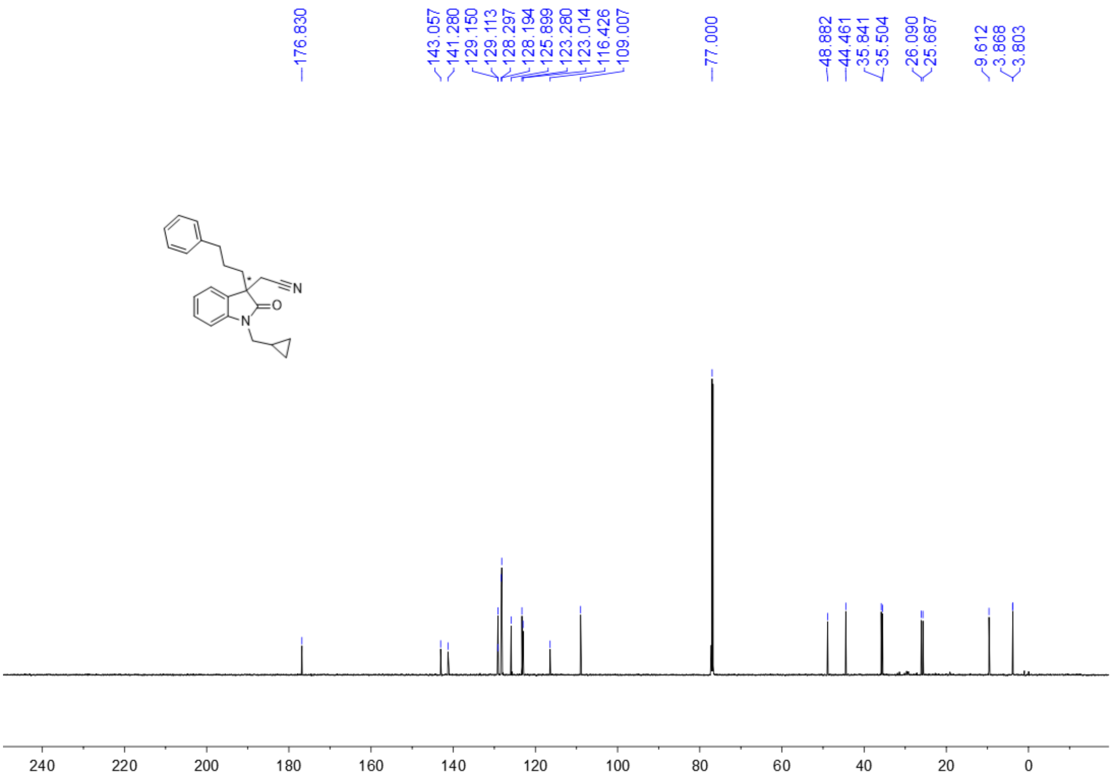
^{13}C NMR spectra of ***2s***



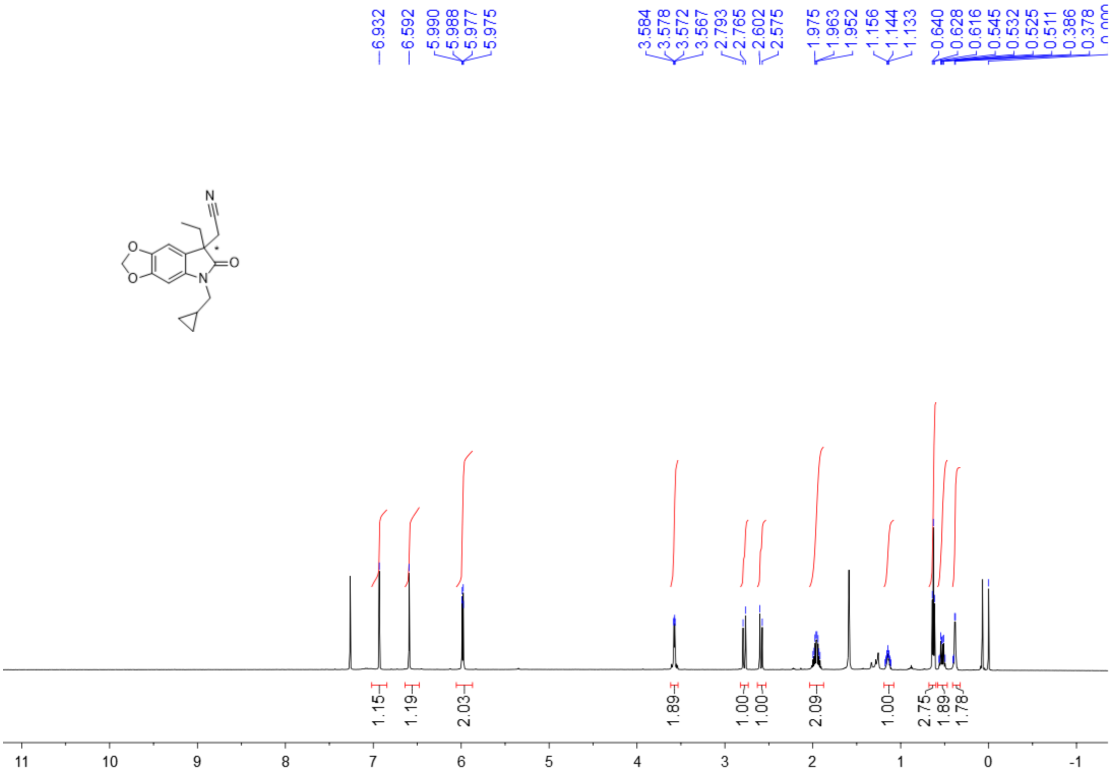
[1]H NMR spectra of ***2t***



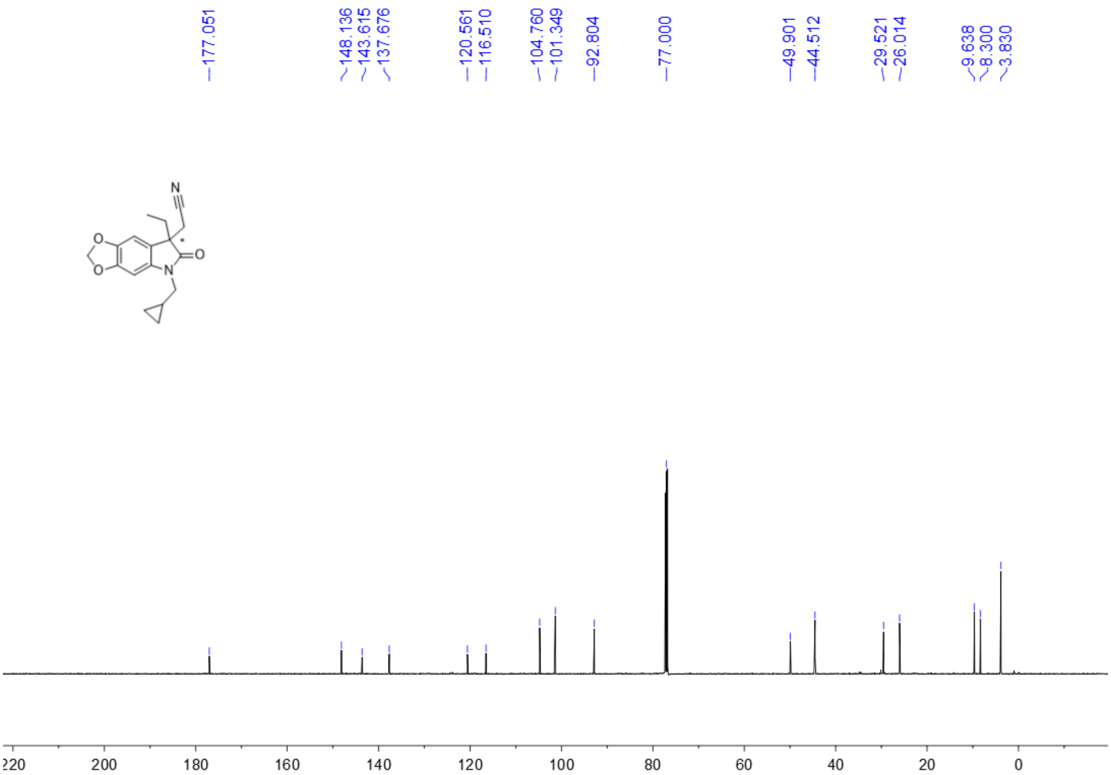
[13]C NMR spectra of ***2t***



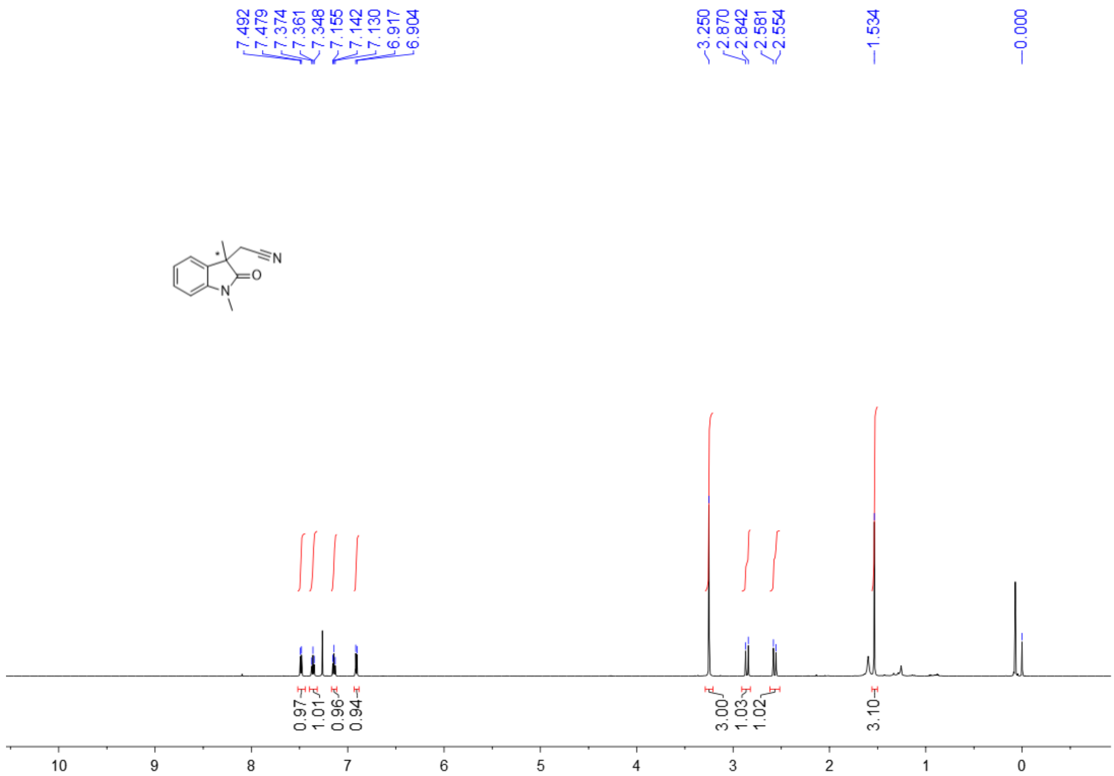
^{1}H NMR spectra of ***2u***



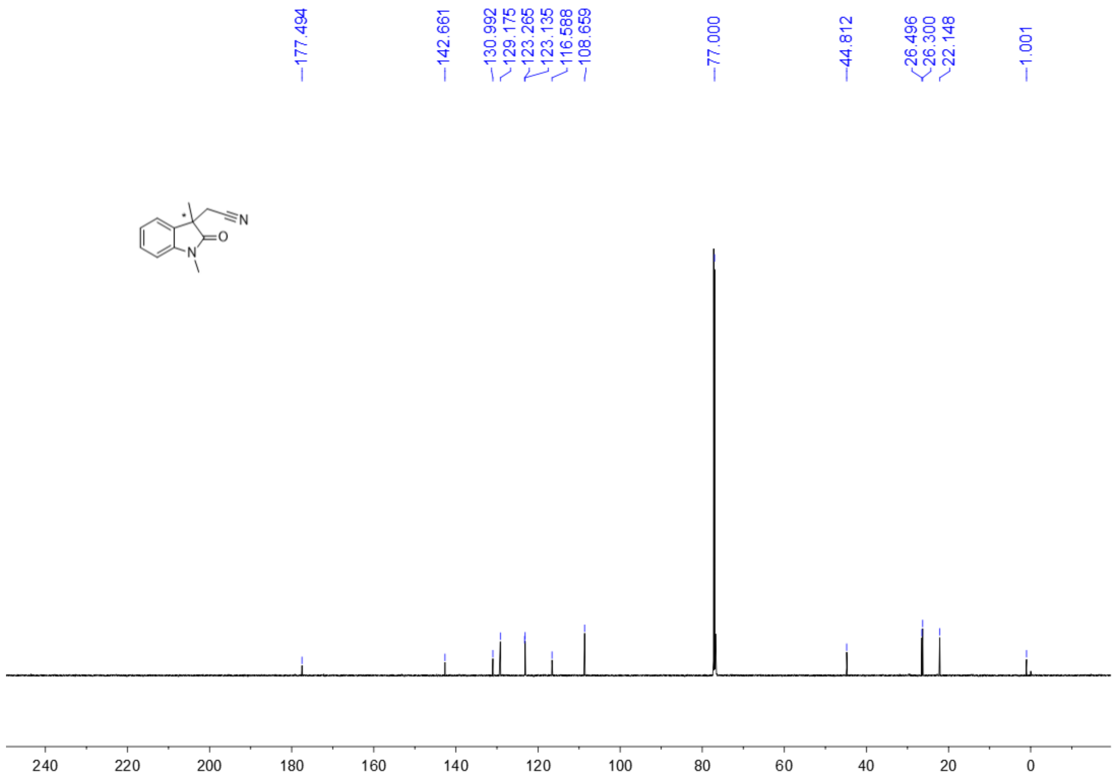
^{13}C NMR spectra of ***2u***



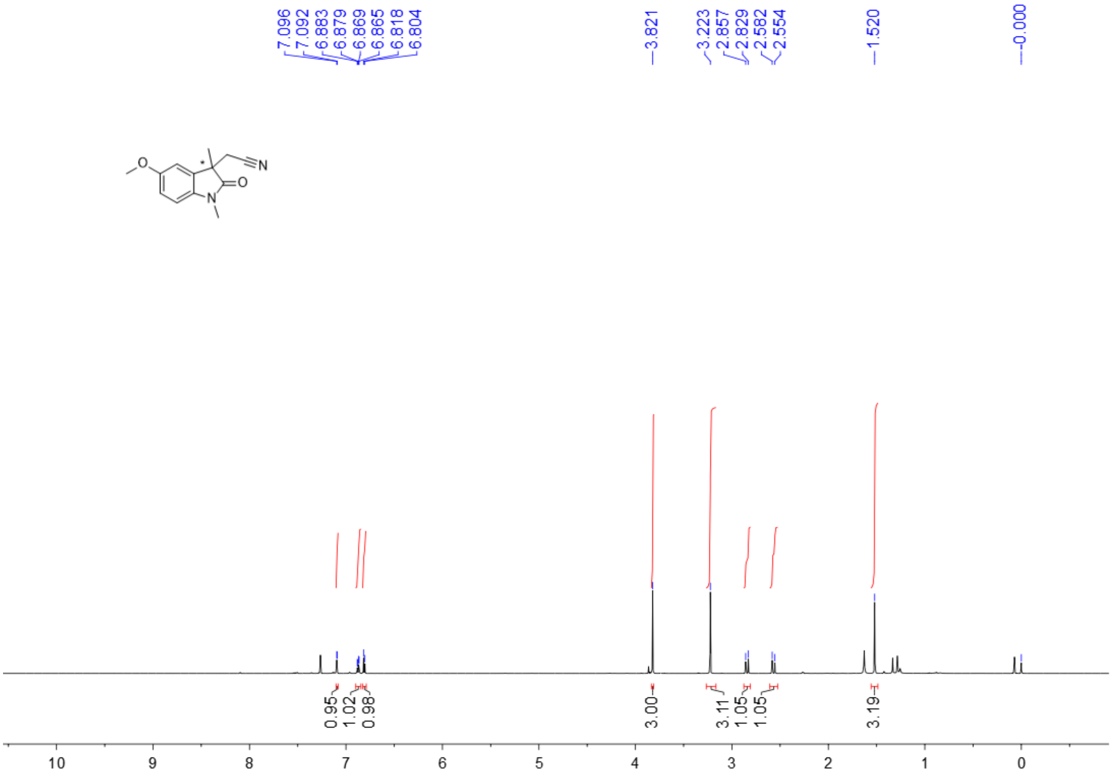
1H NMR spectra of ***2v***



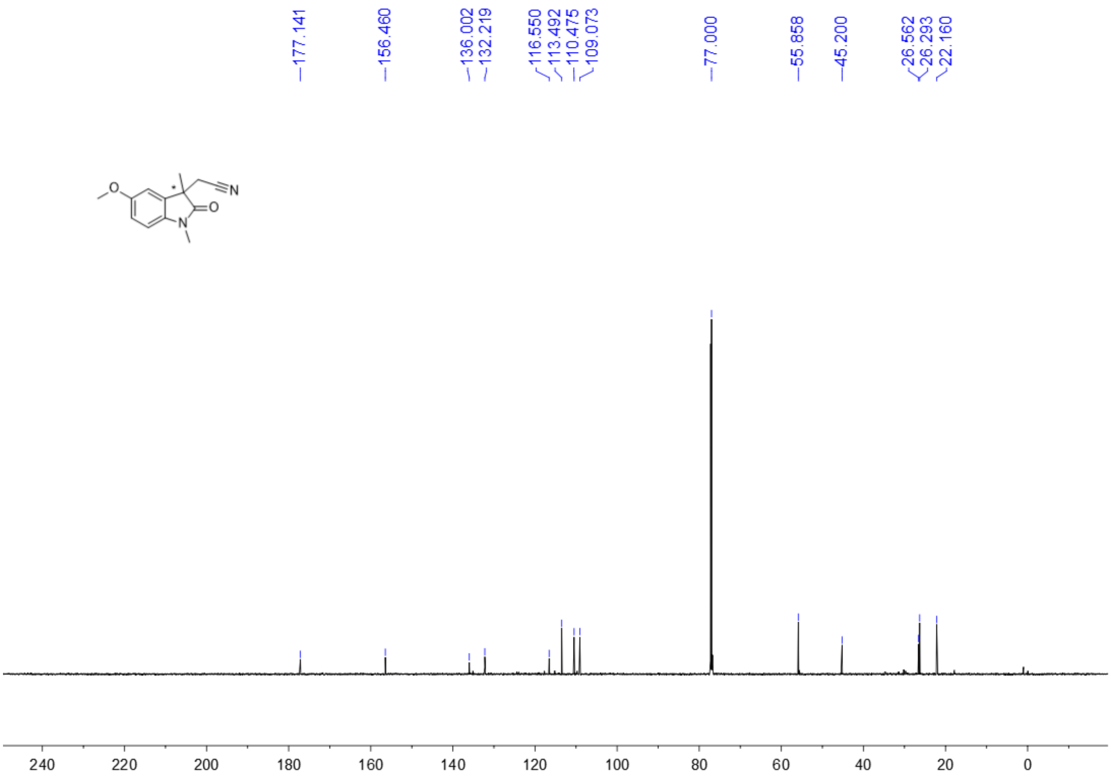
^{13}C NMR spectra of ***2v***



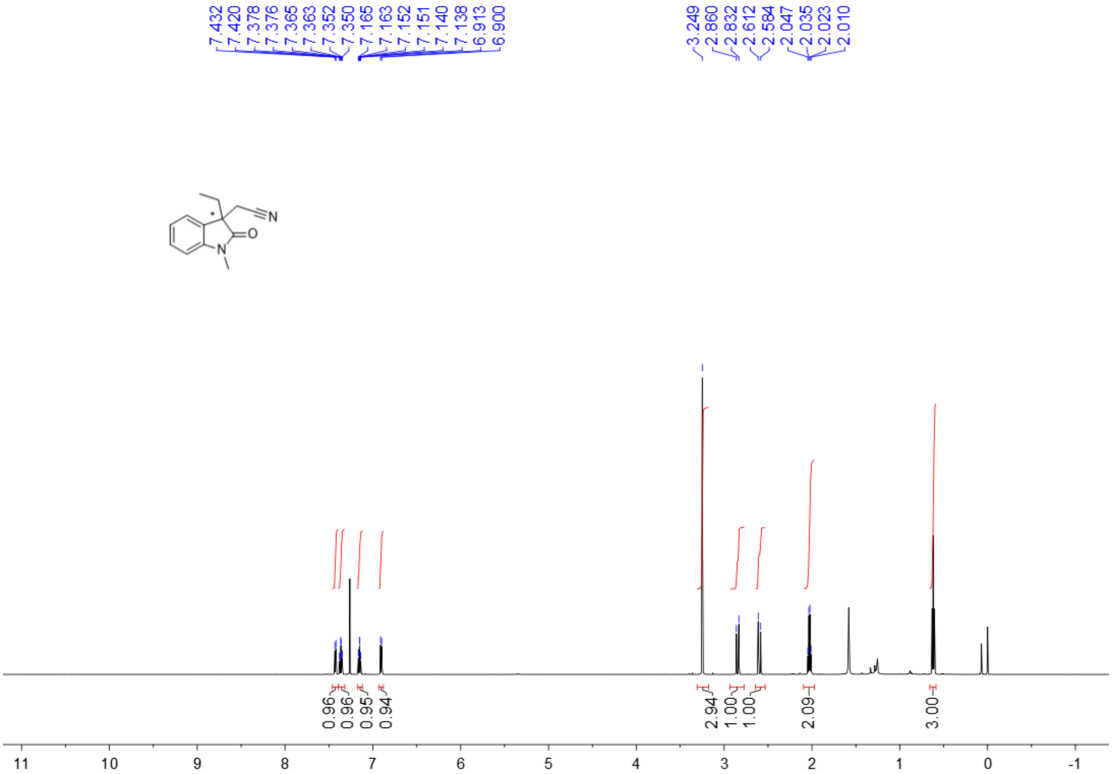
1H NMR spectra of ***2w***



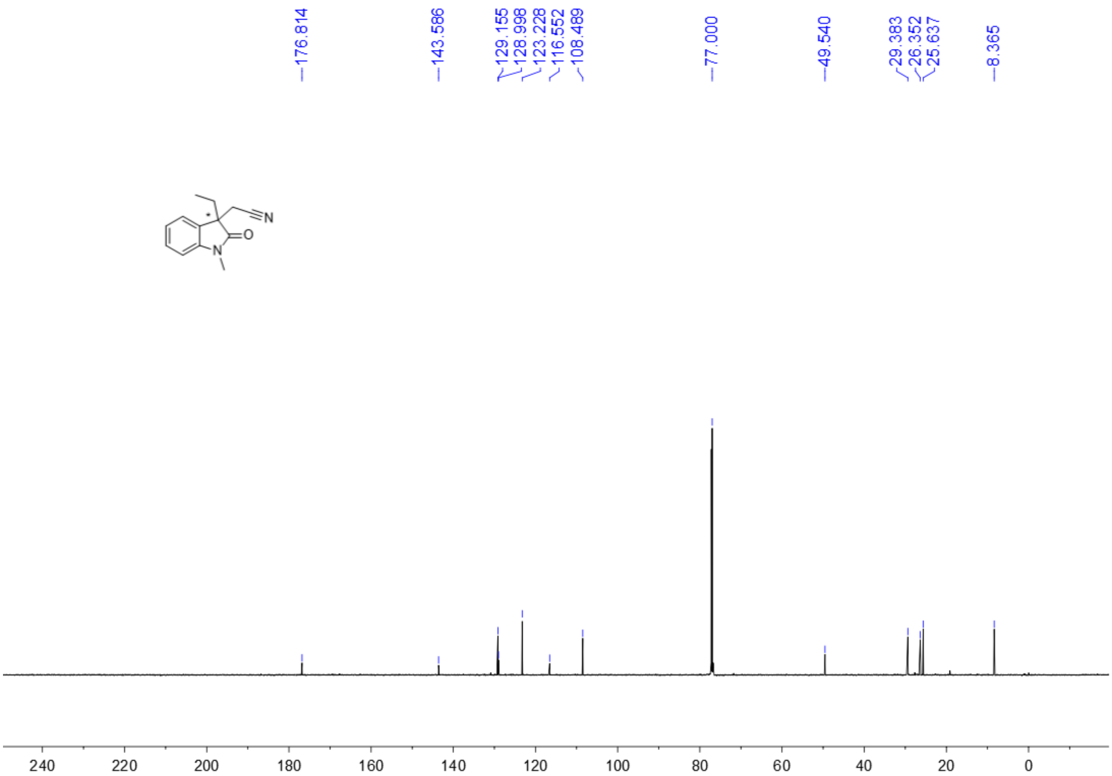
^{13}C NMR spectra of ***2w***



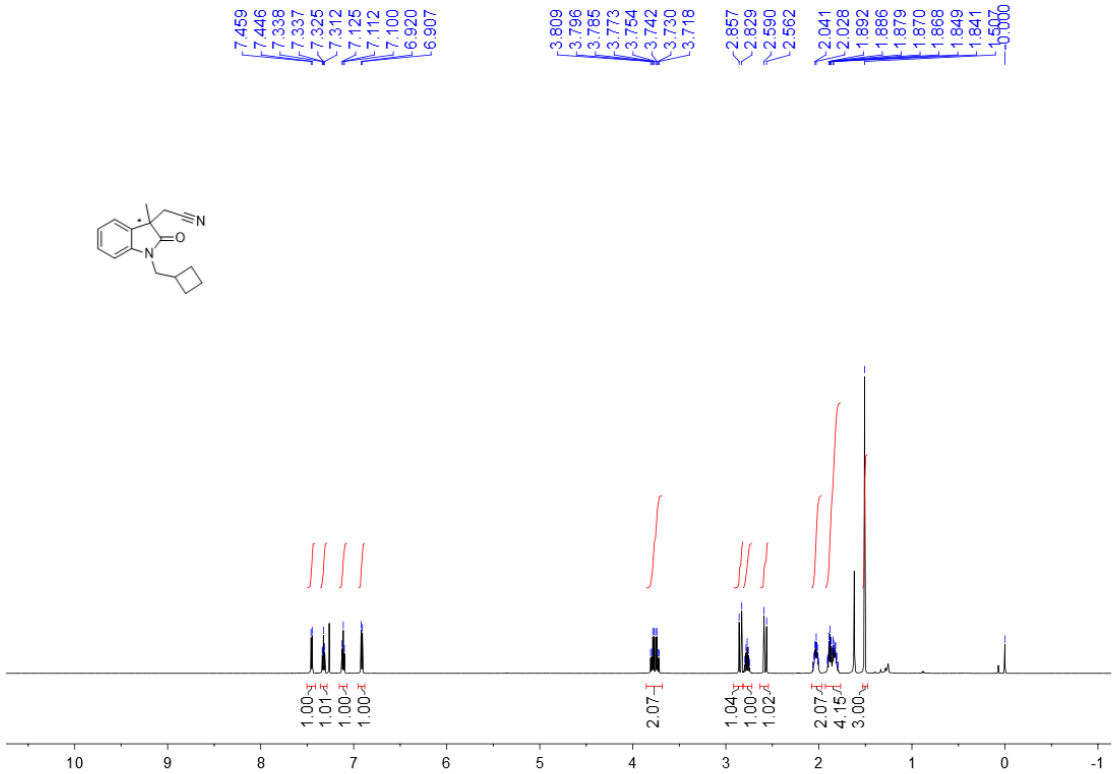
1H NMR spectra of ***2x***



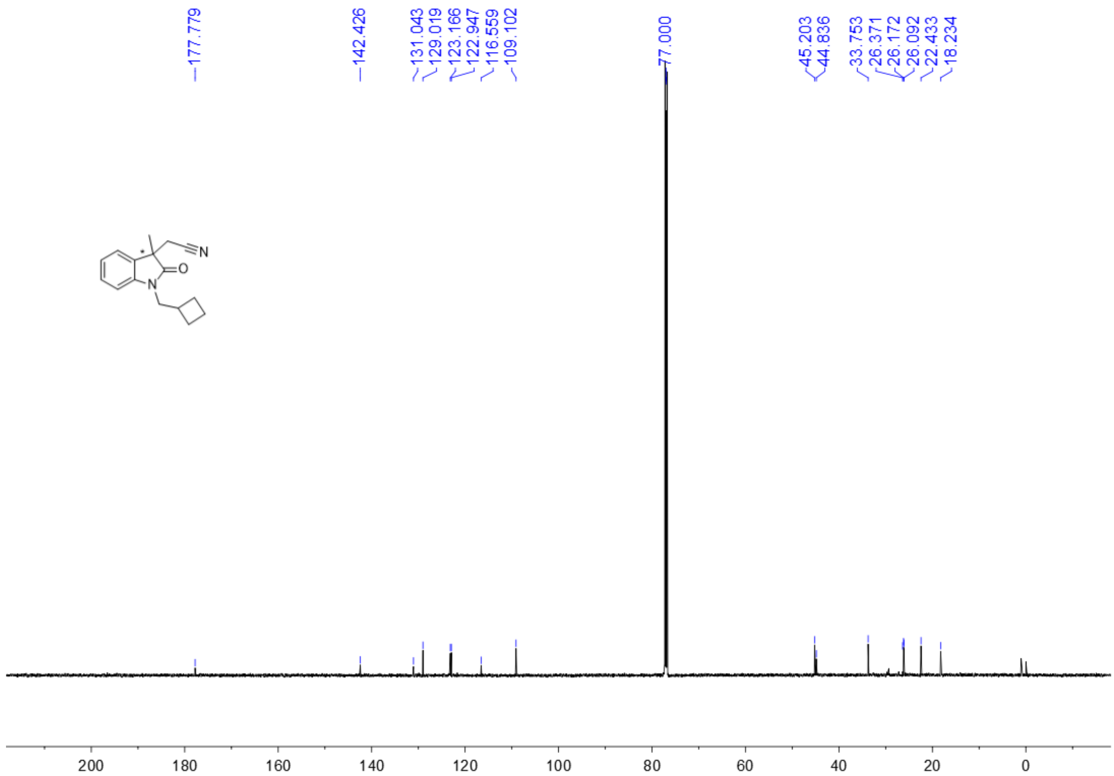
^{13}C NMR spectra of ***2x***



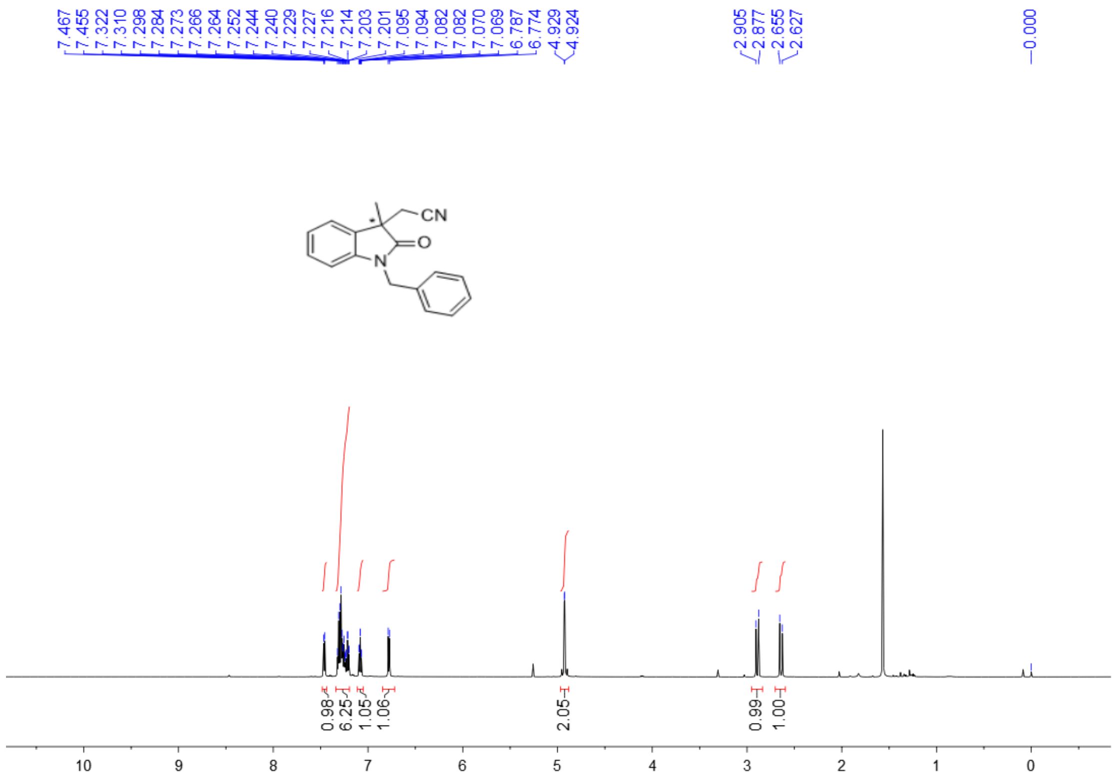
[1]H NMR spectra of ***2y***



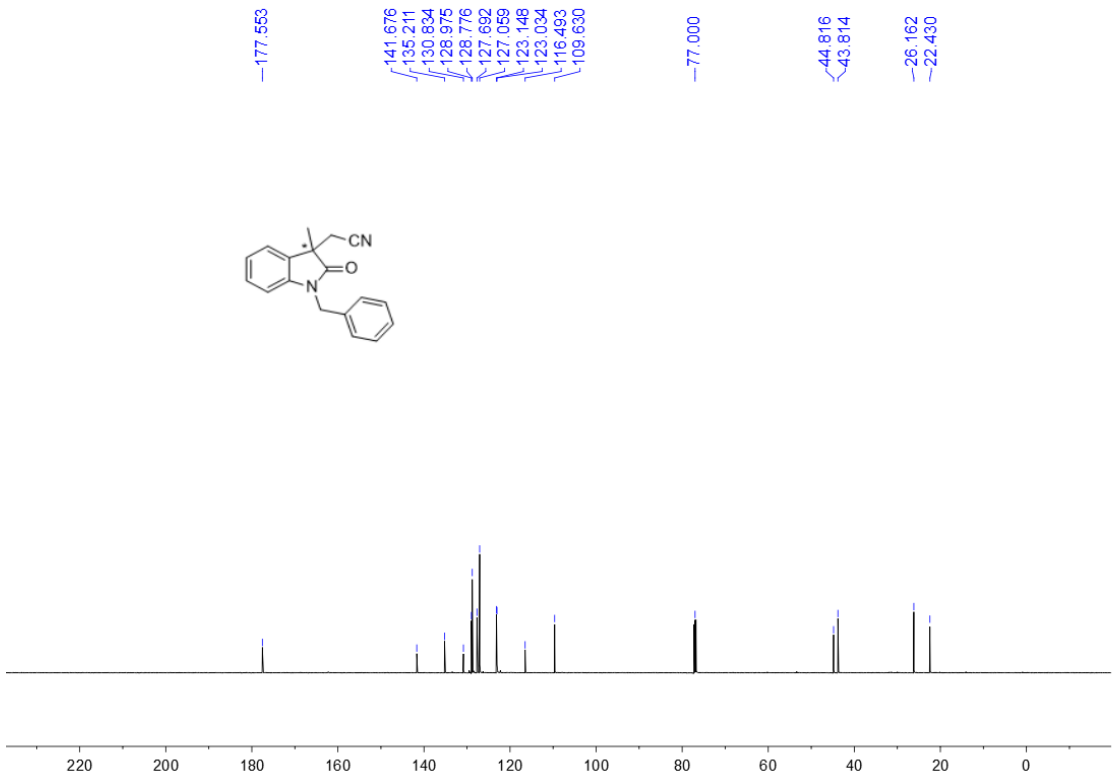
[13]C NMR spectra of ***2y***



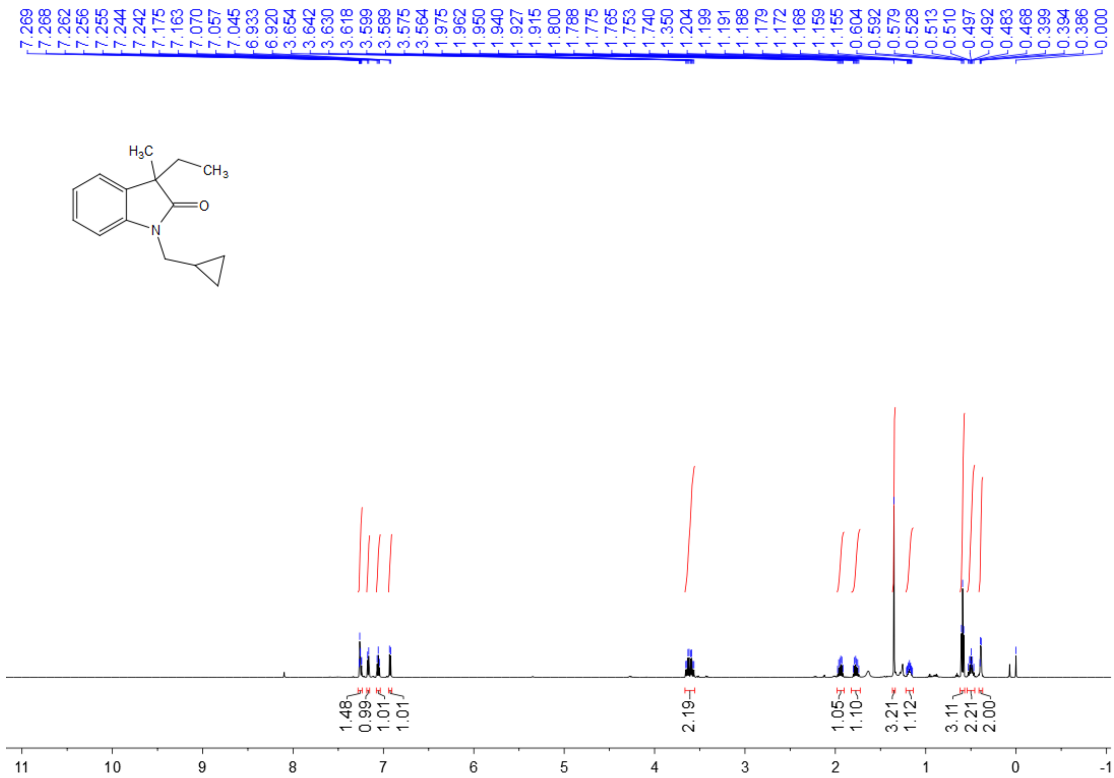
[1]H NMR spectra of ***2z***



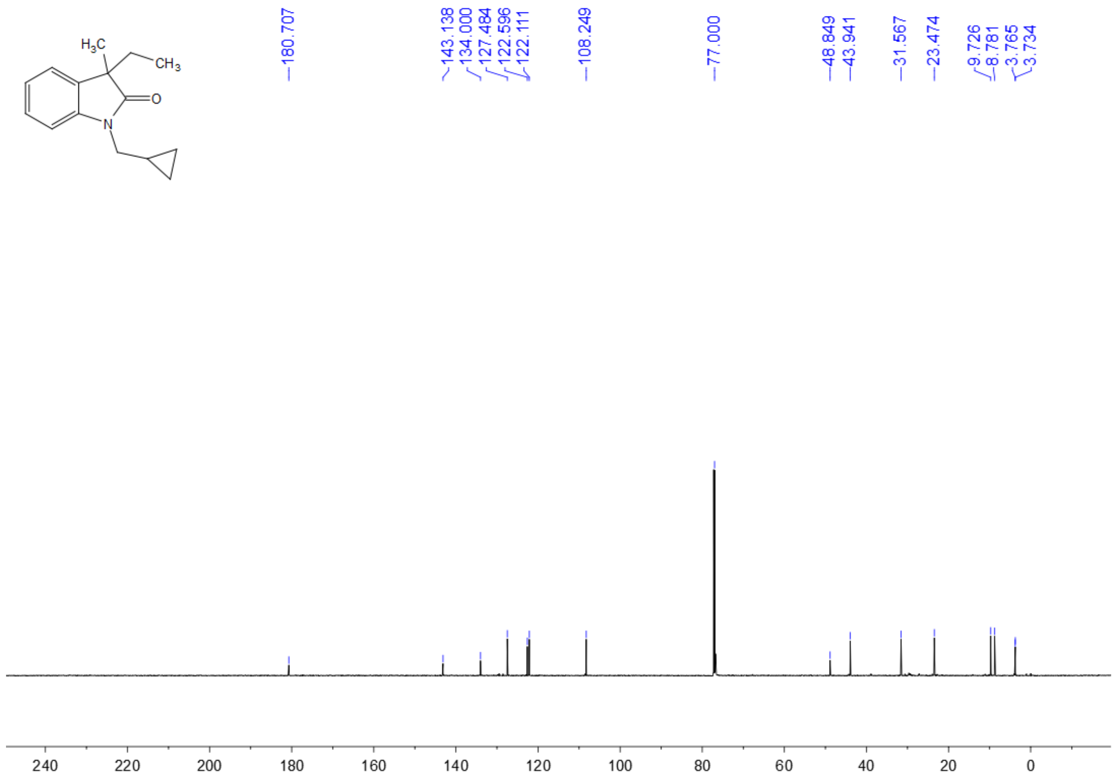
[13]C NMR spectra of ***2z***



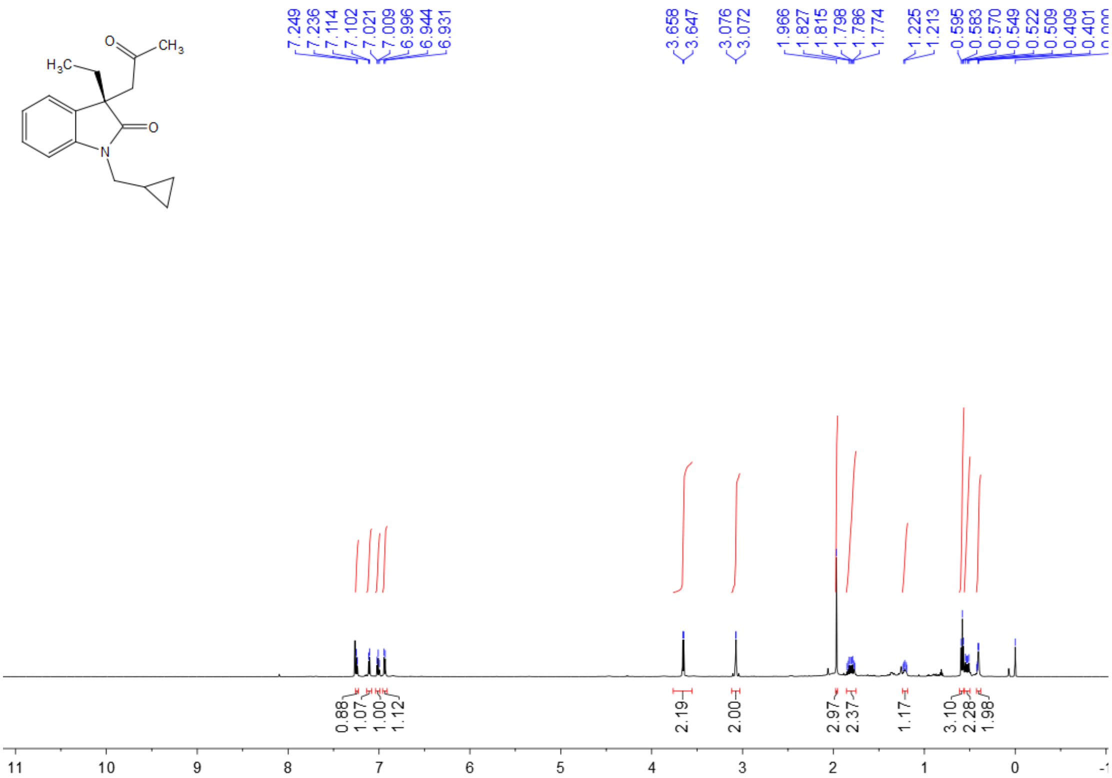
[1]H NMR spectra of ***2ab***



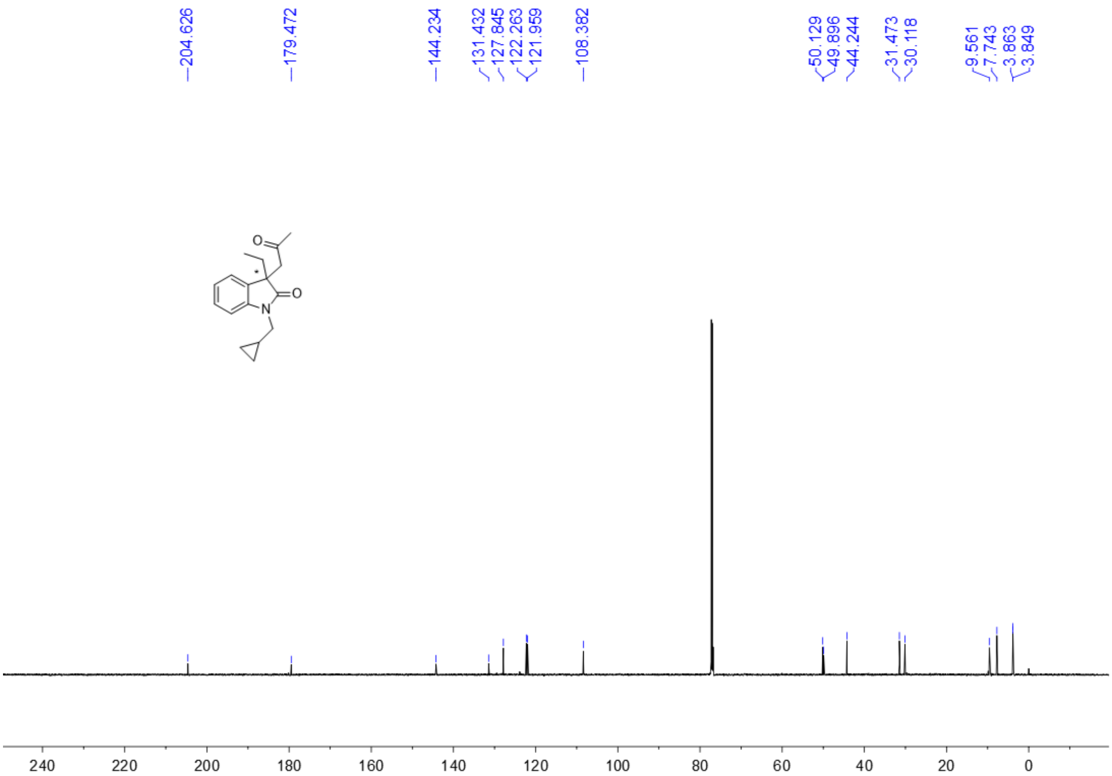
[13]C NMR spectra of ***2ab***



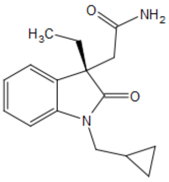
^{1}H NMR spectra of ***3a***

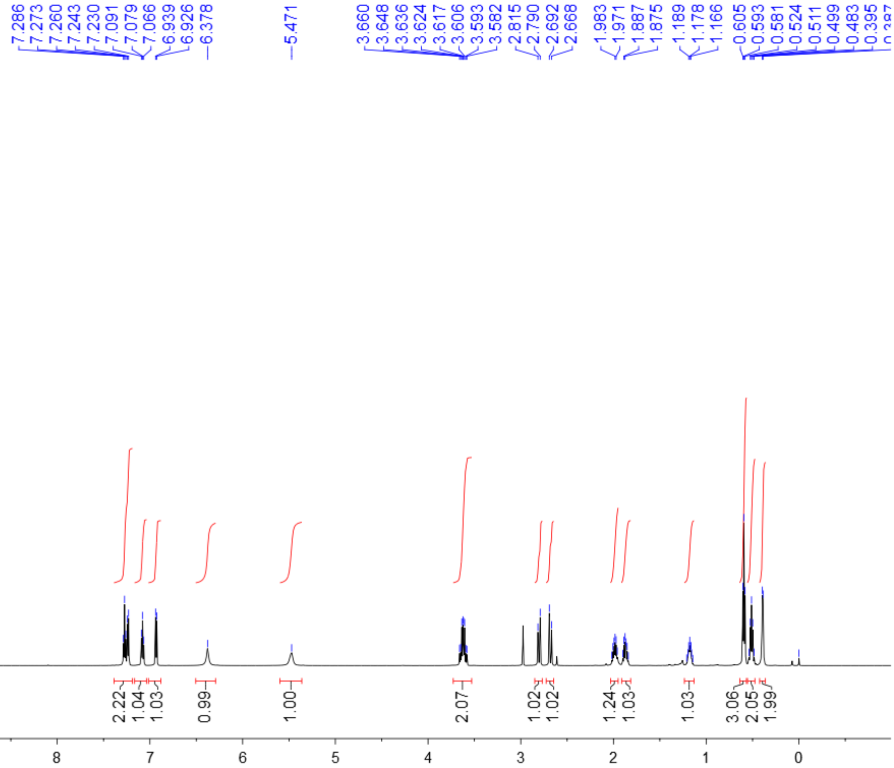


^{13}C NMR spectra of ***3a***

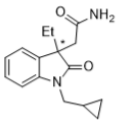


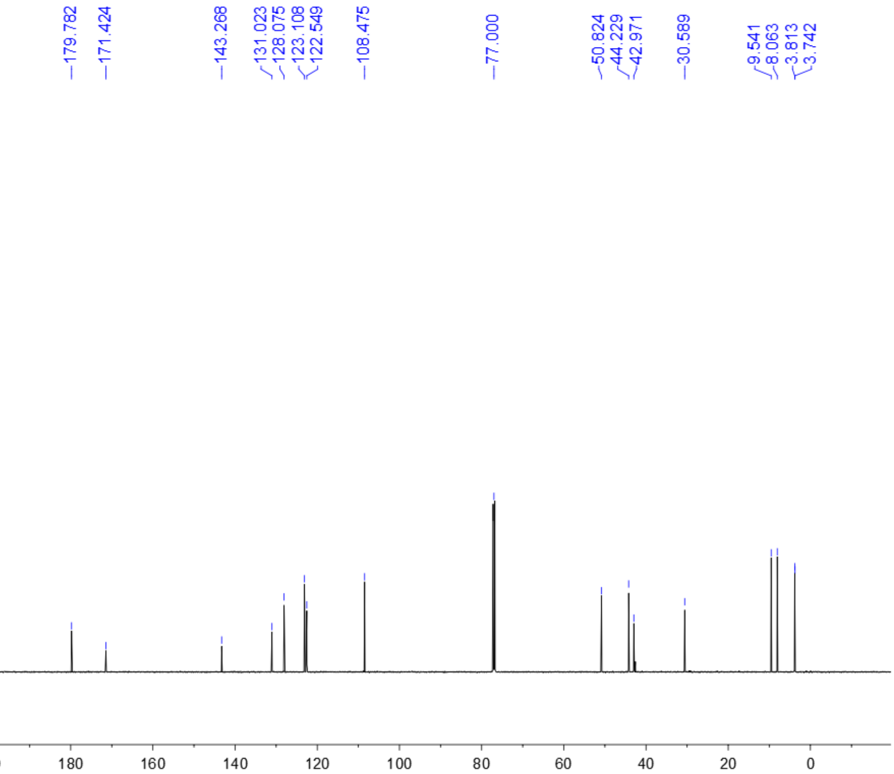
^{1}H NMR spectra of ***3b***



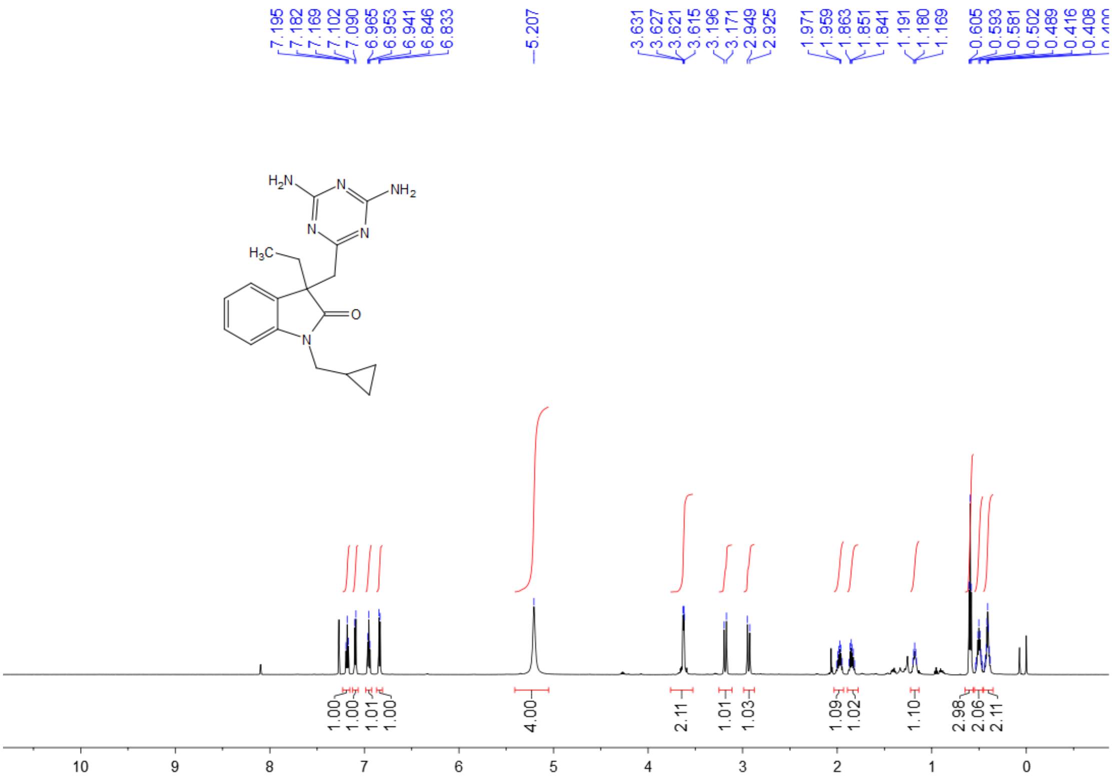


^{13}C NMR spectra of ***3b***

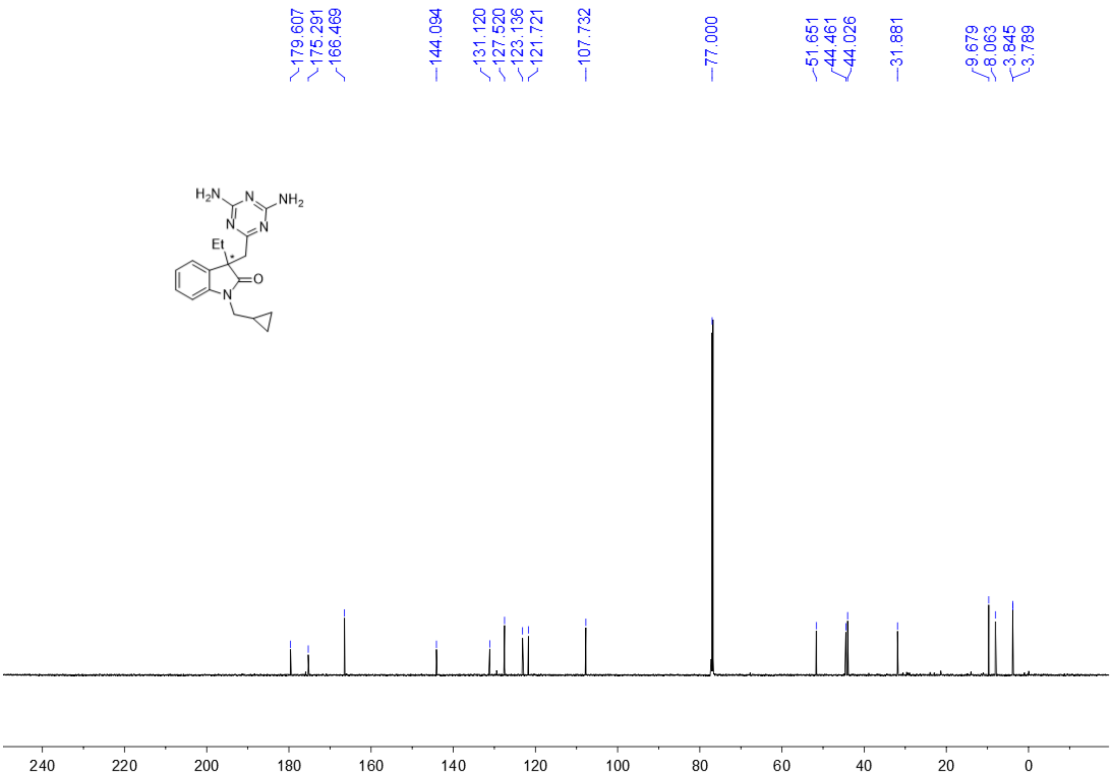




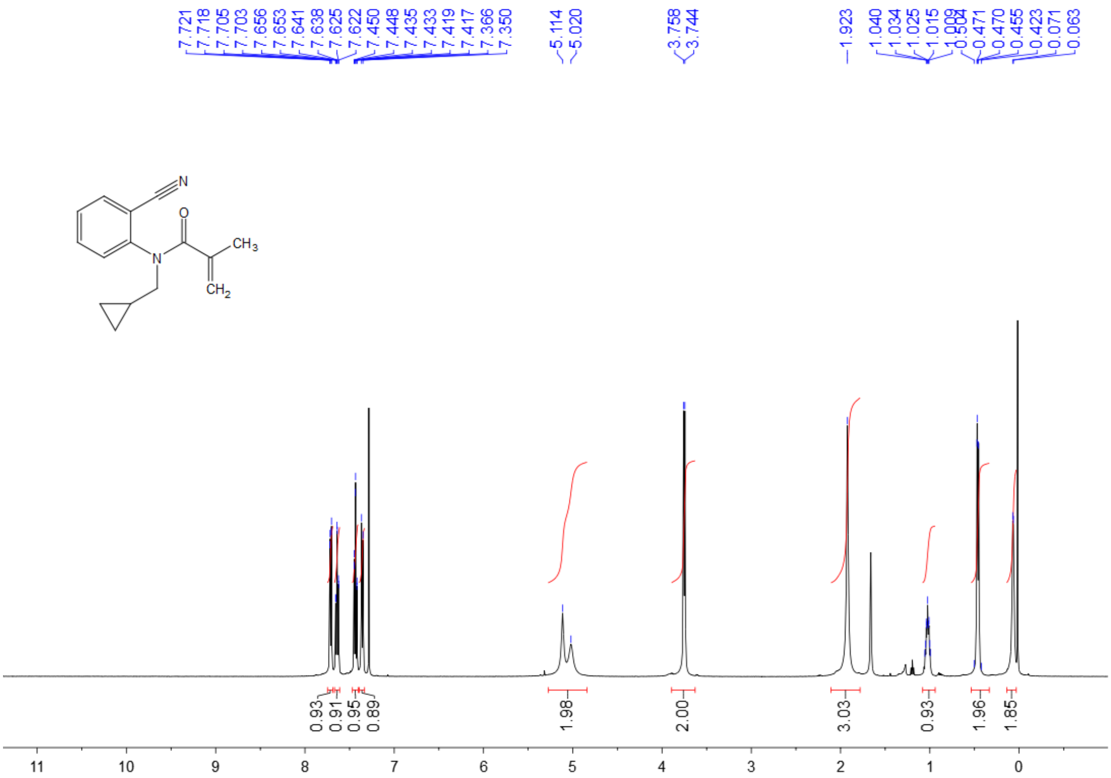
^{1}H NMR spectra of ***3c***



^{13}C NMR spectra of ***3c***



[1]H NMR spectra of ***4***



[13]C NMR spectra of ***4***