

Supplementary Material for:

# Oxidative Cyanation of 2-Oxindoles: Formal Total Synthesis of (±)-Gliocladin C

Arindam Maity,<sup>†a</sup> Avishek Roy,<sup>†a</sup> Mrinal Kanti Das,<sup>a</sup> Subhadip De,<sup>a</sup> Malay Naskar,<sup>a</sup> and Alakesh Bisai<sup>\*,a,b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal - 462 066, Madhya Pradesh, India. e-Mail: [alakesh@iiserb.ac.in](mailto:alakesh@iiserb.ac.in)

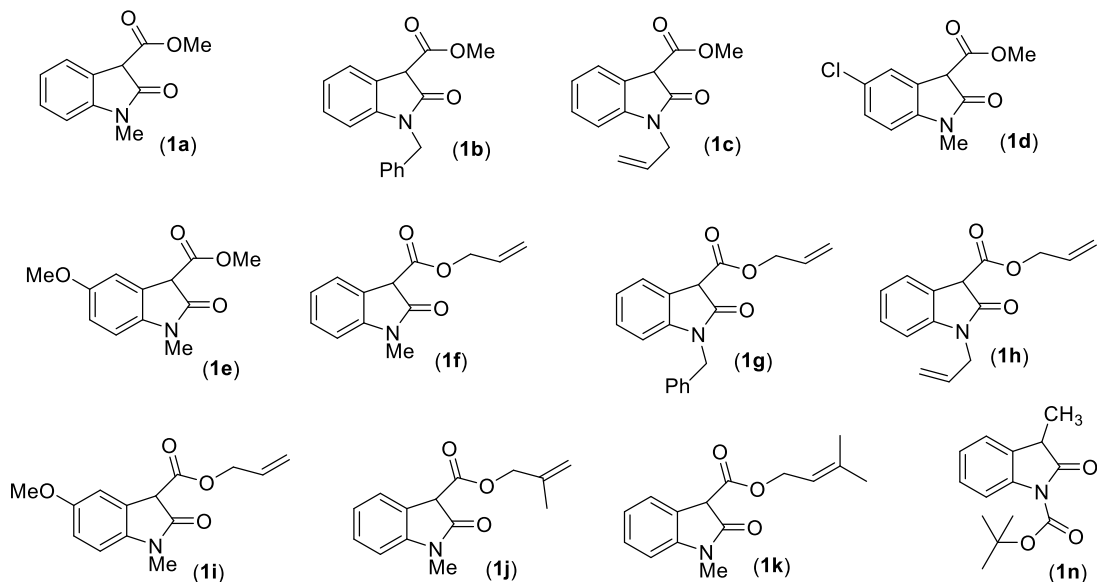
<sup>a</sup>Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, Nadia - 741 246, West Bengal, India. e-Mail: [alakesh@iiserkol.ac.in](mailto:alakesh@iiserkol.ac.in)

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**Substrate preparation for the oxidative cyanation**

1. For syntheses of compounds **1a-k**, **1n** see; S. Ghosh, S. Chaudhuri and A. Bisai, *Org. Lett.*, 2015, **17**, 1373.

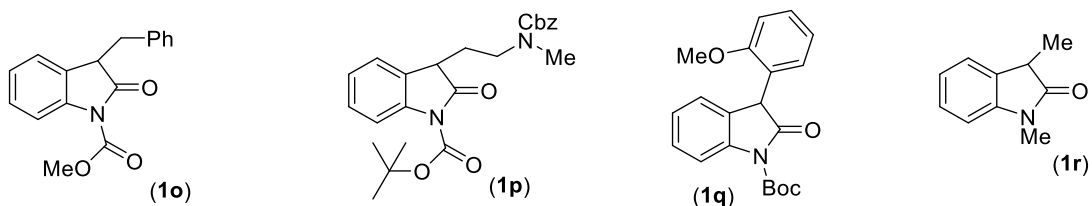


2. For syntheses of compound **1o**, see; Y. Zhang, T. Zhang and B. M. Trost, *J. Org. Chem.*, 2009, **74**, 5115.

3. For synthesis of compound **1p**, see; S. De, M. K. Das, S. Bhunia and A. Bisai, *Org. Lett.*, 2015, **17**, 5922.

4. For syntheses of compound **1q**, see; Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura and M. Sodeoka, *J. Am. Chem. Soc.*, 2005, **127**, 10164.

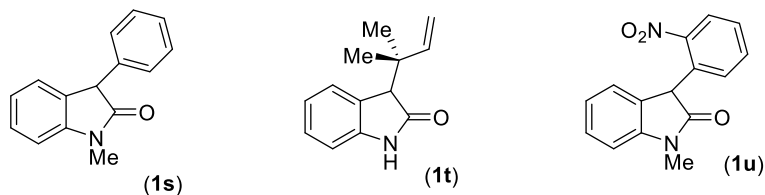
5. For syntheses of compound **1r**, see; N. Kumar, S. Ghosh, S. Bhunia and A. Bisai, *Beilstein J. Org. Chem.*, 2016, **12**, 1153.



6. For syntheses of compound **1s** see; J. Xie, J. D. Sieber and B. M. Trost, *J. Am. Chem. Soc.*, 2011, **133**, 20611.

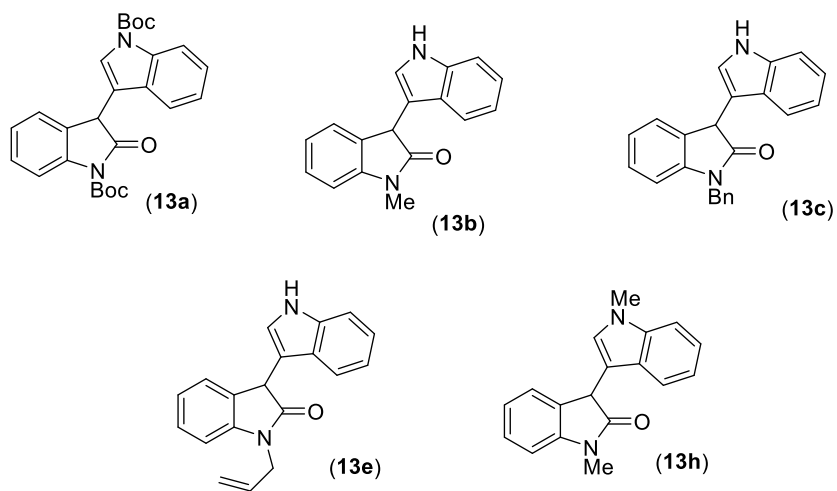
7. For syntheses of compound **1t**, see; C. D. Grant and M. J. Krische, *Org. Lett.*, 2009, **11**, 4485.

8. For syntheses of compound **1u**, see; A. Roy, M. K. Das, S. Chaudhuri and A. Bisai, *J. Org. Chem.*, 2018, **83**, 403.



9. For syntheses of compounds **13a-c**, **13e** see; S. Ghosh, S. Chaudhuri and A. Bisai, *Chem. Eur. J.*, 2015, **21**, 17479.

10. For syntheses of compound **13h** see; D-F. Chen, F. Zhao, Y. Hu and L-Z. Gong, *Angew. Chem. Int. Ed.*, 2014, **53**, 10763.

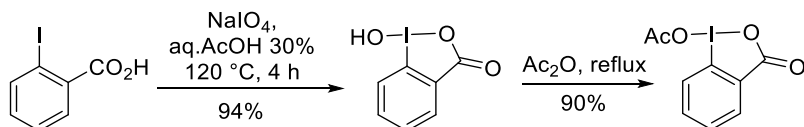


## EXPERIMENTAL SECTION

### Materials and Methods

Unless otherwise stated, reactions were carried out using oven-dried glassware with Teflon-coated magnetic stirring bars were used to stir the reactions. The Syringe was used to transfer the solvents and liquid reagents. Tetrahydrofuran (THF) Diethyl ether (Et<sub>2</sub>O), was distilled over sodium/benzophenone ketyl. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled over calcium hydride. All other solvents like Nitromethane, MeOH, EtOAc, DMF and reagents were used as received. Reaction temperatures above 25 °C were maintained by using an oil bath on a magnetic stirrer. Thin layer chromatography (TLC) analysis was performed by using silica gel precoated plates (0.25 mm) 60 (F-254), Visualized by UV irradiation, yellow dip stain and other stains. Silica gel of particle size 230-400 and 100-200 mesh was used to perform flash chromatography. Digital melting point apparatus is used to record the melting points and are uncorrected. <sup>1</sup>H NMR spectra were recorded by using 400, 500 700 MHz spectrometers, <sup>13</sup>C NMR operating frequencies are 100, 125 175 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvents (CDCl<sub>3</sub>) signal (δ = 7.24 for <sup>1</sup>H NMR and δ = 77.0 for <sup>13</sup>C NMR) and (DMSO-D<sub>6</sub>) signal (δ = 2.50 for <sup>1</sup>H NMR and δ = 39.5 for <sup>13</sup>C NMR). Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on an FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm<sup>-1</sup>). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

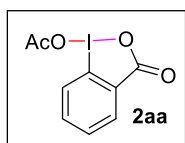
### Synthesis of 1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2aa):



In an oven dried round-bottom flask, 2-iodobenzoic (5 g, 20.15 mmol, 1.0 equiv) was taken 30% aqueous acetic acid (30 mL) at room temperature. To this solution, sodium

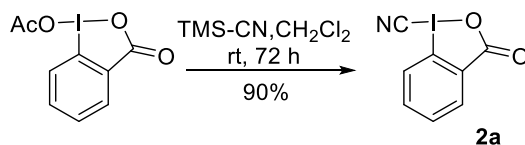
metaperiodate (4.4 g, 20.56 mmol, 1.02 equiv) was added pinch wise over a period of 5 minutes at room temperature. The reaction vessel was placed over a preheated oil-bath maintaining 120 °C. After 4 h of heating at same temperature the reaction mixture was allowed to cool to room temperature and then it was placed on to ice bath to settle down white solid. The solid residue was filtered through sintered crucible and washed with cold acetone (30 mL X 3). Finally, the solid residue was dried *in vacuo* and over calcium chloride desiccator to afford 5.01 g (94% yield) of 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one, which was used further without any purification.

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (5.01 g, 18.9 mmol, 1.0 equiv) was taken in acetic anhydride (18 mL) and the reaction mixture was heated to 130 °C for 30 minutes. The reaction mixture became slightly yellowish clear solution. Later, the reaction mixture was cool to room temperature and then it was placed at -20 °C over 2 hours to get white precipitate. The white suspension was filtered and the white solid was washed with hexane (20 mL X 3) and dried *in vacuo* to afford 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one<sup>6b</sup> (5.2 g, 90%) as a white solid.

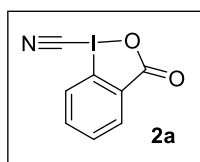


**1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one(2aa):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.20 (dq, *J* = 7.6, 1.5 Hz, 1H), 7.97 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.91 (ddt, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.68 (tt, *J* = 7.4, 1.1 Hz, 1H), 2.23 (s, 3H); **IR** (film) ν<sub>max</sub> 2925, 2867, 2164, 1751, 1682, 1443, 1106, 934, 865, 756 cm<sup>-1</sup>.<sup>6b</sup>

**Synthesis of 1-cyano-1,2-benziodoxol-3-(1*H*)-one (CBX, 2a):**<sup>6b</sup>

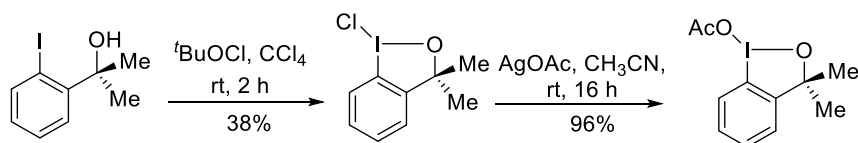


1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (2.0 g, 6.5 mmol, 1.0 equiv.) was dissolved in dry dichloromethane (20 mL) under nitrogen. To this clear colorless solution, trimethylsilyl cyanide (1.63 mL, 13.0 mmol, 2.0 equiv.) was added drop wise over a 10 minutes. Then the reaction mixture was stirred at room temperature for 72 hours under nitrogen atmosphere and thick white suspension was resulted. The white suspension was filtered through sintered crucible and the solid was washed with hexane (10 mL X 3) and dried in *vacuo* affording 1.6 g (90%) 1-cyano-1,2-benziodoxol-3-(1*H*)-one (**2a**) as a white solid.



**1-Cyano-1,2-benziodoxol-3-(1*H*)-one (2a):**  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.26 (d,  $J = 8.3$  Hz, 1H), 8.11 (dd,  $J = 7.5, 1.7$  Hz, 1H), 7.98 (ddd,  $J = 8.5, 7.2, 1.7$  Hz, 1H), 7.87 (td,  $J = 7.3, 0.9$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz, DMSO- $d_6$ )  $\delta$ : 167.5, 137.0, 132.6, 132.3, 130.4, 128.2, 117.6, 87.8; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_8\text{H}_4\text{INO}_2\text{Na}$  : 295.9179, found: 295.9199.<sup>6b</sup>

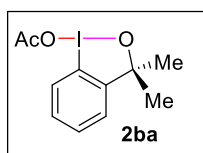
#### Synthesis of 1-acetoxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole(**2ba**):<sup>6c</sup>



In an over dried round bottom flask, 2-(2-iodophenyl)propan-2-ol (4 g, 15.26 mmol, 1.0 equiv) was taken in carbon tetrachloride (20 mL). To this reaction mixture was added *t*-butyl hypochloride (1.99 mL, 18.31 mmol, 1.2 equiv) drop wise at room temperature over 5 minutes and stirring was continued for 2 h. The solid residue was filtered through sintered crucible and washed with *n*-hexane (20 mL X 3). Finally, the solid residue was

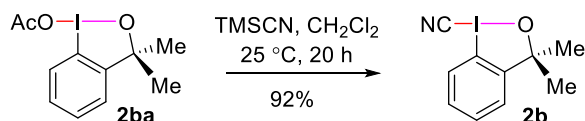
dried *in vacuo* to afford 1.72 g (38% yield) of 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole, which was used further without any purification.

In an oven dried round-bottom flask, 1-chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (1.62 g, 5.46 mmol) was dissolved in dry acetonitrile (15 mL) under N<sub>2</sub> atmosphere. The reaction flask was covered with aluminum foils and protected from light. Silver acetate (957 mg, 5.73 mmol, 1.05 equiv.) was then added. Then the reaction mixture was stirred in the dark at room temperature for 16 h. Filtration of the precipitated silver chloride over a celite plug and evaporation of the solvent afforded 96% yield (1.68 g) of 1-acetoxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole as a light yellow solid.<sup>6e</sup>



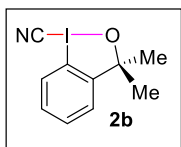
**1-Acetoxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (2ba):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (dtd, *J* = 15.7, 7.2, 1.5 Hz, 2H), 7.18 (dd, *J* = 7.3, 1.8 Hz, 1H), 2.11 (s, 3H), 1.53 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.3, 149.3, 130.4, 129.9, 129.8, 126.1, 115.6, 84.5, 29.2, 21.4; IR (film) ν<sub>max</sub> 3011, 2948, 2104, 1752, 1492, 1143, 975, 834, cm<sup>-1</sup>.

**Synthesis of 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (CDBX, 2b):**<sup>6e</sup>



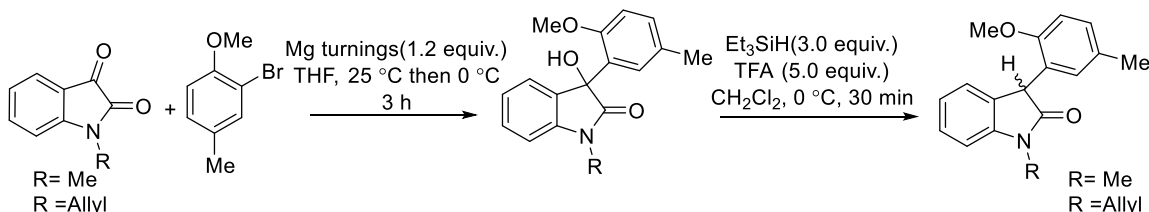
1-Acetoxy-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole **2ba** (1.16 g, 3.6 mmol, 1.00 equiv.) was taken in dichloromethane (12 mL) at room temperature. To this solution was added trimethylsilyl cyanide (0.9 mL, 7.2 mmol, 2.00 equiv.) drop wise over a period of 5 minutes at under N<sub>2</sub> atmosphere. The clear colorless solution was further stirred at room temperature for 20 hours and then solvent was removed to afford a white solid. Later,

pentane (10 mL) was added to the white solid and scratch over 2 minutes. Then it was filtered and dried in *vacuo* to afford 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole **2b** in 92% yield (956 mg) as a white solid.



**1-Cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxole (2b):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.05 (dd,  $J = 8.3, 1.0$  Hz, 1H), 7.62 (td,  $J = 7.3, 1.0$  Hz, 1H), 7.54 (ddd,  $J = 8.6, 7.1, 1.6$  Hz, 1H), 7.34 (dd,  $J = 7.5, 1.6$  Hz, 1H), 1.49 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.0, 131.6, 130.8, 128.2, 126.8, 111.5, 97.9, 80.3, 30.1; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{10}\text{H}_{10}\text{INONa}$  : 309.9699, found: 309.9684.<sup>6e</sup>

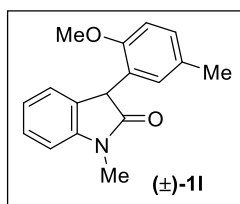
#### Experimental procedure for the synthesis of 3-Aryl 2-Oxindoles ( $\pm$ )-(1):



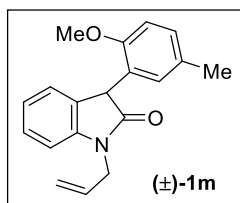
In an oven dried round-bottom flask, 2-Bromo-4-methyl anisole (10.00 mmol; 1.0 equiv.) was dissolved in 10 mL anhydrous THF. Mg turnings (292 mg; 12.00 mmol; 1.2 equiv.) were added. The reaction flask was briefly heated to initiate the reaction. The reaction mixture was then stirred under  $\text{N}_2$  until most of the Mg turnings had disappeared. The resulting Grignard solution was cooled to 0 °C and added dropwise to a solution of N-alkyl isatin (12.0 mmol, 1.2 equiv.) in THF (15 mL). The resulting solution was stirred at 0 °C for 1h, at which point TLC analysis indicated complete consumption of the starting material, and the reaction mixture was then quenched by the addition of saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in *vacuo* to give the crude alcohol.



The crude product (8.8 mmol; 1.0 equiv.) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> under a nitrogen atmosphere at 0 °C. Triethyl silane (4.3 mL; 26.4 mmol; 3.0 equiv.) was added to the solution. To that reaction mixture, TFA (3.4 mL; 44.0 mmol; 5.0 equiv.) was added dropwise over a period of 5 minutes at 0 °C and stirring was continued for 30 minutes. Upon completion of the reaction (Judged by TLC analysis) 5% (w/v) aqueous solution of sodium citrate was added drop wise to make the pH 5 of the mixture. The organic layer was separated, and the aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 x 100 mL). The combined organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude product was purified through flash column chromatography using Hexane-EtOAc mixture as eluent to afford the desired product.



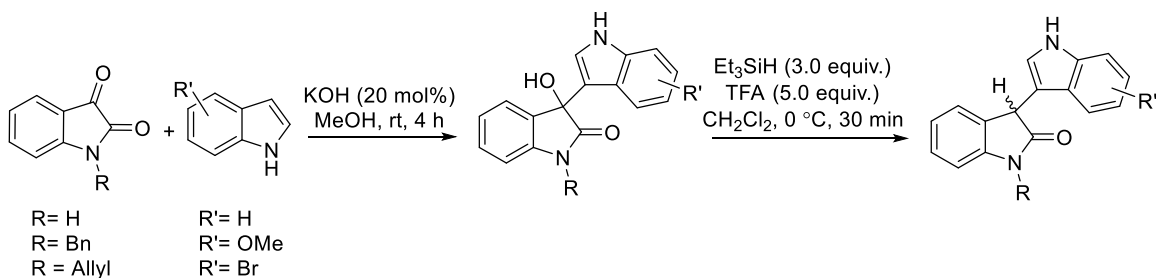
**3-(2-Methoxy-5-methylphenyl)-1-methylindolin-2-one (±)-(11):** 1.7g (overall yield 74% in 2 steps) of (11) as a yellowish gel.  $R_f = 0.40$  (30% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.25 (s, 1H), 7.09 – 7.01 (m, 2H), 6.97 (td,  $J = 7.5, 1.0$  Hz, 1H), 6.85 (d,  $J = 7.9$  Hz, 2H), 6.79 (d,  $J = 8.3$  Hz, 1H), 4.85 (s, 1H), 3.70 (s, 3H), 3.29 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.0, 155.4, 144.3, 130.5, 130.2, 130.0, 129.2, 127.8, 125.7, 124.1, 122.4, 111.5, 107.7, 56.0, 47.9, 26.4, 20.5; IR (film)  $\nu_{max}$  2934, 2762, 1705, 1678, 1037, 934, 864, 756 cm<sup>-1</sup>.



**1-Allyl-3-(2-methoxy-5-methylphenyl)indolin-2-one (±)-(1m):** 1.96g (overall yield 76% in 2 steps) of (1m) as a brownish gel.  $R_f = 0.43$  (30% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.27 – 7.19 (m, 1H), 7.06 (td,  $J = 6.4, 2.9$  Hz, 2H), 6.96 (t,  $J = 7.5$  Hz, 1H), 6.92 – 6.88 (m, 1H), 6.86 (d,  $J = 7.8$  Hz, 1H), 6.79 (d,  $J = 8.3$  Hz, 1H), 5.91 (ddt,  $J = 17.2, 10.5, 5.3$  Hz, 1H), 5.37 – 5.22 (m, 2H), 4.84 (s, 1H), 4.55 – 4.44 (m, 1H),

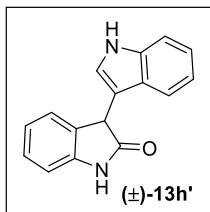
4.37 (ddt,  $J = 16.2, 5.5, 1.7$  Hz, 1H), 3.68 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 176.5, 155.4, 143.4, 131.8, 130.9, 130.2, 129.9, 129.3, 127.6, 125.7, 124.1, 122.3, 117.5, 111.6, 108.6, 55.9, 48.2, 42.5, 20.5; **IR** (film)  $\nu_{\text{max}}$  3014, 2756, 1733, 1674, 1107, 968, 832, 713  $\text{cm}^{-1}$ .

**Procedure for the Synthesis of Compound 3-Indolyl-2-Oxindoles ( $\pm$ )-(13):**

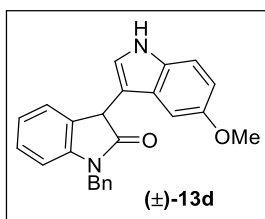


In an oven-dried round-bottom flask this isatin or isatin derivative (2.1 mmol, 1.0 equiv.) was taken in MeOH (10 mL) at 25 °C. To this solution was added indole or indole derivative (2.3 mmol, 1.1 equiv) Afterward (0.42 mmol, 0.2 equiv.) of KOH was added and stirring was continued for 5 h. After completion of the reaction confirmed by TLC, the reaction mixture was quenched with  $\text{H}_2\text{O}$  (100 mL) and diluted with EtOAc (3 X 15mL). The organic layer was collected dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. This was used for next step without further purification.

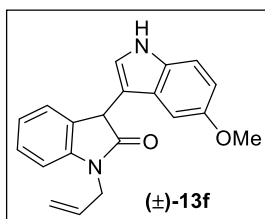
In an oven-dried round-bottom flask was charged with (1.6 mmol; 1.0 equiv.) of the crude product in  $\text{CH}_2\text{Cl}_2$  under a nitrogen atmosphere at 0 °C. Triethyl silane (4.8 mmol; 3.0 equiv.) was added to the solution. To that reaction mixture, TFA (8.0 mmol; 5.0 equiv.) was added drop-wise over a period of 5 minutes at 0 °C and stirring was continued for 30 minutes. Upon completion of the reaction (Judged by TLC analysis) 5% (w/v) aqueous solution of sodium citrate was added drop wise to make the pH 5 of the mixture. The organic layer was separated and the aqueous layer was washed with  $\text{CH}_2\text{Cl}_2$  (2 x 100 mL). The combined organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to afford the desired product.



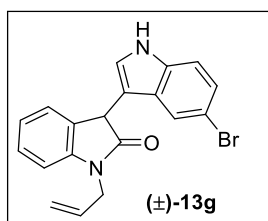
**3-(1H-Indol-3-yl)indolin-2-one (±)-(13h')**: 298 mg (overall yield 75% in 2 steps) of (13h') as a white solid. **m.p.** 111 °C;  $R_f = 0.35$  (50% EtOAc in hexane); **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 7.37 (d,  $J = 8.1$  Hz, 1H), 7.29 (s, 1H), 7.21 (t,  $J = 7.6$  Hz, 1H), 7.07 – 7.02 (m, 1H), 7.01 – 6.94 (m, 3H), 6.91 (t,  $J = 7.4$  Hz, 1H), 6.84 (t,  $J = 7.5$  Hz, 1H), 4.89 (s, 1H); **<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 178.5, 142.6, 142.6, 136.7, 130.8, 128.3, 126.2, 124.9, 122.2, 121.7, 119.1, 118.8, 112.1, 110.2, 109.8, 44.9; **IR** (film)  $\nu_{\max}$  3075, 2934, 2876, 1948, 1718, 1693, 1065, 987, 862, 776  $\text{cm}^{-1}$ .



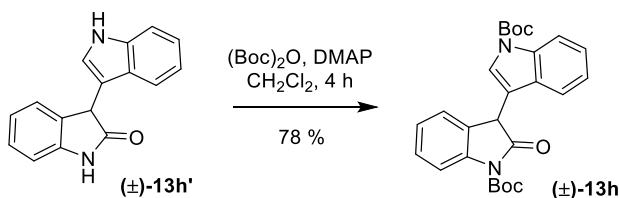
**1-Benzyl-3-(5-methoxy-1H-indol-3-yl)indolin-2-one (±)-(13d)**: 460 mg (overall yield 78% in 2 steps) of (13d) as a brownish gel.  $R_f = 0.40$  (30% EtOAc in hexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.30 (s, 1H), 7.35 (dd,  $J = 8.0, 1.7$  Hz, 2H), 7.33 – 7.26 (m, 3H), 7.23 – 7.14 (m, 3H), 7.01 – 6.97 (m, 2H), 6.86 – 6.81 (m, 1H), 6.78 (dd,  $J = 8.8, 2.4$  Hz, 1H), 6.54 (d,  $J = 2.4$  Hz, 1H), 5.10 (d,  $J = 15.6$  Hz, 1H), 4.94 (s, 1H), 4.89 (d,  $J = 15.6$  Hz, 1H), 3.55 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 176.8, 154.0, 143.4, 136.0, 131.8, 129.0, 128.8, 128.1, 127.7, 127.5, 126.6, 125.0, 124.3, 122.8, 112.6, 112.1, 110.3, 109.0, 100.9, 55.5, 44.7, 44.1; **IR** (film)  $\nu_{\max}$  2954, 2786, 1938, 1702, 1693, 1027, 958, 812, 743, 724  $\text{cm}^{-1}$ .



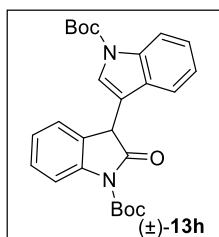
**1-Allyl-3-(5-methoxy-1*H*-indol-3-yl)indolin-2-one (±)-(13f)**: 367 mg (overall yield 72% in 2 steps) of **(13f)** as a brownish gel.  $R_f = 0.35$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.37 (s, 1H), 7.32 – 7.26 (m, 1H), 7.21 (d,  $J = 7.4$  Hz, 1H), 7.16 (d,  $J = 8.8$  Hz, 1H), 7.06 – 7.00 (m, 1H), 6.93 (d,  $J = 7.8$  Hz, 1H), 6.89 (d,  $J = 2.4$  Hz, 1H), 6.78 (dd,  $J = 8.8, 2.4$  Hz, 1H), 6.62 (d,  $J = 2.5$  Hz, 1H), 5.90 (ddt,  $J = 17.1, 10.5, 5.3$  Hz, 1H), 5.36 – 5.19 (m, 2H), 4.87 (s, 1H), 4.52 – 4.44 (m, 1H), 4.39 (ddt,  $J = 16.2, 5.6, 1.6$  Hz, 1H), 3.68 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 176.4, 154.0, 143.4, 131.8, 131.5, 129.1, 128.1, 126.6, 125.0, 124.3, 122.7, 117.8, 112.5, 112.2, 110.1, 108.9, 100.9, 55.6, 44.6, 42.6; **IR** (film)  $\nu_{\text{max}}$  3124, 2983, 2856, 2776, 1713, 1685, 1432, 1105, 952, 834, 773  $\text{cm}^{-1}$ .



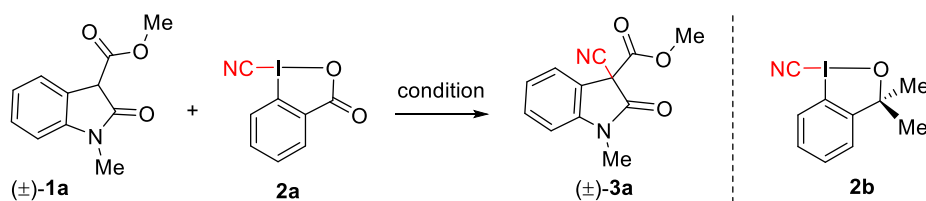
**1-Allyl-3-(5-bromo-1*H*-indol-3-yl)indolin-2-one (±)-(13g)**: 470 mg (overall yield 80% in 2 steps) of **(13g)** as a brownish gel.  $R_f = 0.38$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.75 (s, 1H), 7.35 (t,  $J = 7.9$  Hz, 1H), 7.31 (d,  $J = 8.6$  Hz, 1H), 7.20 (t,  $J = 7.7$  Hz, 2H), 7.08 (dd,  $J = 14.8, 7.8$  Hz, 2H), 7.00 (d,  $J = 7.9$  Hz, 1H), 6.86 (d,  $J = 2.5$  Hz, 1H), 5.97 (ddt,  $J = 16.1, 10.5, 5.4$  Hz, 1H), 5.42 – 5.29 (m, 2H), 4.87 (s, 1H), 4.50 (qd,  $J = 16.3, 5.3$  Hz, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 176.4, 143.2, 135.3, 131.3, 128.6, 128.3, 127.8, 125.0, 124.9, 124.8, 122.9, 121.6, 118.0, 113.0, 112.9, 109.9, 109.2, 44.5, 42.7; **IR** (film)  $\nu_{\text{max}}$  3167, 3034, 2836, 1932, 1718, 1694, 1665, 1045, 975, 854, 737  $\text{cm}^{-1}$ .

**Procedure for the Synthesis of Compound (±)-(13h):**

In an oven-dried round-bottom flask compound **13h'** (250 mg, 1.0 mmol, 1.0 equiv.) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (8 mL). The reaction vessel was placed in a magnetic stirrer and stirred at room temperature then di-*tert*-butyl dicarbonate (Boc anhydride) (735 μL, 3.2 mmol, 3.2 equiv.) and N, N-dimethylaminopyridine (DMAP) (25 mg, 0.2 mmol, 0.2 equiv.) were added sequentially. After 1 h, MeOH (3 mL) was added to the reaction mixture and stirring was continued for 8 h, upon completion of the reaction confirmed by TLC, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl (3 mL). and diluted with EtOAc (3 X 10 mL). The organic layer was collected dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (1:19 ethyl acetate/hexanes) to afford the title compound **13h** as a orange foam (314 mg, 70%).



**tert-Butyl 3-(1-(tert-butoxycarbonyl)-2-oxoindolin-3-yl)-1H-indole-1-carboxylate (±)-(13h):**  $R_f = 0.6$  (30% EtOAc in hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.15 (s, 1H), 7.99 (d,  $J = 8.3$  Hz, 1H), 7.51 (s, 1H), 7.43 – 7.38 (m, 1H), 7.33 (ddd,  $J = 8.4, 7.0, 1.4$  Hz, 2H), 7.24 (dt,  $J = 7.6, 1.4$  Hz, 1H), 7.18 (tdd,  $J = 7.3, 5.7, 1.0$  Hz, 2H), 4.99 (s, 1H), 1.68 (s, 9H), 1.66 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 173.3, 149.4, 140.3, 128.8, 126.5, 125.0, 125.0, 124.8, 124.7, 124.7, 124.7, 122.8, 119.6, 115.5, 115.4, 115.4, 115.2, 84.5, 84.0, 44.7, 28.2, 28.1; IR (film)  $\nu_{max}$  3084, 2986, 2798, 2088, 1744, 1728, 1696, 1678, 1267, 1086, 812, 733 cm<sup>-1</sup>.

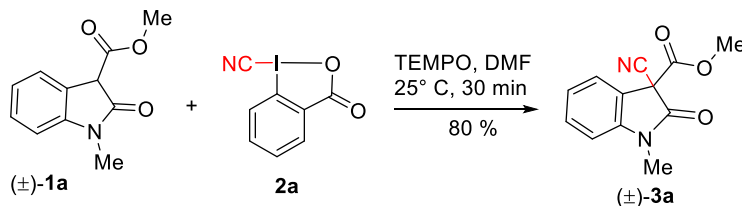
**Table 1:-Optimization of the reaction condition for oxidative cyanide addition of 1a:**

entry <sup>a</sup>	cyanide source	solvent	temp	time	% yield <sup>b</sup> ( <b>3a</b> )
1	<b>2a</b>	THF	25 °C	6 h	26
2	<b>2a</b>	THF	50 °C	4 h	ND
3	<b>2a</b>	Et <sub>2</sub> O	25 °C	8 h	34
4	<b>2a</b>	PhMe	25 °C	8 h	42
5	<b>2a</b>	PhMe	40 °C	5 h	46
6	<b>2a</b>	PhMe	90 °C	5 h	12 <sup>c</sup>
7	<b>2a</b>	CH <sub>2</sub> Cl <sub>2</sub>	25 °C	5 h	28
8	<b>2a</b>	CHCl <sub>3</sub>	25 °C	5 h	30
9	<b>2a</b>	(CH <sub>2</sub> Cl) <sub>2</sub>	25 °C	5 h	42
10	<b>2a</b>	DMF	25 °C	20 min	82
11	<b>2a</b>	DMF	0 °C	8 h	38
12	<b>2a</b>	DMF	40 °C	2 h	64 <sup>c</sup>
13	<b>2a</b>	DMF	60 °C	3 h	58 <sup>c</sup>
14	<b>2a</b>	DMA	25 °C	5 h	36
15	<b>2a</b>	MeNO <sub>2</sub>	25 °C	8 h	17
16	<b>2a</b>	CH <sub>3</sub> CN	25 °C	8 h	26
17	<b>2a</b>	(CH <sub>2</sub> OMe) <sub>2</sub>	25 °C	8 h	24
18	<b>2b</b>	DMF	25 °C	2 h	72
19	<b>2b</b>	DMA	25 °C	4 h	34
20	<b>2b</b>	CHCl <sub>3</sub>	25 °C	3 h	39
21	<b>2b</b>	(CH <sub>2</sub> Cl) <sub>2</sub>	25 °C	4 h	46
22	<b>2b</b>	PhMe	25 °C	4 h	43

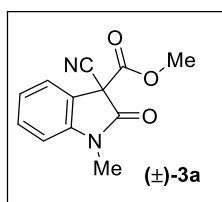
<sup>a</sup>reactions were carried out using 0.20 mmol of **1a** with 0.22 mmol of **2a-b** in 1 mL solvent. <sup>b</sup>yields after column purification. <sup>c</sup>decomposition of cyanation product was observed at higher temperature.

**Experimental procedure A for the synthesis of 3-cyano-2-oxindole:** A 10 mL round bottom flask was charged with a magnetic stir bar, 3-substituted-2-oxindole (0.20 mmol, 1.0 equiv.) and the indicated solvent DMF (1.0 mL). To this solution was added the cyano source (60 mg, 0.22 mmol, 1.1 equiv.). The resulting reaction mixture was stirred with an open flask for 20 minutes at room temperature. The reaction was monitored by TLC analysis UV, Iodine, Cerium Molybdate. After completion, this reaction was quenched by water (2 mL) and extracted with EtOAc (3 x 4 mL). The organic layer was recombined and washed with saturated NaHCO<sub>3</sub> (2 mL), brine (2 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered and evaporated. The crude product was purified through flash column chromatography using Hexane-EtOAc mixture as eluent to afford the desired cyanation product.

**Experimental procedure B for the Synthesis of 3-cyano -2-oxindole:** An oven-dried round bottom flask was charged with a magnetic stir bar, 3-substituted-2-oxindole (0.2 mmol, 1.0 equiv.) and the indicated solvent DMF (1.0 mL). To this solution was added the cyano source (60 mg, 0.22 mmol, 1.1 equiv.) and 1, 1, 3, 3-Tetramethylguanidine (TMG) base (28  $\mu$ L, 0.22 mmol, 1.1 equiv.) was added. The resulting reaction mixture was stirred with an open flask for 30 minutes at room temperature. The reaction was monitored by TLC analysis UV, Iodine, Cerium Molybdate. After completion, this reaction was quenched by water (2 mL) and extracted with EtOAc (3 x 4 mL). The organic layer was recombined and washed with saturated NaHCO<sub>3</sub> (2 mL), brine (2 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered and evaporated. The crude product was purified through flash column chromatography using Hexane-EtOAc mixture as eluent to afford the desired cyanation product.

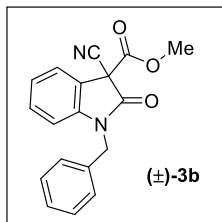
**Experimental procedure for mechanistic investigation of the key reaction:**

A 10 mL round bottom flask was charged with a magnetic stir bar, 3-substituted- 2-oxindole (0.20 mmol, 1.0 equiv.) and the indicated solvent DMF (1.0 mL). To this solution was added (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (35 mg, 0.22 mmol, 1.1 equiv.) and then the cyano source **2a** (60 mg, 0.22 mmol, 1.1 equiv.). The resulting reaction mixture was stirred with an open flask for 30 minutes at room temperature. The reaction was monitored by TLC analysis UV, Iodine, Cerium Molybdate. After completion, this reaction was quenched by water (2 mL) and extracted with EtOAc (3 x 4 mL). The organic layer was recombined and washed with saturated NaHCO<sub>3</sub> (2 mL), brine (2 mL). The combined organic extracts were dried over anhydrous sodium sulphate, filtered and evaporated. The crude product was purified through flash column chromatography using Hexane-EtOAc mixture as eluent, and finally we got the cyanation product **3a** (36.8 mg, 80 % yield).

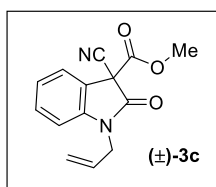


**Methyl 3-cyano-1-methyl-2-oxindole-3-carboxylate (±)-(3a):** According to the experimental procedure **A** The compound **3a** was obtained as yellow gel (0.2 mmol scale of reaction, 38.0 mg of product, 82% yield);  $R_f = 0.55$  (30% EtOAc in hexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.47 – 7.42 (m, 2H), 7.18 (dd,  $J = 7.7, 1.1$  Hz, 1H), 6.91 (dd,  $J = 8.1, 1.0$  Hz, 1H), 3.84 (s, 3H), 3.28 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 165.2, 162.9, 143.7, 131.6, 124.5, 124.2, 121.9, 113.1, 109.6, 54.9, 53.4, 27.4; **IR** (film)  $\nu_{\text{max}}$  3134, 2974, 2896, 2238, 1743, 1687, 1678, 1027, 934 cm<sup>-1</sup>; **HRMS** (ESI-TOF)  $m/z$ : [M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>Na : 253.0584, found: 253.0588.

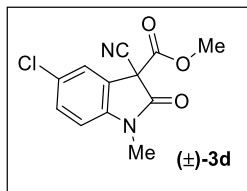




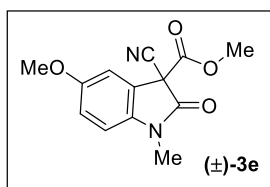
**Methyl 1-benzyl-3-cyano-2-oxindoline-3-carboxylate (±)-(3b):** According to the experimental procedure **A** The compound **3b** was obtained as yellow gel (0.5 mmol scale of reaction, 116.5 mg of product, 76% yield);  $R_f = 0.57$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.50 (dd,  $J = 7.7, 1.2$  Hz, 1H), 7.36 (tdd,  $J = 11.4, 7.5, 5.2$  Hz, 6H), 7.17 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.81 (d,  $J = 7.9$  Hz, 1H), 5.15 (d,  $J = 15.8$  Hz, 1H), 4.84 (d,  $J = 15.8$  Hz, 1H), 3.91 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.6, 163.0, 142.9, 134.1, 131.5, 129.0, 128.2, 127.1, 124.4, 124.2, 121.9, 113.1, 110.7, 54.9, 53.6, 44.8; **IR** (film)  $\nu_{\text{max}}$  3254, 2863, 2841, 2245, 2156, 1767, 1676, 1389, 1179, 1043  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$  : 329.0897, found: 329.0919.



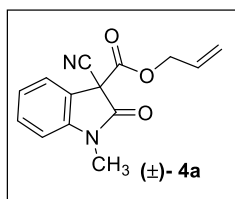
**Methyl 1-allyl-3-cyano-2-oxindoline-3-carboxylate (±)-(3c):** According to the experimental procedure **A** The compound **3c** was obtained as light yellow gel (0.5 mmol scale of reaction, 95.5 mg of product, 73% yield).;  $R_f = 0.53$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.46 – 7.37 (m, 2H), 7.15 (td,  $J = 7.7, 1.1$  Hz, 1H), 6.89 (d,  $J = 8.0$  Hz, 1H), 5.82 (ddd,  $J = 12.2, 10.3, 5.1$  Hz, 1H), 5.30 – 5.19 (m, 2H), 4.51 – 4.39 (m, 1H), 4.33 – 4.23 (m, 1H), 3.84 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.9, 142.9, 141.9, 131.5, 129.7, 124.4, 124.2, 121.9, 118.4, 113.1, 110.5, 54.9, 53.5, 43.3; **IR** (film)  $\nu_{\text{max}}$  3150, 2860, 2758, 2250, 2140, 1746, 1694, 1423, 1251, 1189, 821  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3\text{Na}$  : 279.0740, found: 279.0770.



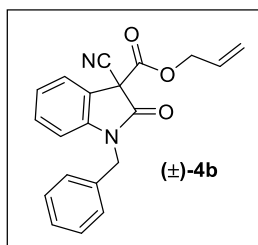
**Methyl 5-chloro-3-cyano-1-methyl-2-oxindoline-3-carboxylate (±)-(3d):** According to the experimental procedure **A** The compound **3d** was obtained as brown gel (0.5 mmol scale of reaction, 87.3 mg of product, 66% yield).;  $R_f = 0.50$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43 (d,  $J = 7.0$  Hz, 2H), 6.87 – 6.82 (m, 1H), 3.87 (s, 3H), 3.26 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.7, 162.3, 142.3, 131.6, 129.6, 125.0, 123.0, 112.5, 110.6, 55.1, 53.2, 27.6; **IR** (film)  $\nu_{\text{max}}$  3134, 2936, 2743, 2218, 2140, 1726, 1676, 1580, 1391, 1154, 1064, 939, 796  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{12}\text{H}_9\text{ClN}_2\text{O}_3\text{Na}$  : 287.0194, found: 287.0222.



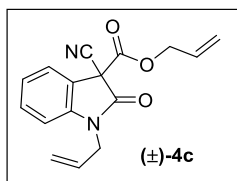
**Methyl 3-cyano-5-methoxy-1-methyl-2-oxindoline-3-carboxylate (±)-(3e):** According to the experimental procedure **A** The compound **3e** was obtained as yellow gel (0.5 mmol scale of reaction, 96.3 mg of product, 74% yield);  $R_f = 0.48$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.03 (d,  $J = 2.5$  Hz, 1H), 6.96 (dd,  $J = 8.6, 2.6$  Hz, 1H), 6.82 (d,  $J = 8.6$  Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.25 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.8, 162.9, 156.9, 136.9, 122.7, 116.4, 113.1, 111.2, 110.2, 56.0, 54.9, 53.8, 27.5; **IR** (film)  $\nu_{\text{max}}$  3146, 2976, 2851, 2265, 2034, 1697, 1680, 1367, 1260, 1129, 964, 741  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4\text{Na}$  : 283.0689, found: 283.0680.



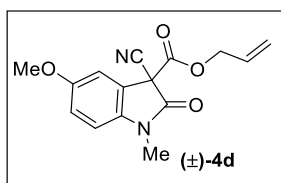
**Allyl 3-cyano-1-methyl-2-oxindoline-3-carboxylate** ( $\pm$ )-(**4a**): According to the experimental procedure **A** The compound **4a** was obtained as yellow gel (0.5 mmol scale of reaction, 111.5 mg of product, 87% yield);  $R_f = 0.55$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.47 – 7.42 (m, 2H), 7.17 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.92 (dd,  $J = 8.2, 1.0$  Hz, 1H), 5.84 (ddt,  $J = 17.3, 10.4, 5.6$  Hz, 1H), 5.33 – 5.21 (m, 2H), 4.71 (dt,  $J = 5.8, 1.5$  Hz, 2H), 3.27 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.2, 162.1, 143.7, 131.6, 130.1, 128.0, 124.2, 121.9, 119.8, 113.0, 109.7, 68.3, 53.6, 27.4; **IR** (film)  $\nu_{\text{max}}$ , 3043, 2763, 2835, 2267, 2138, 1724, 1688, 1481, 1261, 1048, 936, 727  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_3$ : 257.0921, found: 257.0911.



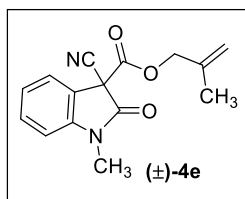
**Allyl 1-benzyl-3-cyano-2-oxindoline-3-carboxylate** ( $\pm$ )-(**4b**): According to the experimental procedure **A** The compound **4b** was obtained as orange gel (0.5 mmol scale of reaction, 136.2 mg of product, 82% yield);  $R_f = 0.58$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.45 (d,  $J = 7.5$  Hz, 1H), 7.30 (h,  $J = 4.2, 3.8$  Hz, 6H), 7.12 (t,  $J = 7.6$  Hz, 1H), 6.76 (d,  $J = 7.9$  Hz, 1H), 5.91 – 5.77 (m, 1H), 5.37 – 5.23 (m, 2H), 5.15 (d,  $J = 15.8$  Hz, 1H), 4.78 (s, 1H), 4.74 – 4.67 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.5, 162.2, 142.9, 134.1, 131.4, 130.0, 129.0, 128.1, 127.1, 124.4, 124.2, 121.9, 120.1, 113.0, 110.7, 68.4, 53.8, 44.8; **IR** (film) 3021, 2978, 2764, 2273, 2151, 1738, 1671, 1654, 1345, 1321, 1143, 1034, 938, 736  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$ : 329.0897, found: 329.0919.



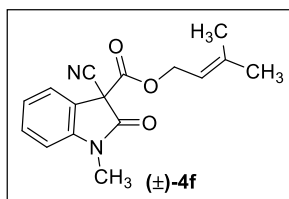
**Allyl 1-allyl-3-cyano-2-oxindoline-3-carboxylate** ( $\pm$ )-(**4c**): According to the experimental procedure **A** The compound **4c** was obtained as light yellow gel (0.5 mmol scale of reaction, 103.0 mg of product, 73% yield);  $R_f = 0.55$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.53 – 7.48 (m, 1H), 7.45 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.20 (td,  $J = 7.7, 1.0$  Hz, 1H), 6.93 (d,  $J = 7.9$  Hz, 1H), 5.93 – 5.80 (m, 2H), 5.39 – 5.26 (m, 4H), 4.75 (tt,  $J = 5.8, 1.4$  Hz, 2H), 4.56 – 4.47 (m, 1H), 4.31 (ddt,  $J = 16.6, 5.2, 1.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.0, 162.1, 143.0, 131.4, 130.0, 129.7, 124.4, 124.1, 121.9, 119.9, 118.3, 113.0, 110.5, 68.3, 53.7, 43.3; **IR** (film)  $\nu_{\text{max}}$  3046, 2864, 2732, 2189, 2128, 1711, 1686, 1294, 1154, 1031, 921, 862  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$  : 305.0897, found: 305.0922.



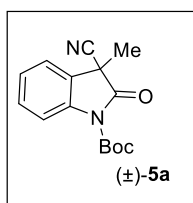
**Allyl 3-cyano-5-methoxy-1-methyl-2-oxindoline-3-carboxylate** ( $\pm$ )-(**4d**): According to the experimental procedure **A** The compound **4d** was obtained as yellow gel (0.5 mmol scale of reaction, 90.2 mg of product, 63% yield);  $R_f = 0.53$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.08 (d,  $J = 2.5$  Hz, 1H), 7.00 (dd,  $J = 8.6, 2.6$  Hz, 1H), 6.86 (d,  $J = 8.6$  Hz, 1H), 5.90 (ddt,  $J = 17.2, 10.5, 5.7$  Hz, 1H), 5.41 – 5.27 (m, 2H), 4.76 (ddt,  $J = 5.9, 4.6, 1.4$  Hz, 2H), 3.84 (s, 3H), 3.29 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.9, 162.1, 156.9, 137.0, 130.1, 122.8, 119.9, 116.4, 113.1, 111.1, 110.2, 68.3, 56.0, 29.7, 27.5; **IR** (film)  $\nu_{\text{max}}$  3084, 2839, 2756, 2259, 2153, 1728, 1588, 1294, 1241, 1184, 823, 798  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4\text{Na}$ : 309.0846, found: 309.0848.



**2-Methylallyl 3-cyano-1-methyl-2-oxoindoline-3-carboxylate** ( $\pm$ )-(**4e**): According to the experimental procedure **A** The compound **4e** was obtained as light yellow gel (0.5 mmol scale of reaction, 97.3 mg of product, 72% yield);  $R_f = 0.52$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.78 (d,  $J = 7.5$  Hz, 1H), 7.41 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.16 (td,  $J = 7.6, 0.9$  Hz, 1H), 6.91 – 6.88 (m, 1H), 5.14 – 4.97 (m, 2H), 4.74 (s, 2H), 3.30 (s, 3H), 1.84 (t,  $J = 1.1$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.4, 157.2, 153.4, 143.2, 139.5, 131.0, 123.4, 121.4, 119.8, 113.57, 108.8, 69.5, 56.4, 25.7, 19.4; **IR** (film)  $\nu_{\text{max}}$  3084, 2996, 2732, 2309, 2118, 1731, 1643, 1195, 1181, 951, 874  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$  : 293.0897, found: 293.0893.

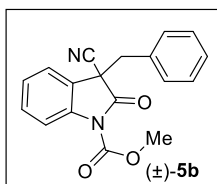


**3-Methylbut-2-en-1-yl 3-cyano-1-methyl-2-oxoindoline-3-carboxylate** ( $\pm$ )-(**4f**): According to the experimental procedure **A** The compound **4f** was obtained as light yellow gel (0.5 mmol scale of reaction, 109.4 mg of product, 77% yield);  $R_f = 0.55$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) 7.48 (t,  $J = 7.8$  Hz, 2H), 7.20 (td,  $J = 7.7, 1.0$  Hz, 1H), 6.94 (dt,  $J = 7.5, 1.0$  Hz, 1H), 5.32 (tdt,  $J = 7.3, 2.9, 1.4$  Hz, 1H), 4.80 – 4.68 (m, 2H), 3.31 (s, 3H), 1.76 (d,  $J = 1.3$  Hz, 3H), 1.69 (d,  $J = 1.4$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.3, 162.4, 143.7, 141.6, 131.4, 124.3, 124.1, 122.1, 116.7, 113.2, 109.6, 65.1, 53.6, 27.4, 25.7, 18.1; **IR** (film)  $\nu_{\text{max}}$  3138, 3054, 2876, 2765, 2306, 2297, 1757, 1648, 1264, 1154, 1039, 928, 776  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$ : 307.1053, found: 307.1070.

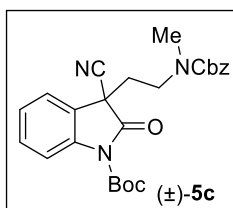


**tert-Butyl 3-cyano-3-methyl-2-oxoindoline-1-carboxylate** ( $\pm$ )-(**5a**): According to the experimental procedure **A** The compound **5a** was obtained as light yellow gel (0.5 mmol

scale of reaction, 114.4 mg of product, 84% yield);  $R_f = 0.48$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.89 – 7.84 (m, 1H), 7.40 (t,  $J = 7.7$  Hz, 2H), 7.28 – 7.20 (m, 1H), 1.84 (s, 3H), 1.62 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 169.0, 148.4, 138.7, 130.5, 125.6, 125.5, 123.5, 117.0, 115.9, 85.7, 43.1, 28.0, 24.5; **IR** (film)  $\nu_{\text{max}}$  2976, 2865, 2761, 2237, 1731, 1671, 1263, 1104, 1013, 873  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$ : 295.1053, found: 295.1078.

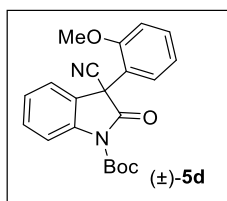


**Methyl 3-benzyl-3-cyano-2-oxoindoline-1-carboxylate (±)-(**5b**)**: According to the experimental procedure **A** The compound **5b** was obtained as yellow solid (0.5 mmol scale of reaction, 110.3 mg of product, 72% yield).; **mp** 115-120 °C;  $R_f = 0.55$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.82 (d,  $J = 8.2$  Hz, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.18 (m, 1H), 7.12 (d,  $J = 7.6$  Hz, 1H), 6.99 (d,  $J = 7.3$  Hz, 2H), 4.01 (s, 3H), 3.59 (dd,  $J = 13.2, 1.8$  Hz, 1H), 3.39 (dd,  $J = 13.3, 1.8$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.1, 150.4, 138.8, 131.5, 130.7, 130.3, 128.4, 128.3, 125.4, 124.7, 123.1, 116.1, 115.7, 54.4, 48.9, 44.0; **IR** (film)  $\nu_{\text{max}}$  3046, 2978, 2836, 2147, 2030, 1712, 1684, 1231, 1163, 1049, 821  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$ : 329.0897, found: 329.0880.



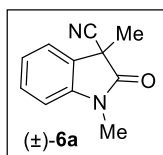
**tert-Butyl 3-(2-(((benzyloxy)carbonyl)(methyl)amino)ethyl)-3-cyano-2-oxoindoline-1-carboxylate (±)-(**5c**)**: According to the experimental procedure **A** The compound **5c** was obtained as colorless gel (0.5 mmol scale of reaction, 191.1 mg of product, 85% yield);  $R_f = 0.56$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.2$  Hz, 1H), 7.55 – 7.41 (m, 1H), 7.31 (q,  $J = 6.5$  Hz, 6H), 7.19 (d,  $J = 31.1$  Hz, 1H), 5.01 (d,

$J = 19.6$  Hz, 2H), 3.43 (d,  $J = 50.9$  Hz, 2H), 2.86 (s, 3H), 2.53 – 2.28 (m, 2H), 1.63 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 171.1, 148.2, 139.2, 132.9, 130.7, 128.5, 128.5, 128.1, 125.6, 115.9, 85.9, 67.3, 60.4, 45.7, 28.0, 21.0, 14.2; IR (film)  $\nu_{\text{max}}$  3030, 2943, 2864, 2198, 2106, 1722, 1680, 1308, 1243, 1021, 978, 721  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{27}\text{N}_3\text{O}_5\text{Na}$ : 472.1843, found: 472.1869.



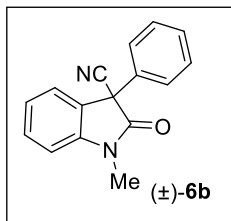
**tert-Butyl 3-cyano-3-(2-methoxyphenyl)-2-oxoindoline-1-carboxylate** (±)-(**5d**):

According to the experimental procedure **A** The compound **5d** was obtained as yellow gel (0.5 mmol scale of reaction, 151.2 mg of product, 83% yield);  $R_f = 0.50$  (30% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.30 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.90 (dd,  $J = 8.1, 1.4$  Hz, 1H), 7.82 (td,  $J = 7.7, 1.4$  Hz, 1H), 7.62 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.46 – 7.40 (m, 1H), 7.10 – 7.01 (m, 2H), 6.97 (d,  $J = 7.9$  Hz, 1H), 3.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.8, 144.2, 141.9, 133.8, 133.0, 132.0, 131.2, 130.7, 128.0, 126.2, 124.0, 123.3, 116.0, 109.5, 52.3, 28.0; IR (film)  $\nu_{\text{max}}$  3018, 2936, 2226, 1719, 1678, 1098, 1012, 852  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}$  : 387.1315, found: 387.1323.

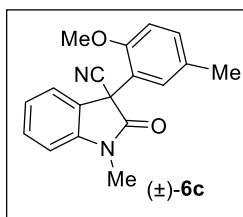


**1,3-Dimethyl-2-oxoindoline-3-carbonitrile** (±)-(**6a**): According to the experimental procedure **B** The compound **6a** was obtained as white solid (0.5 mmol scale of reaction, 75.4 mg of product, 81% yield);  $R_f = 0.42$  (30% EtOAc in hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.47 – 7.41 (m, 2H), 7.20 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.93 (dt,  $J = 7.9, 0.8$  Hz, 1H), 3.29 (s, 3H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 171.0, 142.6, 130.3, 126.8, 123.9, 123.8, 117.6, 109.2, 42.1, 27.0, 23.4; IR (film)  $\nu_{\text{max}}$  2945, 2851, 2238,

2167, 1683, 1289, 1062, 967  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{ONa}$  : 209.0685, found: 209.0705.



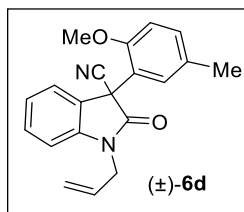
**1-Methyl-2-oxo-3-phenylindoline-3-carbonitrile** ( $\pm$ )-(**6b**): According to the experimental procedure **B** The compound **6b** was obtained as yellow gel (0.5 mmol scale of reaction, 88.1 mg of product, 71% yield);  $R_f = 0.52$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.45 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.35 (dd,  $J = 5.5, 2.8$  Hz, 6H), 7.19 (ddd,  $J = 8.9, 4.2, 1.8$  Hz, 1H), 6.97 (d,  $J = 7.9$  Hz, 1H), 3.25 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 169.7, 143.4, 141.9, 133.7, 130.8, 129.3, 128.0, 126.6, 125.5, 124.2, 116.8, 109.4, 51.8, 27.3; **IR** (film)  $\nu_{\text{max}}$  3128, 2921, 2882, 2265, 1692, 1363, 1714, 1267, 1183, 1091, 854  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}$  : 249.1022, found: 249.1048.



**3-(2-Methoxy-5-methylphenyl)-1-methyl-2-oxoindoline-3-carbonitrile** ( $\pm$ )-(**6c**): According to the experimental procedure **B** The compound **6c** was obtained as light yellow gel (0.5 mmol scale of reaction, 119.9 mg of product, 82% yield);  $R_f = 0.45$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.64 (d,  $J = 2.3$  Hz, 1H), 7.35 (td,  $J = 7.7, 1.4$  Hz, 1H), 7.13 (td,  $J = 8.1, 7.4, 1.7$  Hz, 2H), 7.03 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.90 (d,  $J = 7.9$  Hz, 1H), 6.70 (d,  $J = 8.3$  Hz, 1H), 3.43 (s, 3H), 3.33 (s, 3H), 2.37 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.6, 154.0, 143.6, 131.0, 130.9, 130.0, 129.9, 126.8, 124.0, 123.5, 122.2, 116.4, 112.5, 108.4, 56.1, 50.8, 27.2, 20.6; **IR** (film)  $\nu_{\text{max}}$  3141,

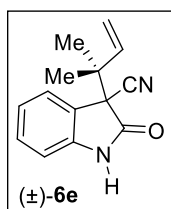


2926, 2761, 2168, 2106, 1717, 1677, 1396, 1028, 989, 877  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$  : 315.1104, found: 315.1093.



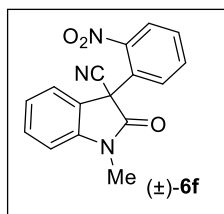
**1-Allyl-3-(2-methoxy-5-methylphenyl)-2-oxoindoline-3-carbonitrile** (±)-(**6d**):

According to the experimental procedure **B** The compound **6d** was obtained as light yellow gel (0.5 mmol scale of reaction, 121.0 mg of product, 76% yield);  $R_f = 0.48$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.66 (d,  $J = 2.1$  Hz, 1H), 7.31 (td,  $J = 7.7, 1.4$  Hz, 1H), 7.13 (ddd,  $J = 13.0, 7.9, 1.7$  Hz, 2H), 7.02 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.91 (d,  $J = 7.9$  Hz, 1H), 6.71 (d,  $J = 8.3$  Hz, 1H), 5.91 (ddt,  $J = 17.2, 10.3, 5.7$  Hz, 1H), 5.40 (dq,  $J = 17.2, 1.5$  Hz, 1H), 5.32 (dq,  $J = 10.3, 1.4$  Hz, 1H), 4.50 (ddt,  $J = 16.0, 5.5, 1.6$  Hz, 1H), 4.39 (ddt,  $J = 16.0, 5.9, 1.6$  Hz, 1H), 3.42 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.1, 154.0, 142.7, 131.0, 131.0, 130.8, 130.2, 129.8, 126.8, 124.0, 123.4, 121.9, 118.7, 112.45, 109.3, 106.9, 55.8, 43.5, 20.6; **IR** (film)  $\nu_{\text{max}}$  3083, 2889, 2764, 2146, 2116, 1701, 1687, 1357, 1258, 1012, 908  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{Na}$  : 341.1260, found: 341.1233.



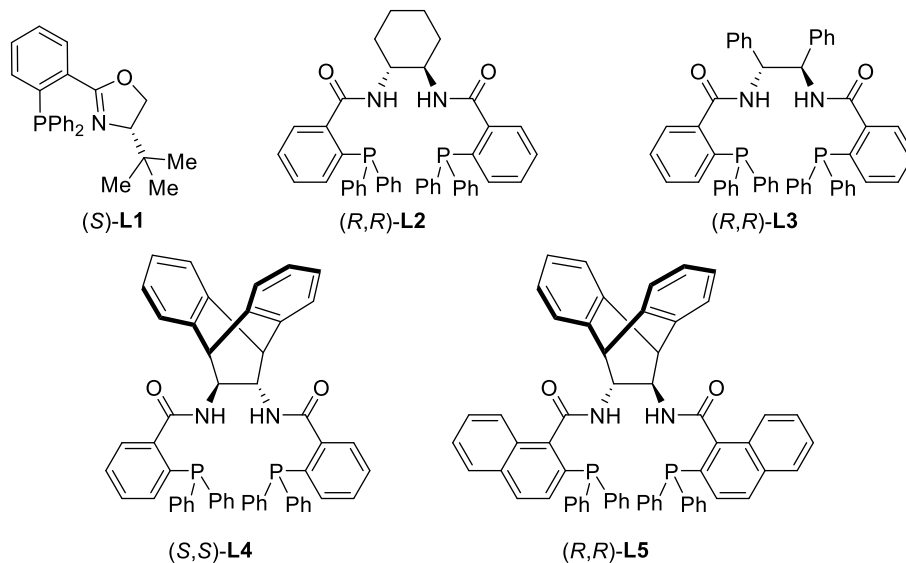
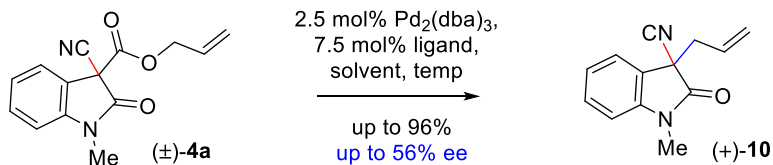
**3-(2-Methylbut-3-en-2-yl)-2-oxoindoline-3-carbonitrile** (±)-(**6e**): According to the experimental procedure **B** The compound **6e** was obtained as light yellow gel (0.5 mmol scale of reaction, 81.5 mg of product, 72% yield);  $R_f = 0.45$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.65 (s, 1H), 7.42 (d,  $J = 7.7$  Hz, 1H), 7.35 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.11 (td,  $J = 7.7, 1.1$  Hz, 1H), 6.96 (d,  $J = 7.8$  Hz, 1H), 5.99 (dd,  $J = 17.3, 10.7$  Hz, 1H), 5.23 (d,  $J = 10.7$  Hz, 1H), 5.10 (d,  $J = 17.3$  Hz, 1H), 1.46 (s, 3H), 1.25 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 171.7, 140.7, 140.1, 130.3, 126.3, 124.6, 122.8, 116.3,

116.2, 110.3, 54.5, 44.1, 23.0, 20.8; **IR** (film)  $\nu_{\max}$  3024, 2967, 2743, 2257, 1727, 1347, 1023, 985, 863  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{Na}$  : 249.0998, found: 249.1022.



**1-Methyl-3-(2-nitrophenyl)-2-oxoindoline-3-carbonitrile (±)-(**6f**):** According to the experimental procedure **A** The compound **6f** was obtained as reddish gel (0.5 mmol scale of reaction, 127.6 mg of product, 87% yield);  $R_f = 0.40$  (30% EtOAc in hexane); **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.30 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.90 (dd,  $J = 8.1, 1.4$  Hz, 1H), 7.82 (td,  $J = 7.7, 1.4$  Hz, 1H), 7.62 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.46 – 7.40 (m, 1H), 7.10 – 7.01 (m, 2H), 6.97 (d,  $J = 7.9$  Hz, 1H), 3.37 (s, 3H); **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 168.8, 144.2, 141.9, 133.8, 133.0, 132.0, 131.2, 130.7, 128.0, 126.2, 124.0, 123.3, 116.0, 109.5, 52.3, 27.5; **IR** (film)  $\nu_{\max}$  3024, 2968, 2864, 2156, 1707, 1157, 1048, 962  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3\text{Na}$  : 316.0693, found: 316.0694.

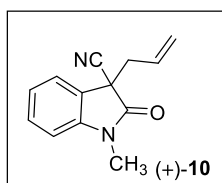
**Optimization of the reaction condition for catalytic decarboxylative allylations (DcA):**



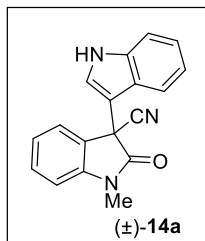
entry <sup>a</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>	ligand	solvent	temp	time	% yield (10) <sup>b</sup>	% ee <sup>c</sup>
1	2.5% mol%	7.5 mol% L1	Et <sub>2</sub> O	25 °C	12 h	89%	02% ee
2	2.5% mol%	7.5 mol% L2	Et <sub>2</sub> O	25 °C	11 h	95%	18% ee
3	2.5% mol%	7.5 mol% L3	Et <sub>2</sub> O	25 °C	12 h	94%	40% ee
4	2.5% mol%	7.5 mol% L4	Et <sub>2</sub> O	25 °C	10 h	93%	50% ee
5	2.5% mol%	7.5 mol% L5	Et <sub>2</sub> O	25 °C	11 h	82%	46% ee
6	2.5% mol%	7.5 mol% L4	PhMe	25 °C	12 h	88%	37% ee
7	2.5% mol%	7.5 mol% L4	1,4-dioxan	25 °C	14 h	32%	ND <sup>d</sup>
8	2.5% mol%	7.5 mol% L4	Ph <sub>2</sub> O	25 °C	16 h	91%	31% ee
9	2.5% mol%	7.5 mol% L4	1,2-DME	25 °C	15 h	90%	30% ee
10	2.5% mol%	7.5 mol% L4	THF	25 °C	18 h	69%	24% ee
11	2.5% mol%	7.5 mol% L4	PhH	25 °C	14 h	92%	38% ee
12	2.5% mol%	7.5 mol% L3	Et <sub>2</sub> O	0 °C	16 h	91%	50% ee
13	2.5% mol%	7.5 mol% L4	Et <sub>2</sub> O	0 °C	16 h	94%	56% ee
14	5% mol%	15 mol% L4	Et <sub>2</sub> O	0 °C	9 h	96%	56% ee
15	2.5% mol%	7.5 mol% L4	Et <sub>2</sub> O	-10 °C	18 h	90%	55% ee
16	2.5% mol%	7.5 mol% L3	Et <sub>2</sub> O	-10 °C	17 h	90%	51% ee

<sup>a</sup>reactions were carried out using 0.09 mmol of **4a** with in 3 mL solvent. <sup>b</sup>yields after column purification. <sup>c</sup>ee's were determined by chiralpak IB column. <sup>d</sup>not determined.

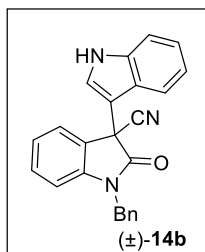
**Procedure for Catalytic Enantioselective Decarboxylative Allylations:** In an oven-dried sealed tube, Et<sub>2</sub>O was degassed by using nitrogen balloon at room temperature over a period of 15 min. 2.5 mol % of Pd<sub>2</sub>(dba)<sub>3</sub> and 7.5 mol % of ligand were added to it and stirring was continued for 15 min to make the complex mixture. After that reaction mixture was cooled to 0 °C. In another vessel ester (±)-**4a** (0.09 mmol; 1.0 equiv.) were dissolved in dry degassed Et<sub>2</sub>O solvent then the resulting solution was added dropwise to the complex solution and stirring was continued for a specified time at same temperature. After complete consumption of starting material (monitored by TLC), the reaction mixture was concentrated and purified by column chromatography to afford the desired enantioenriched compound.



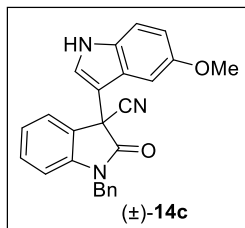
**3-Allyl-1-methyl-2-oxoindoline-3-carbonitrile** -(+)-(**10**): The compound **10** was obtained as light yellow gel (0.09 mmol scale of reaction, 17.9 mg of product, 94% yield);  $R_f = 0.36$  (20% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38 (ddt,  $J = 8.1, 4.1, 2.1$  Hz, 2H), 7.13 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.87 (dd,  $J = 8.1, 1.0$  Hz, 1H), 5.66 (dddd,  $J = 16.8, 10.2, 8.2, 6.5$  Hz, 1H), 5.24 – 5.11 (m, 2H), 3.22 (s, 3H), 2.97 (ddt,  $J = 13.5, 6.4, 1.3$  Hz, 1H), 2.71 (dd,  $J = 13.5, 8.2$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.9, 143.0, 130.3, 129.0, 124.8, 124.5, 123.6, 121.9, 116.7, 109.0, 46.4, 41.0, 26.9; IR (film)  $\nu_{\max}$  3150, 2267, 2125, 1748, 1669, 1265, 1035, 817 cm<sup>-1</sup>; Enantiometric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 99.1/0.9; flow rate: 1.0 mL/min; detection: at 254 nm):  $t_R$  major = 14.56 min,  $t_R$  minor = 16.16 min.  $[\alpha]_D^{26.9} = +9.6$  (c = 0.01, MeOH for 56% ee). HRMS (ESI-TOF) m/z: [M+Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>ONa: 235.0842, found: 235.0841.



**3-(1H-Indol-3-yl)-1-methyl-2-oxoindoline-3-carbonitrile (±)-(14a):** According to the experimental procedure **B** The compound **14a** was obtained as yellowish gel (0.5 mmol scale of reaction, 109.2 mg of product, 76% yield);  $R_f = 0.50$  (50% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.67 (s, 1H), 7.46 (t,  $J = 7.1$  Hz, 1H), 7.39 (d,  $J = 6.7$  Hz, 1H), 7.30 (d,  $J = 8.2$  Hz, 1H), 7.19 – 7.08 (m, 4H), 7.04 – 6.96 (m, 2H), 3.32 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.2, 143.1, 137.0, 130.7, 125.8, 125.4, 124.5, 124.2, 123.8, 122.9, 120.5, 118.9, 116.7, 112.1, 109.3, 108.0, 46.8, 27.3; **IR** (film)  $\nu_{\text{max}}$  2985, 2928, 2753, 2256, 2164, 1710, 1688, 1243, 1175, 928, 724  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}$  : 288.1131, found: 288.1114.

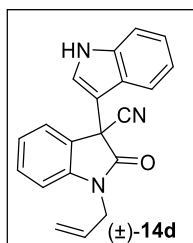


**1-Benzyl-3-(1H-indol-3-yl)-2-oxoindoline-3-carbonitrile (±)-(14b):** According to the experimental procedure **B** The compound **14b** was obtained as reddish gel (0.5 mmol scale of reaction, 147.2 mg of product, 81% yield);  $R_f = 0.48$  (30% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.40 (s, 1H), 7.39 (d,  $J = 7.7$  Hz, 1H), 7.31 (d,  $J = 5.7$  Hz, 7H), 7.12 (dt,  $J = 20.0, 7.6$  Hz, 2H), 6.97 (d,  $J = 8.0$  Hz, 1H), 6.91 (t,  $J = 6.9$  Hz, 2H), 5.08 (d,  $J = 15.5$  Hz, 1H), 4.88 (d,  $J = 15.5$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.1, 142.4, 136.9, 134.7, 130.5, 129.0, 128.1, 127.6, 125.8, 125.5, 124.4, 124.1, 123.9, 123.0, 120.5, 119.3, 116.6, 111.8, 110.2, 108.6, 46.8, 44.9; **IR** (film)  $\nu_{\text{max}}$  3153, 3026, 2853, 2749, 2724, 2143, 2031, 1716, 1678, 1357, 1190, 1034, 945, 867  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{17}\text{N}_3\text{ONa}$  : 386.1264, found: 386.1253.



**1-Benzyl-3-(5-methoxy-1H-indol-3-yl)-2-oxoindoline-3-carbonitrile (±)- (14c):**

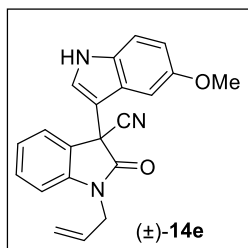
According to the experimental procedure **B** The compound **14c** was obtained as yellowish gel (0.5 mmol scale of reaction, 141.6 mg of product, 72% yield);  $R_f = 0.40$  (40% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.50 (s, 1H), 7.42 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.34 (td,  $J = 7.8, 1.3$  Hz, 1H), 7.29 (s, 5H), 7.22 (d,  $J = 2.8$  Hz, 1H), 7.19 (d,  $J = 8.9$  Hz, 1H), 7.12 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.91 (d,  $J = 7.9$  Hz, 1H), 6.79 (dd,  $J = 8.9, 2.4$  Hz, 1H), 6.35 (d,  $J = 2.4$  Hz, 1H), 5.11 (d,  $J = 15.6$  Hz, 1H), 4.84 (d,  $J = 15.6$  Hz, 1H), 3.43 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.3, 154.3, 142.5, 134.7, 131.9, 130.5, 129.0, 128.1, 127.5, 125.7, 125.7, 125.0, 124.3, 124.2, 116.7, 113.4, 112.6, 110.1, 107.8, 100.6, 55.3, 46.8, 44.9; **IR** (film)  $\nu_{\text{max}}$  3142, 3021, 2938, 2763, 2264, 1710, 1633, 1143, 1075, 928, 864, 794, 726  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{20}\text{N}_3\text{O}_2$ : 394.1550, found: 394.1547.



**1-Allyl-3-(1H-indol-3-yl)-2-oxoindoline-3-carbonitrile (±)-(14d):**

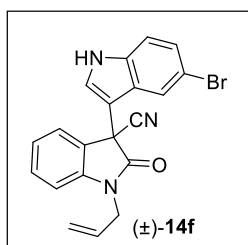
According to the experimental procedure **B** The compound **14d** was obtained as colourless gel (0.5 mmol scale of reaction, 128.5 mg of product, 82% yield);  $R_f = 0.45$  (40% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.49 (s, 1H), 7.43 (ddd,  $J = 10.0, 7.6, 1.9$  Hz, 2H), 7.32 (d,  $J = 8.2$  Hz, 1H), 7.21 (d,  $J = 2.8$  Hz, 1H), 7.19 – 7.07 (m, 3H), 7.05 – 6.95 (m, 2H), 5.91 – 5.79 (m, 1H), 5.36 – 5.24 (m, 2H), 4.47 (ddt,  $J = 16.1, 5.4, 1.7$  Hz, 1H), 4.42 – 4.33 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 169.7, 142.4, 136.9, 130.6, 130.4, 125.8, 125.5, 124.3, 124.1, 123.0, 120.5, 119.1, 118.8, 116.6, 111.9, 110.1, 108.4, 46.7, 43.4; **IR**

(film)  $\nu_{\max}$  3021, 2975, 2864, 2753, 2064, 1721, 1692, 1043, 975, 968, 834, 734  $\text{cm}^{-1}$ ;  
**HRMS** (ESI-TOF)  $m/z$ :  $[M+H]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$  : 314.1288, found: 314.1307.



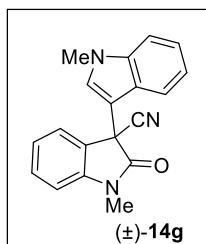
**1-Allyl-3-(5-methoxy-1H-indol-3-yl)-2-oxoindoline-3-carbonitrile** ( $\pm$ )-(14e):

According to the experimental procedure **B** The compound **14e** was obtained as yellowish gel (0.5 mmol scale of reaction, 128.8 mg of product, 75% yield);  $R_f = 0.42$  (40% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.37 (s, 1H), 7.43 (dd,  $J = 8.0$ , 6.9 Hz, 2H), 7.23 – 7.13 (m, 3H), 7.03 – 6.97 (m, 1H), 6.81 (dd,  $J = 8.9$ , 2.5 Hz, 1H), 6.55 (d,  $J = 2.4$  Hz, 1H), 5.85 (ddt,  $J = 17.2$ , 10.7, 5.5 Hz, 1H), 5.34 – 5.23 (m, 2H), 4.47 (ddt,  $J = 16.2$ , 5.3, 1.7 Hz, 1H), 4.34 (ddt,  $J = 16.2$ , 5.8, 1.6 Hz, 1H), 3.64 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 169.6, 154.4, 142.5, 131.9, 130.5, 130.5, 125.6, 124.7, 124.4, 124.0, 118.8, 116.6, 113.5, 112.6, 110.0, 108.0, 100.7, 55.5, 46.6, 43.4; **IR** (film)  $\nu_{\max}$  3174, 3028, 2753, 2156, 1703, 1687, 1143, 1075, 936, 865, 742  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[M+Na]^+$  calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_2\text{Na}$  : 366.1213, found: 366.1209.



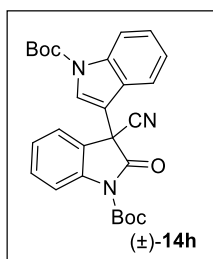
**1-Allyl-3-(5-bromo-1H-indol-3-yl)-2-oxoindoline-3-carbonitrile** ( $\pm$ )-(14f): According to the experimental procedure **B** The compound **14f** was obtained as brownish gel (0.5 mmol scale of reaction, 153.0 mg of product, 78% yield);  $R_f = 0$ . (40% EtOAc in hexane);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.51 (s, 1H), 7.51 – 7.38 (m, 2H), 7.26 (s, 1H), 7.24 – 7.20 (m, 1H), 7.20 – 7.14 (m, 2H), 7.03 (dd,  $J = 8.0$ , 2.6 Hz, 1H), 5.94 – 5.82 (m, 1H), 5.39 – 5.28 (m, 2H), 4.56 – 4.43 (m, 1H), 4.37 (tdt,  $J = 16.1$ , 5.8, 1.6 Hz, 1H);  $^{13}\text{C NMR}$

(100 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.4, 142.3, 135.6, 130.8, 130.2, 126.1, 125.4, 125.4, 124.5, 124.2, 121.8, 119.1, 116.3, 113.9, 113.2, 110.7, 110.3, 108.4, 46.5, 43.5. **IR** (film)  $\nu_{\max}$  3065, 2908, 2853, 2756, 2064, 1710, 1692, 1043, 975, 928, 865, 724 cm<sup>-1</sup>; **HRMS** (ESI-TOF)  $m/z$ : [M+Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>BrN<sub>3</sub>ONa: 414.0212, found: 414.0228.



**1-Methyl-3-(1-methyl-1H-indol-3-yl)-2-oxoindoline-3-carbonitrile** (±)-(**14g**):

According to the experimental procedure **B** The compound **14g** was obtained as yellowish gel (0.5 mmol scale of reaction, 111.5 mg of product, 74% yield);  $R_f = 0.50$  (40% EtOAc in hexane); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.58 – 7.45 (m, 3H), 7.32 (d,  $J = 8.4$  Hz, 1H), 7.27 – 7.22 (m, 1H), 7.20 (d,  $J = 3.2$  Hz, 1H), 7.17 (dt,  $J = 8.2, 1.1$  Hz, 1H), 7.06 – 7.03 (m, 2H), 3.79 (s, 3H), 3.34 (s, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 176.5, 144.2, 137.4, 129.3, 128.1, 127.7, 126.8, 124.78, 122.6, 121.9, 121.6, 119.4, 119.3, 109.4, 109.3, 108.0, 44.4, 32.8, 26.5; **IR** (film)  $\nu_{\max}$  3054, 2965, 2708, 2156, 1710, 1688, 1243, 1175, 928, 774, 728 cm<sup>-1</sup>; **HRMS** (ESI-TOF)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>O: 302.1288, found: 302.1274.

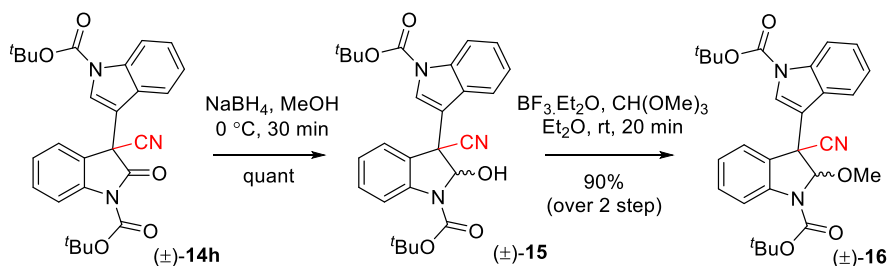


**tert-Butyl 3-(1-(tert-butoxycarbonyl)-3-cyano-2-oxoindolin-3-yl)-1H-indole-1-carboxylate** (±)-(**14h**): According to the experimental procedure **A** The compound **14h** was obtained as reddish gel (3.5 mmol scale of reaction, 1.5 g of product, 92% yield);  $R_f = 0.52$  (30% EtOAc in hexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (d,  $J = 8.4$  Hz, 1H), 8.05 (d,  $J = 8.3$  Hz, 1H), 7.56 (s, 1H), 7.53 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.46 (dd,  $J = 7.7, 1.4$

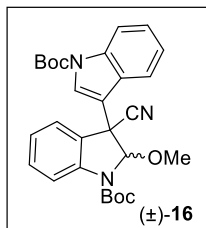


Hz, 1H), 7.37 (s, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.16 (m, 1H), 1.66 (s, 9H), 1.62 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 166.4, 149.1, 148.5, 139.6, 136.1, 131.2, 126.4, 125.9, 125.4, 125.2, 123.4, 120.0, 116.1, 115.6, 115.5, 113.5, 85.9, 84.8, 47.2, 28.1, 28.0; IR (film)  $\nu_{\max}$  3154, 2821, 2793, 2237, 1742, 1713, 1694, 1267, 1090, 1034, 967, 837 cm<sup>-1</sup>; HRMS (ESI-TOF) m/z: [M+Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub>Na : 496.1843, found: 496.1835.

### Synthesis of the compound (16):

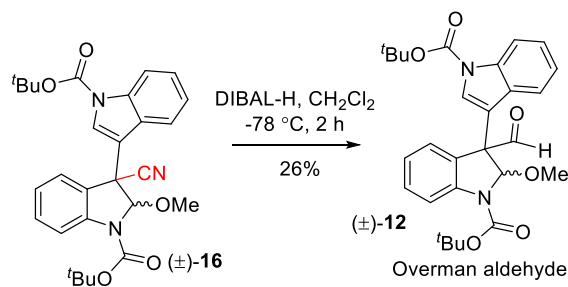


In a solution of compound **14h** (100 mg, 0.211 mmol, 1.0 equiv.) in MeOH (5 mL), sodium borohydride (12 mg, 0.316 mmol, 1.5 equiv.) was added portionwise at 0°C and stirred for 30 minutes. After completion of the reaction, the reaction mixture was quenched by the addition of acetone (1.0 mL), maintained at 0°C for 5 min, then poured into a mixture of ethyl acetate (5 mL) and saturated aqueous NaHCO<sub>3</sub> (5 mL). After the layer separation, the aqueous layer was further extracted with ethyl acetate (2 x 5 mL). The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude products were directly treated for next step without any purification. Next, the crude product was dissolved in Et<sub>2</sub>O (1.5 mL) then trimethoxy methane (1.05 mmol, 5.0 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (1.05 mmol, 5.0 equiv.) were added sequentially. After 30 min, the reaction mixture was poured into H<sub>2</sub>O (1 mL) and extracted with EtOAc (2 x 3 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude products were purified by column chromatography to afford the desired product.



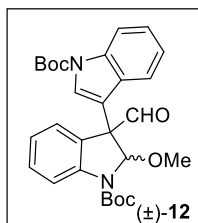
**tert-Butyl 3-(1-(tert-butoxycarbonyl)-3-cyano-2-methoxyindolin-3-yl)-1H-indole-1-carboxylate (±)-(**16**):** 93 mg ( yield 90% over 2 step) of **16** as a yellowish gel.  $R_f = 0.50$  (20% EtOAc in hexane);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.16 (d,  $J = 7.7$  Hz, 1H), 7.75 (d,  $J = 7.9$  Hz, 1H), 7.54 (d,  $J = 7.5$  Hz, 1H), 7.47 – 7.40 (m, 3H), 7.38 – 7.33 (m, 1H), 7.21 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.00 (s, 1H), 5.64 (s, 1H), 3.78 (s, 3H), 1.65 (s, 9H), 1.55 (s, 9H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.3, 136.1, 130.4, 127.0, 125.3, 125.1, 124.9, 124.1, 123.4, 119.0, 117.5, 116.9, 116.3, 115.8, 84.7, 58.2, 28.2, 28.1; **IR** (film)  $\nu_{\text{max}}$  3084, 2893, 2548, 2206, 1694, 1253, 1075, 932, 854, 728  $\text{cm}^{-1}$ ; **HRMS** (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_5\text{Na}$  : 512.2156, found: 512.2179.

### Synthesis of Aldehyde **12**:

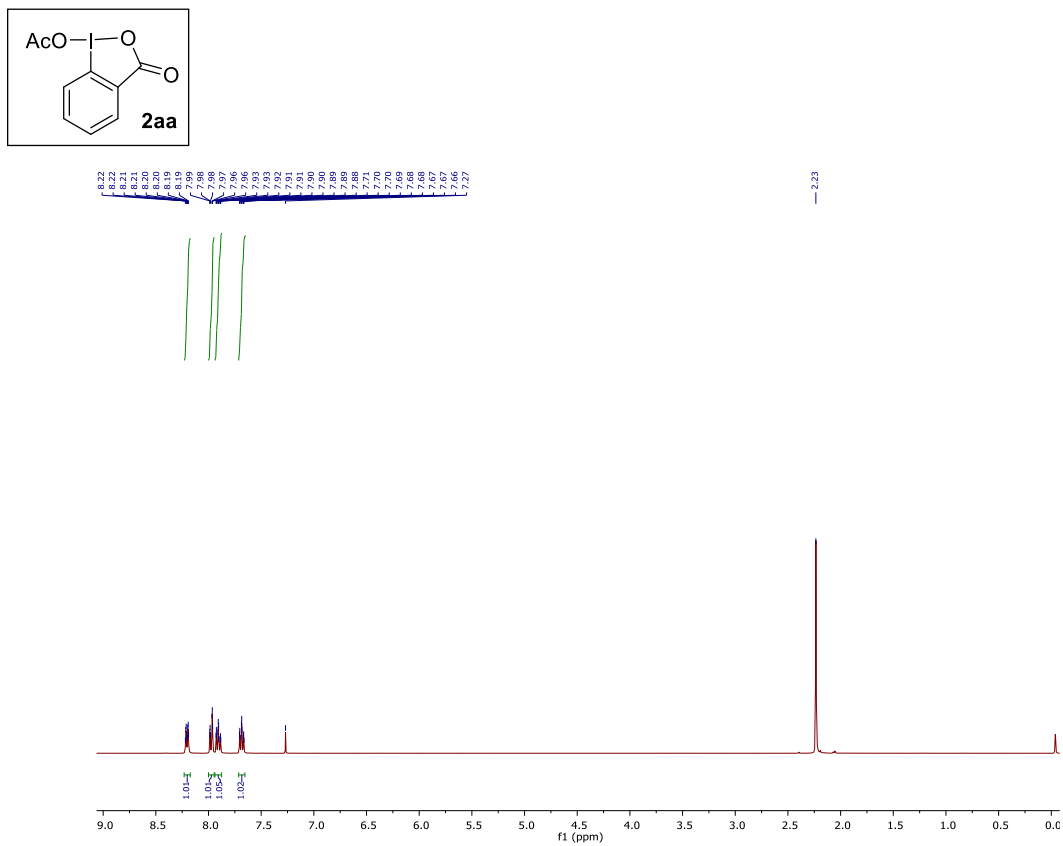


In an oven-dried round bottom flask Compound **16** (50 mg, 0.102 mmol, 1.0 equiv.) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (1.0 mL) and cooled to  $-78$  °C then DIBAL-H (1.0M in Toluene, 0.122 mmol, 1.2 equiv.) was added drop wise. The reaction temperature was allowed to warm up to  $-20$ °C within a period of 2 h and consumption of the starting material was monitored by TLC. Upon completion of the reaction, a saturated solution of Rochelle's salt and EtOAc was added and the reaction mixture was warmed up to room temperature. The solution was further diluted with EtOAc and the suspension was stirred vigorously for 4 h to give a two-phase mixture, which was separated. The aqueous layer was extracted with EtOAc (2 x 2 mL); the combined organic layers were dried over

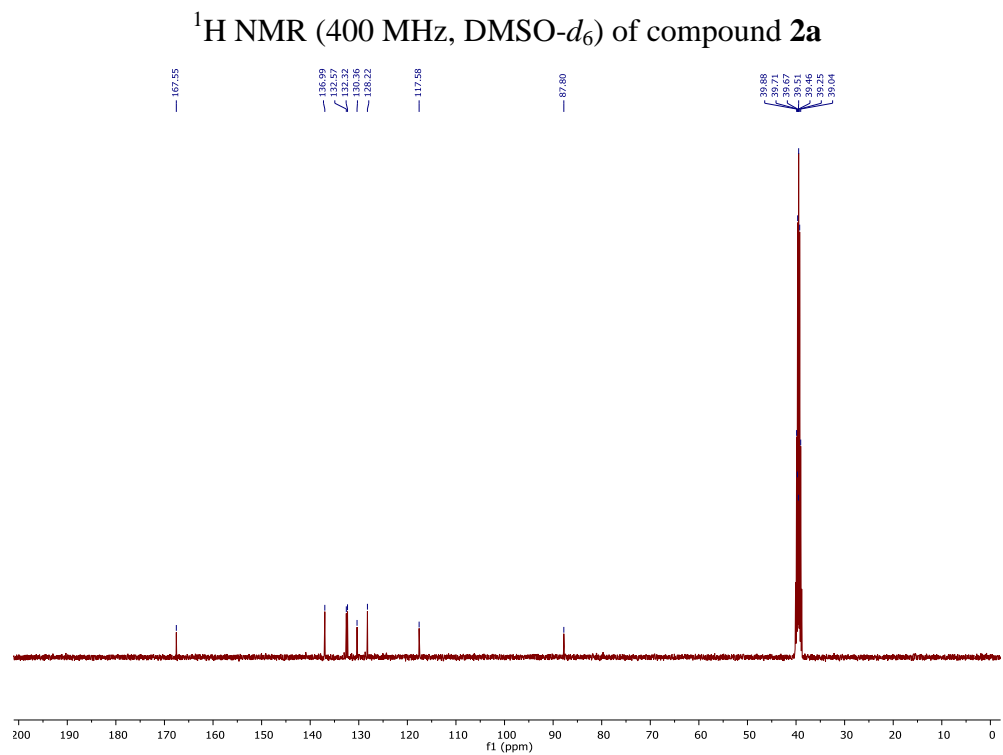
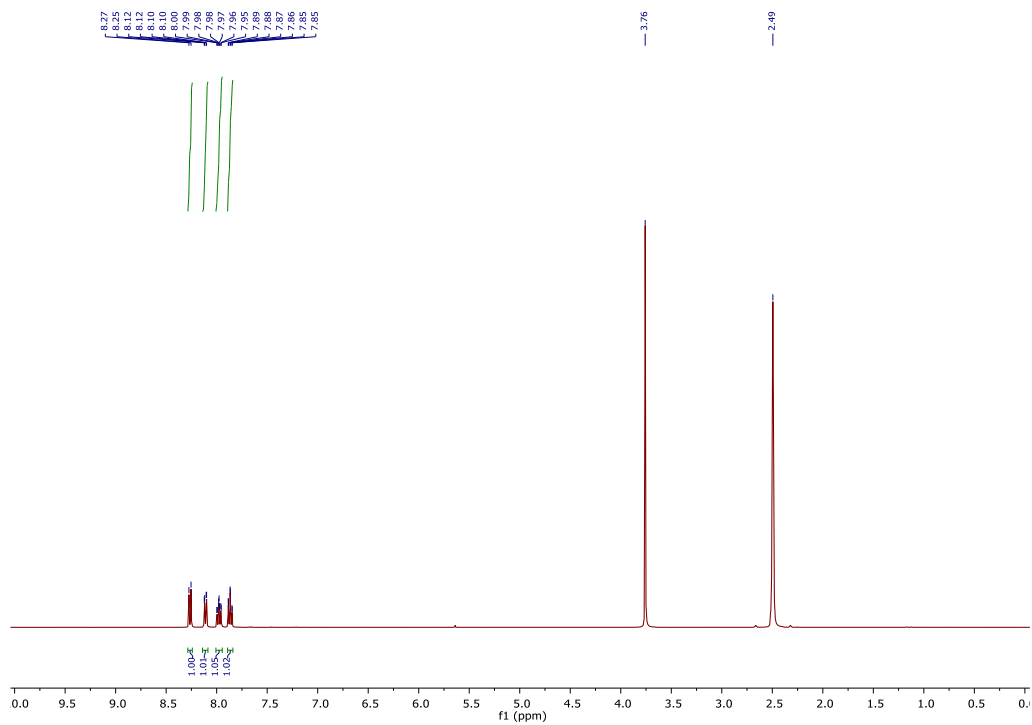
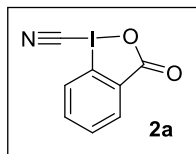
Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude products were purified by column chromatography to afford the desired aldehyde product.



**tert-Butyl 3-(1-(tert-butoxycarbonyl)-3-formyl-2-methoxyindolin-3-yl)-1H-indole-1-carboxylate (±)-(**12**):** 13.0 mg (yield 26%) of **12** as a yellowish gel.  $R_f = 0.50$  (30% EtOAc in hexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.42 (s, 1H), 8.18 (d,  $J = 8.4$  Hz, 1H), 7.63 (s, 1H), 7.41 – 7.36 (m, 1H), 7.32 (ddd,  $J = 8.4, 5.9, 2.4$  Hz, 1H), 7.25 (s, 2H), 7.13 (d,  $J = 6.1$  Hz, 2H), 7.07 (td,  $J = 7.5, 1.0$  Hz, 1H), 6.12 (s, 1H), 3.15 (s, 3H), 1.67 (s, 9H), 1.61 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 192.0, 149.4, 135.9, 130.1, 129.3, 125.7, 124.8, 123.2, 122.7, 121.1, 116.5, 115.3, 112.5, 92.3, 84.3, 82.1, 6.2, 28.4, 28.2; **IR** (film)  $\nu_{\max}$  3034, 2945, 2708, 2156, 1718, 1628, 1254, 1135, 922, 864, 764, 738 cm<sup>-1</sup>; **HRMS** (ESI-TOF)  $m/z$ : [M+Na]<sup>+</sup> calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>Na : 515.2153, found: 515.2148.

**Spectral Graphics**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2aa**



## Display Report

## Analysis Info

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Sample Name Dr A Bisai-AR-01-136  
Comment

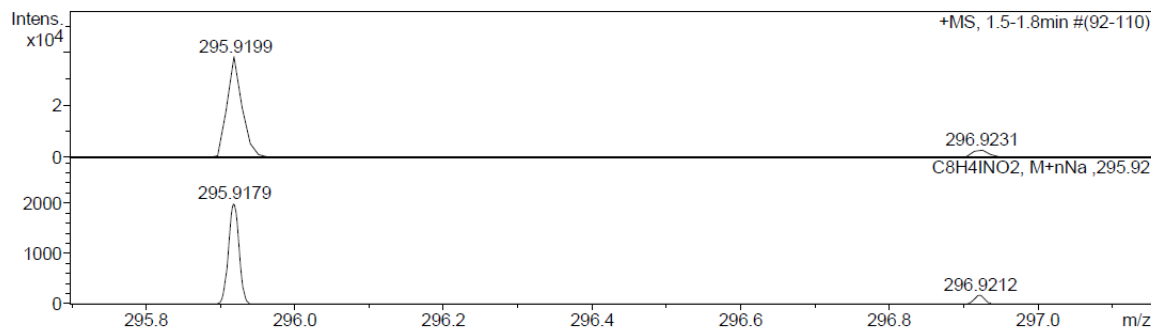
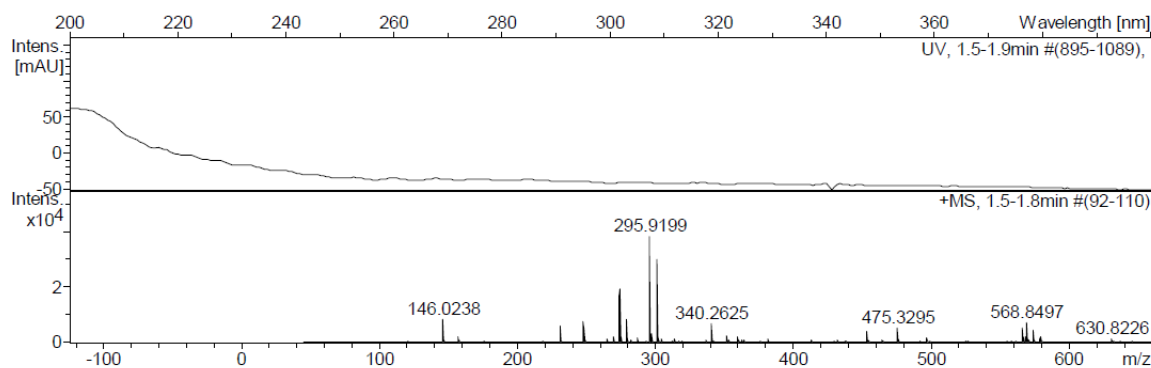
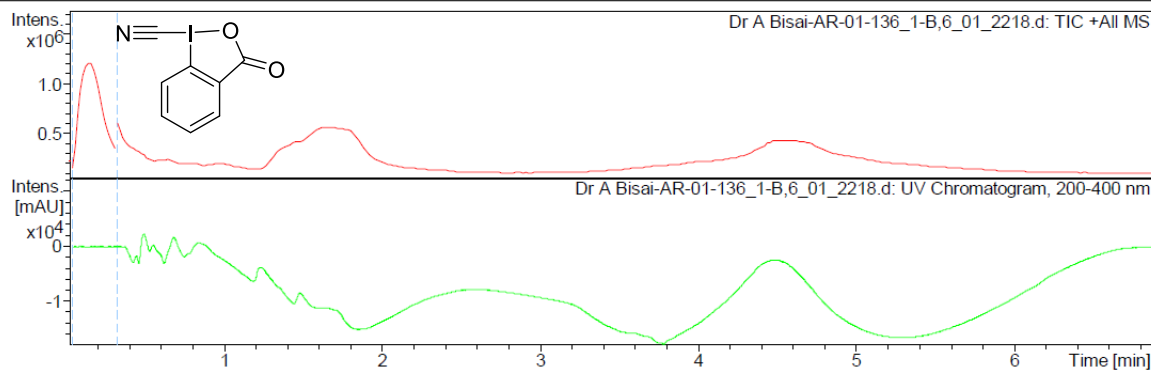
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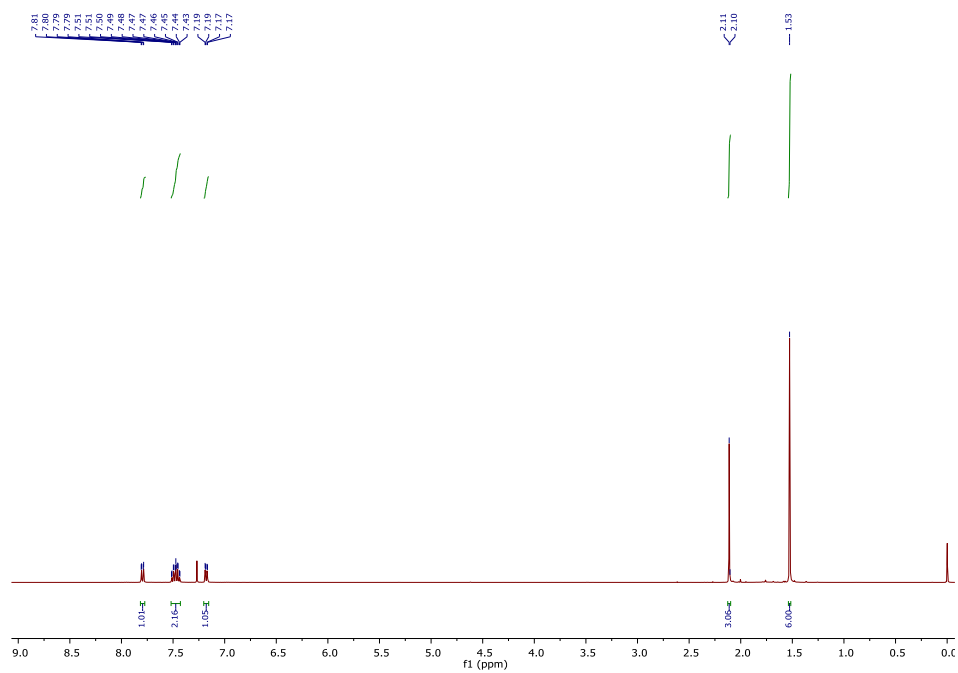
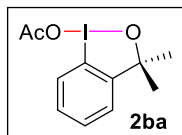
Operator RUCHI SHRIVASTAVA

Instrument micrOTOF-Q II 10330

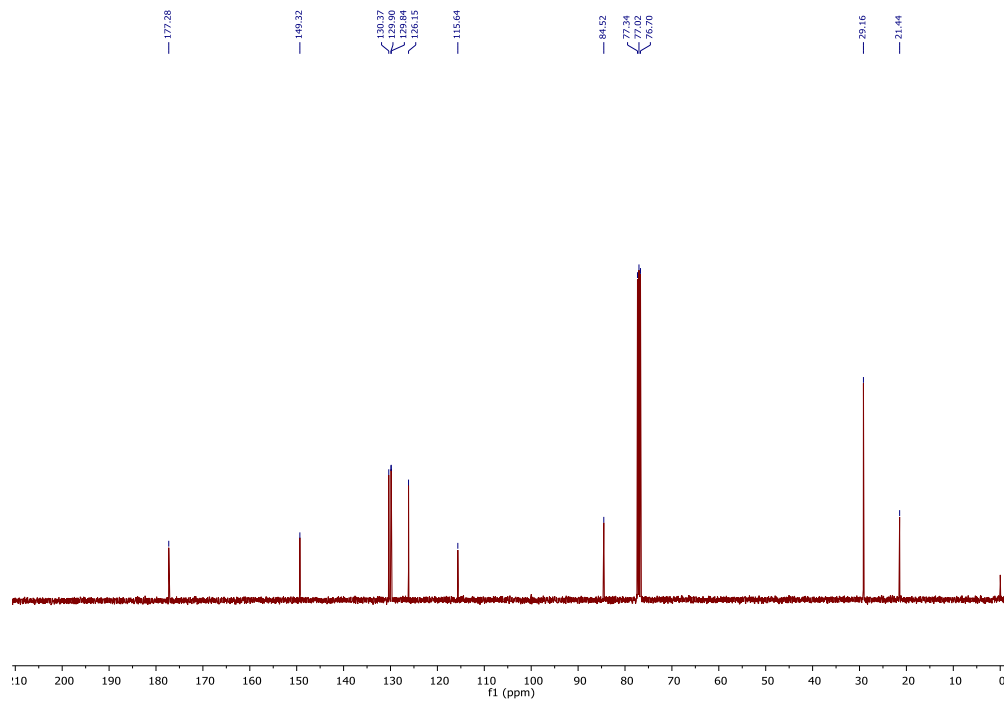
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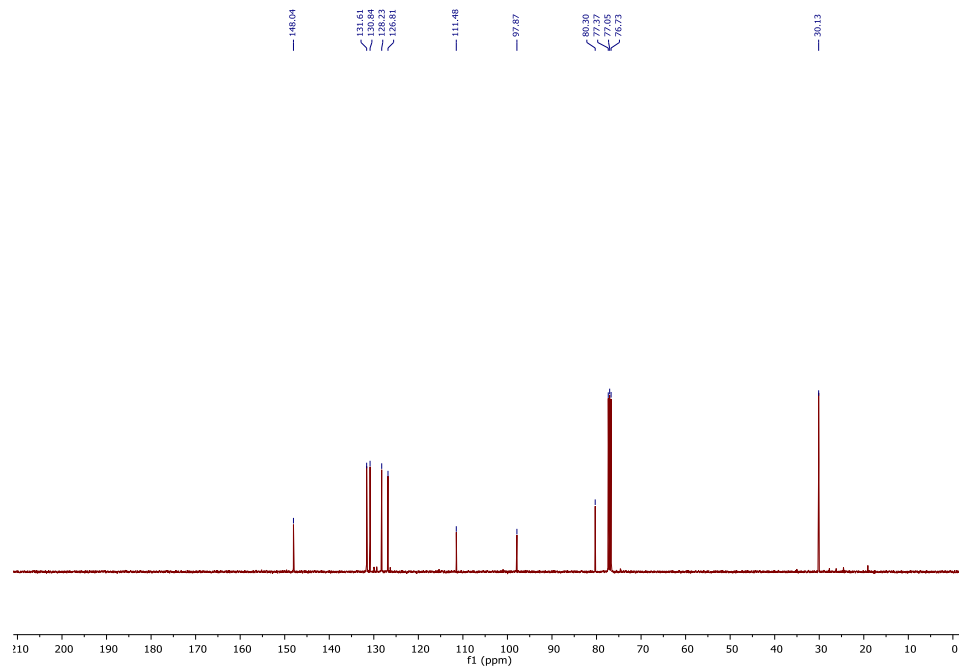
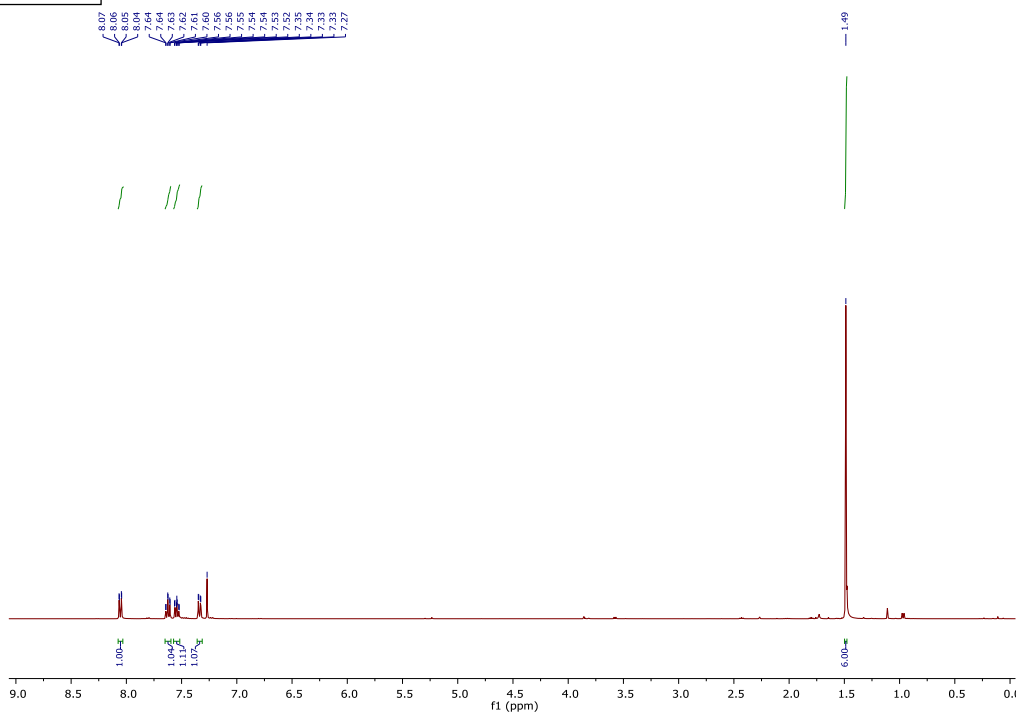
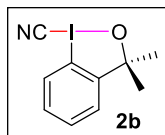
Scanned copy of mass spectrum of **2a**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2ba**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2ba**





## Display Report

## Analysis Info

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Sample Name AB-AR-04-77  
Comment

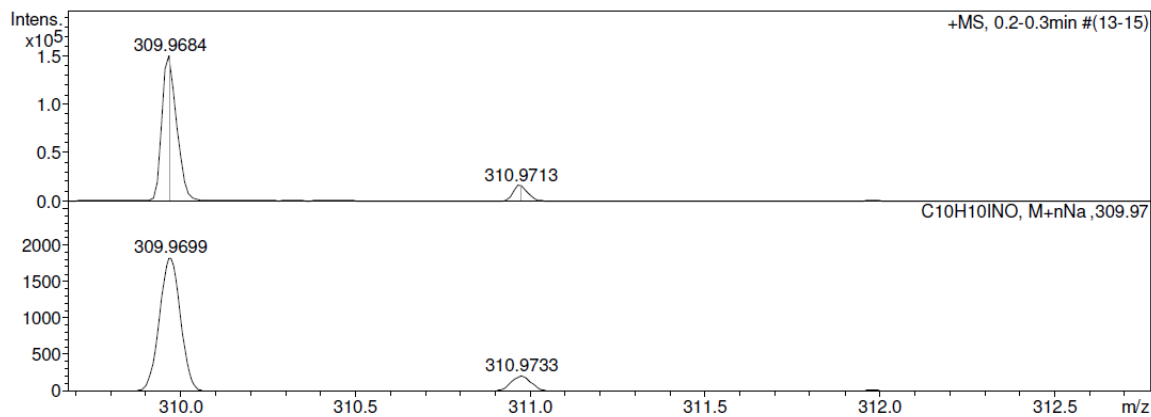
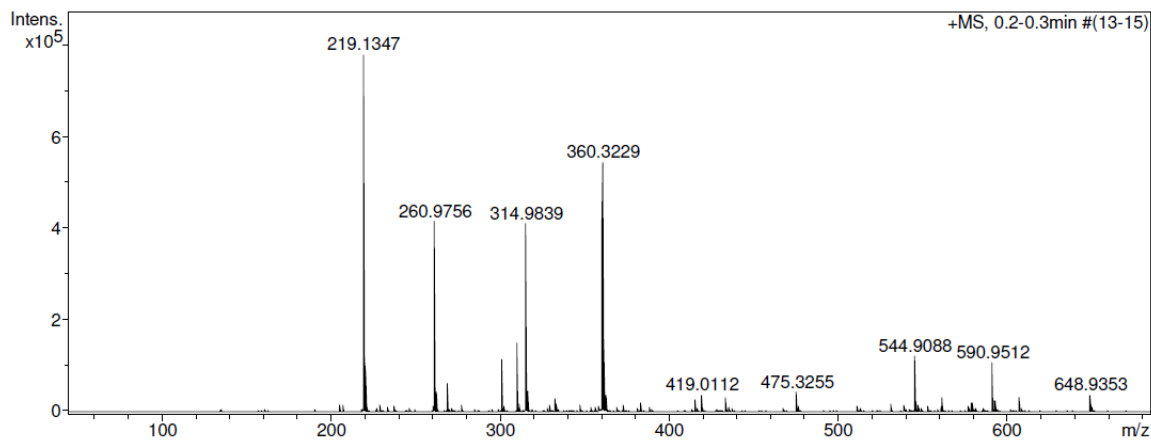
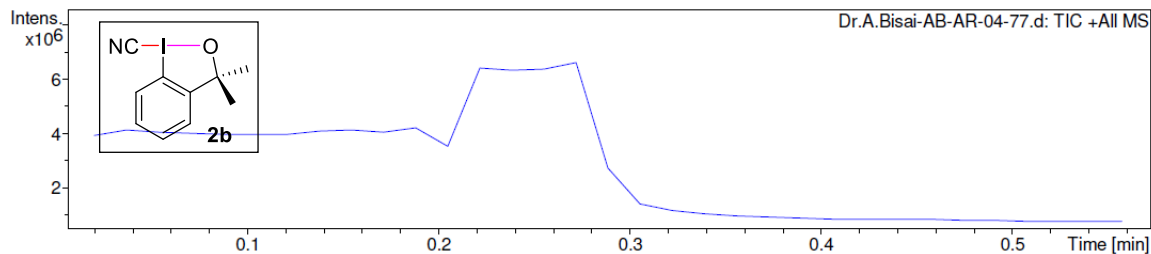
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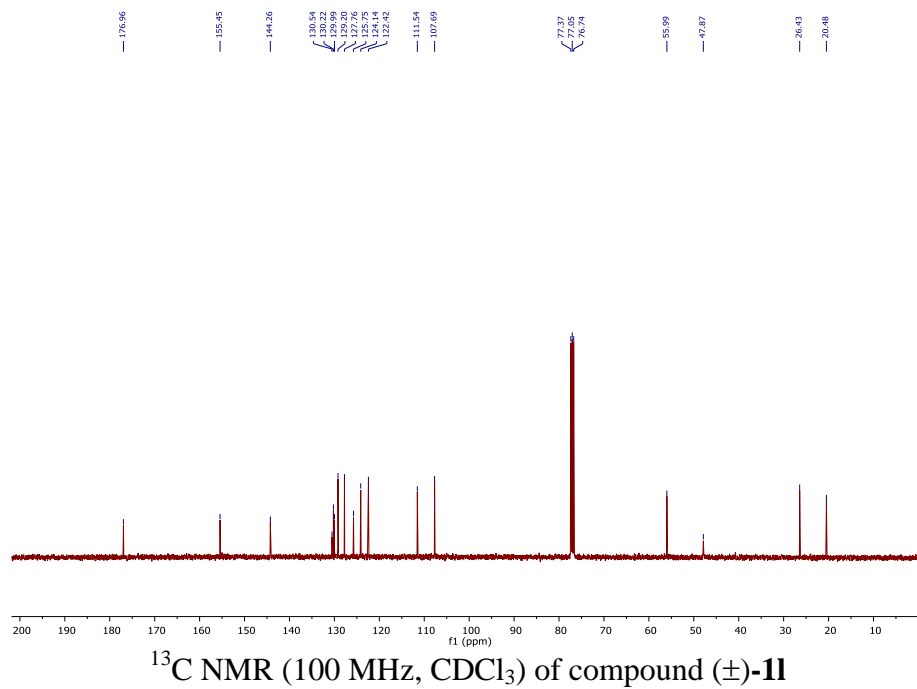
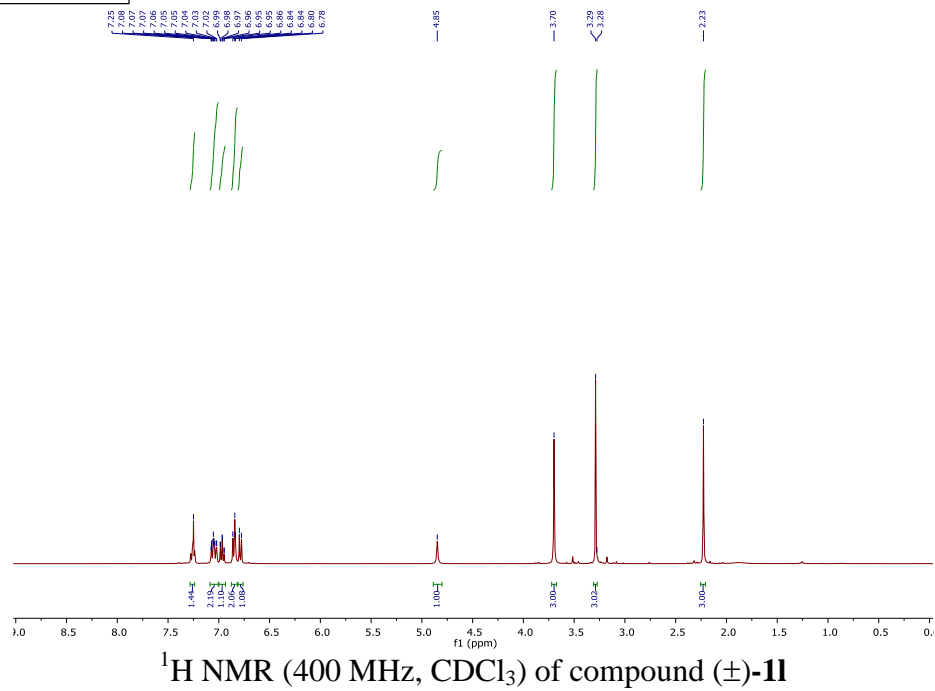
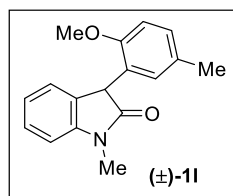
Operator RUCHI

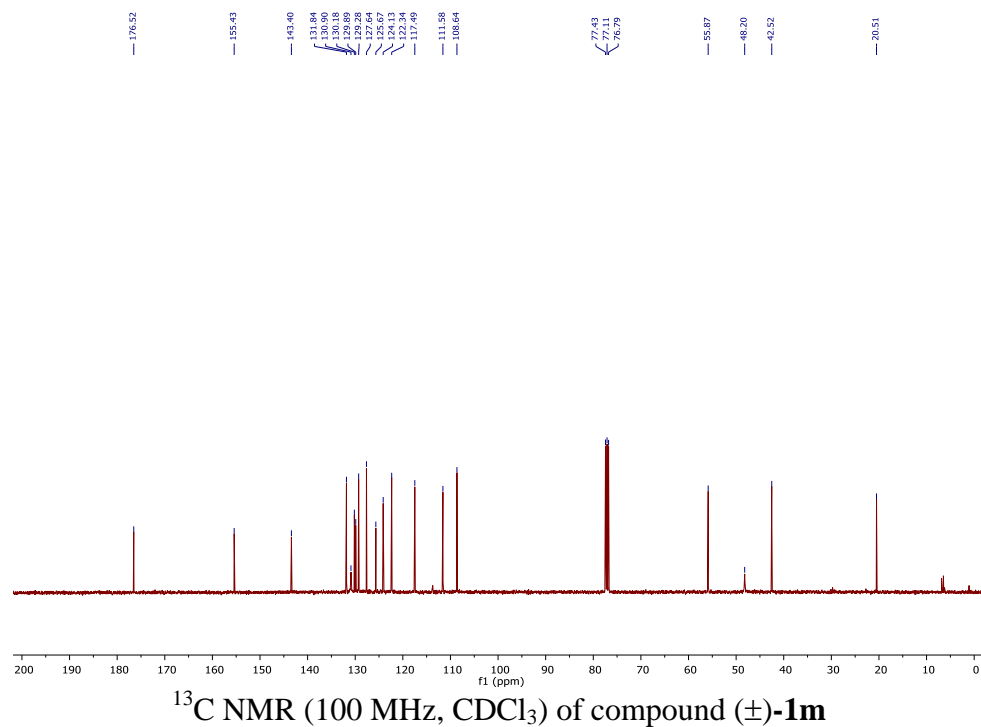
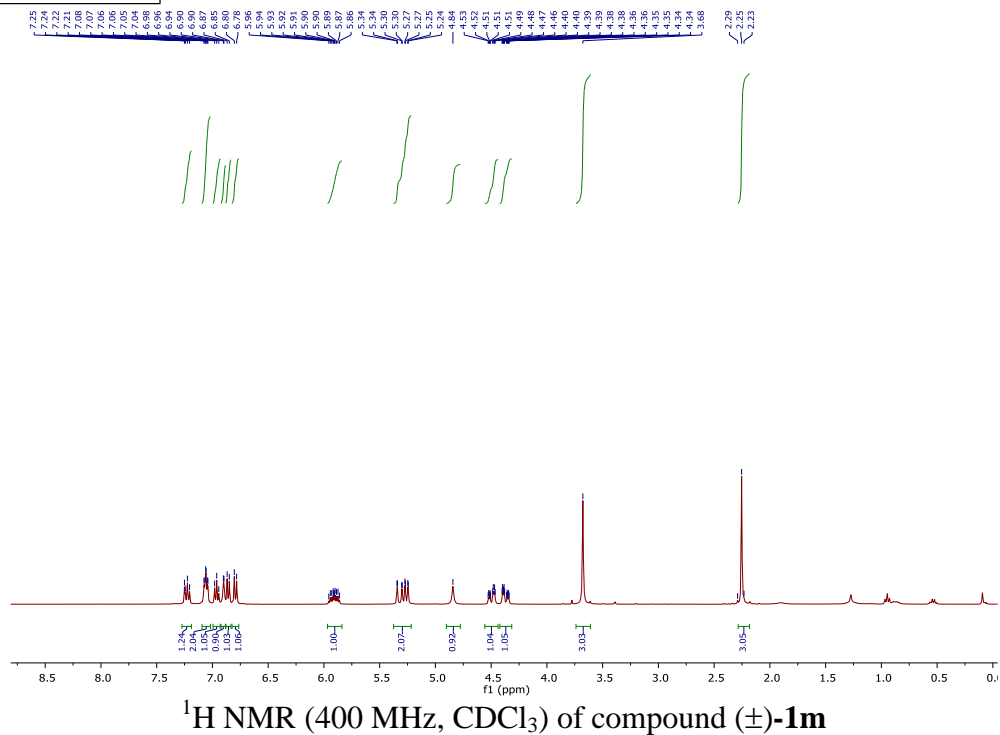
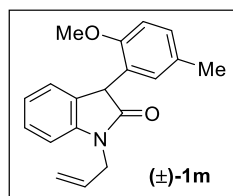
Instrument micrOTOF-Q II 10330

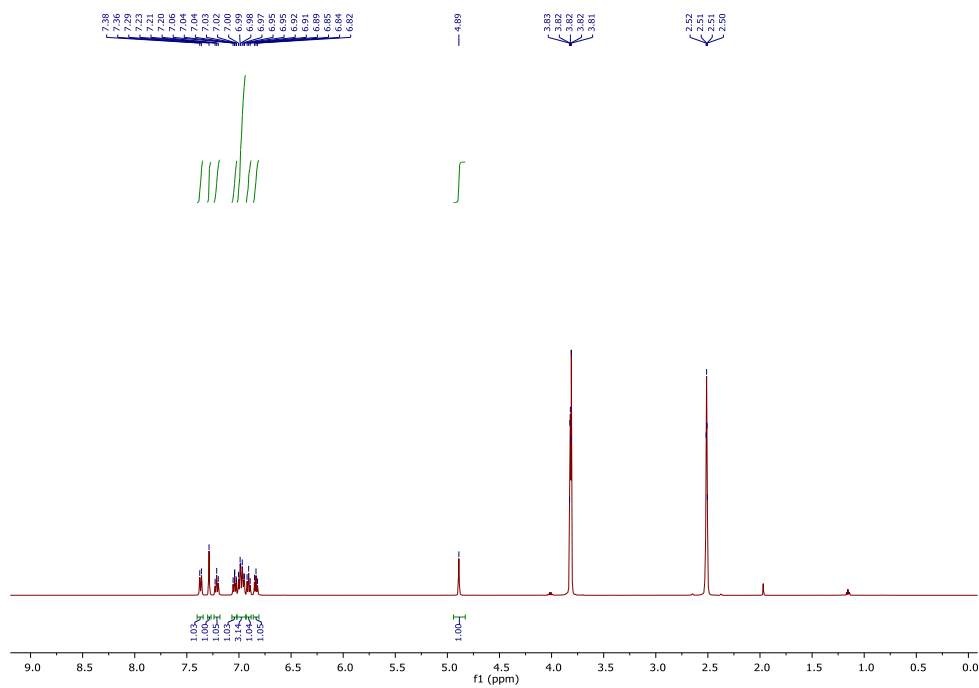
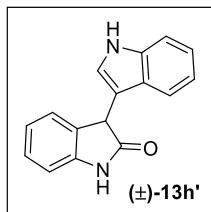
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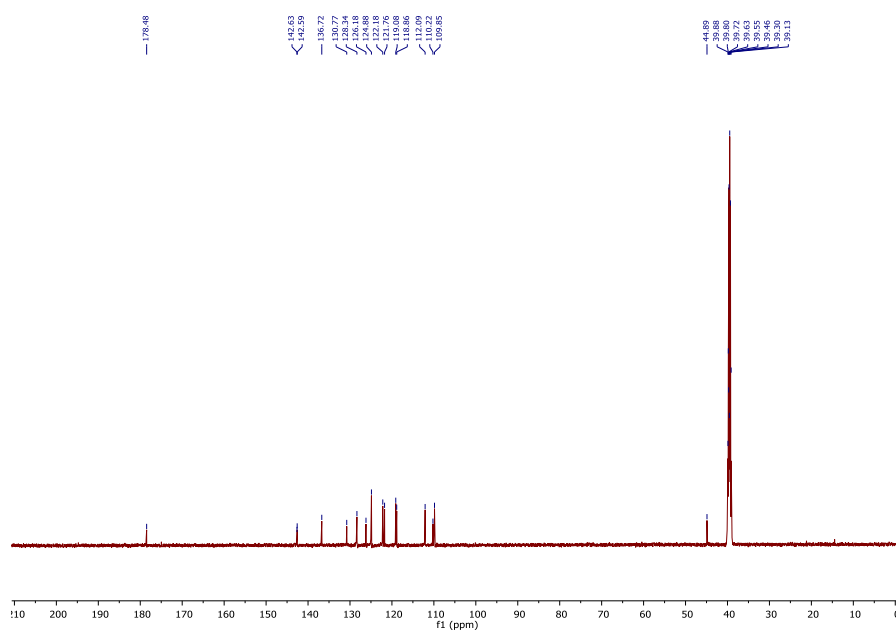
Scanned copy of mass spectrum of **2b**



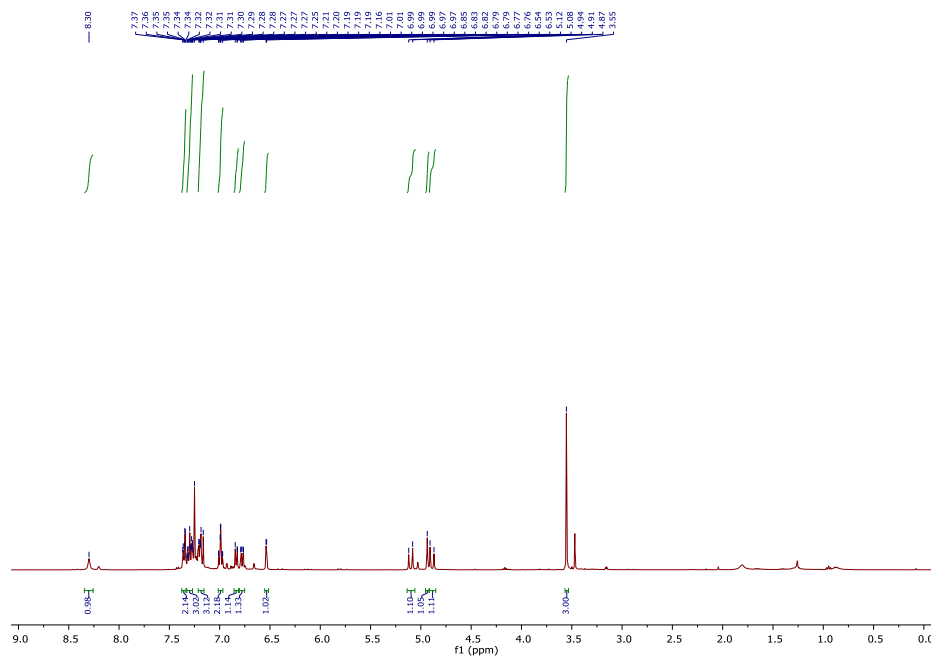
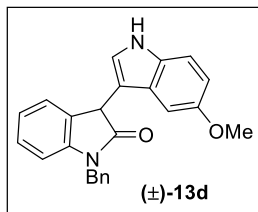




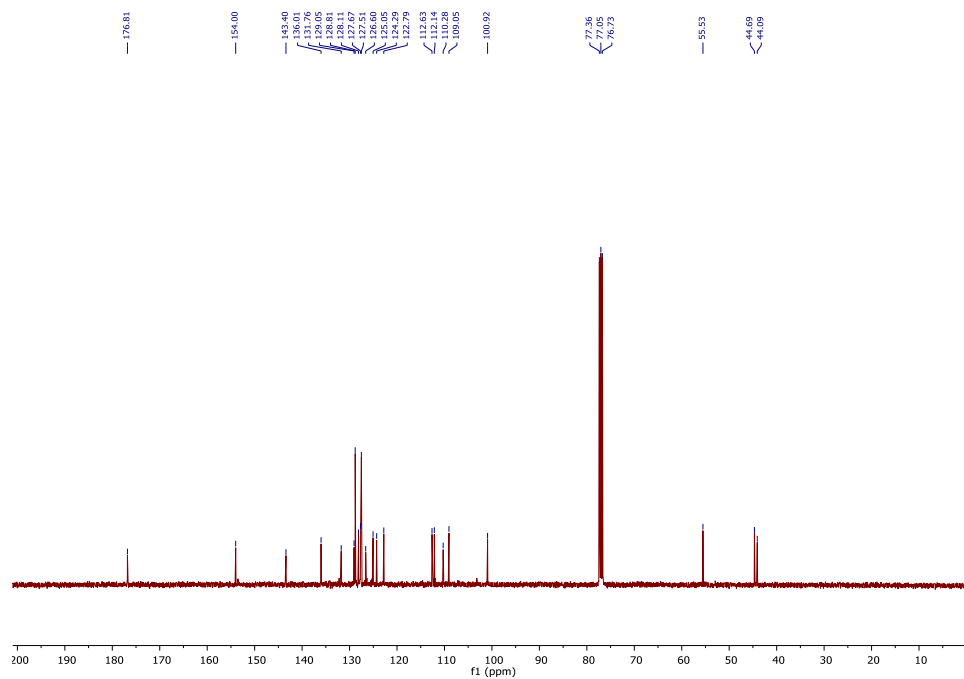
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) of compound (±)-13h'



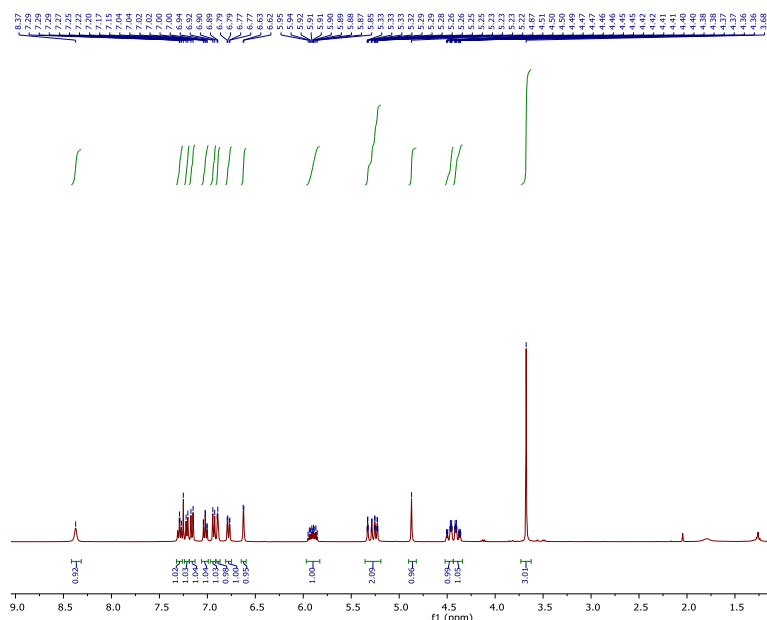
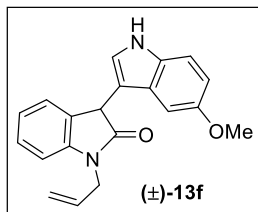
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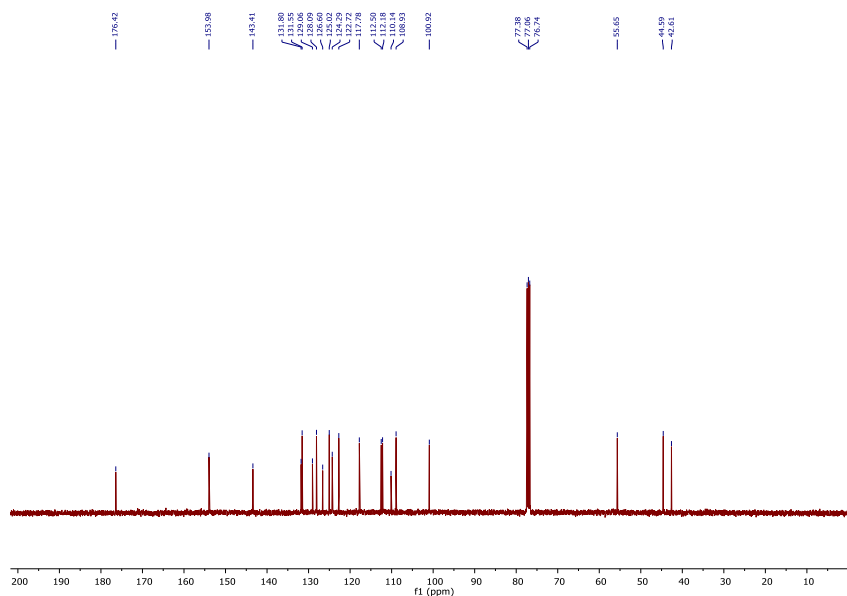
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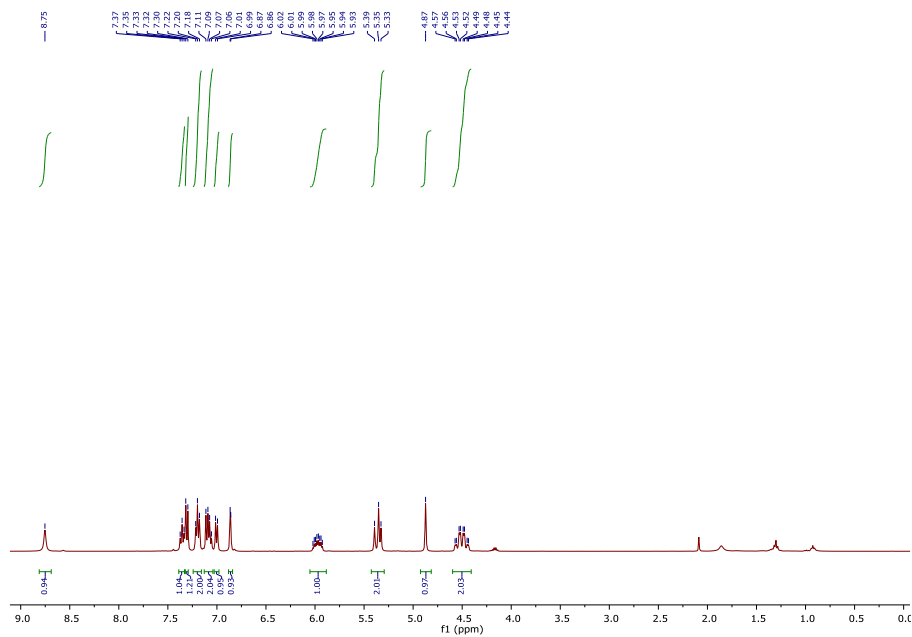
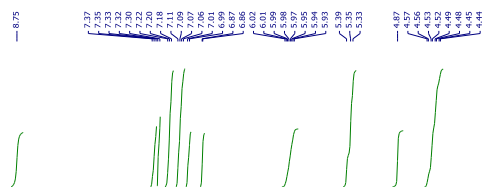
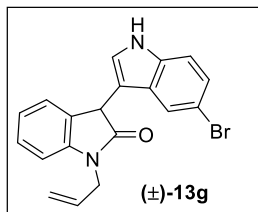
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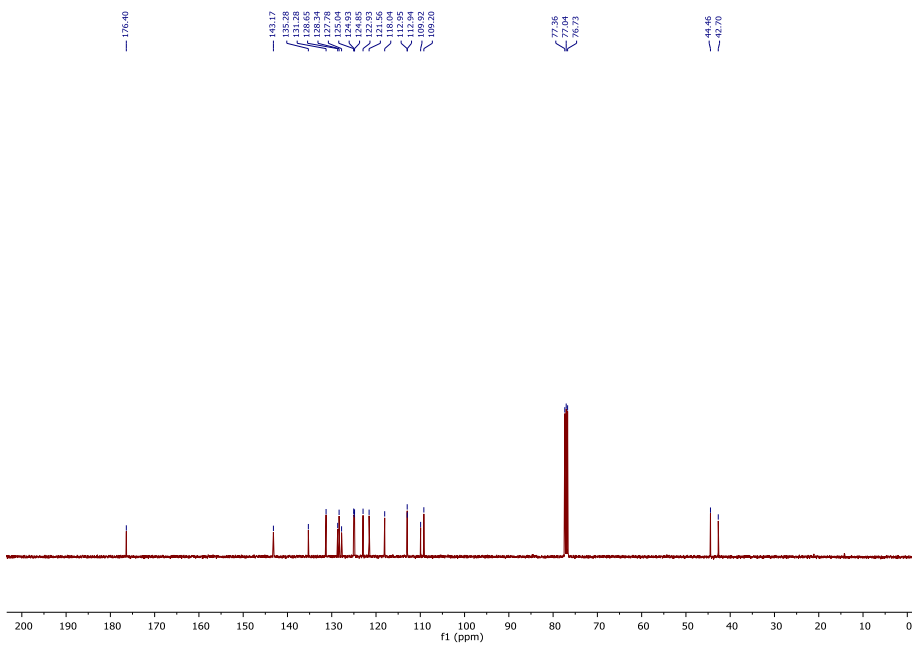
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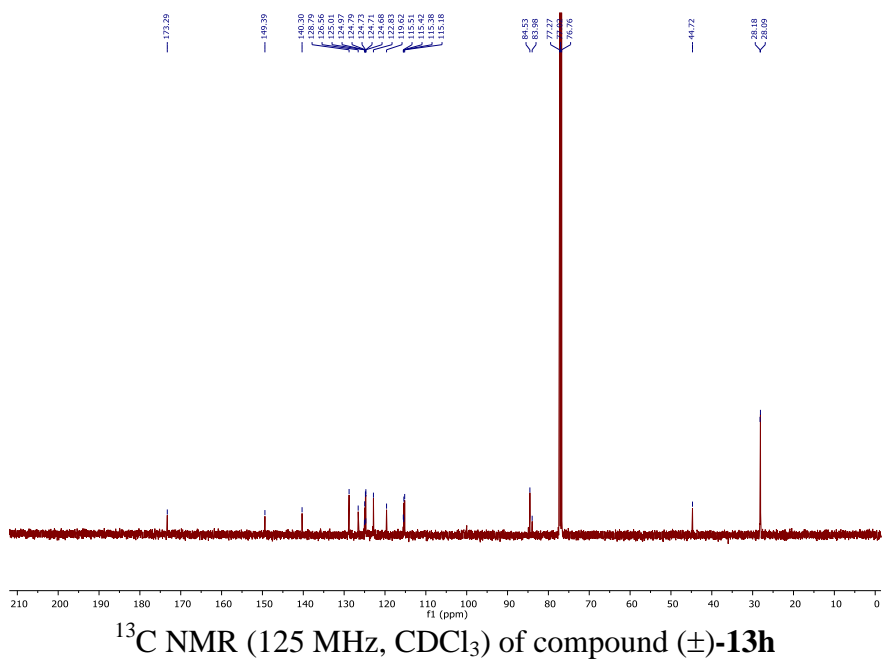
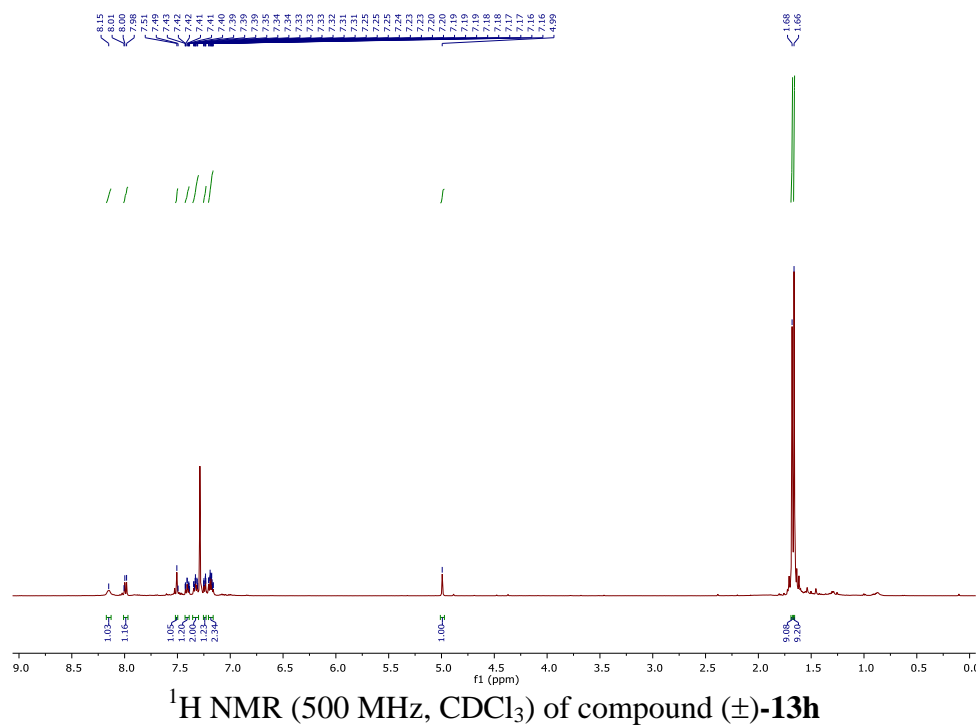
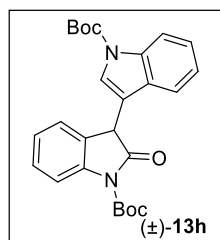
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-13f



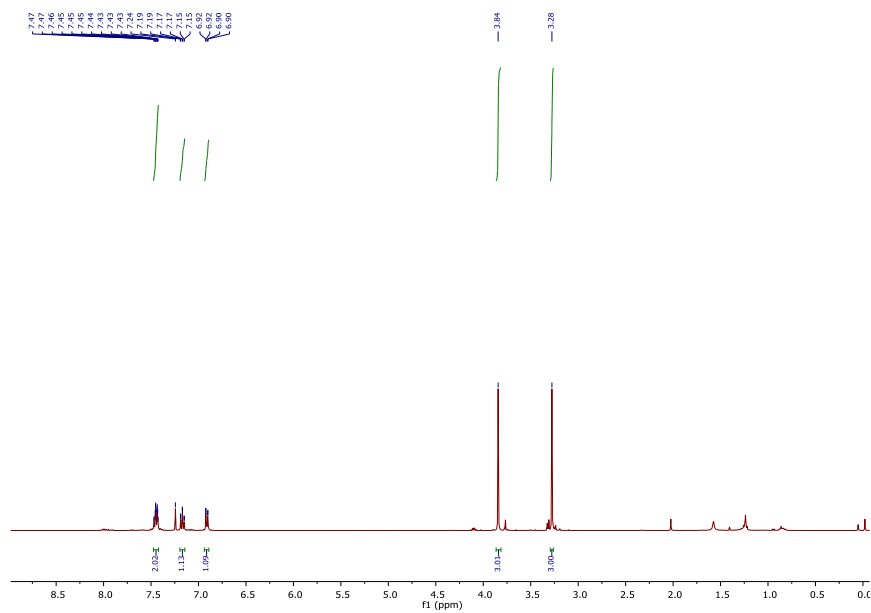
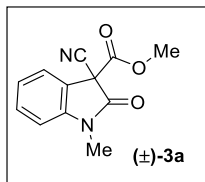
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-**13g**



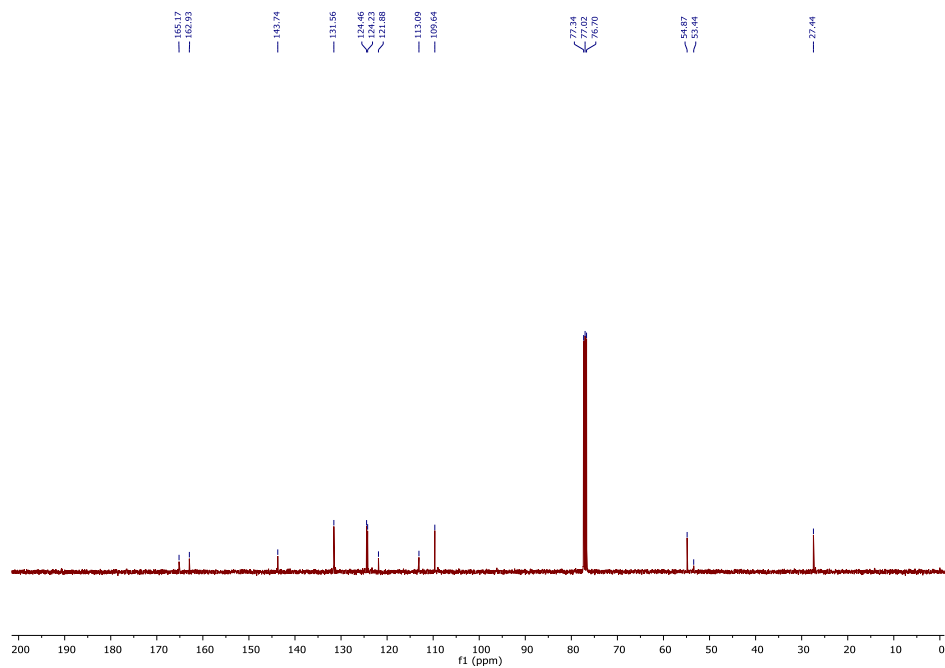
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-**13g**







$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-3a



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-3a

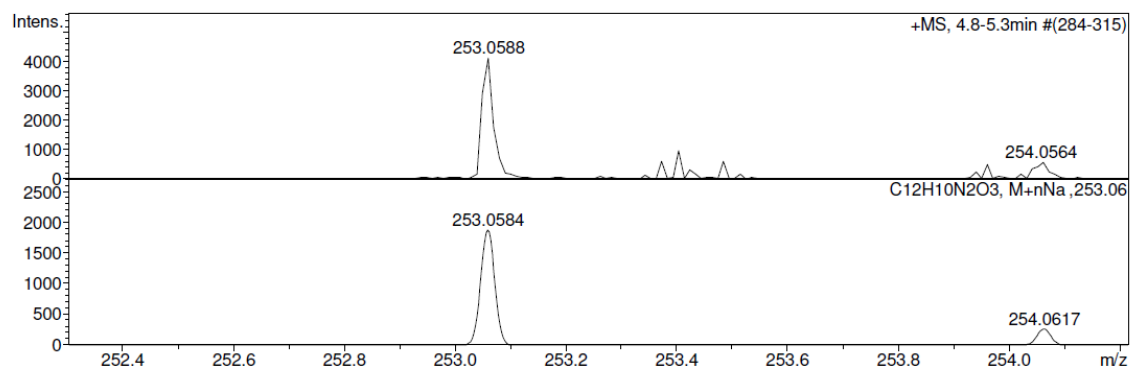
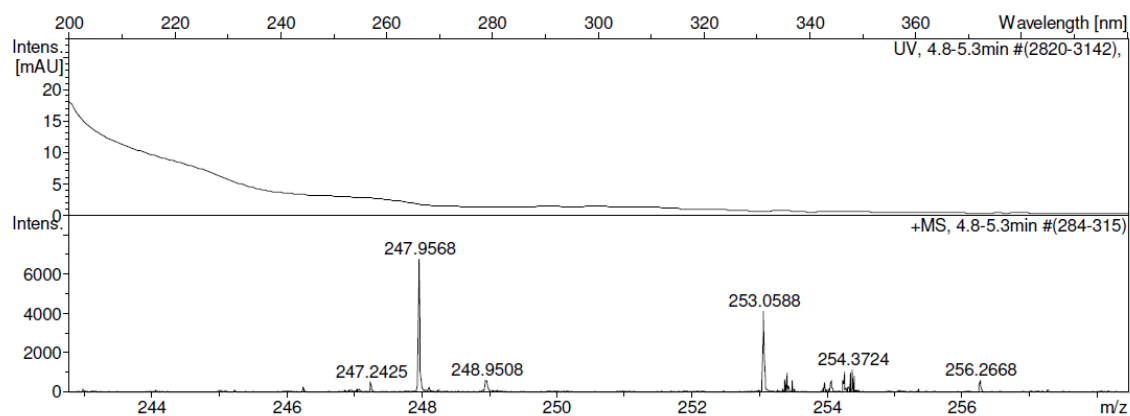
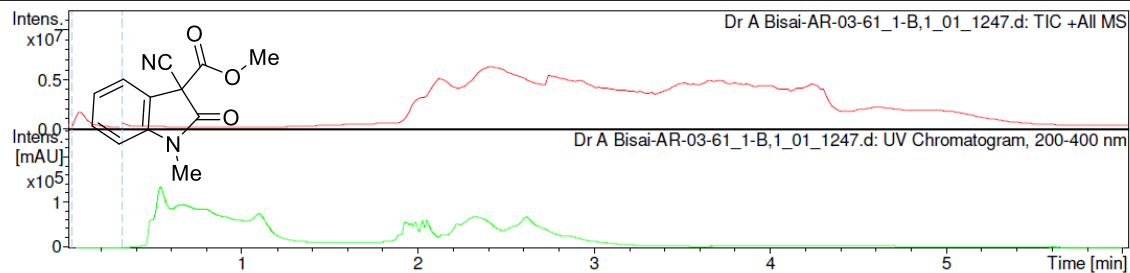
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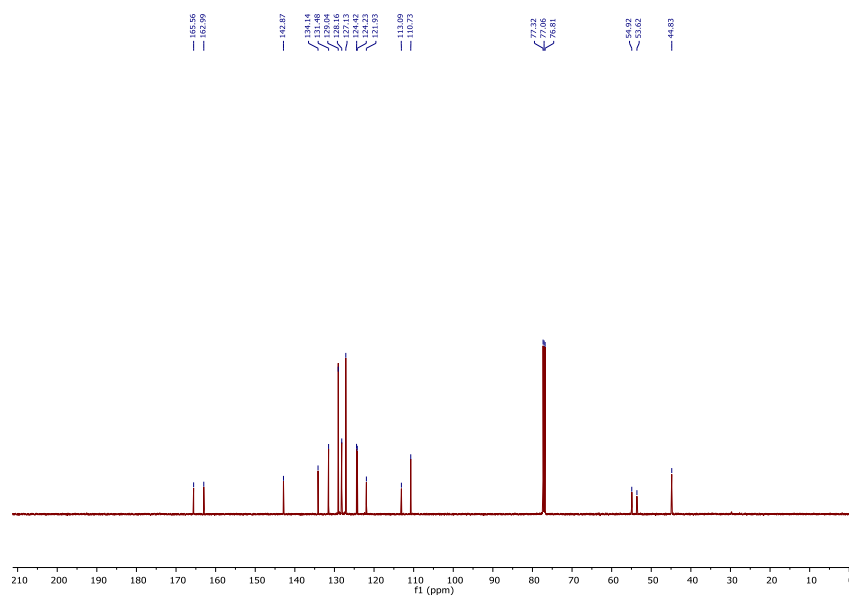
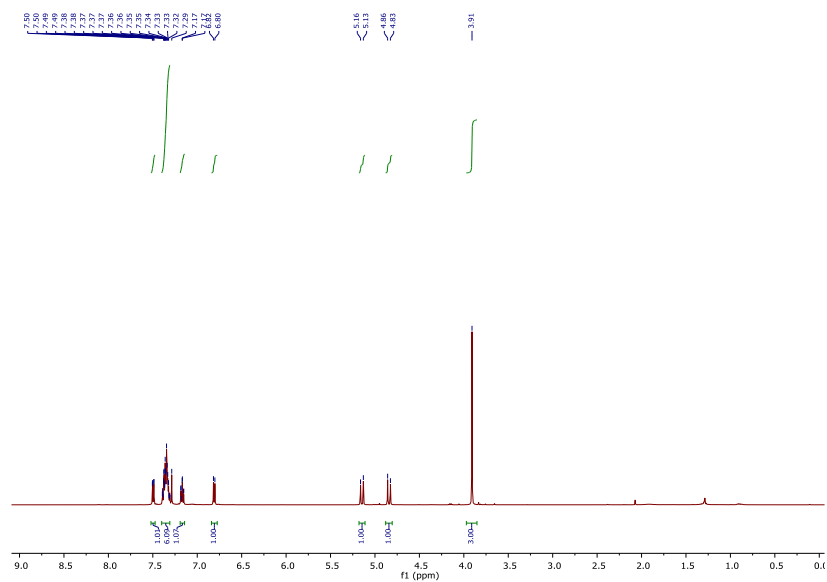
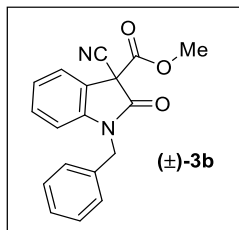
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Method hrlcms-20 sept.m Operator RUCHI  
Sample Name Dr A Bisai-AR-03-61 Instrument micrOTOF-Q II 10330  
Comment

## Acquisition Parameter

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Scanned copy of mass spectrum of (±)-**3a**

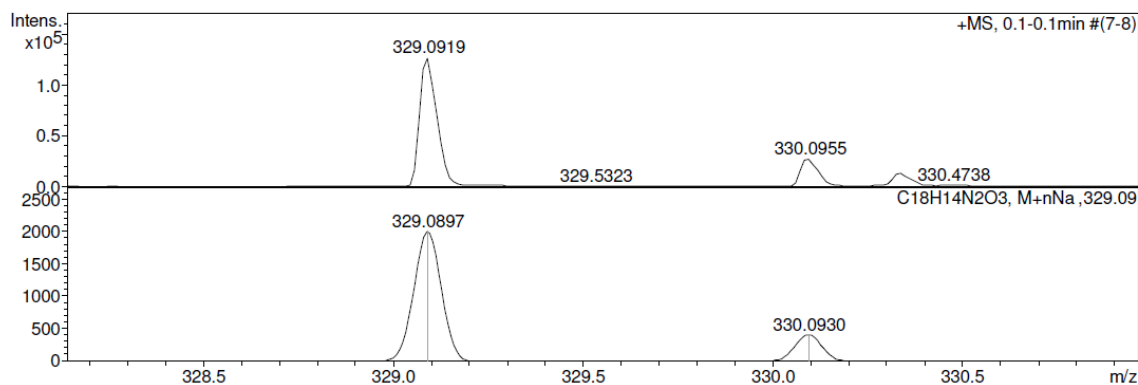
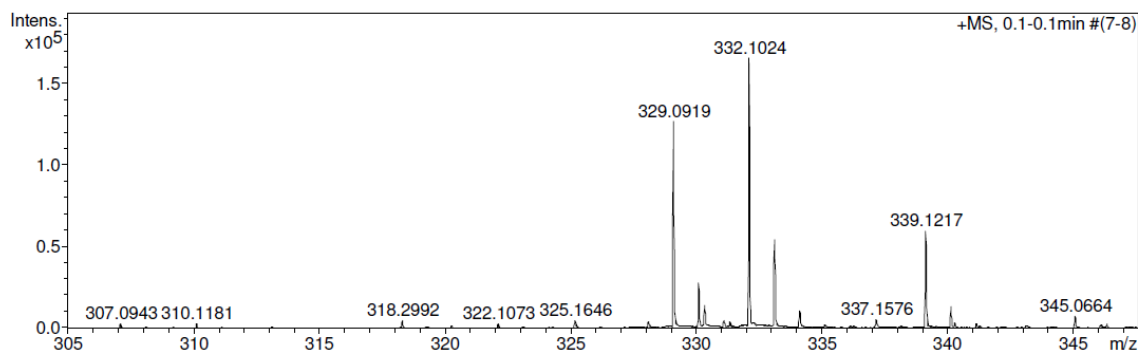
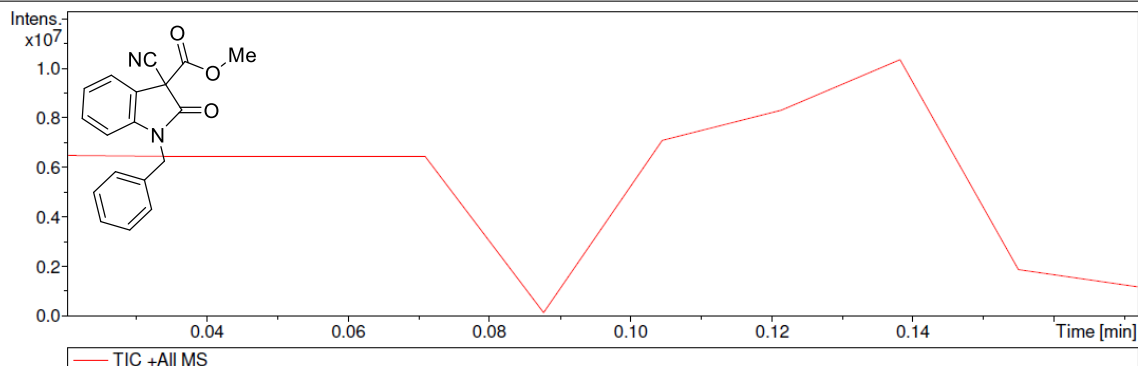


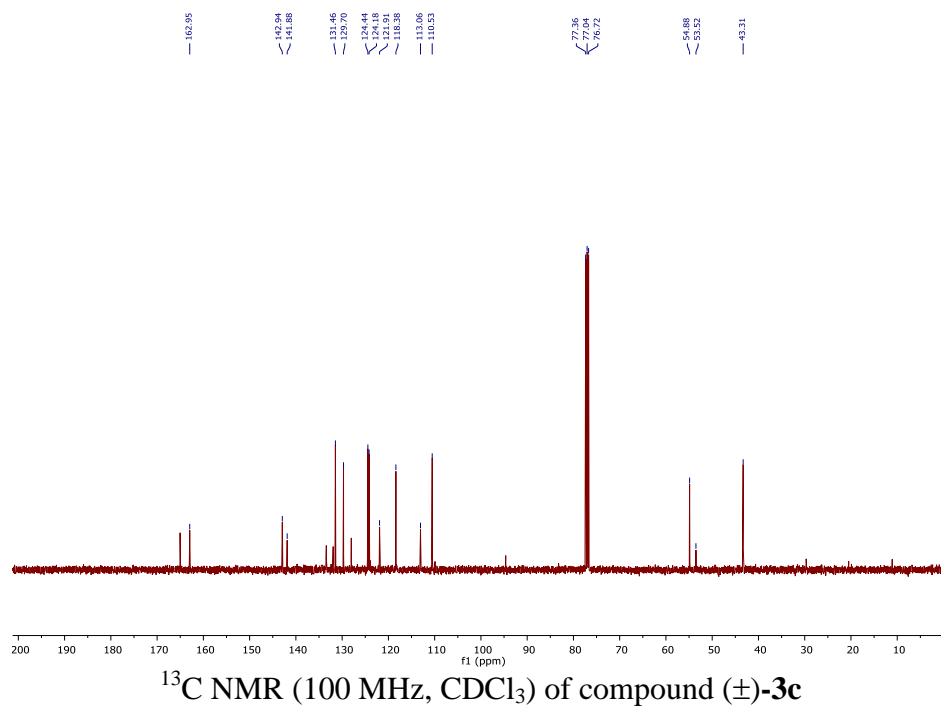
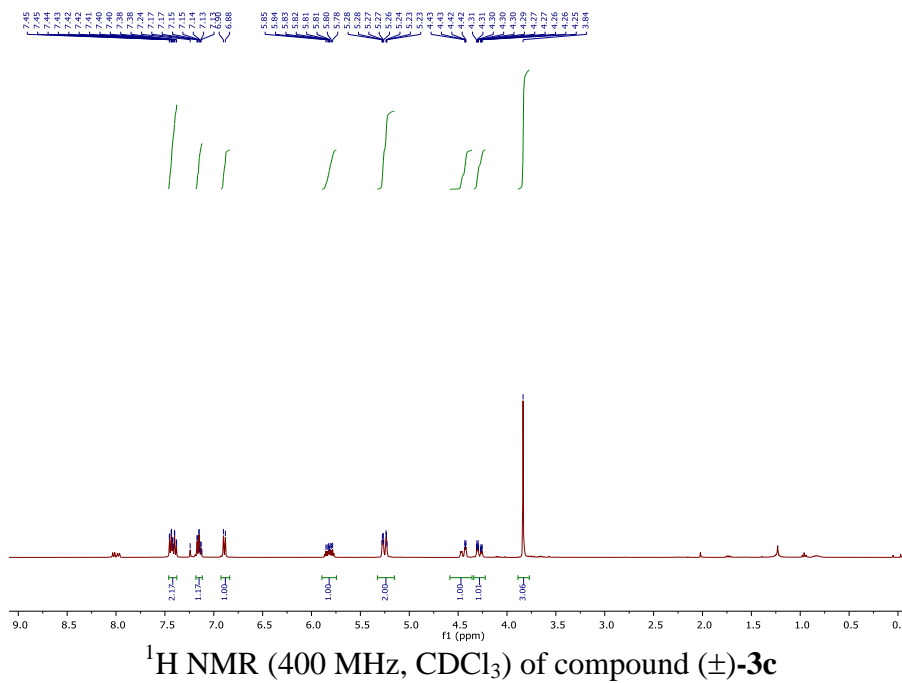
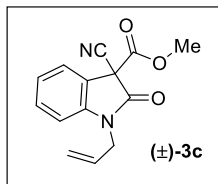
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Scanned copy of mass spectrum of (±)-**3b**



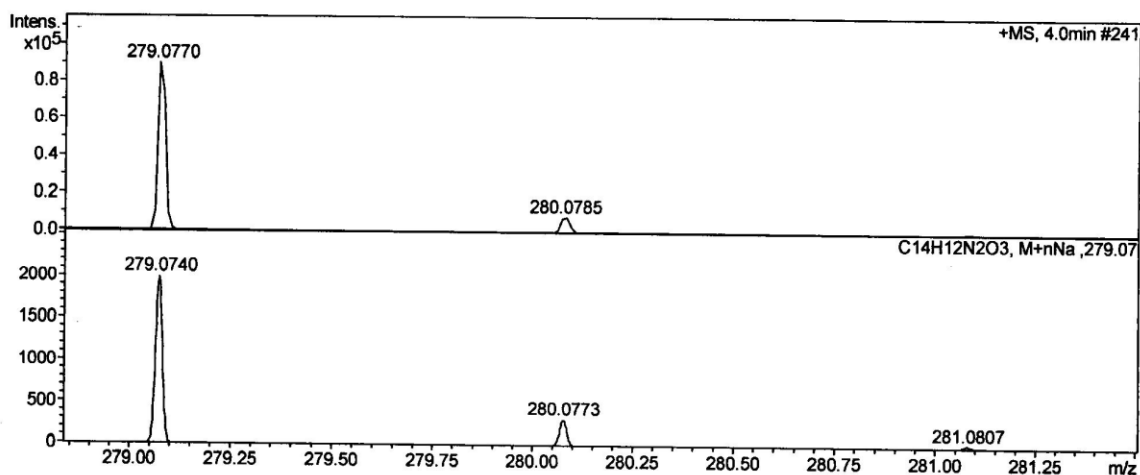
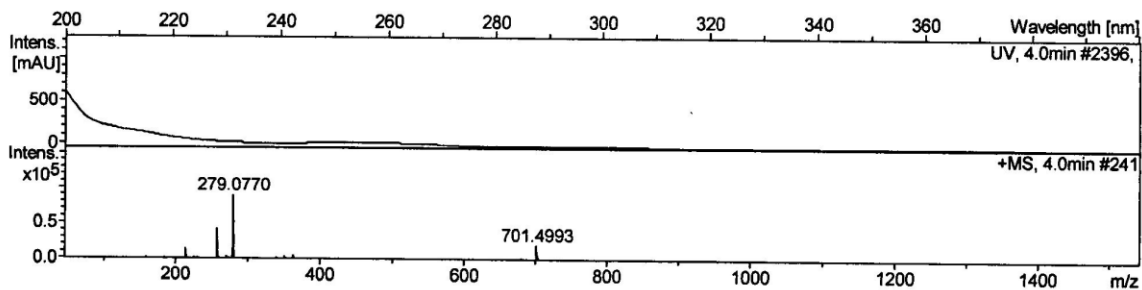
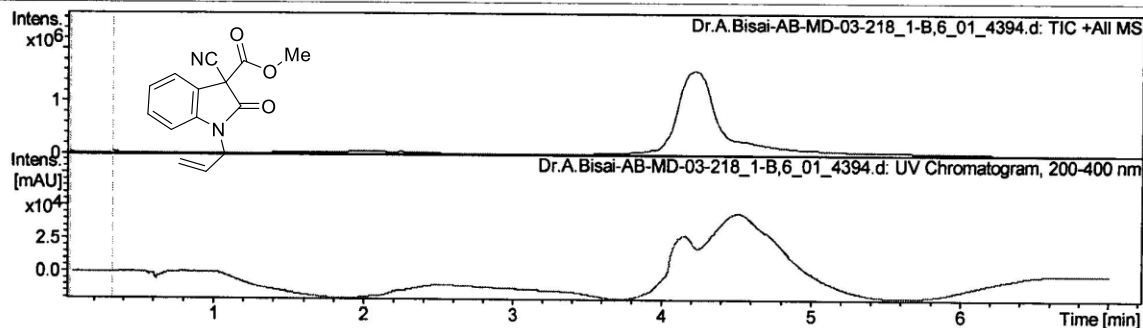
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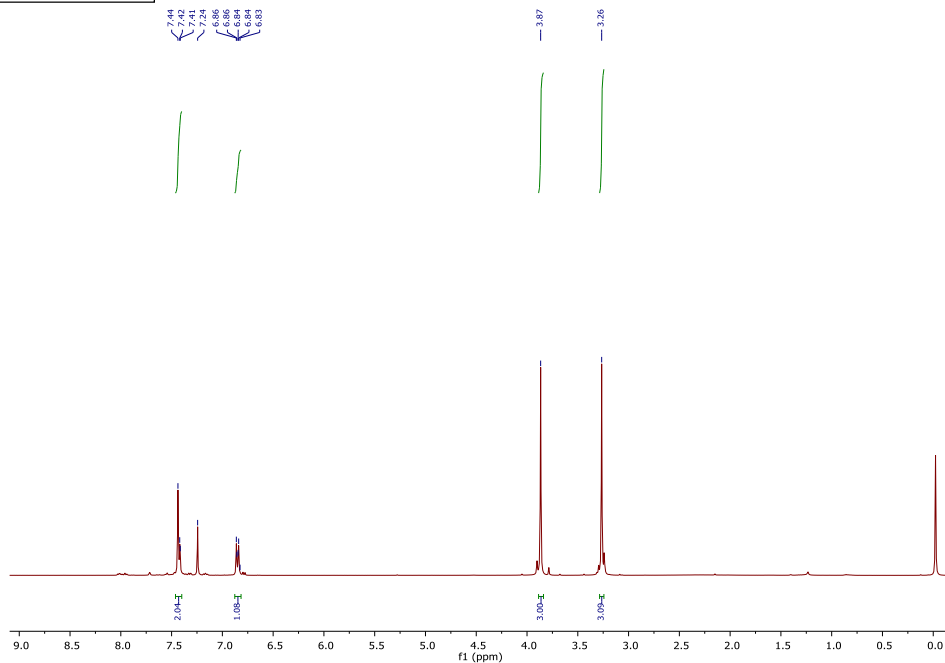
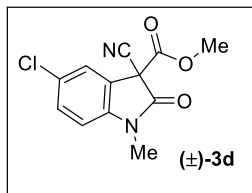
## Analysis Info

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Method	HRLCMS-20 Sept.m	Operator	RUCHI
Sample Name	Dr.A.Bisai-AB-MD-03-218	Instrument	micrOTOF-Q II 10330
Comment			

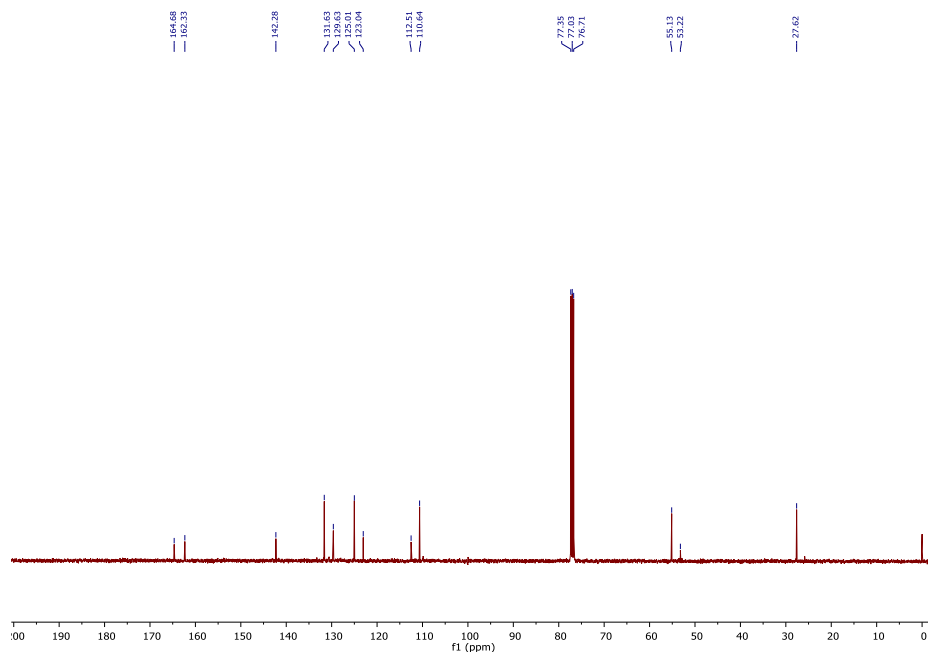
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-3d



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-3d

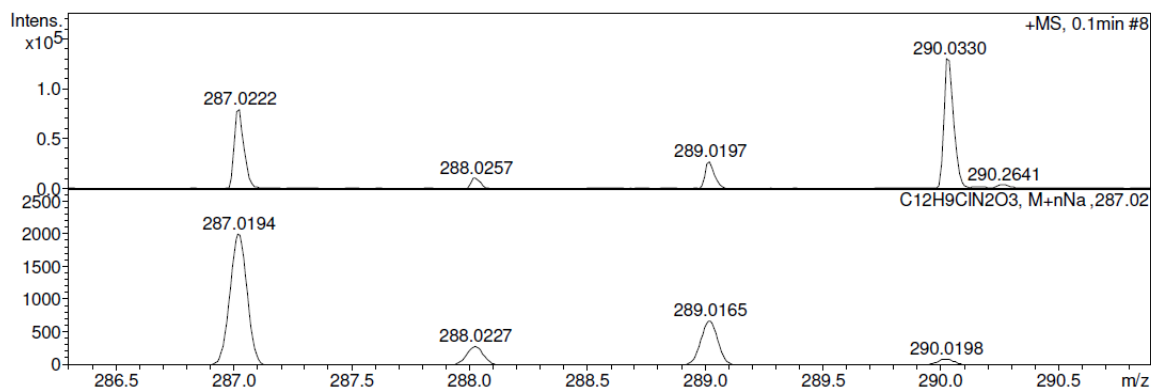
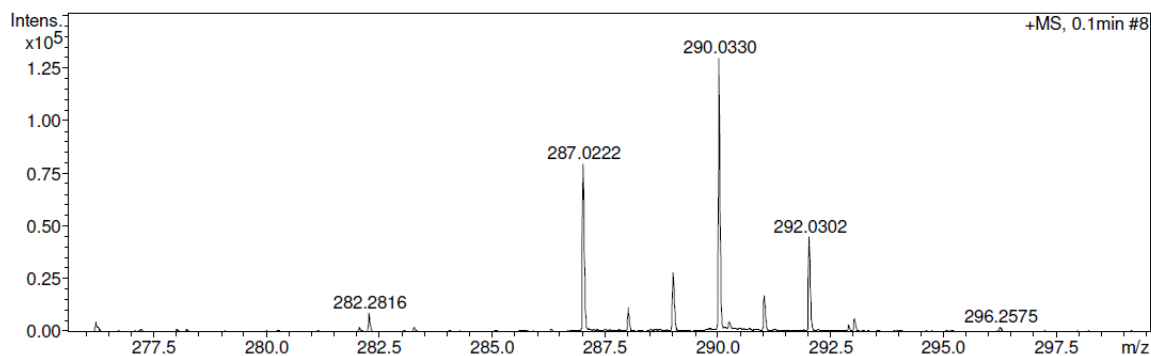
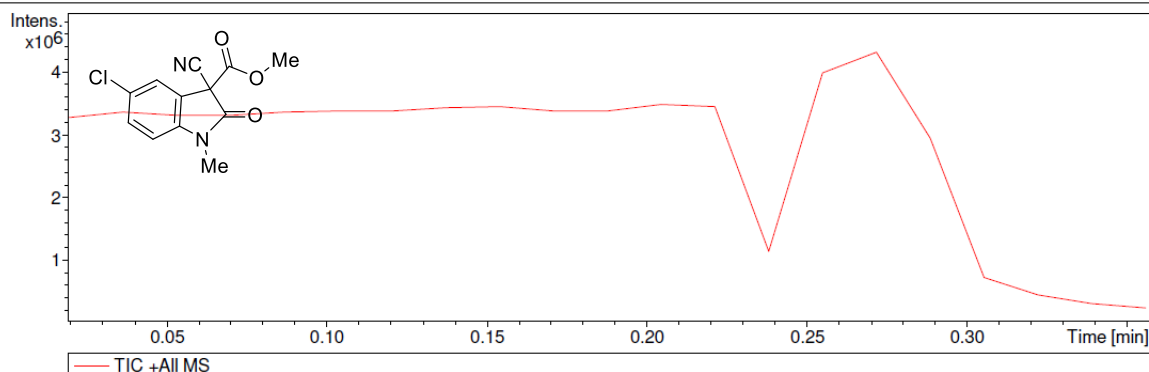
## Display Report

## Analysis Info

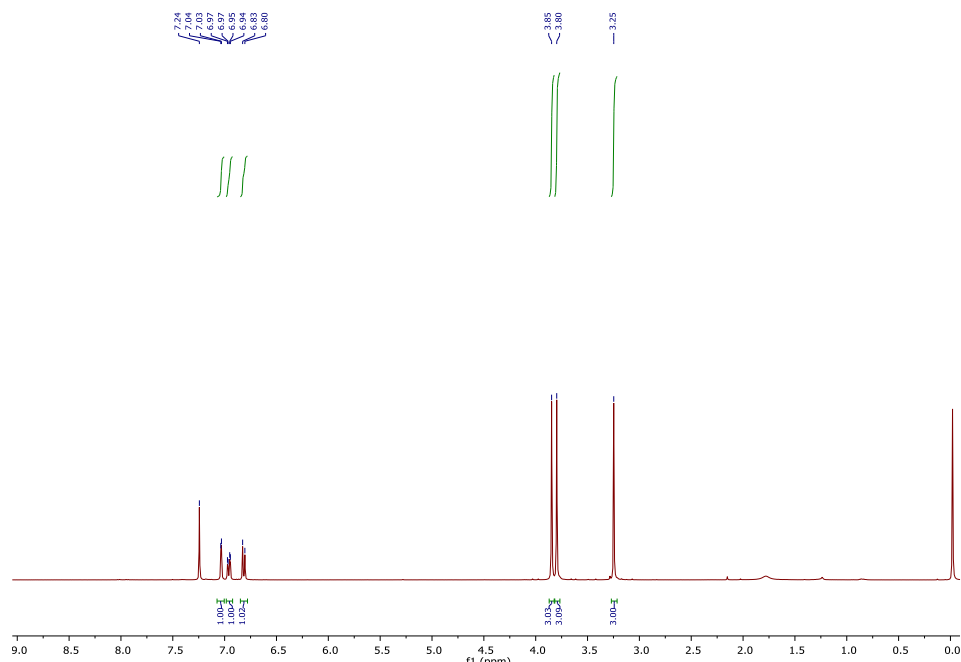
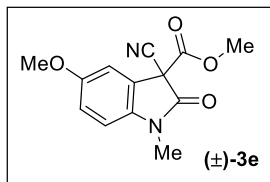
Analysis Name	D:\Data\NEW USER DATA 2017\jan-2018\30 jan\Dr A Bisai-AR-03-62.d	Acquisition Date	1/30/2018 12:37:37 PM
Method	tune_mix_low.New.021117.m	Operator	RUCHI
Sample Name	AR-03-62	Instrument	micrOTOF-Q II 10330
Comment			

## Acquisition Parameter

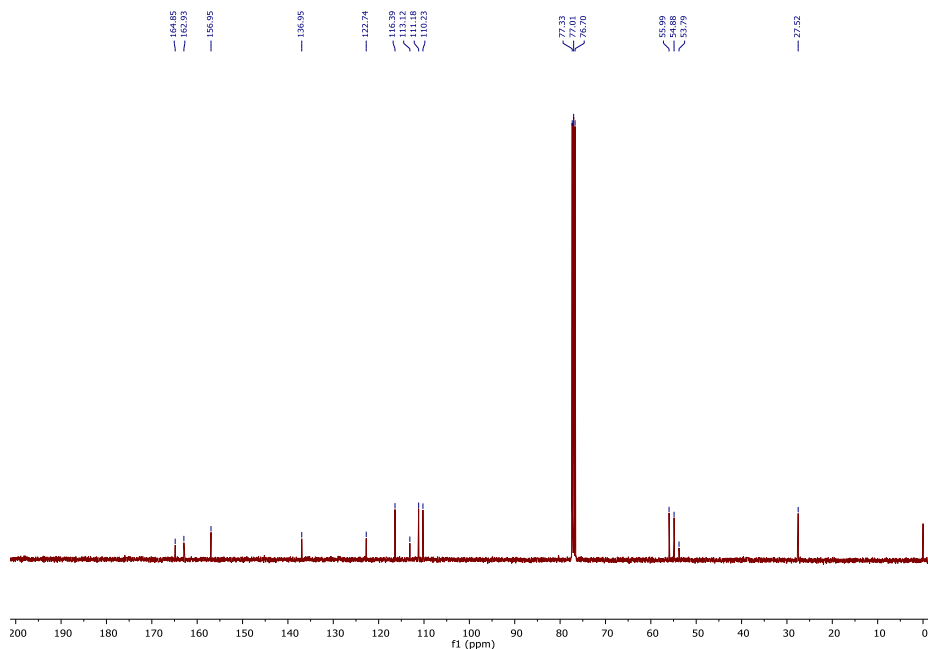
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste







<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (±)-3e



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-3e

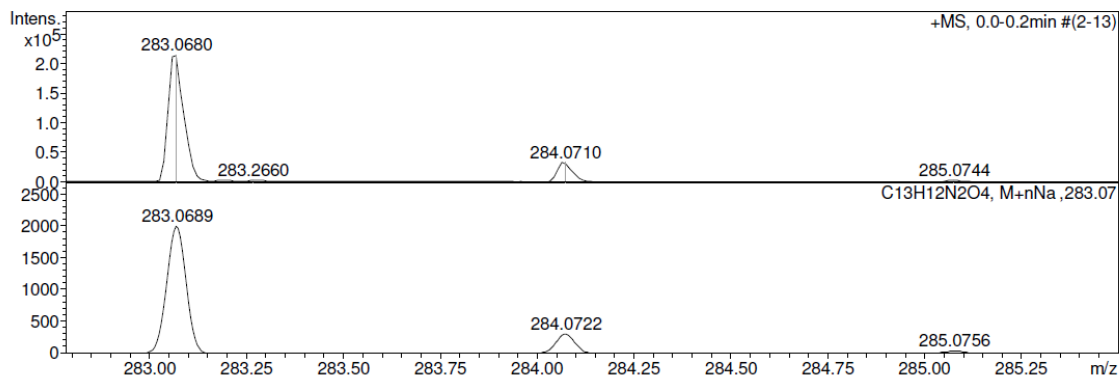
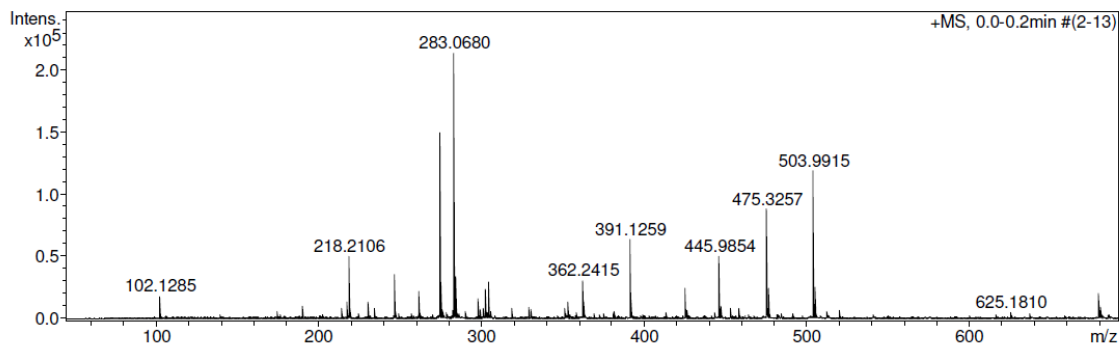
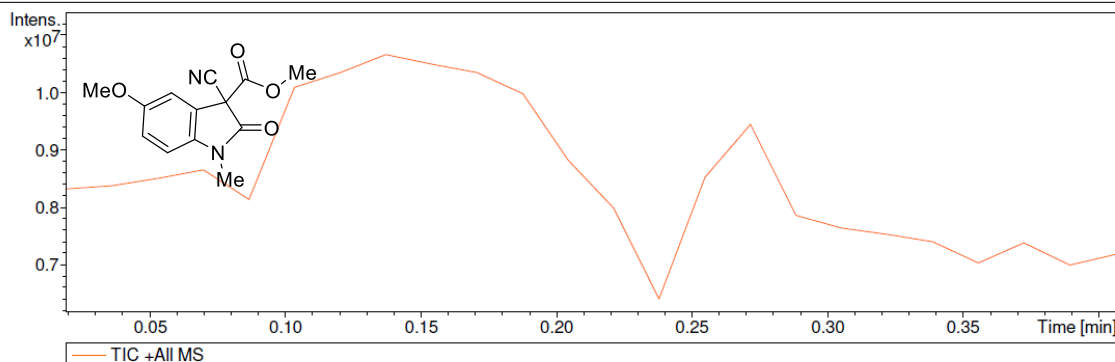
## Display Report

## Analysis Info

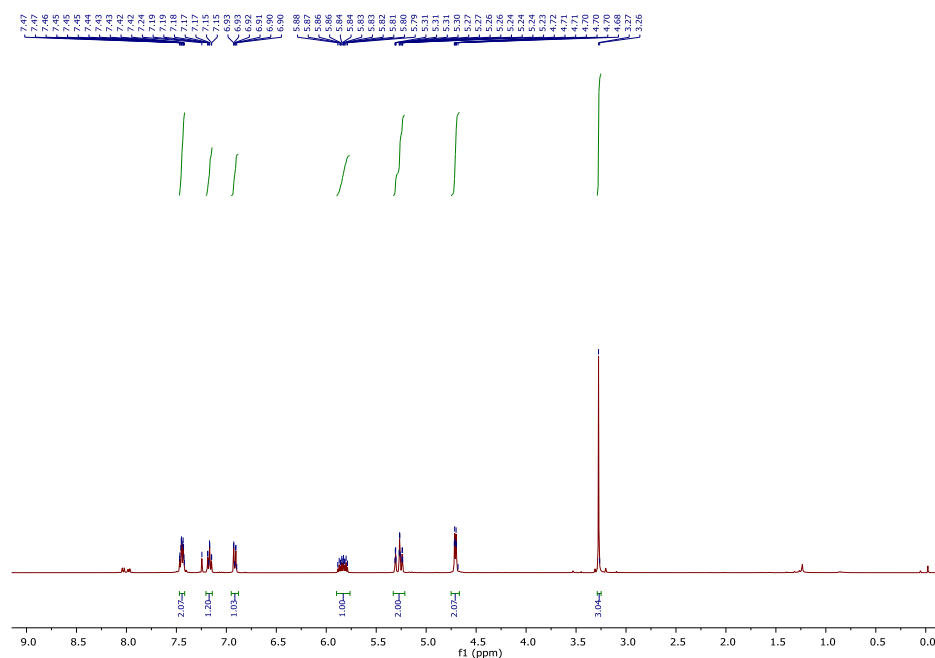
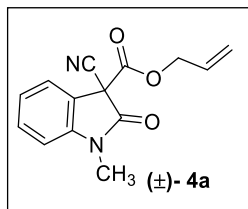
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Method tune\_low.m Operator RUCHI  
Sample Name AB-AR-03-66 Instrument micrOTOF-Q II 10330  
Comment

## Acquisition Parameter

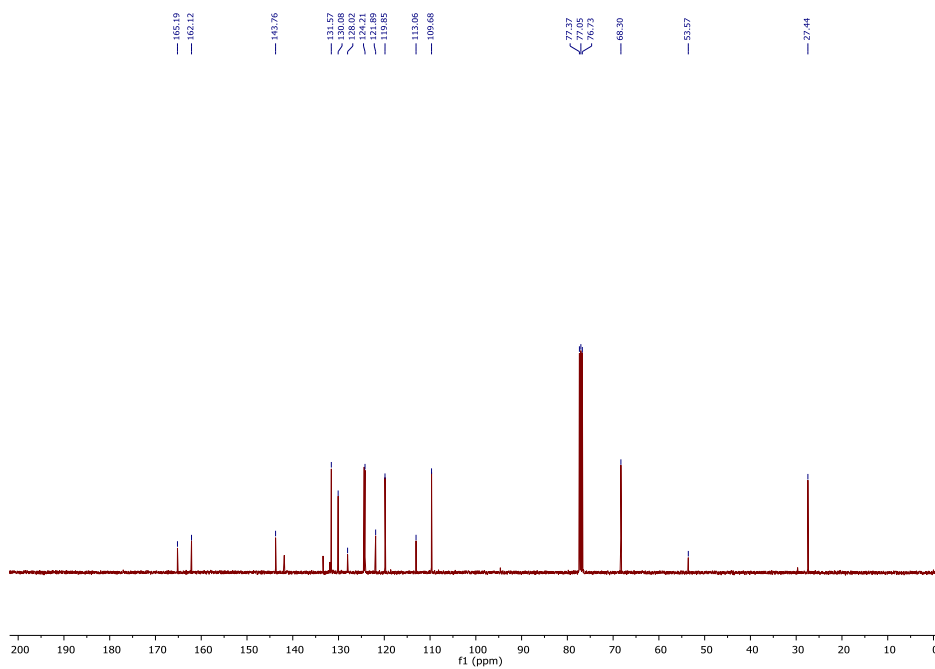
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Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of (±)-3e



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (±)-**4a**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-**4a**

## Display Report

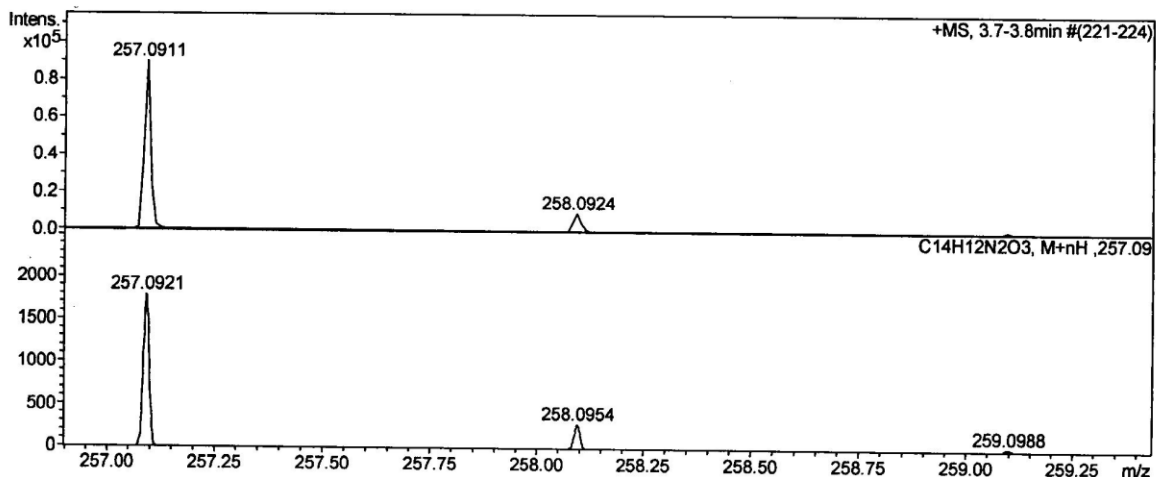
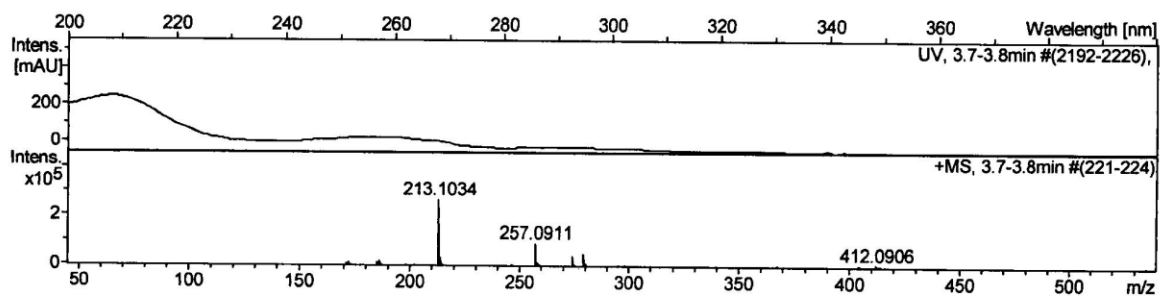
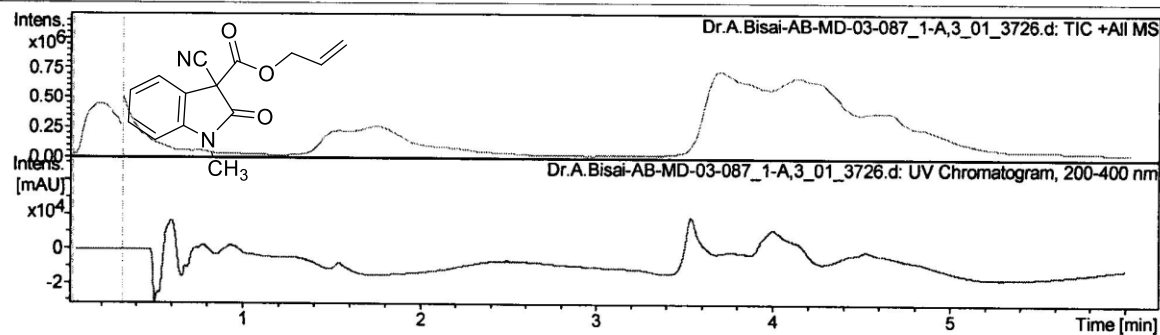
## Analysis Info

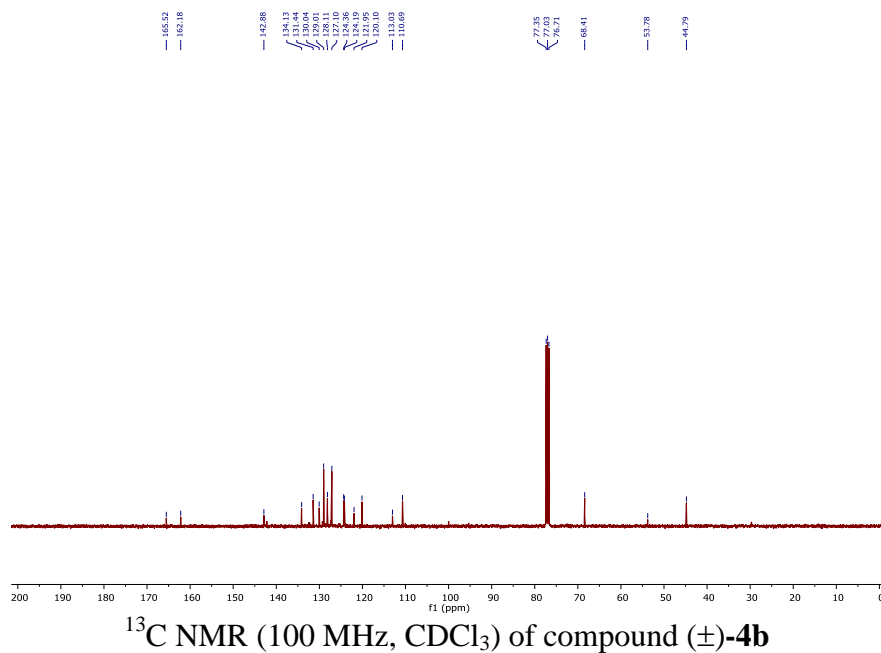
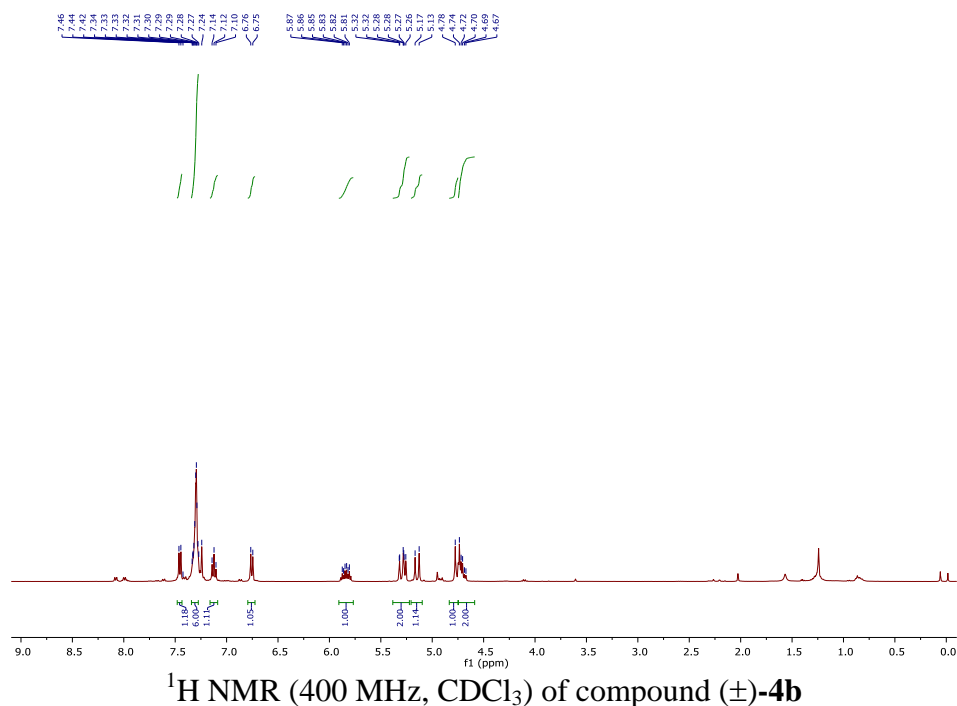
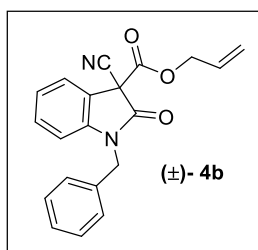
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Method HRLCMS-20 Sept.m  
Sample Name Dr.A.Bisai-AB-MD-03-087  
Comment

Acquisition Date 9/23/2015 11:49:10 AM  
Operator RUCHI  
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



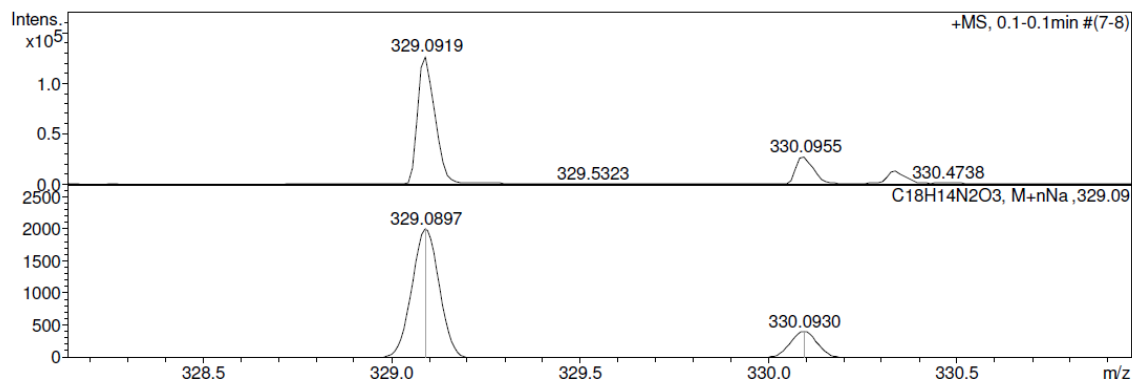
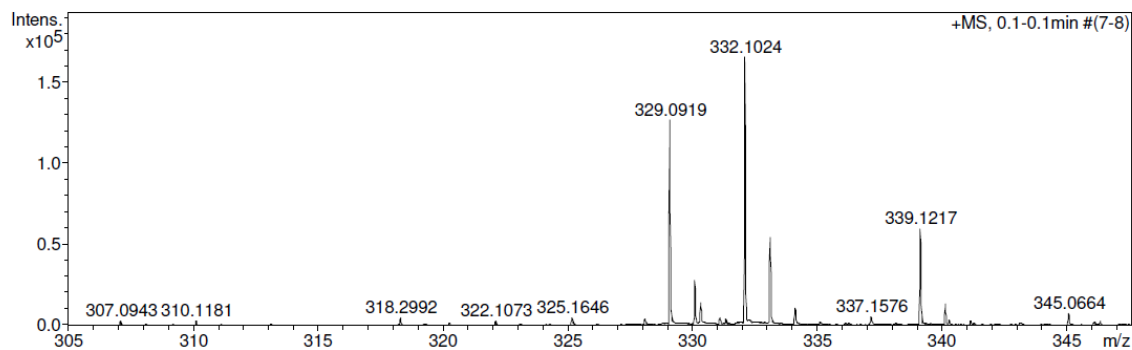
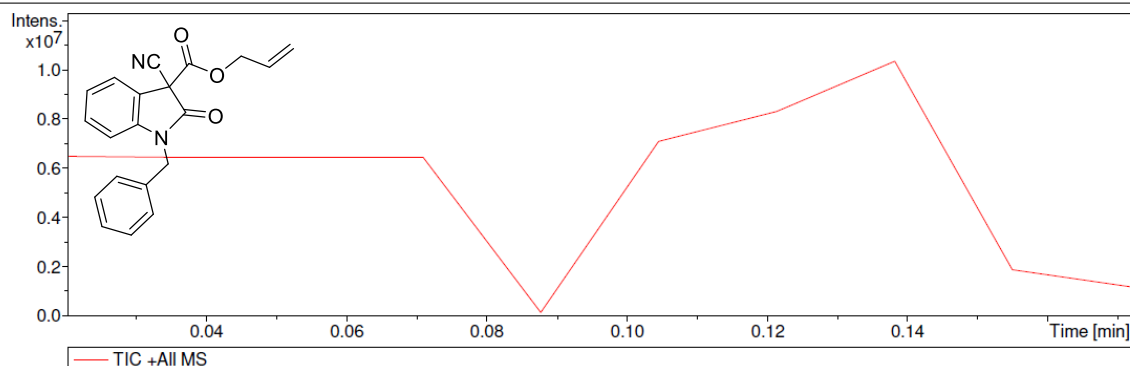


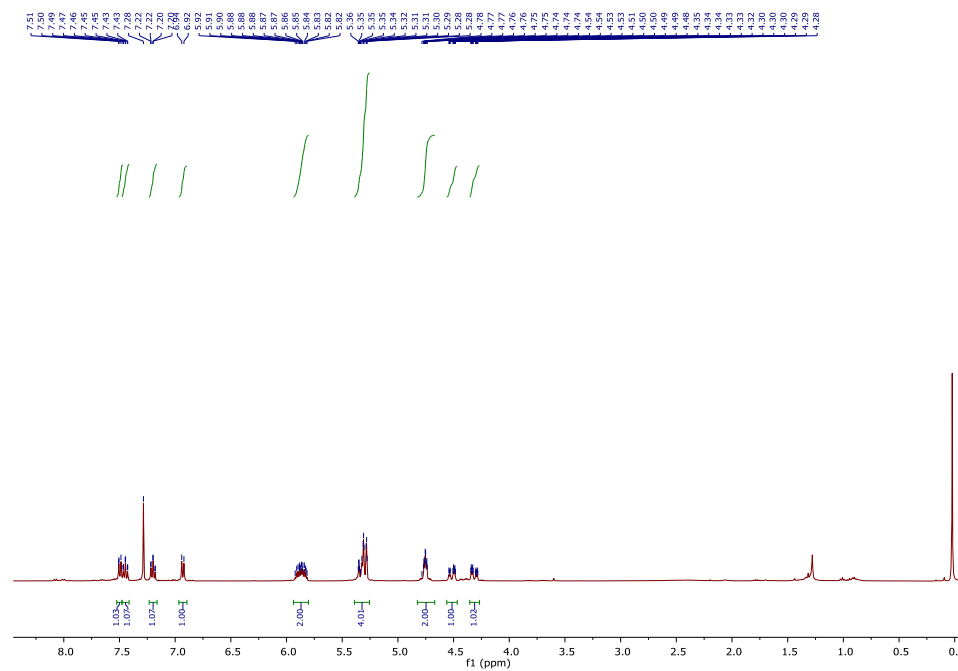
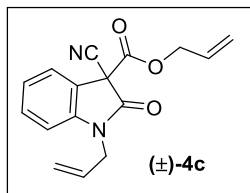
## Display Report

**Analysis Info**  
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Sample Name AR-03-60-R  
Comment  
Acquisition Date 1/30/2018 12:54:58 PM  
Operator RUCHI  
Instrument micrOTOF-Q II 10330

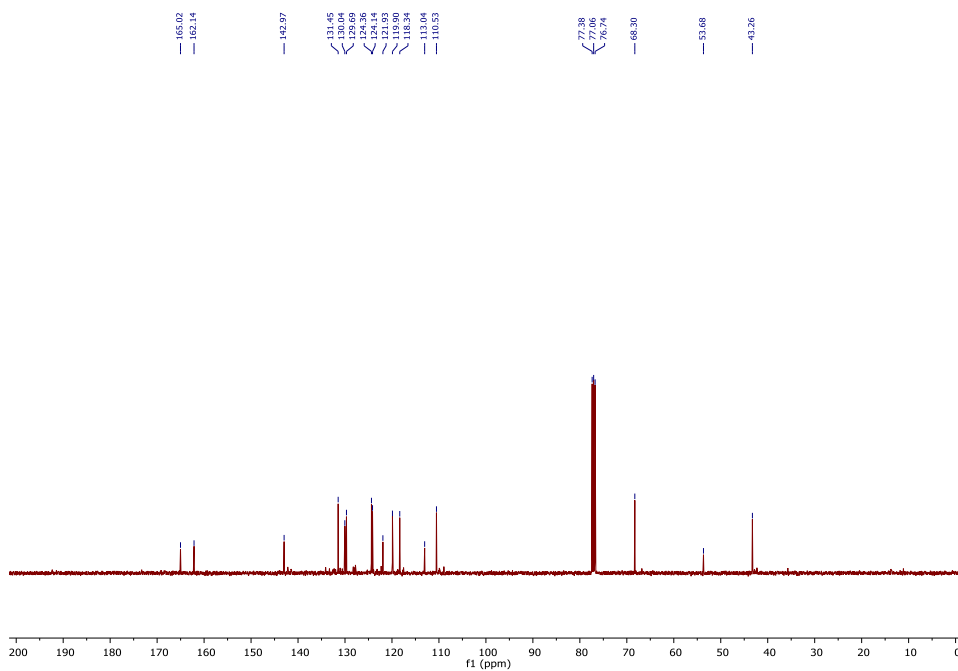
**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste

Scanned copy of mass spectrum of ( $\pm$ )-4b



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-4c



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-4c

## Display Report

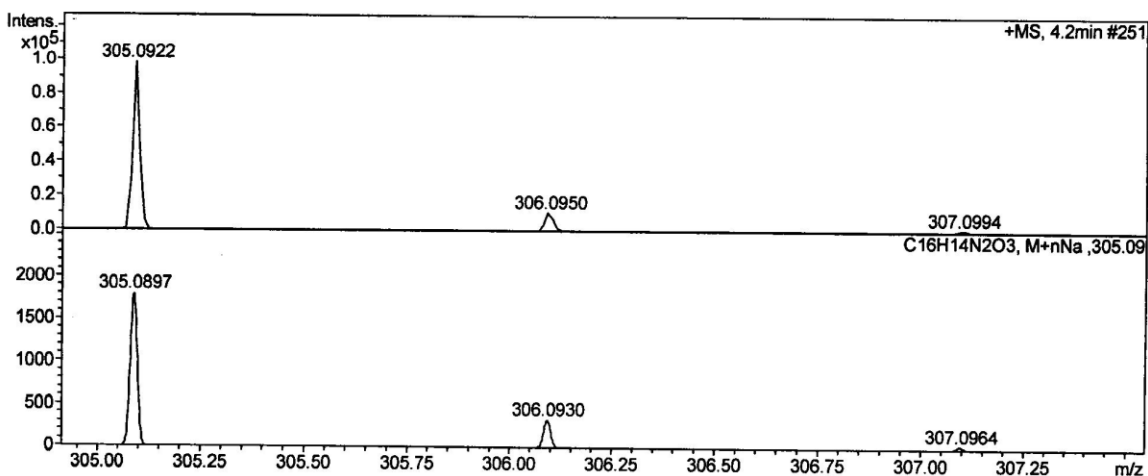
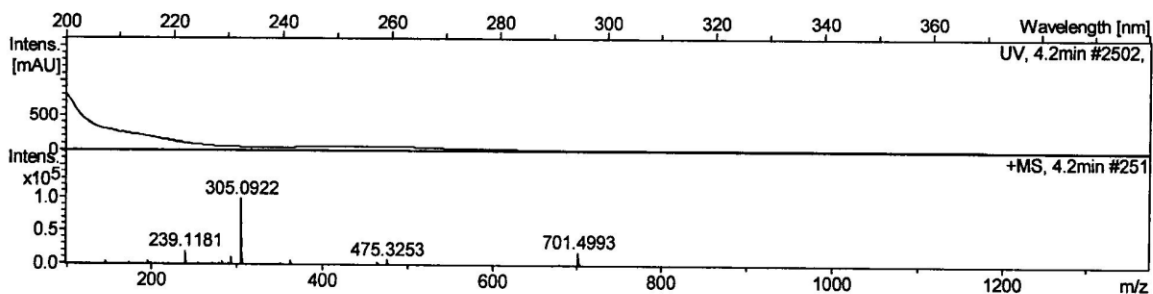
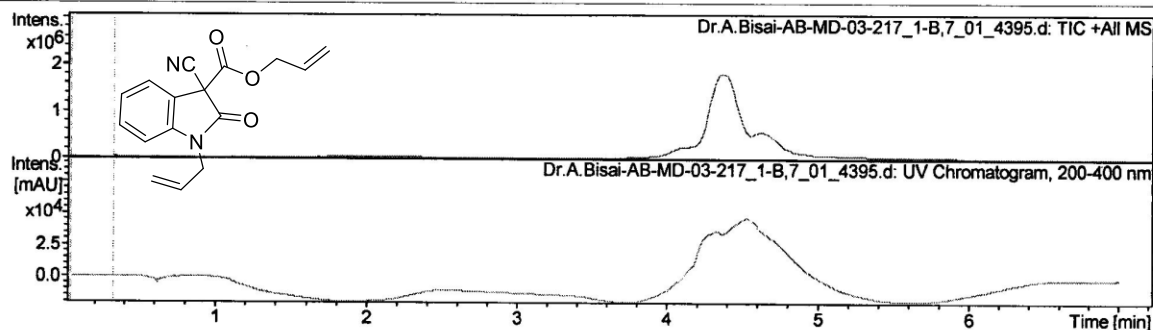
## Analysis Info

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 Sample Name Dr.A.Bisai-AB-MD-03-217  
 Comment

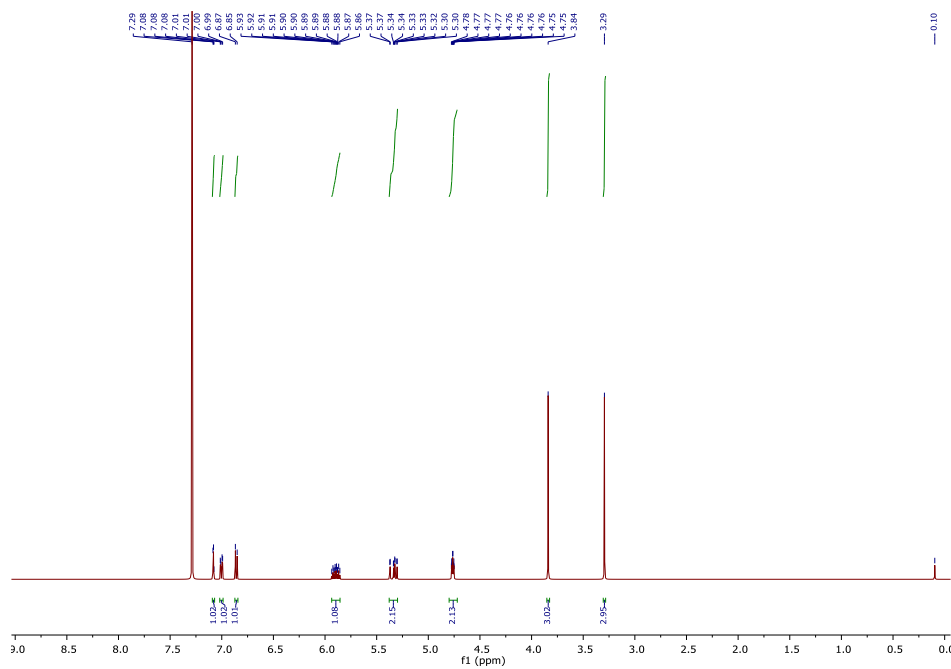
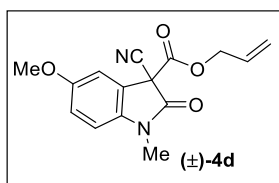
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 Operator RUCHI  
 Instrument micrOTOF-Q II 10330

## Acquisition Parameter

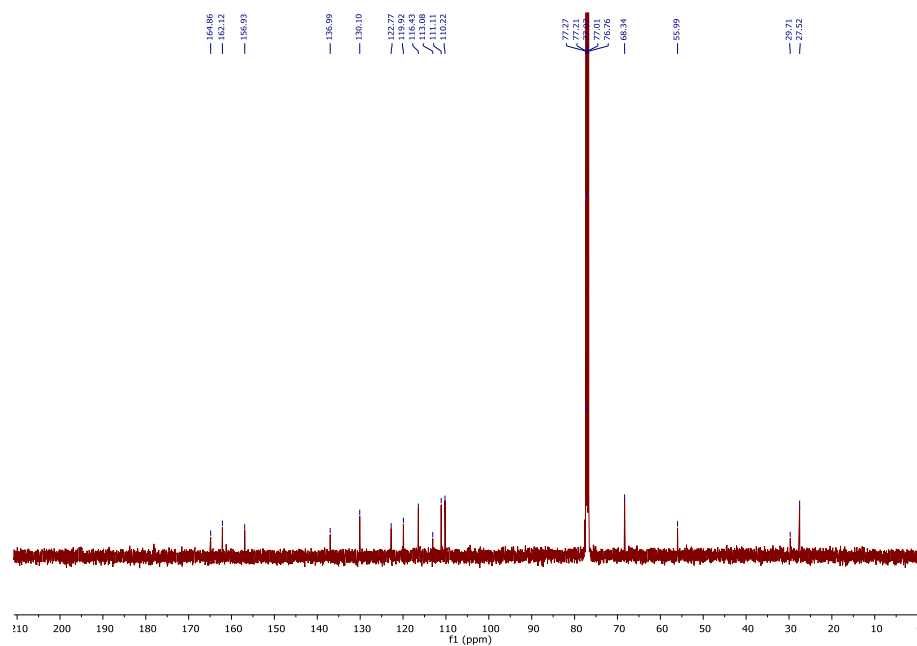
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound (±)-4d



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound (±)-4d

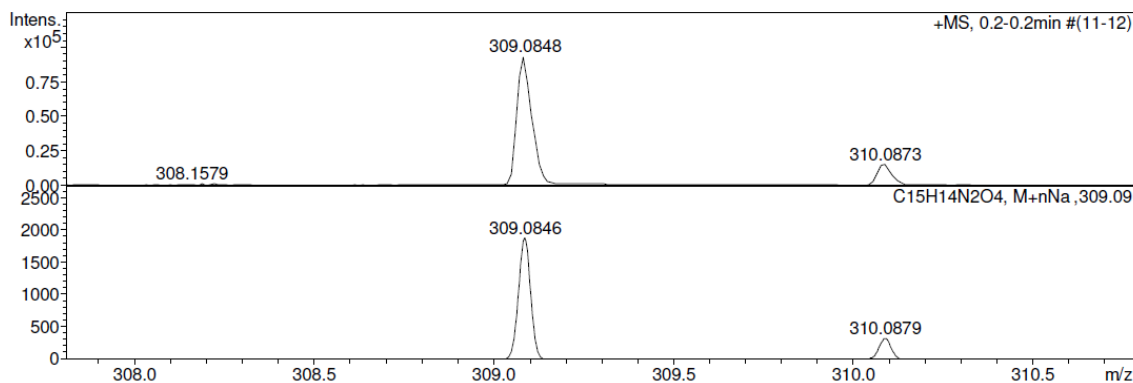
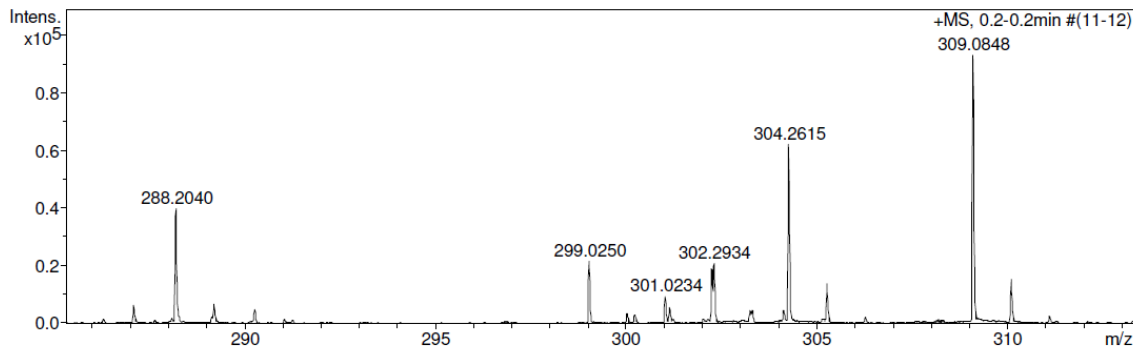
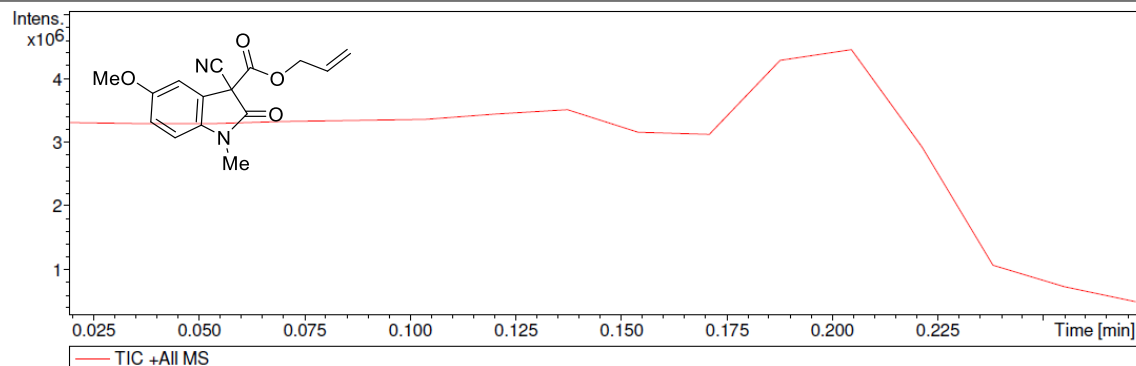
## Display Report

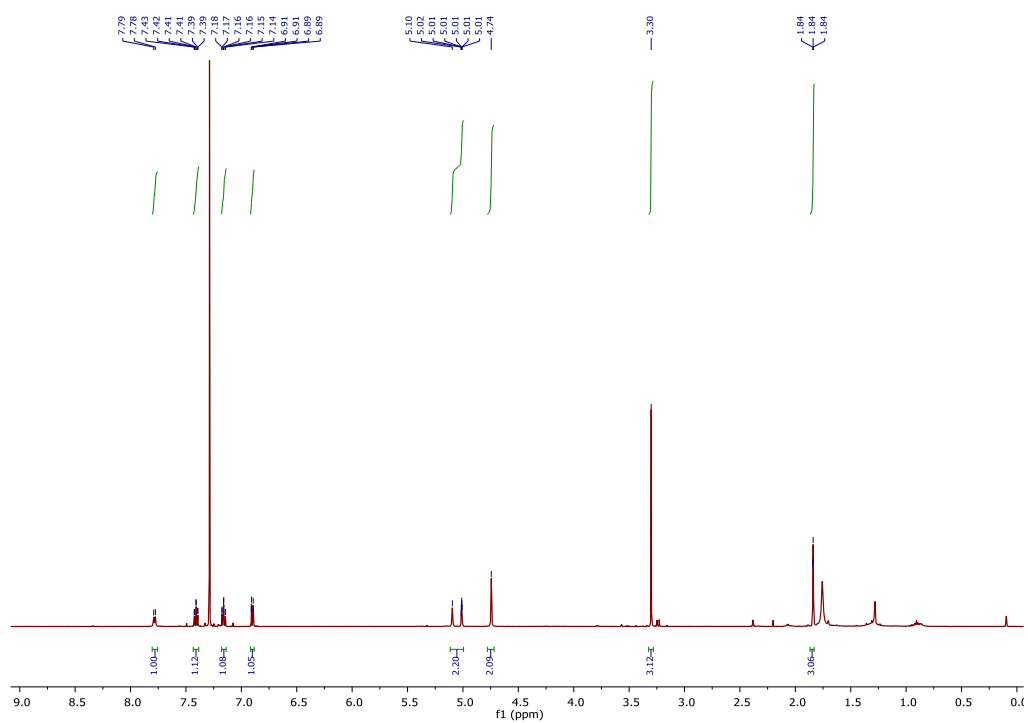
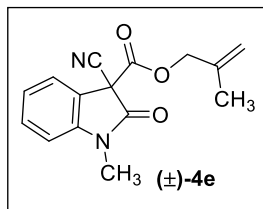
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Method tune mix\_low.New.021117.m Operator RUCHI  
Sample Name AR-03-76 Instrument micrOTOF-Q II 10330  
Comment

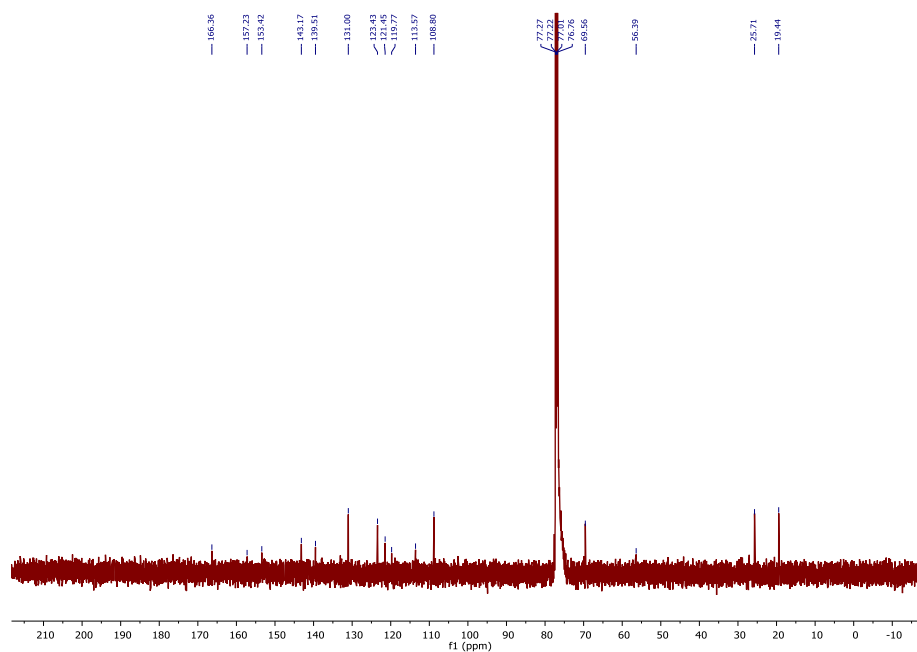
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound (±)-4e



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) of compound (±)-4e

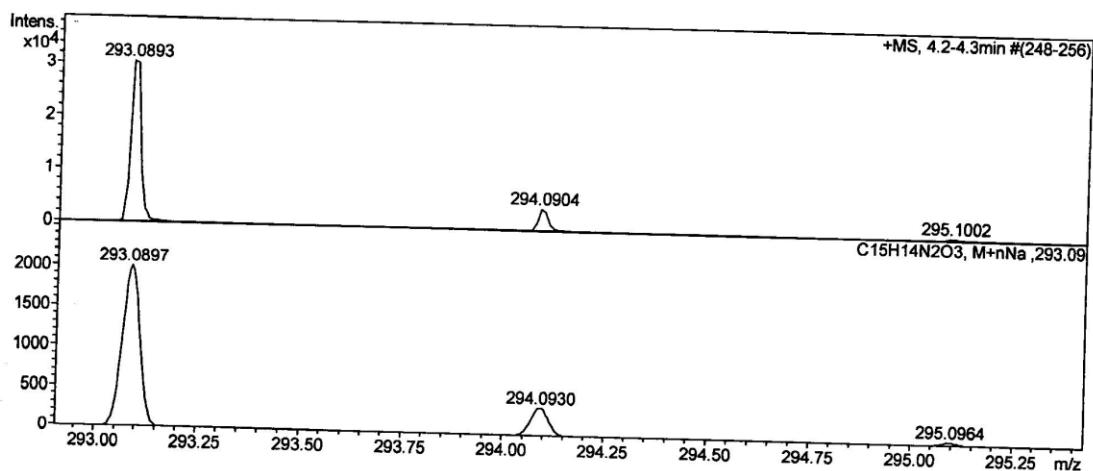
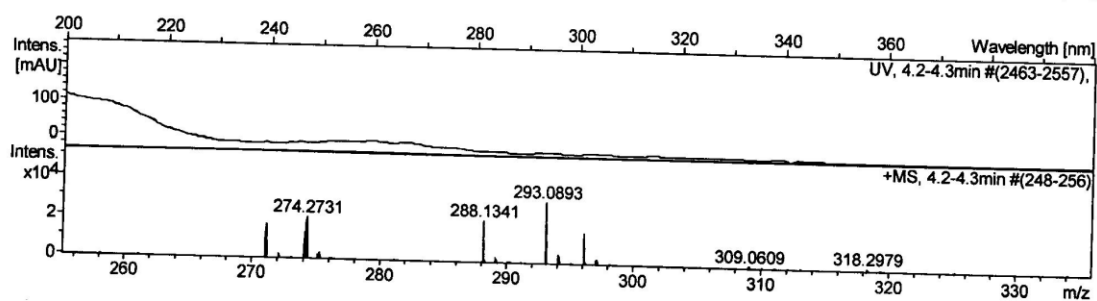
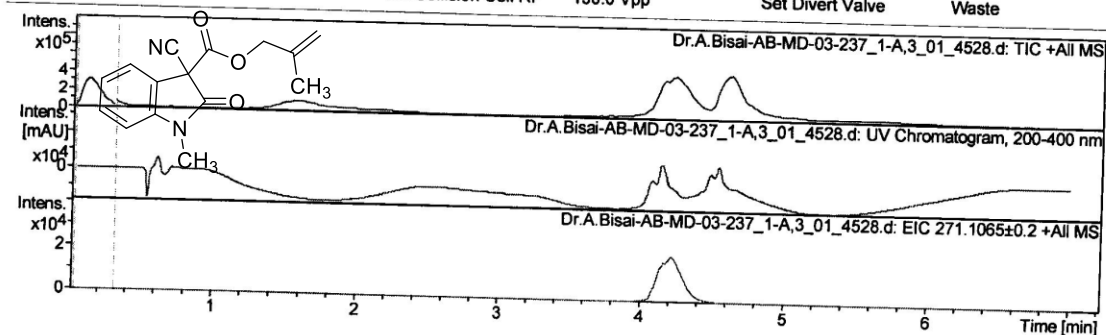
## Display Report

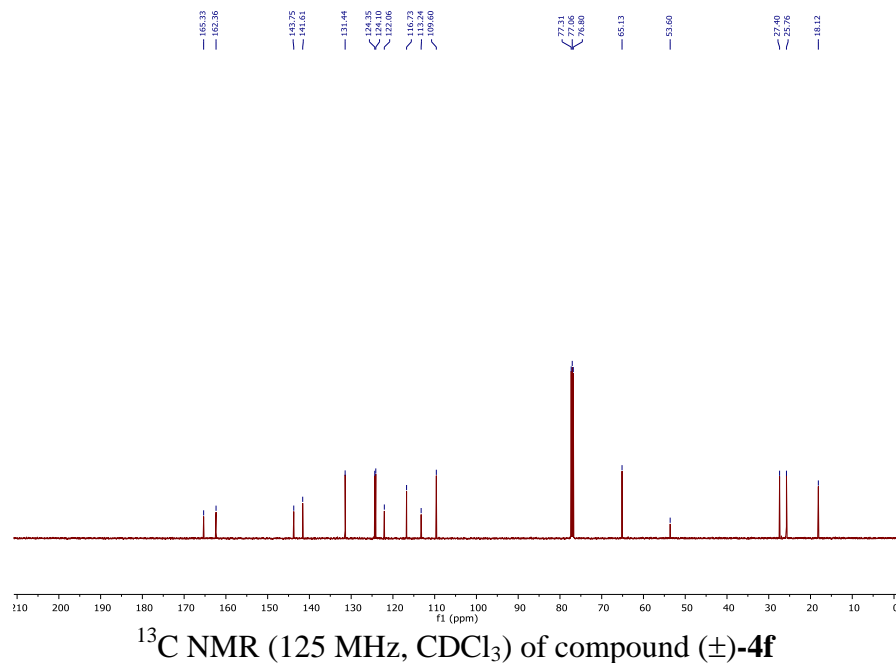
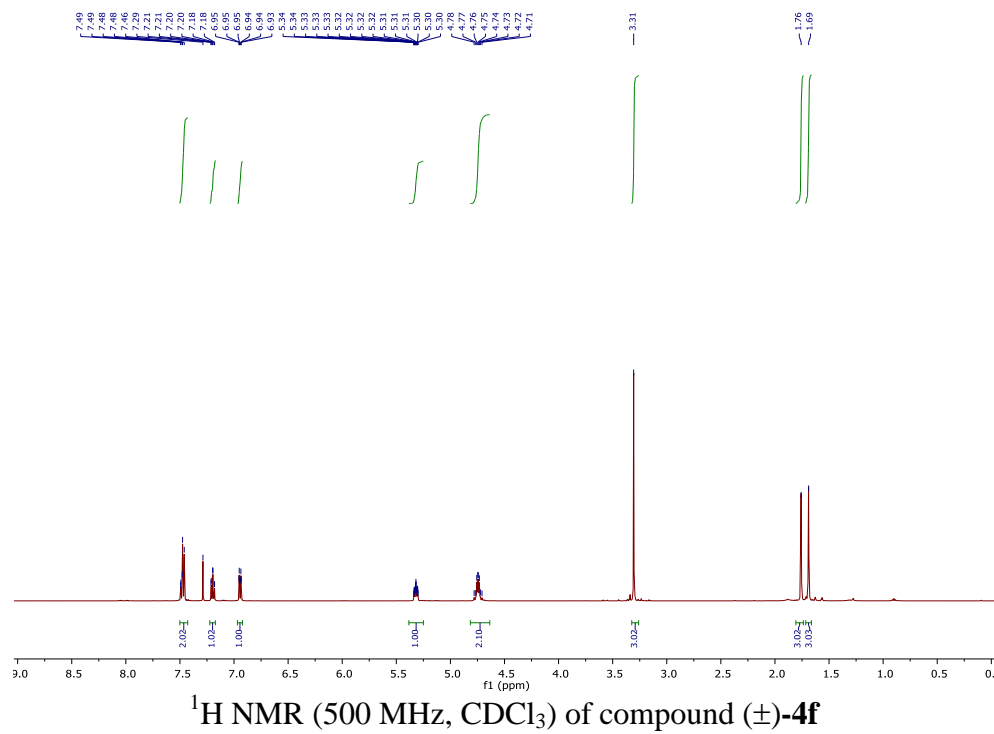
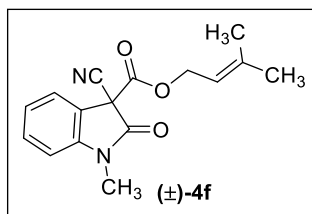
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Method	HRLCMS-20 Sept.m	Operator	RUCHI
Sample Name	Dr.A.Bisai-AB-MD-03-237	Instrument	micrOTOF-Q II 10330
Comment			

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





## Display Report

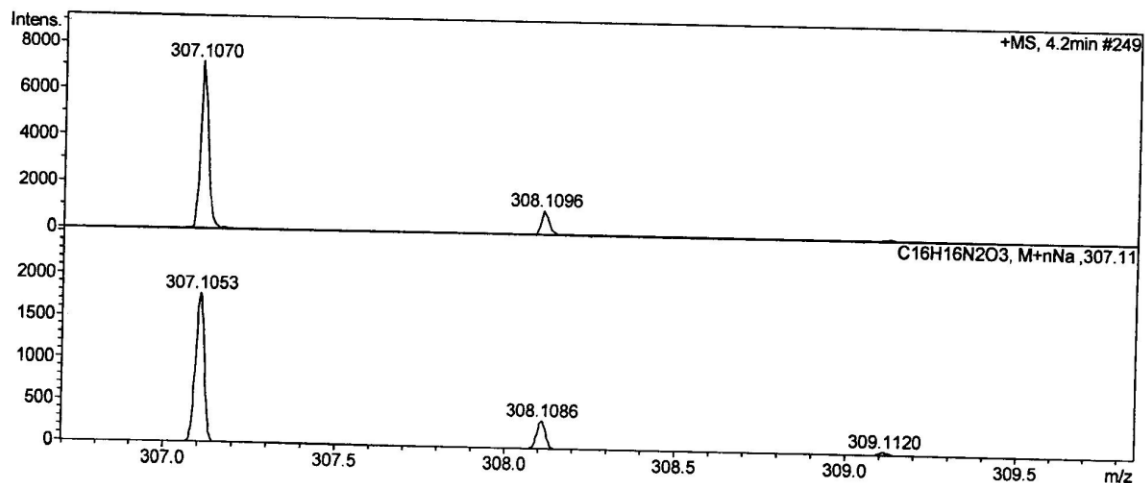
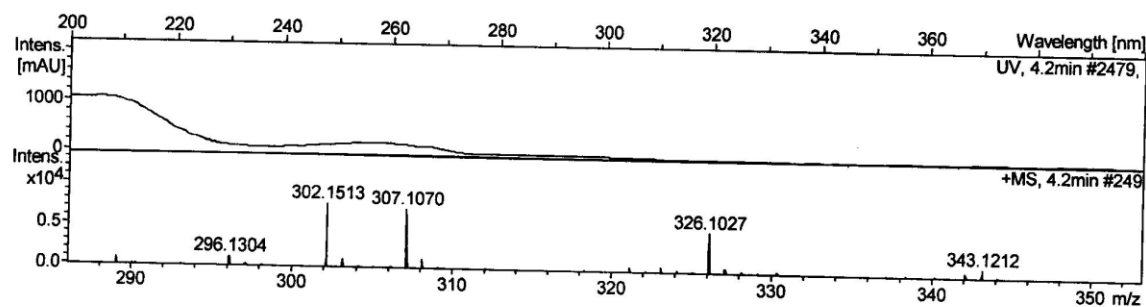
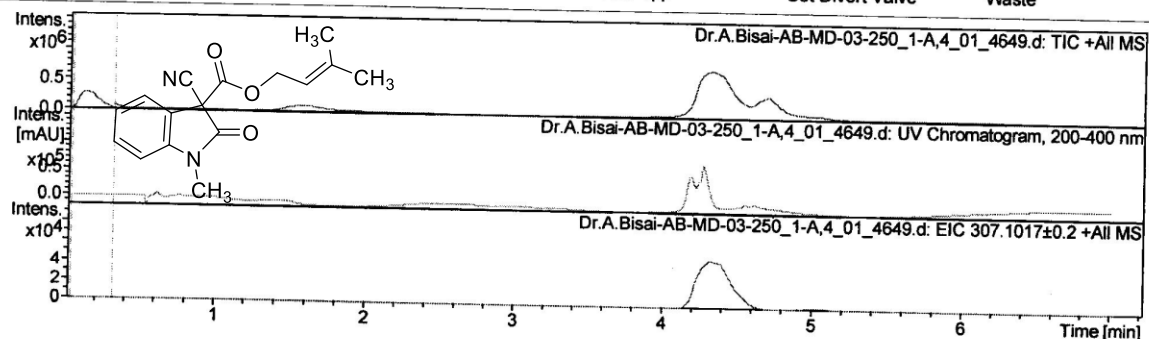
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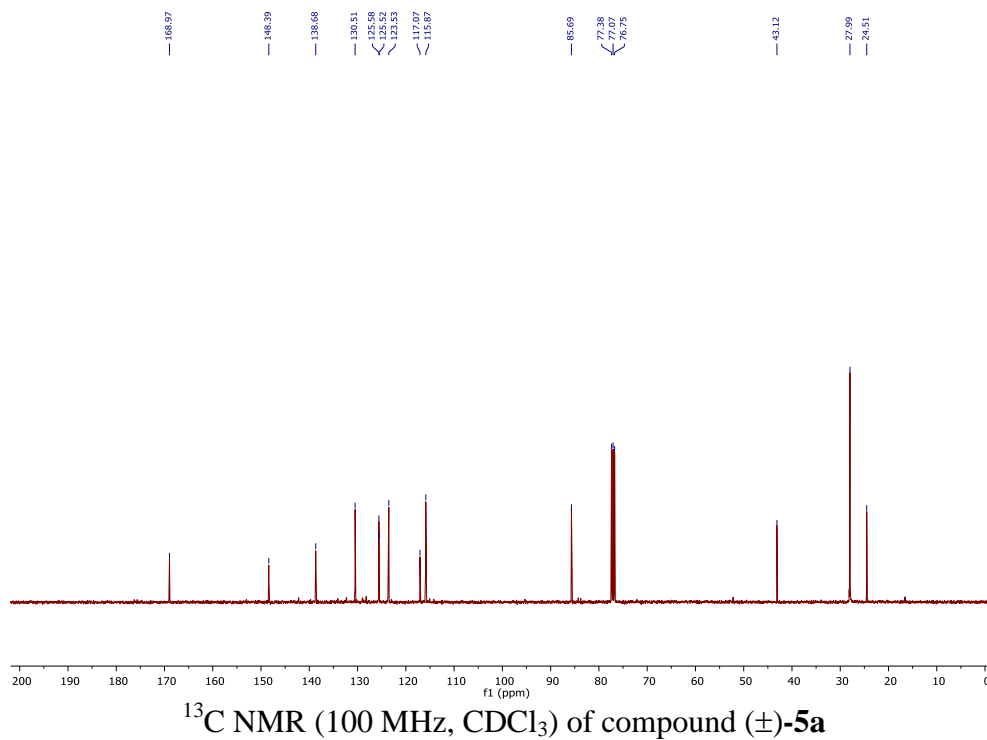
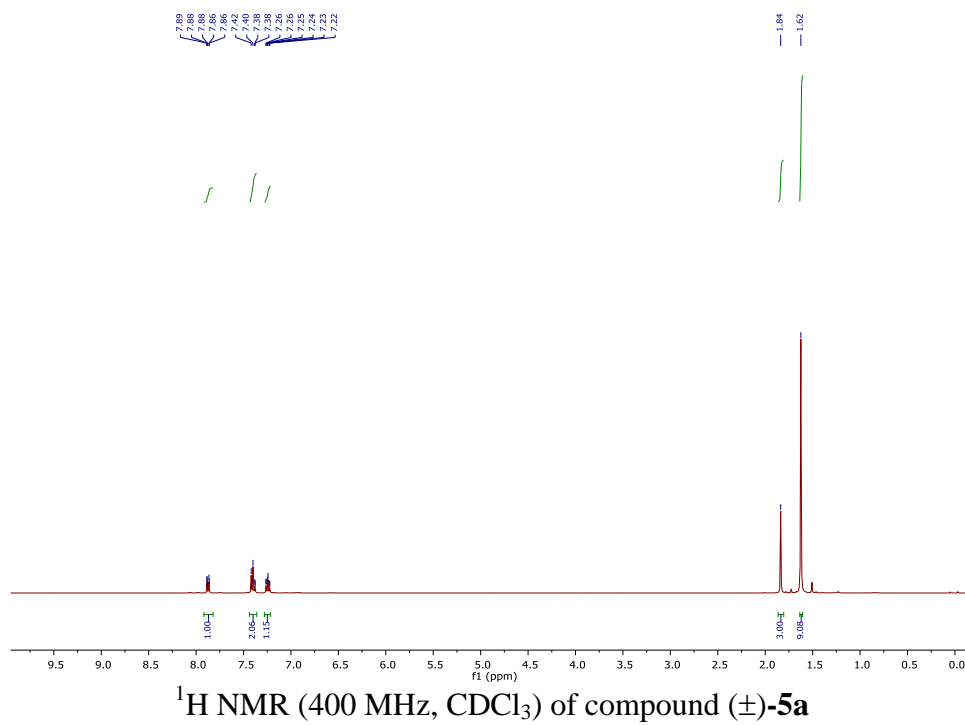
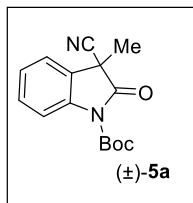
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 Method HRLCMS-20 Sept.m  
 Sample Name Dr.A.Bisai-AB-MD-03-250  
 Comment

Acquisition Date 12/21/2015 11:51:34 AM  
 Operator RUCHI  
 Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





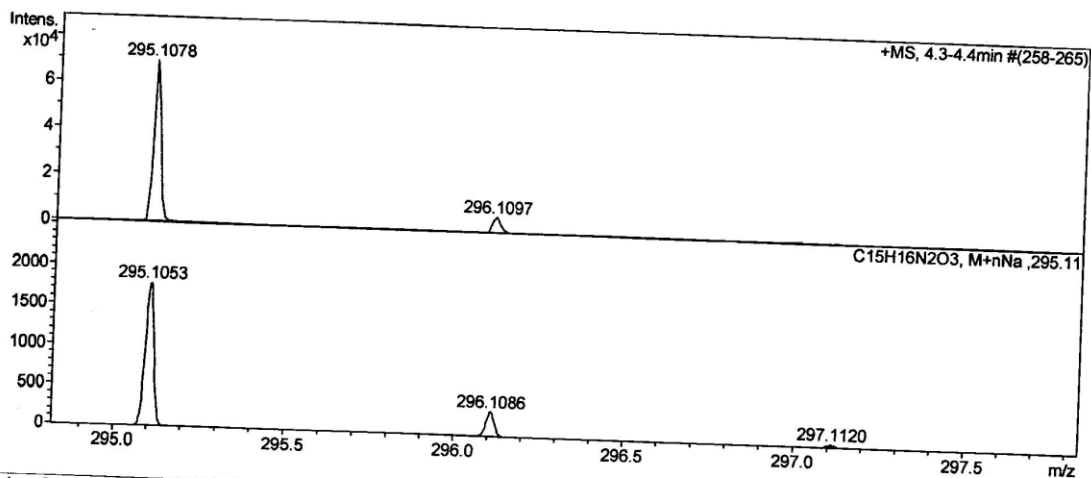
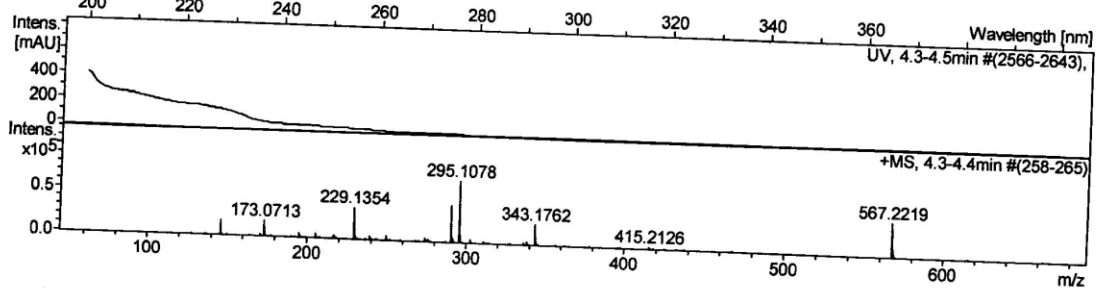
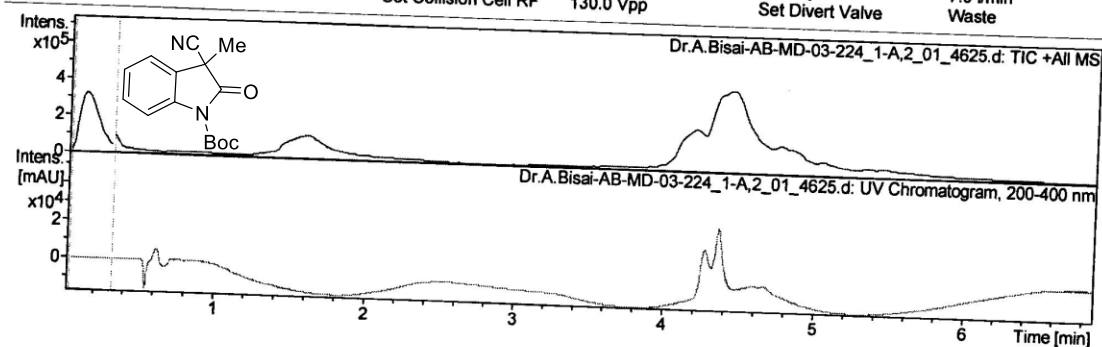
## Display Report

## Analysis Info

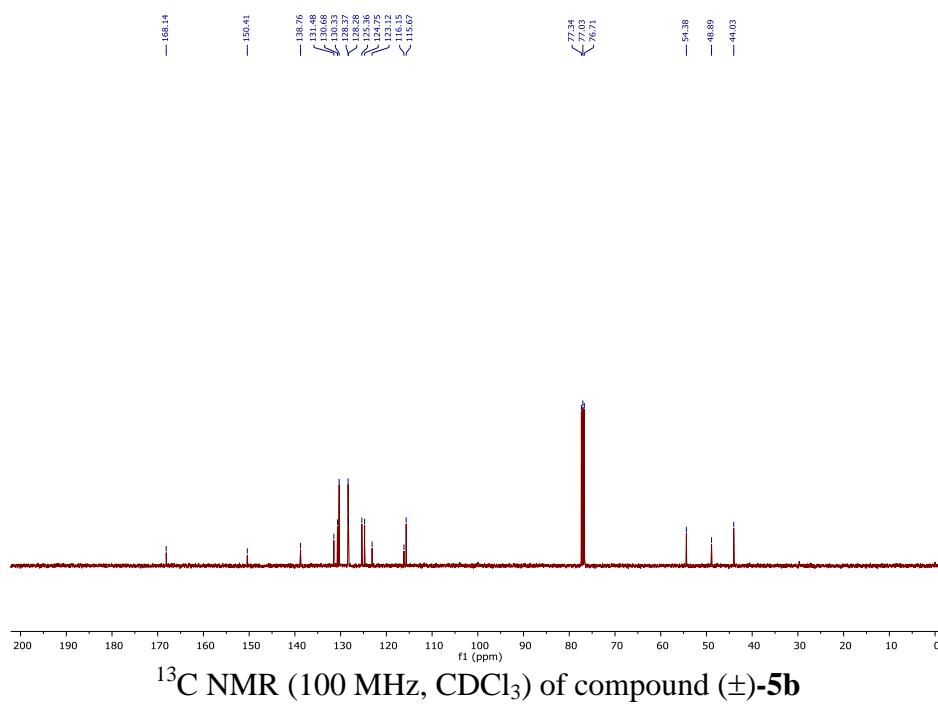
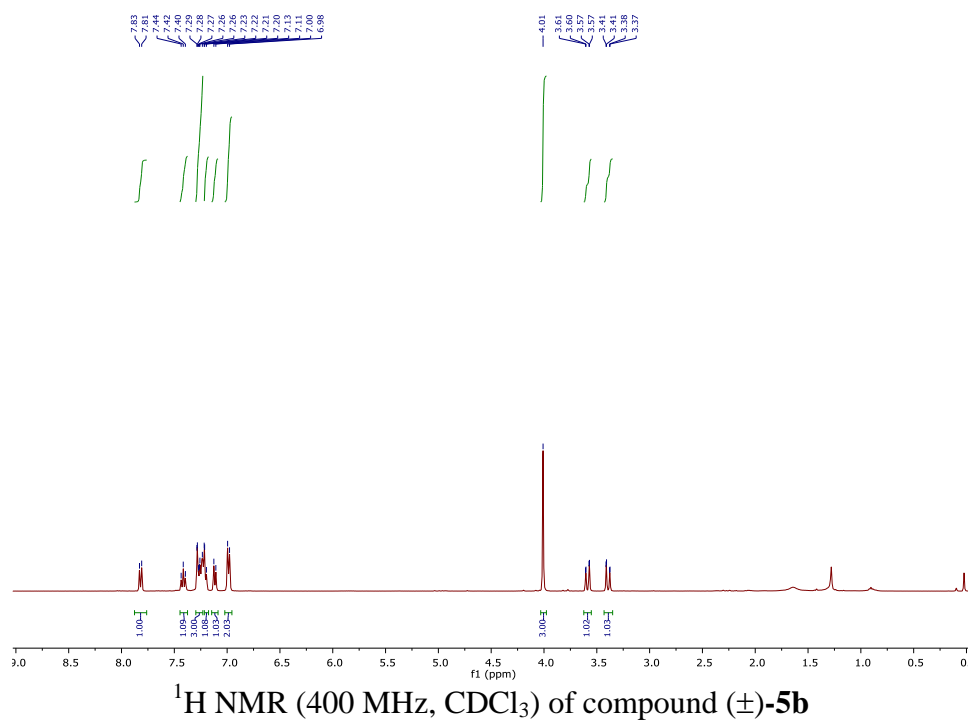
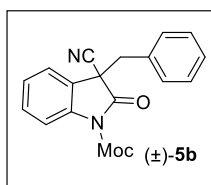
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 Method HRLCMS-20 Sept.m  
 Sample Name Dr.A.Bisai-AB-MD-03-224 Operator RUCHI  
 Comment Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







## Display Report

## Analysis Info

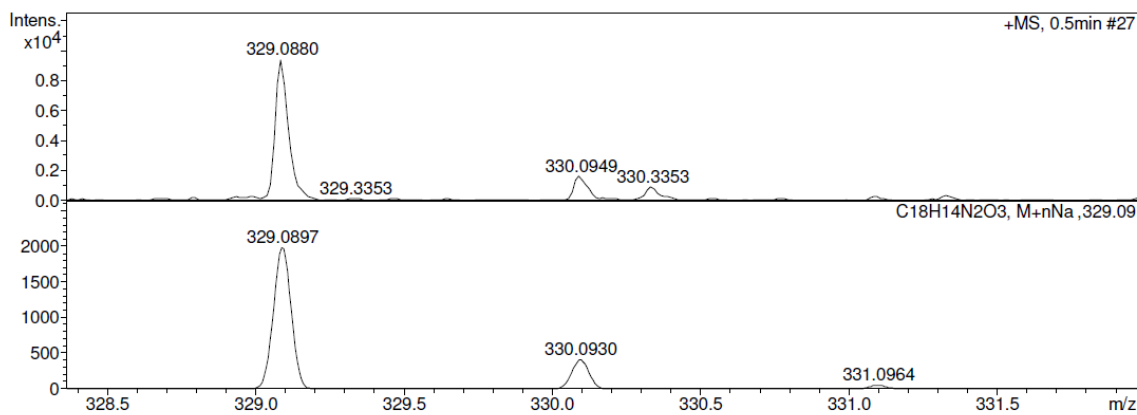
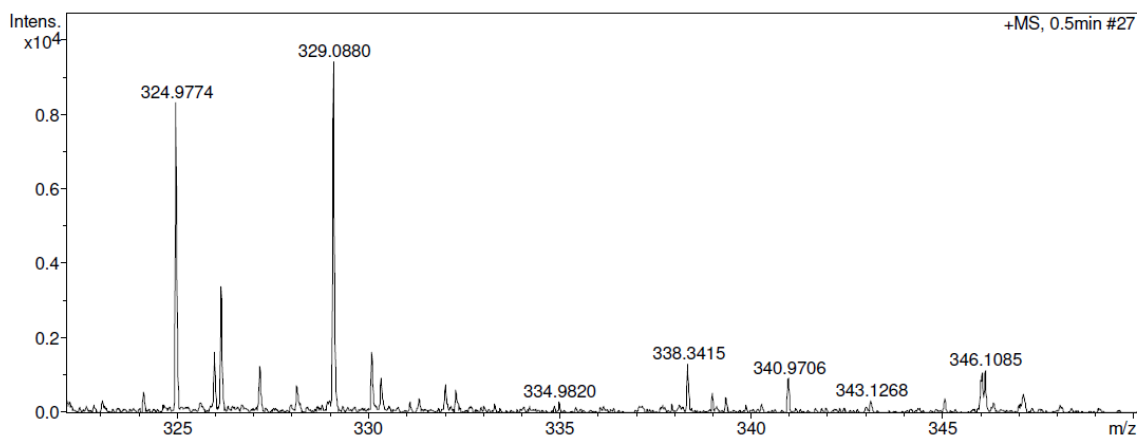
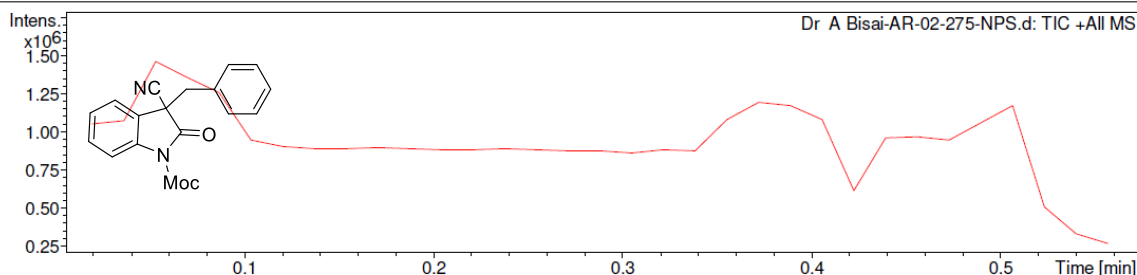
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Sample Name AR-02-275-NPS  
Comment

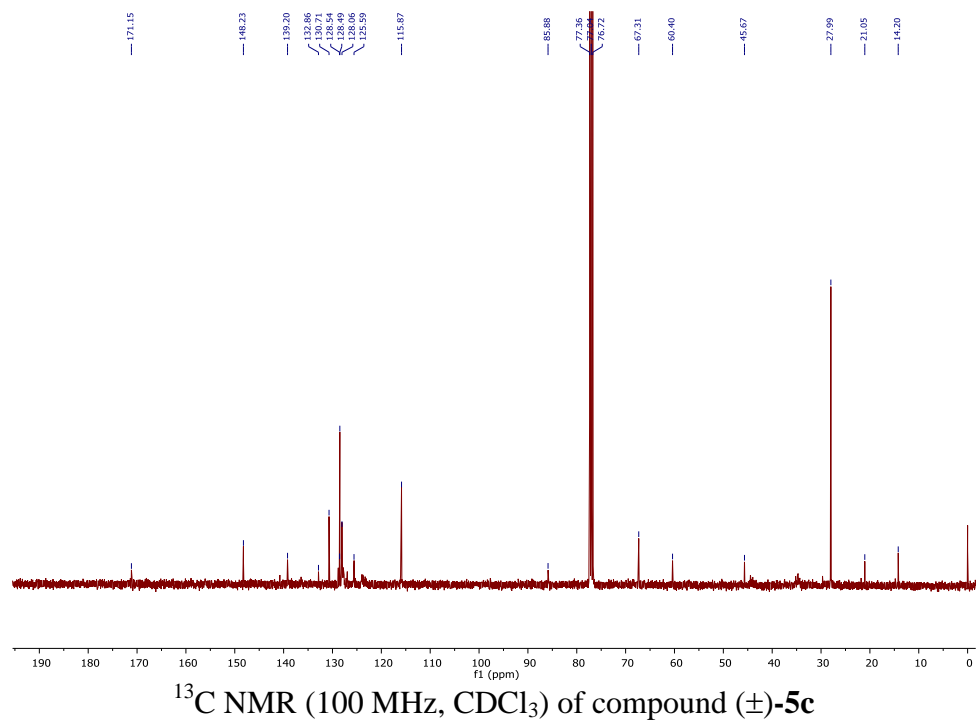
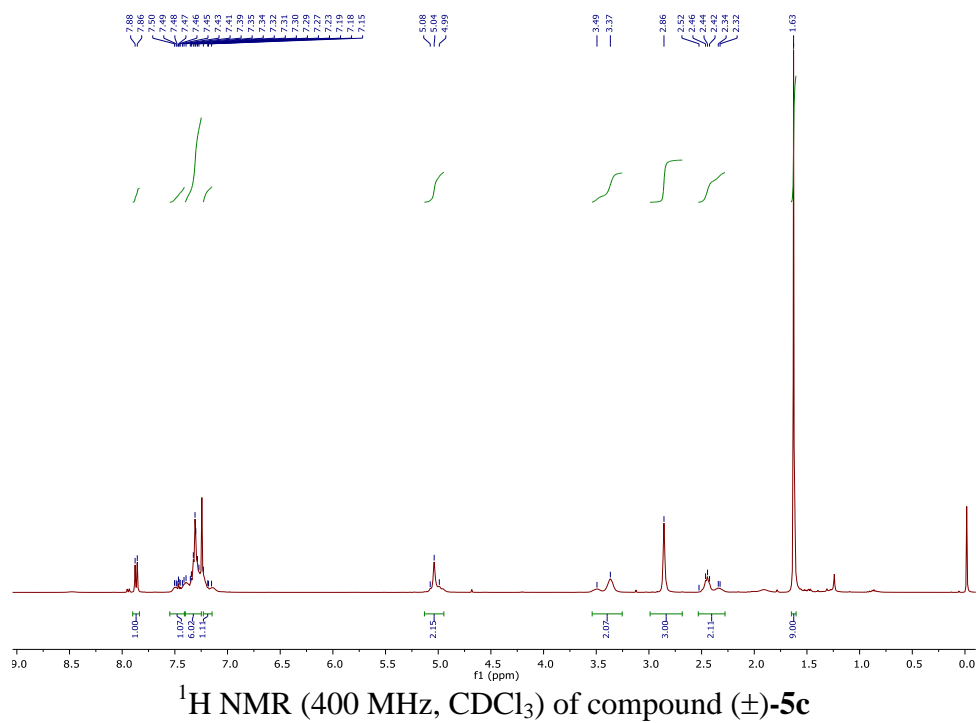
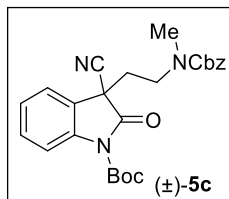
Acquisition Date 3/26/2018 10:56:40 AM

Operator RUCHI  
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\010 Jan\Dr. A Bisai-AR-03-64.d  
Method tune\_low.m  
Sample Name AR-03-64  
Comment

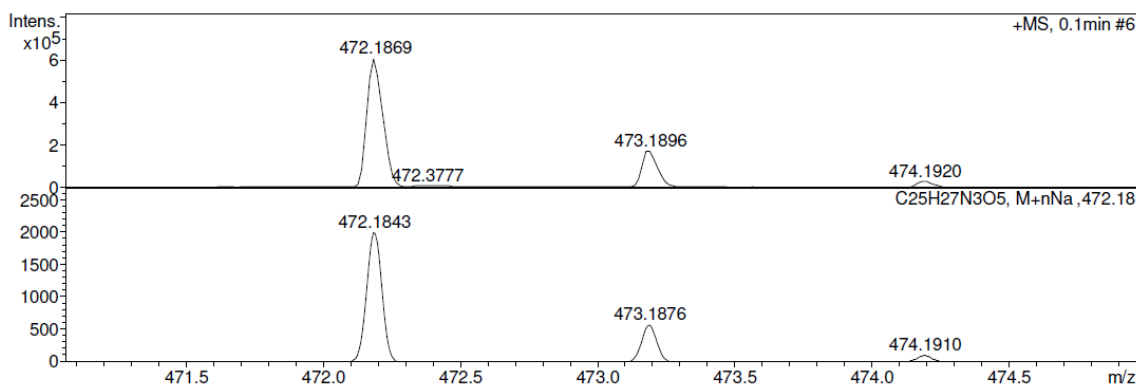
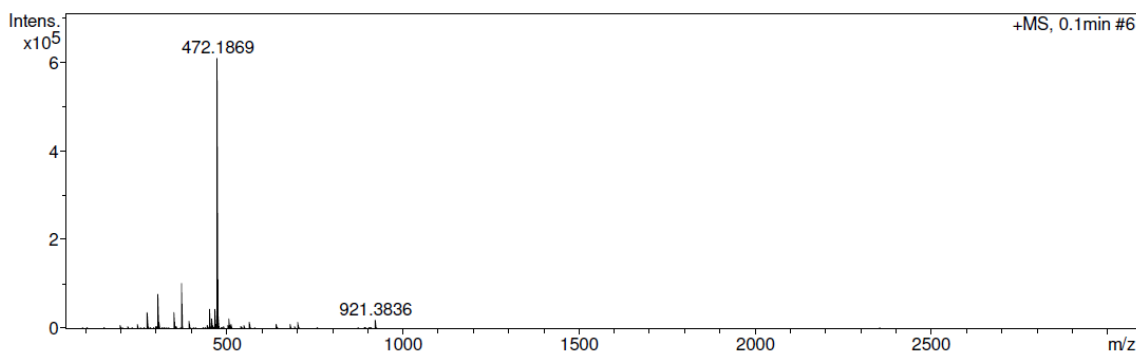
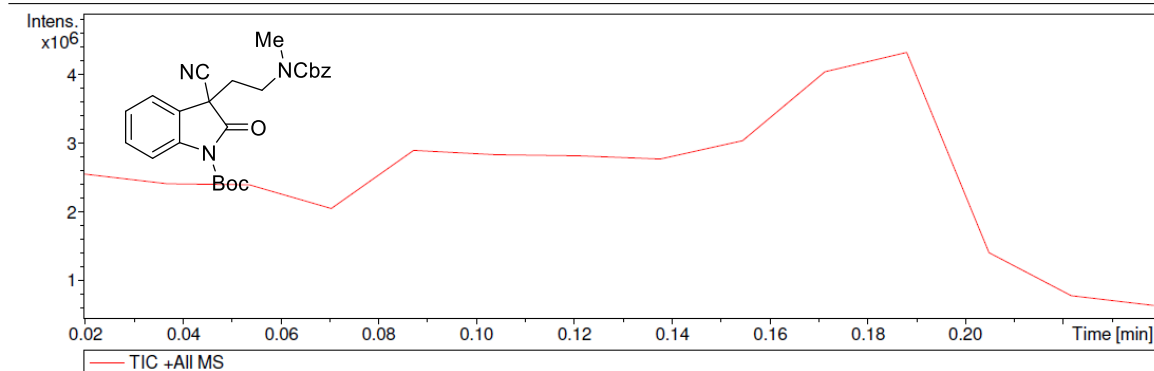
Acquisition Date 1/10/2018 10:01:08 AM

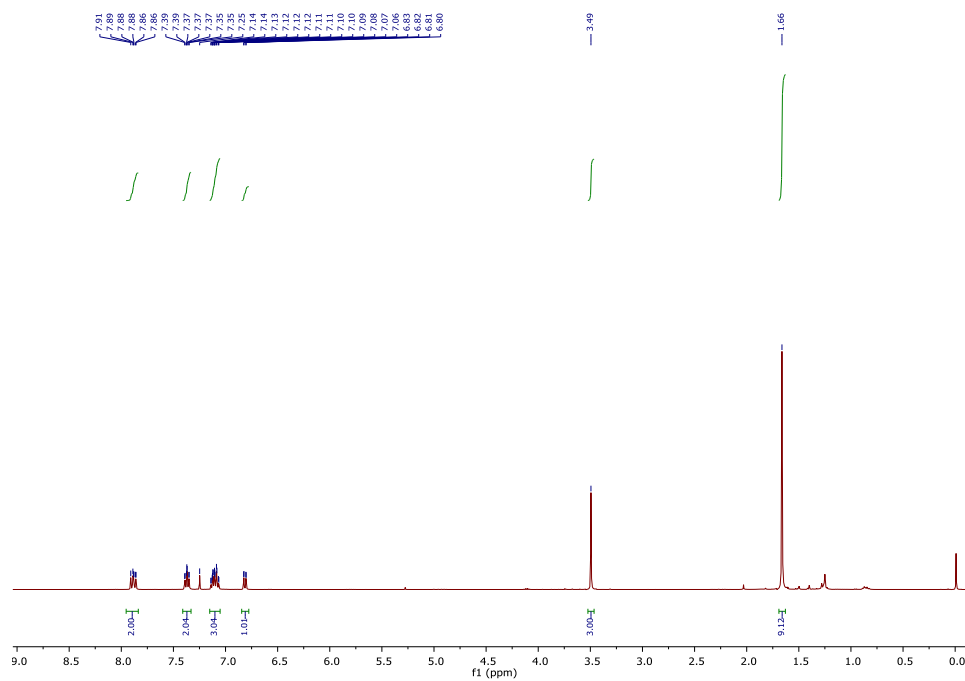
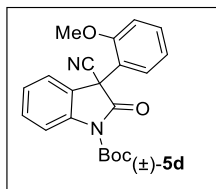
Operator RUCHI

Instrument micrOTOF-Q II 10330

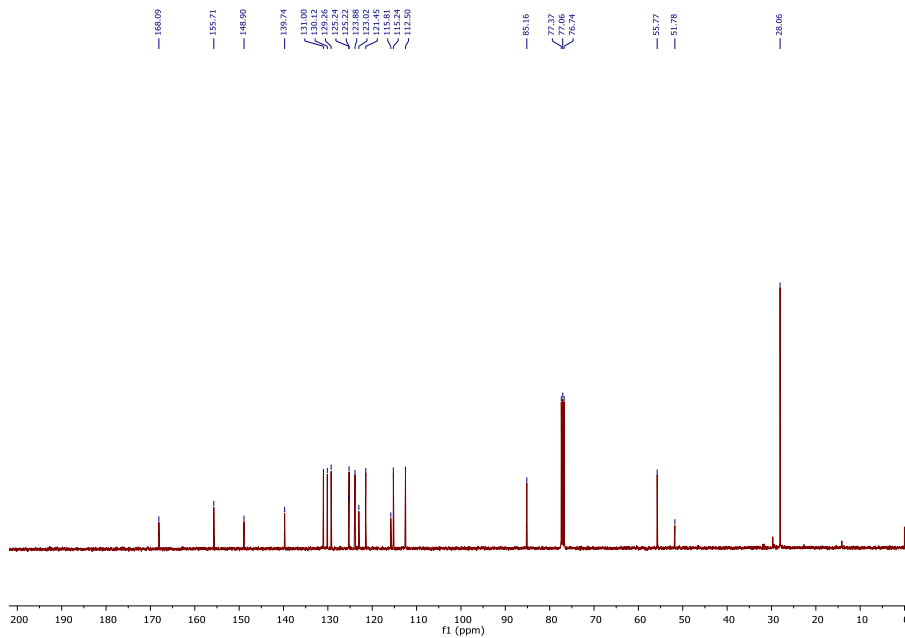
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-5d



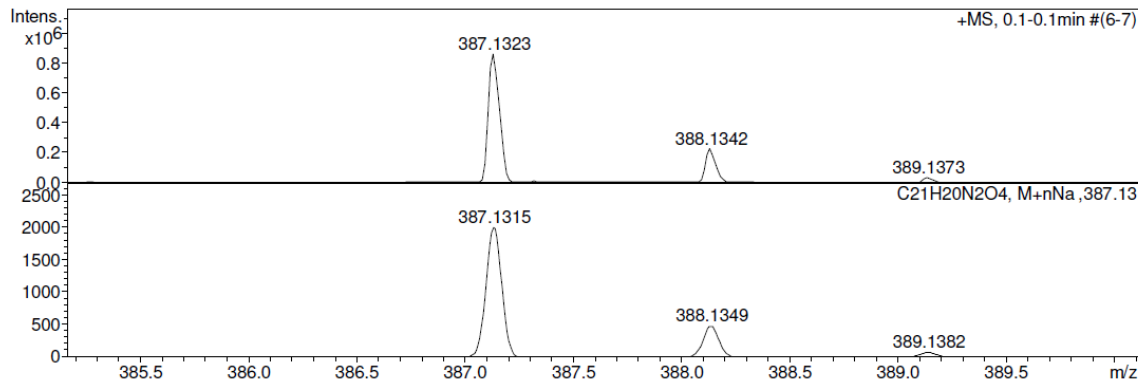
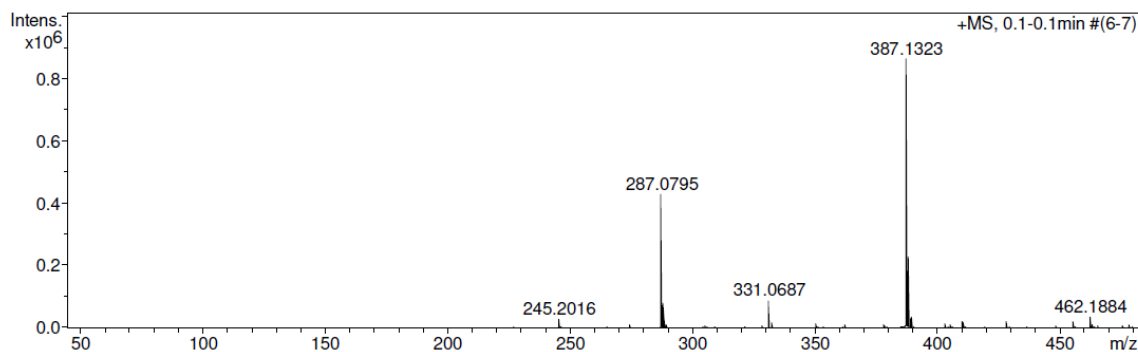
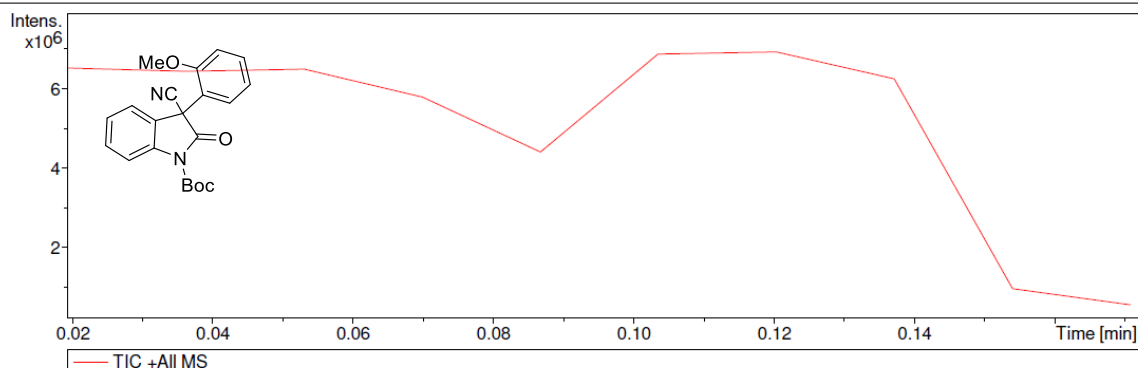
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-5d

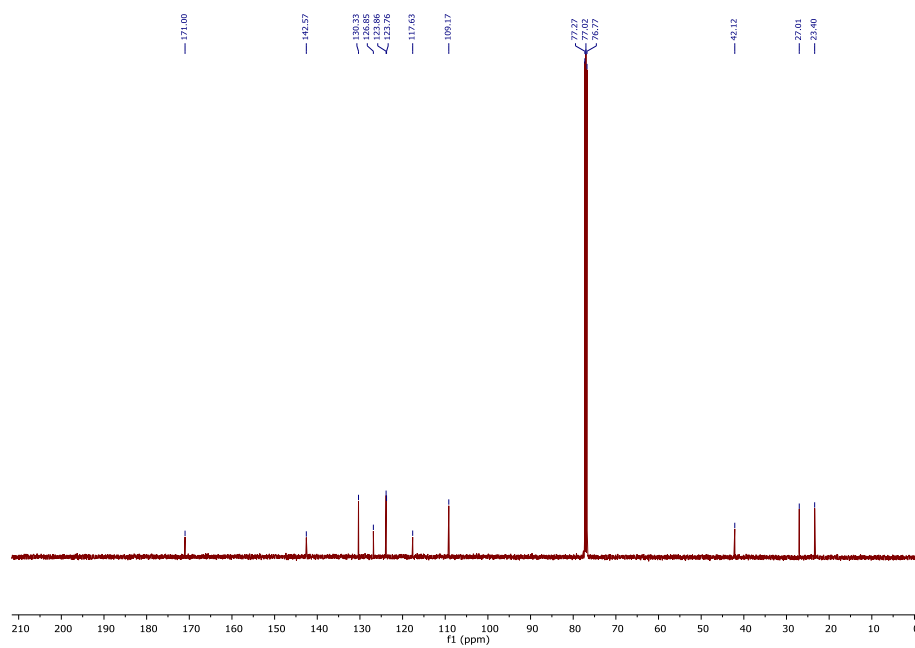
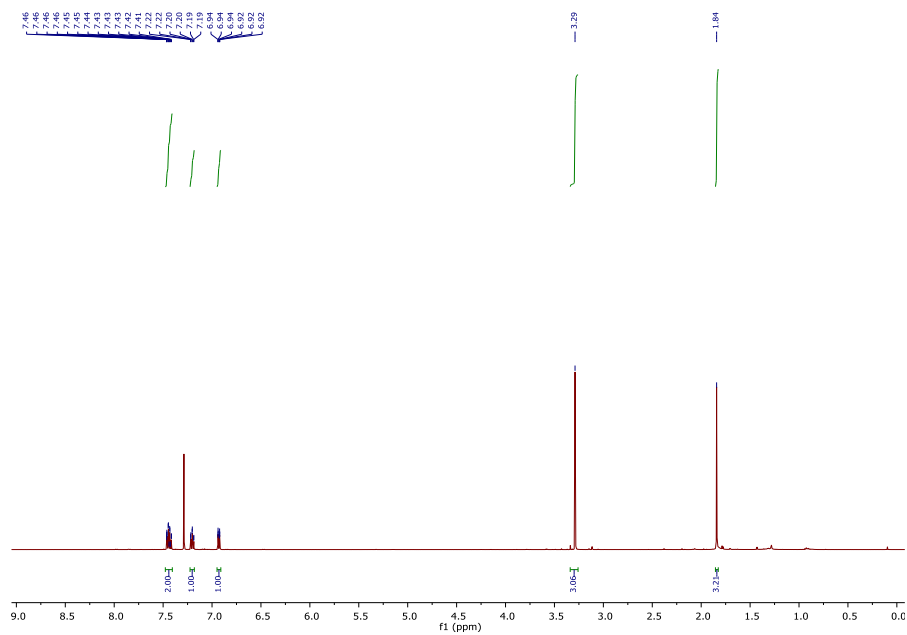
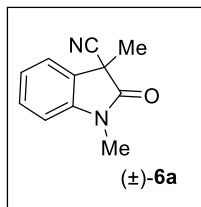
## Display Report

**Analysis Info**  
Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\30 jan\Dr A Bisai-AR-03-115.d Acquisition Date 1/30/2018 11:30:43 AM  
Method tune\_mix\_low.New.021117.m Operator RUCHI  
Sample Name AR-03-115 Instrument micrOTOF-Q II 10330  
Comment

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





## Display Report

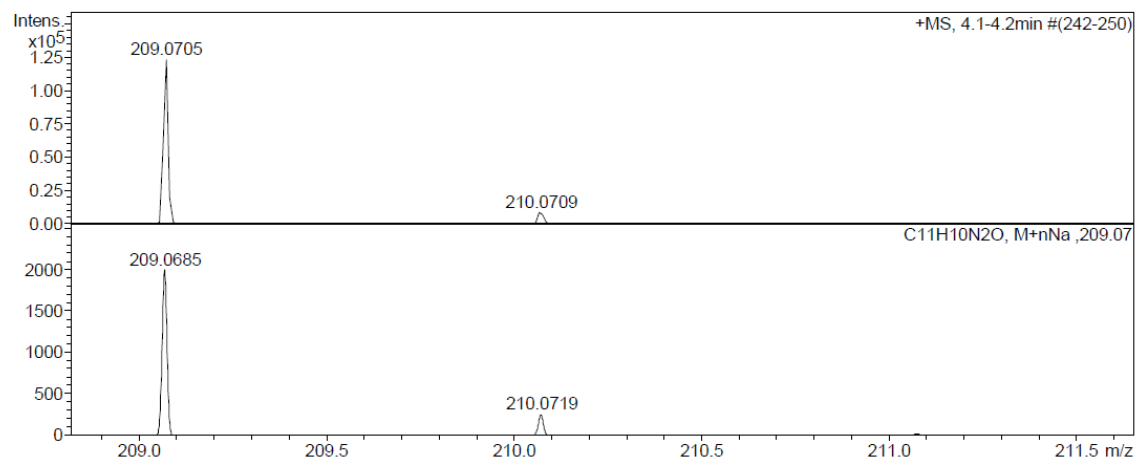
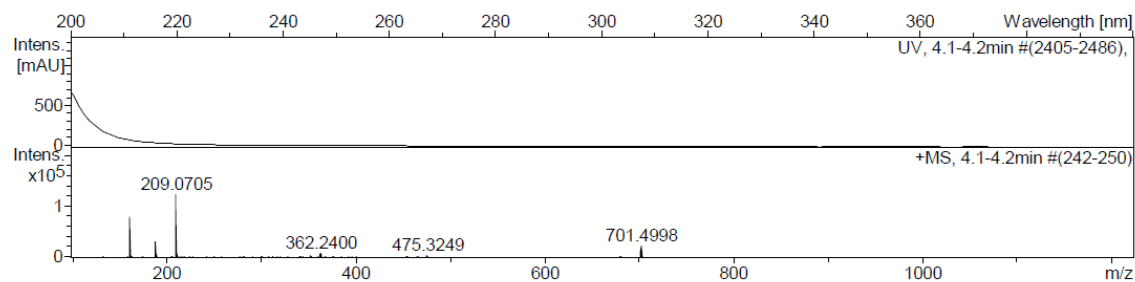
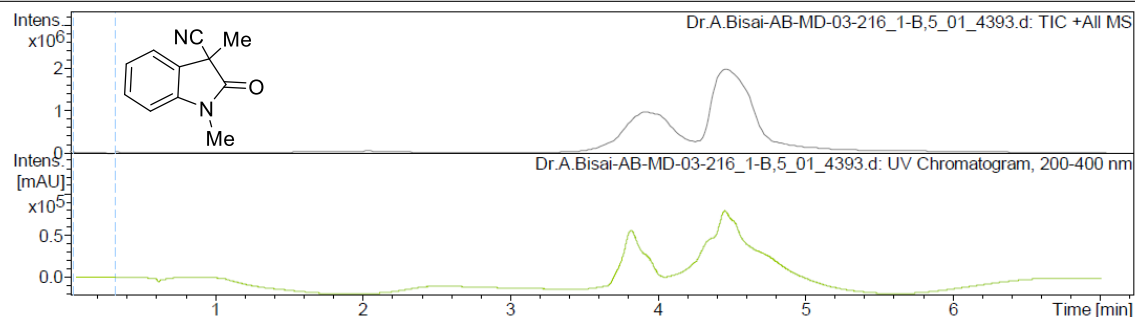
## Analysis Info

Analysis Name D:\Data\user data\2015\December-2015\01-Dec-2015\Dr.A.Bisai-AB-MD-03-216\_1-B,5\_01\_4393.d  
Method HRLCMS-20 Sept.m  
Sample Name Dr.A.Bisai-AB-MD-03-216  
Comment

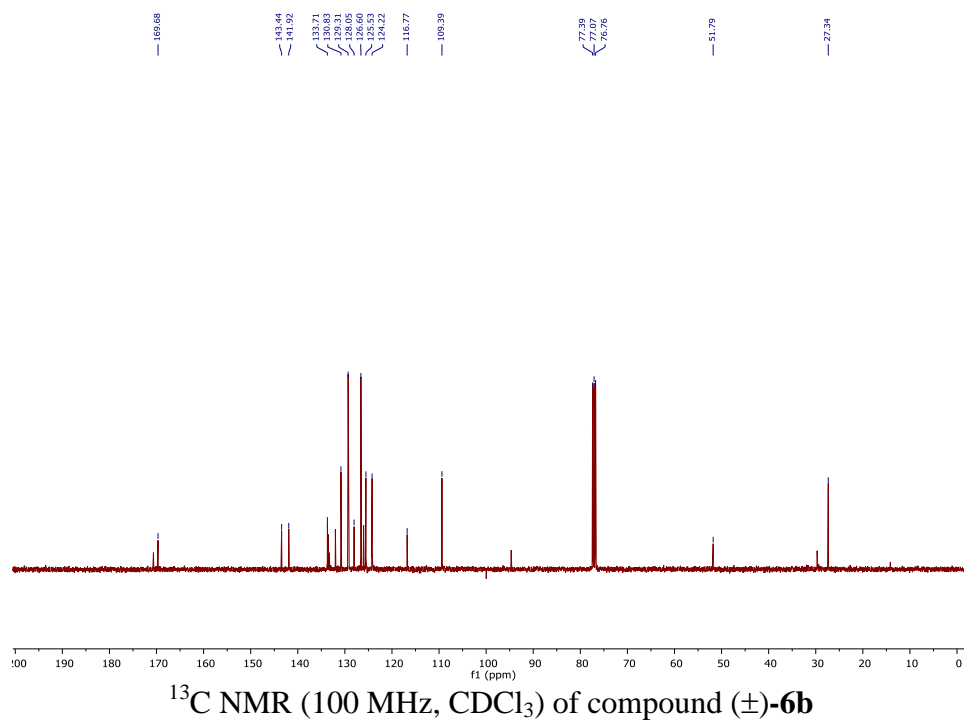
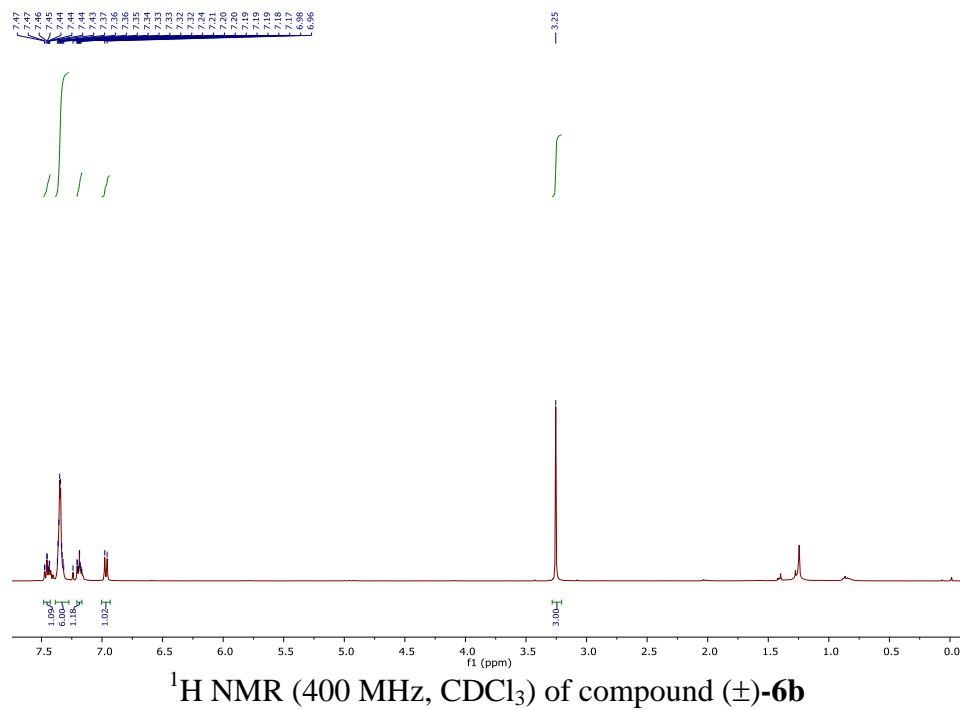
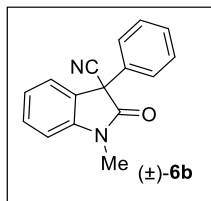
Acquisition Date 12/1/2015 2:55:44 PM  
Operator RUCHI  
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







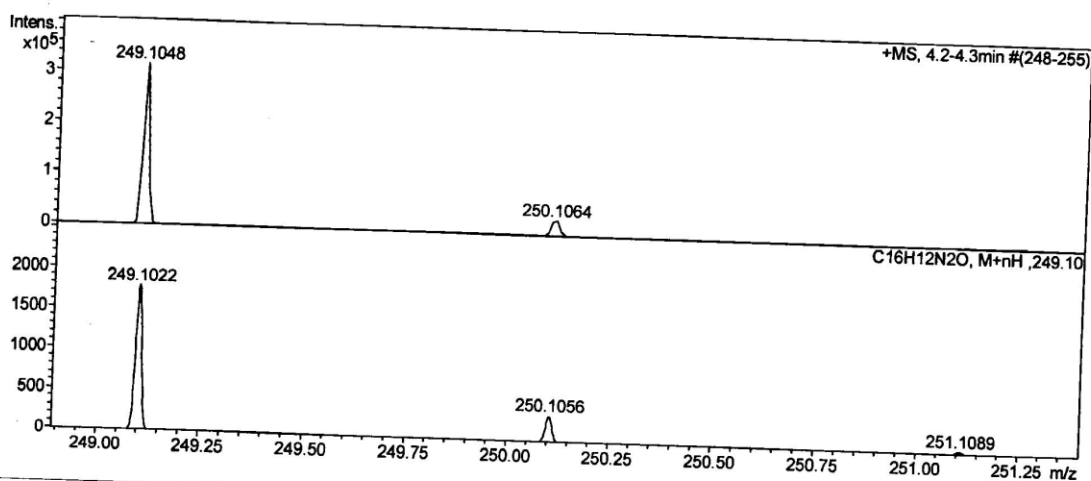
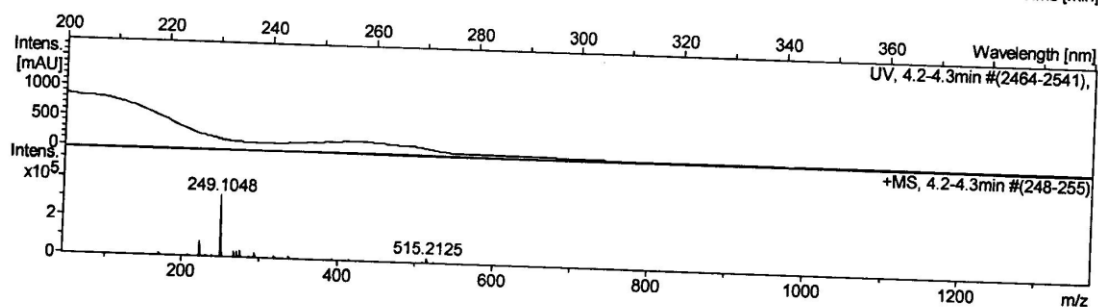
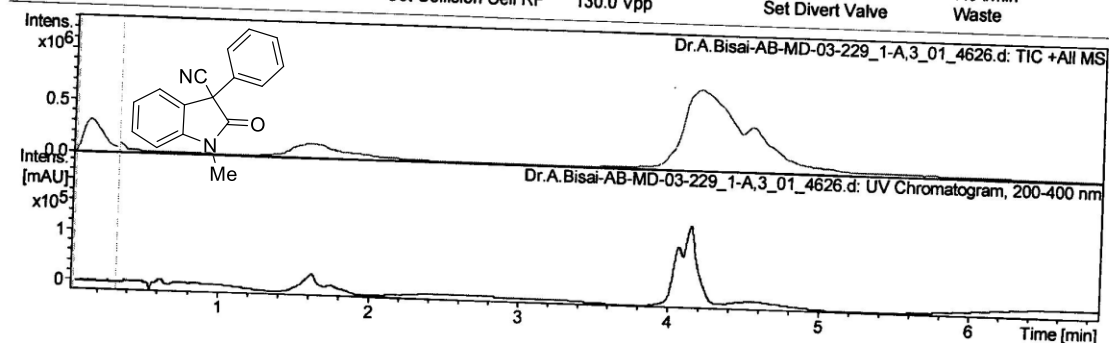
## Display Report

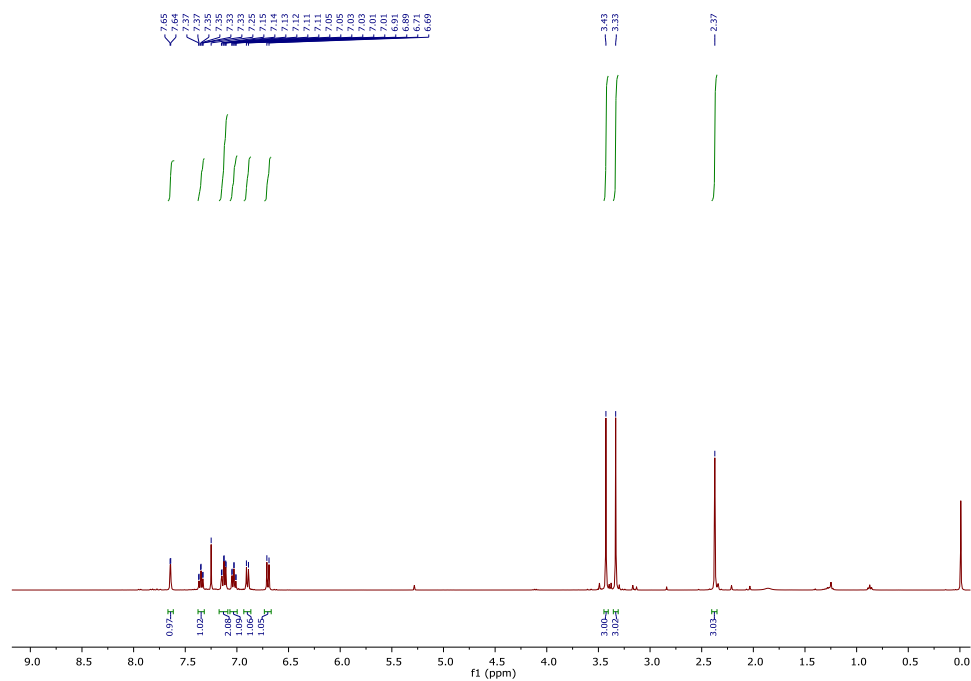
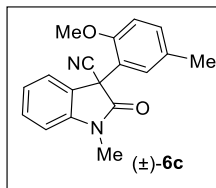
## Analysis Info

Analysis Name D:\Data\user data\2015\December-2015\17-DEC-2015\Dr.A.Bisai-AB-MD-03-229\_1-A,3\_01\_4626.d Acquisition Date 12/17/2015 11:42:03 AM  
 Method HRLCMS-20 Sept.m Operator RUCHI  
 Sample Name Dr.A.Bisai-AB-MD-03-229 Instrument micrOTOF-Q II 10330  
 Comment

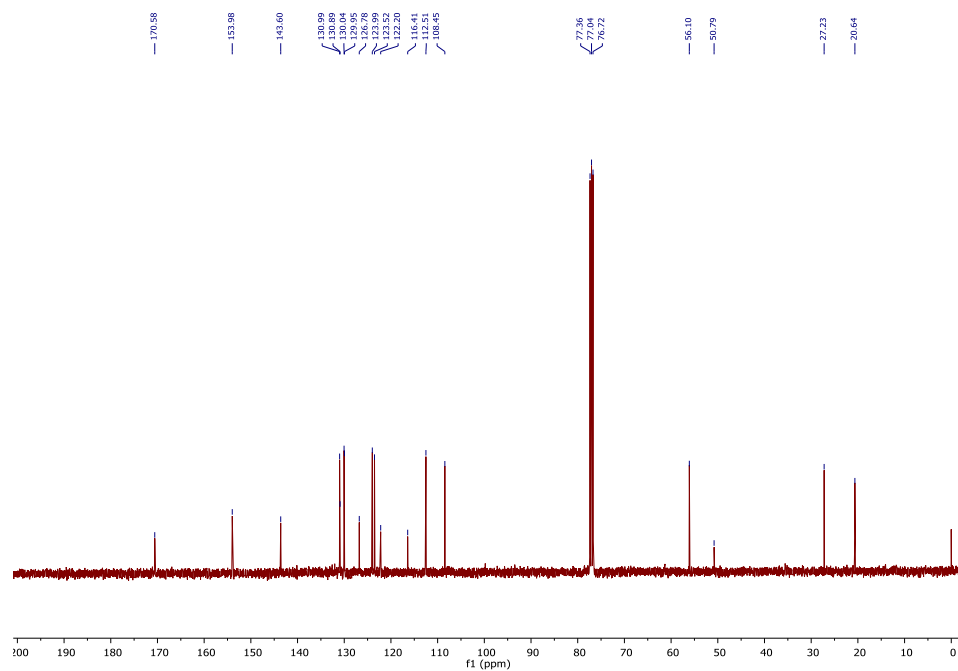
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-6c



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-6c

## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\02 feb\Dr A Bisai-AR-02-264.d  
Method tune mix\_low.New.021117.m  
Sample Name AR-02-264  
Comment

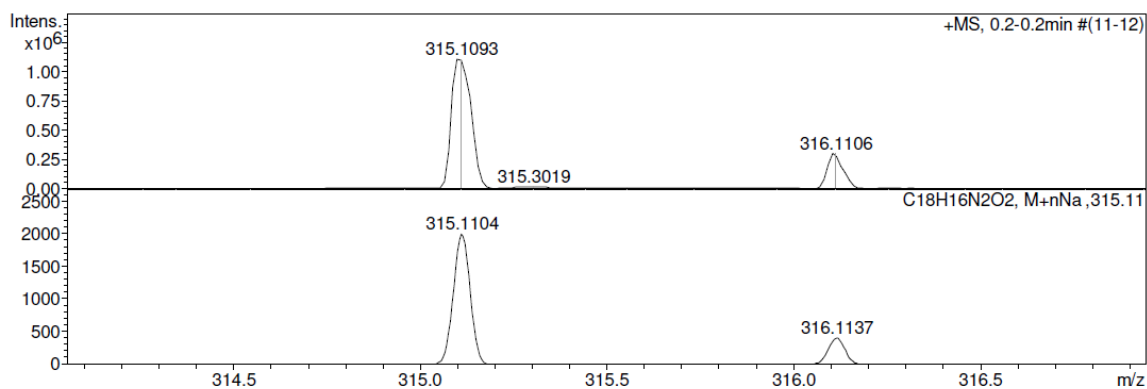
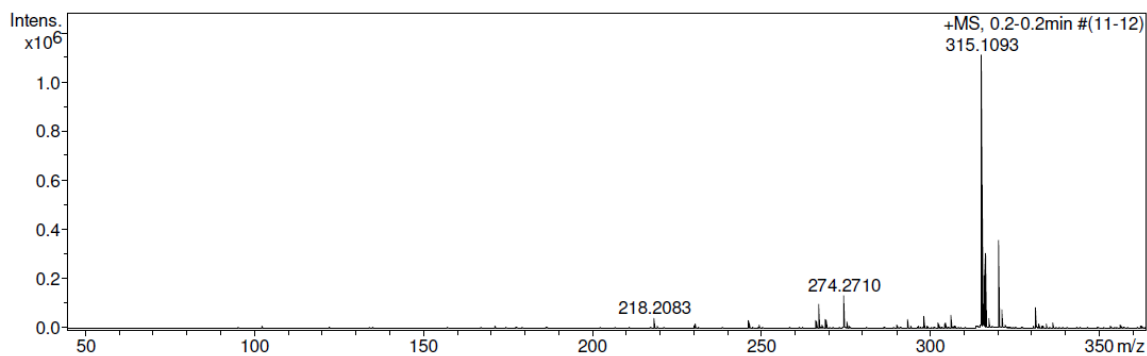
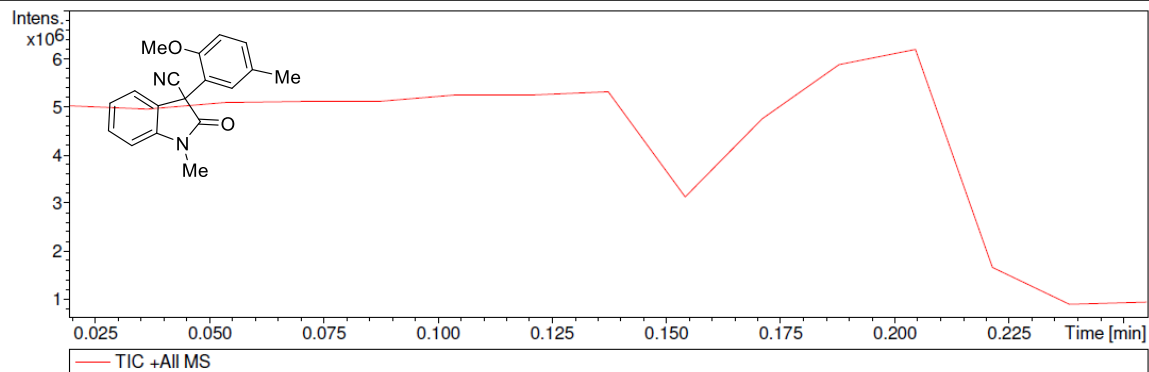
Acquisition Date 2/2/2018 11:49:29 AM

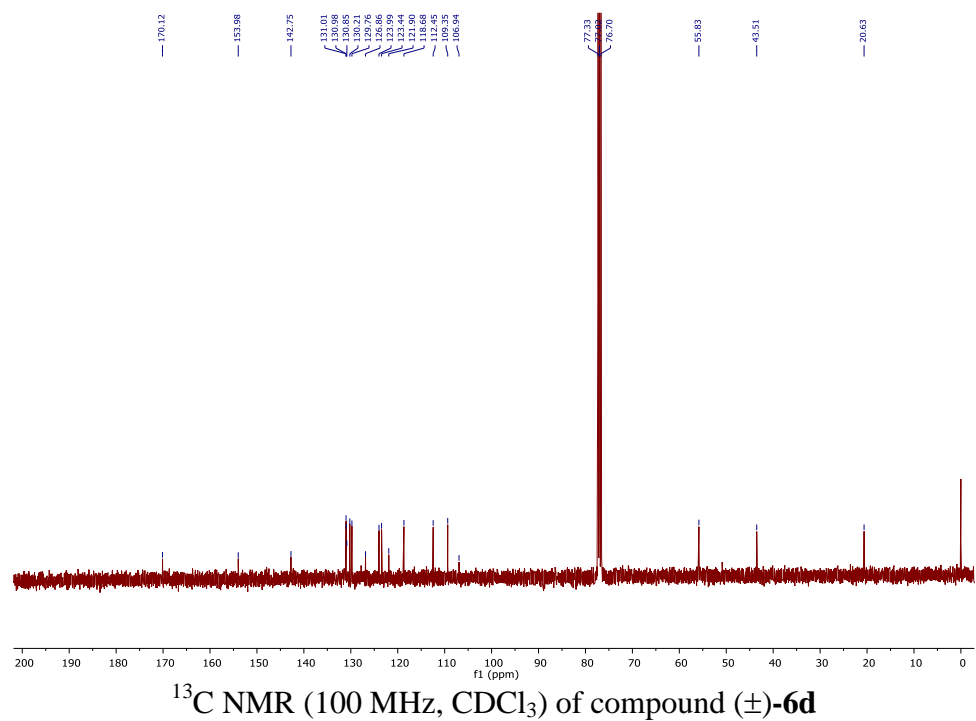
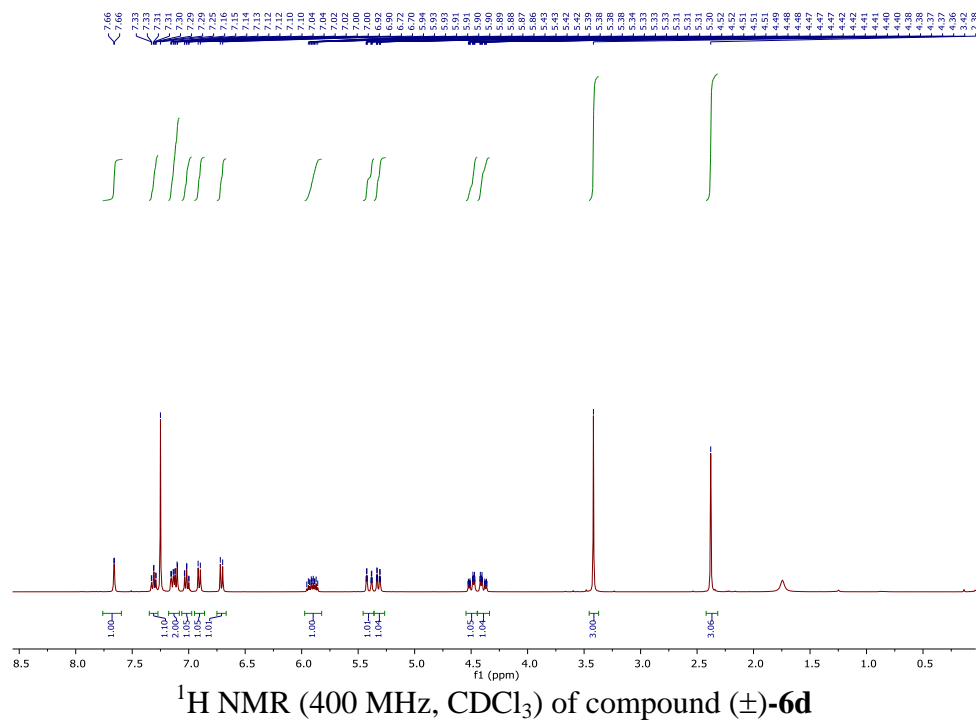
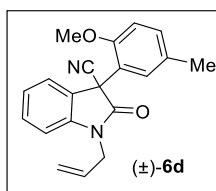
Operator RUCHI

Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\02 feb\Dr A Bisai-AR-02-265.d  
Method tune mix\_low.New.021117.m  
Sample Name AR-02-265  
Comment

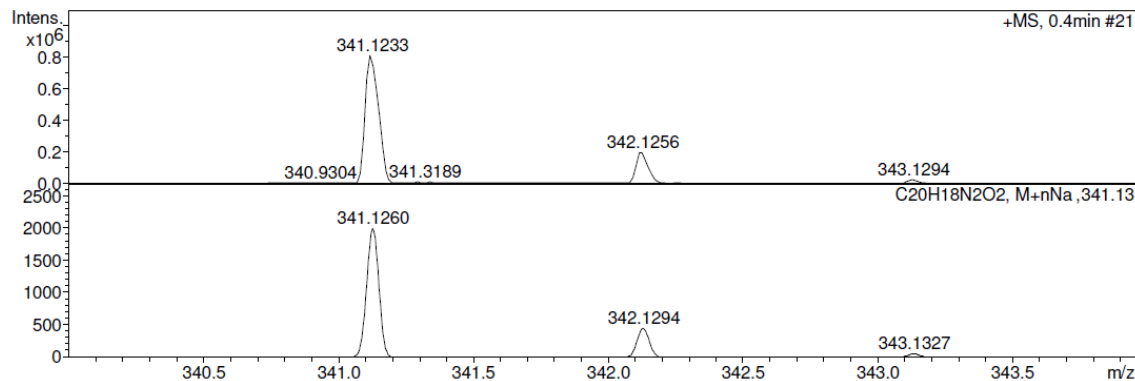
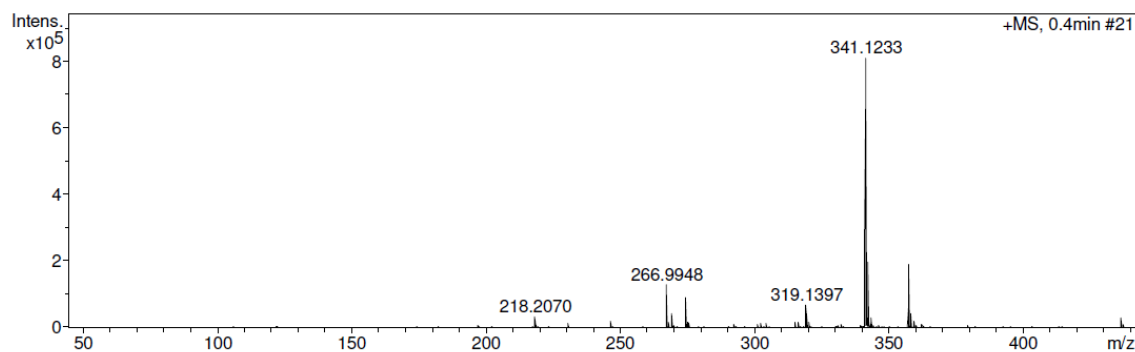
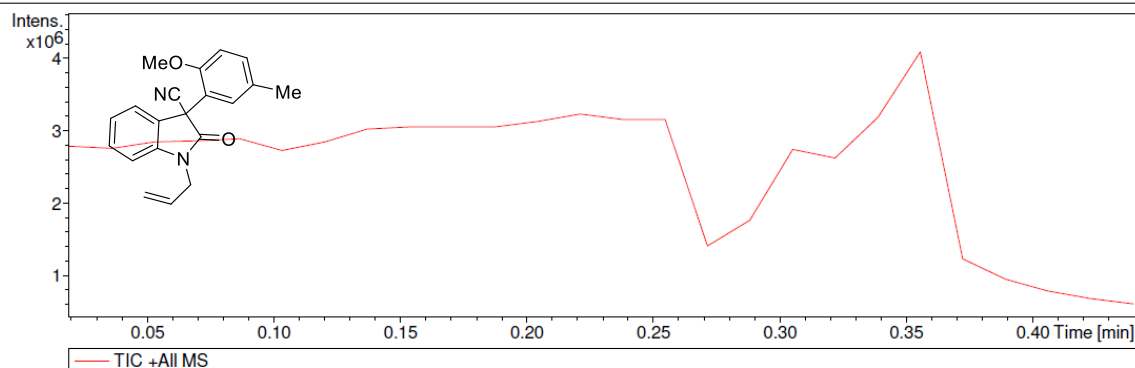
Acquisition Date 2/2/2018 11:54:01 AM

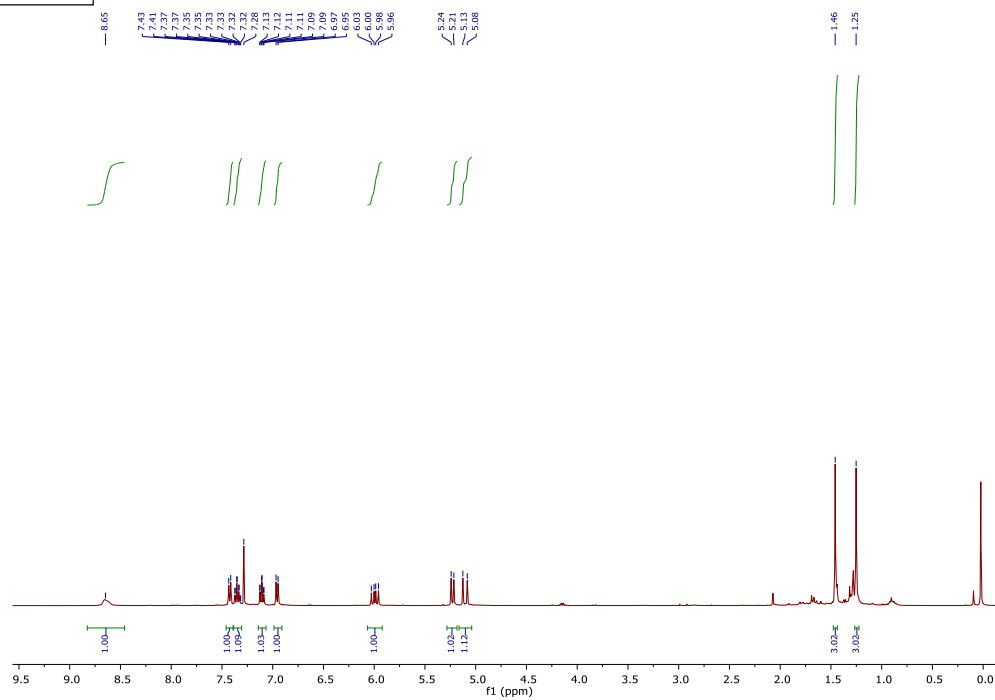
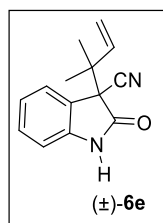
Operator RUCHI

Instrument micrOTOF-Q II 10330

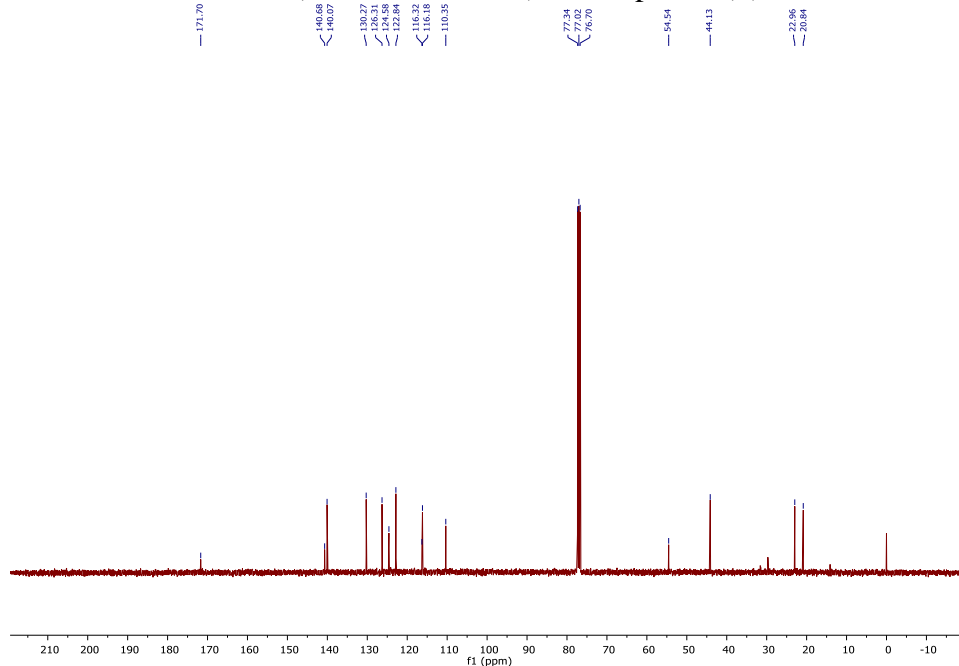
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-6e



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-6e

## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\07 feb\Dr. A.Bisai-AB-AR-03-79.d

Acquisition Date 2/7/2018 3:37:50 PM

Method tune\_low.m

Operator RUCHI

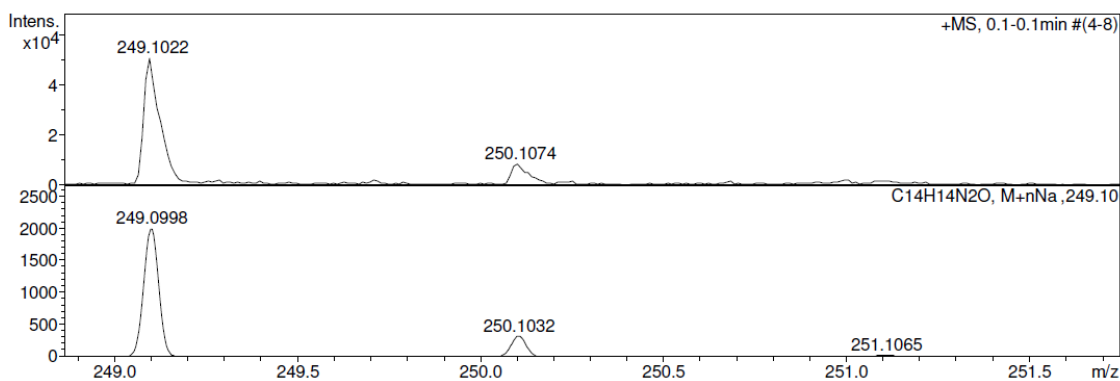
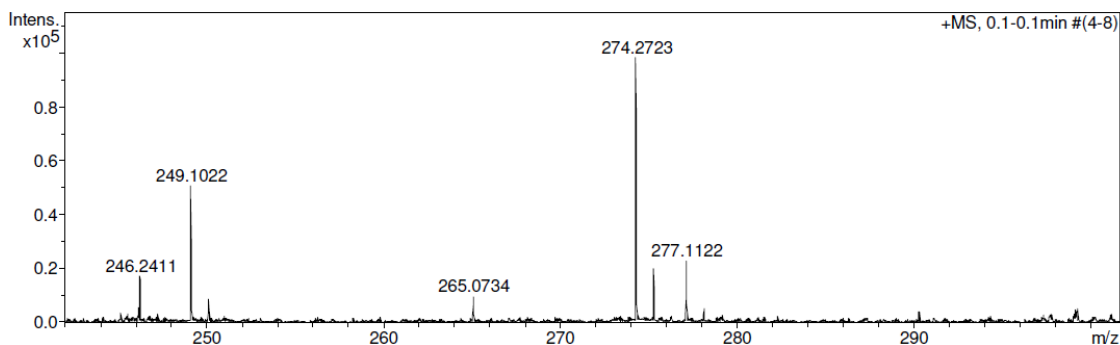
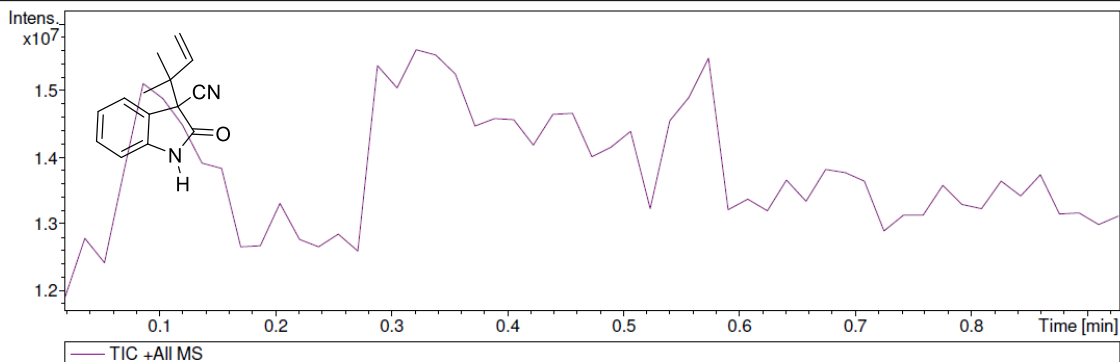
Sample Name AB-AR-03-79

Instrument micrOTOF-Q II 10330

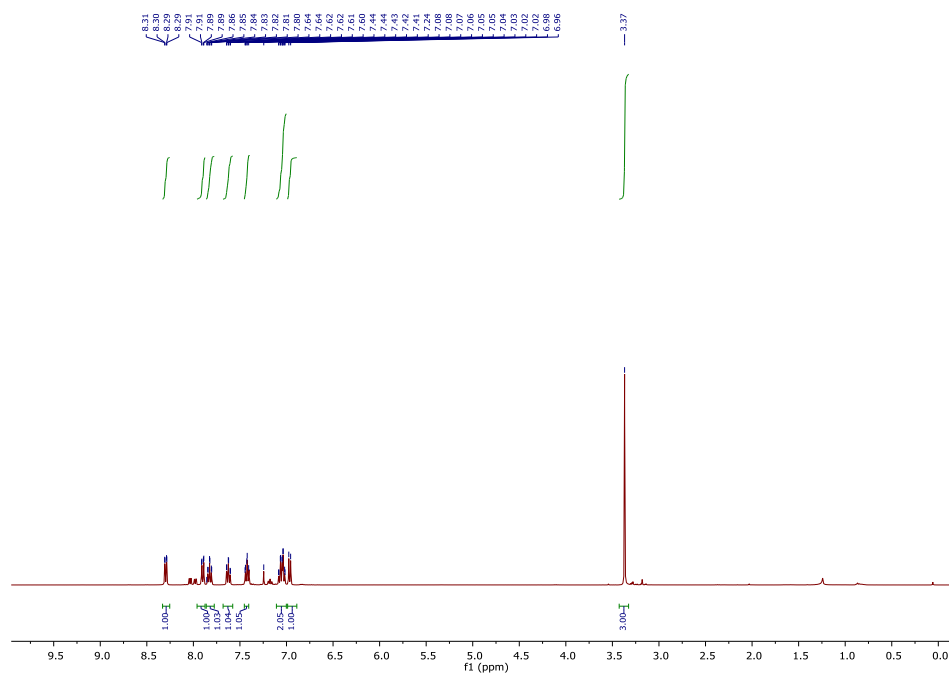
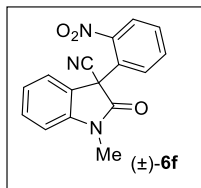
Comment

## Acquisition Parameter

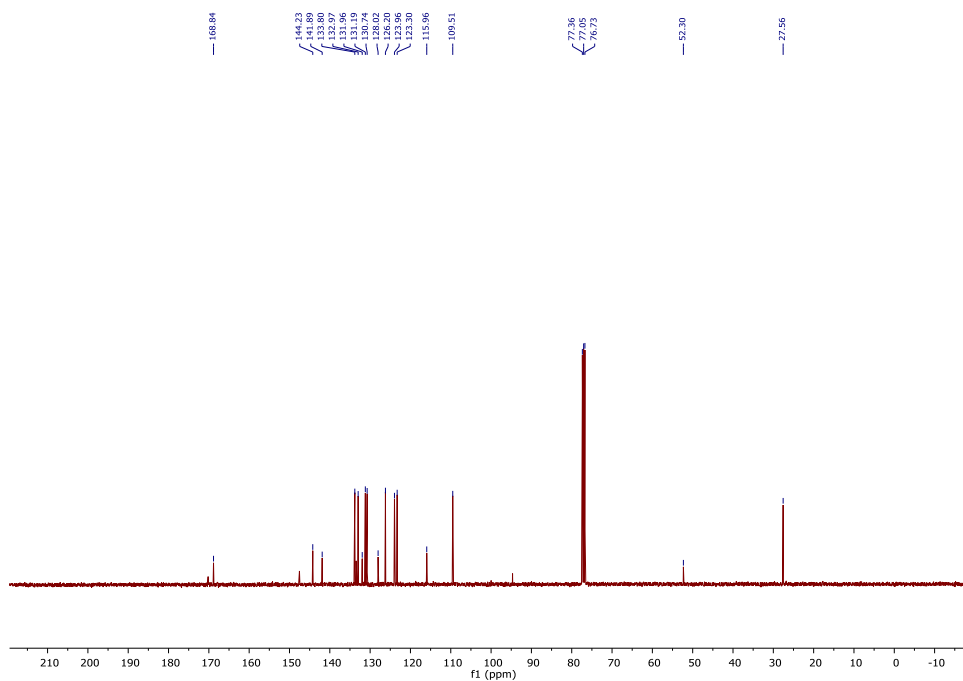
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste







$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (±)-6f



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound (±)-6f

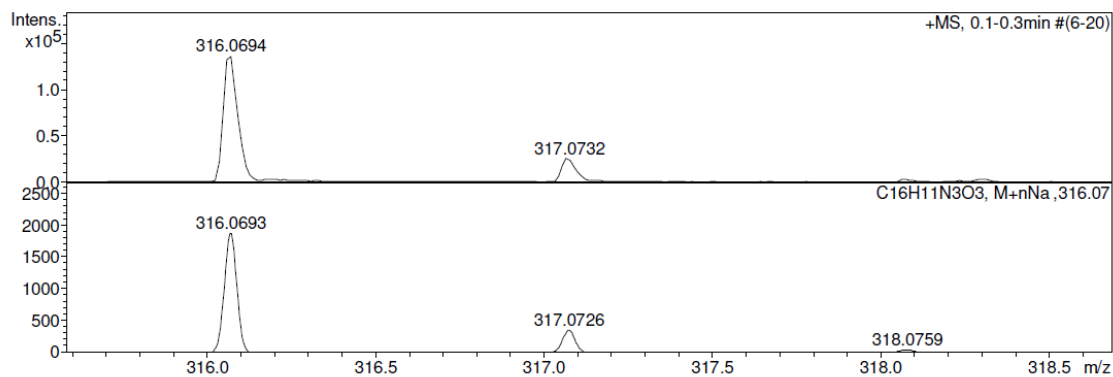
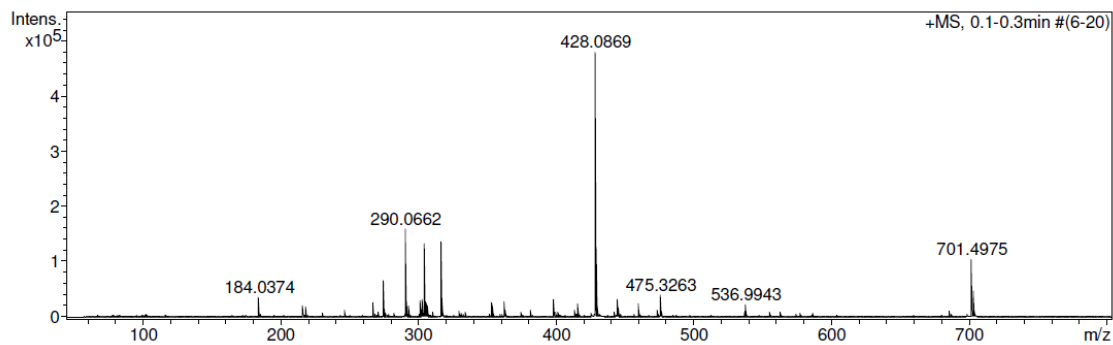
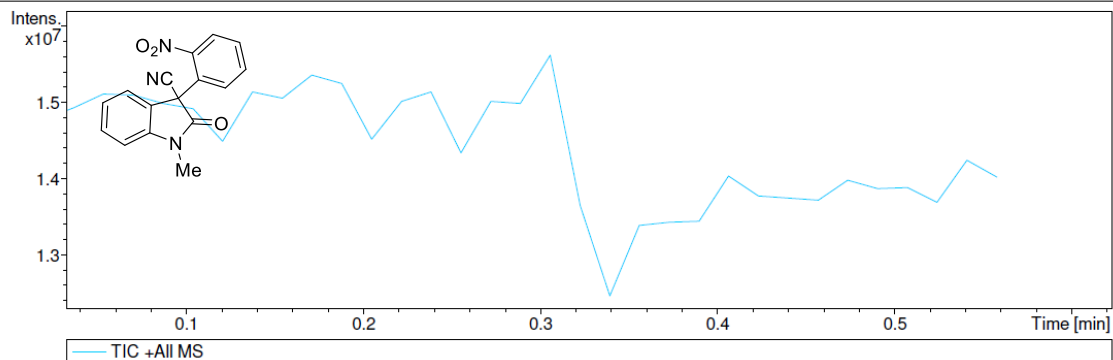
## Display Report

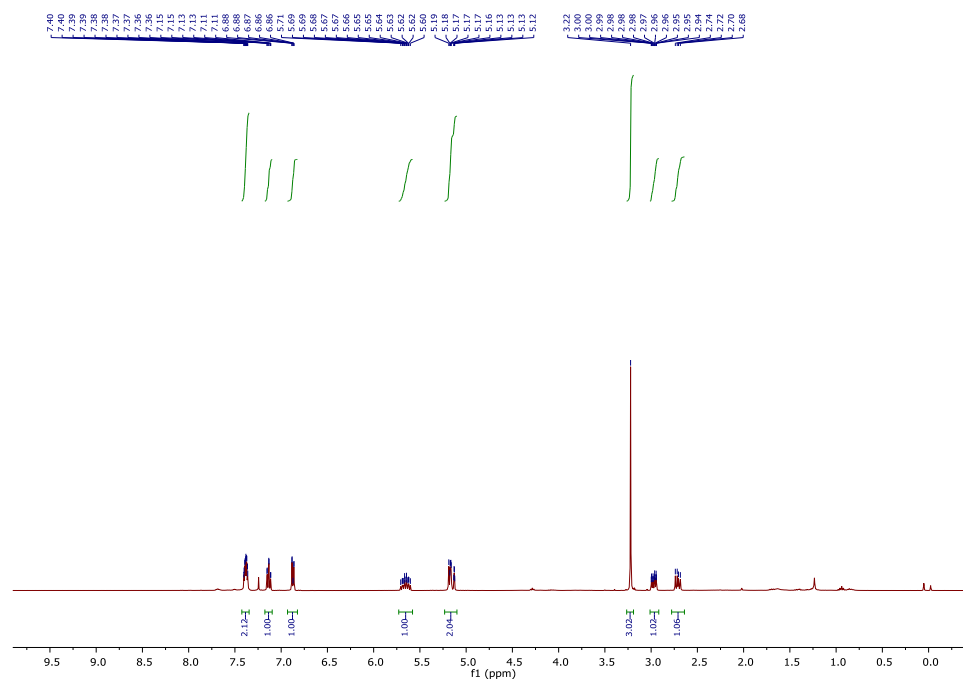
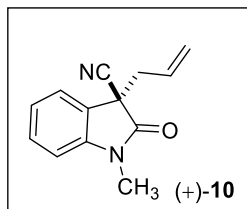
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Analysis Name D:\Data\NEW USER DATA 2017\jan-2018\06 feb\Dr. A.Bisai-AB-MD-03-263.d Acquisition Date 2/6/2018 3:58:08 PM  
Method tune\_low.m Operator RUCHI  
Sample Name AB-MD-03-263 Instrument micrOTOF-Q II 10330  
Comment

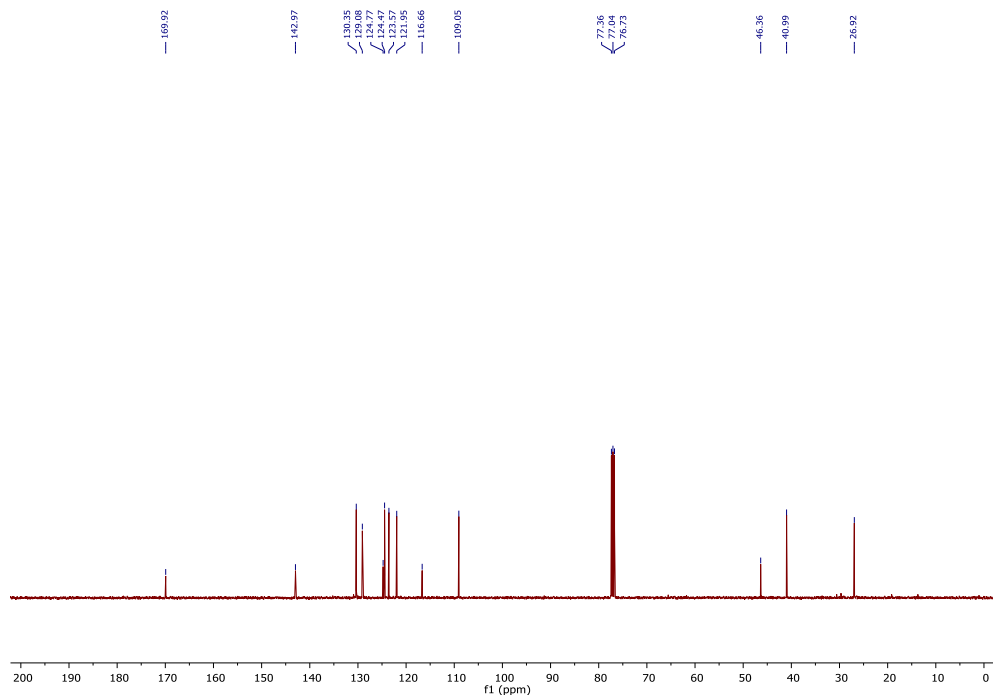
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Scanned copy of mass spectrum of ( $\pm$ )-6f



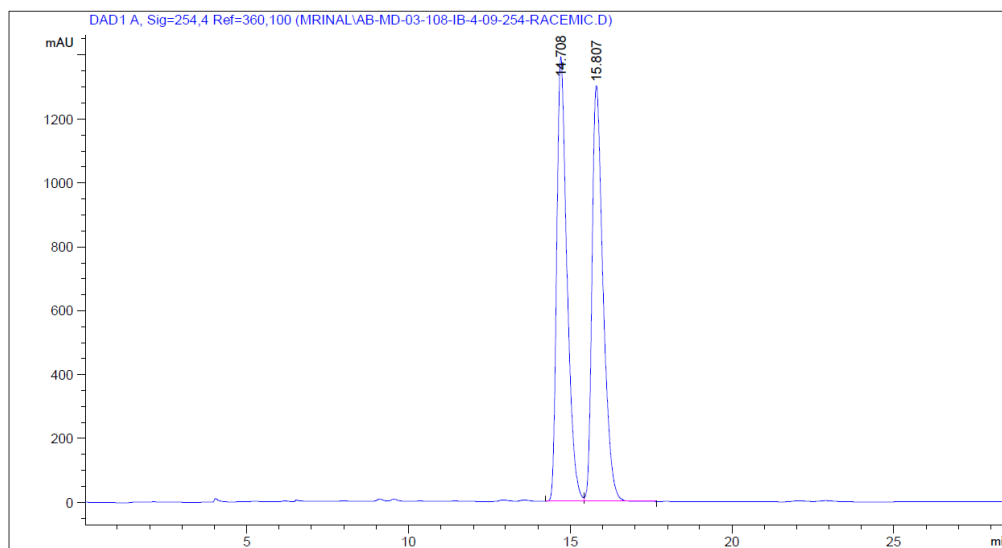
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (+)-10



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (+)-10

Data File C:\CHEM32\1\DATA\MRINAL\AB-MD-03-108-IB-4-09-254-RACEMIC.D

Sample Name: AB-MD-03-108-IB-4-09-254-racemic



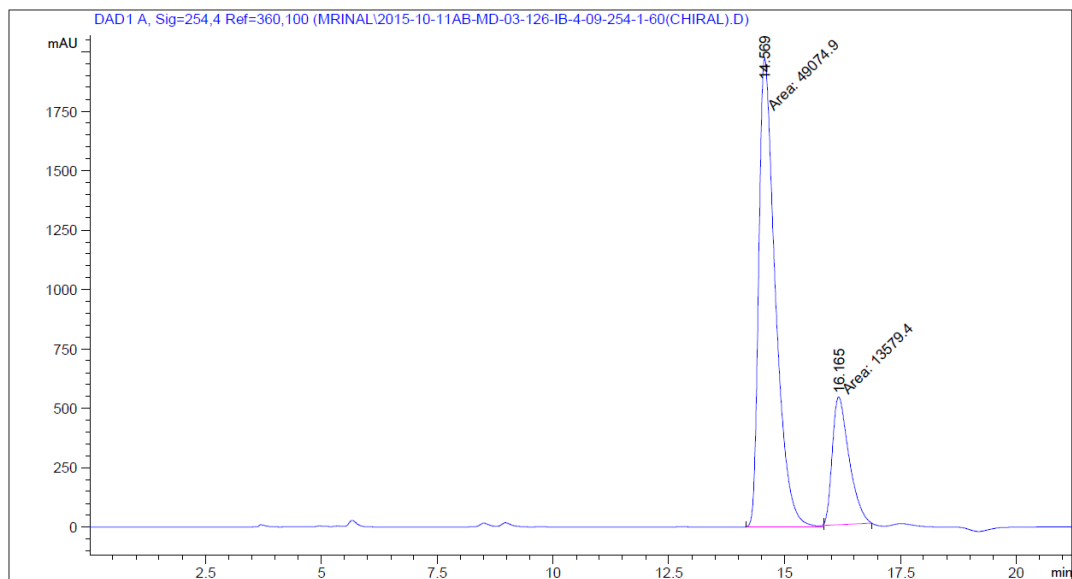
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.708	BV	0.3315	3.06677e4	1389.64111	49.8242
2	15.807	VB	0.3590	3.08842e4	1300.74463	50.1758

Totals : 6.15518e4 2690.38574

\*\*\* End of Report \*\*\*

**HPLC data of (±)-10**

Data File C:\CHEM32\1\DATA\MRINAL\2015-10-11AB-MD-03-126-IB-4-09-254-1-60(CHIRAL).D  
 Sample Name: AB-MD-03-126-IB-4-09-254-1-60(chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.569	MM	0.4149	4.90749e4	1971.50012	78.3264
2	16.165	MM	0.4202	1.35794e4	538.65356	21.6736

Totals : 6.26543e4 2510.15369

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 \*\*\* End of Report \*\*\*

**HPLC data of (+)-10**

## Display Report

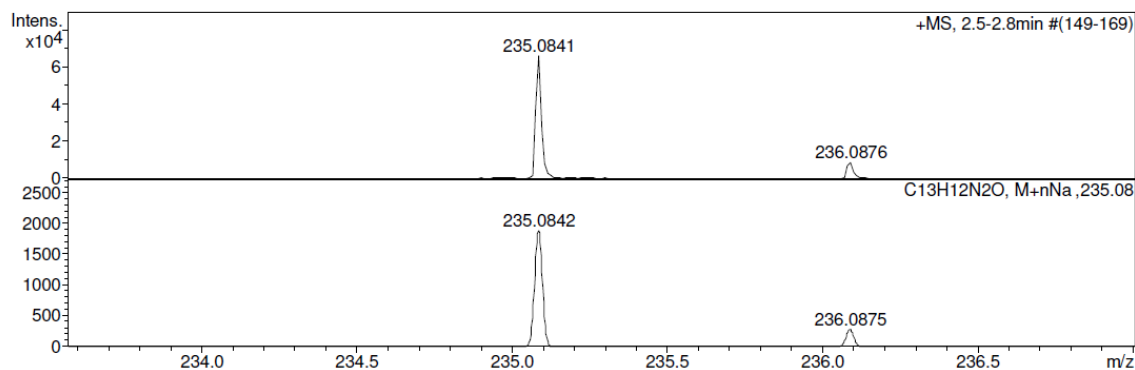
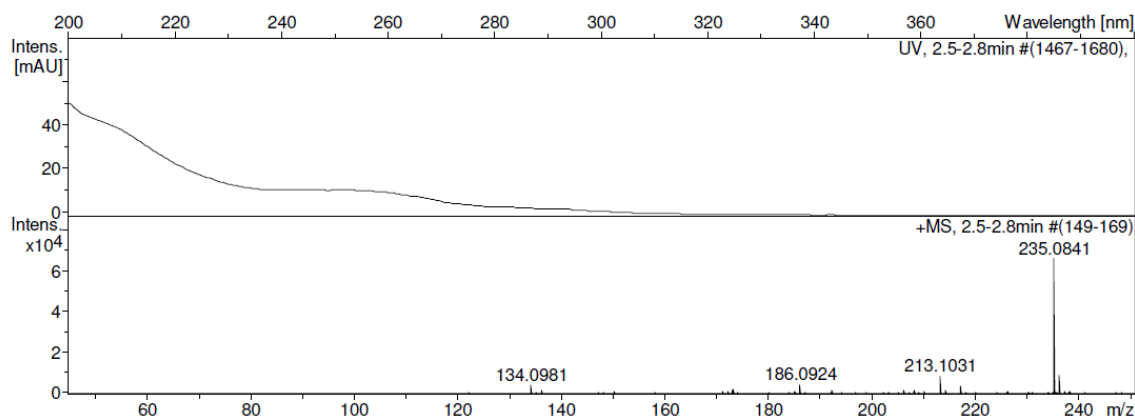
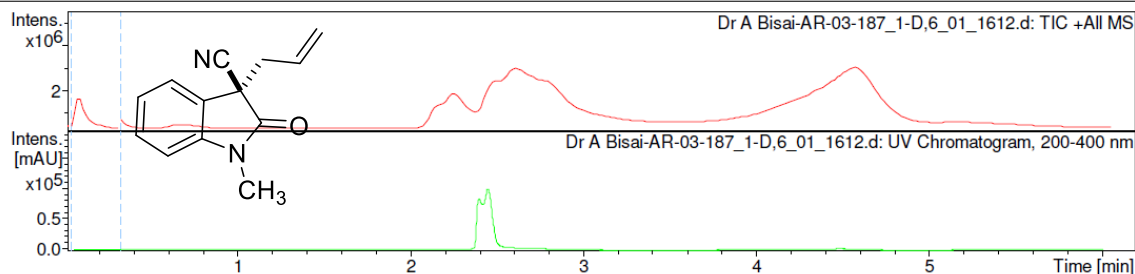
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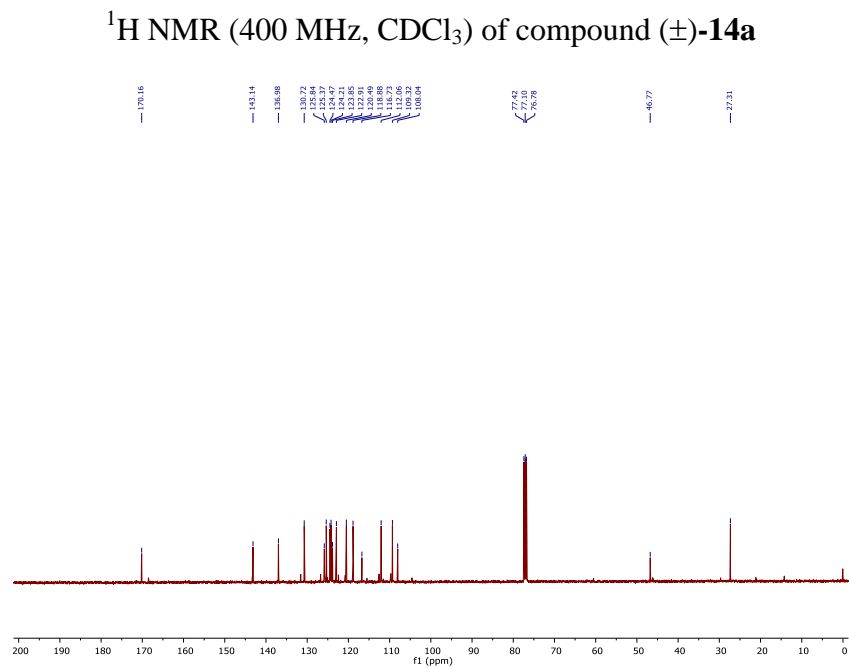
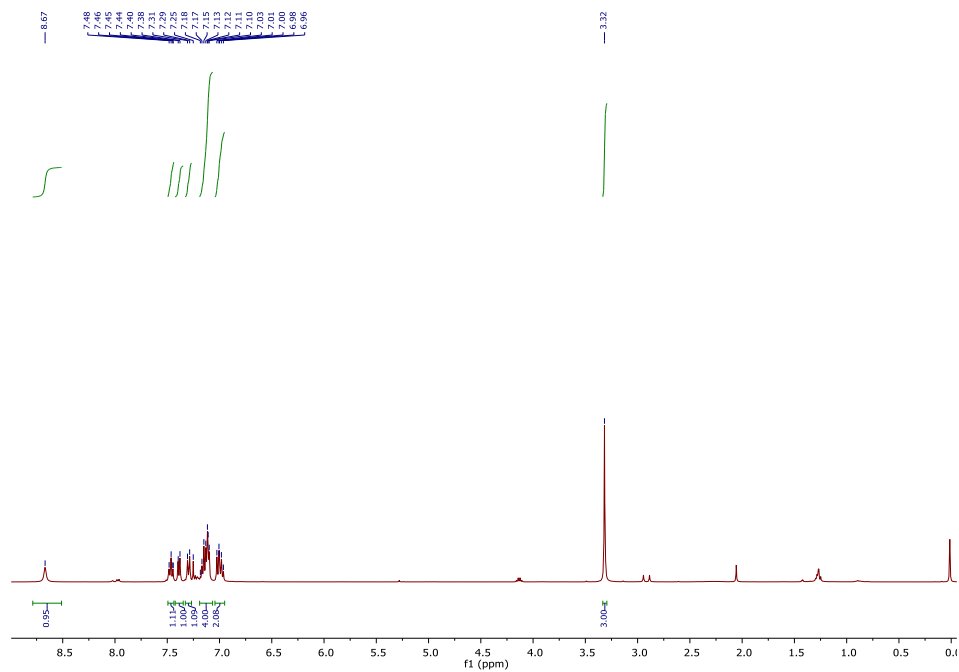
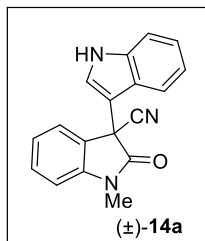
Analysis Name D:\Data\NEW USER DATA 2017\2018\May-2018\07-05-2018\Dr A Bisai-AR-03-187\_1-D,6\_01\_1612.d  
Method hrlcms-20 sept.m  
Sample Name Dr A Bisai-AR-03-187  
Comment

Acquisition Date 5/7/2018 2:11:53 PM  
Operator RUCHI  
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\2018\12 march-2018\Dr A Bisai-AR-03-162\_1-E,6\_01\_1228.d  
Method hrlcms-20 sept.m  
Sample Name Dr A Bisai-AR-03-162  
Comment

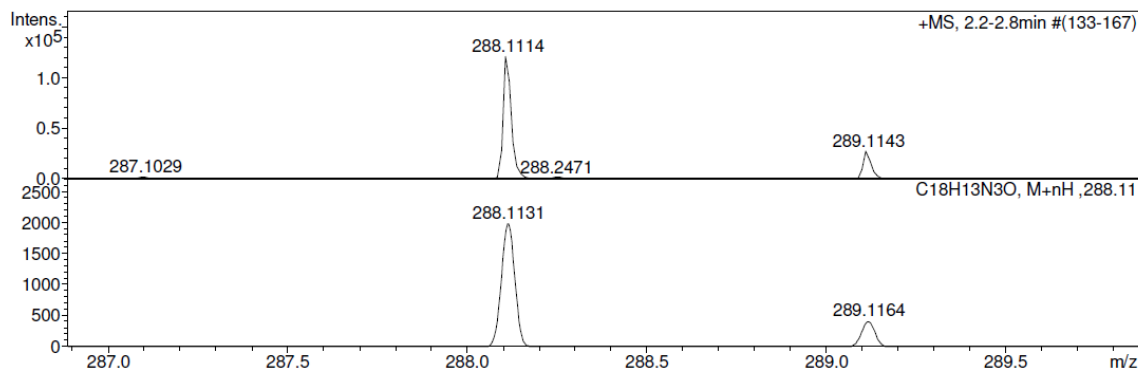
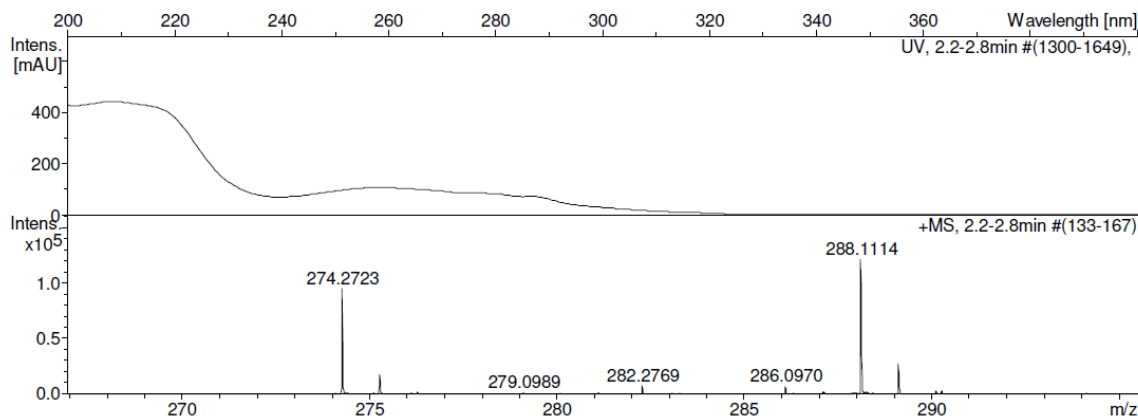
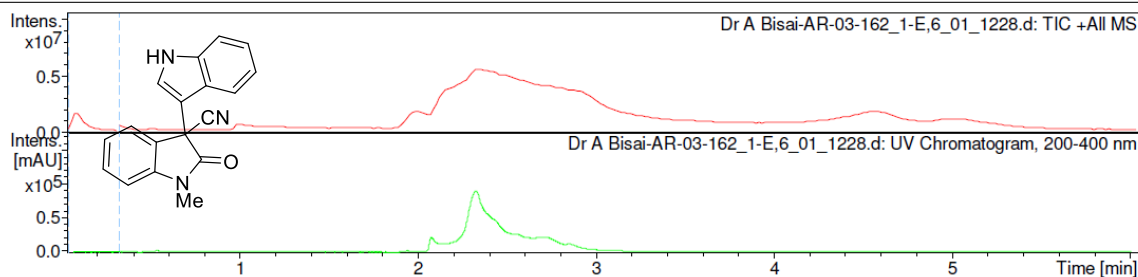
Acquisition Date 3/12/2018 1:45:10 PM

Operator RUCHI

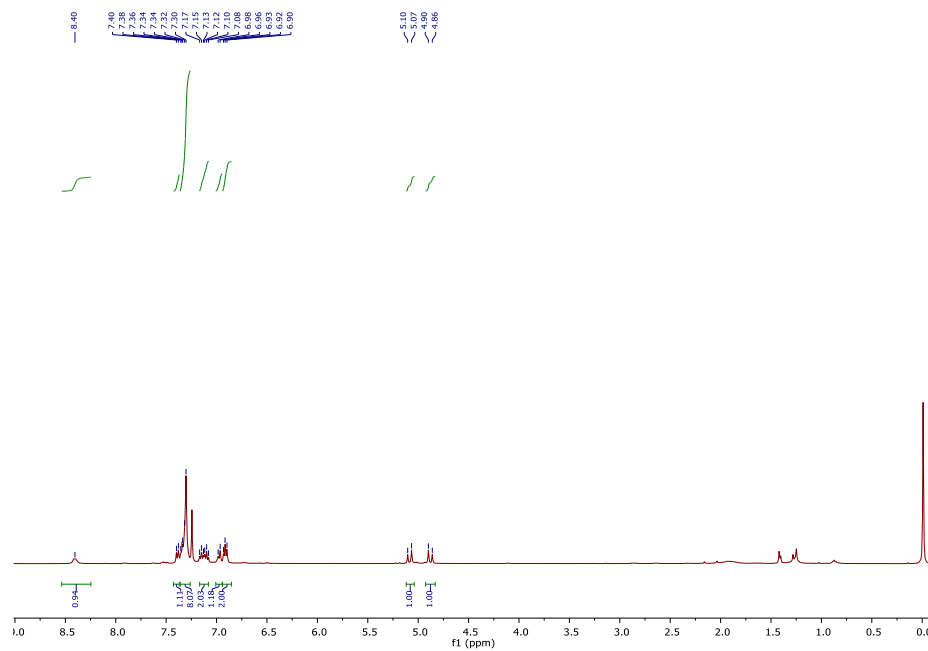
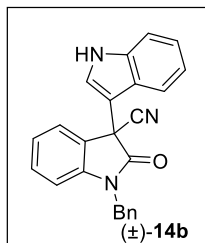
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

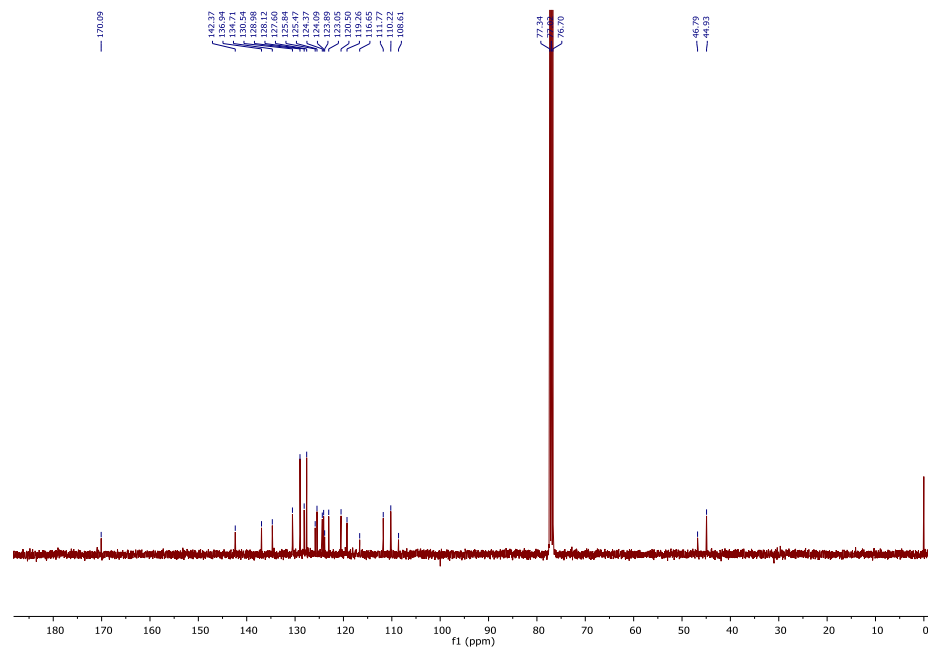
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (±)-14b



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-14b

## Display Report

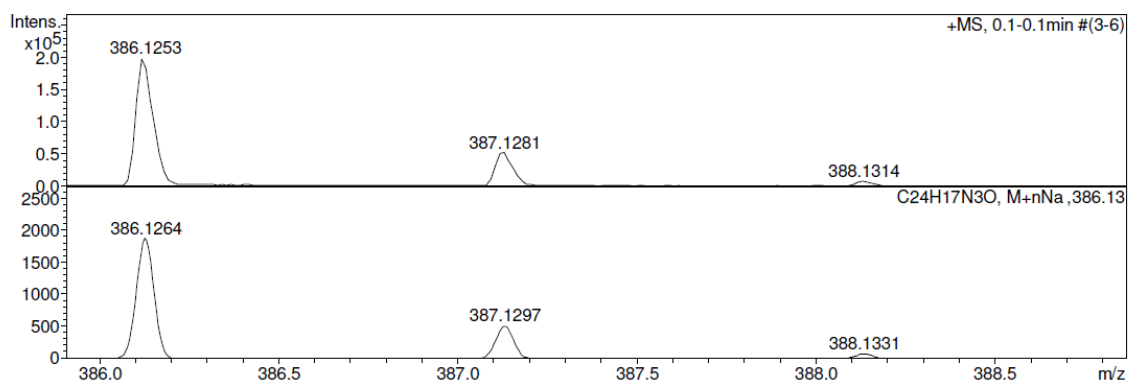
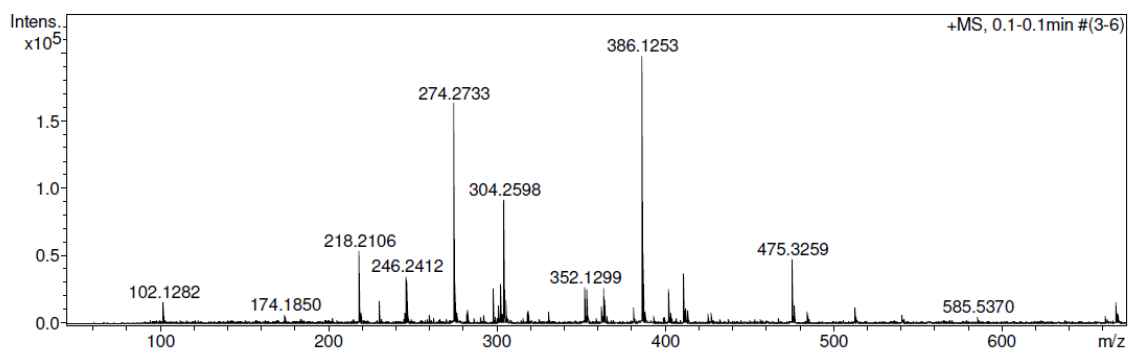
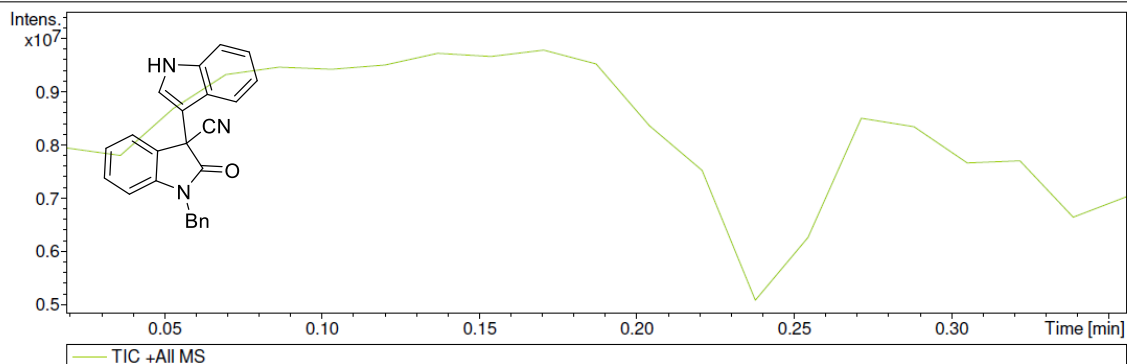
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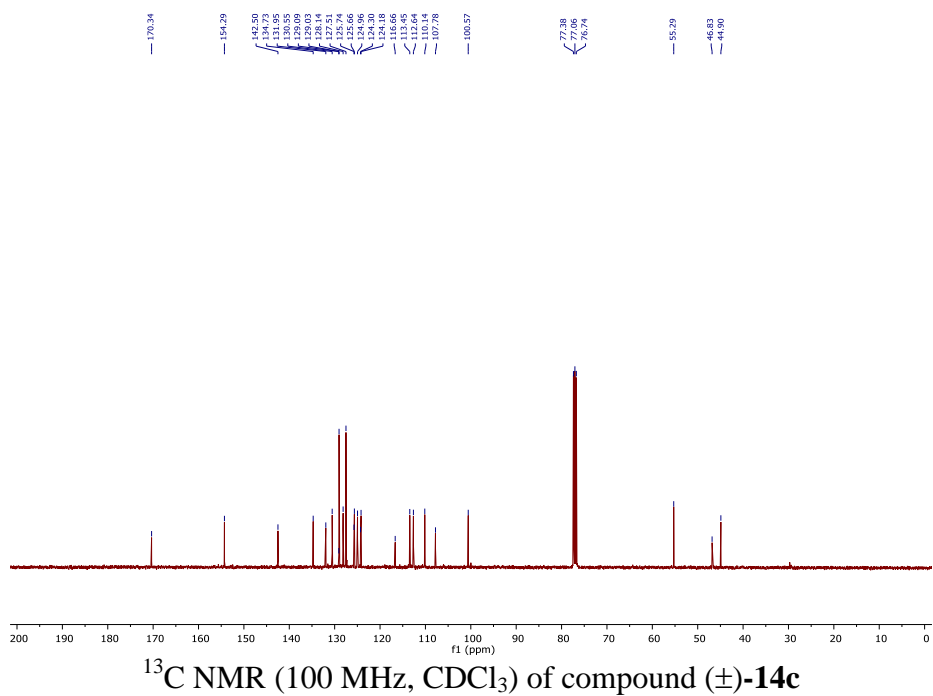
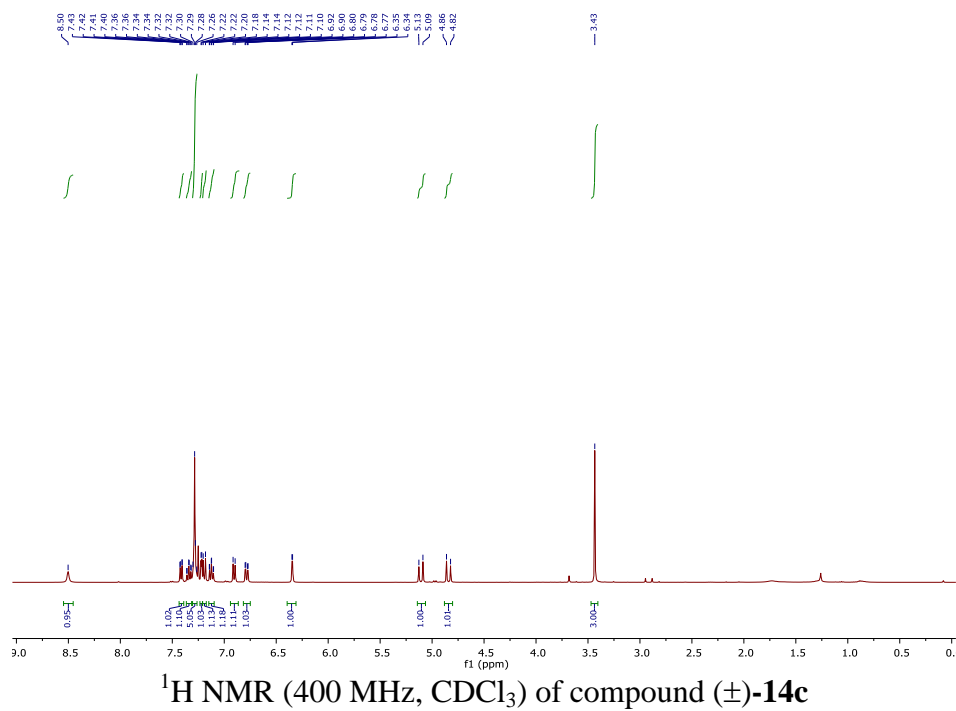
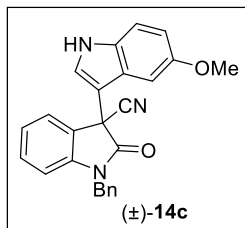
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Sample Name AB-AR-03-95  
Comment

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Operator RUCHI  
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





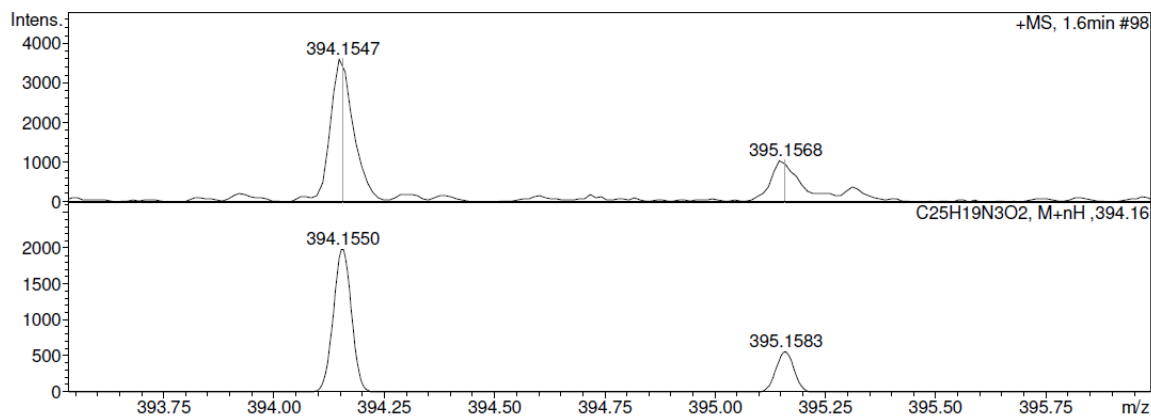
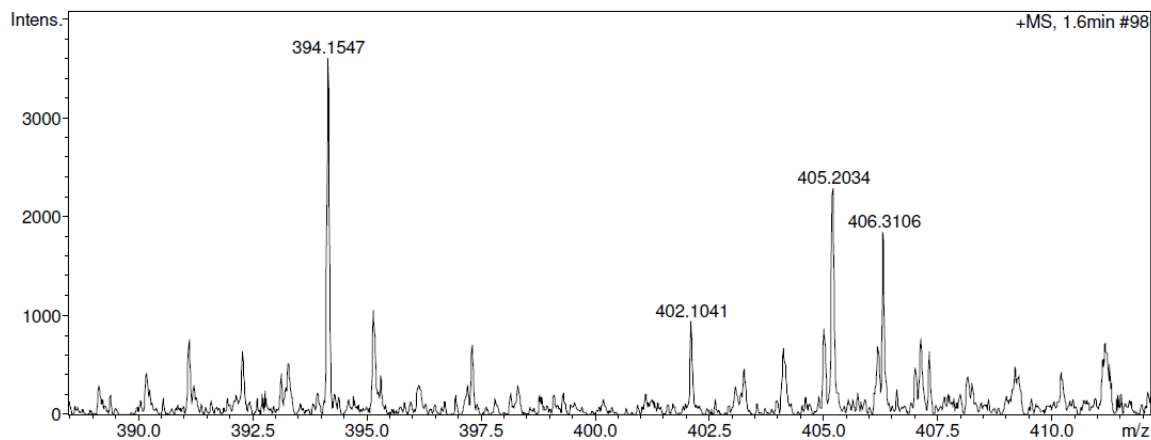
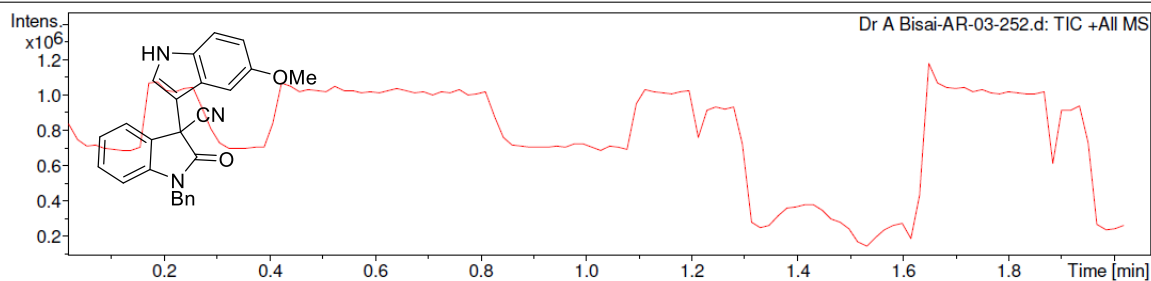
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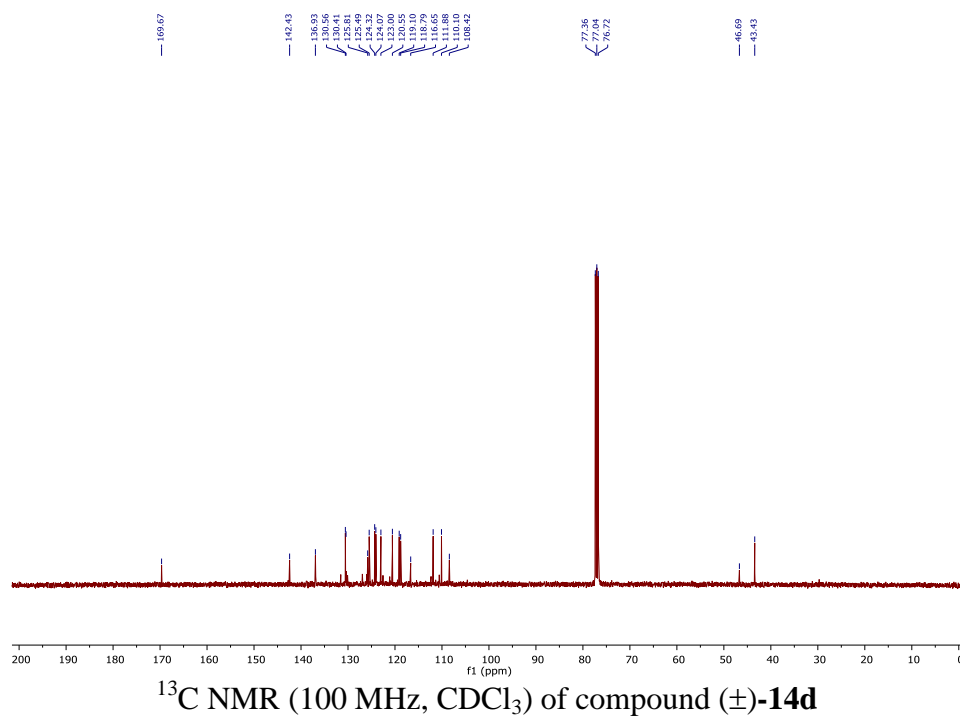
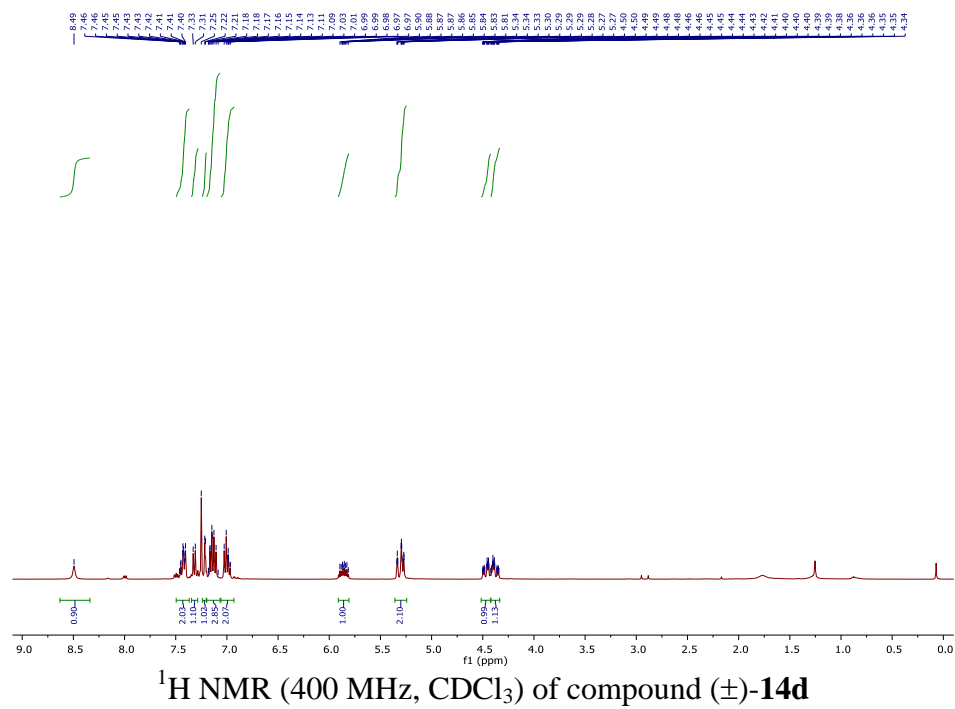
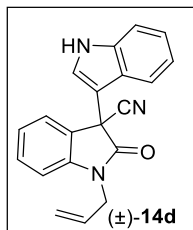
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Method tune\_low.m Operator RUCHI  
Sample Name AR-03-252 Instrument micrOTOF-Q II 10330  
Comment

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Scanned copy of mass spectrum of (±)-**14c**

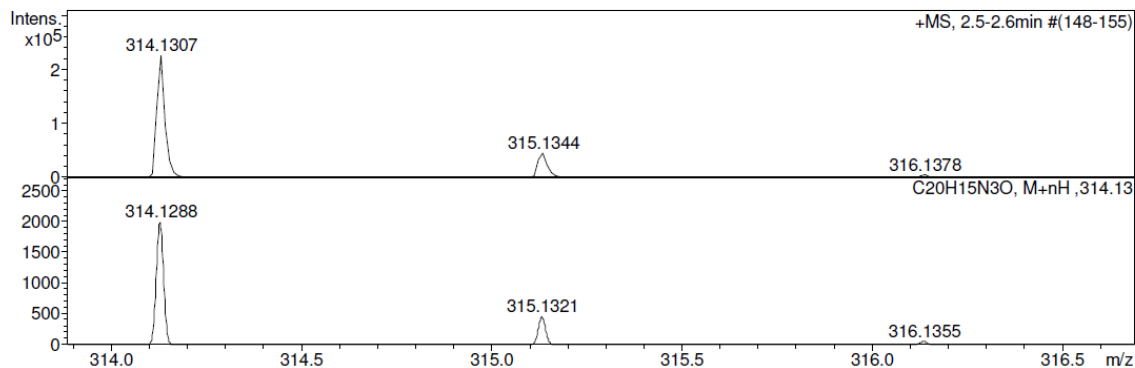
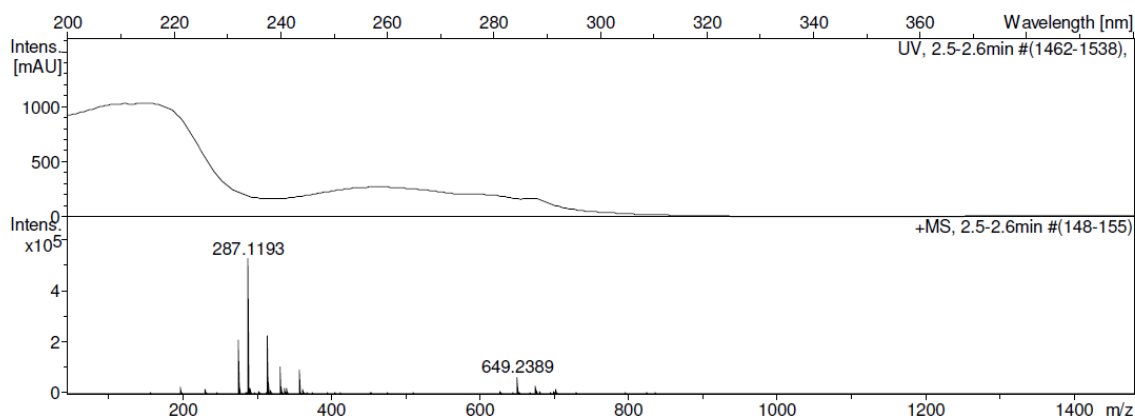
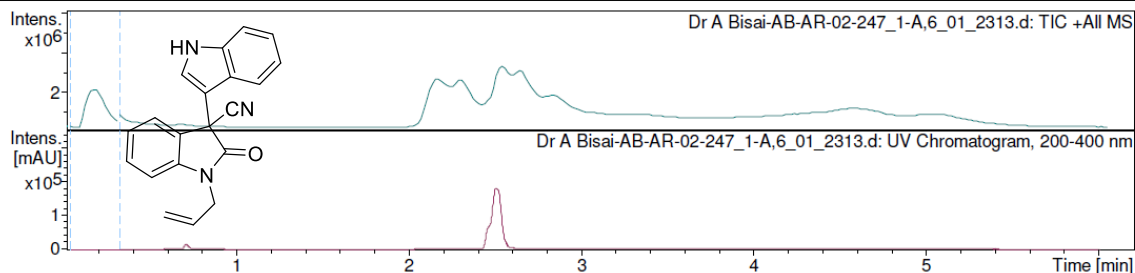


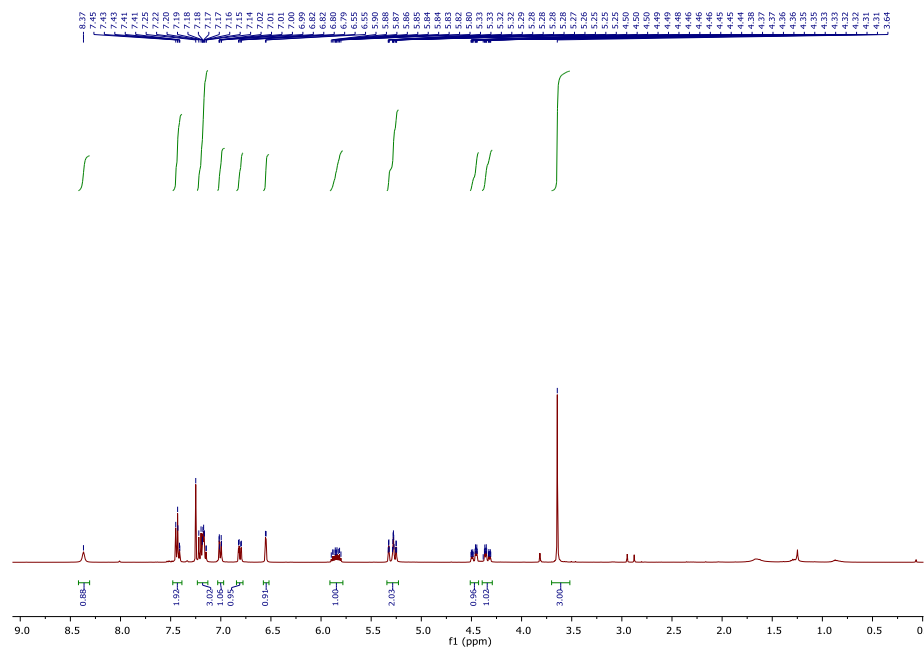
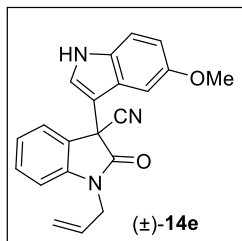
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Comment  
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Operator RUCHI  
Instrument micrOTOF-Q II 10330

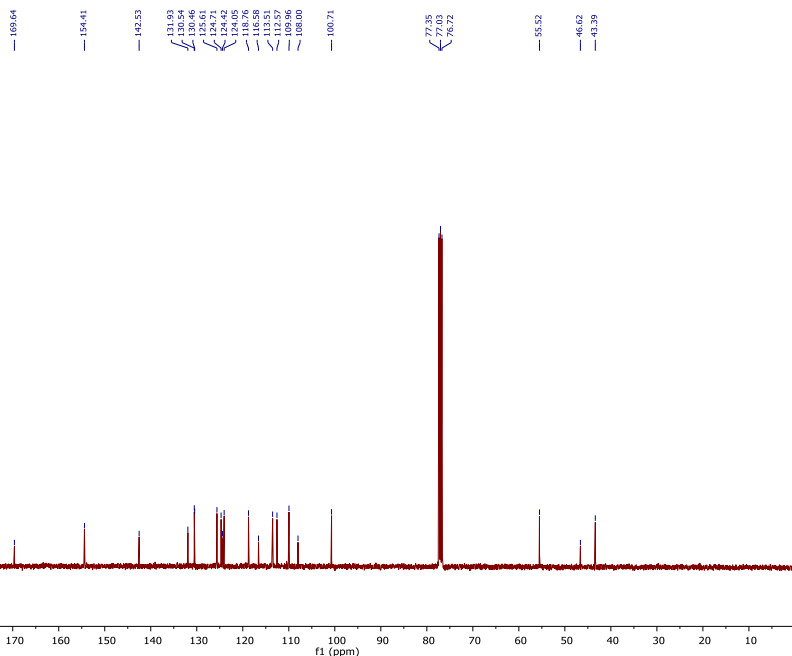
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Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (±)-**14e**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-**14e**

## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\2018\JUNE 2018\26 J\Dr A Bisai-AR-JK-01-27-DI.d  
Method tune\_mix\_low.New.021117.m  
Sample Name AR-JK-01-27-DI  
Comment

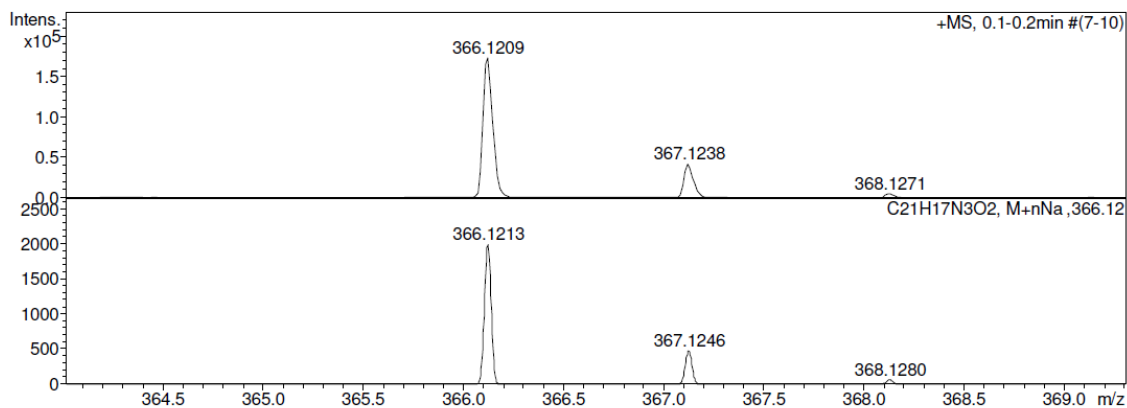
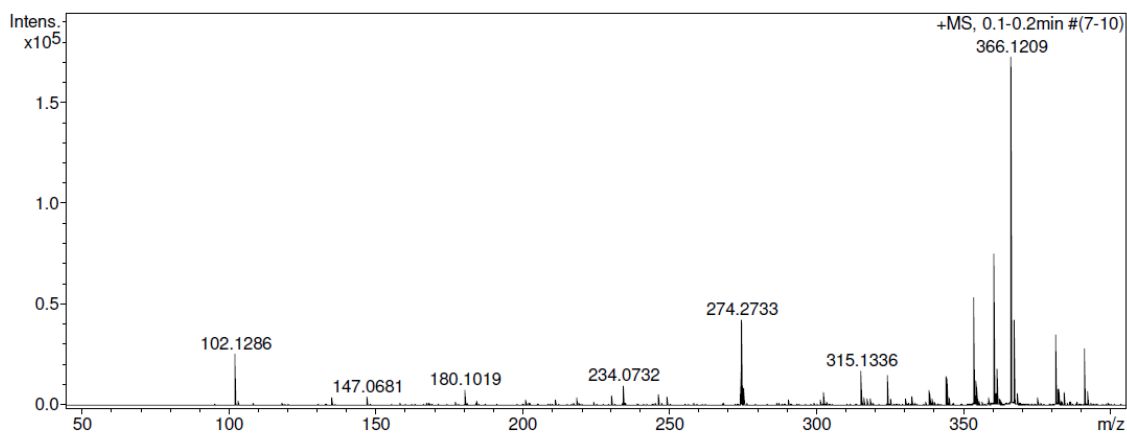
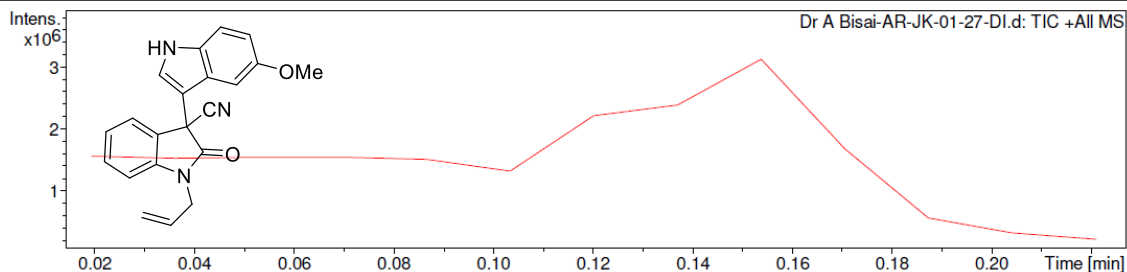
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Operator RUCHI

Instrument micrOTOF-Q II 10330

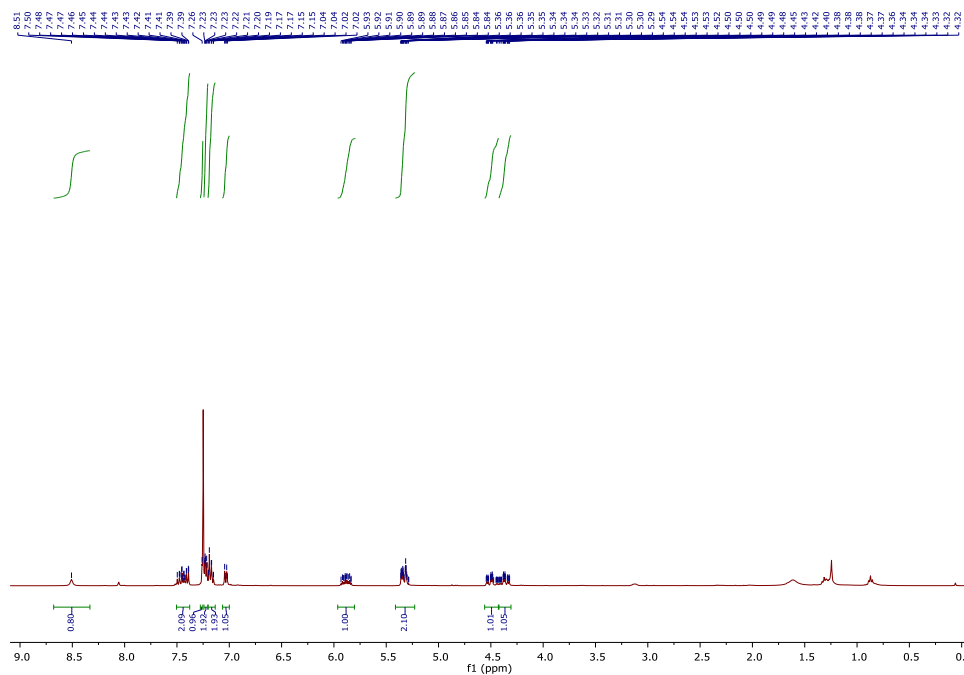
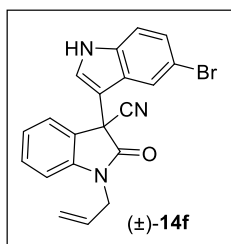
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Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

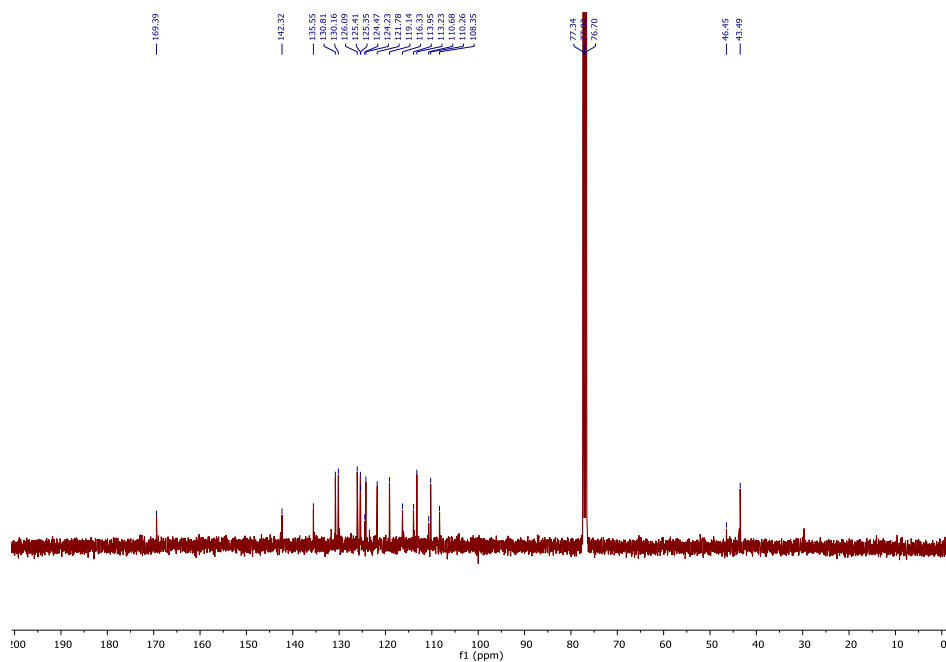


Scanned copy of mass spectrum of (±)-14e





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (±)-**14f**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound (±)-**14f**

## Display Report

## Analysis Info

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Method tune\_low.m

Sample Name AR-03-248R

Comment

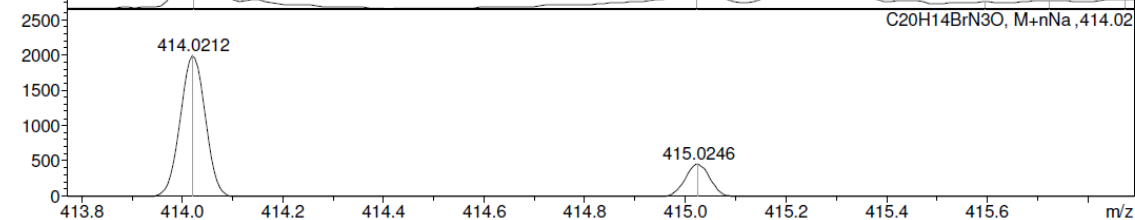
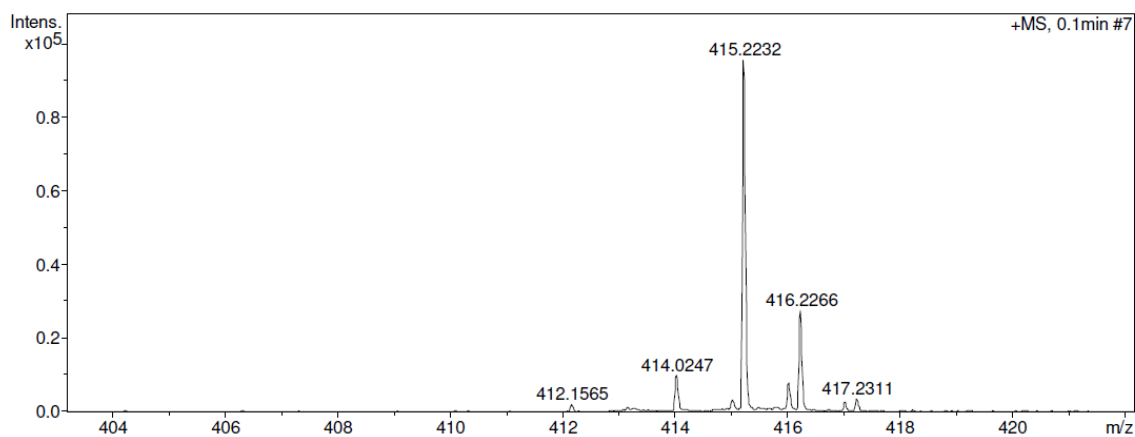
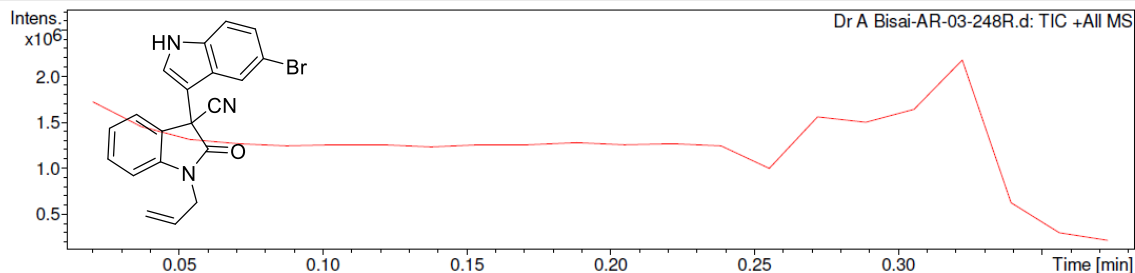
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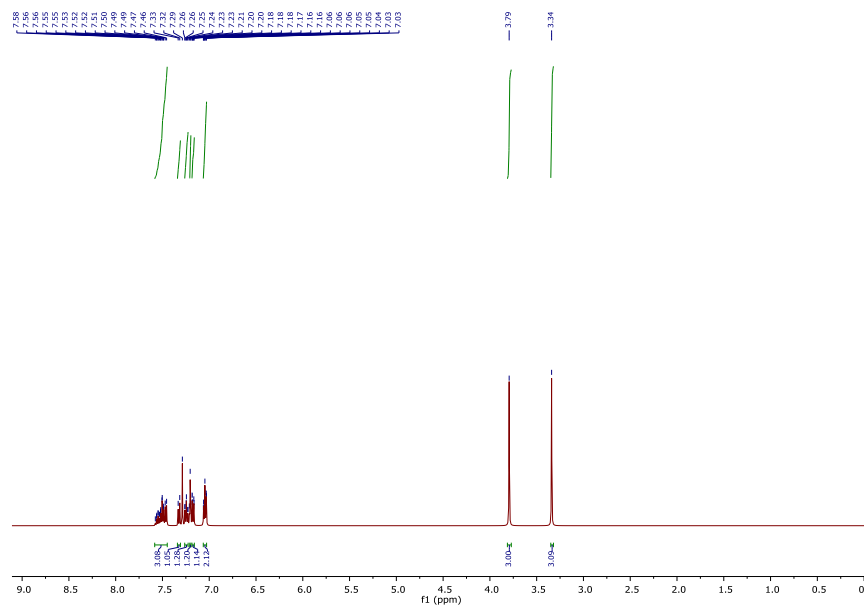
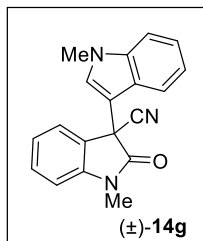
Operator RUCHI

Instrument micrOTOF-Q II 10330

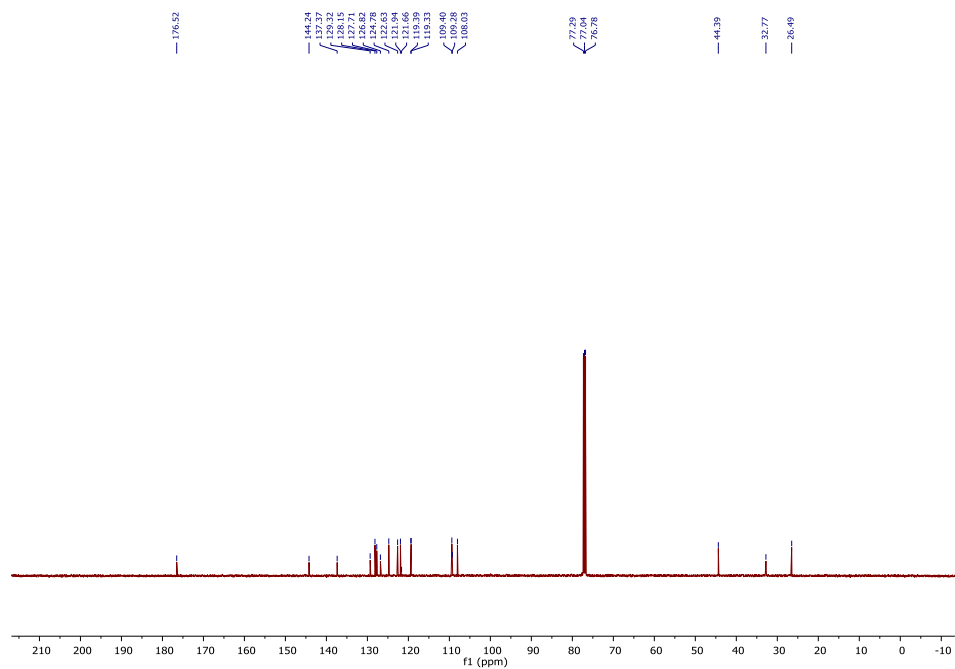
## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste





$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of compound (±)-14g



$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound (±)-14g

## Display Report

## Analysis Info

Analysis Name D:\Data\NEW USER DATA 2017\2018\26 mar\Dr A Bisai-AR-03-169\_1-C,6\_01\_1387.d  
Method hrlcms-20 sept.m  
Sample Name Dr A Bisai-AR-03-169  
Comment

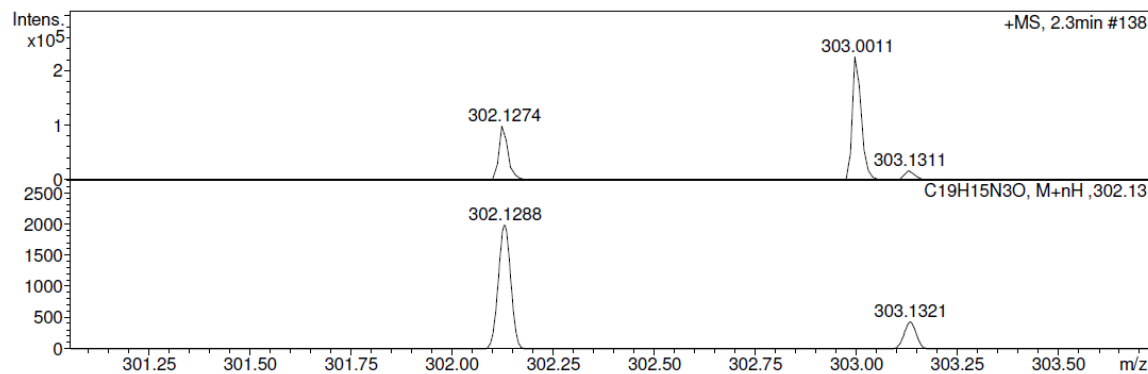
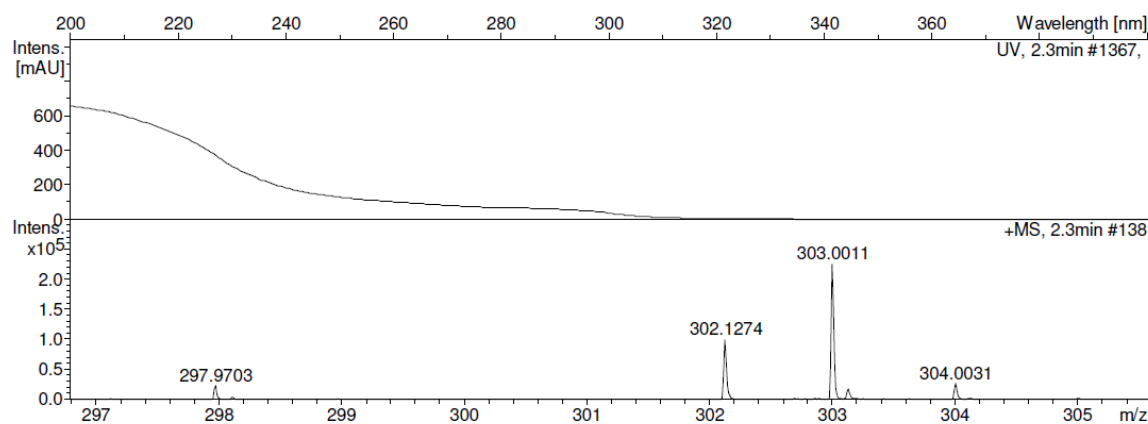
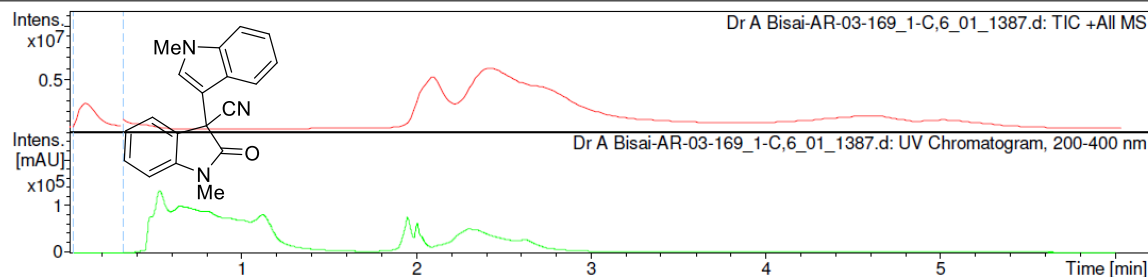
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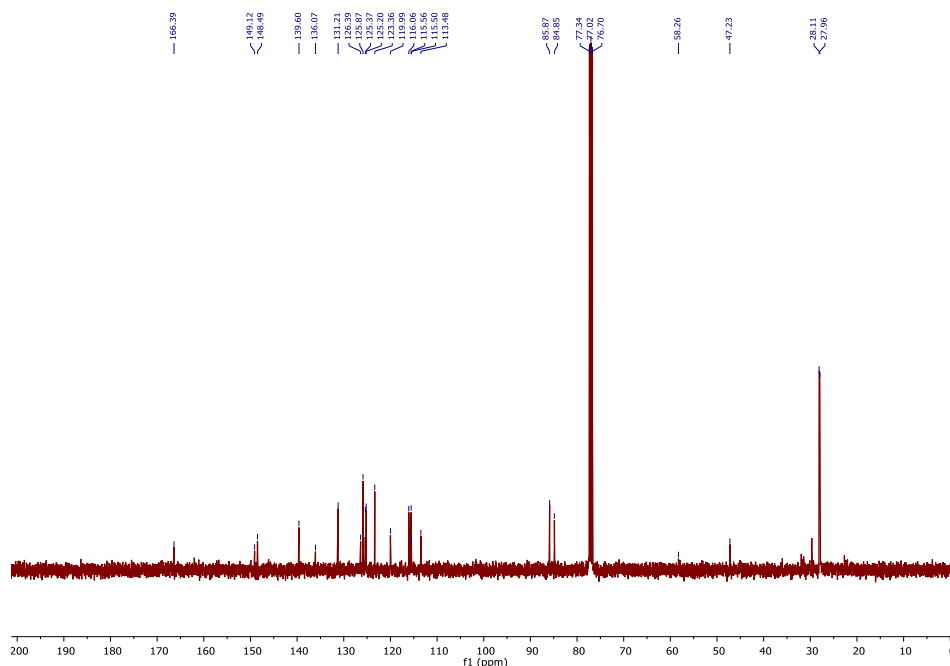
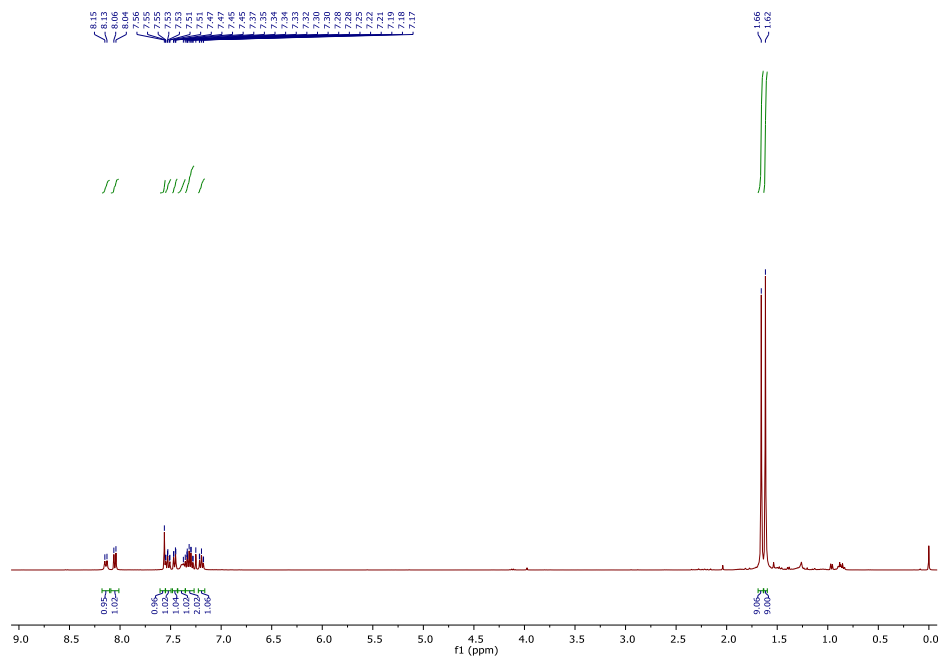
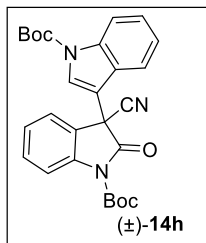
Operator RUCHI

Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





## Display Report

## Analysis Info

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Method tune\_mix\_low.New.021117.m  
Sample Name AR-03-105  
Comment

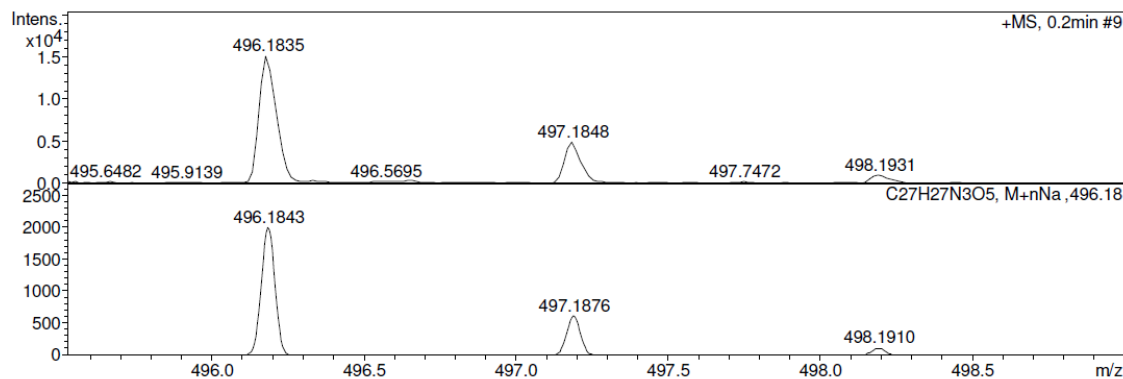
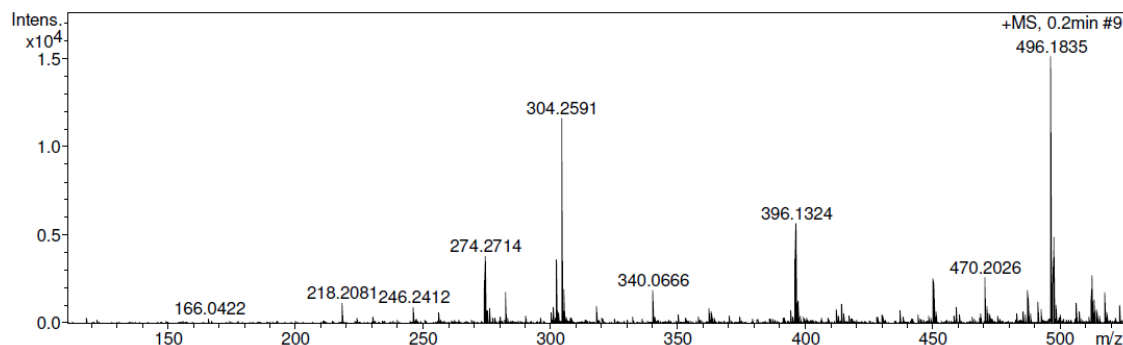
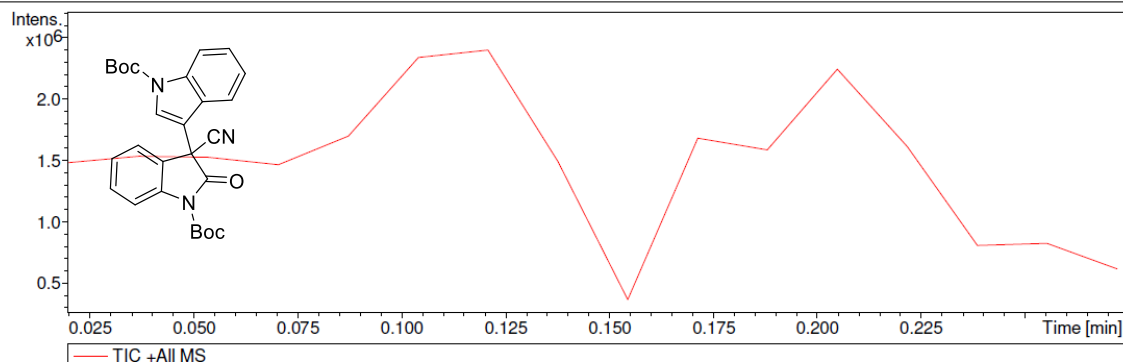
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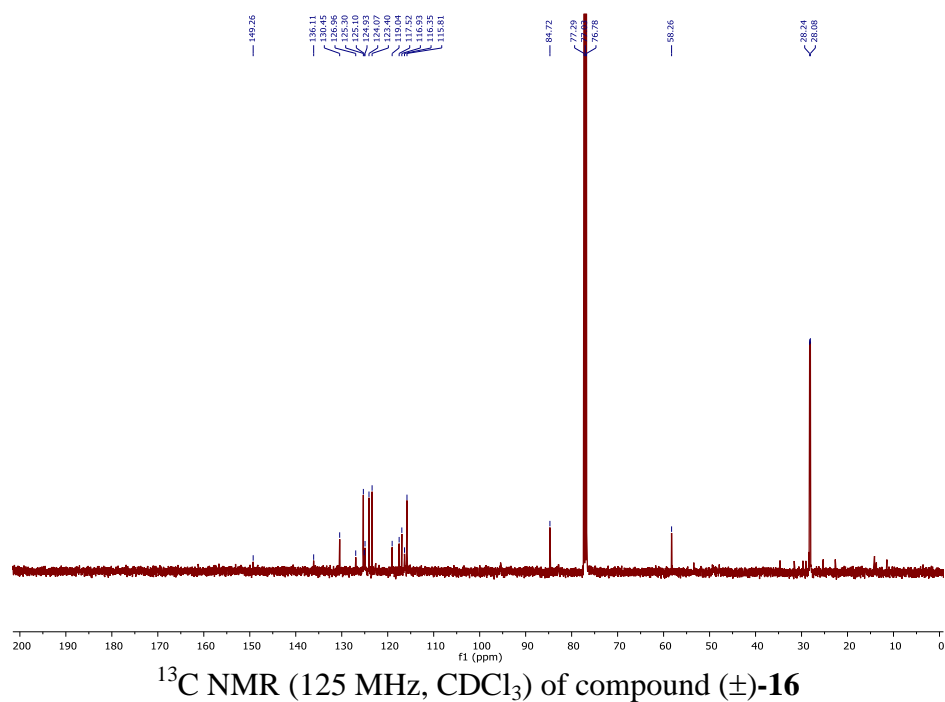
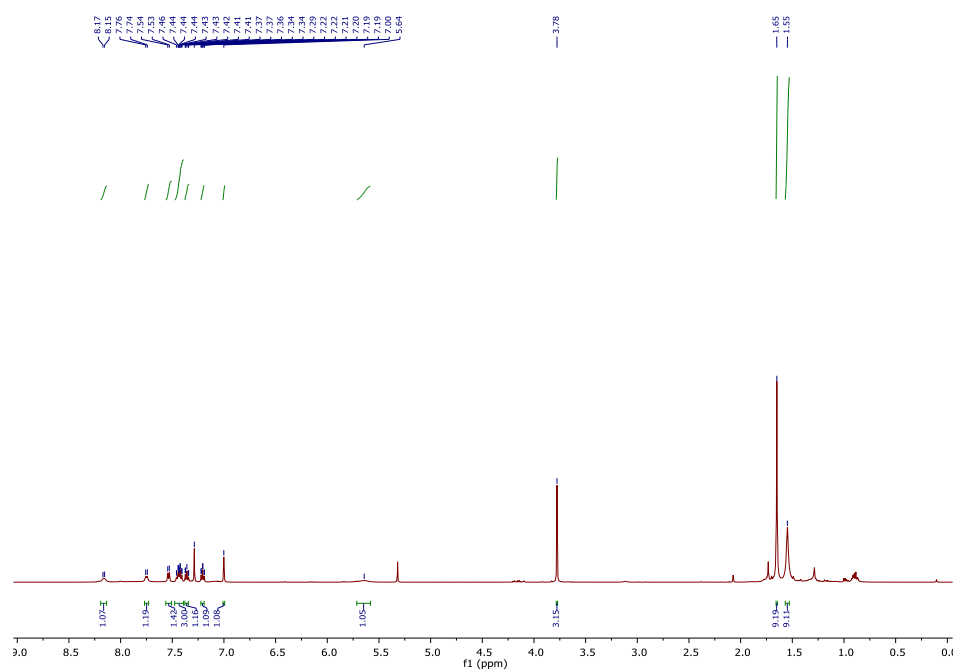
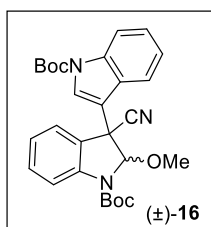
Operator RUCHI

Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	70.0 Vpp	Set Divert Valve	Waste





## Display Report

## Analysis Info

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Sample Name AR-03-232  
Comment

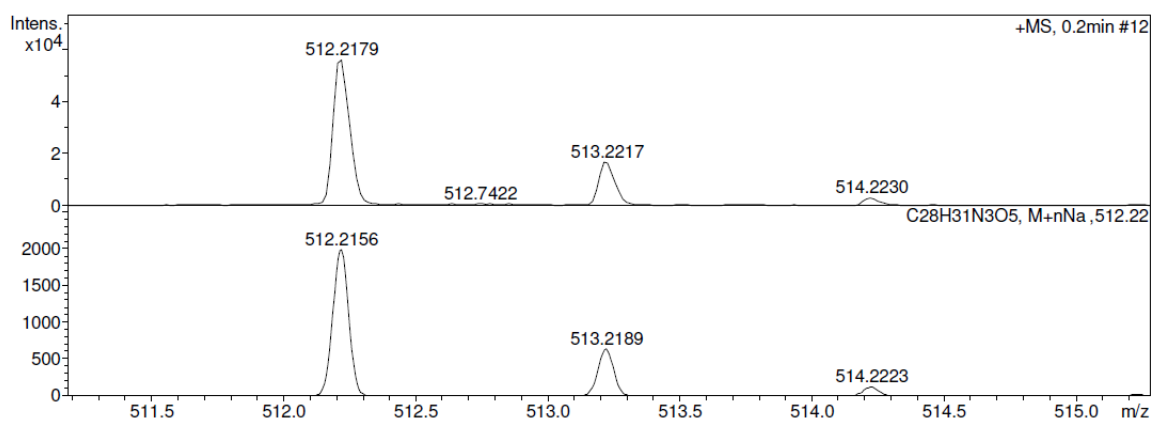
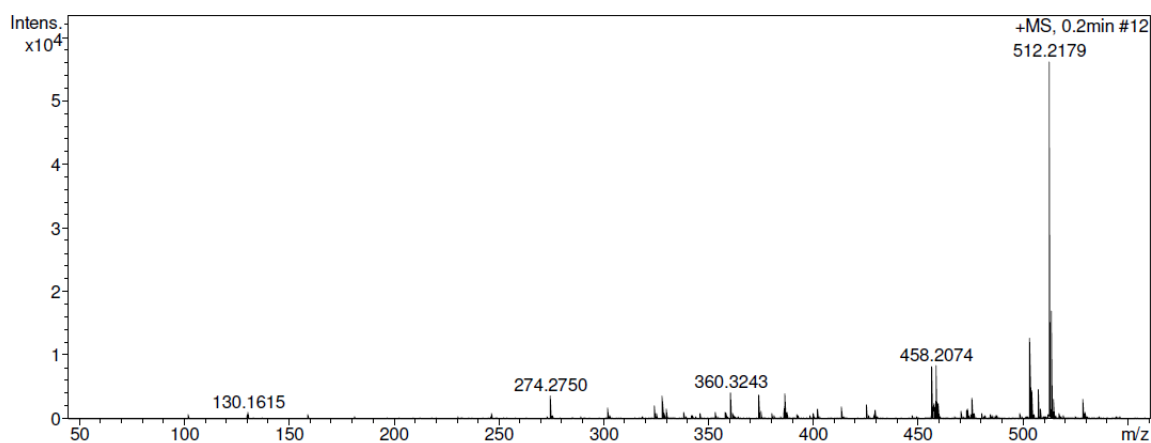
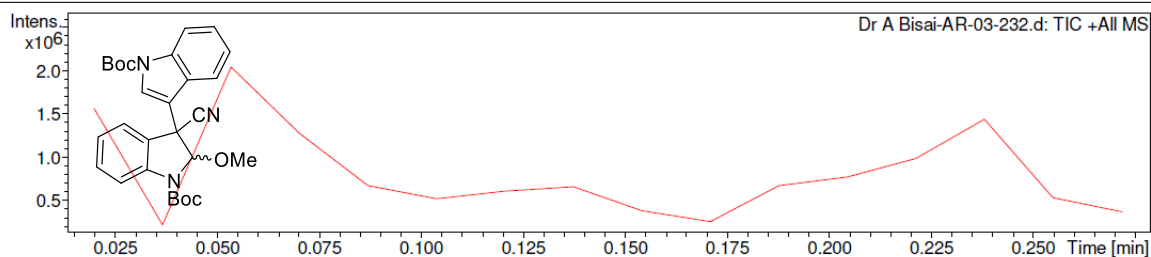
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Operator RUCHI

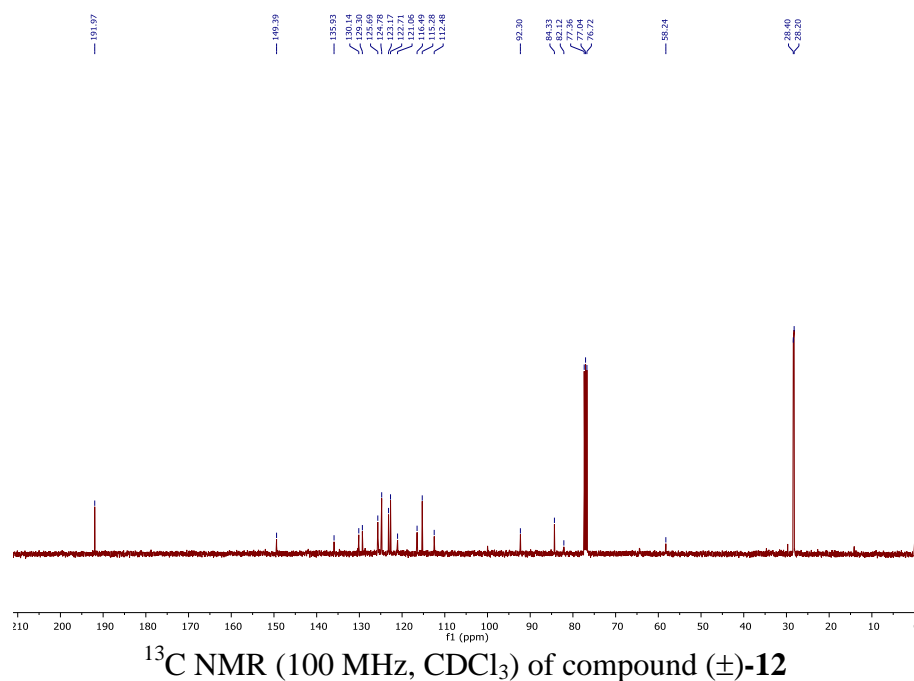
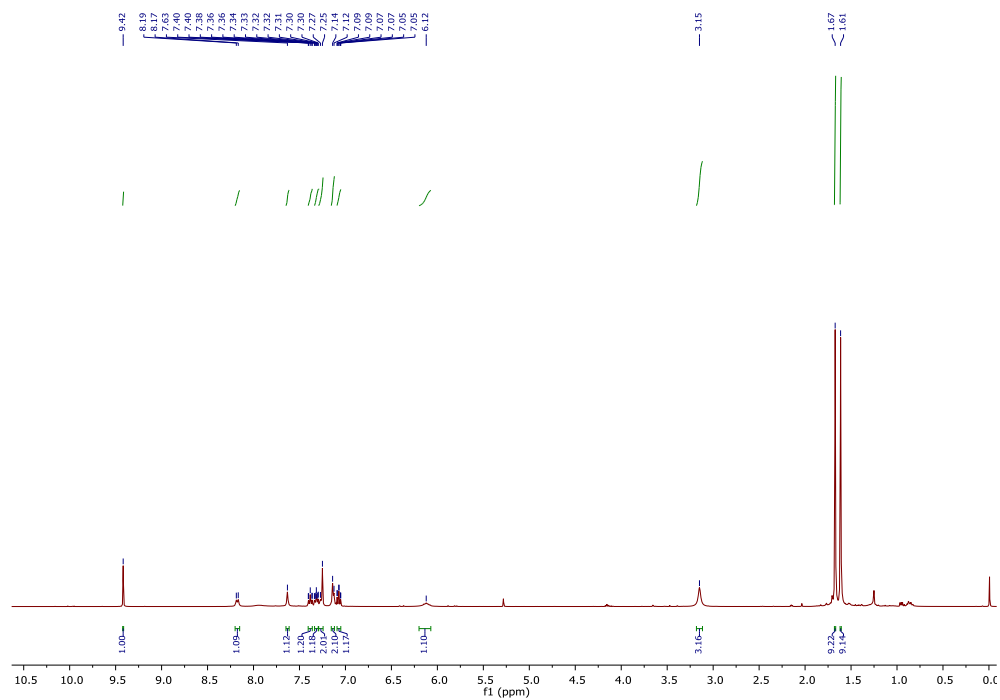
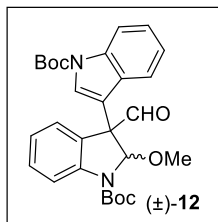
Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste







## Display Report

## Analysis Info

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Sample Name Dr A Bisai-AR-03-227  
Comment

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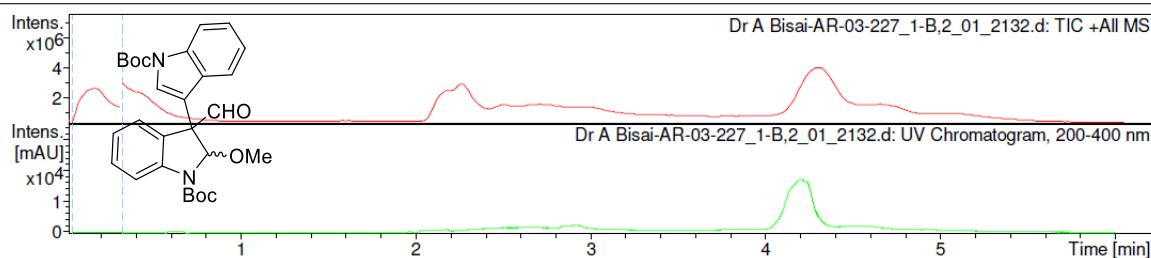
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Operator RUCHI

Instrument micrOTOF-Q II 10330

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Wavelength [nm]

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Intens. [mAU]

+MS, 2.9min #174

Intens.

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1500

1000

500

0

485

490

495

500

505

510

515

520

m/z

Intens.

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515.5

516.0

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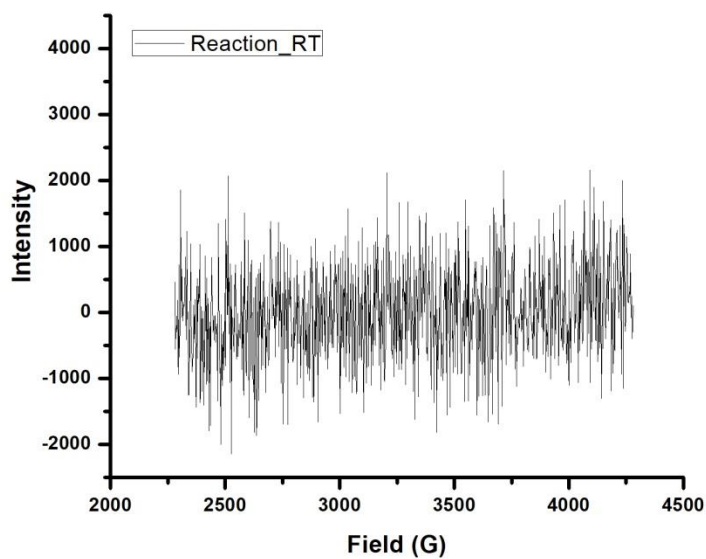
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m/z

**EPR studies for key cyanation reaction of 1a (According to the Experimental procedure A):**



**X-band EPR spectra in DMF at 298K under nitrogen atmosphere (According to the Experimental procedure A)**