Supporting Information

Palladium(II)-Catalyzed Intermolecular C–H Silylation Initiated by Aminopalladation

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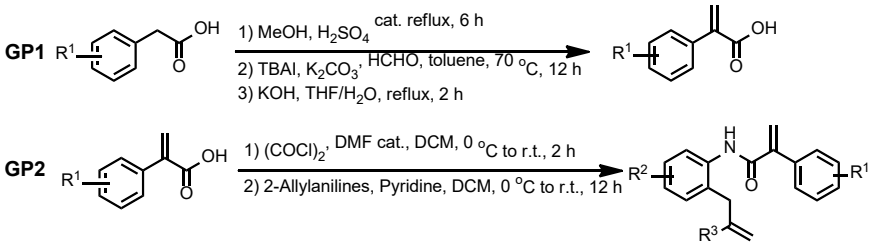
1. General Information

$Pd(OAc)_2$ was purchased from Strem Chemicals. Solvents were purchased from Adamas Reagent and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400 instrument (400 MHz) or Bruker DRX-600 instrument (600 MHz). High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2. General Procedures for the Synthesis of Acrylamide Substrates

Method A



General Procedures 1 (GP1)[1]:

Step 1: A 50 mL round bottom flask equipped with a stir bar was charged with 2-phenylacetic acid derivatives (20 mmol, 1.0 equiv), concentrated sulfuric acid (3 drops), and methanol (20 mL). The mixture was heated to reflux for 6 hours. After that, the reaction mixture was allowed to cool down to room temperature. After the methanol was removed by rotary evaporation, the residue was diluted with EtOAc and treated with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the corresponding methyl 2-phenylacetate derivatives.

Step 2: To a solution of prepared methyl 2-phenylacetate derivatives in anhydrous toluene (20 mL), potassium carbonate (5.53 g, 40 mmol, 2.0 equiv), tetrabutylammonium iodide (2.95 g, 8 mmol, 0.4 equiv), and polyformaldehyde (1.21 g, 40 mmol, 2.0 equiv) were added. The reaction mixture was heated at 70 °C for 12 h, quenched with water, and extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo.* The residue was purified on silica gel column chromatography by using PE/EA as the eluent to afford methyl 2-phenylacrylate derivatives.

Step 3: To a solution of prepared methyl 2-phenylacrylate derivatives in THF (10 mL), a solution of potassium hydrate (4.49 g, 80 mmol, 4.0 equiv) in water (10 mL) was added. The reaction

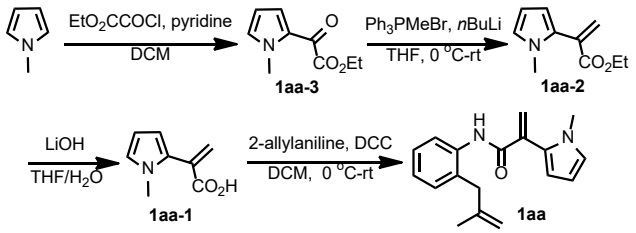
mixture was heated at reflux for 2 hours and then cooled to 0 °C. Addition of concentrated hydrochloric acid resulted in precipitation of a white solid, which was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford 2-phenylacrylic acid derivatives, which was used directly in the next step.

General Procedures 2 (GP2):

Step 1: A solution of 2-phenylacrylic acid derivatives (10 mmol, 1.0 equiv) and DMF (2 drops) in dichloromethane (10 mL) was prepared and cooled to 0 °C. A solution of oxalyl chloride (1.14 mL, 12 mmol, 1.2 equiv) in dichloromethane (5 mL) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 2 hours. The acyl chloride was concentrated *in vacuo* and redissolved in dichloromethane (5 mL).

Step 2: A solution of the 2-allylaniline derivatives[2] (10 mmol, 1.0 equiv) and pyridine (0.8 mL, 10 mmol, 1.0 equiv) was prepared in dichloromethane (10 mL) and cooled to 0 °C. The acyl chloride solution was added dropwise into the vessel containing the 2-allylaniline derivatives. The reaction was allowed to warm to room temperature and stirred for 12 hours. The reaction was quenched with a saturated $NaHCO_3$ solution and extracted with EtOAc. The combined organic layer was treated with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford unsubstituted acrylamide products. The residue was purified on silica gel column chromatography by using petroleum ether/acetone as the eluent to afford acrylamide derivatives.

Method B



Step 1: A solution of pyridine (1.93 mL, 24 mmol) in dry dichloromethane (30 mL) was added dropwise to a stirred solution of ethyl chlorooxoacetate (3.0 g, 22 mmol) in dry dichloromethane (5 mL) at –78°C under nitrogen. A solution of *N*-methyl pyrrole (1.62 g, 20 mmol) in dry dichloromethane (5 mL) was added dropwise to the reaction mixture and the solution was allowed to warm up slowly to room temperature. After being stirred for 48 h, the reaction mixture was washed with dilute hydrochloric acid, water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, PE/EA 5:1) to give product **1aa-3** (2.36g, 65%).

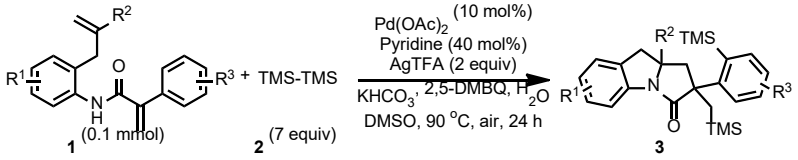
Step 2: To a suspension of triphenylmethylphosphonium bromide (11 mmol) in dry THF (30 mL) at 0 °C was added dropwise *n*-butyllithium (11 mmol) under nitrogen. After stirring at 0 °C for 1 h, product **1aa-3** (10 mmol) in 5 mL of THF was added to the stirred reaction mixture. The reaction was then allowed to warm up to room temperature and stirred for another 30 min and then quenched with water. The organic layer was extracted with ethyl acetate and then combined and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel,

PE/EA 10:1) to give product **1aa-2** as an oil (0.36 g, 20%).

Step 3: A 50 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with product **1aa-2** (6 mmol), LiOH (5 equiv), and THF/H_2O (1:1, 0.25 M) sequentially. The reaction flask was subjected to a 80 °C preheated oil bath and stirred overnight, after which the resulting mixture was cooled down to room temperature and extracted with DCM. The aqueous phase was acidified with 2N HCl and extracted with DCM. The combined organic layers were dried over $MgSO_4$. The volatile compounds were removed *in vacuo* to afford product **1aa-1** as a yellow solid (0.91 g, 100%).

Step 4: To a stirred mixture of DCC (6.6 mmol, 1.1 equiv) and DMAP (0.1 equiv) in DCM (10 mL), product **1aa-1** (6.0 mmol, 1.0 equiv) in 2 mL DCM was added at 0 °C. Then 2-allylaniline derivative (6.0 mmol, 1.0 equiv) in 2 mL DCM was added. The reaction was then allowed to warm up to room temperature and stirred overnight. The precipitated product was filtered off and the solution was then concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, PE/Acetone 10:1) to give product **1aa** as an oil (0.68g, 40%).

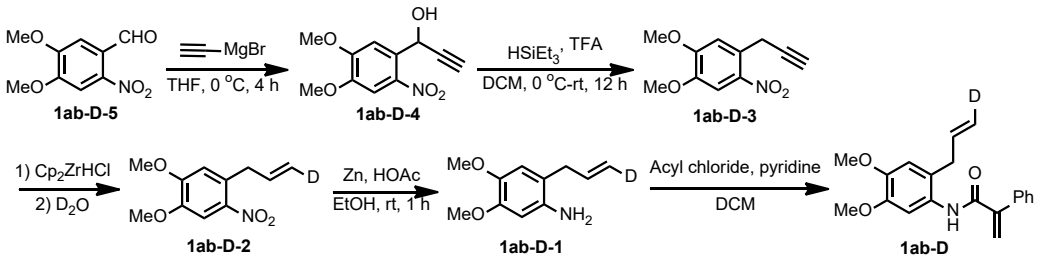
3. General Procedures for the Disilylation of 2-Phenylacrylamide Derivatives



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.25 mg, 0.01 mmol), pyridine (3.2 μL, 0.04 mmol), AgTFA (0.0441 g, 2 equiv), $KHCO_3$ (0.04 g, 4 equiv), 2,5-DMBQ (0.0027 g, 0.02 mmol)，H_2O (14.4 μL, 0.8 mmol)，TMS-TMS **2** (143.5 μL, 0.7 mmol), the corresponding 2-phenylacrylamide derivatives **1** (0.1 mmol) and DMSO (2 mL). The mixture was stirred at 90 °C (preheated oil bath) for 24 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by preparative thin layer chromatography (PTLC) with petroleum ether/ethyl acetate to give the corresponding products.

4. Mechanistic Study on Aminopalladation Step

Preparation of Substrate 1ab-D



Step 1: A 250-mL round-bottom flask was charged with **1ab-D-5** (4.22 g, 20 mmol) and purged with nitrogen. To the flask was added dry tetrahydrofuran (15 mL), and the flask was cooled to 0 °C bath. Ethynyl magnesium bromide (30 mmol) was then added dropwise over 5 min. The mixture was stirred for 4 h at 0 °C. The reaction was quenched with methanol (10 mL) and the solvent removed *in vacuo* before adding aq HCl (100 mL, 1 M) and ethyl acetate (200 mL). The aqueous layer was extracted three times with ethyl acetate. Organic layers were collected, washed with brine, and dried over sodium sulfate. The solution was then concentrated under reduced pressure, and the resulting crude material was purified using flash chromatography to afford a yellow solid **1ab-D-4** (4.6g, 97%).

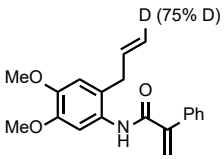
Step 2: A 250-mL round-bottom flask was charged with **1ab-D-4** (4.74 g, 20 mmol) and purged with nitrogen. To the flask was added dry CH_2Cl_2 (50 mL), and the flask was placed in an ice bath. After 5 min on ice, triethylsilane (60 mmol, 3 equiv) was added dropwise over 2 min. Trifluoroacetic acid (270 mmol, 9 equiv) was added, and the reaction was stirred on ice for 15 min and was then allowed to warm up to room temperature. The reaction was stirred for 20 h. Solvents were removed *in vacuo* and the resulting residue was purified using flash chromatography to afford a yellow solid **1ab-D-3** (2.43g, 55%).

Step 3:[3] In a dried Schlenck flask equipped with a stirring bar were introduced under nitrogen Cp_2ZrHCl (Schwartz reagent) (7.5 mmol, 1.25 equiv) and tetrahydrofuran (25 mL). The propargylic derivative **1ab-D-3** (1.0 equiv) in tetrahydrofuran (5 mL) was then added, and the mixture was stirred at room temperature for 2 h. Pure D_2O (3.18 mL) was quickly added, and the mixture was stirred for 2 h. Diethyl ether was added, and the mixture was dried on $MgSO_4$. The product was purified using flash chromatography to afford a yellow oil **1ab-D-2** (1.21g, 90%).

Step 4: A 100-mL round-bottom flask was charged with **1ab-D-2** (10 mmol, 1.0 equiv), Zn (9.9g, 151 mmol), EtOH (60 mL) and purged with nitrogen. HOAc (8.6 mL, 151 mmol) was added. the mixture was stirred at room temperature for 1 h. The solid was filtered off and the solution was then concentrated *in vacuo*. The crude product was purified by column chromatography using flash chromatography to afford a yellow oil **1ab-D-1** (0.582g, 30%).

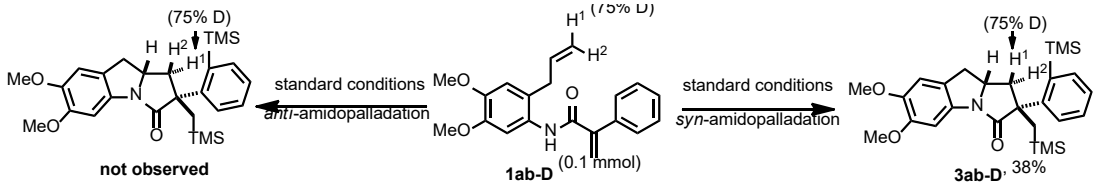
Step 5: A solution of 2-allylaniline derivative **1ab-D-1** (3 mmol, 1.0 equiv) and pyridine (3 mmol, 1.0 equiv) was prepared in dichloromethane (15 mL) and cooled to 0 °C. The acyl chloride solution was added dropwise into the vessel containing the 2-allylaniline derivative. The reaction was allowed to warm up to room temperature and stirred for 12 h. The reaction was quenched with a saturated NaCl solution and extracted with EtOAc. The combined organic layer was treated with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford unsubstituted acrylamide

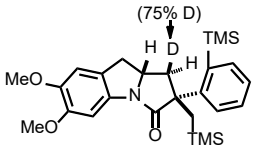
products. The residue was purified on silica gel column chromatography by using petroleum ether/acetone as the eluent to afford acrylamide derivative **1ab-D** (0.729g, 75%).



1ab-D: White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.43 – 7.38 (m, 5H), 7.35 (brs, 1H), 6.61 (s, 1H), 6.33 (d, *J* = 1.0 Hz, 1H), 5.68 (d, *J* = 1.0 Hz, 1H), 5.60 (dt, *J* = 17.2, 5.9 Hz, 1H), 4.74 (dd, *J* = 10.1, 1.4 Hz, 0.25H), 4.46 (d, *J* = 17.2 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.08 (dd, *J* = 5.8, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 147.5, 146.0, 145.0, 136.9, 135.2, 129.0, 128.8, 128.7, 128.6, 123.8, 121.5, 115.7 (t, *J* = 24.2 Hz), 112.9, 107.0, 56.0, 55.9, 36.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{20}DNNaO_3^+$: 347.1476 $(M + Na)^+$, found: 347.1440.

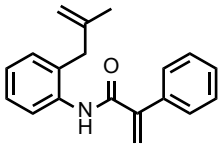
Procedure for Determination of Stereochemistry in the Aminopalladation Step with 1ab-D



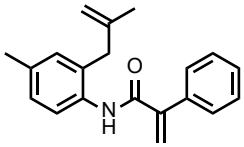


3ab-D: White solid (17.9 mg, 38%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.28 (s, 1H), 7.25 – 7.22 (m, 1H), 7.20 (dd, *J* = 10.6, 4.0 Hz, 1H), 6.76 (s, 1H), 4.71 (dd, *J* = 18.3, 9.5 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.14 (dd, *J* = 15.1, 8.4 Hz, 1H), 2.85 (dd, *J* = 15.1, 9.9 Hz, 1H), 2.79 – 2.74 (m, 1H), 2.36 (d, *J* = 9.5 Hz, 1H), 1.70 (d, *J* = 14.9 Hz, 1H), 1.58 (d, *J* = 14.9 Hz, 1H), 0.38 (s, 9H), -0.13 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 148.7, 148.6, 145.9, 139.7, 137.1, 133.7, 128.0, 127.0, 125.5, 124.8, 108.9, 100.0, 59.3, 57.3, 56.4, 56.3, 44.61 (d, *J* = 25.0 Hz), 35.8, 26.7, 4.0, 0. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{36}DNNaO_3Si_2^+$: 491.2267 $(M + Na)^+$, found: 491.2261.

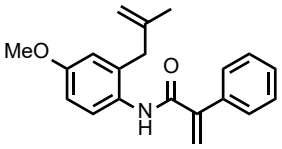
5. Characterization of the Substrates



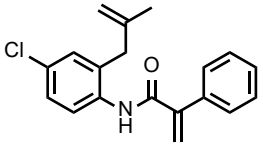
***N*-(2-(2-methylallyl)phenyl)-2-phenylacrylamide (1a).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.53 (brs, 1H), 7.42 – 7.38 (m, 5H), 7.32 – 7.27 (m, 1H), 7.11 – 7.06 (m, 2H), 6.32 (s, 1H), 5.69 (s, 1H), 4.47 (s, 1H), 4.07 (s, 1H), 3.09 (s, 2H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 145.2, 143.0, 137.0, 136.3, 130.8, 129.0, 128.8, 128.7, 128.5, 127.5, 124.8, 123.7, 122.5, 111.9, 40.9, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{19}NNaO^+$: 300.1359 $(M + Na)^+$, found: 300.1366.



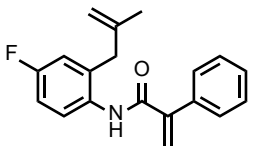
***N*-(4-methyl-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1b).** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.45 (brs, 1H), 7.41 – 7.36 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.31 (s, 1H), 5.67 (d, *J* = 0.7 Hz, 1H), 4.47 (s, 1H), 4.08 (s, 1H), 3.05 (s, 2H), 2.30 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 145.3, 143.1, 137.0, 134.5, 133.7, 131.4, 129.1, 128.8, 128.6, 128.5, 128.0, 123.5, 122.6, 111.7, 40.9, 22.2, 20.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}NNaO^+$: 314.1515 $(M + Na)^+$, found: 314.1522.



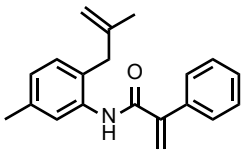
***N*-(4-methoxy-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1c).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.41 (m, 5H), 7.35 (brs, 1H), 6.82 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 6.31 (s, 1H), 5.67 (s, 1H), 4.48 (s, 1H), 4.11 (s, 1H), 3.78 (s, 3H), 3.07 (s, 2H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 156.7, 145.2, 143.0, 137.0, 131.5, 129.3, 128.8, 128.7, 128.5, 124.5, 123.5, 116.4, 112.0, 111.9, 55.4, 41.1, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{22}NO_2^+$: 308.1645 $(M + H)^+$, found: 308.1643.



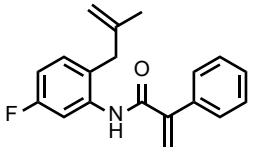
***N*-(4-chloro-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1d).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 1H), 7.50 (brs, 1H), 7.43 – 7.41 (m, 5H), 7.30 – 7.27 (m, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.36 (s, 1H), 5.72 (s, 1H), 4.51 (s, 1H), 4.08 (s, 1H), 3.06 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 145.0, 142.2, 136.7, 135.0, 130.7, 130.5, 129.7, 128.9, 128.8, 128.5, 127.4, 124.3, 123.7, 112.4, 40.7, 22.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}ClNNaO^+$: 334.0969 $(M + Na)^+$, found: 334.0961.



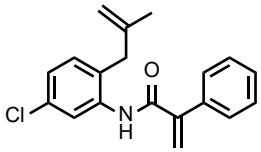
***N*-(4-fluoro-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1e).** Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.9, 5.4 Hz, 1H), 7.41 – 7.38 (m, 6H), 6.98 (td, *J* = 8.6, 2.8 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.8 Hz, 1H), 6.33 (s, 1H), 5.69 (s, 1H), 4.50 (s, 1H), 4.09 (s, 1H), 3.06 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 159.6 (d, *J* = 245.1 Hz), 145.0, 142.3, 136.8, 132.2 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 7.4 Hz), 129.3, 128.9, 128.8, 128.5, 128.2, 124.6 (d, *J* = 8.2 Hz), 124.0, 117.2 (d, *J* = 22.6 Hz), 113.9 (d, *J* = 22.0 Hz), 112.3, 40.8, 22.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}FNNaO^+$: 318.1265 $(M + Na)^+$, found: 318.1259.



***N*-(5-methyl-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1f).** White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.50 (brs, 1H), 7.41 – 7.38 (m, 5H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.31 (s, 1H), 5.68 (s, 1H), 4.46 (s, 1H), 4.07 (s, 1H), 3.05 (s, 2H), 2.36 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 145.3, 143.2, 137.2, 136.9, 136.0, 130.6, 128.8, 128.7, 128.5, 125.9, 125.6, 123.6, 123.0, 111.6, 40.5, 22.1, 21.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}NNaO^+$: 314.1515 $(M + Na)^+$, found: 314.1517.

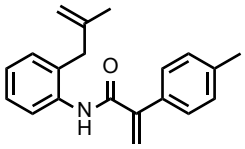


***N*-(5-fluoro-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1g).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 11.1, 2.2 Hz, 1H), 7.60 (brs, 1H), 7.43 – 7.42 (m, 5H), 7.05 – 7.03 (m, 1H), 6.80 (td, *J* = 8.2, 2.5 Hz, 1H), 6.35 (s, 1H), 5.72 (s, 1H), 4.49 (s, 1H), 4.05 (s, 1H), 3.05 (s, 2H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 161.8 (d, *J* = 244.4 Hz), 145.0, 142.6, 137.51 (d, *J* = 11.3 Hz), 136.6, 131.54 (d, *J* = 9.1 Hz), 128.9, 128.8, 128.5, 124.3, 123.75 (d, *J* = 3.2 Hz), 112.0, 111.1 (d, *J* = 21.5 Hz), 109.2 (d, *J* = 27.3 Hz), 40.2, 22.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}FNNaO^+$: 318.1265 $(M + Na)^+$, found: 318.1272.

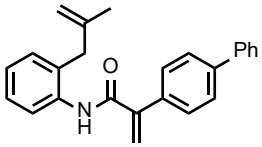


***N*-(5-chloro-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1h).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.51 (brs, 1H), 7.40 – 7.37 (m, 5H), 7.06 – 6.98 (m, 2H), 6.31 (s,

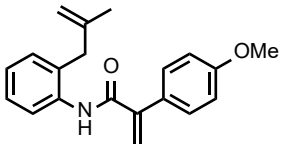
1H), 5.68 (d, J = 0.9 Hz, 1H), 4.45 (s, 1H), 4.01 (s, 1H), 3.01 (s, 2H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 144.9, 142.3, 137.3, 136.6, 133.0, 131.6, 128.9, 128.8, 128.5, 126.9, 124.6, 124.4, 122.1, 112.2, 40.4, 22.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}ClNNaO^+$: 334.0969 (M + Na)$^+$, found: 334.0963.



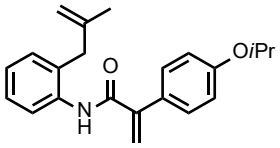
***N*-(2-(2-methylallyl)phenyl)-2-(*p*-tolyl)acrylamide (1i).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 7.54 (brs, 1H), 7.32 – 7.27 (m, 3H), 7.22 (d, J = 7.9 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.28 (s, 1H), 5.65 (d, J = 0.9 Hz, 1H), 4.48 (s, 1H), 4.07 (s, 1H), 3.09 (s, 2H), 2.40 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 145.2, 142.9, 138.7, 136.4, 134.0, 130.8, 129.5, 128.9, 128.4, 127.5, 124.7, 123.1, 122.4, 111.9, 40.9, 22.1, 21.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{21}NNaO^+$: 314.1515 (M + Na)$^+$, found: 314.1526.



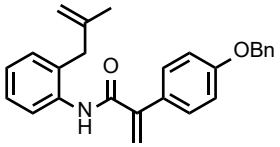
2-([1,1'-Biphenyl]-4-yl)-N-(2-(2-methylallyl)phenyl)acrylamide (1j). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 1H), 7.66 – 7.61 (m, 5H), 7.52 – 7.46 (m, 4H), 7.39 (t, J = 7.3 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.12 – 7.07 (m, 2H), 6.33 (s, 1H), 5.75 (s, 1H), 4.50 (s, 1H), 4.13 (s, 1H), 3.13 (s, 2H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 145.0, 143.0, 141.7, 140.3, 136.4, 135.7, 130.8, 128.9, 128.9, 127.7, 127.5, 127.0, 124.8, 123.5, 122.5, 111.9, 41.0, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{23}NNaO^+$: 376.1672 (M + Na)$^+$, found: 376.1673.



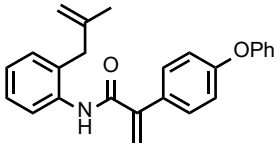
***N*-(4-methoxy-2-(2-methylallyl)phenyl)-2-phenylacrylamide (1k).** Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 7.58 (brs, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.11 – 7.06 (m, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.21 (s, 1H), 5.62 (d, J = 0.9 Hz, 1H), 4.53 (s, 1H), 4.14 (s, 1H), 3.85 (s, 3H), 3.11 (s, 2H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 160.0, 144.9, 143.0, 136.4, 130.8, 129.8, 129.2, 128.9, 127.5, 124.8, 122.4, 122.3, 114.2, 111.9, 55.4, 41.0, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{20}H_{22}NO_2^+$: 308.1645 (M + H)$^+$, found: 308.1648.



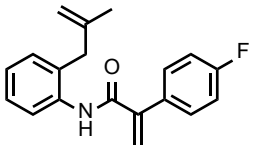
2-(4-Isopropoxyphenyl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1l). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.59 (brs, 1H), 7.36 – 7.27 (m, 3H), 7.13 – 7.05 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.20 (s, 1H), 5.62 (s, 1H), 4.59 (dt, *J* = 12.0, 6.0 Hz, 1H), 4.53 (s, 1H), 4.14 (s, 1H), 3.12 (s, 2H), 1.62 – 1.57 (m, 1H), 1.49 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 158.4, 144.9, 143.0, 136.4, 130.8, 129.8, 128.9, 128.8, 127.5, 124.7, 122.4, 122.2, 115.9, 112.0, 69.9, 41.0, 22.1, 22.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{22}H_{25}NNaO_2^+$: 358.1778 $(M + Na)^+$, found: 358.1765.



2-(4-(Benzyloxy)phenyl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1m). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.59 (brs, 1H), 7.46 – 7.28 (m, 8H), 7.12 – 7.07 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 5.63 (d, *J* = 0.7 Hz, 1H), 5.12 (s, 2H), 4.49 (s, 1H), 4.13 (s, 1H), 3.11 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 159.2, 144.8, 143.0, 136.6, 136.4, 130.8, 129.8, 129.4, 128.9, 128.6, 128.1, 127.5, 127.4, 124.7, 122.4, 122.3, 115.1, 112.0, 70.1, 41.0, 22.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{25}NNaO_2^+$: 406.1778 $(M + Na)^+$, found: 406.1783.

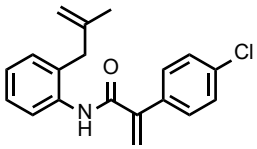


***N*-(2-(2-methylallyl)phenyl)-2-(4-phenoxyphenyl)acrylamide (1n).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.59 (brs, 1H), 7.40 – 7.36 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.01 (m, 7H), 6.23 (s, 1H), 5.68 (s, 1H), 4.60 (s, 1H), 4.21 (s, 1H), 3.15 (s, 2H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 158.1, 156.4, 144.7, 143.2, 136.3, 131.4, 130.8, 129.9, 129.9, 129.0, 127.5, 124.9, 123.9, 122.7, 122.6, 119.4, 118.5, 112.0, 41.1, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{23}NNaO_2^+$: 392.1621 $(M + Na)^+$, found: 392.1622.

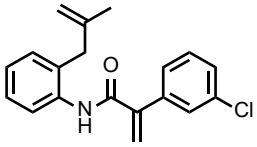


2-(4-Fuorophenyl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1p). Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.53 (brs, 1H), 7.43 – 7.39 (m, 2H), 7.32 – 7.28 (m,

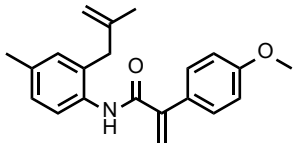
1H), 7.13 – 7.09 (m, 4H), 6.25 (s, 1H), 5.67 (s, 1H), 4.55 (s, 1H), 4.18 (s, 1H), 3.13 (s, 2H), 1.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 163.2 (d, J = 249.7 Hz), 144.7, 143.4, 136.5, 133.1 (d, J = 3.3 Hz), 131.1, 130.5 (d, J = 8.2 Hz), 129.2, 127.8, 125.2, 123.5, 122.8, 116.0 (d, J = 21.7 Hz), 112.2, 41.4, 22.4. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}FNNaO^+$: 318.1265 $(M + Na)^+$, found: 318.1274.



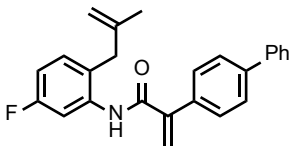
2-(4-Chlorophenyl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1q). Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.1 Hz, 1H), 7.51 (brs, 1H), 7.41 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.13 – 7.08 (m, 2H), 6.26 (s, 1H), 5.70 (s, 1H), 4.56 (s, 1H), 4.18 (s, 1H), 3.14 (s, 2H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 144.4, 143.2, 136.2, 135.2, 134.9, 130.9, 129.8, 129.0, 128.9, 127.6, 125.0, 123.5, 122.5, 111.9, 41.1, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}ClNNaO^+$: 334.0969 $(M + Na)^+$, found: 334.0974.



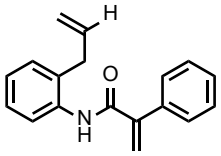
2-(3-Chlorophenyl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1r). Light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 8.1 Hz, 1H), 7.51 (brs, 1H), 7.42 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.12 – 7.09 (m, 2H), 6.31 (s, 1H), 5.72 (s, 1H), 4.56 (s, 1H), 4.17 (s, 1H), 3.14 (s, 2H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 144.2, 143.2, 138.6, 136.2, 134.8, 130.9, 130.1, 128.9, 128.8, 128.6, 127.6, 126.6, 125.0, 124.2, 122.5, 111.9, 41.1, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{18}ClNNaO^+$: 334.0969 $(M + Na)^+$, found: 334.0961.



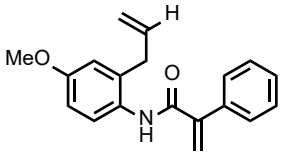
2-(4-Methoxyphenyl)-*N*-(4-methyl-2-(2-methylallyl)phenyl)acrylamide (1s). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 1H), 7.41 –7.37 (m, 5H),7.35 (brs, 1H), 6.83 (dd, J = 8.9, 2.7 Hz, 1H), 6.67 (d, J = 2.7 Hz, 1H), 6.31 (s, 1H), 5.67 (s, 1H), 4.49 (s, 1H), 4.11 (s, 1H), 3.78 (s, 3H), 3.07 (s, 2H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 156.7, 145.2, 143.0, 137.0, 131.5, 129.3, 128.8, 128.7, 128.5, 124.5, 123.5, 116.5, 112.0, 111.9, 55.4, 41.1, 22.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{24}NO_2^+$: 322.1802 $(M + H)^+$, found: 322.1817.



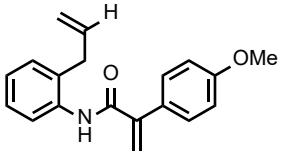
2-([1,1'-Biphenyl]-4-yl)-*N*-(5-fluoro-2-(2-methylallyl)phenyl)acrylamide (1t). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 11.1, 2.0 Hz, 1H), 7.66 – 7.61 (m, 5H), 7.49 – 7.46 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 8.1, 6.5 Hz, 1H), 6.78 (td, *J* = 8.2, 2.6 Hz, 1H), 6.34 (s, 1H), 5.76 (s, 1H), 4.49 (s, 1H), 4.09 (s, 1H), 3.06 (s, 2H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 161.8 (d, *J* = 244.7 Hz), 144.7, 142.7, 141.8, 140.2, 137.6 (d, *J* = 11.3 Hz), 135.5, 131.61 (d, *J* = 9.2 Hz), 129.0, 128.9, 127.8, 127.6, 127.0, 124.1, 123.7 (d, *J* = 3.0 Hz), 112.1, 111.2 (d, *J* = 21.5 Hz), 109.3 (d, *J* = 27.3 Hz), 40.4, 22.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{22}FNNaO^+$: 394.1578 $(M + Na)^+$, found: 394.1571.



***N*-(2-allylphenyl)-2-phenylacrylamide (1w).** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.27 (m, 7H), 7.13 – 7.08 (m, 2H), 6.34 (s, 1H), 5.70 (s, 1H), 5.66 – 5.56 (m, 1H), 4.75 (d, *J* = 9.9 Hz, 1H), 4.48 (d, *J* = 17.1 Hz, 1H), 3.15 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 145.2, 136.9, 136.0, 135.1, 130.2, 129.4, 128.8, 128.8, 128.6, 127.5, 125.1, 123.8, 122.7, 116.3, 36.6. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{17}NNaO^+$: 286.1202 $(M + Na)^+$, found: 286.1219.

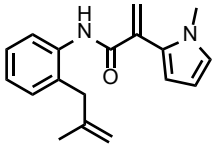


***N*-(2-allyl-4-methoxyphenyl)-2-phenylacrylamide (1x).** White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.30 (brs, 1H), 6.81 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 6.32 (d, *J* = 3.4 Hz, 1H), 5.67 (t, *J* = 2.2 Hz, 1H), 5.66 – 5.61 (m, 1H), 4.78 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.54 (dd, *J* = 17.2, 1.5 Hz, 1H), 3.78 (s, 3H), 3.14 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 157.0, 145.1 137.0, 135.1, 132.1, 128.9, 128.8, 128.7, 128.5, 124.8, 123.5, 116.3, 115.8, 112.0, 55.4, 36.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{19}NNaO_2^+$: 316.1308 $(M + Na)^+$, found: 316.1311.



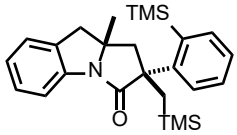
***N*-(2-allylphenyl)-2-(4-methoxyphenyl)acrylamide (1y)**. White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.53 (brs, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.13 (d, *J* = 6.3 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.22 (s, 1H), 5.70 –

5.66 (m, 1H), 5.64 (s, 1H), 4.81 (d, J = 9.3 Hz, 1H), 4.56 (d, J = 17.2 Hz, 1H), 3.85 (s, 3H), 3.18 (d, J = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 160.0, 144.7, 136.0, 135.2, 130.2, 129.8, 129.3, 129.1, 127.4, 125.0, 122.7, 122.3, 116.3, 114.2, 55.4, 36.6. HRMS (ESI-TOF) *m/z*: calcd for $C_{19}H_{19}NNaO_2^+$: 316.1308 $(M + Na)^+$, found: 316.1319.

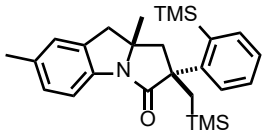


2-(1-Methyl-1*H*-pyrrol-2-yl)-*N*-(2-(2-methylallyl)phenyl)acrylamide (1aa). Light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 8.1 Hz, 1H), 7.75 (brs, 1H), 7.30 – 7.27 (m, 1H), 7.11 – 7.06 (m, 2H), 6.72 (t, J =1.8 Hz, 1H), 6.56 (d, J = 1.8 Hz, 1H), 6.24 (dd, J = 3.6, 1.7 Hz, 1H), 6.19 – 6.18 (m, 1H), 5.66 (d, J = 1.8 Hz, 1H), 4.58 (t, J =1.2 Hz, 1H), 4.10 (d, J = 0.5 Hz, 1H), 3.53 (s, 3H), 3.07 (s, 2H), 1.56 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 142.8, 136.2, 136.0, 130.8, 128.7, 128.3, 127.5, 127.2, 124.7, 124.3, 121.9, 111.6, 111.0, 108.2, 40.6, 34.3, 22.5. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{20}N_2NaO^+$: 303.1468 $(M + Na)^+$, found: 303.1481.

6. Characterization of the Products

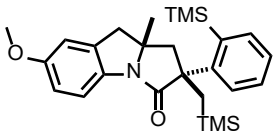


9a-Methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3a). Light yellow oil (33.5 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.5, 1.2 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.15 – 7.12 (m, 2H), 7.08 (t, J = 7.6 Hz, 2H), 2.77 (d, J = 15.1 Hz, 1H), 2.70 – 2.66 (m, 3H), 1.74 (d, J = 14.8 Hz, 1H), 1.66 (d, J = 14.8 Hz, 1H), 1.49 (s, 3H), 0.45 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 152.1, 140.3, 137.7, 137.5, 134.2, 128.2, 127.6, 126.1, 125.3, 125.2, 124.7, 117.1, 66.1, 57.4, 49.1, 44.4, 30.8, 28.5, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{35}NaNOSi_2^+$: 444.2149 $(M + Na)^+$, found: 444.2161.

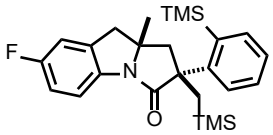


7,9a-Dimethyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3b). Light yellow oil (34.1 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.69 (m, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H),

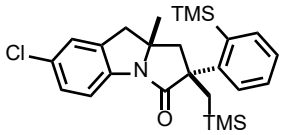
7.08 – 7.06 (m, 2H), 6.95 (s, 1H), 2.72 (d, *J* = 15.0 Hz, 1H), 2.65 (s, 2H), 2.61 (d, *J* = 15.0 Hz, 1H), 2.32 (s, 3H), 1.71 (d, *J* = 14.8 Hz, 1H), 1.64 (d, *J* = 14.8 Hz, 1H), 1.46 (s, 3H), 0.44 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 152.4, 138.0, 137.7, 137.5, 134.3, 134.3, 128.2, 128.0, 126.2, 126.0, 125.2, 116.8, 66.3, 57.4, 49.1, 44.4, 30.9, 28.5, 21.2, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaOSi_2^+$: 458.2306 $(M + Na)^+$, found: 458.2301.



7-Methoxy-9a-methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3c). Light yellow solid (36.0 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.09 – 7.05 (m, 1H), 6.78 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.72 (s, 1H), 3.78 (s, 3H), 2.71 (d, *J* = 15.2 Hz, 1H), 2.66 (d, *J* = 13.2 Hz, 1H), 2.62 (d, *J* = 13.2 Hz, 1H), 2.60 (d, *J* = 15.2 Hz, 1H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.63 (d, *J* = 14.8 Hz, 1H), 1.46 (s, 3H), 0.43 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 157.2, 152.4, 137.7, 137.5, 135.9, 134.0, 128.2, 126.2, 125.2, 117.6, 112.0, 111.7, 66.5, 57.3, 55.6, 48.9, 44.5, 30.8, 28.5, 3.9, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaO_2Si_2^+$: 474.2255 $(M + Na)^+$, found: 474.2254.

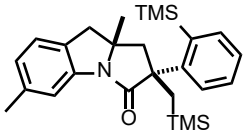


7-Fluoro-9a-methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3d). Light yellow oil (28.6 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.5, 4.7 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.13 – 7.11 (m, 1H), 7.08 – 7.05 (m, 1H), 6.95 (td, *J* = 8.9, 2.3 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 2.74 – 2.62 (m, 4H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.64 (d, *J* = 14.8 Hz, 1H), 1.47 (s, 3H), 0.43 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 160.2 (d, *J* = 242.5 Hz), 152.0, 137.8, 137.6, 136.5 (d, *J* = 2.1 Hz), 136.3 (d, *J* = 8.5 Hz), 128.2, 126.0, 125.4, 117.9 (d, *J* = 8.8 Hz), 113.9 (d, *J* = 23.4 Hz), 112.8 (d, *J* = 24.2 Hz), 66.7, 57.3, 48.7, 44.4, 30.8, 28.4, 3.9, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}FNNaOSi_2^+$: 462.2055 $(M + Na)^+$, found: 462.2062.

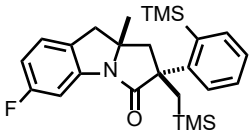


7-Chloro-9a-methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3e). Light yellow oil (25.5 mg, 56%). ^{1}H NMR (600 MHz,

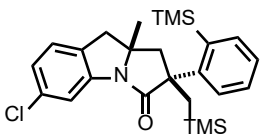
$CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.12 (s, 1H), 7.09 – 7.06 (m, 1H), 2.72 (d, *J* = 15.4 Hz, 1H), 2.69 (d, *J* = 13.2 Hz, 1H), 2.66 – 2.63 (m, 2H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.64 (d, *J* = 14.8 Hz, 1H), 1.47 (s, 3H), 0.43 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 151.9, 139.1, 137.8, 137.7, 136.2, 129.8, 128.3, 127.6, 125.9, 125.6, 125.4, 118.0, 66.4, 57.4, 48.8, 44.2, 30.7, 28.5, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}ClNNaOSi_2^+$: 478.1760 (M + Na)$^+$, found: 478.1755.



6,9a-Dimethyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3f). Light yellow solid (31.5 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.08 (td, *J* = 7.9, 1.4 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 2.72 – 2.61 (m, 4H), 2.39 (s, 3H), 1.73 (d, *J* = 14.8 Hz, 1H), 1.63 (d, *J* = 14.8 Hz, 1H), 1.47 (s, 3H), 0.45 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 152.4, 140.4, 137.6, 137.5, 137.5, 131.2, 128.2, 126.2, 125.3, 125.2, 124.9, 117.8, 66.4, 57.6, 49.3, 44.1, 30.9, 28.5, 21.5, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaOSi_2^+$: 458.2306 (M + Na)$^+$, found: 458.2319.

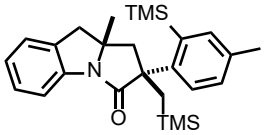


6-Fluoro-9a-methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3g). Light yellow solid (26.5 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.39 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.09 (td, *J* = 8.0, 1.4 Hz, 1H), 7.05 (dd, *J* = 7.9, 5.5 Hz, 1H), 6.76 (td, *J* = 9.1, 2.4 Hz, 1H), 2.72 – 2.64 (m, 4H), 1.72 (d, *J* = 14.8 Hz, 1H), 1.65 (d, *J* = 14.8 Hz, 1H), 1.49 (s, 3H), 0.44 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 162.5 (d, *J* = 244.0 Hz, 1H), 151.7, 141.5 (d, *J* = 12.0 Hz), 137.9, 137.6, 129.4 (d, *J* = 2.7 Hz), 128.2, 126.0, 125.70 (d, *J* = 9.6 Hz), 125.4, 111.1 (d, *J* = 22.7 Hz), 105.4 (d, *J* = 26.6 Hz), 66.9, 57.4, 49.1, 43.9, 30.7, 28.5, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}FNNaOSi_2^+$: 462.2055 (M + Na)$^+$, found: 462.2065.

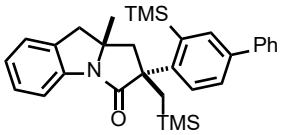


6-Chloro-9a-methyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-

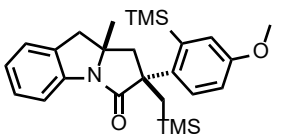
pyrrolo[1,2-*a*]indol-3(2*H*)-one (3h). Light yellow solid (20.5 mg, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.66 (s, 1H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.14 (t, *J* = 6.9 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.04 (s, 2H), 2.71 – 2.63 (m, 4H), 1.71 (d, *J* = 14.8 Hz, 1H), 1.64 (d, *J* = 14.8 Hz, 1H), 1.48 (s, 3H), 0.44 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 151.8, 141.4, 137.8, 137.6, 133.1, 132.7, 128.3, 126.0, 126.0, 125.4, 124.7, 117.6, 66.6, 57.4, 49.0, 44.0, 30.8, 28.5, 3.9, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}ClNNaOSi_2^+$:478.1760 (M + Na)$^+$, found: 478.1775.



9a-Methyl-2-(4-methyl-2-(trimethylsilyl)phenyl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3i). Light yellow oil (26.5 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.48 (s, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.13 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.66 – 2.63 (m, 3H), 2.25 (s, 3H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.62 (d, *J* = 14.8 Hz, 1H), 1.46 (s, 3H), 0.43 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 149.5, 140.4, 138.4, 137.3, 134.3, 128.9, 127.6, 126.1, 125.3, 124.6, 117.1, 66.1, 57.2, 49.1, 44.3, 30.9, 28.5, 20.9, 3.9, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaOSi_2^+$: 458.2306 (M + Na)$^+$, found: 458.2319.

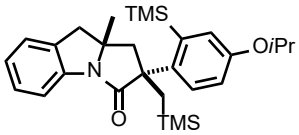


9a-Methyl-2-(3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3j). Light yellow solid (37.3 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.81 (d, *J* = 15.1 Hz, 1H), 2.74 – 2.68 (m, 3H), 1.76 (d, *J* = 14.8 Hz, 1H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.50 (s, 3H), 0.50 (s, 9H), -001 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 151.4, 140.9, 140.3, 138.3, 137.6, 136.4, 134.2, 128.7, 127.6, 127.1, 126.9, 126.8, 126.6, 125.3, 124.7, 117.2, 66.2, 57.2, 49.0, 44.5, 30.8, 28.5, 4.0, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{31}H_{39}NNaOSi_2^+$: 520.2462 (M + Na)$^+$, found: 520.2472.

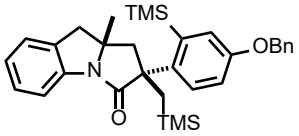


2-(4-Methoxy-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1

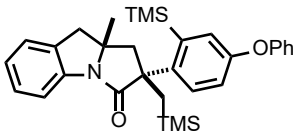
***H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3k).** Light yellow oil (26.2 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 10.3, 7.5 Hz, 3H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.61 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.76 (s, 3H), 2.79 (d, *J* = 15.0 Hz, 1H), 2.71 – 2.68 (m, 3H), 1.72 (d, *J* = 14.8 Hz, 1H), 1.66 (d, *J* = 14.8 Hz, 1H), 1.50 (s, 3H), 0.47 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 156.4, 144.4, 140.4, 139.5, 134.3, 127.6, 127.3, 125.3, 124.6, 124.5, 117.1, 111.5, 66.1, 56.8, 55.0, 49.2, 44.4, 31.0, 28.4, 3.9, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaO_2Si_2^+$: 474.2255 $(M + Na)^+$, found: 474.2266.



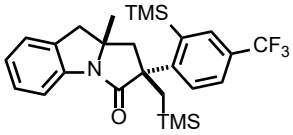
2-(4-Isopropoxy-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3l). Light yellow oil (34.9 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.47 – 4.42 (m, 1H), 2.77 (d, *J* = 15.1 Hz, 1H), 2.66 – 2.61 (m, 3H), 1.68 (d, *J* = 14.8 Hz, 1H), 1.62 (d, *J* = 14.8 Hz, 1H), 1.46 (s, 3H), 1.28 (d, *J* = 4.2 Hz, 3H), 1.27 (d, *J* = 4.2 Hz, 3H), 0.43 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 154.7, 144.2, 140.4, 139.4, 134.3, 127.5, 127.3, 126.2, 125.3, 124.6, 117.1, 113.9, 69.6, 66.1, 56.8, 49.2, 44.4, 30.9, 28.4, 22.0, 21.9, 3.9, 0.2. HRMS (ESI-TOF) *m/z*: calcd for HRMS (ESI-TOF) *m/z*: calcd for $C_{28}H_{41}NNaO_2Si_2^+$: 502.2568 $(M + Na)^+$, found: 502.2590.



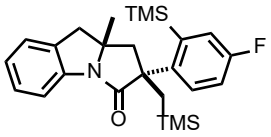
2-(4-(Benzyloxy)-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3m). Light yellow oil (35.2 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.26 (m, 5H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.69 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.02 (s, 2H), 2.80 (d, *J* = 15.1 Hz, 1H), 2.70 (d, *J* = 15.1 Hz, 1H), 2.68 (s, 2H), 1.73 (d, *J* = 14.8 Hz, 1H), 1.66 (d, *J* = 14.8 Hz, 1H), 1.51 (s, 3H), 0.46 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 155.7, 144.6, 140.4, 139.6, 137.0, 134.2, 128.5, 127.9, 127.5, 127.3, 125.3, 125.2, 124.6, 117.1, 112.8, 69.8, 66.0, 56.8, 49.2, 44.4, 30.9, 28.4, 3.8, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{32}H_{41}NNaO_2Si_2^+$: 550.2568 $(M + Na)^+$, found: 550.2582.



9a-Methyl-2-(4-phenoxy-2-(trimethylsilyl)phenyl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3n). Light yellow oil (37.3 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 2.8 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.96 – 6.92 (m, 2H), 6.70 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.82 (d, *J* = 15.1 Hz, 1H), 2.72 (d, *J* = 15.1 Hz, 1H), 2.68 (s, 2H), 1.73 (d, *J* = 14.8 Hz, 1H), 1.68 (d, *J* = 14.8 Hz, 1H), 1.50 (s, 3H), 0.42 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 157.3, 153.9, 146.9, 140.8, 140.2, 134.1, 129.6, 128.2, 127.7, 127.6, 125.3, 124.7, 122.8, 118.3, 118.0, 117.1, 66.0, 56.8, 49.2, 44.8, 31.0, 28.3, 3.8, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{31}H_{39}NNaO_2Si_2^+$: 536.2412 $(M + Na)^+$, found: 536.2432.

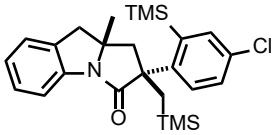


9a-Methyl-2-(4-(trifluoromethyl)-2-(trimethylsilyl)phenyl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3o). Light yellow oil (14.9 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.78 – 2.71 (m, 3H), 2.62 (d, *J* = 13.1 Hz, 1H), 1.72 (d, *J* = 14.8 Hz, 1H), 1.67 (d, *J* = 14.8 Hz, 1H), 1.51 (s, 3H), 0.47 (s, 9H), -0.06 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 155.8, 139.9, 139.8, 134.0, 133.8 (q, *J* = 3.6 Hz, 1H), 127.7, 127.4 (q, *J* = 36.4 Hz), 126.5, 125.4, 125.0 (d, *J* = 3.8 Hz), 124.9, 124.3 (q, *J* = 272.3 Hz), 117.1, 66.1, 57.4, 49.0, 44.8, 30.8, 28.3, 3.8, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{34}F_3NNaOSi_2^+$: 512.2023 $(M + Na)^+$, found: 512.2033.

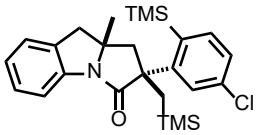


2-(4-Fluoro-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3p). Light yellow solid (25.5 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 10.3, 2.9 Hz, 1H), 7.31 (dd, *J* = 8.9, 5.6 Hz, 1H), 7.24 – 7.23 (m, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.06 (td, *J* = 7.4, 0.5 Hz, 1H), 6.76 – 6.72 (m, 1H), 2.77 – 2.60 (m, 4H), 1.68 (d, *J* = 14.8 Hz, 1H), 1.62 (d, *J* = 14.8 Hz, 1H), 1.47 (s, 3H), 0.43 (s, 9H), -0.08 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 160.3 (d, *J* = 247.3 Hz), 147.5 (d, *J* = 3.1 Hz), 141.6 (d, *J* = 2.8 Hz), 140.0, 134.1, 128.03 (d, *J* = 6.7 Hz), 127.6, 125.3, 124.8, 123.8 (d,

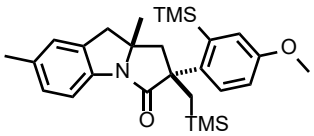
J = 19.3 Hz), 117.1, 114.32 (d, *J* = 19.9 Hz), 66.0, 56.8, 49.3, 44.8, 31.1, 28.3, 3.8, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}FNNaOSi_2^+$: 462.2055 $(M + Na)^+$, found: 462.2076.



2-(4-Chloro-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3q). Light yellow solid (30.0 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.09 – 7.03 (m, 2H), 2.76 (d, *J* = 15.1 Hz, 1H), 2.70 (d, *J* = 15.1 Hz, 1H), 2.67 (d, *J* = 13.1 Hz, 1H), 2.60 (d, *J* = 13.1 Hz, 1H), 1.69 (d, *J* = 14.8 Hz, 1H), 1.62 (d, *J* = 14.8 Hz, 1H), 1.49 (s, 3H), 0.45 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.0, 150.3, 141.2, 140.0, 137.0, 134.1, 131.6, 127.9, 127.9, 127.7, 125.4, 124.8, 117.1, 66.0, 57.0, 49.2, 44.7, 30.9, 28.3, 3.8, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}ClNNaOSi_2^+$: 478.1760 $(M + Na)^+$, found: 478.1776.

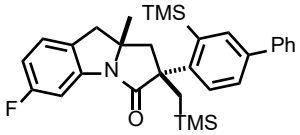


2-(5-Chloro-2-(trimethylsilyl)phenyl)-9a-methyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3r). Light yellow oil (28.6 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.77 (d, *J* = 15.2 Hz, 1H), 2.72 (d, *J* = 12.9 Hz, 1H), 2.60 (d, *J* = 12.9 Hz, 1H), 1.72 (d, *J* = 14.8 Hz, 1H), 1.65 (d, *J* = 14.8 Hz, 1H), 1.52 (s, 3H), 0.42 (s, 9H), -0.08 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 153.3, 139.7, 138.7, 136.8, 134.3, 134.0, 127.7, 126.7, 125.3, 125.3, 124.7, 117.0, 65.7, 56.9, 49.5, 45.3, 31.0, 28.1, 4.0, 0.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{34}ClNNaOSi_2^+$: 478.1760 $(M + Na)^+$, found: 478.1776.

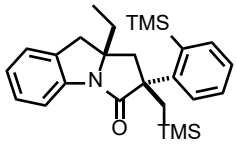


2-(4-Methoxy-2-(trimethylsilyl)phenyl)-7,9a-dimethyl-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3s). Light yellow solid (32.5 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.57 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.73 (s, 3H), 2.71 (d, *J* = 15.0 Hz, 1H), 2.62 – 2.59 (m, 3H), 2.31 (s, 3H), 1.67 (d, *J* = 14.8 Hz, 1H), 1.61 (d, *J* = 4.3 Hz, 1H), 1.45 (s, 3H), 0.43 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 156.4, 144.6, 139.4, 138.1, 134.4, 134.3, 127.9, 127.4,

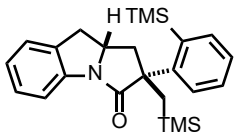
126.0, 124.5, 116.8, 111.5, 66.2, 56.8, 55.0, 49.3, 44.3, 31.0, 28.4, 21.2, 3.8, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{27}H_{39}NNaO_2Si_2^+$: 488.2412 $(M + Na)^+$, found: 488.2427.



6-Fluoro-9a-methyl-2-(3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3t). Light yellow solid (27.2 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.8 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.36 – 7.32 (m, 3H), 7.07 (dd, *J* = 8.0, 5.4 Hz, 1H), 6.79 – 6.76 (m, 1H), 2.77 – 2.66 (m, 4H), 1.75 (d, *J* = 14.8 Hz, 1H), 1.70 (d, *J* = 14.8 Hz, 1H), 1.52 (s, 3H), 0.50 (s, 9H), -0.02 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 162.5 (d, *J* = 244.2 Hz), 151.0, 141.5 (d, *J* = 12.0 Hz), 140.8, 138.4, 137.7, 136.4, 129.4 (d, *J* = 2.7 Hz), 128.7, 127.1, 126.9, 126.8, 126.5, 125.7 (d, *J* = 9.5 Hz), 111.1 (d, *J* = 22.3 Hz), 105.4 (d, *J* = 26.4 Hz), 66.9, 57.1, 49.0, 43.9, 30.7, 28.4, 4.0, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{31}H_{38}FNNaOSi_2^+$: 538.2368 $(M + Na)^+$, found: 538.2360.

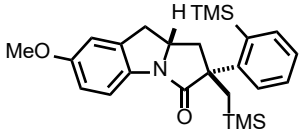


9a-Ethyl-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3u). Light yellow oil (29.6 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.13 – 7.09 (m, 2H), 7.07 – 7.02 (m, 2H), 2.78 (d, *J* = 15.3 Hz, 1H), 2.69 (d, *J* = 13.3 Hz, 1H), 2.59 (d, *J* = 15.3 Hz, 1H), 2.54 (d, *J* = 13.3 Hz, 1H), 1.84 – 1.78 (m, 1H), 1.72 – 1.66 (m, 2H), 1.58 (d, *J* = 14.8 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.45 (s, 9H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2, 152.6, 141.2, 137.6, 137.4, 134.3, 128.3, 127.5, 126.1, 125.2, 125.0, 124.7, 117.0, 69.5, 57.3, 46.4, 40.6, 33.2, 31.1, 8.5, 3.8, 0.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{37}NNaOSi_2^+$: 458.2306 $(M + Na)^+$, found: 458.2318.

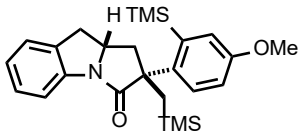


2-((Trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3w). Light yellow solid (21.0 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.72 (dd, *J* = 8.6, 5.7 Hz, 1H), 3.23 (dd, *J* = 15.5, 8.4 Hz, 1H), 2.90 (dd, *J* = 15.5, 10.0 Hz, 1H), 2.81 (dd, *J* = 11.9, 5.6 Hz, 1H), 2.43 – 2.38 (m, 1H), 1.72 (d, *J* = 14.9 Hz, 1H), 1.59

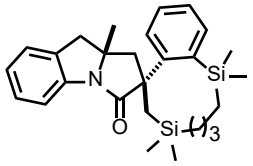
(d, J = 14.9 Hz, 1H), 0.39 (s, 9H), -0.14 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 148.2, 140.1, 140.0, 137.1, 134.1, 127.9, 127.7, 126.8, 125.5, 125.1, 124.0, 115.3, 58.6, 57.3, 45.1, 35.8, 26.6, 4.1, 0. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{33}NNaOSi_2^+$: 430.1993 $(M + Na)^+$, found: 430.2002.



7-Methoxy-2-((trimethylsilyl)methyl)-2-(2-(trimethylsilyl)phenyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3x). Light yellow oil (24.0 mg, 55%, dr: 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, J = 7.5, 1.6 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 7.43 (dd, J = 7.9, 0.9 Hz, 1H), 7.23 (dd, J = 7.8, 1.6 Hz, 1H), 7.20 (dd, J = 7.4, 1.2 Hz, 1H), 6.77 (s, 1H), 6.74 (dd, J = 8.5, 2.4 Hz, 1H), 4.73 – 4.68 (m, 1H), 3.78 (s, 3H), 3.18 (dd, J = 15.6, 8.3 Hz, 1H), 2.90 – 2.86 (m, 1H), 2.79 (dd, J = 12.0, 5.7 Hz, 1H), 2.38 (dd, J = 11.7, 9.8 Hz, 1H), 1.71 (d, J = 14.9 Hz, 1H), 1.58 (d, J = 15.0 Hz, 1H), 0.39 (s, 9H), -0.14 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 156.7, 148.5, 140.0, 137.1, 135.7, 133.6, 127.9, 126.9, 125.5, 115.6, 112.0, 111.8, 59.0, 57.2, 55.7, 45.0, 36.1, 26.8, 4.0, 0.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{35}NNaO_2Si_2^+$: 460.2099 $(M + Na)^+$, found: 460.2101.



2-(4-Methoxy-2-(trimethylsilyl)phenyl)-2-((trimethylsilyl)methyl)-9,9a-dihydro-1*H*-pyrrolo[1,2-*a*]indol-3(2*H*)-one (3y). Light yellow oil (21.0 mg, 50%, dr: 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 2.9 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.03 – 7.01 (m, 1H), 6.76 (dd, J = 8.8, 2.9 Hz, 1H), 4.73 – 4.68 (m, 1H), 3.79 (s, 3H), 3.22 (dd, J = 15.5, 8.4 Hz, 1H), 2.90 (dd, J = 15.5, 10.0 Hz, 1H), 2.78 (dd, J = 11.9, 5.6 Hz, 1H), 2.40 – 2.34 (m, 1H), 1.69 (d, J = 14.9 Hz, 1H), 1.56 (d, J = 14.9 Hz, 1H), 0.39 (s, 9H), -0.12 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 156.7, 141.7, 140.5 140.0, 134.1, 128.1, 127.6, 125.1, 124.0, 123.8, 115.3, 111.8, 58.5, 56.7, 55.0, 45.4, 35.8, 26.7, 4.0, 0.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{35}NNaO_2Si_2^+$: 460.2099 $(M + Na)^+$, found: 460.2096.



1,1,6,6,9a'-Pentamethyl-2,3,4,5,6,7,9',9a'-octahydro-1*H*-spiro[benzo[*b*][1,6]disilecine-8,2'-pyrrolo[1,2-*a*]indol]-3'(1'*H*)-one (5a). Light yellow solid (22.4 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.09 – 7.07 (m, 3H), 6.95 – 6.92 (m,

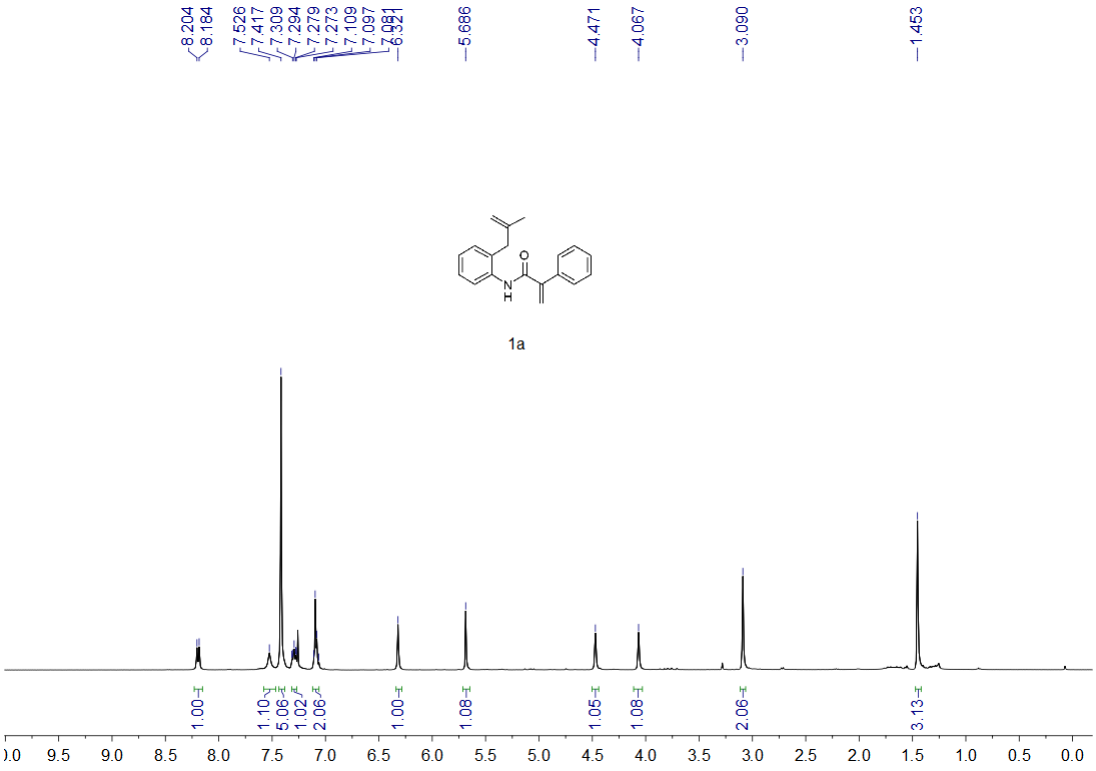
1H), 6.87 (d, *J* = 7.9 Hz, 1H), 2.75 (d, *J* = 13.2 Hz, 1H), 2.72 (d, *J* = 13.2 Hz, 1H), 2.56 (d, *J* = 15.0 Hz, 1H), 2.49 (d, *J* = 15.0 Hz, 1H), 2.05 (d, *J* = 15.5 Hz, 1H), 1.69 – 1.63 (m, 3H), 1.55 – 1.50 (m, 1H), 1.44 (d, *J* = 15.5 Hz, 1H), 1.42 (s, 3H), 1.34 – 1.25 (m, 1H), 0.95 – 0.87 (m, 1H), 0.76 – 0.70 (m, 1H), 0.61 (dt, *J* = 15.2, 4.3 Hz, 1H), 0.41 (s, 3H), 0.38 (s, 3H), 0.11 (s, 3H), -0.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 154.1, 141.2, 138.1, 136.8, 134.3, 128.1, 127.6, 125.6, 125.3, 125.2, 124.9, 117.5, 66.5, 58.6, 48.6, 42.5, 30.6, 29.2, 24.7, 23.5, 13.9, 13.4, 4.0, 0.6, -1.2, -2.2. HRMS (ESI-TOF) *m/z*: calcd for $C_{27}H_{38}NOSi_2^+$: 448.2486 $(M + H)^+$, found: 448.2491.

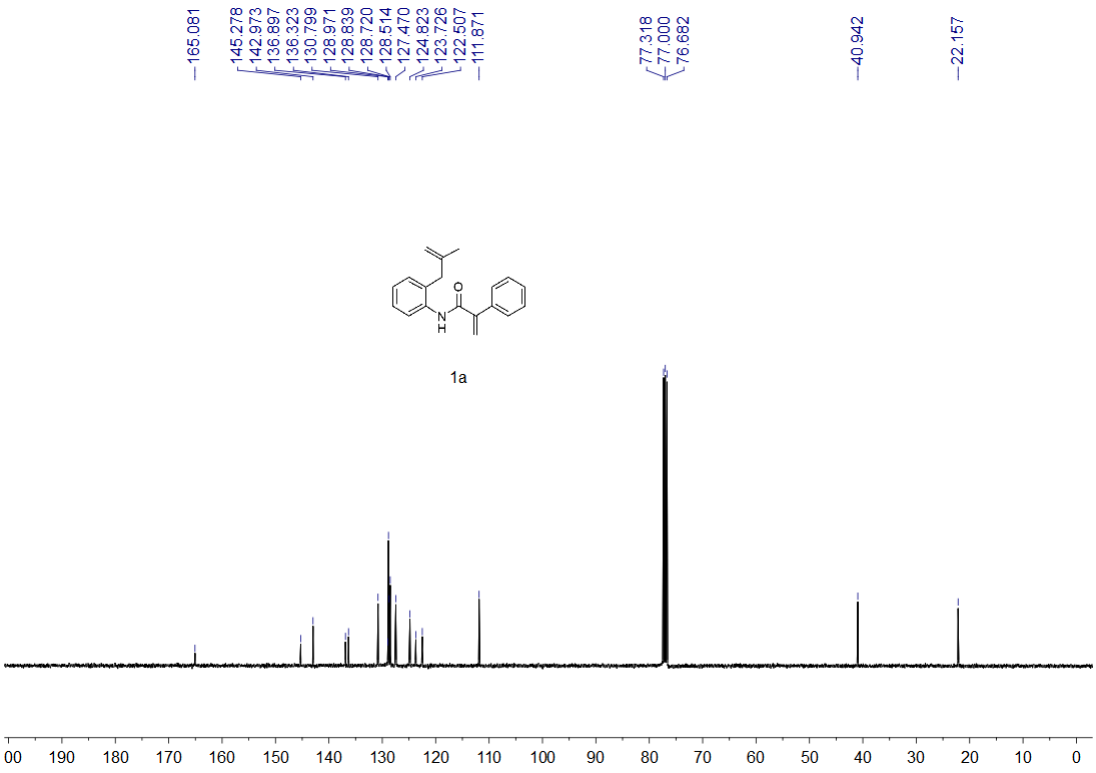
7. References

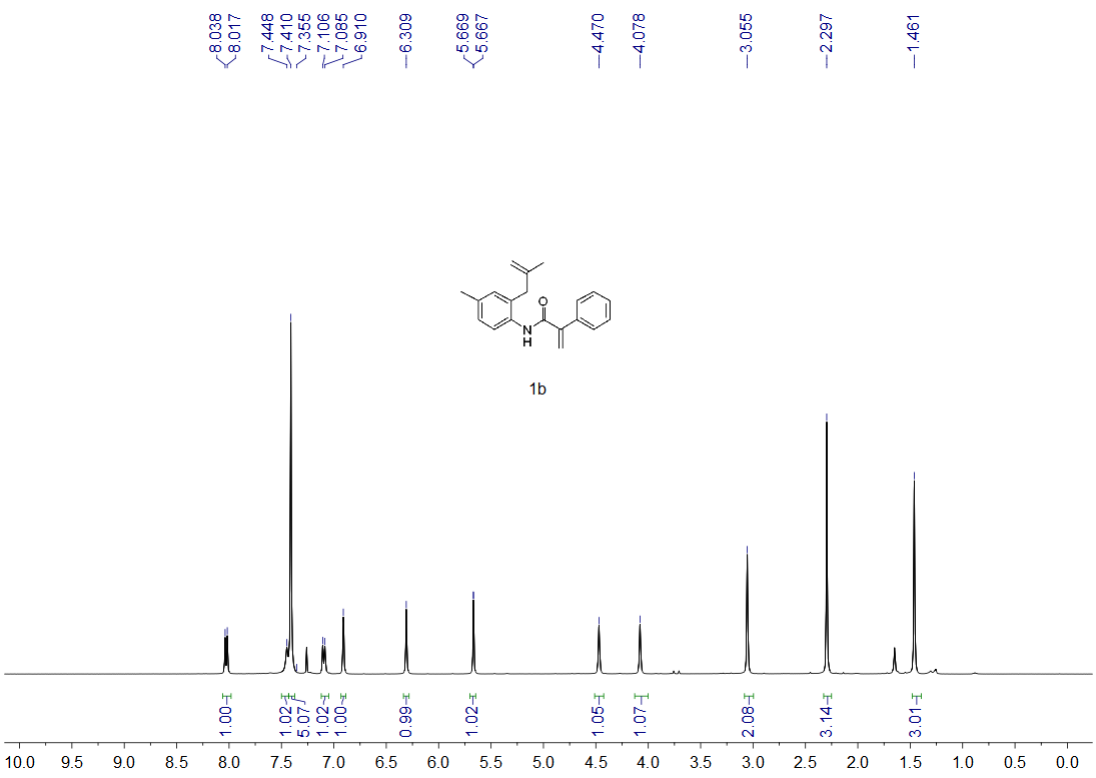
[1] Y. Cao, H. Zhao, D. Zhang-Negrerie, Y. Du and K. Zhao, *Adv. Synth. Catal.*, 2016, **358**, 3610.
[2] W. Du, Q. Gu, Z. Li and D. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 1130.
[3] D. Orain and J.-C. Guillemin, *J. Org. Chem*., 1999, **64**, 3563.

8. NMR Spectra

8.1 NMR Spectra of the Substrates



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1.02
5.07
1.02
1.00
0.99
1.02
1.05
1.07
2.08
3.14
3.01
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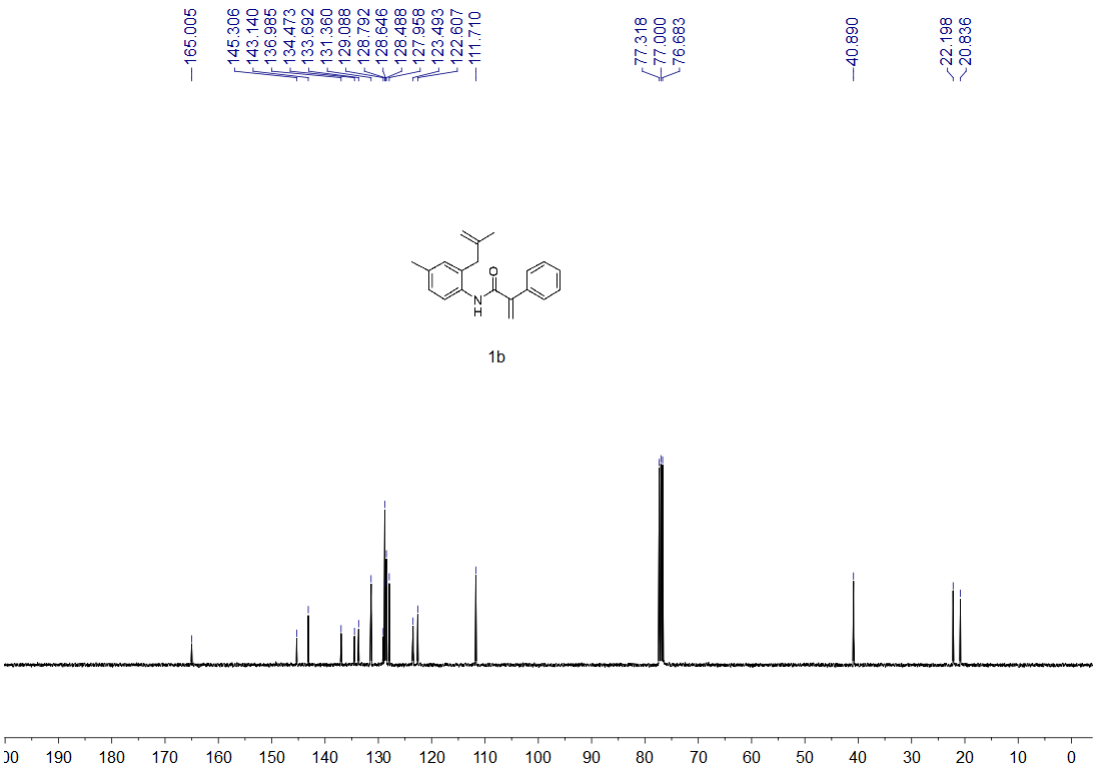
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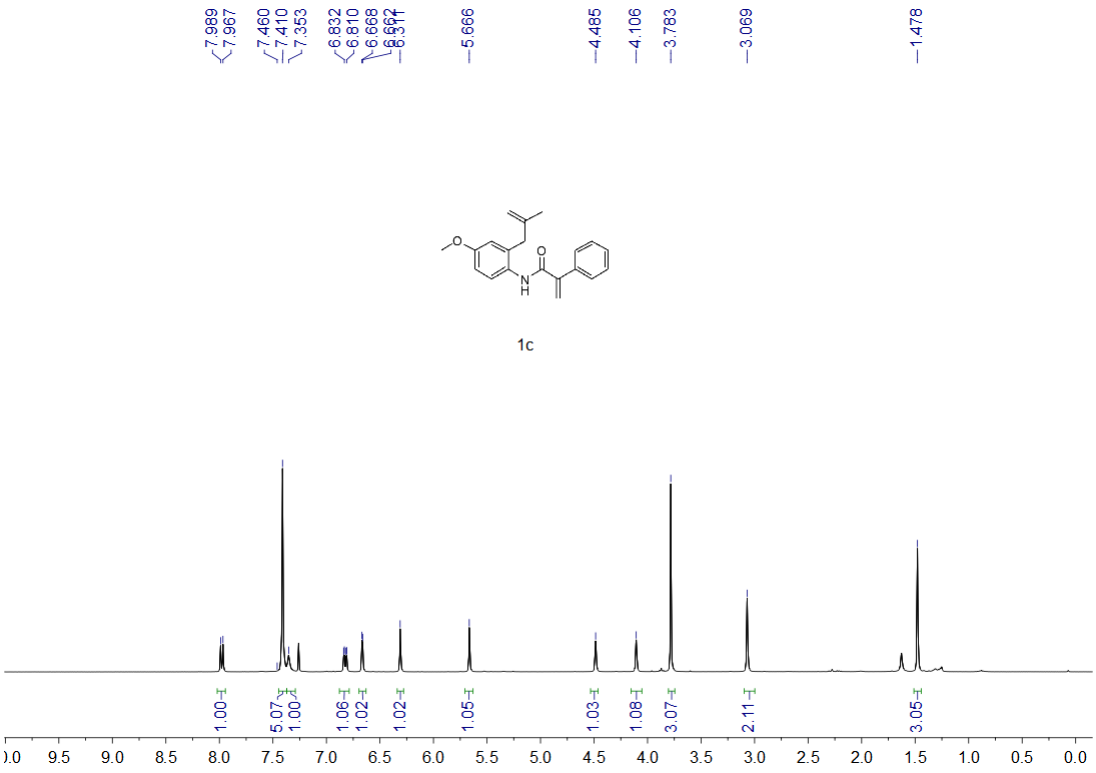
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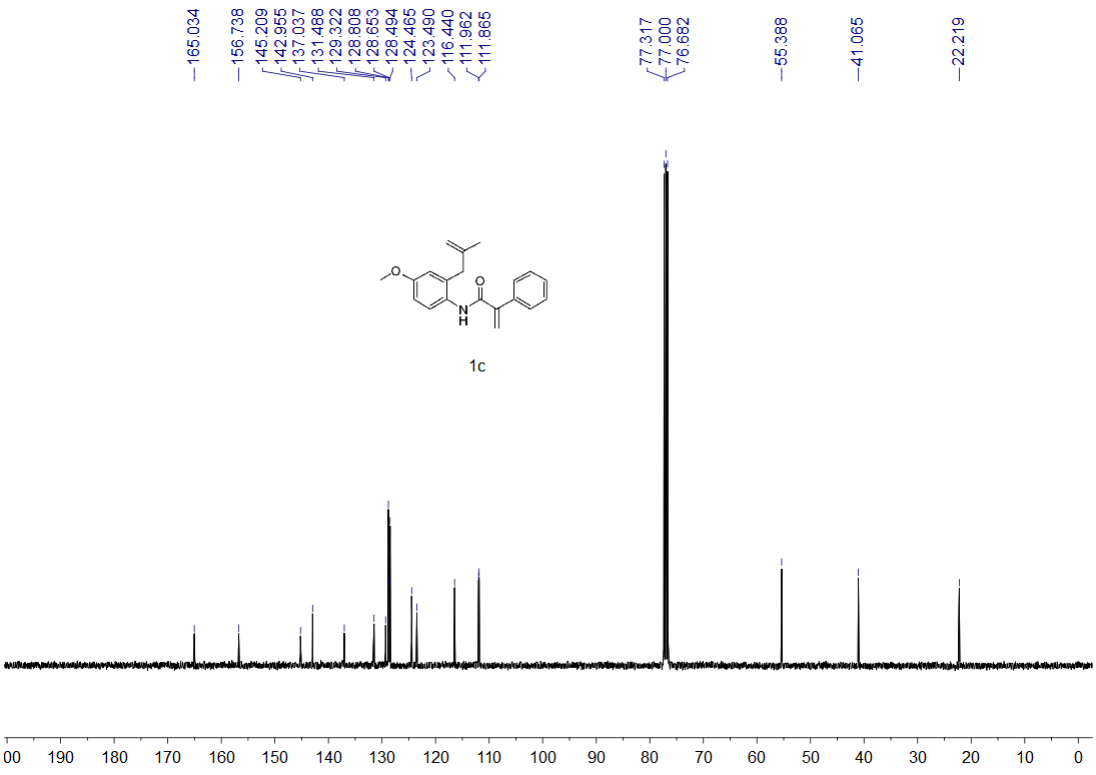
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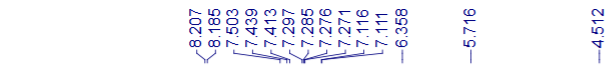
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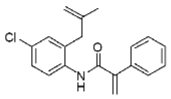
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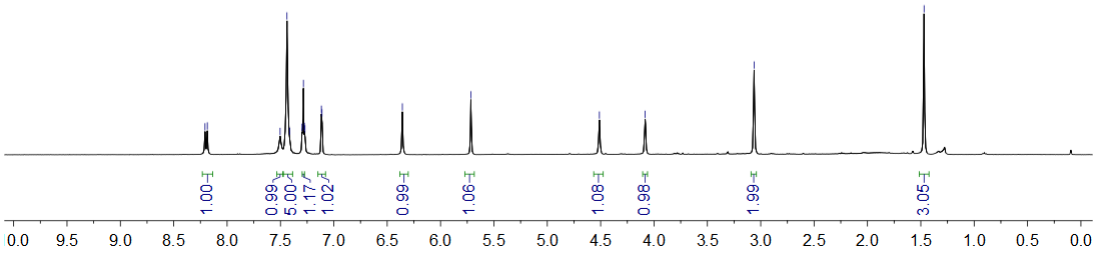
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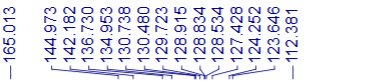
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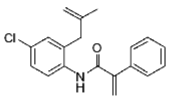
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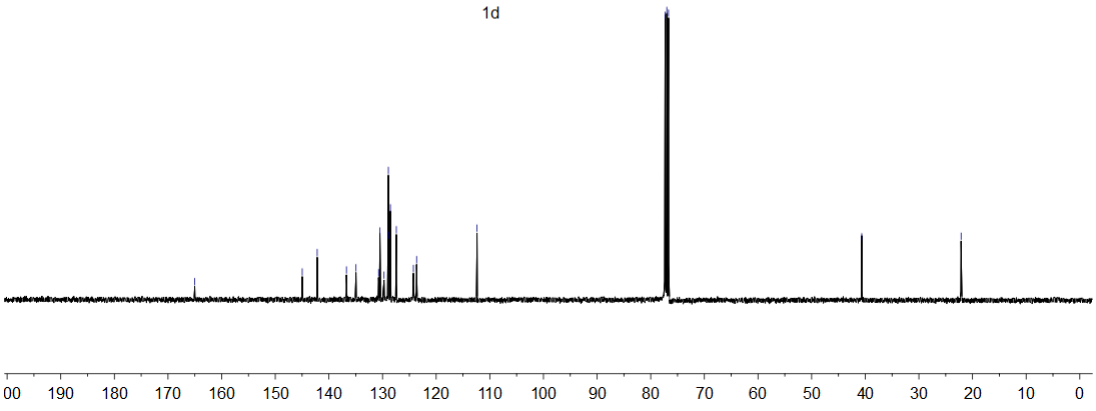
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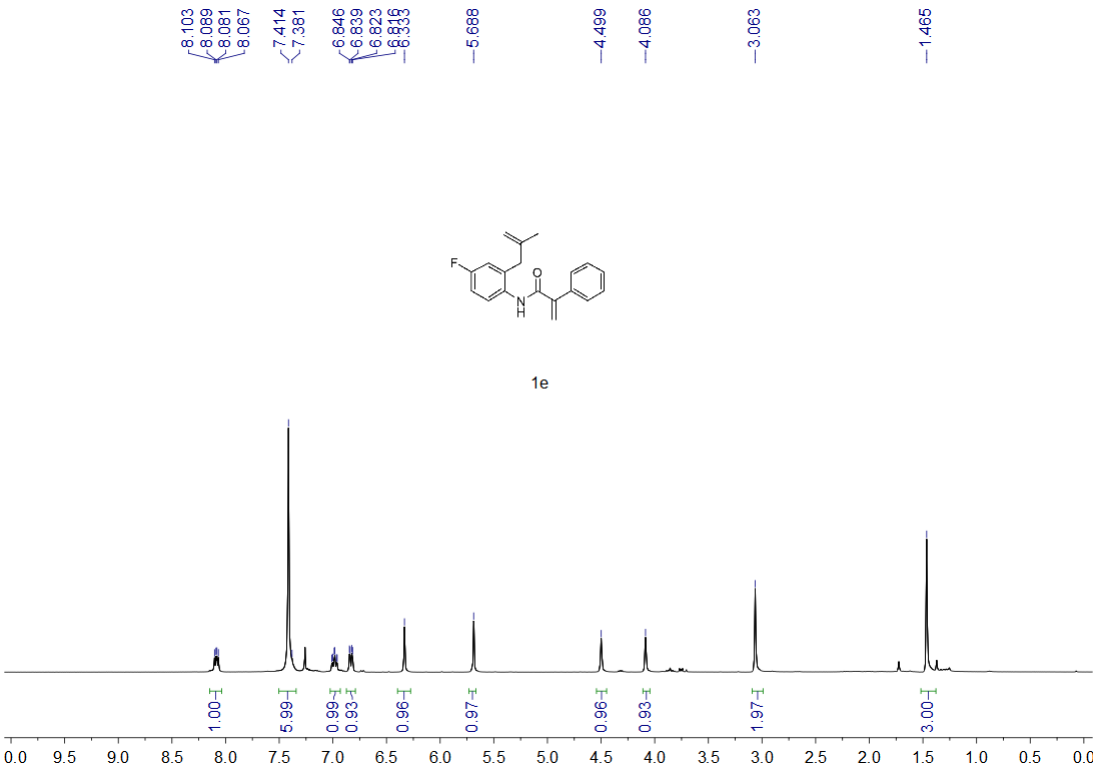
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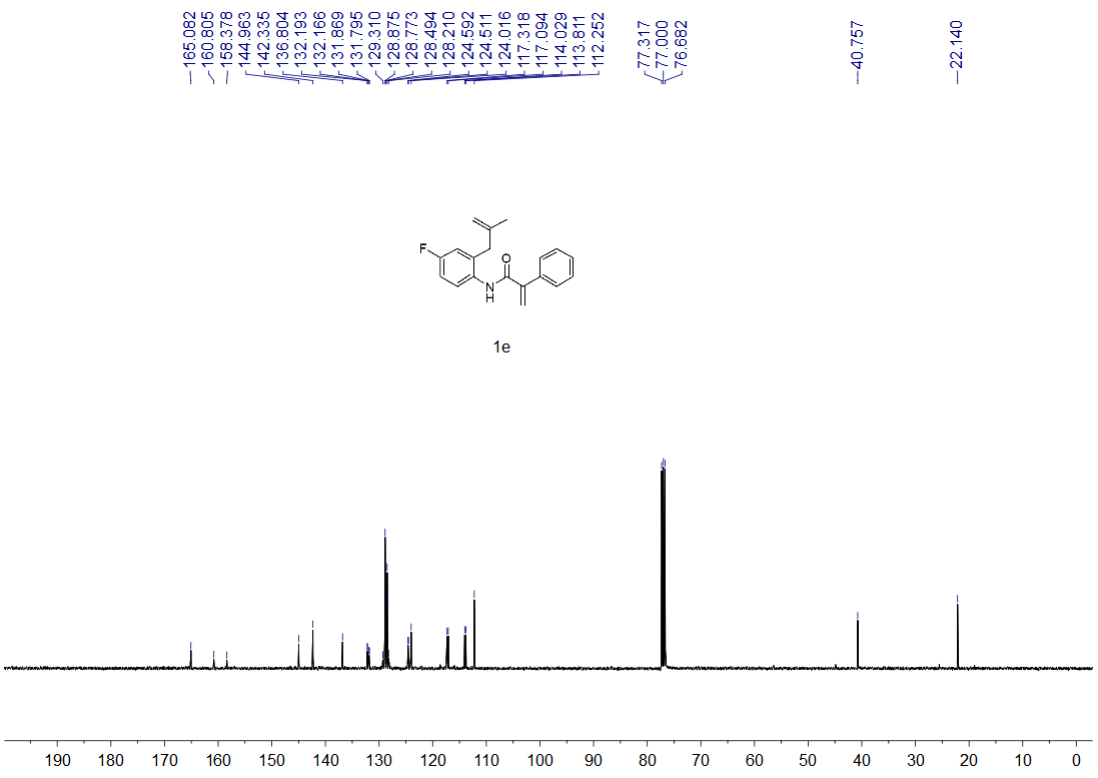
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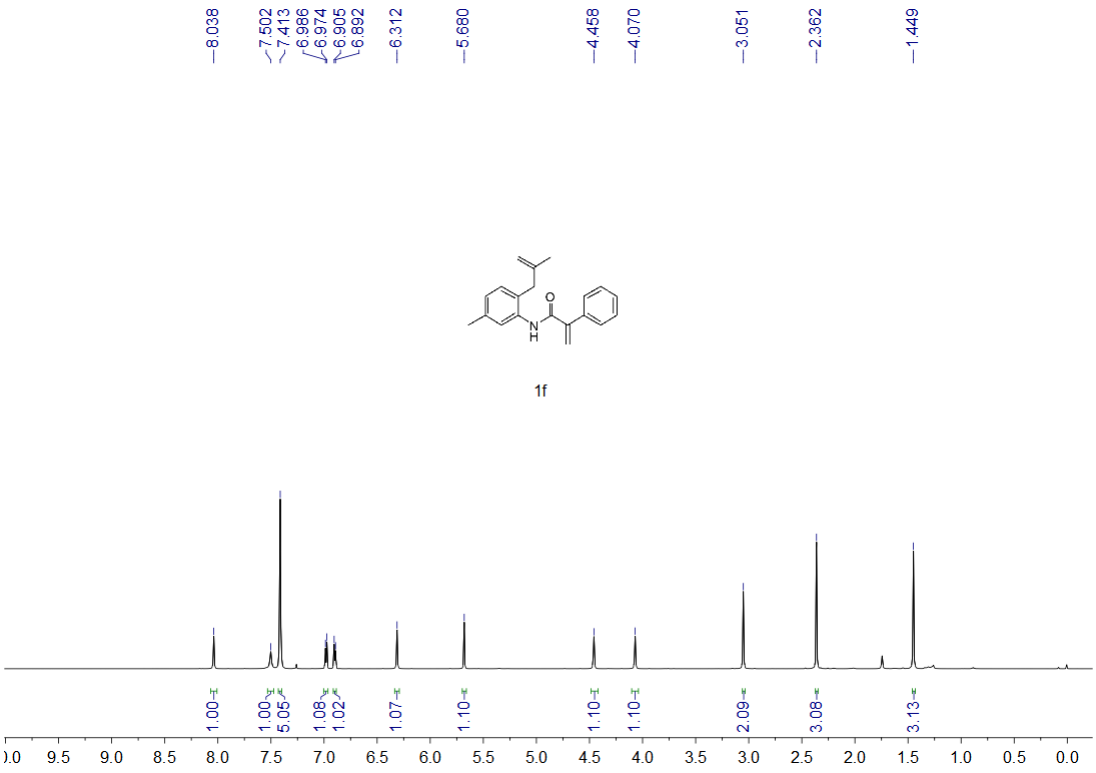
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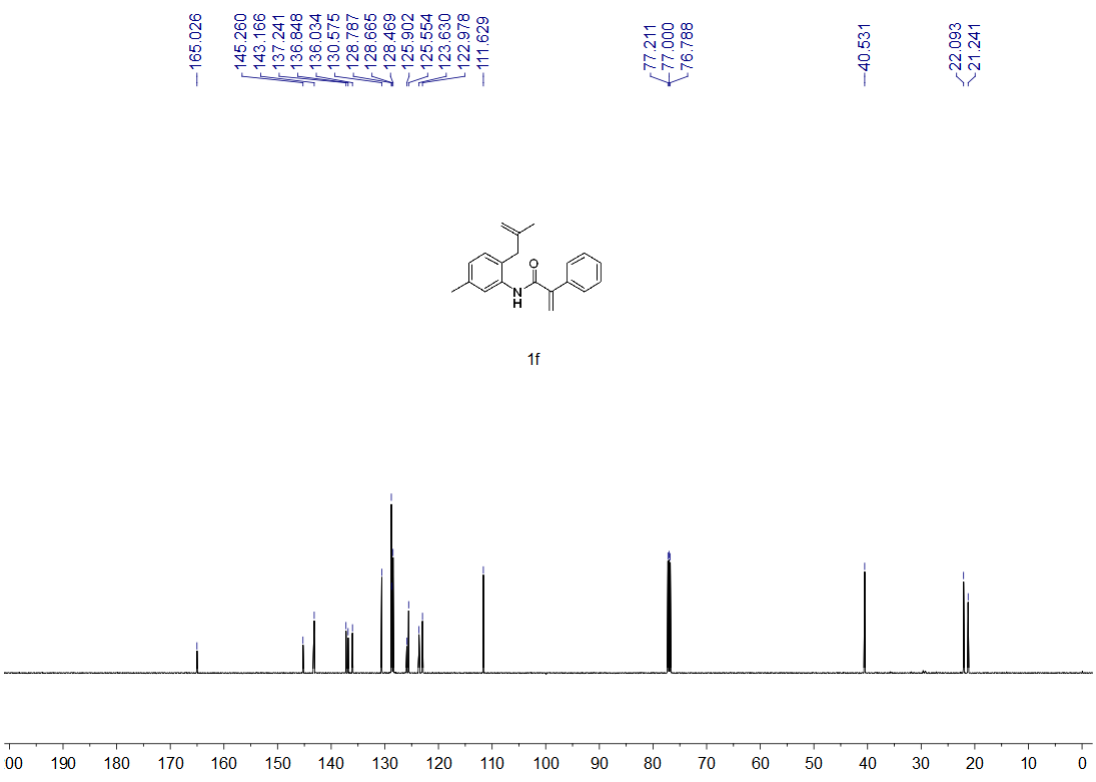
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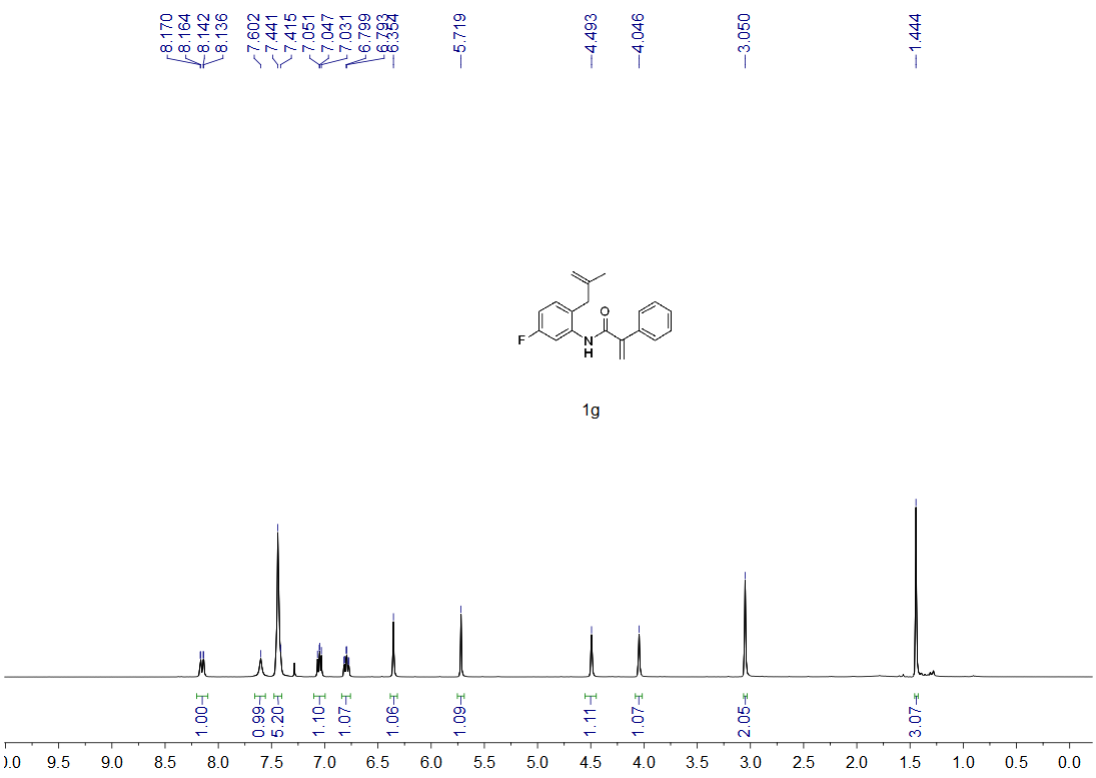
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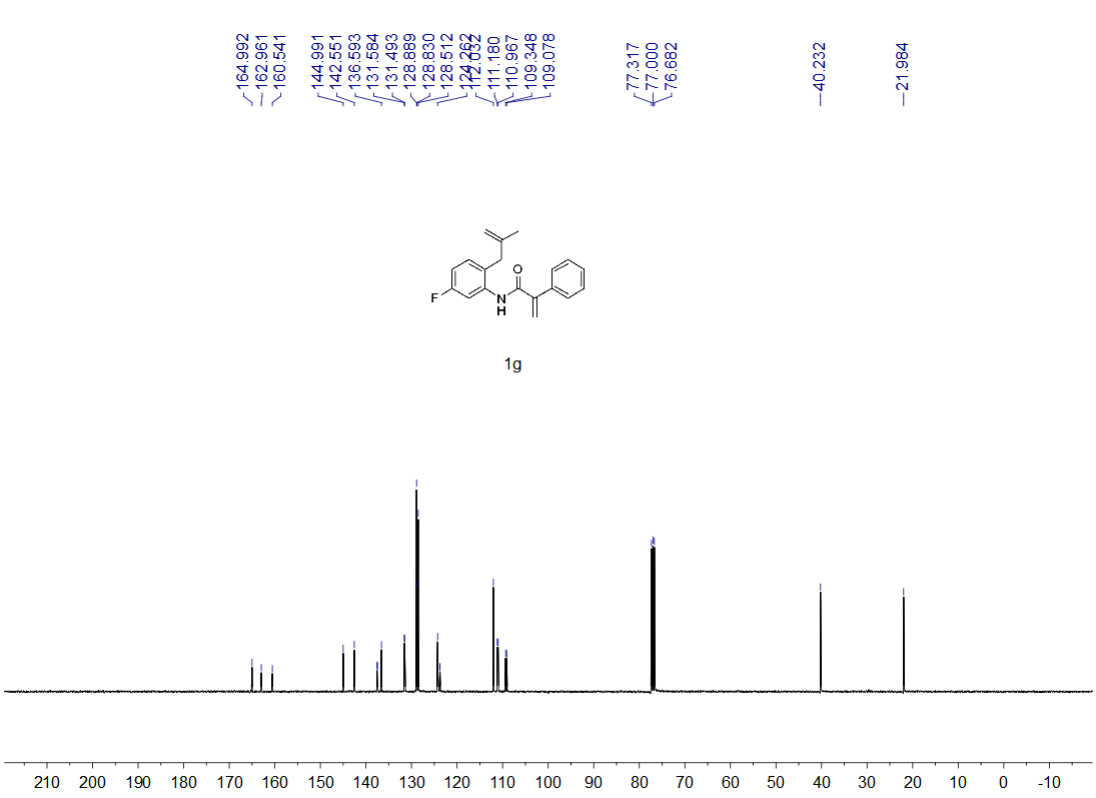
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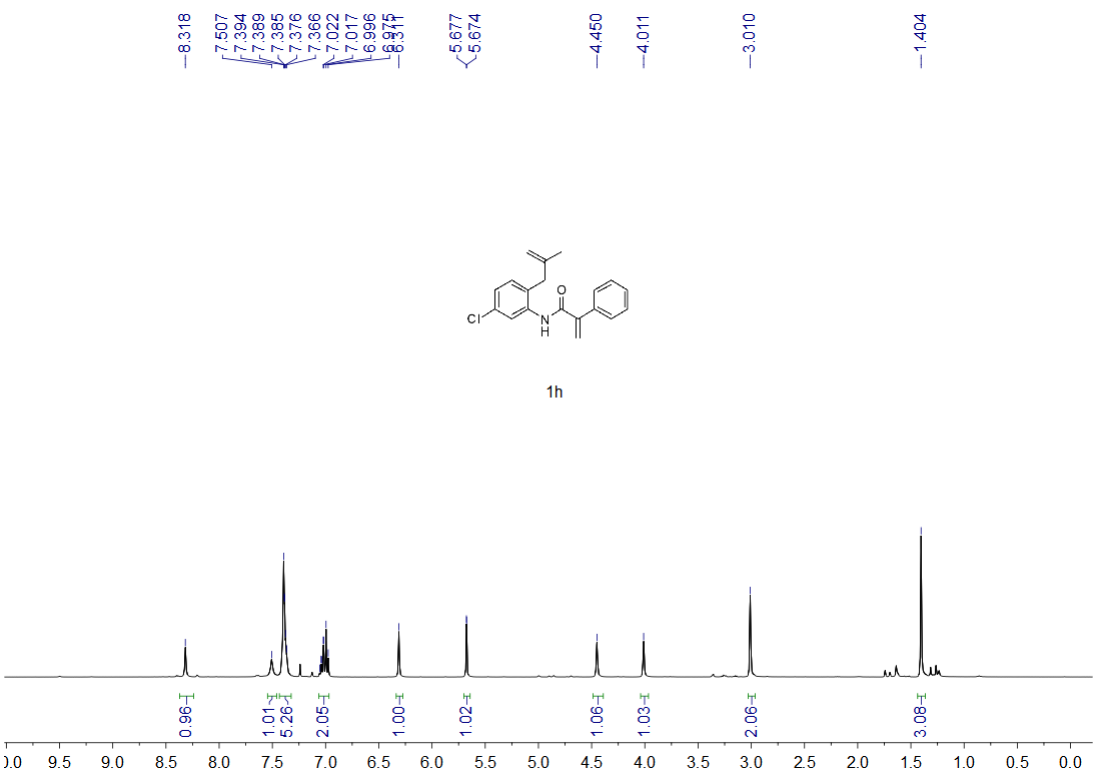
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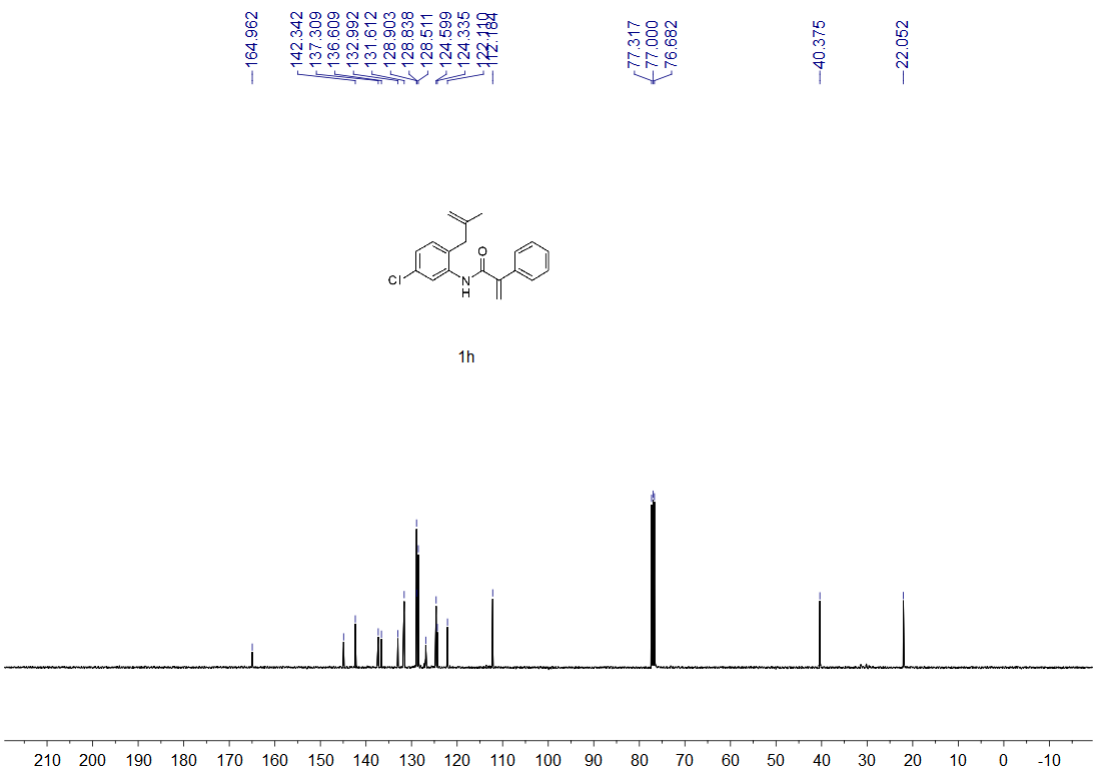
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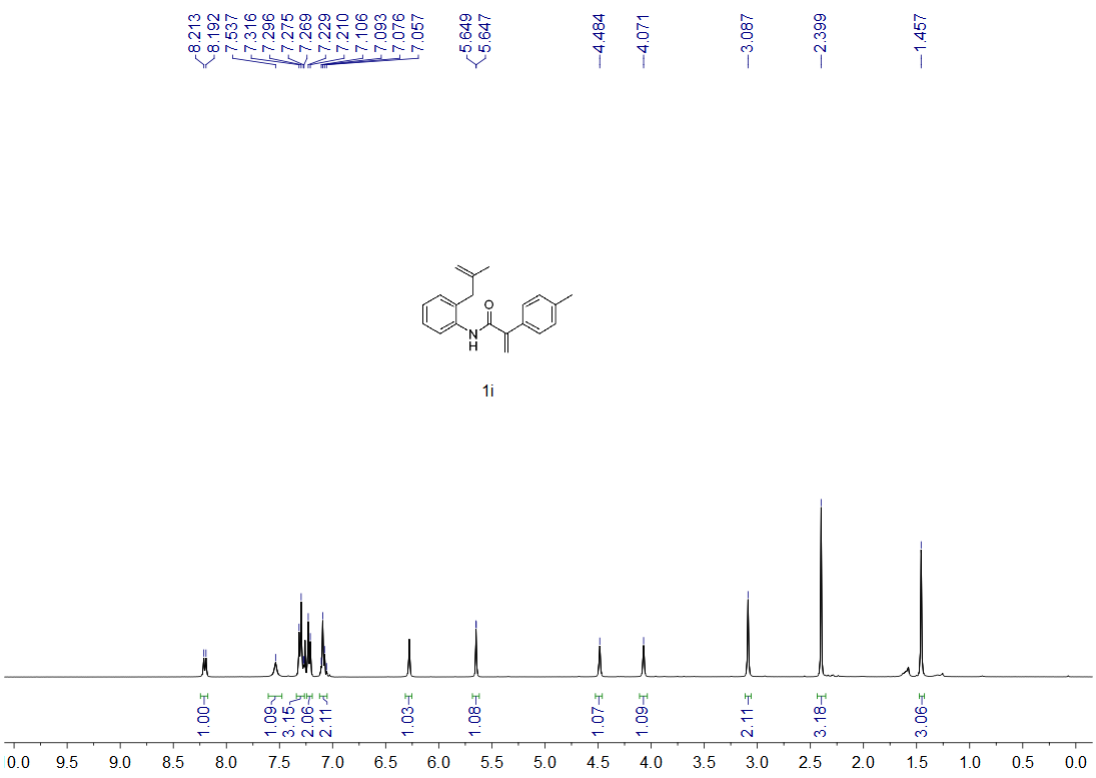
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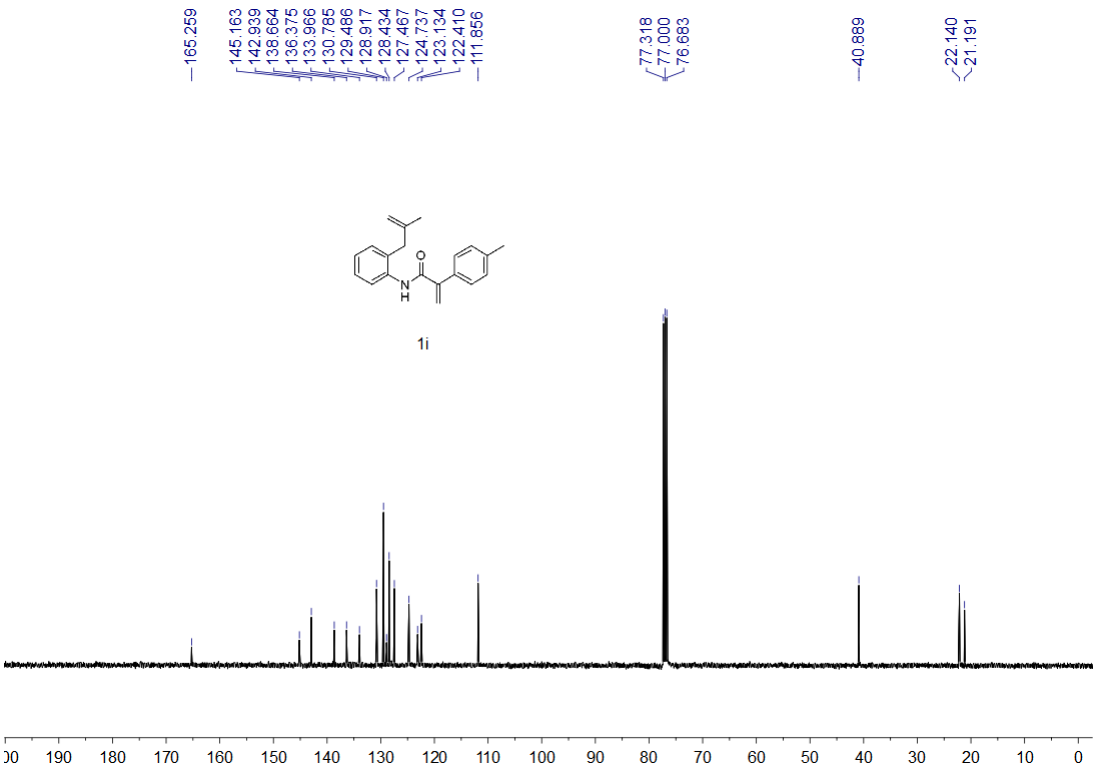
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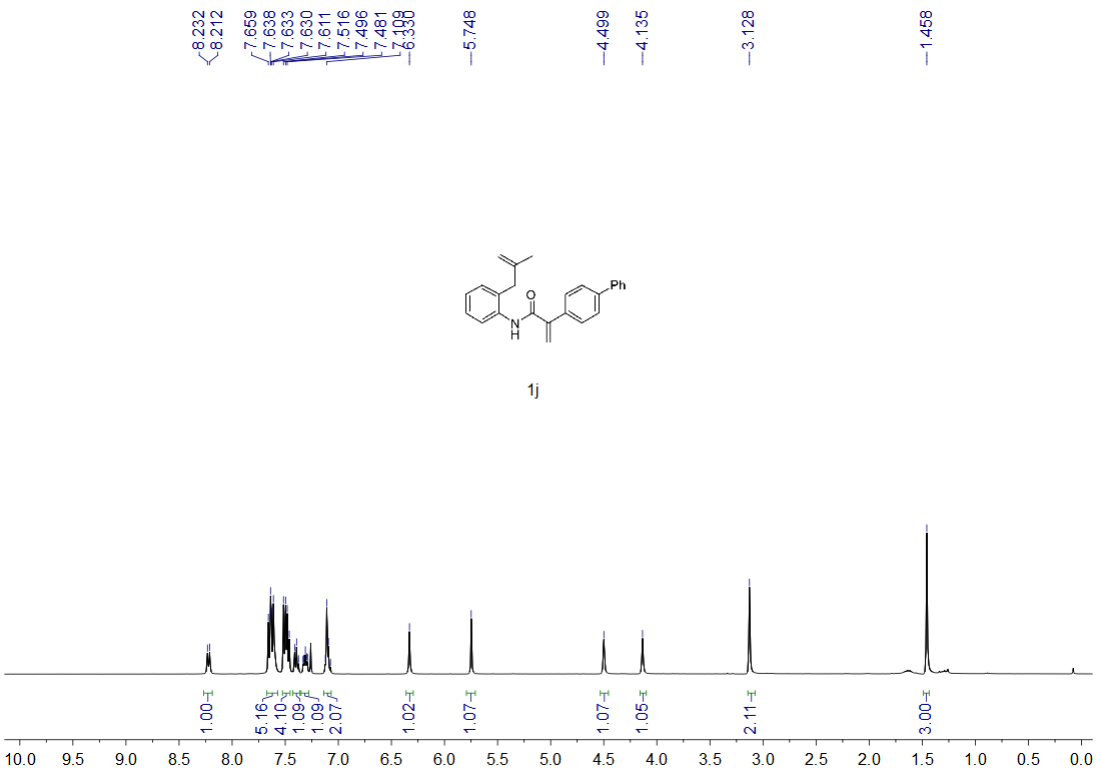
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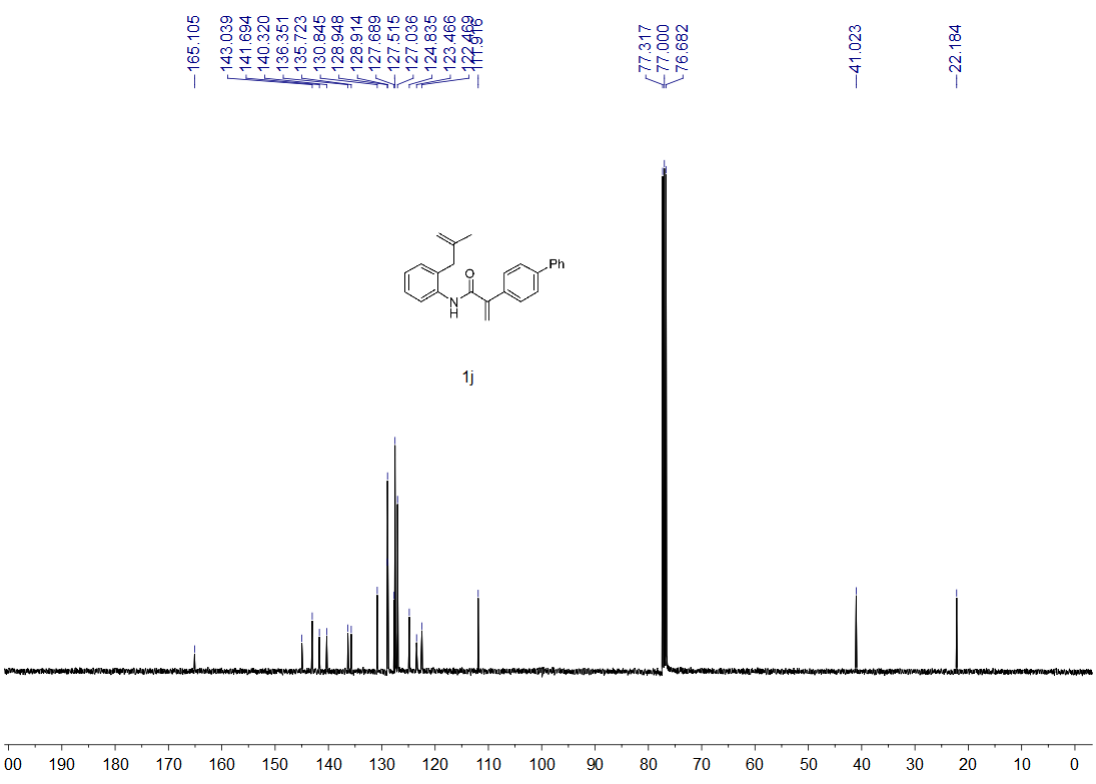
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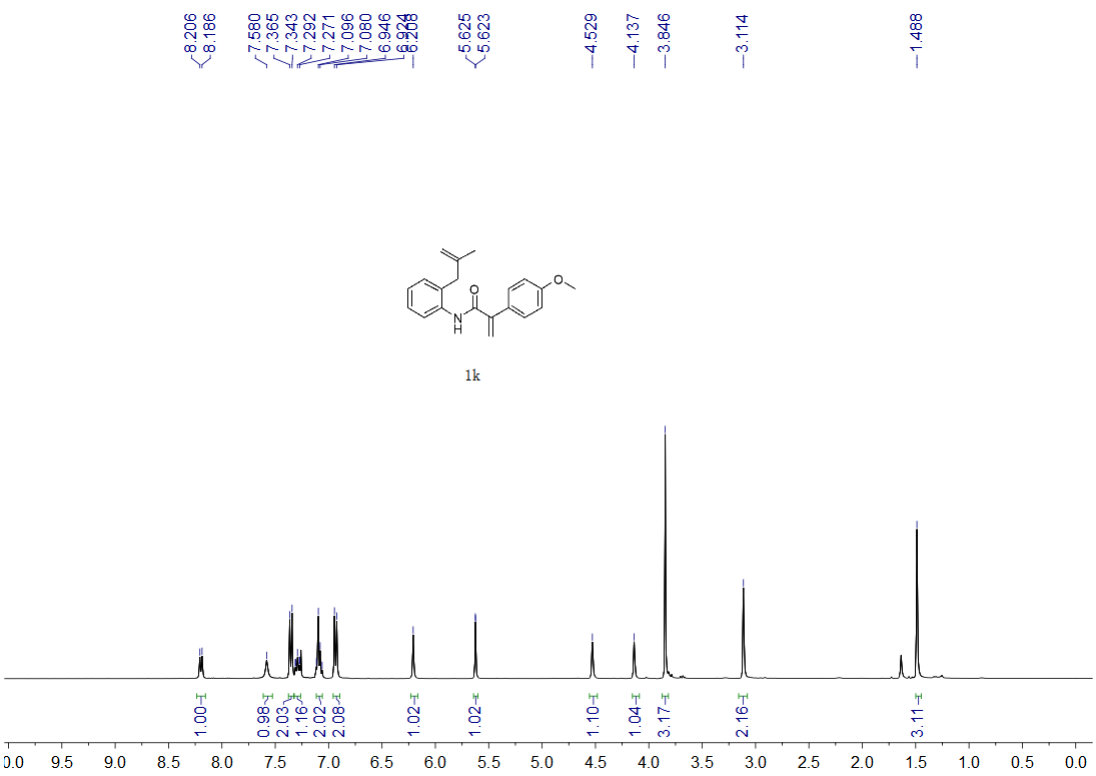
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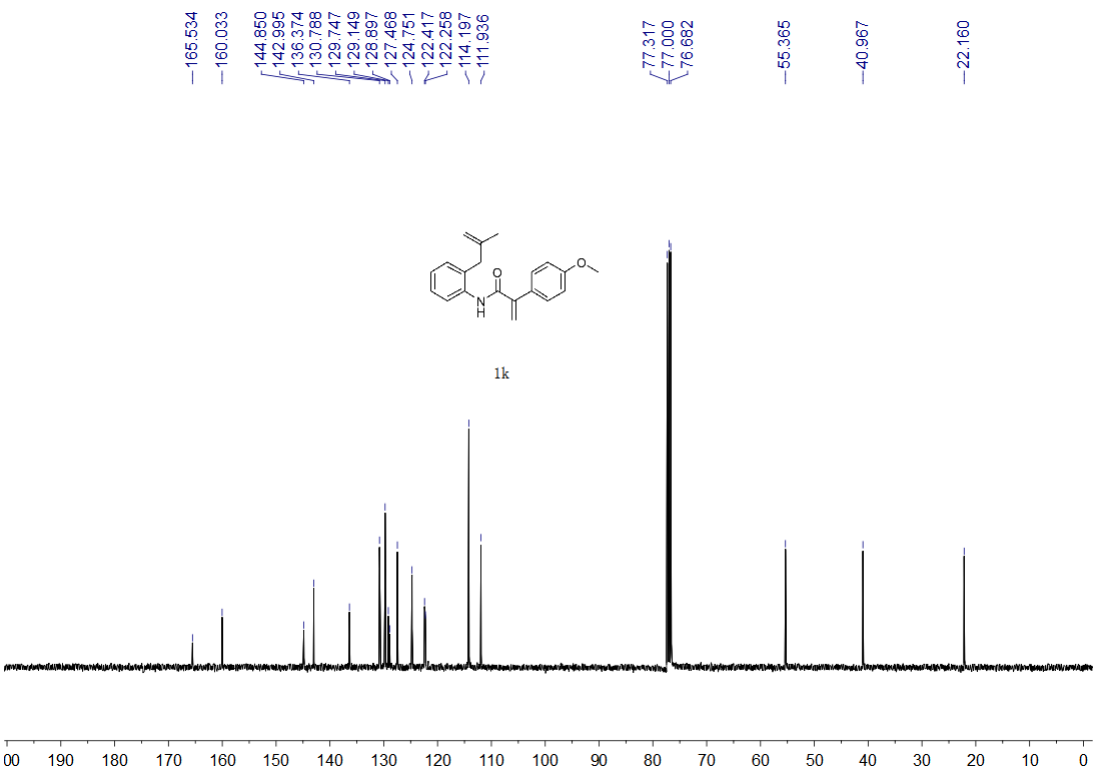
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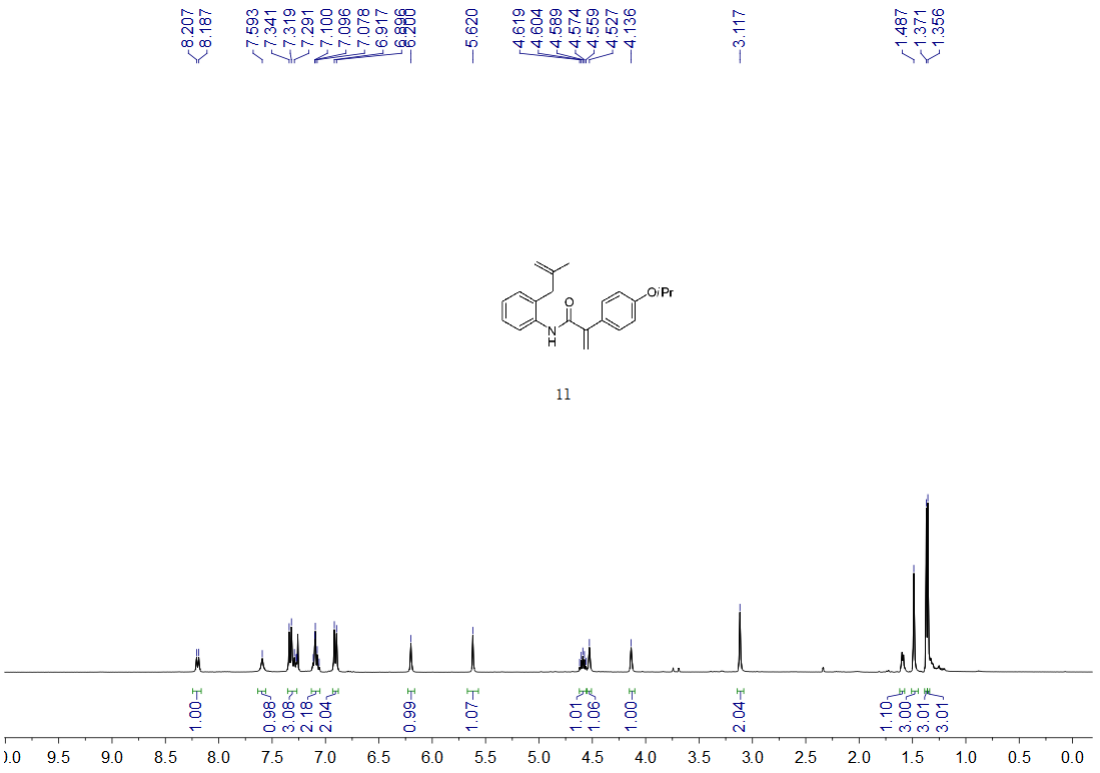
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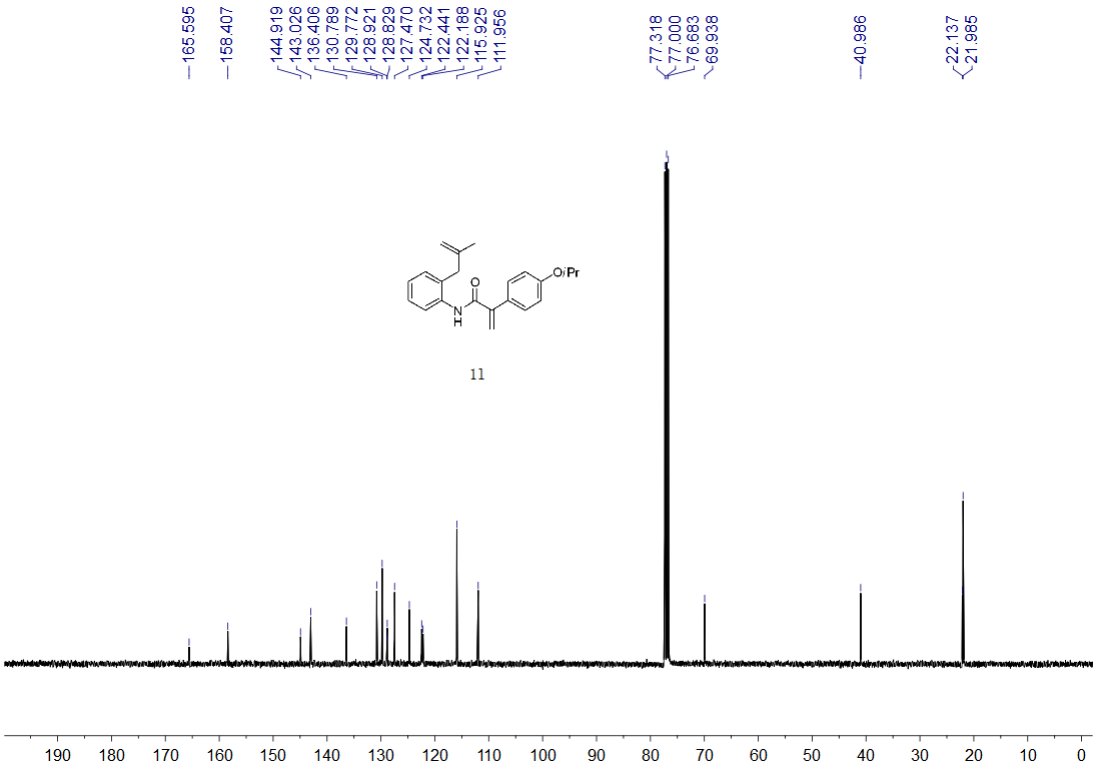
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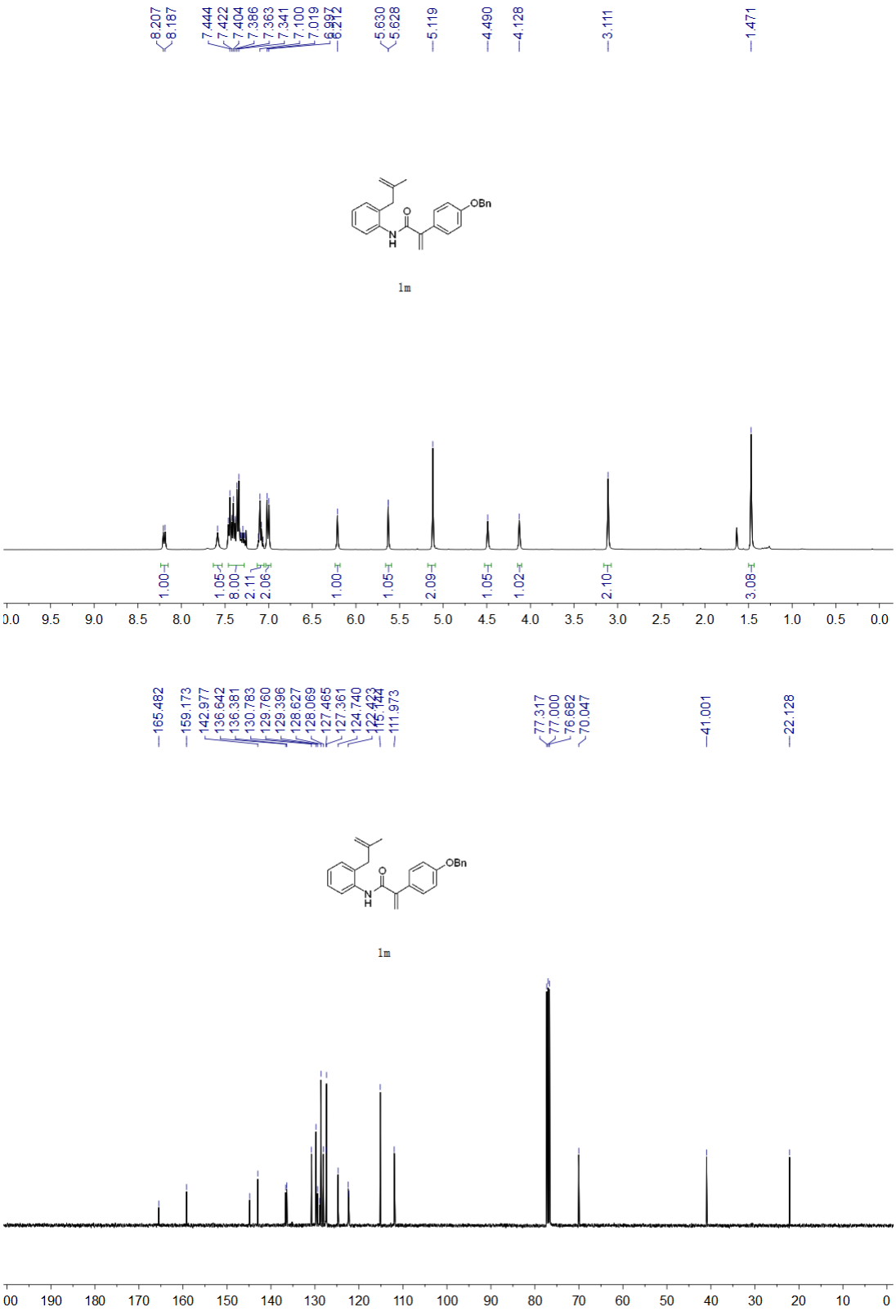
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00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.188
8.168
7.402
7.380
7.359
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7.112
7.067
7.047
7.034
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4.595
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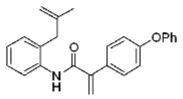
3.154
1.544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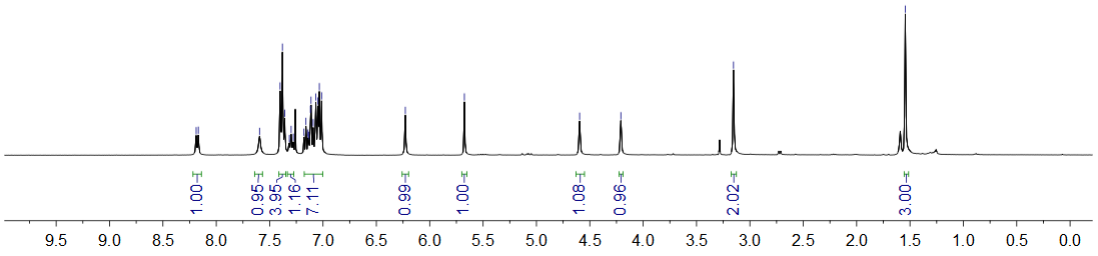
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1.08
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2.02
3.00
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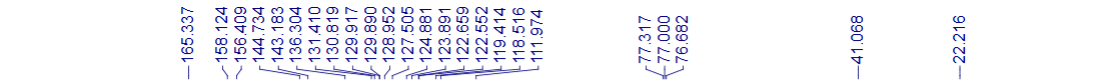
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143.183
136.304
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130.819
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129.890
128.952
127.505
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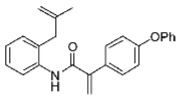
122.552
119.414
118.516
111.974
77.317
77.000
76.682
41.068
22.216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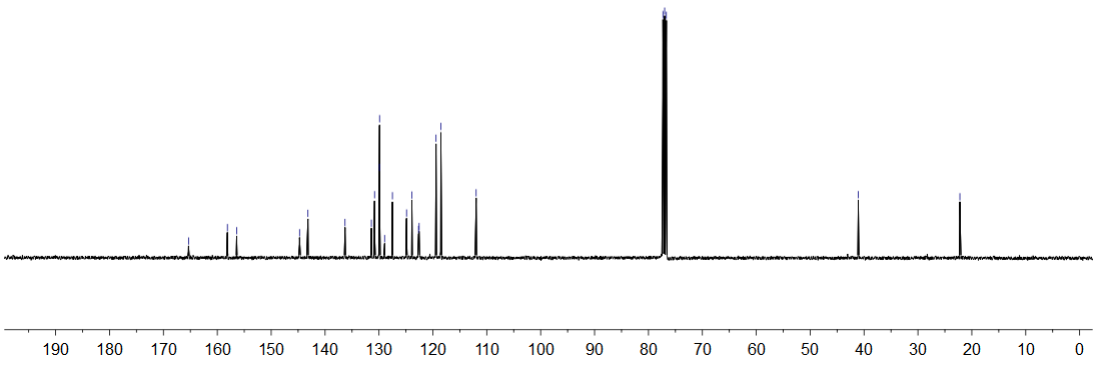
O

1n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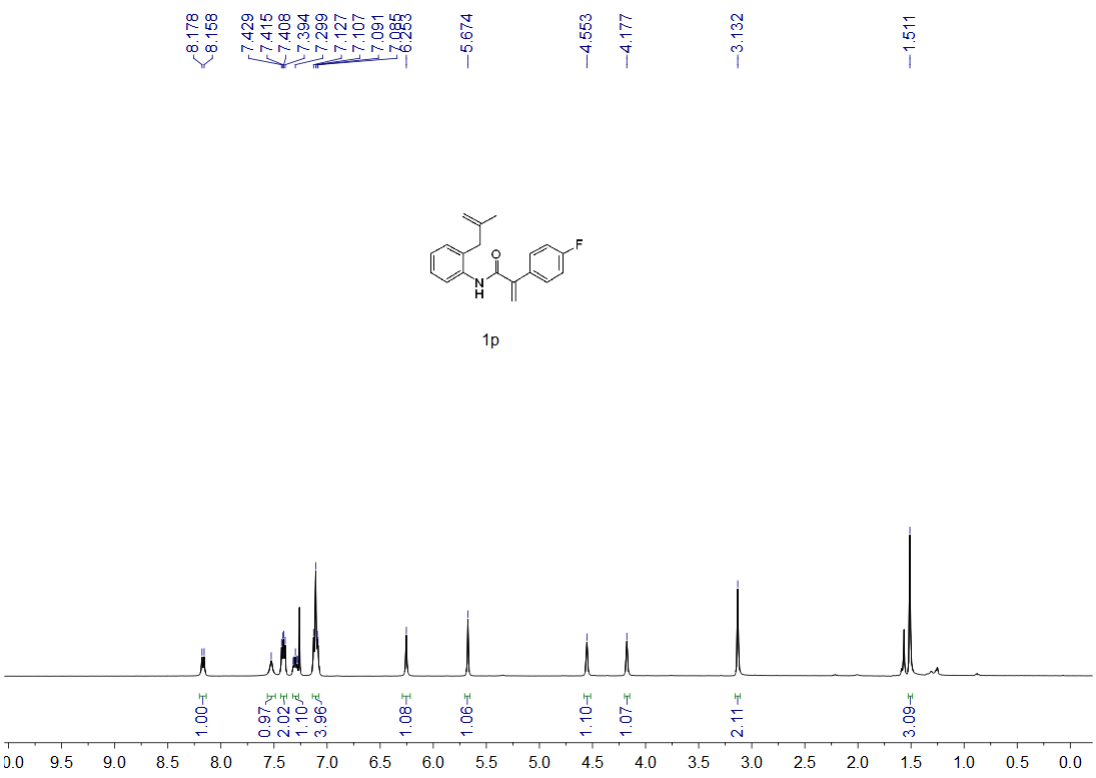
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7.127
7.107
7.091
7.085
6.253
5.674
4.553
4.177
3.132
1.511
1p
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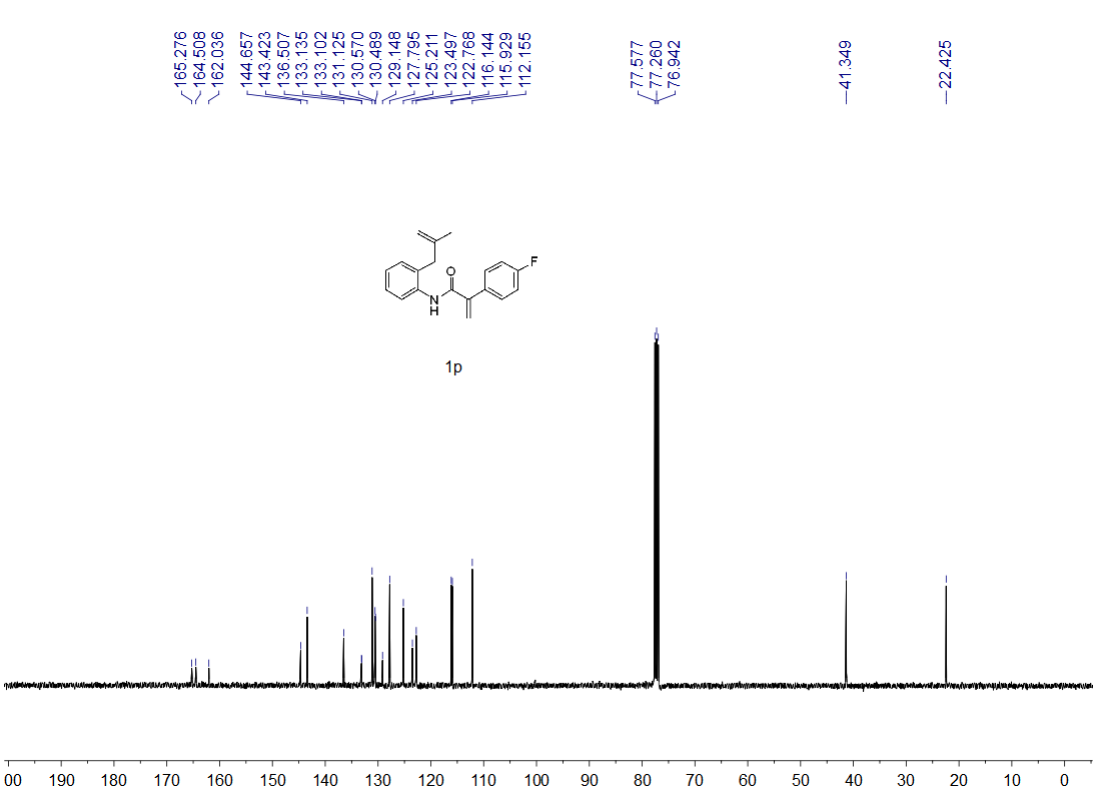
1.10
3.96
1.08
1.06
1.10
1.07
2.11
3.09
0.0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133.102
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130.570
130.489
129.148
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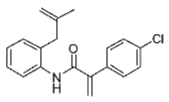
125.211
123.497
122.768
116.144
115.929
112.155
77.577
77.260
76.942
41.349
22.425
1p
00


8.169
8.149
7.514
7.318
7.312
7.296
7.281
7.276
7.126
7.112
7.109
5.697
4.561
4.184
3.136
1.517


Cl
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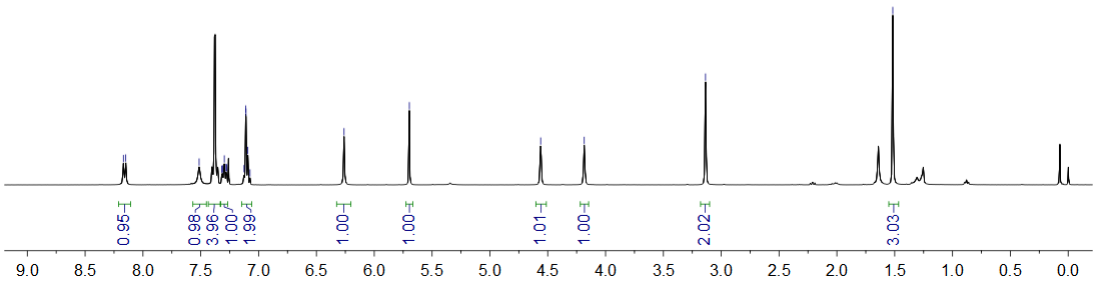
N
H

1q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1.00
1.00
1.01
1.00
2.02
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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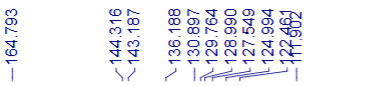
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129.764
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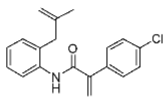
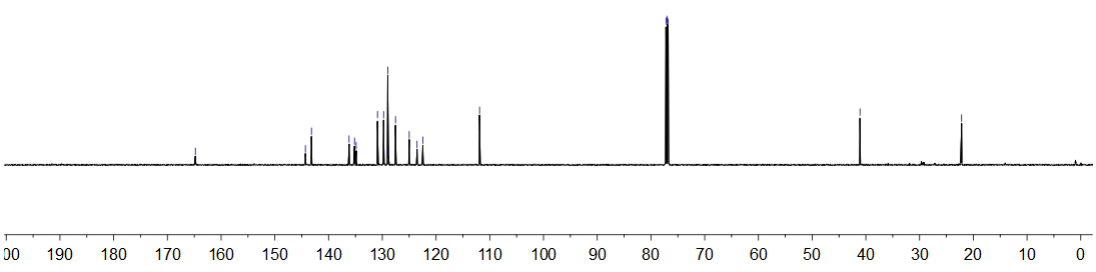
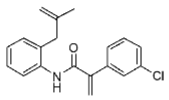
127.549
124.994
77.212
77.000
76.788
41.093
22.182


Cl
O
N
H

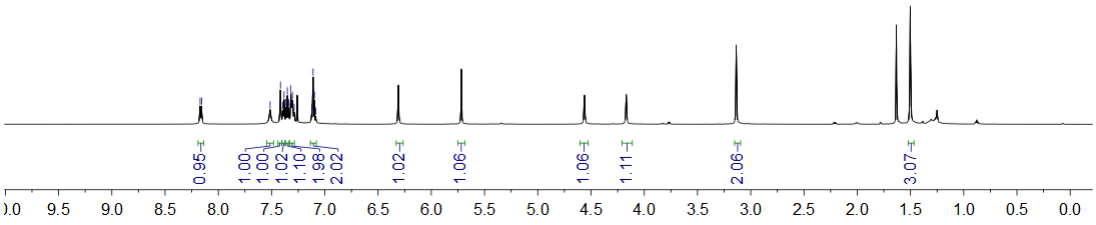
1q


00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.171
8.158
7.514
7.417
7.396
7.382
7.364
7.352
7.339
7.319
7.304
7.288
7.123
7.110
7.098
7.085


O
N
H
Cl

1r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1.98
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1.02
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1.06
1.11
2.06
3.07
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
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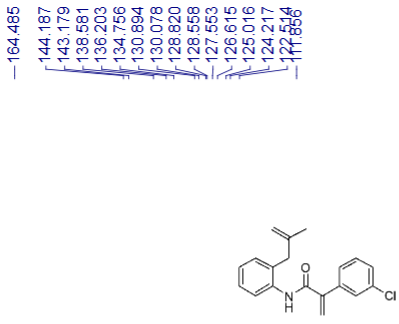
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5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143.179
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130.078
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128.558
127.553
126.615
125.016
124.217
77.318
77.000
76.683
41.119
22.161

O
N
H
Cl

1r

0
10
20
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40
50
60
70
80
90
100
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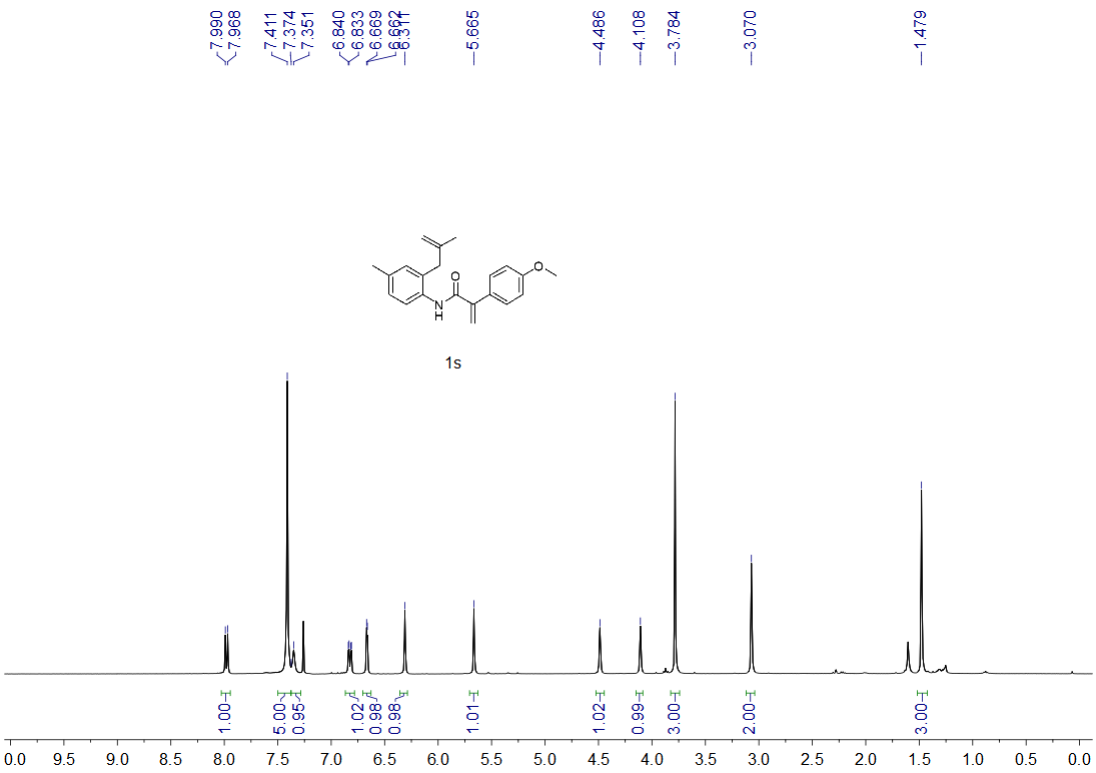
120
130
140
150
160
170
180
190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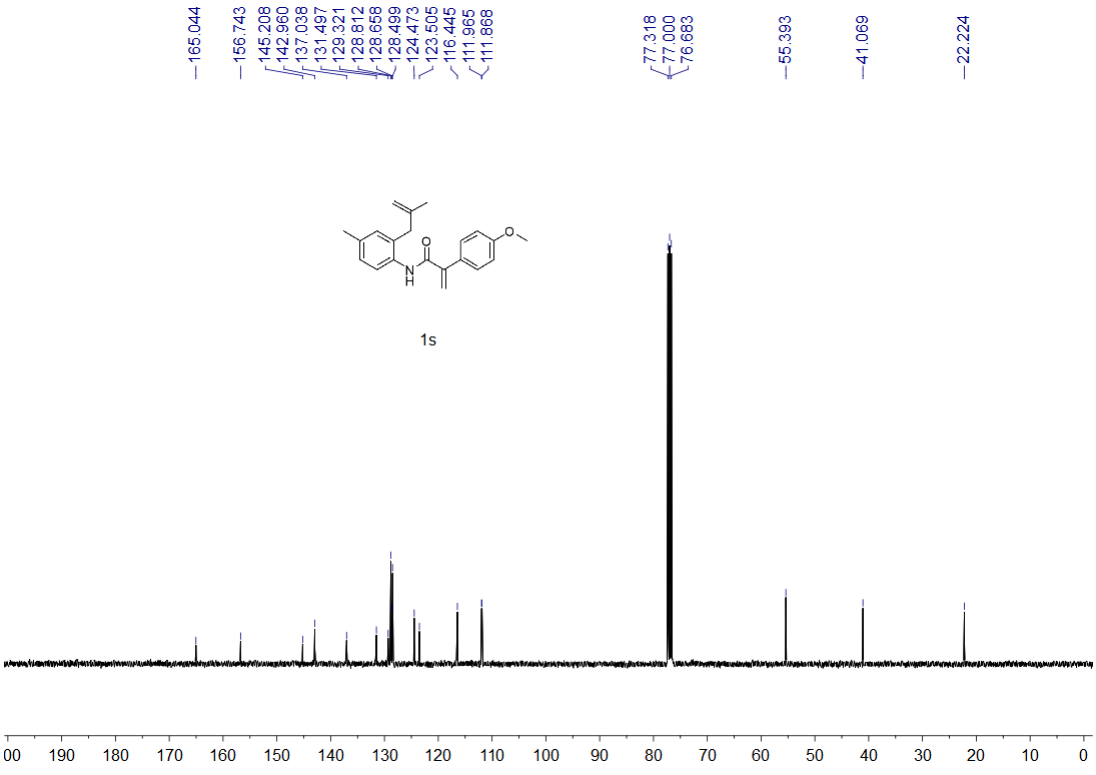
7.351
6.840
6.833
6.669
6.662
5.665
4.486
4.108
3.784
3.070
1.479
1s
1.00
5.00
0.95
1.02
0.98
0.98
1.01
1.02
0.99
3.00
2.00
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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124.473
123.505
116.445
111.965
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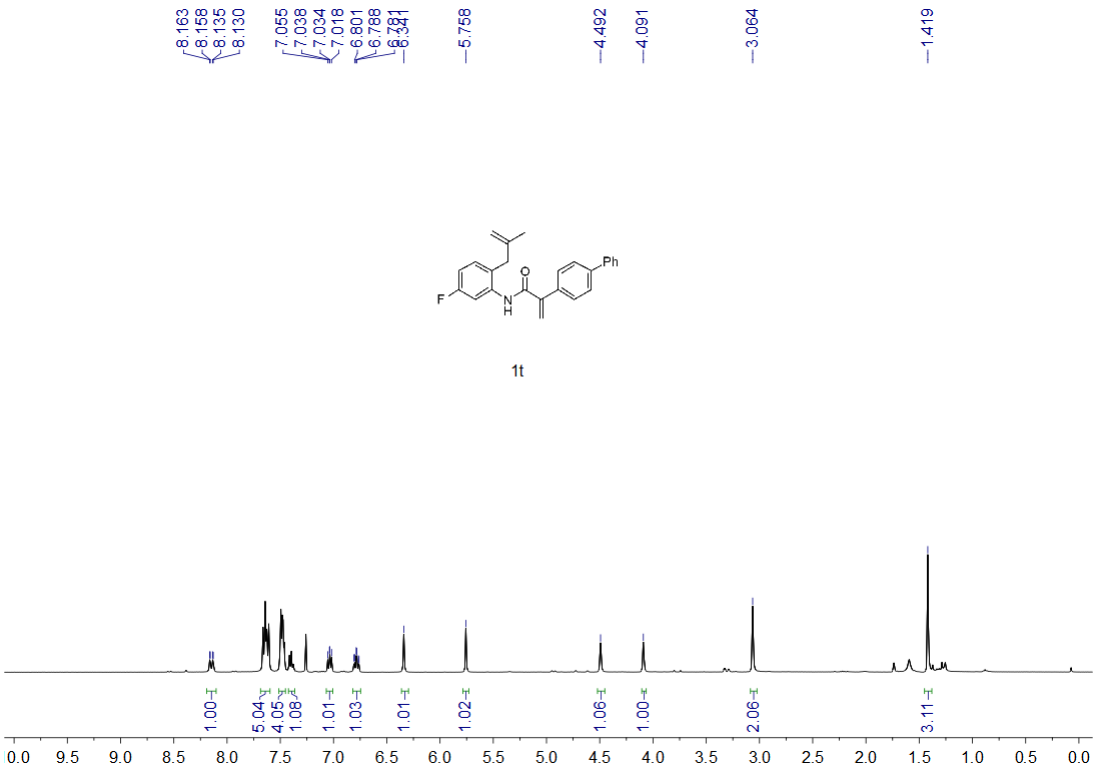
77.318
77.000
76.683
55.393
41.069
22.224
1s
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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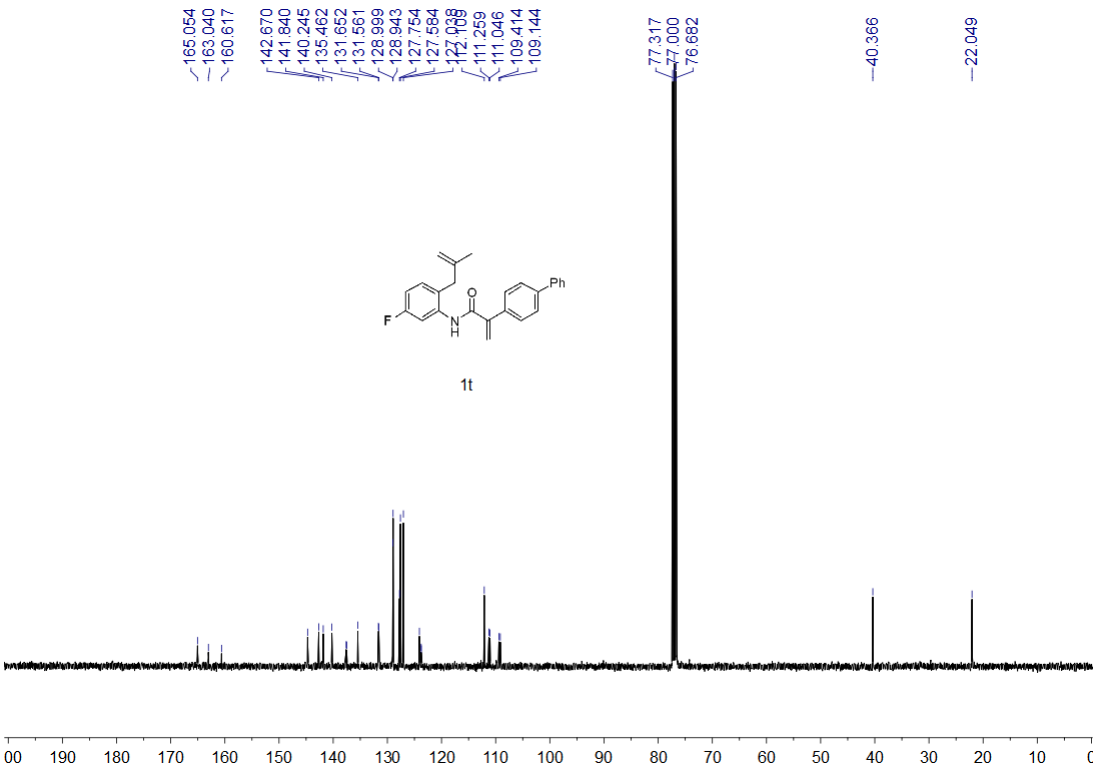
7.038
7.034
7.018
6.801
6.788
6.781
6.341
5.758
4.492
4.091
3.064
1.419
F
N
H
O
Ph
1t
1.00
5.04
4.05
1.08
1.01
1.03
1.01
1.02
1.06
1.00
2.06
3.11
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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127.584
111.259
111.046
109.414
109.144
77.317
77.000
76.682
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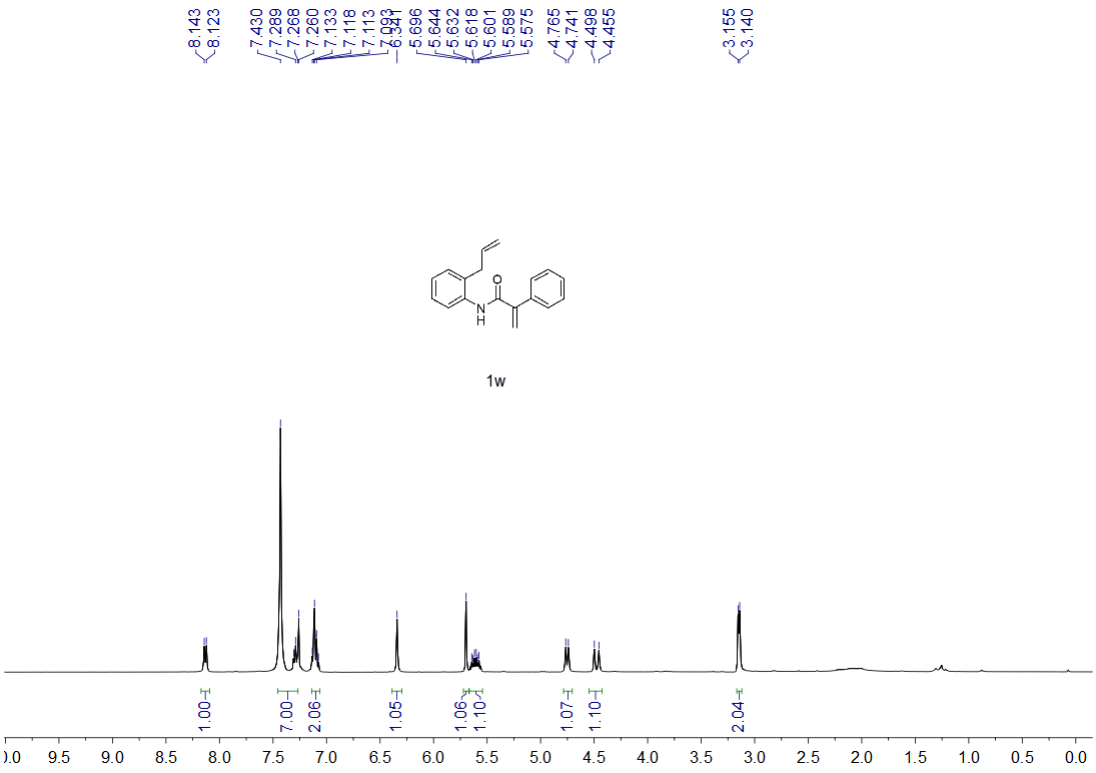
22.049
F
N
H
O
Ph
1t
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.260
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7.118
7.113
7.093
6.341
5.696
5.644
5.632
5.618
5.601
5.589
5.575
4.765
4.741
4.498
4.455
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7.00
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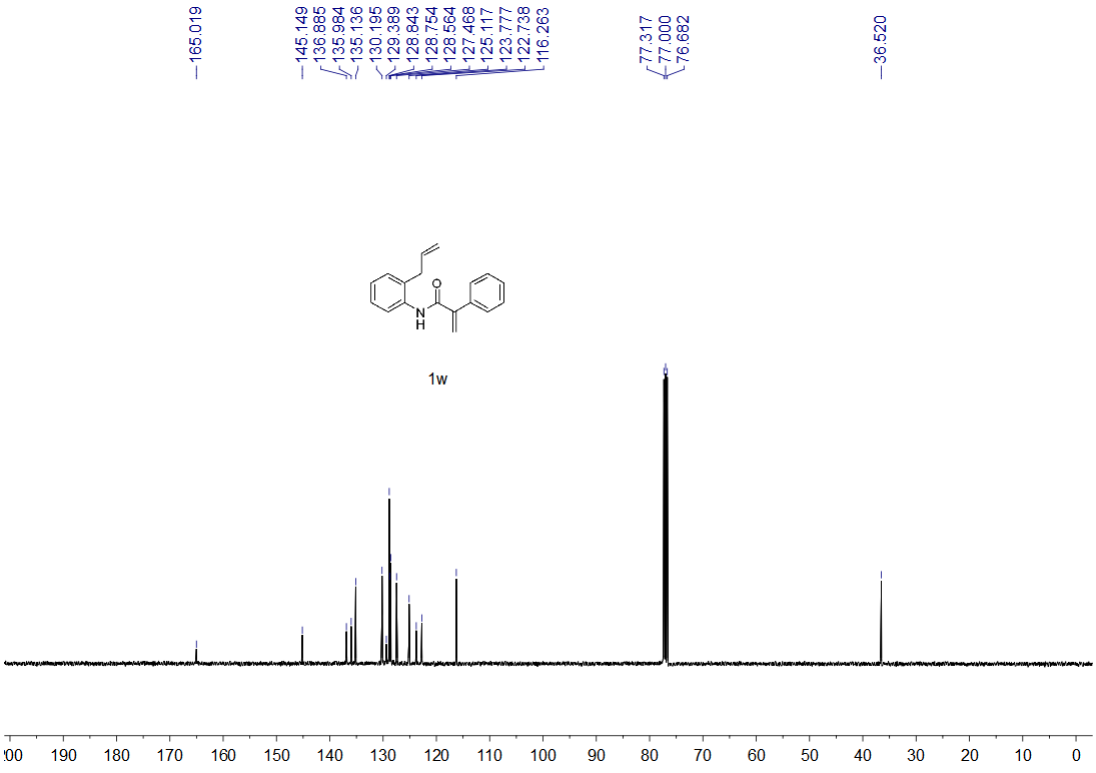
1.05
1.06
1.10
1.07
1.10
2.04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77.000
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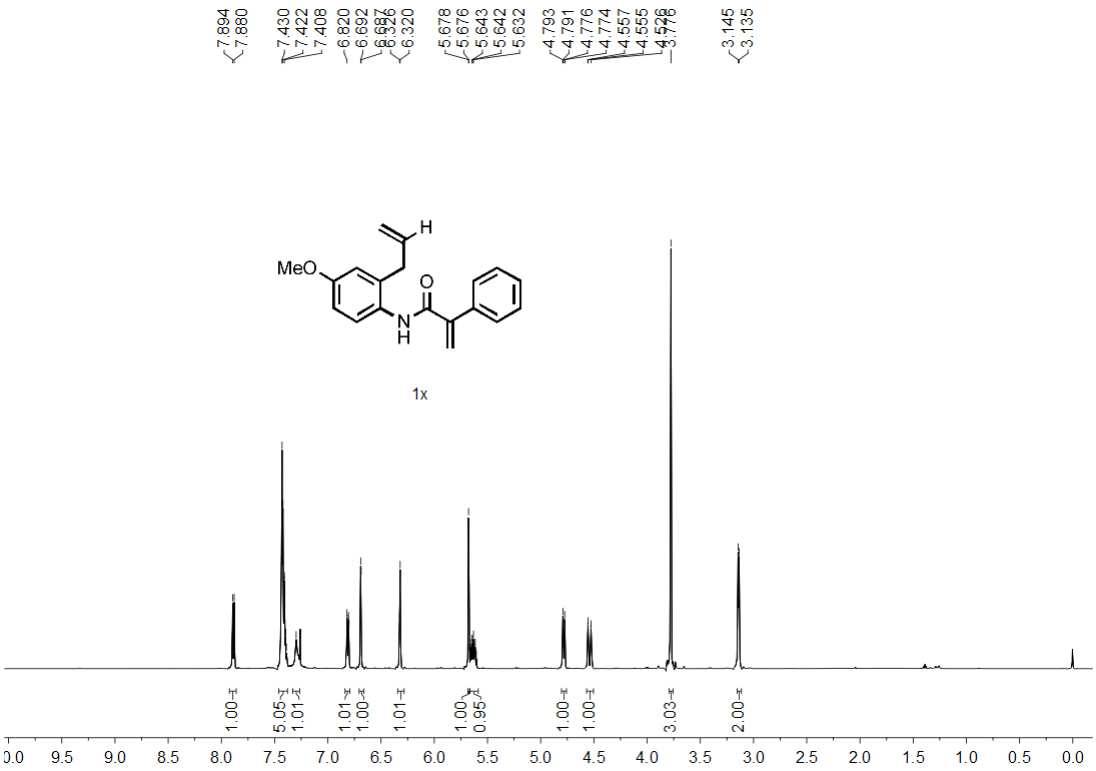
1w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5.676
5.643
5.642
5.632
4.793
4.791
4.776
4.774
4.557
4.555
4.526
3.145
3.135
MeO
H
O
N
H
1x
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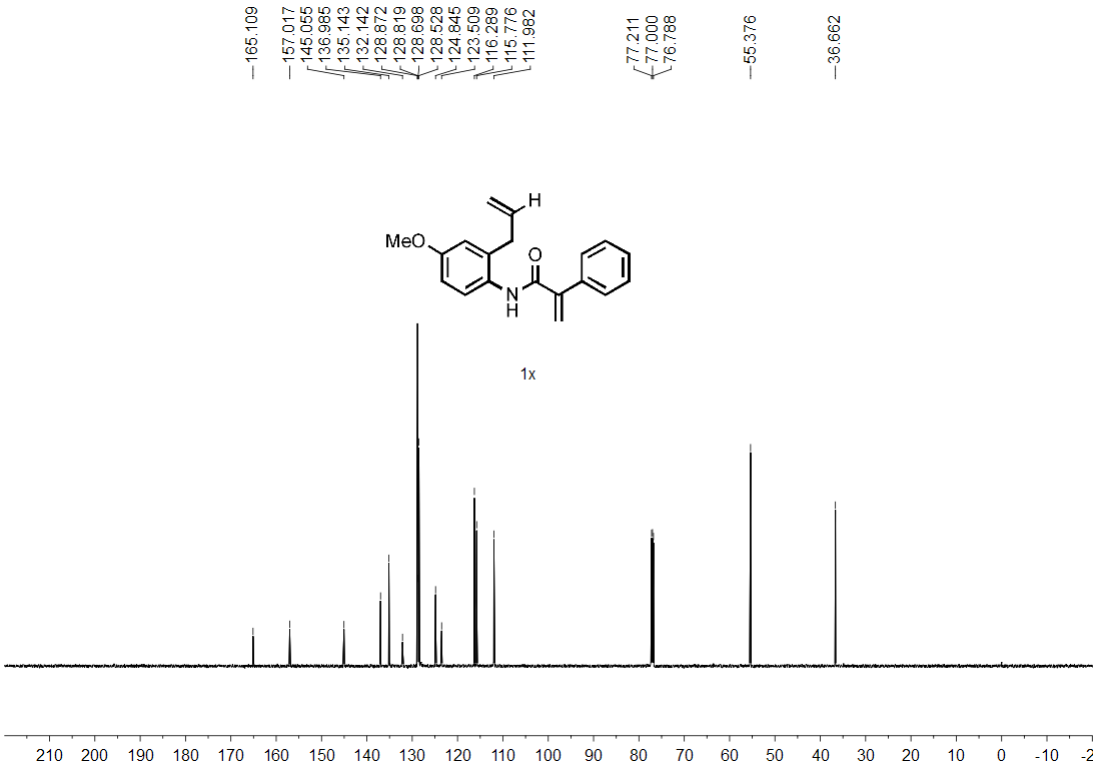
1.01
1.00
1.01
1.00
0.95
1.00
1.00
3.03
2.00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145.055
136.985
135.143
132.142
128.872
128.819
128.698
128.528
124.845
123.509
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115.776
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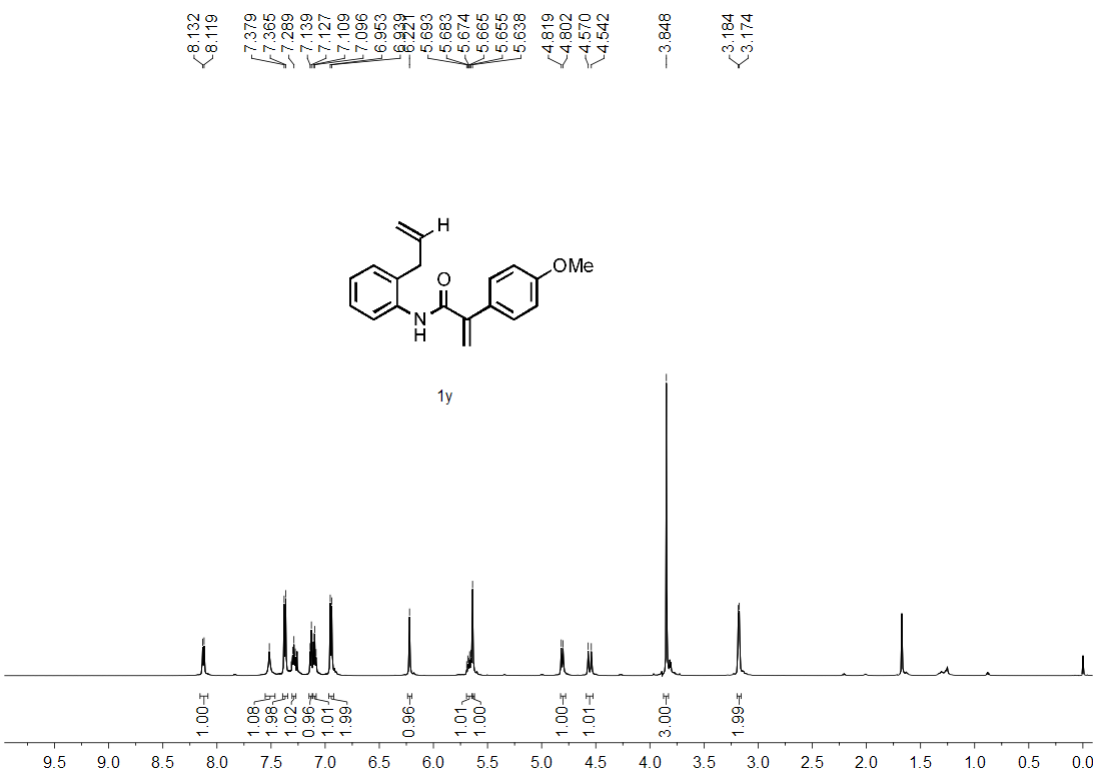
77.211
77.000
76.788
55.376
36.662
MeO
H
O
N
H
1x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7.365
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7.139
7.127
7.109
7.096
6.953
6.939
6.921
5.693
5.683
5.674
5.665
5.655
5.638
4.819
4.802
4.570
4.542
3.848
3.184
3.174
H
O
N
H
OMe
1y
1.00
1.08
1.98
1.02
0.96
1.01
1.99
0.96
1.01
1.00
1.00
1.01
3.00
1.99
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9.0
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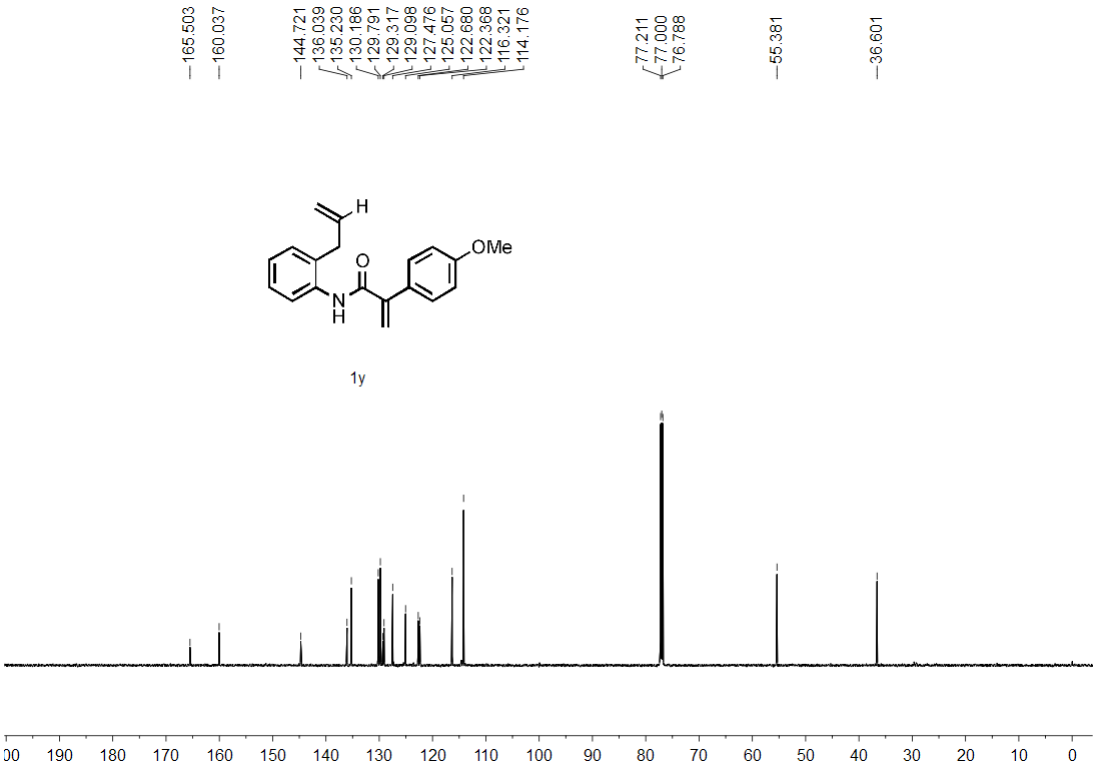
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129.317
129.098
127.476
125.057
122.680
122.368
116.321
114.176
77.211
77.000
76.788
55.381
36.601
H
O
N
H
OMe
1y
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150
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70
60
50
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30
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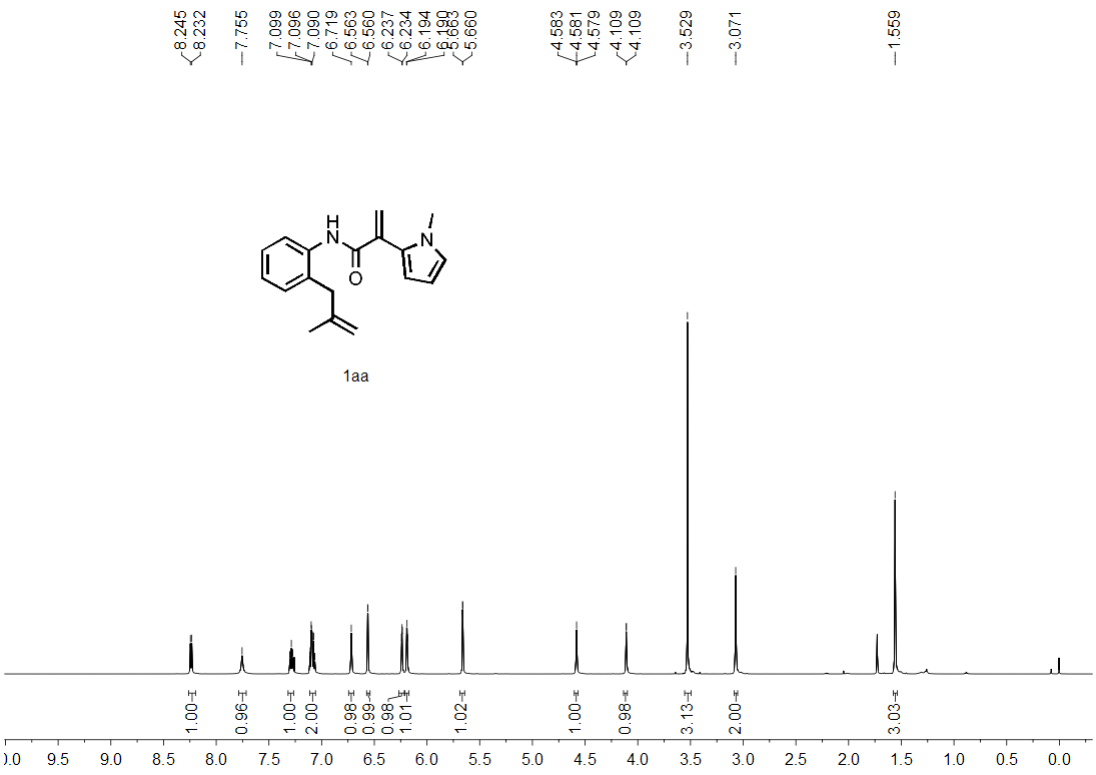
10
0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7.090
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6.563
6.560
6.237
6.234
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6.190
5.663
5.660
4.583
4.581
4.579
4.109
4.109
3.529
3.071
1.559
1aa
1.00
0.96
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0.98
0.99
0.98
1.01
1.02
1.00
0.98
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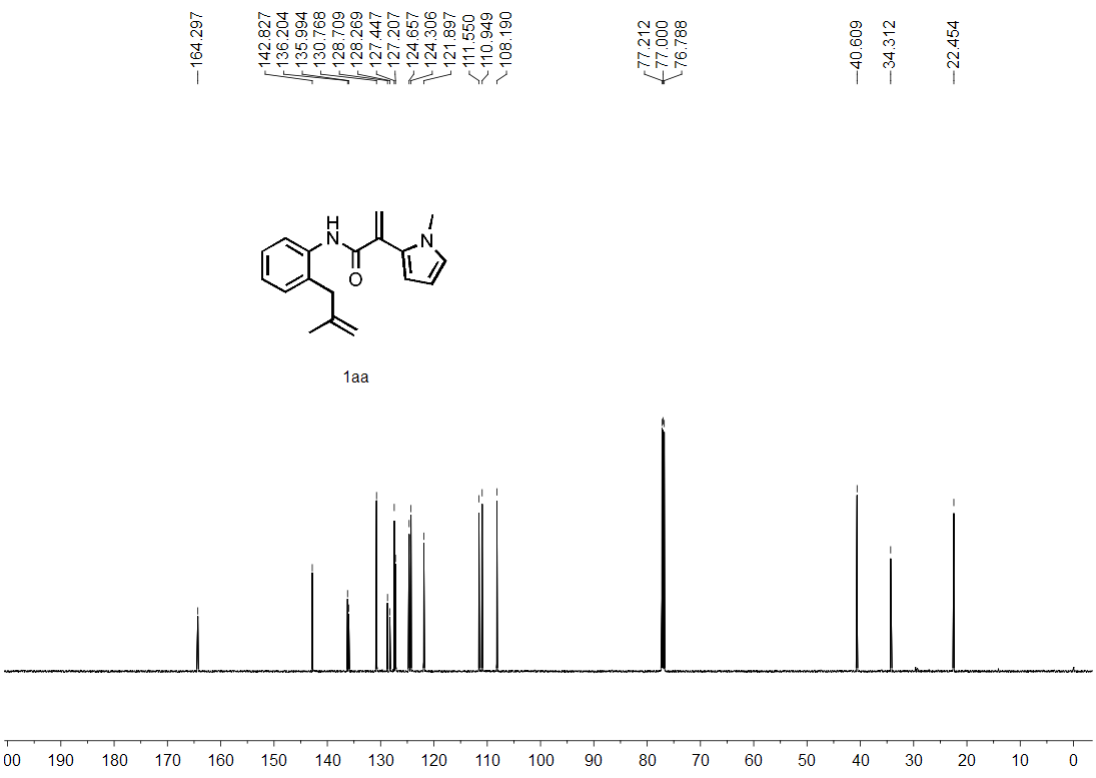
2.00
3.03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135.994
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128.709
128.269
127.447
127.207
124.657
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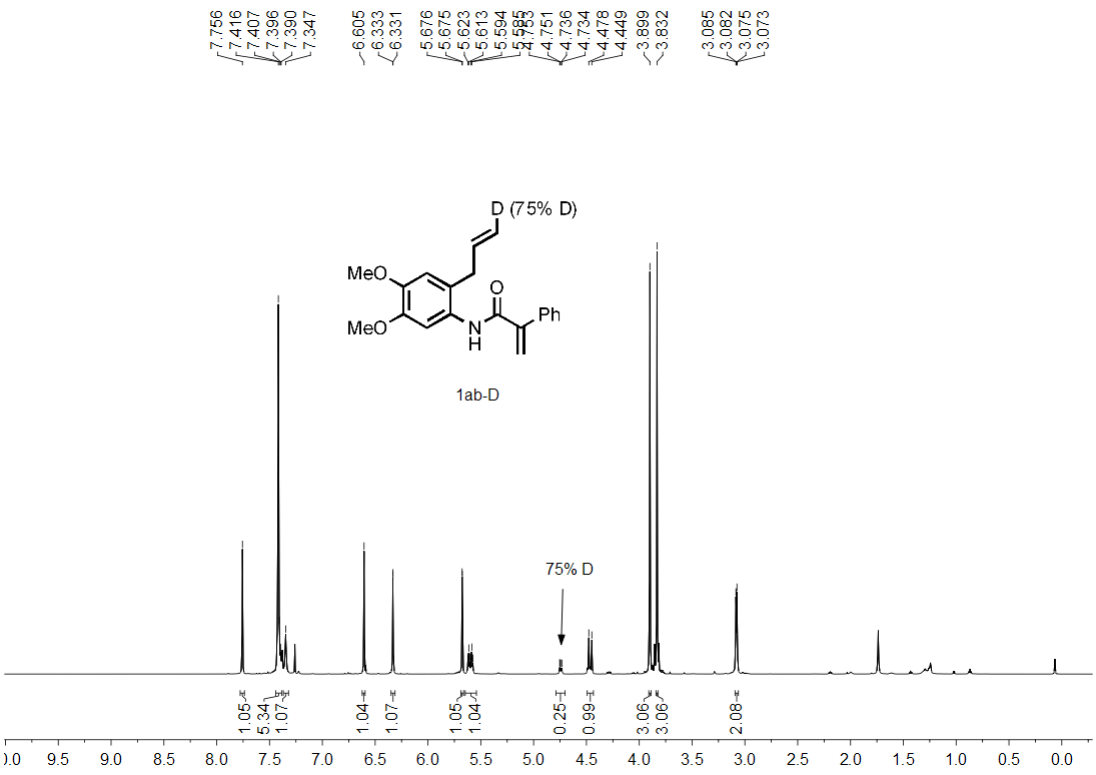
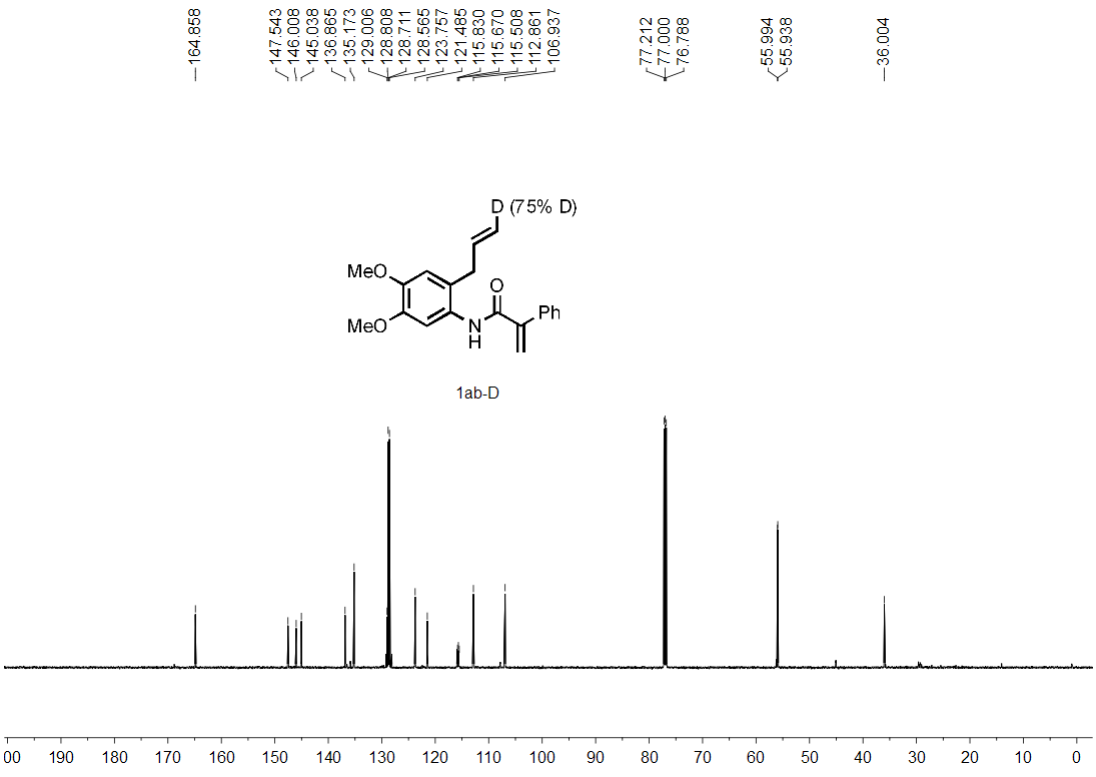
77.000
76.788
40.609
34.312
22.454
1aa


7.756
7.416
7.407
7.396
7.390
7.347
6.605
6.333
6.331
5.676
5.675
5.623
5.613
5.594
4.751
4.736
4.734
4.478
4.449
3.899
3.832
3.085
3.082
3.075
3.073
D (75% D)
MeO
MeO
O
N
H
Ph
1ab-D
75% D
1.05
5.34
1.07
1.04
1.07
1.05
1.04
0.25
0.99
3.06
3.06
2.08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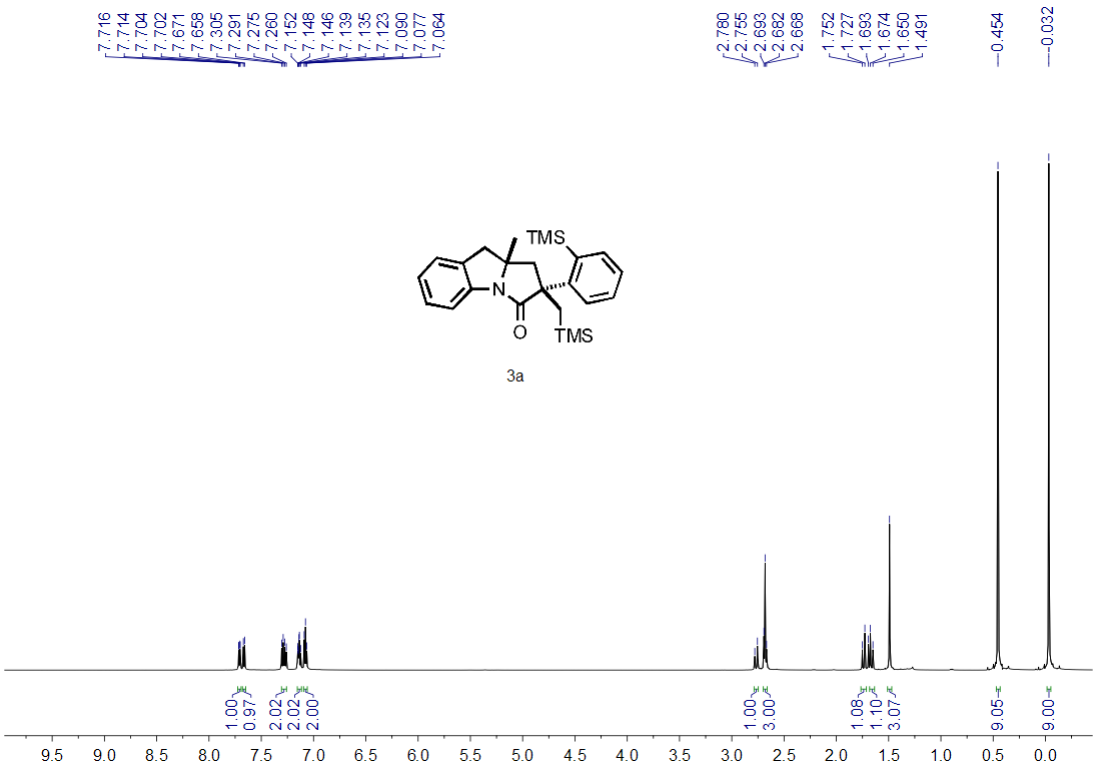
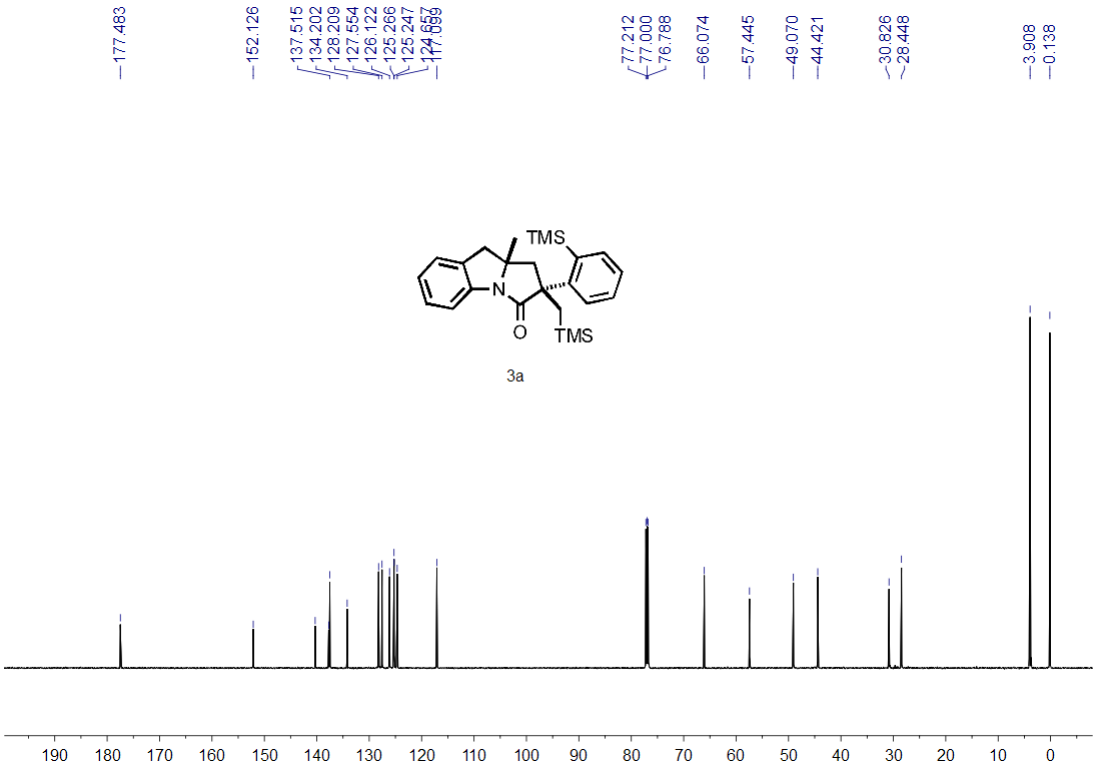
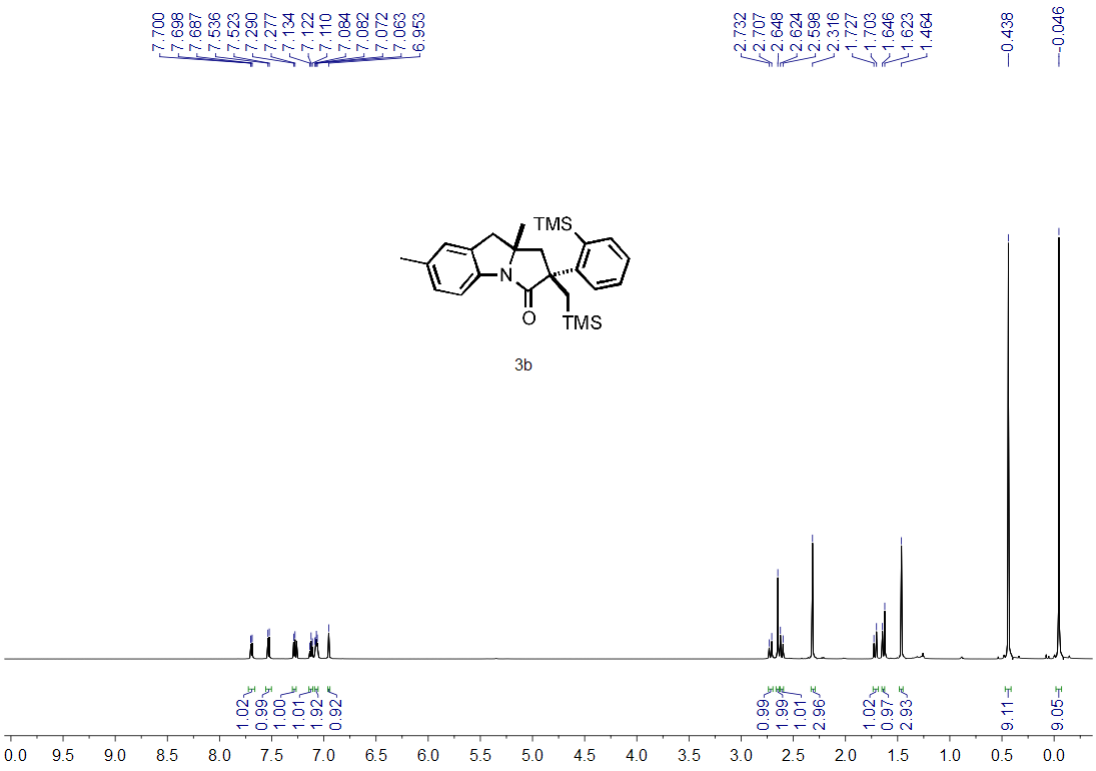
135.173
129.006
128.808
128.711
128.565
123.757
121.485
115.830
115.670
115.508
112.861
106.937
77.212
77.000
76.788
55.994
55.938
36.004
D (75% D)
MeO
MeO
O
N
H
Ph
1ab-D

8.2 NMR Spectra of the Products



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7.687
7.536
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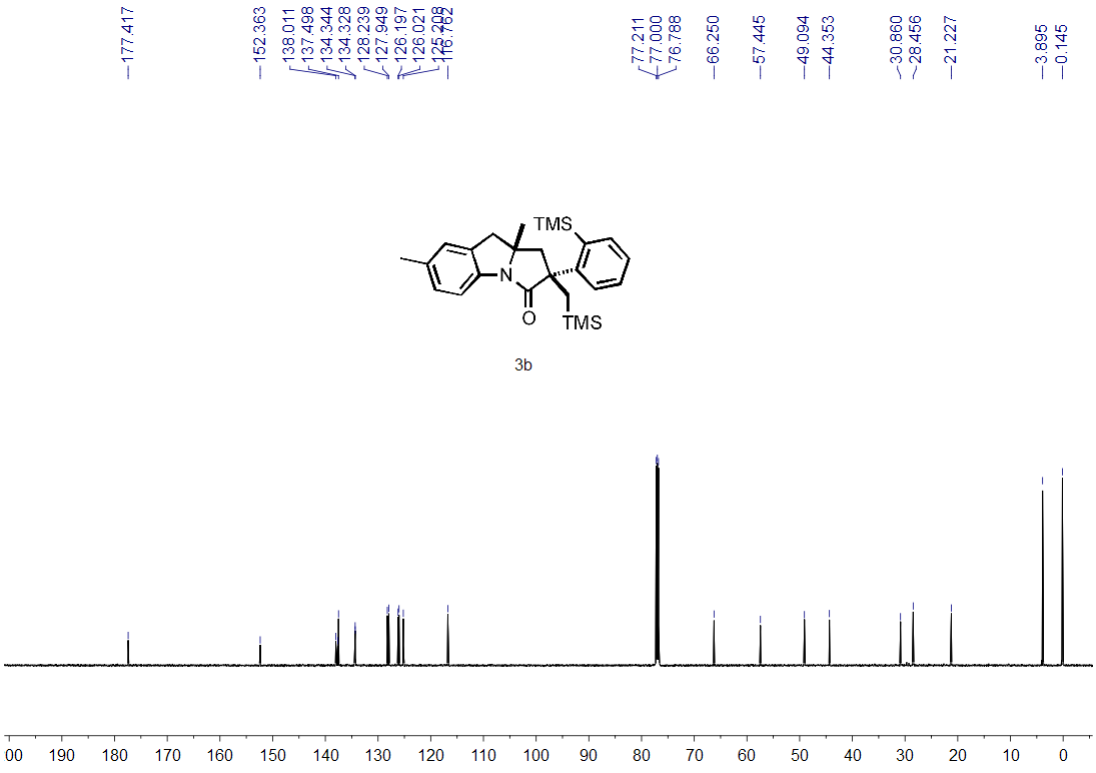
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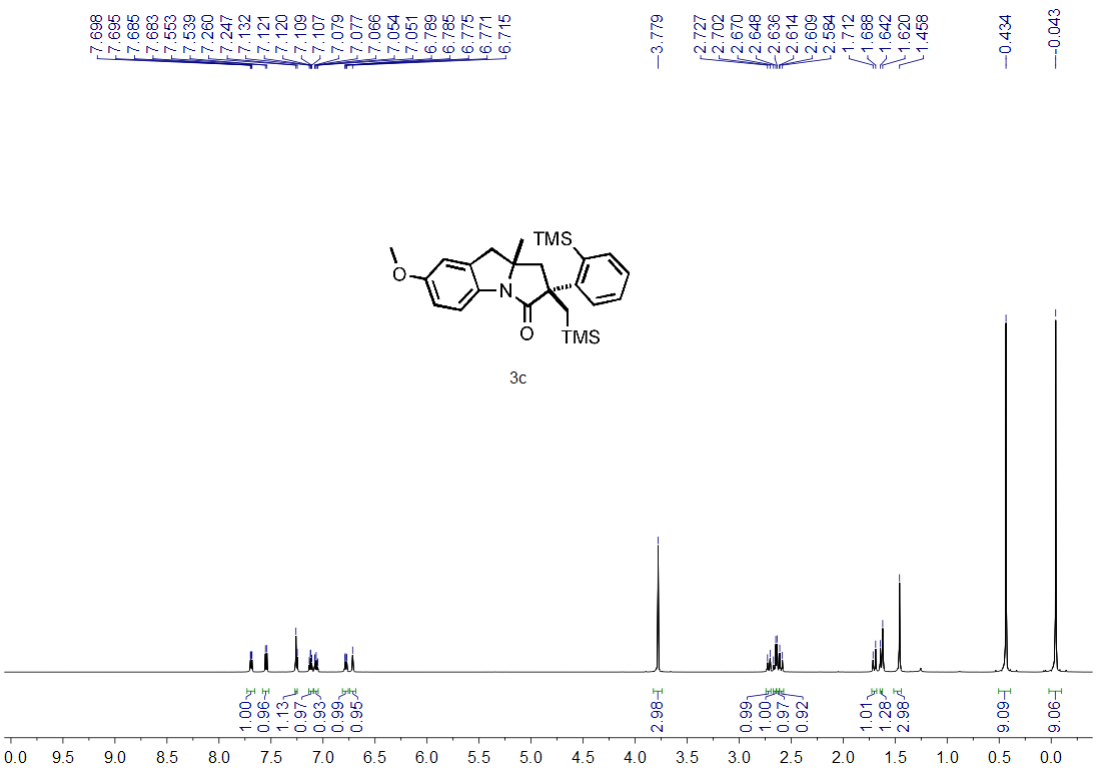
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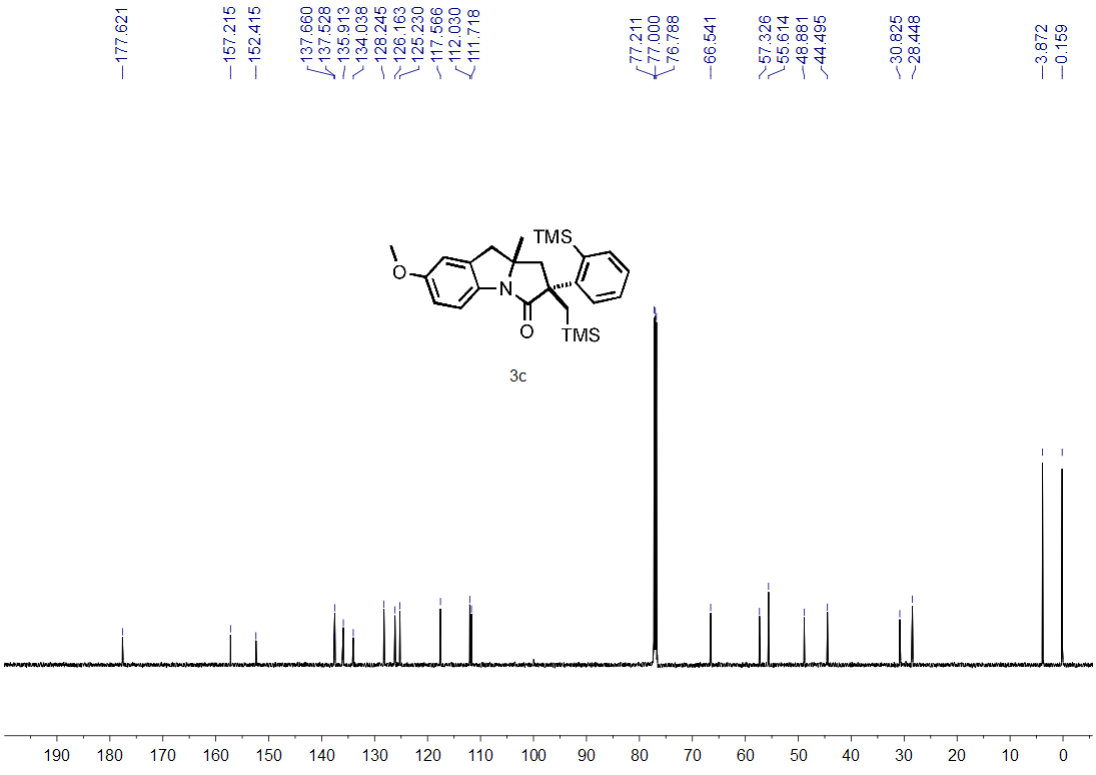
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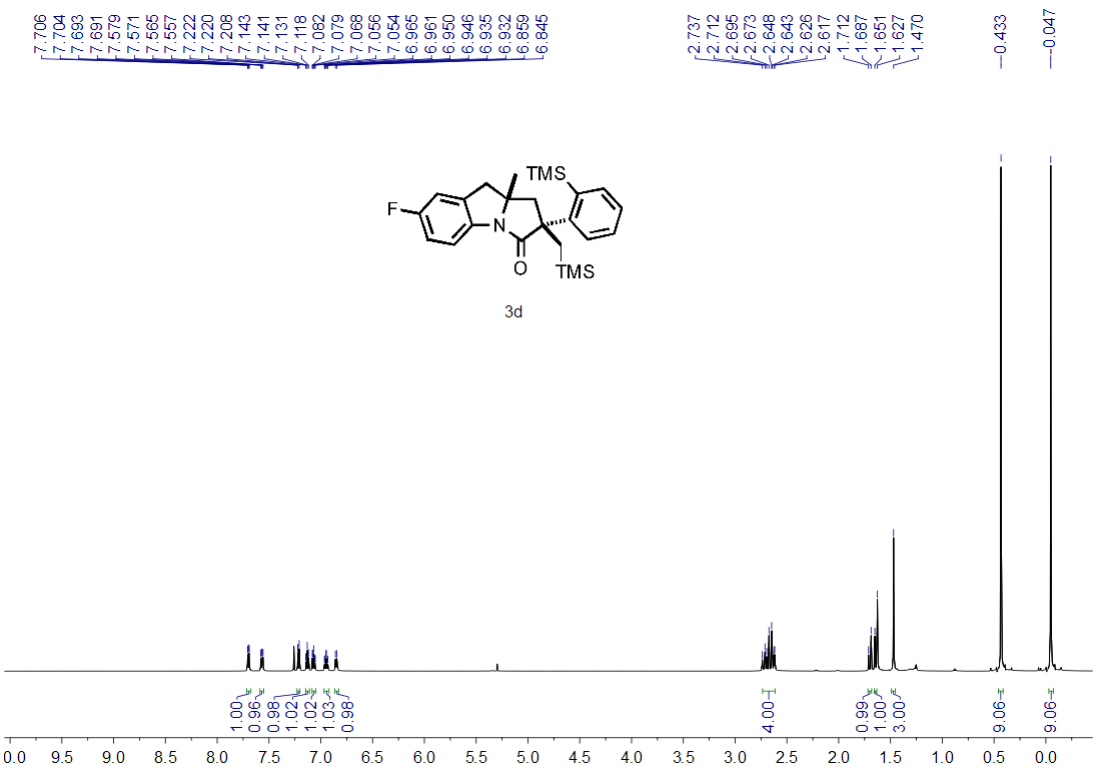
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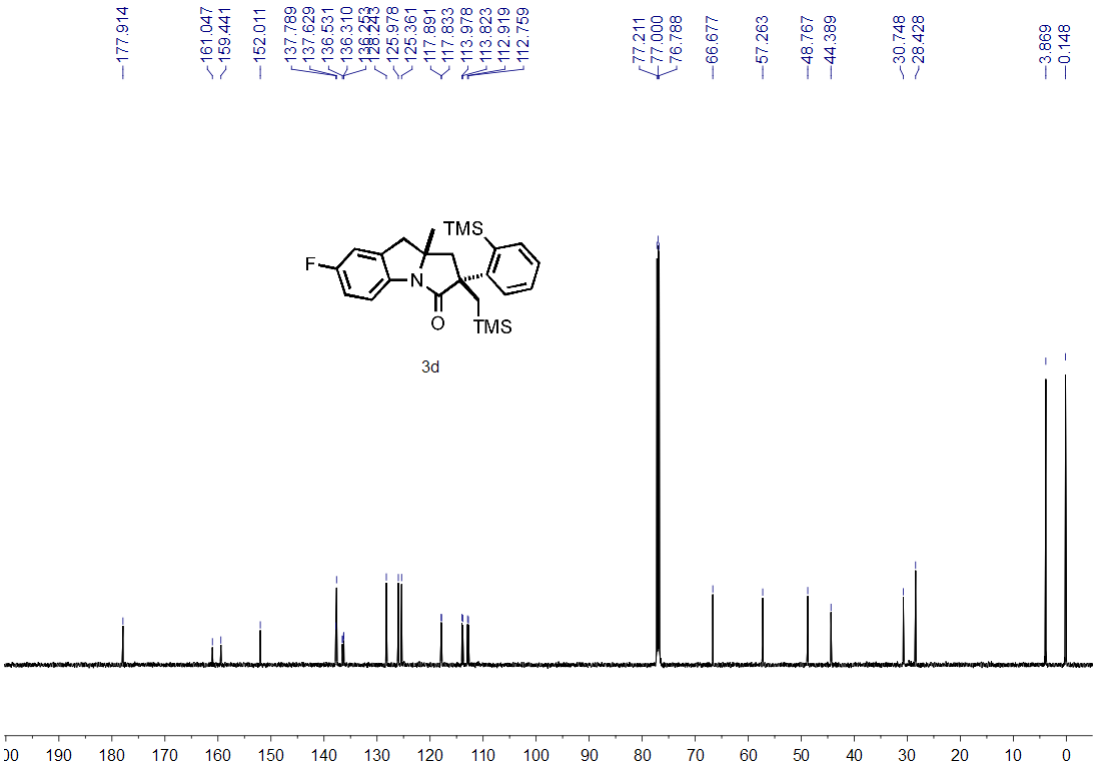
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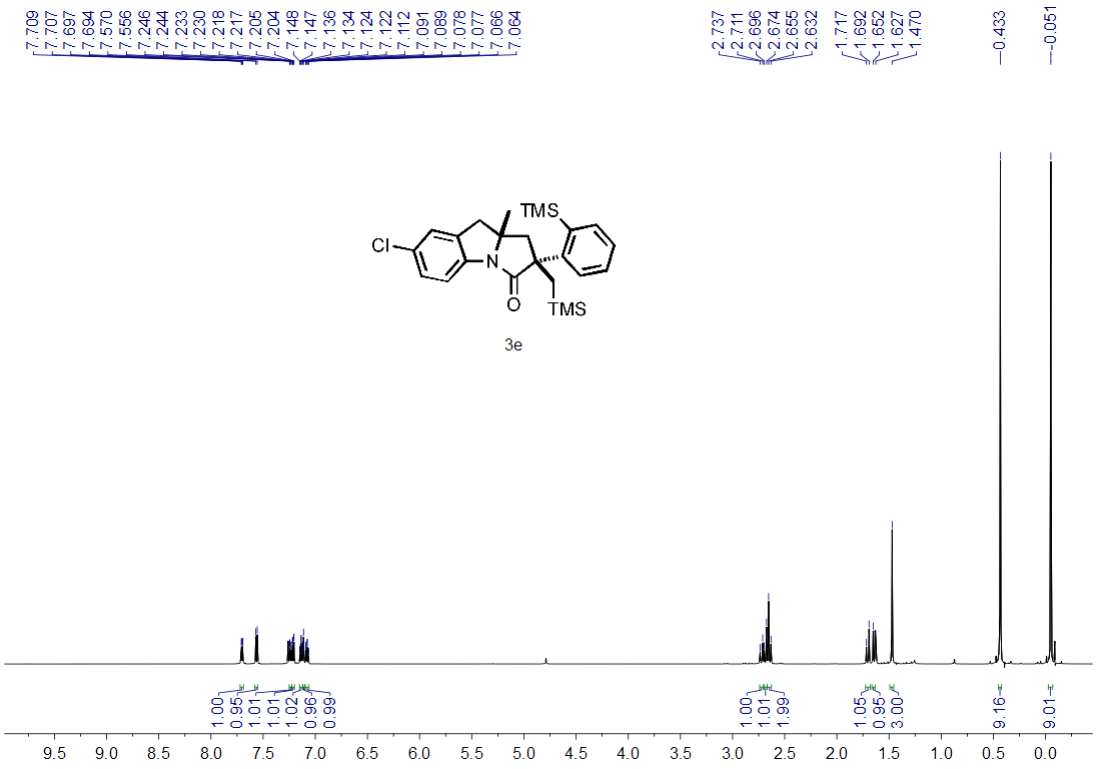
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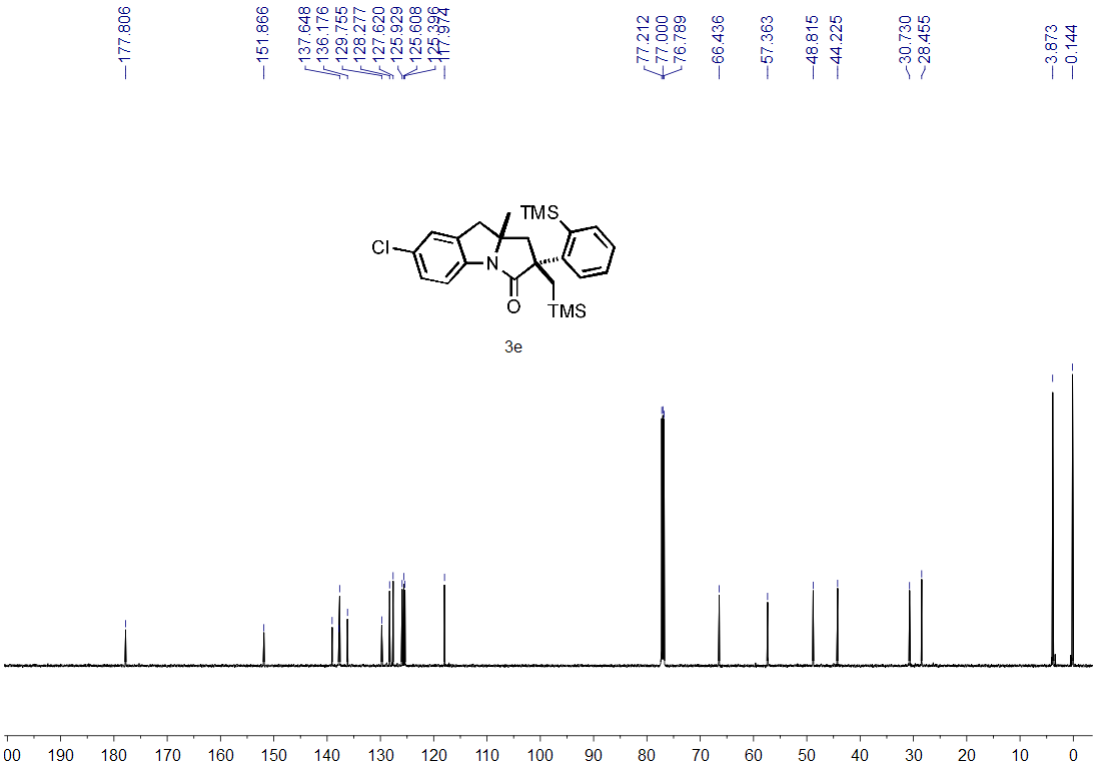
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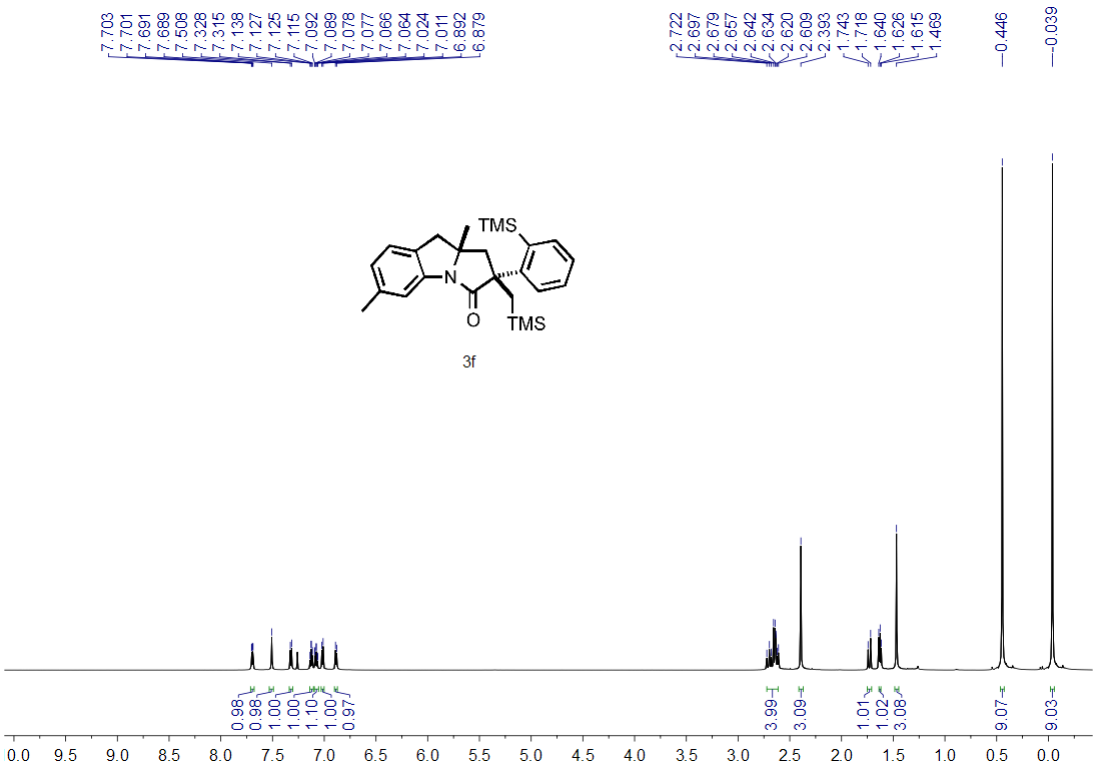
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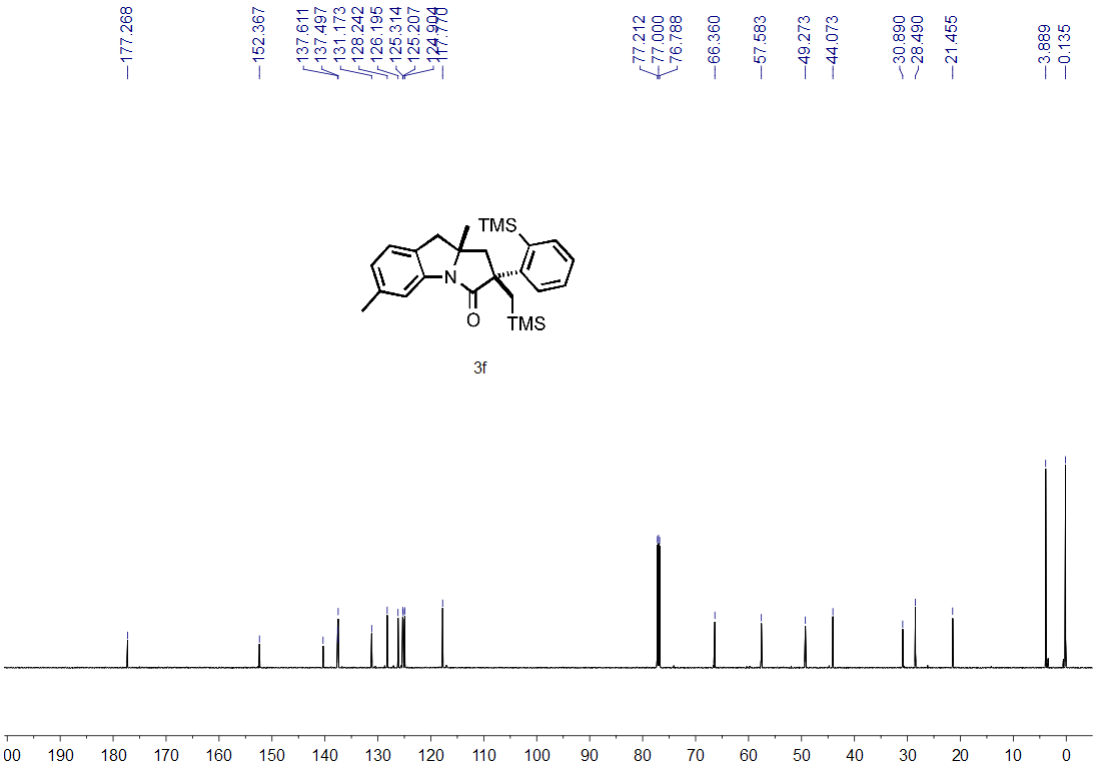
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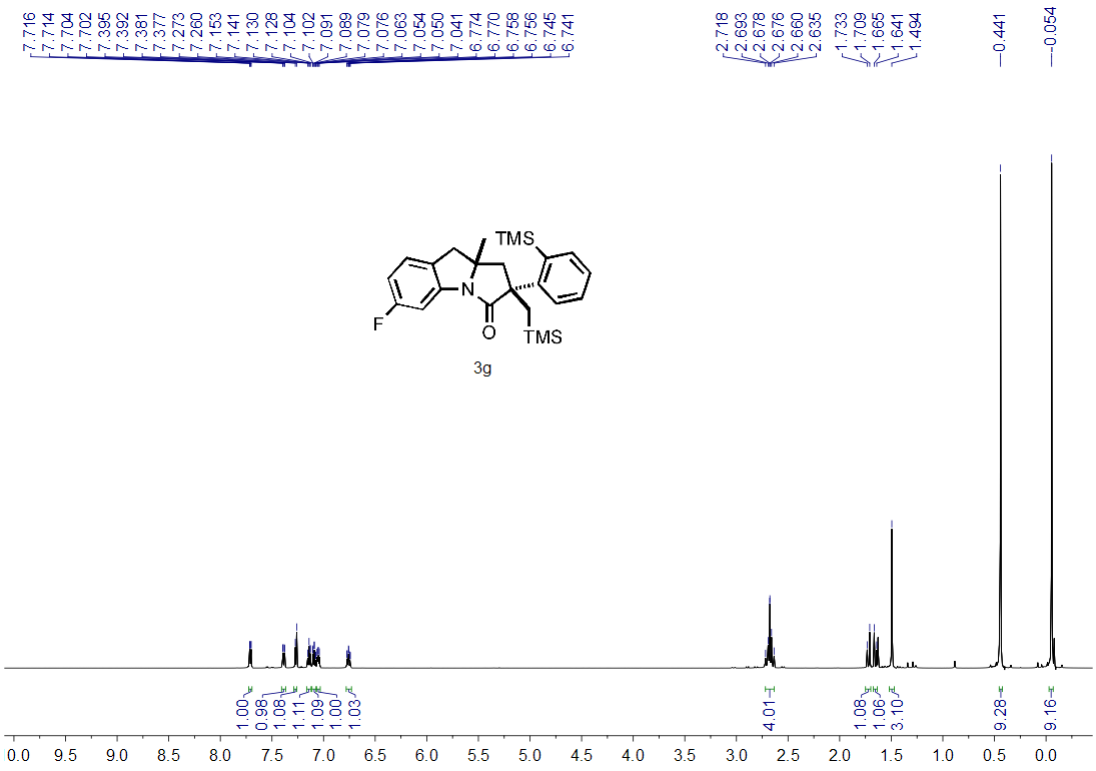
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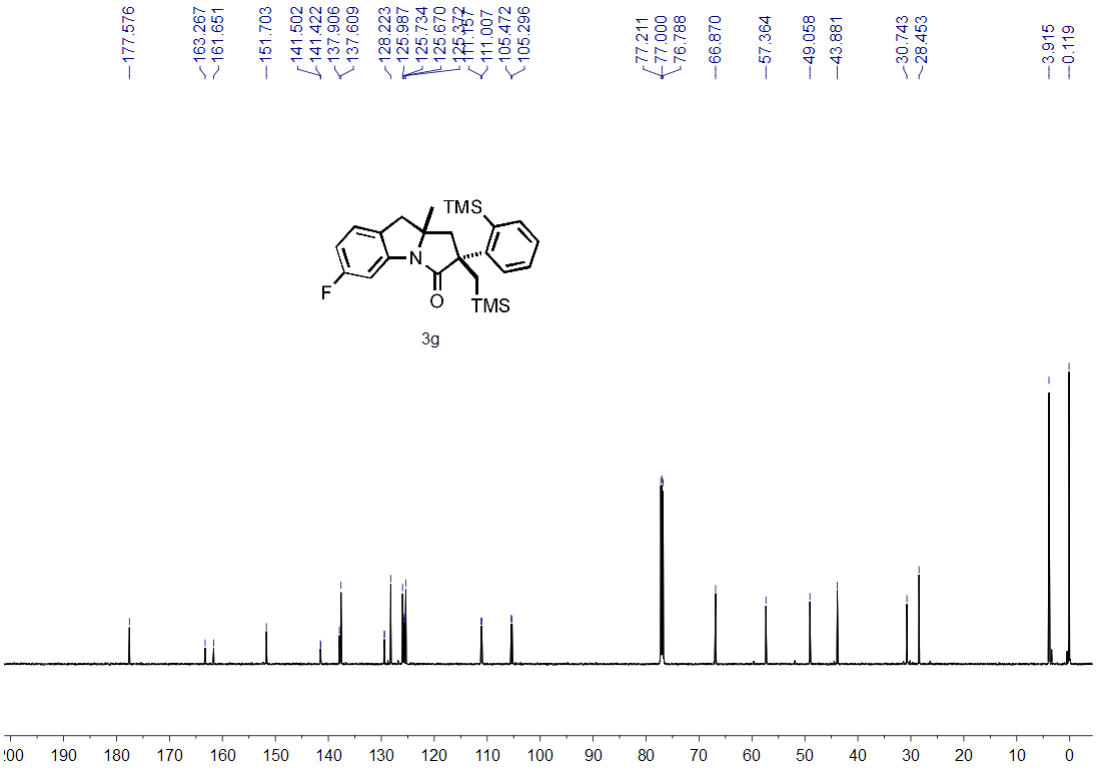
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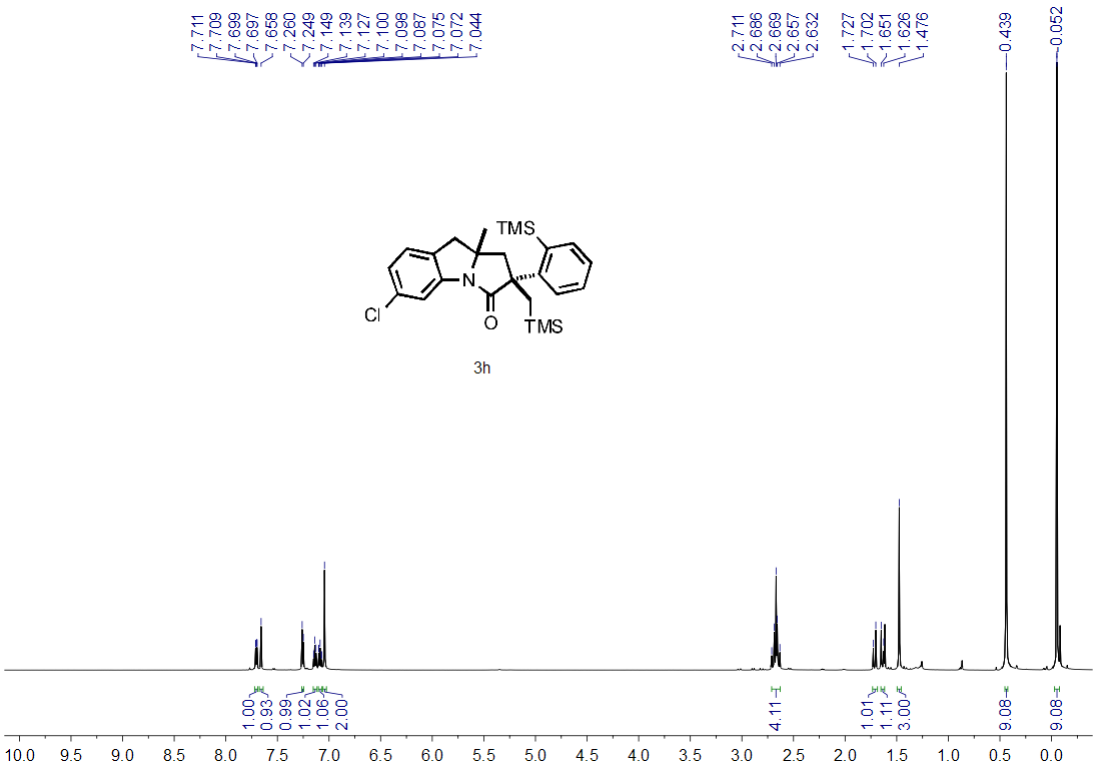
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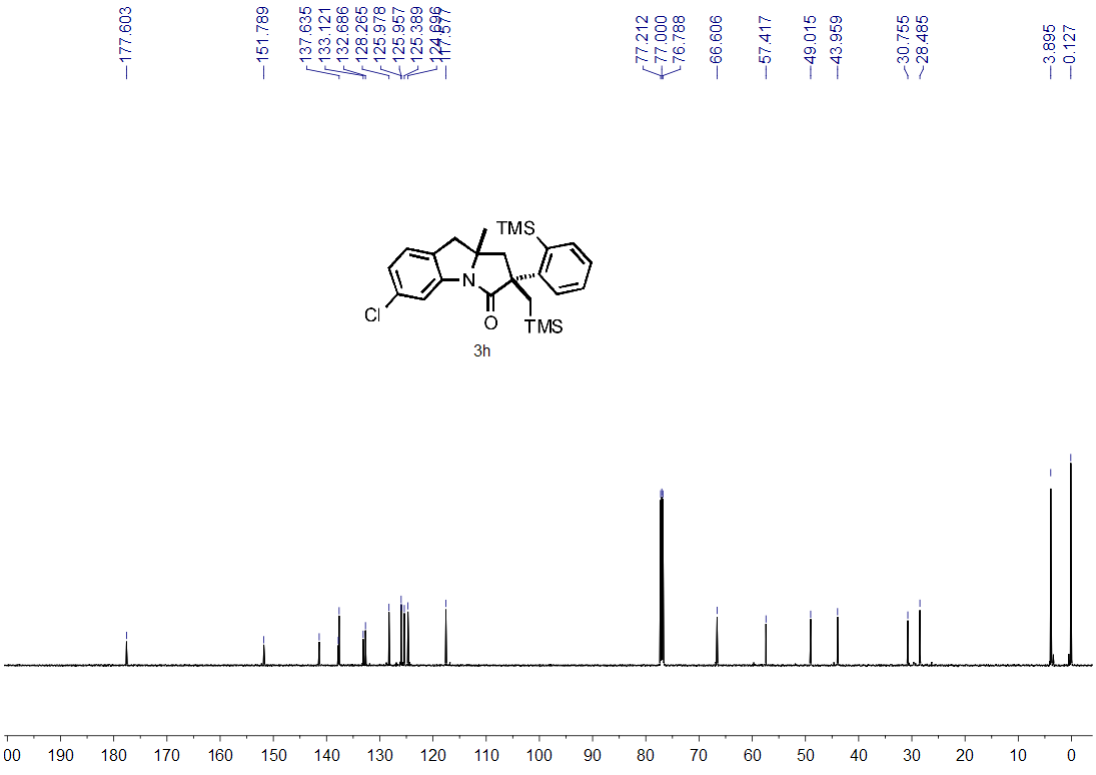
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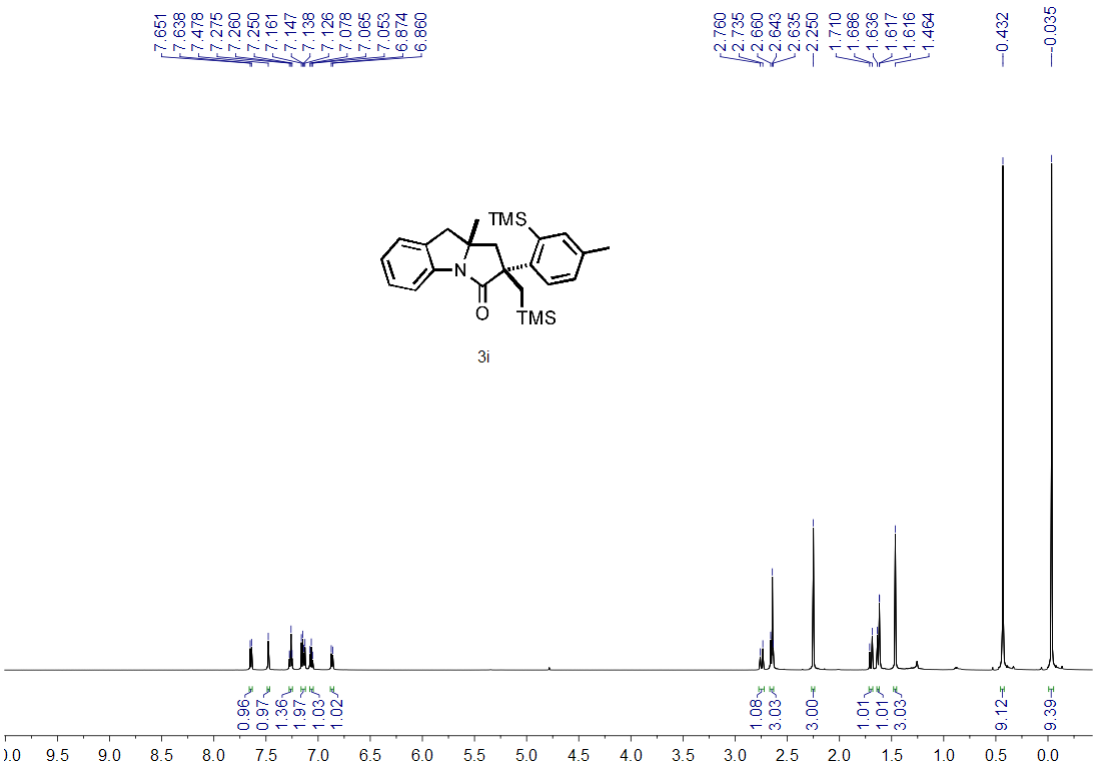
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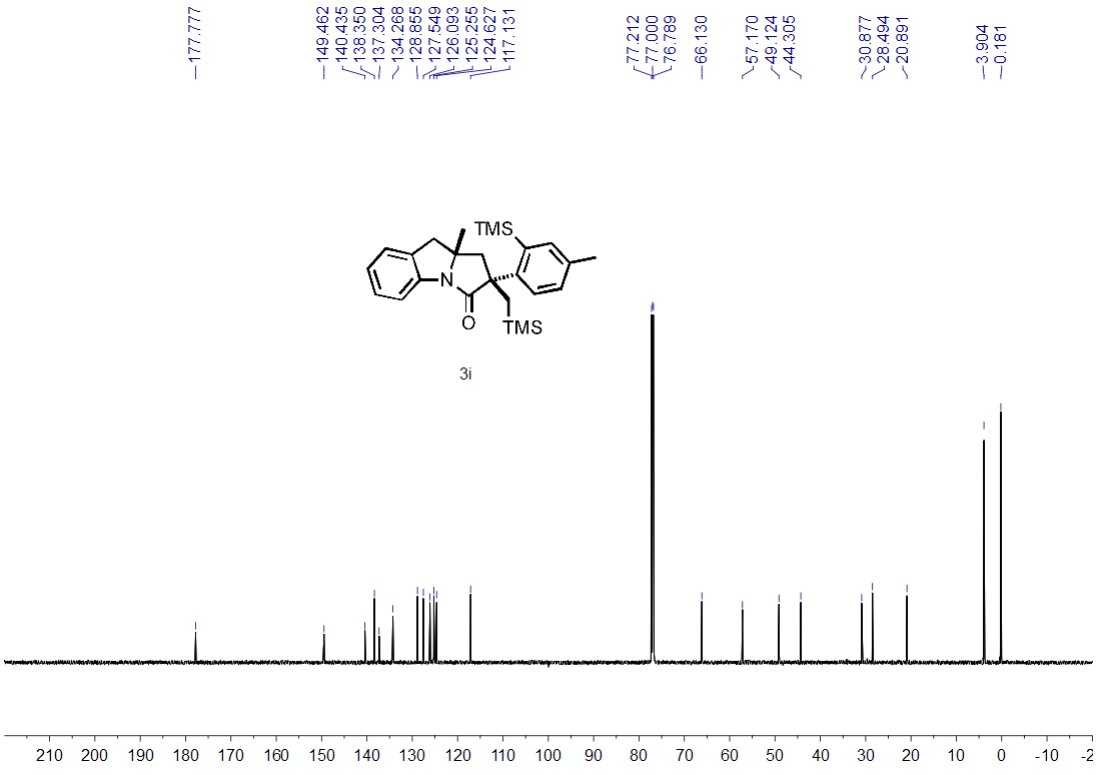
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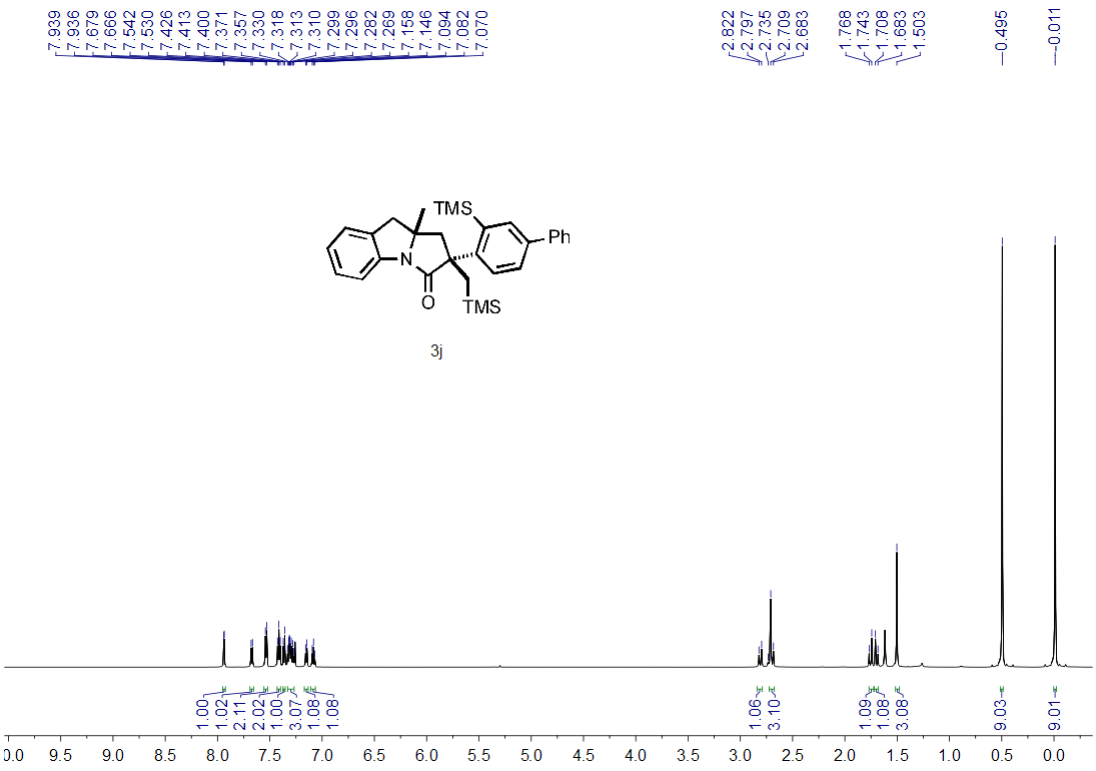
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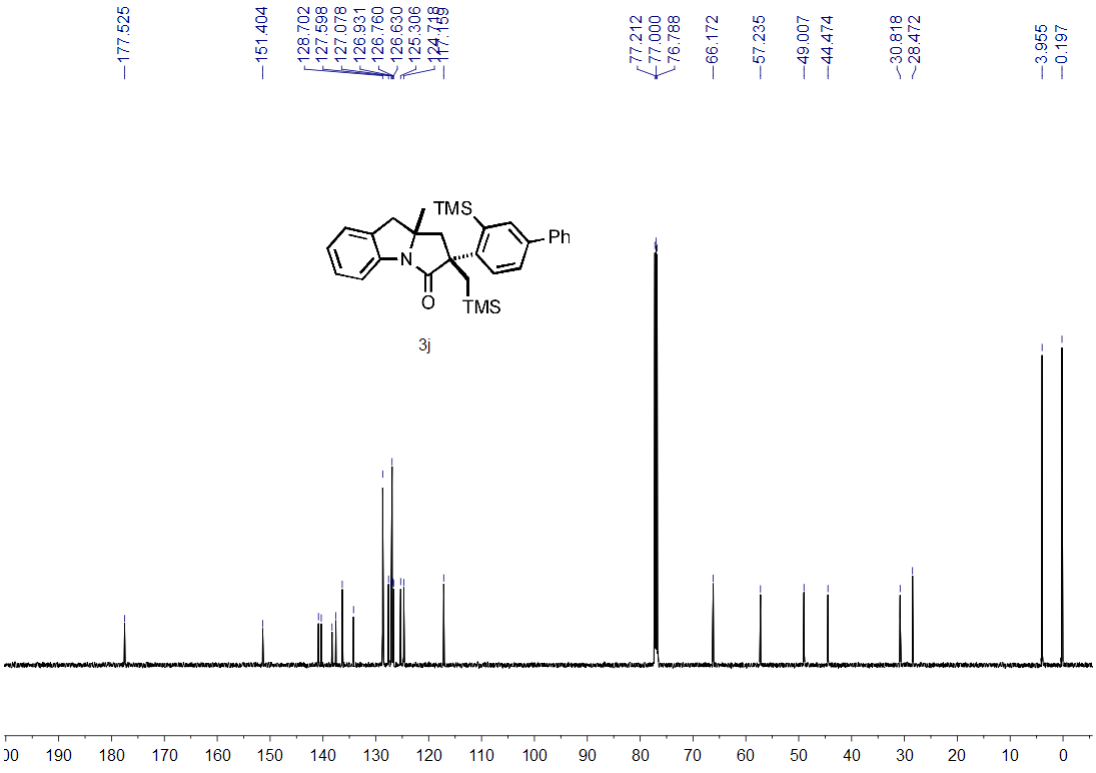
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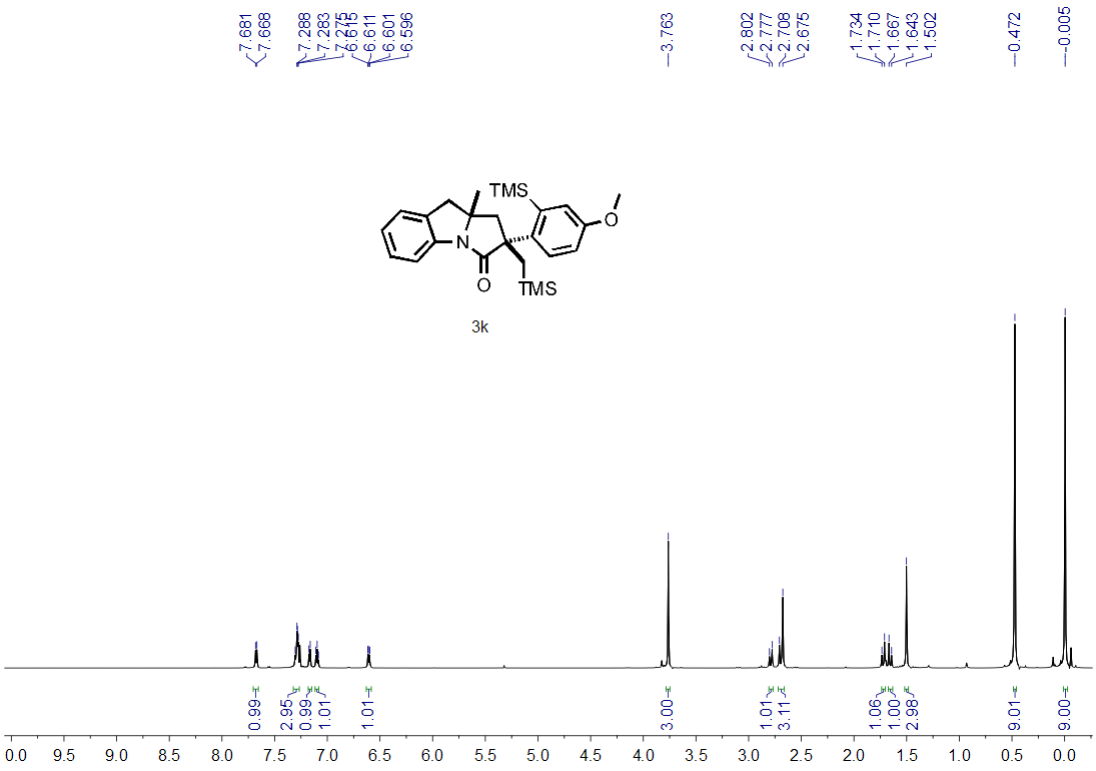
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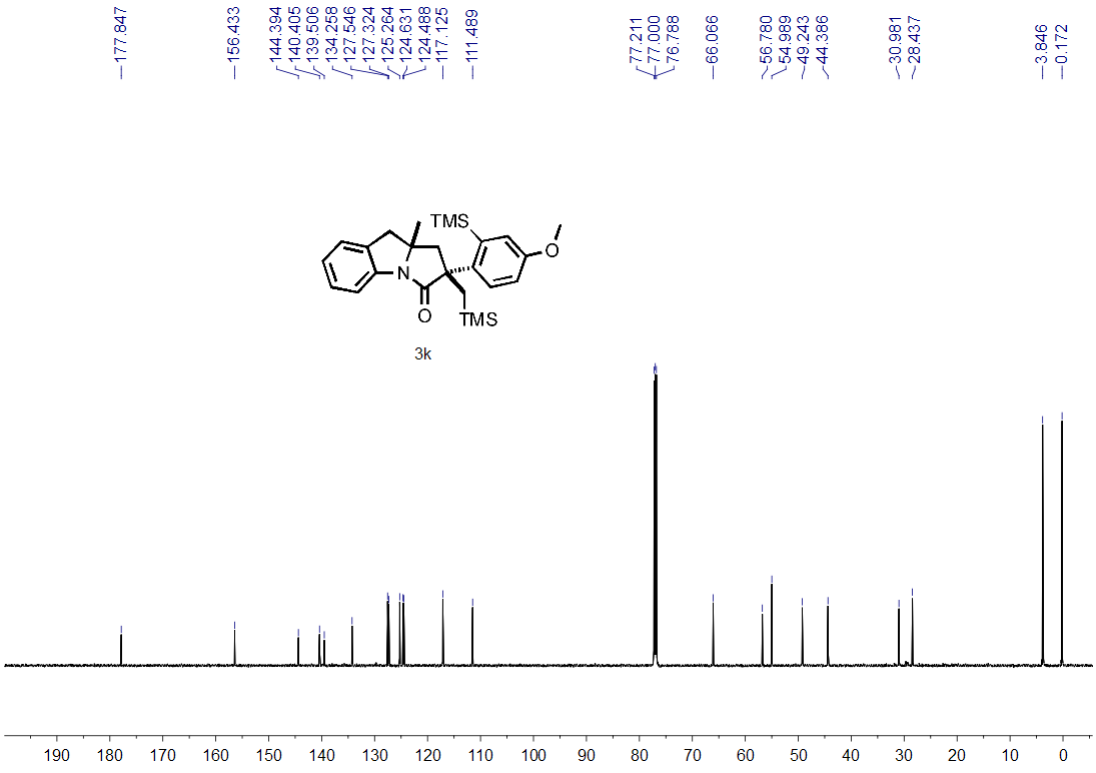
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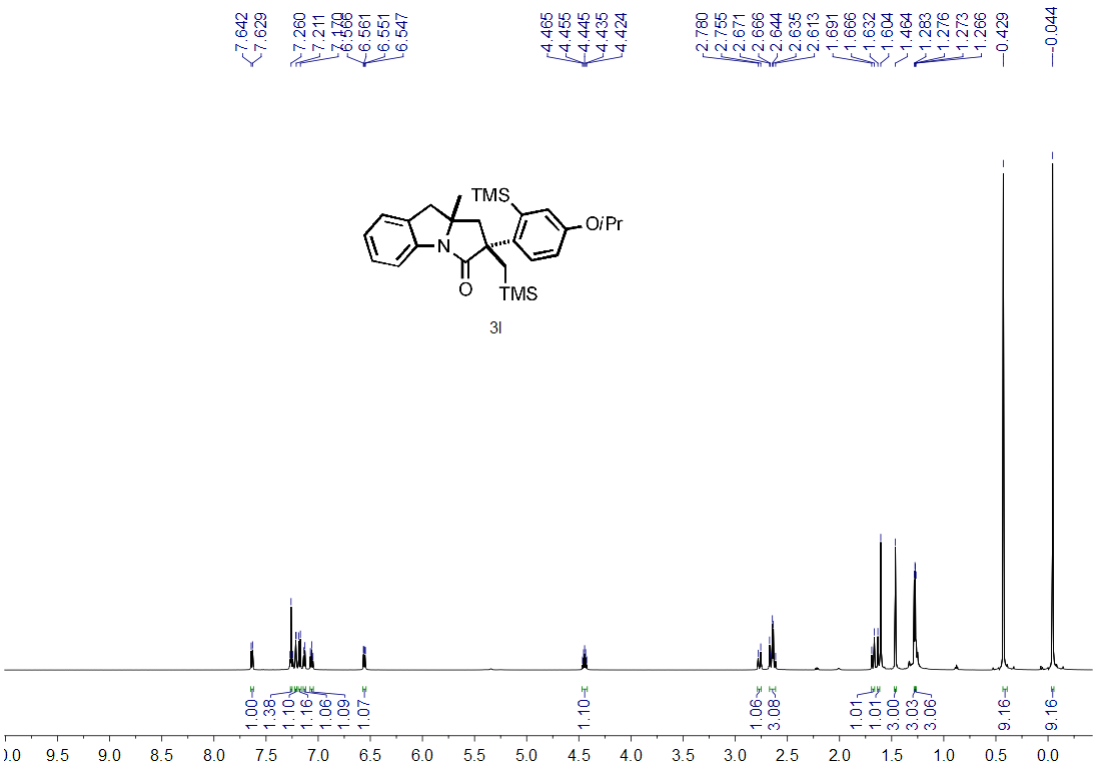
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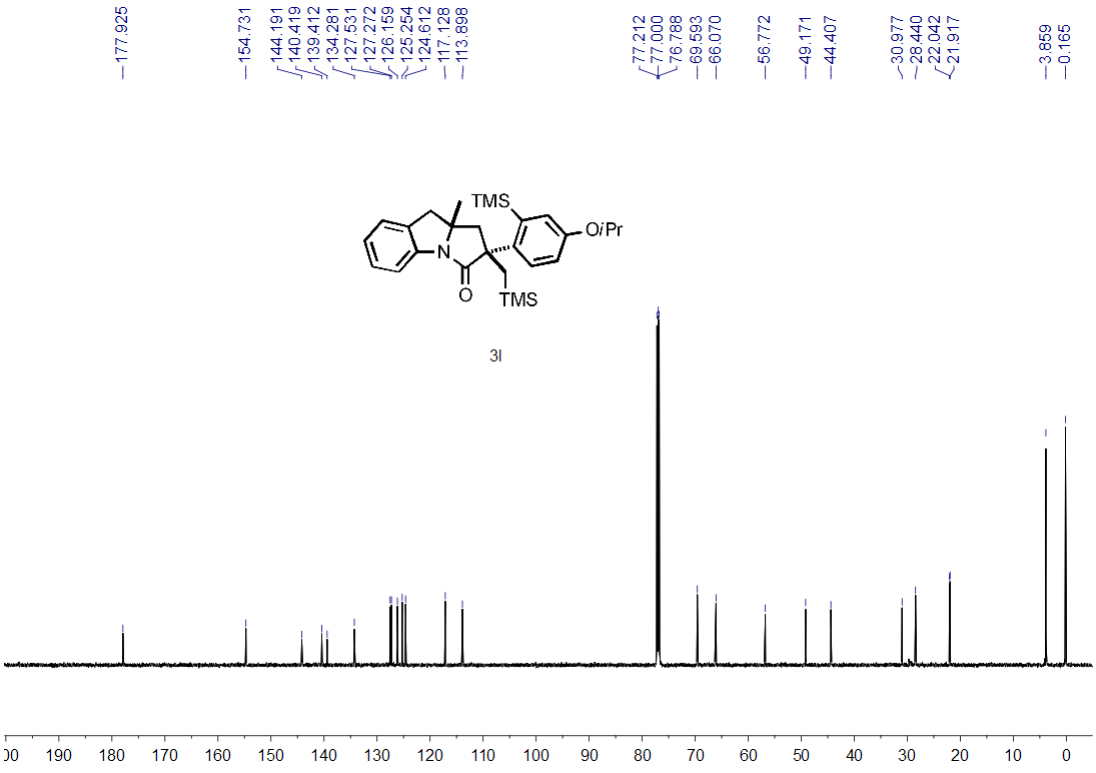
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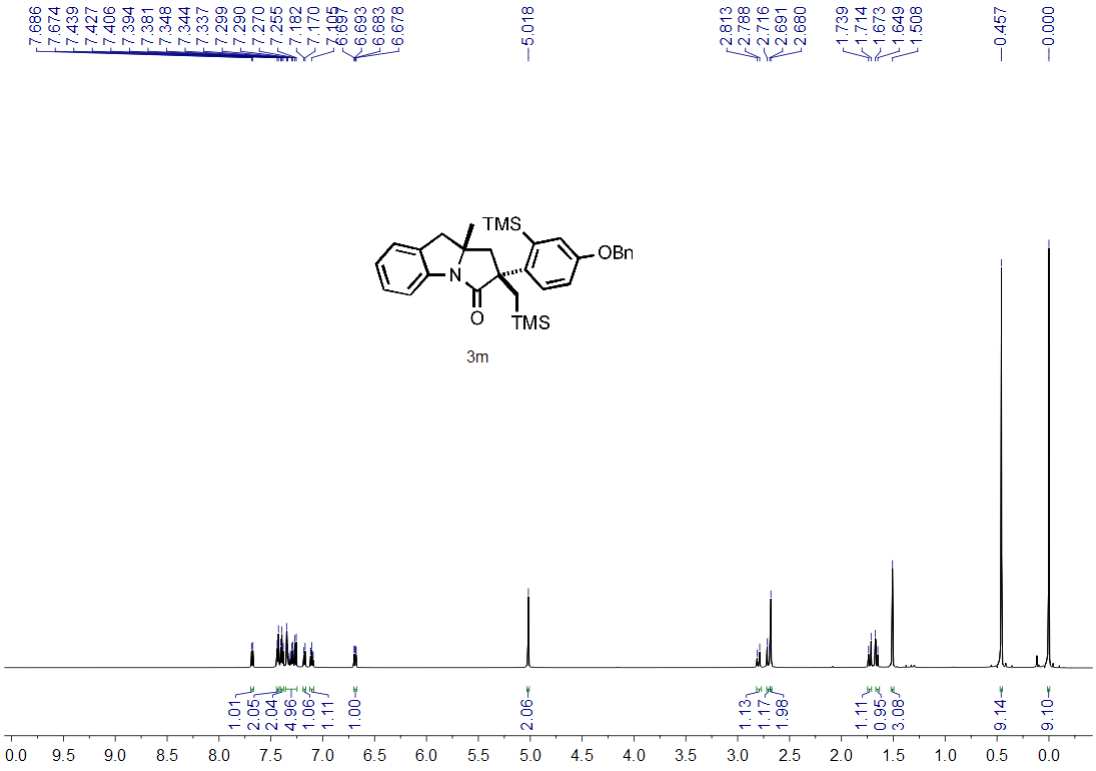
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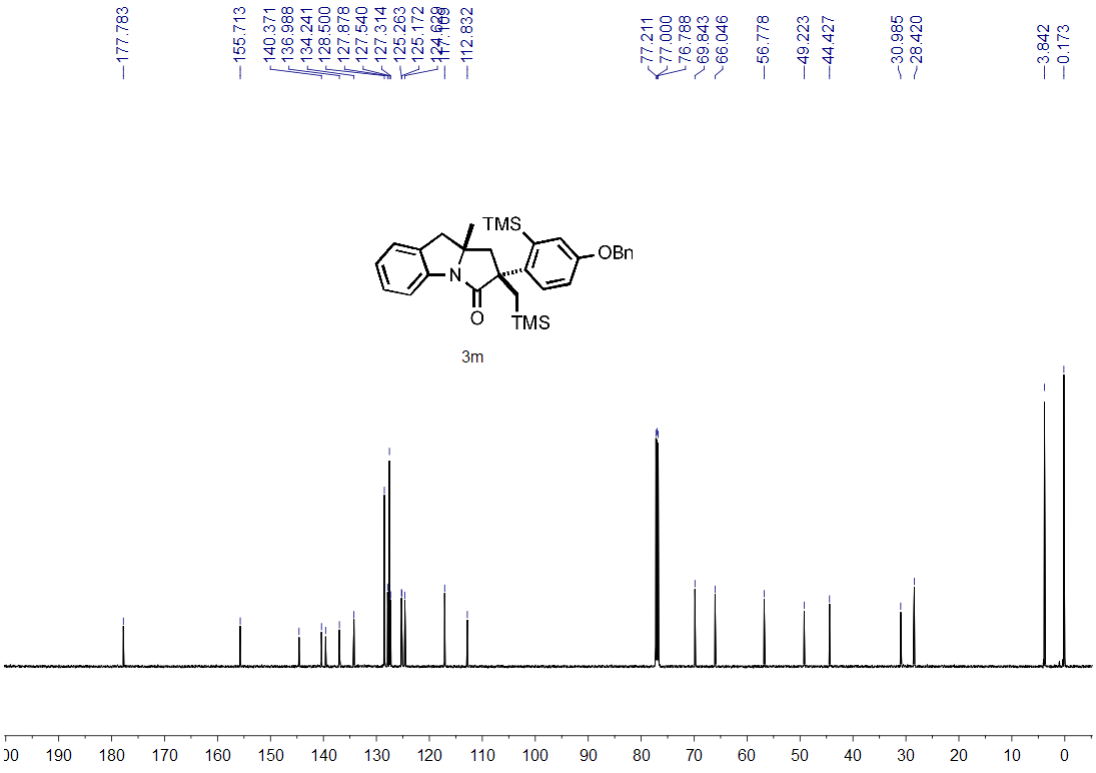
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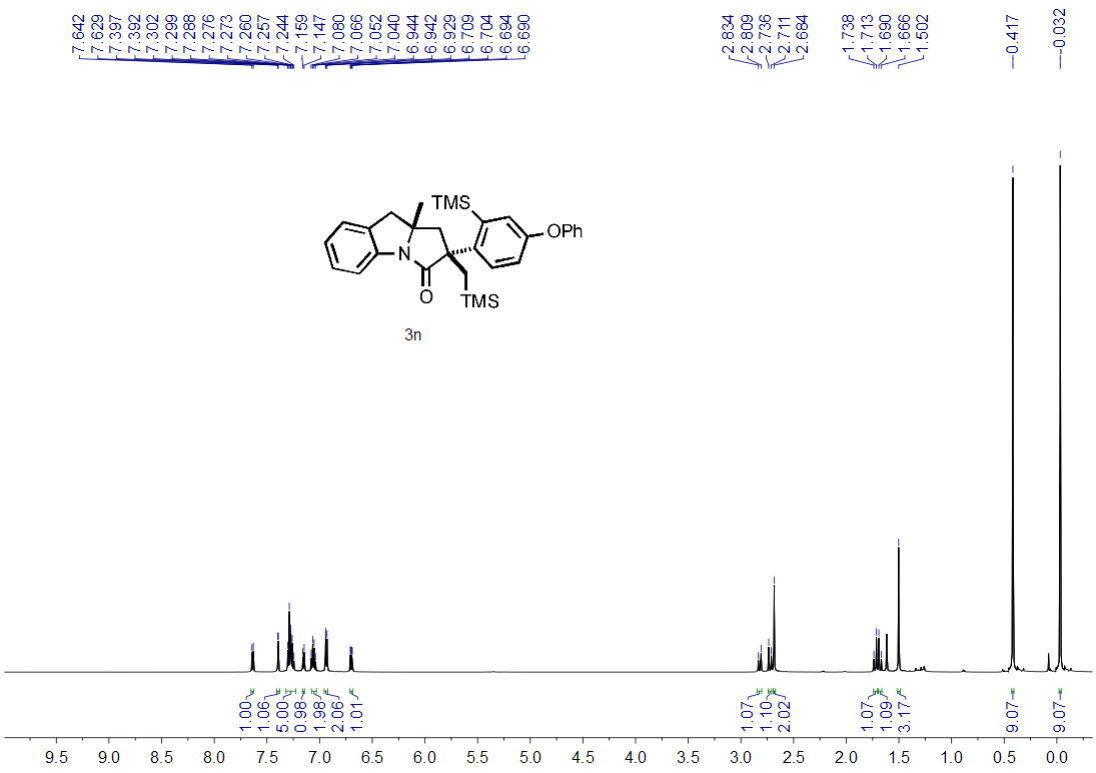
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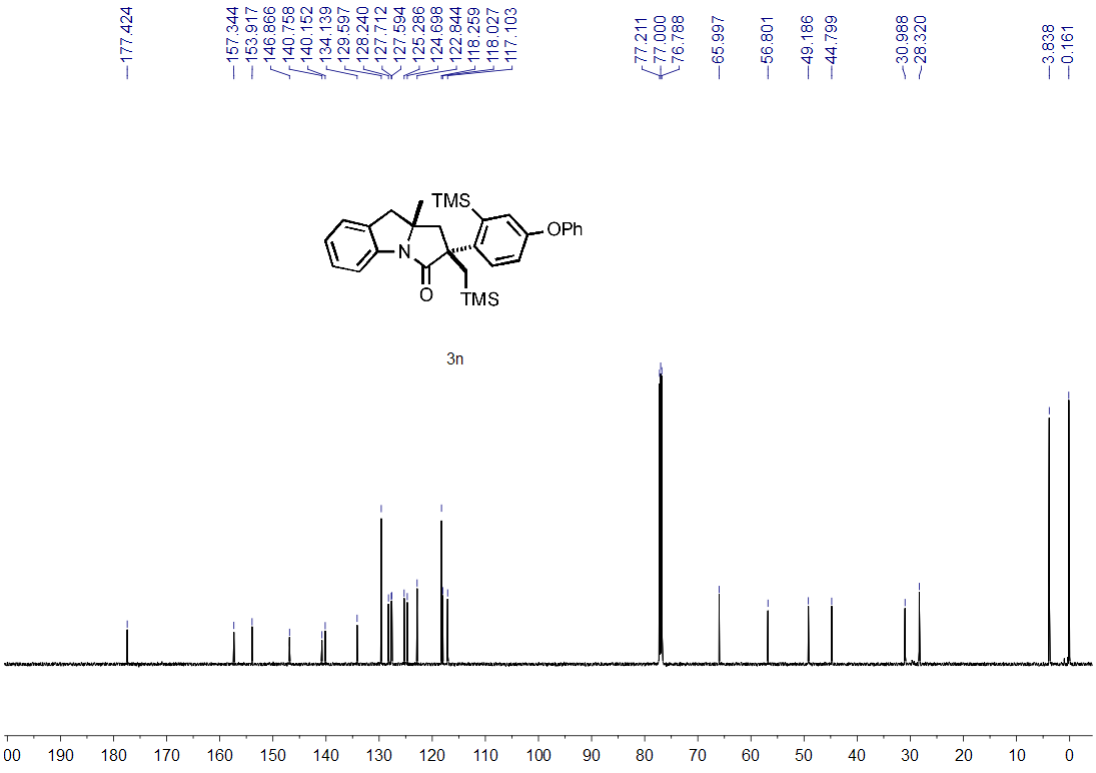
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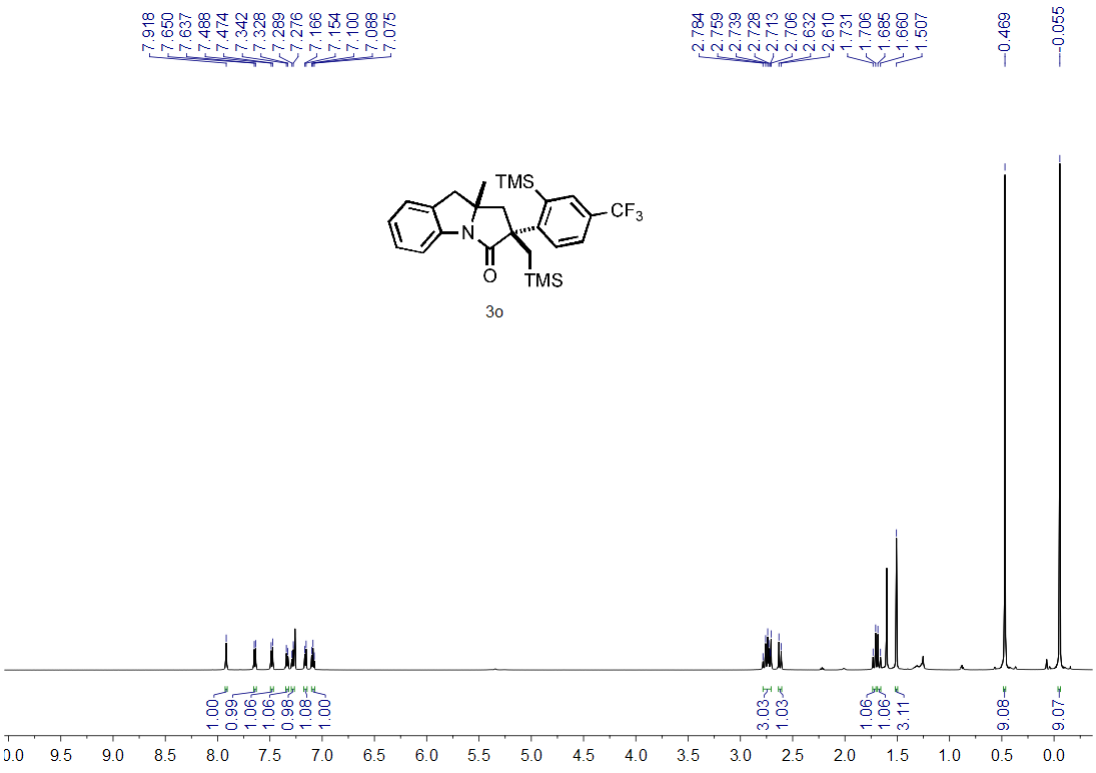
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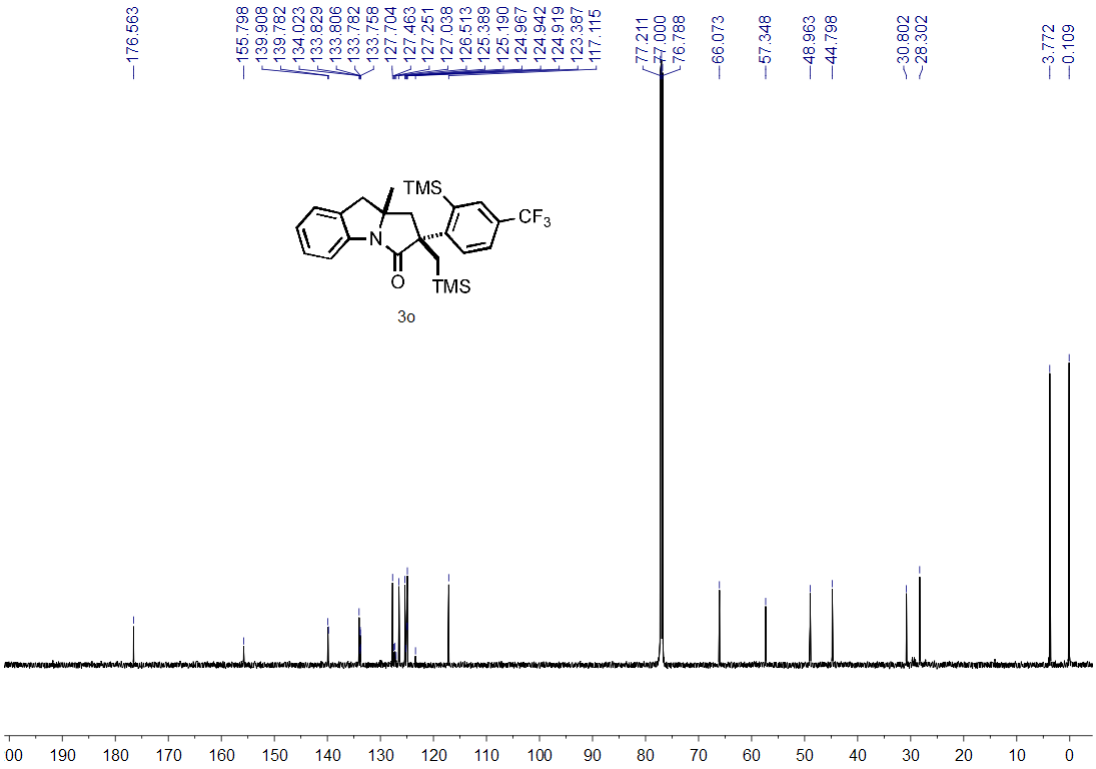
9.08
9.07
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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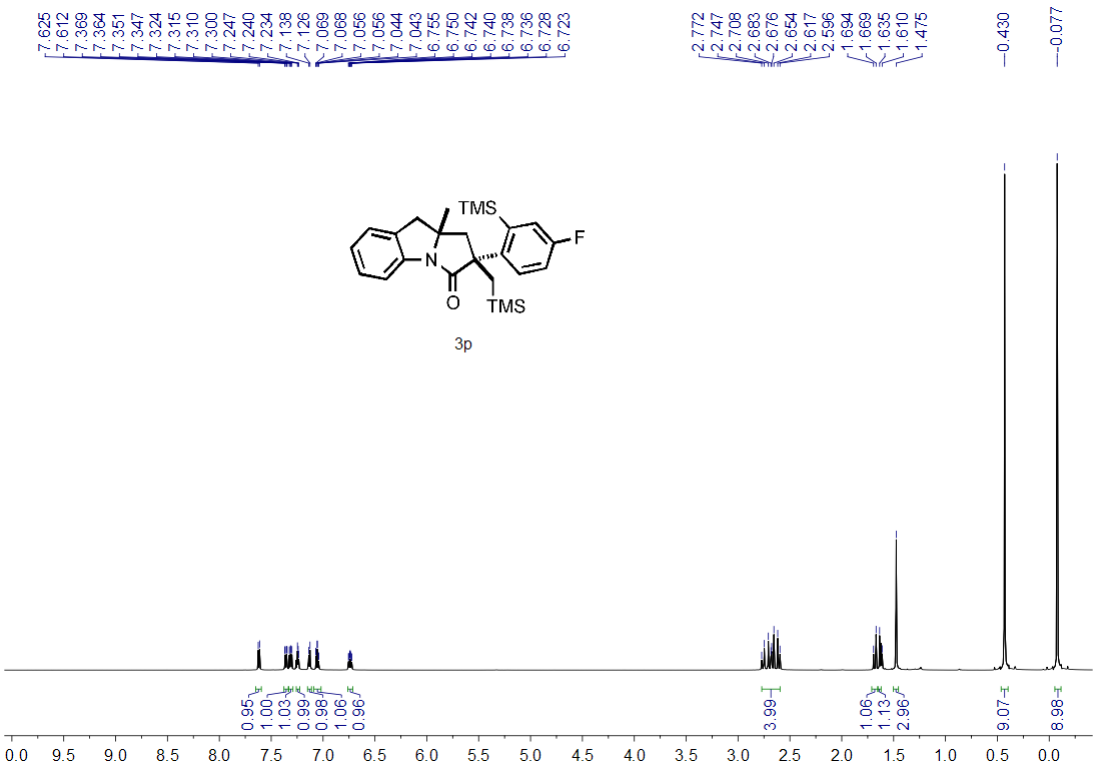
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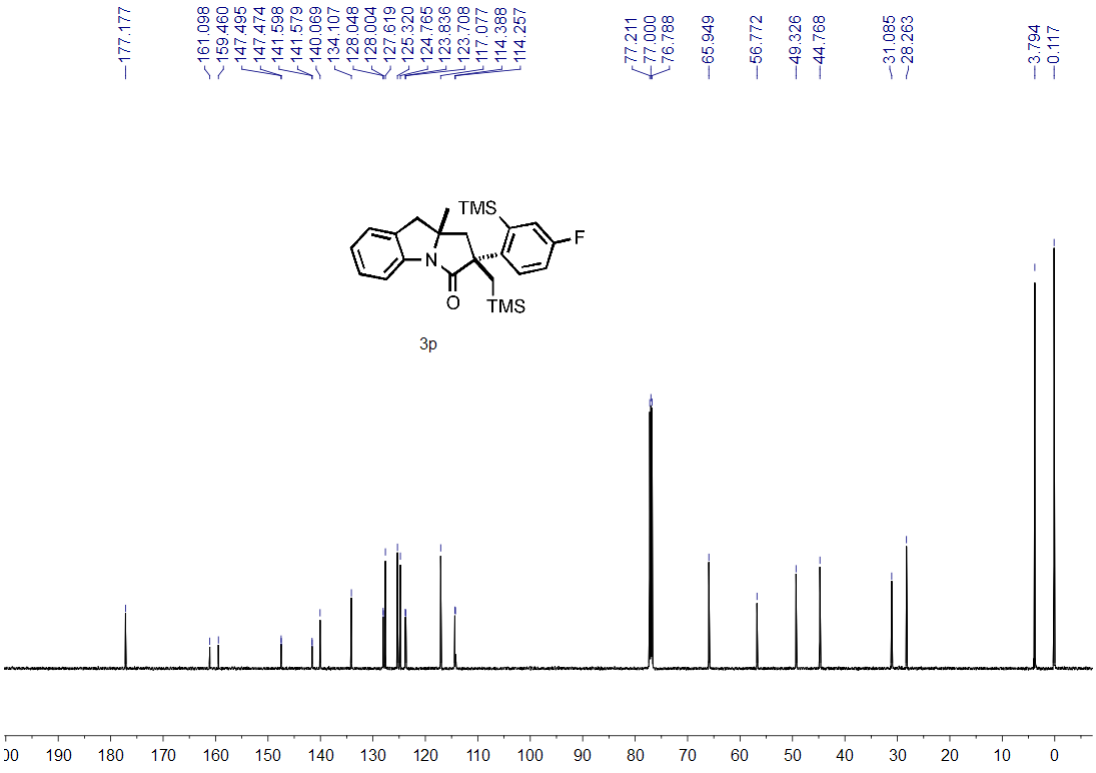
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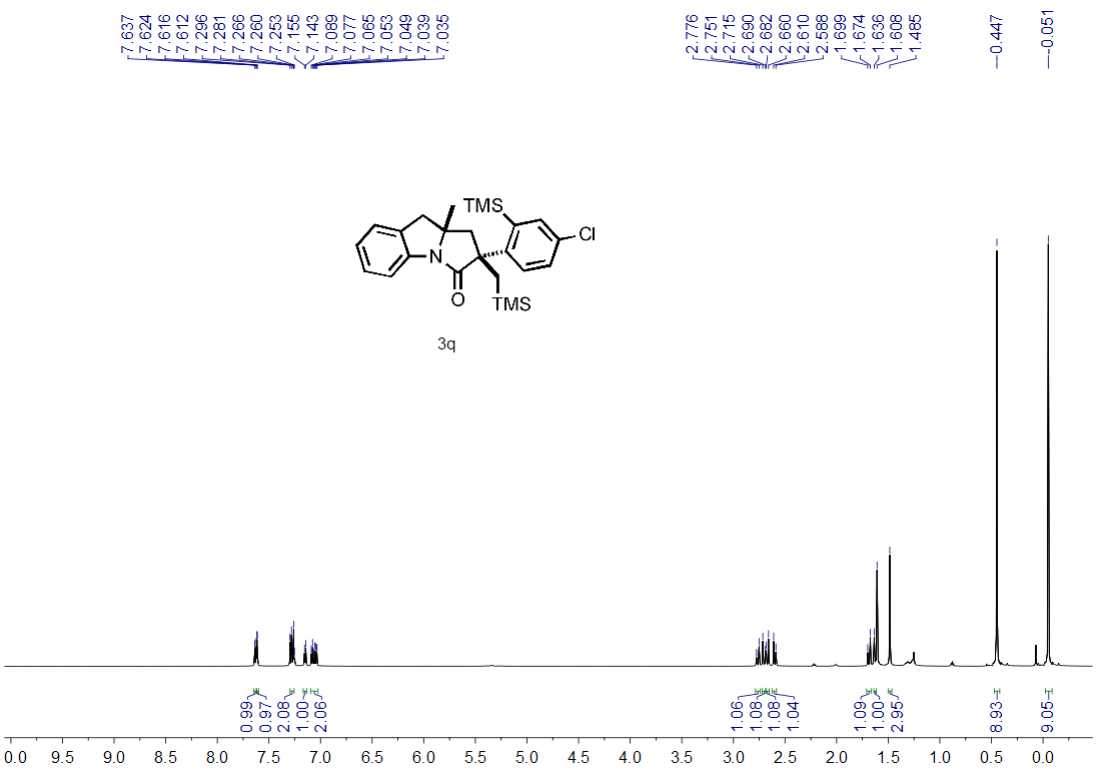
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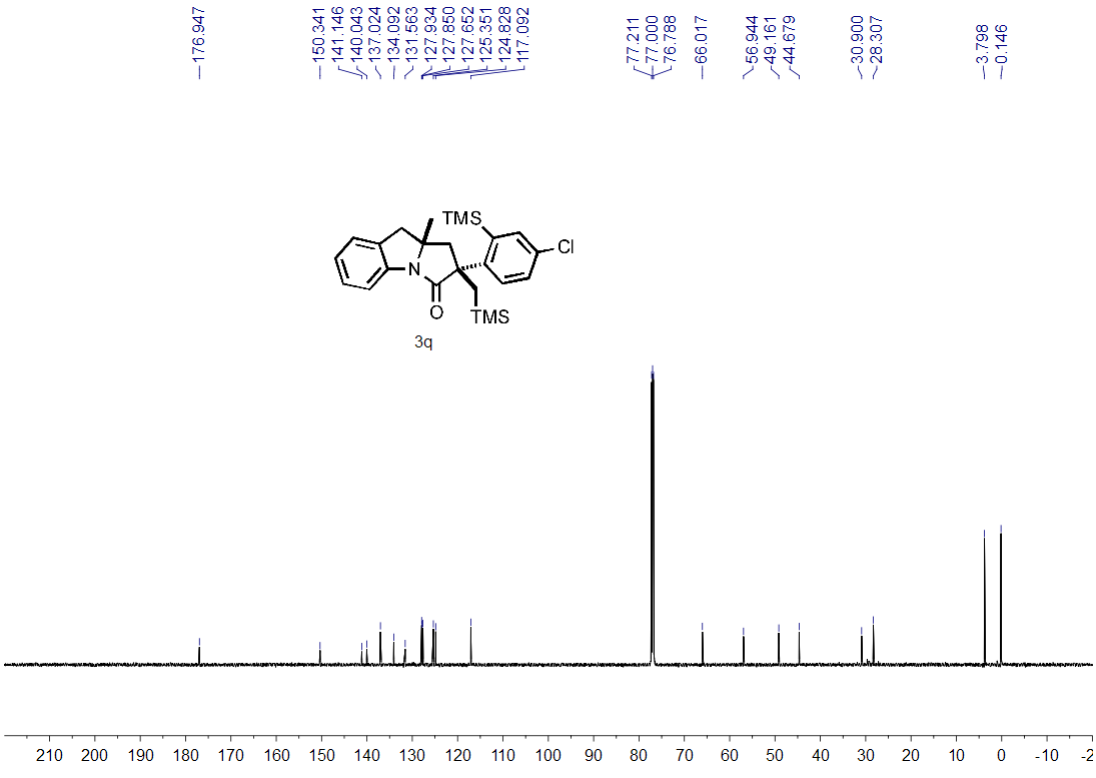
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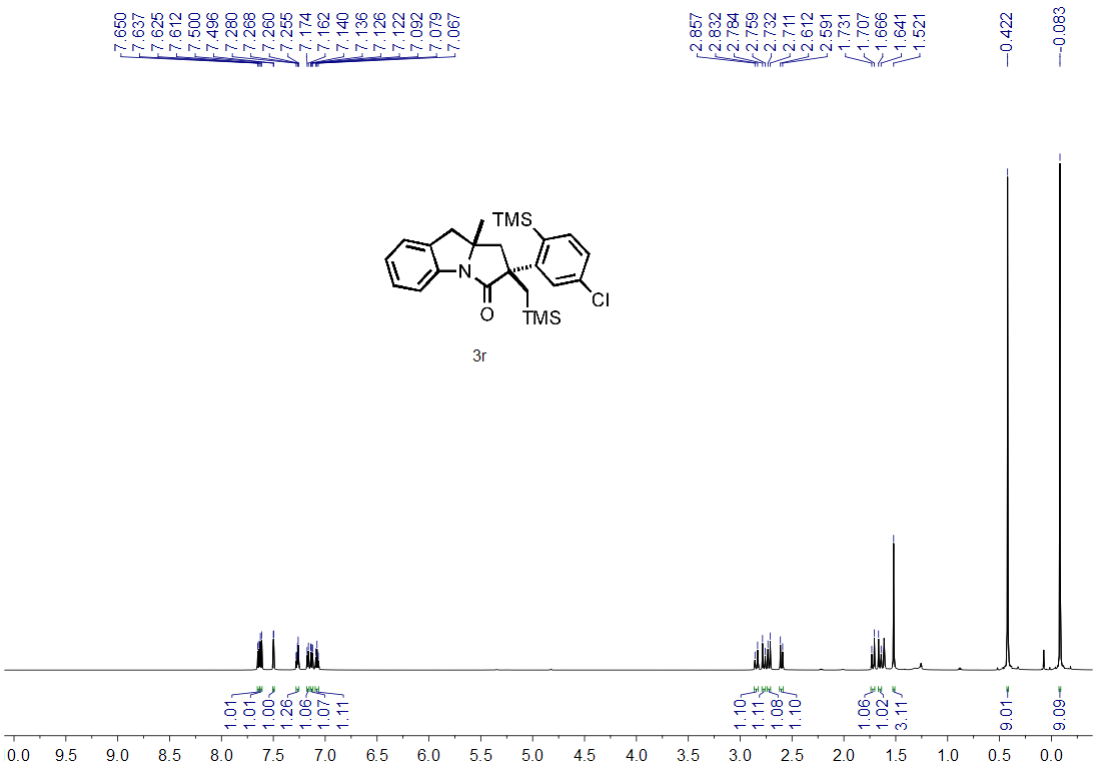
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1.08
1.10
1.06
1.02
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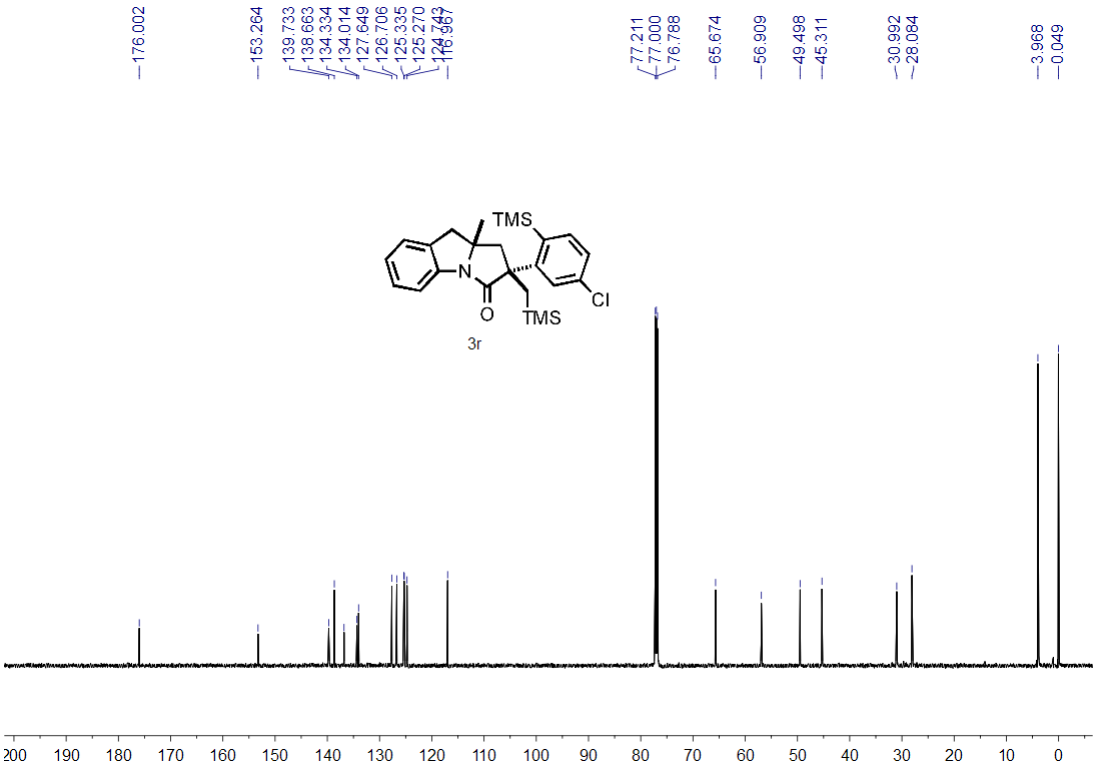
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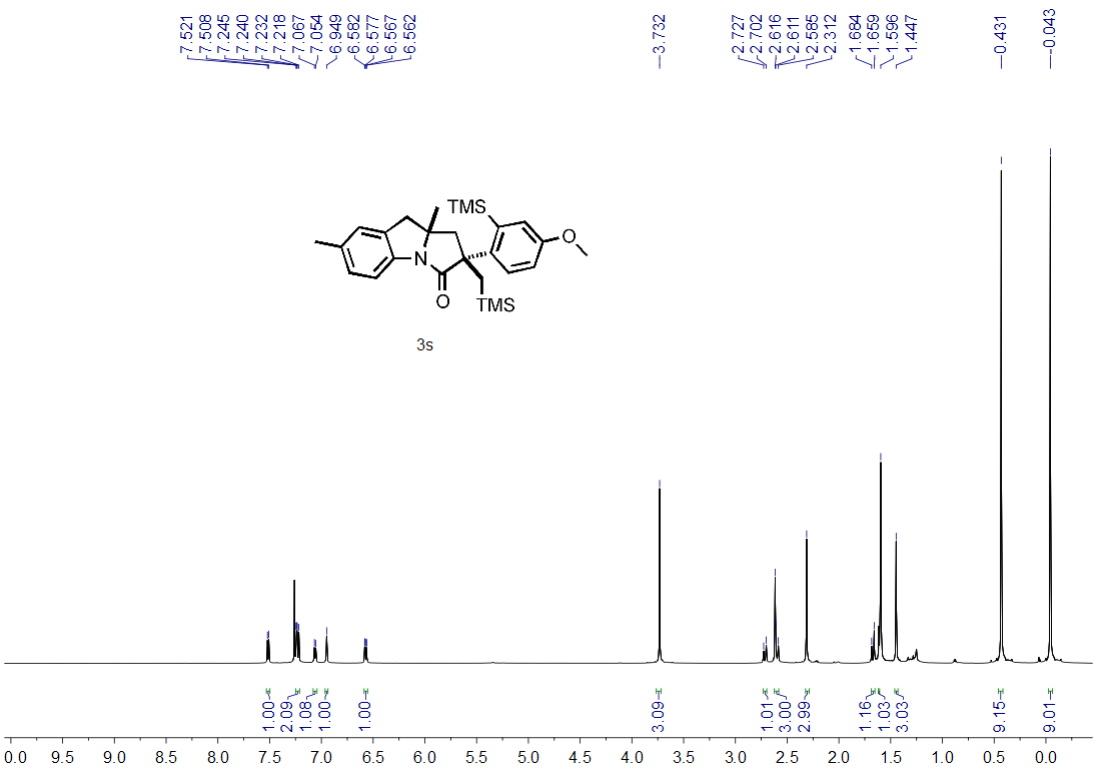
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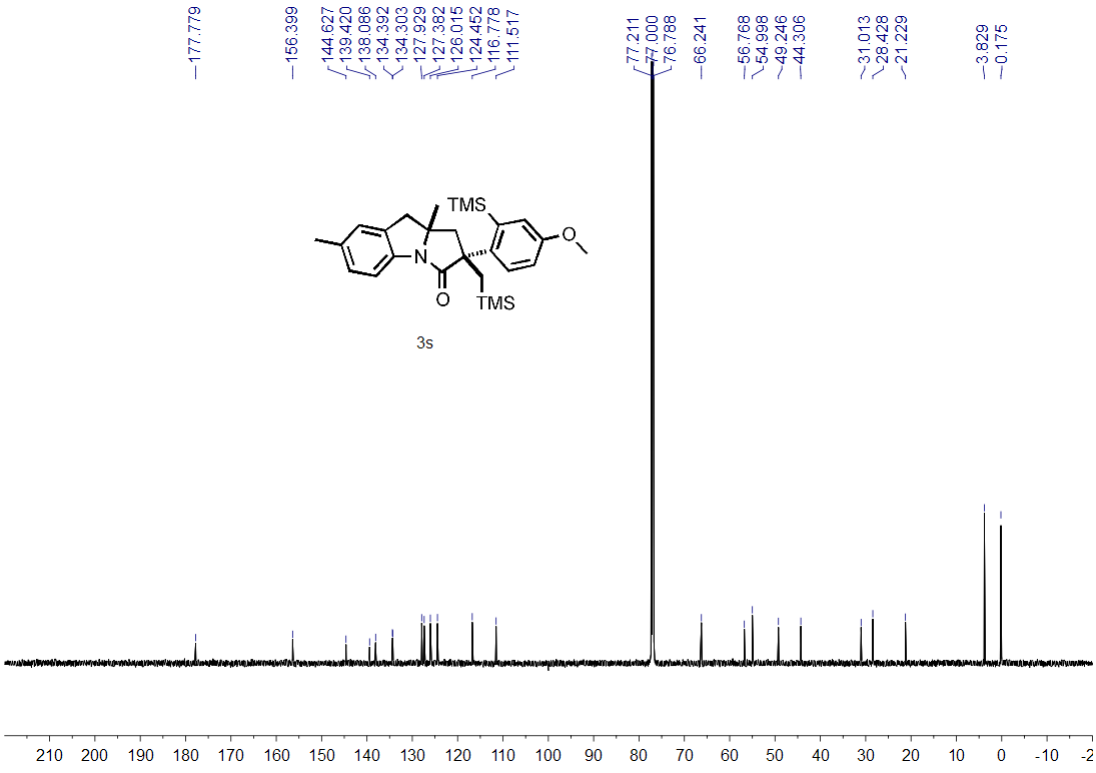
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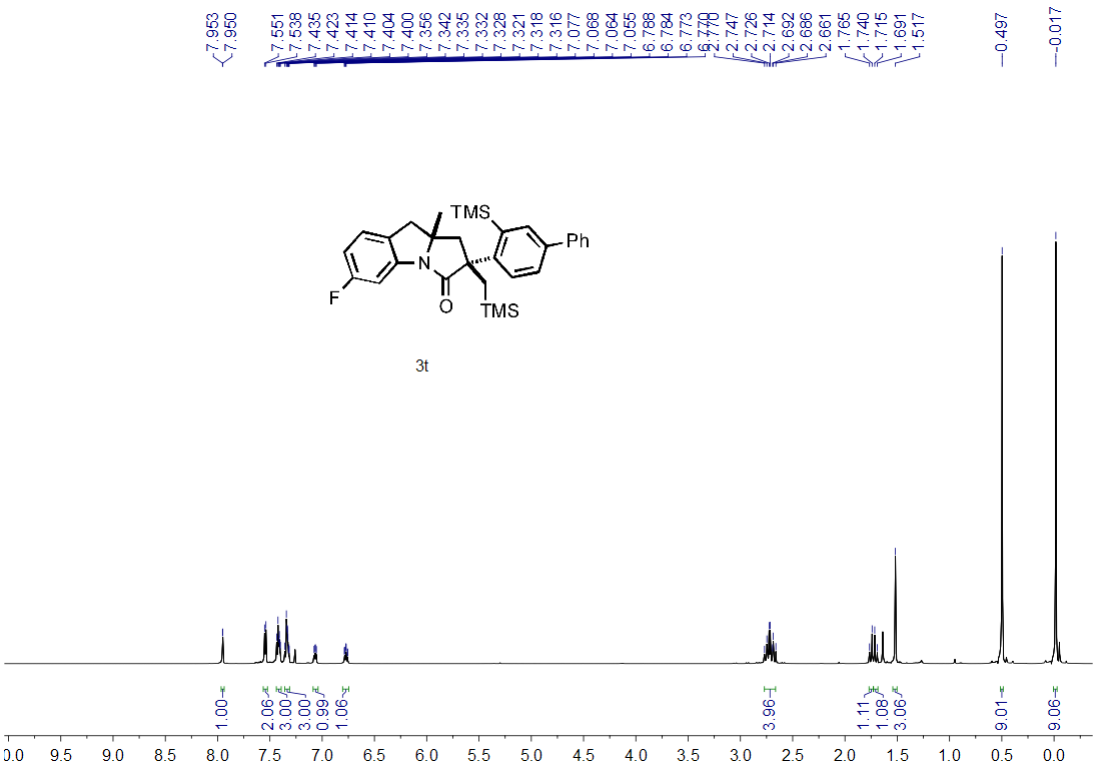
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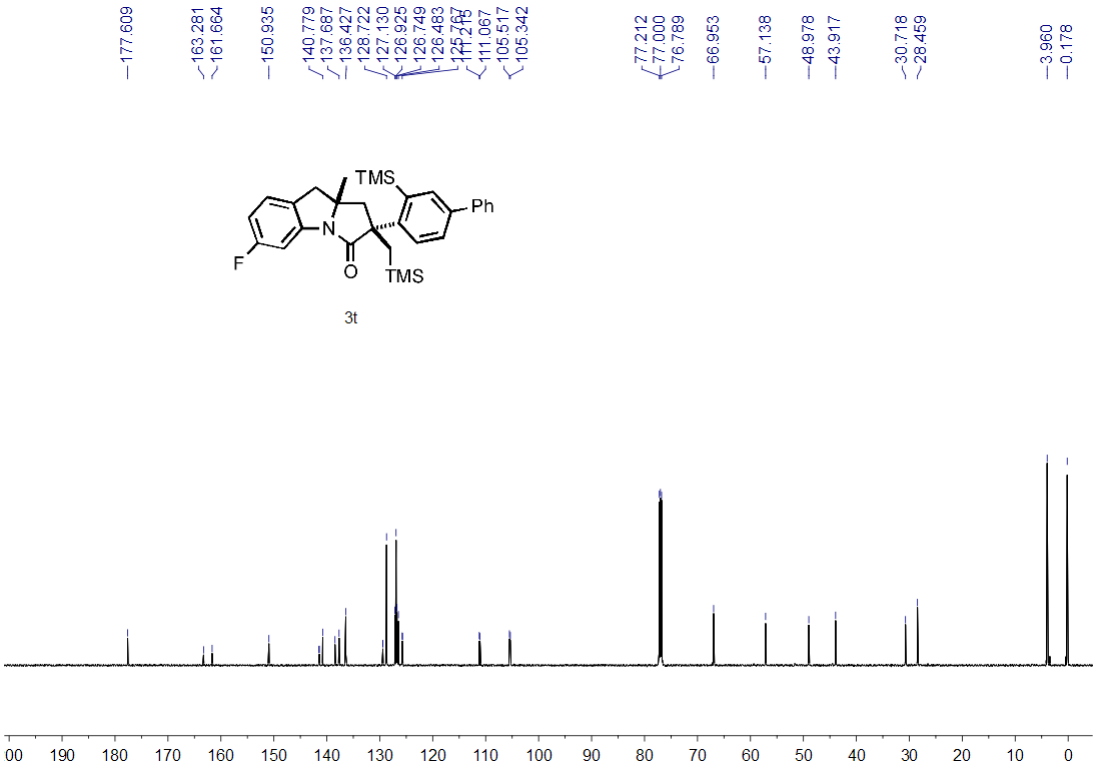
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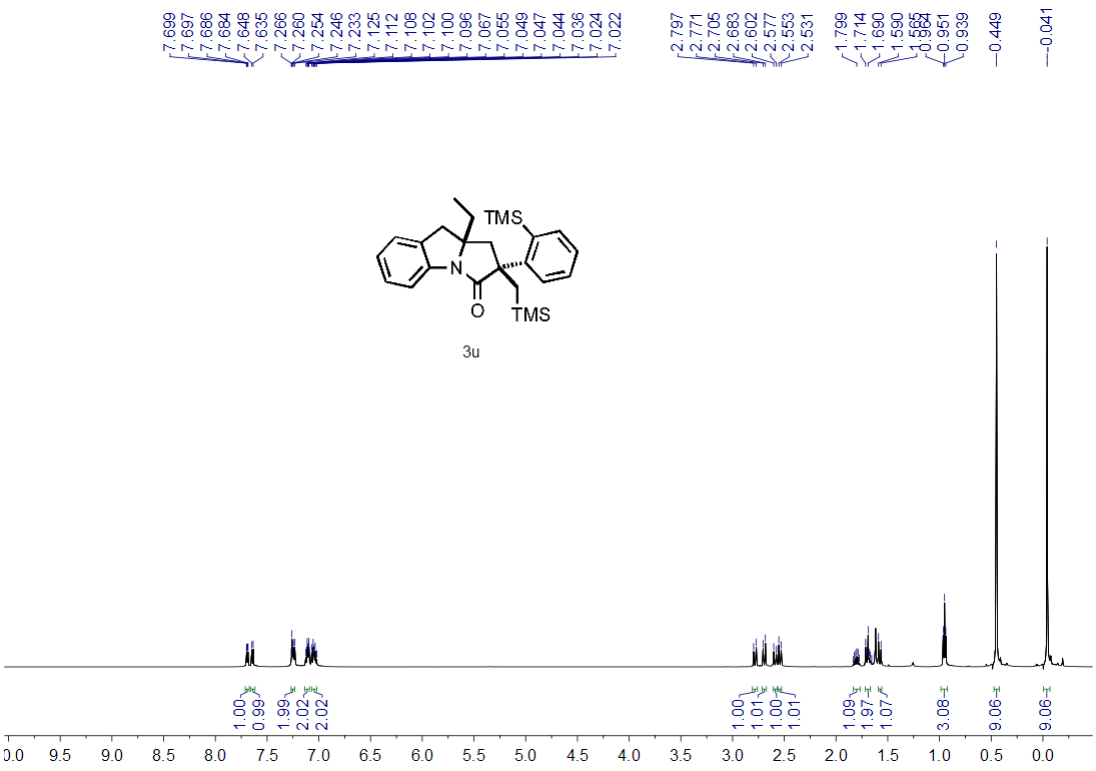
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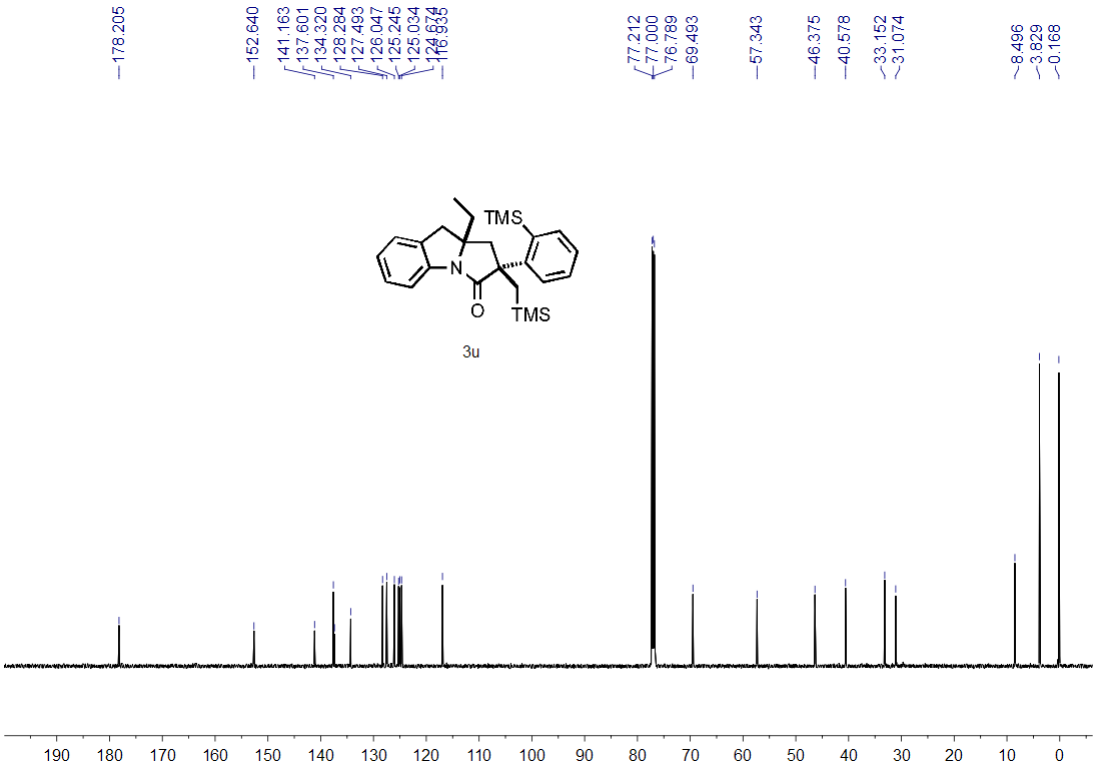
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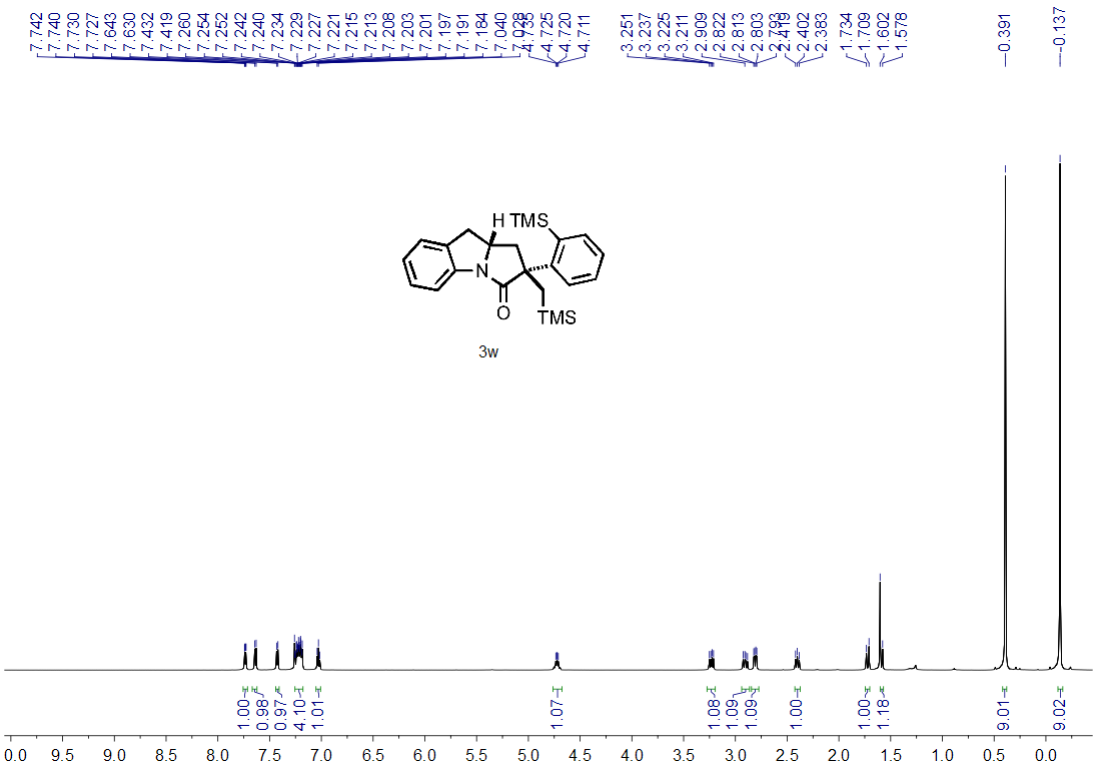
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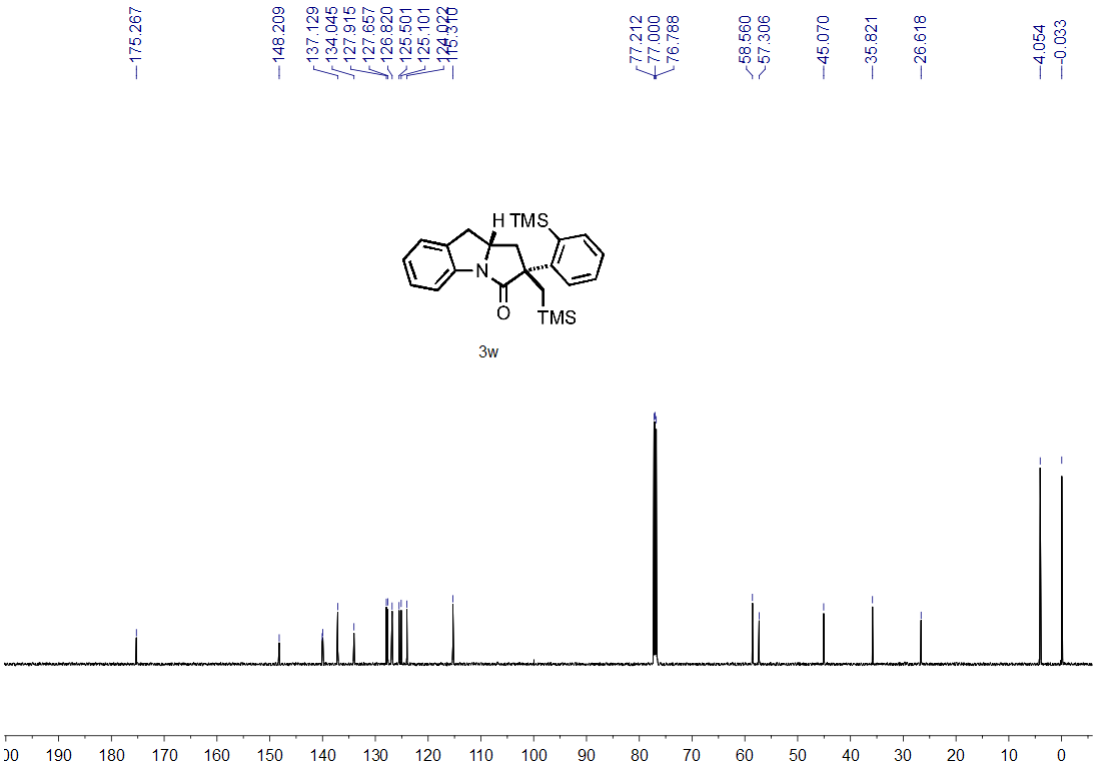
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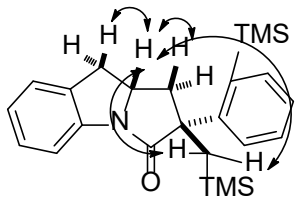
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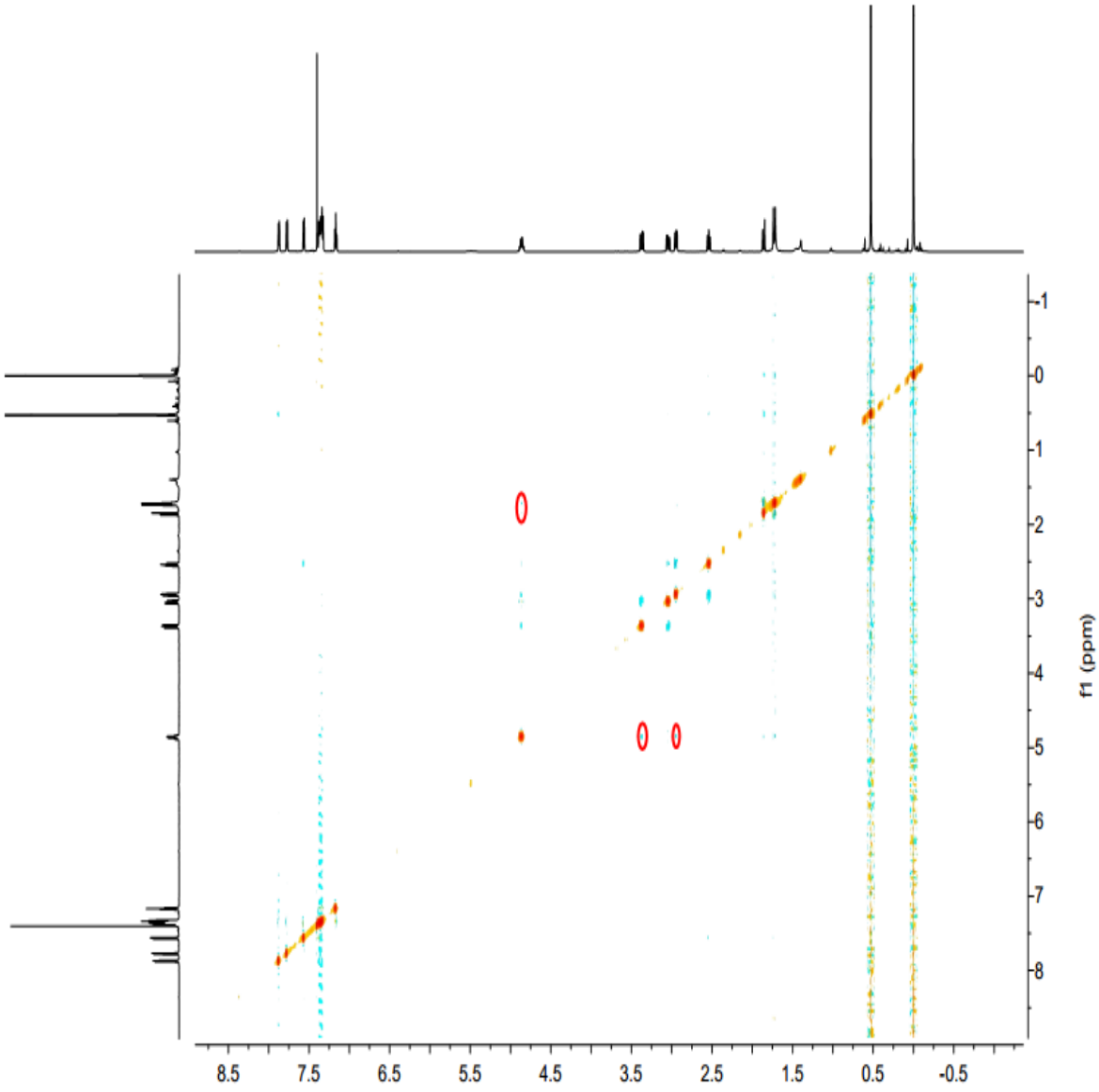
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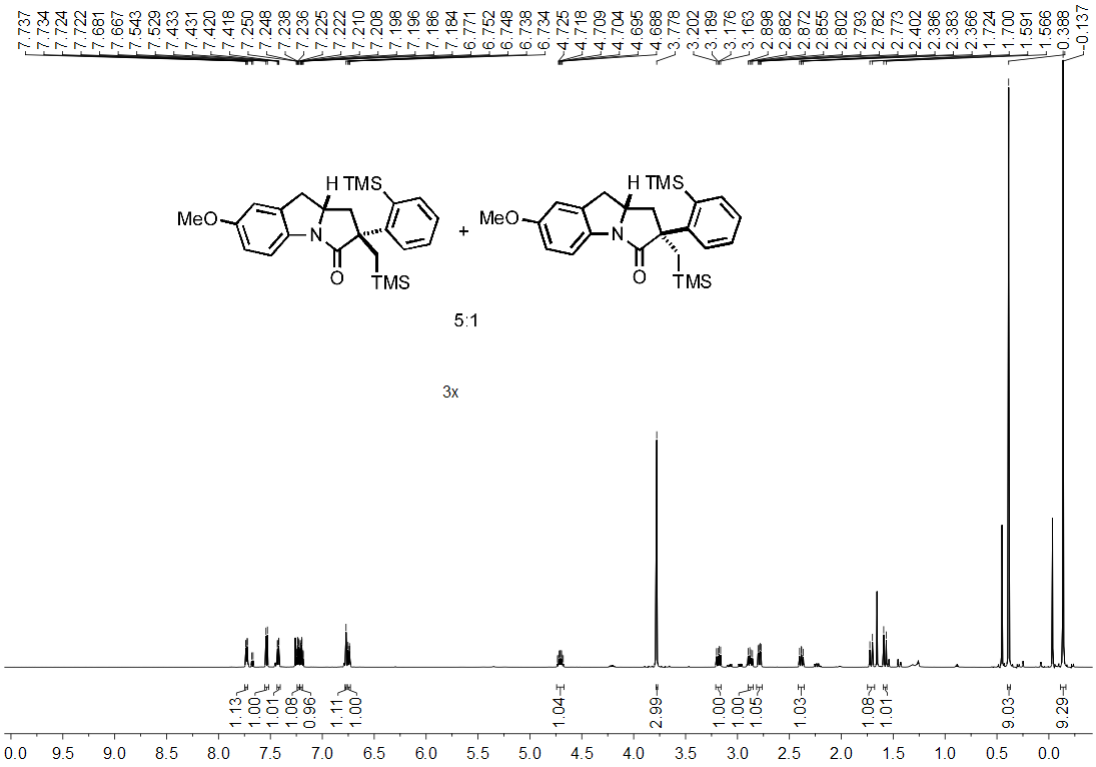
f1 (ppm)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0.137
H TMS
MeO
N
O
TMS
+
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3x
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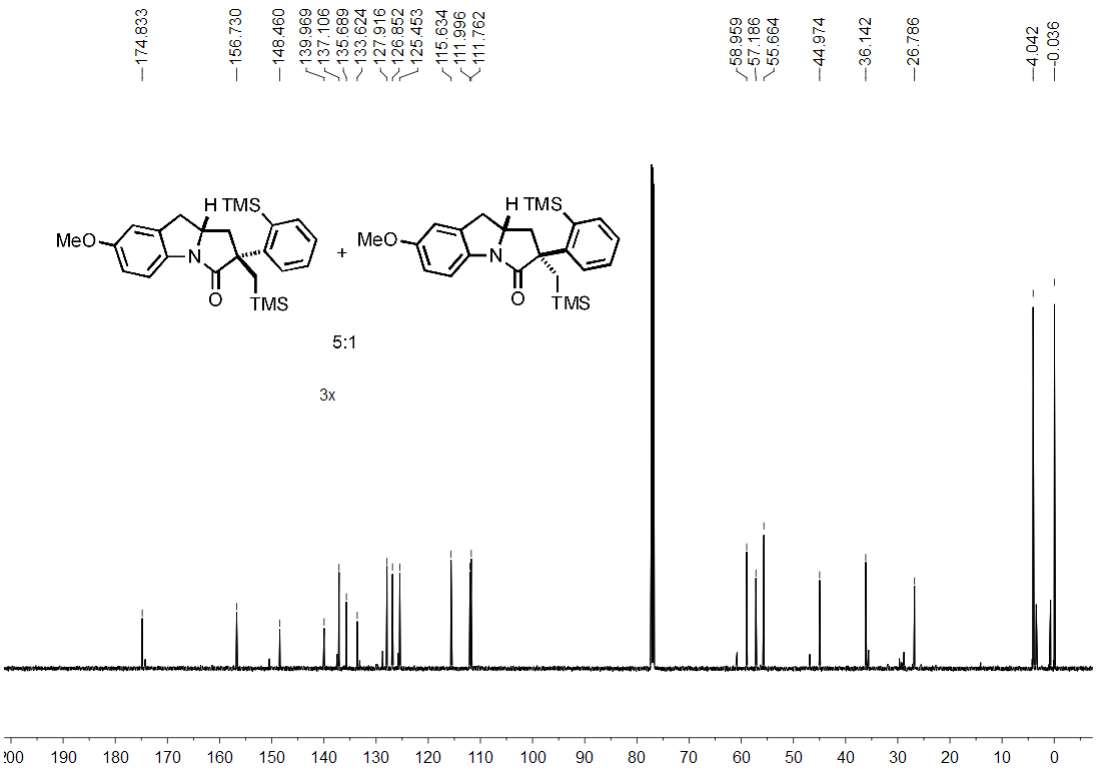
1.01
1.08
0.96
1.11
1.00
1.04
2.99
1.00
1.00
1.05
1.03
1.08
1.01
9.03
9.29
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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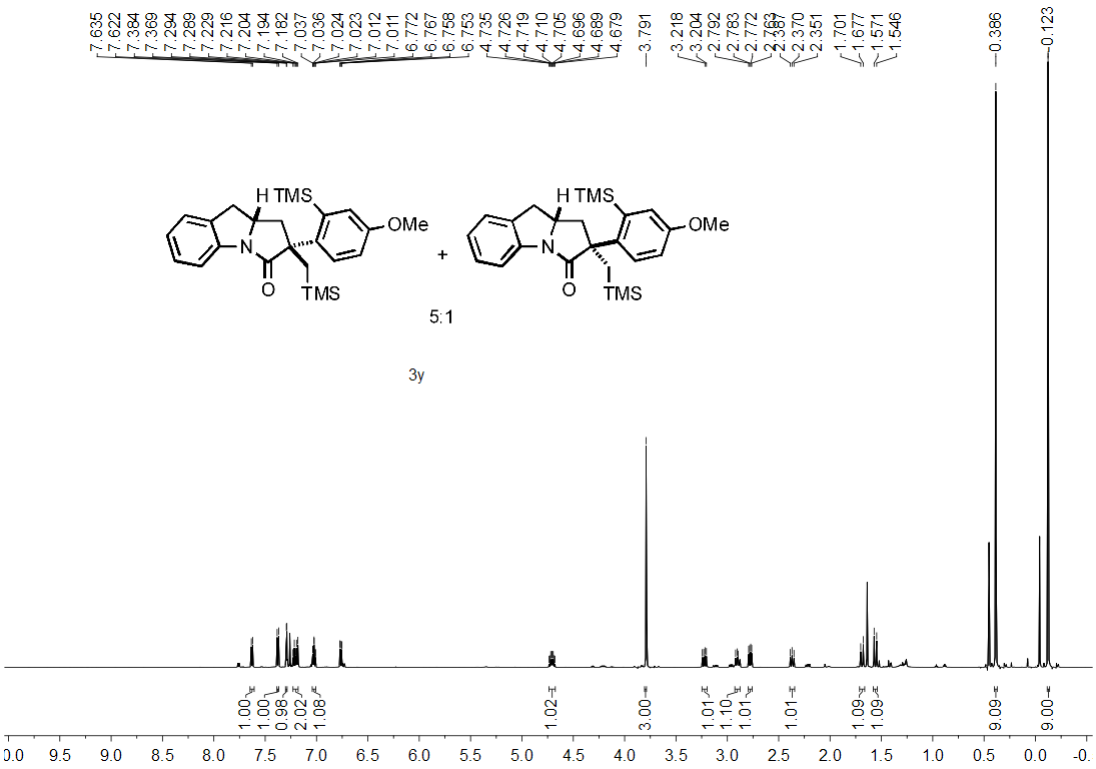
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H TMS
OMe
N
O
TMS
+
H TMS
OMe
N
O
TMS
5:1
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1.00
0.98
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1.08
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9.0
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8.0
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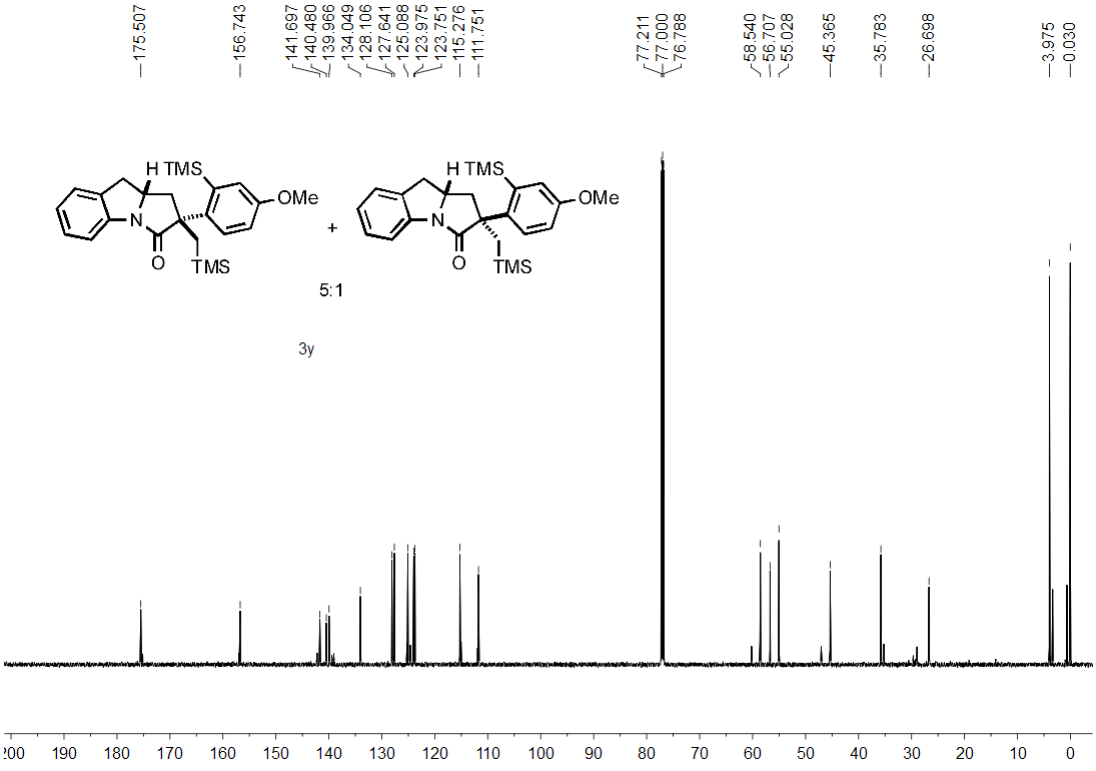
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0.030
H TMS
OMe
N
O
TMS
+
H TMS
OMe
N
O
TMS
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3y
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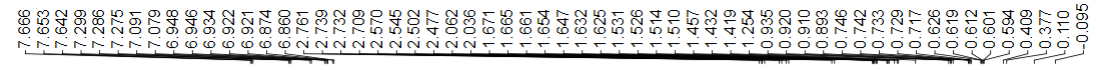
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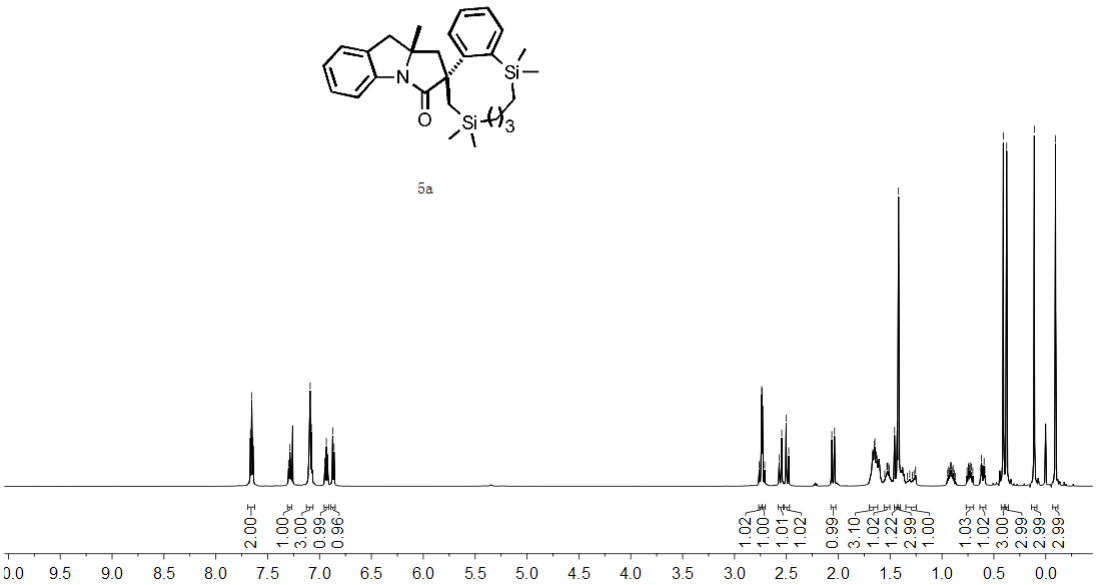
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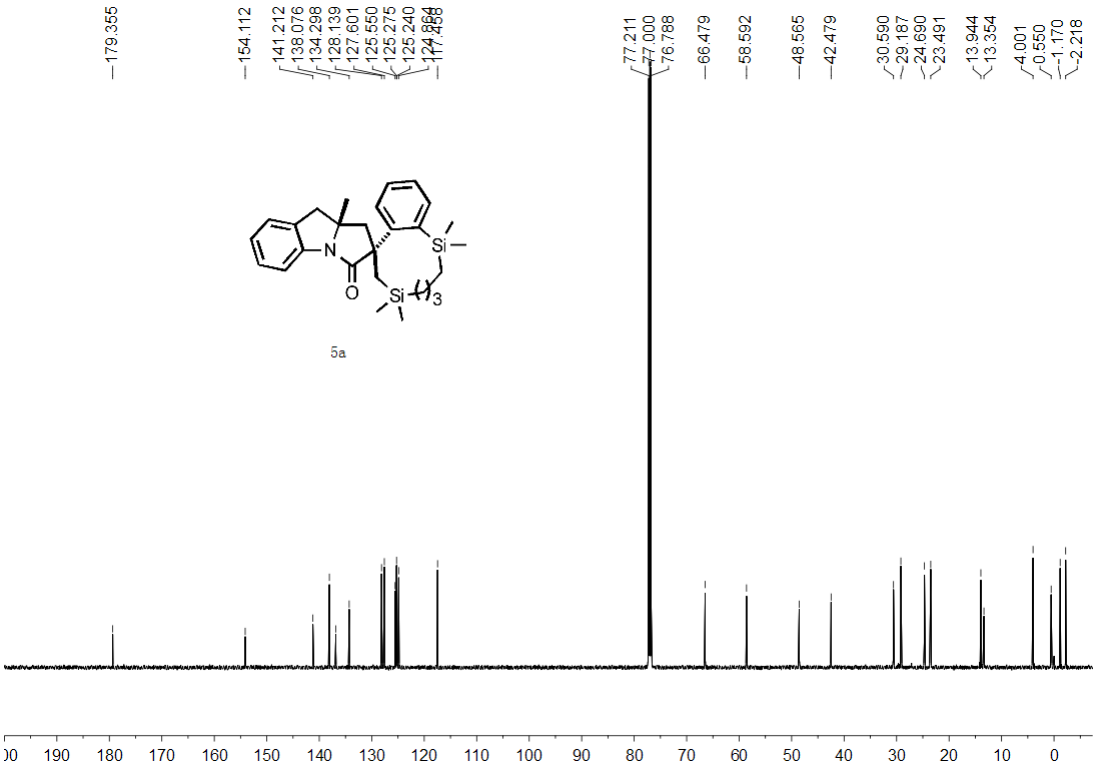
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5a
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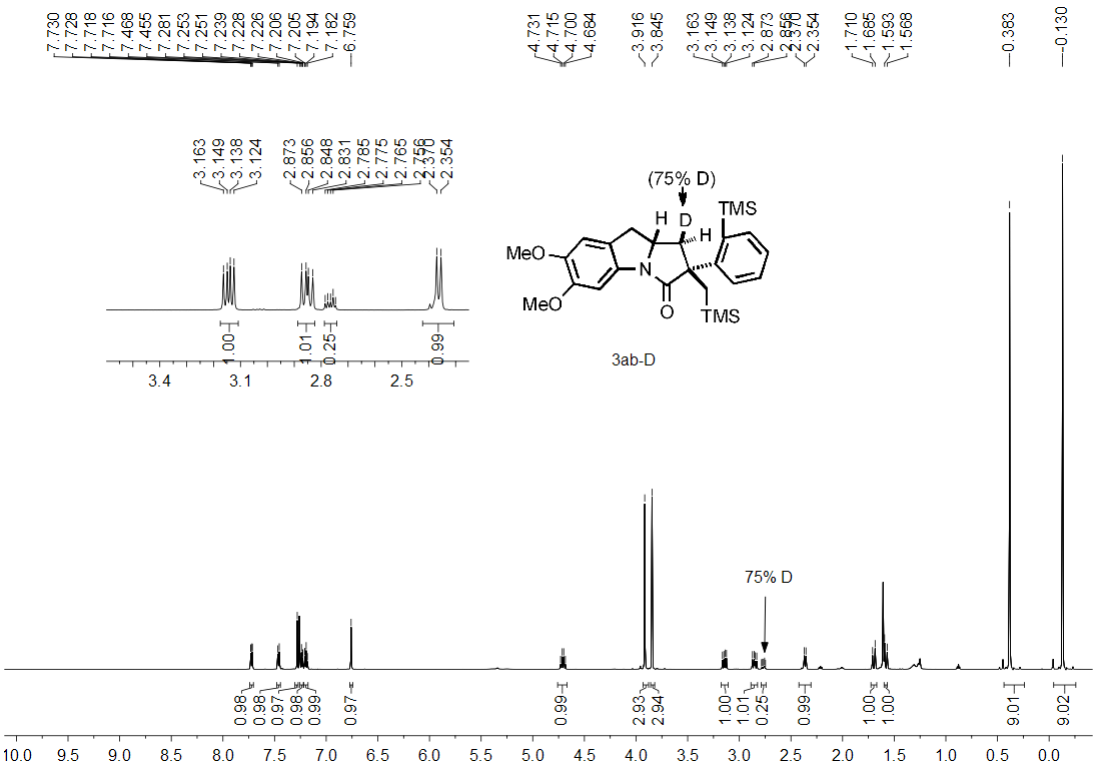
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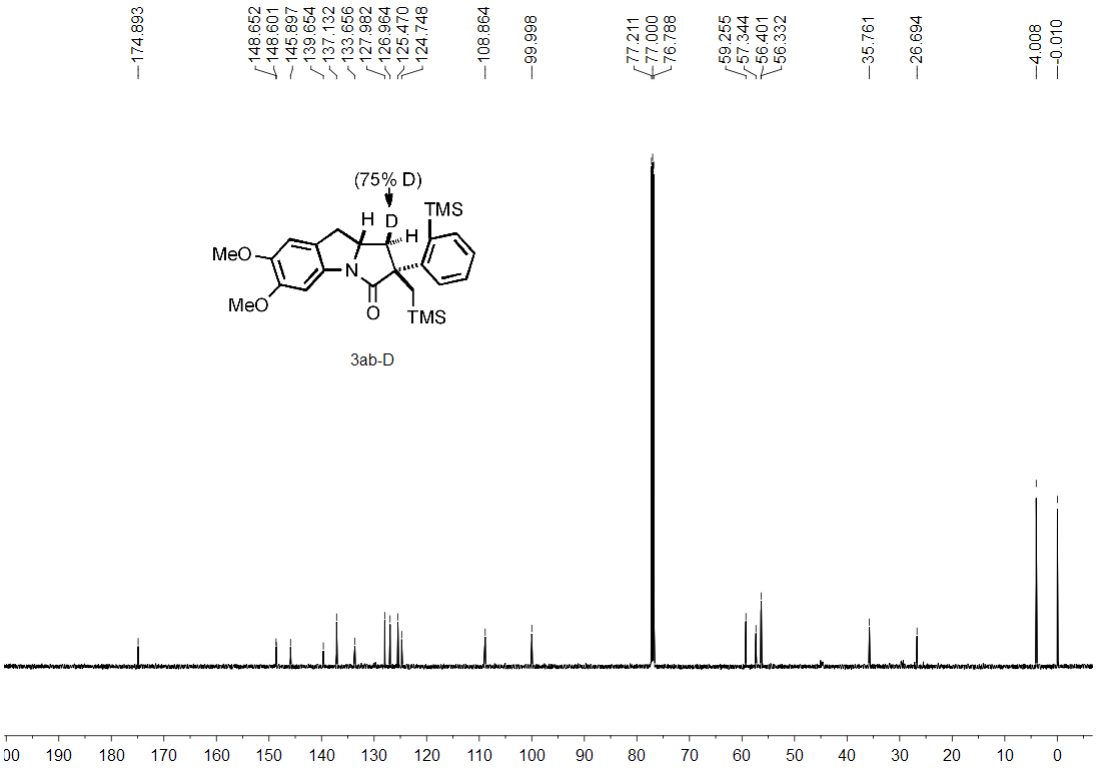
TMS
MeO
MeO
N
O
TMS
3ab-D
75% D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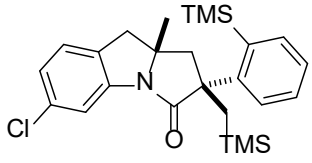
TMS
MeO
MeO
N
O
TMS
3ab-D

9. The X-ray Single-Crystal Diffraction Analysis of 3h



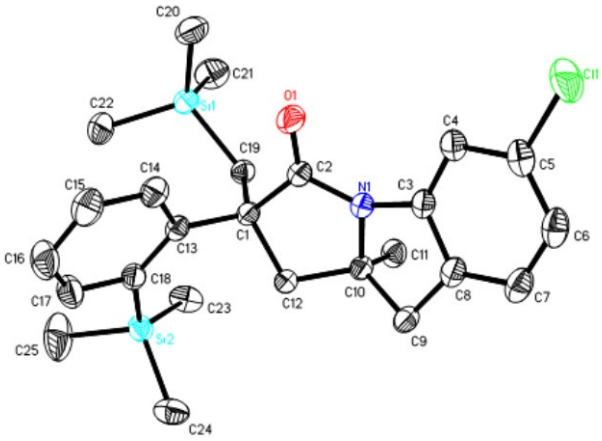


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Table S1 Crystal data and structure refinement for 3h.

Identification code	**3h**
Empirical formula	$C_{25}H_{34}ClNOSi_2$
Formula weight	456.16
Temperature/K	296(2)
Wavelength/Å	1.54178
Crystal system	Triclinic
Space group	P-1
a/Å	8.8523(15)
b/Å	9.551(2)
c/Å	16.927(4)
α/°	81.918(4)
β/°	78.360(4)
γ/°	64.955(6)
Volume/Å^3	1267.5(5)
Z	2
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	2.355
F(000)	488
Crystal size/mm^3	0.150 x 0.080 x 0.060
2Θ range for data collection/°	2.121 to 68.517
Index ranges	-10<=h<=10, -11<=k<=11, -19<=l<=20
Reflections collected	13285
Independent reflections	4607 [R(int) = 0.0299]
Data/restraints/parameters	4607/0/278
Goodness-of-fit on F^2	1.024

Final R indexes [I>=2σ(I)]	R_1 = 0.0377, wR_2 = 0.0975
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.1029
Largest diff. peak and hole / e $Å^{-3}$	0.239 and -0.272