Supporting Information

Palladium-catalyzed Heck-carbonylation of alkene-tethered carbamoyl chlorides with aryl formates

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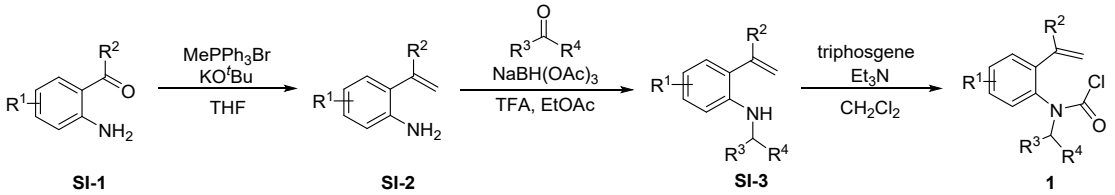
General Information:

The ^{1}H NMR, ^{19}F NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on Agilent 6520 Q-TOF mass spectrometer with ESI resource.

Preparation of Starting Materials:

General Procedure 1:



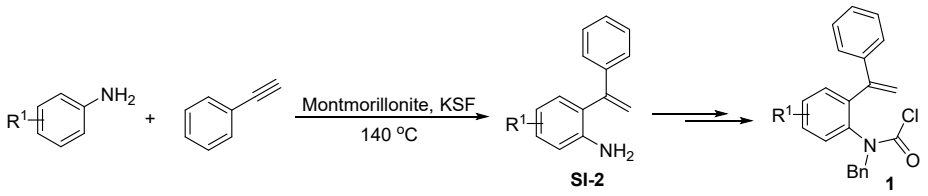
A mixture of $MePPh_3Br$ (1.5 equiv) and KO^{t}Bu (1.5 equiv) in THF (0.3 mmol/mL) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 ^{o}C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2**.

The **SI-2** (1.0 equiv) was dissolved in ethyl acetate (0.25 M). The aldehyde or ketone (1.2 equiv) was added followed by trifluoroacetic acid (2.0 equiv). The reaction was stirred for 30 minutes then sodium triacetoxyborohydride (2.0 equiv) was added. The reduction was stirred for 2 h then quenched with 4 M NaOH. The reaction was diluted with ethyl acetate and washed twice with brine. The organic layer was dried over

magnesium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography to give **SI-3**.

The **SI-3** (1.0 equiv) was dissolved in dichloromethane (0.3 M) and cooled to 0 °C. Then triethylamine (2.0 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC. The reaction was quenched with water and extracted twice with dichloromethane. The organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography in ethyl acetate/petroleum ether mixtures to give **1**.

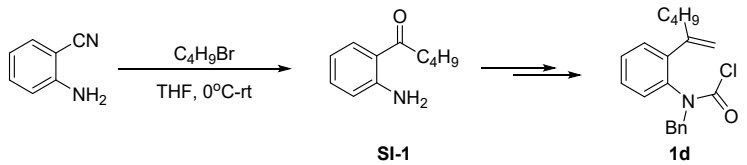
General Procedure 2:



Aniline (1.0 equiv), phenylacetylene (1.1 equiv) and montraorillonite KSF (100.0 mg/mmol) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 °C for 5 hours and then cooled to room temperature. The crude mixtures were dissolved with dichloromethane and filtered. Then the solvents were concentrated in vacuo and the crude was purified by column chromatography (silica gel, appropriate mixture of petroleum ether/ethyl acetate) to give **SI-2**.

(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 3:

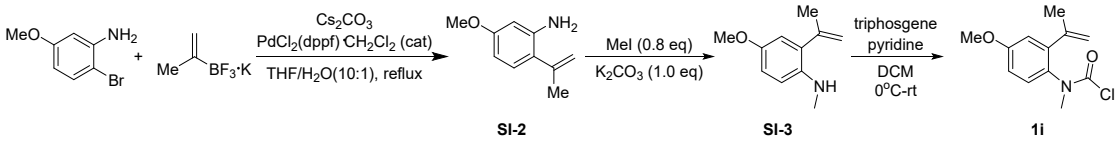


To a solution of 2-amino-benzonitrile (1.0 equiv) in dry THF (0.2 mmol/ mL). Then the solution of the Grignard reagents (2.7 equiv) in THF solution was slowly added dropwise at 0 °C over 30 min. Then the resulting mixture was stirred at ambient temperature overnight. Addition of a saturated aqueous NH_4Cl solution produced a

suspension mixture, then filtered, and extracted with EA. The combined organics were dried over $MgSO_4$. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-1**.

(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 4:

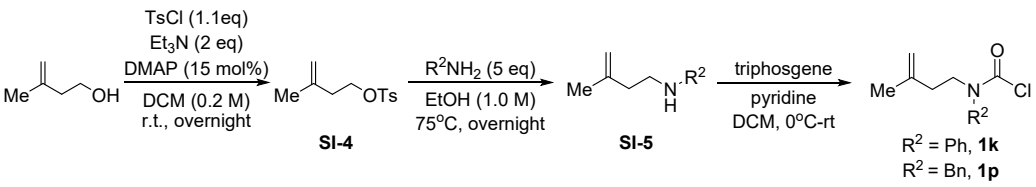


To a suspension of potassium isopropenyltrifluoroborate (1.1 equiv), Cs_2CO_3 (3.0 equiv), $PdCl_2(dppf)•CH_2Cl_2$ (9.0 mol%) in a solvent mixture (THF/H_2O = 10/1) was added 2-bromoaniline (1.0 equiv). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with ethyl acetate (50 mL x 3). The combined organic layer was washed with saturated sodium chloride (50 mL), dried over $MgSO_4$, concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether as an eluent) to give the desired products **SI-2**.

The mixture of **SI-2** (1.0 equiv), MeI (0.8 equiv), K_2CO_3 (1.5 equiv) in MeCN (1 g/45 mL) was stirred at room temperature overnight. The solvent was evaporated under reduced pressure, the mixture was extracted with ethyl acetate, and washed twice with brine, the organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain **SI-3**.

To a solution of **SI-3** (1.0 equiv) and pyridine (2.0 equiv) in DCM at 0 °C, triphosgene (1.0 equiv) was added. The mixture was then allowed to warm to room temperature for 60 min and was washed with 1 M HCl, diluted with DCM, dried over Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give substrate **1i**.

General Procedure 5:

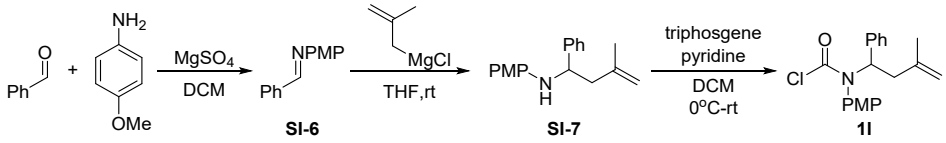


A 250 mL round bottom flask was charged with a mixture of TsCl (1.1 equiv), DMAP (15 mol%). The flask was evacuated and backfilled with N_2 (This process was repeated for three times) before DCM (0.2 M), Et_3N (2.0 equiv), and 3-methylbut-3-en-1-ol (1.0 equiv) were added. The solution was stirred at room temperature overnight. After completion, the mixture was quenched with saturated aqueous NH_4Cl solution. The aqueous layers were extracted with DCM for three times. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated in vacuo, and chromatographed to afford **SI-4** as a colorless oil.

Following the general procedure, **SI-4** (1.0 equiv), in the presence of benzylamine (5.0 equiv), was consumed based on analysis by TLC after 18 hours of stirring and heating. The work up gave a yellow oil, which was purified by flash column chromatography to give **SI-5** as a colourless oil.

To a solution of **SI-5** (1.0 equiv.) in DCM was added pyridine (1.0 equiv) and triphosgene (0.5 equiv) in sequence at 0 °C. The mixture was then allowed to warm to room temperature for enough time (TLC monitor), and then was quenched with 1 M HCl, extracted with DCM, dried over Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give substrate **1k**, **1p**.

General Procedure 6:



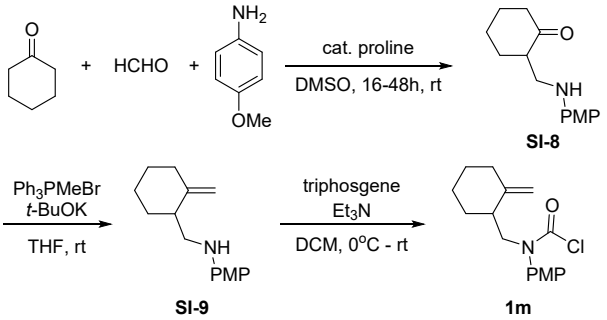
In a round-bottomed flask 0.615 g of *p*-anisidine (5.0 mmol) was taken up in DCM (25 mL), 2.0 g anhydrous magnesium sulfate was added and followed by addition of 0.505 mL of benzaldehyde (5.0 mmol). The reaction was allowed to stir overnight and was then filtered and the solvent removed in vacuo to give **SI-6**.

To a stirred solution of imine **SI-6** (1.0 equiv) in anhydrous THF under N_2 atmosphere at room temperature, Grignard reagent (2.5 equiv), which were freshly

prepared in anhydrous THF, was then added via cannula. The resulting suspension was stirred to additional 30 min. The mixture was cooled to 0 °C and was carefully quenched with saturated aqueous NH_4Cl. The two phases mixture was separated by a separator funnel. The aqueous layer was extracted by EA and the combined organic layers were washed with saturated aqueous NaCl, and dried over Na_2SO_4. After removing the solvent, the residue **SI-7** was used without further purification.

To a solution of **SI-7** (1.0 equiv) and pyridine (2.0 equiv) in DCM at 0 °C, triphosgene (1.0 equiv) was added. The mixture was then allowed to warm to room temperature for 60 min and was washed with 1 M HCl, diluted with DCM, dried over Na_2SO_4. After removing the solvent, the residue was purified by column chromatography to give substrate **1l**.

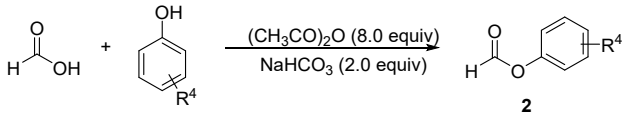
General Procedure 7:



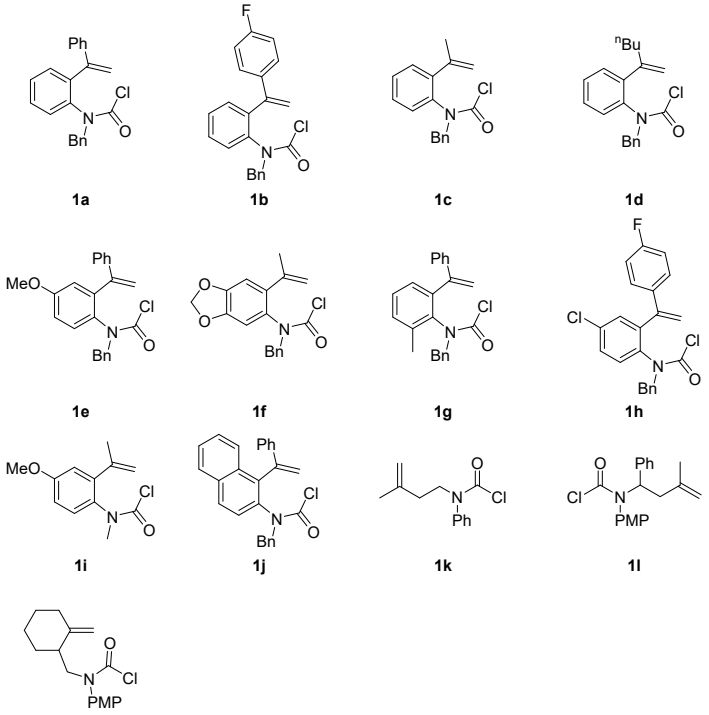
To a solution of cyclohexanone (2.0 equiv) in DMSO were added proline (30 mol%), formaldehyde solution (1.0 equiv) and the *p*-anisidine (1.1 equiv), the solution was vigorous stirred at room temperature during 16-48 h. The reaction mixture was monitored by TLC. When the reaction was completed, the mixture was quenched with saturated aqueous NH_4Cl and extracted with EA. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography to give the **SI-8.**

(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 8:



In a 100 mL flask equipped with a condenser, acetic anhydride (8.0 equiv) was cooled to 0 °C. Then formic acid (10.0 equiv) was added slowly. The solution was warmed up to room temperature and stirred for 10 minutes. Then, the mixture was heated to 60 °C and stirred for 1 h. After cooling to the room temperature, corresponding phenol (1.0 equiv) and $NaHCO_3$ (2.0 equiv) were added. The mixture was stirred at room temperature for 4 h. DCM and water were added to the mixture. The crude was extracted with DCM (three times). Organic layers were combined and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography to give substrate **2**.



1a-1c, **1f**, **1h** were synthesized by **general procedure 1**

1e, **1g**, **1j** were synthesized by **general procedure 2**

1d was synthesized by **general procedure 3**

1i was synthesized by **general procedure 4**

1k was synthesized by **general procedure 5**

1l was synthesized by **general procedure 6**

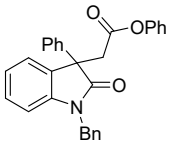
1m was synthesized by **general procedure 7**

General Procedure for the Synthesis of the Esterificated Oxindoles

3 (condition A): In a 38 mL sealed tube, the mixture of **1** (0.2 mmol), **2** (0.4 mmol), $PdCl_2$ (2.5 mg, 0.014 mmol), DPPF (7.7 mg, 0.014 mmol) and Et_3N (40.5 mg, 0.4 mmol) was dissolved in anhydrous MeCN (2.0 mL). The tube was then purged 3 times with N_2 and sealed with a PTEF cap. The reaction mixture was allowed to react at 80 ^oC for 12 h. After the reaction was completed, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate).

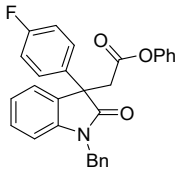
3 (condition B): In a 38 mL sealed tube, the mixture of **1** (0.2 mmol), **2** (0.4 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol), DPPF (5.5 mg, 0.01 mmol) and Et_3N (40.5 mg, 0.4 mmol) was dissolved in anhydrous MeCN (2.0 mL). The tube was then purged 3 times with N_2 and sealed with a PTEF cap. The reaction mixture was allowed to react at 80 ^oC for 12 h. After the reaction was completed, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate).

Characterization of Products:



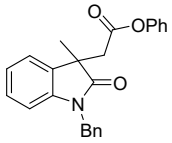
Phenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3aa**)

Colorless oil (condition A: 72 mg, 84%; condition B: 67 mg, 78%) ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 3H), 7.25 – 7.14 (m, 4H), 7.13 – 7.07 (m, 4H), 7.03 – 6.98 (m, 5H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 3.42 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.49, 168.01, 149.99, 143.58, 139.12, 135.48, 130.58, 129.04, 128.62, 128.57, 128.35, 127.62, 127.20, 126.98, 126.38, 125.62, 124.66, 122.50, 121.15, 109.41, 53.36, 44.02, 41.80. ESI-MS: Calcd for $C_{29}H_{23}NO_3$: $[M+H^+]$ 434.1751, found 434.1760.



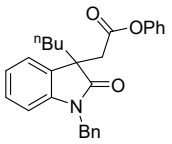
Phenyl-2-(1-benzyl-3-(4-fluorophenyl)-2-oxoindolin-3-yl)acetate (**3ba**)

Colorless oil (condition A: 78 mg, 87%; condition B: 76 mg, 85%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.32 – 7.15 (m, 10H), 7.10 – 7.03 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.65 – 6.57 (m, 2H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.92 (d, *J* = 16.0 Hz, 1H), 3.53 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 168.0, 162.3 (d, *J* = 246.0 Hz), 150.1, 143.7, 135.5, 134.9 (d, *J* = 3.0 Hz), 130.4, 129.2, 128.9, 128.6, 128.4 (d, *J* = 8.0 Hz), 127.5, 127.2, 125.8, 125.0, 122.8, 121.3, 115.6 (d, *J* = 21.0 Hz), 109.8, 52.9, 44.3, 42.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.45. ESI-MS: Calcd for $C_{29}H_{22}FNO_3$: [M+H$^+$] 452.1656, found 4152.1656.



Phenyl-2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetate (**3ca**)

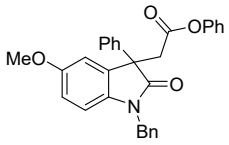
Colorless oil (condition A: 63 mg, 85%; condition B: 63 mg, 85%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (m, 10H), 6.99 – 6.94 (m, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 2H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 3.30 (d, *J* = 15.6 Hz, 1H), 3.02 (d, *J* = 15.6 Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 168.3, 150.2, 142.7, 135.8, 132.5, 129.2, 128.6, 128.2, 127.4, 127.2, 125.7, 122.6, 121.4, 121.3, 109.3, 45.8, 44.0, 41.7, 25.0. ESI-MS: Calcd for $C_{24}H_{21}NO_3$: [M+H$^+$] 372.1594, found 372.1594.



Phenyl-2-(1-benzyl-3-butyl-2-oxoindolin-3-yl)acetate (**3da**)

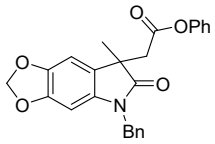
Colorless oil (condition A: 74 mg, 90%; condition B: 72 mg, 87%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 3H), 7.14 – 6.95 (m, 8H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.53 – 6.43 (m, 2H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 3.28 (d, *J* = 15.6 Hz, 1H), 3.00 (d, *J* = 15.6 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.81 – 1.73 (m, 1H), 1.19 – 1.00

(m, 3H), 0.85 – 0.77 (m, 1H), 0.71 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 168.3, 150.1, 143.6, 135.8, 130.9, 129.2, 128.5, 128.2, 127.3, 125.7, 122.8, 122.5, 121.3, 121.3, 109.1, 49.9, 44.1, 41.6, 38.5, 25.8, 22.6, 13.7. ESI-MS: Calcd for $C_{27}H_{27}NO_3$: [M+H$^+$] 414.2064, found 414.2064.



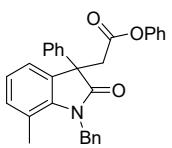
Phenyl-2-(1-benzyl-5-methoxy-2-oxo-3-phenylindolin-3-yl)acetate (**3ea**)

Yellow oil (condition A: 74 mg, 80%; condition B: 71 mg, 77%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.6 Hz, 2H), 7.27 – 7.19 (m, 3H), 7.15 – 7.09 (m, 4H), 7.06 – 7.01 (m, 4H), 6.94 (d, J = 2.4 Hz, 1H), 6.70 – 6.66 (m, 1H), 6.58 – 6.51 (m, 3H), 4.85 (d, J = 15.6 Hz, 1H), 4.70 (d, J = 16.0 Hz, 1H), 3.82 (d, J = 16.0 Hz, 1H), 3.64 (s, 3H), 3.42 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 168.1, 156.0, 150.1, 139.2, 137.1, 135.6, 132.1, 129.2, 128.8, 128.5, 127.8, 127.3, 127.1, 126.5, 125.8, 121.3, 113.0, 112.2, 112.1, 110.0, 55.7, 53.82, 44.3, 41.8. ESI-MS: Calcd for $C_{30}H_{25}NO_4$: [M+H$^+$] 464.1856, found 464.1856.



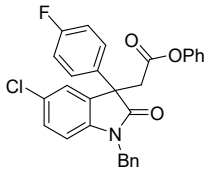
Phenyl-2-(5-benzyl-7-methyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,4,5-f]indol-7-yl)acetate (**3fa**)

Colorless oil (condition A: 68 mg, 82%; condition B: 67 mg, 81%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (m, 8H), 6.77 (s, 1H), 6.66 (d, J = 8.0 Hz, 2H), 6.24 (s, 1H), 5.79 (s, 2H), 4.85 (d, J = 15.6 Hz, 1H), 4.74 (d, J = 16.0 Hz, 1H), 3.24 (d, J = 16.0 Hz, 1H), 2.96 (d, J = 16.0 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 179.8 168.3, 150.1, 147.2, 143.2 136.9 135.6, 129.3 128.7 127.1, 125.8, 124.3 121.4 104.37, 101.0, 93.3, 46.1, 44.1, 41.7, 25.1, 25.1. ESI-MS: Calcd for $C_{25}H_{21}NO_5$: [M+H$^+$] 416.1492, found 416.1492.



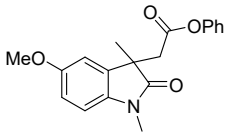
Phenyl-2-(1-benzyl-7-methyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ga**)

Colorless oil (condition A: 80 mg, 90%; condition B: 81 mg, 91%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.28 (m, 6H), 7.23 – 7.08 (m, 8H), 6.69 (d, *J* = 8.0 Hz, 2H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 4.01 (d, *J* = 16.0 Hz, 1H), 3.54 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 168.3, 150.2, 142.0, 139.7, 137.8, 132.7, 131.5, 129.3, 128.8, 128.6, 127.8, 126.9, 126.7, 125.8, 125.7, 122.7, 121.4, 120.2, 52.9, 45.5, 42.2, 18.9. ESI-MS: Calcd for $C_{30}H_{25}NO_3$: [M+H$^+$] 448.1907, found 448.1907.



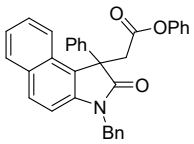
Phenyl-2-(1-benzyl-5-chloro-3-(4-fluorophenyl)-2-oxoindolin-3-yl)acetate (**3ha**)

White solid (condition A: 60 mg, 62%; condition B: 58 mg, 60%) M.P.: 154-156 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.33 (m, 1H), 7.26 – 7.15 (m, 9H), 7.11 – 6.98 (m, 4H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 3.80 (d, *J* = 16.0 Hz, 1H), 3.64 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 167.9, 161.1 (d, *J* = 247.0 Hz), 150.1, 142.1, 135.2, 132.8, 130.0 (d, *J* = 8.0 Hz), 129.3, 128.7, 128.6, 128.2, 127.6, 127.2, 125.9, 124.7, 124.5 (d, *J* = 6.0 Hz), 121.3, 116.9 (d, *J* = 23.0 Hz), 110.4, 52.2, 44.6, 39.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.45. ESI-MS: Calcd for $C_{29}H_{21}ClFNO_3$: [M+H$^+$] 486.1267, found 486.1267.

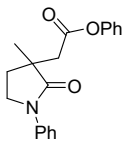


Phenyl-2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**3ia**)

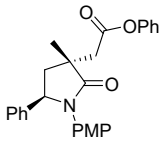
Colorless oil (condition A: 47 mg, 72%; condition B: 45 mg, 70%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.86 – 6.84 (m, 1H), 6.76 – 6.72 (m, 1H), 6.66 (t, *J* = 8.8 Hz, 3H), 3.70 (s, 3H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.10 (s, 3H), 2.95 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 168.2, 156.0, 150.1, 137.1, 133.9, 129.2, 125.7, 121.2, 112.3, 110.3, 108.5, 55.8, 46.0, 41.7, 26.4, 24.3. ESI-MS: Calcd for $C_{19}H_{19}NO_4$: [M+H$^+$] 326.1387, found 326.1392.



Phenyl-2-(3-benzyl-2-oxo-1-phenyl-2,3-dihydro-1H-benzo[e]indol-1-yl)acetate (**3ja**)
White solid (condition A: 63 mg, 66%; condition B: 58 mg, 60%) M.P.: 196-198 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.29 (m, 9H), 7.24 – 7.19 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.62 (d, *J* = 17.2 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 4.11 (d, *J* = 16.0 Hz, 1H), 3.71 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 168.1, 150.1, 139.7, 139.3, 137.1, 134.8, 129.2, 128.9, 128.7, 127.9, 127.1, 126.7, 126.6, 125.9, 125.7, 125.7, 123.6, 122.2, 121.7, 121.2, 120.7, 53.3, 46.7, 42.1. ESI-MS: Calcd for $C_{33}H_{25}NO_3$: [M+H$^+$] 484.1907, found 484.1907.

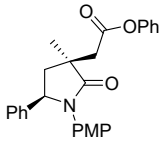


Phenyl-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (**3ka**)
Colorless oil (condition A: 28 mg, 45%; condition B: 27 mg, 44%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 4H), 7.18 – 7.13 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.99 (m, 2H), 3.82 – 3.71 (m, 2H), 2.91 (d, *J* = 16.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.08 – 2.01 (m, 1H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 169.8, 150.5, 139.6, 129.4, 128.8, 125.8, 124.6, 121.5, 120.0, 45.2, 43.9, 41.9, 30.5, 23.2. ESI-MS: Calcd for $C_{19}H_{19}NO_3$: [M+H$^+$] 310.1438, found 310.1438.



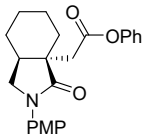
Phenyl-2-((3R,5R)-1-(4-methoxyphenyl)-3-methyl-2-oxo-5-phenylpyrrolidin-3-yl)acetate (**3la**)
Colorless oil (condition A: 35 mg, 43%; condition B: 34 mg, 41%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 2H), 7.22 – 7.12 (m, 8H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 9.2 Hz, 2H), 5.15 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.62 (s, 3H), 3.01 (d, *J* = 16.4 Hz, 1H), 2.87 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.75 (d, *J* = 16.4 Hz, 1H), 1.91 (dd, *J* = 13.2, 5.6

Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 169.9, 157.1, 150.5, 142.1, 131.3, 129.4, 128.8, 127.6, 126.5, 125.9, 124.9, 121.5, 113.9, 61.5, 55.3, 43.0, 42.7, 41.3, 26.3. ESI-MS: Calcd for $C_{26}H_{25}NO_4$: [M+H$^+$] 416.1856, found 416.1860.



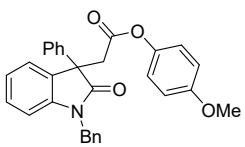
Phenyl-2-((3S,5R)-1-(4-methoxyphenyl)-3-methyl-2-oxo-5-phenylpyrrolidin-3-yl)acetate (**3la'**)

Colorless oil (condition A: 24 mg, 29%; condition B: 23 mg, 28%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 2H), 7.22 – 7.05 (m, 8H), 7.05 – 6.94 (m, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 5.08 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.60 (s, 3H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.41 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.27 (dd, *J* = 12.8, 9.2 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 169.8, 156.9, 150.5, 140.6, 130.7, 129.5, 128.7, 127.7, 127.2, 125.9, 125.0, 121.6, 113.8, 60.9, 55.2, 43.1, 42.4, 41.6, 23.1. ESI-MS: Calcd for $C_{26}H_{25}NO_4$: [M+H$^+$] 416.1856, found 416.1865.



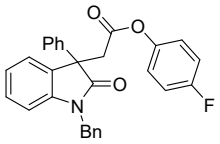
Phenyl-2-((3aS,7aS)-2-(4-methoxyphenyl)-3-oxooctahydro-3aH-isoindol-3a-yl)acetate (**3ma**)

Colorless oil (condition A: 46 mg, 61%; condition B: 45 mg, 60%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 3.68 – 3.63 (m, 1H), 3.58 – 3.50 (m, 1H), 2.90 (d, *J* = 16.0 Hz, 1H), 2.81 (d, *J* = 15.6 Hz, 1H), 2.74 – 2.62 (m, 1H), 1.74 – 1.63 (m, 3H), 1.56 – 1.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 169.7, 156.5, 150.6, 133.1, 129.3, 125.8, 121.6, 121.6, 114.0, 55.5, 49.8, 46.3, 38.2, 34.2, 30.3, 24.5, 21.6, 21.3. ESI-MS: Calcd for $C_{23}H_{25}NO_4$: [M+Na$^+$] 402.1676, found 402.1678.



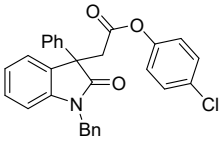
4-Methoxyphenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ab**)

White solid (condition A: 48 mg, 52%; condition B: 44 mg, 48%) M.P.: 156-158 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 10H), 7.08 – 7.02 (m, 4H), 6.70 – 6.63 (m, 3H), 6.39 – 6.33 (m, 2H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.73 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 3.65 (s, 3H), 3.41 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 168.5, 157.2, 143.8, 143.6, 139.3, 135.6, 130.8, 128.8, 128.7, 128.6, 127.8, 127.4, 127.2, 126.6, 124.9, 122.7, 122.1, 114.3, 109.6, 55.5, 53.5, 44.3, 42.1. ESI-MS: Calcd for $C_{30}H_{25}NO_4$: [M+H$^+$] 464.1856, found 464.1856.



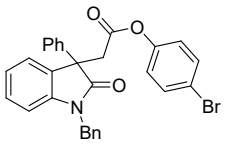
4-Fluorophenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ac**)

White solid (condition A: 74 mg, 83%; condition B: 72 mg, 80%) M.P.: 130-132 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 9H), 7.22 – 7.14 (m, 4H), 6.97 – 6.89 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.57 – 6.45 (m, 2H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 3.99 (d, *J* = 15.6 Hz, 1H), 3.56 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 168.2, 160.1 (d, *J* = 242.0 Hz), 145.8, 143.7, 139.1, 135.5, 130.6, 128.8, 128.8, 128.5, 127.8, 127.4, 127.2, 126.5, 124.8, 122.7, 122.6 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 23.0 Hz), 109.6, 53.4, 44.2, 42.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.78. ESI-MS: Calcd for $C_{29}H_{22}FNO_3$: [M+H$^+$] 452.1656, found 452.1656.



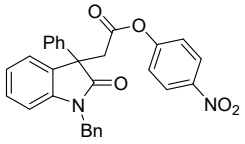
4-Chlorophenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ad**)

Colorless oil (condition A: 57 mg, 62%; condition B: 57 mg, 62%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.12 (m, 9H), 7.10 – 7.01 (m, 6H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 8.8 Hz, 2H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 16.0 Hz, 1H), 3.84 (d, *J* = 15.6 Hz, 1H), 3.41 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 168.0, 148.5, 143.7, 139.1, 135.5, 131.2, 130.6, 129.3, 128.9, 128.6, 127.9, 127.5, 127.3, 126.5, 124.9, 122.7, 122.7, 116.7, 109.7, 53.5, 44.3, 42.0. ESI-MS: Calcd for $C_{29}H_{22}ClNO_3$: [M+H$^+$] 468.1361, found 468.1361.



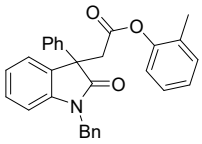
4-Bromophenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ae**)

Colorless oil (condition A: 52 mg, 51%; condition B: 51 mg, 50%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 10H), 7.09 – 7.01 (m, 4H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 6.29 (d, *J* = 8.8 Hz, 2H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 3.41 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 168.0, 155.4, 149.0, 143.6, 138.8, 135.3, 132.3, 130.6, 128.9, 128.6, 127.9, 127.5, 127.2, 126.5, 124.8, 123.1, 119.0, 117.3, 109.8, 53.5, 44.3, 41.8. ESI-MS: Calcd for $C_{29}H_{22}BrNO_3$: [M+H$^+$] 512.0856, found 512.0860.



4-Nitrophenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3af**)

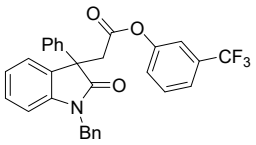
Yellow oil (condition A: 36 mg, 38%; condition B: 35 mg, 37%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.21 (m, 7H), 7.17 – 7.13 (m, 2H), 7.08 – 7.04 (m, 3H), 6.78 – 6.70 (m, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.85 (d, *J* = 15.6 Hz, 1H), 4.79 (d, *J* = 15.6 Hz, 1H), 3.89 (d, *J* = 15.6 Hz, 1H), 3.46 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.4, 154.7, 145.3, 143.6, 138.6, 135.3, 130.4, 129.0, 128.6, 128.1, 127.6, 127.3, 126.5, 126.0, 125.0, 123.0, 122.2, 115.6, 109.8, 53.5, 44.4, 41.8. ESI-MS: Calcd for $C_{29}H_{22}N_2O_5$: [M+H$^+$] 479.1601, found 479.1600.



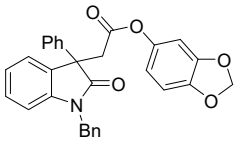
o-Tolyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ag**)

White solid (condition A: 59 mg, 66%; condition B: 55 mg, 62%) M.P.: 129-131 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.41 – 7.24 (m, 6H), 7.20 – 7.06 (m, 7H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 6.8 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.01 (d, *J* = 16.0 Hz, 1H), 3.62 (d, *J* = 16.0 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.9, 148.9, 143.8, 139.2, 135.6, 130.9, 130.8,

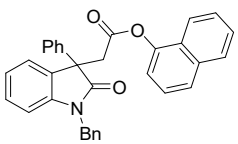
130.1, 128.8, 128.7, 128.5, 127.8, 127.3, 127.1, 126.7, 126.5, 126.0, 124.7, 122.6, 121.5, 109.7, 53.3, 44.2, 41.8, 15.8. ESI-MS: Calcd for $C_{30}H_{25}NO_3$: [M+H$^+$] 448.1907, found 448.1907.



3-(Trifluoromethyl)phenyl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ah**)
White solid (condition A: 74 mg, 74%; condition B: 70 mg, 70%) M.P.: 116-118 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.32 (m, 9H), 7.29 –7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.11 (m, 3H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.03 (d, *J* = 15.6 Hz, 1H), 3.56 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.8, 150.1, 143.7, 139.0, 135.4, 131.7 (q, *J* = 33.0 Hz), 130.4, 129.8, 128.9, 128.9, 128.5, 127.9, 127.5, 127.4, 126.5, 124.9, 123.3 (q, *J* = 271.0 Hz), 122.8, 122.6 (q, *J* = 4.0 Hz), 118.7 (q, *J* = 4.0 Hz), 109.7, 53.4, 44.3, 42.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65. ESI-MS: Calcd for $C_{30}H_{22}F_3NO_3$: [M+H$^+$] 502.1625, found 502.1625.



Benzo[*d*][1,3]dioxol-5-yl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3ai**)
White solid (condition A: 68 mg, 72%; condition B: 63 mg, 66%) M.P.: 146-148 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 9H), 7.24 – 7.14 (m, 4H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.09 – 6.05 (m, 1H), 6.00 (d, *J* = 2.4 Hz, 1H), 5.93 – 5.92 (m, 2H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 3.95 (d, *J* = 15.6 Hz, 1H), 3.53 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 168.4, 147.7, 145.2, 144.3, 143.7, 139.1, 135.6, 130.6, 128.8, 128.7, 128.5, 127.8, 127.4, 127.2, 126.5, 124.8, 122.7, 113.7, 109.6, 107.7, 103.3, 101.5, 53.4, 44.2, 42.0. ESI-MS: Calcd for $C_{30}H_{23}NO_5$: [M+H$^+$] 478.1649, found 478.1646.

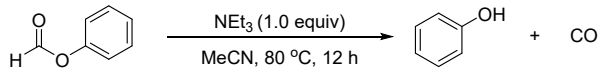


Naphthalen-1-yl-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (**3aj**)

Colorless oil (condition A: 42 mg, 44%; condition B: 42 mg, 44%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.31 (m, 10H), 7.26 – 7.18 (m, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 3.74 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 168.2, 146.2, 143.9, 139.2, 135.5, 134.4, 130.8, 128.9, 128.8, 128.4, 127.9, 127.7, 127.2, 127.1, 126.6, 126.5, 126.4, 126.3, 126.0, 125.2, 124.9, 122.7, 121.1, 117.7, 109.9, 53.4, 44.3, 42.1. ESI-MS: Calcd for $C_{33}H_{25}NO_3$: [M+H$^+$] 484.1907, found 484.1907.

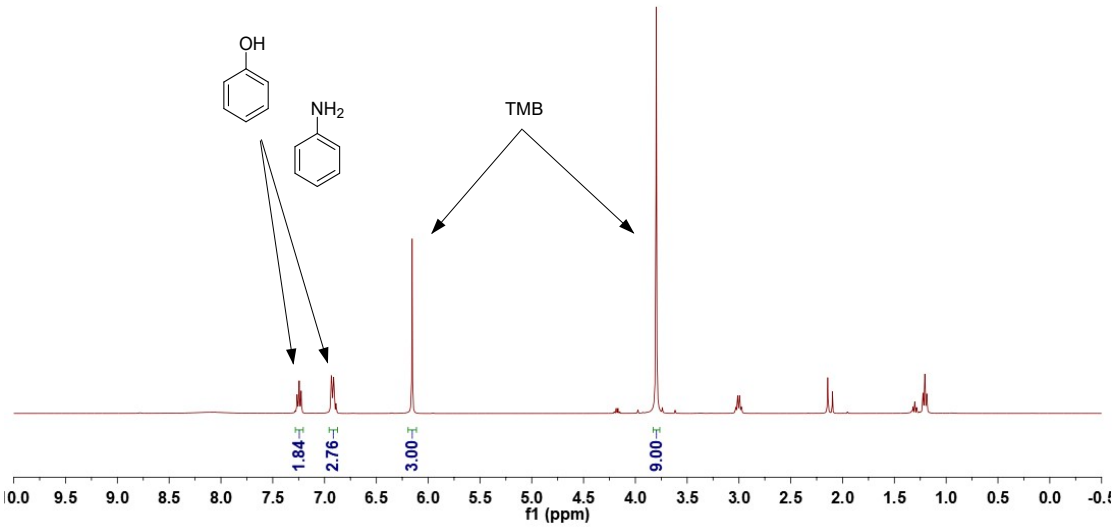
Control Experiments

Decarbonylation of phenyl formate with NEt_3:

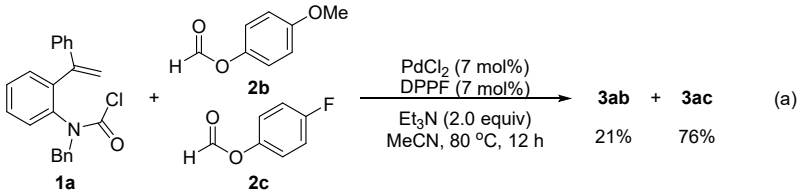


2a 92%

In a 38 mL sealed tube, the mixture of **2a** (0.4 mmol) and NEt_3 (0.4 mmol) was dissolved in anhydrous MeCN (2.0 mL). The tube was then purged 3 times with N_2 and sealed with a PTEF cap. The reaction mixture was allowed to react at 80 °C for 12 h. The solvent was removed in vacuum and ^{1}H NMR was taken using 0.4 mmol 1,3,5-trimethoxybenzene as the internal standard. The reaction provided the product phenol in 92% yield.

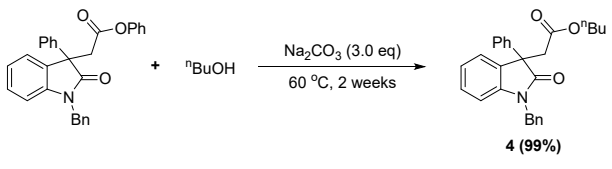


Competition experiment: electron-deficient *vs.* electron-rich



In a 38 mL sealed tube, the mixture of **1** (0.2 mmol), **2b** (0.4 mmol), **2c** (0.4 mmol), $PdCl_2$ (2.5 mg, 0.014 mmol), DPPF (7.7 mg, 0.014 mmol) and Et_3N (40.5 mg, 0.4 mmol) was dissolved in anhydrous MeCN (2.0 mL). The tube was then purged 3 times with N_2 and sealed with a PTEF cap. The reaction mixture was allowed to react at 80 ^oC for 12 h. After the reaction was completed, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give product **3ab** (19 mg, 21%) and **3ac** (68 mg, 76%).

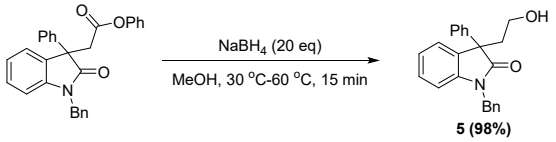
Application Investigation:



In a 38 mL sealed tube, Na_2CO_3 (0.6 mmol, 3.0 equiv) was added to a solution of

3aa (86.6 mg, 0.2 mmol) in *n*-butanol (2.0 mL). The reaction mixture was carried out at 60 °C for 2 weeks. After the reaction was completed, 10 mL of water was added and the mixture was extracted with DCM (20 mL × 3). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude was purified via column chromatography on silica gel. The target compound was isolated as colorless oil **4** (81.8 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.09 (m, 12H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.97 (d, *J* = 16.0 Hz, 1H), 4.73 (d, *J* = 16.0 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.75 – 3.67 (m, 1H), 3.55 (d, *J* = 16.0 Hz, 1H), 3.22 (d, *J* = 16.0 Hz, 1H), 1.25 – 1.16 (m, 2H), 1.11 – 1.01 (m, 2H), 0.72 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 169.6, 143.6, 139.4, 135.9, 131.2, 128.7, 128.6, 128.4, 127.6, 127.4, 127.3, 126.5, 124.5, 122.5, 109.4, 64.4, 53.3, 44.1, 41.8, 30.3, 18.8, 13.6. ESI-MS: Calcd for $C_{27}H_{27}NO_3$: [M+Na$^+$] 436.1883, found 436.1874.

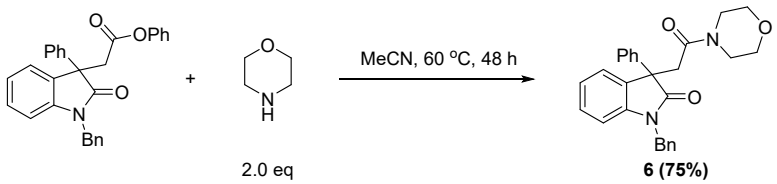


5 (98%)

In a 25 mL round bottomed flask equipped with magnetic stir bar, **3aa** (86.6 mg, 0.2 mmol) was dissolved in 2.5 mL methanol with stirring at 30 °C. To this solution was slowly added 151.3 mg (4 mmol, 20 equiv) of sodium borohydride with stirring. A reflux condenser was attached to the flask and the reaction was heated to 60 °C over 15 min. Once the starting material was consumed (TLC analysis), 6 mL H_2O was added and some of the methanol was removed on a rotary evaporator. The resulting aqueous solution was extracted with five 10 mL portions of DCM; the combined organic extracts were dried ($MgSO_4$), concentrated on a rotary evaporator and purified by flash chromatography to afford **5** (67.2 mg, 98%) of the product as a white solid.

M.P.: 131-133 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.07 (m, 12H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 16.0 Hz, 1H), 4.08 (d, *J* = 16.0 Hz, 1H), 3.54 – 3.31 (m, 2H), 2.78 – 2.71 (m, 1H), 2.45 – 2.30 (m, 1H), 2.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 142.7, 140.1, 135.7, 131.9, 128.7, 128.6, 128.2, 127.5, 127.3, 127.2, 126.6, 124.6, 122.8, 109.5, 59.3, 54.9, 44.0, 40.0. ESI-MS: Calcd for

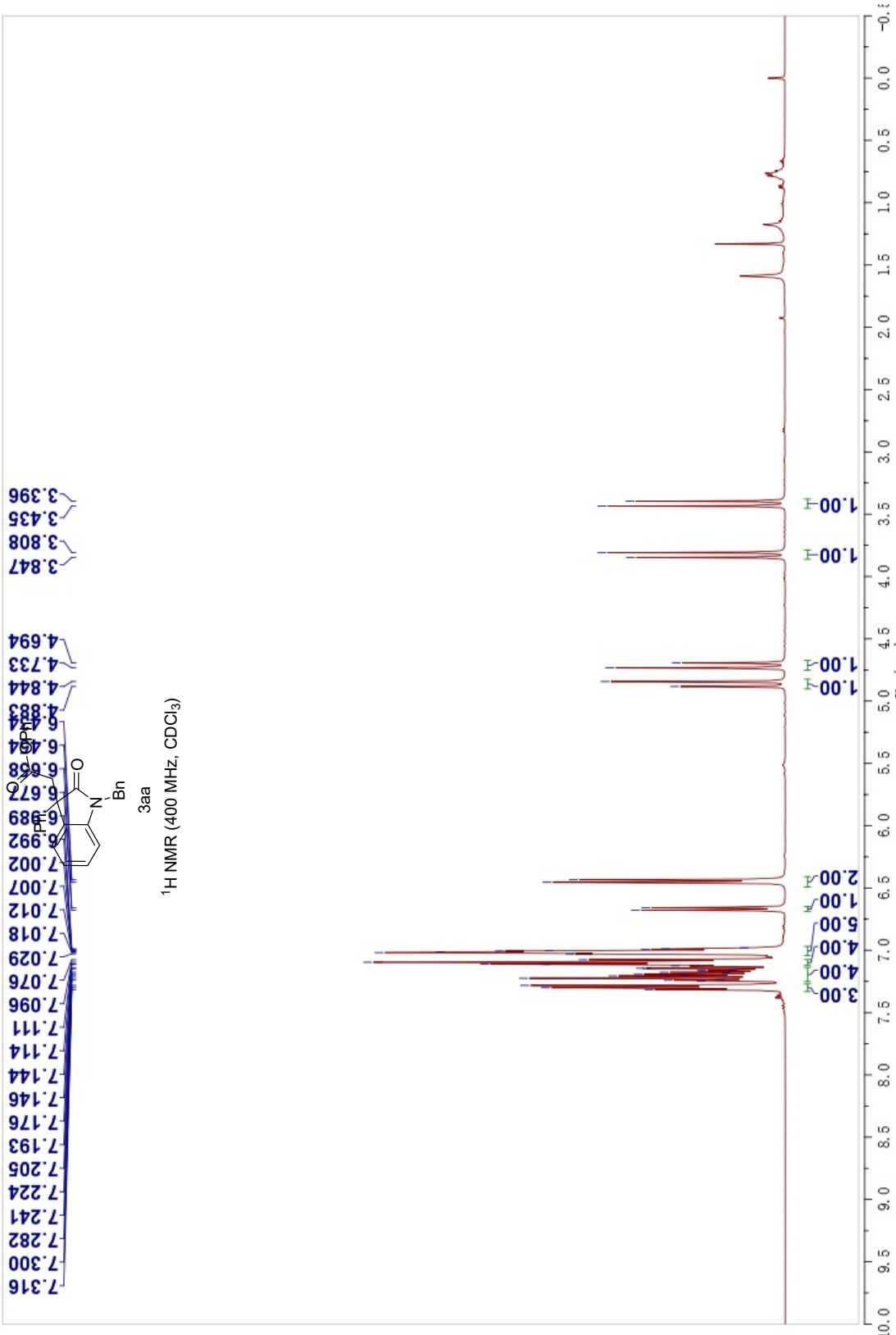
$C_{23}H_{21}NO_2$: [M+H$^+$] 344.1645, found 344.1647.

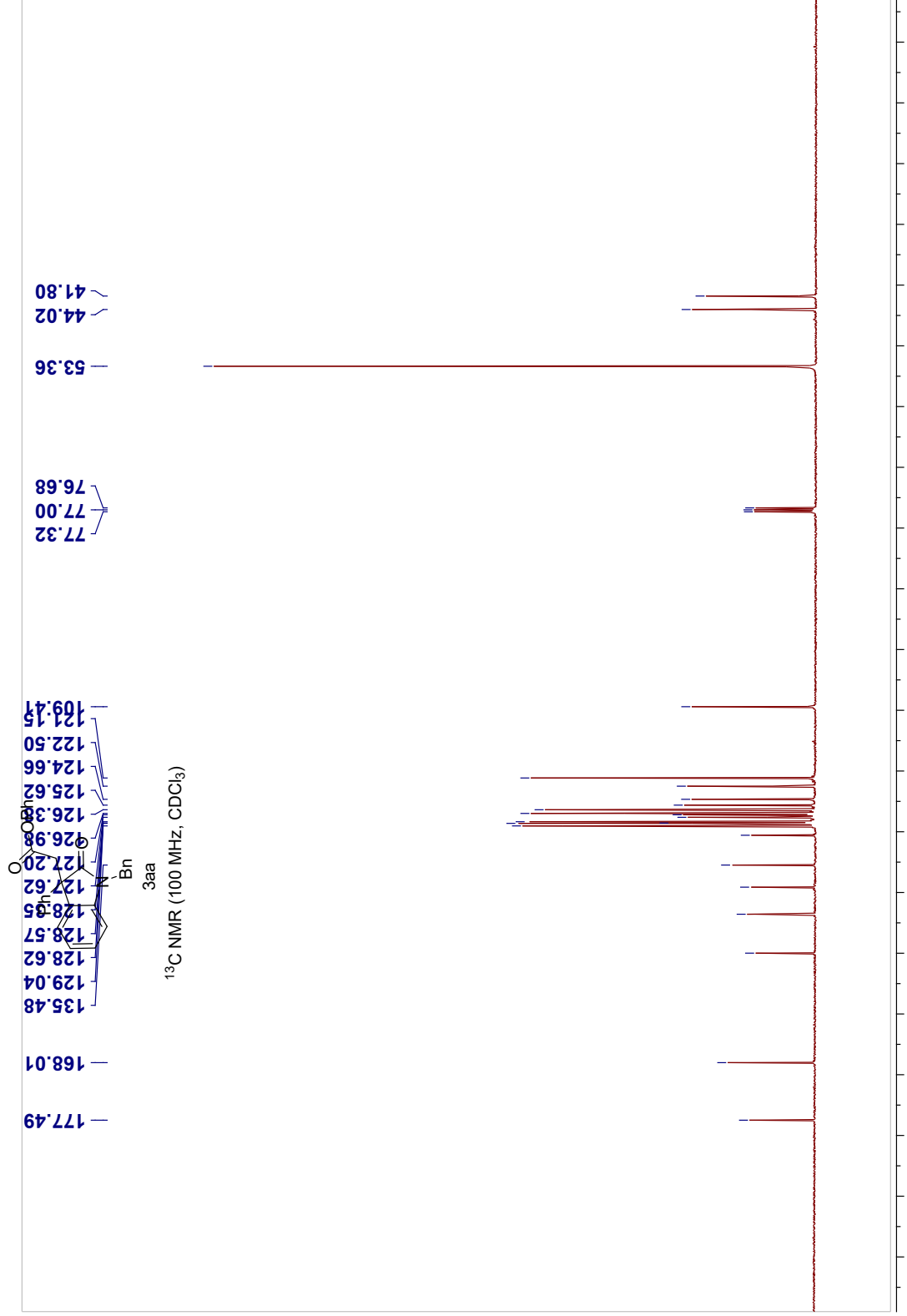


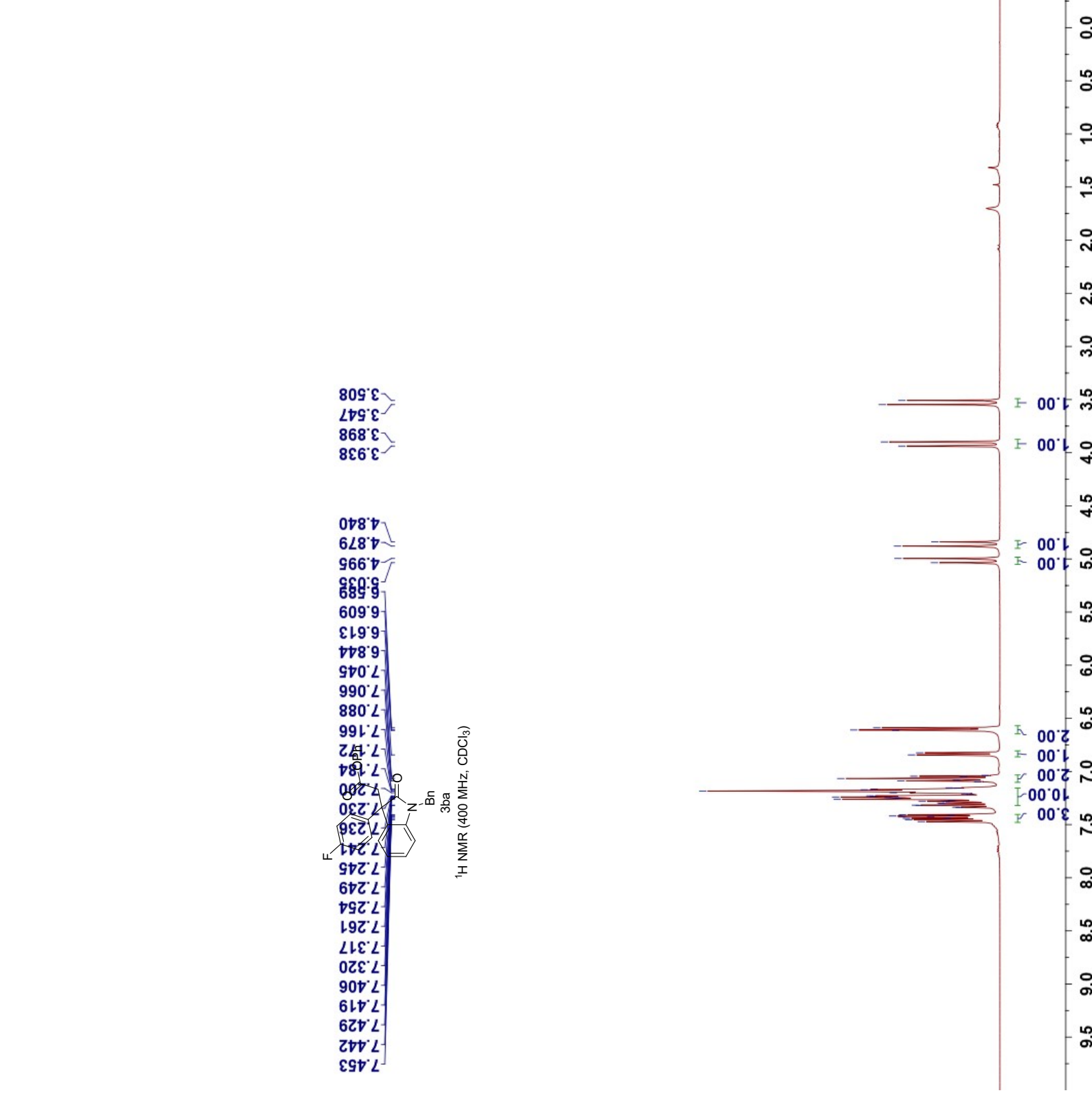
In a 38 mL sealed tube, **3aa** (86.6 mg, 0.2 mmol) and morpholine (0.4 mmol, 2.0 equiv) were dissolved and mixed in acetonitrile (1.0 mL). The reaction mixture was carried at 60 °C for 48 h. After the reaction was completed, 5 mL of brine was added and the mixture was extracted with ethyl acetate (8 mL × 3). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude was purified via column chromatography on silica gel. The target compound was isolated as white solid **6** (63.9 mg, 75%).

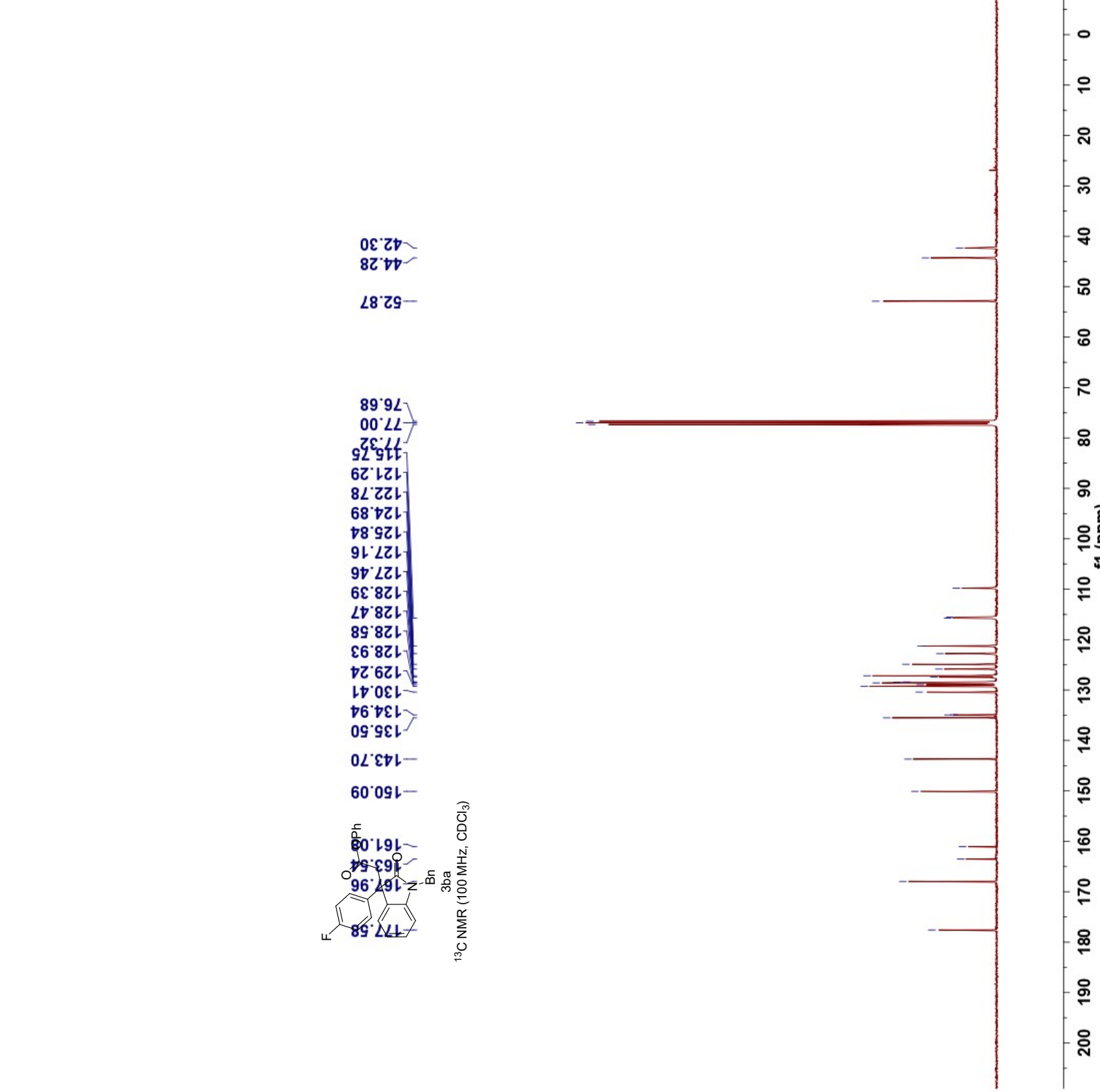
M.P.: 177-179 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.07 (m, 10H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 16.0 Hz, 1H), 3.56 – 3.29 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 167.3, 143.8, 139.8, 136.1, 131.9, 128.6, 128.6, 128.1, 127.5, 127.2, 127.0, 126.7, 123.8, 122.1, 109.5, 66.7, 66.4, 53.6, 45.9, 44.1, 41.8, 41.0. ESI-MS: Calcd for $C_{27}H_{26}N_2O_3$: [M+Na$^+$] 449.1836, found 449.1841.

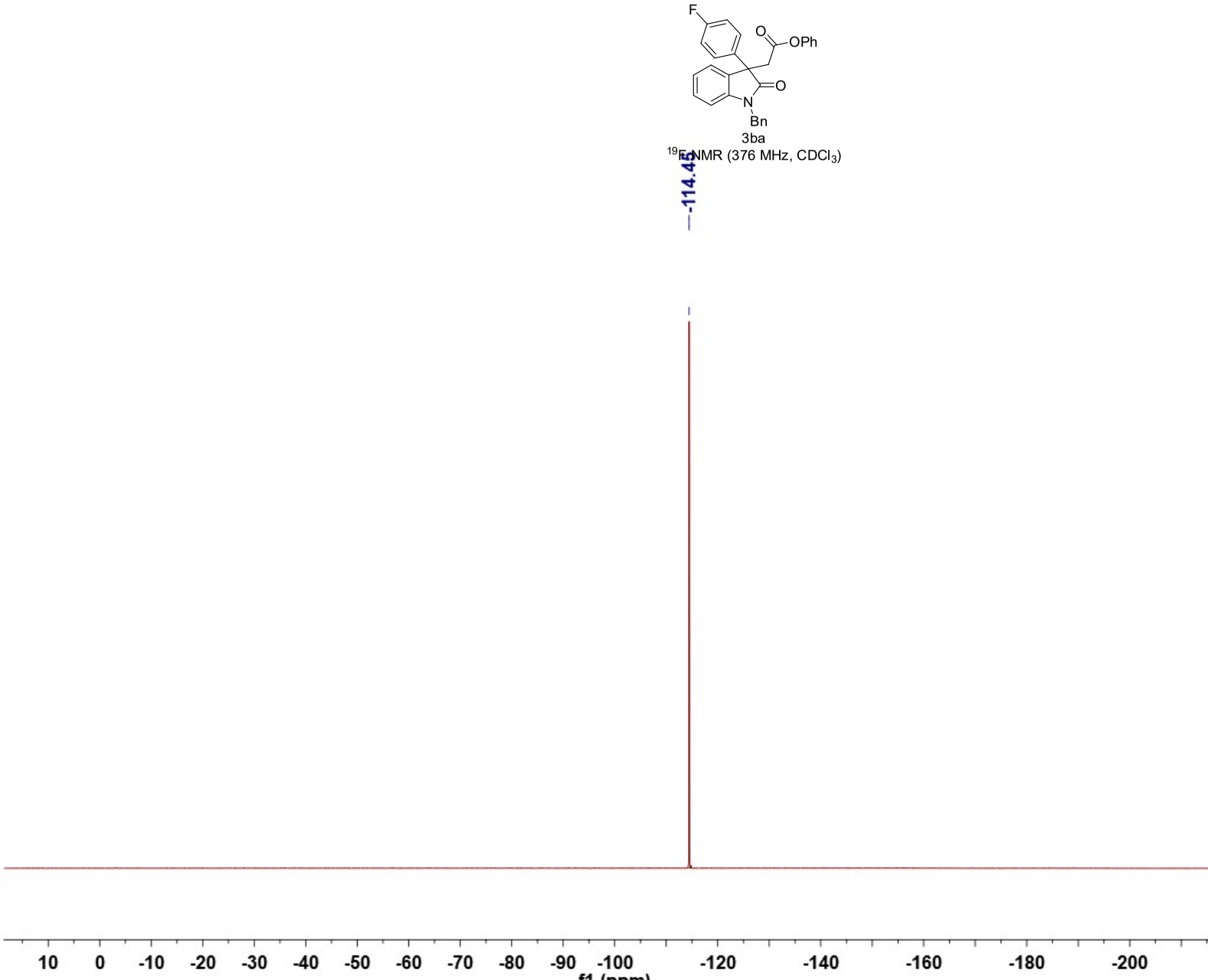
NMR Spectra:

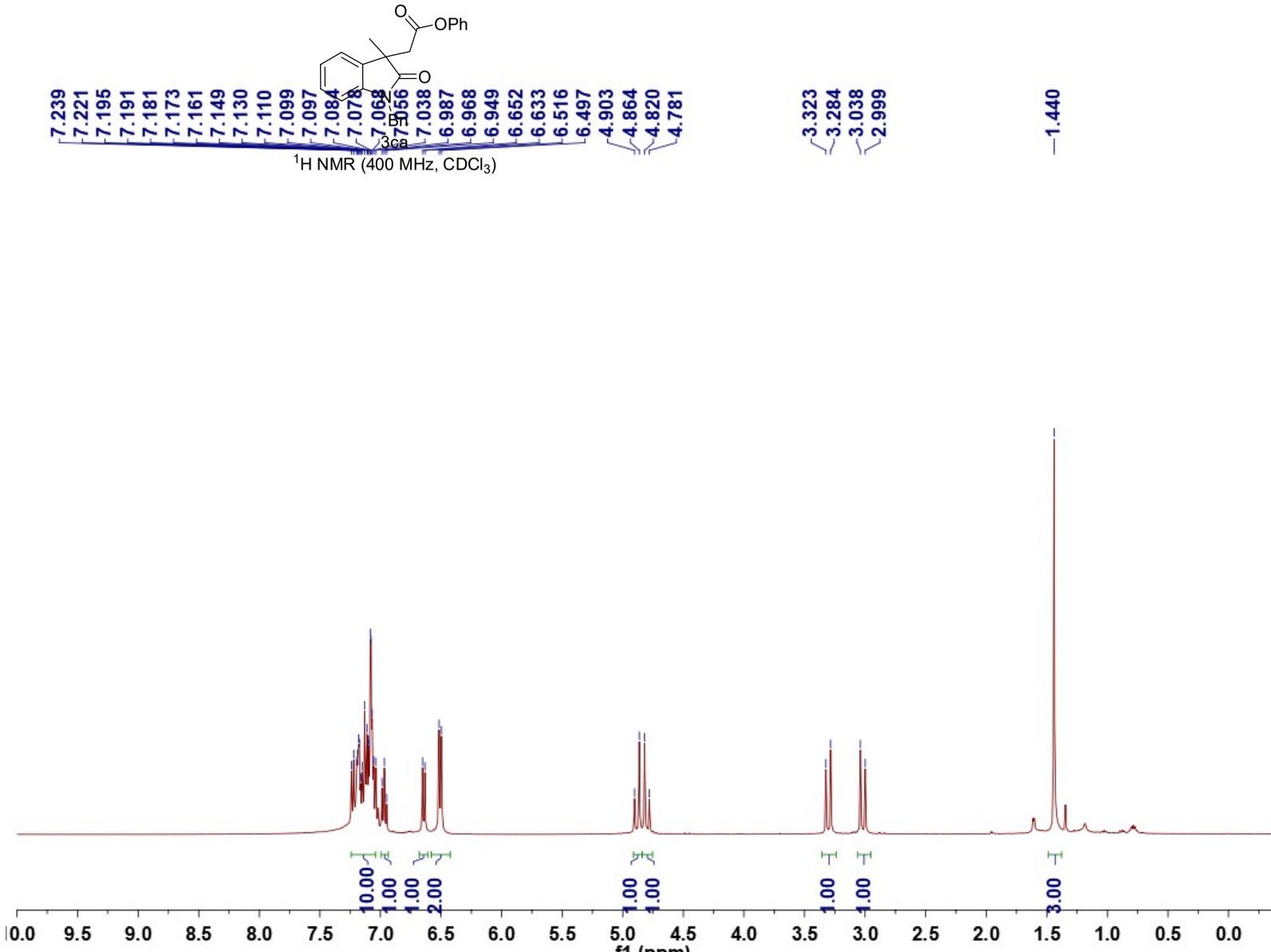

3.396
3.435
3.808
3.847
4.694
4.733
4.844
4.883
6.424
6.464
6.658
6.672
6.689
6.992
7.002
7.007
7.012
7.018
7.029
7.076
7.096
7.111
7.114
7.144
7.146
7.176
7.193
7.205
7.224
7.241
7.282
7.300
7.316
Ph
O
O
N
Bn
3aa
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.00
1.00
1.00
2.00
1.00
5.00
4.00
4.00
3.00


41.80
44.02
53.36
76.68
77.00
77.32
109.47
121.15
122.50
124.66
125.62
126.38
126.98
127.20
127.62
128.45
128.57
128.62
129.04
135.48
168.01
177.49
^{13}C NMR (100 MHz, CDCl$_3$)
3aa
Bn
OBn
O
N
O
Bn

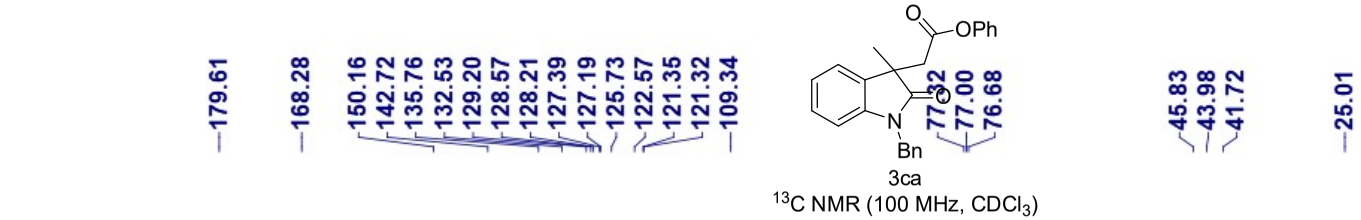

3.508
3.547
3.898
3.938
4.840
4.879
4.995
5.035
6.589
6.609
6.613
6.844
7.045
7.066
7.088
7.166
7.172
7.184
7.200
7.230
7.236
7.241
7.245
7.249
7.254
7.261
7.317
7.320
7.406
7.419
7.429
7.442
7.453
F
O
N
Bn
3ba
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.00
1.00
1.00
2.00
1.00
2.00
10.00
3.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5


42.30
44.28
52.87
76.68
77.00
77.32
115.75
121.29
122.78
124.89
125.84
127.16
127.46
128.39
128.47
128.58
128.93
129.24
130.41
134.94
135.50
143.70
150.09
161.08
163.54
167.96
177.58
Ph
O
O
N
Bn
F
3ba
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


F
O
OPh
O
N
Bn
3ba
^{19}F NMR (376 MHz, $CDCl_3$)
-114.45
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

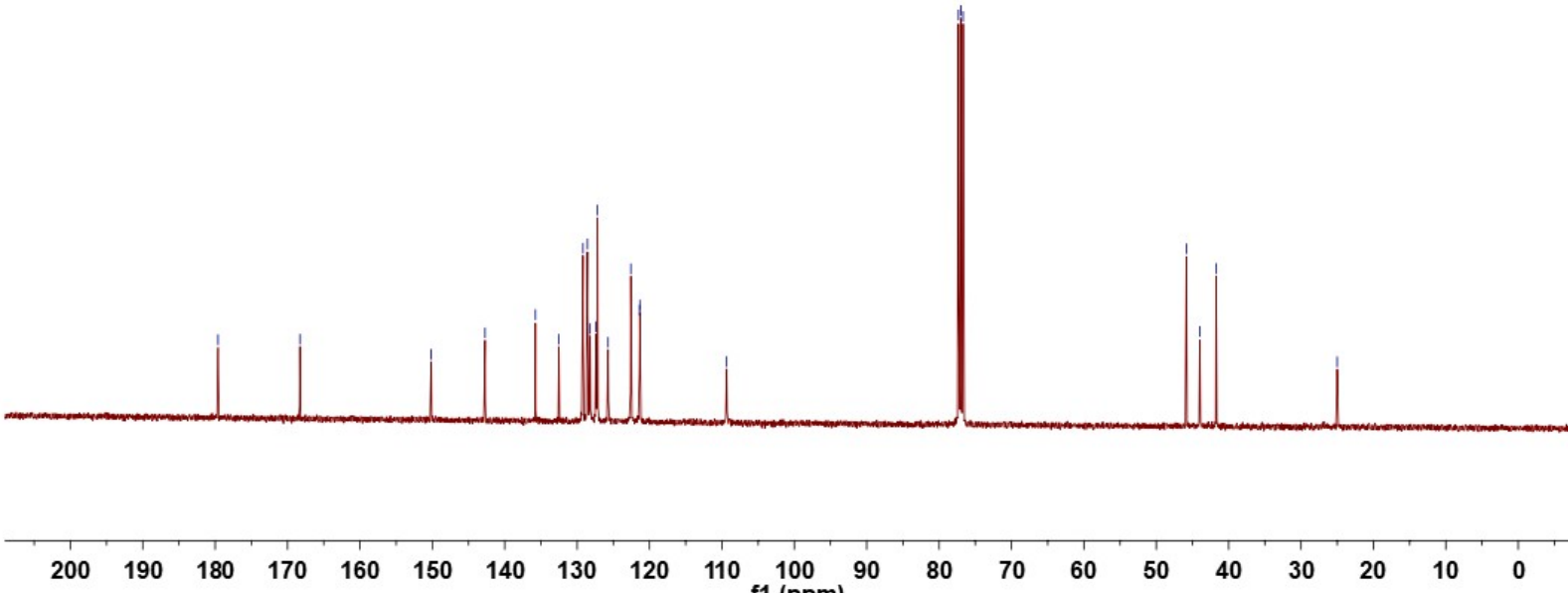


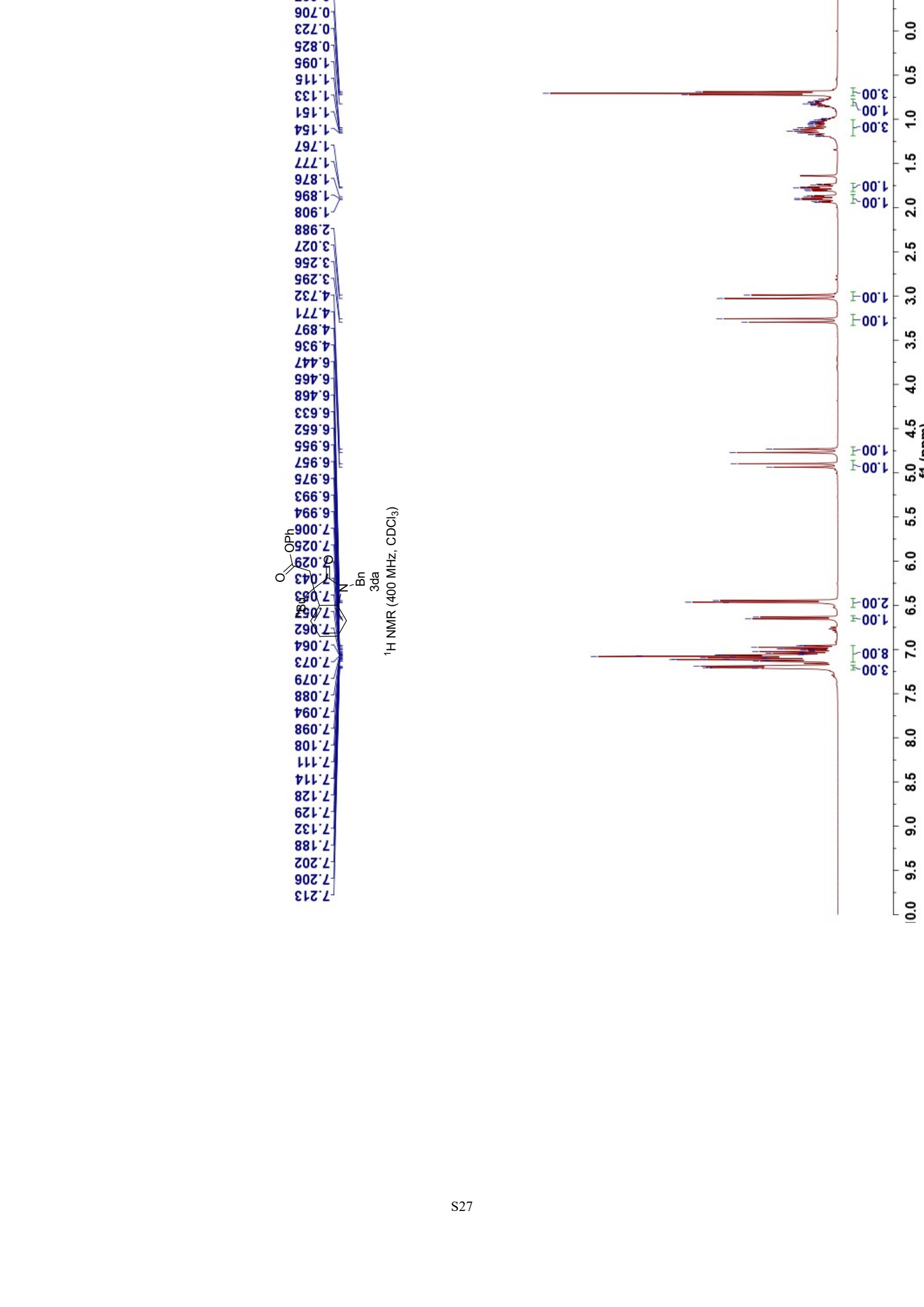
^{1}H NMR (400 MHz, $CDCl_3$)



3ca

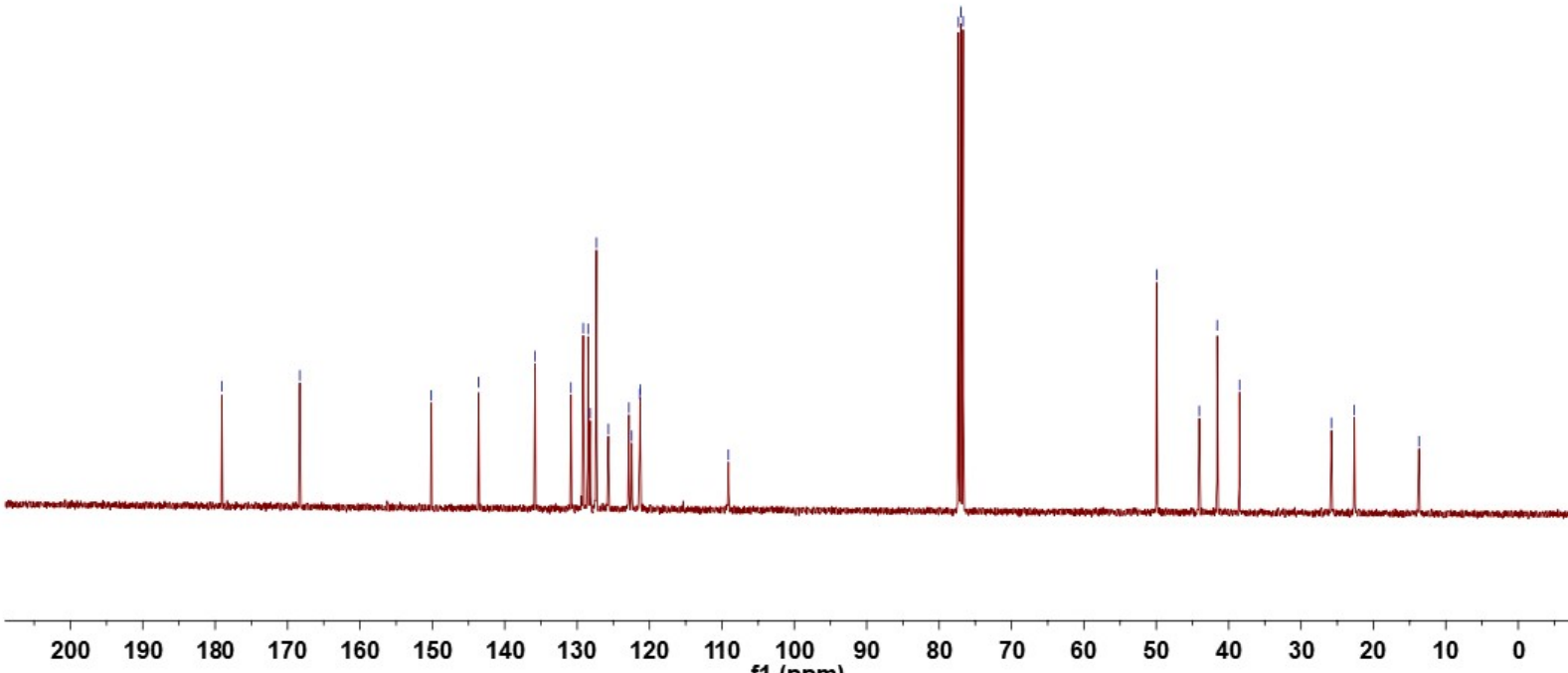
^{13}C NMR (100 MHz, $CDCl_3$)

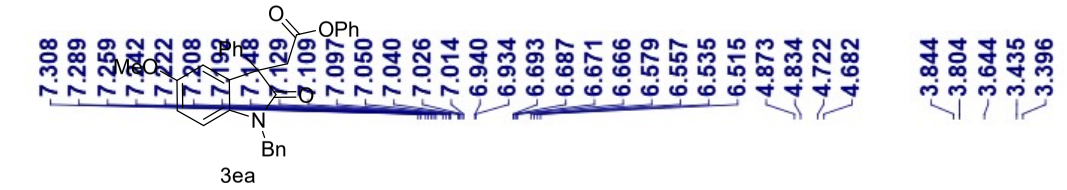



OPh
O
O
N
Bn
Br
3da
^{1}H NMR (400 MHz, CDCl$_3$)

3da

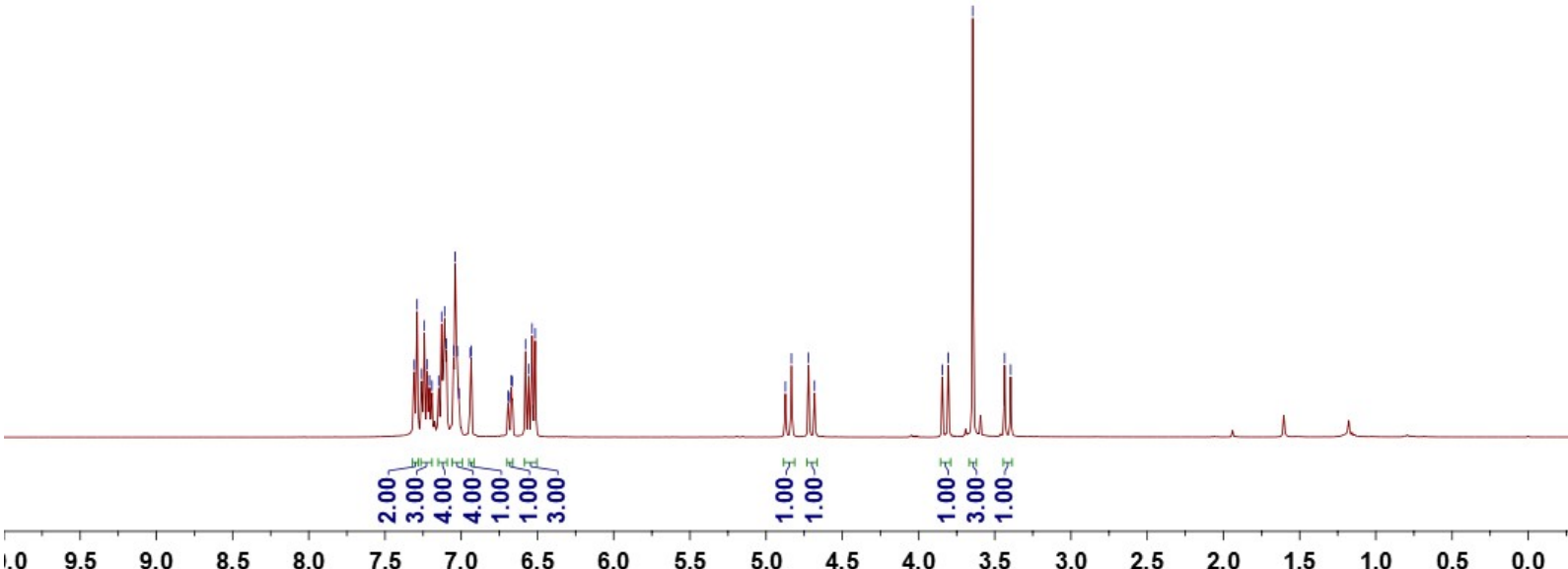
^{13}C NMR (100 MHz, $CDCl_3$)

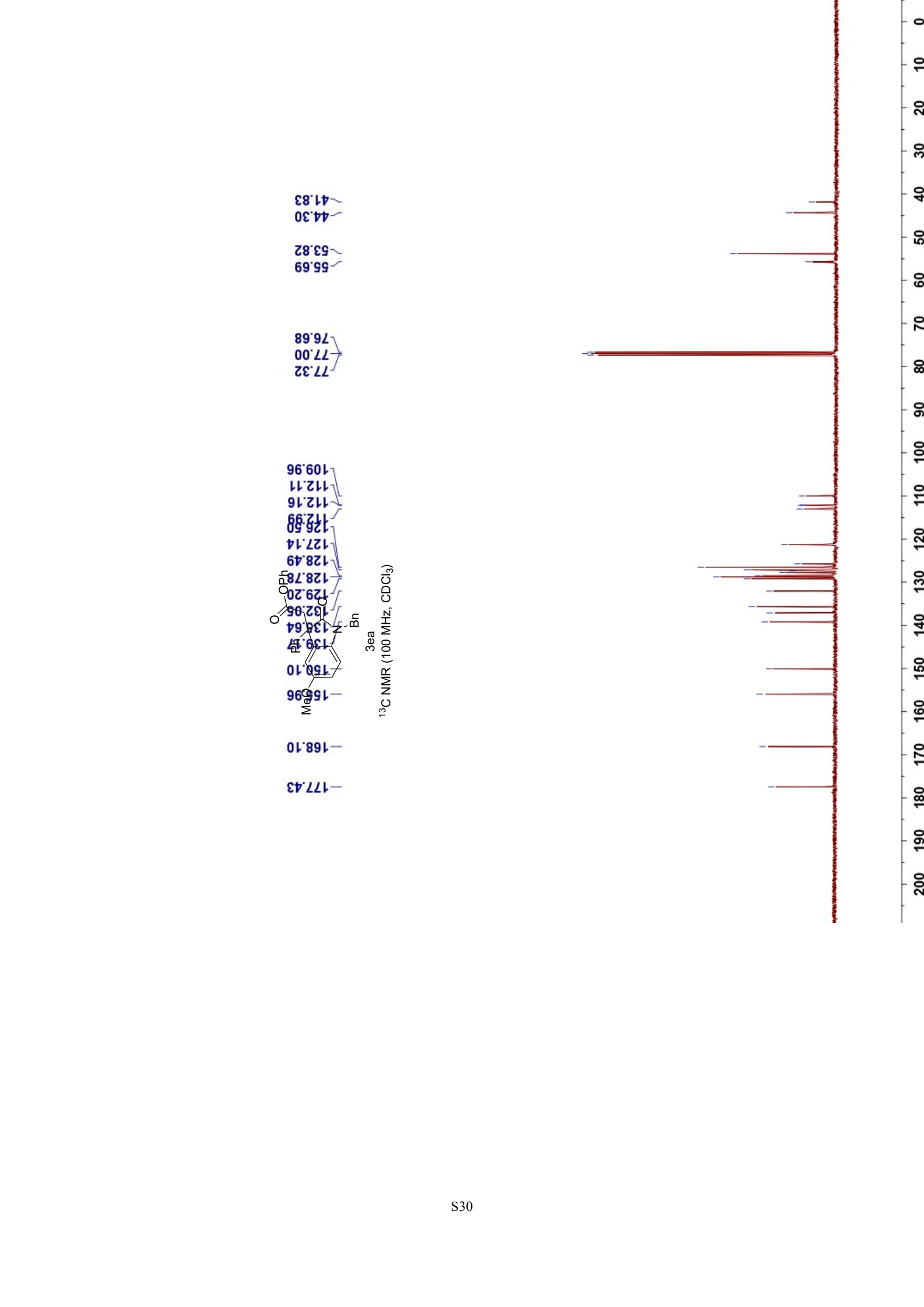


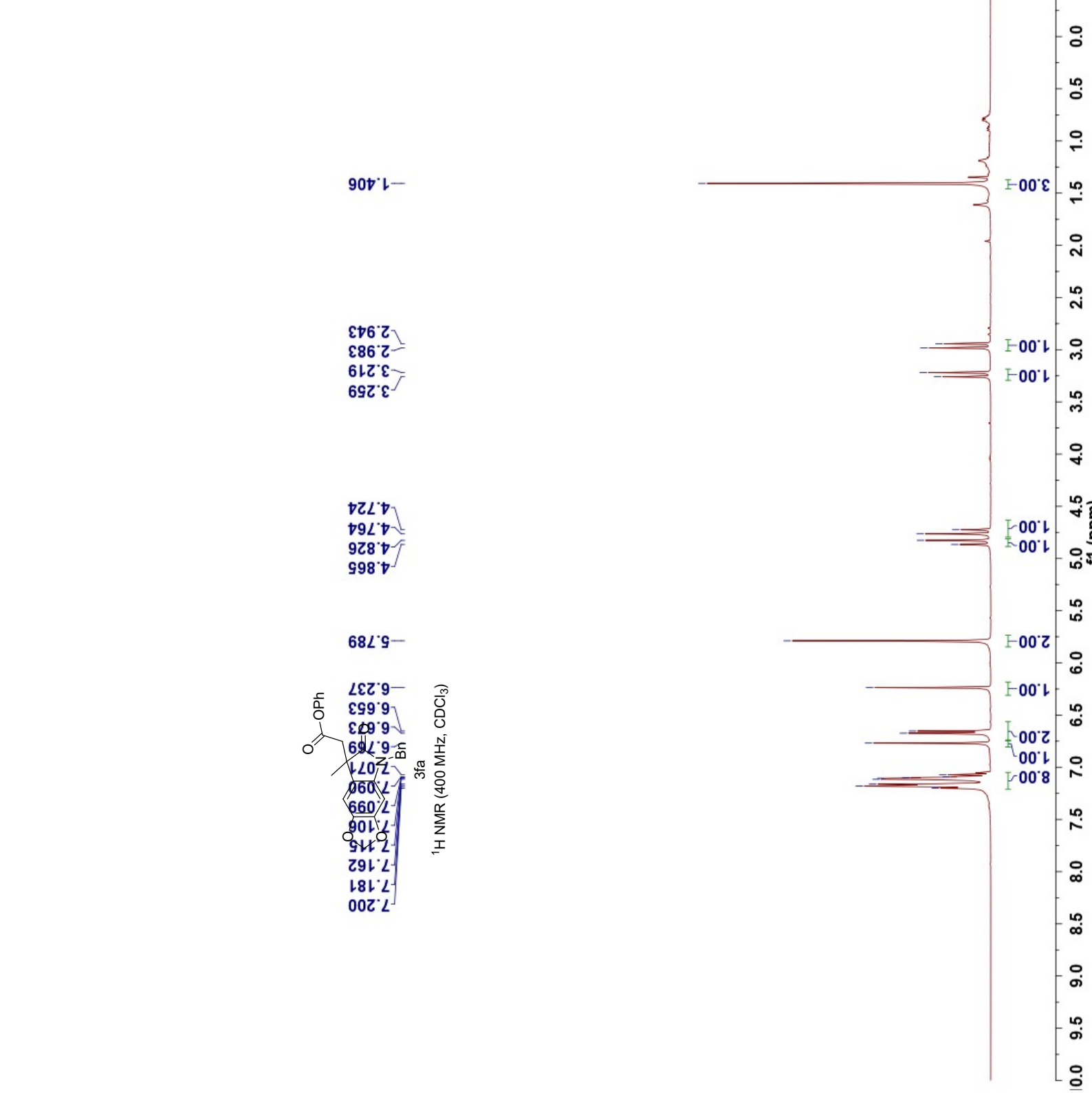


3ea

^{1}H NMR (400 MHz, $CDCl_3$)

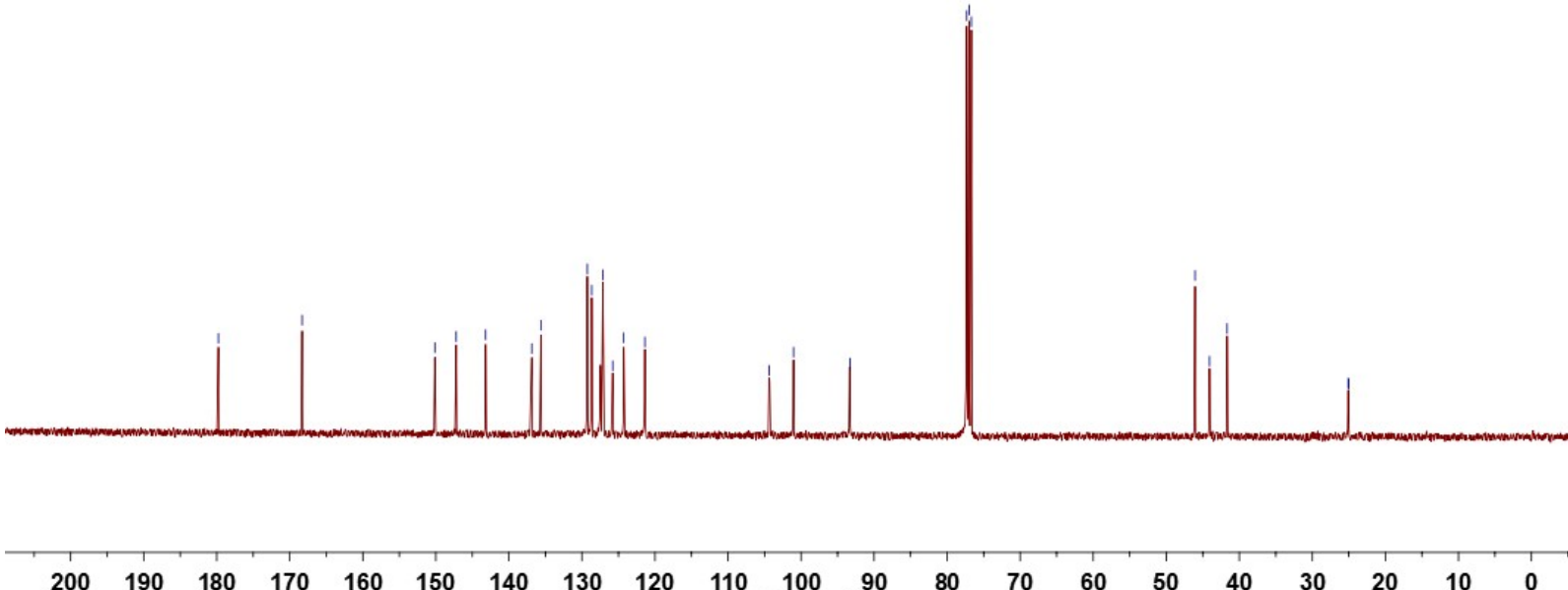


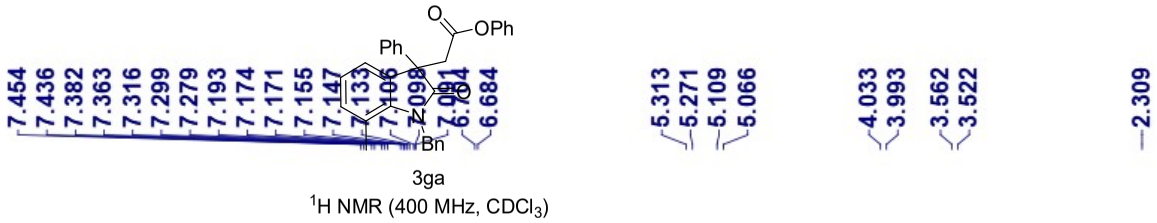

41.83
44.30
53.82
55.69
76.68
77.00
77.32
109.96
112.11
112.16
112.99
126.50
127.14
128.49
128.78
129.20
132.05
133.64
139.47
150.10
155.96
168.10
177.43
OPh
O
O
N
Bn
Ph
MeO
3ea
^{13}C NMR (100 MHz, CDCl$_3$)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


1.406
2.943
2.983
3.219
3.259
4.724
4.764
4.826
4.865
5.789
6.237
6.653
6.693
6.759
7.071
7.090
7.099
7.106
7.115
7.162
7.181
7.200
3fa
^{1}H NMR (400 MHz, CDCl$_3$)
3.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
1.00
8.00

3fa

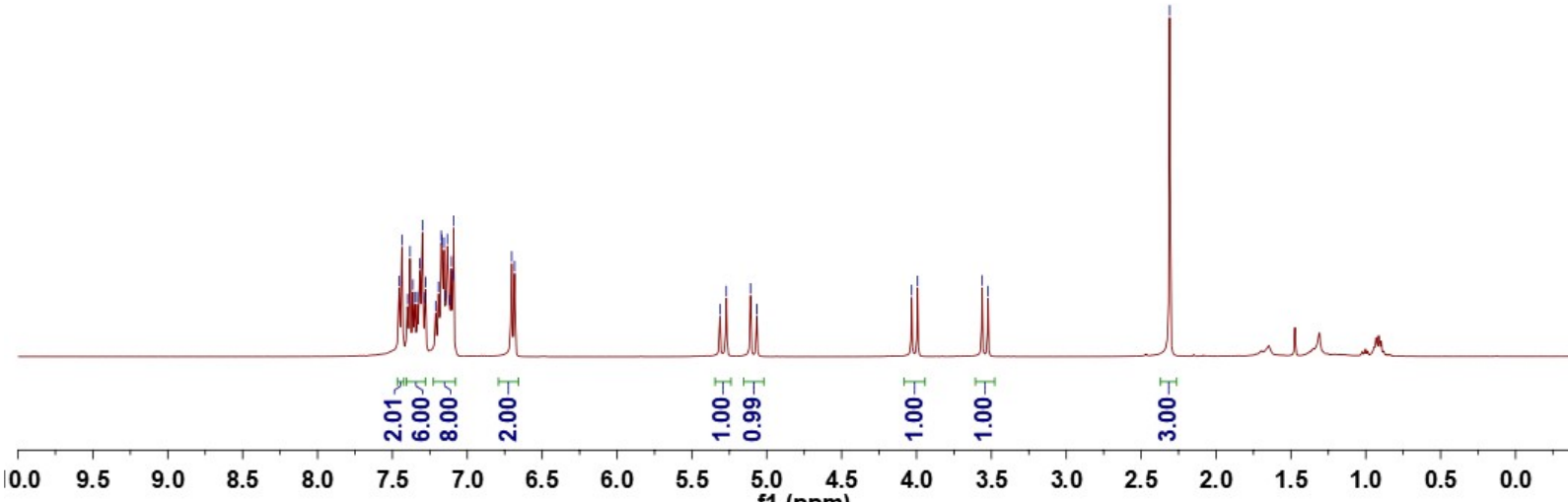
^{13}C NMR (100 MHz, $CDCl_3$)

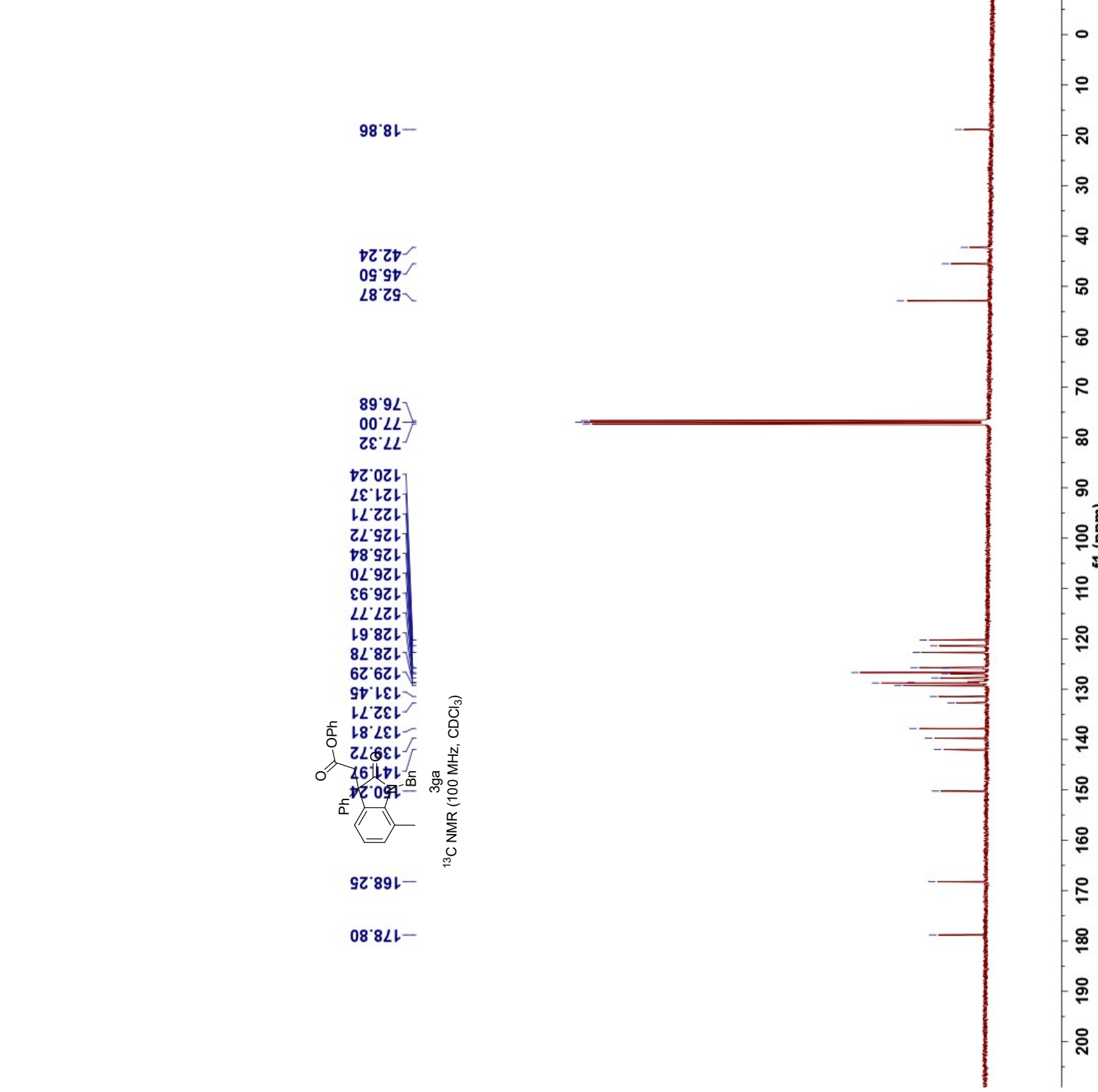


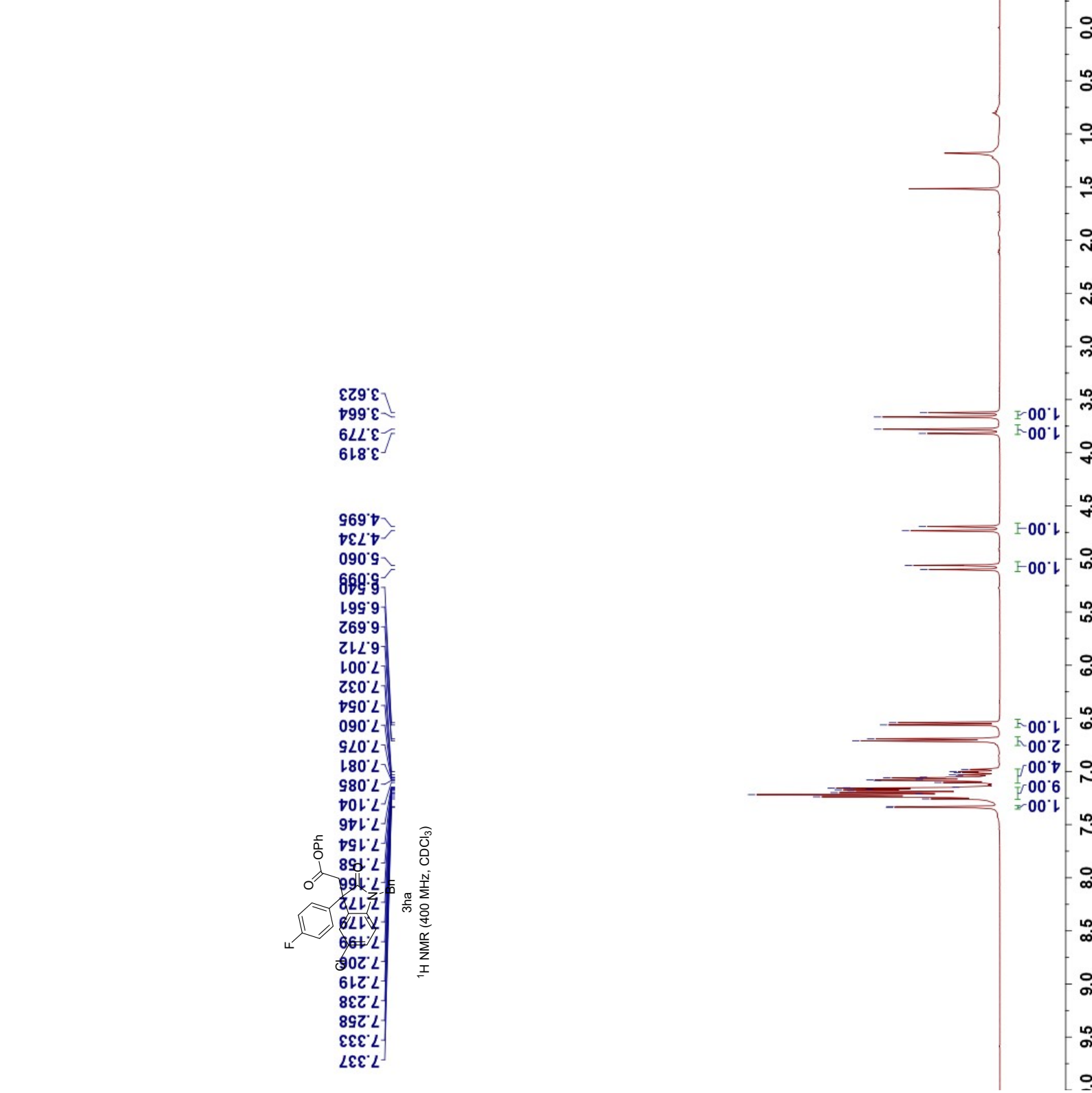


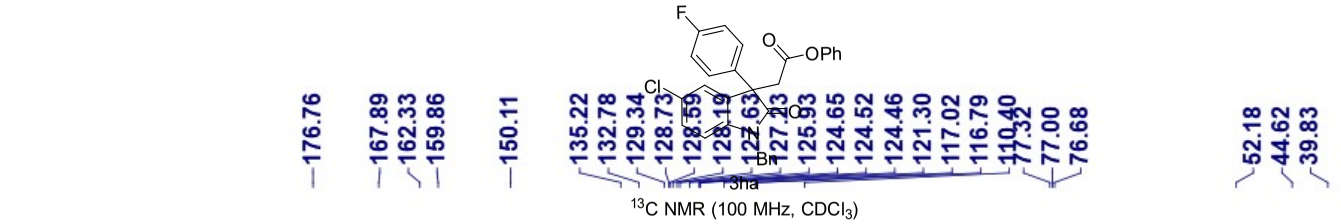
3ga

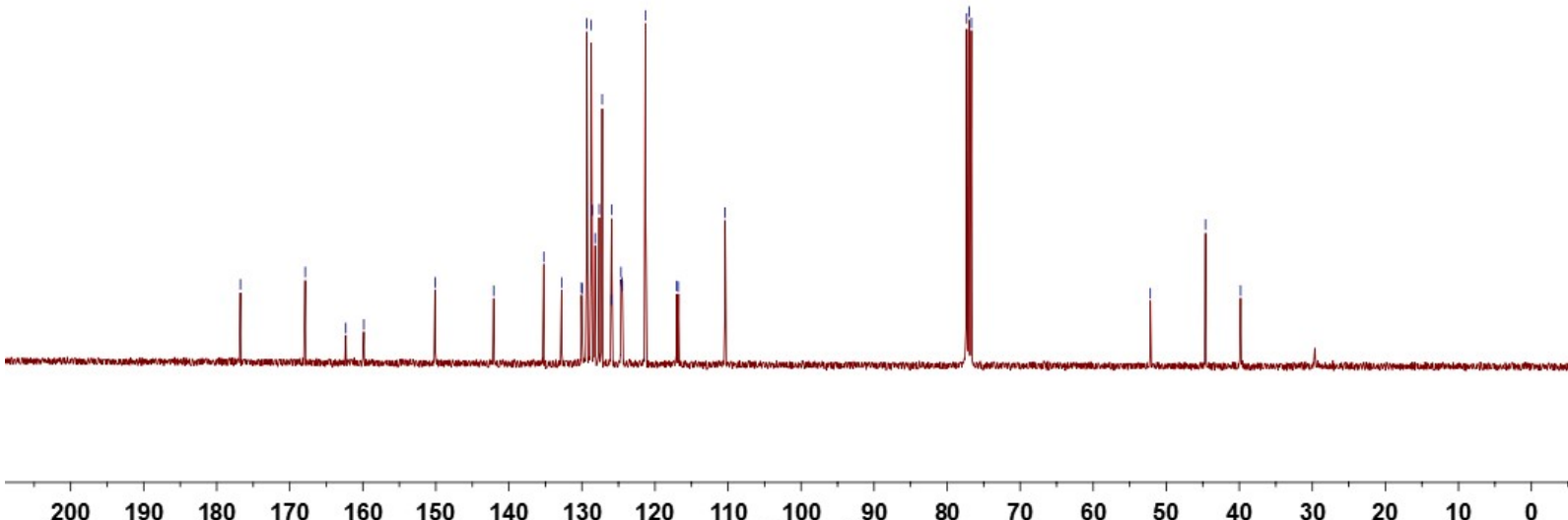
^{1}H NMR (400 MHz, $CDCl_3$)

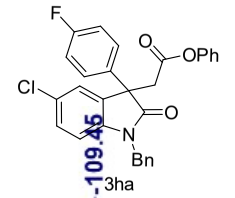



18.86
42.24
45.50
52.87
76.68
77.00
77.32
120.24
121.37
122.71
125.72
125.84
126.70
126.93
127.77
128.61
128.78
129.29
131.45
132.71
137.81
139.72
141.97
150.24
168.25
178.80
OPh
O
Ph
Bn
3ga
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


3.623
3.664
3.779
3.819
4.695
4.734
5.060
5.099
6.540
6.561
6.692
6.712
7.001
7.032
7.054
7.060
7.075
7.081
7.085
7.104
7.146
7.154
7.158
7.166
7.172
7.179
7.199
7.206
7.219
7.238
7.258
7.333
7.337
1.00
1.00
1.00
1.00
1.00
2.00
4.00
9.00
1.00
O
OPh
F
Cl
N
Bn
3ha
^{1}H NMR (400 MHz, CDCl$_3$)

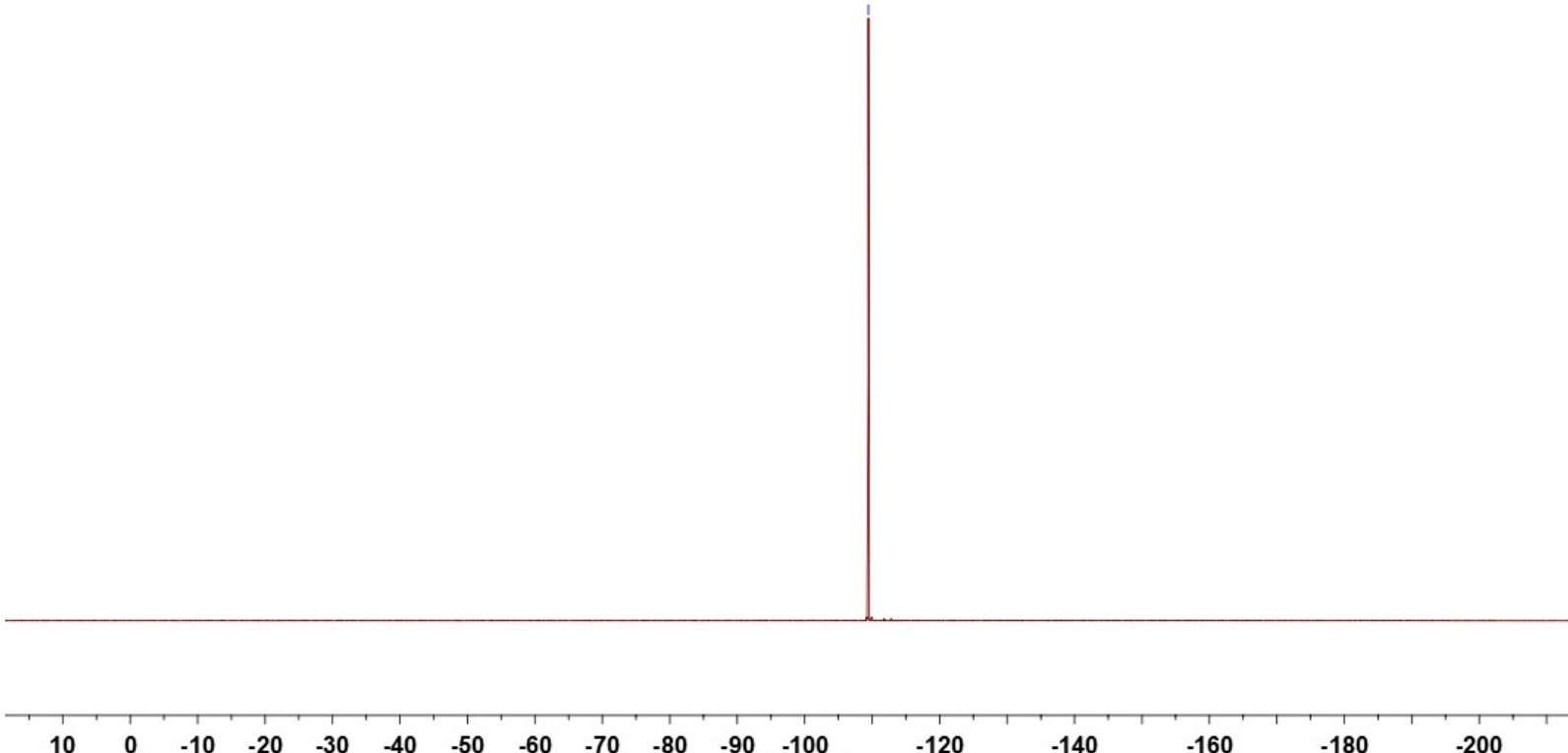

F
O
OPh
Cl
HO
Br
3ha
176.76
167.89
162.33
159.86
150.11
135.22
132.78
129.34
128.73
128.59
128.19
127.63
127.13
125.93
124.65
124.52
124.46
121.30
117.02
116.79
110.40
77.32
77.00
76.68
52.18
44.62
39.83
^{13}C NMR (100 MHz, CDCl$_3$)

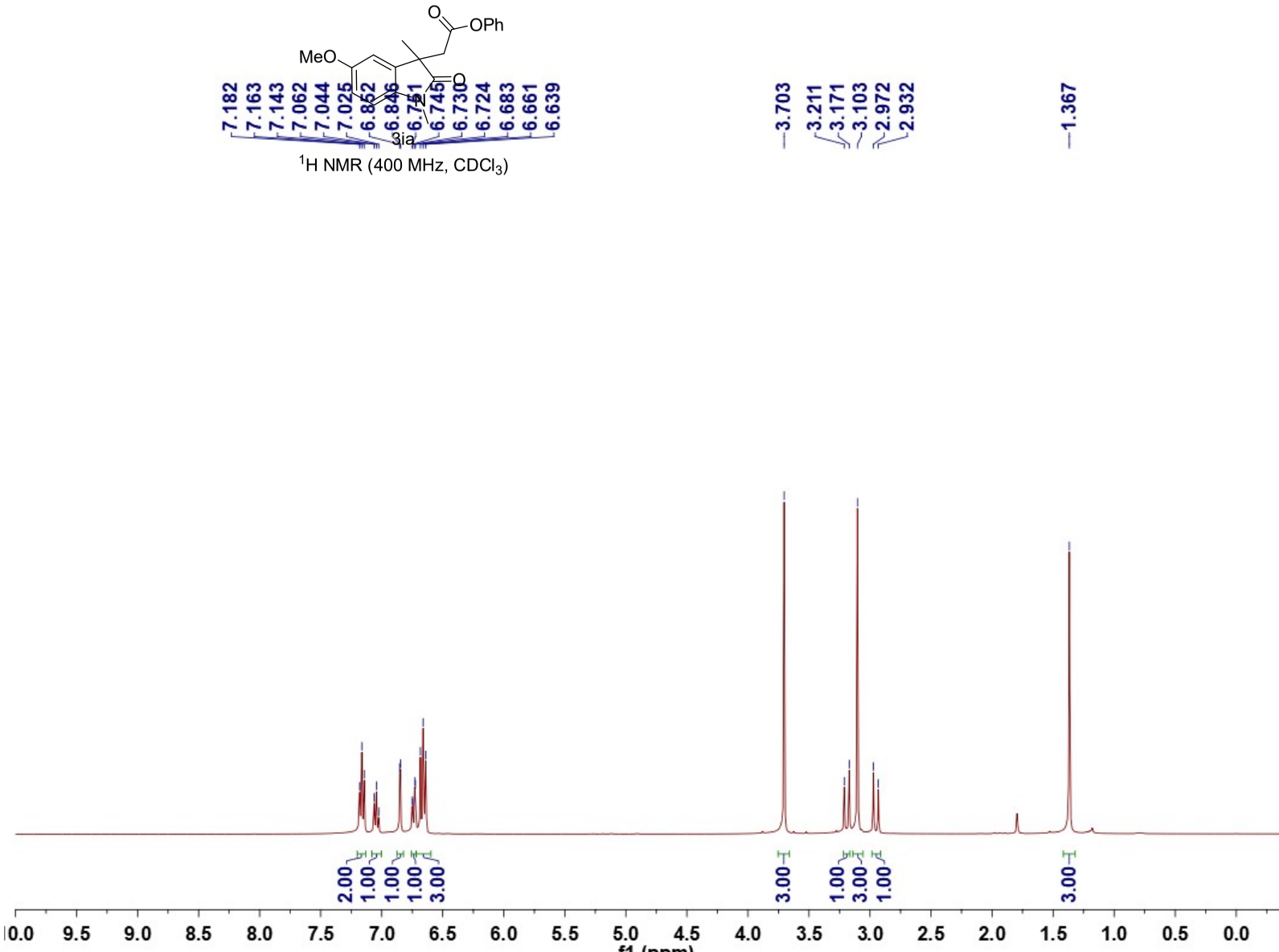

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



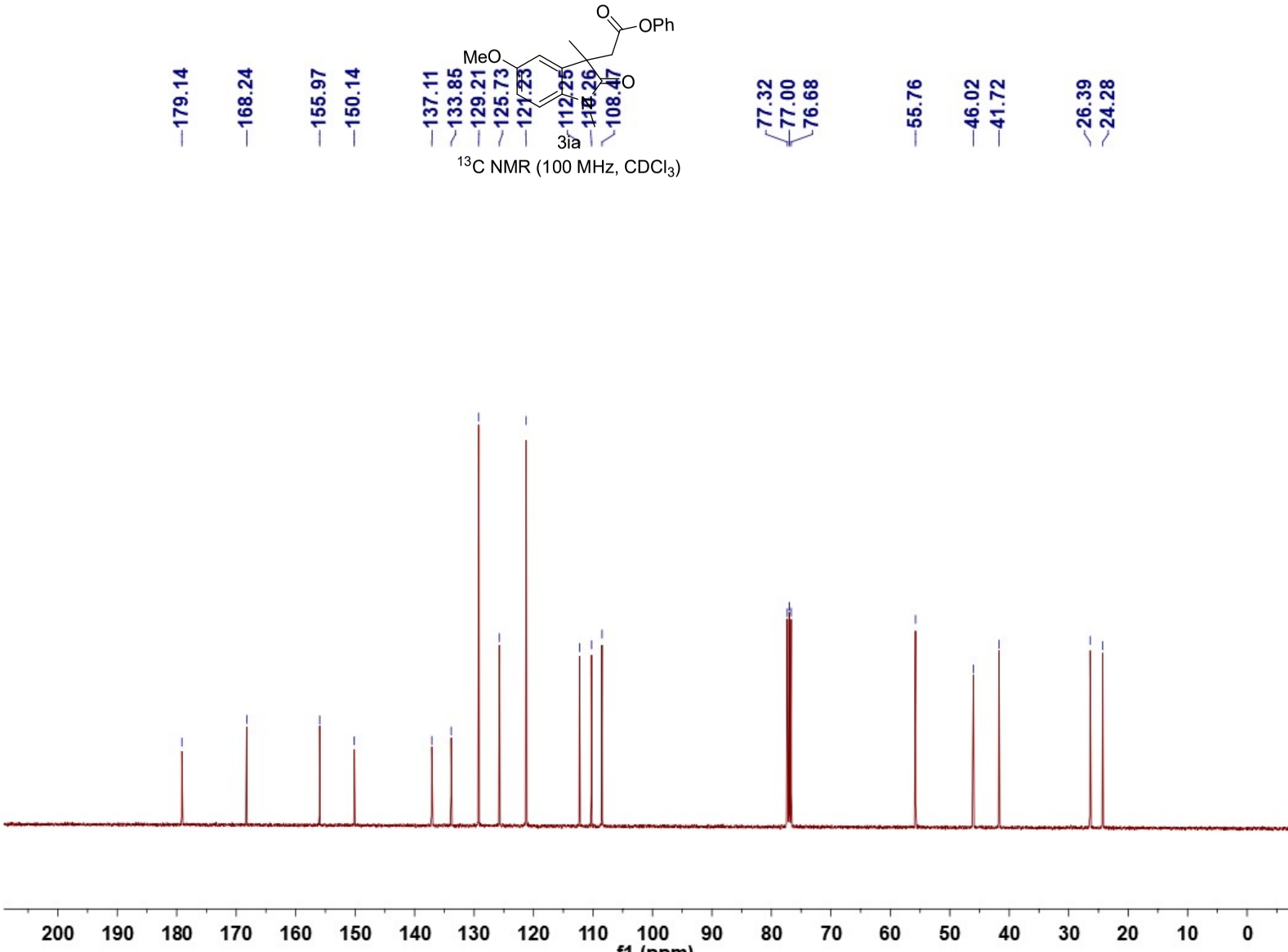
3ha

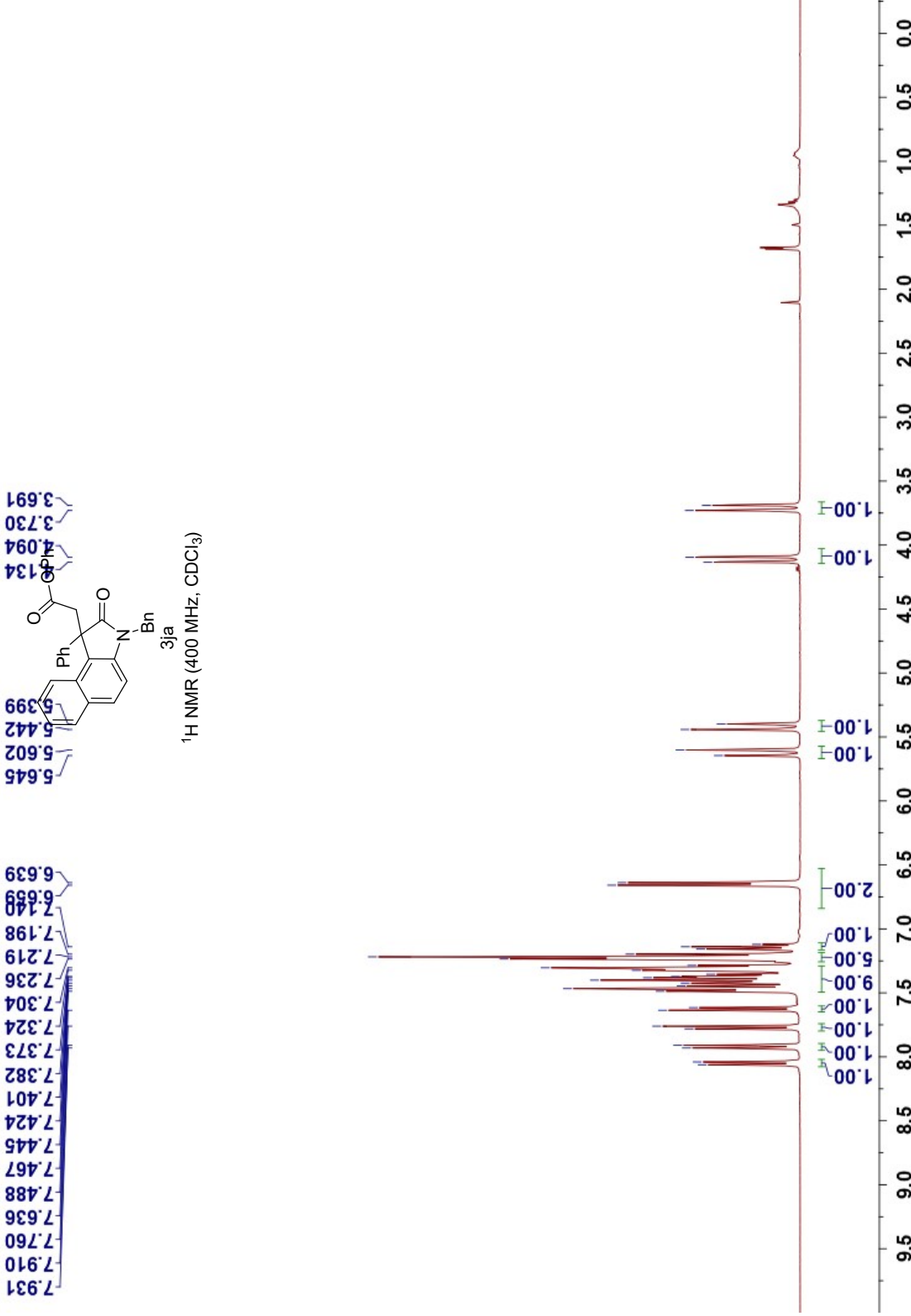
^{19}F NMR (376 MHz, $CDCl_3$)

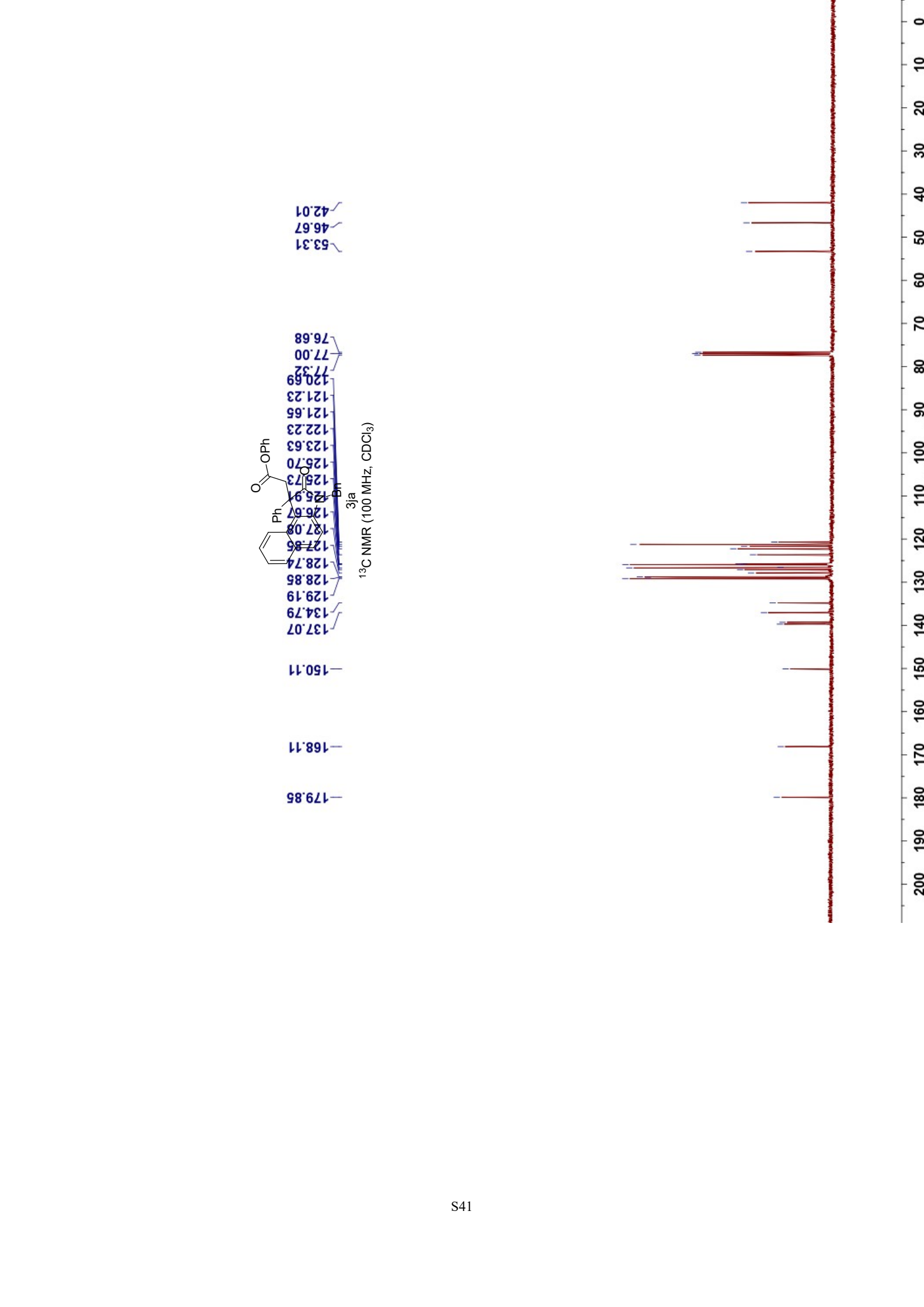


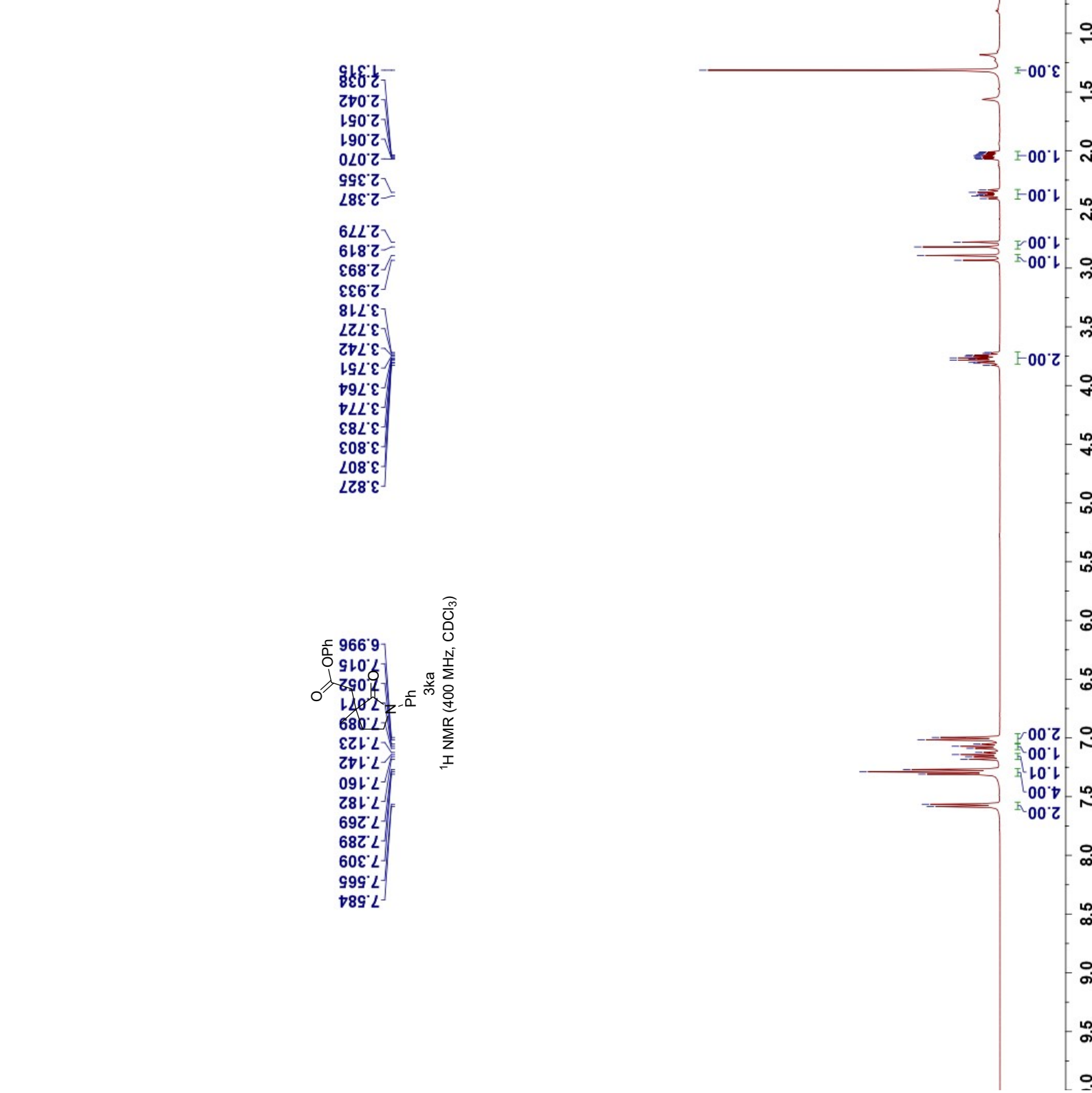


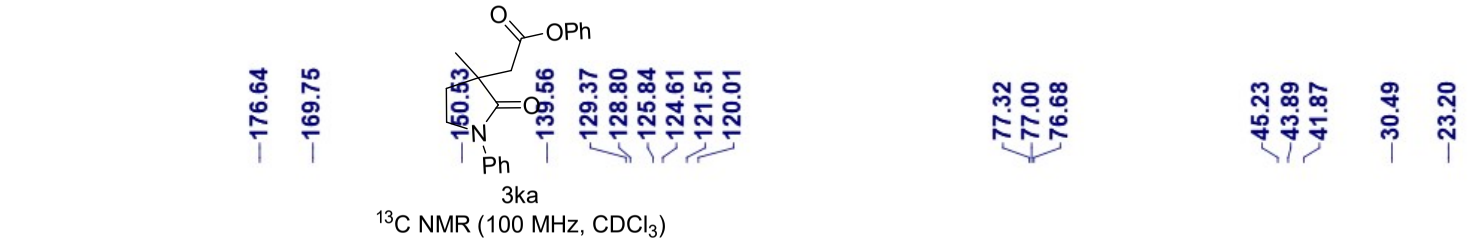
^{1}H NMR (400 MHz, $CDCl_3$)


179.14
168.24
155.97
150.14
137.11
133.85
129.21
125.73
121.23
112.25
108.47
77.32
77.00
76.68
55.76
46.02
41.72
26.39
24.28
MeO
OPh
O
O
3ia
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3.691
3.730
4.094
4.134
5.399
5.442
5.602
5.645
6.639
6.659
7.140
7.198
7.219
7.236
7.304
7.324
7.373
7.382
7.401
7.424
7.445
7.467
7.488
7.636
7.760
7.910
7.931
Ph
O
O
O
N
Bn
3ja
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.00
1.00
1.00
2.00
1.00
5.00
9.00
1.00
1.00
1.00
1.00
1.00

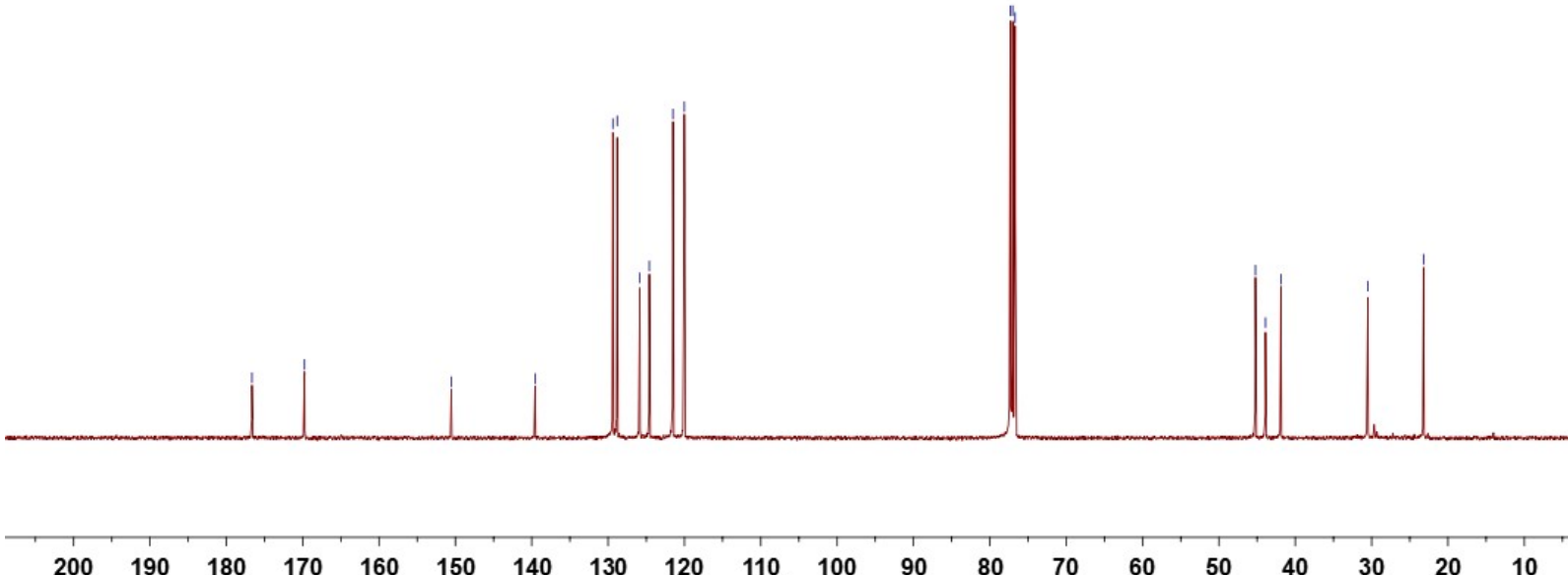

42.01
46.67
53.31
76.68
77.00
77.32
120.69
121.23
121.65
122.23
123.63
125.70
125.73
125.97
126.67
127.08
127.85
128.74
128.85
129.19
134.79
137.07
150.11
168.11
179.85
OPh
O
O
N
Bn
Ph
3ja
^{13}C NMR (100 MHz, CDCl$_3$)

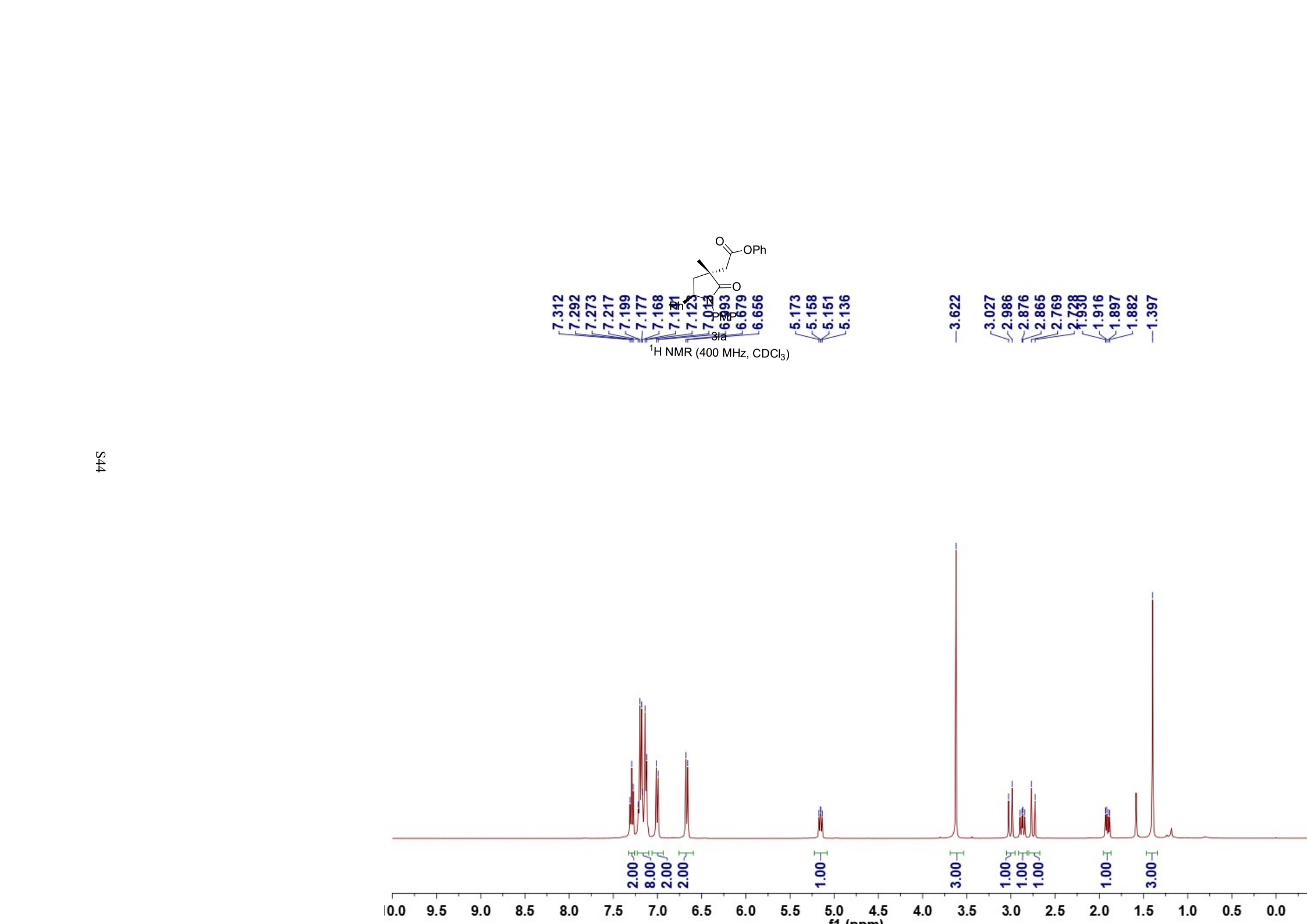

OPh
O
O
N
Ph
3ka
^{1}H NMR (400 MHz, CDCl$_3$)

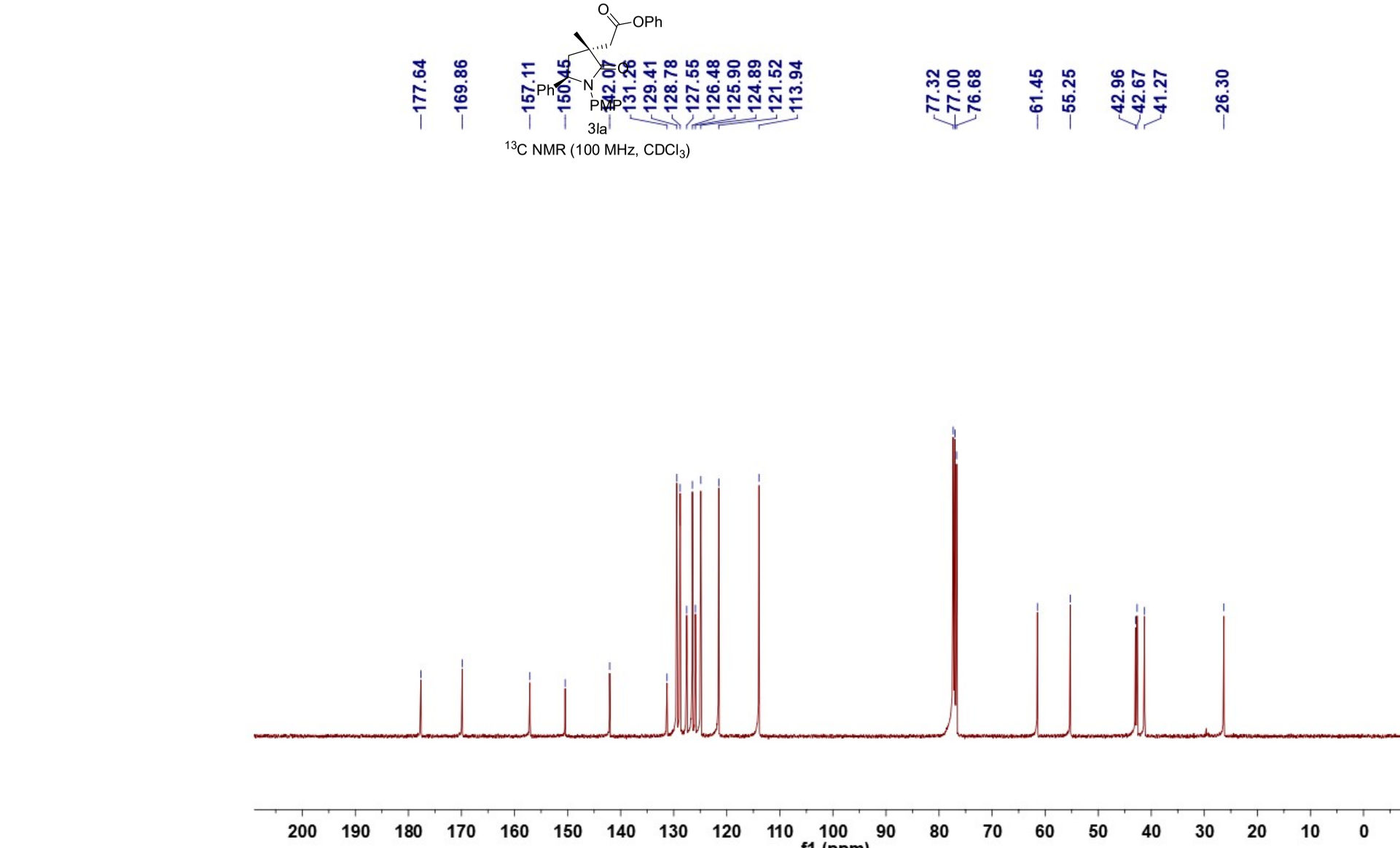


3ka

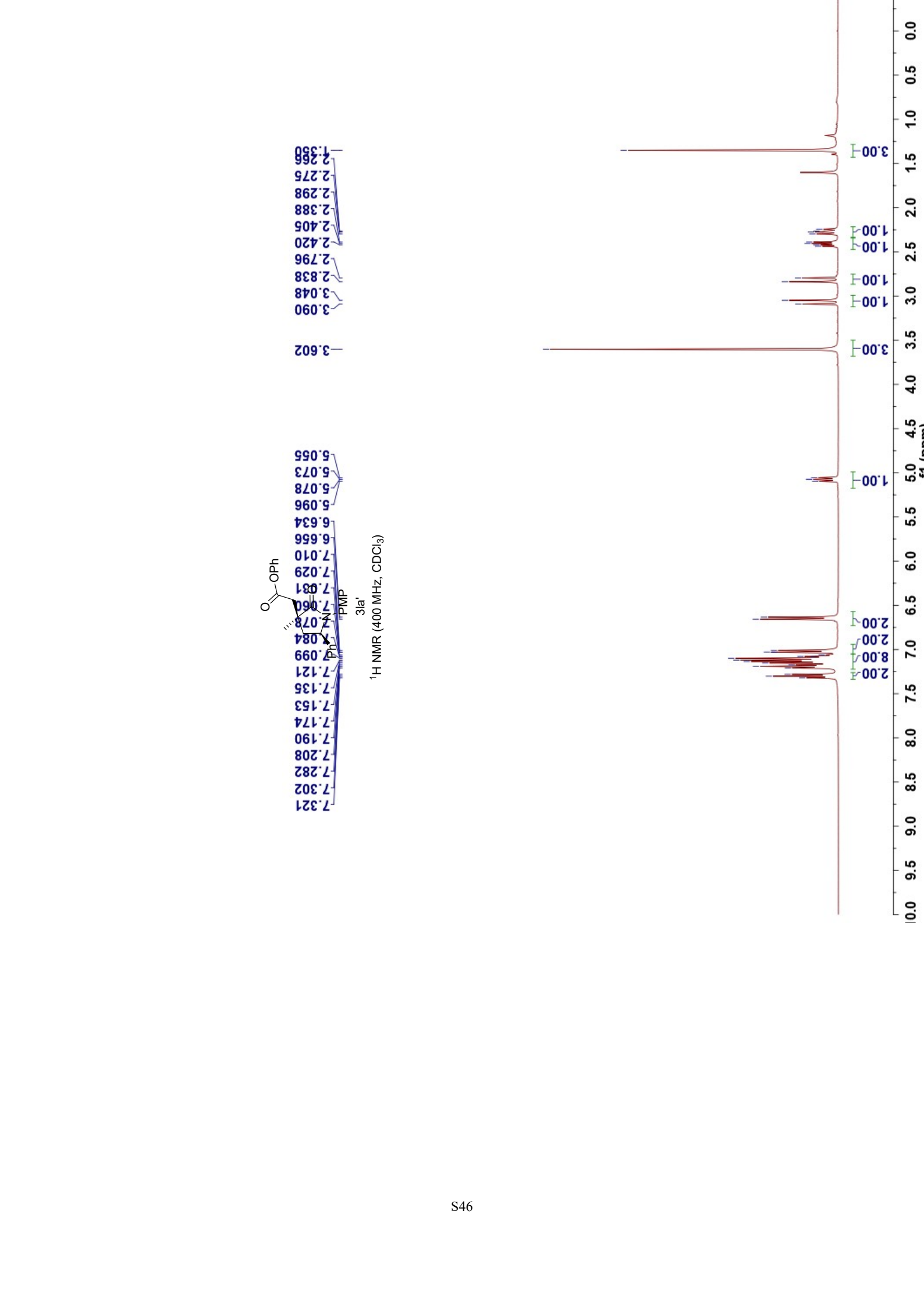
^{13}C NMR (100 MHz, $CDCl_3$)

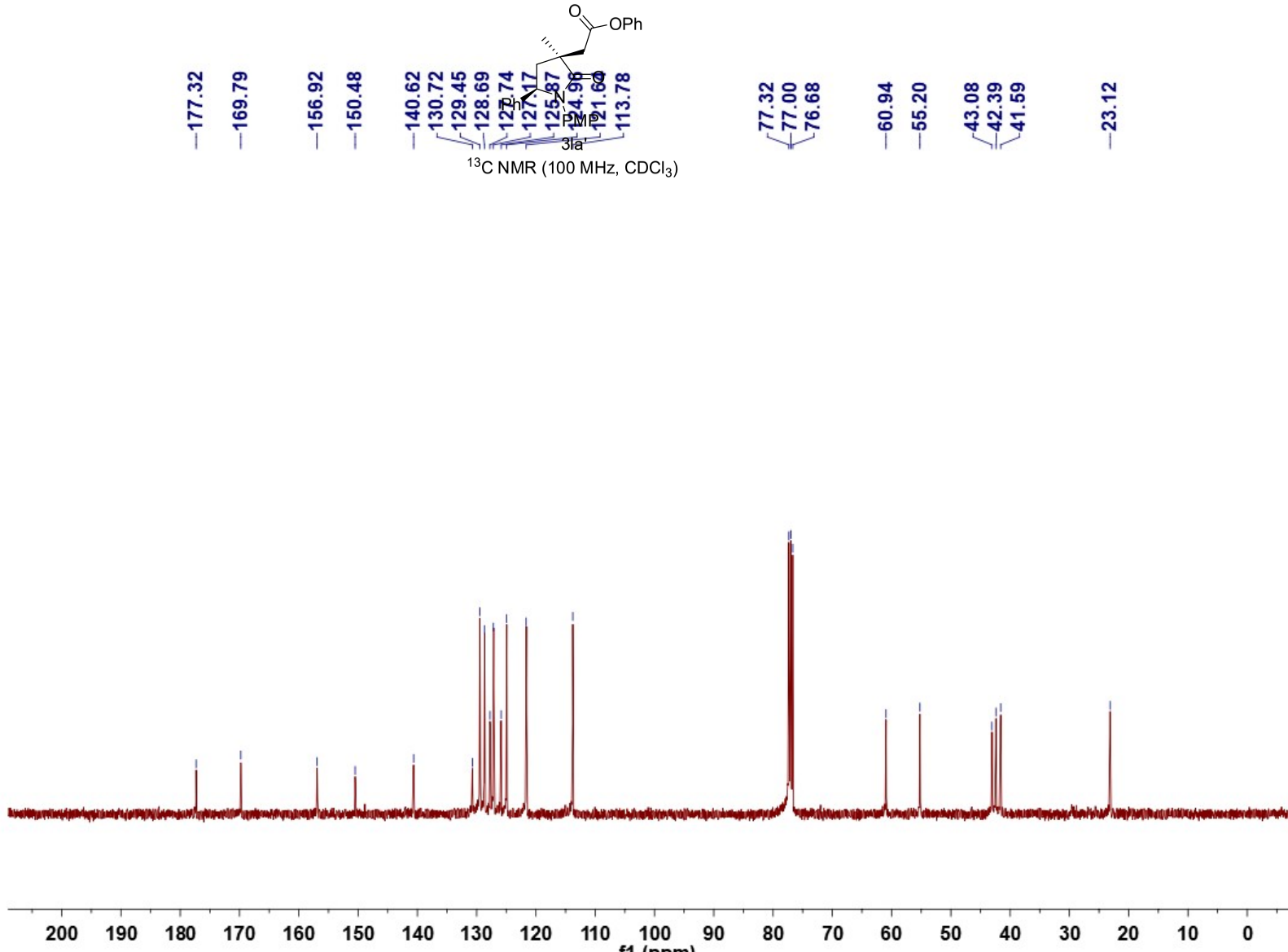


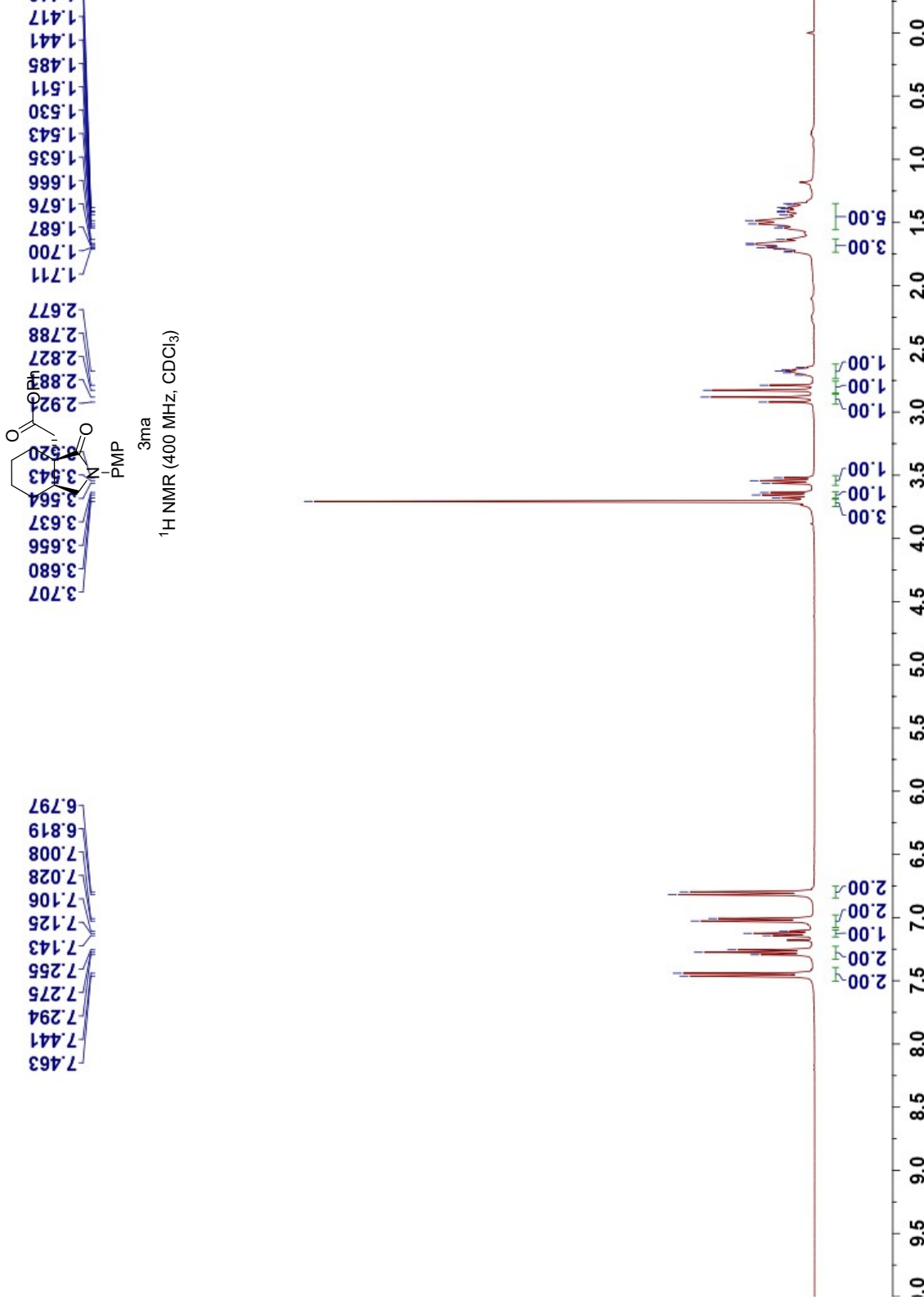

O
OPh
O
Ph
PMP
3la
7.312
7.292
7.273
7.217
7.199
7.177
7.168
7.151
7.123
7.012
6.993
6.679
6.656
5.173
5.158
5.151
5.136
3.622
3.027
2.986
2.876
2.865
2.769
2.728
1.930
1.916
1.897
1.882
1.397
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
8.00
2.00
2.00
1.00
3.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

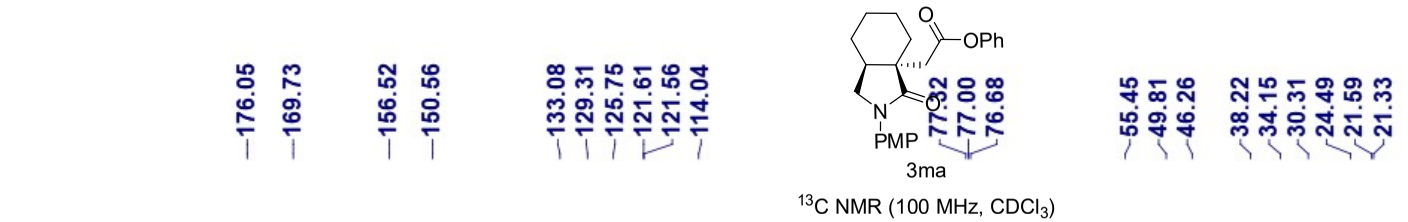


^{13}C NMR (100 MHz, $CDCl_3$)


1.350
2.266
2.275
2.298
2.388
2.405
2.420
2.796
2.838
3.048
3.090
3.602
5.055
5.073
5.078
5.096
6.634
6.656
7.010
7.029
7.031
7.060
7.078
7.084
7.099
7.121
7.135
7.153
7.174
7.190
7.208
7.282
7.302
7.321
OPh
O
N
Ph
PMP
3la'
^{1}H NMR (400 MHz, $CDCl_3$)
3.00
1.00
1.00
1.00
1.00
3.00
1.00
2.00
2.00
8.00
2.00
f1 (ppm)

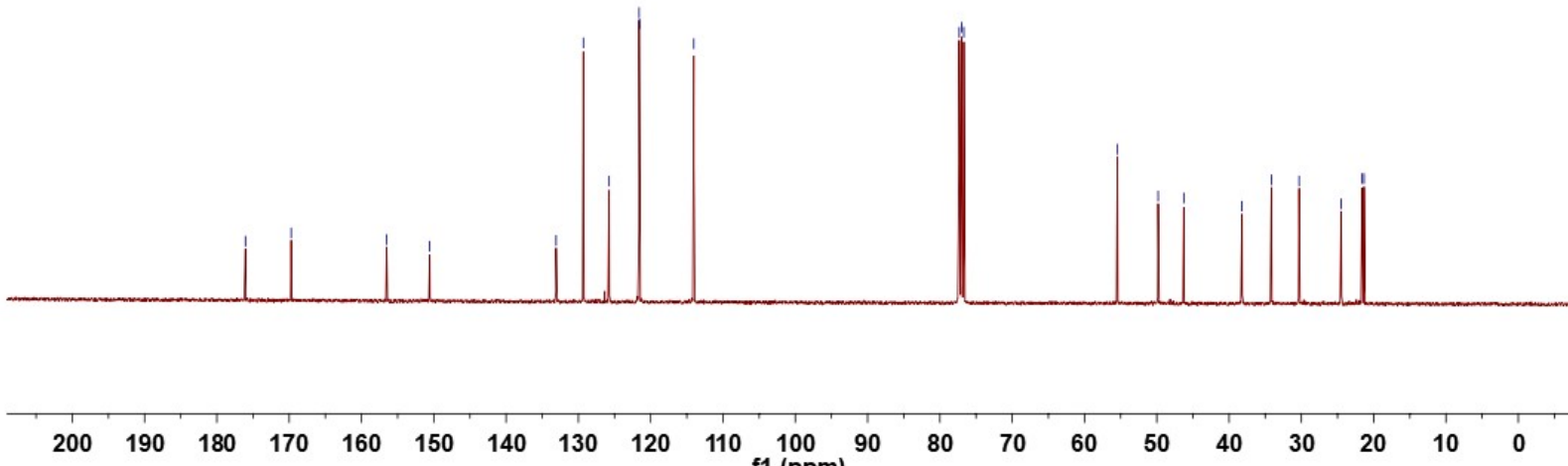

O
OPh
Ph
PMP
3la'
177.32
169.79
156.92
150.48
140.62
130.72
129.45
128.69
127.74
127.17
125.87
124.90
121.64
113.78
77.32
77.00
76.68
60.94
55.20
43.08
42.39
41.59
23.12
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

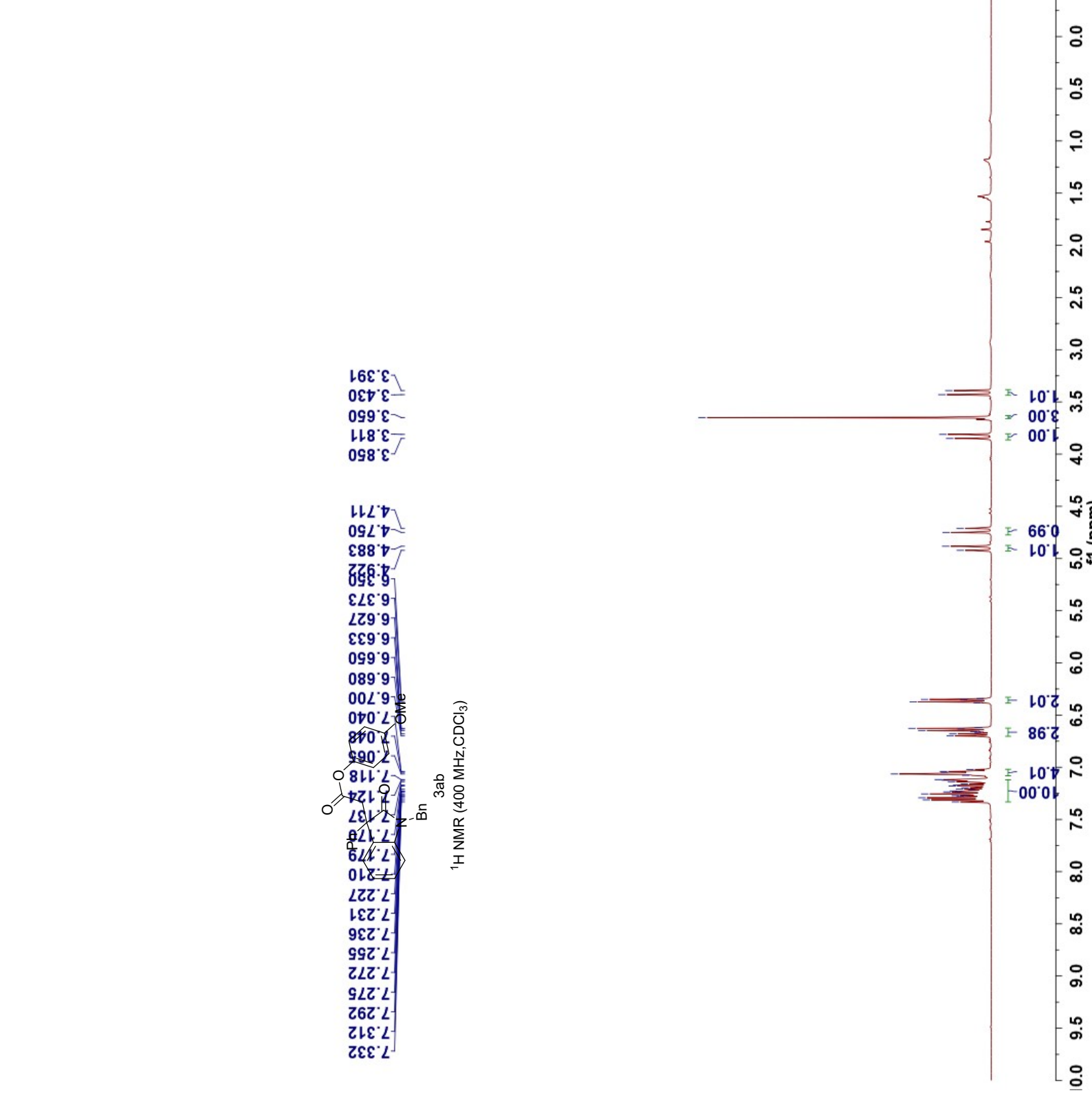

PMP
3ma
^{1}H NMR (400 MHz, CDCl$_3$)

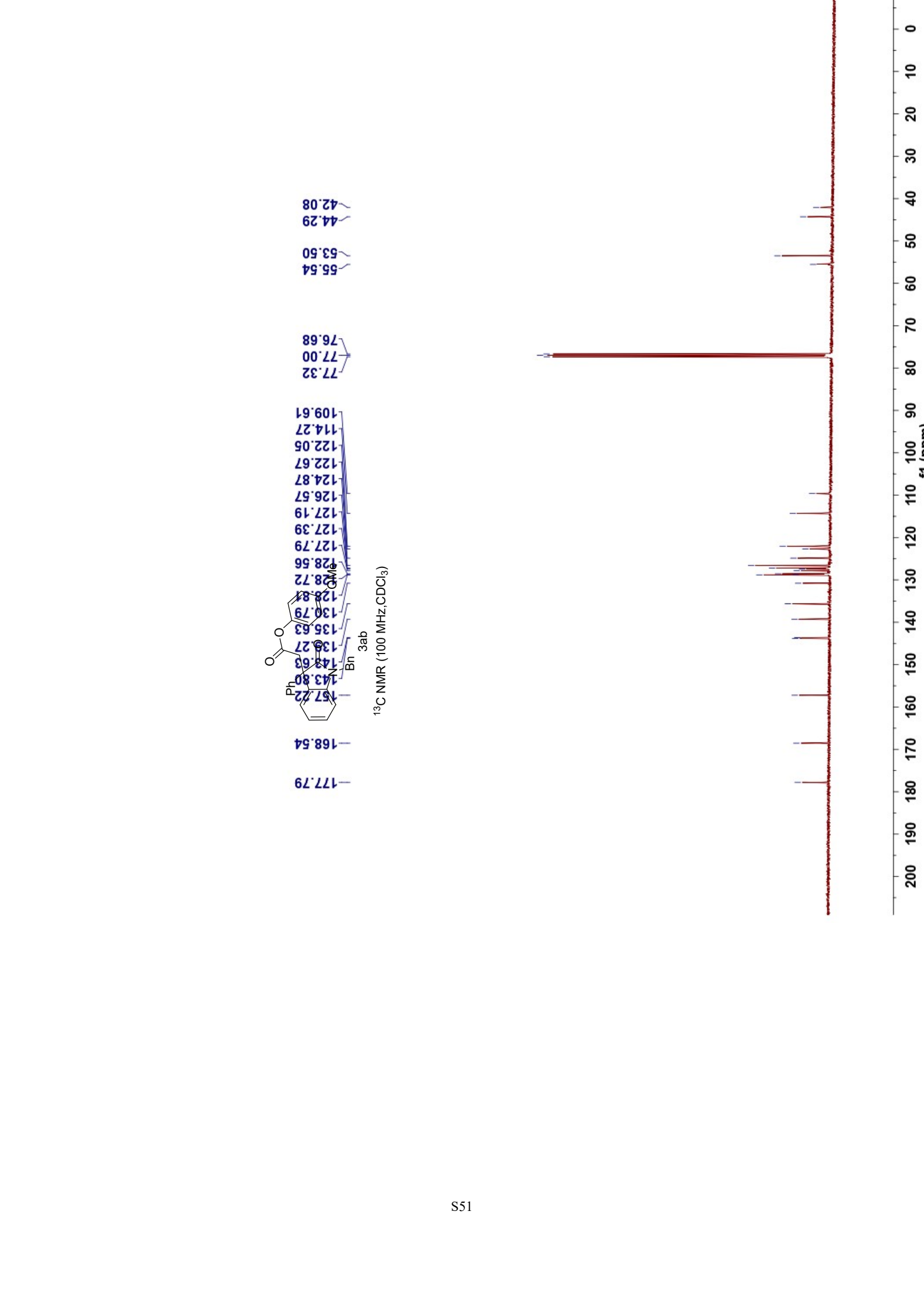


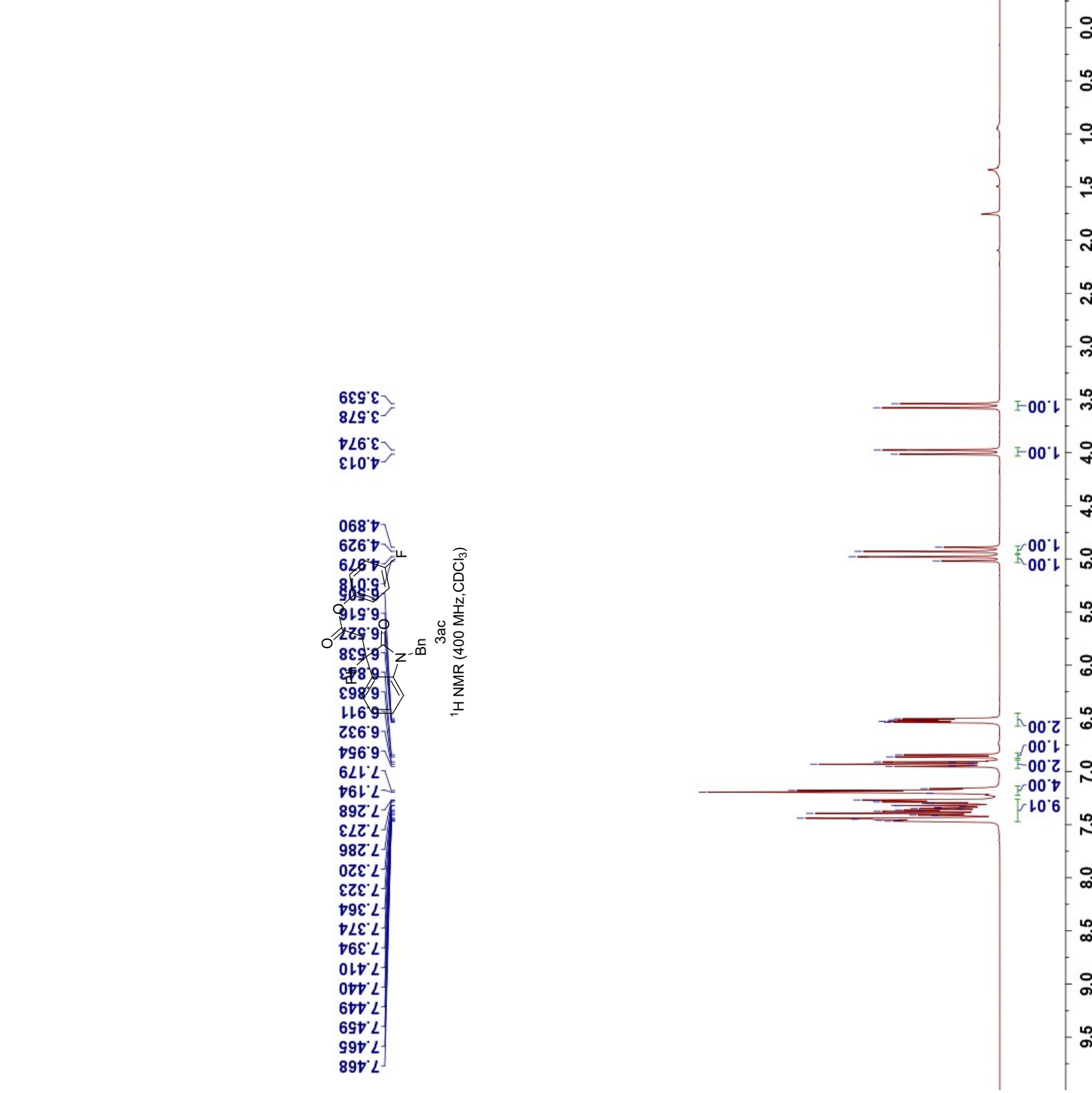
3ma

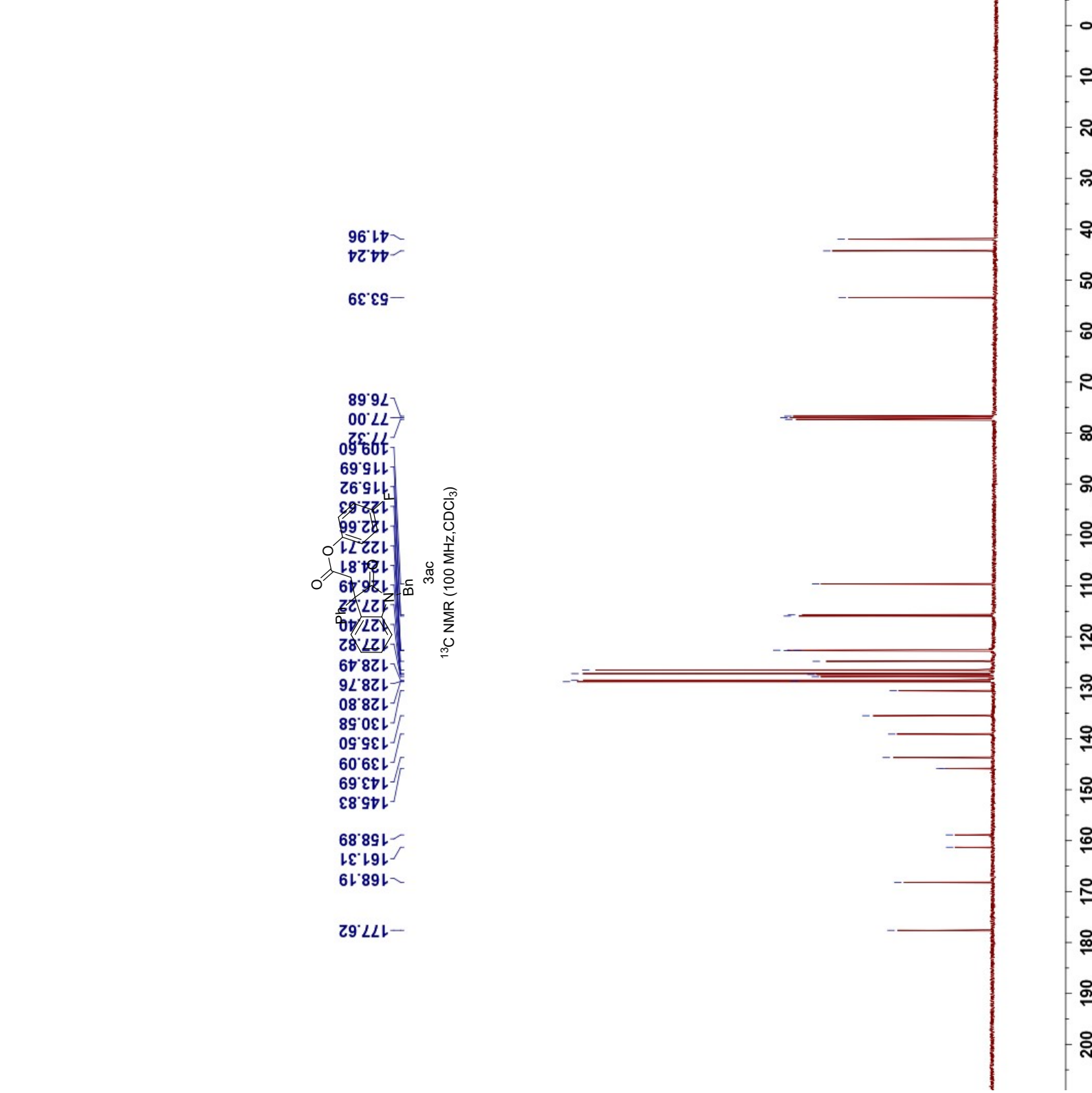
^{13}C NMR (100 MHz, $CDCl_3$)

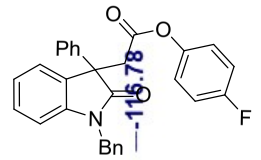



3ab
^{1}H NMR (400 MHz,CDCl$_3$)
Bn
OMe
Ph
3.391
3.430
3.650
3.811
3.850
4.711
4.750
4.883
4.922
6.350
6.373
6.627
6.633
6.650
6.680
6.700
7.040
7.048
7.065
7.118
7.124
7.137
7.178
7.179
7.210
7.227
7.231
7.236
7.255
7.272
7.275
7.292
7.312
7.332
1.01
3.00
1.00
0.99
1.01
2.01
2.98
4.01
10.00


42.08
44.29
53.50
55.54
76.68
77.00
77.32
109.61
114.27
122.05
122.67
124.87
126.57
127.19
127.39
127.79
128.56
128.72
128.81
130.79
135.63
139.27
143.63
143.80
157.22
168.54
177.79
OMe
Bn
Ph
3ab
^{13}C NMR (100 MHz,CDCl$_3$)
f1 (ppm)

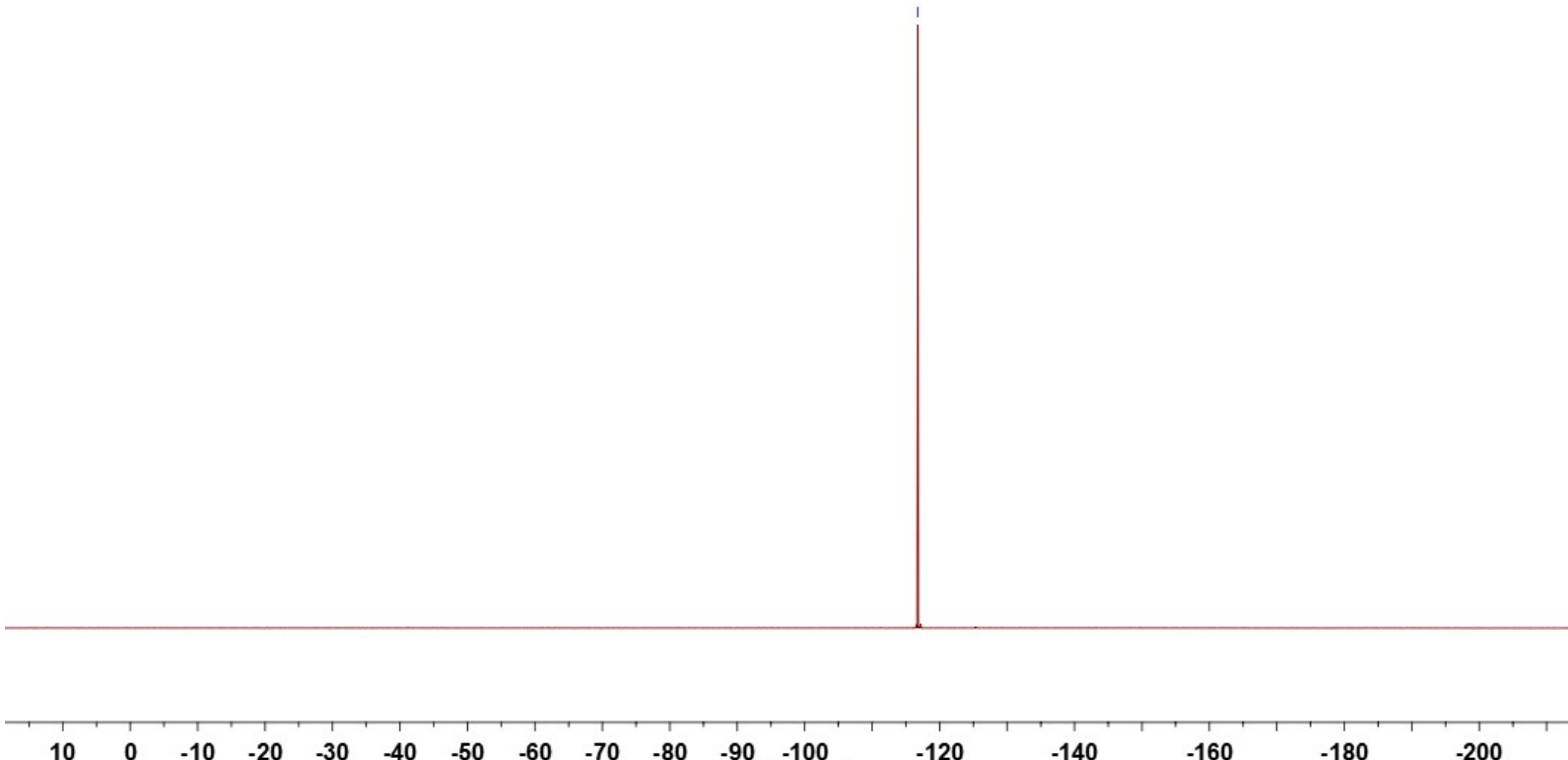

3ac
^{1}H NMR (400 MHz,CDCl$_3$)
Bn
F
O
N
3.539
3.578
3.974
4.013
4.890
4.929
4.979
5.018
6.516
6.527
6.538
6.853
6.863
6.911
6.932
6.954
7.179
7.194
7.268
7.273
7.286
7.320
7.323
7.364
7.374
7.394
7.410
7.440
7.449
7.459
7.465
7.468
1.00
1.00
1.00
1.00
2.00
1.00
2.00
4.00
9.01

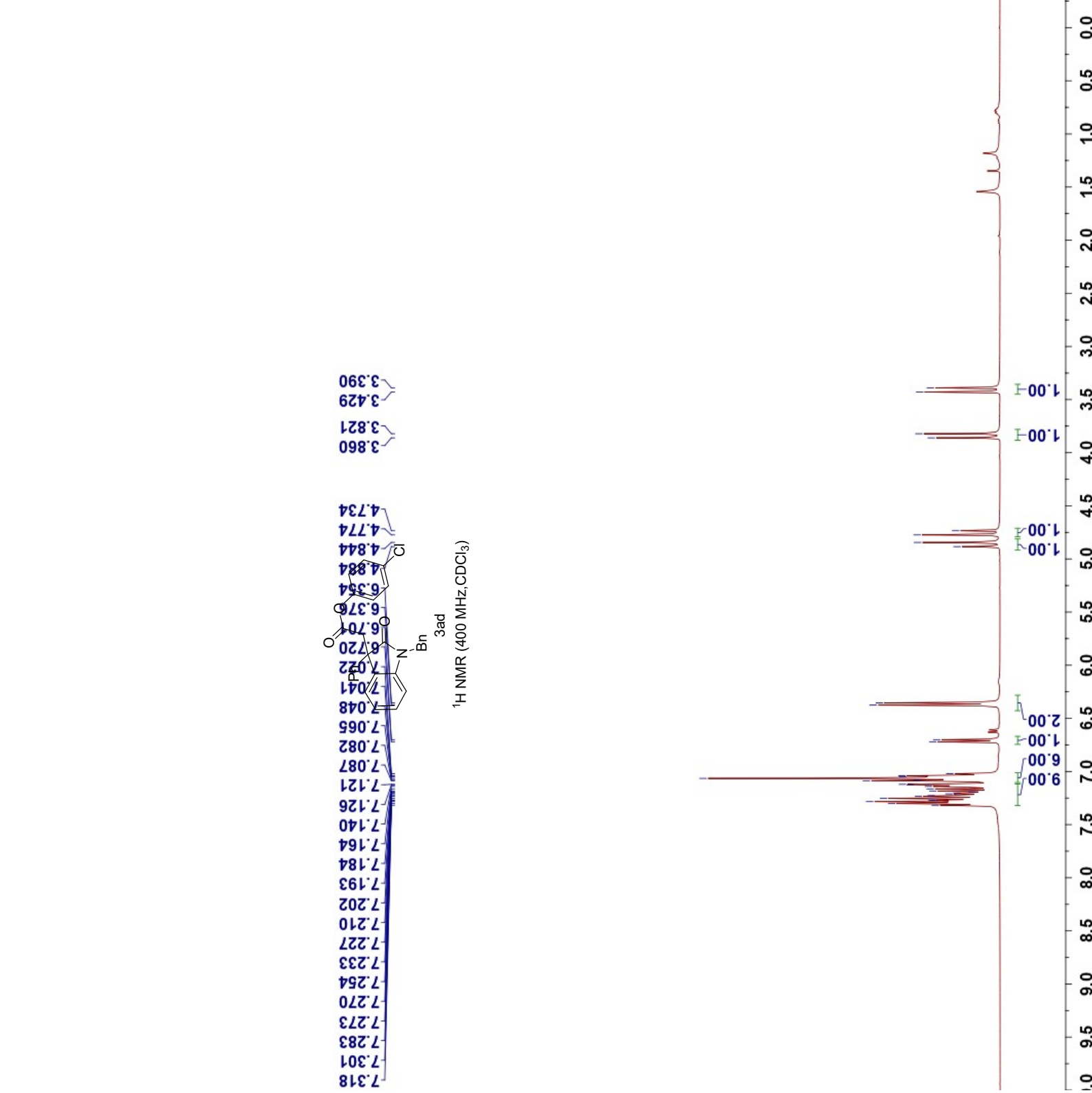

41.96
44.24
53.39
76.68
77.00
77.32
109.60
115.69
115.92
122.63
122.66
122.71
124.81
126.49
127.22
127.40
127.82
128.49
128.76
128.80
130.58
135.50
139.09
143.69
145.83
158.89
161.31
168.19
177.62
3ac
^{13}C NMR (100 MHz,CDCl$_3$)
F
O
O
N
Bn
Ph

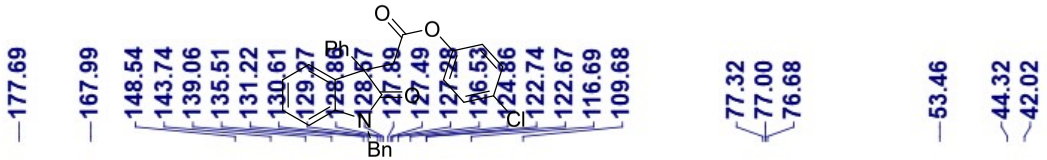


3ac

^{19}F NMR (376 MHz,$CDCl_3$)

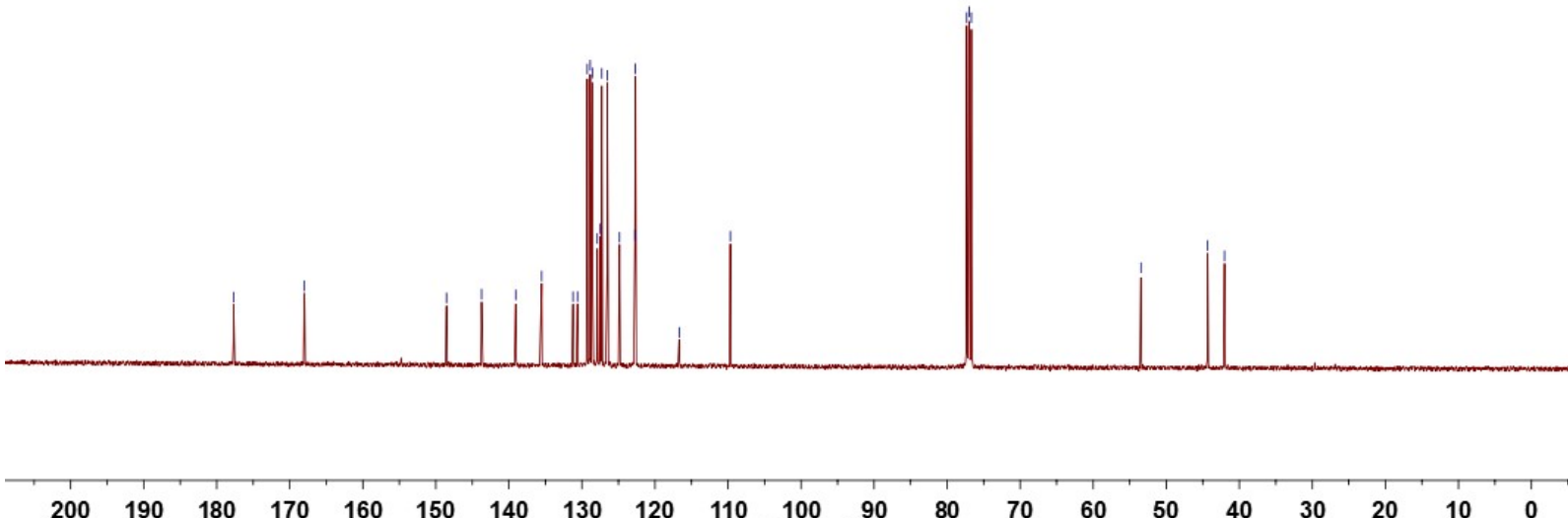


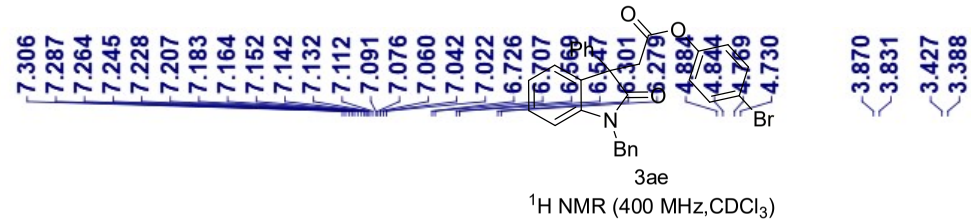

3.390
3.429
3.821
3.860
4.734
4.774
4.844
4.884
6.354
6.376
6.701
6.720
7.022
7.041
7.048
7.065
7.082
7.087
7.121
7.126
7.140
7.164
7.184
7.193
7.202
7.210
7.227
7.233
7.254
7.270
7.273
7.283
7.301
7.318
Cl
O
O
O
N
Bn
Ph
3ad
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.00
1.00
1.00
2.00
1.00
6.00
9.00



3ad

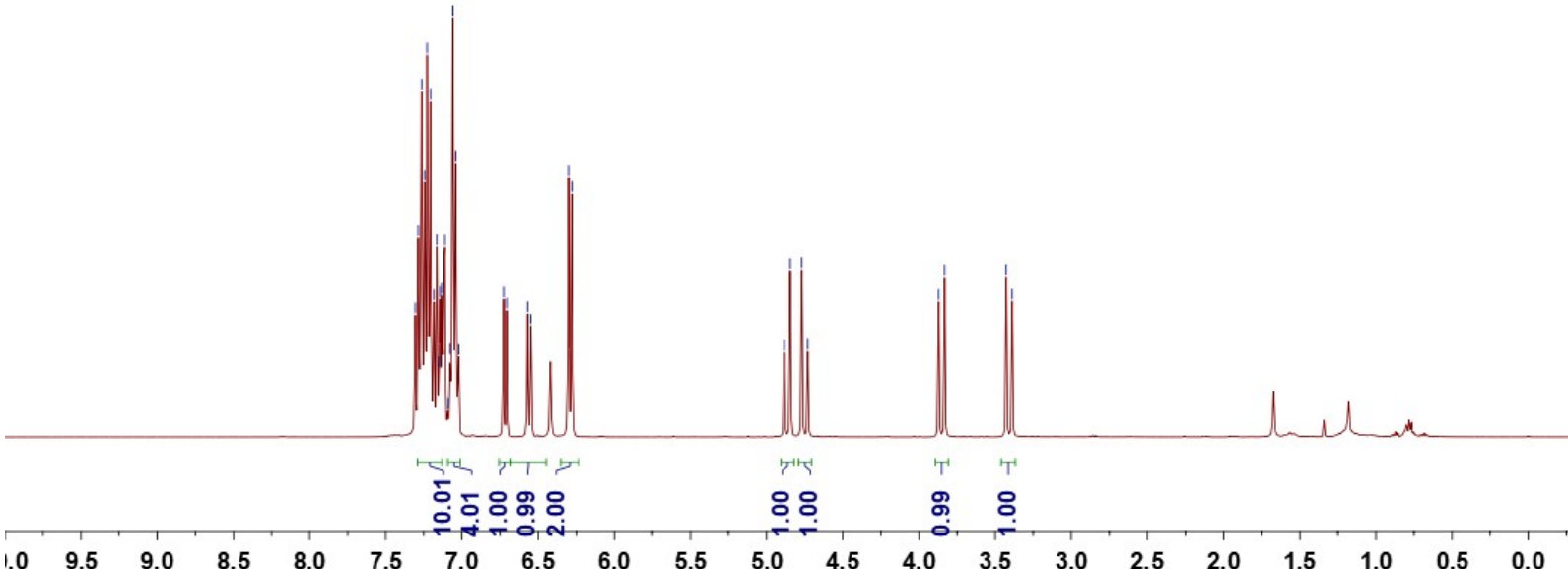
^{13}C NMR (100 MHz,$CDCl_3$)

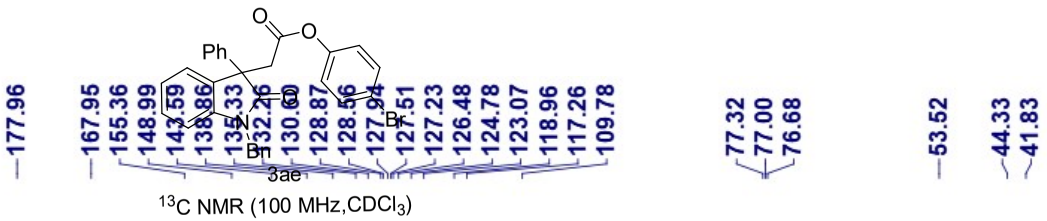




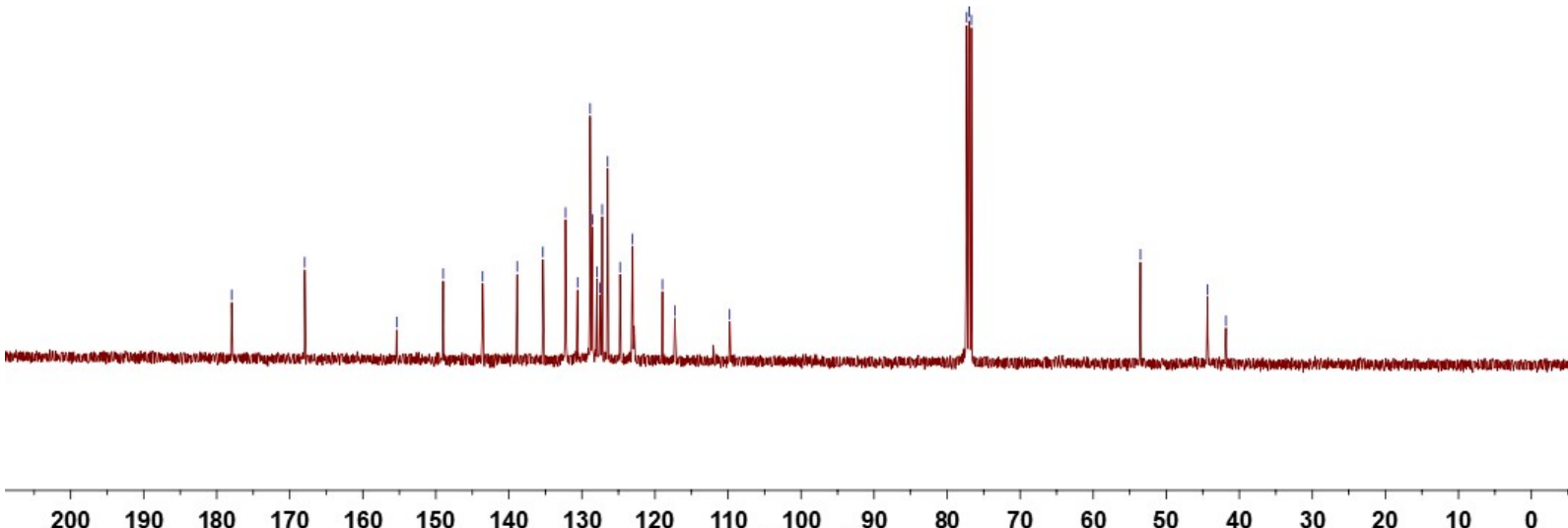
3ae

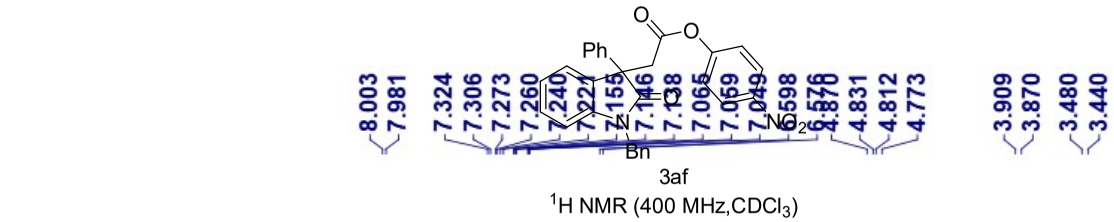
^{1}H NMR (400 MHz,$CDCl_3$)





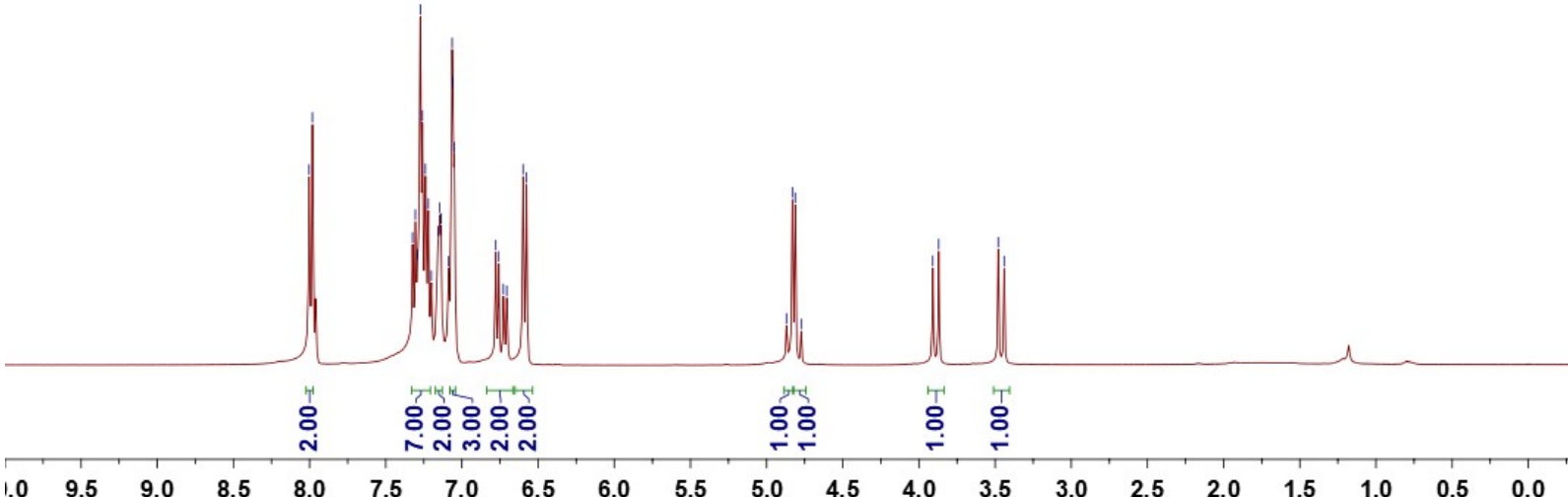
^{13}C NMR (100 MHz,$CDCl_3$)

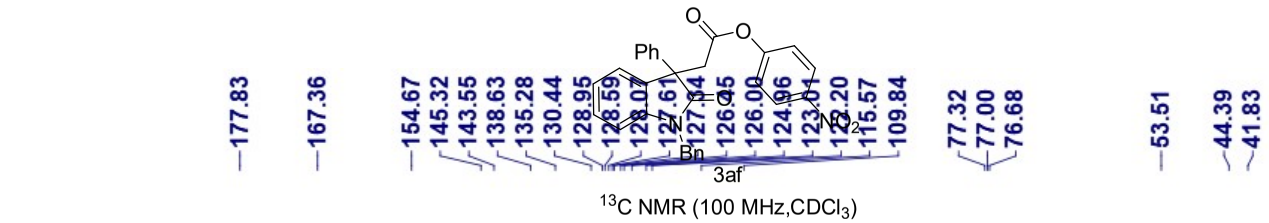


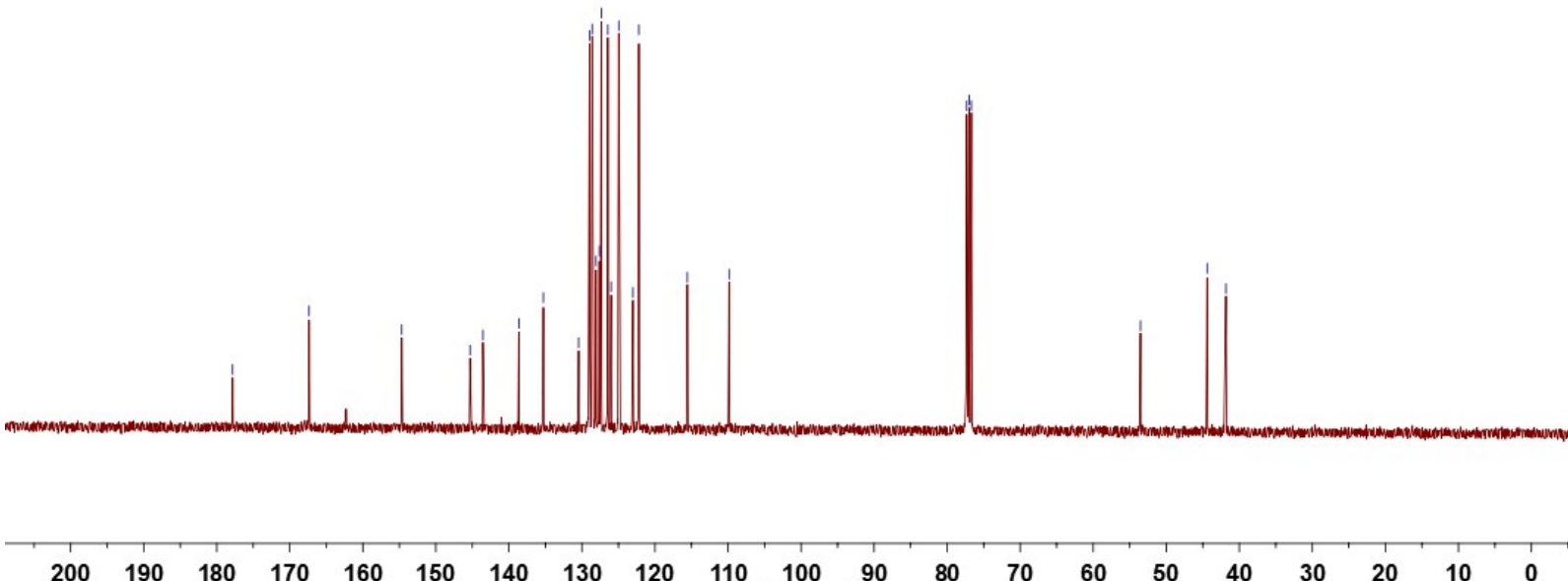


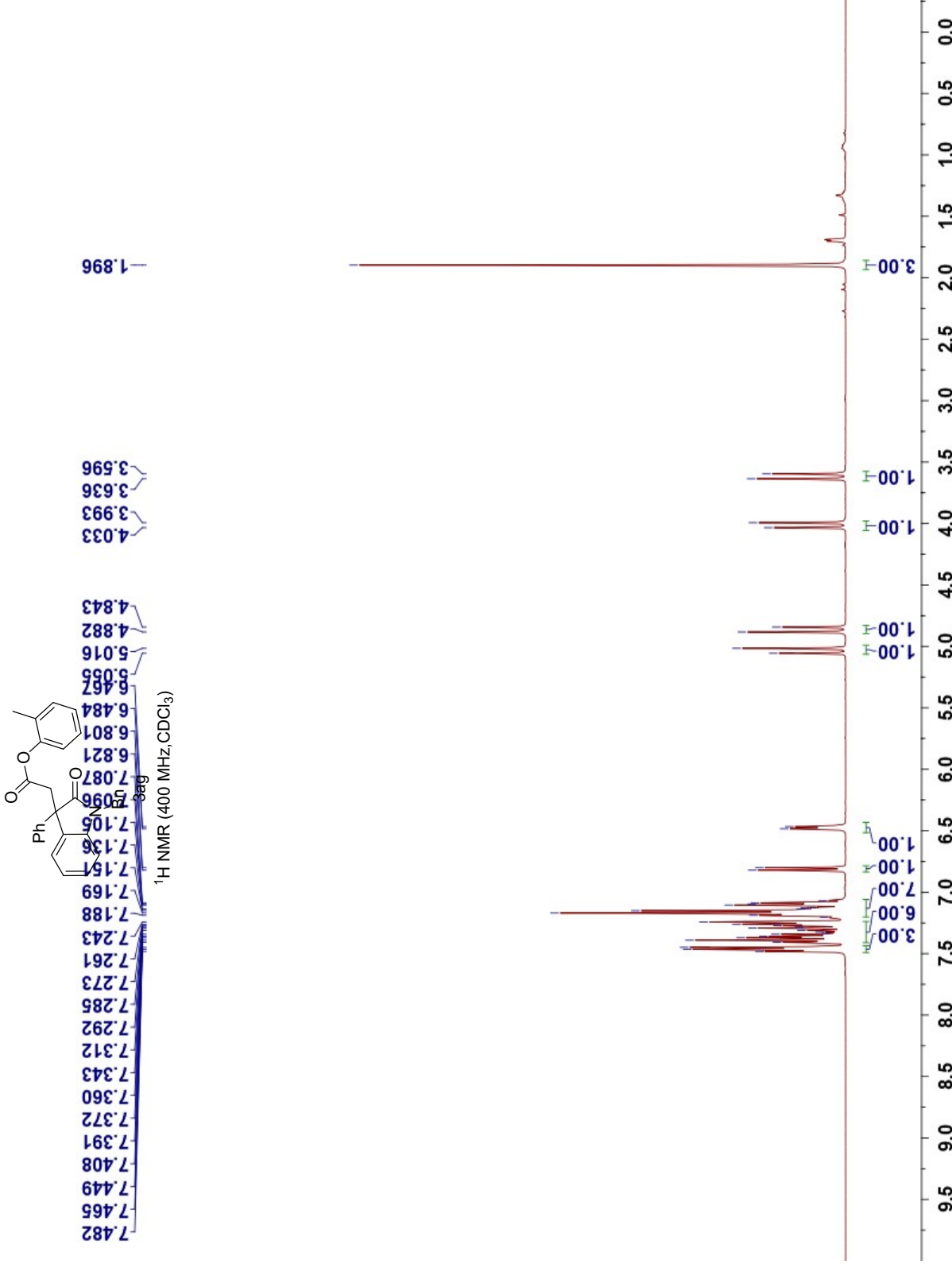
3af

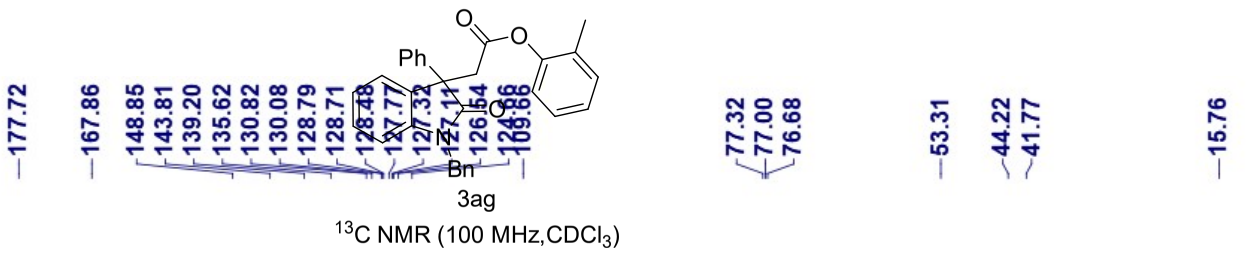
^{1}H NMR (400 MHz,$CDCl_3$)

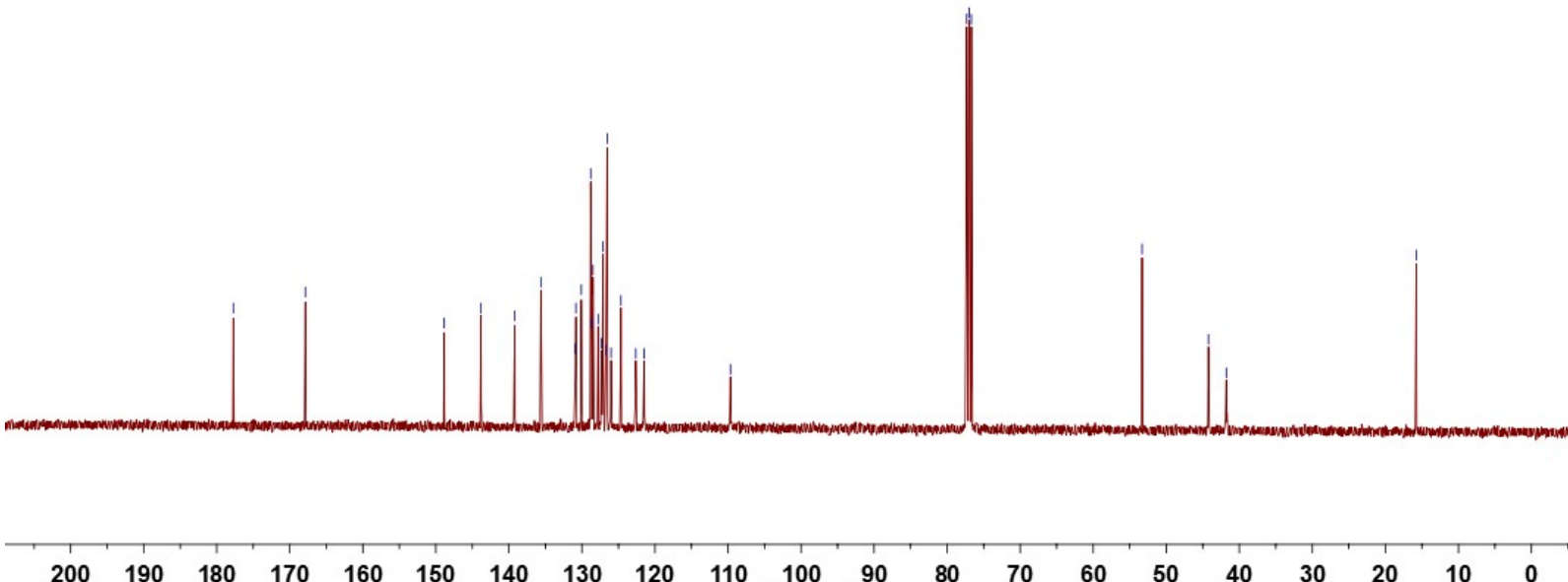


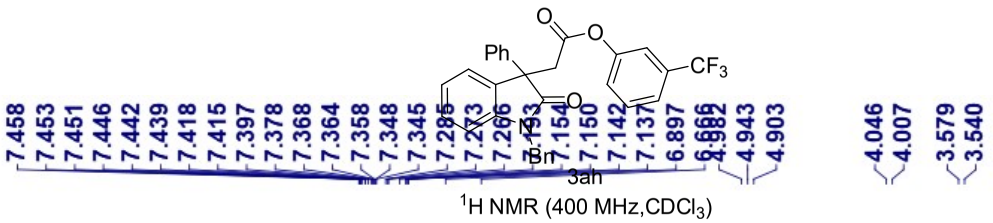

O
O
Ph
N
Bn
NO2
177.83
167.36
154.67
145.32
143.55
138.63
135.28
130.44
128.95
128.59
128.07
127.61
127.34
126.45
126.00
124.96
123.01
122.20
115.57
109.84
77.32
77.00
76.68
53.51
44.39
41.83
3af
13C NMR (100 MHz,CDCl3)

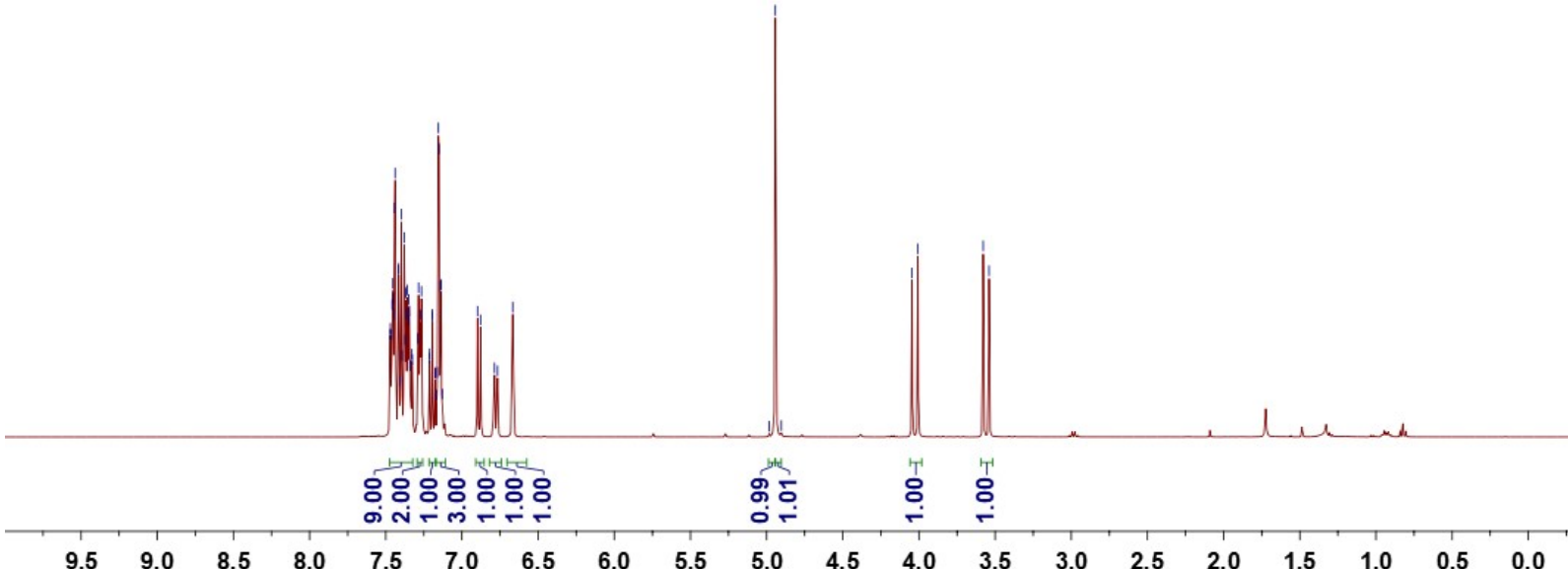

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

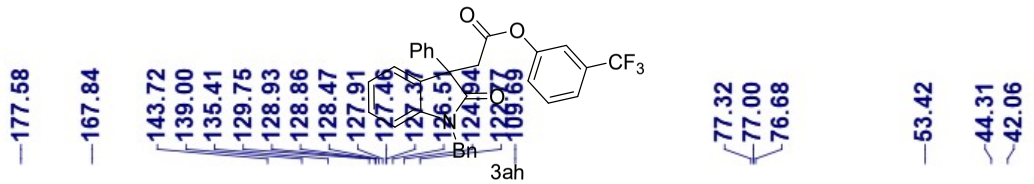

1.896
3.596
3.636
3.993
4.033
4.843
4.882
5.016
5.055
6.467
6.484
6.801
6.821
7.087
7.096
7.105
7.136
7.151
7.169
7.188
7.243
7.261
7.273
7.285
7.292
7.312
7.343
7.360
7.372
7.391
7.408
7.449
7.465
7.482
3.00
1.00
1.00
1.00
1.00
1.00
7.00
6.00
3.00
Ph
O
O
O
O
^{1}H NMR (400 MHz,CDCl$_3$)


177.72
167.86
148.85
143.81
139.20
135.62
130.82
130.08
128.79
128.71
128.48
127.77
127.32
127.11
126.54
124.66
109.88
77.32
77.00
76.68
53.31
44.22
41.77
15.76
Ph
Bn
3ag
^{13}C NMR (100 MHz,$CDCl_3$)

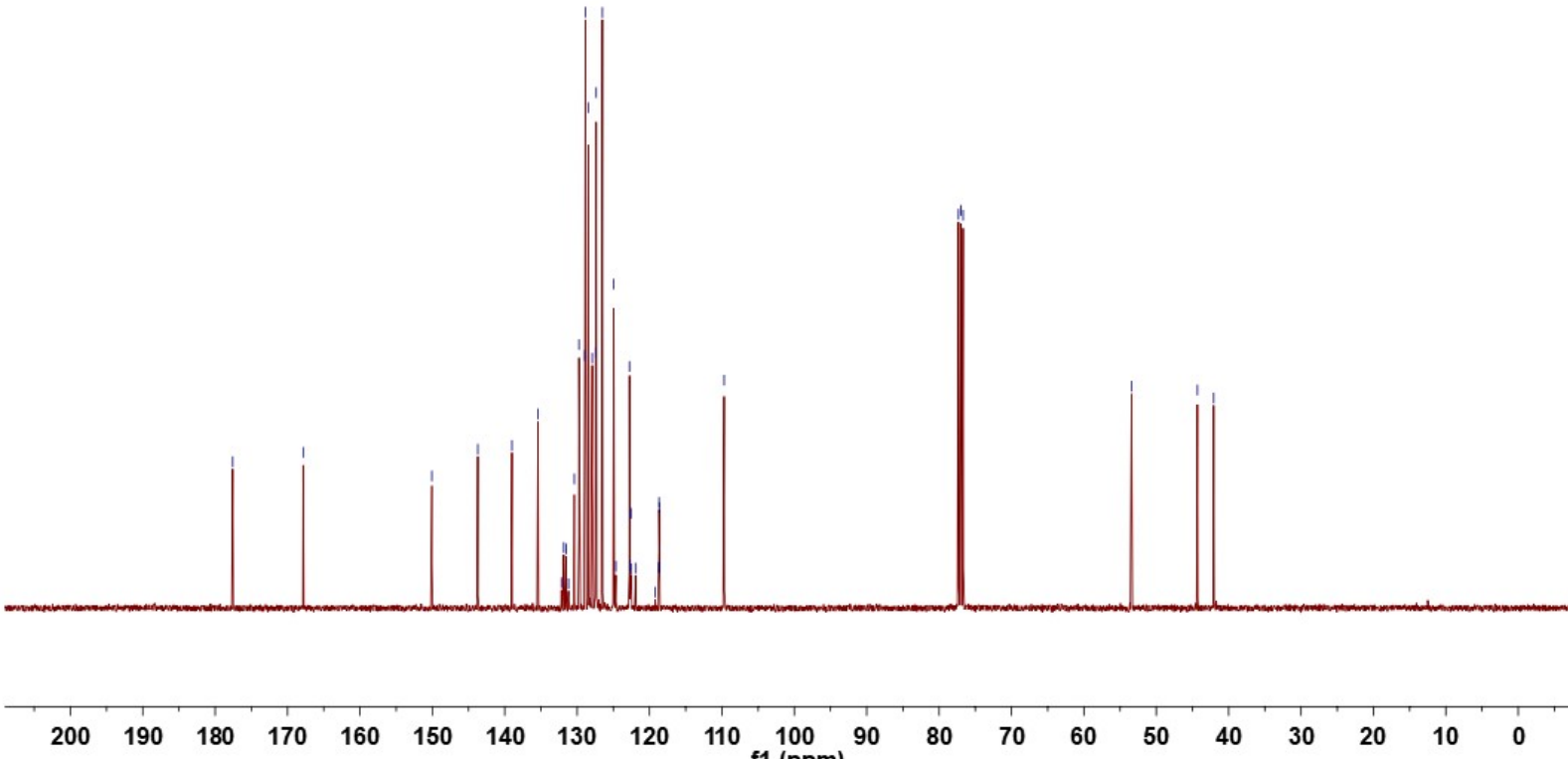

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

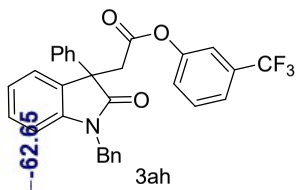

O
O
Ph
CF3
O
N
Bn
7.458
7.453
7.451
7.446
7.442
7.439
7.418
7.415
7.397
7.378
7.368
7.364
7.358
7.348
7.345
7.154
7.150
7.142
7.137
6.897
4.943
4.903
4.046
4.007
3.579
3.540
3ah
1H NMR (400 MHz,CDCl3)


9.00
2.00
1.00
3.00
1.00
1.00
1.00
0.99
1.01
1.00
1.00
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



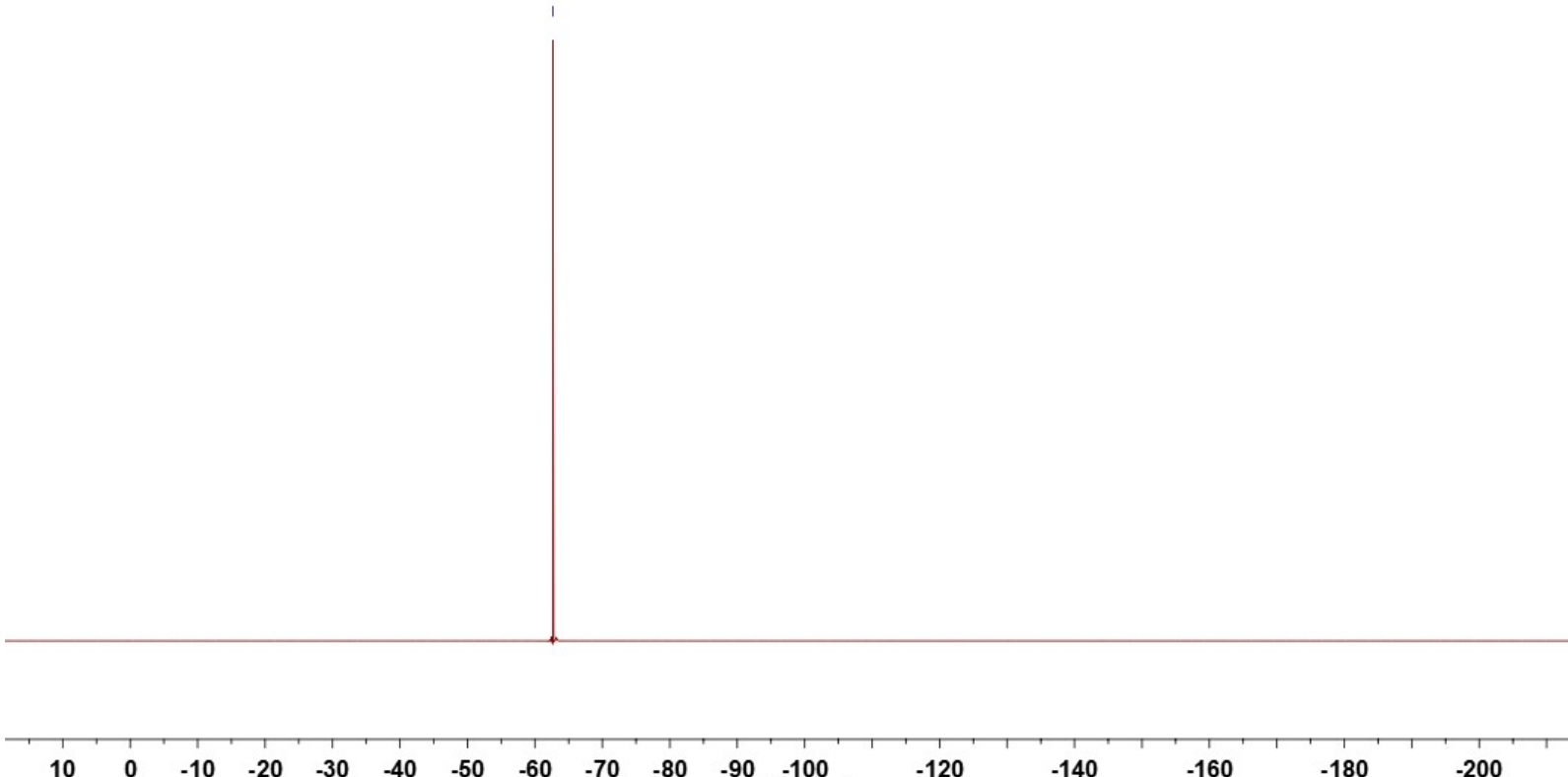
^{13}C NMR (100 MHz,$CDCl_3$)

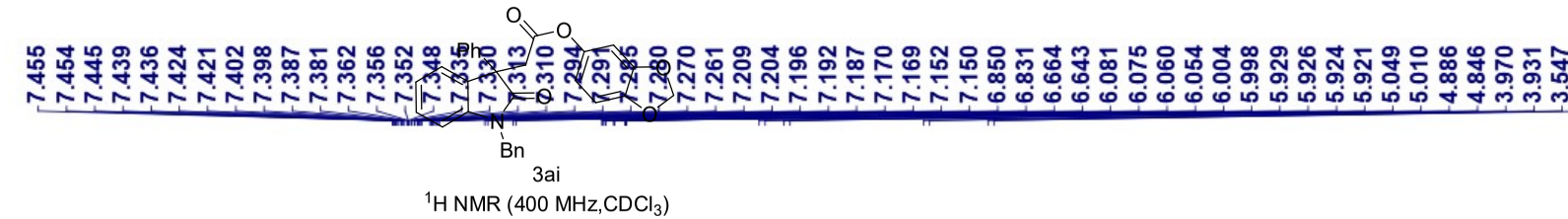




3ah

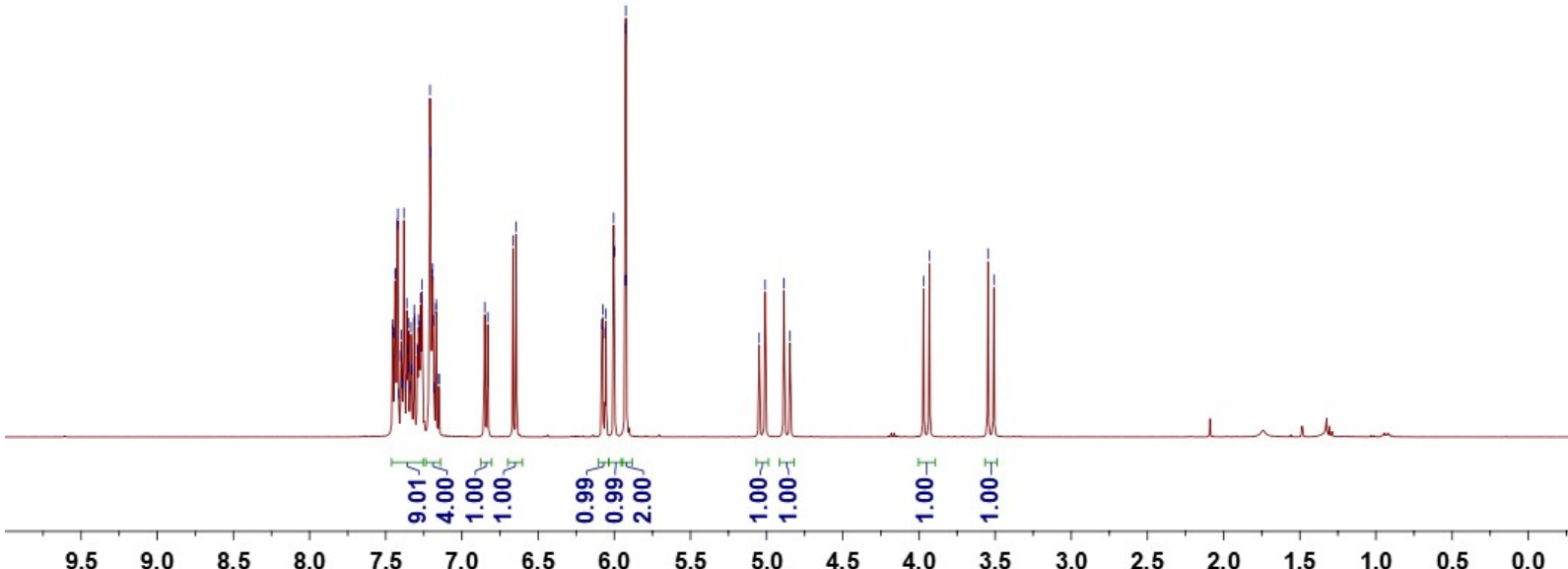
^{19}F NMR (376 MHz,$CDCl_3$)

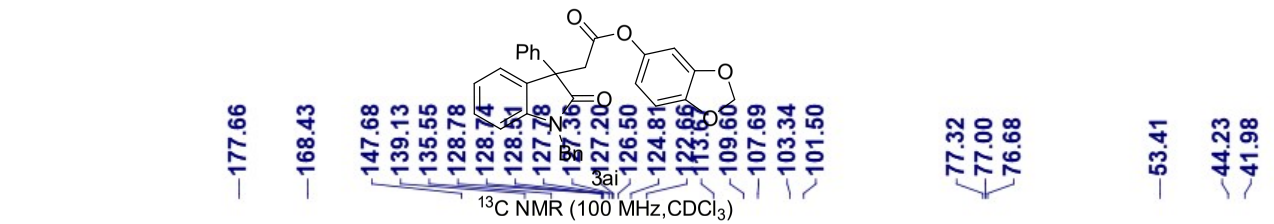


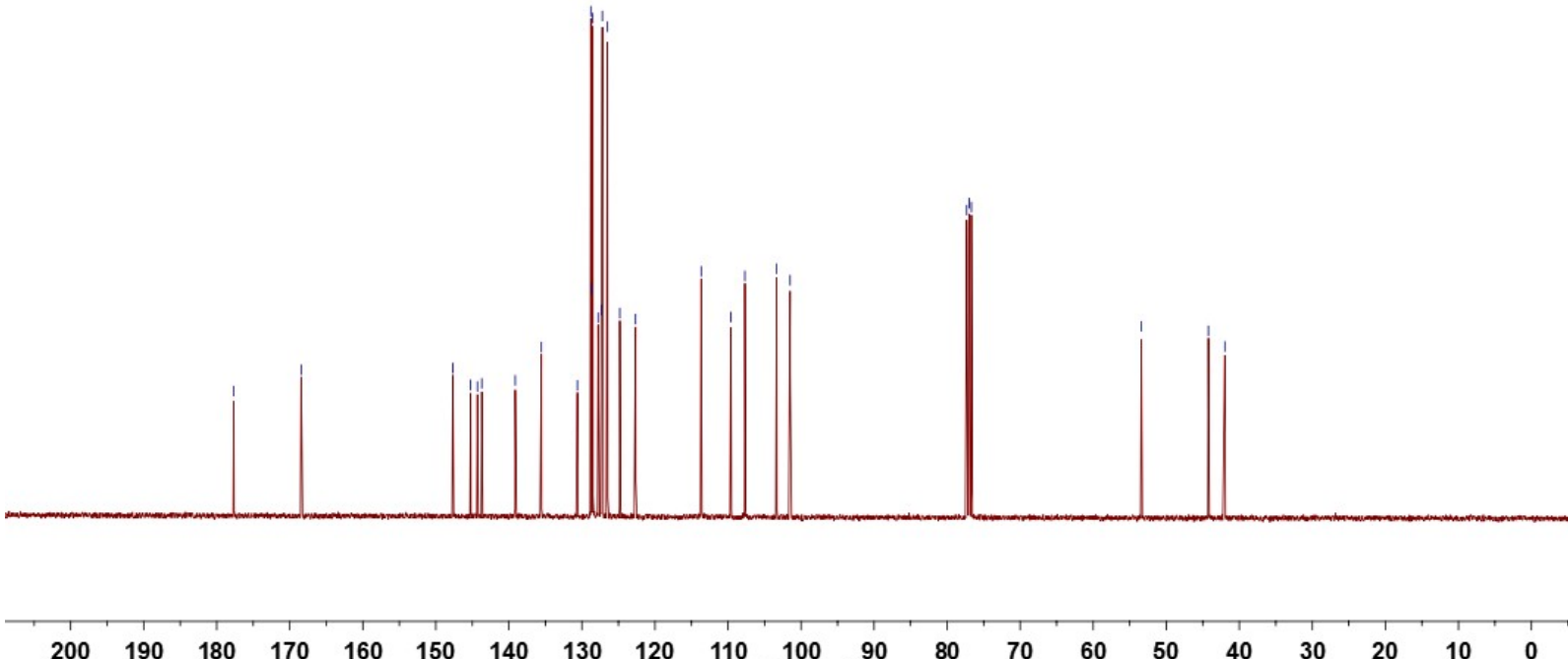


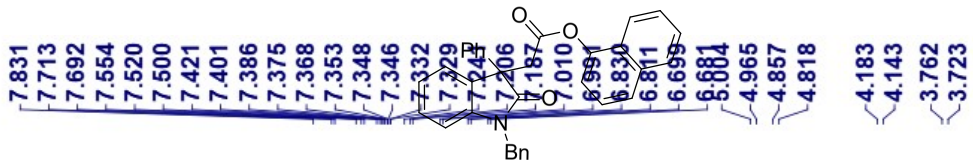
3ai

^{1}H NMR (400 MHz,$CDCl_3$)



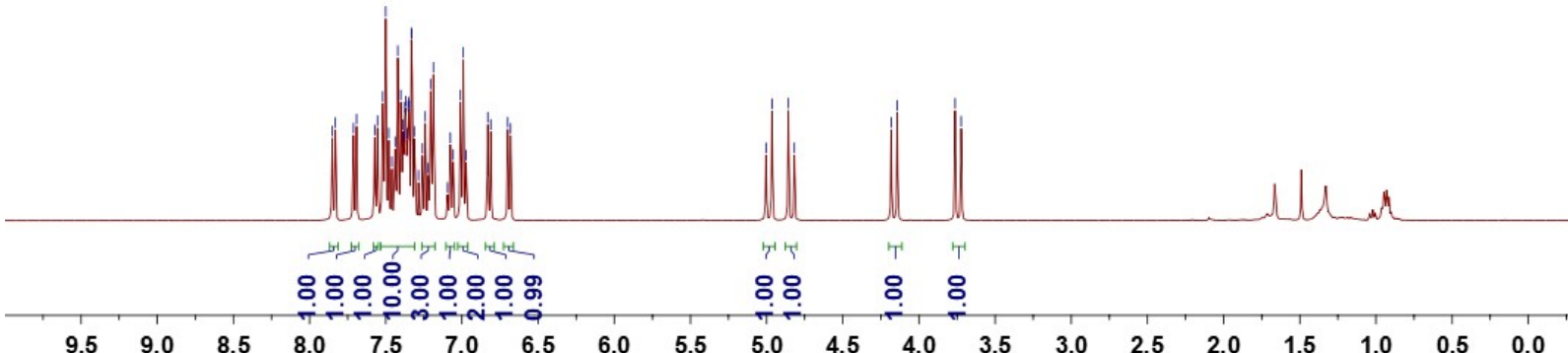

177.66
168.43
147.68
139.13
135.55
128.78
128.74
128.51
127.78
127.36
127.20
126.50
124.81
122.66
113.62
109.60
107.69
103.34
101.50
77.32
77.00
76.68
53.41
44.23
41.98
Ph
O
O
O
O
O
N
Bn
3ai
13C NMR (100 MHz,CDCl3)

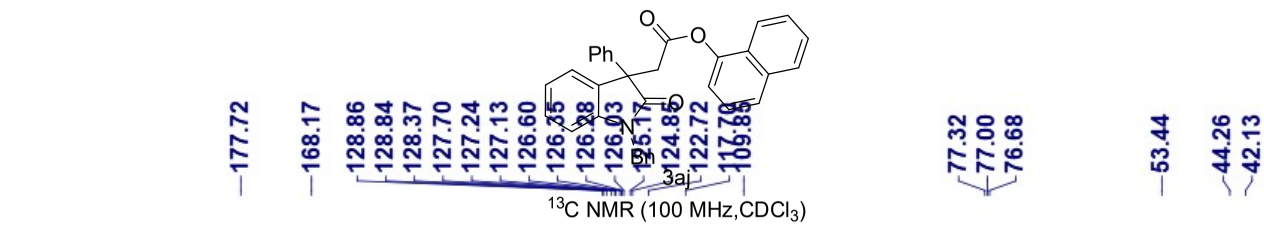

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

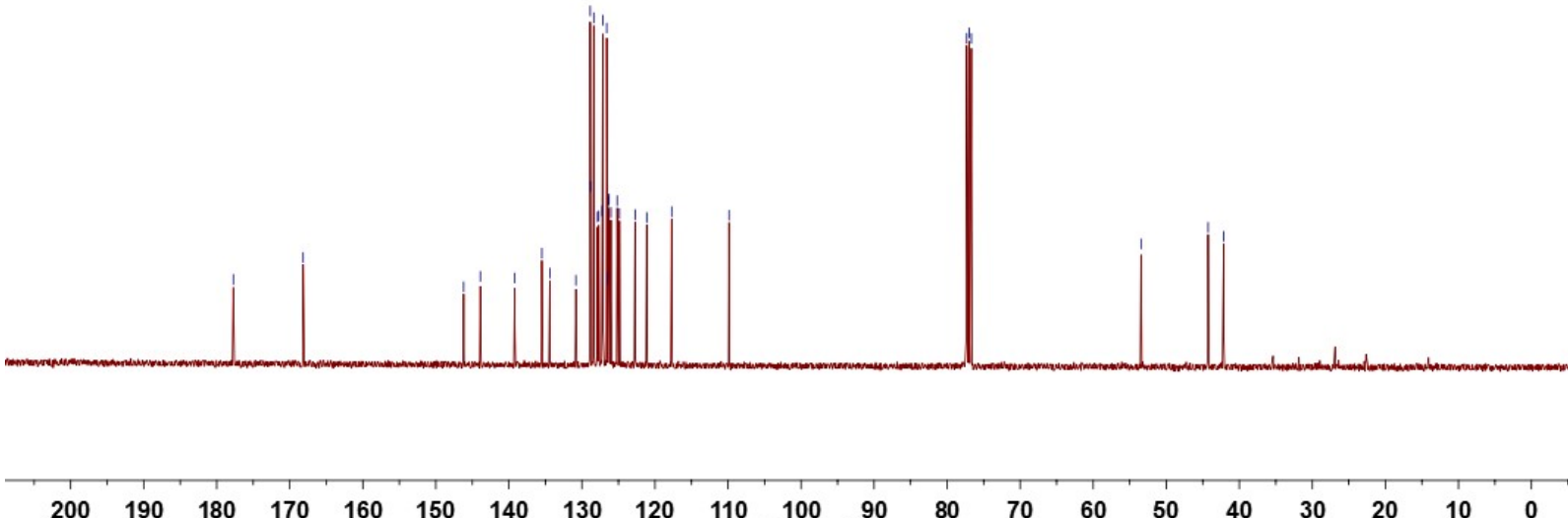


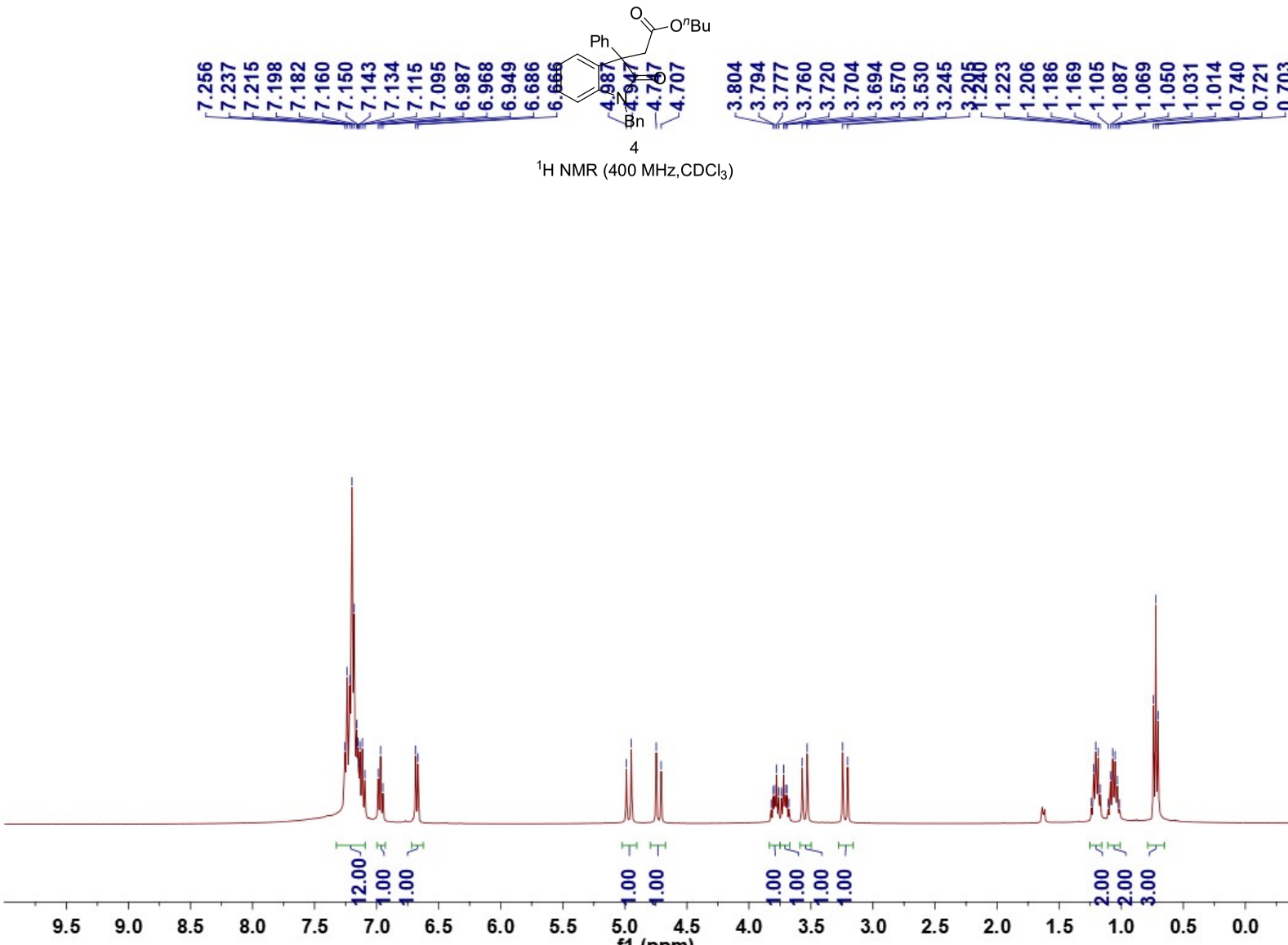
3aj

^{1}H NMR (400 MHz,$CDCl_3$)

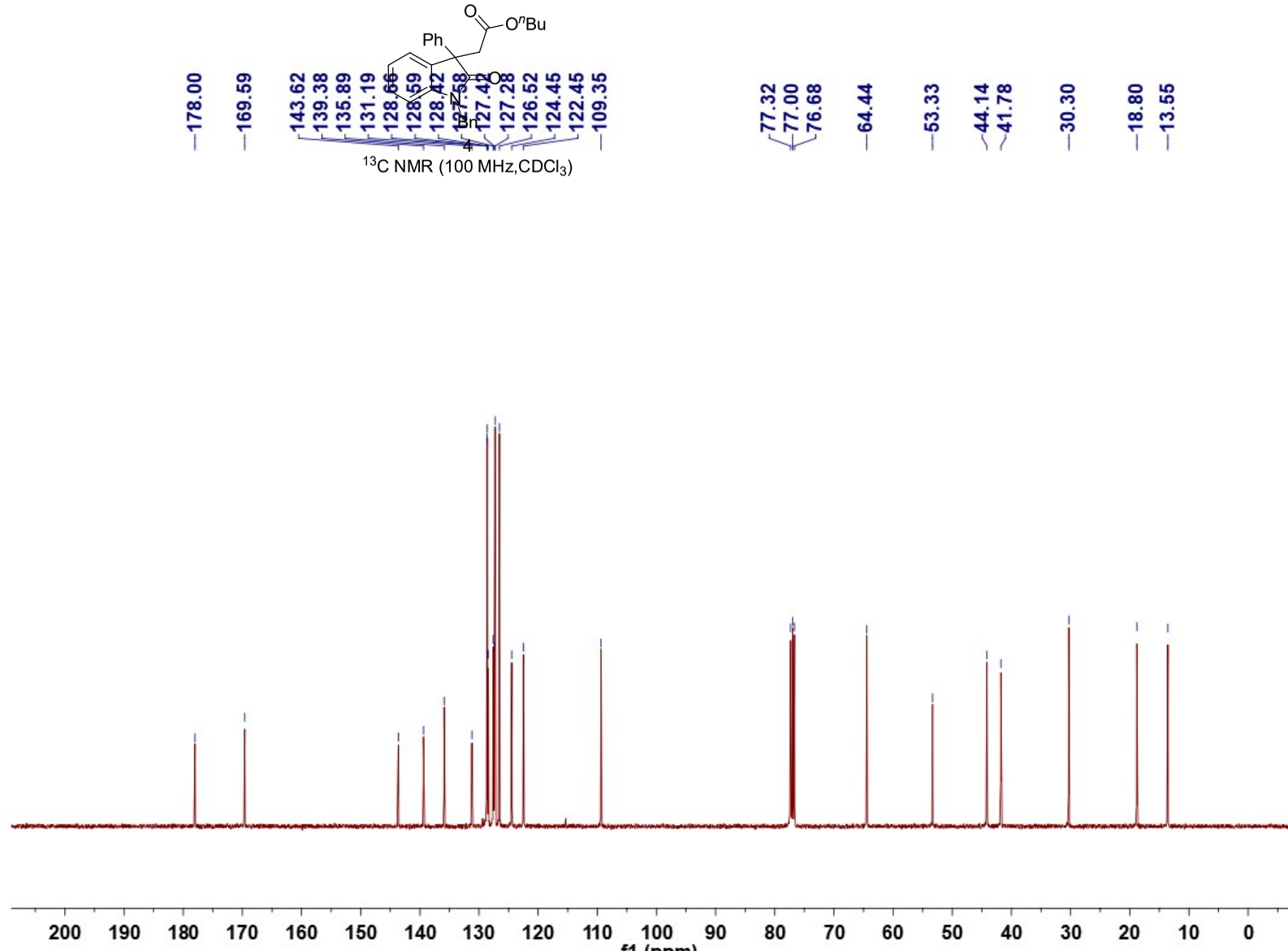


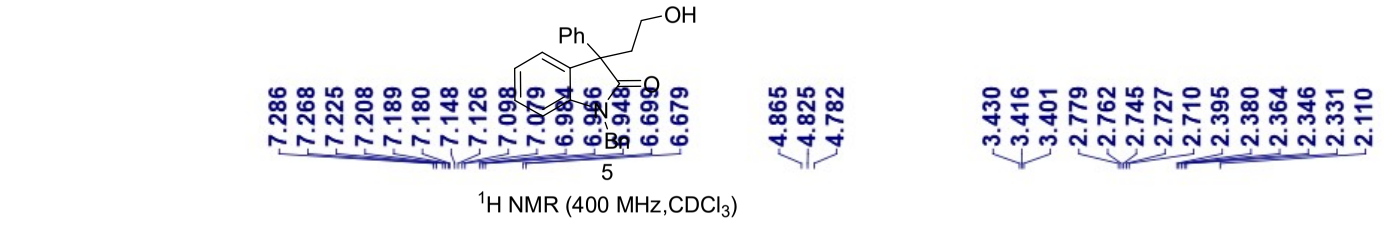

O
O
Ph
O
N
Br
3aj
177.72
168.17
128.86
128.84
128.37
127.70
127.24
127.13
126.60
126.55
126.48
126.03
125.17
124.85
122.72
117.76
109.85
77.32
77.00
76.68
53.44
44.26
42.13
^{13}C NMR (100 MHz,CDCl$_3$)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

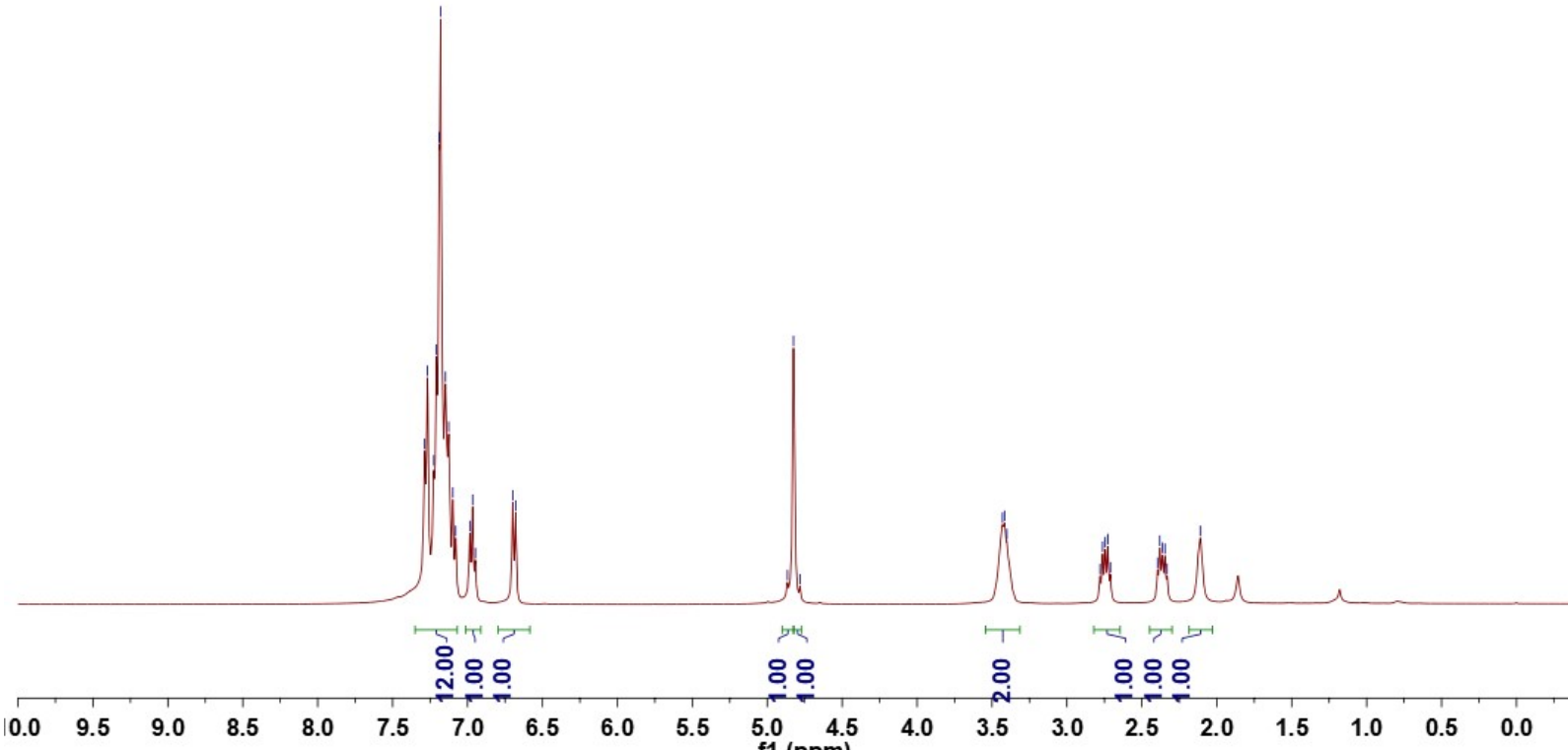


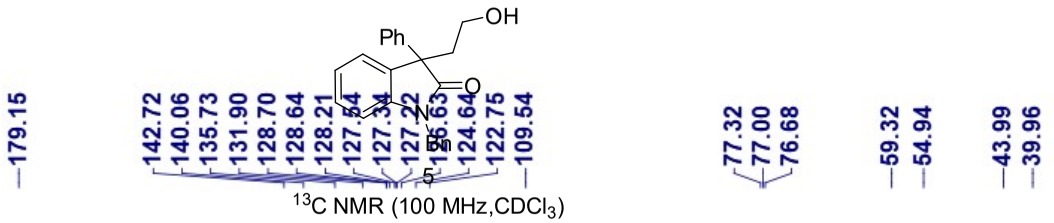
^{1}H NMR (400 MHz,$CDCl_3$)

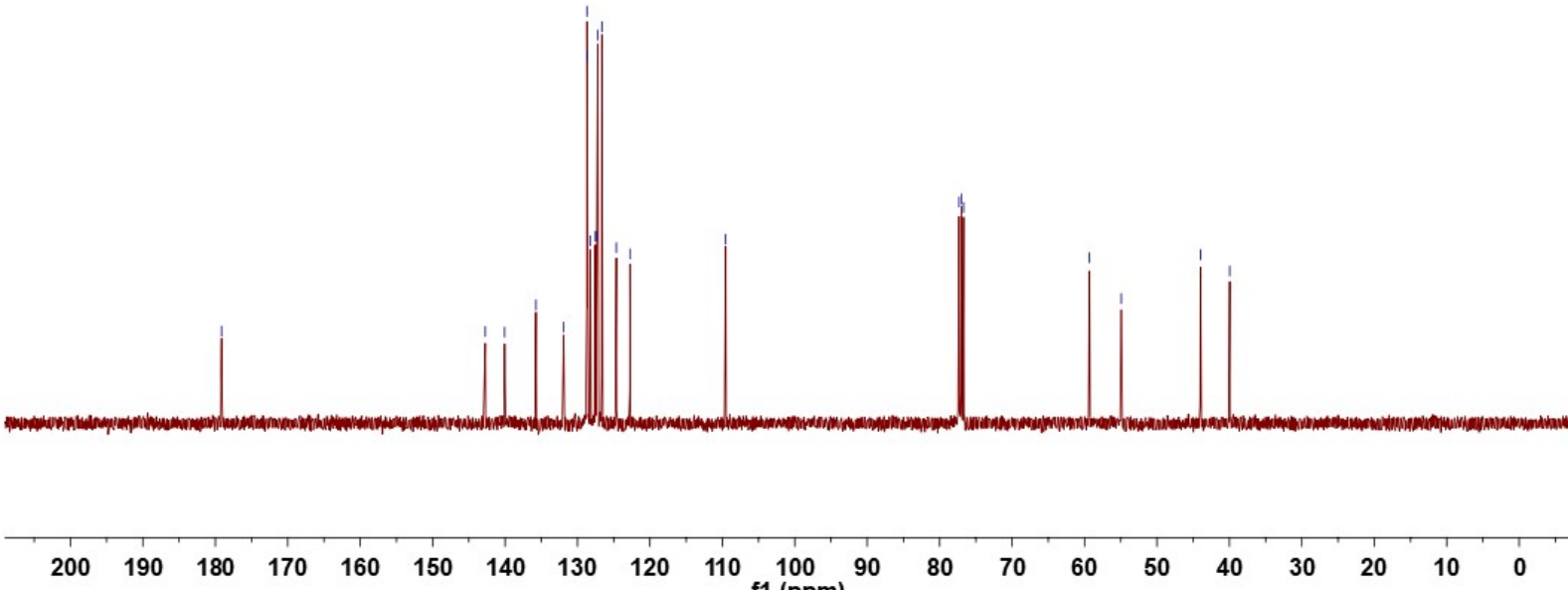

O
O^{n}Bu
Ph
O
Br
4
178.00
169.59
143.62
139.38
135.89
131.19
128.66
128.59
128.42
127.58
127.41
127.28
126.52
124.45
122.45
109.35
77.32
77.00
76.68
64.44
53.33
44.14
41.78
30.30
18.80
13.55
^{13}C NMR (100 MHz,CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

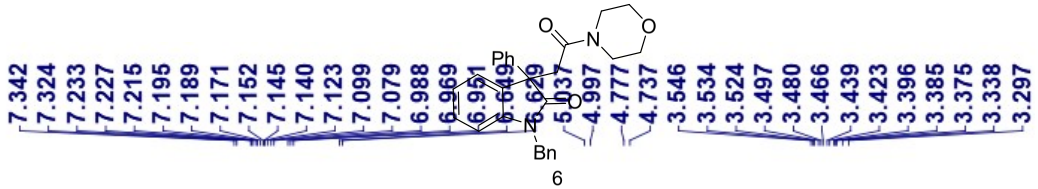


^{1}H NMR (400 MHz,$CDCl_3$)



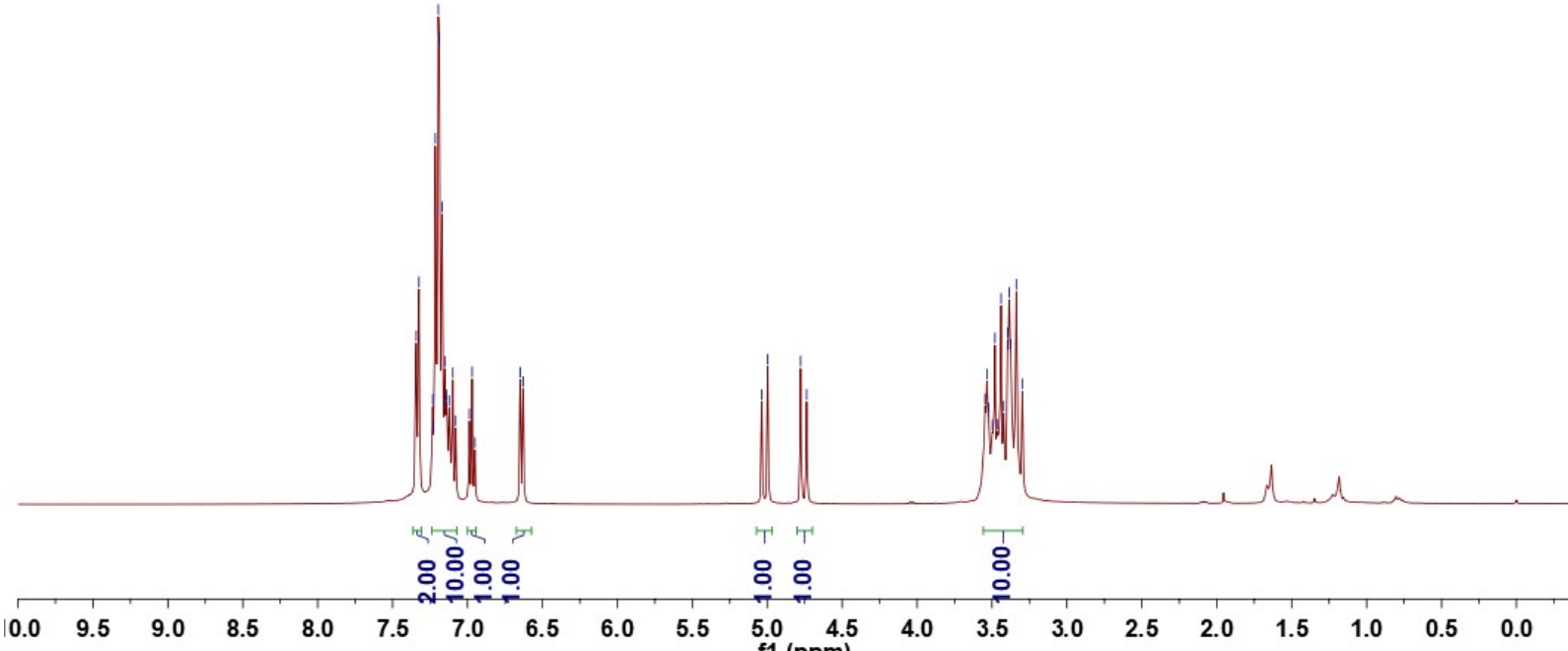

OH
Ph
O
N
5
179.15
142.72
140.06
135.73
131.90
128.70
128.64
128.21
127.54
127.34
127.22
126.63
124.64
122.75
109.54
77.32
77.00
76.68
59.32
54.94
43.99
39.96
^{13}C NMR (100 MHz,CDCl$_3$)

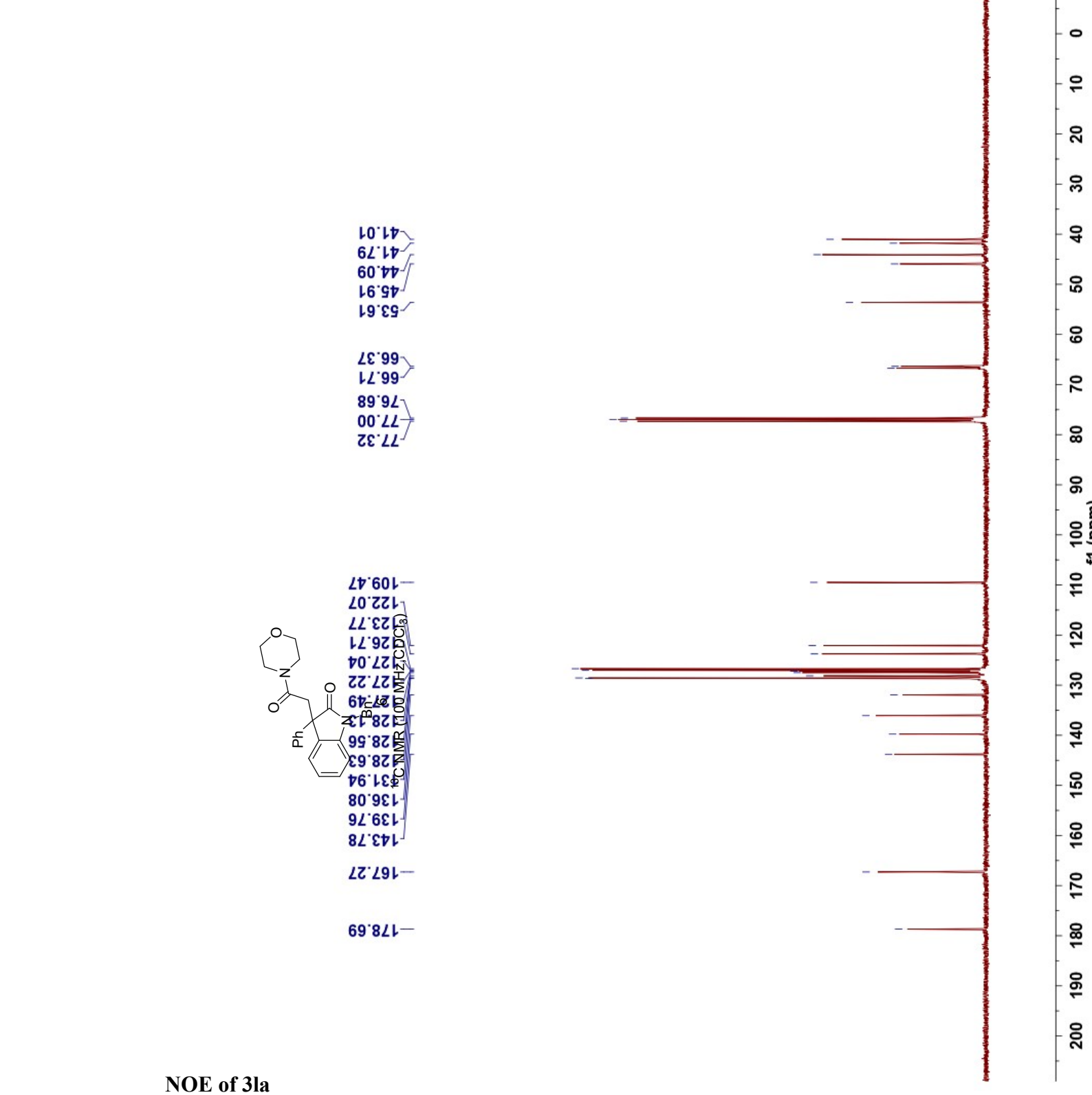

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



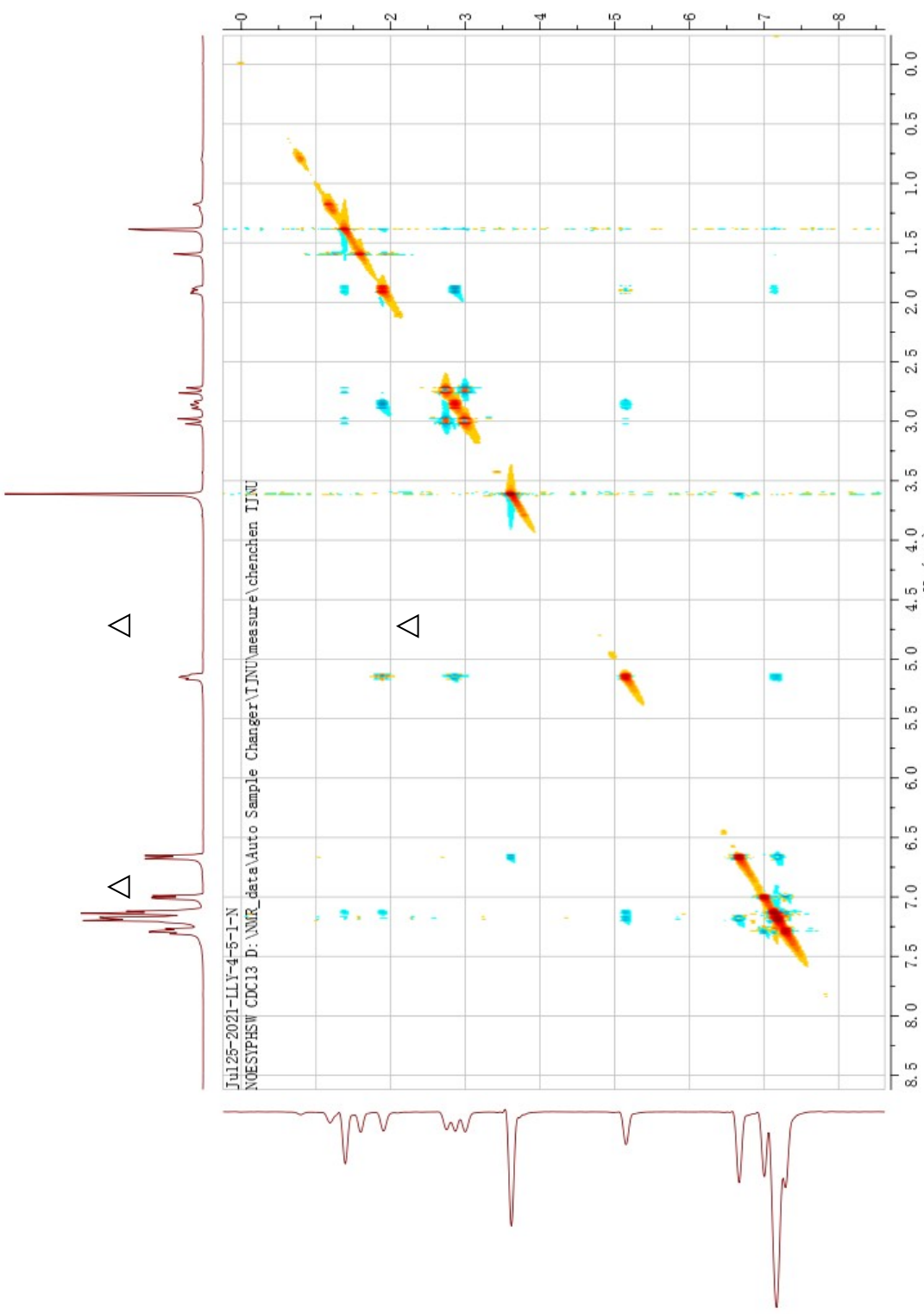
6

^{1}H NMR (400 MHz,$CDCl_3$)




41.01
41.79
44.09
45.91
53.61
66.37
66.71
76.68
77.00
77.32
109.47
122.07
123.77
126.71
127.04
127.22
127.49
128.13
128.56
128.63
131.94
136.08
139.76
143.78
167.27
178.69
Ph
N
O
O
O
N
13C NMR (100 MHz, CDCl3)
f1 (ppm)

NOE of 3la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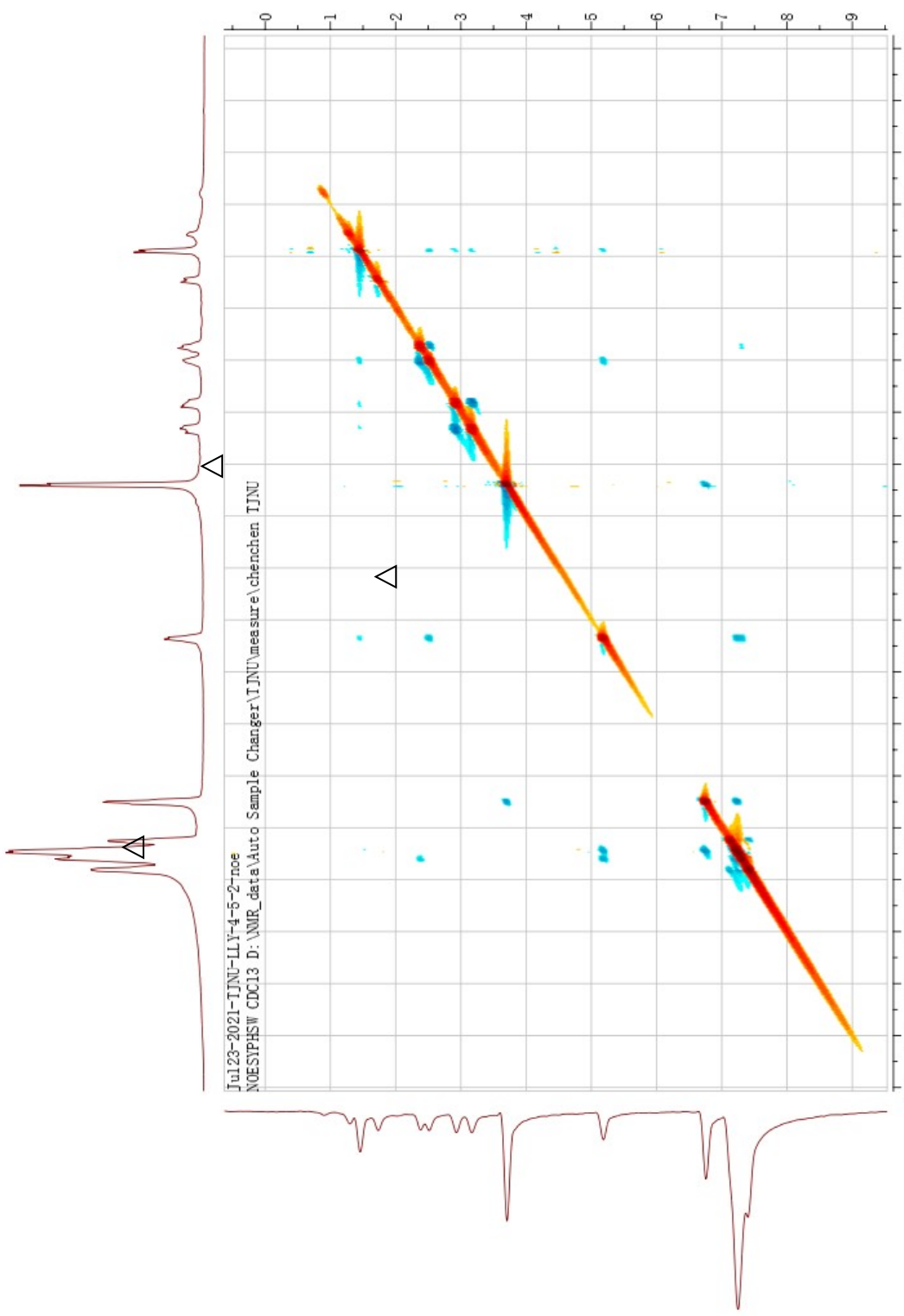
NOESYPHSW CDCl3 D:\NMR_data\Auto Sample Changer\TJNU\measure\chenchen TJNU

NOE of 3la'


Jul23-2021-TJNU-LLY-4-5-2-noe
NOESYPHSW CDCl3 D:\NMR_data\Auto Sample Changer\TJNU\measure\chenchen TJNU