Electronic Supplementary Information

Benzylic C(sp^3)–C(sp^2) Cross-Coupling of Indoles Enabled by Oxidative Radical Generation and Nickel Catalysis

Weonjeong Kim,‡ Jangwoo Koo‡ and Hong Geun Lee*

Department of Chemistry, College of Natural Sciences, Seoul National University, 1 Gwanak-ro, Seoul 08826, Republic of Korea

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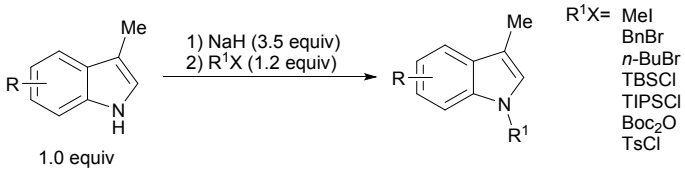
1. General Experimental Details

Unless otherwise noted, all reactions were performed under inert conditions. Analytical TLC was performed on a Merck 60 F254 silica gel plates (0.25mm thickness), and visualized either using UV light (254 nm) or by staining with potassium permanganate and heating. Column chromatography was performed on Merck 60 silica gel (230–400 mesh). NMR spectroscopy experiments were conducted with a Varian 400 and 500 MHz or a Bruker 300 MHz system. Gas chromatography (GC) was carried out using a GC-2030 (Shimadzu) equipped with an Rxi®-5Sil MS column and a flame ionization detector (FID). Liquid chromatography-mass spectrometry (LC-MS) spectra were obtained on an Agilent 6120 Quadrupole LC/MS. NMR spectra were processed with ACD NMR Processor or MestReNova. Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H, 77.16 ppm for ^{13}C; CH_2Cl_2 in CD_2Cl_2: 5.32 ppm for ^1H, 53.84 ppm for ^{13}C; $(CH_3)_2SO$ in $(CD_3)_2SO$: 2.50 ppm for ^1H, 39.52 ppm for ^{13}C). ^{19}F NMR spectra were calibrated to an external standard of neat $CFCl_3$ (0.0 ppm for ^{19}F). Coupling constants are reported in Hertz. Deuterated compounds were purchased from Cambridge Isotope Laboratories, Inc. All anhydrous solvents and chemicals were purchased from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar, TCI, or Strem) and used without further purification. The iridum-based photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was synthesized according to literature procedure.[1] 34 W Blue LED lamps purchased from Kessil (Kessil H150 Grow Light-Blue) were used for all the visible light photocatalytic reactions. Cyclic voltammetry was measured using a CH Instruments, CHI620E potentiostat using a three-electrode-cell assembly. High resolution mass spectroscopy (HRMS) analyses were performed by the ultrahigh resolution ESI Q-TOF mass spectrometer at the Organic Chemistry Research Center in Sogang University and the Mass Spectrometry Laboratory of National Instrumentation Center for Environmental Management (NICEM) in Seoul National University. UV–Vis spectra were recorded on an Agilent 8453 UV–Vis spectrophotometer with ChemStation software. Fluorescence spectra were recorded on a Photon Technology International (PTI) QM-400 spectrofluorometer with FelixGX software. The quenching constant (k_q) was determined following the Stern-Volmer relationship.[2]

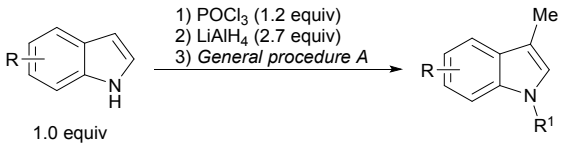
2. Substrate Preparations

General procedure A[3]



To a stirred solution of NaH (454 mg, 11.3 mmol, 3.5 equiv, 60% suspension in mineral oil) in dry DMF (10 mL), 3-methylindole (425 mg, 3.2 mmol, 1.0 equiv) in DMF (5 mL) was added dropwise at 0°C. The mixture was allowed to warm up to room temperature and stirred for 30 min. After cooling down to 0 °C, R^1X (3.9 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at room temperature for another 6 h and then it was quenched by the addition of water and was extracted with ethyl acetate (10 mL, 3 times). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding compounds.

General procedure B[4]



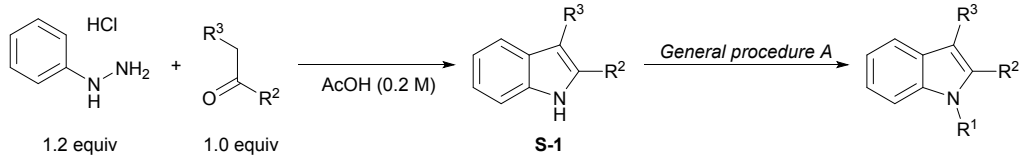
1) Phosphorus oxychloride (0.56 mL, 6.0 mmol, 1.2 equiv) was added dropwise to DMF (20 mL) with ice-bath. The mixture was stirred for 5 min then added to a solution of *1H*-indole (5.0 mmol, 1.0 equiv) in DMF (10 mL) at 0 °C. The mixture was then to warm to room temperature and stirred for 30 min. The reaction became a heavy suspension that required vigorous stirring 5.0 M aqueous potassium hydroxide was added until pH>9 and the mixture was heated at 100 °C for 2 h. The resulting suspension was cooled down to 0 °C, the precipitate was filtered off, washed with water then dried under vacuum overnight and used in the next step without further purification.

2) To a suspension of $LiAlH_4$ (0.50 g, 13 mmol, 2.7 equiv) in THF (55 mL) at 0 °C under argon atmosphere was added previously synthesized 3-formyl-*1H*-indole (5.0 mmol, 1.0 equiv) over spatula. The suspension was then to warm to room temperature and stirred for 4 h. The reaction was cooled down at 0 °C, distillated water (0.5 mL) was added dropwise then aqueous solution of NaOH 10% (0.5

mL) then again H_2O (1.0 mL). The resulting slurry was strirred vigorously for 30 min, diluted with Et_2O and anhydrous $MgSO_4$ was added. The white precipitate was filtered on Celite then washed with Et_2O. The solvent was removed under vacuum and the product was used in the next step without further purification.

3) The crude 3-methyl-*1H*-indole was protected following *General procedure A*. Flash column chromatography purification led to indoles as the starting materials.

General procedure C[5]

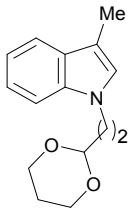


1) The suspension of phenylhydrazine hydrochloride (0.87g, 6.0 mmol, 1.2 equiv) in AcOH (25 mL) was heated in 50 °C for 30 min, then corresponding ketone (5.0 mmol, 1.0 equiv) was added in one portion and the reaction mixture was refluxed for 3 h. After cooling to room temperature, AcOH was removed under vacuum and the residue was dissolved in ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum to give gray residue, which was purified by flash chromatography on silica gel to afford the S-1.

2) Synthesized indole, at the previous stage, was protected following *General procedure A*. Flash column chromatography purification led to indoles as the starting materials.

Characterization data of substrates

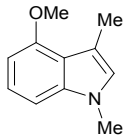
Previously reported N-protected indoles (**1a**,[6] **1c**,[6] **1d**,[7] **1f**,[8] **1g**,[9] **1h**,[10] **1i**,[11] **1j**,[12] **1l**,[13] **1m**,[14] **1p**,[6] **1r**,[6] **1s**,[15] **1t**,[16] **1v**,[17] **1x**,[18] **1y**,[7] **1za**,[19] **1zb**,[20] **1zc**,[17] **6aa**[21]) were characterized by spectral comparison with literature data. New N-protected indoles (**1e**, **1k**, **1n**, **1o**, **1q**, **1u**, **1w**, **1z**, **D-1a**) and aryl halides (**2t**) were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR. The **[Ni]-1**,[22] **3wt**[23] was confirmed by ^{1}H NMR and ^{19}F NMR spectral comparison with literature data, while new products were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS-ESI.



1-(2-(1,3-dioxan-2-yl)ethyl)-3-methyl-1*H*-indole (**1e**)

Following the general procedure A, compound **1e** was prepared from 3-methylindole and 2-(2-bromoethyl)-1,3-dioxane as R^1X.

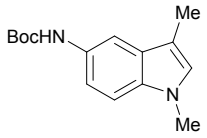
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (1H, d, *J* 7.8), 7.53 (1H, d, *J* 8.2), 7.42 (1H, t, *J* 7.6), 7.33 (1H, t, *J* 7.4), 7.01 (1H, s), 4.52 (1H, t, *J* 5.2), 4.35 (2H, t, *J* 6.9), 4.23 (2H, dd, *J* 11.8, 4.9), 3.76 (2H, t, *J* 12.1), 2.56 (3H, s), 2.30 – 2.15 (3H, m), 1.38 (1H, d, *J* 13.5) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.28, 128.64, 125.32, 121.32, 118.84, 118.45, 110.17, 109.17, 99.45, 66.57, 40.75, 35.67, 25.63, 9.55 ppm.



4-methoxy-1,3-dimethyl-1*H*-indole (**1k**)

Following the general procedure B, compound **1k** was prepared from 4-methoxyindole and iodomethane as R^1X.

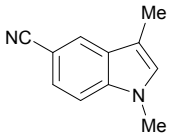
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (1H, t, *J* 8.0), 6.89 (1H, d, *J* 8.2), 6.68 (1H, s), 6.48 (1H, d, *J* 7.7), 3.93 (3H, s), 3.69 (3H, s), 2.49 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.39, 138.93, 125.35, 122.35, 118.36, 110.75, 102.64, 98.95, 55.33, 32.77, 12.13 ppm.



tert-butyl (1,3-dimethyl-1*H*-indol-5-yl)carbamate (**1n**)

Compound **1n** was prepared following slightly modified literature procedures using 5-nitro-1*H*-indole.[4, 24]

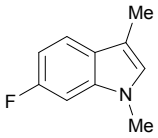
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (1H, s), 7.17 (1H, d, *J* 8.7), 7.09 (1H, d, *J* 8.2), 6.80 (1H, s), 6.50 (1H, s), 3.69 (3H, s), 2.29 (3H, s), 1.55 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.70, 134.24, 130.13, 128.93, 127.45, 115.18, 110.15, 109.88, 109.21, 79.97, 32.68, 28.60, 9.67 ppm.



1,3-dimethyl-1*H*-indole-5-carbonitrile (**1o**)

Compound **1o** was prepared following slightly modified literature procedures using 5-bromo-1,3-dimethyl-1*H*-indole (**1p**).[25]

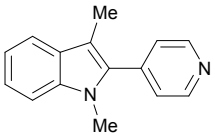
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (1H, s), 7.40 (1H, dd, *J* 8.5, 1.2), 7.28 (1H, d, *J* 8.5), 6.93 (1H, s), 3.75 (3H, s), 2.31 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.45, 128.81, 128.51, 124.67, 124.36, 121.19, 111.50, 109.88, 101.44, 32.79, 9.36 ppm.



6-fluoro-1,3-dimethyl-1*H*-indole (**1q**)

Following the general procedure B, compound **1q** was prepared from 6-fluoroindole and iodomethane as R^1X.

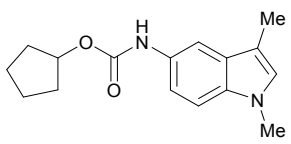
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (1H, dd, *J* 8.6, 5.3), 6.98 (1H, dd, *J* 10.0, 2.2), 6.91 (1H, ddd, *J* 9.7, 8.7, 2.3), 6.83 – 6.79 (1H, m), 3.69 (3H, s), 2.35 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.13 (d, $J_{C–F}$ 237.0), 137.14 (d, $J_{C–F}$ 12.2), 126.89 (dd, $J_{C–F}$ 3.5), 125.39, 119.77 (d, $J_{C–F}$ 10.3), 110.52, 107.25 (d, $J_{C–F}$ 24.6), 95.47 (d, $J_{C–F}$ 26.1), 32.62, 9.60 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –121.59 ppm.



1,3-dimethyl-2-(pyridin-4-yl)-1*H*-indole (**1u**)

Following the general procedure C, compound **1u** was prepared from phenylhydrazine hydrochloride, 4-propionylpyridine, and iodomethane as R^1X.

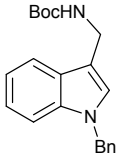
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (2H, d, *J* 5.7), 7.65 (1H, d, *J* 7.9), 7.38 – 7.30 (4H, m), 7.20 (1H, t, *J* 7.3), 3.66 (3H, s), 2.36 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.85, 140.18, 138.00, 134.60, 128.36, 125.04, 122.90, 119.65, 119.35, 110.73, 109.57, 31.27, 9.49 ppm.



cyclopentyl (1,3-dimethyl-1*H*-indol-5-yl)carbamate (**1w**)

Compound **1w** was prepared following slightly modified literature procedures using 5-nitro-1*H*-indole.[4, 26]

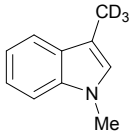
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, s), 7.17 (1H, d, *J* 8.6), 7.11 (1H, d, *J* 7.9), 6.80 (1H, s), 6.60 (1H, s), 5.33 – 5.18 (1H, m), 3.69 (3H, s), 2.29 (3H, s), 1.96 – 1.87 (2H, m), 1.84 – 1.71 (4H, m), 1.68 – 1.58 (2H, m) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.40, 134.30, 129.87, 128.90, 127.49, 115.10, 110.14, 109.80, 109.22, 77.81, 32.95, 32.65, 23.82, 9.60 ppm.



tert-butyl ((1-benzyl-1*H*-indol-3-yl)methyl)carbamate (**1z**)

Compound **1z** was prepared following slightly modified literature procedures using Indole-3-carboxaldehyde.[27-28]

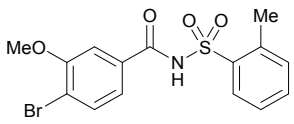
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, d, *J* 7.8), 7.33 – 7.25 (4H, m), 7.24 – 7.17 (1H, m), 7.17 – 7.09 (3H, m), 7.07 (1H, s), 5.28 (2H, s), 4.49 (2H, s), 1.47 (9H, s) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.61, 138.31, 136.11, 128.47, 127.29, 127.22, 127.09, 126.99, 121.29, 119.15, 118.68, 113.13, 110.06, 77.46, 48.88, 35.19, 28.29 ppm.



1-methyl-3-(methyl-d_3)-1*H*-indole (**D-1a**)

Following the general procedure B, compound **D-1a** was prepared from indole, DMF-d_7 instead of DMF, $LiAlD_4$ instead of $LiAlH_4$, and iodomethane as R^1X.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* 8.6), 7.33 (2H, dt, *J* 14.2, 7.7), 7.22 – 7.17 (1H, m), 6.88 (1H, s), 3.78 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.10, 128.78, 126.63, 121.50, 119.04, 118.59, 110.05, 109.09, 32.53, 8.88 (hept, *J* 19.4) ppm.



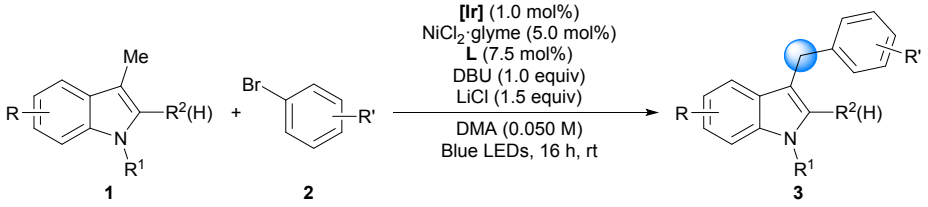
4-bromo-3-methoxy-*N*-(*o*-tolylsulfonyl)benzamide (**2t**)

Compound **2t** was prepared following slightly modified literature procedures using methyl 4-bromo-3-hydroxybenzoate.[23, 29]

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 (1H, dd, *J* 7.9, 1.4), 7.63 (1H, d, *J* 8.2), 7.58 (1H, d, *J* 1.9), 7.49 – 7.41 (2H, m), 7.36 (1H, td, *J* 7.7, 1.4), 7.31 (1H, d, *J* 7.5), 3.88 (3H, s), 2.59 (3H, s) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.92, 155.09, 140.23, 136.46, 135.40, 132.60, 131.99, 131.75, 129.56, 125.57, 121.89, 114.85, 111.90, 56.25, 19.75 ppm.

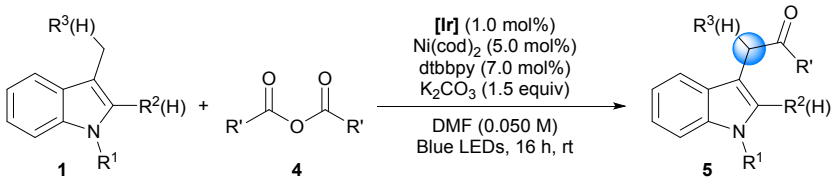
3. General Procedure for Arylation and Acylation

General procedure D: Arylation of indole



The reaction was set up in a nitrogen-filled glove box. To a 8 mL vial equipped with a PTFE-coated stirrer bar were added the corresponding indole **1** (0.30 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.0020 mmol, 1.0 mol%), $NiCl_2$·glyme (2.2 mg, 0.010 mmol, 5.0 mol%), 1,10-phenanthroline (2.7 mg, 0.015 mmol, 7.5 mol%), DBU (30 µL, 0.20 mmol, 1.0 equiv), LiCl (12.7 mg, 0.30 mmol, 1.5 equiv), aryl halide **2** (0.20 mmol, 1.0 equiv), and DMA (4.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography purification provided the arylated indoles as the desired products.

General procedure E: Acylation of indole

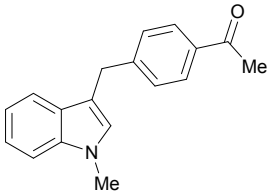


The reaction was set up in a nitrogen-filled glove box. To a 8 mL vial equipped with a PTFE-coated stirring bar were added the corresponding indole **1** (0.20 mmol, 1.0 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.0020 mmol, 1.0 mol%), $Ni(cod)_2$ (2.8 mg, 0.010 mmol, 5.0 mol%), 4,4'-di-tert-butyl-2,2'-bipyridine (3.8 mg, 0.014 mmol, 7.0 mol%), K_2CO_3 (42 mg, 0.30 mmol, 1.5 equiv), acid anhydride **4** (0.24 mmol, 1.2 equiv), and DMF (4.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The

organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography purification provided the acylated indoles as the desired products.

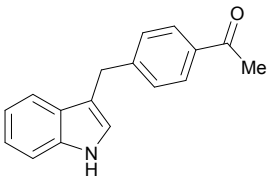
4. Characterization Data

Characterization data of arylation products



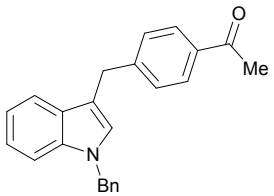
1-(4-((1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3aa**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.2), 7.49 (1H, d, *J* 7.9), 7.39 (2H, d, *J* 8.1), 7.32 (1H, d, *J* 8.2), 7.25 (1H, t, *J* 7.3), 7.10 (1H, t, *J* 7.2), 6.80 (1H, s), 4.18 (2H, s), 3.76 (3H, s), 2.59 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.97, 147.39, 137.29, 135.23, 128.93, 128.64, 127.75, 127.33, 121.86, 119.14, 119.06, 113.21, 109.37, 32.73, 31.70, 26.66 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO$: 286.1202, found: 286.1202.



1-(4-((1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ba**)

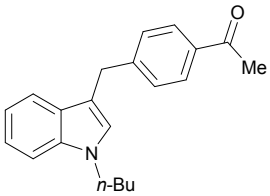
^{1}H NMR (500 MHz, DMSO-d_6) δ 10.89 (1H, s), 7.88 – 7.82 (2H, m), 7.37 (4H, m), 7.20 (1H, s), 7.04 (1H, t, *J* 7.5), 6.92 (1H, t, *J* 7.5), 4.11 (2H, s), 2.52 (3H, s) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 197.44, 147.59, 136.40, 134.63, 128.62, 128.27, 126.85, 123.35, 121.00, 118.42, 118.35, 112.93, 111.43, 31.02, 26.58 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO$: 272.1046, found: 272.1046.



1-(4-((1-benzyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ca**)

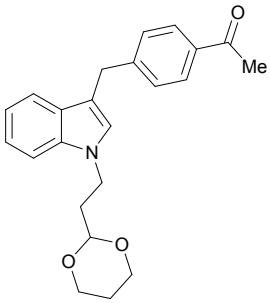
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (2H, m), 7.51 – 7.44 (1H, m), 7.36 (2H, d, *J* 8.0), 7.34 – 7.23 (4H, m), 7.17 (1H, ddd, *J* 8.3, 6.9, 1.2), 7.12 – 7.02 (3H, m), 6.87 (1H, s), 5.25 (2H, s), 4.16 (2H, s), 2.55 (3H, s)

ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.95, 147.23, 137.68, 136.96, 135.22, 128.91, 128.84, 128.64, 128.02, 127.67, 126.81, 126.73, 122.07, 119.33, 119.28, 113.85, 109.87, 49.99, 31.73, 26.64 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{21}NNaO$: 362.1515, found: 362.1515.



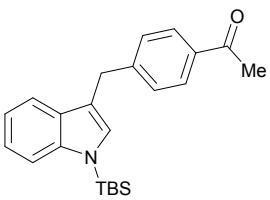
1-(4-((1-butyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3da**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.1), 7.48 (1H, d, *J* 7.9), 7.39 (2H, d, *J* 8.1), 7.35 (1H, d, *J* 8.2), 7.22 (1H, t, *J* 7.6), 7.08 (1H, t, *J* 7.4), 6.86 (1H, s), 4.18 (2H, s), 4.08 (2H, t, *J* 7.1), 2.59 (3H, s), 1.82 (2H, p, *J* 7.3), 1.36 (2H, h, *J* 7.5), 0.96 (3H, t, *J* 7.4) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.94, 147.46, 136.68, 135.29, 128.95, 128.64, 127.89, 126.32, 121.69, 119.23, 118.98, 113.10, 109.57, 46.09, 32.49, 31.77, 26.61, 20.32, 13.81 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{23}NNaO$: 328.1672, found: 328.1672.



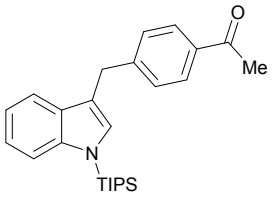
1-(4-((1-(2-(1,3-dioxan-2-yl)ethyl)-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ea**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* 8.2), 7.47 (1H, d, *J* 7.9), 7.40 – 7.33 (3H, m), 7.21 (1H, t, *J* 7.6), 7.07 (1H, t, *J* 7.5), 6.81 (1H, s), 4.37 (1H, t, *J* 5.2), 4.21 (2H, t, *J* 6.9), 4.16 (2H, s), 4.09 (2H, dd, *J* 10.8, 5.0), 3.66 (2H, td, *J* 12.4, 2.3), 2.58 (3H, s), 2.07 (2H, q, *J* 7.0), 1.33 (1H, d, *J* 13.5), 1.26 (1H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.02, 147.39, 136.64, 135.25, 128.98, 128.67, 127.82, 126.38, 121.88, 119.18, 119.09, 113.56, 109.66, 99.68, 66.95, 41.20, 35.72, 31.77, 26.71, 25.83 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{25}NNaO_3$: 386.1727, found: 386.1727.



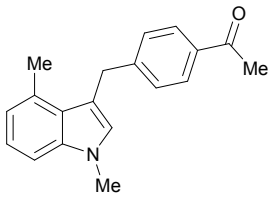
1-(4-((1-(*tert*-butyldimethylsilyl)-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3fa**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (2H, d, *J* 8.2), 7.50 (1H, d, *J* 8.3), 7.41 (1H, d, *J* 7.8), 7.36 (2H, d, *J* 8.3), 7.15 (1H, t, *J* 7.6), 7.06 (1H, t, *J* 7.4), 6.96 (1H, s), 4.16 (2H, s), 2.57 (3H, s), 0.93 (9H, s), 0.59 (6H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.08, 147.27, 141.81, 135.24, 130.81, 129.35, 128.89, 128.65, 121.74, 119.65, 119.07, 116.33, 114.14, 31.83, 26.70, 26.46, 19.65, –3.78 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{29}NNaOSi$: 386.1911, found: 386.1911.



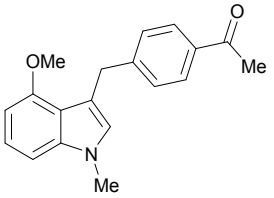
1-(4-((1-(triisopropylsilyl)-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ga**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.1), 7.51 (1H, d, *J* 8.3), 7.43 (1H, d, *J* 7.7), 7.36 (2H, d, *J* 8.0), 7.16 (1H, t, *J* 7.5), 7.07 (1H, t, *J* 7.4), 7.03 (1H, s), 4.19 (2H, s), 2.58 (3H, s), 1.70 (3H, p, *J* 7.5), 1.16 (18H, d, *J* 7.5) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.08, 147.36, 141.65, 135.18, 130.85, 129.58, 128.86, 128.63, 121.71, 119.59, 118.93, 116.19, 114.15, 31.82, 26.69, 18.26, 12.93 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{35}NNaOSi$: 428.2380, found: 428.2380.



1-(4-((1,4-dimethyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ja**)

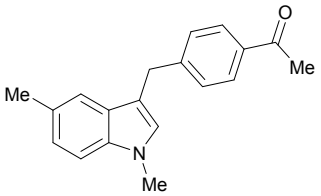
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.2), 7.31 (2H, d, *J* 8.1), 7.19 – 7.10 (2H, m), 6.83 (1H, d, *J* 6.8), 6.68 (1H, s), 4.35 (2H, s), 3.73 (3H, s), 2.59 (3H, s), 2.53 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.99, 148.22, 137.90, 135.29, 131.09, 128.87, 128.65, 128.19, 126.50, 122.02, 120.76, 113.35, 107.30, 33.41, 32.82, 26.64, 20.19 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.



1-(4-((4-methoxy-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ka**)

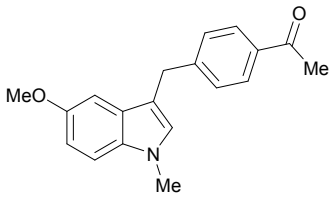
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* 8.2), 7.38 (2H, d, *J* 8.2), 7.13 (1H, t, *J* 8.0), 6.90 (1H, d, *J* 8.2), 6.58 (1H, s), 6.48 (1H, d, *J* 7.8,), 4.32 (2H, s), 3.84 (3H, s), 3.69 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (126

MHz, $CDCl_3$) δ 198.10, 155.01, 148.92, 138.98, 134.93, 129.06, 128.45, 126.03, 122.68, 117.71, 113.90, 102.72, 99.37, 55.14, 33.12, 32.90, 26.62 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_2$: 316.1308, found: 316.1308.



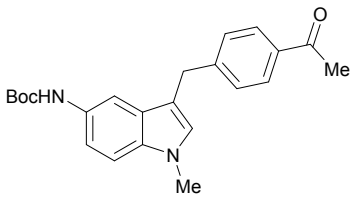
1-(4-((1,5-dimethyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3la**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.2), 7.38 (2H, d, *J* 8.2), 7.27 (1H, s), 7.21 (1H, d, *J* 8.3), 7.07 (1H, d, *J* 8.3), 6.75 (1H, s), 4.14 (2H, s), 3.72 (3H, s), 2.59 (3H, s), 2.44 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.02, 147.55, 135.74, 135.19, 128.91, 128.65, 128.30, 127.98, 127.44, 123.49, 118.73, 112.57, 109.10, 32.78, 31.65, 26.68, 21.59 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.



1-(4-((5-methoxy-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ma**)

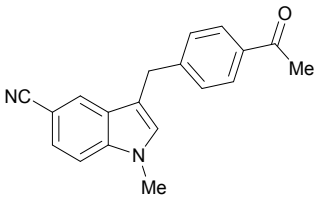
^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.1), 7.38 (2H, d, *J* 8.1), 7.20 (1H, d, *J* 8.5), 6.90 (2H, d, *J* 8.9), 6.75 (1H, s), 4.12 (2H, s), 3.81 (3H, s), 3.71 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.02, 153.90, 147.36, 135.22, 132.71, 128.92, 128.66, 128.05, 127.98, 112.61, 111.89, 110.15, 101.14, 56.05, 32.91, 31.70, 26.67 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_2$: 316.1308, found: 316.1308.



tert-butyl (3-(4-acetylbenzyl)-1-methyl-1*H*-indol-5-yl)carbamate (**3na**)

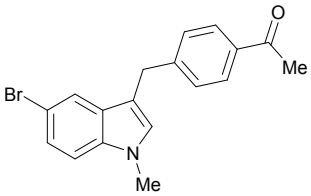
^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (2H, d, *J* 8.1), 7.49 (1H, s), 7.35 (2H, d, *J* 8.1), 7.20 (2H, d, *J* 8.3), 6.72 (1H, s), 6.48 (1H, s), 4.10 (2H, s), 3.70 (3H, s), 2.57 (3H, s), 1.51 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.97, 153.65, 147.35, 135.26, 134.36, 130.57, 128.93, 128.66, 128.11, 127.92, 115.61, 113.12, 109.65,

109.52, 80.04, 32.86, 31.58, 28.54, 26.63 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{26}N_2NaO_3$: 401.1836, found: 401.1836.



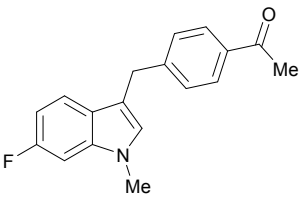
3-(4-acetylbenzyl)-1-methyl-1*H*-indole-5-carbonitrile (**3oa**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* 8.3), 7.77 (1H, s), 7.41 (1H, dd, *J* 8.5, 1.4), 7.33 (3H, d, *J* 8.4), 6.93 (1H, s), 4.12 (2H, s), 3.78 (3H, s), 2.57 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.75, 146.12, 138.79, 135.61, 129.56, 128.83, 128.81, 127.53, 124.81, 124.79, 114.61, 110.27, 102.18, 33.00, 31.37, 26.62 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{16}N_2NaO$: 311.1155, found: 311.1155.



1-(4-((5-bromo-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3pa**)

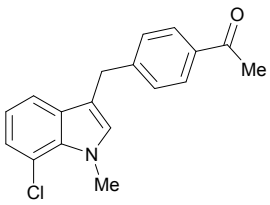
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* 8.2), 7.58 (1H, d, *J* 1.8), 7.34 (2H, d, *J* 8.1), 7.29 (1H, dd, *J* 8.7, 1.8), 7.16 (1H, d, *J* 8.7), 6.78 (1H, s), 4.09 (2H, s), 3.72 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.03, 146.82, 135.95, 135.35, 129.40, 128.86, 128.76, 128.53, 124.70, 121.65, 112.88, 112.54, 110.93, 32.96, 31.46, 26.72 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{16}BrNNaO$: 364.0308, found: 364.0307.



1-(4-((6-fluoro-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3qa**)

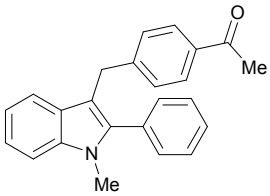
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* 8.2), 7.36 (3H, d, *J* 7.9), 6.97 (1H, dd, *J* 9.9, 2.2), 6.84 (1H, td, *J* 9.3, 2.2), 6.78 (1H, s), 4.13 (2H, s), 3.68 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.84, 160.11 (d, J_{C-F} 237.8), 147.02, 137.43, 137.38 (d, J_{C-F} 12.3), 128.86, 128.64, 127.60 (d, J_{C-F} 3.5), 124.31, 119.90 (d, J_{C-F} 10.3), 113.51, 107.73 (d, J_{C-F} 24.7), 95.75 (d, J_{C-F} 26.1), 32.74, 31.63, 26.56 ppm. ^{19}F NMR

(376 MHz, $CDCl_3$) δ –120.79 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{16}FNNaO$: 304.1108, found: 304.1108.



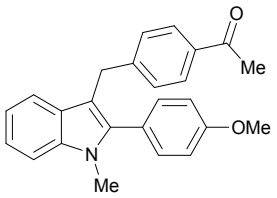
1-(4-((7-chloro-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ra**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (2H, d, *J* 8.0), 7.33 (3H, t, *J* 7.5), 7.14 (1H, d, *J* 7.6), 6.94 (1H, t, *J* 7.7), 6.73 (1H, s), 4.11 (2H, s), 4.09 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.90, 146.81, 135.37, 132.57, 130.87, 130.12, 128.87, 128.69, 123.39, 119.90, 117.92, 117.14, 113.31, 36.55, 31.47, 26.65 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{16}ClNNaO$: 320.0813, found: 320.0813.



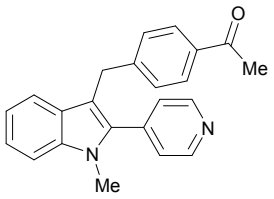
1-(4-((1-methyl-2-phenyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3sa**)

^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (2H, d, *J* 8.1), 7.49 (4H, dt, *J* 20.5, 7.4), 7.41 (3H, t, *J* 6.7), 7.30 (3H, dd, *J* 13.9, 7.7), 7.14 (1H, t, *J* 7.4), 4.18 (2H, s), 3.69 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.86, 147.95, 139.03, 137.48, 135.06, 131.77, 130.60, 128.59, 128.53, 128.49, 128.36, 127.78, 122.03, 119.63, 119.28, 110.64, 109.55, 31.00, 30.92, 26.54 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{21}NNaO$: 362.1515, found: 362.1515.



1-(4-((2-(4-methoxyphenyl)-1-methyl-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ta**)

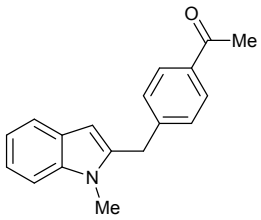
^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (2H, d, *J* 8.3), 7.43 (1H, d, *J* 7.9), 7.39 (1H, d, *J* 8.2), 7.28 (5H, dd, *J* 13.3, 8.5), 7.11 (1H, t, *J* 7.5), 7.02 (2H, d, *J* 8.7), 4.14 (2H, s), 3.89 (3H, s), 3.65 (3H, s), 2.57 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.92, 159.76, 148.10, 138.93, 137.33, 135.04, 131.81, 128.54, 128.51, 127.79, 123.93, 121.83, 119.55, 119.13, 114.11, 110.39, 109.49, 55.42, 30.98, 30.91, 26.57 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{23}NNaO_2$: 392.1621, found: 392.1621.



1-(4-((1-methyl-2-(pyridin-4-yl)-1*H*-indol-3-yl)methyl)phenyl)ethan-1-one (**3ua**)

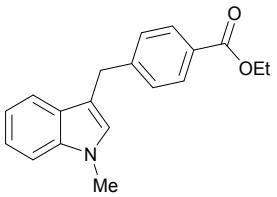
3ua was prepared according to the general procedure D *with the following modifications*: The reaction was conducted for 23 h with 4CzIPN instead of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$.

^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (2H, s), 7.82 (2H, d, *J* 8.2), 7.42 (2H, dd, *J* 11.7, 8.1), 7.35 – 7.28 (3H, m), 7.22 (2H, d, *J* 8.1), 7.12 (1H, t, *J* 7.4), 4.16 (2H, s), 3.70 (3H, s), 2.55 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89, 149.78, 147.15, 140.15, 138.16, 135.75, 135.30, 128.73, 128.39, 127.72, 125.14, 123.20, 120.22, 119.76, 112.48, 109.89, 31.41, 30.72, 26.66 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd $C_{23}H_{21}N_2O$: 341.1648, found: 341.1648.



1-(4-((1-methyl-1*H*-indol-2-yl)methyl)phenyl)ethan-1-one (**3va**)

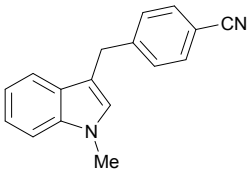
^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (2H, d, *J* 7.1), 7.57 (1H, d, *J* 7.8), 7.31 – 7.25 (3H, m), 7.19 (1H, t, *J* 7.5), 7.10 (1H, t, *J* 7.4), 6.29 (1H, s), 4.20 (2H, s), 3.55 (3H, s), 2.58 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.88, 144.22, 138.05, 137.81, 135.77, 128.92, 128.85, 127.79, 121.28, 120.24, 119.64, 109.05, 101.64, 33.56, 29.87, 26.72 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd $C_{18}H_{18}NO$: 264.1383, found: 264.1379.



ethyl 4-((1-methyl-1*H*-indol-3-yl)methyl)benzoate (**3ab**)

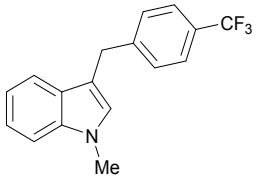
^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (2H, d, *J* 8.2), 7.49 (1H, d, *J* 7.9), 7.36 (2H, d, *J* 8.1), 7.31 (1H, d, *J* 8.2), 7.23 (1H, d, *J* 7.6), 7.09 (1H, t, *J* 7.4), 6.78 (1H, s), 4.38 (2H, q, *J* 7.1), 4.17 (2H, s), 3.75 (3H, s), 1.40 (3H, t, *J* 7.1) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.81, 146.95, 137.30, 129.79, 128.77, 128.36, 127.78, 127.34,

121.84, 119.19, 119.04, 113.41, 109.35, 60.88, 32.76, 31.75, 14.48 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_2$: 316.1308, found: 316.1308.



4-((1-methyl-1*H*-indol-3-yl)methyl)benzonitrile (**3ac**)

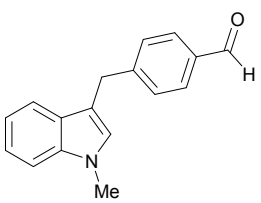
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (2H, d, *J* 8.0), 7.50 – 7.33 (4H, m), 7.30 (1H, d, *J* 6.9), 7.13 (1H, t, *J* 7.3), 6.86 (1H, s), 4.20 (2H, s), 3.80 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.22, 137.23, 132.18, 129.36, 127.52, 127.33, 121.90, 119.17, 119.11, 118.92, 112.38, 109.75, 109.37, 32.68, 31.70 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}N_2Na$: 269.1049, found: 269.1049.



1-methyl-3-(4-(trifluoromethyl)benzyl)-1*H*-indole (**3ad**)

3ad was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

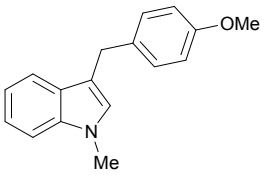
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* 8.0), 7.51 (1H, dt, *J* 7.9, 0.9), 7.42 (2H, d, *J* 7.9), 7.35 (1H, dt, *J* 8.3, 0.8), 7.28 (1H, ddd, *J* 8.3, 7.0, 1.2), 7.13 (1H, ddd, *J* 8.0, 7.0, 1.0), 6.81 (1H, s), 4.19 (2H, s), 3.77 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.76, 137.34, 129.04, 128.34 (q, J_{C-F} 32.0), 127.76, 127.37, 125.38 (q, J_{C-F} 3.8), 124.55 (q, J_{C-F} 271.8), 121.93, 119.14, 119.13, 113.23, 109.42, 32.75, 31.52 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.24 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}F_3NNa$: 312.0971, found: 312.0971.



4-((1-methyl-1*H*-indol-3-yl)methyl)benzaldehyde (**3ae**)

3ae was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

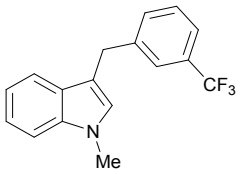
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (1H, s), 7.79 (2H, d, *J* 8.0), 7.45 (3H, t, *J* 8.5), 7.32 (1H, d, *J* 8.2), 7.24 (1H, t, *J* 7.6), 7.08 (1H, t, *J* 7.4), 6.81 (1H, s), 4.19 (2H, s), 3.76 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.20, 149.09, 137.31, 134.70, 130.11, 129.43, 129.39, 127.74, 127.41, 121.91, 119.15, 112.94, 109.45, 32.84, 31.93 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO$: 272.1046, found: 272.1046.



3-(4-methoxybenzyl)-1-methyl-1*H*-indole (**3af**)

3af was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

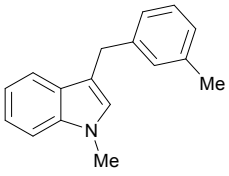
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (1H, d, *J* 7.9), 7.29 (1H, d, *J* 8.2), 7.20 (3H, d, *J* 8.3), 7.07 (1H, t, *J* 7.9), 6.83 (2H, d, *J* 8.6), 6.74 (1H, s), 4.04 (2H, s), 3.78 (3H, s), 3.73 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.91, 137.31, 133.64, 129.70, 127.92, 127.14, 121.67, 119.34, 118.85, 114.89, 113.86, 109.25, 55.39, 32.72, 30.74 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO$: 274.1202, found: 274.1202.



1-methyl-3-(3-(trifluoromethyl)benzyl)-1*H*-indole (**3ag**)

3ag was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

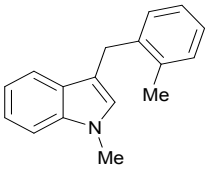
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (1H, s), 7.47 (3H, dd, *J* 11.5, 8.0), 7.42 – 7.36 (1H, m), 7.32 (1H, d, *J* 8.2), 7.23 (1H, d, *J* 8.1), 7.09 (1H, t, *J* 7.4), 6.78 (1H, s), 4.16 (2H, s), 3.76 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.56, 137.41, 132.19, 130.78 (q, J_{C-F} 31.9), 128.87, 127.81, 127.35, 125.50 (q, J_{C-F} 3.9), 122.94 (q, J_{C-F} 3.8), 122.30 (q, J_{C-F} 272.2), 121.93, 119.15, 119.13, 113.39, 109.41, 32.75, 31.54 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.48 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}F_3NNa$: 312.0971, found: 312.0971.



1-methyl-3-(3-methylbenzyl)-1*H*-indole (**3ah**)

3ah was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

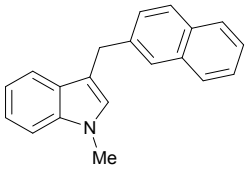
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, d, *J* 8.7), 7.31 (1H, d, *J* 8.2), 7.26 – 7.21 (1H, m), 7.18 (1H, d, *J* 7.4), 7.15 – 7.07 (3H, m), 7.03 (1H, d, *J* 7.4), 6.77 (1H, s), 4.08 (2H, s), 3.75 (3H, s), 2.33 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.49, 137.98, 137.28, 129.61, 128.34, 128.01, 127.23, 127.21, 126.72, 125.86, 121.66, 119.34, 118.87, 114.55, 109.24, 32.74, 31.56, 21.57 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{17}NNa$: 258.1253, found: 258.1253.



1-methyl-3-(2-methylbenzyl)-1*H*-indole (**3ai**)

3ai was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

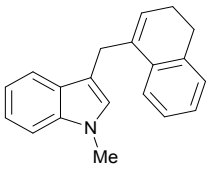
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, d, *J* 7.9), 7.31 (1H, d, *J* 8.2), 7.25 – 7.06 (6H, m), 6.57 (1H, s), 4.08 (2H, s), 3.71 (3H, s), 2.34 (3H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.24, 137.14, 136.41, 130.09, 129.41, 127.89, 127.12, 127.10, 126.11, 125.90, 121.53, 119.08, 118.69, 113.58, 109.11, 32.59, 29.13, 19.49 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{17}NNa$: 258.1253, found: 258.1253.



1-methyl-3-(naphthalen-2-ylmethyl)-1*H*-indole (**3aj**)

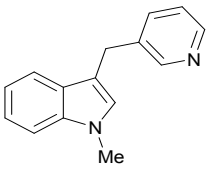
3aj was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.76 (4H, m), 7.59 (1H, d, *J* 7.9), 7.50 – 7.41 (3H, m), 7.33 (1H, d, *J* 8.2), 7.29 – 7.23 (1H, m), 7.11 (1H, t, *J* 7.8), 6.79 (1H, s), 4.30 (2H, s), 3.75 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.10, 137.38, 133.83, 132.26, 128.06, 128.01, 127.80, 127.75, 127.69, 127.43, 126.79, 125.95, 125.28, 121.75, 119.36, 118.98, 114.37, 109.29, 32.72, 31.90 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{17}NNa$: 294.1253, found: 294.1253.



3-((3,4-dihydronaphthalen-1-yl)methyl)-1-methyl-1*H*-indole (**3ak**)

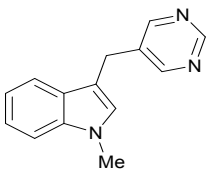
3ak was prepared according to the general procedure D *with the following modifications*: The reaction was conducted using alkenyl triflate with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (1H, d, *J* 7.9), 7.35 – 7.32 (1H, m), 7.30 (1H, d, *J* 8.2), 7.23 (1H, t, *J* 7.6), 7.18 – 7.09 (4H, m), 6.80 (1H, s), 5.90 (1H, t, *J* 4.5), 3.90 (2H, s), 3.72 (3H, s), 2.80 (2H, t, *J* 8.0), 2.33 – 2.26 (2H, m) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.33, 136.82, 135.39, 135.22, 128.27, 127.58, 127.44, 127.43, 126.70, 126.45, 123.31, 121.58, 119.39, 118.80, 113.06, 109.24, 32.75, 28.86, 28.60, 23.41 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{19}NNa$: 296.1410, found: 296.1410.



1-methyl-3-(pyridin-3-ylmethyl)-1*H*-indole (**3al**)

3al was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with the reaction temperature reaching 53 °C (without fan-cooling).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (1H, s), 8.46 (1H, d, *J* 3.9), 7.57 (1H, d, *J* 7.7), 7.48 (1H, d, *J* 7.9), 7.31 (1H, d, *J* 8.2), 7.26 – 7.18 (2H, m), 7.09 (1H, t, *J* 7.4), 6.78 (1H, s), 4.11 (2H, s), 3.75 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.94, 147.28, 137.36, 137.07, 136.50, 127.64, 127.33, 123.54, 121.97, 119.17, 119.06, 113.04, 109.42, 32.76, 28.89 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{15}N_2$: 223.1230, found: 223.1230.

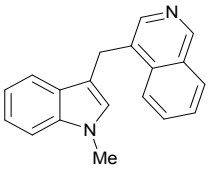


1-methyl-3-(pyrimidin-5-ylmethyl)-1*H*-indole (**3am**)

3am was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with the reaction temperature reaching 53 °C (without fan-cooling).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (1H, s), 8.66 (2H, s), 7.46 (1H, d, *J* 7.9), 7.32 (1H, d, *J* 8.2), 7.25 (1H, t, *J* 7.5), 7.10 (1H, t, *J* 7.4), 6.80 (1H, s), 4.09 (2H, s), 3.76 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.00,

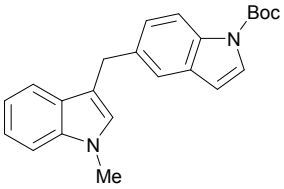
156.85, 156.83, 137.38, 134.64, 127.33, 122.20, 119.42, 118.77, 111.66, 109.56, 32.81, 26.48 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{14}N_3$: 224.1182, found: 224.1182.



4-((1-methyl-1*H*-indol-3-yl)methyl)isoquinoline (**3an**)

3an was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with the reaction temperature reaching 53 °C (without fan-cooling).

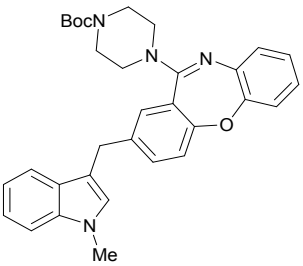
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (1H, s), 8.53 (1H, s), 8.02 (2H, dd, *J* 19.5, 8.2), 7.70 (1H, d, *J* 7.9), 7.62 (2H, dt, *J* 25.6, 7.2), 7.35 – 7.25 (2H, m), 7.17 (1H, t, *J* 7.2), 6.52 (1H, s), 4.50 (2H, s), 3.64 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.62, 143.22, 137.11, 135.04, 130.32, 130.17, 128.58, 128.21, 127.60, 127.41, 126.95, 123.70, 121.83, 119.05, 118.94, 113.12, 109.33, 32.65, 26.24 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{17}N_2$: 273.1386, found: 273.1386.



tert-butyl 5-((1-methyl-1*H*-indol-3-yl)methyl)-1*H*-indole-1-carboxylate (**3ao**)

3ao was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with 4,4‘-dimethoxy-2,2‘-bipyridine instead of 1,10-phenanthroline.

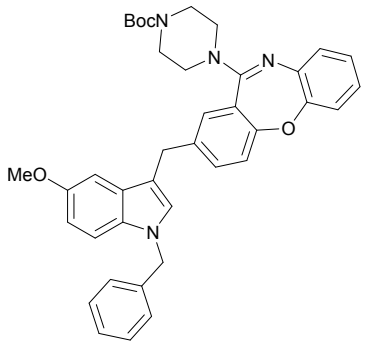
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (1H, s), 7.58 – 7.56 (1H, m), 7.54 (1H, d, *J* 7.9), 7.46 (1H, s), 7.32 – 7.25 (2H, m), 7.22 (1H, t, *J* 8.0), 7.07 (1H, t, *J* 7.8), 6.75 (1H, s), 6.49 (1H, d, *J* 3.7), 4.20 (2H, s), 3.73 (3H, s), 1.67 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.00, 137.36, 135.91, 130.94, 128.01, 127.29, 127.28, 126.08, 125.44, 121.67, 120.78, 119.41, 118.87, 115.10, 115.03, 109.23, 107.39, 83.61, 32.72, 31.54, 28.35 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{24}N_2NaO_2$: 383.1730, found: 383.1730.



tert-butyl 4-(2-((1-methyl-1*H*-indol-3-yl)methyl)dibenzo[*b,f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate (**3ap**)

3ap was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 4,4'-dimethoxy-2,2'-bipyridine (15.0 mol%), DMA (0.033 M) and corresponding aryl chloride instead of aryl bromide.

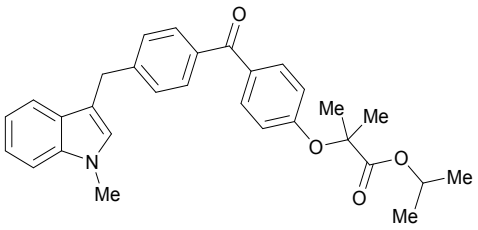
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (1H, d, *J* 6.9), 7.36 (1H, d, *J* 7.9), 7.32 (1H, d, *J* 8.2), 7.23 (1H, t, *J* 7.6), 7.19 – 7.09 (4H, m), 7.06 (2H, q, *J* 7.2, 6.7), 6.99 (1H, t, *J* 7.6), 6.82 (1H, s), 4.07 (2H, s), 3.76 (3H, s), 3.26 (8H, s), 1.50 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.62, 159.43, 154.87, 152.47, 140.37, 138.50, 137.43, 133.09, 129.38, 127.54, 127.29, 127.04, 125.58, 124.56, 123.00, 121.97, 121.06, 120.32, 119.12, 119.10, 113.38, 109.50, 80.01, 47.29, 43.47, 32.78, 30.83, 28.56 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{35}N_4O_3$: 523.2704, found: 524.2704.



tert-butyl 4-(2-((1-benzyl-5-methoxy-1*H*-indol-3-yl)methyl)dibenzo[*b,f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate (**3xp**)

3xp was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 4,4'-dimethoxy-2,2'-bipyridine (15.0 mol%), DMA (0.033 M) and corresponding aryl chloride instead of aryl bromide.

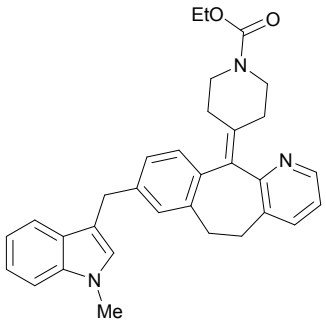
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (1H, d, *J* 8.1), 7.29 (3H, m), 7.23 – 7.05 (8H, m), 6.98 (1H, t, *J* 7.5), 6.91 (1H, s), 6.84 (1H, dd, *J* 8.8, 1.9), 6.73 (1H, s), 5.24 (2H, s), 4.06 (2H, s), 3.71 (3H, s), 3.25 (8H, s), 1.49 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.57, 159.47, 154.80, 154.06, 152.45, 138.23, 137.73, 133.03, 132.52, 129.37, 128.89, 128.20, 127.81, 127.42, 127.08, 126.87, 125.56, 124.50, 123.15, 121.05, 120.29, 113.38, 112.01, 110.75, 101.63, 79.94, 55.98, 50.27, 47.37, 43.17, 30.94, 28.57 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{39}H_{41}N_4O_4$: 629.3122, found: 629.3122.



isopropyl 2-methyl-2-(4-(4-((1-methyl-1*H*-indol-3-yl)methyl)benzoyl)phenoxy)propanoate (**3aq**)

3aq was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 4,4'-dimethoxy-2,2'-bipyridine (15.0 mol%), DMA (0.033 M) and corresponding aryl chloride instead of aryl bromide.

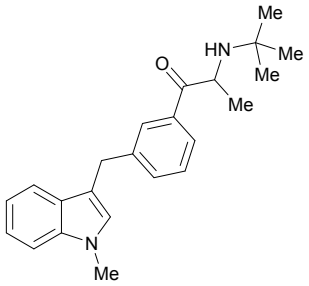
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (2H, d, *J* 8.2), 7.70 (2H, d, *J* 7.5), 7.52 (1H, d, *J* 7.7), 7.39 (2H, d, *J* 7.5), 7.32 (1H, d, *J* 8.0), 7.27 – 7.21 (1H, m), 7.10 (1H, t, *J* 7.1), 6.87 (2H, d, *J* 8.2), 6.82 (1H, s), 5.13 – 5.04 (1H, m), 4.19 (2H, s), 3.76 (3H, s), 1.67 (6H, s), 1.21 (6H, d, *J* 6.0) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.44, 173.30, 159.47, 146.23, 137.28, 135.91, 132.07, 130.98, 130.18, 128.58, 127.79, 127.37, 121.82, 119.19, 119.03, 117.23, 113.37, 109.36, 79.44, 69.37, 32.73, 31.67, 25.48, 21.62 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{31}NNaO_4$: 492.2145, found: 492.2145.



ethyl 4-(8-((1-methyl-1*H*-indol-3-yl)methyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (**3ar**)

3ar was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 4,4'-dimethoxy-2,2'-bipyridine (15.0 mol%), DMA (0.033 M) and corresponding aryl chloride instead of aryl bromide.

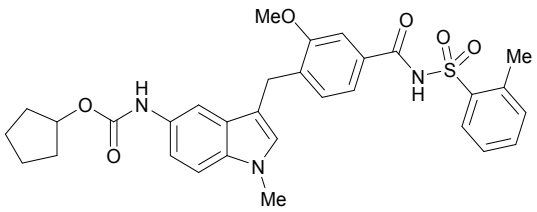
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (1H, dd, *J* 4.8, 1.6), 7.53 (1H, dt, *J* 7.9, 0.9), 7.44 (1H, d, *J* 7.5), 7.28 (1H, dt, *J* 8.2, 0.8), 7.21 (1H, ddd, *J* 8.1, 7.1, 1.0), 7.14 – 7.03 (5H, m), 6.78 (1H, s), 4.13 (2H, q, *J* 7.5), 4.04 (2H, s), 3.82 (2H, s), 3.73 (3H, s), 3.43 – 3.26 (2H, m), 3.20 – 3.06 (2H, m), 2.88 – 2.72 (2H, m), 2.53 – 2.22 (4H, m), 1.25 (3H, t, *J* 7.2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.76, 155.64, 146.18, 140.87, 137.80, 137.48, 137.24, 136.93, 136.56, 134.95, 134.14, 129.51, 129.41, 127.98, 127.23, 126.45, 122.23, 121.68, 119.28, 118.88, 114.10, 109.26, 61.38, 45.01, 44.92, 32.73, 32.00, 31.83, 31.18, 30.84, 30.71, 14.81 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{34}N_3O_2$: 492.2646, found: 492.2646.



2-(*tert*-butylamino)-1-(3-((1-methyl-1*H*-indol-3-yl)methyl)phenyl)propan-1-one (**3as**)

3as was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 4,4'-dimethoxy-2,2'-bipyridine (15.0 mol%), DMA (0.033 M) and corresponding aryl chloride instead of aryl bromide.

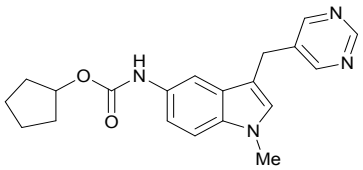
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (1H, s), 7.82 (1H, d, *J* 7.7), 7.52 – 7.48 (2H, m), 7.39 (1H, t, *J* 7.7), 7.30 (1H, d, *J* 8.2), 7.25 – 7.21 (1H, m), 7.08 (1H, ddd, *J* 7.9, 7.1, 0.9), 6.79 (1H, d, *J* 1.0), 4.33 (1H, q, *J* 7.1), 4.18 (2H, s), 3.75 (3H, s), 2.75 (1H, d, *J* 6.9), 1.24 (3H, d, *J* 7.1), 1.04 (9H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.29, 142.43, 137.36, 135.25, 133.80, 128.88, 128.69, 127.78, 127.30, 126.12, 121.87, 119.15, 119.06, 113.60, 109.38, 52.06, 50.89, 32.74, 31.58, 29.88, 22.85 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{29}N_2O$: 349.2274, found: 349.2274.



cyclopentyl (3-(2-methoxy-4-((*o*-tolylsulfonyl)carbamoyl)benzyl)-1-methyl-1*H*-indol-5-yl)carbamate (**3wt**)

3wt was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 1,10-phenanthroline (15.0 mol%) and DMA (0.033 M).

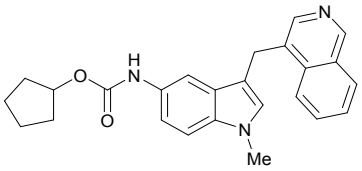
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (1H, s), 8.25 (1H, d, *J* 7.8), 7.55 – 7.46 (2H, m), 7.40 (1H, t, *J* 7.6), 7.33 – 7.27 (2H, m), 7.17 (2H, dd, *J* 12.7, 8.5), 7.10 (2H, t, *J* 10.0), 6.77 (1H, s), 6.52 (1H, s), 5.24 – 5.16 (1H, m), 4.03 (2H, s), 3.84 (3H, s), 3.70 (3H, s), 2.68 (3H, s), 1.86 (2H, s), 1.75 (4H, m), 1.60 (2H, s) ppm.



cyclopentyl (1-methyl-3-(pyrimidin-5-ylmethyl)-1*H*-indol-5-yl)carbamate (**3wm**)

3wm was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 1,10-phenanthroline (15.0 mol%) and DMA (0.033 M) and the reaction temperature reaching 53 °C (without fan-cooling).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (1H, s), 8.64 (2H, s), 7.59 (1H, s), 7.21 (1H, d, *J* 8.6), 7.14 (1H, d, *J* 7.1), 6.75 (1H, s), 6.68 (1H, s), 5.19 (1H, s), 4.03 (2H, s), 3.71 (3H, s), 1.92 – 1.83 (2H, m), 1.75 (4H, m), 1.65 – 1.54 (2H, m) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.98, 156.78, 154.26, 134.62, 134.42, 130.72, 128.16, 127.54, 115.71, 111.55, 109.79, 109.26, 77.94, 32.94, 26.34, 23.80 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{22}N_4NaO_2$: 373.1635, found: 373.1635.

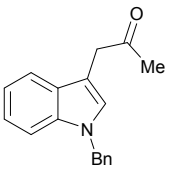


cyclopentyl (3-(isoquinolin-4-ylmethyl)-1-methyl-1*H*-indol-5-yl)carbamate (**3wn**)

3wn was prepared according to the general procedure D *with the following modifications*: The reaction was conducted with $NiCl_2$·glyme (10.0 mol%), 1,10-phenanthroline (15.0 mol%) and DMA (0.033 M) and the reaction temperature reaching 53 °C (without fan-cooling).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, s), 8.42 (1H, s), 8.02 (2H, dd, *J* 7.9, 3.6), 7.75 (1H, s), 7.68 (1H, t, *J* 7.6), 7.61 (1H, t, *J* 7.4), 7.22 – 7.13 (2H, m), 6.64 (1H, s), 6.49 (1H, s), 5.27 – 5.17 (1H, m), 4.44 (2H, s), 3.62 (3H, s), 1.95 – 1.83 (2H, m), 1.83 – 1.67 (4H, m), 1.67 – 1.53 (2H, m) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.35, 150.92, 141.90, 135.40, 134.30, 131.03, 130.90, 130.45, 128.53, 128.41, 128.39, 127.76, 127.40, 123.82, 115.48, 112.63, 109.66, 109.38, 77.90, 32.96, 32.89, 26.21, 23.82 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{26}N_3O_2$: 400.2020, found: 400.2020.

Characterization data of acylation products

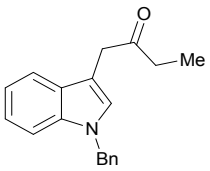


1-(1-benzyl-1*H*-indol-3-yl)propan-2-one (**5ca**)

5ca was prepared according to the general procedure E *with the following modifications*: The reaction was conducted in the absence of K_2CO_3.

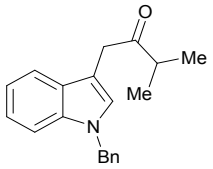
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (1H, d, *J* 7.9), 7.31 – 7.22 (4H, m), 7.21 – 7.15 (1H, m), 7.15 – 7.08 (3H, m), 7.07 (1H, s), 5.29 (2H, s), 3.80 (2H, s), 2.16 (3H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.43, 137.50,

136.77, 128.92, 128.10, 127.80, 127.32, 126.94, 122.22, 119.71, 119.05, 109.97, 108.09, 50.15, 40.92, 29.01 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO$: 286.1202, found: 286.1202.



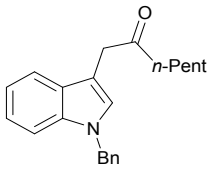
1-(1-benzyl-1*H*-indol-3-yl)butan-2-one (**5cb**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (1H, d, *J* 7.8), 7.33 – 7.22 (4H, m), 7.18 (1H, t, *J* 7.2), 7.16 – 7.09 (3H, m), 7.07 (1H, s), 5.28 (2H, s), 3.80 (2H, s), 2.51 (2H, q, *J* 7.3), 1.01 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.43, 137.50, 136.77, 128.92, 127.80, 127.32, 126.94, 122.22, 119.71, 119.05, 109.97, 108.09, 50.15, 40.92, 29.01 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.



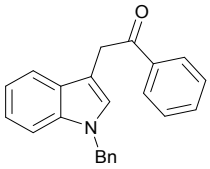
1-(1-benzyl-1*H*-indol-3-yl)-3-methylbutan-2-one (**5cc**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (1H, d, *J* 7.9), 7.34 – 7.24 (4H, m), 7.20 (1H, t, *J* 7.6), 7.14 (3H, dd, *J* 11.3, 7.3), 7.12 (1H, s), 5.31 (2H, s), 3.90 (2H, s), 2.93 – 2.68 (1H, m), 1.13 (6H, d, *J* 6.9) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.63, 137.61, 136.71, 128.87, 128.28, 127.73, 127.36, 126.93, 122.09, 119.57, 119.01, 109.90, 108.06, 50.13, 39.66, 37.67, 18.69 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO$: 314.1515, found: 314.1515.



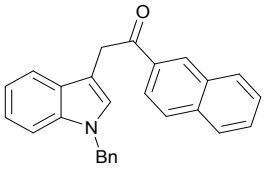
1-(1-benzyl-1*H*-indol-3-yl)heptan-2-one (**5cd**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (1H, d, *J* 7.5), 7.33 – 7.23 (4H, m), 7.22 – 7.16 (1H, m), 7.16 – 7.09 (3H, m), 7.08 (1H, s), 5.29 (2H, s), 3.81 (2H, s), 2.48 (2H, t, *J* 7.4), 1.62 – 1.50 (2H, m), 1.29 – 1.14 (4H, m), 0.85 (3H, t, *J* 7.0) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.49, 137.55, 136.72, 128.86, 128.18, 127.73, 127.28, 126.90, 122.12, 119.61, 119.06, 109.90, 108.14, 50.09, 41.52, 39.99, 31.43, 23.69, 22.52, 14.00 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{25}NNaO$: 342.1828, found: 342.1828.



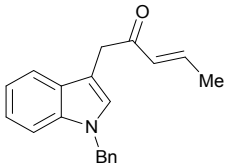
2-(1-benzyl-1*H*-indol-3-yl)-1-phenylethan-1-one (**5ce**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (2H, m), 7.67 – 7.62 (1H, m), 7.56 – 7.49 (1H, m), 7.43 (2H, t, *J* 7.7), 7.28 – 7.22 (4H, m), 7.20 – 7.12 (2H, m), 7.08 (1H, s), 7.06 (2H, dd, *J* 7.9, 1.5), 5.24 (2H, s), 4.41 (2H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.91, 137.57, 136.78, 136.66, 133.05, 128.81, 128.69, 128.65, 128.17, 127.65, 127.44, 126.84, 122.09, 119.58, 119.11, 109.91, 108.17, 50.07, 35.70 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{23}H_{19}NNaO$: 348.1359, found: 348.1359.



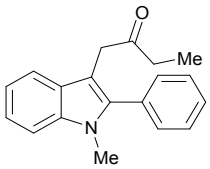
2-(1-benzyl-1*H*-indol-3-yl)-1-(naphthalen-2-yl)ethan-1-one (**5cf**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (1H, s), 8.10 (1H, dd, *J* 8.6, 1.8), 7.93 (1H, d, *J* 8.1), 7.87 (2H, dd, *J* 8.4, 4.4), 7.70 (1H, dd, *J* 6.8, 1.0), 7.57 (2H, dtd, *J* 16.2, 6.9, 1.2), 7.29 – 7.22 (4H, m), 7.18 (2H, ddd, *J* 14.4, 8.2, 2.6), 7.13 (1H, s), 7.06 (2H, dd, *J* 6.4, 2.9), 5.27 (2H, s), 4.55 (2H, s) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.99, 137.56, 136.68, 135.65, 134.09, 132.62, 130.41, 129.75, 128.83, 128.55, 128.51, 128.19, 127.86, 127.67, 127.46, 126.85, 126.82, 124.51, 122.14, 119.63, 119.15, 109.95, 108.37, 50.11, 35.89 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{27}H_{21}NNaO$: 398.1515, found: 398.1515.



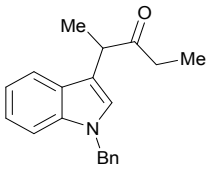
(*E*)-1-(1-benzyl-1*H*-indol-3-yl)pent-3-en-2-one (**5cg**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, d, *J* 7.8), 7.38 – 7.23 (4H, m), 7.20 (1H, t, *J* 7.1), 7.14 (3H, dd, *J* 12.3, 7.3), 7.08 (1H, s), 6.98 (1H, dq, *J* 18.2, 6.9), 6.25 (1H, dd, *J* 15.6, 1.6), 5.31 (2H, s), 3.94 (2H, s), 1.86 (3H, dd, *J* 6.9, 1.6) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.77, 143.19, 137.60, 136.75, 130.68, 128.88, 128.27, 127.74, 127.36, 126.95, 122.12, 119.60, 119.14, 109.91, 108.15, 50.15, 37.86, 18.37 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{19}NNaO$: 312.1359, found: 312.1359.



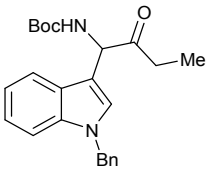
1-(1-methyl-2-phenyl-1*H*-indol-3-yl)butan-2-one (**5sb**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (3H, m), 7.48 (1H, dd, *J* 10.3, 4.4), 7.44 – 7.35 (3H, m), 7.32 – 7.27 (1H, m), 7.18 (1H, td, *J* 7.5, 0.8), 3.75 (2H, s), 3.64 (3H, s), 2.40 (2H, q, *J* 7.3), 0.97 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.28, 139.38, 137.38, 131.57, 130.66, 128.72, 128.54, 127.77, 122.19, 119.93, 119.04, 109.62, 106.44, 39.57, 34.76, 31.03, 7.95 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.



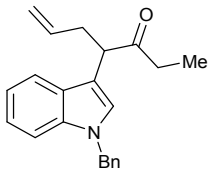
2-(1-benzyl-1*H*-indol-3-yl)pentan-3-one (**5yb**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, d, *J* 7.9), 7.36 – 7.23 (4H, m), 7.19 (1H, t, *J* 7.3), 7.12 (3H, dd, *J* 16.3, 7.9), 7.00 (1H, s), 5.29 (2H, s), 4.04 (1H, q, *J* 7.0), 2.58 – 2.30 (2H, m), 1.49 (3H, d, *J* 7.0), 0.96 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.53, 137.51, 136.93, 128.92, 127.79, 127.37, 126.90, 126.04, 122.22, 119.66, 119.28, 115.16, 110.03, 50.21, 43.97, 33.53, 17.13, 8.28 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO$: 314.1515, found: 314.1515.



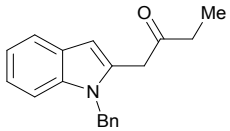
tert-butyl (1-(1-benzyl-1*H*-indol-3-yl)-2-oxobutyl)carbamate (**5zb**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, d, *J* 7.9), 7.32 – 7.22 (4H, m), 7.18 (1H, t, *J* 7.5), 7.14 (1H, s), 7.12 (1H, d, *J* 6.6), 7.07 (2H, d, *J* 6.7), 5.64 (2H, m), 5.26 (2H, s), 2.60 – 2.38 (2H, m), 1.40 (9H, s), 0.99 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.69, 155.30, 137.00, 136.97, 128.93, 127.90, 127.90, 126.91, 126.51, 122.59, 120.29, 119.35, 110.55, 110.21, 79.74, 56.39, 50.28, 32.96, 28.46, 8.01 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{29}N_2O_3$: 393.2173, found: 393.2167.



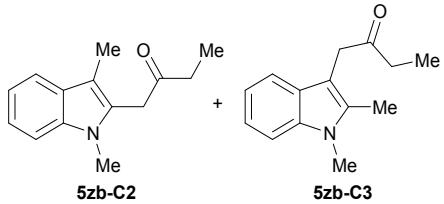
4-(1-benzyl-1*H*-indol-3-yl)hept-6-en-3-one (**5zab**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* 7.7), 7.29 (4H, t, *J* 8.0), 7.18 (2H, dt, *J* 14.7, 7.1), 7.09 (2H, d, *J* 6.8), 7.03 (1H, s), 5.79 (1H, dt, *J* 24.0, 12.0), 5.31 (2H, s), 5.06 (1H, d, *J* 17.0), 4.98 (1H, d, *J* 10.2), 4.03 (1H, t, *J* 7.5), 2.89 (1H, dt, *J* 14.5, 7.3), 2.65 – 2.34 (3H, m), 0.98 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.12, 137.46, 136.85, 136.56, 128.89, 127.77, 127.52, 126.79, 126.65, 122.21, 119.70, 119.28, 116.41, 112.85, 110.04, 50.17, 49.55, 36.14, 34.60, 8.13 ppm. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NO$: 318.1852, found: 318.1853.



1-(1-benzyl-1*H*-indol-2-yl)butan-2-one (**5zbb**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (1H, d, *J* 7.6), 7.34 – 7.19 (4H, m), 7.15 (2H, dt, *J* 14.7, 7.0), 6.95 (2H, d, *J* 7.0), 6.49 (1H, s), 5.33 (2H, s), 3.77 (2H, s), 2.45 (2H, q, *J* 7.3), 0.97 (3H, t, *J* 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.64, 137.73, 137.63, 133.34, 128.91, 128.01, 127.53, 126.11, 121.83, 120.42, 119.99, 109.77, 102.94, 46.86, 41.77, 35.03, 7.72 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.



1-(1,3-dimethyl-1*H*-indol-2-yl)butan-2-one(**5zcb-C2**) & 1-(1,2-dimethyl-1*H*-indol-3-yl)butan-2-one (**5zcb-C3**)

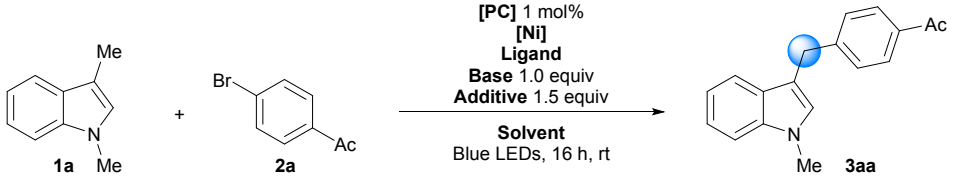
Regioisomers were obtained in **5zcb-C2** and **5zcb-C3** at a ratio of 4:3, respectively.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (1H, d, *J* 7.9, **5zcb-C2**), 7.49 (0.72H, d, *J* 6.9, **5zcb-C3**), 7.28 (1.81H, d, *J* 7.7), 7.25 – 7.16 (1.70H, m), 7.16 – 7.08 (1.66H, m), 3.84 (2H, s, **5zcb-C2**), 3.75 (1.45H, s, **5zcb-C3**), 3.68 (2.15H, s, **5zcb-C3**), 3.64 (3H, s, **5zcb-C2**), 2.45 (3.44H, qd, *J* 7.3, 1.6), 2.39 (2.15H, s, **5zcb-C3**), 2.34 (3H, s, **5zcb-C2**), 1.01 (5.17H, dt, *J* 16.6, 7.3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.03, 207.96, 137.15, 136.79, 134.58, 129.63, 128.28, 127.72, 121.63, 121.02, 119.41, 119.04, 118.61, 117.89, 108.98, 108.85, 108.72,

104.28, 39.71, 39.35, 34.83, 34.38, 30.02, 29.72, 10.49, 9.16, 7.92, 7.73 ppm. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{17}NNaO$: 238.1202, found: 238.1202.

5. Optimization of Reaction Conditions

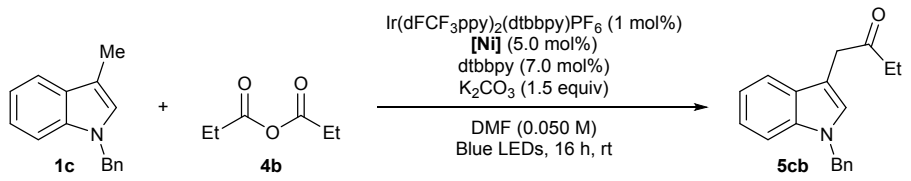
Table S1. Optimization of the reaction with **1a** and **2a**.[a]



entry	[PC]	[Ni] (mol%)	ligand (mol%)	base	additive	solvent (M)	result (%)
1	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiCl_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	29
2	$Ir(ppy)_3$	$NiCl_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	0
3	$Ru(bpy)_3Cl_2$	$NiCl_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	0
4	4-CzIPN	$NiCl_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	4
5	2,4,6-triphenylpyrylium BF_4	$NiCl_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	0
6	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	29
7	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$Ni(cod)_2$ (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	20
8	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$Ni(acac)_2$ (10)	dtbbpy (15)	DABCO	-	DMF (0.1M)	trace
9	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	K_3PO_4	-	DMF (0.1M)	0
10	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	K_2CO_3	-	DMF (0.1M)	13
11	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	DMF (0.1M)	35
12	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	2,4,6-collidine	-	DMF (0.1M)	0
13	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	BTMG	-	DMF (0.1M)	31
14	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	DMA (0.1M)	40
15	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	DMSO (0.1M)	21
16	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	CH_3CN (0.1M)	30
17	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	CH_2Cl_2 (0.1M)	trace
18	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	dtbbpy (15)	DBU	-	toluene (0.1M)	27
19	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	2,2'-bipyridine (15)	DBU	-	DMA (0.1M)	27
20	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	2,2-bisoxazole (15)	DBU	-	DMA (0.1M)	14
21	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	Terpyridine (15)	DBU	-	DMA (0.1M)	35
22	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	-	DMA (0.1M)	44
23[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	$ZnBr_2$	DMA (0.1M)	12
24[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	$MgBr_2$	DMA (0.1M)	trace
25[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	LiCl	DMA (0.1M)	73
26[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	LiBr	DMA (0.1M)	22
27[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	TBACl	DMA (0.1M)	70
28[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (10)	1,10-phenanthroline (15)	DBU	TBABr	DMA (0.1M)	38
29[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiBr_2$ glyme (5)	1,10-phenanthroline (7.5)	DBU	LiCl	DMA (0.05M)	78
30[b]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	$NiCl_2$ glyme (5)	1,10-phenanthroline (7.5)	DBU	LiCl	DMA (0.05M)	83 (73)[c]

[a] Reaction condition: **1a** (0.13 mmol), **2a** (0.10 mmol), **[PC]** (1.0 mol%), **[Ni]**, **ligand**, **base** (0.10 mmol), **additive** (0.15 mmol) and **solvent** irradiated with 34W blue LEDs. Yields are determined by gas chromatography using dodecane as an internal standard. [b] **1a** (0.15 mmol). [c] The reaction was carried out under air conditions. glyme=1,2-dimethoxyethane. dtbbpy=4,4'-di-*tert*-butyl-2,2'-bipyridine. DBU=1,8-diazabicyclo[5.4.0]undec-7-ene. DABCO=1,4-diazabicyclo[2.2.2]octane. DMF=*N,N*-dimethylformamide. 4CzIPN=1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene. DMA=*N,N*-dimethylacetamide. BTMG=2-*tert*-butyl-1,1,3,3-tetramethyl-guanidine. DMSO=dimethyl sulfoxide.

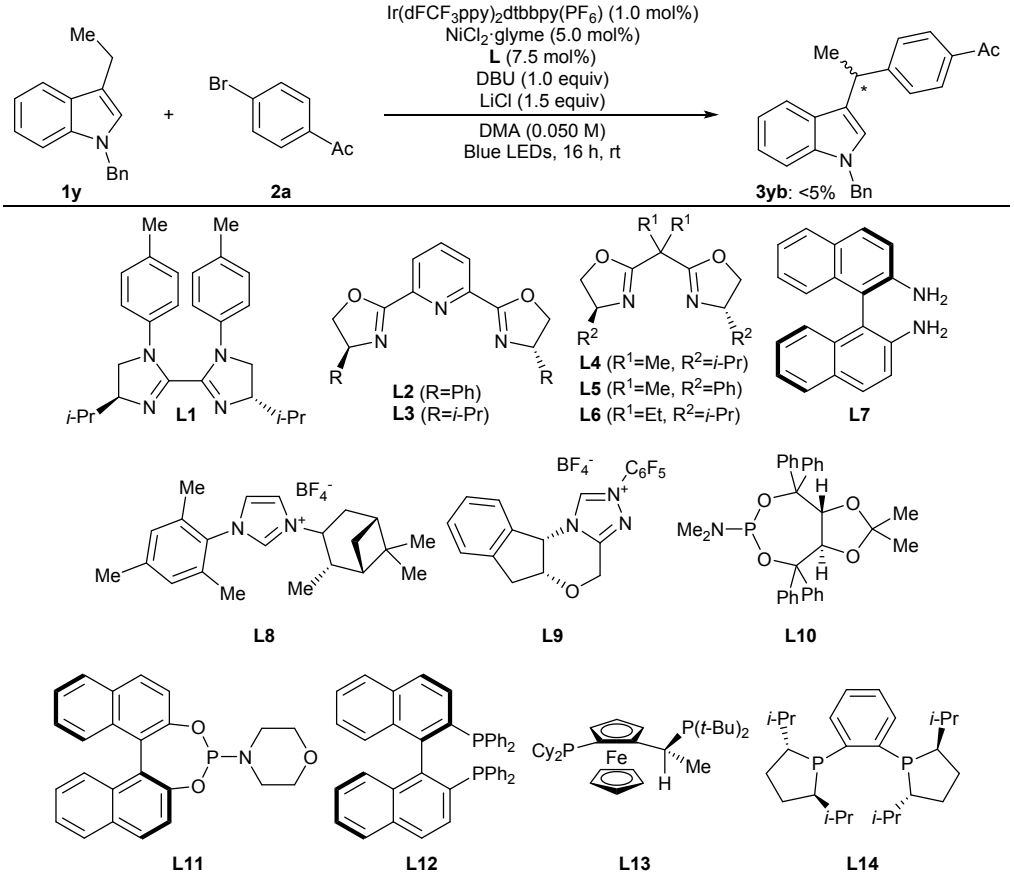
Table S2. Evaluation of other Ni sources.[a]



[Ni]	yield (%)
$NiCl_2$·glyme	76
$NiBr_2$·glyme	73
$NiSO_4·6H_2O$	87
$Ni(acac)_2$	77
$Ni(TMHD)_2$	80
$Ni(cod)_2$	99

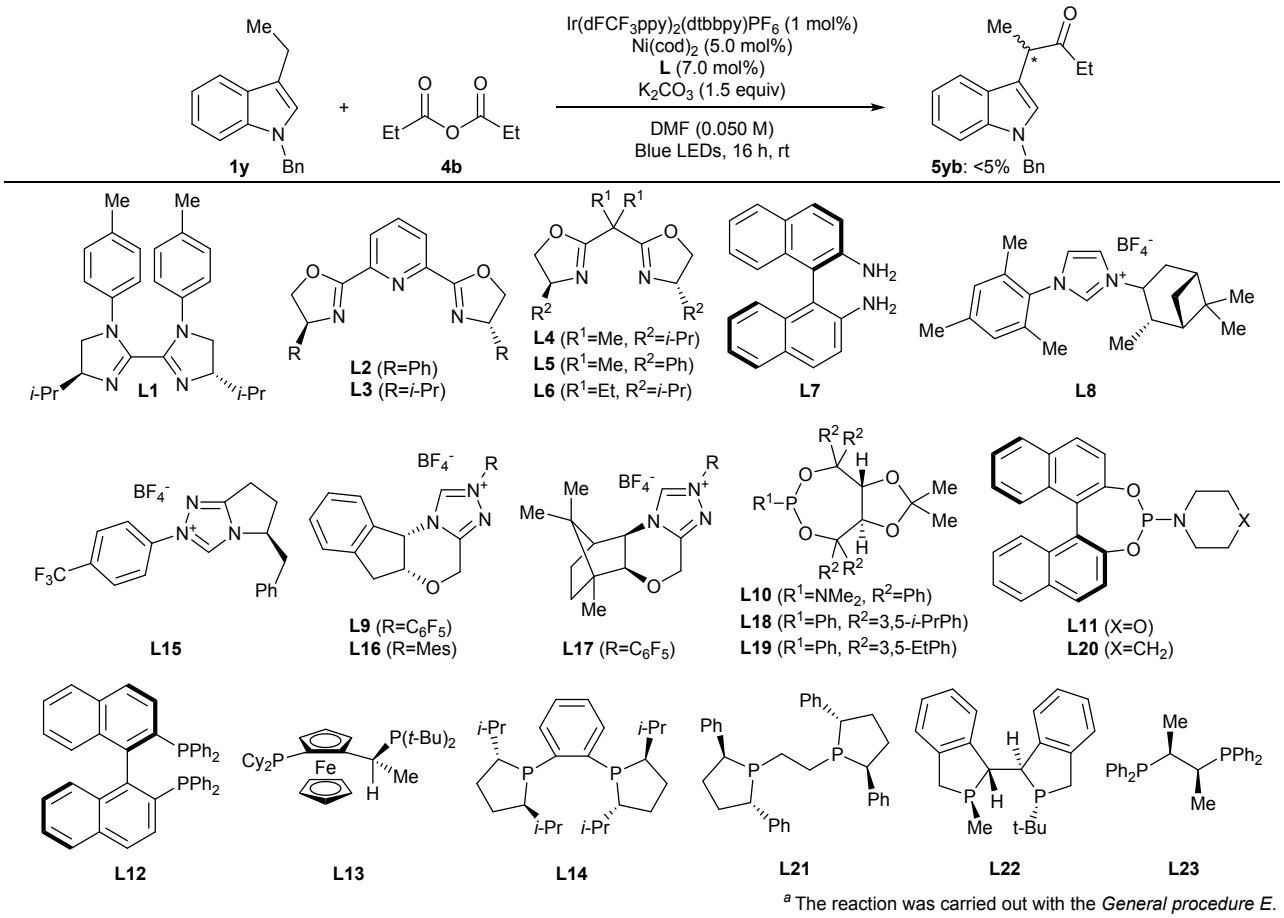
[a] The reaction was carried out with the *General procedure E*.

Table S3. Attempted enantioselective arylation with chiral ligands.



All reactions performed in the presence of a chiral ligand did not show the required level of reactivity in the first place. Hence, the enantioselective benzylic functionalization has been excluded from the scope of the current study.

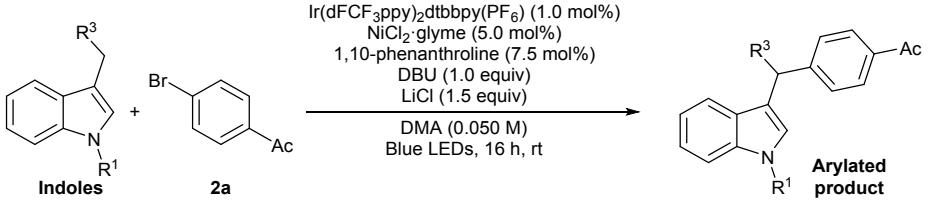
Table S4. Attempted enantioselective acylation with chiral ligands.



[a] The reaction was carried out with the *General procedure E*.

All reactions performed in the presence of a chiral ligand did not show the required level of reactivity in the first place. Hence, the enantioselective benzylic functionalization has been excluded from the scope of the current study.

Table S5. Unsuccessful substrates for the arylation reaction.



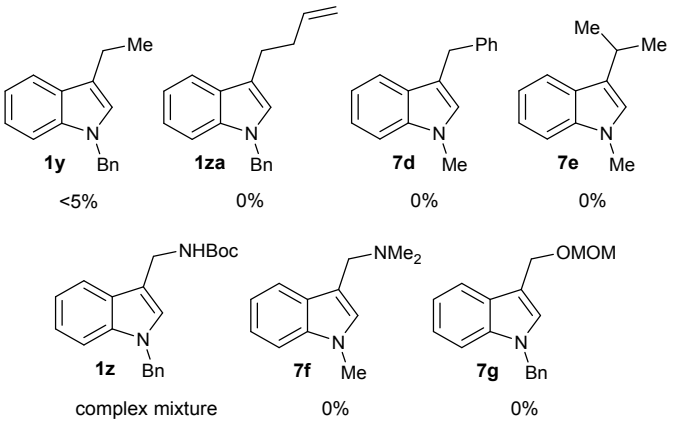
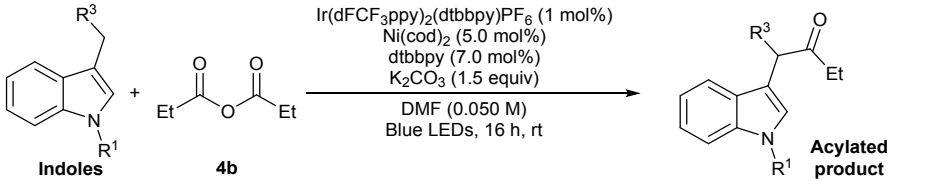
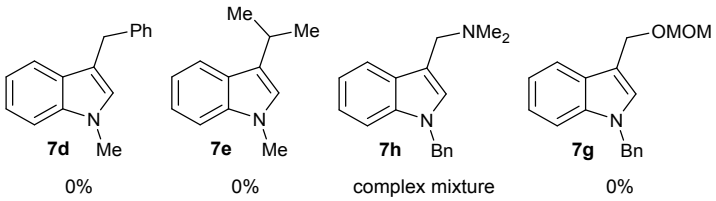
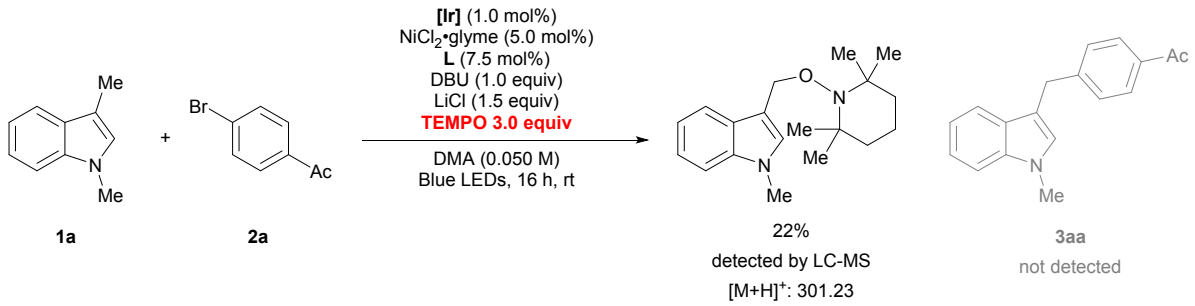


Table S6. Unsuccessful substrates for the acylation reaction.





6. Radical Trapping Experiments



The reaction was set up in a nitrogen-filled glove box. To a 8 mL vial equipped with a PTFE-coated stirrer bar were added the corresponding indole **1a** (0.30 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.0020 mmol, 1.0 mol%), $NiCl_2$·glyme (2.2 mg, 0.010 mmol, 5.0 mol%), 1,10-phenanthroline (2.7 mg, 0.015 mmol, 7.5 mol%), DBU (30 µL, 0.20 mmol, 1.0 equiv), LiCl (12.7 mg, 0.30 mmol, 1.5 equiv), aryl halide **2a** (0.20 mmol, 1.0 equiv), (2,2,6,6-tetramethylpiperidine-1-yl)oxy (93.7 mg, 0.60 mmol, 3.0 equiv) and DMA (4.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was analyzed by ^1H NMR relative to 1,1,2,2-tetrachloroethane(10 µL, 0.094 mmol) as an external standard to determine the existence of product **3aa**.[30]

In the LC-MS analysis, product **3aa** was not detected and the TEMPO-indole adduct was detected. This indicates that the reaction indeed proceeds through a radical pathway and indole radical is generated during the reaction. Figure S2 depicts the selective ion chromatogram with peaks showing molecular weight values of 301.23. The peak eluted at 13.120 min was determined to be the TEMPO-indole adduct. The mass spectrum is shown in Figure S2.

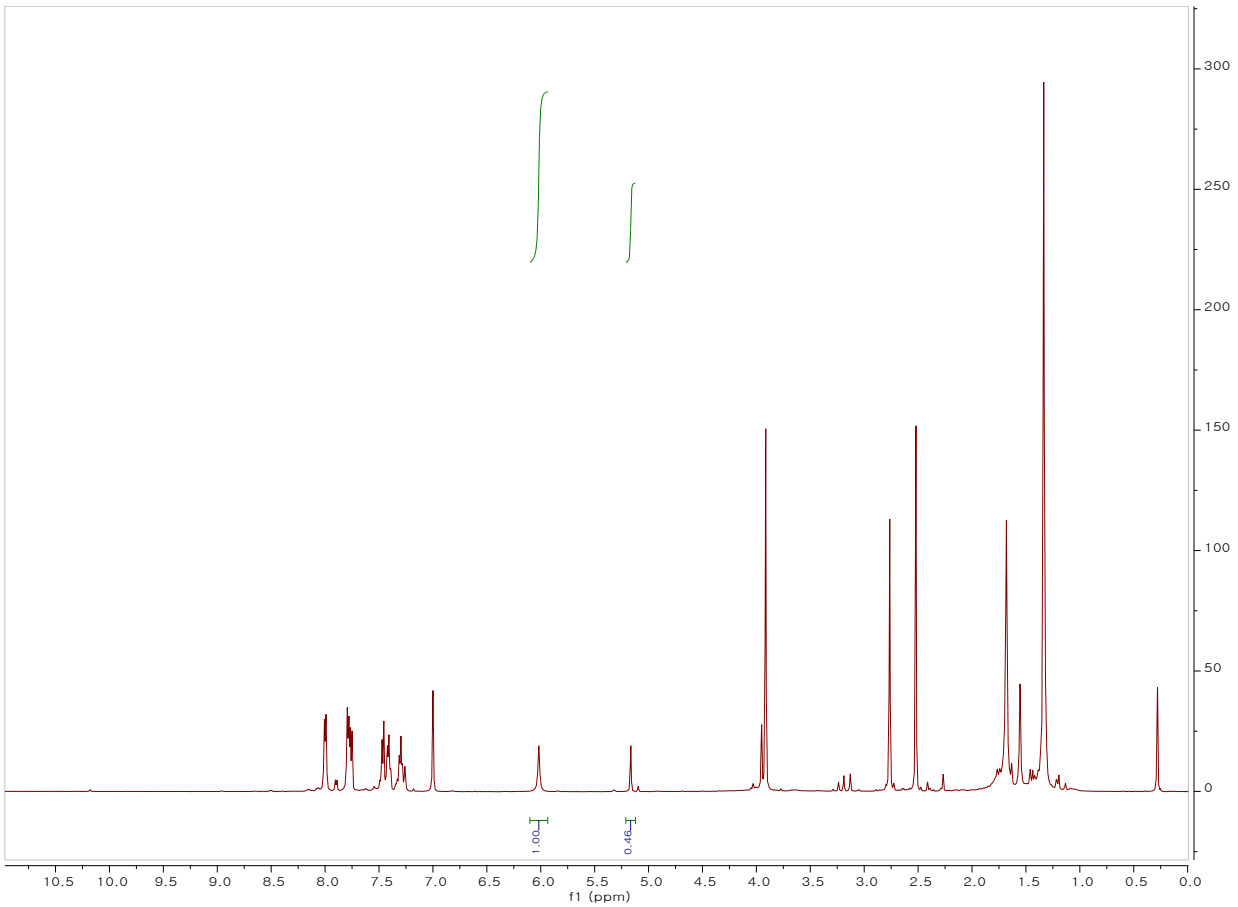


Figure S1. ^{1}H-NMR spectrum of the crude reaction mixture.

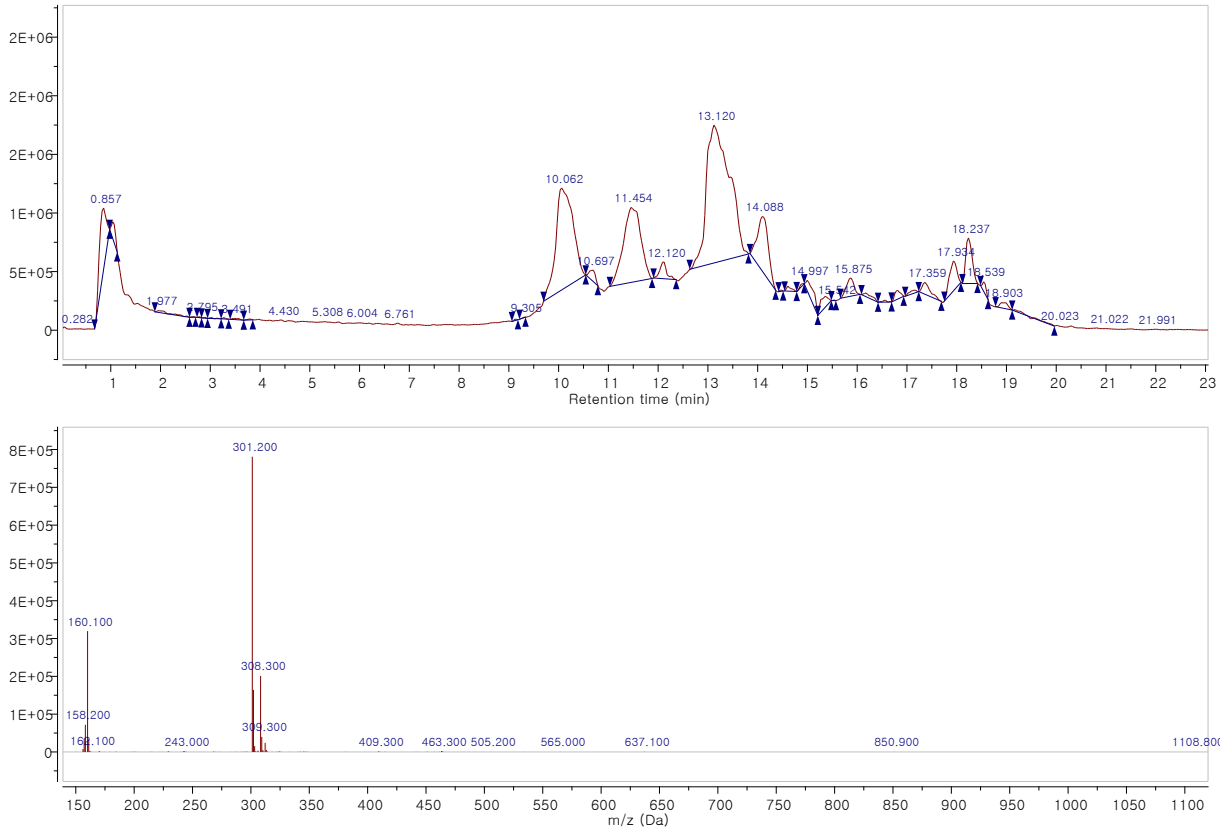
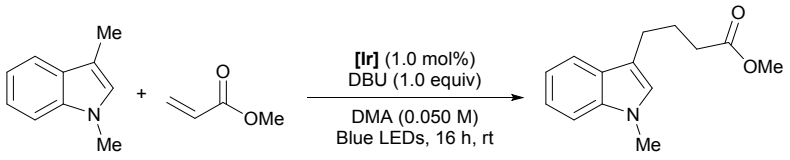


Figure S2. LC-MS spectrum of the crude mixture showing ions of mass 301.2.

7. Control Experiments to Exclude the HAT Process (Scheme 3)

Giese addition with LiCl

For the experiments shown in Scheme 3a, the following procedure was employed.

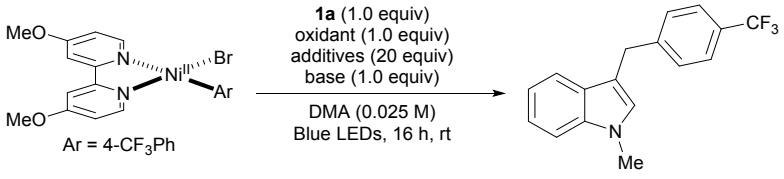


The reaction was set up in a nitrogen-filled glove box. To a 4 mL vial equipped with a PTFE-coated stirring bar were added the corresponding indole **1a** (14.6 mg, 0.10 mmol, 1.0 equiv), methyl acrylate (10.8 µL, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.1 mg, 0.0010 mmol, 1.0 mol%), DBU (15 µL, 0.10 mmol, 1.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1.5 equiv), and DMF (2.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was analyzed by ^1H NMR relative to 1,1,2,2-tetrachloroethane as an external standard.

Stoichiometric experiment with **[Ni]-1**

The oxidative addition complex **[Ni]-1** was prepared following the literature procedure.[22] For the experiments shown in Scheme 3b, the following procedure was employed.

Table S7. Stoichiometric experiment result of nickel complex [Ni]-1 with various oxidants and additives.



[Ni]-1 **3ad**: N.D.

entry	oxidant	additives	base	result
1	$(TBPA)SbCl_6$	-	-	N.D.
2	$(TBPA)SbCl_6$ (dark)	-	-	N.D.
3	$(TBPA)SbCl_6$	LiCl	-	N.D.
4	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	-	-	N.D.
5	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiCl	-	N.D.
6	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiCl	DBU	N.D.

The reaction was set up in a nitrogen-filled glove box. To a 4 mL vial equipped with a PTFE-coated stirring bar were added the corresponding **[Ni]-1** (25 mg, 0.050 mmol, 1.0 equiv), indole **1a** (7.3 mg, 0.050 mmol, 1.0 equiv), oxidant (0.050 mmol, 1.0 equiv), LiCl (42.39 mg, 1.0 mmol, 20 equiv), DBU (7.5 µL, 0.050 mmol, 1.0 equiv), and DMF (2.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was analyzed by ^1H NMR relative to 1,1,2,2-tetrachloroethane as an external standard.

8. Fluorescence Quenching Experiment (Stern-Volmer Relationship)

Fluoresence quenching experiment was conducted with 25 μM $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in DMA. Various substrates were used as quenchers (see below in more detail). Samples were excited at 400 nm and peak emissions were recorded at 500 nm to construct the Stern-Volmer regression.

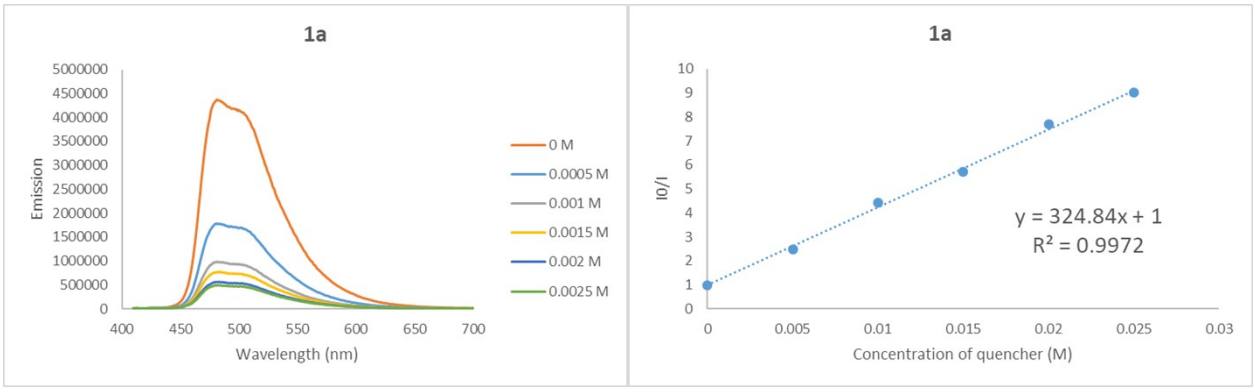


Figure S3. Stern-Volmer quenching study with 1,3-dimethyl-1*H*-indole, **1a**.

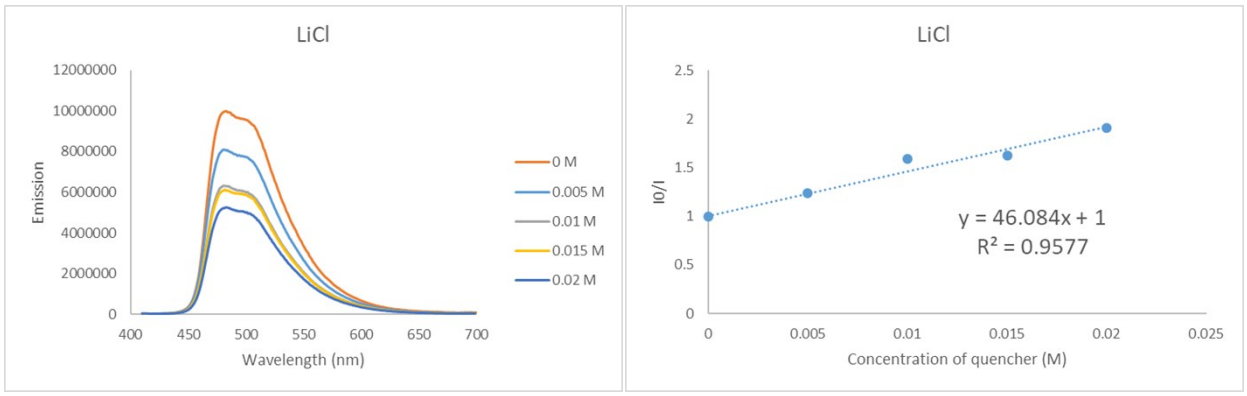


Figure S4. Stern-Volmer quenching study with LiCl.

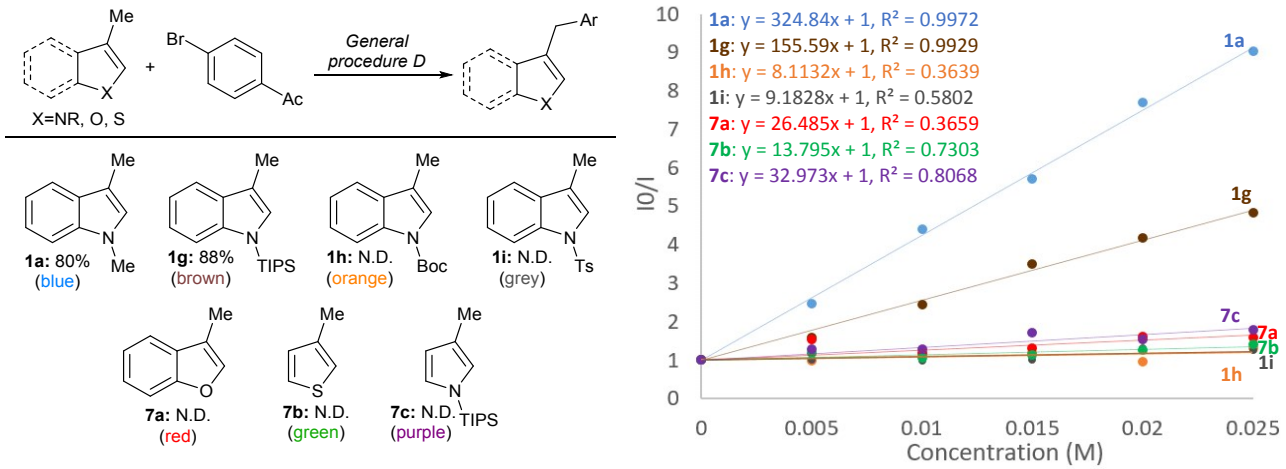


Figure S5. Stern-Volmer quenching studies with various indoles (**1a**, **1g**–**1i**) and other heterocyclic compounds (**7a**–**7c**).

9. Electrochemical Characterizations

The electrochemical properties of the substrates and photocatalyst were characterized by standard cyclic voltammetry (CV) techniques. The samples were dissolved in Ar-saturated CH_3CN (10 mL) to a concentration of 10.0 mM of photocatalyst and 5.0 mM of other substrates. The solution contained 0.10 M $TBAPF_6$ supporting electrolyte. A three-electrode cell assembly consisting of a glassy carbon (GC) working electrode, a Pt coiled counter electrode, and Ag/AgCl pseudo reference electrode was employed for the voltammetric measurements.

9.1. Procedure for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

The cyclic voltammogram was acquired at a scan rate of 0.10 V s^{-1} and a scan range of –1.8 to 0.0 V. The excited-state reduction potential of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was calculated from the triplet state energy (2.57 eV) and ground-state redox reduction potential. The cyclic voltammograms indicates that a reversible reduction occurred at –1.32 V vs. Ag/AgCl. As a result, the excited-state reduction potential of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ is +1.24 V vs. Ag/AgCl.

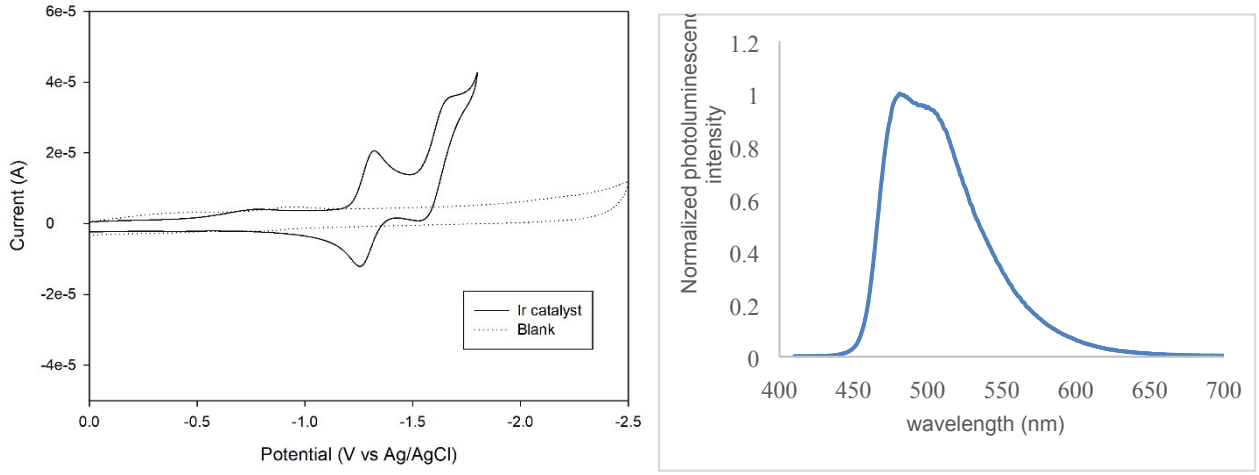


Figure S6. Left, cyclic voltammograms (grey line) of 10.0 mM of **[Ir]** obtained in Ar-saturated CH_3CN. The dotted line is an electrochemical response of a blank CH_3CN solution. Right, the phosphorescence spectrum of **[Ir]**. The photoexcitation wavelength was 400 nm.

9.2. Procedure for 1,3-dimethyl-1*H*-indole (**1a**)

The cyclic voltammogram was acquired at a scan rate of 0.10 V s^{-1} and a scan range of 0.0 to +2.0 V. The cyclic voltammograms indicates that an irreversible oxidation occurred at +1.00 V vs. Ag/AgCl.

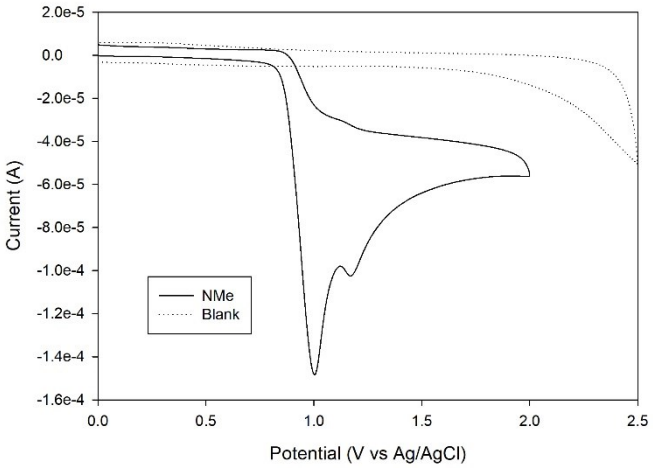


Figure S7. The cyclic voltammograms (grey line) of 5.0 mM of 1,3-dimethyl-1*H*-indole obtained in Ar-saturated CH_3CN. The dotted line is an electrochemical response of a blank CH_3CN solution.

9.3. Procedure for *tert*-butyl 3-methyl-1*H*-indole-1-carboxylate (**1h**)

The cyclic voltammogram was acquired at a scan rate of 0.10 V s^{-1} and a scan range of 0.0 to +2.0 V. The cyclic voltammograms indicates that an irreversible oxidation occurred at +1.49 V vs. Ag/AgCl.

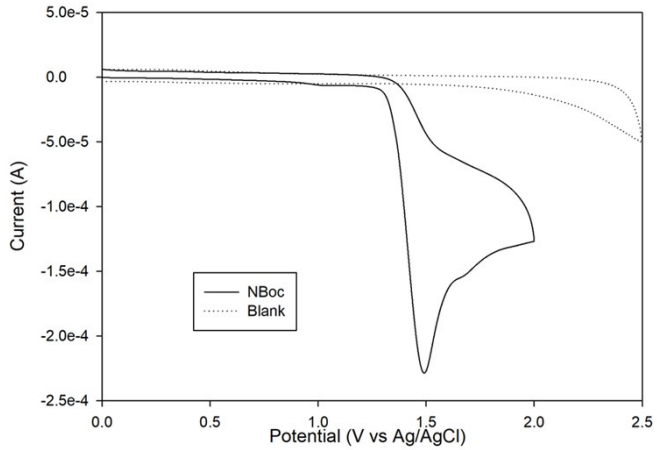


Figure S8. The cyclic voltammograms (grey line) of 5.0 mM of *tert*-butyl 3-methyl-1*H*-indole-1-carboxylate obtained in Ar-saturated CH_3CN. The dotted line is an electrochemical response of a blank CH_3CN solution.

9.4. Procedure for lithium chloride (LiCl)

The cyclic voltammogram was acquired at a scan rate of 0.10 V s^{-1} and a scan range of 0.0 to +2.5 V. The cyclic voltammograms indicates that an irreversible oxidation occurred at +1.31 V vs. Ag/AgCl.

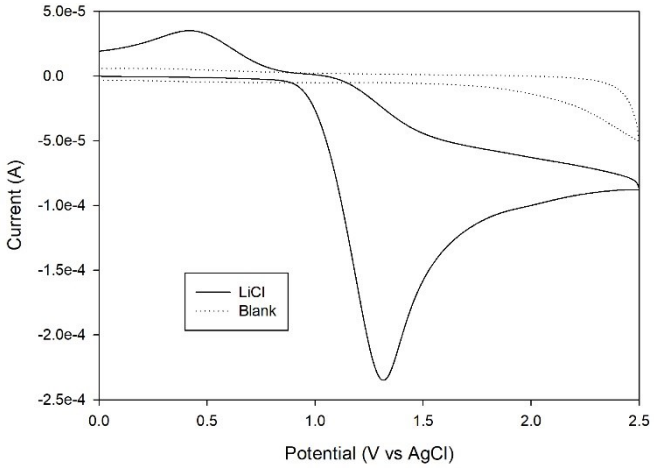


Figure S9. The cyclic voltammograms (grey line) of 5.0 mM of lithium chloride obtained in Ar-saturated CH_3CN. The dotted line is an electrochemical response of a blank CH_3CN solution.

9.5. Procedure for 3-methyl-1-(triisopropylsilyl)-1*H*-pyrrole (**7c**)

The cyclic voltammogram was acquired at a scan rate of 0.10 V s^{-1} and a scan range of 0.0 to +2.0 V. The cyclic voltammograms indicates that an irreversible oxidation occurred at +1.32 V vs. Ag/AgCl.

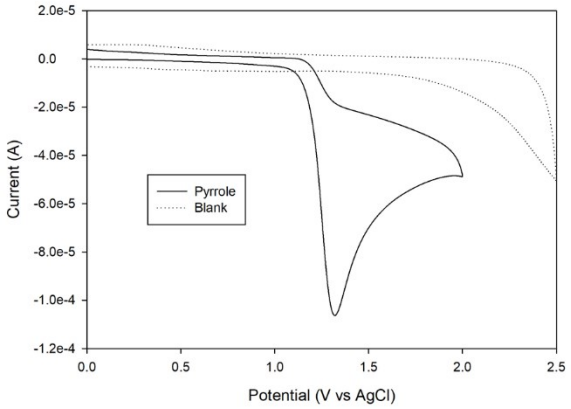
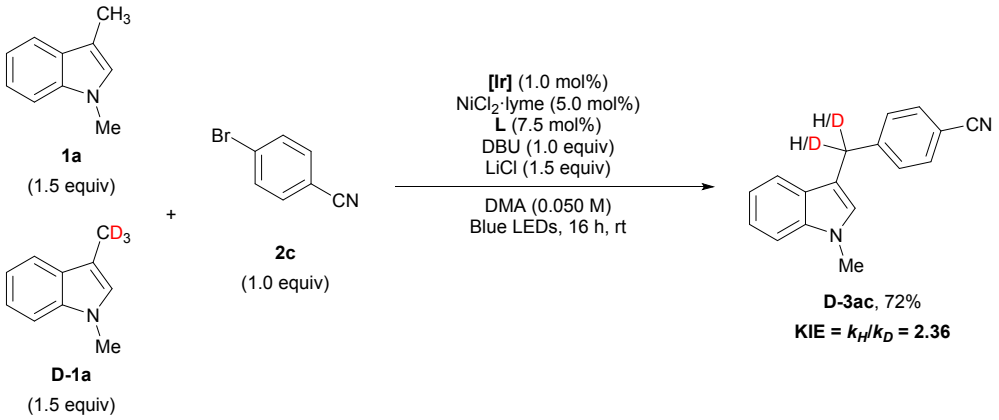


Figure S10. The cyclic voltammograms (grey line) of 5.0 mM of 3-methyl-1-(triisopropylsilyl)-1*H*-pyrrole obtained in Ar-saturated CH_3CN. The dotted line is an electrochemical response of a blank CH_3CN solution.

10. Kinetic Isotope Effect (KIE) Experiment



The reaction was set up in a nitrogen-filled glove box. To a 8 mL vial equipped with a PTFE-coated stirrer bar were added the corresponding indole **1a** (0.30 mmol, 1.5 equiv) deutrated indole **D-1a** (0.30 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (2.2 mg, 0.0020 mmol, 1.0 mol%), $NiCl_2$·glyme (2.2 mg, 0.010 mmol, 5.0 mol%), 1,10-phenanthroline (2.7 mg, 0.015 mmol, 7.5 mol%), DBU (30 µL, 0.20 mmol, 1.0 equiv), LiCl (12.7 mg, 0.30 mmol, 1.5 equiv) the corresponding aryl halide **2c** (0.20 mmol, 1.0 equiv), and DMA (4.0 mL). The reaction vial was removed from the glove box, set to stir for 16 h under 34 W blue LED irradiation with fan cooling. At the end of the reaction, the resulting solution was transferred to a separatory funnel and partitioned between water (7 mL) and Et_2O (20 mL). The organic extract was washed with water (7 mL x 2) and brine (7 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography purification led to the 72% of the combined arylated products. The KIE value was k_H/k_D=2.36 determined by ^{1}H NMR spectrum (Figure S11).

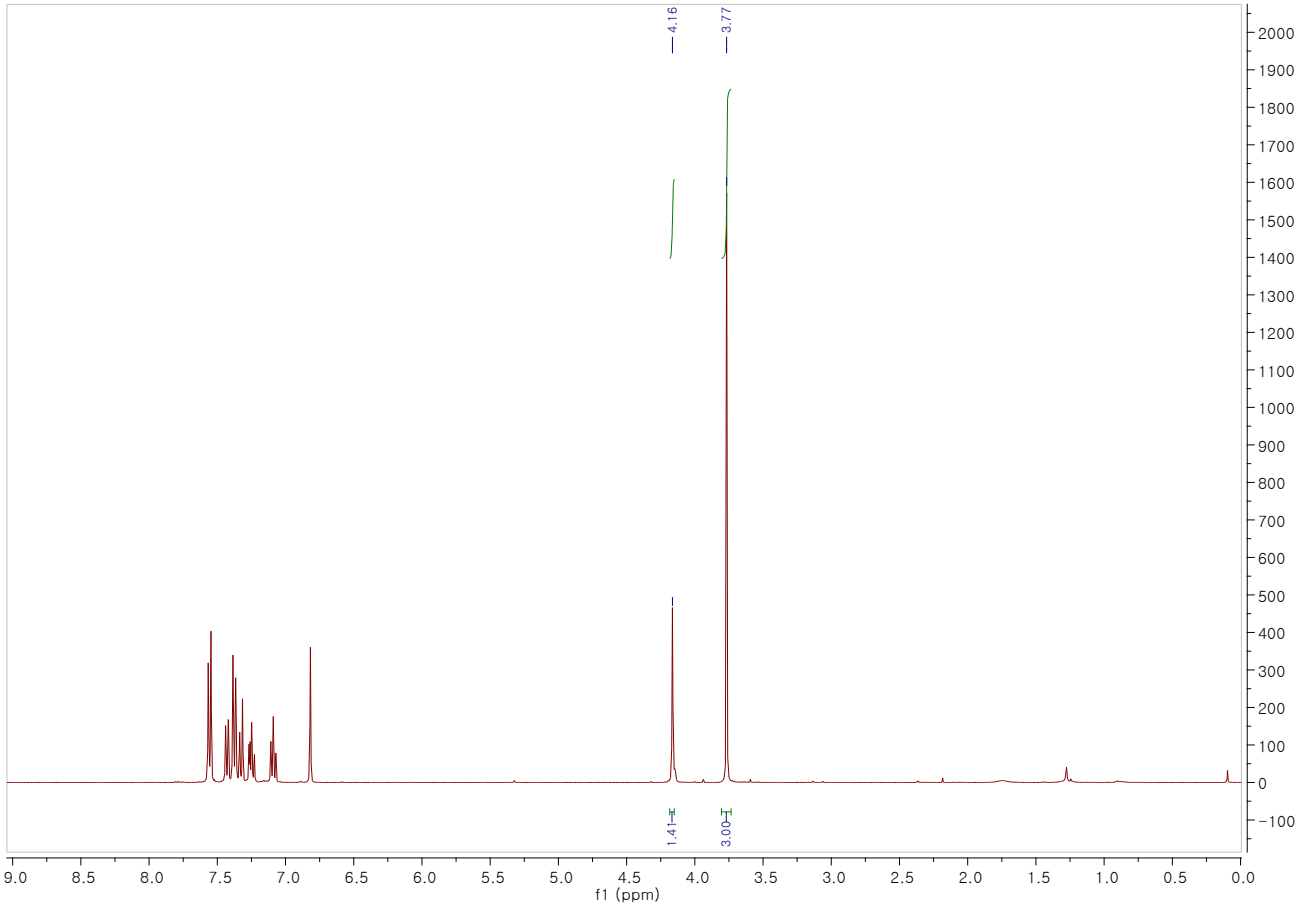


Figure S11. ^{1}H-NMR spectrum of KIE experiment, **D-3ac**.

11. References

1. M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712-5719.
2. D. M. Arias-Rotondo and J. K. McCusker, *Chem. Soc. Rev.*, 2016, **45**, 5803-5820.
3. R. B. Bedford, N. Fey, M. F. Haddow and R. F. Sankey, *Chem. Commun.*, 2011, **47**, 3649-3651.
4. T. Tomakinian, R. Guillot, C. Kouklovsky and G. Vincent, *Angew. Chem. Int. Ed.*, 2014, **53**, 11881-11885.
5. L. Wang, J. Zhou, T.-M. Ding, Z.-Q. Yan, S.-H. Hou, G.-D. Zhu and S.-Y. Zhang, *Org. Lett.*, 2019, **21**, 2795-2799.
6. Y.-M. Su, Y. Hou, F. Yin, Y.-M. Xu, Y. Li, X. Zheng and X.-S. Wang, *Org. Lett.*, 2014, **16**, 2958-2961.
7. M. Taddei, M. G. Mura, S. Rajamäki, L. D. Luca and A. Porcheddu, *Adv. Synth. Catal.*, 2013, **355**, 3002-3013.
8. D. Dhanak and C. B. Reese, *J. Chem. Soc., Perkin Trans. 1*, 1986, 2181-2186.
9. Y. Feng, D. Holte, J. Zoller, S. Umemiya, L. R. Simke and P. S. Baran, *J. Am. Chem. Soc.*, 2015, **137**, 10160-10163.
10. S. Rohrbach, R. S. Shah, T. Tuttle and J. A. Murphy, *Angew. Chem. Int. Ed.*, 2019, **58**, 11454-11458.
11. Qiang-Liu, Y.-X. Liu, H.-J. Song and Q.-M. Wang, *Adv. Synth. Catal.*, 2020, **362**, 3110-3115.
12. J. Ni, H. Wang and S. E. Reisman, *Tetrahedron*, 2013, **69**, 5622-5633.
13. L. M. Repka, J. Ni and S. E. Reisman, *J. Am. Chem. Soc.*, 2010, **132**, 14418-14420.
14. J. J. Newsome, E. Swann, M. Hassani, K. C. Bray, A. M. Z. Slawin, H. D. Beall and C. J. Moody, *Org. Biomol. Chem.*, 2007, **5**, 1629-1640.
15. M. Peña-López, H. Neumann and M. Beller, *Chem. Eur. J.*, 2014, **20**, 1818-1824.
16. X. Zeng, R. Kinjo, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, **49**, 942-945.
17. D. Zhang, T. Iwai and M. Sawamura, *Org. Lett.*, 2020, **22**, 5240-5245.
18. T. Mandal, G. Chakraborti and J. Dash, *Tetrahedron Lett.*, 2020, **61**, 152109.
19. B. E. Daniels, J. Ni and S. E. Reisman, *Angew. Chem. Int. Ed.*, 2016, **55**, 3398-3402.
20. A. J. Smith, A. Young, S. Rohrbach, E. F. O'Connor, M. Allison, H.-S. Wang, D. L. Poole, T. Tuttle and J. A. Murphy, *Angew. Chem. Int. Ed.*, 2017, **56**, 13747-13751.
21. C. L. Hansen, R. G. Ohm, L. B. Olsen, E. Ascic, D. Tanner and T. E. Nielsen, *Org. Lett.*, 2016, **18**, 5990-5993.
22. S.-Z. Sun and R. Martin, *Angew. Chem. Int. Ed.*, 2018, **57**, 3622-3625.
23. G. Goverdhan, A. R. Reddy, V. Himabindu and G. M. Reddy, *Synth. Commun.*, 2013, **43**, 498-504.
24. S. Laufer and F. Lehmann, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 1461-1464.
25. T. Utsumi, K. Noda, D. Kawauchi, H. Ueda and H. Tokuyama, *Adv. Synth. Catal.*, 2020, **362**, 3583-3588.
26. A. A. Martinez, B. A. Espinosa, R. N. Adamek, B. A. Thomas, J. Chau, E. Gonzalez, N. Keppetipola and N. T. Salzameda, *Eur. J. Med. Chem.*, 2018, **157**, 1202-1213.
27. X. Zhong, N. Chen and J. Xu, *New J. Chem.*, 2018, **42**, 13549-13557.
28. M. Géraldy, M. Morgen, P. Sehr, R. R. Steimbach, D. Moi, J. Ridinger, I. Oehme, O. Witt, M. Malz, M. S. Nogueira, O. Koch, N. Gunkel and A. K. Miller, *J. Med. Chem.*, 2019, **62**, 4426-4443.
29. A. Klinkebiel, O. Beyer, B. Malawko and U. Lüning, *Beilstein J. Org. Chem.*, 2016, **12**, 2267-2273.
30. L. Buzzetti, A. Prieto, S. R. Roy and P. Melchiorre, *Angew. Chem. Int. Ed.*, 2017, **56**, 15039-15043.

12. NMR spectra

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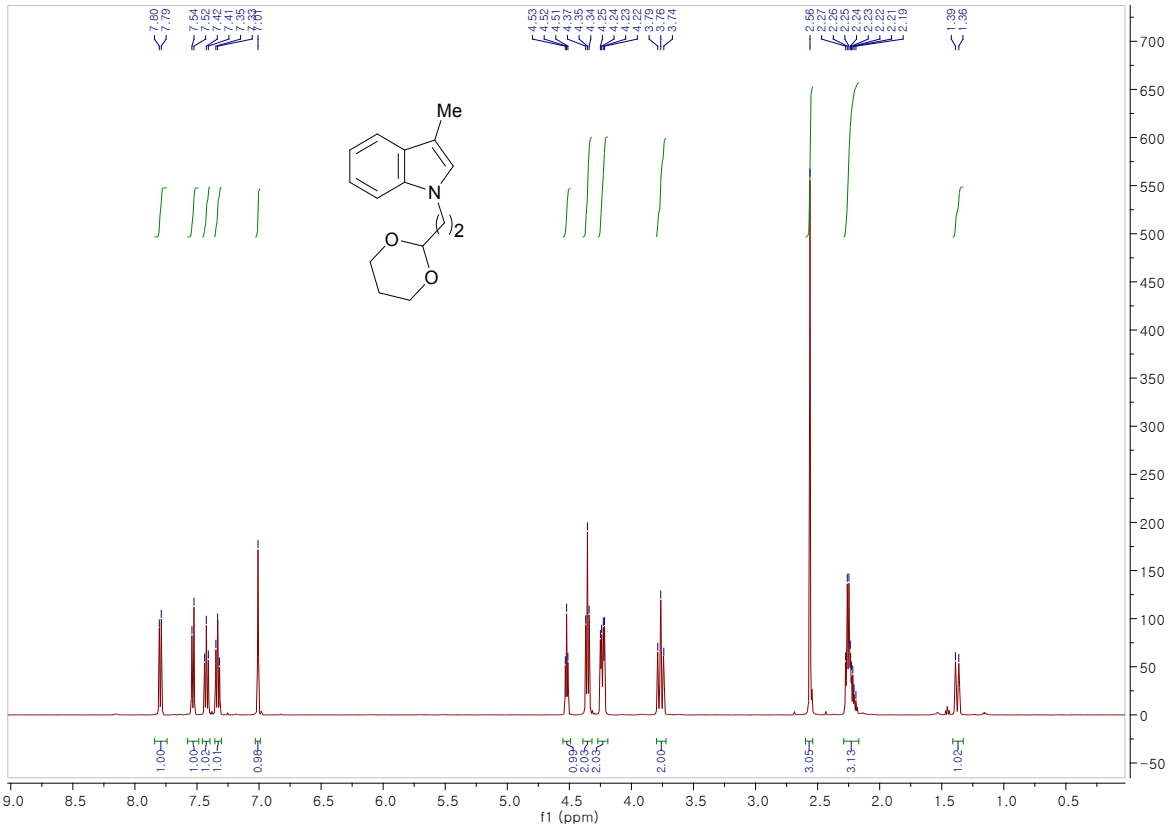

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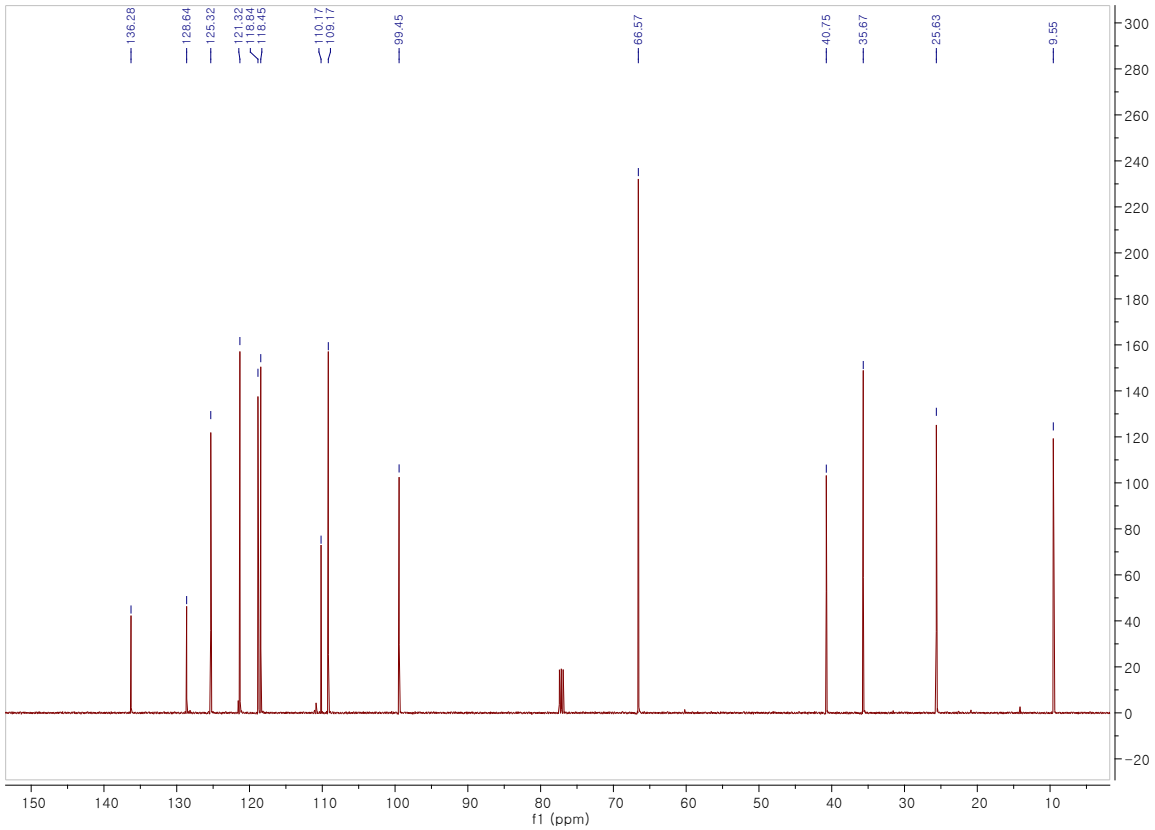

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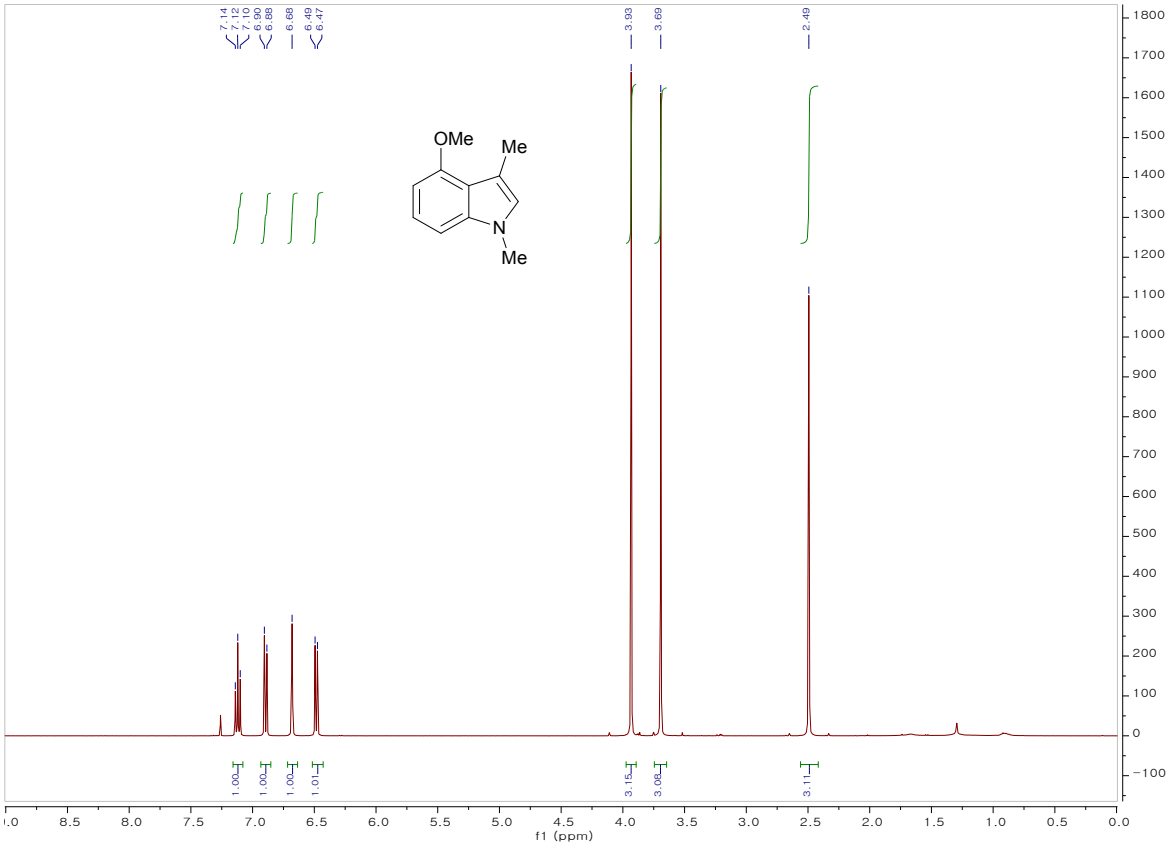

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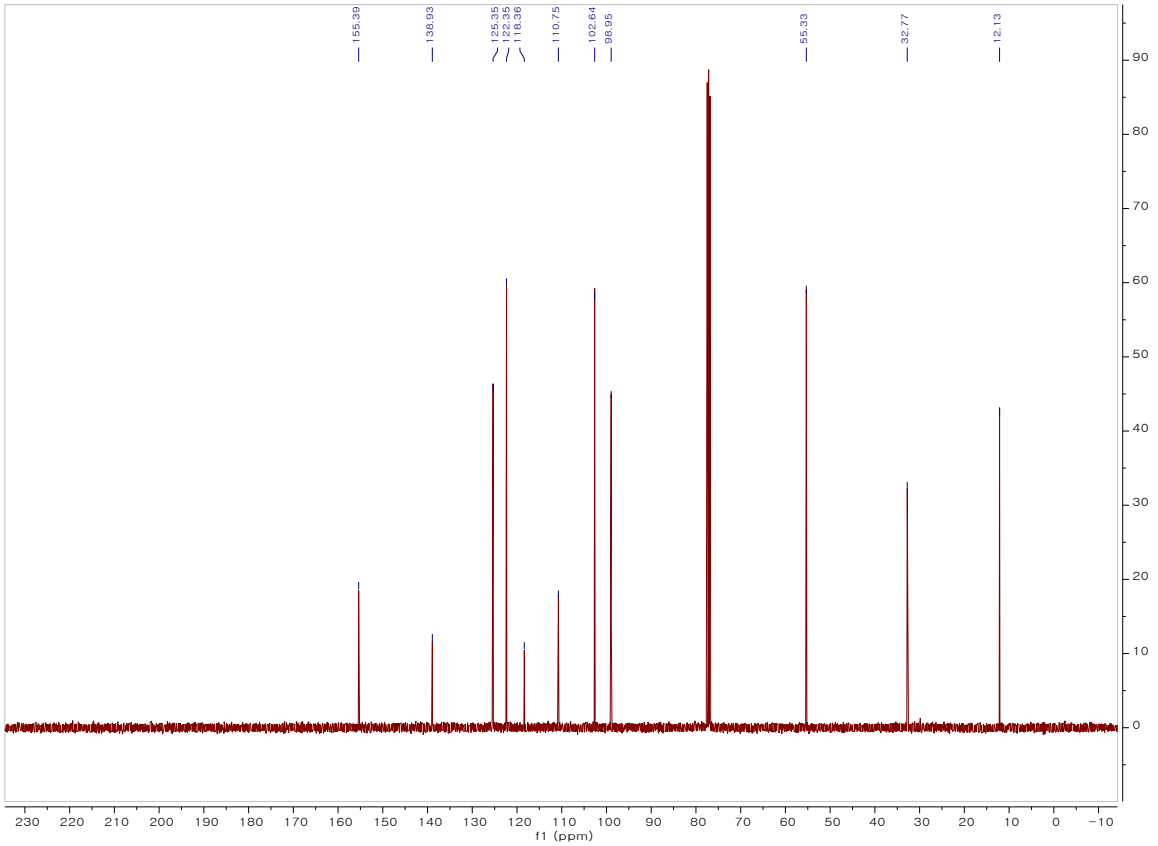

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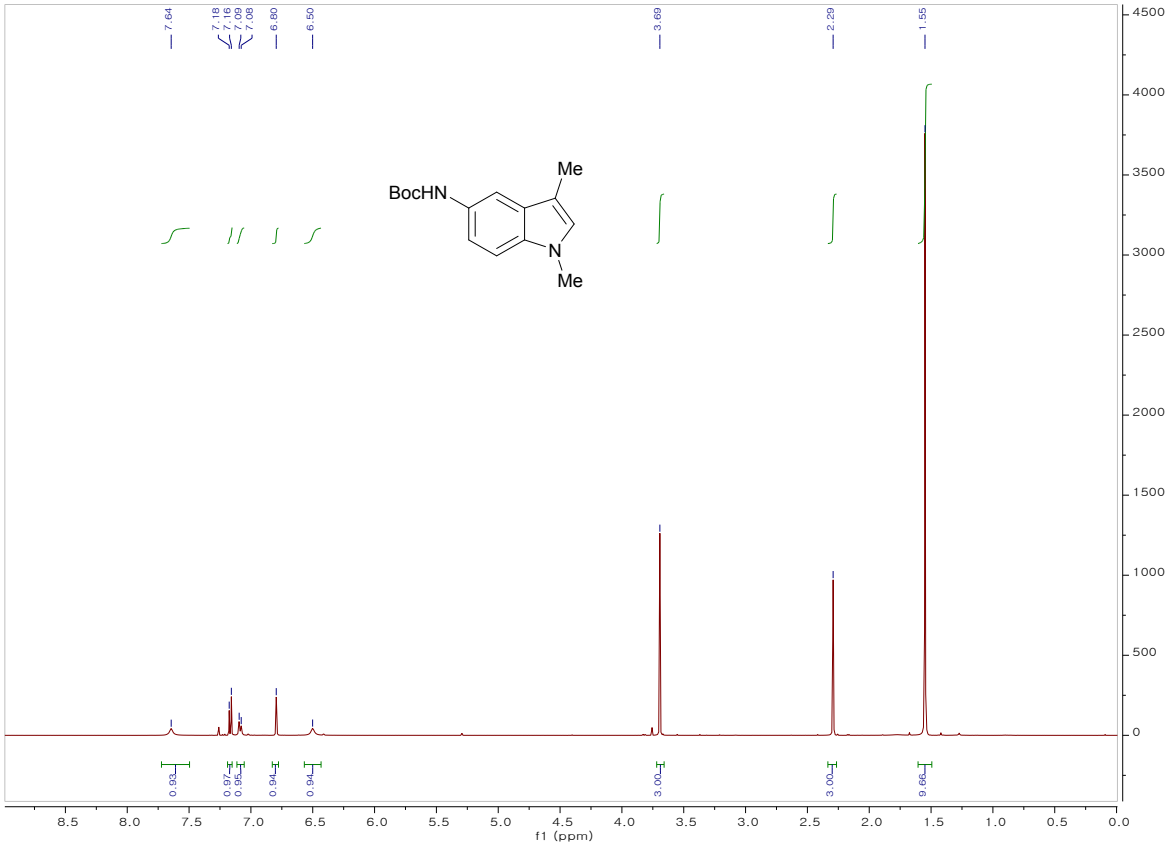

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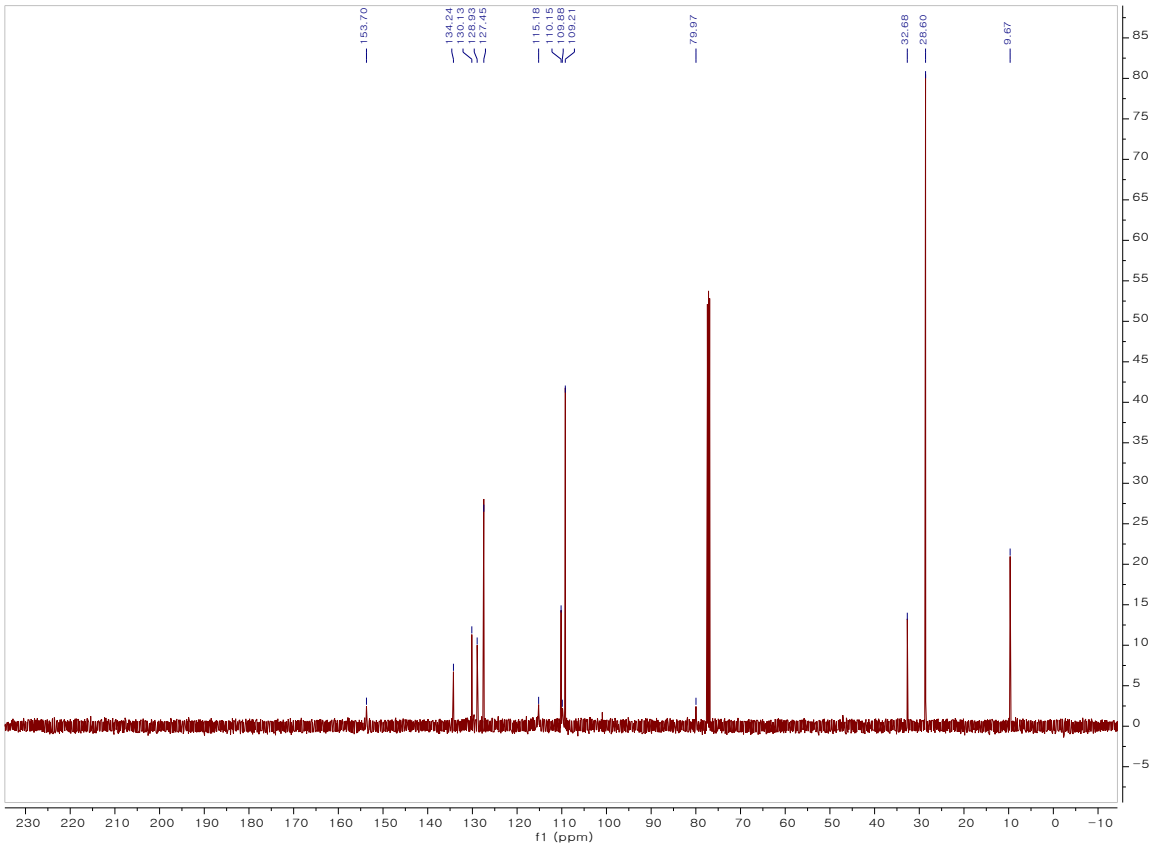

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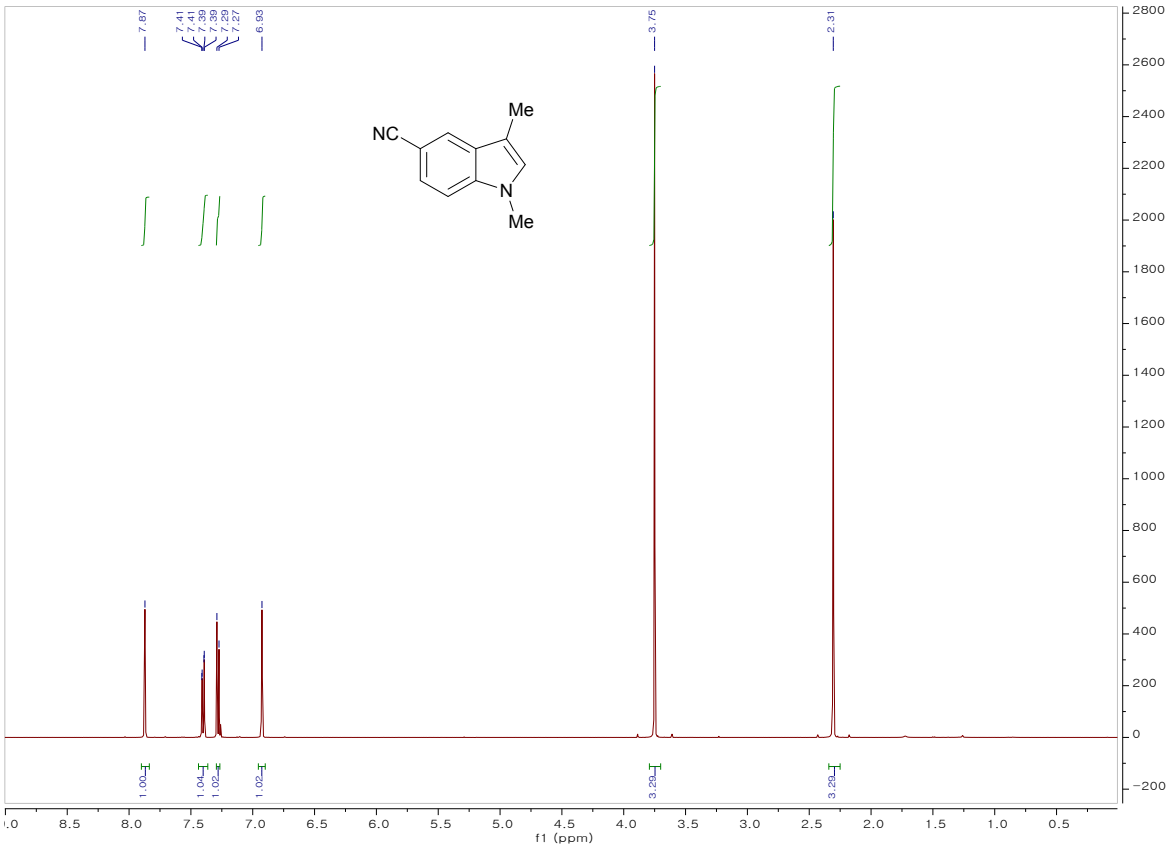

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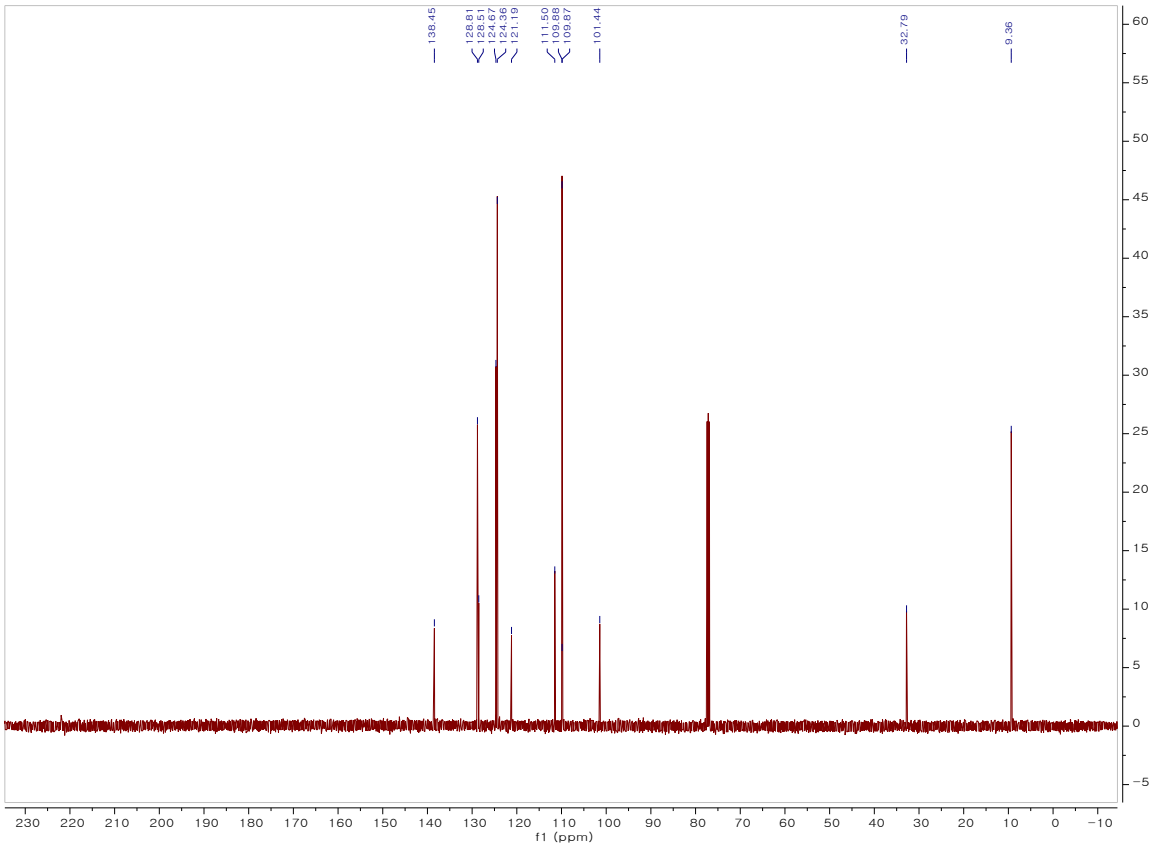

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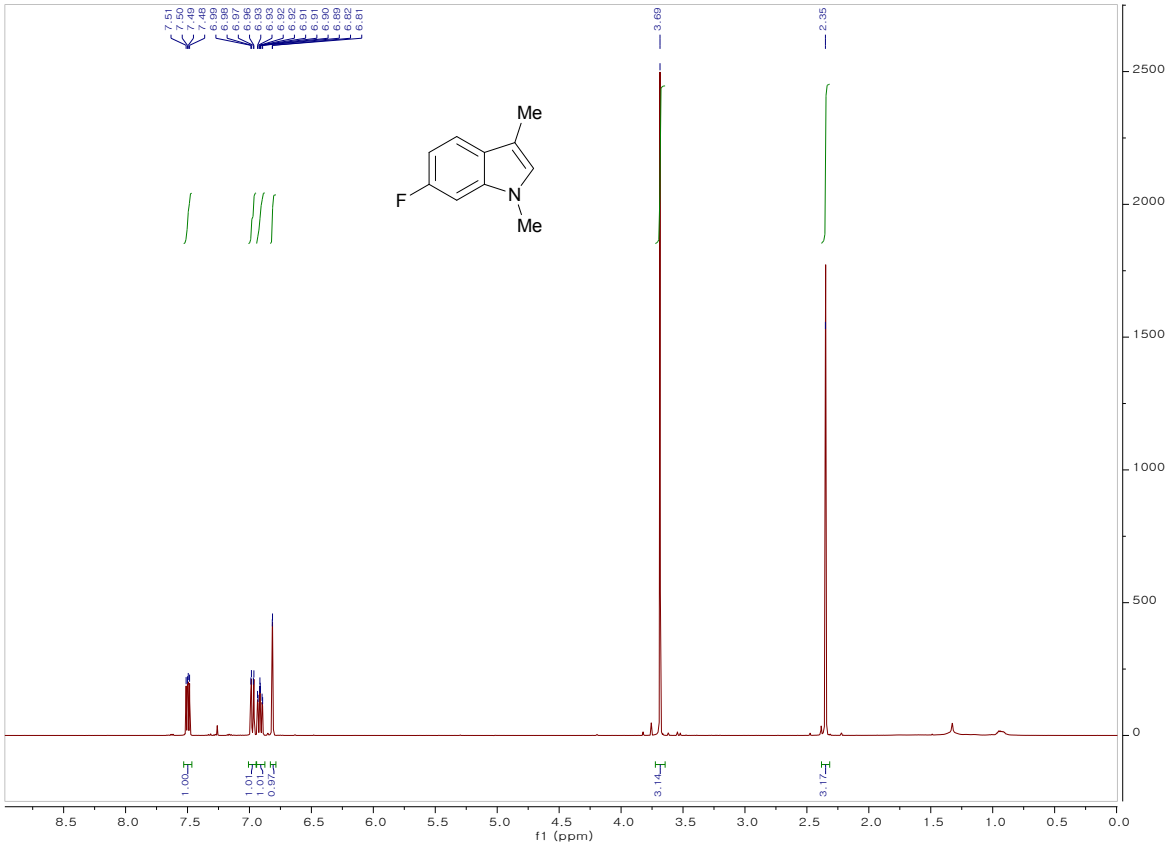

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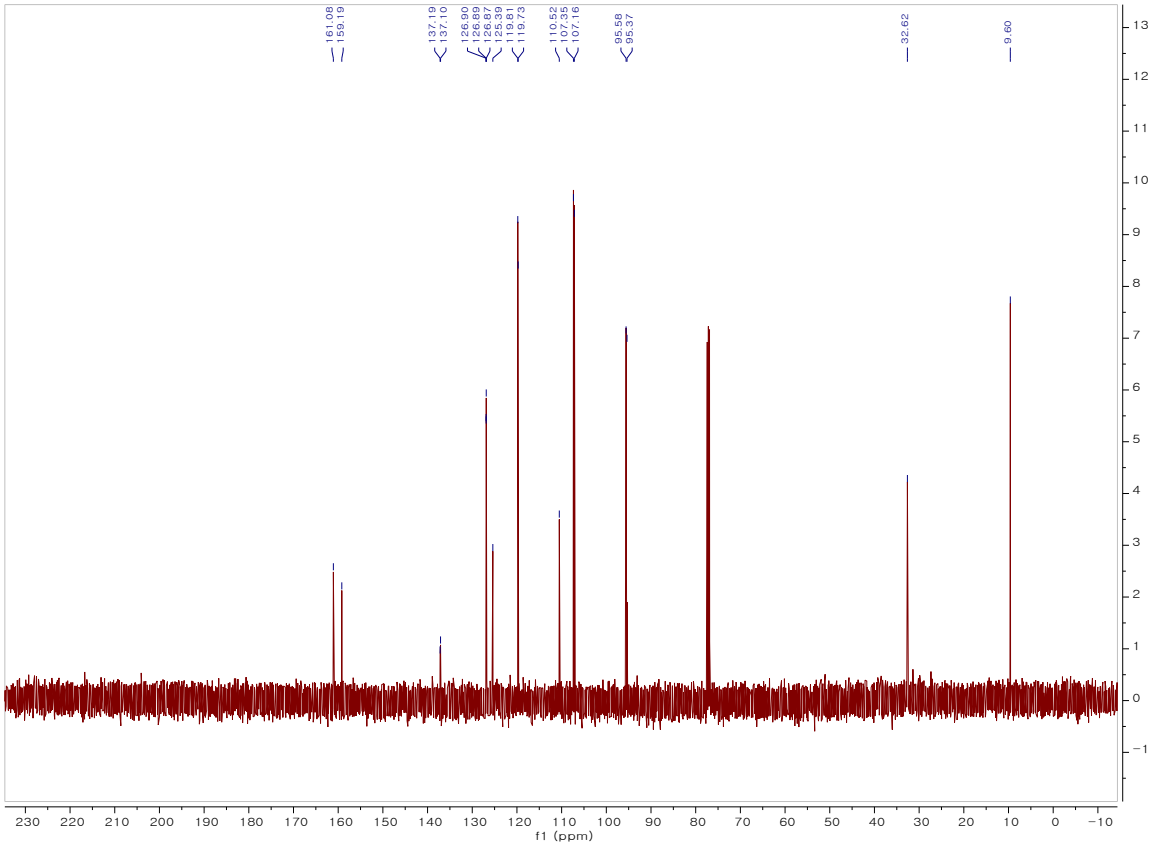

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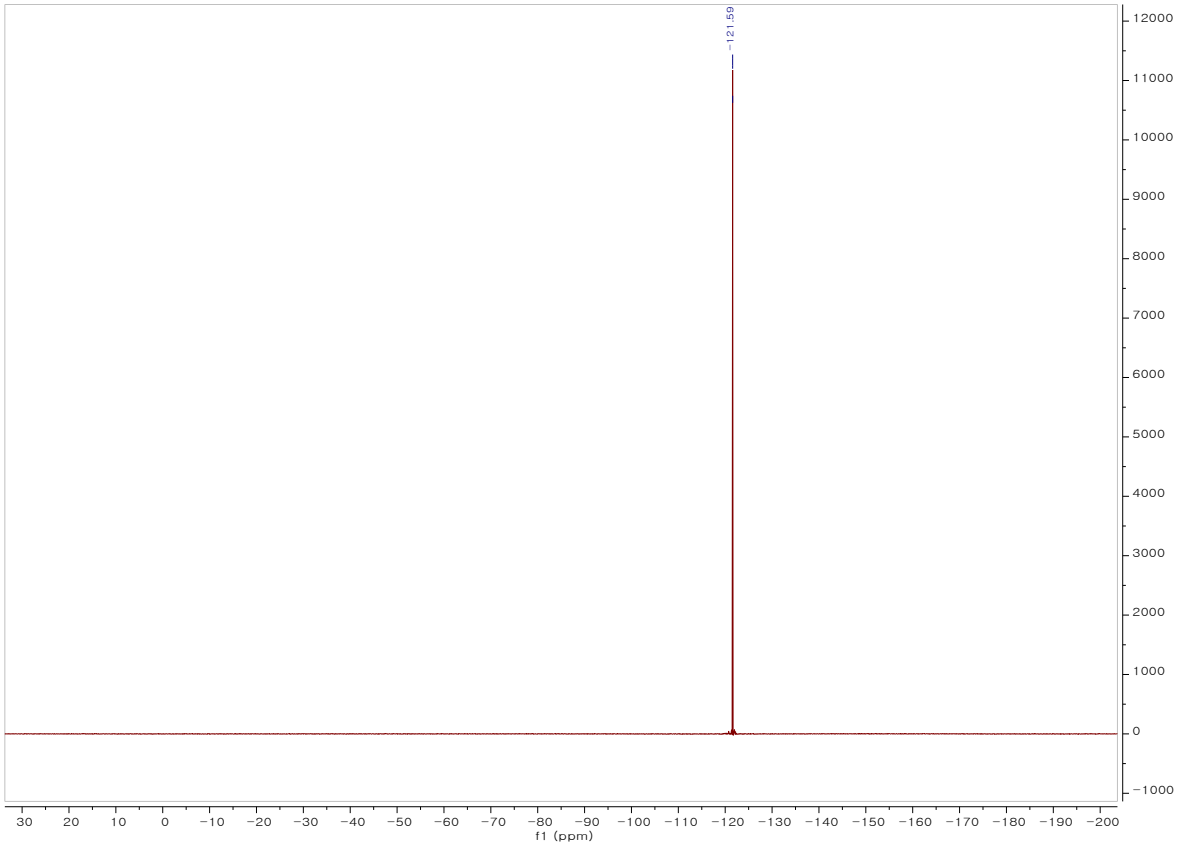
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f1 (ppm)

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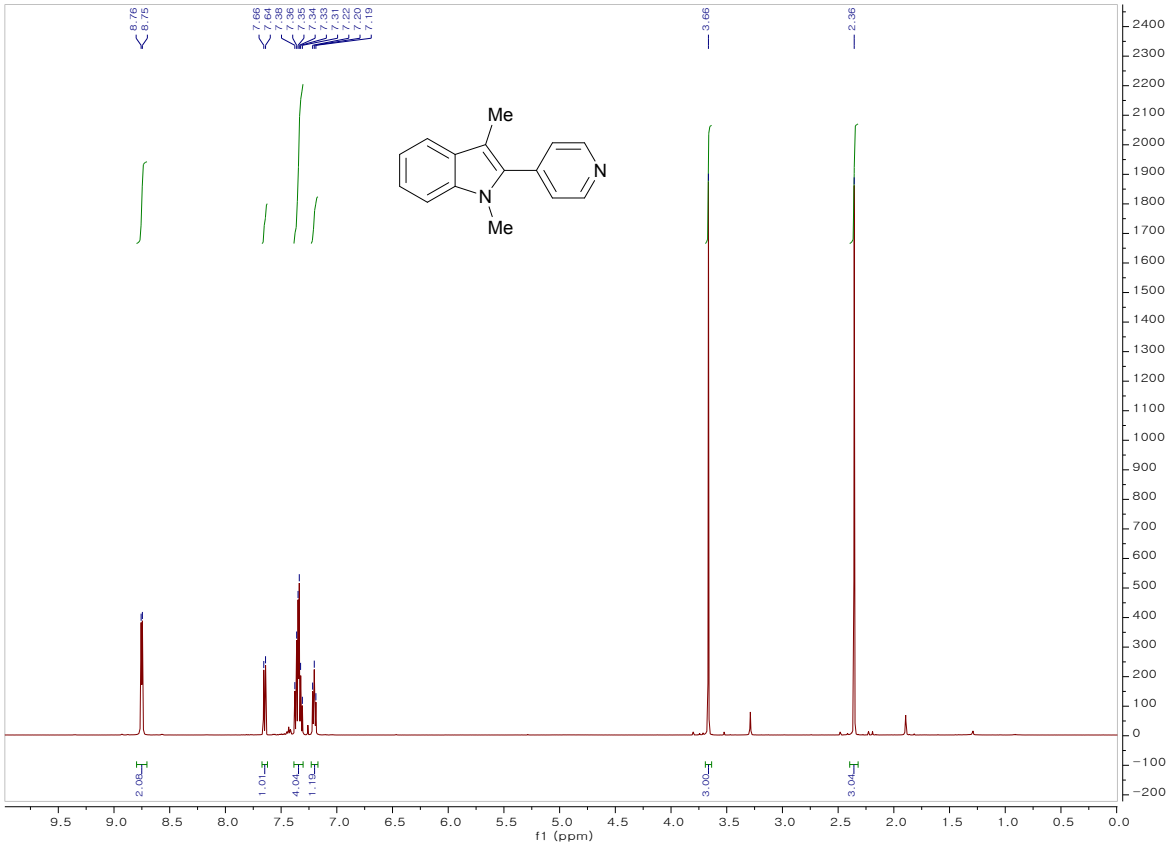

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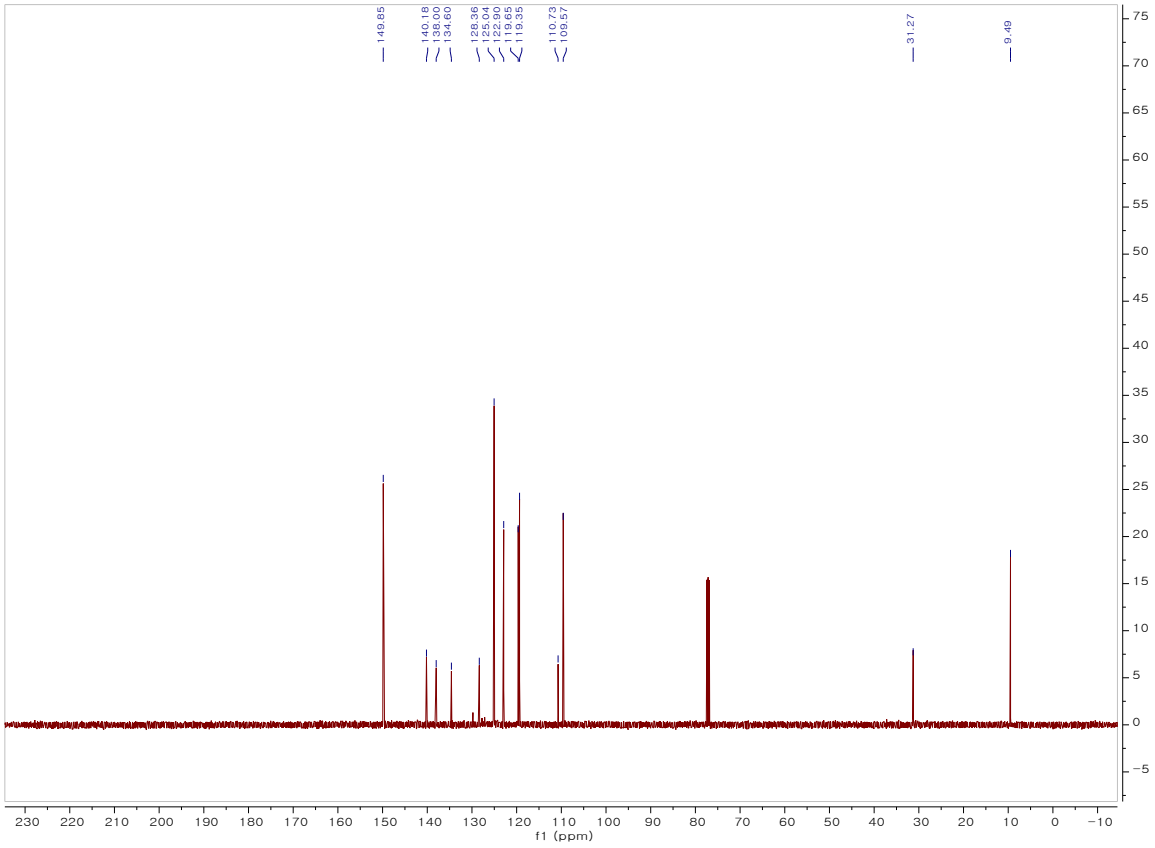

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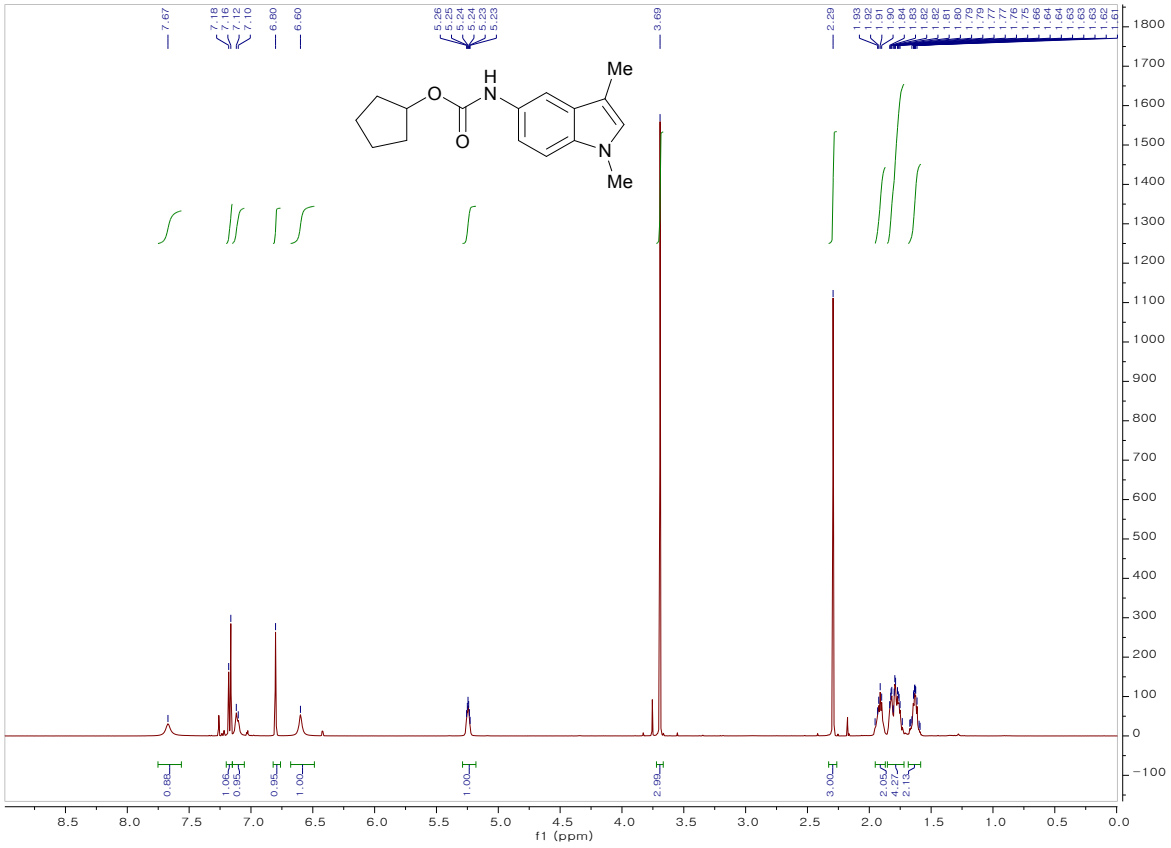

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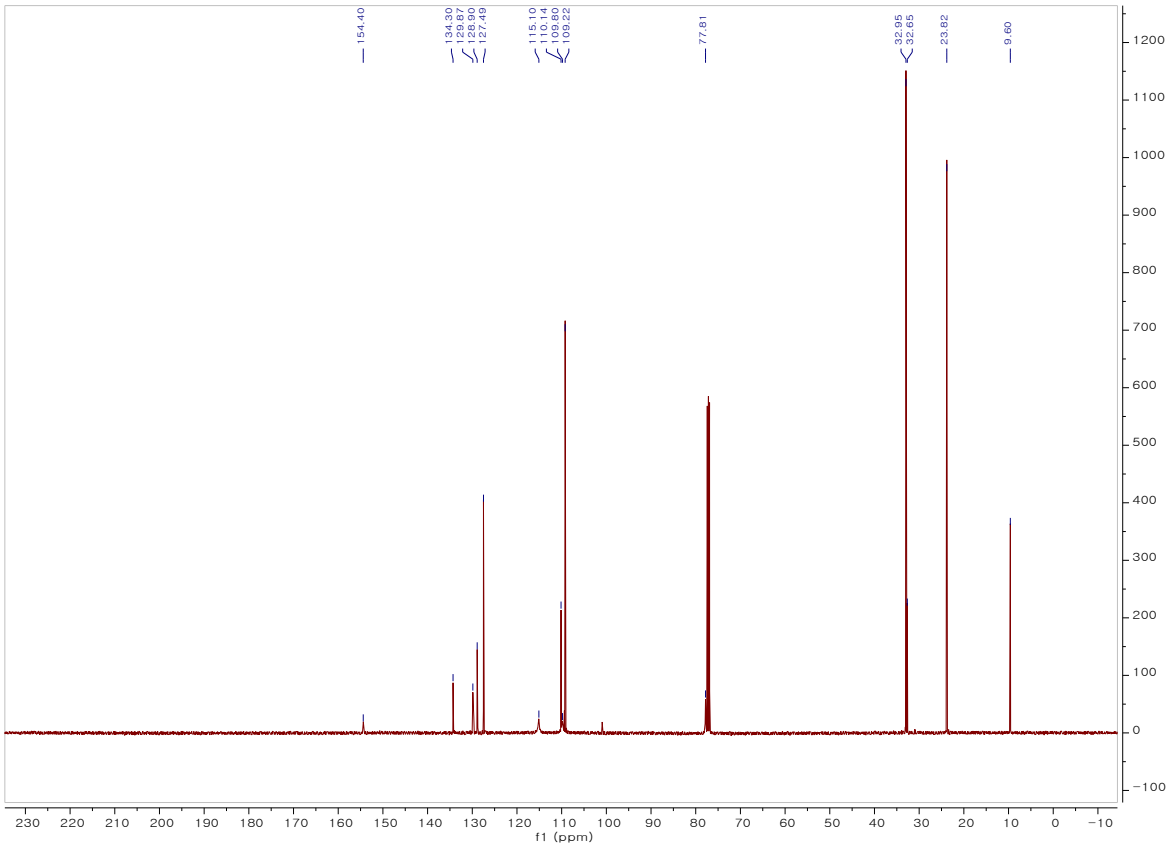

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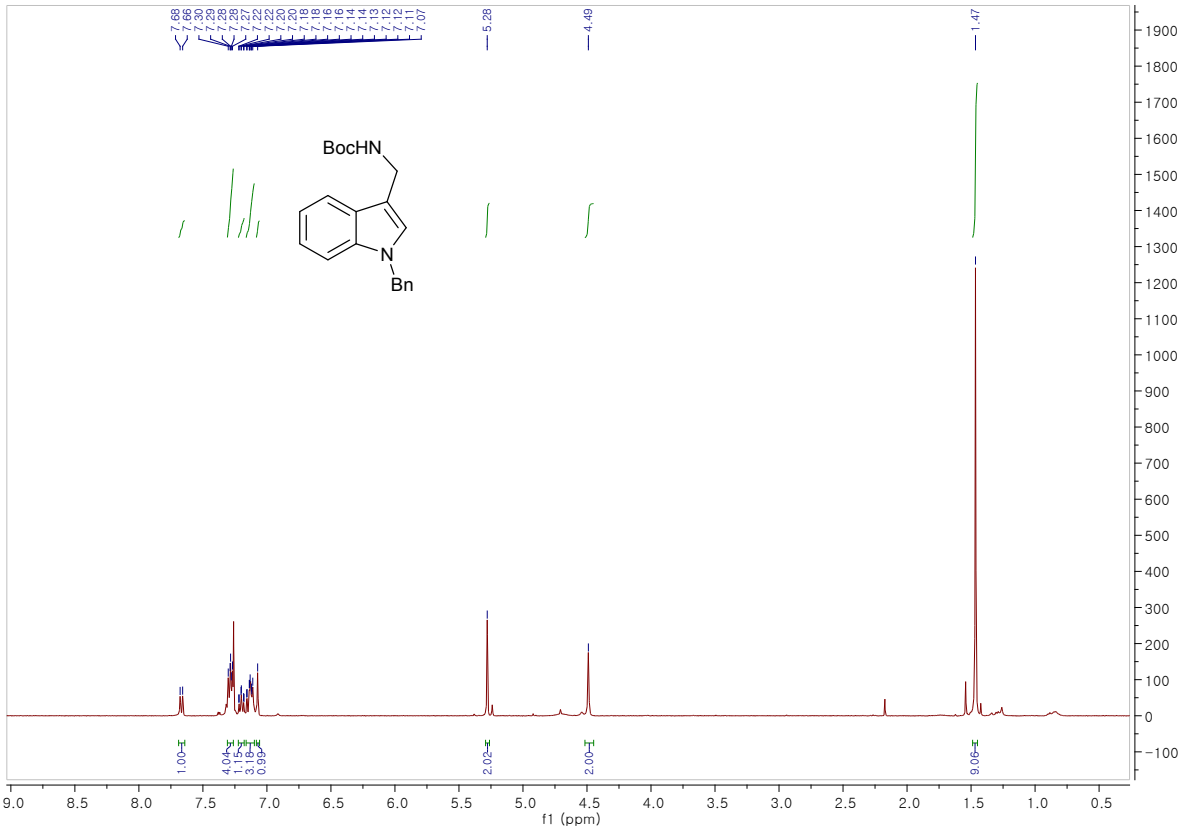

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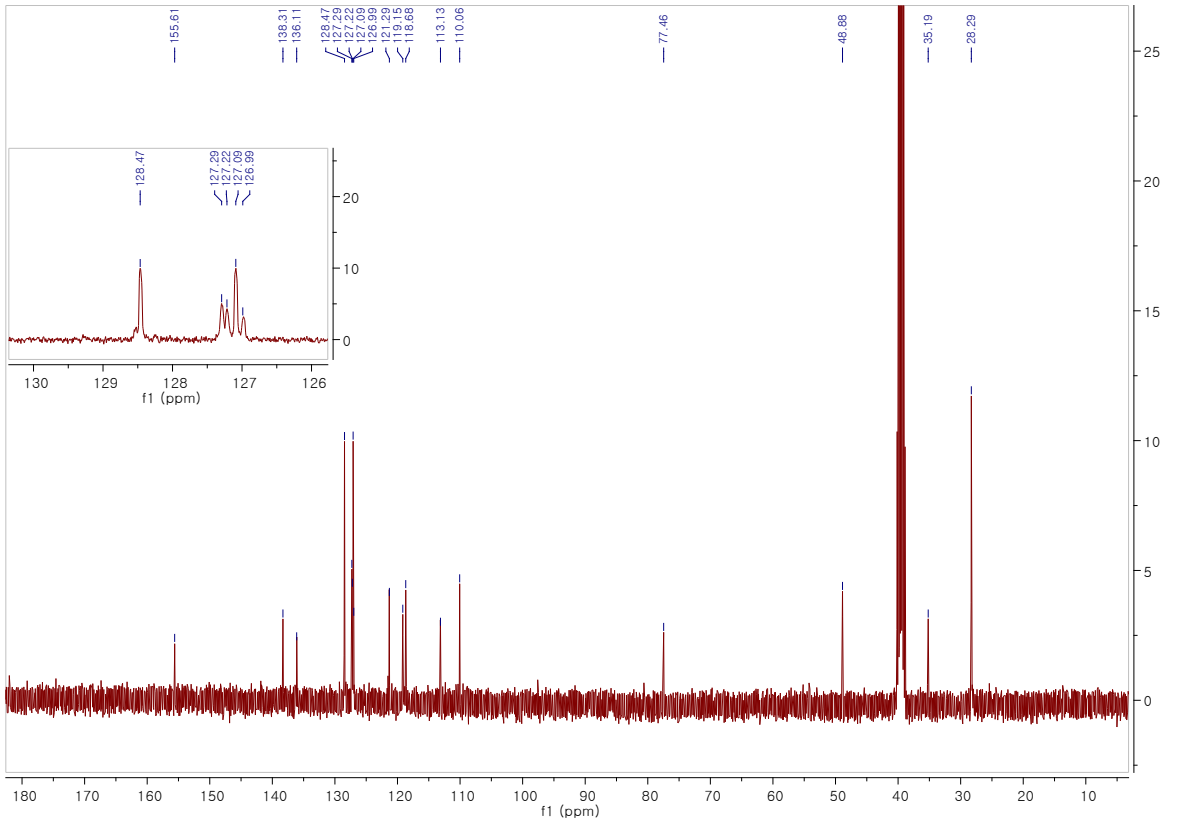

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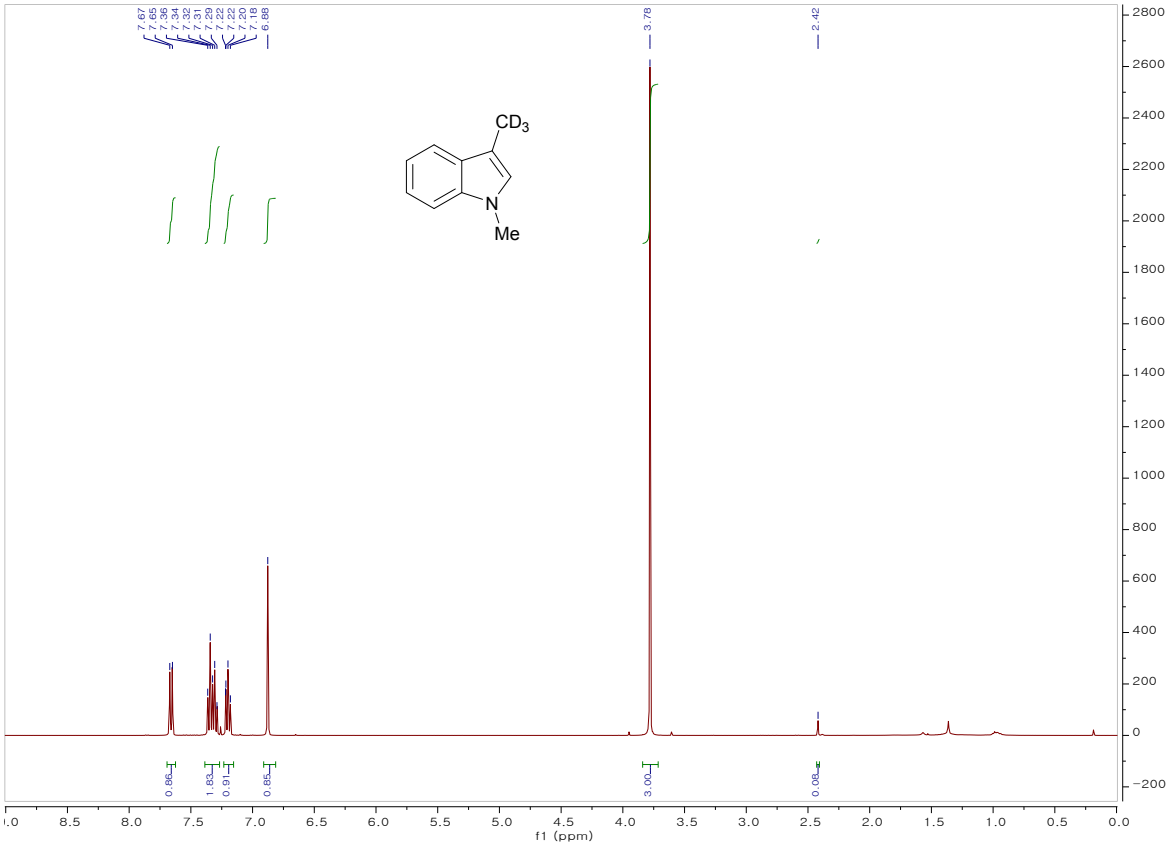

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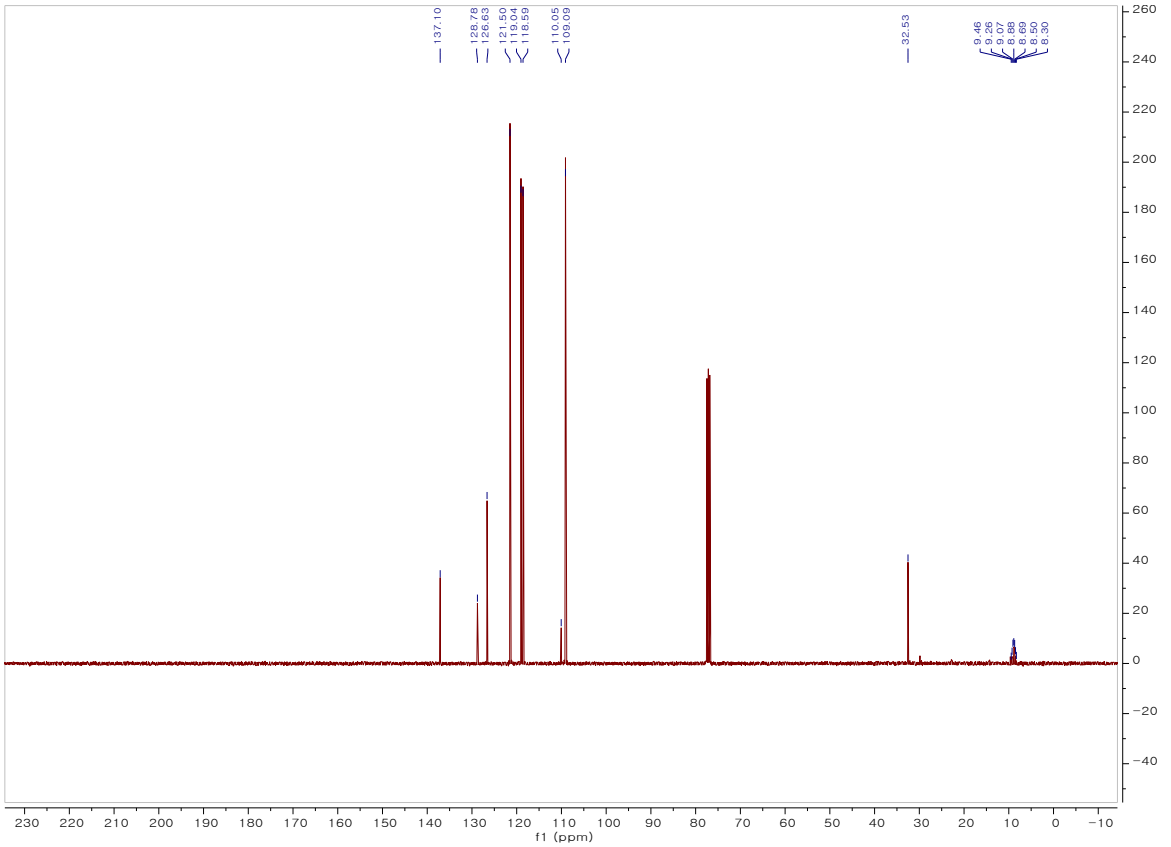

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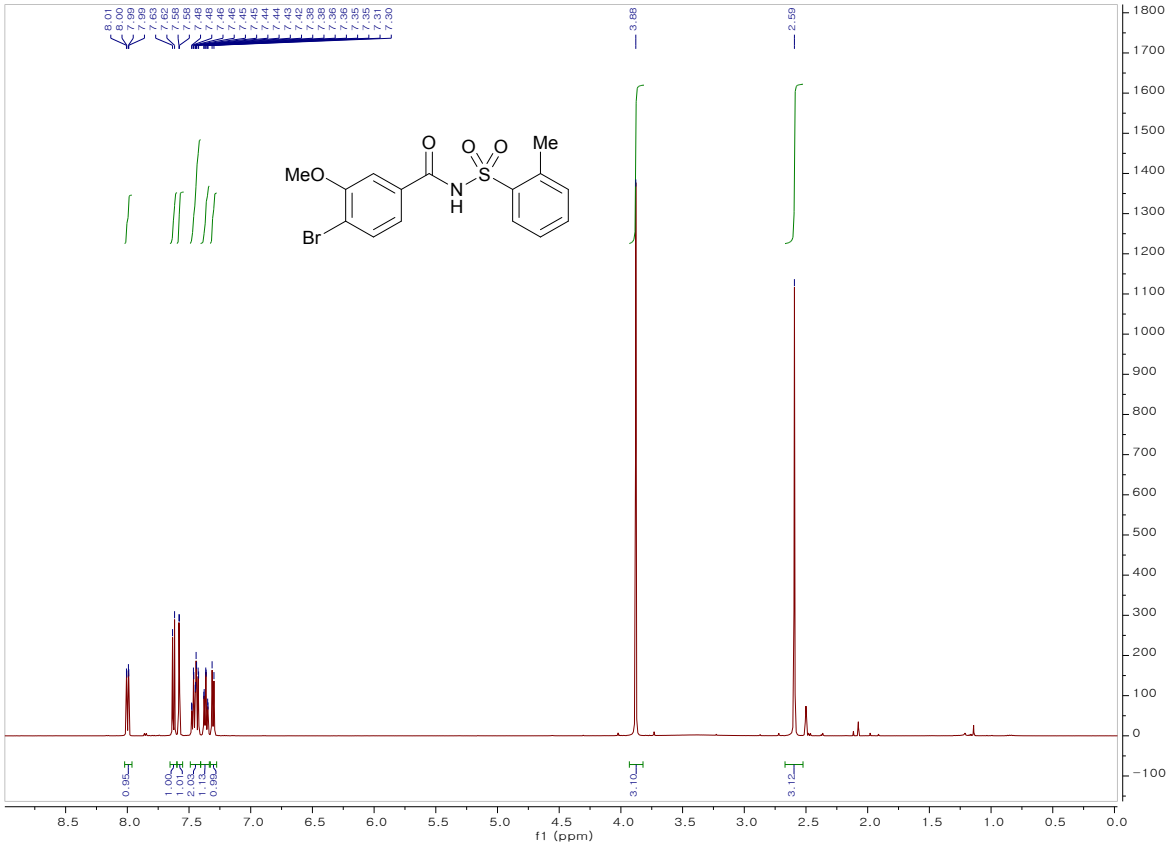

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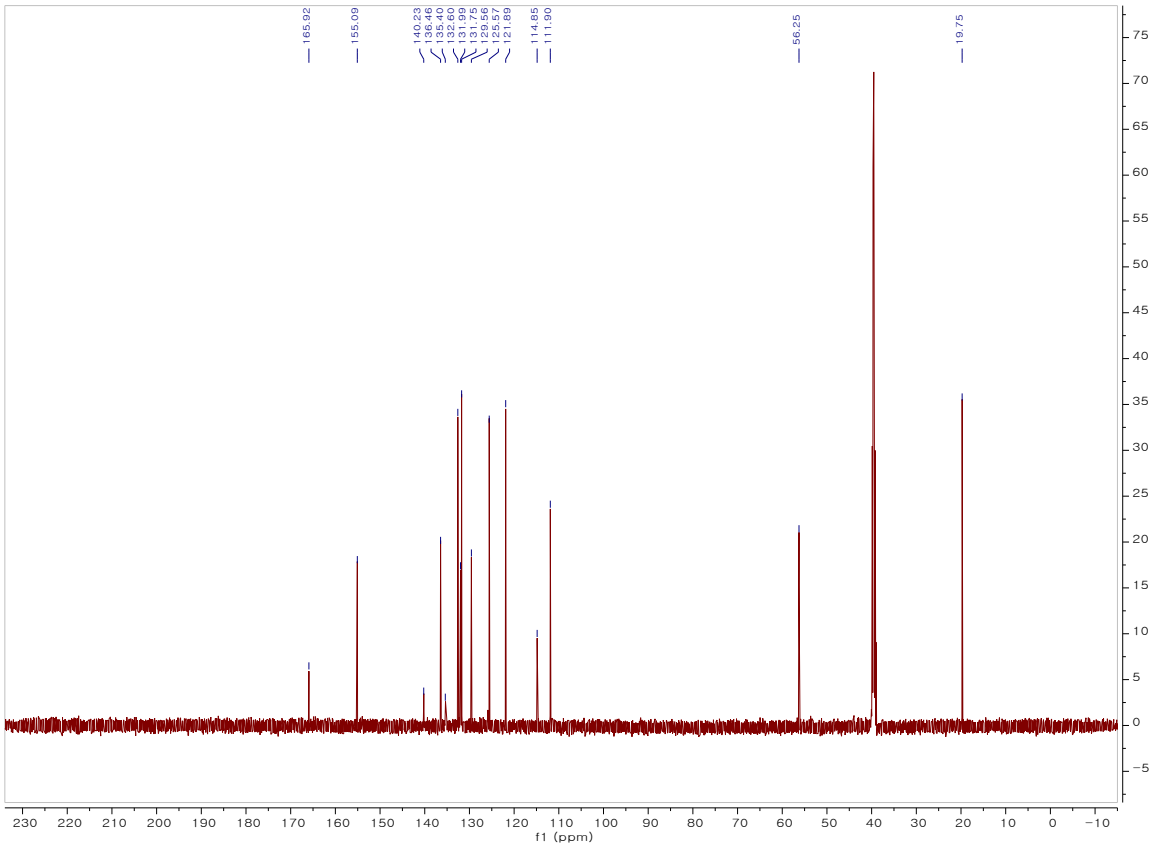

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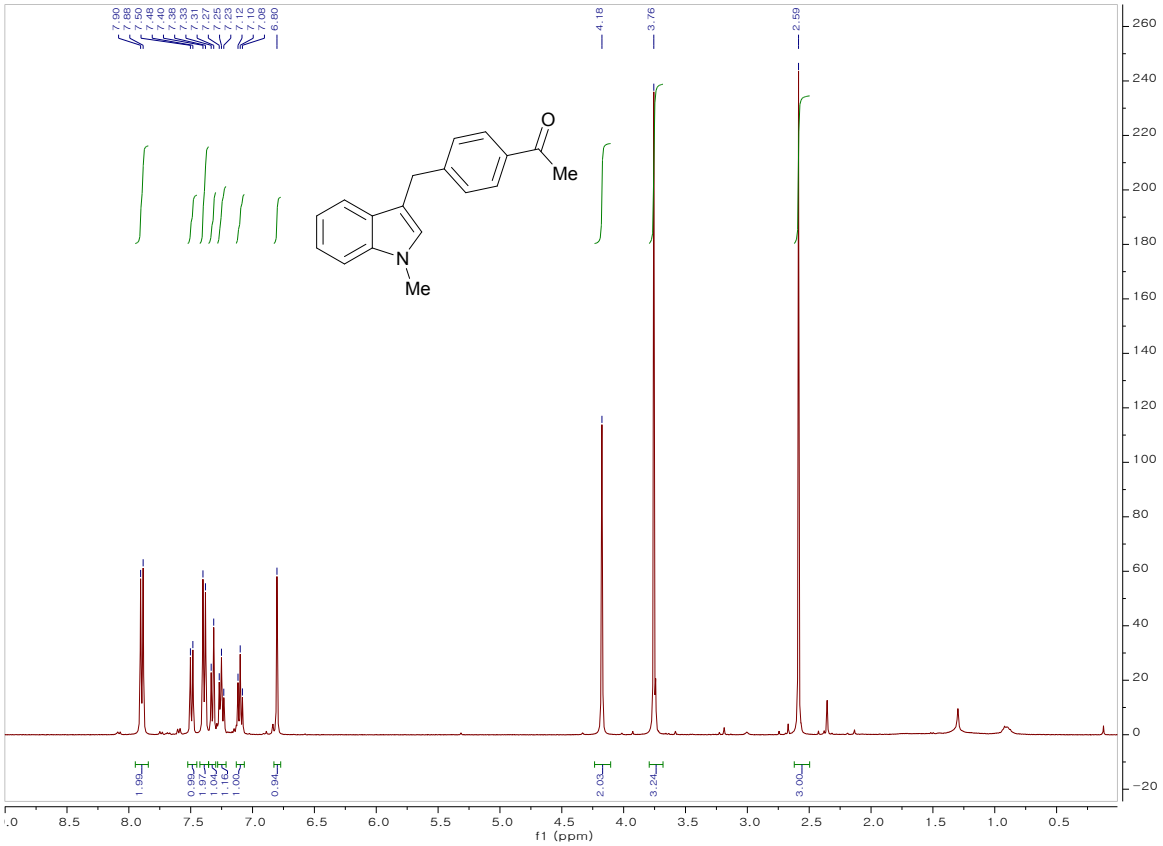

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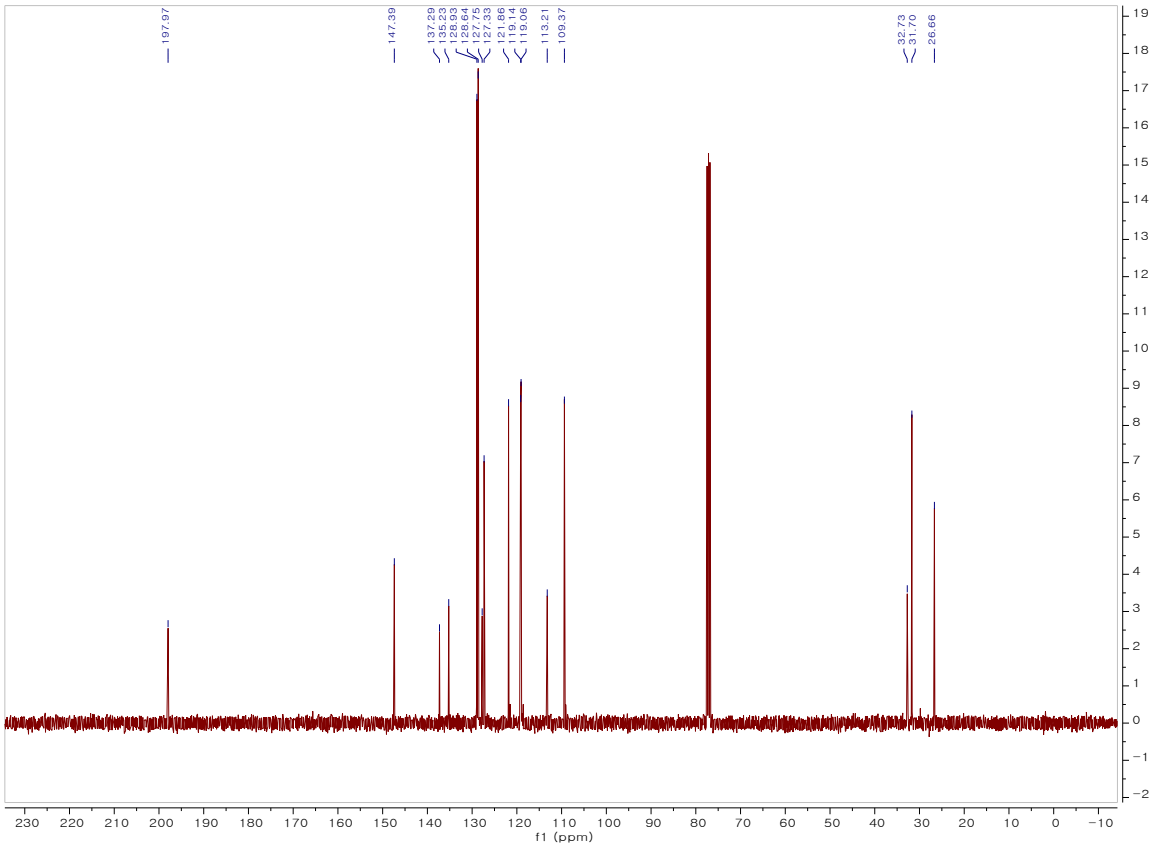

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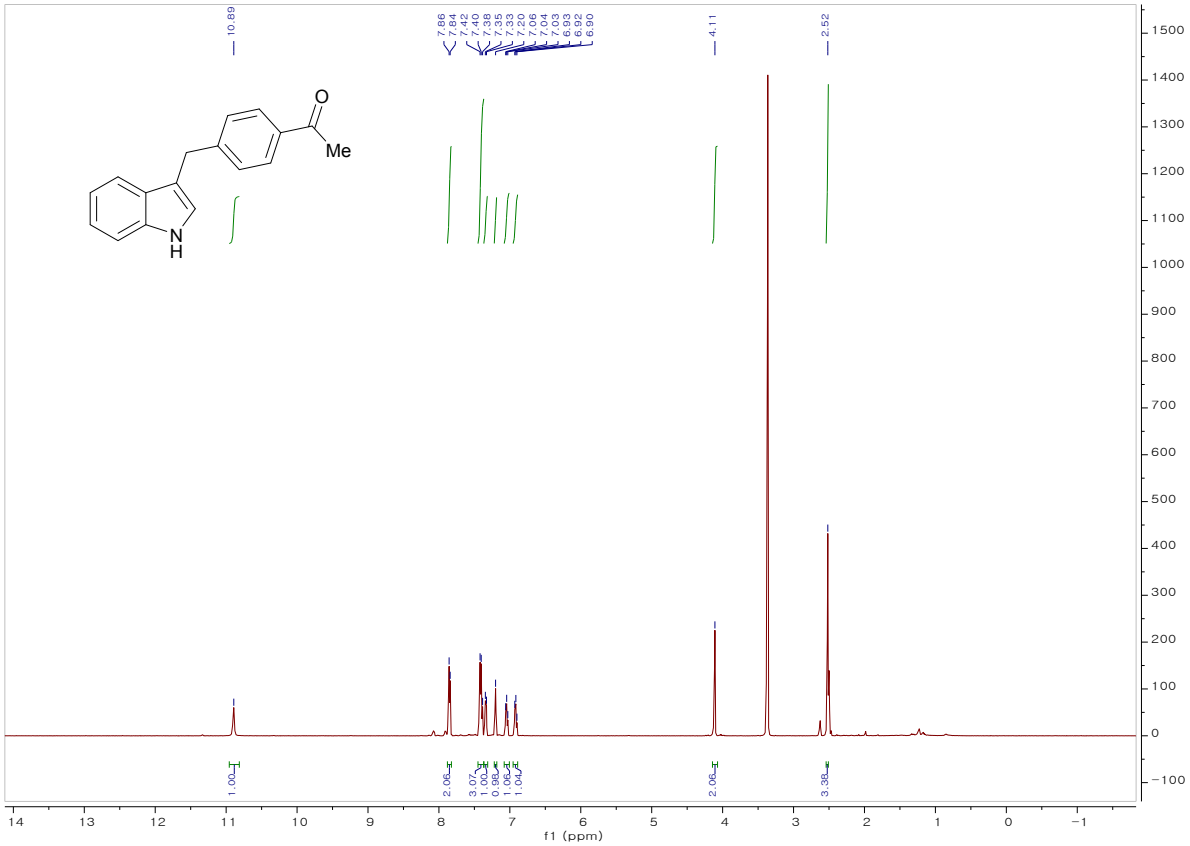

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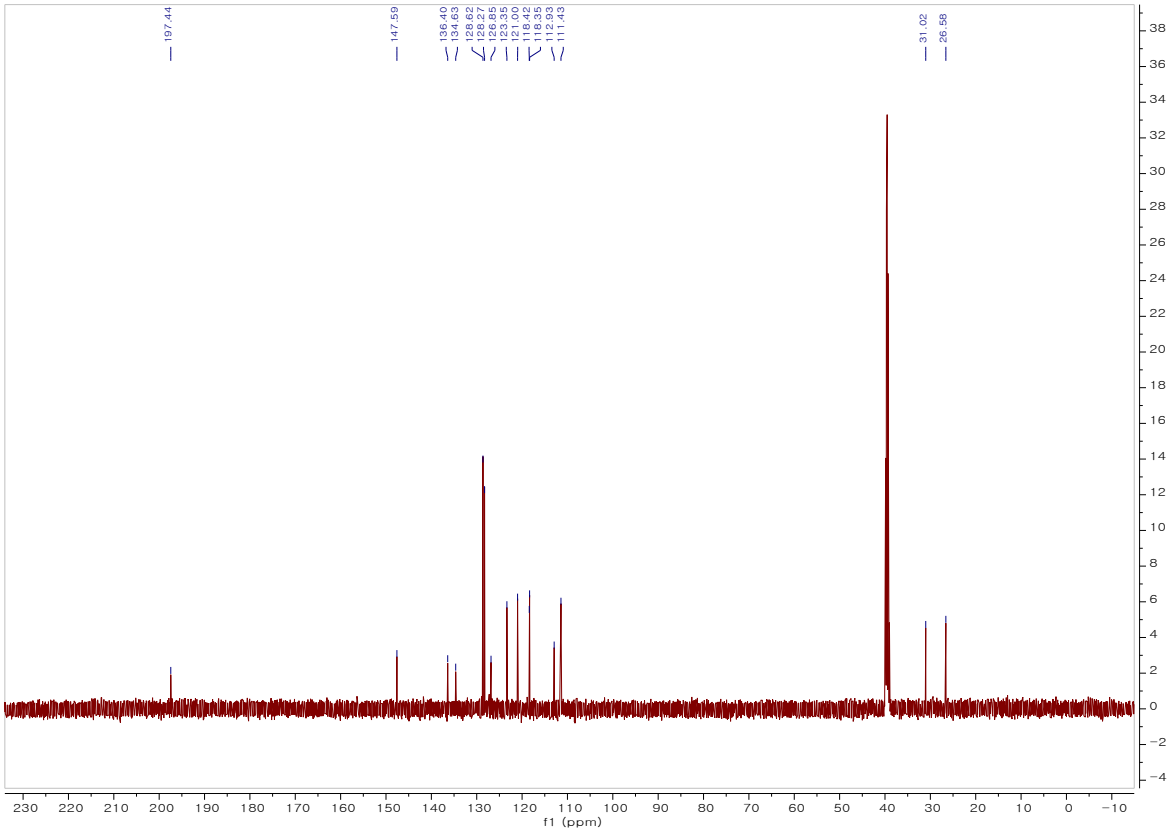
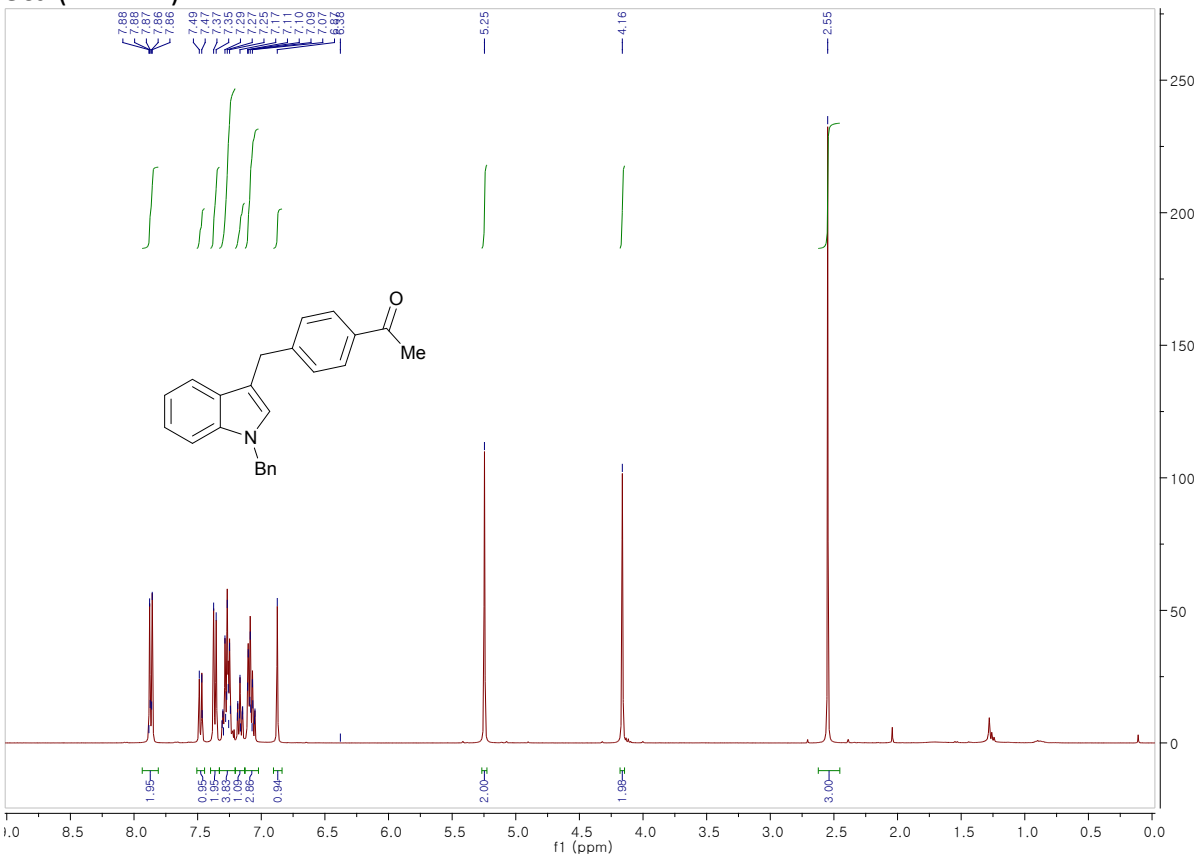
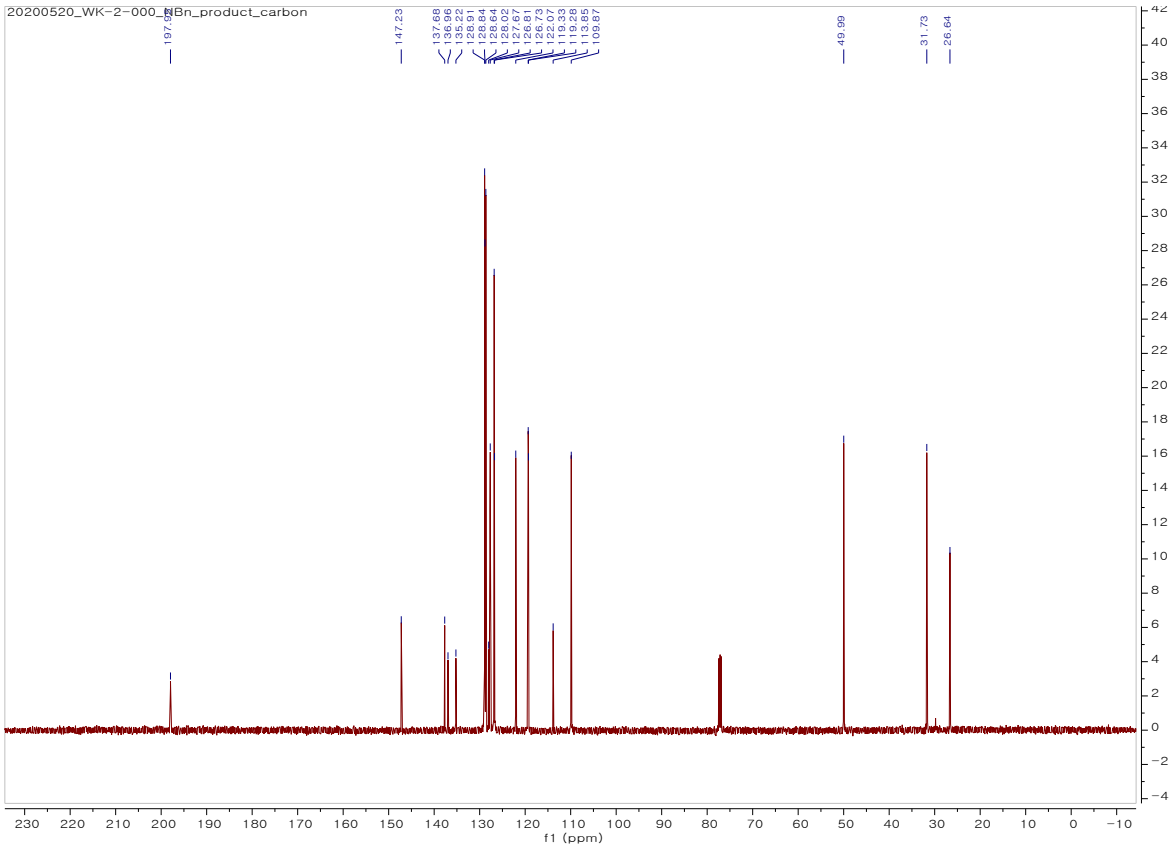


3ca (^{1}H NMR)



3ca (^{13}C NMR)



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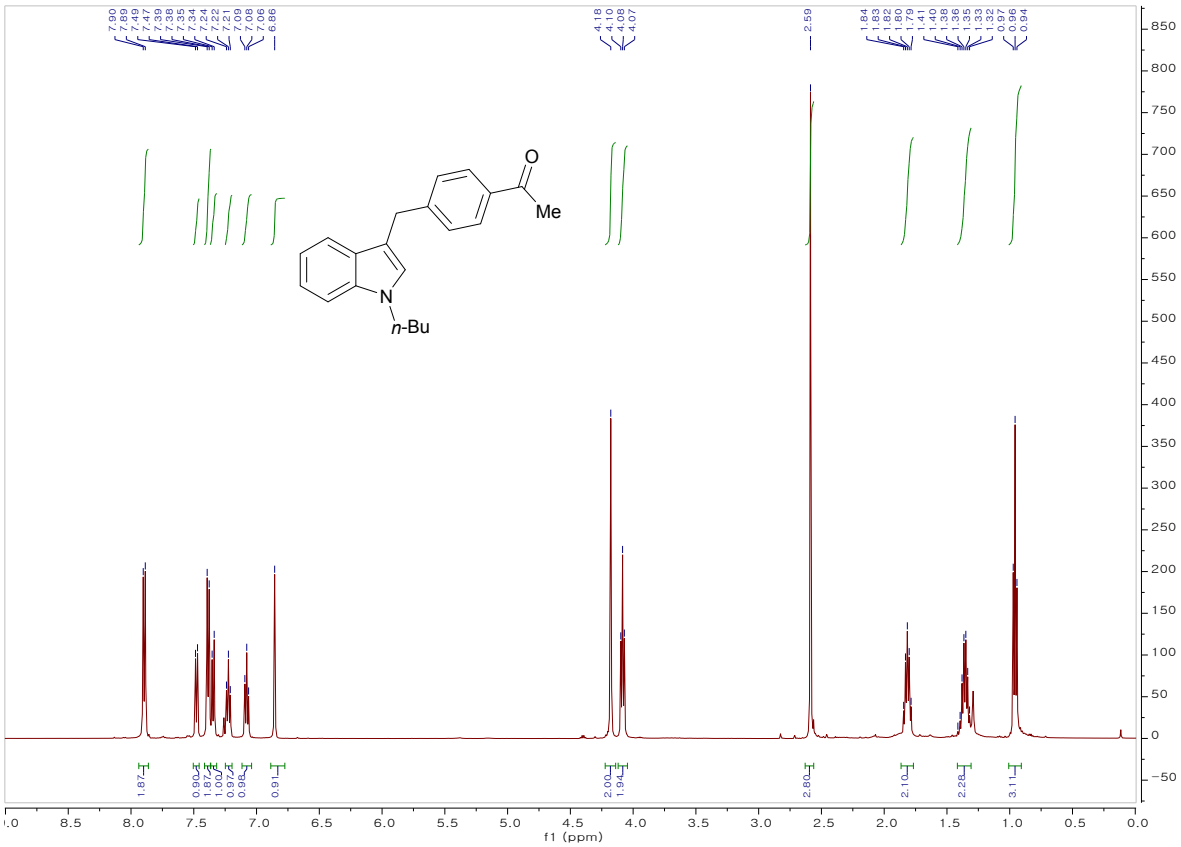

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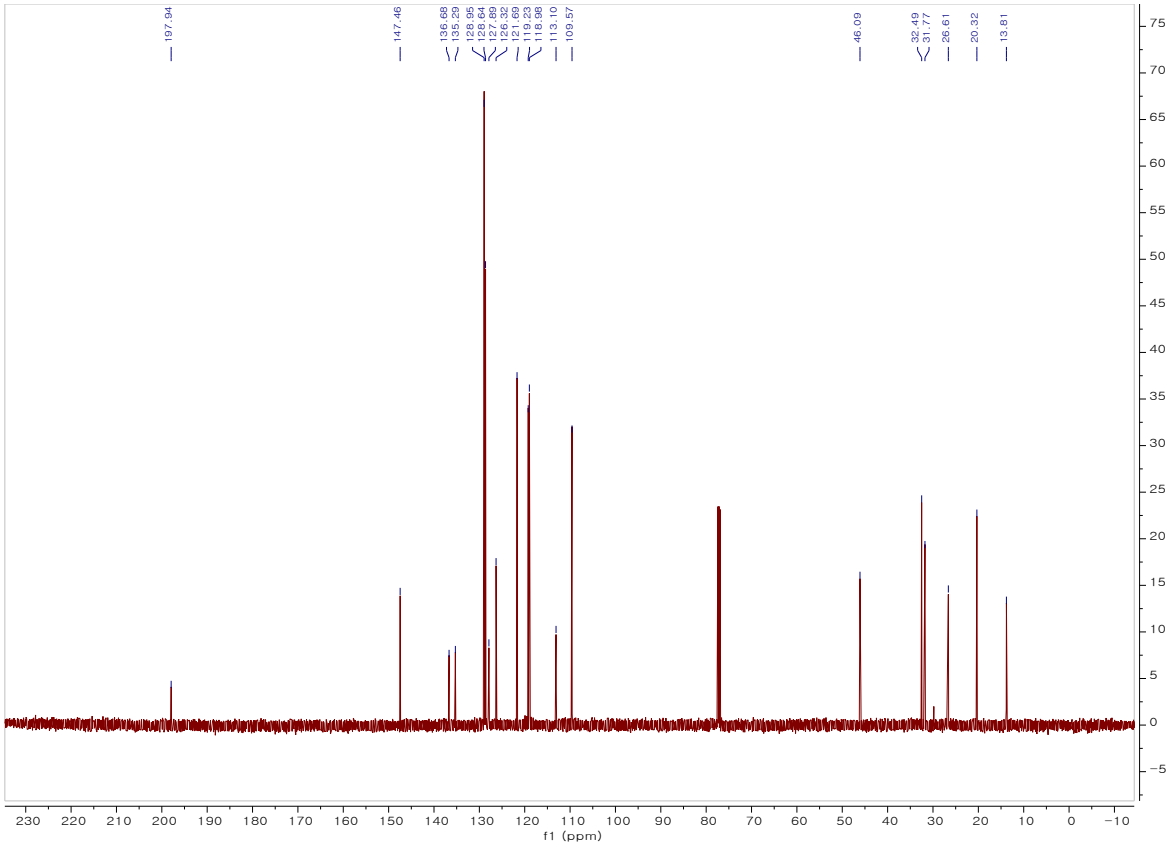

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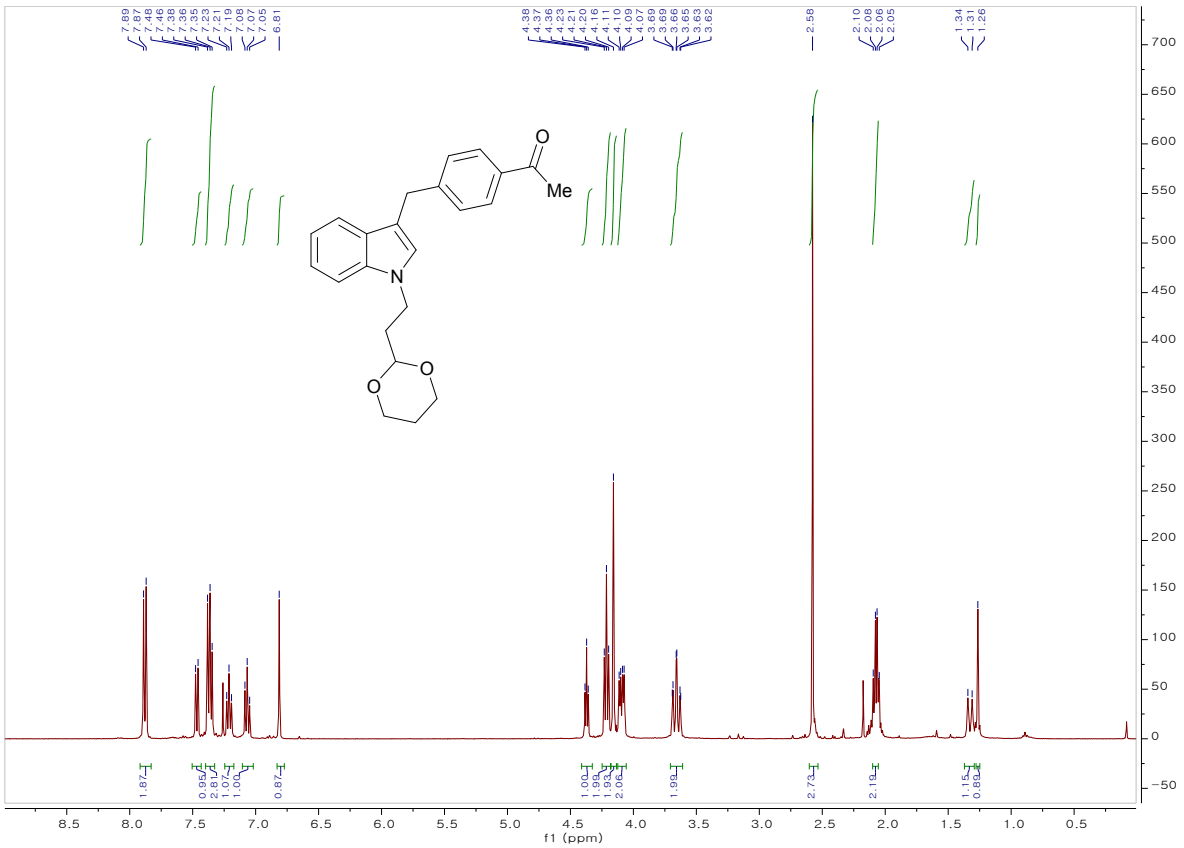

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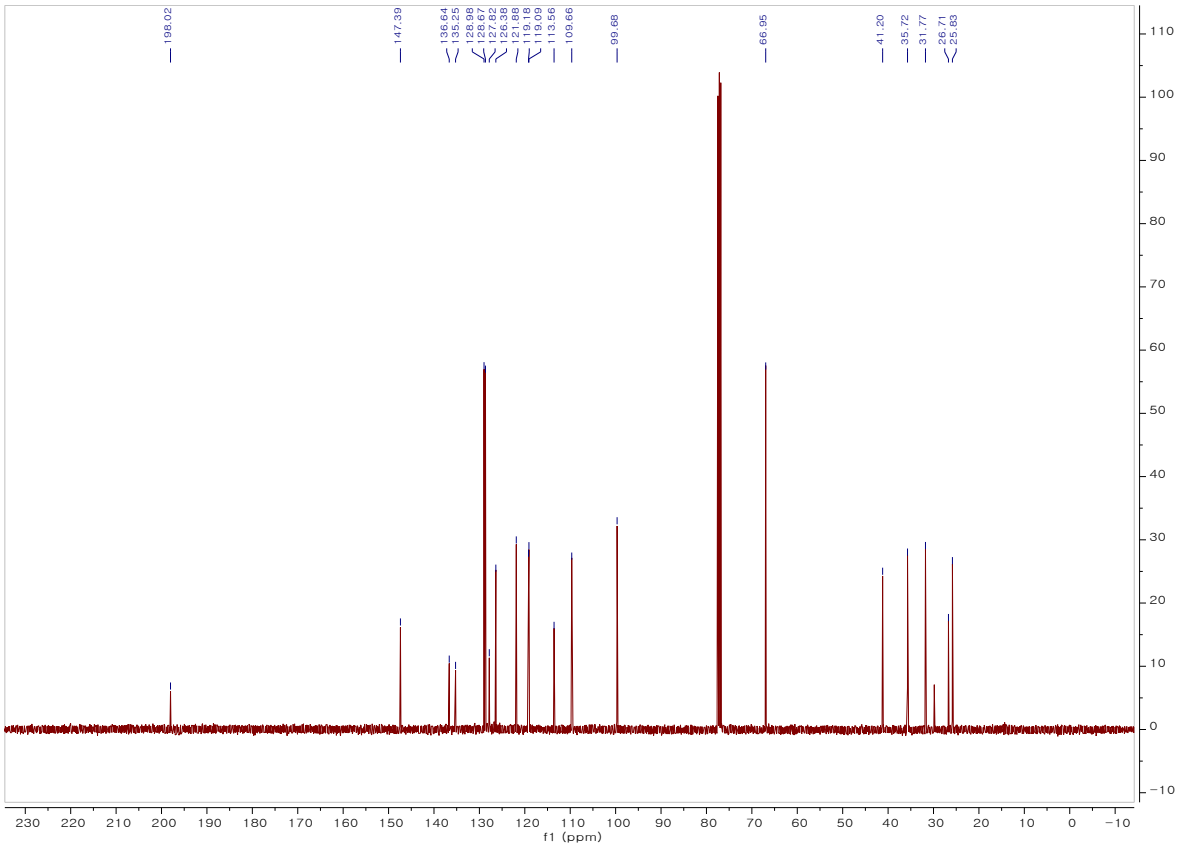

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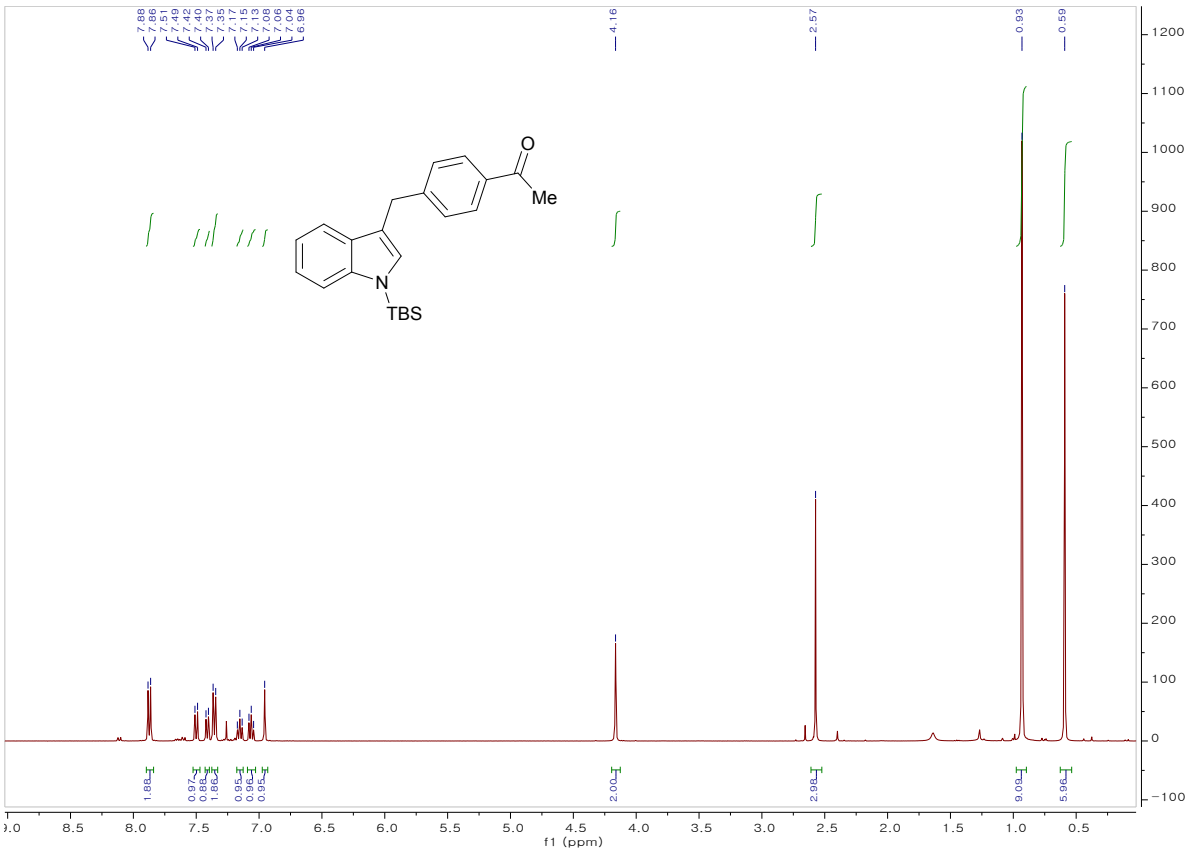

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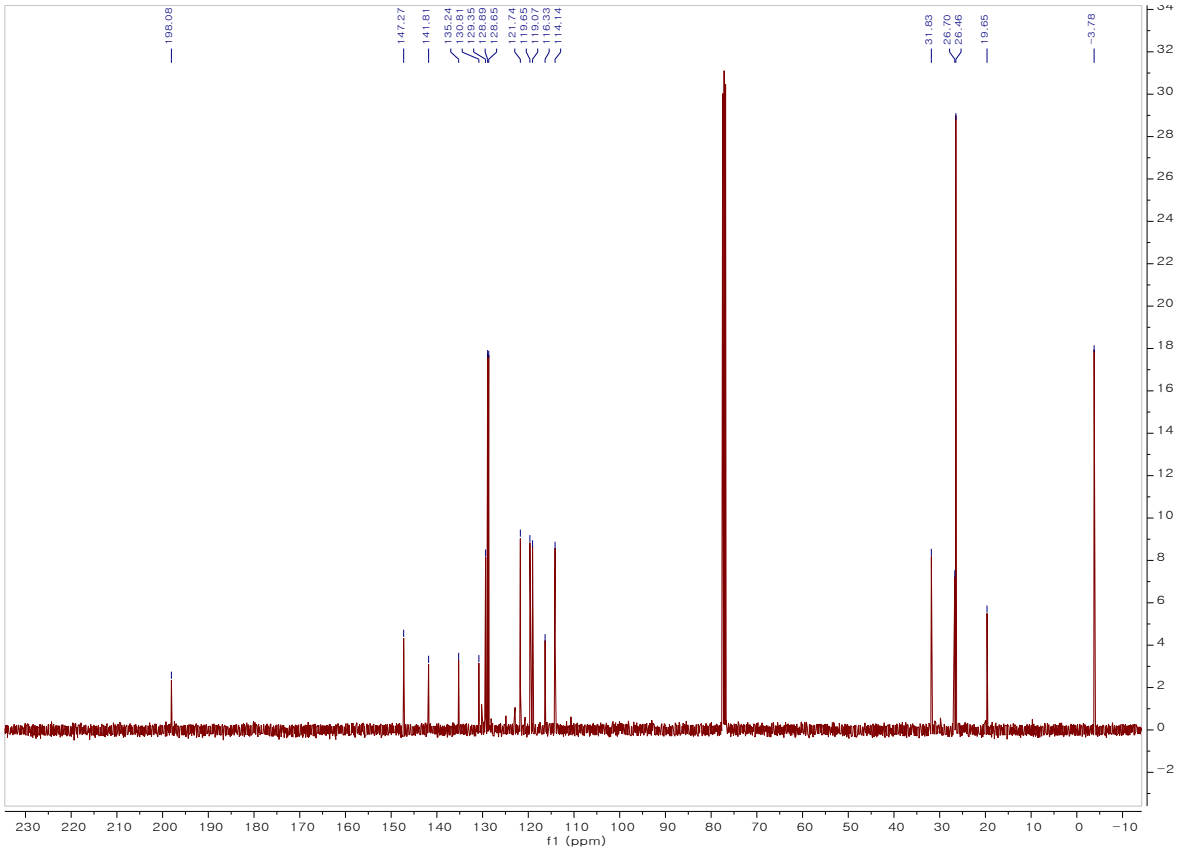
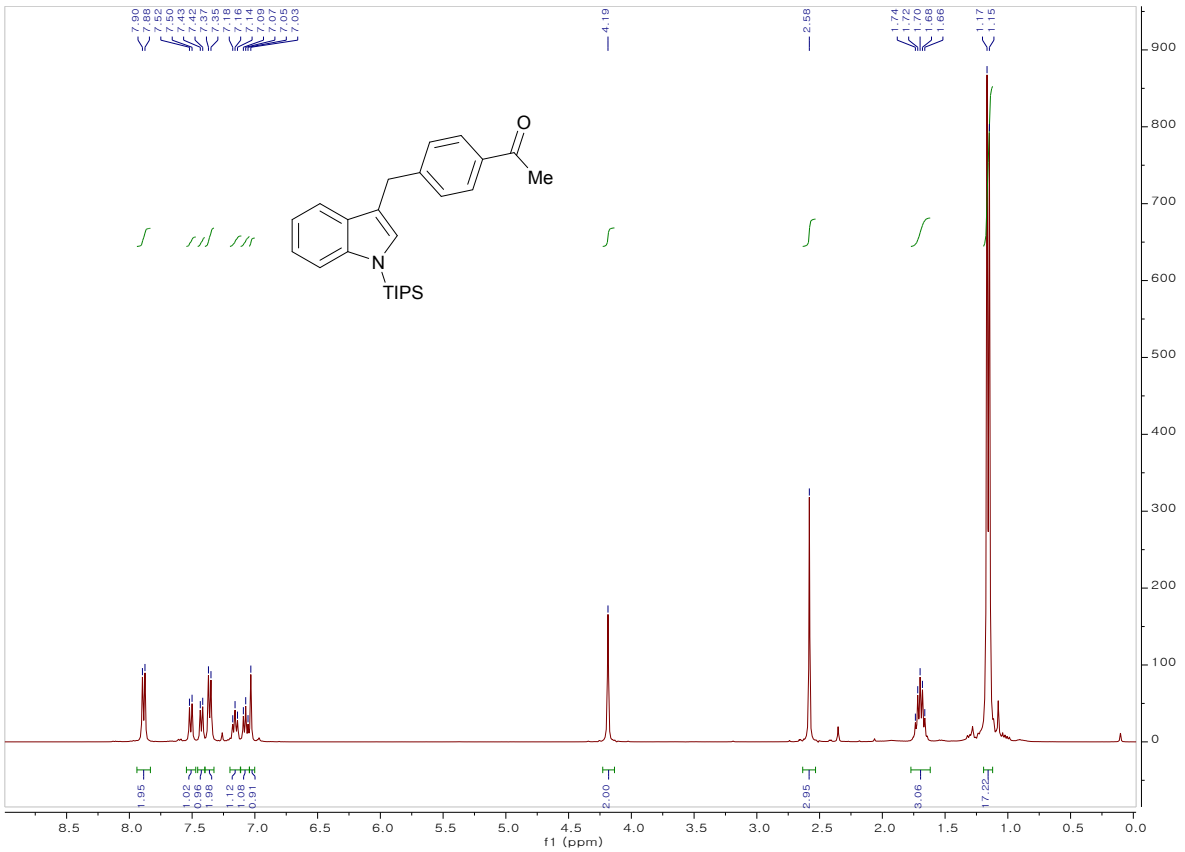


3ga (^{1}H NMR)



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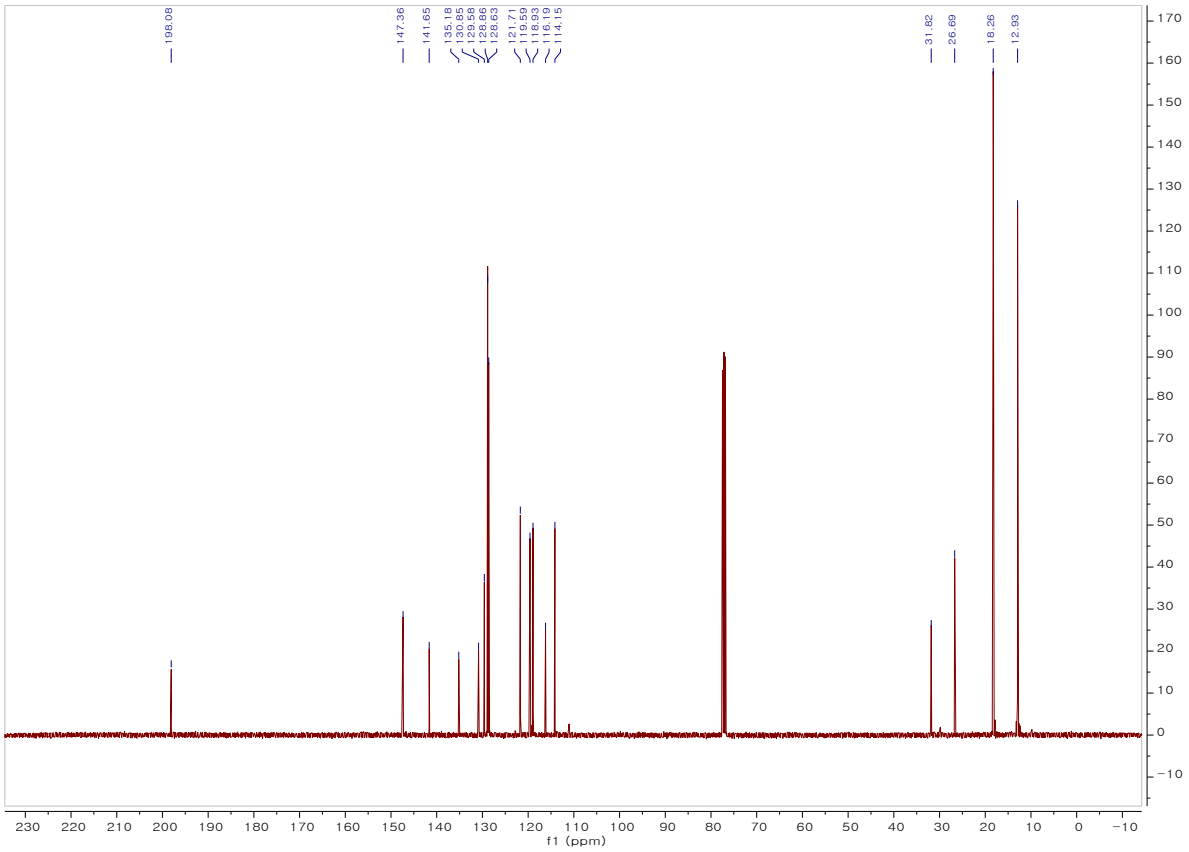
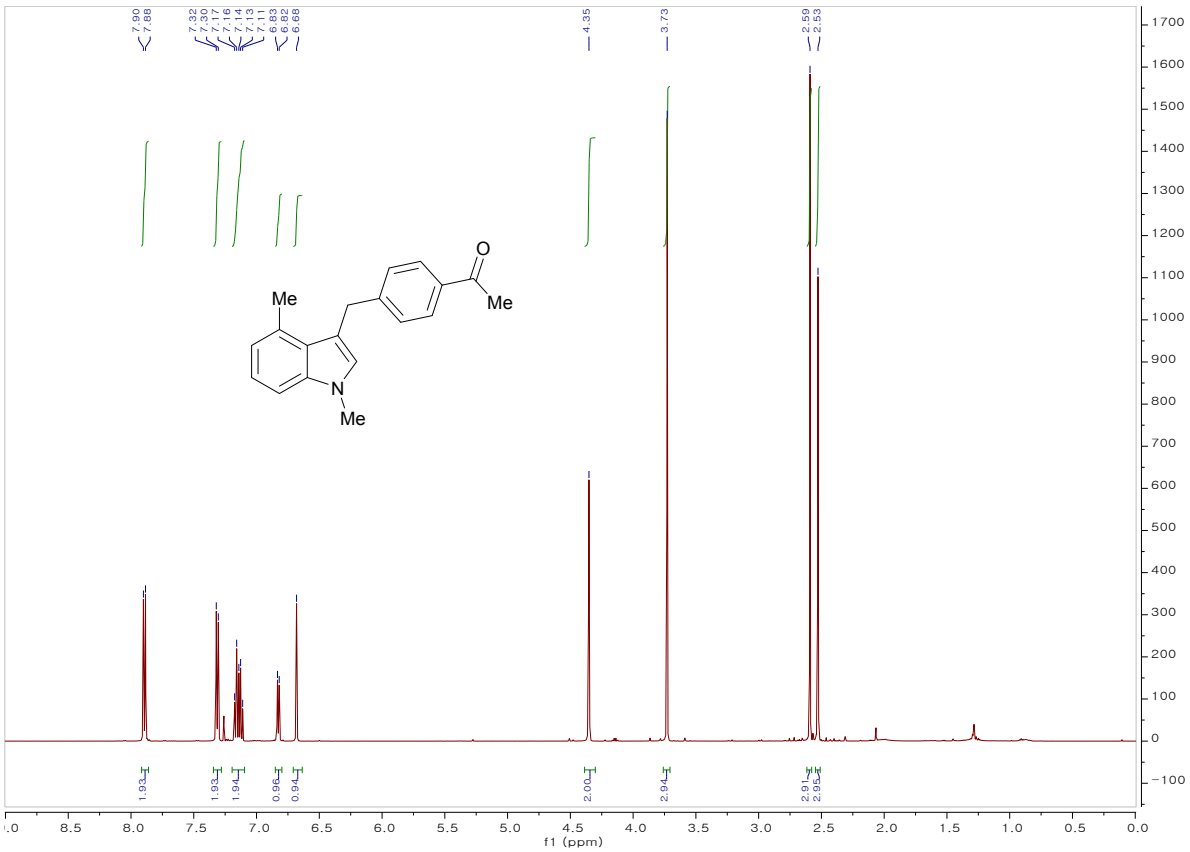


3ja (^{1}H NMR)



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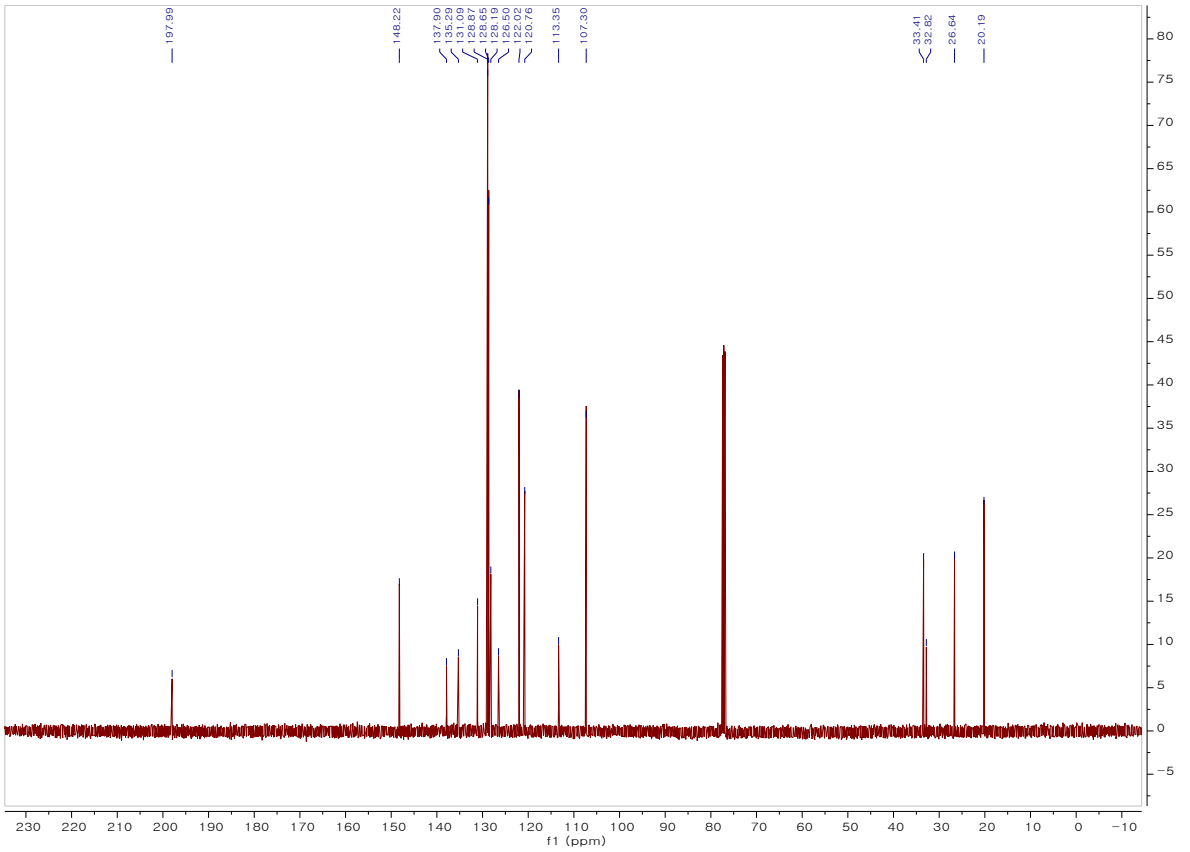

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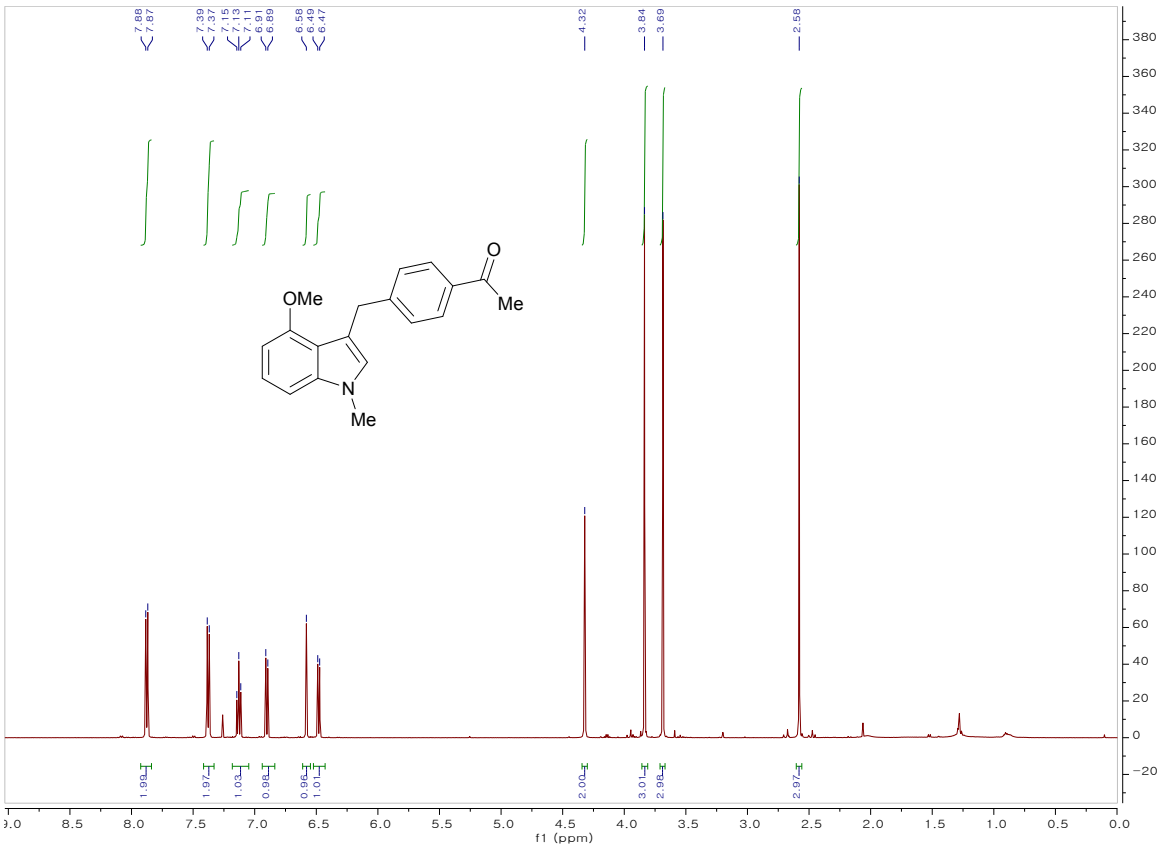

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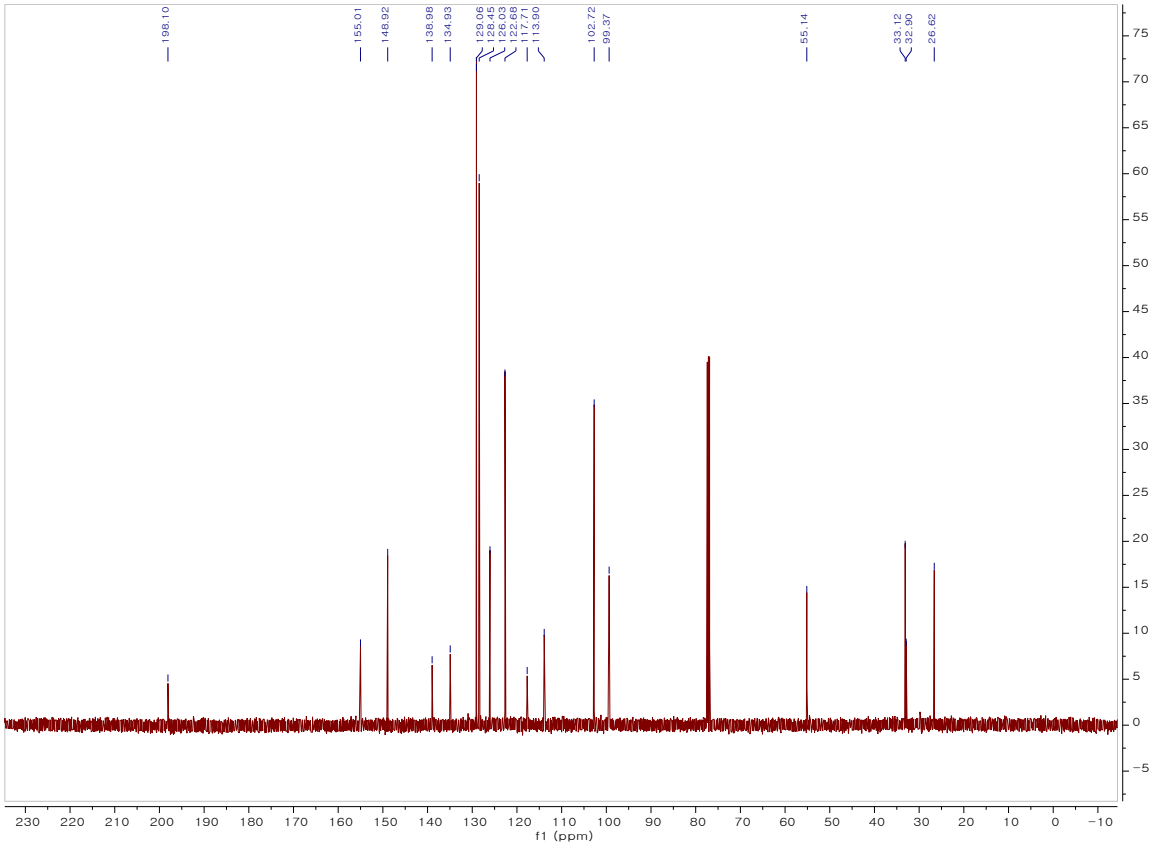

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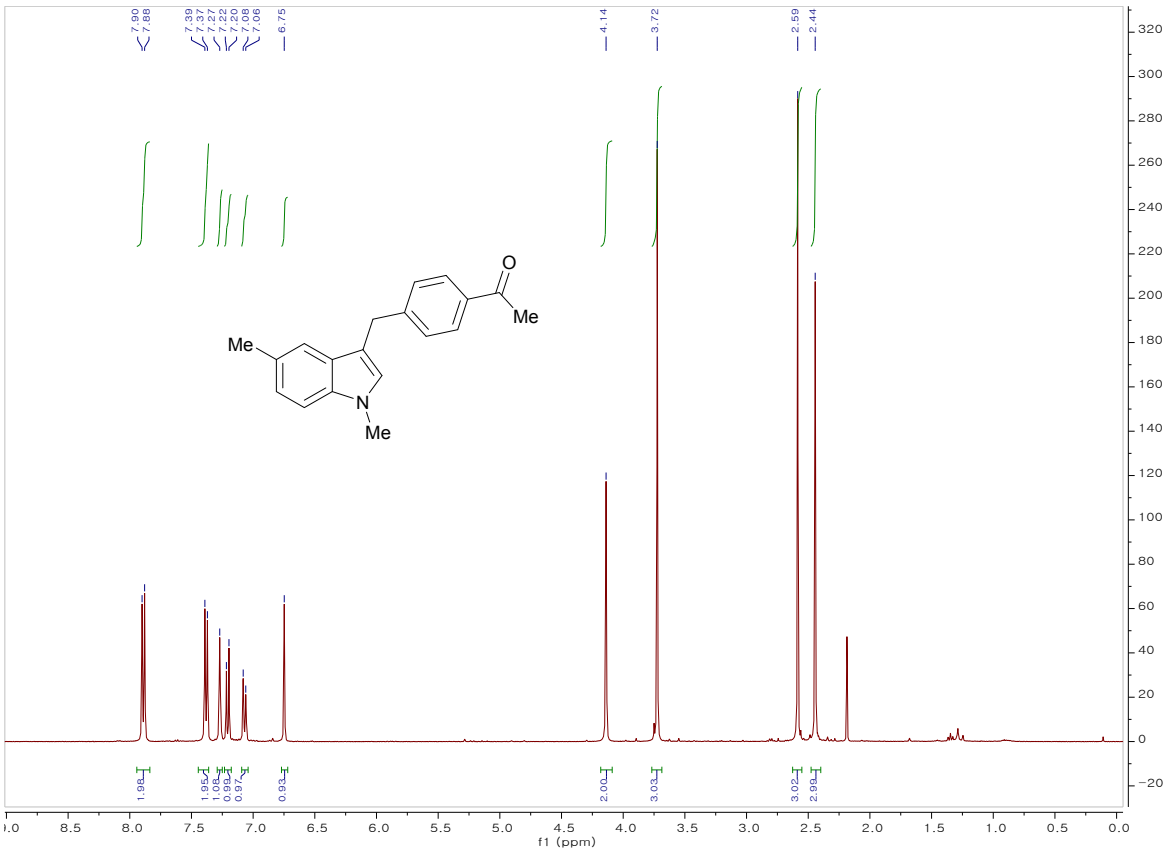

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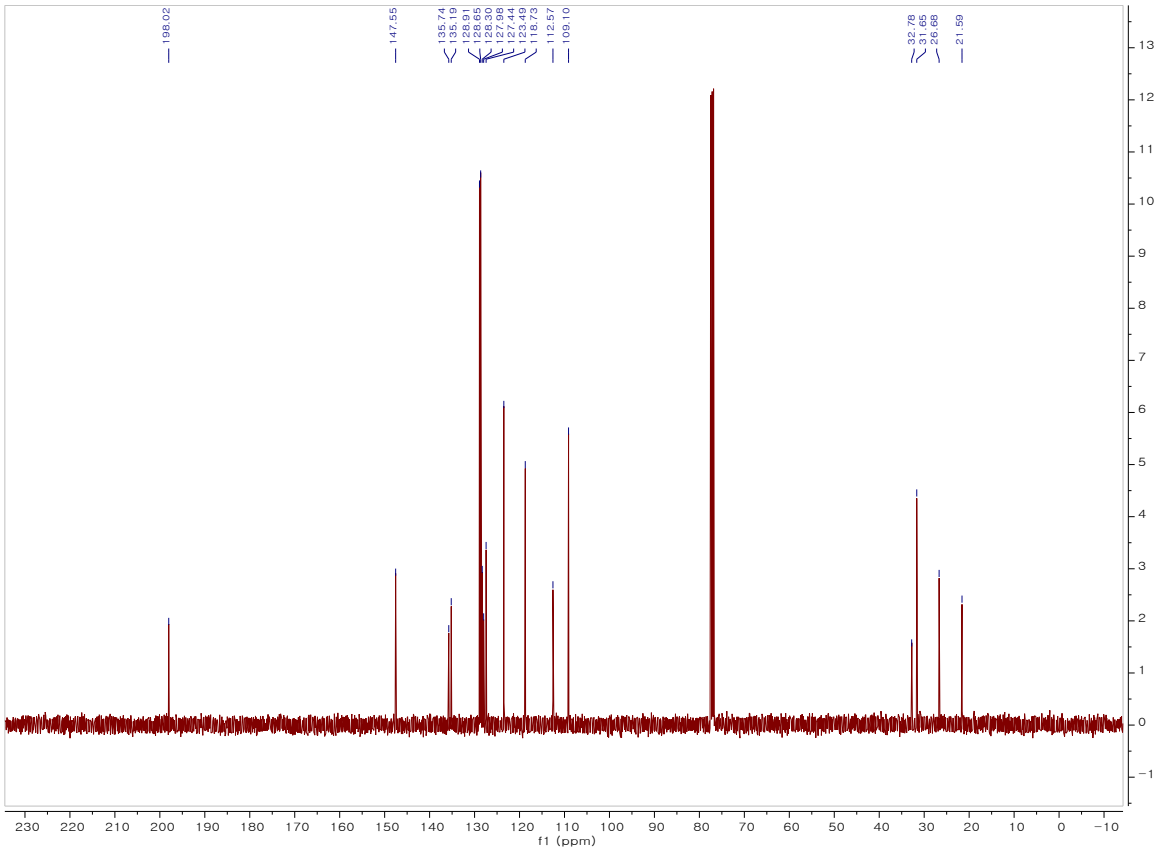
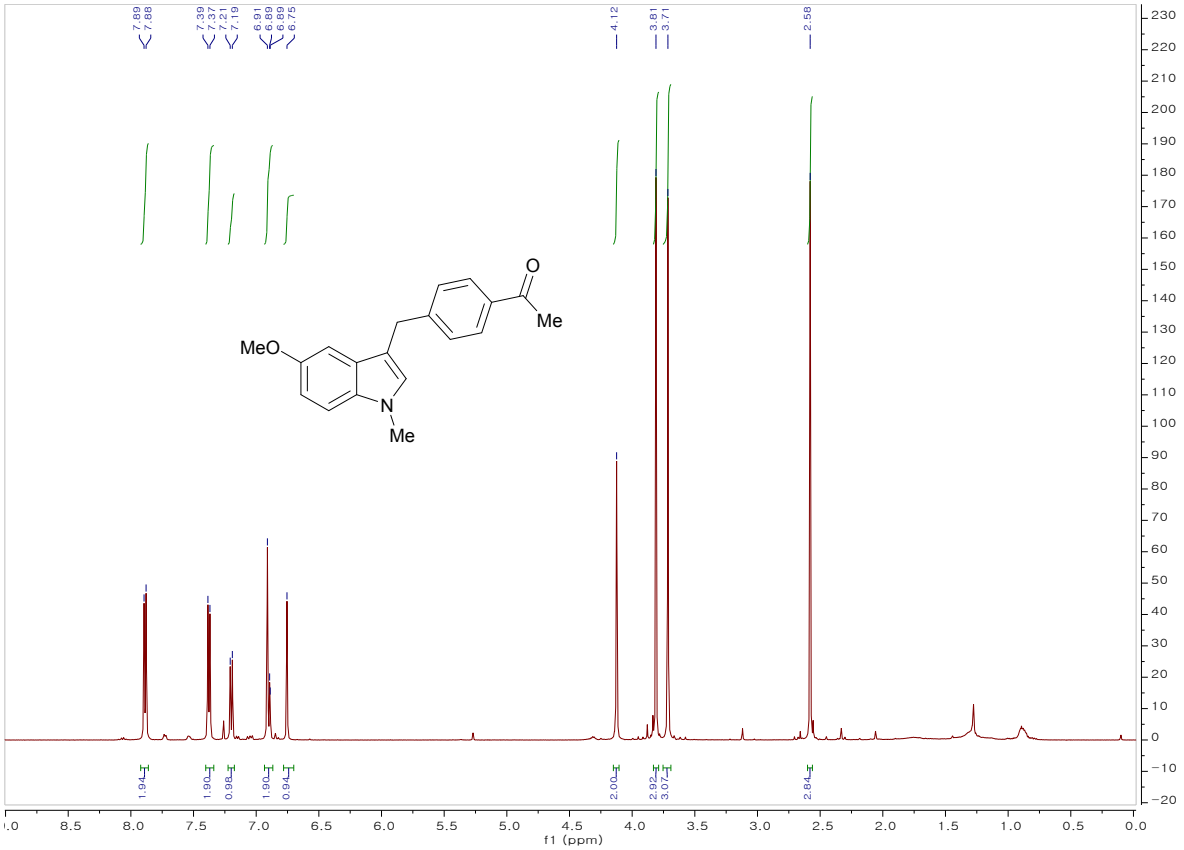


3ma (^{1}H NMR)



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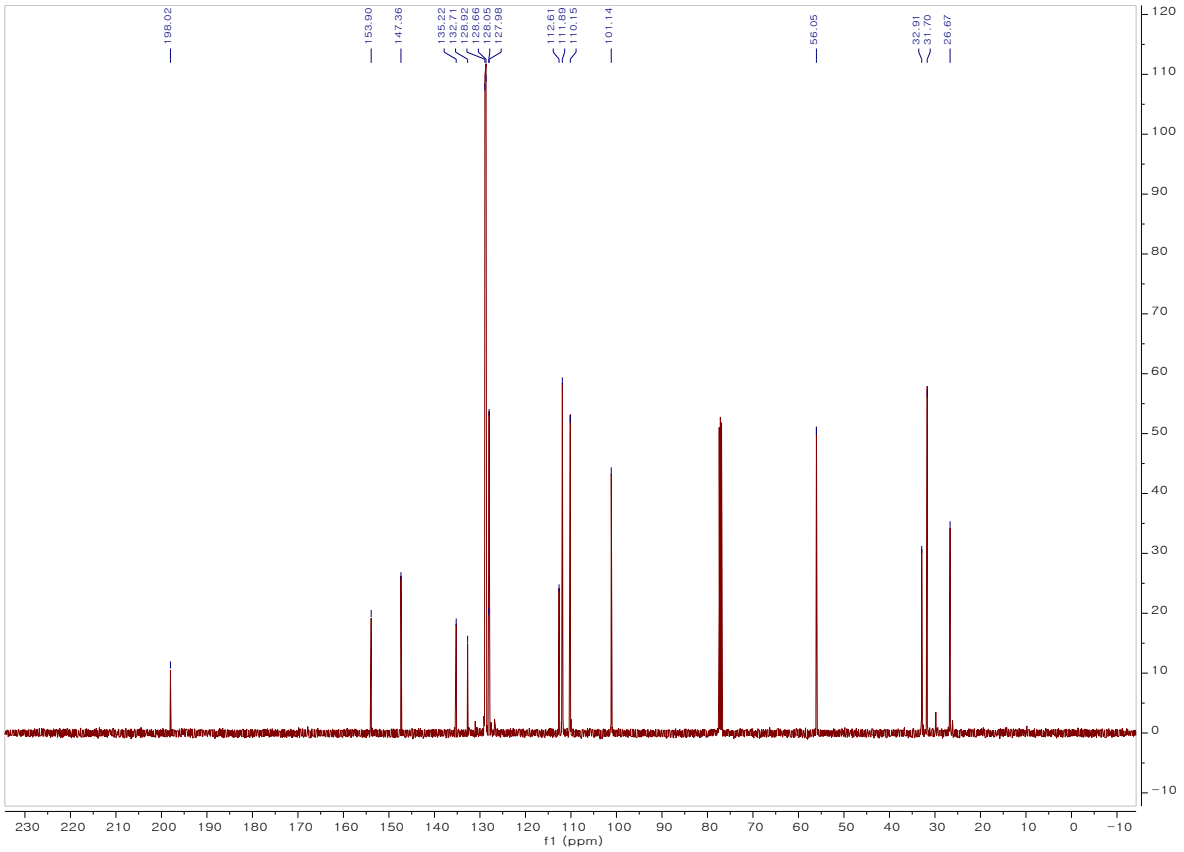

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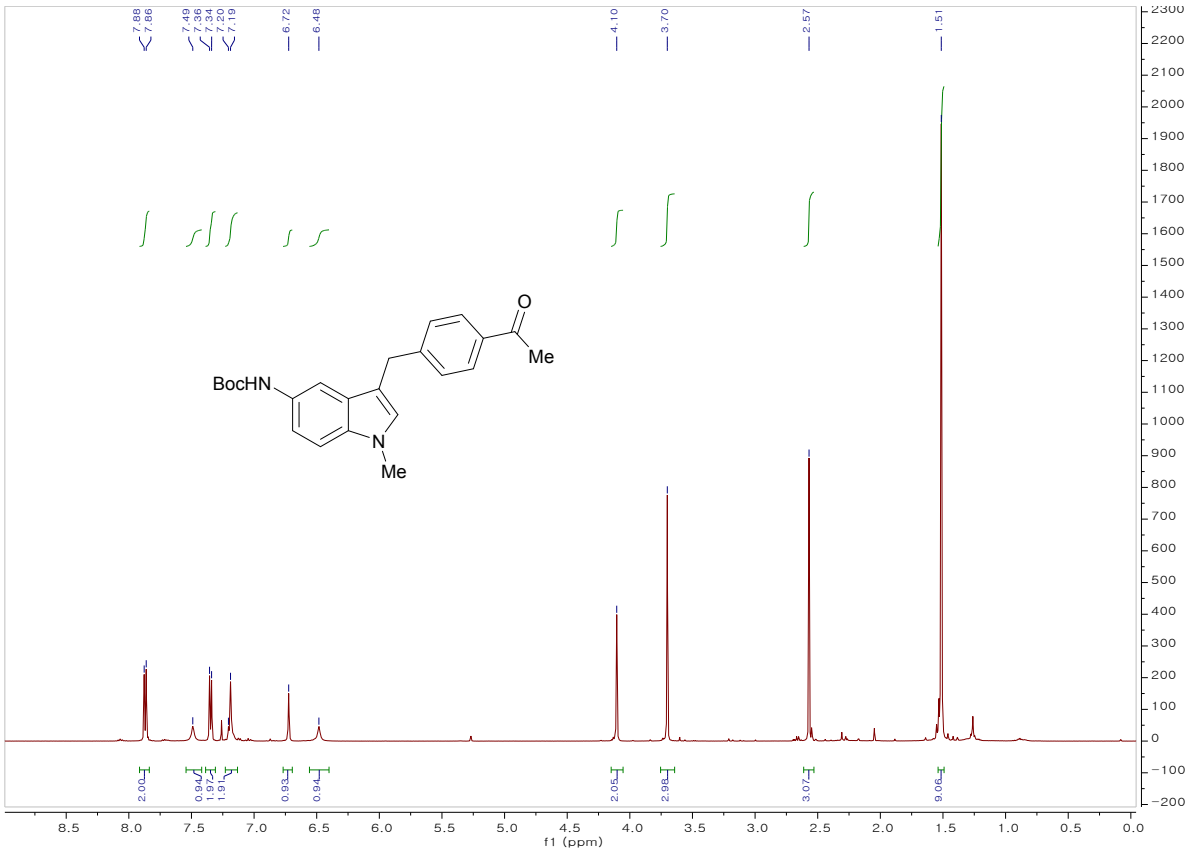

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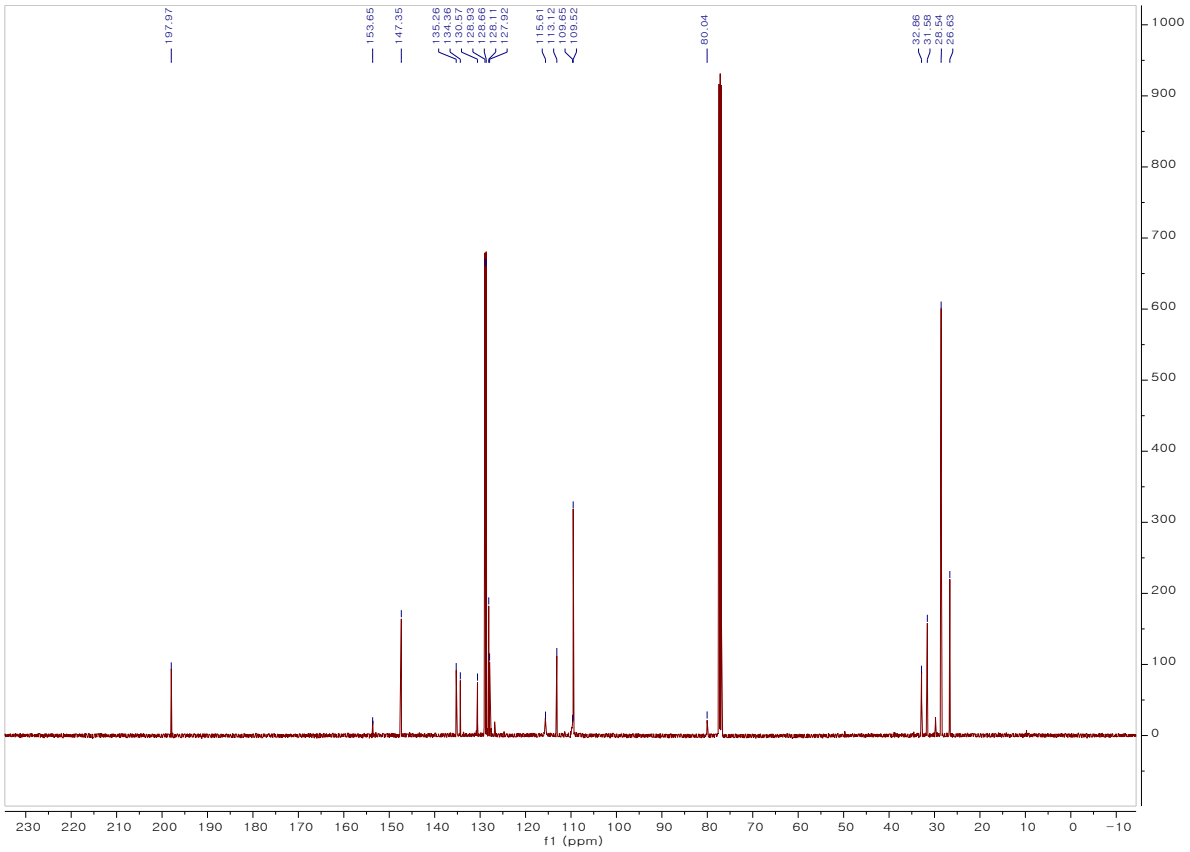

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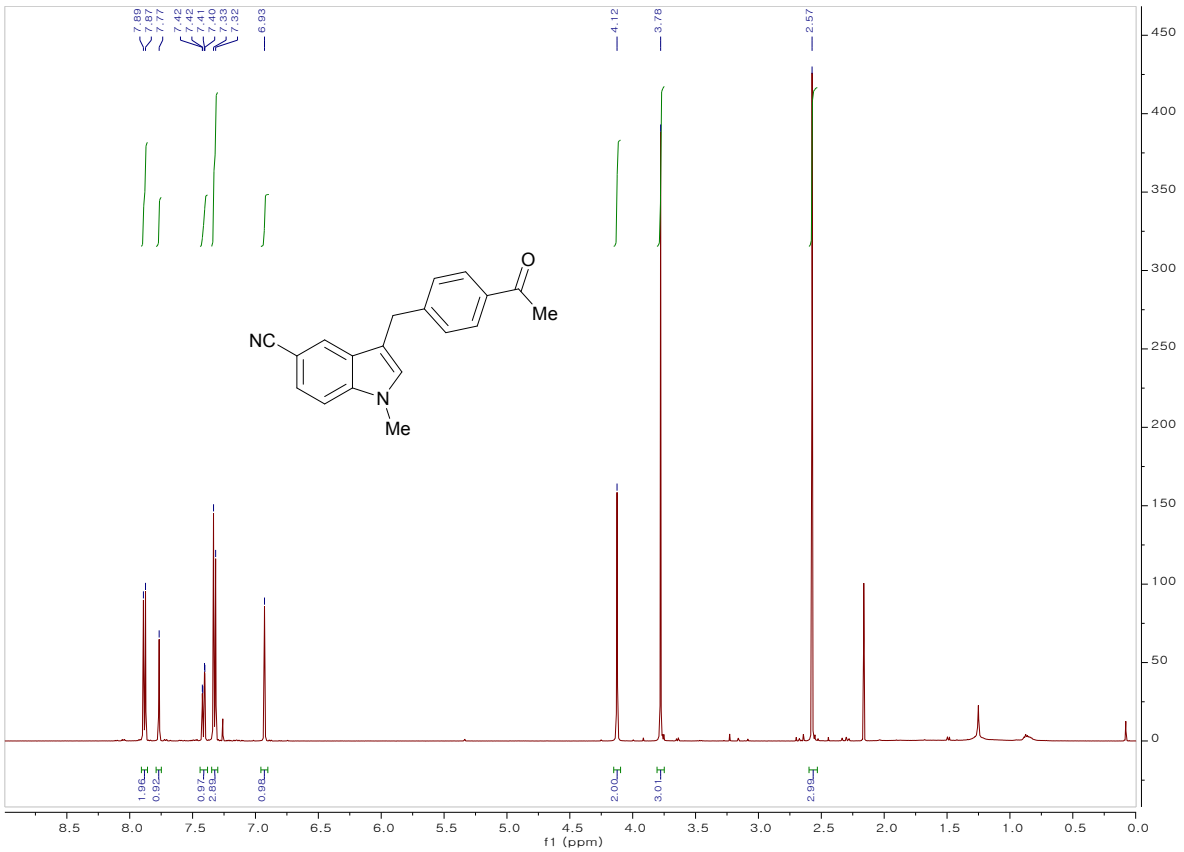

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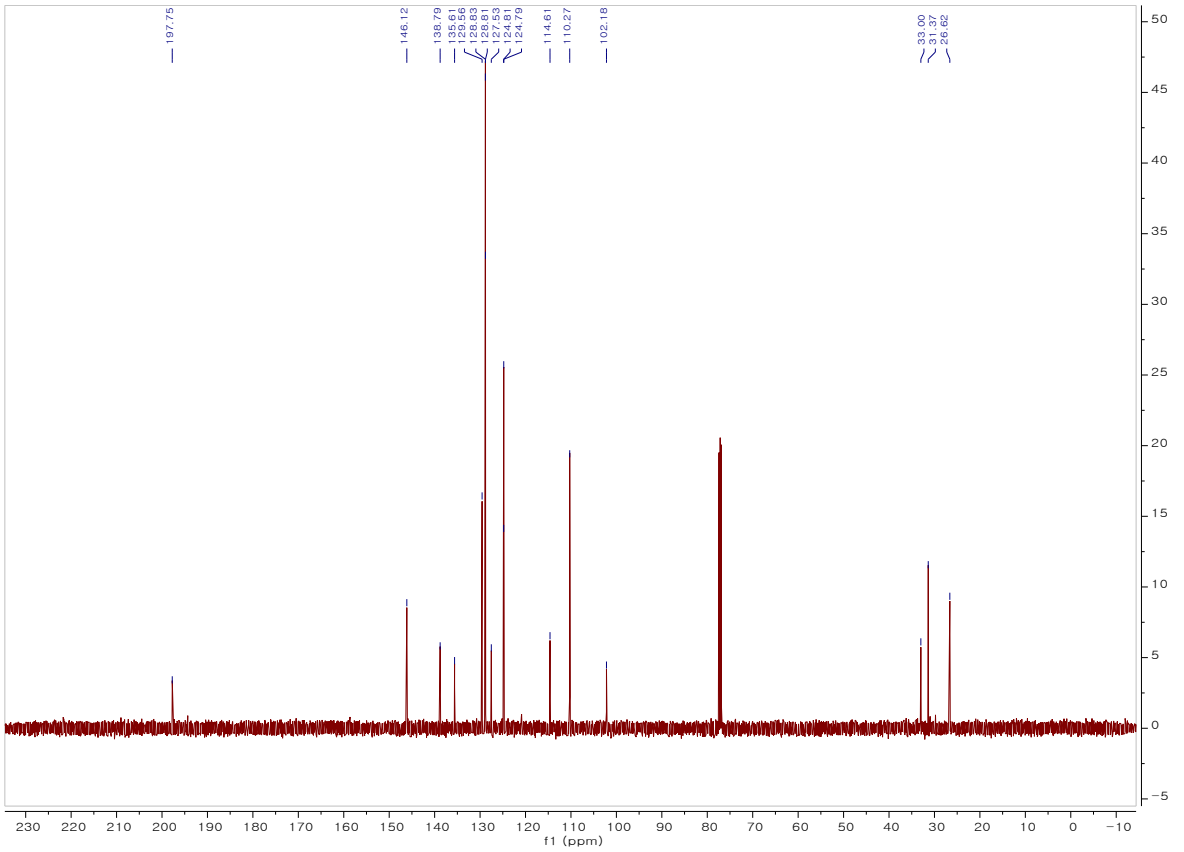

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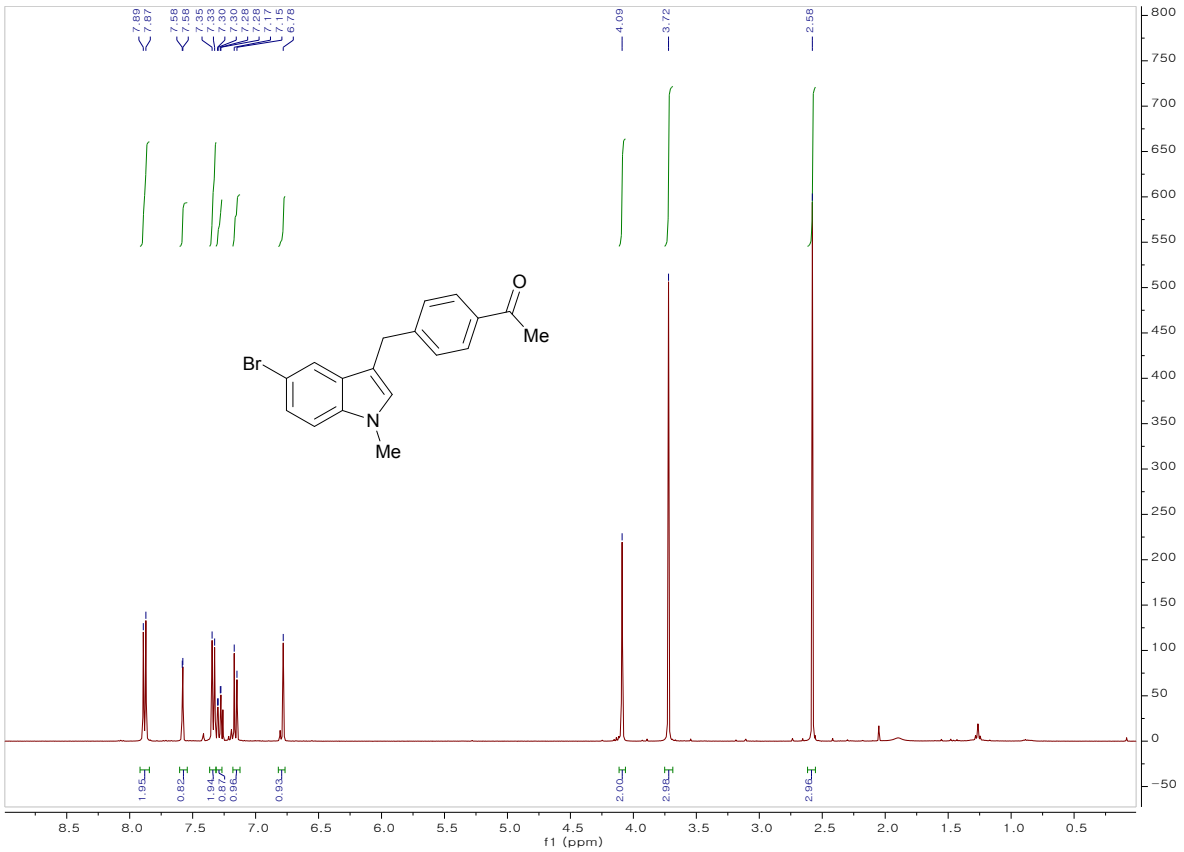

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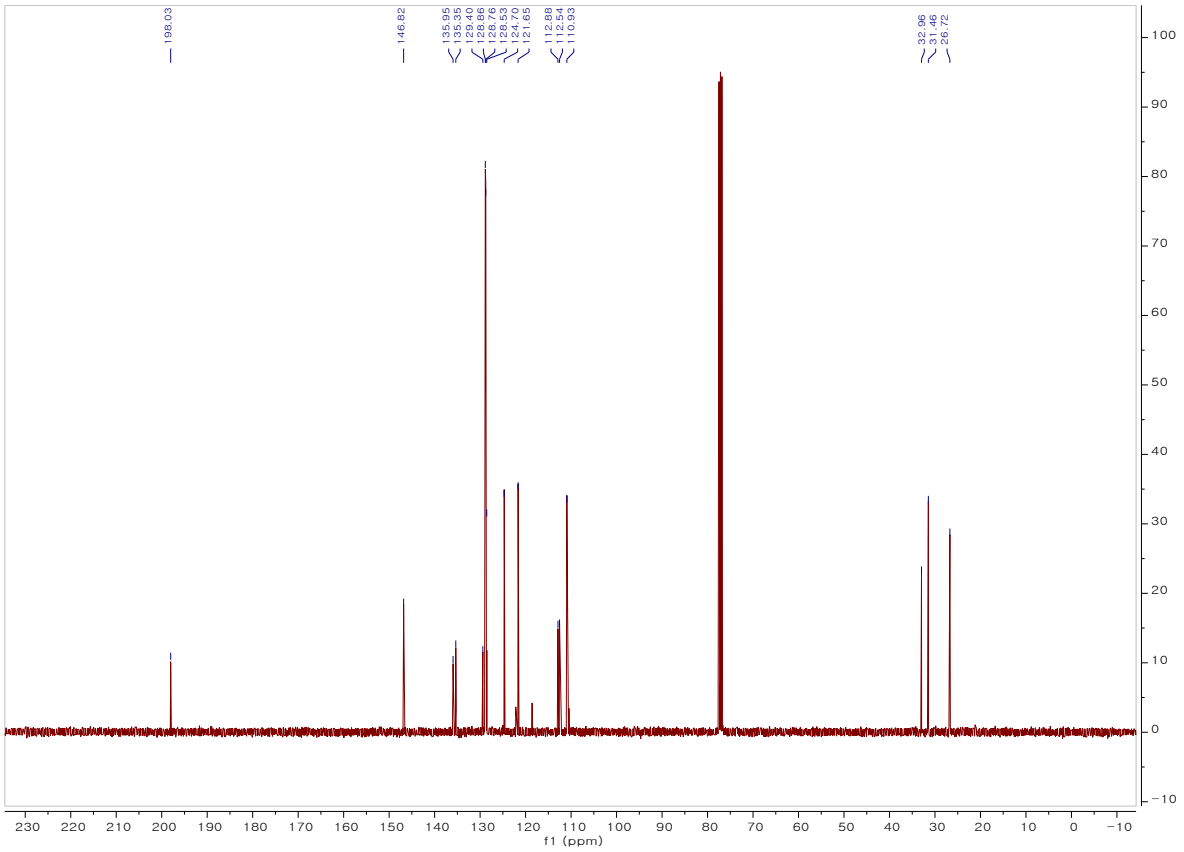

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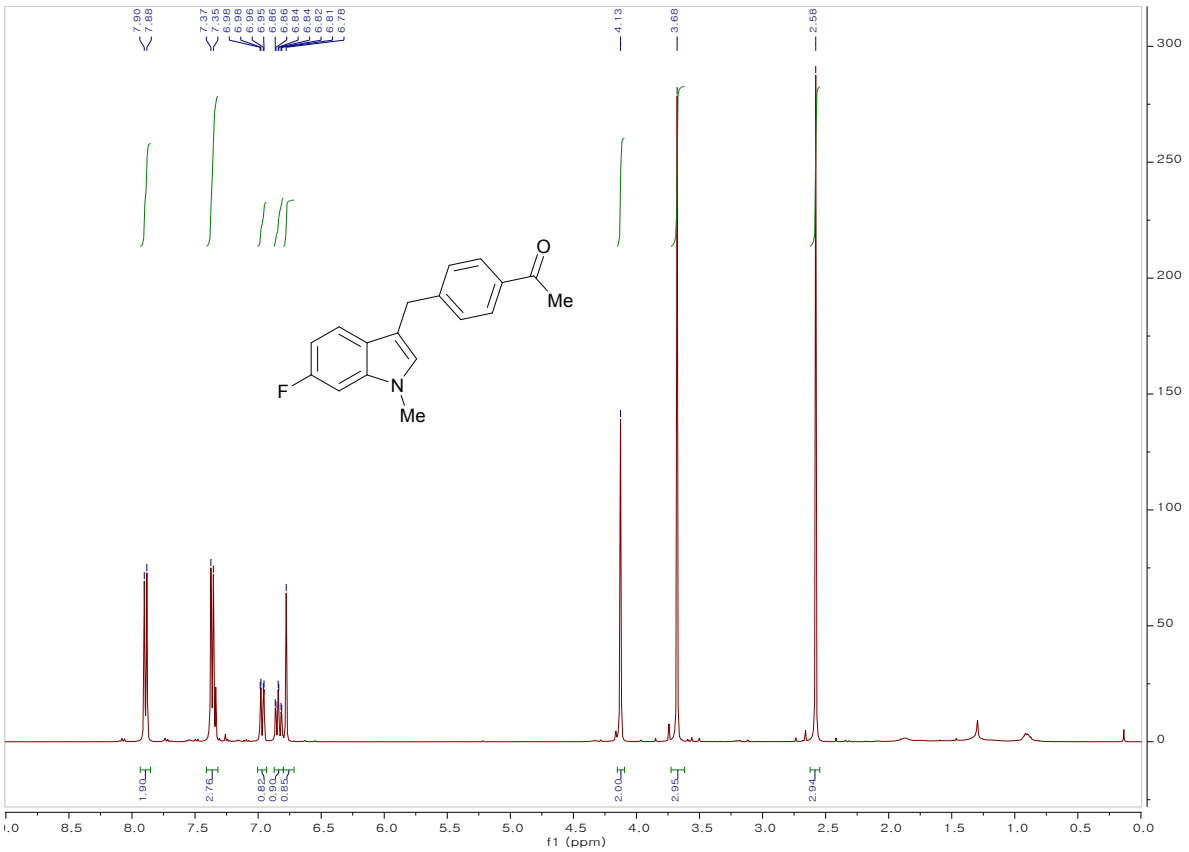

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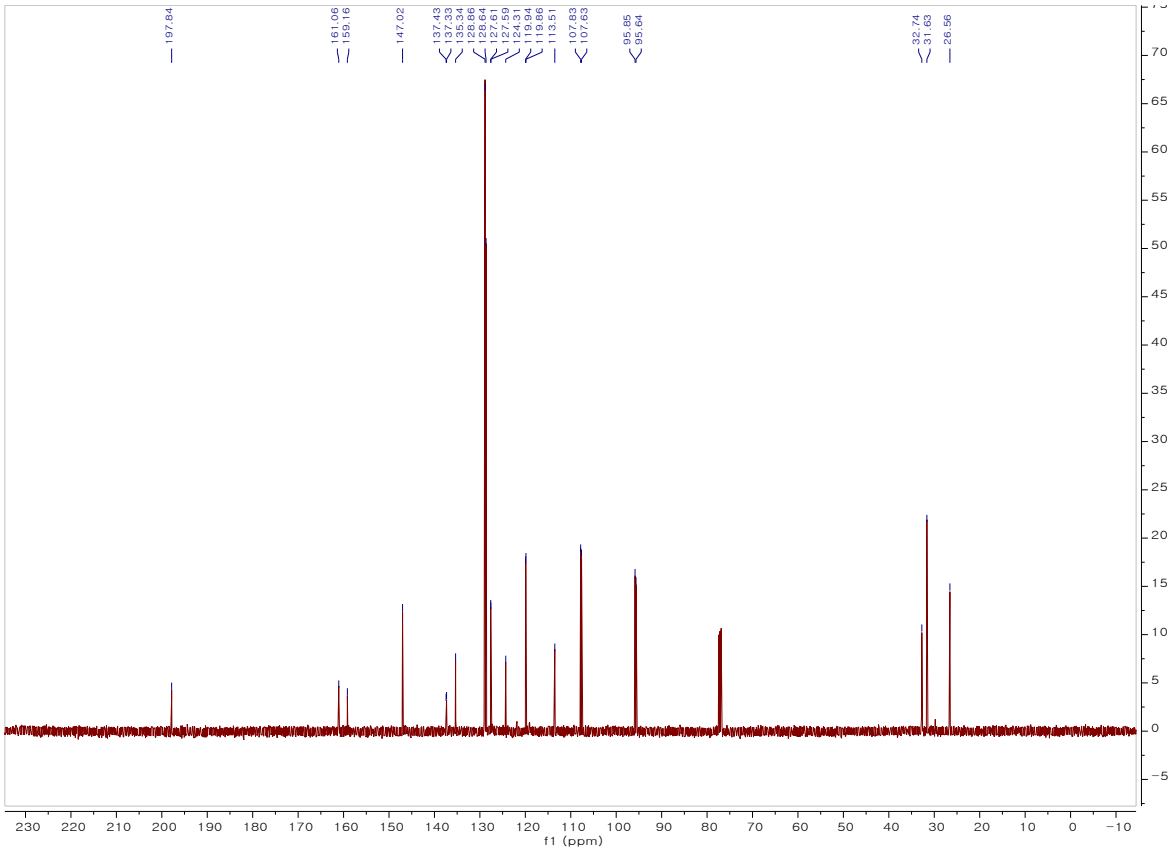
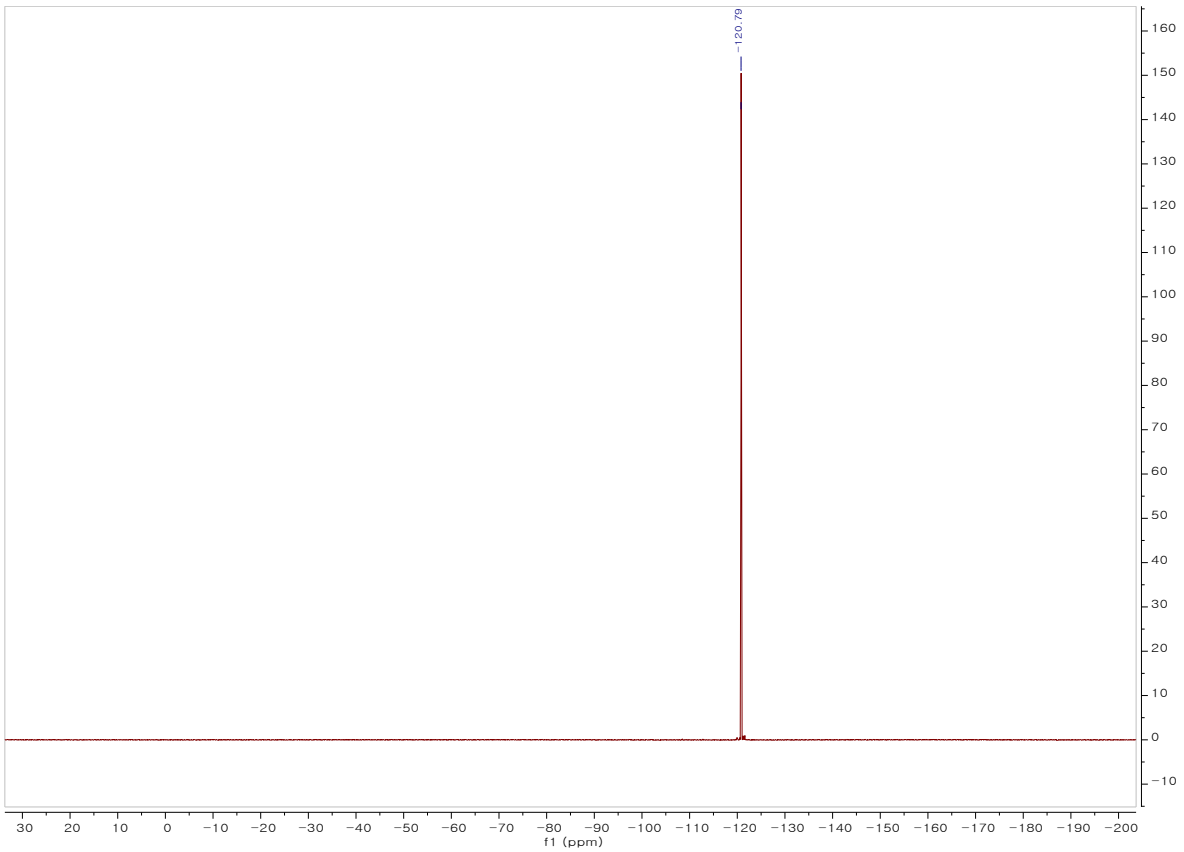


3qa (^{19}F NMR)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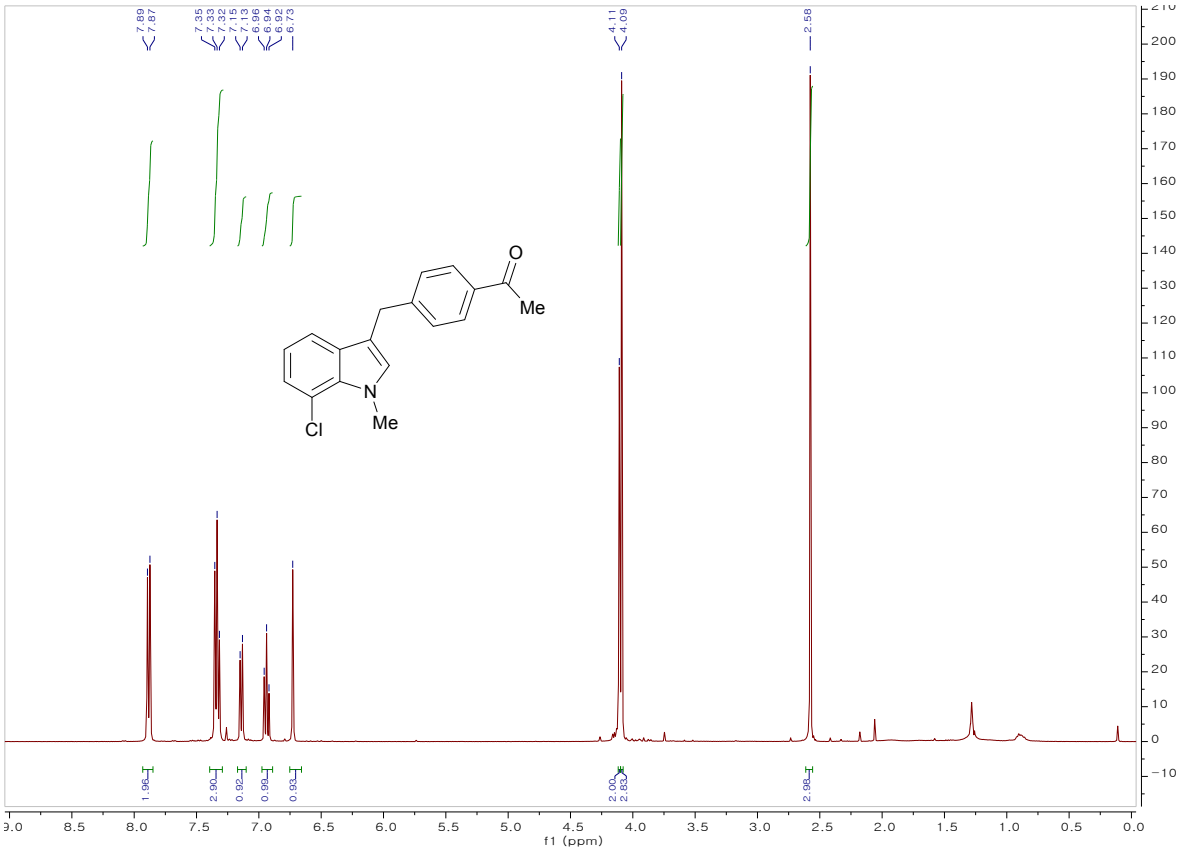
f1 (ppm)

3ra (^{1}H NMR)



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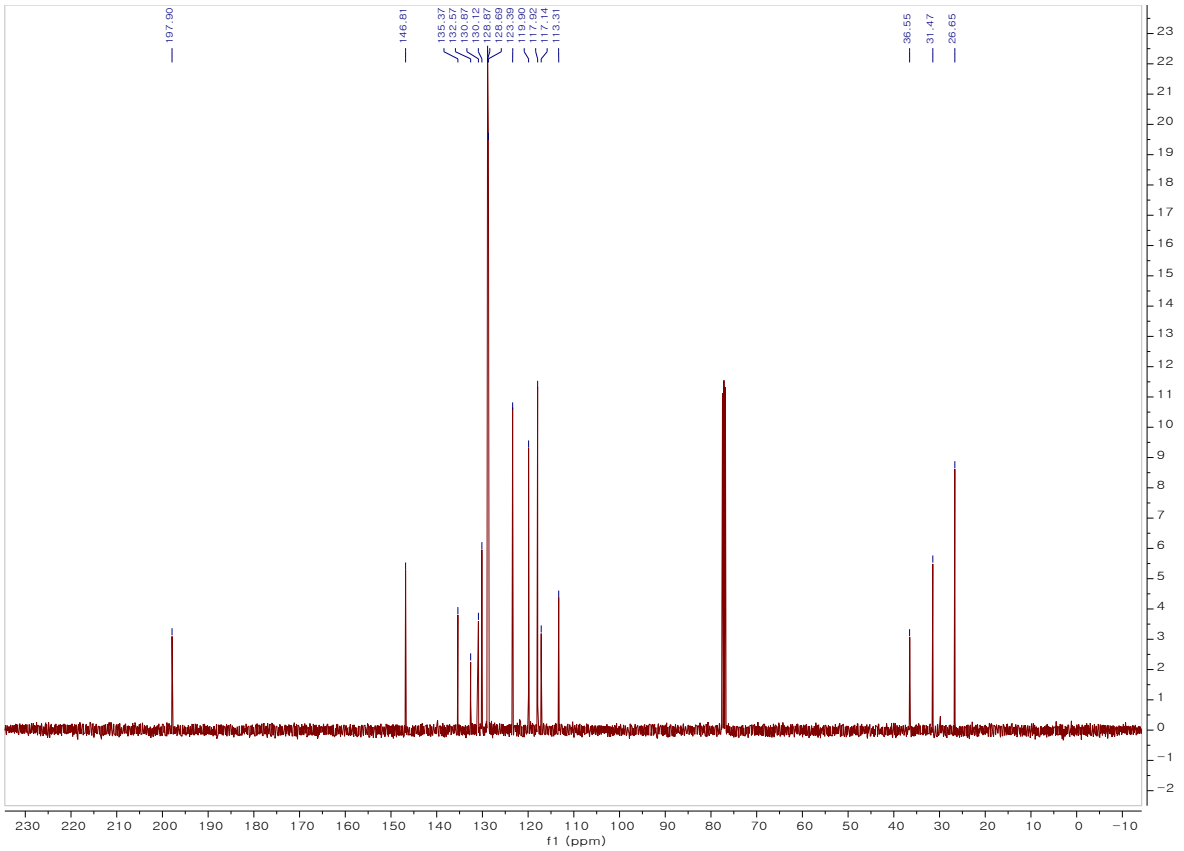

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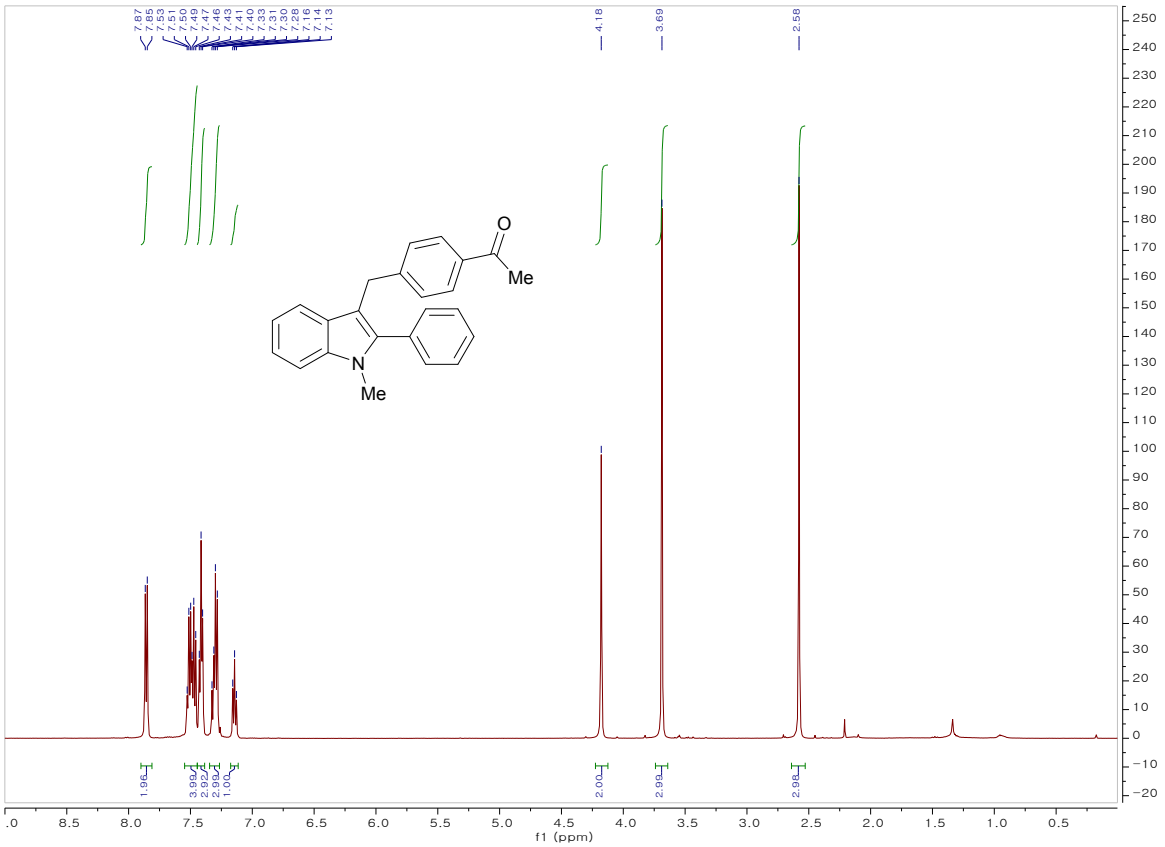

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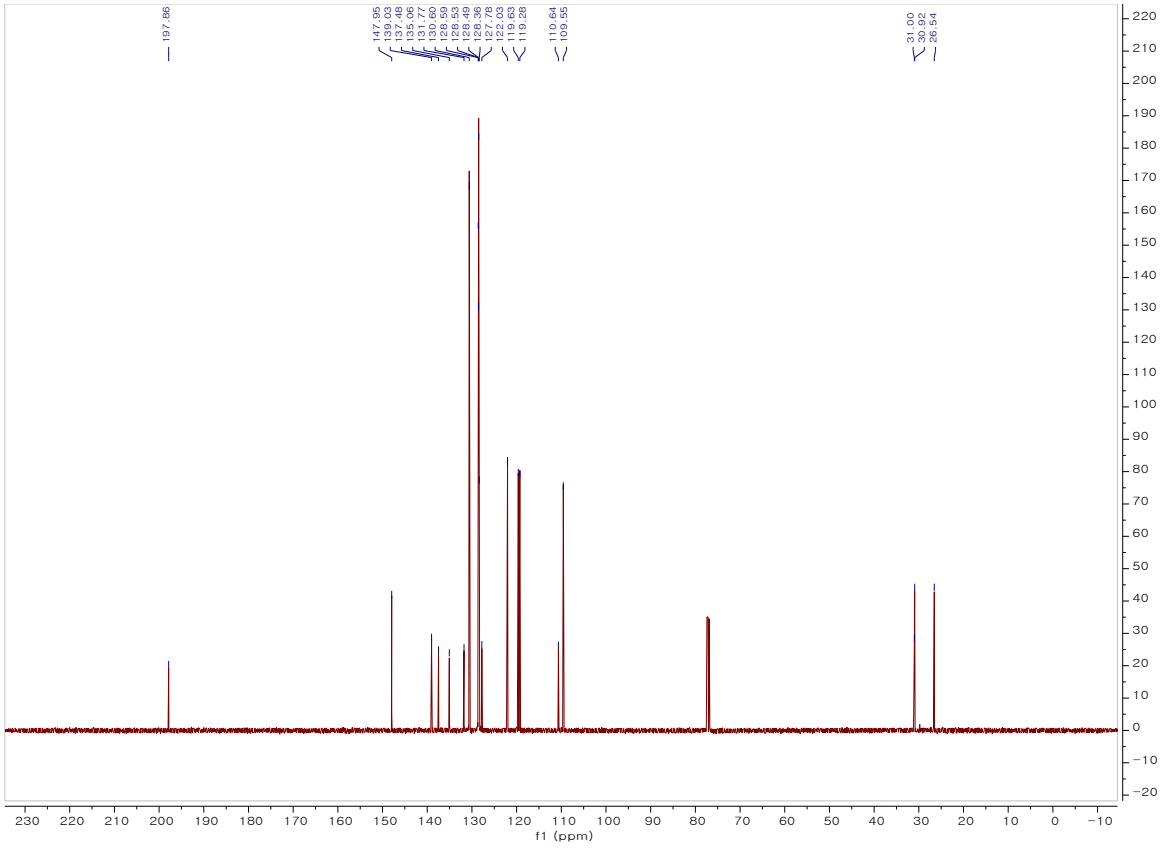

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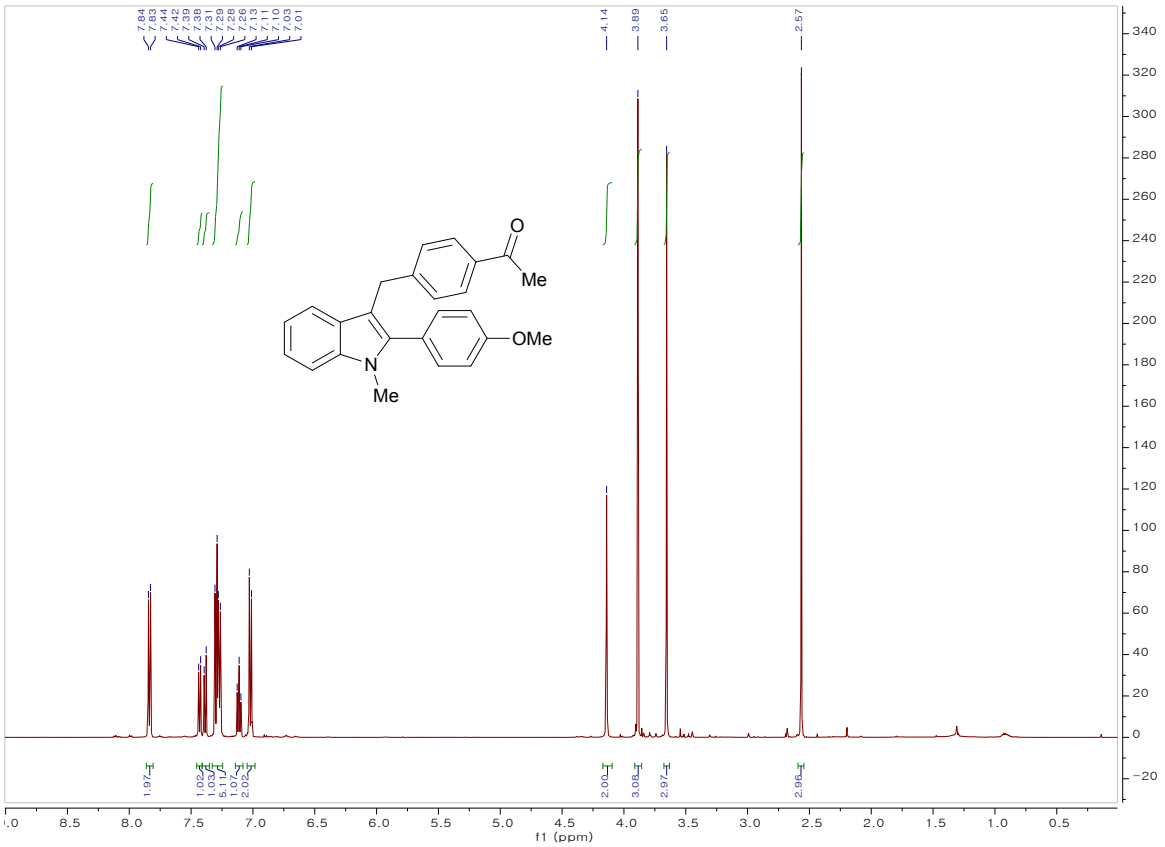

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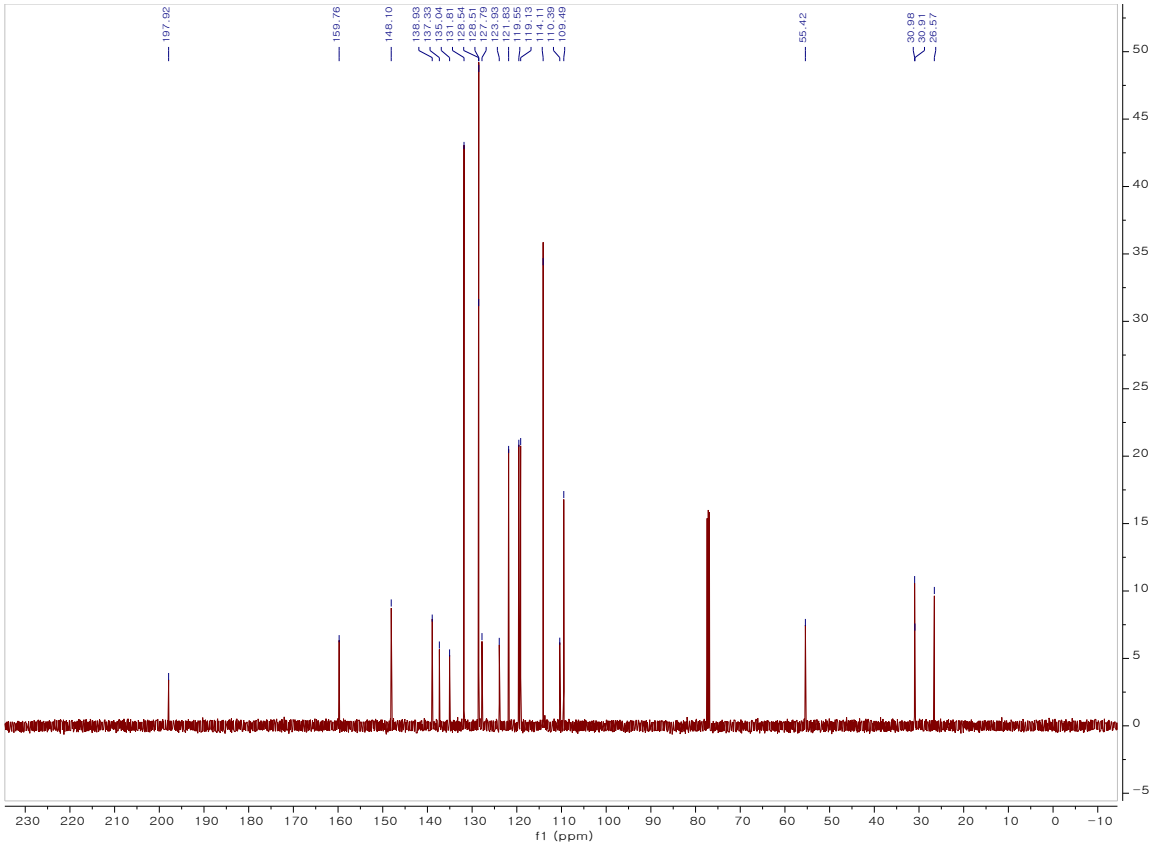

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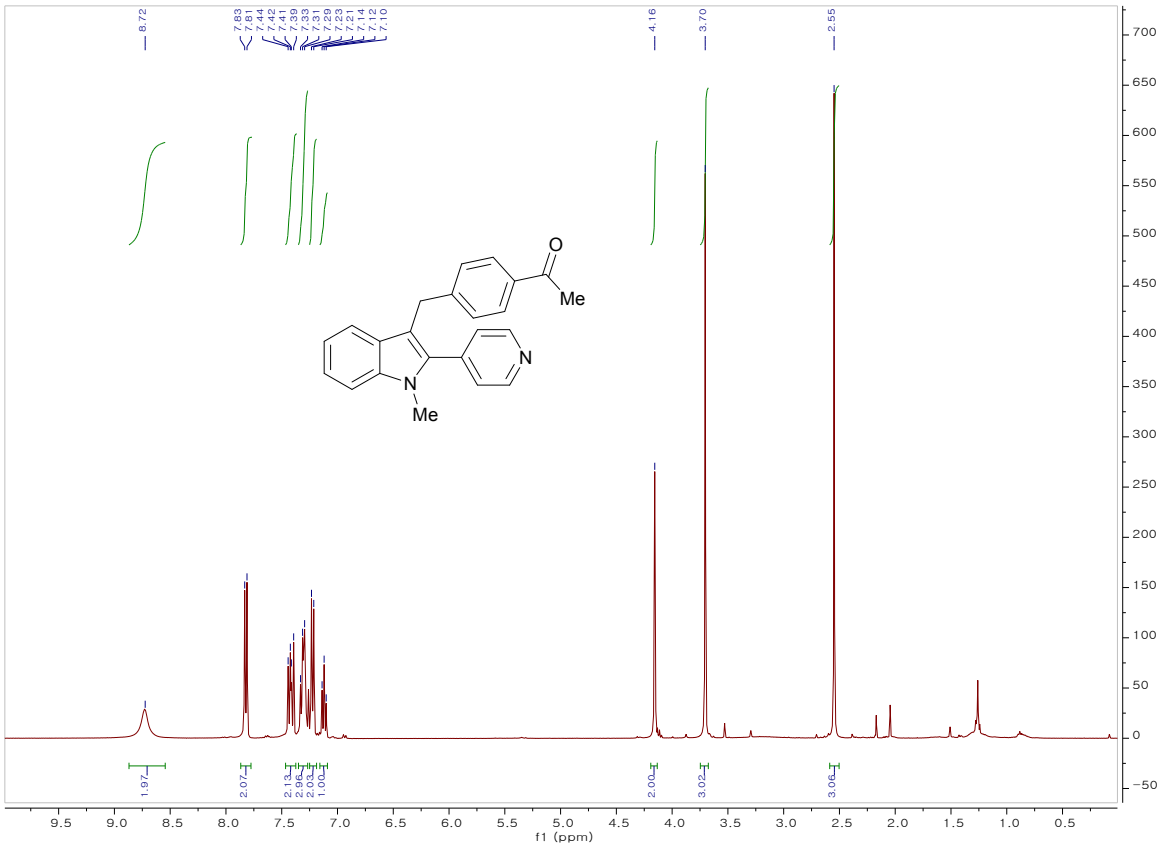

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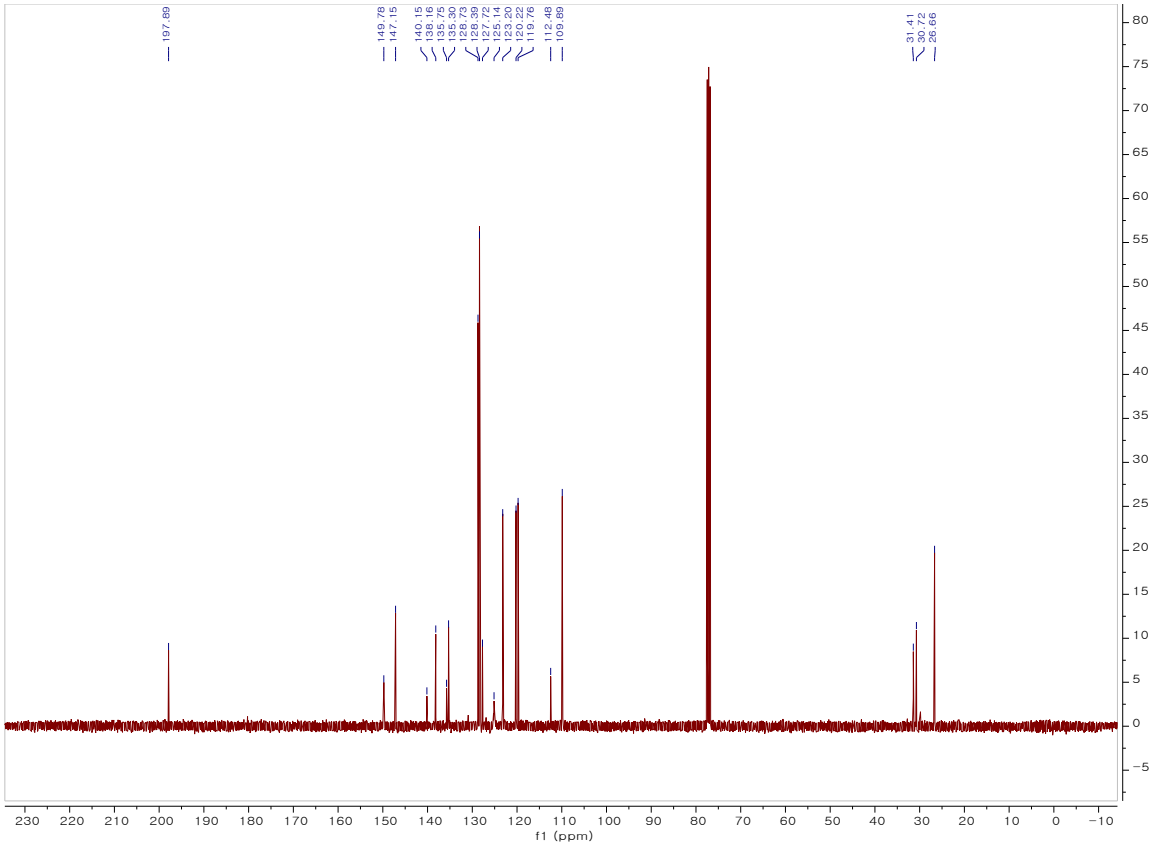

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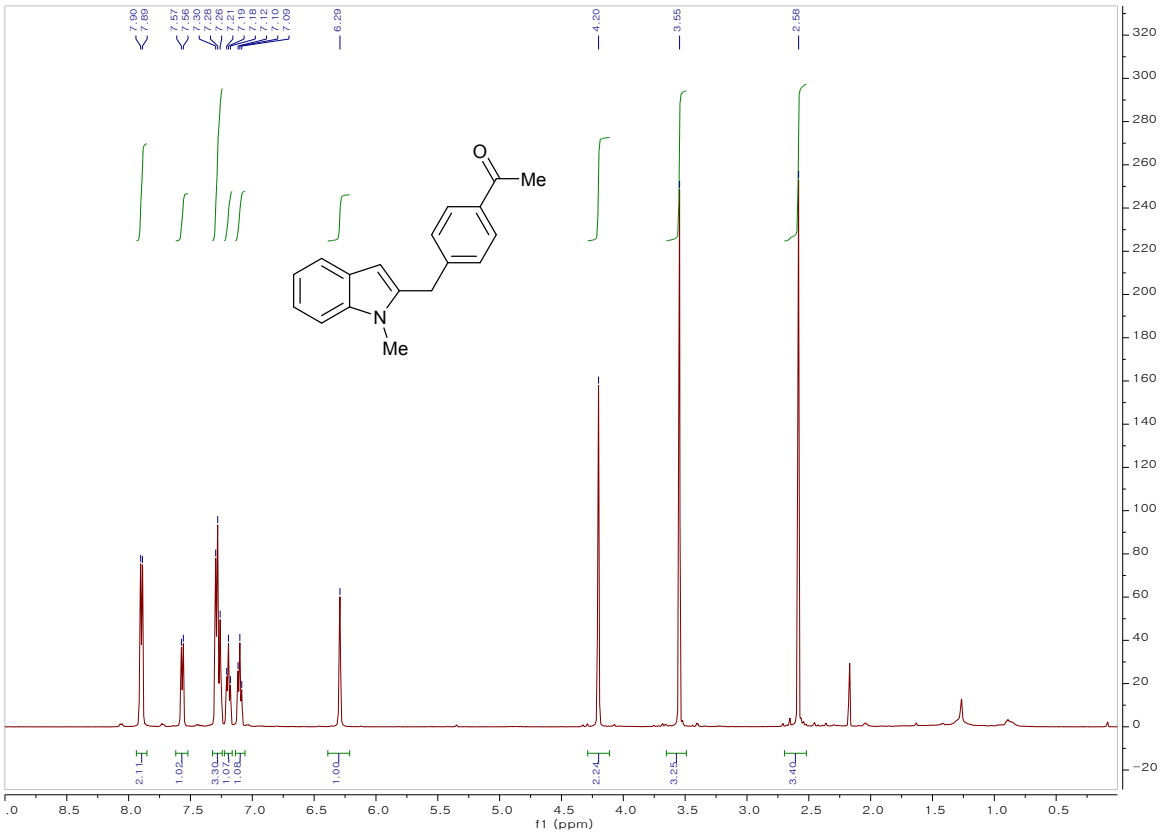

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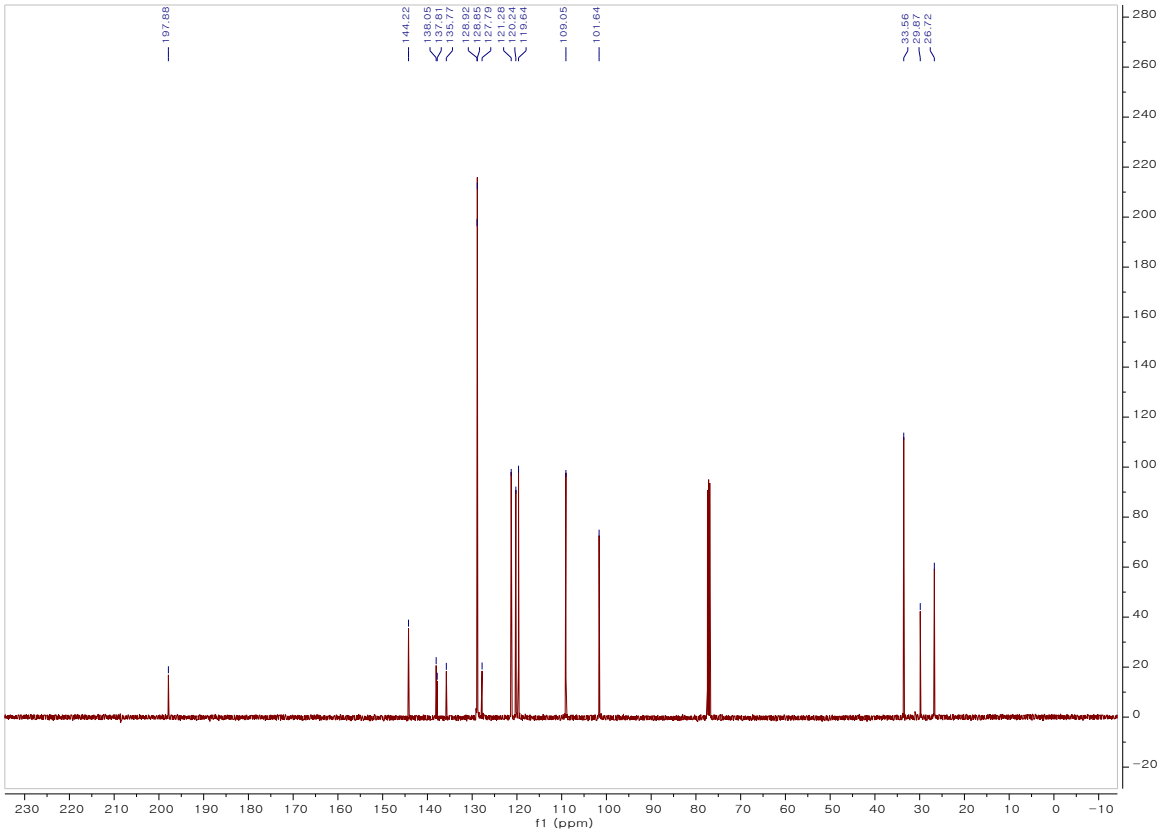
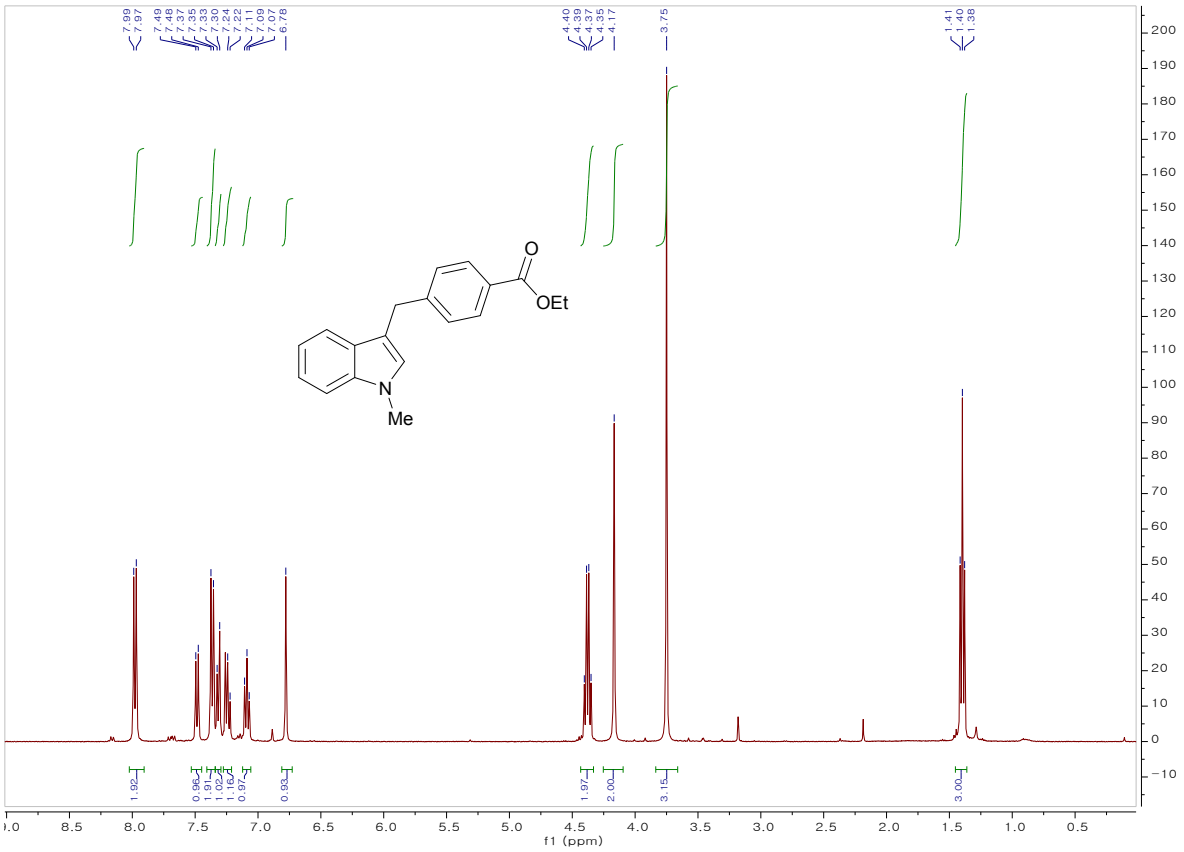
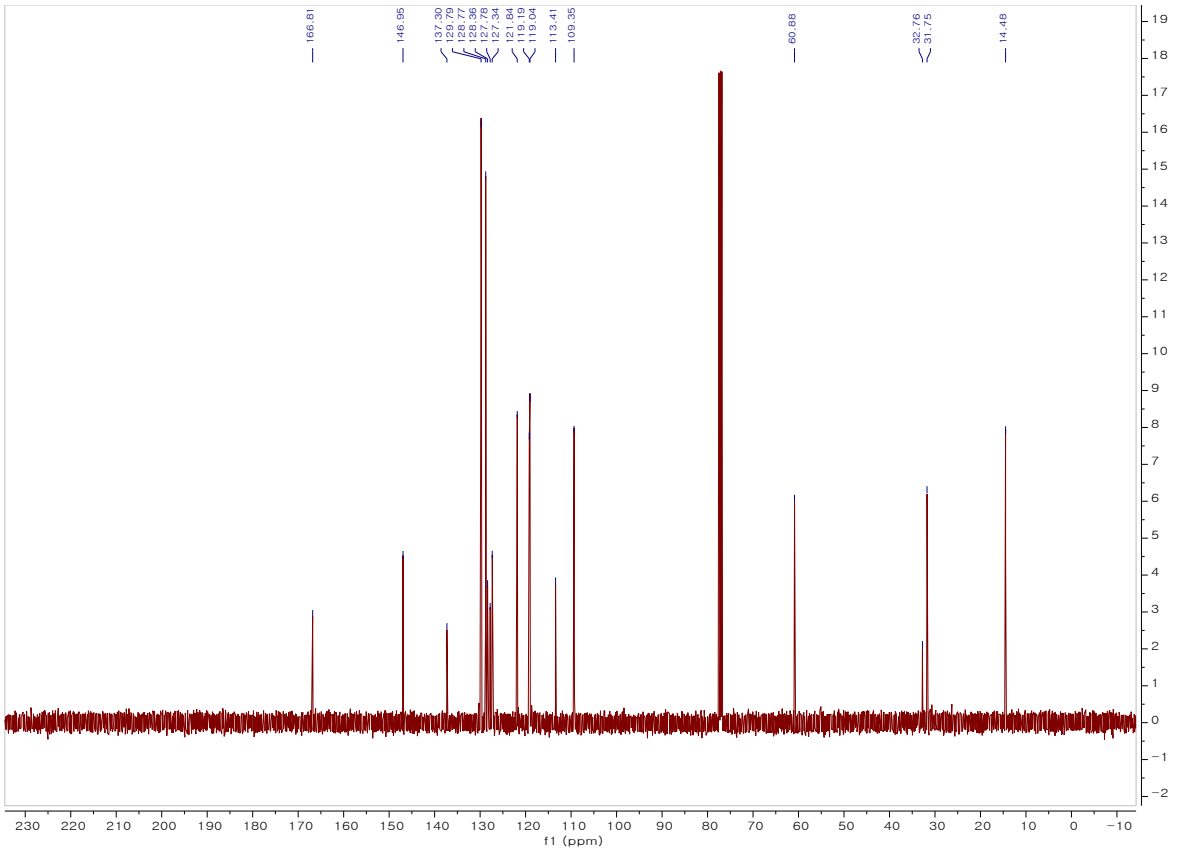


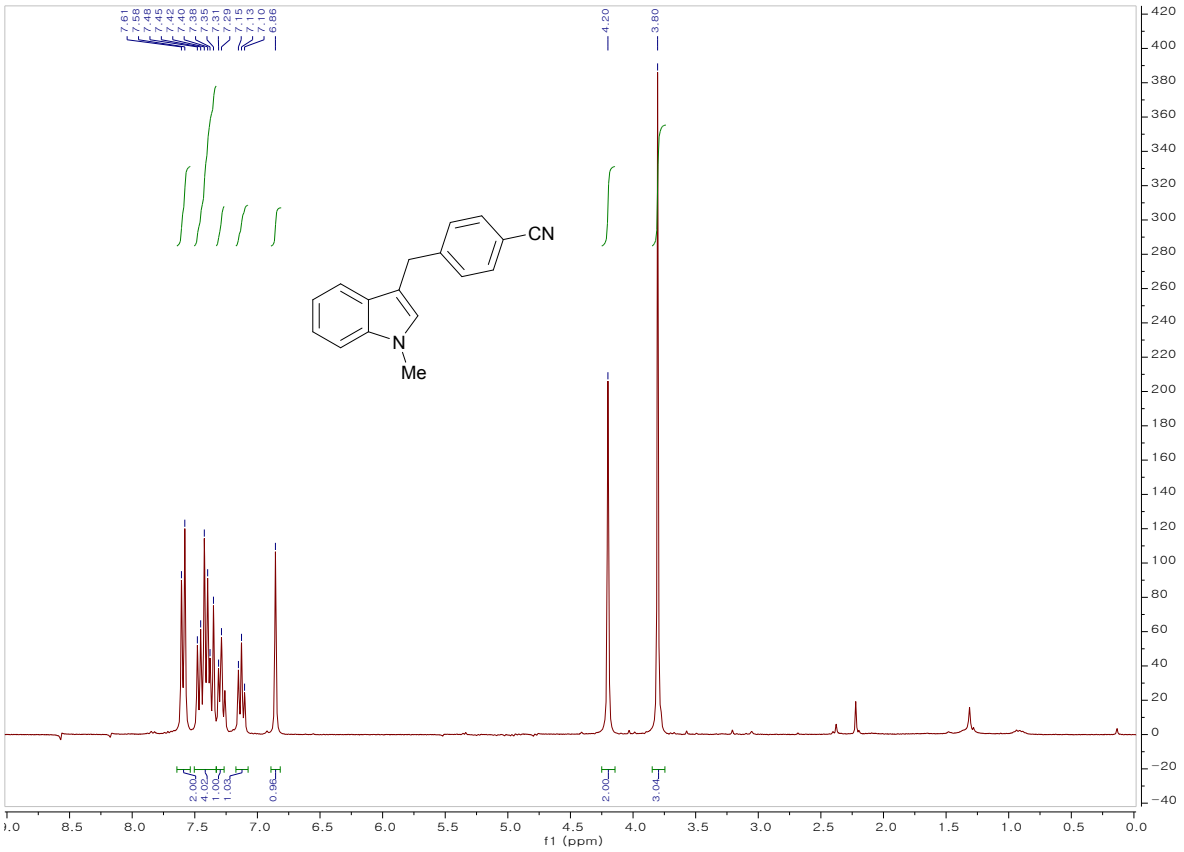
3ab (^{1}H NMR)



3ab (^{13}C NMR)



3ac (^{1}H NMR)



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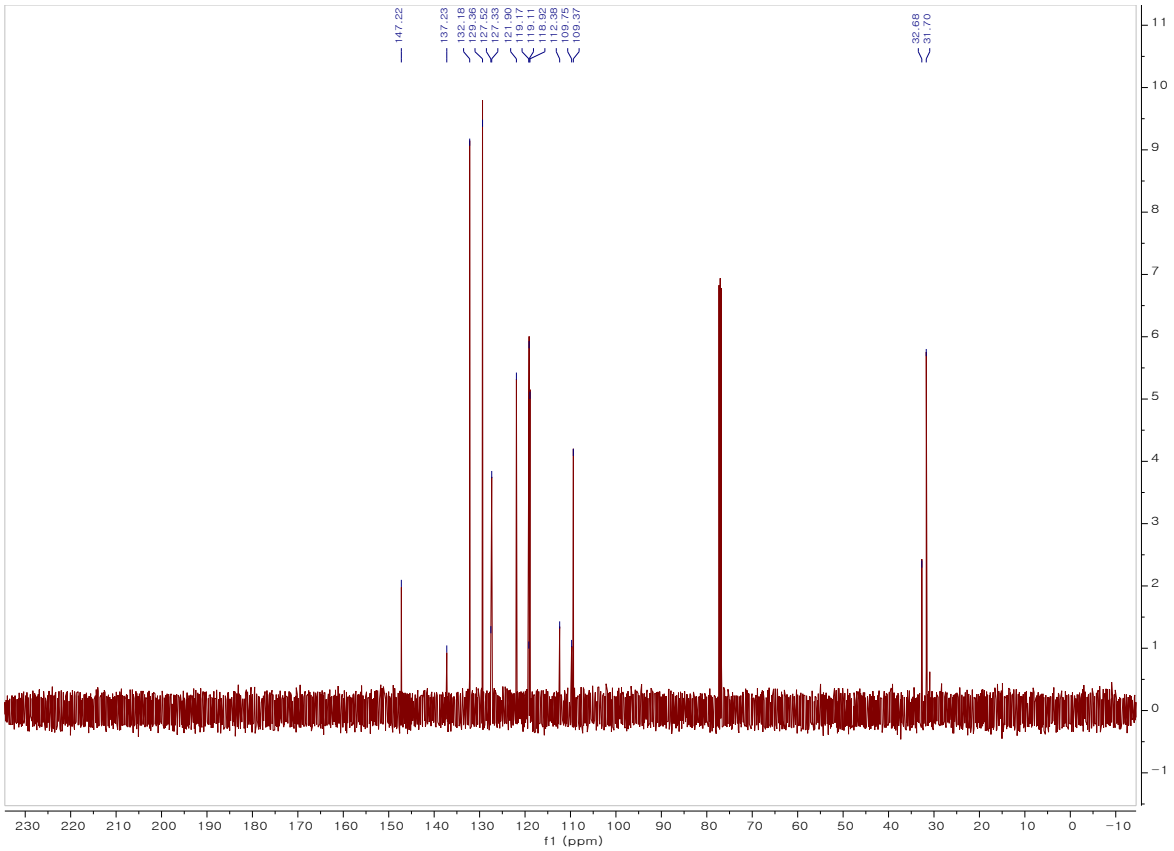
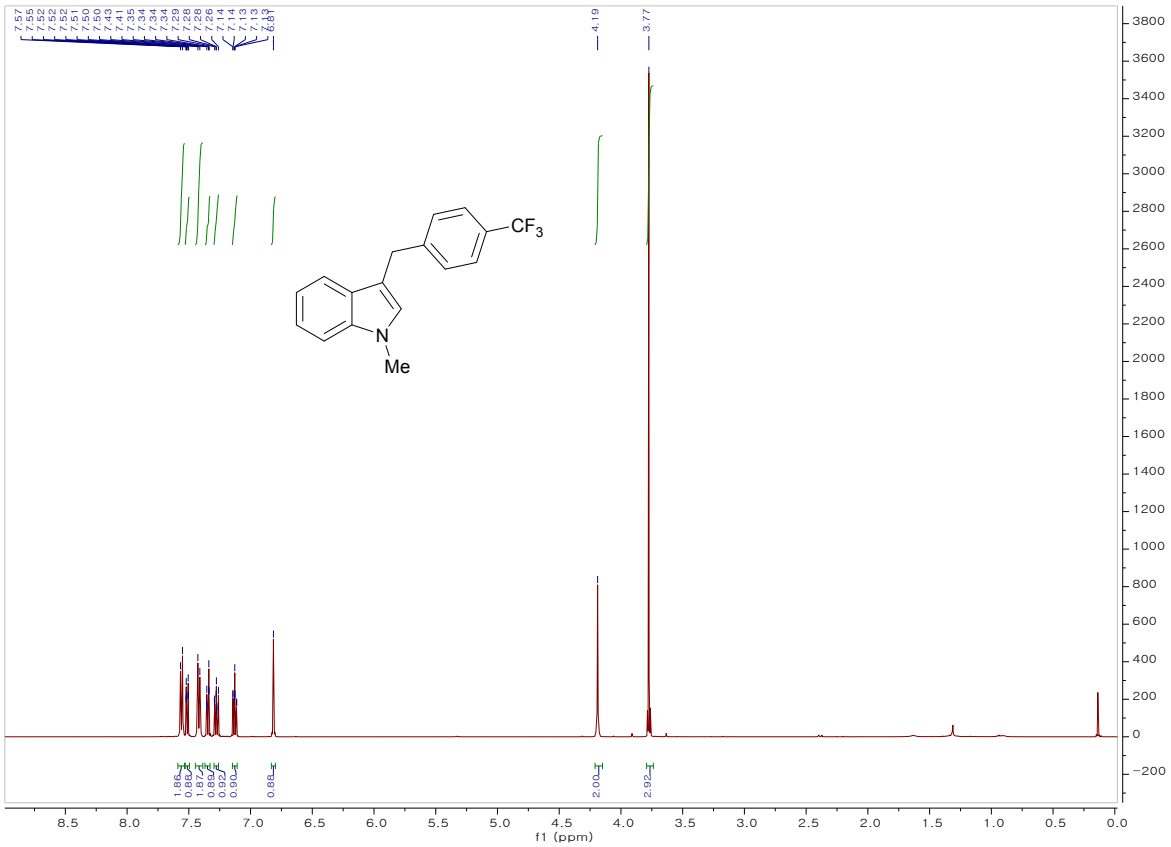
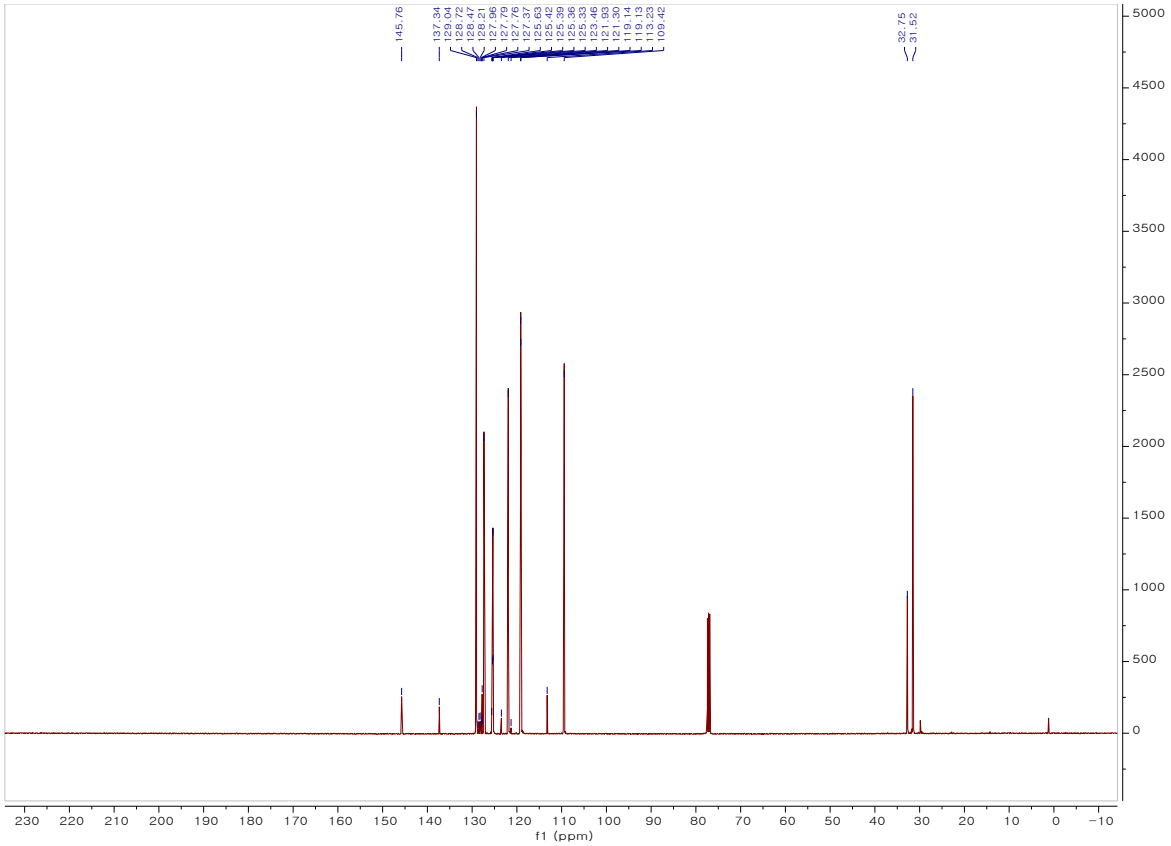


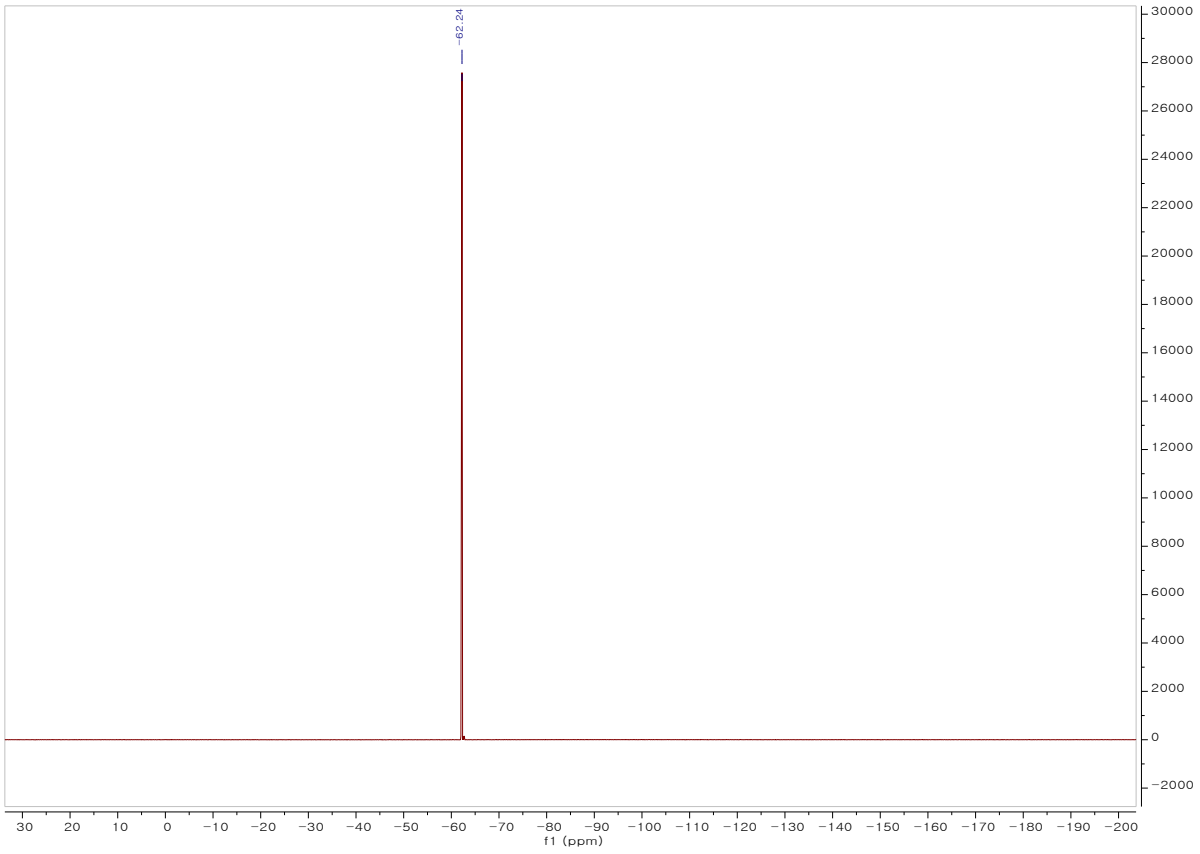
3ad (^{1}H NMR)



3ad (^{13}C NMR)



3ad (^{19}F NMR)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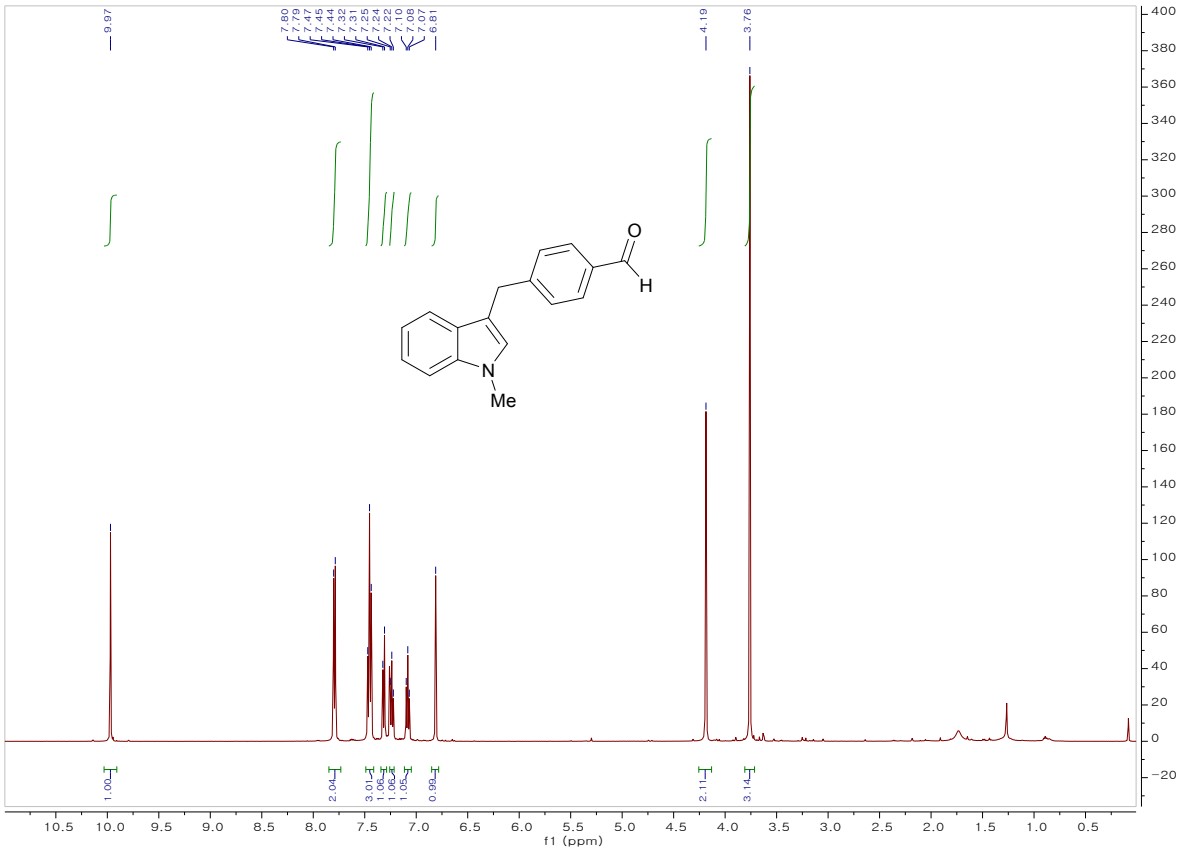
f1 (ppm)

3ae (^{1}H NMR)



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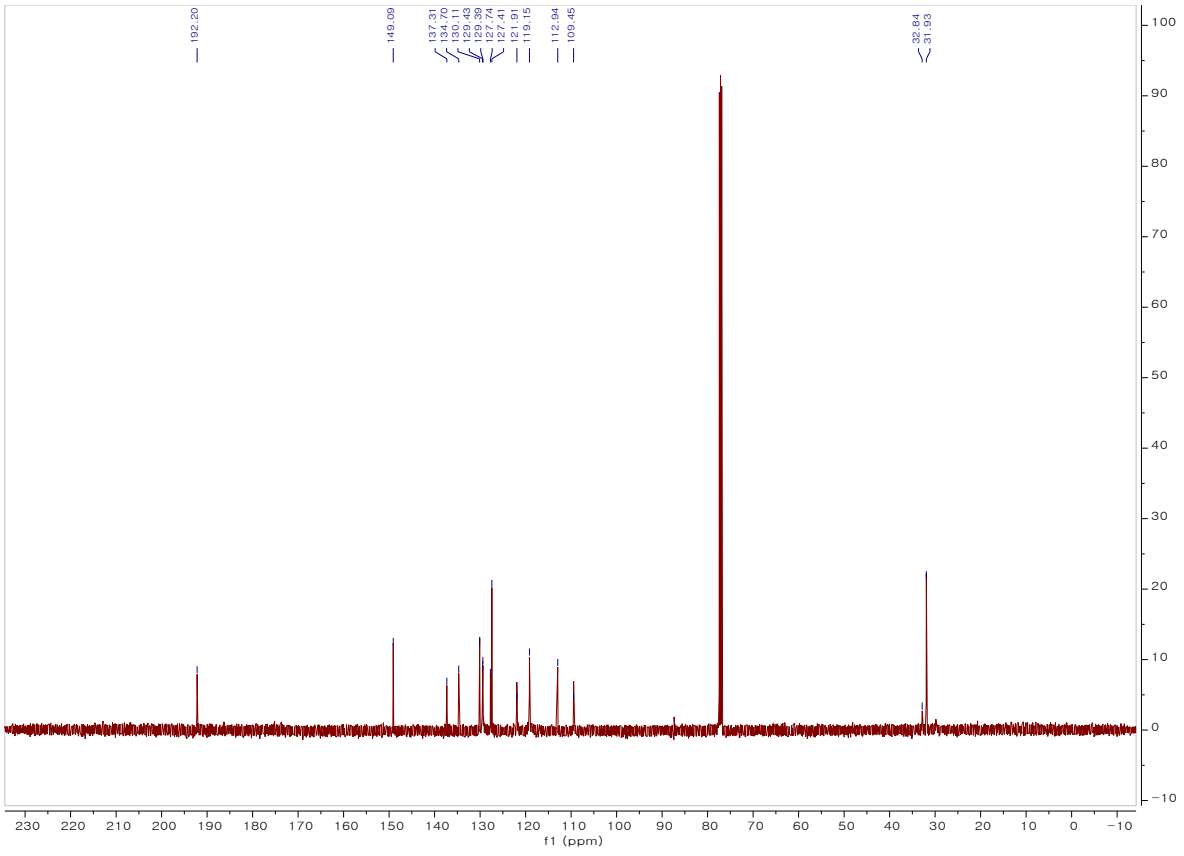

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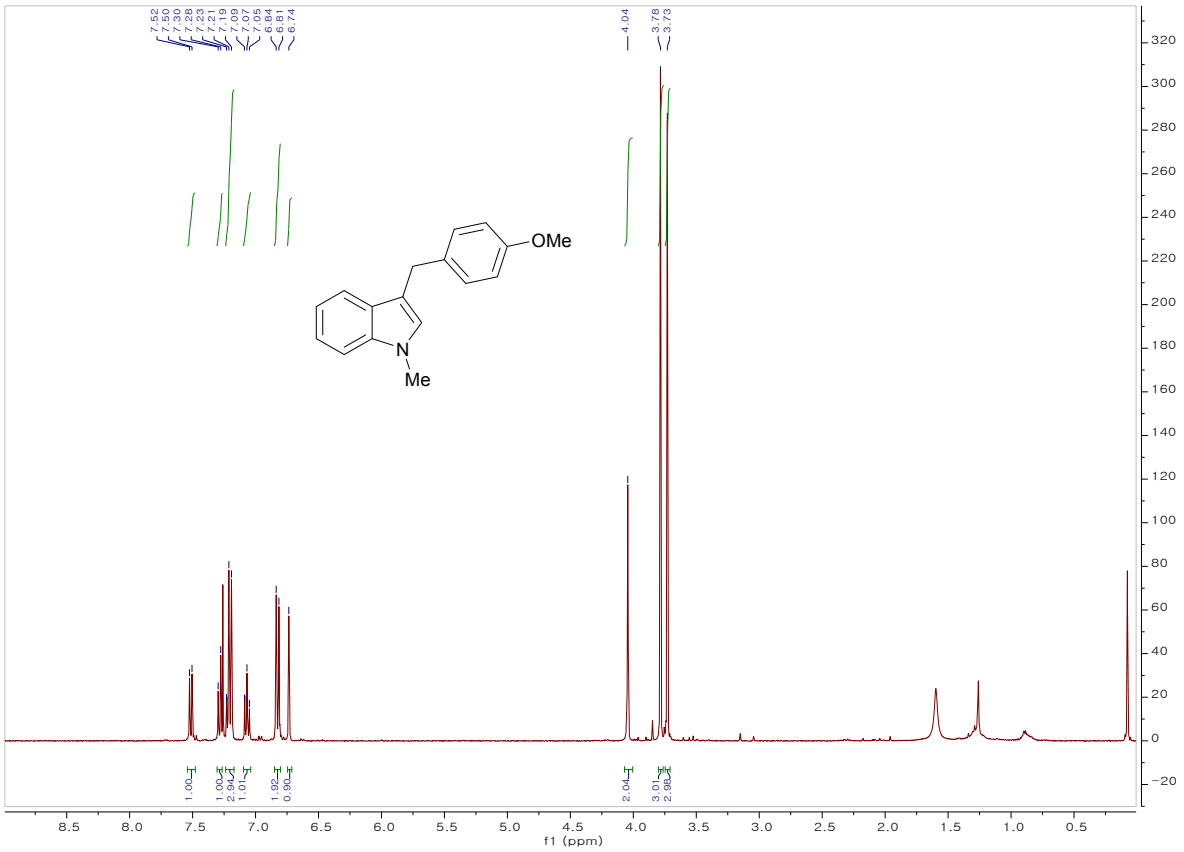

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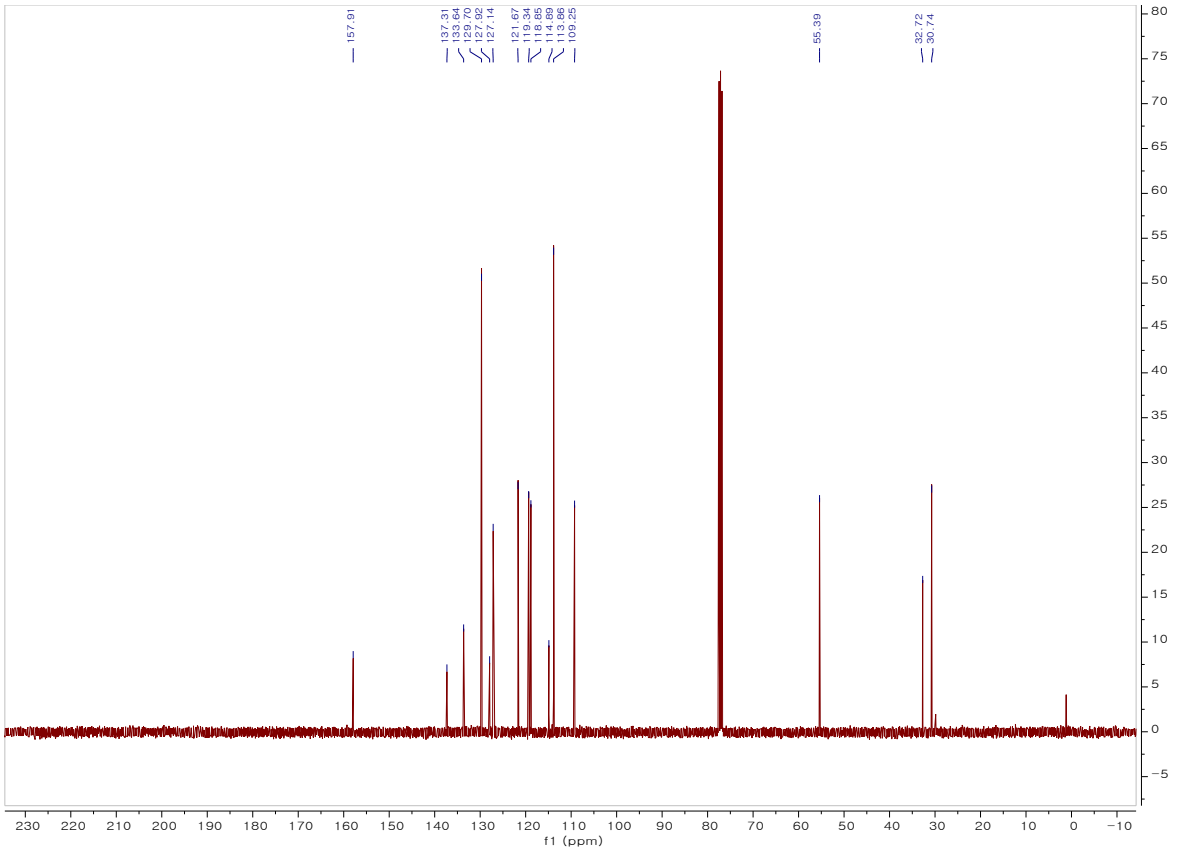
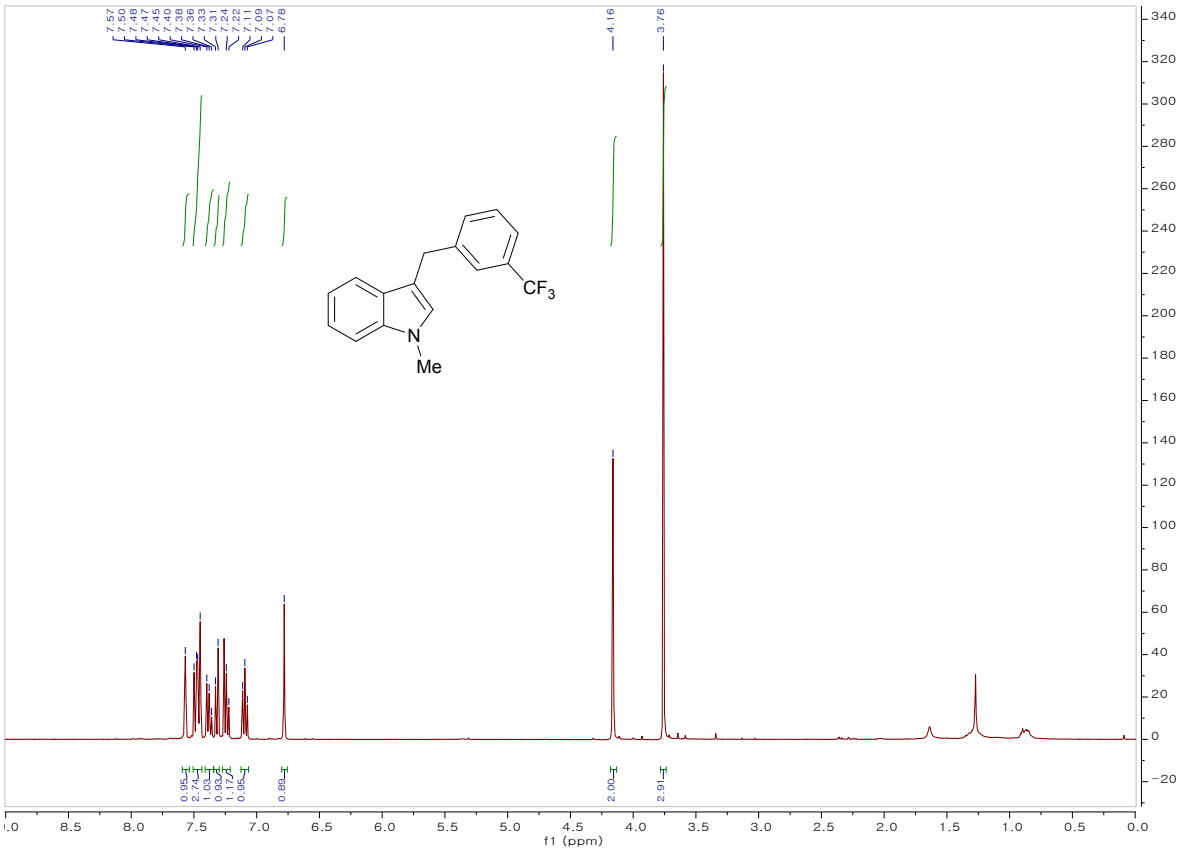
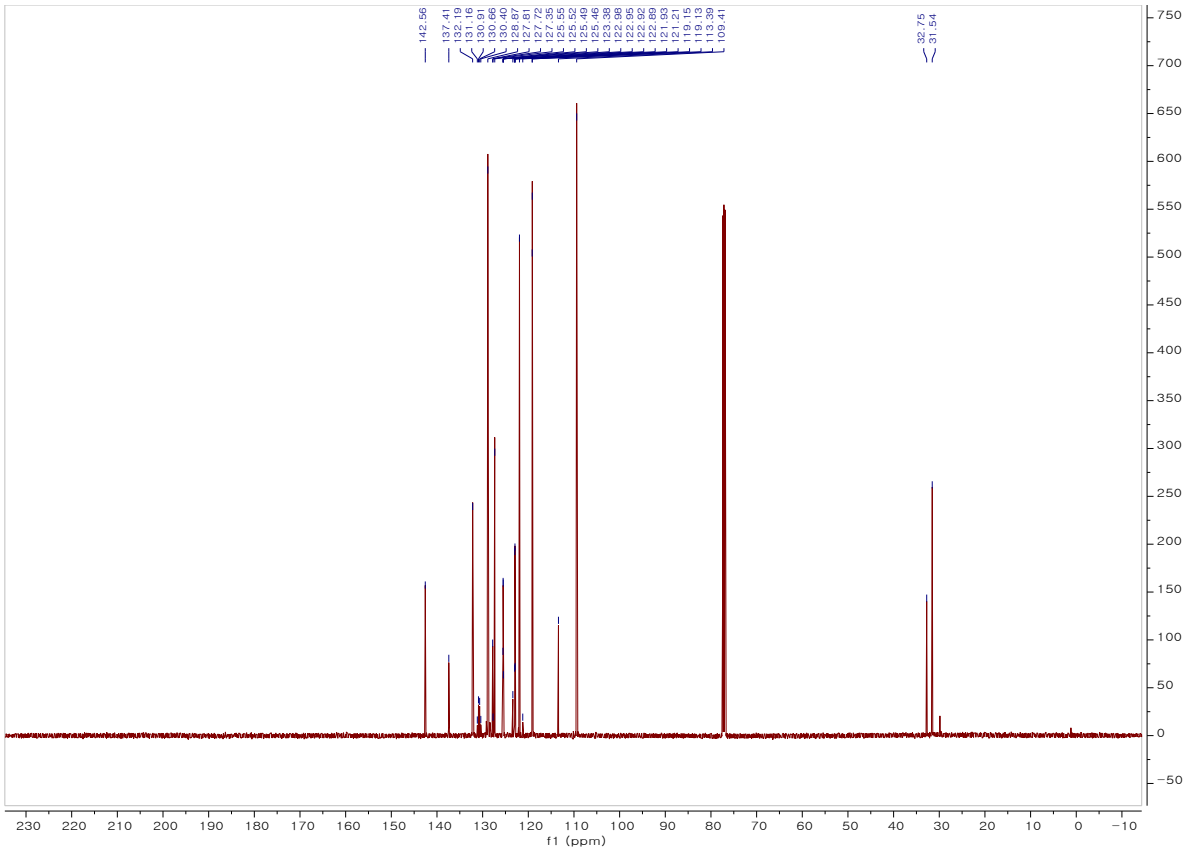


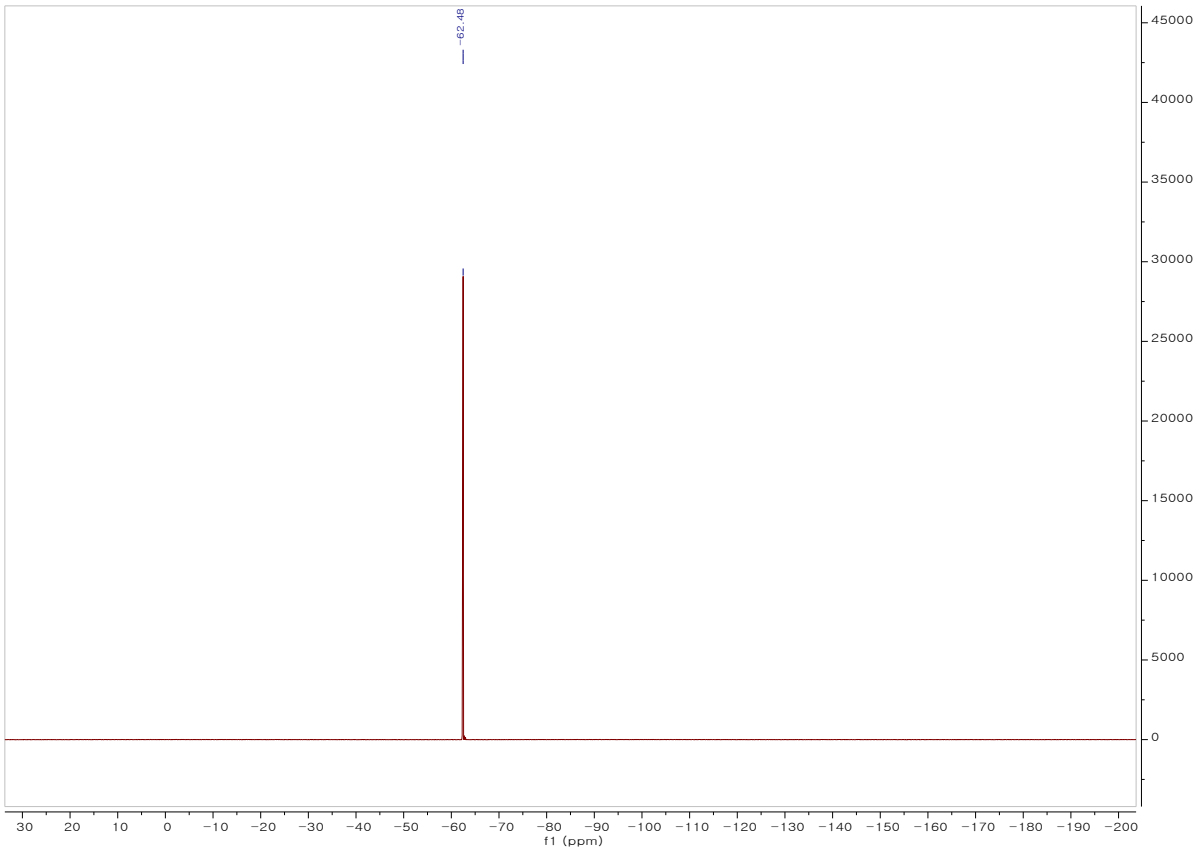
3ag (^{1}H NMR)



3ag (^{13}C NMR)



3ag (^{19}F NMR)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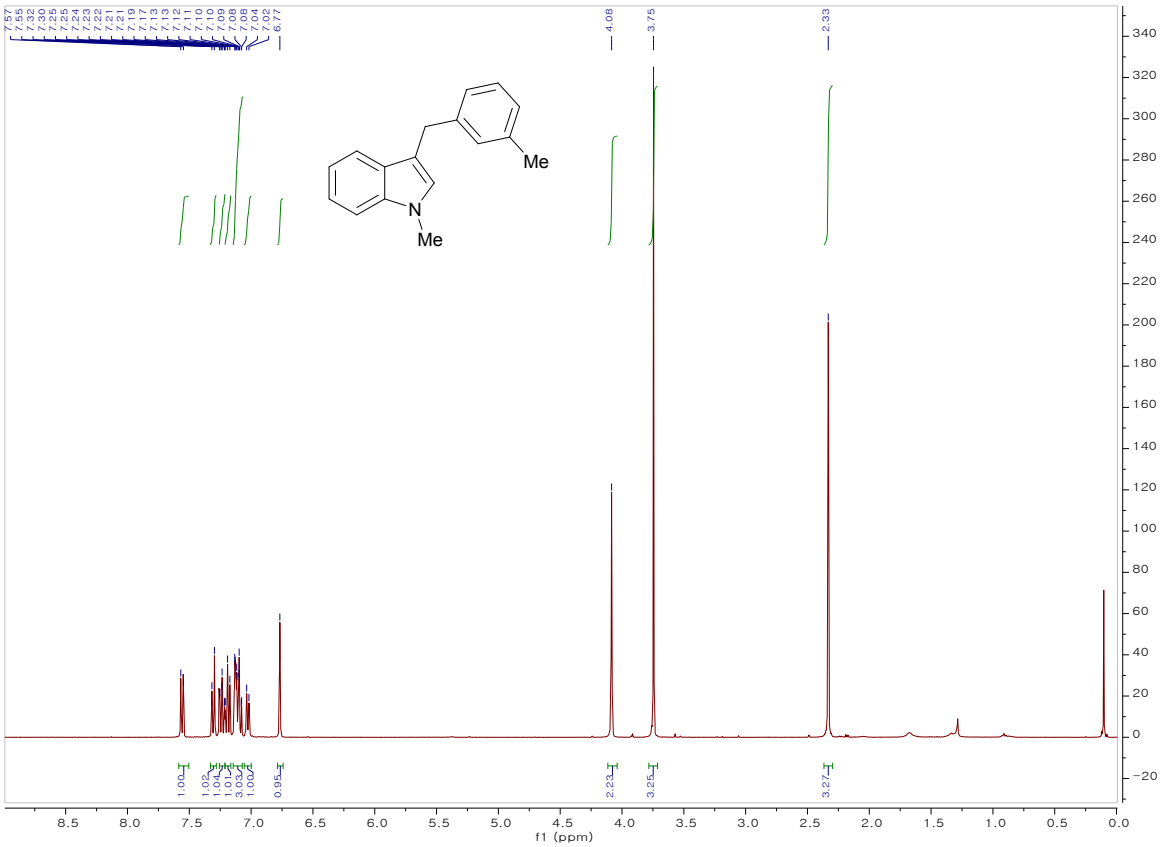
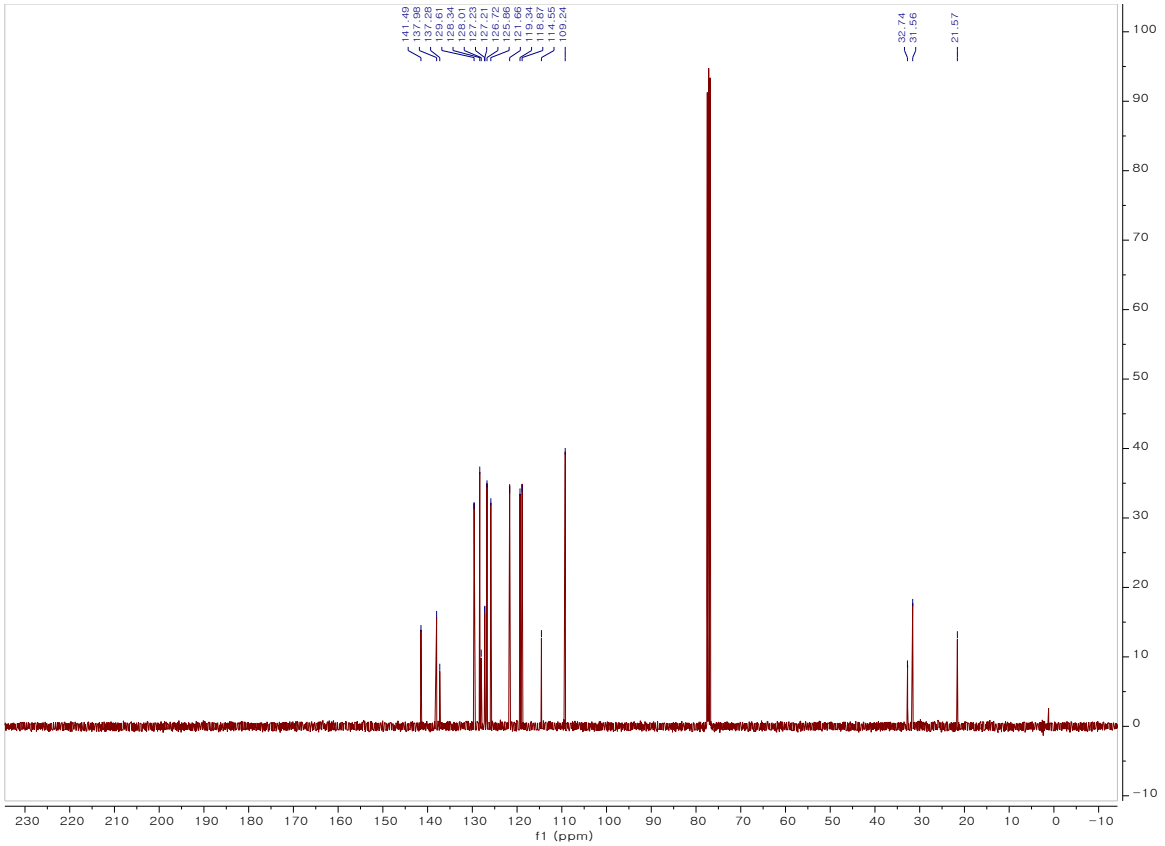
f1 (ppm)

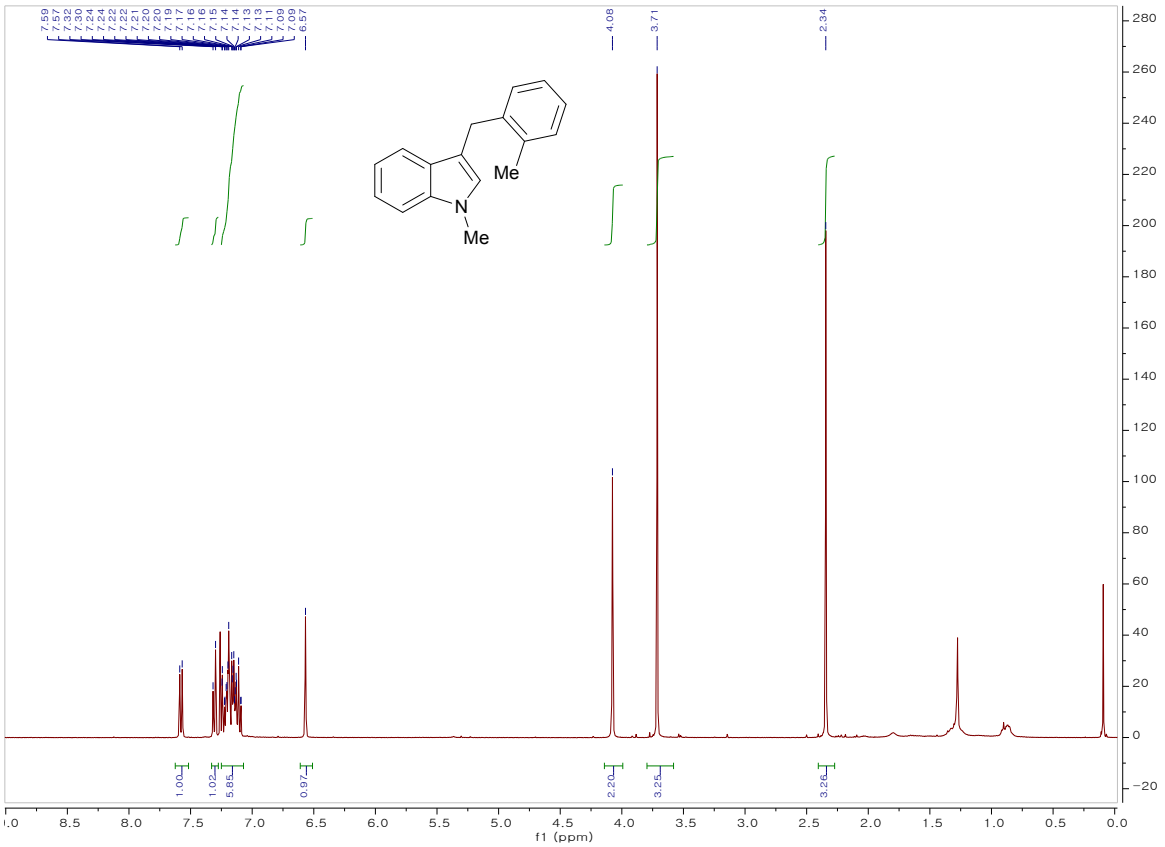
3ah (^{1}H NMR)



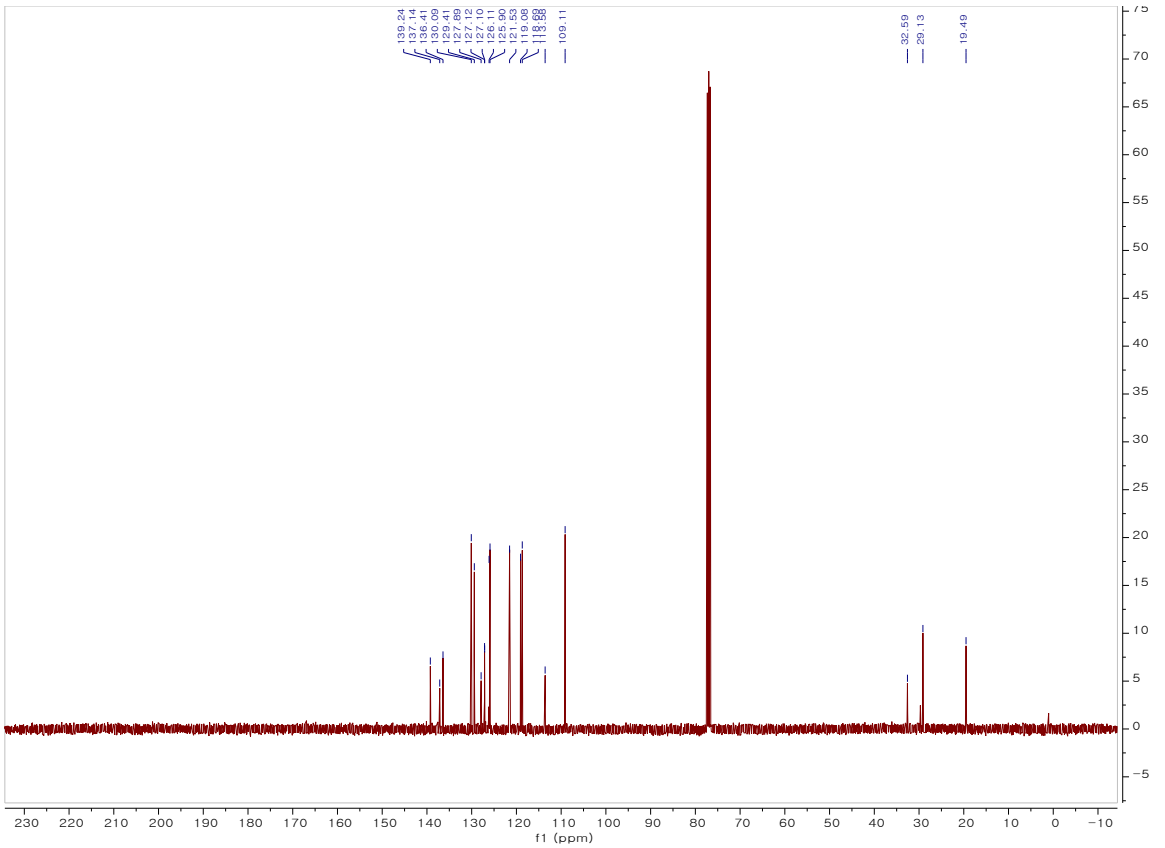
3ah (^{13}C NMR)



3ai (^{1}H NMR)



3ai (^{13}C NMR)



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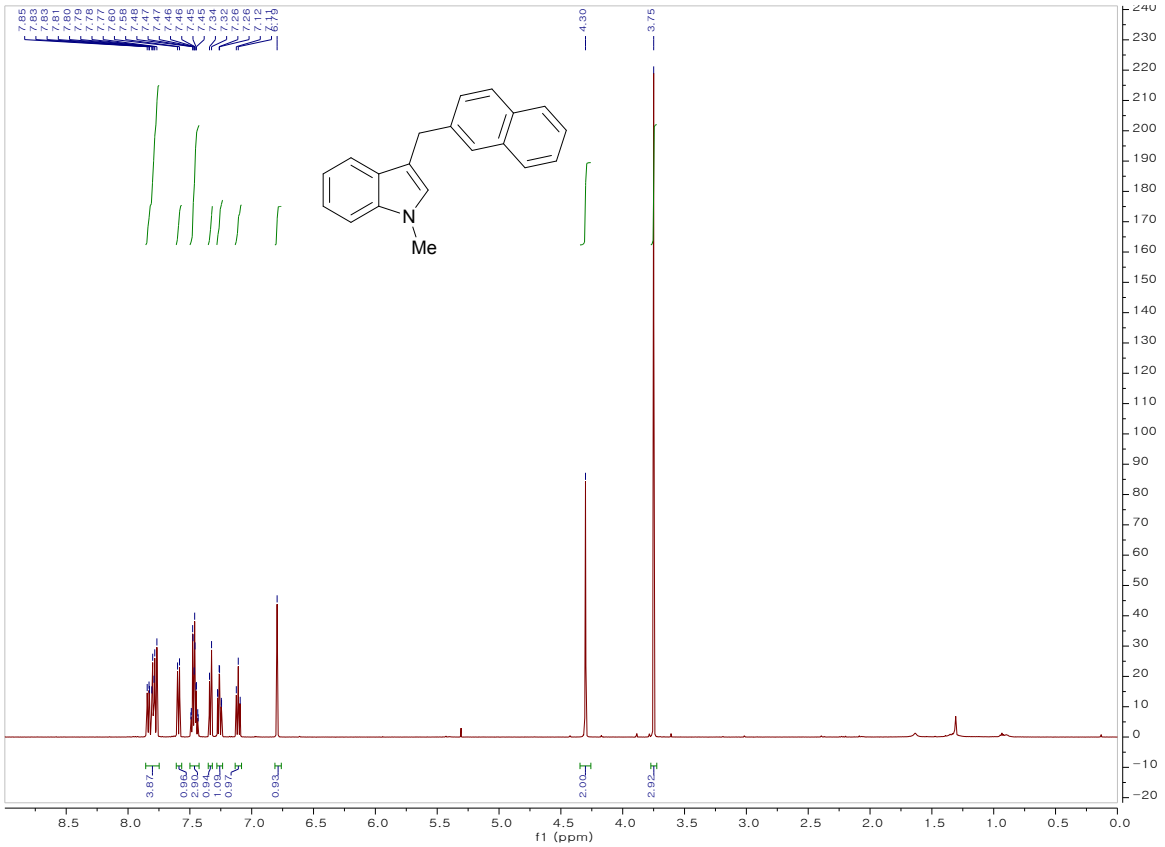

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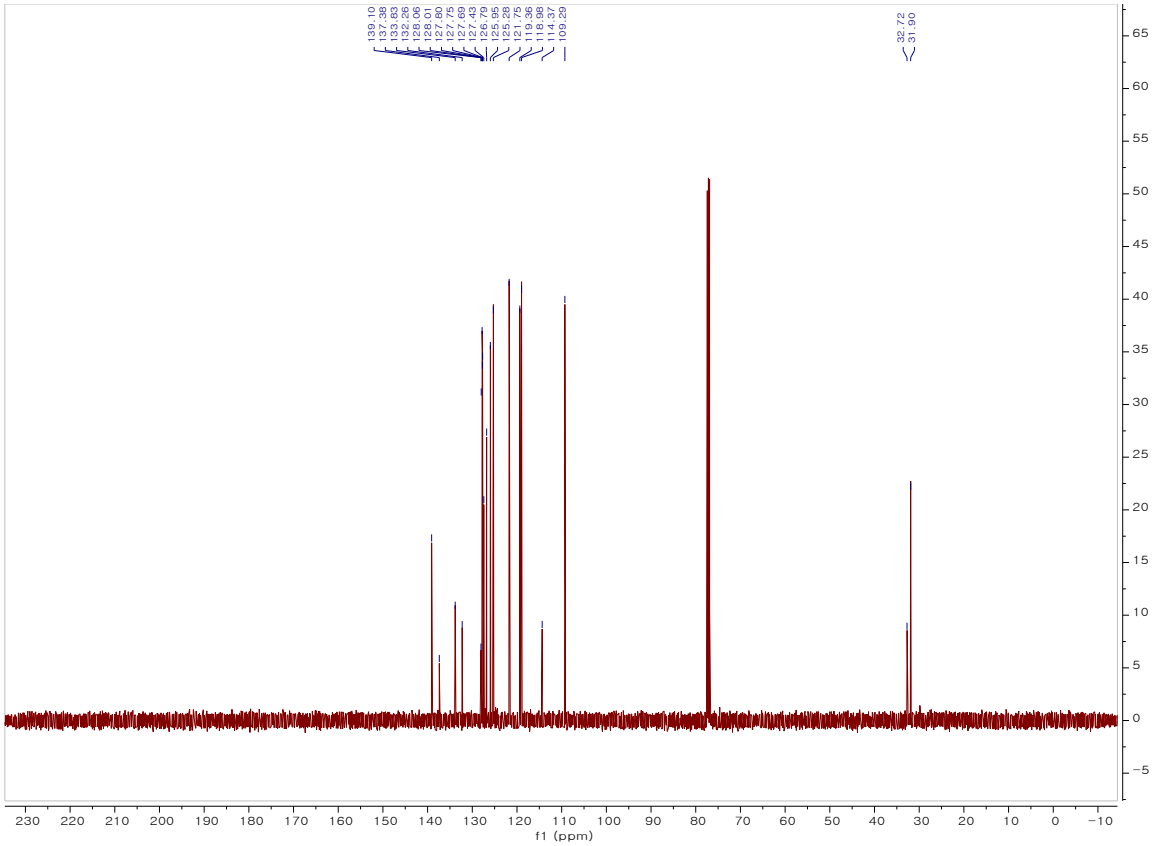

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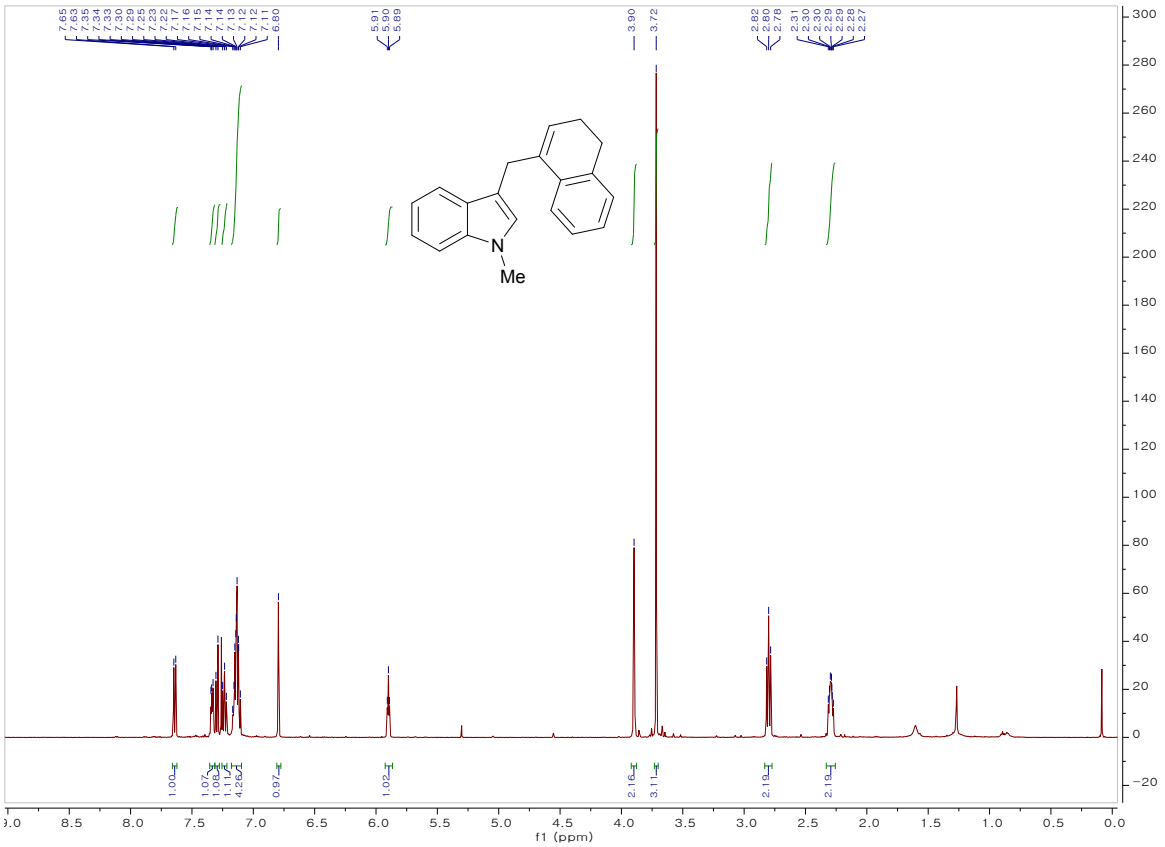

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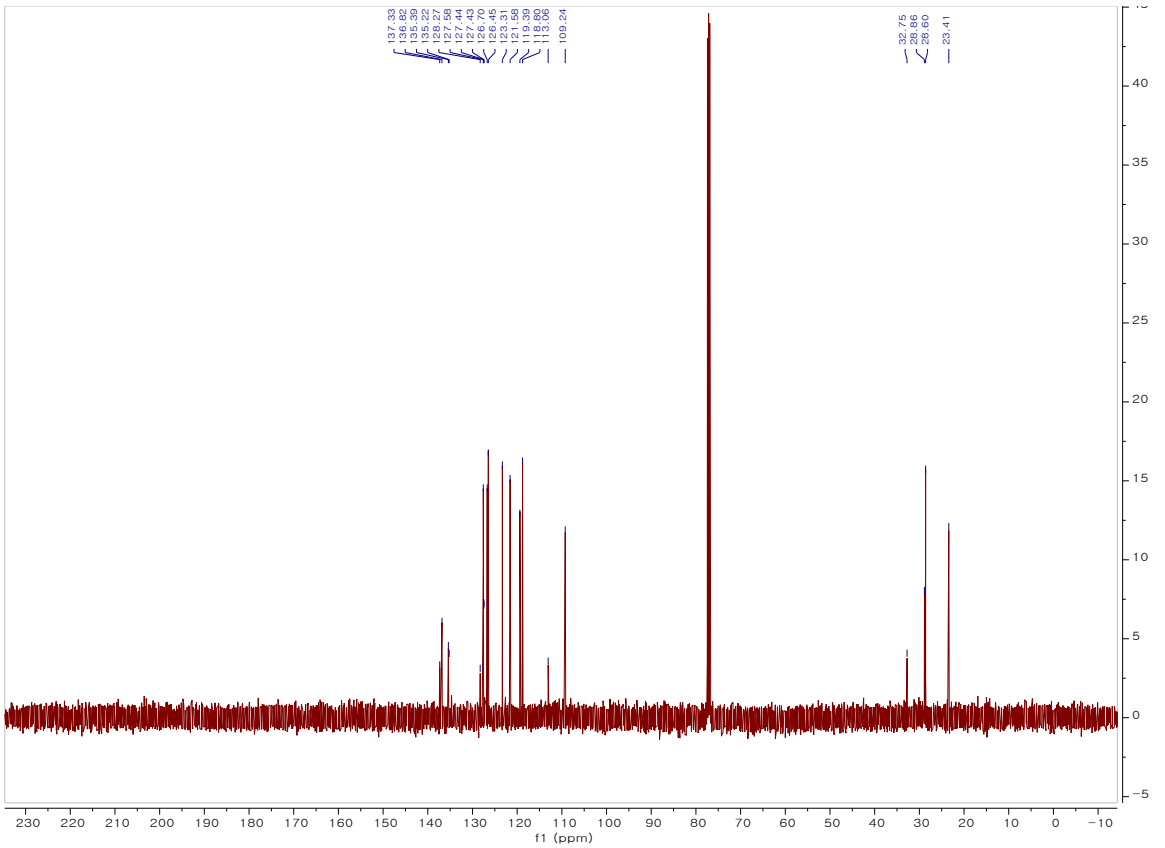

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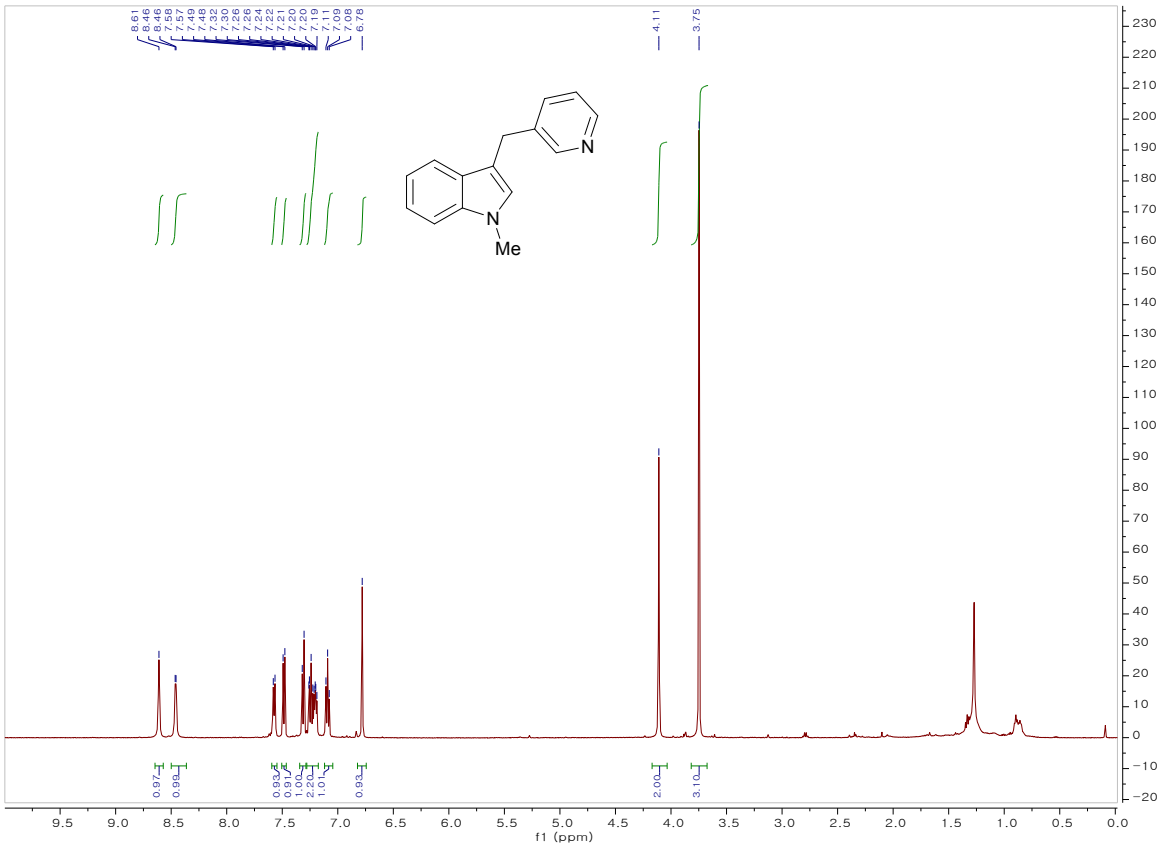

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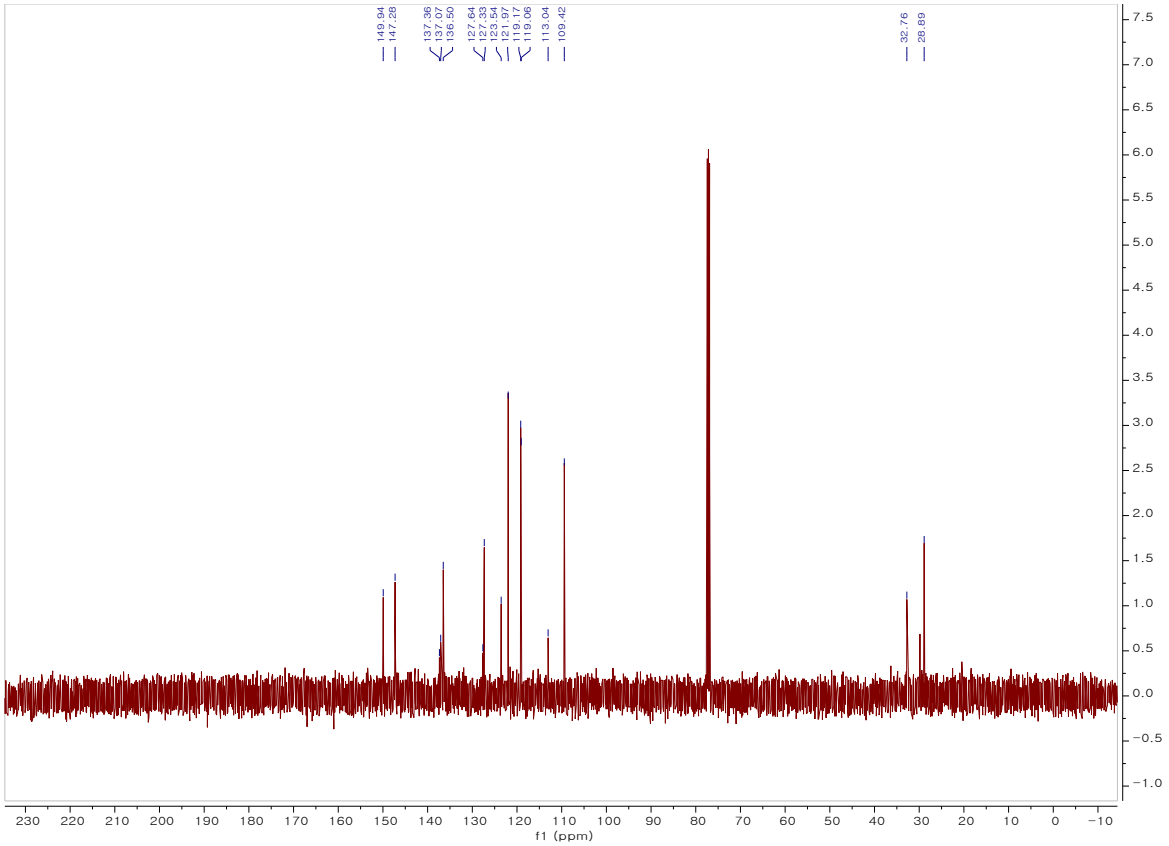

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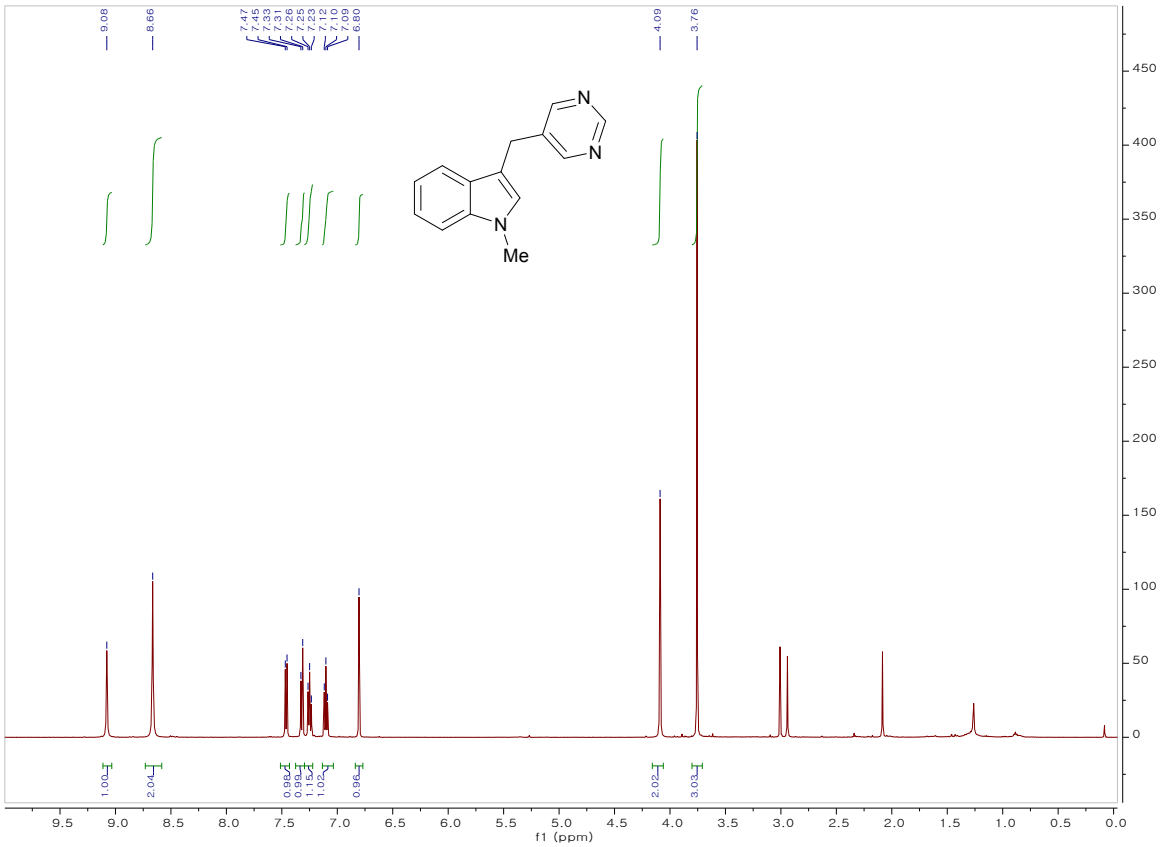

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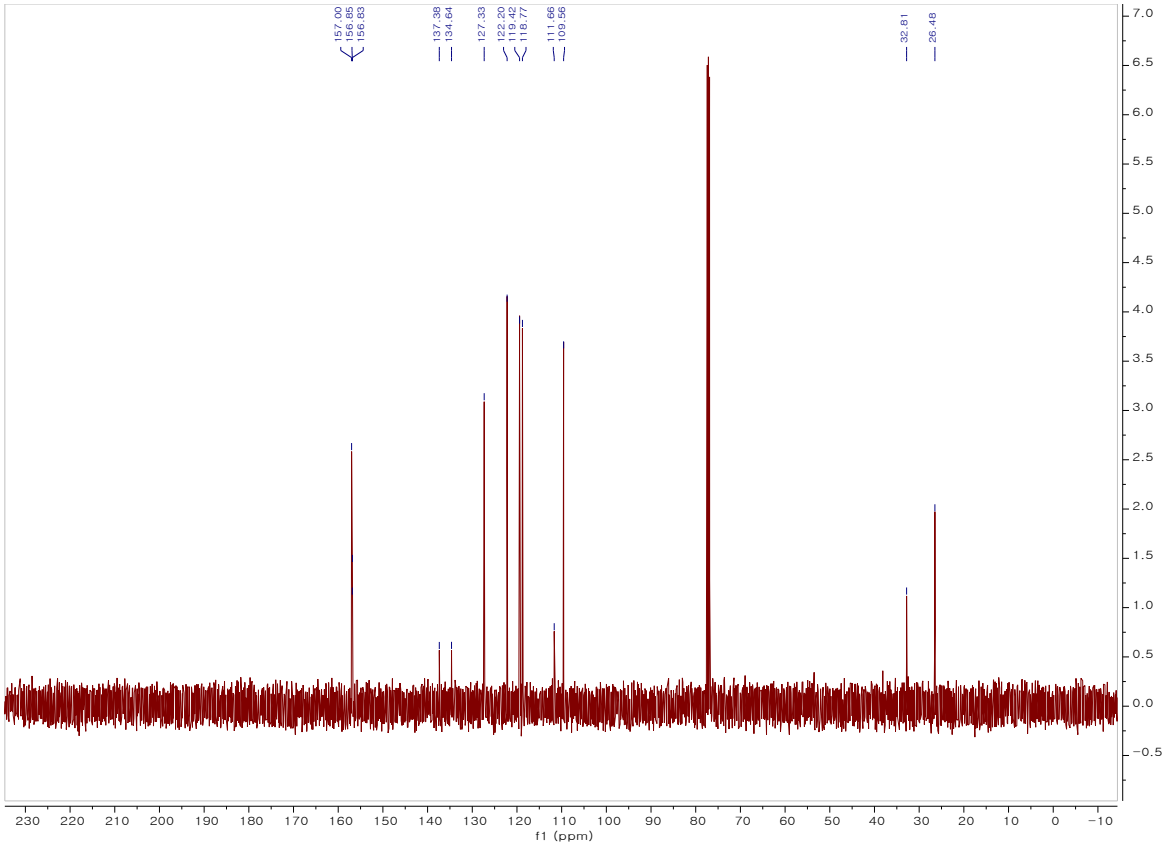

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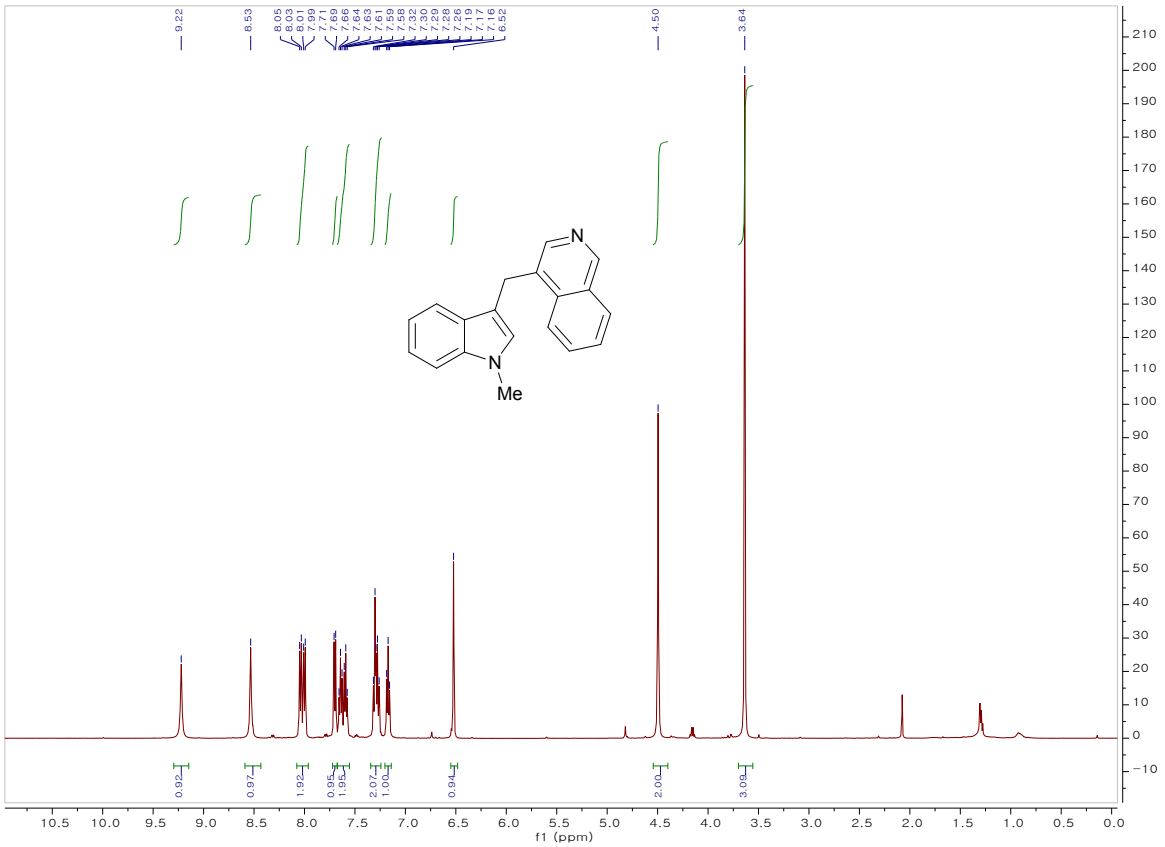

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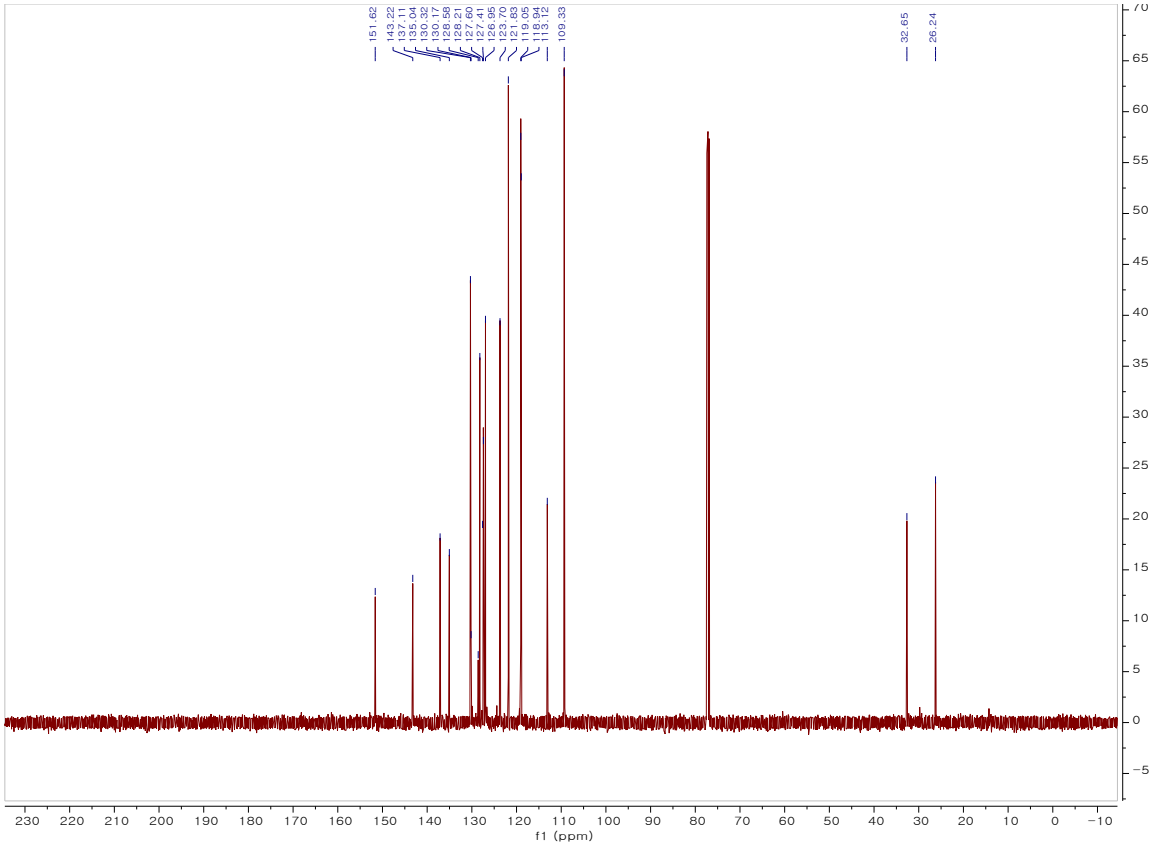

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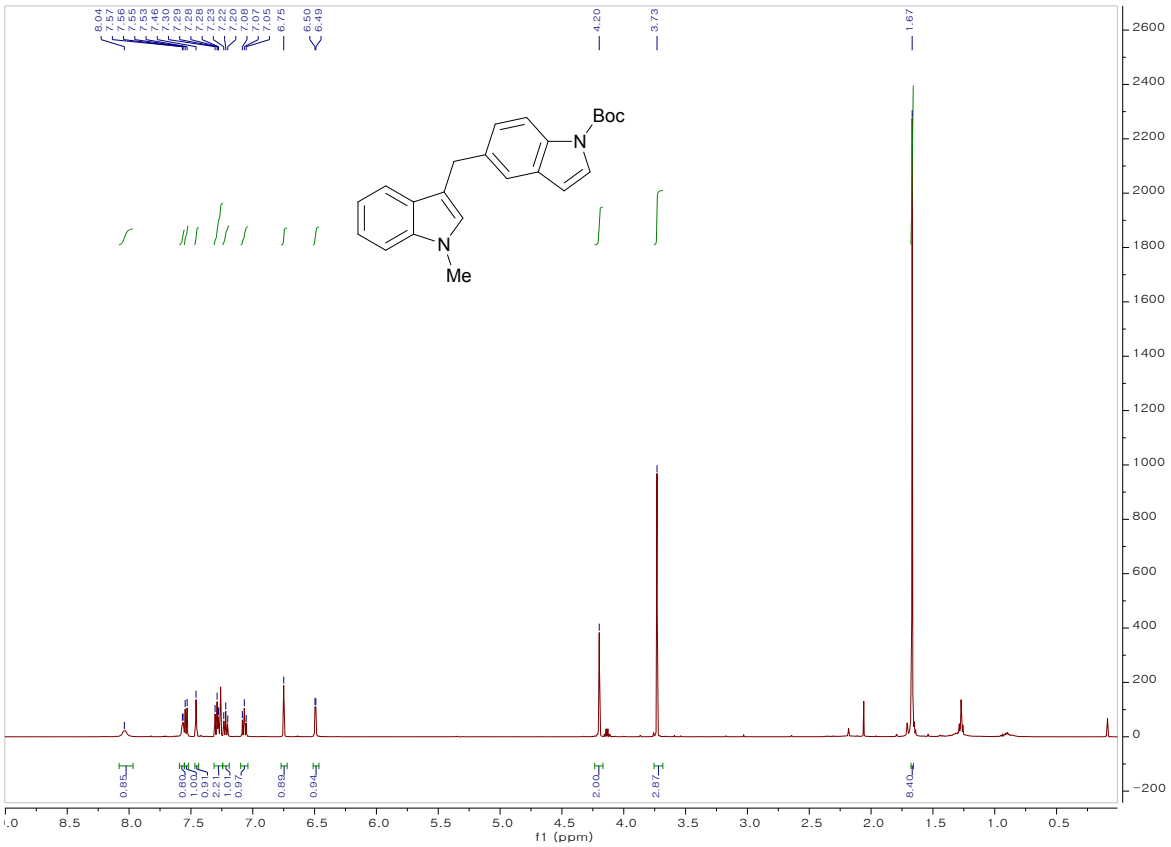

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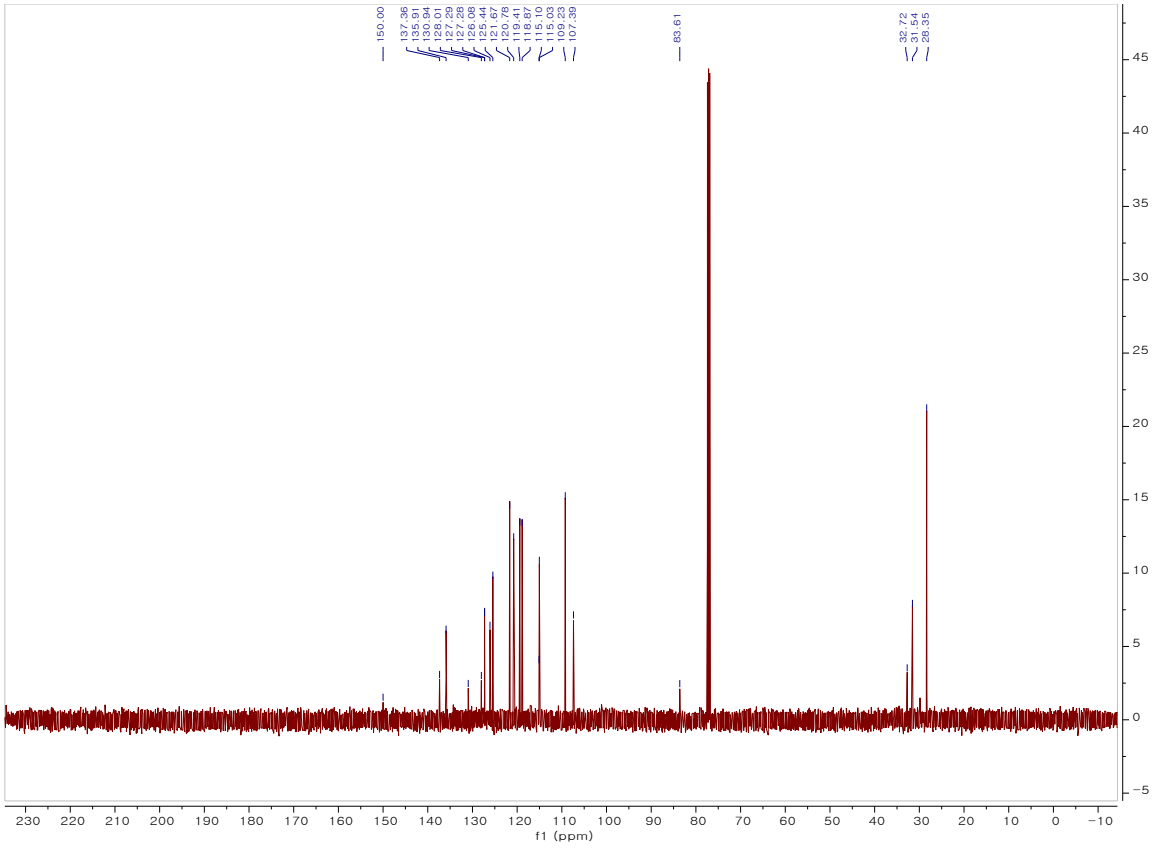

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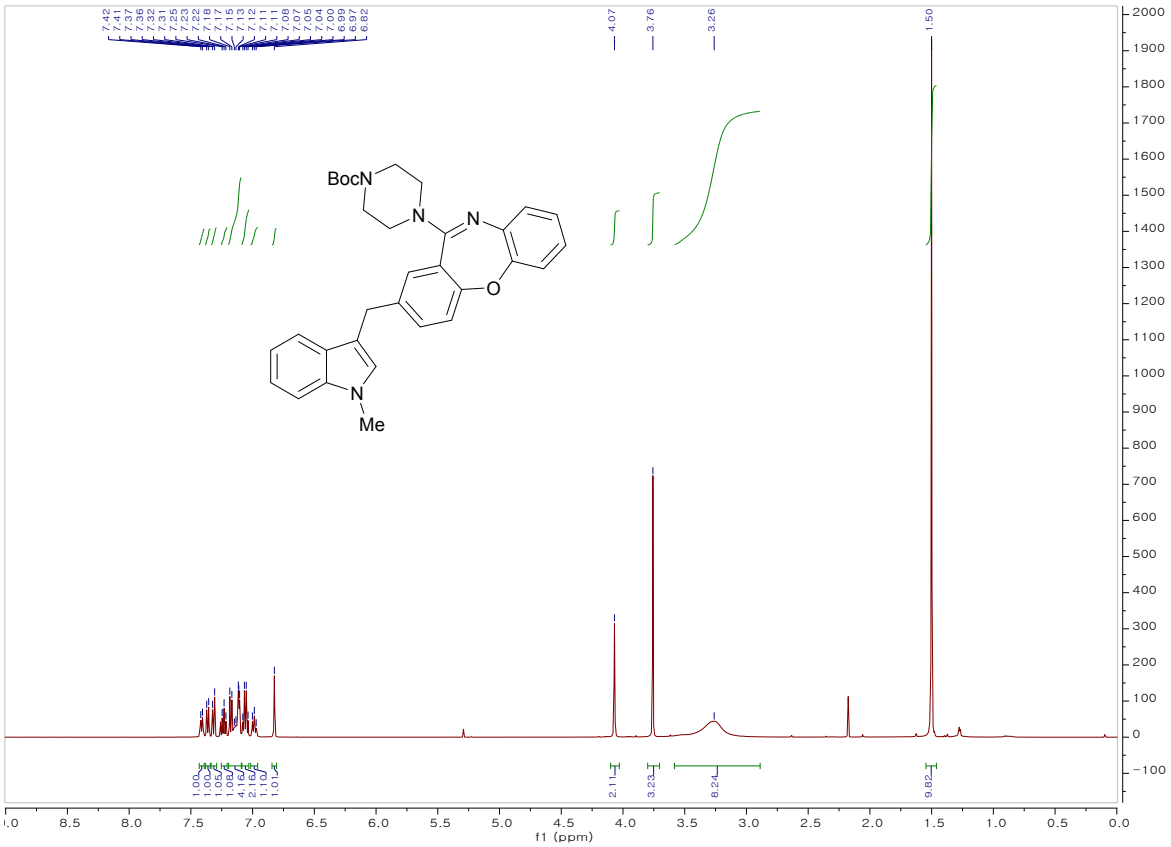
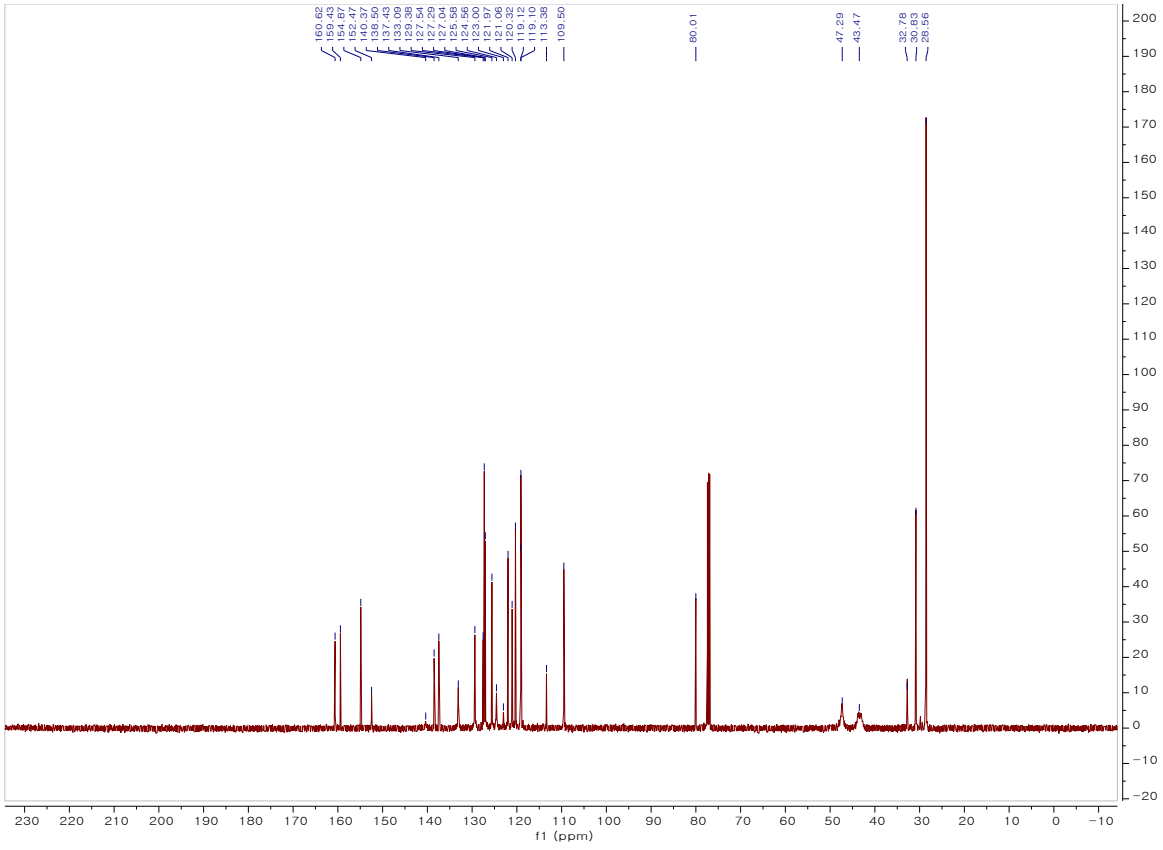
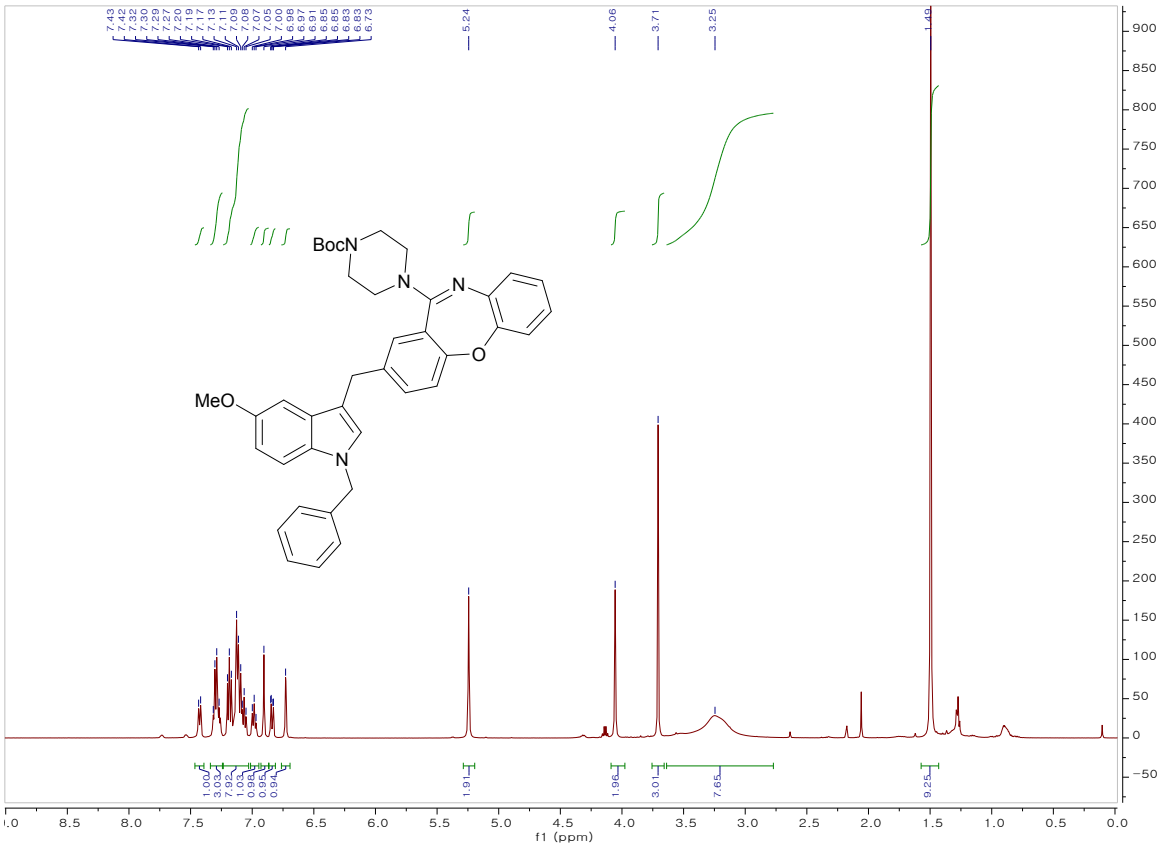


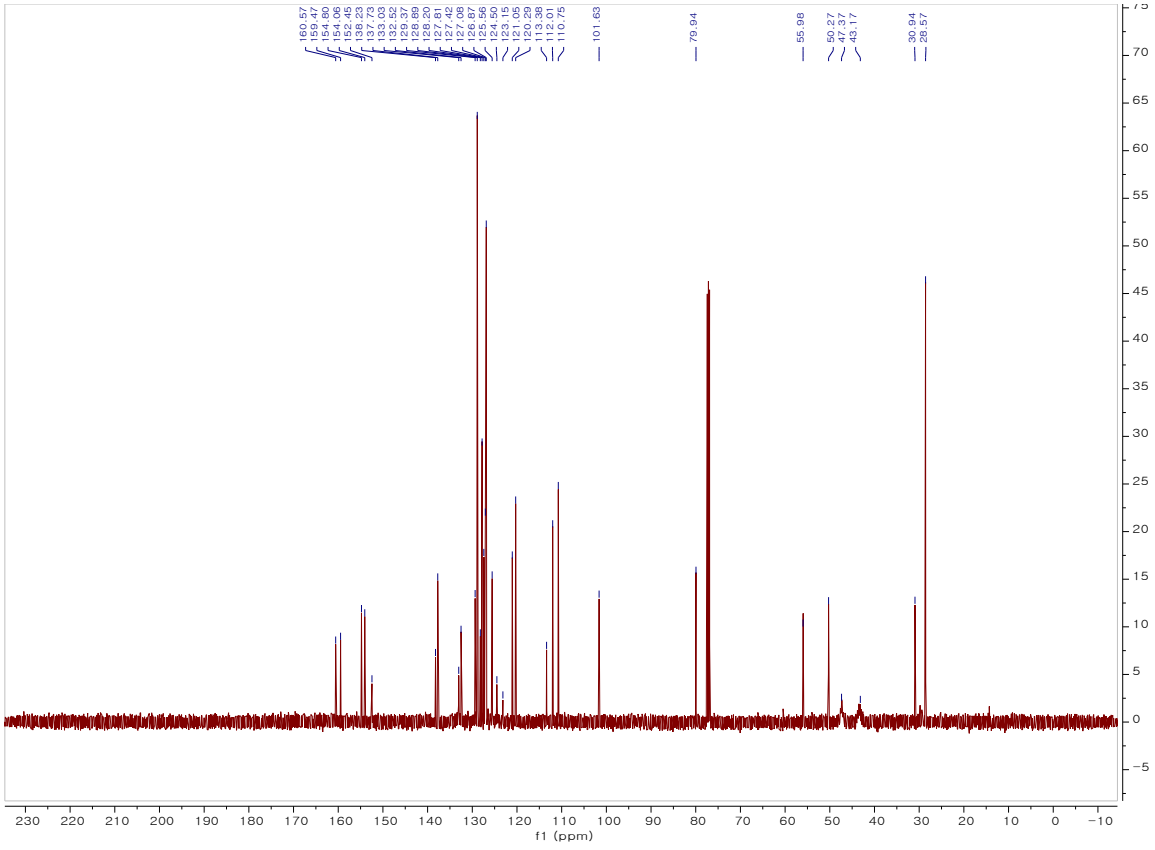
3ap (^{13}C NMR)



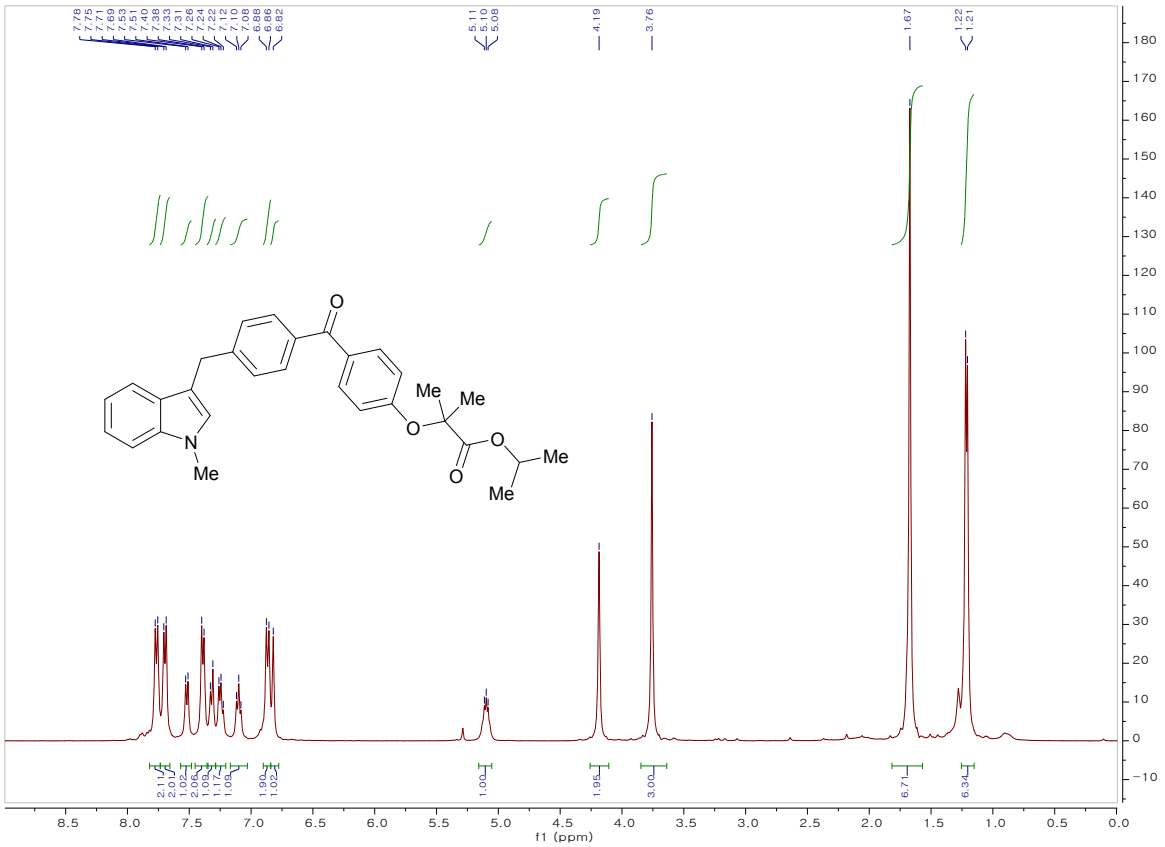
3xp (^{1}H NMR)



3xp (^{13}C NMR)



3aq (^{1}H NMR)



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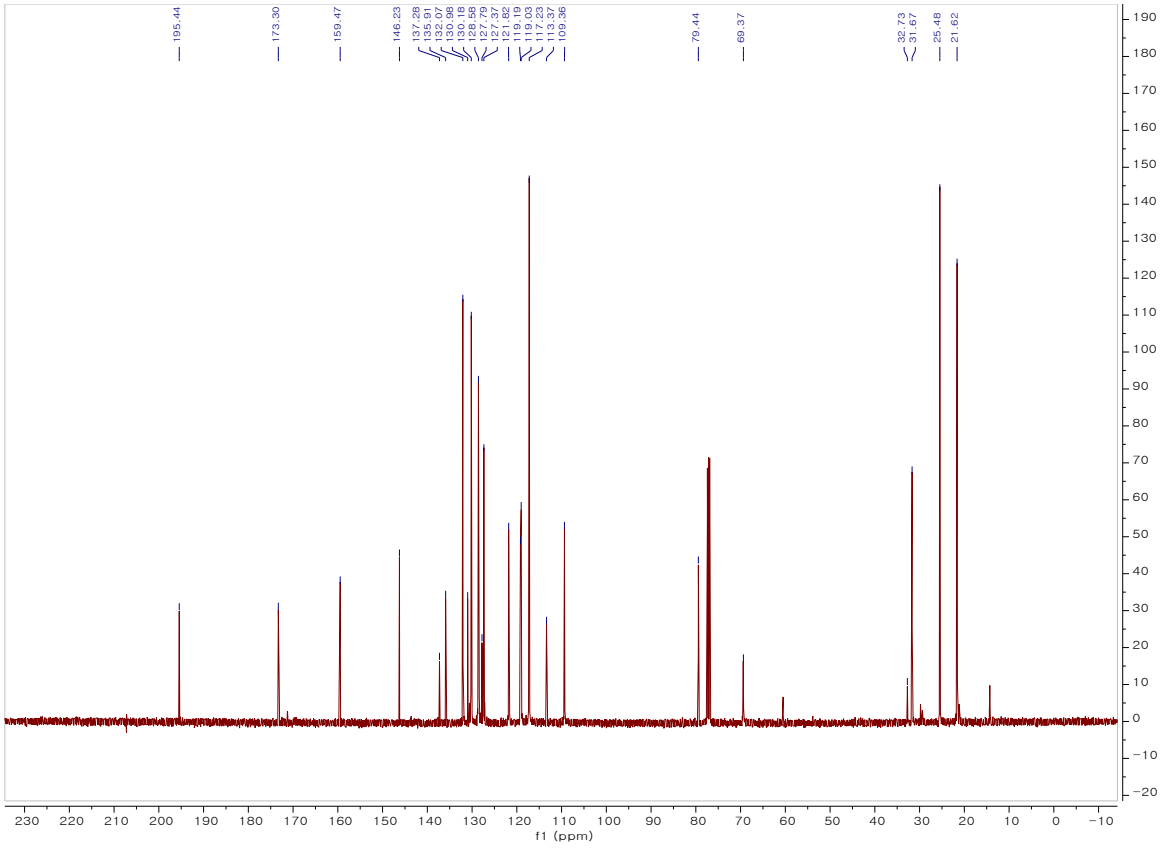
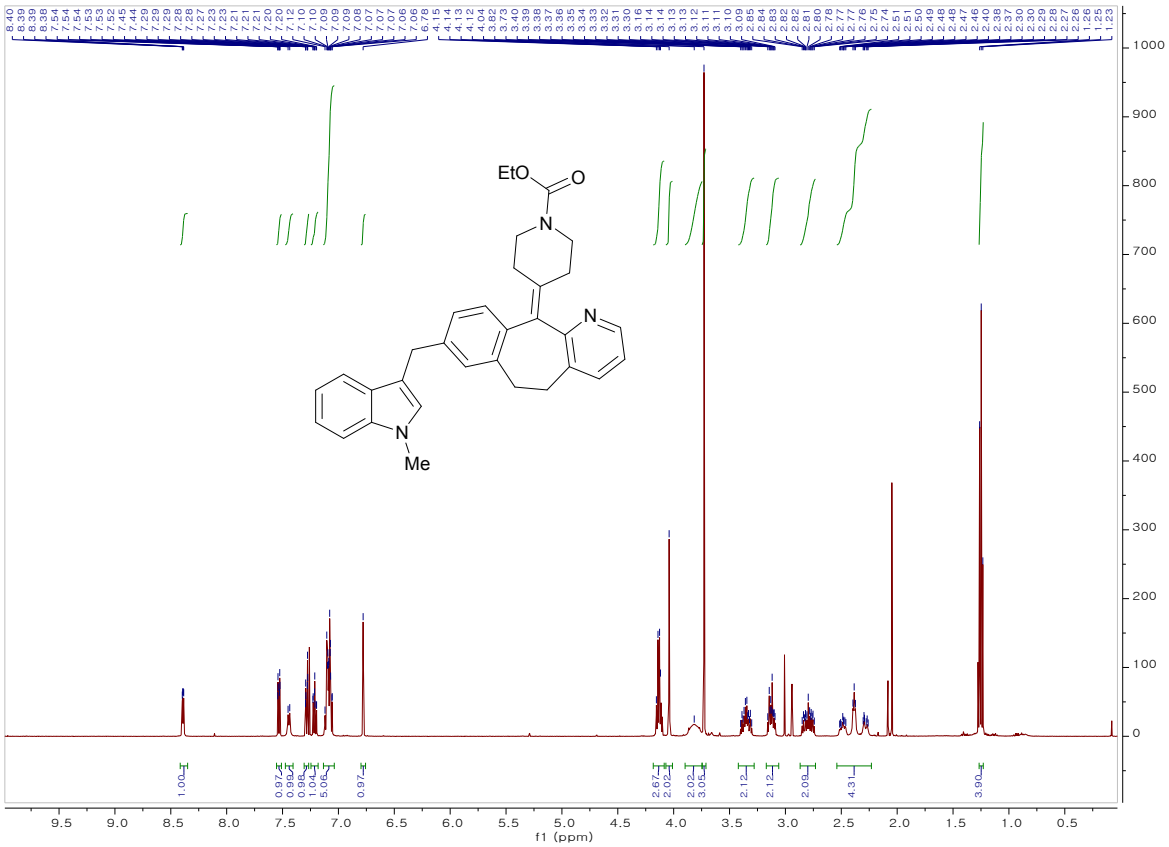


3ar (^{1}H NMR)



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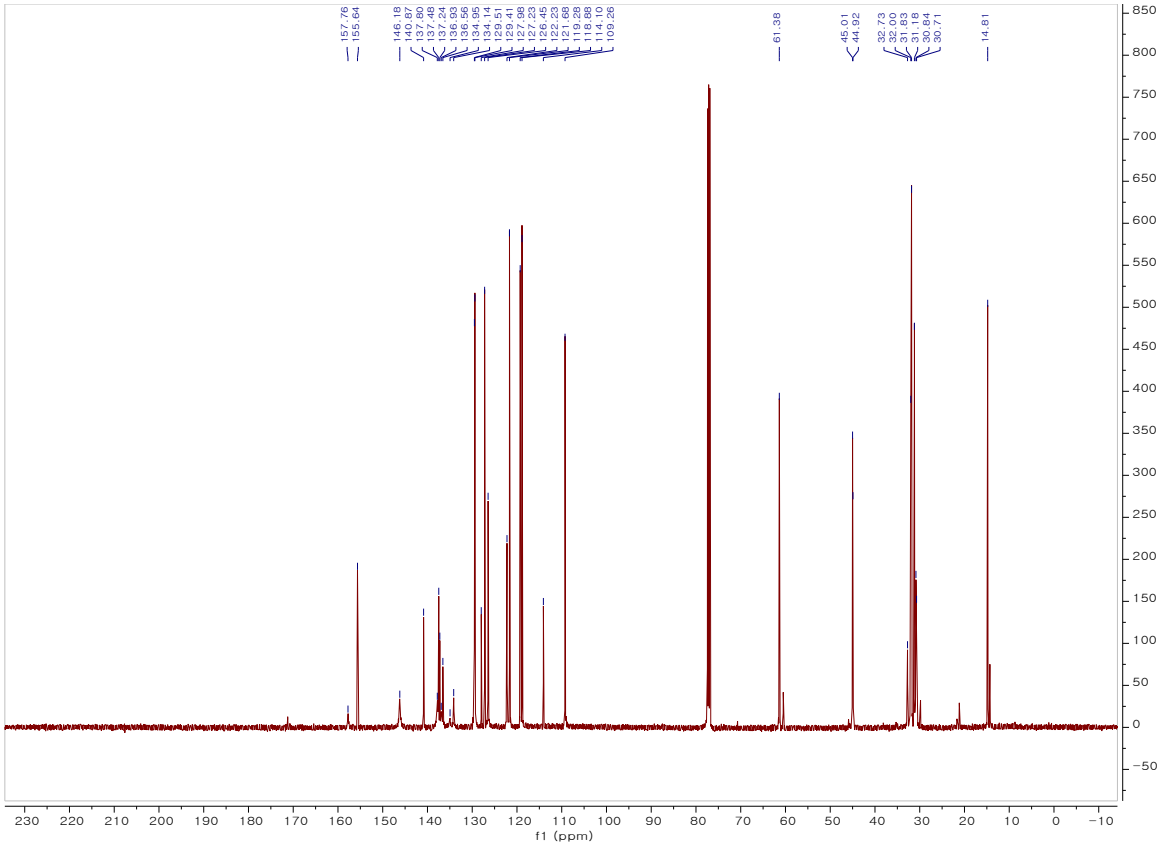

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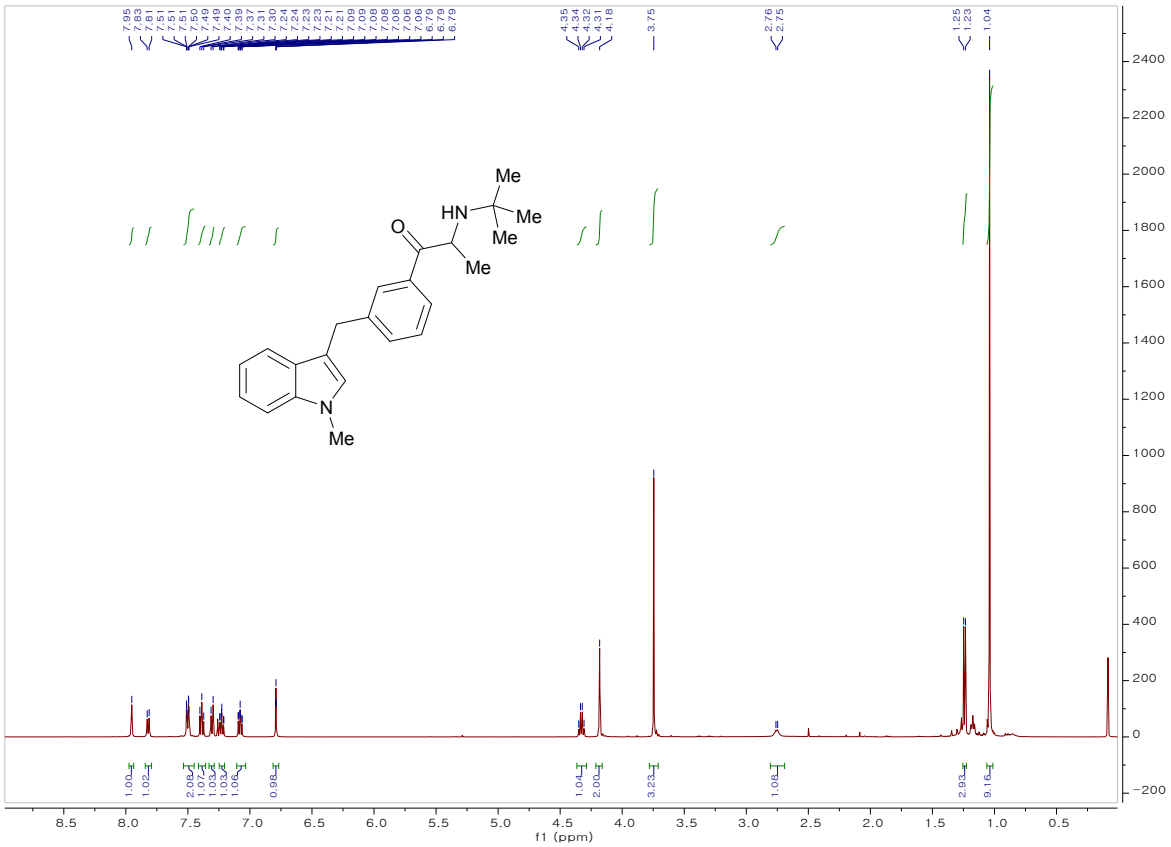

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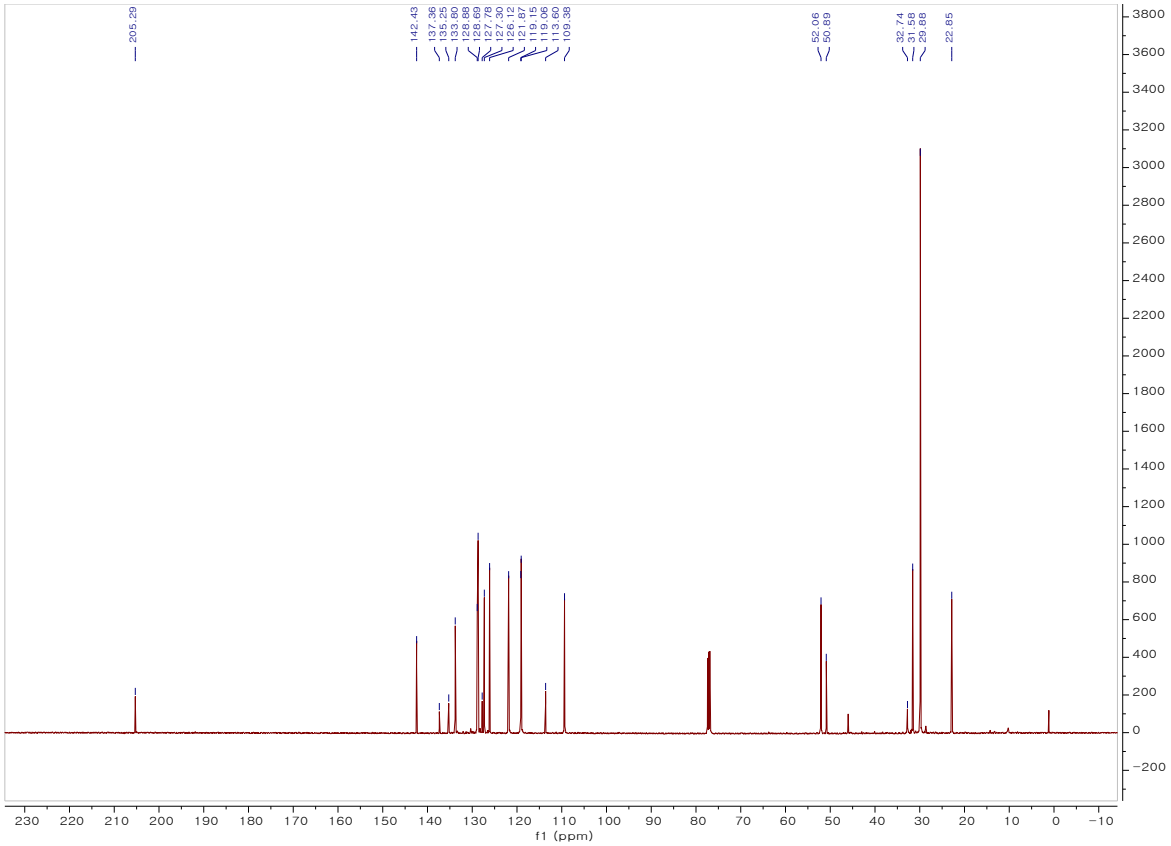

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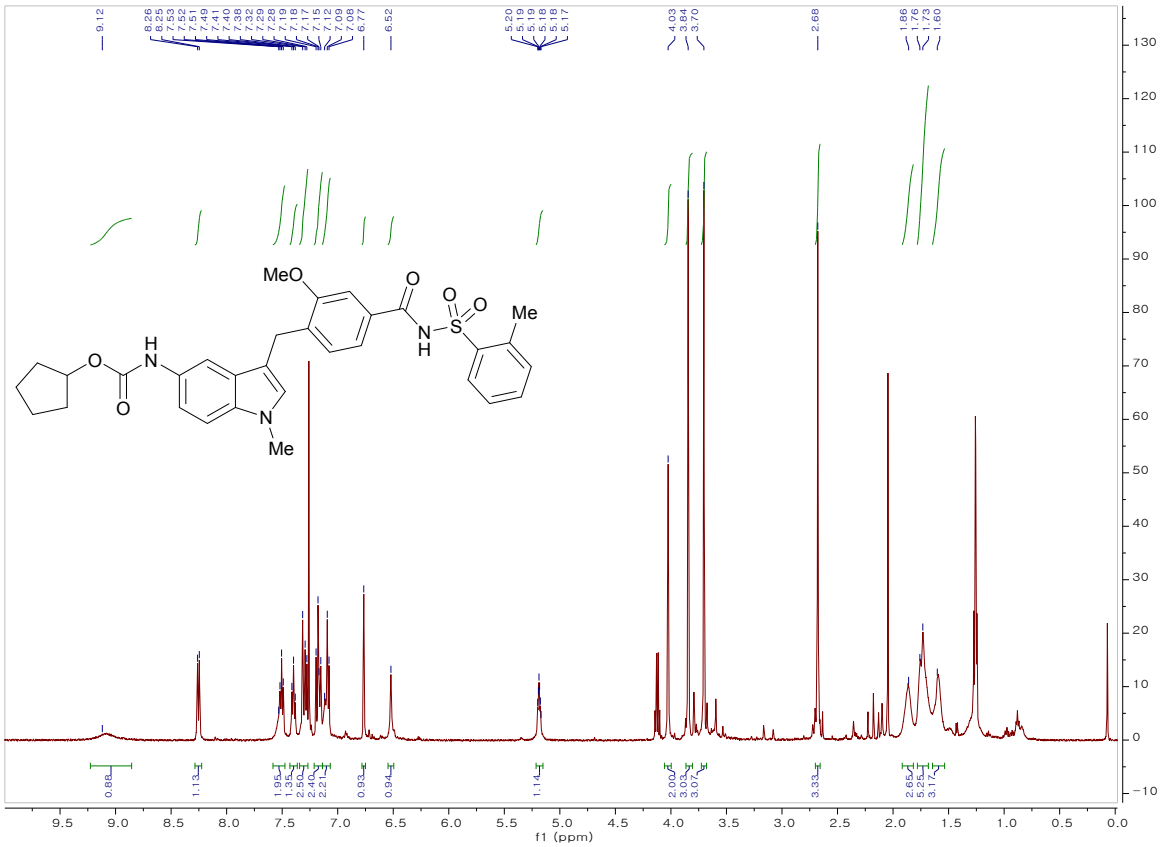
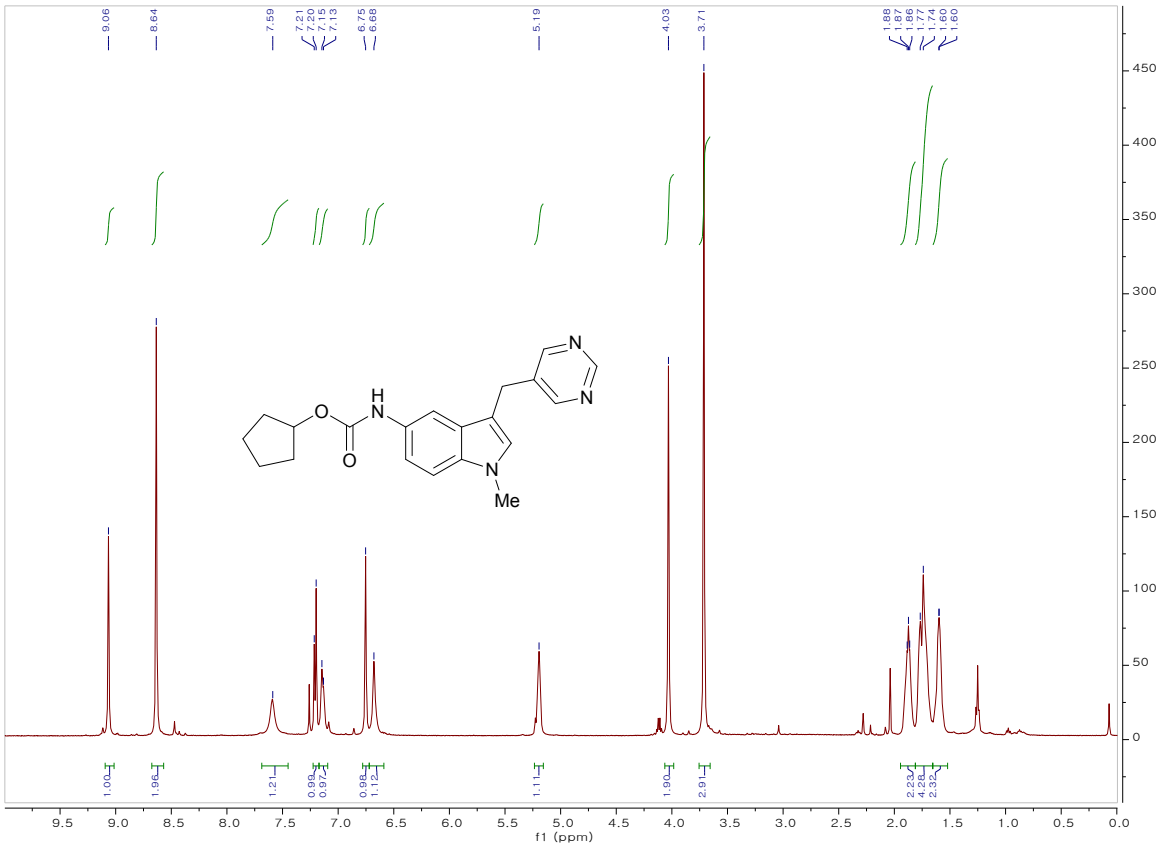


3wm (^{1}H NMR)



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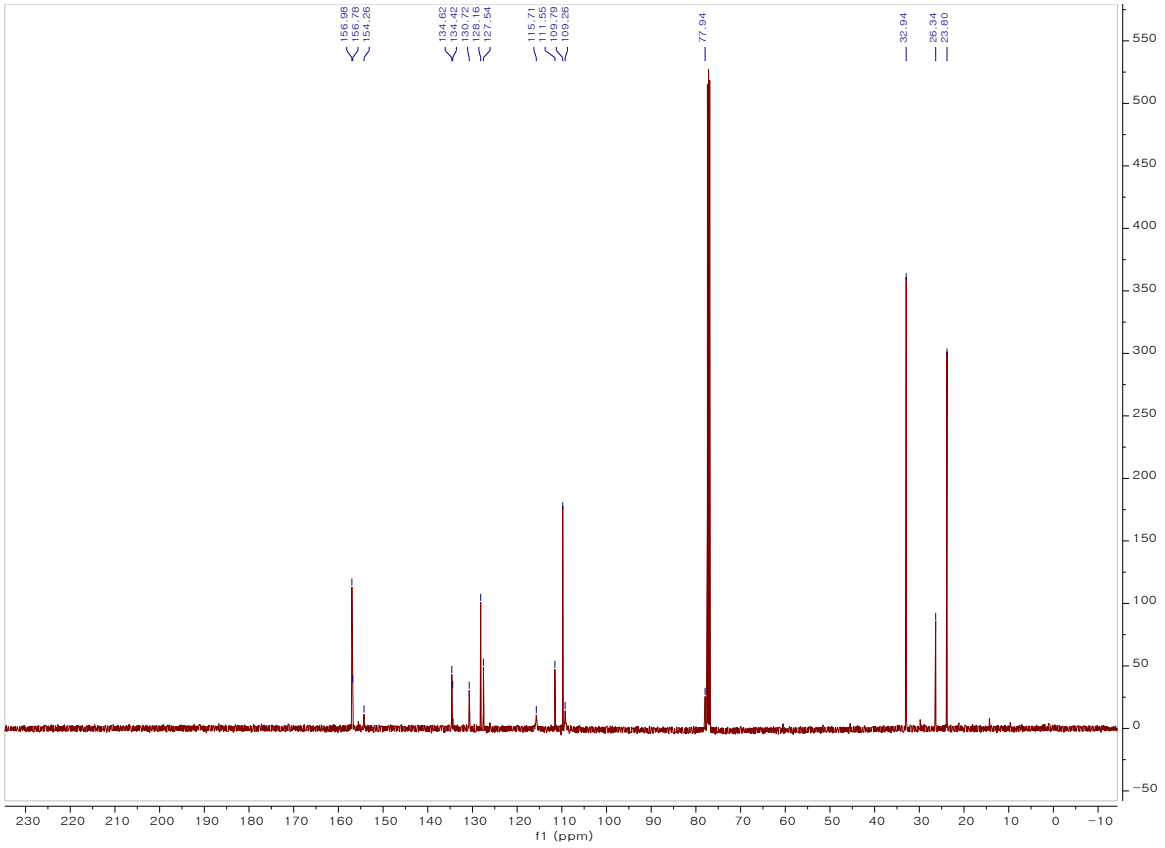

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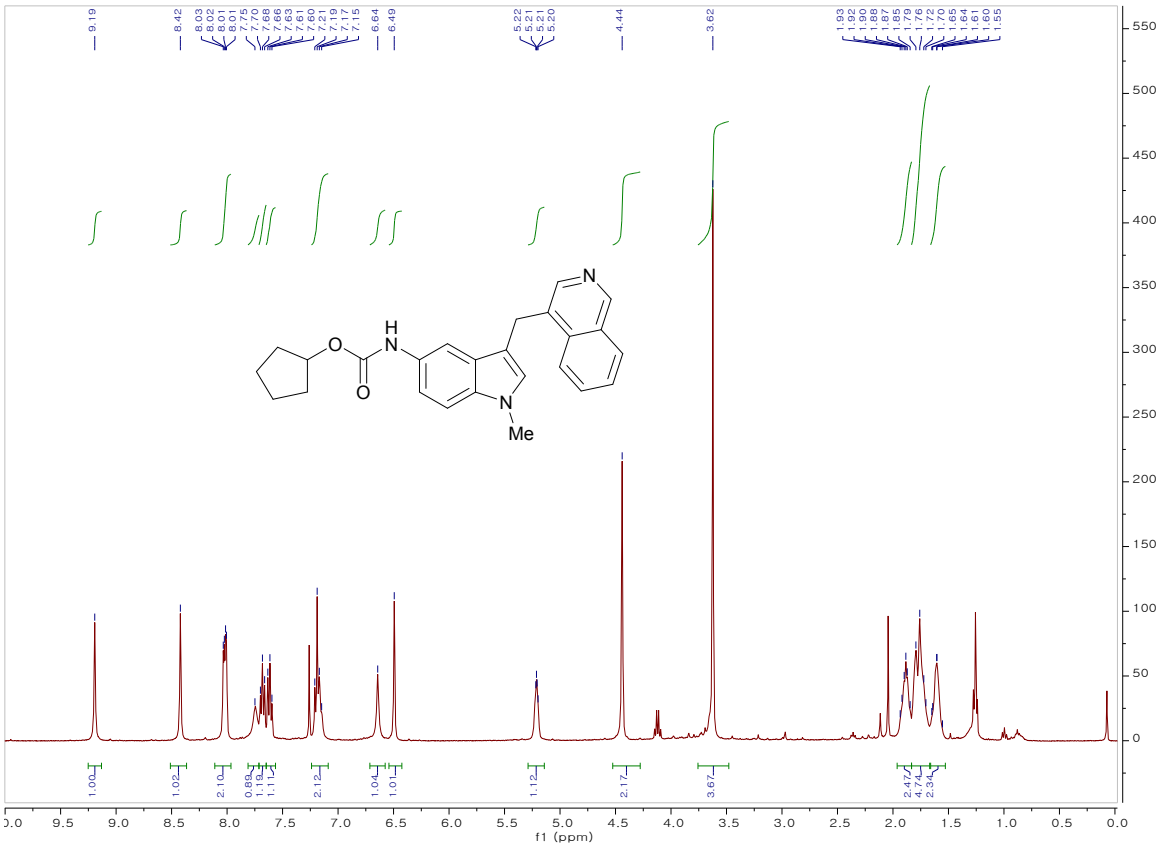

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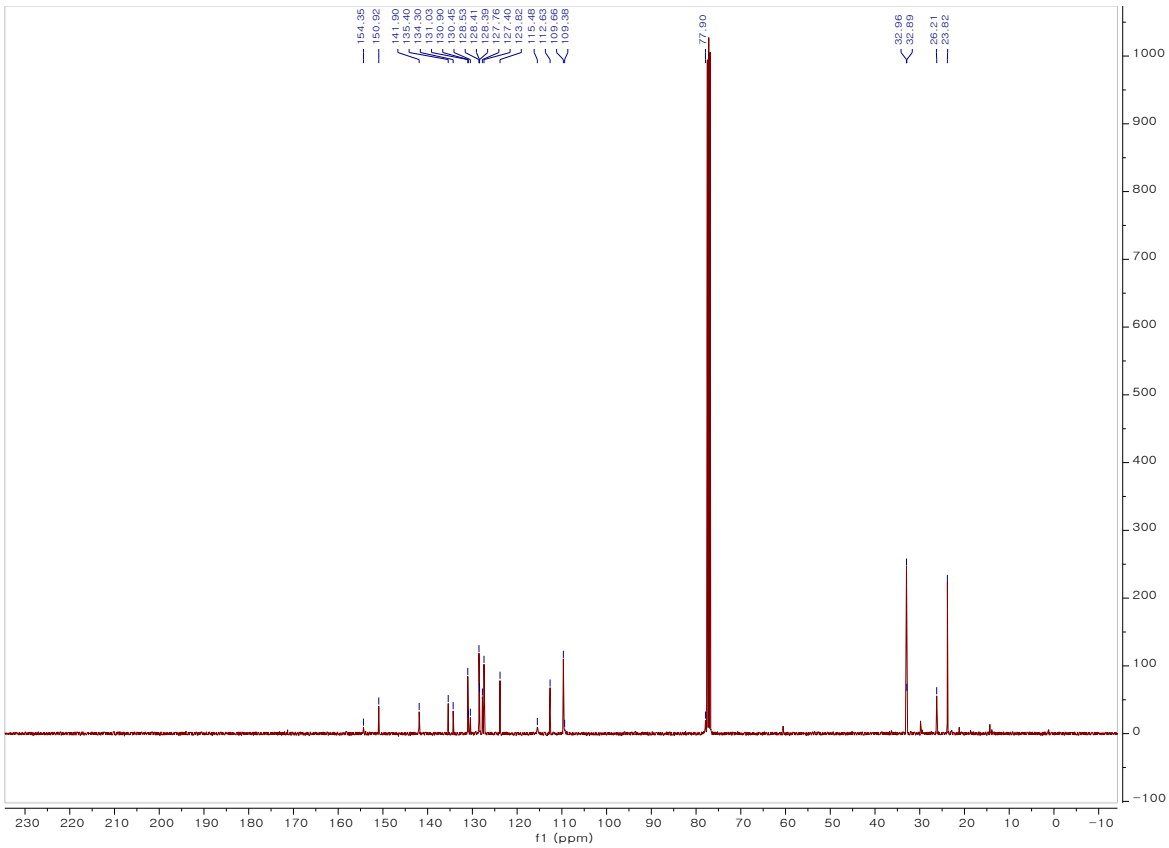

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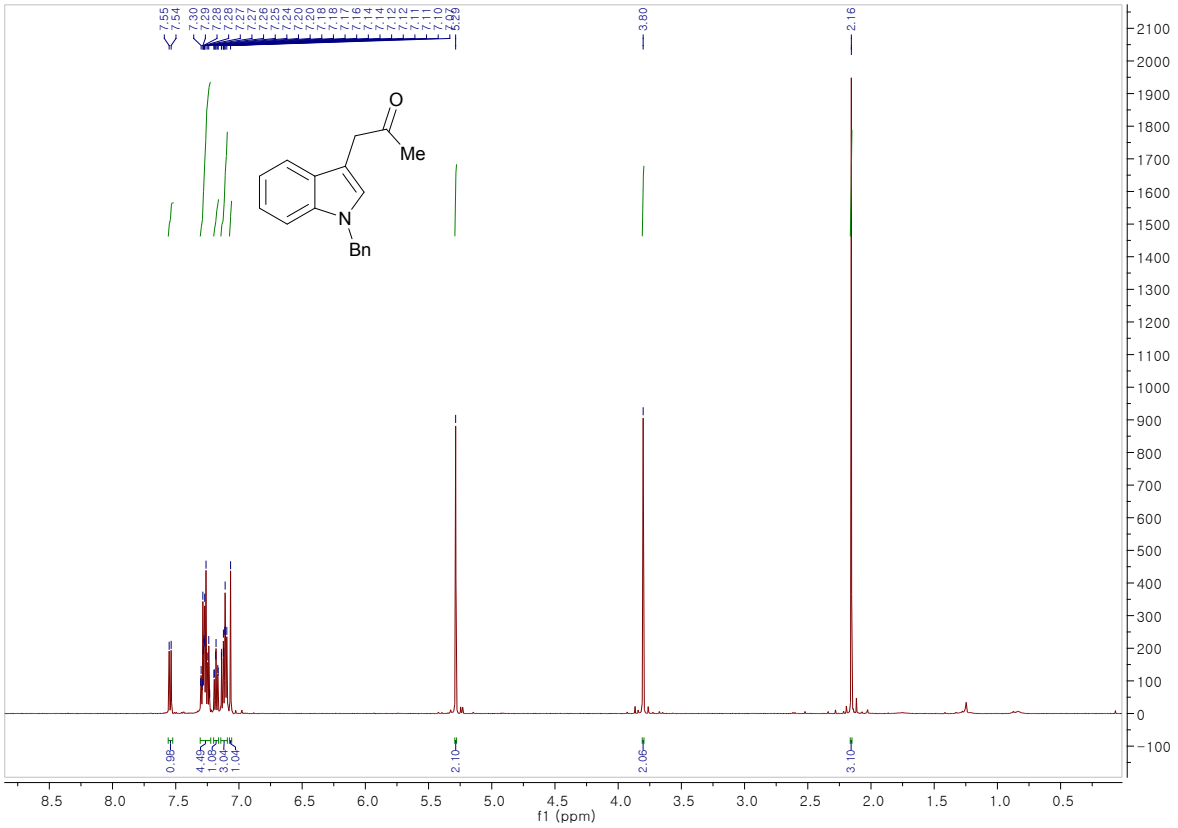

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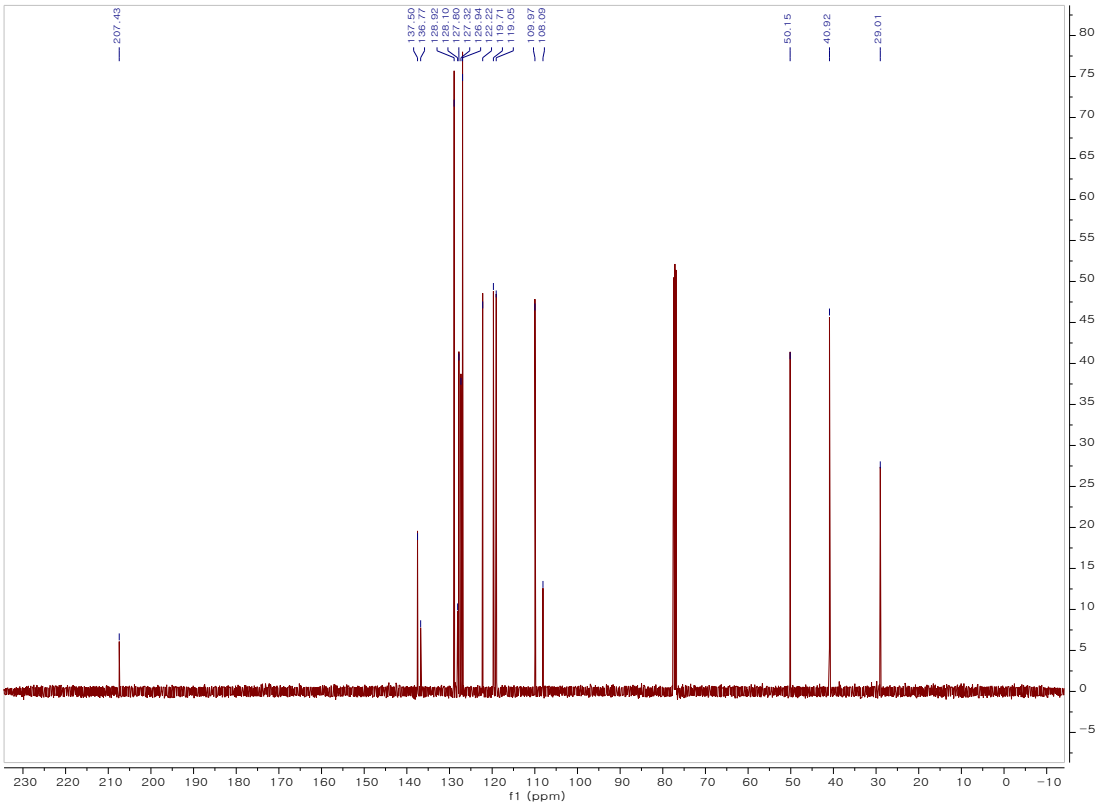
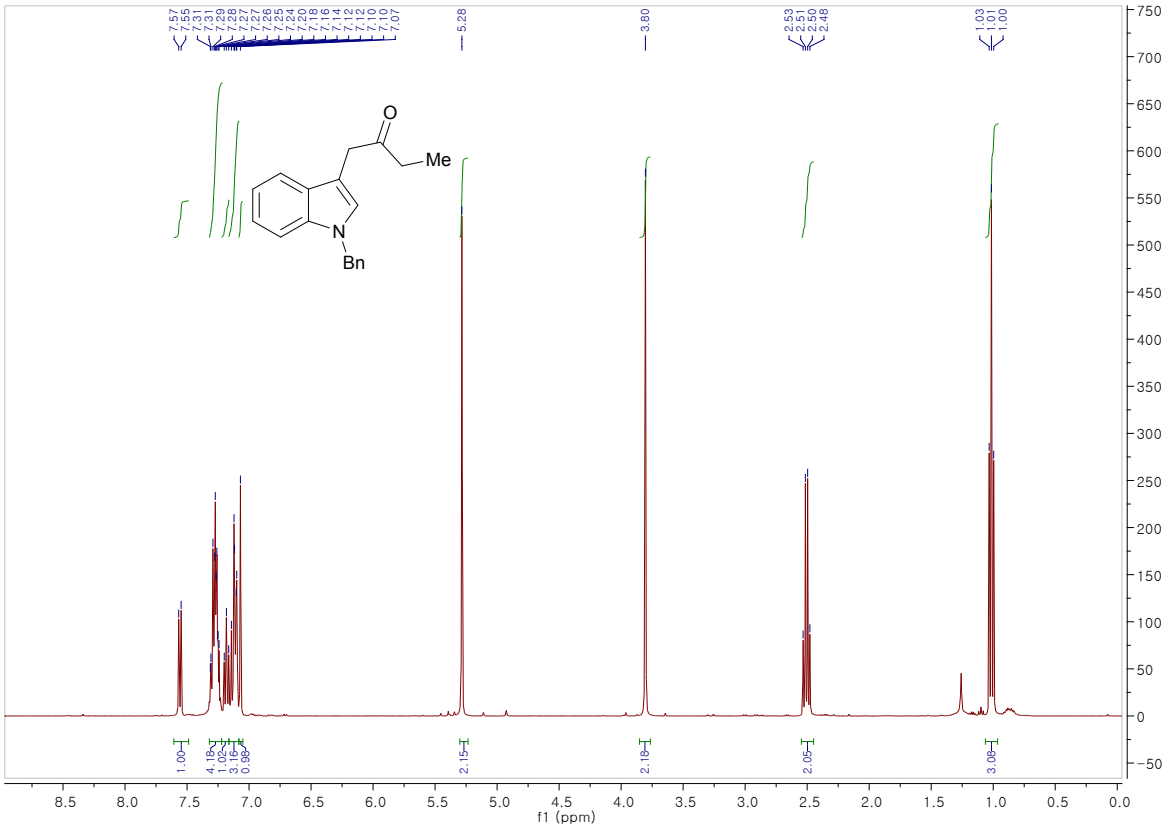
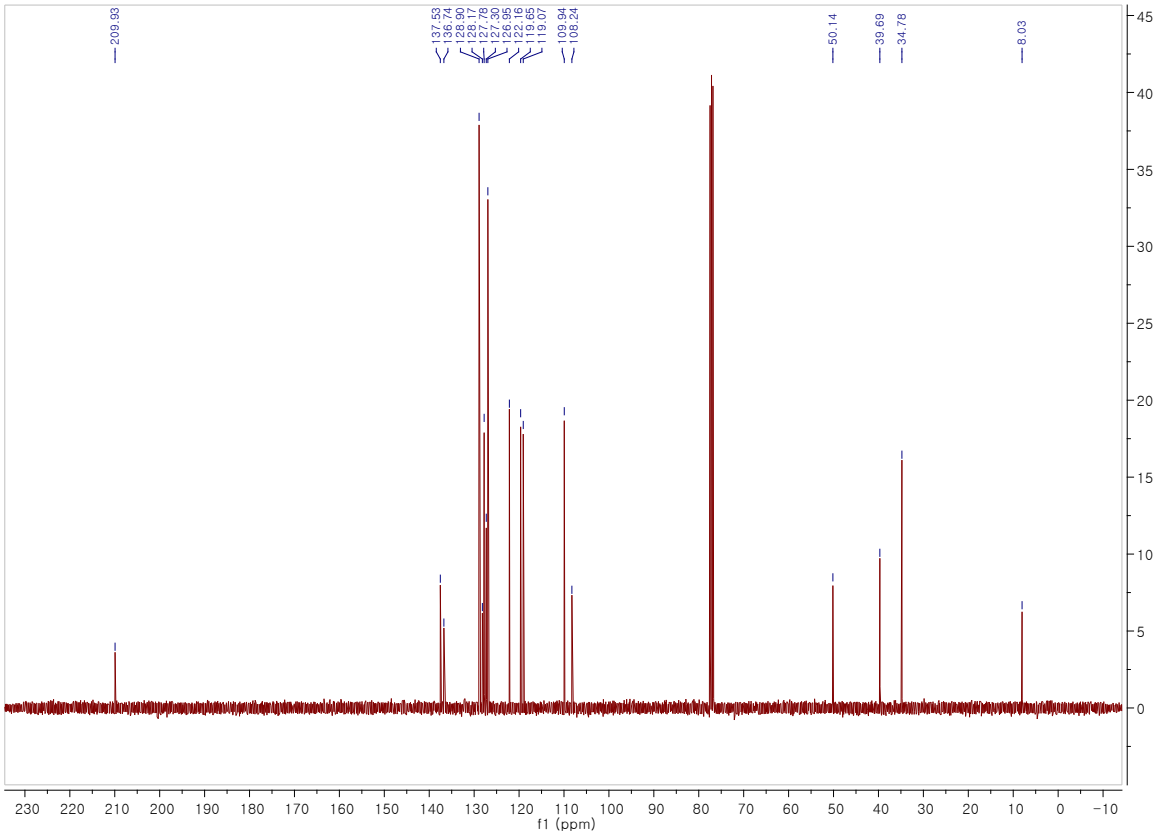


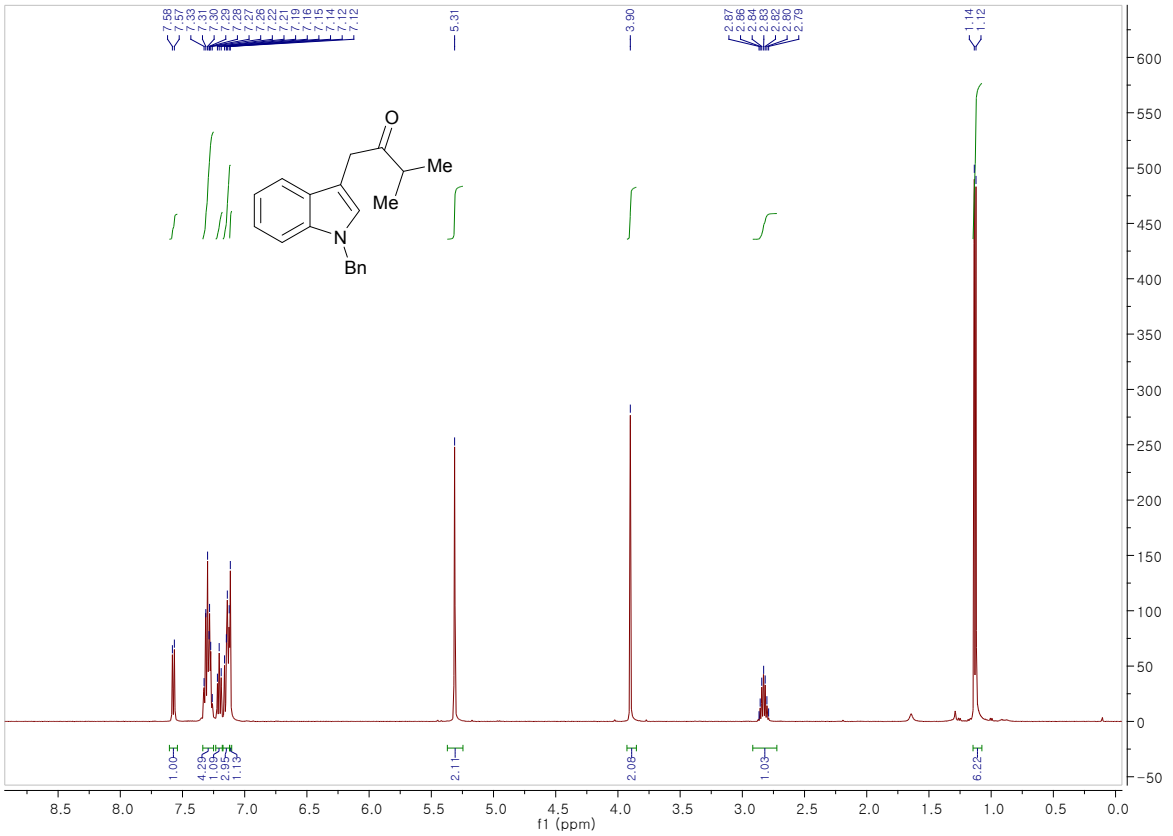
5cb (^{1}H NMR)



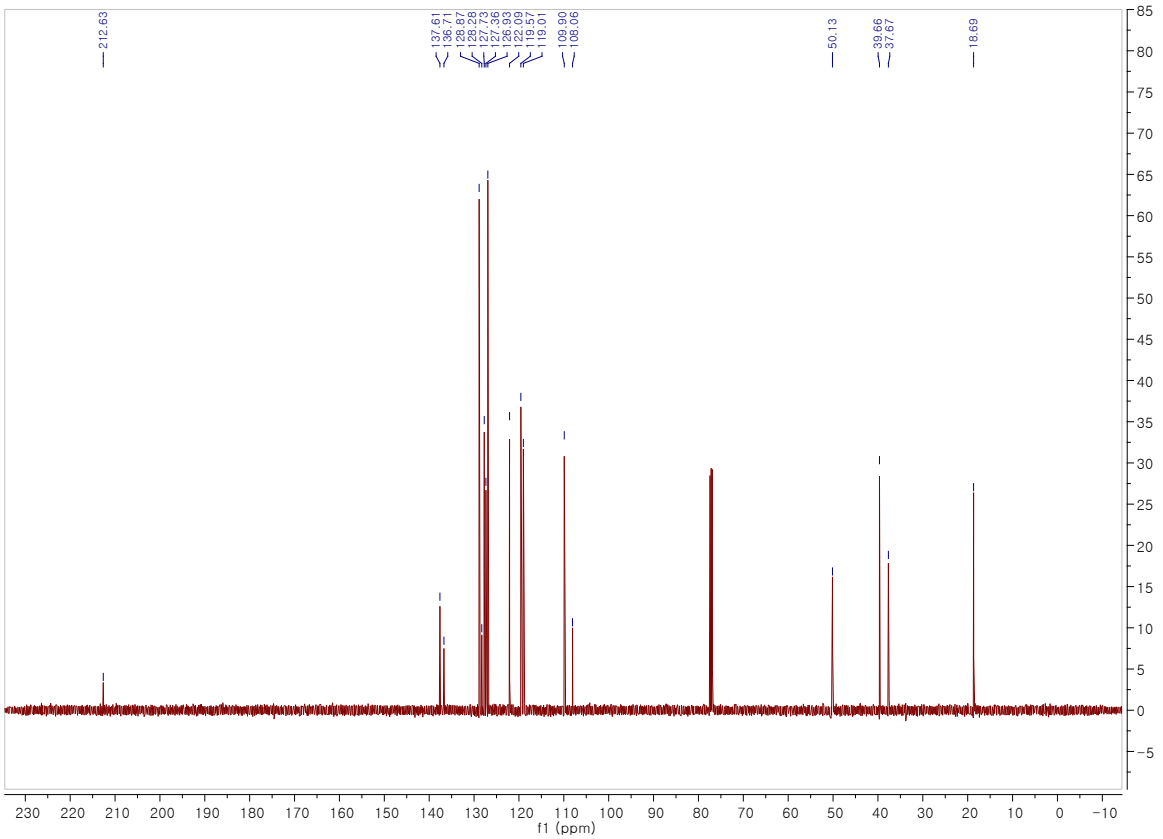
5cb (^{13}C NMR)



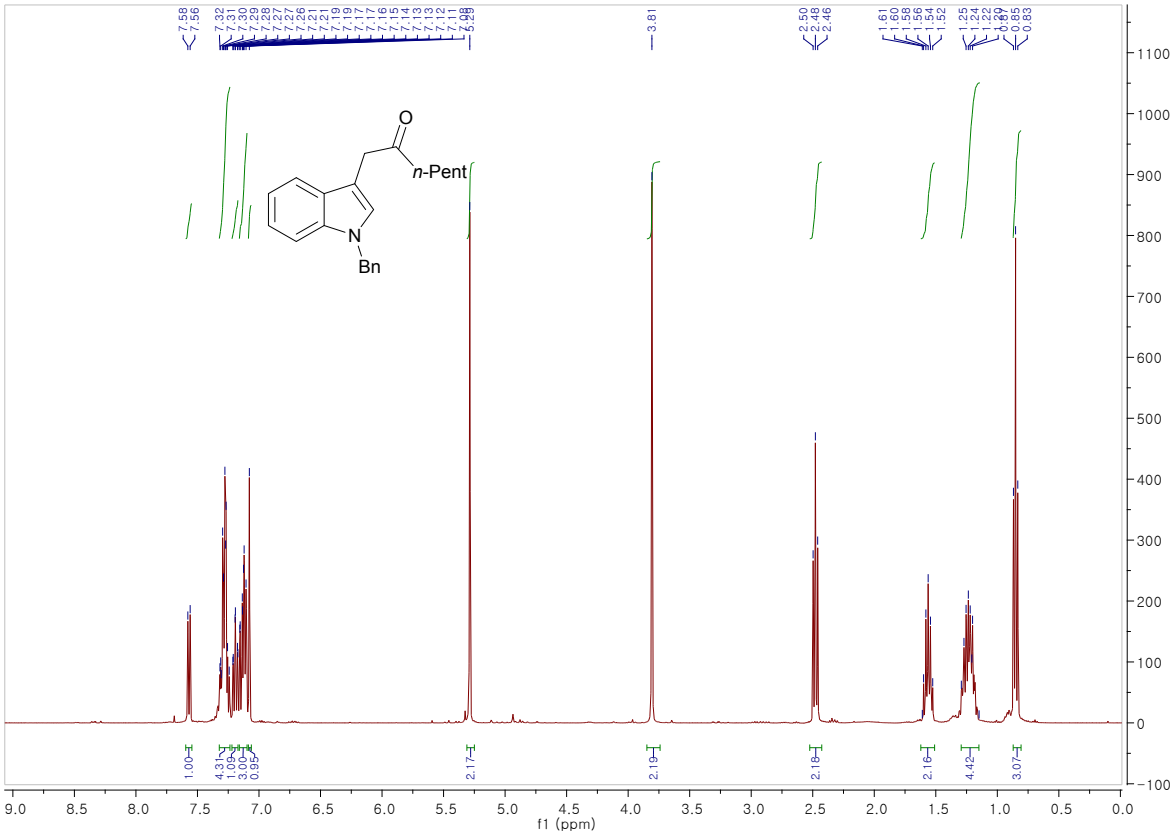
5cc (^{1}H NMR)


7.58
7.57
7.33
7.31
7.30
7.29
7.28
7.27
7.26
7.22
7.21
7.19
7.16
7.15
7.14
7.12
7.12
5.31
3.90
2.87
2.86
2.84
2.83
2.83
2.80
2.79
1.14
1.12
O
Me
Me
N
Bn
1.00
4.29
1.09
2.95
1.13
2.11
2.09
1.03
6.22
f1 (ppm)

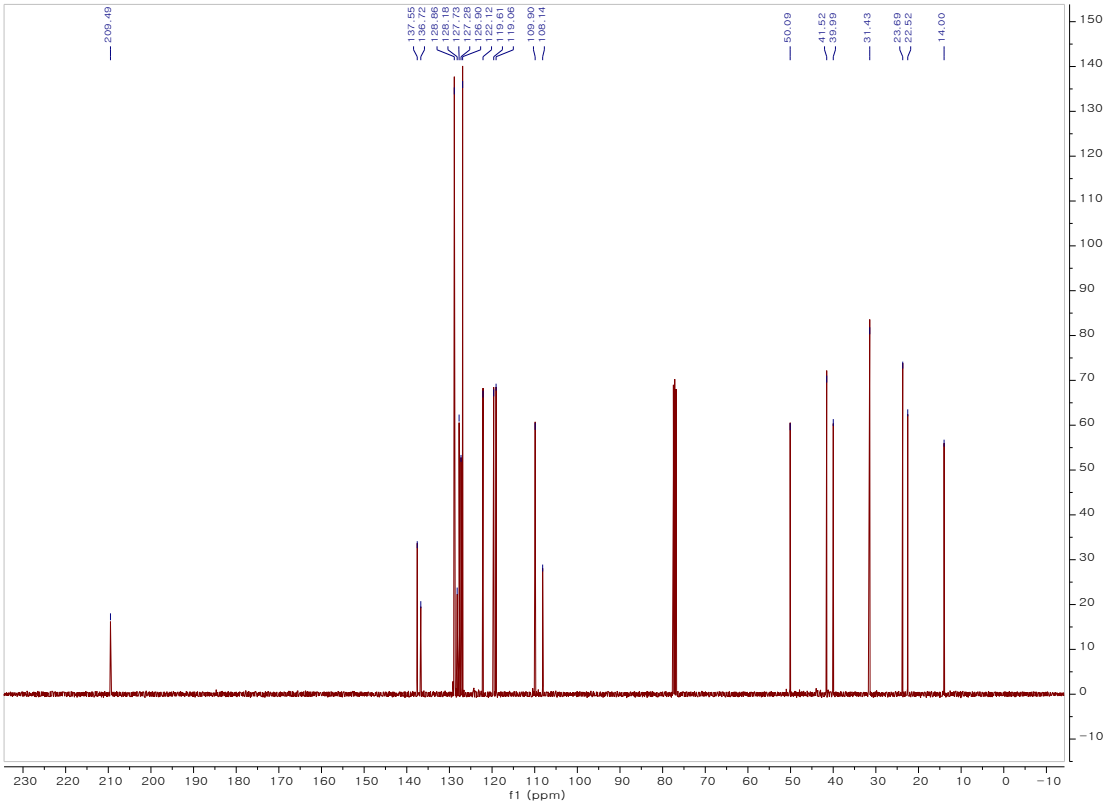
5cc (^{13}C NMR)


212.63
137.61
136.71
128.87
128.28
127.23
127.36
126.93
122.09
119.57
119.01
109.90
108.06
50.13
39.66
37.67
18.69
f1 (ppm)

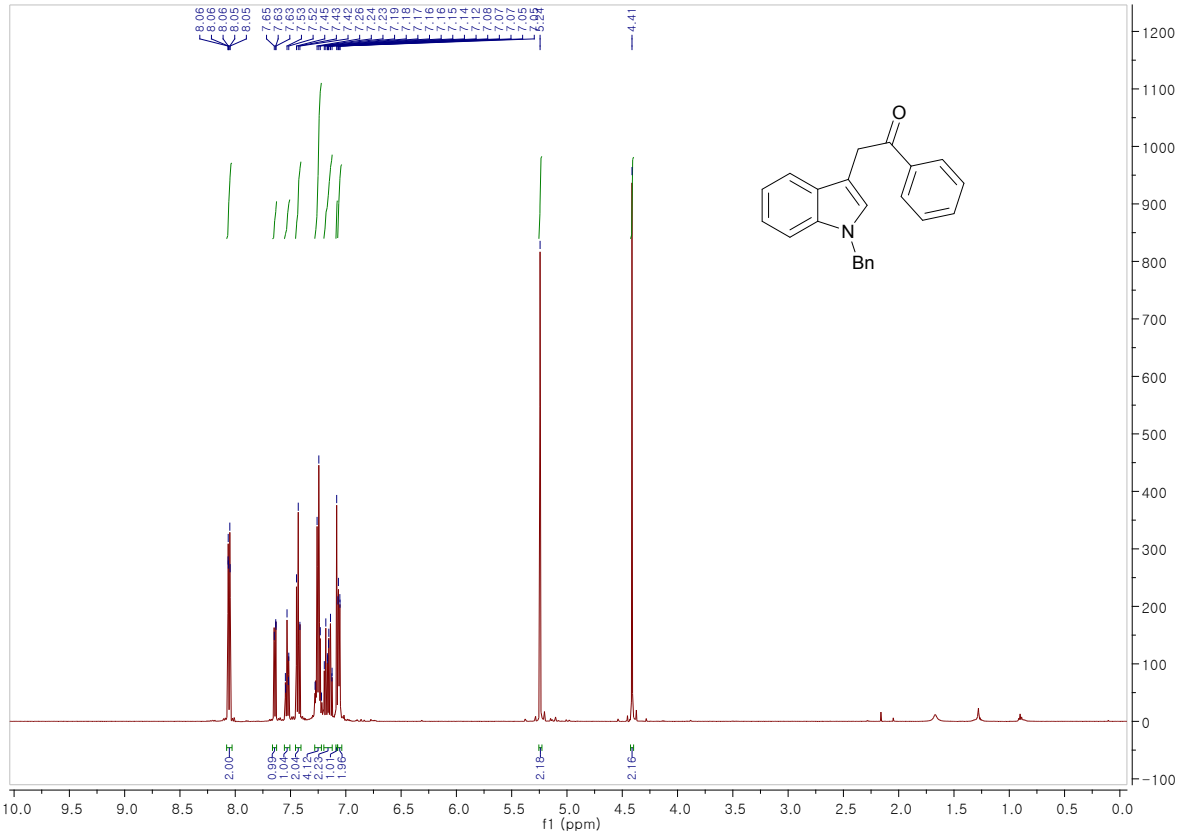
5cd (^{1}H NMR)



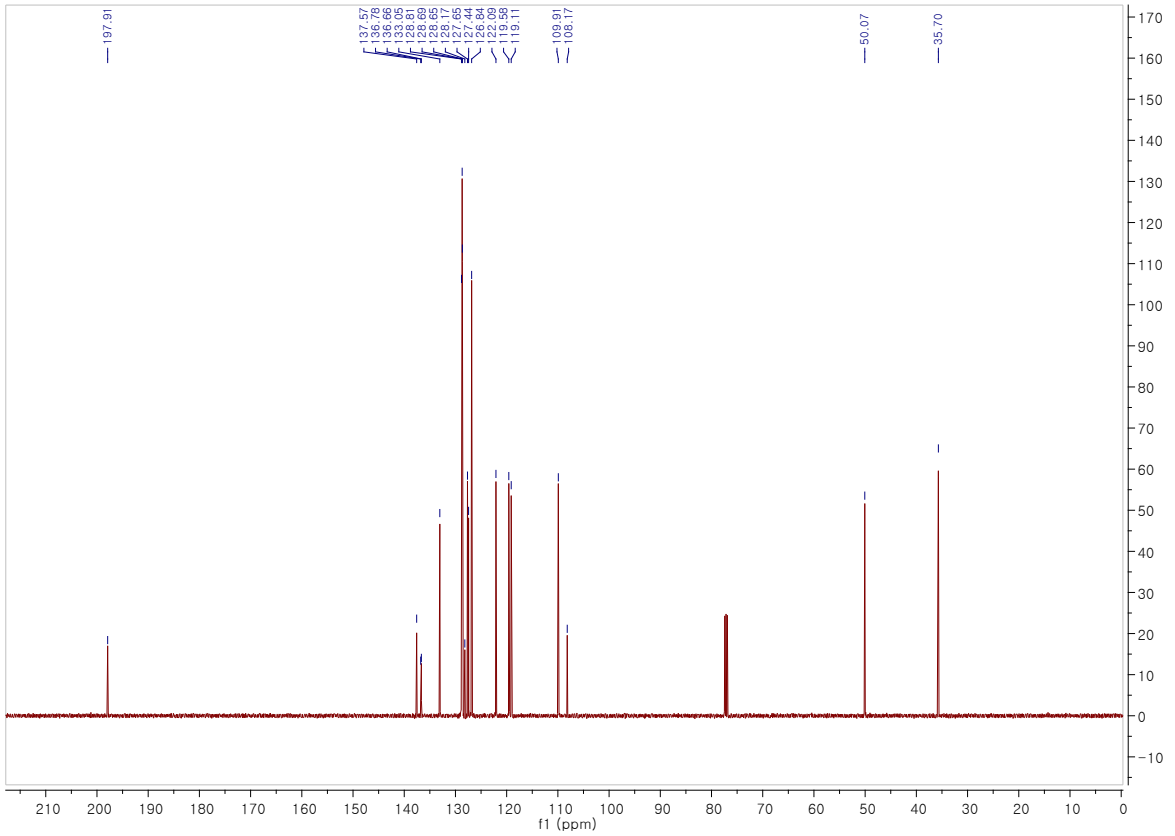
5cd (^{13}C NMR)



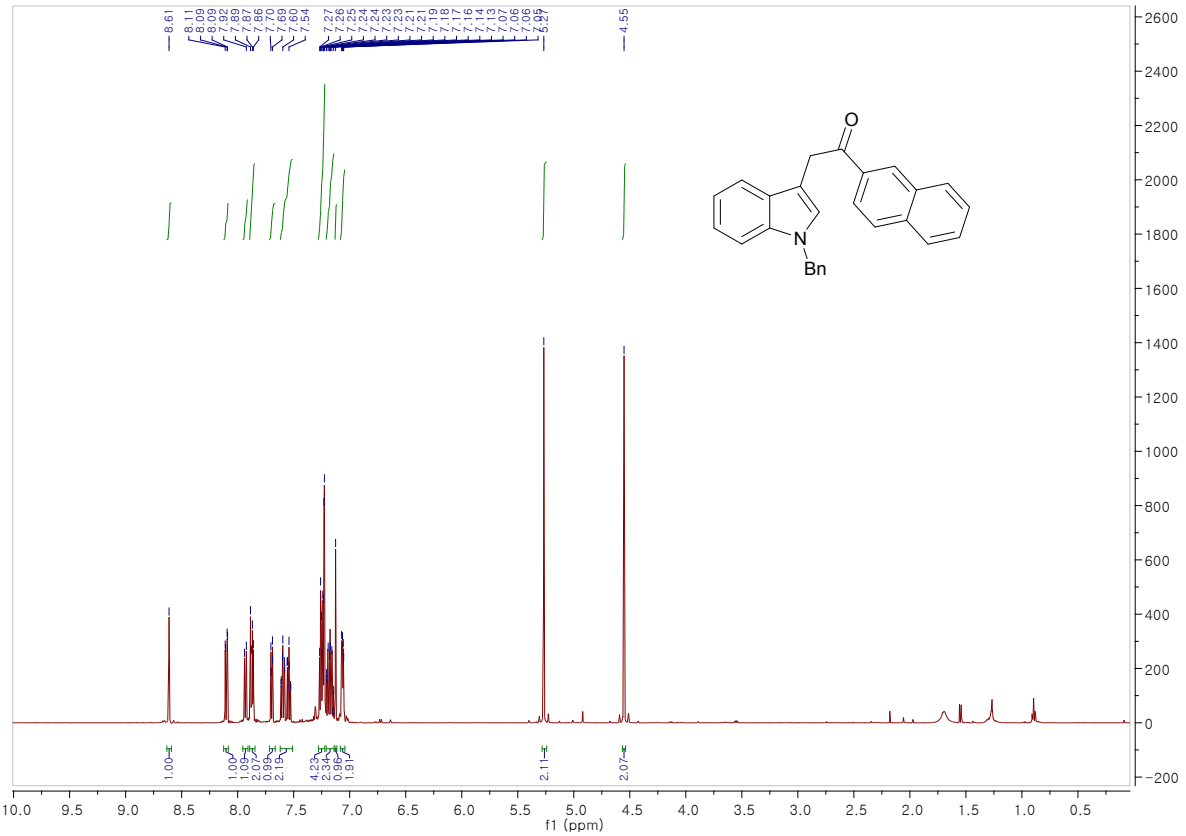
5ce (^{1}H NMR)



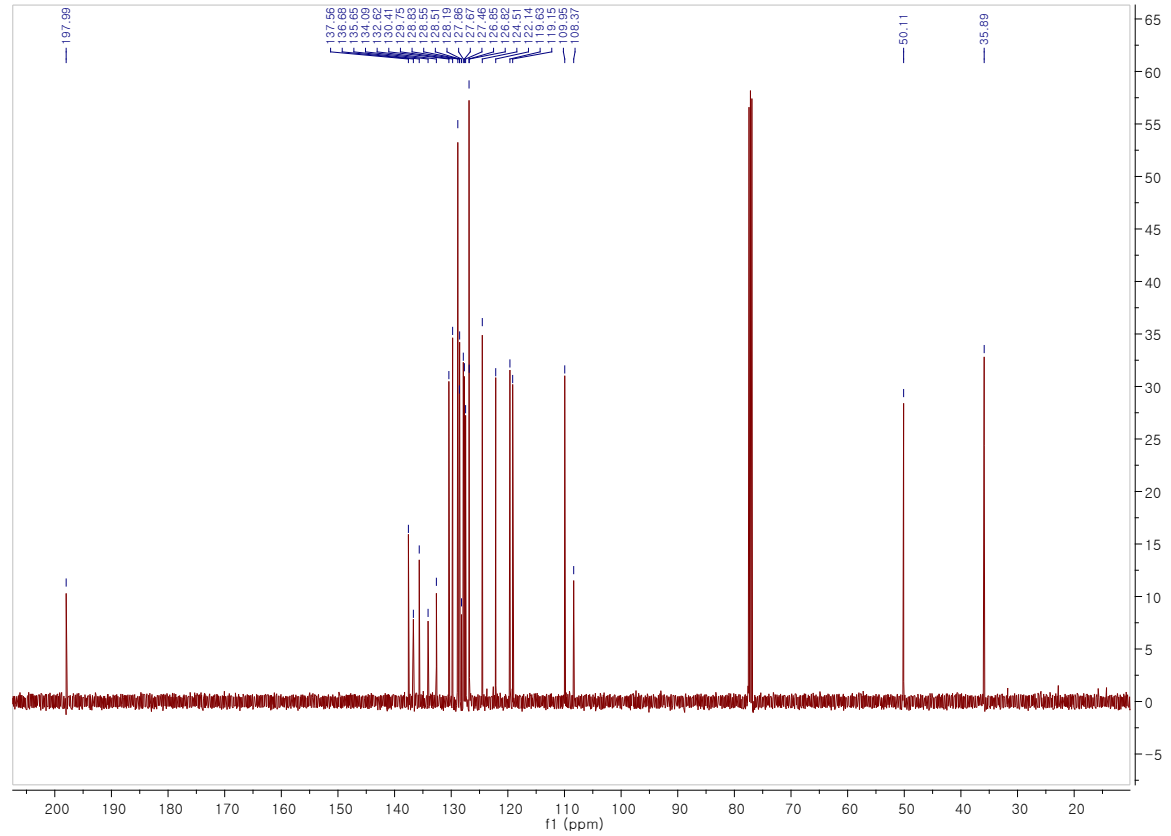
5ce (^{13}C NMR)



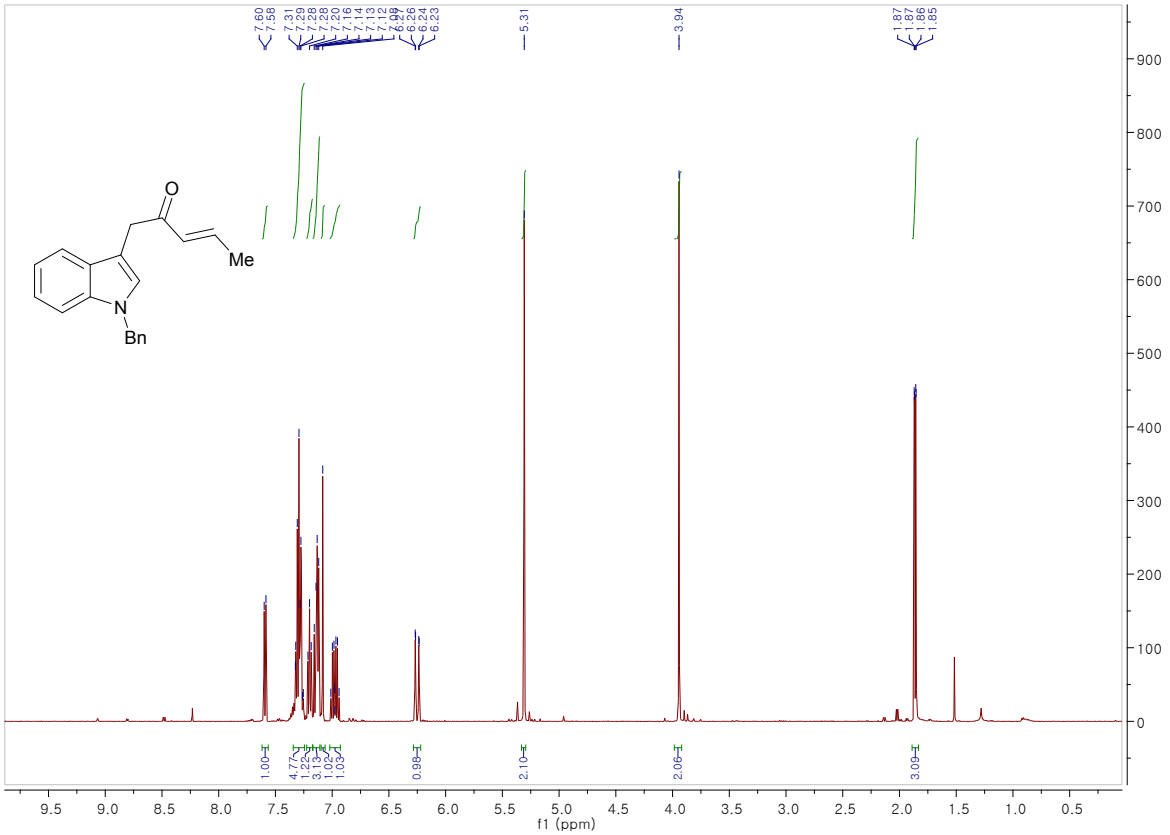
5cf (^{1}H NMR)



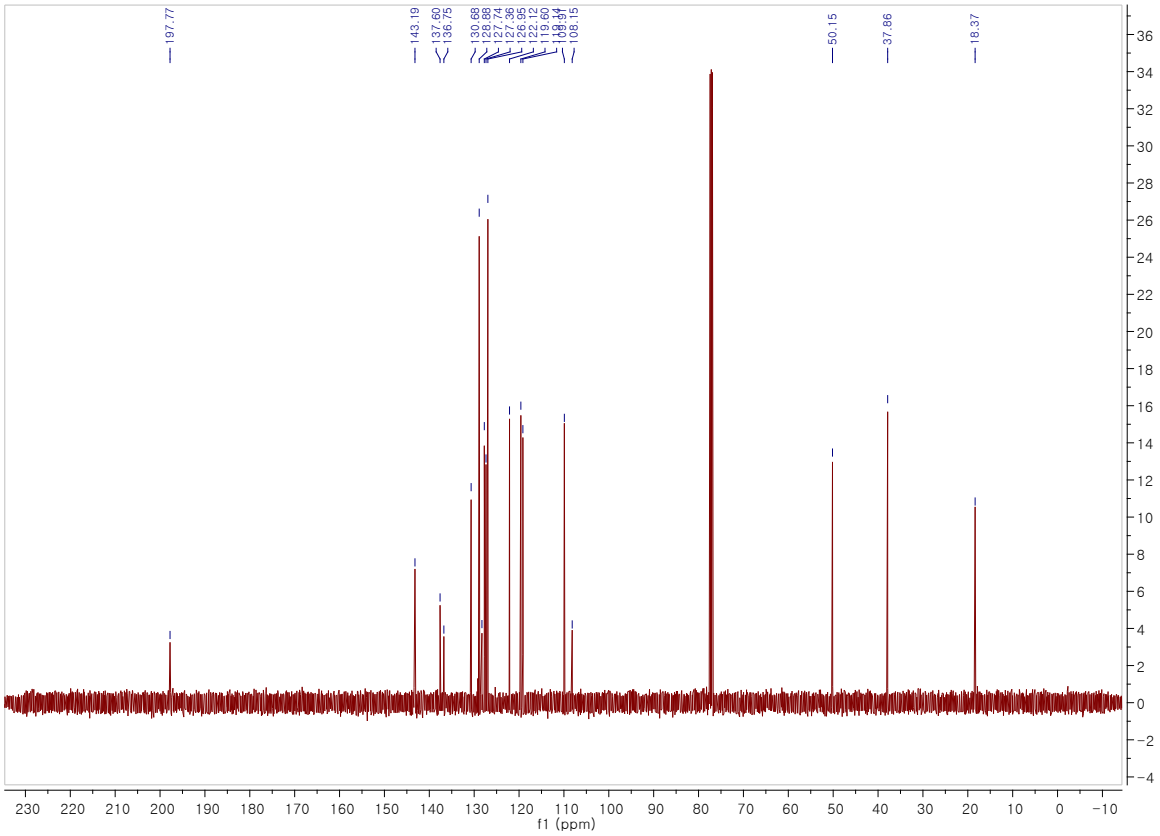
5cf (^{13}C NMR)



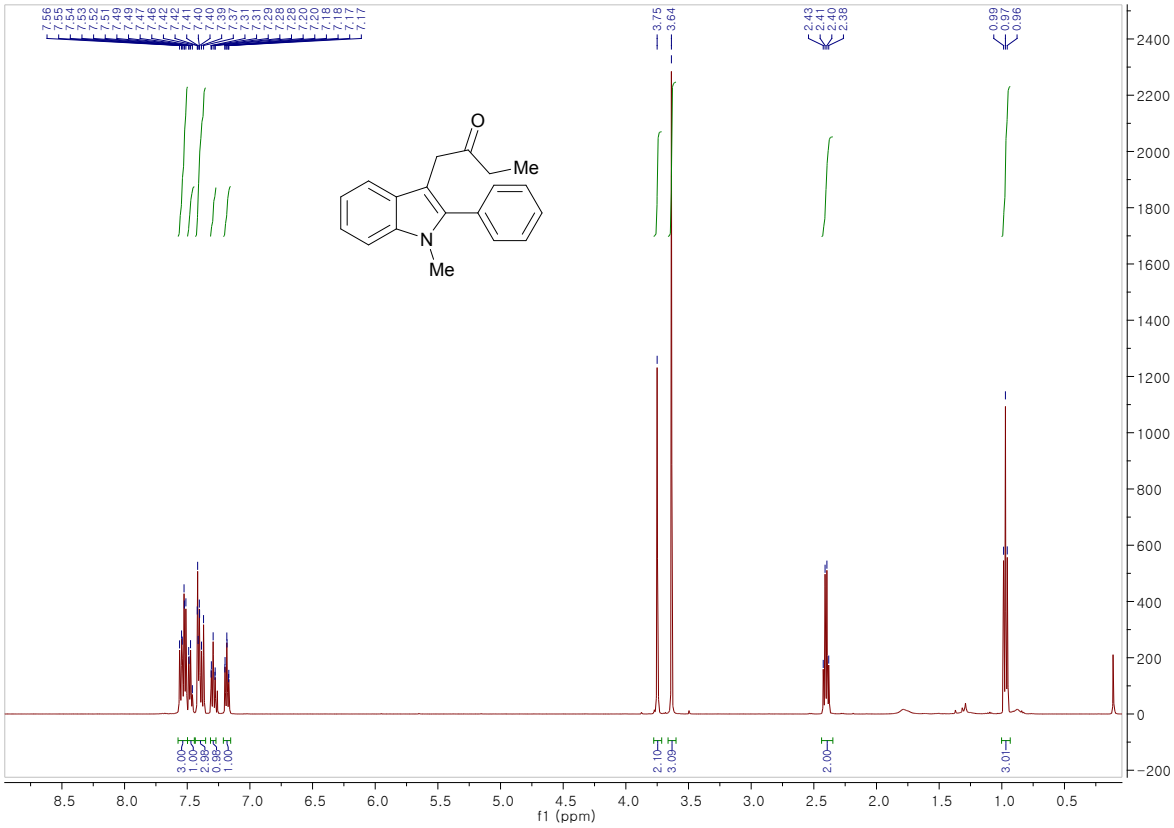
5cg (^{1}H NMR)



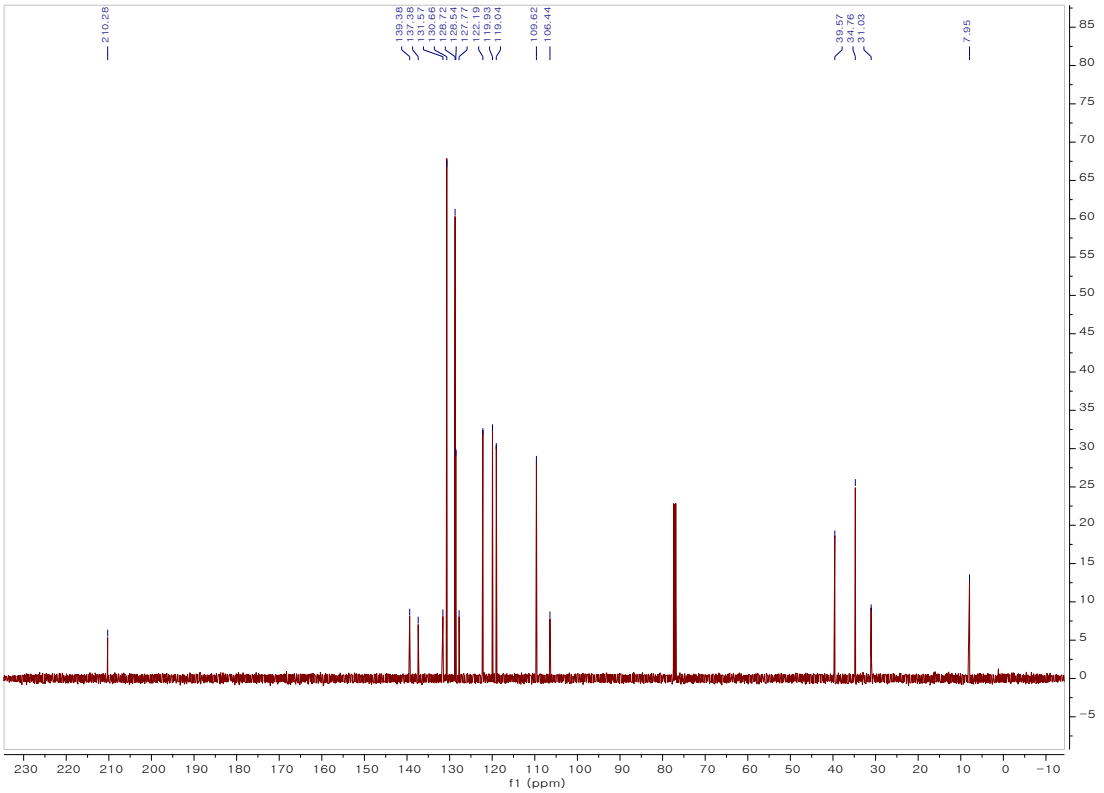
5cg (^{13}C NMR)



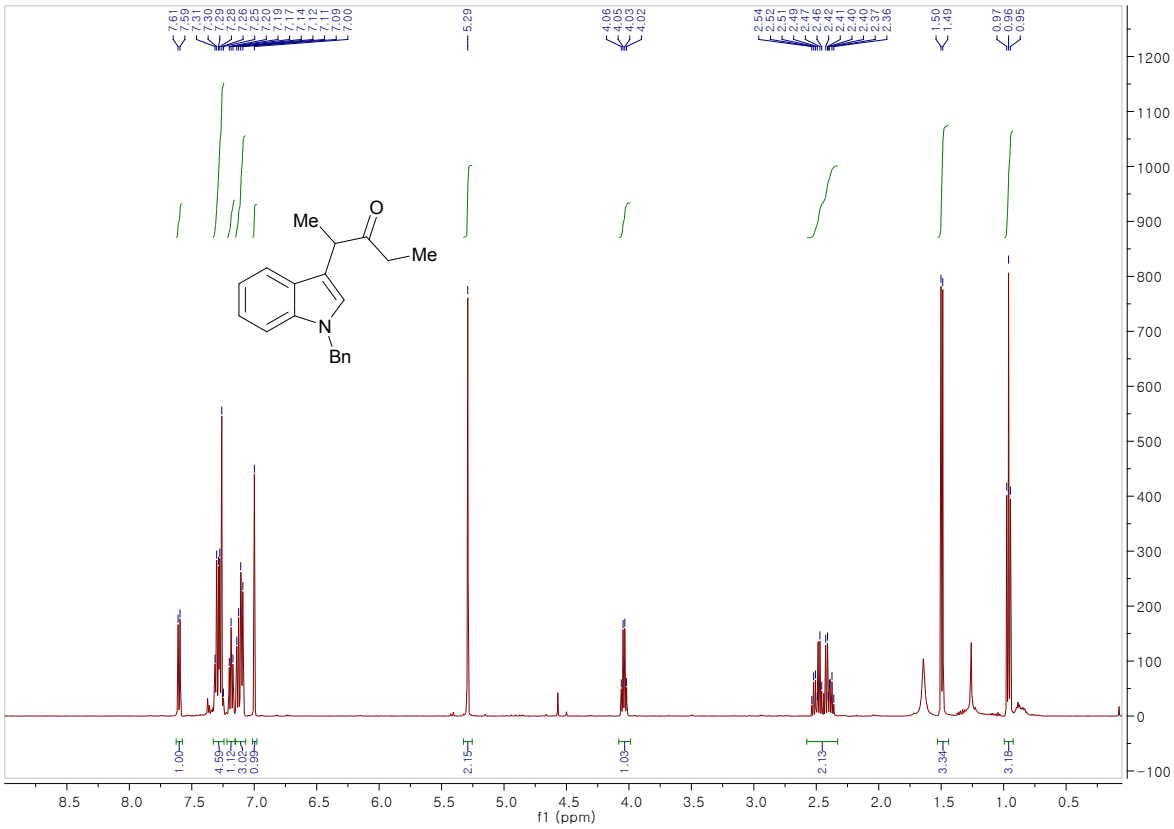
5sb (^{1}H NMR)



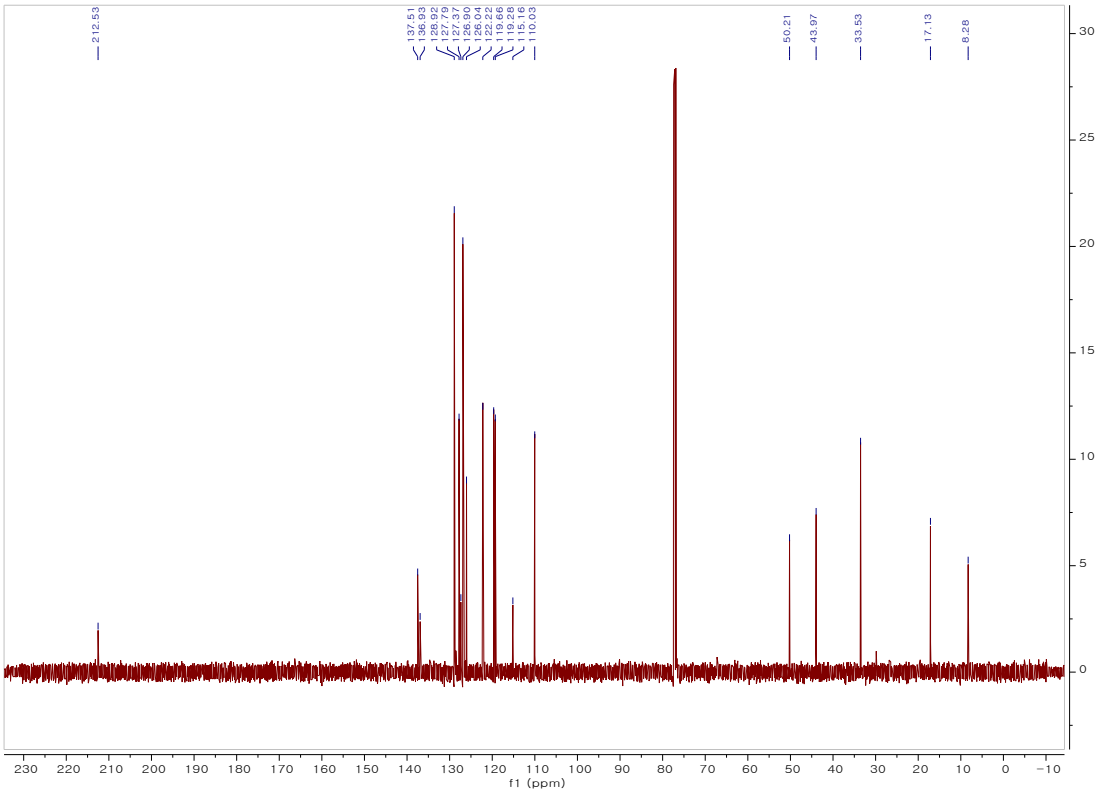
5sb (^{13}C NMR)



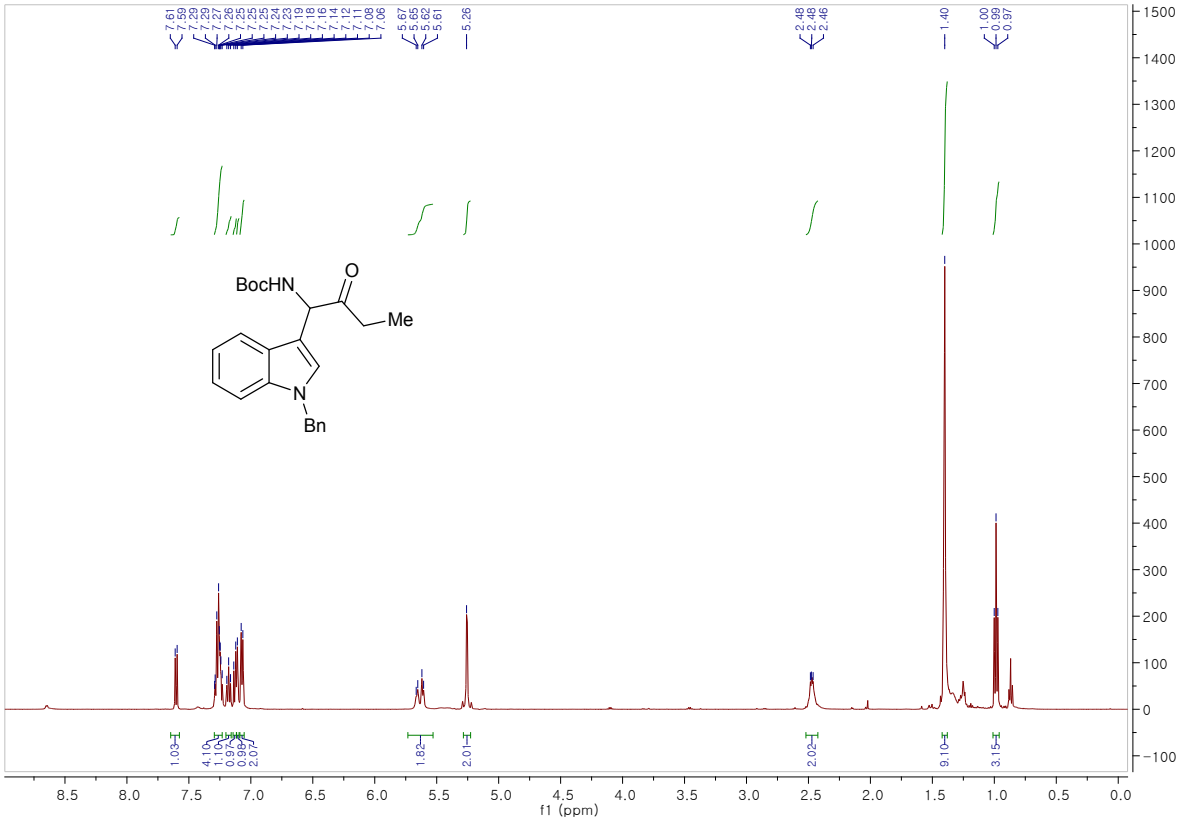
5yb (^{1}H NMR)



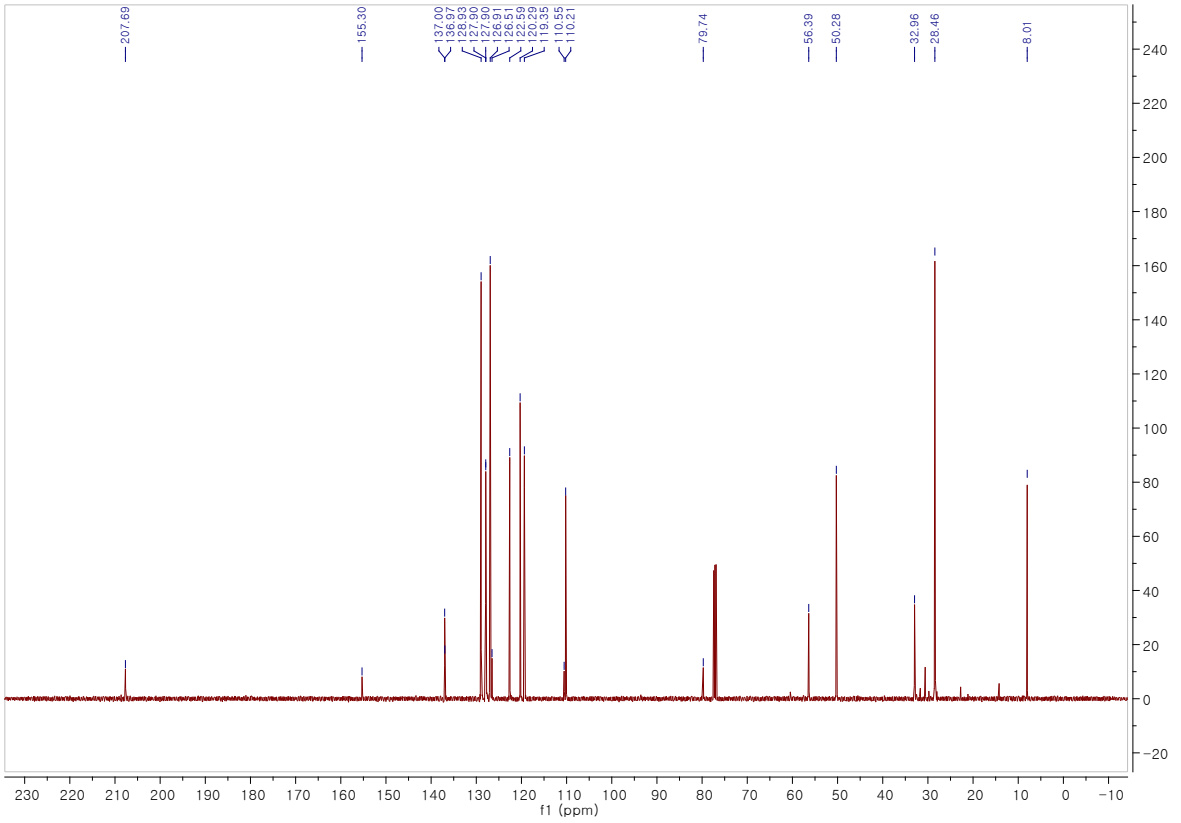
5yb (^{13}C NMR)



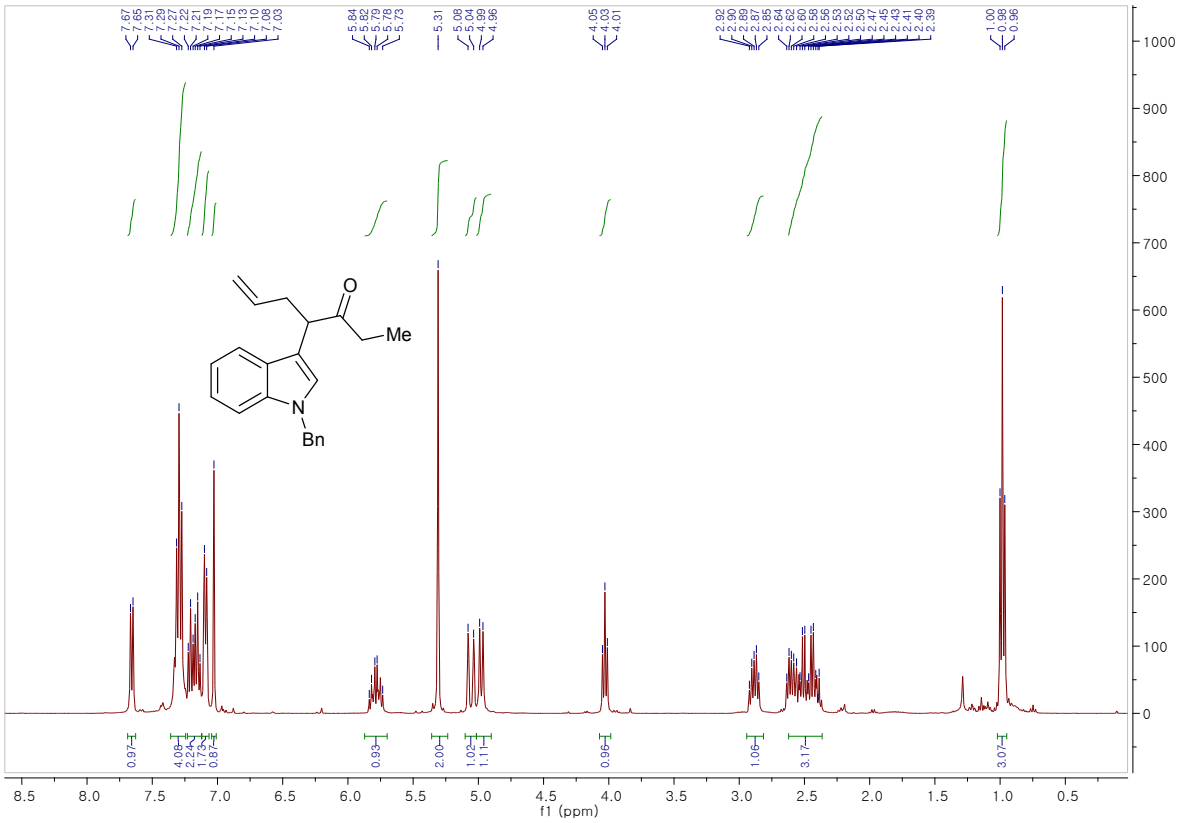
5zb (^{1}H NMR)



5zb (^{13}C NMR)



5zab (^{1}H NMR)



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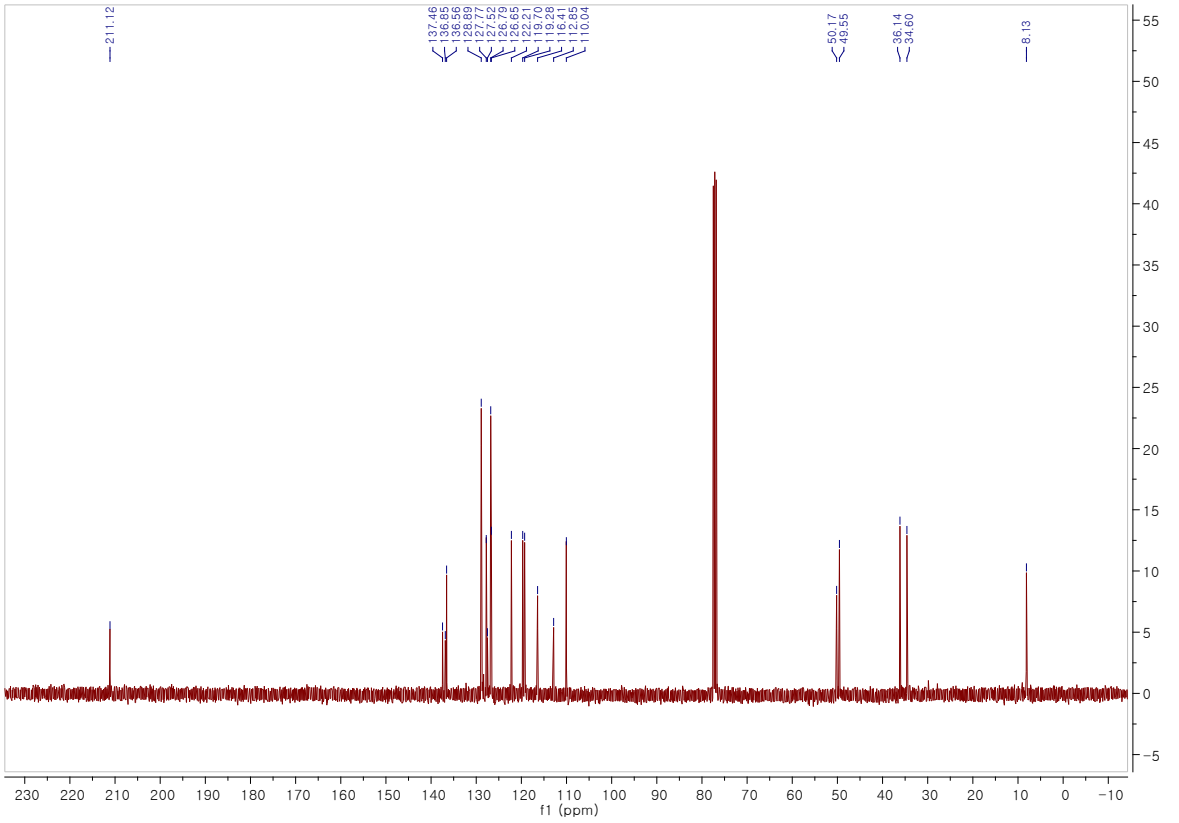
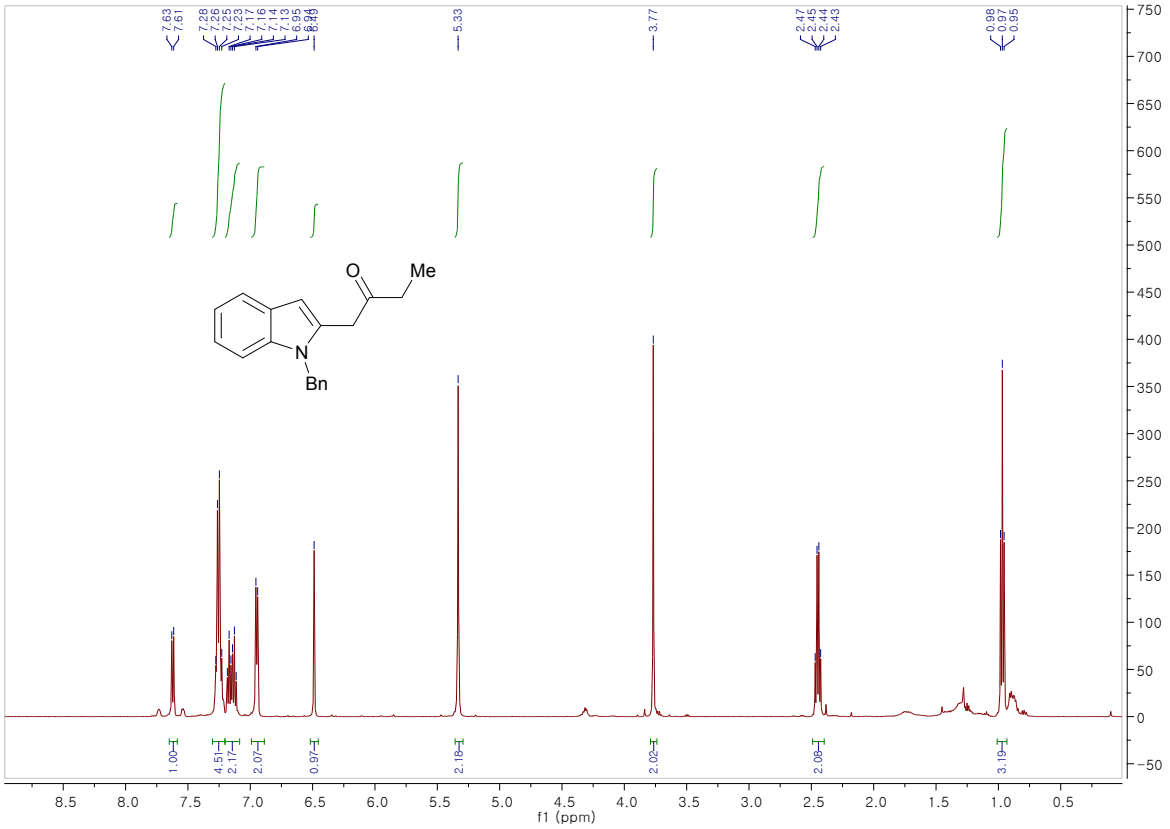
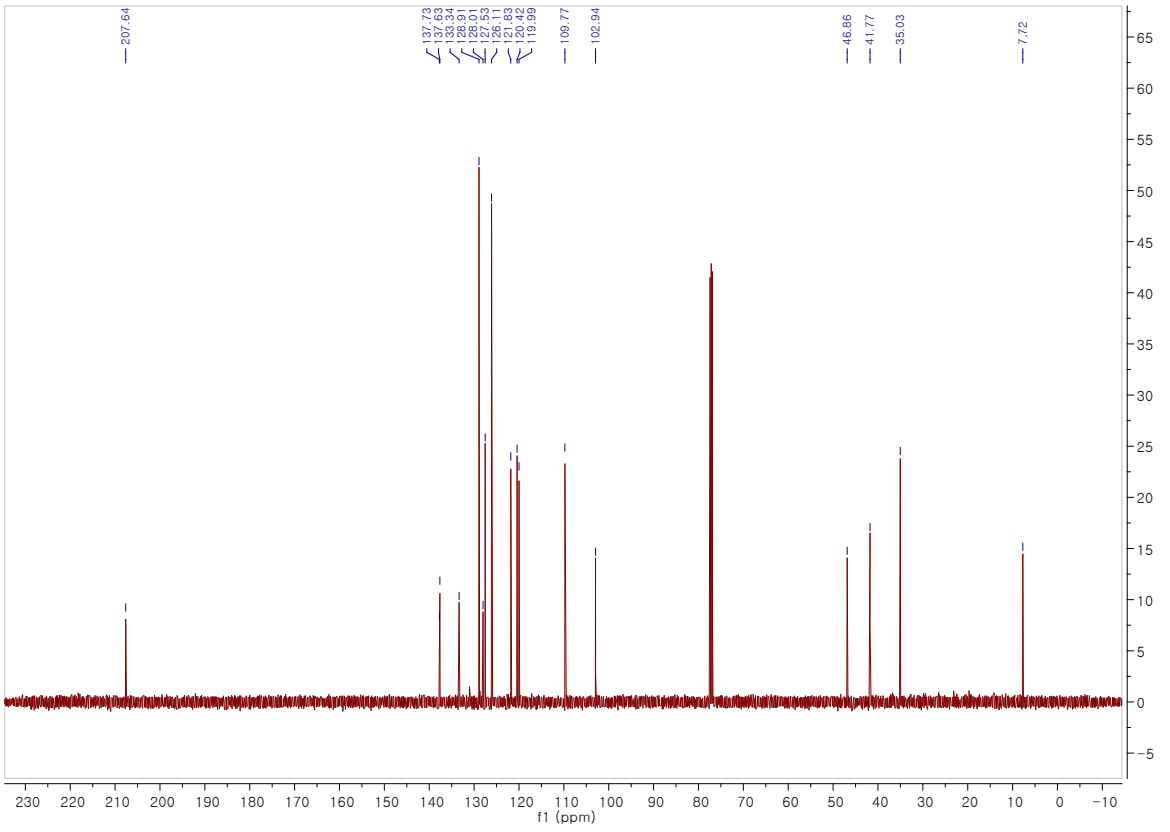


5zbb (^{1}H NMR)



5zbb (^{13}C NMR)



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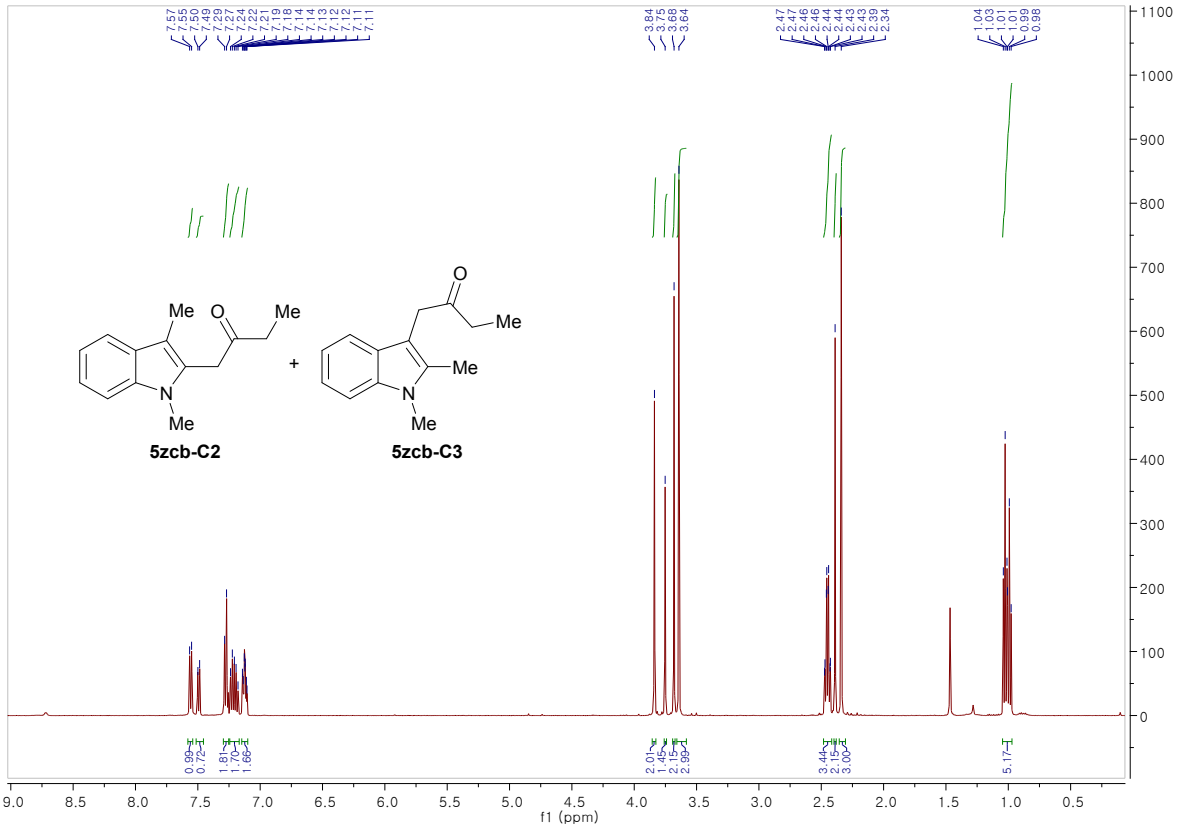
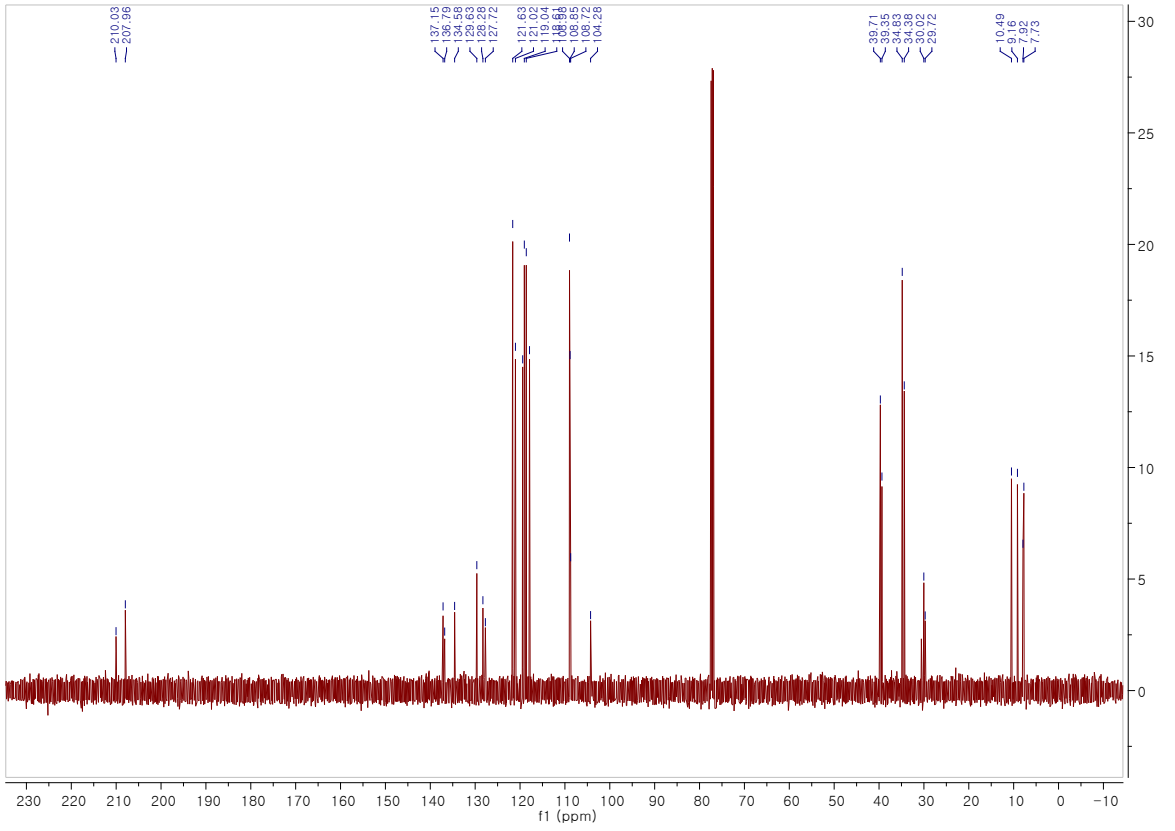
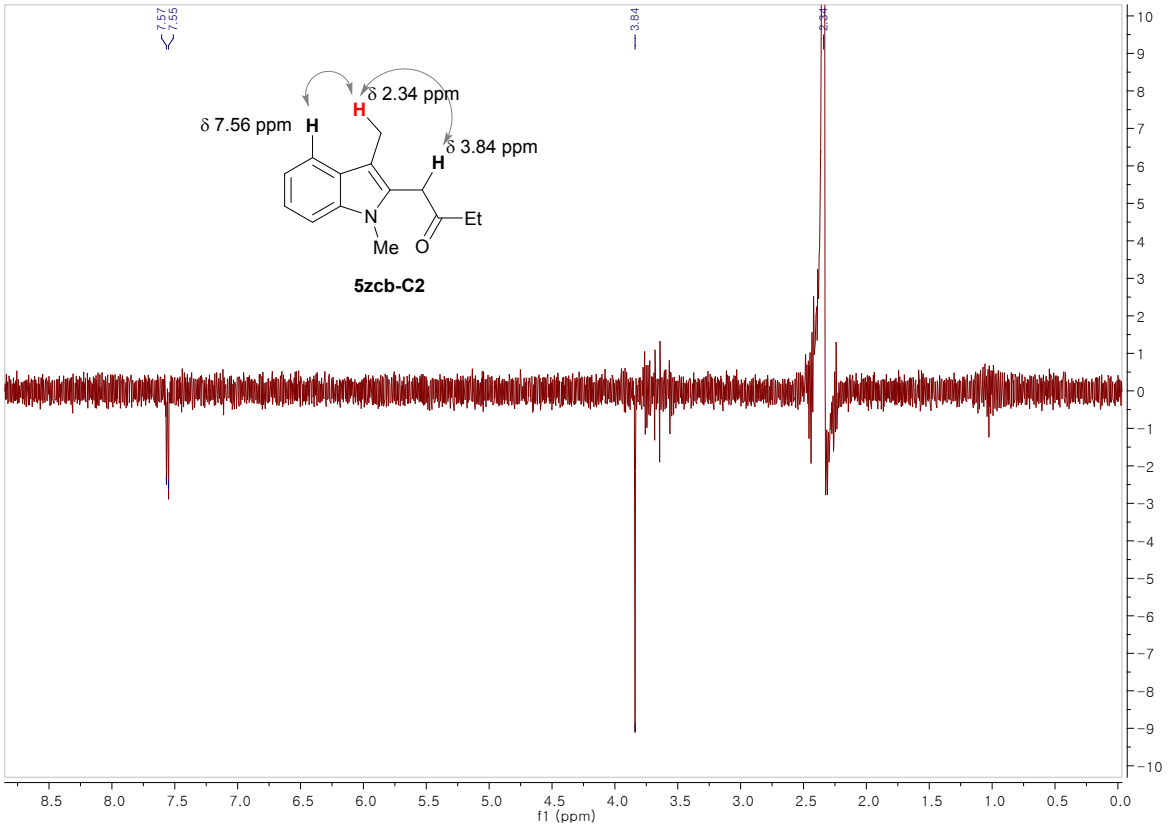


5zcb (^{13}C NMR)



5zcb-C2 (NOSEY)



5zcb-C3 (NOSEY)