

Supporting Information

Palladium-Catalyzed Cascade Reactions of Alkene-tethered Carbamoyl Chlorides with *N*-Tosyl Hydrazones: Synthesis of Alkene-functionalized Oxindoles

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Table of Contents

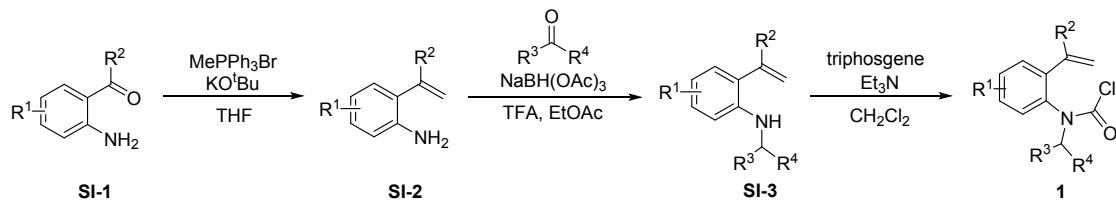
General Information-----	S02
Preparation of Starting Materials-----	
S02	
Characterization of Starting Materials-----	S04
General Procedures for the Synthesis of Alkene-functionalized Oxindoles-----	S08
Characterization of Products-----	S08
Synthetic Transformations-----	S21
NMR Spectra-----	S23

General information:

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

Preparation of Starting Materials:

General Procedure 1:



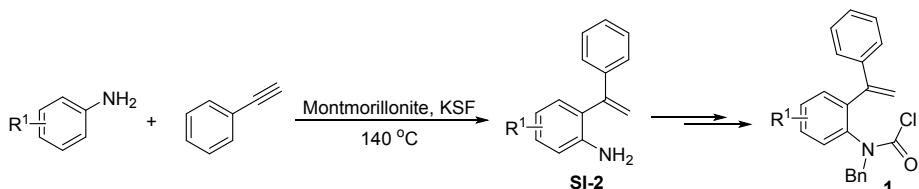
A mixture of MePPh₃Br (1.5 equiv) and KO^tBu (1.5 equiv) in THF (0.3 mmol/mL) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2**.

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

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

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

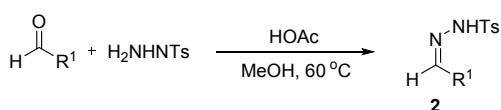
General Procedure 2:



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

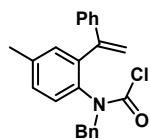
(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 3:



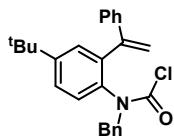
To a solution of aldehyde (1.0 equiv) and *p*-toluene sulfonylhydrazide (1.0 equiv) in methanol, a catalytic amount of acetic acid was added. The mixture was stirred at 60 °C for 3 h and the reaction was monitored by TLC. After the completion of the reaction, methanol slowly evaporates in the air to precipitate solids to give **2**.

Characterization of Starting Materials (New Compounds):



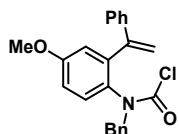
benzyl(4-methyl-2-(1-phenylvinyl)phenyl)carbamic chloride (**1b**) was synthesized by **General Procedure 2.** ^1H and ^{13}C NMR data listed is for the major rotamer.

White solid; M.P.: 71–76 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.39 (m, 5H), 7.35 – 7.31 (m, 4H), 7.22 – 7.19 (m, 2H), 7.10 – 7.06 (m, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.85 (s, 1H), 5.53 (s, 1H), 5.03 (d, J = 14.4 Hz, 1H), 3.77 (d, J = 14.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.75, 146.98, 140.15, 139.44, 138.73, 136.47, 135.67, 131.93, 130.44, 128.89, 128.36, 128.34, 128.11, 127.81, 127.75, 126.83, 117.41, 54.61, 21.00. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}$: $[\text{M}+\text{H}^+]$ 362.1306, found 362.1306. IR (neat): ν = 703, 776, 832, 908, 1020, 1195, 1371, 1490, 1738, 3679.



benzyl(4-(tert-butyl)-2-(1-phenylvinyl)phenyl)carbamic chloride (**1c**) was synthesized by **General Procedure 2.** ^1H and ^{13}C NMR data listed is for the major rotamer.

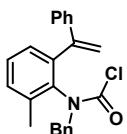
Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 2.0 Hz, 1H), 7.24 (s, 5H), 7.15 – 7.09 (m, 4H), 7.04 – 6.98 (m, 2H), 6.61 (d, J = 8.4 Hz, 1H), 5.67 (s, 1H), 5.34 (s, 1H), 4.77 (d, J = 14.4 Hz, 1H), 3.58 (d, J = 14.4 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.89, 149.85, 147.42, 140.21, 139.05, 136.52, 135.76, 129.95, 128.83, 128.40, 128.36, 128.14, 127.79, 126.82, 125.21, 117.45, 54.70, 34.62, 31.22. ESI-MS: Calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}$: $[\text{M}+\text{H}^+]$ 404.1776, found 404.1778. IR (neat): ν = 472, 790, 907, 1020, 1499, 2578, 3684.



benzyl(4-methoxy-2-(1-phenylvinyl)phenyl)carbamic chloride (**1d**) was synthesized by **General Procedure 2.** ^1H and ^{13}C NMR data listed is for the major rotamer.

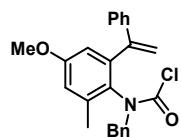
Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 4.0 Hz, 5H), 7.32 – 7.28 (m,

3H), 7.17 – 7.14 (m, 2H), 6.99 (d, J = 2.8 Hz, 1H), 6.76 (dd, J = 8.8, 3.2 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 5.82 (s, 1H), 5.50 (s, 1H), 4.98 (d, J = 14.4 Hz, 1H), 3.84 (s, 3H), 3.67 (d, J = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.31, 150.15, 146.86, 141.03, 139.91, 135.72, 131.88, 131.75, 128.98, 128.44, 128.39, 128.23, 127.87, 126.85, 117.60, 116.48, 113.23, 55.35, 54.69. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_2$: [M+H $^+$] 378.1255, found 378.1259. IR (neat): ν = 476, 607, 700, 778, 833, 910, 1025, 1224, 1315, 1375, 1492, 1573, 1732, 3668.



benzyl(2-methyl-6-(1-phenylvinyl)phenyl)carbamic chloride (**1e**) was synthesized by **General Procedure 2**. ^1H and ^{13}C NMR data listed is for the major rotamer.

White solid; M.P.: 102-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.28 (m, 5H), 7.25 – 7.16 (m, 5H), 7.08 – 7.03 (m, 3H), 5.75 (s, 1H), 5.43 (s, 1H), 5.08 (d, J = 14.0 Hz, 1H), 3.91 (d, J = 14.0 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.96, 147.39, 139.89, 139.63, 138.52, 137.71, 135.14, 130.60, 129.93, 129.39, 128.46, 128.42, 128.41, 128.23, 126.86, 126.62, 117.52, 55.09, 17.79. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}$: [M+H $^+$] 362.1306, found 362.1310. IR (neat): ν = 509, 614, 700, 780, 947, 1017, 1200, 1365, 1445, 1602, 1730, 2357, 3664.



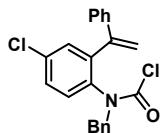
benzyl(4-methoxy-2-methyl-6-(1-phenylvinyl)phenyl)carbamic chloride (**1f**) was synthesized by **General Procedure 2**. ^1H and ^{13}C NMR data listed is for the major rotamer.

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.19 (m, 5H), 7.13 – 7.11 (m, 1H), 7.10 – 7.07 (m, 2H), 7.01 – 6.95 (m, 2H), 6.69 (d, J = 2.8 Hz, 1H), 6.52 (d, J = 2.8 Hz, 1H), 5.67 (s, 1H), 5.36 (s, 1H), 4.99 (d, J = 14.0 Hz, 1H), 3.78 (d, J = 14.0 Hz, 1H), 3.67 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.68, 150.30, 147.28, 140.69, 139.69, 139.59, 135.18, 130.75, 129.86, 128.33, 128.30, 128.14, 128.08,

126.76, 117.24, 115.17, 114.48, 55.21, 55.15, 17.99. ESI-MS: Calcd for C₂₄H₂₂ClNO₂: [M+H⁺] 392.1412, found 392.1410. IR (neat): ν = 473, 592, 703, 845, 986, 1086, 1224, 1648, 2171, 3493.

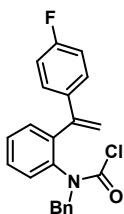


benzyl(4-fluoro-2-(1-phenylvinyl)phenyl)carbamic chloride (**1g**) was synthesized by **General Procedure 2**. ¹H, ¹⁹F and ¹³C NMR data listed is for the major rotamer. White solid; M.P.: 87-91 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 5H), 7.25 (s, 3H), 7.14 – 7.06 (m, 3H), 6.89 – 6.85 (m, 1H), 6.69 – 6.64 (m, 1H), 5.79 (s, 1H), 5.46 (s, 1H), 4.94 (d, *J* = 14.4 Hz, 1H), 3.60 (d, *J* = 14.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.03 (d, *J* = 249.0 Hz), 149.73, 146.05, 142.07 (d, *J* = 9.0 Hz), 139.48, 135.39, 134.94 (d, *J* = 3.0 Hz), 132.57 (d, *J* = 9.0 Hz), 128.97, 128.59, 128.53, 128.49, 128.08, 126.84, 118.41, 118.16 (d, *J* = 21.0 Hz), 115.16 (d, *J* = 23.0 Hz), 54.53. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.73. ESI-MS: Calcd for C₂₂H₁₇ClFNO: [M+H⁺] 366.1055, found 366.1055. IR (neat): ν = 497, 556, 606, 701, 779, 837, 908, 965, 1021, 1083, 1194, 1312, 1374, 1486, 1582, 1743, 1890, 1960, 2071, 2356, 3021, 3612.



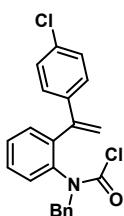
benzyl(4-chloro-2-(1-phenylvinyl)phenyl)carbamic chloride (**1h**) was synthesized by **General Procedure 1**. ¹H and ¹³C NMR data listed is for the major rotamer.

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 2.8 Hz, 1H), 7.41 – 7.34 (m, 5H), 7.30 – 7.26 (m, 3H), 7.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.12 – 7.09 (m, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.83 (s, 1H), 5.49 (s, 1H), 4.97 (d, *J* = 14.4 Hz, 1H), 3.63 (d, *J* = 14.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.45, 145.95, 141.56, 139.43, 137.42, 135.30, 134.63, 132.14, 131.29, 128.96, 128.61, 128.56, 128.53, 128.42, 128.13, 126.84, 118.56, 54.44. ESI-MS: Calcd for C₂₂H₁₇Cl₂NO: [M+H⁺] 382.0760, found 382.0766. IR (neat): ν = 472, 700, 901, 1017, 1090, 1224, 1485, 1641, 1737, 2110, 2349, 2560, 3622.



benzyl(2-(1-(4-fluorophenyl)vinyl)phenyl)carbamic chloride (**1k**) was synthesized by **General Procedure 1.** ^1H , ^{19}F and ^{13}C NMR data listed is for the major rotamer.

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.32 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.17 (m, 3H), 7.16 – 7.15 (m, 1H), 7.07 – 7.02 (m, 2H), 6.99 – 6.95 (m, 2H), 6.70 (d, $J = 7.6$ Hz, 1H), 5.66 (s, 1H), 5.36 (s, 1H), 4.92 (d, $J = 14.4$ Hz, 1H), 3.67 (d, $J = 14.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.69 (d, $J = 247.0$ Hz), 149.58, 146.02, 139.25 (d, $J = 63.0$ Hz), 136.21, 135.45, 131.42, 130.92, 128.94, 128.91, 128.58, 128.47, 128.01, 117.76, 115.38 (d, $J = 22.0$ Hz), 54.73. ^{19}F NMR (376 MHz, CDCl_3) δ -113.28. ESI-MS: Calcd for $\text{C}_{22}\text{H}_{17}\text{ClFNO}$: $[\text{M}+\text{H}^+]$ 366.1055, found 366.1055. IR (neat): ν = 480, 596, 701, 760, 835, 906, 1021, 1221, 1500, 1739, 2353, 3665.



benzyl(2-(1-(4-chlorophenyl)vinyl)phenyl)carbamic chloride (**1l**) was synthesized by **General Procedure 1.** ^1H and ^{13}C NMR data listed is for the major rotamer.

White solid; M.P.: 85-87 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.29 (m, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.18 – 7.13 (m, 6H), 7.03 – 6.97 (m, 2H), 6.67 (d, $J = 7.6$ Hz, 1H), 5.68 (s, 1H), 5.36 (s, 1H), 4.90 (d, $J = 14.4$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.60, 145.81, 139.27, 138.96, 138.53, 135.40, 134.14, 131.46, 130.92, 128.96, 128.93, 128.63, 128.57, 128.48, 128.11, 128.04, 118.31, 54.78. ESI-MS: Calcd for $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{NO}$: $[\text{M}+\text{H}^+]$ 382.0760, found 382.0766. IR (neat): ν = 488, 612, 684, 741, 836, 915, 967, 1019, 1091, 1229, 1374, 1484, 1605, 1721, 2352, 2592, 3669.



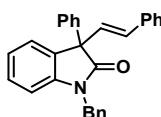
benzyl(4-chloro-2-(1-(2-fluorophenyl)vinyl)phenyl)carbamic chloride (**1m**) was synthesized by **General Procedure 1**. ^1H , ^{19}F and ^{13}C NMR data listed is for the major rotamer.

Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 2.4$ Hz, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.14 (m, 3H), 7.11 – 7.07 (m, 1H), 7.05 – 6.98 (m, 4H), 6.47 (d, $J = 8.4$ Hz, 1H), 5.68 (s, 1H), 5.59 (s, 1H), 4.95 (d, $J = 14.4$ Hz, 1H), 3.68 (d, $J = 14.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.67 (d, $J = 248.0$ Hz), 149.46, 141.12, 141.07, 136.78, 135.24, 134.74, 132.16, 130.71, 130.36 (d, $J = 3.0$ Hz), 130.20 (d, $J = 8.0$ Hz), 129.16, 128.56, 128.37, 128.18, 127.67 (d, $J = 13.0$ Hz), 124.45 (d, $J = 4.0$ Hz), 122.68, 116.13 (d, $J = 21.0$ Hz), 54.44. ^{19}F NMR (376 MHz, CDCl_3) δ -113.23. ESI-MS: Calcd for $\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{FNO}$: [M+H $^+$] 400.0666, found 400.0669. IR (neat): ν = 479, 559, 608, 692, 755, 832, 895, 1021, 1094, 1212, 1317, 1376, 1483, 1611, 1730, 2071, 2357, 2949, 3613.

General Procedure for the Synthesis of Alkene-functionalized Oxindoles:

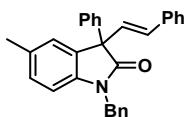
In a 38 mL sealed tube, the mixture of **1** (0.20 mmol), **2** (0.40 mmol), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol), $\text{P}(4\text{-F-C}_6\text{H}_4)_3$ (12.7 mg, 0.04 mmol), $\text{LiO}'\text{Bu}$ (48.0 mg, 0.60 mmol) were dissolved in anhydrous MeCN (2.0 mL). The reaction mixture was heated to 90 °C for 30 min. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the products **3**.

Characterization of Products:



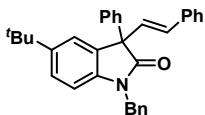
(E)-1-benzyl-3-phenyl-3-styrylindolin-2-one (3aa**)**

Yellow solid (76 mg, 95%); M.P.: 112-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 4H), 7.45 – 7.29 (m, 13H), 7.20 (d, *J* = 6.8 Hz, 1H), 6.92 (s, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 5.11 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 176.69, 142.23, 140.15, 136.36, 135.72, 131.67, 131.55, 129.06, 128.70, 128.66, 128.47, 128.20, 127.81, 127.50, 127.47, 127.41, 127.04, 126.55, 125.47, 122.78, 109.59, 59.62, 43.79. ESI-MS: Calcd for C₂₉H₂₃NO: [M+H⁺] 402.1852, found 402.1855. IR (neat): ν = 475, 592, 730, 901, 1019, 1093, 1227, 1510, 1643, 2023, 2353, 2561, 3200, 3634.



(E)-1-benzyl-5-methyl-3-phenyl-3-styrylindolin-2-one (3ba**)**

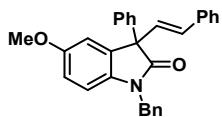
White solid (67 mg, 81%); M.P.: 59-62 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.25 – 7.16 (m, 8H), 7.02 – 6.94 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 4.93 (s, 2H), 2.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.72, 140.38, 139.90, 136.52, 135.90, 132.40, 131.84, 131.53, 129.26, 128.73, 128.71, 128.57, 128.51, 127.82, 127.52, 127.47, 127.10, 126.62, 126.20, 126.19, 109.40, 59.78, 43.88, 21.15. ESI-MS: Calcd for C₃₀H₂₅NO: [M+H⁺] 416.2009, found 416.2011. IR (neat): ν = 478, 595, 695, 736, 801, 901, 1022, 1090, 1188, 1342, 1442, 1492, 1610, 1707, 2565, 2916, 3643.



(E)-1-benzyl-5-(tert-butyl)-3-phenyl-3-styrylindolin-2-one (3ca**)**

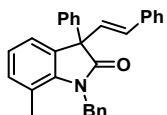
Yellow solid (73 mg, 80%); M.P.: 59-62 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.27 (m, 4H), 7.25 – 7.20 (m, 3H), 7.18 (d, *J* = 6.0 Hz, 7H), 7.15 – 7.11 (m, 3H), 6.67 – 6.63 (m, 1H), 6.65 (d, *J* = 14.0 Hz, 1H), 6.48 (d, *J* = 14.0 Hz, 1H), 4.88 (d, *J* = 16.4 Hz, 1H), 4.84 (d, *J* = 16.4 Hz, 1H), 1.18 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 176.76, 146.02, 140.28, 139.92, 136.52, 135.96, 131.46, 131.26, 129.34, 128.71, 128.67, 128.51, 127.80, 127.56, 127.50, 127.43, 127.18, 126.60, 124.80, 122.74, 108.95, 59.87, 43.91, 34.54, 31.52. ESI-MS: Calcd for C₃₃H₃₁NO: [M+H⁺] 458.2478,

found 458.2484. IR (neat): ν = 484, 596, 694, 746, 811, 910, 983, 1024, 1194, 1341, 1492, 1610, 1707, 2357, 2959, 3615.



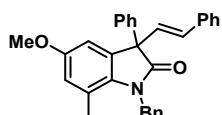
(E)-1-benzyl-5-methoxy-3-phenylindolin-2-one (3da)

Yellow oil (47 mg, 55%); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 7.2 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.24 – 7.20 (m, 4H), 7.19 (s, 3H), 7.18 – 7.15 (m, 2H), 6.76 (d, J = 2.0 Hz, 1H), 6.66 – 6.64 (m, 1H), 6.65 (d, J = 16.0 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 4.91 (d, J = 16.0 Hz, 1H), 4.87 (d, J = 16.0 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.52, 156.09, 140.19, 136.46, 135.86, 135.77, 133.09, 131.67, 129.09, 128.76, 128.54, 127.88, 127.55, 127.49, 127.12, 126.65, 112.90, 112.55, 110.03, 60.12, 55.75, 43.99. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{25}\text{NO}_2$: [M+H $^+$] 432.1958, found 432.1960. IR (neat): ν = 479, 597, 696, 738, 801, 908, 1022, 1183, 1342, 1490, 1706, 2356, 3666.



(E)-1-benzyl-7-methyl-3-phenylindolin-2-one (3ea)

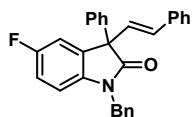
Yellow oil (60 mg, 72%); ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, J = 7.2 Hz, 4H), 7.26 – 7.19 (m, 5H), 7.17 – 7.11 (m, 4H), 7.07 – 7.01 (m, 3H), 6.95 – 6.88 (m, 2H), 6.66 (d, J = 16.4 Hz, 1H), 6.50 (d, J = 16.4 Hz, 1H), 5.22 (d, J = 16.8 Hz, 1H), 5.14 (d, J = 16.8 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.73, 140.51, 137.75, 136.56, 132.44, 132.21, 131.62, 129.71, 128.83, 128.69, 128.53, 127.84, 127.63, 127.49, 127.13, 126.64, 125.60, 123.68, 122.91, 120.30, 59.16, 45.13, 18.91. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{25}\text{NO}$: [M+H $^+$] 416.2009, found 416.2011. IR (neat): ν = 476, 592, 693, 738, 901, 1020, 1181, 1346, 1448, 1598, 1706, 1953, 2355, 2576, 3654.



(E)-1-benzyl-5-methoxy-7-methyl-3-phenylindolin-2-one (3fa)

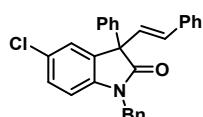
Yellow solid (78 mg, 88%); M.P.: 68–73 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.22 – 7.17 (m, 3H), 7.15 (d,

J = 7.6 Hz, 3H), 7.12 – 7.10 (m, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 16.8 Hz, 1H), 3.63 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.48, 155.65, 140.46, 137.71, 136.50, 133.85, 133.77, 131.65, 129.63, 128.78, 128.70, 128.51, 127.83, 127.60, 127.48, 127.08, 126.62, 125.58, 121.25, 116.73, 110.21, 59.64, 55.58, 45.05, 18.91. ESI-MS: Calcd for $\text{C}_{31}\text{H}_{27}\text{NO}_2$: [M+H $^+$] 446.2115, found 446.2119. IR (neat): ν = 471, 592, 733, 845, 986, 1087, 1218, 1648, 2025, 3521.



(E)-1-benzyl-5-fluoro-3-phenyl-3-styrylindolin-2-one (3ga)

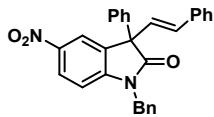
Yellow oil (83 mg, 99%); ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.34 (m, 2H), 7.30 – 7.27 (m, 5H), 7.27 – 7.15 (m, 8H), 6.94 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.67 – 6.64 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.95 (d, *J* = 16.0 Hz, 1H), 4.91 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.51, 159.24 (d, *J* = 240.0 Hz), 139.66, 138.17, 136.17, 135.46, 133.37 (d, *J* = 8.0 Hz), 131.92, 128.86, 128.83, 128.58, 128.48, 128.04, 127.73 (d, *J* = 7.0 Hz), 127.35, 127.07, 126.64, 114.67 (d, *J* = 23.0 Hz), 113.46 (d, *J* = 25.0 Hz), 110.22 (d, *J* = 8.0 Hz), 60.03, 44.02. ^{19}F NMR (376 MHz, CDCl_3) δ -119.52. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{22}\text{FNO}$: [M+H $^+$] 420.1758, found 420.1762. IR (neat): ν = 478, 592, 693, 738, 844, 908, 977, 1023, 1074, 1211, 1259, 1343, 1395, 1491, 1641, 1699, 2025, 2070, 2357, 3033, 3589.



(E)-1-benzyl-5-chloro-3-phenyl-3-styrylindolin-2-one (3ha)

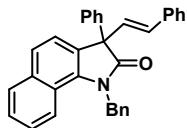
White solid (78 mg, 89%); M.P.: 63–68 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.31 (m, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.26 – 7.16 (m, 12H), 7.13 – 7.12 (m, 1H), 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.62 (s, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.91 (d, *J* = 16.4 Hz, 1H), 4.87 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.34, 140.84, 139.53, 136.15, 135.32, 133.52, 132.01, 128.89, 128.87, 128.59,

128.38, 128.28, 128.08, 127.81, 127.75, 127.38, 127.06, 126.67, 125.82, 110.63, 59.83, 44.00. ESI-MS: Calcd for $C_{29}H_{22}ClNO$: [M+H⁺] 436.1463, found 436.1468. IR (neat): ν = 476, 592, 691, 906, 981, 1019, 1090, 1210, 1339, 1487, 1700, 2024, 2071, 2356, 3017, 3607.



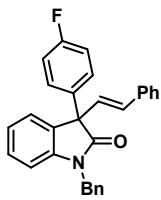
(E)-1-benzyl-5-nitro-3-phenyl-3-styrylindolin-2-one (3ia)

Yellow solid (67 mg, 75%); M.P.: 58-63 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.01 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.24 – 7.12 (m, 13H), 6.77 (d, J = 8.8 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 16.4 Hz, 1H), 4.94 (d, J = 16.8 Hz, 1H), 4.89 (d, J = 17.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.72, 147.77, 143.56, 138.64, 135.67, 134.60, 132.68, 132.42, 129.03, 128.96, 128.58, 128.26, 128.10, 127.99, 127.37, 127.19, 127.00, 126.62, 125.38, 121.07, 109.25, 59.39, 44.15. ESI-MS: Calcd for $C_{29}H_{22}N_2O_3$: [M+H⁺] 447.1703, found 447.1707. IR (neat): ν = 493, 644, 696, 744, 821, 958, 1177, 1331, 1514, 1612, 1722, 2359, 2918, 3029, 3630.



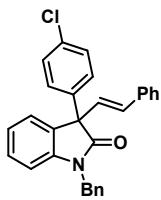
(E)-1-benzyl-3-phenyl-3-styryl-1,3-dihydro-2H-benzo[g]indol-2-one (3ja)

Yellow solid (30 mg, 33%); M.P.: 78-82 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 5H), 7.27 – 7.15 (m, 13H), 6.76 (d, J = 16.0 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 5.54 (d, J = 17.2 Hz, 1H), 5.47 (d, J = 16.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 178.68, 140.14, 137.91, 137.01, 136.48, 134.57, 131.98, 129.26, 128.96, 128.82, 128.57, 127.92, 127.83, 127.68, 127.30, 126.66, 126.00, 125.89, 125.65, 123.88, 122.73, 122.15, 120.86, 59.63, 46.23. ESI-MS: Calcd for $C_{33}H_{25}NO$: [M+H⁺] 452.2009, found 452.2015. IR (neat): ν = 515, 620, 820, 859, 951, 1057, 1140, 1265, 1519, 1614, 1714, 2069, 2359, 2448, 2903, 3081, 3452, 3649.



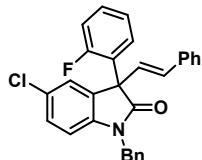
(E)-1-benzyl-3-(4-fluorophenyl)-3-styrylindolin-2-one (3ka)

White solid (78 mg, 93%); M.P.: 57-61 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 7.26 – 7.16 (m, 9H), 7.08 – 7.04 (m, 1H), 7.01 – 6.95 (m, 2H), 6.78 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 4.96 (d, J = 16.4 Hz, 1H), 4.92 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.62, 162.24 (d, J = 245.0 Hz), 142.28, 136.30, 135.85, 135.71, 131.76, 131.52, 129.29 (d, J = 8.0 Hz), 128.92, 128.79, 128.56, 128.43, 127.97, 127.62, 127.11, 126.62, 125.45, 122.93, 115.55 (d, J = 21.0 Hz), 109.76, 59.01, 43.91. ^{19}F NMR (376 MHz, CDCl_3) δ -114.79. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{22}\text{FNO}$: [M+H $^+$] 420.1758, found 420.1760. IR (neat): ν = 481, 749, 824, 920, 1018, 1505, 1711, 2322, 3657.



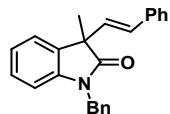
(E)-1-benzyl-3-(4-chlorophenyl)-3-styrylindolin-2-one (3la)

White solid (83 mg, 96%); M.P.: 52-58 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.10 (m, 14H), 7.02 – 6.97 (m, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 4.90 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.37, 142.25, 138.64, 136.19, 135.63, 133.58, 131.95, 131.22, 128.97, 128.83, 128.79, 128.55, 128.50, 128.01, 127.63, 127.09, 126.62, 125.43, 122.97, 109.79, 59.10, 43.91. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{22}\text{ClNO}$: [M+H $^+$] 436.1463, found 436.1468. IR (neat): ν = 469, 740, 817, 923, 1017, 1179, 1351, 1483, 1605, 1711, 2919, 3031, 3652.



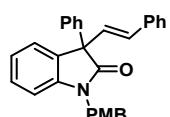
(E)-1-benzyl-5-chloro-3-(2-fluorophenyl)-3-styrylindolin-2-one (3ma)

White solid (67 mg, 74%); M.P.: 136-139 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.48 (m, 1H), 7.38 – 7.34 (m, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.16 (m, 8H), 7.13 (dd, J = 7.6, 1.2 Hz, 1H), 7.09 (dd, J = 8.4, 1.2 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.65 (d, J = 16.0 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.96 (d, J = 15.6 Hz, 1H), 4.88 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.17, 160.23 (d, J = 247.0 Hz), 141.18, 135.89, 135.35, 132.97, 132.25, 130.03 (d, J = 3.0 Hz), 129.90 (d, J = 9.0 Hz), 128.79, 128.65, 128.42, 128.31, 128.00, 127.66, 127.36, 127.26, 127.14, 126.80, 125.22, 124.38 (d, J = 3.0 Hz), 116.10 (d, J = 22.0 Hz), 110.58, 56.94, 44.24. ^{19}F NMR (376 MHz, CDCl_3) δ -111.85. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{21}\text{ClFNO}$: [M+H $^+$] 454.1368, found 454.1371. IR (neat): ν = 469, 743, 809, 918, 1020, 1347, 1484, 1607, 1712, 2024, 3653.



(E)-1-benzyl-3-methyl-3-styrylindolin-2-one (3na)

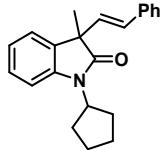
Yellow oil (67 mg, 99%); ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.17 (m, 12H), 7.09 – 7.05 (m, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.94 (d, J = 16.0 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 178.69, 142.00, 136.52, 135.84, 132.86, 130.15, 129.90, 128.70, 128.41, 127.99, 127.60, 127.47, 127.05, 126.44, 123.92, 122.58, 109.31, 50.59, 43.61, 23.30. ESI-MS: Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}$: [M+H $^+$] 340.1696, found 340.1700. IR (neat): ν = 473, 693, 743, 897, 1016, 1089, 1179, 1354, 1483, 1611, 1709, 2108, 2556, 2970, 3029, 3625.



(E)-1-(4-methoxybenzyl)-3-phenyl-3-styrylindolin-2-one (3oa)

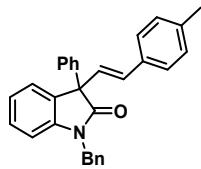
White solid (49 mg, 57%); M.P.: 165-167 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 4H), 7.25 – 7.19 (m, 4H), 7.17 (d, J = 8.0 Hz, 4H), 7.04 – 7.00 (m, 1H), 6.80 – 6.75 (m, 3H), 6.68 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.85 (d, J = 15.6 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.76, 159.08, 142.39, 140.28, 136.51, 131.84, 131.60, 129.16,

128.72, 128.54, 128.23, 127.90, 127.86, 127.49, 126.65, 125.55, 122.78, 114.21, 109.68, 59.68, 55.24, 43.42. ESI-MS: Calcd for $C_{30}H_{25}NO_2$: [M+H⁺] 432.1958, found 432.1960. IR (neat): ν = 477, 595, 696, 745, 910, 973, 1024, 1183, 1249, 1353, 1495, 1609, 1708, 2024, 2321, 2915, 3623.



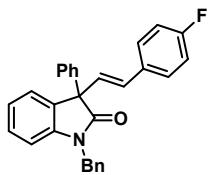
(E)-1-cyclopentyl-3-methyl-3-styrylindolin-2-one (3pa)

Red oil (62 mg, 99%); ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 7.2 Hz, 2H), 7.19 – 7.14 (m, 4H), 7.09 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.23 (d, J = 16.0 Hz, 1H), 4.78 – 4.60 (m, 1H), 2.04 – 1.94 (m, 2H), 1.85 (s, 4H), 1.66 – 1.57 (m, 2H), 1.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.54, 141.44, 136.58, 133.41, 130.08, 129.83, 128.36, 127.68, 127.50, 126.40, 124.13, 122.01, 109.88, 52.28, 50.33, 27.66, 27.53, 25.19, 23.18. ESI-MS: Calcd for C₂₂H₂₃NO: [M+H⁺] 318.1852, found 318.1855. IR (neat): ν = 480, 691, 745, 916, 965, 1023, 1166, 1212, 1357, 1469, 1604, 1706, 2870, 2959, 3664.



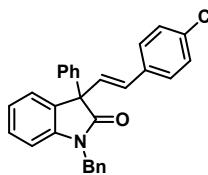
(E)-1-benzyl-3-(4-methylstyryl)-3-phenylindolin-2-one (3ab)

Yellow solid (68 mg, 82%); M.P.: 153–157 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (s, 1H), 7.25 – 7.07 (m, 13H), 7.03 – 6.94 (m, 3H), 6.70 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 4.91 (d, J = 16.0 Hz, 1H), 4.87 (d, J = 16.0 Hz, 1H), 2.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.87, 142.29, 140.34, 137.71, 135.81, 133.66, 131.87, 131.47, 129.22, 128.75, 128.68, 128.18, 128.06, 127.53, 127.47, 127.10, 126.52, 125.55, 122.79, 109.61, 59.68, 43.86, 21.15. ESI-MS: Calcd for C₃₀H₂₅NO: [M+H⁺] 416.2009, found 416.2011. IR (neat): ν = 480, 547, 598, 694, 747, 797, 845, 914, 980, 1030, 1087, 1173, 1352, 1470, 1604, 1702, 2026, 2069, 2357, 2964, 3527.



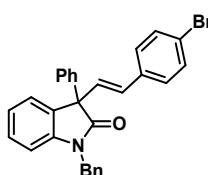
(E)-1-benzyl-3-(4-fluorostyryl)-3-phenylindolin-2-one (3ac)

White solid (65 mg, 78%); M.P.: 153-157 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.26 (m, 5H), 7.25 – 7.12 (m, 9H), 7.01 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 8.4 Hz, 2H), 6.75 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 4.94 (d, J = 16.0 Hz, 1H), 4.89 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.74, 162.50 (d, J = 246.0 Hz), 142.35, 140.13, 135.80, 132.64, 131.71, 130.47, 128.94, 128.79, 128.76, 128.32, 128.22, 128.14, 127.60 (d, J = 3.0 Hz), 127.46, 127.15, 125.54, 122.87, 115.46 (d, J = 21.0 Hz), 109.70, 59.62, 43.93. ^{19}F NMR (376 MHz, CDCl_3) δ -113.85. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{22}\text{FNO}$: [M+H $^+$] 420.1758, found 420.1760. IR (neat): ν = 526, 621, 694, 746, 853, 924, 980, 1083, 1162, 1216, 1270, 1350, 1494, 1600, 1708, 1893, 2069, 2357, 3056, 3378.



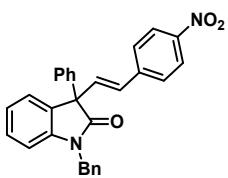
(E)-1-benzyl-3-(4-chlorostyryl)-3-phenylindolin-2-one (3ad)

White solid (57 mg, 66%); M.P.: 167-171 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.17 (m, 16H), 7.07 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 5.00 (d, J = 16.0 Hz, 1H), 4.94 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.65, 142.35, 140.00, 135.77, 134.99, 133.58, 131.57, 130.45, 129.84, 128.81, 128.80, 128.72, 128.39, 127.86, 127.64, 127.46, 127.16, 125.56, 122.92, 109.75, 59.66, 43.96. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{22}\text{ClNO}$: [M+H $^+$] 436.1463, found 436.1468. IR (neat): ν = 492, 696, 742, 801, 922, 970, 1020, 1091, 1180, 1351, 1483, 1604, 1710, 2358, 2919, 3029, 3646.



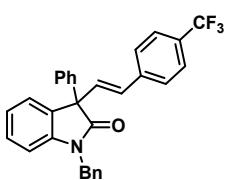
(E)-1-benzyl-3-(4-bromostyryl)-3-phenylindolin-2-one (3ae)

White solid (59 mg, 62%); M.P.: 163-167 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.18 (m, 14H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.4 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.94 (d, *J* = 15.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.60, 142.34, 139.95, 135.75, 135.42, 131.67, 131.53, 130.50, 129.96, 128.81, 128.39, 128.17, 127.64, 127.45, 127.15, 125.55, 122.92, 121.73, 109.75, 59.67, 43.96. ESI-MS: Calcd for C₂₉H₂₂BrNO: [M+H⁺] 480.0958, found 480.0958. IR (neat): ν = 464, 695, 742, 800, 913, 971, 1019, 1176, 1347, 1482, 1605, 1709, 2586, 3675.



(E)-1-benzyl-3-(4-nitrostyryl)-3-phenylindolin-2-one (3af)

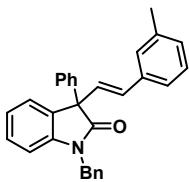
Yellow solid (29 mg, 33%); M.P.: 169-173 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.27 (m, 12H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 16.4 Hz, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.17, 147.20, 142.89, 142.40, 139.44, 135.64, 134.03, 130.98, 129.69, 128.92, 128.84, 128.68, 127.86, 127.73, 127.41, 127.21, 127.18, 125.55, 123.96, 123.07, 109.91, 59.75, 44.05. ESI-MS: Calcd for C₂₉H₂₂N₂O₃: [M+H⁺] 447.1703, found 447.1693. IR (neat): ν = 471, 741, 904, 1019, 1215, 1340, 1511, 1603, 1707, 2358, 2597, 3734.



(E)-1-benzyl-3-phenyl-3-(4-(trifluoromethyl)styryl)indolin-2-one (3ag)

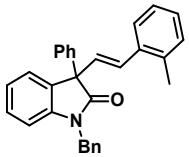
Yellow solid (51 mg, 55%); M.P.: 159-162 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.33 (m, 3H), 7.30 – 7.21 (m, 9H), 7.12 – 7.07 (m, 1H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* =

16.4 Hz, 1H), 5.02 (d, J = 15.6 Hz, 1H), 4.97 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.44, 142.34, 139.92, 139.75, 135.69, 131.84, 131.30, 130.32, 129.66 (q, J = 32.0 Hz), 128.84, 128.81, 128.49, 127.72, 127.66, 127.42, 127.13, 126.80, 126.78 (q, J = 268.0 Hz), 125.52, 125.48, 122.98, 109.80, 59.68, 43.95. ^{19}F NMR (376 MHz, CDCl_3) δ -62.45. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{22}\text{F}_3\text{NO}$: [M+H $^+$] 470.1726, found 470.1730. IR (neat): ν = 474, 593, 689, 744, 909, 1019, 1110, 1174, 1327, 1488, 1611, 1710, 2024, 2355, 2940, 3622.



(E)-1-benzyl-3-(3-methylstyryl)-3-phenylindolin-2-one (3ah)

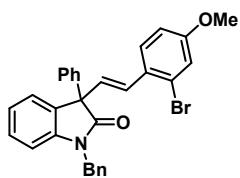
Yellow oil (55 mg, 67%); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (s, 1H), 7.25 – 7.08 (m, 14H), 7.01 – 6.94 (m, 2H), 6.70 (d, J = 7.6 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 4.91 (d, J = 16.0 Hz, 1H), 4.87 (d, J = 16.4 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.83, 142.30, 140.26, 138.09, 136.37, 135.80, 131.78, 131.69, 128.88, 128.77, 128.71, 128.65, 128.43, 128.22, 127.55, 127.48, 127.26, 127.11, 125.57, 123.85, 122.81, 109.64, 59.71, 43.88, 21.27. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{25}\text{NO}$: [M+H $^+$] 416.2009, found 416.2011. IR (neat): ν = 476, 592, 691, 906, 981, 1019, 1090, 1210, 1339, 1487, 1700, 2024, 2071, 2356, 3017, 3607.



(E)-1-benzyl-3-(2-methylstyryl)-3-phenylindolin-2-one (3ai)

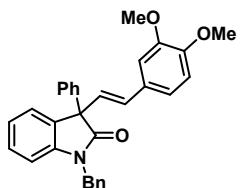
Yellow oil (77 mg, 93%); ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.42 (m, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.14 (m, 8H), 7.13 – 6.98 (m, 5H), 6.75 (d, J = 16.0 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 4.99 (d, J = 16.0 Hz, 1H), 4.85 (d, J = 16.0 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.72, 142.26, 140.16, 135.80, 135.67, 135.61, 131.83, 130.46, 130.16, 129.67, 128.72, 128.68, 128.22, 127.71, 127.53, 127.49, 127.06, 126.05, 125.78, 125.39, 122.77, 109.60, 59.87, 43.80, 19.64. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{25}\text{NO}$: [M+H $^+$] 416.2009,

found 416.2011. IR (neat): ν = 500, 697, 744, 850, 977, 1031, 1083, 1176, 1350, 1480, 1603, 1710, 2356, 2925, 3049, 3538.



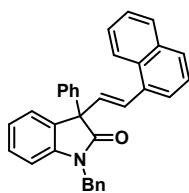
(E)-1-benzyl-3-(2-bromo-4-methoxystyryl)-3-phenylindolin-2-one (3aj)

Yellow oil (58 mg, 57%); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 8.8 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.21 (m, 4H), 7.20 – 7.16 (m, 3H), 7.13 – 7.10 (m, 1H), 7.03 – 7.00 (m, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.79 (d, J = 16.0 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 4.98 (d, J = 15.6 Hz, 1H), 4.87 (d, J = 15.6 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.76, 159.63, 142.26, 140.17, 135.75, 131.54, 130.35, 130.03, 129.06, 128.81, 128.75, 128.31, 127.73, 127.55, 127.53, 127.45, 127.12, 125.66, 124.29, 122.86, 117.64, 114.03, 109.70, 59.86, 55.50, 43.90. ESI-MS: Calcd for $\text{C}_{30}\text{H}_{24}\text{BrNO}_2$: [M+H $^+$] 510.1063, found 510.1068. IR (neat): ν = 472, 595, 697, 740, 899, 1023, 1091, 1242, 1352, 1484, 1604, 1709, 2108, 2356, 2557, 2917, 3637.



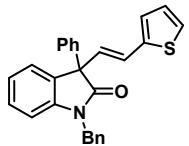
(E)-1-benzyl-3-(3,4-dimethoxystyryl)-3-phenylindolin-2-one (3ak)

White solid (48 mg, 52%); M.P.: 175–178 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.17 (m, 12H), 7.06 (t, J = 7.6 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.78 (dd, J = 8.0, 3.6 Hz, 2H), 6.58 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.95 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.02, 149.12, 149.09, 142.34, 140.42, 135.83, 131.91, 131.38, 129.54, 128.80, 128.75, 128.22, 127.60, 127.52, 127.15, 127.09, 125.63, 122.84, 119.90, 111.11, 109.68, 109.06, 59.73, 55.91, 43.94. ESI-MS: Calcd for $\text{C}_{31}\text{H}_{27}\text{NO}_3$: [M+H $^+$] 462.2064, found 462.2066. IR (neat): ν = 477, 558, 600, 701, 748, 805, 853, 918, 982, 1024, 1087, 1156, 1261, 1352, 1462, 1508, 1601, 1699, 2356, 2846, 2952, 3006, 3606.



(E)-1-benzyl-3-(2-(naphthalen-1-yl)vinyl)-3-phenylindolin-2-one (3al)

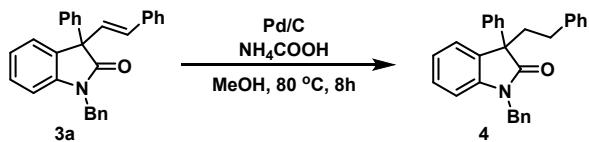
Yellow solid (52 mg, 57%); M.P.: 65-68 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.80 (m, 1H), 7.72 – 7.69 (m, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.26 – 7.07 (m, 11H), 7.00 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.67 (d, J = 15.6 Hz, 1H), 4.99 (d, J = 15.6 Hz, 1H), 4.85 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.71, 142.34, 140.09, 135.81, 134.27, 133.51, 132.23, 131.81, 131.18, 129.09, 128.79, 128.76, 128.45, 128.34, 128.19, 127.54, 127.08, 126.08, 125.76, 125.54, 125.45, 123.99, 123.67, 122.93, 109.70, 60.05, 43.84. ESI-MS: Calcd for $\text{C}_{33}\text{H}_{25}\text{NO}$: [M+H $^+$] 452.2009, found 452.2011. IR (neat): ν = 593, 741, 839, 905, 1021, 1221, 1515, 1694, 2070, 2356, 3628.



(E)-1-benzyl-3-phenyl-3-(2-(thiophen-2-yl)vinyl)indolin-2-one (3am)

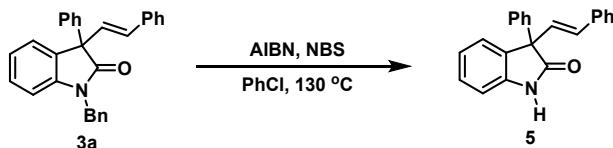
Yellow solid (55 mg, 68%); M.P.: 86-90 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.11 (m, 12H), 7.06 (d, J = 4.4 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.72 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.53, 142.29, 141.45, 140.00, 135.72, 131.55, 128.77, 128.72, 128.37, 128.31, 127.56, 127.44, 127.34, 127.10, 126.27, 125.46, 125.03, 124.63, 122.88, 109.67, 59.50, 43.89. ESI-MS: Calcd for $\text{C}_{27}\text{H}_{21}\text{NOS}$: [M+H $^+$] 408.1417, found 408.1422. IR (neat): ν = 492, 698, 746, 803, 848, 914, 974, 1029, 1081, 1178, 1267, 1354, 1485, 1604, 1701, 2069, 2356, 3027, 3235, 3539.

Synthetic Transformations:



To an oven-dried 50 mL screw-capped vial was added substrate **3a** (80.2 mg, 0.2 mmol, 1.0 equiv), HCO_2NH_4 (126.0 mg, 2.0 mmol, 10.0 equiv), Pd/C (2.1 mg, 0.02 mmol, 0.1 equiv) in MeOH (2.0 mL). The mixture was stirred at 80 °C for 8 h followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by silica gel chromatography to give **4** (64 mg, 79%) as a colourless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.6$ Hz, 2H), 7.23 – 7.09 (m, 12H), 7.09 – 6.97 (m, 4H), 6.72 (d, $J = 8.0$ Hz, 1H), 4.86 (d, $J = 15.6$ Hz, 1H), 4.81 (d, $J = 16.0$ Hz, 1H), 2.76 – 2.63 (m, 1H), 2.48 – 2.33 (m, 2H), 2.20 – 2.11 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 178.32, 143.11, 141.31, 140.13, 135.93, 132.04, 128.71, 128.56, 128.31, 128.28, 128.16, 127.56, 127.29, 126.82, 125.93, 124.71, 122.74, 109.40, 56.56, 43.92, 39.78, 31.03. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{25}\text{NO}$: [M+H $^+$] 404.2009, found 404.2008. IR (neat): ν = 481, 697, 741, 902, 1020, 1089, 1189, 1352, 1484, 1610, 1709, 2108, 2355, 2567, 2855, 2923, 3027, 3614.

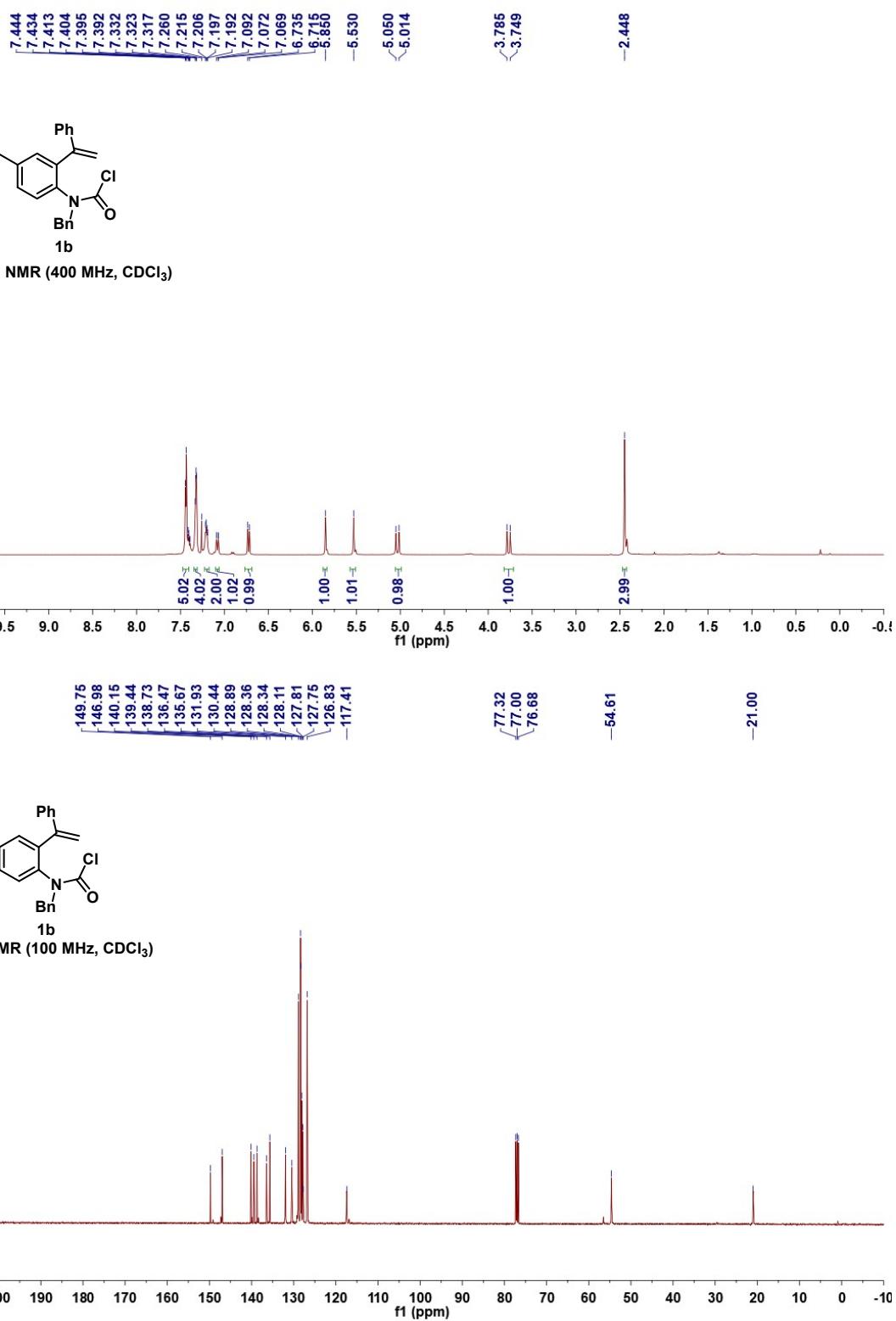


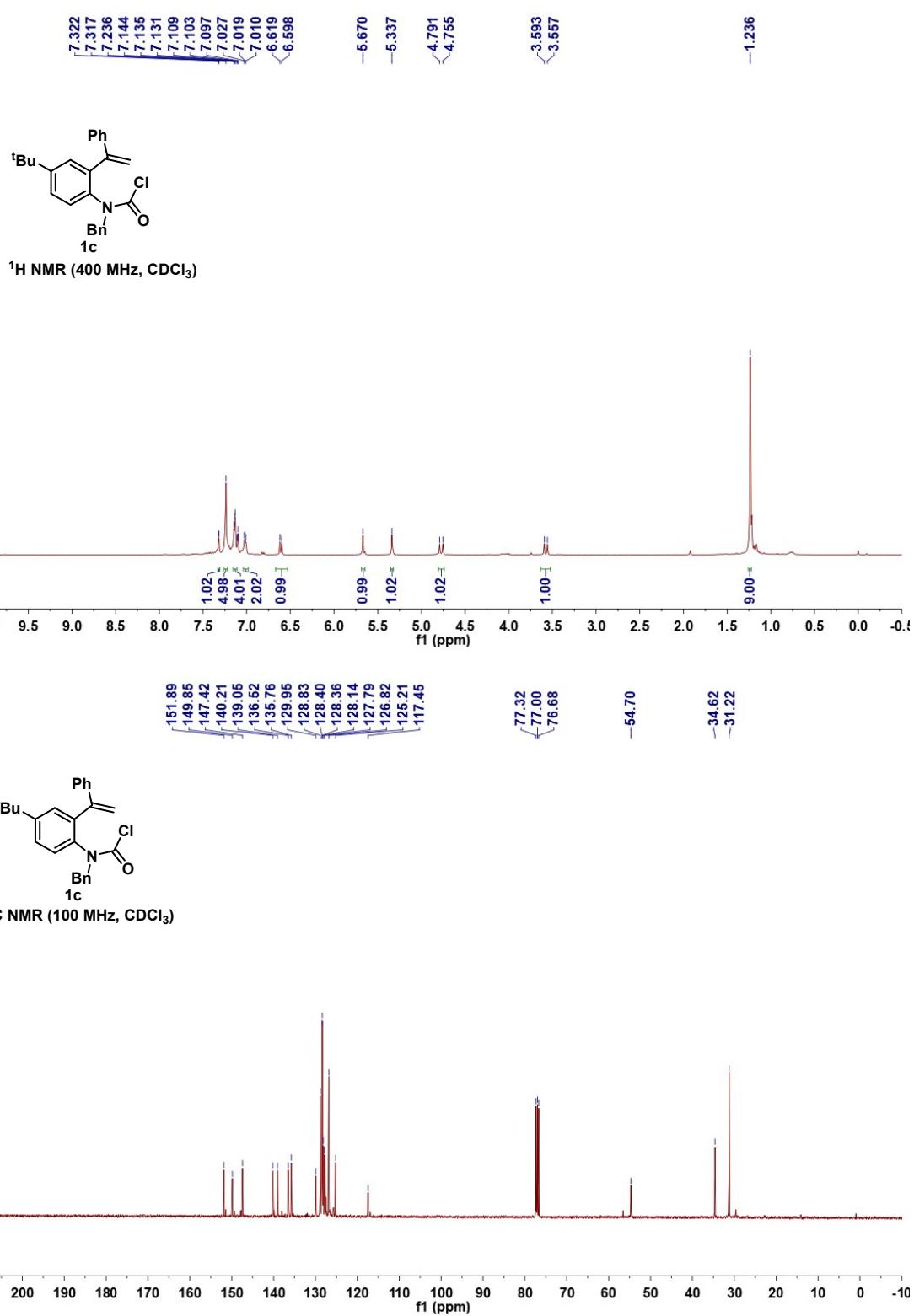
To a solution of **3a** (157.0 mg, 0.39 mmol, 1.0 equiv) in chlorobenzene (8.0 mL) containing NBS (86.0 mg, 0.46 mmol, 1.2 equiv) and AIBN (15.0 mg, 0.09 mmol, 0.2 equiv) was heated to reflux under a nitrogen atmosphere. After 4 h, AIBN (3.0 mg, 0.02 mmol, 0.05 equiv) and NBS (20.0 mg, 0.11 mmol, 0.3 equiv) were added. The solution was heated overnight then cooled to room temperature. Diethyl ether (10.0 mL) and water (20.0 mL) were added to the solution, which was stirred for 4 h, then the organic layer was separated, dried over anhydrous Na_2SO_4 , and evaporated and the crude product was purified by silica gel chromatography to give **5** (99 mg, 82%) as a yellow solid (M.P.: 186–191 °C).

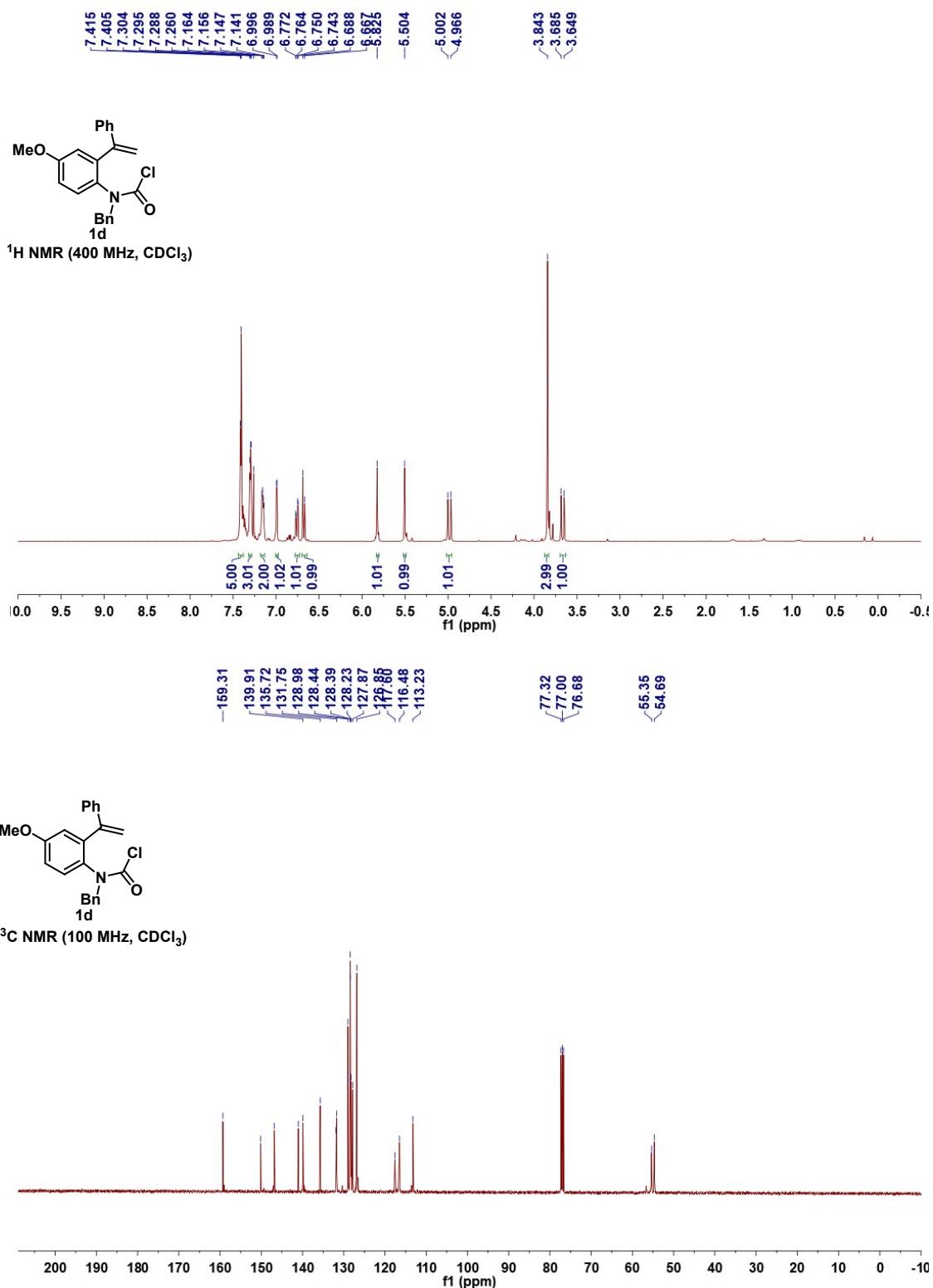
^1H NMR (400 MHz, CDCl_3) δ 9.79 (s, 1H), 7.34 – 7.31 (m, 4H), 7.28 – 7.27 (m, 1H),

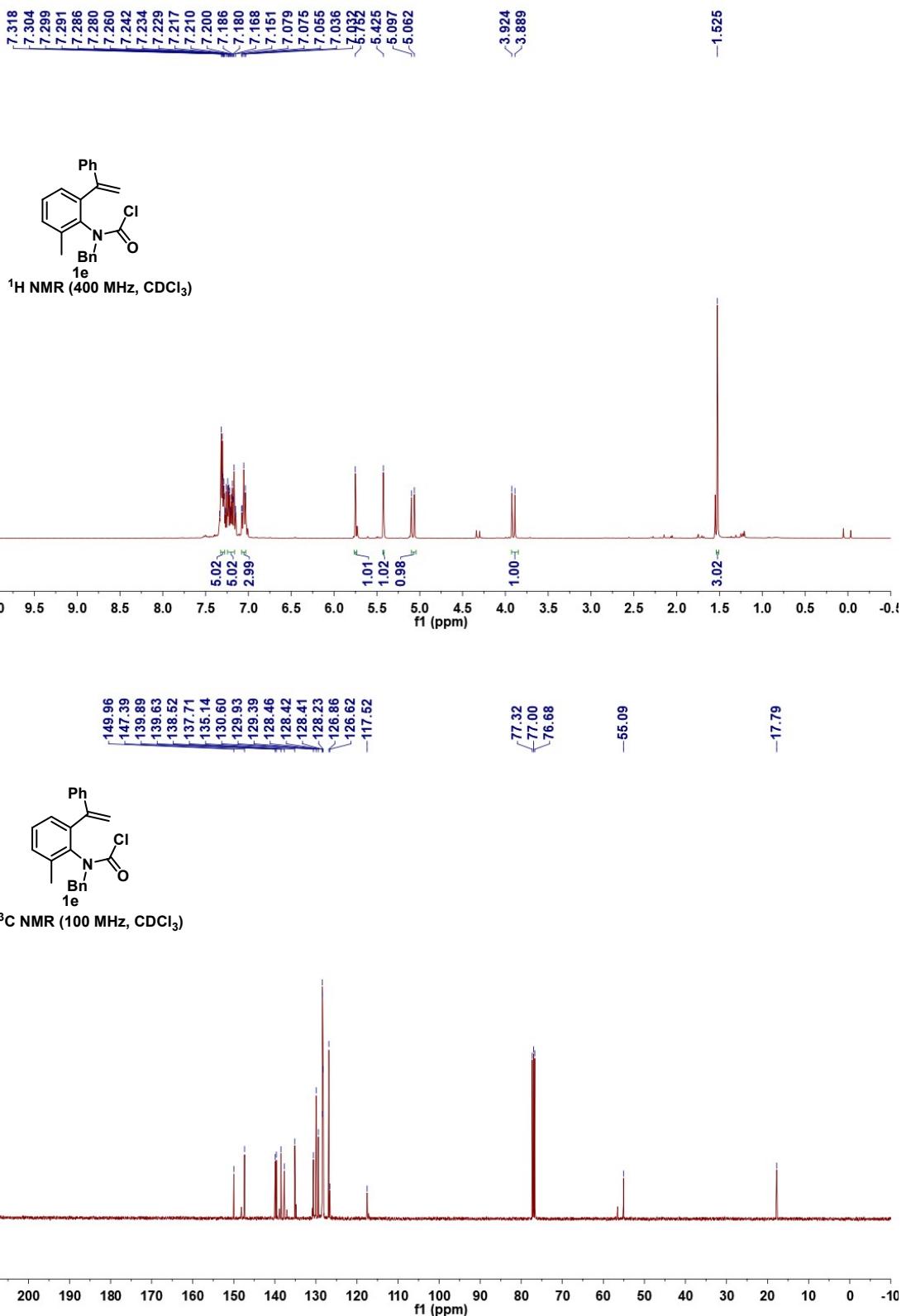
7.24 – 7.20 (m, 3H), 7.20 – 7.10 (m, 4H), 7.03 – 6.99 (m, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.51 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 179.97, 140.60, 140.06, 136.35, 132.37, 131.86, 128.72, 128.63, 128.49, 128.31, 127.84, 127.52, 127.40, 126.60, 125.63, 122.71, 110.73, 60.34. ESI-MS: Calcd for $\text{C}_{22}\text{H}_{17}\text{NO}$: [M+H $^+$] 312.1383, found 312.1380. IR (neat): ν = 492, 605, 692, 745, 841, 985, 1080, 1207, 1313, 1406, 1473, 1608, 1705, 2359, 3186, 3527.

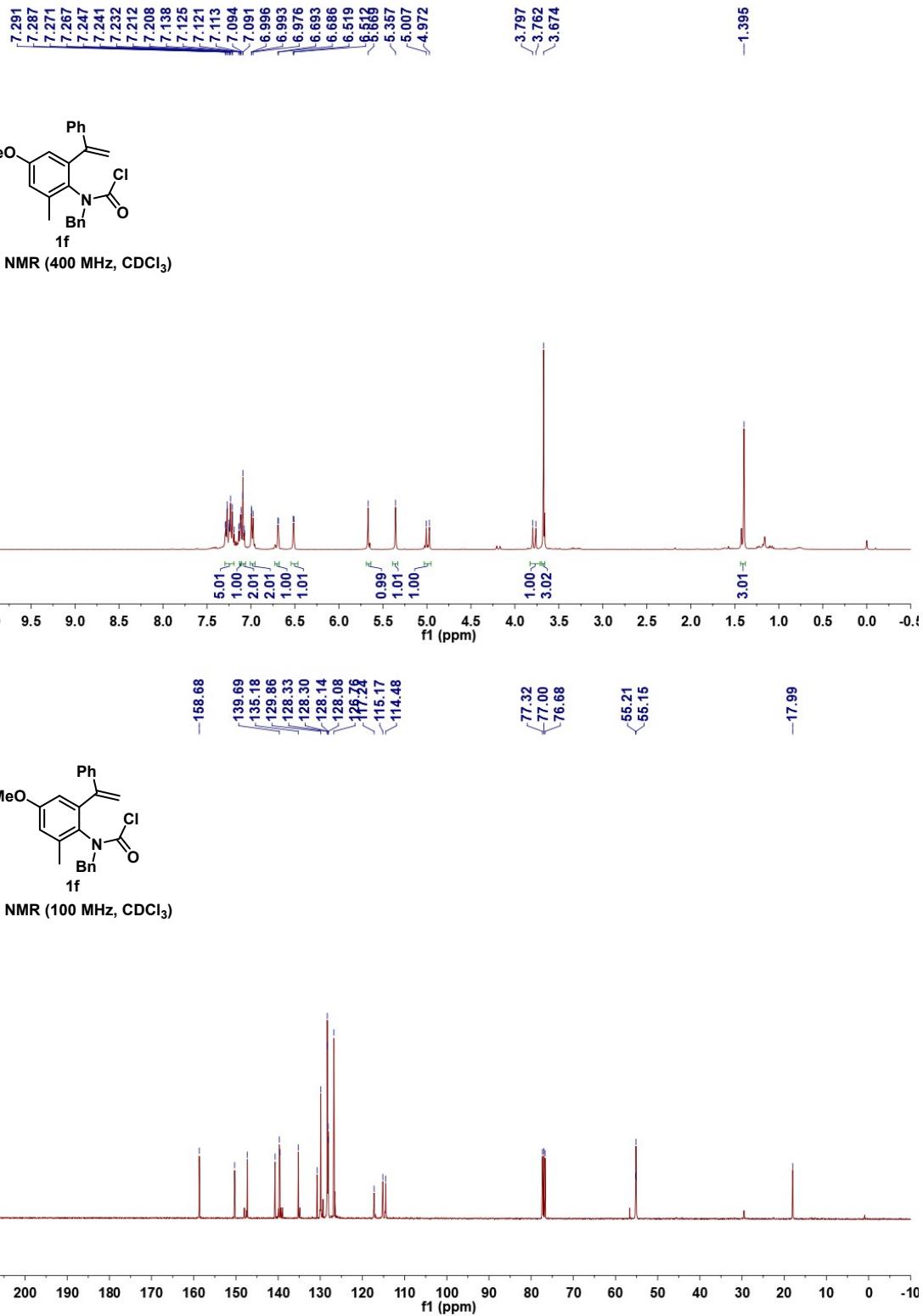
NMR Spectra:

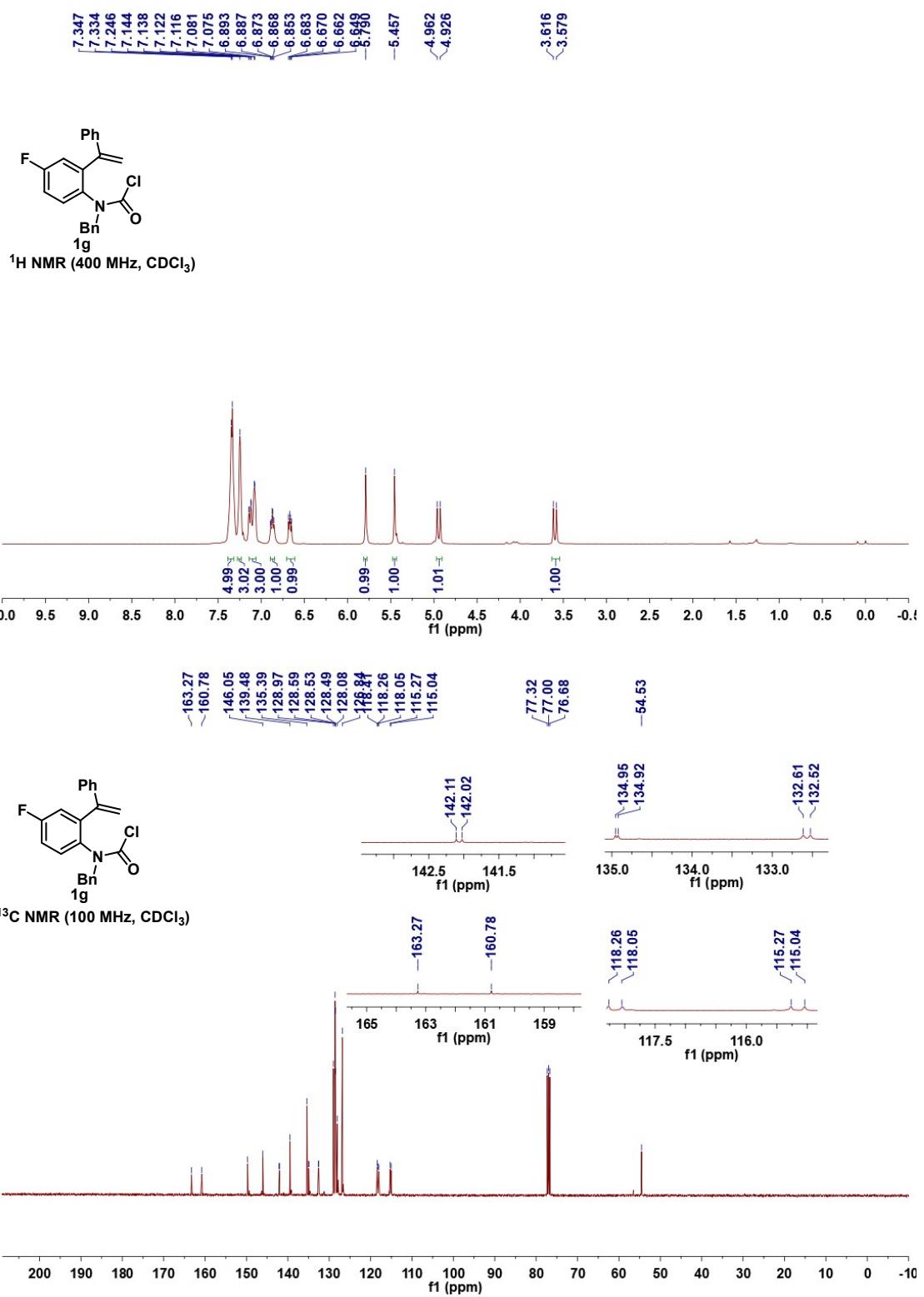


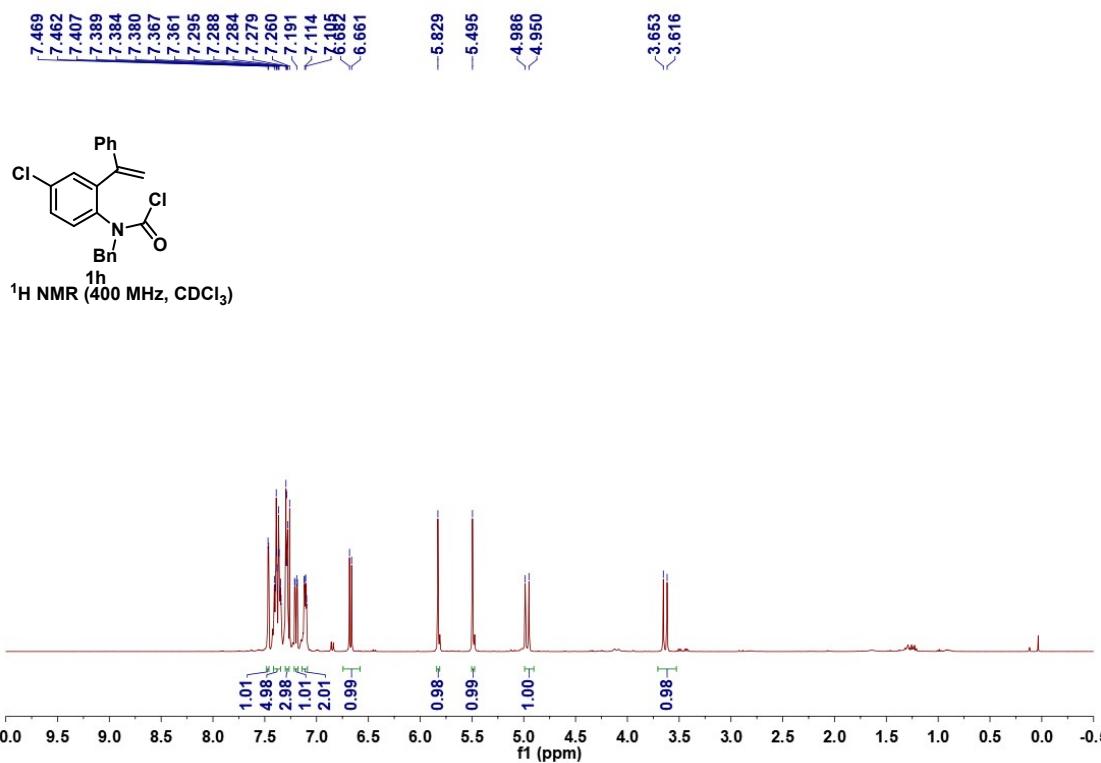
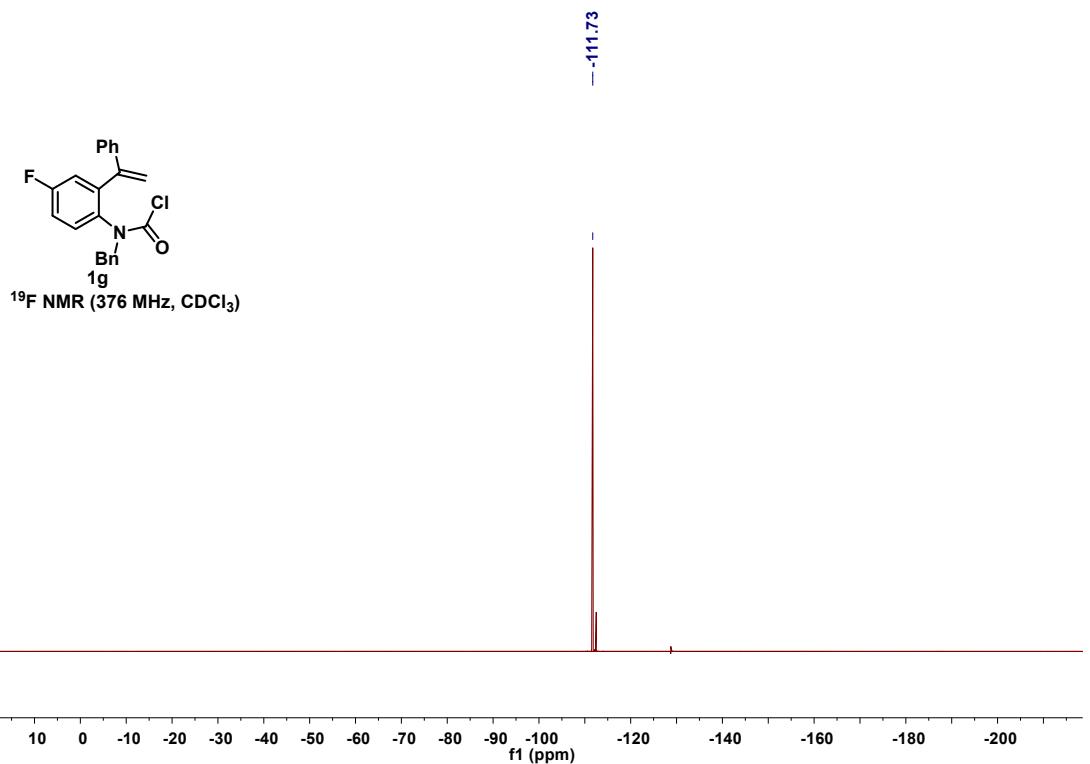


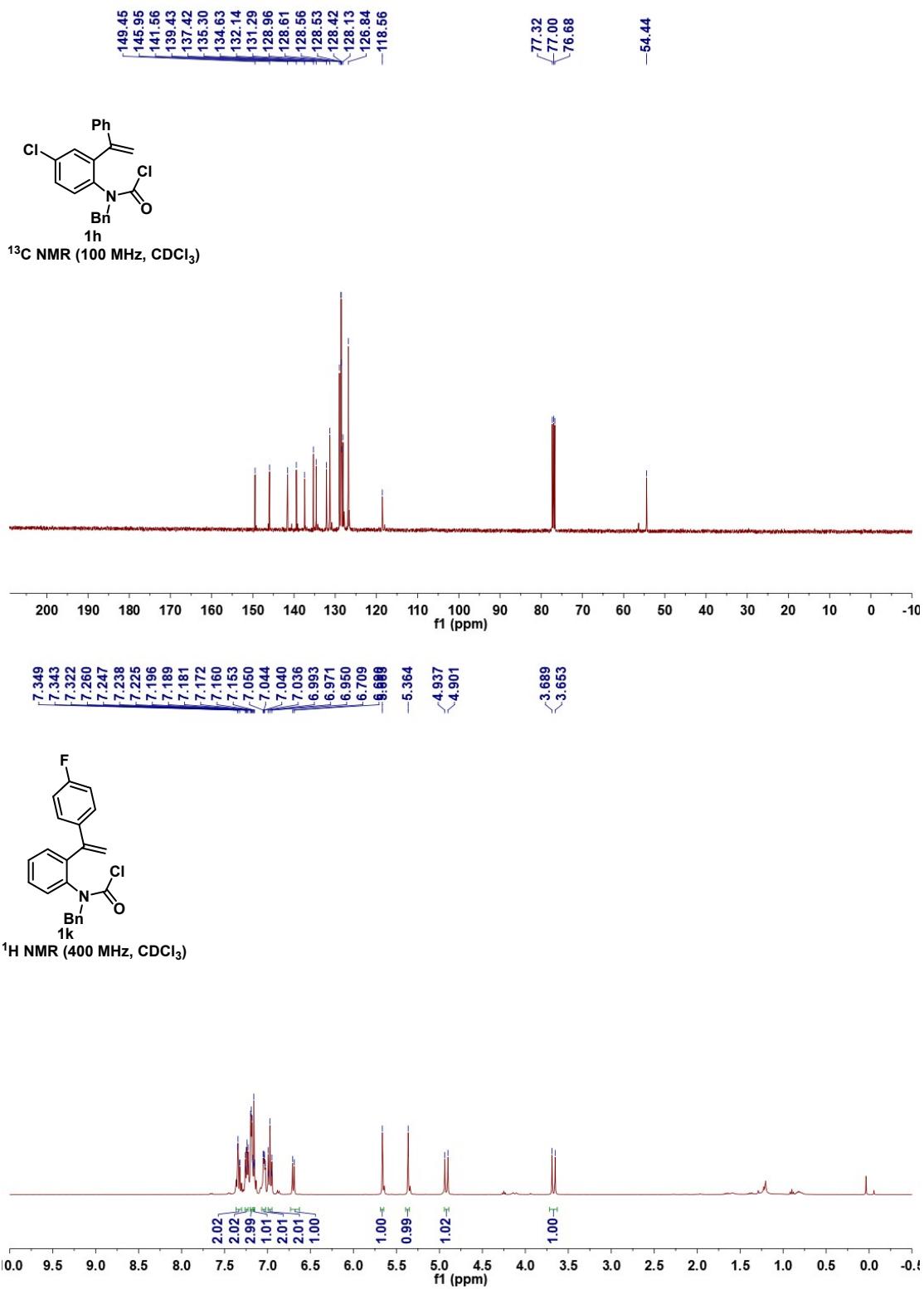


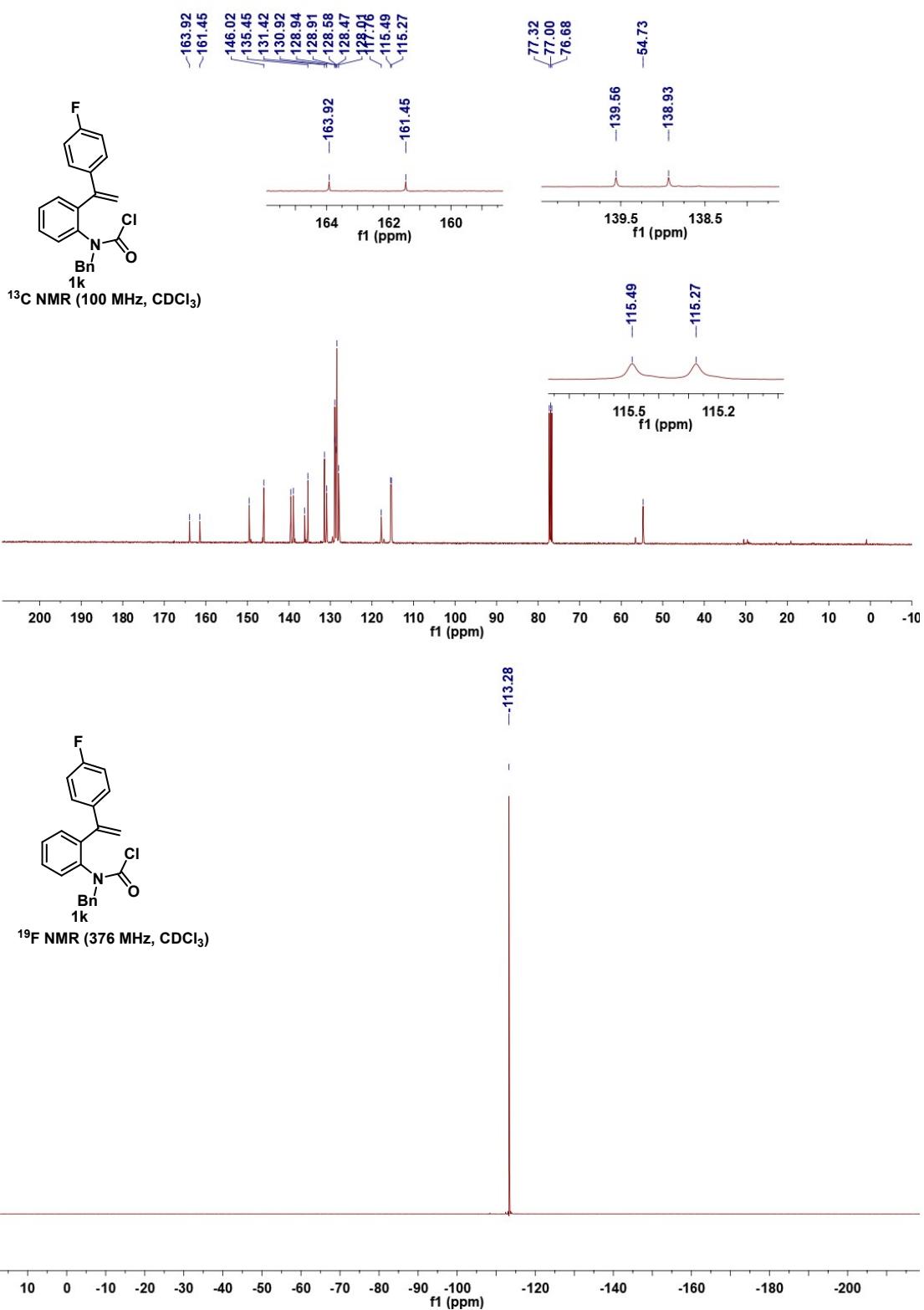


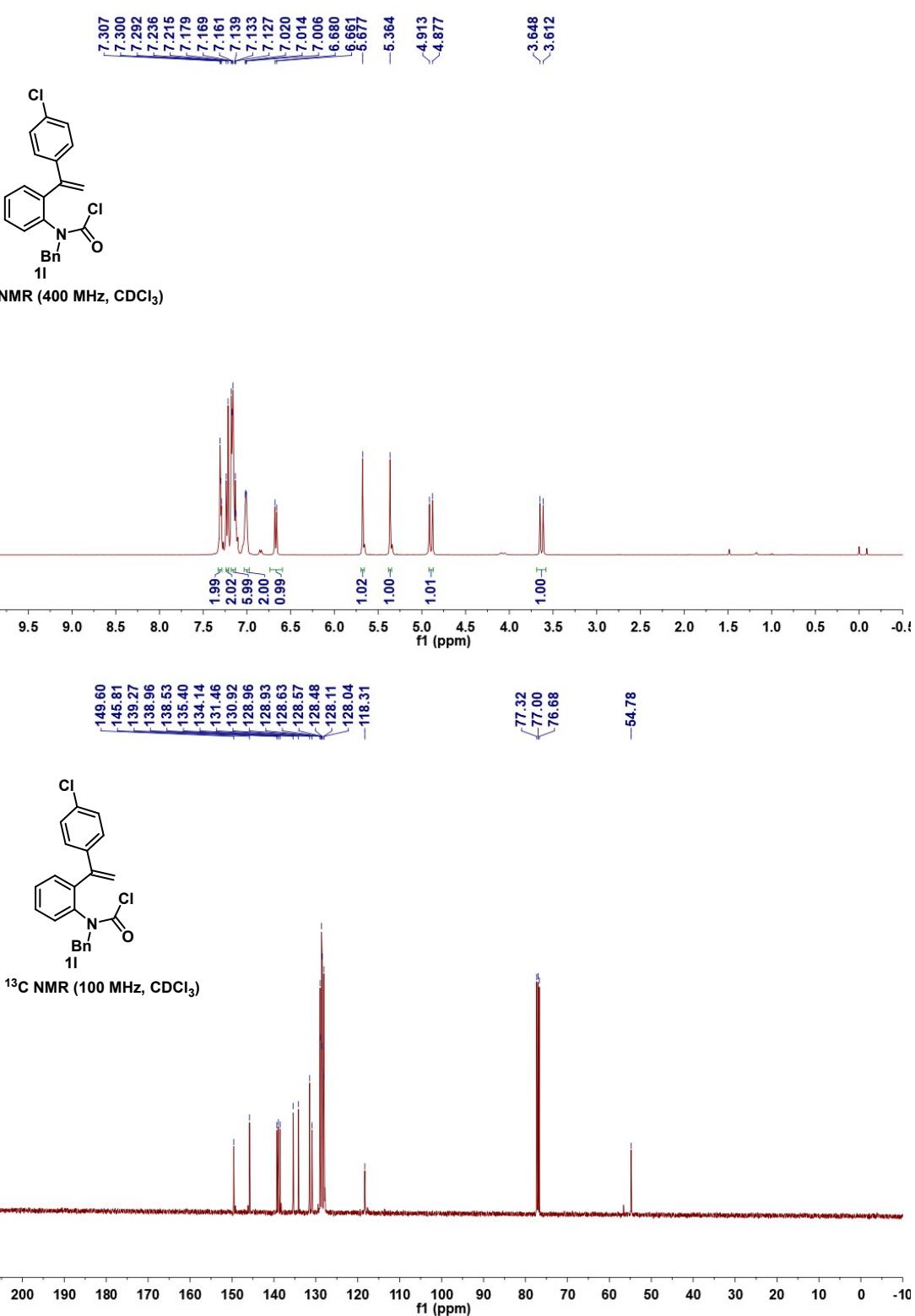


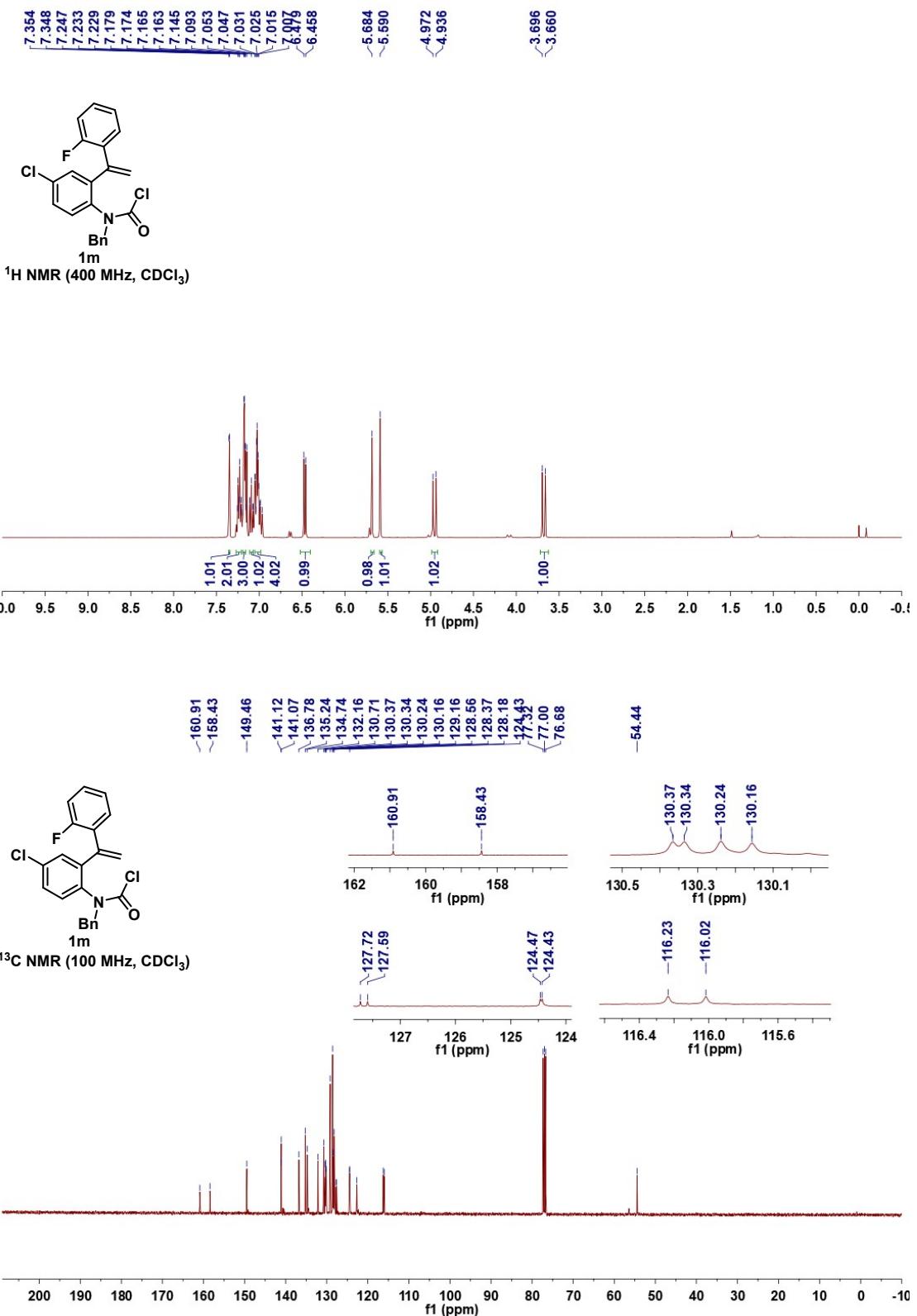


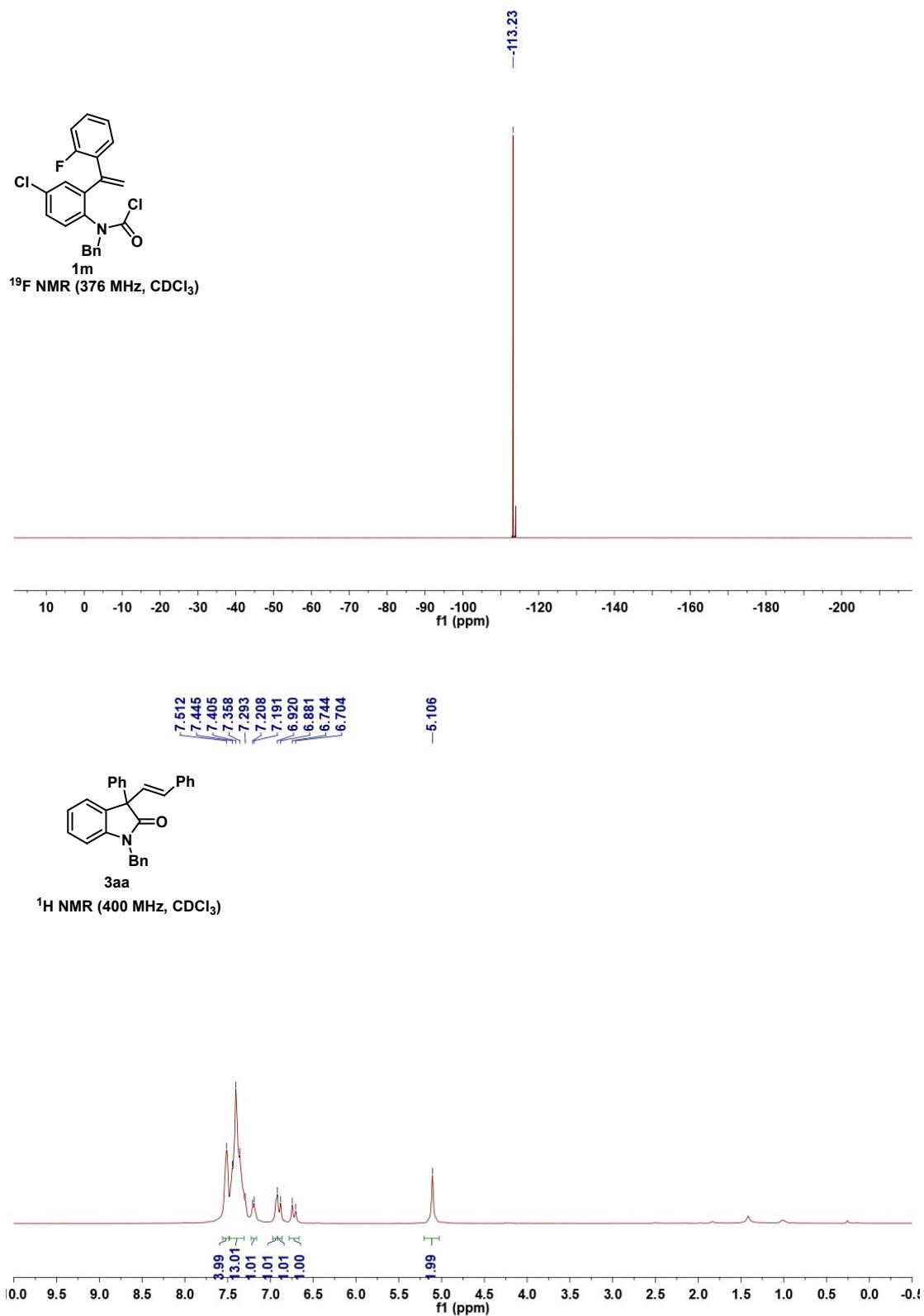


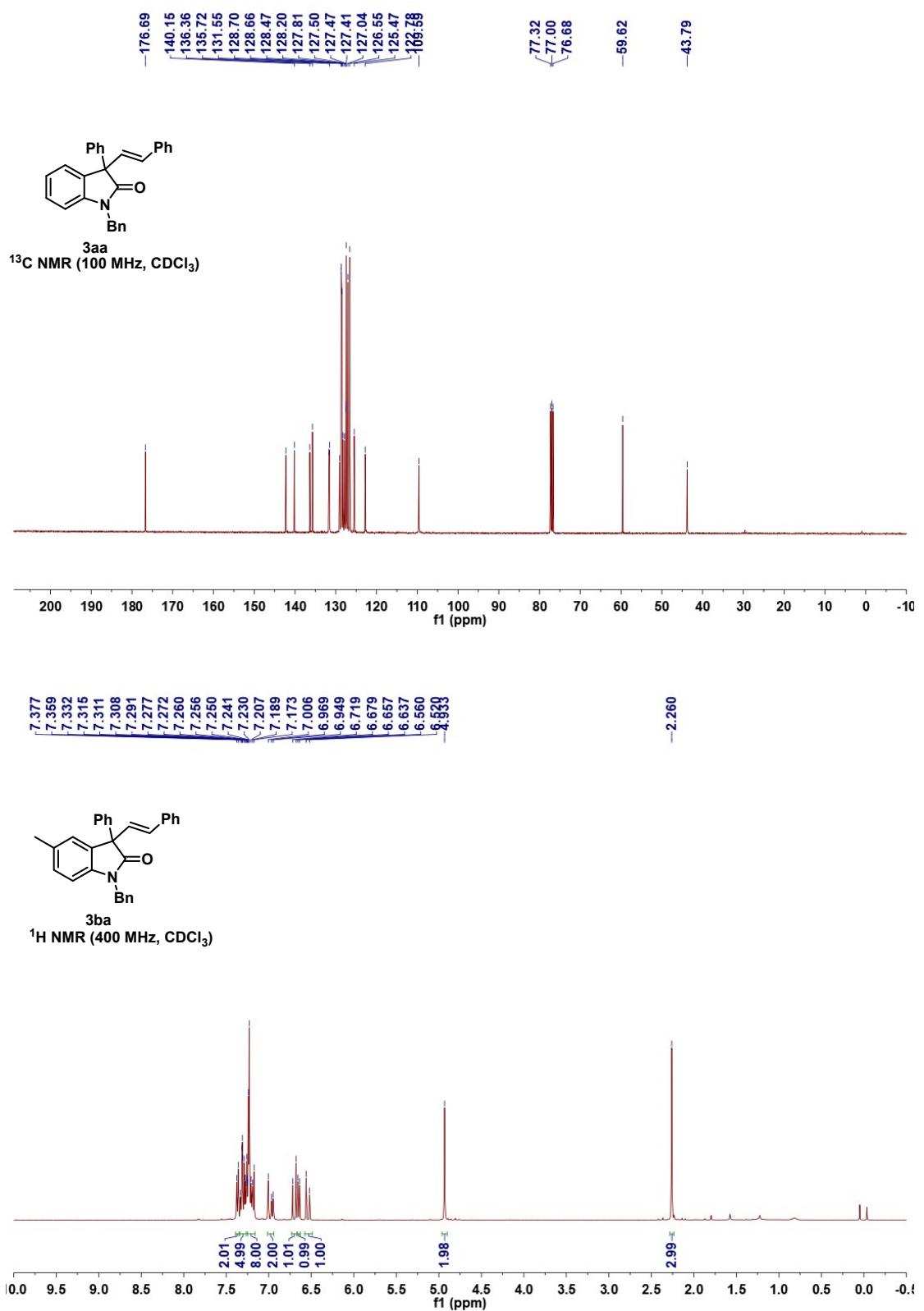


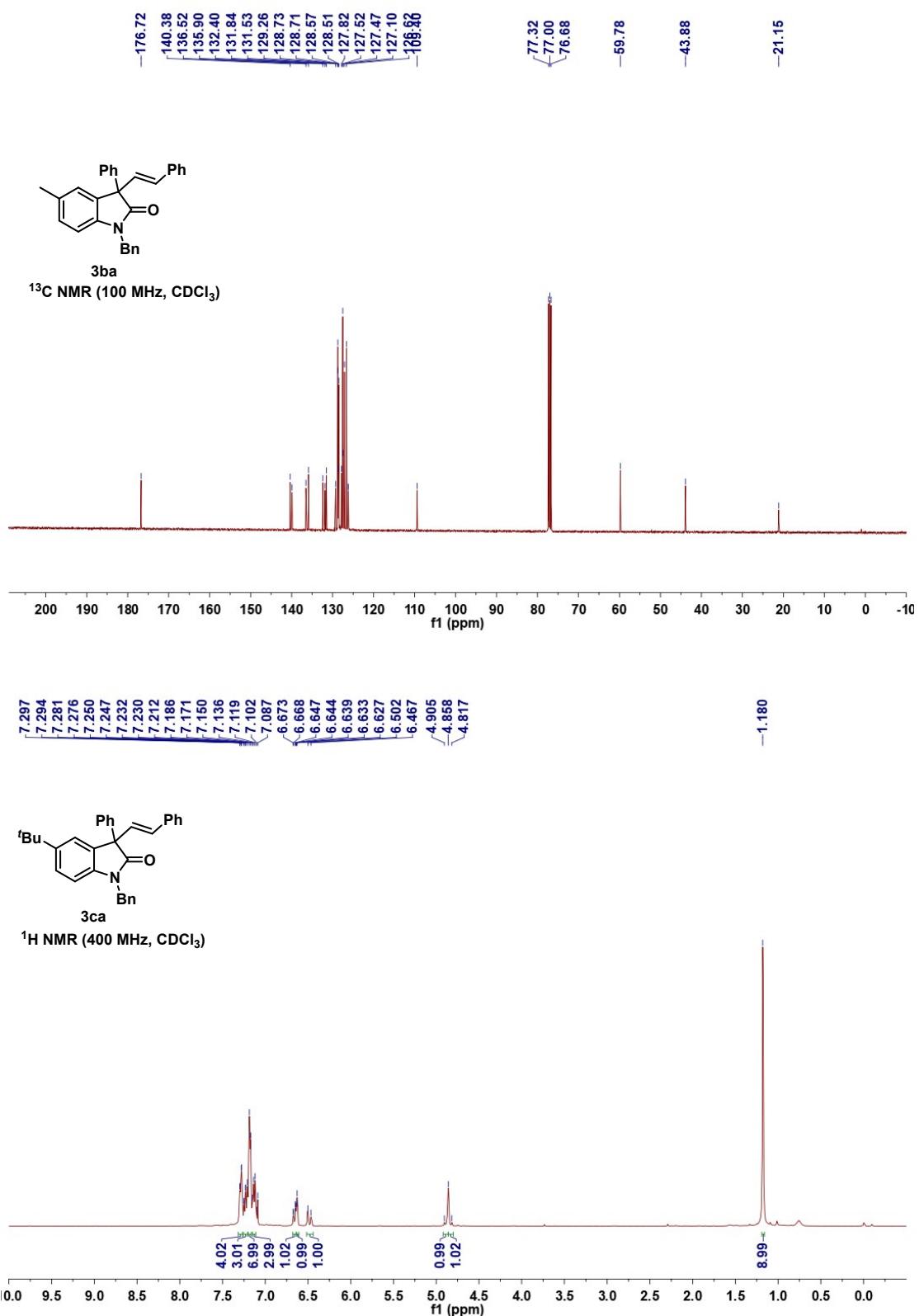


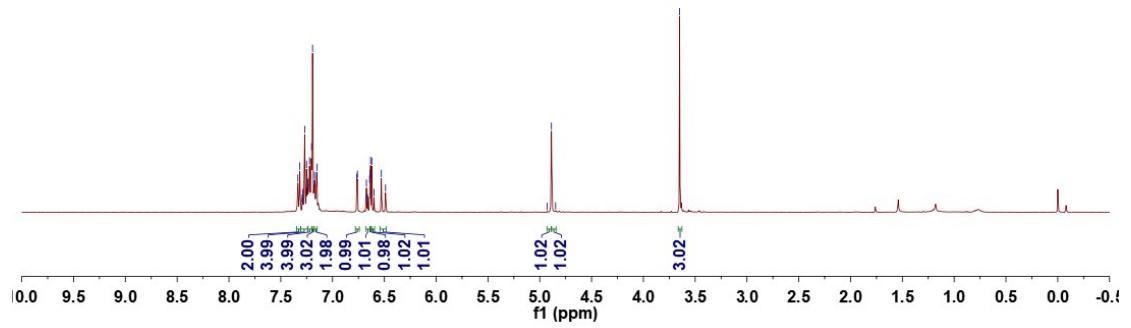
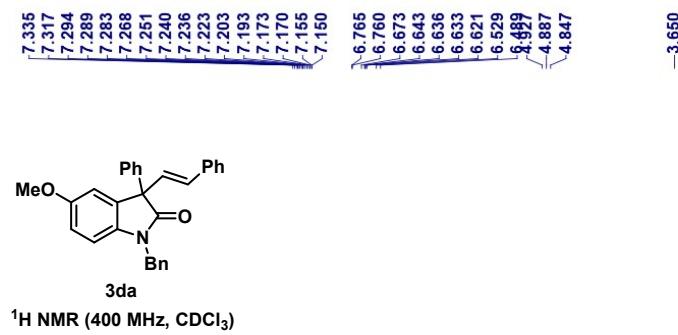
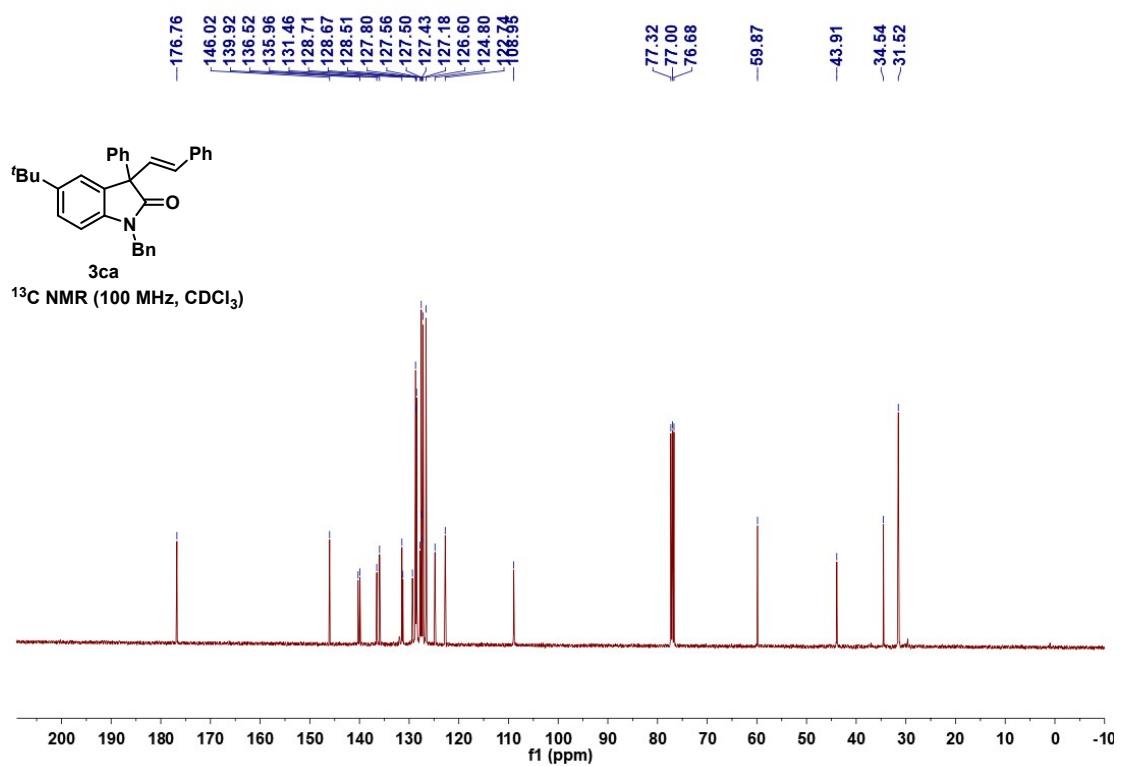


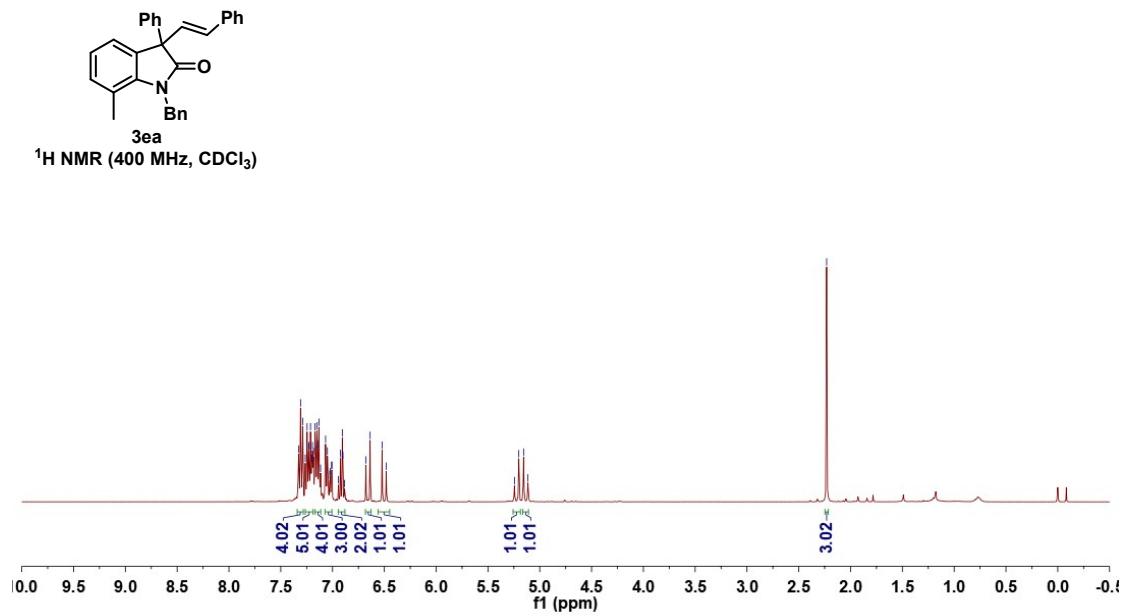
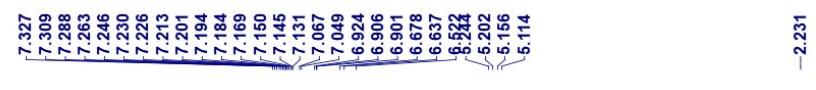
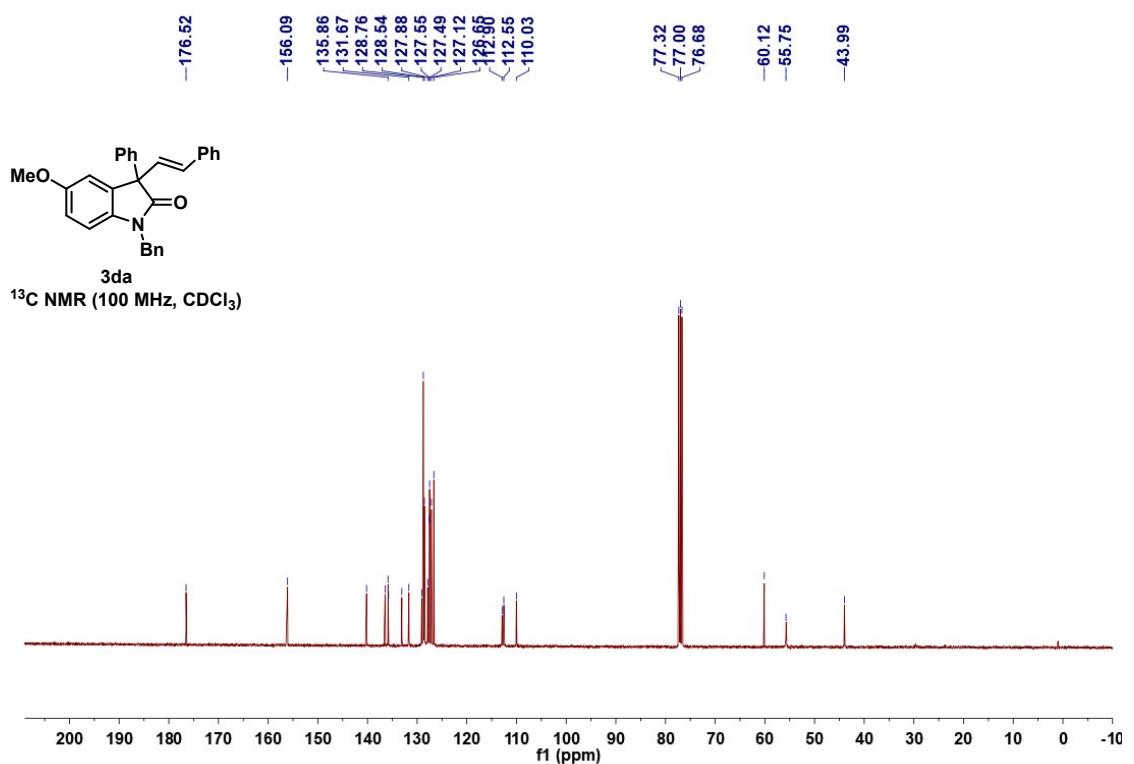


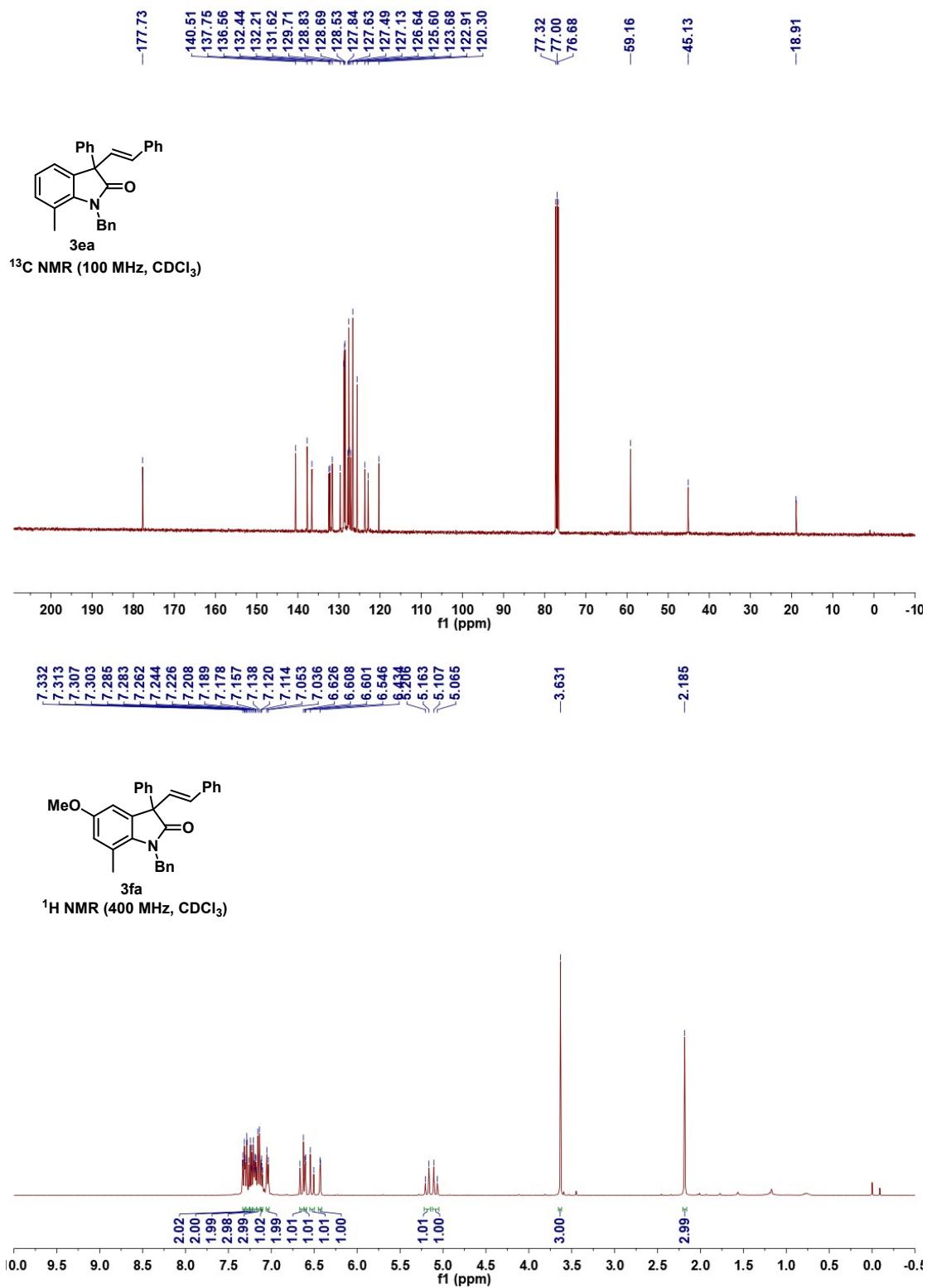


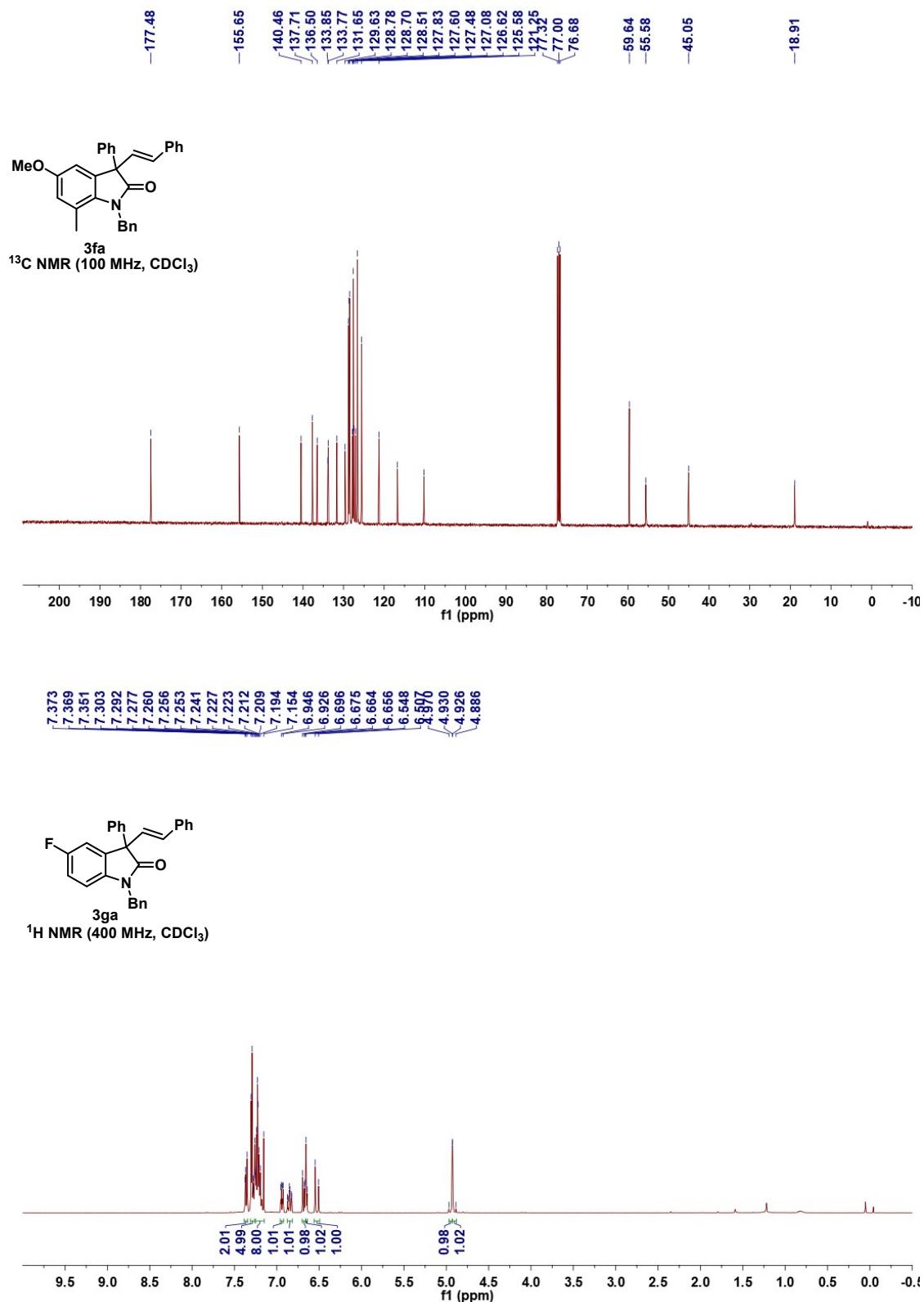


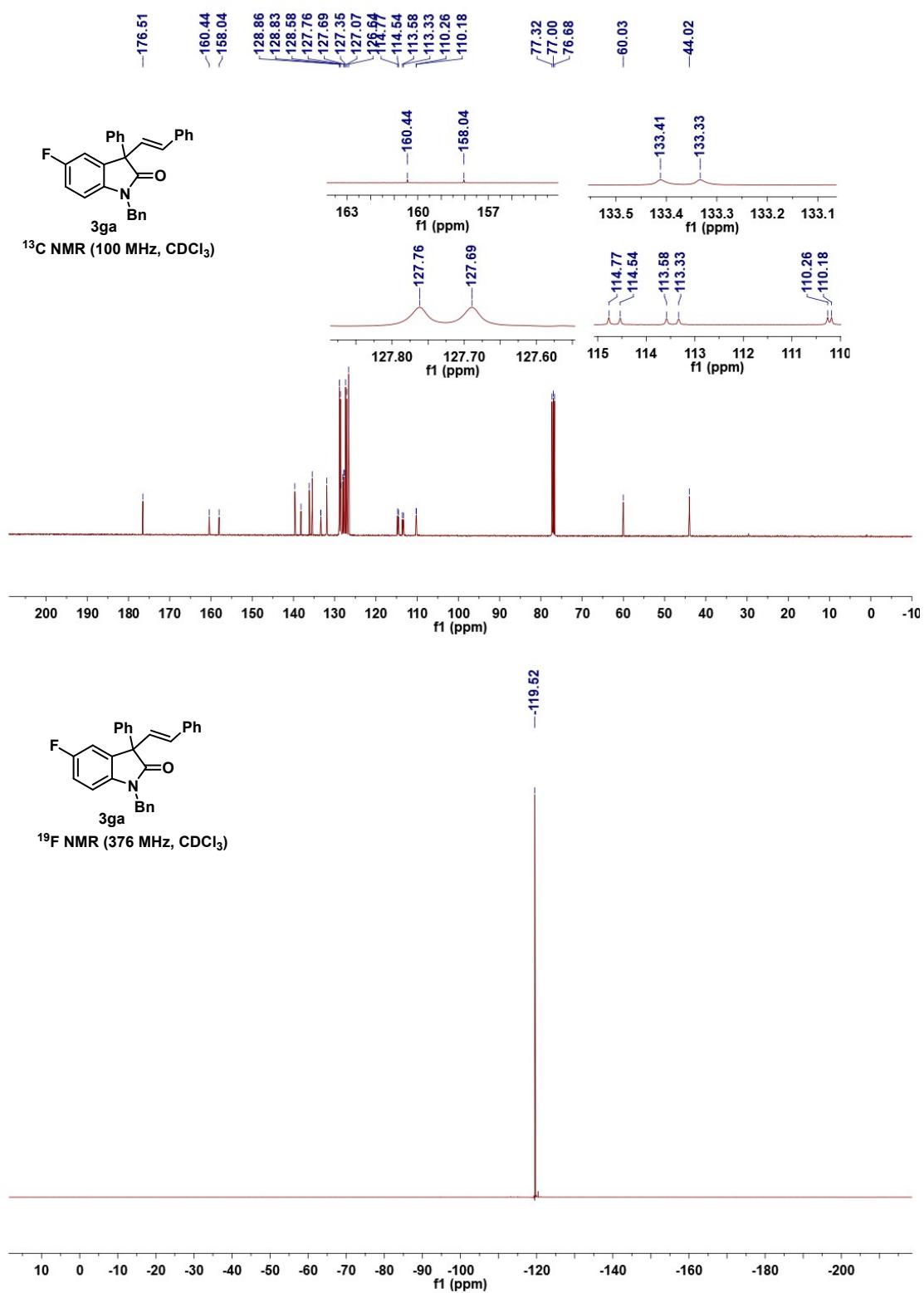


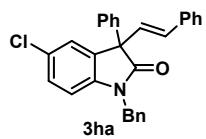




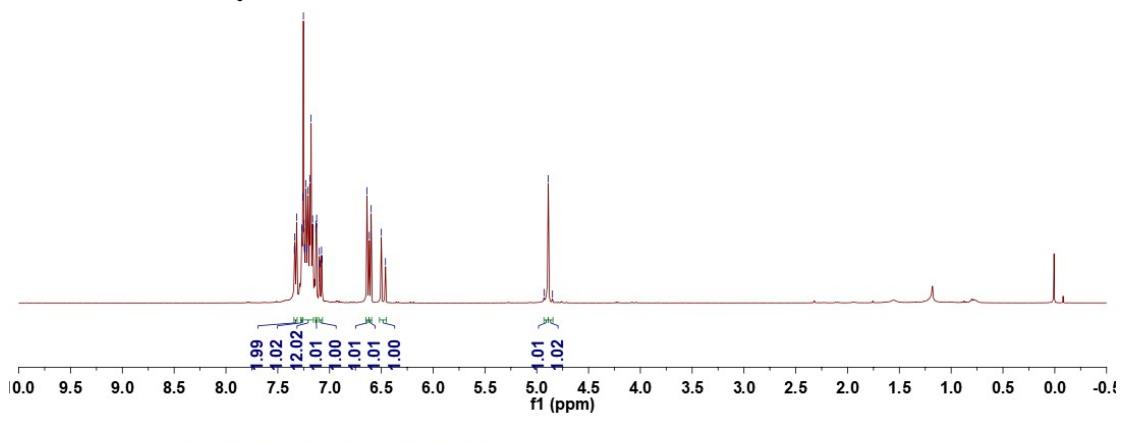




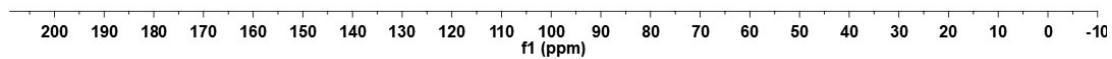


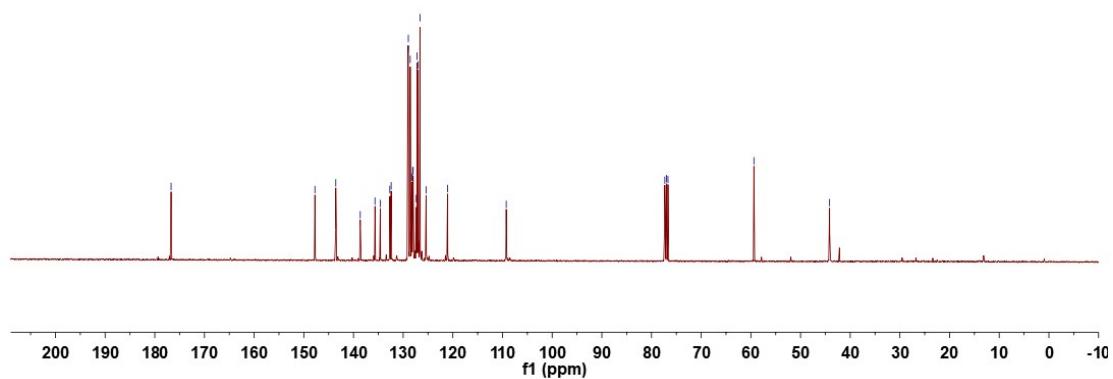
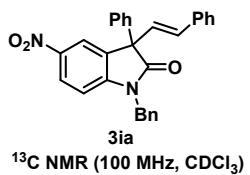
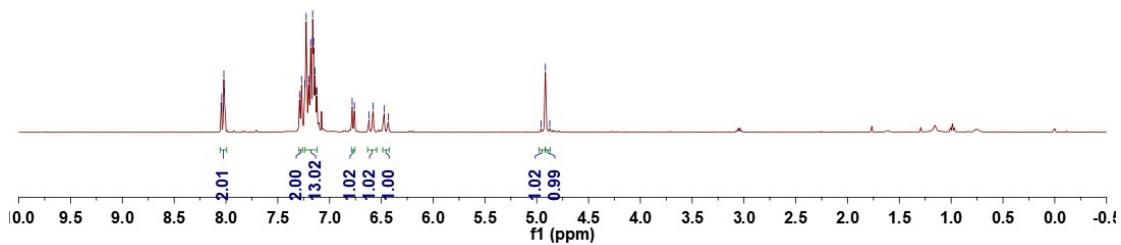
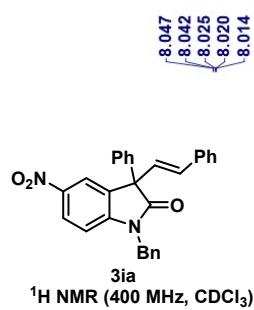


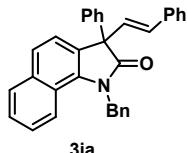
¹H NMR (400 MHz, CDCl₃)



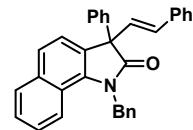
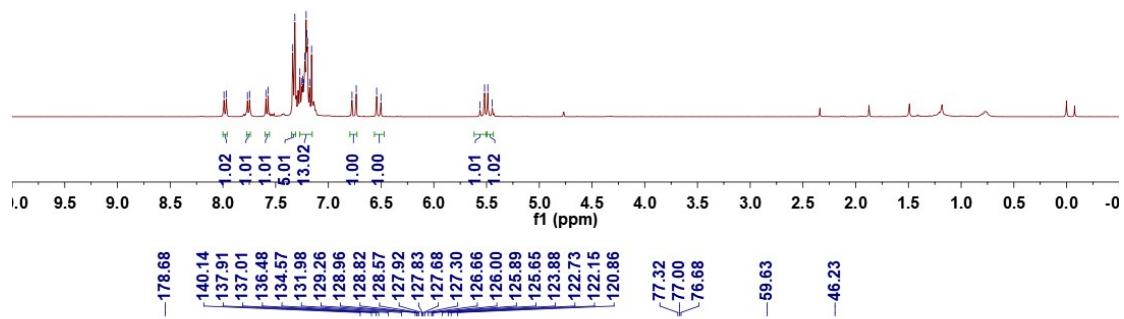
¹³C NMR (100 MHz, CDCl₃)



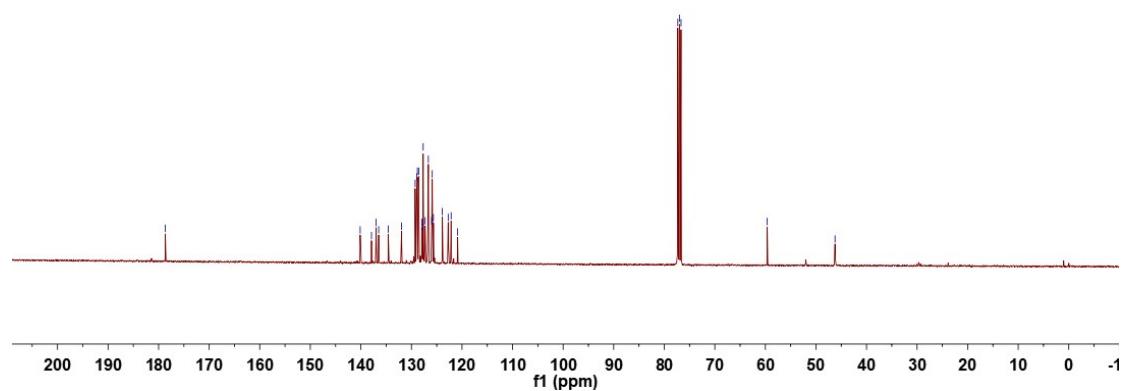


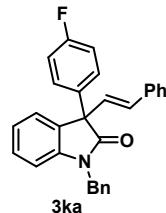


¹H NMR (400 MHz, CDCl₃)

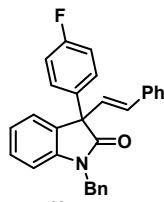
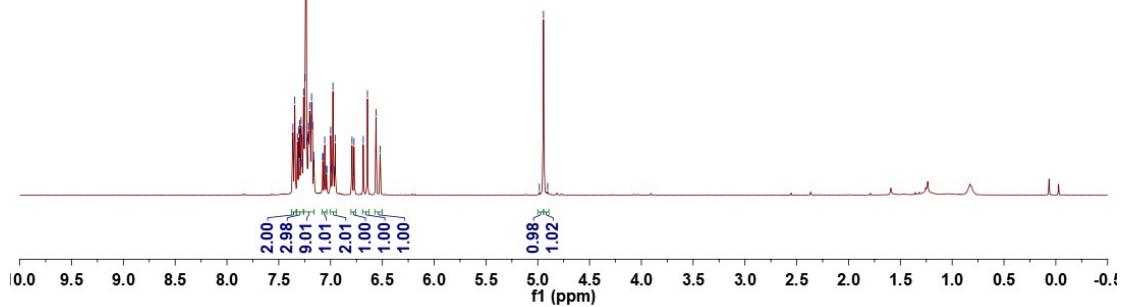


¹³C NMR (100 MHz, CDCl₃)

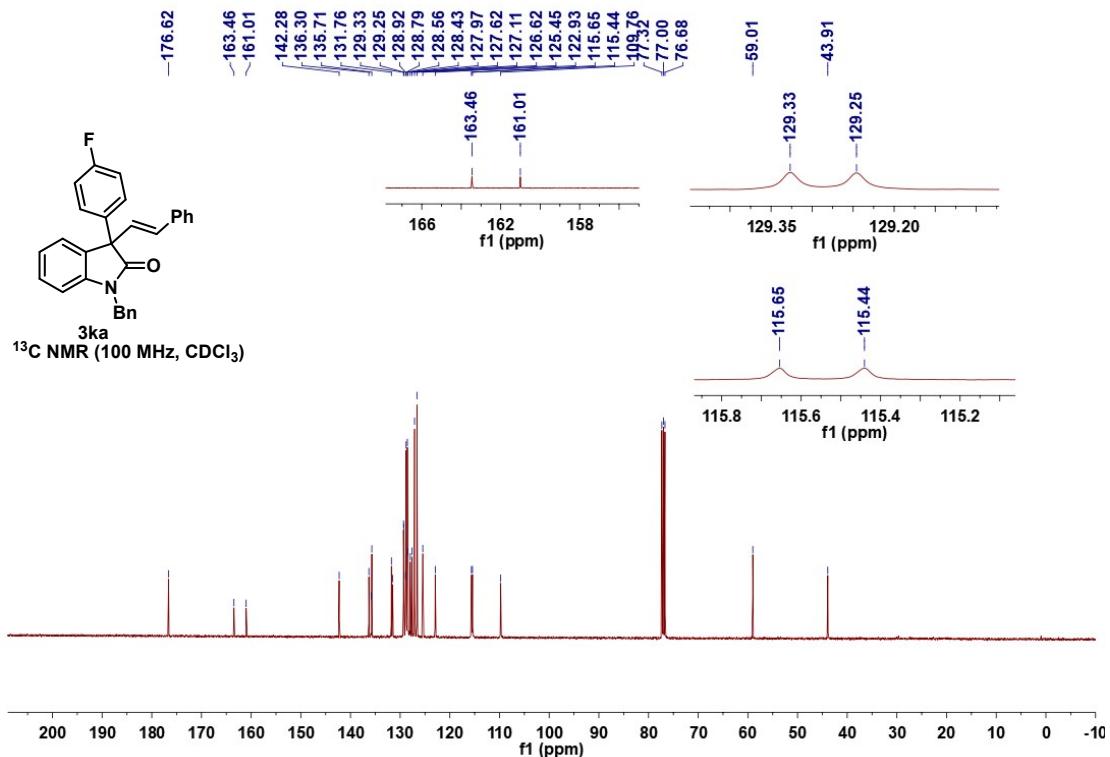


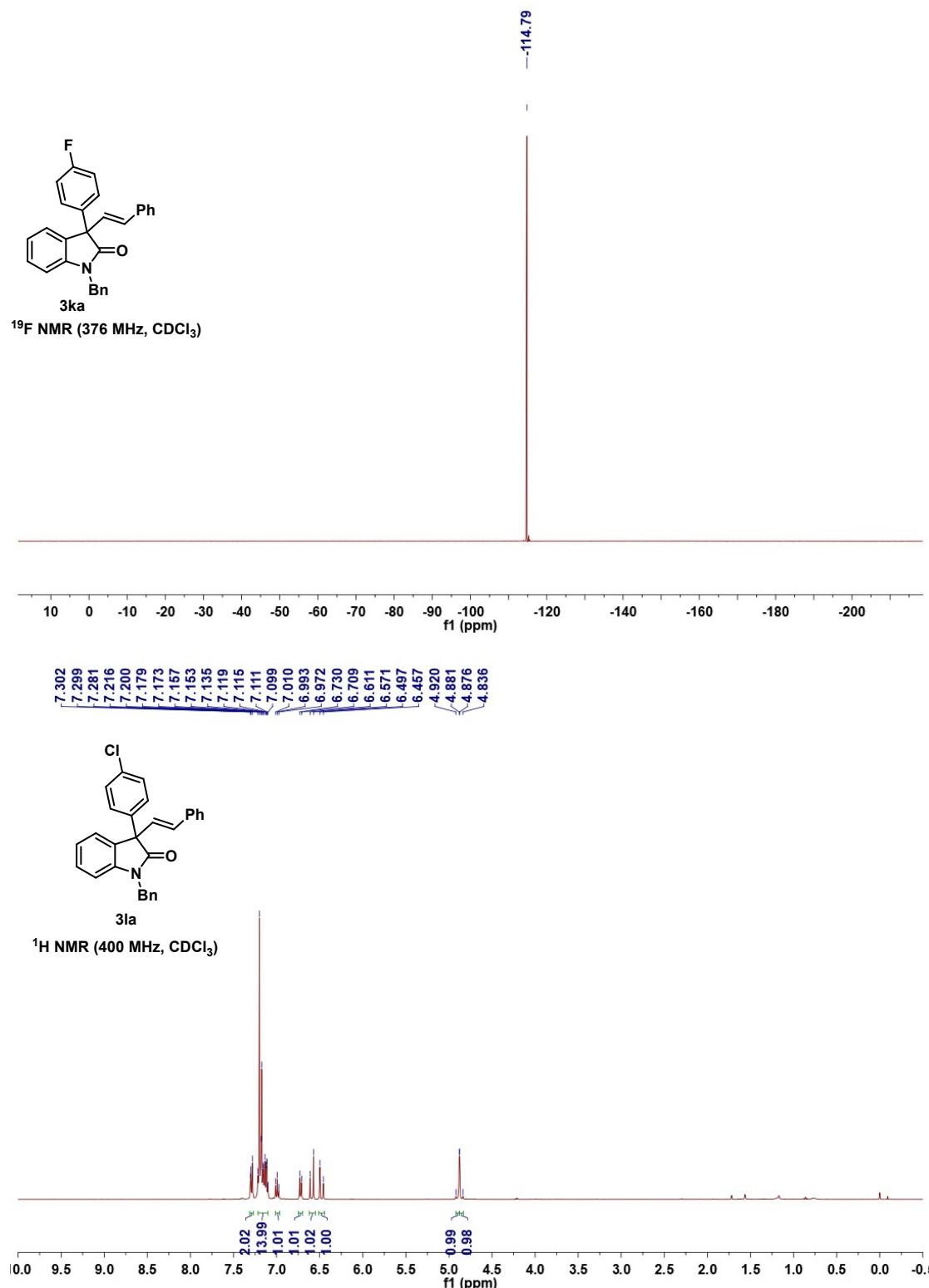


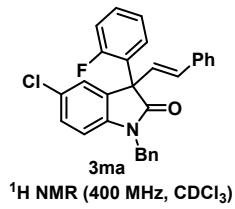
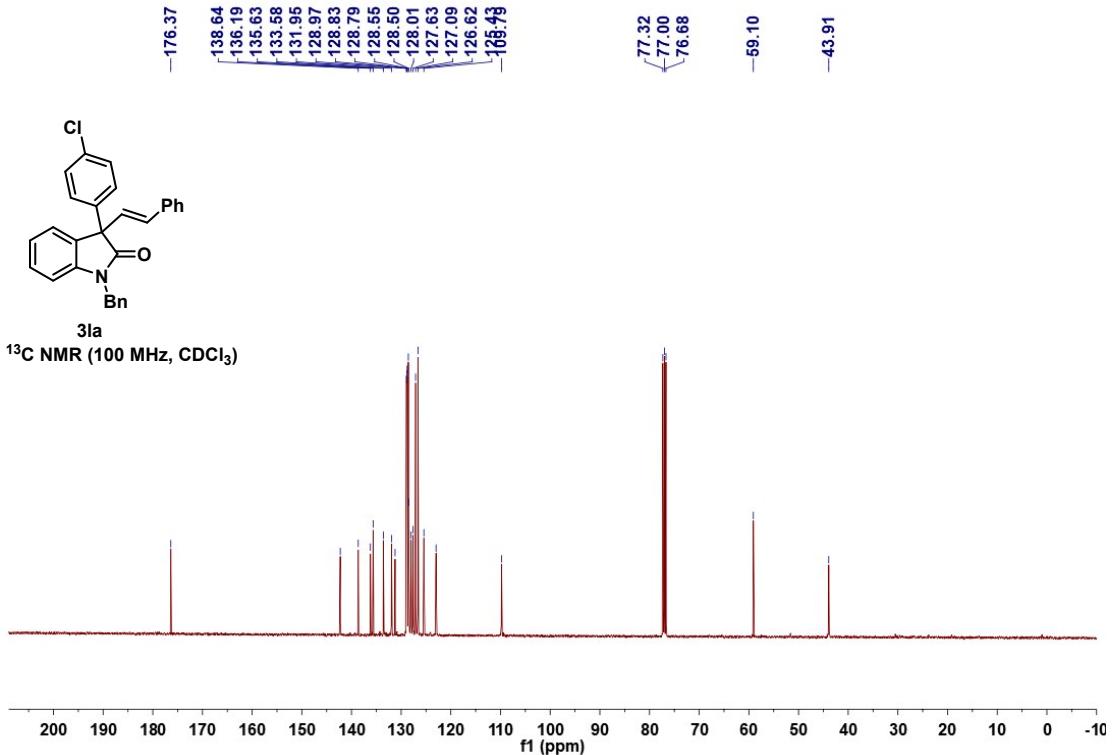
¹H NMR (400 MHz, CDCl₃)



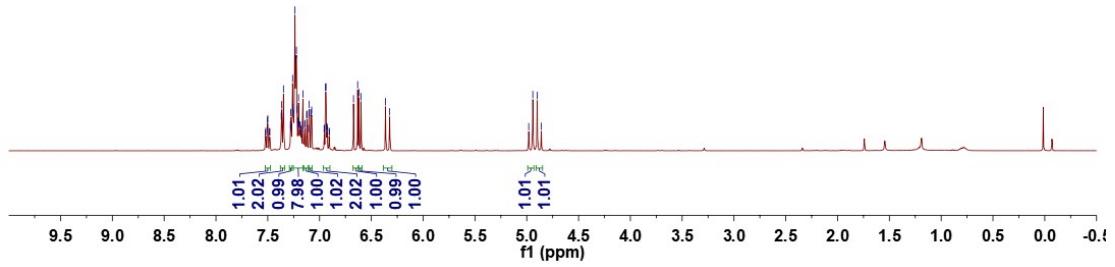
¹³C NMR (100 MHz, CDCl₃)

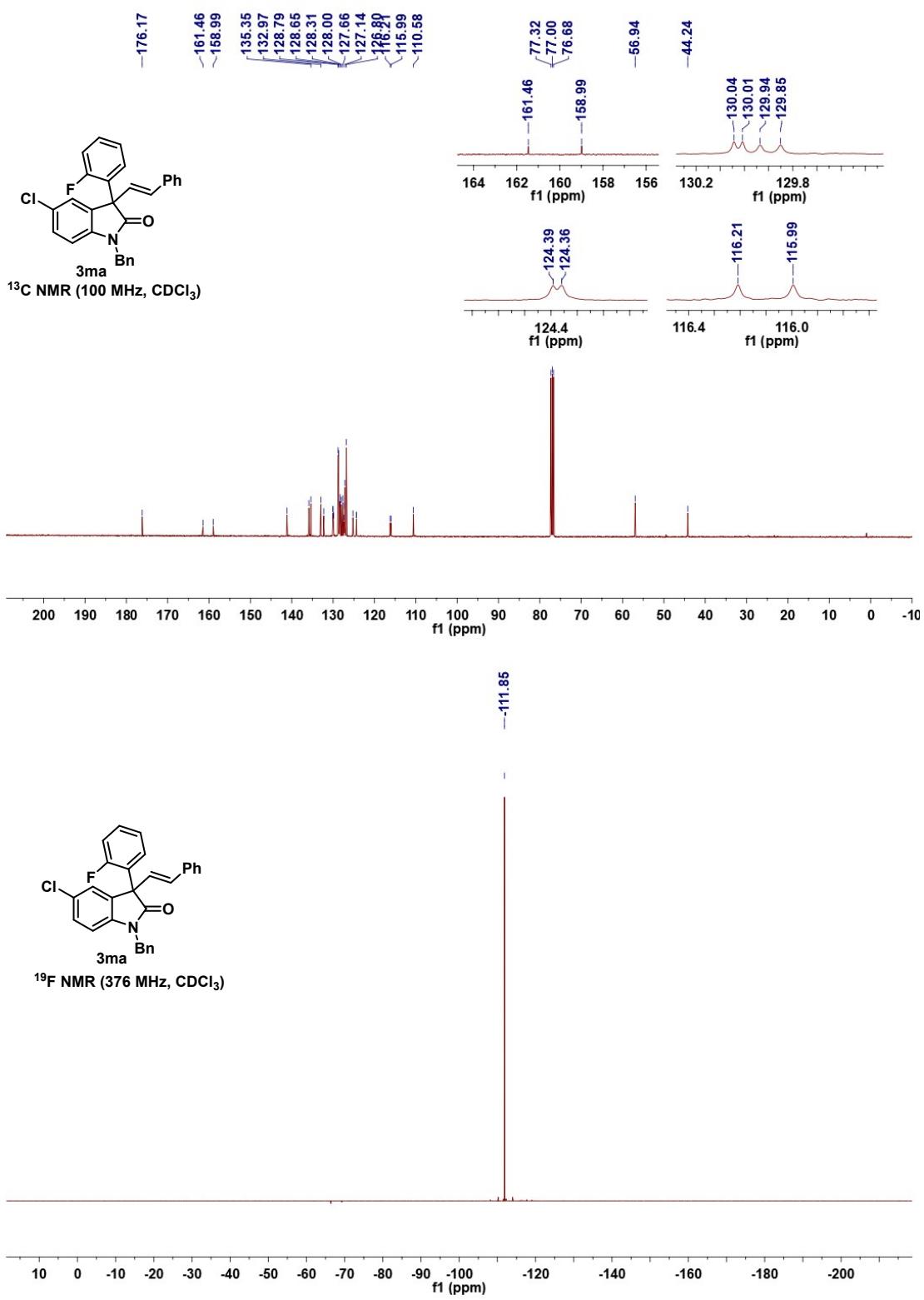


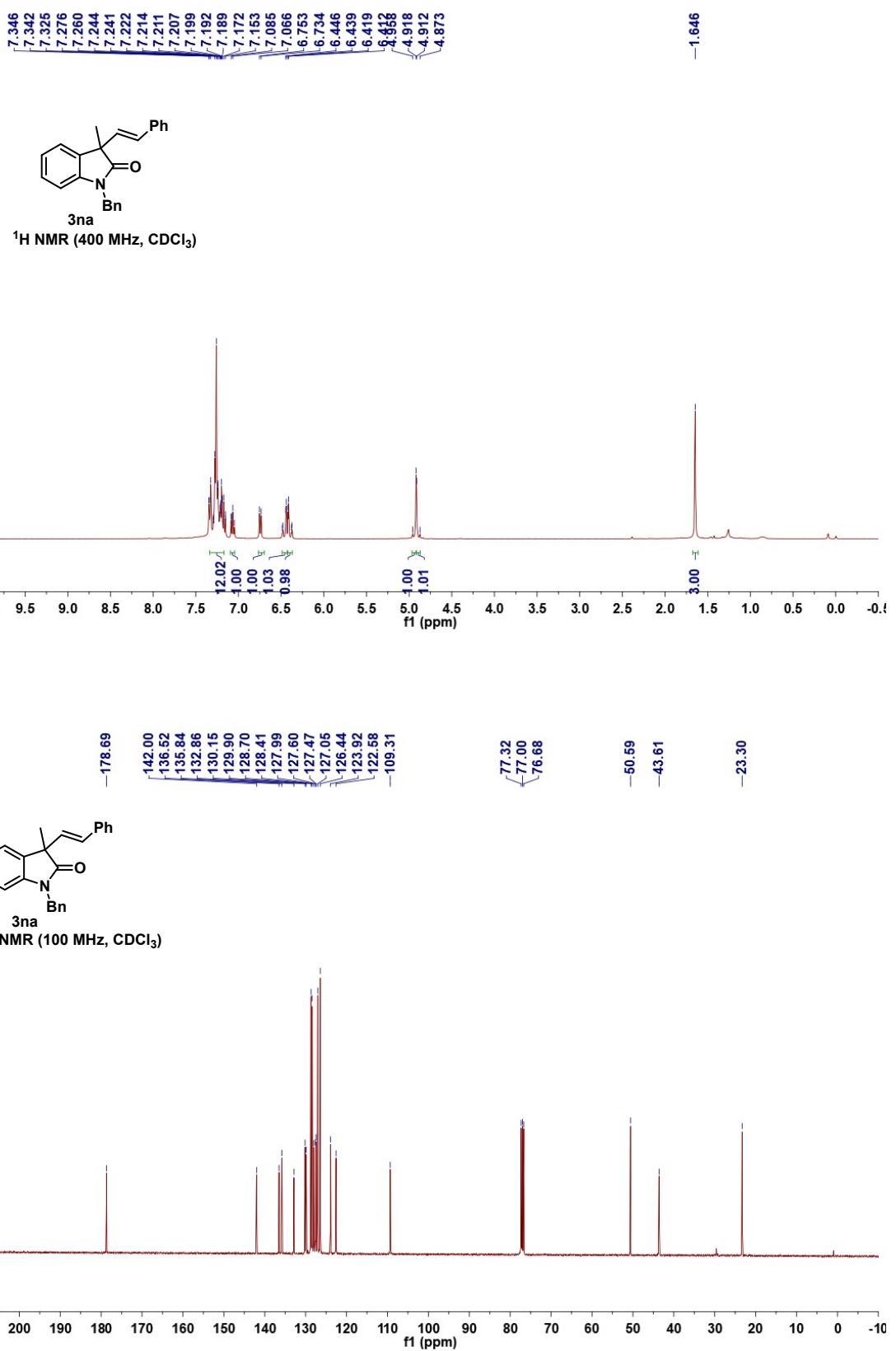


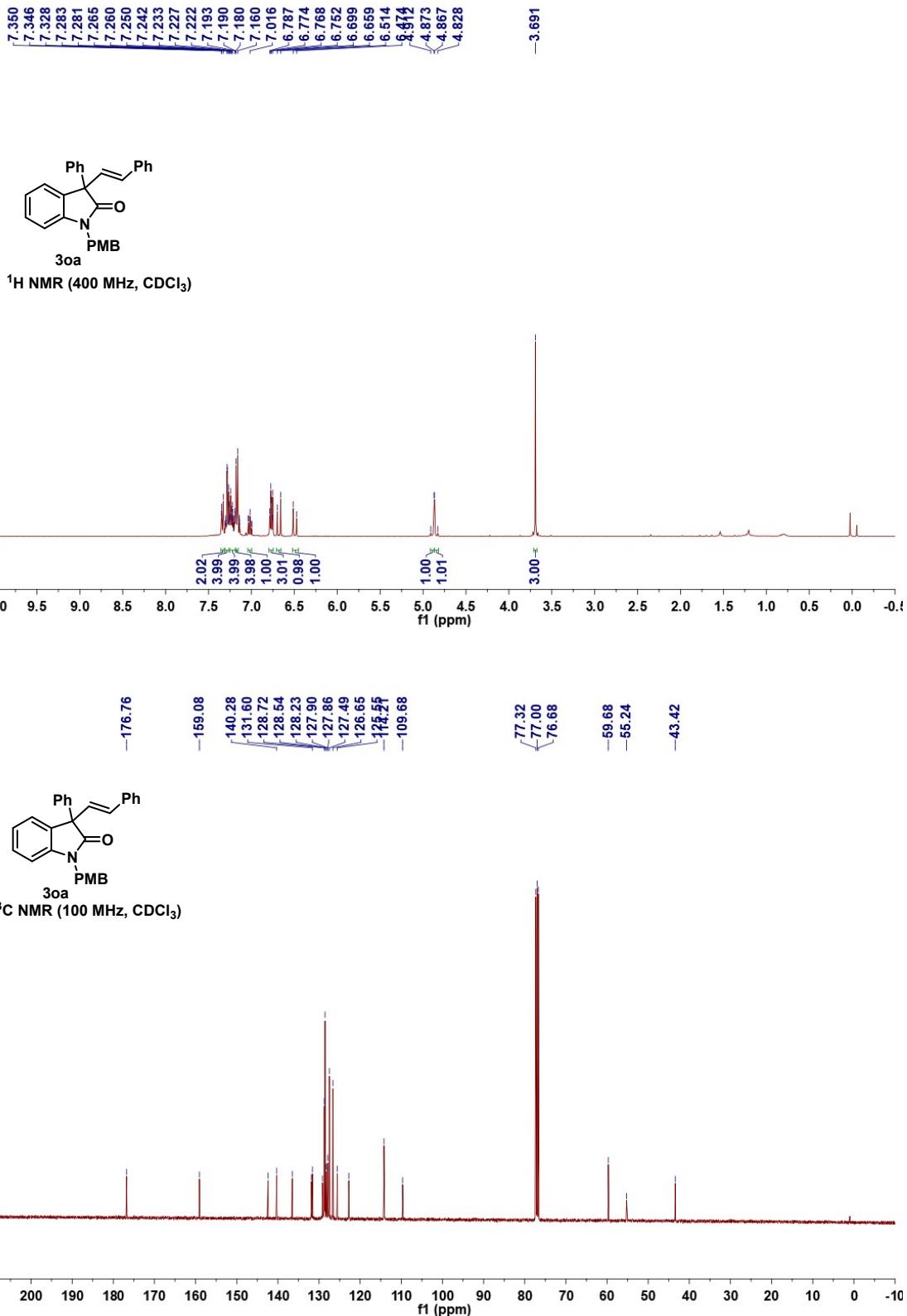


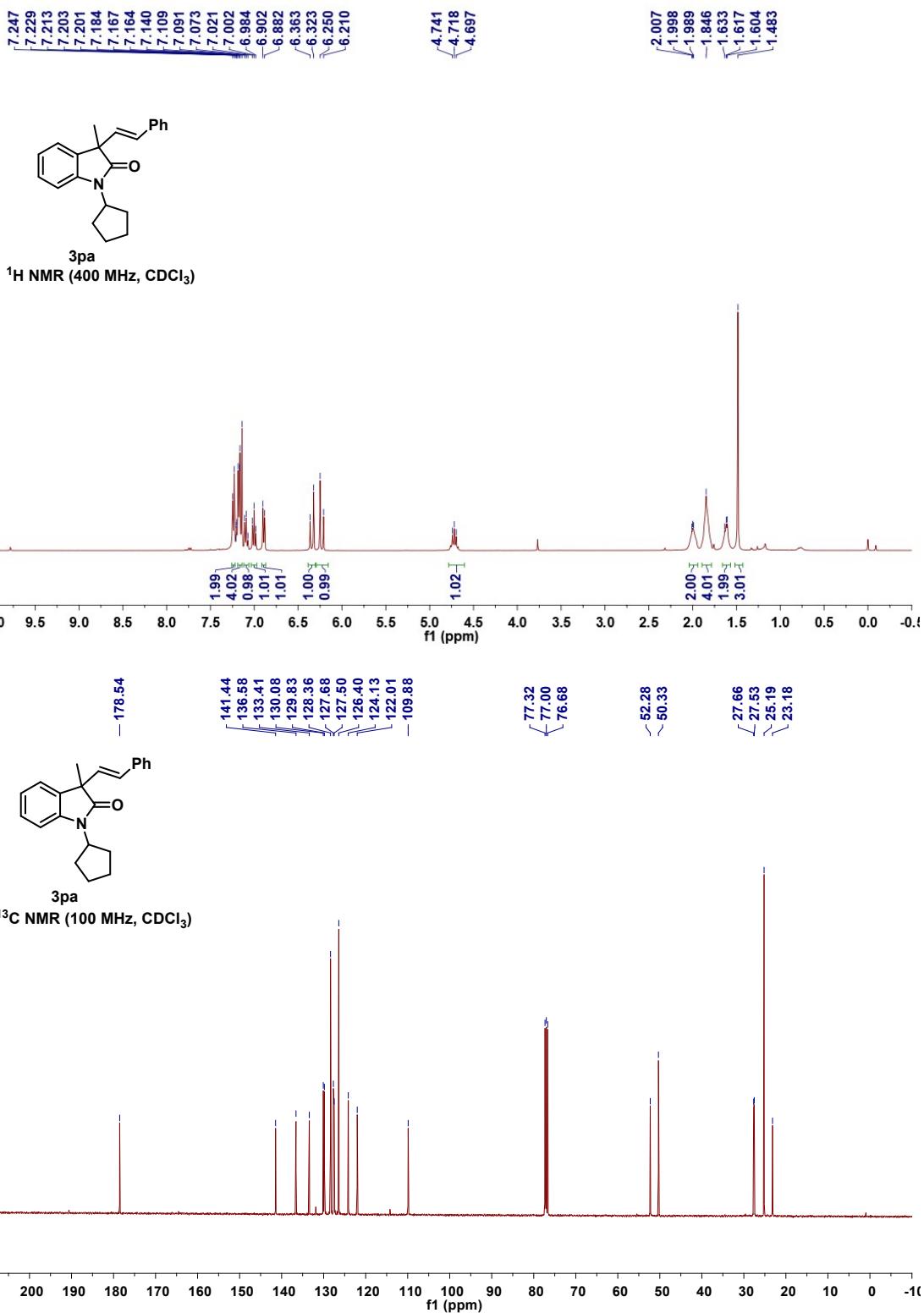
¹H NMR (400 MHz, CDCl₃)

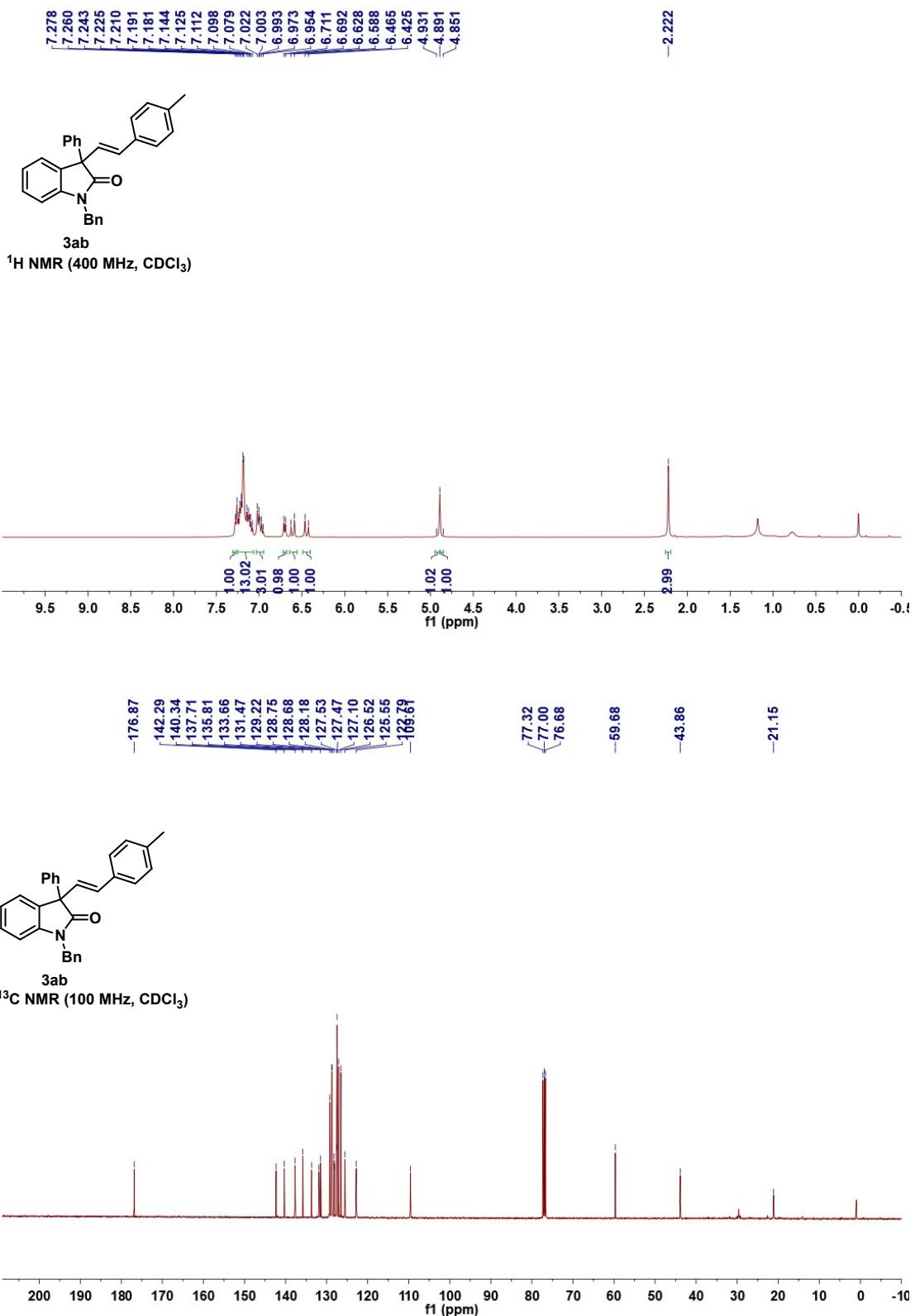


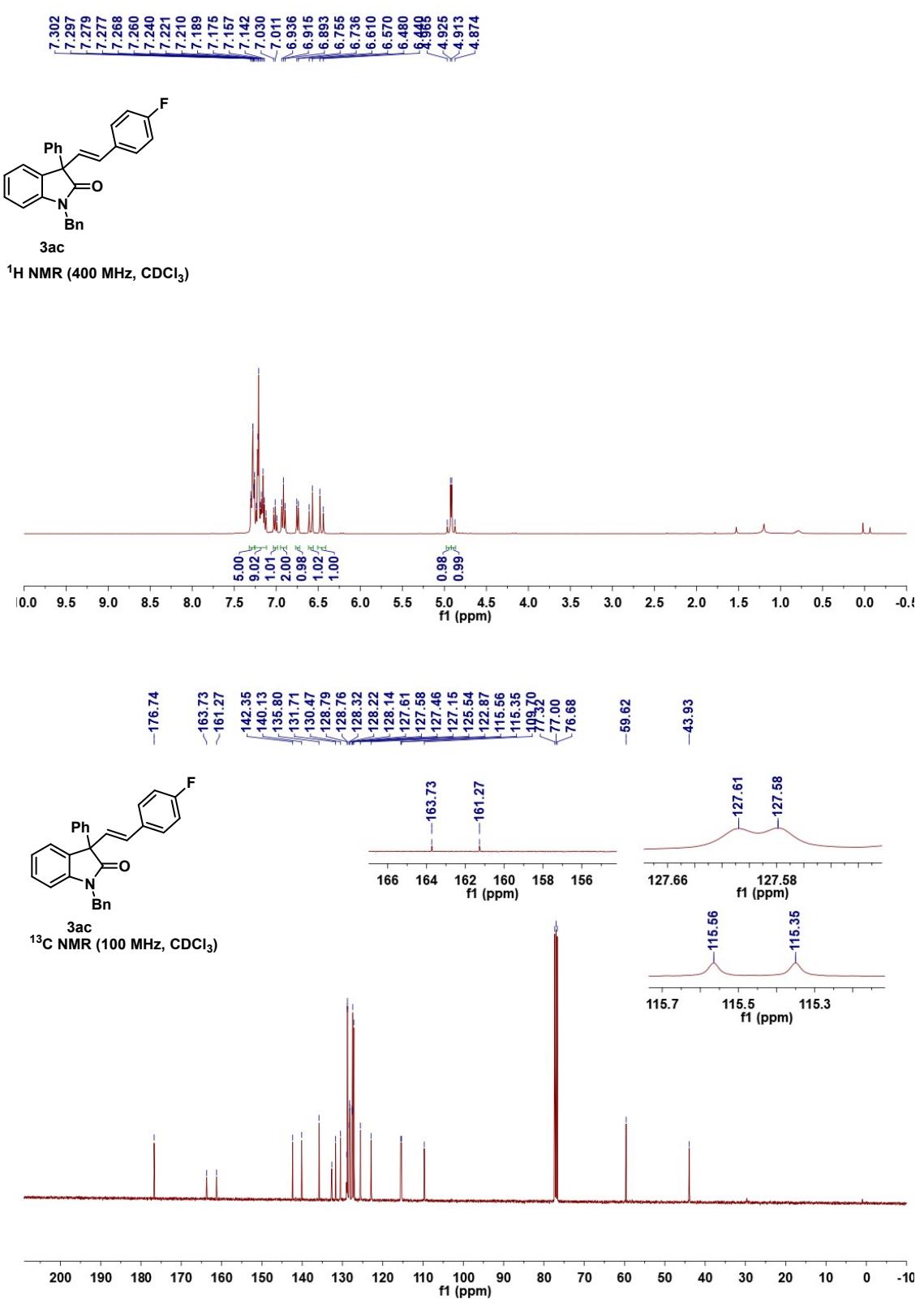


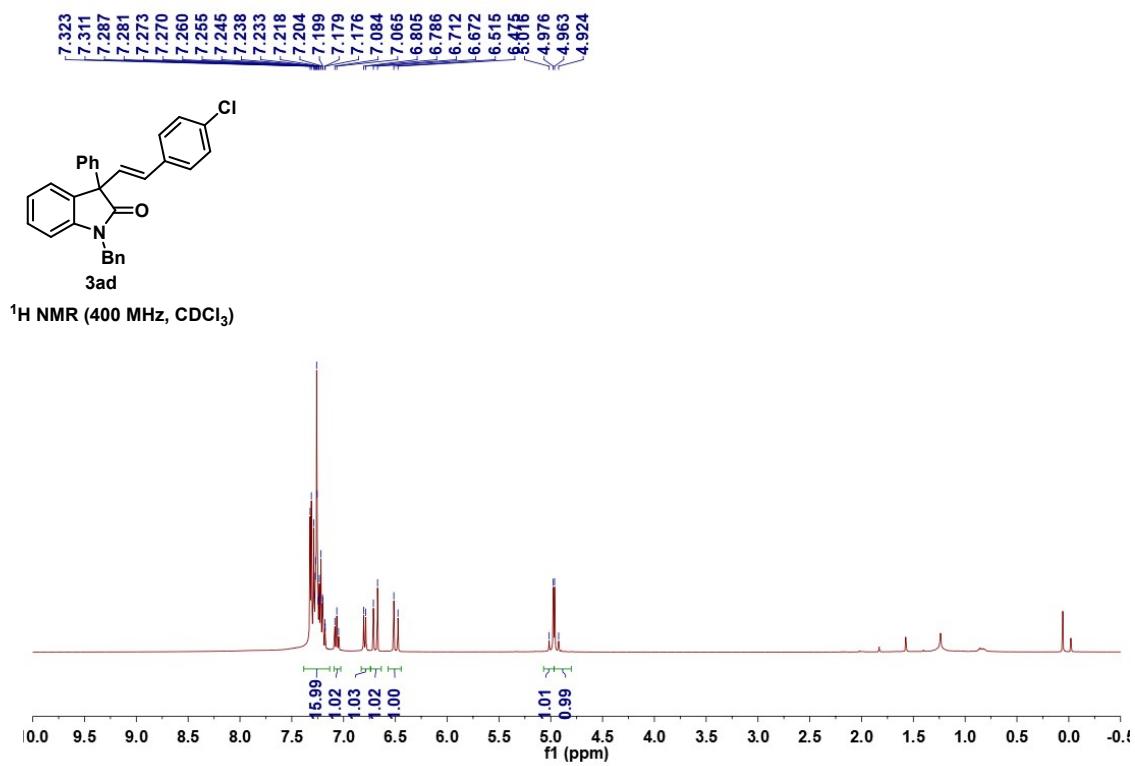
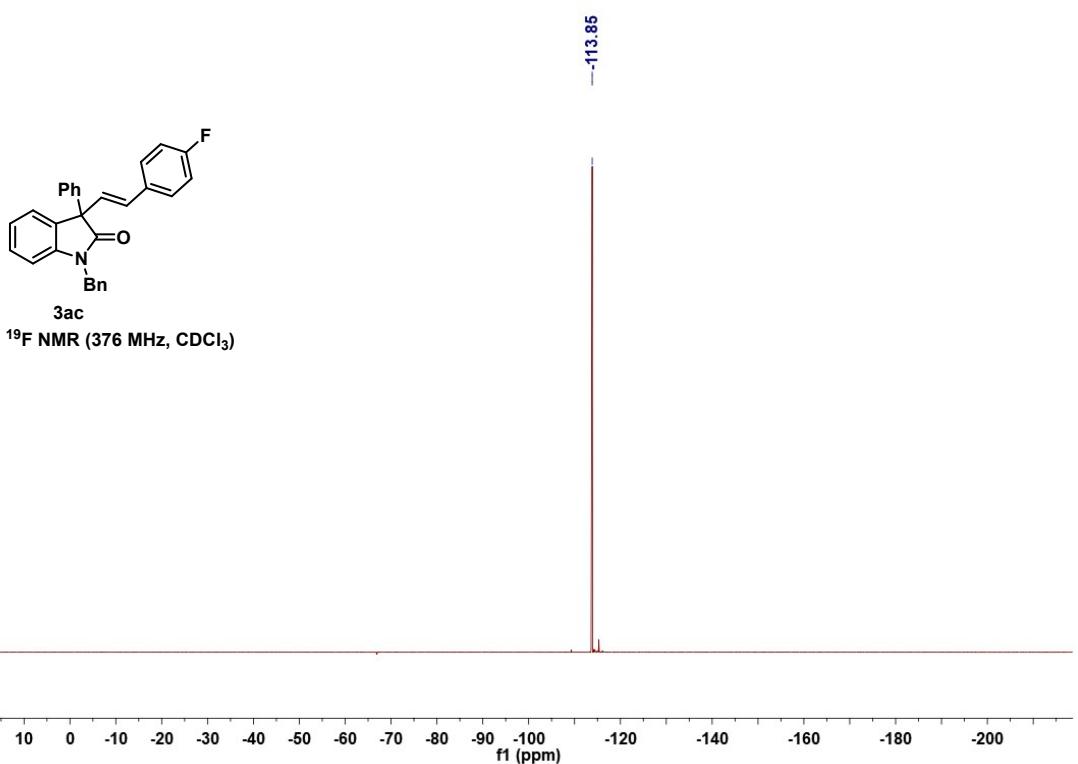


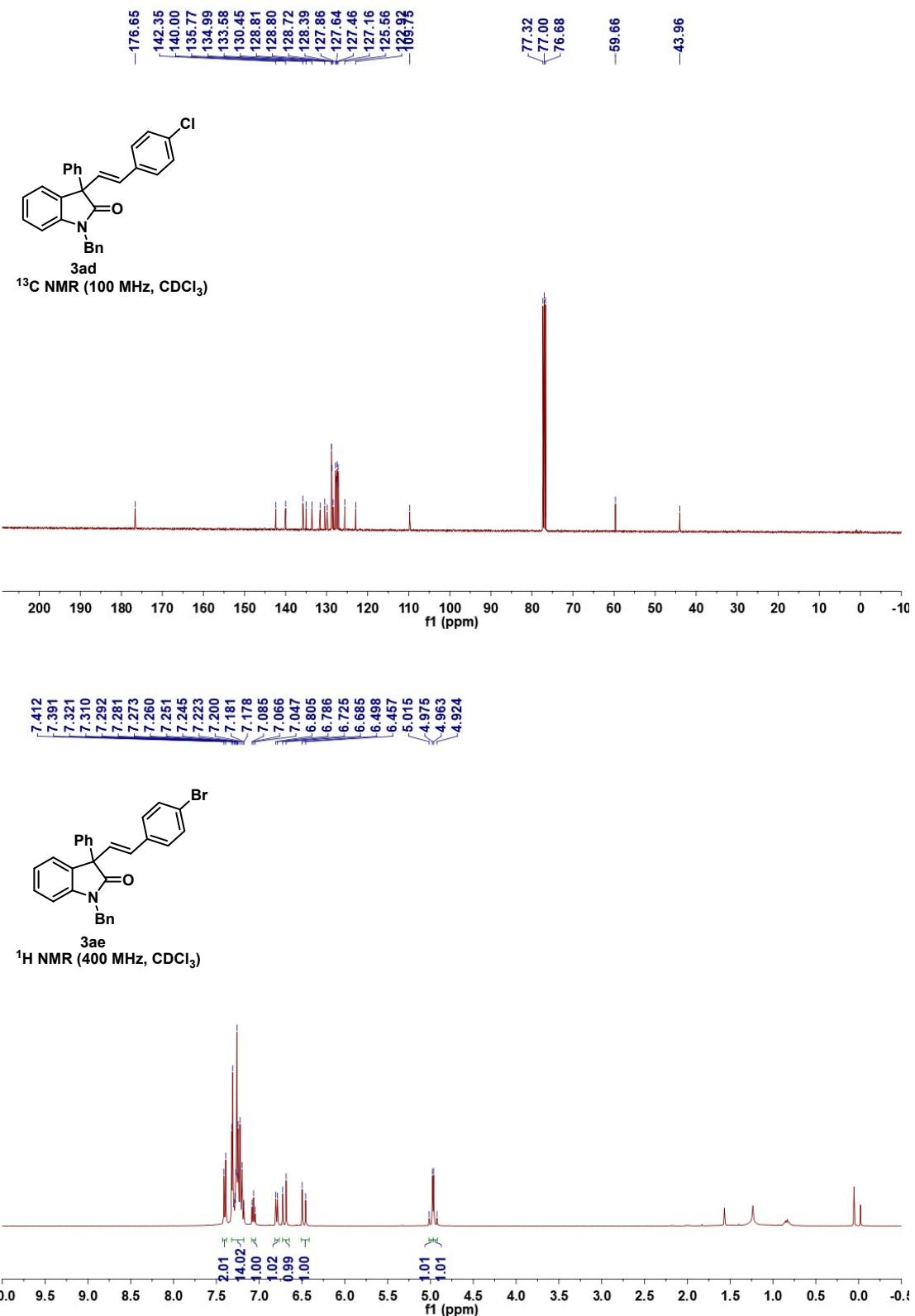


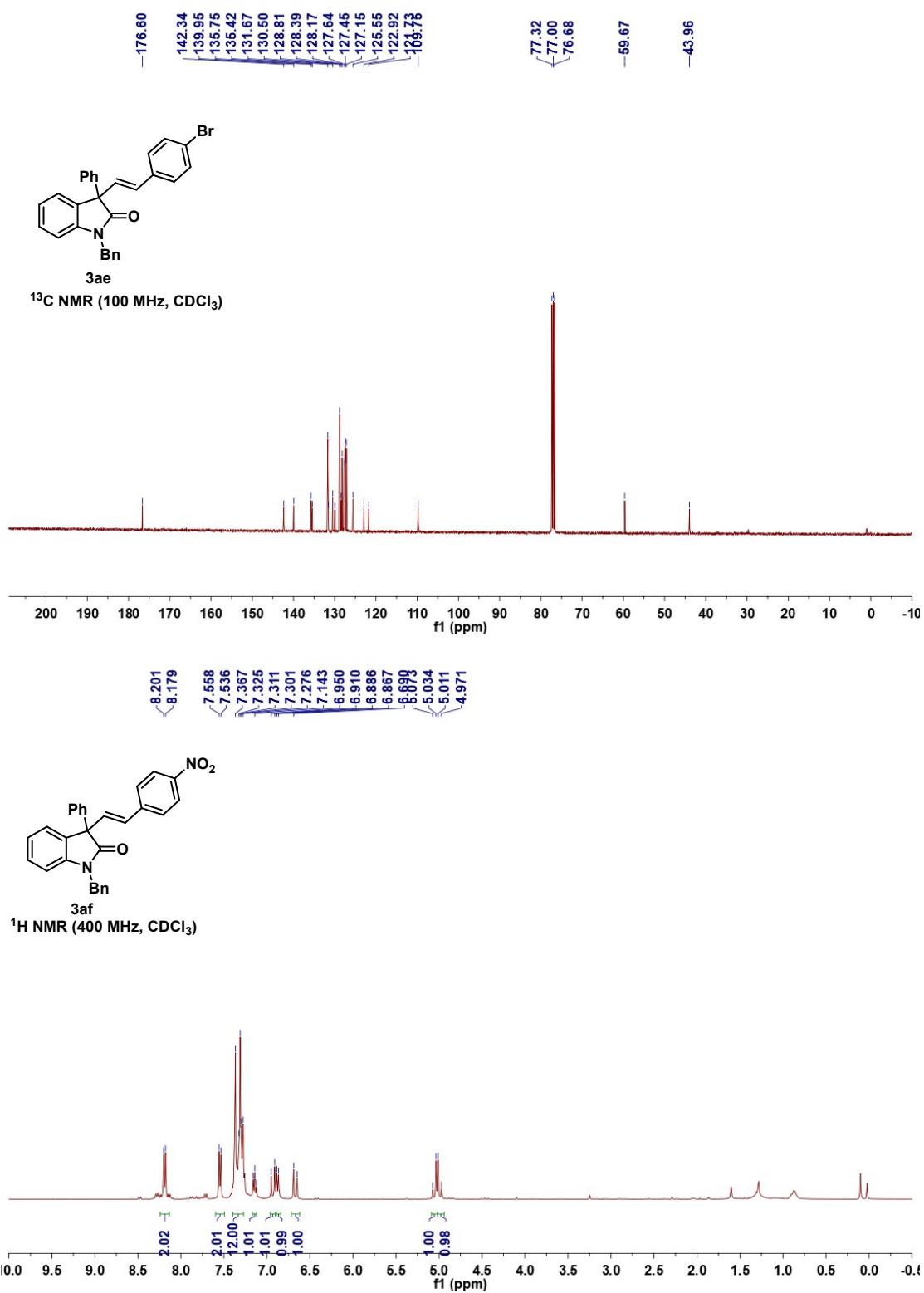


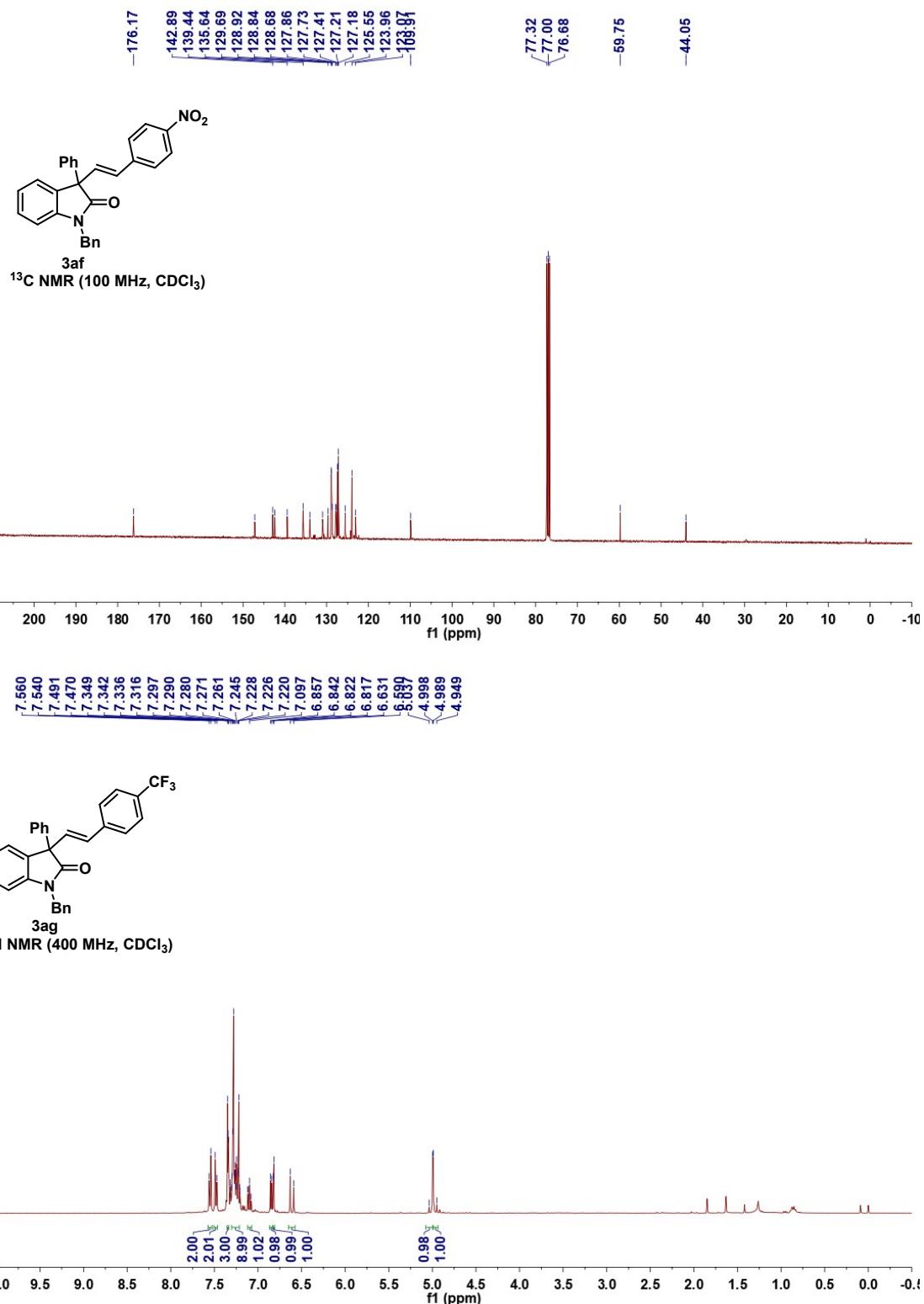


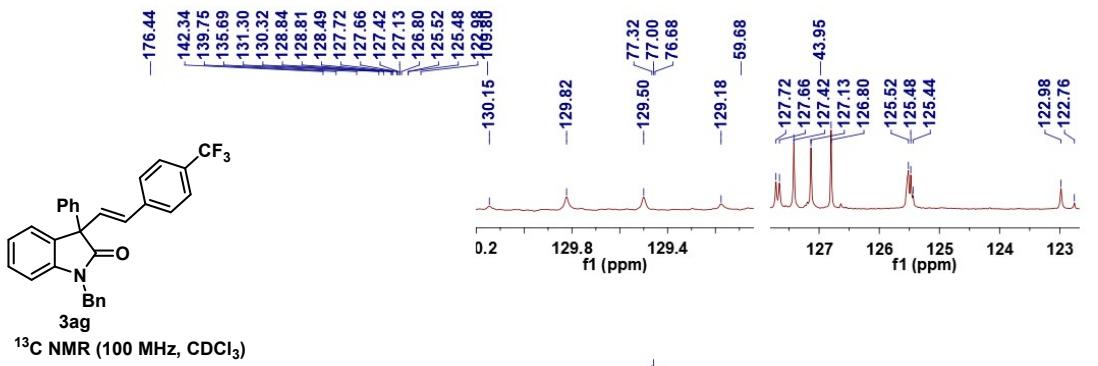




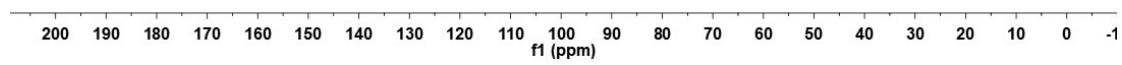




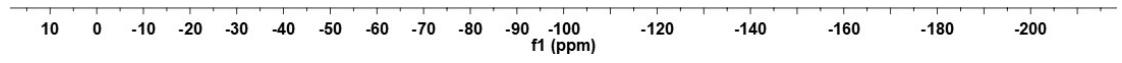


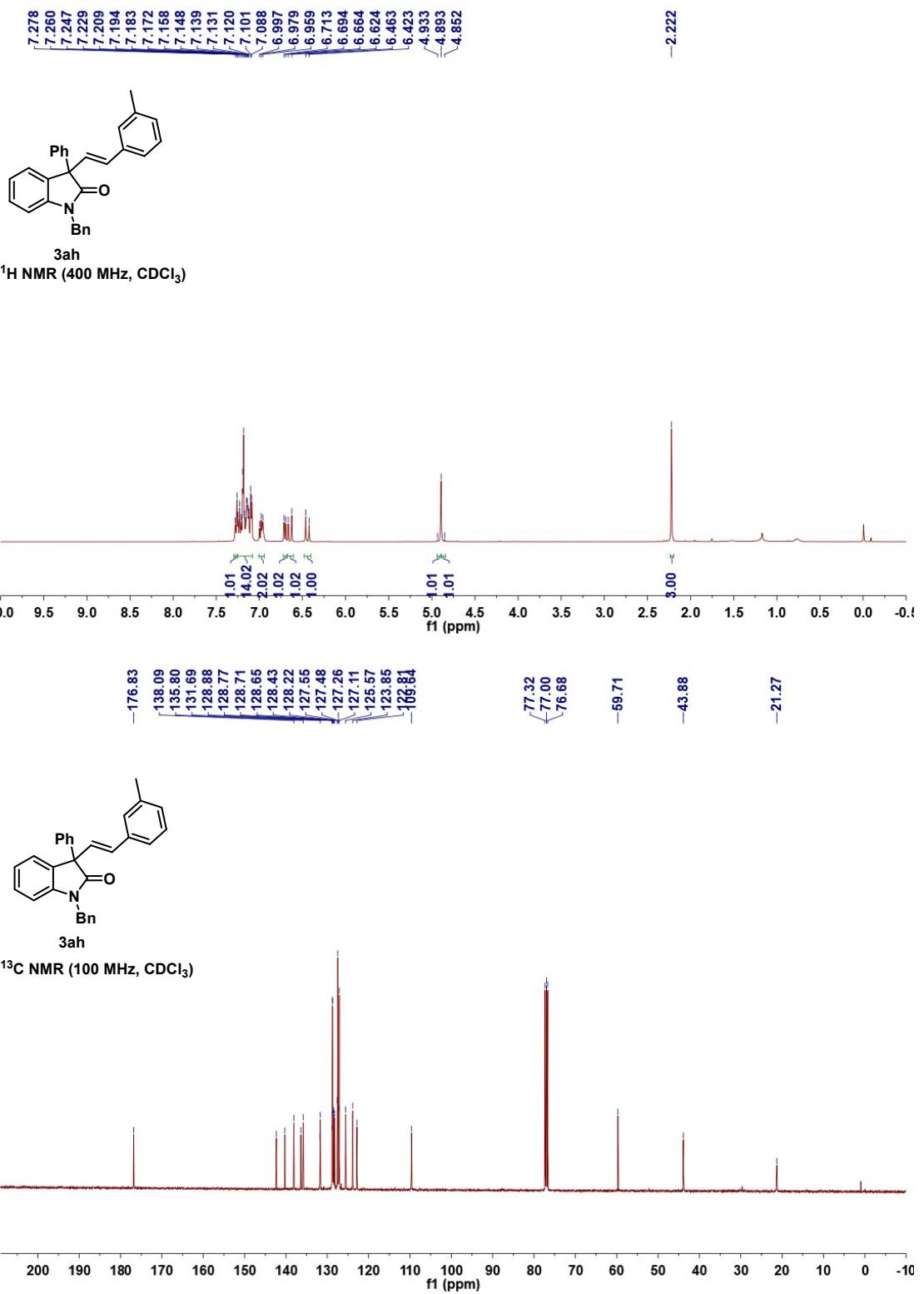


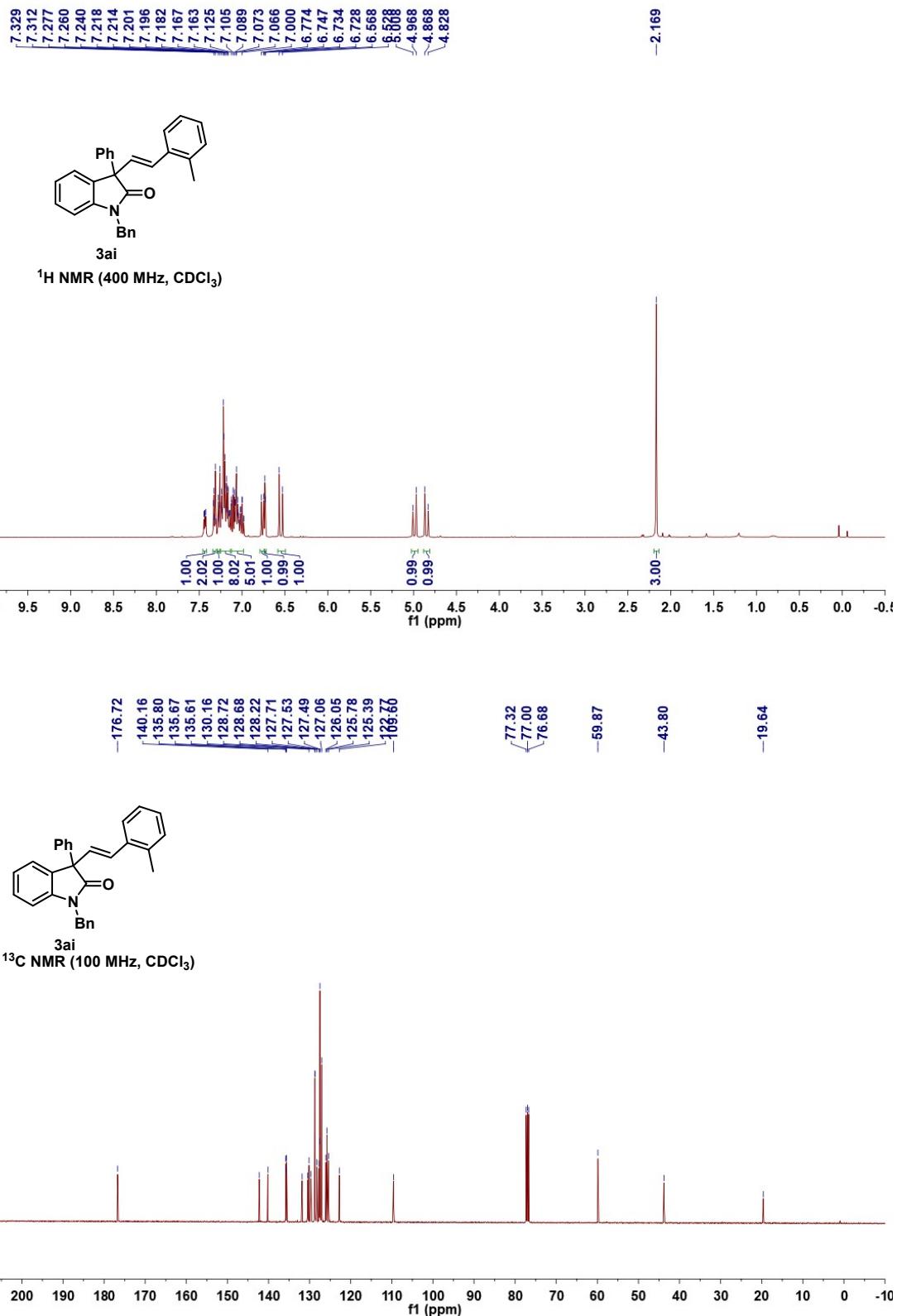
^{13}C NMR (100 MHz, CDCl_3)

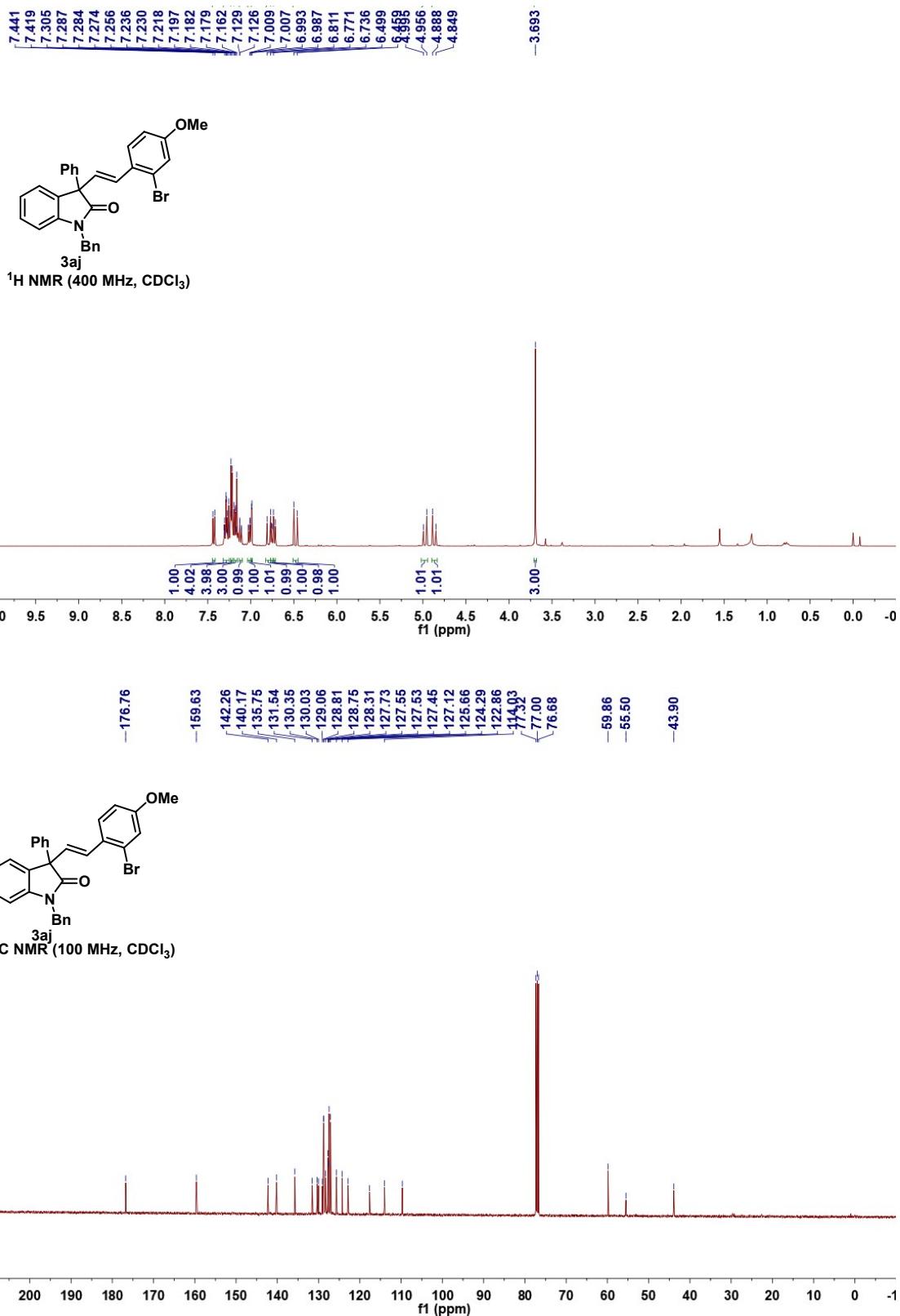


^{19}F NMR (376 MHz, CDCl_3)

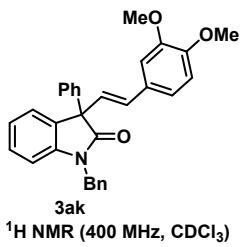




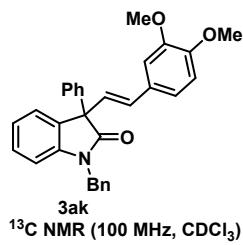
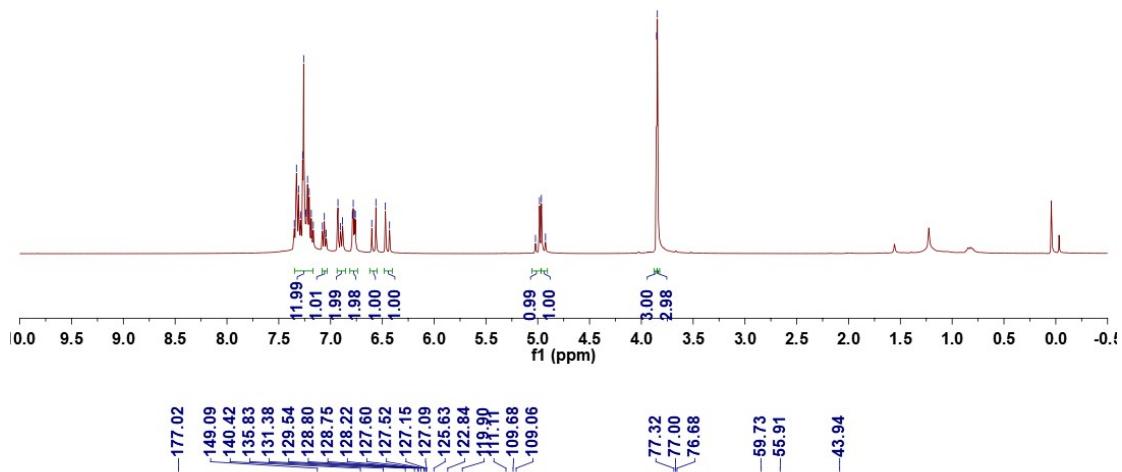




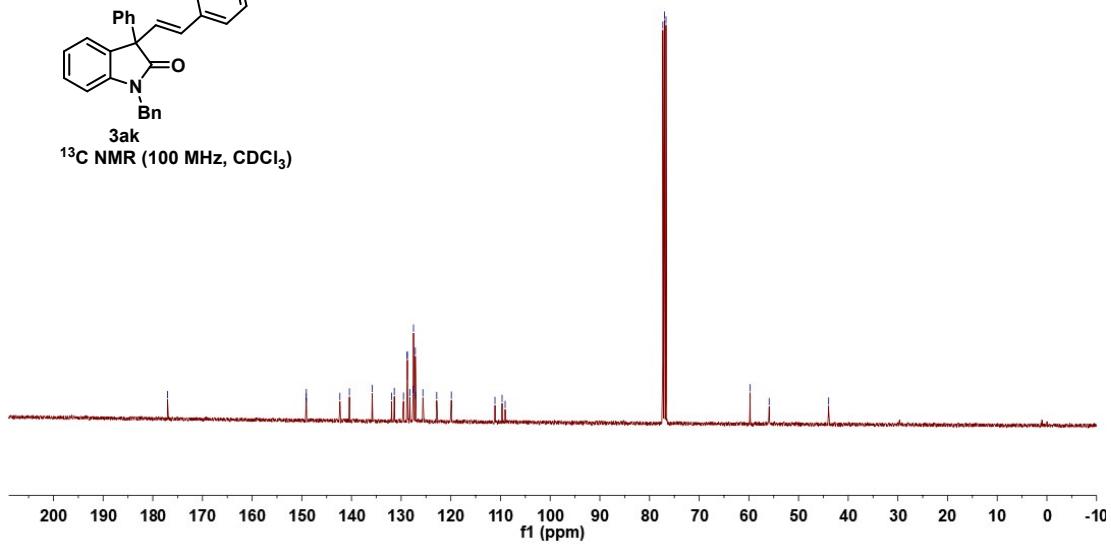
7.350
7.329
7.309
7.289
7.270
7.260
7.238
7.222
7.206
7.186
7.167
7.079
7.060
6.929
6.905
6.884
6.750
6.711
6.770
6.761
6.602
6.562
6.471
6.032
4.983
4.965
4.956



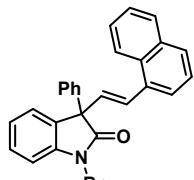
^1H NMR (400 MHz, CDCl_3)



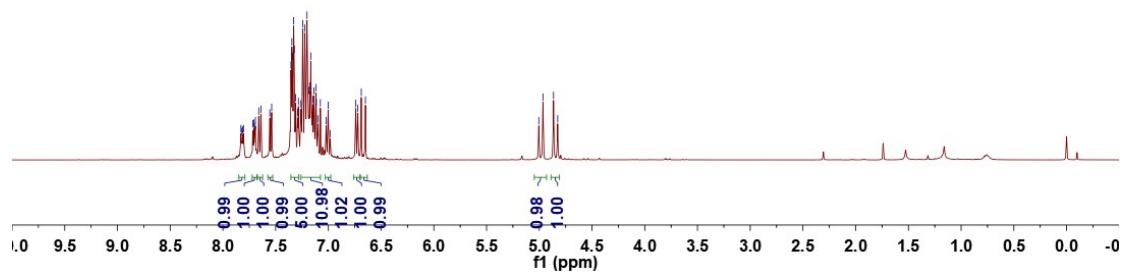
^{13}C NMR (100 MHz, CDCl_3)



7.537
7.354
7.346
7.339
7.330
7.323
7.311
7.284
7.260
7.243
7.223
7.202
7.183
7.177
7.167
7.148
7.136
7.118
7.114
7.076
7.002
6.740
6.721
6.688
6.649
6.605
4.966
4.866
4.825



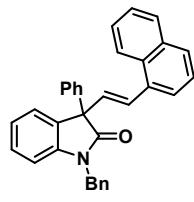
¹H NMR (400 MHz, CDCl₃)



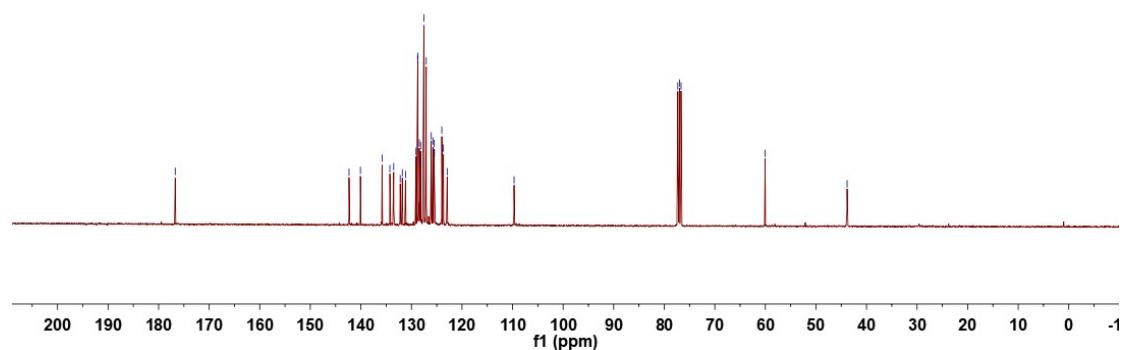
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-135.81
-133.51
-129.09
-128.79
-128.76
-128.45
-128.34
-128.19
-127.54
-127.54
-127.08
-126.08
-125.76
-125.54
-125.45
-123.99
-123.97

77.32
77.00
76.68

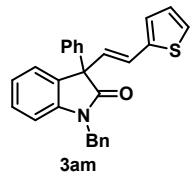
-60.05
-43.84



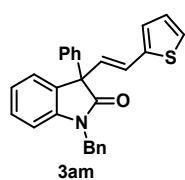
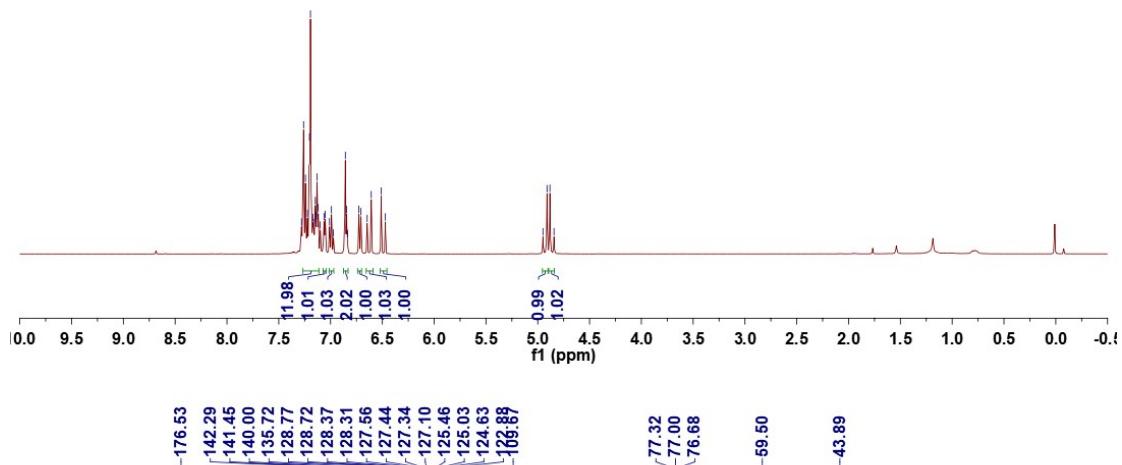
¹³C NMR (100 MHz, CDCl₃)



7.281
 7.260
 7.243
 7.223
 7.204
 7.194
 7.172
 7.164
 7.147
 7.137
 7.130
 7.119
 7.100
 7.063
 7.052
 7.010
 6.991
 6.887
 6.845
 6.727
 6.707
 6.647
 6.607
 6.511
 5.816
 4.911
 4.883
 4.843

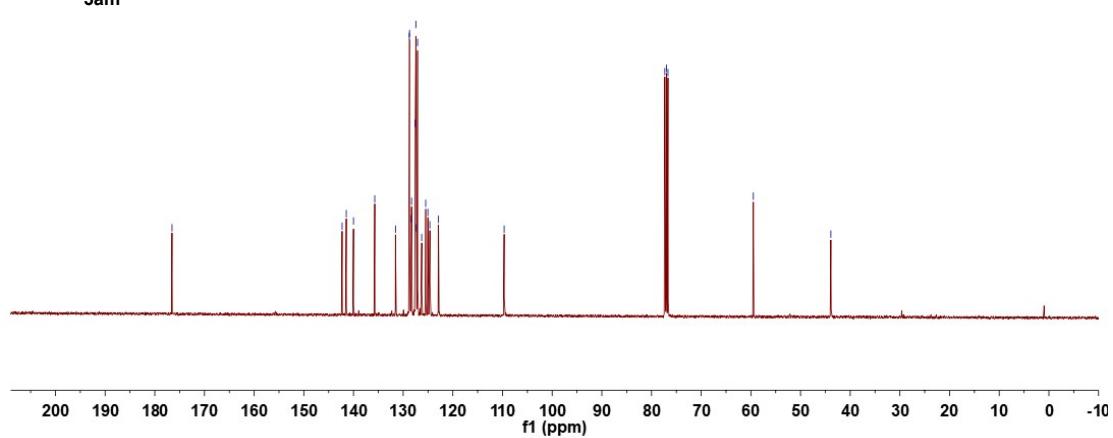


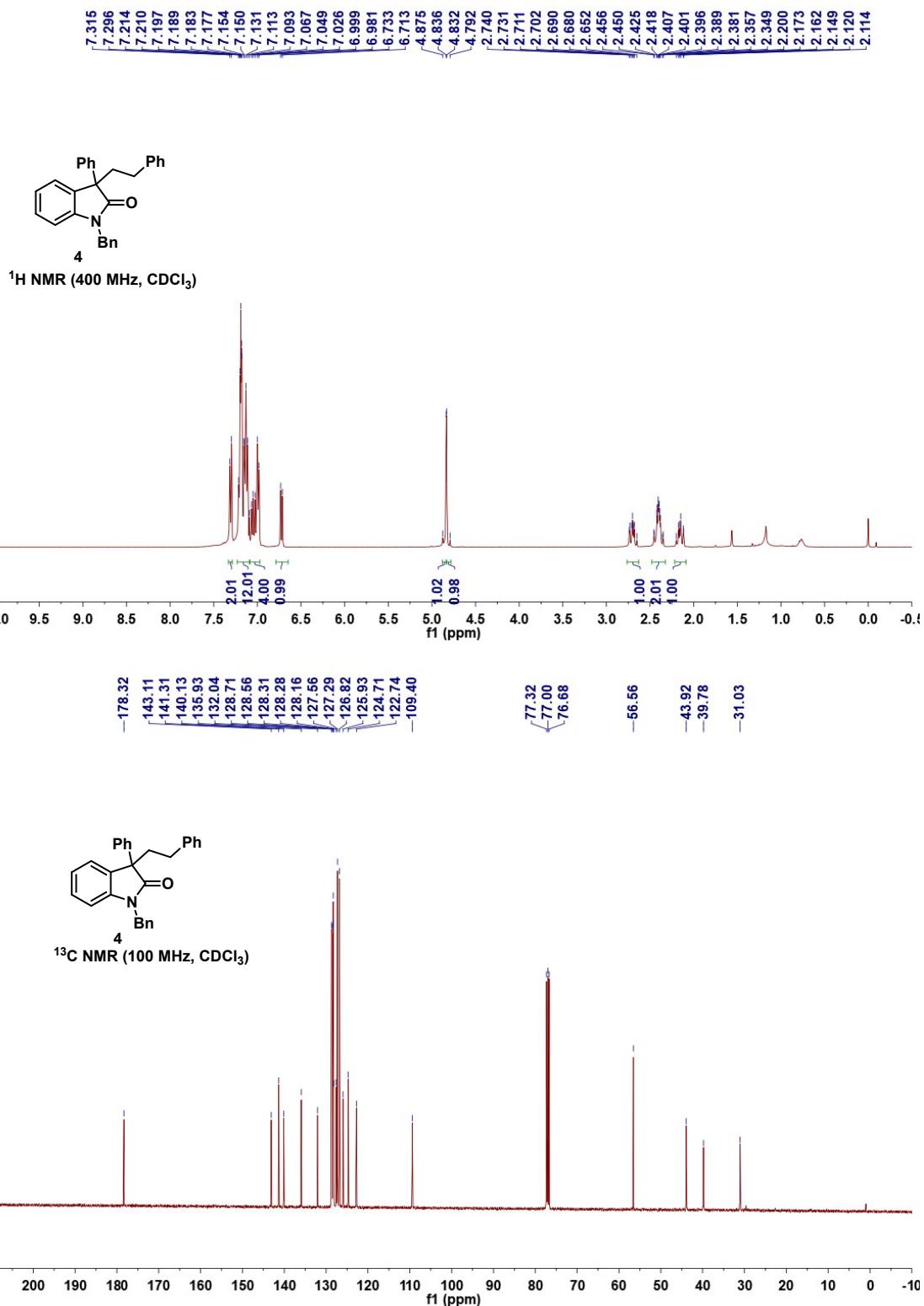
¹H NMR (400 MHz, CDCl₃)



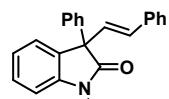
-176.53
 -142.29
 -141.45
 -140.00
 -135.72
 -128.77
 -128.72
 -128.37
 -128.31
 -127.56
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 -127.34
 -127.10
 -125.46
 -125.03
 -124.63
 -123.88

-59.50
-43.89

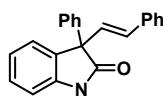
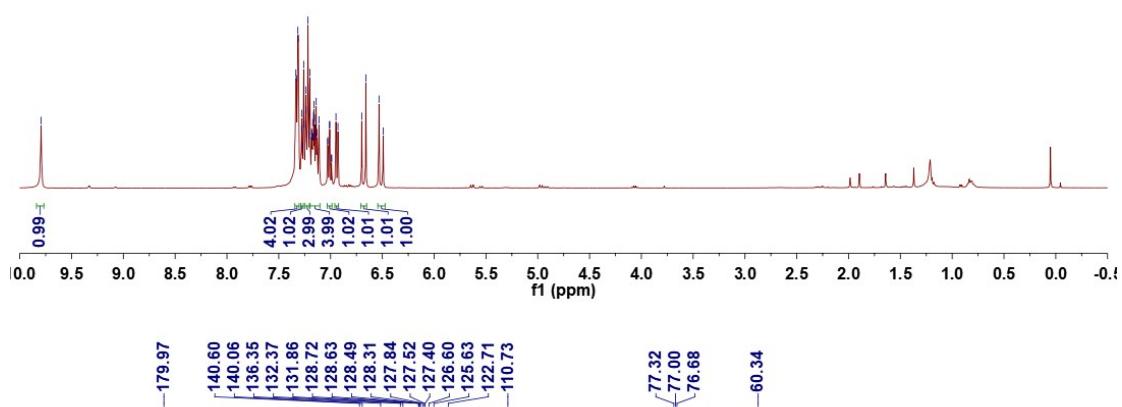




9.794
7.335
7.329
7.316
7.311
7.280
7.277
7.272
7.260
7.266
7.240
7.236
7.218
7.207
7.200
7.183
7.180
7.176
7.172
7.169
7.164
7.161
7.154
7.029
7.027
7.010
7.008
7.129
7.111
6.948
6.938
6.899
6.639
6.533
6.492



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

