

Supporting Information

Weak Coordination Enabled Switchable C4-Alkenylation and Alkylation of Indoles with Allyl Alcohols

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General Information. Indoles, $[\text{Cp}^*\text{RhCl}_2]_2$, AgSbF_6 (99%), $\text{Cu}(\text{OAc})_2$ (98%), AgOTf ($\geq 98.0\%$), AgBF_4 (98%), $\text{NaOPiv}\cdot\text{H}_2\text{O}$ (99%) and Ag_2CO_3 (98%) were purchased from Aldrich and used as received. All the solvents were dried prior to use according to the standard procedure.¹ Substituted allyl alcohols were prepared according to the literature.² Merck silica gel G/GF254 plates were utilized for analytical thin-layer chromatography (TLC). Rankem silica gel (60–120 mesh) was employed for column chromatography. Bruker Avance III 600 and 400 MHz spectrometers were used for recording NMR spectra utilizing CDCl_3 and $\text{DMSO}-d_6$ as the solvent and tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts (δ) and spin–spin coupling constant (J) are reported in parts per million and hertz (Hz), respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet and br s = broad singlet. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. IR spectra were collected on a PerkinElmer Fourier transform infrared (FT-IR) spectrometer. Quadrupole time-of-flight electrospray ionization (ESI) mass spectrometry instrument (model HAB 273) was used for mass spectra. Single-crystal X-ray data were collected on a Bruker SMART APEX II equipped with a charge-coupled device area detector MoK α radiation, and the structure was solved by direct method using SHELXL-16 (Göttingen, Germany).

Crystal Data and Structure Refinement for 5d

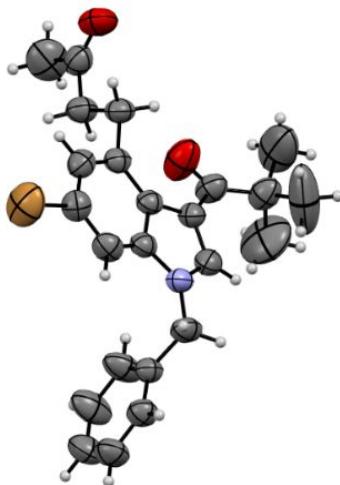
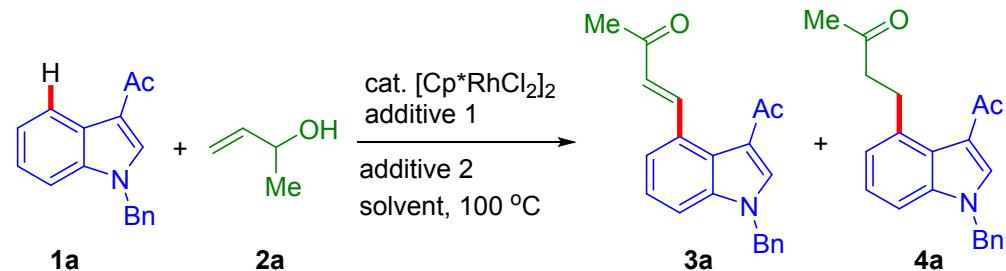


Figure S1. ORTEP diagram of methyl 4-(1-benzyl-6-bromo-3-pivaloyl-1*H*-indol-4-yl)butan-2-one **5d** with 50% ellipsoid (CCDC 1959139).

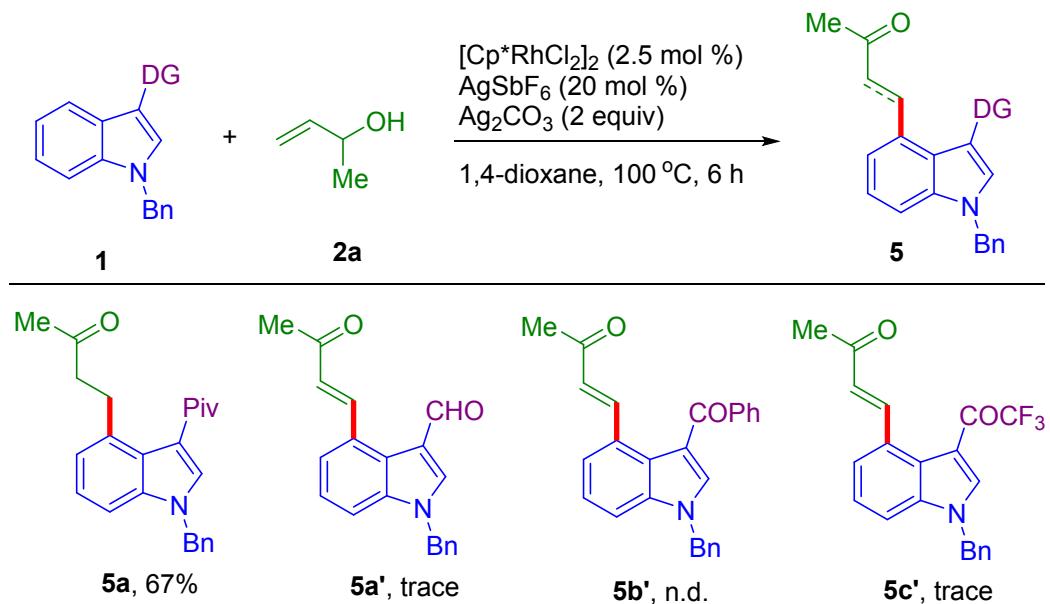
Identification code	5d
Empirical formula	C ₂₄ H ₂₆ BrNO ₂
Solvent for crystal growth	Ethyl acetate
Formula weight	440.36
Crystal habit, colour	block /colorless
Temperature, <i>T</i> /K	296 K
Wavelength, $\lambda/\text{\AA}$	0.71073
Crystal system	monoclinic
Space group	'P 21/c'
Unit cell dimensions	$a = 20.911(3) \text{ \AA}$ $b = 10.7246(13) \text{ \AA}$ $c = 10.0860(12) \text{ \AA}$ $\alpha = 90$ $\beta = 102.188(4)$ $\gamma = 90$
Volume, <i>V</i> /\AA ³	2211.0(5)
<i>Z</i>	4
Calculated density, Mg·m ⁻³	1.323
Absorption coefficient, μ/mm^{-1}	1.877
<i>F</i> (000)	996
θ range for data collection	2.14 to 17.10°
Limiting indices	-25 ≤ <i>h</i> ≤ 25, -13 ≤ <i>k</i> ≤ 13, -12 ≤ <i>l</i> ≤ 12
Reflection collected / unique	4198/1880
Completeness to θ	99.80% ($\theta = 25.96^\circ$)
Absorption correction	multi-scan
Refinement method	'SHELXL-2014/7 (Sheldrick, 2014)'
Data / restraints / parameters	4198/0/ 258
Goodness-of-fit on <i>F</i> ²	0.958
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	<i>R</i> 1 = 0.1564, <i>wR</i> 2 = 0.1987
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0558, <i>wR</i> 2 = 0.1437

Table S1. Optimization of the Reaction Conditions^a

Entry	Additive 1	Additive 2	Solvent	Yield ^b	
				3a	4a
1	AgSbF_6	Cu(OAc)_2	$(\text{CH}_2\text{Cl})_2$	17	trace
2	AgSbF_6	Cu(OAc)_2	THF	57	12
3	AgSbF_6	Cu(OAc)_2	toluene	trace	n.d.
4	AgSbF_6	Cu(OAc)_2	CH_3CN	n.d.	n.d.
5	AgSbF_6	Cu(OAc)_2	1,4-dioxane	68	trace
6	AgOTf	Cu(OAc)_2	1,4-dioxane	61	10
7	AgBF_4	Cu(OAc)_2	1,4-dioxane	trace	n.d.
8	NaOAc	Cu(OAc)_2	1,4-dioxane	n.d.	n.d.
9	AgSbF_6	Ag_2CO_3	1,4-dioxane	74	trace
10	AgSbF_6	AgOAc	1,4-dioxane	43	trace
11	AgSbF_6	Ag_2CO_3	HFIP	41	47
12	AgSbF_6	Ag_2CO_3	TFE	23	55
13	AgSbF_6	Ag_2CO_3	${}^t\text{BuOH}$	21	59
14	AgOTf	Ag_2CO_3	${}^t\text{BuOH}$	16	61
15	AgOTf	$\text{NaOPiv}\cdot\text{H}_2\text{O}$	${}^t\text{BuOH}$	trace	69
16	AgOTf	PivOH	${}^t\text{BuOH}$	trace	61
17	AgOTf	AcOH or 1-AdCO ₂ H	${}^t\text{BuOH}$	n.d.	n.d.
18 ^c	-	Ag_2CO_3	1,4-dioxane	n.d.	n.d.
19 ^d	-	$\text{NaOPiv}\cdot\text{H}_2\text{O}$	1,4-dioxane	n.d.	n.d.
20 ^e	AgSbF_6	Ag_2CO_3	${}^t\text{BuOH}$	n.d.	n.d.
21 ^e	AgOTf	$\text{NaOPiv}\cdot\text{H}_2\text{O}$	${}^t\text{BuOH}$	n.d.	n.d.

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %), additive 1 (20 mol %), additive 2 (0.2 mmol), solvent (1.5 mL), 100 °C, 6 h, air. ^bIsolated yields. ^cWithout AgSbF_6 . ^dWithout AgOTf . ^eWithout Rh-catalyst. n.d. = not detected. Ac = acetyl.

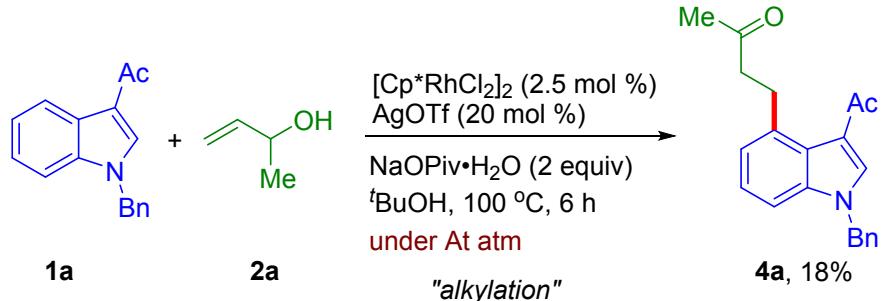
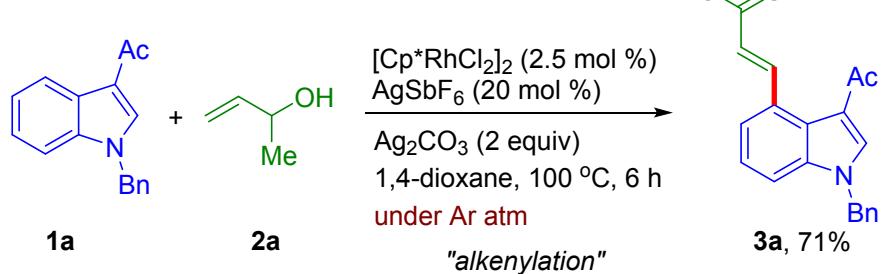
Scheme S1. Evaluation of Different Directing Groups



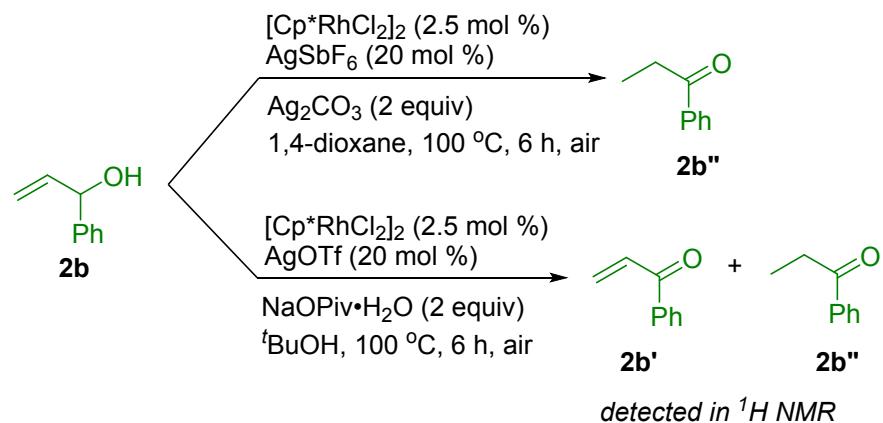
Scheme S2. Preliminary Mechanistic Investigations

Control experiments

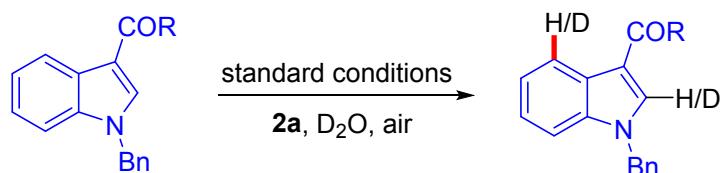
a. Reaction under N₂ atm



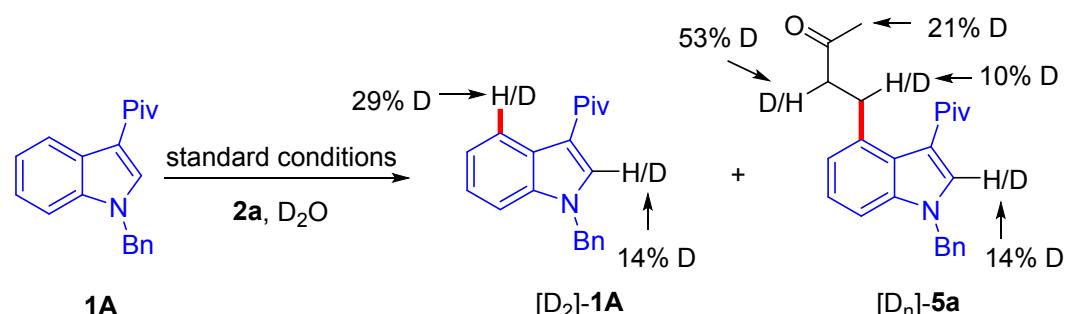
b. Enone detection



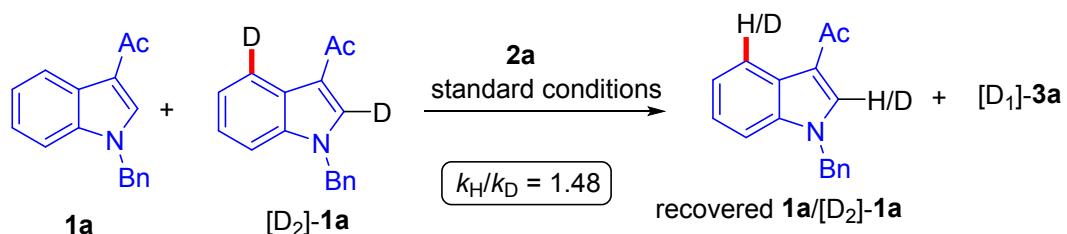
c. H/D-Exchange experiments



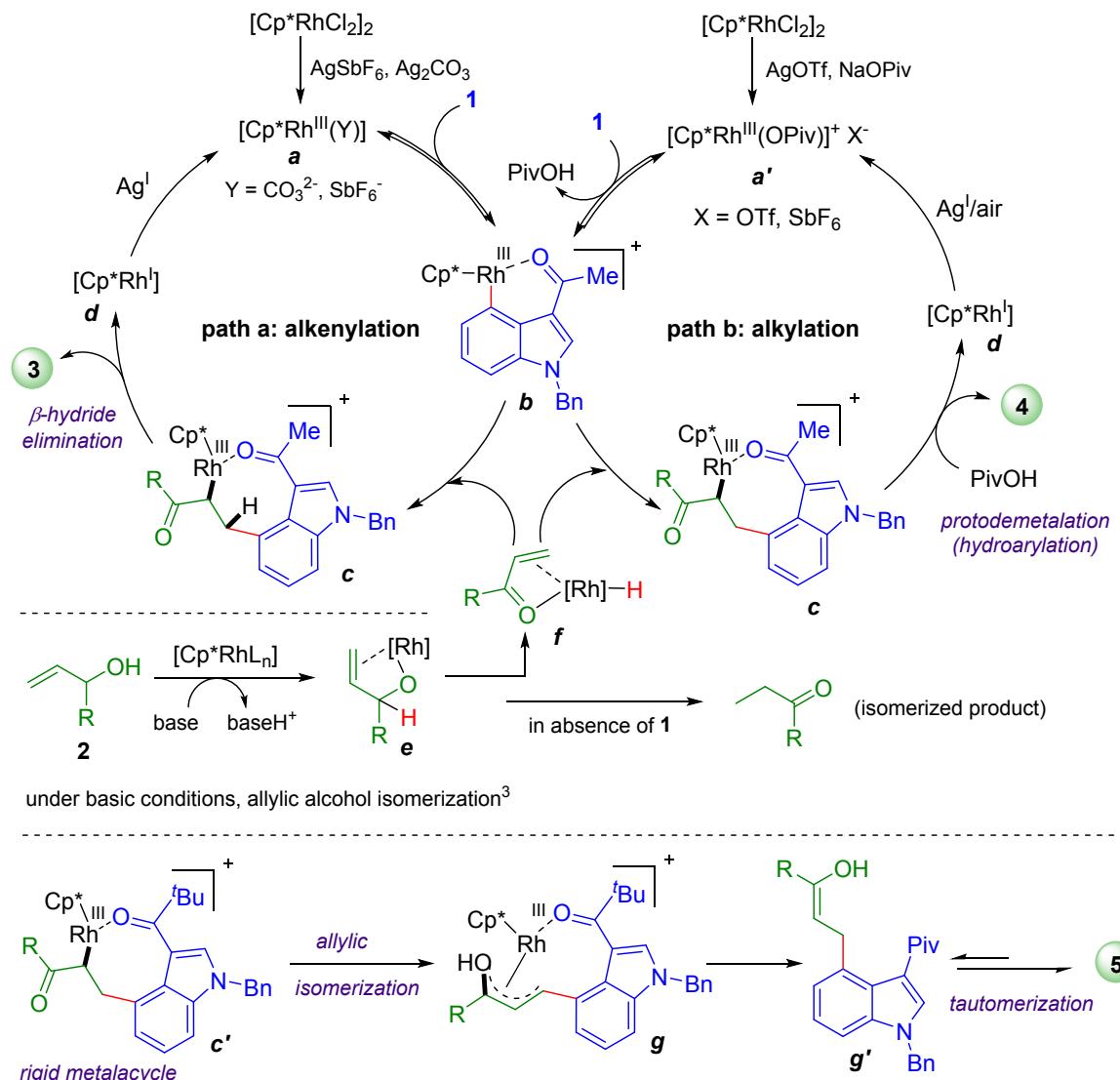
variation	R	C2-H deuteration	C4-H deuteration
none	Me 1a	16%	49%
without 2a	Me 1a	79%	80%
without 2a	t-Bu 1A	78%	76%



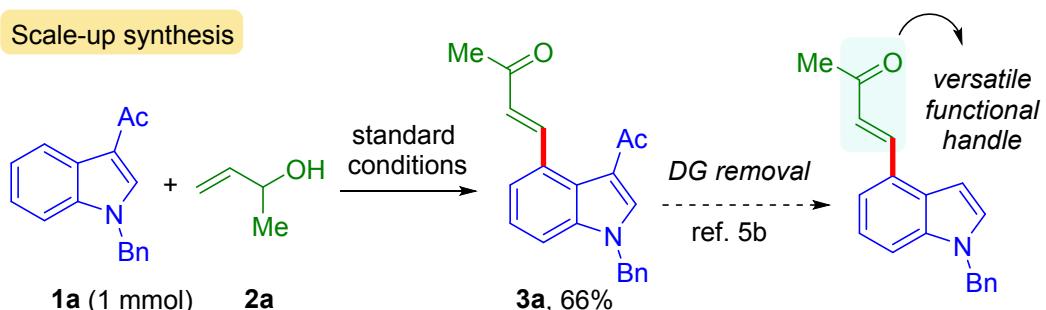
d. Kinetic isotope experiment



Scheme S3. Proposed Reaction Mechanism



Scheme S4. Synthetic Application



General Procedure for the Preparation of Indole Substrates 1. Indole substrates **1a-s** and **1A-G** were prepared according to the reported literature method.⁴

To a stirred solution of indole (2 mmol) in CH₂Cl₂ (10 mL), was added Et₂AlCl (1.5 mL, 3 mmol, 2 mol/L in hexane) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 h. Then, a solution of corresponding acid chloride (3 mmol) in CH₂Cl₂ (5 mL) was added dropwise at 0 °C. The resulting mixture was further stirred at the same temperature for an appropriate time (2-4 h). After completion, as judged by the TLC, the reaction mixture was quenched with aqueous buffer (pH 7) and extracted with CH₂Cl₂ (2 x 20 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford 3-acyl indoles. Then, to a suspension of NaH (1.05 mmol, 60% dispersion in mineral oil) in THF at 0 °C, a solution of 3-acyl indole (1 mmol) in THF (5 mL) was added dropwise. The corresponding alkyl bromide (1.1 mmol) was then added dropwise to this solution and allowed to stir at room temperature for an appropriate time. After completion, it was quenched with water and extracted by EtOAc (30 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford *N*-alkyl 3-acyl indole **1**. To show the purity of the synthesized acyl indoles [**1a-s**]^{4a, 4c} and pivaloyl indoles [**1A-G**]^{4b} NMR spectra are provided.

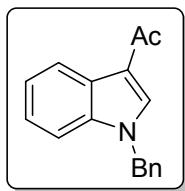
General Procedure for the Rh(III)-Catalyzed C4-Alkenylation of Indoles. A mixture of *N*-alkyl 3-acetyl indole **1** (0.1 mmol), [Cp*RhCl₂]₂ (2.5 mol %, 0.0025 mmol, 1.5 mg), AgSbF₆ (0.02 mmol, 7 mg), Ag₂CO₃ (0.2 mmol, 55 mg) and allyl alcohol **2** (0.2 mmol) in 1,4-dioxane (1.5 mL) was stirred at 100 °C in a preheated oil bath under air for 6 h. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as an eluent. The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂ (10 mL) and passed through a short pad of celite using CH₂Cl₂ (2 x 10 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford C4-alkenylated indoles **3a-z**.

General Procedure for the Rh(III)-Catalyzed C4-Alkylation of Indoles. A mixture of *N*-alkyl 3-acetyl indole **1** (0.1 mmol), [Cp*RhCl₂]₂ (2.5 mol %, 0.0025 mmol, 1.5 mg), AgOTf (0.02 mmol, 5 mg), NaOPiv•H₂O (0.2 mmol, 25 mg) and allyl alcohol **2** (0.2 mmol, 14.5 mg) in 2,2,2-trifluoroethanol (TFE) or ^tBuOH (1.5 mL) was stirred at 120 °C in a preheated oil bath under air for 12 h. The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂ (10 mL) and passed through a short pad of celite using CH₂Cl₂ (2 x 10 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford C4-alkylated indoles **4a-n**.

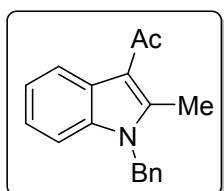
General Procedure for the Rh(III)-Catalyzed C4-Alkylation of 3-Pivaloyl Indoles. A mixture of *N*-alkyl 3-pivaloyl indole **1A-G** (0.1 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %, 0.0025 mmol, 1.5 mg), AgSbF_6 (0.02 mmol, 7 mg), Ag_2CO_3 (0.2 mmol, 55 mg) and allyl alcohol **2** (0.2 mmol) in 1,4-dioxane (1.5 mL) was stirred at 100 °C in a preheated oil bath under air for 6 h. The work up was followed as described earlier. Purification by silica gel column chromatography using *n*-hexane and ethyl acetate afforded C4-alkylated indoles **5a-h**.

Procedure for the Scale-up Synthesis of **3a.** A mixture of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (1 mmol, 249 mg), but-3-en-2-ol **2a** (2 mmol, 145 mg), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol %, 15.5 mg), AgSbF_6 (0.2 mmol, 68.8 mg) and Ag_2CO_3 (2 mmol, 550 mg) in 1,4-dioxane (10 mL) was stirred at 100 °C in a preheated oil bath under air for 6 h. Progress of the reaction was monitored by TLC using ethyl acetate and hexane as an eluent. Then the work up procedure was followed as described in the general procedure for alkenylation. Purification using hexane and ethyl acetate as an eluent (70/30, v/v) furnished **3a** in 66% (209 mg) yield.

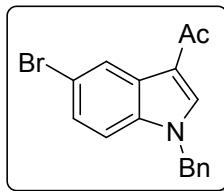
Characterization Data of Indole Substrates



1-(1-Benzyl-1*H*-indol-3-yl)ethan-1-one **1a.** Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.32-8.29 (m, 1H), 7.64 (s, 1H), 7.26-7.13 (m, 6H), 7.06-7.04 (m, 2H), 5.22 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 137.1, 135.9, 135.1, 129.1, 128.3, 127.0, 126.5, 123.5, 122.77, 122.74, 117.5, 110.2, 50.7, 27.7.

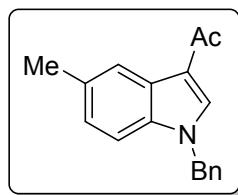


1-(1-Benzyl-2-methyl-1*H*-indol-3-yl)ethan-1-one **1b.** Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.90 (m, 1H), 7.18-7.12 (m, 5H), 7.10-7.06 (m, 1H), 6.87-6.85 (m, 2H), 5.21 (s, 2H), 2.60 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.8, 144.9, 136.5, 136.1, 129.0, 127.7, 126.5, 125.9, 122.3, 122.1, 120.8, 114.7, 110.0, 46.3, 31.8, 12.7.

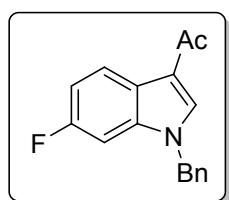


1-(1-Benzyl-5-bromo-1*H*-indol-3-yl)ethan-1-one **1c.** Light yellow solid; ^1H NMR (600 MHz, CDCl_3) δ 8.56 (d, $J = 1.8$ Hz, 1H), 7.72 (s, 1H), 7.36-7.31 (m, 4H), 7.14-7.12 (m,

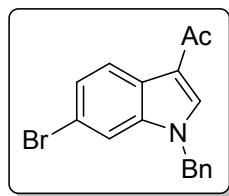
3H), 5.31 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 192.8, 135.8, 135.7, 135.4, 129.2, 128.5, 128.0, 127.0, 126.6, 125.4, 117.0, 116.5, 111.7, 51.0, 27.7.



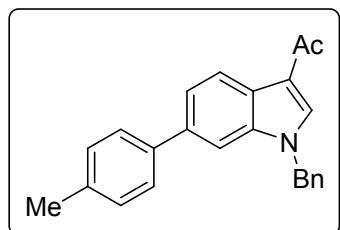
1-(1-Benzyl-5-methyl-1*H*-indol-3-yl)ethan-1-one 1d. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.23 (bs, 1H), 7.71 (s, 1H), 7.35-7.28 (m, 3H), 7.18-7.13 (m, 3H), 7.09 (dd, $J = 8.4, 1.2$ Hz, 1H), 5.29 (s, 2H), 2.50 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 136.0, 135.5, 135.2, 132.4, 129.1, 128.2, 127.0, 126.7, 125.1, 122.4, 117.1, 109.9, 50.8, 27.7, 21.6.



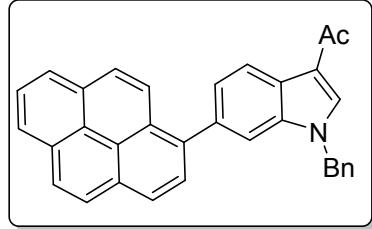
1-(1-Benzyl-6-fluoro-1*H*-indol-3-yl)ethan-1-one 1e. Colorless solid; ^1H NMR (600 MHz, CDCl_3) δ 8.39 (dd, $J = 9.0, 5.4$ Hz, 1H), 7.75 (s, 1H), 7.38-7.33 (m, 3H), 7.17 (d, $J = 6.6$ Hz, 2H), 7.07-7.03 (m, 1H), 6.97 (dd, $J = 9.0, 1.8$ Hz, 1H), 5.29 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.0, 161.7 ($J_{\text{C}-\text{F}} = 239.1$ Hz), 135.4, 129.2, 129.0, 128.5, 128.0, 127.0, 126.66, 124.0 ($J_{\text{C}-\text{F}} = 9.8$ Hz), 117.6, 111.5 ($J_{\text{C}-\text{F}} = 23.6$ Hz), 97.06 ($J_{\text{C}-\text{F}} = 26.3$ Hz), 51.0, 27.5.



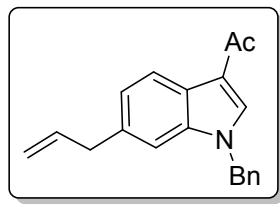
1-(1-Benzyl-6-bromo-1*H*-indol-3-yl)ethan-1-one 1f. Light yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.4$ Hz, 1H), 7.69 (s, 1H), 7.45 (d, $J = 1.6$ Hz, 1H), 7.40-7.33 (m, 4H), 7.15-7.13 (m, 2H), 5.30 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.0, 138.0, 135.37, 135.36, 129.3, 128.5, 127.0, 126.1, 125.3, 124.2, 117.6, 117.3, 113.2, 50.8, 27.7.



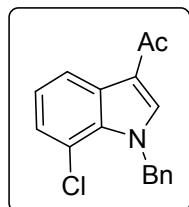
1-(1-Benzyl-6-(*p*-tolyl)-1*H*-indol-3-yl)ethan-1-one 1g. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 8.4$ Hz, 1H), 7.76 (s, 1H), 7.55 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.50-7.46 (m, 3H), 7.37-7.31 (m, 3H), 7.25-7.22 (m, 2H), 7.20-7.18 (m, 2H), 5.39 (s, 2H), 2.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.1, 138.9, 137.8, 137.1, 136.9, 135.8, 135.4, 129.6, 129.2, 128.3, 127.4, 127.1, 125.5, 122.9, 122.5, 117.6, 108.4, 50.8, 27.8, 21.2.



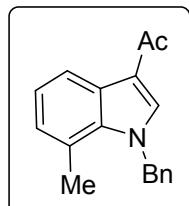
1-(1-Benzyl-6-(pyren-1-yl)-1H-indol-3-yl)ethan-1-one 1h. Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, $J = 8.0$ Hz, 1H), 8.22-8.18 (m, 2H), 8.16 (d, $J = 7.2$ Hz, 1H), 8.09-8.07 (m, 3H), 8.03-7.98 (m, 2H), 7.94 (d, $J = 9.2$ Hz, 1H), 7.87 (s, 1H), 7.61 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.55 (bs, 1H), 7.38-7.32 (m, 3H), 7.21 (dd, $J = 8.0, 2.8$ Hz, 2H), 5.41 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 193.2, 138.1, 137.3, 136.7, 135.7, 135.6, 131.6, 131.0, 130.6, 129.2, 128.7, 128.4, 128.0, 127.59, 127.56, 127.52, 127.2, 126.1, 125.9, 125.7, 125.4, 125.2, 125.1, 125.0, 124.9, 124.7, 122.5, 117.7, 112.3, 51.0, 27.9.



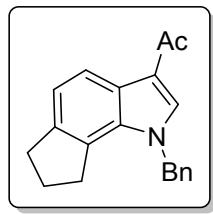
1-(6-Allyl-1-benzyl-1H-indol-3-yl)ethan-1-one 1i. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 8.2$ Hz, 1H), 7.69 (s, 1H), 7.37-7.31 (m, 3H), 7.17-7.14 (m, 3H), 7.12 (s, 1H), 6.03-5.93 (m, 1H), 5.32 (s, 2H), 5.09-5.05 (m, 2H), 3.48 (d, $J = 6.4$ Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 193.1, 137.7, 137.6, 135.9, 135.8, 134.8, 129.1, 128.2, 127.1, 124.8, 124.0, 122.5, 117.5, 115.8, 109.7, 50.6, 40.5, 27.7.



1-(1-Benzyl-7-chloro-1H-indol-3-yl)ethan-1-one 1j. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.62 (s, 1H), 7.27-7.21 (m, 3H), 7.16-7.09 (m, 2H), 6.99-6.97 (m, 2H), 5.72 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 192.9, 137.6, 137.5, 132.5, 129.4, 129.0, 128.0, 126.3, 125.5, 123.6, 121.6, 117.4, 117.0, 52.7, 27.7.

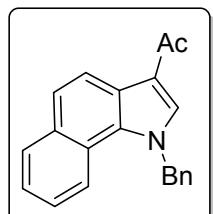


1-(1-Benzyl-7-methyl-1H-indol-3-yl)ethan-1-one 1k. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 1H), 7.36-7.30 (m, 3H), 7.23-7.19 (m, 1H), 7.01-6.96 (m, 3H), 5.62 (s, 2H), 2.53 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.1, 137.9, 137.2, 135.9, 129.2, 127.9, 127.5, 126.6, 125.5, 123.0, 121.4, 120.8, 117.2, 53.0, 27.7, 19.5.

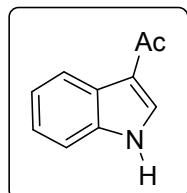


1-(1-Benzyl-1,6,7,8-tetrahydrocyclopenta[g]indol-3-yl)ethan-1-one 1l.

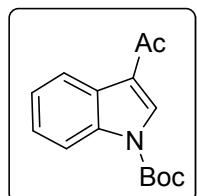
Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.0$ Hz, 1H), 7.64 (s, 1H), 7.35-7.22 (m, 3H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.03-7.01 (m, 2H), 5.48 (s, 2H), 3.07 (t, $J = 7.2$ Hz, 2H), 2.98 (t, $J = 7.2$ Hz, 2H), 2.49 (s, 3H), 2.12-2.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.1, 141.0, 137.6, 135.6, 134.7, 129.1, 127.9, 126.0, 125.5, 125.4, 120.8, 119.8, 117.7, 51.9, 32.7, 31.1, 27.6, 25.2.



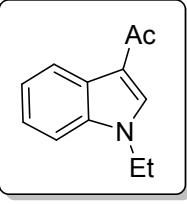
1-(1-Benzyl-1H-benzo[g]indol-3-yl)ethan-1-one 1m. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.96 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.73-7.71 (m, 2H), 7.43-7.29 (m, 5H), 7.11-7.09 (m, 2H), 5.82 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.7, 136.3, 135.3, 132.0, 130.9, 129.4, 129.3, 128.1, 126.1, 125.9, 124.5, 124.4, 124.3, 122.1, 121.6, 120.9, 117.9, 54.4, 27.9.



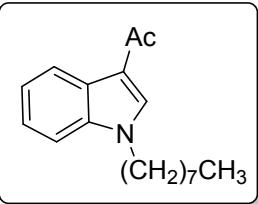
1-(1H-indol-3-yl)ethan-1-one 1n. Grey solid; ^1H NMR (400 MHz, CDCl_3) δ 8.86 (bs, 1H), 8.41-8.38 (m, 1H), 7.86 (d, $J = 3.2$ Hz, 1H), 7.43-7.40 (m, 1H), 7.31-7.28 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 193.8, 136.4, 131.7, 125.5, 123.8, 122.8, 122.5, 118.6, 111.4, 27.7.



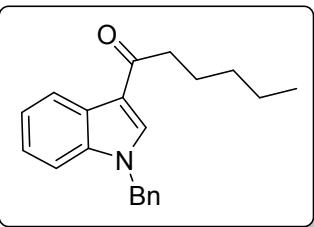
tert-Butyl 3-acetyl-1H-indole-1-carboxylate 1o. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.37-8.35 (m, 1H), 8.21 (s, 1H), 8.11 (d, $J = 7.2$ Hz, 1H), 7.39-7.32 (m, 2H), 2.56 (s, 3H), 1.71 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.0, 149.2, 135.6, 132.5, 127.4, 125.5, 124.4, 122.7, 120.7, 115.0, 85.5, 28.2, 27.8.



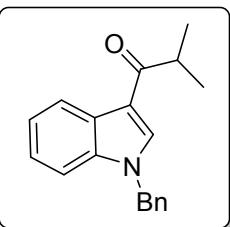
1-(1-Ethyl-1*H*-indol-3-yl)ethan-1-one 1p. Light brown liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.40-8.36 (m, 1H), 7.75 (s, 1H), 7.37-7.35 (m, 1H), 7.32-7.27 (m, 2H), 4.22-4.16 (m, 2H), 2.52 (s, 3H), 1.52 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 193.0, 136.6, 134.2, 126.4, 123.2, 122.6, 122.5, 117.0, 109.8, 41.7, 27.7, 15.2.



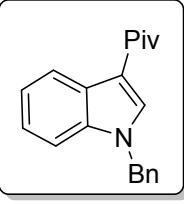
1-(1-Octyl-1*H*-indol-3-yl)ethan-1-one 1q. Light brown solid; ¹H NMR (400 MHz, CDCl₃) δ 8.39-8.35 (m, 1H), 7.74 (s, 1H), 7.38-7.33 (m, 1H), 7.32-7.28 (m, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 1.92-1.84 (m, 2H), 1.33-1.25 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 193.1, 136.9, 134.8, 126.4, 123.2, 122.7, 122.5, 117.0, 109.9, 47.2, 31.8, 30.0, 29.2, 27.8, 27.0, 22.7, 14.2.



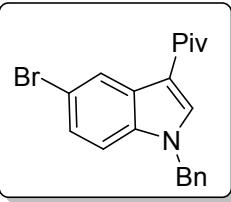
1-(1-Benzyl-1*H*-indol-3-yl)hexan-1-one 1r. Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.35-8.33 (m, 1H), 7.68 (s, 1H), 7.27-7.14 (m, 6H), 7.07 (dd, *J* = 8.0, 2.0 Hz, 2H), 5.25 (s, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 1.73-1.65 (m, 2H), 1.30-1.26 (m, 4H), 0.83-0.80 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 196.3, 137.1, 135.9, 134.6, 129.1, 128.2, 127.0, 126.6, 123.5, 122.8, 122.7, 117.2, 110.2, 50.8, 40.0, 31.8, 24.9, 22.7, 14.1.



1-(1-Benzyl-1*H*-indol-3-yl)-2-methylpropan-1-one 1s. Light yellow solid; ¹H NMR (600 MHz, CDCl₃) δ 8.47-8.46 (m, 1H), 7.82 (s, 1H), 7.38-7.31 (m, 5H), 7.29-7.27 (m, 1H), 7.18 (d, *J* = 6.6 Hz, 2H), 5.38 (s, 2H), 3.37-3.30 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 200.4, 137.2, 135.9, 134.4, 129.1, 128.3, 127.0, 126.9, 123.5, 122.9, 122.8, 115.9, 110.2, 50.8, 37.3, 19.9.

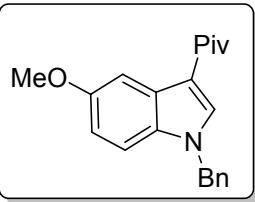


1-(1-Benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one 1A. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J = 7.2$ Hz, 1H), 7.75 (s, 1H), 7.22-7.09 (m, 6H), 7.01 (d, $J = 6.4$ Hz, 2H), 5.22 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.2, 136.1, 136.1, 133.7, 129.0, 128.5, 128.1, 126.8, 123.4, 123.4, 122.6, 113.2, 109.9, 50.6, 44.2, 29.0.



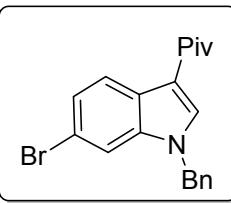
1-(1-Benzyl-5-bromo-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one 1B.

Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, $J = 2.0$ Hz, 1H), 7.83 (s, 1H), 7.36-7.29 (m, 4H), 7.11 (d, $J = 8.4$ Hz, 3H), 5.34 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.0, 135.6, 134.8, 134.3, 130.1, 129.2, 128.4, 126.7, 126.5, 126.2, 116.5, 112.9, 111.3, 51.0, 44.2, 28.9.



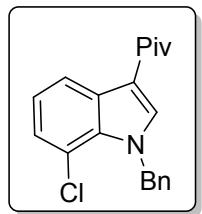
1-(1-Benzyl-5-methoxy-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one 1C.

Light brown solid; ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.4$ Hz, 1H), 7.84 (s, 1H), 7.37-7.29 (m, 3H), 7.14-7.11 (m, 3H), 6.89 (dd, $J = 8.8, 2.4$ Hz, 1H), 5.33 (s, 2H), 3.89 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.4, 156.6, 136.1, 134.0, 131.0, 129.3, 129.1, 128.2, 126.8, 114.3, 112.8, 110.8, 104.2, 55.8, 51.0, 44.2, 29.1.

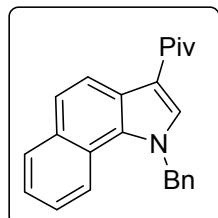


1-(1-Benzyl-6-bromo-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one 1D. Light

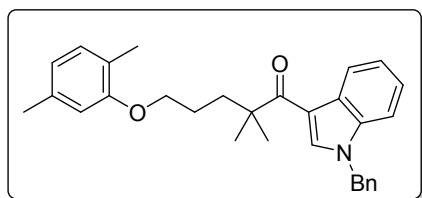
yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, $J = 8.4$ Hz, 1H), 7.80 (s, 1H), 7.42 (d, $J = 1.6$ Hz, 1H), 7.38-7.33 (m, 4H), 7.12-7.10 (m, 2H), 5.31 (s, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.1, 137.0, 135.6, 134.0, 129.2, 128.4, 127.4, 126.8, 125.9, 124.9, 117.1, 113.4, 112.9, 50.8, 44.3, 28.9.



1-(1-Benzyl-7-chloro-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one 1E. Light yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.50 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.80 (s, 1H), 7.37-7.28 (m, 3H), 7.22-7.16 (m, 2H), 7.05-7.03 (m, 2H), 5.82 (s, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.0, 137.7, 136.2, 131.5, 129.0, 127.95, 127.91, 126.2, 125.4, 123.4, 122.2, 116.9, 113.3, 52.7, 44.4, 28.9.

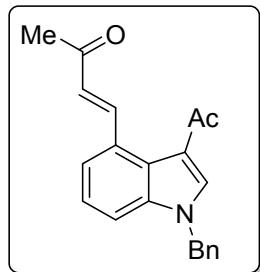


1-(1-Benzyl-1*H*-benzo[g]indol-3-yl)-2,2-dimethylpropan-1-one 1F. Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (dd, $J = 8.8, 2.0$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 9.2$ Hz, 1H), 7.85 (s, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.42-7.35 (m, 2H), 7.34-7.27 (m, 3H), 7.11 (d, $J = 6.8$ Hz, 2H), 5.84 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.8, 136.5, 133.8, 131.9, 130.0, 129.3, 129.2, 128.0, 126.5, 126.1, 125.7, 124.1, 122.1, 122.0, 120.9, 113.9, 54.3, 44.5, 29.0.

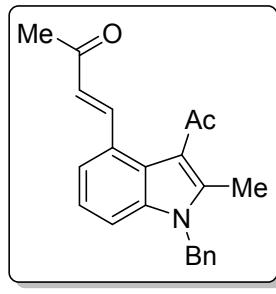


1-(1-Benzyl-1*H*-indol-3-yl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one 1G. Thick brown liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.47 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.79 (s, 1H), 7.23-7.12 (m, 6H), 7.02-7.00 (m, 2H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 6.42 (s, 1H), 5.23 (s, 2H), 3.75 (t, $J = 6.0$ Hz, 2H), 2.15 (s, 3H), 2.02 (s, 3H), 1.94-1.90 (m, 2H), 1.71-1.64 (m, 2H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.6, 157.0, 136.5, 136.14, 136.11, 133.3, 130.3, 129.1, 128.5, 128.1, 126.7, 123.55, 123.52, 123.4, 122.7, 120.7, 113.8, 111.9, 109.9, 68.1, 50.7, 47.6, 39.0, 27.0, 25.1, 21.4, 15.8.

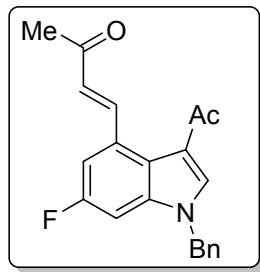
Characterization Data of the Products



(E)-4-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)but-3-en-2-one 3a. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.42$; light yellow solid; mp 165-166 °C; yield 74% (23.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.49 (d, $J = 16.4$ Hz, 1H), 7.93 (s, 1H), 7.60 (d, $J = 7.6$ Hz, 1H), 7.37-7.27 (m, 5H), 7.15-7.13 (m, 2H), 6.59 (d, $J = 16.4$ Hz, 1H), 5.39 (s, 2H), 2.58 (bs, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.9, 192.3, 147.2, 138.7, 138.4, 135.3, 130.4, 129.3, 128.6, 128.5, 126.9, 125.1, 124.1, 121.4, 118.8, 112.1, 51.0, 28.6, 26.3; FT-IR (KBr) 2925, 2853, 1667, 1650, 1524, 1440, 1395 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2$: 318.1489, found 318.1495.

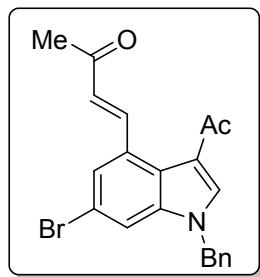


(E)-4-(3-Acetyl-1-benzyl-2-methyl-1*H*-indol-4-yl)but-3-en-2-one 3b. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.46$; colorless solid; mp 155-156 °C; yield 70% (23 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 16.0$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.32-7.26 (m, 4H), 7.24-7.20 (m, 1H), 6.98-6.96 (m, 2H), 6.67 (d, $J = 16.0$ Hz, 1H), 5.38 (s, 2H), 2.57 (s, 6H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 197.9, 144.7, 142.2, 137.3, 136.0, 129.2, 128.0, 128.0, 128.0, 125.9, 124.8, 122.9, 121.4, 118.0, 111.6, 46.9, 32.3, 27.0, 12.5; FT-IR (KBr) 2925, 1659, 1639, 1509, 1494, 1401, 1263 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2$: 332.1645, found 332.1640.



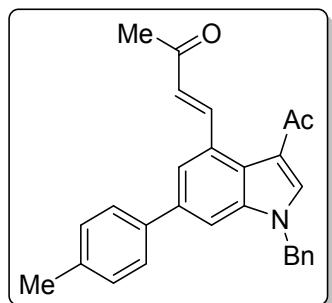
(E)-4-(3-Acetyl-1-benzyl-6-fluoro-1*H*-indol-4-yl)but-3-en-2-one 3e. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; colorless solid; mp 167-168 °C; yield 79% (26.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.41 (d, $J = 17.6$ Hz, 1H), 7.92 (s, 1H), 7.39-7.34 (m, 3H), 7.30 (dd, $J = 10.8, 2.4$ Hz, 1H), 7.14-7.12 (m, 2H), 7.00 (dd, $J = 8.4, 2.4$ Hz, 1H),

6.53 (d, $J = 16.4$ Hz, 1H), 5.33 (s, 2H), 2.573 (s, 3H), 2.571 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.5, 192.2, 161.4 ($J_{\text{C}-\text{F}} = 240.8$ Hz), 145.7, 139.0 ($J_{\text{C}-\text{F}} = 2.1$ Hz), 138.9 ($J_{\text{C}-\text{F}} = 11.9$ Hz), 134.8, 131.9 ($J_{\text{C}-\text{F}} = 9.1$ Hz), 129.5, 129.4, 128.7, 126.9, 121.7, 119.0, 109.4 ($J_{\text{C}-\text{F}} = 24.3$ Hz), 98.8 ($J_{\text{C}-\text{F}} = 26.3$ Hz), 51.2, 28.5, 26.4; ^{19}F NMR (377 MHz, CDCl_3) δ -117.28; FT-IR (KBr) 2923, 1667, 1649, 1526, 1488, 1399, 1264 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{FNO}_2$: 336.1394, found 336.1397.



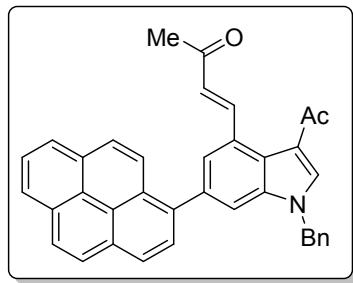
(*E*)-4-(3-Acetyl-1-benzyl-6-bromo-1*H*-indol-4-yl)but-3-en-2-one **3f**

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; grey solid; mp 170-171°C; yield 67% (26 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.33 (d, $J = 16.4$ Hz, 1H), 7.87 (s, 1H), 7.66 (d, $J = 1.6$ Hz, 1H), 7.47 (d, $J = 1.6$ Hz, 1H), 7.38-7.35 (m, 3H), 7.14-7.12 (m, 2H), 6.54 (d, $J = 16.4$ Hz, 1H), 5.34 (s, 2H), 2.563 (s, 3H), 2.561 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.2, 191.9, 145.3, 139.0, 138.6, 134.7, 131.9, 129.5, 129.3, 128.6, 126.8, 124.2, 123.8, 118.8, 117.6, 114.5, 50.9, 28.4, 26.3; FT-IR (KBr) 2924, 2852, 1710, 1638, 1528, 1470, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{BrNO}_2$: 396.0594, found 396.0595.

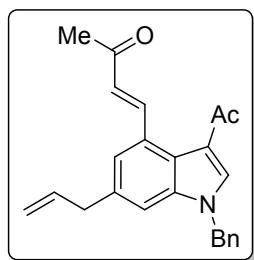


(*E*)-4-(3-Acetyl-1-benzyl-6-(*p*-tolyl)-1*H*-indol-4-yl)but-3-en-2-one

3g. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.45$; yellow solid; mp 155-156 °C; yield 72% (29 mg); ^1H NMR (600 MHz, CDCl_3) δ 9.52 (d, $J = 16.2$ Hz, 1H), 7.93 (s, 1H), 7.82 (s, 1H), 7.49-7.46 (m, 3H), 7.37-7.32 (m, 3H), 7.26-7.24 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 6.66 (d, $J = 16.2$ Hz, 1H), 5.42 (s, 2H), 2.60 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.9, 192.3, 147.2, 139.1, 138.9, 137.7, 137.5, 135.3, 130.9, 130.6, 129.7, 129.3, 128.9, 128.6, 127.2, 126.9, 124.1, 120.9, 118.7, 110.1, 51.0, 28.5, 26.3, 21.2; FT-IR (KBr) 2925, 2854, 1651, 1636, 1520, 1399, 1264 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_2$: 408.1958, found 408.1962.

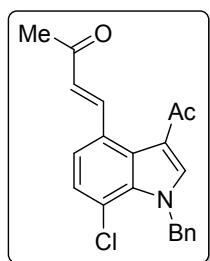


(E)-4-(3-Acetyl-1-benzyl-6-(pyren-1-yl)-1H-indol-4-yl)but-3-en-2-one 3h. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.45$; light yellow liquid; yield 61% (31.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.59 (d, $J = 16.4$ Hz, 1H), 8.23-8.20 (m, 2H), 8.17 (d, $J = 7.2$ Hz, 1H), 8.10 (s, 2H), 8.04 (s, 1H), 8.02-7.98 (m, 2H), 7.98-7.92 (m, 2H), 7.896-7.894 (m, 1H), 7.595-7.592 (m, 1H), 7.39-7.37 (m, 3H), 7.20-7.18 (m, 2H), 6.65 (d, $J = 16.4$ Hz, 1H), 5.44 (s, 2H), 2.66 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.7, 192.3, 146.9, 139.0, 138.6, 137.2, 136.8, 135.2, 131.6, 131.0, 131.0, 130.9, 130.4, 129.4, 129.0, 128.68, 128.65, 128.0, 127.8, 127.7, 127.5, 127.1, 126.2, 125.4, 125.1, 125.0, 124.9, 124.8, 124.8, 124.3, 118.9, 114.2, 51.3, 28.6, 26.4; FT-IR (neat) 2927, 1644, 1638, 1400, 1262 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{37}\text{H}_{28}\text{NO}_2$: 518.2115, found 518.2119.



(E)-4-(3-Acetyl-6-allyl-1-benzyl-1H-indol-4-yl)but-3-en-2-one 3i.

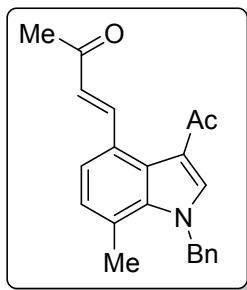
Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; colorless solid; mp 135-136 °C; yield 69% (24.6 mg); ^1H NMR (600 MHz, CDCl_3) δ 9.48 (d, $J = 16.2$ Hz, 1H), 7.86 (s, 1H), 7.44 (s, 1H), 7.38-7.33 (m, 3H), 7.15-7.13 (m, 3H), 6.58 (d, $J = 16.8$ Hz, 1H), 5.97-5.90 (m, 1H), 5.36 (s, 2H), 5.09-5.08 (m, 1H), 5.07-5.06 (m, 1H), 3.47 (d, $J = 6.6$ Hz, 2H), 2.58 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.9, 192.2, 147.2, 138.9, 138.4, 137.0, 136.4, 135.4, 130.2, 129.3, 128.7, 128.5, 127.0, 123.5, 122.5, 118.8, 116.5, 111.8, 50.8, 40.2, 28.5, 26.2; FT-IR (KBr) 2927, 1648, 1638, 1524, 1399, 1265 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_2$: 358.1802, found 358.1801.



(E)-4-(3-Acetyl-1-benzyl-7-chloro-1H-indol-4-yl)but-3-en-2-one 3j. Analytical

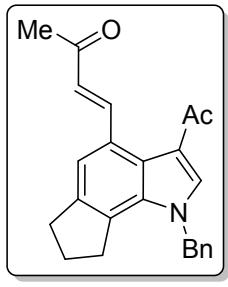
TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; light grey liquid; yield 71% (25 mg); ^1H NMR

(400 MHz, CDCl₃) δ 9.27 (d, *J* = 16.4 Hz, 1H), 7.87 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.36-7.30 (m, 3H), 7.27-7.25 (m, 1H), 7.04-7.01 (m, 2H), 6.53 (d, *J* = 16.4 Hz, 1H), 5.86 (s, 2H), 2.57 (s, 3H), 2.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.5, 192.2, 146.0, 141.1, 137.0, 133.6, 129.4, 129.2, 128.8, 128.2, 127.7, 126.3, 126.2, 122.2, 119.1, 118.8, 53.3, 28.9, 26.4; FT-IR (neat) 2961, 2853, 1710, 1658, 1638, 1590, 1388 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₁H₁₉ClNO₂: 352.1099, found 352.1098.



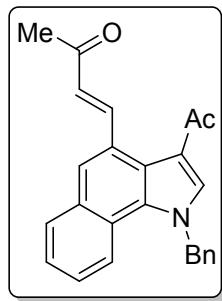
(E)-4-(3-Acetyl-1-benzyl-7-methyl-1*H*-indol-4-yl)but-3-en-2-one 3k.

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; light yellow liquid; yield 74% (25 mg); ¹H NMR (400 MHz, CDCl₃) δ 9.40 (d, *J* = 16.4 Hz, 1H), 7.87 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.35-7.28 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93-6.91 (m, 2H), 6.56 (d, *J* = 16.4 Hz, 1H), 5.66 (s, 2H), 2.58 (s, 3H), 2.57 (s, 3H), 2.54 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 200.9, 192.4, 147.2, 140.8, 137.5, 137.1, 129.4, 128.5, 128.2, 127.9, 127.6, 126.1, 125.4, 123.8, 121.8, 118.6, 53.4, 28.8, 26.3, 19.9; FT-IR (neat) 2931, 1650, 1637, 1588, 1532, 1400, 1260 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₂₂NO₂: 332.1645, found 332.1650.



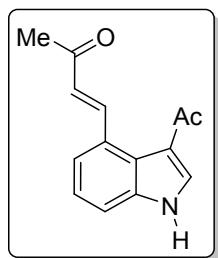
(E)-4-(3-Acetyl-1-benzyl-1,6,7,8-tetrahydrocyclopenta[g]indol-4-yl)but-3-en-2-one 3l.

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; yellow solid; mp 152-153 °C; yield 66% (23.6 mg); ¹H NMR (600 MHz, CDCl₃) δ 9.48 (d, *J* = 16.8 Hz, 1H), 7.83 (s, 1H), 7.51 (s, 1H), 7.35-7.29 (m, 3H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 16.2 Hz, 1H), 5.54 (s, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.577 (s, 3H), 2.570 (s, 3H), 2.10 (p, *J* = 7.2 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 201.0, 192.4, 147.6, 142.0, 139.3, 137.2, 135.8, 129.3, 128.7, 128.3, 128.2, 127.7, 125.7, 124.4, 119.0, 118.3, 52.2, 32.5, 31.6, 28.7, 26.3, 25.3; FT-IR (KBr) 2926, 1648, 1639, 1596, 1529, 1400, 1261 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₄H₂₄NO₂: 358.1802, found 358.1805.

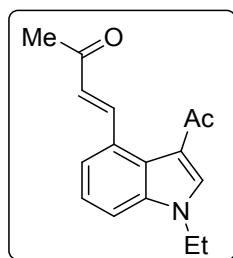


(E)-4-(3-Acetyl-1-benzyl-1*H*-benzo[*g*]indol-4-yl)but-3-en-2-one 3m.

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.45$; light yellow liquid; yield 64% (23 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.26 (d, $J = 16.4$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.95-7.93 (m, 2H), 7.90 (s, 1H), 7.46-7.41 (m, 1H), 7.39-7.37 (m, 1H), 7.35-7.29 (m, 3H), 7.11-7.09 (m, 2H), 6.68 (d, $J = 16.4$ Hz, 1H), 5.90 (s, 2H), 2.63 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.6, 193.0, 147.4, 138.1, 135.9, 132.4, 131.7, 129.9, 129.53, 129.50, 128.9, 128.4, 127.1, 126.1, 125.2, 123.5, 122.5, 122.3, 121.0, 119.4, 54.8, 28.9, 26.4; FT-IR (neat) 1582, 1655, 1638, 1529, 1400, 1261 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{25}\text{H}_{22}\text{NO}_2$: 368.1645, found 368.1644.

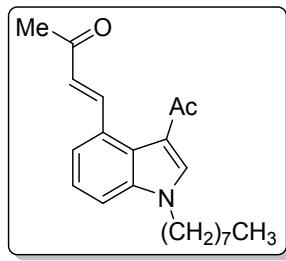


(E)-4-(3-Acetyl-1*H*-indol-4-yl)but-3-en-2-one 3n. Analytical TLC on silica gel, 1:1 ethyl acetate/hexane $R_f = 0.48$; colorless solid; mp 147-148 °C; yield 67% (15.2 mg); ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 12.3 (s, 1H), 9.51 (d, $J = 16.2$ Hz, 1H), 8.56 (s, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 7.8$ Hz, 1H), 6.57 (d, $J = 16.2$ Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 199.2, 192.9, 147.2, 138.8, 138.6, 128.7, 127.2, 124.4, 123.7, 120.7, 118.5, 114.9, 28.8, 26.7; FT-IR (KBr) 2923, 2256, 2129, 1643, 1625, 1504, 1400 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_2$: 228.1019, found 228.1013.



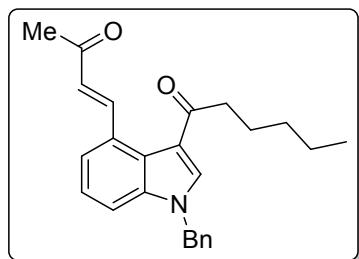
(E)-4-(3-Acetyl-1-ethyl-1*H*-indol-4-yl)but-3-en-2-one 3p. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.47$; brown thick liquid; yield 69% (18 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.50 (d, $J = 16.4$ Hz, 1H), 7.92 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.34-7.30 (m, 1H), 6.57 (d, $J = 16.4$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.58 (s, 3H), 2.57 (s, 3H), 1.54 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 192.1, 147.3, 137.9, 137.7,

130.3, 128.4, 125.1, 123.8, 121.2, 118.3, 111.6, 42.0, 28.5, 26.3, 15.1; FT-IR (neat) 2930, 1663, 1637, 1524, 1399 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₆H₁₈NO₂: 256.1332, found 256.1332.



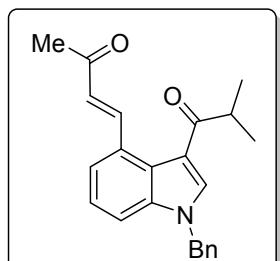
(E)-4-(3-Acetyl-1-octyl-1*H*-indol-4-yl)but-3-en-2-one 3q. Analytical

TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.47; brown thick liquid; yield 74% (25 mg); ¹H NMR (400 MHz, CDCl₃) δ 9.50 (d, *J* = 16.4 Hz, 1H), 7.89 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 16.4 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 2.58 (s, 3H), 2.57 (s, 3H), 1.89-1.84 (m, 2H), 1.33-1.24 (m, 10H), 0.86 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 192.1, 147.3, 138.4, 138.1, 130.3, 128.5, 125.0, 123.8, 121.2, 118.2, 111.8, 47.4, 31.8, 29.85, 29.82, 29.2, 28.5, 26.9, 26.2, 22.7, 14.1; FT-IR (neat) 2917, 2850, 1521, 1638, 1395 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₃₀NO₂: 340.2271, found 340.2273.



(E)-1-(1-Benzyl-4-(3-oxobut-1-en-1-yl)-1*H*-indol-3-yl)hexan-1-

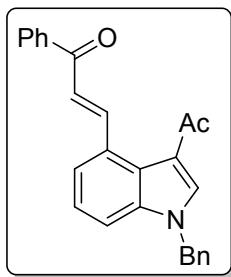
one 3r. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; yellow thick liquid; yield 73% (27.6 mg); ¹H NMR (400 MHz, CDCl₃) δ 9.40 (d, *J* = 16.4 Hz, 1H), 7.92 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.37-7.32 (m, 4H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.14-7.12 (m, 2H), 6.58 (d, *J* = 16.4 Hz, 1H), 5.39 (s, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 1.81-1.73 (m, 2H), 1.38-1.33 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 195.6, 147.0, 138.3, 137.6, 135.4, 130.4, 129.2, 128.6, 128.5, 126.9, 125.2, 124.0, 121.3, 118.6, 112.1, 51.0, 40.9, 31.8, 26.3, 25.7, 22.6, 14.1; FT-IR (neat) 2926, 2855, 1664, 1651, 1638, 1399 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₅H₂₈NO₂: 374.2115, found 374.2115.



(E)-4-(1-Benzyl-3-isobutyryl-1*H*-indol-4-yl)but-3-en-2-one 3s. Analytical

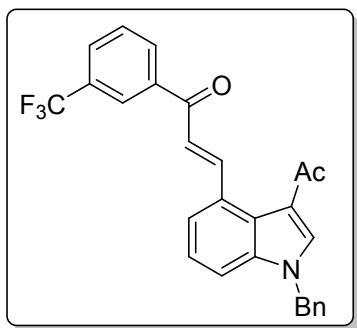
TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 145-146 °C; yield 78%

(27 mg); ^1H NMR (600 MHz, CDCl_3) δ 9.31 (d, $J = 16.2$ Hz, 1H), 7.93 (s, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.36-7.31 (m, 4H), 7.27 (t, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 6.6$ Hz, 2H), 6.57 (d, $J = 16.2$ Hz, 1H), 5.39 (s, 2H), 3.39-3.32 (m, 1H), 2.56 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.8, 199.7, 146.9, 138.4, 137.0, 135.5, 130.4, 129.2, 128.5, 128.4, 126.8, 125.5, 124.0, 121.3, 117.6, 112.1, 51.0, 38.0, 26.3, 20.2; FT-IR (neat) 2969, 2928, 1646, 1601, 1522, 1391 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2$: 346.1802, found 346.1805.



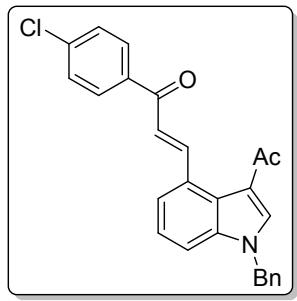
(E)-3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-phenylprop-2-en-1-one **3t.**

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; brown thick liquid; yield 64% (24 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.30 (d, $J = 15.6$ Hz, 1H), 8.09-8.06 (m, 2H), 7.86 (s, 1H), 7.67-7.65 (m, 1H), 7.58-7.54 (m, 1H), 7.51-7.47 (m, 2H), 7.35-7.28 (m, 6H), 7.15-7.13 (m, 2H), 5.38 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 191.7, 147.3, 138.7, 138.4, 137.5, 135.5, 132.3, 131.2, 129.2, 128.9, 128.53, 128.51, 127.0, 125.1, 123.9, 123.4, 121.7, 119.2, 112.0, 51.0, 28.4; FT-IR (neat) 2927, 2853, 1654, 1523, 1398 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_2$: 380.1645, found 380.1648.



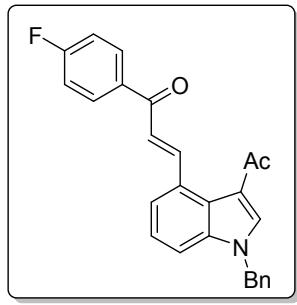
(E)-3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(3-trifluoromethylphenyl)prop-2-en-1-one **3u.**

Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.43$; yellow thick liquid; yield 58% (26 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.37 (d, $J = 16.0$ Hz, 1H), 8.29-8.25 (m, 2H), 7.88 (s, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.68-7.62 (m, 2H), 7.38-7.32 (m, 5H), 7.30-7.29 (m, 1H), 7.15-7.13 (m, 2H), 5.39 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 191.0, 148.8, 139.2, 138.4, 137.8, 135.4, 132.2, 130.7, 130.1, 129.3, 129.1, 128.8 ($J_{\text{C}-\text{F}} = 3.7$ Hz), 128.5, 126.9, 125.8 ($J_{\text{C}-\text{F}} = 3.0$ Hz), 125.2, 123.9, 123.0, 121.8, 119.1, 112.4, 51.0, 28.3; ^{19}F NMR (377 MHz, CDCl_3) δ -62.60; FT-IR (neat) 2849, 1654, 1590, 1523, 1400, 1332 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{F}_3\text{NO}_2$: 448.1519, found 448.1521.



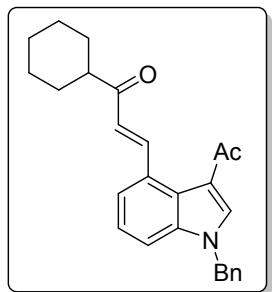
(E)-3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(4-chlorophenyl)prop-2-en-1-one 3v.

1-one 3v. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.45$; yellow thick liquid; yield 63% (26 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.30 (d, $J = 15.6$ Hz, 1H), 8.05-8.01 (m, 2H), 7.87 (s, 1H), 7.66 (d, $J = 6.8$ Hz, 1H), 7.48-7.46 (m, 2H), 7.36-7.32 (m, 3H), 7.30-7.24 (m, 3H), 7.15-7.12 (m, 2H), 5.39 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 190.7, 147.9, 138.7, 138.4, 137.7, 136.9, 135.4, 131.0, 130.4, 129.3, 128.8, 128.5, 127.0, 125.2, 123.9, 123.1, 121.8, 119.2, 112.1, 51.0, 28.4; FT-IR (neat) 1654, 1591, 1565, 1523, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{ClNO}_2$: 414.1255, found 414.1262.



(E)-3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(4-fluorophenyl)prop-2-en-1-one 3w.

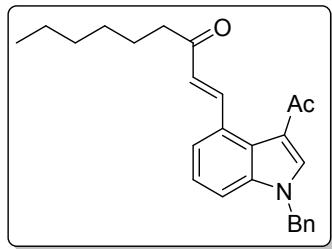
1-one 3w. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane $R_f = 0.45$; light yellow liquid; yield 51% (21.4 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.30 (d, $J = 15.6$ Hz, 1H), 8.13-8.09 (m, 2H), 7.88 (s, 1H), 7.66 (d, $J = 7.2$ Hz, 1H), 7.36-7.32 (m, 5H), 7.303-7.300 (m, 1H), 7.189-7.184 (m, 1H), 7.16-7.13 (m, 3H), 5.39 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 191.9, 190.4, 166.3 ($J_{\text{C}-\text{F}} = 251.5$ Hz), 147.6, 138.4, 137.7, 135.4, 134.9 ($J_{\text{C}-\text{F}} = 2.8$ Hz), 131.5 ($J_{\text{C}-\text{F}} = 9.0$ Hz), 131.0, 129.2, 128.5, 126.9, 125.1, 123.9, 123.1, 121.7, 119.1, 115.6 ($J_{\text{C}-\text{F}} = 21.6$ Hz), 112.1, 51.0, 28.4; FT-IR (neat) 3017, 2853, 1654, 1598, 1524, 1400 cm^{-1} ; HRMS (ESI) m/z [M+Na] $^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{FNNaO}_2$: 420.1370, found 420.1358.



(E)-3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-cyclohexylprop-2-en-1-one 3x.

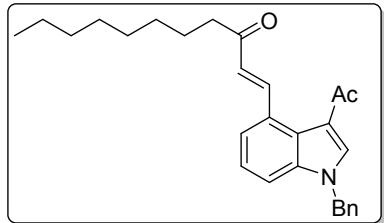
Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.45$; colorless solid; mp 134-135 °C;

yield 53% (20.4 mg); ^1H NMR (600 MHz, CDCl_3) δ 9.40 (d, $J = 16.2$ Hz, 1H), 7.90 (s, 1H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.36-7.30 (m, 4H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 2H), 6.58 (d, $J = 16.2$ Hz, 1H), 5.38 (s, 2H), 3.23-3.19 (m, 1H), 2.57 (s, 3H), 1.96-1.95 (m, 2H), 1.84-1.82 (m, 2H), 1.76-1.72 (m, 1H), 1.63-1.62 (m, 2H), 1.53-1.46 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 205.7, 192.1, 145.0, 138.4, 138.1, 135.4, 130.7, 129.2, 128.5, 126.9, 126.7, 125.1, 124.0, 121.3, 119.0, 111.9, 51.0, 46.7, 29.6, 28.6, 26.2, 26.0; FT-IR (KBr) 2930, 2853, 1650, 1598, 1523, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_2$: 386.2115, found 386.2112.



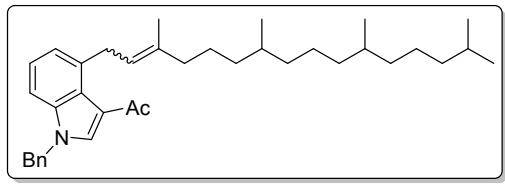
(E)-1-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)non-1-en-3-one **3y.**

Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.44$; light yellow liquid; yield 65% (25 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.42 (d, $J = 16.4$ Hz, 1H), 7.90 (s, 1H), 7.59 (d, $J = 6.4$ Hz, 1H), 7.35-7.28 (m, 5H), 7.15-7.13 (m, 2H), 6.58 (d, $J = 16.4$ Hz, 1H), 5.38 (s, 2H), 2.94 (t, $J = 7.2$ Hz, 2H), 2.57 (s, 3H), 1.77-1.69 (m, 2H), 1.45-1.38 (m, 2H), 1.35-1.31 (m, 4H), 0.90-0.87 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.0, 192.1, 145.6, 138.4, 138.3, 135.4, 130.7, 129.3, 128.5, 128.3, 126.9, 125.1, 124.1, 121.4, 119.0, 111.9, 51.0, 38.7, 31.9, 29.3, 28.5, 25.0, 22.7, 14.2; FT-IR (neat) 2925, 2853, 1714, 1650, 1602, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_2$: 388.2271, found 388.2278.

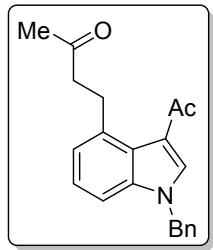


(E)-1-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)undec-1-en-3-one **3z.**

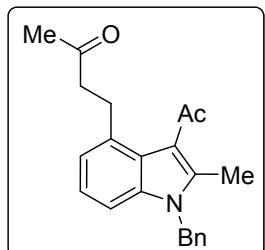
Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.44$; yellow liquid; yield 68% (28 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.42 (d, $J = 16.4$ Hz, 1H), 7.91 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.38-7.28 (m, 5H), 7.15-7.13 (m, 2H), 6.58 (d, $J = 16.4$ Hz, 1H), 5.38 (s, 2H), 2.94 (t, $J = 7.2$ Hz, 2H), 2.57 (s, 3H), 1.77-1.69 (m, 2H), 1.43-1.25 (m, 10H), 0.89-0.83 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.1, 192.1, 145.6, 138.4, 138.3, 135.4, 130.8, 129.3, 128.5, 128.4, 126.9, 124.1, 121.4, 119.0, 111.9, 100.1, 51.0, 38.7, 32.0, 29.7, 29.6, 29.3, 28.5, 25.1, 22.8, 14.2; FT-IR (neat) 2923, 2854, 1653, 1647, 1522, 1398 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{28}\text{H}_{34}\text{NO}_2$: 416.2584, found 416.2590.



1-(1-Benzyl-4-(3,7,11,15-tetramethylhexadec-2-en-1-yl)-1*H*-indol-3-yl)ethan-1-one 3aa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; light yellow liquid; yield 41% (21.6 mg); dr = 1.7:1; ^1H NMR (400 MHz, CDCl_3) δ (*E*+*Z*) 7.77-7.76 (m, 1H), 7.36-7.30 (m, 3H), 7.20-7.09 (m, 5H), 5.33 (s, 2H), 4.08 (d, $J = 7.2$ Hz, 2H), 2.53 (s, 3H), 2.15 (t, $J = 7.6$ Hz, 1H), 1.98 (t, $J = 7.6$ Hz, 1H), 1.72-1.70 (m, 3H), 1.42-1.32 (m, 5H), 1.29-1.24 (m, 6H), 1.15-1.00 (m, 8H), 0.86-0.82 (m, 13H); ^{13}C NMR (150 MHz, CDCl_3) δ (*E*+*Z*) 192.25, 192.24, 138.3, 138.2, 137.8, 137.7, 136.5, 136.4, 135.96, 135.94, 135.8, 135.6, 129.1, 128.2, 127.0, 124.7, 124.69, 124.63, 124.0, 123.97, 123.91, 123.5, 123.1, 119.4, 119.3, 107.9, 50.8, 40.3, 39.5, 37.6, 37.59, 37.58, 37.55, 37.52, 37.4, 37.3, 37.2, 37.0, 36.9, 33.9, 32.94, 32.92, 32.88, 32.86, 32.4, 28.85, 28.81, 28.1, 25.75, 25.74, 25.67, 25.66, 24.97, 24.96, 24.6, 23.7, 22.8, 22.7, 19.9, 19.88, 19.84, 19.81, 16.3; FT-IR (neat) 3017, 2925, 2857, 1655, 1525, 1400, 1259 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{37}\text{H}_{54}\text{NO}$: 528.4200, found 528.4206.

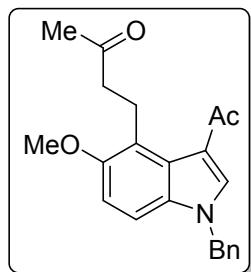


4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)butan-2-one 4a. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.41$; thick brown liquid; yield 69% (22 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.37-7.29 (m, 3H), 7.19-7.14 (m, 4H), 7.09 (dd, $J = 6.4, 1.6$ Hz, 1H), 5.33 (s, 2H), 3.55 (t, $J = 7.6$ Hz, 2H), 2.79 (t, $J = 8.0$ Hz, 2H), 2.53 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.6, 192.0, 138.4, 137.1, 137.0, 135.7, 129.2, 128.3, 127.0, 124.4, 124.4, 124.0, 118.7, 108.4, 50.8, 46.9, 30.9, 30.1, 28.6.; FT-IR (neat) 2923, 2851, 1706, 1658, 1521, 1400 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_2$: 320.1645, found 320.1641.

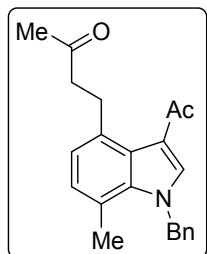


4-(3-Acetyl-1-benzyl-2-methyl-1*H*-indol-4-yl)butan-2-one 4b. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.45$; yellow liquid; yield 53% (17.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.27 (m, 3H), 7.14-7.09 (m, 2H), 7.03-6.97 (m, 3H), 5.34 (s, 2H), 3.23 (t, $J = 7.6$ Hz, 2H), 2.78 (t, $J = 8.0$ Hz, 2H), 2.62 (s, 3H), 2.53 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (150

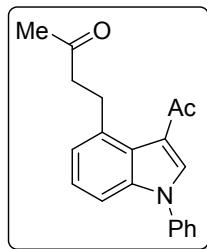
MHz, CDCl₃) δ 209.0, 198.8, 139.4, 137.3, 136.4, 134.3, 129.1, 127.8, 126.0, 124.0, 123.1, 122.9, 118.2, 107.9, 46.8, 45.2, 32.6, 30.0, 29.1, 12.6; FT-IR (neat) 2926, 2854, 2090, 1710, 1637, 1400 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₂₄NO₂: 334.1802, found 334.1810.



4-(3-Acetyl-1-benzyl-5-methoxy-1H-indol-4-yl)butan-2-one 4d. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; colorless solid; mp 115-116 °C; yield 66% (23 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.36-7.30 (m, 3H), 7.15-7.13 (m, 2H), 7.09 (d, *J* = 9.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.29 (s, 2H), 3.82 (s, 3H), 3.54 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.50 (s, 3H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 191.8, 153.8, 138.0, 135.8, 133.5, 129.1, 128.3, 127.0, 126.2, 124.2, 118.6, 109.8, 108.4, 57.1, 50.9, 45.3, 29.8, 28.6, 23.4; FT-IR (KBr) 2925, 2853, 1709, 1658, 1526, 1399 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₂₄NO₃: 350.1751, found 350.1755.

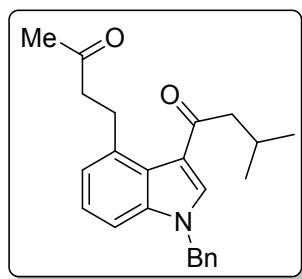


4-(3-Acetyl-1-benzyl-7-methyl-1H-indol-4-yl)butan-2-one 4e. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; light yellow solid; mp 110-111 °C; yield 63% (21 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 1H), 7.34-7.32 (m, 1H), 7.30-7.28 (m, 2H), 6.98-6.94 (m, 2H), 6.93-6.88 (m, 2H), 5.62 (s, 2H), 3.51 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 2.49 (s, 3H), 2.18 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 209.7, 192.2, 139.2, 137.9, 137.2, 134.7, 129.2, 128.0, 127.3, 125.5, 125.4, 124.6, 119.3, 118.7, 53.2, 46.8, 30.5, 30.1, 28.8, 19.6; FT-IR (KBr) 2924, 2852, 1704, 1652, 1533, 1401 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₂₄NO₂: 334.1802, found 334.1799.



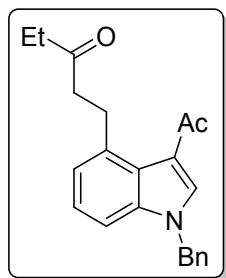
4-(3-Acetyl-1-phenyl-1H-indol-4-yl)butan-2-one 4f. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 145-146 °C; yield 64% (19.5 mg); ¹H

NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.56-7.52 (m, 2H), 7.47-7.44 (m, 3H), 7.24-7.22 (m, 1H), 7.19-7.15 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 3.54 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.5, 192.4, 138.6, 138.3, 136.99, 136.91, 130.1, 130.0, 128.4, 125.6, 124.8, 124.4, 120.0, 109.1, 46.9, 30.8, 30.1, 28.7; FT-IR (KBr) 1704, 1659, 1596, 1522, 1400 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₀H₂₀NO₂: 306.1489, found 306.1492.

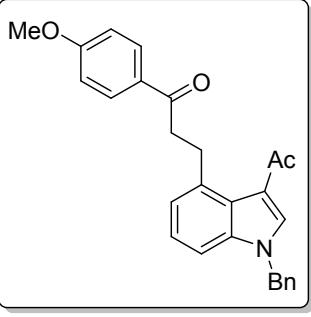


1-(1-Benzyl-4-(3-oxobutyl)-1*H*-indol-3-yl)-3-methylbutan-1-one 4g.

Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 120-121 °C; yield 69% (25 mg); ¹H NMR (600 MHz, CDCl₃) δ 7.81 (s, 1H), 7.35-7.31 (m, 3H), 7.18-7.13 (m, 4H), 7.09 (d, *J* = 6.6 Hz, 1H), 5.34 (s, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.71 (d, *J* = 7.2 Hz, 2H), 2.33-2.26 (m, 1H), 2.17 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.6, 194.9, 138.4, 137.0, 136.4, 135.8, 129.1, 128.3, 126.9, 124.5, 124.3, 123.9, 119.2, 108.4, 50.8, 49.9, 46.7, 30.8, 30.1, 26.4, 22.9; FT-IR (KBr) 2955, 2924, 2868, 1705, 1646, 1397 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₄H₂₈NO₂: 362.2115, found 362.2112.

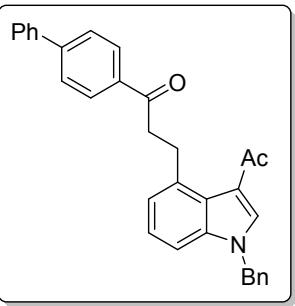


1-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)pentan-3-one 4h. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; colorless solid; mp 118-119 °C; yield 69% (23 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.37-7.31 (m, 3H), 7.19-7.14 (m, 4H), 7.10-7.08 (m, 1H), 5.34 (s, 2H), 3.55 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.52 (s, 3H), 2.47 (q, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.1, 192.0, 138.4, 137.2, 137.1, 135.7, 129.2, 128.3, 127.0, 124.54, 124.51, 124.0, 108.4, 50.9, 45.6, 36.0, 30.9, 28.6, 7.9; FT-IR (KBr) 2851, 1709, 1644, 1525, 1397 cm⁻¹; HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₂H₂₄NO₂: 334.1802, found 334.1805.



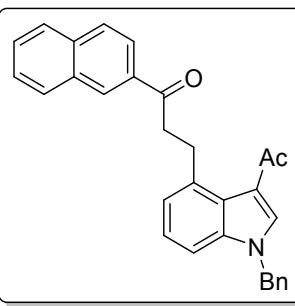
3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(4-methoxyphenyl)propan-1-one **4i**

one 4i. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.41$; brown thick liquid; yield 68% (28 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.93 (m, 2H), 7.81 (s, 1H), 7.37-7.29 (m, 3H), 7.20-7.13 (m, 5H), 6.89-6.86 (m, 2H), 5.33 (s, 2H), 3.83 (s, 3H), 3.70 (t, $J = 7.6$ Hz, 2H), 3.32 (t, $J = 7.6$ Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.9, 192.0, 163.2, 138.4, 137.5, 137.0, 135.8, 130.6, 130.5, 129.1, 128.3, 127.0, 124.7, 124.6, 124.0, 118.9, 113.5, 108.3, 55.5, 50.8, 41.5, 30.9, 28.5; FT-IR (neat) 2931, 2838, 1656, 1599, 1524, 1395, 1259, 1170 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_3$: 412.1907, found 412.1912.



1-([1,1'-Biphenyl]-4-yl)-3-(3-acetyl-1-benzyl-1*H*-indol-4-yl)propan-1-one **4j**

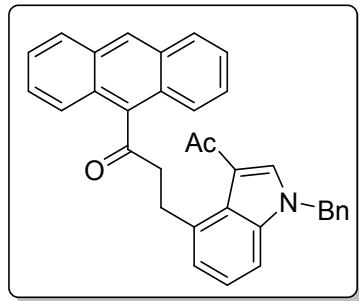
one 4j. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.41$; brown thick liquid; yield 66% (30.2 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.83 (s, 1H), 7.63-7.60 (m, 4H), 7.45 (t, $J = 7.2$ Hz, 2H), 7.38-7.31 (m, 4H), 7.19-7.15 (m, 5H), 5.35 (s, 2H), 3.74 (t, $J = 7.2$ Hz, 2H), 3.41 (t, $J = 7.8$ Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 199.9, 192.0, 145.3, 140.2, 138.4, 137.4, 137.1, 136.1, 135.7, 129.2, 129.0, 128.9, 128.3, 128.1, 127.4, 127.3, 127.1, 127.0, 124.7, 124.0, 118.8, 108.4, 50.8, 42.0, 30.8, 28.6; FT-IR (neat) 1651, 1603, 1524, 1400, 1265 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{32}\text{H}_{28}\text{NO}_2$: 458.2115, found 458.2120.



3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(naphthalen-2-yl)propan-1-one **4k**

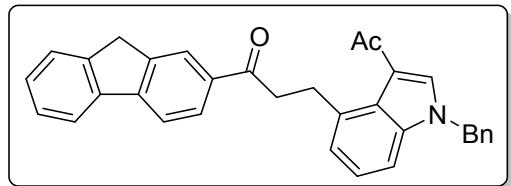
one 4k. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.46$; brown thick liquid; yield 72% (31 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.06 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.90 (d, J

= 8.0 Hz, 1H), 7.85-7.83 (m, 3H), 7.58-7.48 (m, 3H), 7.35-7.31 (m, 3H), 7.20-7.15 (m, 4H), 5.34 (s, 2H), 3.78 (t, J = 7.2 Hz, 2H), 3.52 (t, J = 7.6 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.3, 192.1, 138.4, 137.4, 137.0, 135.7, 135.5, 134.8, 132.7, 129.9, 129.6, 129.2, 128.3, 128.2, 128.2, 127.8, 127.08, 127.04, 126.5, 124.8, 124.3, 124.0, 118.9, 108.4, 50.9, 42.1, 31.0, 28.6; FT-IR (neat) 2927, 2851, 1677, 1655, 1525, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_2$: 432.1958, found 432.1964.



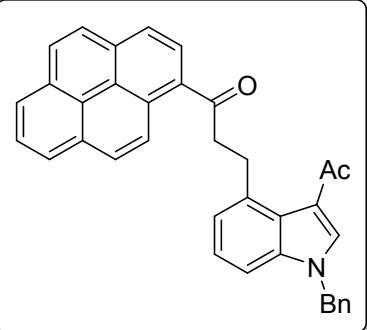
3-(3-Acetyl-1-benzyl-1H-indol-4-yl)-1-(anthracen-9-yl)propan-1-one 4l.

4l. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.43; brown thick liquid; yield 68% (32.7 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.39 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.77-7.75 (m, 3H), 7.41 (t, J = 7.2 Hz, 2H), 7.37-7.34 (m, 2H), 7.31-7.30 (m, 3H), 7.28-7.26 (m, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.11-7.10 (m, 2H), 5.31 (s, 2H), 3.99 (t, J = 7.2 Hz, 2H), 3.39 (t, J = 7.8 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 210.2, 191.9, 138.3, 137.2, 137.1, 136.8, 135.8, 131.0, 129.1, 128.5, 128.2, 127.7, 127.07, 127.04, 126.9, 126.4, 125.4, 124.9, 124.5, 124.0, 118.8, 108.5, 50.8, 49.3, 30.2, 28.6; FT-IR (neat) 2925, 1694, 1653, 1523, 1398 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{34}\text{H}_{28}\text{NO}_2$: 482.2115, found 482.2120.



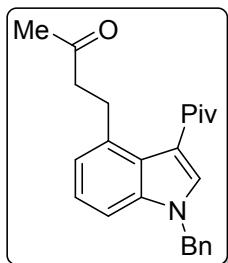
3-(3-Acetyl-1-benzyl-1H-indol-4-yl)-1-(9H-fluoren-2-yl)propan-1-one 4m.

4m. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.44; brown thick liquid; yield 65% (30 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.82-7.77 (m, 3H), 7.57 (d, J = 7.2 Hz, 1H), 7.40-7.33 (m, 5H), 7.19-7.14 (m, 5H), 5.34 (s, 2H), 3.90 (s, 2H), 3.75 (t, J = 7.2 Hz, 2H), 3.44 (t, J = 7.6 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.1, 192.0, 145.9, 144.6, 143.2, 140.8, 138.4, 137.5, 137.0, 136.0, 135.8, 129.2, 128.3, 127.8, 127.6, 127.0, 125.3, 125.0, 124.8, 124.6, 124.0, 120.8, 119.6, 118.9, 108.4, 50.9, 42.0, 37.0, 30.9, 28.6; FT-IR (neat) 2927, 1675, 1656, 1606, 1438, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{33}\text{H}_{28}\text{NO}_2$: 470.2115, found 470.2119.

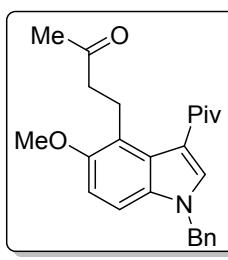


3-(3-Acetyl-1-benzyl-1*H*-indol-4-yl)-1-(pyren-1-yl)propan-1-one

4n. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.42$; brown thick liquid; yield 63% (31.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.83 (d, $J = 9.6$ Hz, 1H), 8.30 (d, $J = 8.0$ Hz, 1H), 8.22 (dd, $J = 7.6, 2.8$ Hz, 2H), 8.15-8.09 (m, 3H), 8.05-8.01 (m, 2H), 7.76 (s, 1H), 7.34-7.30 (m, 3H), 7.19-7.12 (m, 5H), 5.30 (s, 2H), 3.88 (t, $J = 7.2$ Hz, 2H), 3.59 (t, $J = 7.6$ Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.4, 192.0, 138.4, 137.2, 137.0, 135.8, 133.7, 133.4, 131.2, 130.8, 129.24, 129.22, 129.20, 129.1, 128.3, 127.2, 127.0, 126.3, 126.2, 126.0, 125.8, 125.3, 125.0, 124.7, 124.6, 124.5, 124.1, 124.0, 118.9, 108.4, 50.8, 45.7, 31.5, 28.5; FT-IR (neat) 2925, 2851, 1721, 1655, 1524, 1400 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{36}\text{H}_{28}\text{NO}_2$: 506.2115, found 506.2119.



4-(1-Benzyl-3-pivaloyl-1*H*-indol-4-yl)butan-2-one 5a. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.45$; colorless solid; mp 120-121 °C; yield 67% (24 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.35-7.27 (m, 3H), 7.18-7.12 (m, 4H), 7.03-7.01 (m, 1H), 5.32 (s, 2H), 3.20 (t, $J = 7.6$ Hz, 2H), 2.80 (t, $J = 8.0$ Hz, 2H), 2.17 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.1, 205.8, 137.0, 136.2, 135.6, 130.6, 129.0, 128.1, 126.9, 125.7, 123.4, 122.9, 115.9, 108.3, 50.6, 45.2, 44.9, 29.9, 29.0, 28.6; FT-IR (KBr) 2982, 2886, 1709, 1646, 1524, 1400 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{24}\text{H}_{28}\text{NO}_2$: 362.2115, found 362.2112.

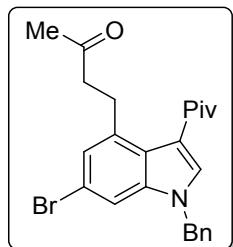


4-(1-Benzyl-5-methoxy-3-pivaloyl-1*H*-indol-4-yl)butan-2-one

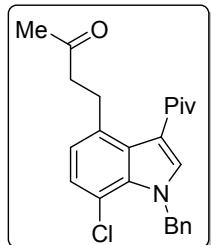
5c.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.43$; brown thick liquid; yield 69% (27 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1H), 7.35-7.28 (m, 3H), 7.14-7.12 (m, 2H), 7.08 (d, $J = 8.8$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 1H), 5.27 (s, 2H), 3.82 (s, 3H), 3.07-3.03 (m, 2H), 2.84-2.80 (m,

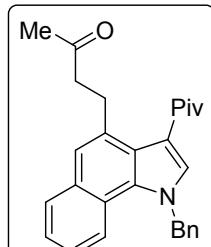
2H), 2.21 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 209.9, 206.2, 153.0, 136.4, 132.4, 131.0, 129.0, 128.1, 127.3, 126.9, 122.7, 115.9, 109.6, 108.2, 57.2, 50.7, 44.9, 43.6, 29.7, 28.5, 22.4; FT-IR (KBr) 2925, 2853, 1709, 1658, 1524, 1436, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{25}\text{H}_{30}\text{NO}_3$: 392.2220, found 392.2223.



4-(1-Benzyl-6-bromo-3-pivaloyl-1H-indol-4-yl)butan-2-one 5d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.43; colorless solid; mp 160-161 °C; yield 63% (27.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1H), 7.37-7.31 (m, 3H), 7.29 (d, J = 1.6 Hz, 1H), 7.13-7.09 (m, 3H), 5.27 (s, 2H), 3.11 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 2.17 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 205.7, 137.7, 137.5, 135.7, 130.7, 129.2, 128.3, 126.8, 125.9, 124.7, 117.0, 116.2, 111.1, 50.6, 45.0, 44.9, 29.9, 28.58, 28.51; FT-IR (KBr) 2961, 2929, 1710, 1655, 1526, 1401, 1359 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{BrNO}_2$: 440.1220, found 440.1226.

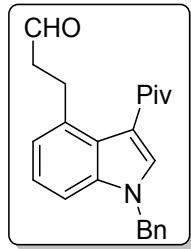


4-(1-Benzyl-7-chloro-3-pivaloyl-1H-indol-4-yl)butan-2-one 5e. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.44; colorless solid; mp 99-100 °C; yield 71% (28 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (s, 1H), 7.26-7.18 (m, 3H), 7.05 (d, J = 7.6 Hz, 1H), 6.96-6.94 (m, 2H), 6.83 (d, J = 7.6 Hz, 1H), 5.71 (s, 2H), 2.97 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 8.0 Hz, 2H), 2.08 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 208.5, 206.6, 138.0, 134.1, 132.14, 132.12, 129.0, 128.6, 127.8, 126.3, 125.2, 123.2, 116.5, 115.1, 52.6, 45.2, 44.7, 29.9, 28.2, 28.1; FT-IR (KBr) 2963, 2928, 1715, 1707, 1655, 1643, 1401 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{ClNO}_2$: 396.1725, found 396.1725.

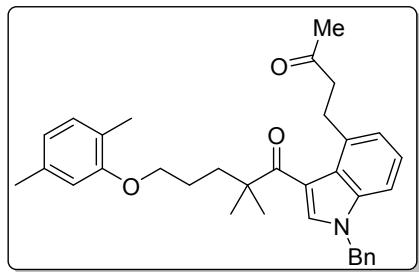


4-(1-Benzyl-3-pivaloyl-1H-benzo[g]indol-4-yl)butan-2-one 5f. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 138-139 °C; yield 65% (26.7

mg); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.8$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.45 (s, 1H), 7.39-7.38 (m, 1H), 7.36-7.33 (m, 2H), 7.32-7.26 (m, 3H), 7.11 (d, $J = 6.8$ Hz, 2H), 5.83 (s, 2H), 3.20 (t, $J = 7.2$ Hz, 2H), 2.90 (t, $J = 8.0$ Hz, 2H), 2.20 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 208.7, 208.0, 136.7, 133.8, 131.9, 130.7, 129.5, 129.3, 128.6, 128.0, 126.2, 125.3, 124.3, 123.9, 122.8, 121.1, 120.9, 117.3, 54.2, 45.3, 44.6, 30.0, 28.7, 28.3; FT-IR (KBr) 2958, 2925, 2853, 1706, 1650, 1531, 1400 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{NO}_2$: 412.2271, found 412.2270.



3-(1-Benzyl-3-pivaloyl-1H-indol-4-yl)propanal 5g. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.42$; colorless solid; mp 100-101 °C; yield 67% (23 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.81 (t, $J = 1.6$ Hz, 1H), 7.61 (s, 1H), 7.36-7.29 (m, 3H), 7.17-7.16 (m, 2H), 7.14-7.12 (m, 2H), 7.03-7.01 (m, 1H), 5.33 (s, 2H), 3.31 (t, $J = 7.2$ Hz, 2H), 2.77 (t, $J = 7.6$ Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 205.4, 202.9, 137.1, 136.2, 135.1, 131.1, 129.1, 128.2, 126.9, 125.7, 123.5, 123.0, 116.0, 108.5, 50.7, 45.1, 44.9, 28.8, 27.4; FT-IR (KBr) 2931, 2725, 1717, 1650, 1523, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_2$: 348.1958, found 348.1957.



1-(1-Benzyl-4-(3-oxobutyl)-1H-indol-3-yl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one 5h. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.43$; colorless liquid; yield 70% (35.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.33-7.27 (m, 3H), 7.18-7.10 (m, 4H), 7.04-7.02 (m, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 7.6$ Hz, 1H), 6.58 (s, 1H), 5.30 (s, 2H), 3.91 (t, $J = 6.4$ Hz, 2H), 3.22 (t, $J = 7.6$ Hz, 2H), 2.84 (t, $J = 8.0$ Hz, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H), 2.01-1.96 (m, 2H), 1.86-1.81 (m, 2H), 1.39 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 209.0, 204.7, 157.0, 137.1, 136.6, 136.2, 135.8, 130.7, 130.4, 129.0, 128.1, 126.8, 126.1, 125.8, 123.5, 123.1, 120.8, 116.3, 112.2, 108.3, 68.2, 50.6, 48.1, 45.4, 38.0, 29.9, 29.1, 26.9, 25.2, 21.4, 15.8; FT-IR (neat) 2963, 2925, 1713, 1647, 1524, 1399 cm^{-1} ; HRMS (ESI) m/z [M+H] $^+$ calcd for $\text{C}_{34}\text{H}_{40}\text{NO}_3$: 510.3003, found 510.3009.

H/D Exchange Experiment of **1a with D₂O in the Absence of **2a**.** To a stirred solution of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (0.1 mmol, 24.9 mg), [Cp*RhCl₂]₂ (2.5 mol %, 1.6 mg), AgSbF₆ (0.02 mmol, 6.9 mg) and Ag₂CO₃ (0.2 mmol, 55 mg) in 1,4-dioxane (1.5 mL), D₂O (0.4 mmol, 80 μ L) was added. The reaction mixture was stirred at 100 °C in a preheated oil bath under air for 6 h under air. The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂ (10 mL), and passed through a short pad of celite using CH₂Cl₂ (25 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to give [D₂]-**1a** in 89% (22.3 mg) yield with 80% and 79% deuterium incorporation at C4-H and C2-H, respectively, as estimated by 400 MHz ¹H NMR.

H/D Exchange Experiment of **1a with D₂O in the Presence of **2a**.** To a stirred solution of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (0.1 mmol, 24.9 mg), but-3-en-2-ol **2a** (0.2 mmol, 14.5 mg), [Cp*RhCl₂]₂ (2.5 mol %, 1.6 mg), AgSbF₆ (0.02 mmol, 6.9 mg) and Ag₂CO₃ (0.2 mmol, 55 mg) in 1,4-dioxane (1.5 mL), D₂O (0.4 mmol, 80 μ L) was added. The reaction mixture was stirred at 100 °C in a preheated oil bath under air for 4 h under air. Work up as described above was followed. Drying (Na₂SO₄) and evaporation of the solvent produced a residue, which was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to give [D₂]-**1a** and [D₁]-**3a**. The deuterium incorporation was observed as 49% at C4-H and 16% at C2-H from 400 MHz ¹H NMR analysis of recovered [D₂]-**1a**.

H/D Exchange Experiment of **1A with D₂O in the Absence of **2a**.** To a stirred solution of 1-(1-benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1A** (0.1 mmol, 29.1 mg), [Cp*RhCl₂]₂ (2.5 mol %, 1.6 mg), AgSbF₆ (0.02 mmol, 6.9 mg) and Ag₂CO₃ (0.2 mmol, 55 mg) in 1,4-dioxane (1.5 mL), D₂O (0.4 mmol, 80 μ L) was added. The reaction mixture was stirred at 100 °C in a preheated oil bath under air for 6 h under air. Work up as described above was followed. Drying (Na₂SO₄) and evaporation of the solvent produced a residue, which was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to give [D₂]-**1A** in 91% yield. The deuterium incorporation was observed as 76% at C4-H and 78% at C2-H from ¹H NMR analysis of recovered [D₂]-**1A**.

H/D Exchange Experiment of **1A with D₂O in the Presence of **2a**.** To a stirred solution of 1-(1-benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1A** (0.1 mmol, 29.1 mg), but-3-en-2-ol **2a** (0.2 mmol, 14.5 mg), [Cp*RhCl₂]₂ (2.5 mol %, 1.6 mg), AgSbF₆ (0.02 mmol, 6.9 mg) and Ag₂CO₃ (0.2 mmol, 55 mg) in 1,4-dioxane (1.5 mL), D₂O (0.4 mmol, 80 μ L) was added. The reaction mixture was stirred at 100 °C in a preheated oil bath under air for 4 h under air. Work up as described above was followed. Drying (Na₂SO₄) and evaporation of the solvent produced a residue, which was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to give

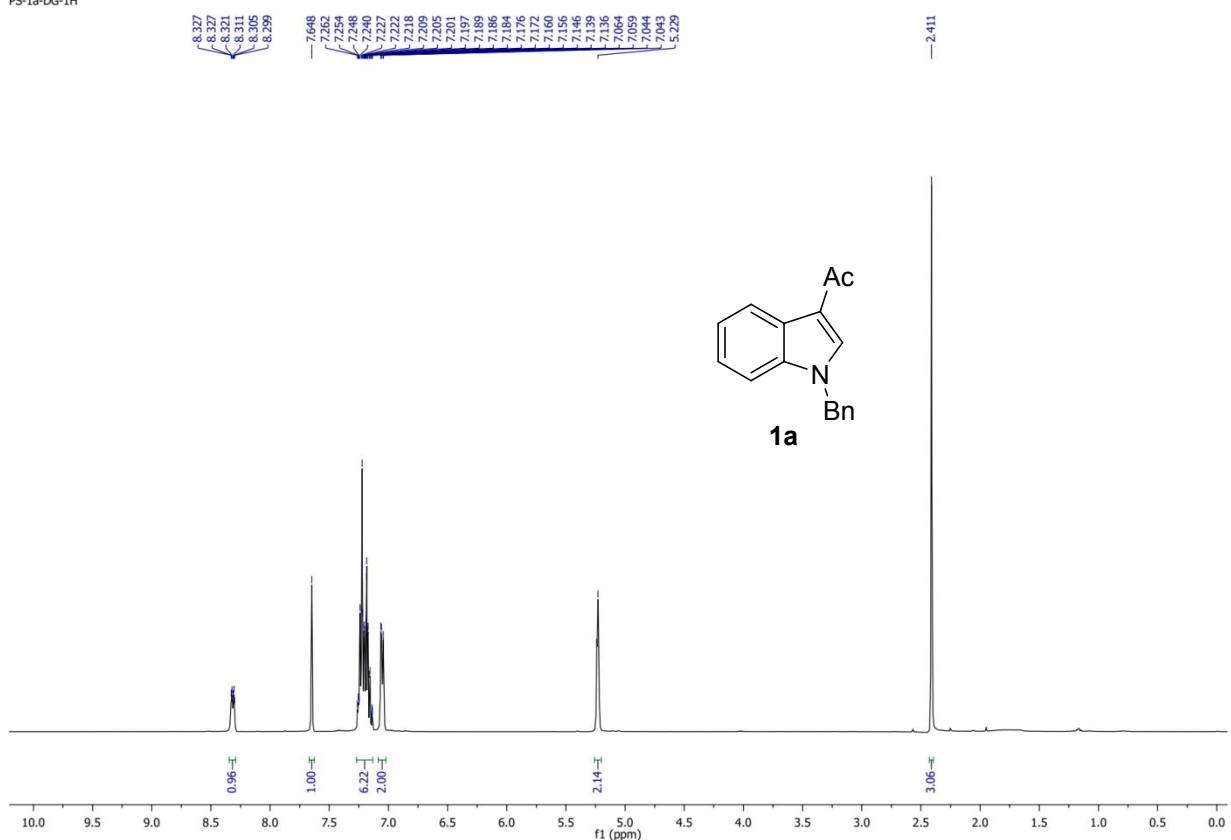
[D₂]-**1A** and [D_n]-**5a**. The deuterium incorporation was observed as 29% at C4-H and 14% at C2-H from 600 MHz ¹H NMR analysis of recovered [D₂]-**1A**.

Kinetic Isotope Effect Experiment. A mixture of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (0.1 mmol, 24.9 mg) and 1-(1-benzyl-1*H*-indol-3-yl-2,4-*d*₂)ethan-1-one [D₂]-**1a** (0.1 mmol, 25.1 mg) were reacted with but-3-en-2-ol **2a** (0.2 mmol, 14.5 mg) for 35 min under the standard reaction conditions. The resulting mixture was then diluted with CH₂Cl₂ (10 mL) and passed through a short pad of celite using CH₂Cl₂ (2 x 10 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford [D₁]-**3a** and a mixture of unreacted **1a** and [D₂]-**1a** as a colourless solid. The intermolecular *k*_H/*k*_D was found to be 1.48 after 35 min at 15% conversion, based on 600 MHz ¹H NMR of the recovered substrate **1a** and [D₂]-**1a**.

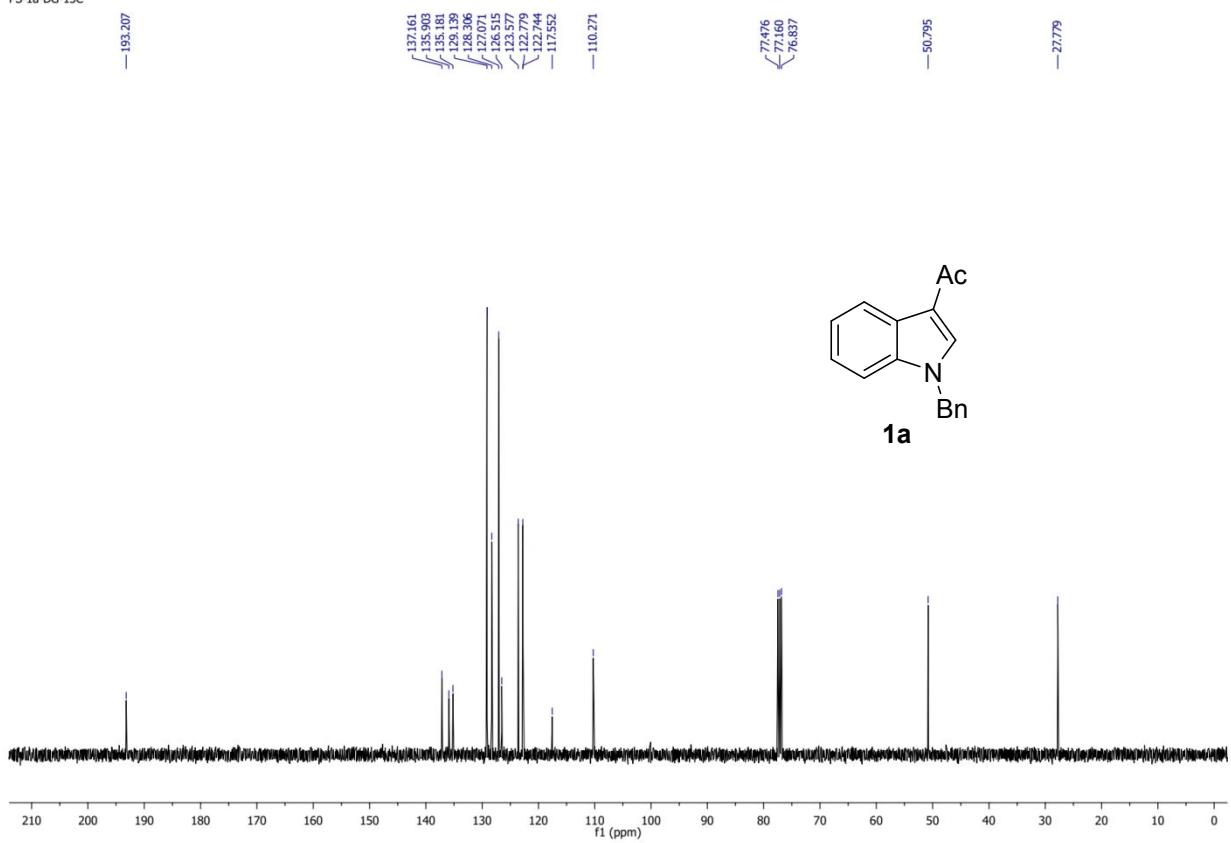
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4. (a) Borah, A. J.; Shi, Z. *Chem. Commun.* **2017**, *53*, 3945. (b) Yang, Y.; Gao, P.; Zhao, Y.; Shi, Z. *Angew. Chem. Int. Ed.* **2017**, *56*, 3966. (c) Maity, S.; Karmakar, U.; Samanta, R. *Chem. Commun.* **2019**, *55*, 8102.

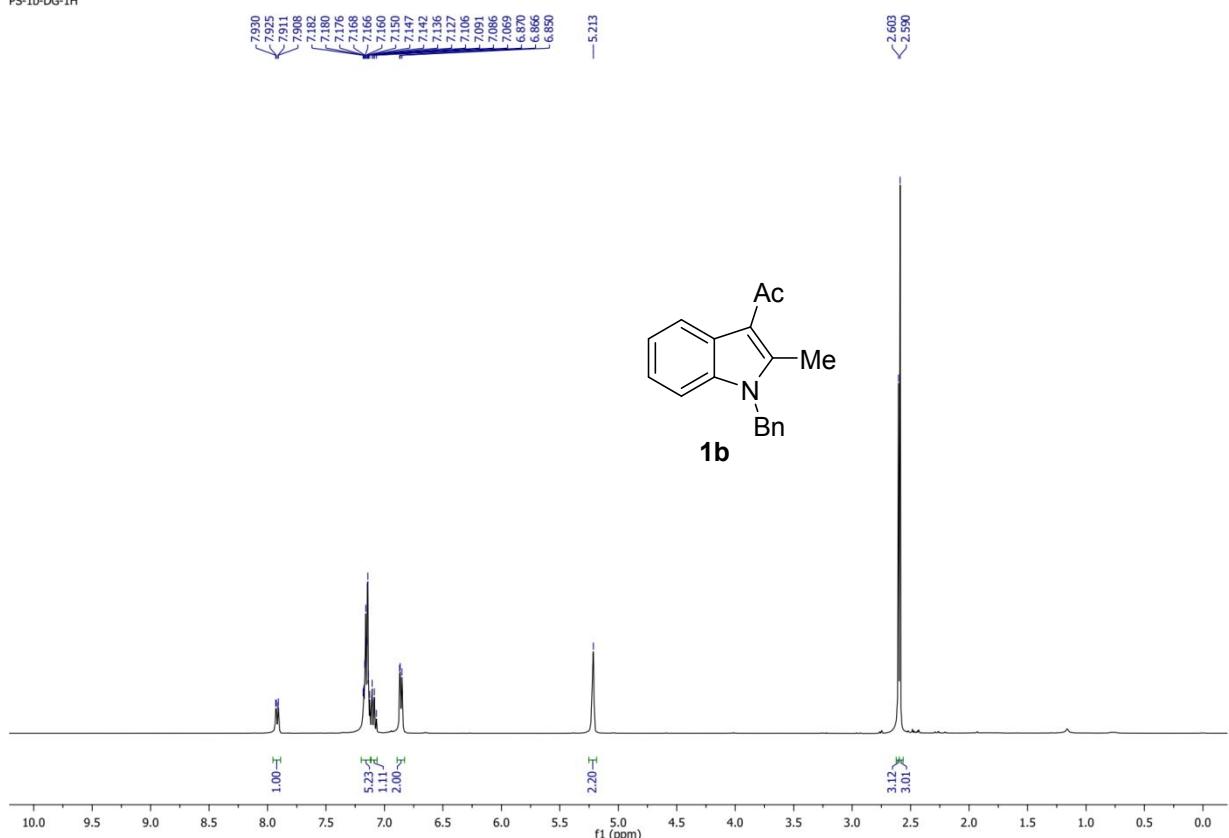
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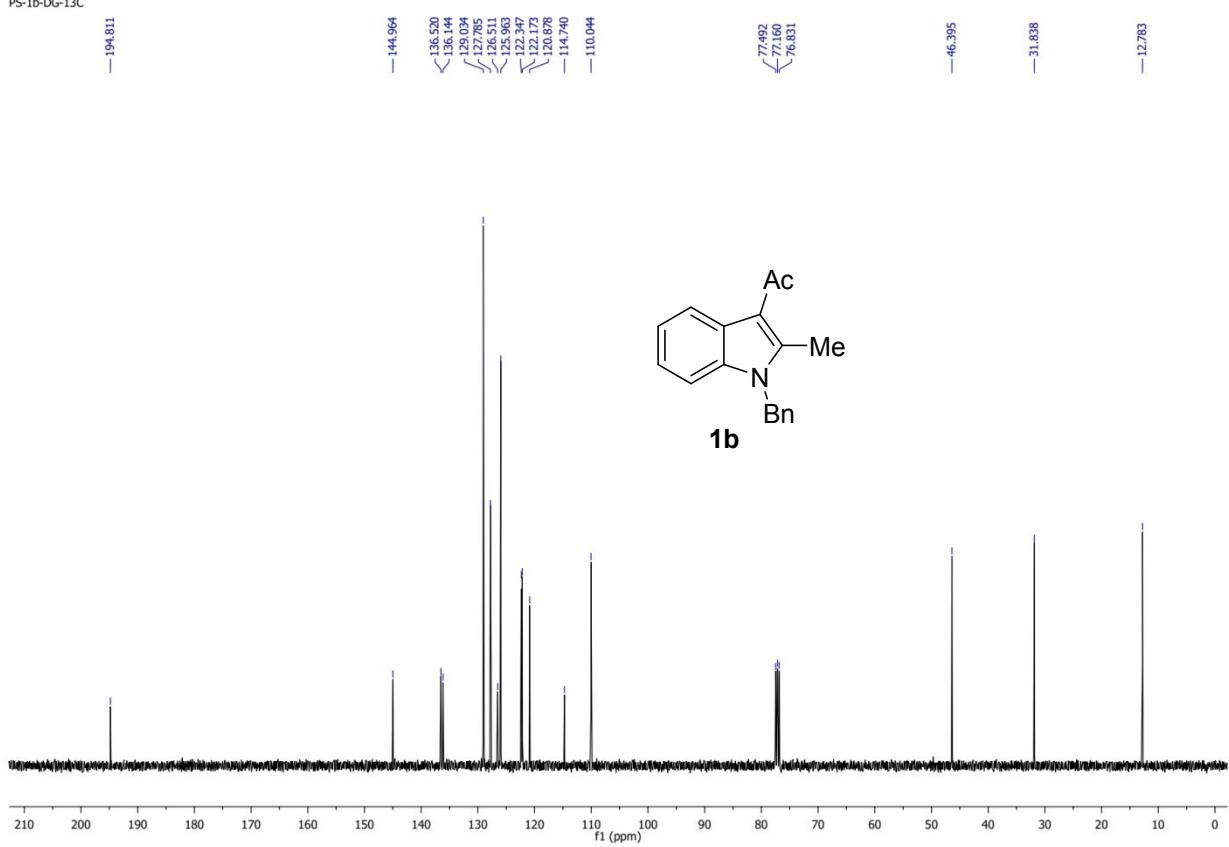
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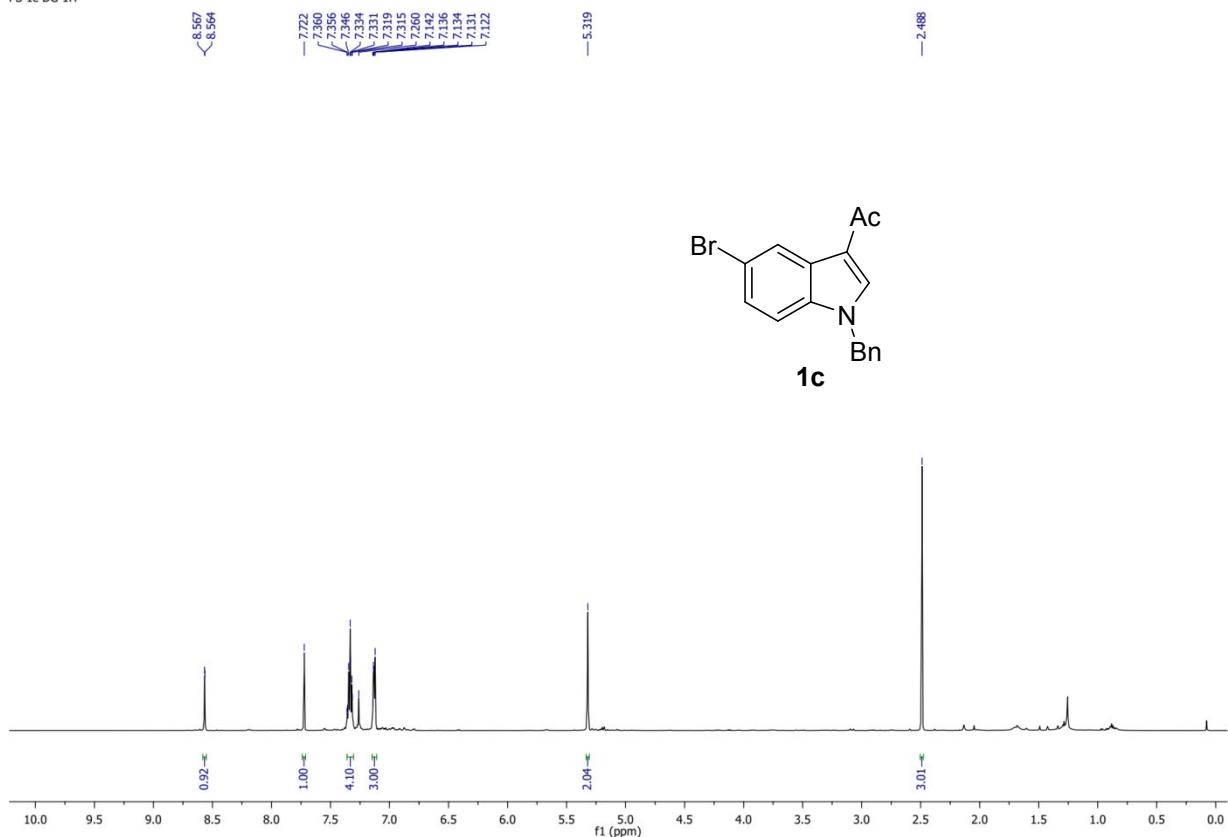
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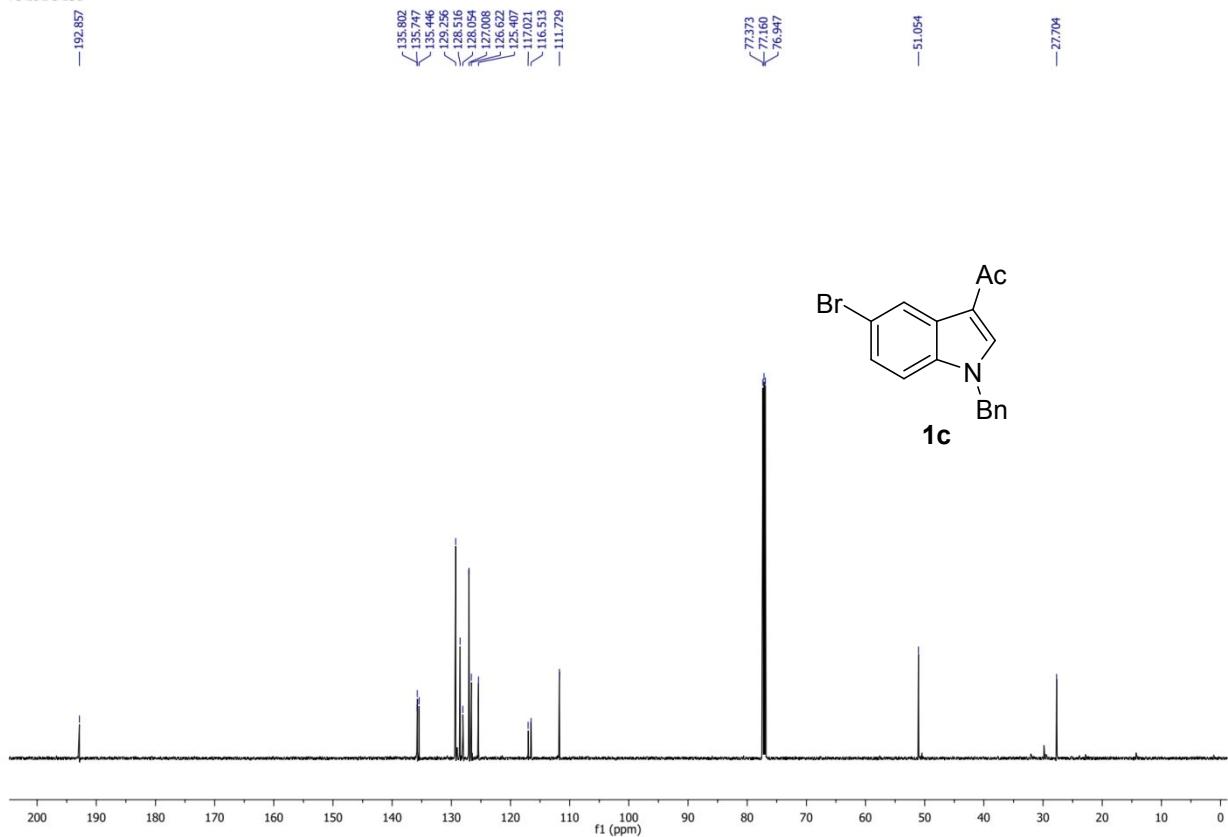
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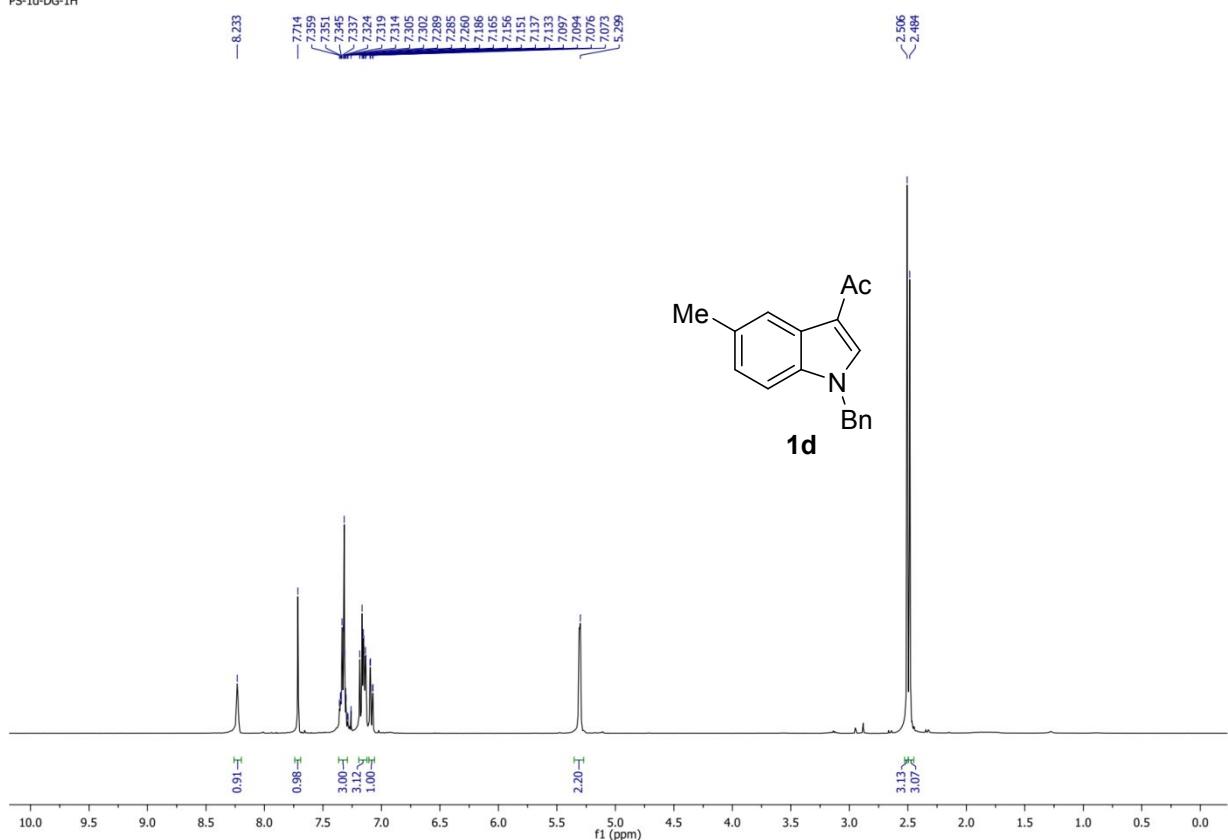
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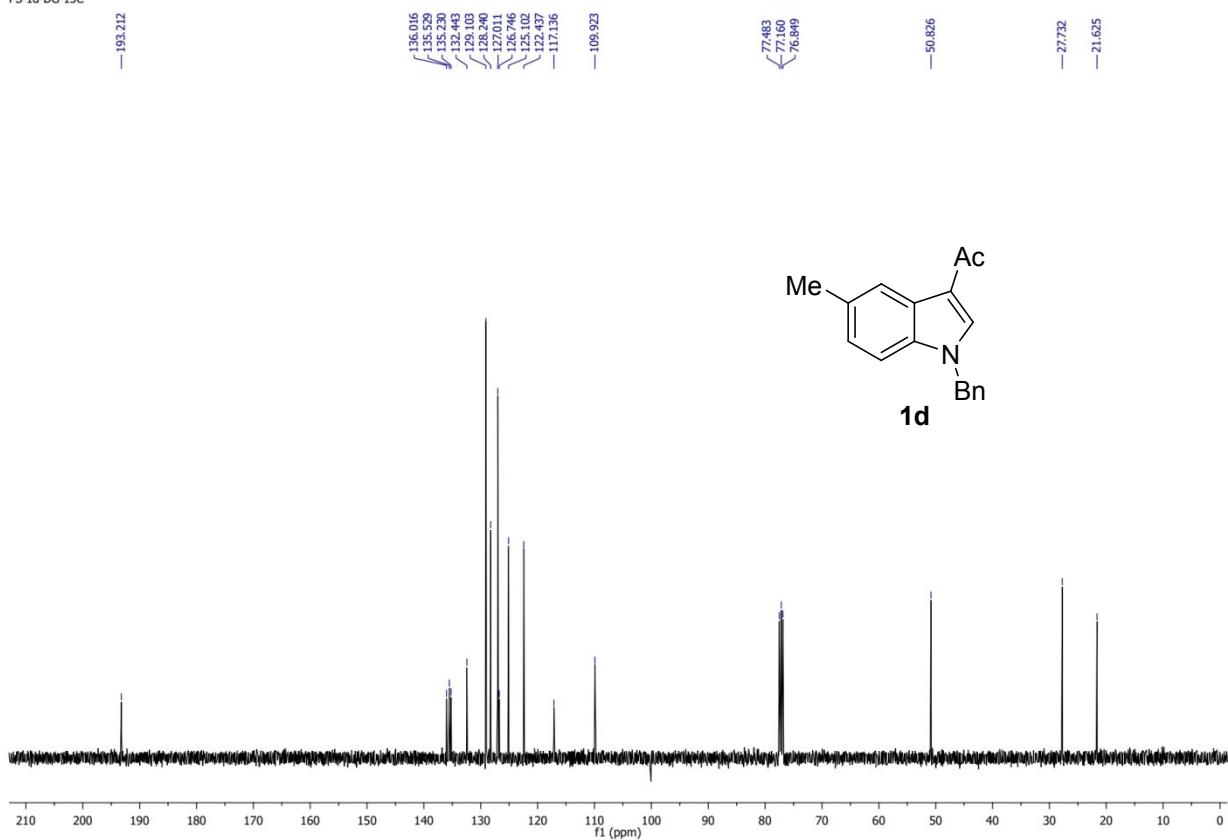
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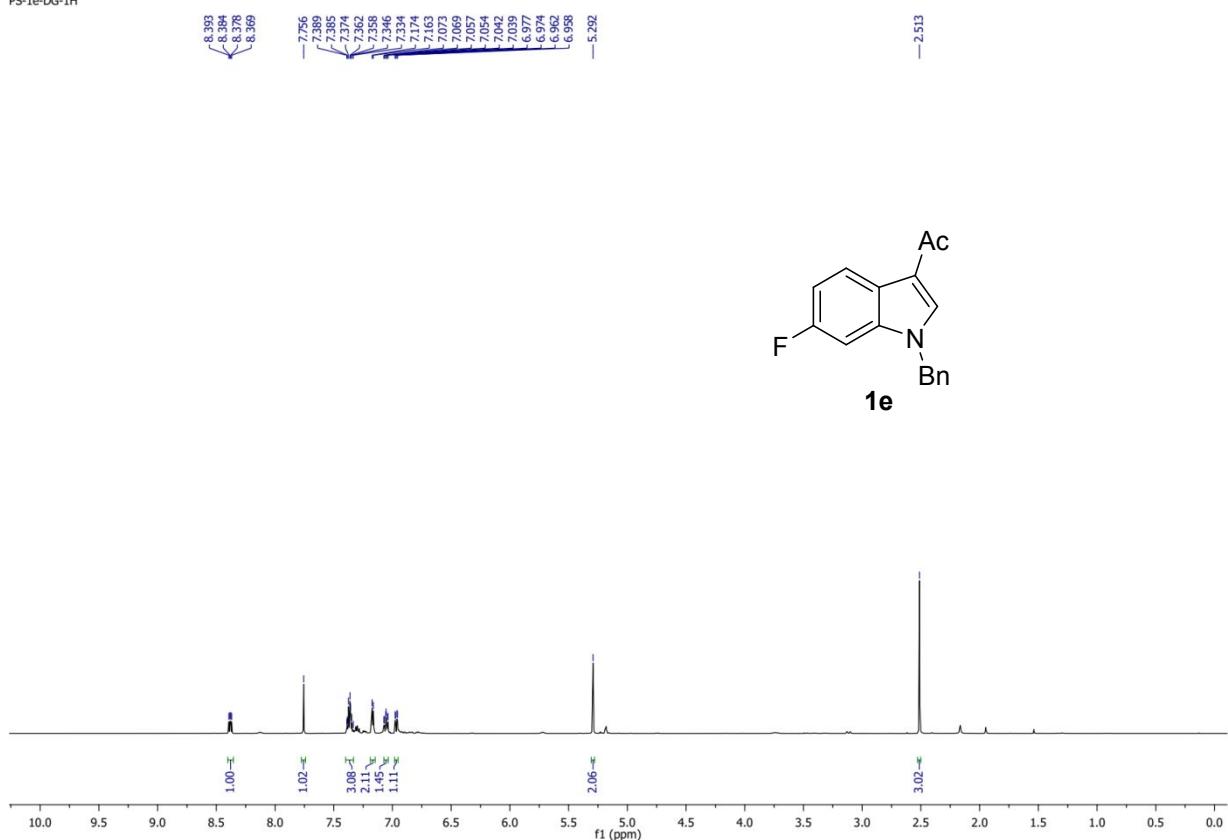
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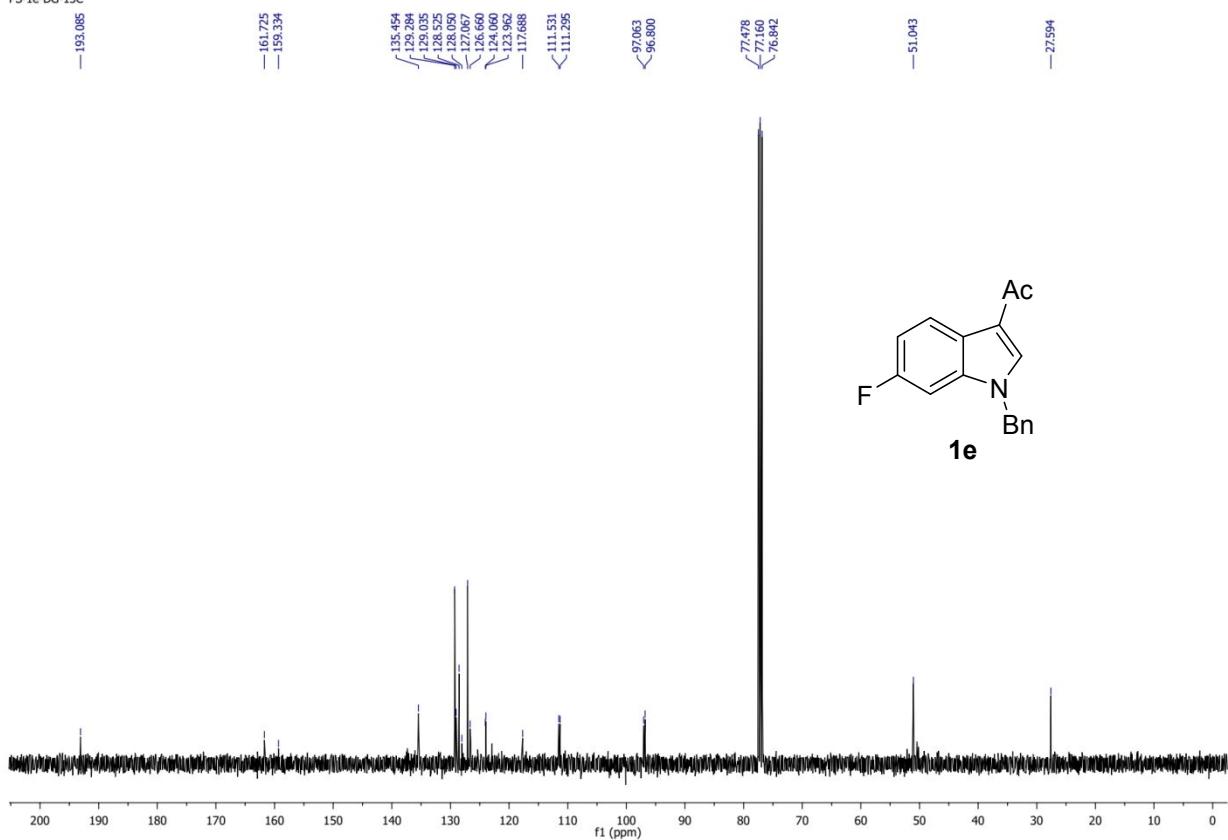
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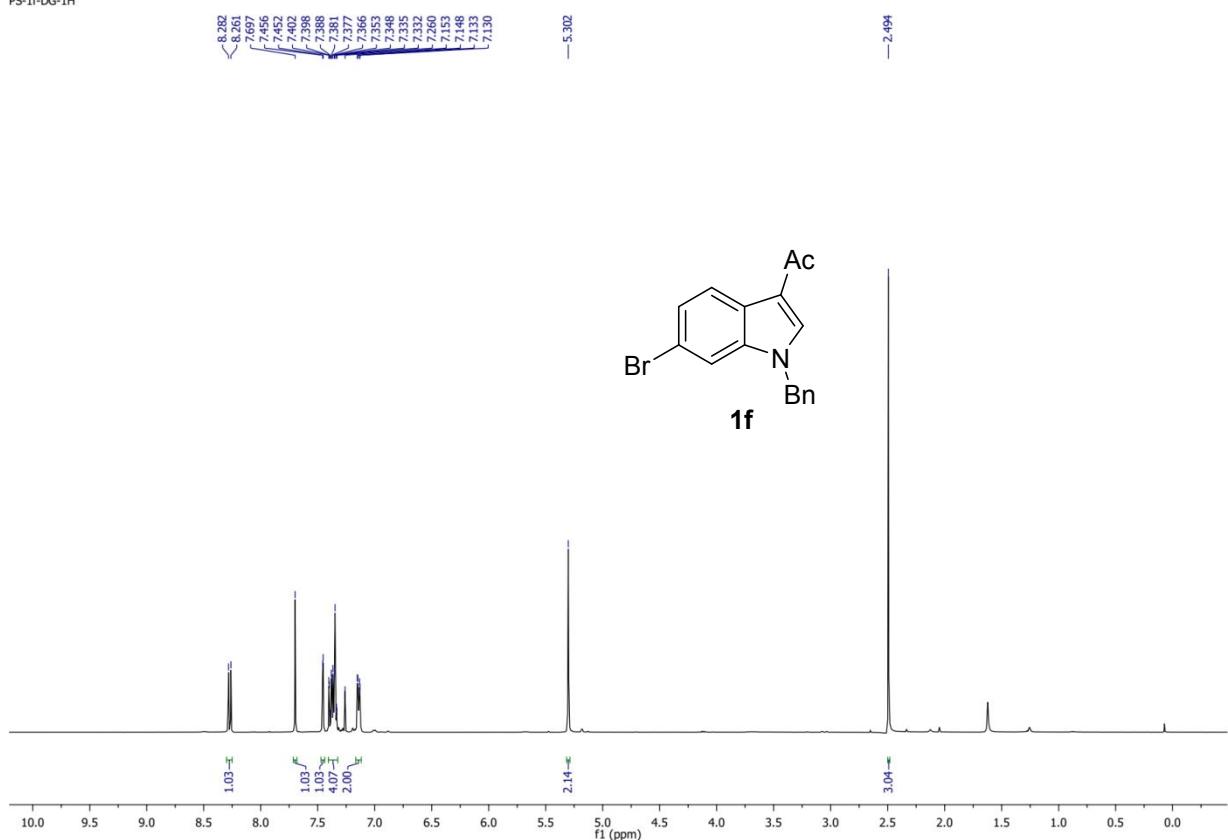
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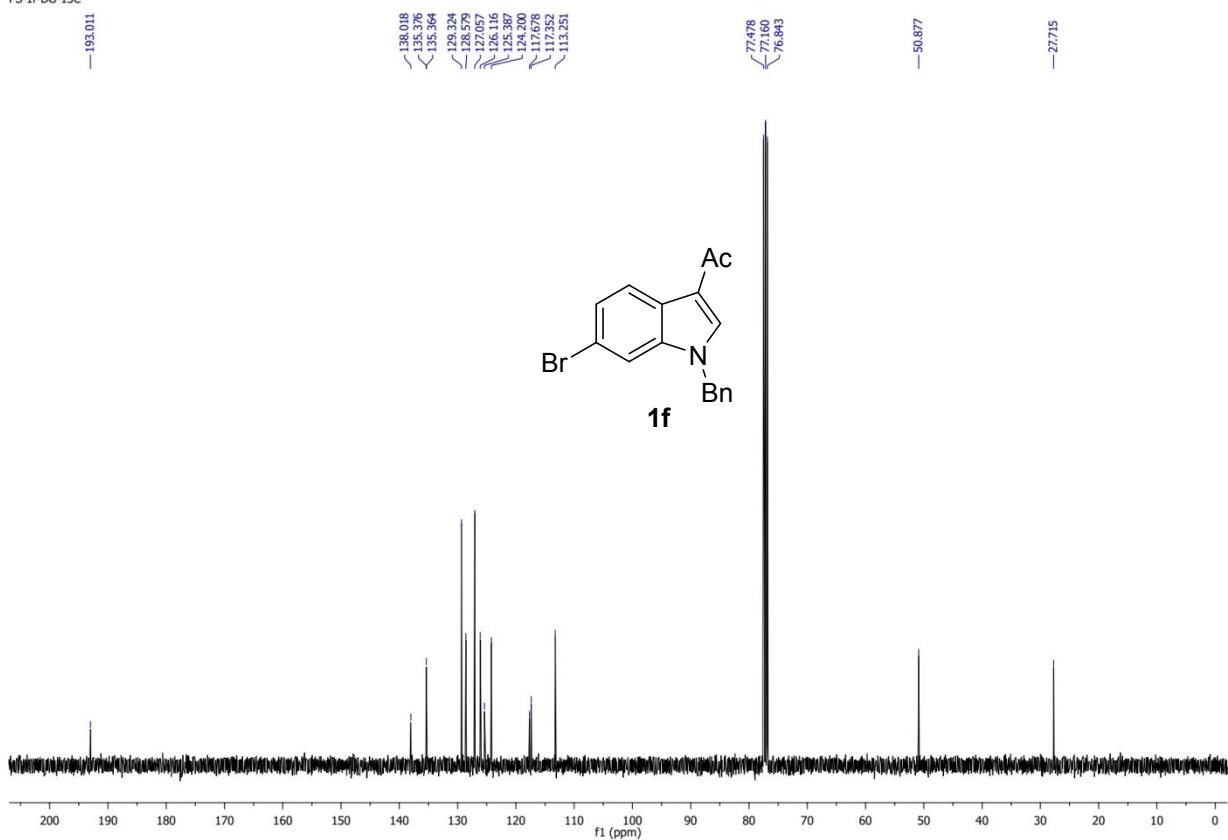
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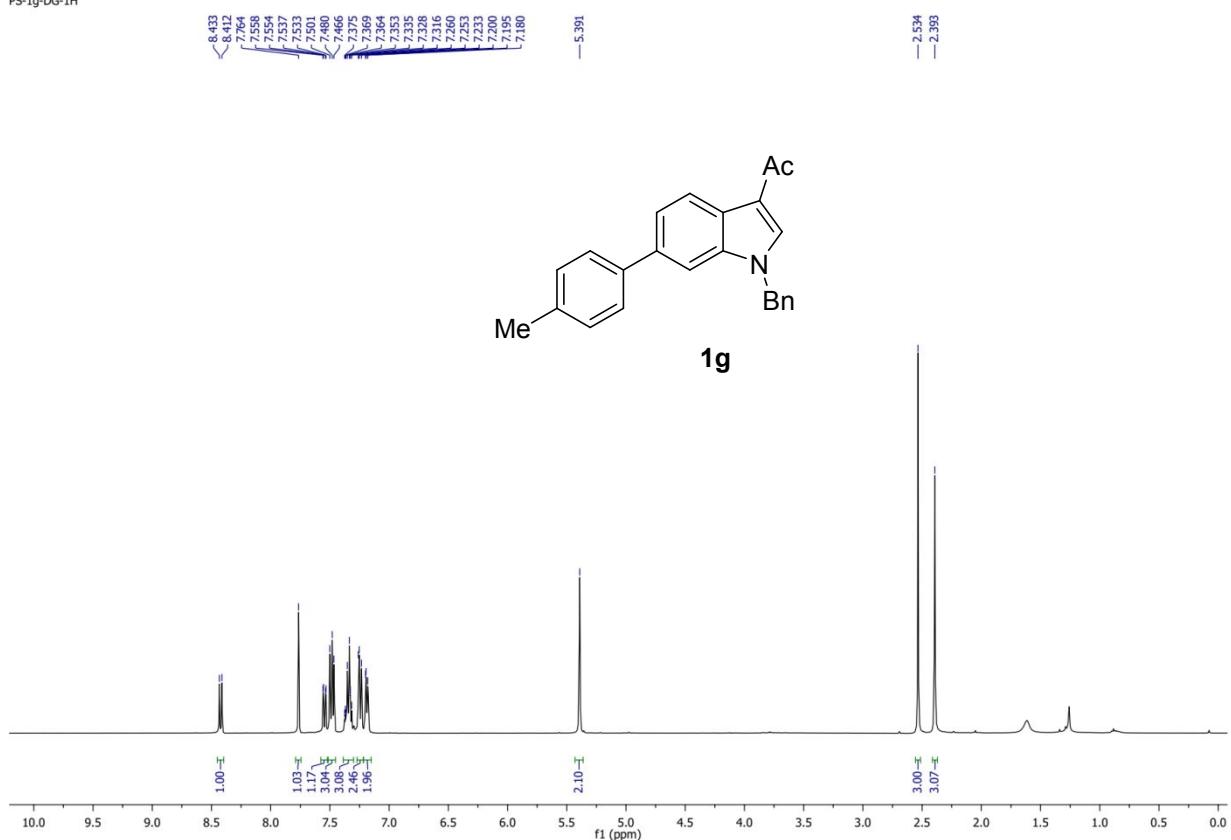
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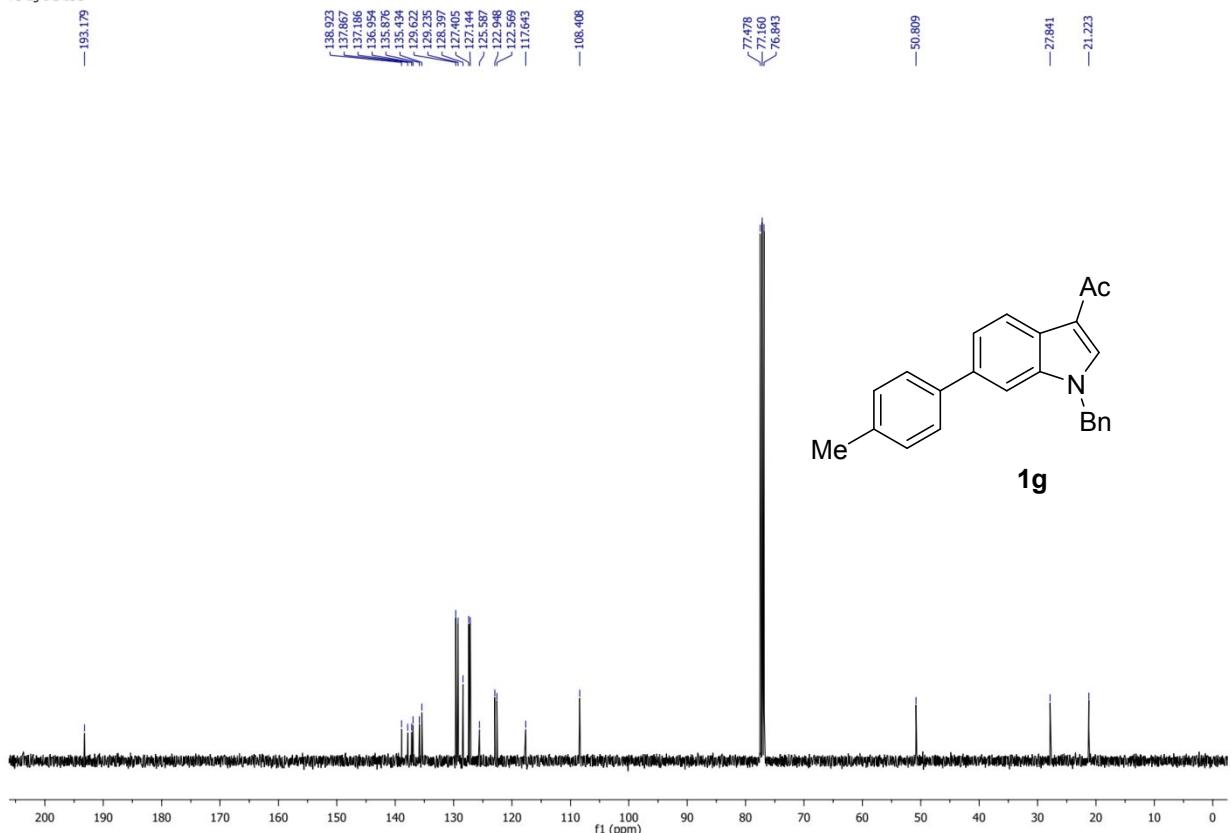
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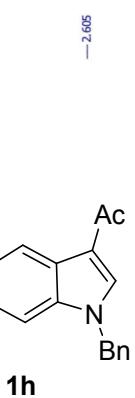
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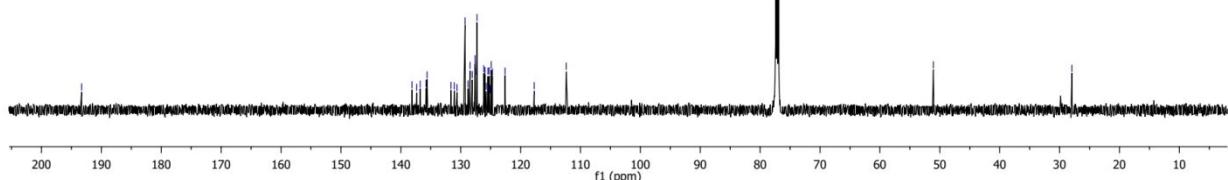
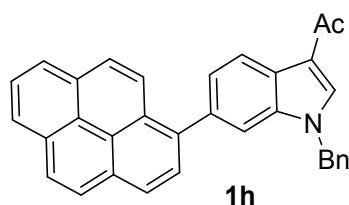
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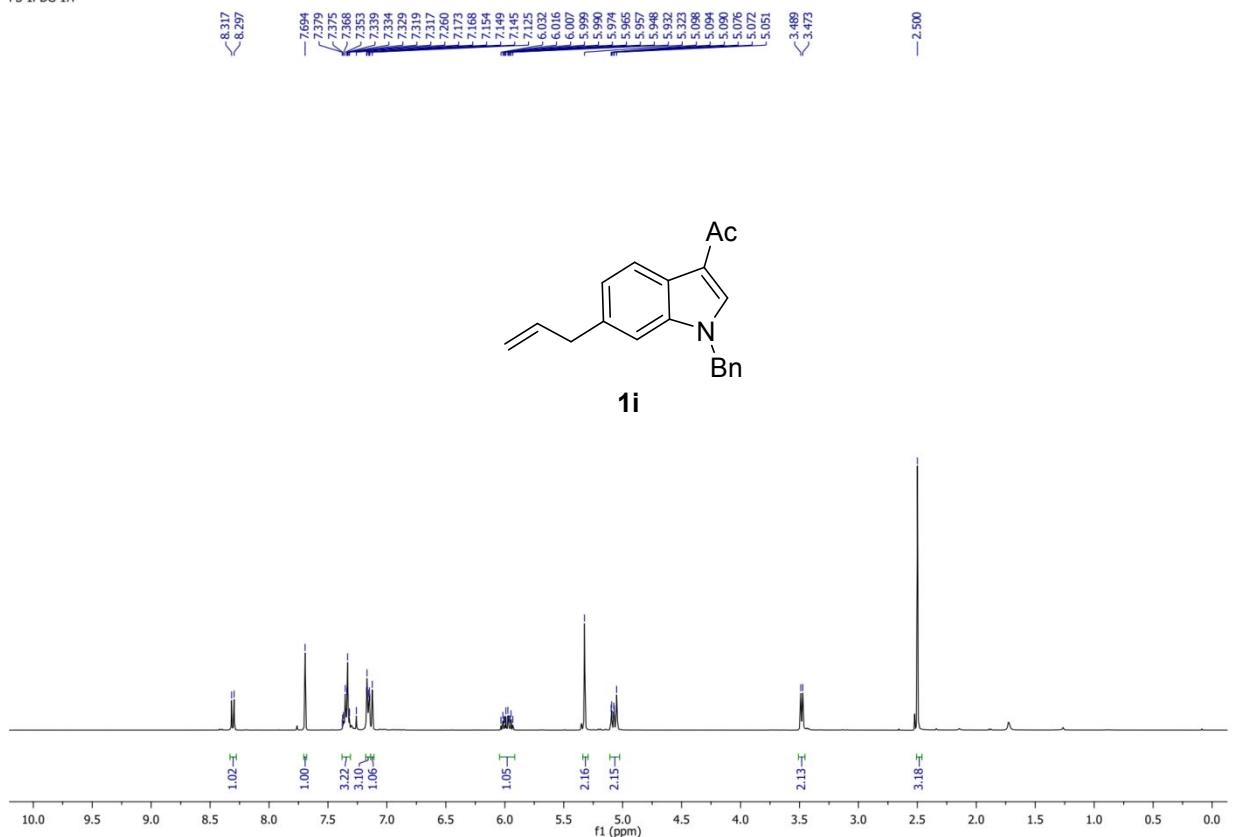
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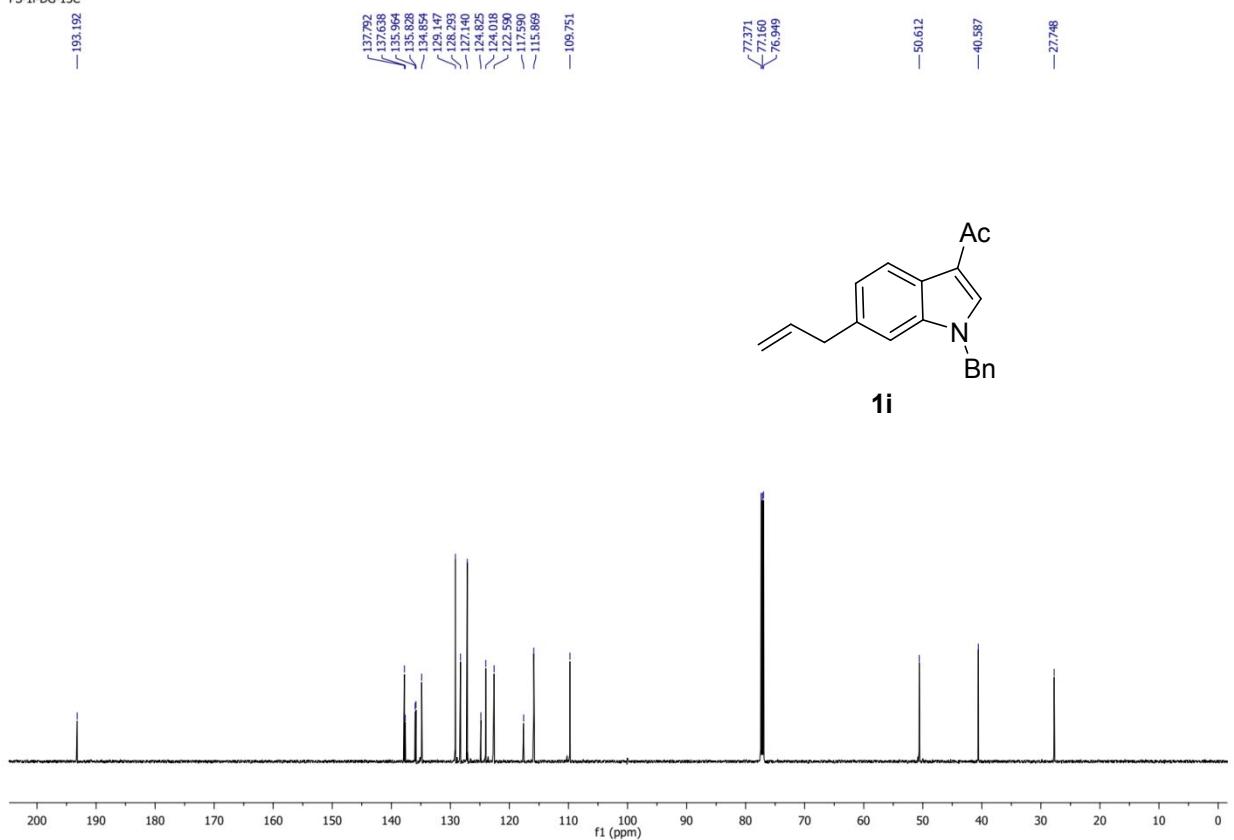
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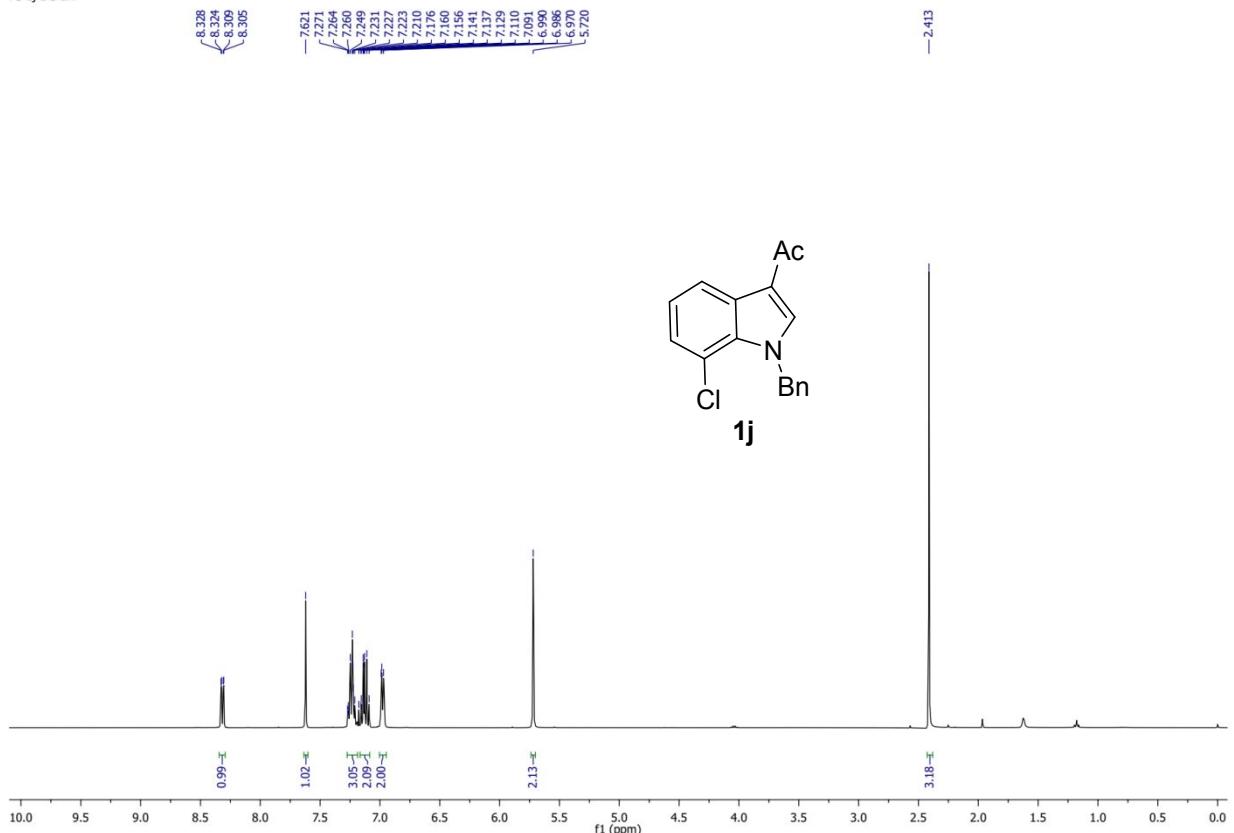
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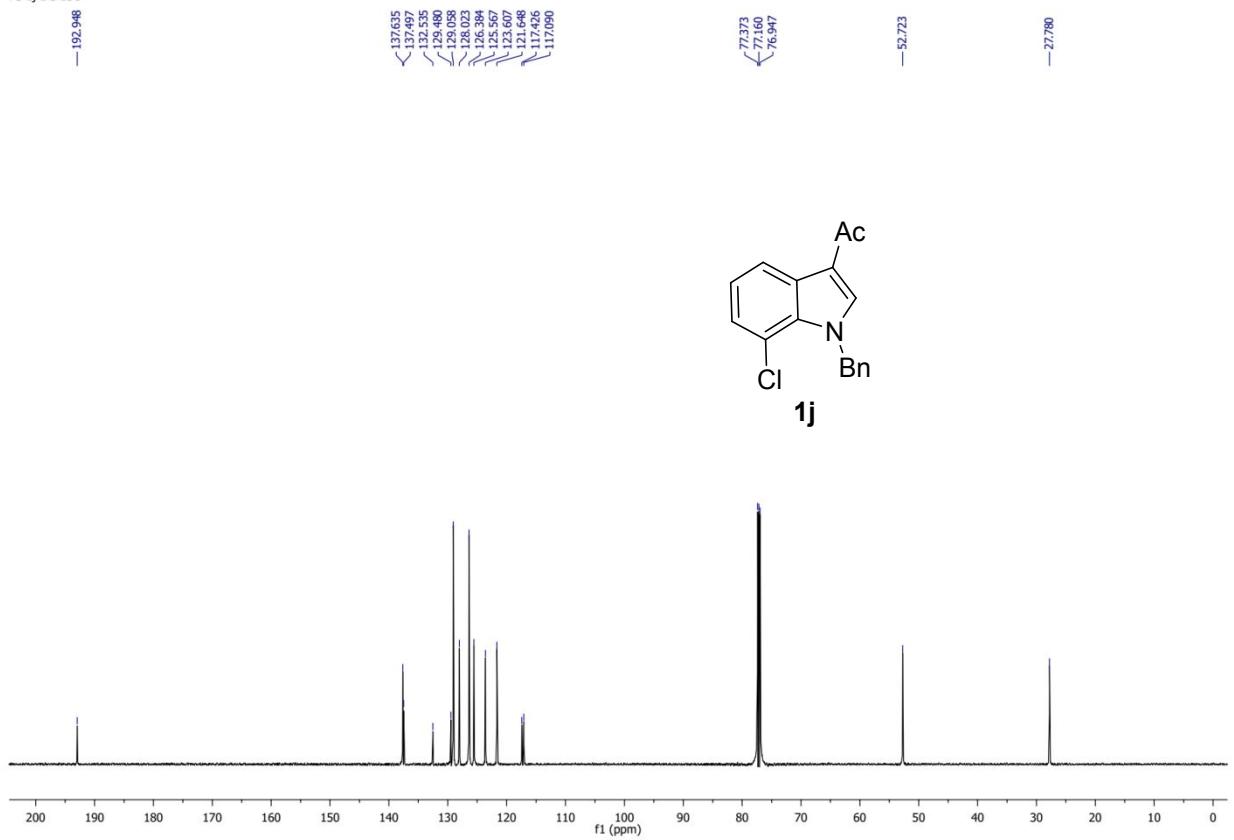
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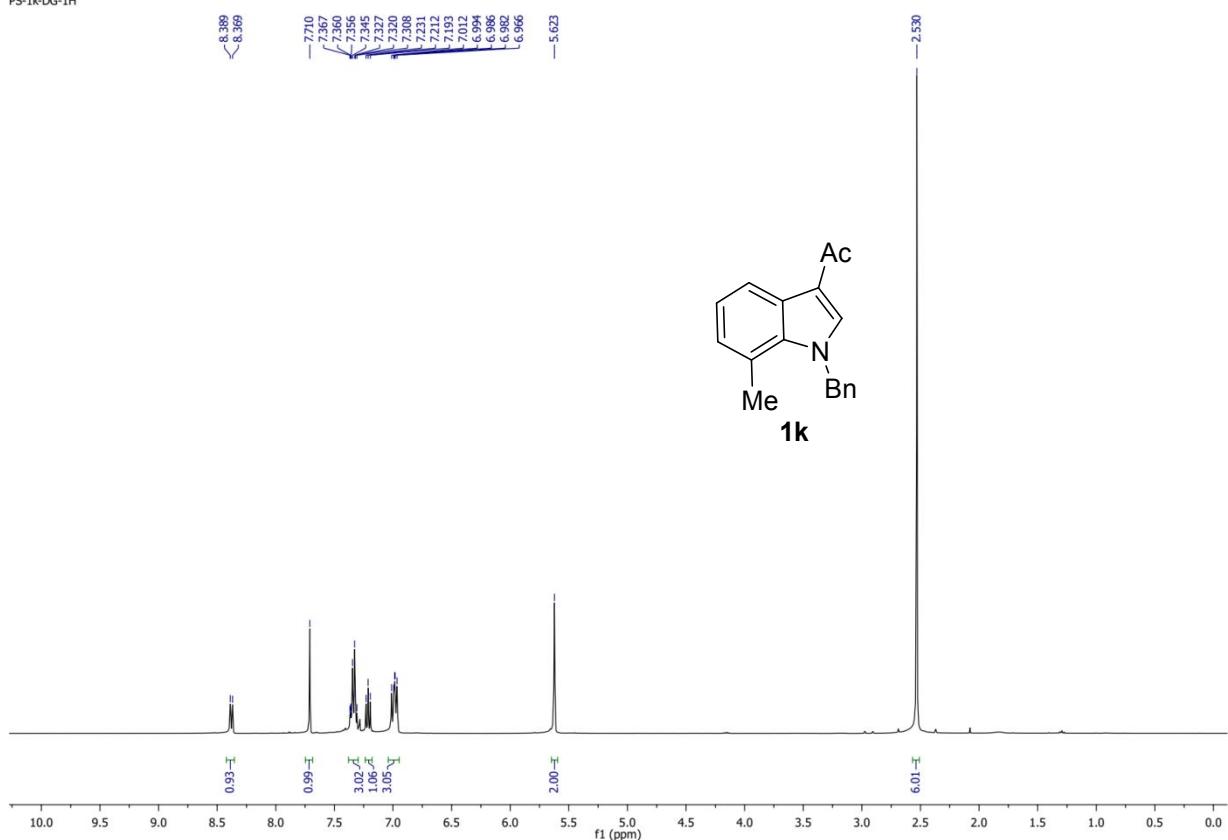
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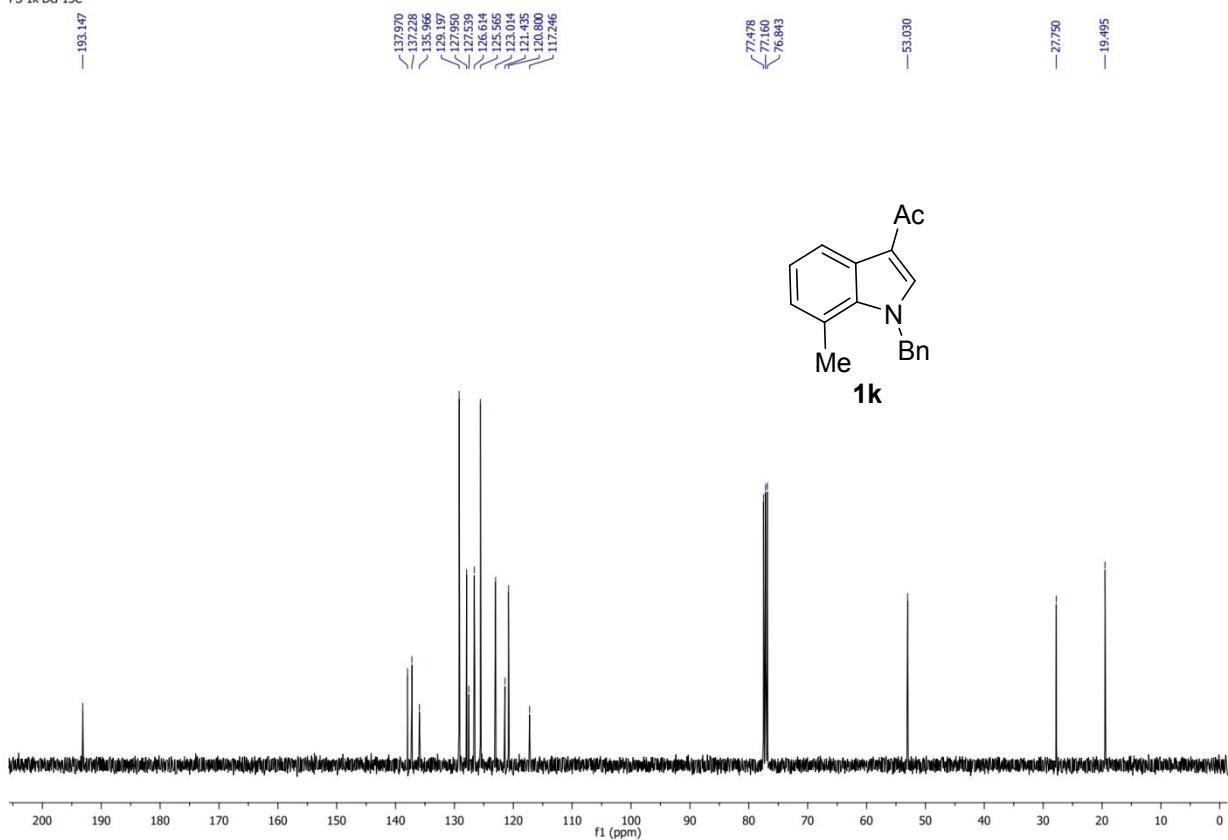
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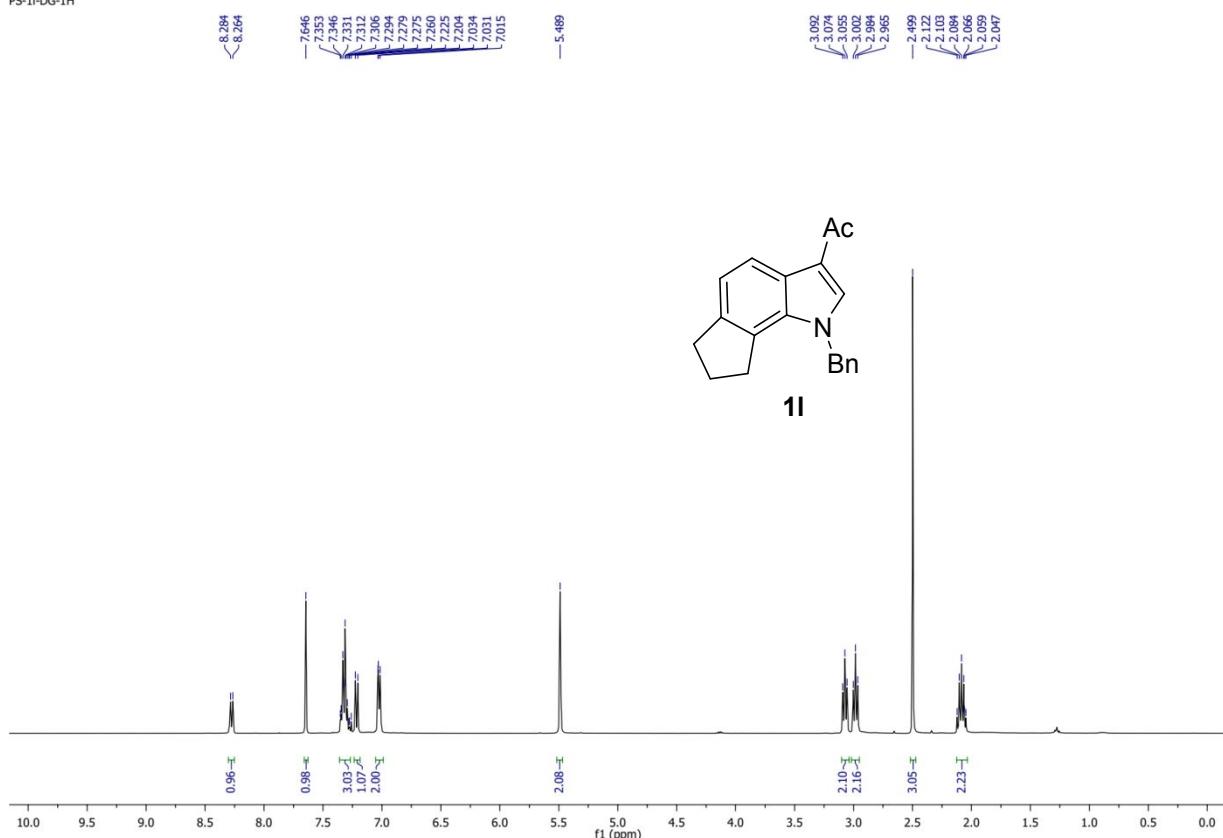
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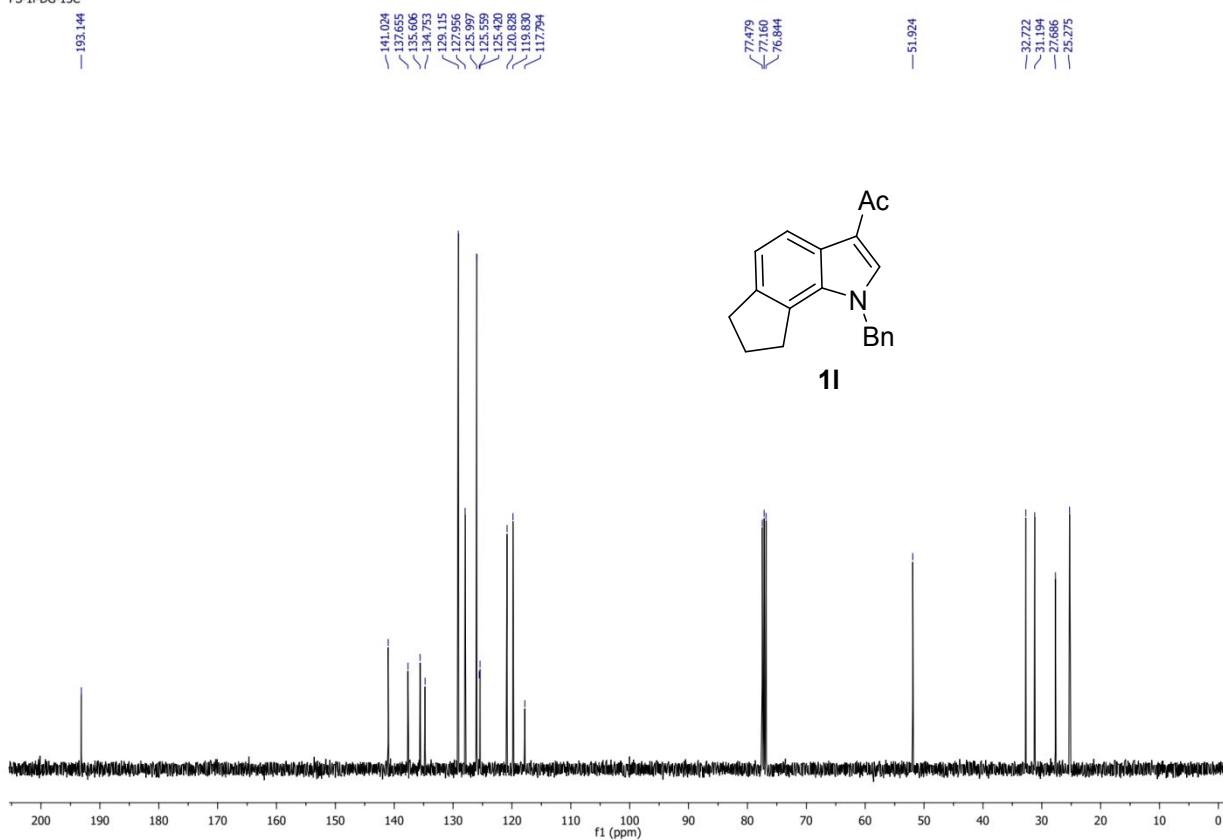
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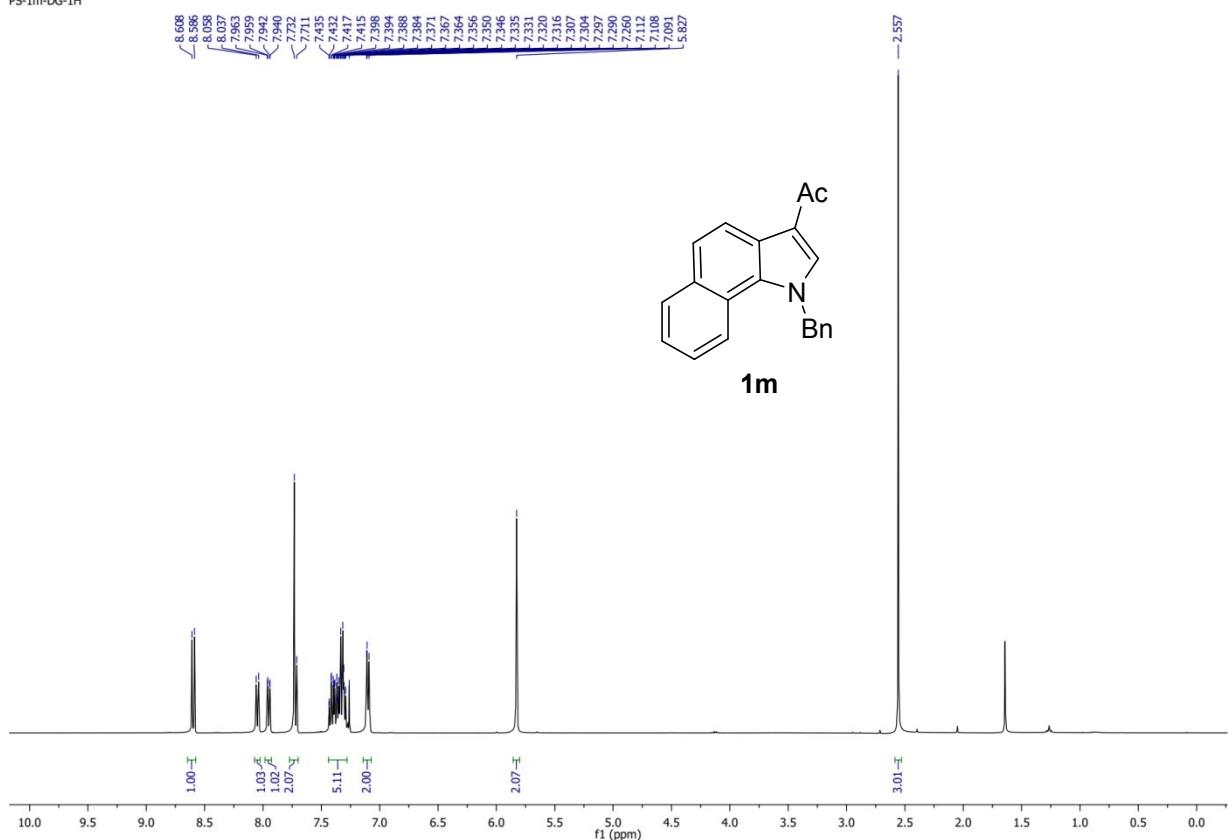
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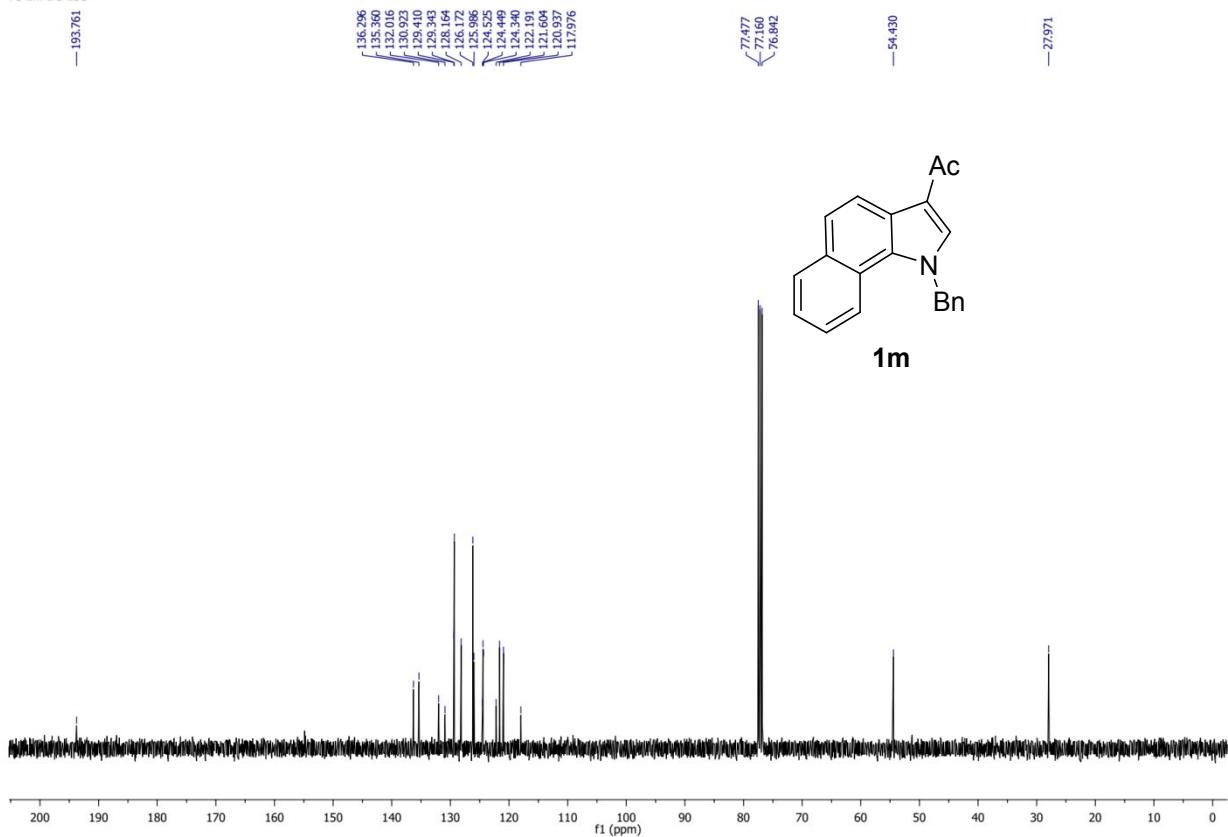
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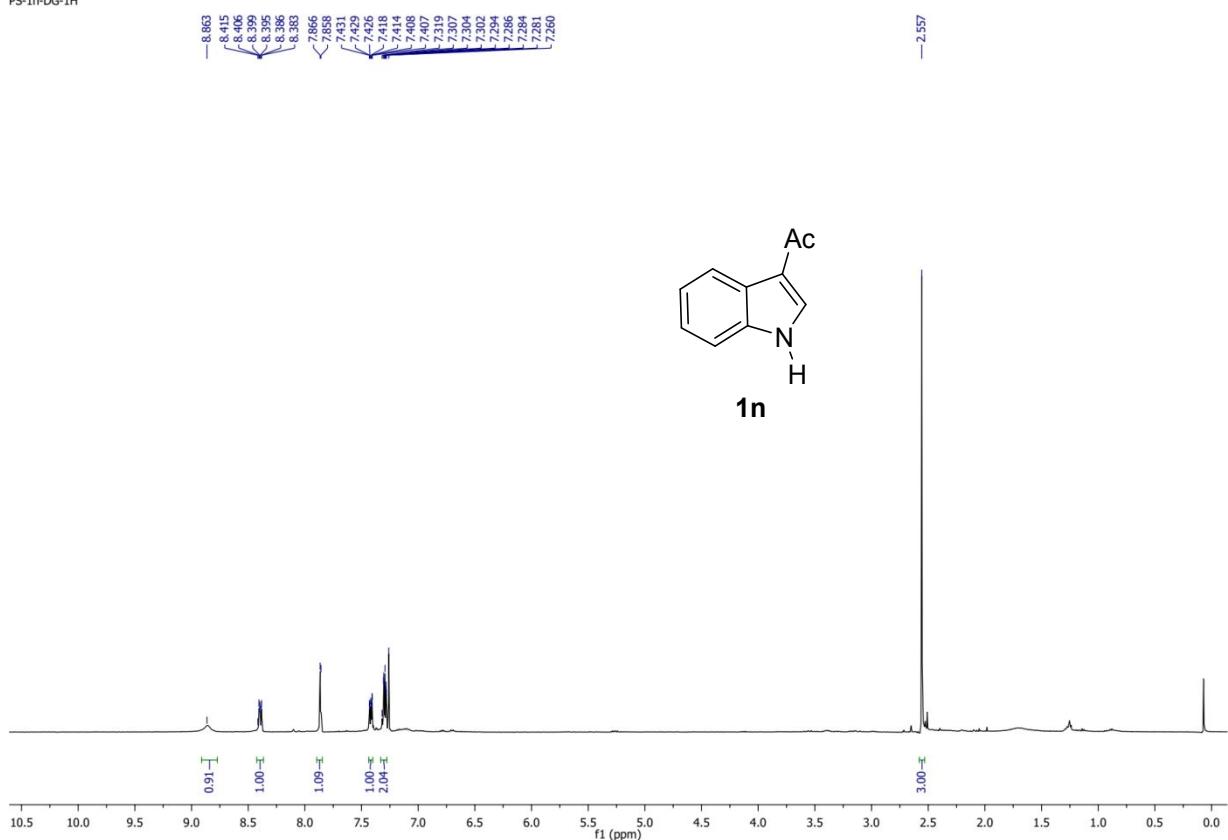
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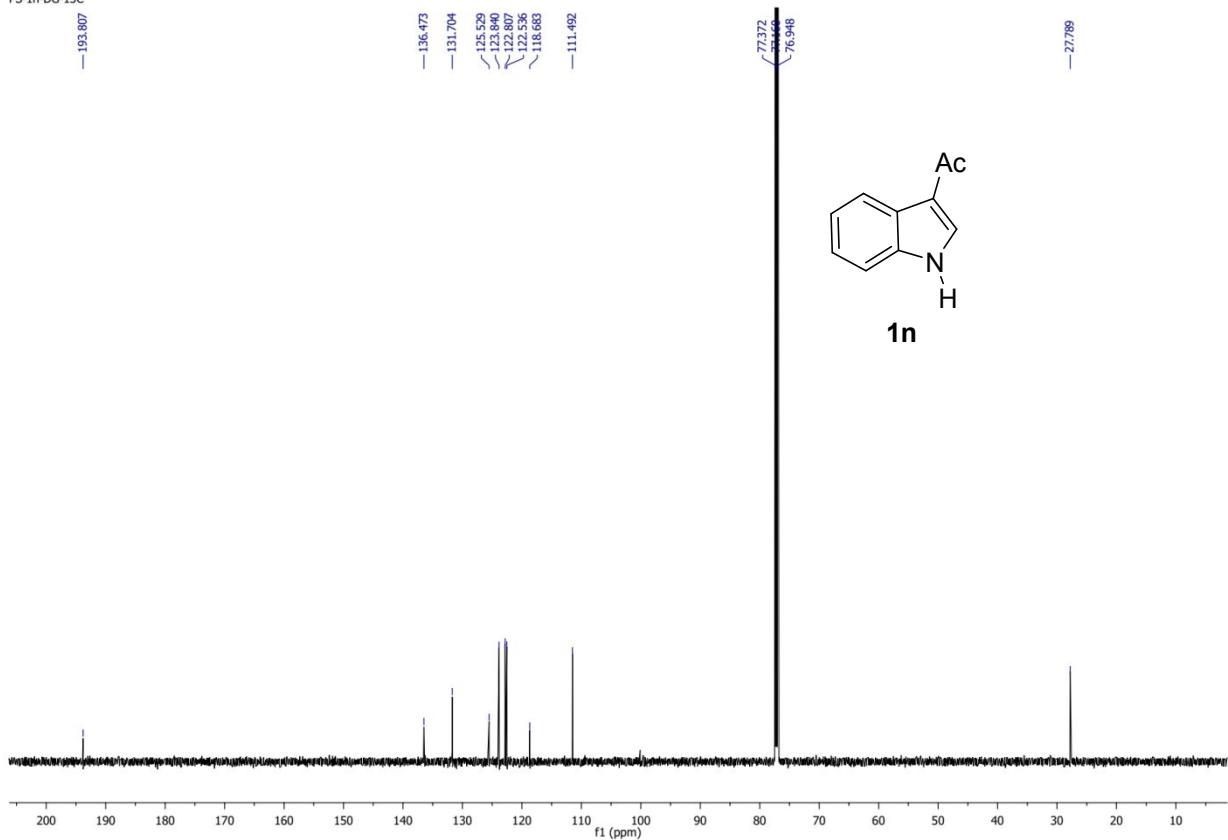
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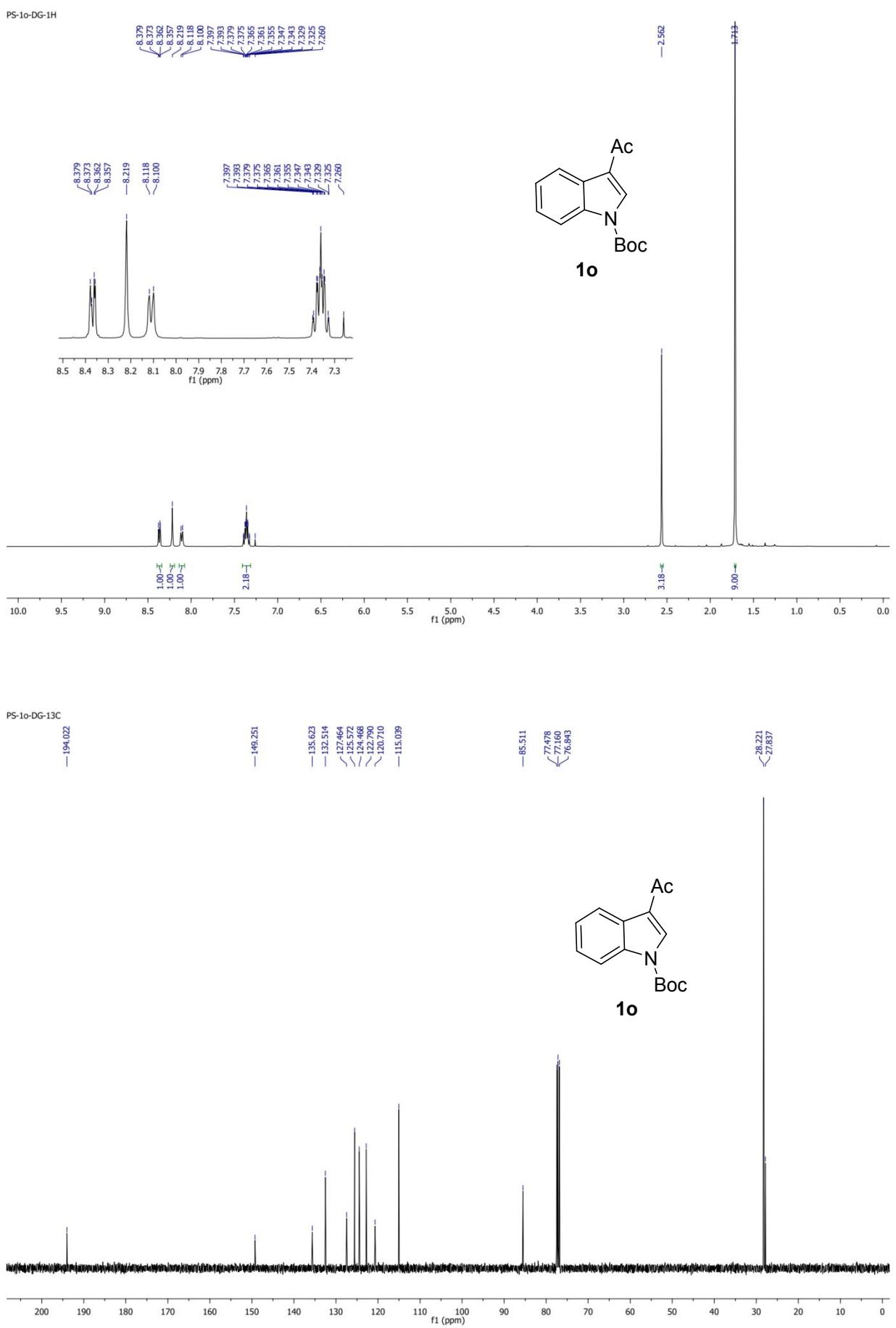


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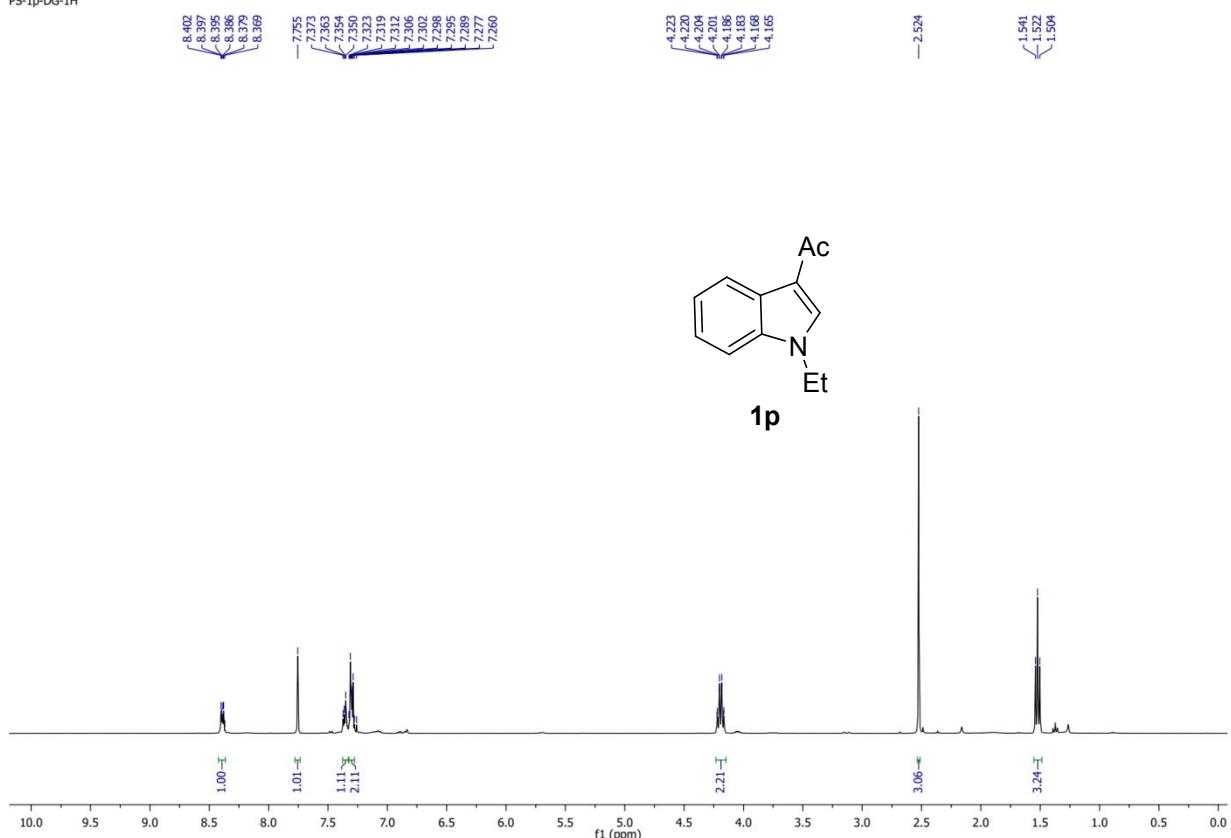


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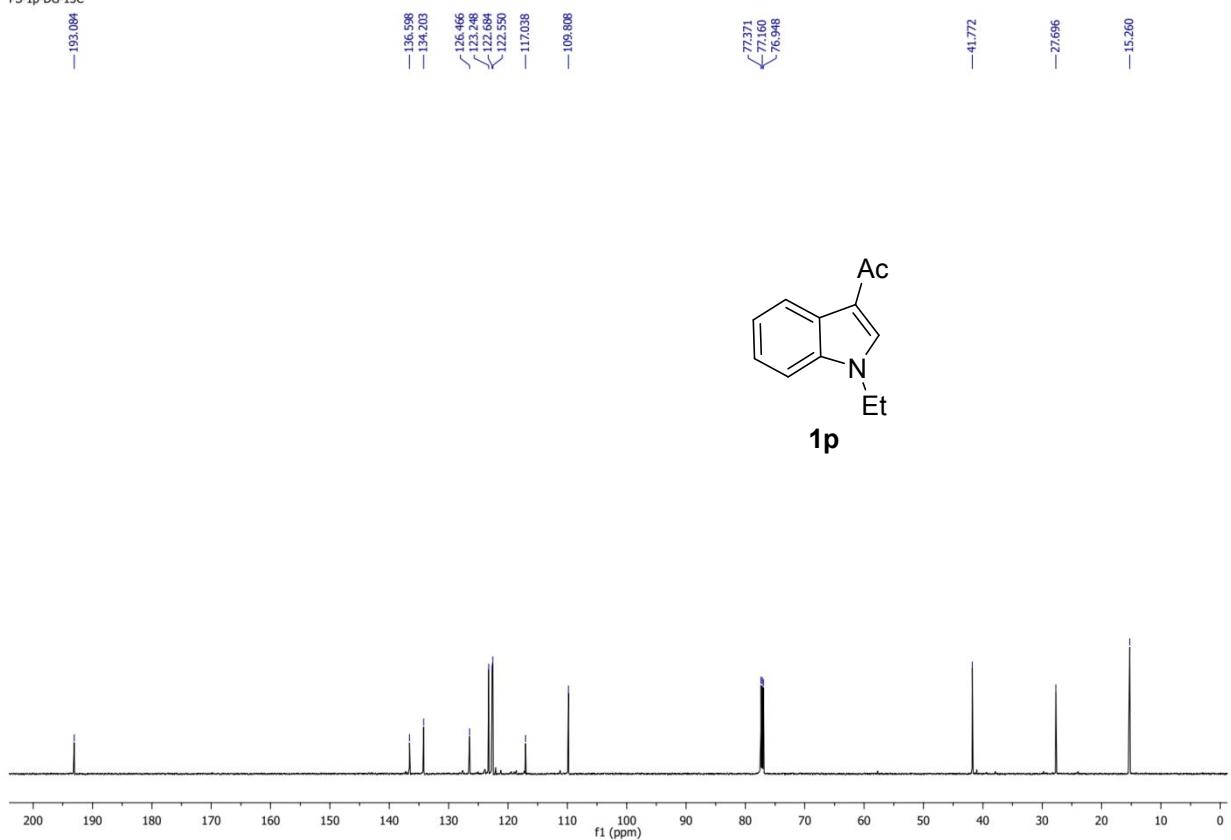




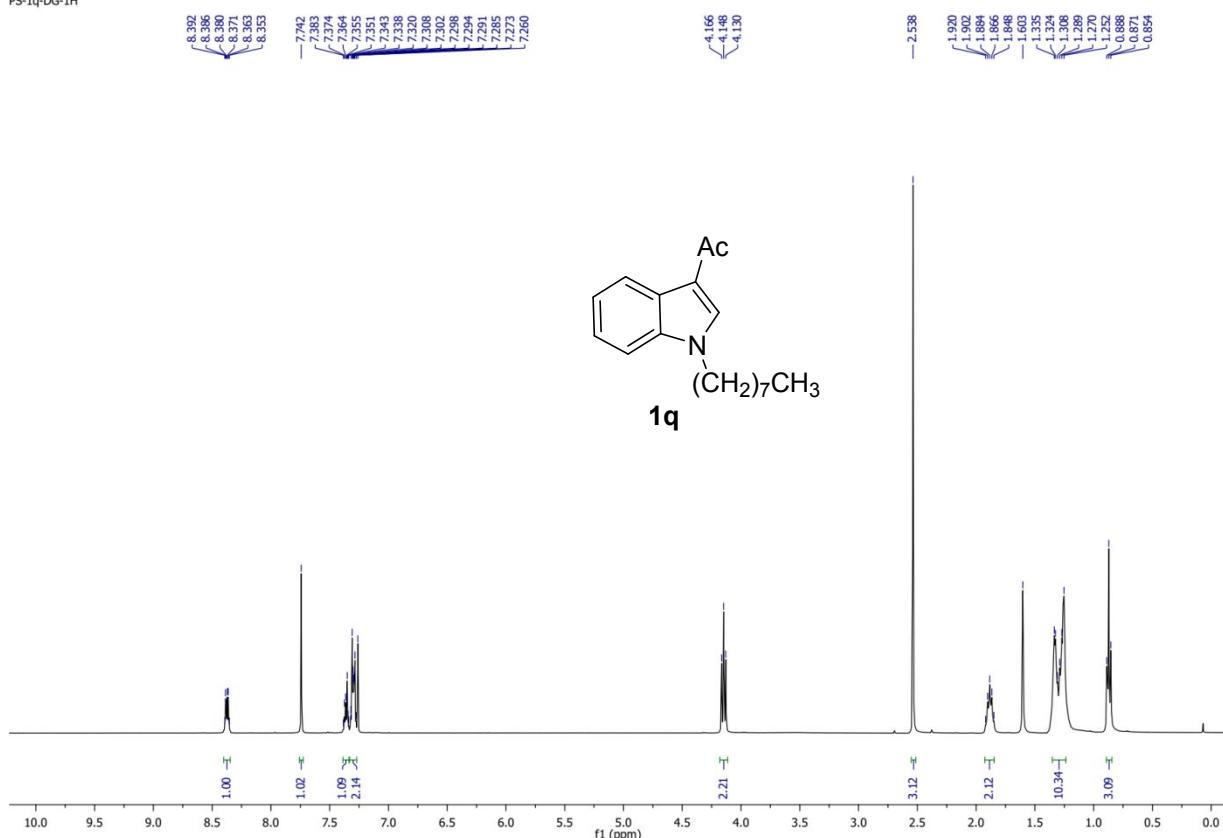
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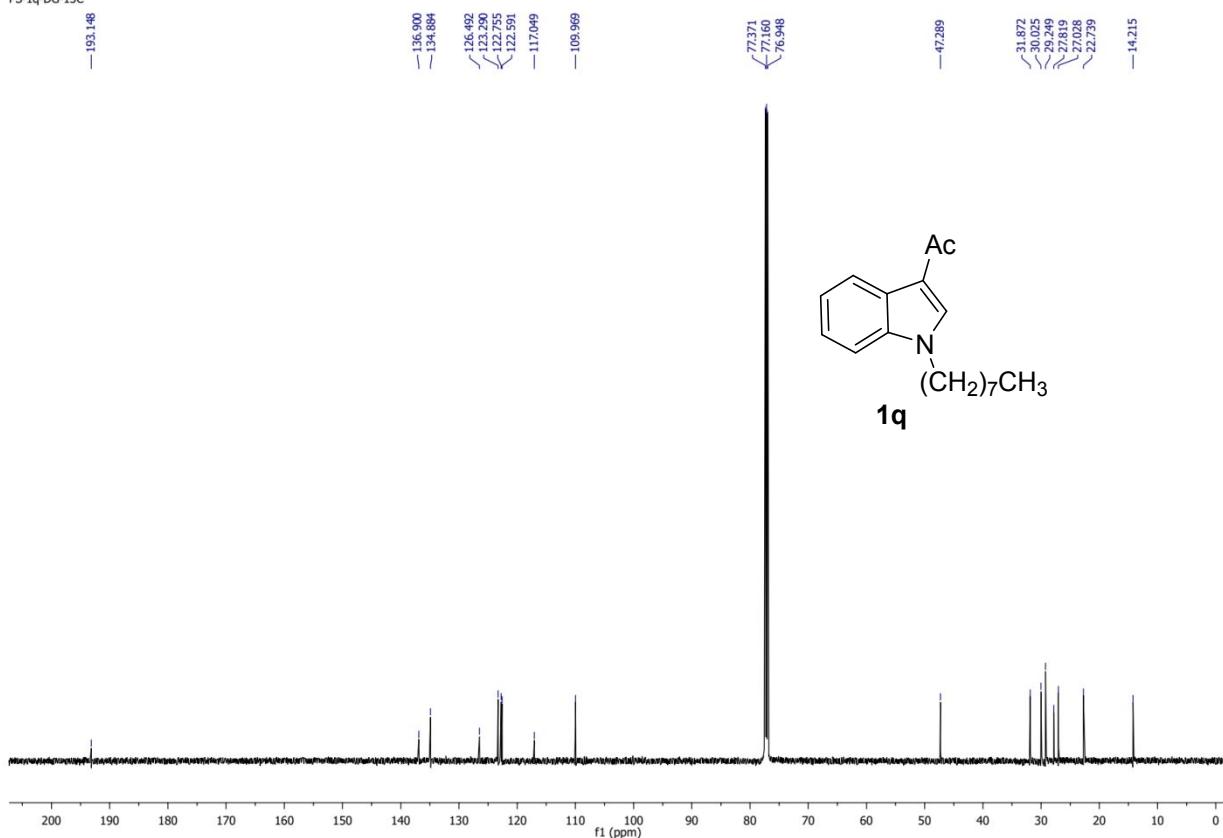
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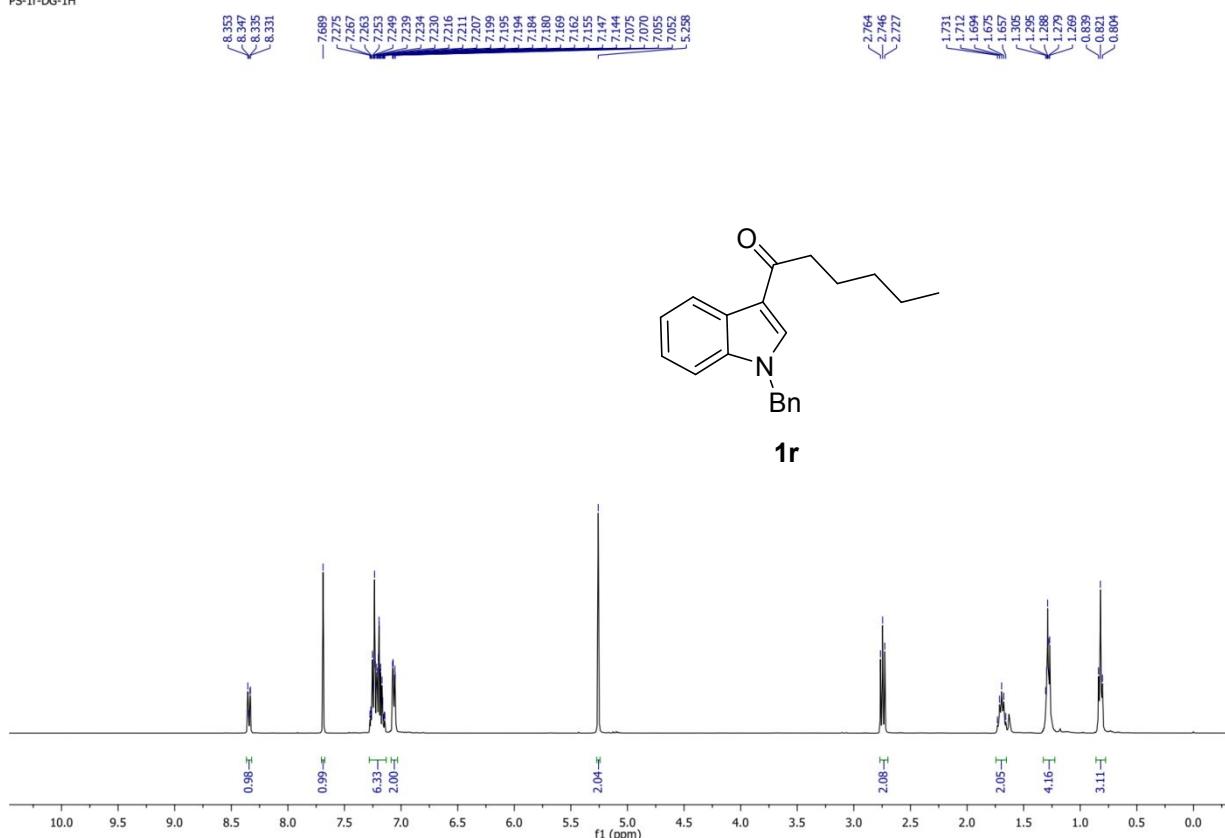
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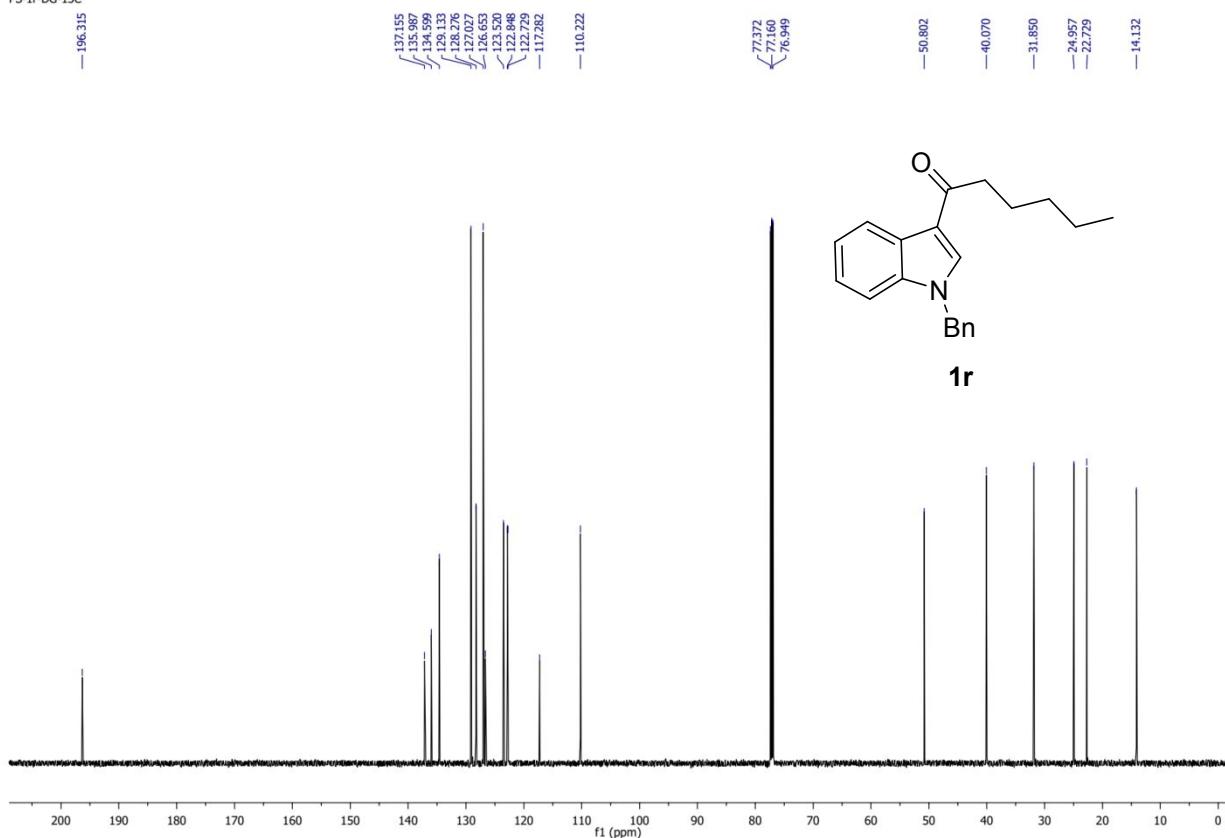
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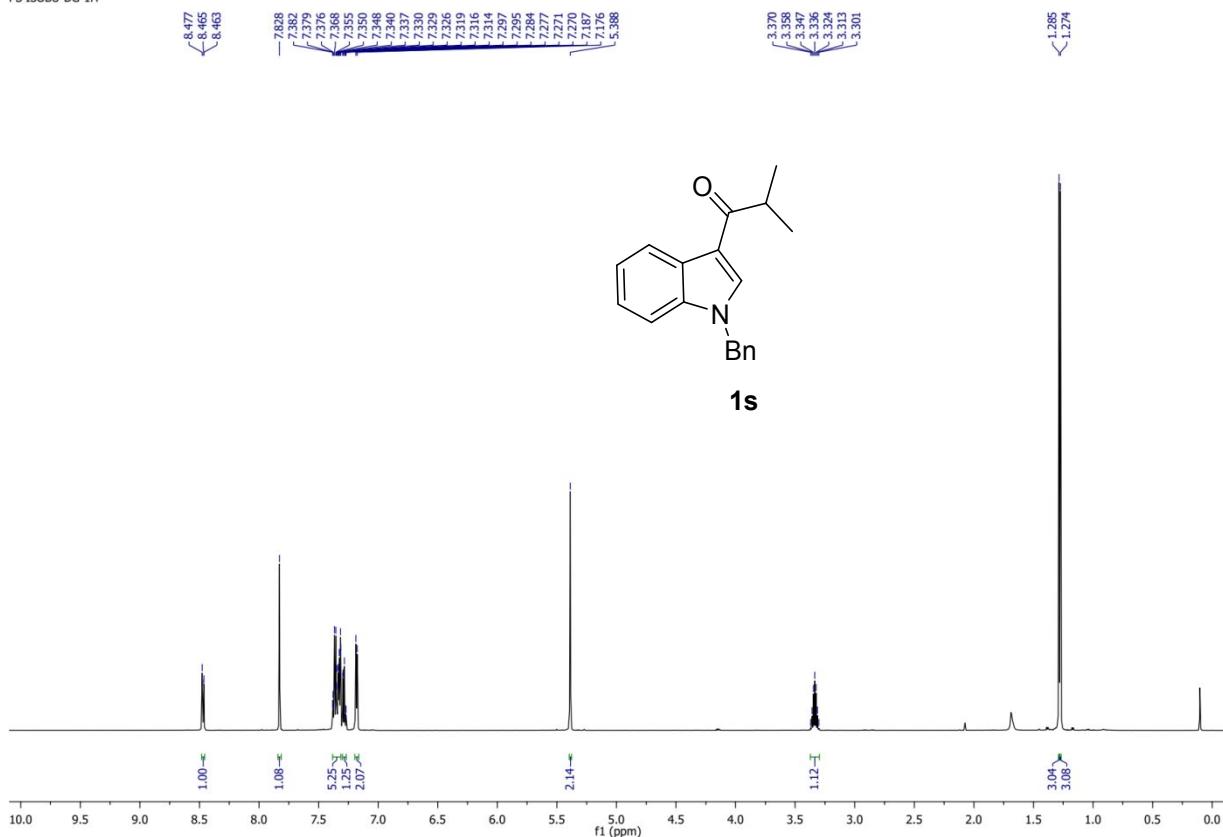
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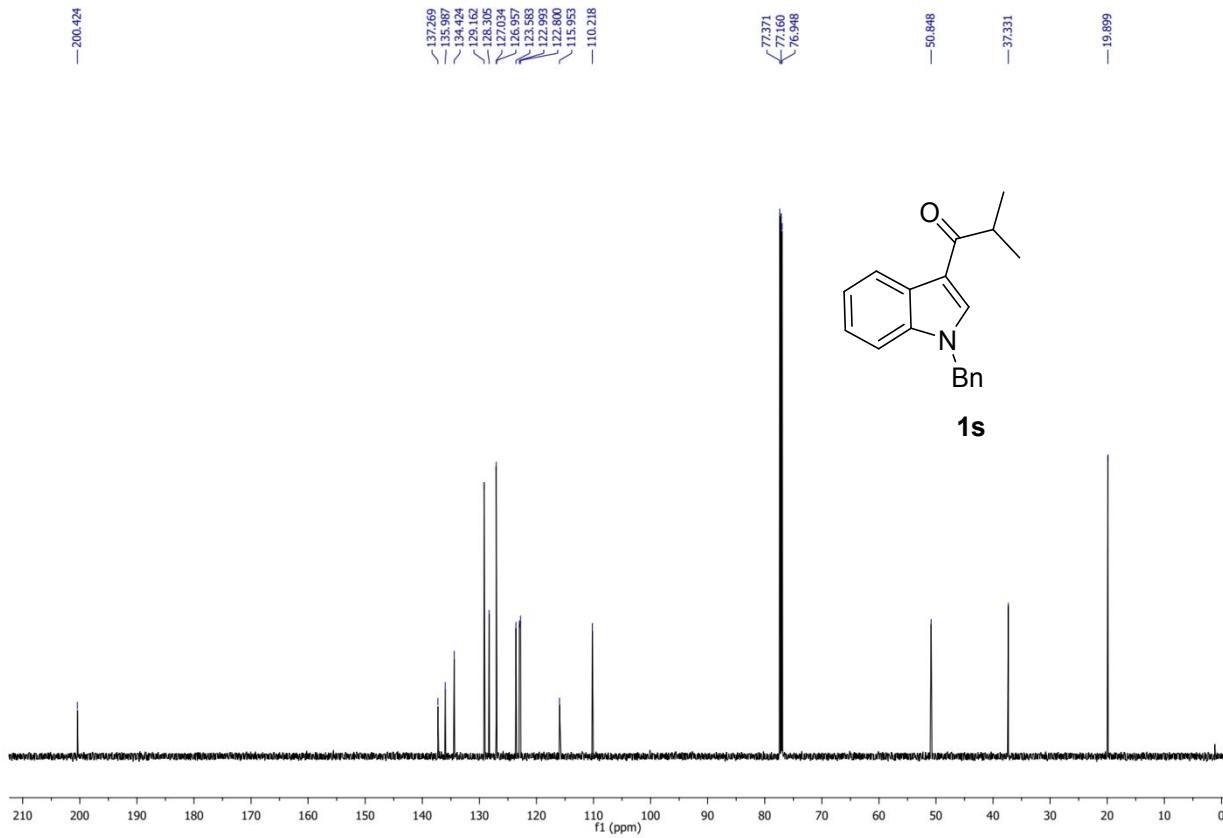
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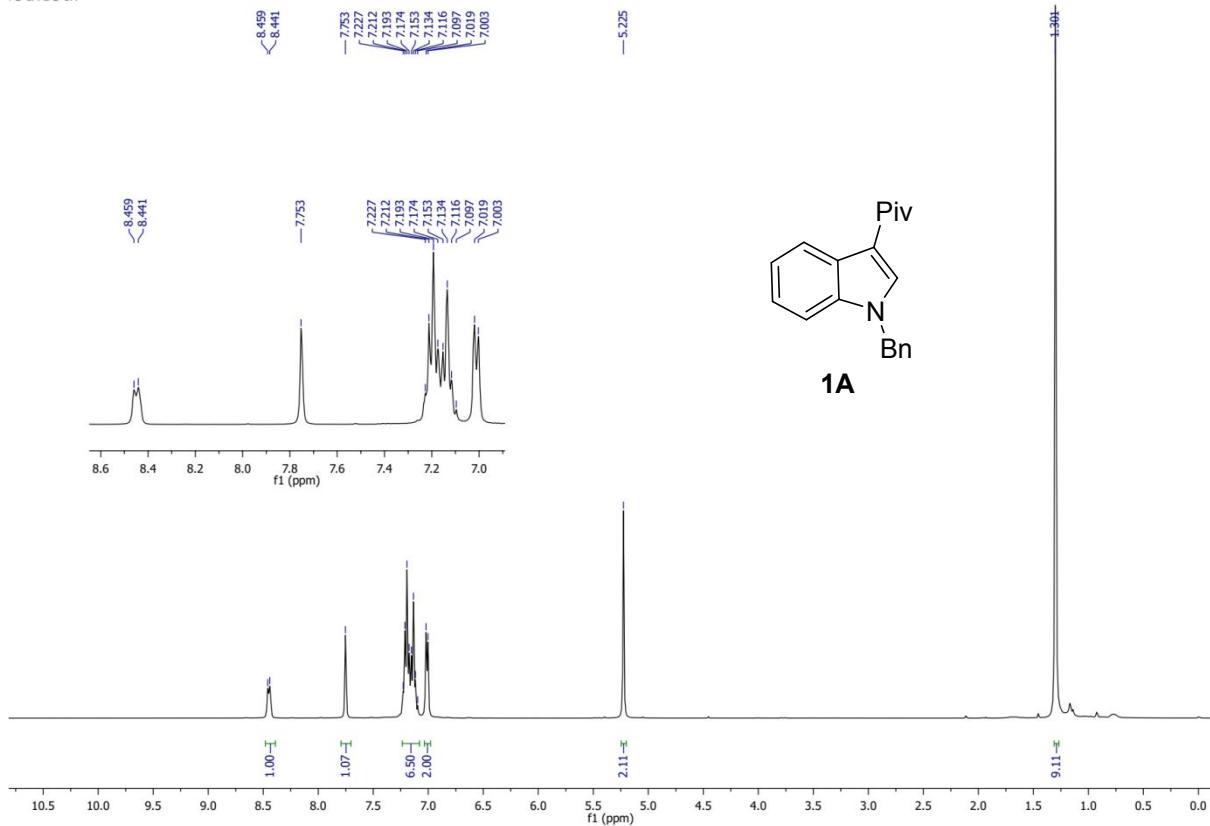
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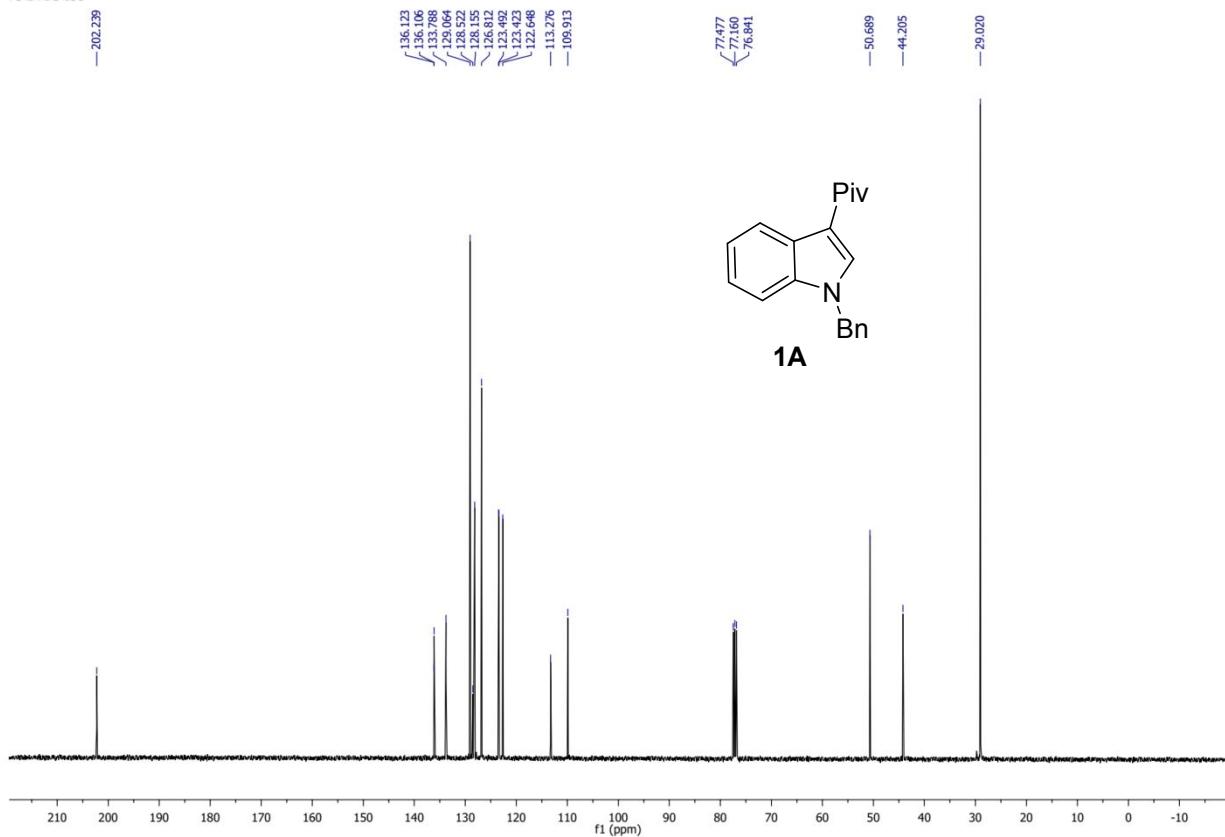
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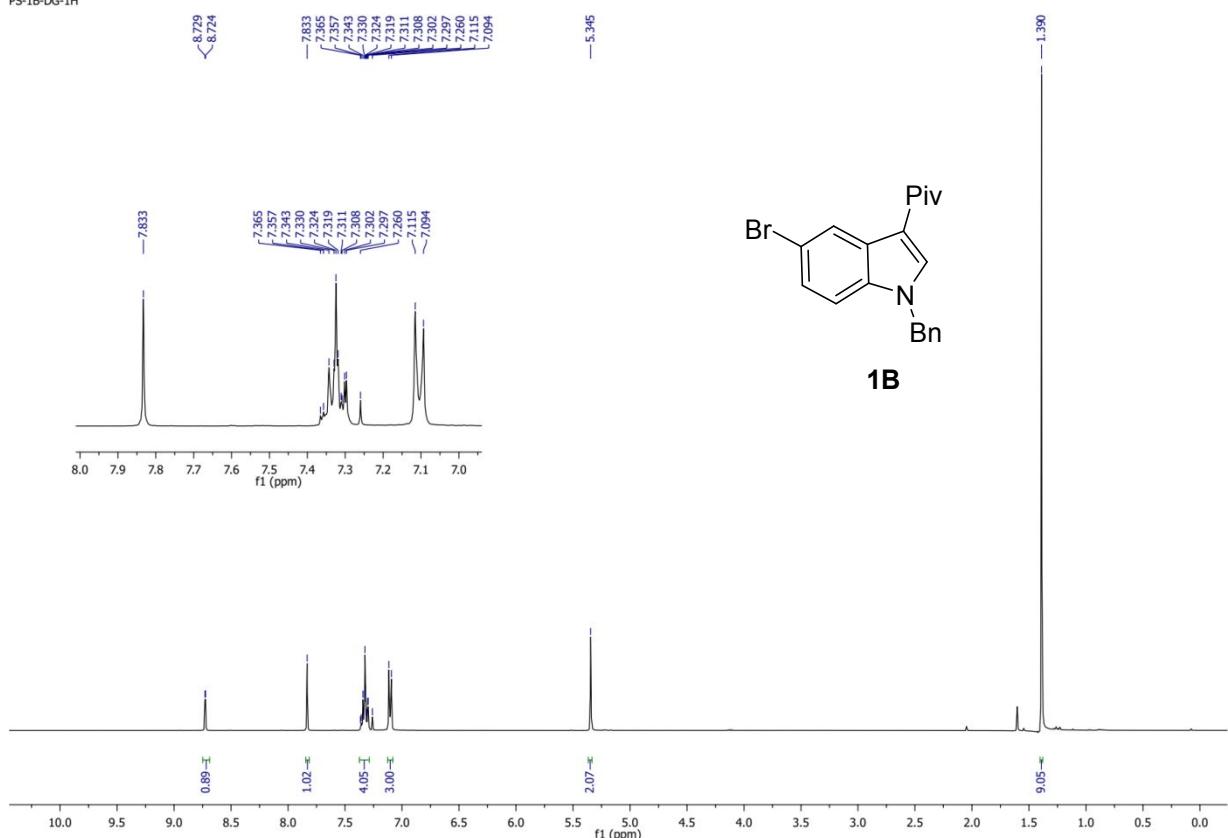
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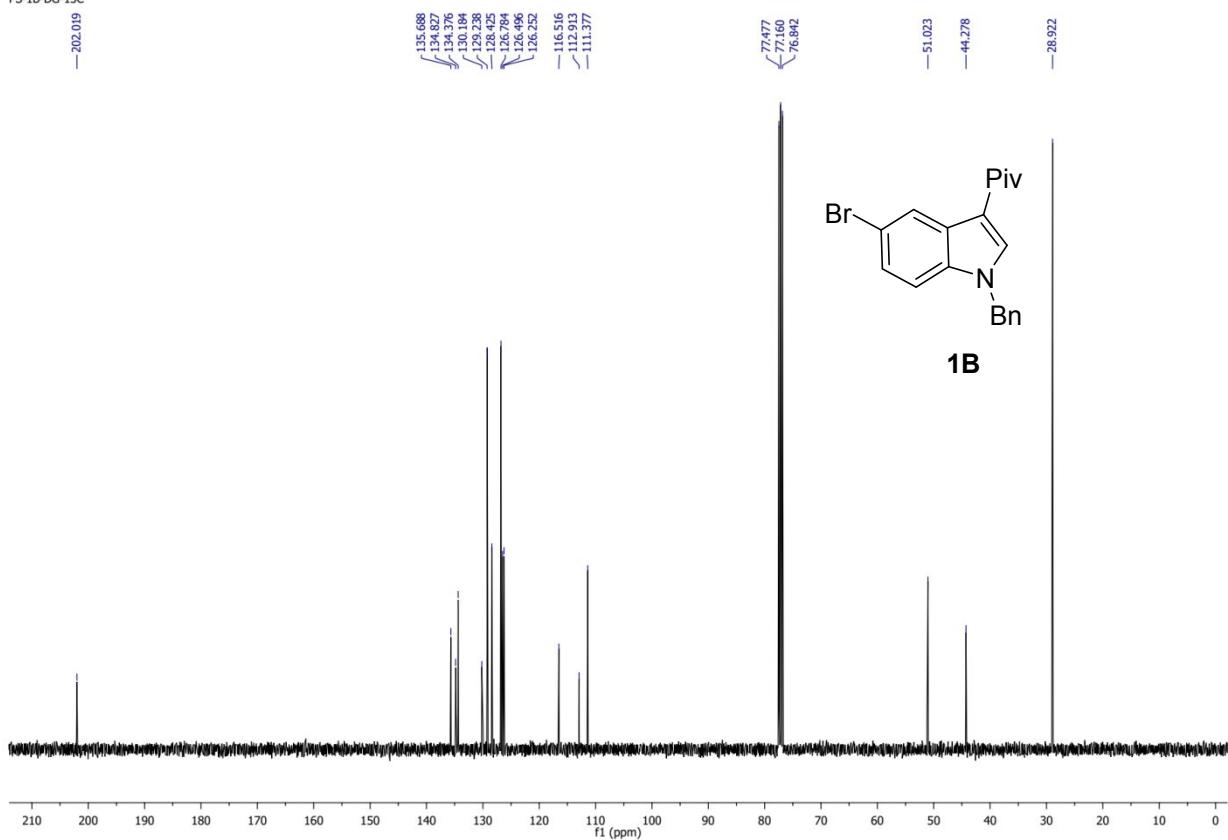
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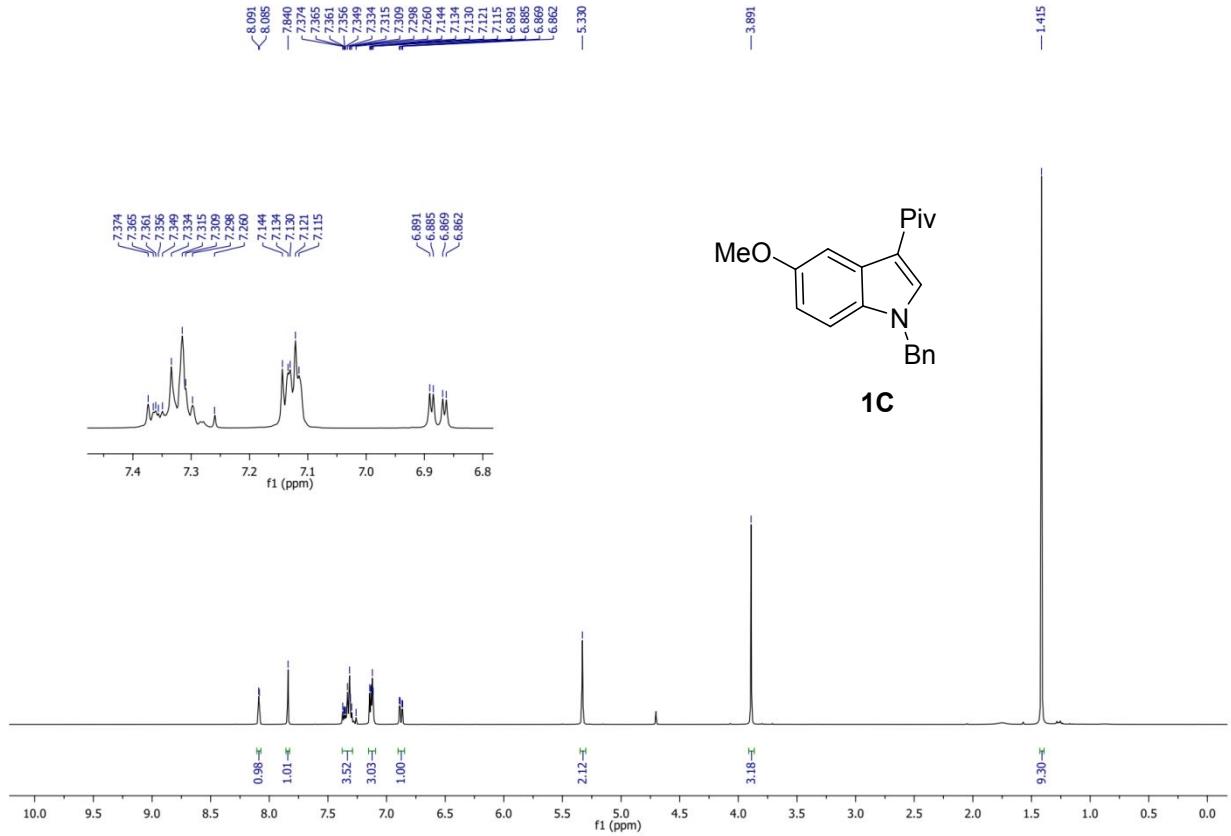
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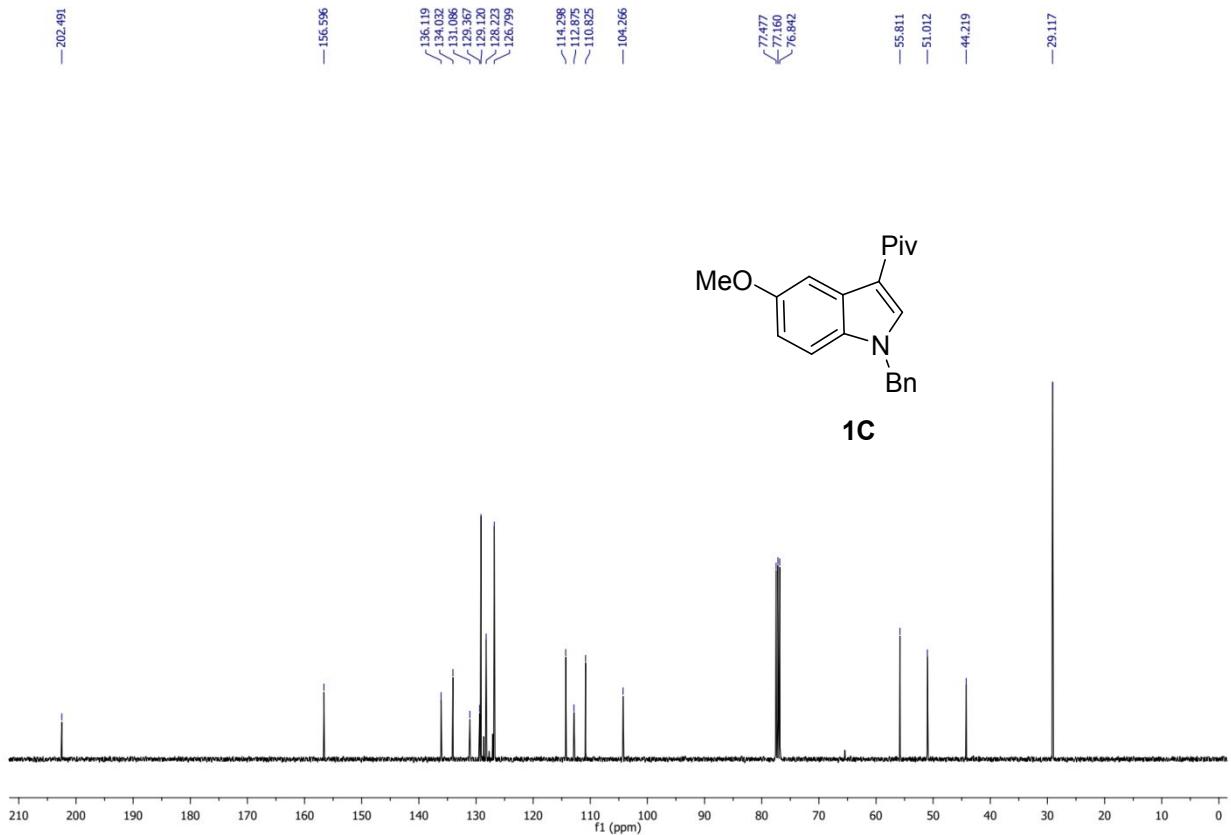
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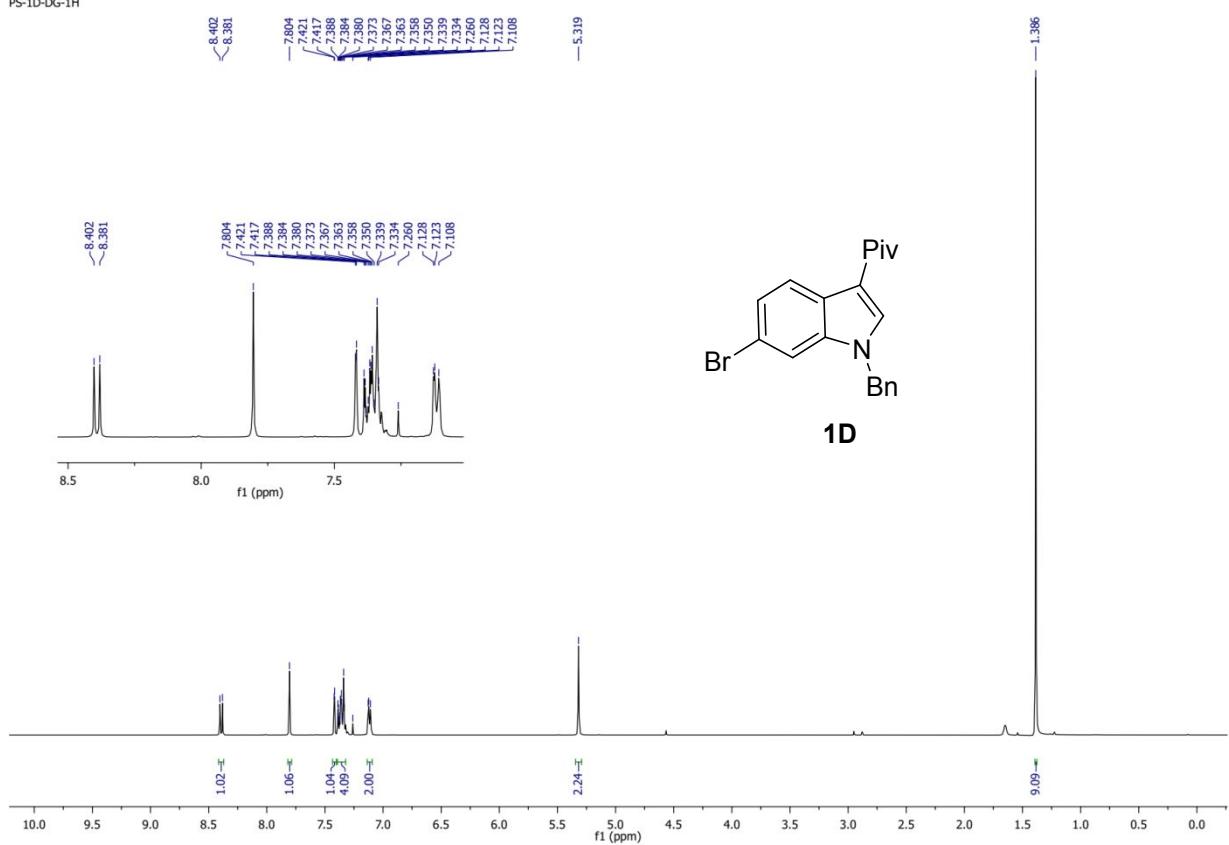
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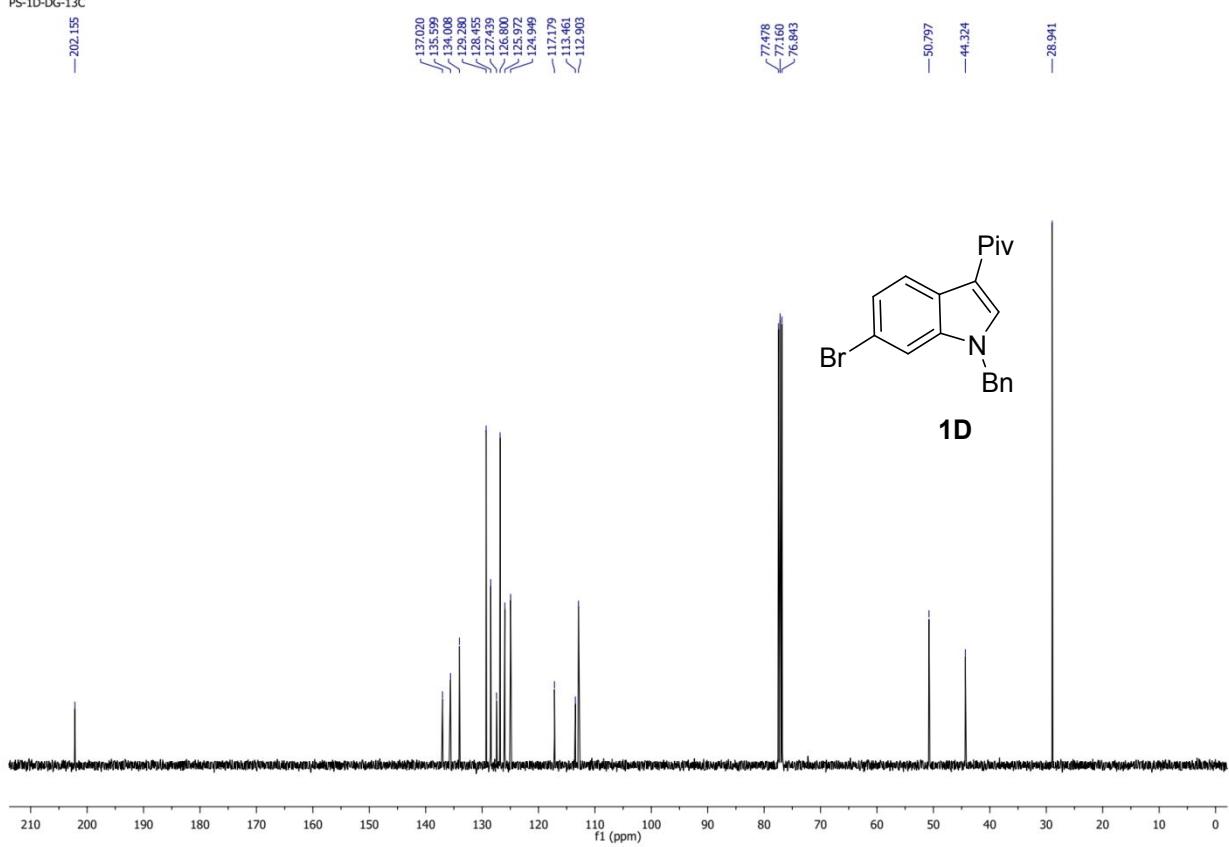
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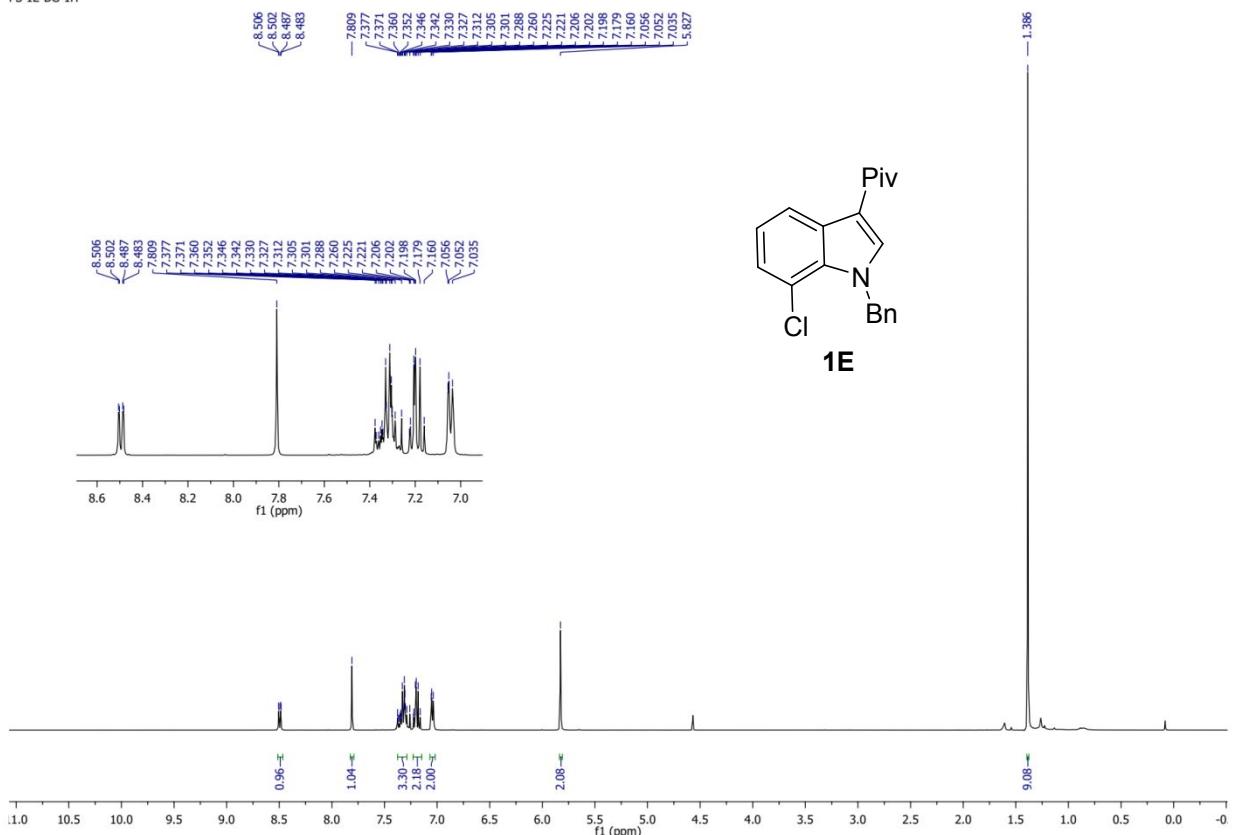
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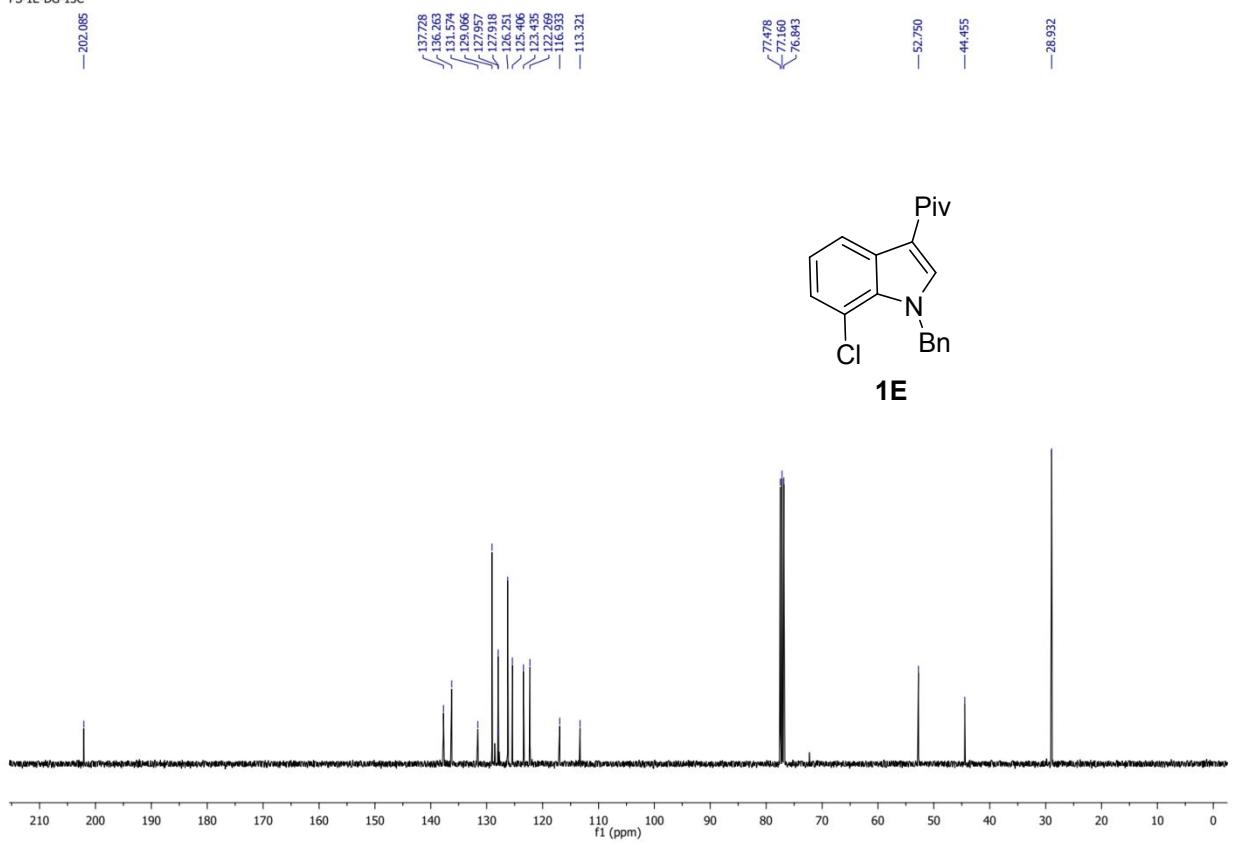
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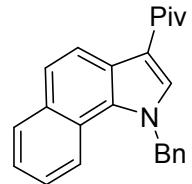
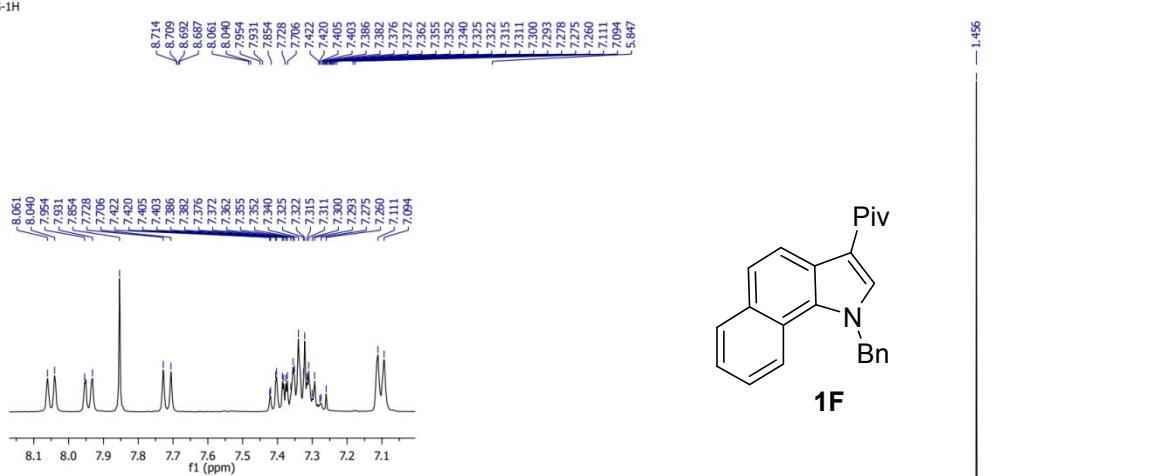
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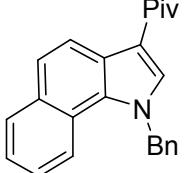
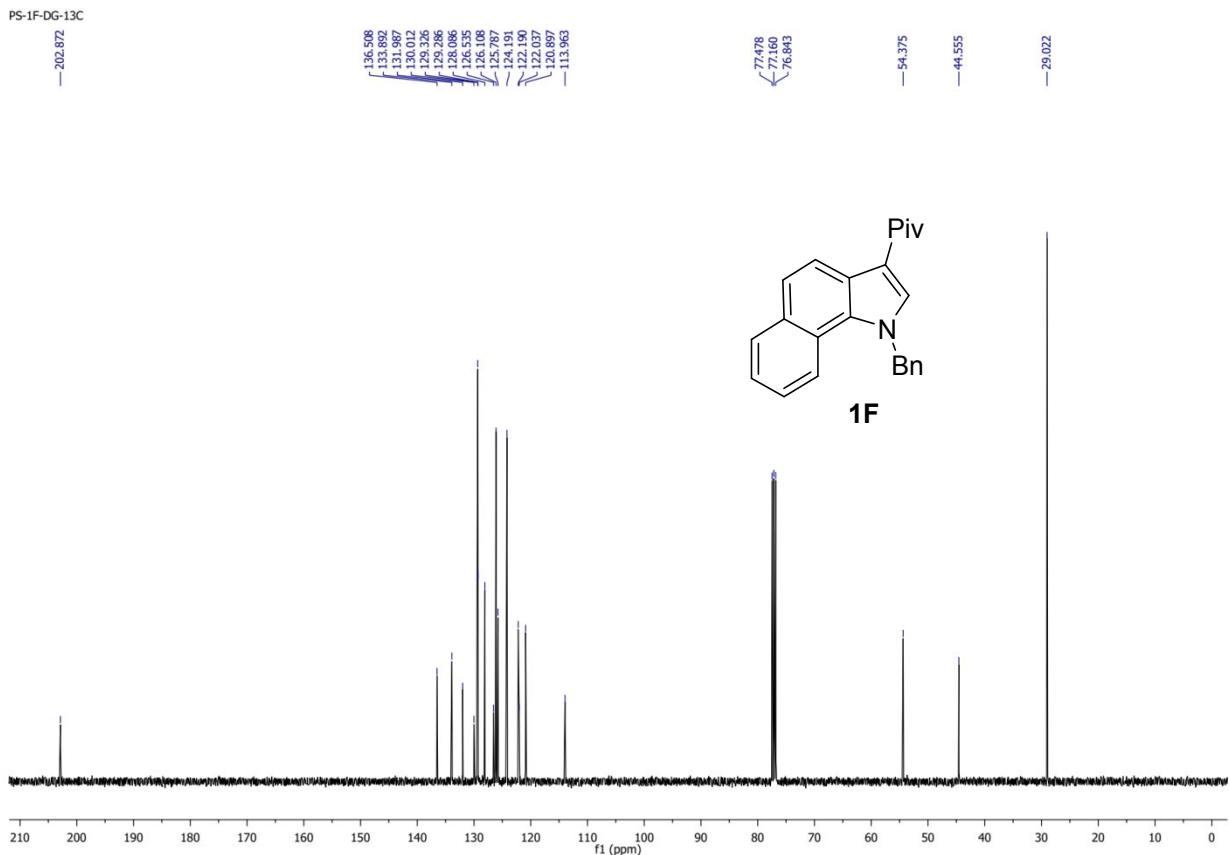


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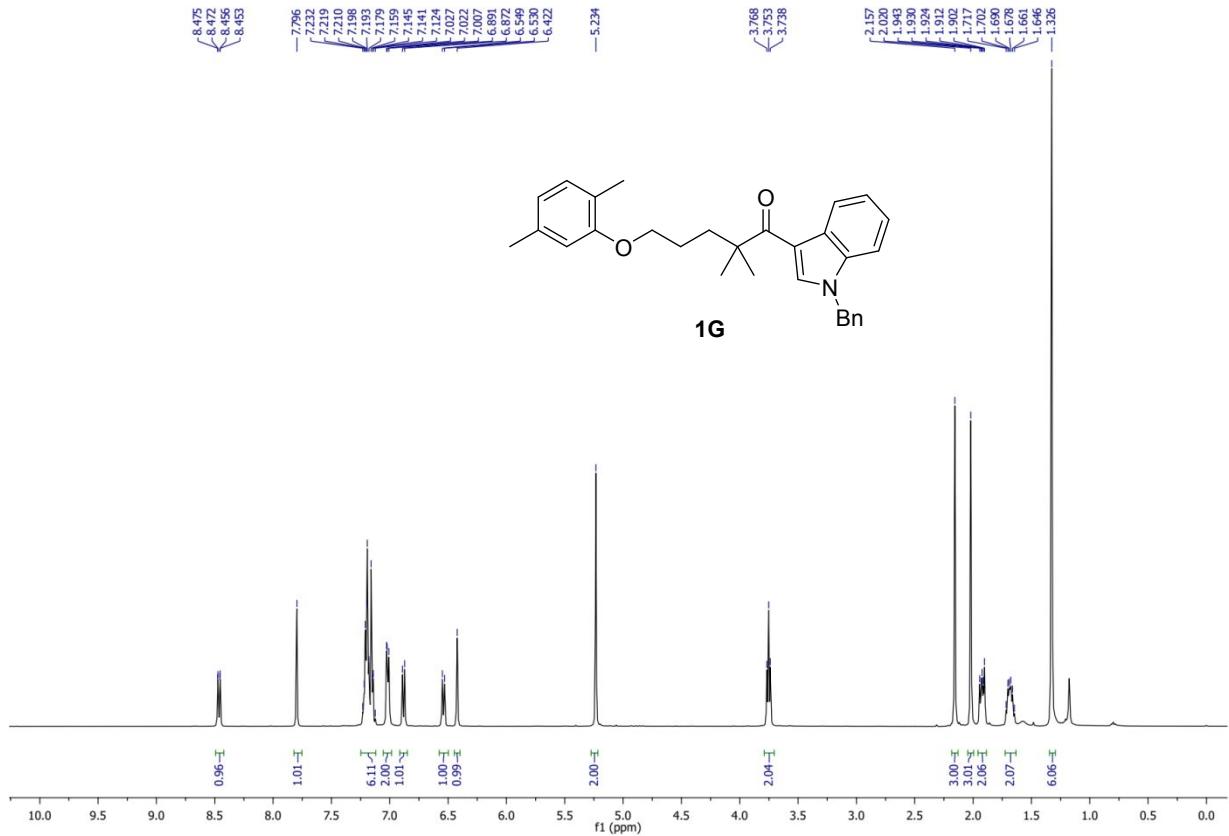
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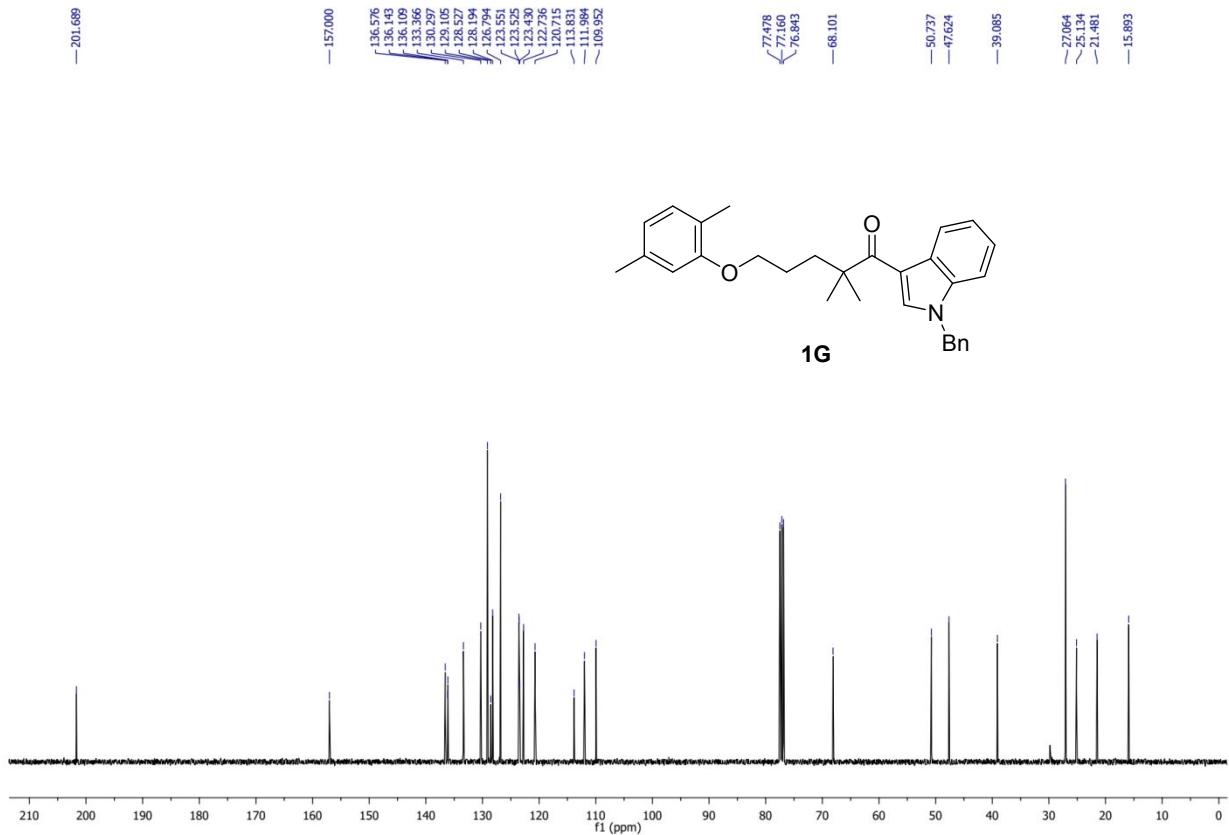


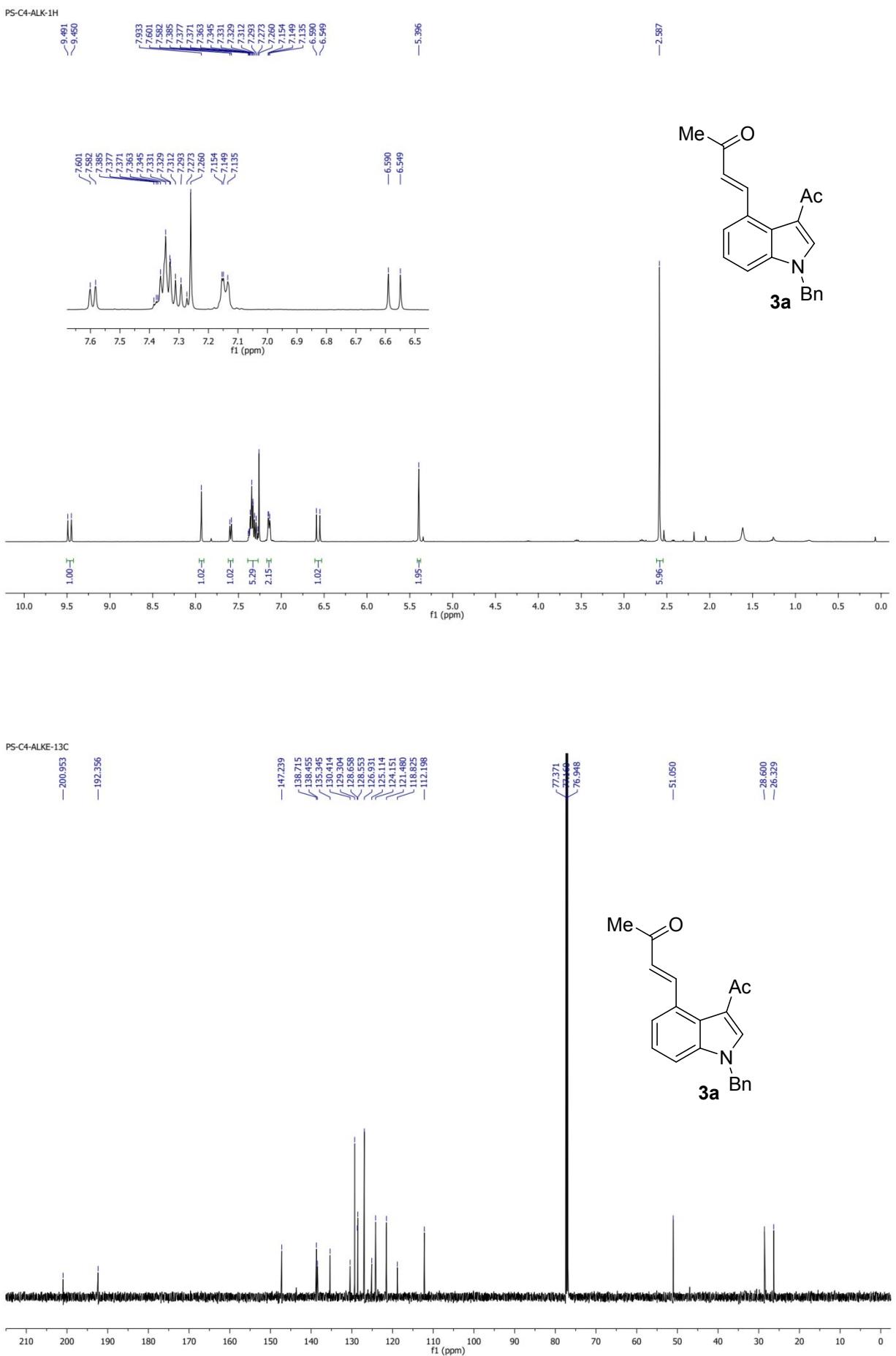
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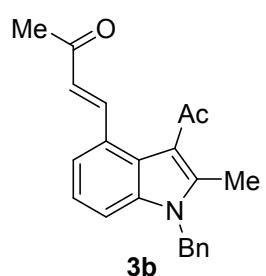
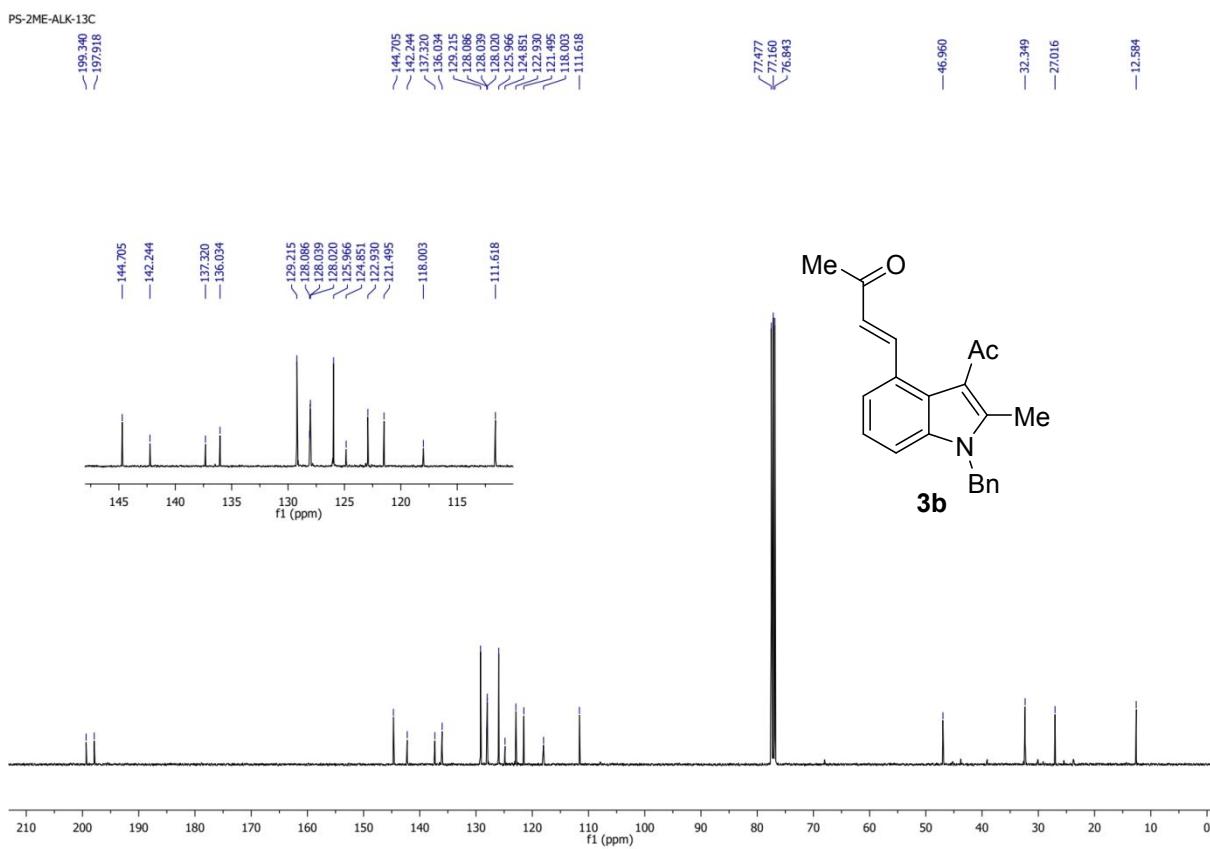
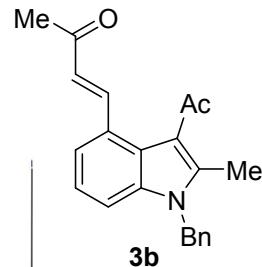
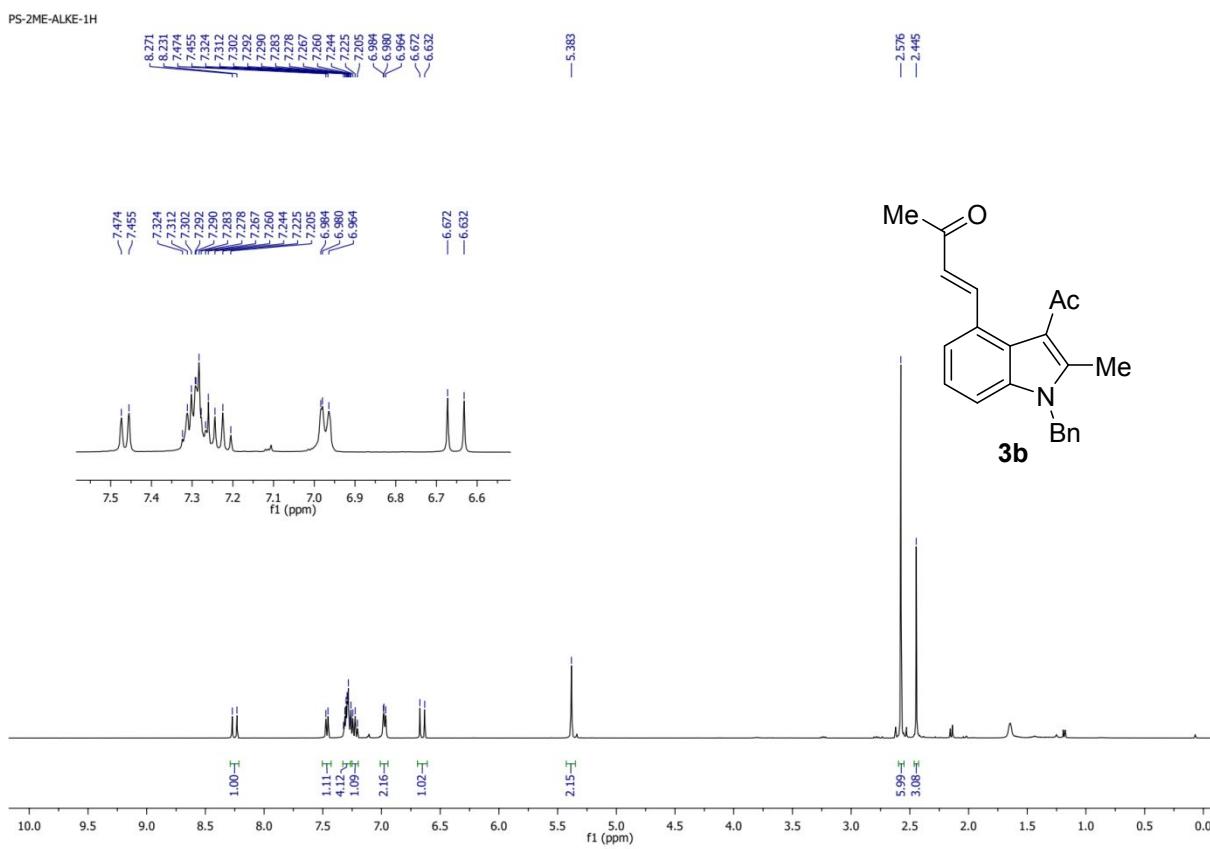
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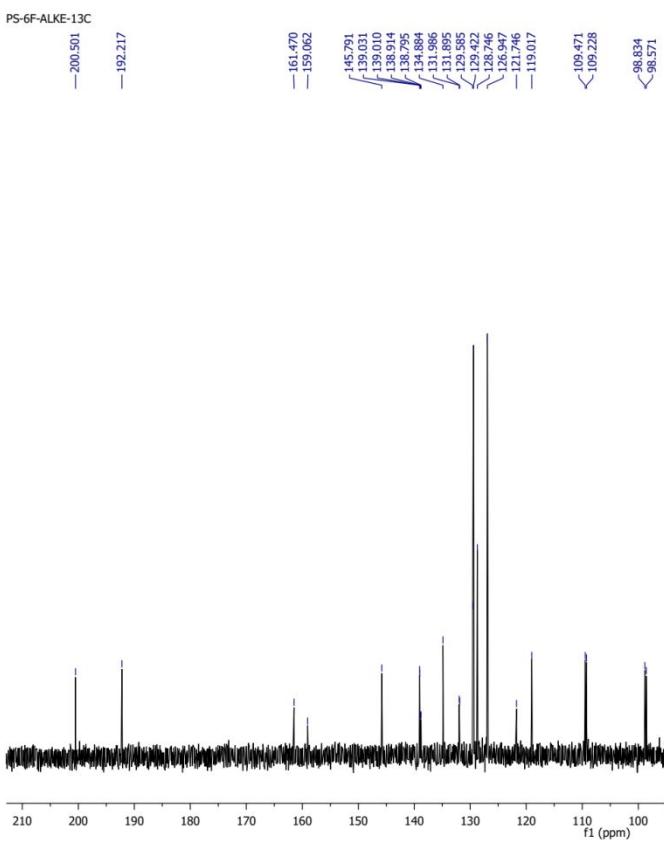
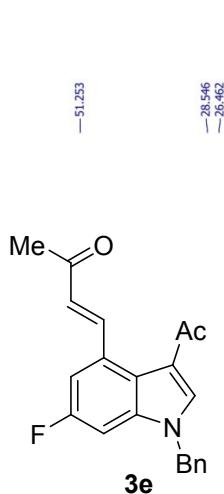
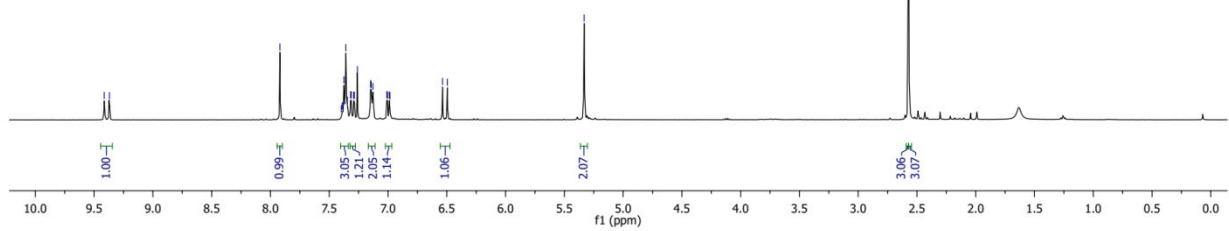
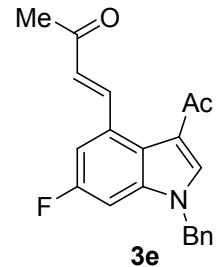
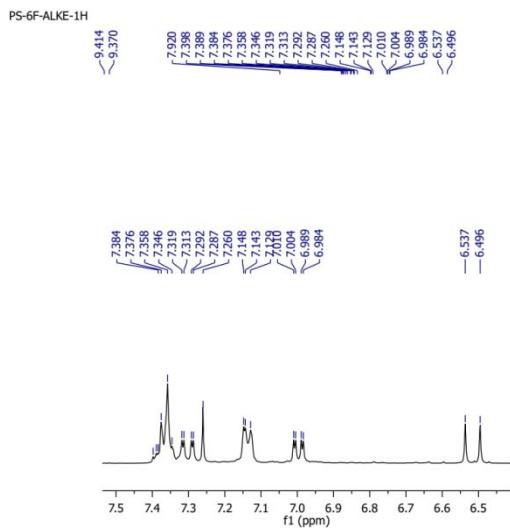


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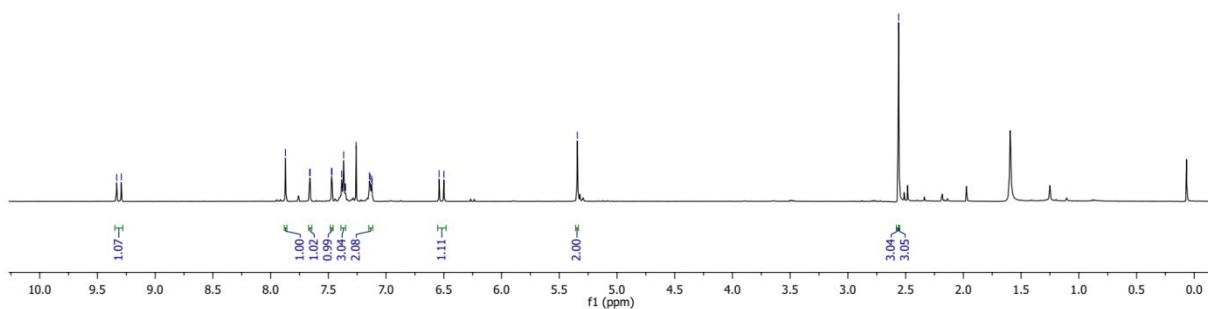
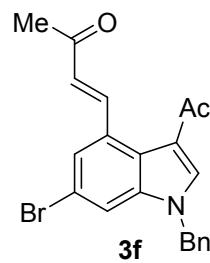
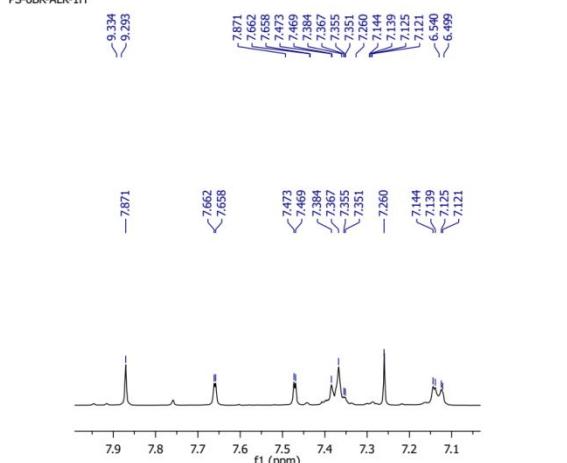




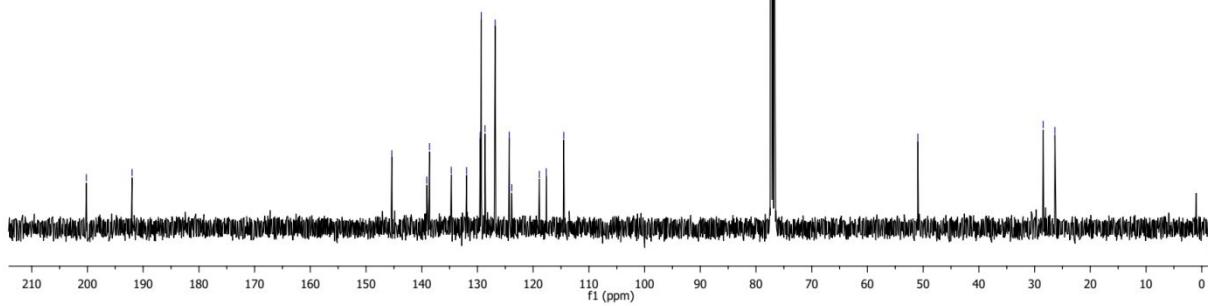
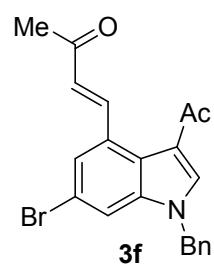


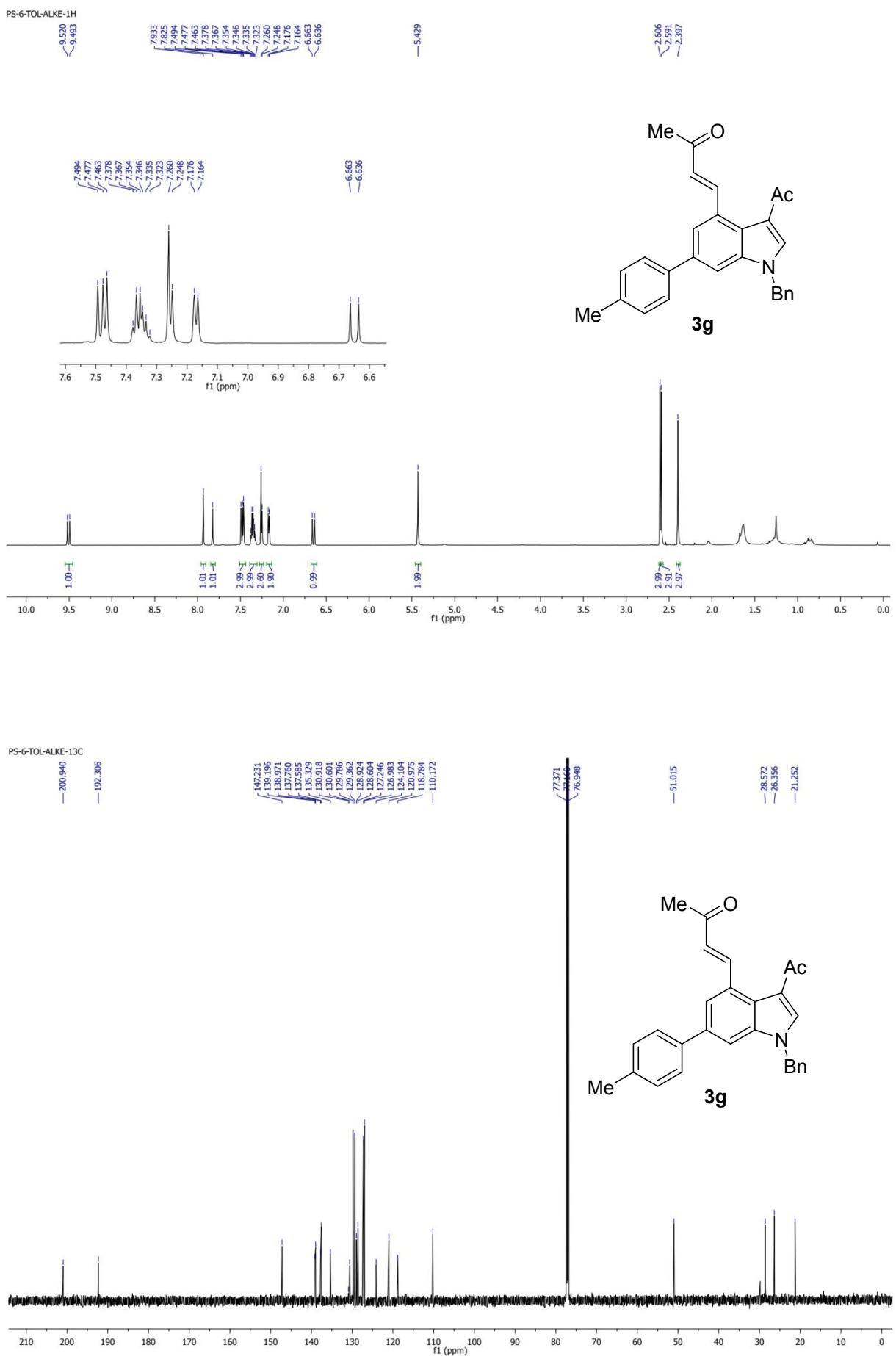


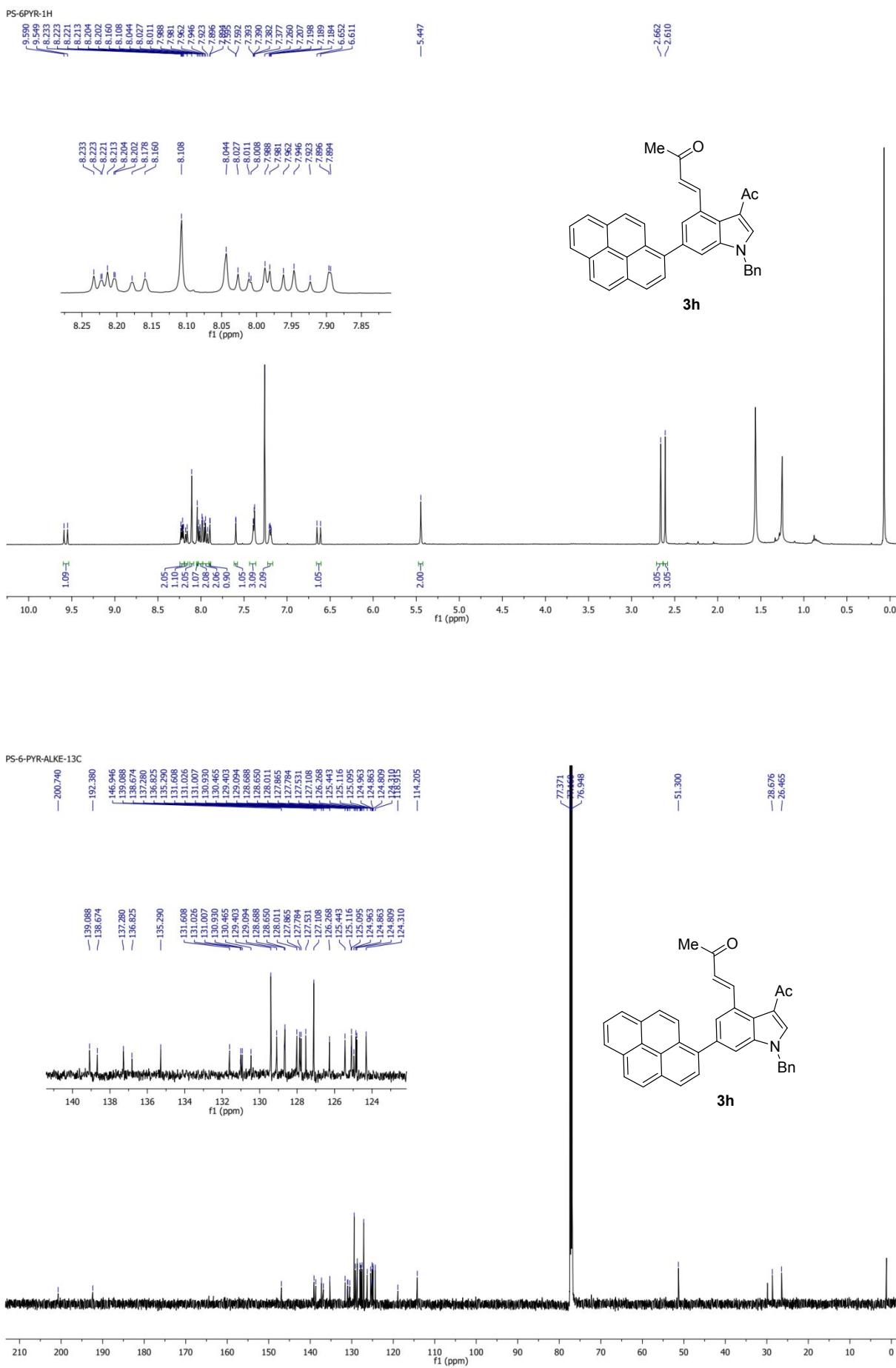
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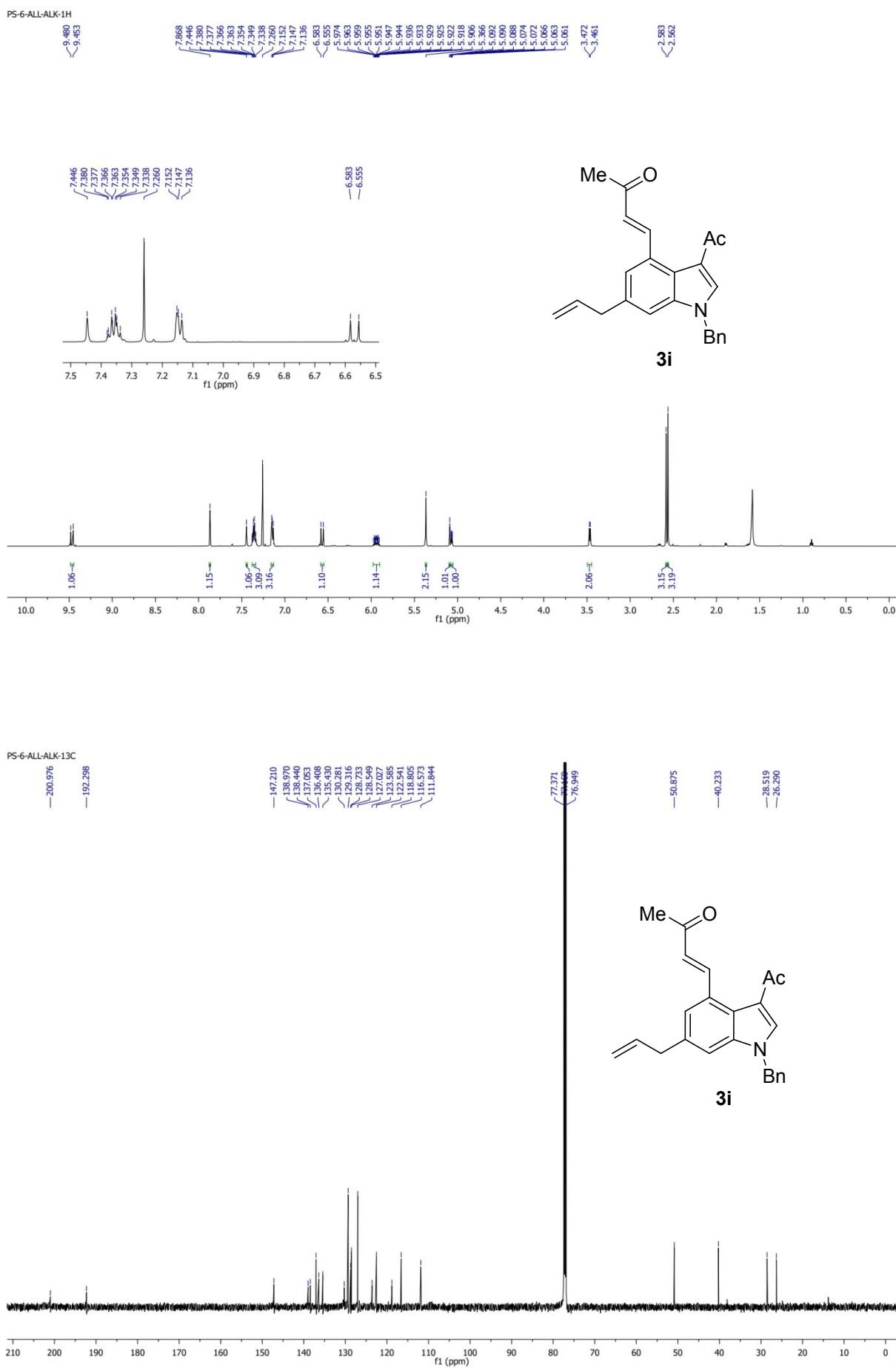


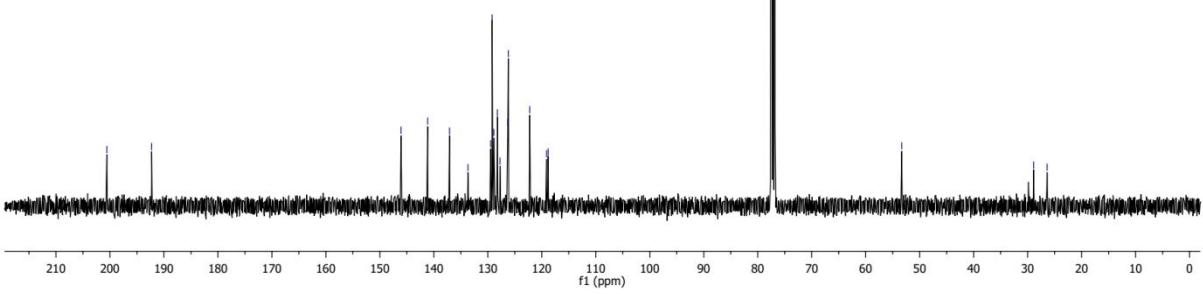
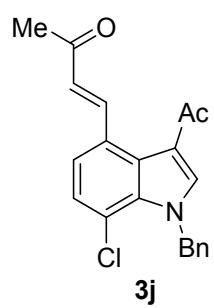
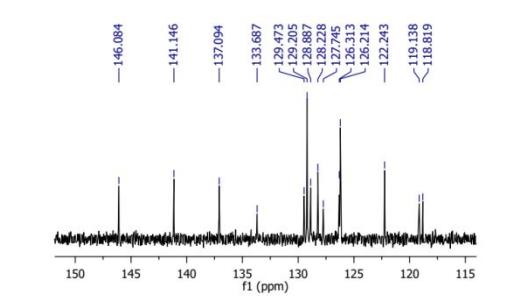
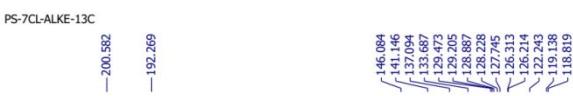
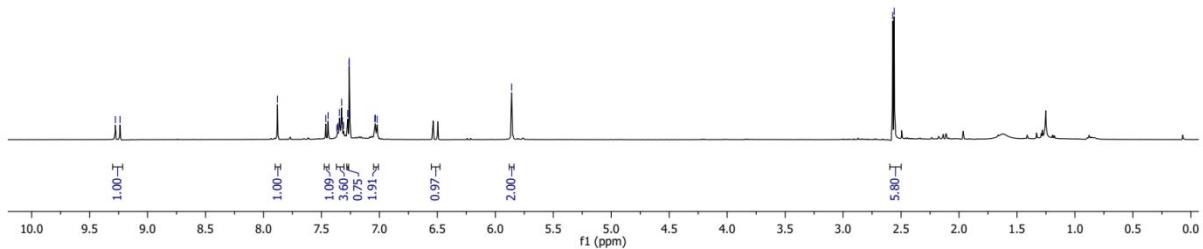
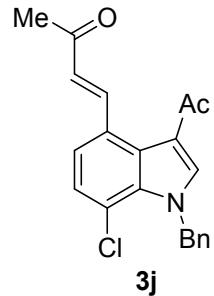
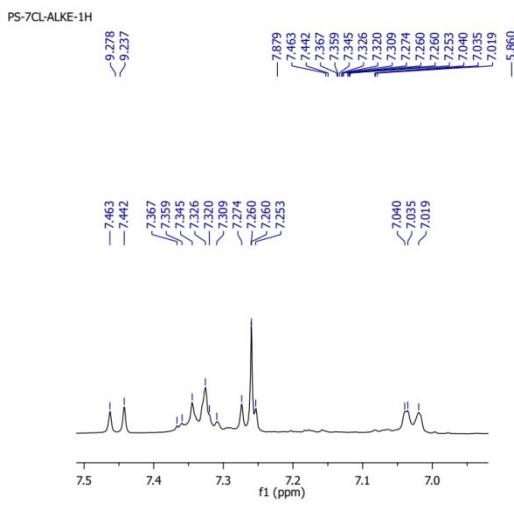
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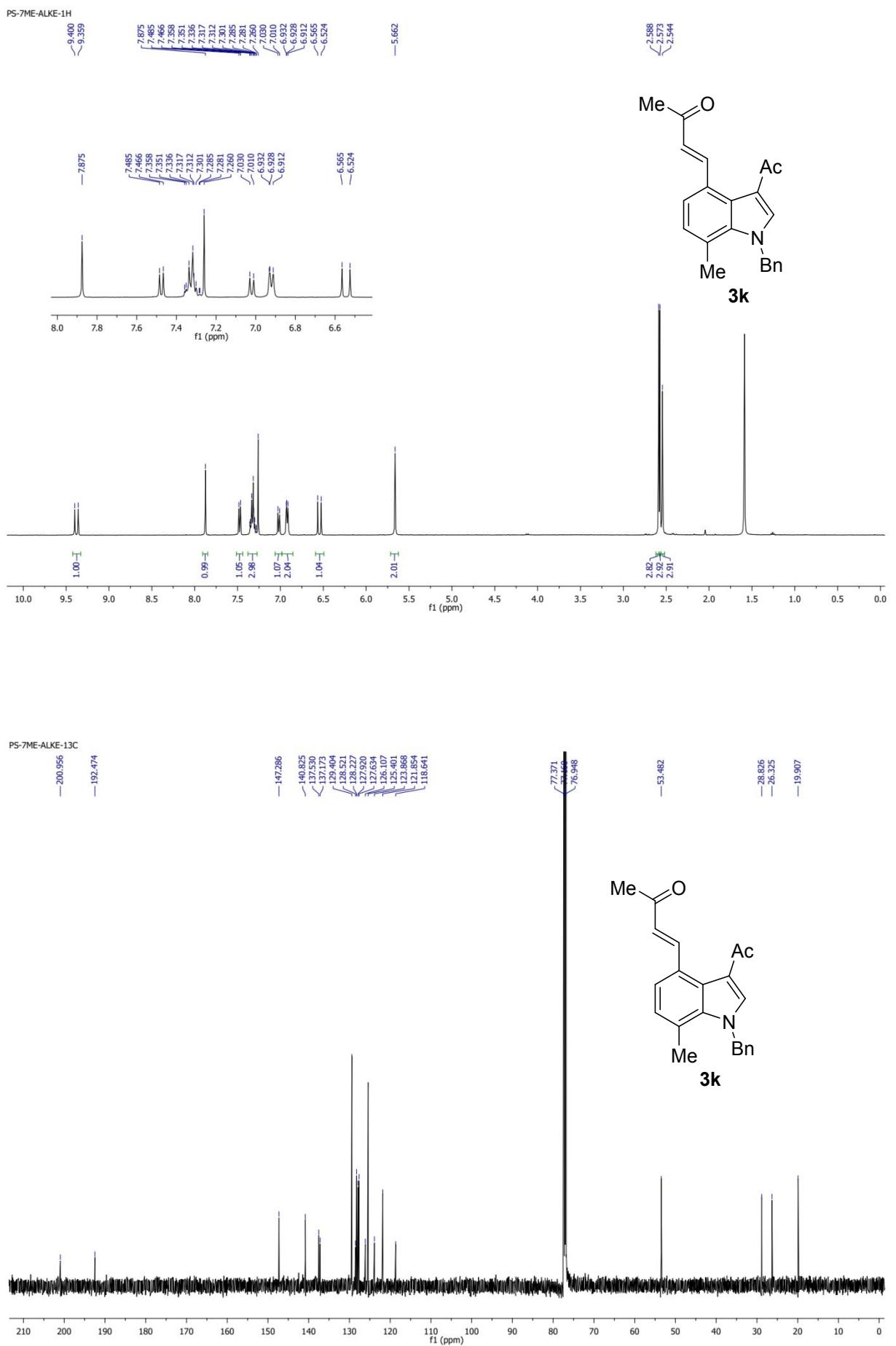


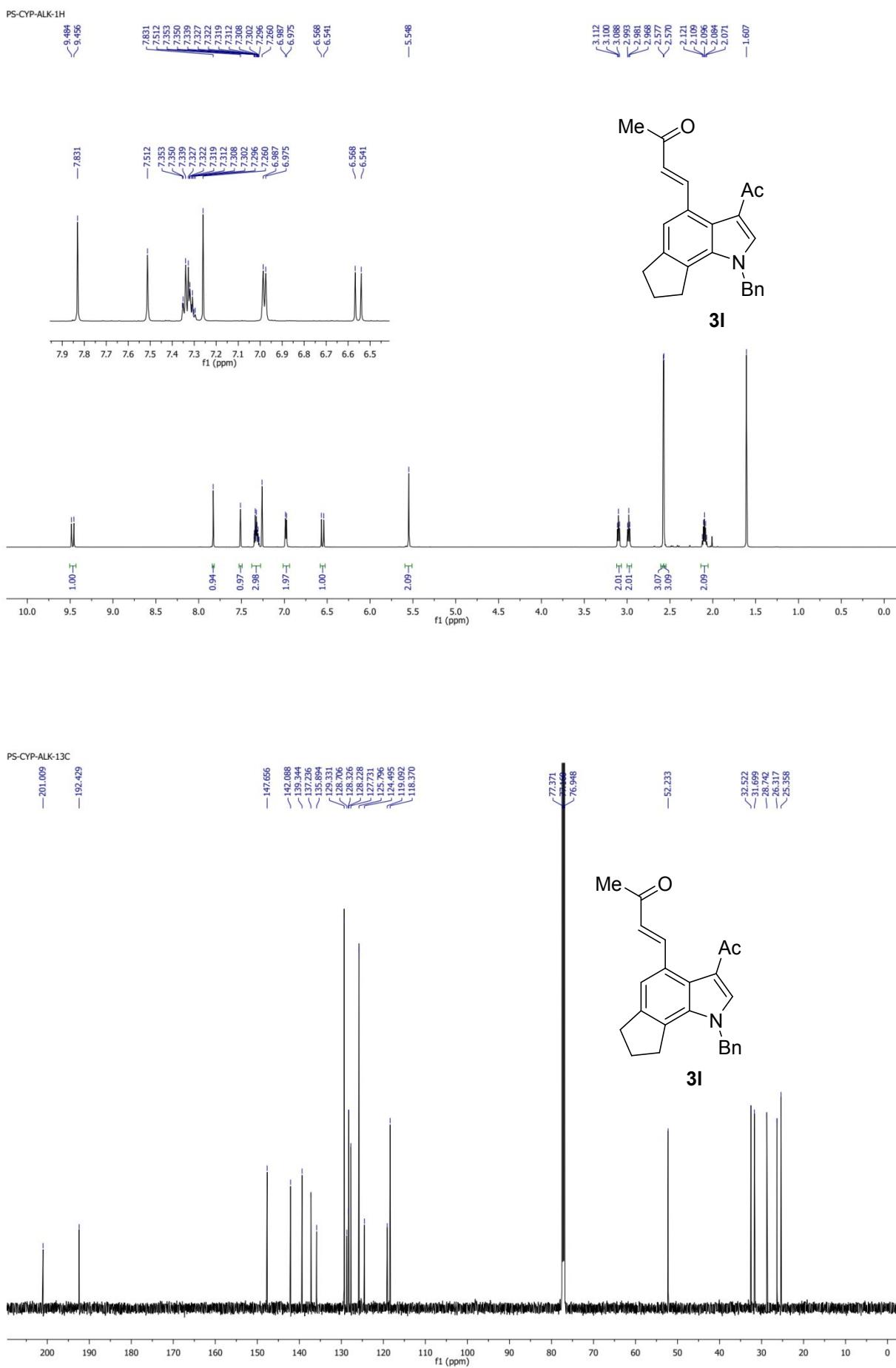


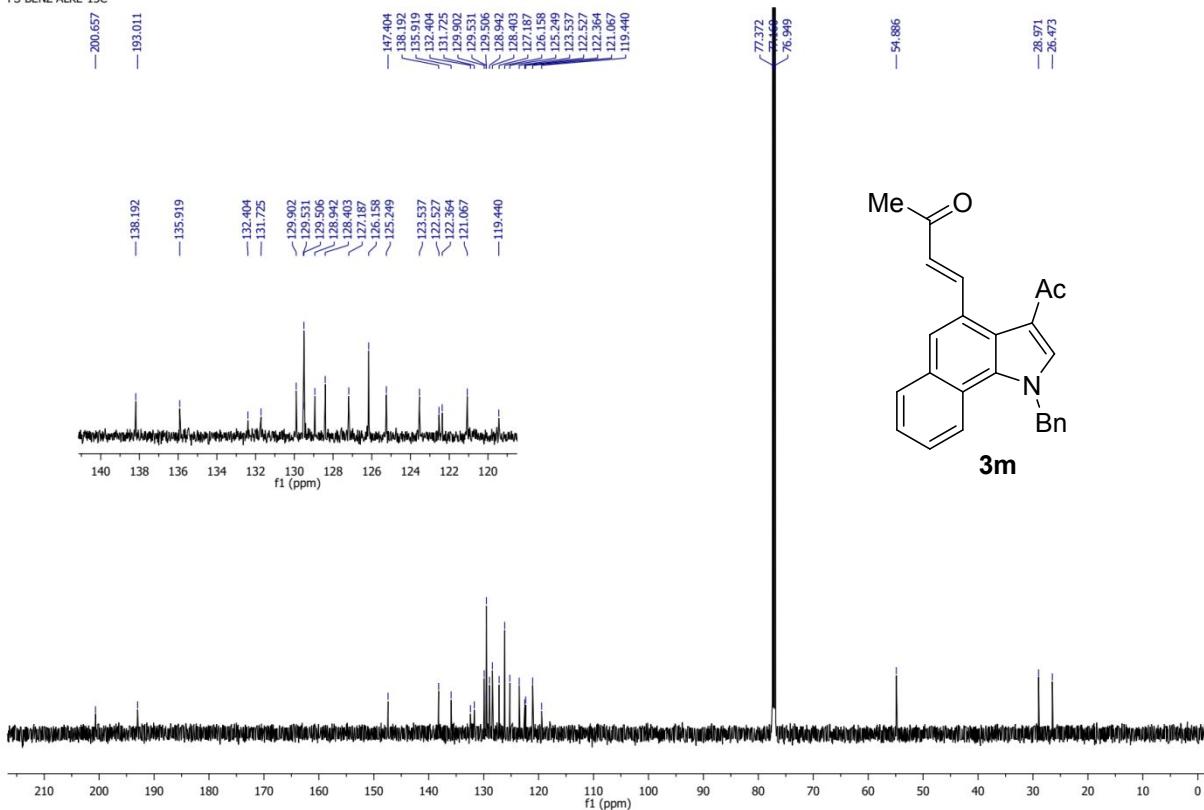
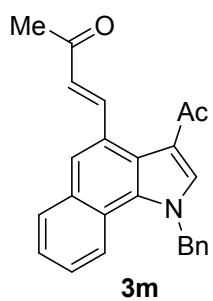
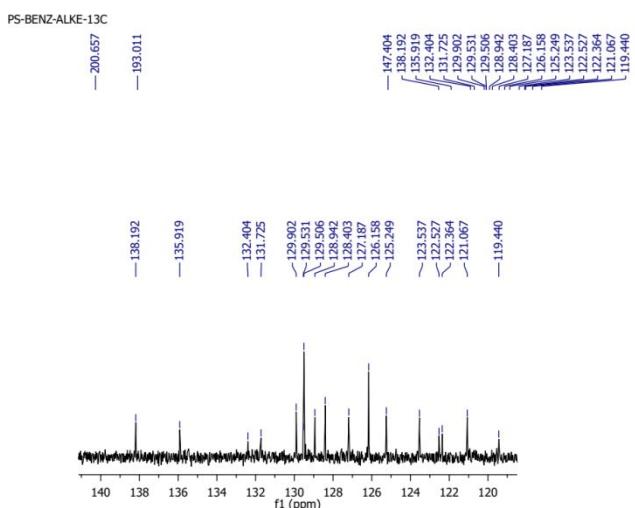
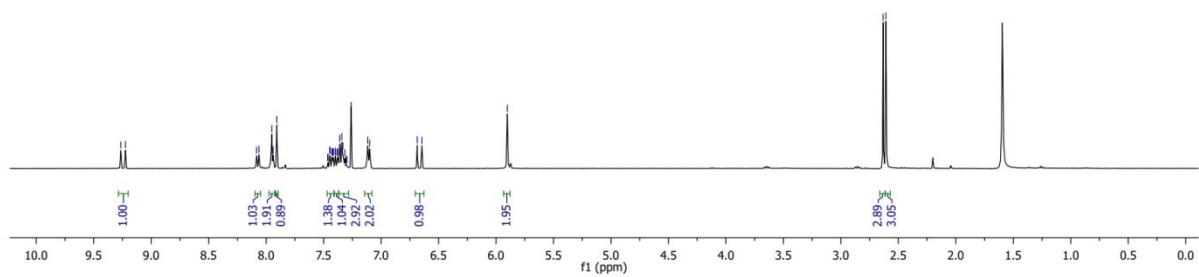
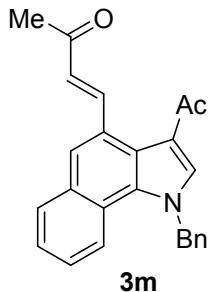
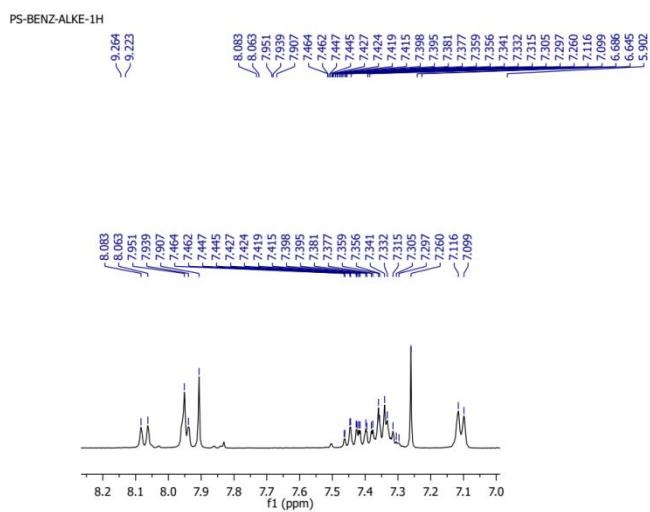




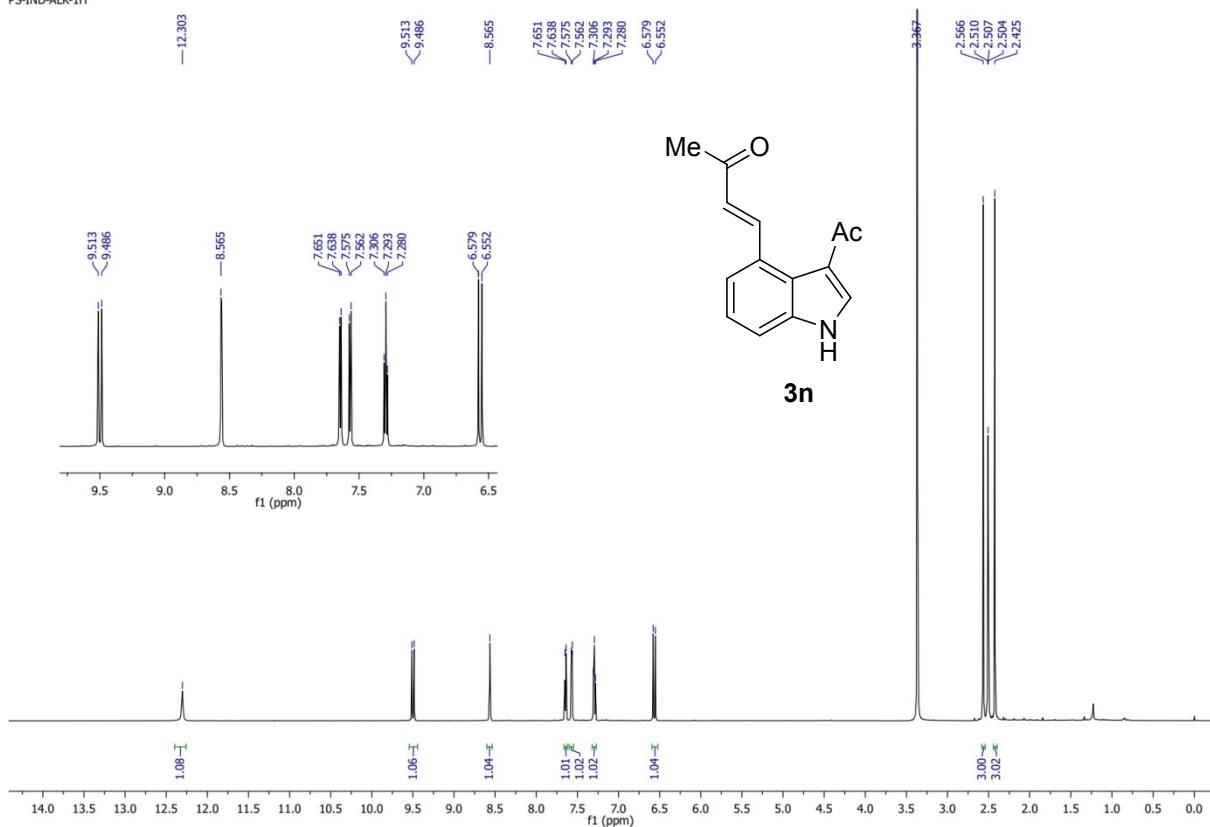




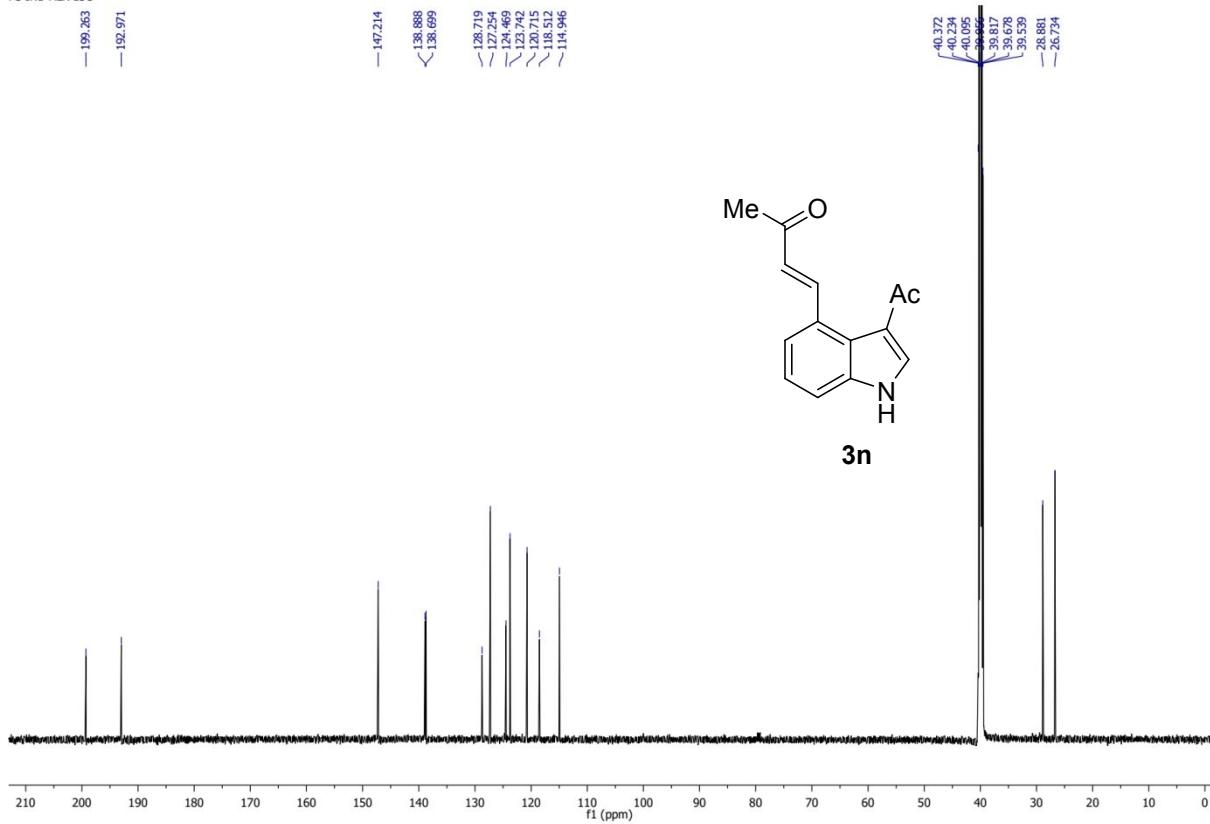


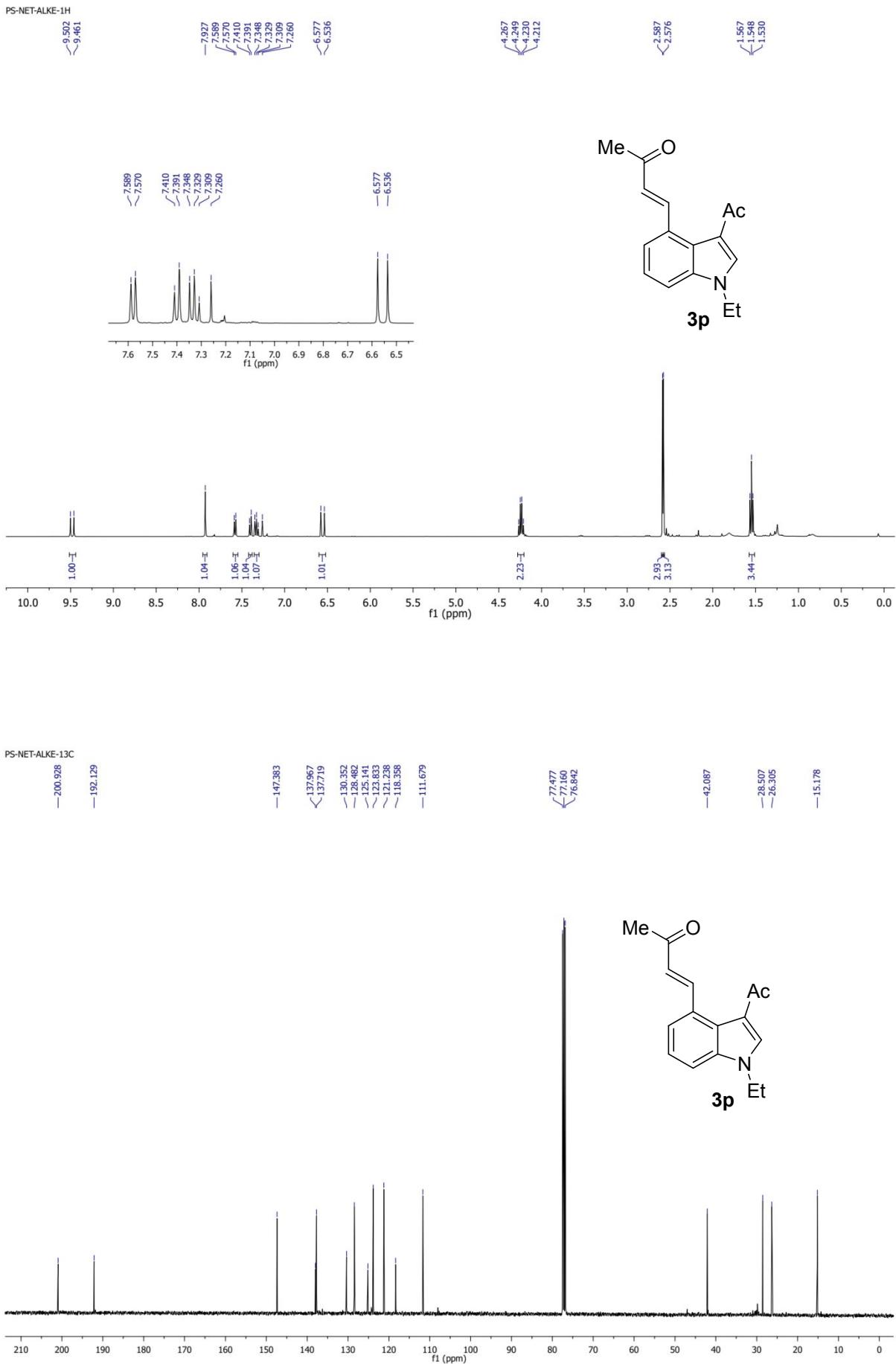


PS-IND-ALK-1H

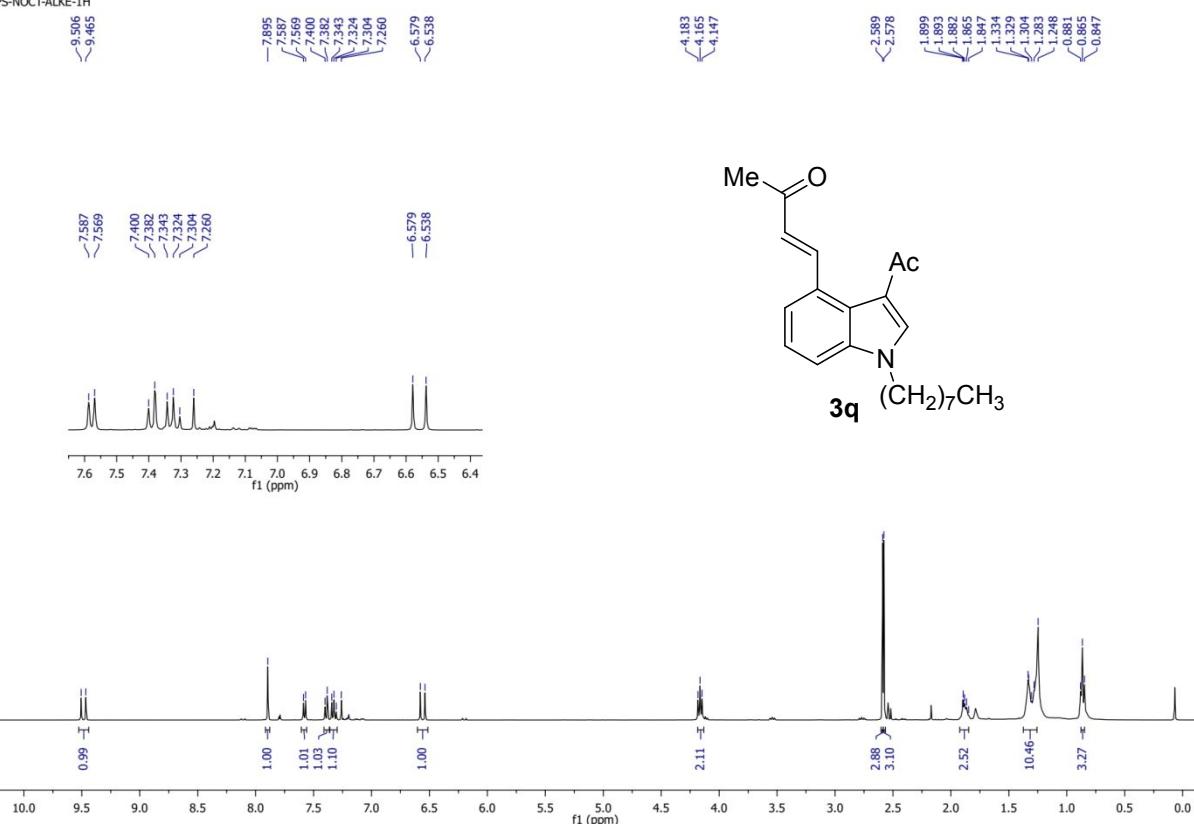


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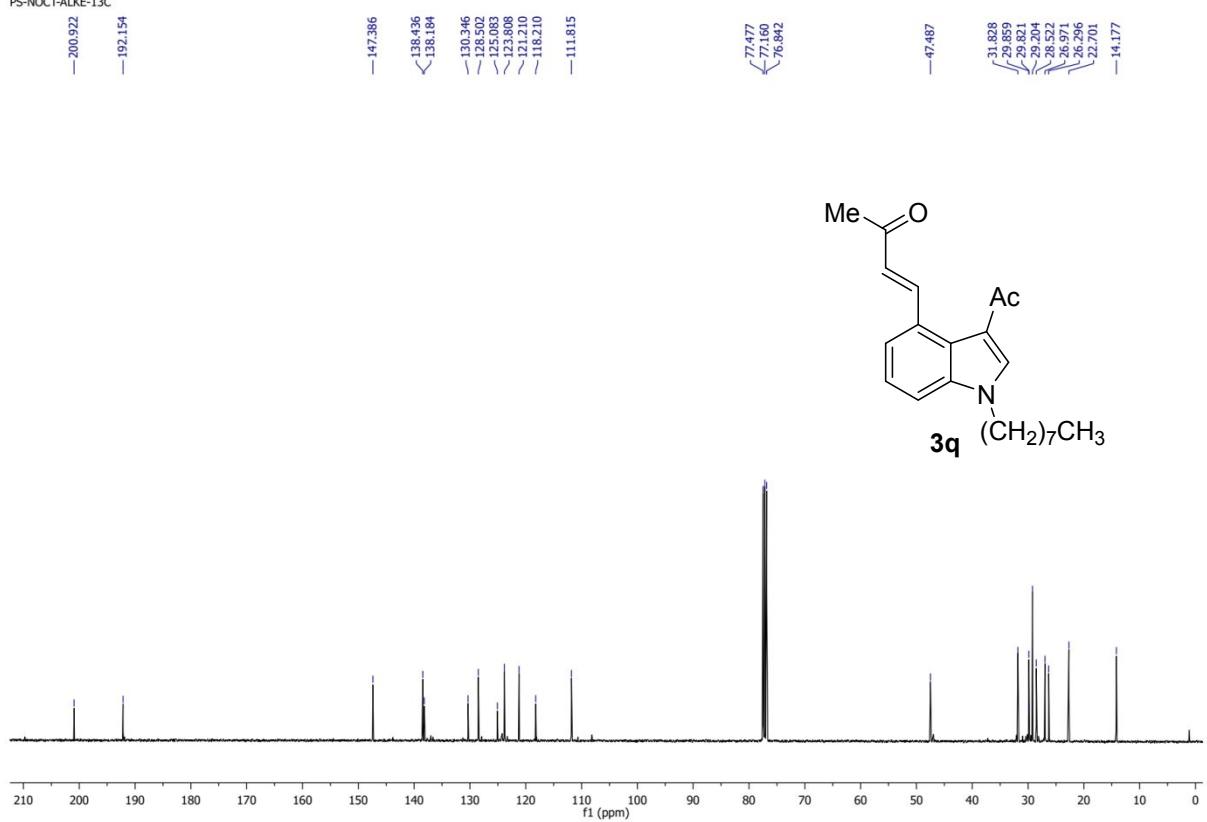




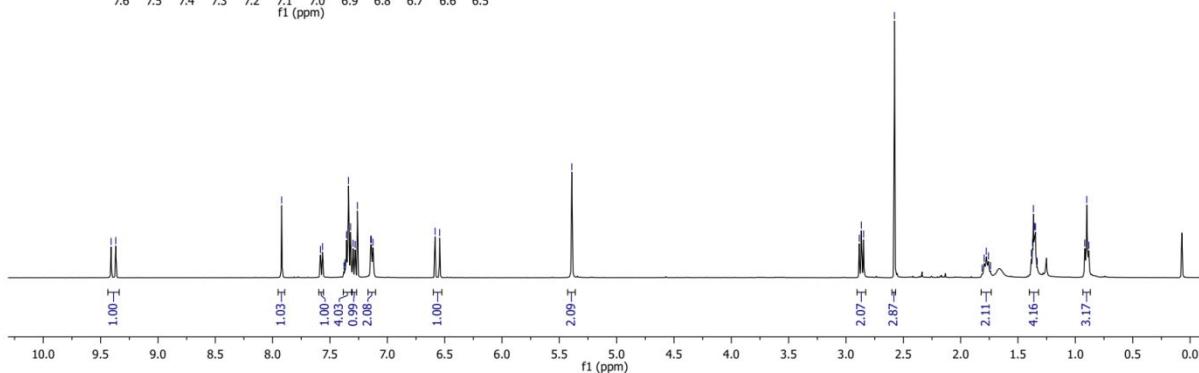
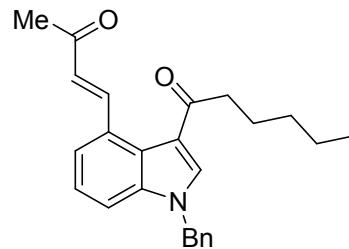
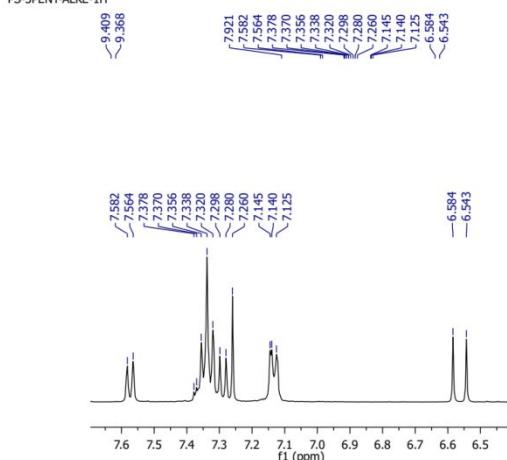
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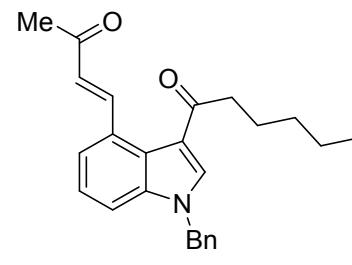
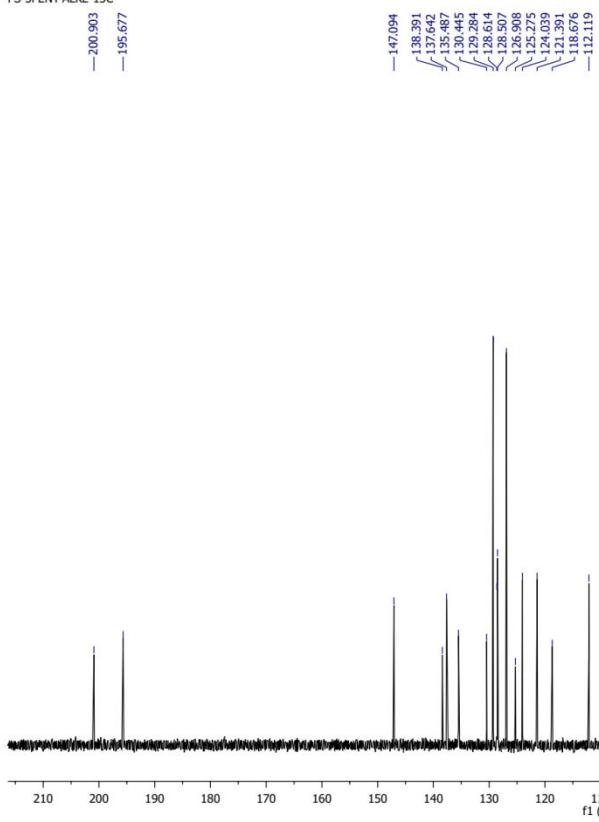
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PS-3PENT-ALKE-1H

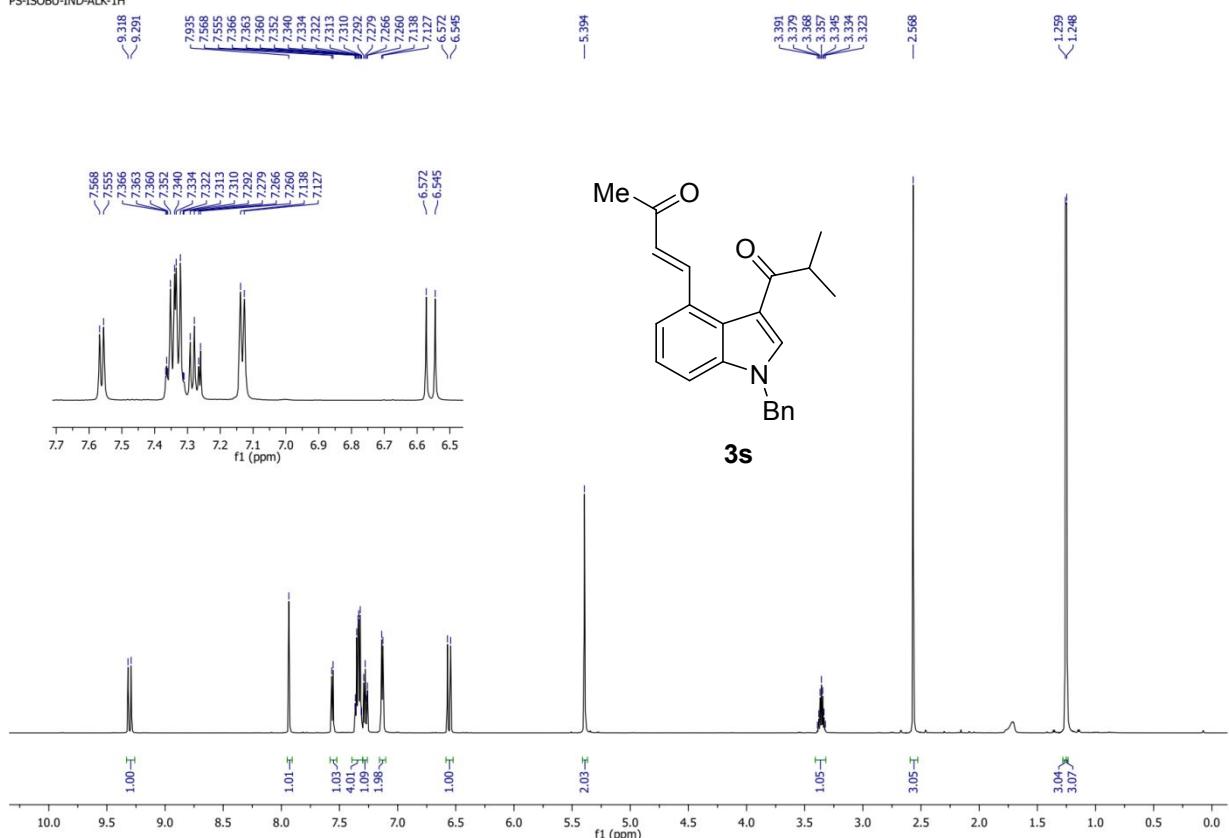


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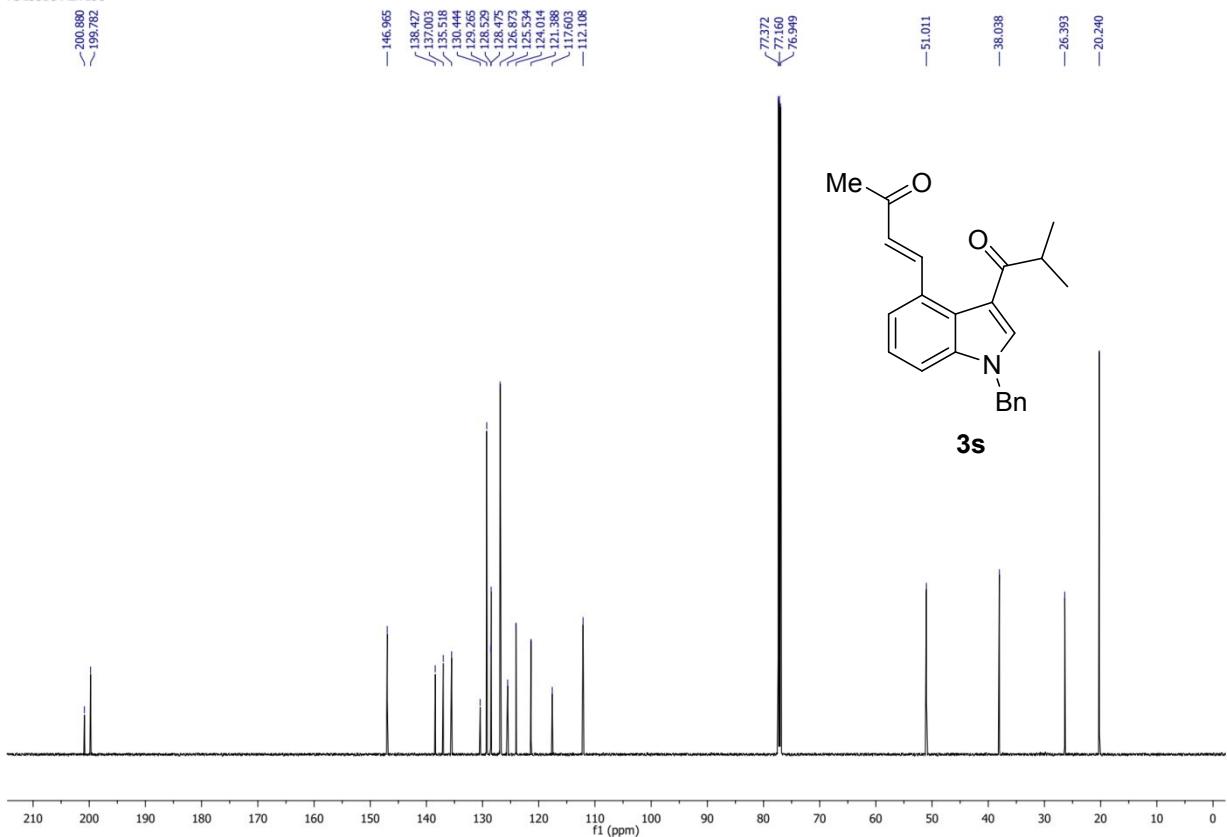


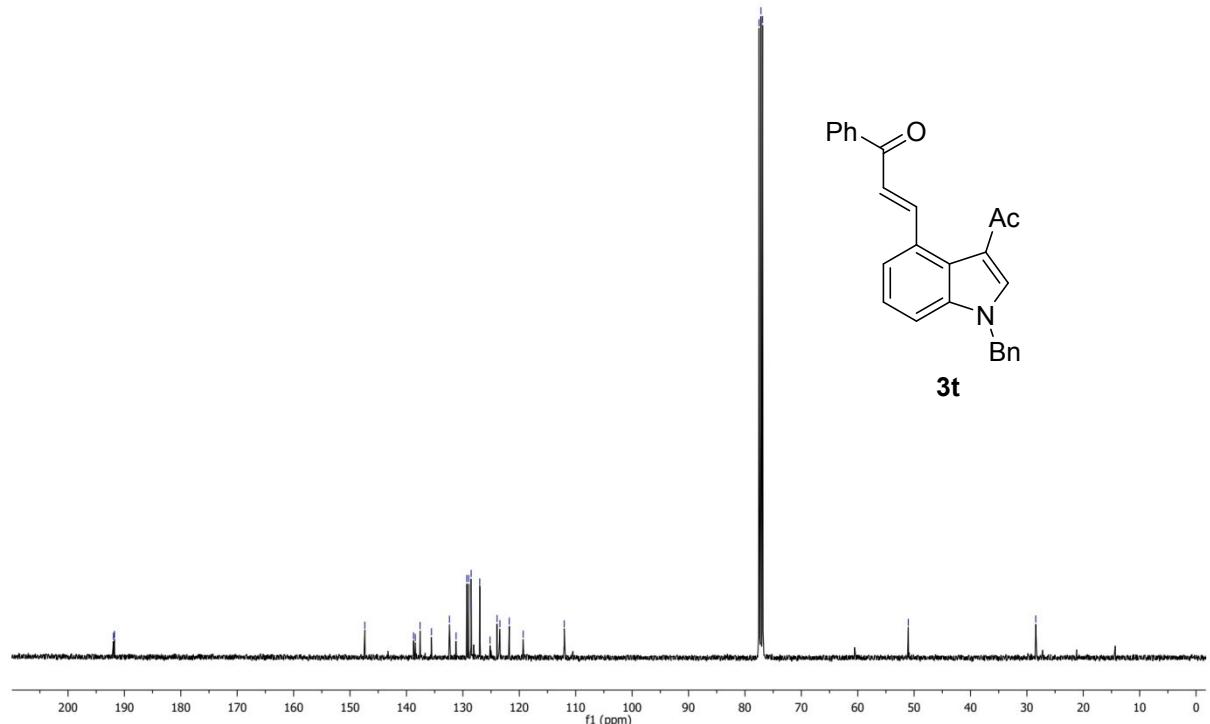
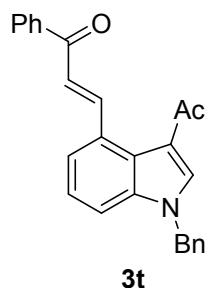
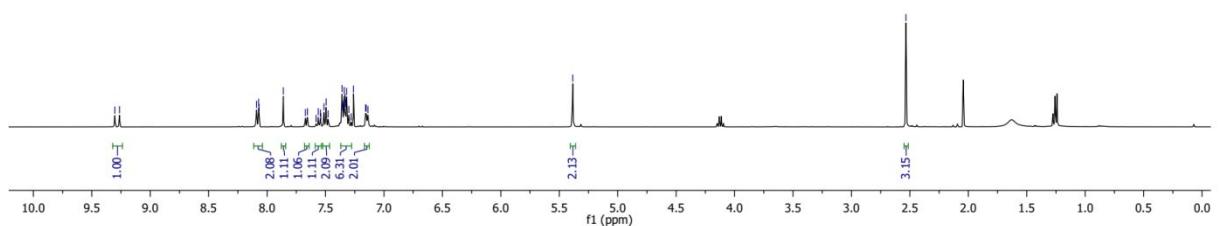
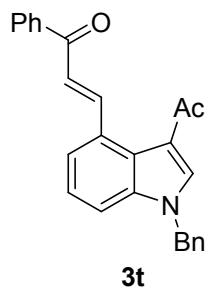
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—195.677
—147.094
—138.391
—137.642
—135.487
—130.445
—129.284
—128.614
—128.507
—126.908
—125.275
—124.039
—121.391
—118.676
—112.119
—77.478
—76.542
—51.024
—49.957
—31.846
—26.371
—25.756
—22.586
—14.141

PS-ISOBU-IND-ALK-1H

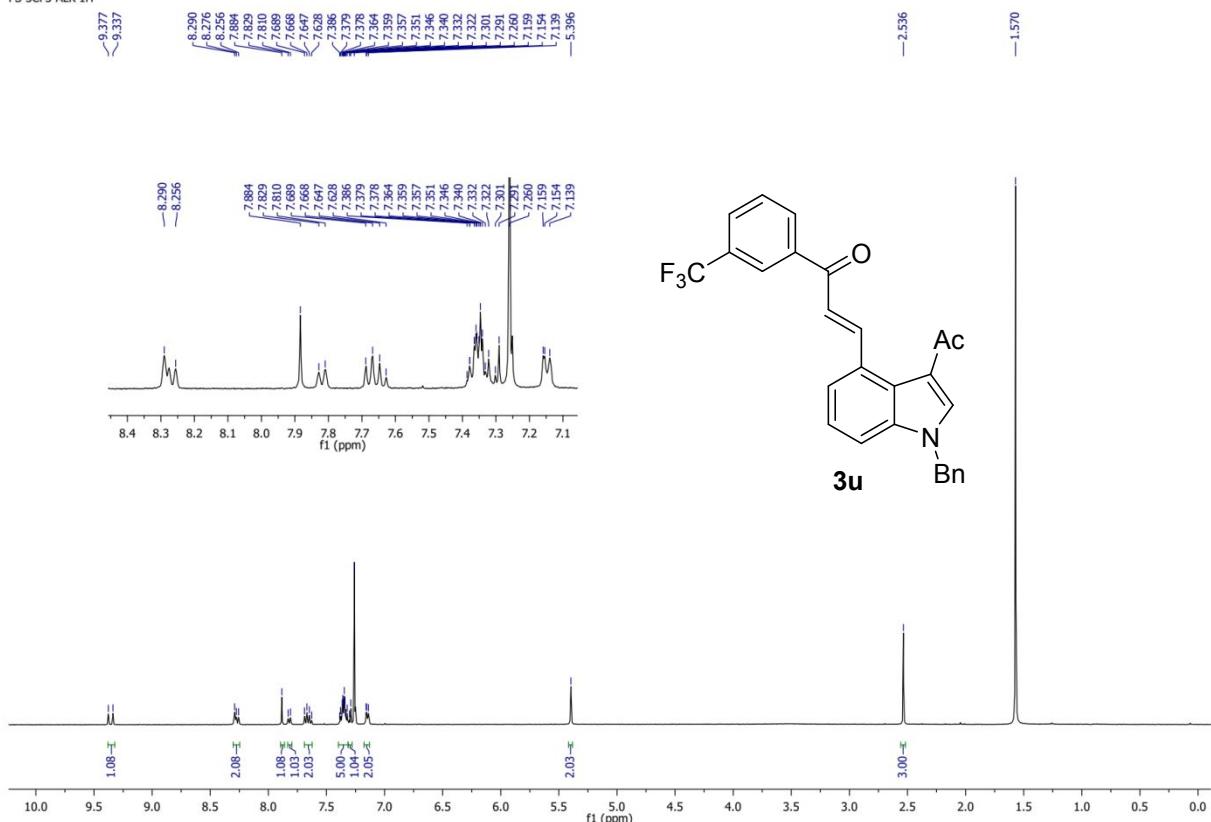


PS-ISOBU-ALK-13C

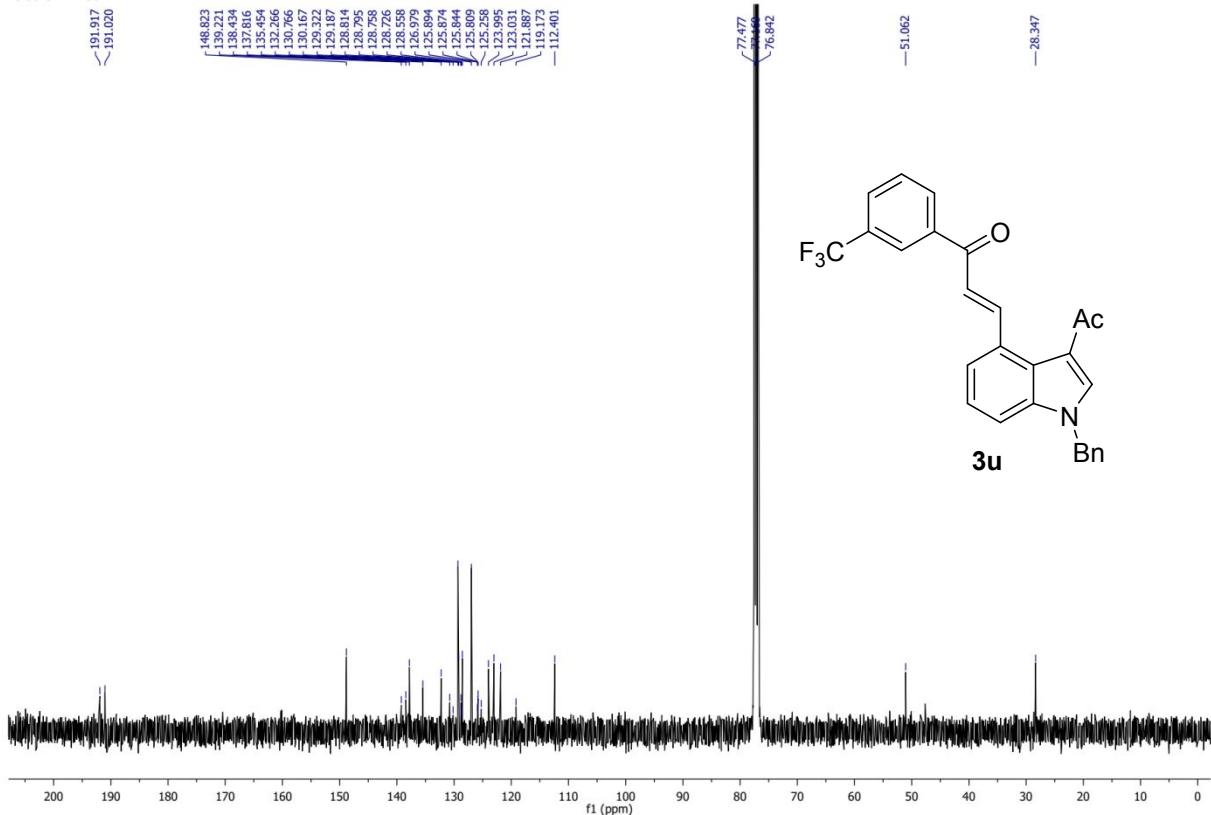


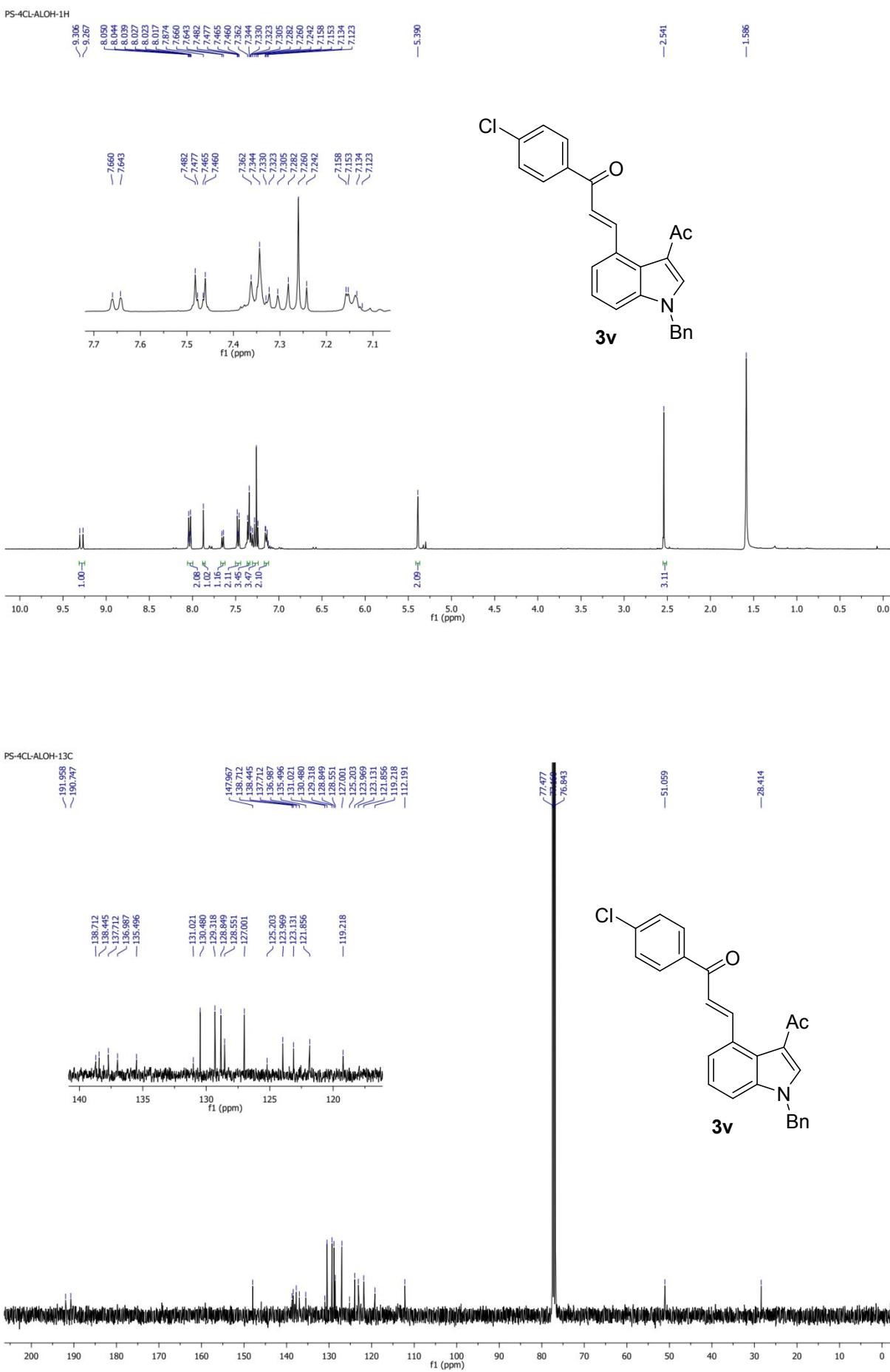


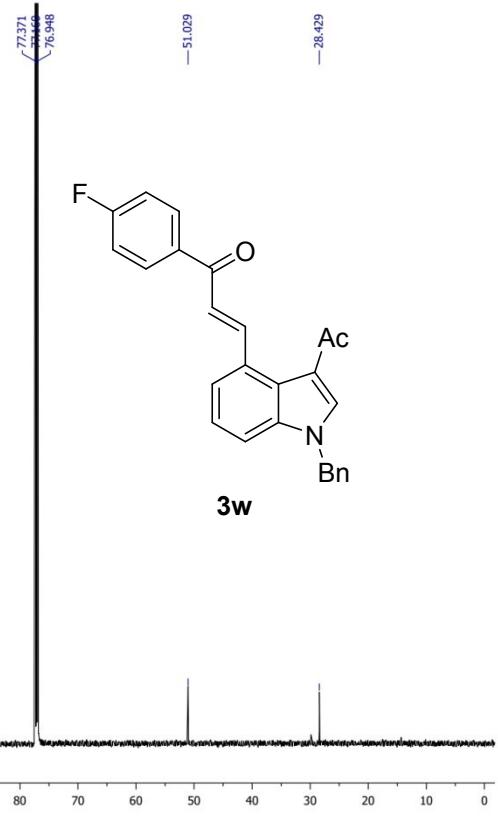
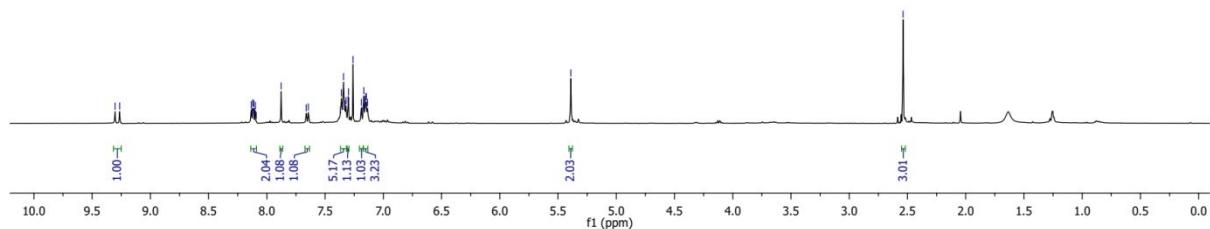
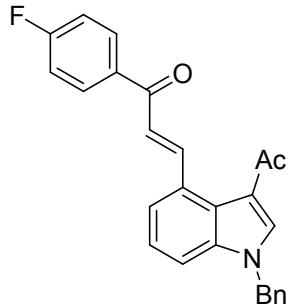
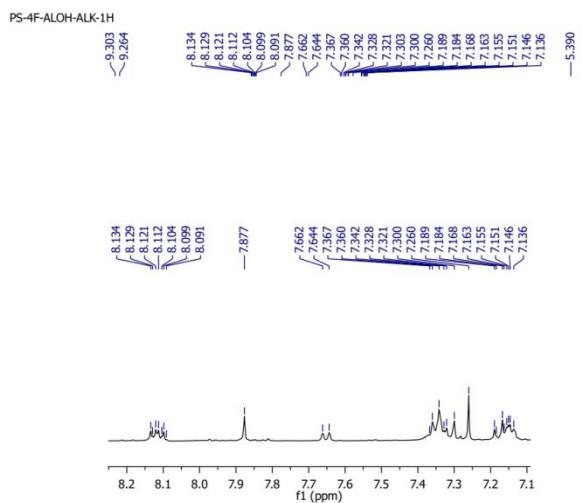
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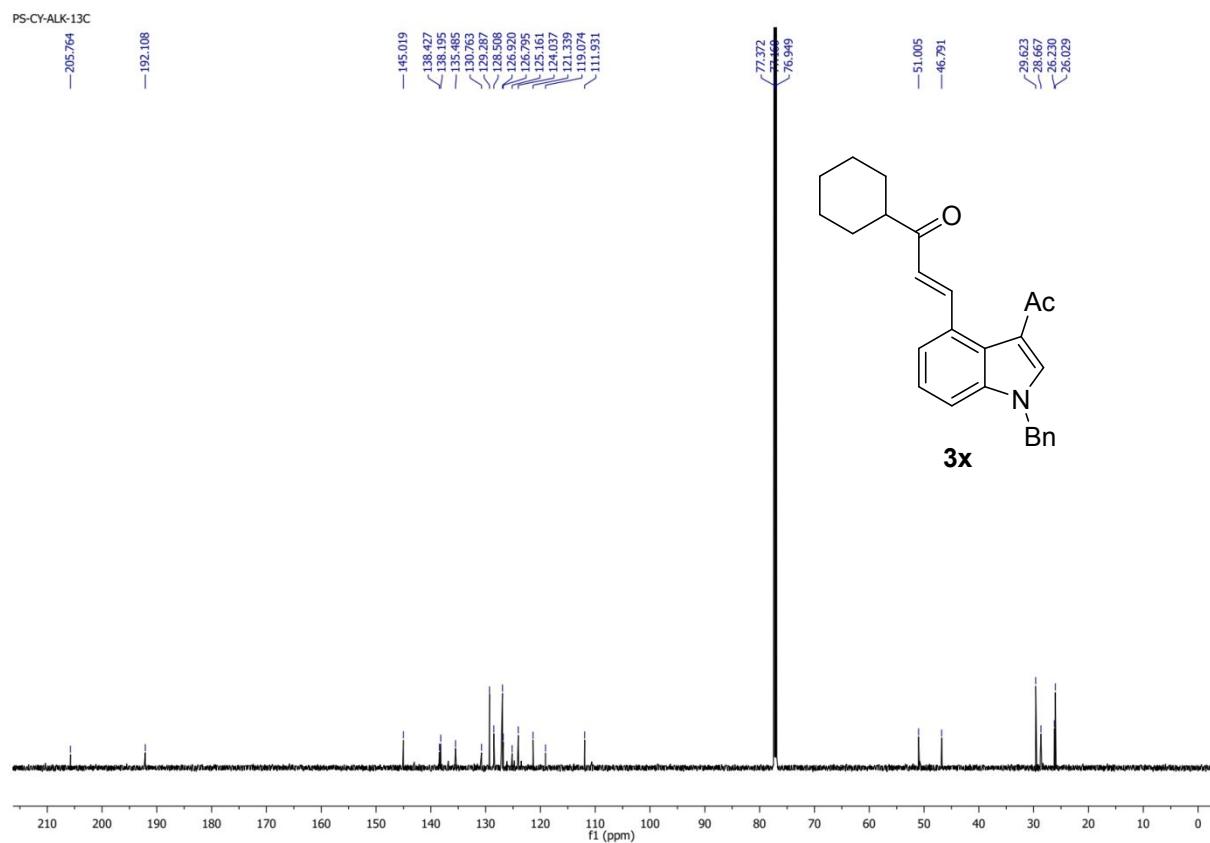
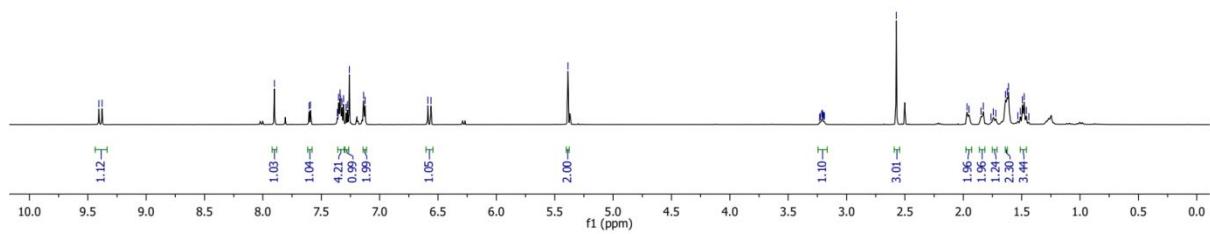


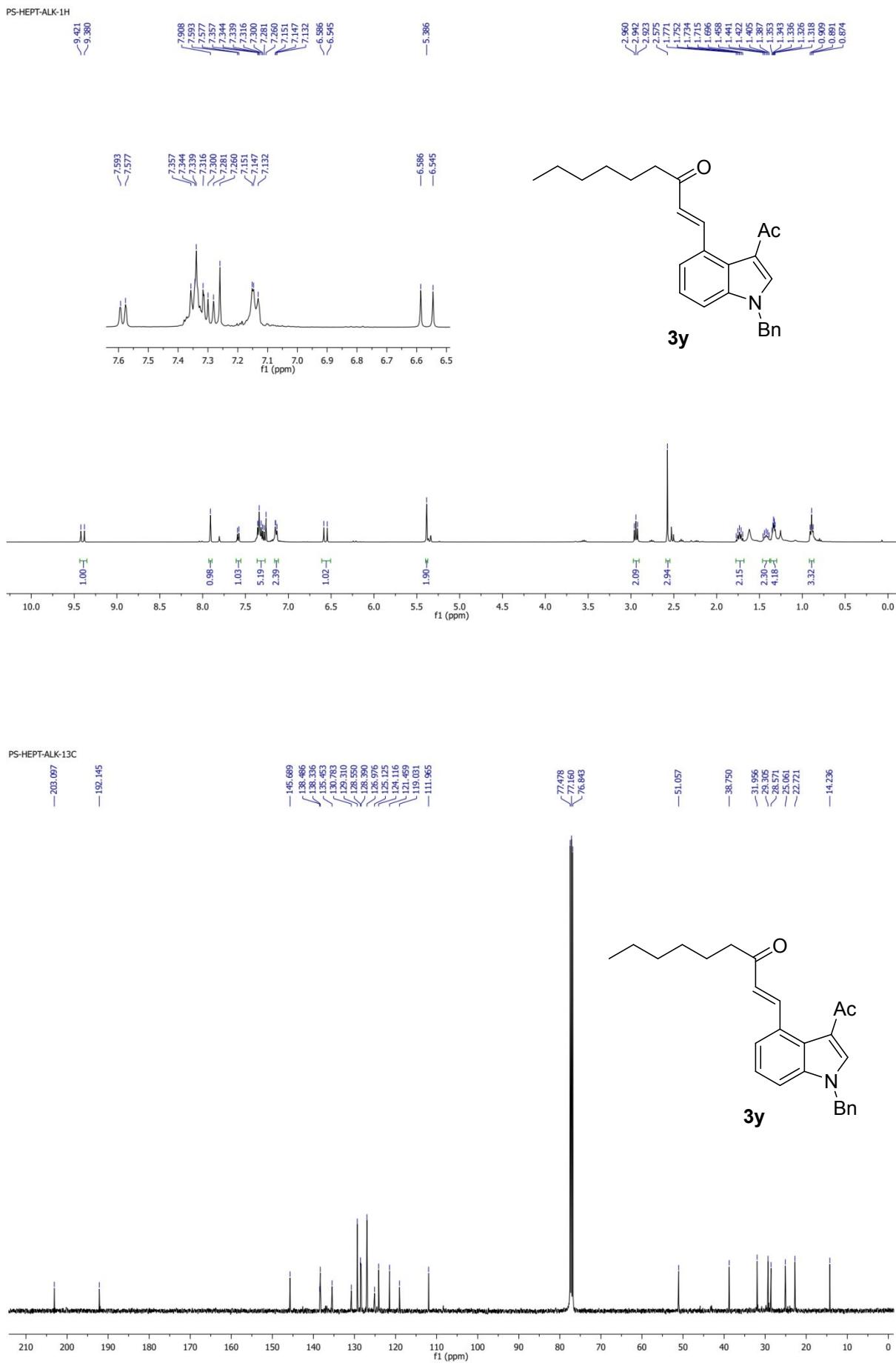
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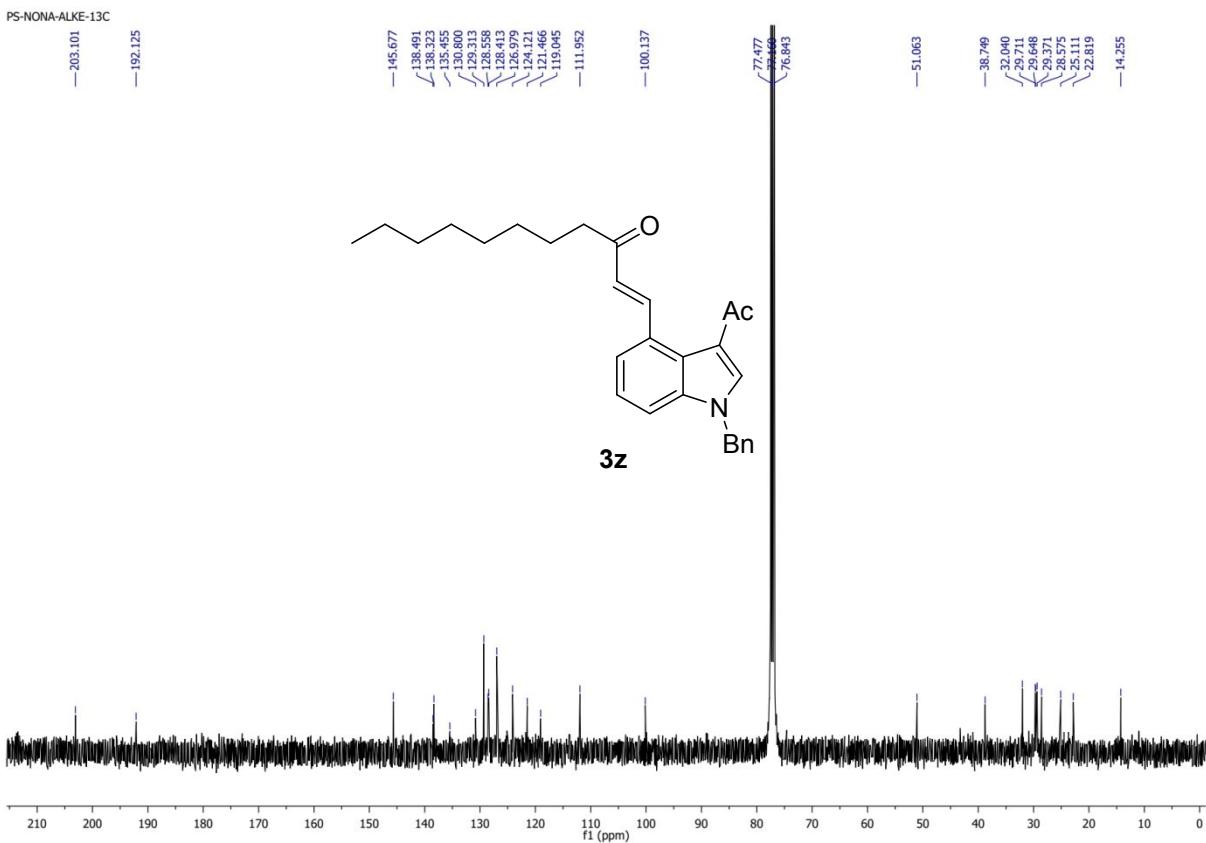
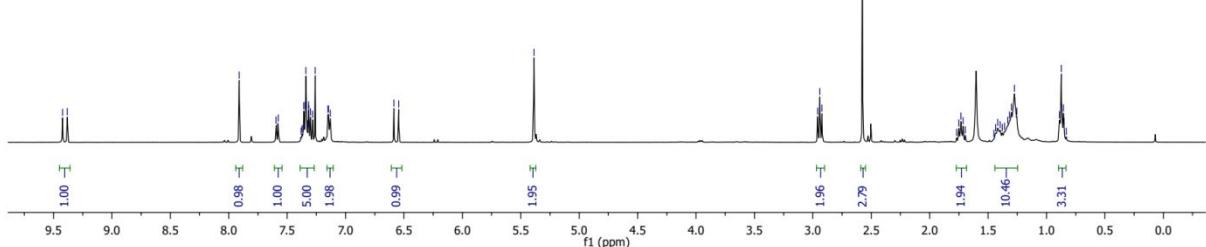
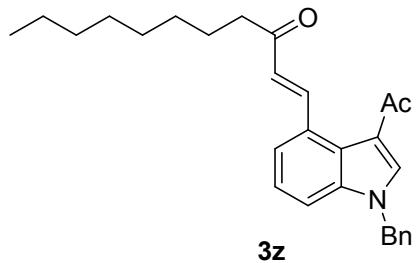




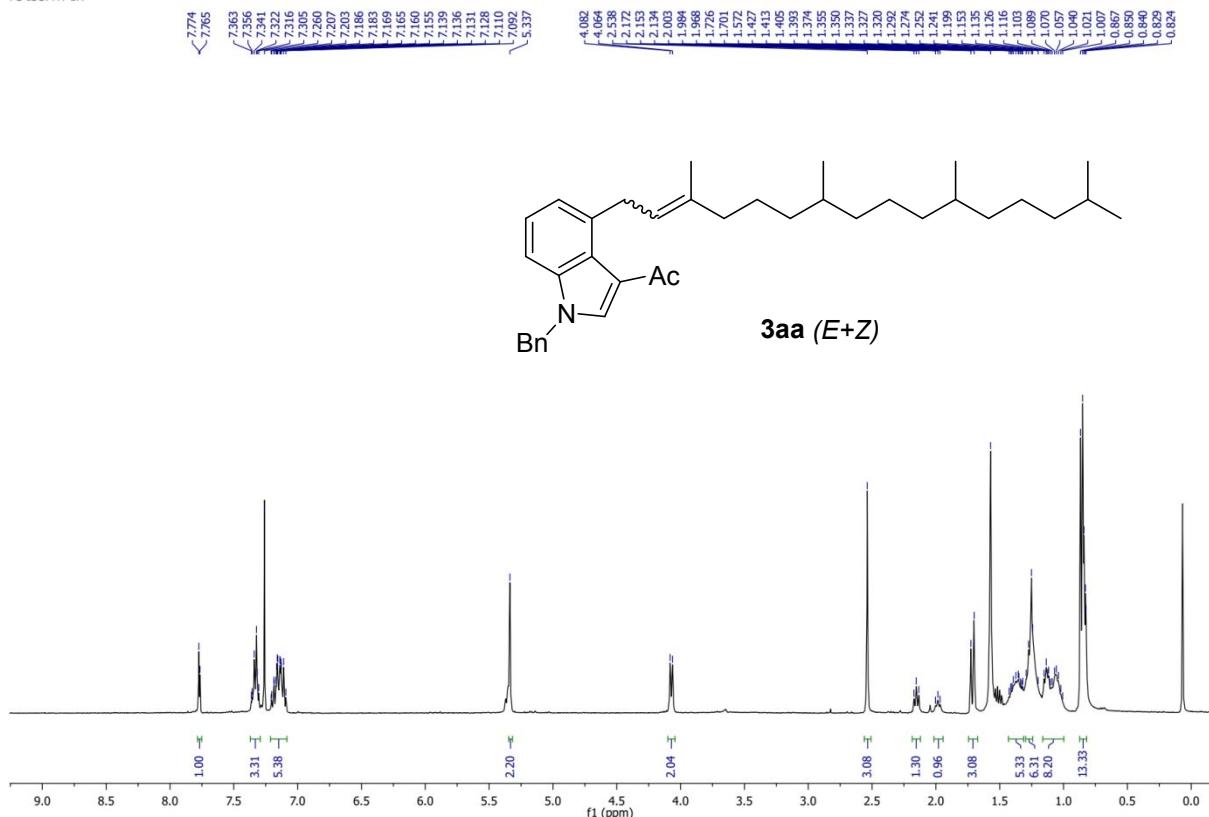




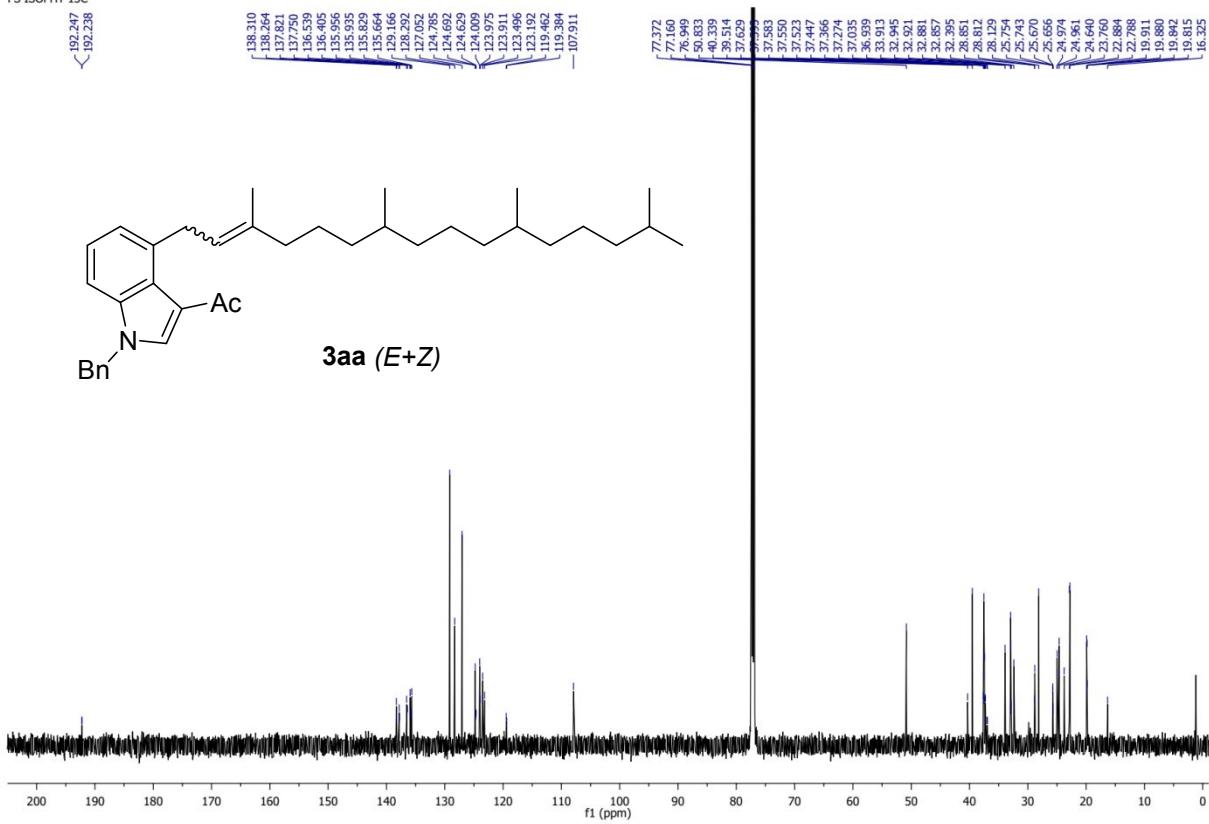




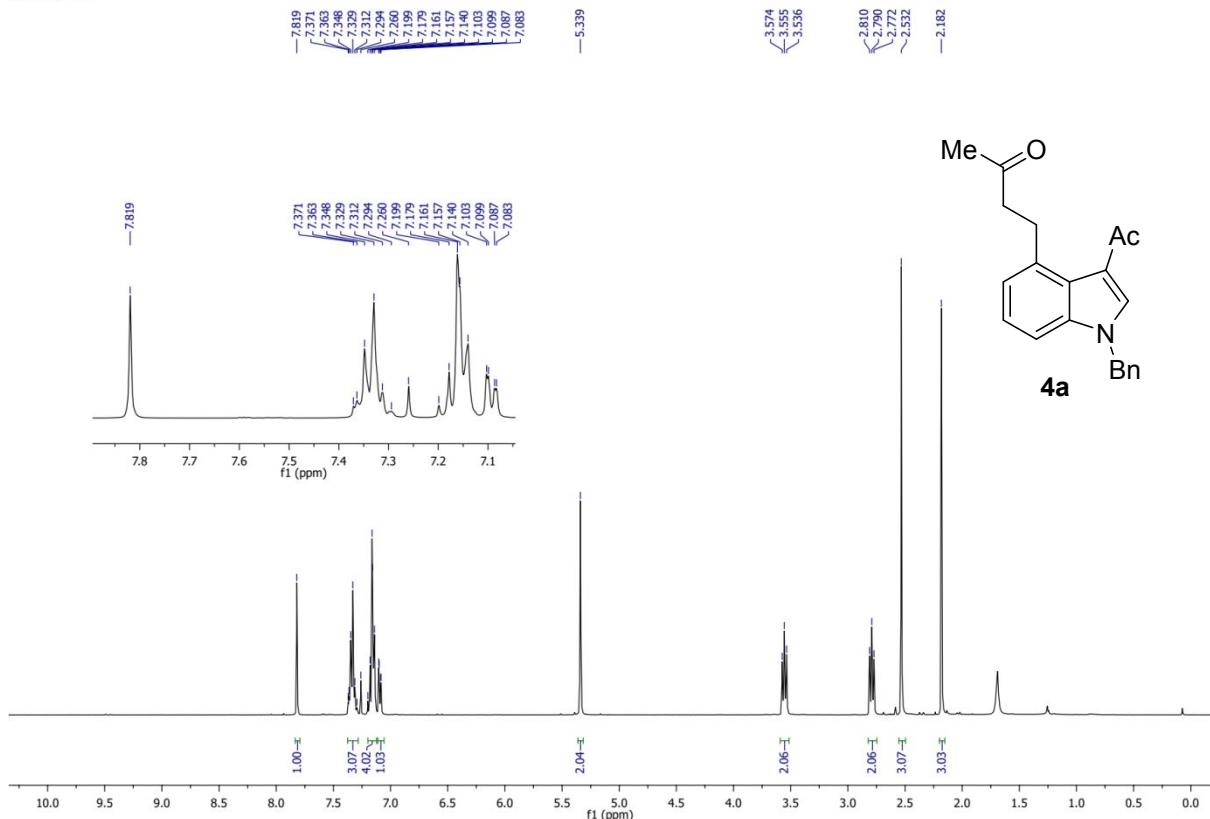
PS-ISOPHY-1H



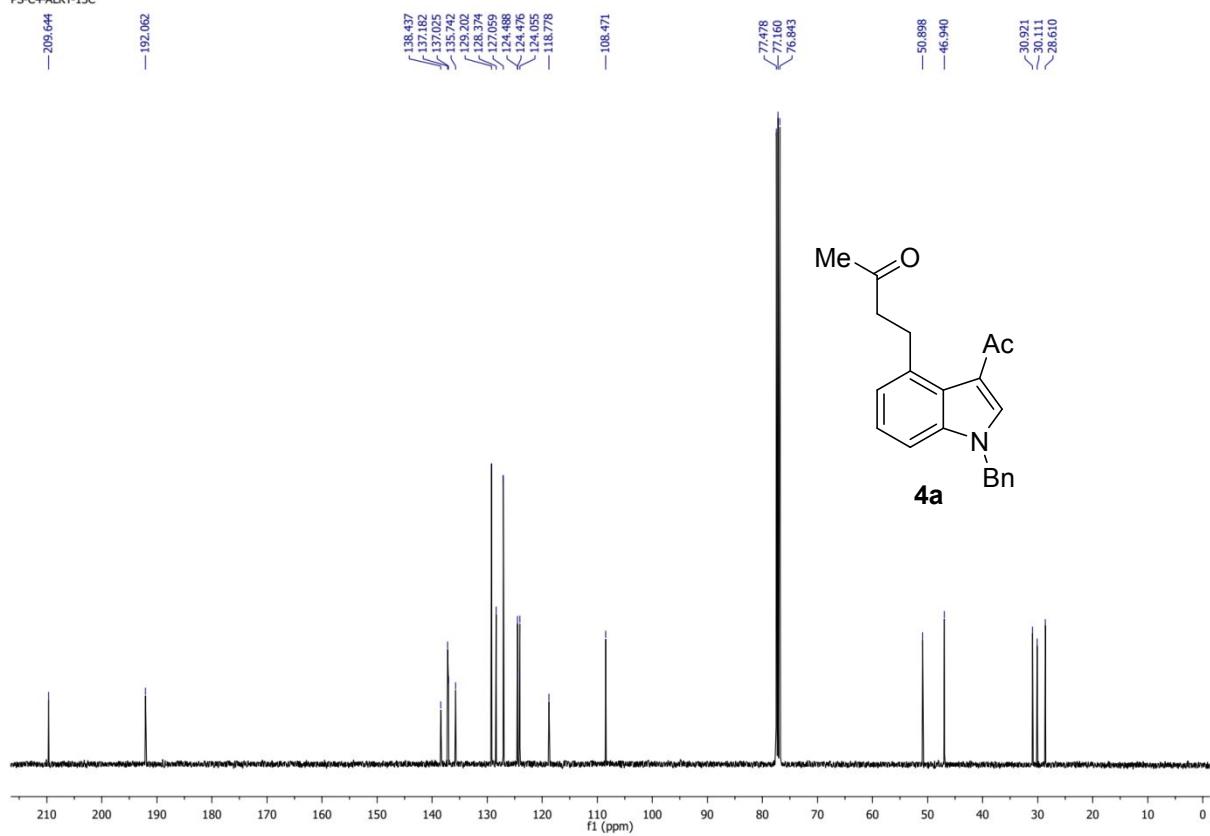
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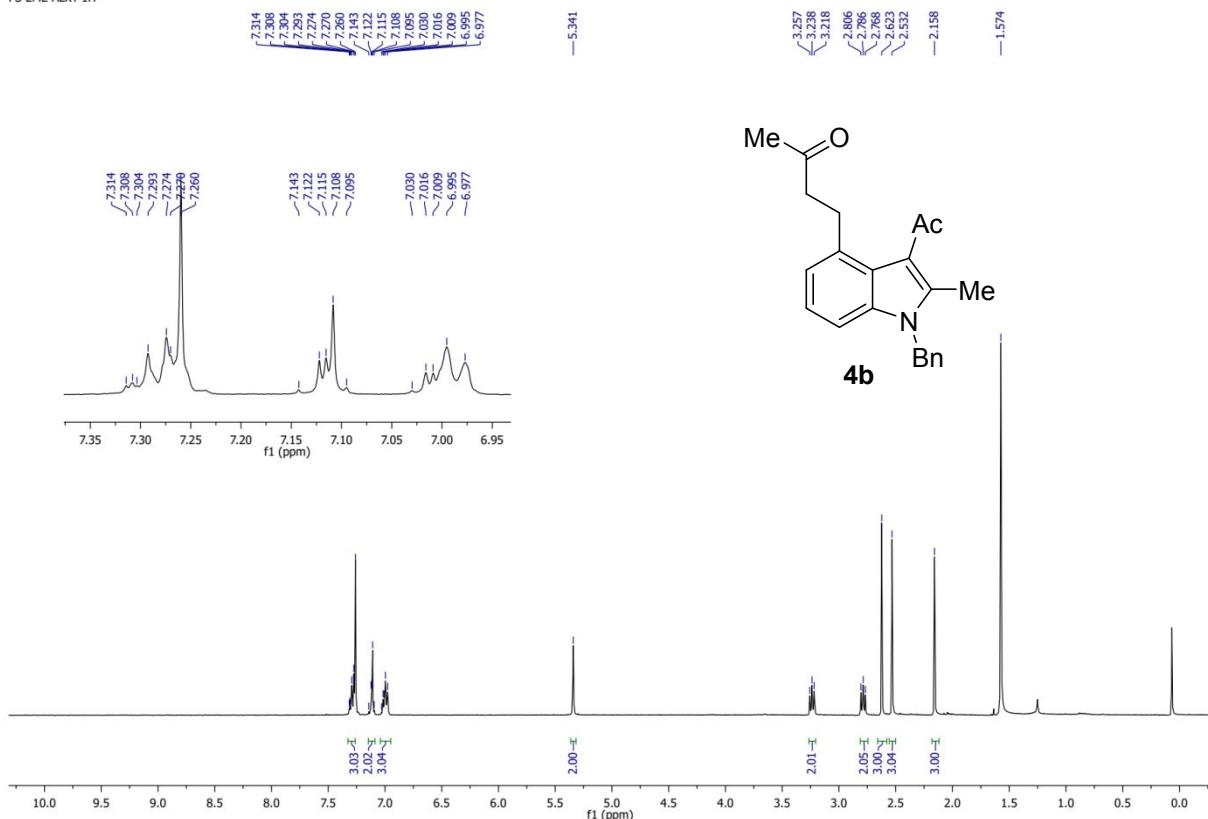
PS-C4-ALKY-1H



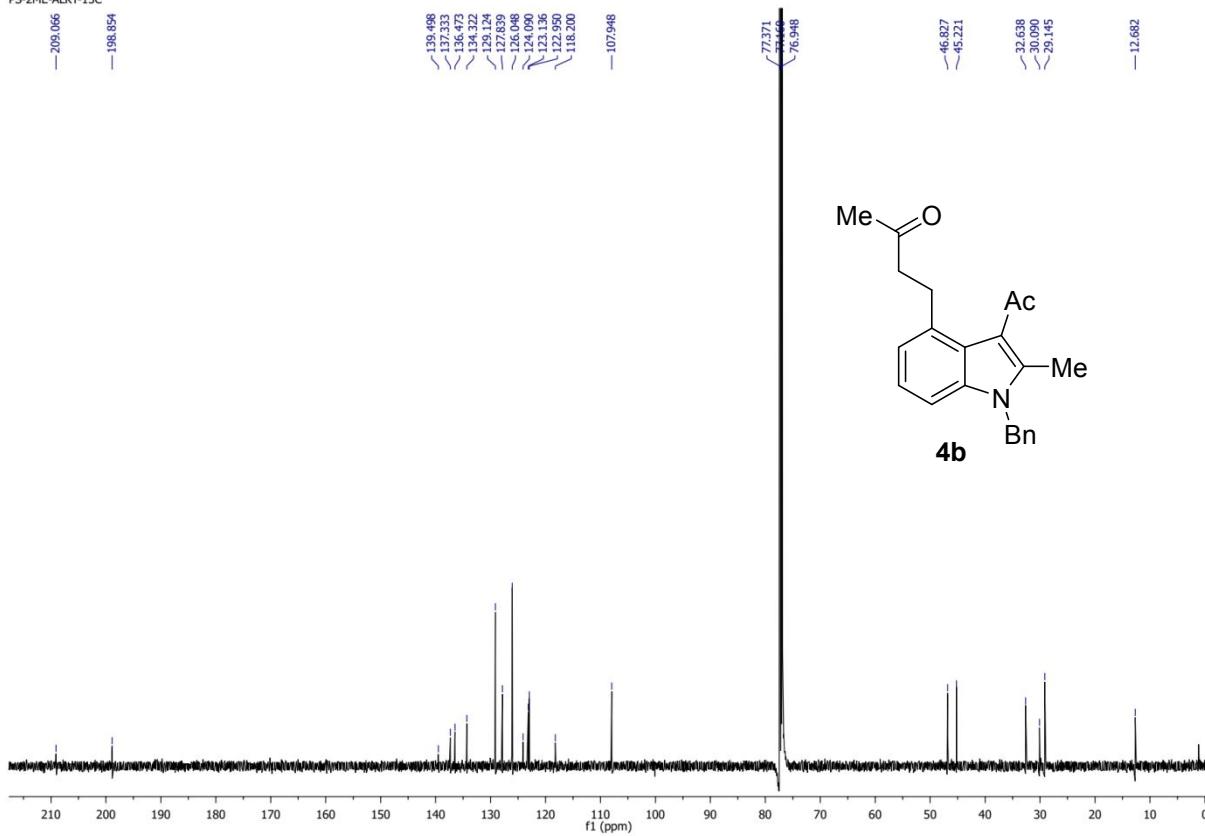
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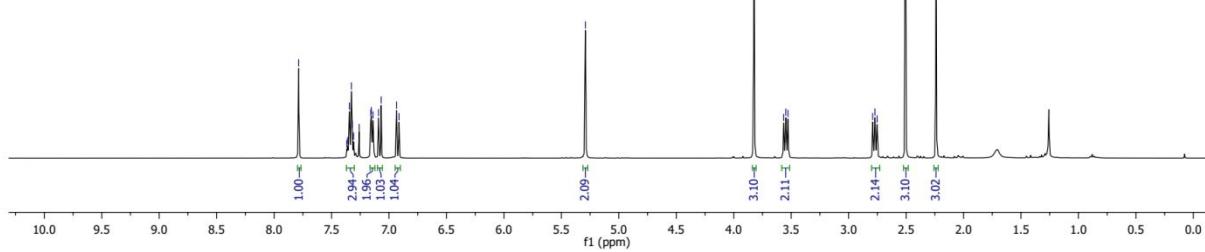
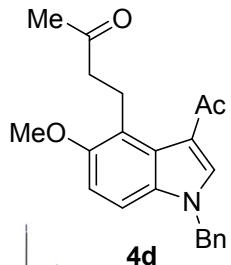
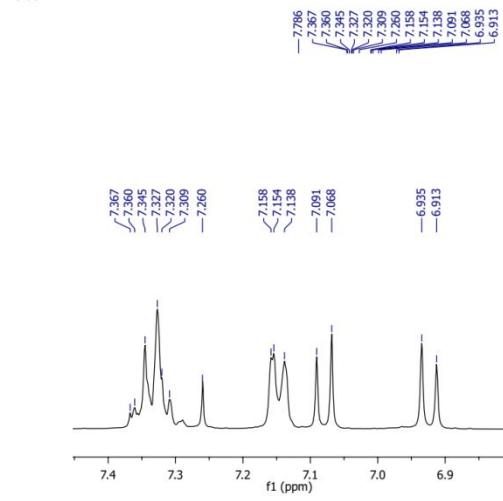
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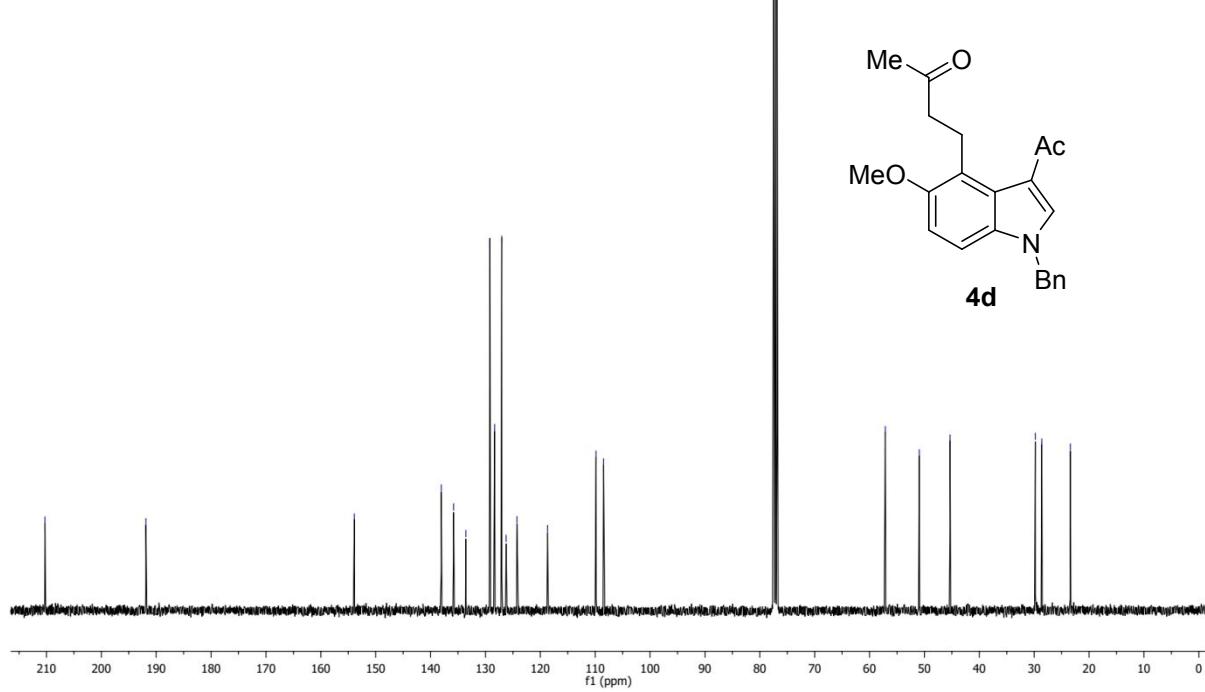
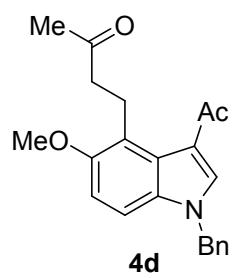
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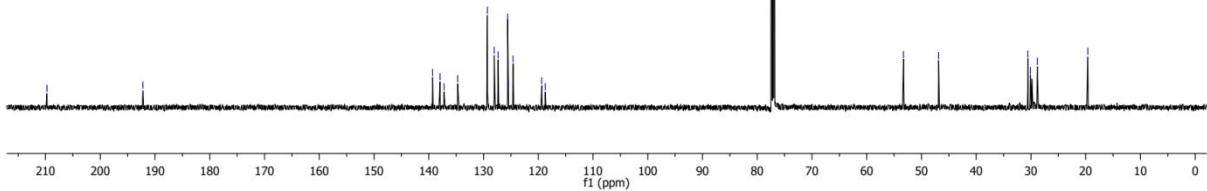
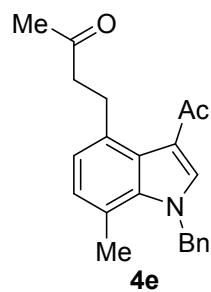
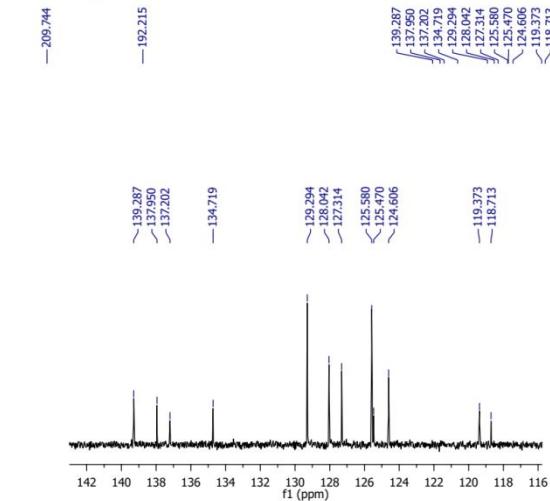
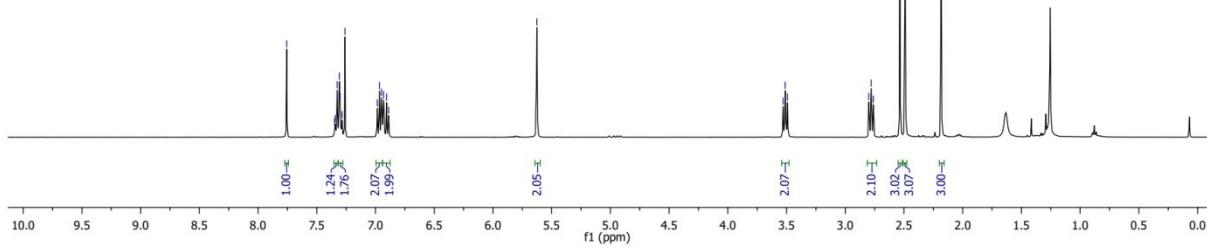
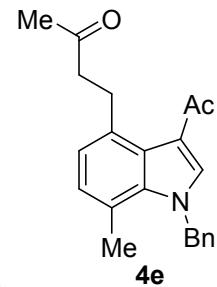
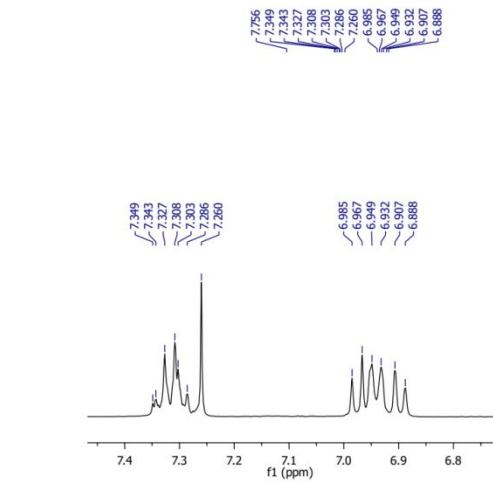
PS-SOME-ALKY-1H



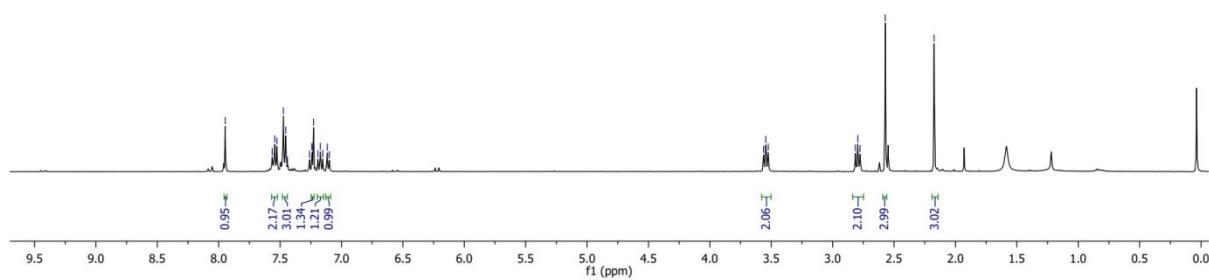
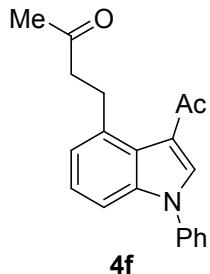
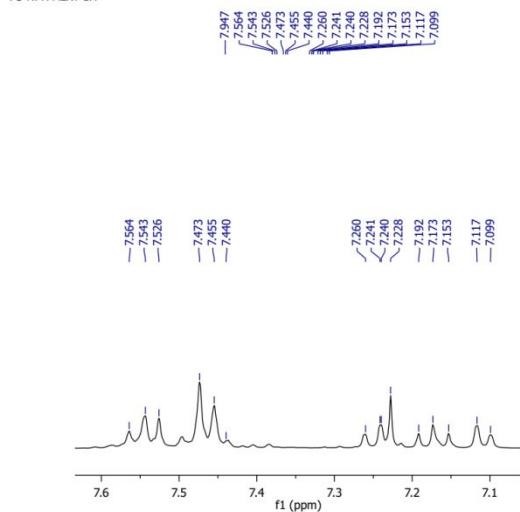
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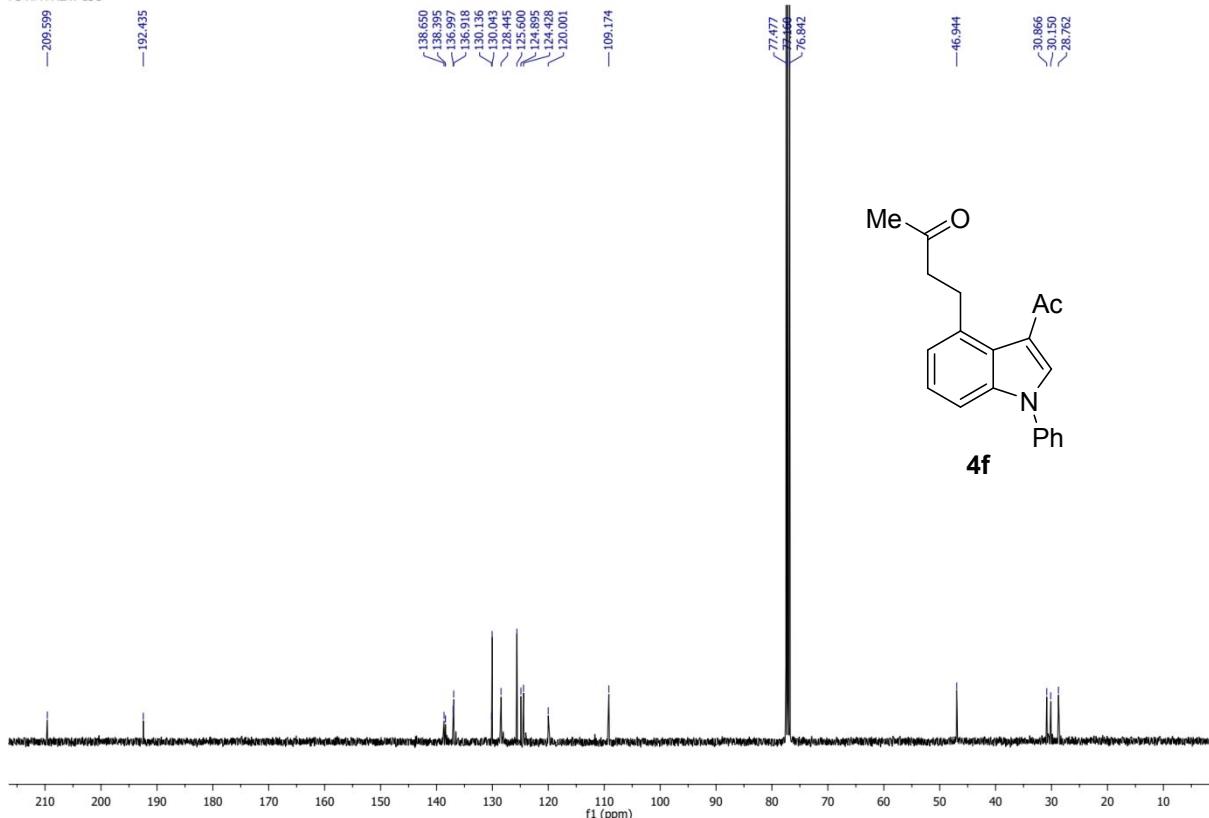
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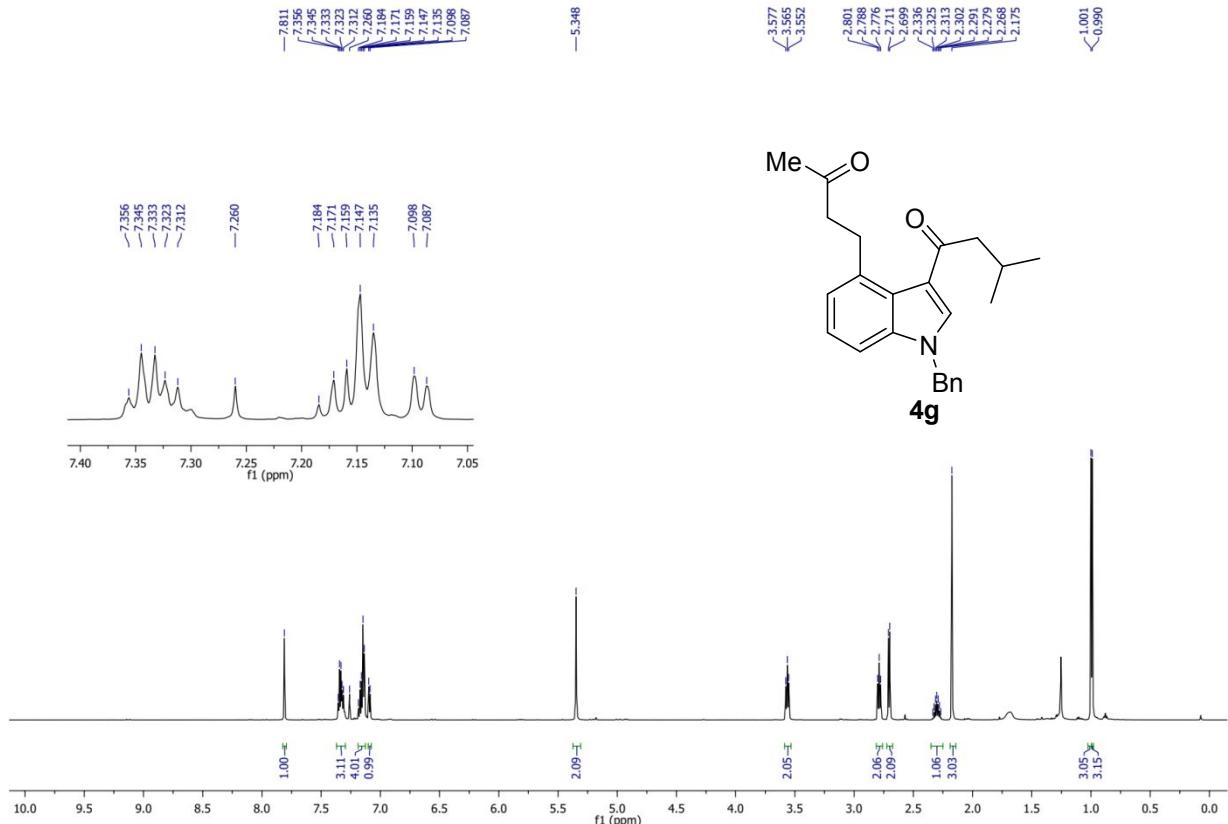
PS-NPH-ALKY-1H



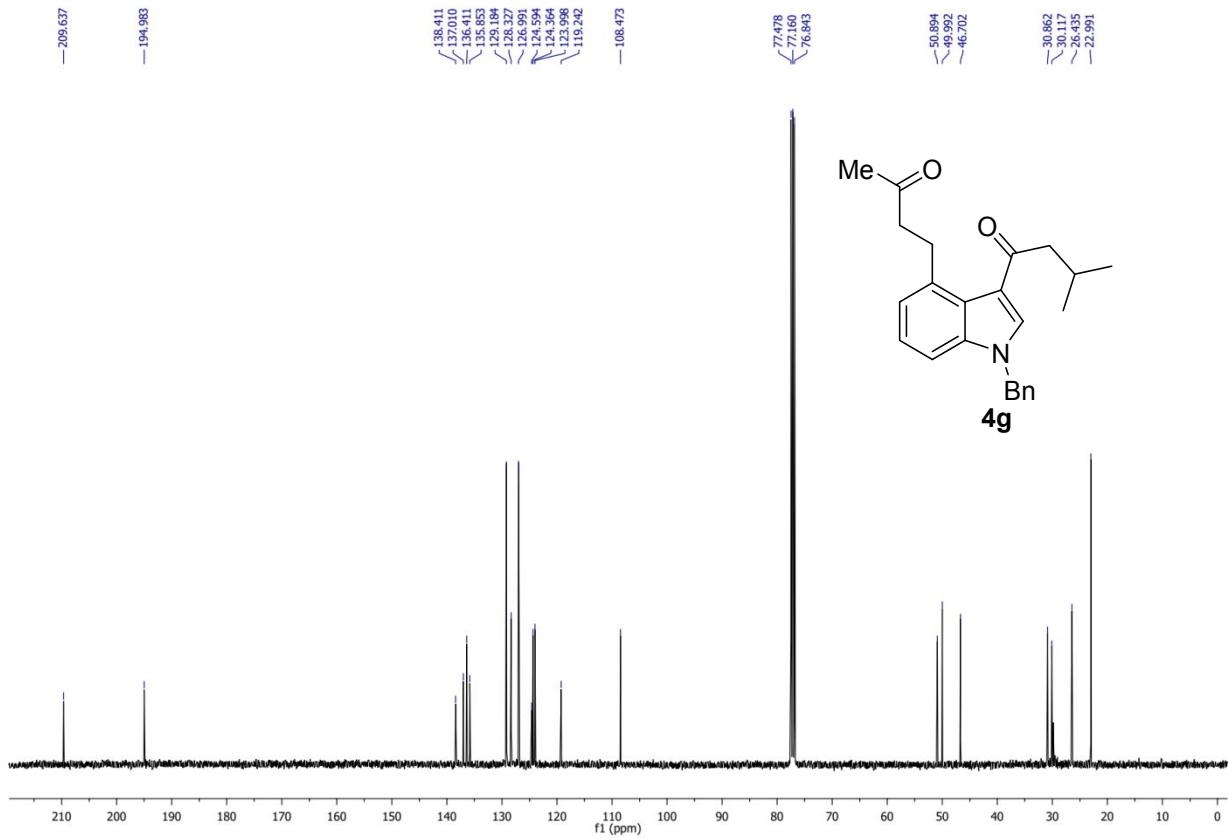
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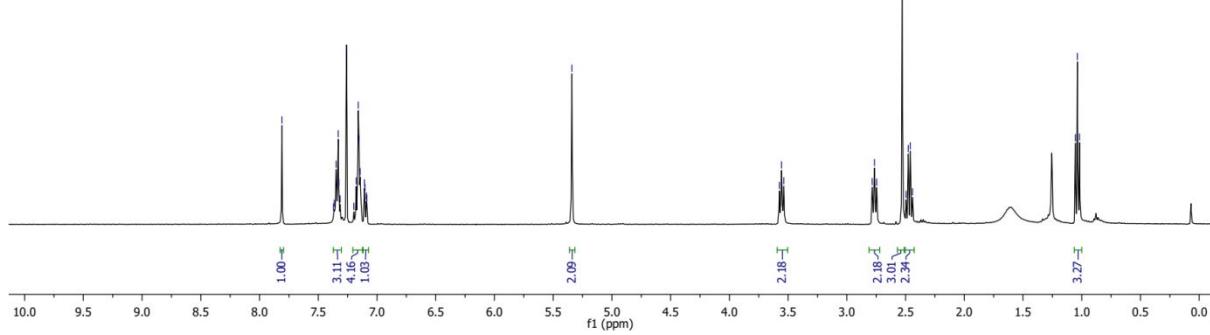
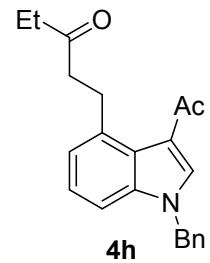
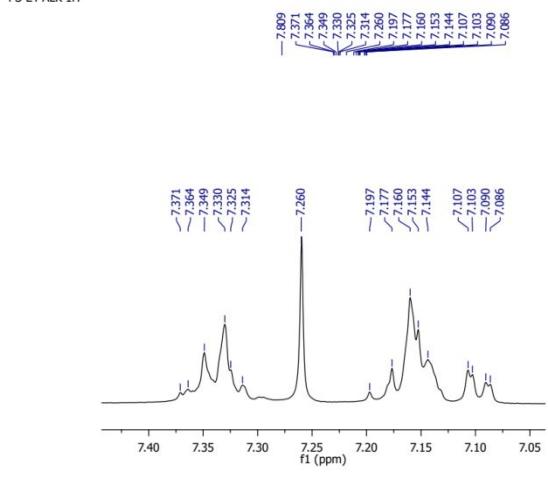
PS-ISOVAL-ALK-1H



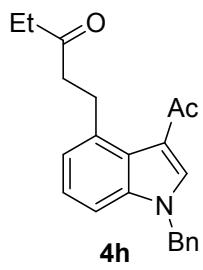
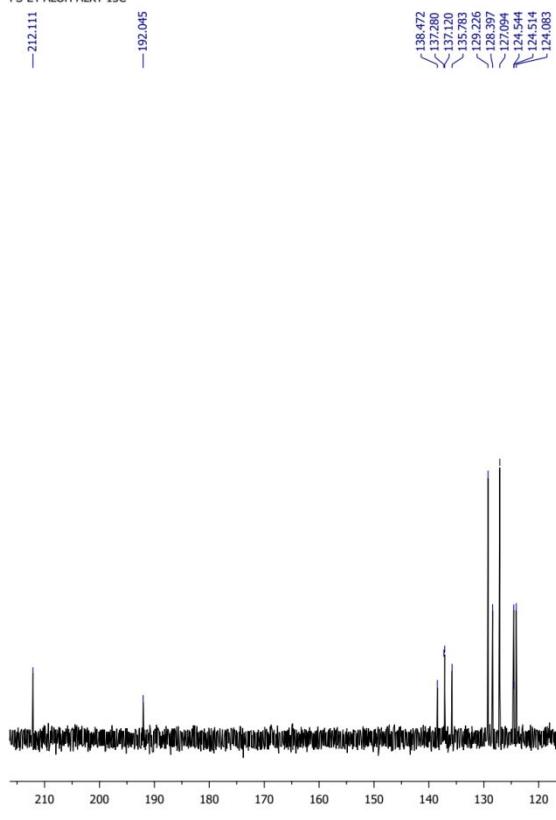
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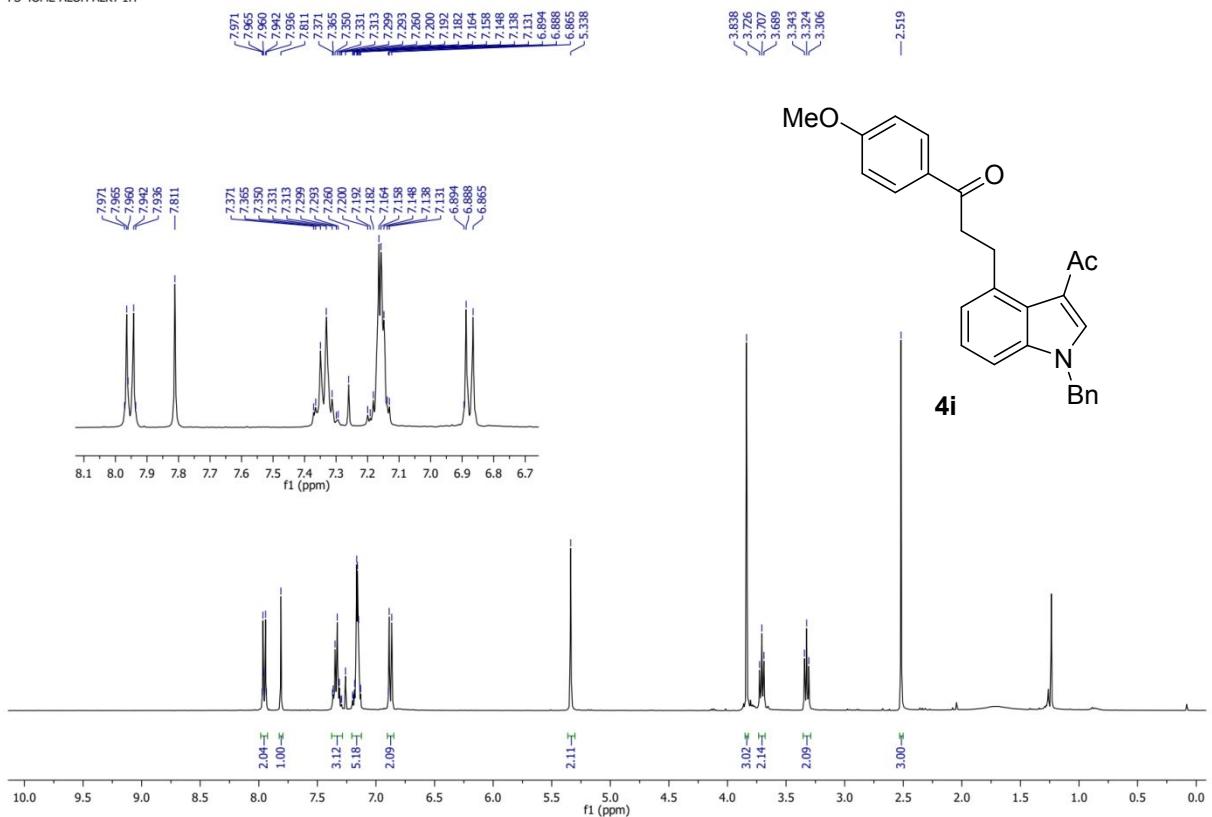
PS-ET-ALK-1H



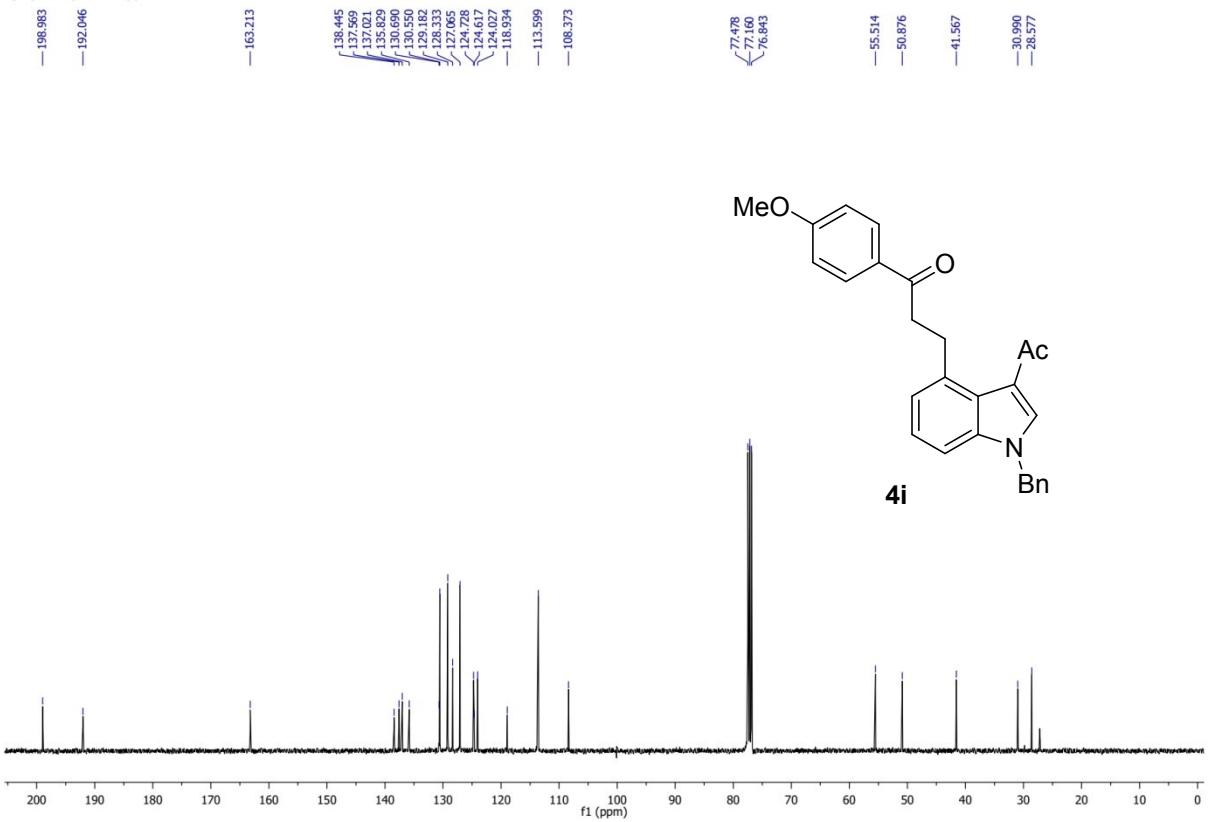
PS-ET-ALOH-ALKY-13C



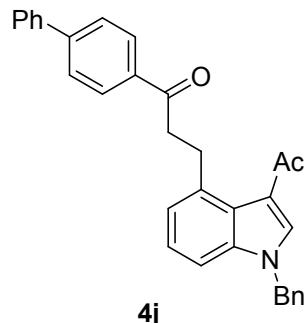
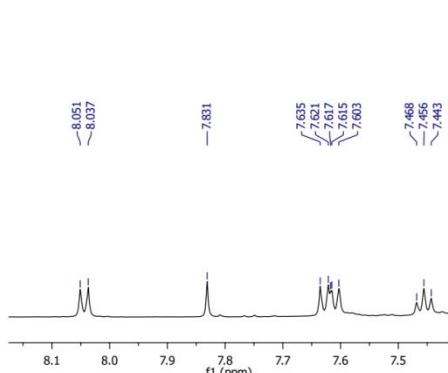
PS-4OME-ALOH-ALKY-1H



PS-4OME-ALOH-ALKY-13C



PS-4PH-ALOH-ALKY-1H



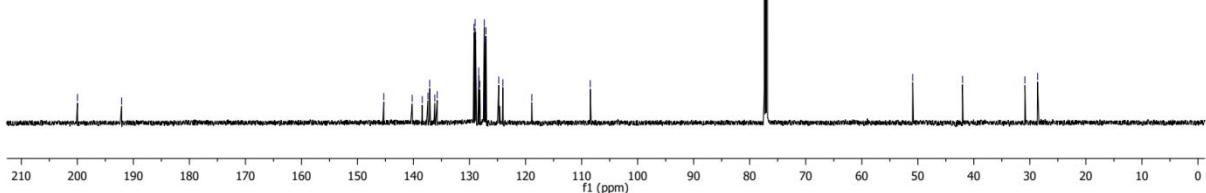
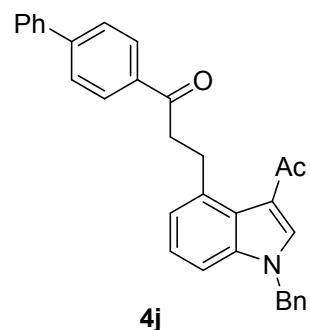
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— 196.972

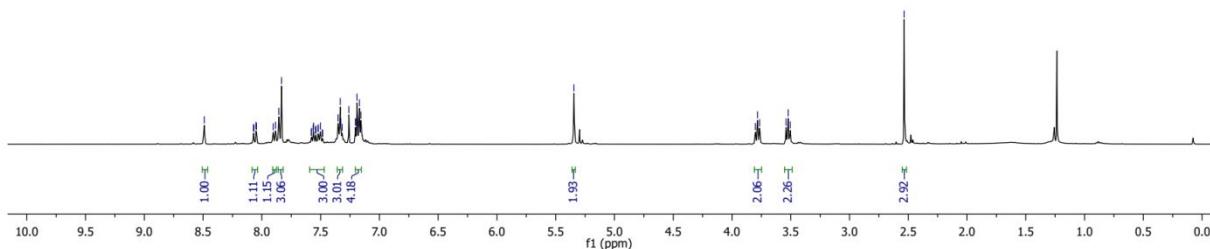
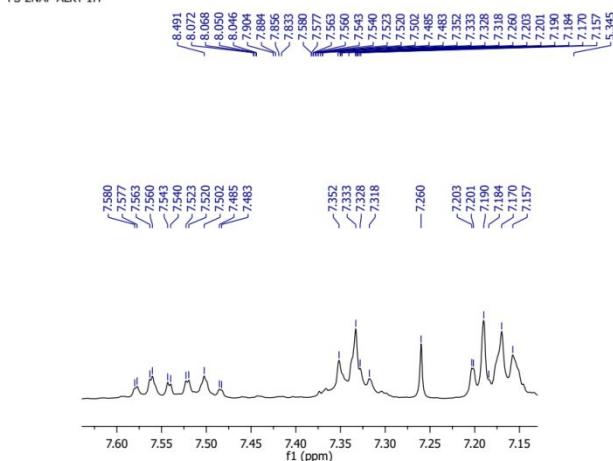
— 192.096

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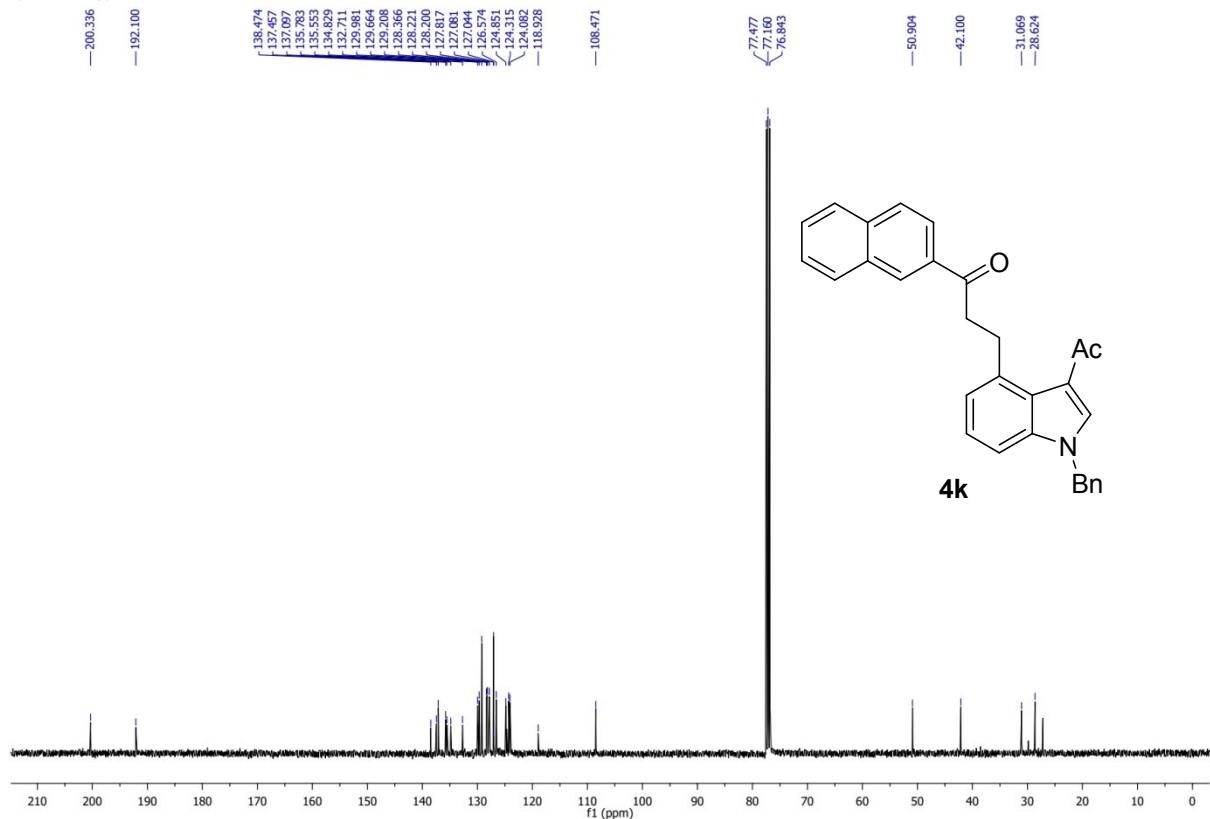
— 77.371
— 76.948
— 50.898
— 42.017
— 30.883
— 28.630

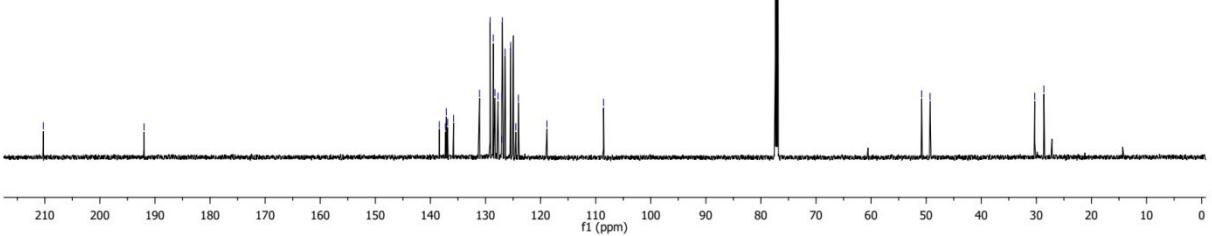
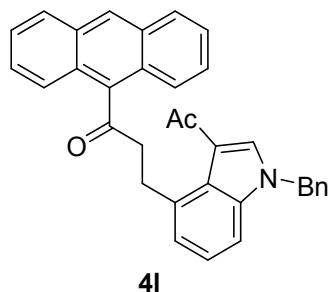
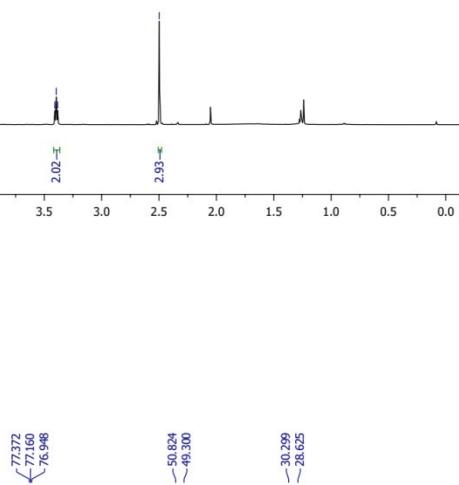
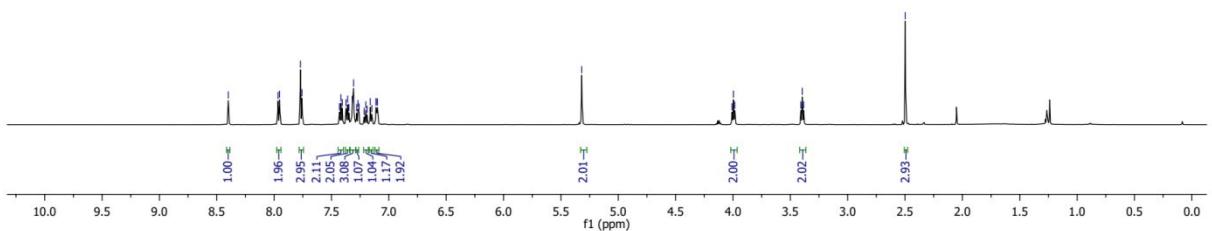
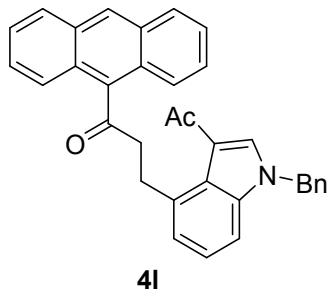
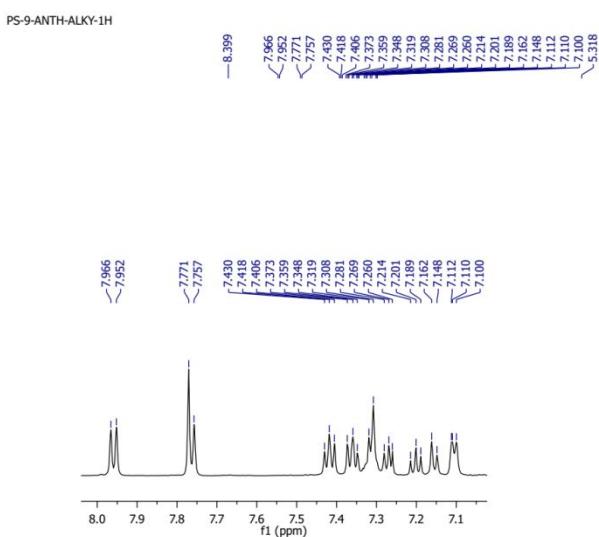


PS-2NAP-ALKY-1H

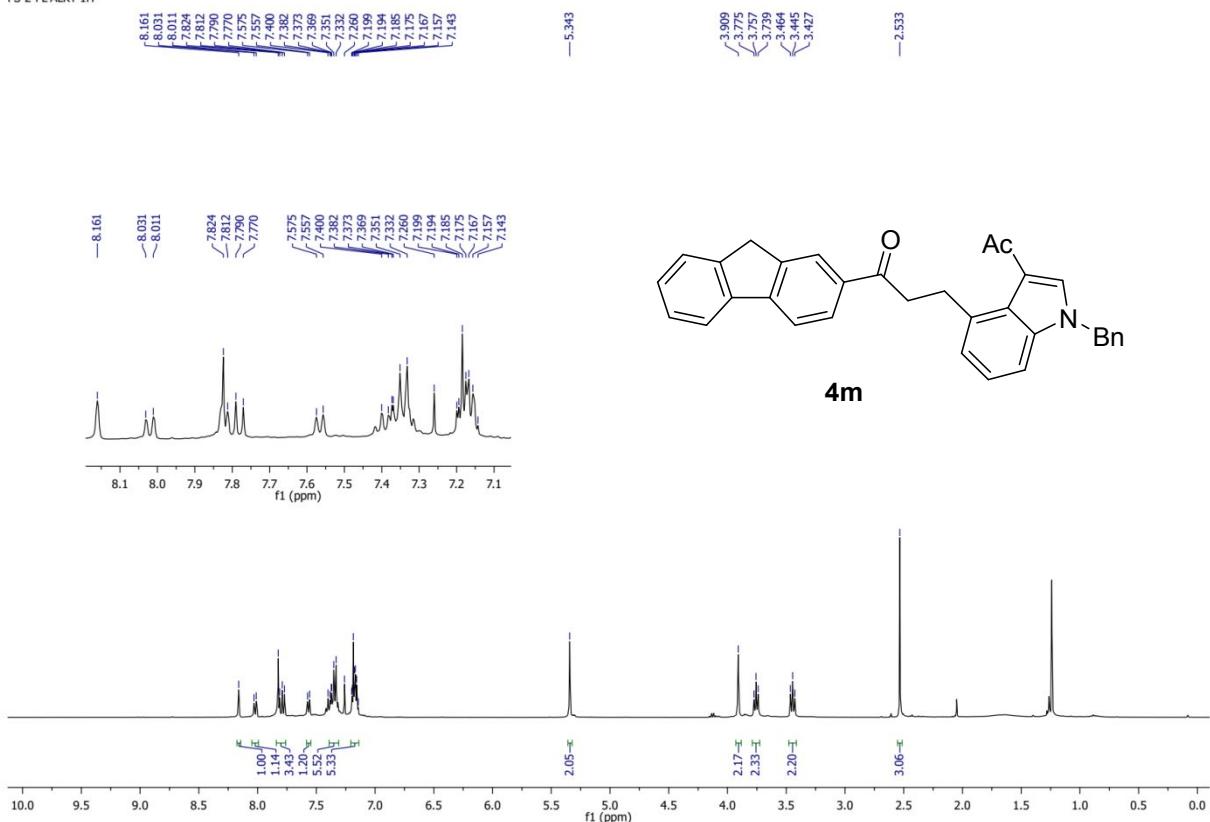


PS-2NAP-ALKY-13C

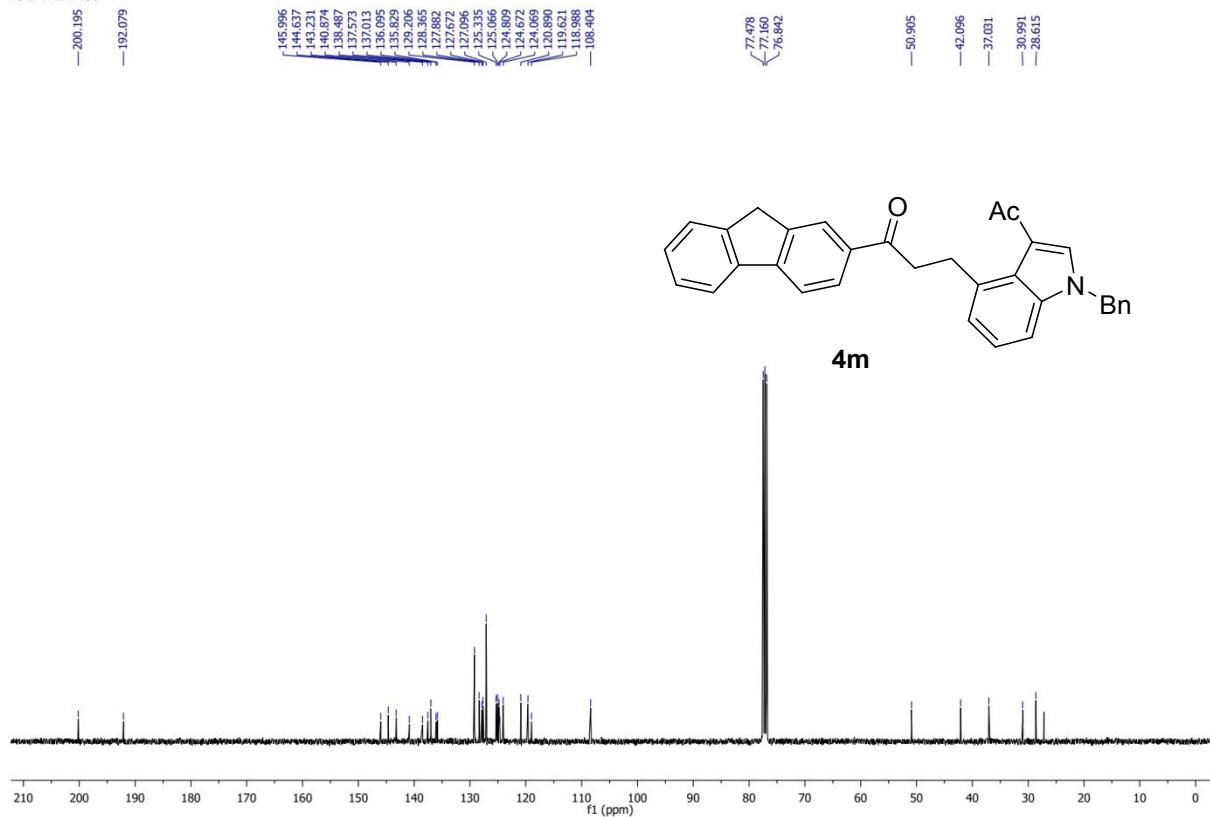


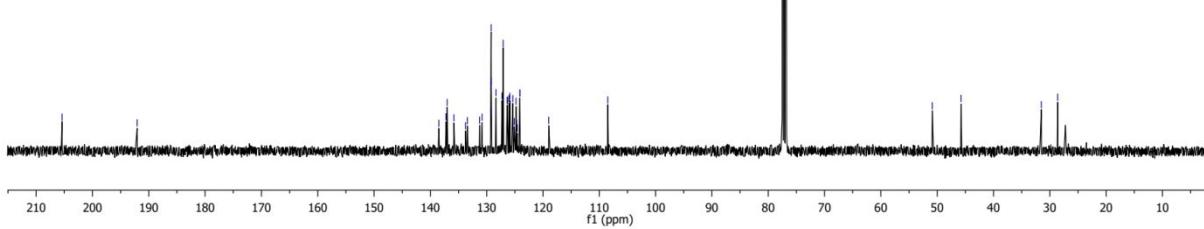
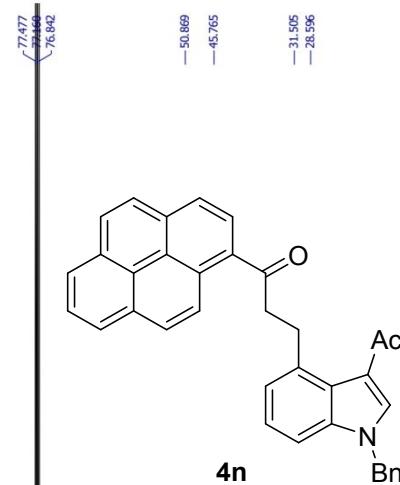
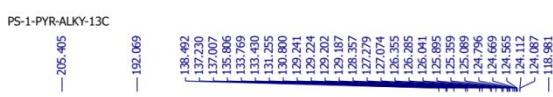
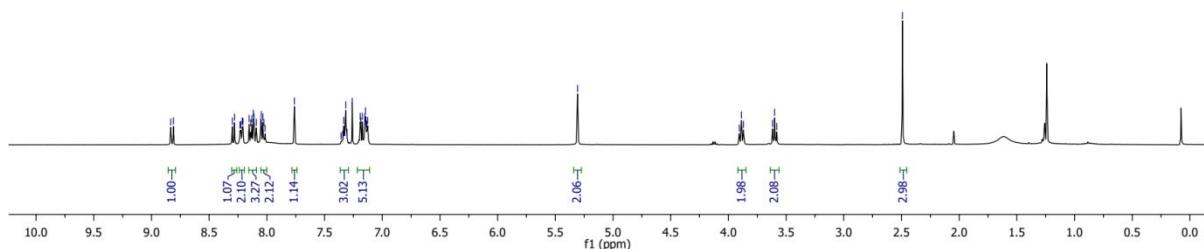
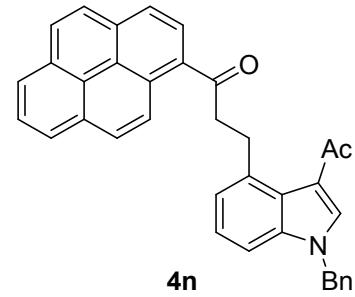
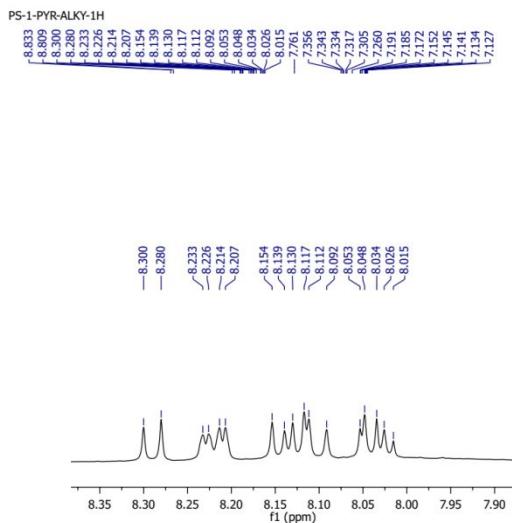


PS-2-FL-ALKY-1H

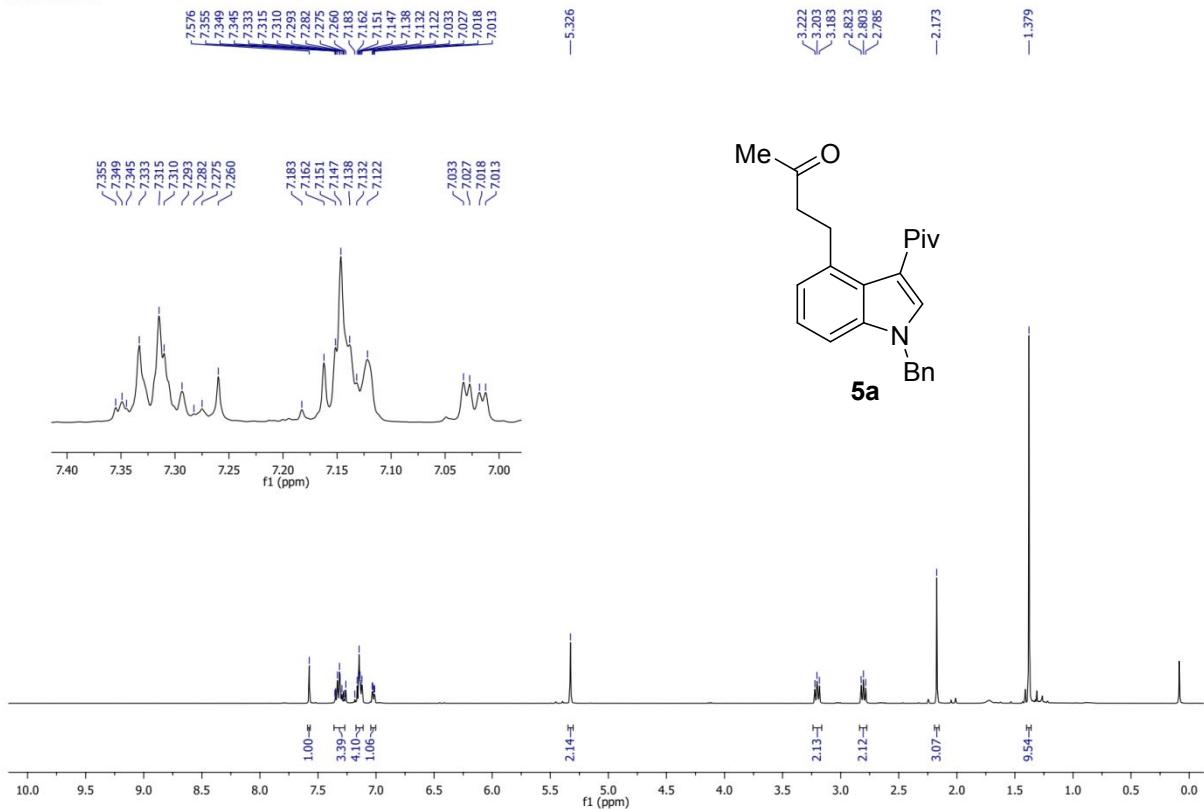


PS-2FL-ALKY-13C

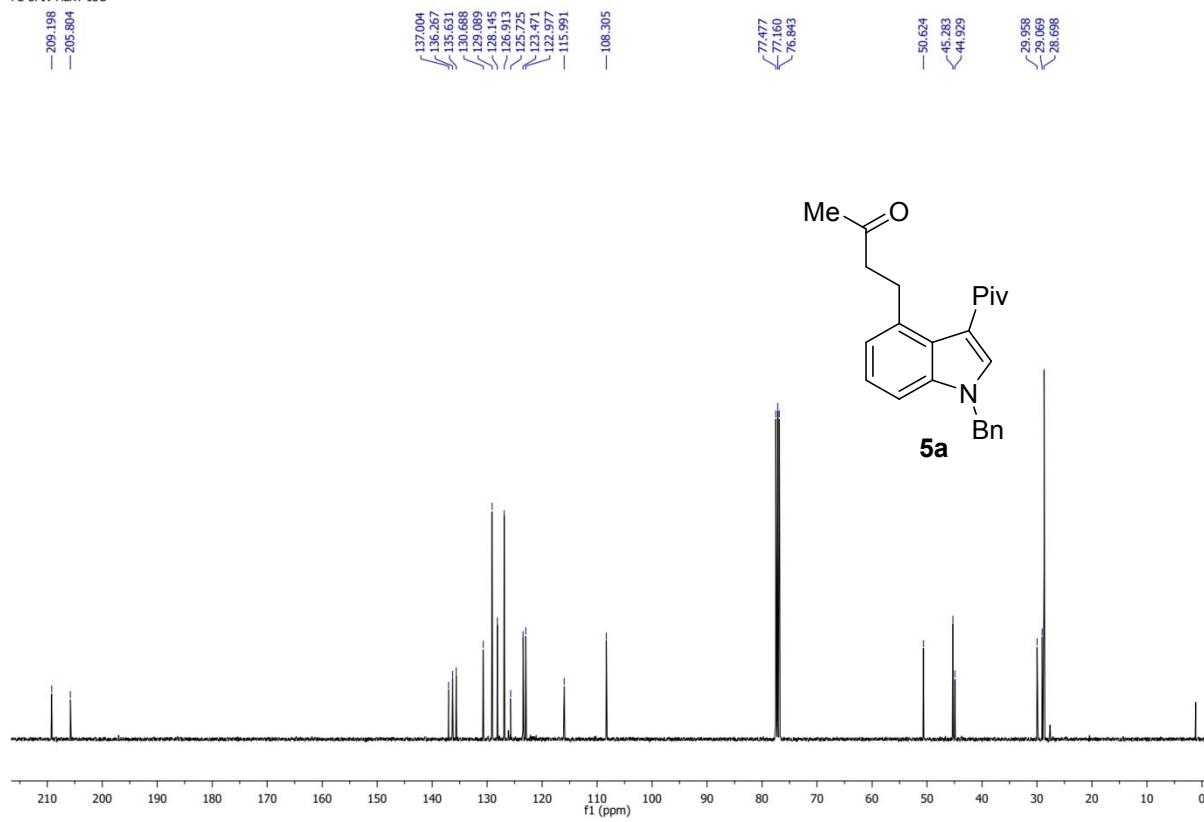




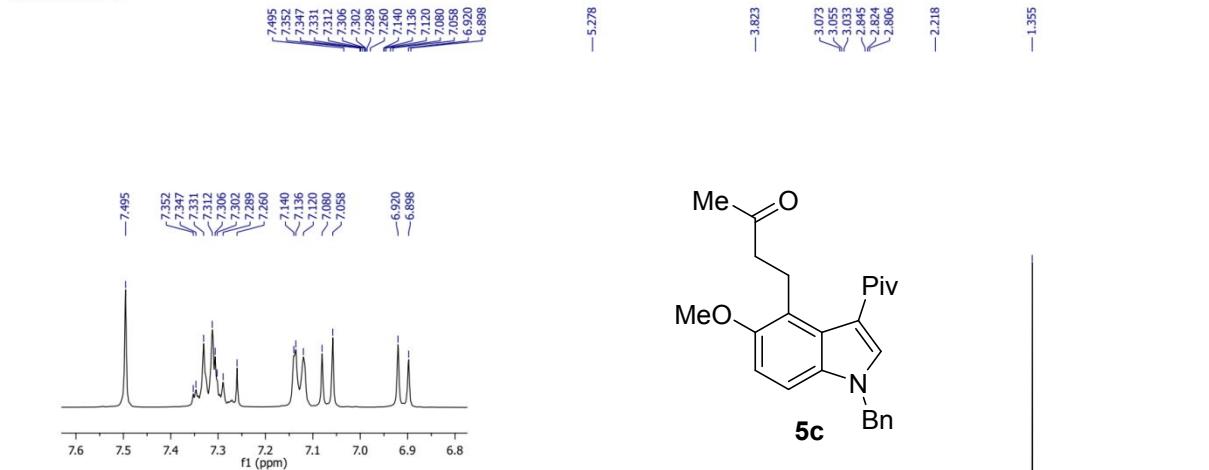
PS-3PIV-ALKY-1H



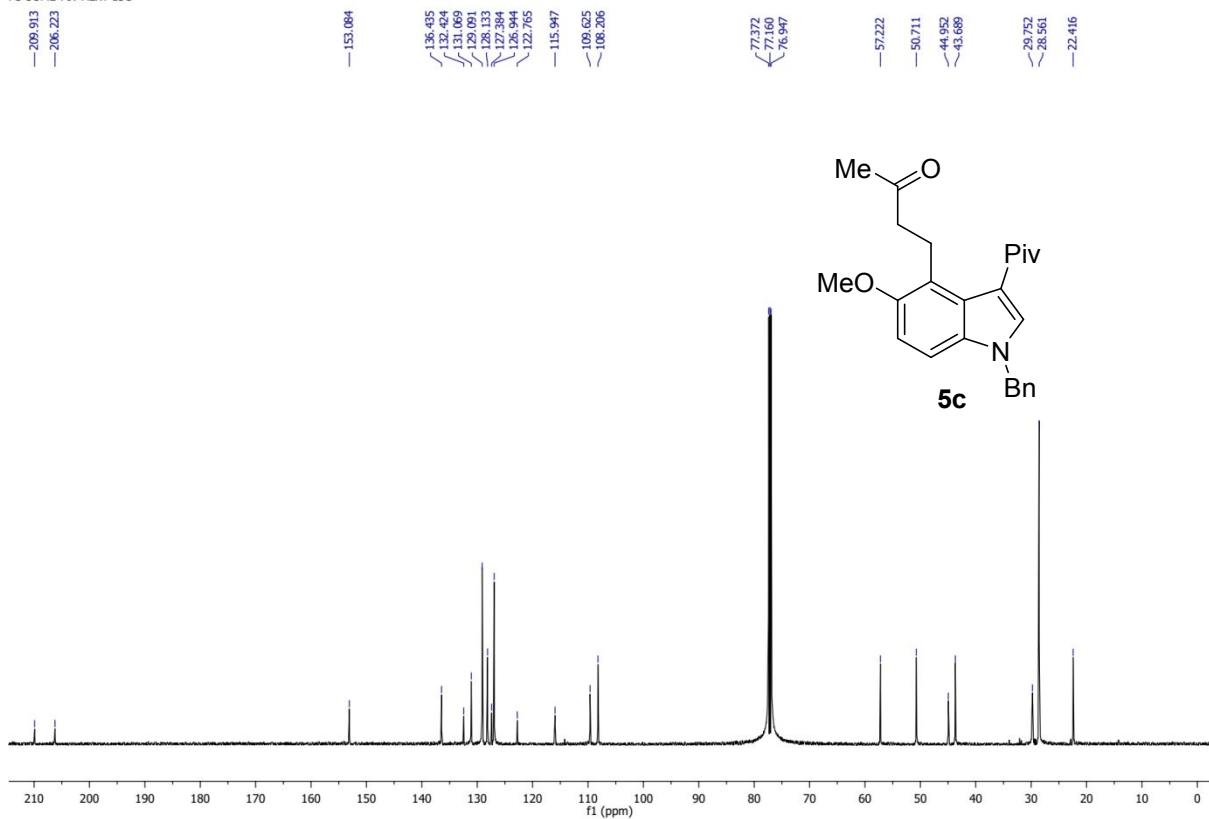
PS-3PIV-ALKY-13C



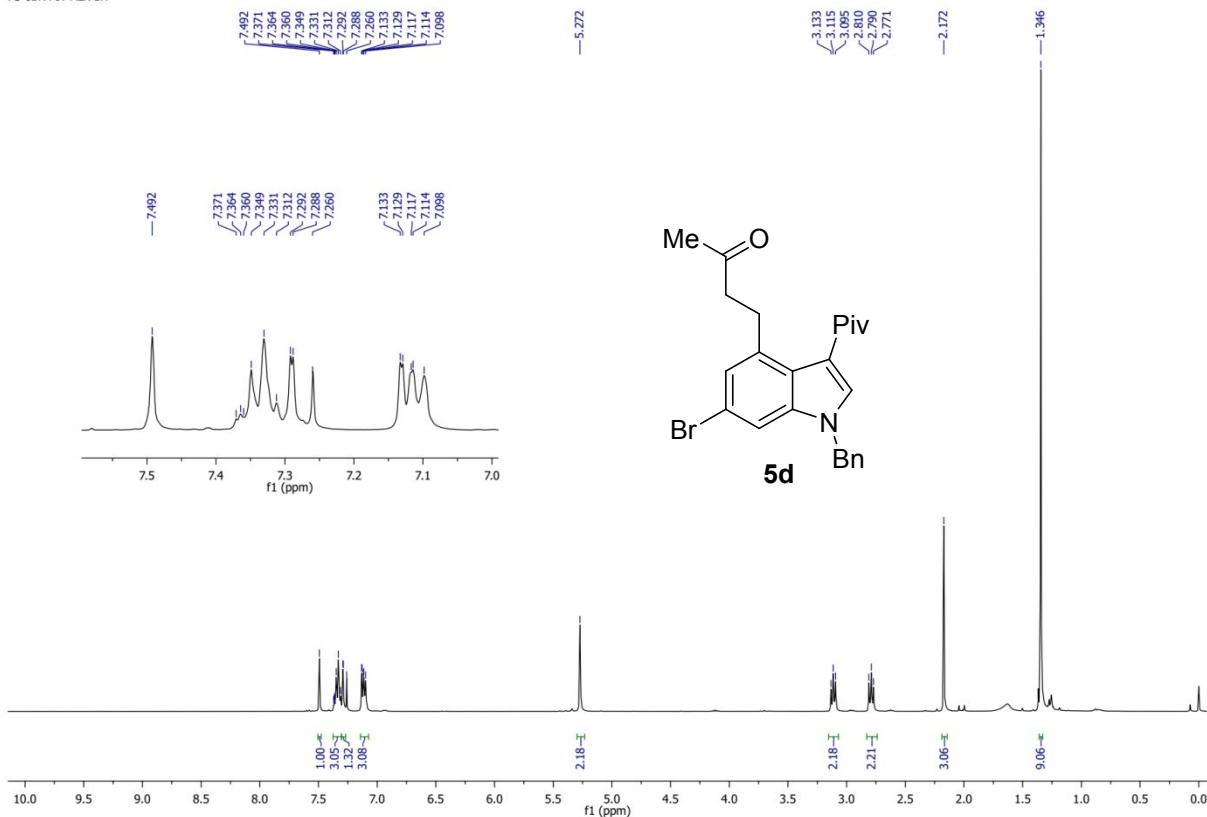
PS-SOME-PIV-ALKY-1H



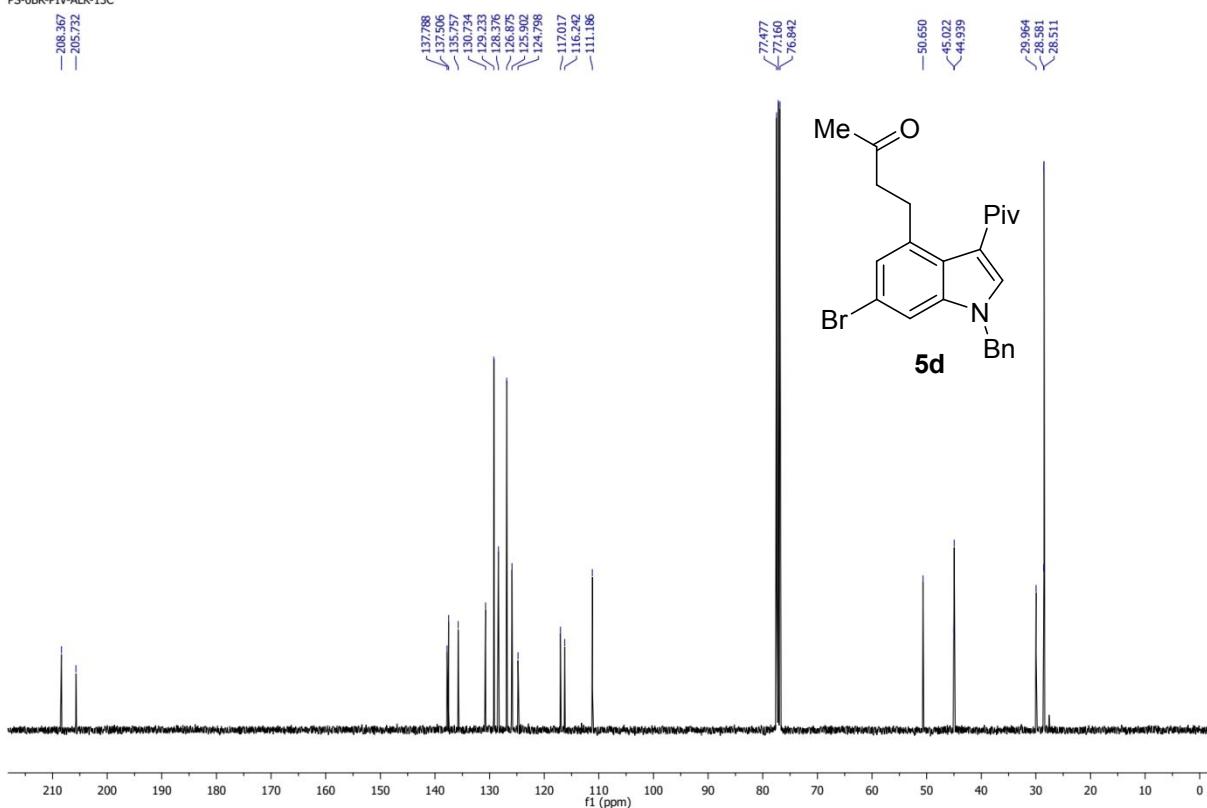
PS-SOME-PIV-ALKY-13C



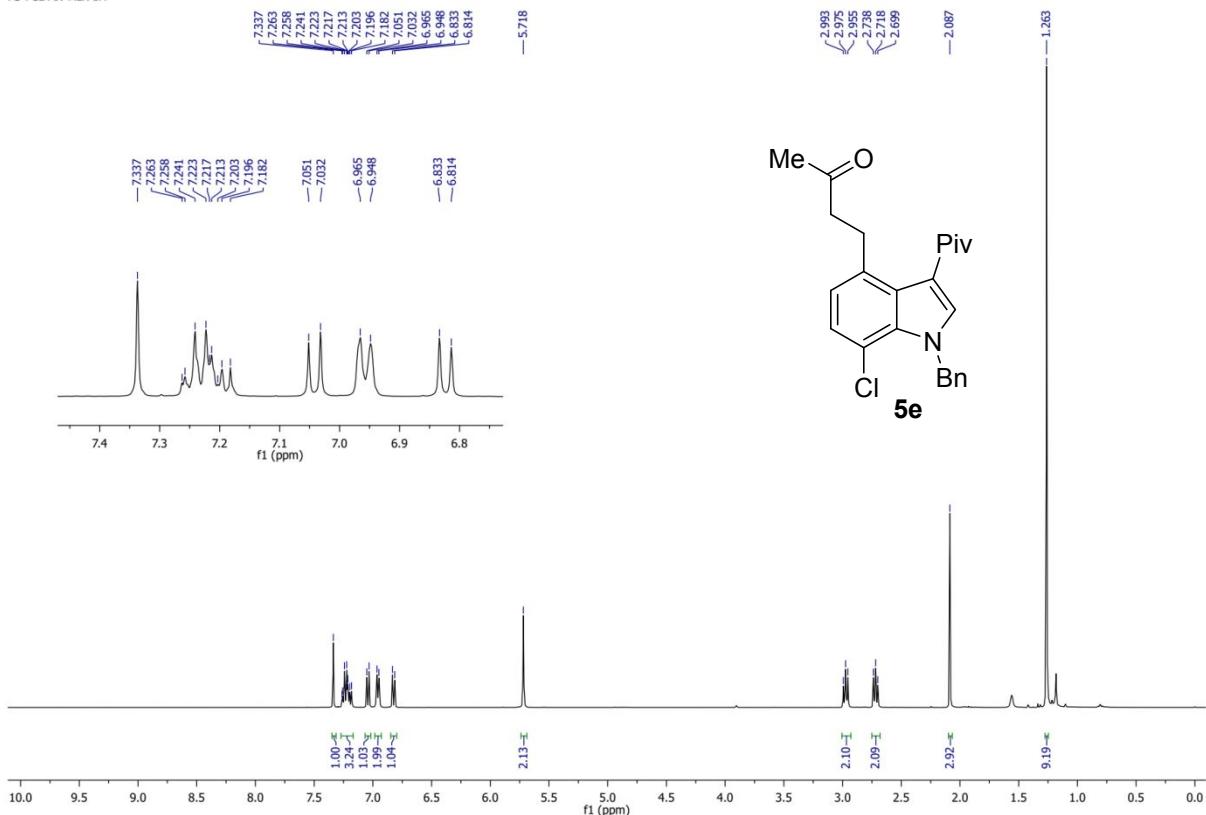
PS-6BR-PIV-ALK-1H



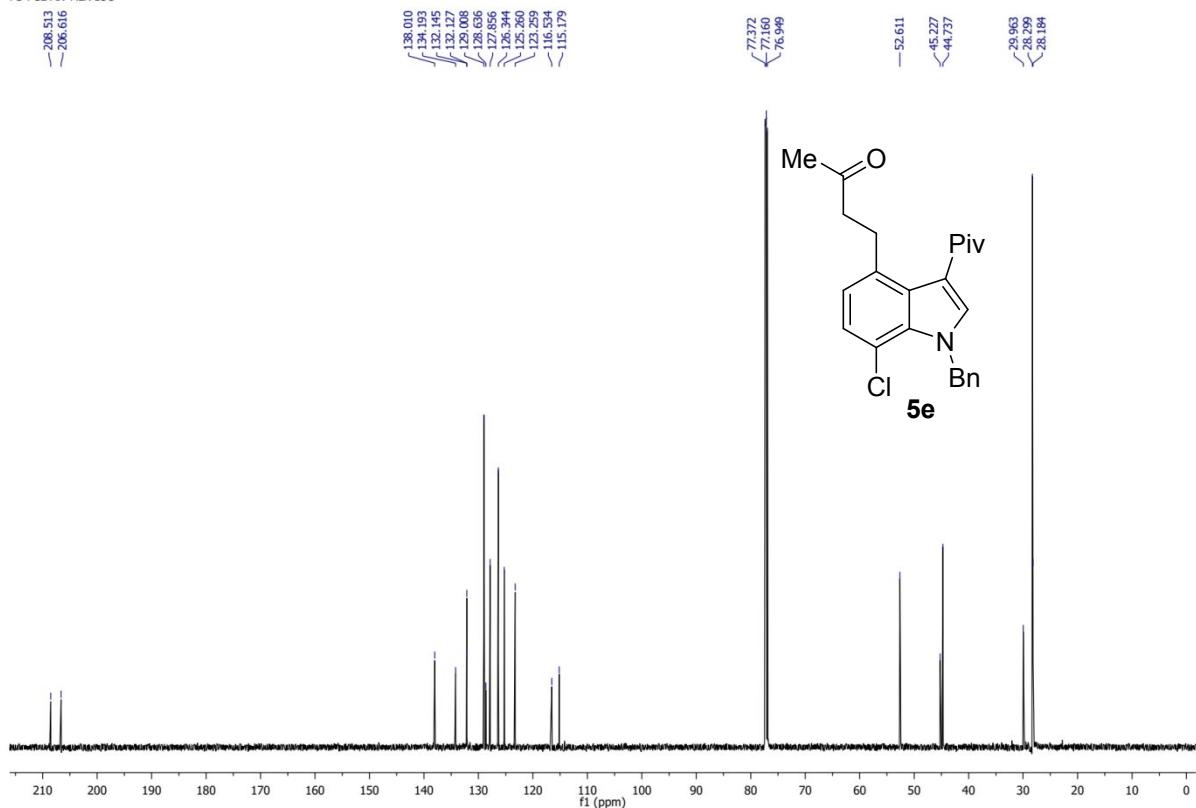
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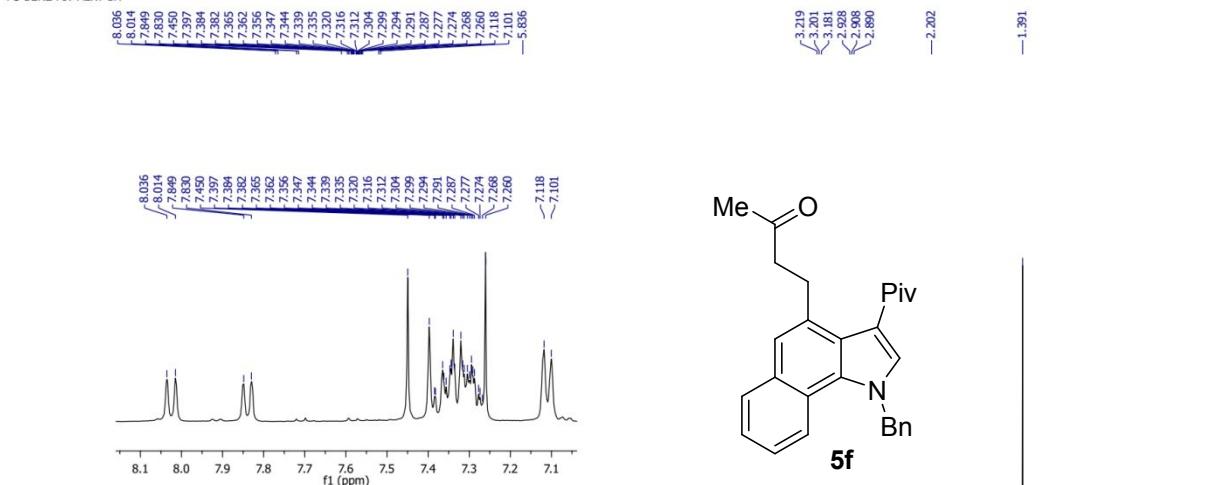
PS-7CL-PIV-ALK-1H



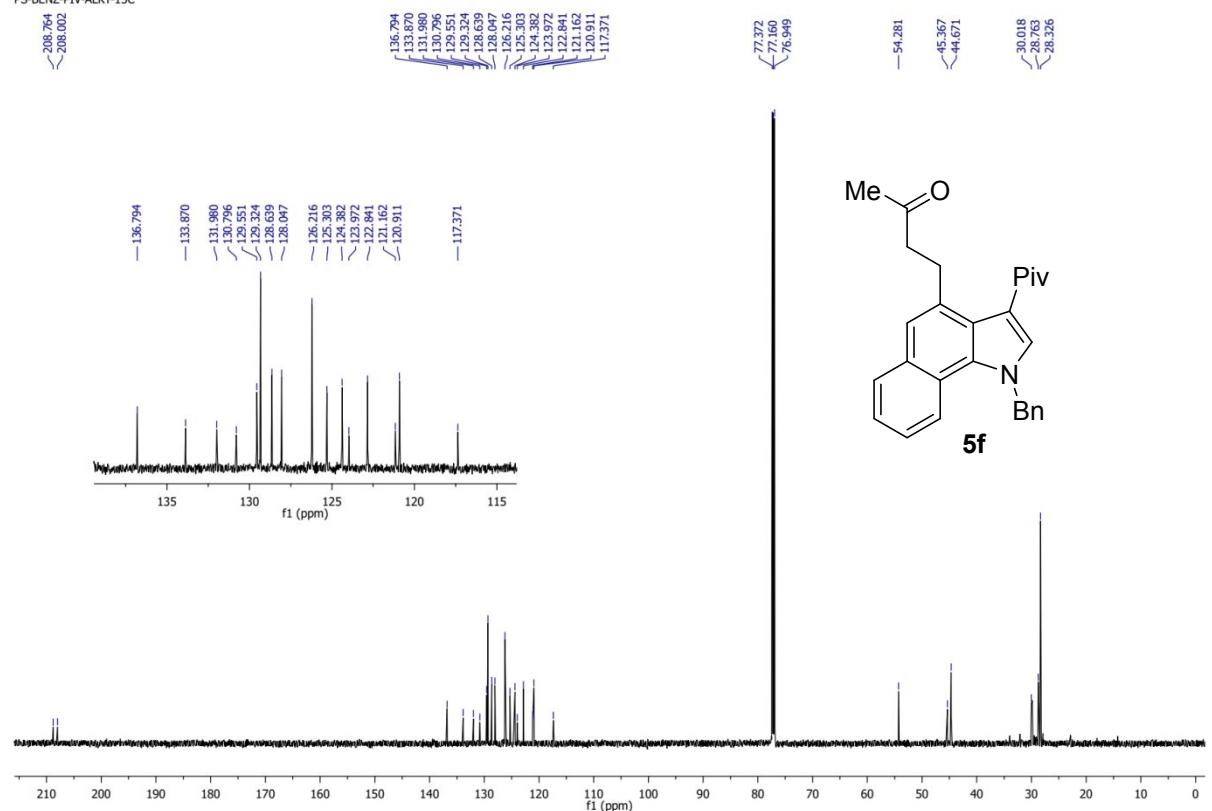
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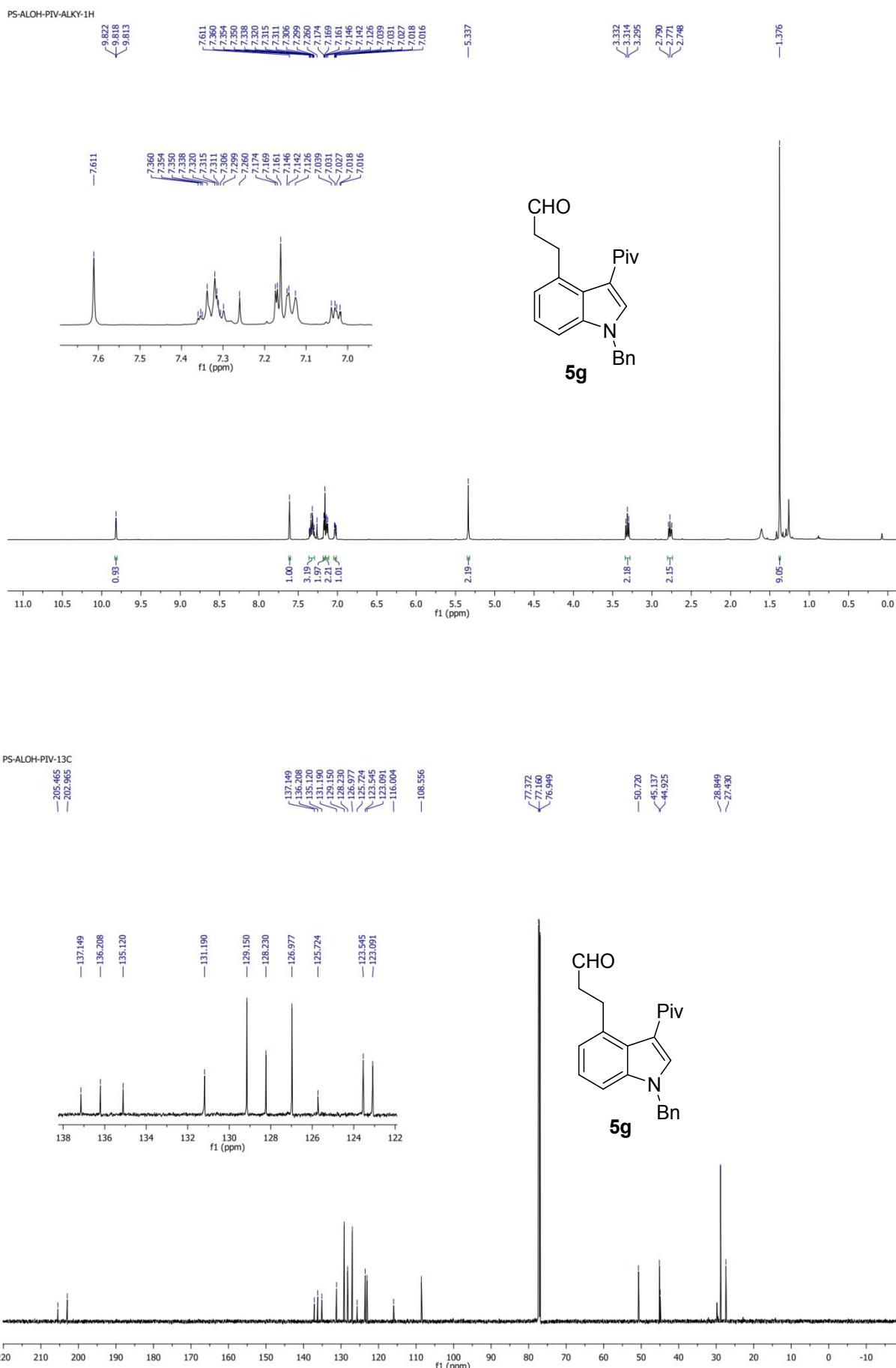


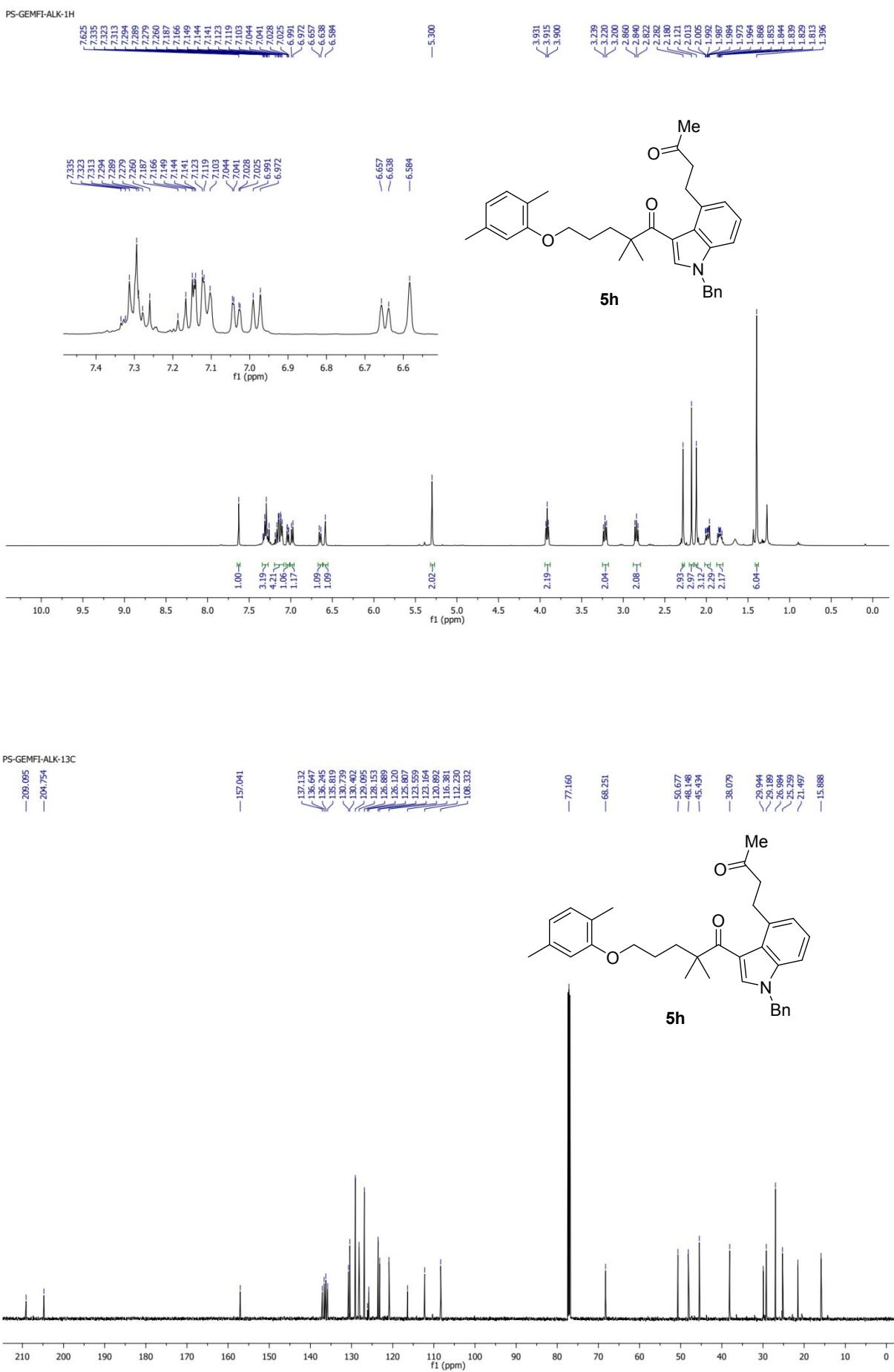
PS-BENZ-PIV-ALKY-1H



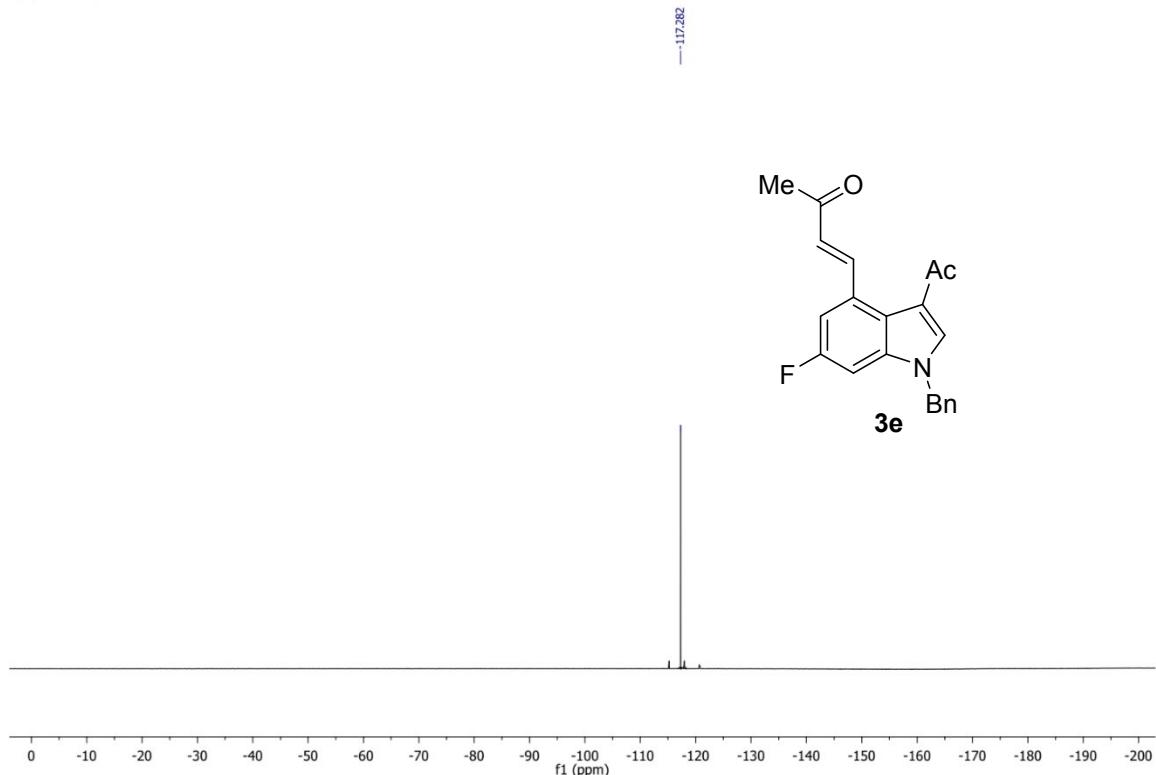
PS-BENZ-PIV-ALKY-13C



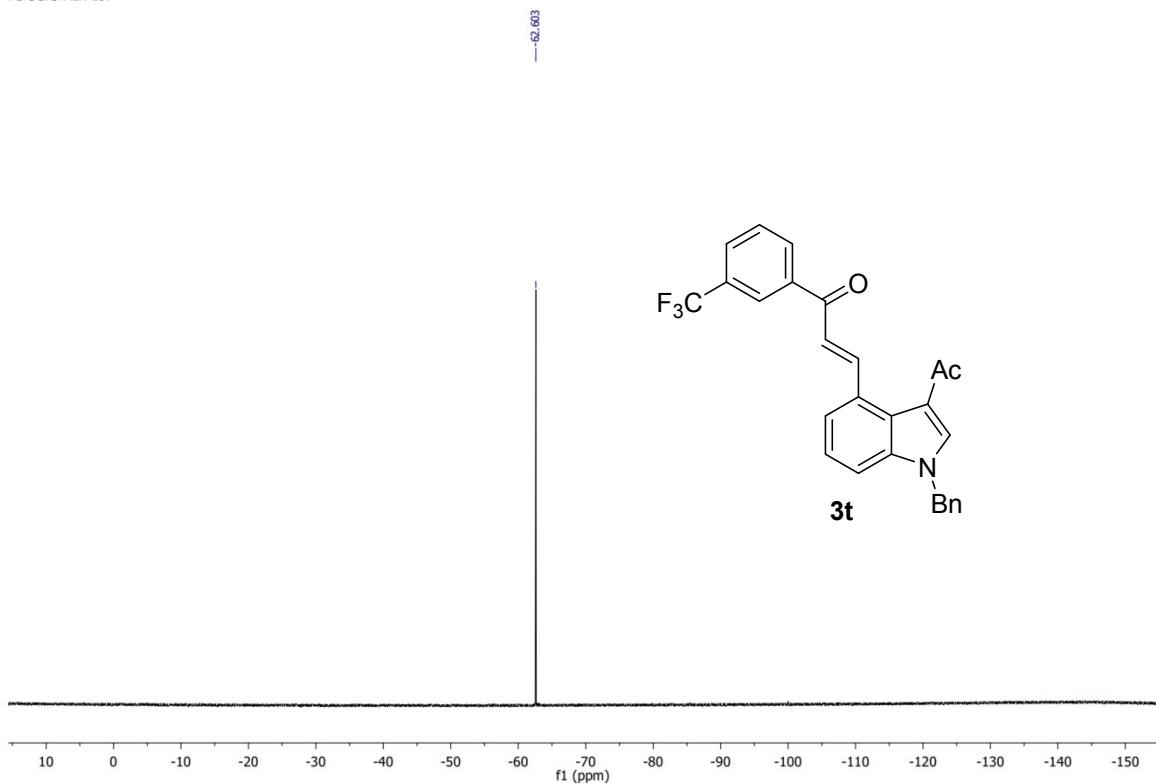




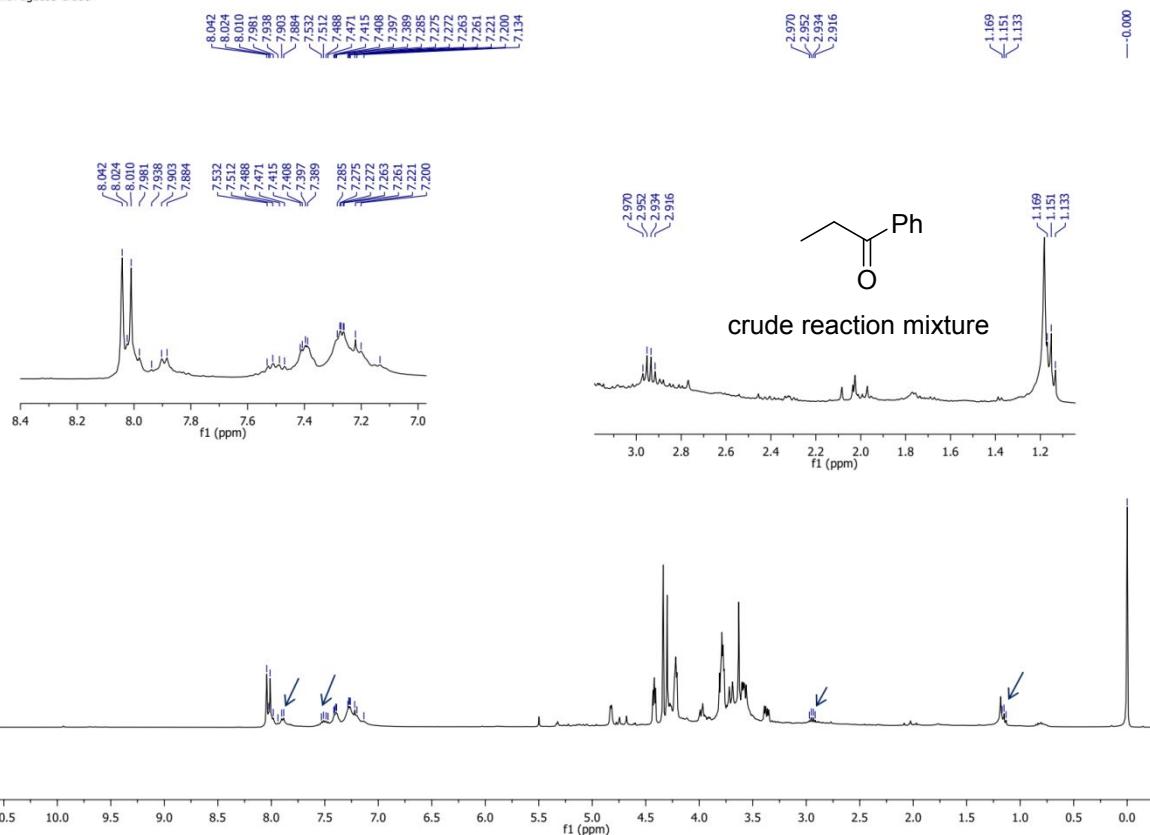
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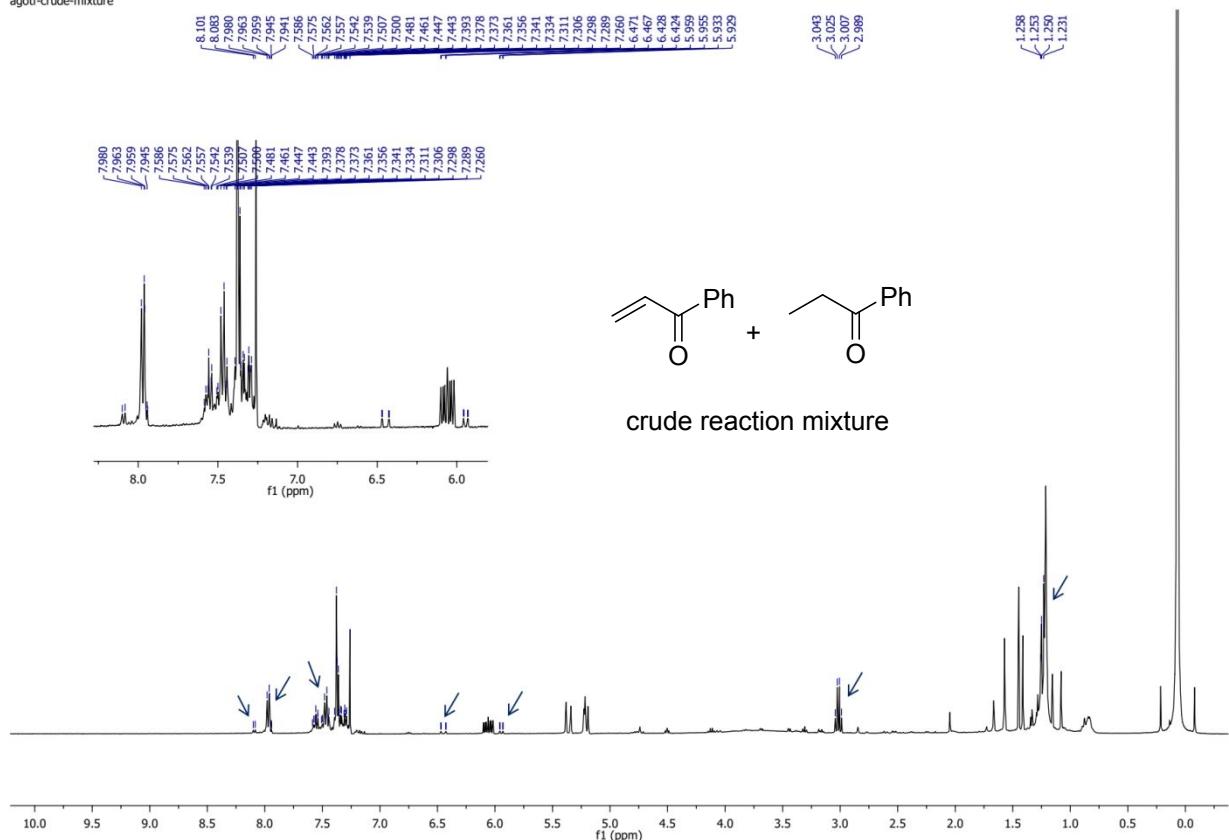
PS-3CF3-ALK-19F

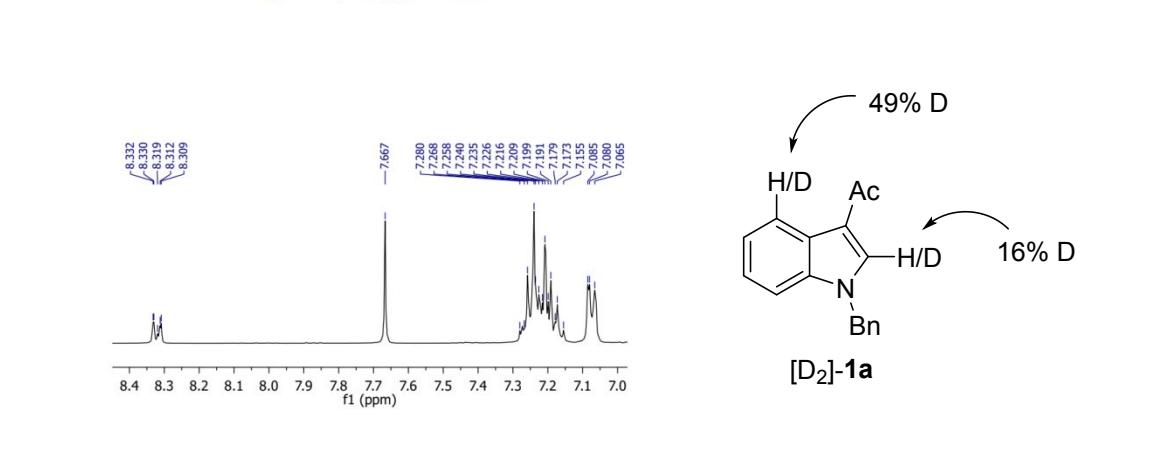


PS-with ag2co3-crude

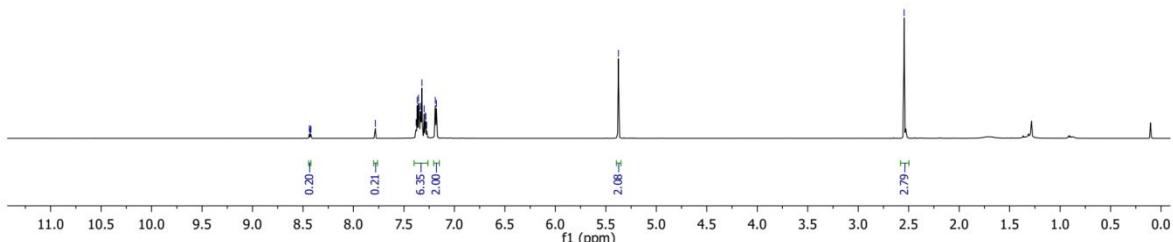
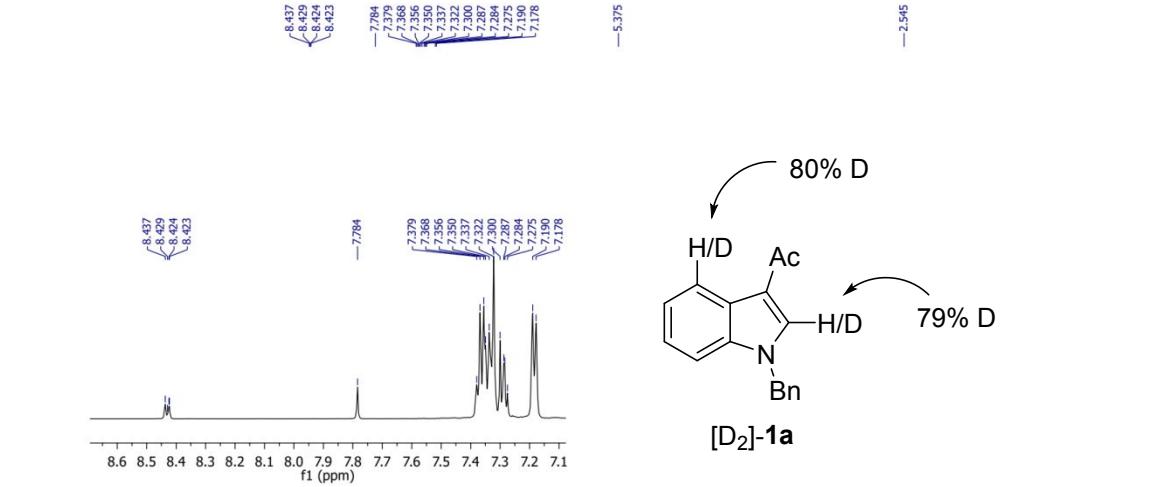


agotf-crude-mixture

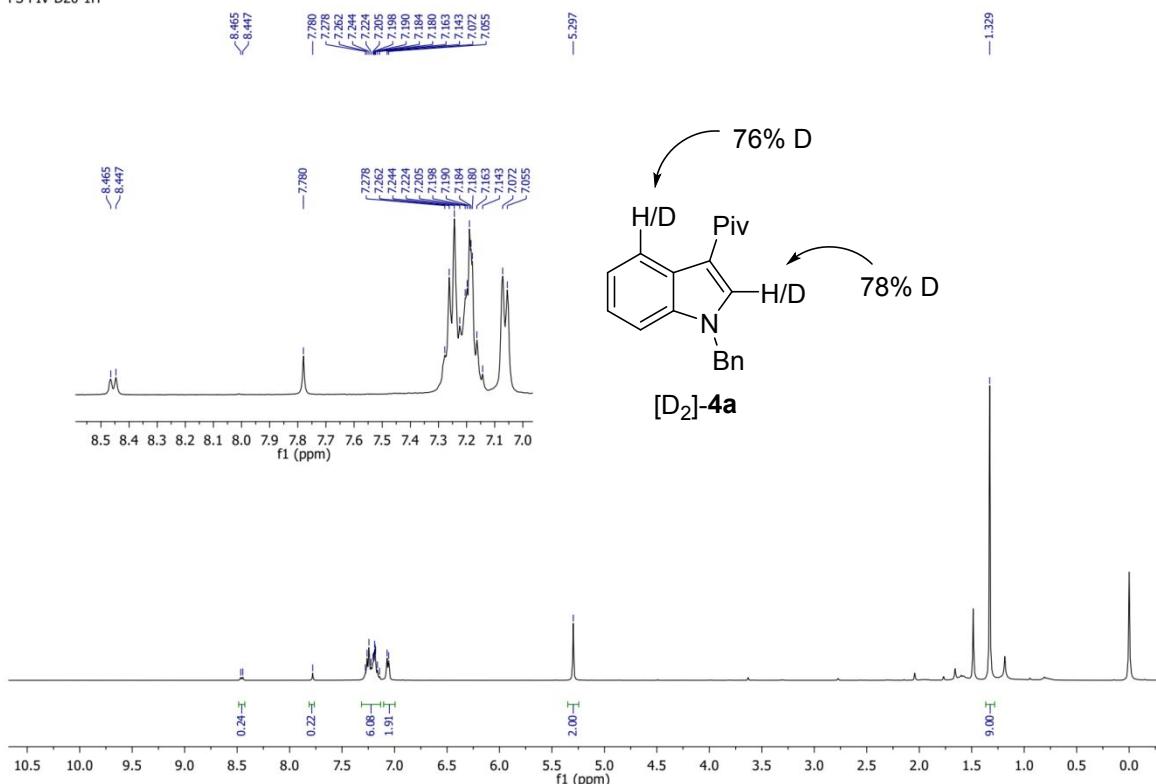




D2-1a-1H



PS-PIV-D20-1H



PIV-ALK-HDEX-WITH ALOH

