Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A redox-neutral weak carbonyl chelation assisted C4-H allylation of indoles with vinylcyclopropanes

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General Information. Indoles, [Ru(*p*-cymene)Cl_2]$_2$ (>97%), $RuCl_3 \cdot 3H_2O$ (>98%), $MesCO_2H$ (99%), 1-$AdCO_2H$ (99%), PivOH (99%), K_3PO_4 (98%), CS_2CO_3 (98%), K_2CO_3 (≥98%) Na_2CO_3 (99.5%), 3,4-dihydro-1(2*H*)-naphthalenone (97%), 3,4-epoxy-1-butene (98%), TFE and HFIP of Aldrich and TCI Chemicals were used as received. Methanol, tetrahydrofuran, 1,2-dichloroethane and chlorobenzene were dried prior as per the standard procedure. Merck silica gel G/GF254 plates were used for analytical thin-layer chromatography. Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record spectra using $CDCl_3$ 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 to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer Fourier transform infrared spectrometer. Quadrupole time-of-flight electrospray ionization mass spectrometer (Agilent 6546) and Xevo XS mass spectrometer were used for recording HRMS.

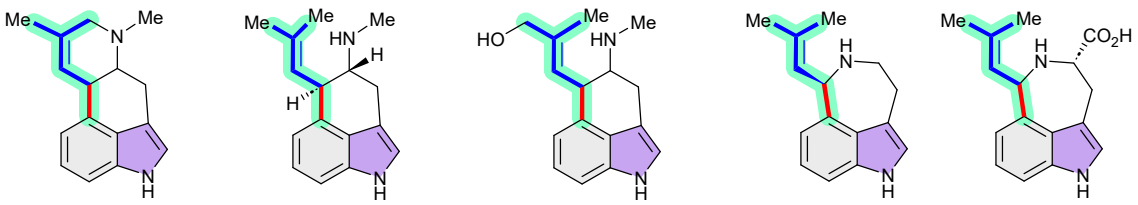
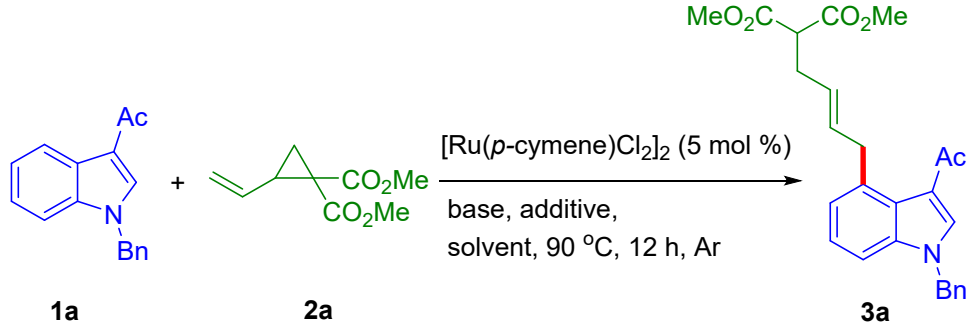


Fig. S1 Representative Natural Products of C4-Allylated Indoles.

Table S1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

Entry	base	additive	solvent	yield (%) [b]	*E/Z* ratio [c]
1	K_3PO_4	---	HFIP	32	8:1
2	CS_2CO_3	---	HFIP	41	12:1
3	K_2CO_3	---	HFIP	65	14:1
4	Na_2CO_3	---	HFIP	50	10:1
5	**K_2CO_3**	**$MesCO_2H$**	**HFIP**	**79**	**25:1**
6	K_2CO_3	1-$AdCO_2H$	HFIP	68	18:1
7	K_2CO_3	PivOH	HFIP	64	16:1
8	K_2CO_3	TsOH	HFIP	61	13:1
9	K_2CO_3	$(PhO)_2POOH$	HFIP	52	10:1
10	K_2CO_3	$MesCO_2H$	TFE	25	7:1
11	K_2CO_3	$MesCO_2H$	MeOH	trace	---
12	K_2CO_3	$MesCO_2H$	H_2O	n.d.	---
13	K_2CO_3	$MesCO_2H$	$(CH_2Cl)_2$	45	5:1
14	K_2CO_3	$MesCO_2H$	THF	trace	---
15	K_2CO_3	$MesCO_2H$	PhCl	n.d.	---
16	---	$MesCO_2H$	HFIP	n.d.	---
17[d]	K_2CO_3	$MesCO_2H$	HFIP	41	25:1
18[e]	K_2CO_3	$MesCO_2H$	HFIP	23	25:1
19[f]	K_2CO_3	$MesCO_2H$	HFIP	n.d.	---
20[g]	K_2CO_3	$MesCO_2H$	HFIP	n.d.	---
21[h]	K_2CO_3	$MesCO_2H$	HFIP	55	25:1

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), base (0.2 mmol), additive (30 mol %), solvent (1 mL), 90 °C, 12 h, Ar, pressure tube. [b] Isolated yield. [c]

Determined by ^{1}H NMR. [d] 1.0 equiv base used. [e] Reaction at 25 °C. [f] Without [Ru]-catalyst. [g] 5 mol % $RuCl_3 \cdot 3H_2O$ used. [h] Under air. n.d. = not detected

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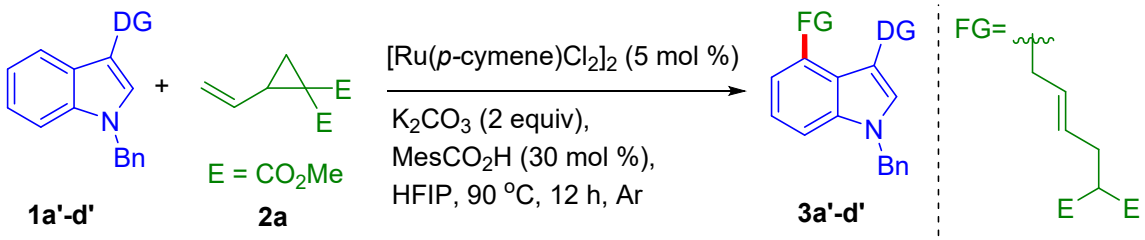
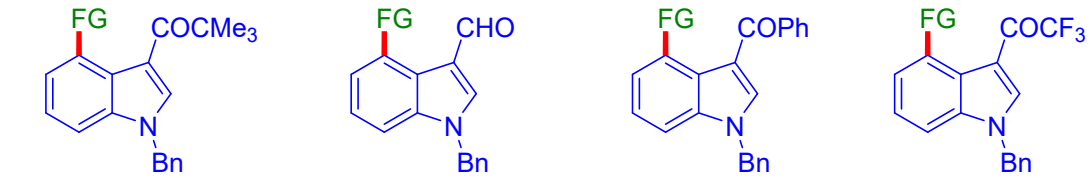
Scheme S1. Directing Groups Screening[a,b]





[a]Reaction conditions: **1a′-d′** (0.1 mmol), **2a** (0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), K_2CO_3 (0.2 mmol), $MesCO_2H$ (30 mol %), HFIP (1 mL), 90 °C, 12 h, Ar, pressure tube . [b]Isolated yield.

General Procedure for the Preparation of Indole Substrates 1.[1] To a stirred solution of indole (2 mmol) in CH_2Cl_2 (10 mL), Et_2AlCl (1.5 mL, 3 mmol, 2 mol/L in hexane) was added dropwise under argon atmosphere at 0 °C. The resulting solution was allowed to stir for 30 min at 0 °C. Then, the solution of corresponding acid chloride (3 mmol) in CH_2Cl_2 (5 mL) was added dropwise at 0 °C and was further stirred at the same temperature for an appropriate time (2-4 h). The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was quenched with aqueous buffer (pH 7) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying over Na_2SO_4 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.

Next, to a stirred suspension of NaH (1.05 mmol, 60 % dispersion in mineral oil) in THF (5 mL) at 0 °C, 3-acyl indole (1 mmol) was added and stirred for 15 minutes. Then, corresponding

alkyl bromide (1.1 mmol) was added slowly to the reaction mixture and allowed to warm at room temperature and stirred for the appropriate time. Upon completion (as monitored by TLC), the reaction mixture was quenched with water and extracted with EtOAc (3 x 10 mL). The combined solution was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and *n*-hexane as an eluent to give *N*-alkyl 3-acyl indole **1**.

Substrate **1k** is new, the complete characterization data are provided, whereas **1a-j**, **1l-u**, **1a′-d′**, **1A-C** and **1E** are known, synthesized according to the reported procedure and ^{1}H NMR are given to show the purity.

General Procedure for the Synthesis of Vinylcyclopropanes 2.[2]

Preparation of 2a:[2d] To an oven-dried round bottom flask, Na-metal (10.3 mmol, 240 mg) was added portion-wise in dry MeOH (10 mL) and stirred at room temperature until complete dissolution. The resulting solution was added dropwise to a stirring solution of (*E*)-1,4-dibromobut-2-ene (4.7 mmol, 1g) and dimethyl malonate (5.1 mmol, 0.59 mL) in dry MeOH (5 mL) at room temperature under argon atmosphere and allowed to stir for 16 h. Upon completion (monitored by TLC), the reaction mixture was quenched with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined solution was washed with brine (1 x 10 mL) and water (1 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and *n*-hexane (10/90, v/v) as an eluent to give vinylcyclopropane **2a** in 80% (691 mg) yield.

Preparation of 2b-i:[2b] To a stirred solution of (*E*)-1,4-dibromobut-2-ene (2.5 mmol, 535 mg) and corresponding malonate (2.5 mmol) in dry THF (15 mL), Cs_2CO_3 (6.25 mmol, 2 g) was added and allowed to stir at 60 °C for an appropriate time (24-48 h). Upon completion, monitored by TLC, the reaction mixture was cooled to room temperature, diluted with diethyl ether (20 mL) and passed through a short pad of celite. The organic part was washed with saturated aq. $NaHCO_3$ solution (5 mL) and brine (5 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and *n*-hexane (20/80, v/v) as an eluent to give VCPs **2b-i**.

Preparation of 2k:[2a,e]

To a stirred solution of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (5.88 mmol, 1.08 g) in MeOH (5 mL) at room temperature, 1.7N NaOH solution (7 mmol, 5 mL) was added and

allowed the solution to stir for 1.5 h. Upon completion, the reaction mixture was diluted with EtOAc (10 mL) and water (5 mL) to get two separate layers. Then, the aqueous part was acidified with 5% HCl solution as monitored by pH paper. The organic layer was extracted with EtOAc (3 x 10 mL) and washed with brine (10 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was concentrated under vacuum to get the mono-saponified VCP and used for the next step without purification.

Next, to a stirred solution of 1-(methoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid (1.1 mmol, 190 mg) in dry CH_2Cl_2 (5 mL), *vitamin E* (1 mmol, 430 mg), DMAP (0.2 mmol, 25 mg) and DCC (1.3 mmol, 268 mg) were added in a sequence at 0 °C. Then, the reaction mixture was allowed to cool to room temperature and stirred for 12 h at the same temperature. Upon completion, monitored by TLC, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. Evaporation of the solvent gave a residue which was purified on silica gel column chromatography using ethyl acetate and *n*-hexane (10/90, v/v) as an eluent to give VCP **2k**.

Substrate **2k** is new whose characterization data are provided whereas **2a-j** are known and prepared according to the reported procedure whose ^{1}H NMR are given to show the purity.

General Procedure for the Synthesis of Vinylaziridine 2A.[3] To a stirred solution of buta-1,3-diene (5 mmol, 0.44 mL) and Chloramine-T trihydrate (5.5 mmol, 1.55 g) in dry CH_3CN (25 mL), pyridinium hydrobromide perbromide (0.5 mmol, 160 mg) was added and allowed to stir at room temperature for 12 h under argon atmosphere. Upon completion, monitored by TLC, the reaction mixture was quenched with water (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic solution was washed with brine (1 x 10 mL) and water (1 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (90/10, v/v) as an eluent to give vinylaziridine **2A** in 52% (557 mg) yield.

General Procedure for Ru(II)-Catalyzed C4-Allylation of Indoles. In an oven-dried pressure tube, a mixture of indole **1** (0.1 mmol), vinylcyclopropane **2** (0.2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3 mg), K_2CO_3 (0.2 mmol, 28 mg) and $MesCO_2H$ (0.03 mmol, 5 mg) were stirred in HFIP (1 mL) at 90 ^{o}C in a preheated oil bath for 12 h under Ar atmosphere. The reaction progress was monitored by TLC using ethyl acetate and hexane as an eluent. Upon completion, the reaction mixture was allowed to cool to room temperature and was diluted with EtOAc and passed through a celite pad. The filtrate was concentrated under

reduced pressure and the residue was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford C4-allylated indole **3** in moderate to good yields.

Scale-up Synthesis of 3a. In an oven-dried pressure tube, a mixture of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (2 mmol, 498 mg), dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (4 mmol, 736 mg), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%, 0.1 mmol, 61 mg), K_2CO_3 (4 mmol, 552 mg), $MesCO_2H$ (0.6 mmol, 98 mg) and HFIP (15 mL) were subjected to the aforementioned general procedure. Upon completion, monitored by TLC, the reaction mixture was cooled to room temperature and was diluted with EtOAc and passed through a short pad of celite. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent (85/15, v/v) to afford **3a** in 65% (0.56 g) yield.

Procedures for the Post-Synthetic Modifications

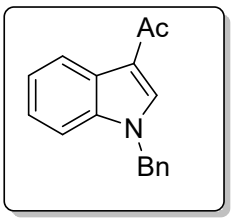
Removal of Acetyl Directing Group.[1a] In an oven-dried round bottom flask, a mixture of dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate **3a** (0.1 mmol, 43 mg), ethylene glycol (0.1 mL) and *p*-toluenesulfonic acid monohydrate (0.1 mmol, 21 mg) was refluxed in benzene (2 mL) for 3 h. After completion, monitored by TLC, the reaction mixture was cooled to room temperature, washed with saturated $NaHCO_3$ solution (5 mL) and extracted using EtOAc (3 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent under reduced pressure gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (97/3, v/v) as an eluent to afford **5** in 73 % (28.5 mg) yield.

Synthesis of 6.[4] In an oven-dried round bottom flask, a mixture of dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate **3a** (0.1 mmol, 43 mg) and LiCl (0.5 mmol, 21 mg) in DMSO (1 mL) and H_2O (0.5 mmol, 10 µL) was stirred at 150 °C for 12 h under argon atmosphere. Upon completion, the reaction mixture was cooled to room temperature and extracted with EtOAc (3 x 10 mL). The organic layer was washed with brine (1 x 10 mL) and water (1 x 10 mL). Drying over Na_2SO_4 and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (90/10, v/v) as an eluent to afford **6** in 70 % (26.2 mg) yield.

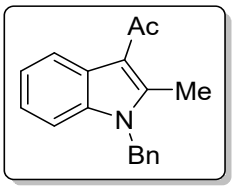
Synthesis of 7.[5] To a stirred solution of dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate **3a** (0.1 mmol, 43 mg) and a suspension of NaH (0.11 mmol, 4.5 mg, 60 % dispersion in mineral oil) in THF (2 mL) at 0 °C for 20 min, allyl bromide (0.1 mmol, 9 µL) was added and the stirring was continued for 3 h at room temperature. Upon completion, monitored by TLC, the reaction mixture was quenched with saturated aq. NH_4Cl solution (1

mL) and diluted with EtOAc (5 mL) and water (5 mL), The organic layer was extracted using EtOAc (2 x 10 mL), dried over Na_2SO_4 and evaporation of the solvent under reduced pressure gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (90/10, v/v) as an eluent to afford **7** in 66 % (31.2 mg) yield.

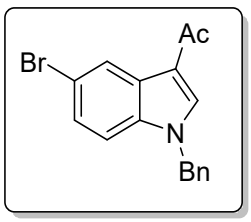
Characterization Data of the Indole Substrates



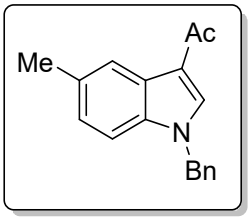
1-(1-Benzyl-1*H*-indol-3-yl)ethan-1-one 1a. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41-8.39 (m, 1H), 7.75 (s, 1H), 7.35-7.27 (m, 5H), 7.16-7.15 (m, 2H), 5.35 (s, 2H), 2.52 (s, 3H).



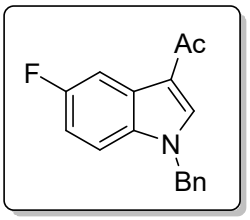
1-(1-Benzyl-2-methyl-1*H*-indol-3-yl)ethan-1-one 1b. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.29-7.25 (m, 5H), 7.22-7.19 (m, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 5.38 (s, 2H), 2.74 (s, 3H), 2.71 (s, 3H).



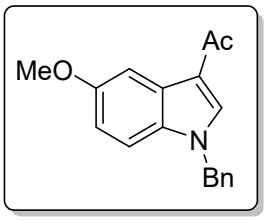
1-(1-Benzyl-5-bromo-1*H*-indol-3-yl)ethan-1-one 1c. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57-8.56 (m, 1H), 7.72 (s, 1H), 7.37-7.32 (m, 4H), 7.15-7.12 (m, 3H), 5.32 (s, 2H), 2.49 (s, 3H).



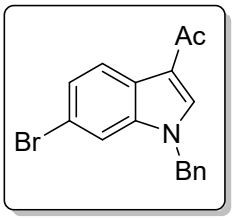
1-(1-Benzyl-5-methyl-1*H*-indol-3-yl)ethan-1-one 1d. Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.71 (s, 1H), 7.35-7.30 (m, 3H), 7.18-7.13 (m, 3H), 7.09-7.06 (m, 1H), 5.32 (s, 2H), 2.50 (s, 3H), 2.47 (s, 3H).



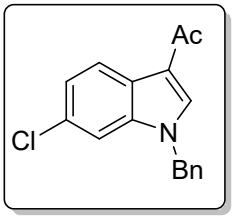
1-(1-Benzyl-5-fluoro-1*H*-indol-3-yl)ethan-1-one 1e. Light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.76 (s, 1H), 7.37-7.31 (m, 3H), 7.19-7.13 (m, 3H), 6.99-6.94 (m, 1H), 5.32 (s, 2H), 2.48 (s, 3H).



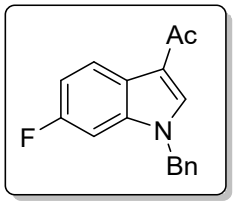
1-(1-Benzyl-5-methoxy-1*H*-indol-3-yl)ethan-1-one 1f. Brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.91 (m, 1H), 7.70 (s, 1H), 7.33-7.29 (m, 3H), 7.15-7.12 (m, 3H), 6.88-6.87 (m, 1H), 5.28 (s, 2H), 3.87 (s, 3H), 2.48 (s, 3H).



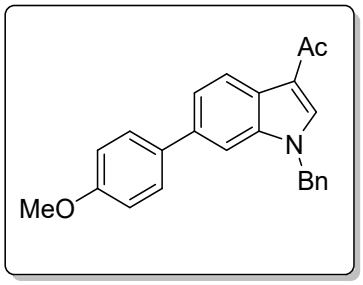
1-(1-Benzyl-6-bromo-1*H*-indol-3-yl)ethan-1-one 1g. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.46-7.45 (m, 1H), 7.40-7.33 (m, 4H), 7.15-7.13 (m, 2H), 5.30 (s, 2H), 2.49 (s, 3H).



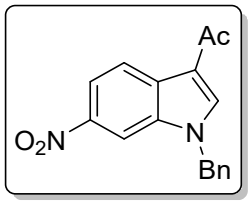
1-(1-Benzyl-6-chloro-1*H*-indol-3-yl)ethan-1-one 1h. Light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.69 (s, 1H), 7.37-7.32 (m, 3H), 7.27-7.22 (m, 2H), 7.14-7.12 (m, 2H), 5.27 (s, 2H), 2.47 (s, 3H).



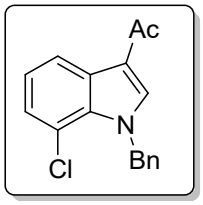
1-(1-Benzyl-6-fluoro-1*H*-indol-3-yl)ethan-1-one 1i. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26-8.23 (m, 1H), 7.62 (s, 1H), 7.26-7.21 (m, 3H), 7.05-7.04 (m, 2H), 6.94-6.91 (m, 1H), 6.85-6.83 (m, 1H), 5.17 (s, 2H), 2.38 (s, 3H).



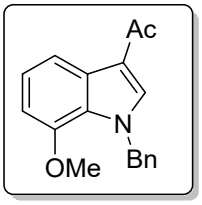
1-(1-Benzyl-6-(4-methoxyphenyl)-1*H*-indol-3-yl)ethan-1-one 1j. Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.41-7.39 (m, 3H), 7.31 (s, 1H), 7.25-7.18 (m, 3H), 7.07-7.06 (m, 2H), 6.87 (d, J = 9.0 Hz, 2H), 5.24 (s, 2H), 3.73 (s, 3H), 2.40 (s, 3H).



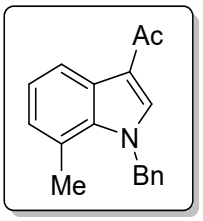
1-(1-Benzyl-6-nitro-1*H*-indol-3-yl)ethan-1-one 1k. Analytical TLC on silica gel, 1:5 ethyl acetate/hexane R_f = 0.43; yellow solid; mp 145-146 °C; yield 84% (246.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 8.4 Hz, 1H), 8.29-8.28 (m, 1H), 8.18-8.17 (m, 1H), 7.95 (s, 1H), 7.40-7.36 (m, 3H), 7.20-7.18 (m, 2H), 5.44 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 144.5, 138.8, 136.0, 134.7, 131.2, 129.5, 128.9, 127.2, 123.2, 118.0, 117.9, 107.0, 51.3, 27.8; FT-IR (KBr) 2925, 1653, 1515, 1388, 1336, 1177, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_3$: 295.1077, found 295.1073.



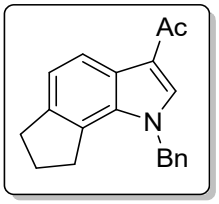
1-(1-Benzyl-7-chloro-1*H*-indol-3-yl)ethan-1-one 1l. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1H), 7.59 (s, 1H), 7.24-7.18 (m, 3H), 7.13-7.08 (m, 2H), 6.97-6.95 (m, 2H), 5.69 (s, 2H), 2.39 (s, 3H).



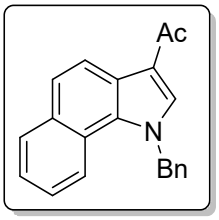
1-(1-Benzyl-7-methoxy-1*H*-indol-3-yl)ethan-1-one 1m. Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.32-7.30 (m, 2H), 7.28-7.27 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.13-7.12 (m, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.65 (s, 2H), 3.82 (s, 3H), 2.49 (s, 3H).



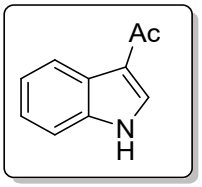
1-(1-Benzyl-7-methyl-1*H*-indol-3-yl)ethan-1-one 1n. Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.25-7.18 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.91-6.87 (m, 3H), 5.53 (s, 2H), 2.44-2.43 (m, 6H).



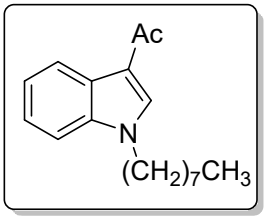
1-(1-Benzyl-1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)ethan-1-one 1o. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.23-7.18 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.93-6.91 (m, 2H), 5.39 (s, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 2.00-1.96 (m, 2H).



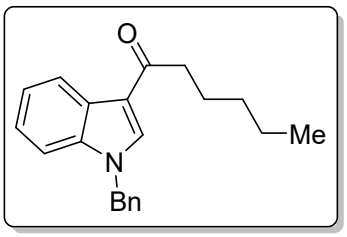
1-(1-Benzyl-1*H*-benzo[*g*]indol-3-yl)ethan-1-one 1p. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.62-7.58 (m, 2H), 7.32-7.29 (m, 1H), 7.27-7.17 (m, 4H), 6.98-6.97 (m, 2H), 5.66 (s, 2H), 2.43 (s, 3H).



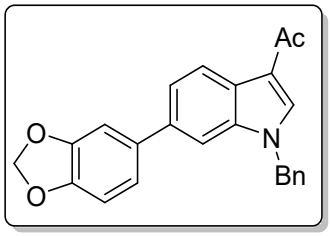
1-(1*H*-indol-3-yl)ethan-1-one 1q. Grey solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.40-8.38 (m, 1H), 7.86-7.85 (m, 1H), 7.42-7.40 (m, 1H), 7.31-7.28 (m, 2H), 2.55 (s, 3H).



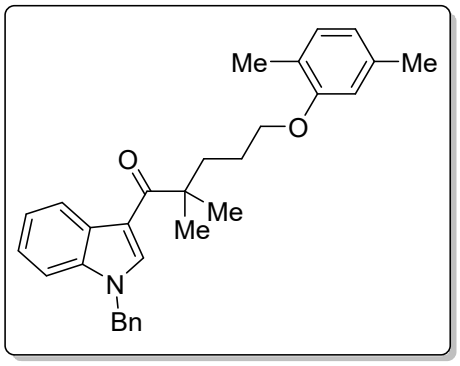
1-(1-Octyl-1*H*-indol-3-yl)ethan-1-one 1r. Light brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38-8.36 (m, 1H), 7.74 (s, 1H), 7.37-7.34 (m, 1H), 7.31-7.28 (m, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 1.90-1.86 (m, 2H), 1.60-1.58 (m, 2H), 1.35-1.31 (m, 2H), 1.30-1.23 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H).



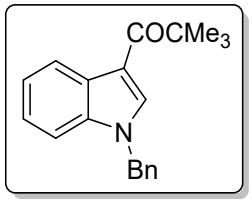
1-(1-Benzyl-1*H*-indol-3-yl)hexan-1-one 1s. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.29-7.19 (m, 6H), 7.10-7.08 (m, 2H), 5.23 (s, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.78-1.71 (m, 2H), 1.36-1.32 (m, 4H), 0.90-0.86 (m, 3H).



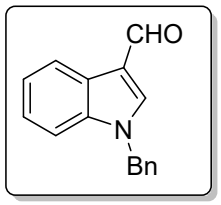
1-(6-(Benzo[*d*][1,3]dioxol-5-yl)-1-benzyl-1*H*-indol-3-yl)ethan-1-one 1t. Light brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 1H), 7.48-7.46 (m, 1H), 7.39 (s, 1H), 7.36-7.32 (m, 3H), 7.19-7.18 (m, 2H), 7.05-7.04 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 2H), 5.38 (s, 2H), 2.53 (s, 3H).



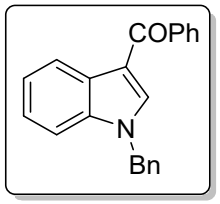
1-(1-Benzyl-1*H*-indol-3-yl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-one 1u. Brown sticky liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.8 Hz, 1H), 7.79 (s, 1H), 7.22-7.15 (m, 6H), 7.03-7.02 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.42 (s, 1H), 5.24 (s, 2H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H), 2.02 (s, 3H), 1.93-1.91 (m, 2H), 1.70-1.67 (m, 2H), 1.33 (s, 6H).



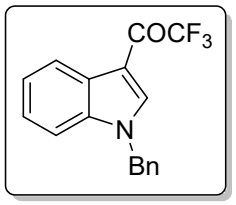
1-(1-benzyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one 1a′. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.34-7.22 (m, 6H), 7.13-7.12 (m, 2H), 5.36 (s, 2H), 1.40 (s, 9H).



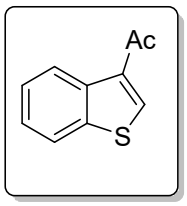
1-Benzyl-1*H*-indole-3-carbaldehyde 1b′. Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.69 (s, 1H), 7.36-7.29 (m, 6H), 7.18-7.17 (m, 2H), 5.33 (s, 2H).



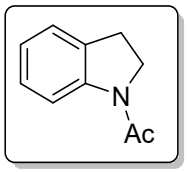
(1-Benzyl-1*H*-indol-3-yl)(phenyl)methanone 1c′. Brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.74-7.73 (m, 2H), 7.54 (s, 1H), 7.46-7.44 (m, 1H), 7.40-7.37 (t, *J* = 7.5 Hz, 2H), 7.25-7.19 (m, 6H), 7.05-7.04 (m, 2H), 5.27 (s, 2H).



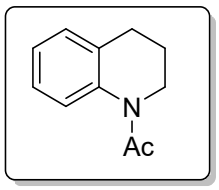
1-(1-Benzyl-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one 1d′. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H), 7.39-7.33 (m, 6H), 7.18-7.17 (m, 2H), 5.41 (s, 2H).



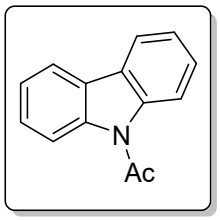
1-(Benzo[*b*]thiophen-3-yl)ethan-1-one 1A. Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.50-7.47 (m, 1H), 7.43-7.40 (m, 1H), 2.64 (s, 3H).



1-(Indolin-1-yl)ethan-1-one 1B. Light yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.19-7.16 (m, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 4.03 (t, *J* = 9.0 Hz, 2H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.21 (s, 3H).

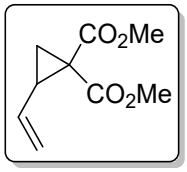


1-(3,4-Dihydroquinolin-1(2*H*)-yl)ethan-1-one 1C. Yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19-7.10 (m, 4H), 3.79-3.77 (m, 2H), 2.72-2.70 (m, 2H), 2.22 (s, 3H), 1.97-1.93 (m, 2H).

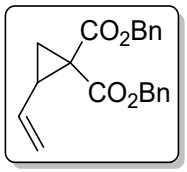


1-(9*H*-carbazol-9-yl)ethan-1-one 1E. Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.49-7.46 (m, 2H), 7.40-7.37 (m, 2H), 2.87 (s, 3H).

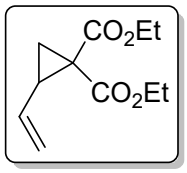
Characterization Data of the Vinylcyclopropanes and Vinylaziridine



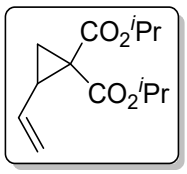
Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate 2a. Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45-5.38 (m, 1H), 5.29-5.26 (m, 1H), 5.13-5.11 (m, 1H), 3.72 (s, 6H), 2.57 (q, *J* = 8.5 Hz, 1H), 1.72-1.69 (m, 1H), 1.58-1.55 (m, 1H).



Dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate 2b. Colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.29 (m, 10H), 5.46-5.39 (m, 1H), 5.31-5.28 (m, 1H), 5.22-5.11 (m, 5H), 2.66 (q, *J* = 8.4 Hz, 1H), 1.79-1.77 (m, 1H), 1.64-1.61 (m, 1H).

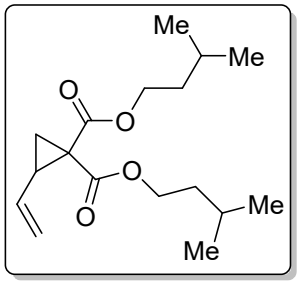


Diethyl 2-vinylcyclopropane-1,1-dicarboxylate 2c. Colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.41-5.37 (m, 1H), 5.25-5.22 (m, 1H), 5.09-5.07 (m, 1H), 4.20-4.09 (m, 4H), 2.54-2.49 (m, 1H), 1.64-1.62 (m, 1H), 1.51-1.48 (m, 1H), 1.23-1.20 (m, 6H).

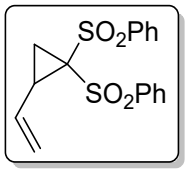


Diisopropyl 2-vinylcyclopropane-1,1-dicarboxylate 2d. Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43-5.36 (m, 1H), 5.27-5.23 (d, *J* = 17.0 Hz, 1H), 5.10-5.08 (m,

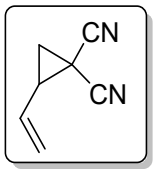
1H), 5.06-5.00 (m, 2H), 2.52 (q, J = 8.5 Hz, 1H), 1.62-1.59 (m, 1H), 1.47-1.44 (m, 1H), 1.25-1.17 (m, 12H).



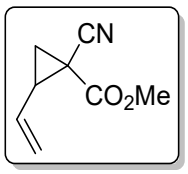
Diisopentyl 2-vinylcyclopropane-1,1-dicarboxylate 2e. Colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.44-5.38 (m, 1H), 5.28-5.26 (m, 1H), 5.12-5.10 (m, 1H), 4.19-4.09 (m, 4H), 2.55 (q, J = 9.0 Hz, 1H), 1.70-1.65 (m, 4H), 1.53-1.48 (m, 4H), 0.90-0.88 (m, 12H).



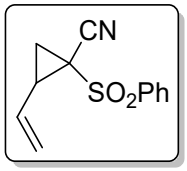
(2-vinylcyclopropane-1,1-disulfonyl)dibenzene 2f. Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.70-7.64 (m, 2H), 7.58-7.52 (m, 4H), 6.07-5.99 (m, 1H), 5.42-5.39 (m, 1H), 5.32-5.30 (m, 1H), 3.25 (q, J = 9.5 Hz, 1H), 2.35-2.32 (m, 1H), 2.13-2.10 (m, 1H).



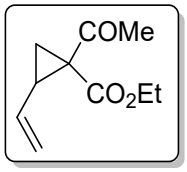
2-vinylcyclopropane-1,1-dicarbonitrile 2g. Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64-5.57 (m, 1H), 5.54-5.49 (m, 2H), 2.69 (q, J = 8.5 Hz, 1H), 2.07-2.04 (m, 1H), 1.84-1.81 (m, 1H).



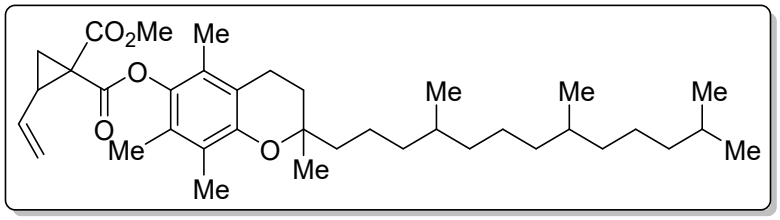
Methyl 1-cyano-2-vinylcyclopropane-1-carboxylate 2h. Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65-5.58 (m, 1H), 5.44-5.35 (m, 2H), 3.81 (s, 3H), 2.56 (q, J = 8.5 Hz, 1H), 1.99-1.95 (m, 1H), 1.67-1.64 (m, 1H).



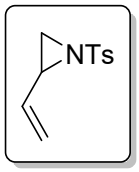
1-(phenylsulfonyl)-2-vinylcyclopropane-1-carbonitrile 2i. Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.77-7.74 (m, 1H), 7.66-7.62 (m, 2H), 5.59-5.52 (m, 1H), 5.44-5.36 (m, 2H), 2.89 (q, *J* = 8.0 Hz, 1H), 2.16-2.13 (m, 1H), 1.71-1.68 (m, 1H).



Ethyl 1-acetyl-2-vinylcyclopropane-1-carboxylate 2j. Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51-5.44 (m, 1H), 5.29-5.26 (m, 1H), 5.13-5.11 (m, 1H), 4.24-4.19 (m, 2H), 2.59 (q, *J* = 8.5 Hz, 1H), 2.38 (s, 3H), 1.75-1.72 (m, 1H), 1.57-1.54 (m, 1H), 1.28 (t, *J* = 7.5 Hz, 3H).

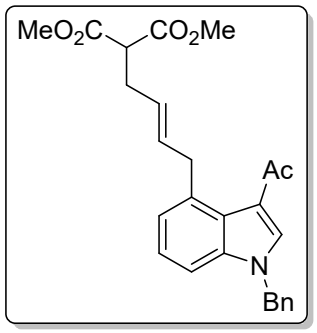


1-Methyl 1-(2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl) 2-vinylcyclopropane-1,1-dicarboxylate 2k. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless liquid; yield 75% (480 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.55-5.50 (m, 1H), 5.38-5.35 (m, 1H), 5.21-5.19 (m, 1H), 3.80 (s, 3H), 2.75 (q, *J* = 8.4 Hz, 1H), 2.60-2.57 (m, 2H), 2.11-1.95 (m, 9H), 1.88-1.79 (m, 2H), 1.77-1.69 (m, 2H), 1.59-1.50 (m, 3H), 1.38-1.24 (m, 14H), 1.16-1.05 (m, 7H), 0.88-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 167.9, 149.7, 140.5, 132.9, 119.0, 117.6, 75.2, 52.7, 39.5, 37.7, 37.67, 37.60, 37.53, 37.4, 35.9, 32.94, 32.92, 32.86, 32.84, 31.2, 28.1, 24.96, 24.94, 24.5, 22.8, 22.7, 21.1, 21.0, 20.7, 19.89, 19.83, 19.79, 19.73, 12.8, 12.0, 11.9; FT-IR (neat) 2925, 1736, 1459, 1332, 1240, 1203, 1108, 911 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$calcd for $C_{37}H_{59}O_5$: 583.4357, found 583.4368.

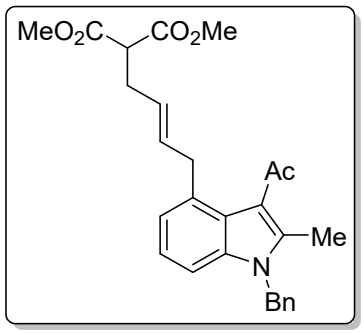


1-Tosyl-2-vinylaziridine 2A. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.55-5.39 (m, 2H), 5.24-5.22 (m, 1H), 3.29-3.24 (m, 1H), 2.78 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.21 (d, *J* = 4.8 Hz, 1H).

Characterization Data of the Products

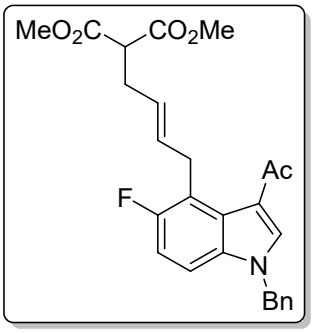


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3a. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.45; brown sticky liquid; yield 79% (34.2 mg, *E/Z* = 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.35-7.30 (m, 3H), 7.19-7.17 (m, 1H), 7.14-7.13 (m, 3H), 7.05-7.03 (m, 1H), 5.79-5.74 (m, 1H), 5.39-5.34 (m, 1H), 5.33 (s, 2H), 4.07 (d, *J* = 7.2 Hz, 2H), 3.64 (s, 6H), 3.39 (t, *J* = 7.8 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 169.6, 138.3, 136.7, 136.2, 135.8, 134.2, 129.1, 128.3, 127.0, 125.3, 124.5, 124.0, 123.8, 119.2, 108.2, 52.4, 52.1, 50.8, 38.7, 32.1, 28.7; FT-IR (neat) 2922, 1732, 1654, 1524, 1438, 1376, 1231, 1191, 972, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}NO_5$: 434.1962, found 434.1967.

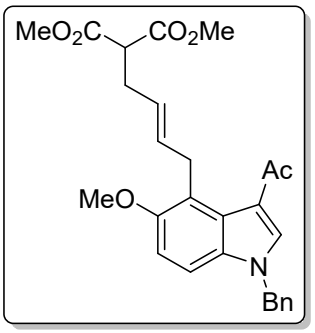


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-2-methyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3b. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.48; ; brown sticky liquid; yield 72% (32 mg, *E/Z* = 7:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.24-7.23 (m, 1H), 7.16-7.09 (m, 2H), 6.98-6.97 (m, 3H), 5.70-5.65 (m, 1H), 5.42-5.37 (m, 1H), 5.32 (s, 2H), 3.76-3.66 (m, 8H), 3.42 (t, *J* = 7.8 Hz, 1H), 2.61-2.58 (m, 5H),

2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.9, 169.5, 139.1, 137.1, 136.5, 133.2, 132.7, 129.0, 127.7, 126.5, 126.0, 124.2, 122.8, 122.7, 118.3, 107.8, 52.5, 51.9, 46.7, 37.5, 32.5, 32.1, 12.3; FT-IR (neat) 2952, 1733, 1653, 1435, 1351, 1230, 1195, 972, 734 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}NO_5$: 448.2118, found 448.2124.

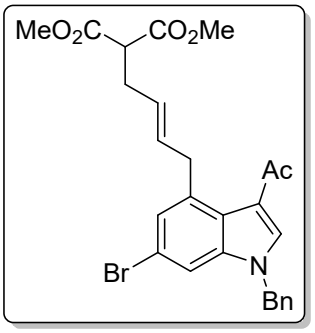


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-5-fluoro-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3e. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; ; brown sticky liquid; yield 70% (31.5 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.36-7.31 (m, 3H), 7.14-7.12 (m, 2H), 7.06-7.04 (m, 1H), 6.99-6.96 (m, 1H), 5.74-5.69 (m, 1H), 5.36-5.31 (m, 3H), 4.11 (d, *J* = 6 Hz, 2H), 3.61 (s, 6H), 3.34 (t, *J* = 7.8 Hz, 1H), 2.53-2.50 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 169.6, 158.6 ($J_{C\text{-}F}$ = 234.4 Hz), 137.8, 135.5, 134.5, 133.0, 129.2, 128.4, 127.0, 125.8 ($J_{C\text{-}F}$ = 6.0 Hz), 125.2, 121.7 ($J_{C\text{-}F}$ = 18.4 Hz), 119.3 ($J_{C\text{-}F}$ = 4.3 Hz), 112.4 ($J_{C\text{-}F}$ = 28.5 Hz),108.9 ($J_{C\text{-}F}$ = 10.3 Hz), 52.3, 52.1, 51.0, 32.1, 30.0 ($J_{C\text{-}F}$ = 4.5 Hz), 28.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -124.53; FT-IR (neat) 2952, 1730, 1655, 1523, 1438, 1392, 1204, 970, 796 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}FNO_5$: 452.1868, found 452.1866.

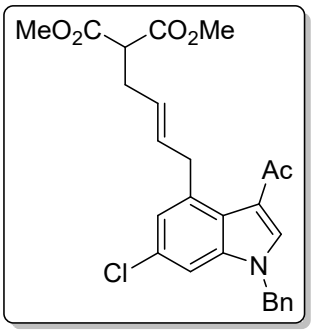


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-5-methoxy-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3f. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.39; brown sticky liquid; yield 68% (31.4 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.35-7.29 (m, 3H), 7.14-7.13 (m, 2H), 7.07-7.06 (m, 1H), 6.94-6.93 (m, 1H), 5.73-5.68 (m, 1H), 5.31-5.26 (m, 3H), 4.14 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 3H), 3.60 (s, 6H), 3.33 (t, *J* = 7.8

Hz, 1H), 2.51-2.49 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 169.6, 153.9, 137.8, 135.9, 133.9, 133.6, 129.1, 128.3, 127.0, 126.0, 124.4, 123.8, 118.8, 110.6, 108.4, 57.6, 52.3, 50.9, 32.2, 30.5, 28.8; FT-IR (neat) 2952,1733, 1656, 1506, 1435, 1385, 1265, 1091, 943, 730 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}NO_6$: 464.2068, found 464.2064.

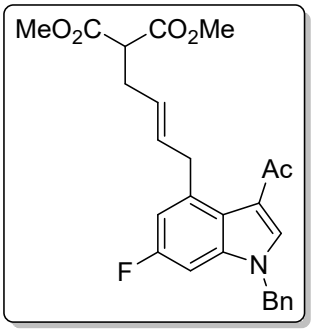


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-6-bromo-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3g. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.43; light yellow sticky liquid; yield 64% (32.7 mg, *E/Z* = 13:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.37-7.33 (m, 3H), 7.29 (s, 1H), 7.15-7.12 (m, 3H), 5.74-5.69 (m, 1H), 5.40-5.36 (m, 1H), 5.29 (s, 2H), 4.01 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 6H), 3.40 (t, *J* = 7.8 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 169.5, 139.0, 138.1, 136.9, 135.3, 133.3, 129.3, 128.5, 127.0, 126.8, 126.1, 123.6, 119.3, 117.6, 111.1, 52.5, 52.0, 50.8, 38.4, 32.1, 28.7; FT-IR (neat) 2918, 1730, 1657, 1523, 1432, 1376, 1254, 1189, 923, 701 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{26}H_{26}BrNaNO_5$: 534.0887, found 534.0878.

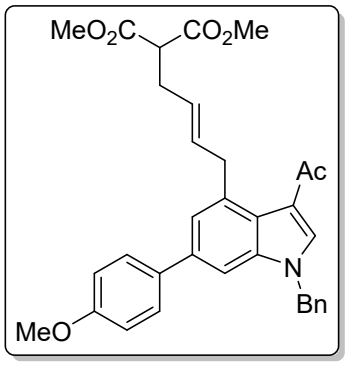


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-6-chloro-1H-indol-4-yl)but-2-en-1-yl)malonate 3h. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.41; brown sticky liquid; yield 66% (30.8 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.37-7.33 (m, 3H), 7.13-7.12 (m, 3H), 7.01 (s, 1H), 5.74-5.70 (m, 1H), 5.41-5.36 (m, 1H), 5.29 (s, 2H), 4.02 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 6H), 3.40 (t, *J* = 7.8 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 169.5, 138.7, 137.9, 137.0, 135.3, 133.2, 129.8, 129.3, 128.5, 126.9, 126.2, 124.1, 123.2, 119.3, 108.1, 52.5, 52.0, 50.9, 38.4, 32.1, 28.7;

FT-IR (neat) 2924, 1732, 1657, 1524, 1434, 1375, 1187, 1028, 972, 700 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}ClNO_5$: 468.1572, found 468.1578.

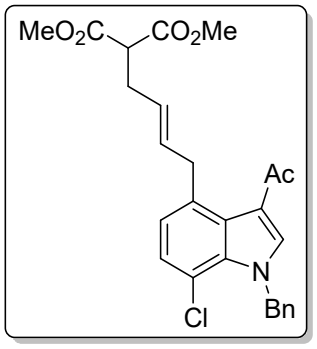


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-6-fluoro-1H-indol-4-yl)but-2-en-1-yl)malonate 3i. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.42; brown sticky liquid; yield 68% (30.6 mg, *E/Z* = 17:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.36-7.32 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.81-6.78 (m, 2H), 5.75-5.70 (m, 1H), 5.42-5.37 (m, 1H), 5.27 (s, 2H), 4.03 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 6H), 3.40 (t, *J* = 7.8 Hz, 1H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 169.5, 161.3 ($J_{C\text{-}F}$ = 239.7 Hz), 138.5 ($J_{C\text{-}F}$ = 12.0 Hz), 138.4, 137.0 ($J_{C\text{-}F}$ = 2.5 Hz), 135.4, 133.2, 129.2, 128.5, 127.0, 126.3, 121.0, 119.4, 112.1 ($J_{C\text{-}F}$ = 23.5 Hz), 94.7 ($J_{C\text{-}F}$ = 25.9 Hz), 52.5, 52.0, 51.0, 38.4, 32.1, 28.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.34.; FT-IR (neat) 2917, 1734, 1657, 1526, 1435, 1378, 1258, 1101, 955, 729 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}FNO_5$: 452.1868, found 452.1869.

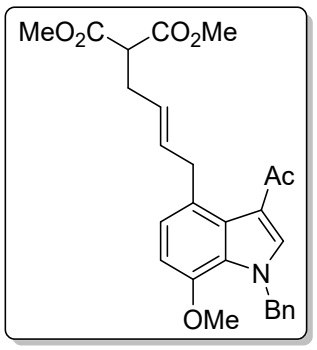


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-6-(4-methoxyphenyl)-1H-indol-4-yl)but-2-en-1-yl)malonate 3j. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.36; brown sticky liquid; yield 73% (39.3 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 3H), 7.26-7.25 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 5.83-5.78 (m, 1H), 5.43-5.38 (m, 1H), 5.36 (s, 2H), 4.11 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.60 (s, 6H), 3.39 (t, *J* = 7.8 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 169.6, 159.1, 139.0, 137.1,

137.0, 136.4, 135.8, 134.2, 134.1, 129.2, 128.5, 128.3, 127.0, 125.4, 123.5, 123.4, 119.1, 114.3, 106.0, 55.5, 52.4, 52.1, 50.8, 38.8, 32.1, 28.6; FT-IR (neat) 2919, 1735, 1656, 1520, 1435, 1247, 1183, 1030, 733 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{34}NO_6$: 540.2381, found 540.2380.

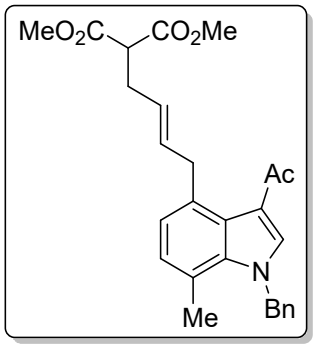


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-7-chloro-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3l. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.42; brown sticky liquid; yield 70% (32.6 mg, *E/Z* > 25:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.33-7.27 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.82 (s, 2H), 5.72-5.67 (m, 1H), 5.36-5.32 (m, 1H), 3.97 (d, *J* = 6.6 Hz, 2H), 3.66 (s, 6H), 3.38 (t, *J* = 7.8 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 169.5, 139.0, 137.6, 135.0, 133.5, 133.3, 129.0, 128.0, 127.4, 126.3, 125.91, 125.90, 124.5, 119.3, 115.1, 53.0, 52.5, 52.0, 38.1, 32.1, 29.0; FT-IR (neat) 2925, 1733, 1662, 1532, 1435, 1383, 1205, 968, 735 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}ClNO_5$: 468.1572, found 468.1577.

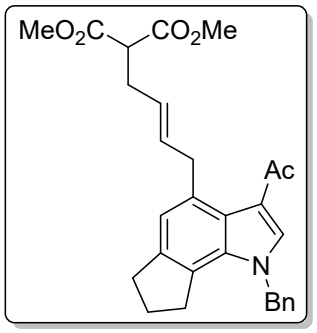


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-7-methoxy-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3m. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.38 brown sticky liquid; yield 77% (35.6 mg, *E/Z* = 21:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.31-7.29 (m, 2H), 7.27-7.26 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.74-5.70 (m, 1H), 5.65 (s, 2H), 5.34-5.30 (m, 1H), 3.94 (d, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.65 (s, 6H), 3.38 (t, *J* = 7.8 Hz, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.49

(s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 169.6, 146.0, 138.2, 137.6, 134.5, 128.8, 127.9, 127.8, 127.7, 126.7, 126.6, 124.9, 123.9, 119.2, 105.1, 55.6, 53.6, 52.4, 52.2, 38.0, 32.1, 28.8; FT-IR (neat) 2952, 1733, 1656, 1506, 1435, 1385, 1265, 943, 730 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}NO_6$: 464.2068, found 464.2059.

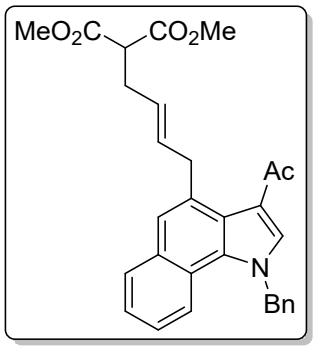


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-7-methyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3n. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; light brown sticky liquid; yield 75% (33.5 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.32-7.27 (m, 3H), 6.93-6.89 (m, 4H), 5.76-5.72 (m, 1H), 5.61 (s, 2H), 5.38-5.33 (m, 1H), 3.99 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 6H), 3.39 (d, *J* = 7.8 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.5, 169.6, 138.6, 138.0, 136.9, 134.2, 133.9, 129.2, 127.9, 127.2, 125.5, 125.3, 123.9, 119.19, 119.17, 53.2, 52.5, 52.1, 38.3, 32.1, 28.9, 19.5; FT-IR (neat) 2953, 1733, 1656, 1534, 1436, 1375, 1206, 1154, 944, 731 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}NO_5$: 448.2118, found 448.2101.

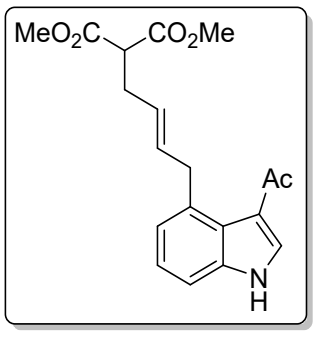


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1,6,7,8-tetrahydrocyclopenta[*g*]indol-4-yl)but-2-en-1-yl)malonate 3o. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; brown sticky liquid; yield 68% (32.1 mg, *E/Z* = 19:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.33-7.28 (m, 3H), 7.00-6.96 (m, 3H), 5.78-5.74 (m, 1H), 5.50 (s, 2H), 5.40-5.35 (m, 1H), 4.01 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 6H), 3.40 (t, *J* = 7.8 Hz, 1H), 3.05 (t, *J* = 7.8 Hz, 2H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 2.07-2.03 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 169.6, 141.6, 137.7, 137.1, 135.7,

134.4, 134.2, 129.1, 128.0, 125.9, 125.1, 123.5, 123.3, 120.8, 119.6, 52.5, 52.2, 52.0, 38.5, 32.6, 32.2, 31.3, 28.8, 25.4; FT-IR (neat) 2952, 1732, 1656, 1529, 1436, 1378, 1206, 1155, 965, 731 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{32}NO_5$: 474.2275, found 474.2283.

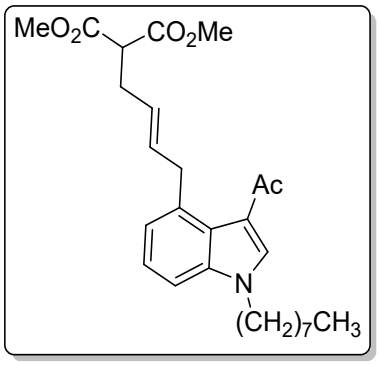


Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-benzo[g]indol-4-yl)but-2-en-1-yl)malonate 3p. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.40; colorless amorphous solid; mp 110-111 °C; yield 66% (31.8 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.45 (s, 1H), 7.39-7.36 (m, 1H), 7.35-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.85 (s, 2H), 5.83-5.80 (m, 1H), 5.45-5.40 (m, 1H), 4.10 (d, *J* = 6.6 Hz, 2H), 3.66 (s, 6H), 3.42 (t, *J* = 7.8 Hz, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 169.6, 136.6, 136.3, 134.4, 133.5, 132.2, 132.1, 129.3, 128.6, 128.1, 126.1, 126.0, 125.3, 124.6, 124.0, 123.1, 120.92, 120.91, 120.0, 54.6, 52.5, 52.1, 38.6, 32.2, 29.3; FT-IR (neat) 2952, 1732, 1661, 1529, 1435, 1369, 1231, 1151, 945, 736 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{30}NO_5$: 484.2118, found 484.2126.

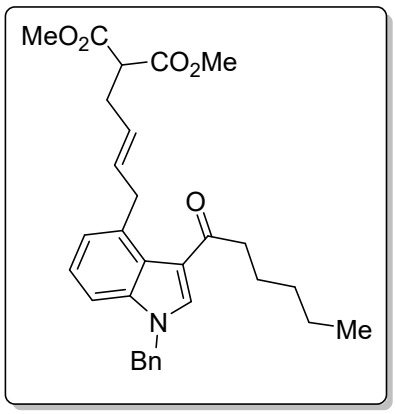


Dimethyl (*E*)-2-(4-(3-acetyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3q. Analytical TLC on silica gel, 1:1 ethyl acetate/hexane R_f = 0.35; brown amorphous solid; mp 115-116 °C; yield 57% (19.5 mg, *E/Z* = 17:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.86 (s, 1H), 7.23-7.19 (m, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 5.78-5.73 (m, 1H), 5.37-5.32 (m, 1H), 4.05 (d, *J* = 6.6 Hz, 2H), 3.65 (s, 6H), 3.38 (t, *J* = 7.8 Hz, 1H), 2.58-2.56 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 169.6, 137.6, 135.9, 134.2, 132.9, 125.3,

124.2, 123.8, 123.5, 120.4, 109.5, 52.5, 52.1, 38.6, 32.1, 28.7; FT-IR (KBr) 2954, 1733, 1634, 1518, 1408, 1232, 1155, 934, 751 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{22}NO_5$: 344.1492, found 344.1505.

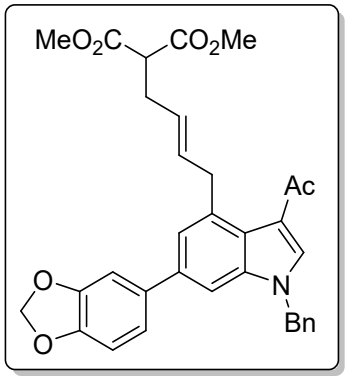


Dimethyl (*E*)-2-(4-(3-acetyl-1-octyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3r. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; light yellow sticky liquid; yield 61% (27.7 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.23-7.18 (m, 2H), 7.04 (d, *J* = 6.6 Hz, 1H), 5.78-5.73 (m, 1H), 5.39-5.34 (m, 1H), 4.12 (t, *J* = 7.8 Hz, 2H), 4.06 (d, *J* = 6.6 Hz, 2H), 3.65 (s, 6H), 3.38 (t, *J* = 7.8 Hz, 1H), 2.57-2.54 (m, 5H), 1.89-1.84 (m, 2H), 1.34-1.25 (m, 10H), 0.89-0.85 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 169.6, 137.9, 136.5, 136.2, 134.3, 125.2, 124.5, 123.7, 123.6, 118.5, 107.9, 52.5, 52.1, 47.3, 38.7, 32.1, 32.0, 31.8, 29.8, 29.2, 28.6, 27.0, 22.7, 14.2; FT-IR (neat) 2925, 1734, 1654, 1524, 1434, 1376, 1275, 1152, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{38}NO_5$: 456.2744, found 456.2750.

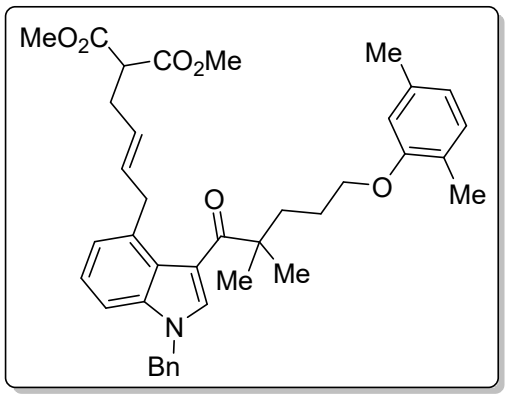


Dimethyl (*E*)-2-(4-(1-benzyl-3-hexanoyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3s. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.47; colorless sticky liquid; yield 59% (28.8 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.36-7.30 (m, 3H), 7.19-7.16 (m, 1H), 7.13-7.12 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 5.78-5.74 (m, 1H), 5.42-5.36 (m, 1H), 5.34 (s, 2H), 4.05 (d, *J* = 6.6 Hz, 2H), 3.65 (s, 6H), 3.39

(t, *J* = 7.8 Hz, 1H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.76-1.73 (m, 2H), 1.37-1.33 (m, 4H), 0.91-0.87 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 169.6, 138.2, 136.2, 136.0, 135.8, 134.1, 129.1, 128.3, 126.9, 125.5, 124.7, 123.9, 123.6, 119.1, 108.2, 52.5, 52.1, 50.8, 40.9, 38.6, 32.1, 31.8, 25.3, 22.7, 14.1; FT-IR (neat) 2921, 2852, 1735, 1657, 1524, 1455, 1260, 1019, 799 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{36}NO_5$: 490.2588, found 490.2593.

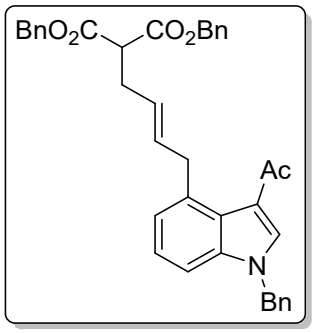


Dimethyl (*E*)-2-(4-(3-acetyl-6-(benzo[*d*][1,3]dioxol-5-yl)-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3t. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.37; brown sticky liquid; yield 68% (37.6 mg, *E/Z* = 11:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.36-7.31 (m, 3H), 7.23-7.22 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.05-7.03 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.98 (s, 2H), 5.82-5.77 (m, 1H), 5.43-5.39 (m, 1H), 5.37 (s, 2H), 4.10 (d, *J* = 6.6 Hz, 2H), 3.61 (s, 6H), 3.39 (t, *J* = 7.8 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.1, 169.6, 148.1, 147.0, 138.9, 137.2, 137.1, 136.5, 135.9, 135.8, 134.1, 129.2, 128.4, 127.0, 125.5, 123.6, 123.5, 120.9, 119.1, 108.6, 108.0, 106.2, 101.2, 52.4, 52.1, 50.8, 38.8, 32.1, 28.6; FT-IR (neat) 2924, 1733, 1655, 1524, 1478, 1377, 1231, 1038, 933, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{32}NO_7$: 554.2173, found 554.2179.

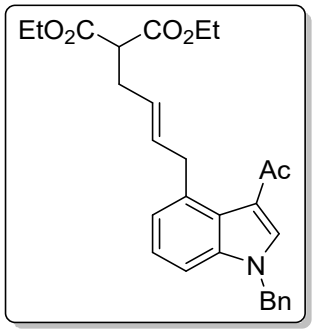


Dimethyl (*E*)-2-(4-(1-benzyl-3-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3u.

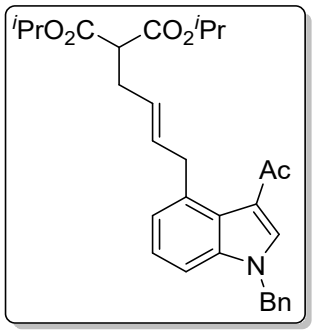
Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.42; colorless amorphous solid; mp 105-106 °C; yield 61% (38.0 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.31-7.28 (m, 3H), 7.18-7.15 (m, 1H), 7.13-7.08 (m, 3H), 7.00-6.96 (m, 2H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 5.78-5.73 (m, 1H), 5.43-5.38 (m, 1H), 5.29 (s, 2H), 3.90 (t, *J* = 6.0 Hz, 2H), 3.69-3.68 (m, 8H), 3.42 (t, *J* = 7.8 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 2.11 (s, 3H), 1.98-1.95 (m, 2H), 1.84-1.80 (m, 2H), 1.37 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.5, 169.5, 157.0, 136.9, 136.6, 136.3, 135.1, 133.0, 130.7, 130.3, 129.0, 128.1, 126.8, 126.4, 125.7, 123.5, 123.4, 122.7, 120.8, 116.6, 112.1, 108.2, 68.2, 52.5, 52.0, 50.6, 48.0, 38.0, 37.3, 32.1, 29.8, 27.0, 25.2, 21.5, 15.9; FT-IR (KBr) 2953, 1736, 1649, 1253, 1436, 1389, 1264, 1156, 1129, 1042, 731 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{39}H_{46}NO_6$: 624.3320, found 624.3328.



Dibenzyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3v. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.42; brown sticky liquid; yield 66% (38.6 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.33-7.28 (m, 9H), 7.23-7.22 (m, 4H), 7.18-7.15 (m, 1H), 7.13-7.12 (m, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 5.78-5.74 (m, 1H), 5.41-5.36 (m, 1H), 5.32 (s, 2H), 5.07-5.02 (m, 4H), 4.05 (d, *J* = 6.6 Hz, 2H), 3.48 (t, *J* = 7.8 Hz, 1H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 168.8, 138.3, 136.7, 136.2, 135.8, 135.5, 134.3, 129.1, 128.6, 128.33, 128.31, 128.2, 127.0, 125.2, 124.5, 124.0, 123.9, 119.2, 108.2, 67.0, 52.4, 50.8, 38.7, 32.0, 28.7; FT-IR (neat) 2925, 1731, 1655, 1524, 1453, 1389, 1207, 1151, 748 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{38}H_{36}NO_5$: 586.2588, found 586.2595.

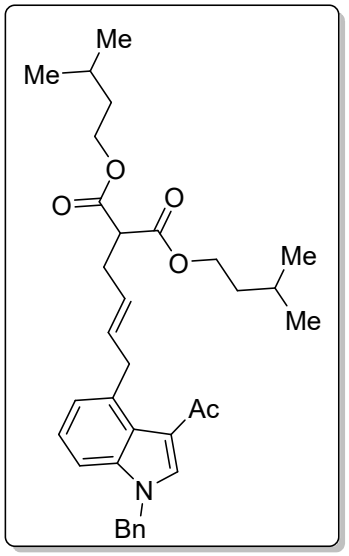


Diethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3w. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; brown sticky liquid; yield 73% (33.6 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.35-7.29 (m, 3H), 7.19-7.16 (m, 1H), 7.15-7.12 (m, 3H), 7.05 (d, *J* = 7.2 Hz, 1H), 5.78-5.74 (m, 1H), 5.40-5.36 (m, 1H), 5.33 (s, 2H), 4.14-4.08 (m, 4H), 4.06 (d, *J* = 6.6 Hz, 2H), 3.34 (t, *J* = 7.8 Hz, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 169.2, 138.3, 136.6, 136.3, 135.8, 133.9, 129.1, 128.3, 127.0, 125.6, 124.5, 124.0, 123.9, 119.2, 108.2, 61.3, 52.4, 50.8, 38.7, 32.1, 28.7, 14.1; FT-IR (neat) 2918, 2850, 1729, 1656, 1524, 1441, 1373, 1150, 1030, 748 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{32}NO_5$: 462.2275, found 462.2279.

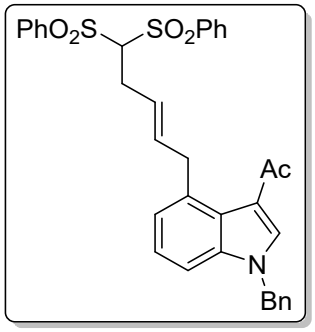


Diisopropyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3x. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.45; light brown sticky liquid; yield 46% (22.4 mg, *E/Z* = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 0.56H), 7.77 (s, 1H), 7.40-7.30 (m, 5.42H), 7.19-7.11 (m, 6.38H), 7.05-7.04 (m, 1.05H), 6.09-6.04 (m, 0.63H), 5.77-5.72 (m, 1.17H), 5.42-5.39 (m, 0.60H), 5.38-5.35 (m, 1.14H), 5.34-5.33 (m, 3.28H), 5.07-5.03 (m, 1.25H), 5.00-4.95 (m, 2.31H), 4.15 (d, *J* = 6.6 Hz, 0.85H), 4.06 (d, *J* = 6.6 Hz, 1.93H), 3.38 (t, *J* = 7.8 Hz, 0.63H), 3.27 (t, *J* = 7.8 Hz, 1.16H), 2.55-2.51 (m, 6.49H), 2.39-2.35 (m, 0.64H), 2.13-2.10 (m, 1.19H), 1.25-1.15 (m, 18H);^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 192.2, 169.3, 168.8, 138.4, 138.4, 138.3, 137.0, 136.6, 136.3, 135.9, 135.8, 133.8, 133.7, 132.5, 129.38, 129.36, 129.1, 128.3, 127.0, 126.9, 125.7, 124.6, 124.03, 124.00, 123.9, 123.6, 120.3, 119.3, 119.2, 108.9, 108.2, 68.8, 68.7, 52.8, 52.0, 50.8, 38.6, 31.9, 31.0, 28.75,

28.72, 21.8, 21.76, 21.74, 21.6; FT-IR (neat) 2926, 1724, 1656, 1524, 1441, 1374, 1189, 1102, 746 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{36}NO_5$: 490.2588, found 490.2595.

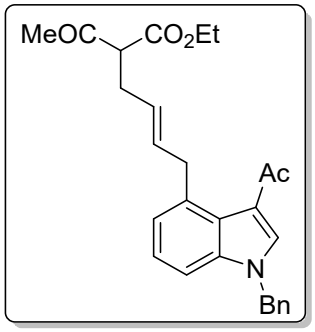


Diisopentyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3y. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.46; brown sticky liquid; yield 52% (28.3 mg, *E/Z* = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.35-7.30 (m, 3H), 7.19-7.12 (m, 4H), 7.05 (d, *J* = 7.2 Hz, 1H), 5.79-5.74 (m, 1H), 5.41-5.36 (m, 1H), 5.33 (s, 2H), 4.12-4.05 (m, 4H), 3.74-3.70 (m, 2H), 3.38-3.33 (m, 1H), 2.58-2.55 (m, 2H), 2.52 (s, 3H), 1.66-1.62 (m, 2H), 1.52-1.45 (m, 4H), 0.90-0.85 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 169.3, 138.3, 136.6, 136.3, 135.8, 133.9, 129.1, 128.3, 127.1, 127.0, 125.6, 124.6, 124.0, 123.9, 108.2, 64.0, 52.6, 50.8, 38.6, 37.2, 32.1, 28.7, 25.0, 22.5; FT-IR (neat) 2957, 1729, 1655, 1525, 1440, 1388, 1190, 971, 746 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{34}H_{44}NO_5$: 546.3214, found 546.3218.

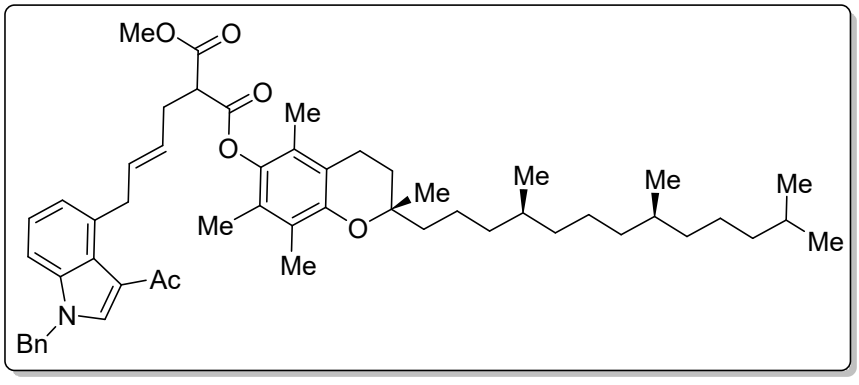


(*E*)-1-(1-benzyl-4-(5,5-bis(phenylsulfonyl)pent-2-en-1-yl)-1*H*-indol-3-yl)ethan-1-one 3z. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.41; colorless sticky liquid; yield 61% (36.4 mg, *E/Z* > 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 4H), 7.81 (s, 1H), 7.64-7.60 (m, 2H), 7.51-7.47 (m, 4H), 7.34-7.29 (m, 3H), 7.20-7.14

(m, 4H), 7.01-6.99 (m, 1H), 5.64-5.57 (m, 1H), 5.35-5.28 (m, 3H), 4.41 (t, J = 6.4 Hz, 1H), 4.01 (d, J = 6.4 Hz, 2H), 2.80 (t, J = 6.4 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 138.3, 138.1, 137.0, 135.85, 135.81, 135.6, 134.5, 129.8, 129.2, 129.1, 128.3, 127.0, 124.6, 124.2, 124.0, 123.4, 119.1, 108.4, 84.2, 50.9, 38.7, 29.8, 29.0, 28.7; FT-IR (neat) 2924, 2854, 1652, 1524, 1447, 1376, 1330, 1153, 1079, 734 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{34}H_{32}S_2NO_5$: 598.1716, found 598.1719.

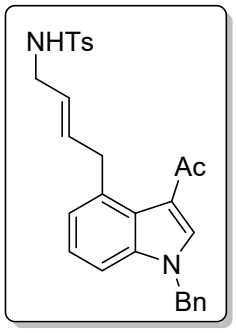


Ethyl (*E*)-2-acetyl-6-(3-acetyl-1-benzyl-1*H*-indol-4-yl)hex-4-enoate 3ad. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; light yellow sticky liquid; yield 45% (19.3 mg, *E/Z* = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.35-7.30 (m, 3H), 7.18-7.12 (m, 4H), 7.04-7.02 (m, 1H), 5.79-5.72 (m, 1H), 5.37-5.29 (m, 3H), 4.21-4.09 (m, 2H), 4.08-4.04 (m, 2H), 3.44 (t, J = 7.6 Hz, 1H), 2.52 (s, 3H), 2.27-2.21 (m, 2H), 2.16 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 192.2, 169.5, 138.3, 136.7, 136.2, 135.8, 134.0, 129.1, 128.3, 127.0, 125.6, 124.5, 124.0, 123.9, 119.1, 108.2, 61.3, 60.0, 50.8, 38.6, 31.5, 29.3, 28.7, 14.1; FT-IR (neat) 2923, 2853, 1712, 1653, 1524, 1440, 1373, 1189, 1022, 970, 736 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{27}H_{29}NaNO_4$: 454.1989, found 454.1986.

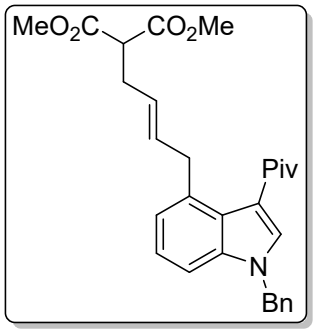


1-Methyl 3-((*S*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl) 2-((*E*)-4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3ae. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.43; brown sticky liquid; yield 57% (47.4 mg, *E/Z* = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.35-7.30 (m, 3H), 7.20-7.14 (m, 4H), 7.07 (d, J = 7.2 Hz, 1H),

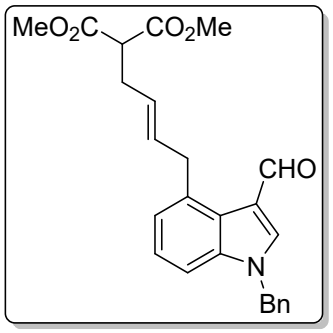
5.88-5.84 (m, 1H), 5.49-5.44 (m, 1H), 5.33 (s, 2H), 4.11-4.09 (m, 2H), 3.70 (s, 3H), 3.66 (t, *J* = 7.8 Hz, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.58-2.54 (m, 2H), 2.53 (s, 3H), 2.06 (s, 3H), 1.98-1.92 (m, 6H), 1.82-1.77 (m, 2H), 1.56-1.49 (m, 3H), 1.37-1.22 (m, 14H), 1.15-1.09 (m, 7H), 0.87-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 169.4, 167.6, 149.6, 140.4, 138.3, 136.7, 136.1, 135.8, 134.4, 132.9, 129.1, 128.3, 127.0, 125.4, 124.6, 124.0, 123.1, 120.4, 119.2, 117.5, 109.0, 108.2, 75.2, 52.4, 52.2, 50.8, 39.5, 38.7, 37.7, 37.6, 37.5, 37.4, 32.93, 32.91, 32.8, 32.2, 28.7, 28.1, 24.95, 24.94, 24.5, 22.8, 22.7, 21.1, 20.7, 19.9, 19.8, 19.79, 19.76, 19.72, 11.9; FT-IR (neat) 2925, 1740, 1658, 1525, 1440, 1376, 1191, 1151, 741 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{54}H_{74}NO_6$: 832.5511, found 832.5501.



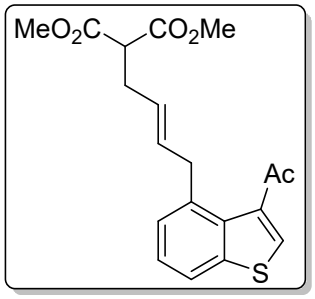
(*E*)-*N*-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3A. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 50% (23.6 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.35-7.30 (m, 4H), 7.26 (s, 1H), 7.19-7.14 (m, 4H), 6.98-6.97 (m, 1H), 5.85-5.81 (m, 1H), 5.34 (s, 2H), 5.30-5.25 (m, 1H), 4.28 (t, *J* = 6.0 Hz, 1H), 4.02 (d, *J* = 6.6 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.50 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 143.4, 138.3, 137.1, 137.0, 135.9, 135.7, 135.3, 129.7, 129.2, 128.4, 127.2, 127.0, 126.6, 124.5, 124.3, 124.0, 118.9, 108.5, 50.9, 45.6, 38.5, 28.6, 21.6; FT-IR (neat) 3267, 2924, 1644, 1524, 1442, 1379, 1326, 1157, 1093 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{29}N_2O_3S$: 473.1893, found 473.1893.



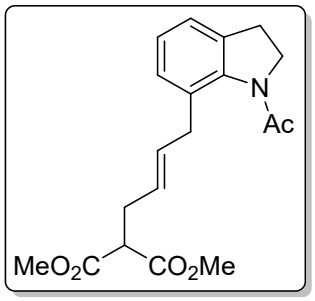
Dimethyl (*E*)-2-(4-(1-benzyl-3-pivaloyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3a′. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.46; light brown amorphous solid; mp 103-104 °C; yield 55% (26.1 mg, *E/Z* > 25:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.33-7.28 (m, 3H), 7.18-7.11 (m, 4H), 6.99 (d, *J* = 6.5 Hz, 1H), 5.75-5.69 (m, 1H), 5.41-5.35 (m, 1H), 5.33 (s, 2H), 3.68-3.65 (m, 8H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.6, 169.6, 136.9, 136.3, 135.0, 132.9, 130.6, 129.1, 128.1, 126.9, 126.3, 125.7, 123.4, 122.5, 116.3, 108.2, 52.5, 52.0, 50.6, 44.8, 37.1, 32.1, 28.7; FT-IR (KBr) 2953, 1735, 1650, 1524, 1437, 1390, 1183, 971, 731 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{34}NO_5$: 476.2431, found 476.2438.



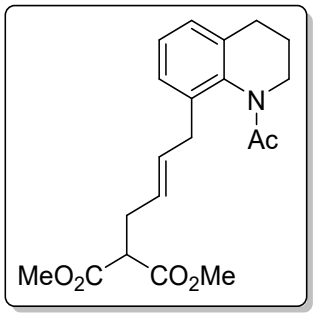
Dimethyl (*E*)-2-(4-(1-benzyl-3-formyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 3b′. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.44; brown sticky liquid; yield 41% (17.1 mg, *E/Z* = 15:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.81 (s, 1H), 7.36-7.32 (m, 3H), 7.23-7.17 (m, 4H), 7.08 (d, *J* = 6.6 Hz, 1H), 5.83-5.78 (m, 1H), 5.43-5.38 (m, 1H), 5.34 (s, 2H), 3.99 (d, *J* = 6.0 Hz, 2H), 3.66 (s, 6H), 3.39 (t, *J* = 7.8 Hz, 1H), 2.59 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.4, 169.5, 139.2, 138.3, 135.3, 135.1, 132.7, 129.2, 128.5, 127.3, 126.5, 124.6, 124.1, 123.8, 119.7, 108.8, 52.5, 52.0, 51.2, 38.4, 32.0; FT-IR (neat) 1734, 1669, 1526, 1439, 1389, 1275, 1162, 750 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{26}NO_5$: 420.1805, found 420.1811.



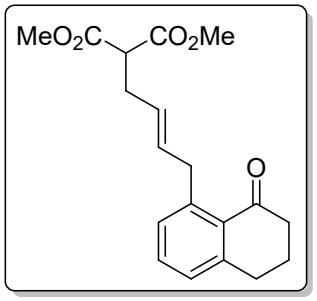
Dimethyl (*E*)-2-(4-(3-acetylbenzo[*b*]thiophen-4-yl)but-2-en-1-yl)malonate 4A. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; light yellow liquid; yield 55% (19.8 mg, *E/Z* > 25:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.24-7.22 (m, 1H), 5.63-5.57 (m, 1H), 5.31-5.26 (m, 1H), 3.70 (d, *J* = 6.5 Hz, 2H), 3.66 (s, 6H), 3.38 (t, *J* = 8.0 Hz, 1H), 2.66 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.3, 169.4, 141.4, 140.1, 137.3, 134.2, 132.9, 132.4, 127.3, 127.0, 125.6, 120.9, 52.5, 51.8, 38.1, 32.0, 30.3; FT-IR (neat) 2923, 1735, 1681, 1435, 1209, 1155, 975, 760 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_5S$: 361.1104, found 361.1113.



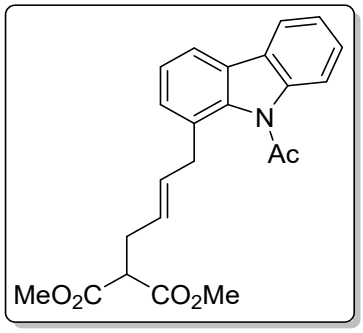
Dimethyl (*E*)-2-(4-(1-acetylindolin-7-yl)but-2-en-1-yl)malonate 4B. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.48; brown sticky liquid; yield 70% (24.1 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07-6.99 (m, 3H), 5.63-5.58 (m, 1H), 5.47-5.43 (m, 1H), 4.07-4.04 (m, 2H), 3.70 (s, 6H), 3.42 (t, *J* = 7.8 Hz, 1H), 3.35-3.34 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 140.9, 131.8, 128.8, 126.9, 125.4, 122.3, 52.5, 52.0, 51.3, 37.0, 32.0, 30.1, 23.9; FT-IR (neat) 2954, 1733, 1662, 1435, 1386, 1232, 1152, 974, 732 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}NO_5$: 346.1649, found 346.1643.



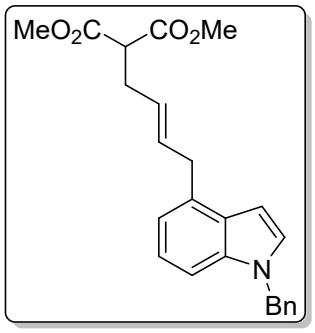
Dimethyl (*E*)-2-(4-(1-acetyl-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-yl)malonate 4C. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.49; brown liquid; yield 39% (14.0 mg, *E/Z* = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17-7.14 (m, 1.36H), 7.11-7.08 (m, 1.53H), 7.06-6.99 (m, 1.63H), 5.62-5.54 (m, 1.57H), 5.47-5.41 (m, 1.57H), 4.81-4.76 (m, 1.57H), 3.74-3.70 (m, 8.95H), 3.44-3.41 (m, 1.49H), 3.37-3.33 (m, 1.55H), 3.21 (d, *J* = 7.2 Hz, 1H), 3.18 (d, *J* = 7.2 Hz, 0.51H), 2.78-2.73 (m, 1.57H), 2.66-2.63 (m, 1.49H), 2.62-2.59 (m, 3.25H), 2.44-2.39 (m, 1.61H), 2.29-2.23 (m, 3.13H), 1.86 (s, 3.64H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.13, 171.10, 169.43, 169.40, 139.5, 137.7, 135.6, 132.1, 131.3, 130.5, 128.1, 127.7, 127.4, 127.0, 126.9, 126.5, 126.3, 126.2, 125.8, 122.9, 52.65, 52.63, 52.0, 51.8, 46.1, 41.5, 35.2, 34.0, 32.0, 31.9, 26.6, 26.0, 24.7, 24.0, 22.5, 21.6; FT-IR (neat) 2924, 1736, 1659, 1437, 1378, 1234, 1154, 971, 766 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{26}NO_5$: 360.1805, found 360.1813.



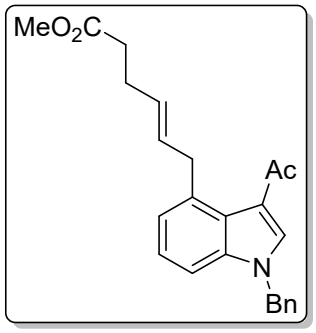
Dimethyl (*E*)-2-(4-(8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)but-2-en-1-yl)malonate 4D. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.46; colorless sticky liquid; yield 41% (13.5 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 5.77-5.72 (m, 1H), 5.43-5.38 (m, 1H), 3.76 (d, *J* = 6.6 Hz, 2H), 3.68 (s, 6H), 3.40 (t, *J* = 7.8 Hz, 1H), 2.94 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.6 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.10-2.04 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 169.5, 146.0, 143.4, 132.9, 132.5, 130.8, 129.5, 127.3, 126.3, 52.5, 52.0, 41.1, 38.0, 32.0, 31.2, 23.0; FT-IR (neat) 2925, 2853, 1737, 1678, 1591, 1436, 1273, 1155, 762 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{23}O_5$: 331.1540, found 331.1546.



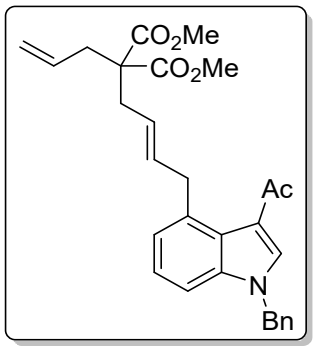
Dimethyl (*E*)-2-(4-(9-acetyl-9H-carbazol-1-yl)but-2-en-1-yl)malonate 4E. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.43; colorless liquid; yield 36% (14.4 mg, *E/Z* > 25:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.37-7.34 (m, 2H), 7.28-7.27 (m, 1H), 5.59-5.55 (m, 1H), 5.52-5.47 (m, 1H), 3.66 (s, 6H), 3.58 (d, *J* = 6.0 Hz, 2H), 3.42 (t, *J* = 7.8 Hz, 1H), 2.74 (s, 3H), 2.62 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.4, 139.6, 138.3, 131.1, 129.3, 129.1, 128.0, 127.7, 127.1, 126.9, 124.4, 123.4, 120.2, 117.9, 114.4, 52.6, 51.8, 37.7, 31.9, 27.2; FT-IR (neat) 2924, 2853, 1737, 1435, 1364, 1272, 1205, 758 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{24}NO_5$: 394.1649, found 394.1650.



Dimethyl (*E*)-2-(4-(1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)malonate 5. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.46; yellow sticky liquid; yield 73% (28.5 mg, *E/Z* > 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 3H), 7.15-7.07 (m, 5H), 6.88 (d, *J* = 6.4 Hz, 1H), 6.55-6.54 (m, 1H), 5.85-5.78 (m, 1H), 5.58-5.50 (m, 1H), 5.30 (s, 2H), 3.67 (s, 6H), 3.61 (d, *J* = 6.8 Hz, 2H), 3.44 (t, *J* = 7.6 Hz, 1H), 2.62 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 137.6, 136.4, 132.7, 132.4, 128.8, 128.1, 127.8, 127.7, 126.9, 126.5, 122.0, 119.0, 108.0, 100.2, 52.5, 52.0, 50.3, 36.6, 32.0; FT-IR (neat) 2961, 1732, 1493, 1435, 1259, 1152, 1017, 795 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{26}NO_4$: 392.1856, found 392.1862.



Methyl (*E*)-6-(3-acetyl-1-benzyl-1*H*-indol-4-yl)hex-4-enoate 6. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.46; yellow sticky liquid; yield 70% (26.2 mg, *E/Z* > 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.36-7.30 (m, 3H), 7.21-7.17 (m, 1H), 7.15-7.13 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 1H), 5.74-5.67 (m, 1H), 5.46-5.39 (m, 1H), 5.33 (s, 2H), 4.07 (d, *J* = 6.8 Hz, 2H), 3.61 (s, 3H), 2.52 (s, 3H), 2.37-2.27 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 173.9, 138.3, 136.6, 135.8, 131.8, 129.1, 128.32, 128.30, 127.0, 124.6, 124.0, 123.8, 119.2, 108.2, 51.5, 50.8, 38.6, 34.3, 28.7, 28.1; FT-IR (neat) 2920, 1731, 1652, 1524, 1438, 1374, 1190, 970, 735 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{26}NO_3$: 376.1907, found 376.1914.



Dimethyl (*E*)-2-(4-(3-acetyl-1-benzyl-1*H*-indol-4-yl)but-2-en-1-yl)-2-allylmalonate 7. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.47; colorless sticky liquid; yield 66% (31.2 mg, *E/Z* > 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.34-7.30 (m, 3H), 7.20-7.16 (m, 1H), 7.13-7.11 (m, 3H), 7.05 (d, *J* = 6.8 Hz, 1H), 5.76-5.69 (m, 1H), 5.64-5.55 (m, 1H), 5.34 (s, 2H), 5.25-5.17 (m, 1H), 5.03-4.97 (m, 2H), 4.09 (d, *J* = 6.4 Hz, 2H), 3.59 (s, 6H), 2.57-2.55 (m, 4H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 171.4, 138.33, 138.30, 136.8, 136.2, 135.9, 135.8, 132.7, 129.1, 128.3, 126.9, 124.6, 124.0, 123.4, 119.2, 119.0, 108.2, 58.1, 52.3, 50.8, 38.8, 36.9, 35.9, 28.7; FT-IR (neat) 2924, 1732, 1656, 1525, 1440, 1376, 1207, 748 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{32}NO_5$: 474.2275, found 474.2283.

Mechanistic Investigation

Radical Trapping Experiments. In an oven-dried pressure tube, a mixture of indole **1a** (0.1 mmol, 24.9 mg), dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (0.2 mmol, 36.8 mg), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3 mg), K_2CO_3 (0.2 mmol, 28 mg), MesCO_2H (0.03 mmol, 5 mg) and TEMPO (0.1 mmol, 15.6 mg) or BHT (0.1 mmol, 22 mg) were stirred in HFIP (1 mL) at 90 ^oC in a preheated oil bath for 12 h under argon atmosphere. Upon completion, the reaction mixture was allowed to cool to room temperature and was diluted with EtOAc and passed through a celite pad. The purification was performed as described in the general procedure to afford **3a**.

H/D Exchange Experiment of 1a with D_2O in Presence of 2a. In an oven-dried pressure tube, a mixture of indole **1a** (0.1 mmol, 24.9 mg), dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (0.2 mmol, 36.8 mg), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3 mg), K_2CO_3 (0.2 mmol, 28 mg), MesCO_2H (0.03 mmol, 5 mg), D_2O (1 mmol, 0.2 mL) and HFIP (1 mL) were stirred at 90 ^oC in a preheated oil bath for 12 h under argon atmosphere. Upon completion, the reaction mixture was allowed to cool to room temperature and was diluted with EtOAc and passed through a celite pad. The purification was performed as described in the general procedure to afford [D_n]-**1a** and [D_n]-**3a**. The deuterium incorporation was observed as 15% at C4-H, 5% at C2-H of **1a** based on 500 MHz ^{1}H NMR spectrum.

H/D Exchange Experiment of 1a with D_2O in Absence of 2a. In an oven-dried pressure tube, a mixture of indole **1a** (0.1 mmol, 24.9 mg), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %, 0.005 mmol, 3 mg), K_2CO_3 (0.2 mmol, 28 mg), MesCO_2H (0.03 mmol, 5 mg), D_2O (1 mmol, 0.2 mL) and HFIP (1 mL) were stirred at 90 ^oC in a preheated oil bath for 12 h under argon atmosphere. Upon completion, the reaction mixture was allowed to cool to room temperature and was diluted with EtOAc and passed through celite pad. The purification was performed as described in the general procedure to give [D_n]-**1a**. The deuterium incorporation was observed as 26% at C4-H and 11% at C2-H based on 500 MHz ^{1}H NMR spectrum.

Preparation of 1-(1-Benzyl-1*H*-indol-3-yl-2,4-*d*$_2$)ethan-1-one [D_2]-**1a.** In an oven-dried pressure tube, 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (0.1 mmol, 24.9 mg), [Cp*RhCl_2]$_2$ (2.5 mol %, 0.0025 mmol, 1.5 mg), $AgSbF_6$ (0.02 mmol, 6.8 mg), Cu(OAc)$_2$ (0.1 mmol, 18 mg), D_2O (0.4 mmol, 80 μL) and 1,4-dioxane (1.5 mL) were stirred at 120 ^oC in a preheated oil bath for 14 h. The resulting reaction mixture was allowed to cool to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. Drying over Na_2SO_4 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 [D_2]-**1a** as a light-yellow solid. The deuterium incorporation was determined using 600 MHz ^{1}H NMR as 85% at C4-H.

Kinetic Isotope Effect Experiment. A mixture of 1-(1-benzyl-1*H*-indol-3-yl)ethan-1-one **1a** (0.05 mmol, 12.4 mg) and 1-(1-Benzyl-1*H*-indol-3-yl-2,4-*d*$_2$)ethan-1-one [D_2]-**1a** (0.05 mmol, 12.5 mg) was stirred with dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (0.2 mmol, 36.8 mg) for 0.5 h under standard reaction condition. The reaction mixture was allowed to cool to room temperature and was diluted with EtOAc and passed through celite pad. The purification was performed as described in the general procedure to afford [D_1]-**3a** and a mixture of unreacted **1a** and [D_2]-**1a** as a colorless solid. The intermolecular k_H/k_D was found to be 2.18, based on 400 MHz ^{1}H NMR of the recovered substrate **1a** and [D_2]-**1a**.

References

1. (a) A. J. Borah and Z. Shi, *Chem. Commun*., 2017, **53**, 3945; (b) L. Tu, W. Che, S. Li, X. Li, Y. Xie and Z. Li, *J. Mater. Chem. C*, 2021, **9**, 12124; (c) T. Paul, S. Basak and T. Punniyamurthy, *Org. Lett.*, 2022, **24**, 6000.
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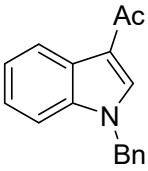
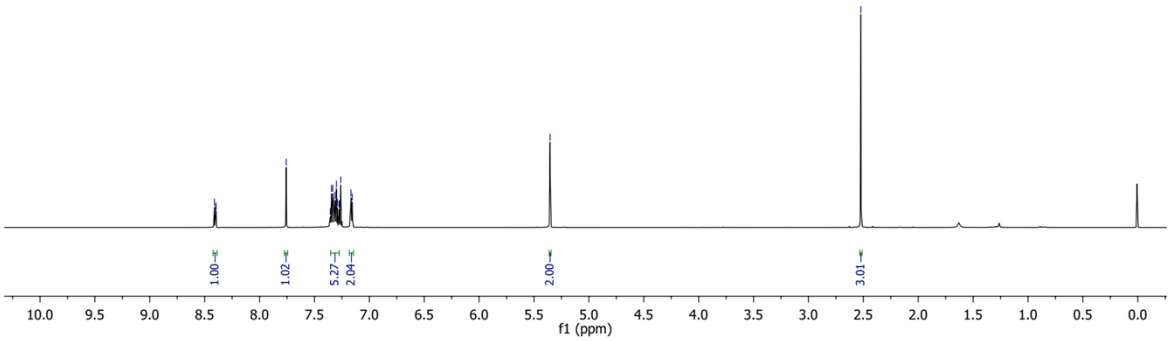
SBT-AC-DG-1H



1a

^{1}H NMR (600 MHz, $CDCl_3$)



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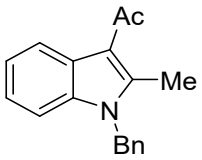

1b

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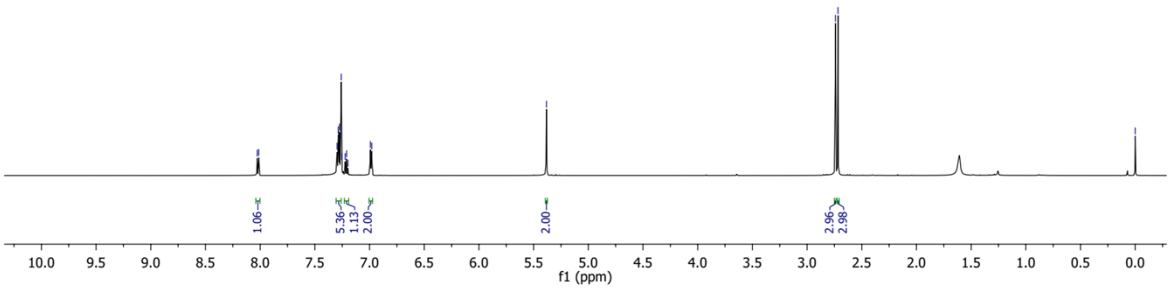

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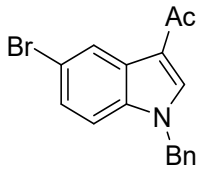

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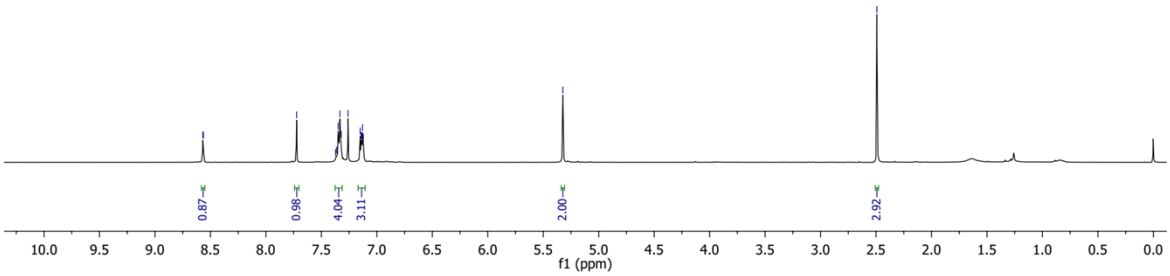

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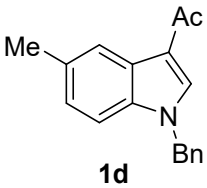
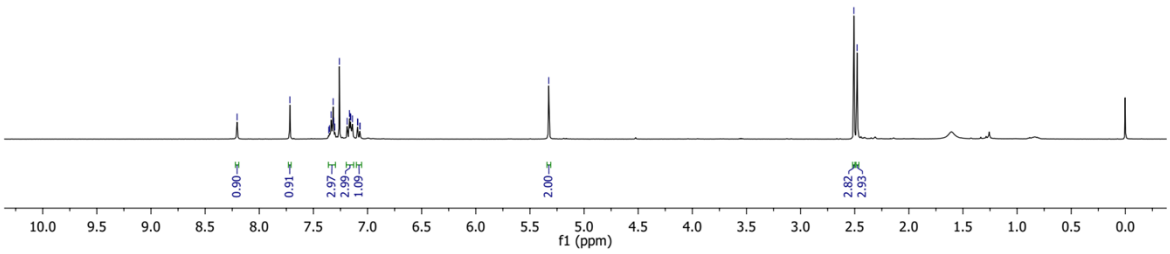


1d

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



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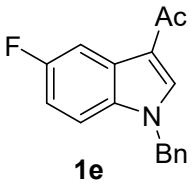

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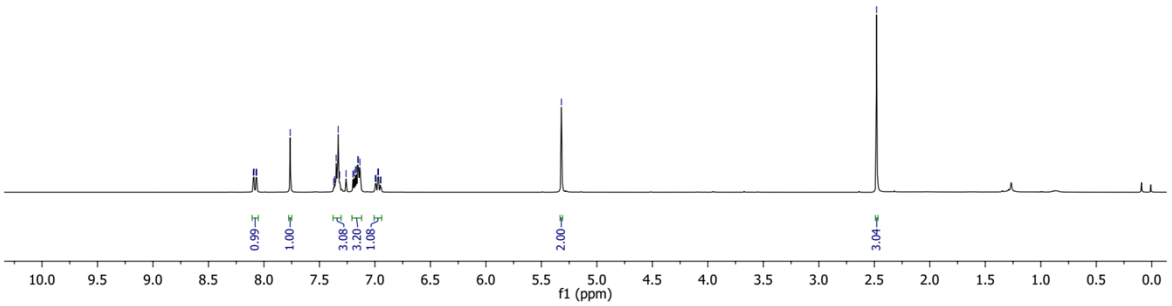

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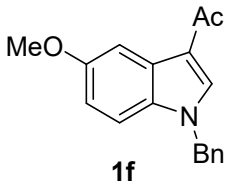
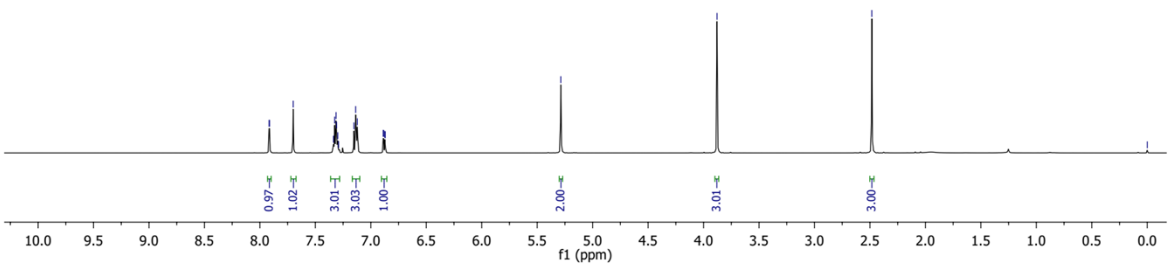


1f

^{1}H NMR (600 MHz, $CDCl_3$)



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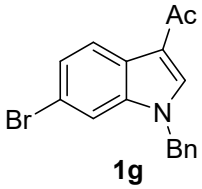

1g

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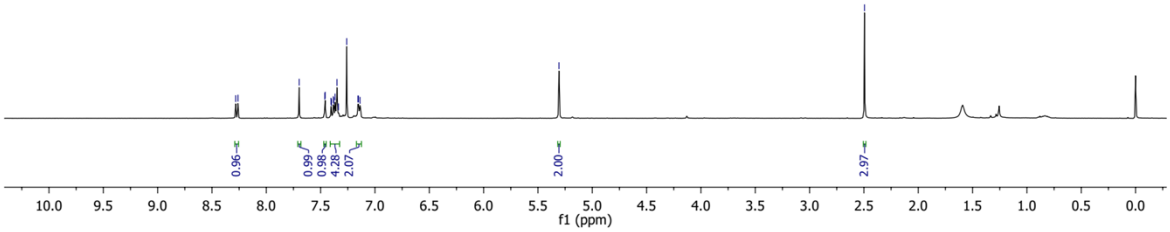

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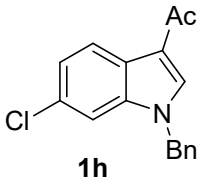
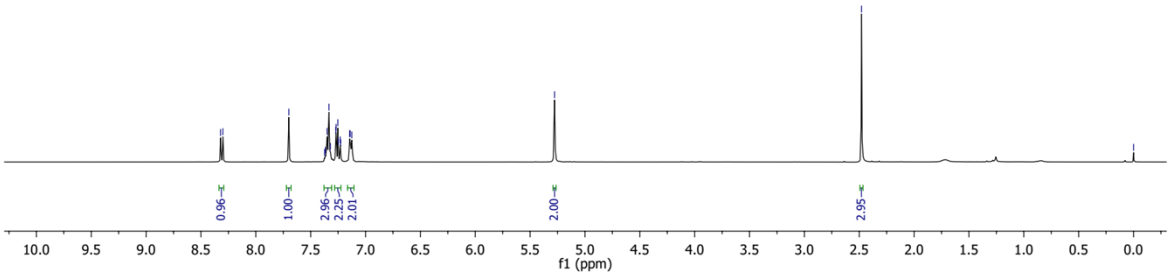


1h

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



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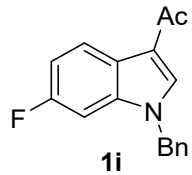
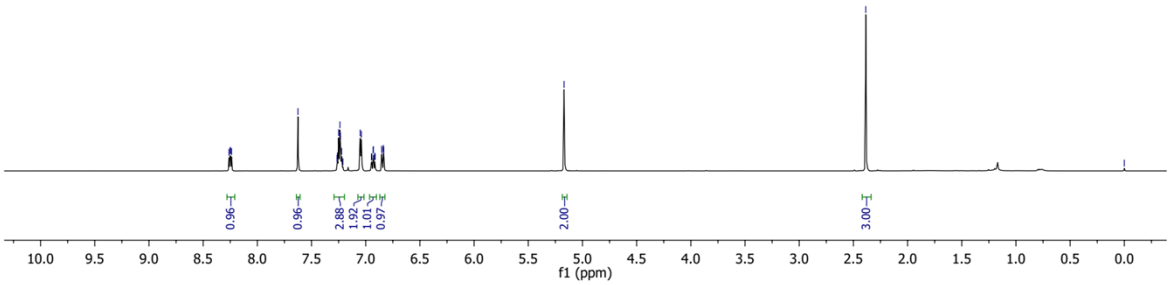


1i

^{1}H NMR (600 MHz, $CDCl_3$)



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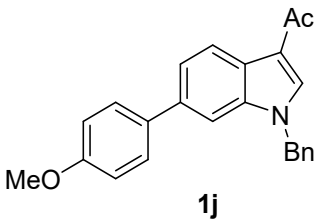
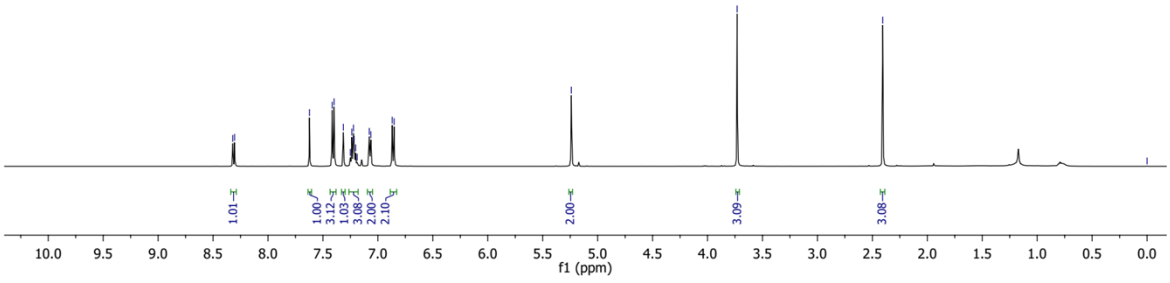


1j

^{1}H NMR (500 MHz, $CDCl_3$)



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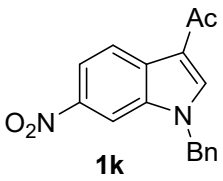

1k

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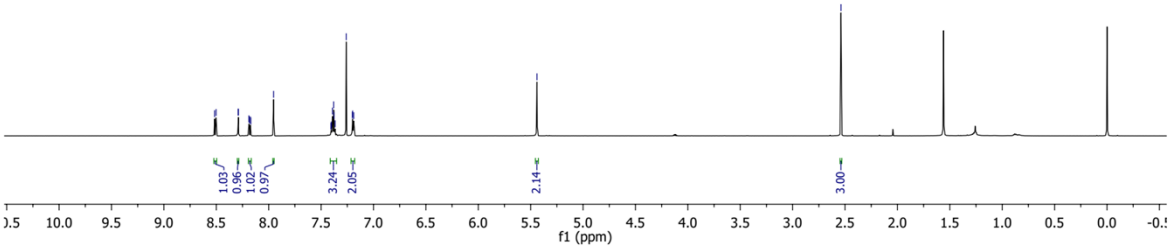

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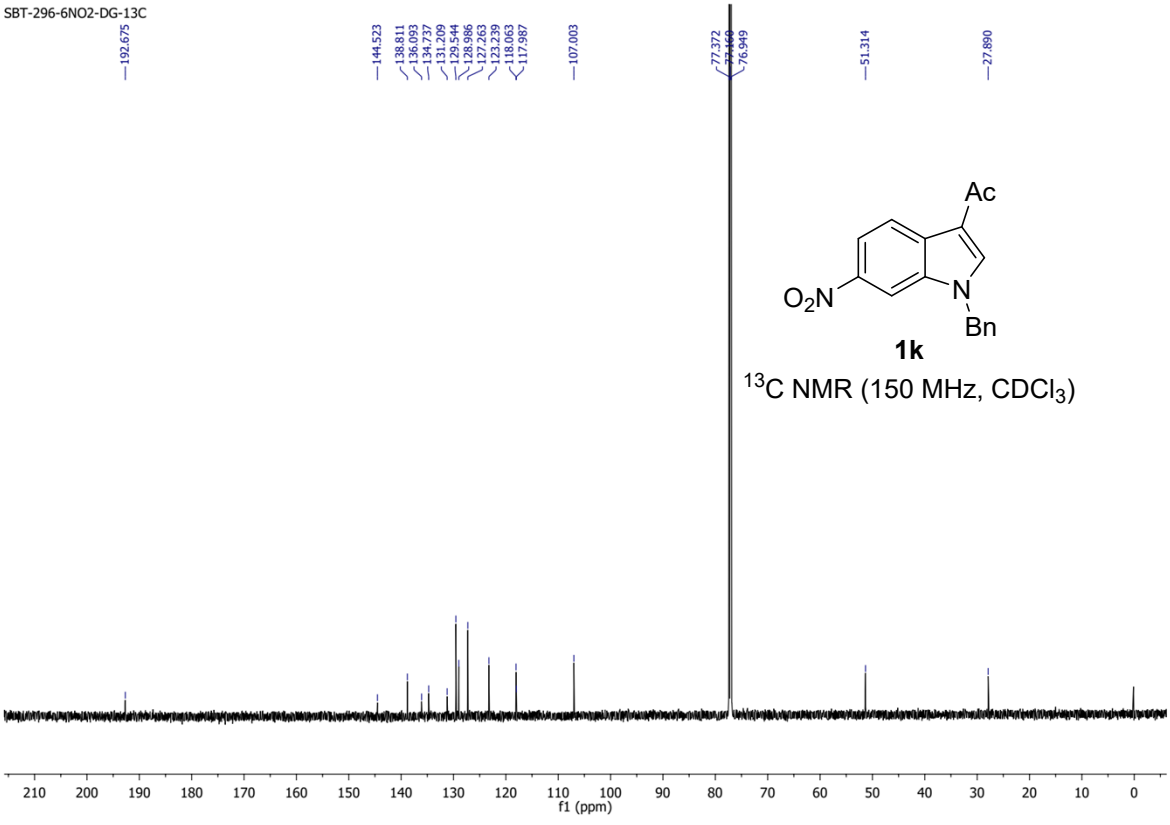

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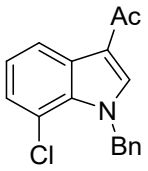
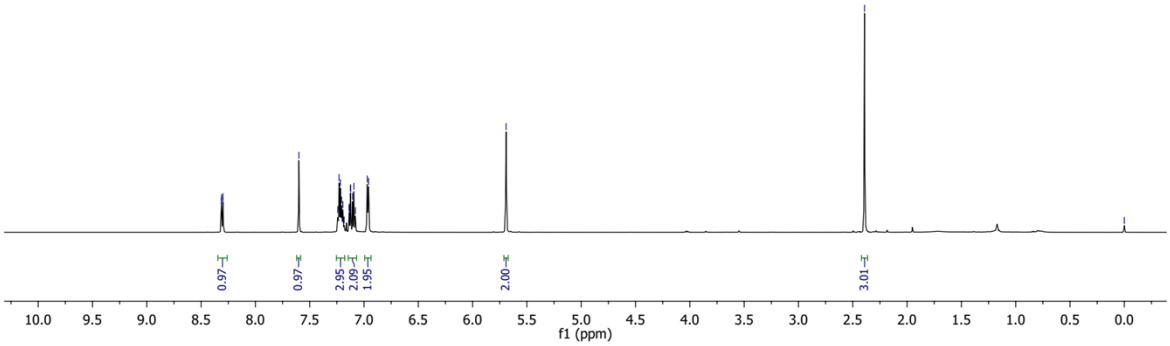
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-7Cl-DG-1H



1l

^{1}H NMR (600 MHz, $CDCl_3$)



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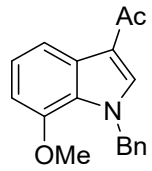

1m

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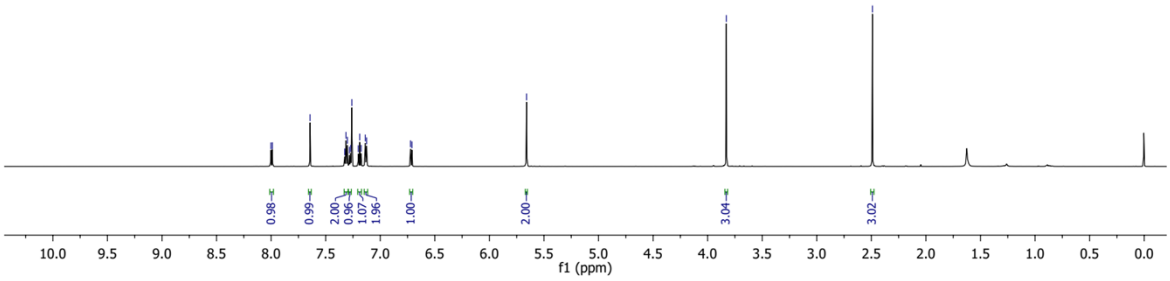

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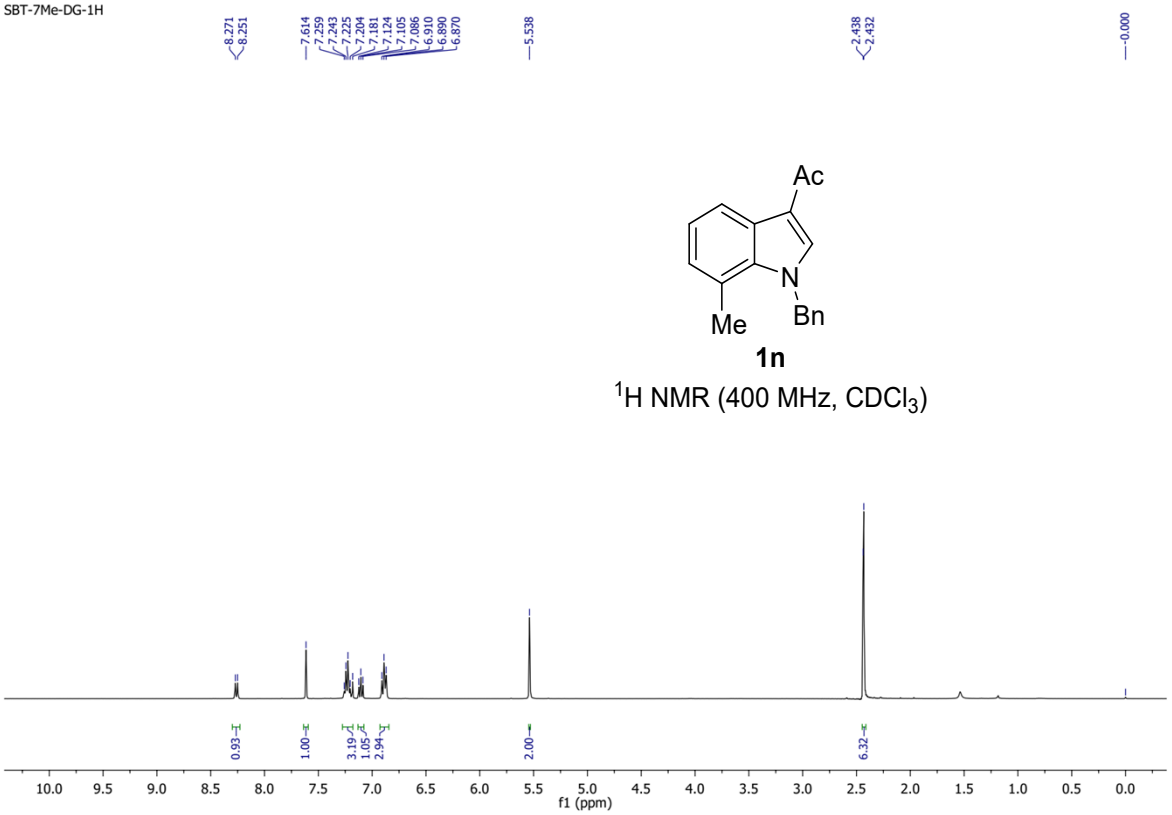

1n

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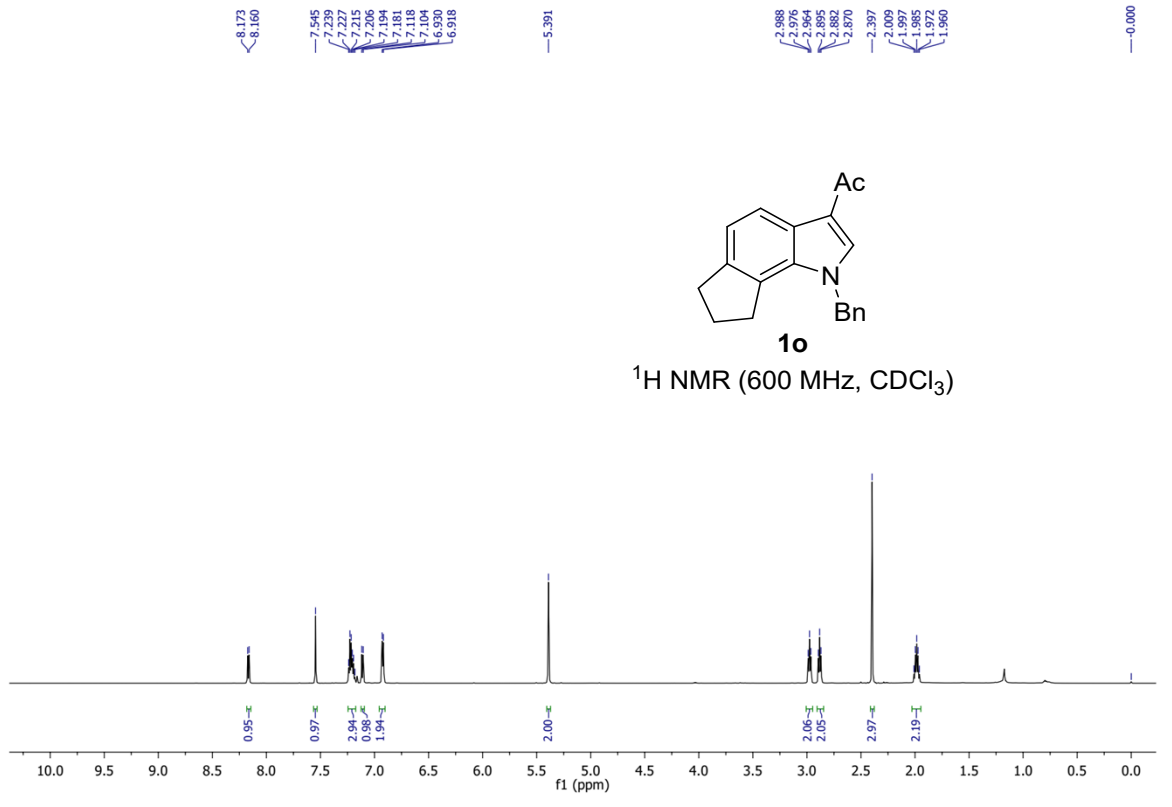
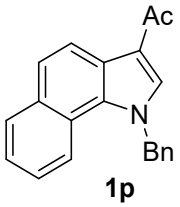
SBT-Penta[g]-DG-1H



1o

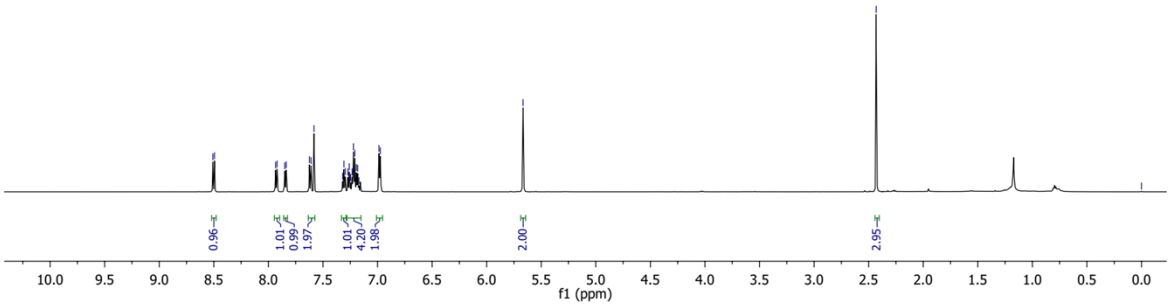
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-Benzo[g]-DG-1H

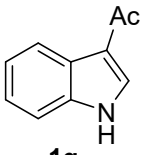


1p

^{1}H NMR (600 MHz, $CDCl_3$)

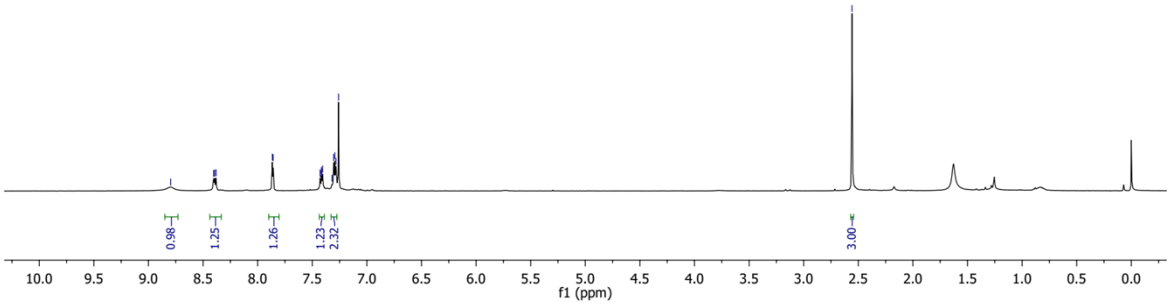


SBT-NH-AC-DG-1H

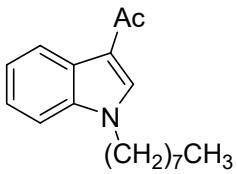


1q

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

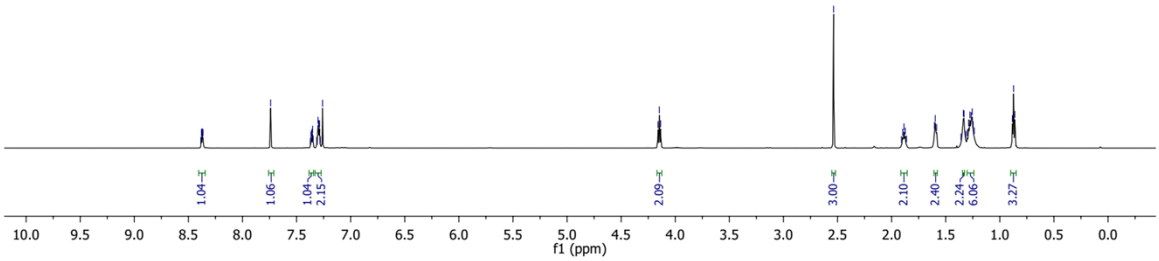


SBT-N-Oct-DG-1H

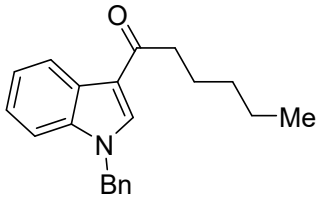


1r

^{1}H NMR (600 MHz, $CDCl_3$)

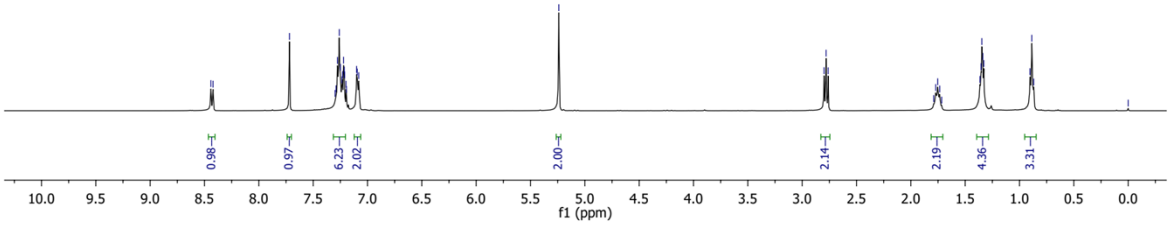


SBT-hexanoyl-DG-1H

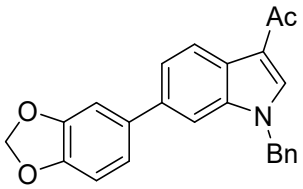


1s

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

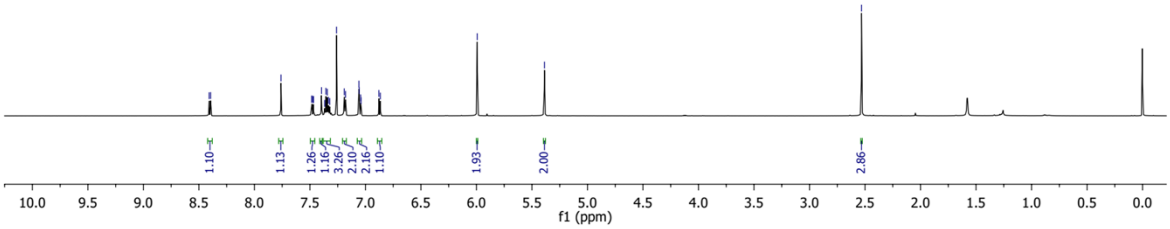


SBT-Sesa-DG-1H

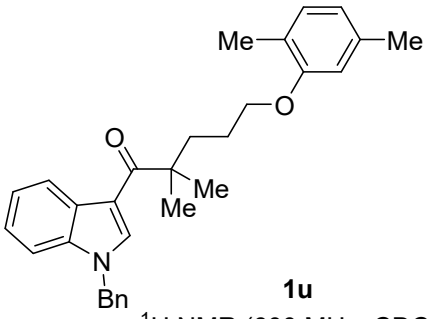


1t

^{1}H NMR (600 MHz, $CDCl_3$)

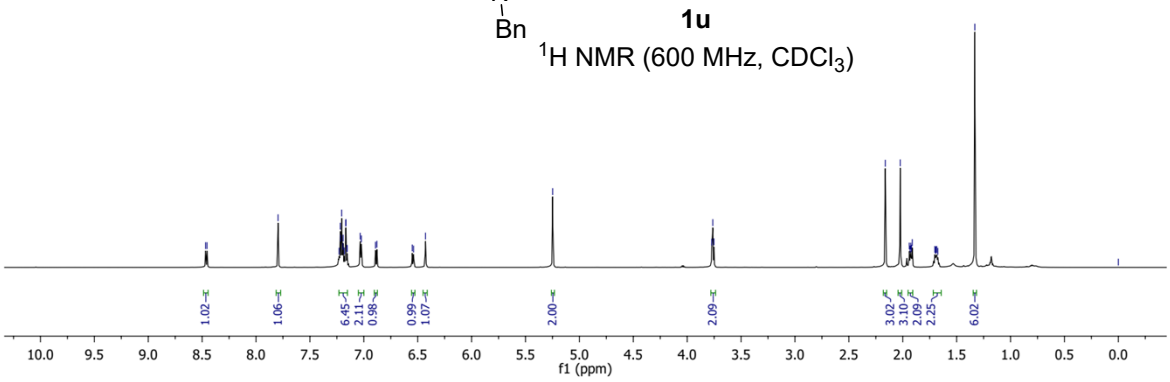


SBT-Gemfibrozil-DG-1H

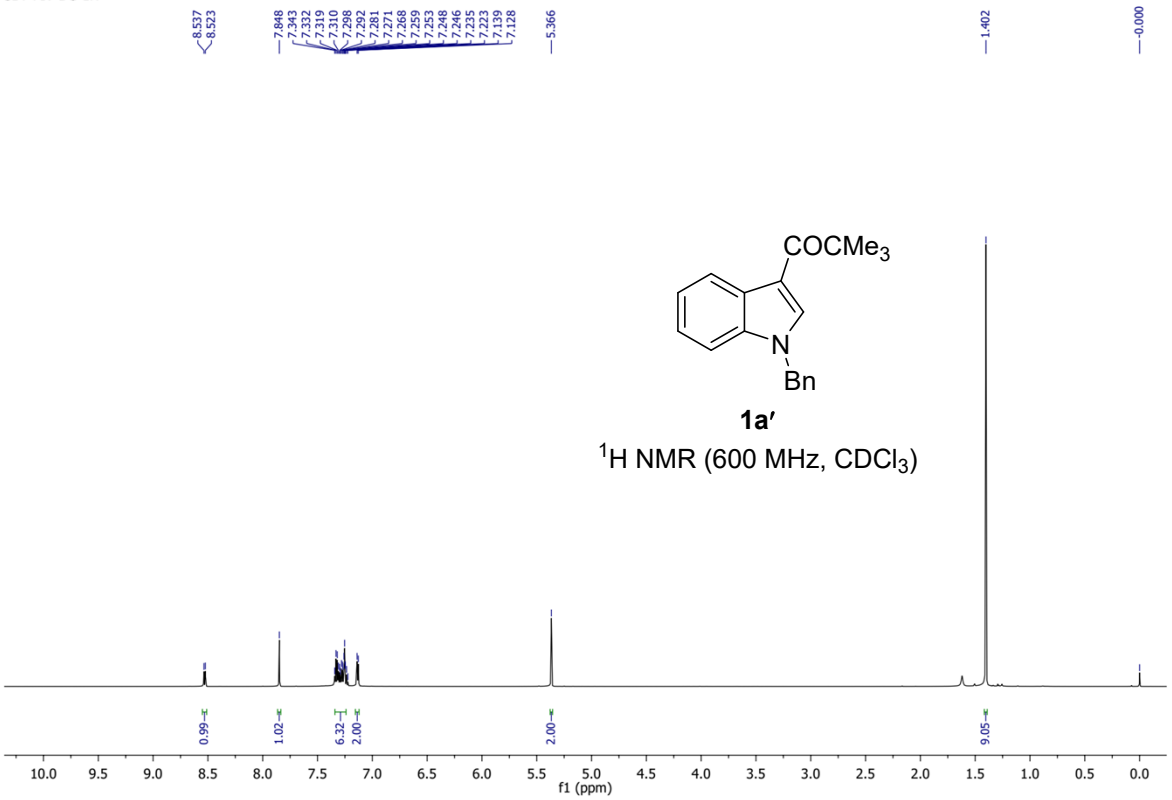


1u

^{1}H NMR (600 MHz, $CDCl_3$)



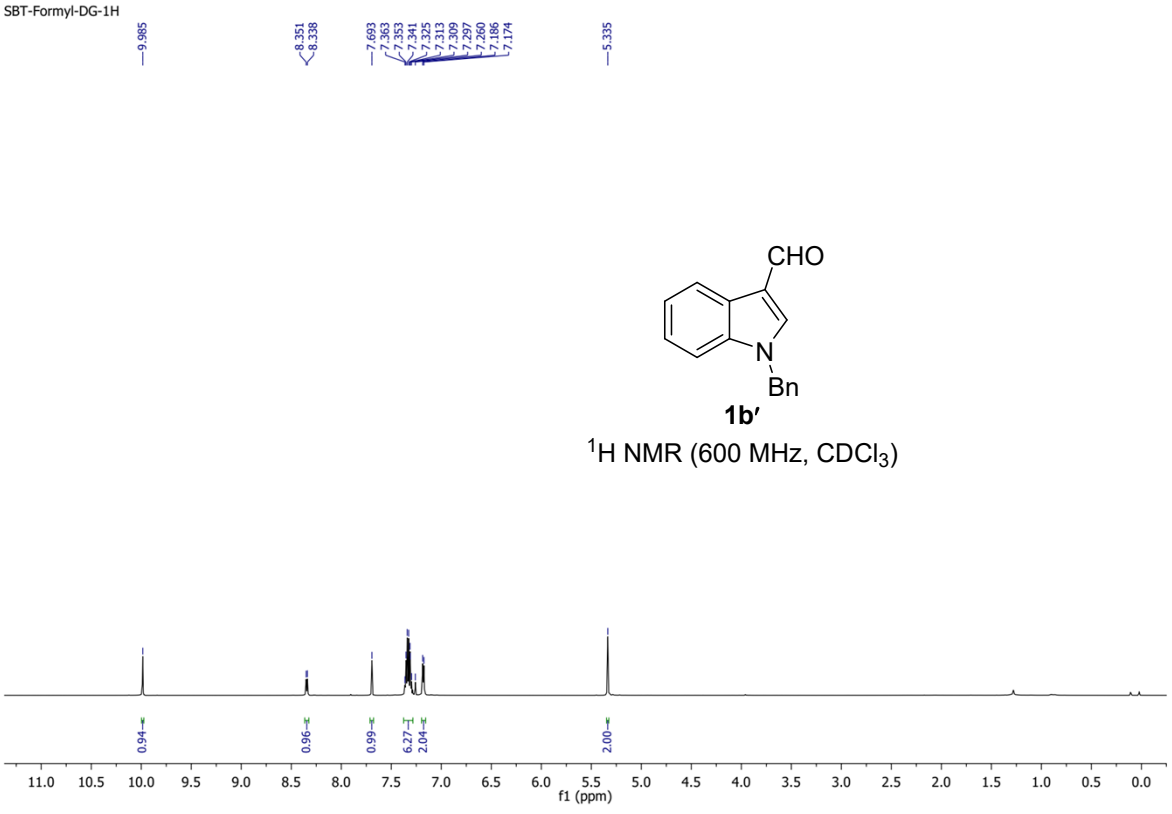
SBT-PIV-DG-1H



1a′

^{1}H NMR (600 MHz, $CDCl_3$)

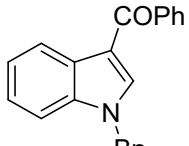
SBT-Formyl-DG-1H



1b′

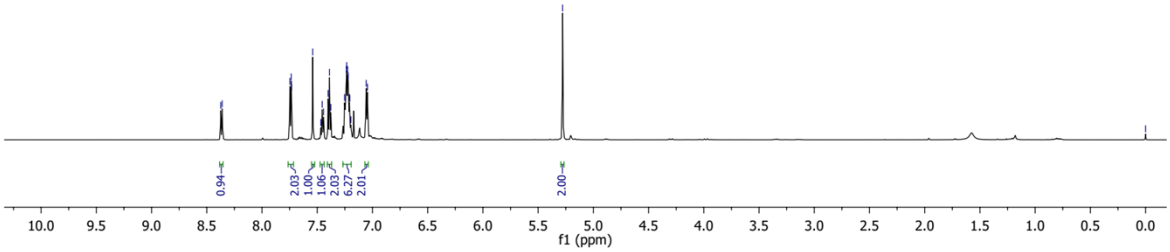
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-BZ-DG-1H

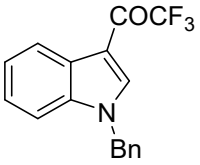


1c′

^{1}H NMR (600 MHz, $CDCl_3$)

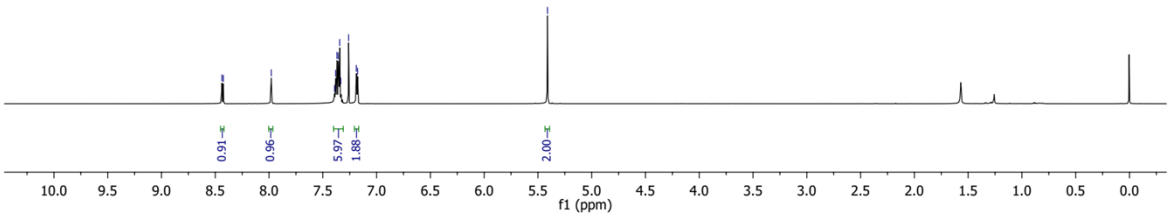


SBT-COCF3-DG-1H

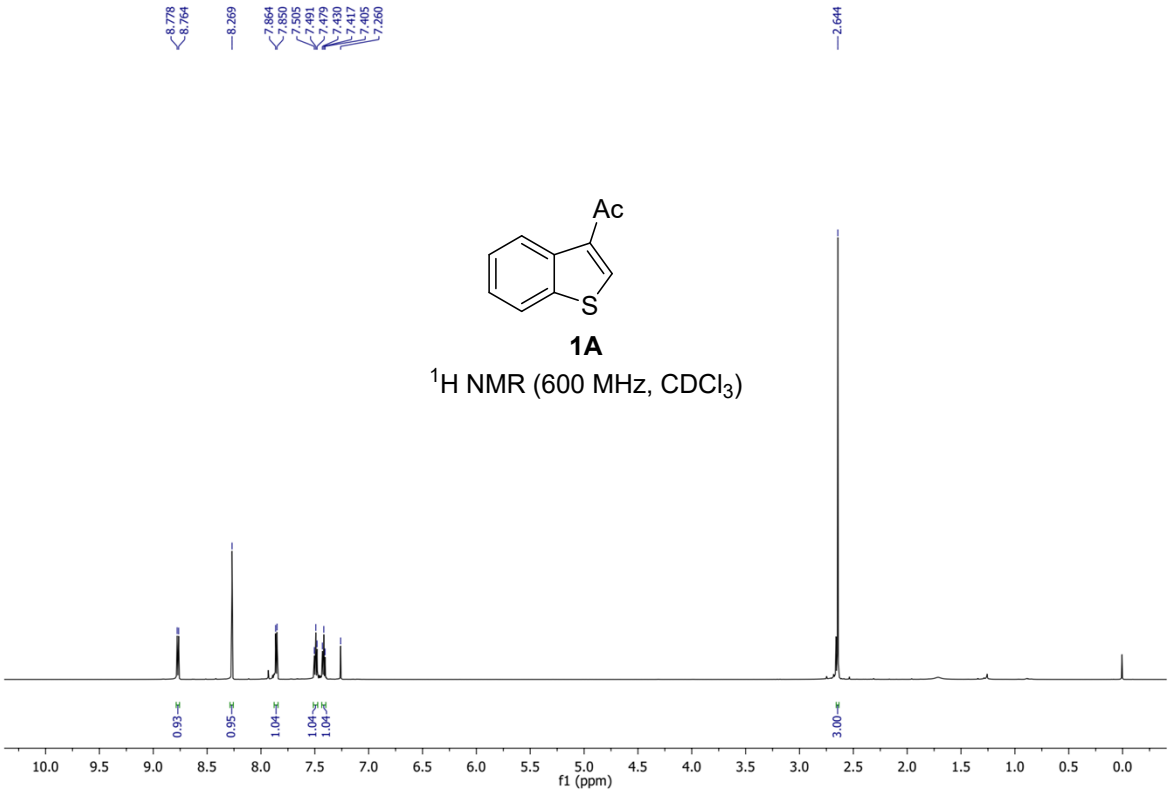


1d′

^{1}H NMR (600 MHz, $CDCl_3$)



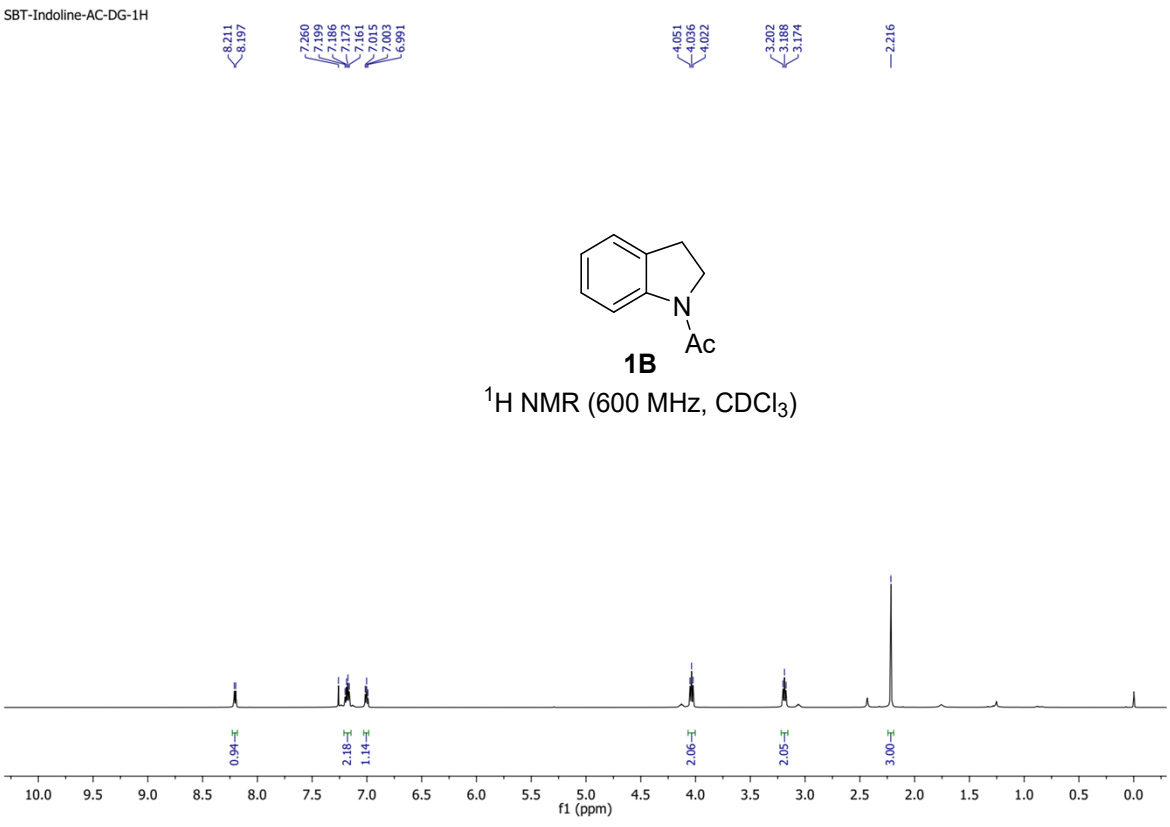
SBT-THIA-AC-DG-1H



1A

^{1}H NMR (600 MHz, $CDCl_3$)

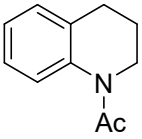
SBT-Indoline-AC-DG-1H



1B

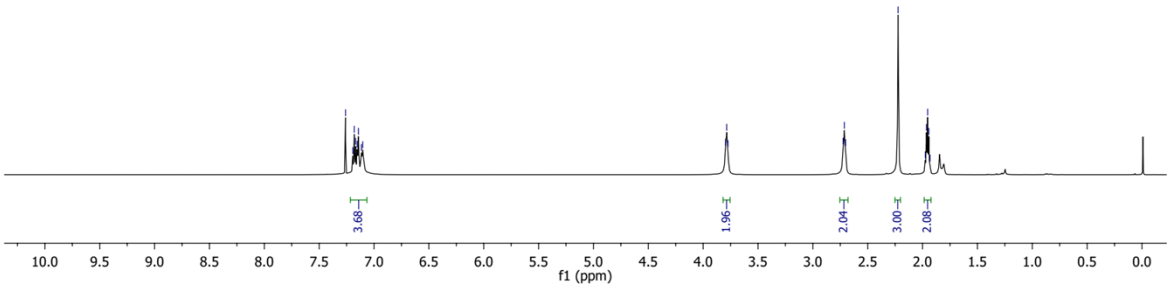
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-THQ-AC-DG-1H

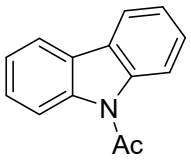


1C

^{1}H NMR (600 MHz, $CDCl_3$)

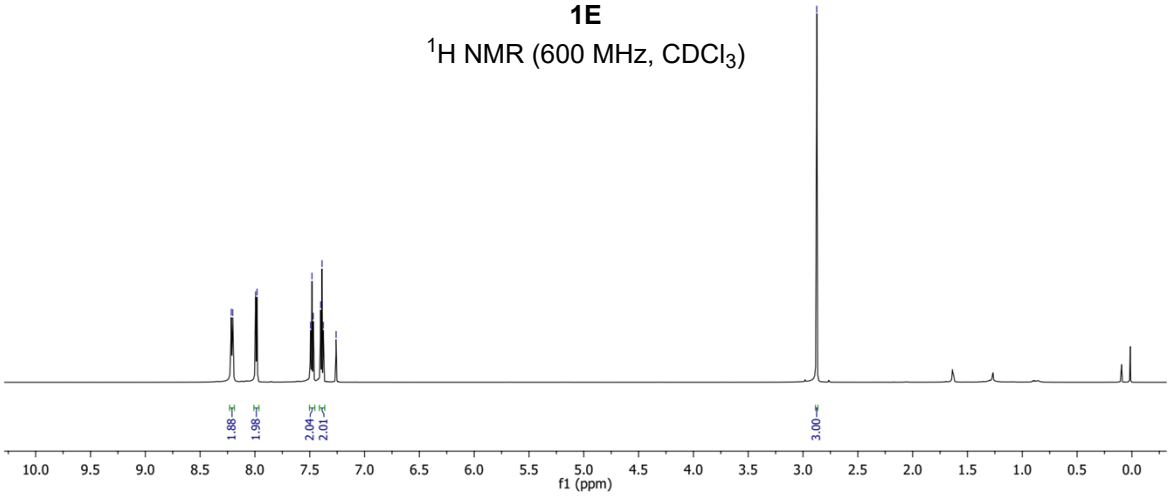


SBT-CARBA-AC-DG-1H

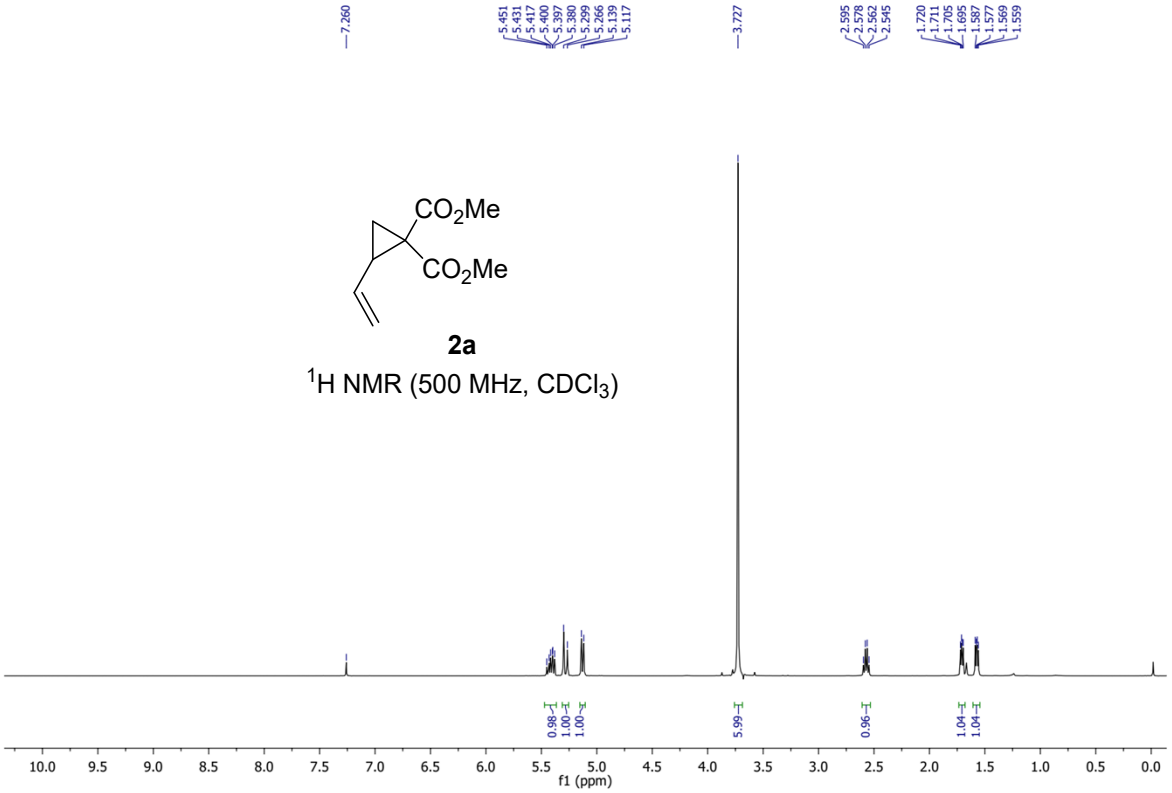


1E

^{1}H NMR (600 MHz, $CDCl_3$)



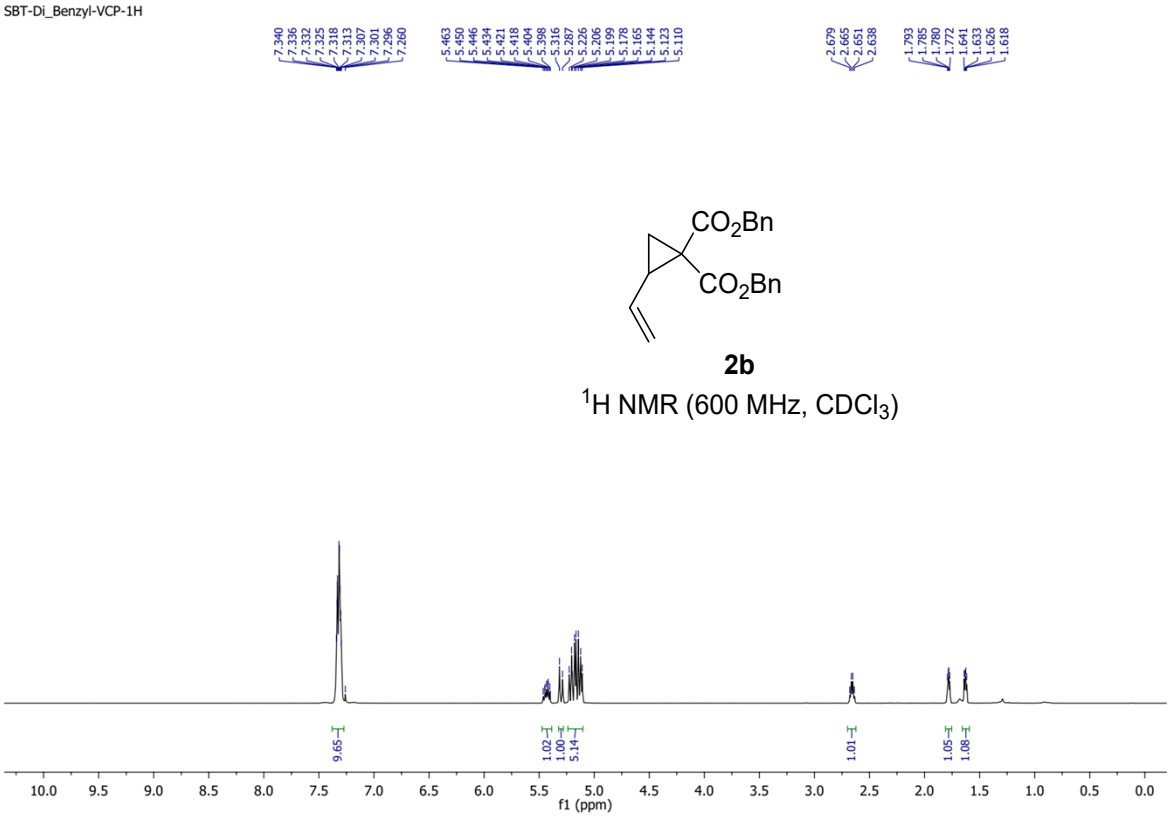
SBT-Di_CO2Me-VCP-1H



2a

^{1}H NMR (500 MHz, $CDCl_3$)

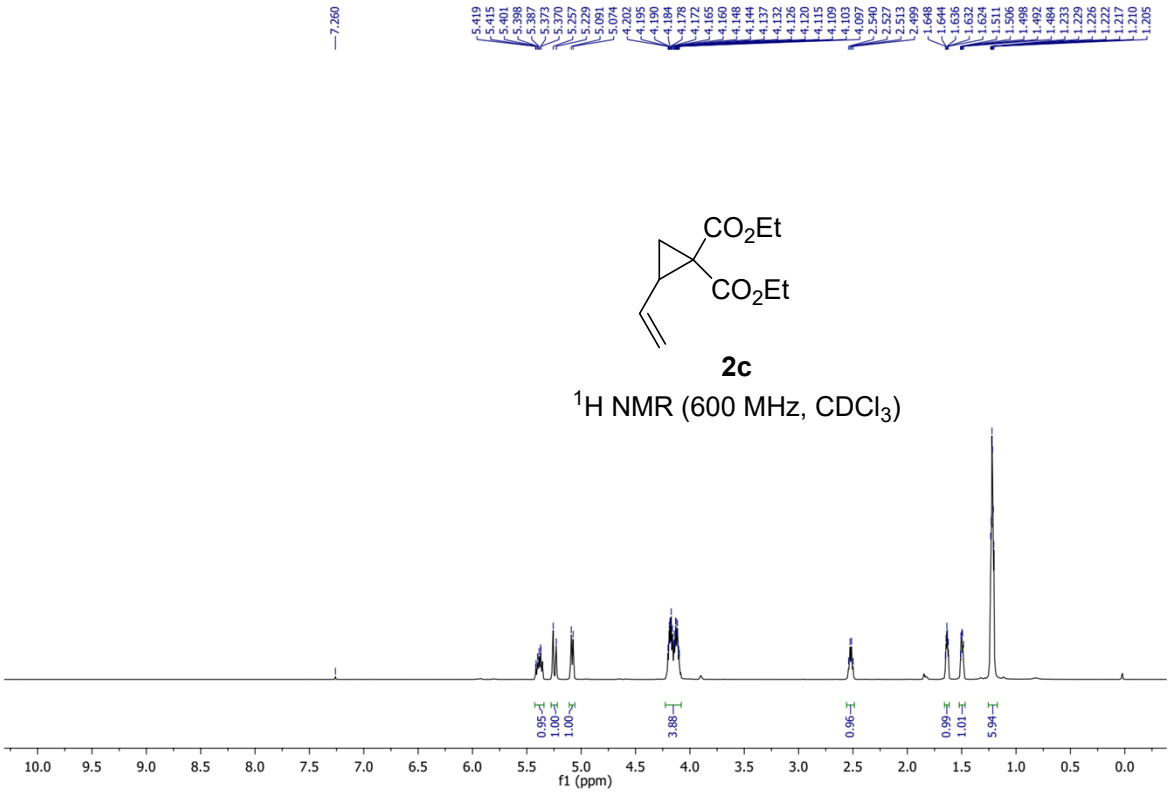
SBT-Di_Benzyl-VCP-1H



2b

^{1}H NMR (600 MHz, $CDCl_3$)

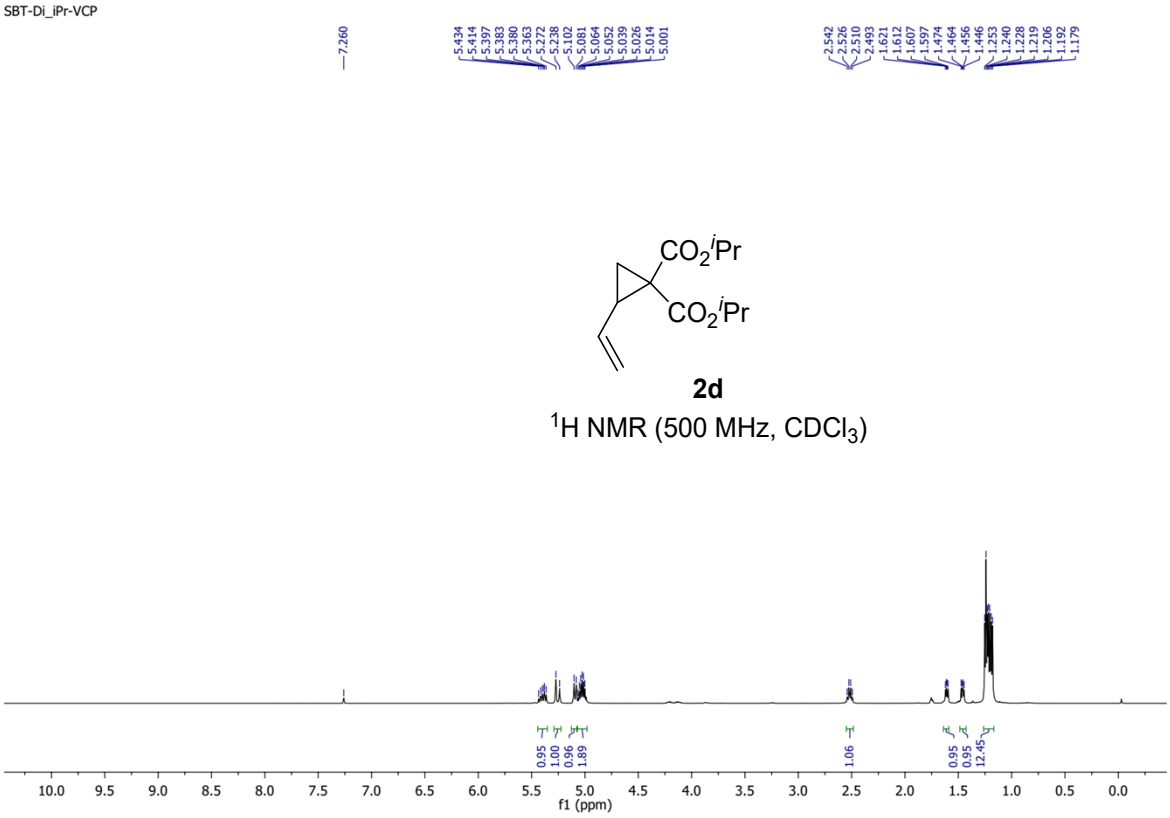
SBT-Di_CO2Et-VCP-1H



2c

^{1}H NMR (600 MHz, $CDCl_3$)

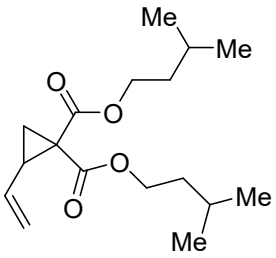
SBT-Di_iPr-VCP



2d

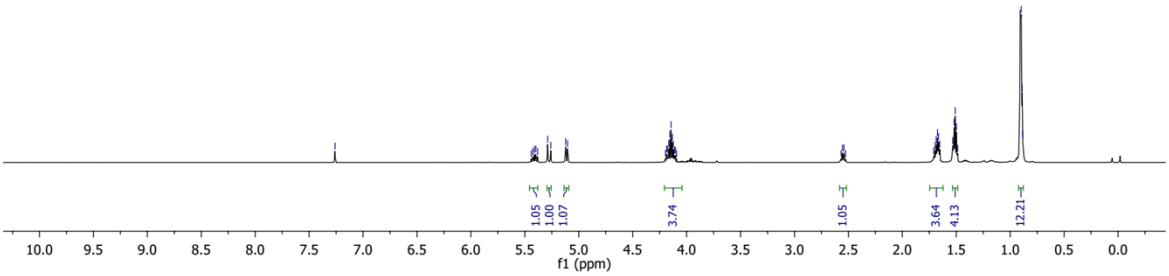
^{1}H NMR (500 MHz, $CDCl_3$)

SBT-Di_isoamyl-VCP-1H

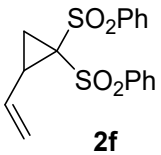


2e

^{1}H NMR (600 MHz, $CDCl_3$)

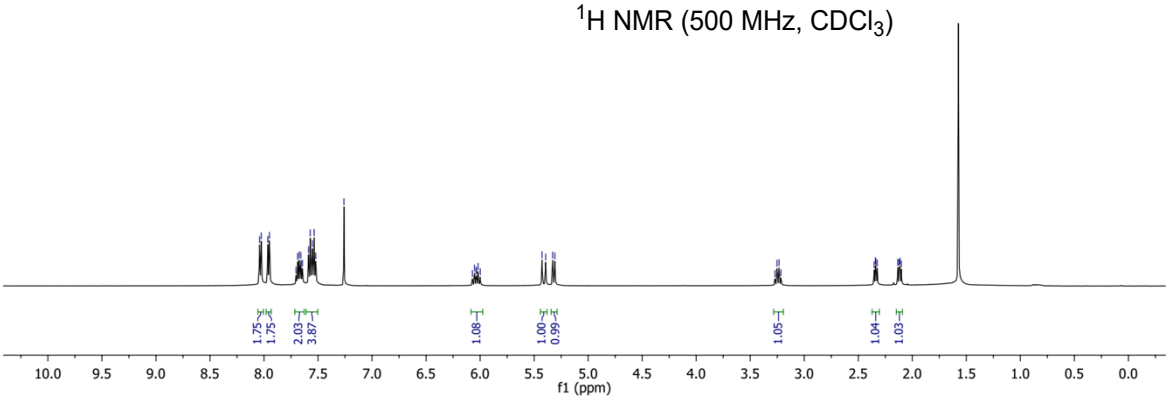


SBT-Di_SO2Ph-VCP-1H

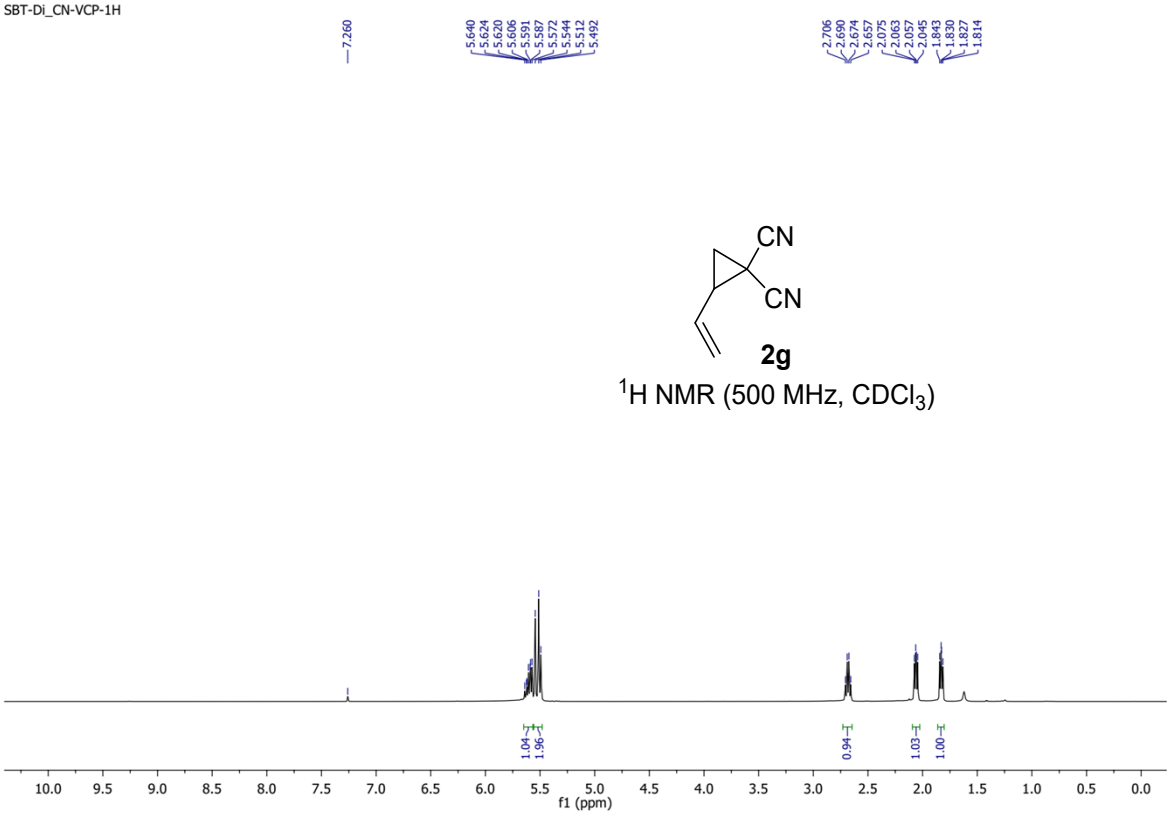


2f

^{1}H NMR (500 MHz, $CDCl_3$)



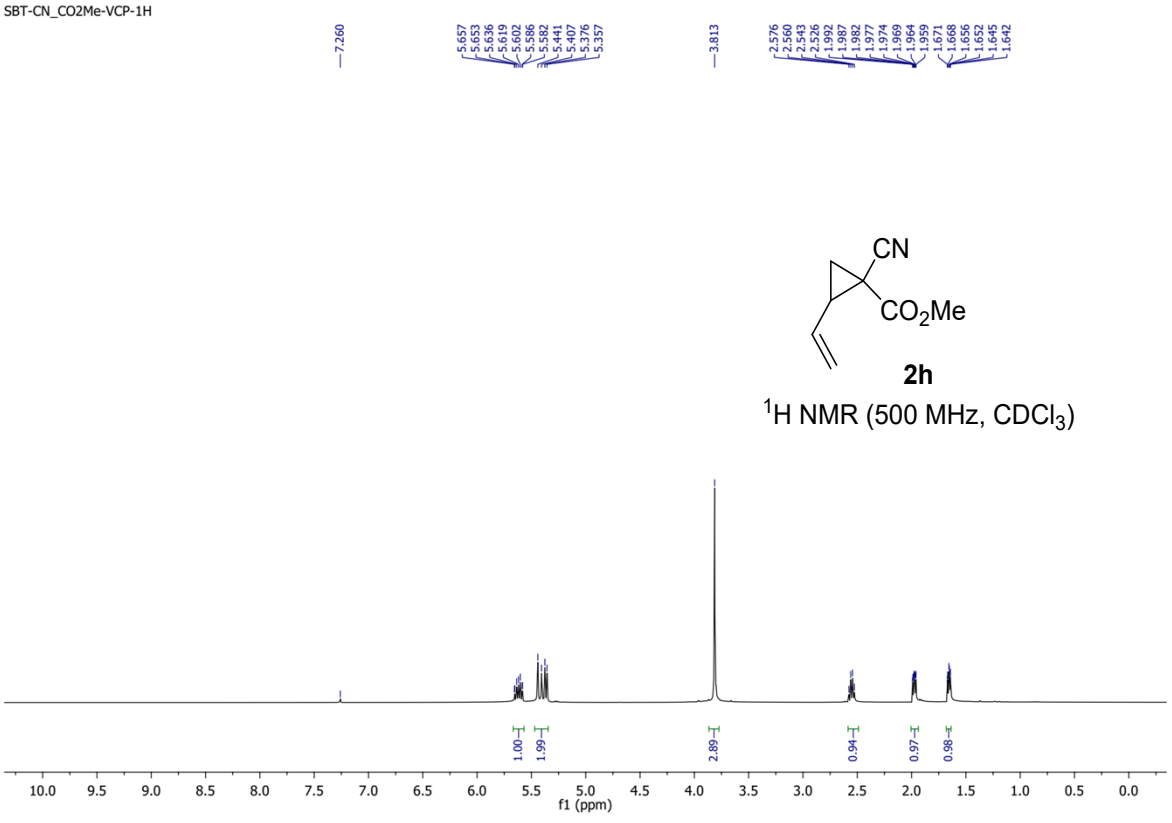
SBT-Di_CN-VCP-1H



2g

^{1}H NMR (500 MHz, $CDCl_3$)

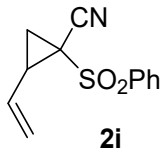
SBT-CN_CO2Me-VCP-1H



2h

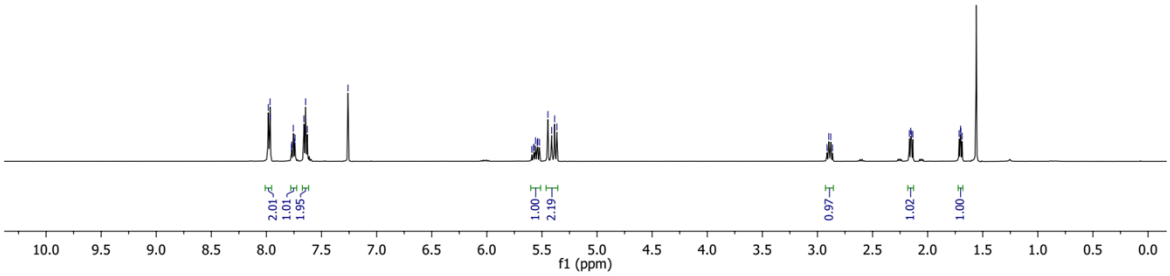
^{1}H NMR (500 MHz, $CDCl_3$)

SBT-CN_SO2Ph-VCP-1H

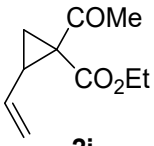


2i

^{1}H NMR (500 MHz, $CDCl_3$)

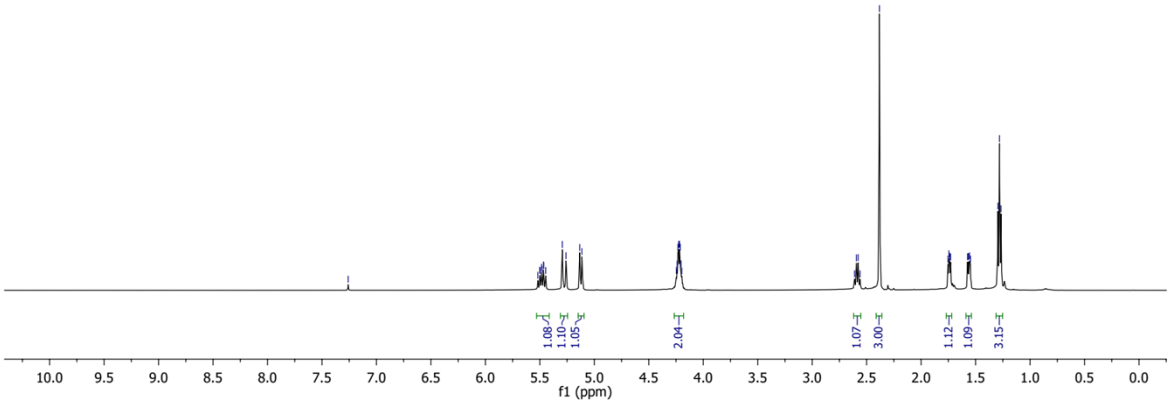


SBT-EAA_VCP-1H

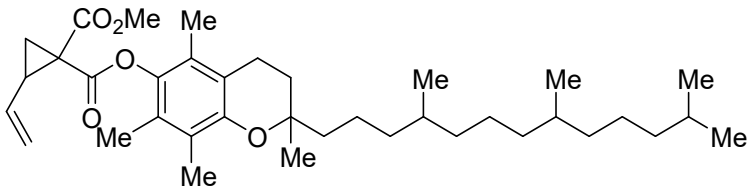


2j

^{1}H NMR (500 MHz, $CDCl_3$)

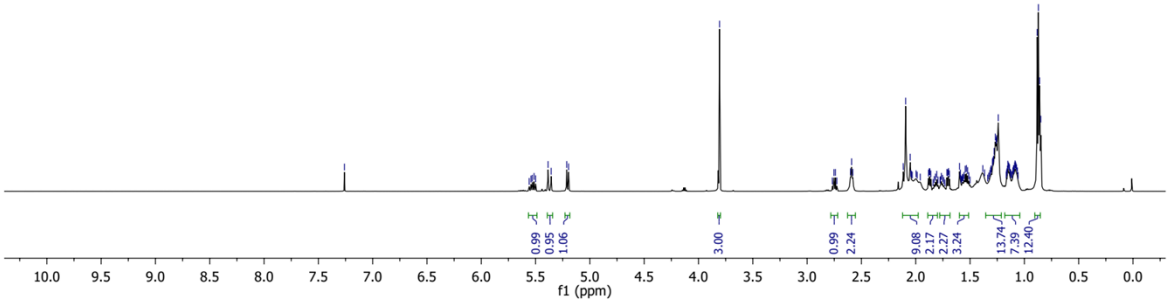


SBT-CO2Me_Vit E-VCP-1H

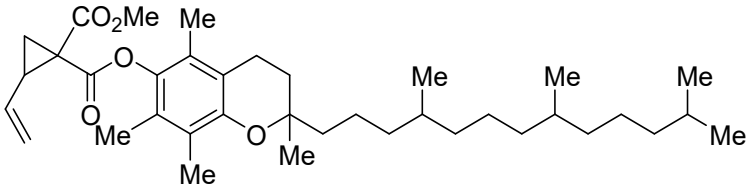


2k

^{1}H NMR (600 MHz, $CDCl_3$)

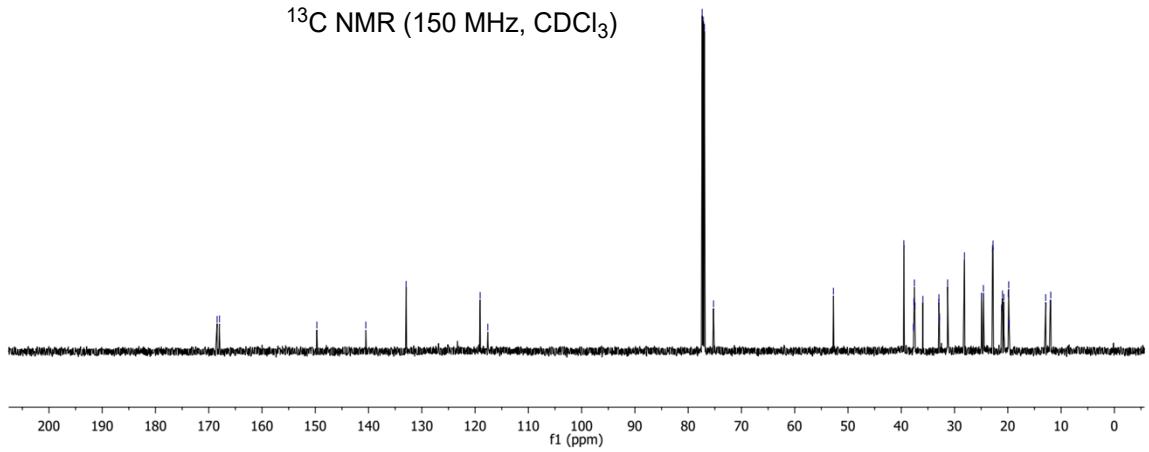


SBT-CO2Me_Vit E-VCP-13C

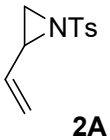


2k

^{13}C NMR (150 MHz, $CDCl_3$)

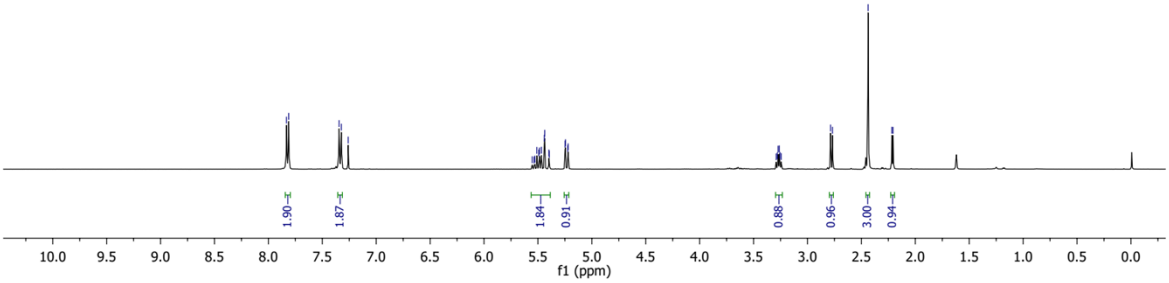


SBT-VAZ-1H

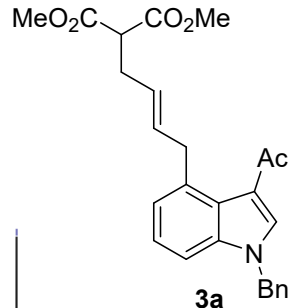


2A

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

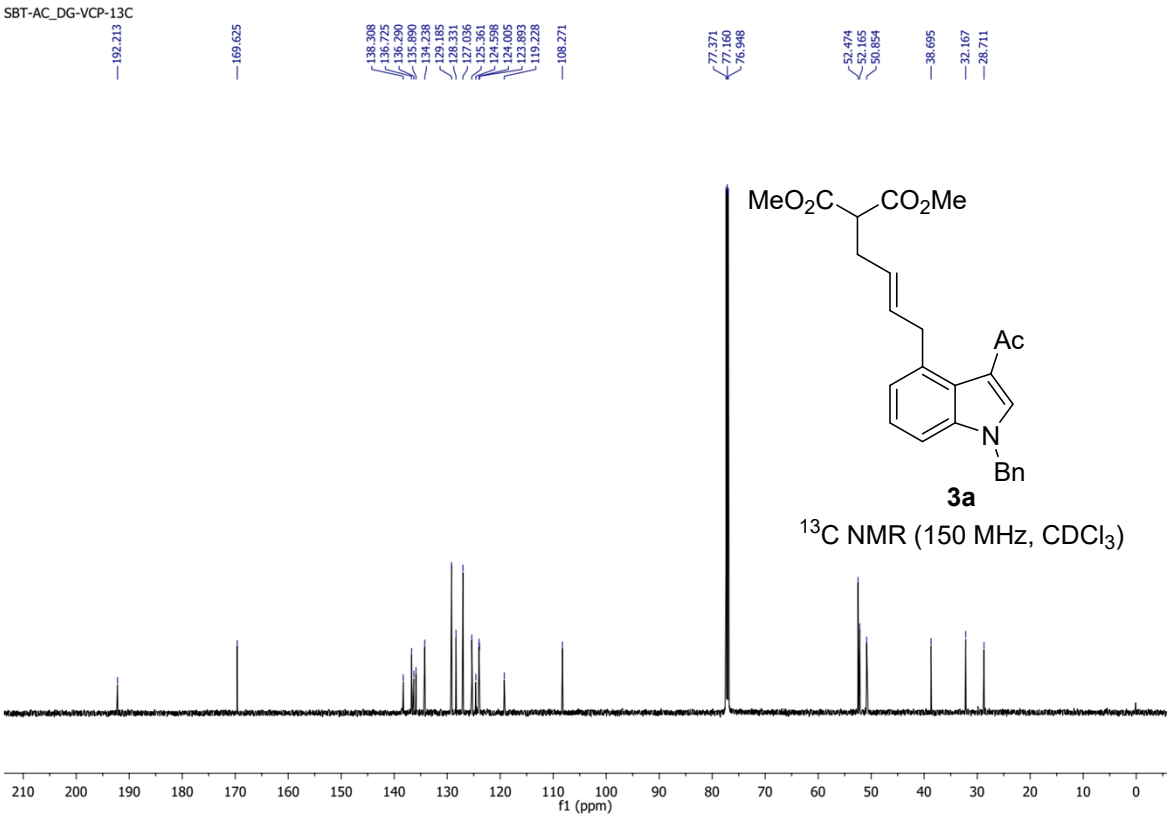


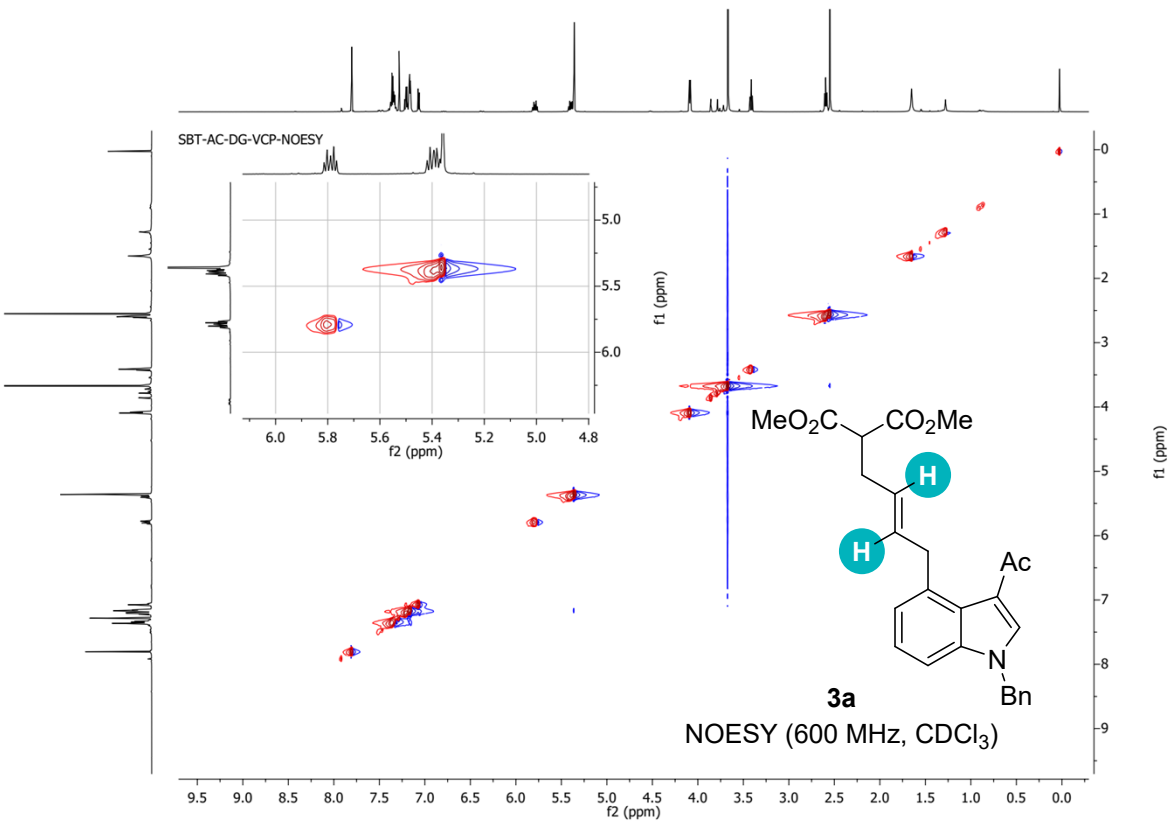
SBT-AC_DG-VCP-1H

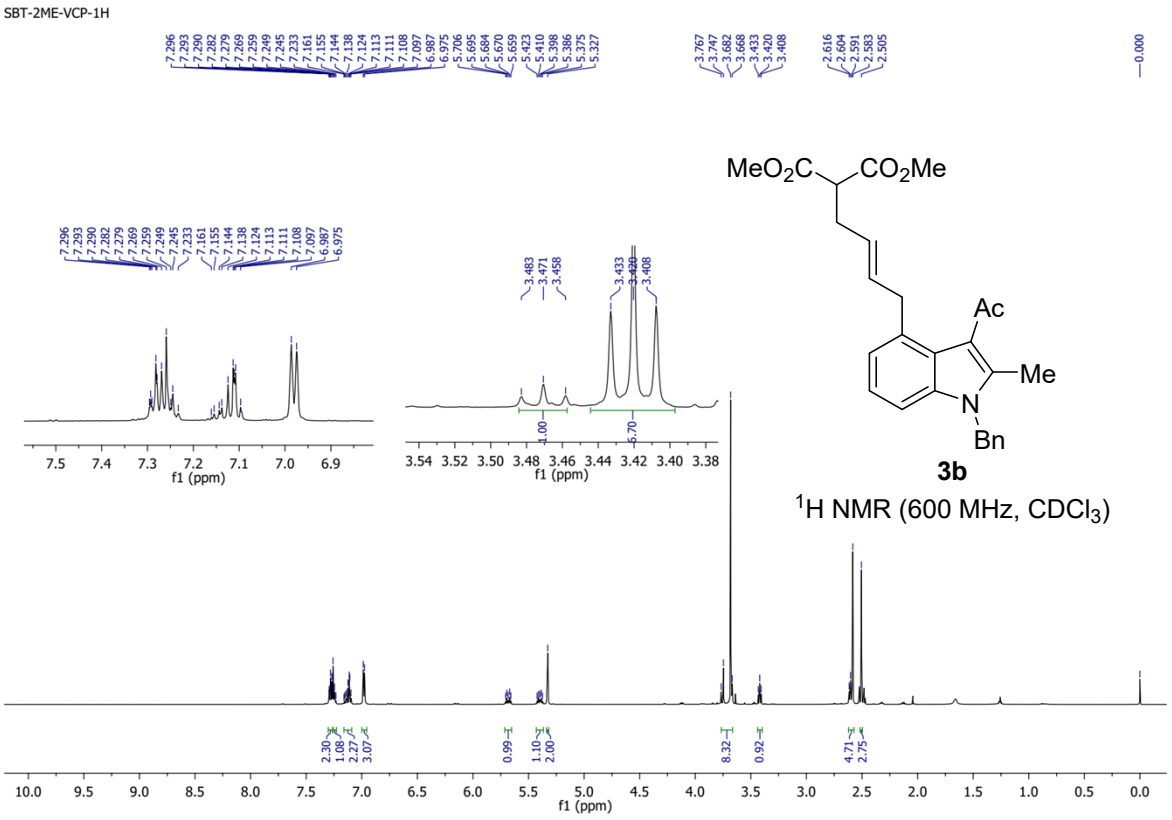


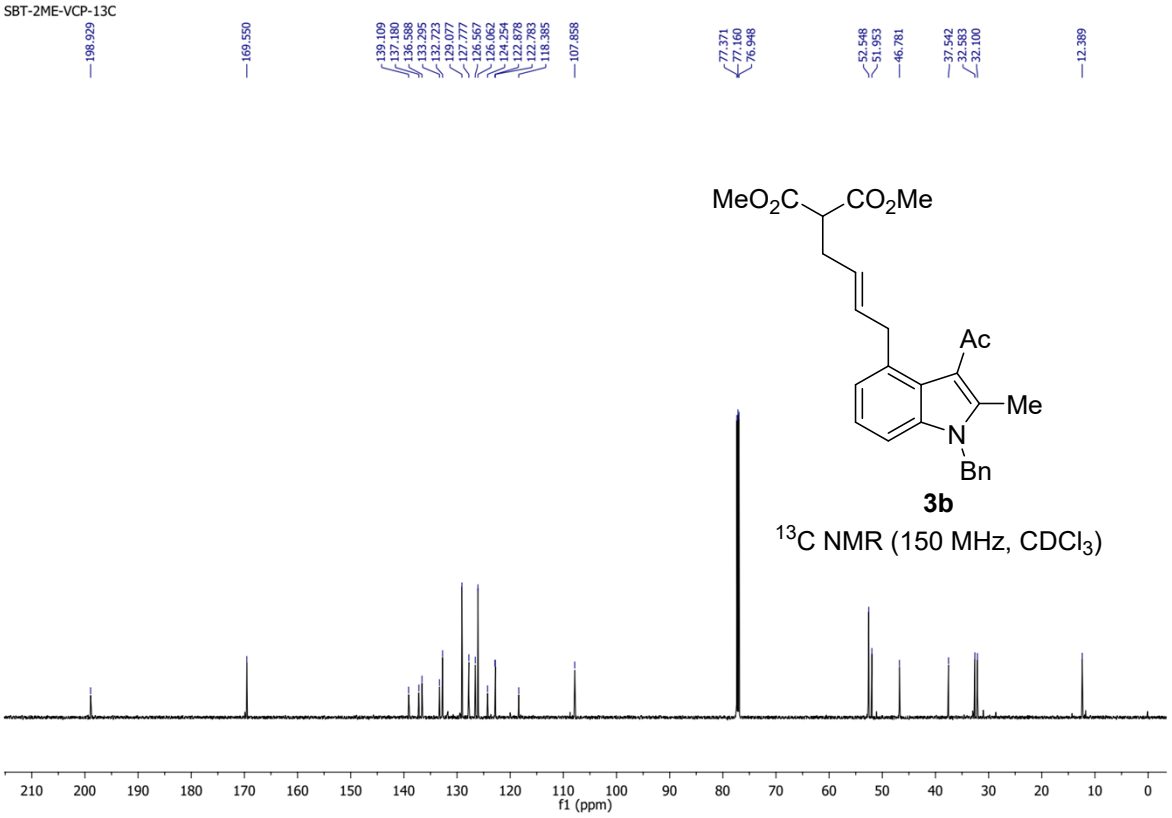
3a

^{1}H NMR (600 MHz, $CDCl_3$)

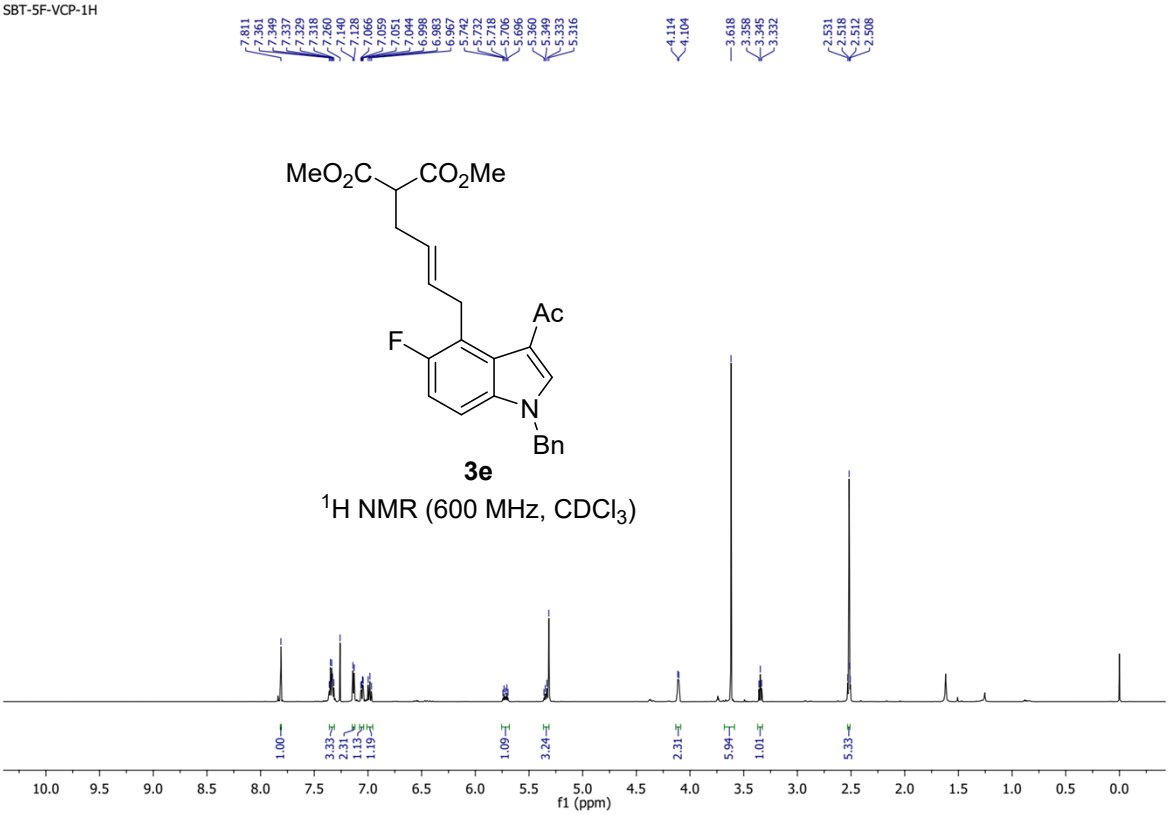

SBT-AC_DG-VCP-13C
192.213
169.625
138.308
136.725
136.290
135.890
134.238
129.185
128.331
127.036
125.361
124.598
124.005
123.893
119.228
108.271
77.371
77.160
76.948
52.474
52.165
50.854
38.695
32.167
28.711
MeO2C
CO2Me
Ac
N
Bn
3a
13C NMR (150 MHz, CDCl3)
f1 (ppm)


SBT-AC-DG-VCP-NOESY
f2 (ppm)
f1 (ppm)
MeO2C
CO2Me
H
H
Ac
N
Bn
3a
NOESY (600 MHz, CDCl3)


SBT-2ME-VCP-1H
MeO2C
CO2Me
Ac
Me
N
Bn
3b
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-2ME-VCP-13C
MeO2C
CO2Me
Ac
Me
N
Bn
3b
13C NMR (150 MHz, CDCl3)
f1 (ppm)

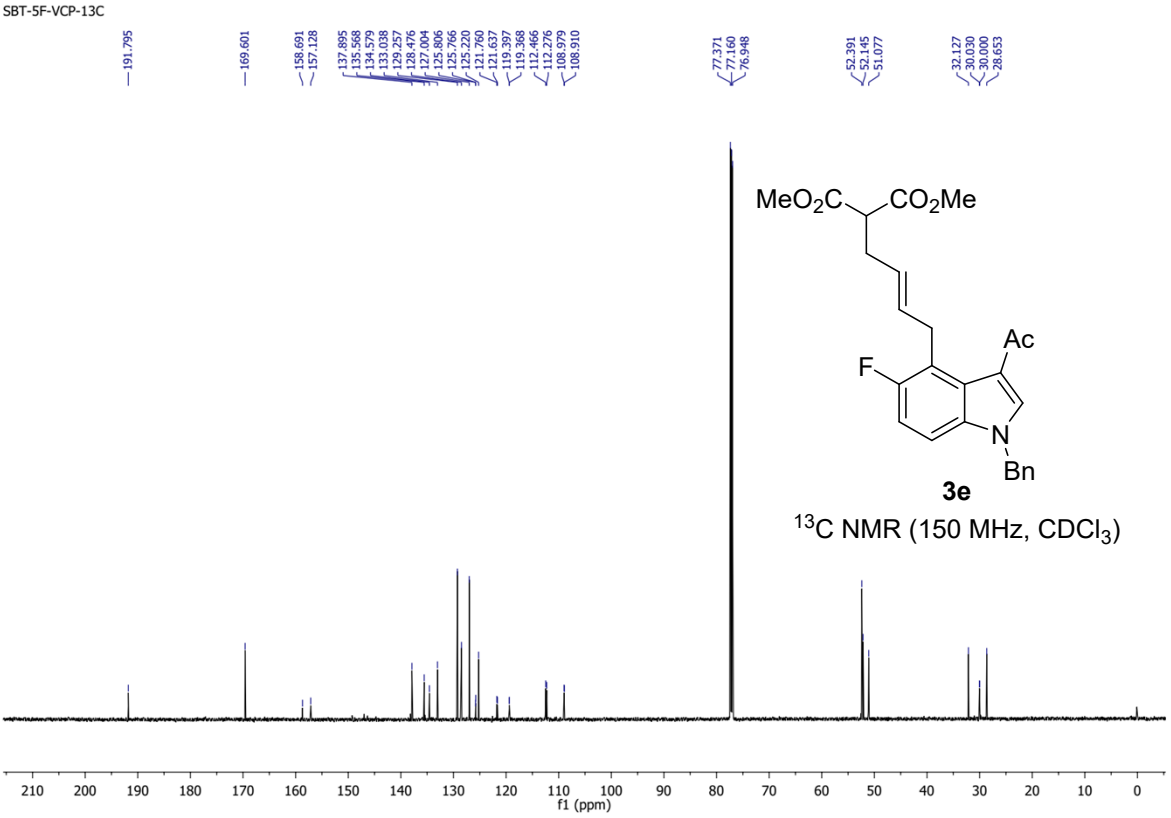
SBT-5F-VCP-1H



3e

^{1}H NMR (600 MHz, $CDCl_3$)

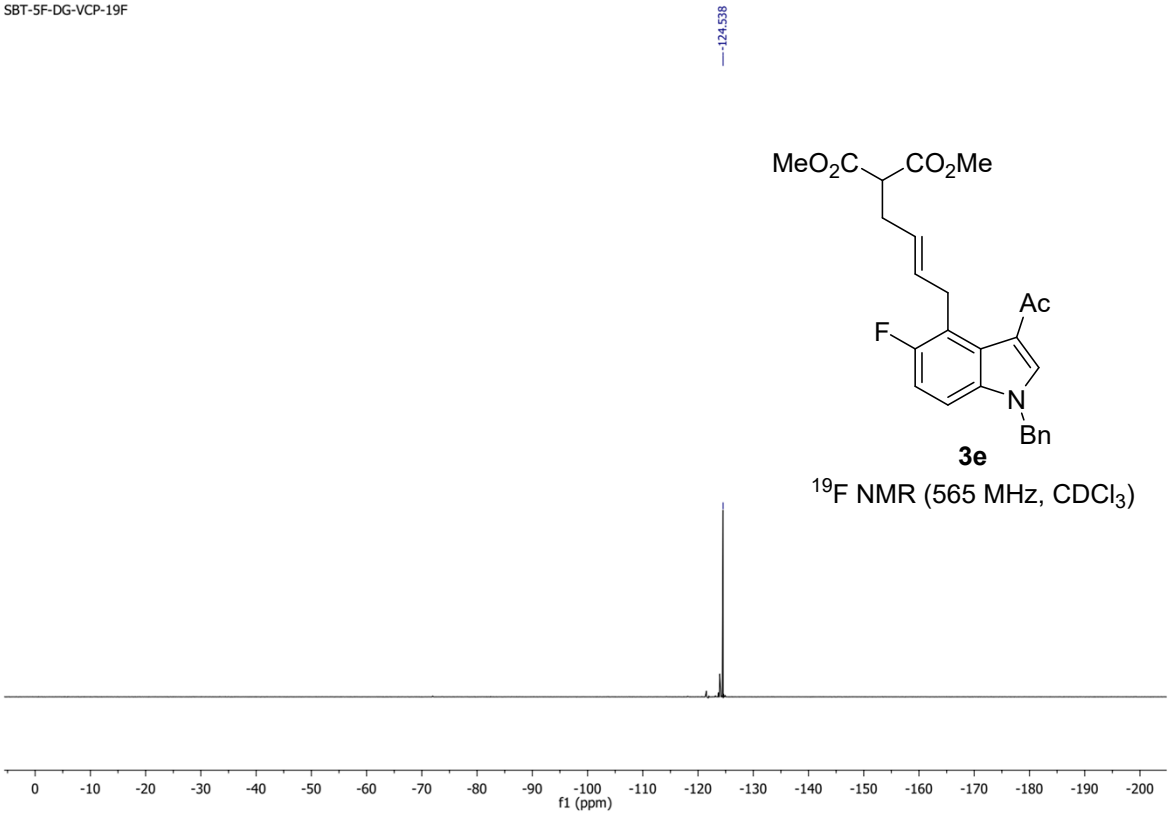
SBT-5F-VCP-13C



3e

^{13}C NMR (150 MHz, $CDCl_3$)

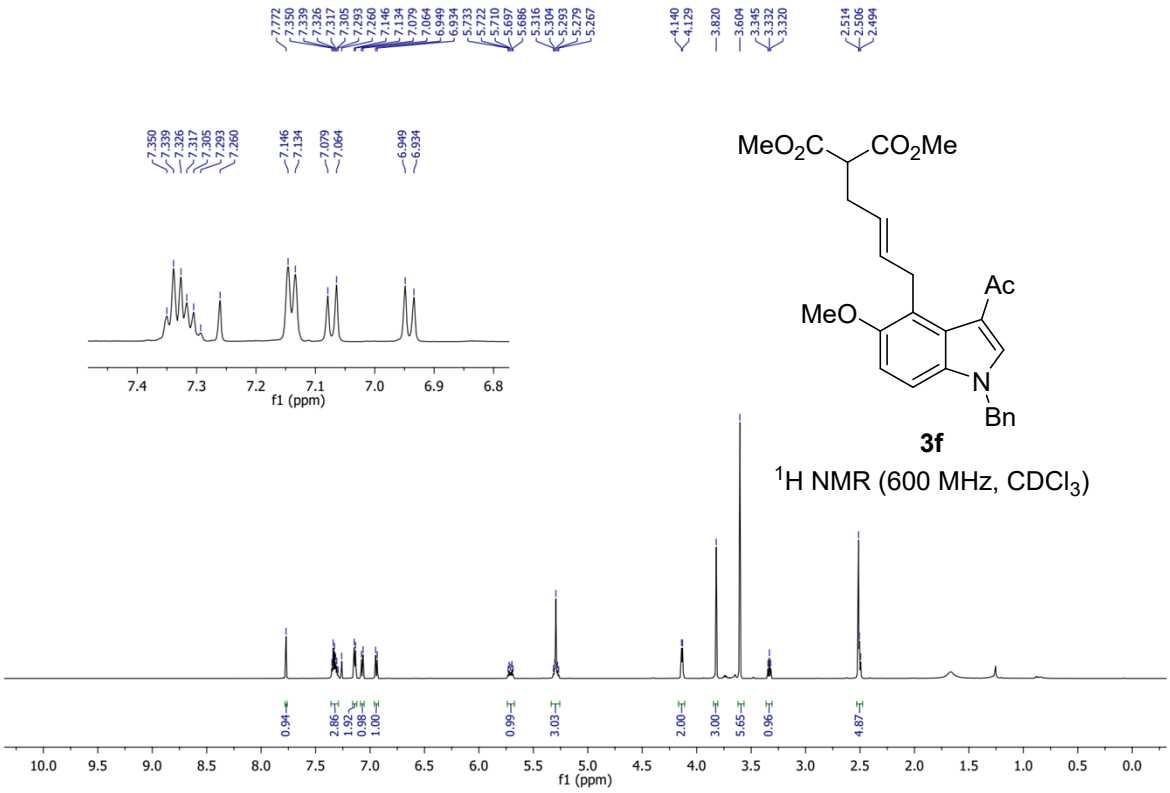
SBT-5F-DG-VCP-19F



3e

^{19}F NMR (565 MHz, $CDCl_3$)

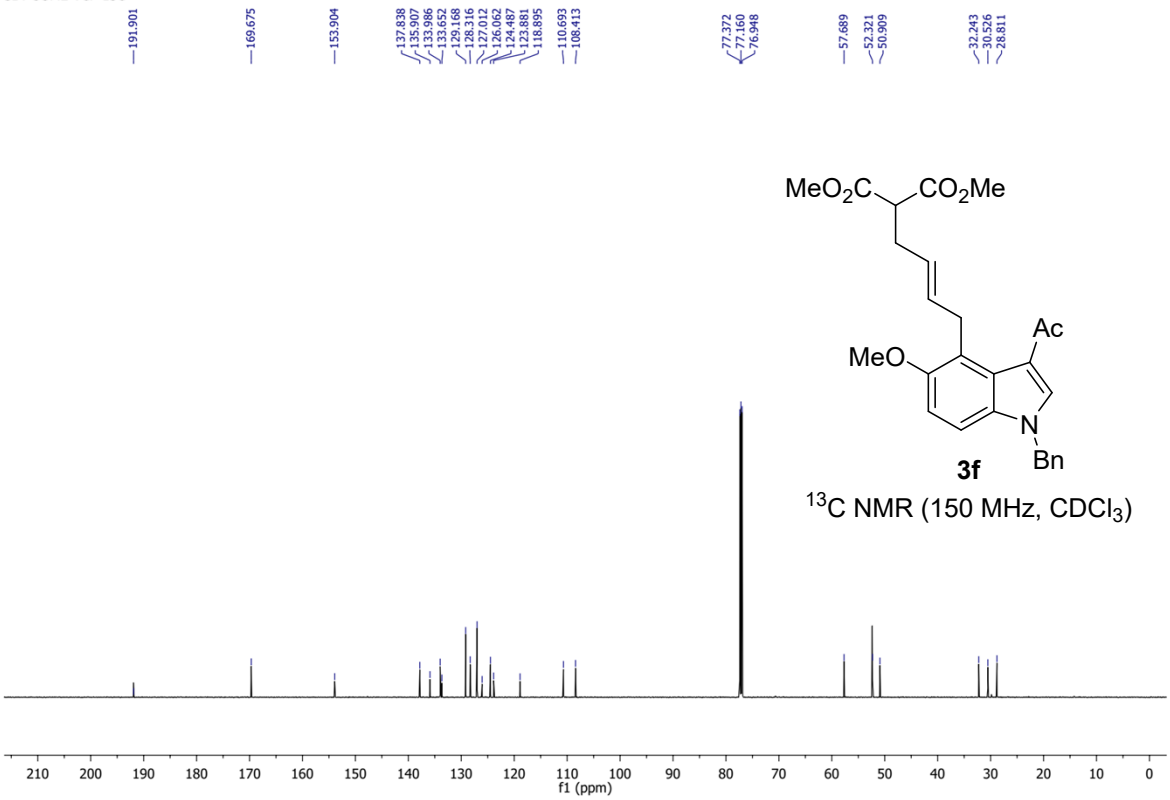
SBT-5OME-VCP-1H



3f

^{1}H NMR (600 MHz, $CDCl_3$)

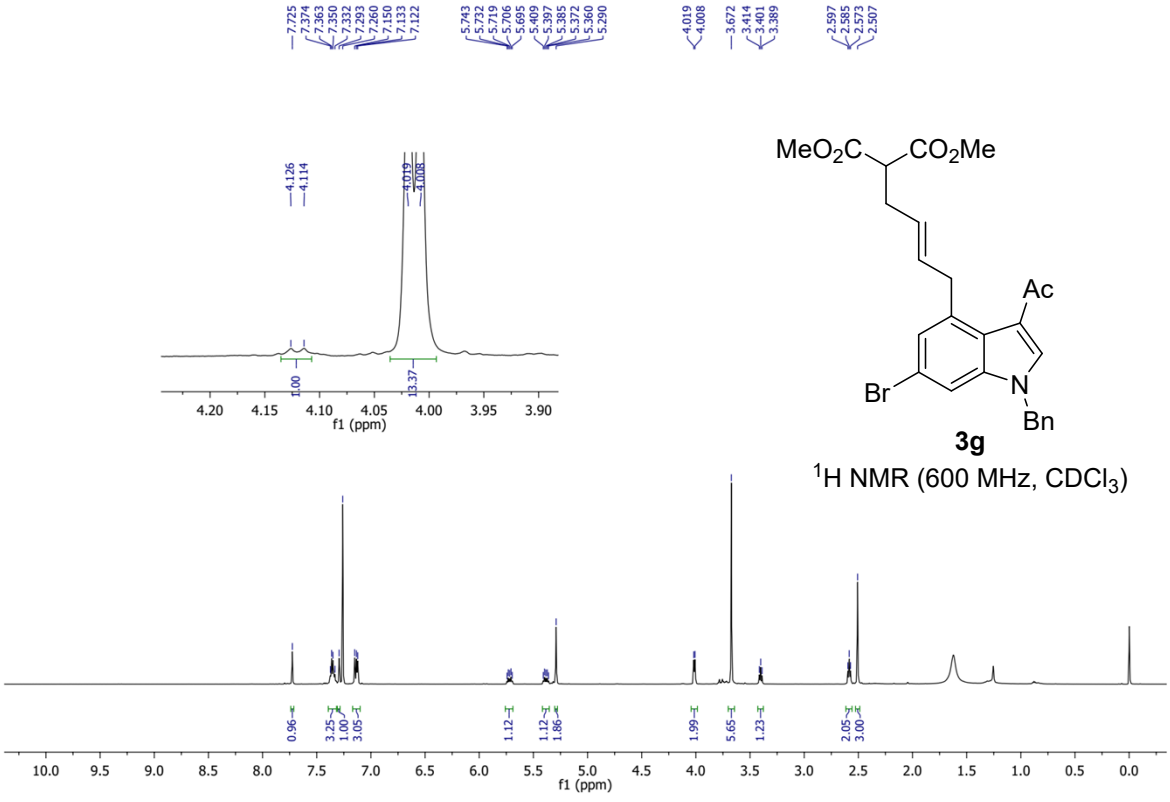
SBT-5OME-VCP-13C



3f

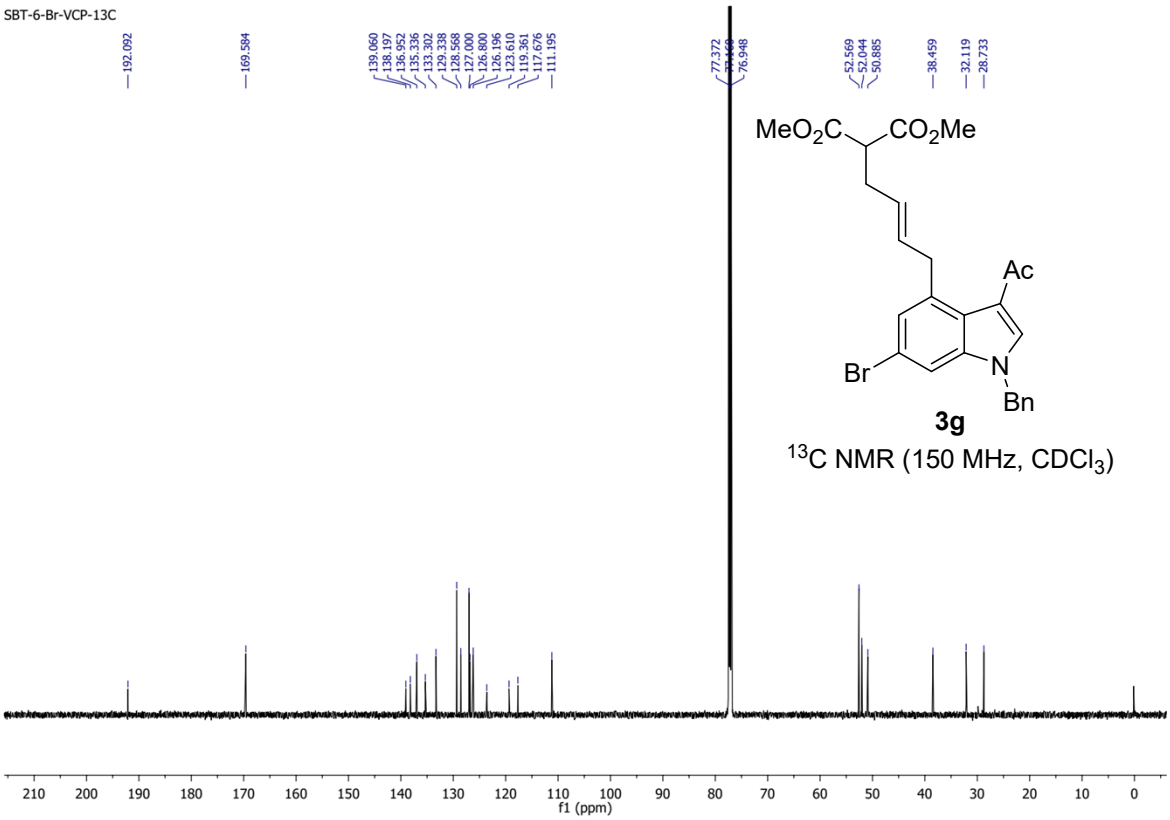
^{13}C NMR (150 MHz, $CDCl_3$)

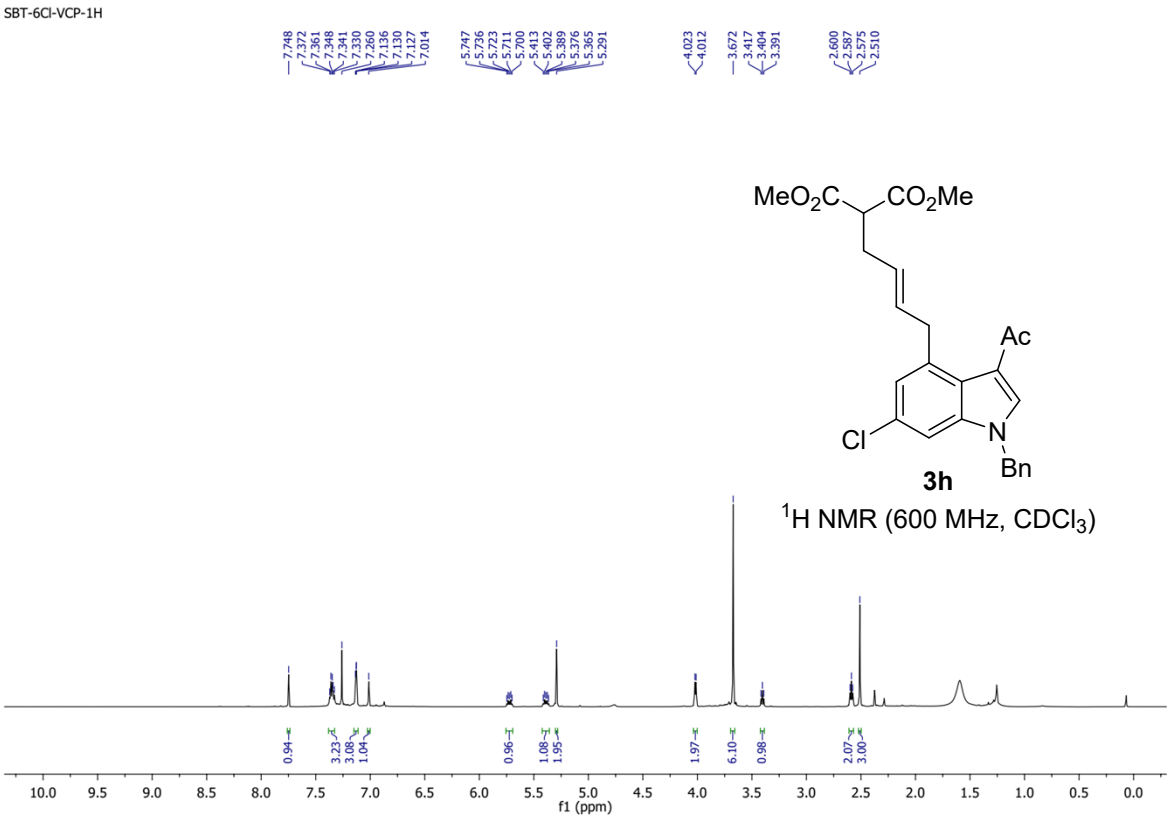
SBT-6-Br-VCP-1H

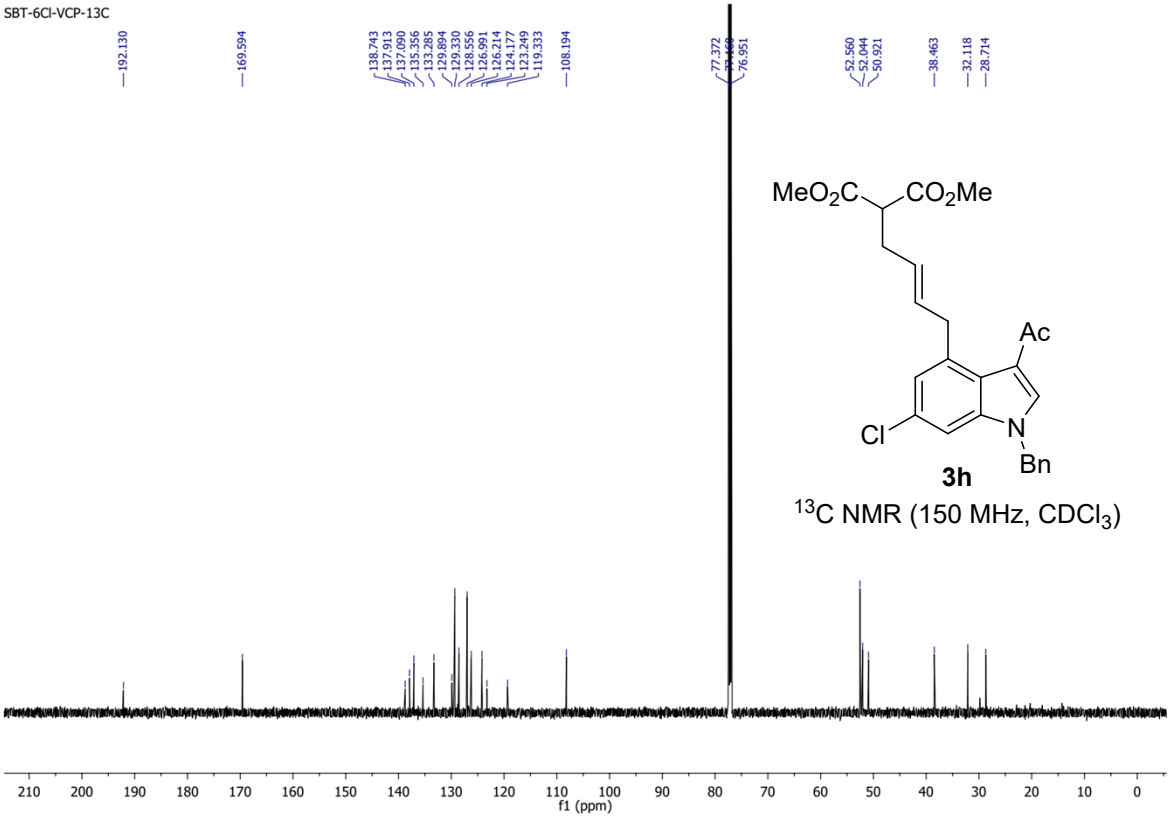


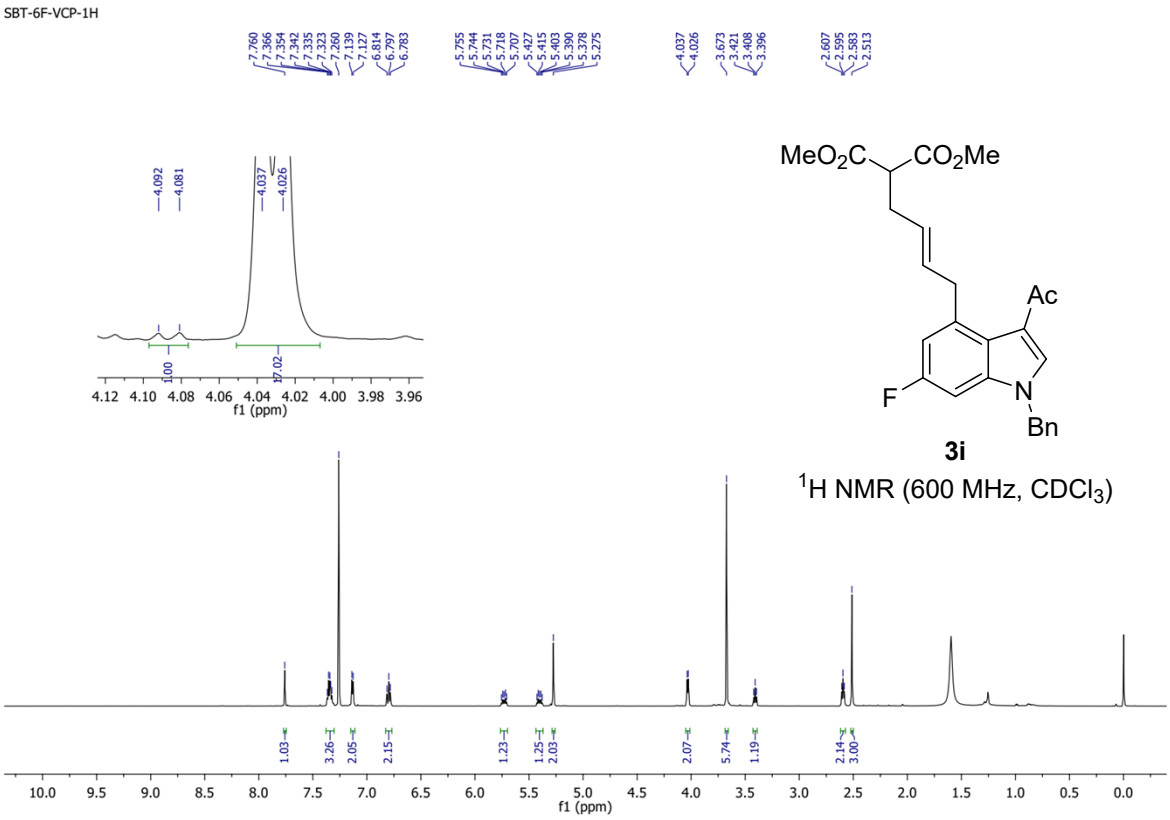
3g

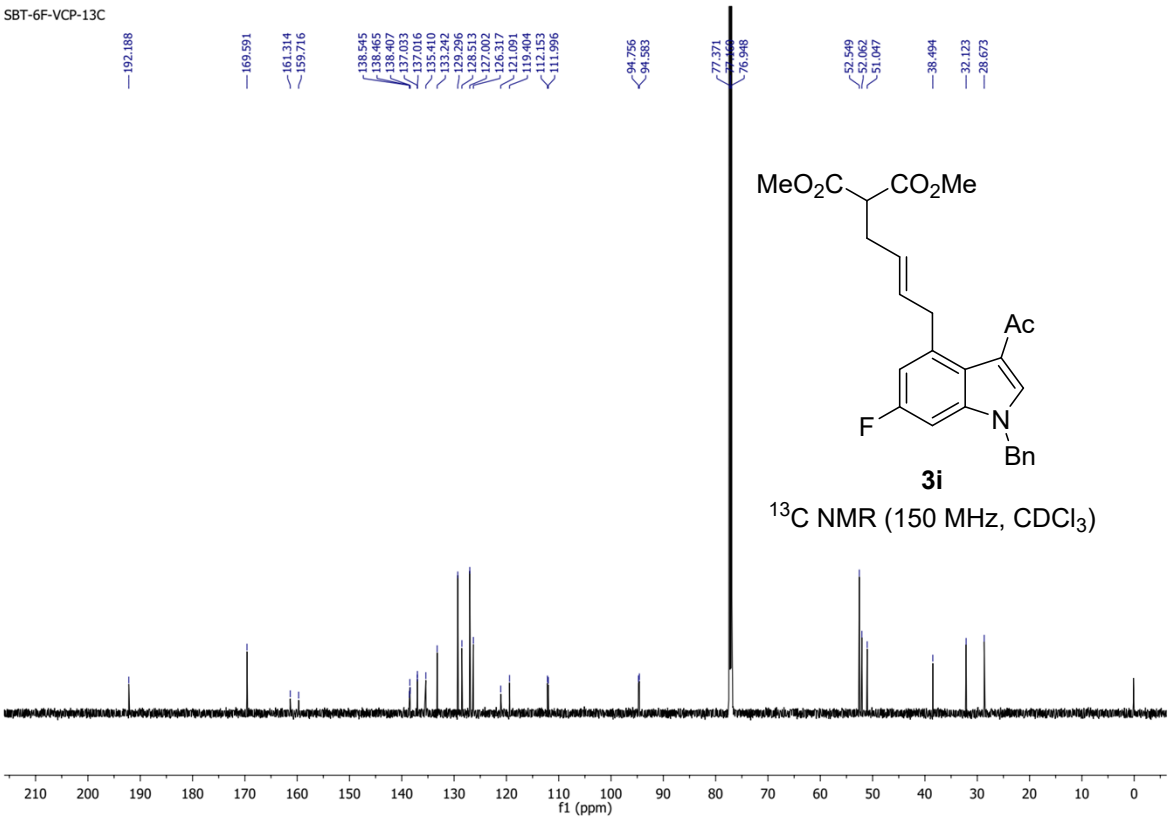
^{1}H NMR (600 MHz, $CDCl_3$)


SBT-6-Br-VCP-13C
192.092
169.584
139.060
138.197
136.952
135.336
133.302
129.338
128.568
127.000
126.800
126.196
123.610
119.361
117.676
111.195
77.372
77.046
76.948
52.569
52.044
50.885
38.459
32.119
28.733
MeO2C
CO2Me
Ac
Br
N
Bn
3g
13C NMR (150 MHz, CDCl3)
f1 (ppm)


SBT-6Cl-VCP-1H
7.748
7.372
7.361
7.348
7.341
7.330
7.260
7.136
7.130
7.127
7.014
5.747
5.736
5.723
5.711
5.700
5.413
5.402
5.389
5.376
5.365
5.291
4.023
4.012
3.672
3.417
3.404
3.391
2.600
2.587
2.575
2.510
MeO2C
CO2Me
Ac
Cl
N
Bn
3h
1H NMR (600 MHz, CDCl3)
0.94
3.23
3.08
1.04
0.96
1.08
1.95
1.97
6.10
0.98
2.07
3.00
f1 (ppm)

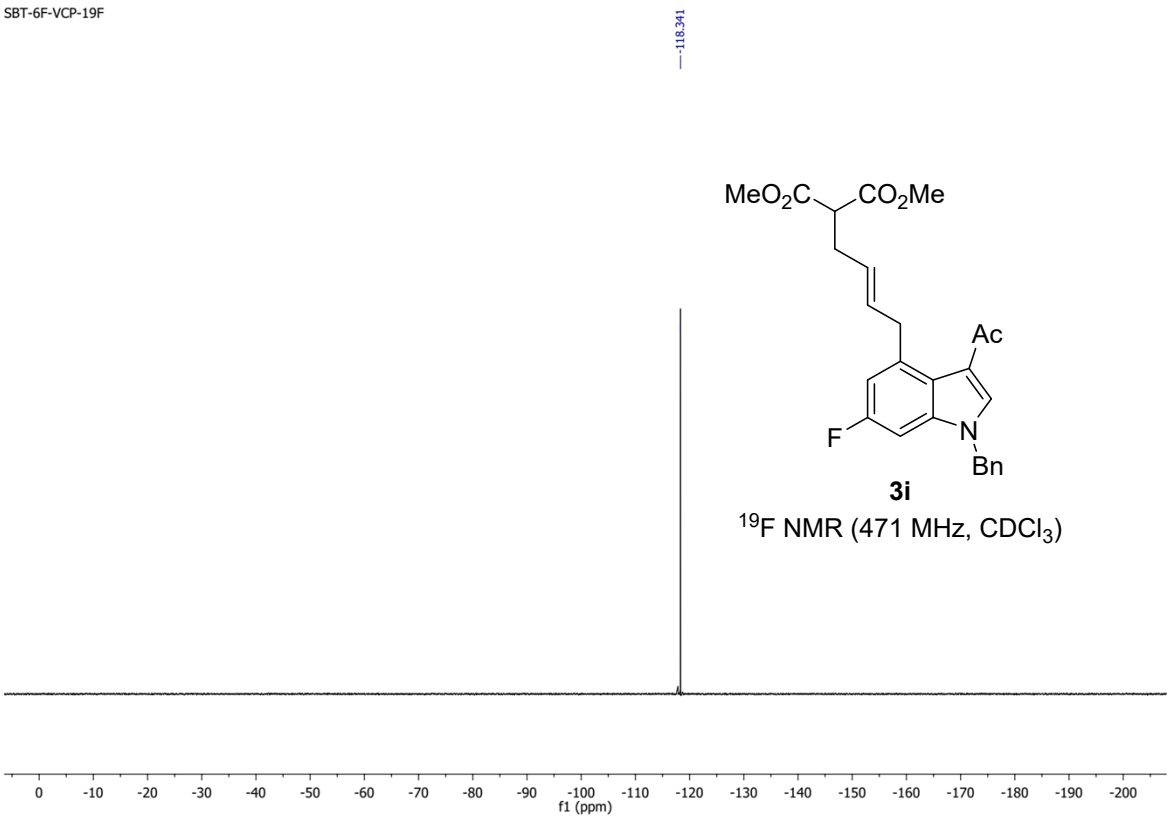

SBT-6Cl-VCP-13C
192.130
169.594
138.743
137.913
137.090
135.356
133.285
129.894
129.330
128.556
126.991
126.214
124.177
123.249
119.333
108.194
77.372
77.160
76.951
52.560
52.044
50.921
38.463
32.118
28.714
MeO2C
CO2Me
Ac
Cl
N
Bn
3h
13C NMR (150 MHz, CDCl3)
f1 (ppm)


SBT-6F-VCP-1H
7.760
7.366
7.354
7.342
7.335
7.323
7.260
7.139
7.127
6.814
6.797
6.783
5.755
5.744
5.731
5.718
5.707
5.427
5.415
5.403
5.390
5.378
5.275
4.037
4.026
3.673
3.421
3.408
3.396
2.607
2.595
2.583
2.513
4.092
4.081
4.037
4.026
1.00
17.02
f1 (ppm)
MeO2C
CO2Me
Ac
F
N
Bn
3i
1H NMR (600 MHz, CDCl3)
1.03
3.26
2.05
2.15
1.23
1.25
2.03
2.07
5.74
1.19
2.14
3.00
f1 (ppm)



3i

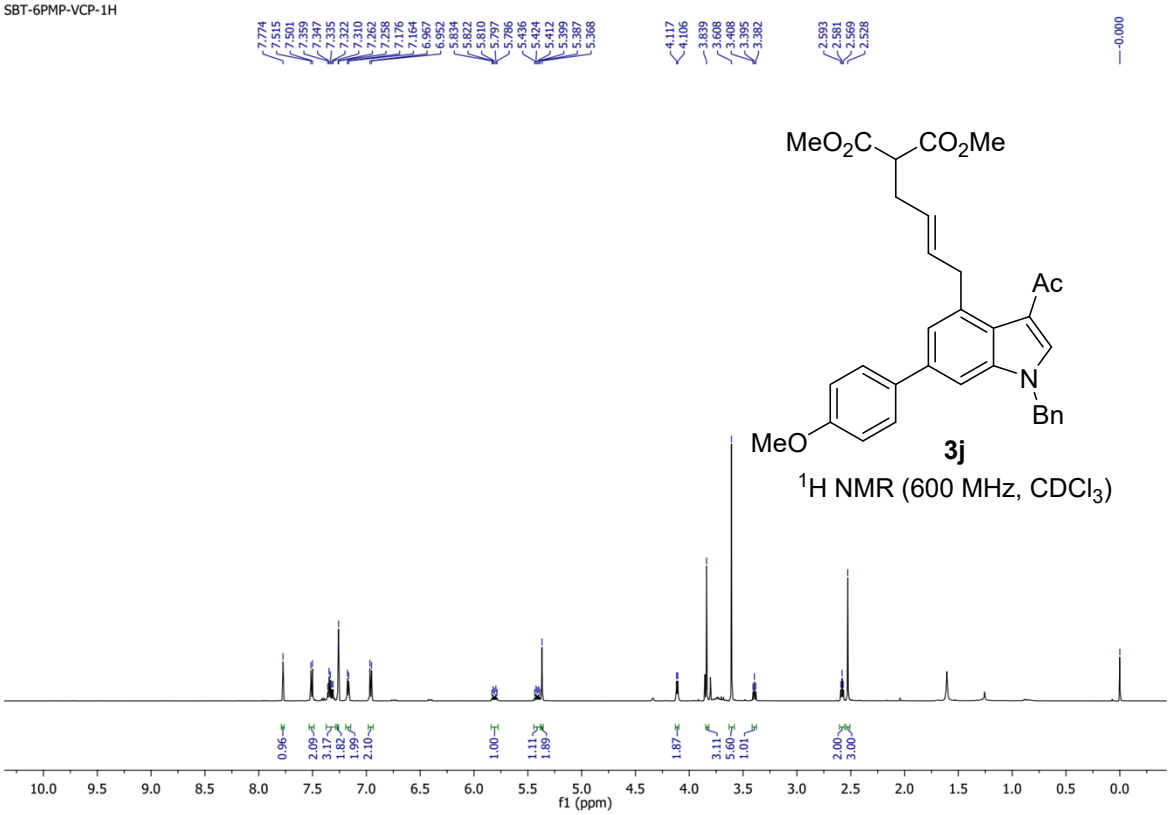
^{13}C NMR (150 MHz, $CDCl_3$)



3i

^{19}F NMR (471 MHz, $CDCl_3$)

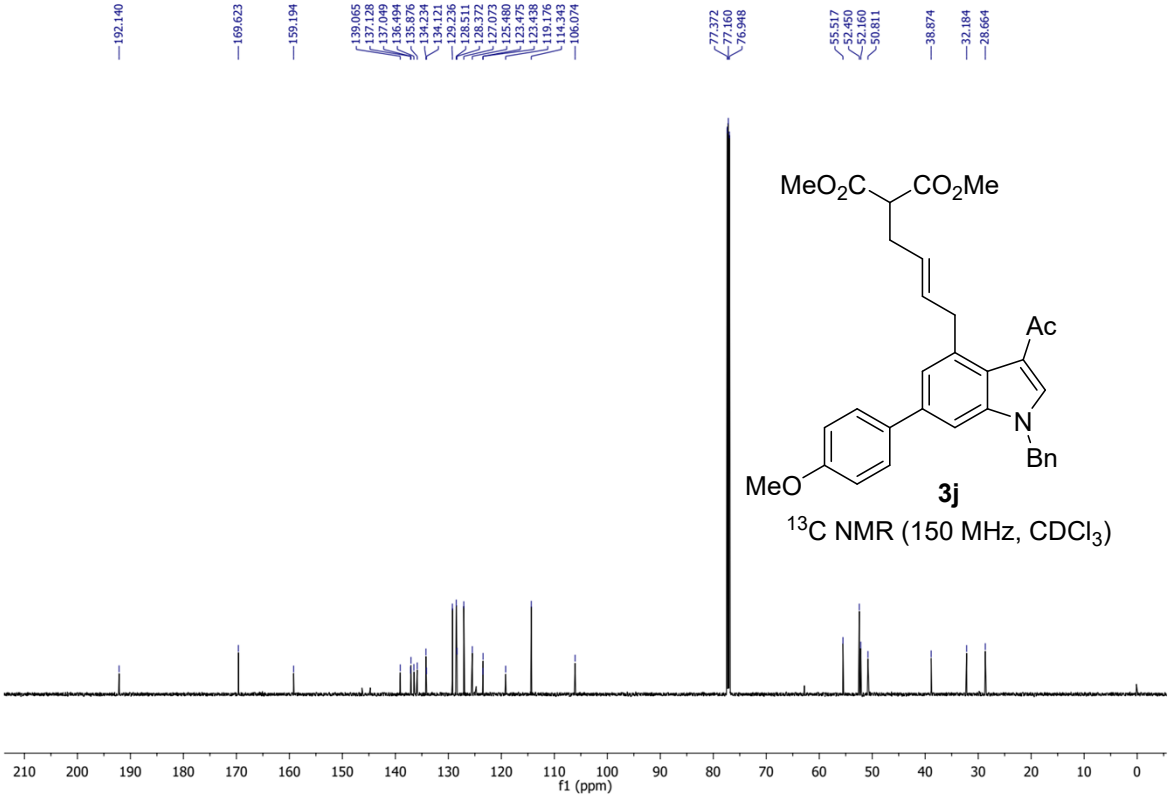
SBT-6PMP-VCP-1H



3j

^{1}H NMR (600 MHz, $CDCl_3$)

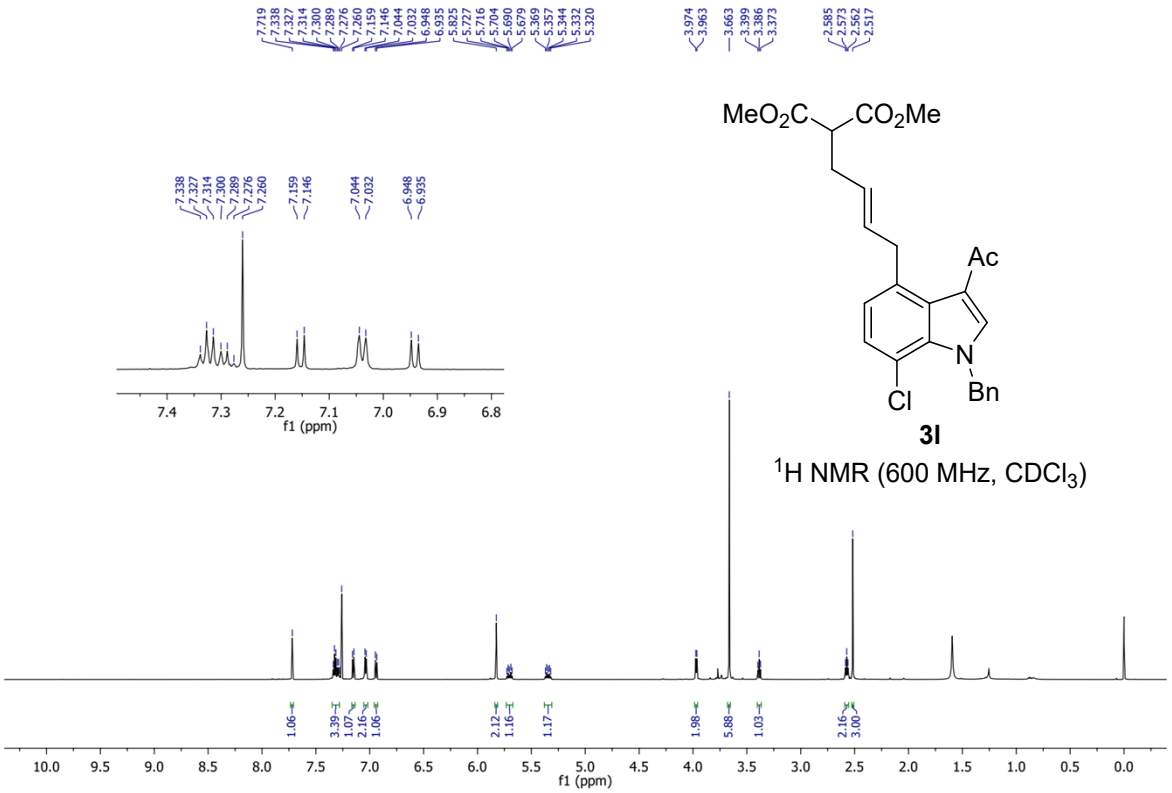
SBT-6PMP-VCP-13C



3j

^{13}C NMR (150 MHz, $CDCl_3$)

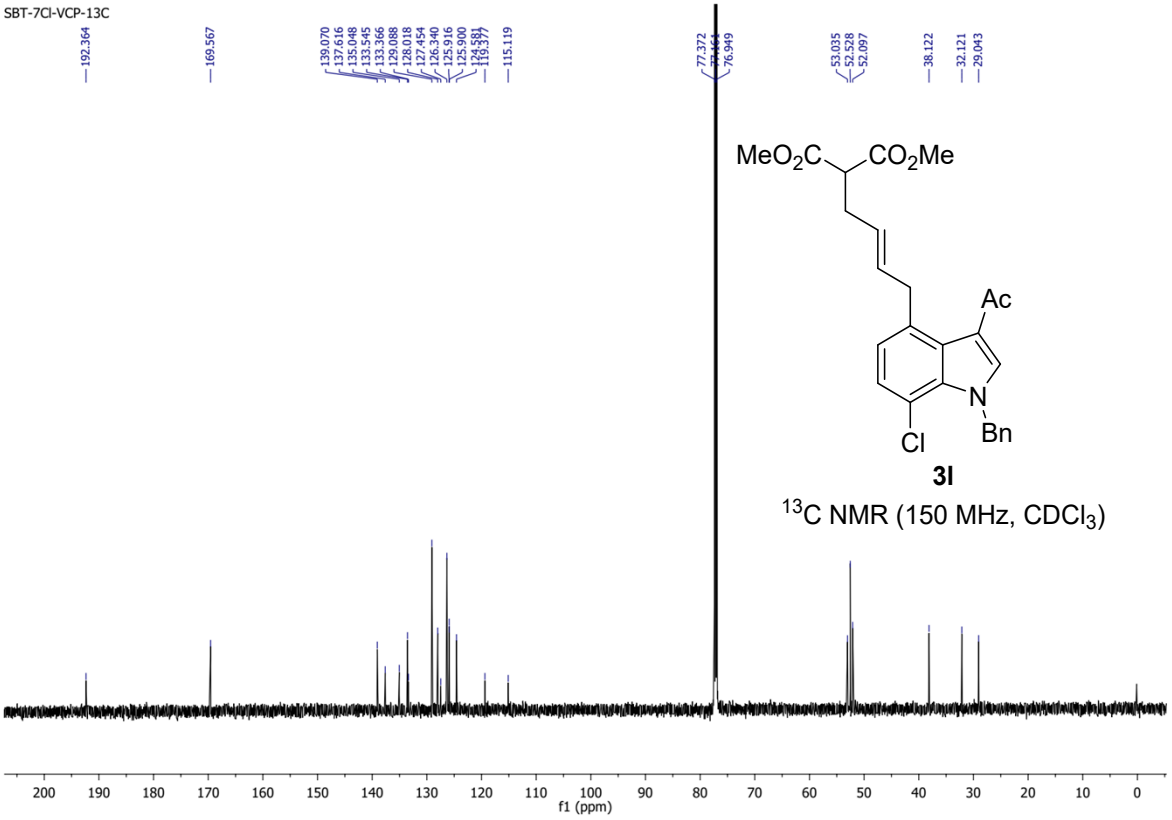
SBT-7Cl-VCP-1H



3l

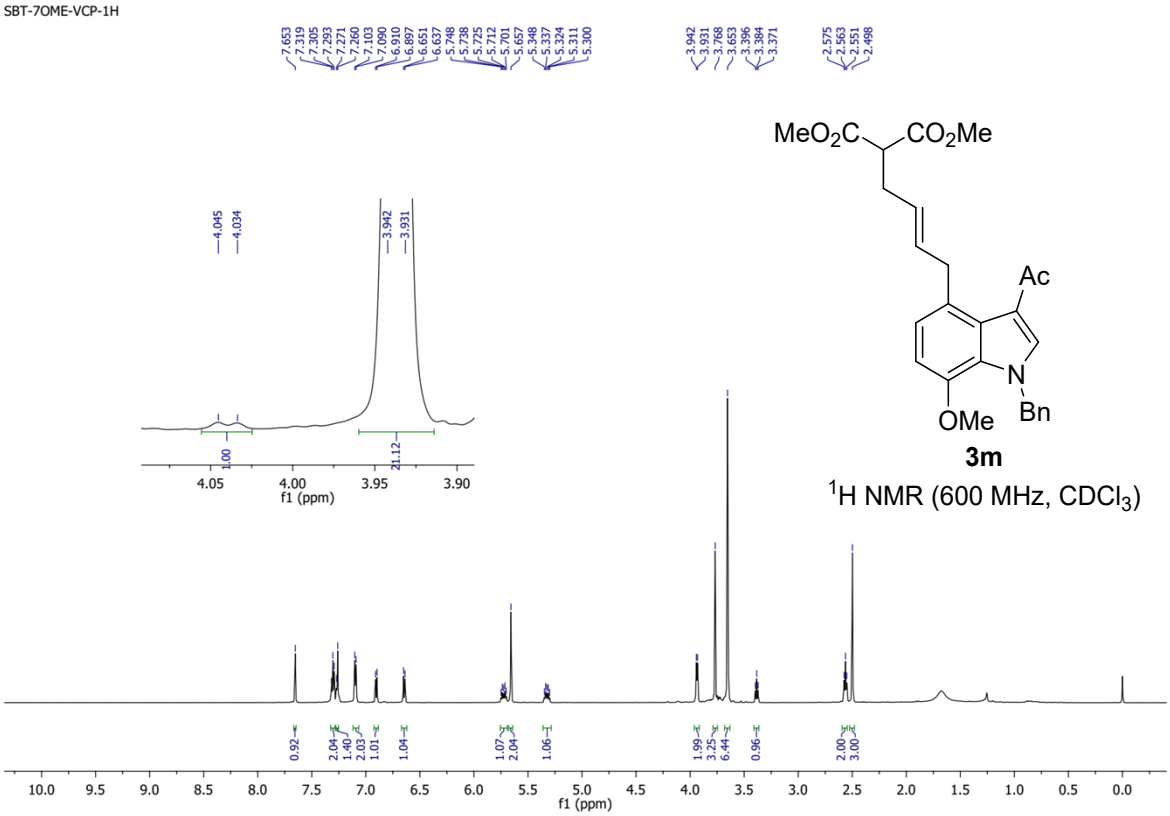
^{1}H NMR (600 MHz, $CDCl_3$)

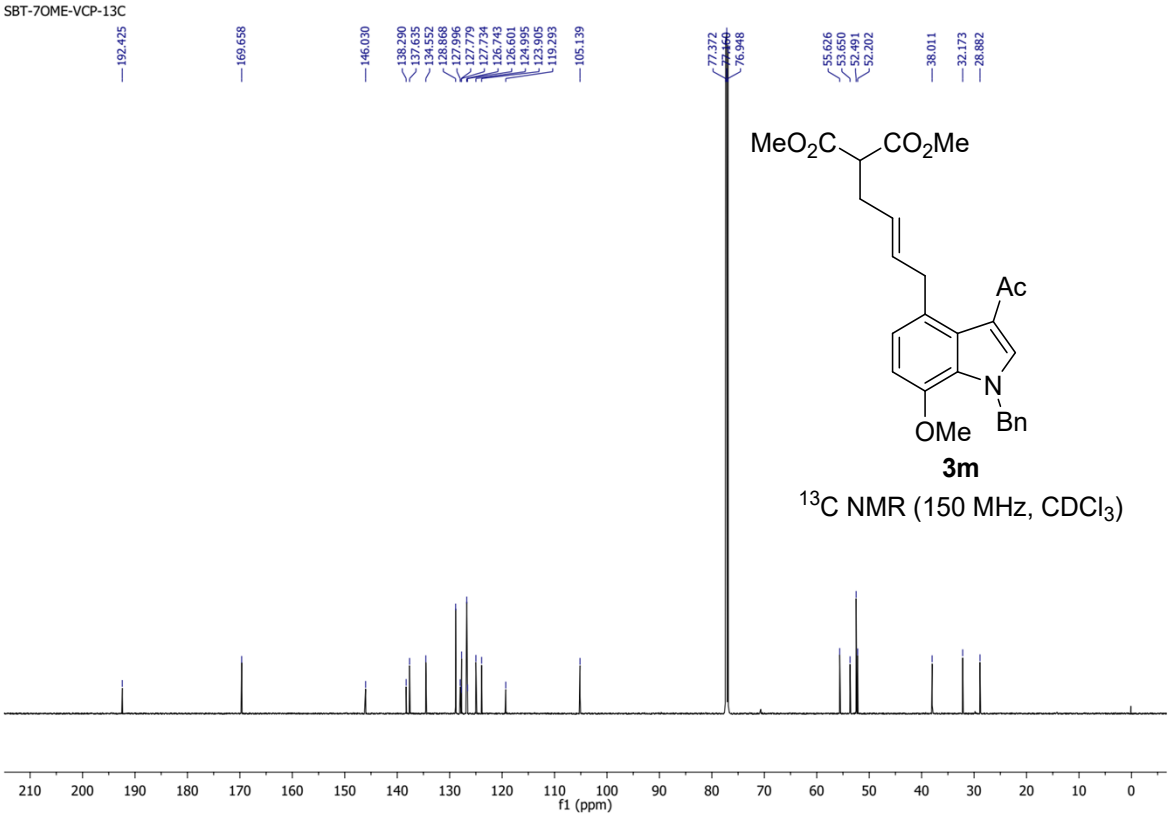
SBT-7Cl-VCP-13C



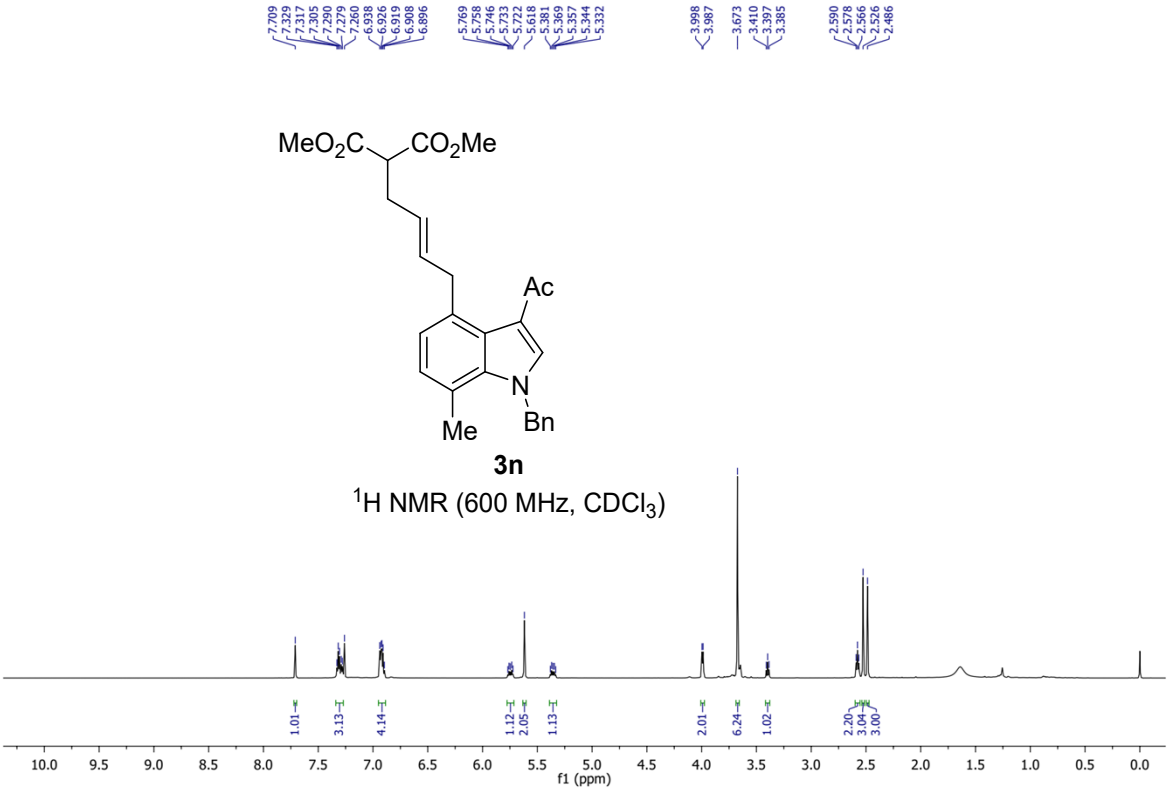
3l

^{13}C NMR (150 MHz, $CDCl_3$)


SBT-7OME-VCP-1H
MeO2C
CO2Me
Ac
N
Bn
OMe
3m
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-7OME-VCP-13C
MeO2C
CO2Me
Ac
N
Bn
OMe
3m
13C NMR (150 MHz, CDCl3)
f1 (ppm)

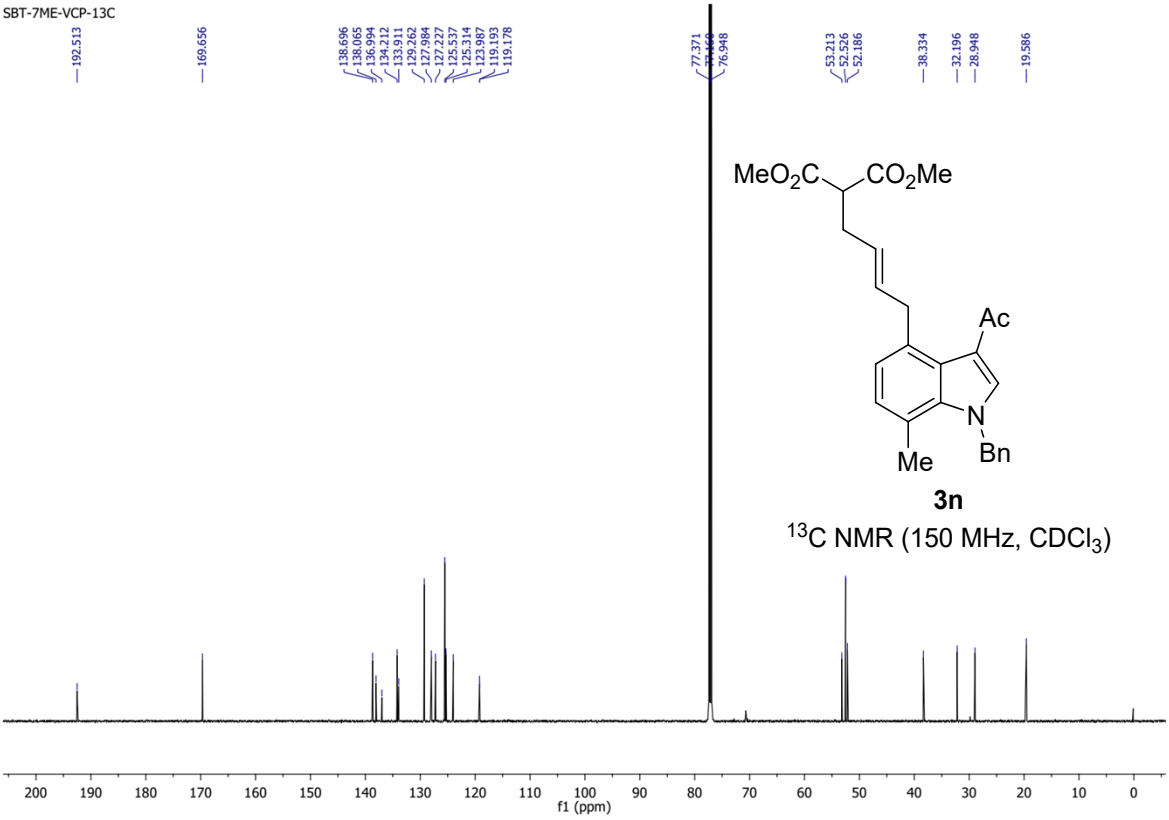
SBT-7ME-VCP-1H



3n

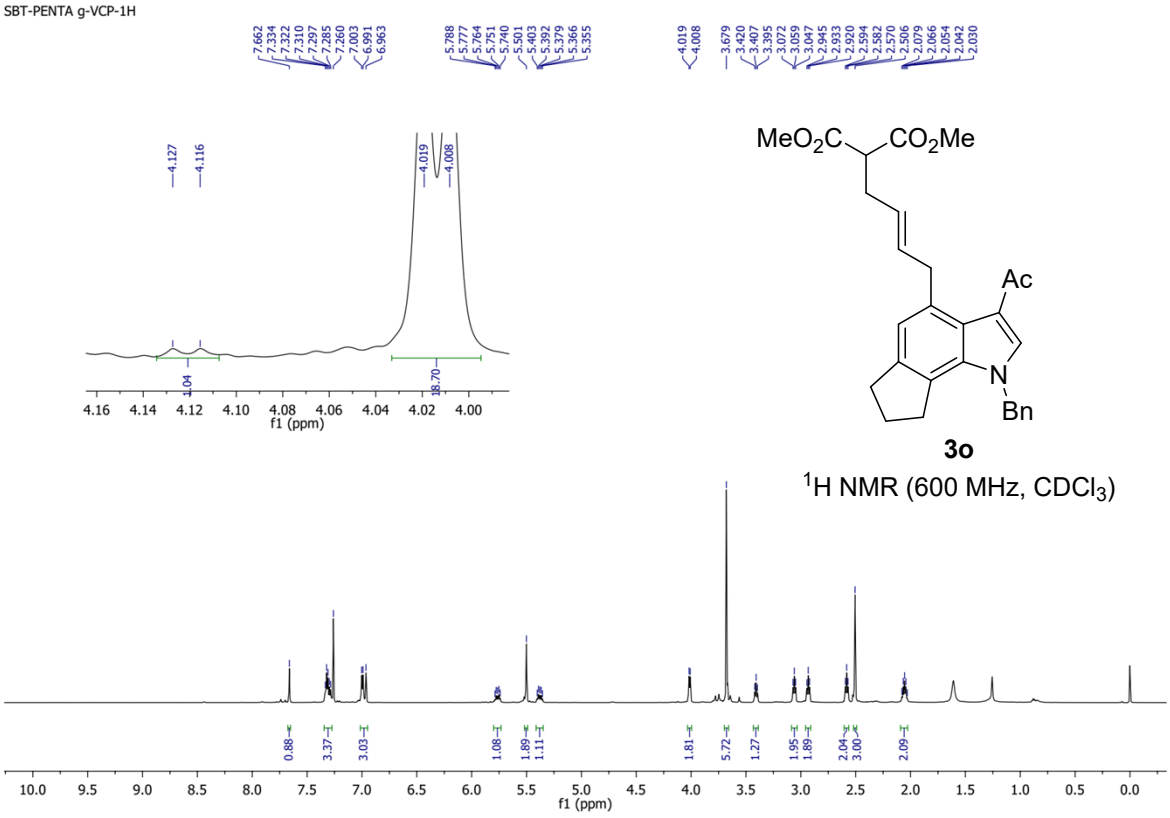
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-7ME-VCP-13C



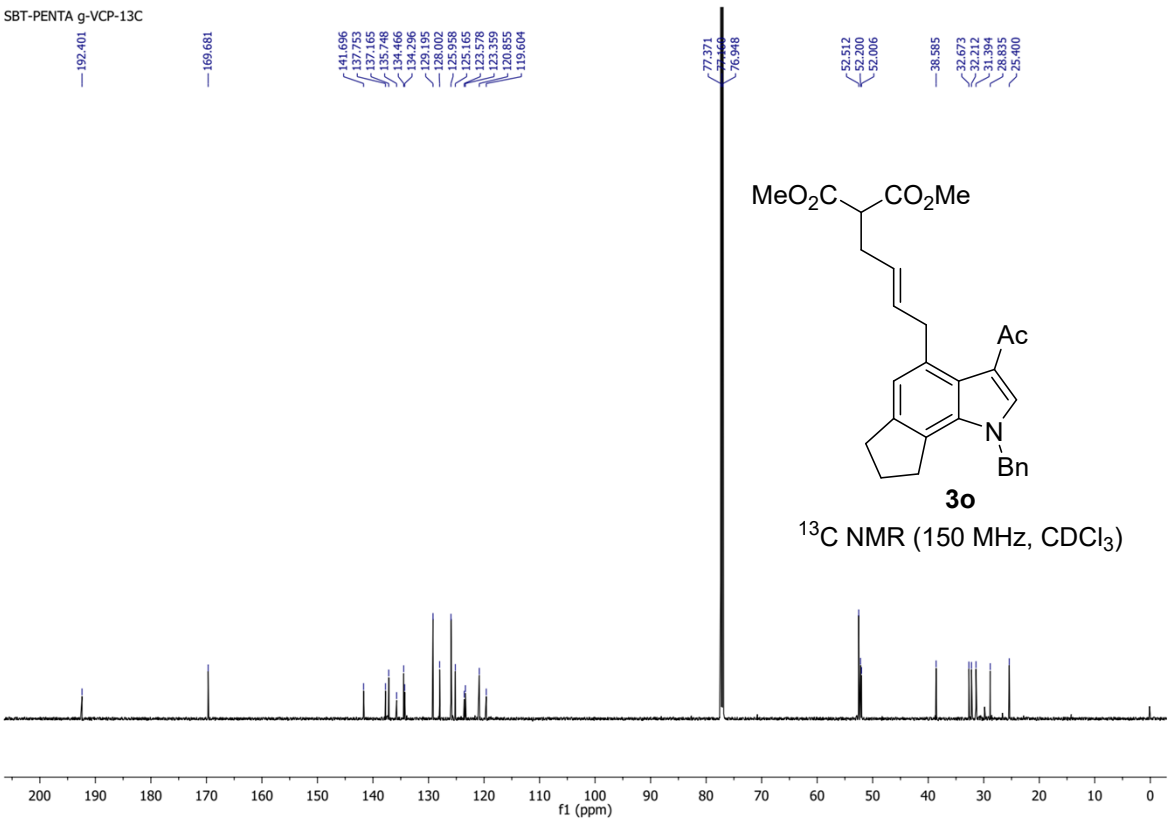
3n

^{13}C NMR (150 MHz, $CDCl_3$)



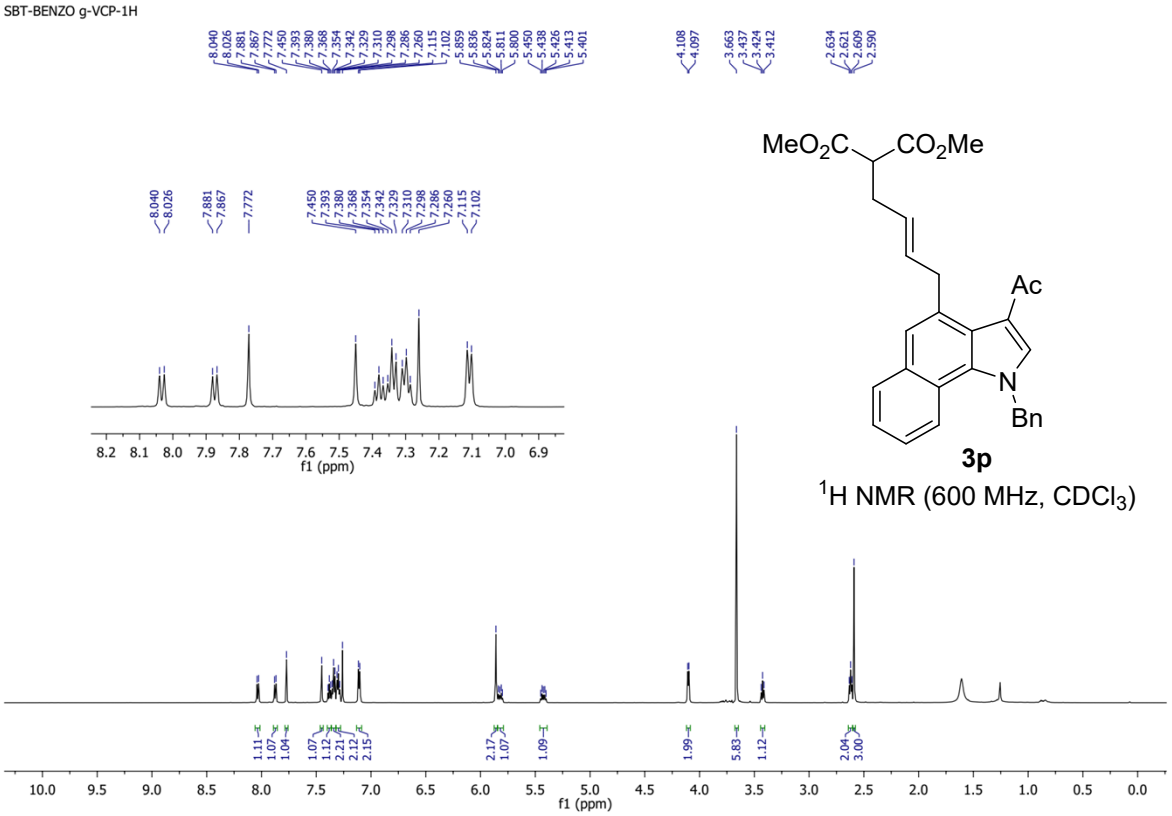
3o

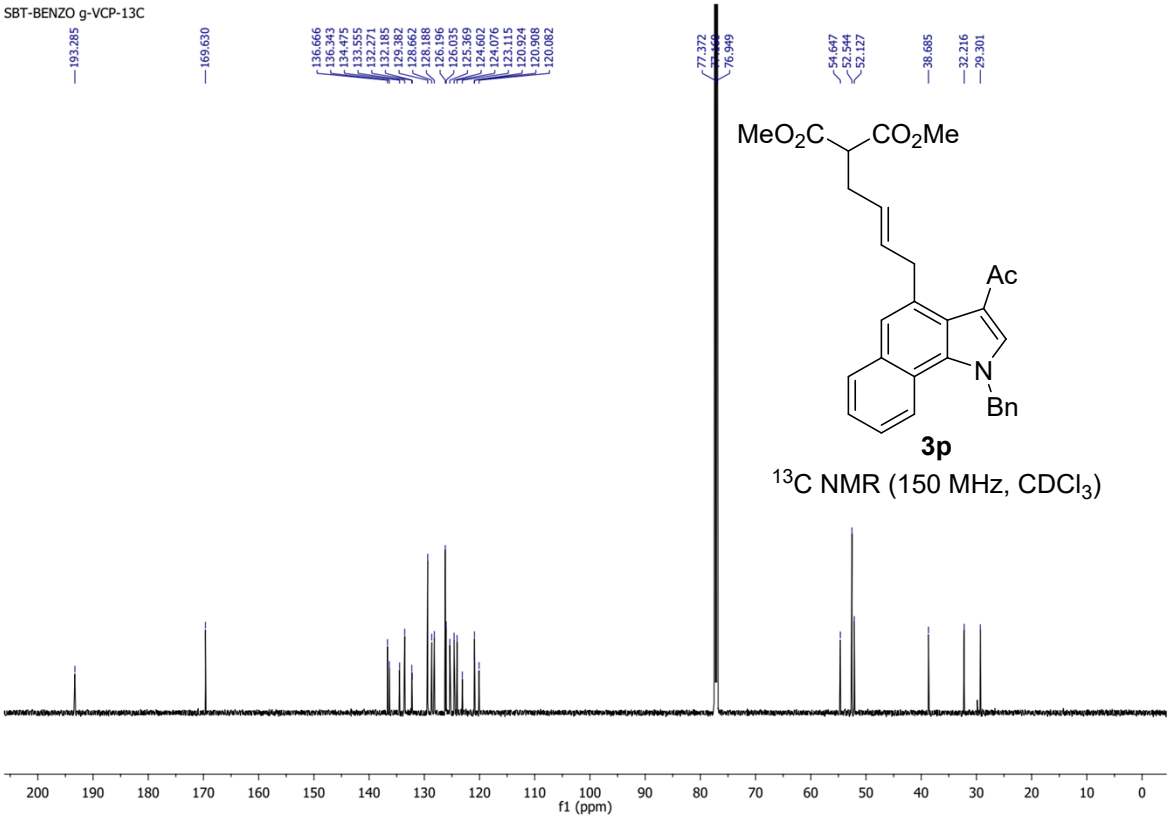
^{1}H NMR (600 MHz, $CDCl_3$)

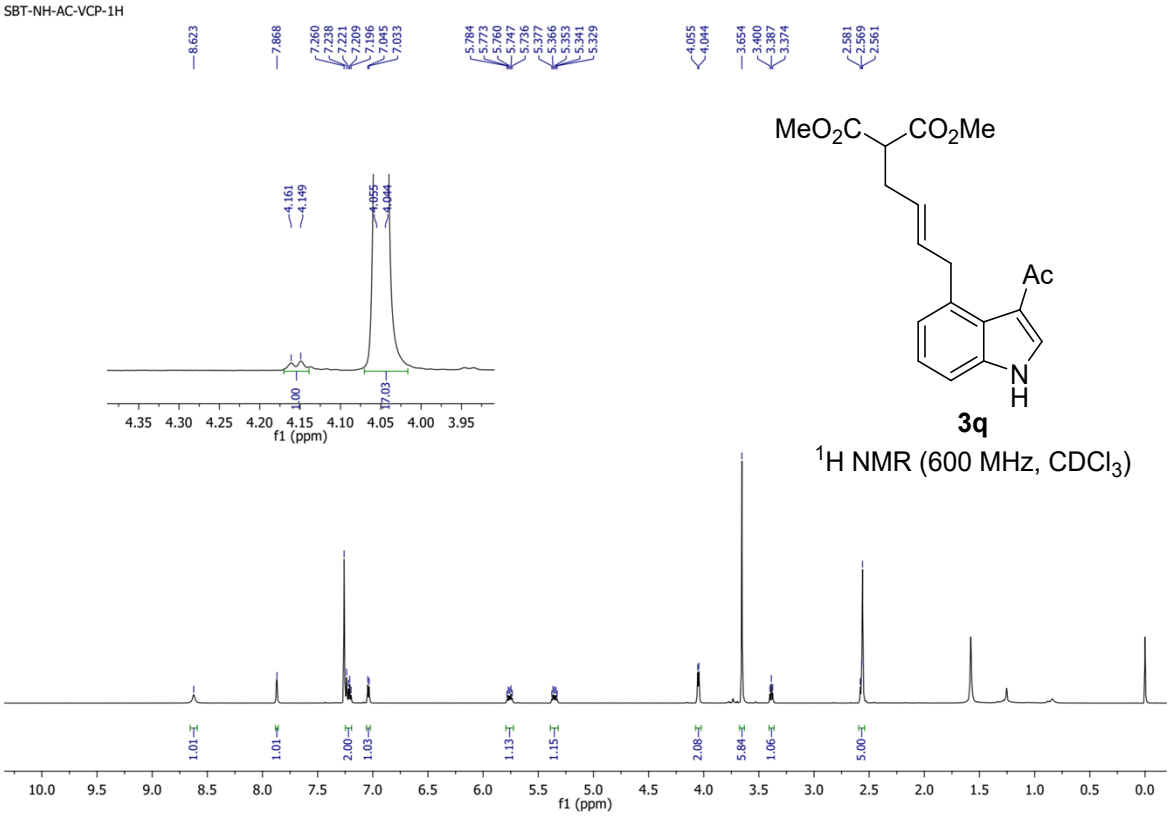


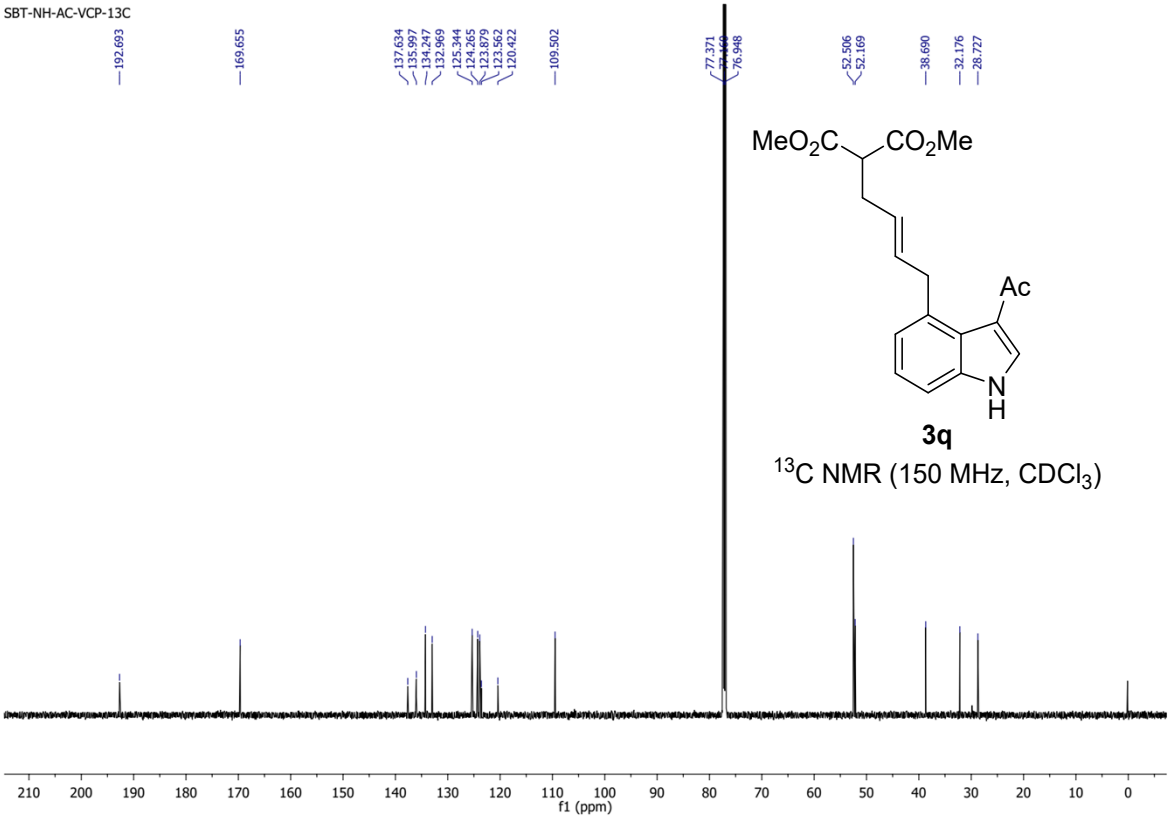
3o

^{13}C NMR (150 MHz, $CDCl_3$)

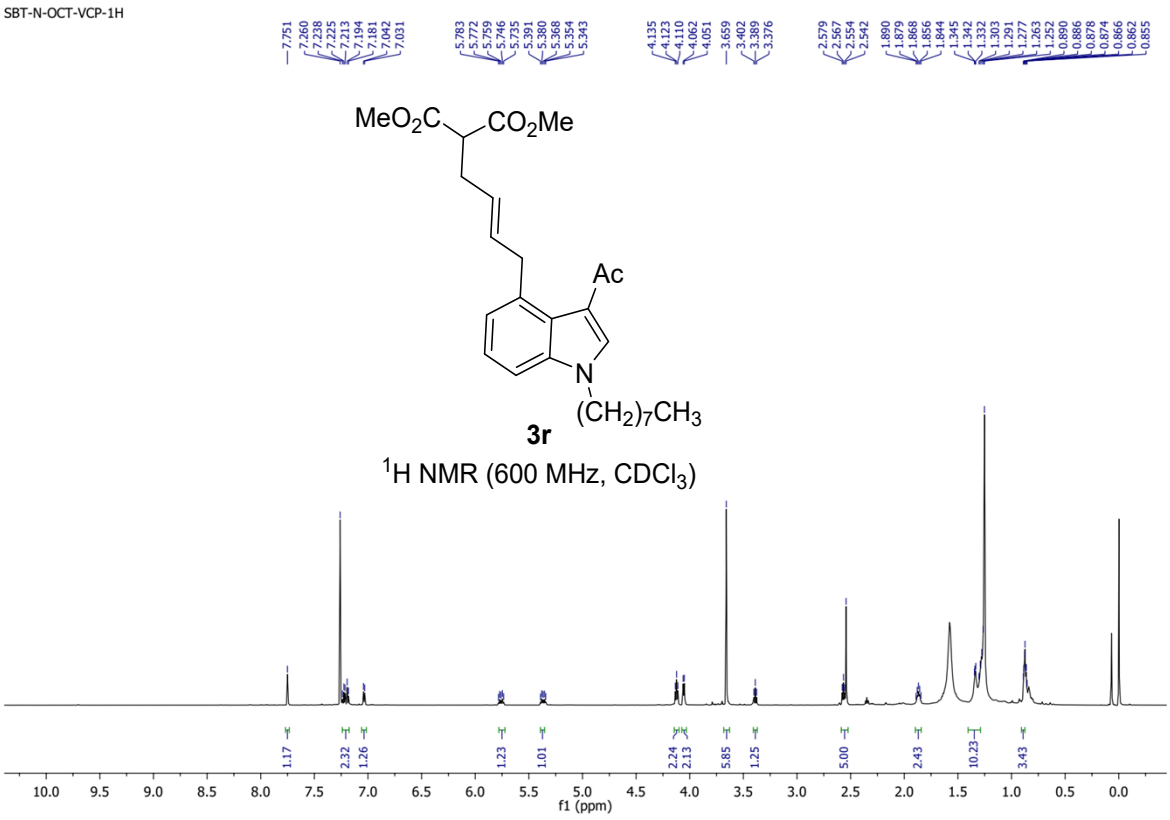

SBT-BENZO g-VCP-1H
MeO2C
CO2Me
Ac
N
Bn
3p
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-BENZO g-VCP-13C
MeO2C
CO2Me
Ac
N
Bn
3p
13C NMR (150 MHz, CDCl3)
f1 (ppm)

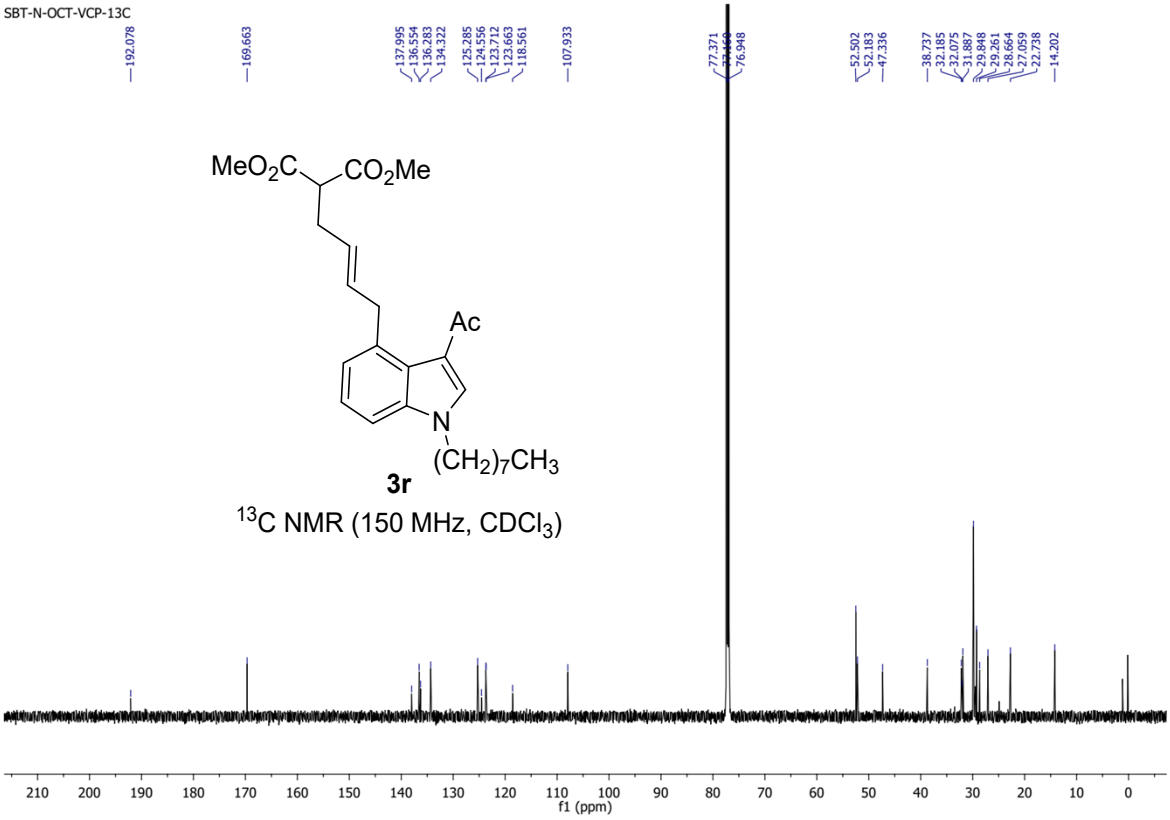

SBT-NH-AC-VCP-1H
8.623
7.868
7.260
7.238
7.221
7.209
7.196
7.045
7.033
5.784
5.773
5.760
5.747
5.736
5.377
5.366
5.353
5.341
5.329
4.055
4.044
3.654
3.400
3.387
3.374
2.581
2.569
2.561
4.161
4.149
4.055
4.044
1.00
17.03
4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95
f1 (ppm)
MeO2C
CO2Me
Ac
N
H
3q
1H NMR (600 MHz, CDCl3)
1.01
1.01
2.00
1.03
1.13
1.15
2.08
5.84
1.06
5.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

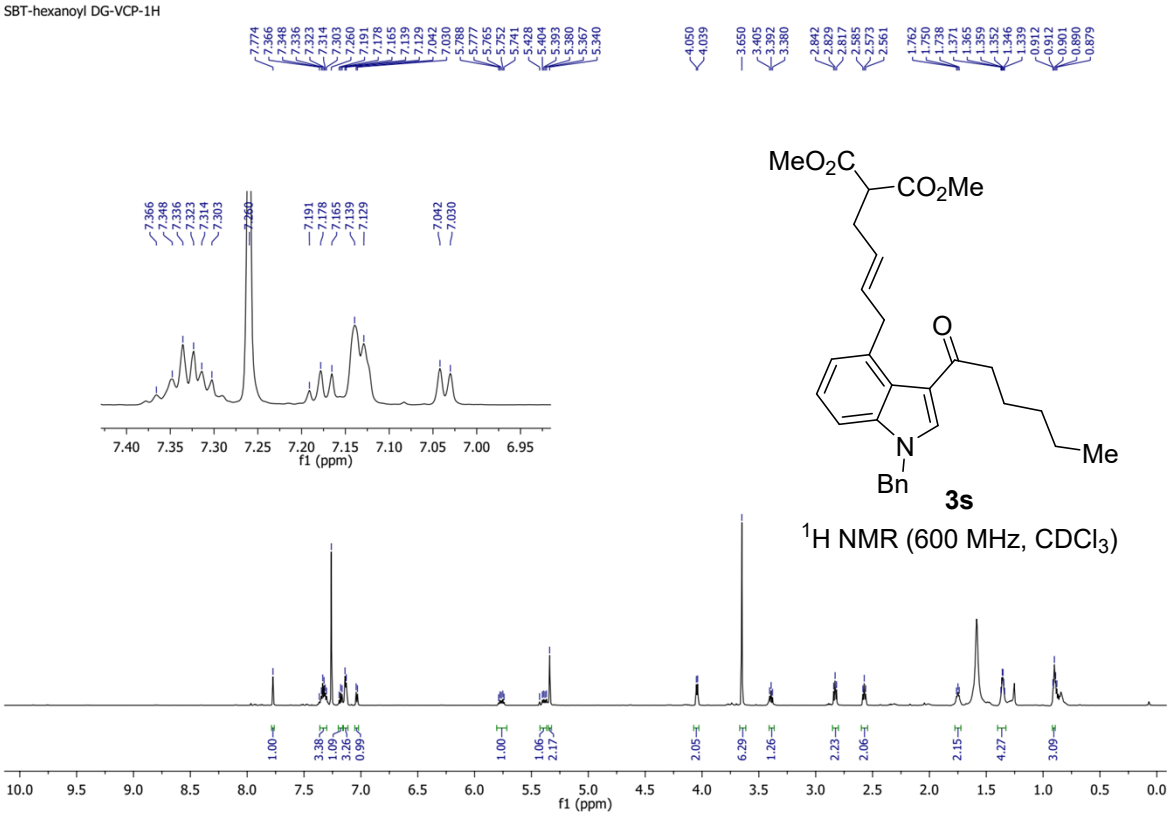

SBT-NH-AC-VCP-13C
192.693
169.655
137.634
135.997
134.247
132.969
125.344
124.265
123.879
123.562
120.422
109.502
77.371
77.169
76.948
52.506
52.169
38.690
32.176
28.727
MeO2C
CO2Me
Ac
N
H
3q
13C NMR (150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

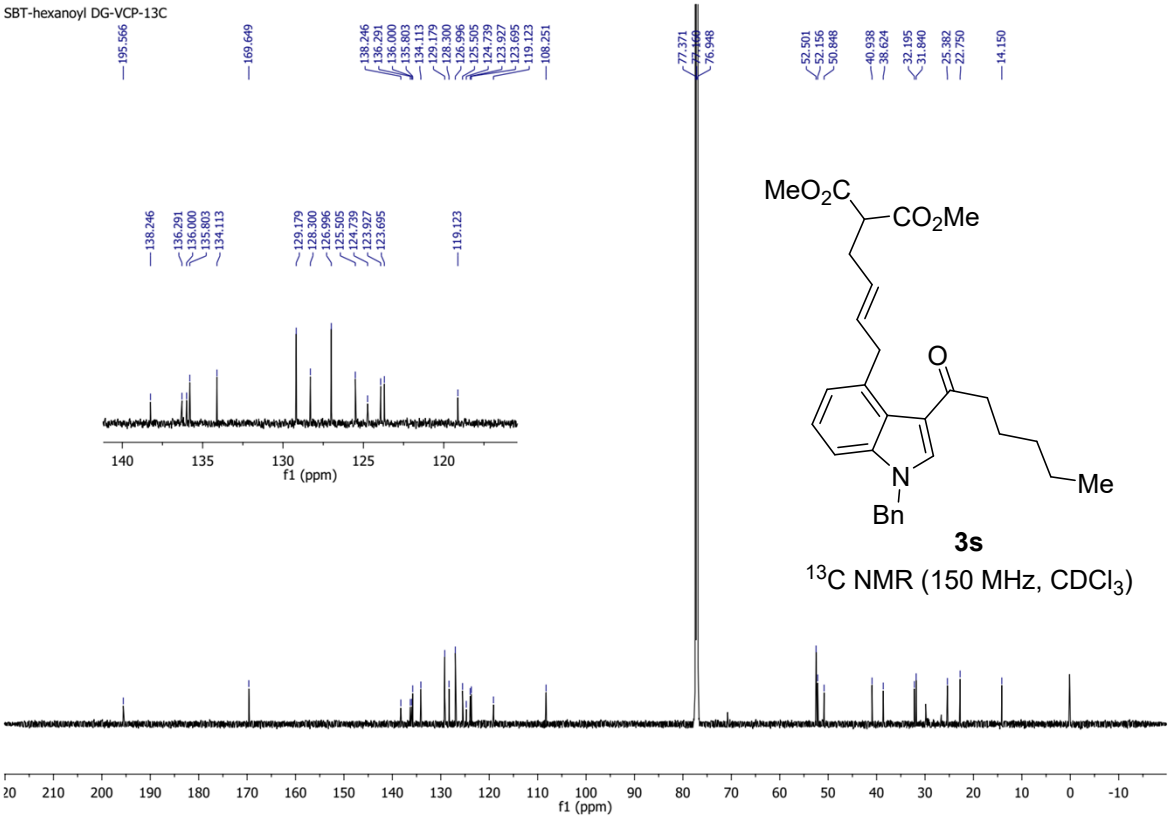
SBT-N-OCT-VCP-1H

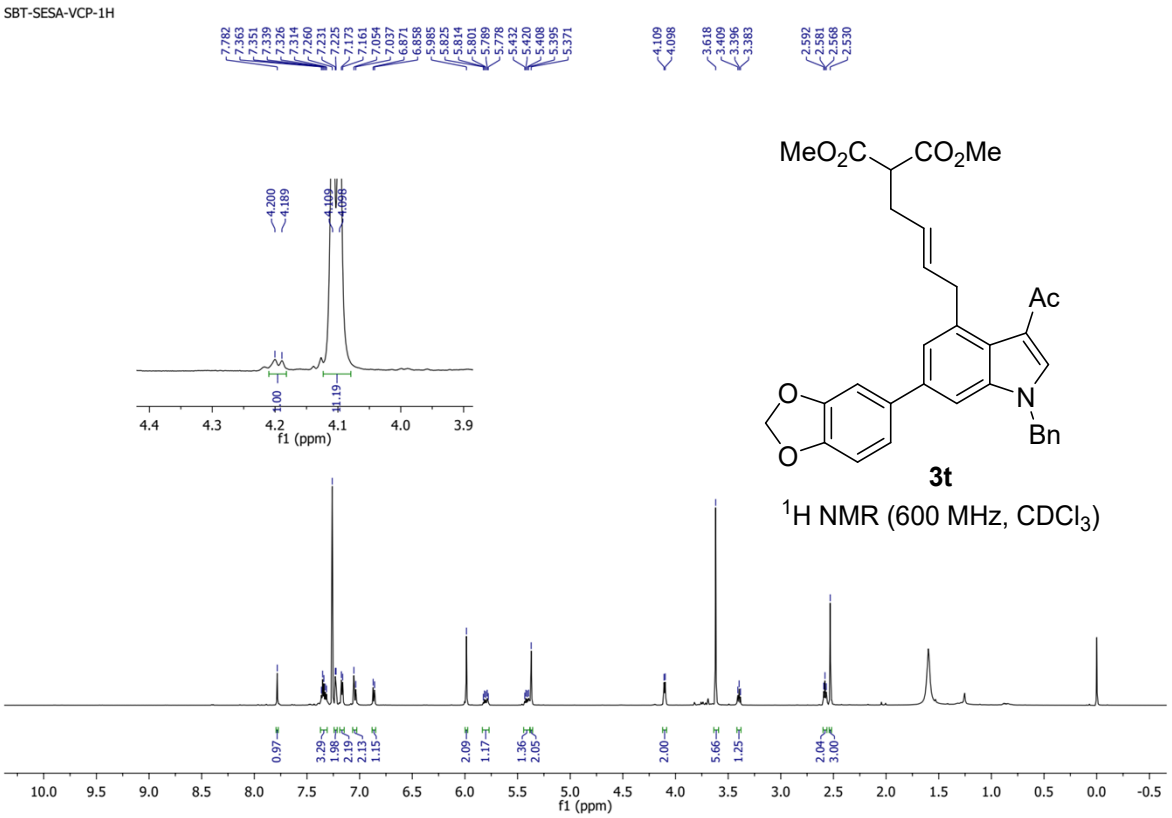


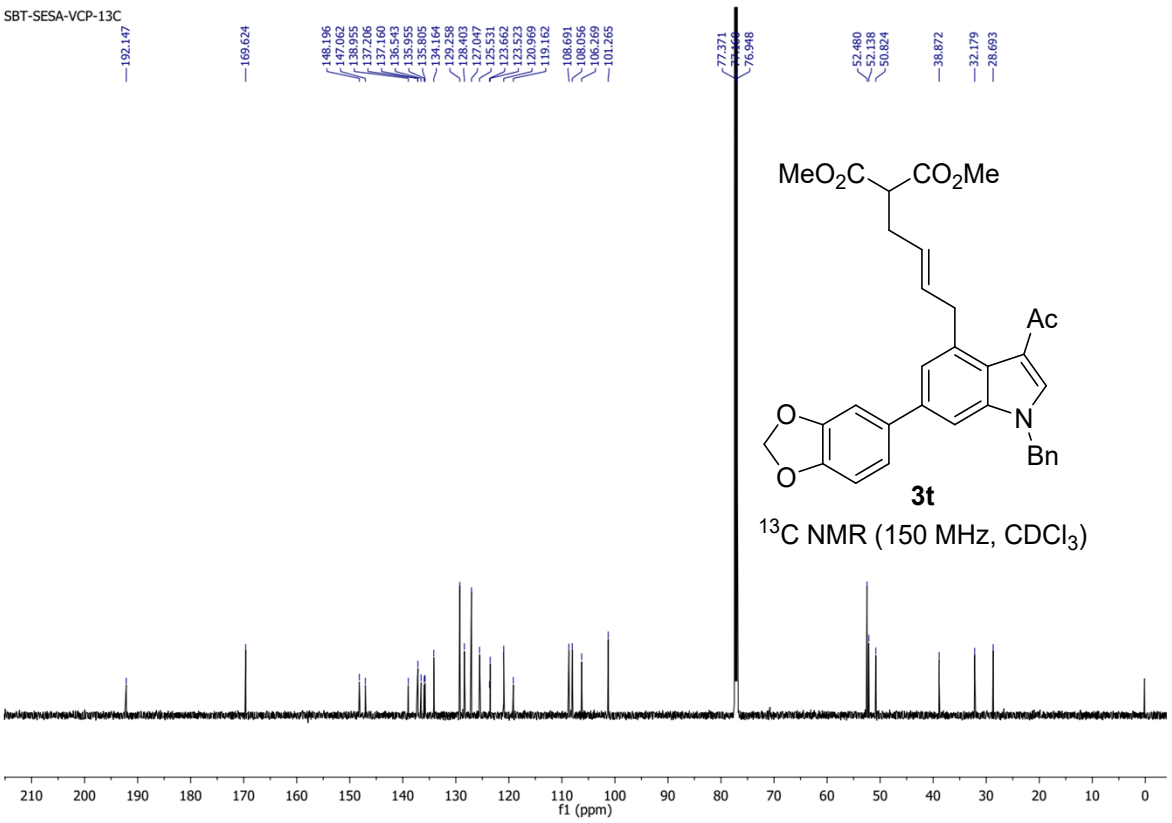
SBT-N-OCT-VCP-13C



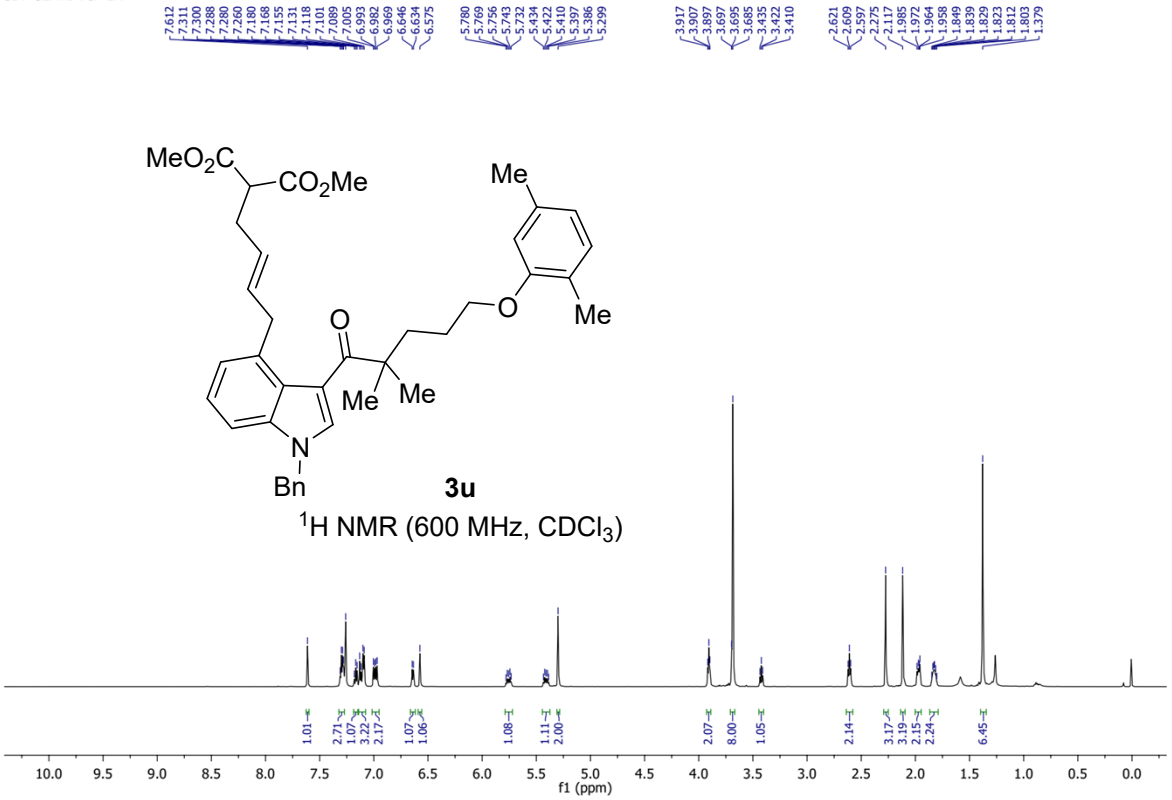

SBT-hexanoyl DG-VCP-1H
MeO2C
CO2Me
O
N
Bn
Me
3s
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-hexanoyl DG-VCP-13C
MeO2C
CO2Me
O
N
Bn
Me
3s
13C NMR (150 MHz, CDCl3)
f1 (ppm)

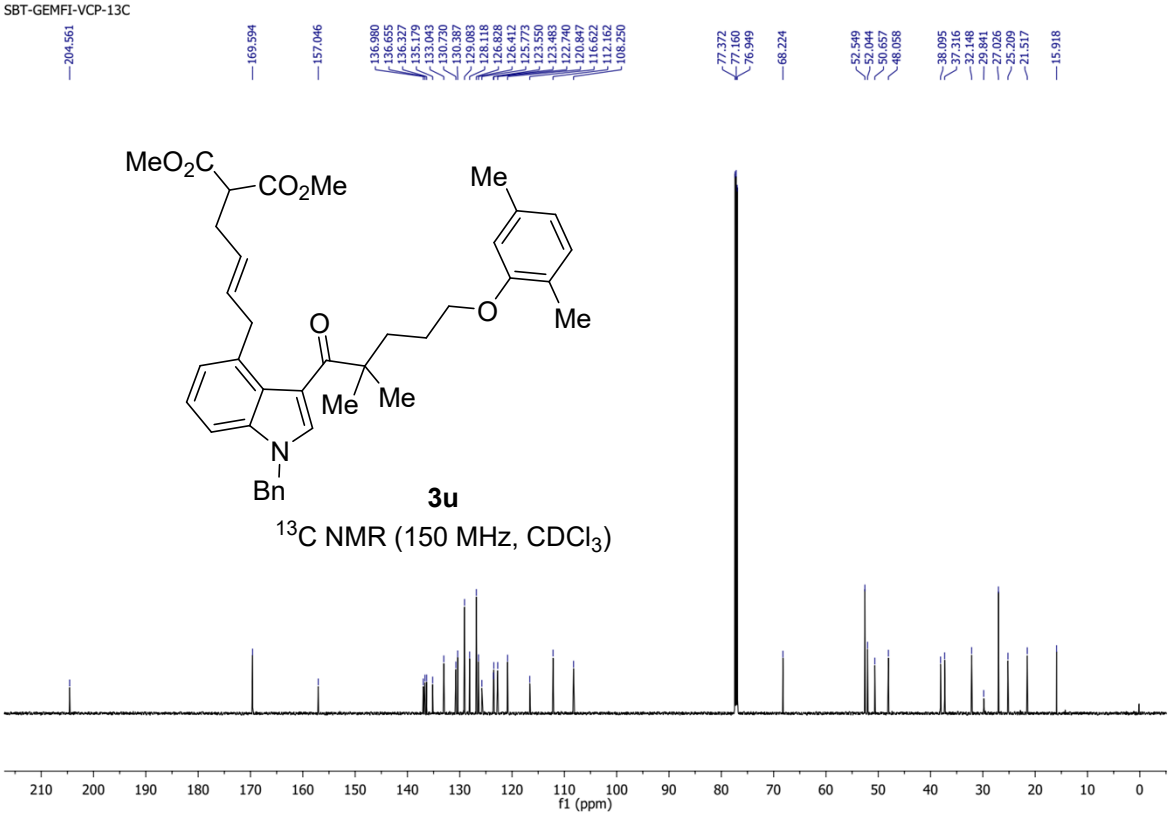

SBT-SESA-VCP-1H
MeO2C
CO2Me
Ac
N
Bn
O
O
3t
1H NMR (600 MHz, CDCl3)
f1 (ppm)

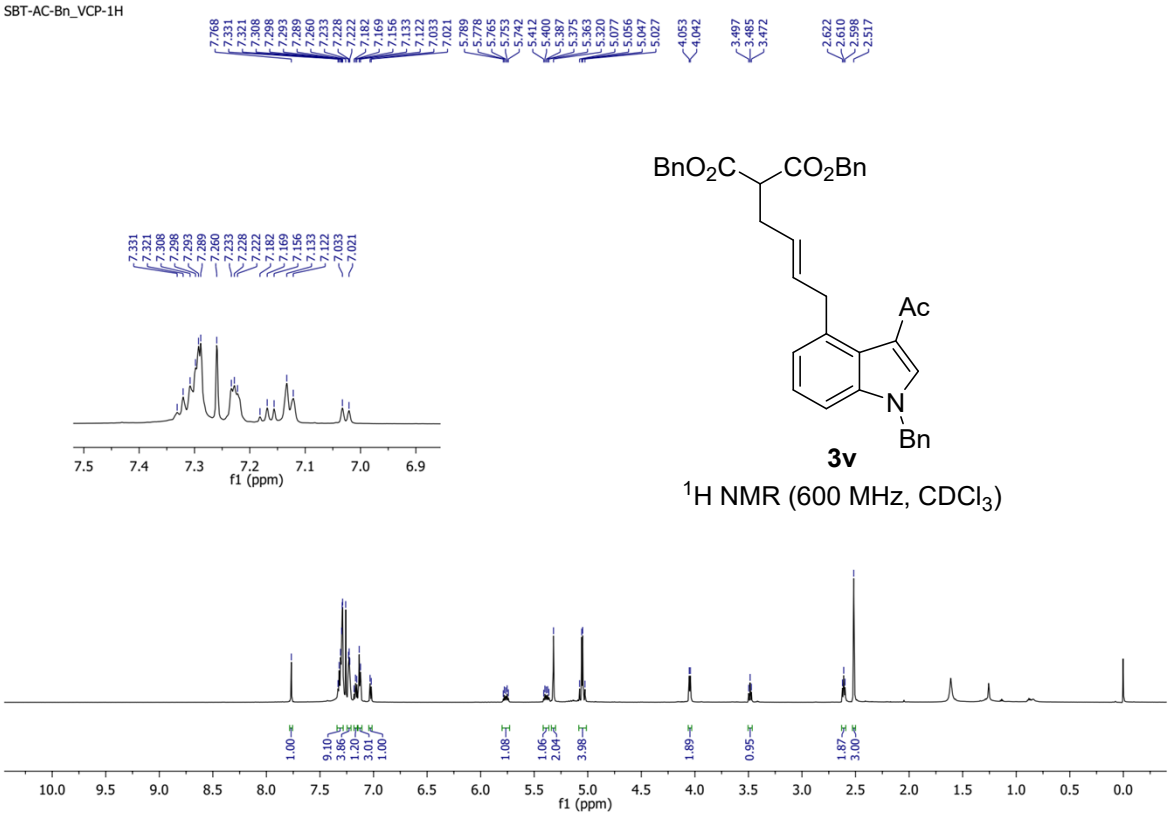

SBT-SESA-VCP-13C
MeO2C
CO2Me
Ac
N
Bn
O
O
3t
13C NMR (150 MHz, CDCl3)
f1 (ppm)

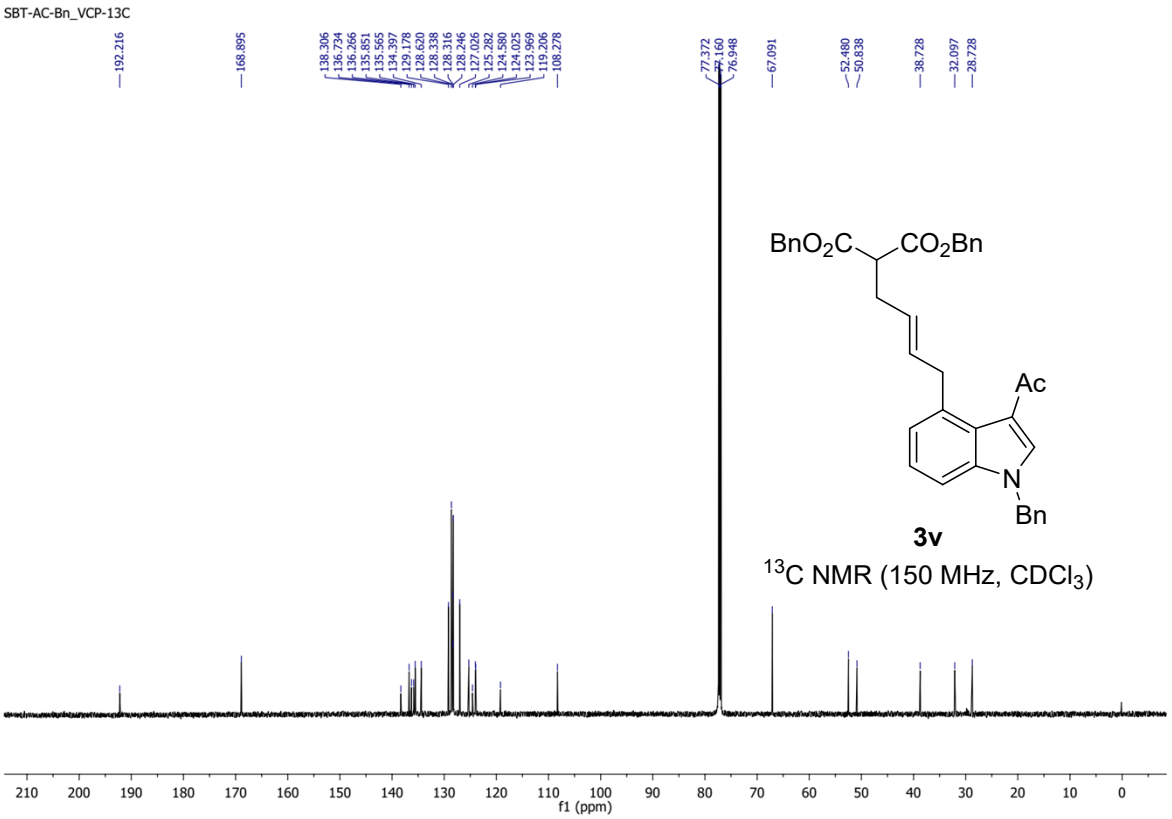
SBT-GEMFI-VCP-1H



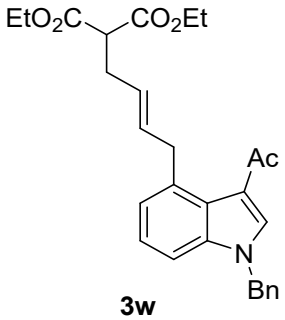
SBT-GEMFI-VCP-13C




SBT-AC-Bn_VCP-1H
BnO2C
CO2Bn
Ac
N
Bn
3v
1H NMR (600 MHz, CDCl3)
f1 (ppm)

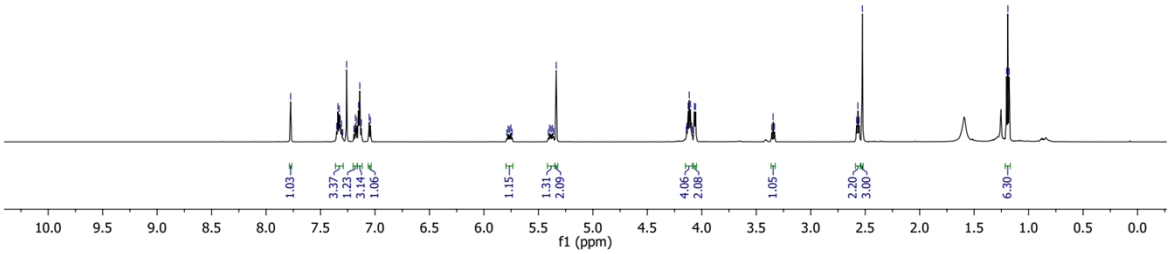

SBT-AC-Bn_VCP-13C
BnO2C
CO2Bn
Ac
N
Bn
3v
13C NMR (150 MHz, CDCl3)
f1 (ppm)

SBT-AC-ET-VCP-1H

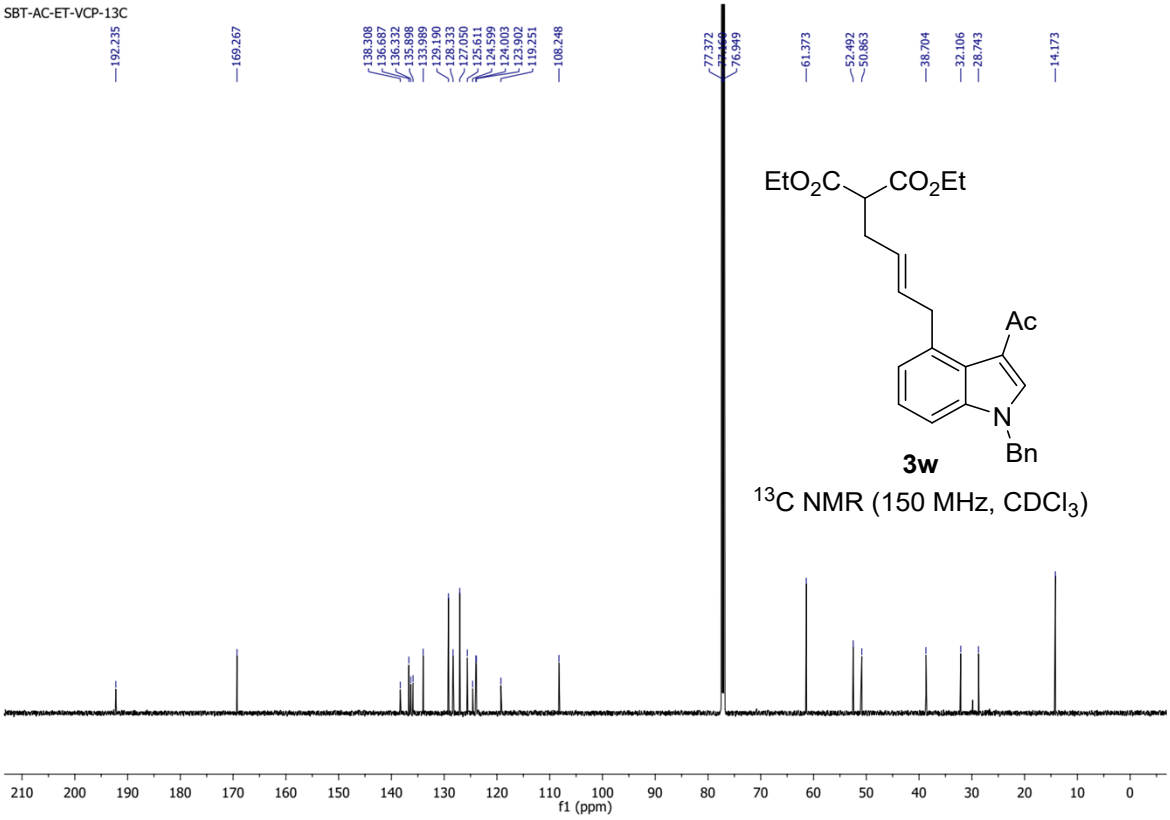


3w

^{1}H NMR (600 MHz, $CDCl_3$)

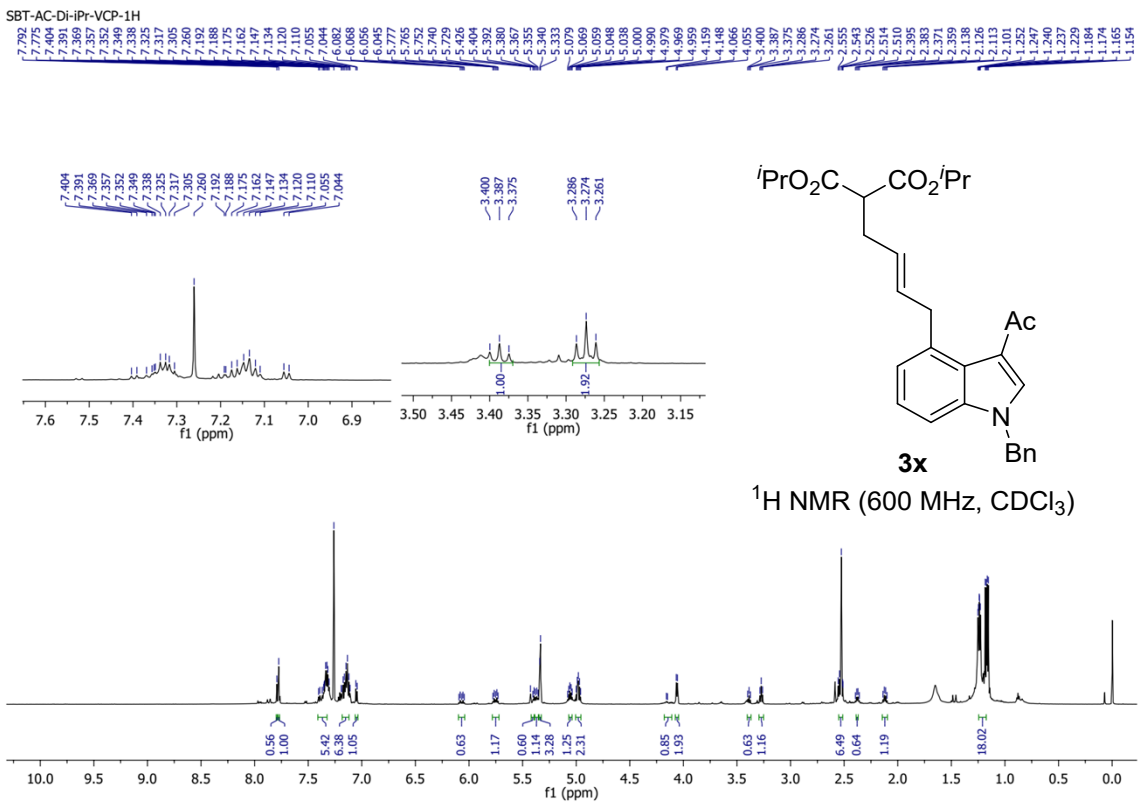


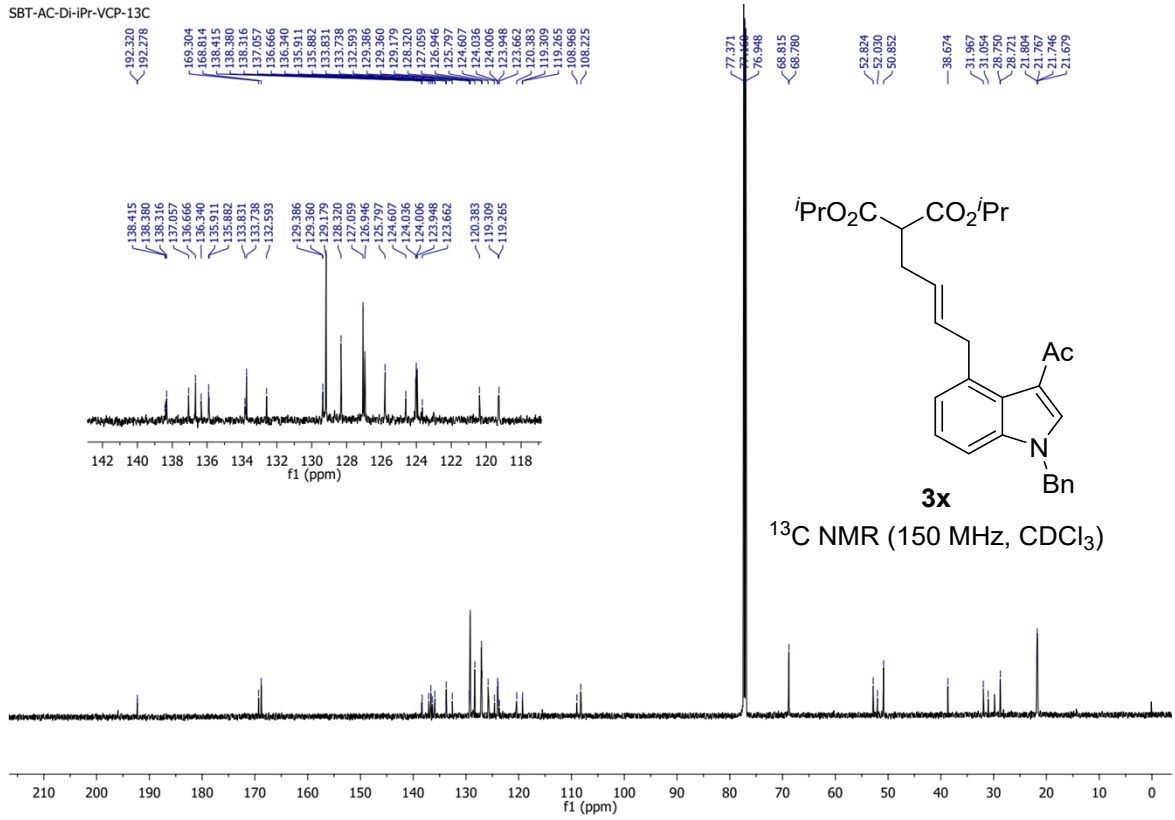
SBT-AC-ET-VCP-13C

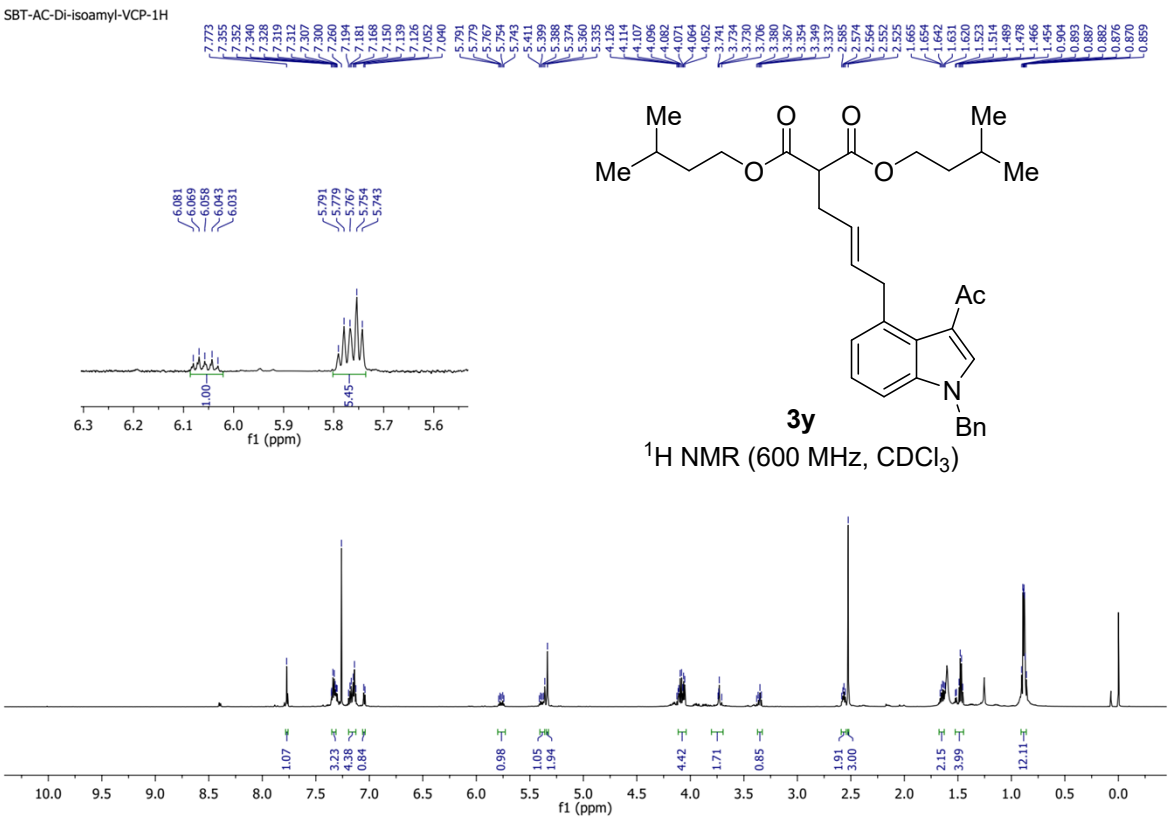


3w

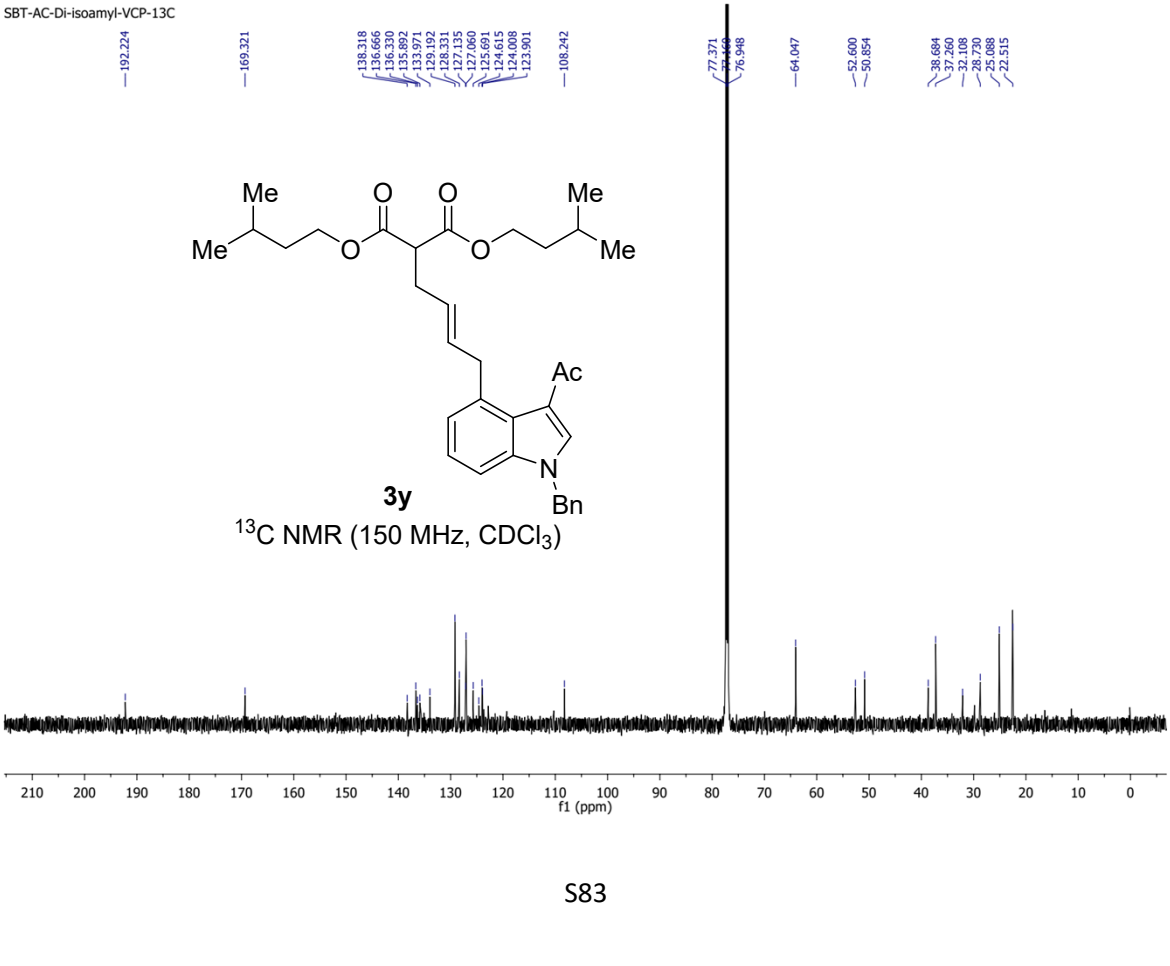
^{13}C NMR (150 MHz, $CDCl_3$)


SBT-AC-Di-iPr-VCP-1H
f1 (ppm)
$^{i}PrO_2C$
$CO_2{}^{i}Pr$
Ac
N
Bn
3x
^{1}H NMR (600 MHz, $CDCl_3$)

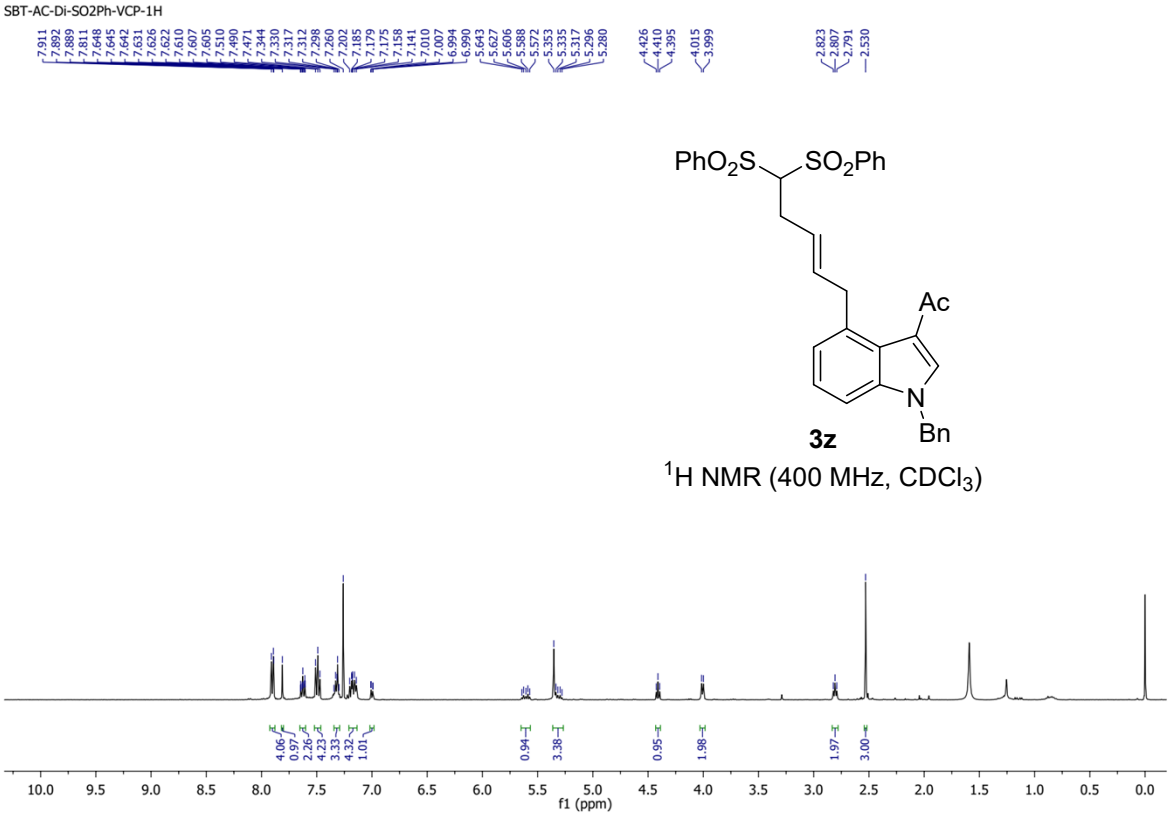

SBT-AC-Di-iPr-VCP-13C
f1 (ppm)
$^{i}PrO_2C$
$CO_2{}^{i}Pr$
Ac
N
Bn
3x
^{13}C NMR (150 MHz, $CDCl_3$)

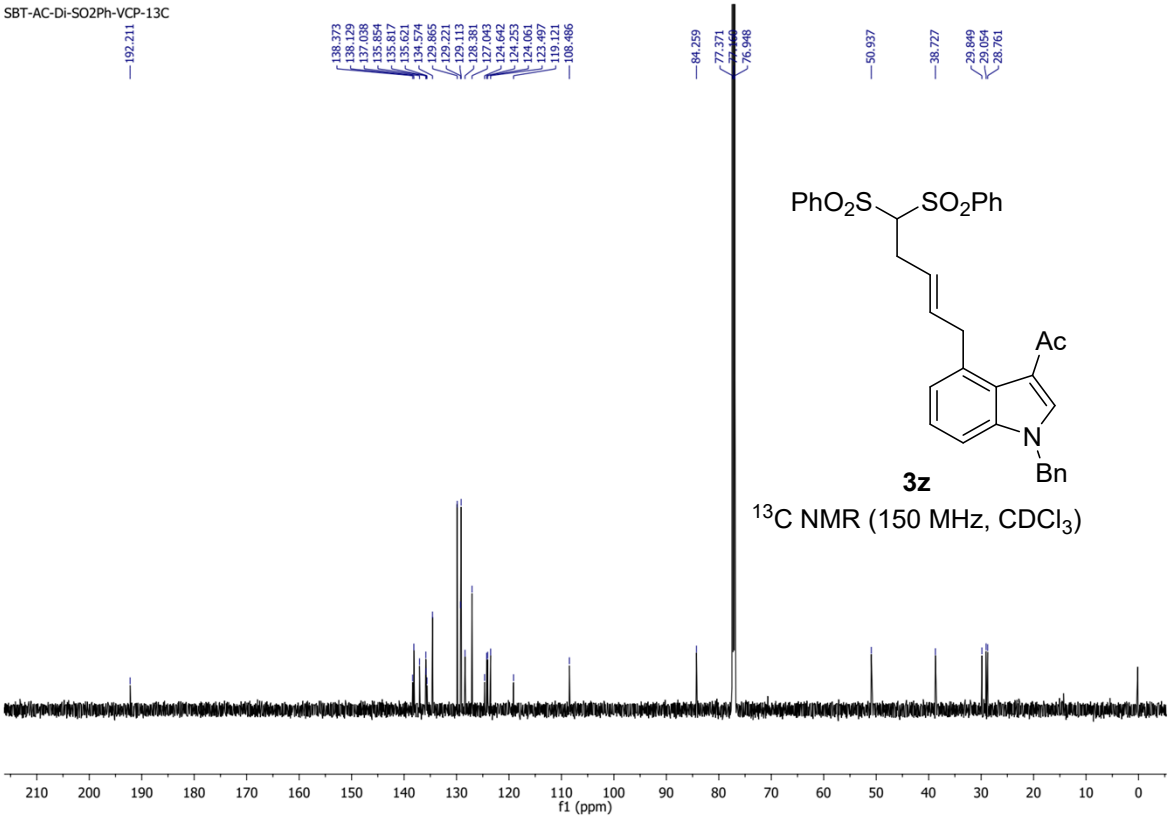


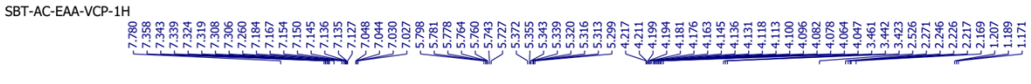
^{1}H NMR (600 MHz, $CDCl_3$)

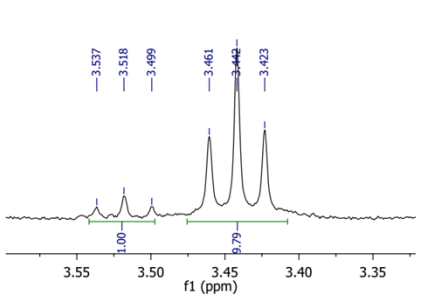


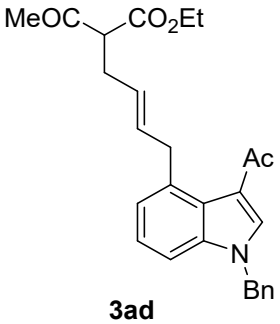
^{13}C NMR (150 MHz, $CDCl_3$)


SBT-AC-Di-SO2Ph-VCP-1H
PhO2S
SO2Ph
Ac
N
Bn
3z
1H NMR (400 MHz, CDCl3)
f1 (ppm)


SBT-AC-Di-SO2Ph-VCP-13C
PhO2S
SO2Ph
Ac
N
Bn
3z
13C NMR (150 MHz, CDCl3)
f1 (ppm)

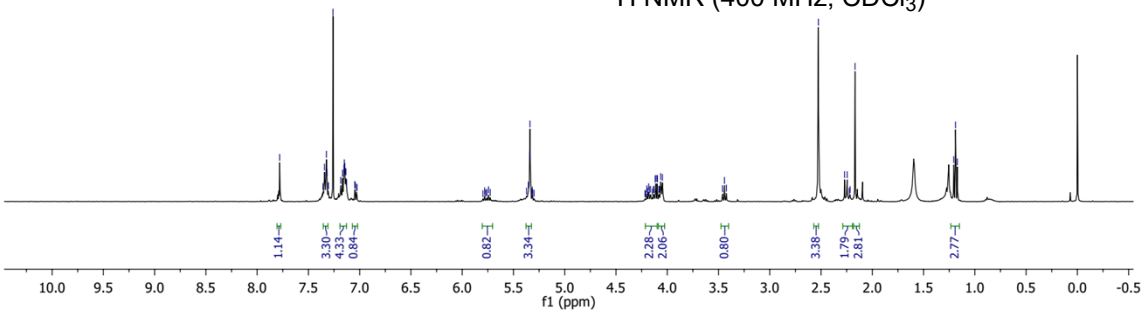


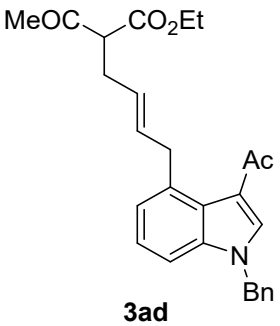




3ad

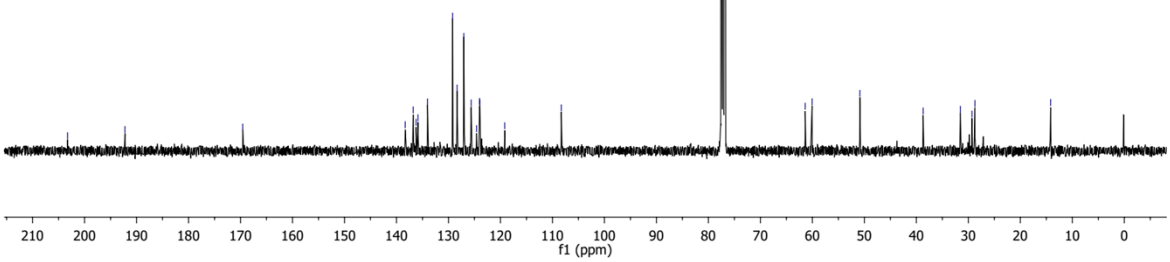
^{1}H NMR (400 MHz, $CDCl_3$)

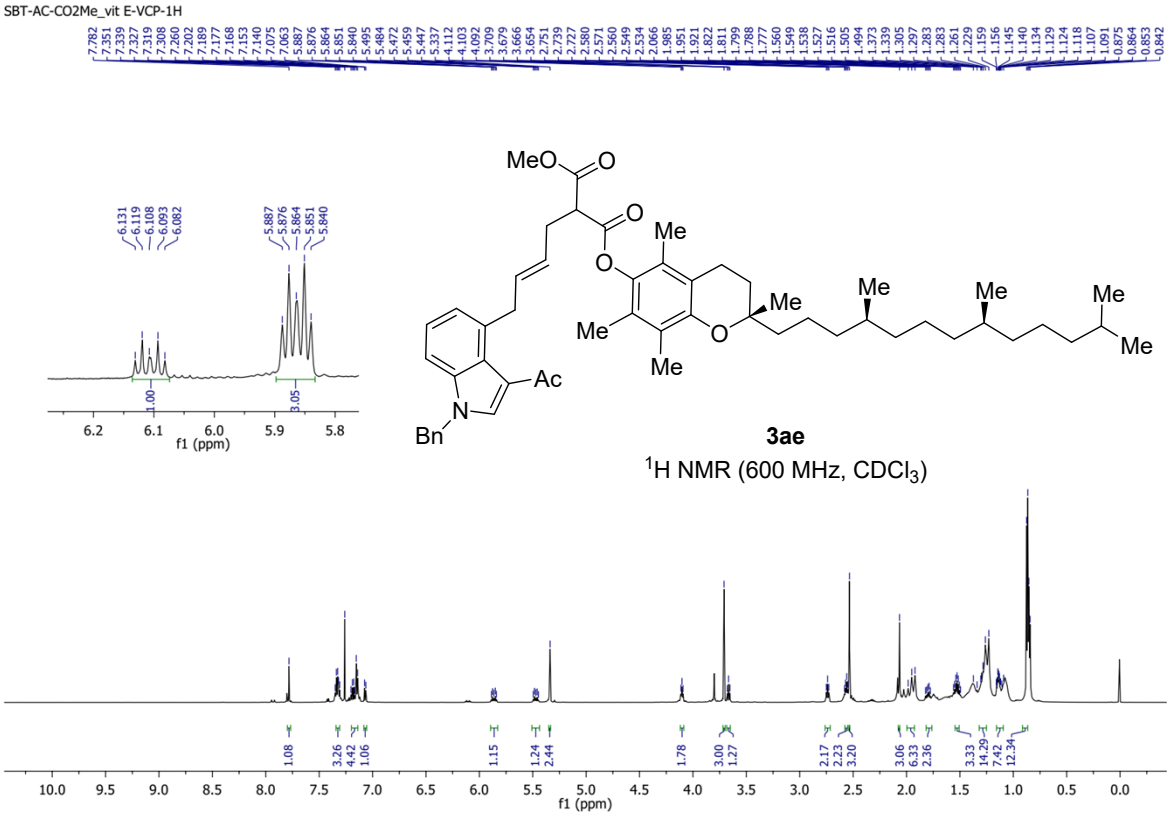


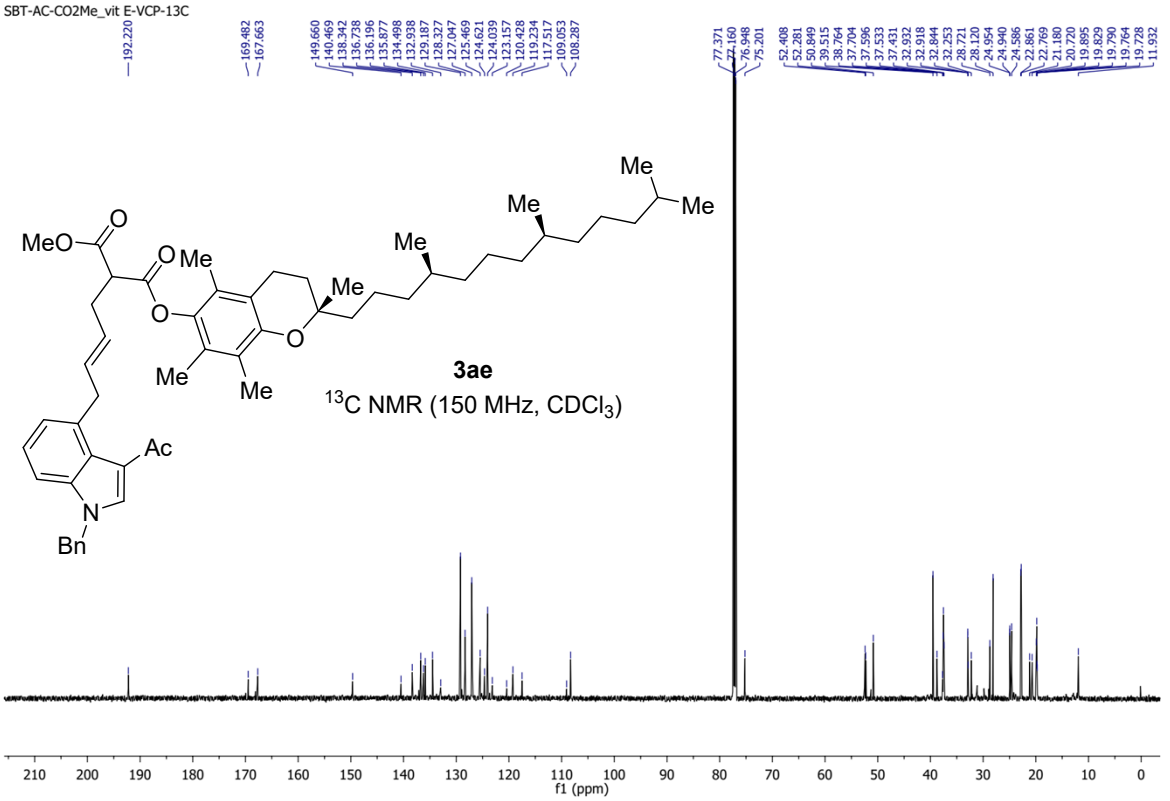


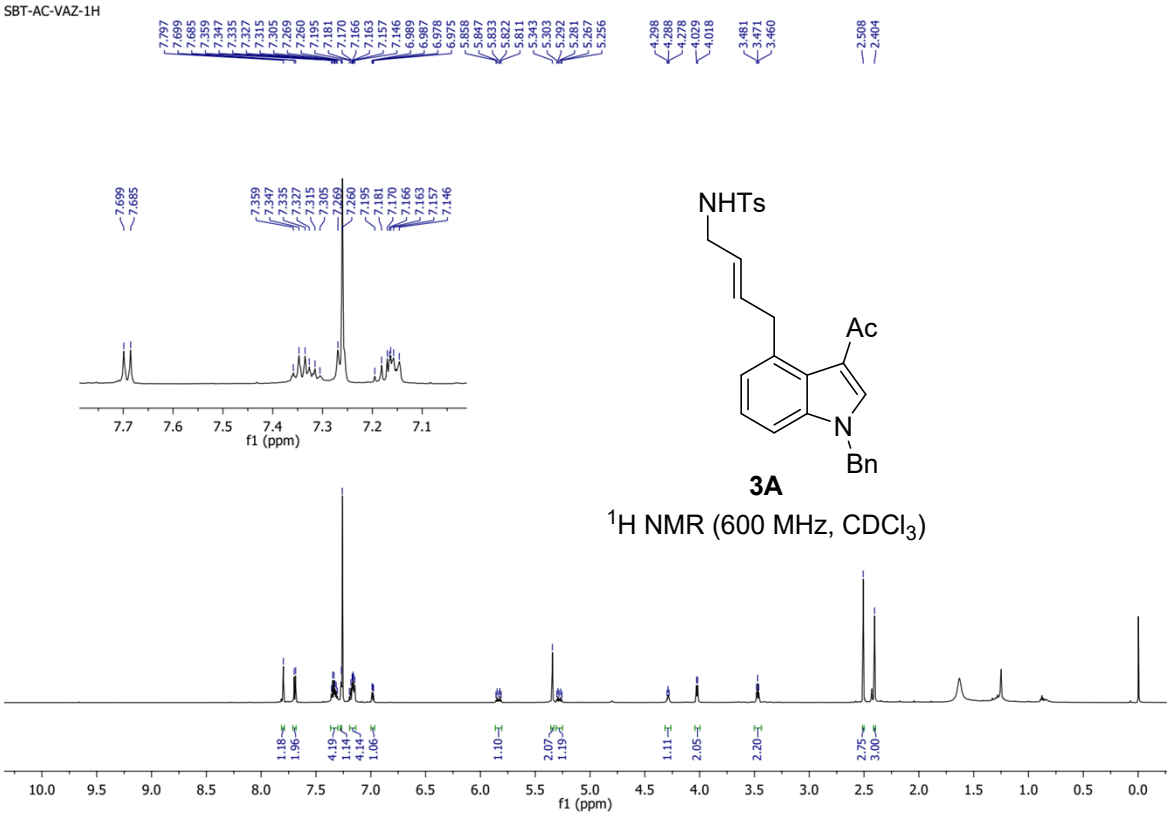
3ad

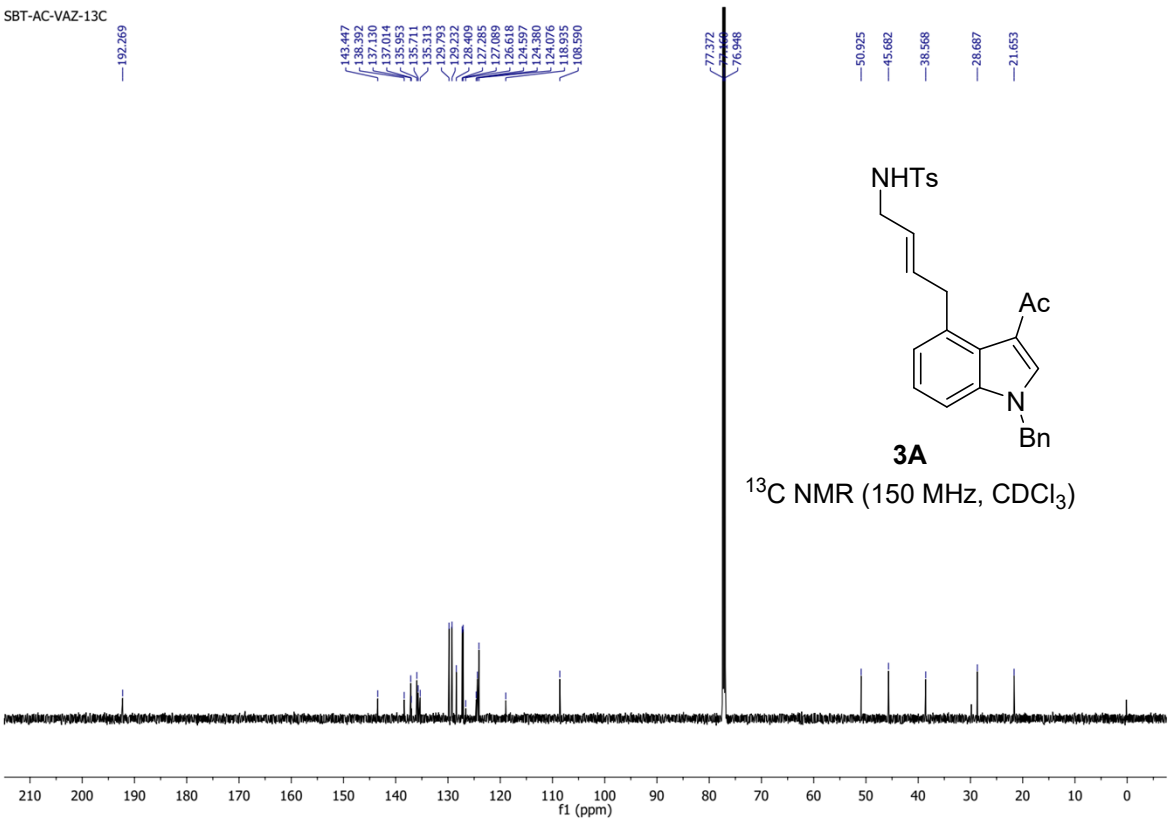
^{13}C NMR (100 MHz, $CDCl_3$)



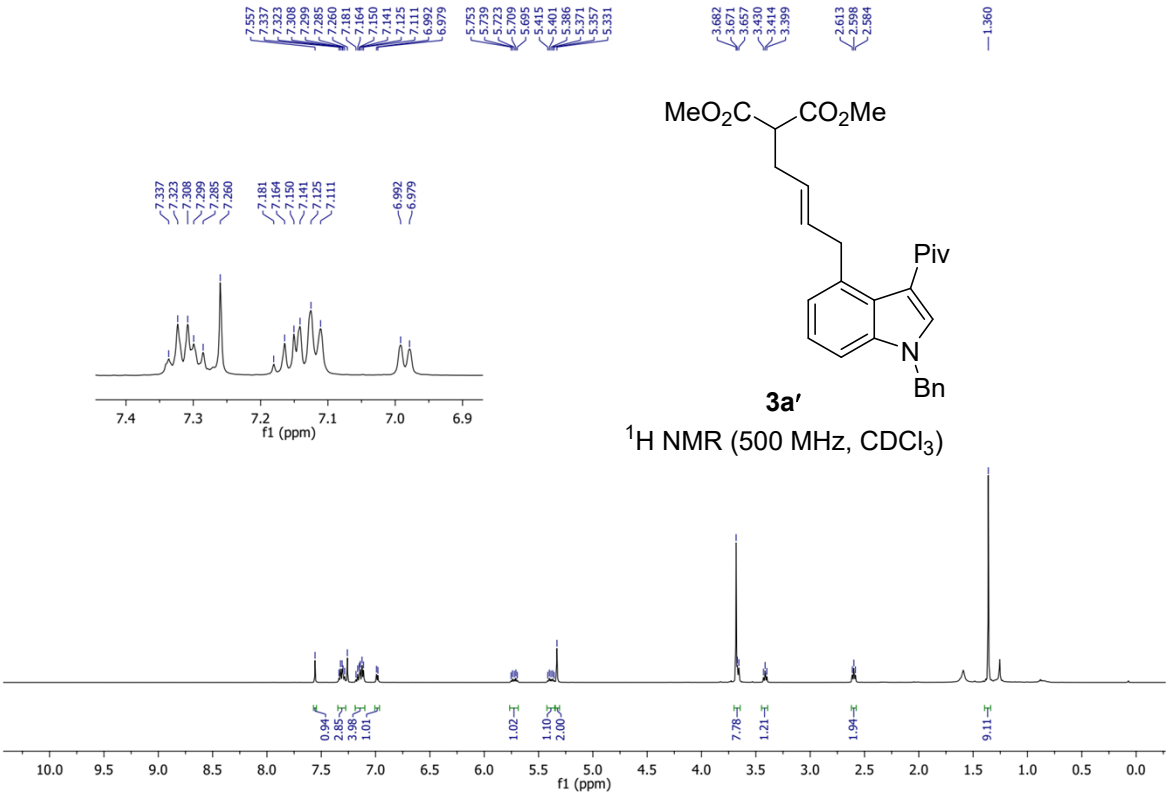

SBT-AC-CO2Me_vit E-VCP-1H
MeO
O
Me
Ac
N
Bn
3ae
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


SBT-AC-CO2Me_vit E-VCP-13C
MeO
Me
Ac
N
Bn
3ae
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

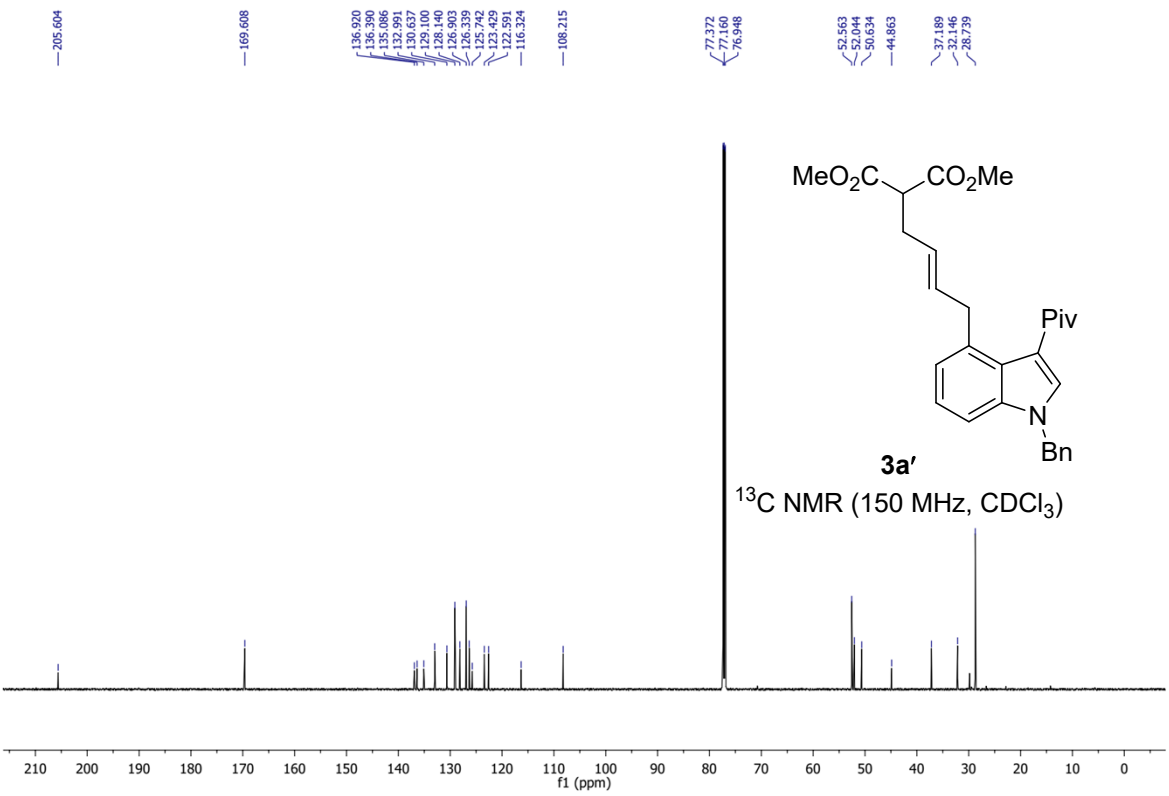

SBT-AC-VAZ-1H
NHTs
Ac
N
Bn
3A
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

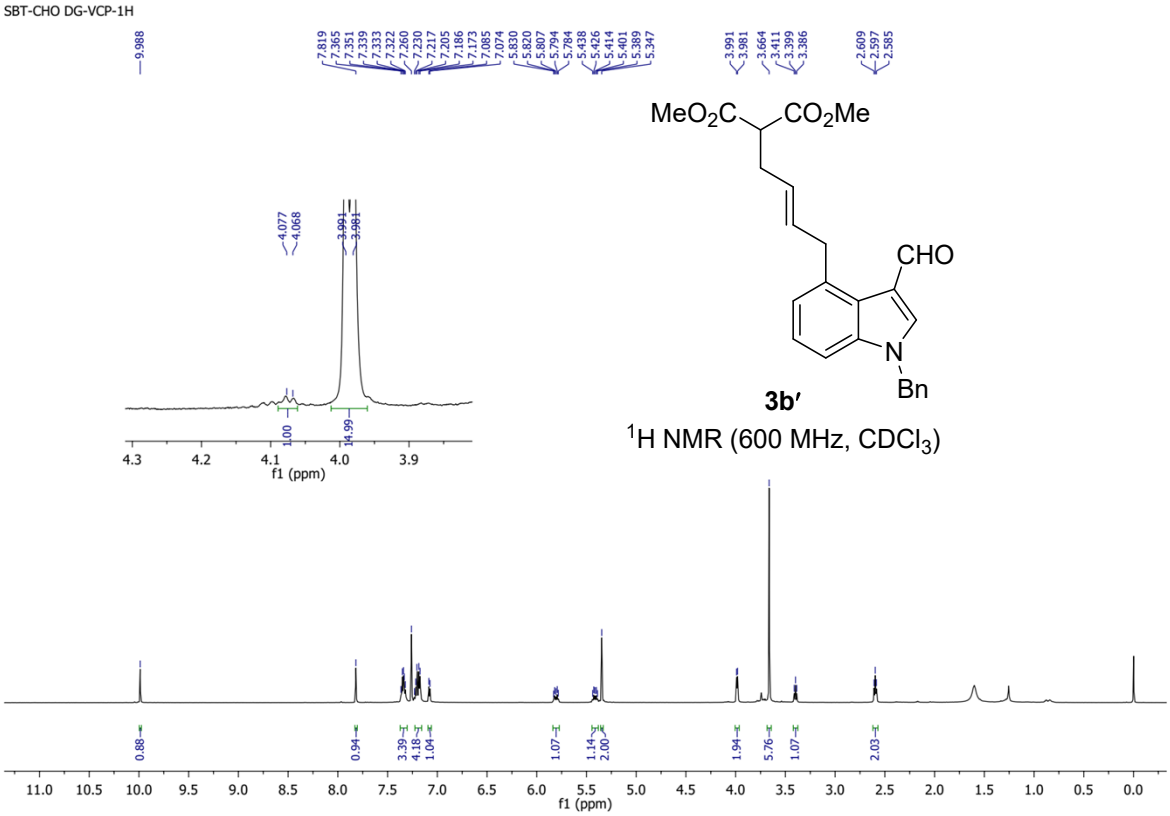

SBT-AC-VAZ-13C
NHTs
Ac
N
Bn
3A
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

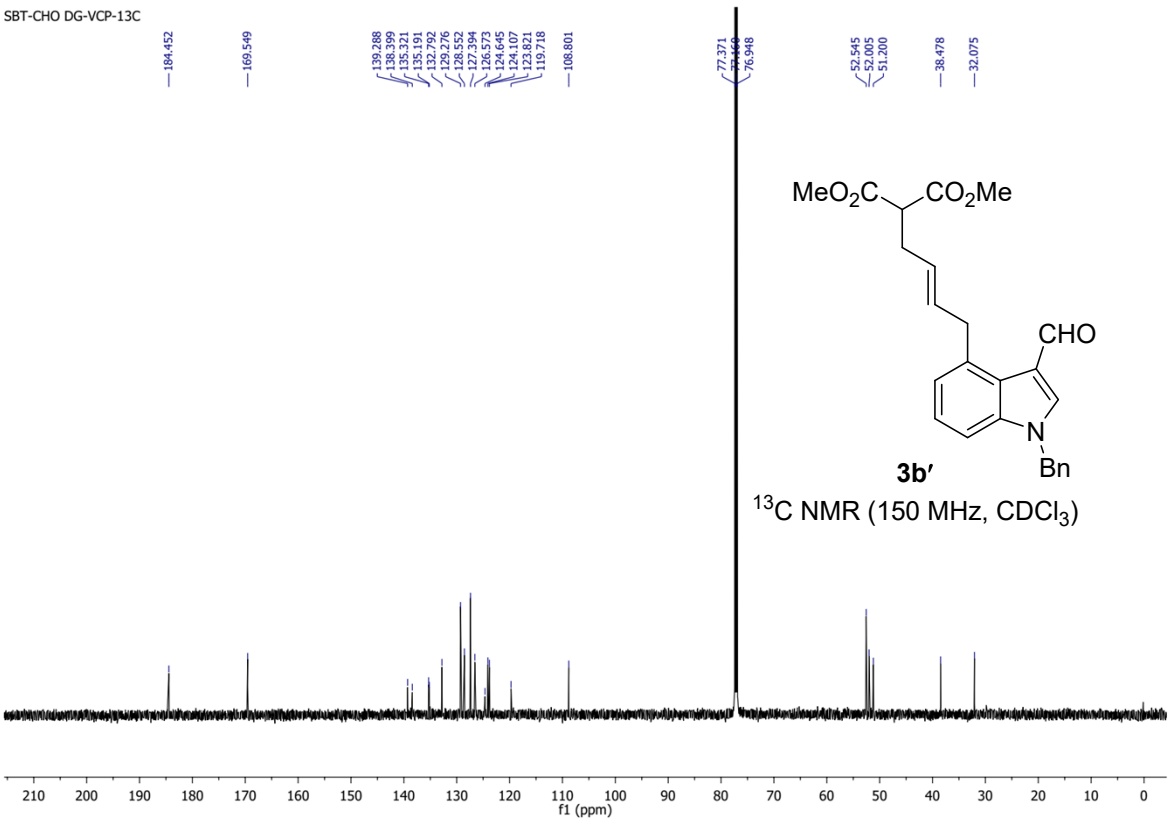
SBT-PIV DG-VCP-1H



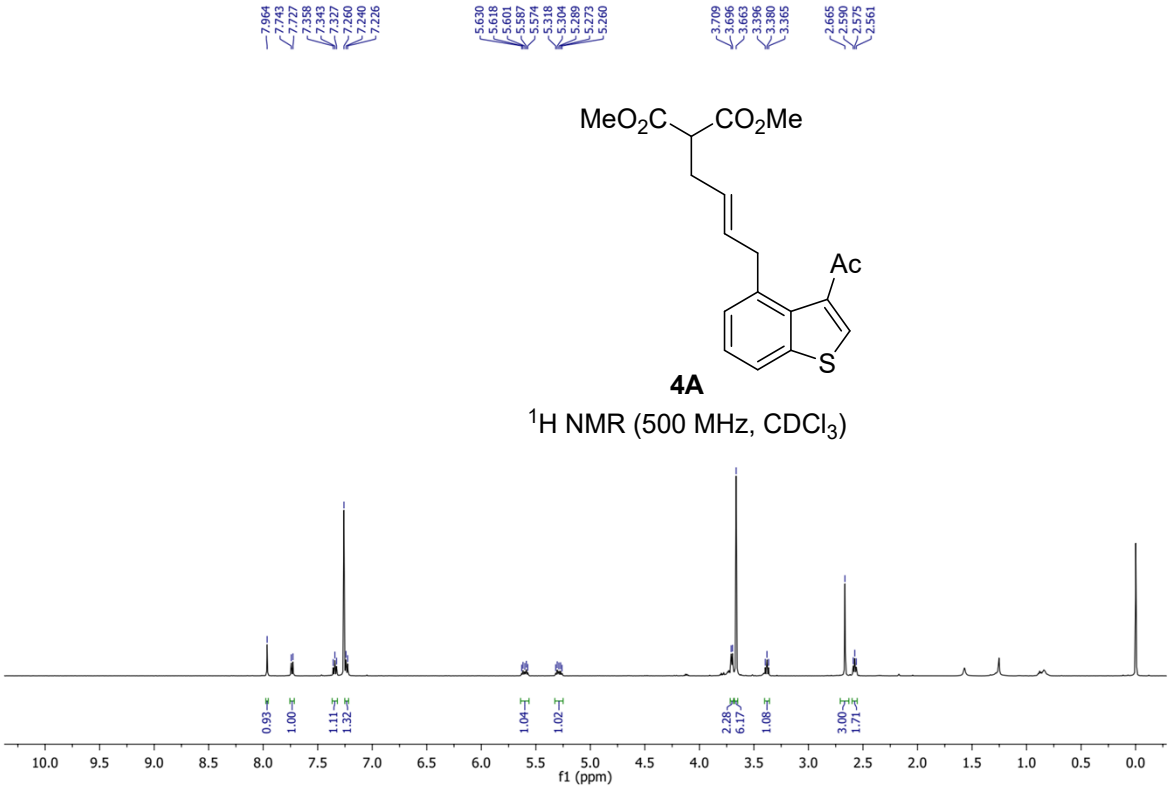
SBT-PIV DG-VCP-13C




SBT-CHO DG-VCP-1H
MeO2C
CO2Me
CHO
N
Bn
3b′
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-CHO DG-VCP-13C
MeO2C
CO2Me
CHO
N
Bn
3b′
13C NMR (150 MHz, CDCl3)
f1 (ppm)

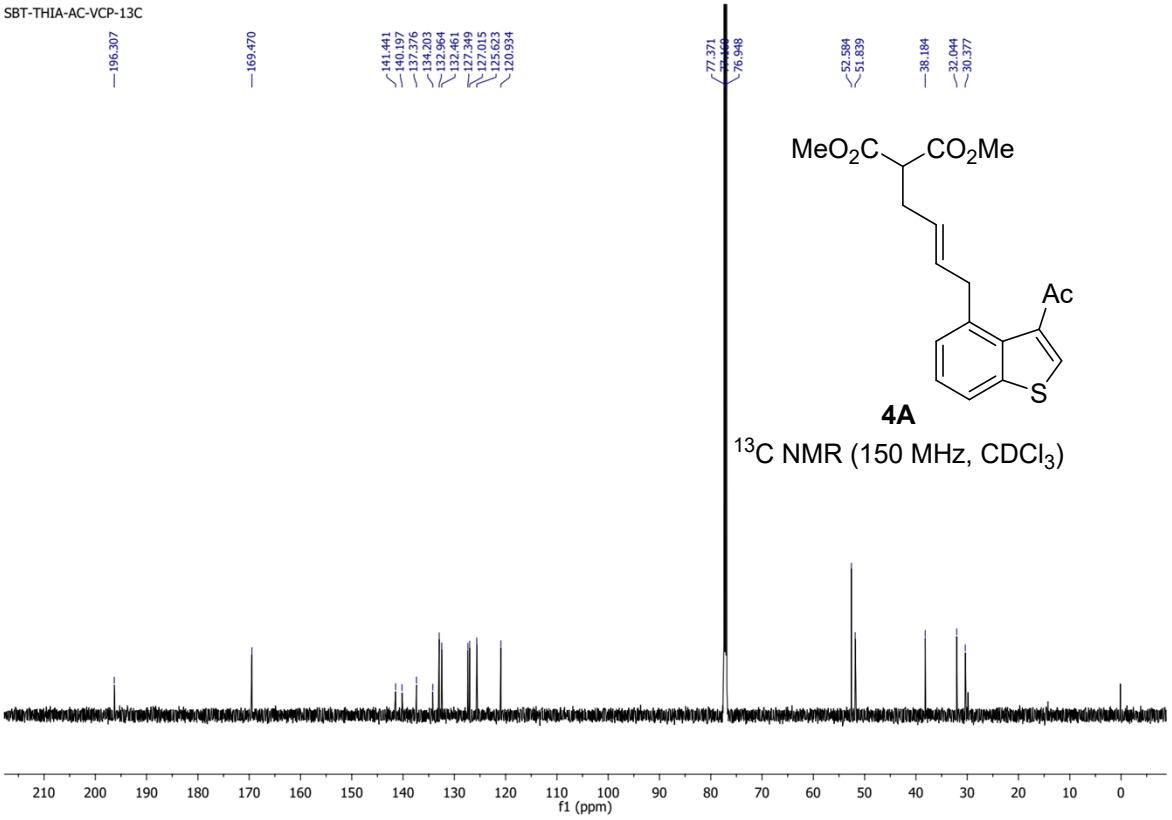
SBT-THIA-AC-VCP-1H



4A

^{1}H NMR (500 MHz, $CDCl_3$)

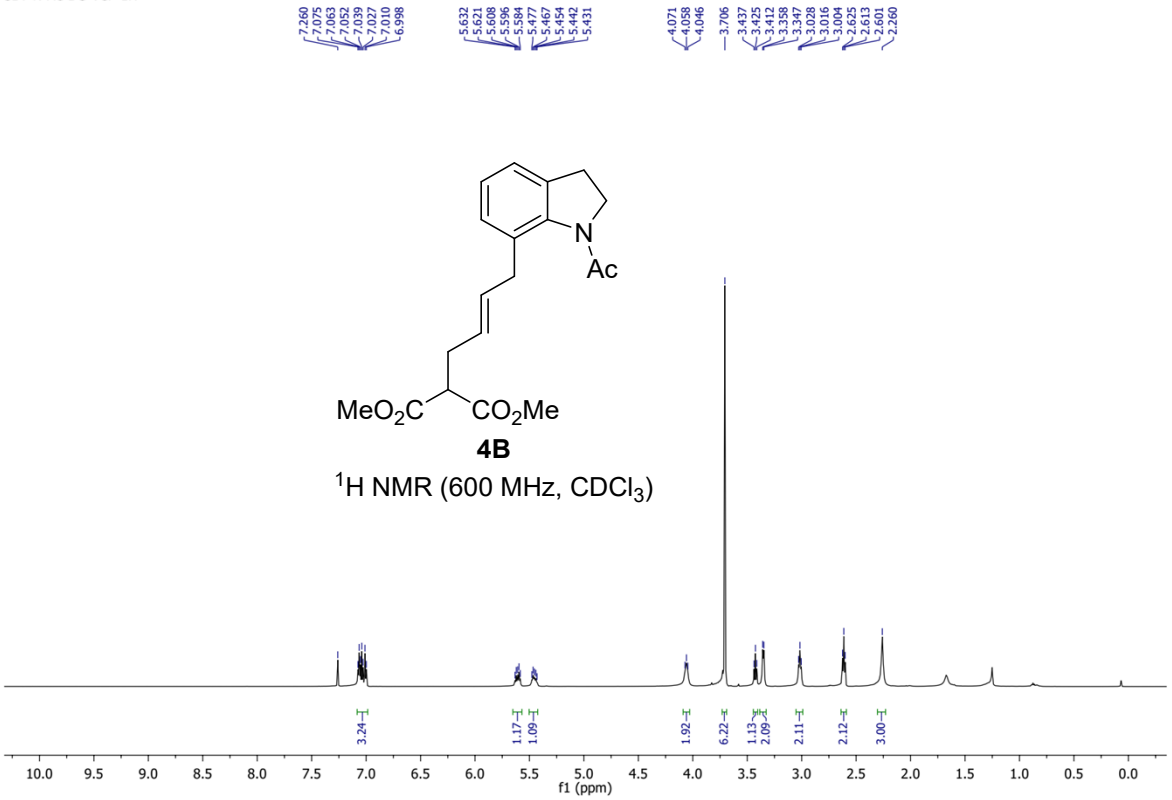
SBT-THIA-AC-VCP-13C



4A

^{13}C NMR (150 MHz, $CDCl_3$)

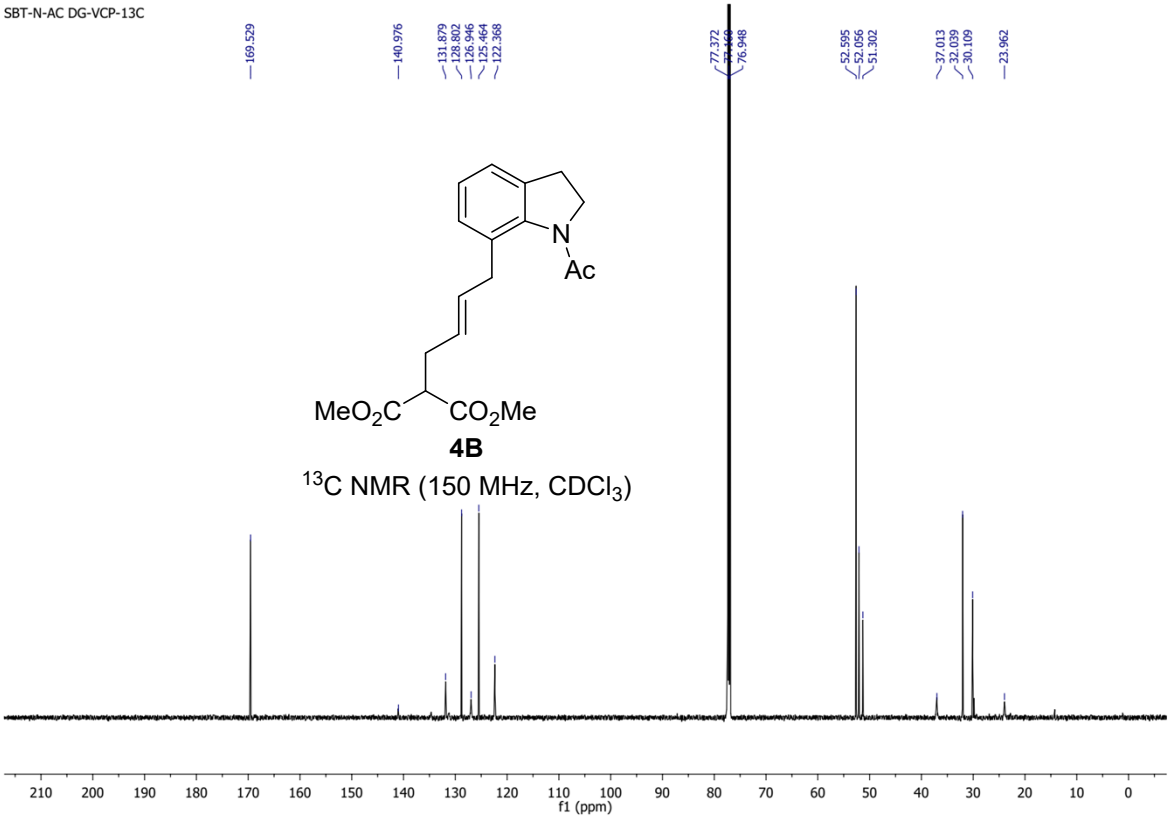
SBT-N-AC DG-VCP-1H



4B

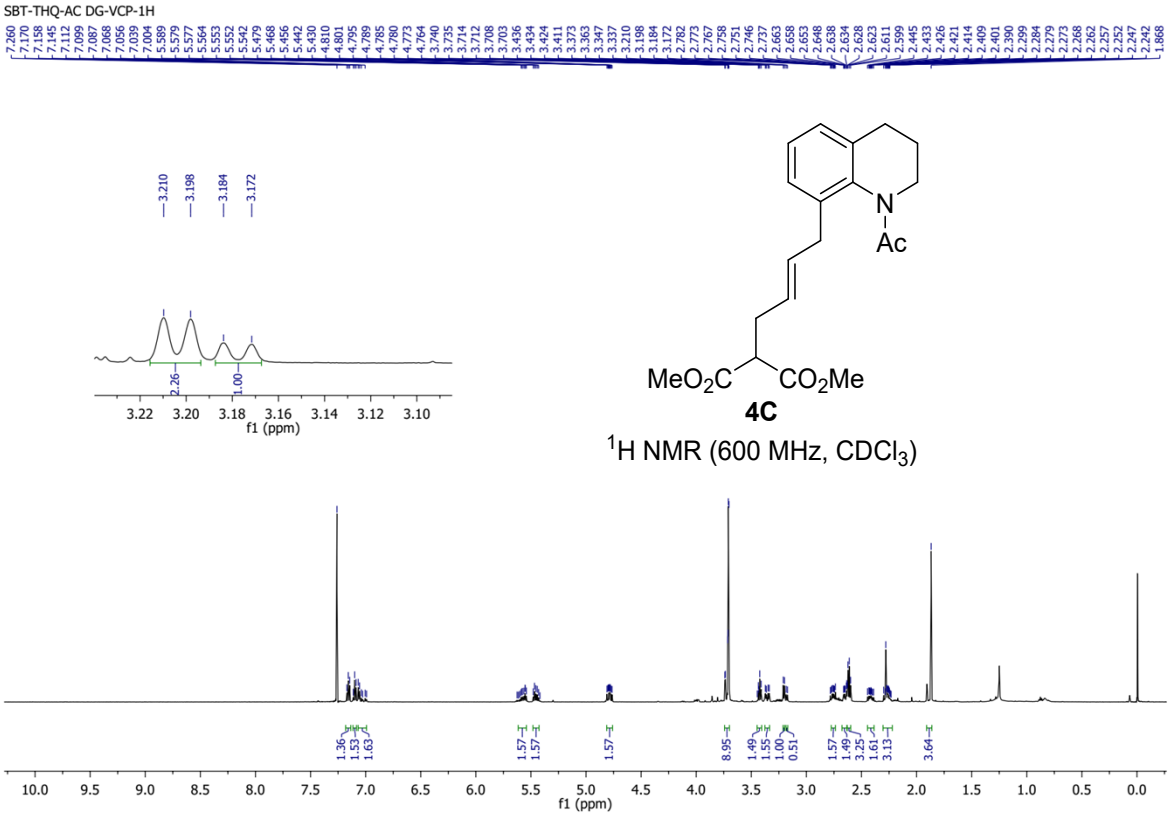
^{1}H NMR (600 MHz, $CDCl_3$)

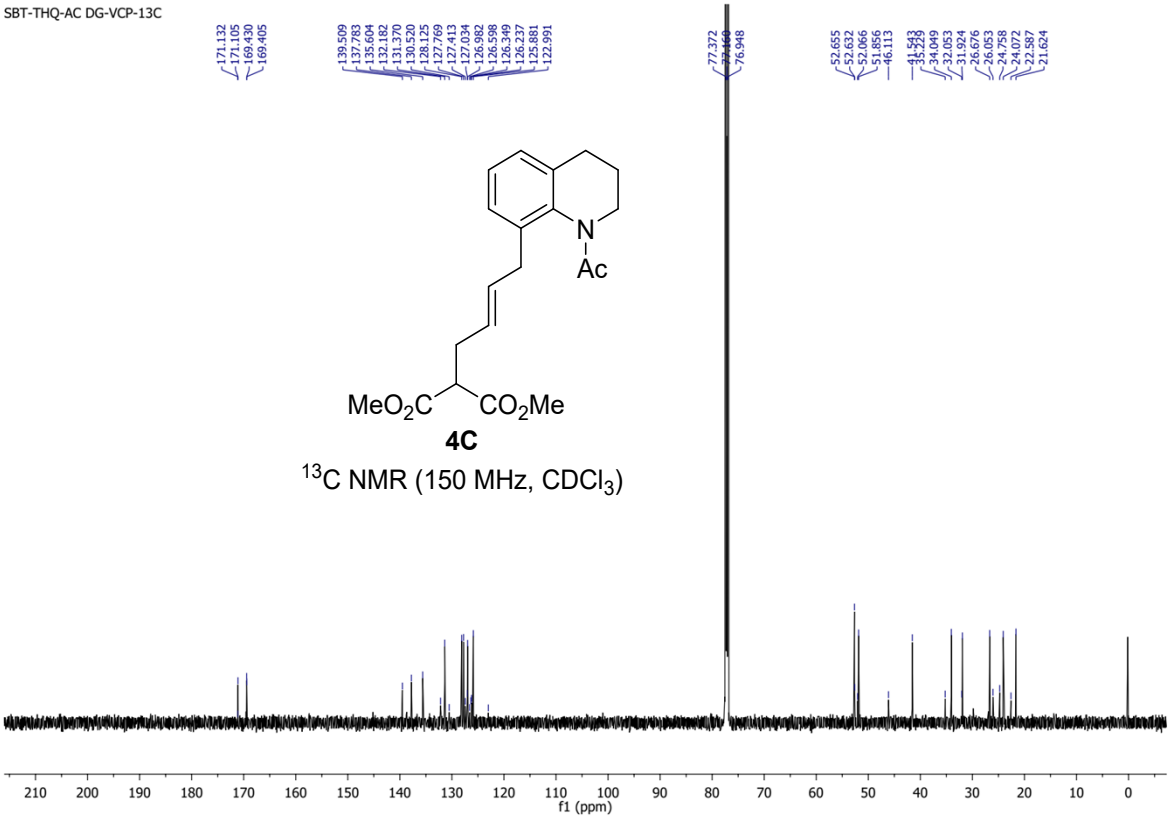
SBT-N-AC DG-VCP-13C



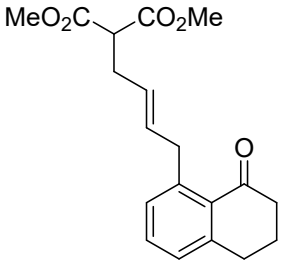
4B

^{13}C NMR (150 MHz, $CDCl_3$)


SBT-THQ-AC DG-VCP-1H
N
Ac
MeO2C
CO2Me
4C
1H NMR (600 MHz, CDCl3)
f1 (ppm)

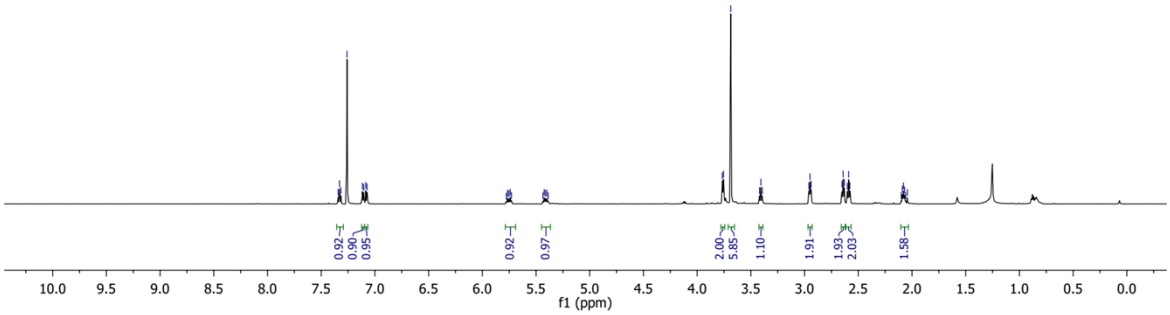

SBT-THQ-AC DG-VCP-13C
N
Ac
MeO2C
CO2Me
4C
13C NMR (150 MHz, CDCl3)
f1 (ppm)

SBT-TETRA-VCP-1H

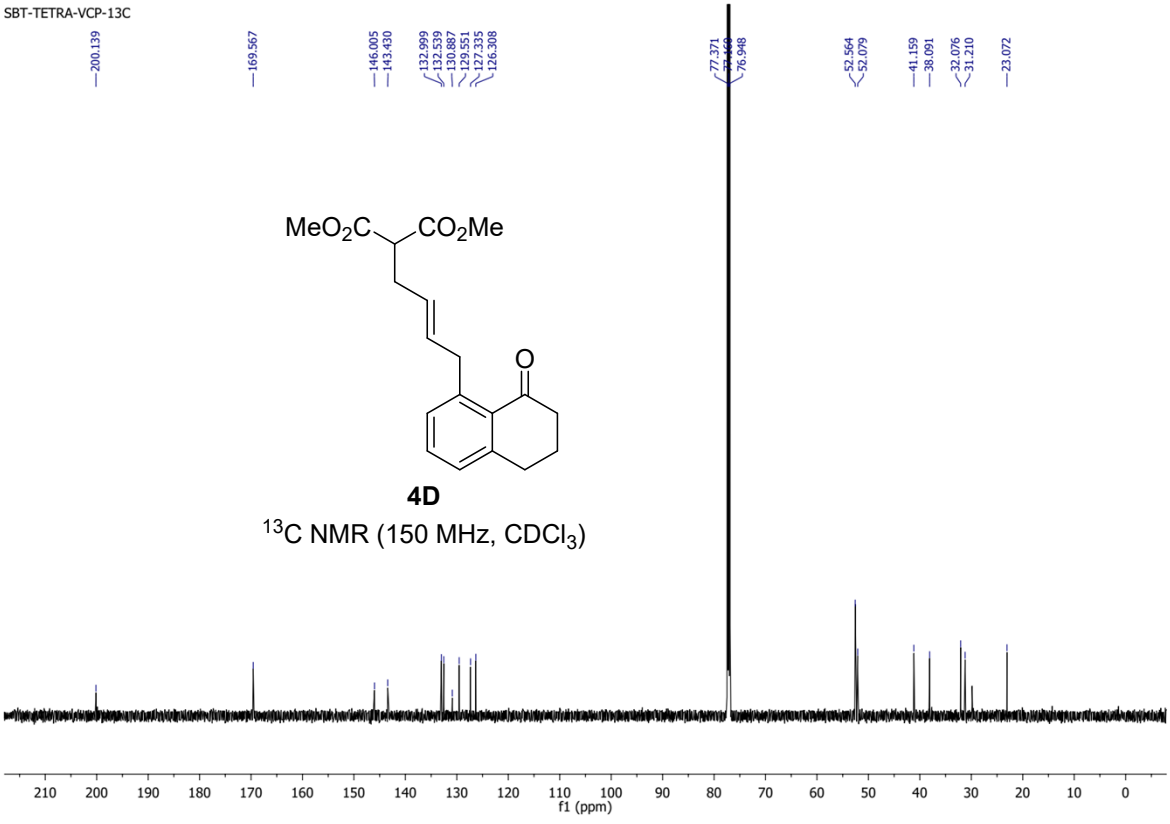


4D

^{1}H NMR (600 MHz, $CDCl_3$)

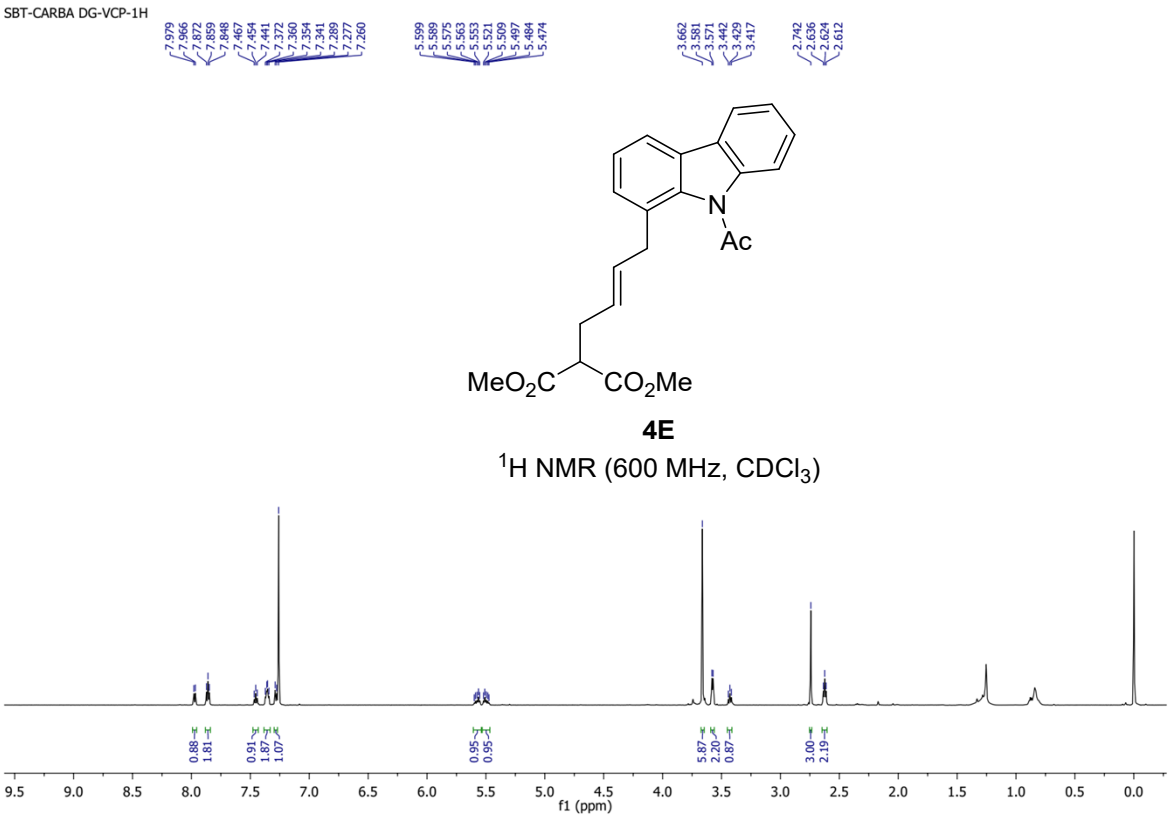


SBT-TETRA-VCP-13C



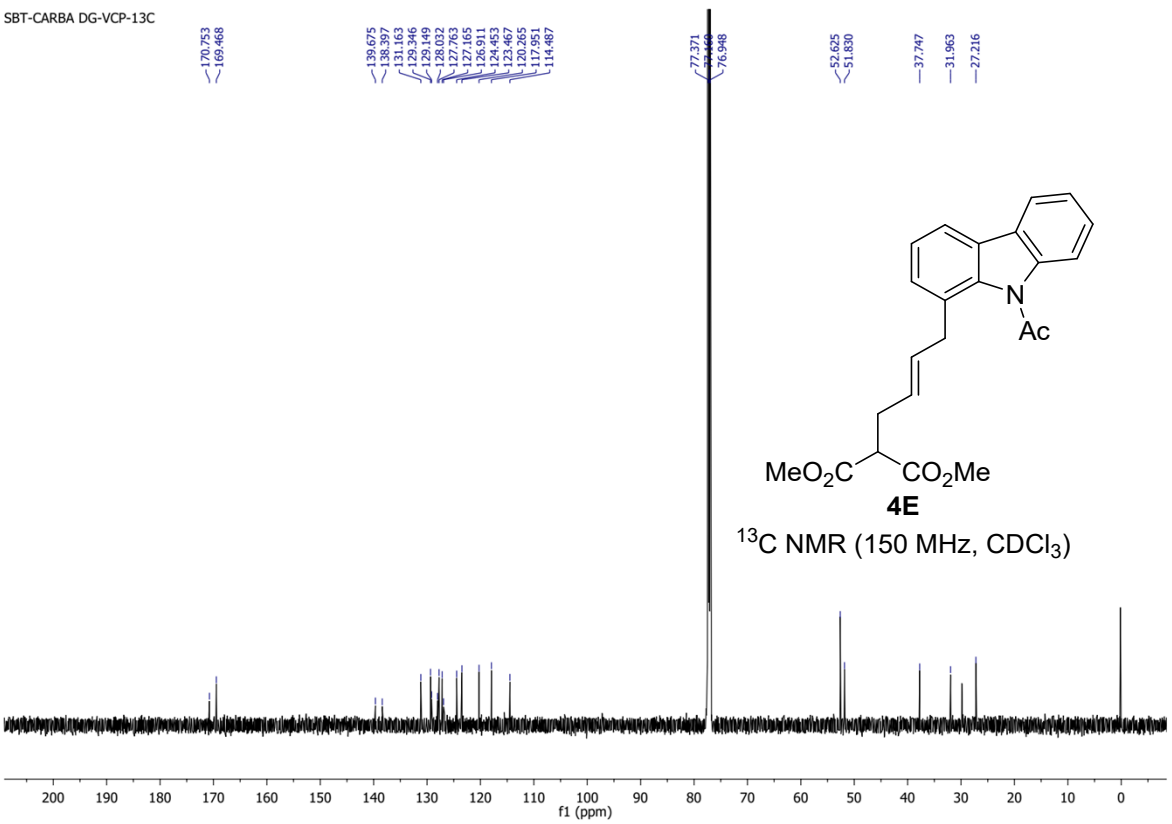
4D

^{13}C NMR (150 MHz, $CDCl_3$)



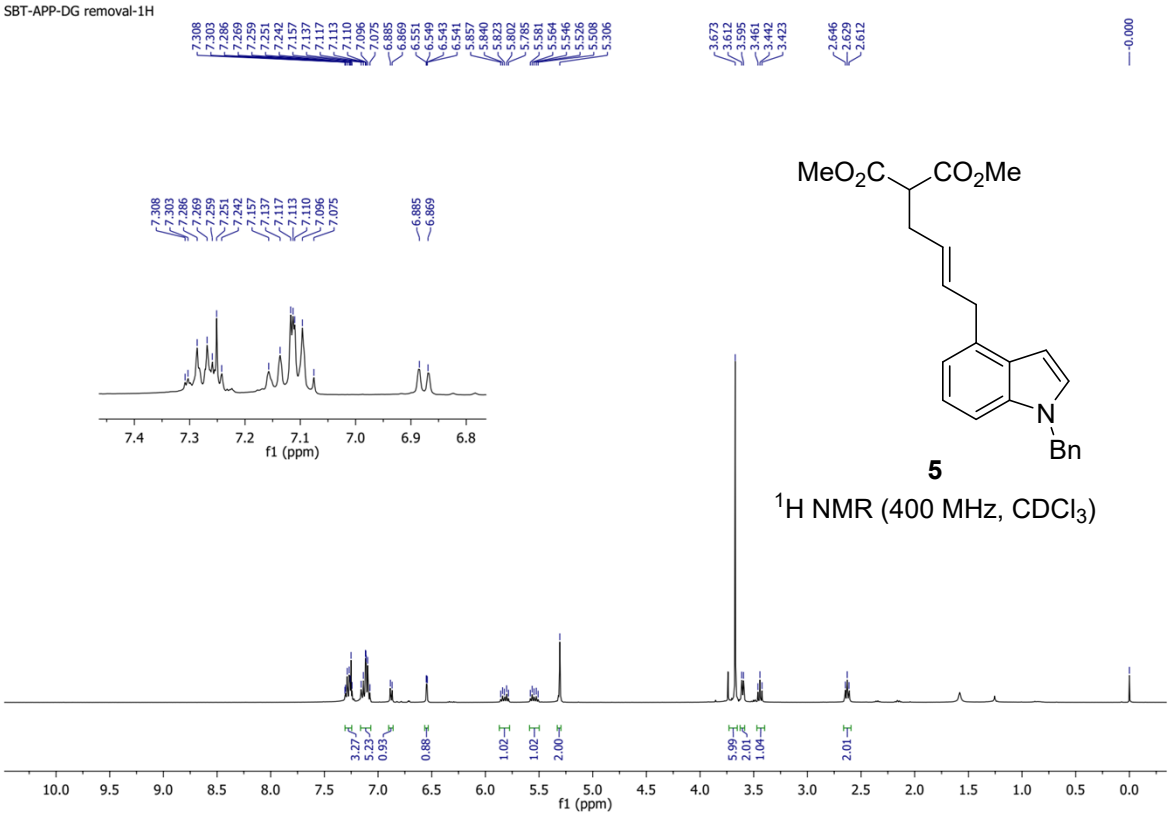
4E

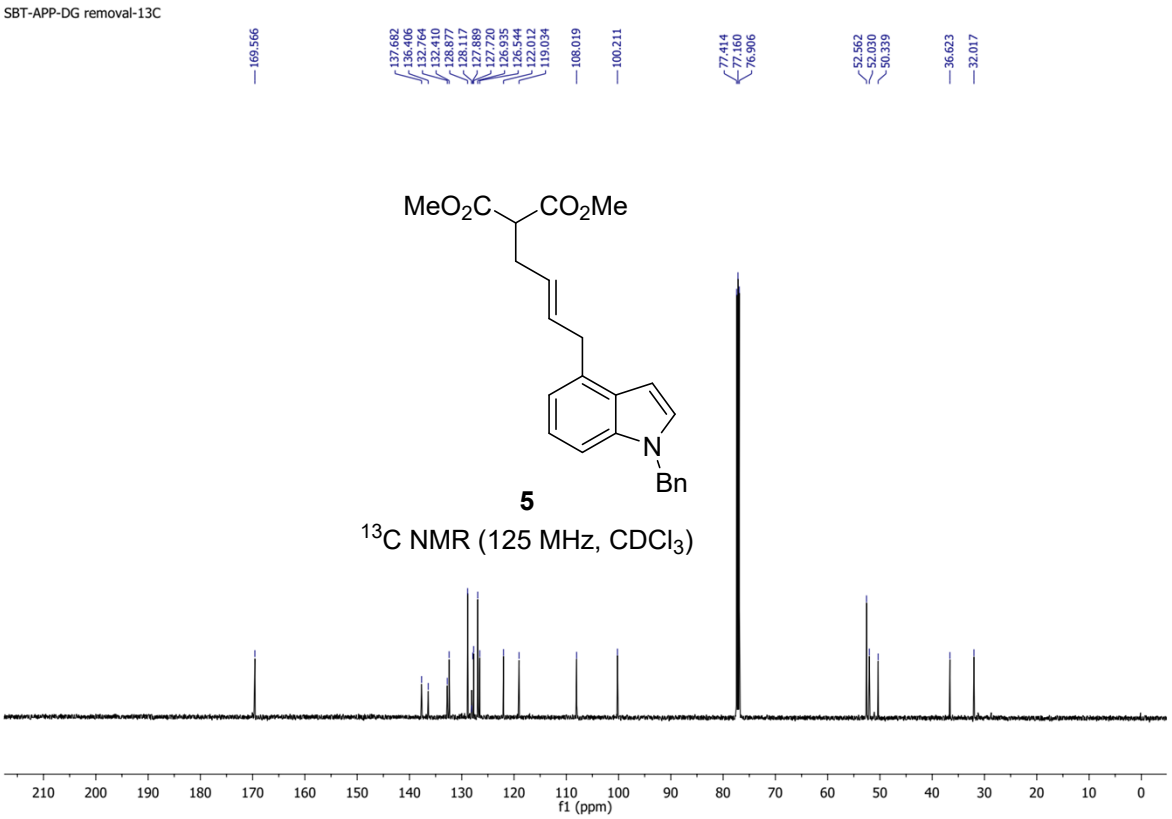
^{1}H NMR (600 MHz, $CDCl_3$)

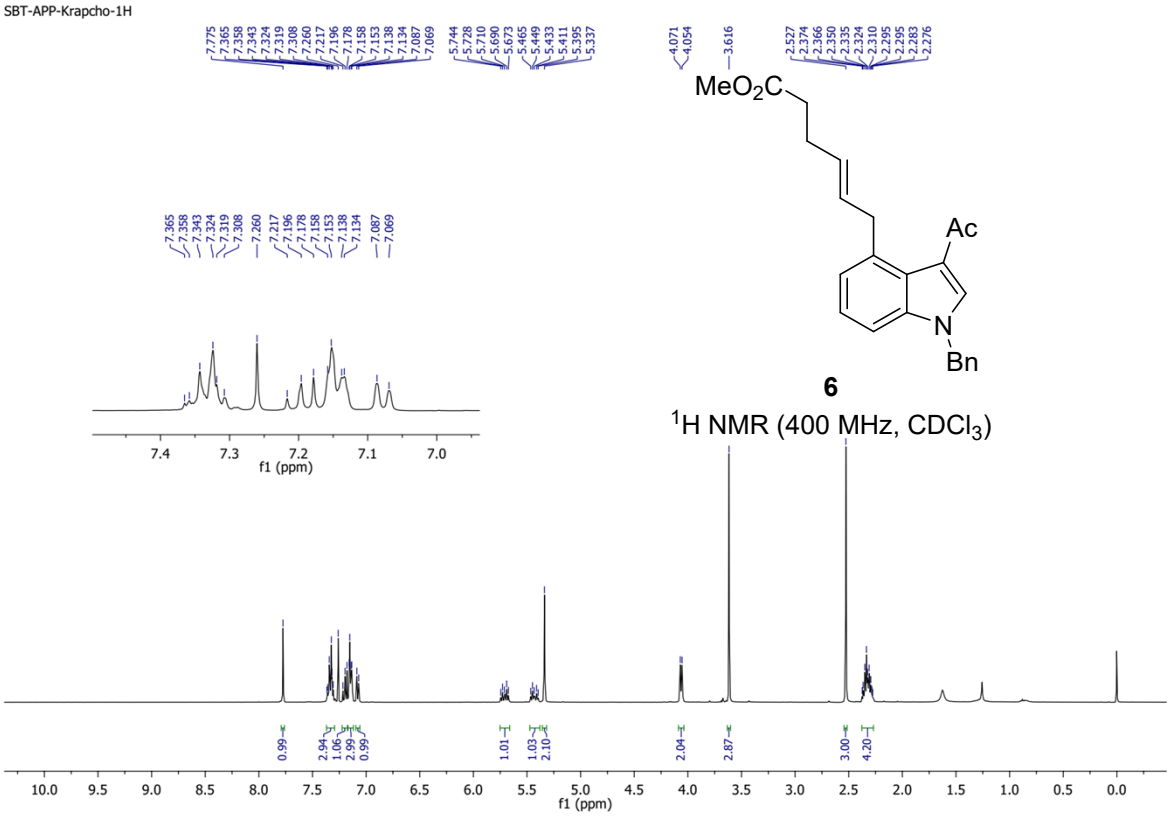


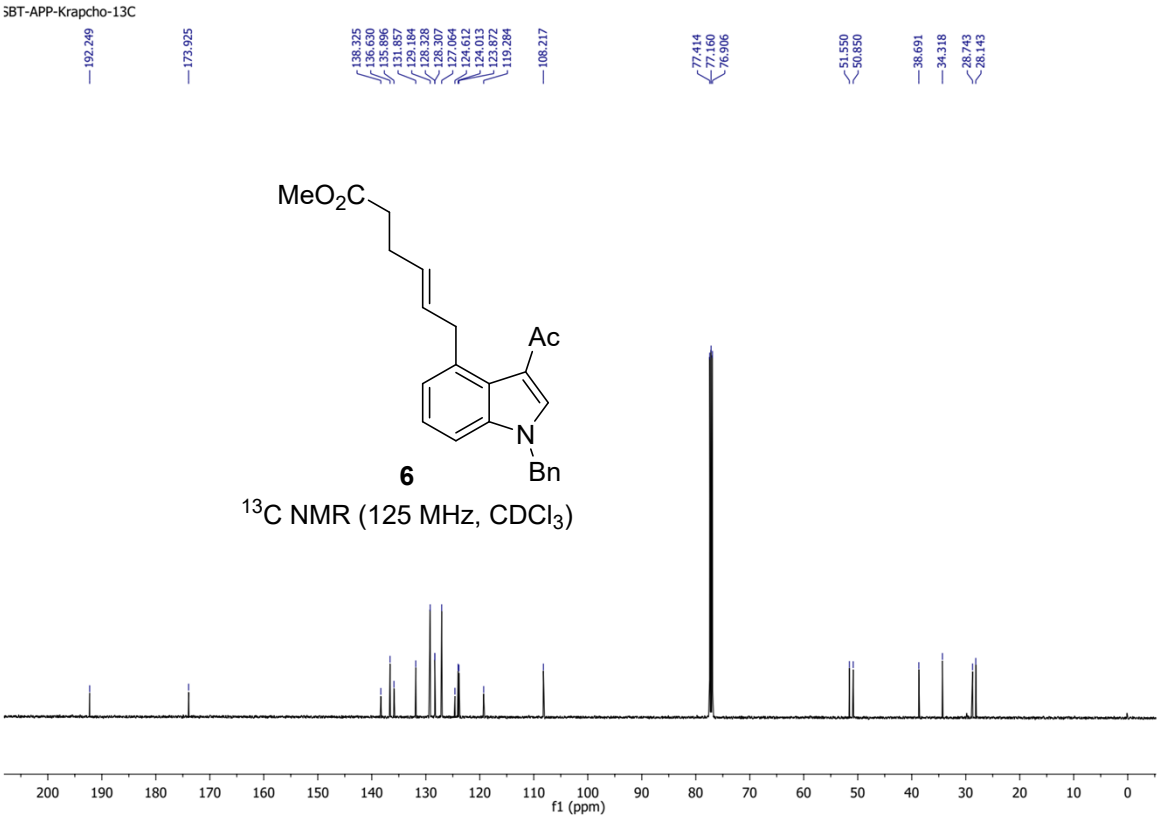
4E

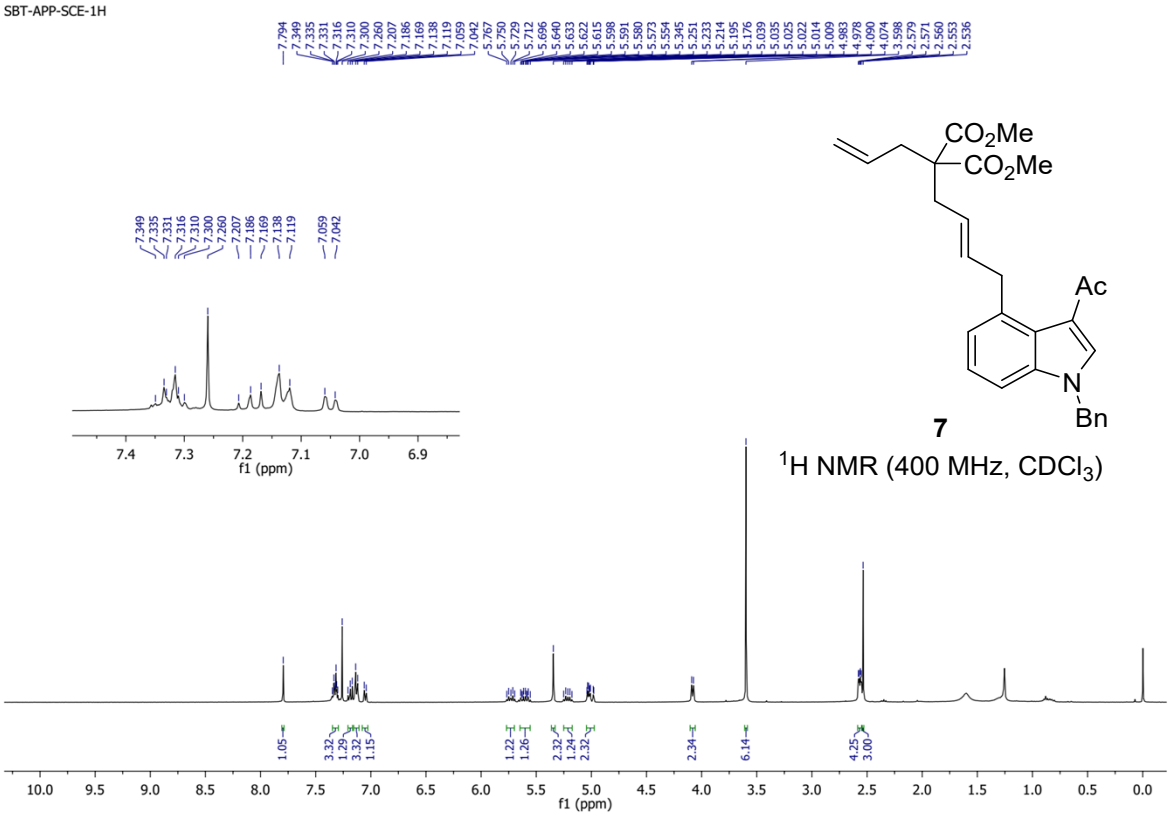
^{13}C NMR (150 MHz, $CDCl_3$)

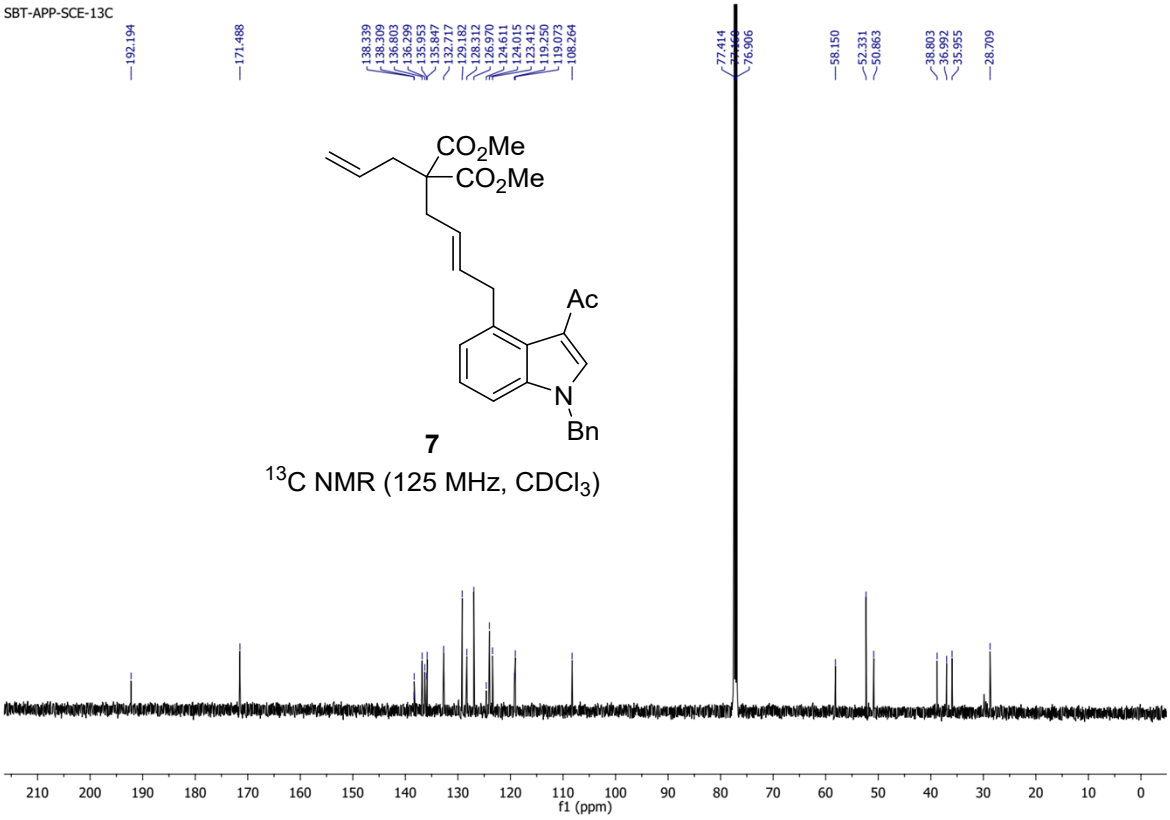

SBT-APP-DG removal-1H
MeO2C
CO2Me
N
Bn
5
1H NMR (400 MHz, CDCl3)
f1 (ppm)

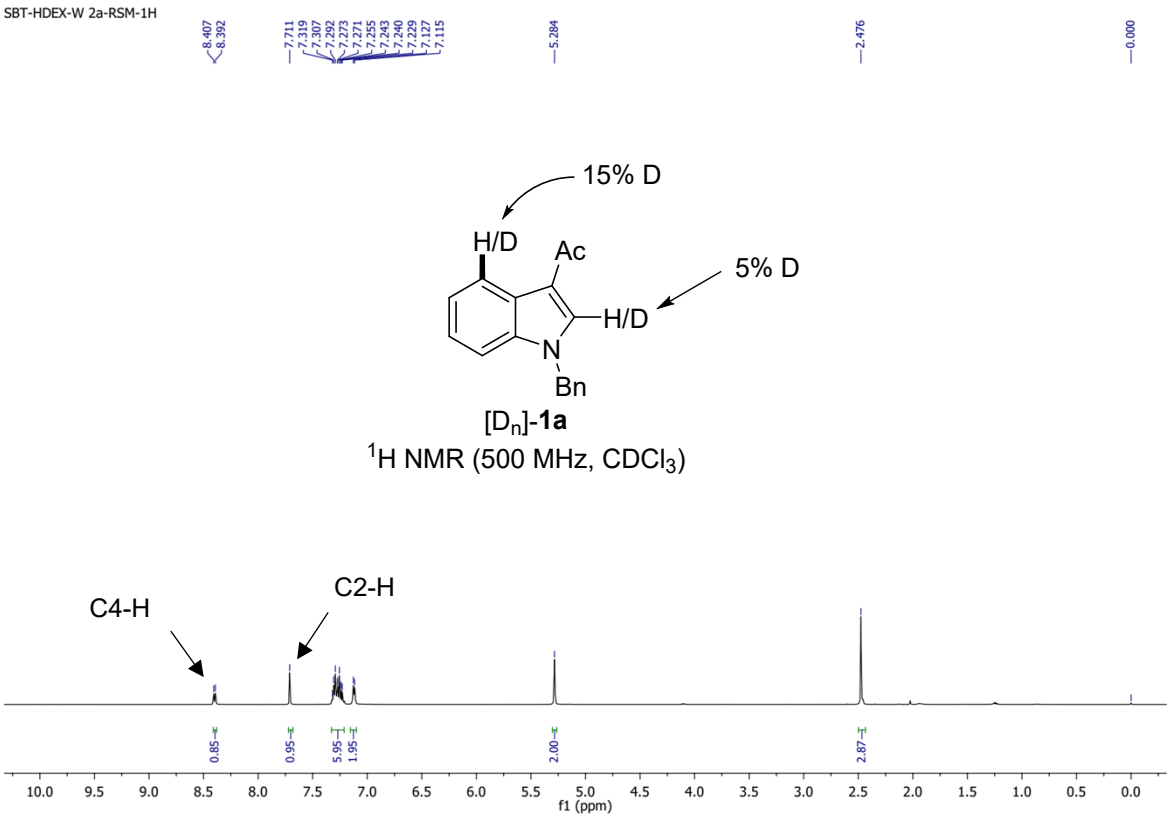

SBT-APP-DG removal-13C
MeO2C
CO2Me
N
Bn
5
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SBT-APP-Krapcho-1H
MeO2C
Ac
N
Bn
6
1H NMR (400 MHz, CDCl3)
f1 (ppm)


SBT-APP-Krapcho-13C
MeO2C
Ac
N
Bn
6
13C NMR (125 MHz, CDCl3)
f1 (ppm)

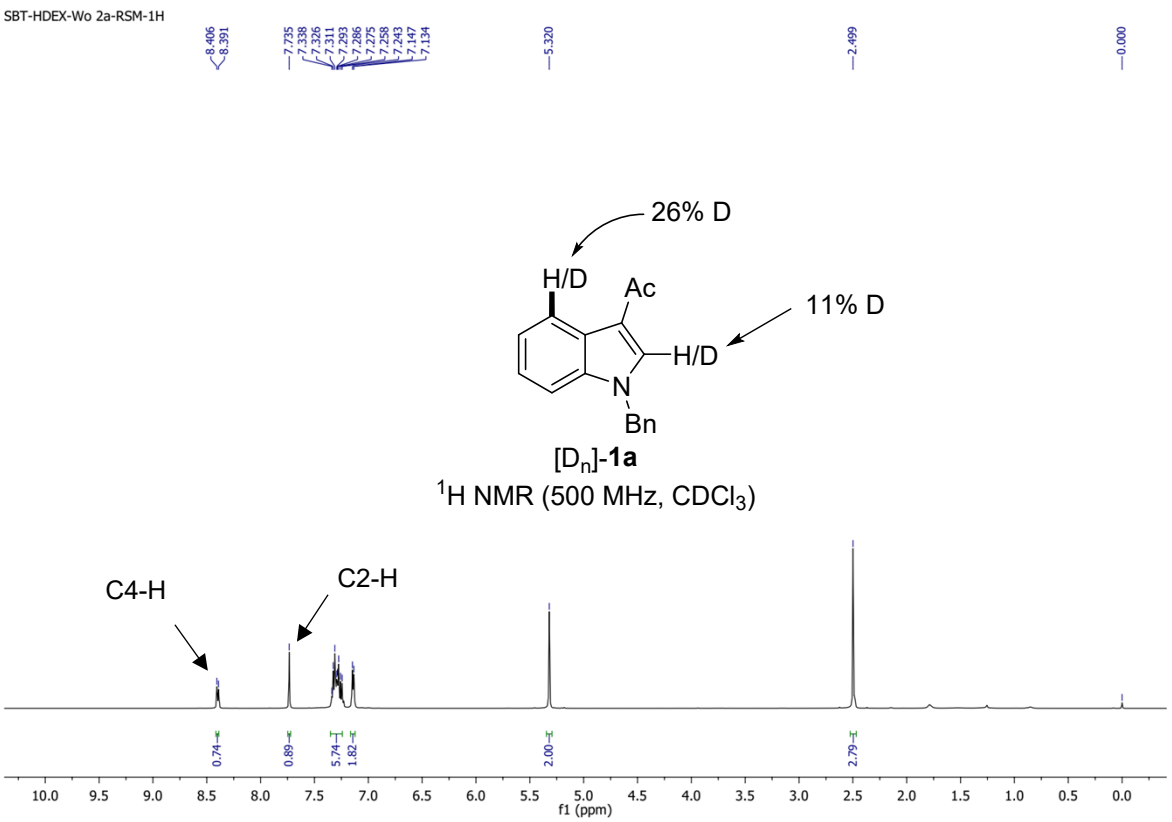

SBT-APP-SCE-1H
CO2Me
CO2Me
Ac
N
Bn
7
1H NMR (400 MHz, CDCl3)
f1 (ppm)


SBT-APP-SCE-13C
CO2Me
CO2Me
Ac
N
Bn
7
13C NMR (125 MHz, CDCl3)
f1 (ppm)



[D_n]-**1a**

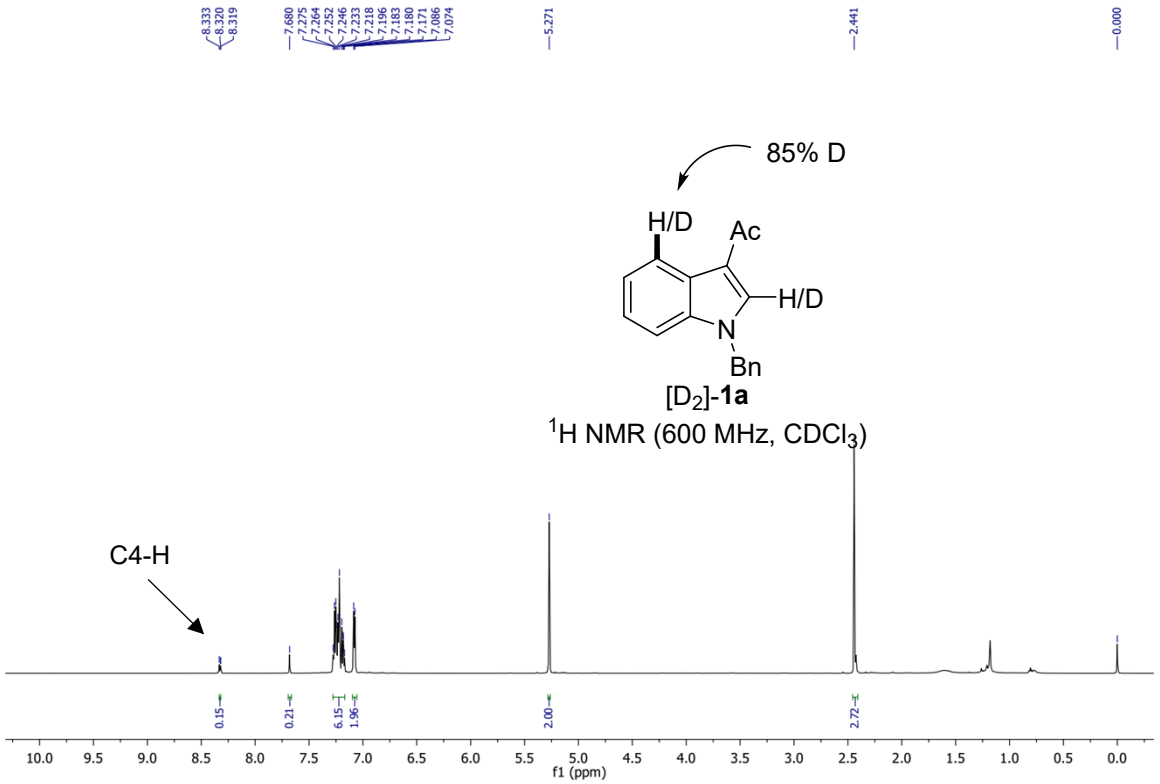
^{1}H NMR (500 MHz, $CDCl_3$)



[D_n]-**1a**

^{1}H NMR (500 MHz, $CDCl_3$)

SBT-D2-1a-1H



SBT-308-KHKD-RSM-1H