Catalytic Use of Elemental Gallium for Carbon–Carbon Bond Formation

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General and Additional Information

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1 General Experimental

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVA 400, Bruker AVA 500, Bruker PRO 500, and Bruker AVA 600 spectrometers, respectively. These spectrometers operate at the following frequencies: 400 MHz, 500 MHz, or 600 MHz for ^{1}H NMR; 100 MHz, 125 MHz, or 150 MHz for ^{13}C NMR; 77 MHz for ^{2}H NMR; 128 MHz or 160 MHz for ^{11}B NMR; 128 MHz for ^{19}F NMR; 162 MHz or 203 MHz for ^{31}P NMR; 152 MHz for ^{71}Ga NMR. Chemical shifts (δ) were quoted in parts per million (ppm) down-field to tetramethylsilane (TMS; δ = 0 ppm), or in the scale relative to the corresponding NMR solvent used as an internal reference. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Infrared (IR) spectra were recorded on a Shimadzu IR Affinity–1 instrument using the corresponding isolated NMR sample in $CDCl_3$ (attenuated total reflectance sampling technique). High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 900 XLT spectrometer [electrospray ionization (ESI) technique]. Chiral HPLC analyses were performed on a Shimadzu LC–20AT apparatus with an SPD–20A detector using 4.6 x 250 mm columns from DAICEL CHIRALPAK. Thin layer chromatography (TLC) was carried out on pre-coated silica gel plates from Merck (DF ALufolien 60F_{254}; 0.2 mm). Preparative thin-layer Chromatography (PTLC) was carried out on self-prepared plates using silica gel from Wakogel (B–5F; particle size: 45 μm). Flash column chromatography was carried out using silica gel from Fisher Scientific (60 Å; particle size: 40–63 μm). Product spots were visualized by UV light at 254 nm or with an appropriate stain solution.

Allyl boronic esters **2**[1] and **2**–[d_2][2] were prepared according to literature methods, respectively. The analytical data were in full agreement with the reported data. In this context, allyl magnesium bromide (1.0 M in Et_2O, Aldrich), trimethyl borate (99%, Aldrich), pinacol (99%, Alfa Aesar), vinyl boronic acid pinacol ester (95%, Aldrich), and chloroiodomethane–[d_2] (OMX Laboratories) were used. Octyl pinacol boronic ester was also synthesized according to a literature report;[3] the analytical data were in full agreement with the reported data. Allyl boronic ester MIDA complex (**4**; Aldrich), potassium allyl trifluoroborate (**5**; 95%, Aldrich), allenyl boronic ester **14** (97%, Aldrich), phenyl pinacol boronic ester (97%, Aldrich), 1-(trimethylsiloxy)cyclopentene (97%, Aldrich), and 2,6-di-*tert*-butylpyridine (97%, Aldrich) were purchased. Acetals **1a** (99%, Aldrich), **1h** (97%, Aldrich), **1o** (97%, TCI), **1v** (98%, Alfa Aesar), and ketal **1z'** (99%, Acros Organics) were purchased. Acetals **1b–g**,[4] **1i–n**,[4] **1p**,[5] **1q**,[6] **1r**,[7] **1s–u**,[4] **1y–z**,[4] and ketal **1z**[4] are literature-known and were prepared accordingly. In this context, trimethylorthoformate (99%, Aldrich) was used. Aminal *rac*-**12**[8] is literature-known and was prepared accordingly. The analyses of these substrates were in full agreement with the reported data. Gallium metal (99.9999%, Strem) and gallium(III) triflate (98%, Strem) were purchased; likewise, all other metal triflates for control experiments were purchased with the highest available purity. Silver triflate (99.95%, Aldrich), silver tetrafluoroborate (99.95%, Aldrich), silver carbonate (99.999%, Aldrich), silver nitrate (99.995%, Alfa Aesar), silver bistriflimide (97%, Aldrich), silver phosphate (99%, Alfa Aesar), silver hexafluorophosphate (99.99%, Aldrich), silver

hexafluoroantimonate (99%, Alfa Aesar), silver oxide (99.99%, Alfa Aesar), silver cyanate (99.995%, Aldrich), silver perchlorate (anhydrous, Alfa Aesar), silver fluoride (99.9%, Aldrich), silver chloride (99%, Acros Organics), silver bromide (99.9%, Alfa Aesar), silver iodide (99.999%, Alfa Aesar), and silver metal (powder, 99.9%, –35+45 mesh, Alfa Aesar) were purchased. [18]Crown-6 (99%, Alfa Aesar), dibenzo[18]crown-6 (98%, Alfa Aesar), [15]crown-5 (98%, Alfa Aesar), [12]crown-4 (98%, Aldrich), Mes–NHC (97%, Aldrich), Dipp–NHC (97%, Aldrich), and triphenylphosphine (99%, Alfa Aesar) were purchased. The corresponding (*R*)-BINOL precursor to silver phosphate (*R*)-**17** was purchased from Apollo Scientific Support Research Library. Unless otherwise stated, all reagents purchased from commercial suppliers were used directly without further purification. THF, toluene, and diethyl ether were distilled over sodium–benzophenone and stored over molecular sieves (4 Å) in a nitrogen glove box. All other solvents –including dioxane, benzene, mesitylene, DME, DCM, DCE, and MeCN– were used non-distilled, but stored over molecular sieves (4 Å) in a nitrogen glove box. Solvent dryness was confirmed using a Karl–Fischer apparatus.

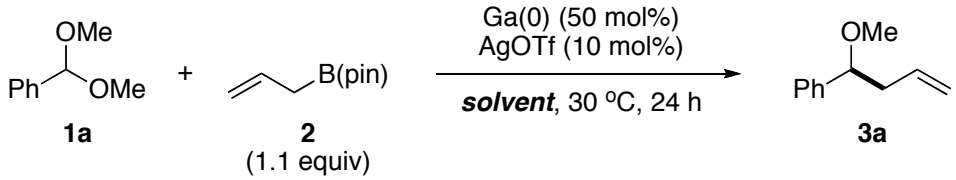
All catalytic reactions were carried out in in oven-dried glassware (typically sealed 10 mL test tubes) under an inert atmosphere. Conventional heating and stirring was performed using a magnetic stirring bar and a hot plate magnetic stirrer (sand bath). Ultrasonic activation was carried out –in the absence of a magnetic stirring bar– using the ultrasonicator bath FB15049 from Fisherbrand (power level: 37 kHz).

2 Additional Experiments

2.1 Conventional Heating and Stirring: Initial Solvent Screening (Table S–1)

Results for the initial screening of aromatic, etheral, and chlorinated solvents –with conventional heating and stirring– are summarized in Table S–1.

Table S–1: Initial solvent screening (conventional heating and stirring).



entry	***solvent***	yield (%)[a]
1	C_6H_6	32
2	C_6D_6	31
3	$H_3C–C_6H_5$	12
4	$F_3C–C_6H_5$	14
5	Et_2O	36
6	dioxane	50
7	THF	16
8	CH_2Cl_2	27
9	$C_2H_4Cl_2$	16

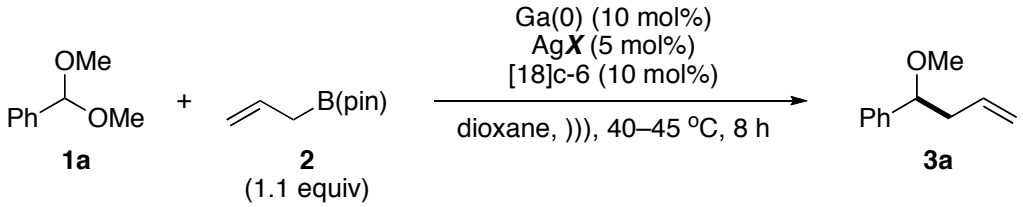
[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol%).

Among all solvents examined, the use of benzene, C_6D_6, Et_2O, and dioxane proved to be most effective (TON = 3–5; entries 1, 2, 5, and 6).

2.2 Ultrasonic Activation: Screening of Silver Salts (Table S–2)

Results for the screening of silver salts –under ultrasonic activation– are summarized in Table S–2.

Table S–2: Screening of silver salts (ultrasonic activation).



entry	Ag***X***	yield (%)[a]
1	AgOTf	99[b]
2	$AgBF_4$	21
3	Ag_2CO_3	NR[c]
4	$AgNO_3$	NR[c]
5	$AgNTf_2$	NR[c]
6	Ag_3PO_4	NR[c]
7	$AgPF_6$	NR[c]
8	$AgSbF_6$	22
9	Ag_2O	NR[c]
10	AgOCN	4
11	$AgClO_4$	2
12	AgF	63
13	AgCl	60
14	AgBr	5
15	AgI	NR[c]

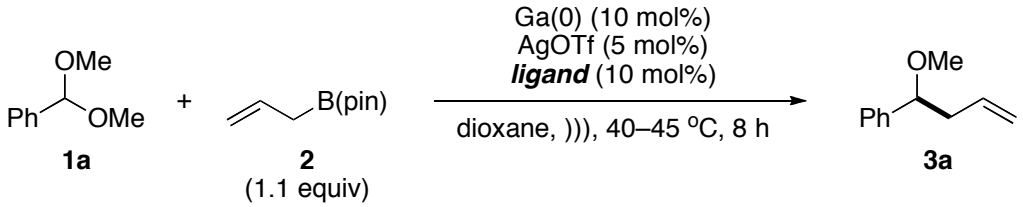
[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol%). [b] The same result was obtained when the experiment was carried out in the presence of 2,6-di-*tert*-butylpyridine (10 mol%). [c] NR = no reaction; the desired product **3a** was not detected – only starting materials were recovered (^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture).

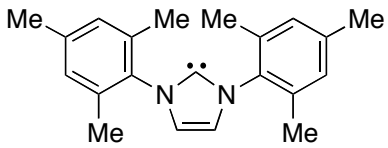
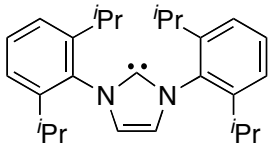
Among all silver salts examined, AgOTf proved to be the most effective co-catalyst (99% yield; entry 1); the participation of protons in this Ga(I) catalysis was ruled out through conducting the same experiment in the presence of a proton-trapping agent (*same result*). Most other salts displayed no catalytic activity, or provided **3a** in only up to 22% yield (entries 2–11, 14, and 15). AgF and AgCl displayed moderate catalytic activity (60–63% yields; entries 12 and 13).

2.3 Ultrasonic Activation: Screening of Ligands (Table S–3)

Results for the screening of ligands –under ultrasonic activation– are summarized in Table S–3.

Table S–3: Screening of ligands (ultrasonic activation).



Entry	***Ligand***	yield (%)[a]
1	–	67
2	[18]crown-6	99
3	dibenzo[18]crown-6	67
4	[15]crown-5	17
5	[12]crown-4	73
6		NR[b]
7		NR[b]
8	PPh_3	NR[b]

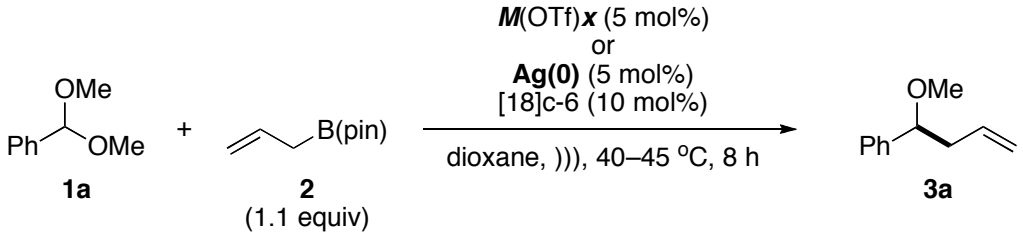
[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol%). [b] NR = no reaction; the desired product **3a** was not detected – only starting materials were recovered (^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture).

Under standard conditions, in the absence of [18]crown-6, product **3a** was obtained in 53% yield, whereas [18]crown-6 ligation gave **3a** in 99% yield (entry 1 vs. entry 2). Other crown ether ligands proved to be less efficient (17–73% yields; entries 3–5). Strong σ donor ligands, such as carbenes and phosphines, shut down completely the reaction (entries 6–8).

2.4 Ultrasonic Activation: Control Experiments with $M(OTf)_x$ or Ag(0) (Table S–4)

Results for the control experiments with other metal triflates or Ag(0) [*being the stoichiometric by-product of the Ga(I) catalyst formation*] –under ultrasonic activation– are summarized in Table S–4.

Table S–4: Control experiments with other metal triflates or Ag(0) (ultrasonic activation).



entry	$\underline{M}(OTf)_{\underline{x}}$	yield (%)[a]
1	LiOTf	NR[b]
2	$Mg(OTf)_2$	NR[b]
3	$Ca(OTf)_2$	NR[b]
4	$Al(OTf)_3$	NR[b]
5	$Ga(OTf)_3$	3
6	$Sn(OTf)_2$	NR[b]
7	$Sc(OTf)_3$	NR[b]
8	$Mn(OTf)_2$	NR[b]
9	$Fe(OTf)_2$	NR[b]
10	$Ni(OTf)_2$	NR[b]
11	$(CuOTf)_2$•toluene	4
12	$Cu(OTf)_2$	NR[b]
13	$Zn(OTf)_2$	NR[b]
14	AgOTf	NR[b]
15	Ag(0)	NR[b]

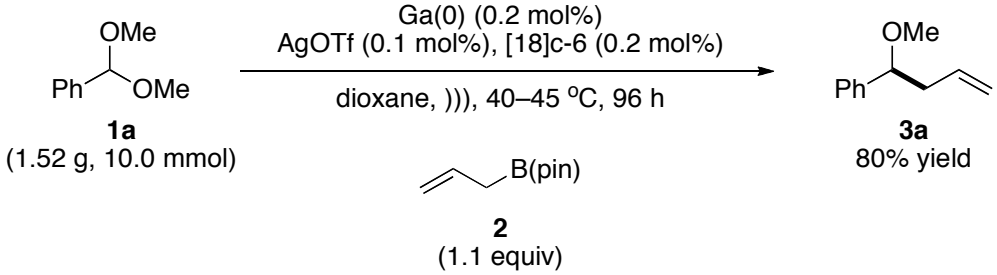
[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol%). [b] NR = no reaction; the desired product **3a** was not detected – only starting materials were recovered (^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture).

Among all commercially available metal triflates examined, the vast majority led only to the recovery of starting materials; the formation of product **3a** was not observed (entries 1–4, 6–10, and 12–14). In two cases, traces of product **3a** were detected: Ga(III) and Cu(I) (entries 5 and 11). In this context, the use of Ag(0) also failed to give **3a** (entry 15).

2.5 Gram-Scale Reaction at Low Catalyst Loading (Scheme S–1)

The result for an appropriate gram-scale experiment at low catalyst loading is summarized in Scheme S–1.

Scheme S–1: Gram-scale experiment at low catalyst loading.

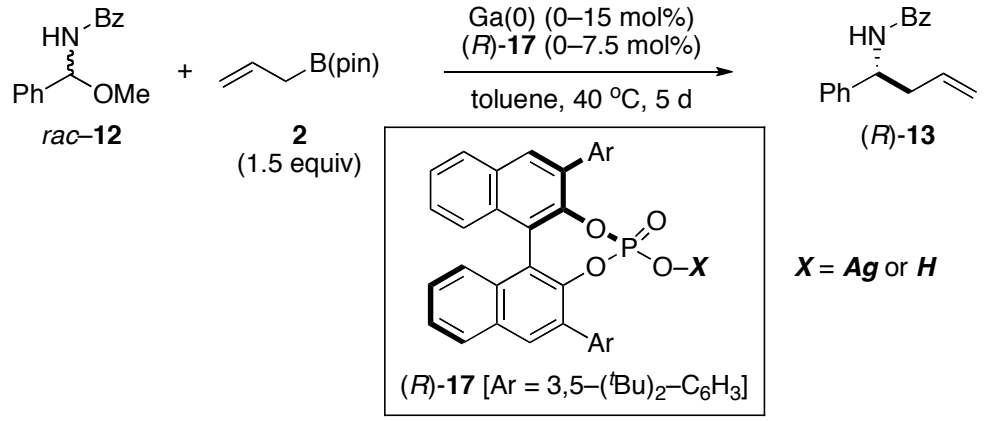


The use of 0.2 mol% of elemental gallium –combined with 0.1 mol% of silver(I) triflate and 0.2 mol% of [18]crown-6– is expected to give 0.1 mol% of the *in situ* gallium(I) catalyst = actual catalyst loading.

2.6 Control Experiments for Asymmetric Catalysis (Table S–5)

Results regarding control experiments for asymmetric catalysis –with conventional heating and stirring– are summarized in Table S–5.

Table S–5: Control experiments for asymmetric catalysis (conventional heating and stirring).



Entry	Ga(0) (15 mol%)	(*R*)-17 (7.5 mol%)	yield (%)[a] / *ee* (%)[b]
1	+	+ [***X*** = ***Ag***]	60 / 40
2	+	+ [***X*** = ***H***]	NR[c]
3	+	–	NR[c]
4	–	+ [***X*** = ***Ag***]	18 / 17
5	–	+ [***X*** = ***H***]	NR[c]

[a] The yield was determined by ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture; internal standard: dibenzyl ether (25 mol%). [b] The enantiomeric excess (*ee*) was determined by chiral HPLC analysis of a purified sample of **13**. [c] NR = no reaction; the desired product **13** was not detected – only starting materials were recovered (^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture).

The combined use of gallium(0) and silver salt (*R*)-**17** (***X*** = ***Ag***) gave product (*R*)-**13** in 60% yield with 40% *ee* (entry 1). The combination of gallium(0) and acid (*R*)-**17** (***X*** = ***H***) or the sole use of gallium(0) failed to catalyze this reaction (entries 2 and 3). In the absence of gallium(0), the sole use of silver salt (*R*)-**17** (***X*** = ***Ag***) or acid (*R*)-**17** (***X*** = ***H***) gave poor results (entries 4 and 5).

3 General Procedures for *In Situ* Gallium(I) Catalysis

General Procedure A **[Standard Conditions = Ultrasonic Activation]**

Gallium(0) (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%) or silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%), the corresponding acetal/ketal **1** (0.20 mmol), allyl boronic ester **2** (37.0–50.4 mg, 0.22–0.30 mmol, 1.1–1.5 equiv), and dioxane (200µL, 1.0 M) or toluene (400–800 µL, 0.25–0.50 M) were added to an oven-dried 10 mL test tube in a nitrogen-filled glove box. The mixture was reacted under ultrasonic activation at 40–50 °C for 8–78 h (inert atmosphere), at which point ^{1}H NMR spectroscopic analysis indicated the complete consumption of **1**. The solvent was removed *in vacuo*, and the residue was purified by PTLC on silica gel –as indicated– to give the corresponding homoallyl ether **3**.

Alternatively, allyl boronic ester **2**–[d_2] (51.0 mg, 0.30 mmol, 1.5 equiv) and allenyl boronic ester **14** (39.9 mg, 0.24 mmol, 1.2 equiv) have been used instead of **2** under otherwise identical conditions. Likewise, aminal *rac*-**12** (48.3 mg, 0.20 mmol) has been used instead of **1**; in this specific case ultrasonic activation was *not* required.

General Procedure B **[Gram-Scale & Low Catalyst Loading]**

Gallium(0) (1.4 mg, 0.02 mmol, 0.20 mol%), silver triflate (2.8 mg, 0.01 mmol, 0.10 mol%), [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%), acetal **1a** (1.52 g, 10.0 mmol), allyl boronic ester **2** (1.85 g, 11.0 mmol, 1.1 equiv), and dioxane (10 mL, 1.0 M) were added to an oven-dried 50 mL round-bottom flask in a nitrogen-filled glove box. The mixture was reacted under ultrasonic activation at 40–45 °C for 96 h (inert atmosphere). The solvent was removed *in vacuo*, and the residue was purified by flash column chromatography on silica gel (eluent: heptane/EtOAc = 19:1) to give homoallyl ether **3a** in 80% yield (1.30 g) as a pale yellow liquid.

General Procedure C **[Asymmetric Version]**

Gallium(0) (2.1 mg, 0.03 mmol, 15 mol%), silver phosphate (*R*)-**17** (8.3 mg, 0.015 mmol, 7.5 mol%), aminal *rac*-**12** (48.3 mg, 0.20 mmol), allyl boronic ester **2** (50.4 mg, 0.30 mmol, 1.5 equiv), and toluene (200 µL, 1.0 M) were added to an oven-dried 10 mL test tube with a magnetic stirring bar in a nitrogen-filled glove box. The reaction mixture was stirred at 40 °C for 5 days (inert atmosphere). The solvent was removed *in vacuo*, and the residue was purified by PTLC on silica gel [eluent: PE(40–60)/Et_2O = 5:1, *eluted 4 times*] to give homoallyl amide **13** –with predominant *R* configuration– as a colorless solid. The optical purity of the product was determined by chiral HPLC analysis (DAICEL CHIRALPAK IF).

4 Mechanistic Experiments

4.1 *In Situ* Generation of Gallium(I) Catalyst 6 from Gallium(0)

Gallium metal (27.9 mg, 0.40 mmol), silver triflate (51.4 mg, 0.20 mmol, 0.5 equiv), [18]crown-6 (106 mg, 0.40 mmol, 1 equiv), and dioxane (400 µL, 1.0 M) were added to an oven-dried 10 mL test tube in a nitrogen-filled glove box. The mixture was reacted under ultrasonic activation at 40–45 °C for 36 h (inert atmosphere), at which point the reaction mixture (*100 µL aliquot*) was analyzed by ^{71}Ga NMR spectroscopy (Young NMR tube). The spectrum displayed a single resonance at –566 ppm, which has been ascribed –in analogy to literature– to a novel gallium(I) species, i.e., gallium(I) catalyst **6**: [18]c-6–Ga(I)•(dioxane)$_n$OTf (n = 1,2,3). *Efforts to isolate or further characterize this highly reactive species by ^{1}H NMR and ^{13}C NMR spectroscopy, HRMS, or X-ray analysis failed to give conclusive results.* Evidence for Ga(II) or Ga(III) species were not detected under these conditions.

^{71}Ga NMR (C_6D_6, 152 MHz): δ = –566 ppm (**6**).

4.2 Detection of Gallium(I) Catalyst 6 after C–C Bond Formation

Acetal **1a** (30.4 mg, 0.20 mmol, 1 equiv) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) were added to the pre-formed solution of gallium(I) catalyst **6** (0.20 mmol; *see 4.1*) in a nitrogen-filled glove box and kept at 40 °C for 4 h (Young NMR tube), at which point the reaction mixture was analyzed by ^{11}B and ^{71}Ga NMR spectroscopy (*100 µL aliquot*). The ^{11}B NMR spectrum displayed the appearance of a novel major resonance at 22 ppm, which has been ascribed to the stoichiometric by-product of the C–C bond formation between **1a** and **2**, MeO–B(pin) (**7**); a second minor signal at 33 ppm, corresponding to residual **2**, was detected as well. *In this context, ^{1}H NMR spectroscopy confirmed the formation of homoallyl ether **3a** in >99% yield*. The ^{71}Ga NMR spectrum displayed a single resonance at –587 ppm, which has been ascribed to the regenerated gallium(I) catalyst **6** (which is now in a slightly different medium, hence, a slightly different chemical shift was observed). Evidence for Ga(II) or Ga(III) species were not detected under these conditions.

^{11}B NMR (C_6D_6, 128 MHz): δ = 33 ppm (*minor = residual **2***), 22 ppm (*major = **7***).
^{71}Ga NMR (C_6D_6, 152 MHz): δ = –587 ppm (regenerated **6**).

4.3 Stoichiometric Activation of Acetal 1a by Gallium(I) Catalyst 6

Acetal **1a** (30.4 mg, 0.20 mmol, 1 equiv) was added to the pre-formed solution of gallium(I) catalyst **6** (0.20 mmol; *see 4.1*) in a nitrogen-filled glove box and kept at 40 °C for 2 h (Young NMR tube), at which point the reaction mixture was analyzed by HRMS (ESI) and ^{71}Ga NMR spectroscopy (*100 µL aliquot*). The analysis by HRMS (ESI) revealed the formation of the corresponding oxocarbenium ion species **8**. [*In this context, **8** was not detected when a mixture of **1a**, AgOTf, and [18]c-6 was used under otherwise identical*

conditions (no gallium)]. Accordingly, the concomitant formation of a gallium(I) methoxide species **9**, [Ga(I)]–OMe, may be concluded. The ^{71}Ga NMR spectrum did not display any signal, which is in accordance with literature precedents of electron-rich gallium(I) complexes bearing phosphine or carbene ligands. *Efforts to isolate or further characterize this highly reactive species by ^{1}H NMR and ^{13}C NMR spectroscopy, HRMS, or X-ray analysis failed to give conclusive results.* Evidence for Ga(II) or Ga(III) species were not detected under these conditions. *After addition of **2** to the mixture of **8** and **9**, homoallyl ether **3a** was smoothly formed in >99% yield (^{1}H NMR spectroscopy).*

HRMS (ESI): calculated for $C_8H_9O^+ = [M]^+$: *m/z* = 121.0679, found: *m/z* = 121.0671 (**8**).
^{71}Ga NMR (C_6D_6, 152 MHz): *no signal* (**9**).

4.4 Attempted Activation of Boronic Ester 2 by Gallium(I) Catalyst 6

Allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) was added to the pre-formed solution of gallium(I) catalyst **6** (0.20 mmol; *see 4.1*) in a nitrogen-filled glove box and kept at 40 °C for 24 h (Young NMR tube), at which point the reaction mixture was analyzed by ^{11}B and ^{71}Ga NMR spectroscopy (*100 µL aliquot*). The ^{11}B NMR spectrum displayed a single resonance at 33 ppm, which corresponds to remaining **2**. The ^{71}Ga NMR spectrum displayed a single resonance at –566 ppm, which corresponds to remaining **6**. Thus, a reaction did not occur under these conditions; evidence for Ga(II) or Ga(III) species were not detected neither.

^{11}B NMR (C_6D_6, 128 MHz): δ = 33 ppm (**2**; *no change*).
^{71}Ga NMR (C_6D_6, 152 MHz): δ = –566 ppm (**6**; *no change*).

4.5 Stoichiometric Activation of Boron–Ate Complex 10 by Gallium(I) Catalyst 6

Allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) and K–OMe (14.0 mg, 0.20 mmol) were reacted in dioxane (200 µL, 1.0 M) at 40 °C for 18 h to form the corresponding boron–ate complex **10**, allyl–B$^-$(OMe)(pin) K$^+$. The generation of this species was confirmed by ^{11}B NMR spectroscopic analysis, which displayed two signals at 33 ppm (minor; residual **2**) and 7 ppm (major; **10**). The solution of **10** was added to the pre-formed solution of gallium(I) catalyst **6** (0.20 mmol; *see 4.1*) in a nitrogen-filled glove box and kept at 40 °C for 2 h (Young NMR tube), at which point the reaction mixture was analyzed by ^{11}B and ^{71}Ga NMR spectroscopy (*100 µL aliquot*). The ^{11}B NMR spectrum displayed the appearance of a novel major resonance at 22 ppm, which has been ascribed to the stoichiometric by-product of the B–Ga transmetalation between **10** and **6**, MeO–B(pin) (**7**); a second minor signal at 33 ppm, corresponding to residual **2**, was detected alongside with a trace of **10** (7 ppm). The ^{71}Ga NMR spectrum revealed a novel single resonance at –624 ppm, which has been ascribed to unprecedented allyl gallium(I) species **11** (likely σ and π complexes in equilibrium). *Efforts to isolate or further characterize this highly reactive species by ^{1}H NMR and ^{13}C NMR spectroscopy, HRMS, or X-ray analysis failed to give*

conclusive results. Evidence for Ga(II) or Ga(III) species were not detected under these conditions.

^{11}B NMR (C_6D_6, 128 MHz): δ = 33 ppm (*minor = residual **2***), 22 ppm (*major = **7***), 7 ppm (*trace = **10***).

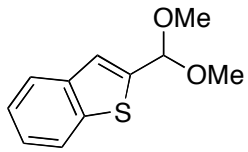
^{71}Ga NMR (C_6D_6, 152 MHz): δ = –624 ppm (**11**).

5 Analytical Data for Unknown Compounds

5.1 Analytical Data for Acetals 1a–y, Ketals 1z–z', and Aminal *rac*-12

The synthesized acetals **1b**,[9] **1c**,[10] **1d**,[11] **1e–g**,[12] **1i**,[13] **1j–n**,[12] **1p**,[5] **1q**,[6] **1r**,[7] **1s–t**,[14] **1w–y**,[12] ketal **1z**,[15] and aminal *rac*-**12**[8] are literature-known, and thee obtained analytical data are in full agreement with the reported data. The obtained analytical data for the novel acetals **1u–v** and ketal **1z'** are listed below.

2-(Dimethoxymethyl)benzo[*b*]thiophene (1u)



1u

Pale yellow liquid.

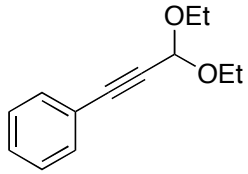
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.41 (s, 6H), 5.71 (s, 1H), 7.29–7.37 (m, 3H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 52.7 (2C), 100.2, 122.3, 122.5, 123.8, 124.3, 124.4, 139.4, 140.0, 142.3 ppm.

IR (neat): ν = 2933, 1458, 1435, 1346, 1186, 1139, 1042, 977, 744, 725 cm^{-1}.

HRMS (ESI): calculated for $C_{11}H_{12}NaO_2S^+$ = $[M+Na]^+$: *m/z* = 231.0450, found: *m/z* = 231.0453.

(3,3-Diethoxyprop-1ynyl)benzene (1v)



1v

Pale yellow liquid.

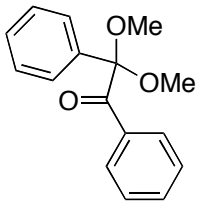
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.25 (t, *J* = 8.5 Hz, 6H), 3.45–3.60 (m, 2H), 3.79–3.93 (m, 2H), 5.49 (s, 1H), 7.27–7.34 (m, 3H), 7.40–7.51 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.2 (2C), 61.0 (2C), 84.4, 85.2, 91.8, 121.9 (2C), 128.3, 128.8 (2C), 132.0 ppm.

IR (neat): ν = 2927, 2237, 1489, 1354, 1327, 1093, 1042, 1006, 754, 680 cm^{-1}.

HRMS (ESI): calculated for $C_{13}H_{16}NaO_2^+$ = $[M+Na]^+$: *m/z* = 227.1043, found: *m/z* = 227.1057.

2,2-Dimethoxy-1,2-diphenylethanone (1z')



1z'

Colorless solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.22 (s, 6H), 7.27–7.33 (m, 3H), 7.33–7.38 (m, 2H), 7.38–7.45 (m, 1H), 7.59–7.65 (m, 2H), 8.03–8.08 (m, 2H) ppm.

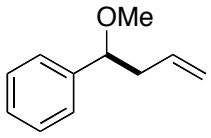
^{13}C NMR ($CDCl_3$, 150 MHz): δ = 50.1 (2C), 103.6, 127.0 (2C), 128.1 (2C), 128.5 (2C), 128.9, 130.0 (2C), 132.9, 134.3, 136.9, 195.2 ppm.

IR (neat): ν = 2974, 1689, 1448, 1234, 1040, 1018, 866, 758, 688, 659 cm^{-1}.

HRMS: Mass spectroscopic analyses (various techniques) failed to give the molecular signal, resulting only in fragmentation.

5.2 Analytical Data for Homoallyl Ethers 3a–z', 3a–[d_2], and 3'a–[d_2]

(1-Methoxybut-3-enyl)benzene (3a)[12]

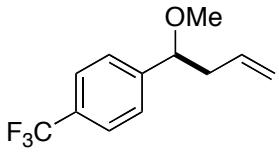


3a

Prepared from acetal **1a** (30.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3a** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 29.4 mg (91%).

1-(1-Methoxybut-3-enyl)-4-(trifluoromethyl)benzene (3b)



3b

Prepared from acetal **1b** (44.0 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3b** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Colorless liquid.
Yield: 42.5 mg (92%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.39–2.42 (m, 1H), 2.53–2.56 (m, 1H), 3.24 (s, 3H), 4.23 (dd, *J* = 6.3, 7.0 Hz, 1H), 5.03–5.06 (m, 2H), 5.74 (dddd, *J* = 6.9, 7.0, 9.7, 17.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H) ppm.

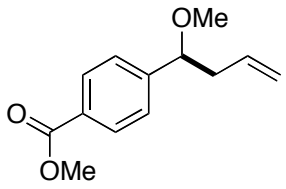
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 42.3, 56.9, 83.1, 117.5, 124.2 (q, *J* = 271.8 Hz), 125.4 (q, *J* = 3.8 Hz, 2C), 127.0 (2C), 129.9 (q, *J* = 32.4 Hz), 134.0, 145.9 ppm.

^{19}F NMR ($CDCl_3$, 128 MHz): δ = –62.4 ~ –62.5 (m) ppm.

IR (neat): ν = 1320, 1163, 1122, 1097, 1064, 916, 837 cm^{-1}.

HRMS: Mass spectroscopic analyses (various techniques) failed to give the molecular signal, resulting only in fragmentation.

Methyl 4-(1-methoxybut-3-enyl)benzoate (3c)[14]

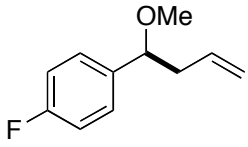


3c

Prepared from acetal **1c** (42.0 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3c** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[14]

Colorless liquid.
Yield: 40.3 mg (92%).

1-Fluoro-4-(1-methoxybut-3-enyl)benzene (3d)[16]

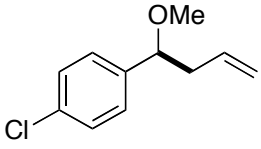


3d

Prepared from acetal **1d** (34.0 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2,8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3d** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[16]

Pale yellow liquid.
Yield: 32.0 mg (89%).

1-Chloro-4-(1-methoxybut-3-enyl)benzene (3e)[12]



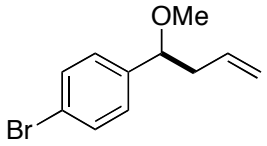
3e

Prepared from acetal **1e** (37.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol,

10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3e** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 36 mg (92%).

1-Bromo-4-(1-methoxybut-3-enyl)benzene (3f)[12]

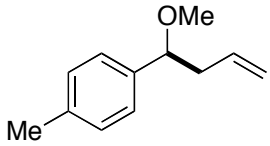


3f

Prepared from acetal **1f** (46.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3f** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 44.2 mg (92%).

1-(1-Methoxybut-3-enyl)-4-methylbenzene (3g)[12]

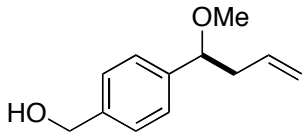


3g

Prepared from acetal **1g** (33.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 20 h. **3g** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 33.0 mg (94%).

[4-(1-Methoxybut-3-enyl)phenyl]methanol (3h)



3h

Prepared from acetal **1h** (36.4 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in toluene (200 µL, 1.0 M) under ultrasonication at 50 °C for 20 h. **3h** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 9:1; *eluted twice*).

Colorless liquid.

Yield: 20.0 mg (57%).

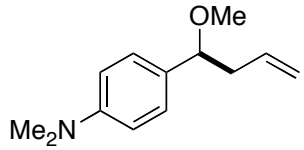
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.64 (br s, 1H), 2.38–2.42 (m, 1H), 2.54–2.59 (m, 1H), 3.22 (s, 3H), 4.17 (dd, *J* = 6.0, 7.3 Hz, 1H), 4.70 (s, 2H), 5.01–5.08 (m, 2H), 5.71–5.81 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 42.5, 56.7, 65.2, 83.4, 117.0, 127.0 (2C), 127.1 (2C), 134.7, 140.2, 141.2 ppm.

IR (neat): ν = 3421, 2862, 2849, 1463, 1095, 1016, 914, 819 cm^{-1}.

HRMS (ESI): calculated for $C_{12}H_{16}NaO_2^+$ = $[M+Na]^+$: *m/z* = 215.1043, found: *m/z* = 215.1053.

4-(1-Methoxybut-3-enyl)-*N*,*N*-dimethylaniline (3i)



3i

Prepared from acetal **1i** (39.1 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in toluene (800 µL, 0.25 M) under ultrasonication at 40–45 °C for 20 h. **3i** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Pale yellow liquid.

Yield: 22.1 mg (54%).

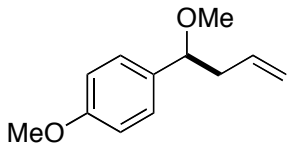
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.37–2.42 (m, 1H), 2.54–2.59 (m, 1H), 2.95 (s, 6H), 3.18 (s, 3H), 4.07 (dd, *J* = 6.2, 7.4 Hz, 1H), 5.00–5.07 (m, 2H), 5.75–5.80 (m, 1H), 6.71 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 40.6 (2C), 42.4, 56.2, 83.3, 112.3 (2C), 116.5, 127.8 (2C), 129.3, 135.4, 150.2 ppm.

IR (neat): ν = 2918, 2828, 1614, 1521, 1346, 1274, 1261, 1093, 912, 756 cm^{-1}.

HRMS (ESI): calculated for $C_{13}H_{19}NaNO^+$ = $[M+Na]^+$: *m/z* = 228.1359, found: *m/z* = 228.1358.

1-Methoxy-4-(1-methoxybut-3-enyl)benzene (3j)[12]

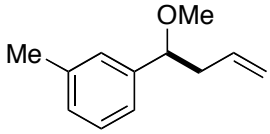


3j

Prepared from acetal **1j** (36.4 mg, 0.20 mmol) and allyl boronic acid **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 20 h. **3j** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 35.6 mg (93%).

1-(1-Methoxybut-3-enyl)-3-methylbenzene (3k)[12]

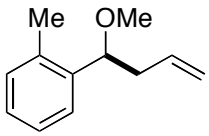


3k

Prepared from acetal **1k** (33.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3k** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 32.1 mg (91%).

1-(1-Methoxybut-3-enyl)-2-methylbenzene (3l)[12]



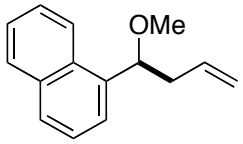
3l

Prepared from acetal **1l** (33.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol,

10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3l** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 32.0 mg (90%).

1-(1-Methoxybut-3-enyl)naphthalene (3m)[12]

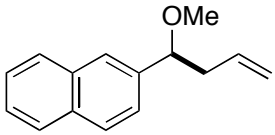


3m

Prepared from acetal **1m** (40.4 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3m** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 38.5 mg (91%).

2-(1-Methoxybut-3-enyl)naphthalene (3n)[12]

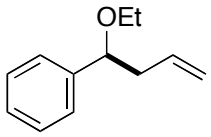


3n

Prepared from acetal **1n** (40.4 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 8 h. **3n** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 38.1 mg (91%).

(1-Ethoxybut-3-enyl)benzene (3o)[17]

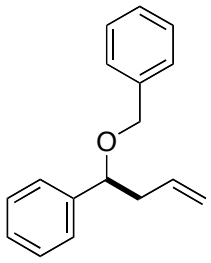


3o

Prepared from acetal **1o** (36.0 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 μL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3o** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[17]

Colorless liquid.
Yield: 31.4 mg (87%).

[1-(Benzyloxy)but-3-enyl]benzene (3p)[5,18]

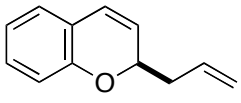


3p

Prepared from acetal **1p** (54.4 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 μL, 1.0 M) under ultrasonication at 40–45 °C for 20 h. **3p** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[5,18]

Colorless liquid.
Yield: 42.0 mg (88%).

2-Allyl-2*H*-chromene (3q)[19]



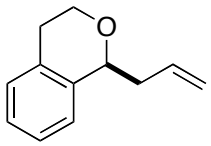
3q

Prepared from acetal **1q** (32.8 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol,

10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 52 h. **3q** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[19]

Colorless liquid.
Yield: 27.5 mg (80%).

1-Allylisochroman (3r)[14]

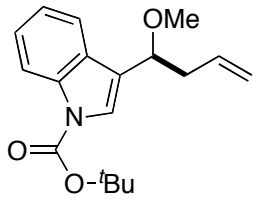


3r

Prepared from acetal **1r** (32.8 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 12 h. **3r** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[14]

Colorless liquid.
Yield: 31.2 mg (90%).

***Tert*-butyl-3-(1-methyoxybut-3-enyl)-1*H*-indole-1-carboxylate (3s)**[14]

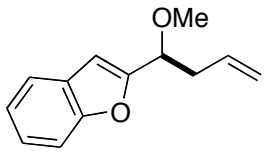


3s

Prepared from acetal **1s** (58.2 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in toluene (400 µL, 0.5 M) under ultrasonication at 50 °C for 16 h. **3s** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[14]

Pale yellow liquid.
Yield: 51.0 mg (84%).

2-(1-Methoxybut-3-enyl)benzofuran (3t)[14]

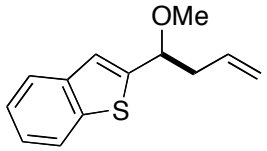


3t

Prepared from acetal **1t** (38.4 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 20 h. **3t** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[14]

Pale yellow liquid.
Yield: 37.0 mg (90%).

2-(1-Methoxybut-3-enyl)benzo[*b*]thiophene (3u)



3u

Prepared from acetal **1u** (41.6 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in toluene (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 20 h. **3u** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Pale yellow liquid.
Yield: 35.0 mg (80%).

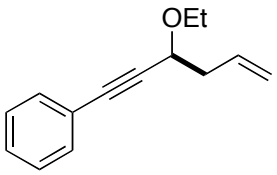
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.54–2.60 (m, 1H), 2.68–2.75 (m, 1H), 3.32 (s, 3H), 4.49 (dd, *J* = 6.7, 6.8 Hz, 1H), 5.04–5.13 (m, 2H), 5.80 (dddd, *J* = 6.9, 7.0. 10.3, 17.2 Hz, 1H), 7.18 (s, 1H), 7.27–7.35 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 42.3, 56.8, 79.7, 117.6, 122.0, 122.6, 123.4, 124.2 (2C), 133.9, 139.3, 139.7, 146.5 ppm.

IR (neat): ν = 2924, 1458, 1436, 1350, 1193, 1110, 916, 827, 746, 727 cm^{-1}.

HRMS (ESI): calculated for $C_{13}H_{14}NaOS^+$ = $[M+Na]^+$: *m/z* = 241.0658, found: *m/z* = 241.0667.

(3-Ethoxyhex-5-en-1-ynyl)benzene (3v)



3v

Prepared from acetal **1v** (40.9 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 78 h. **3v** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Colorless liquid.
Yield: 33.6 mg (85%).

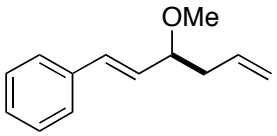
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.25 (dd, *J* = 7.0, 7.0 Hz, 3H), 2.53–2.61 (m, 2H), 3.50–3.56 (m, 1H), 3.84–3.90 (m, 1H), 4.29 (dd, *J* = 6.5, 6.6 Hz, 1H), 5.12–5.21 (m, 2H), 5.95 (dddd, *J* = 6.9, 7.0, 10.2, 17.2 Hz, 1H), 7.28–7.31 (m, 3H), 7.42–7.44 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 15.1, 40.3, 64.3, 69.5, 85.9, 88.1, 117.6, 122.8, 128.2 (2C), 128.3, 131.8 (2C), 133.8 ppm.

IR (neat): ν = 2976, 2358, 2339, 1489, 1334, 1089, 914, 760, 690 cm^{-1}.

HRMS (ESI): calculated for $C_{14}H_{16}NaO^+$ = $[M+Na]^+$: *m/z* = 223.1093, found: *m/z* = 223.1118.

(*E*)-(3-Methoxyhexa-1,5-dienyl)benzene (3w)[12]

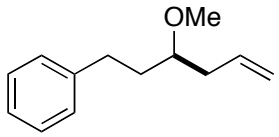


3w

Prepared from acetal **1w** (35.6 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 50 °C for 20 h. **3w** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Pale yellow liquid.
Yield: 27.0 mg (72%).

(3-Methoxyhex-5-enyl)benzene (3x)[12]

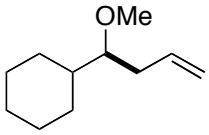


3x

Prepared from acetal **1x** (36.5 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 50 °C for 20 h. **3x** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Pale yellow liquid.
Yield: 32.0 mg (84%).

(1-Methoxybut-3-enyl)cyclohexane (3y)[12]

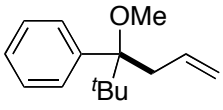


3y

Prepared from acetal **1y** (31.6 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 50 °C for 20 h. **3y** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[12]

Colorless liquid.
Yield: 26.9 mg (80%).

(3-Methoxy-2,2-dimethylhex-5-en-3-yl)benzene (3z)



3z

Prepared from acetal **1z** (41.6 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 50 °C for 40 h. **3z** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Colorless liquid.

Yield: 39.8 mg (91%).

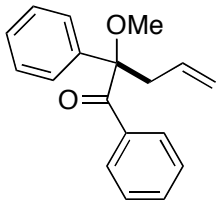
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (s, 9H), 2.94–3.03 (m, 2H), 3.22 (s, 3H), 4.97 (ddd, *J* = 2.2, 3.4, 10.2 Hz, 1H), 5.13 (ddd, *J* = 2.2, 3.4, 17.2 Hz, 1H), 5.93–6.00 (m, 1H), 7.21–7.32 (m, 5H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 26.5 (3C), 37.0, 39.5, 52.6, 85.3, 115.3, 126.2, 126.8 (2C), 129.3 (2C), 137.3. 140.8 ppm.

IR (neat): ν = 2958, 1483, 1444, 1392, 1363, 1097, 1074, 906, 748, 705 cm^{-1}.

HRMS (ESI): calculated for $C_{15}H_{22}NaO^+$ = $[M+Na]^+$: *m/z* = 241.1563, found: *m/z* =241.1557.

2-Methoxy-1,2-diphenylpent-4-en-1-one (3z')



3z'

Prepared from acetal **1z'** (51.3 mg, 0.20 mmol) and allyl boronic ester **2** (37.0 mg, 0.22 mmol, 1.1 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45°C for 60 h. **3z'** was purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1).

Colorless liquid.

Yield: 43.6 mg (82%).

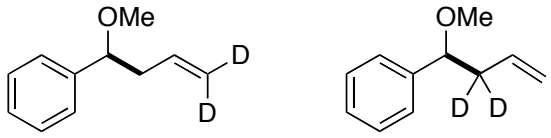
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.08 (s, 3H), 3.41–3.43 (m, 2H), 5.00 (ddd, *J* = 1.6, 3.1, 17.2 Hz, 1H), 5.08 (ddd, *J* = 1.6, 3.1, 10.2 Hz, 1H), 5.83 (dddd, *J* = 6.8, 6.9, 10.2, 17.2 Hz, 1H), 7.26–7.42 (m, 10H) ppm.

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 42.4, 53.0, 91.4, 118.2, 128.0, 128.1 (6C), 129.0 (4C), 131.1, 138.7, 208.3 ppm.

IR (neat): ν = 2916, 2356, 2341, 1718, 1490, 1446, 1066, 914, 738, 680 cm^{-1}.

HRMS (ESI): calculated for $C_{18}H_{18}NaO_2^+$ = $[M+Na]^+$: *m/z* = 289.1199, found: *m/z* = 289.1212.

(4,4-Dideuterio-1-methoxybut-3-enyl)benzene (3a–[d_2])[14] /
(2,2-Dideuterio-1-methoxybut-3-enyl)benzene (3'a–[d_2])[14]



3a–[d_2] **3'a**–[d_2]

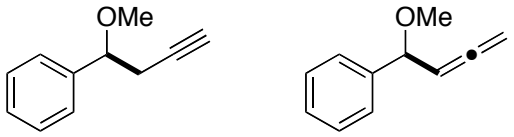
3a–[d_2]:**3'a**–[d_2] = 1:1

Prepared from acetal **1a** (30.4 mg, 0.20 mmol) and allyl boronic ester **2–**[d_2] (51.0 mg, 0.30 mmol, 1.5 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (2.8 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45°C for 8 h. **3'a–[*d*$_2$]** and **3'a–[*d*$_2$]** were purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[14]

Pale yellow liquid.
Yield: 26.0 mg {80%; **3a**–[d_2]:**3'a**–[d_2] = 1:1]}.

5.3 Analytical Data for Homopropargyl Ethers 15a and 15x

(1-Methoxybut-3-ynyl)benzene (15a)[20]



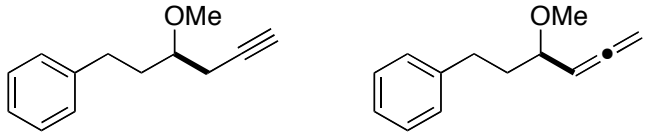
15a **16a**

15a:**16a** = 49:1

Prepared from acetal **1a** (30.4 mg, 0.20 mmol) and allenyl boronic ester **14** (39.9 mg, 0.24 mmol, 1.2 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 52 h. **15a** and **16a** were purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[20]

Pale yellow liquid.
Yield: 29.0 mg (91%; **15a**:**16a** = 49:1).

(3-Methoxyhex-5-ynyl)benzene (15x)[21,22]



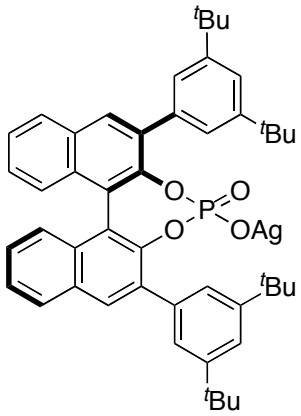
15x **16x**

15x:**16x** = >30:1

Prepared from acetal **1x** (36.4 mg, 0.20 mmol) and allenyl boronic ester **14** (39.9 mg, 0.24 mmol, 1.2 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver fluoride (1.3 mg, 0.01 mmol, 5 mol%), and [18]crown-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) under ultrasonication at 40–45 °C for 72 h. **15x** and **16x** were purified by PTLC on silica gel (eluent: heptane/EtOAc = 19:1). *The obtained analytical data were in full agreement with the reported data.*[21,22]

Colorless liquid.
Yield: 31.1 mg (82%; **15x**:**16x** = >30:1).

5.4 Analytical Data for Silver Phosphate (*R*)-17[23]



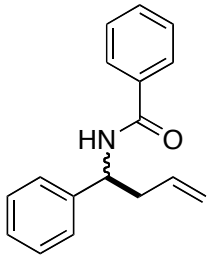
(*R*)-**17**

Silver phosphate (*R*)-**17** was obtained from the corresponding enantiopure phosphoric acid and silver carbonate (Ag_2CO_3) according to a literature report.[24] *The phosphoric acid was prepared from the enantiopure diol and phosphoryl chloride ($POCl_3$) according to a literature report.*[25] (*R*)-**17** was purified by filtration over activated celite, followed by rigorous drying *in vacuo*. *The obtained analytical data were in full agreement with the reported data.*[23]

Colorless solid.

5.5 Analytical Data for Homoallyl Amides *rac*-13 and (*R*)-13

Rac-N-(1-Phenylbut-3-enyl)benzamide (*rac*-13)[23]

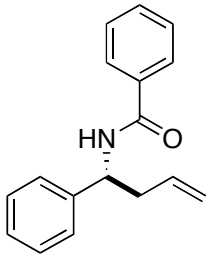


rac-**13**

Prepared from aminal *rac*-**12** (48.3 mg, 0.20 mmol) and allyl boronic ester **2** (40.0 mg, 0.24 mmol, 1.2 equiv) according to *general procedure A* using gallium metal (1.4 mg, 0.02 mmol, 10 mol%), silver triflate (1.3 mg, 0.01 mmol, 5 mol%), and 18[crown]-6 (5.2 mg, 0.02 mmol, 10 mol%) in dioxane (200 µL, 1.0 M) at 50 °C for 24 h. *Rac*-**13** was purified by PTLC on silica gel [eluent: PE (40–60)/Et_2O = 5:1; *eluted three times*]. *The obtained analytical data were in full agreement with the reported data.*[23]

Colorless solid.
Yield: 41.6 mg (83%).

(*R*)-*N*-(1-Phenylbut-3-enyl)benzamide [(*R*)-13][23]



(*R*)-**13**

Prepared from aminal *rac*-**12** (48.3 mg, 0.20 mmol) and allyl boronic ester **2** (50.4 mg, 0.30 mmol, 1.5 equiv), according to *general procedure C*, using gallium metal (2.1 mg, 0.03 mmol, 15 mol%) and silver salt (*R*)-**17** (8.3 mg, 0.015 mmol, 7.5 mol%), in toluene (200 µL, 1.0 M) at 40 °C for 5 d. (*R*)-**13** was purified by PTLC on silica gel [eluent: PE (40–60)/Et_2O = 5:1; *eluted four times*]. *The obtained analytical data were in full agreement with the reported data.*[23]

Colorless solid.
Yield: 30.1 mg (60%); 40% *ee*.

HPLC (DAICEL CHIRALPAK IF; eluent: hexane/^{i}PrOH = 9:1; flow rate: 1.0 mL/min): t_r = 15.4 (*R*), 21.0 (*S*) min.
*The absolute configuration of **13** was assigned in analogy to literature.*[23]

6 References

(1) Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.

(2) Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.

(3) Challinor, A. J.; Calin, M.; Nichol, G. S.; Carter, N. B.; Thomas, S. P. *Adv. Synth. Catal.* **2016**, *15*, 2404.

(4) Williams, D. B. G.; Lawton, M. C. *Green Chem.* **2008**, *10*, 914.

(5) Madabhushi, S.; Mallu, K. K. R.; Chinthala, N.; Beeram, C. R.; Vangipuram, V. S. *Tetrahedron Lett.* **2012**, *53*, 697.

(6) Moquist, P. N.; Kodama, T.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2010**, *49*, 7096.

(7) Reisman, S. E.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008**, *130*, 7198.

(8) Katritzky, A. R.; Fan, W.-Q.; Black, M.; Pernak, J. *J. Org. Chem.* **1992**, *52*, 547.

(9) Fujioka, H.; Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T. *Chem. Commun.* **2011**, *47*, 9894.

(10) Wiles, C.; Watts, P.; Haswell, S. J. *Tetrahedron* **2005**, *61*, 5209.

(11) Sakai, N.; Moritaka, K.; Konakahara, T. *Eur. J. Org. Chem.* **2009**, *2009*, 4123.

(12) Ito, S.; Hayashi, A.; Komai, H.; Yamaguchi, H.; Kubota, Y.; Asami, M. *Tetrahedron* **2011**, *67*, 2081.

(13) Kumar, D.; Kumar, R.; Chakraborti, A. K. *Synthesis* **2008**, 1249.

(14) Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.

(15) Ortholand, J.-Y.; Vicart, N.; Greiner, A. *J. Org. Chem.* **1995**, *60*, 1880.

(16) Merisor, E.; Conrad, J.; Malakar, C. C.; Beifuss, U. *Synlett* **2008**, 903.

(17) Yang, M.-S.; Xu, L.-W.; Zhang, F.-B.; Qiu, H.-Y.; Jiang, J.-X.; Lai, G.-Q. *Appl. Organomet. Chem.* **2008**, *22*, 177.

(18) Watahiki, T.; Akabane, Y.; Mori, S.; Oriyama, T. *Org. Lett.* **2003**, *5*, 3045.

(19) Clausen, D. J.; Floreancig, P. E. *J. Org. Chem.* **2012**, *77*, 6574.

(20) Niimi, L.; Hiraoka, S.; Yokozawa, T. *Tetrahedron* **2002**, *58*, 245.

(21) Motodate, S.; Kobayashi, T.; Fujii, M.; Mochida, T.; Kusakabe, T.; Katoh, S.; Akita, H.; Kato, K. *Chem. – Asian J.* **2010**, *5*, 2221.

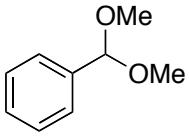
(22) Pragani, R.; Roush, W. R. *Org. Lett.* **2008**, *10*, 4613.

(23) Huang, Y.-Y.; Chakrabarti, A.; Morita, N.; Schneider, U.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 11121.

(24) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science* **2007**, *317*, 496.

(25) Liu, W.-J.; Chen, X.-H.; Gong, L.-Z. *Org. Lett.* **2008**, *10*, 5357.

7 Copies of NMR Spectra and Chiral HPLC Charts of Substrates and Products



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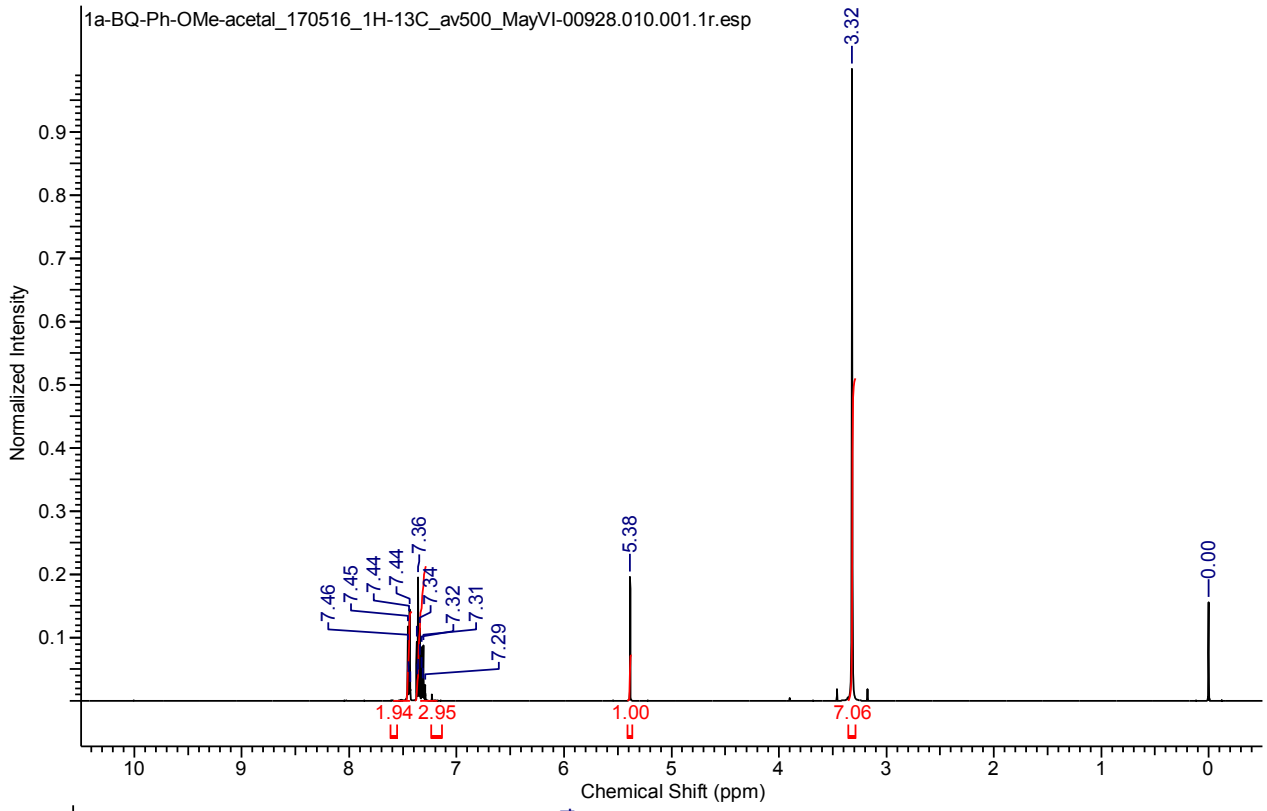
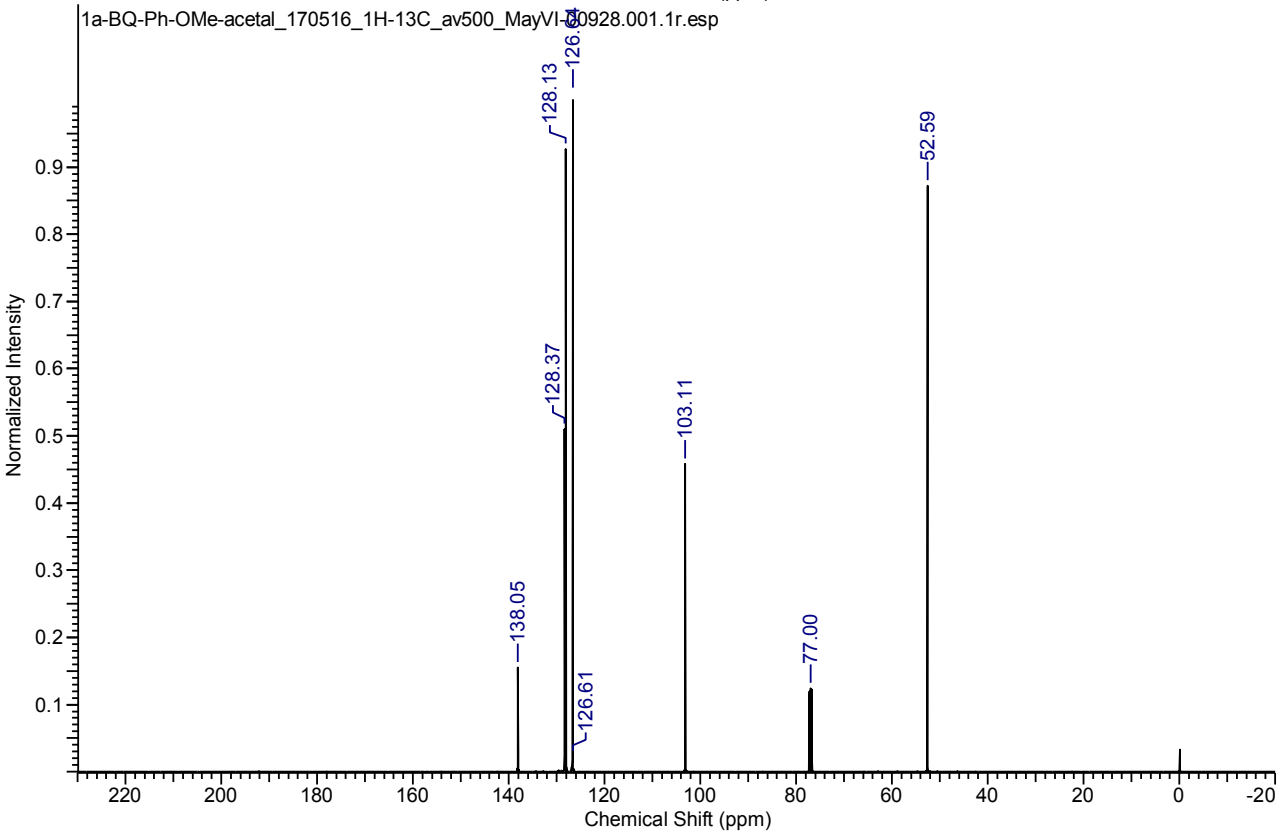
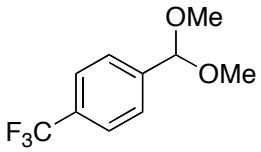
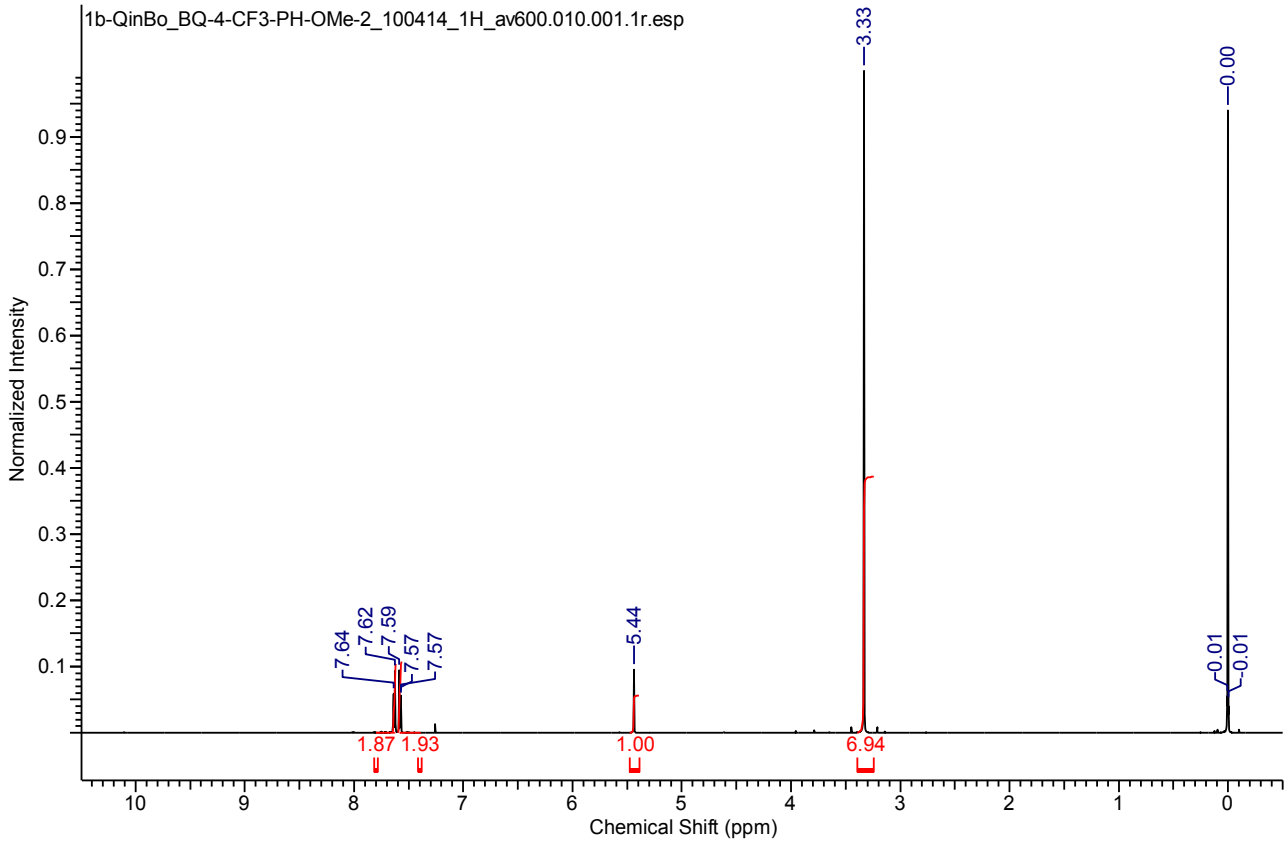





OMe
OMe
F3C

1b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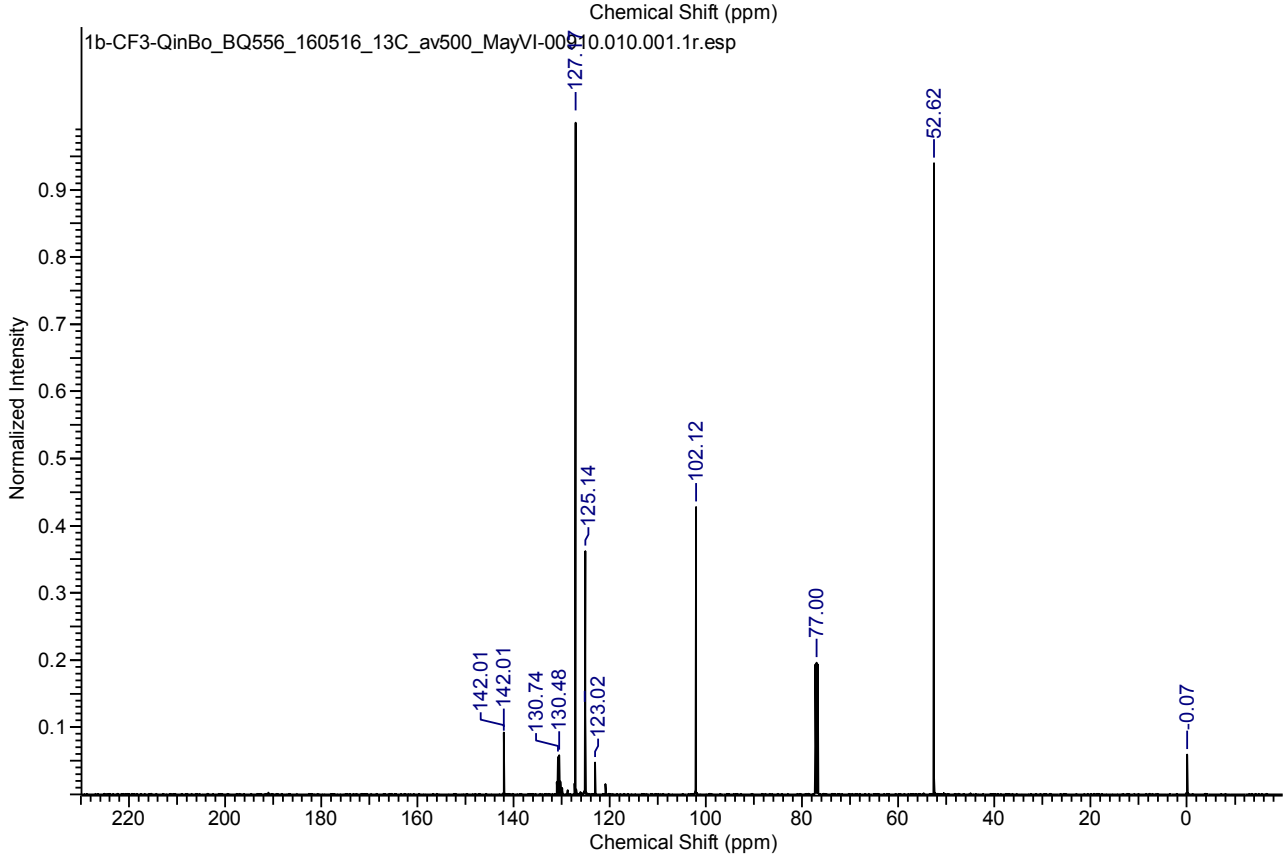
Chemical Shift (ppm)
7.64
7.62
7.59
7.57
7.57
5.44
3.33
0.00
0.01
-0.01
1.87
1.93
1.00
6.94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Chemical Shift (ppm)
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142.01
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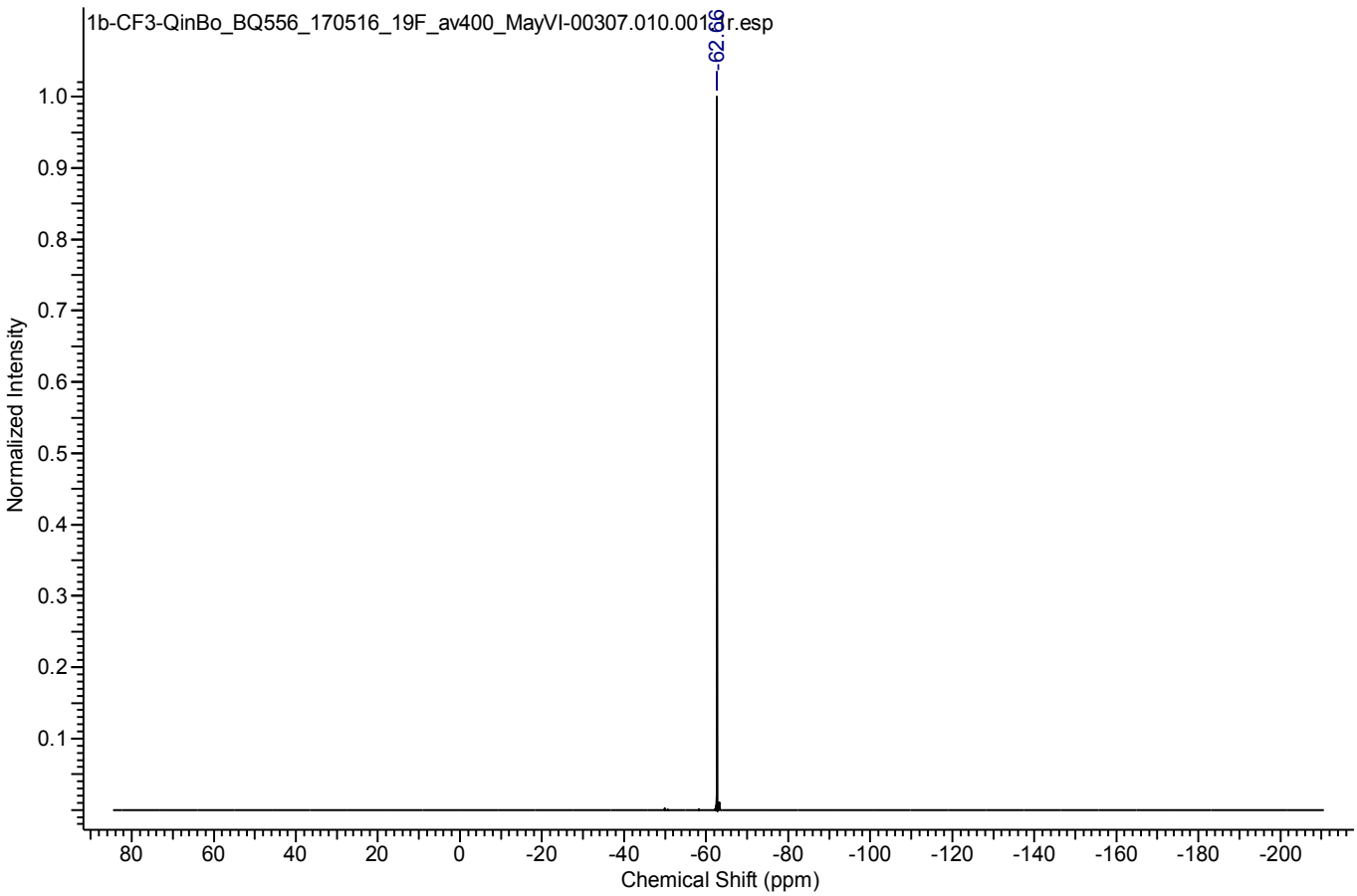
130.48
102.12
77.00
52.62
-0.07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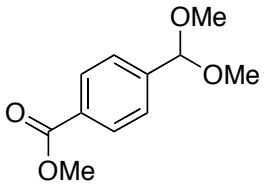
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)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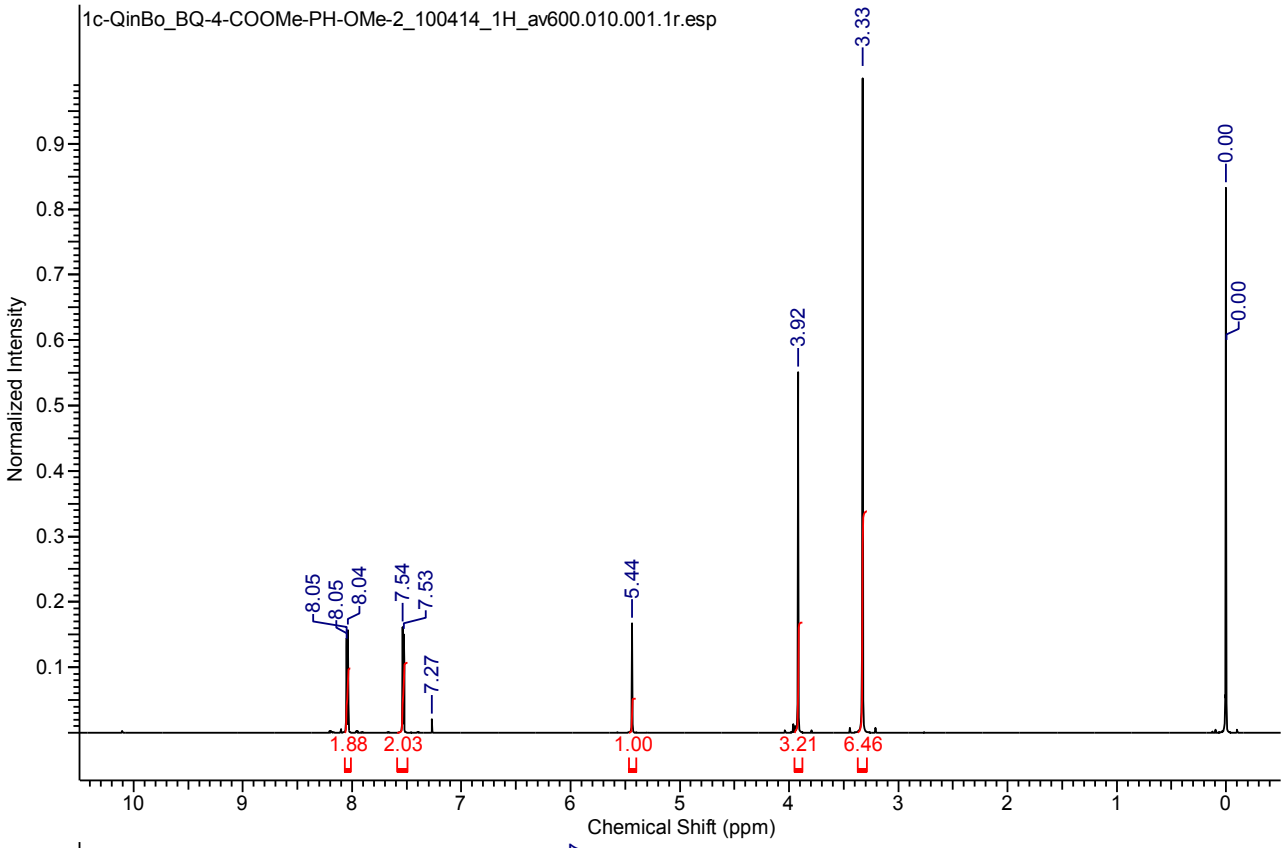
OMe
O
OMe

1c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Normalized Intensity
Chemical Shift (ppm)
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8.05
8.04
7.54
7.53
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3.92
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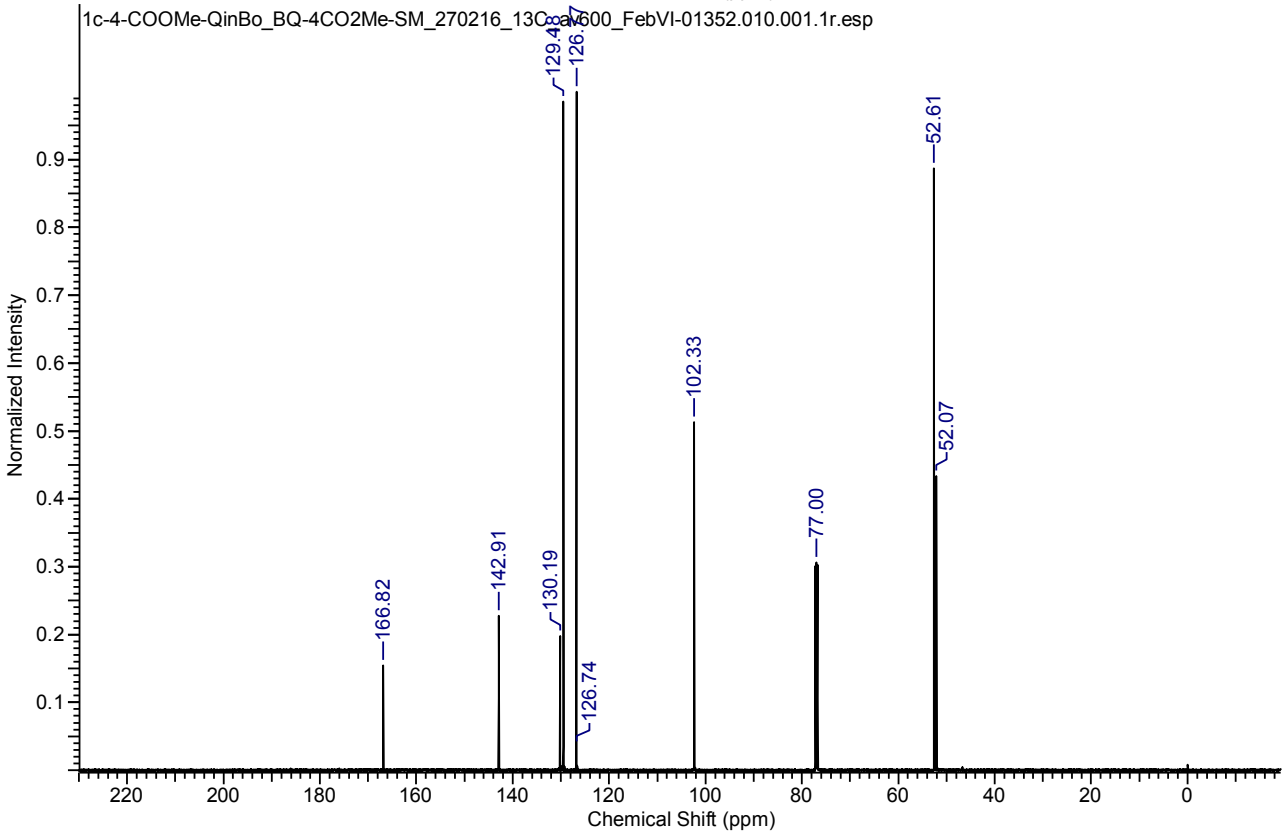
0.00
1.88
2.03
1.00
3.21
6.46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Normalized Intensity
Chemical Shift (ppm)
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126.74
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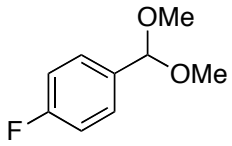
77.00
52.61
52.07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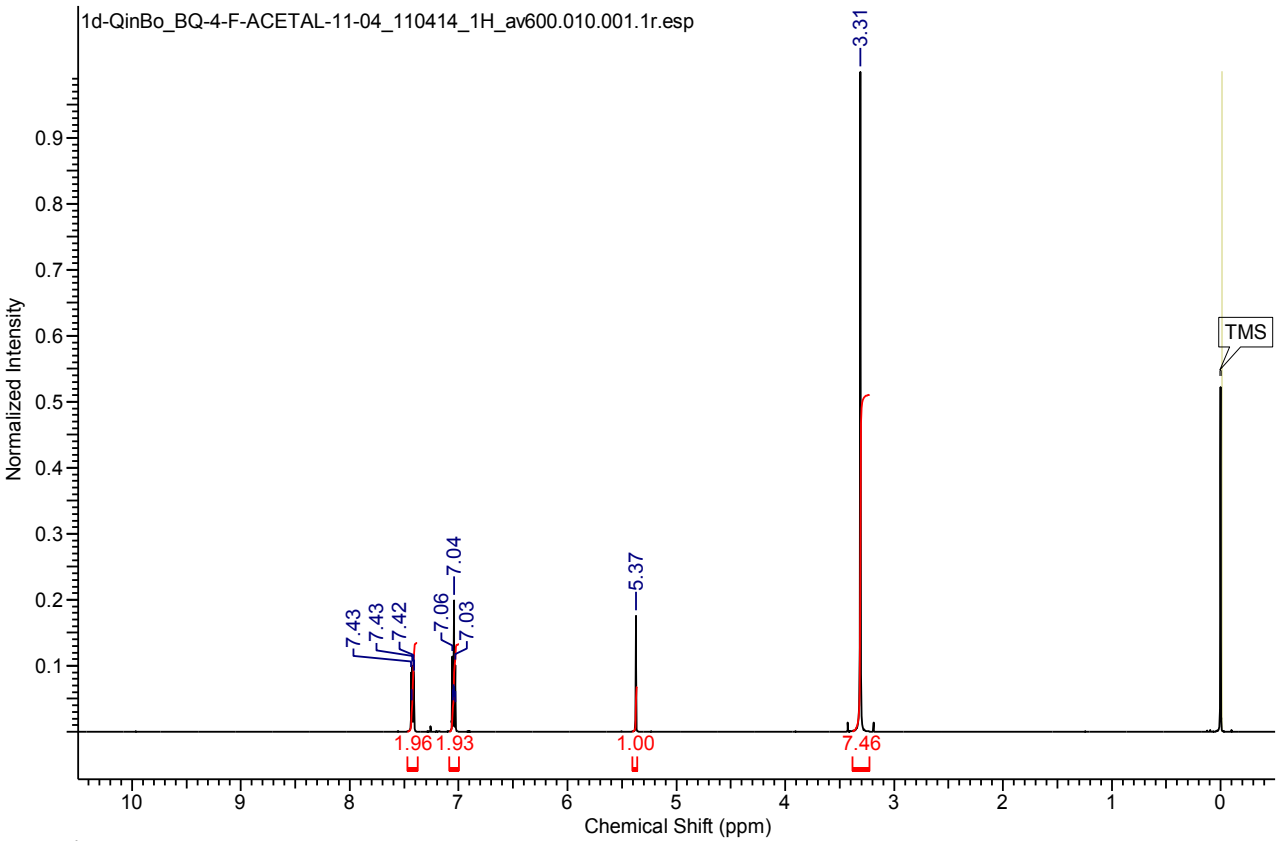
OMe
F

1d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Normalized Intensity
Chemical Shift (ppm)
3.31
TMS
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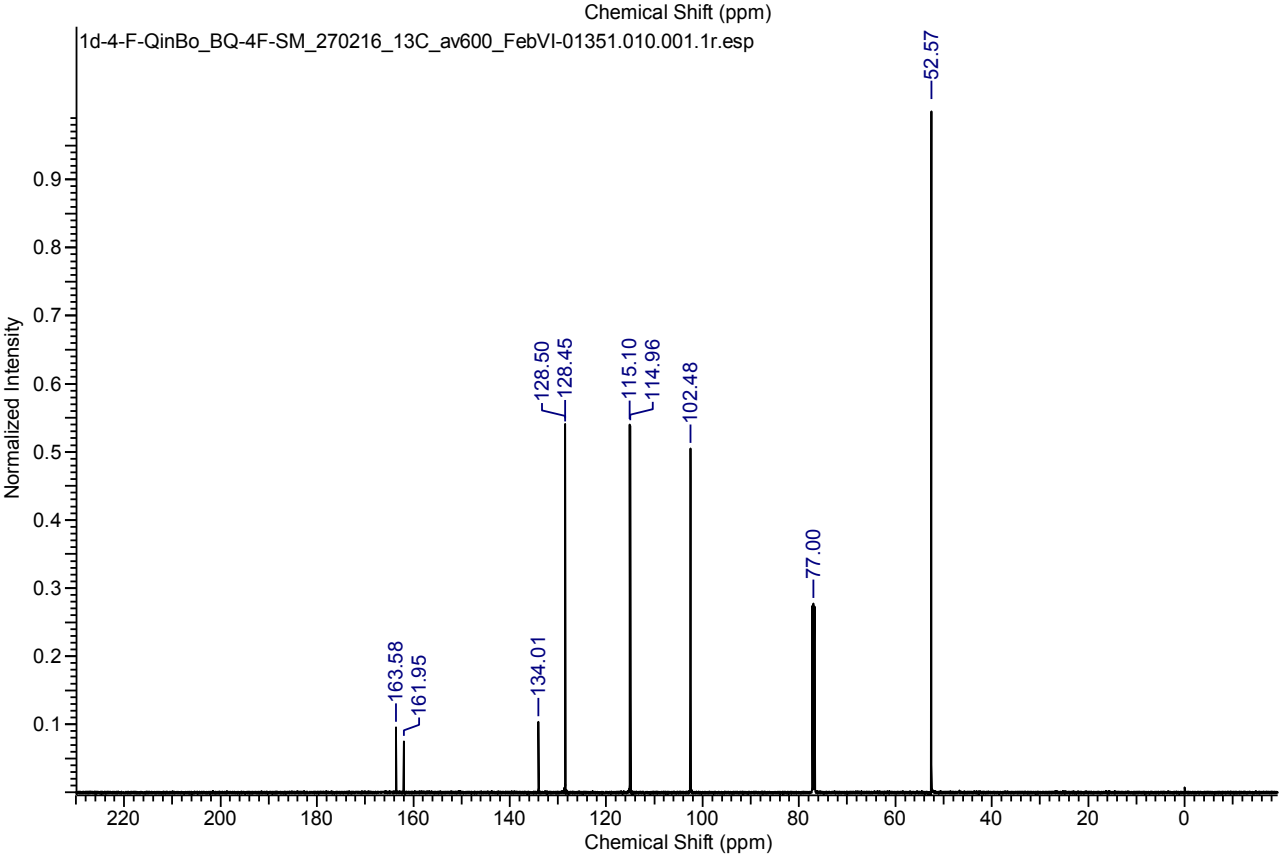
7.43
7.42
7.06
7.04
7.03
5.37
1.96
1.93
1.00
7.46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102.48
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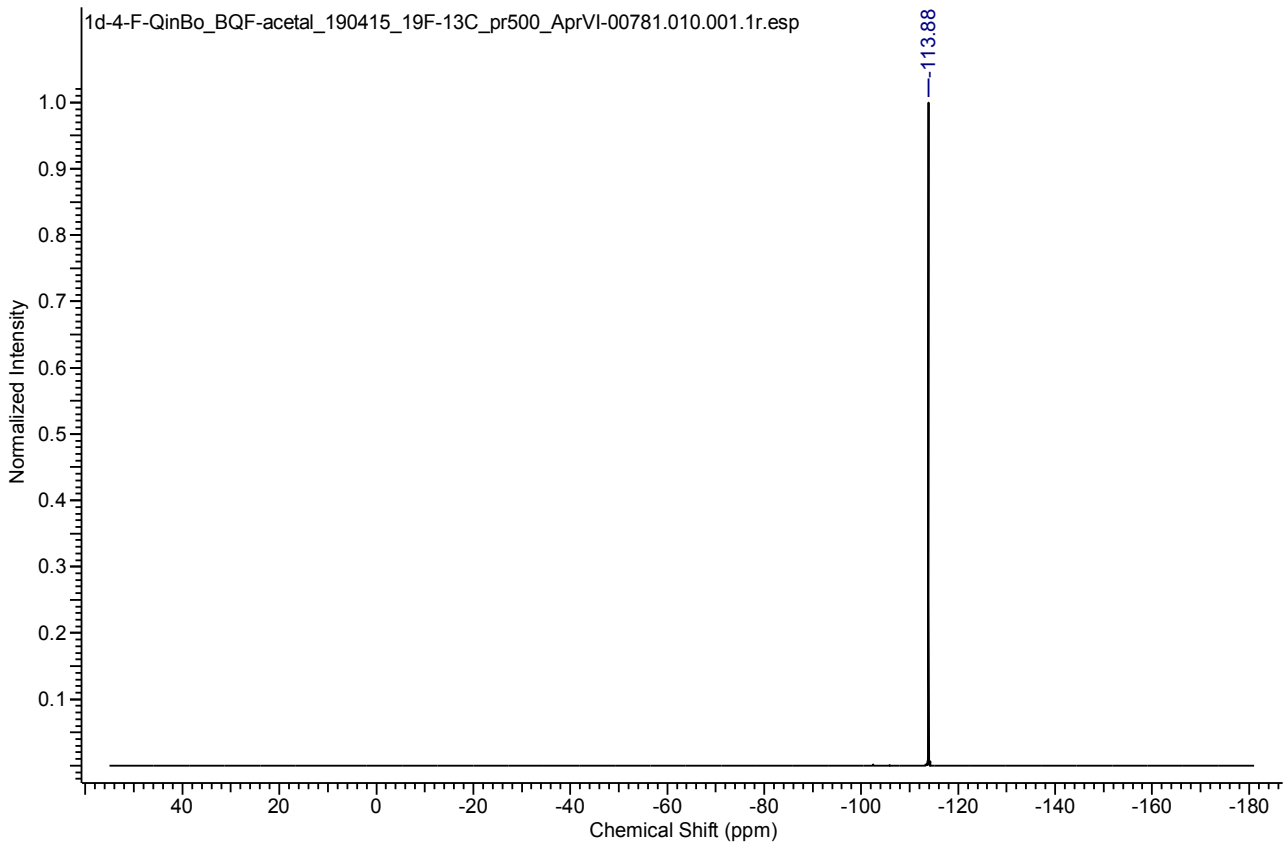
163.58
161.95
134.01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0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
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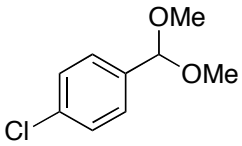
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)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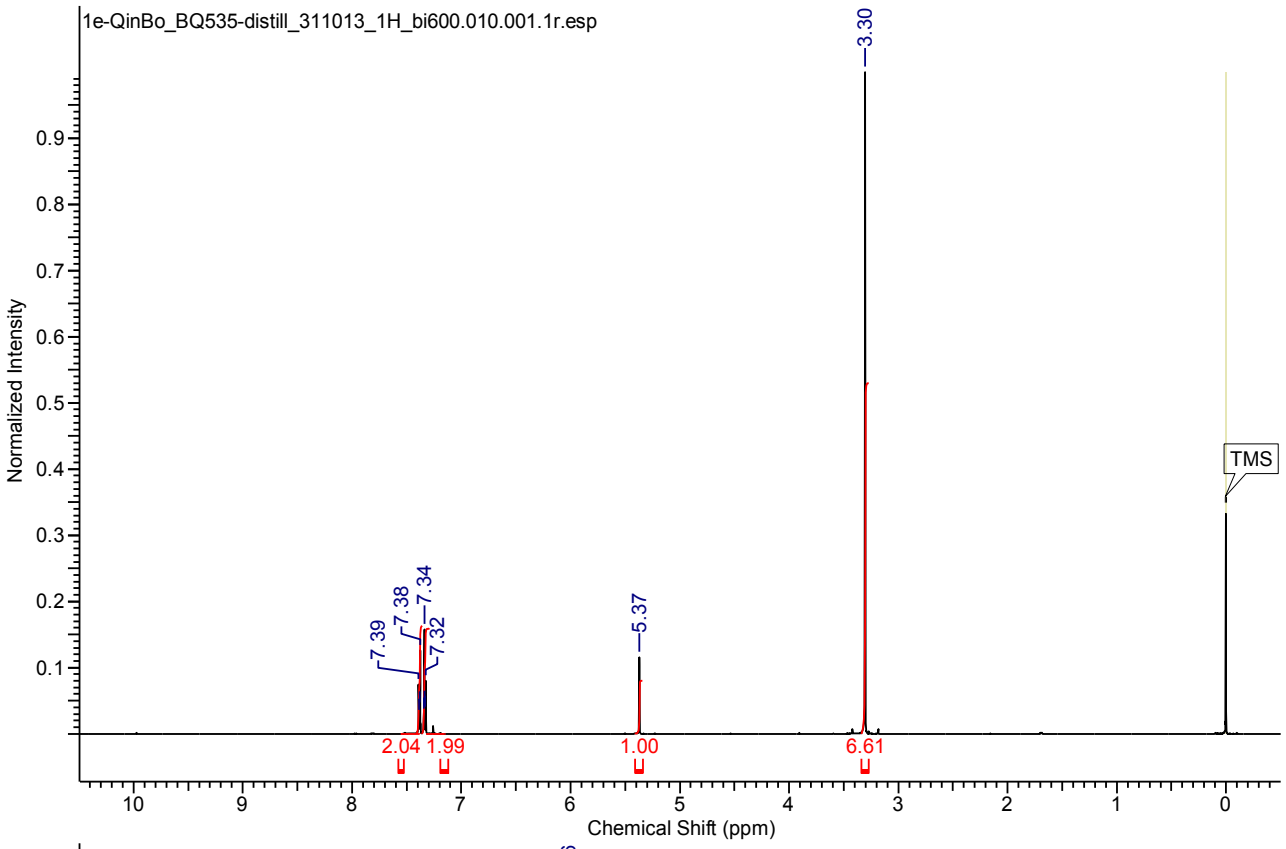
OMe
Cl

1e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7.32
5.37
TMS
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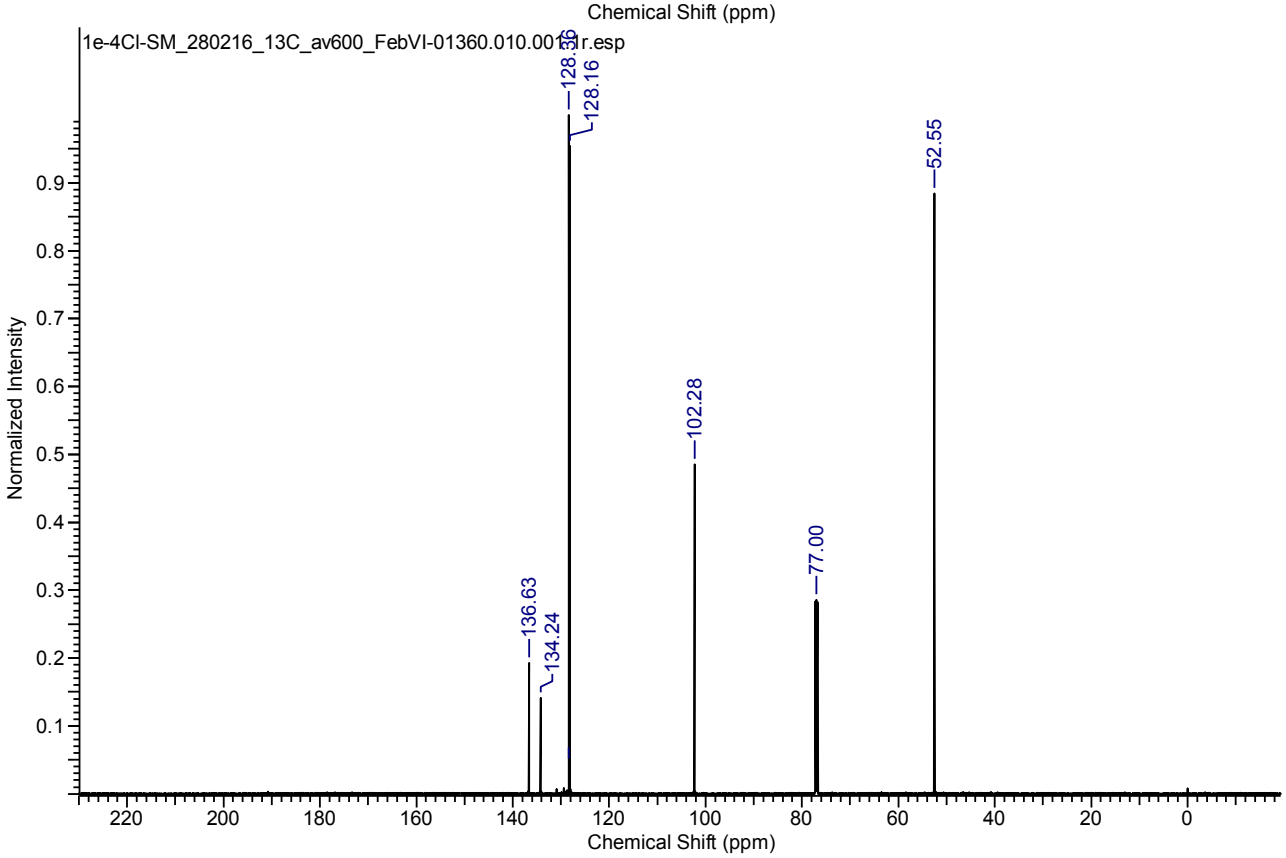
1.99
1.00
6.61
Normalized Intensity
Chemical Shift (ppm)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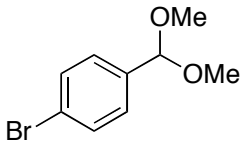
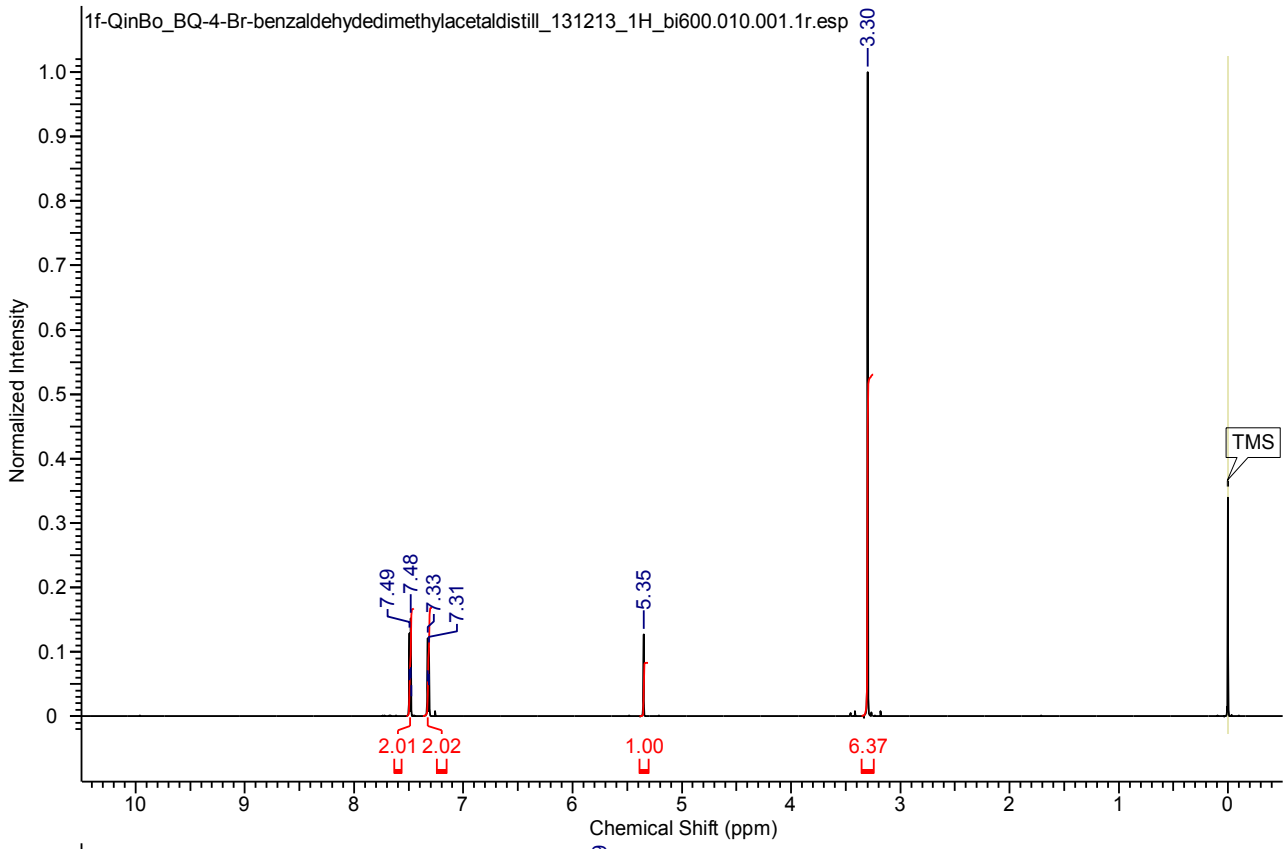
136.63
134.24
Normalized Intensity
Chemical Shift (ppm)


OMe
OMe
Br

1f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Normalized Intensity
Chemical Shift (ppm)
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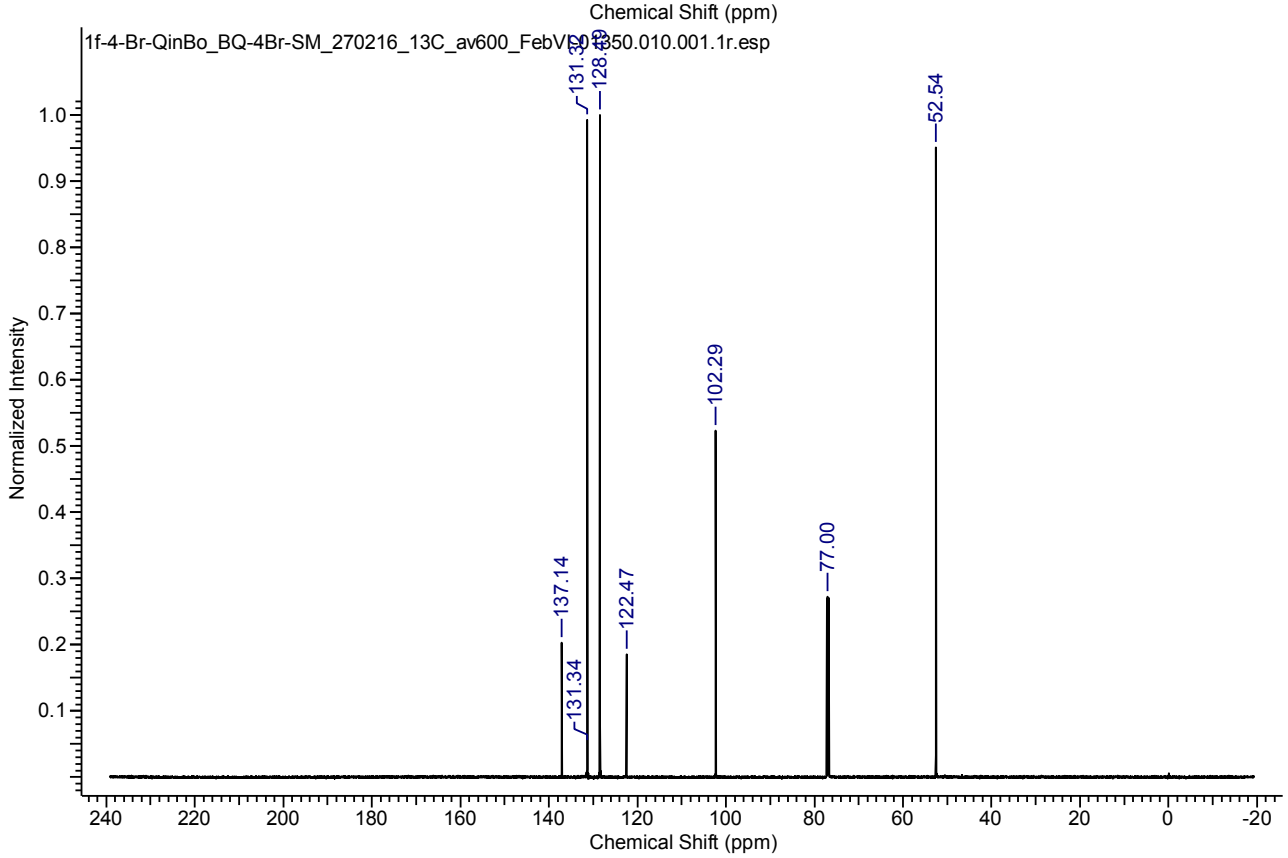
7.49
7.48
7.33
7.31
5.35
TMS
2.01
2.02
1.00
6.37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Chemical Shift (ppm)
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102.29
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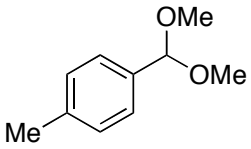
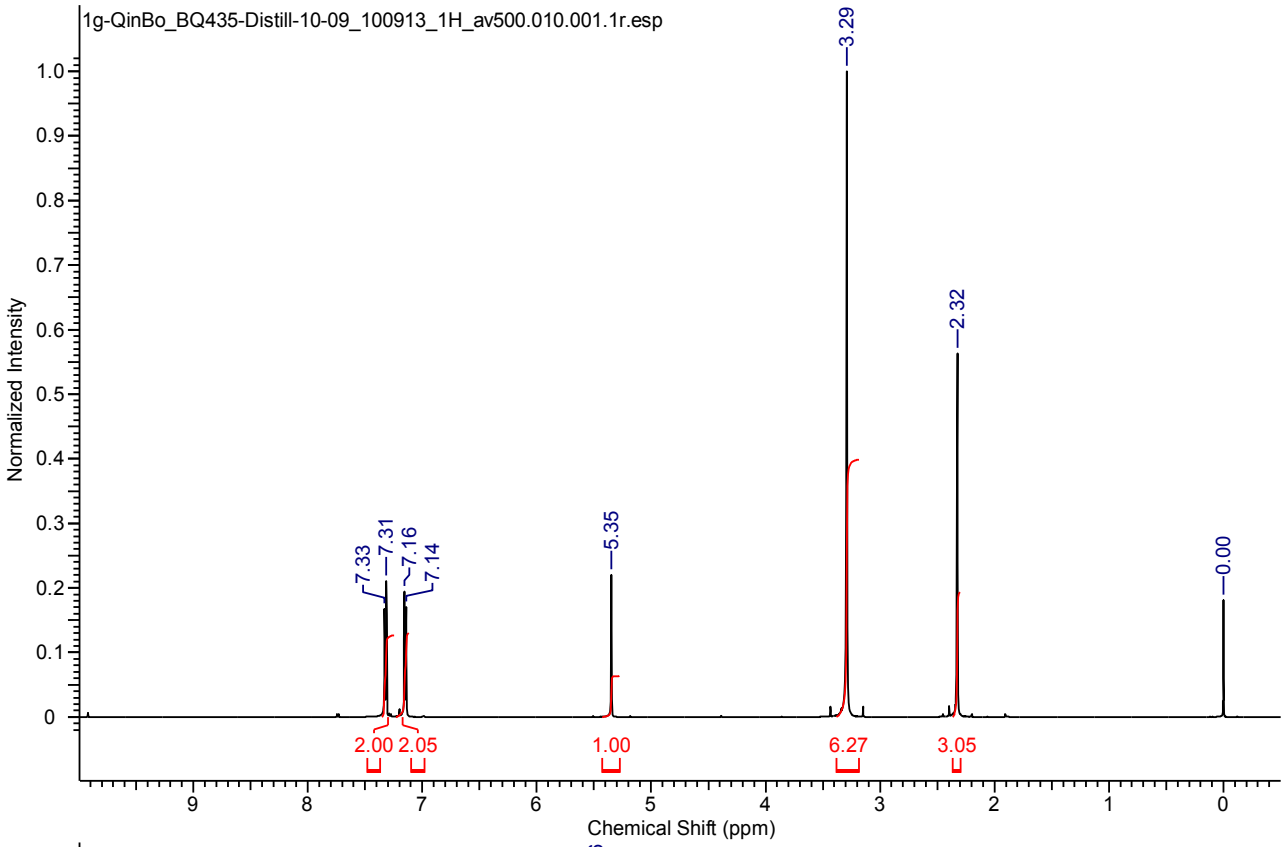
137.14
131.34
122.47


OMe
OMe
Me

1g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Normalized Intensity
Chemical Shift (ppm)
3.29
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7.33
7.31
7.16
7.14
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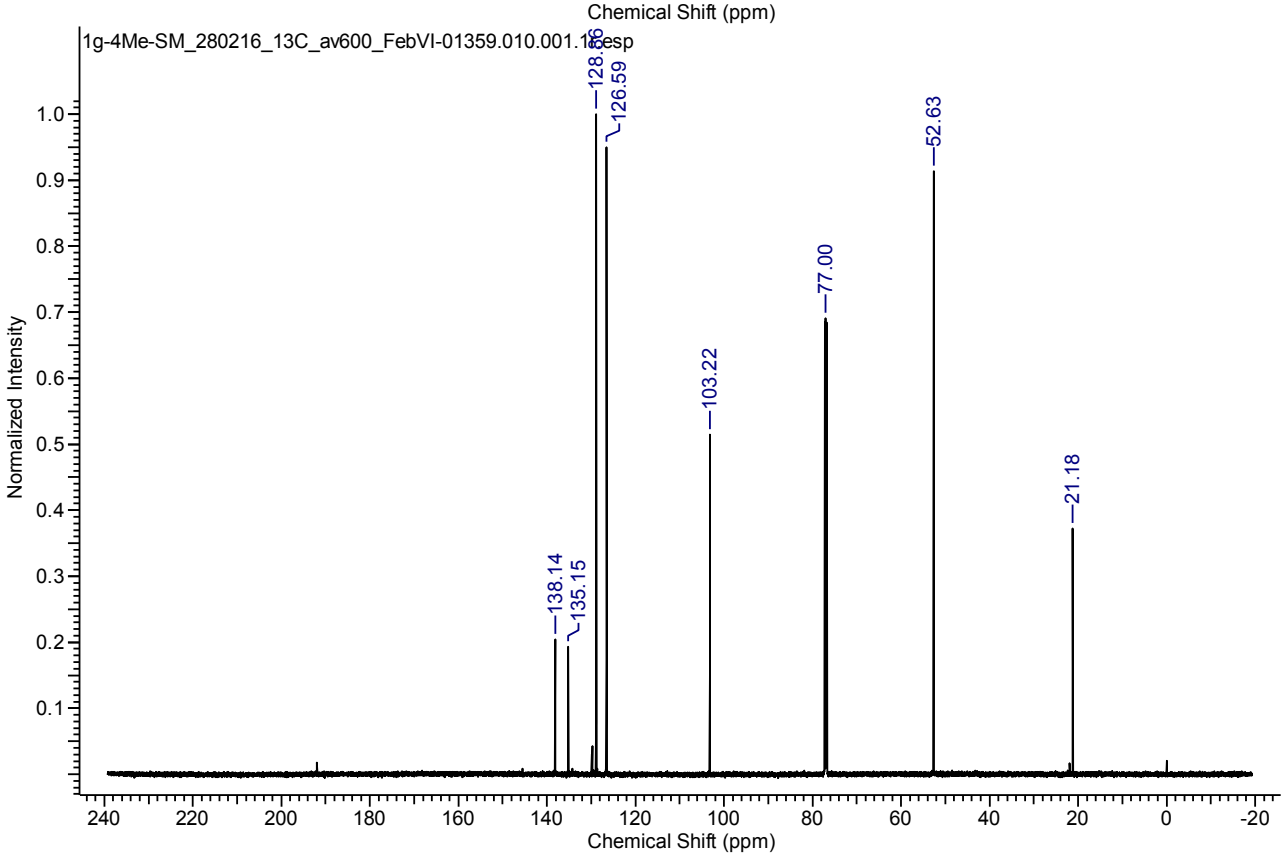
2.00
2.05
1.00
6.27
3.05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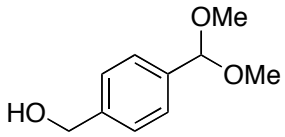
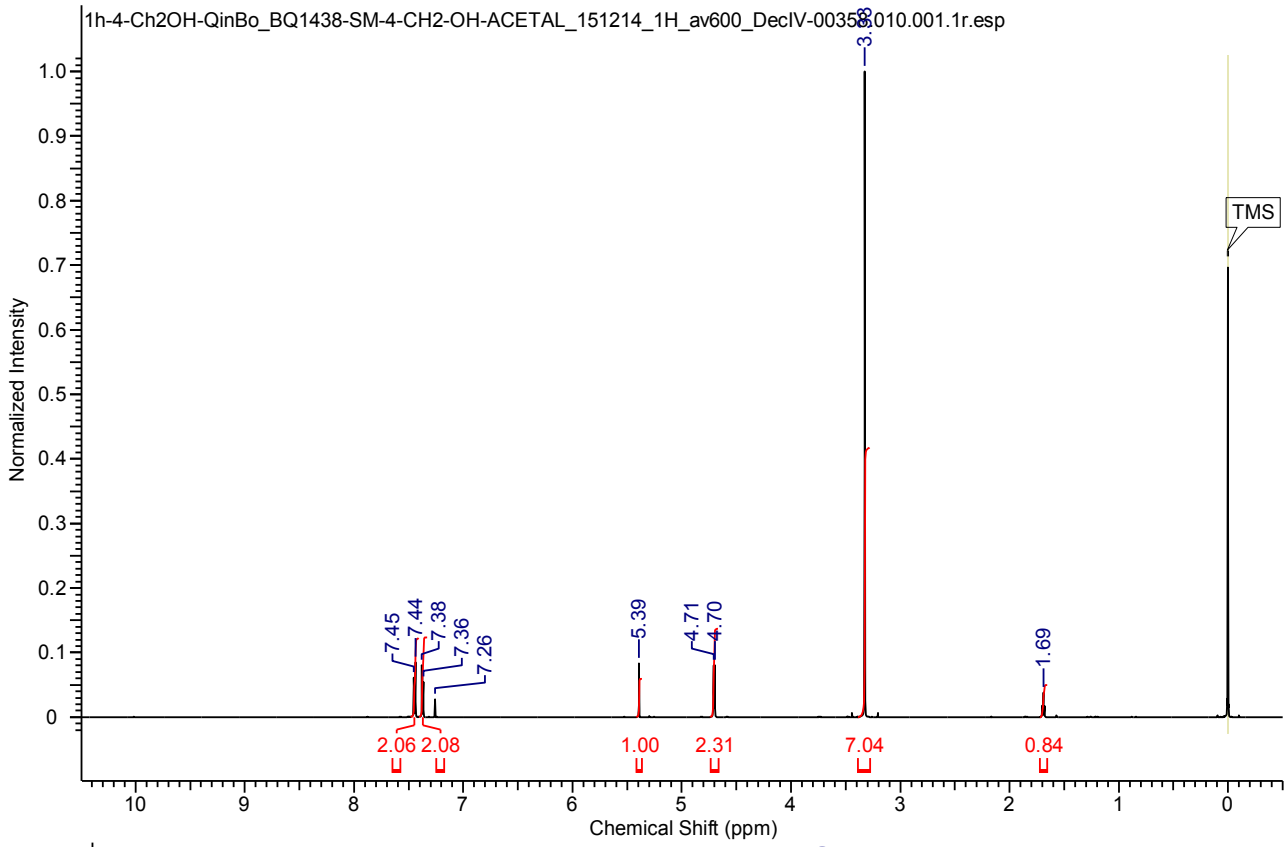
52.63
77.00
103.22
21.18
138.14
135.15


OMe
OMe
HO

1h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Normalized Intensity
Chemical Shift (ppm)
7.45
7.44
7.38
7.36
7.26
5.39
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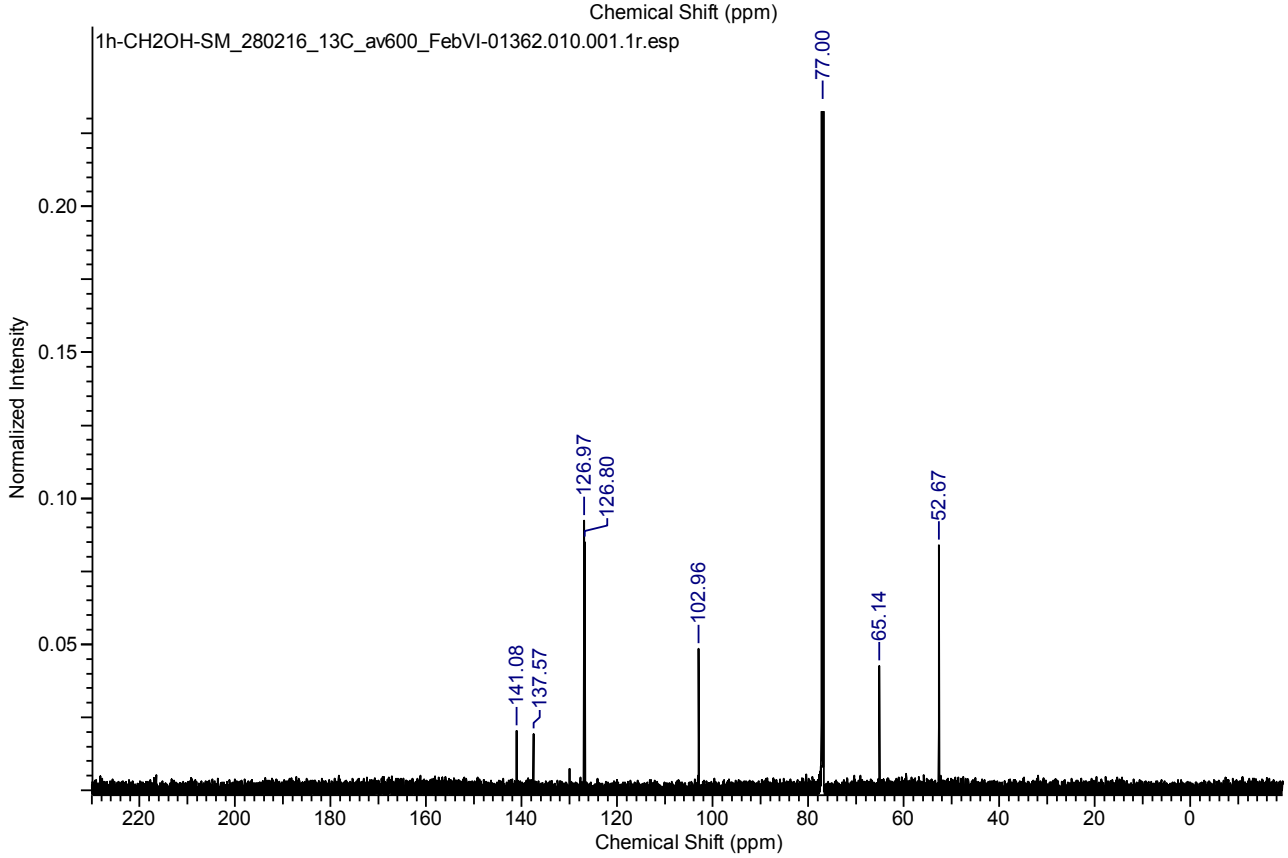
4.70
3.88
1.69
TMS
2.06
2.08
1.00
2.31
7.04
0.84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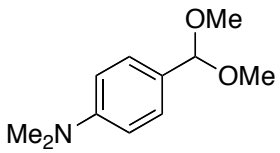
141.08
137.57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OMe
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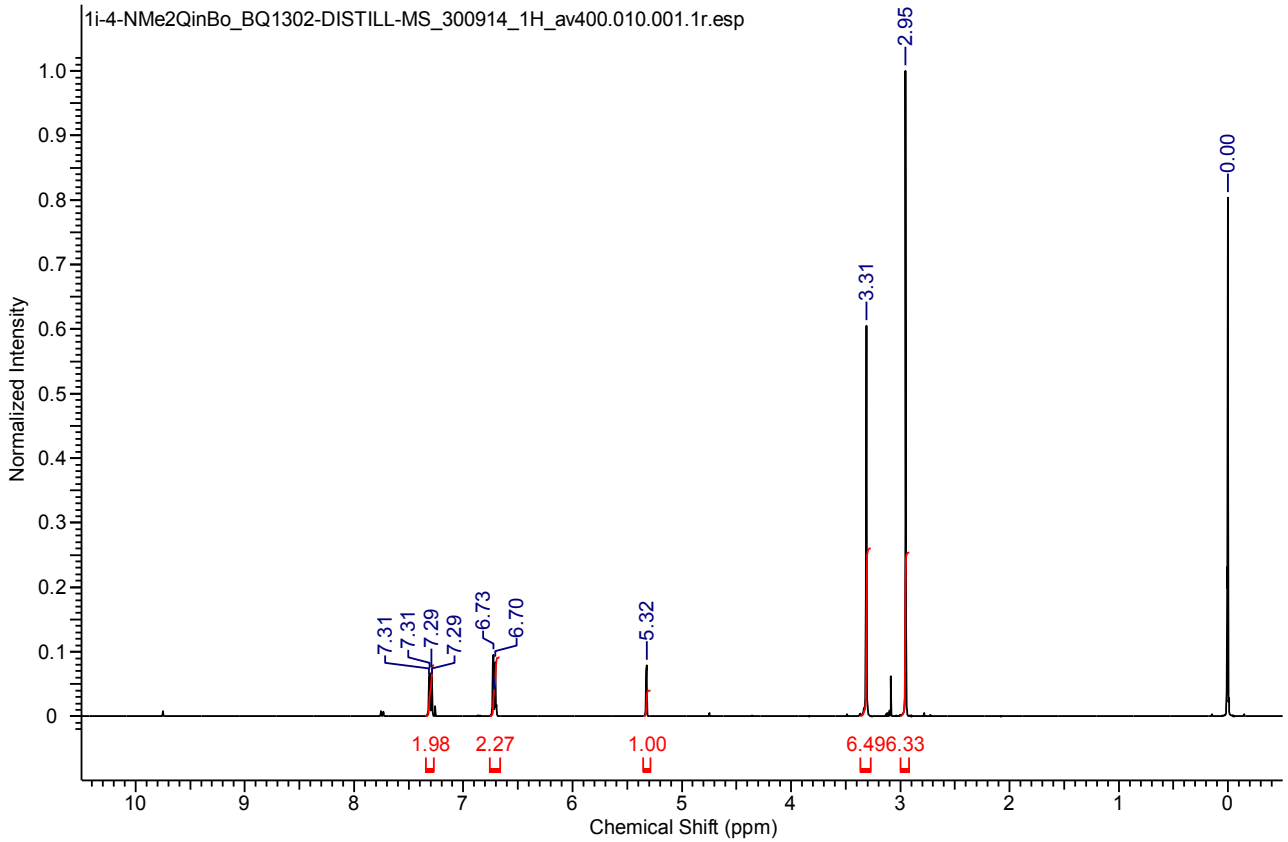
1i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Normalized Intensity
Chemical Shift (ppm)
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7.31
7.29
7.29
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6.70
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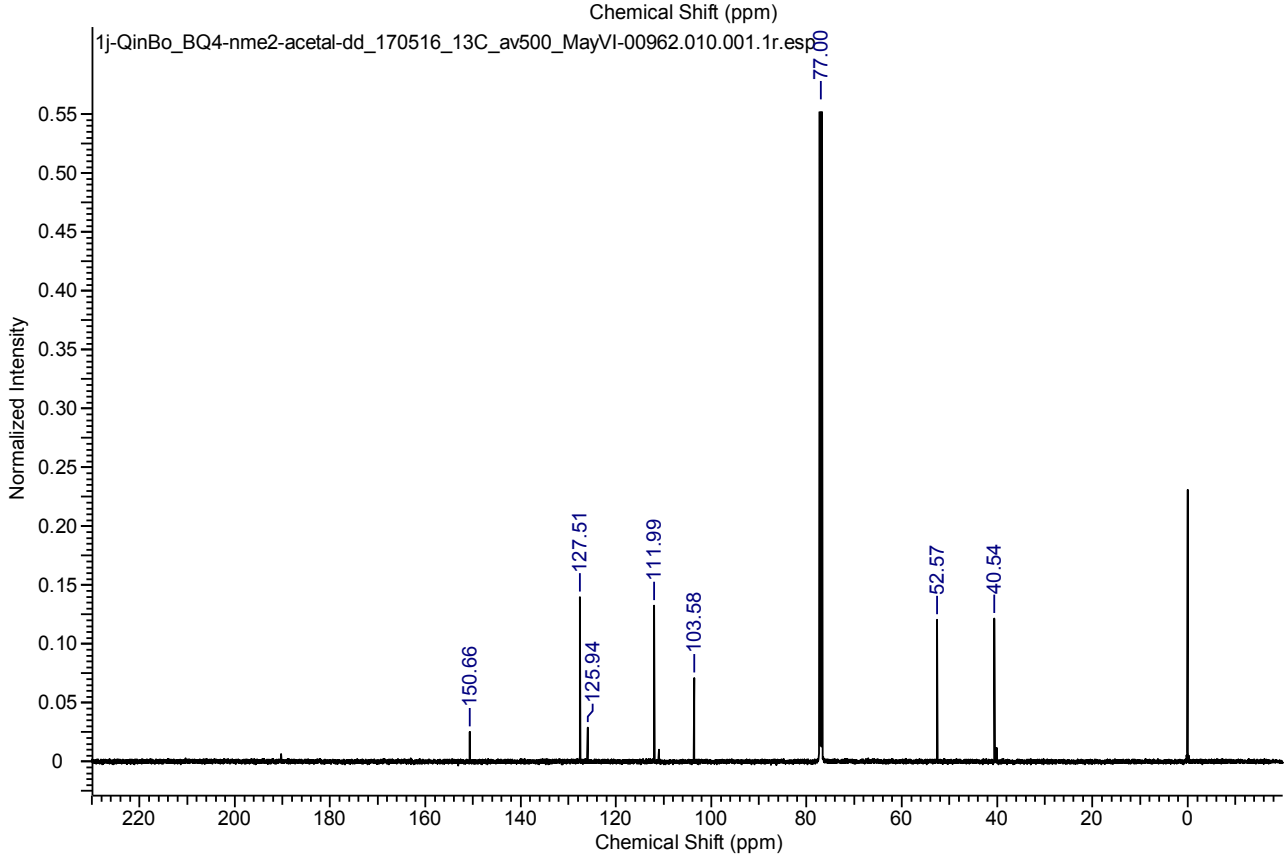
1.98
2.27
1.00
6.49
6.33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125.94
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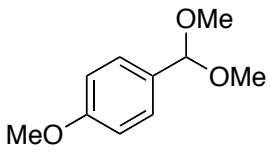
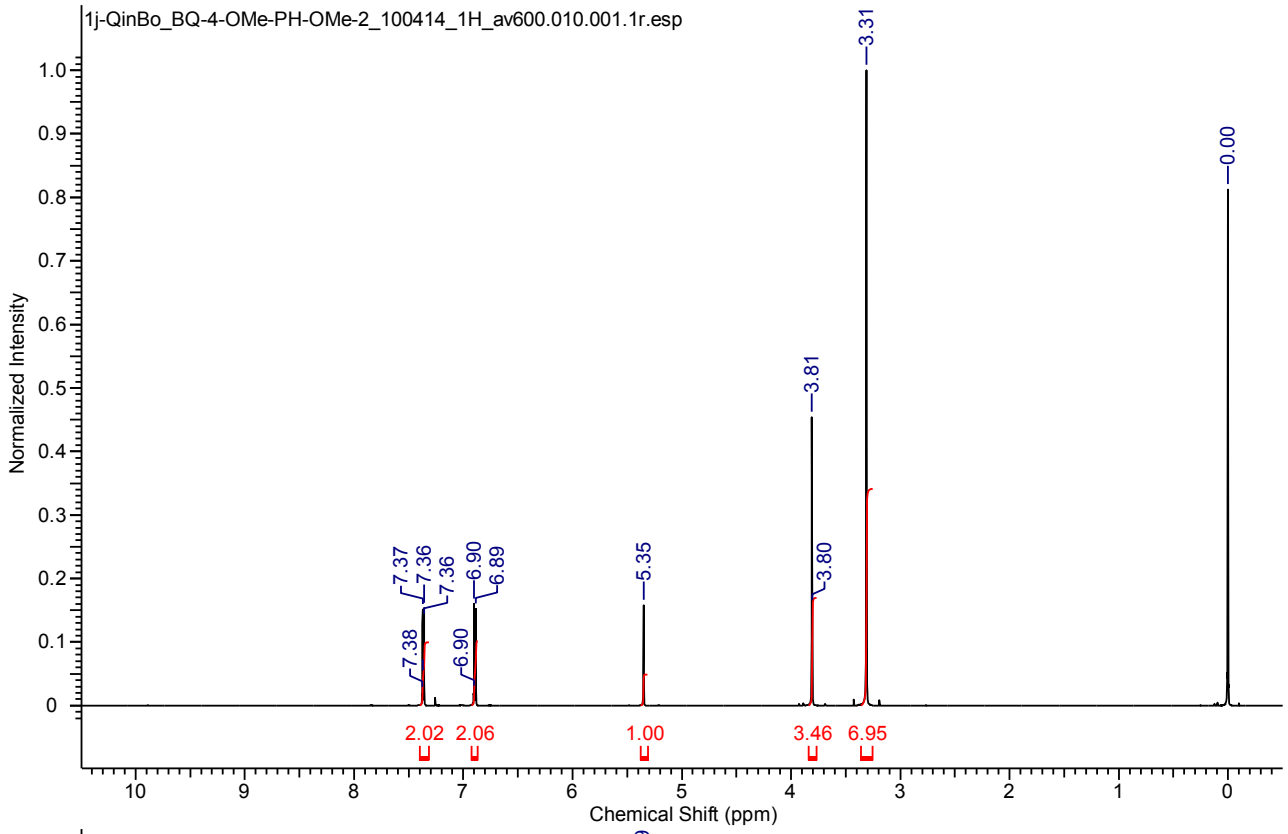
103.58
52.57
40.54


OMe
OMe
MeO

1j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Normalized Intensity
Chemical Shift (ppm)
7.38
7.37
7.36
7.36
6.90
6.90
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3.81
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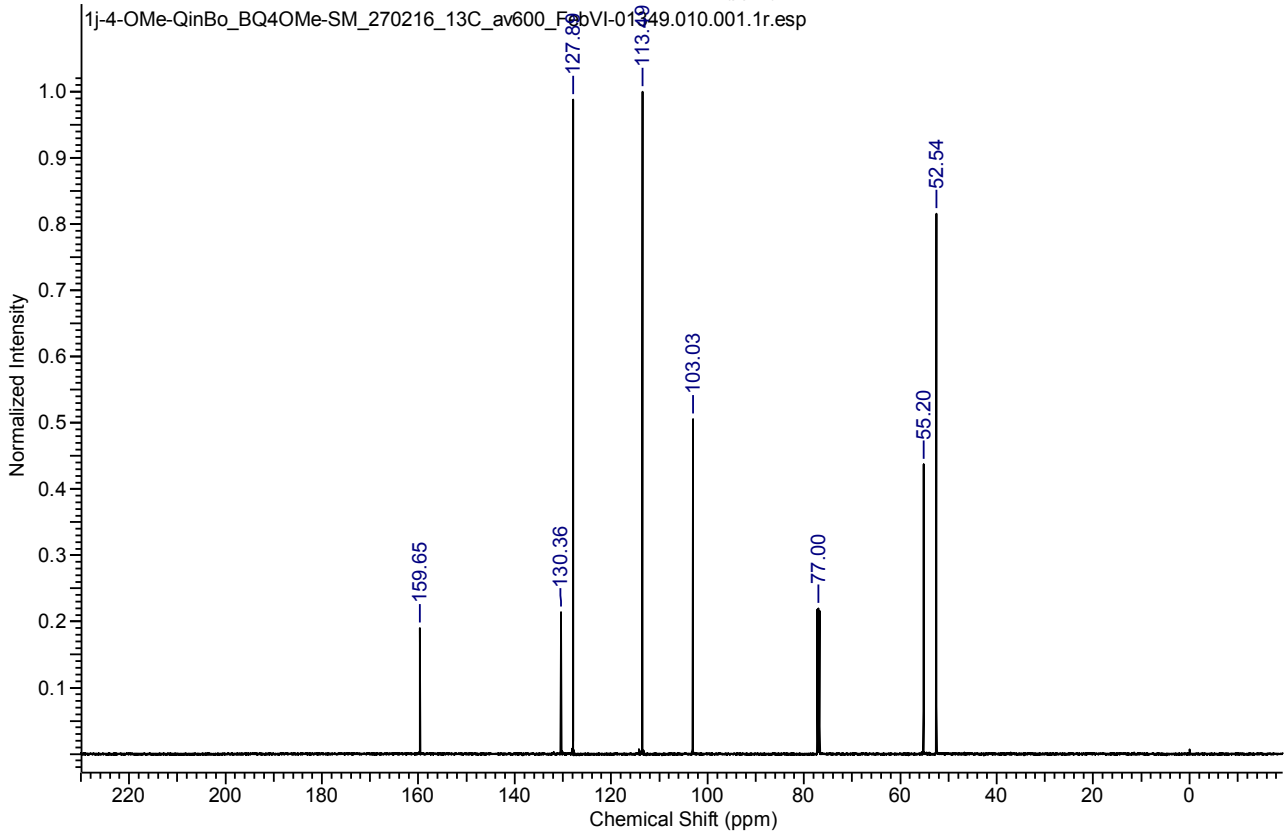
2.02
2.06
1.00
3.46
6.95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Chemical Shift (ppm)
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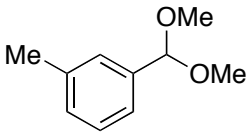
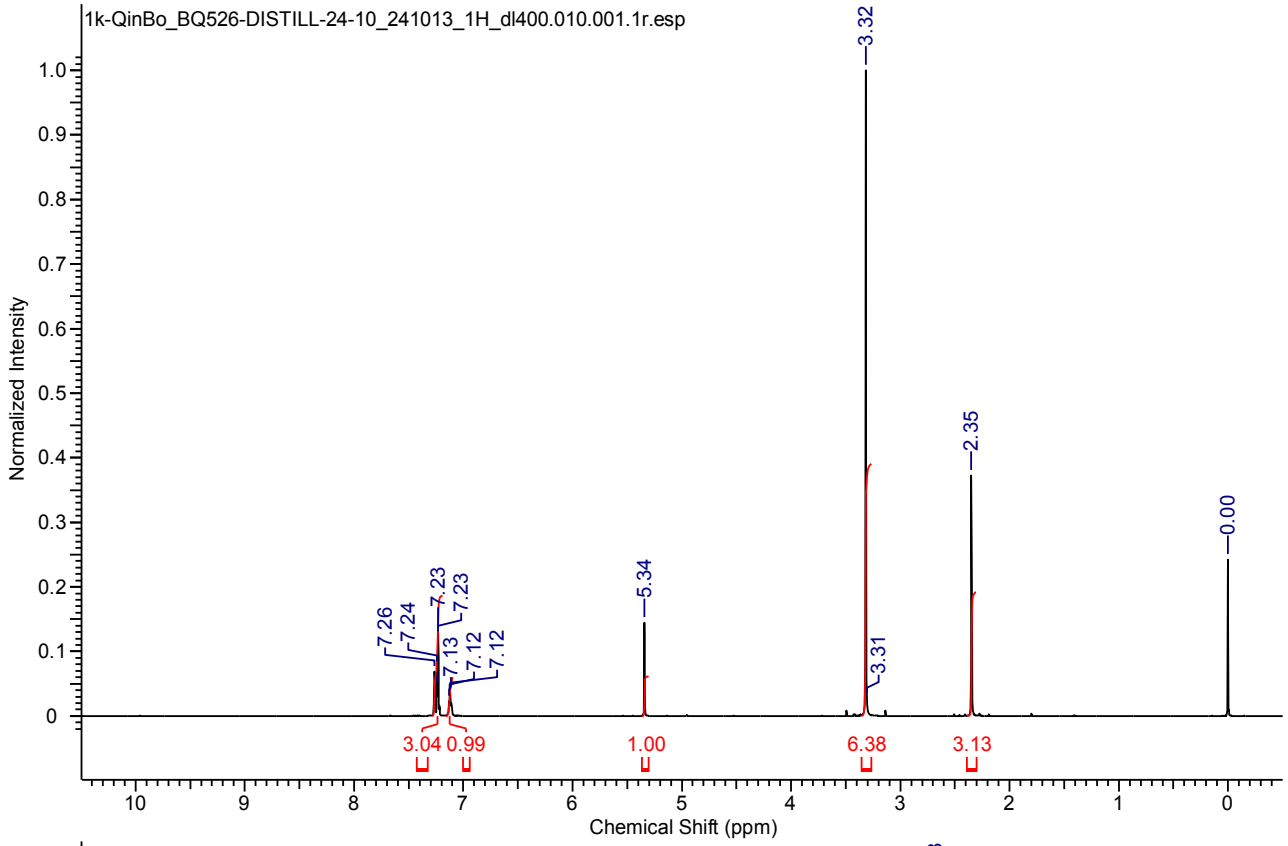
113.49
103.03
77.00
55.20
52.54


OMe
Me
OMe

1k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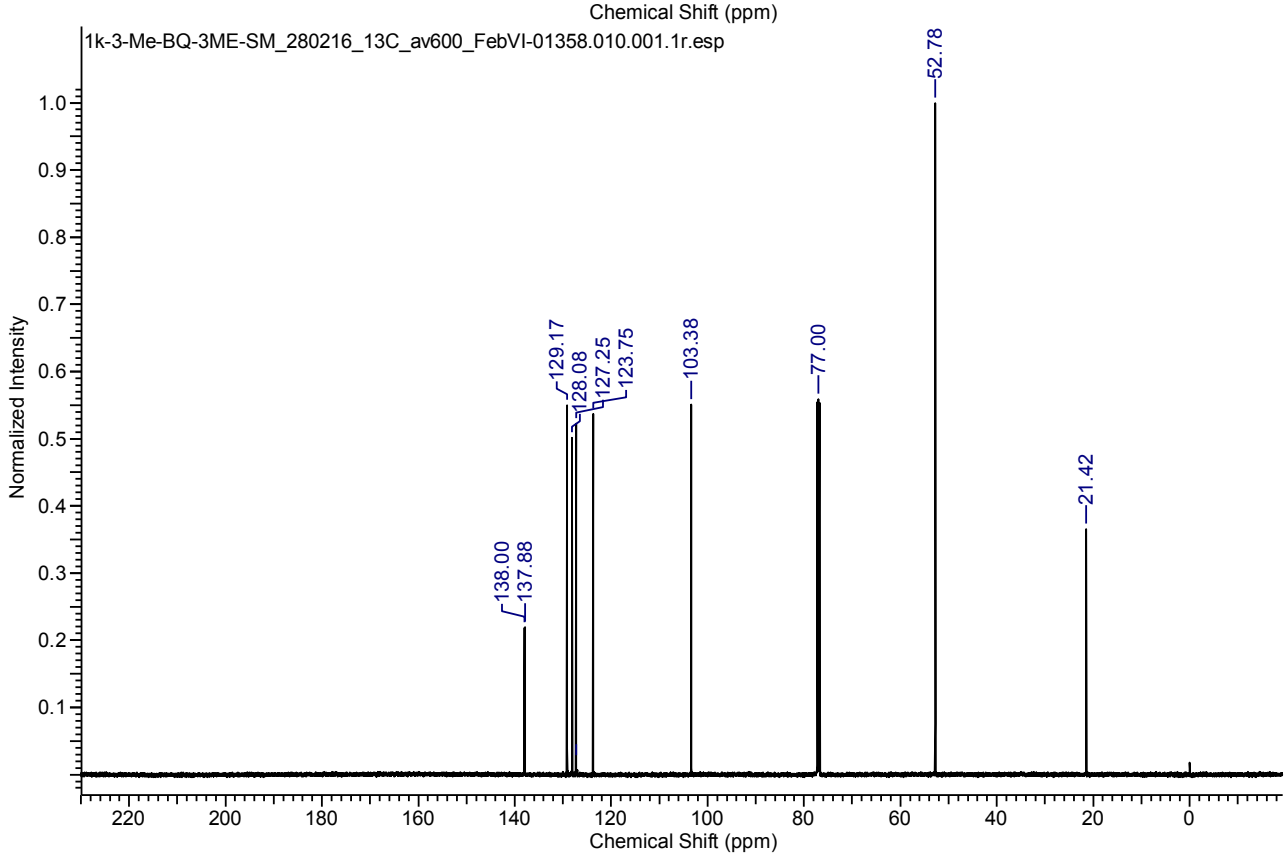
Normalized Intensity
Chemical Shift (ppm)
3.32
2.35
0.00
5.34
3.31
7.26
7.24
7.23
7.23
7.13
7.12
7.12
3.04
0.99
1.00
6.38
3.13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Normalized Intensity
Chemical Shift (ppm)
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21.42
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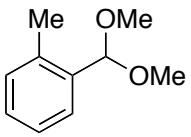
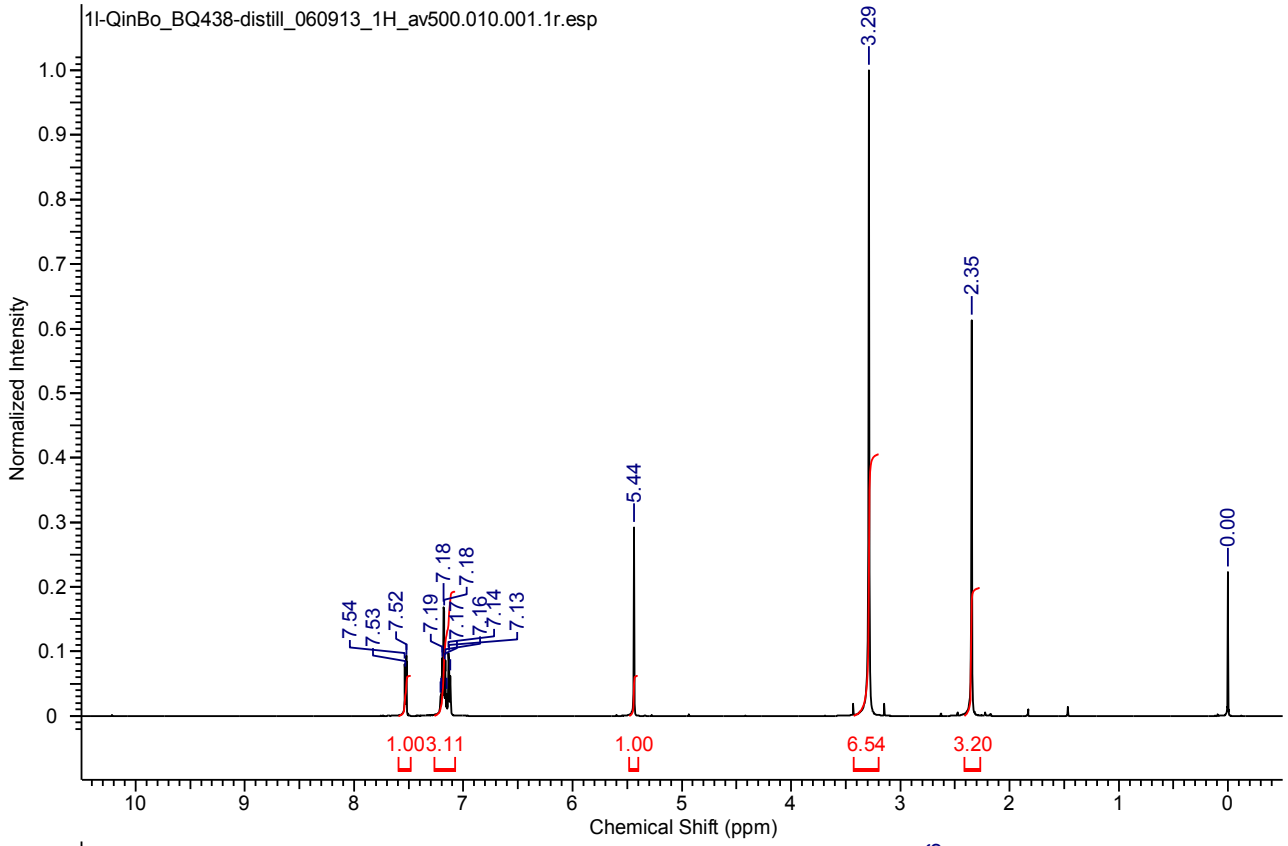
103.38
77.00
138.00
137.88


Me
OMe
OMe

1l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Normalized Intensity
Chemical Shift (ppm)
3.29
2.35
5.44
0.00
7.54
7.53
7.52
7.19
7.18
7.18
7.17
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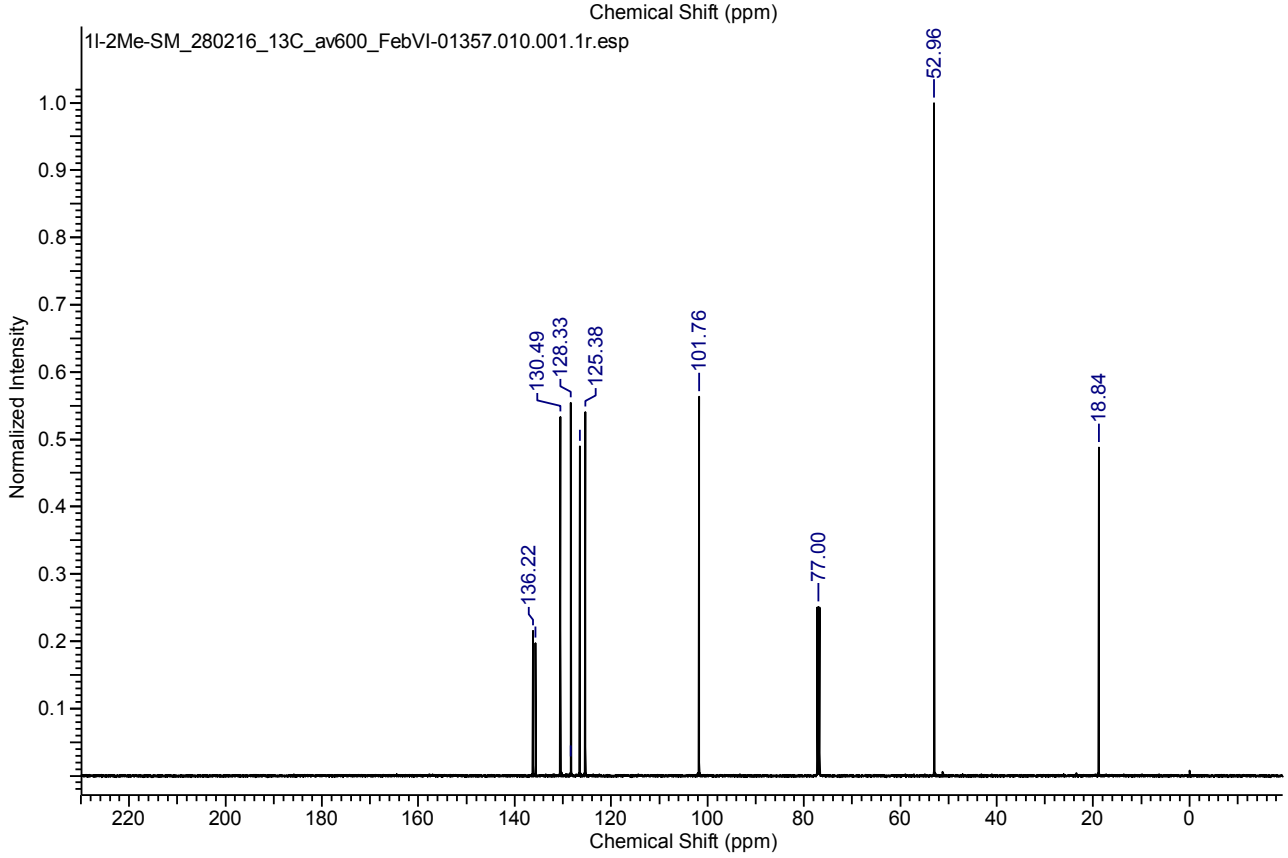
7.13
1.00
3.11
1.00
6.54
3.20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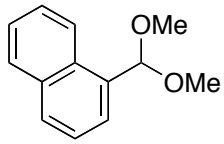
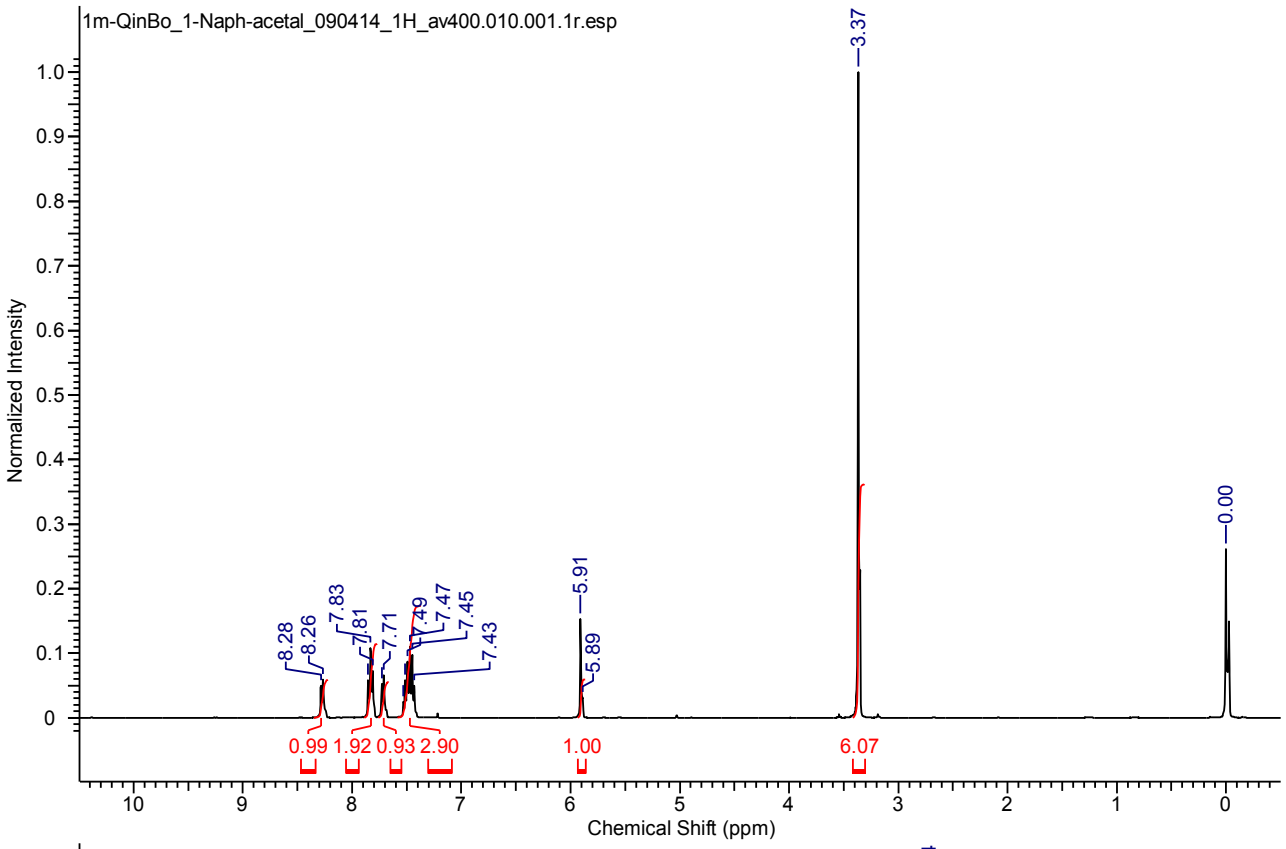
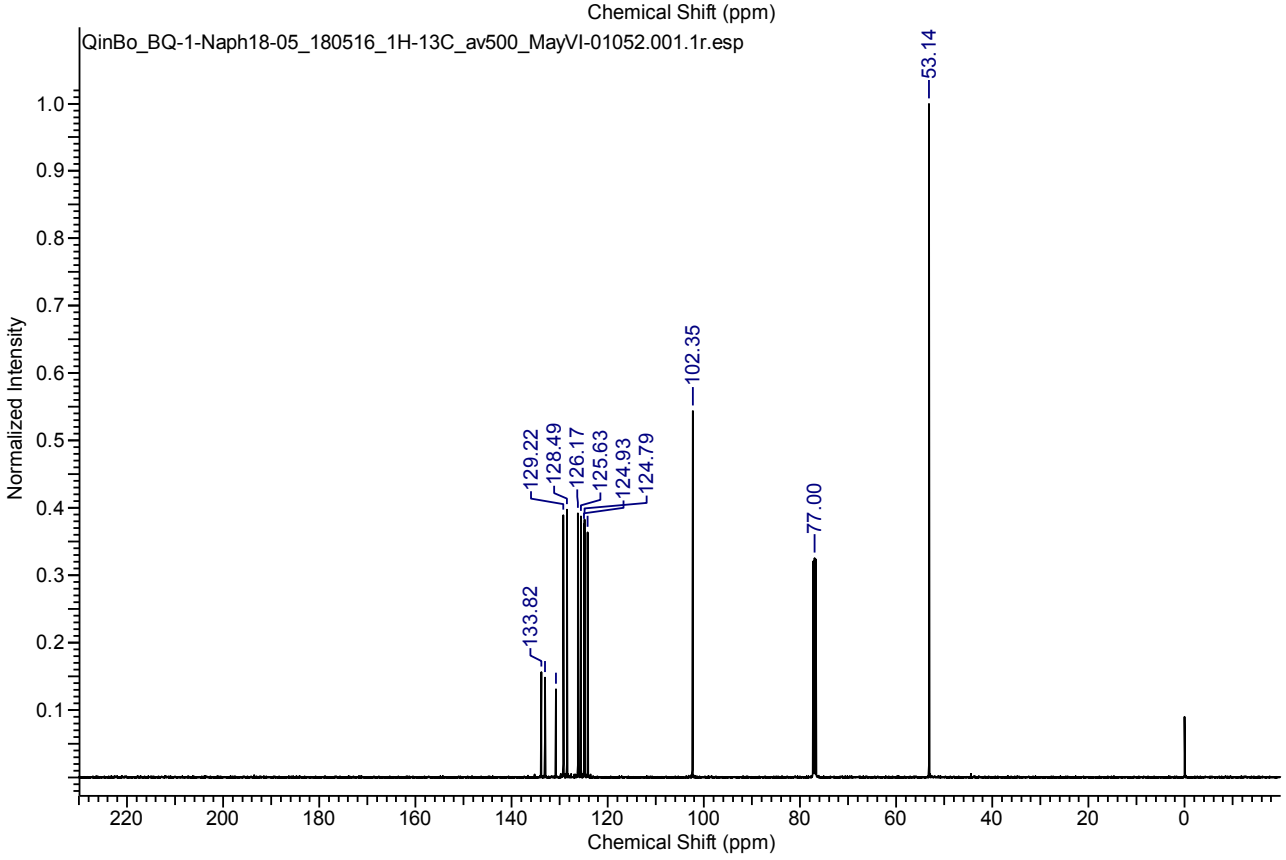
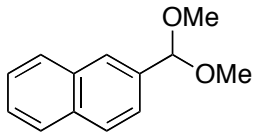
Normalized Intensity
Chemical Shift (ppm)
52.96
130.49
128.33
125.38
101.76
136.22
77.00
18.84


OMe
OMe

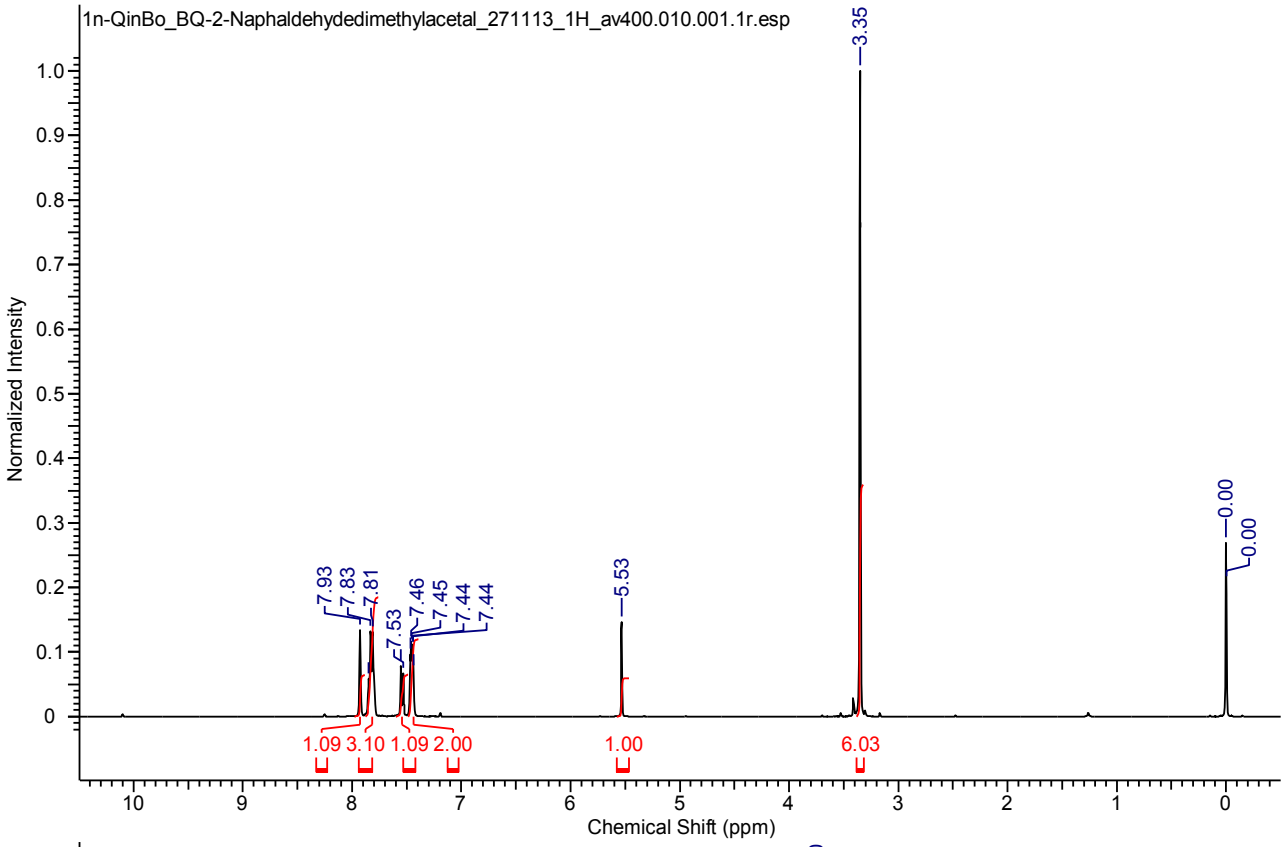
1m

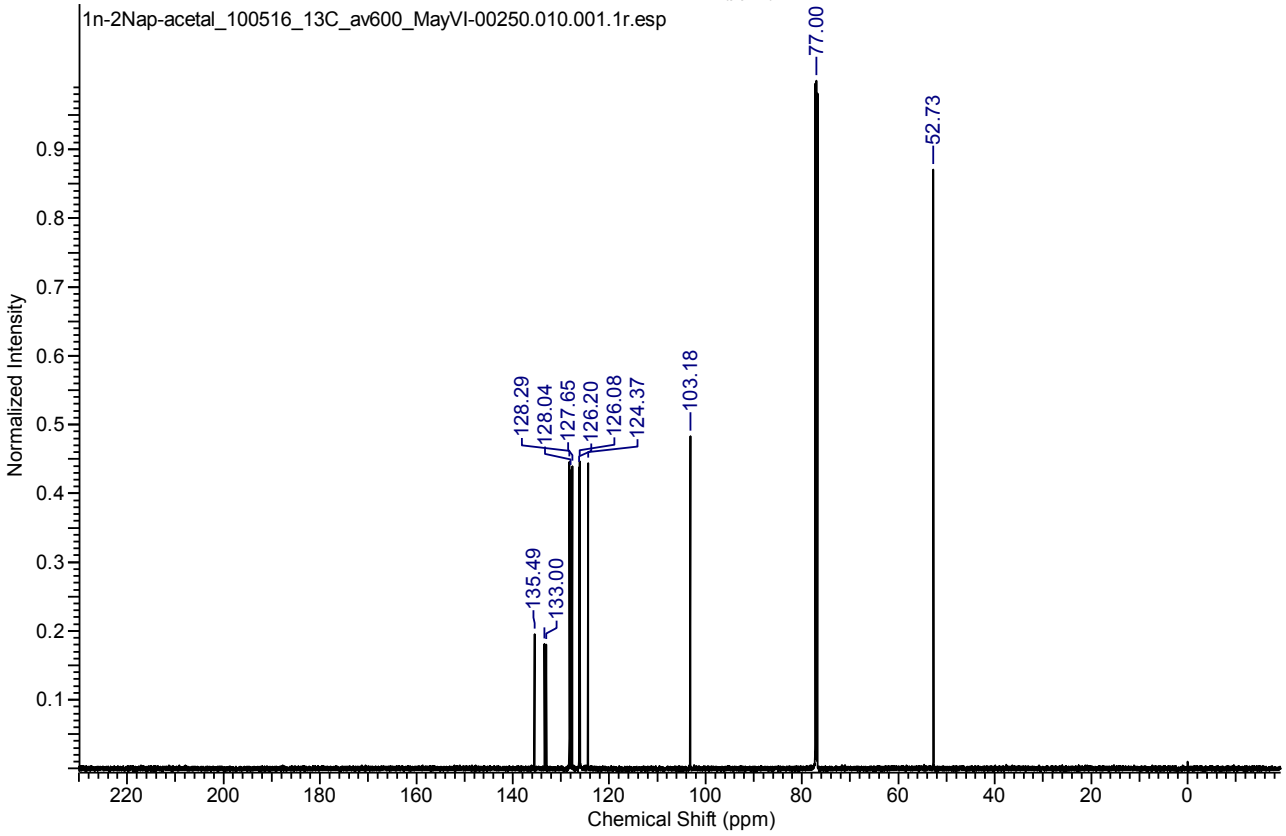

1m-QinBo_1-Naph-acetal_090414_1H_av400.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.37
0.00
5.91
5.89
8.28
8.26
7.83
7.81
7.71
7.49
7.47
7.45
7.43
0.99
1.92
0.93
2.90
1.00
6.07

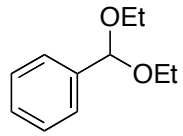

QinBo_BQ-1-Naph18-05_180516_1H-13C_av500_MayVI-01052.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
53.14
102.35
77.00
129.22
128.49
126.17
125.63
124.93
124.79
133.82


OMe
OMe

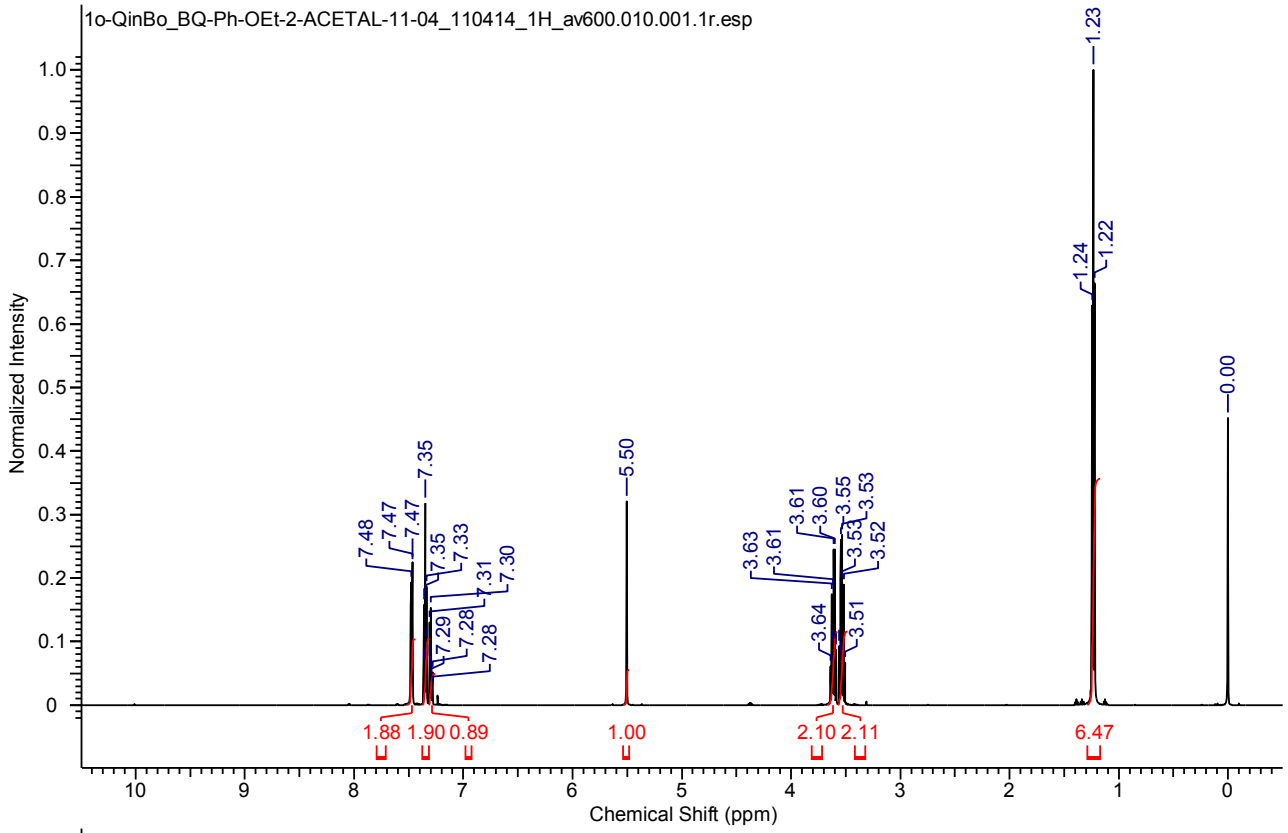
1n

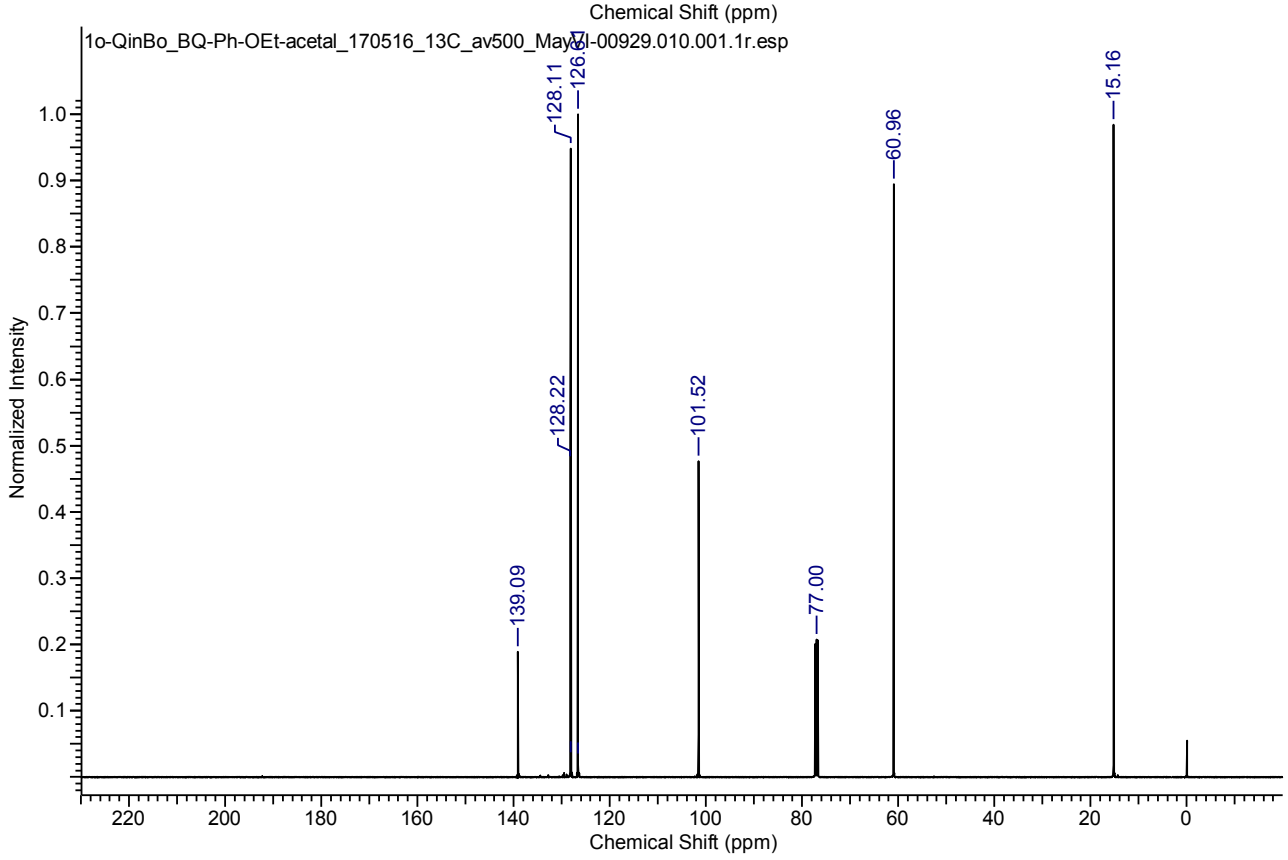

1n-QinBo_BQ-2-Naphaldehydedimethylacetal_271113_1H_av400.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.93
7.83
7.81
7.53
7.46
7.45
7.44
7.44
5.53
3.35
0.00
0.00
1.09 3.10 1.09 2.00
1.00
6.03

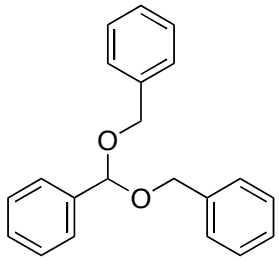

1n-2Nap-acetal_100516_13C_av600_MayVI-00250.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
52.73
128.29
128.04
127.65
126.20
126.08
124.37
103.18
135.49
133.00


OEt
OEt

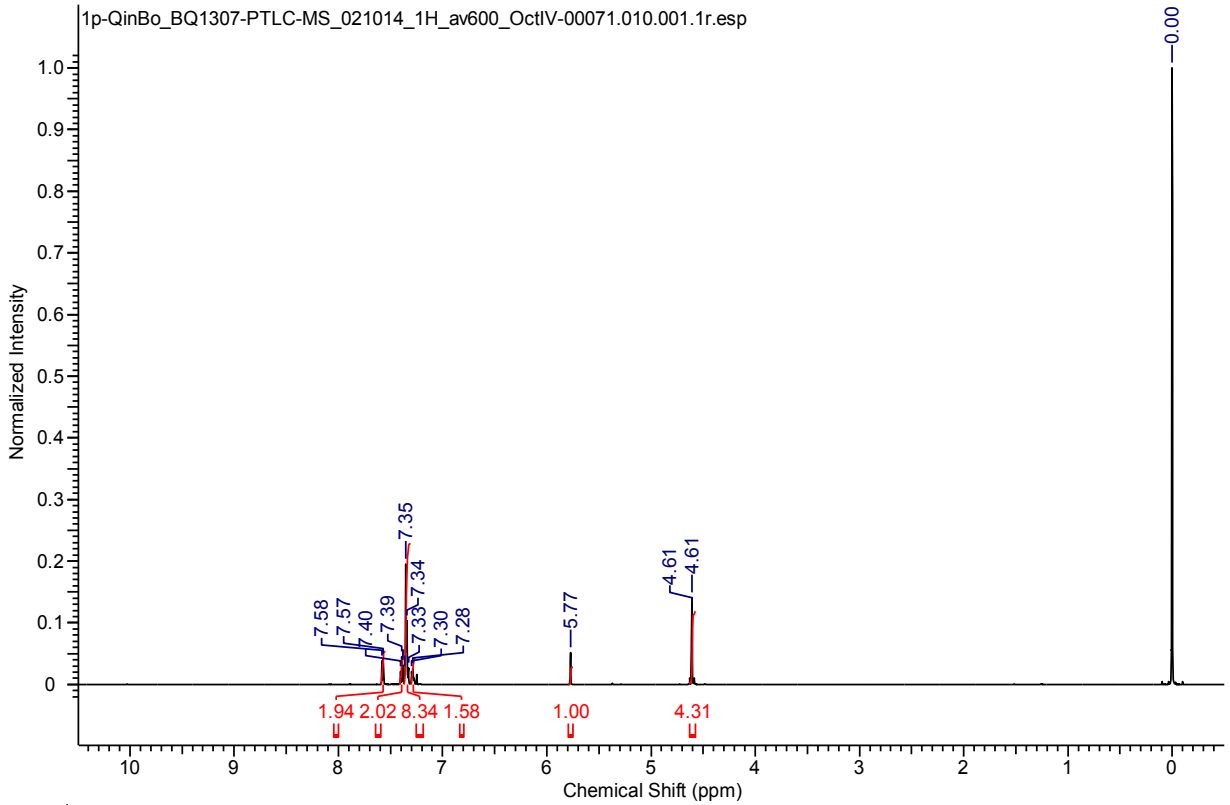
1o

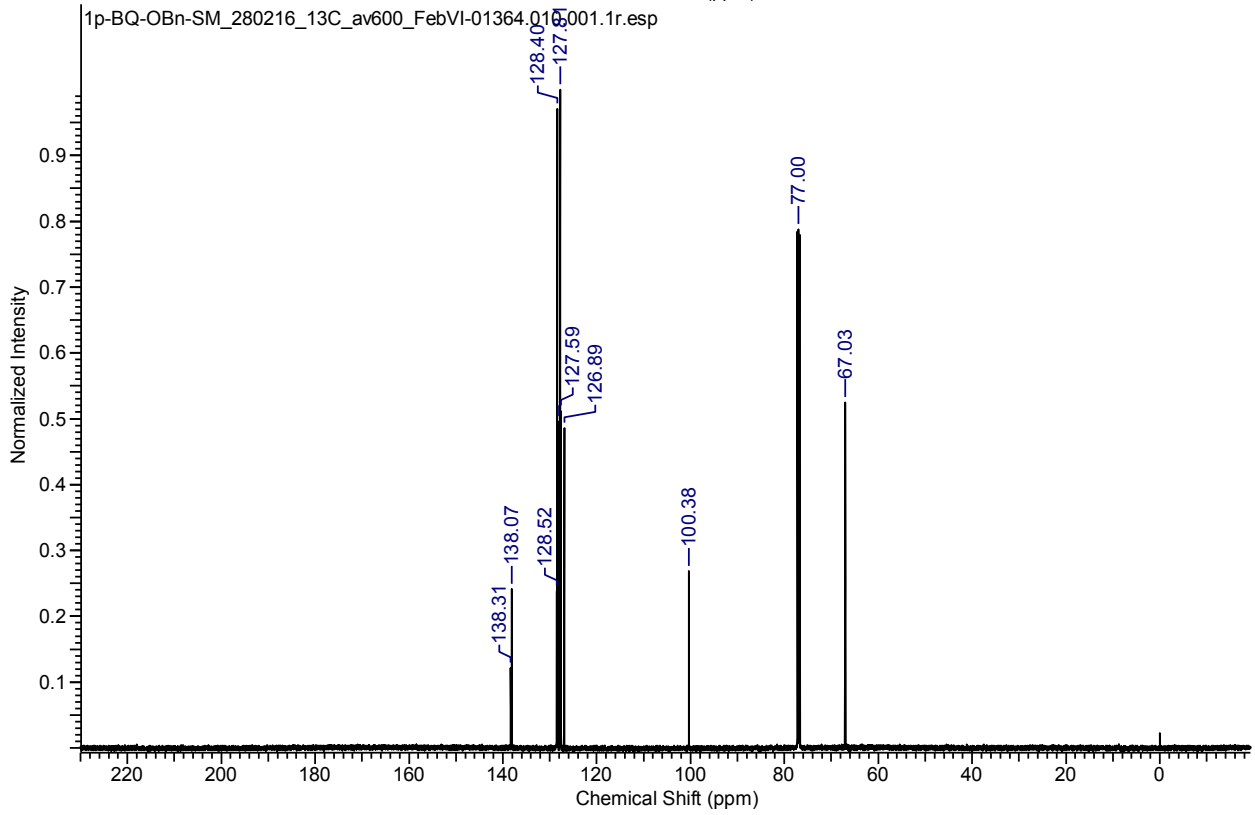

1o-QinBo_BQ-Ph-OEt-2-ACETAL-11-04_110414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
1.23
1.24
1.22
0.00
7.48
7.47
7.47
7.35
7.35
7.33
7.31
7.30
7.29
7.28
7.28
5.50
3.63
3.61
3.61
3.60
3.55
3.53
3.53
3.52
3.64
3.51
1.88
1.90
0.89
1.00
2.10
2.11
6.47

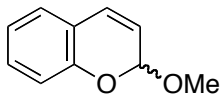

1o-QinBo_BQ-Ph-OEt-acetal_170516_13C_av500_May
-00929.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.11
126.67
15.16
60.96
128.22
101.52
139.09
77.00



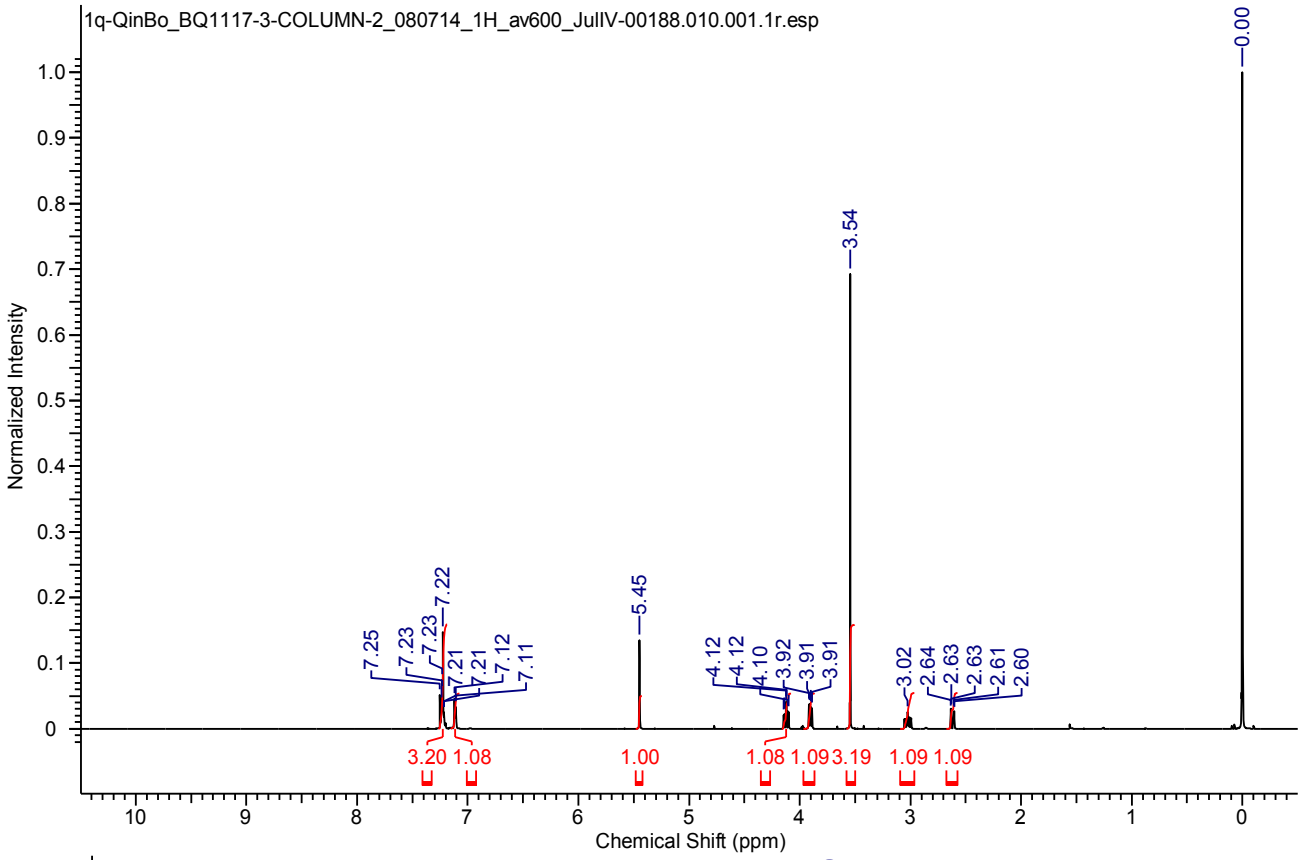
1p

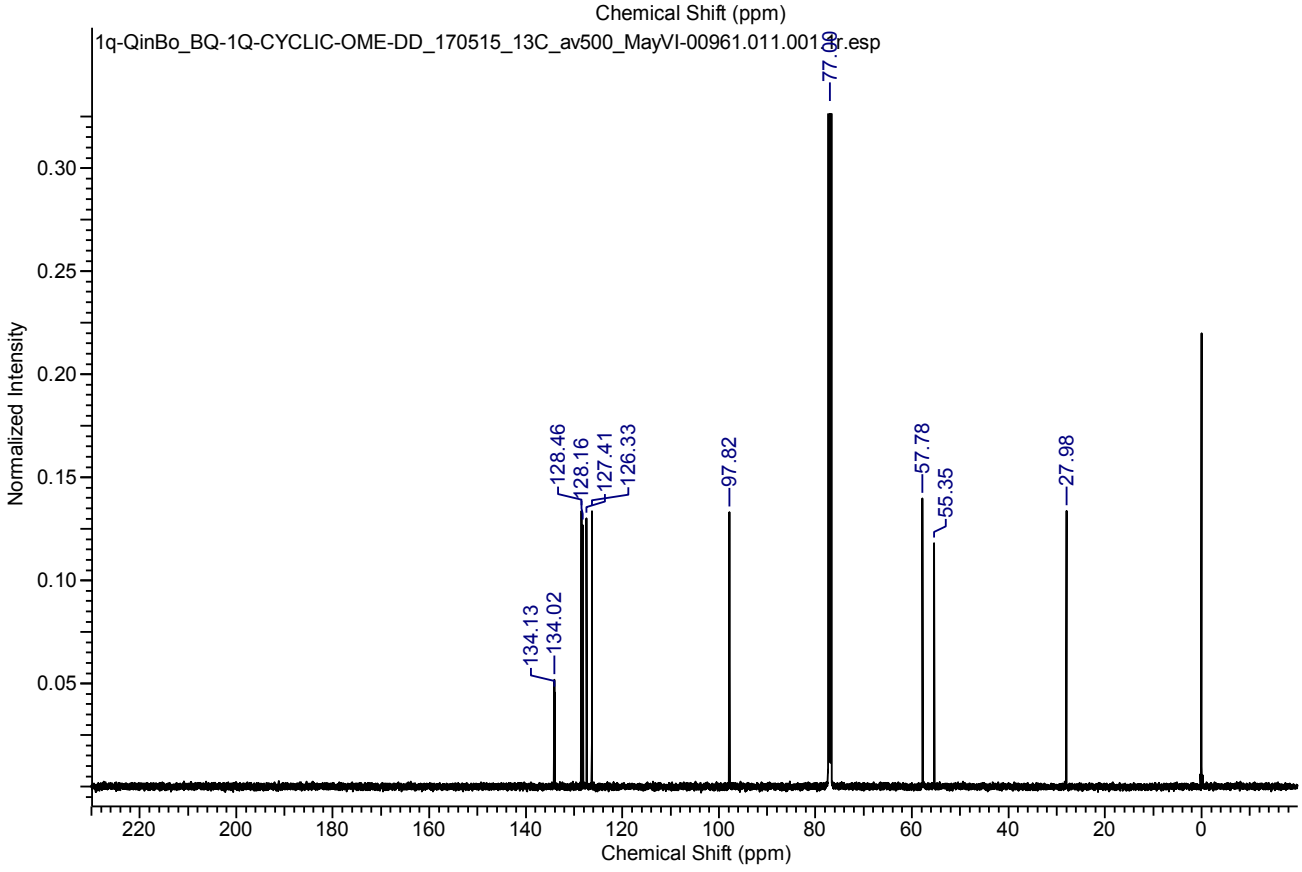

1p-QinBo_BQ1307-PTLC-MS_021014_1H_av600_OctIV-00071.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
7.58
7.57
7.40
7.39
7.35
7.34
7.33
7.30
7.28
5.77
4.61
4.61
1.94
2.02
8.34
1.58
1.00
4.31

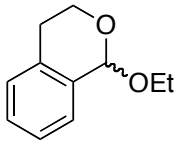

1p-BQ-OBn-SM_280216_13C_av600_FebVI-01364.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.40
127.91
77.00
127.59
126.89
67.03
138.07
128.52
100.38
138.31


O
OMe

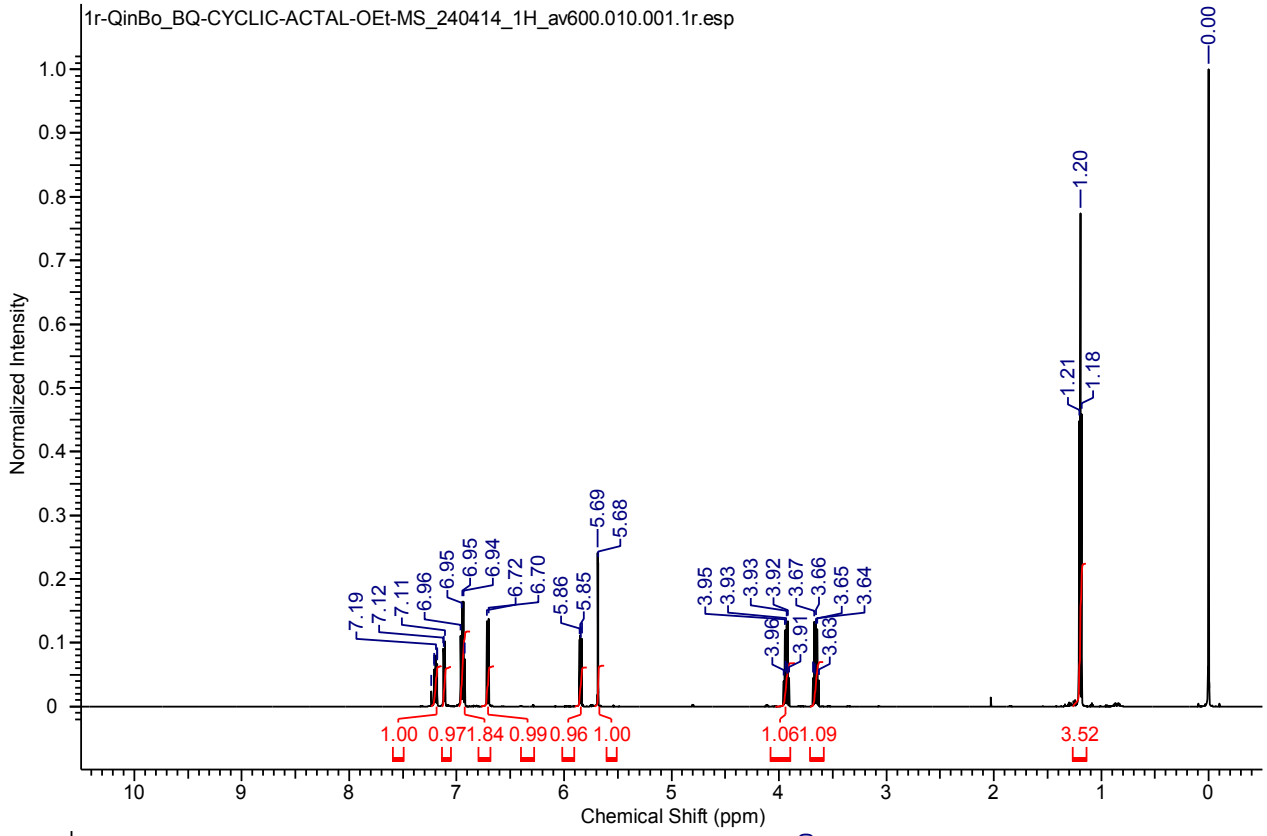
rac-**1q**

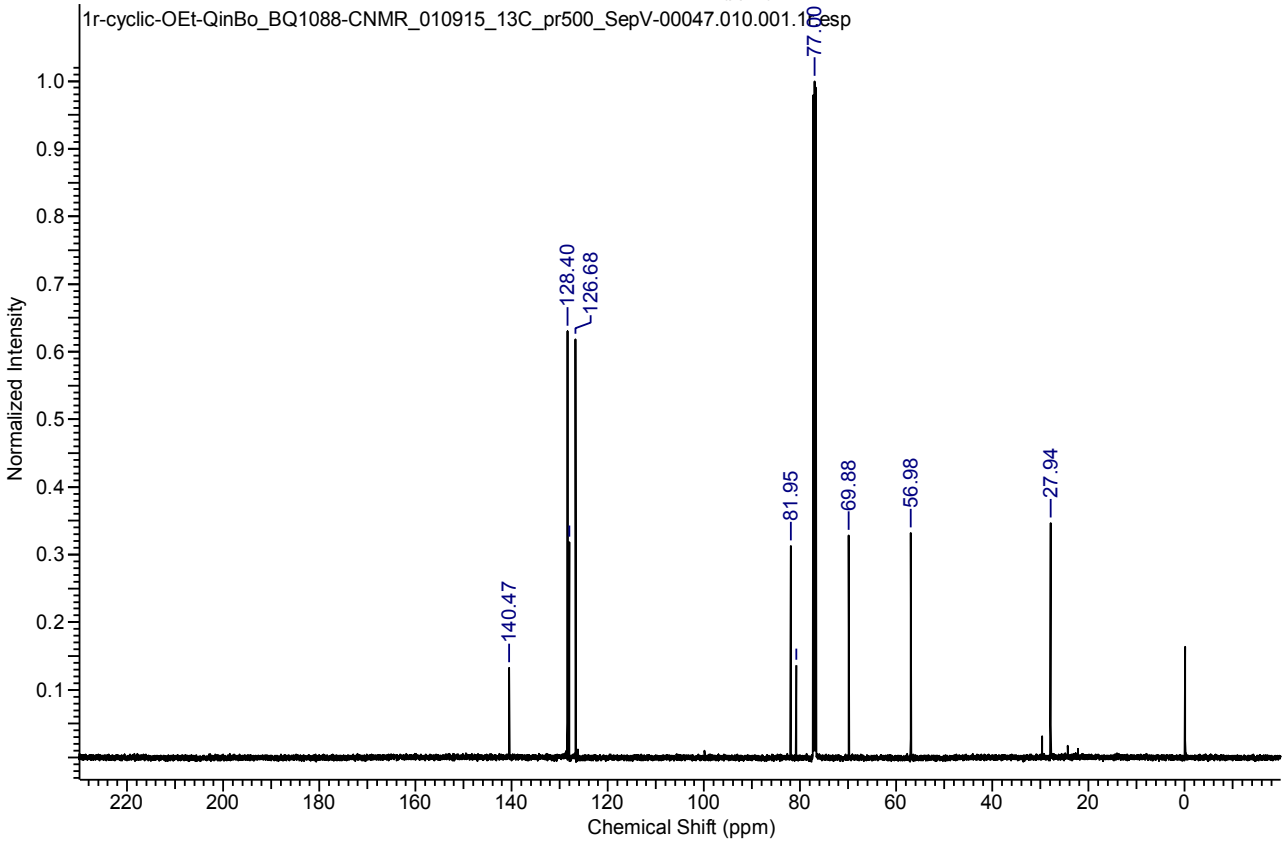

1q-QinBo_BQ1117-3-COLUMN-2_080714_1H_av600_JulIV-00188.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
3.54
5.45
7.25
7.23
7.23
7.22
7.21
7.21
7.12
7.11
4.12
4.12
4.10
3.92
3.91
3.91
3.02
2.64
2.63
2.63
2.61
2.60
3.20
1.08
1.00
1.08
1.09
3.19
1.09
1.09

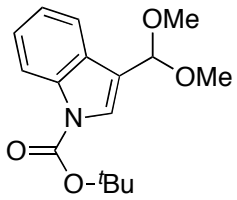

1q-QinBo_BQ-1Q-CYCLIC-OME-DD_170515_13C_av500_MayVI-00961.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.26
134.13
134.02
128.46
128.16
127.41
126.33
97.82
57.78
55.35
27.98


O
OEt

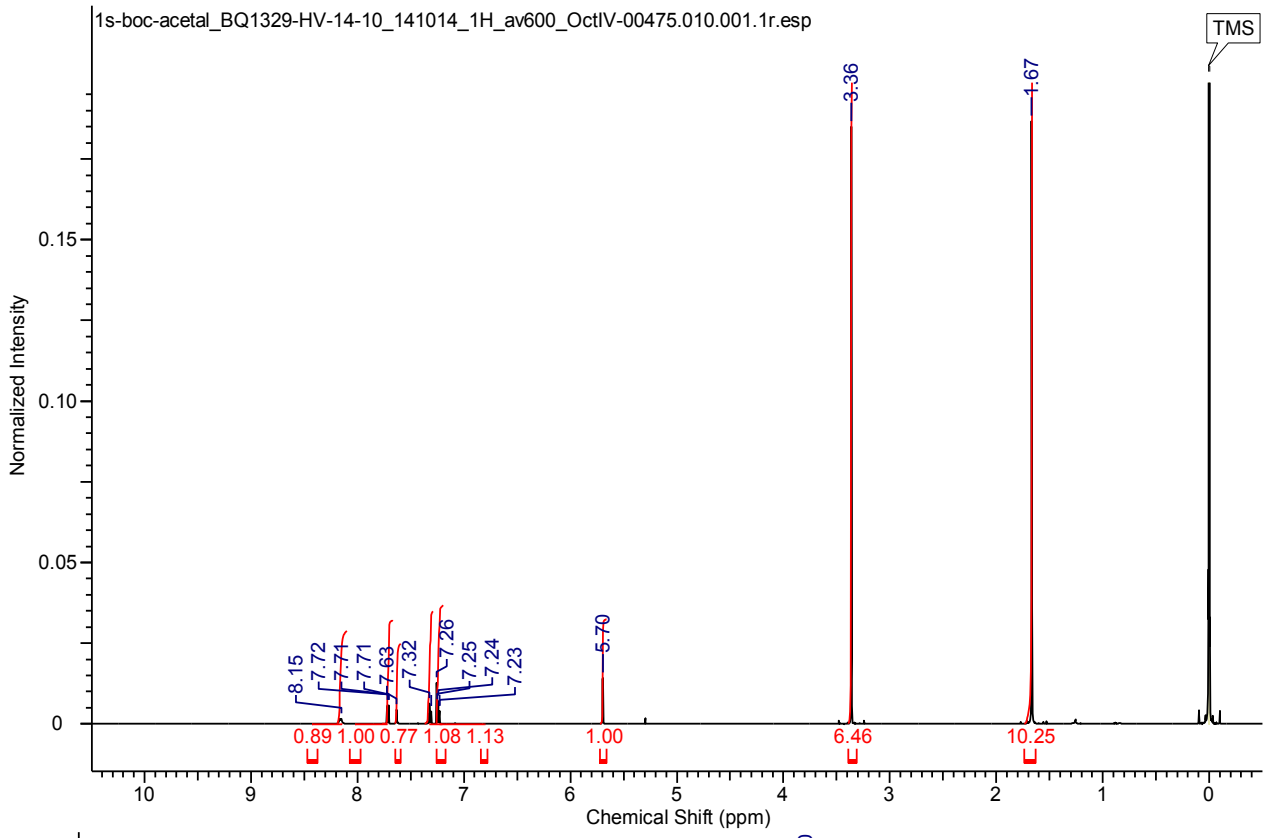
rac-**1r**

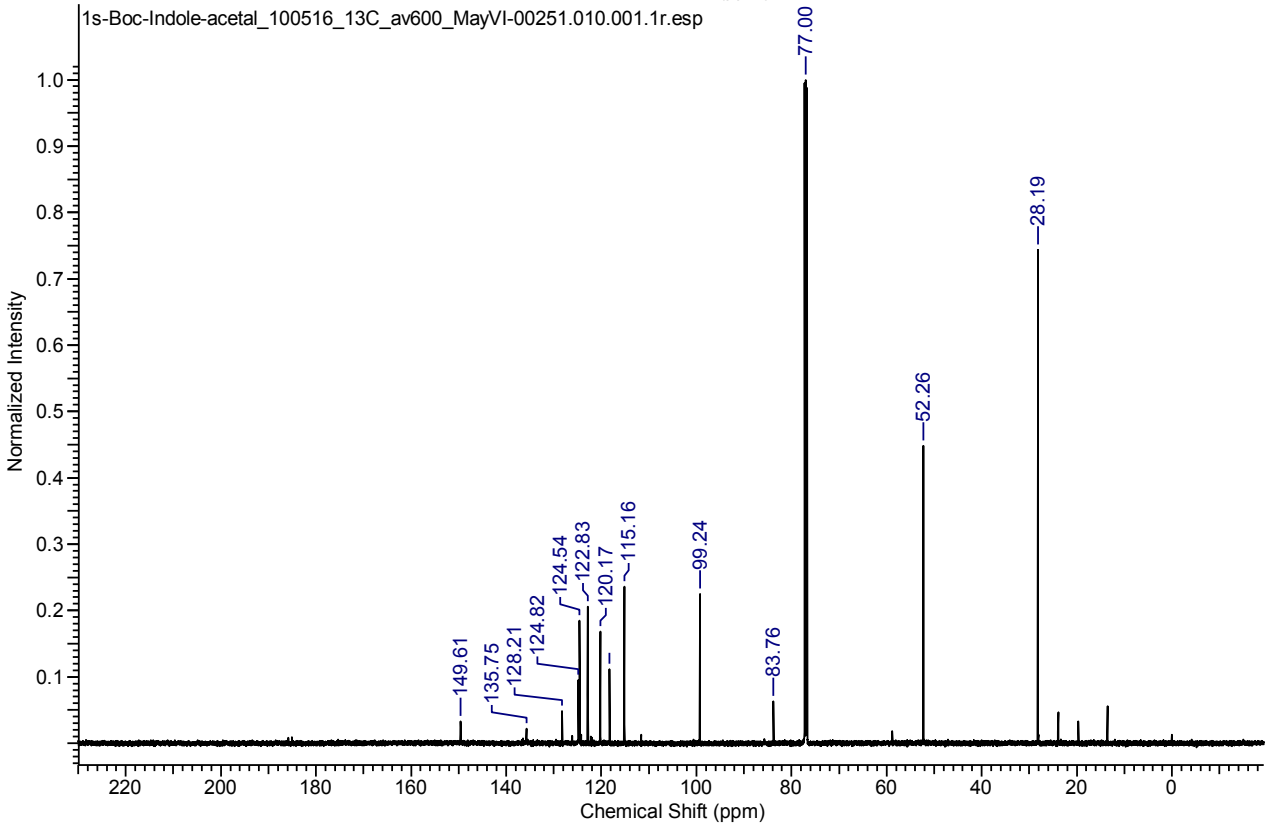

1r-QinBo_BQ-CYCLIC-ACTAL-OEt-MS_240414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
1.20
1.21
1.18
7.19
7.12
7.11
6.96
6.95
6.95
6.94
6.72
6.70
5.86
5.85
5.69
5.68
3.95
3.93
3.93
3.92
3.67
3.66
3.65
3.64
3.96
3.91
3.63
1.00
0.97
1.84
0.99
0.96
1.00
1.06
1.09
3.52

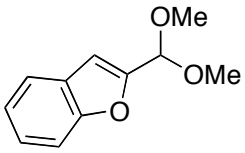

1r-cyclic-OEt-QinBo_BQ1088-CNMR_010915_13C_pr500_SepV-00047.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
128.40
126.68
140.47
81.95
69.88
56.98
27.94


OMe
OMe
N
O
O-tBu

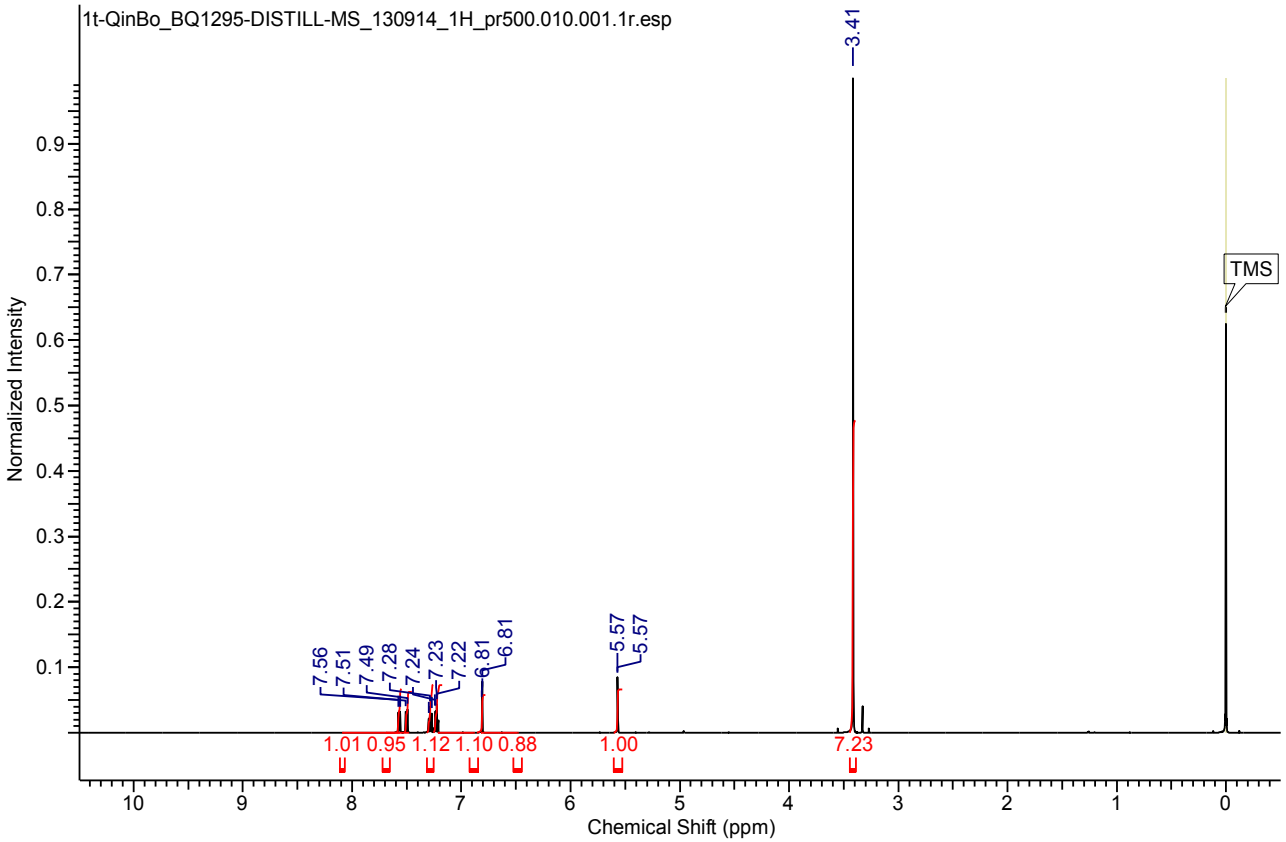
1s

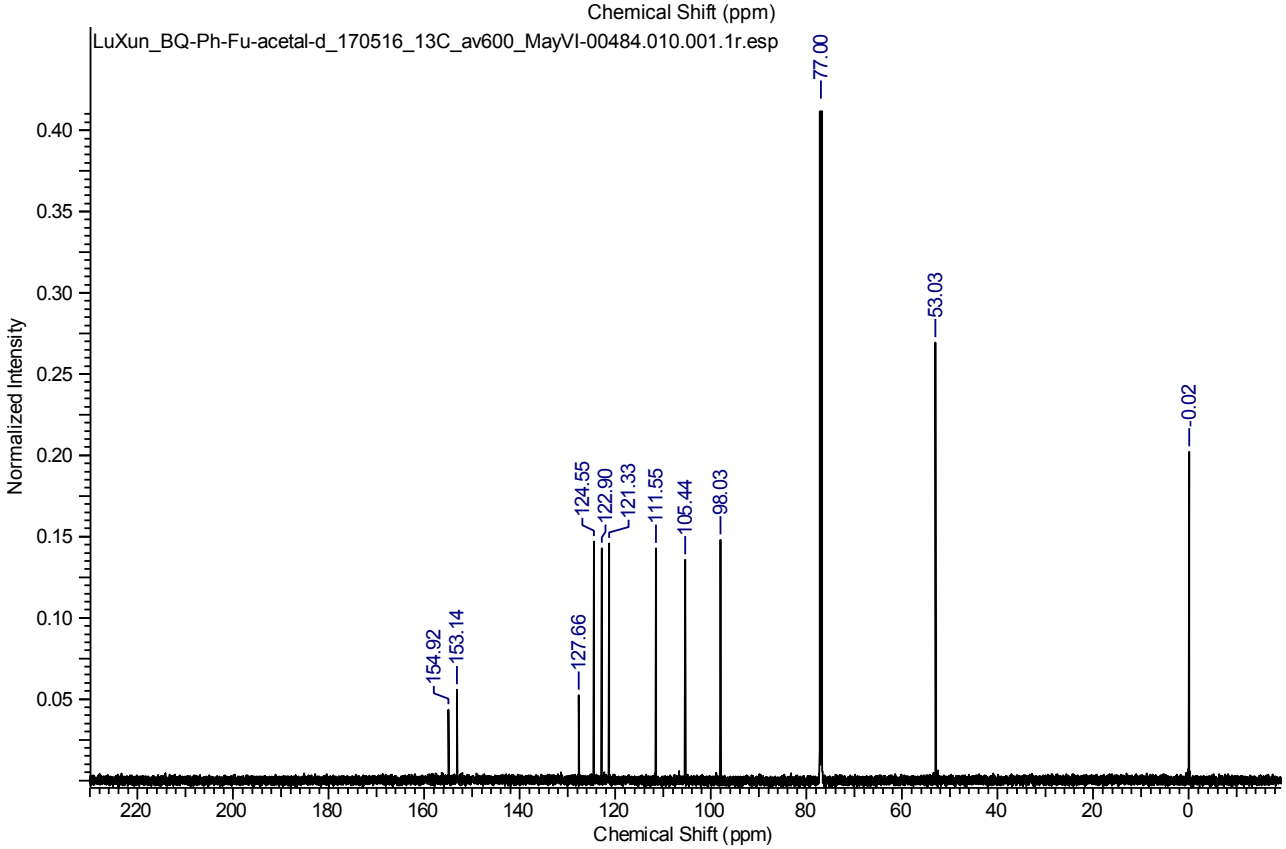

1s-boc-acetal_BQ1329-HV-14-10_141014_1H_av600_OctIV-00475.010.001.1r.esp
TMS
3.36
1.67
8.15
7.72
7.71
7.71
7.63
7.32
7.26
7.25
7.24
7.23
5.70
0.89 1.00 0.77 1.08 1.13
1.00
6.46
10.25
Normalized Intensity
Chemical Shift (ppm)

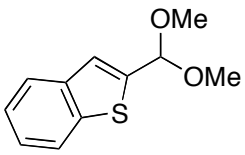

1s-Boc-Indole-acetal_100516_13C_av600_MayVI-00251.010.001.1r.esp
77.00
28.19
52.26
149.61
135.75
128.21
124.82
124.54
122.83
120.17
115.16
99.24
83.76
Normalized Intensity
Chemical Shift (ppm)


OMe
OMe
O

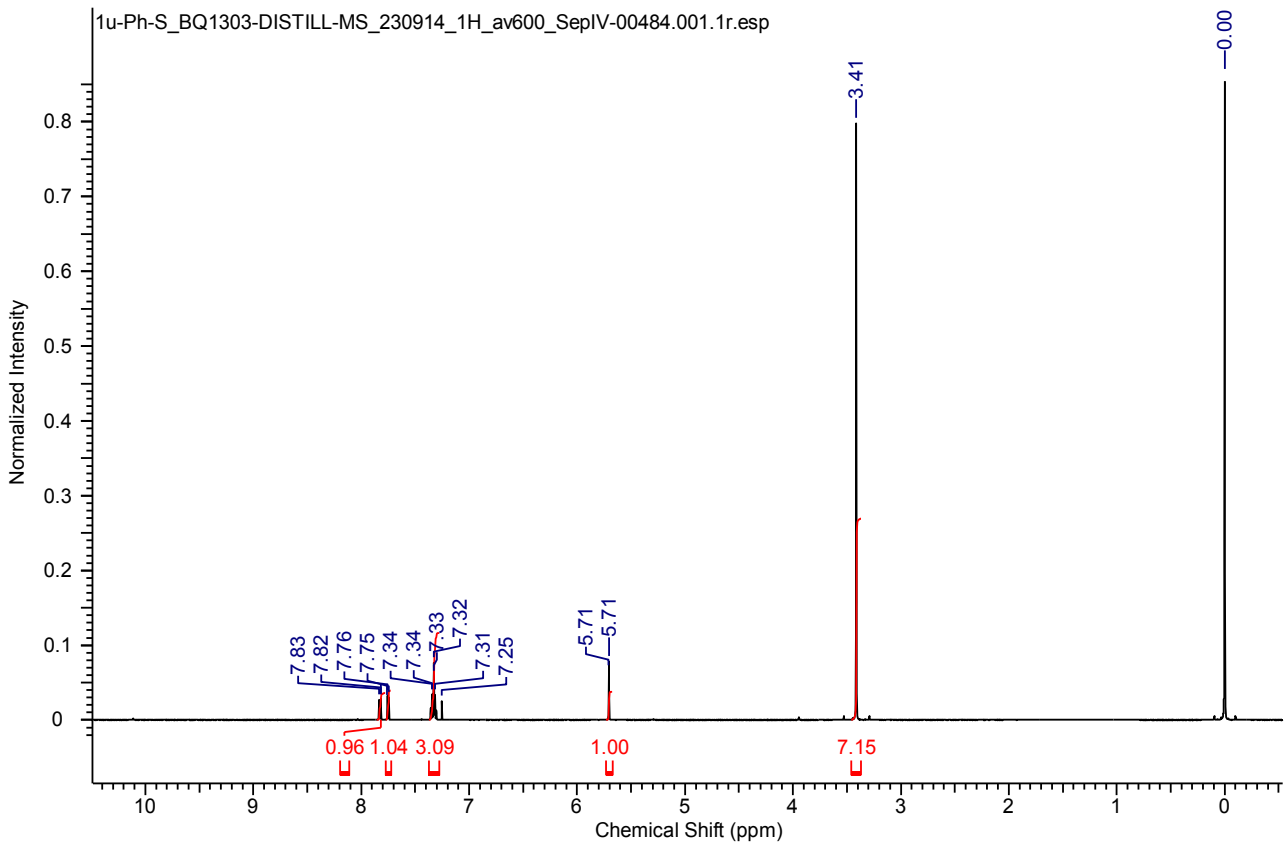
1t

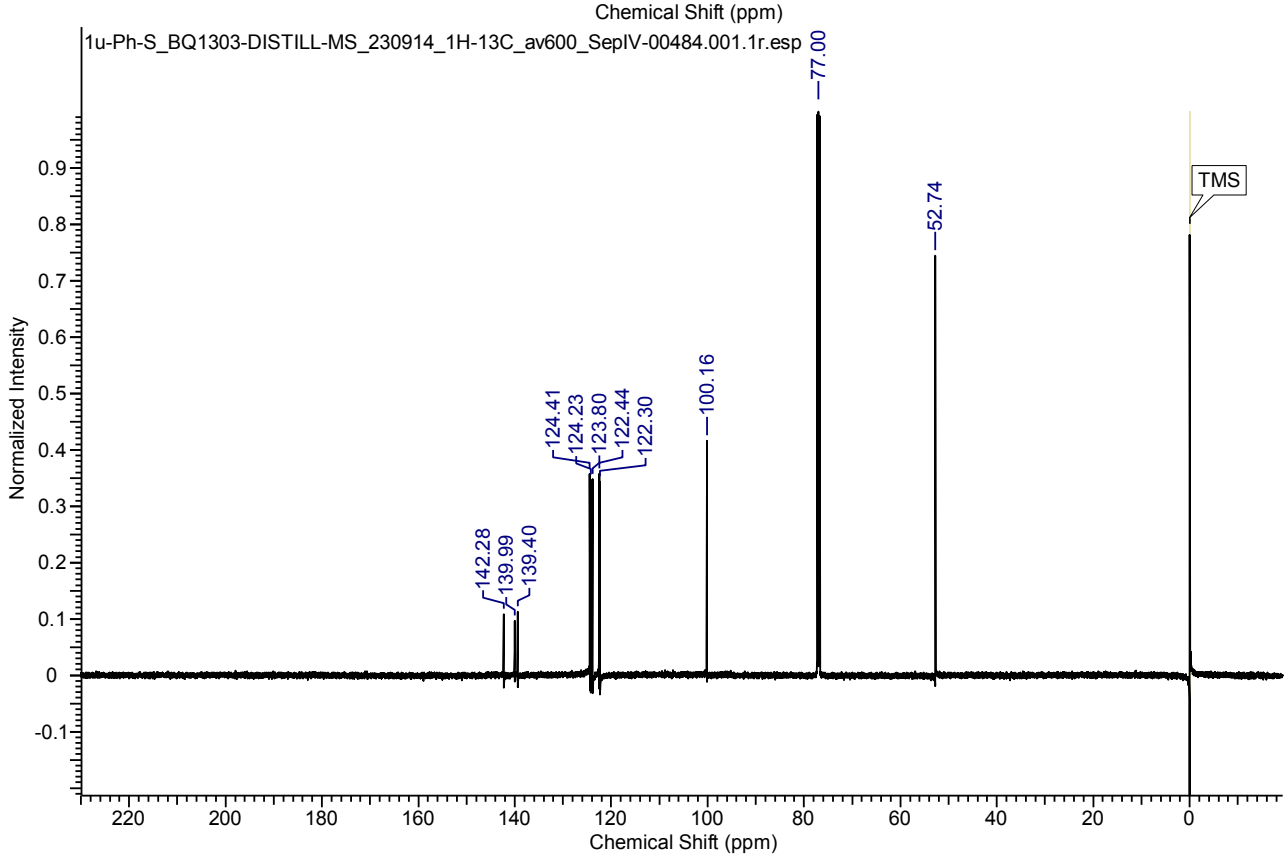

1t-QinBo_BQ1295-DISTILL-MS_130914_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.41
TMS
7.56
7.51
7.49
7.28
7.24
7.23
7.22
6.81
6.81
5.57
5.57
1.01 0.95 1.12 1.10 0.88
1.00
7.23

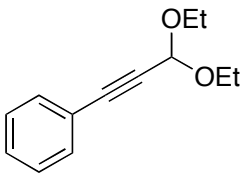

LuXun_BQ-Ph-Fu-acetal-d_170516_13C_av600_MayVI-00484.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
53.03
0.02
124.55
122.90
121.33
111.55
105.44
98.03
154.92
153.14
127.66


OMe
OMe
S

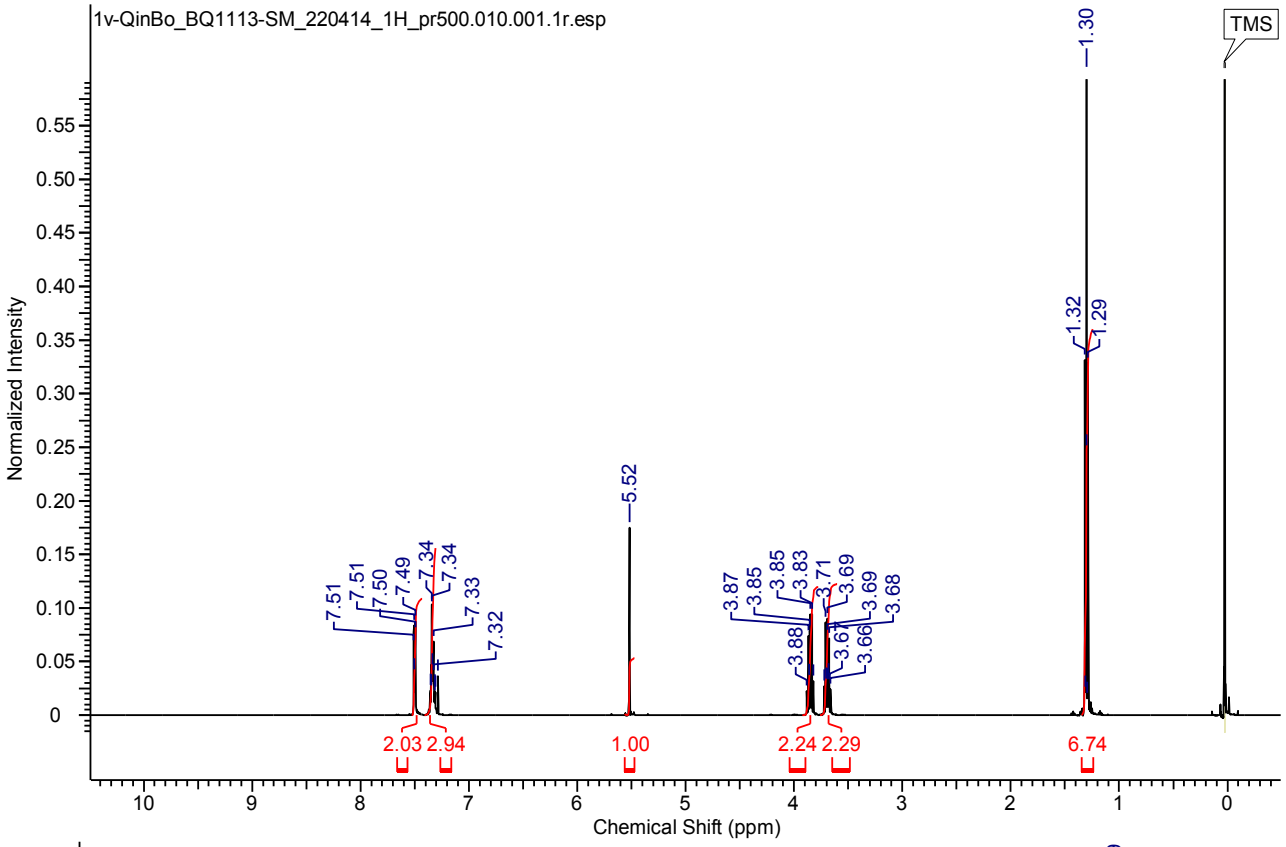
1u

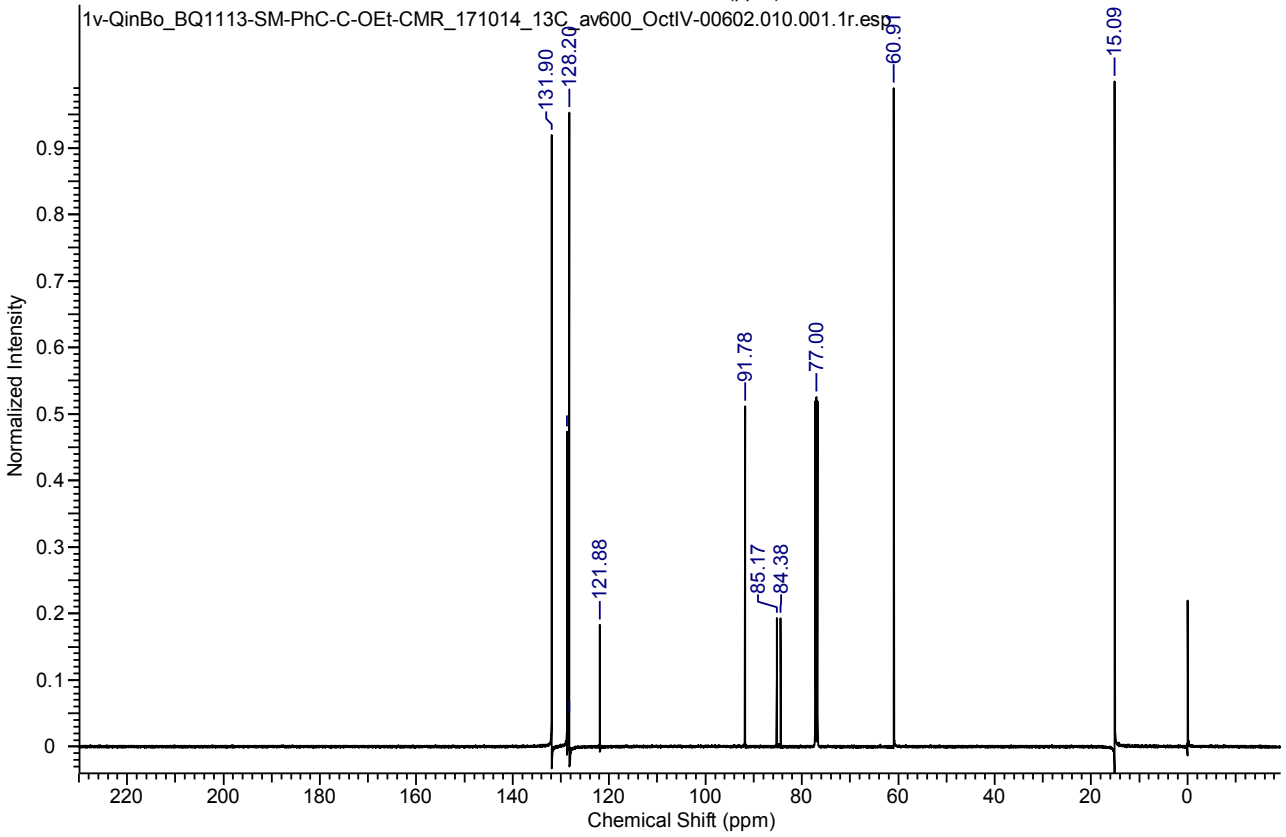

1u-Ph-S_BQ1303-DISTILL-MS_230914_1H_av600_SepIV-00484.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.83
7.82
7.76
7.75
7.34
7.34
7.33
7.32
7.31
7.25
5.71
5.71
3.41
0.00
0.96
1.04
3.09
1.00
7.15

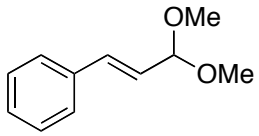

1u-Ph-S_BQ1303-DISTILL-MS_230914_1H-13C_av600_SepIV-00484.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
52.74
TMS
100.16
124.41
124.23
123.80
122.44
122.30
142.28
139.99
139.40


OEt
OEt

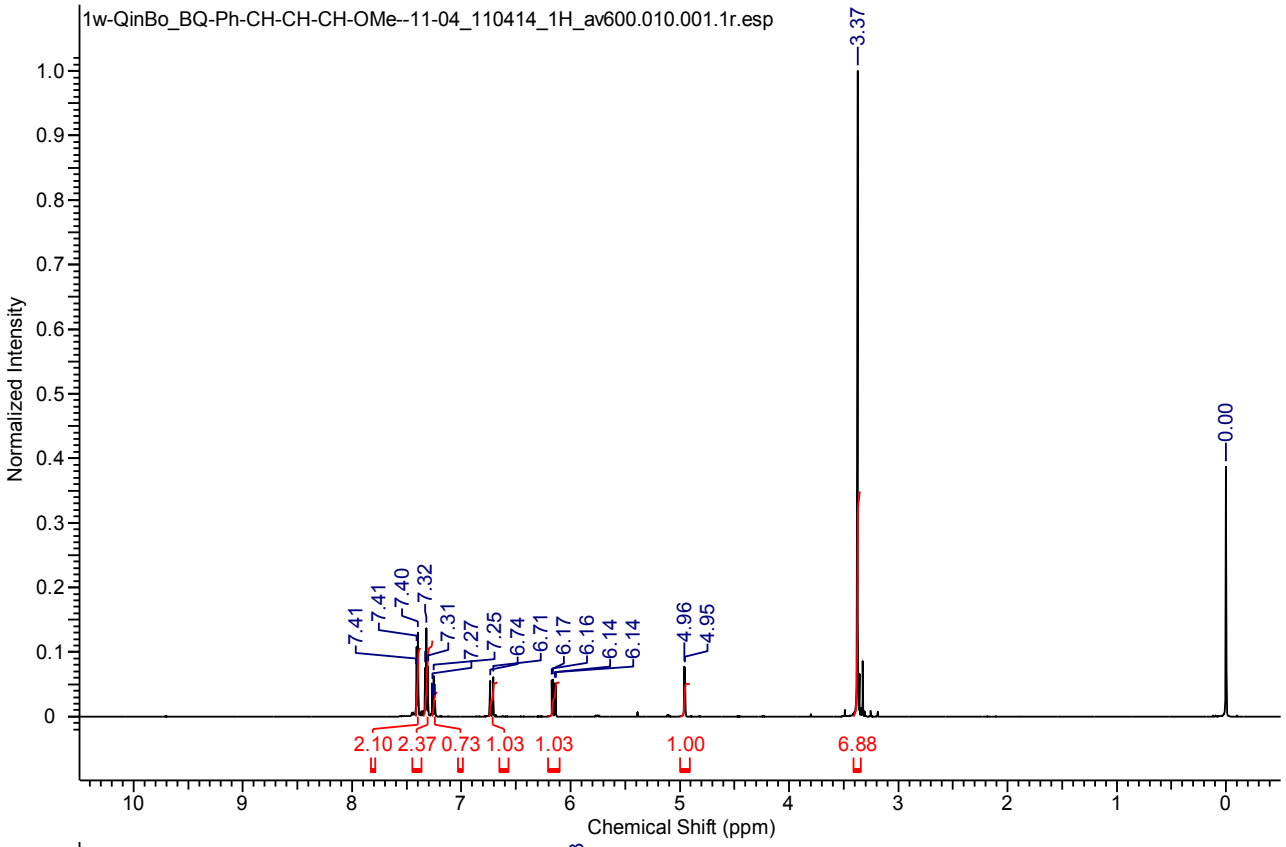
1v

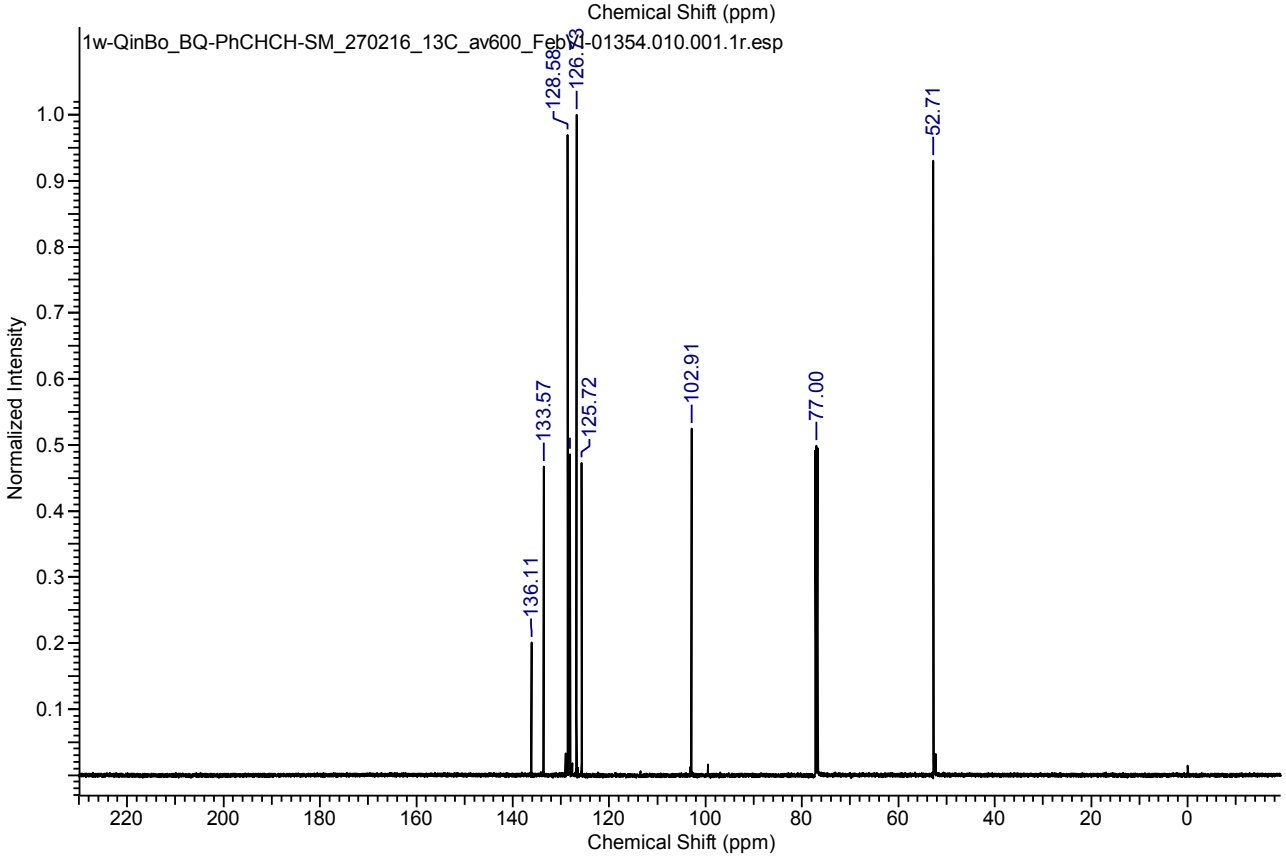

1v-QinBo_BQ1113-SM_220414_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
1.30
1.32
1.29
5.52
7.51
7.51
7.50
7.49
7.34
7.34
7.33
7.32
3.87
3.85
3.85
3.83
3.71
3.69
3.69
3.68
3.88
3.67
3.66
2.03
2.94
1.00
2.24
2.29
6.74

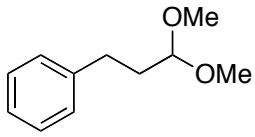

1v-QinBo_BQ1113-SM-PhC-C-OEt-CMR_171014_13C_av600_OctIV-00602.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
131.90
128.20
121.88
91.78
85.17
84.38
77.00
60.97
15.09


OMe
OMe

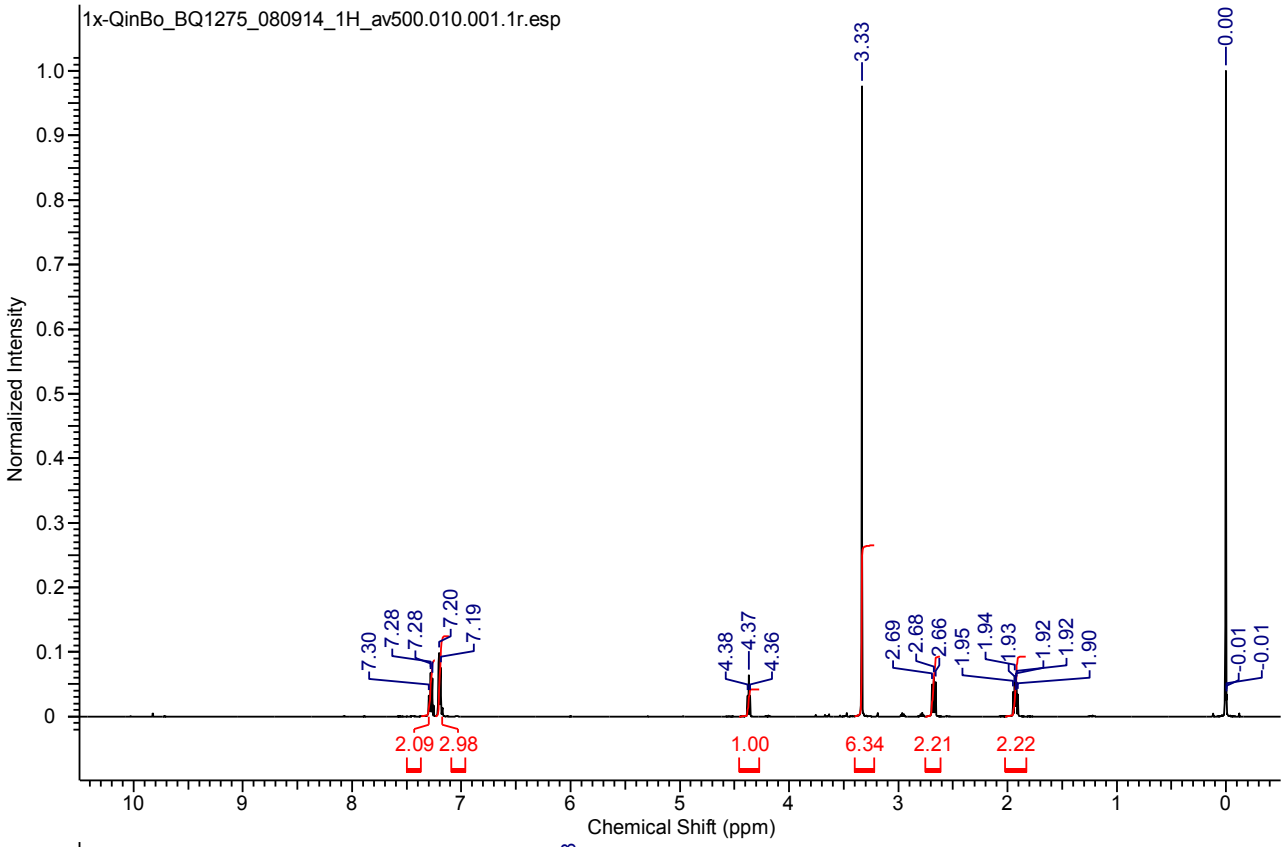
1w

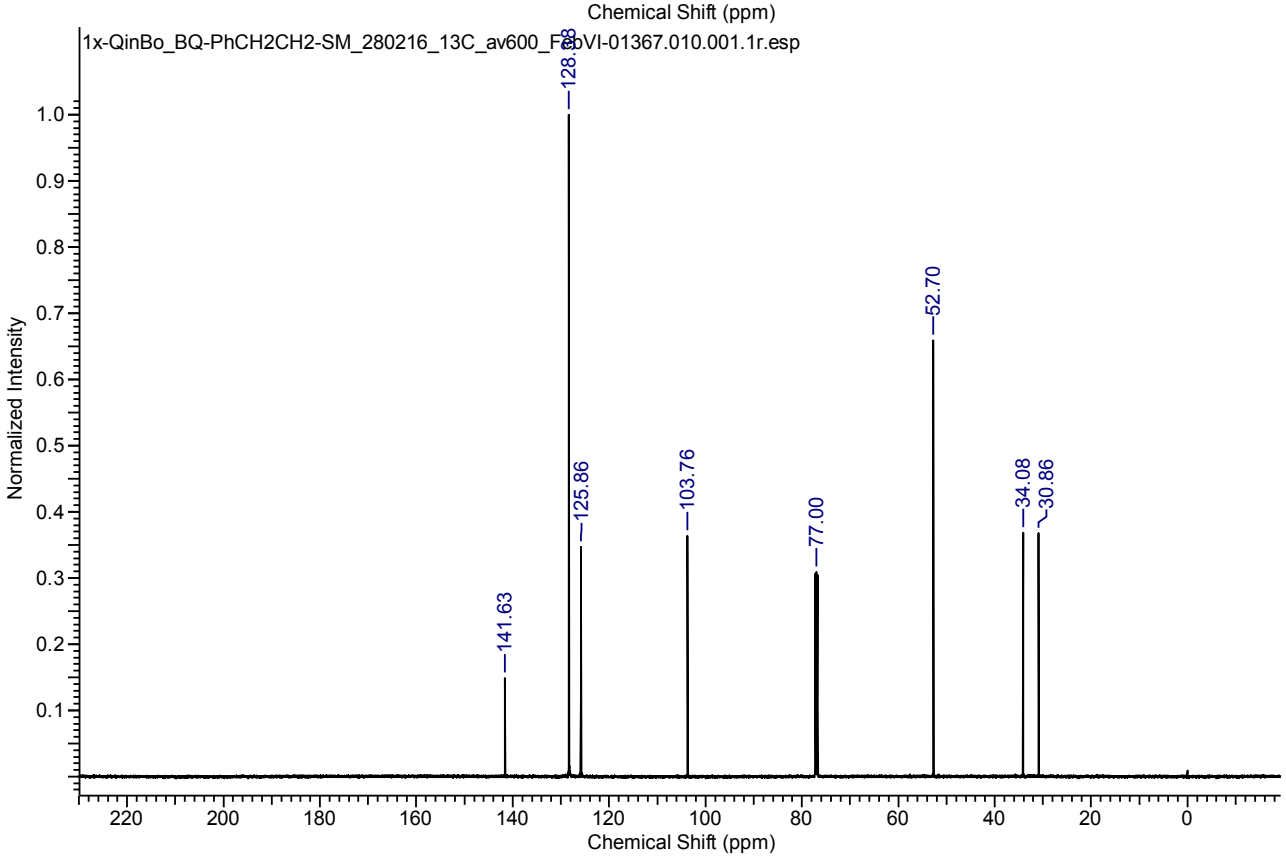

1w-QinBo_BQ-Ph-CH-CH-CH-OMe--11-04_110414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.37
0.00
7.41
7.41
7.40
7.32
7.31
7.27
7.25
6.74
6.71
6.17
6.16
6.14
6.14
4.96
4.95
2.10 2.37 0.73 1.03 1.03 1.00 6.88

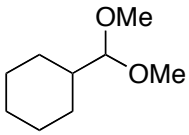

1w-QinBo_BQ-PhCHCH-SM_270216_13C_av600_Feb-01354.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.58
126.63
52.71
133.57
125.72
102.91
77.00
136.11


OMe
OMe

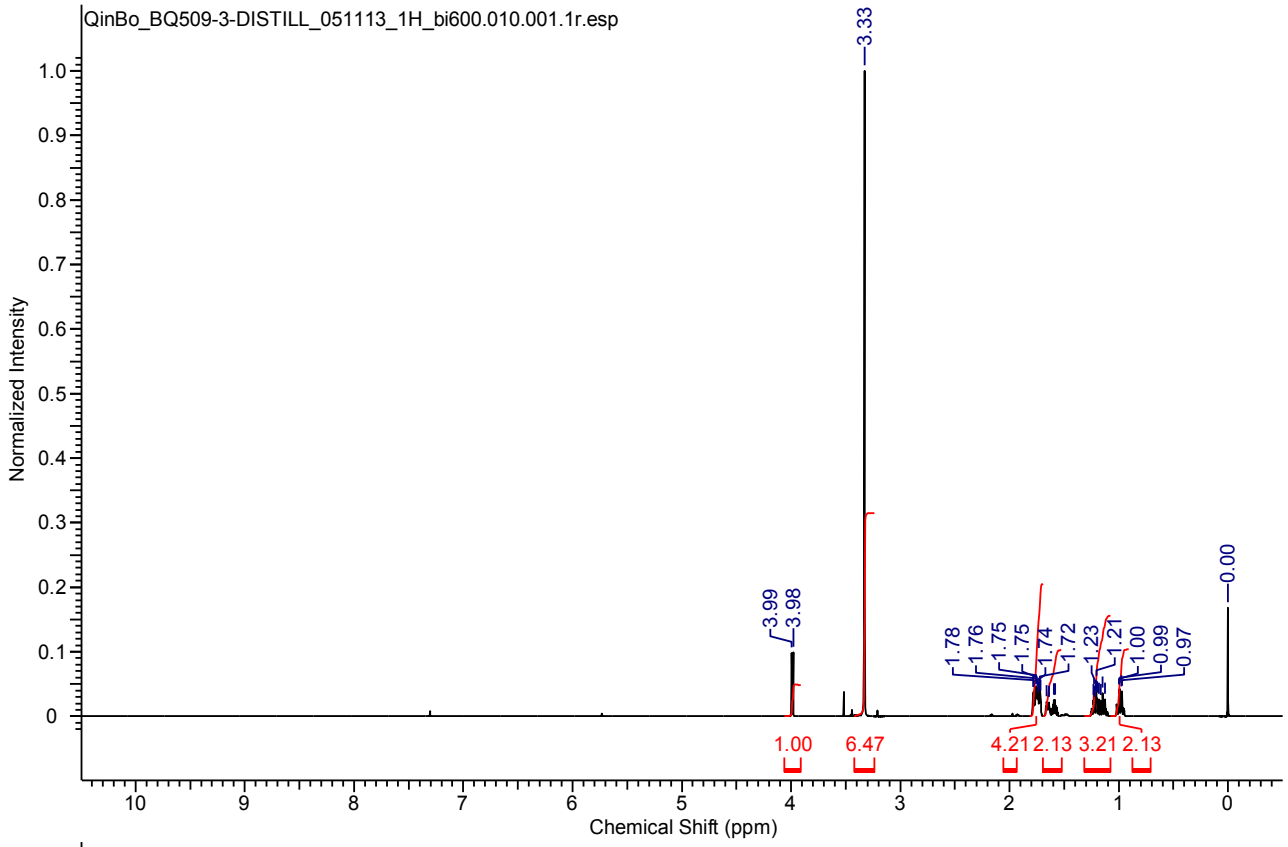
1x

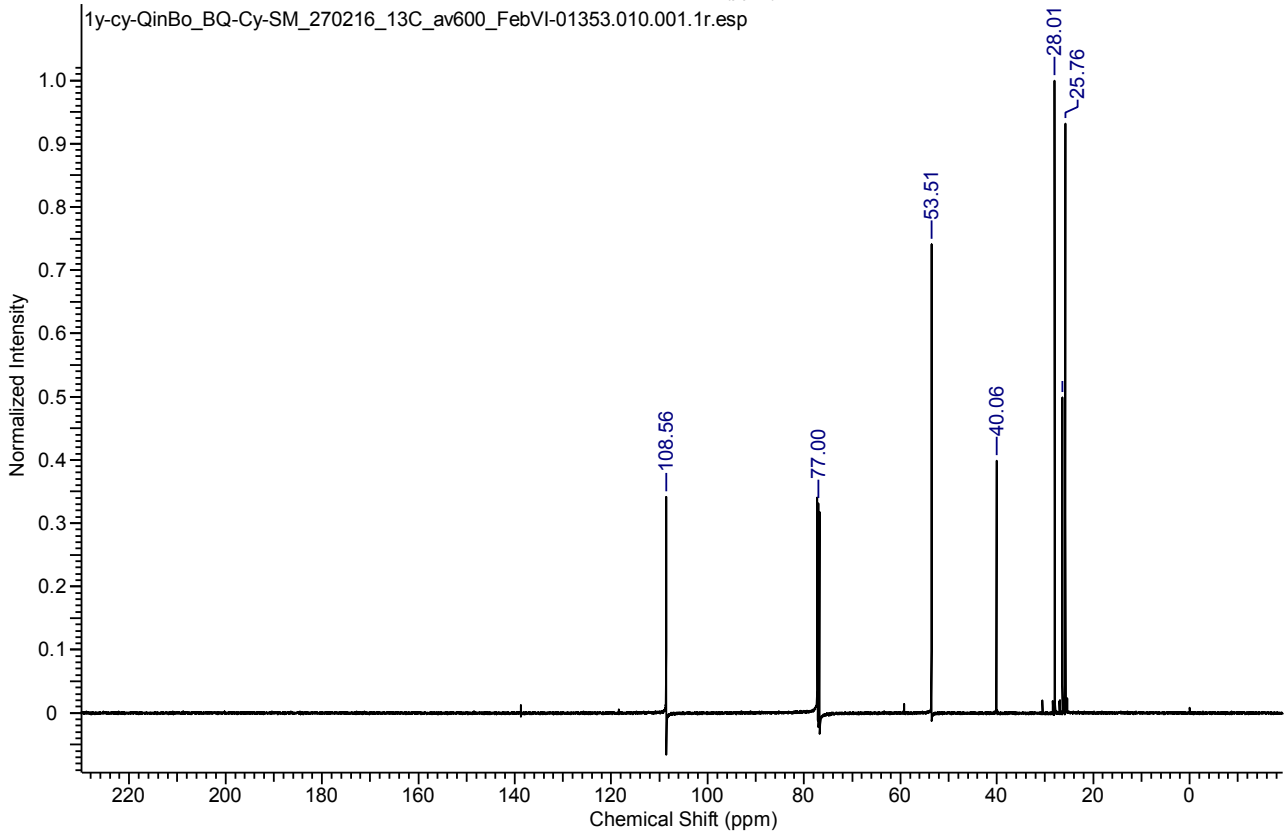

1x-QinBo_BQ1275_080914_1H_av500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.33
0.00
7.30
7.28
7.28
7.20
7.19
4.38
4.37
4.36
2.69
2.68
2.66
1.95
1.94
1.93
1.92
1.92
1.90
0.01
0.01
2.09
2.98
1.00
6.34
2.21
2.22

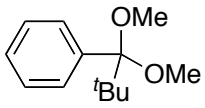

1x-QinBo_BQ-PhCH2CH2-SM_280216_13C_av600_FebVI-01367.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.88
125.86
141.63
103.76
77.00
52.70
34.08
30.86


OMe
OMe

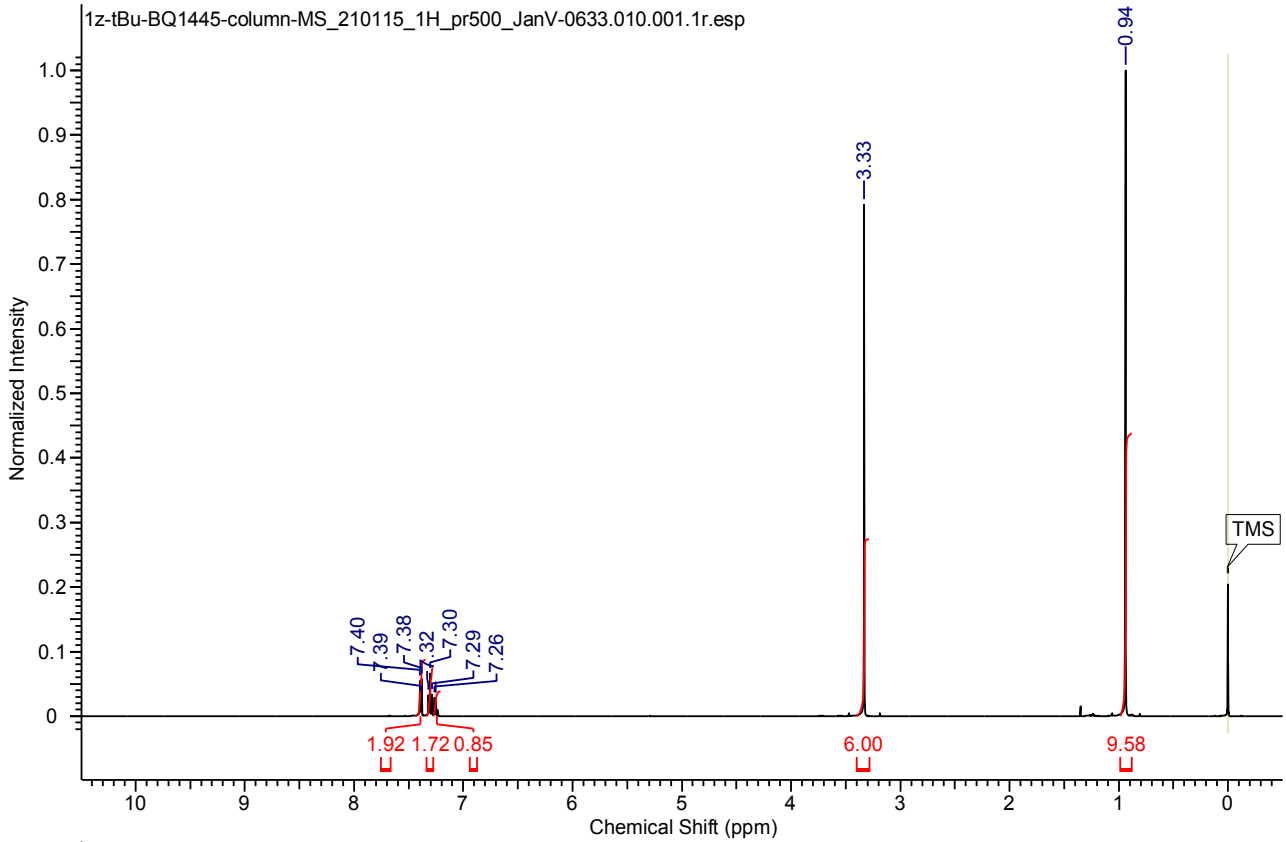
1y

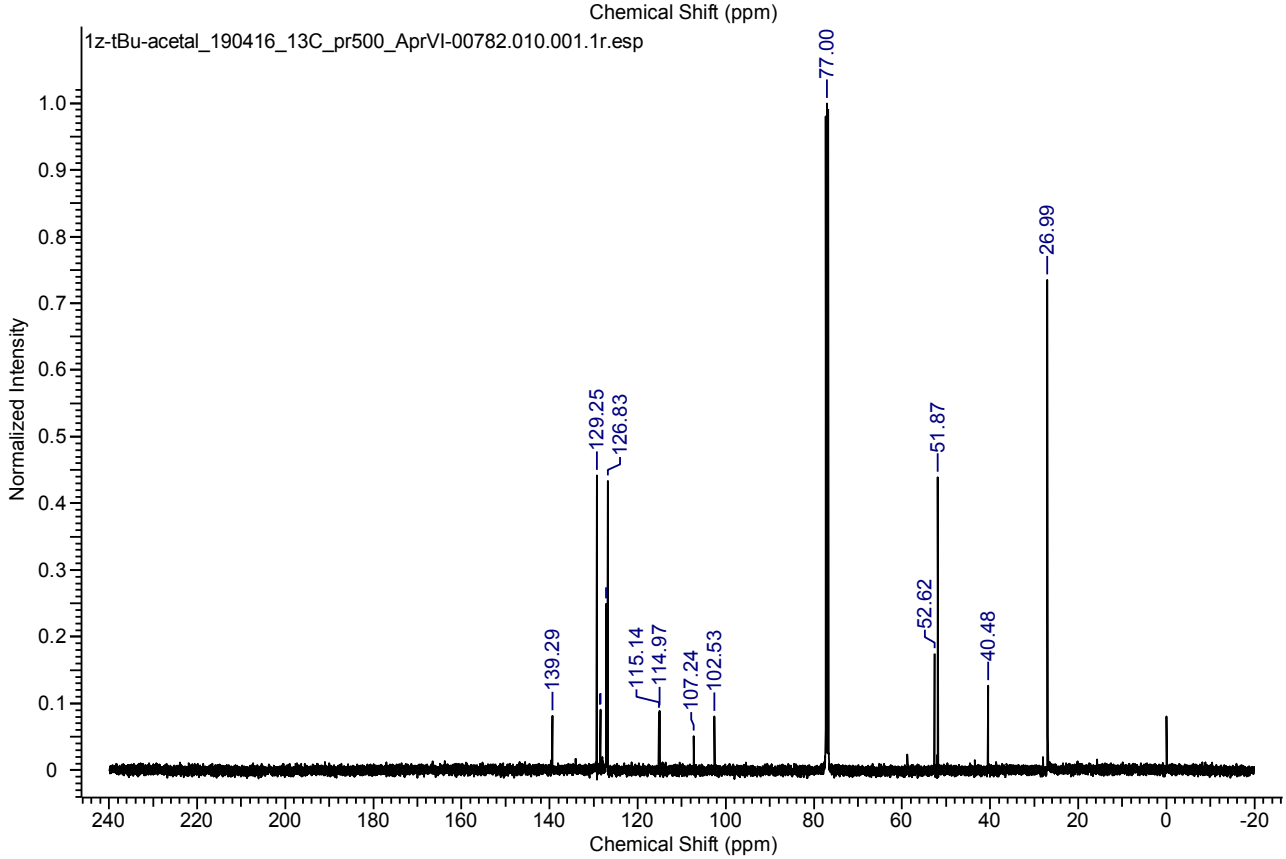

QinBo_BQ509-3-DISTILL_051113_1H_bi600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.33
3.99
3.98
1.78
1.76
1.75
1.75
1.74
1.72
1.23
1.21
1.00
0.99
0.97
0.00
1.00
6.47
4.21
2.13
3.21
2.13

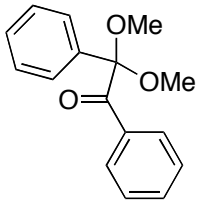

1y-cy-QinBo_BQ-Cy-SM_270216_13C_av600_FebVI-01353.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
28.01
25.76
53.51
40.06
108.56
77.00


OMe
OMe
tBu

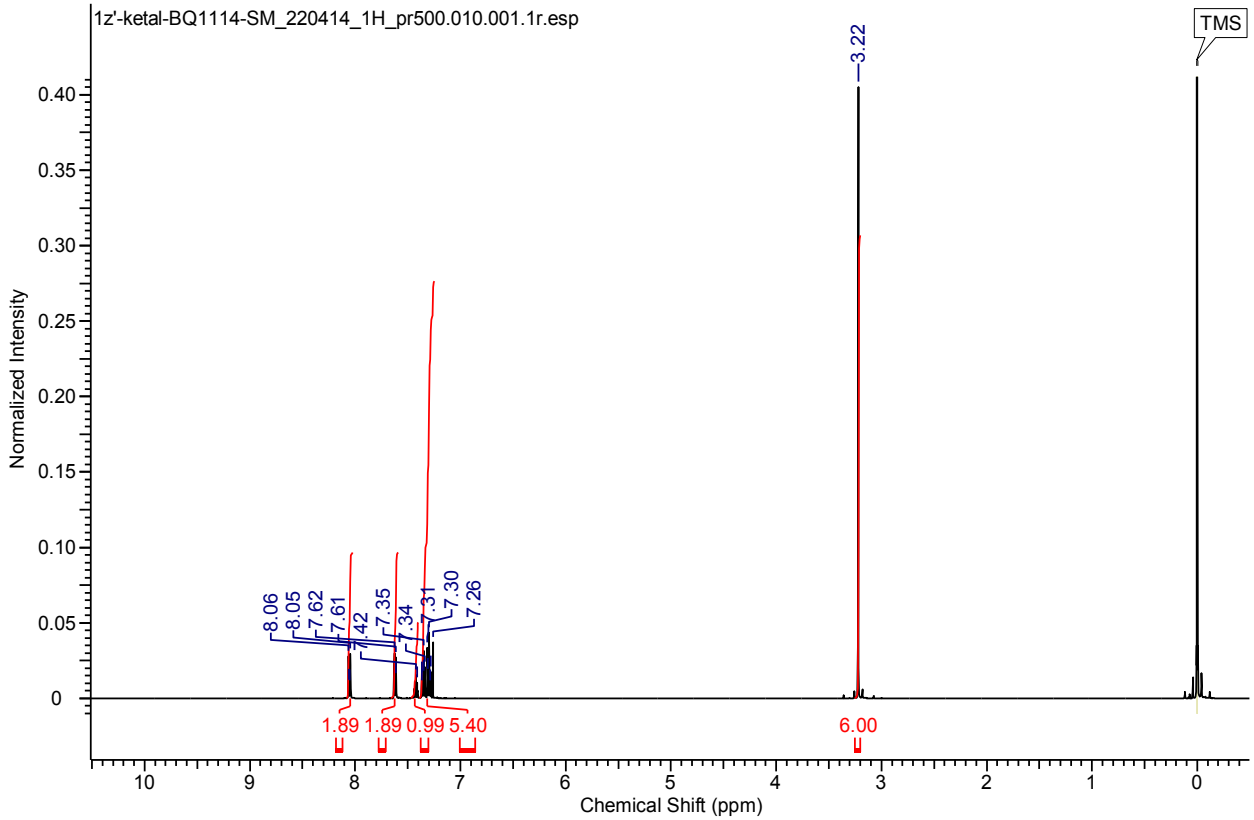
1z

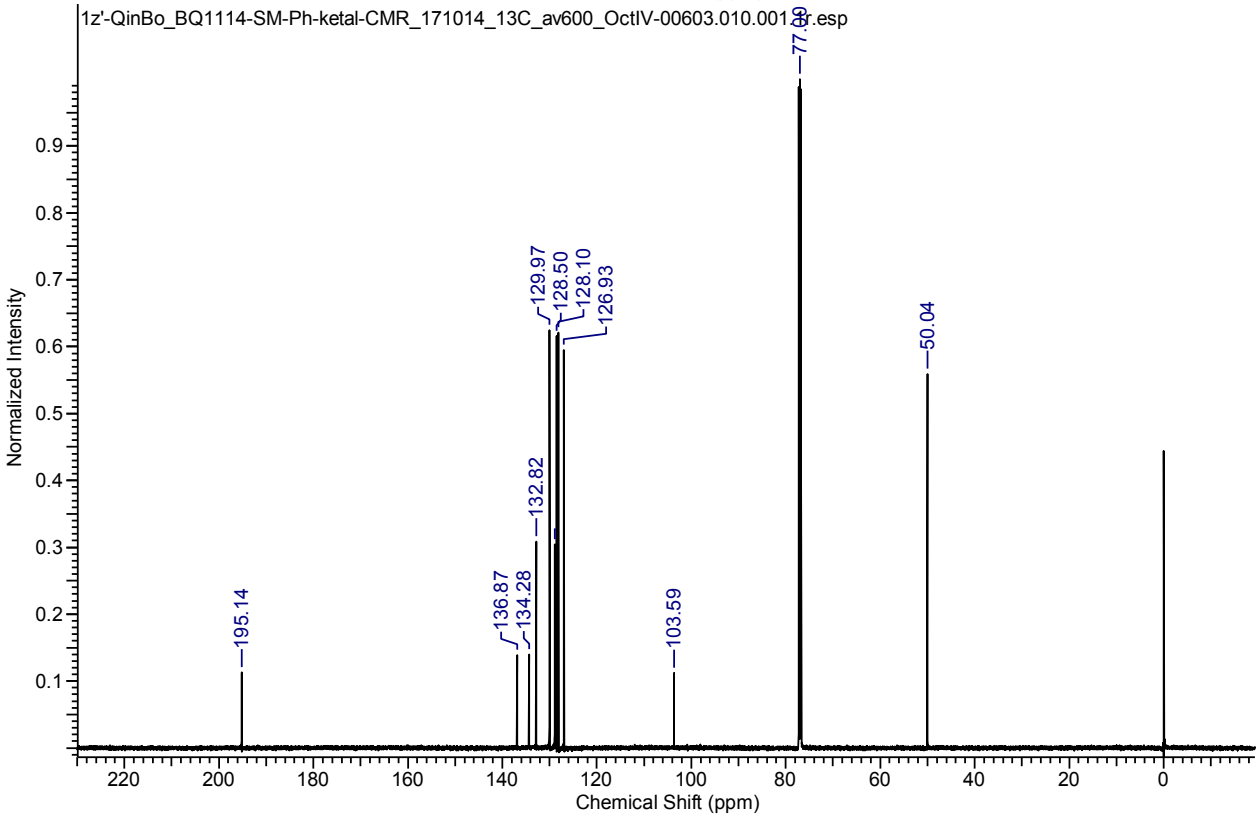

1z-tBu-BQ1445-column-MS_210115_1H_pr500_JanV-0633.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.40
7.39
7.38
7.32
7.30
7.29
7.26
3.33
0.94
TMS
1.92
1.72
0.85
6.00
9.58

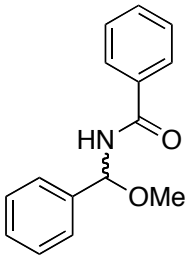

1z-tBu-acetal_190416_13C_pr500_AprVI-00782.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
129.25
126.83
139.29
115.14
114.97
107.24
102.53
52.62
51.87
40.48
26.99


OMe
OMe
O

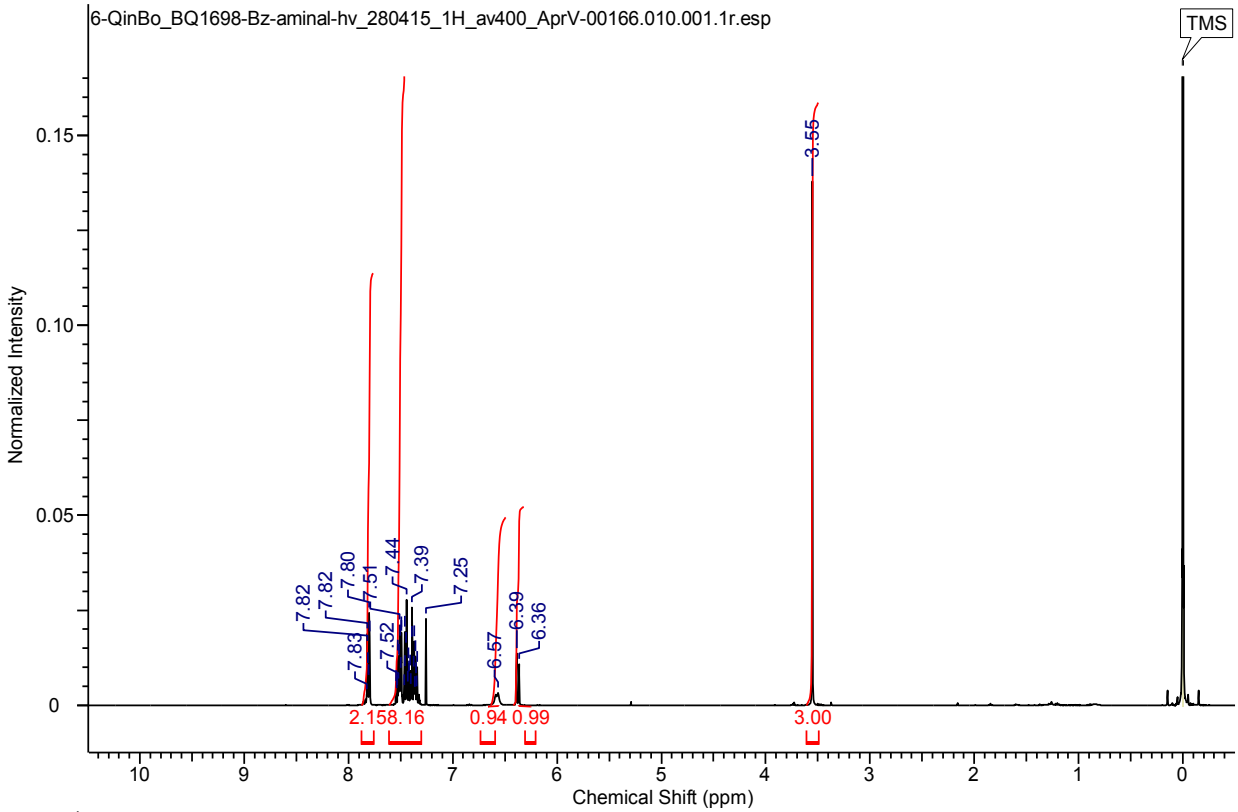
1z'

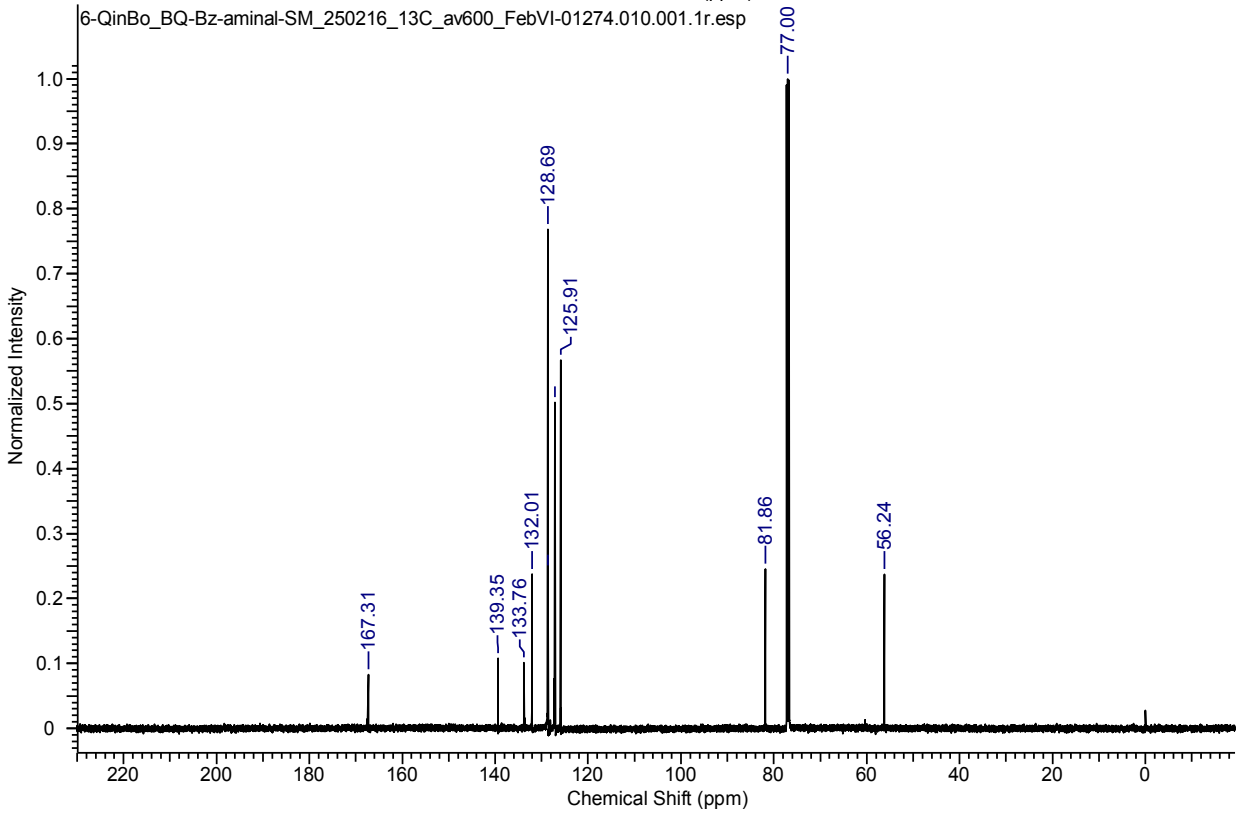

1z'-ketal-BQ1114-SM_220414_1H_pr500.010.001.1r.esp
TMS
3.22
8.06
8.05
7.62
7.61
7.42
7.35
7.34
7.31
7.30
7.26
1.89 1.89 0.99 5.40
6.00
Normalized Intensity
Chemical Shift (ppm)

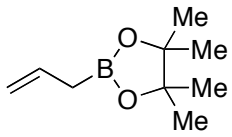

1z'-QinBo_BQ1114-SM-Ph-ketal-CMR_171014_13C_av600_OctIV-00603.010.001.1r.esp
77.00
129.97
128.50
128.10
126.93
50.04
132.82
136.87
134.28
195.14
103.59
Normalized Intensity
Chemical Shift (ppm)


HN
O
OMe

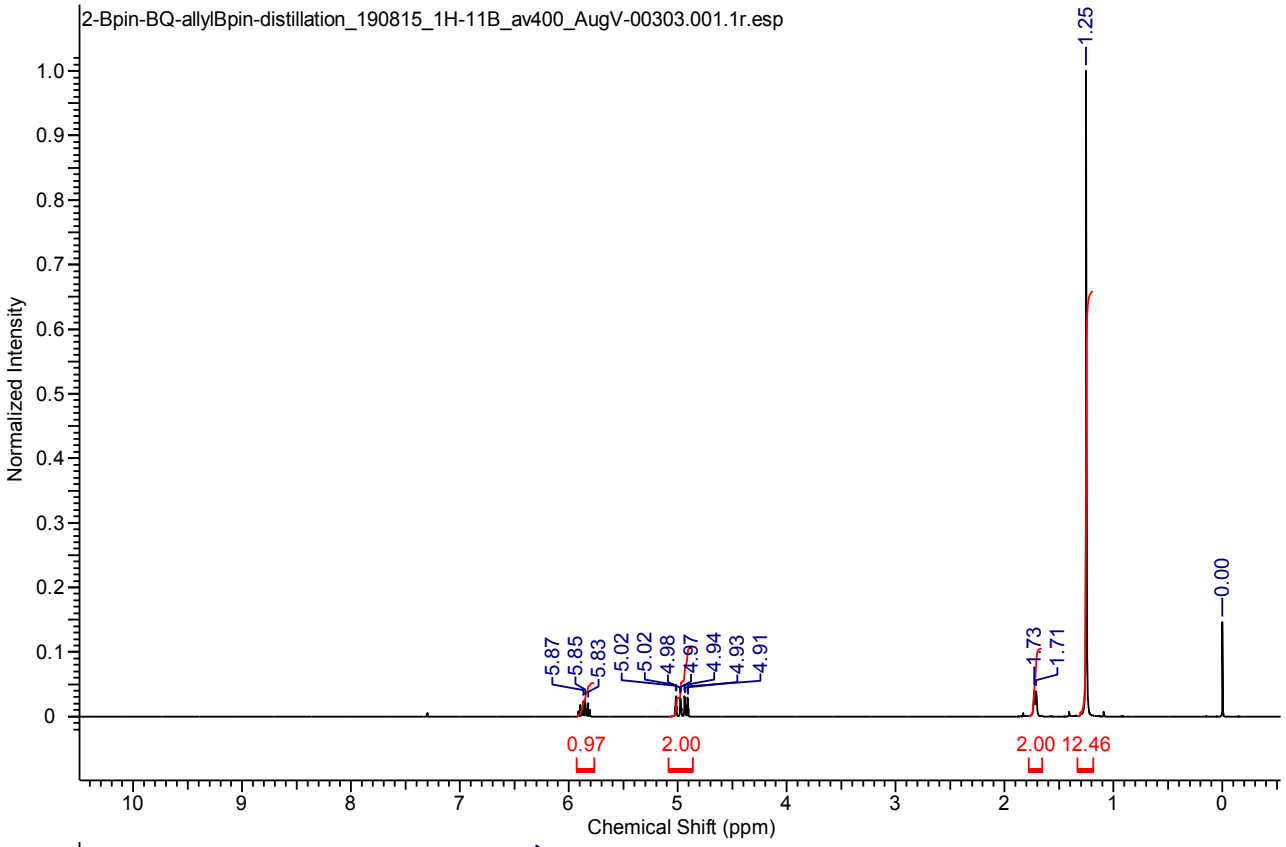
rac-**12**

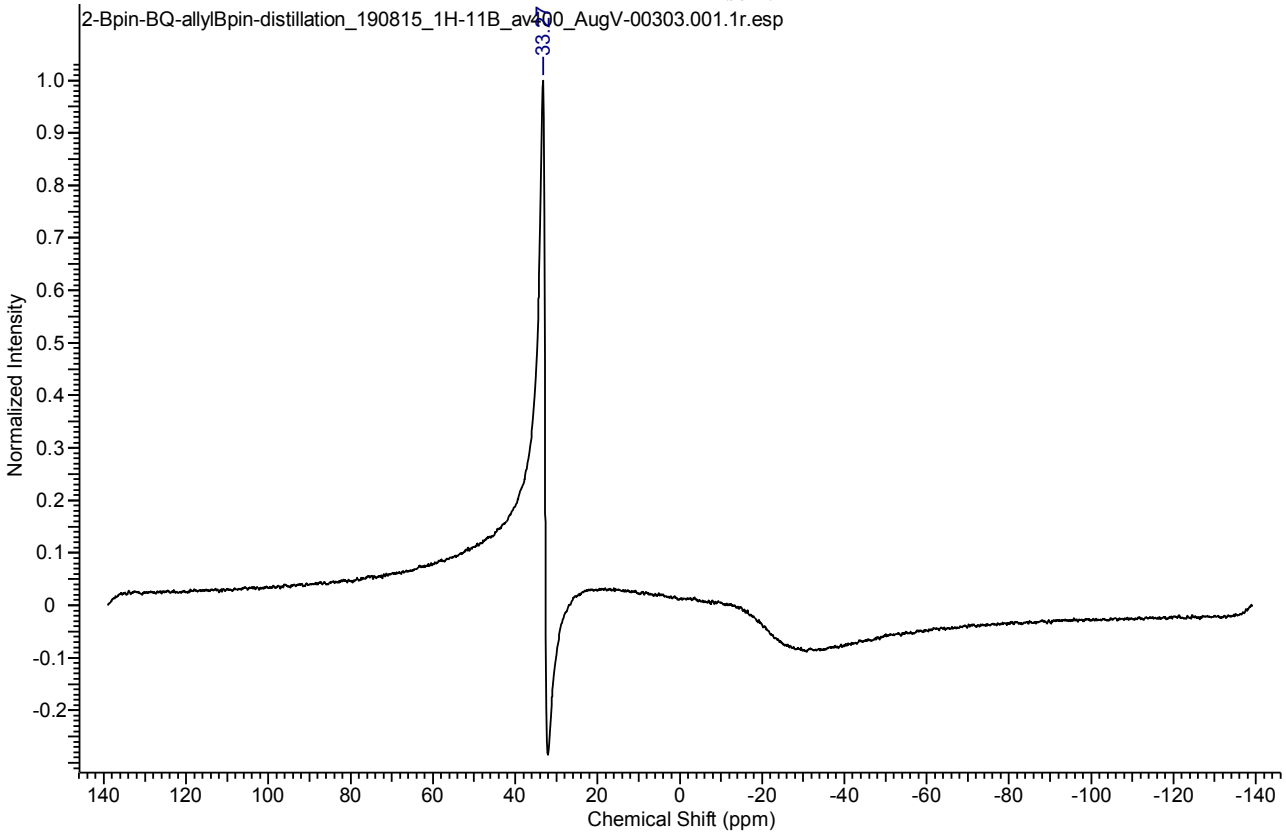

6-QinBo_BQ1698-Bz-aminal-hv_280415_1H_av400_AprV-00166.010.001.1r.esp
TMS
Normalized Intensity
Chemical Shift (ppm)
7.82
7.82
7.80
7.51
7.44
7.39
7.25
7.83
7.52
6.57
6.39
6.36
3.55
2.15
8.16
0.94
0.99
3.00

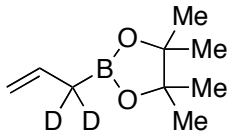

6-QinBo_BQ-Bz-aminal-SM_250216_13C_av600_FebVI-01274.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
128.69
125.91
132.01
139.35
133.76
167.31
81.86
56.24


Me
O
Me
B
Me
O
Me

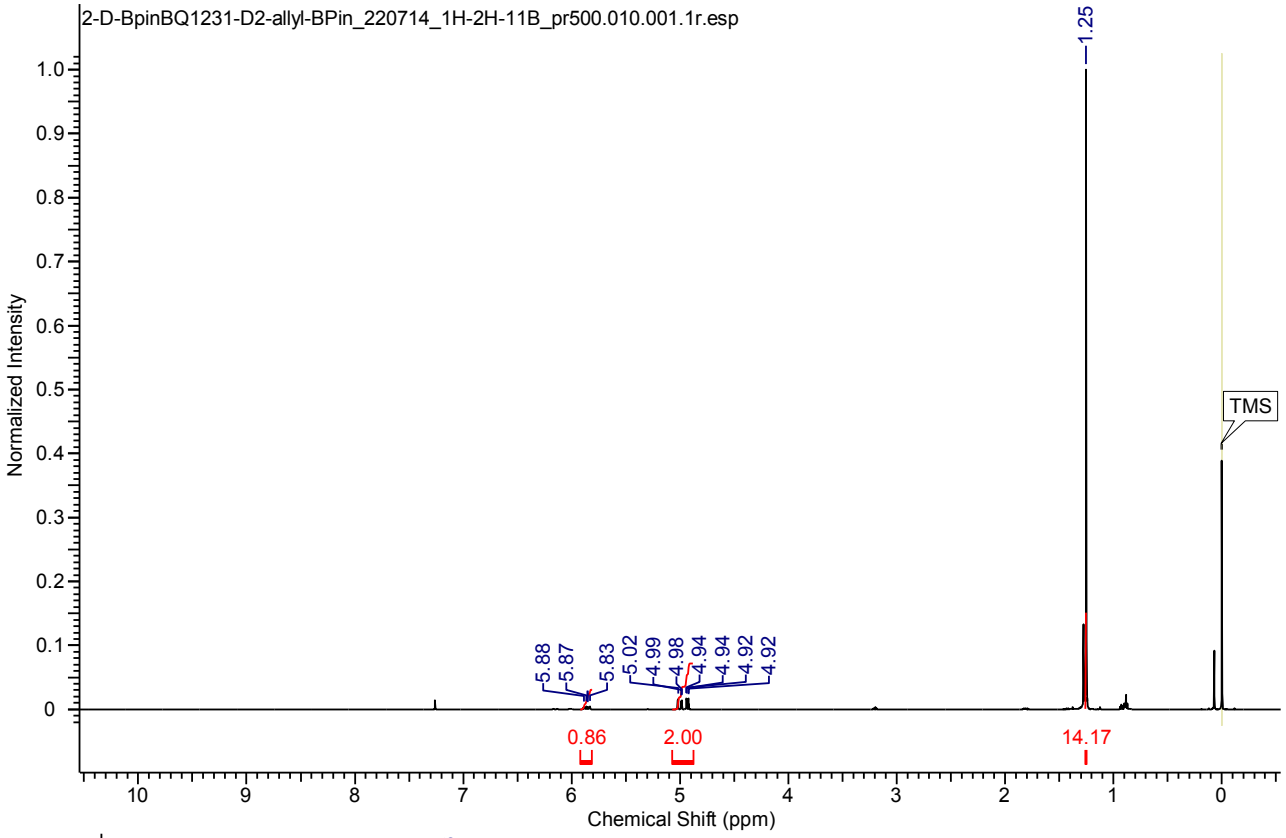
2

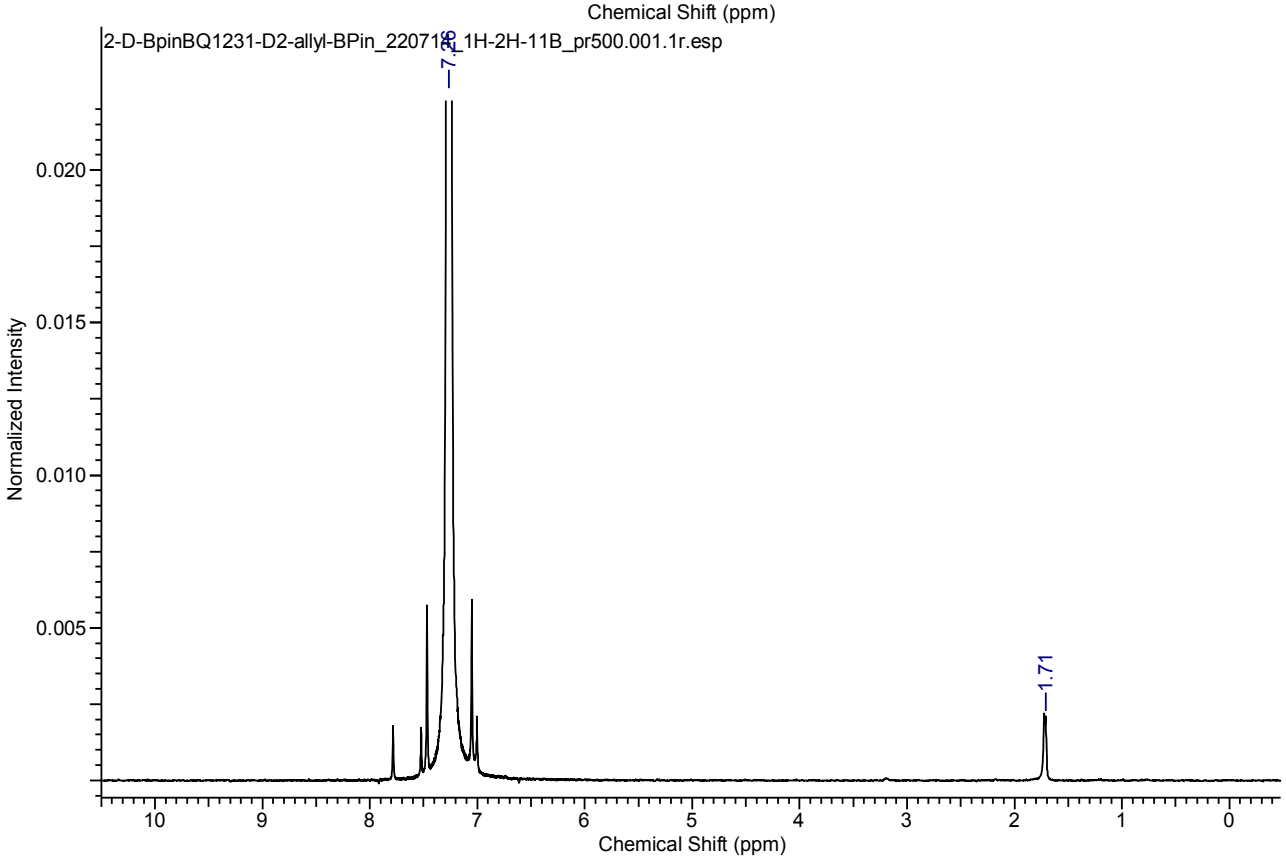

2-Bpin-BQ-allylBpin-distillation_190815_1H-11B_av400_AugV-00303.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
1.25
0.00
5.87
5.85
5.83
5.02
5.02
4.98
4.97
4.94
4.93
4.91
1.73
1.71
0.97
2.00
2.00
12.46

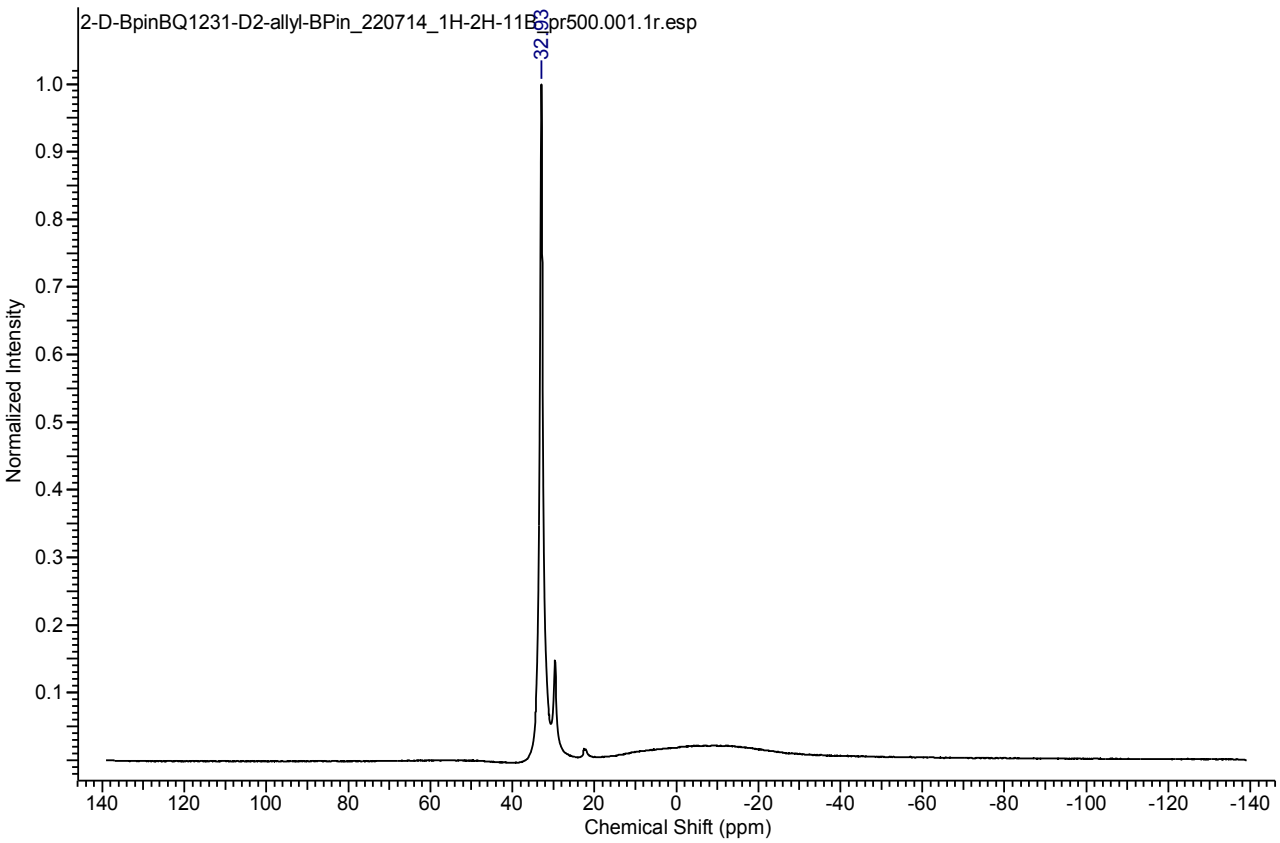

2-Bpin-BQ-allylBpin-distillation_190815_1H-11B_av400_AugV-00303.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
33.47

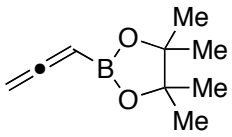

Me
O
Me
B
Me
O
D
D
Me

2–[d_2]

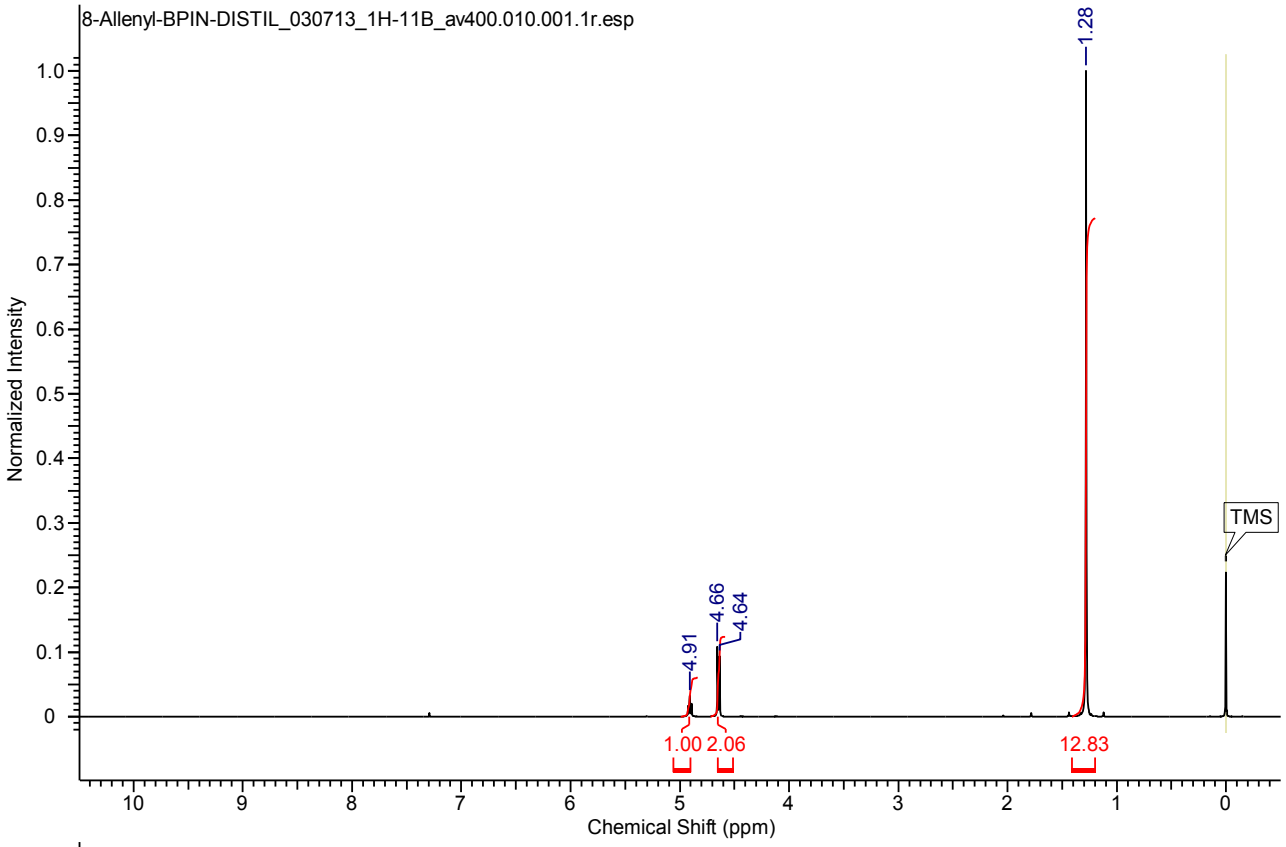

2-D-BpinBQ1231-D2-allyl-BPin_220714_1H-2H-11B_pr500.010.001.1r.esp
Normalized Intensity
1.25
TMS
5.88
5.87
5.83
5.02
4.99
4.98
4.94
4.94
4.92
4.92
0.86
2.00
14.17
Chemical Shift (ppm)

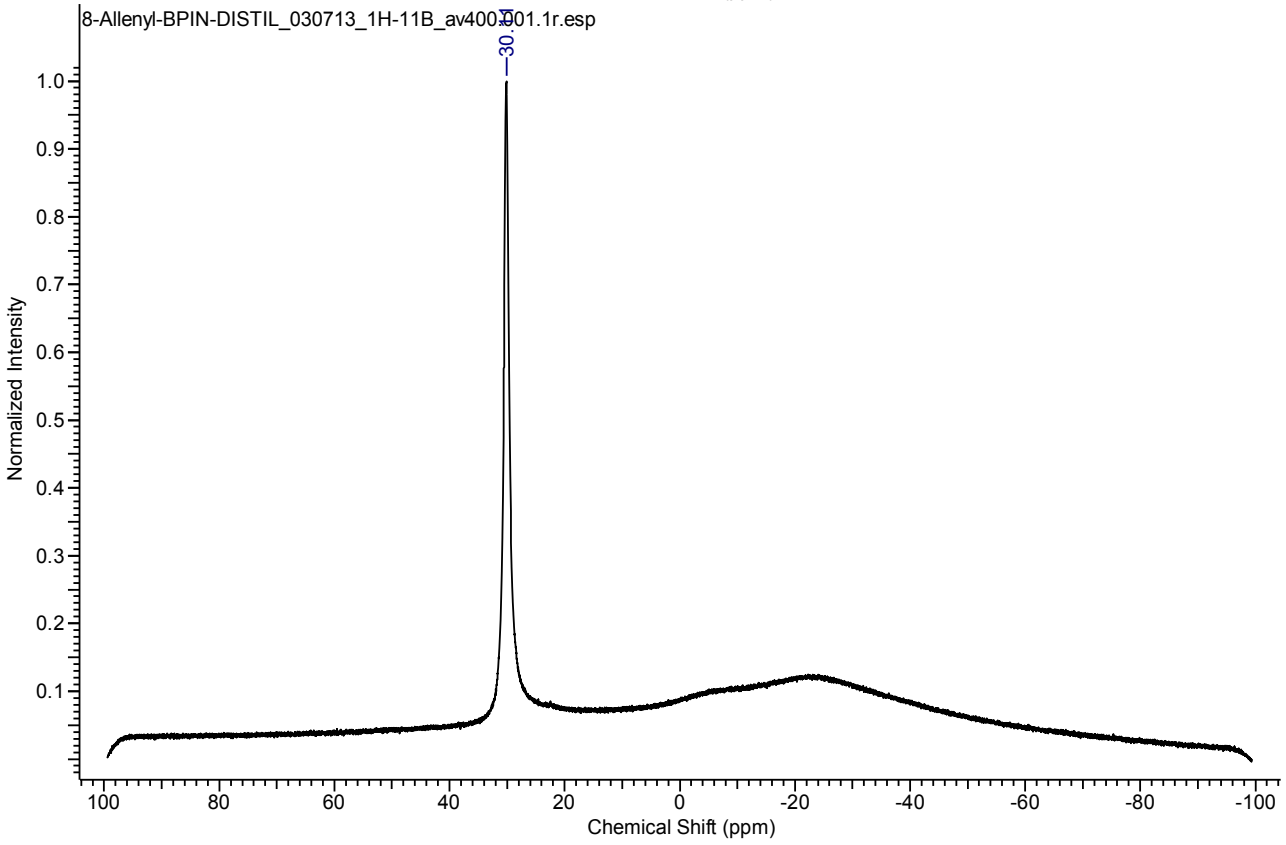

2-D-BpinBQ1231-D2-allyl-BPin_220714_1H-2H-11B_pr500.001.1r.esp
Normalized Intensity
7.26
1.71
Chemical Shift (ppm)

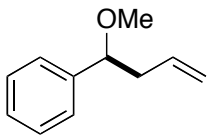

2-D-BpinBQ1231-D2-allyl-BPin_220714_1H-2H-11B-pr500.001.1r.esp
32.83
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)


Me
O
Me
B
Me
O
Me

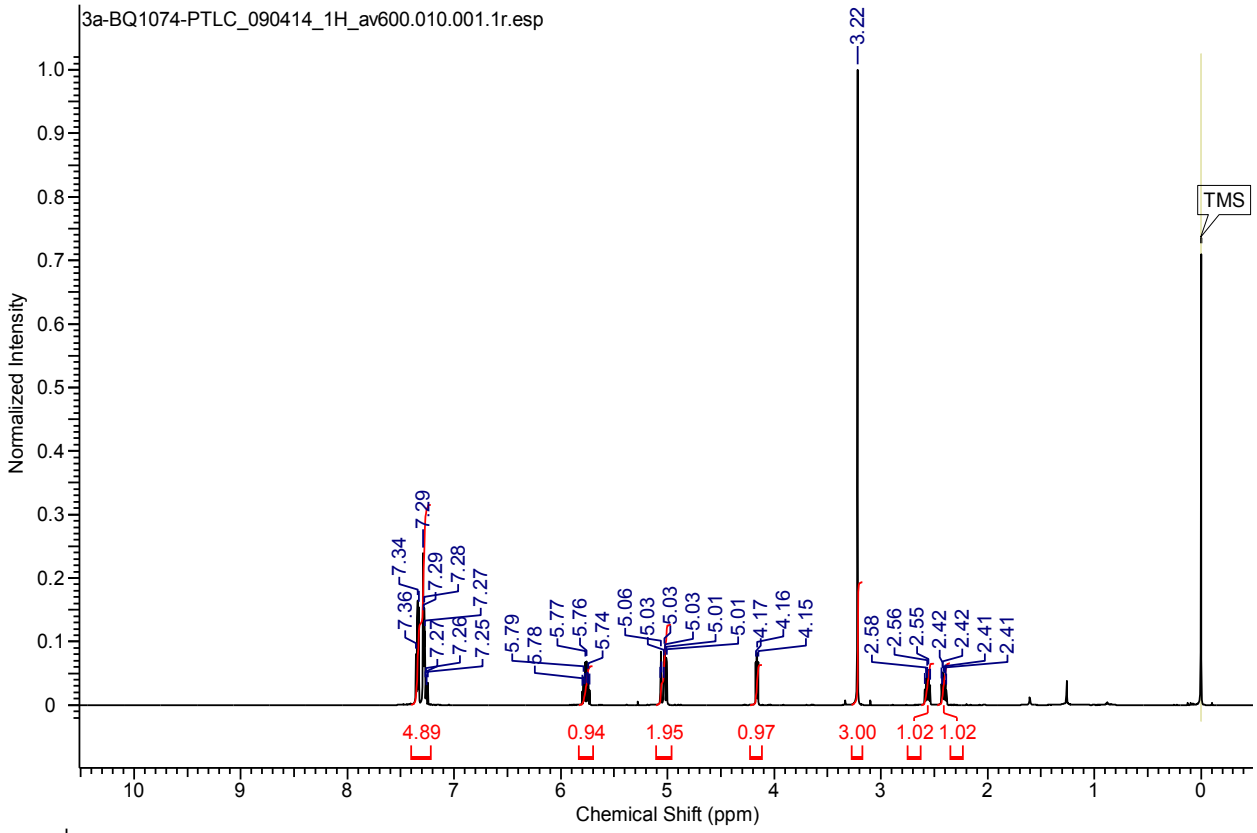
14

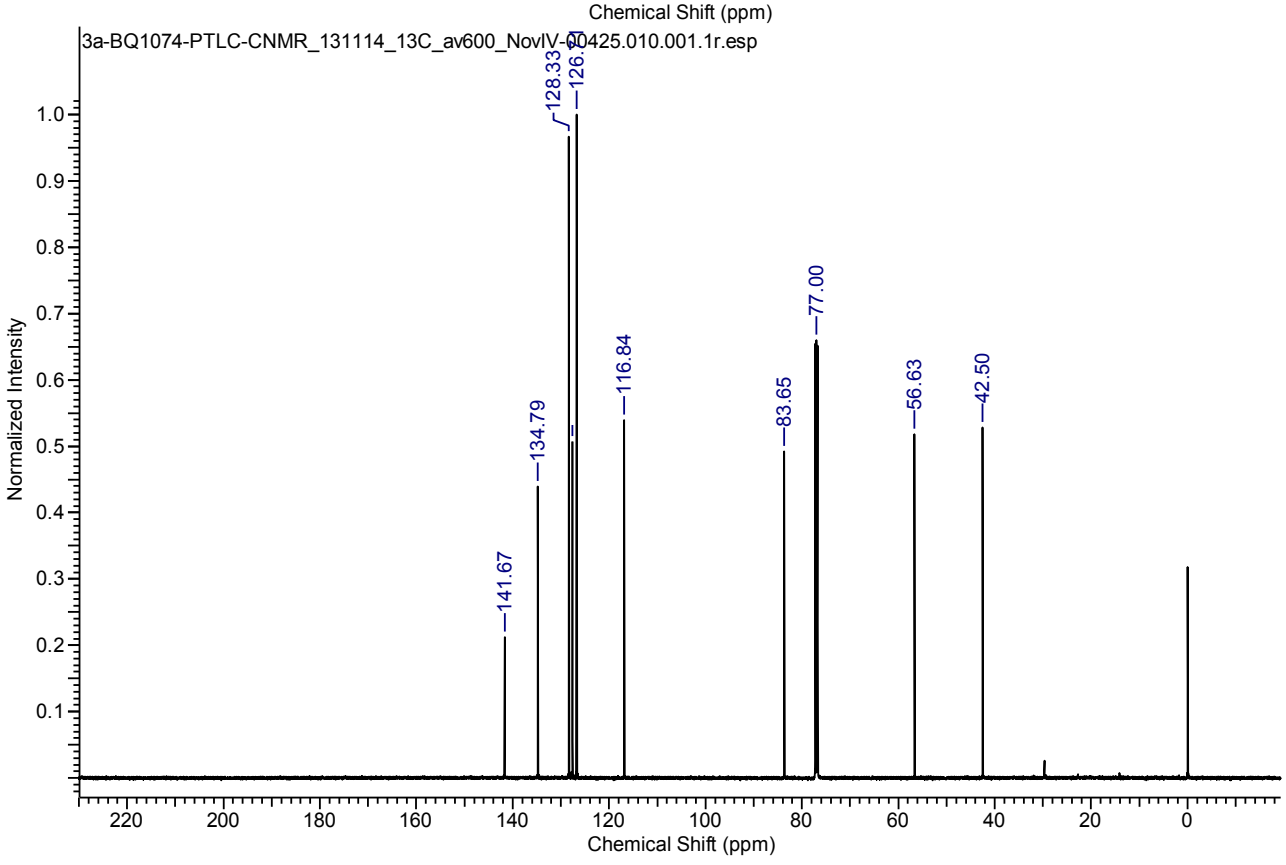

8-Allenyl-BPIN-DISTIL_030713_1H-11B_av400.010.001.1r.esp
1.28
TMS
4.66
4.64
4.91
1.00
2.06
12.83
Normalized Intensity
Chemical Shift (ppm)

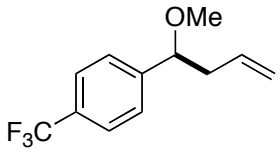

8-Allenyl-BPIN-DISTIL_030713_1H-11B_av400.001.1r.esp
30.71
Normalized Intensity
Chemical Shift (ppm)


OMe

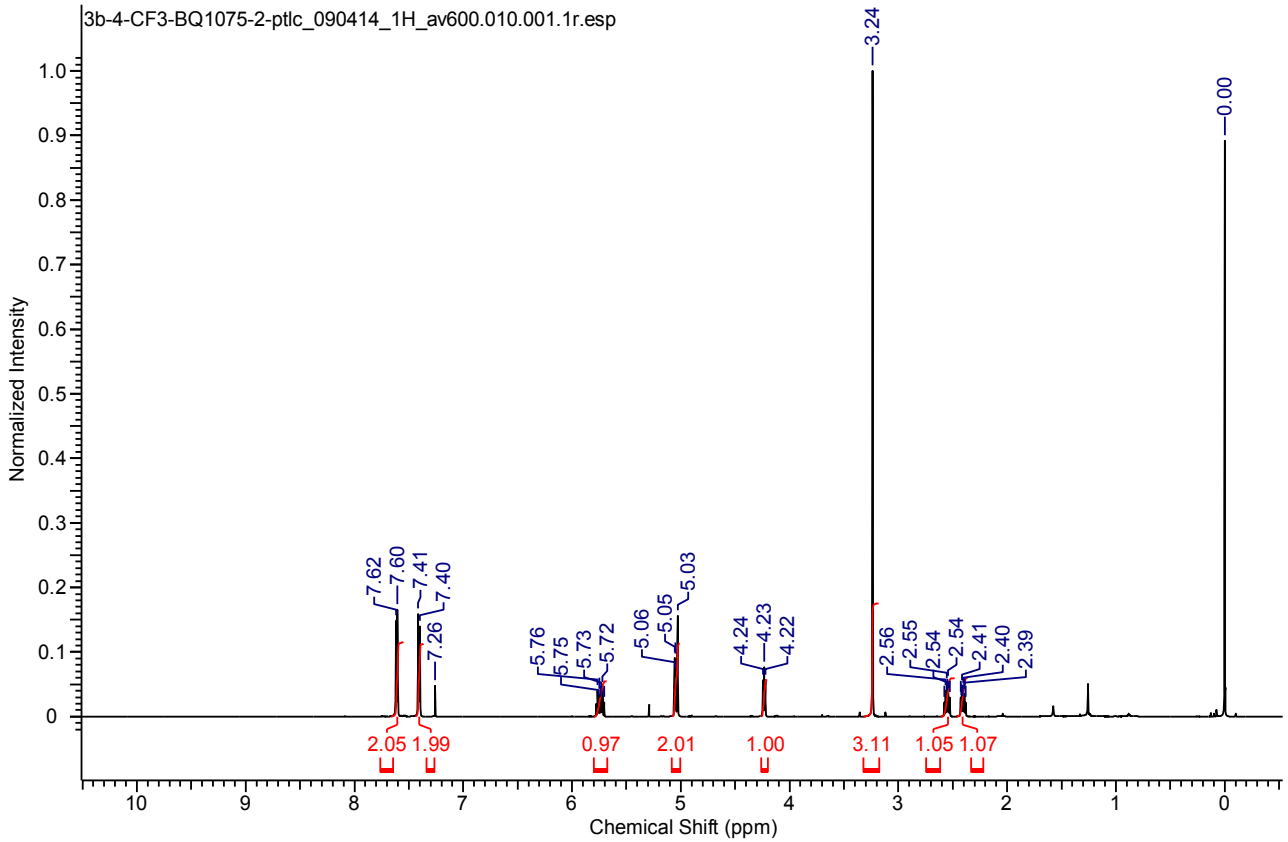
3a

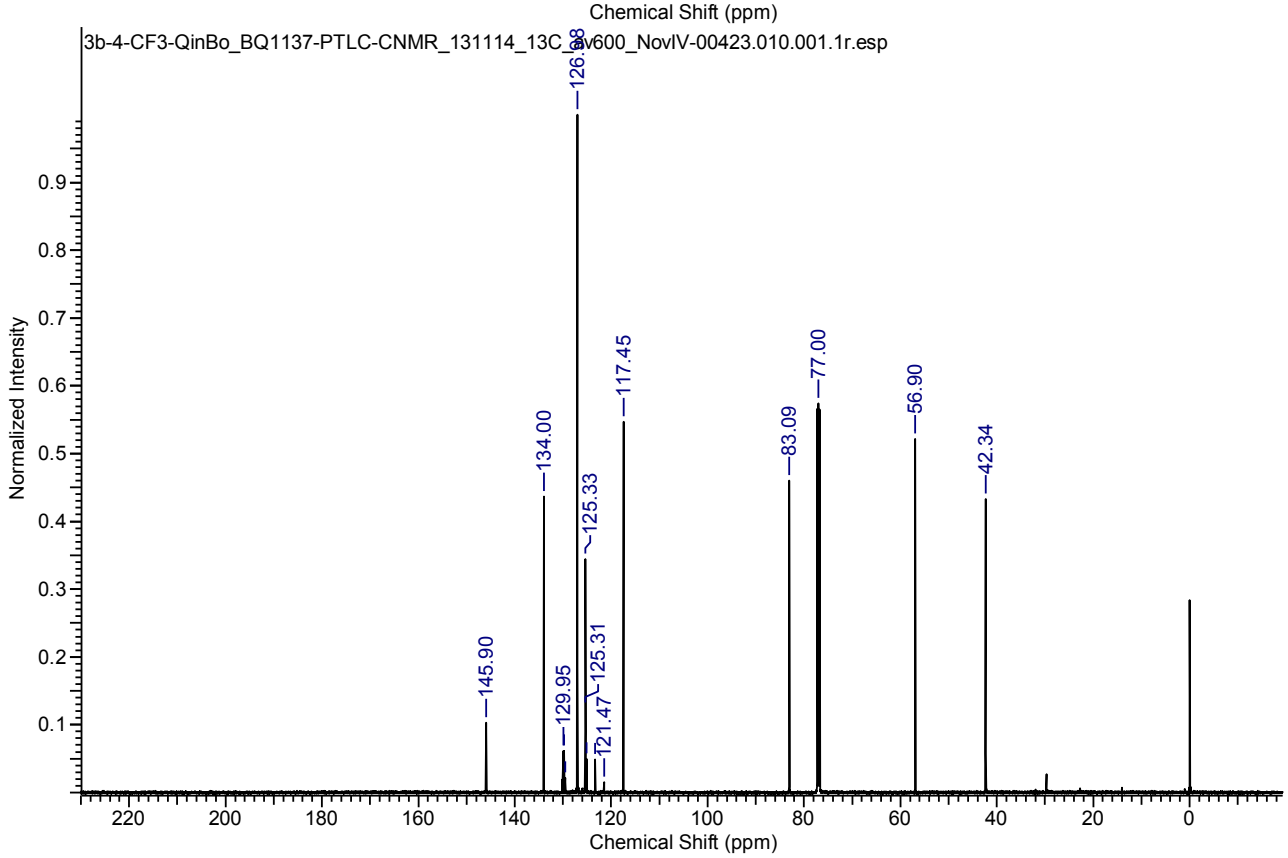

3a-BQ1074-PTLC_090414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.22
7.34
7.29
7.36
7.29
7.28
7.27
7.27
7.26
7.25
5.79
5.78
5.77
5.76
5.74
5.06
5.03
5.03
5.03
5.01
5.01
4.17
4.16
4.15
2.58
2.56
2.55
2.42
2.42
2.41
2.41
4.89
0.94
1.95
0.97
3.00
1.02
1.02

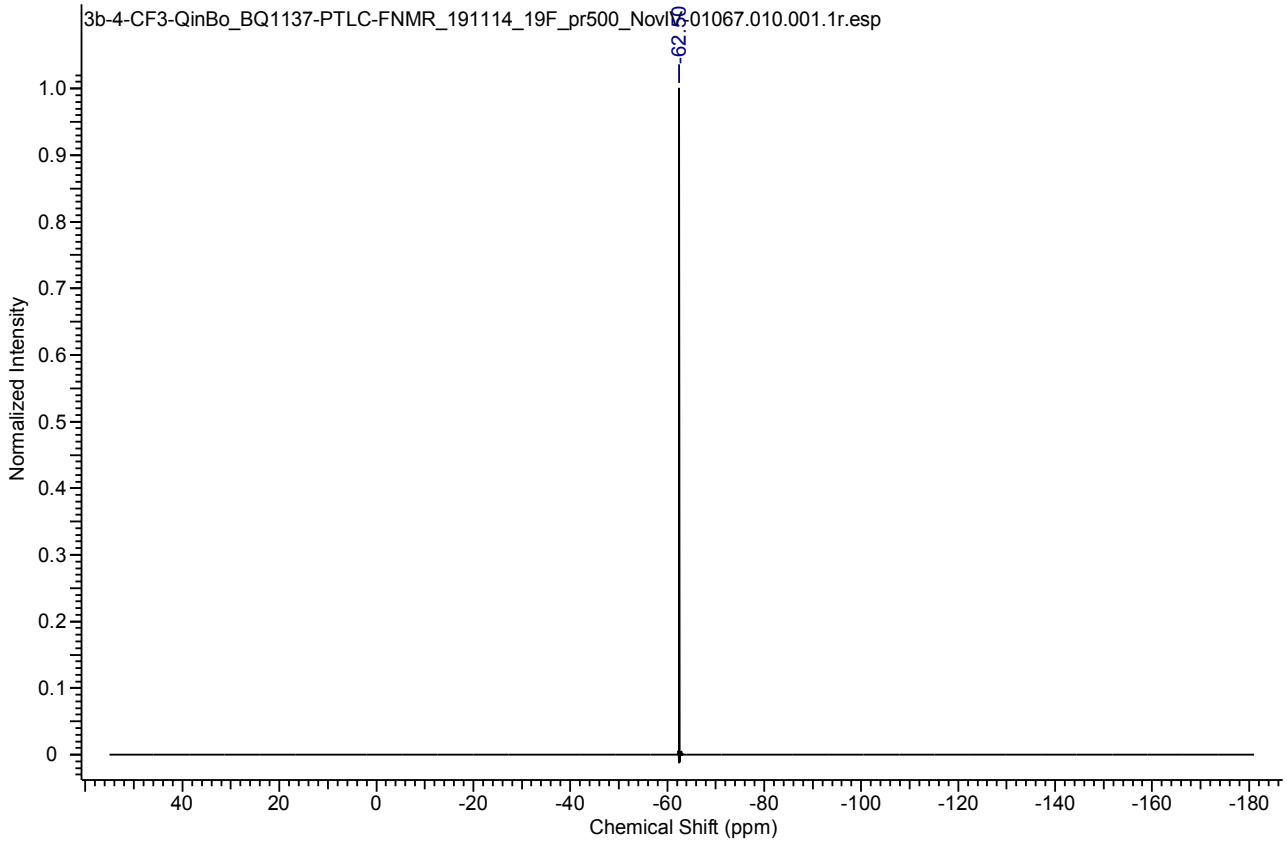

3a-BQ1074-PTLC-CNMR_131114_13C_av600_NovIV-10425.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.33
126.
141.67
134.79
116.84
83.65
77.00
56.63
42.50

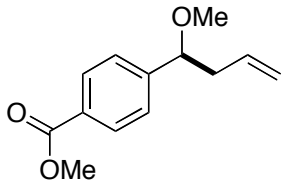

OMe
F3C

3b

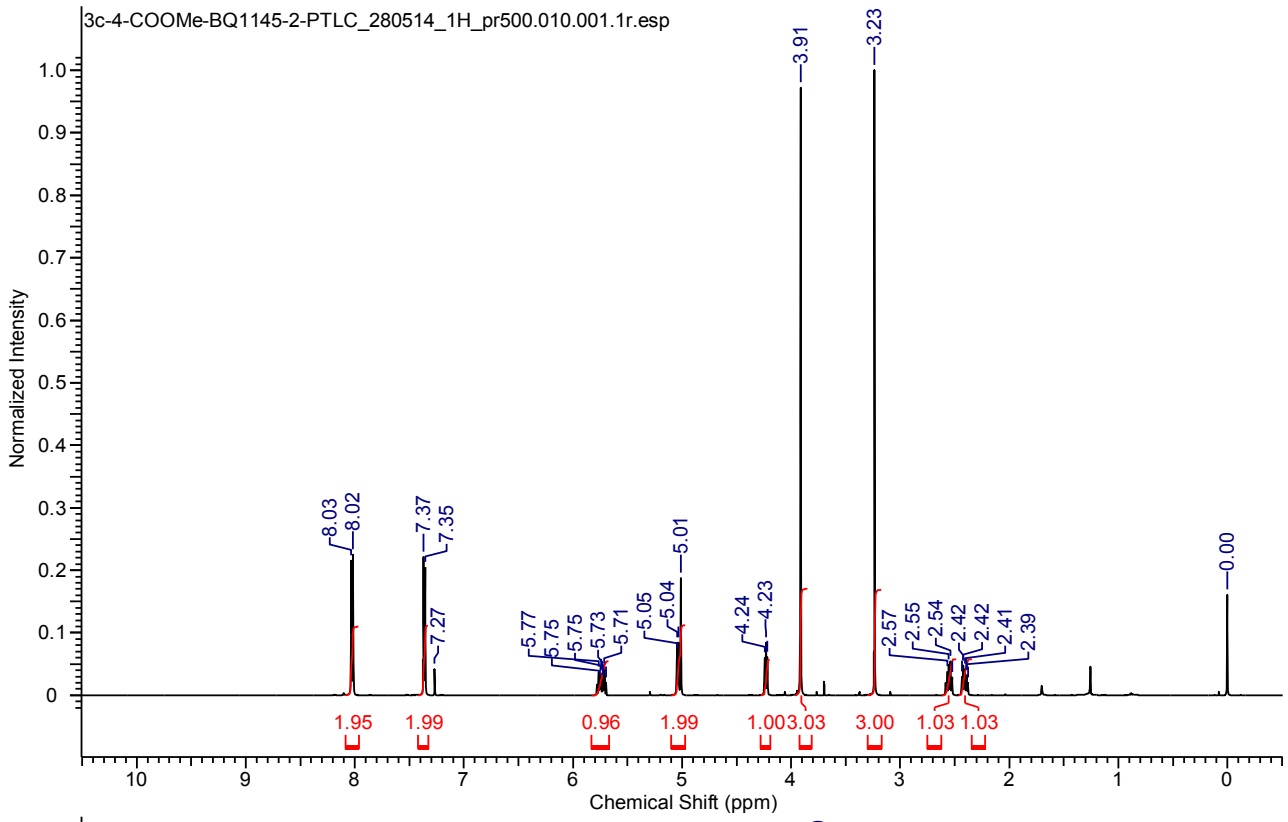

3b-4-CF3-BQ1075-2-ptlc_090414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.62
7.60
7.41
7.40
7.26
5.76
5.75
5.73
5.72
5.06
5.05
5.03
4.24
4.23
4.22
3.24
2.56
2.55
2.54
2.54
2.41
2.40
2.39
0.00
2.05
1.99
0.97
2.01
1.00
3.11
1.05
1.07

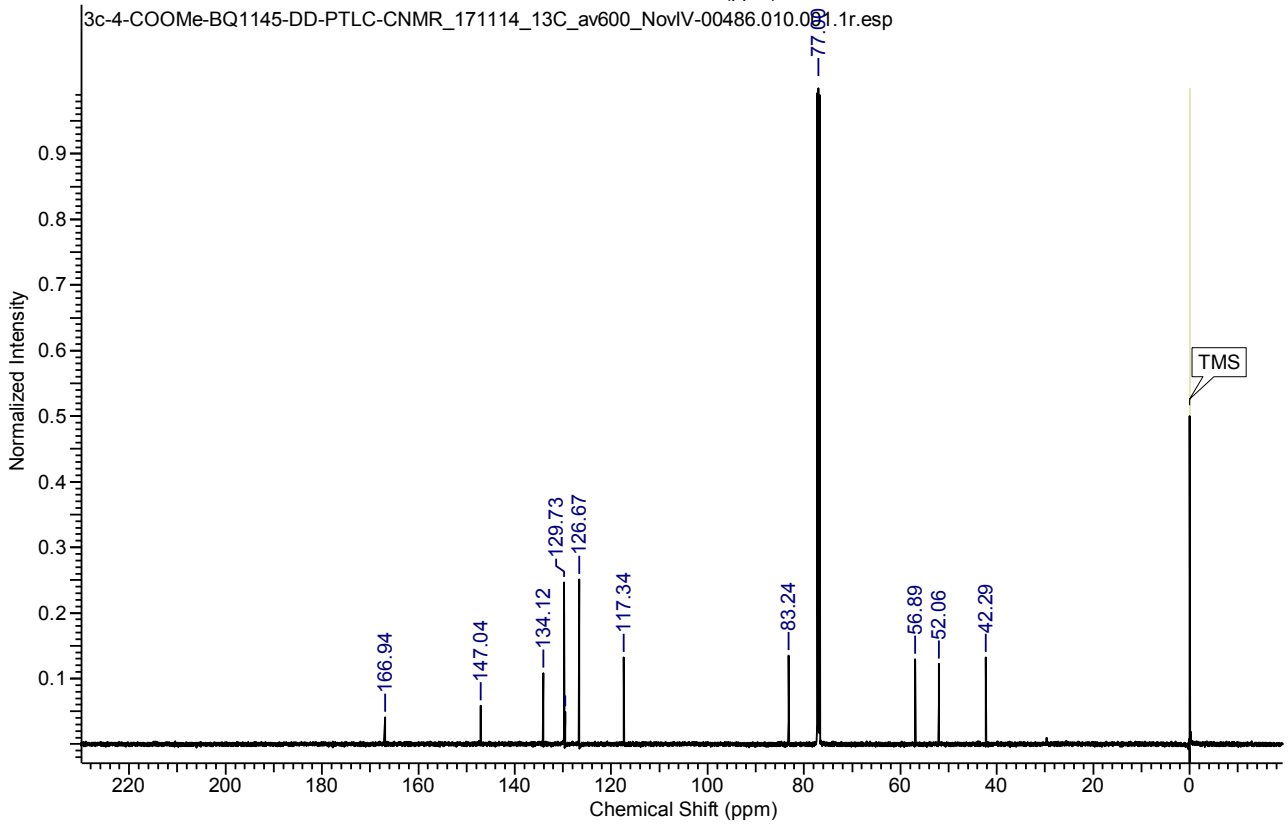

3b-4-CF3-QinBo_BQ1137-PTLC-CNMR_131114_13C_av600_NovIV-00423.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
126.98
145.90
134.00
129.95
125.33
125.31
121.47
117.45
83.09
77.00
56.90
42.34

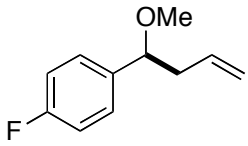

3b-4-CF3-QinBo_BQ1137-PTLC-FNMR_191114_19F_pr500_Novl_01067.010.001.1r.esp
-62.50
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)


OMe
O
OMe

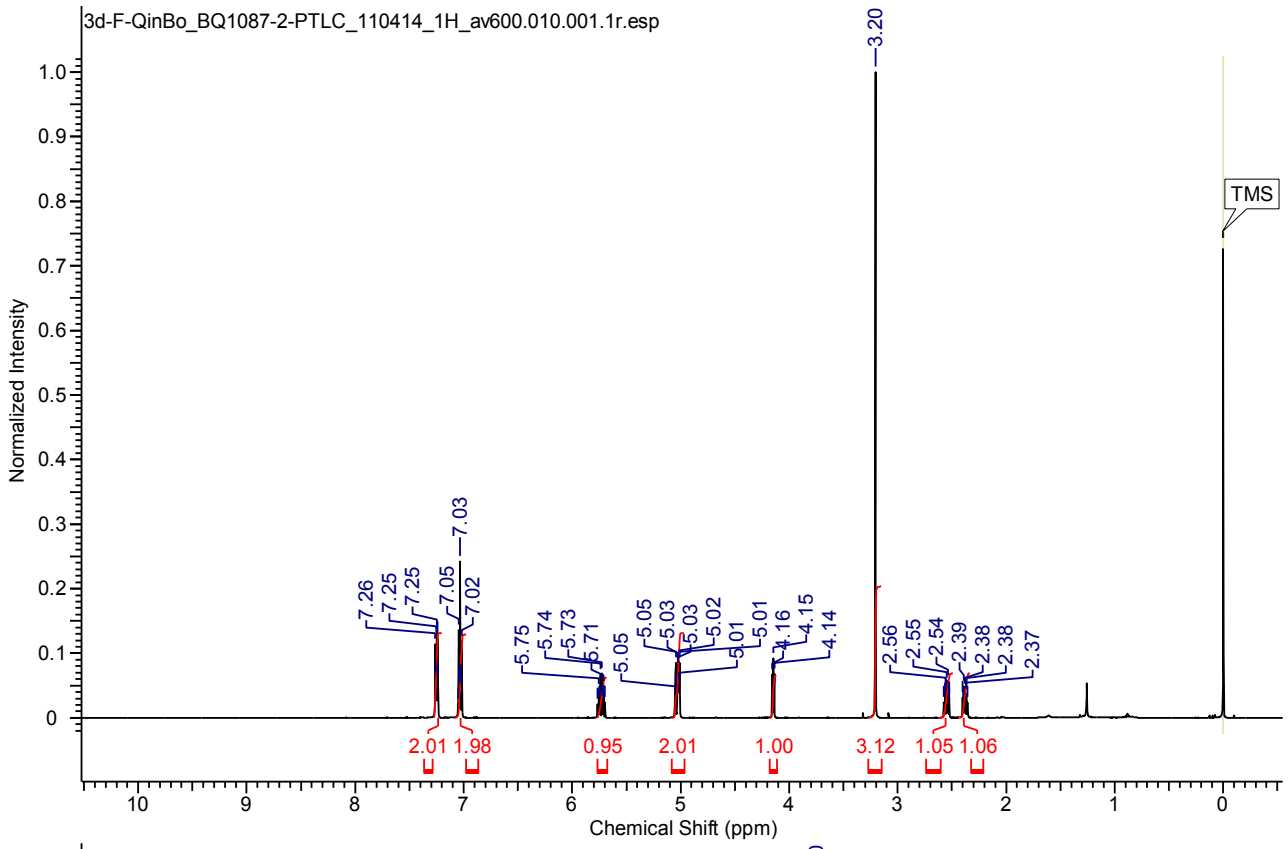
3c

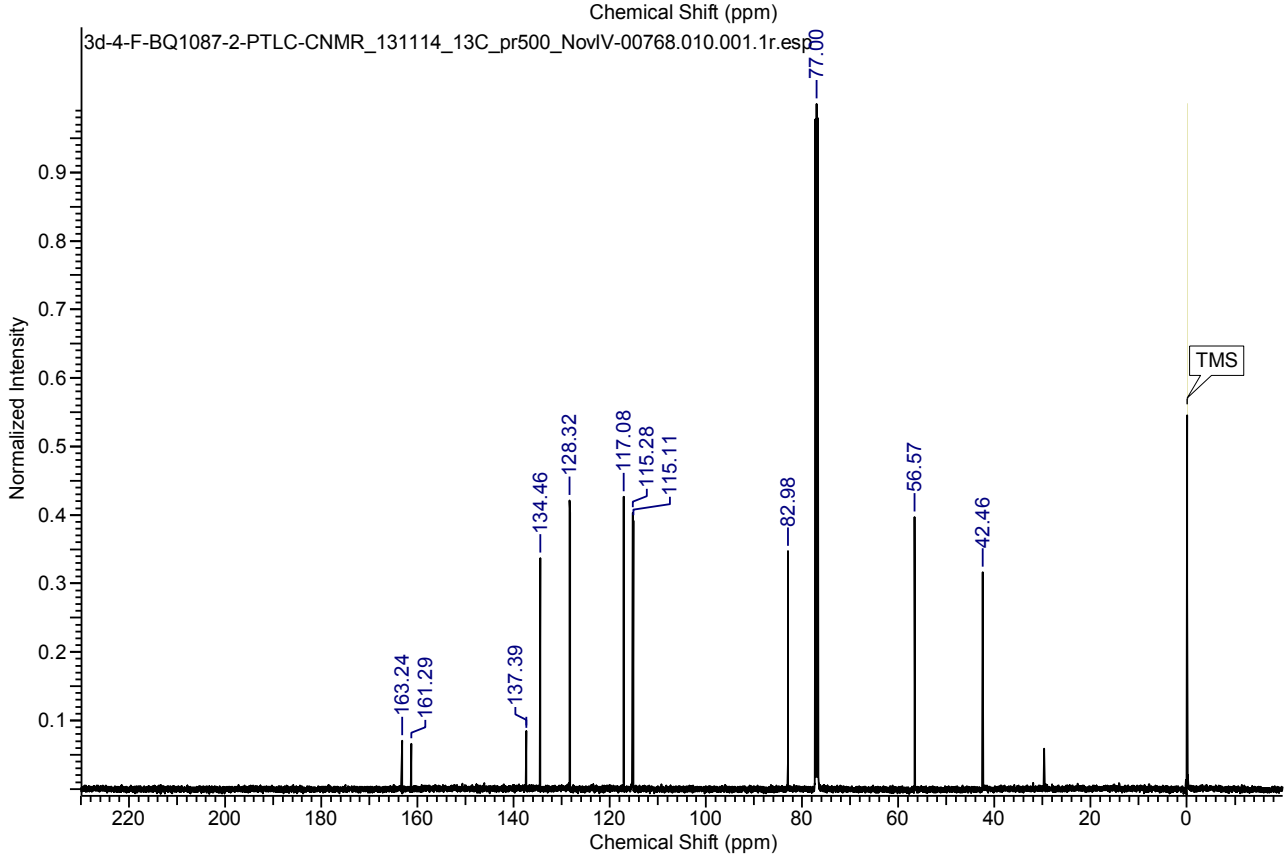

3c-4-COOMe-BQ1145-2-PTLC_280514_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.03
8.02
7.37
7.35
7.27
5.77
5.75
5.75
5.73
5.71
5.05
5.04
5.01
4.24
4.23
3.91
3.23
2.57
2.55
2.54
2.42
2.42
2.41
2.39
0.00
1.95
1.99
0.96
1.99
1.00
3.03
3.00
1.03
1.03

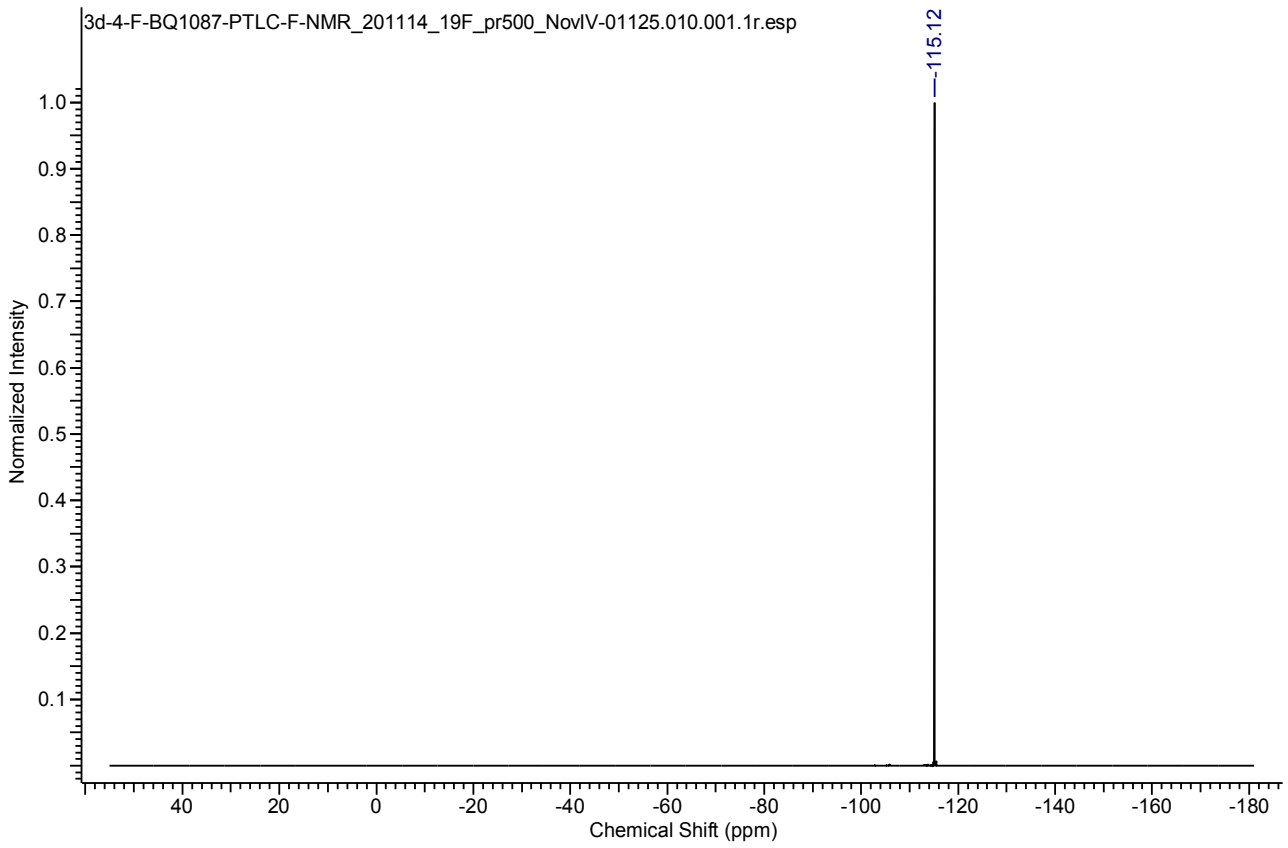

3c-4-COOMe-BQ1145-DD-PTLC-CNMR_171114_13C_av600_NovIV-00486.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
TMS
166.94
147.04
134.12
129.73
126.67
117.34
83.24
56.89
52.06
42.29

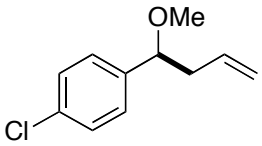

OMe
F

3d

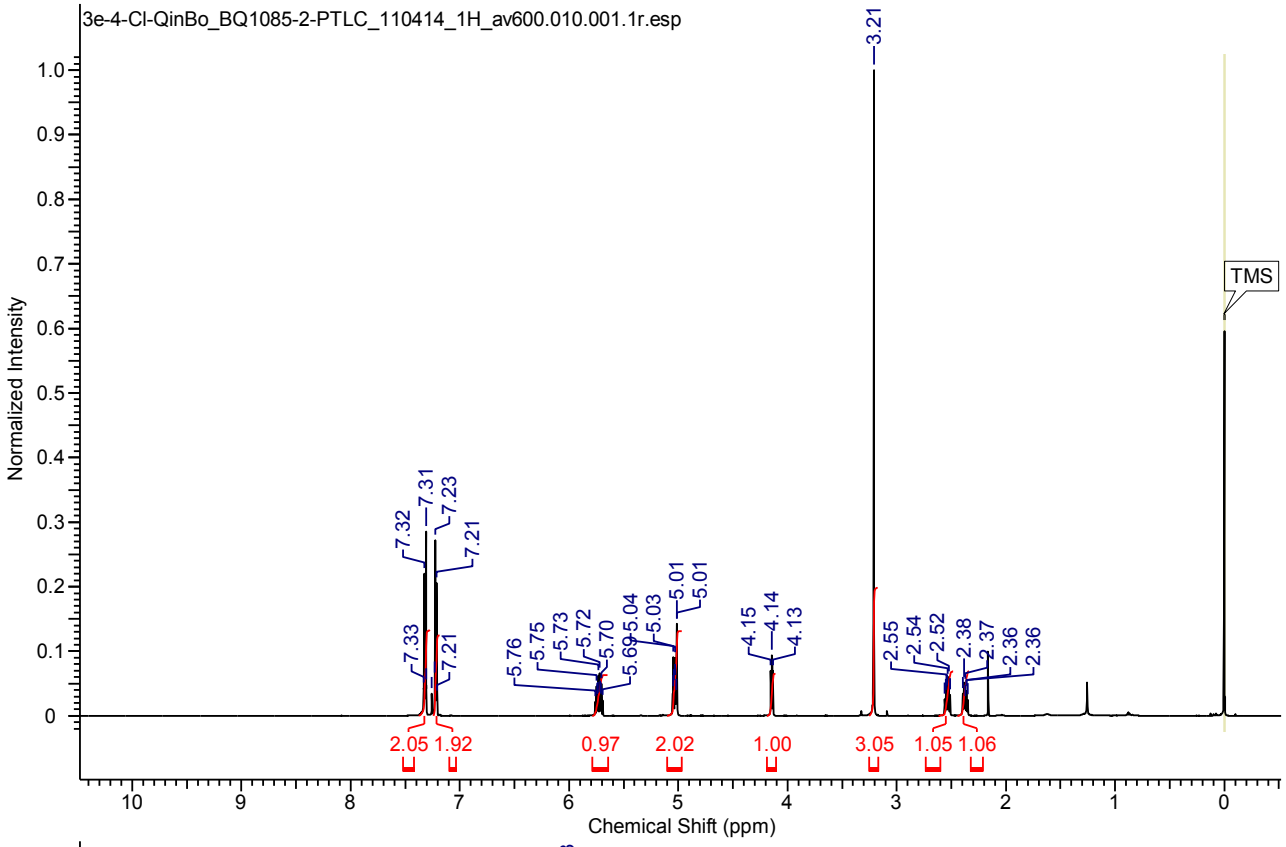

3d-F-QinBo_BQ1087-2-PTLC_110414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.20
7.26
7.25
7.25
7.05
7.03
7.02
5.75
5.74
5.73
5.71
5.05
5.05
5.03
5.03
5.02
5.01
5.01
4.16
4.15
4.14
2.56
2.55
2.54
2.39
2.38
2.38
2.37
2.01
1.98
0.95
2.01
1.00
3.12
1.05
1.06

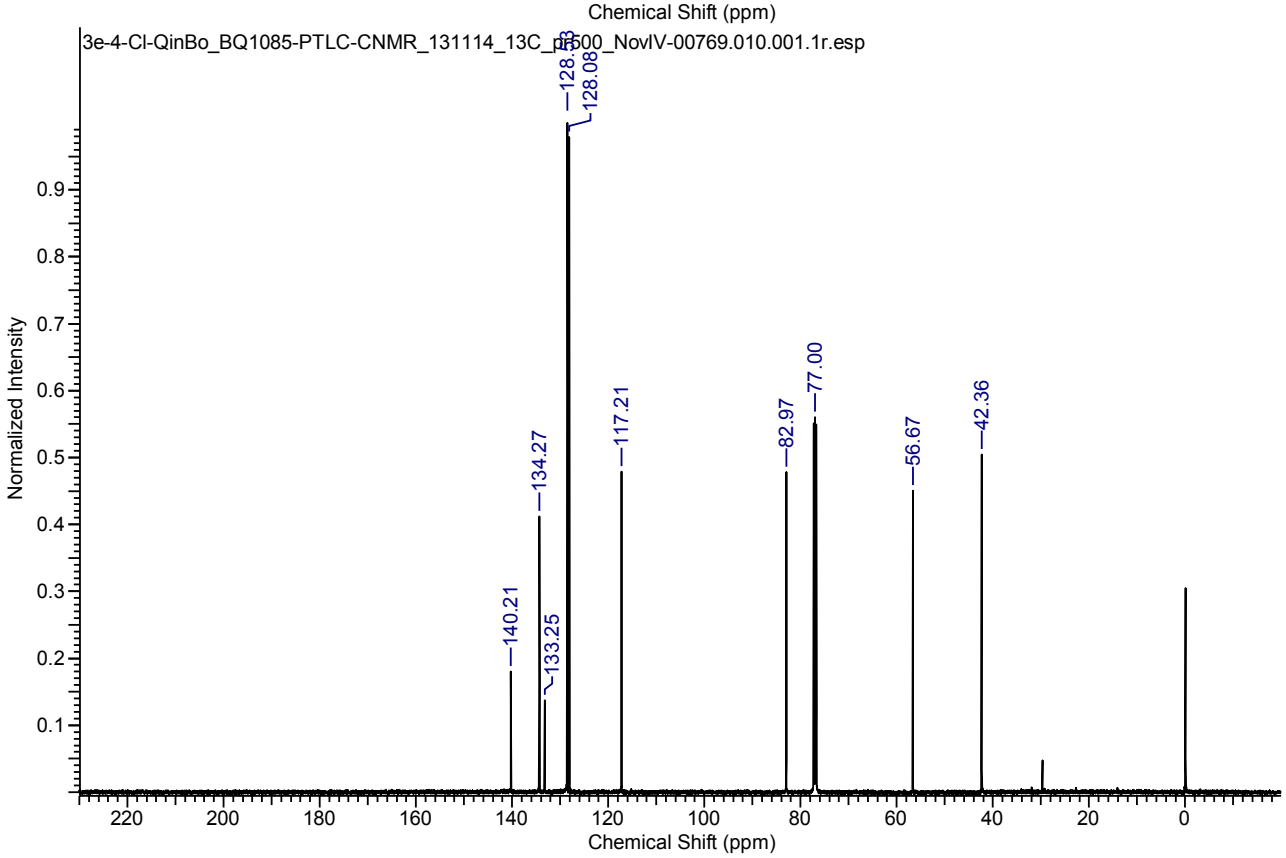

3d-4-F-BQ1087-2-PTLC-CNMR_131114_13C_pr500_NovIV-00768.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
77.00
163.24
161.29
137.39
134.46
128.32
117.08
115.28
115.11
82.98
56.57
42.46

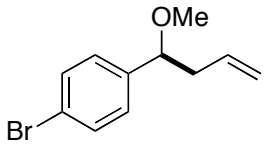

3d-4-F-BQ1087-PTLC-F-NMR_201114_19F_pr500_NovIV-01125.010.001.1r.esp
-115.12
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)


OMe
Cl

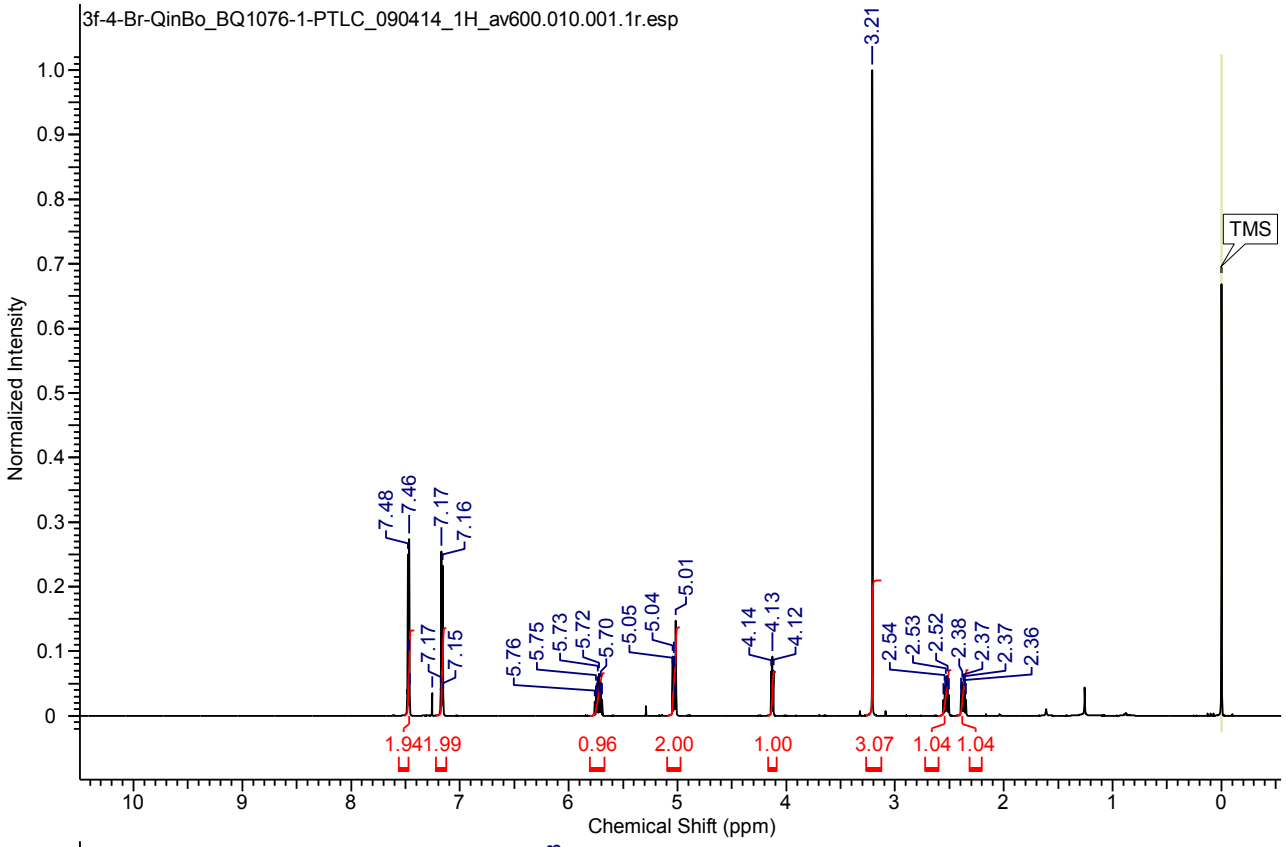
3e

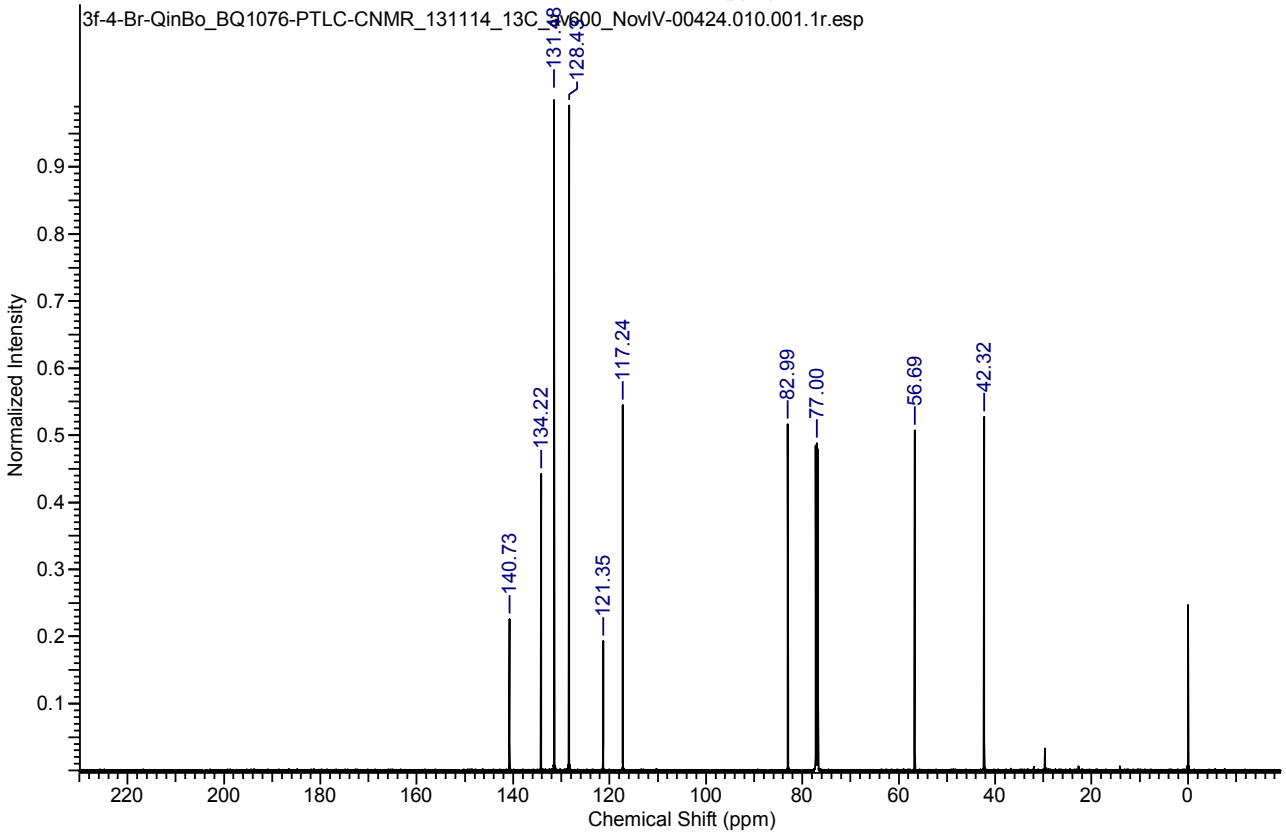

3e-4-Cl-QinBo_BQ1085-2-PTLC_110414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.21
7.32
7.31
7.23
7.21
7.33
7.21
5.76
5.75
5.73
5.72
5.70
5.69
5.04
5.03
5.01
5.01
4.15
4.14
4.13
2.55
2.54
2.52
2.38
2.37
2.36
2.36
2.05
1.92
0.97
2.02
1.00
3.05
1.05
1.06

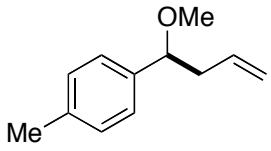

3e-4-Cl-QinBo_BQ1085-PTLC-CNMR_131114_13C_d500_NovIV-00769.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
128.33
128.08
140.21
134.27
133.25
117.21
82.97
77.00
56.67
42.36


OMe
Br

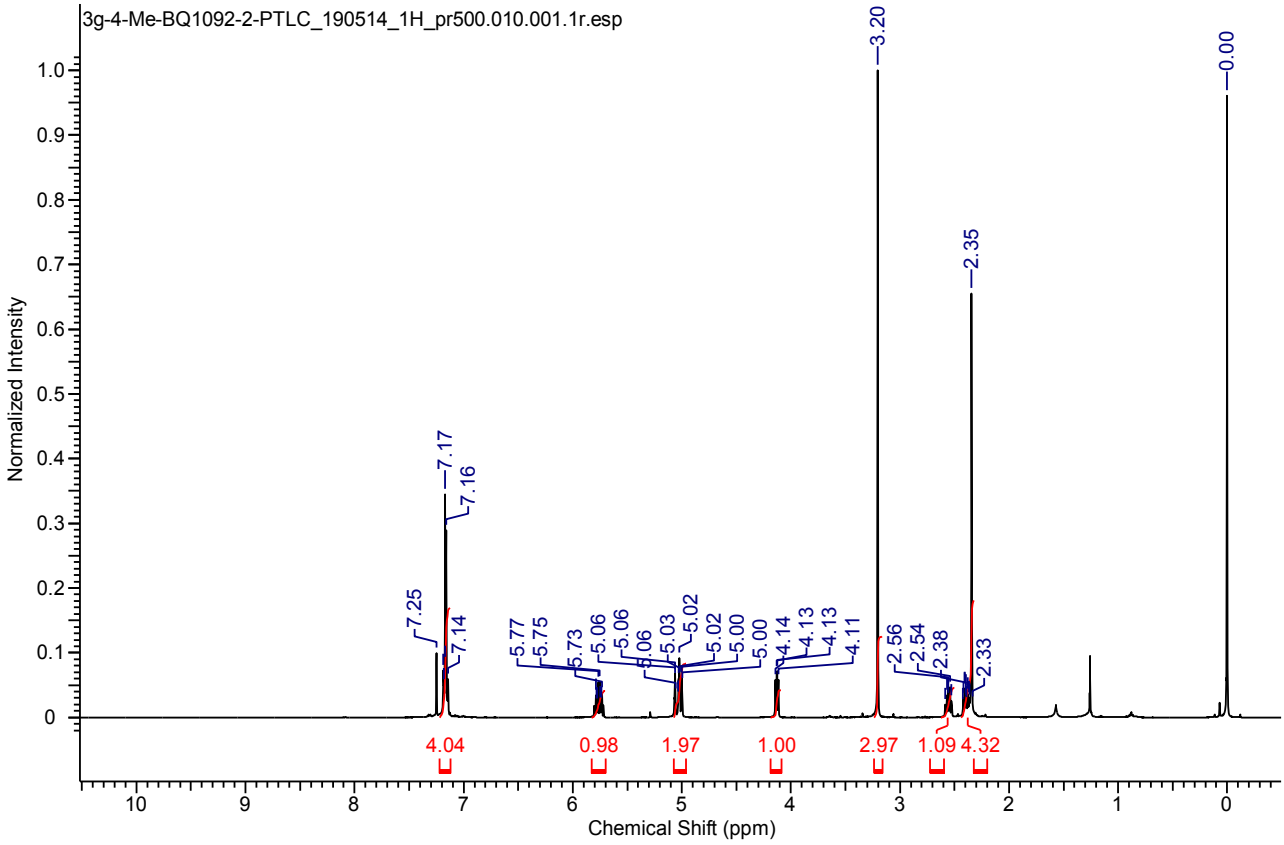
3f

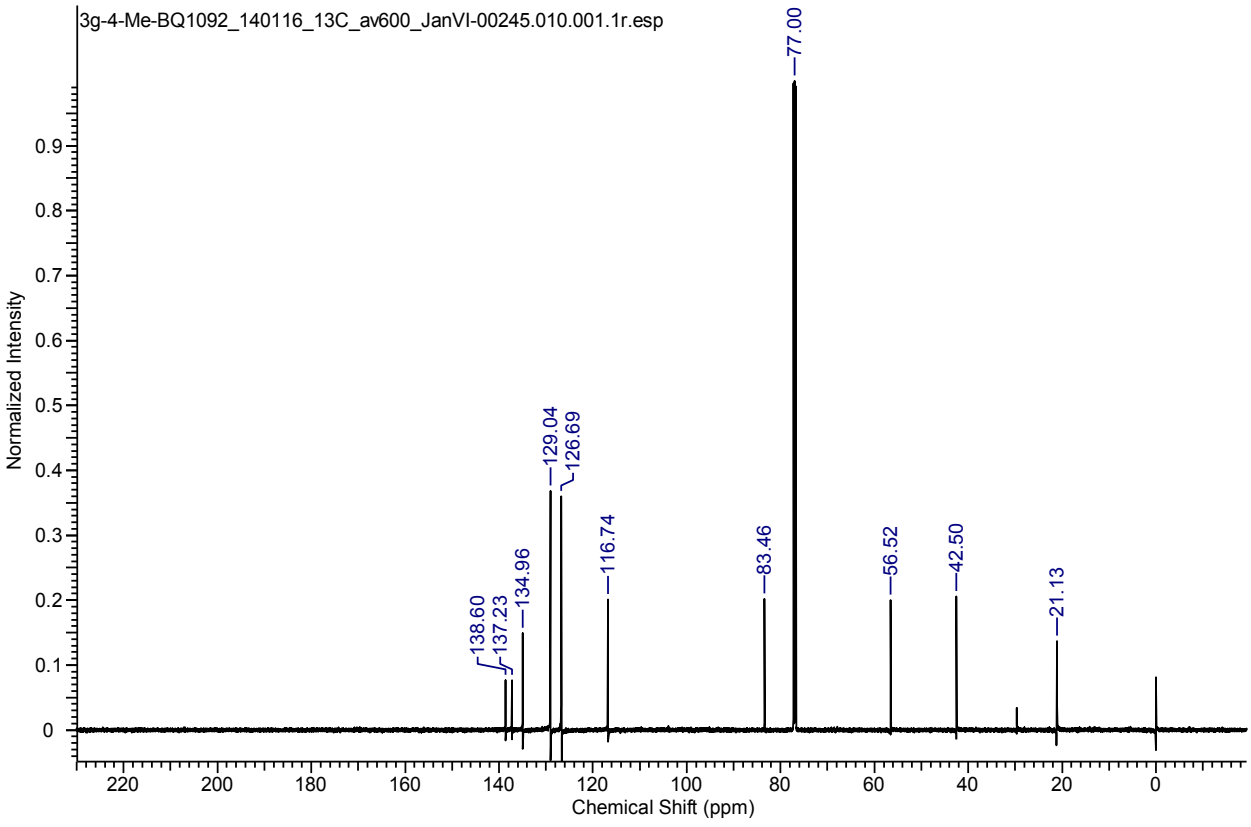

3f-4-Br-QinBo_BQ1076-1-PTLC_090414_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.21
7.48
7.46
7.17
7.16
7.17
7.15
5.76
5.75
5.73
5.72
5.70
5.05
5.04
5.01
4.14
4.13
4.12
2.54
2.53
2.52
2.38
2.37
2.37
2.36
1.94
1.99
0.96
2.00
1.00
3.07
1.04
1.04

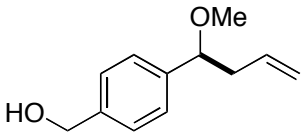

3f-4-Br-QinBo_BQ1076-PTLC-CNMR_131114_13C_av600_NovIV-00424.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
131.46
128.46
140.73
134.22
121.35
117.24
82.99
77.00
56.69
42.32


OMe
Me

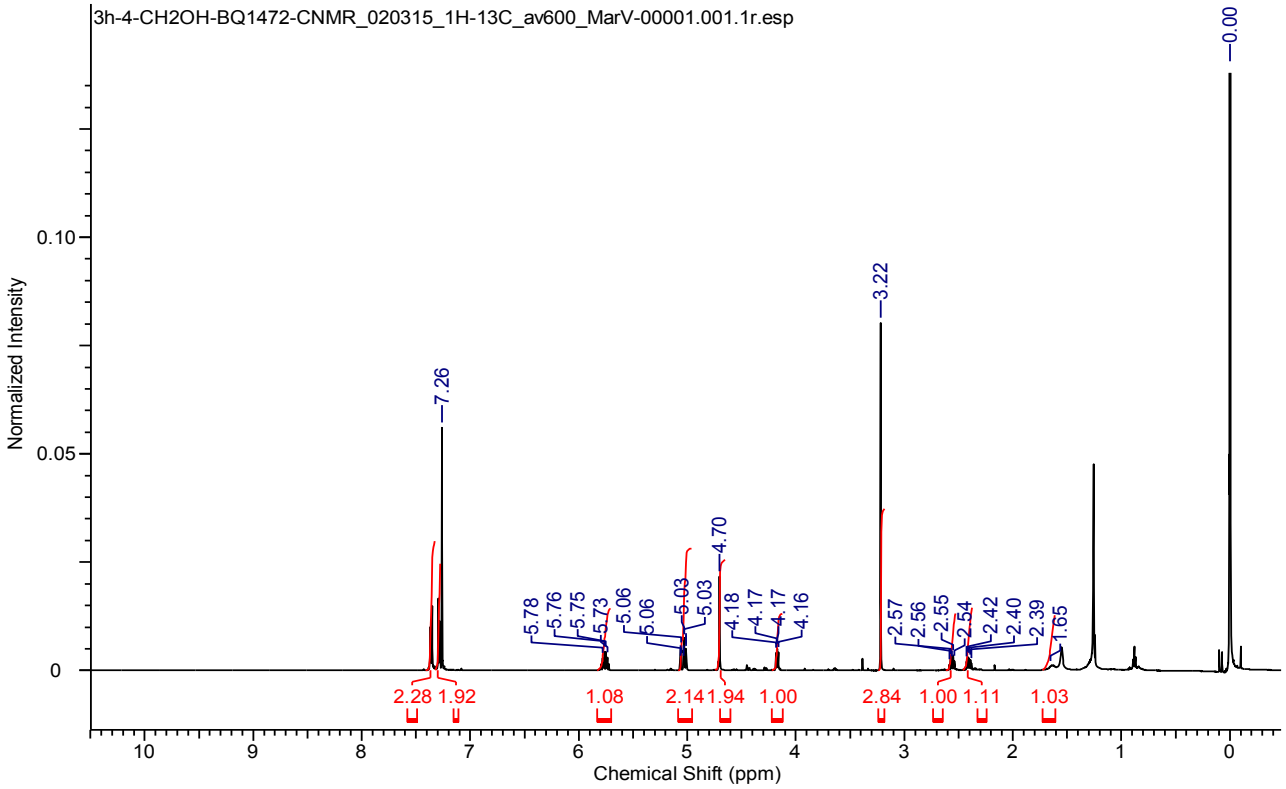
3g

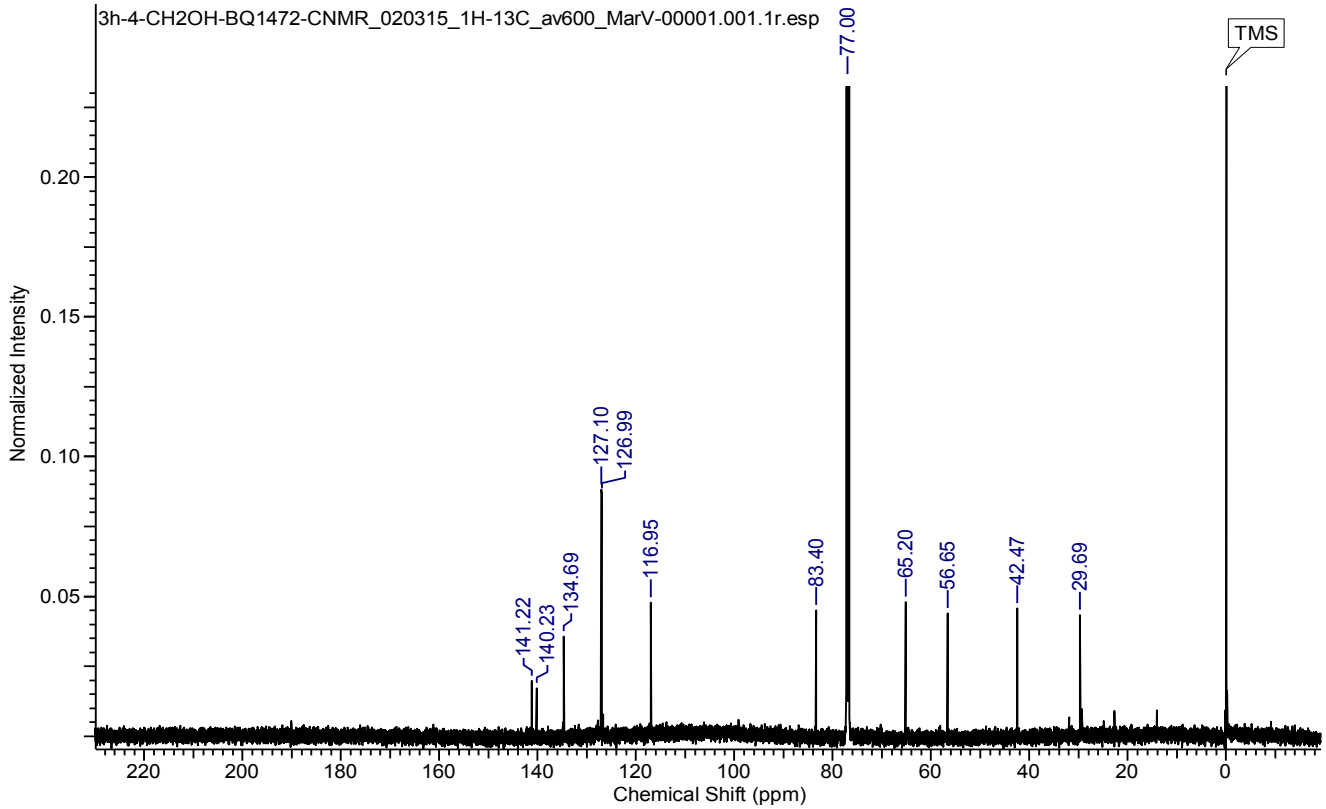

3g-4-Me-BQ1092-2-PTLC_190514_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.20
0.00
2.35
7.17
7.16
7.25
7.14
5.77
5.75
5.73
5.06
5.06
5.06
5.03
5.02
5.02
5.00
5.00
4.14
4.13
4.13
4.11
2.56
2.54
2.38
2.33
4.04
0.98
1.97
1.00
2.97
1.09
4.32

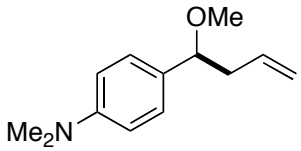

3g-4-Me-BQ1092_140116_13C_av600_JanVI-00245.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
129.04
126.69
116.74
83.46
56.52
42.50
21.13
138.60
137.23
134.96


OMe
HO

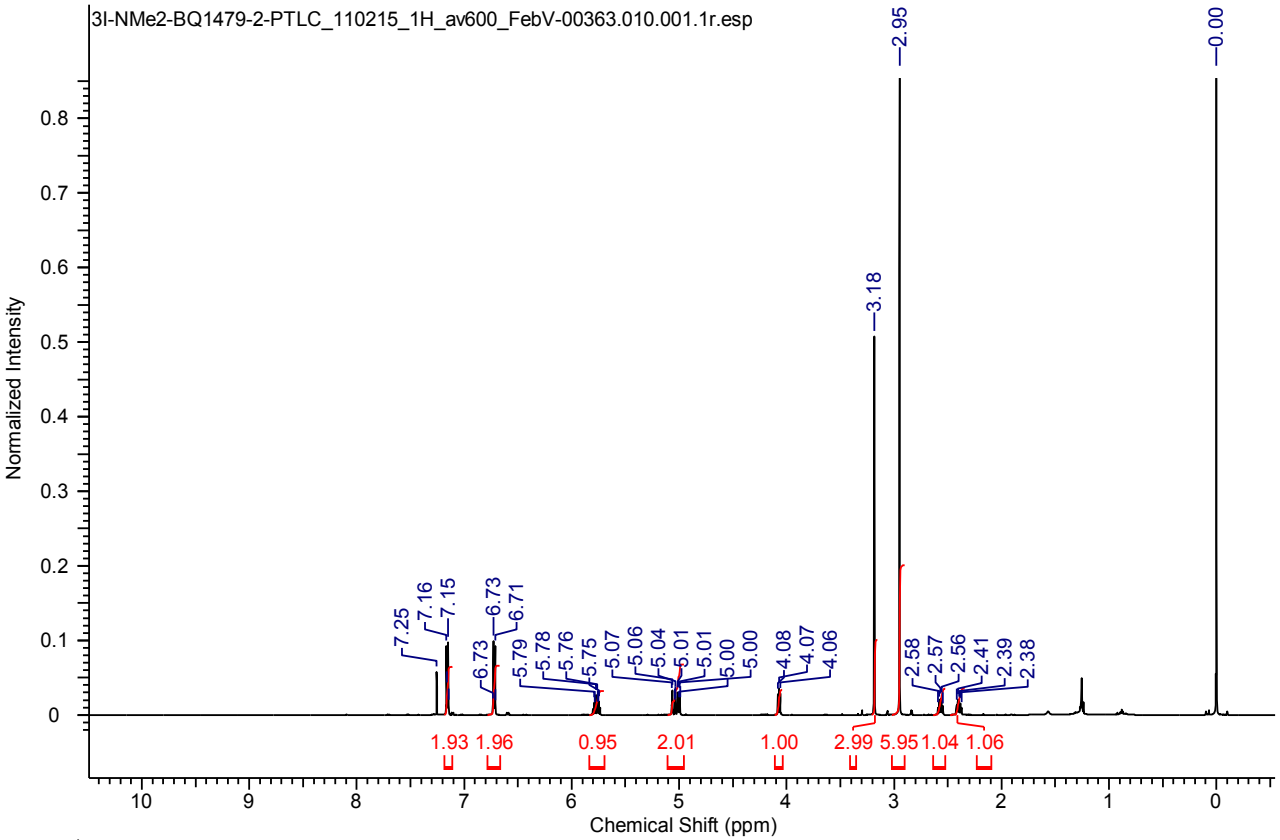
3h

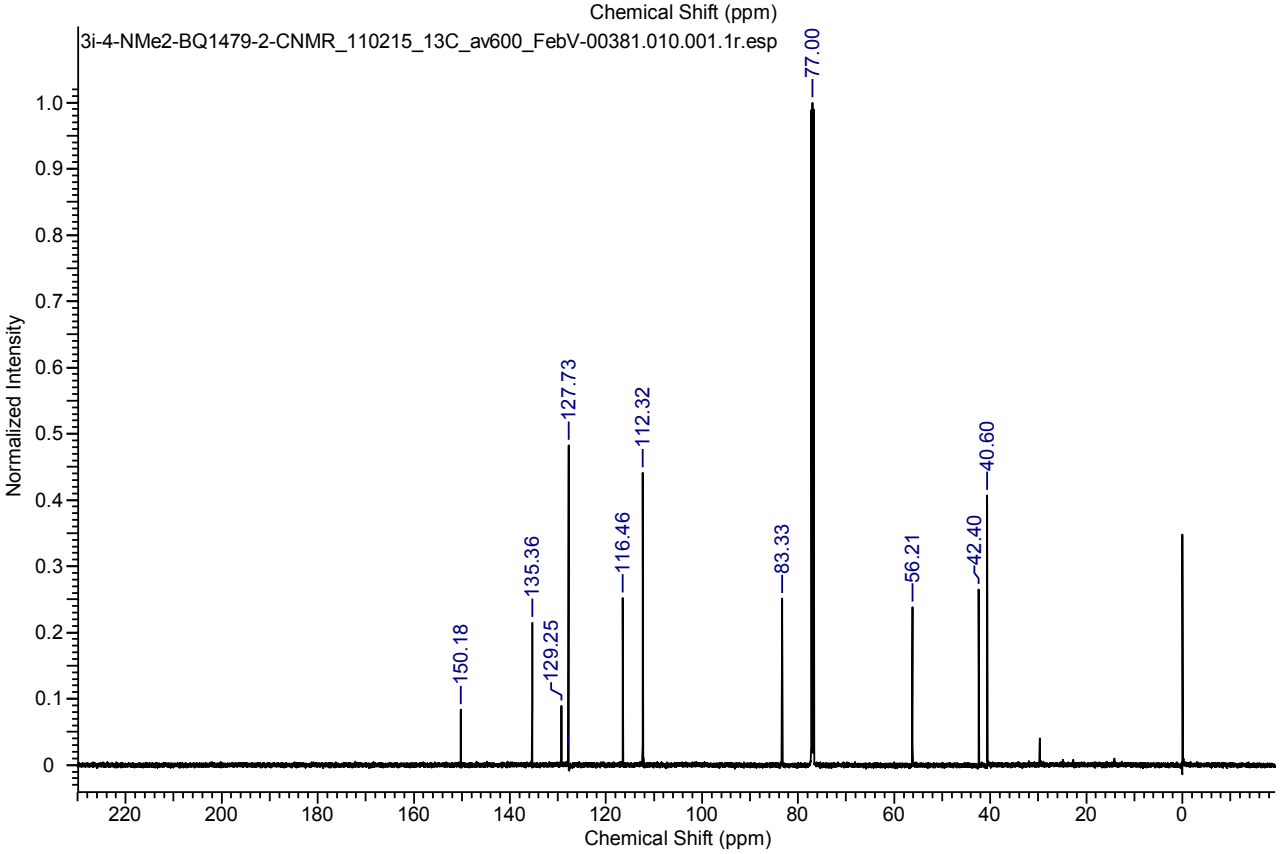

3h-4-CH2OH-BQ1472-CNMR_020315_1H-13C_av600_MarV-00001.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.26
0.00
3.22
5.78
5.76
5.75
5.73
5.06
5.06
5.03
5.03
4.70
4.18
4.17
4.17
4.16
2.57
2.56
2.55
2.54
2.42
2.40
2.39
1.65
2.28
1.92
1.08
2.14
1.94
1.00
2.84
1.00
1.11
1.03

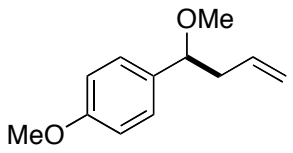

3h-4-CH2OH-BQ1472-CNMR_020315_1H-13C_av600_MarV-00001.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
TMS
127.10
126.99
141.22
140.23
134.69
116.95
83.40
65.20
56.65
42.47
29.69


OMe
Me2N

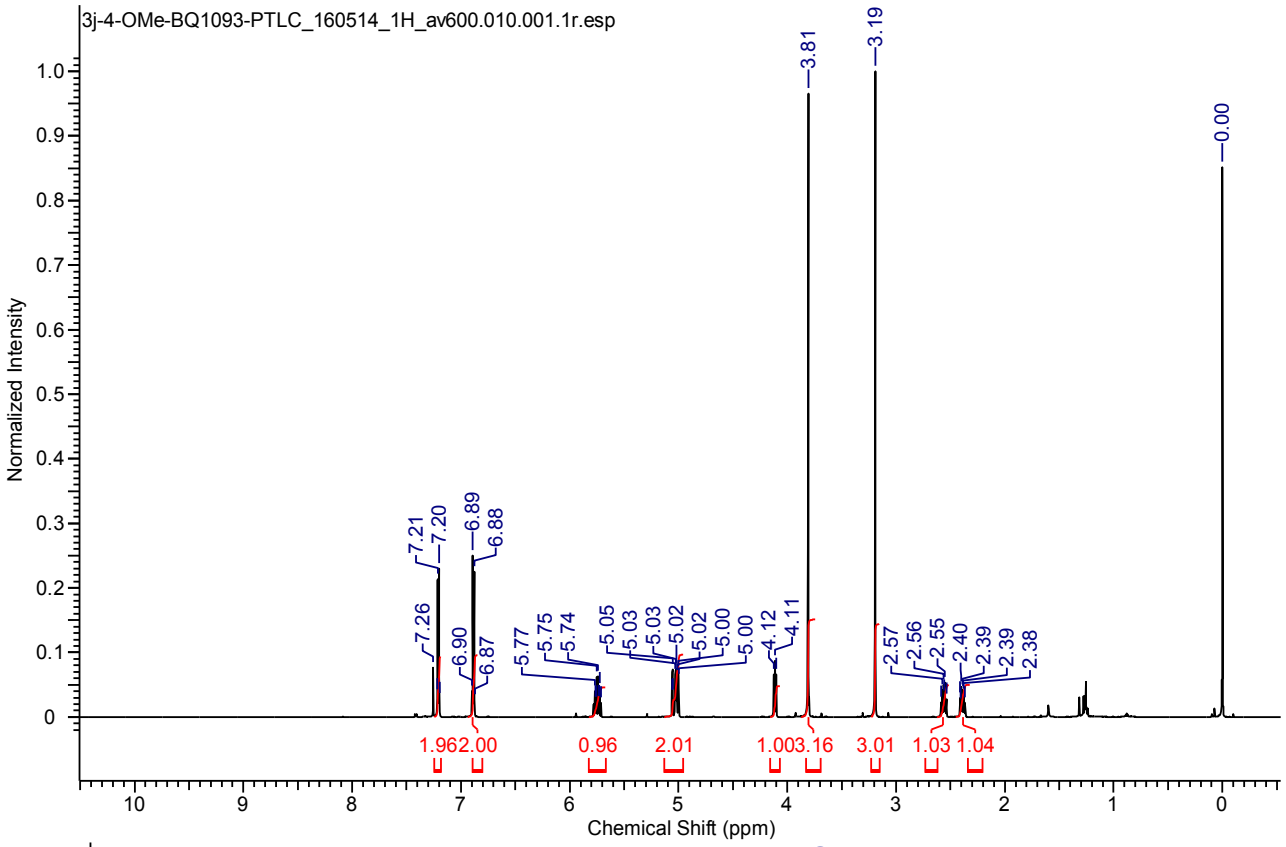
3i

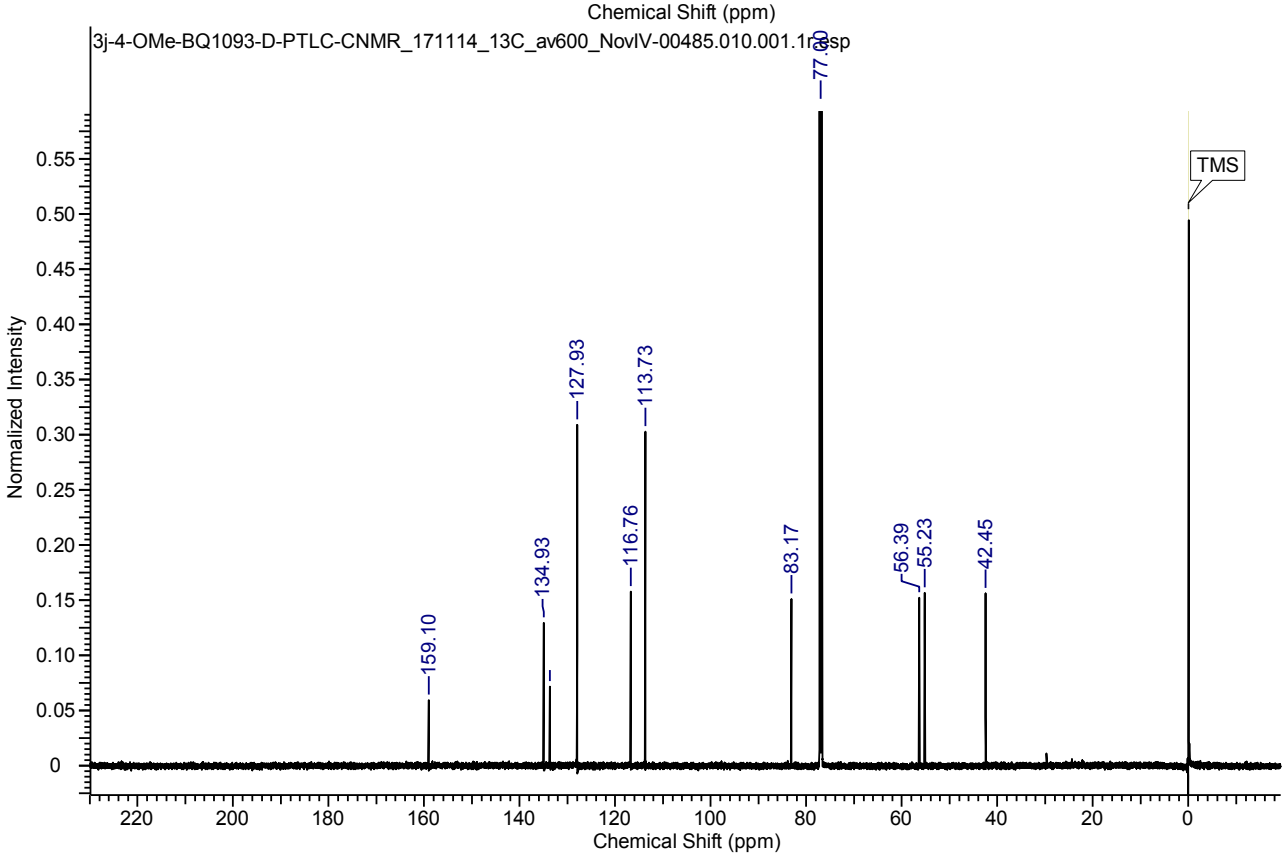

3I-NMe2-BQ1479-2-PTLC_110215_1H_av600_FebV-00363.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
2.95
0.00
3.18
7.25
7.16
7.15
6.73
6.71
6.73
5.79
5.78
5.76
5.75
5.07
5.06
5.04
5.01
5.01
5.00
5.00
4.08
4.07
4.06
2.58
2.57
2.56
2.41
2.39
2.38
1.93 1.96 0.95 2.01 1.00 2.99 5.95 1.04 1.06

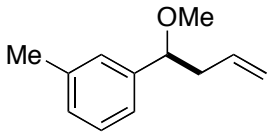

3i-4-NMe2-BQ1479-2-CNMR_110215_13C_av600_FebV-00381.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
127.73
112.32
135.36
116.46
83.33
56.21
42.40
40.60
150.18
129.25


OMe
MeO

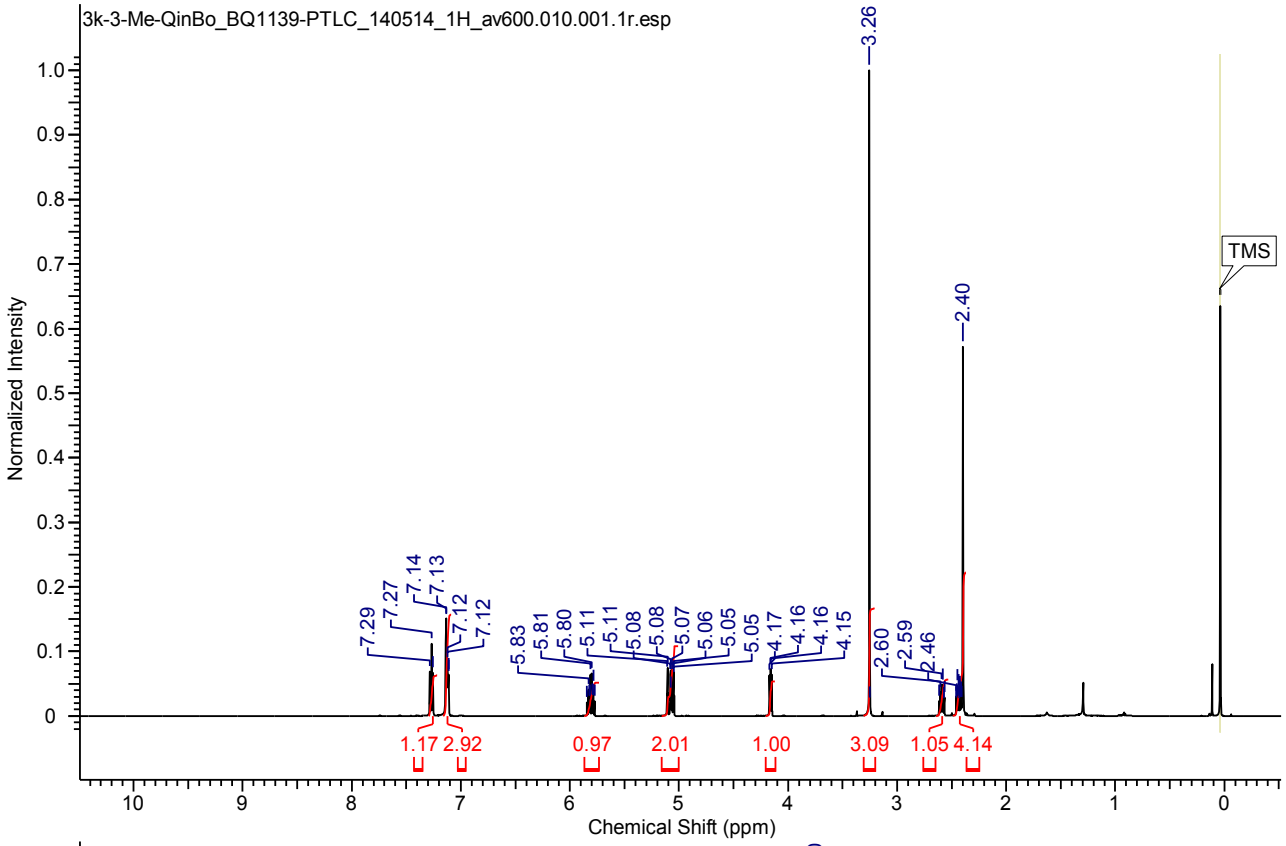
3j

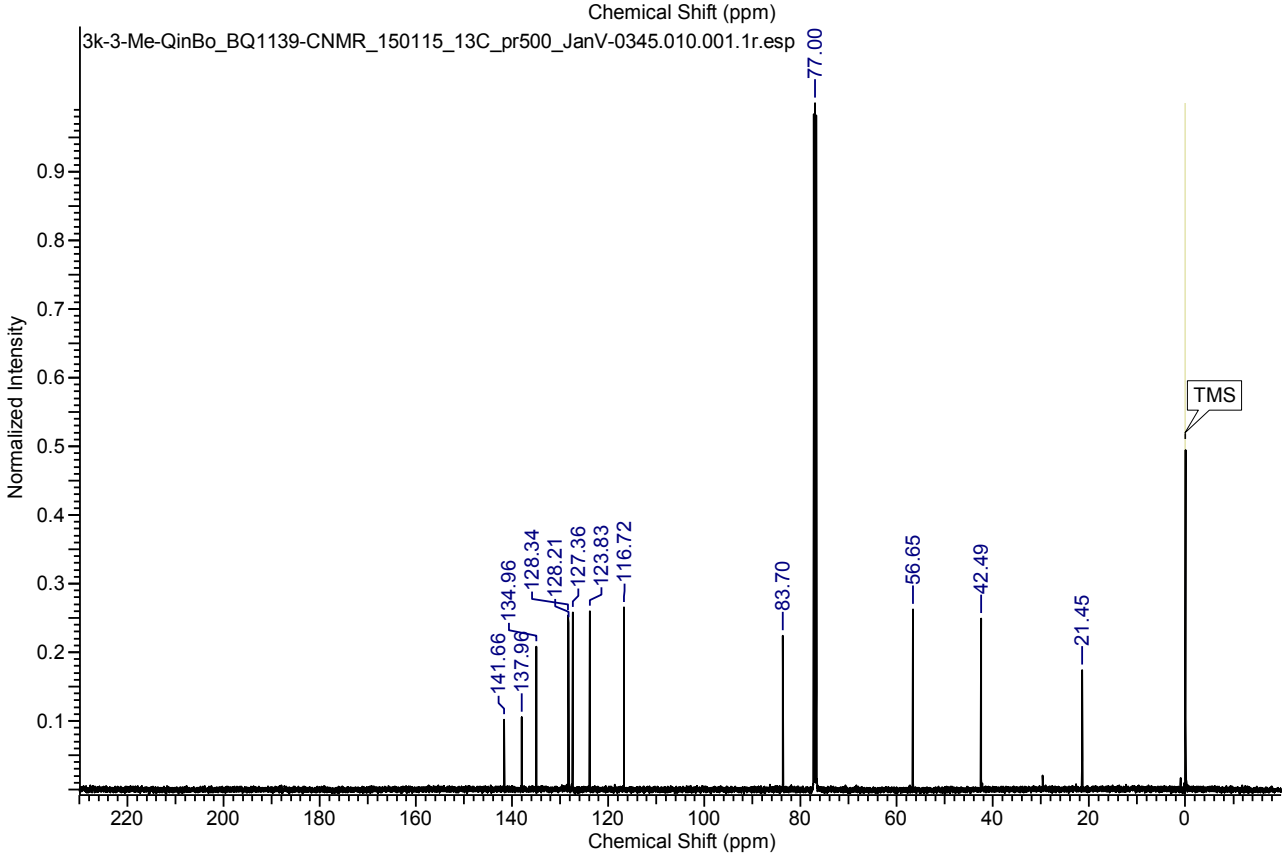

3j-4-OMe-BQ1093-PTLC_160514_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.21
7.20
6.89
6.88
7.26
6.90
6.87
5.77
5.75
5.74
5.05
5.03
5.03
5.02
5.02
5.00
5.00
4.12
4.11
3.81
3.19
2.57
2.56
2.55
2.40
2.39
2.39
2.38
0.00
1.96
2.00
0.96
2.01
1.00
3.16
3.01
1.03
1.04

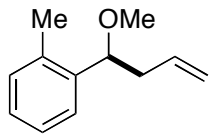

3j-4-OMe-BQ1093-D-PTLC-CNMR_171114_13C_av600_NovIV-00485.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
159.10
134.93
127.93
116.76
113.73
83.17
77.00
56.39
55.23
42.45
TMS


OMe
Me

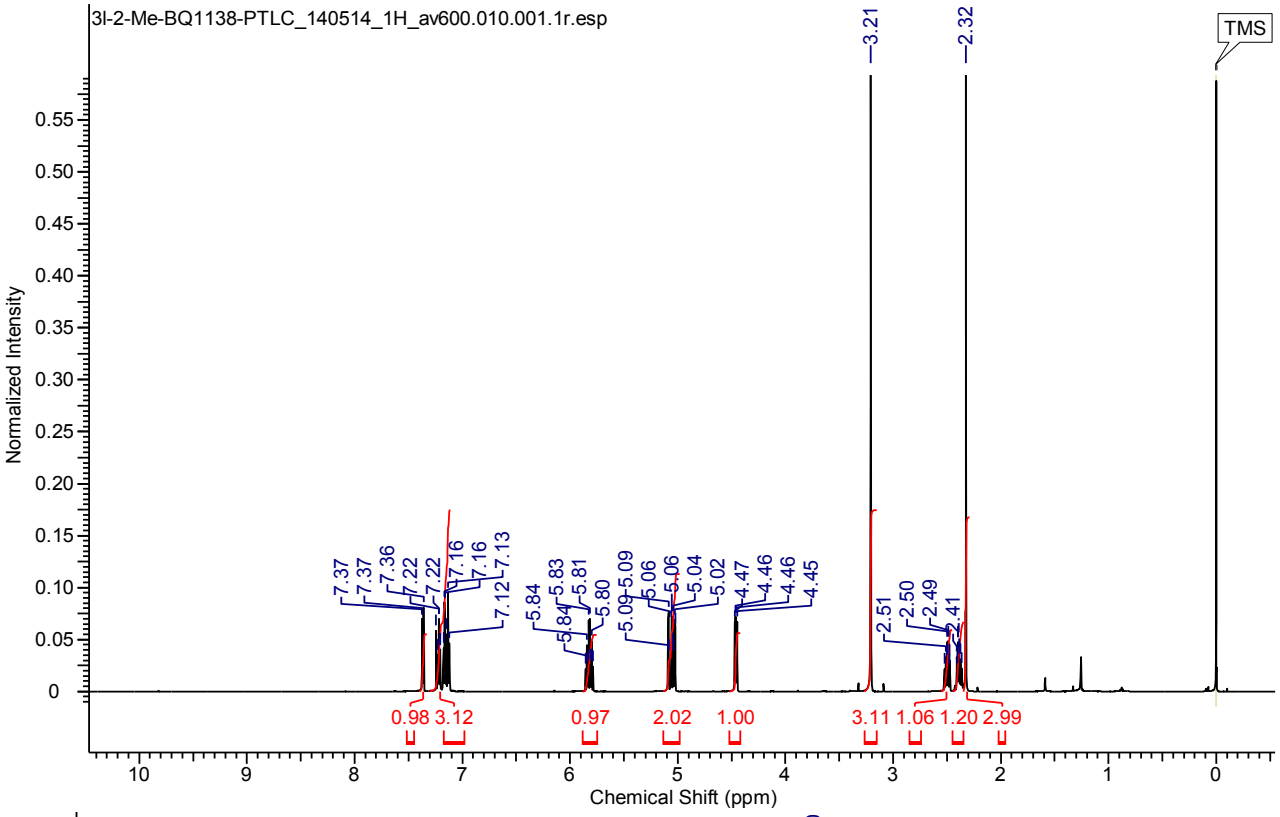
3k

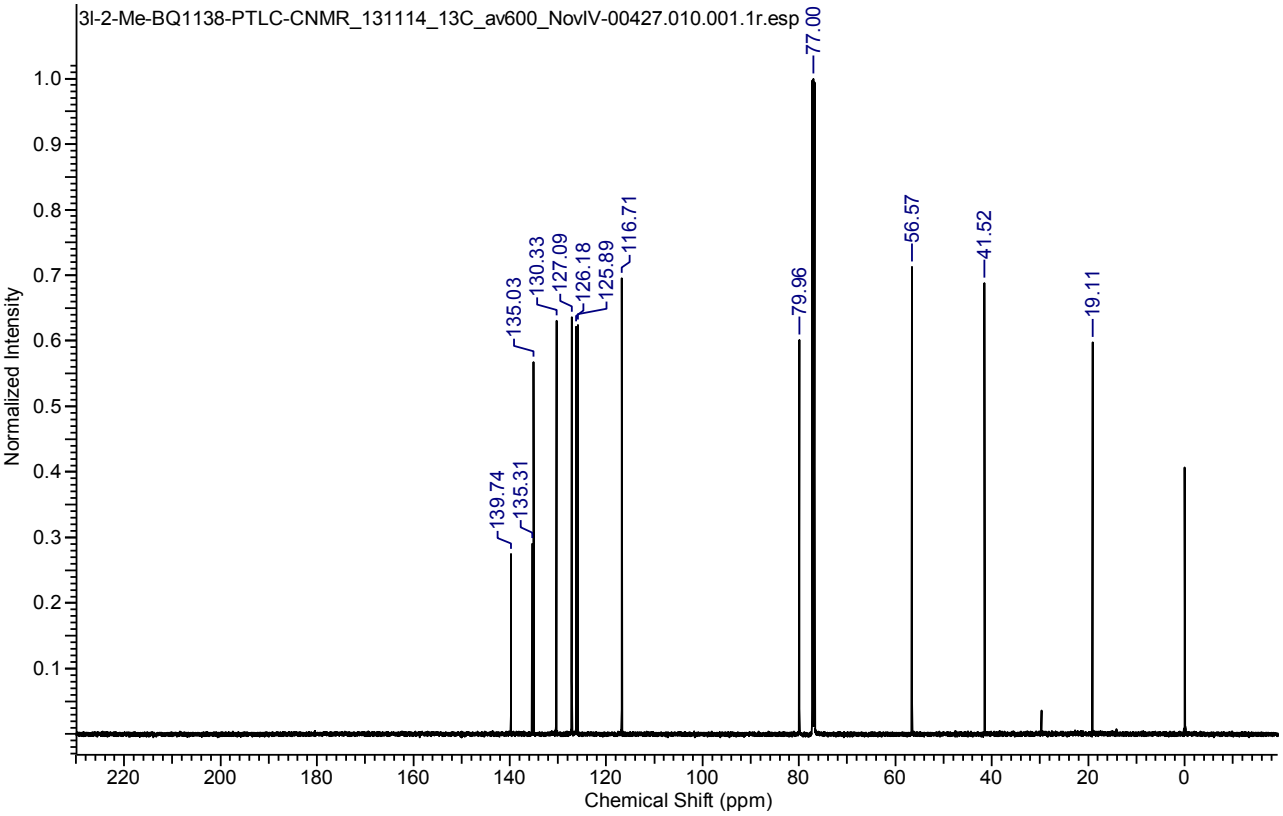

3k-3-Me-QinBo_BQ1139-PTLC_140514_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.26
2.40
7.29
7.27
7.14
7.13
7.12
7.12
5.83
5.81
5.80
5.11
5.11
5.08
5.08
5.07
5.06
5.05
5.05
4.17
4.16
4.16
4.15
2.60
2.59
2.46
1.17
2.92
0.97
2.01
1.00
3.09
1.05
4.14

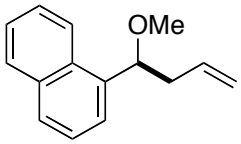

3k-3-Me-QinBo_BQ1139-CNMR_150115_13C_pr500_JanV-0345.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
77.00
141.66
137.96
134.96
128.34
128.21
127.36
123.83
116.72
83.70
56.65
42.49
21.45


Me
OMe

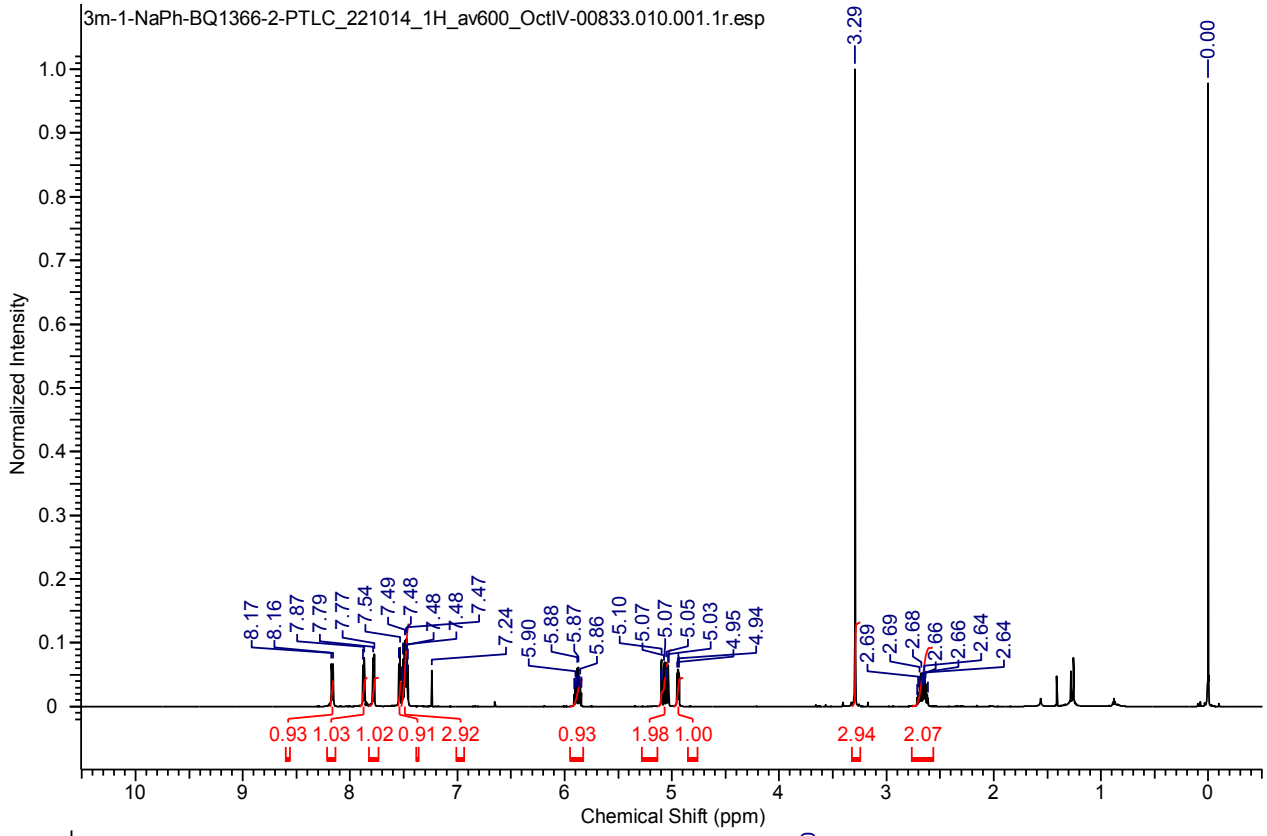
3l

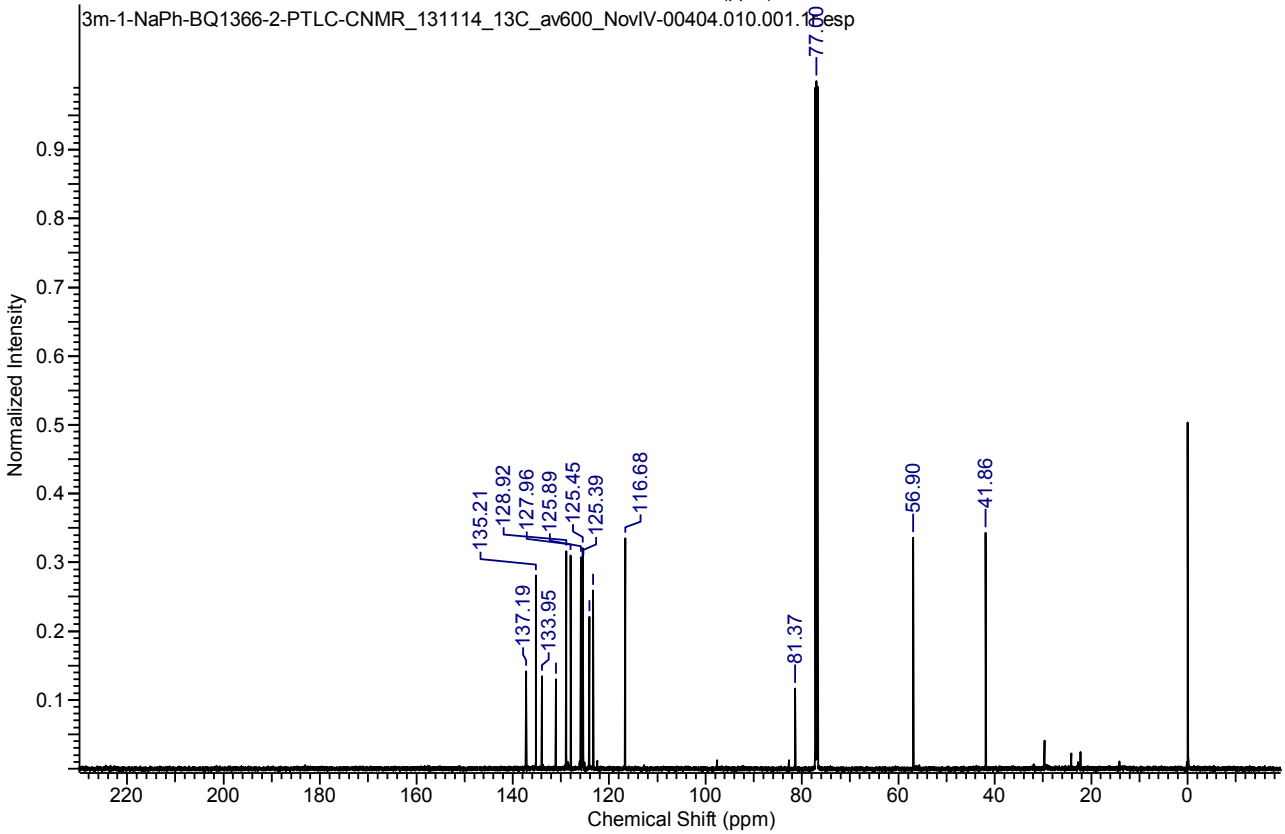

3l-2-Me-BQ1138-PTLC_140514_1H_av600.010.001.1r.esp
TMS
3.21
2.32
Normalized Intensity
Chemical Shift (ppm)
0.98 3.12 0.97 2.02 1.00 3.11 1.06 1.20 2.99

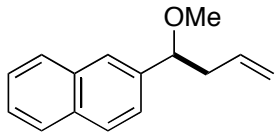

3l-2-Me-BQ1138-PTLC-CNMR_131114_13C_av600_NovIV-00427.010.001.1r.esp
77.00
139.74
135.31
135.03
130.33
127.09
126.18
125.89
116.71
79.96
56.57
41.52
19.11
Normalized Intensity
Chemical Shift (ppm)


OMe

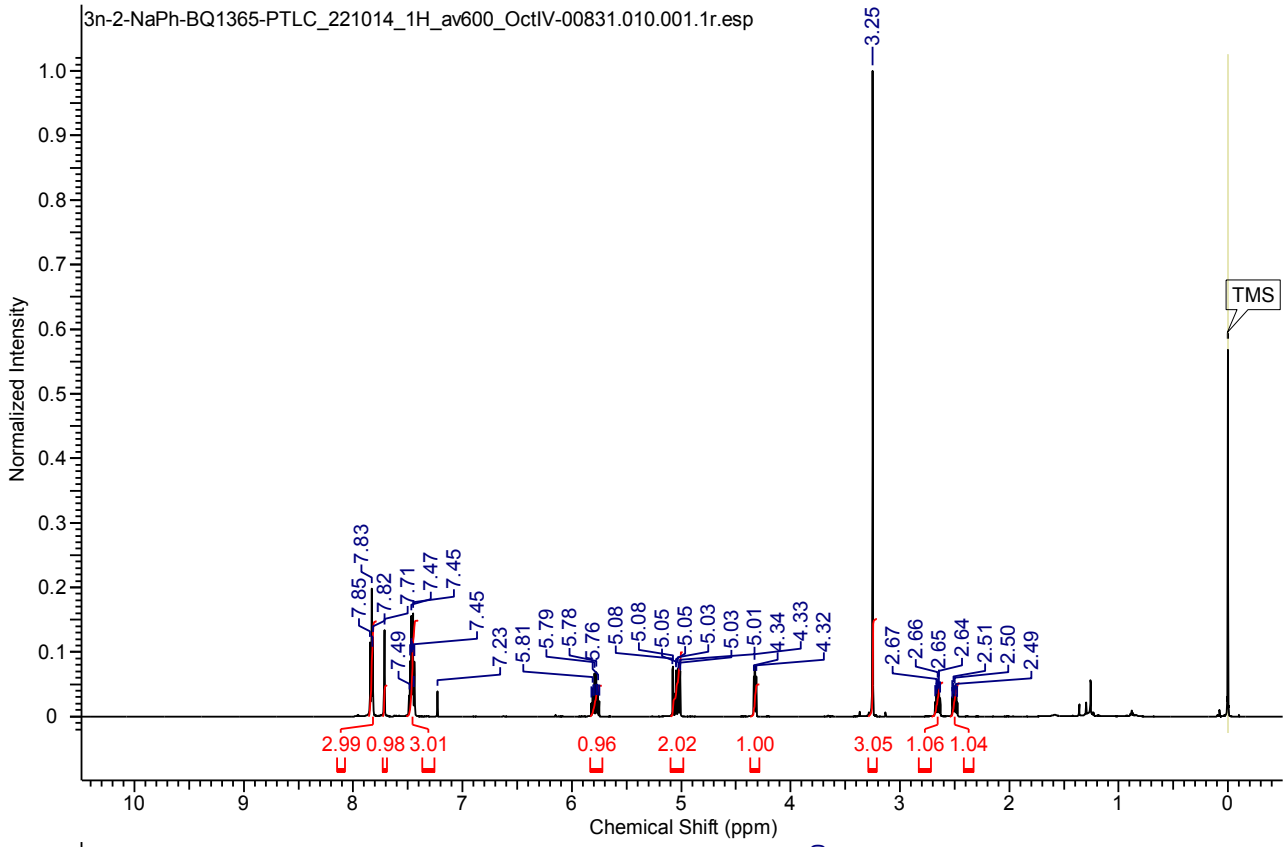
3m

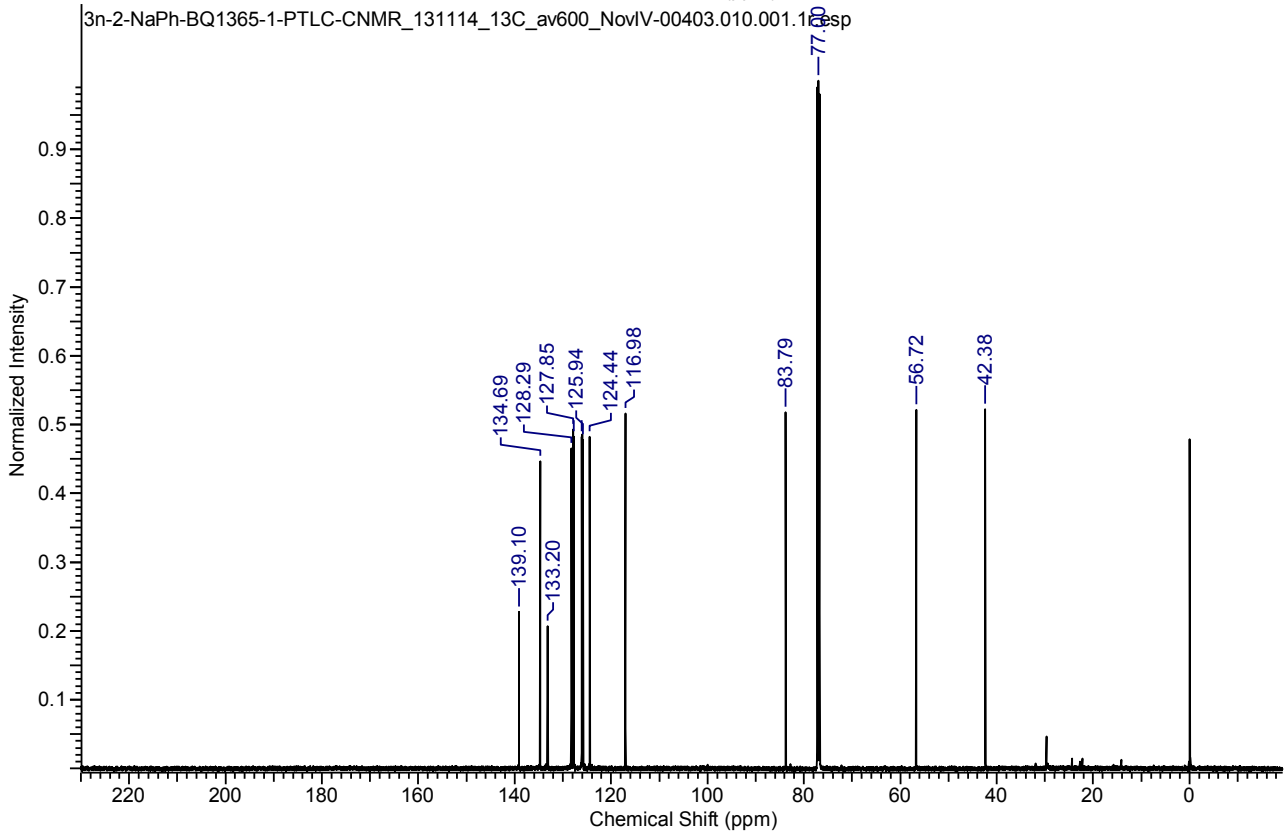

3m-1-NaPh-BQ1366-2-PTLC_221014_1H_av600_OctIV-00833.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.29
0.00
8.17
8.16
7.87
7.79
7.77
7.54
7.49
7.48
7.48
7.48
7.47
7.24
5.90
5.88
5.87
5.86
5.10
5.07
5.07
5.05
5.03
4.95
4.94
2.69
2.69
2.68
2.66
2.66
2.64
2.64
0.93 1.03 1.02 0.91 2.92
0.93
1.98 1.00
2.94
2.07

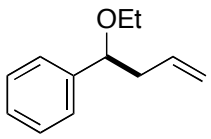

3m-1-NaPh-BQ1366-2-PTLC-CNMR_131114_13C_av600_NovIV-00404.010.001.1esp
Normalized Intensity
Chemical Shift (ppm)
77.00
135.21
128.92
127.96
125.89
125.45
125.39
116.68
137.19
133.95
81.37
56.90
41.86


OMe

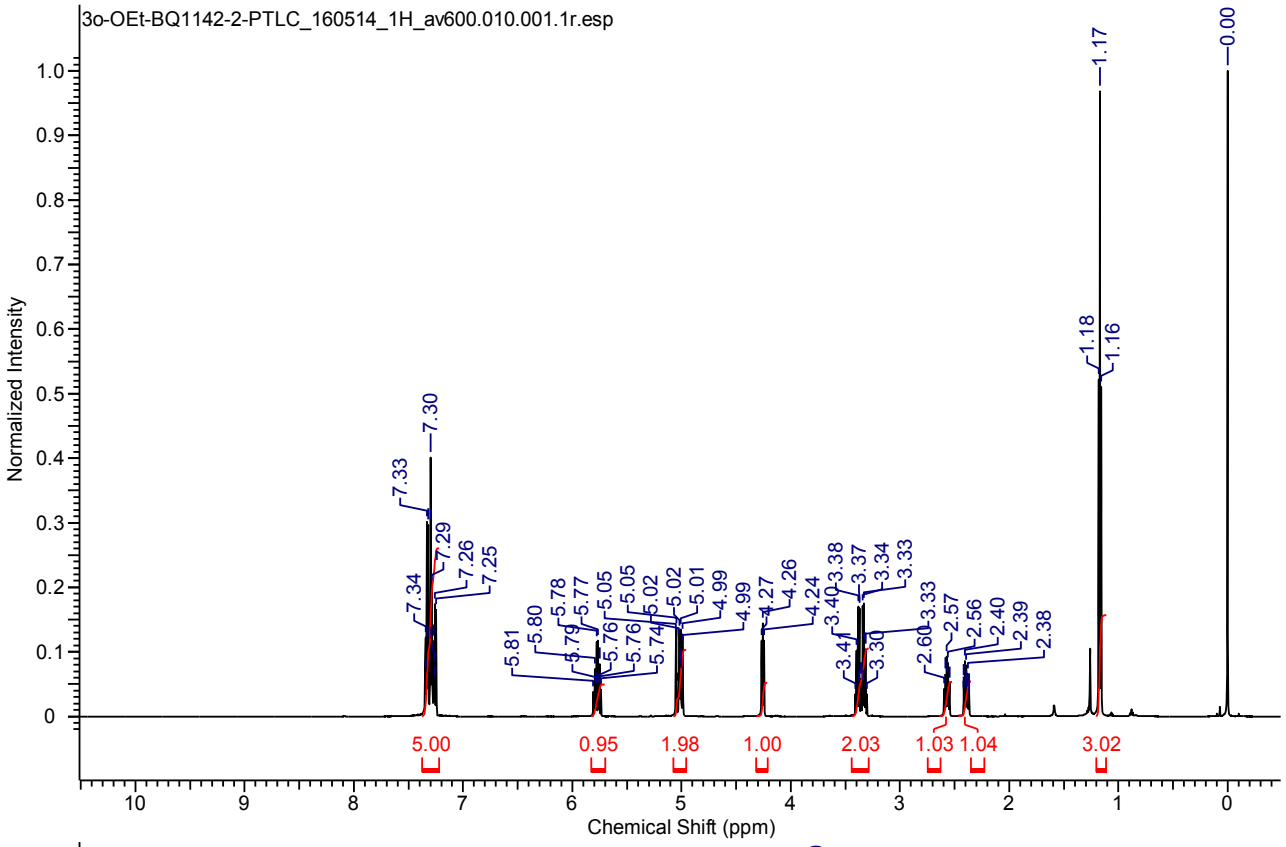
3n

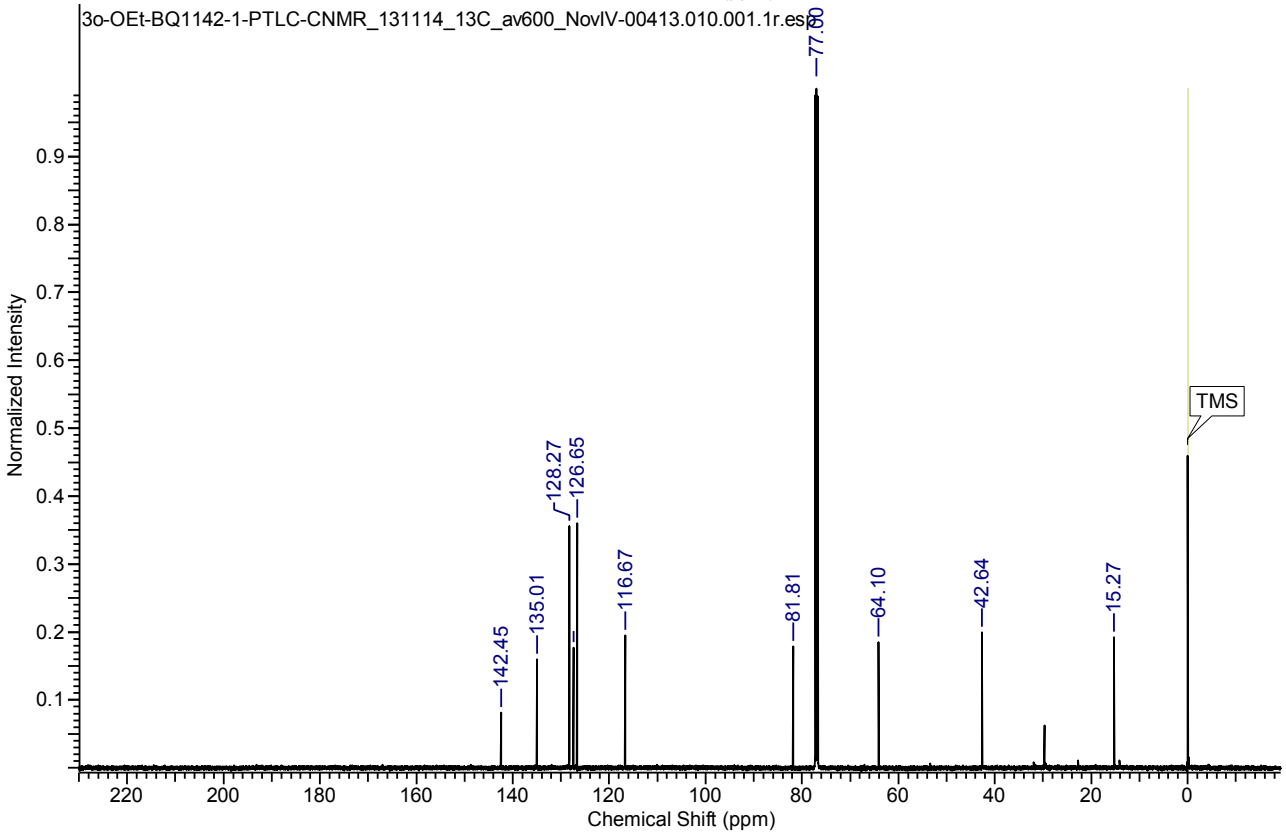

3n-2-NaPh-BQ1365-PTLC_221014_1H_av600_OctIV-00831.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.25
TMS
7.85
7.83
7.82
7.71
7.49
7.47
7.45
7.45
7.23
5.81
5.79
5.78
5.76
5.08
5.08
5.05
5.05
5.03
5.03
5.01
4.34
4.33
4.32
2.67
2.66
2.65
2.64
2.51
2.50
2.49
2.99
0.98
3.01
0.96
2.02
1.00
3.05
1.06
1.04

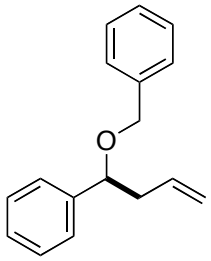

3n-2-NaPh-BQ1365-1-PTLC-CNMR_131114_13C_av600_NovIV-00403.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
134.69
128.29
127.85
125.94
124.44
116.98
83.79
56.72
42.38
139.10
133.20


OEt

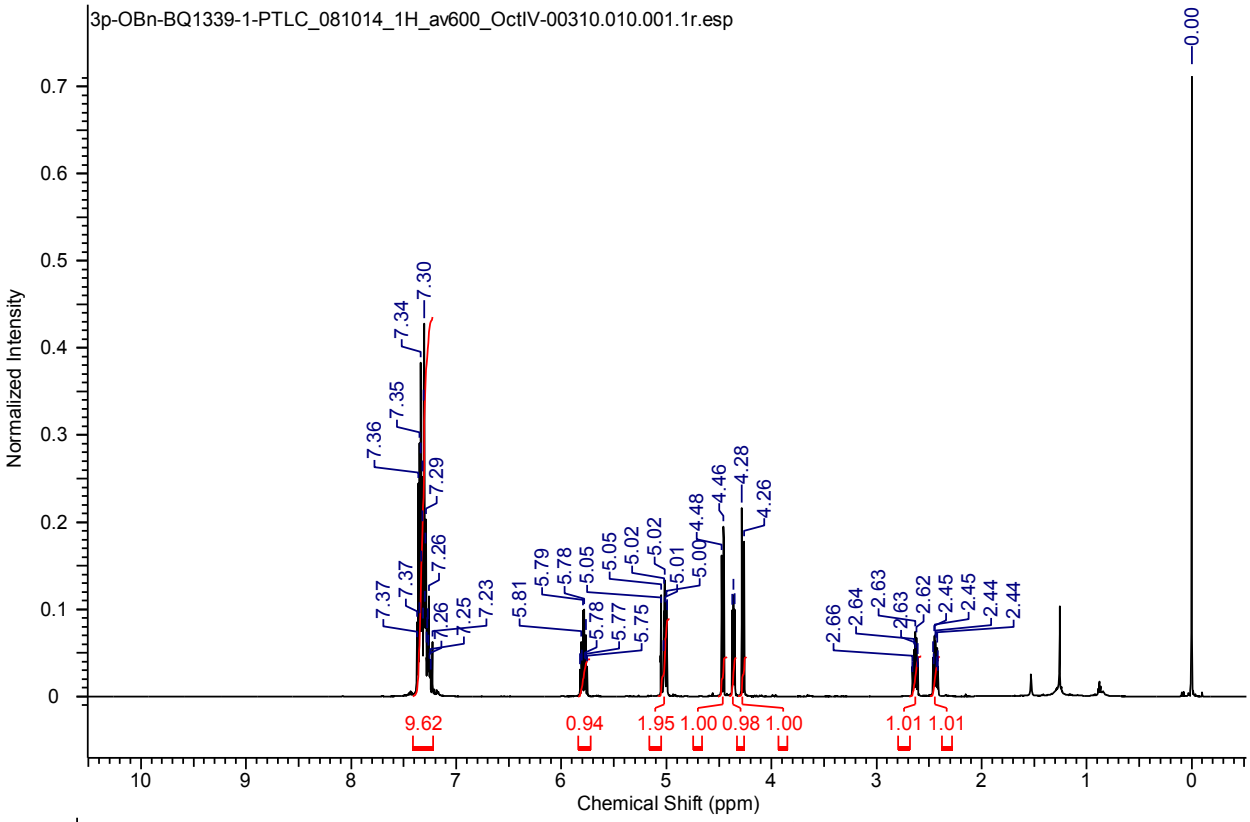
3o

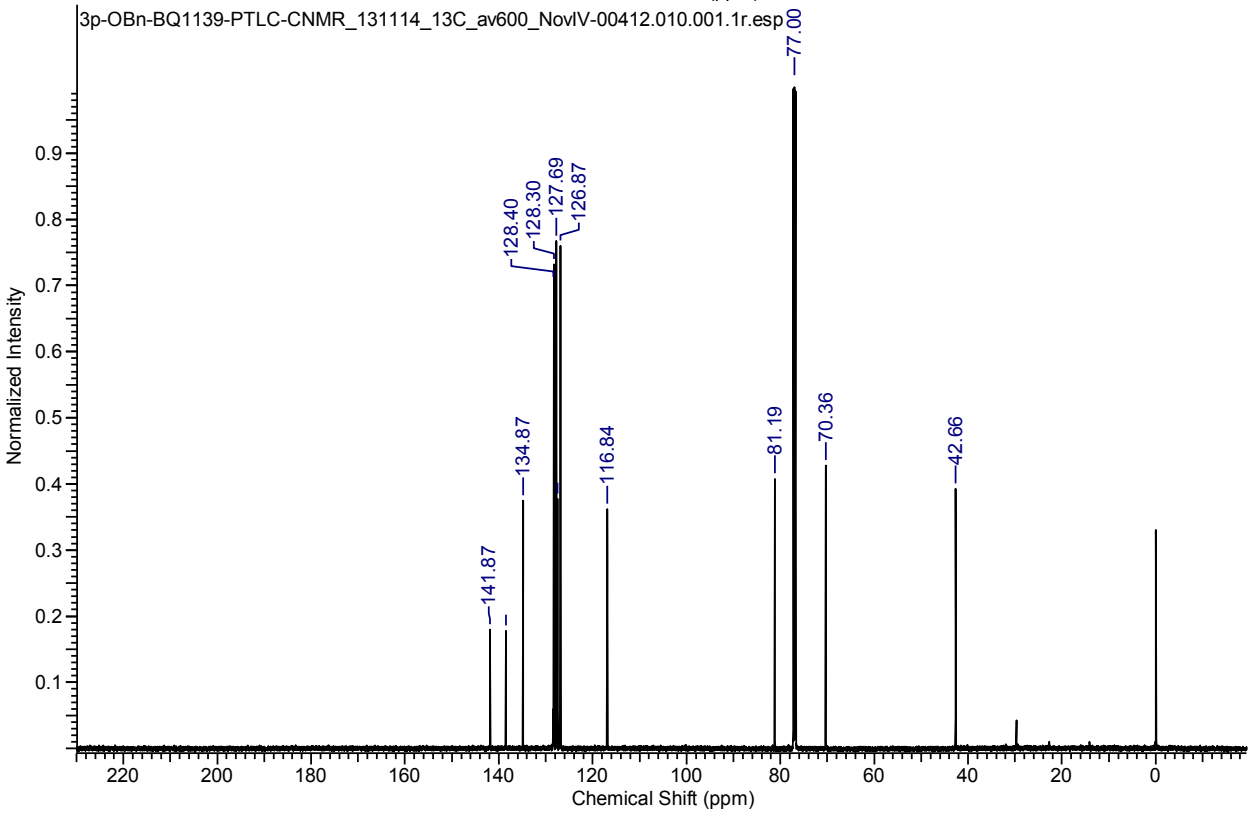

3o-OEt-BQ1142-2-PTLC_160514_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.34
7.33
7.30
7.29
7.26
7.25
5.81
5.80
5.78
5.77
5.76
5.74
5.05
5.05
5.02
5.02
5.01
4.99
4.99
4.27
4.26
4.24
3.41
3.40
3.38
3.37
3.34
3.33
3.30
2.60
2.57
2.56
2.40
2.39
2.38
1.18
1.16
1.17
0.00
5.00
0.95
1.98
1.00
2.03
1.03
1.04
3.02

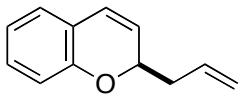

3o-OEt-BQ1142-1-PTLC-CNMR_131114_13C_av600_NovIV-00413.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
142.45
135.01
128.27
126.65
116.67
81.81
64.10
42.64
15.27
TMS



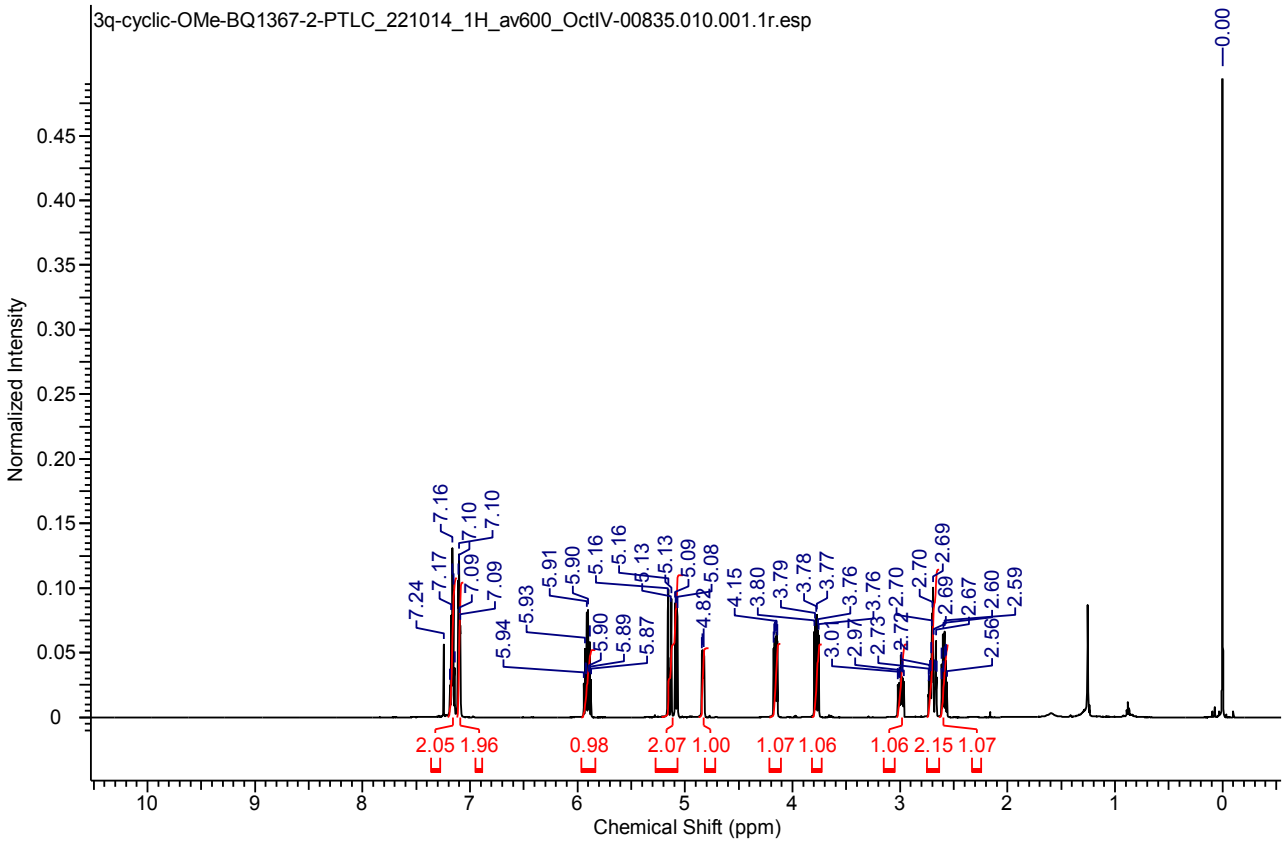
3p

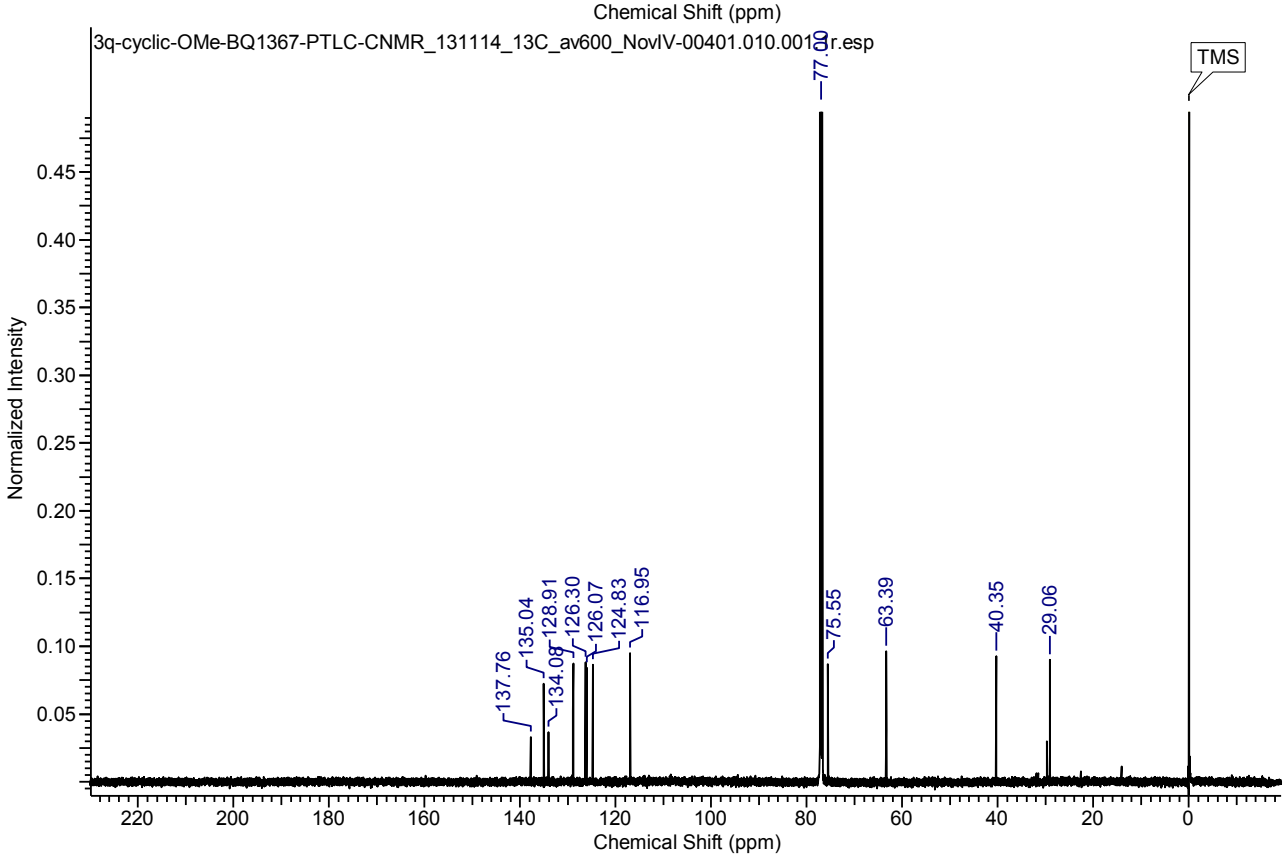

3p-OBn-BQ1339-1-PTLC_081014_1H_av600_OctIV-00310.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
7.30
7.34
7.35
7.36
7.29
7.26
7.37
7.37
7.26
7.25
7.23
5.81
5.79
5.78
5.05
5.05
5.02
5.02
5.01
5.00
4.48
4.46
4.28
4.26
2.66
2.64
2.63
2.63
2.62
2.45
2.45
2.44
2.44
9.62
0.94
1.95
1.00
0.98
1.00
1.01
1.01

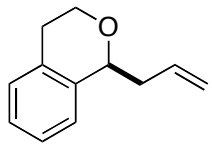

3p-OBn-BQ1139-PTLC-CNMR_131114_13C_av600_NovIV-00412.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
128.40
128.30
127.69
126.87
141.87
134.87
116.84
81.19
70.36
42.66



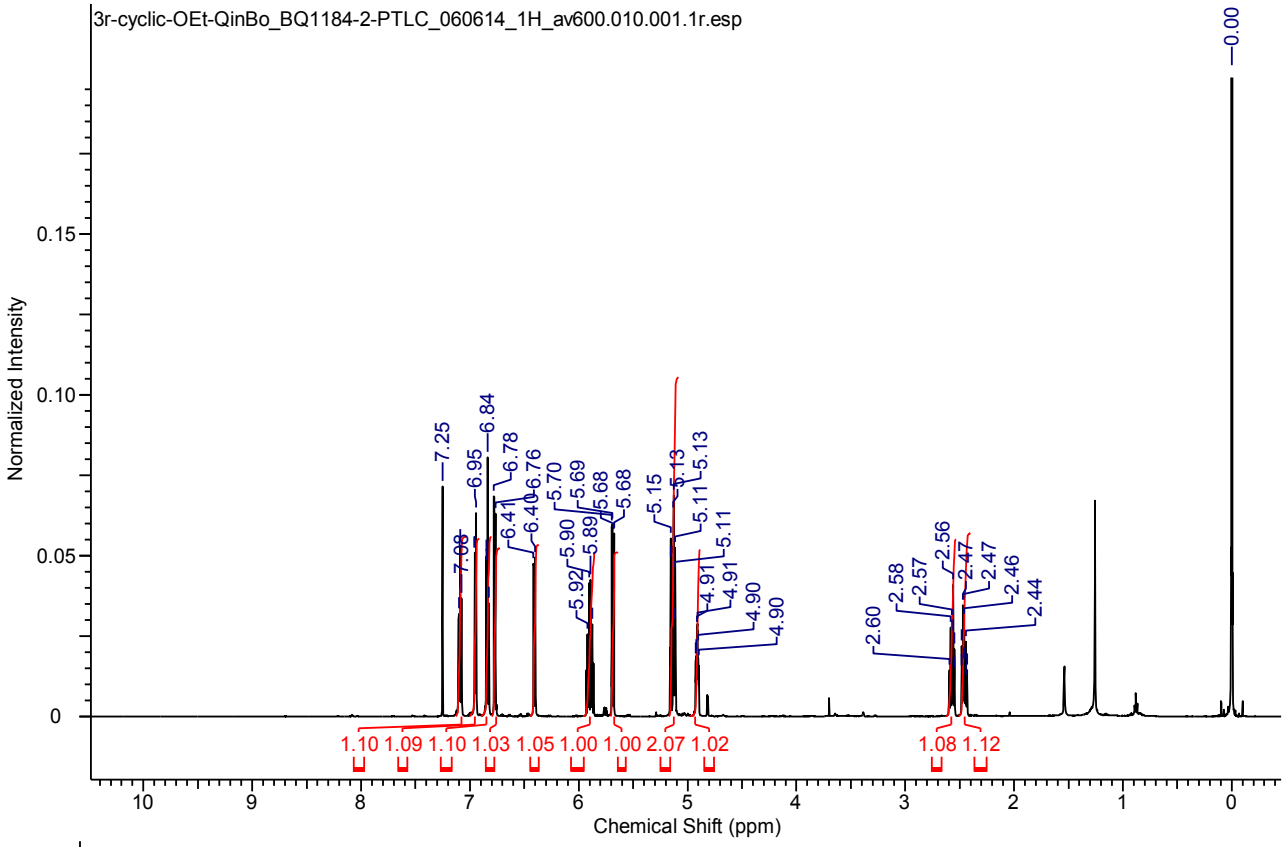
3q

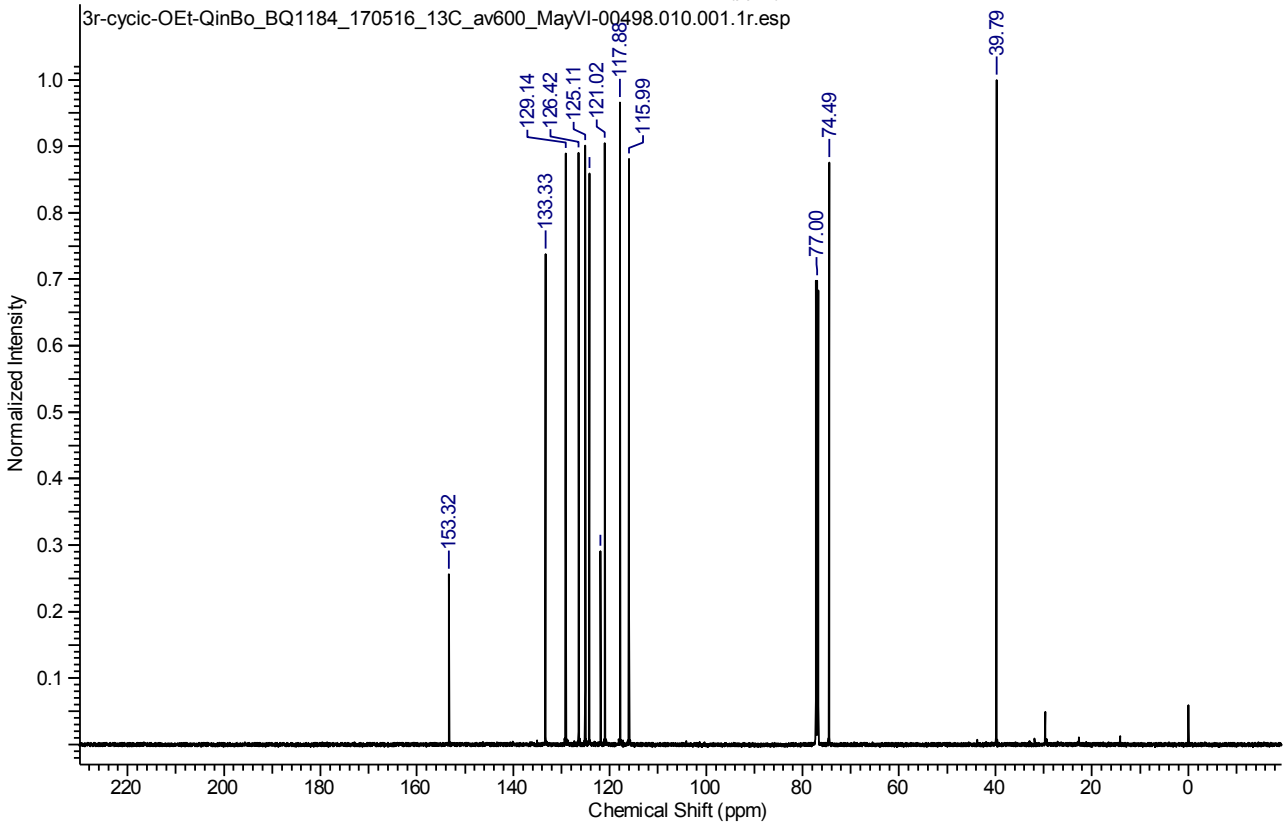

3q-cyclic-OMe-BQ1367-2-PTLC_221014_1H_av600_OctIV-00835.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
7.24
7.17
7.16
7.10
7.10
7.09
7.09
5.94
5.93
5.91
5.90
5.90
5.89
5.87
5.16
5.16
5.13
5.13
5.09
5.08
4.82
4.15
3.80
3.79
3.78
3.77
3.76
3.76
3.07
2.97
2.73
2.72
2.70
2.70
2.69
2.69
2.67
2.60
2.59
2.56
2.05
1.96
0.98
2.07
1.00
1.07
1.06
1.06
2.15
1.07

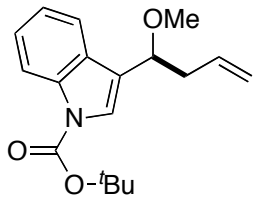

3q-cyclic-OMe-BQ1367-PTLC-CNMR_131114_13C_av600_NovIV-00401.010.001r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
77.00
137.76
135.04
134.08
128.91
126.30
126.07
124.83
116.95
75.55
63.39
40.35
29.06



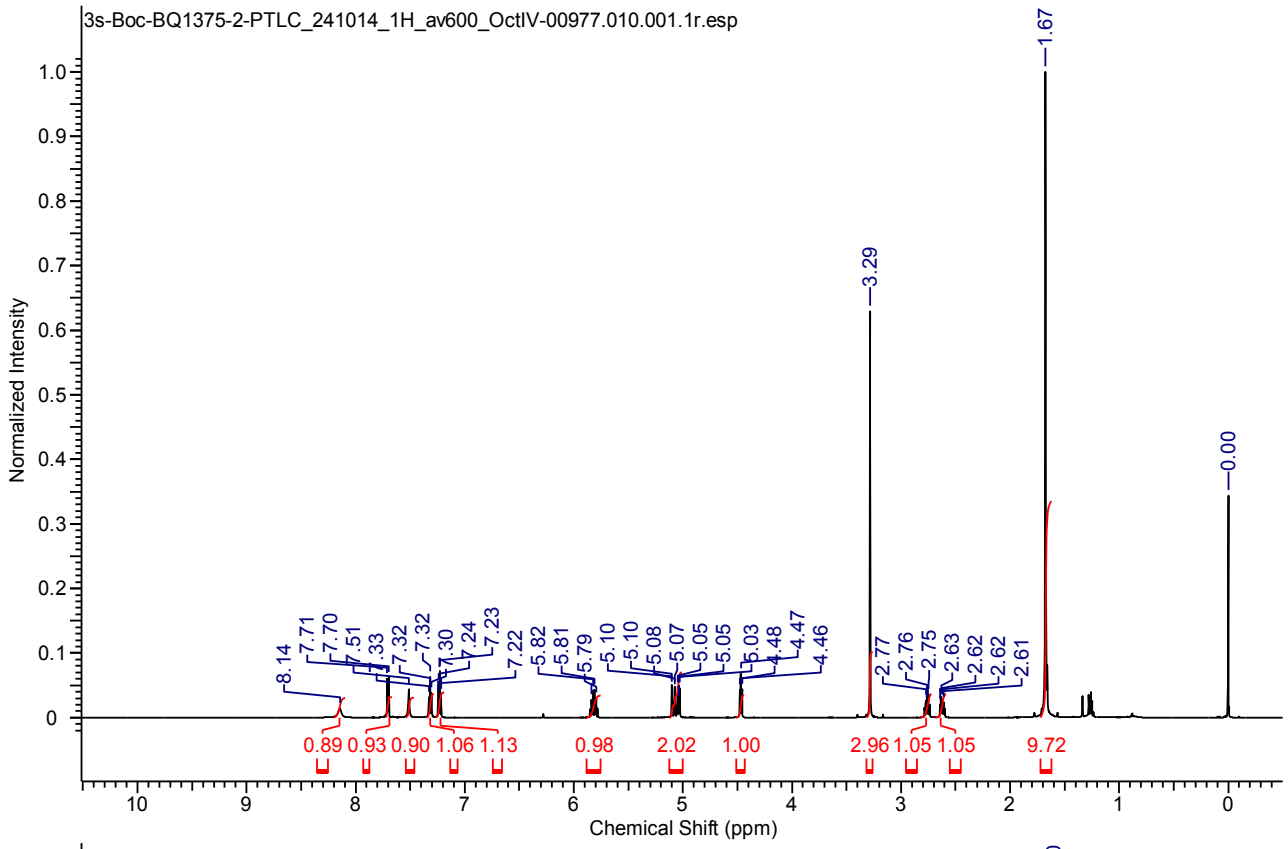
3r

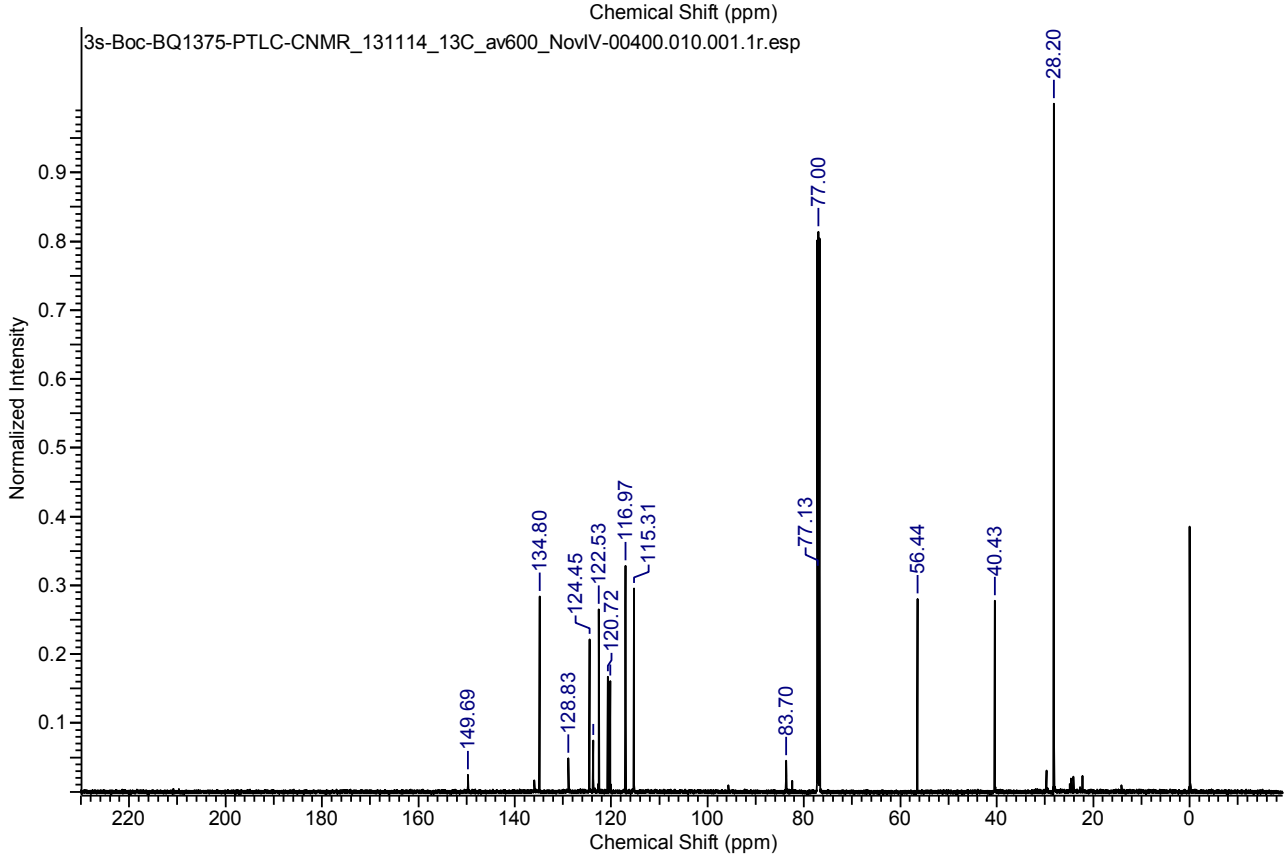

3r-cyclic-OEt-QinBo_BQ1184-2-PTLC_060614_1H_av600.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
7.25
7.06
6.95
6.84
6.78
6.76
6.41
6.40
5.92
5.90
5.89
5.70
5.69
5.68
5.68
5.15
5.13
5.13
5.11
5.11
4.91
4.91
4.90
4.90
2.60
2.58
2.57
2.56
2.47
2.47
2.46
2.44
1.10 1.09 1.10 1.03 1.05 1.00 1.00 2.07 1.02
1.08 1.12

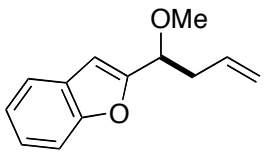

3r-cycic-OEt-QinBo_BQ1184_170516_13C_av600_MayVI-00498.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
153.32
133.33
129.14
126.42
125.11
121.02
117.88
115.99
77.00
74.49
39.79


OMe
N
O
O-tBu

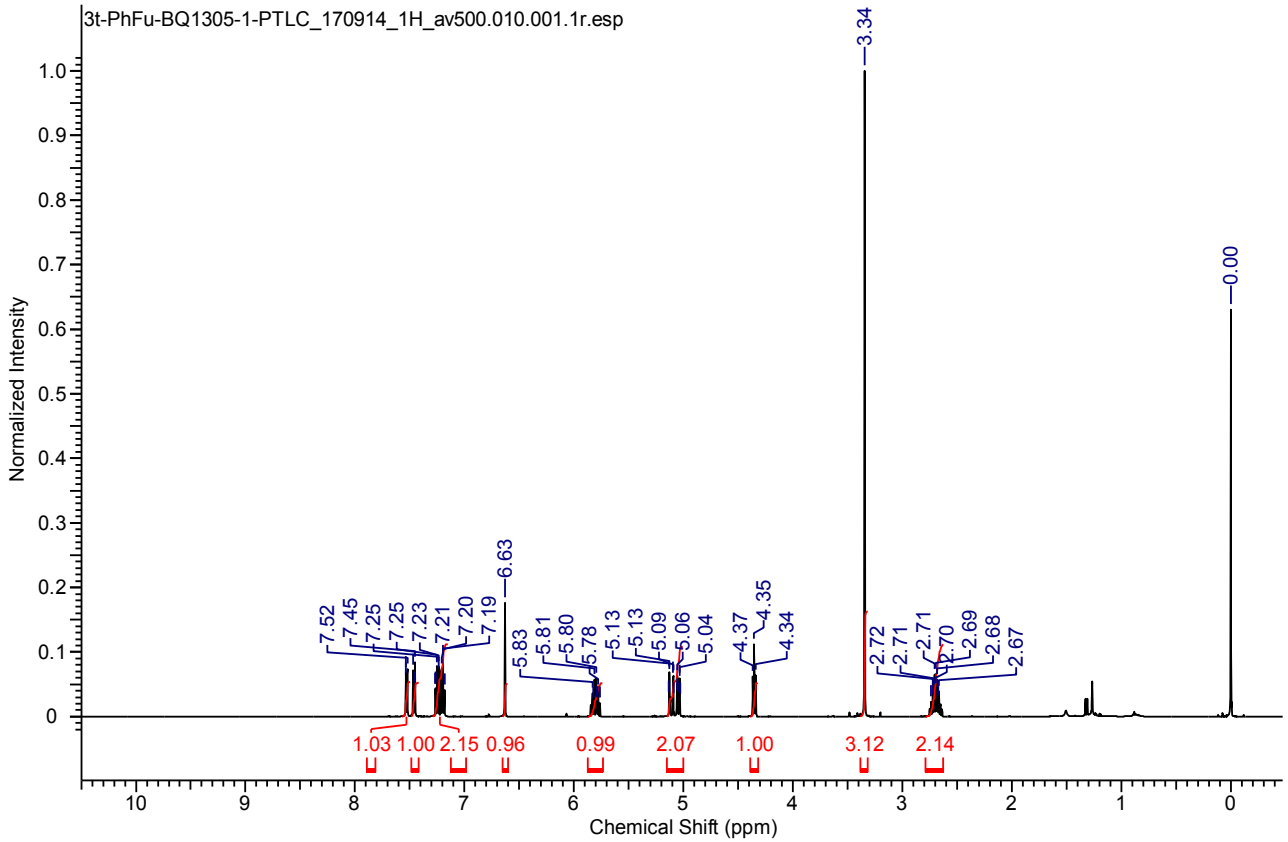
3s

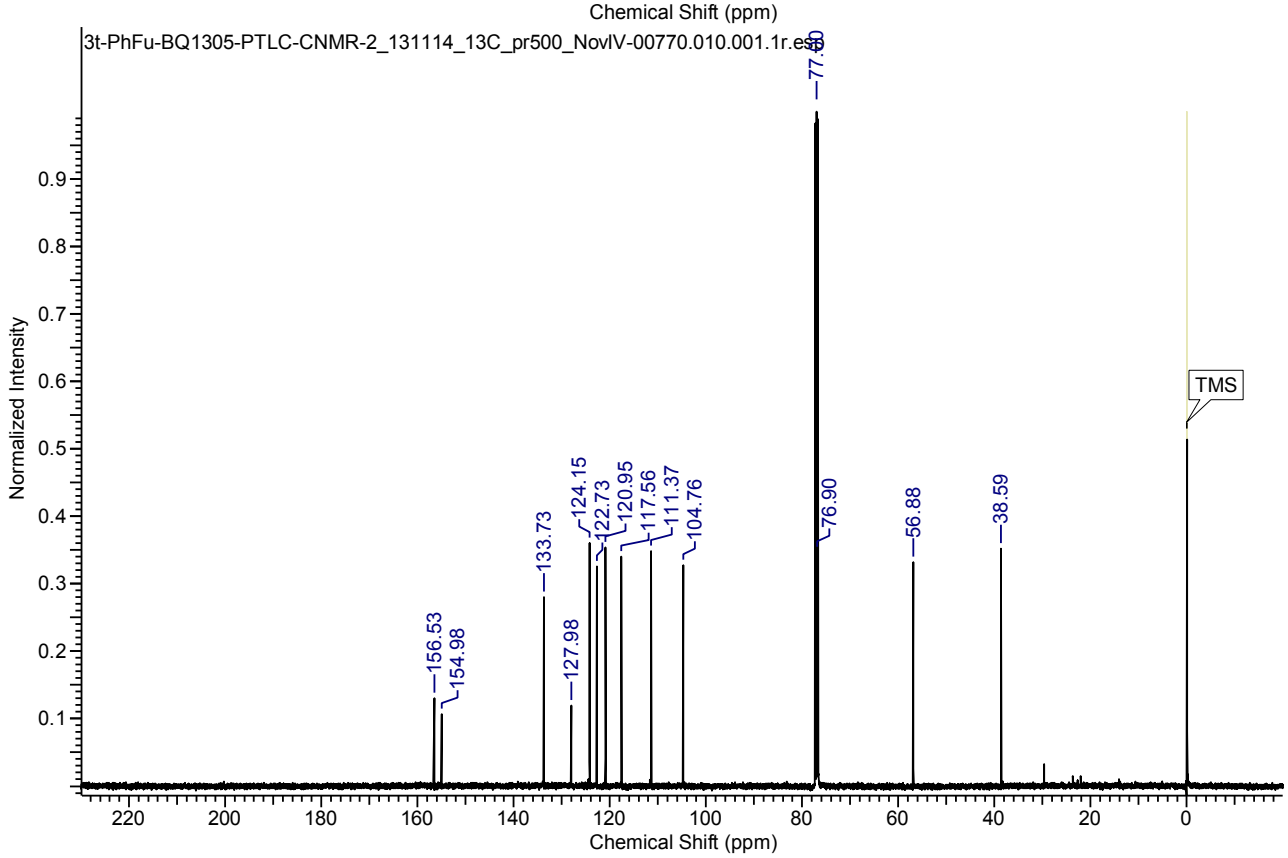

3s-Boc-BQ1375-2-PTLC_241014_1H_av600_OctIV-00977.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
8.14
7.71
7.70
7.51
7.33
7.32
7.32
7.30
7.24
7.23
7.22
5.82
5.81
5.79
5.10
5.10
5.08
5.07
5.05
5.05
5.03
4.48
4.47
4.46
3.29
2.77
2.76
2.75
2.63
2.62
2.62
2.61
1.67
0.00
0.89 0.93 0.90 1.06 1.13 0.98 2.02 1.00 2.96 1.05 1.05 9.72

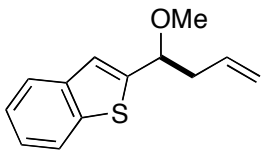

3s-Boc-BQ1375-PTLC-CNMR_131114_13C_av600_NovIV-00400.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
149.69
134.80
128.83
124.45
122.53
120.72
116.97
115.31
83.70
77.13
77.00
56.44
40.43
28.20


OMe
O

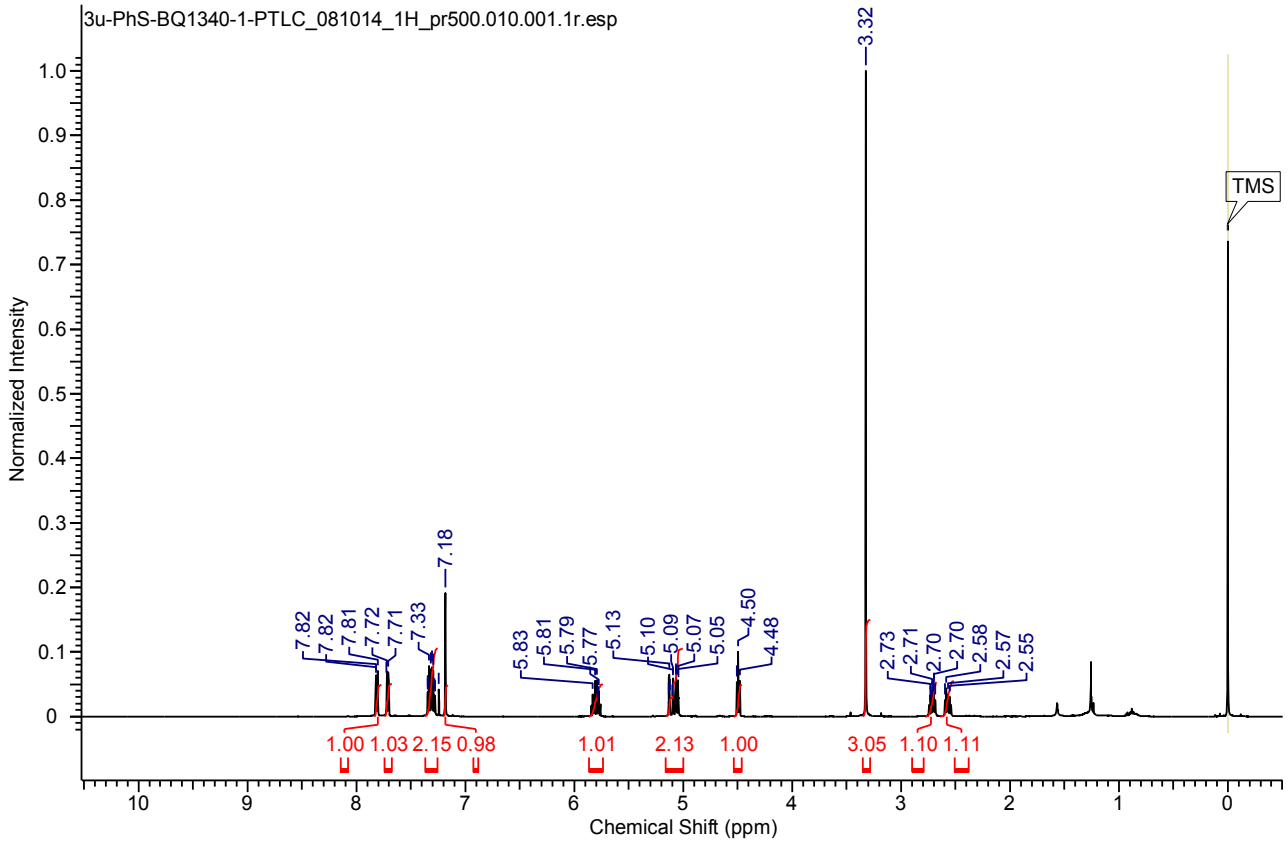
3t

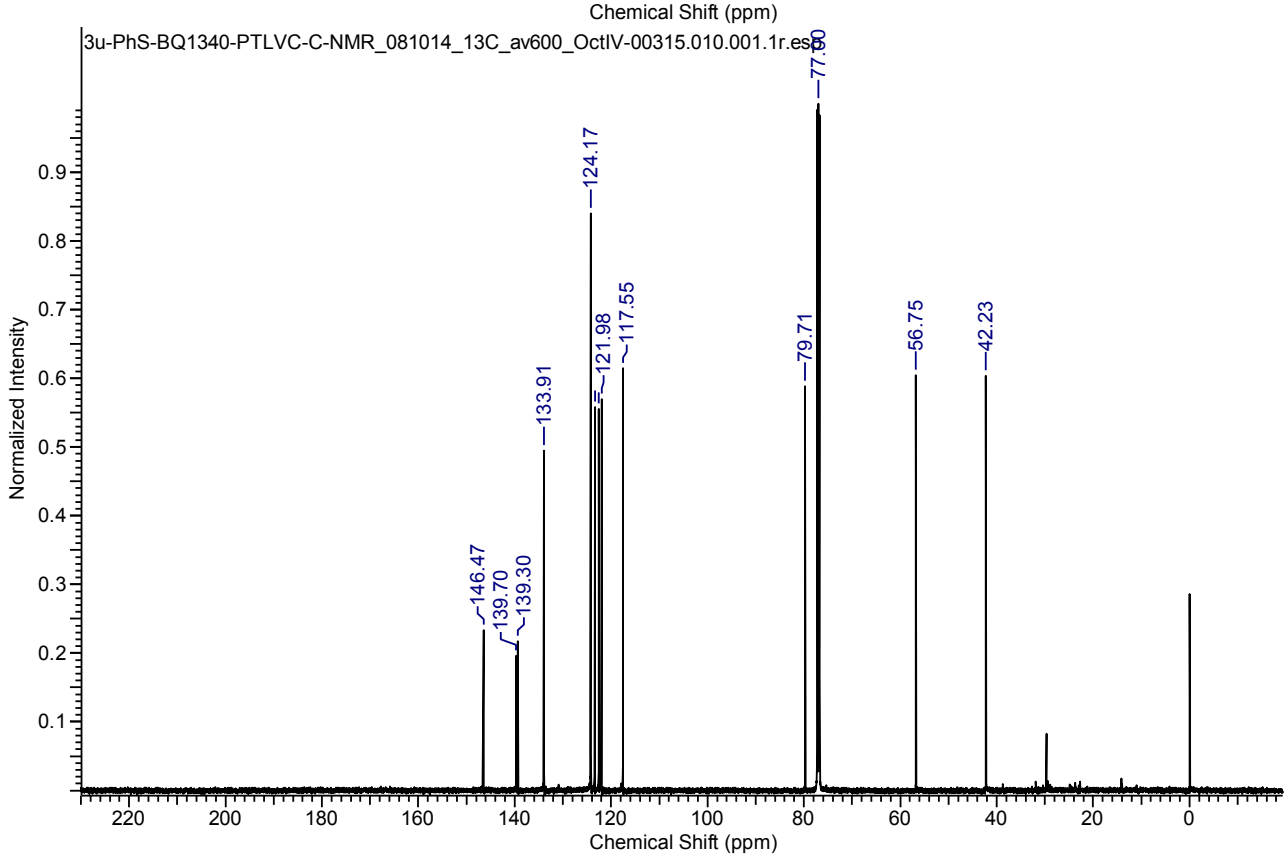

3t-PhFu-BQ1305-1-PTLC_170914_1H_av500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.34
0.00
6.63
7.52
7.45
7.25
7.25
7.23
7.21
7.20
7.19
5.83
5.81
5.80
5.78
5.13
5.13
5.09
5.06
5.04
4.37
4.35
4.34
2.72
2.71
2.71
2.70
2.69
2.68
2.67
1.03 1.00 2.15 0.96 0.99 2.07 1.00 3.12 2.14

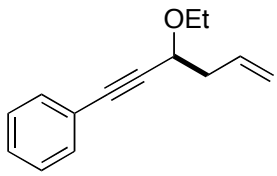

3t-PhFu-BQ1305-PTLC-CNMR-2_131114_13C_pr500_NovIV-00770.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.40
TMS
156.53
154.98
133.73
127.98
124.15
122.73
120.95
117.56
111.37
104.76
76.90
56.88
38.59


OMe
S

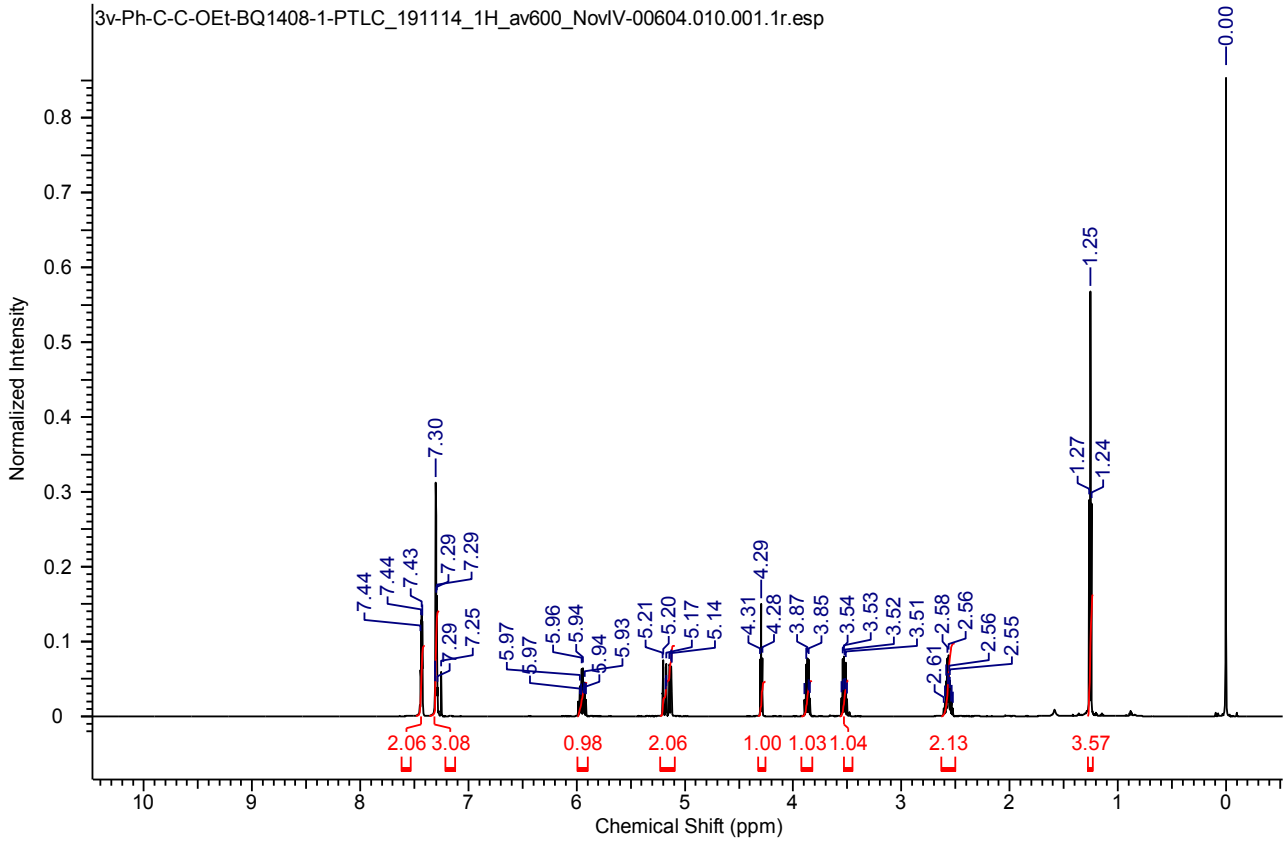
3u

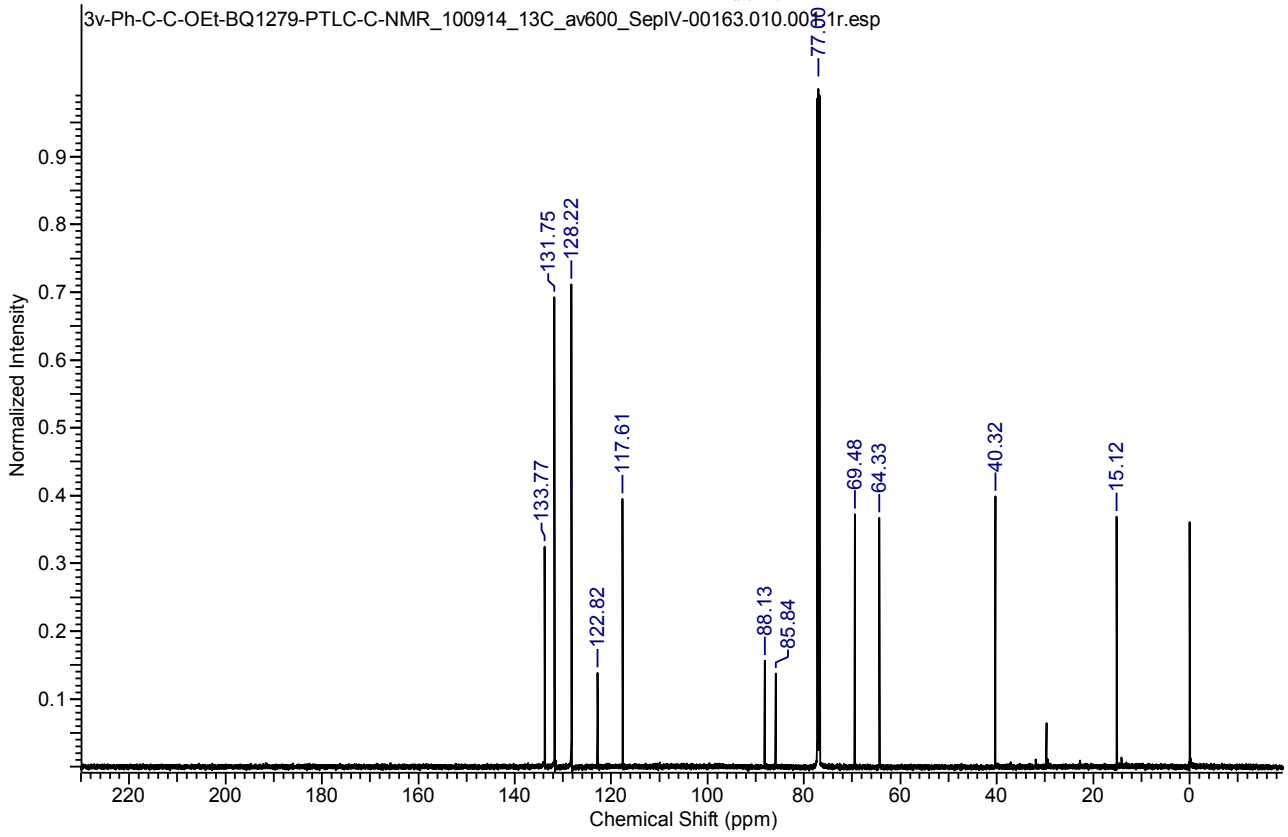

3u-PhS-BQ1340-1-PTLC_081014_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
TMS
3.32
7.18
7.82
7.82
7.81
7.72
7.71
7.33
5.83
5.81
5.79
5.77
5.13
5.10
5.09
5.07
5.05
4.50
4.48
2.73
2.71
2.70
2.70
2.58
2.57
2.55
1.00 1.03 2.15 0.98
1.01
2.13
1.00
3.05
1.10 1.11

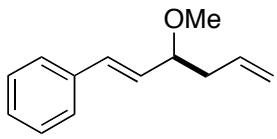

3u-PhS-BQ1340-PTLVC-C-NMR_081014_13C_av600_OctIV-00315.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
124.17
121.98
117.55
133.91
146.47
139.70
139.30
79.71
56.75
42.23


OEt

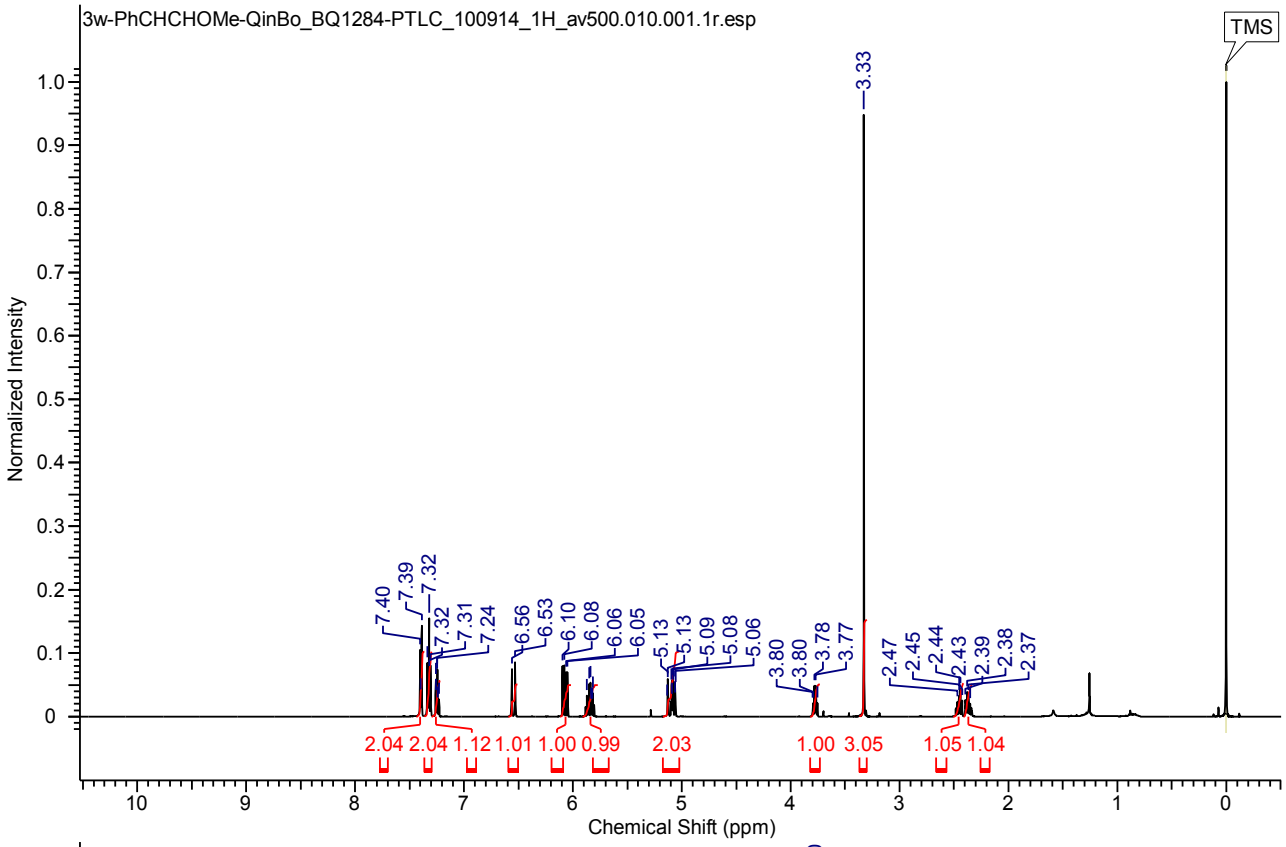
3v

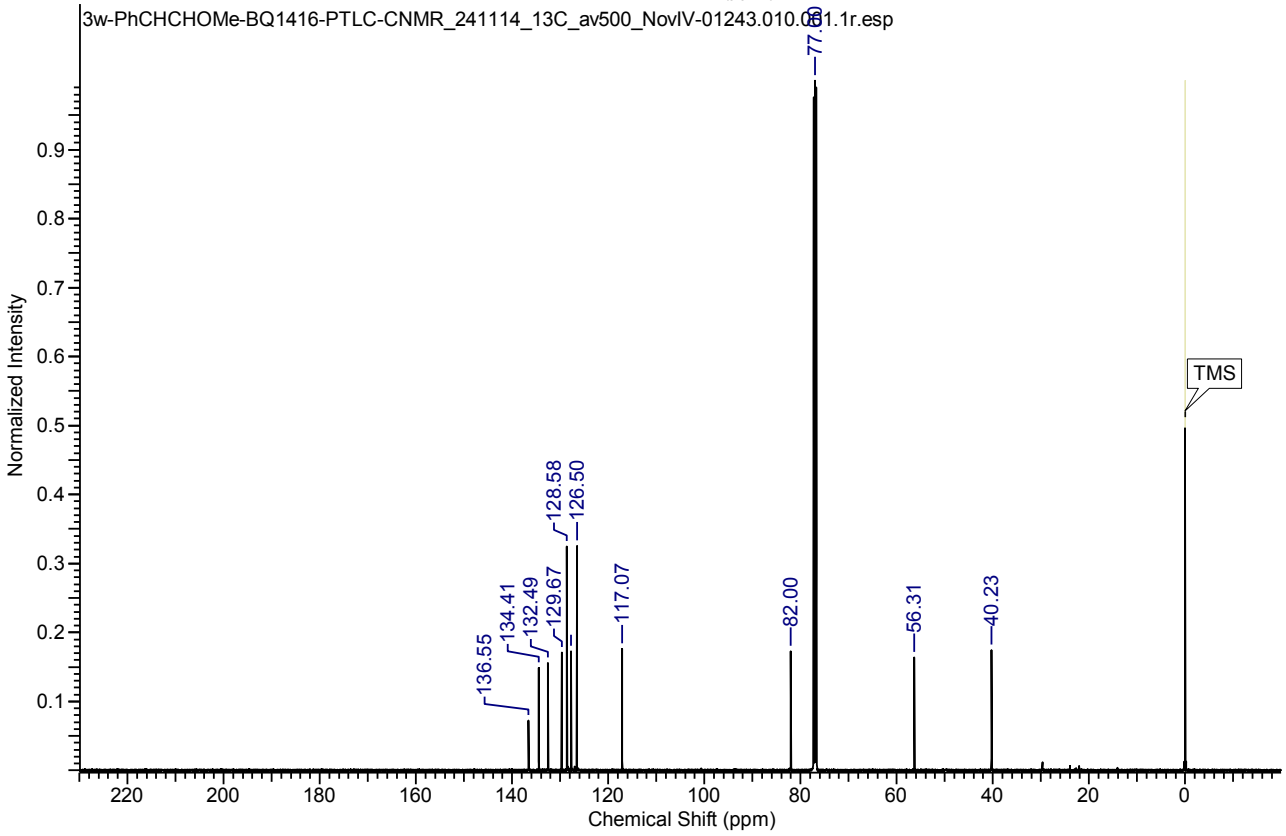

3v-Ph-C-C-OEt-BQ1408-1-PTLC_191114_1H_av600_NovIV-00604.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.44
7.44
7.43
7.30
7.29
7.29
7.29
7.25
5.97
5.97
5.96
5.94
5.94
5.93
5.21
5.20
5.17
5.14
4.31
4.29
4.28
3.87
3.85
3.54
3.53
3.52
3.51
2.61
2.58
2.56
2.56
2.55
1.27
1.25
1.24
0.00
2.06
3.08
0.98
2.06
1.00
1.03
1.04
2.13
3.57

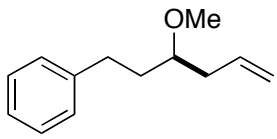

3v-Ph-C-C-OEt-BQ1279-PTLC-C-NMR_100914_13C_av600_SepIV-00163.010.001r.esp
Normalized Intensity
Chemical Shift (ppm)
133.77
131.75
128.22
122.82
117.61
88.13
85.84
77.00
69.48
64.33
40.32
15.12


OMe

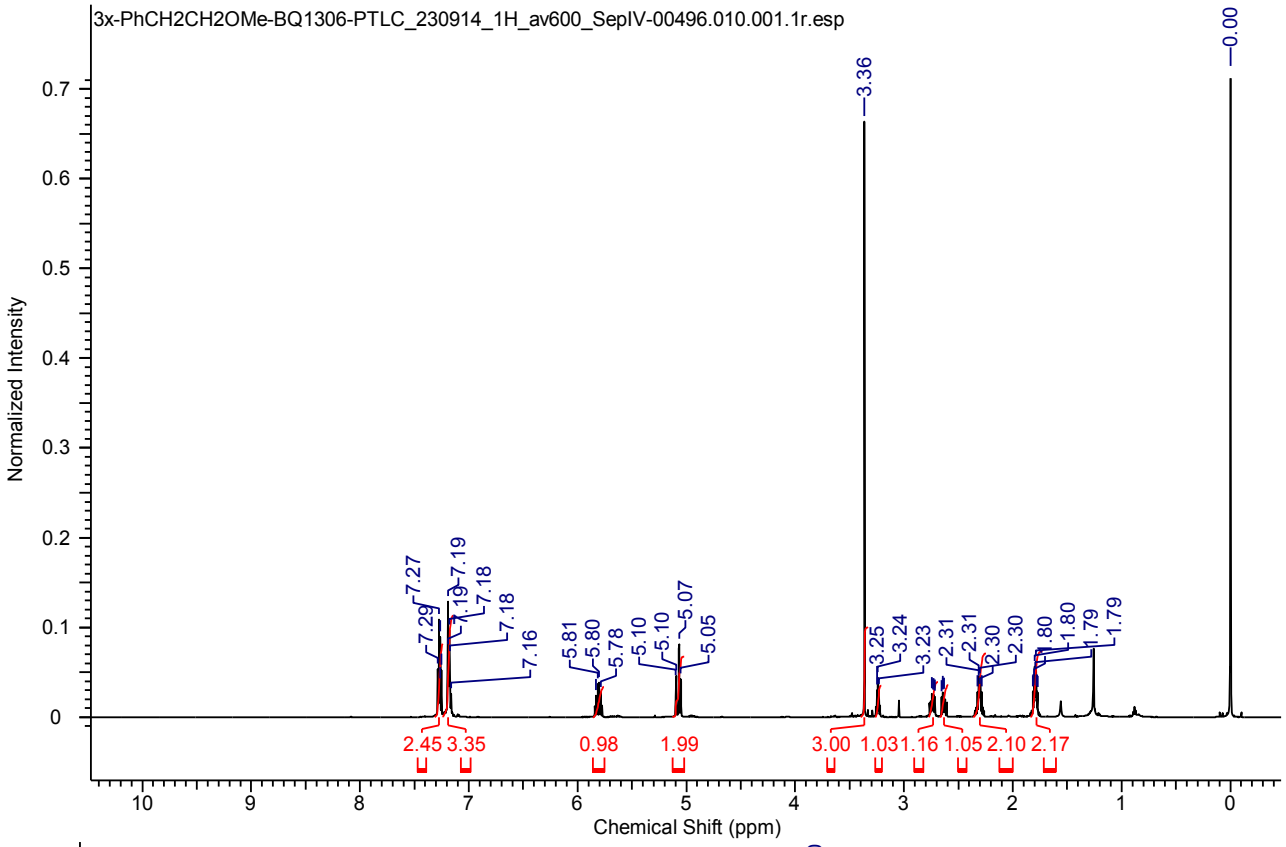
3w

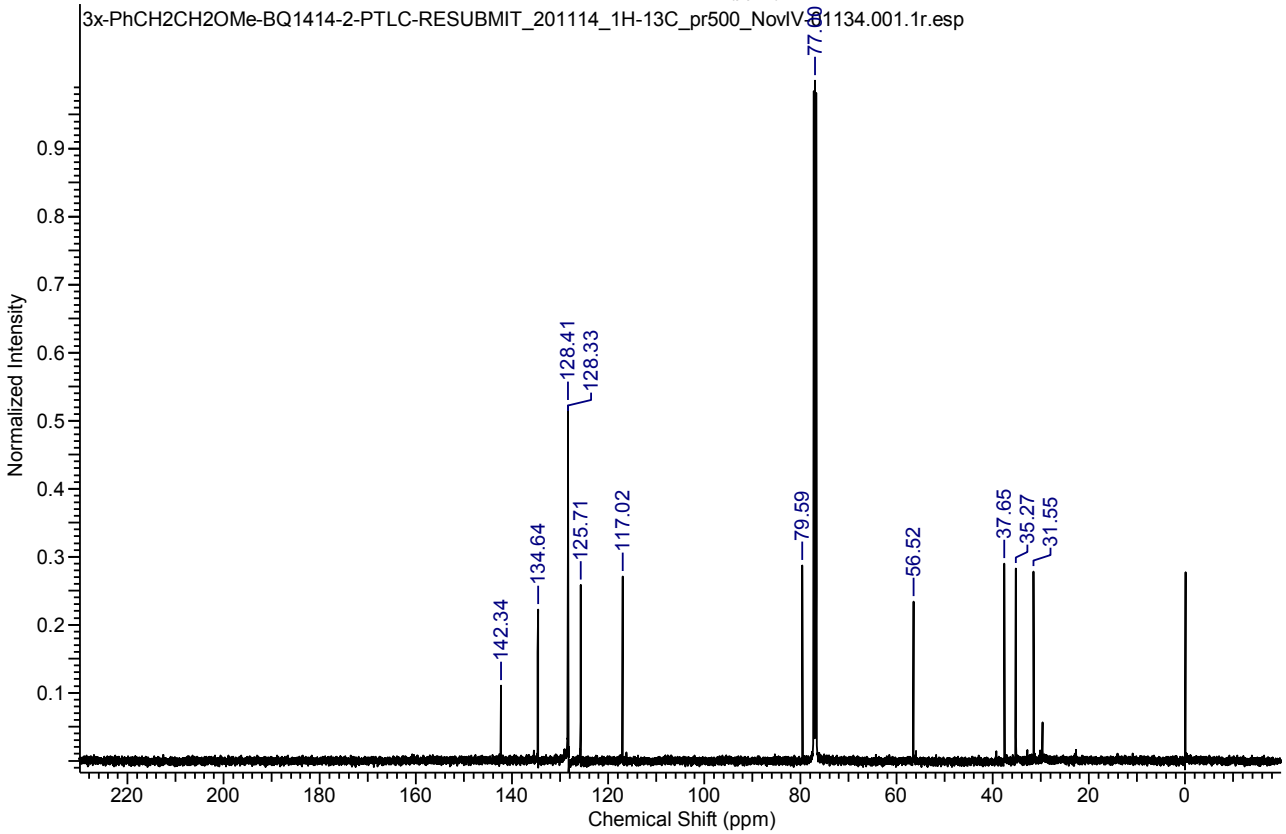

3w-PhCHCHOMe-QinBo_BQ1284-PTLC_100914_1H_av500.010.001.1r.esp
TMS
3.33
7.40
7.39
7.32
7.32
7.31
7.24
6.56
6.53
6.10
6.08
6.06
6.05
5.13
5.13
5.09
5.08
5.06
3.80
3.80
3.78
3.77
2.47
2.45
2.44
2.43
2.39
2.38
2.37
2.04 2.04 1.12 1.01 1.00 0.99 2.03 1.00 3.05 1.05 1.04
Normalized Intensity
Chemical Shift (ppm)

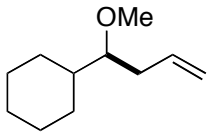

3w-PhCHCHOMe-BQ1416-PTLC-CNMR_241114_13C_av500_NovIV-01243.010.001.1r.esp
77.00
TMS
128.58
126.50
136.55
134.41
132.49
129.67
117.07
82.00
56.31
40.23
Normalized Intensity
Chemical Shift (ppm)


OMe

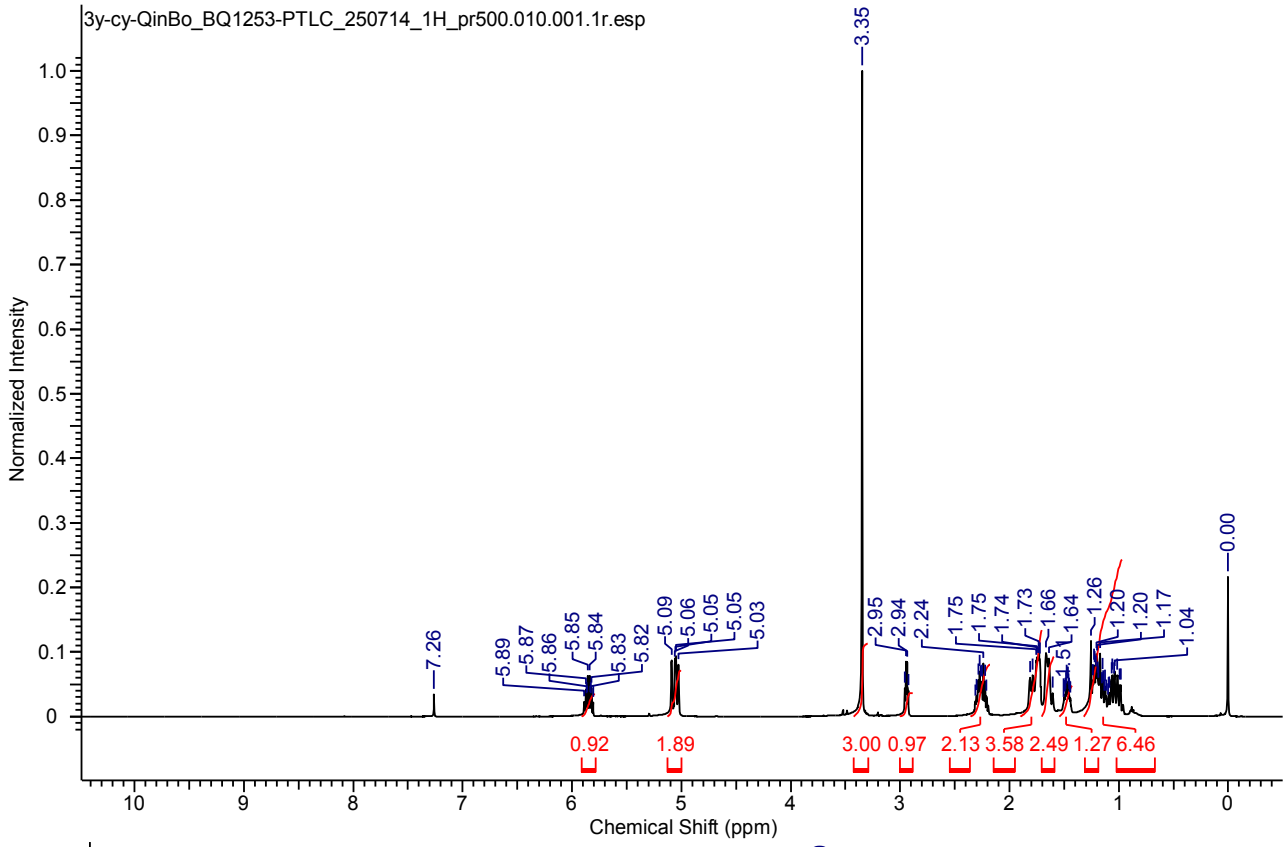
3x

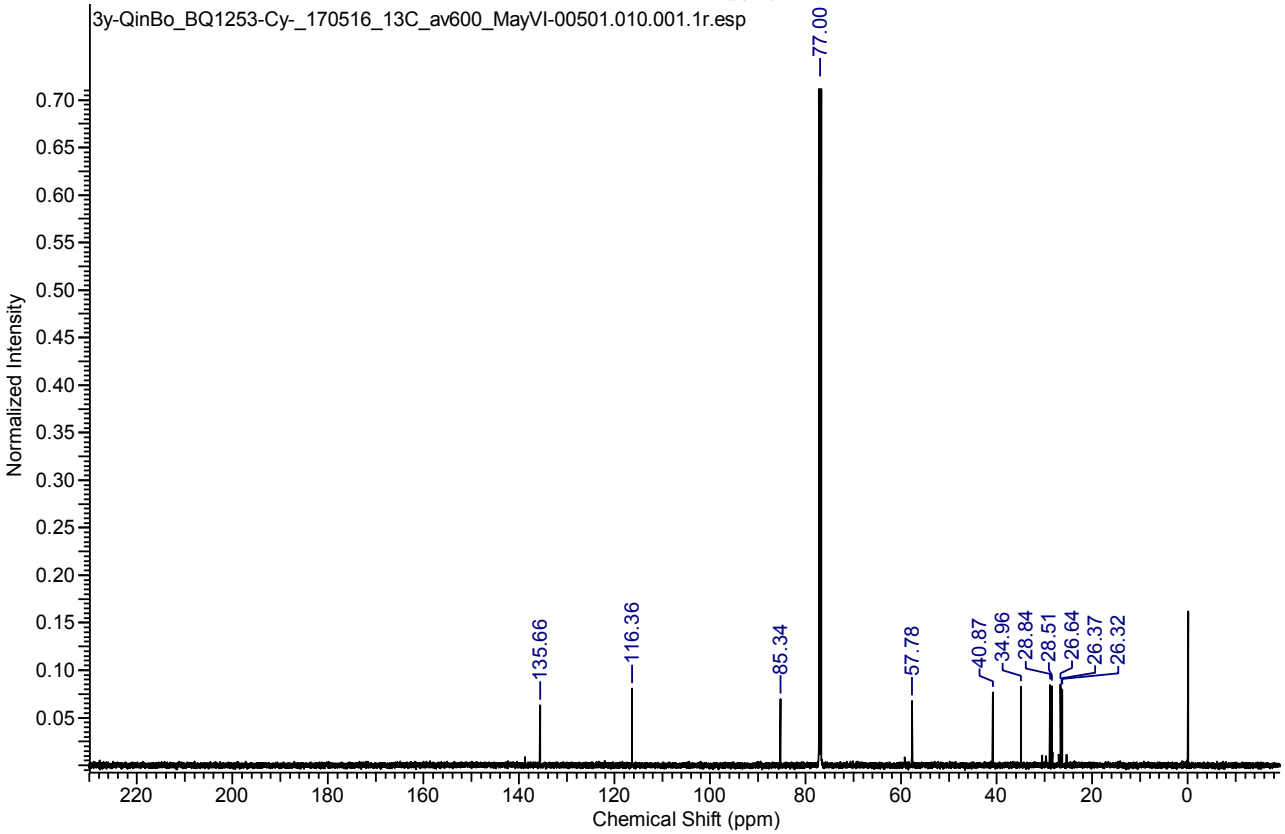

3x-PhCH2CH2OMe-BQ1306-PTLC_230914_1H_av600_SepIV-00496.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
3.36
7.27
7.29
7.19
7.19
7.18
7.18
7.16
5.81
5.80
5.78
5.10
5.10
5.07
5.05
3.25
3.24
3.23
2.31
2.31
2.30
2.30
1.80
1.80
1.79
1.79
2.45
3.35
0.98
1.99
3.00
1.03
1.16
1.05
2.10
2.17

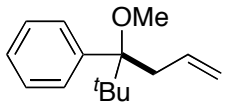

3x-PhCH2CH2OMe-BQ1414-2-PTLC-RESUBMIT_201114_1H-13C_pr500_NovIV-01134.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
128.41
128.33
142.34
134.64
125.71
117.02
79.59
56.52
37.65
35.27
31.55


OMe

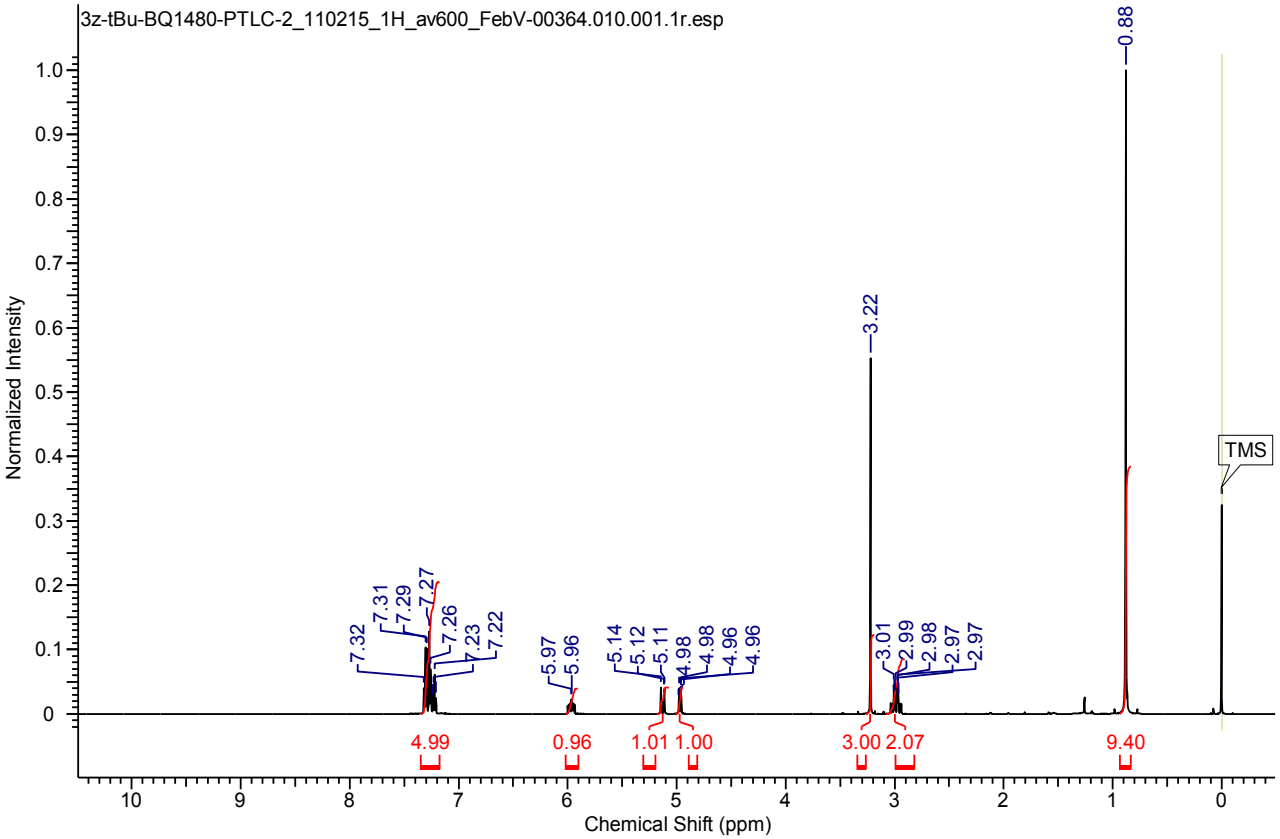
3y

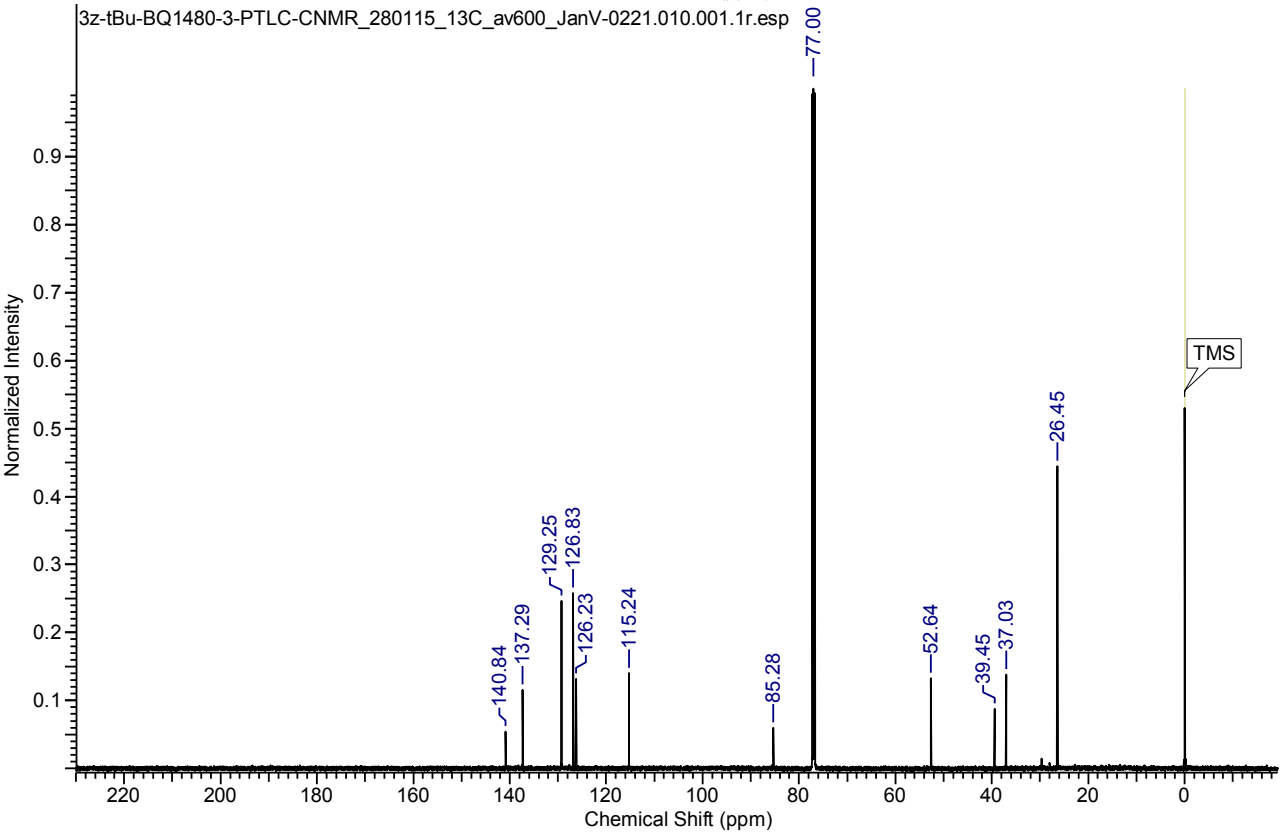

3y-cy-QinBo_BQ1253-PTLC_250714_1H_pr500.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
3.35
7.26
0.00
0.92
1.89
3.00
0.97
2.13
3.58
2.49
1.27
6.46

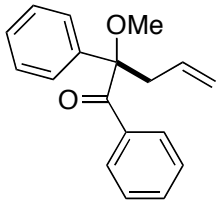

3y-QinBo_BQ1253-Cy-_170516_13C_av600_MayVI-00501.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
135.66
116.36
85.34
57.78
40.87
34.96
28.84
28.51
26.64
26.37
26.32


OMe
tBu

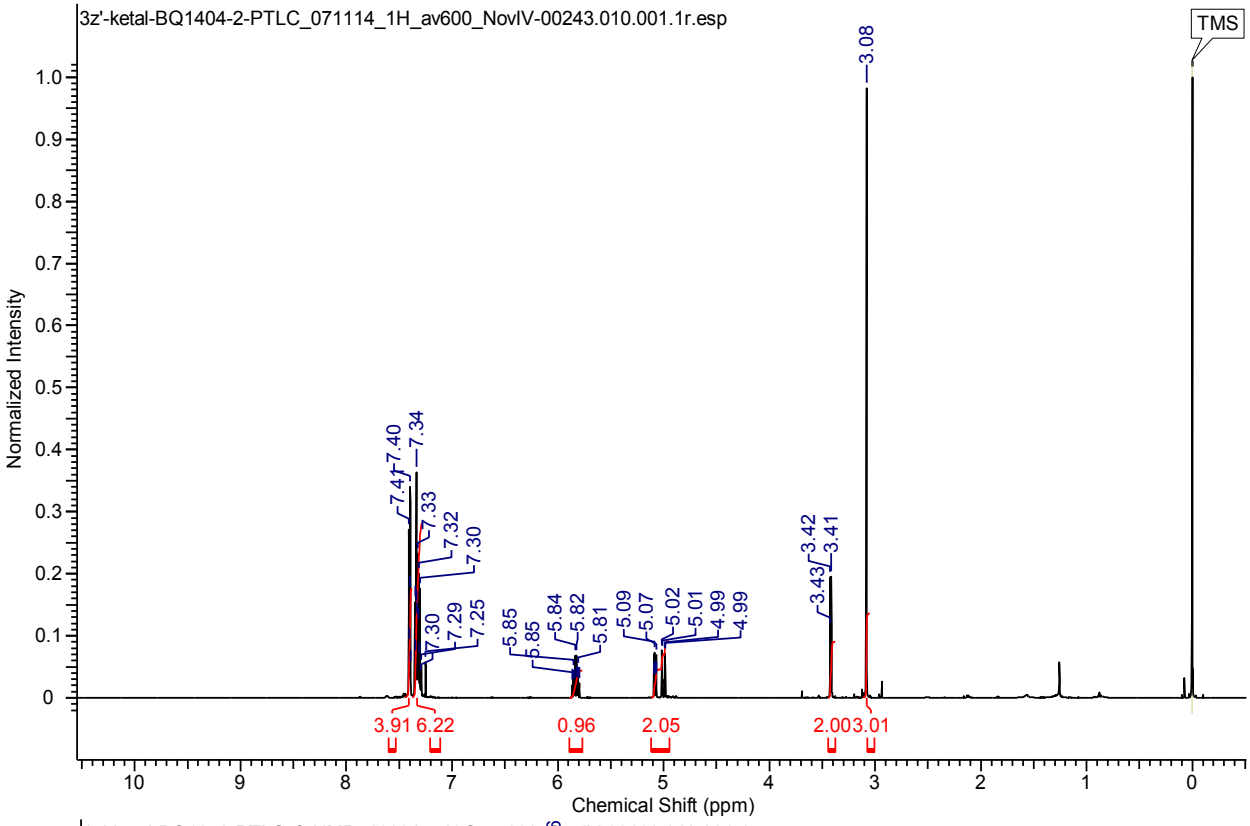
3z

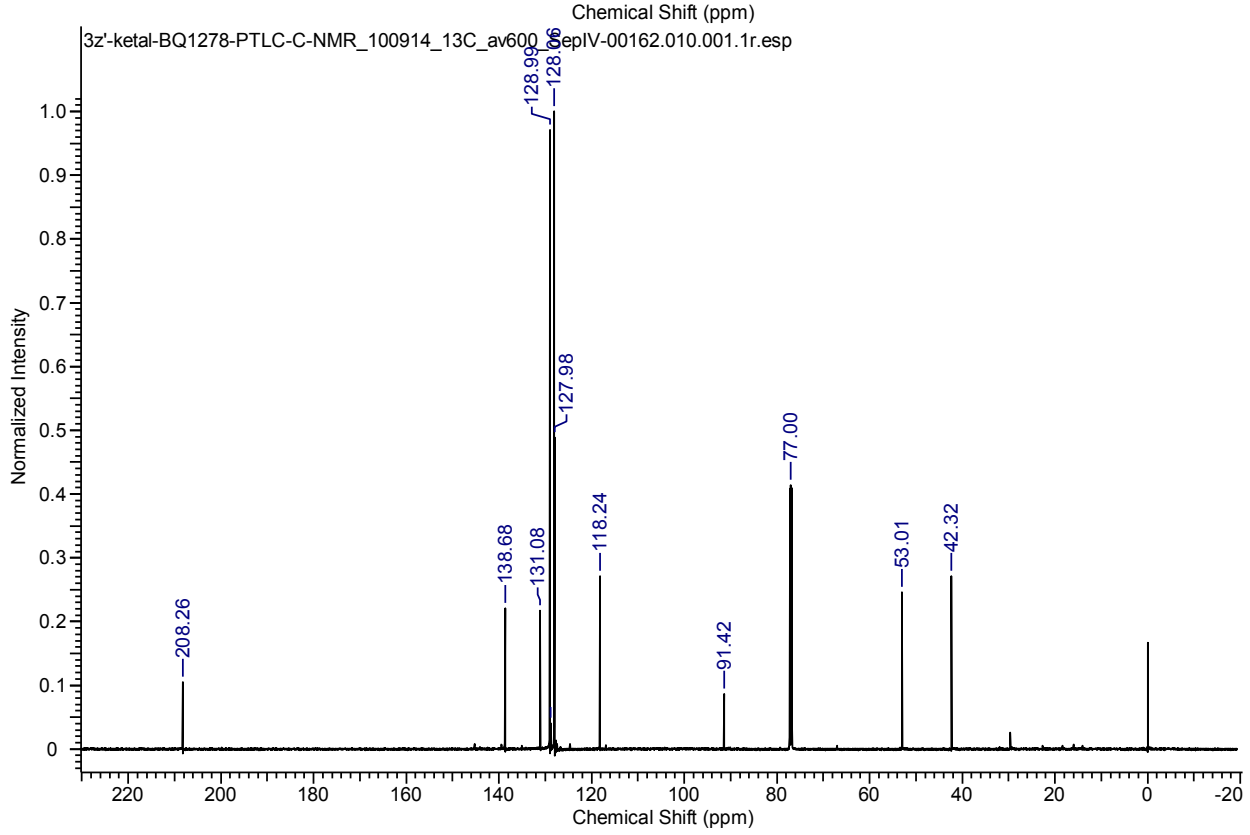

3z-tBu-BQ1480-PTLC-2_110215_1H_av600_FebV-00364.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.88
3.22
TMS
7.32
7.31
7.29
7.27
7.26
7.23
7.22
5.97
5.96
5.14
5.12
5.11
4.98
4.98
4.96
4.96
3.01
2.99
2.98
2.97
2.97
4.99
0.96
1.01
1.00
3.00
2.07
9.40

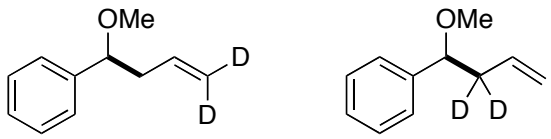

3z-tBu-BQ1480-3-PTLC-CNMR_280115_13C_av600_JanV-0221.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
TMS
26.45
140.84
137.29
129.25
126.83
126.23
115.24
85.28
52.64
39.45
37.03


OMe
O

3z'

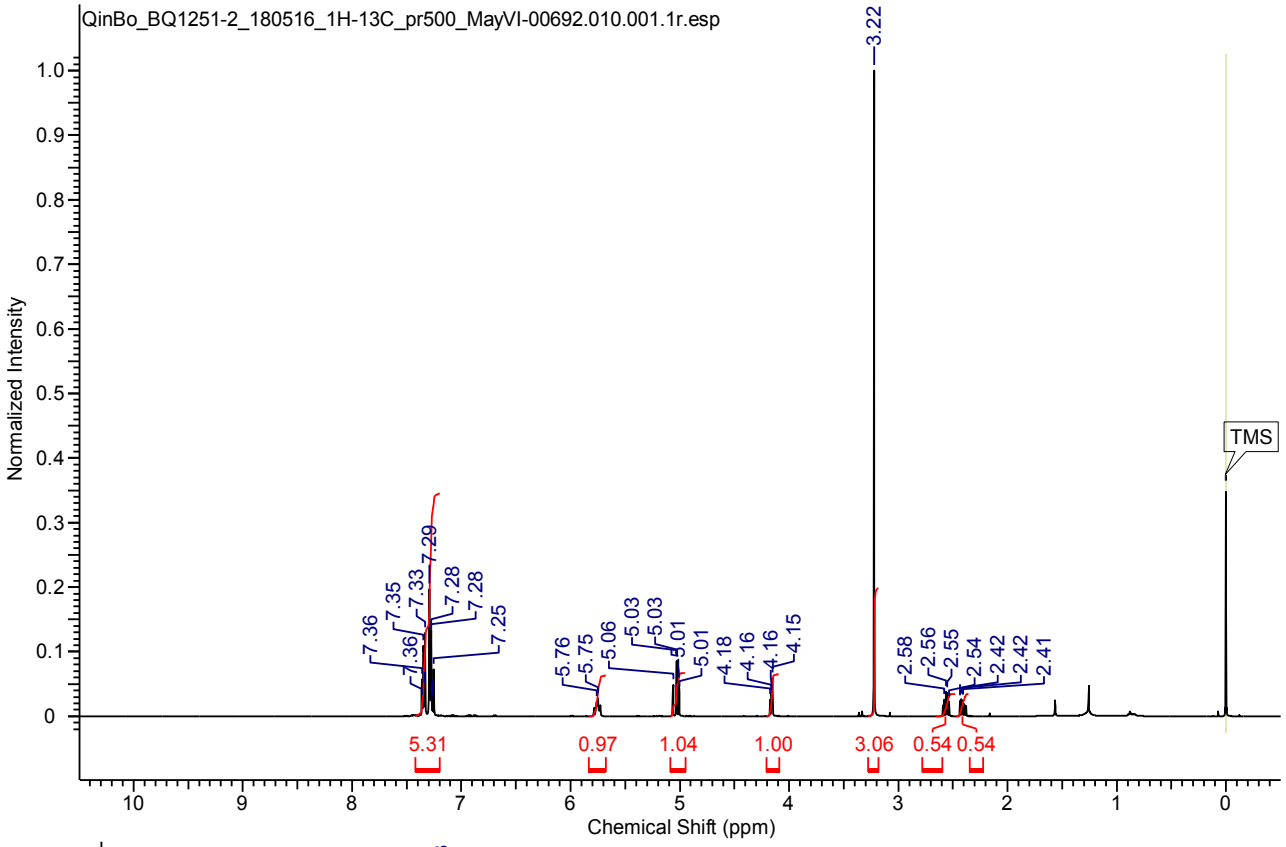

3z'-ketal-BQ1404-2-PTLC_071114_1H_av600_NovIV-00243.010.001.1r.esp
TMS
3.08
7.40
7.34
7.41
7.33
7.32
7.30
7.30
7.29
7.25
5.85
5.85
5.84
5.82
5.81
5.09
5.07
5.02
5.01
4.99
4.99
3.42
3.41
3.43
3.91
6.22
0.96
2.05
2.00
3.01
Normalized Intensity
Chemical Shift (ppm)

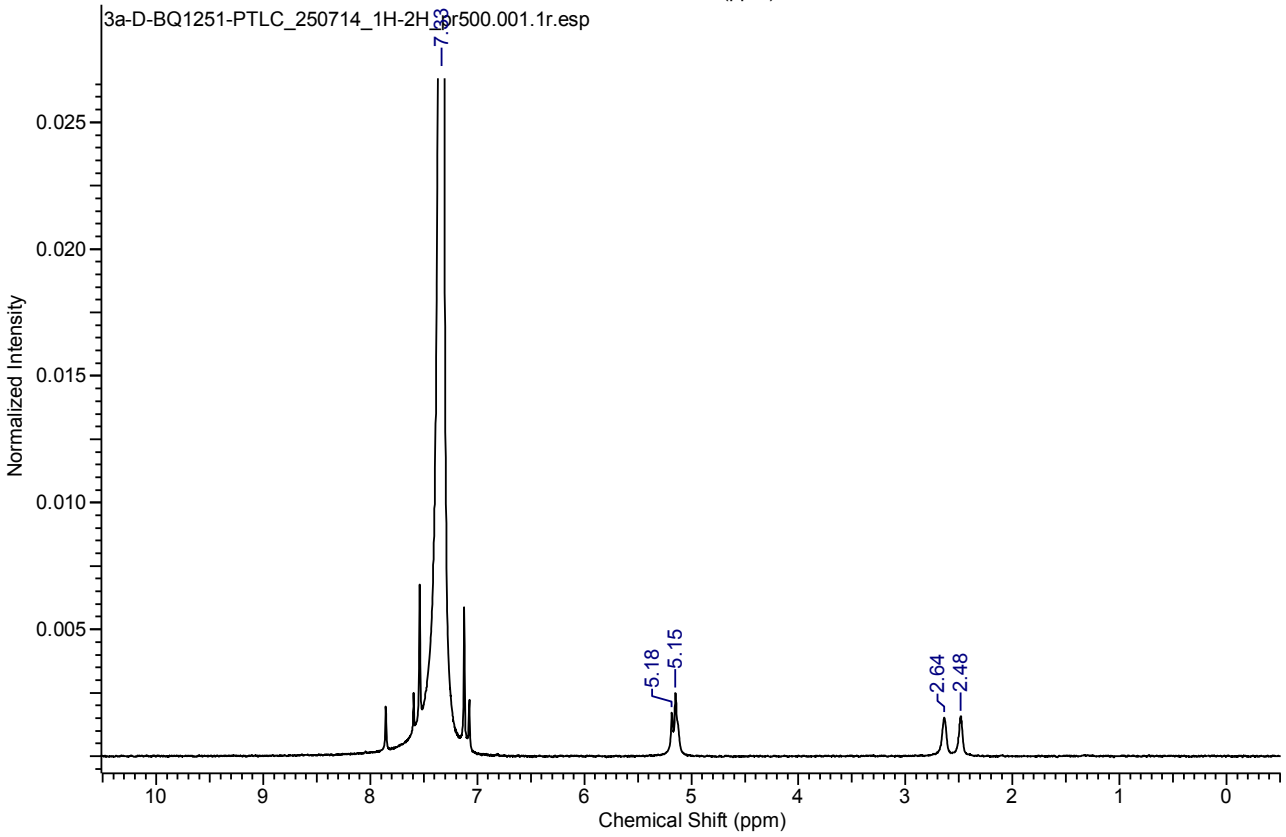

3z'-ketal-BQ1278-PTLC-C-NMR_100914_13C_av600_SepIV-00162.010.001.1r.esp
128.99
128.66
127.98
208.26
138.68
131.08
118.24
91.42
77.00
53.01
42.32
Normalized Intensity
Chemical Shift (ppm)

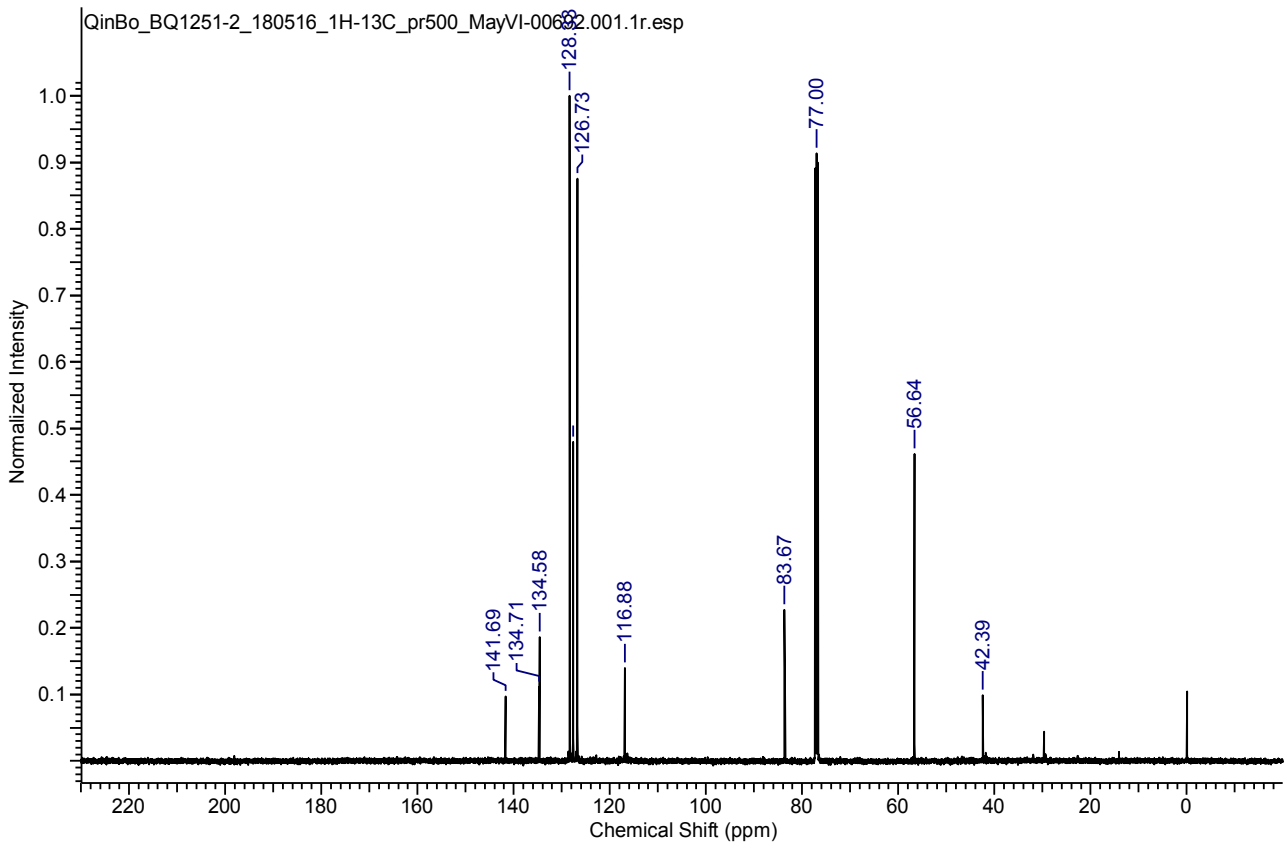


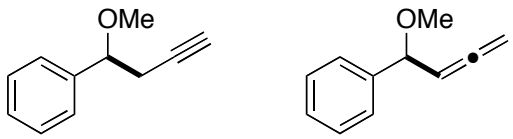
3a–[d_2] **3'a**–[d_2]

3a–[d_2]:**3'a**–[d_2] = 1:1



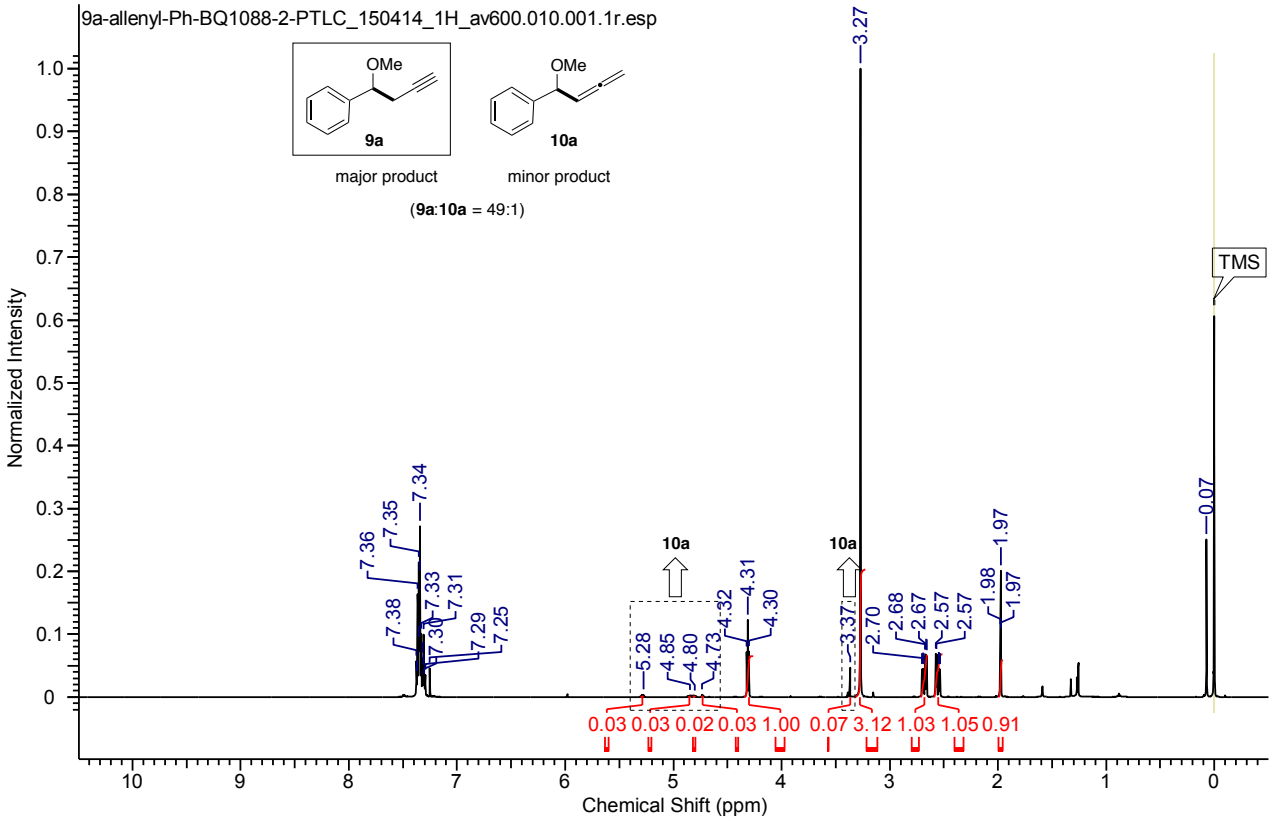


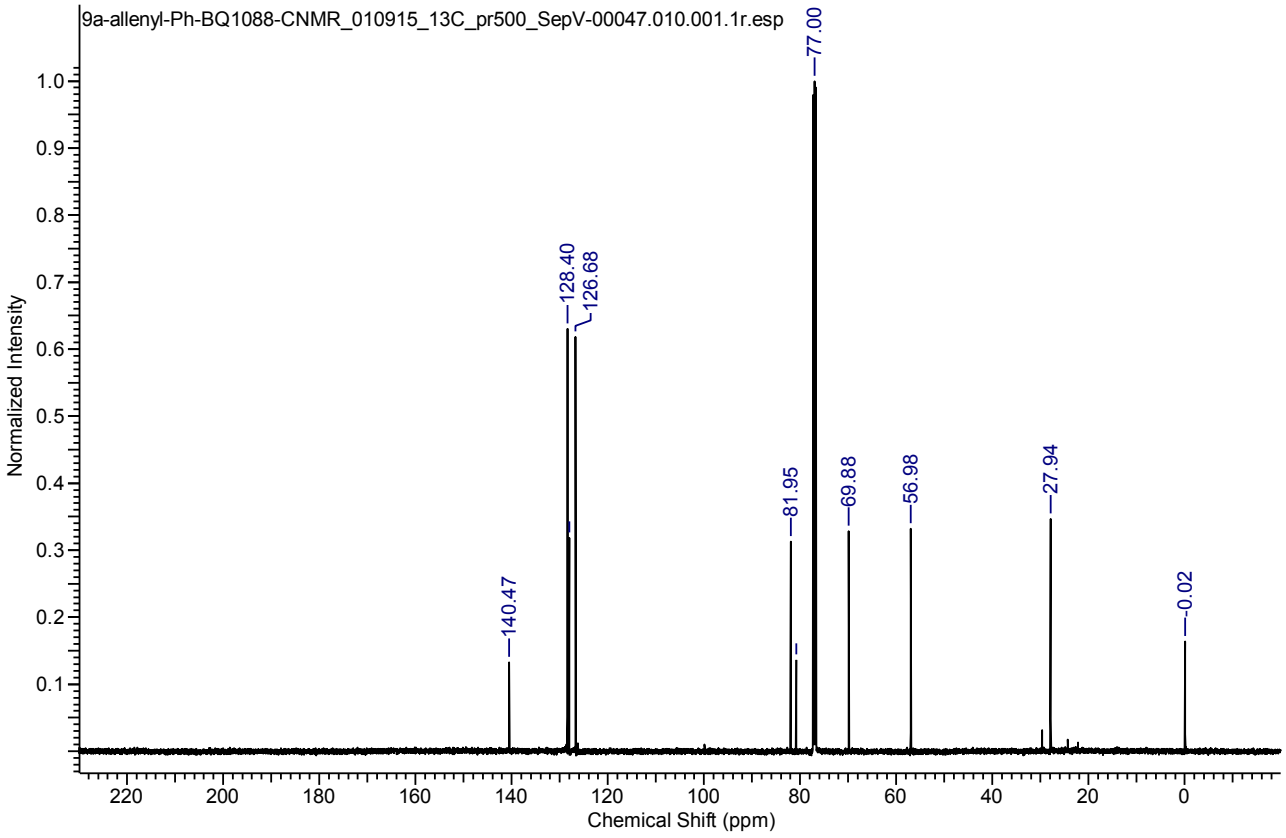

QinBo_BQ1251-2_180516_1H-13C_pr500_MayVI-00682.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
141.69
134.71
134.58
128.88
126.73
116.88
83.67
77.00
56.64
42.39

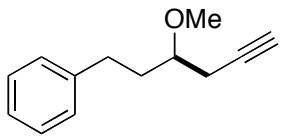


15a **16a**

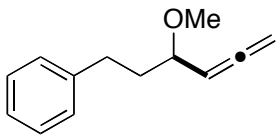
15a:**16a** = 49:1





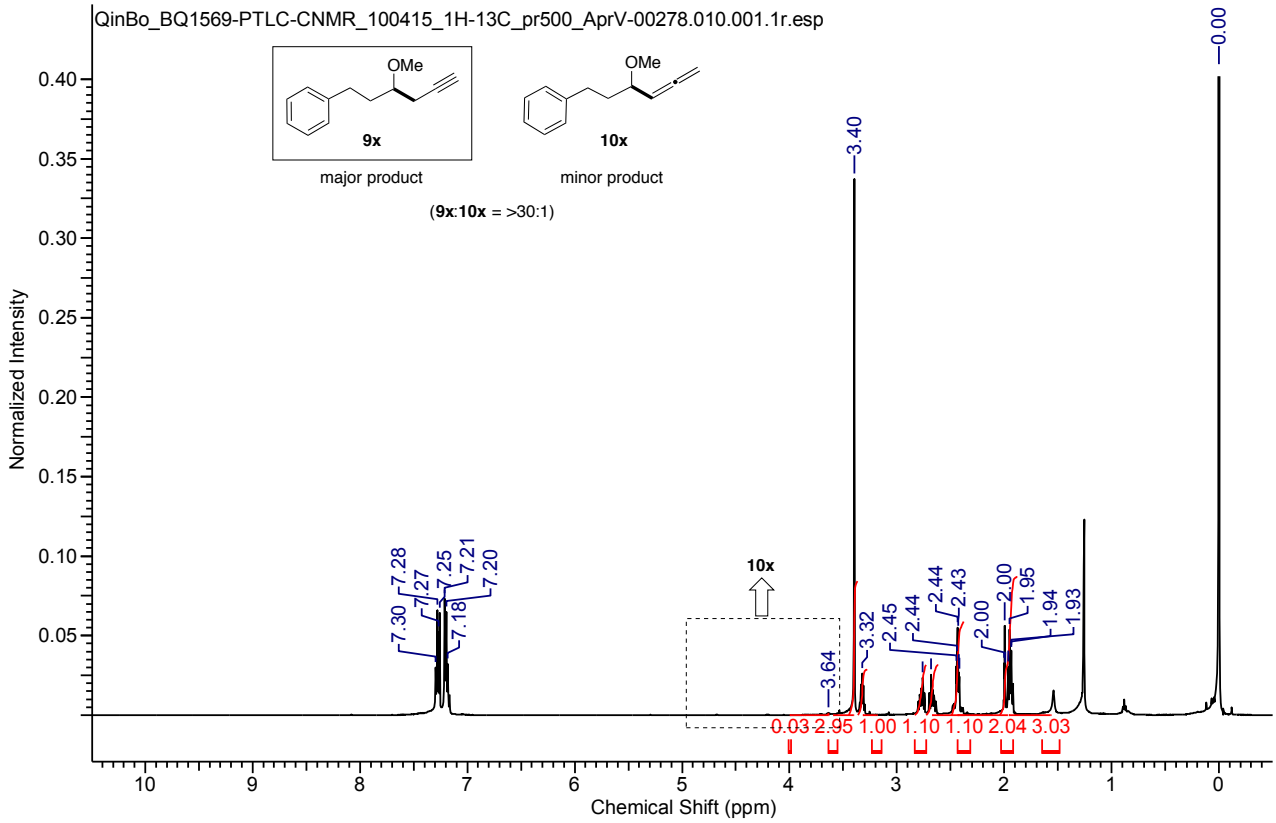


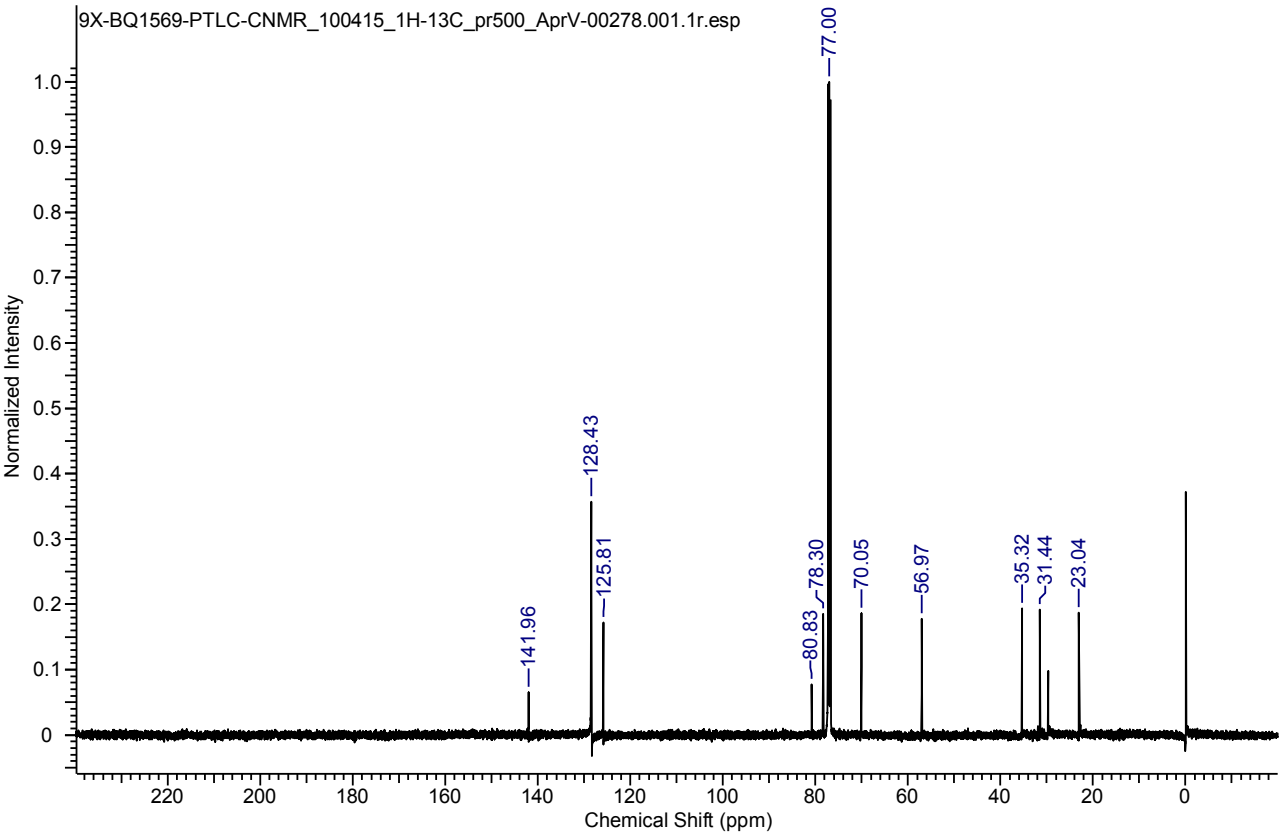
15x

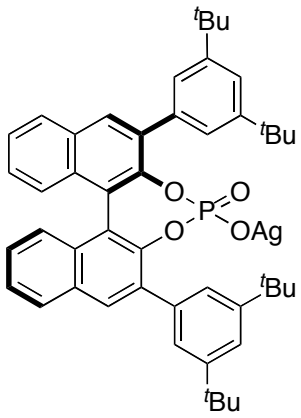


16x

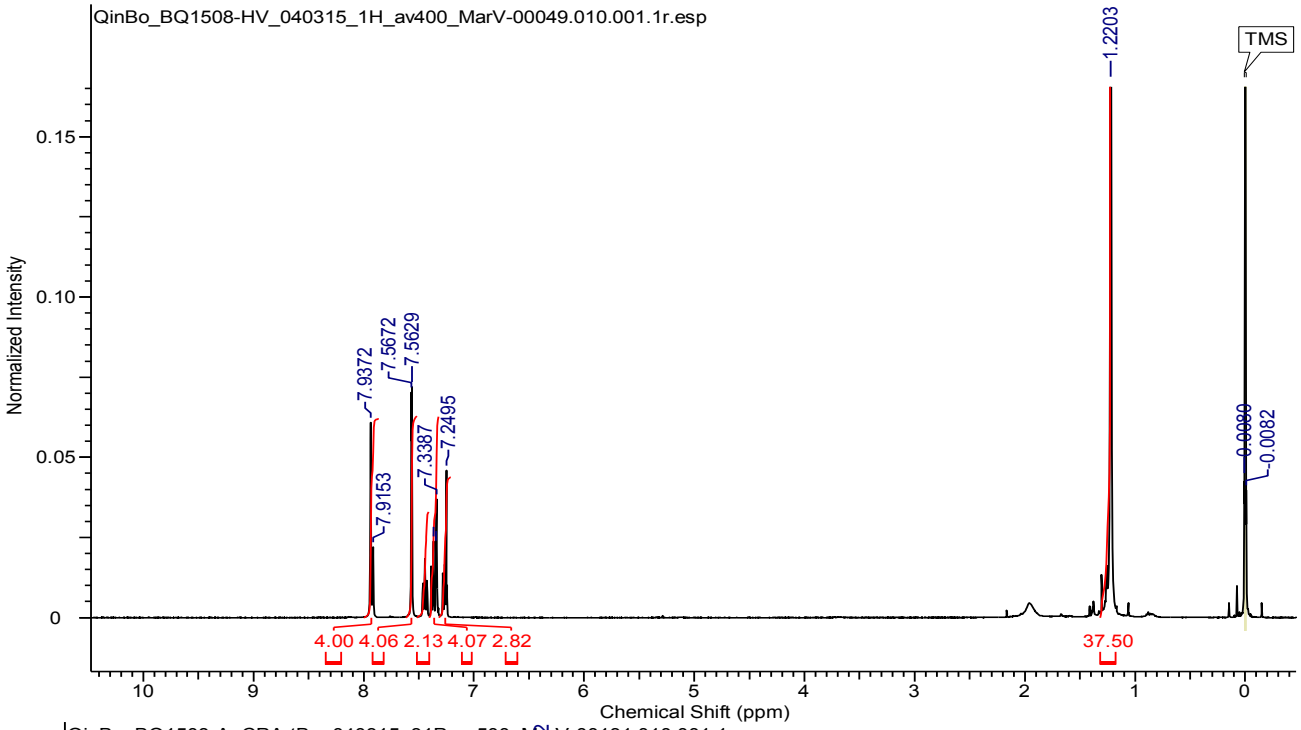
15x:**16x** = >30:1

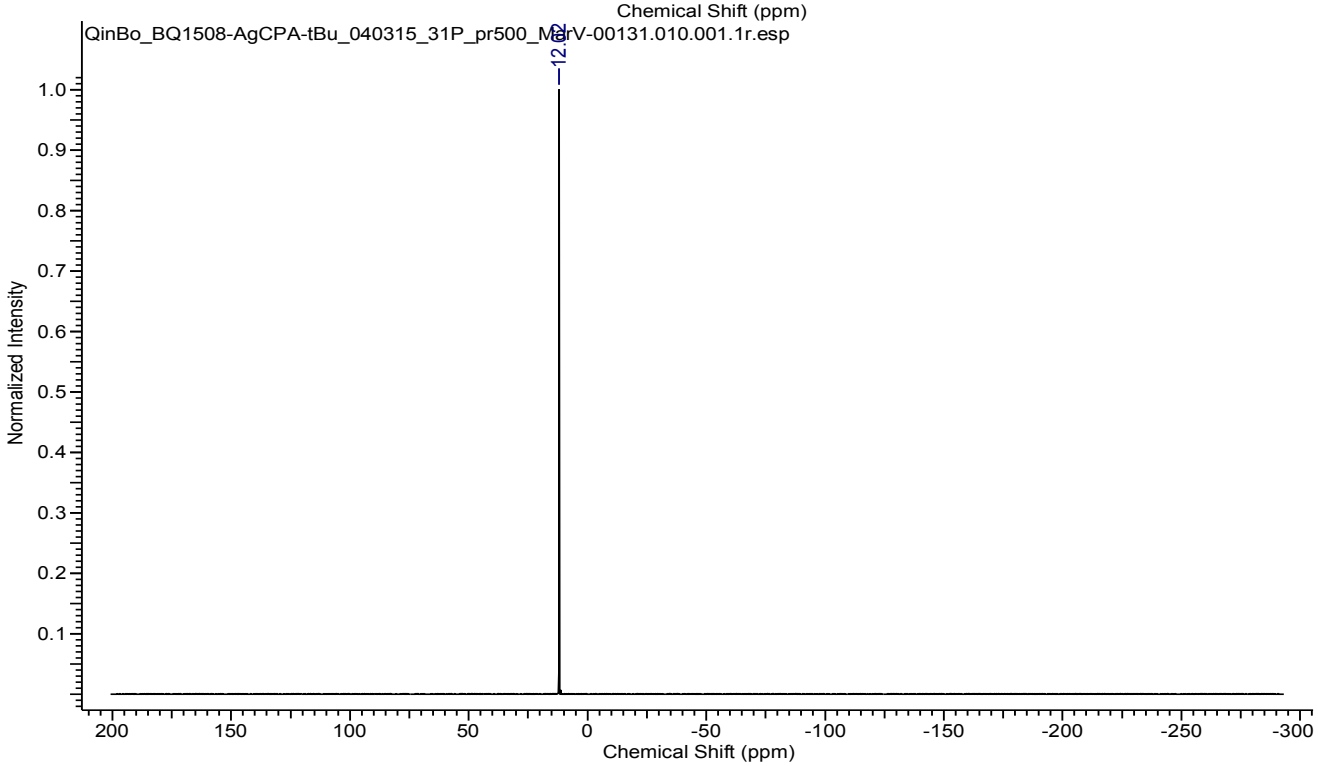


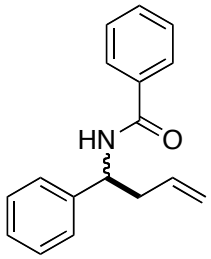



tBu
tBu
O
P
O
O
OAg
tBu
tBu

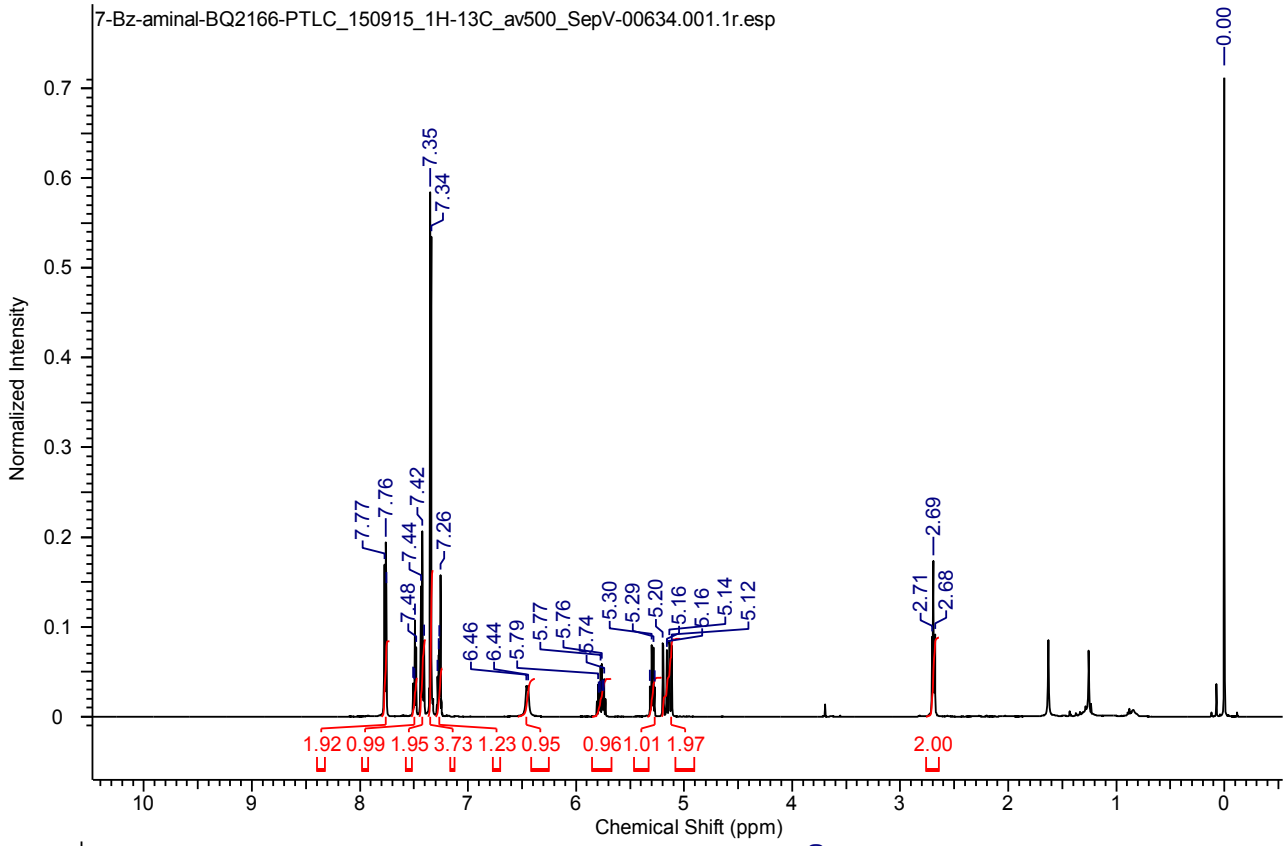
(*R*)-**17**

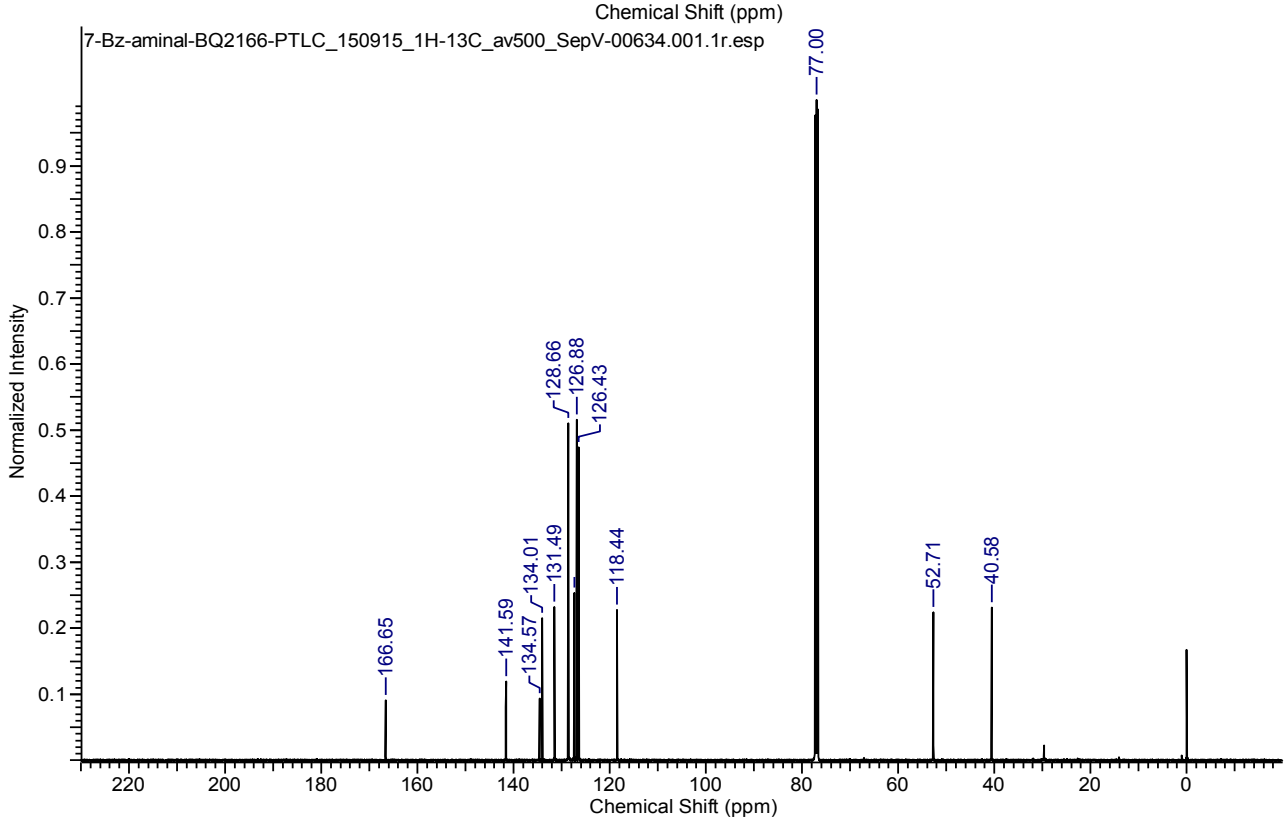

QinBo_BQ1508-HV_040315_1H_av400_MarV-00049.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
7.9372
7.5672
7.5629
7.9153
7.3387
7.2495
1.2203
TMS
0.0080
0.0082
4.00 4.06 2.13 4.07 2.82
37.50

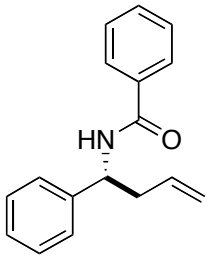

QinBo_BQ1508-AgCPA-tBu_040315_31P_pr500_MarV-00131.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
12.82


HN
O

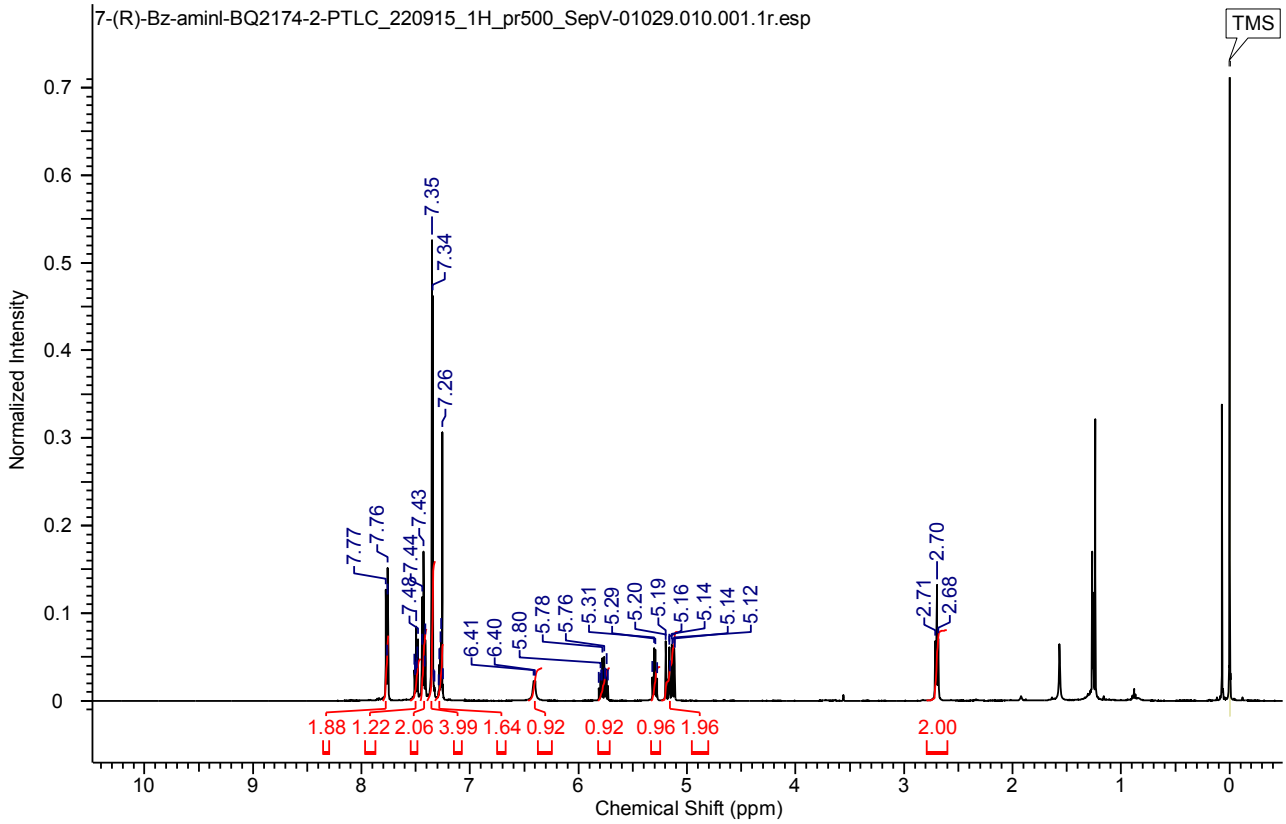
rac-**13**

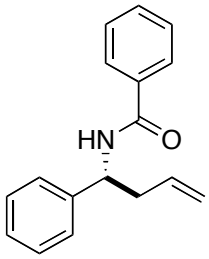

7-Bz-aminal-BQ2166-PTLC_150915_1H-13C_av500_SepV-00634.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
0.00
7.77
7.76
7.44
7.42
7.48
7.35
7.34
7.26
6.46
6.44
5.79
5.77
5.76
5.74
5.30
5.29
5.20
5.16
5.16
5.14
5.12
2.69
2.71
2.68
1.92 0.99 1.95 3.73 1.23 0.95 0.96 1.01 1.97
2.00


7-Bz-aminal-BQ2166-PTLC_150915_1H-13C_av500_SepV-00634.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
77.00
166.65
141.59
134.57
134.01
131.49
128.66
126.88
126.43
118.44
52.71
40.58


HN
O

(*R*)-**13**


7-(R)-Bz-aminl-BQ2174-2-PTLC_220915_1H_pr500_SepV-01029.010.001.1r.esp
TMS
Normalized Intensity
Chemical Shift (ppm)
7.77
7.76
7.48
7.44
7.43
7.35
7.34
7.26
6.41
6.40
5.80
5.78
5.76
5.31
5.29
5.20
5.19
5.16
5.14
5.14
5.12
2.71
2.70
2.68
1.88 1.22 2.06 3.99 1.64 0.92 0.92 0.96 1.96
2.00



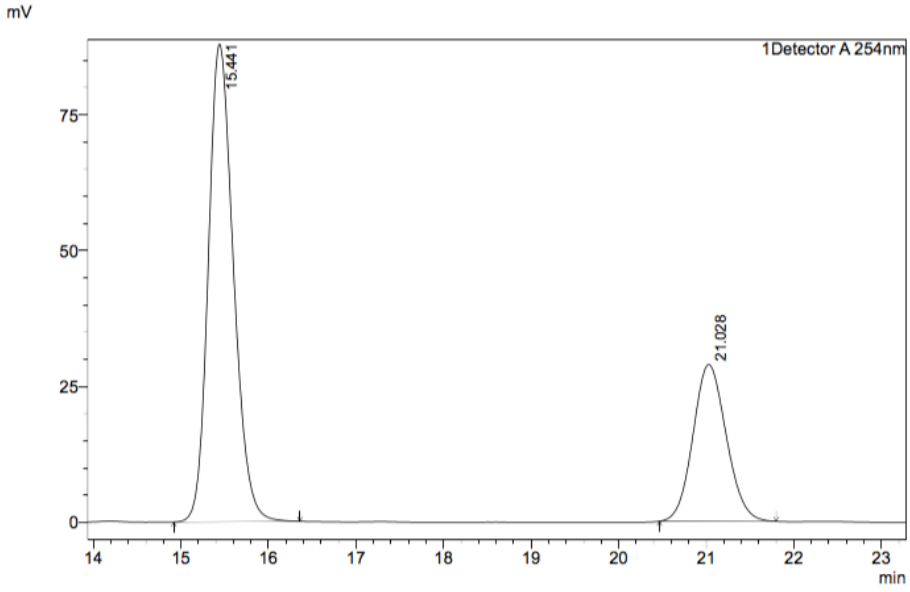
(*R*)-**13**

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: BQ2174-3		
Sample ID	:		
Data Filename	: BQ2174-3.lcd		
Method Filename	: wash.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 22/09/2015 16:57:02	Acquired by	: System Administrator
Date Processed	: 22/09/2015 17:22:06	Processed by	: System Administrator

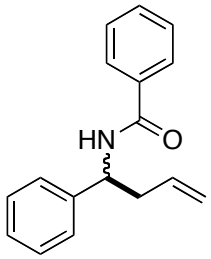
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.441	1751303	87854	70.051		M	
2	21.028	748731	28640	29.949		M	
Total		2500034	116494				



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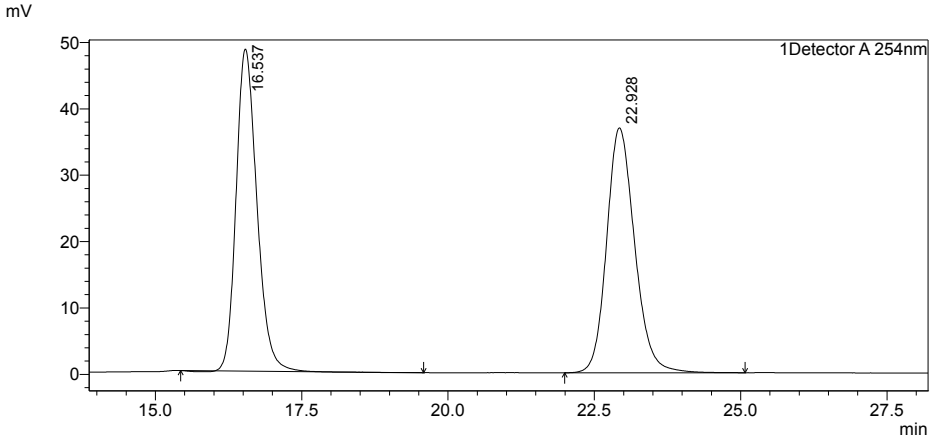
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: BQ1786-IPROH-HEX-90-10-1.0-1		
Sample ID	:		
Data Filename	: BQ1786-IPROH-HEX-90-10-1.0-1.lcd		
Method Filename	: wash.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 19/05/2015 14:41:08	Acquired by	: System Administrator
Date Processed	: 19/05/2015 15:10:38	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Mark	Name	Area%
1	16.537	1198694	48529	M		49.984
2	22.928	1199469	36694	M		50.016
Total		2398163	85223			100.000