

Ni-Catalyzed Electrochemical C(sp²)–C(sp³) Cross-Coupling Reactions

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Nickel (Ni) catalyzed carbon-carbon (C–C) cross-coupling has been considerably developed in last decades and has demonstrated unique reactivities compared to palladium. However, existing Ni catalyzed cross-coupling reactions, despite success in organic synthesis, are still subject to the use of air-sensitive nucleophiles (i.e. Grignard and organozinc reagents), or catalysts (i.e. Ni⁰ pre-catalysts), significantly limiting their academic and industrial adoption. Herein, we report that, through electrochemical voltammetry screening and optimization, the redox neutral C(sp²)–C(sp³) cross-coupling can be accomplished in an undivided cell configuration using bench-stable aryl halide or β-bromostyrene (electrophiles) and benzylic trifluoroborate (nucleophiles) reactants, non-precious, bench stable catalysts consisting of NiCl₂•glyme pre-catalyst and polypyridine ligands under ambient conditions. The broad reaction scope and good yields of the Ni-catalyzed electrochemical coupling reaction were confirmed by 48 examples of aryl/β-styrenyl chloride/bromide and benzylic trifluoroborates. Its potential applications were demonstrated by late-stage functionalization of pharmaceuticals and natural amino acid modification. Furthermore, this electrochemical C–C cross-coupling reaction was demonstrated at gram-scale in a flow-cell electrolyzer for practical industrial adoption. Finally, an array of chemical and electrochemical studies mechanistically indicates that electrochemical C–C cross-coupling reaction proceeds through an unconventional radical trans-metalation mechanism.

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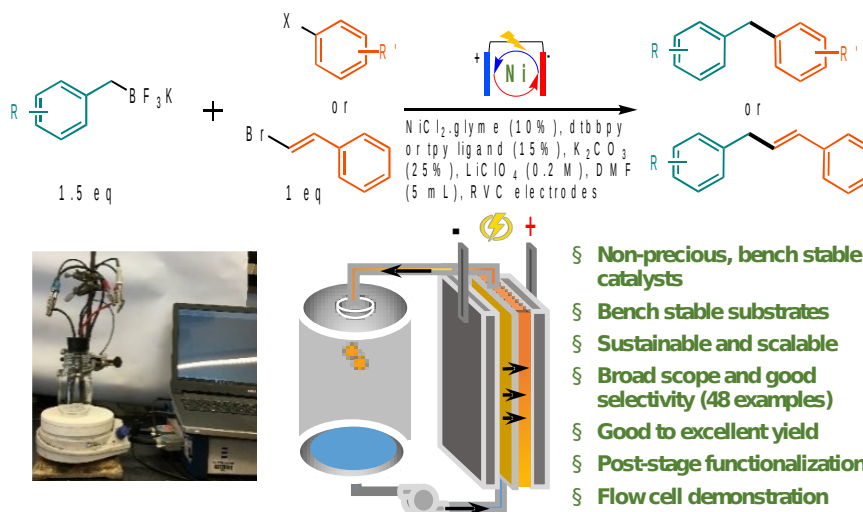
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Ni-Catalyzed Electrochemical C(sp²)-C(sp³) Cross-Coupling Reactions

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Abstract: Nickel (Ni) catalyzed carbon-carbon (C-C) cross-coupling has been considerably developed in last decades and has demonstrated unique reactivities compared to palladium. However, existing Ni catalyzed cross-coupling reactions, despite success in organic synthesis, are still subject to the use of air-sensitive nucleophiles (i.e. Grignard and organozinc reagents), or catalysts (i.e. Ni^0 pre-catalysts), significantly limiting their academic and industrial adoption. Herein, we report that, through electrochemical voltammetry screening and optimization, the redox neutral C(sp²)-C(sp³) cross-coupling can be accomplished in an undivided cell configuration using bench-stable aryl halide or β -bromostyrene (electrophiles) and benzylic trifluoroborate (nucleophiles) reactants, non-precious, stable catalysts consisting of $\text{NiCl}_2 \cdot \text{glyme}$ pre-catalyst and polypyridine ligands under ambient conditions. The broad reaction scope and good yields of the Ni-catalyzed electrochemical coupling reaction were confirmed by 48 examples of aryl/ β -styrenyl chloride/bromide and benzylic trifluoroborates. Its potential applications were demonstrated by late-stage functionalization of pharmaceuticals and natural amino acid modification. Furthermore, this electrochemical C-C cross-coupling reaction was demonstrated at gram-scale in a flow-cell electrolyzer for practical industrial adoption. Finally, an array of chemical and electrochemical studies mechanistically indicates that electrochemical

C–C cross-coupling reaction proceeds through an unconventional radical trans-metalation mechanism.

In the past half-century, transition metal catalyzed carbon-carbon (C–C) cross-coupling reactions have gained significance advances regarding reaction scopes, selectivity, and catalytic mechanisms, and achieved tremendous success in organic synthesis of pharmaceutical molecules, agrochemicals, and organic materials.¹⁻³ Catalyzed C–C cross-coupling reactions have historically been dominated by Pd-based catalysts.^{4, 5} In addition to replacing the expensive, precious Pd metal, Ni metal is characteristic of more negative 2+/0 and 1+/0 redox potential than Pd^{2+/0} to enable unique oxidative addition reactivities in activating C–X (X = Cl and Br) bonds⁶ and has found increasing importance in C–C cross coupling reactions.^{7, 8} However, Ni catalyzed C–C cross-coupling reactions are still limited by a number of well-known synthetic limitations. Ni-based Kumada, Negishi, and Suzuki, and reductive couplings are practically hampered by the use of either strong nucleophiles, sacrificed reductants, or sensitive Ni⁰ pre-catalysts, e.g. widely used Ni(COD)₂ (where COD is 1,5-cyclooctadiene) and typically require rigid reaction conditions using inert atmosphere glovebox or Schlenk-line techniques. It remains a long-standing challenge to develop Ni-catalyzed cross-coupling reactions using bench stable chemicals and easy-handling conditions for widespread academic and industrial adoption.⁸ Efforts have been made to develop well-defined air stable Ni^{II} and Ni⁰ pre-catalysts⁹⁻¹¹ and encapsulated Ni⁰ pre-catalysts.¹² However, these practices are limited by the pre-formation of Ni pre-catalysts under rigid air-free conditions and the need of special stabilization ligands for most of them.

On the other side, literature has witnessed the powerful applications of electrochemistry in organic synthesis.¹³⁻¹⁵ By precisely controlling redox potentials in an electrolyzer cell, substrates or catalysts can be selectively anodically or cathodically activated to participate desired reaction sequences.¹³⁻¹⁵ Thereby, electrochemical reactions not only migrate the use of reactive (even dangerous and toxic) oxidants and reductants and enable the access of highly reactive catalytic intermediates which are not easily handled in traditional thermal reactions, representing a green, atomically economical synthetic strategy. In spite of being known for many decades, until very recently electrochemical synthesis has aroused recurrent attention and is believed to impart

profound impacts on organic syntheses.¹³⁻¹⁵ For instance, anodic reactions including alcohol oxidation,¹⁶ C–H functionalization,¹⁷⁻¹⁹ alkene functionalization,^{20, 21} cyclization,^{22, 23} and C–O²⁴ and C–N^{25, 26} couplings, and cathodic reactions including arene or alkene hydrogenation,^{27, 28} and arylboronic acid hydroxylation²⁹ were demonstrated with good selectivity and yields. We envisioned that the synergic coupling of single electron transfer (SET) anodic oxidation and cathodic reduction process could enable unprecedented electrochemical C–C cross-coupling reactions which hold promise to address the above-mentioned limitations of two-electron redox based traditional Ni-catalyzed thermal coupling reactions. Ni-catalyzed cathodic Heck-type³⁰ and reductive³¹ C–C couplings were recently demonstrated, still requiring the use of a sacrificed anode electrode.

Instead of randomly testing combinations of nucleophiles, electrophiles, and catalysts, we first set out to identify individual anodic and cathodic SET half-cell reactions for the proposed full-cell C–C coupling reactions using the electrochemical cyclic voltammetry (CV) method. For the cathodic half-cell reaction, we aimed to explore for the SET reduction of Ni^{II}-based catalysts to activate aryl and vinyl halide electrophiles by the Ni^{III/I(II/O)} redox cycle to achieve R–Ni^{III(II)}–X intermediate, which is mechanistically accessible in traditional Ni-based thermal couplings.⁶ For the anodic half-reaction, nucleophiles including carboxylic acid¹³ and organic trifluoroborate³² are well documented as carbon radical precursors (R'• in Figure 1) upon SET oxidation. Herein, we chosen potassium butyrate, pivalate, phenylacetate, butyltrifluoroborate and benzyltrifluoroborate as C(sp³) sources; potassium benzoate, 3-methylcrotonate, and phenyltrifluoroborate as C(sp²) sources; potassium 2-butyrate as C(sp) source (Figure 2A). The proposed concept is illustrated in Figure 1. In principle, if adopting a Ni^{III/I} redox cycle, a bench stable Ni^{II} precursor can be activated by one electron reduction using a catalytic amount of a redox active nucleophile to access the R–Ni^{III}–X intermediate through oxidative addition. Then after another electron reduction while a R'• radical is generated anodically, the R–Ni^{II}–X intermediate can trap the R'• radical to form a high-valent R–Ni^{III}(X)–R' intermediate through single-electron transmetallation. Finally, the desired C–C cross-coupling product would be produced accompanying with the regeneration of the Ni^I catalyst through a reductive elimination reaction. The designed electrochemical C–C cross coupling reaction is (1) fundamentally attractive as a new means to forge C–C bonds, (2) practically attractive without involving reactive reactants and expensive metals, and (3) atomically economic and environmentally

friendly by avoiding the use of sensitive (even dangerous and toxic) sacrificial chemical reductants or oxidants.

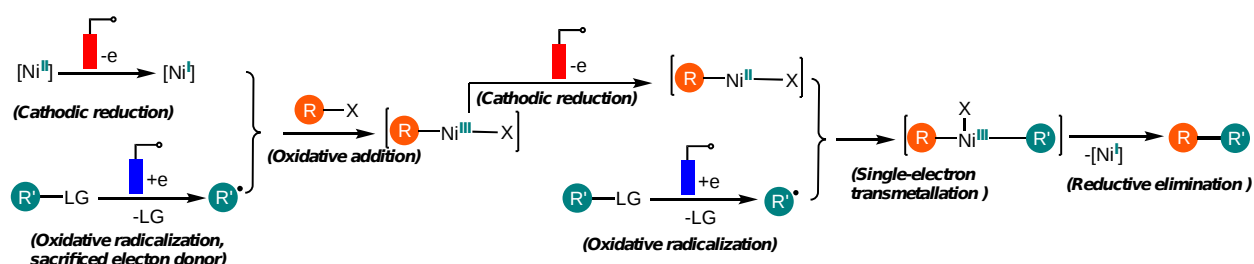


Figure 1. Designed Ni-catalyzed electrochemical C-C cross-coupling reaction. X, halide; LG, leaving group.

Electrochemical screening of the proposed half-cell reactions was conducted through the cyclic voltammetry (CV) method using a three-electrode system. As shown in Figure 2B(i) (gray curve), in the presence of 3 equivalents 2,2'-bipyridine (2,2'-bpy) ligand, $\text{NiCl}_2\cdot\text{glyme}$ displayed a reversible redox signal at $E_{1/2} = -1.49$ V (vs. $\text{Fc}^{+/0}$), which corresponding to the $\text{Ni}^{\text{III/I}}$ redox couple. Then, 10 equivalents of organic halides (R-X) were added to the electrolyte and CV curves were collected again. Among tested organic halides, $\text{C}(\text{sp}^2)$ precursors (aryl halide and alkenyl bromide) or $\text{C}(\text{sp})$ precursors (alkynyl bromide) could be activated by the Ni^{I} intermediate while $\text{C}(\text{sp}^3)$ precursors were inactive. For example, when methyl 4-bromobenzoate was added (green trace in Figure 2B(i)), the reductive peak current intensity was obviously increased, meanwhile, the return peak disappeared which indicates that an irreversible chemical reaction happened between Ni^{I} species and the aryl halide. The same screening experiments were conducted to the anodic substrates. As shown in Figure 2B(ii), in 0 – 1.25 V (vs. $\text{Fc}^{+/0}$) potential range, only potassium benzyltrifluoroborate, phenylacetate, and pivalate displayed remarkable electrochemical reactivity with peak potentials at +0.75 V, +0.94 V, and +1.02 V (vs $\text{Fc}^{+/0}$), respectively. Other substrates were electrochemically inert in the scanned potential range. Based on the CV screening results for both cathodic and anodic substrates, $\text{C}(\text{sp}^2)$ precursors (aryl halide and alkenyl bromide) or $\text{C}(\text{sp})$ precursors (alkynyl bromide) and $\text{C}(\text{sp}^3)$ sources (potassium benzyltrifluoroborate, phenylacetate, and pivalate) were possible combinations for electrochemical $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ or $\text{C}(\text{sp})\text{-C}(\text{sp}^3)$ cross-coupling reactions.

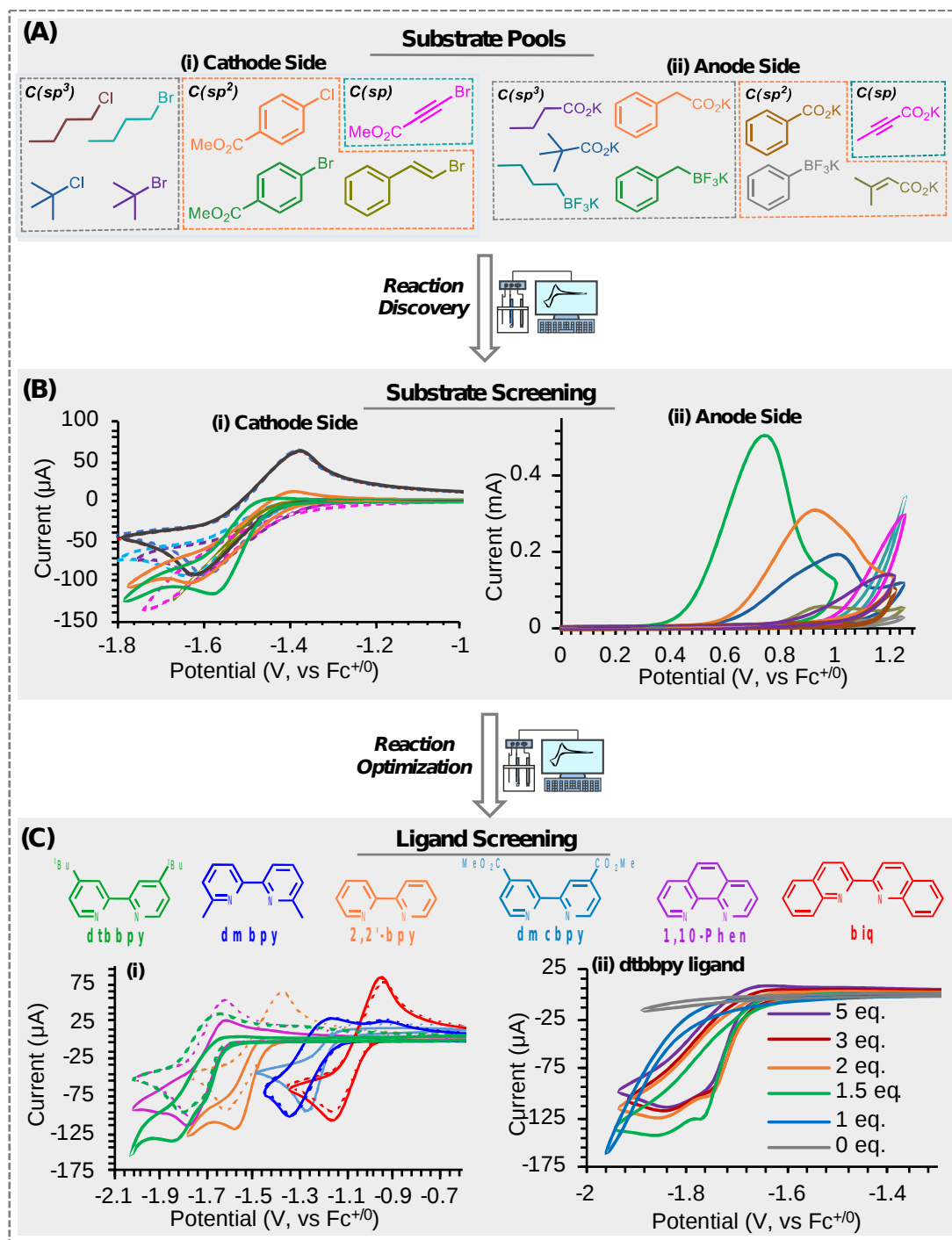


Figure 2. Electrochemical voltammetry screening of cathodic and anodic half-reactions. (A) Selected substrate pools. (B) CV screening to identify reactive substrates of cathodic (i) and anodic (ii) half-reactions. The CV curves were recorded with 5 mM $NiCl_2 \cdot glyme$, 15 mM 2,2'-bpy, and 50 mM organic halides for the cathode side screening, 0.1 M potassium trifluoroborates or carboxylates for the anode side screening. DMF solvent, 0.2 M $LiClO_4$ supporting electrolyte,

GC working electrode, 100 mV/s scan rate, room temperature. (C) CV screening of the ligand (i) and Ni/ligand ratio (ii) to optimize the cathodic half-reaction. The ligand screening curves were recorded with 5 mM NiCl₂.glyme and 15 mM ligand in the presence (dash line) and absence (solid line) of 50 mM methyl 4-bromobenzoate. The Ni/ligand ratio screening curves were recorded with 5 mM NiCl₂.glyme and 50 mM methyl 4-bromobenzoate by adding various ratio of dtbbpy ligand.

We then optimized the NiCl₂.glyme/polypyridine catalyst system using cyclic voltammetry with methyl 4-bromobenzoate as a model electrophile. As shown in Figure 2C(i), seven different polypyridine ligands including 4,4'-di-tert-butyl-2,2'-bipyridyl (dtbbpy), 6,6'-dimethyl-2,2'-bipyridyl (dmbpy), 2,2'-bpy, dimethyl 2,2'-bipyridine-4,4'-dicarboxylate (dmcbpy), 1,10-phenanthroline (1,10-Phen), and 2,2'-biquinoline (biq) were screened to identify the most suitable ligand for the Ni-catalyst. Among all the ligands, dtbbpy prompted the strongest current intensity increase (green curve), indicating that Ni^I(dtbbpy)⁺ is the most reactive species to oxidative addition of the C–Br bond of methyl 4-bromobenzoate. Besides 2,2'-bpy and dtbbpy, 1,10-Phen also aroused strong current response (purple curve) and thus can also be a suitable ligand. We further investigated the effect of Ni/ligand ratio on the reactivity of the Ni-catalyst. The CV curves of NiCl₂.glyme with addition of various ratio of dtbbpy ligand showed continuous change (Figure S5). In the absence of dtbbpy ligand, no reversible redox signal was observed. When 1 ~ 3 equivalents of dtbbpy ligand was added, there were two set of quasi-reversible redox signals. Further increase the ligand ratio to 5 equivalents, the redox signals overlapped to one set of fully reversible redox signal. It indicates that there is an equilibrium for Ni^{II} complexes in the solution: Ni^{II} ↔ Ni^{II}(dtbbpy) ↔ Ni^{II}(dtbbpy)₂ ↔ Ni^{II}(dtbbpy)₃, which is consistent with a previous UV-vis study. In the presence of methyl 4-bromobenzoate substrate, the addition of 1.5 equivalent of dtbbpy ligand (Figure 2C(ii), green curve) yielded the highest cathodic current. Adding more ligand (2 – 5 equivalents), the reductive peak current intensity slightly decreased and the return peak gradually showed up, which is most likely due to the decreased reactivity of Ni-catalyst after coordination to multiple dtbbpy ligands (Ni(dtbbpy)₂ and Ni(dtbbpy)₃).

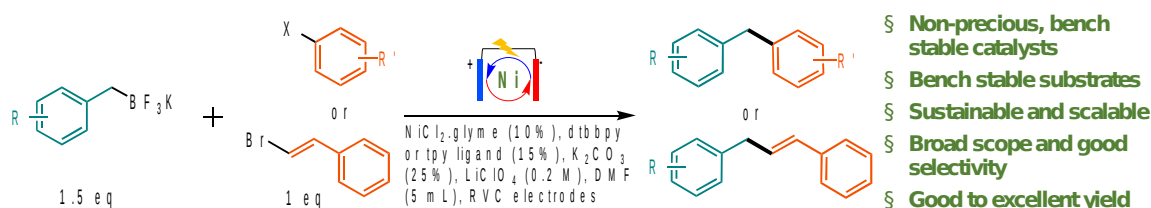
Encouraged by the positive observations in the electrochemical voltammetry studies, we proceeded to test the C(sp²)–C(sp³) cross-coupling full-reaction by combining the oxidative

radicalization of benzylic trifluoroborates and Ni-catalyzed C–X activation of aryl halides in an undivided cell. A starting electrolysis system consisting of $\text{NiCl}_2\cdot\text{glyme}$ catalyst, dtbbpy ligand, and LiClO_4 supporting electrolyte confirmed the cross-coupling of methyl 4-bromobenzoate and potassium benzyltrifluoroborate in 47% yield (produce methyl 4-benzylbenzoate, **1**) after galvanostatic electrolysis at 3.0 mA for 28 h. Dimethyl 4,4'-biphenyldicarboxylate (**1'**) from the homo-coupling of methyl 4-bromobenzoate was isolated as the main by-product in 38% yield. To further improve the reaction yield, a number of supporting electrolytes (TBAPF_6 , KPF_6 , and NaBF_4) and salt additives (K_2CO_3 , Na_2CO_3 , and KOAc) were tested to optimize the reaction efficiency (Table S1). It was found that the yield for **1** was further improved to 93% using K_2CO_3 additive. The essentiality of $\text{NiCl}_2\cdot\text{glyme}$ catalyst, dtbbpy ligand, and electrolysis was determined by control experiments (Table S1, SI). In addition, both reaction selectivity and rate were largely affected by current intensity. Poorer selectivity was obtained under a higher or lower current intensity (64% under 1.0 mA, 77% under 5.0 mA current). Under 1.0 mA current electrolysis, the reaction was significantly decelerated as a reaction time of 48 h needs to fully convert the substrate. Other solvents, such as THF, MeCN, CH_2Cl_2 , MeOH, and DMSO were not effective to this reaction (only 0 – 15% yield was observed, Table S2, SI). Moreover, similar as under thermal reaction conditions,¹⁶ the reactivity and selectivity of this reaction is highly sensitive to the ligand structure (Table S3, SI). In particular, dtbbpy and 2,2'-bpy ligands exhibited the best efficiencies with isolated yields of 93% and 87%, respectively. 1,10-Phen and tridentate terpyridine (tpy) ligands gave moderate yields of 67% and 73%, respectively. It is noteworthy that the best selectivity between cross-coupling product **1** and homo-coupling product **1'** (96:4) was obtained by using tpy ligand, which tends to suppress the homo-coupling of strong electrophiles. However, other ligands (dmbpy, dmcbpy, and biq) were not effective.

After establishing optimal reaction conditions for the Ni-catalyzed electrochemical $\text{C}(\text{sp}^2)$ – $\text{C}(\text{sp}^3)$ cross-coupling reaction, we next tested the reaction scope on both aryl halide and benzylic trifluoroborate. As shown in Figure 3, a wide range of aryl chlorides including both electron-rich and electron-deficient arenes were suitable to this Ni-catalyzed electrosynthesis system (**1** to **5**). The electron-deficient aryl chlorides (**1** to **3**, 74% to 86% yield) delivered better yield than the electron-rich ones (**4** and **5**, 46% and 31% yield). It is probably due to the low activity of electron-rich aryl chloride substrates with the Ni^{I} intermediate. Aryl bromides displayed better efficiencies than the corresponding aryl chlorides, as **1** to **5** were isolated in 77% to 93% yield by

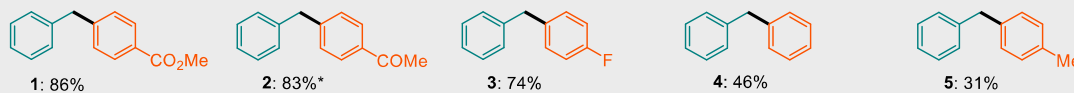
using aryl bromide substrates. The reaction exhibited comparable efficiency upon scale-up, for example, 89% yield was obtained on a 2.5 mmol scale reaction of **1** (0.5 g). The substituent position of aryl bromide displayed moderate effect to the reaction efficiency, as the para-, meta- and ortho-substituted methyl bromobenzoate delivered 93%, 71%, and 89% yield (**1**, **6** and **7**), respectively. Aryl bromides with functional groups as diverse as ester (**1**, **6**, **7**, and **10**), ketone (**2**), fluoride (**3**), methoxy group (**9** and **10**), amide (**14** and **15**), aldehyde (**11**), nitrile (**12**) and alkenyl (**19**) were effective in this reaction. Substrates possessing strongly electron-donating substituents such as ^tBu and methoxy groups could also provide moderate to good yield (72% for **8** and 53% for **9**). It is interesting that for the substrates possessing strong electron-withdrawing substituents such as aldehyde, acetyl, and cyano groups, best results were obtained by using 2,2'-bpy ligand (83% and 91% yield for **2** from chloride and bromide, respectively, 82% yield for **11**, and 74% yield for **12**). Furthermore, in the case of 4-bromo(trifluoromethyl)benzene, homo-coupling product, 4,4'-bis-(trifluoromethyl)biphenyl (**13'**), was obtained as the only product when using dtbbpy and 2'2-bpy ligands. Interestingly, 21% yield of cross-coupling product **13** was obtained by using the tpy ligand.

In addition to examine the substituent positions and functional groups of the aryl halide substrates, we also investigated the tolerance of this electrosynthesis system to common protecting groups which are widely used in organic synthesis, such as amide, tert-butyloxycarbonyl (Boc), benzyl ether (BnO), and acetal. All of these protecting groups were well tolerated, as evidenced by good isolation yield of **14** to **18** (67% to 86% yield). The π -conjugation extended aryl bromide substrates including 4-bromophenylethene, 3-bromofluorene, and 2-bromonaphthalene also smoothly proceeded this cross-coupling reaction with moderate to good yield (**19** to **21**, 43% to 84% yield). Moreover, a variety of aryl bromides consisting nitrogen-containing heterocyclic including 6-bromoquinoline, 6-bromoisquinoline, and Boc protected 6-bromotetrahydroisoquinoline, and 5-bromoindole, which are prevalent building blocks in bio-active molecules, delivered moderate to good yield (**22** to **25**, 52% to 81% yield).

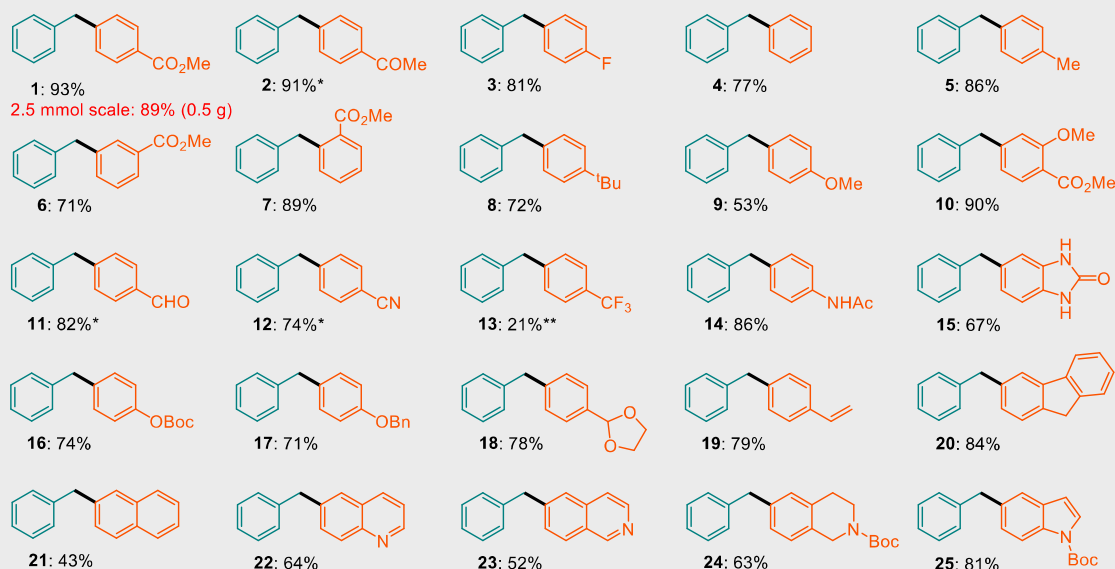


Ar-X scope

X = Cl

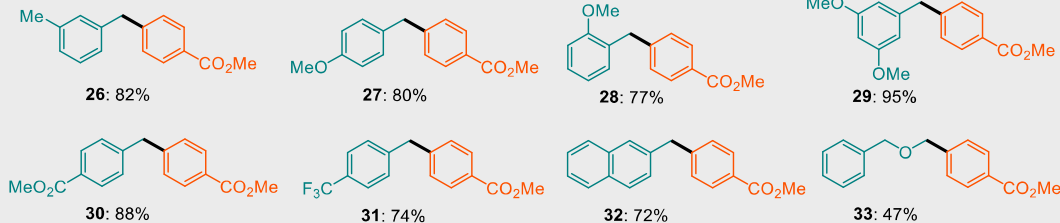


X = Br



R-BF₃K scope

Ar-Br



Alkenyl-Br

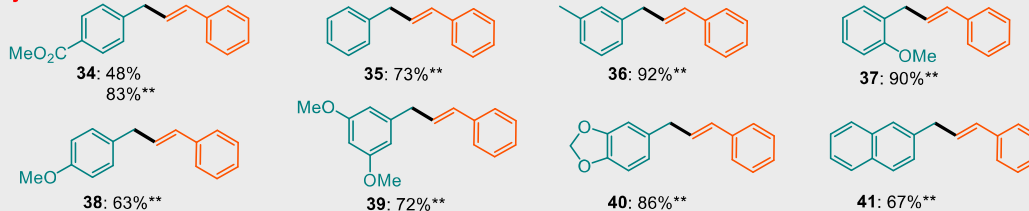


Figure 3. Substrate scope of the Ni-catalyzed electrochemical C(sp²)-C(sp³) cross-coupling reaction. Yields refer to isolated yields of products after chromatography on silica gel. Standard

conditions: aryl halide or β -bromostyrene substrate (0.5 mmol), trifluoroborate substrate (0.75 mmol), $\text{NiCl}_2\cdot\text{glyme}$ (50 μmol), dtbbpy ligand (75 μmol), K_2CO_3 (1.25 mmol), LiClO_4 (0.2 M), DMF (5 mL), RVC as anode and cathode, 3 mA current electrolysis under Ar at room temperature for 20 – 36 h. *75 μmol 2,2'-bppy as ligand. **50 μmol tpy as ligand. In case of **13**, an inseparable mixture of **13** and **13'** was obtained, 41% purity.

The substrate scope of benzylic trifluoroborate salts was also investigated. As shown in Figure 3, both electron-rich and electron-deficient benzylic trifluoroborates were approved efficient carbon radical precursors in this cross-coupling reaction (**26** to **31**, 74% to 95% yield). Functional groups, including esters, methoxy group, and trifluoromethyl group were tolerant to this Ni-catalyzed electrosynthesis. The substituent positions displayed negligible effects to the reaction efficiency, as comparable yield was obtained for the para-, meta-, and ortho-substituted benzylic trifluoroborates (**26** to **28**, 77% to 82% yield). In the presence of two strong electron-donating methoxy (MeO-) groups, the highest yield, 95%, was gained for **29**, which is interpreted as the favorable oxidation kinetics of the corresponding trifluoroborate substrate. The π -conjugation extended naphthalen-2-ylmethyl trifluoroborate is also highly productive in this electrochemical $\text{C}(\text{sp}^2)\text{--}\text{C}(\text{sp}^3)$ cross-coupling reaction, as 72% yield was obtained for **32**. Beside the benzylic trifluoroborates, ((benzyloxy)methyl)trifluoroborate also manifested reasonable reactivity in this reaction with a yield of 47% (**33**).

In the CV screening studies (Figure 2B), some other substrates also showed reactivity in the anodic half-reaction. For example, β -bromostyrene and methyl 3-bromopropiolate showed reactivity in the anodic half-cell reaction (Figure S4, SI). When β -bromostyrene was used as an electrophile to react with potassium trifluoro(4-(methoxycarbonyl)benzyl)borate, 48% yield of the Heck-like $\text{C}(\text{sp}^2)\text{--}\text{C}(\text{sp}^3)$ cross-coupling product **34** and 47% yield of the homo-coupling product **34'** were obtained by using dtbbpy as ligand. To suppress the homo-coupling product, best yield and selectivity for the cross-coupling product **34** was obtained in the presence of tpy ligand (83% yield, 90% selectivity) (Table S4, SI). As shown in Figure 3, both electron-rich and electron-deficient benzylic trifluoroborates were efficient in this cross-coupling reaction (**34** to **40**, 63% to 92% yield). Functional groups including esters, methoxy group, and benzodioxol group were tolerant in this Ni-catalyzed electrochemical reaction. The π -conjugation extended naphthalen-2-ylmethyl trifluoroborate also provided good reactivity in this reaction, as 67% yield

was obtained for **41**. However, other anodic nucleophiles (3-bromopropiolate, phenylacetic acid, potassium pivalate, and potassium phenyltrifluoroborate) didn't provide satisfactory results (see Figure S7 and the SI for more discussions).

To demonstrate potential applications of this Ni-catalyzed electrochemical C(sp²)-C(sp³) cross-coupling reaction, we utilized it in late-stage functionalization of pharmaceuticals which is a popular way for fast discovery of new drug candidates. Fenofibrate is a pharmaceutical molecule of the fibrate class and used to treat abnormal blood lipid levels. As shown in Figure 4A, using our electrosynthesis method, Fenofibrate was successfully converted to a series of brand-new compounds (**42** to **46**, 41% to 86% yield) in up to 2.5 mmol (0.93 g) scale from a regular vial electrolyzer cell. To testify the potential industrial adoption of this innovative electrochemical C-C cross-coupling reaction, the synthesis of **46** was further scaled up to 8 mmol (3.2 g) using a flow-cell electrolyzer (Figure 4D and 4E). Under the flow-cell condition, an even better reaction efficiency (84% yield) was obtained compared to the vial reaction (81% yield). Another new Clofibrate derivative (a lipid-lowering agent) was synthesized using this electrochemical approach (**47**, 63% yield) (Figure 4B). Furthermore, the electrochemical C-C cross-coupling reaction was also effective in modification of brominated natural amino acid, e.g. phenylalanine, (Figure 4C) (**48**, 83% yield).

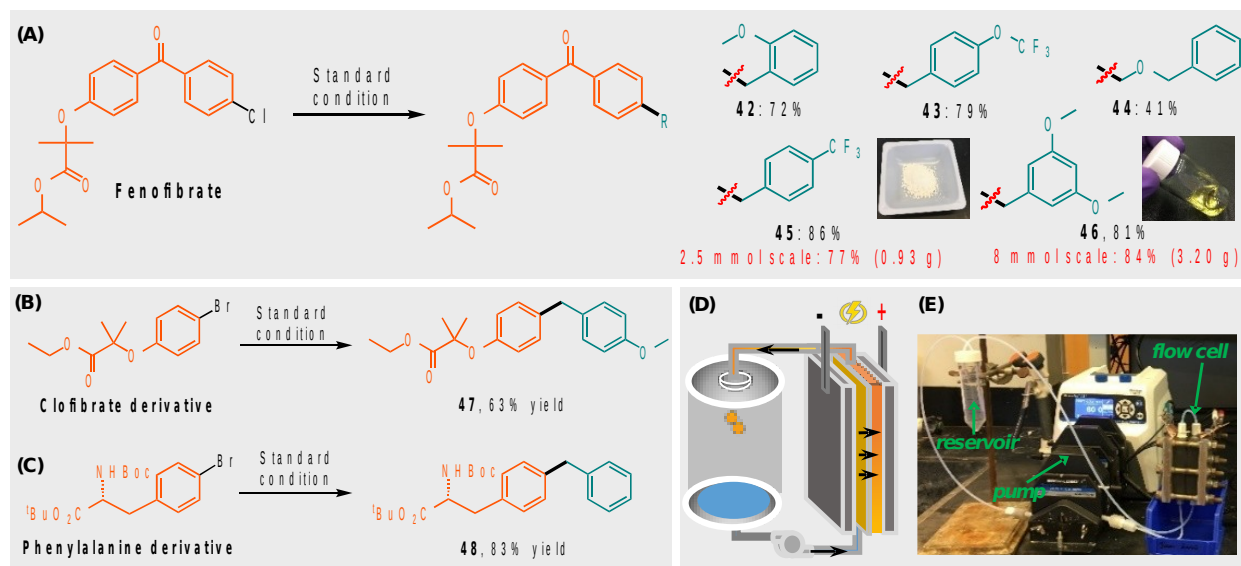


Figure 4. Applications of the Ni-catalyzed electrochemical C(sp²)-C(sp³) cross-coupling reaction. Late-stage functionalization of Fenofibrate (A), Clofibrate derivative (B), and modification of brominated phenylalanine (C). (D) schematic drawing and (E) experimental

setup of the electrosynthesis flow-cell. Yields refer to isolated yields of products after chromatography on silica gel.

To gain mechanism understandings of this Ni-catalyzed electrochemical C(sp²)-C(sp³) cross-coupling reaction, radical-trapping experiment was conducted for the anodic half-reaction. As shown in Figure 5A, controlled potential electrolysis (at 1.2 V, vs. Fc^{+/0}) of the potassium trifluoro(4-(methoxycarbonyl)benzyl)borate and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in a divided-cell produced radical coupling product **49** with 86% isolated yield, which confirms the formation of 4-(methoxycarbonyl)benzyl free radical in the anodic oxidation process. In addition, plots of overpotential over the logarithm of kinetic current and the corresponding fitted Tafel plots were constructed to determine charge transfer rate constants (k^0) of potassium benzyltrifluoroborate and cesium phenylacetate in the anodic oxidation process (Figure 5B and see the SI for detail). k^0 of potassium benzyltrifluoroborate and cesium phenylacetate were calculated as 5.56×10^{-5} cm/s and 1.39×10^{-5} cm/s, respectively. The higher charge transfer rate constant of potassium benzyltrifluoroborate indicates faster electrochemical reactivity to generate carbon radicals than cesium phenylacetate, which is consistent with the better efficiency of potassium benzyltrifluoroborate in the cross-coupling reaction than cesium phenylacetate. It is believed that the quick formation of the carbon radical is critical to trap the R-Ni^{II}-X intermediate, otherwise the R-Ni^{II}-X intermediate can promote the homo-coupling side reaction.

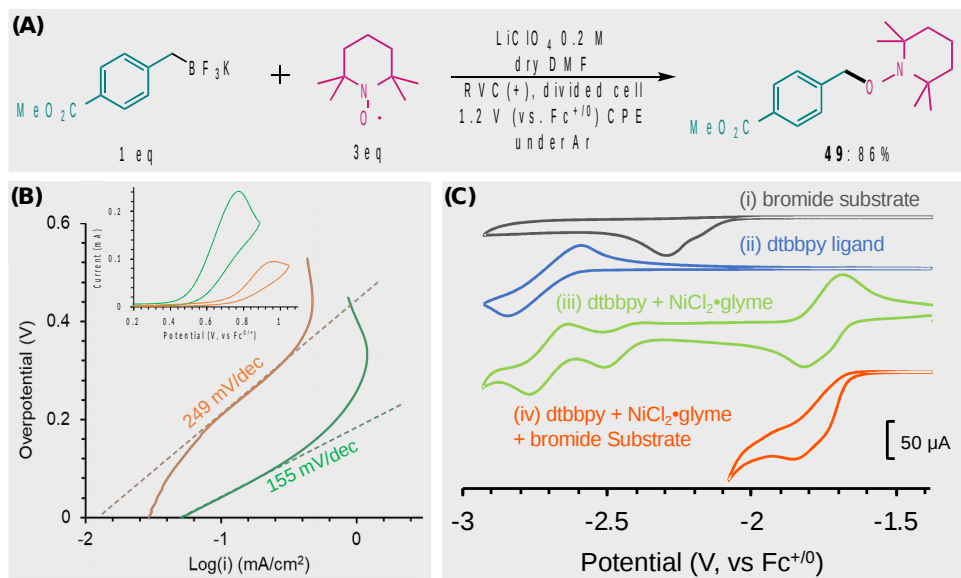


Figure 5. Reaction mechanism studies of the Ni-catalyzed electrosynthesis system. (A) Carbon free radical trapping reaction. **(B)** Plots of overpotential over the logarithm of kinetic current and the fitted Tafel plots of phenyl trifluoroborate (green) and cesium phenylacetate (orange). Inset: CV curves of potassium phenyl trifluoroborate (green) and cesium phenylacetate (orange); conditions: 10 mM in DMF, LiClO₄ (0.2 M) supporting electrolyte, GC working electrode, and 100 mV/s scan rate. **(C)** CV curves of 50 mM methyl 4-bromobenzoate (gray), 15 mM dtbbpy ligand (blue), 5 mM NiCl₂•glyme + 25 mM dtbbpy (green), and 5 mM NiCl₂•glyme + 15 mM dtbbpy + 50 mM methyl 4-bromobenzoate (orange) in DMF with 0.2 M LiClO₄ supporting electrolyte.

Additional CV studies were conducted to gain additional mechanistic insights for the cathodic process. As shown in Figure 5B, methyl 4-bromobenzoate substrate displayed irreversible redox signal with onset potential at -2.05 V (vs Fc⁺⁰) and dtbbpy ligand delivered reversible redox signal with $E_{1/2} = -2.70$ V (vs. Fc⁺⁰), respectively. The mixture of NiCl₂•glyme and dtbbpy ligand delivered three redox peaks at $E_{1/2} = -1.74$ V, -2.44 V, and -2.70 V (vs. Fc⁺⁰), which corresponding to Ni^{III/I}, Ni^{I/0} redox couples, and the free ligand. When the methyl 4-bromobenzoate substrate was added, significant increase of reductive current and disappearing of the return peak was observed for the Ni^{III/I} redox couples. It indicated that the Ni^I is the reactive species for oxidative addition to aryl halide. In addition, CV curves of the reaction mixture displayed -1.60 V and 0.33 V (vs. Fc⁺⁰) onset potentials for cathodic and anodic half-reactions, respectively (Figure S8). The potential of cathode kept between -1.7 and -1.9 V (vs. Fc⁺⁰) during the reaction (Figure S9), which indicates the Ni^{I/0} redox couple is not involved in the cathodic process.

Based on the chemical and electrochemical studies, a possible reaction mechanism for this Ni-catalyzed electrochemical C(sp²)-C(sp³) cross-coupling is proposed and illustrated in Figure 6. The reaction is initiated by the electrochemical reduction of Ni^{II} catalyst **A** to Ni^I species **B**, the latter further oxidative addition to aryl halide substrate **C** to generate an Ar-Ni^{III} complex **D**. **D** is subsequently electrochemically reduced to Ar-Ni^{II} species **E**. Simultaneously, a benzylic carbon free radical **G** generated through oxidative degradation of benzylic trifluoroborate or phenylacetate substrate **F** in the anode side is captured by **E** to form a high-valent Ar-Ni^{III}-Bn

species **H**. Then, **H** undergoes reductive elimination to produce the cross-coupling product **I** and recover the Ni^I catalyst **B**.

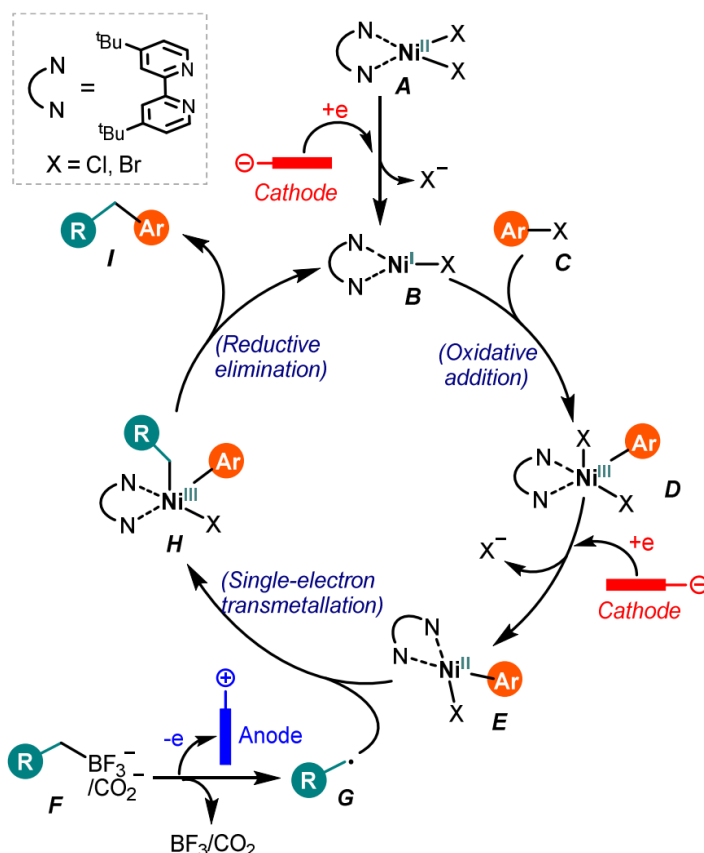


Figure 6. Proposed reaction mechanism for the Ni-catalyzed electrochemical C(sp²)–C(sp³) cross-coupling reaction.

In summary, a Ni-catalyzed electrochemical cross-coupling methodology was developed to forge the C(sp²)–C(sp³) bond with broad substrate scope, excellent functional group tolerance, selectivity, and good yield. In addition, the cyclic voltammetry proved an effective and efficient way for the discovery, optimization, and mechanistic understanding of anodic and cathodic half-reactions and can be used as a go-to method for developing other useful electrosynthesis methodologies. Compared to traditional thermal Ni catalyzed cross-coupling reactions, the present electrochemical approach is advantageous as all reactants and catalysts are bench stable without using reactive oxidants/reductants and complex inert atmosphere techniques. As exemplified in gram-scale synthesis in flow-cell and late-stage functionalization of

pharmaceuticals, this electrochemical C–C coupling methodology are expected to be widely applied to the construction of C(sp²)–C(sp³) bonds in developing pharmaceutical molecules, agrochemicals, and organic materials. The Ni-catalyzed electrochemical C–C cross reactions can be further advanced for broader substrates and extended to other types of coupling reactions. Moreover, the present new C–C bond formation paradigm (and also extended reactions) can offer rich opportunities to pursue fundamental mechanistic studies and thus lead to the discovery of new catalytic knowledge at the interface of synthetic chemistry and electrochemistry.

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Supporting Information for

Ni-Catalyzed Electrochemical C(sp²)-C(sp³) Cross-Coupling Reactions

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1. Materials

All solvents and reagents were purchased from commercial sources (Sigma Aldrich, TCI Chemicals, and Oakwood Chemicals) and, unless otherwise noted, used without further purification. ^1H -NMR, ^{13}C -NMR, and ^{19}F -NMR measurements were performed on a Bruker FT-NMR spectrometer (500 MHz). Mass spectra (MS) were collected on a 2020 Shimadzu LC-MS with APCI ion source. Electrochemical measurements were performed on a Gamry Instruments 1000 electrochemical workstation. The electrochemical catalytic reactions were investigated using the Chronopotentiometry (CP) method by a Gamry Instruments 5000 electrochemical workstation or a Land battery testing system. Thin-layer chromatography (TLC) was conducted to monitor the reactions. All compounds were purified by flash column chromatography with silica gel.

2. Substrate Synthesis and Characterization

Potassium benzyltrifluoroborates were synthesized similar to previously reported procedures.¹

Method A: Bis(pinacolato)diboron (11.58g, 45 mmol, 1.5 equiv), triphenylphosphine (1.02 g, 3.9 mmol, 13 mol%), CuI (0.57 g, 3.0 mmol, 10 mol%), and LiOMe (2.28 g, 60 mmol, 2 equiv), were mixed in 50 mL dry DMF under Ar. Then, benzylic bromide (30 mmol, 1 equiv) was added. The reaction mixture was stirred at room temperature for 24 h under inert atmosphere. The resultant black mixture was decanted into 200 mL water and extracted by 3 x 150 mL EtOAc. The organic phases were combined and washed with 3 x 100 mL saturated NaCl solution. After drying under vacuum, the residue was suspended in 100 mL CH_3OH . And then, KHF_2 (1:1 ratio of KF and HF) (18.7 g, 240 mmol, 8 equiv) in 60 mL water solution was added dropwise at 0 °C over 30 min. The obtained suspension was warmed up to room temperature and concentrated under reduced pressure. The resultant residue was suspended in 50 mL EtOH and dried by rotary evaporation, which was repeated for 3 times to remove pinacol and H_2O . The obtained solid was further suspended in hot acetone (3 x 200 mL) and filtered. The filtrate was dried by rotary evaporation. The resultant residue was further purified by washing with CH_2Cl_2 (2 x 20 mL) and hexane (2 x 30 mL) to afford the desired potassium benzylic trifluoroborate salts.

Method B: Benzylic bromide (30 mmol, 1 equiv), KOAc (4.41 g, 45 mmol, 1.5 equiv), (4-MeC₆H₄)₃P (0.547 g, 1.8 mmol, 6 mol%), Pd(dba)₂ (0.518 g, 0.9 mmol, 3 mol%), and bis(pinacolato)diboron (11.58g, 45 mmol, 1.5 equiv) were mixed in 100 mL dry toluene under Ar. The reaction mixture was stirred at room temperature for 2 days under inert atmosphere. The resultant brown mixture was dried by rotary evaporation and suspended in 100 mL CH_3OH . And then, KHF_2 (18.7 g, 240 mmol, 8 equiv) in 60 mL water solution was added dropwise at 0 °C over 30 min. The obtained suspension was warm to room temperature and concentrated under reduced pressure. The resultant residue was suspended in 50 mL EtOH and dried by rotary evaporation, which was repeated for 3 time to remove the pinacol and H_2O . The obtained solid

was further suspended in hot acetone (3 x 200 mL) and filtered. The filtrate was dried by rotary evaporation. The resultant residue was further purified by washing with CH₂Cl₂ (2 x 20 mL) and hexane (2 x 30 mL) to afford the desired potassium benzylic trifluoroborate salts.

Potassium benzyltrifluoroborate

The titled compound was synthesized following Method A using benzyl bromide (5.13 g) as the starting material. The titled compound was obtained as a white powder, 4.4 g (74 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.41 ~ 1.53 (m, 2H), 6.87 (t, *J* = 5.0 Hz, 1H), 6.99 (d, *J* = 10.0 Hz, 2H), 7.04 (t, *J* = 5.0 Hz, 2H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.29 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.63 (br, 3F).

APCI-MS *m/z* calcd for C₇H₇BF₃⁻ ([M]⁻) 159.06, found: 159.10.

Potassium trifluoro(3-methylbenzyl)borate

The titled compound was synthesized following Method A using 3-methylbenzyl bromide (1.11 g) as the starting material. The titled compound was obtained as a white powder, 0.86 g (68 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.33 ~ 1.48 (m, 2H), 2.19 (s, 3H), 6.68 (d, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.92 (t, *J* = 7.5 Hz, 1H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.24 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.45 (br, 3F).

APCI-MS *m/z* calcd for C₈H₉BF₃⁻ ([M]⁻) 173.07, found: 173.05.

Potassium trifluoro(4-methoxybenzyl)borate

The titled compound was synthesized following Method A using 4-methoxybenzyl bromide (1.20 g) as the starting material. The titled compound was obtained as a white powder, 1.15 g (84 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.30 ~ 1.44 (m, 2H), 3.66 (s, 3H), 6.63 (d, *J* = 10.0 Hz, 2H), 6.90 (d, *J* = 10.0 Hz, 2H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.13 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.69 (br, 3F).

APCI-MS *m/z* calcd for C₈H₉BF₃O⁻ ([M]⁻) 189.07, found: 189.00.

Potassium trifluoro(2-methoxybenzyl)borate

The titled compound was synthesized following Method A using 2-methoxybenzyl bromide (3.01 g) as the starting material. The titled compound was obtained as a white powder, 1.30 g (38 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.39 ~ 1.49 (m, 2H), 3.66 (s, 3H), 6.67 (t, *J* = 10.0 Hz, 1H), 6.73 (d, *J* = 5.0 Hz, 1H), 6.86 (t, *J* = 5.0 Hz, 1H), 7.06 (d, *J* = 5.0 Hz, 1H). ¹¹B NMR

(DMSO-*d*₆, 160 MHz, ppm): δ 11.01 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -135.50 (br, 3F).

APCI-MS *m/z* calcd for C₈H₉BF₃O⁻ ([M]⁻) 189.07, found: 189.05.

Potassium trifluoro(3,5-dimethoxybenzyl)borate

The titled compound was synthesized following Method A using 3,5-dimethoxybenzyl bromide (6.93 g) as the starting material. The titled compound was obtained as a white powder, 6.81 g (88 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.34 ~ 1.47 (m, 2H), 3.65 (s, 6H), 6.04 (s, 1H), 6.17 (s, 2H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.48 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.33 (br, 3F).

APCI-MS *m/z* calcd for C₉H₁₁BF₃O₂⁻ ([M]⁻) 219.08, found: 219.10.

Potassium trifluoro(4-(methoxycarbonyl)benzyl)borate

The titled compound was synthesized following Method B using 4-(methoxycarbonyl)benzyl bromide (6.87 g) as the starting material. The titled compound was obtained as a white powder, 4.07 g (53 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.50 ~ 1.66 (m, 2H), 3.80 (s, 3H), 7.10 (d, *J* = 10.0 Hz, 2H), 7.68 (d, *J* = 10.0 Hz, 4H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.06 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.72 (br, 3F).

APCI-MS *m/z* calcd for C₉H₉BF₃O₂⁻ ([M]⁻) 217.06, found: 217.10.

Potassium trifluoro(4-(trifluoromethyl)benzyl)borate

The titled compound was synthesized following Method B using 4-(trifluoromethyl)benzyl bromide (7.17 g) as the starting material. The titled compound was obtained as a white powder, 4.87 g (61 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.50 ~ 1.66 (m, 2H), 7.17 (d, *J* = 5.0 Hz, 2H), 7.38 (d, *J* = 5.0 Hz, 2H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 10.98 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -137.04 (br, 3F), -60.01 (s, 3F).

APCI-MS *m/z* calcd for C₈H₆BF₆⁻ ([M]⁻) 227.05, found: 227.00.

Potassium trifluoro(naphthalen-2-ylmethyl)borate

The titled compound was synthesized following Method A using 2-(bromomethyl)naphthalene (3.32 g) as the starting material. The titled compound was obtained as a white powder, 2.05 g (55 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.77 ~ 1.92 (m, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.85 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -140.23 (br, 3F).

APCI-MS *m/z* calcd for C₁₁H₉BF₃⁻ ([M]⁻) 209.07, found: 209.05.

potassium (4-(trifluoromethoxy)benzyl)trifluoroborate

The titled compound was synthesized following Method A using 4-(trifluoromethoxy)benzyl bromide (2.55 g) as the starting material. The titled compound was obtained as a white powder, 1.32 g (47 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.41 ~ 1.53 (m, 2H), 7.01 (brs, 2H), 7.05 (brs, 2H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.46 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -137.09 (br, 3F), -56.83 (s, 3F).

APCI-MS *m/z* calcd for C₈H₆BOF₆⁻ ([M]⁻) 243.04, found: 243.00.

Potassium (1,3-benzodioxol-5-ylmethyl)trifluoroborate

The titled compound was synthesized following Method A using 5-(Bromomethyl)-1,3-benzodioxole (2.15 g) as the starting material. The titled compound was obtained as a white powder, 1.52 g (63 % yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 1.37 ~ 1.42 (m, 2H), 5.83 (s, 2H), 6.42 (d, *J* = 10.0 Hz, 1H), 6.55 (s, 1H), 6.59 (d, *J* = 10.0 Hz, 1H). ¹¹B NMR (DMSO-*d*₆, 160 MHz, ppm): δ 11.03 (br, 1B). ¹⁹F NMR (DMSO-*d*₆, 470 MHz, ppm): δ -136.83 (br, 3F).

APCI-MS *m/z* calcd for C₈H₇BO₂F₃⁻ ([M]⁻) 203.05, found: 203.00.

3. C-C cross-coupling reactions between benzylic trifluoroborates and aryl halides

3.1 General Procedure

In the Ar filled glovebox, a reaction vial was charged with the aryl bromide (0.5 mmol, 1.0 eq.), trifluoroborate salt (0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy ligand (20 mg, 75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL). Two homemade RVC electrodes were immersed into the reaction mixture as anode and cathode. The electrocatalysis was performed at room temperature with a constant current of 3.0 mA maintained for 20 ~36 h. Monitor the reaction with TLC. After the reaction was done,

wash the RVC electrodes with EtOAc (2×5 mL) in an ultrasonic bath and combined with reaction mixture. The reaction mixture was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO_4 . Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel) or preparative TLC to afford the desired product.

3.2 Aryl halide scope

Methyl 4-benzylbenzoate (1)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl 4-bromobenzoate (108 mg) or methyl 4-chlorobenzoate (85.3 mg) as the starting material. The titled compound was obtained as colorless oil, 105 mg (93% yield) from methyl 4-bromobenzoate and 97 mg (86% yield) from methyl 4-chlorobenzoate.

A 2.5 mmol scale reaction was conducted in a 150 mL glass bottle, as shown in Figure S1. 0.75 g potassium benzyltrifluoroborate, 0.54 g methyl 4-bromobenzoate, 0.875 g K_2CO_3 , 55 mg $\text{NiCl}_2 \cdot \text{glyme}$, 0.1 g dtbbpy ligand, and 0.53 g LiClO_4 were dissolved in 30 mL dry DMF. The electrocatalysis was performed at room temperature with a constant current of 20 mA. The titled compound was obtained as colorless oil, 0.50 g (89% yield)

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.92 (s, 3H), 4.06 (s, 2H), 7.20 (d, $J = 10.0$ Hz, 2H), 7.24 (t, $J = 5.0$ Hz, 1H), 7.25 (d, $J = 10.0$ Hz, 2H), 7.32 (t, $J = 10.0$ Hz, 2H), 7.99 (d, $J = 5.0$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 41.93, 52.01, 126.38, 128.11, 128.36, 128.61, 128.95, 129.58, 129.83, 132.91, 140.12, 146.51, 167.05.

APCI-MS m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2^+$ ($[\text{M} + \text{H}]^+$) 227.10, found: 227.00.

Dimethyl 4,4'-biphenyldicarboxylate (1')

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.97 (s, 6H), 7.72 (d, $J = 5.0$ Hz, 4H), 8.16 (d, $J = 5.0$ Hz, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 52.23, 127.25, 129.70, 130.20, 144.36, 166.80.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4^+$ ($[\text{M}]^+$) 270.09, found: 270.00.

4-Acetyldiphenylmethane (2)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4'-bromoacetophenone (99.5 mg) or 4'-chloroacetophenone (77.3 mg) as the starting material and 2,2'-bpy as ligand. The titled compound was obtained as white solid, 96 mg (91% yield) from 4'-bromoacetophenone and 87 mg (83%) from 4'-chloroacetophenone.

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 2.60 (s, 3H), 4.06 (s, 2H), 7.20 (d, J = 10.0 Hz, 2H), 7.25 (t, J = 5.0 Hz, 1H), 7.28 ~ 7.34 (m, 4H), 7.91 (d, J = 10.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 26.58, 41.91, 126.41, 128.64, 128.94, 129.11, 135.27, 140.04, 146.80, 197.78.

APCI-MS m/z calcd for $\text{C}_{15}\text{H}_{15}\text{O}^+$ ($[\text{M} + \text{H}]^+$) 211.10, found: 211.05.

4-Benzylfluorobenzene (3)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromofluorobenzene (87.5 mg) or 4-chlorofluorobenzene (65.3 mg) as the starting material. The titled compound was obtained as light brown oil, 75 mg (81 % yield) from 4-bromofluorobenzene and 69 mg (74% yield) from 4-chlorofluorobenzene.

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.99 (s, 2H), 7.00 (t, J = 8.7 Hz, 2H), 7.14 ~ 7.23 (m, 4H), 7.24 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 41.10, 115.13, 115.30, 126.21, 128.54, 128.84, 130.26, 130.32, 136.76, 136.79, 140.95, 160.46, 162.40. ^{19}F NMR (CDCl_3 , 470 MHz, ppm): δ -117.43 ~ -117.37 (m, 1F).

APCI-MS m/z calcd for $\text{C}_{13}\text{H}_{11}\text{F}^+$ ($[\text{M}]^+$) 186.08, found: 186.05.



4-Benzylbenzene (4)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and bromobenzene (78.5 mg) or chlorobenzene (56.3 mg) as the starting material. The titled compound was obtained as colorless oil, 65 g (77 % yield) from bromobenzene and 39 mg (46% yield) from chlorobenzene.

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 4.03 (s, 2H), 7.20 ~ 7.27 (m, 6H), 7.33 (t, J = 10.0 Hz, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 41.97, 126.08, 128.47, 128.95, 141.13.

APCI-MS m/z calcd for $\text{C}_{13}\text{H}_{12}^+$ ($[\text{M}]^+$) 168.09, found: 168.05.

1-Methyl-4-benzylbenzene (5)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromotoluene (85.5 mg) or 4-chlorotoluene (63.3 mg) as the starting material. The titled compound was obtained as colorless oil, 78 g (86 % yield) from 4-bromotoluene and 28 mg (31% yield) from 4-chlorotoluene.

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 2.35 (s, 3H), 3.98 (s, 2H), 7.08 ~ 7.16 (m, 4H), 7.18 ~ 7.26 (m, 3H), 7.26 ~ 7.35 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 21.02, 41.53, 125.98, 128.43, 128.81, 128.87, 129.15, 135.54, 138.08, 141.42.

APCI-MS m/z calcd for $\text{C}_{14}\text{H}_{14}^+$ ($[\text{M}]^+$) 182.11, found: 182.10.

Methyl 3-benzylbenzoate (6)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl 3-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 80 mg (71% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.93 (s, 3H), 4.06 (s, 2H), 7.17 ~ 7.27 (m, 3H), 7.32 (t, *J* = 5.0 Hz, 2H), 7.37 ~ 7.42 (m, 2H), 7.92 (d, *J* = 5.0 Hz, 1H), 7.94 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.74, 52.09, 126.31, 127.45, 128.36, 128.56, 128.59, 128.89, 129.58, 130.05, 133.55, 140.50, 141.48, 167.15.

APCI-MS *m/z* calcd for C₁₅H₁₅O₂⁺ ([M + H]⁺) 227.10, found: 227.00.

Methyl 2-benzylbenzoate (7)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl 2-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 100 mg (89% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.85 (s, 3H), 4.42 (s, 2H), 7.15 ~ 7.24 (m, 3H), 7.27 ~ 7.36 (m, 4H), 7.46 (t, *J* = 5.0 Hz, 1H), 7.93 (d, *J* = 10.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 39.63, 51.94, 125.95, 126.26, 128.34, 128.91, 130.68, 131.57, 131.98, 140.92, 142.18, 168.10.

APCI-MS *m/z* calcd for C₁₅H₁₅O₂⁺ ([M + H]⁺) 227.10, found: 227.00.

1-Benzyl-4-tert-butylbenzene (8)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 1-bromo-4-tert-butylbenzene (106.6 mg) as the starting material. The titled compound was obtained as colorless oil, 81 mg (72% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.34 (s, 9H), 4.00 (s, 2H), 7.16 (d, *J* = 10.0 Hz, 2H), 7.20 ~ 7.26 (m, 3H), 7.29 ~ 7.36 (m, 4H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 31.41, 41.45, 125.36, 126.00, 128.43, 128.51, 128.98, 138.08, 141.29, 148.84.

APCI-MS *m/z* calcd for C₁₇H₂₀⁺ ([M]⁺) 224.06, found: 224.10.

1-Benzyl-4-methoxybenzene (9)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromoanisole (93.5 mg) as the starting material. The titled compound was obtained as colorless oil, 52 mg (53% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.81 (s, 3H), 3.95 (s, 2H), 6.86 (d, *J* = 10.0 Hz, 2H), 7.13 (d, *J* = 10.0 Hz, 2H), 7.17 ~ 7.24 (m, 3H), 7.31 (t, *J* = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.04, 55.26, 113.87, 125.97, 128.42, 128.81, 129.95, 133.25, 141.58, 157.96.

APCI-MS m/z calcd for $C_{14}H_{14}O^+$ ($[M]^+$) 189.10, found: 198.05.

Methyl 4-benzyl-2-methoxybenzoate (10)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl 4-bromo-2-methoxybenzoate (122.5 mg) as the starting material. The titled compound was obtained as white solid, 115 mg (90% yield).

1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.88 (s, 3H), 3.89 (s, 3H), 4.03 (s, 2H), 6.77 ~ 6.87 (m, 2H), 7.20 (d, J = 10.0 Hz, 2H), 7.25 (t, J = 5.0 Hz, 1H), 7.32 (t, J = 5.0 Hz, 2H), 7.77 (d, J = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 42.13, 51.91, 55.96, 112.69, 117.75, 120.85, 126.41, 128.59, 128.89, 131.97, 139.98, 147.42, 159.44, 166.56.

APCI-MS m/z calcd for $C_{16}H_{17}O_3^+$ ($[M + H]^+$) 257.11, found: 257.00.

4-Benzylbenzaldehyde (11)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromobenzaldehyde (92.5 mg) as the starting material and 2,2'-bpy as ligand. The titled compound was obtained as white solid, 80 mg (82% yield).

1H NMR ($CDCl_3$, 500 MHz, ppm): δ 4.09 (s, 2H), 7.22 (d, J = 5.0 Hz, 2H), 7.26 (t, J = 5.0 Hz, 1H), 7.34 (t, J = 10.0 Hz, 2H), 7.38 (d, J = 10.0 Hz, 2H), 7.84 (d, J = 5.0 Hz, 2H), 10.00 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 42.11, 126.53, 128.71, 128.99, 129.57, 130.05, 134.70, 139.77, 148.43, 191.93.

APCI-MS m/z calcd for $C_{14}H_{13}O^+$ ($[M + H]^+$) 197.09, found: 197.00.

4-Benzylbenzonitrile (12)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromobenzonitrile (91 mg) as the starting material and 2,2'-bpy as ligand. The titled compound was obtained as white solid, 71 mg (74% yield).

1H NMR ($CDCl_3$, 500 MHz, ppm): δ 4.06 (s, 2H), 7.19 (d, J = 10.0 Hz, 2H), 7.26 ~ 7.36 (m, 5H), 7.60 (d, J = 5.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 41.99, 110.07, 119.00, 126.68, 128.78, 128.97, 129.65, 132.31, 139.34, 146.74.

APCI-MS m/z calcd for $C_{14}H_{11}N^+$ ($[M]^+$) 193.09, found: 193.05.

1-Benzyl-4-(trifluoromethyl)benzene (13)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromobenzotrifluoride (113 mg) as the starting material and tpy as ligand. The titled compound was obtained as a mixture with 4,4'-bis-(trifluoromethyl)biphenyl (**13'**), 71 mg (21% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 4.06 (s, 2H), 7.20 (d, J = 10.0 Hz, 2H), 7.25 (t, J = 5.0 Hz, 1H), 7.30 ~ 7.36 (m, 4H), 7.56 (d, J = 10.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 41.72, 123.01, 125.40 (m), 126.46, 128.44 (m), 128.65, 128.92, 129.18, 139.96. ^{19}F NMR (CDCl_3 , 470 MHz, ppm): δ -62.38 (s, 3F).

APCI-MS m/z calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3^+$ ($[\text{M}]^+$) 236.08, found: 236.05.

4,4'-Bis-(trifluoromethyl)biphenyl (13'**)**

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromobenzotrifluoride (113 mg) as the starting material and dtbbpy as ligand. The titled compound was obtained as a white powder, 63 mg (87% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 7.75 (m, 8H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 125.17, 125.93 (m), 127.63, 130.17 (m), 143.25. ^{19}F NMR (CDCl_3 , 470 MHz, ppm): δ -62.60 (s, 6F).

APCI-MS m/z calcd for $\text{C}_{14}\text{H}_8\text{F}_6^+$ ($[\text{M}]^+$) 290.05, found: 290.00.

N-[4-(Phenylmethyl)phenyl]acetamide (14**)**

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4'-bromoacetanilide (107 mg) as the starting material. The titled compound was obtained as white powder, 97 mg (86% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 2.17 (s, 3H), 3.96 (s, 2H), 7.11 ~ 7.16 (m, 3H), 7.16 ~ 7.23 (m, 3H), 7.33 (t, J = 5.0 Hz, 1H), 7.51 (d, J = 10.0 Hz, 2H), 7.74 (brs, 1H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 24.52, 41.33, 120.31, 121.45, 126.11, 128.48, 128.87, 129.42, 131.89, 135.89, 137.11, 141.04, 168.59.

APCI-MS m/z calcd for $\text{C}_{15}\text{H}_{16}\text{NO}^+$ ($[\text{M} + \text{H}]^+$) 226.12, found: 226.00.

5-Benzyl-1,3-dihydro-2H-benzimidazol-2-one (15**)**

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 5-bromo-1,3-dihydrobenzimidazol-2-one (106.5 mg) as the starting material. The titled compound was obtained as white solid, 75 mg (67% yield).

¹H NMR (DMSO-*d*₆, 500 MHz, ppm): δ 3.90 (s, 2H), 6.73 (s, 1H), 6.76 ~ 6.85 (m, 2H), 7.17 (t, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 10.0 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 2H), 10.48 (s, 1H), 10.76 (s, 1H). ¹³C NMR (DMSO-*d*₆, 125 MHz, ppm): δ 41.51, 108.72, 109.19, 121.28, 126.28, 128.35, 128.81, 129.10, 129.46, 134.09, 142.36, 155.51.

APCI-MS *m/z* calcd for C₁₄H₁₂N₂O⁺ ([M]⁺) 224.09, found: 224.05.

4-Acetoxydiphenylmethane (16)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-bromophenyl tert-butyl carbonate (136.6 mg) as the starting material. The titled compound was obtained as colorless oil, 105 g (74 % yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.60 (s, 9H), 4.01 (s, 2H), 7.13 (d, *J* = 10.0 Hz, 2H), 7.20 ~ 7.26 (m, 5H), 7.33 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 27.74, 41.29, 83.44, 121.25, 126.22, 128.54, 128.97, 129.40, 129.82, 138.65, 140.80, 152.11.

APCI-MS *m/z* calcd for C₁₃H₁₁O⁺ ([M - Boc]⁺) 183.08, found: 183.10.

(4-benzyl)phenylbenzyl ether (17)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 4-benzylloxybromobenzene (131.6 mg) as the starting material. The titled compound was obtained as colorless oil, 97 g (71 % yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.03 (s, 2H), 5.12 (s, 2H), 7.01 (d, *J* = 10.0 Hz, 2H), 7.21 (d, *J* = 5.0 Hz, 2H), 7.27 ~ 7.32 (m, 3H), 7.38 (t, *J* = 5.0 Hz, 2H), 7.43 ~ 7.50 (m, 3H), 7.52 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.16, 70.12, 114.94, 126.09, 127.56, 127.99, 128.54, 128.66, 128.94, 129.99, 133.65, 137.28, 141.62, 157.33.

APCI-MS *m/z* calcd for C₂₀H₁₈O⁺ ([M]⁺) 274.14, found: 274.05.

2-(4-Benzylphenyl)-1,3-dioxolane (18)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 2-(4-bromophenyl)-1,3-dioxolane (114 mg) as the starting material. The titled compound was obtained as colorless oil, 170 g (83 % yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.02 (s, 2H), 4.04 ~ 4.08 (m, 2H), 4.12 ~ 4.18 (m, 2H), 5.82 (s, 1H), 7.20 (d, *J* = 10.0 Hz, 2H), 7.21 ~ 7.27 (m, 3H), 7.30 (t, *J* = 10.0 Hz, 2H), 7.43 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.73, 65.31, 103.73, 126.13, 126.62, 128.47, 128.95, 129.01, 135.71, 140.90, 142.23.

APCI-MS *m/z* calcd for C₁₆H₁₇O₂⁺ ([M + H]⁺) 241.12, found: 241.00.

Phenyl(p-vinylphenyl)methane (19)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl 4-bromostyrene (91.5 mg) as the starting material. The titled compound was obtained as colorless oil, 77 mg (79% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.02 (s, 2H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.76 (d, *J* = 20.0 Hz, 1H), 6.75 (dd, *J*₁ = 10.0 Hz, *J*₂ = 20.0 Hz, 1H), 7.17 ~ 7.27 (m, 5H), 7.34 (t, *J* = 5.0 Hz, 2H), 7.39 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.69, 113.23, 126.13, 126.36, 128.51, 128.93, 129.13, 135.55, 136.62, 140.84, 141.03.

APCI-MS *m/z* calcd for C₁₅H₁₄⁺ ([M]⁺) 194.11, found: 194.05.

3-Benzylfluorene (20)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 3-bromofluorene (122.5 mg) as the starting material. The titled compound was obtained as white solid, 111 mg (84% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.89 (s, 2H), 4.10 (s, 2H), 7.23 ~ 7.30 (m, 4H), 7.31 ~ 7.36 (m, 3H), 7.37 ~ 7.43 (m, 2H), 7.56 (d, *J* = 5.0 Hz, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 7.79 (d, *J* = 10.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 36.86, 42.11, 119.69, 119.80, 124.99, 125.64, 126.09, 126.40, 126.70, 127.64, 128.51, 128.96, 139.83, 139.85, 141.43, 141.63, 143.21, 143.69.

APCI-MS *m/z* calcd for C₂₀H₁₆⁺ ([M]⁺) 256.13, found: 256.00.

2-Benzylanthracene (21)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 2-bromonaphthalene (103 mg) as the starting material. The titled compound was obtained as white solid, 47 mg (43% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.20 (s, 2H), 7.15 ~ 7.30 (m, 3H), 7.32 ~ 7.38 (m, 3H), 7.46 ~ 7.52 (m, 2H), 7.69 (s, 1H), 7.80 ~ 7.88 (m, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 42.15, 125.38, 126.01, 126.18, 127.13, 127.58, 127.65, 127.67, 128.11, 128.53, 129.06, 132.12, 133.64, 138.63, 141.01.

APCI-MS *m/z* calcd for C₁₇H₁₄⁺ ([M]⁺) 218.11, found: 218.05.

6-Benzylquinoline (22)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 6-bromoquinoline (104 mg) as the starting material. The titled compound was obtained as white solid, 70 mg (64% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.18 (s, 2H), 7.20 ~ 7.28 (m, 3H), 7.32 ~ 7.38 (m, 3H), 7.56 ~ 7.62 (m, 2H), 8.07 (t, *J* = 10.0 Hz, 2H), 8.89 (d, *J* = 5.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.90, 121.17, 126.38, 126.80, 128.34, 128.63, 129.06, 129.56, 131.25, 135.67, 139.57, 140.44, 147.25, 149.91.

APCI-MS *m/z* calcd for C₁₆H₁₄N⁺ ([M + H]⁺) 220.10, found: 219.95.

6-Benzylisoquinoline (23)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 6-bromoisoquinoline (104 mg) as the starting material. The titled compound was obtained as white solid, 57 mg (52% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 4.19 (s, 2H), 7.21 ~ 7.28 (m, 3H), 7.34 (t, *J* = 5.0 Hz, 2H), 7.46 (d, *J* = 10.0 Hz, 1H), 7.72 (t, *J* = 10.0 Hz, 2H), 7.99 (d, *J* = 10.0 Hz, 1H), 8.51 (d, *J* = 5.0 Hz, 1H), 9.21 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 42.31, 120.47, 125.54, 126.48, 127.25, 127.64, 128.67, 129.06, 135.79, 139.97, 143.00, 143.19, 152.50.

APCI-MS *m/z* calcd for C₁₆H₁₄N⁺ ([M + H]⁺) 220.10, found: 220.00.

6-Benzyl-2-Boc-1,2,3,4-tetrahydroisoquinoline (24)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and 6-brom-2-Boc-1,2,3,4-tetrahydroisoquinoline (156 mg) as the starting material. The titled compound was obtained as white solid, 102 mg (63% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.52 (s, 9H), 2.82 (brs, 2H), 3.66 (brs, 2H), 3.97 (s, 2H), 4.56 (brs, 2H), 6.96 (s, 1H), 7.03 (d, *J* = 10.0 Hz, 1H), 7.08 (d, *J* = 10.0 Hz, 1H), 7.17 ~ 7.26 (m, 3H), 7.32 (t, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 28.52, 28.66, 40.70 ~ 41.97 (m), 41.60, 45.32 ~ 46.01 (m), 79.74, 126.11, 126.59, 127.01, 128.50, 128.74, 128.88, 132.50 ~ 133.64 (m), 139.15, 141.07, 154.92.

APCI-MS *m/z* calcd for C₂₁H₂₅NO₂⁺ ([M]⁺) 323.19, found: 323.10.

N-Boc-5-benzylindole (25)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and N-Boc-5-bromoindole (147.5 mg) as the starting material. The titled compound was obtained as white solid, 124 mg (81% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.69 (s, 9H), 4.10 (s, 2H), 6.52 (d, *J* = 5.0 Hz, 1H), 7.18 ~ 7.25 (m, 4H), 7.28 ~ 7.34 (m, 2H), 7.39 (s, 1H), 7.56 ~ 7.62 (s, 1H), 8.06 (d, *J* = 5.0 Hz, 1H). ¹³C

NMR (CDCl₃, 125 MHz, ppm): δ 28.21, 41.81, 83.55, 107.18, 115.06, 120.98, 125.46, 125.96, 126.09, 128.41, 128.89, 130.87, 133.73, 135.49, 141.73, 149.80.

APCI-MS m/z calcd for C₁₅H₁₃N⁺ ([M + H - Boc]⁺) 206.10, found: 207.10.

3.3 Benzylic trifluoroborates scope

4-Methoxycarbonyl-3'-methylphenylmethane (26)

The titled compound was synthesized following the general procedure using potassium trifluoro(3-methylbenzyl)borate (159 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 98 mg (82% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.34 (s, 3H), 3.92 (s, 3H), 4.02 (s, 2H), 6.95 ~ 7.03 (m, 2H), 7.06 (d, J = 10.0 Hz, 1H), 7.21 (t, J = 10.0 Hz, 1H), 7.28 (d, J = 10.0 Hz, 2H), 7.98 (d, J = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 21.40, 41.88, 52.01, 125.98, 127.12, 128.36, 128.49, 128.94, 129.72, 129.81, 138.24, 140.05, 146.67, 167.09.

APCI-MS m/z calcd for C₁₆H₁₇O₂⁺ ([M + H]⁺) 241.12, found: 241.05.

Methyl 4-[(4-methoxyphenyl)methyl]benzoate (27)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-methoxybenzyl)borate (171 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 102 mg (80% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.81 (s, 3H), 3.92 (s, 3H), 4.00 (s, 2H), 6.87 (d, J = 10.0 Hz, 2H), 7.12 (d, J = 10.0 Hz, 2H), 7.27 (d, J = 10.0 Hz, 2H), 7.99 (d, J = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.05, 52.01, 55.26, 114.04, 128.03, 128.84, 129.82, 129.93, 132.24, 147.05, 158.20, 167.10.

APCI-MS m/z calcd for C₁₆H₁₆O₃⁺ ([M]⁺) 256.11, found: 256.05.

Methyl 4-[(2-methoxyphenyl)methyl]benzoate (28)

The titled compound was synthesized following the general procedure using potassium trifluoro(2-methoxybenzyl)borate (171 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 98 mg (77% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.82 (s, 3H), 3.92 (s, 3H), 4.04 (s, 2H), 6.87 ~ 6.96 (m, 2H), 7.11 (d, J = 10.0 Hz, 1H), 7.16 (t, J = 10.0 Hz, 1H), 7.31 (d, J = 10.0 Hz, 2H), 7.97 (d, J = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 36.13, 51.94, 55.31, 110.52, 120.56, 127.81, 128.66, 128.88, 129.61, 130.50, 157.34, 161.00, 167.10.

APCI-MS m/z calcd for C₁₆H₁₇O₃⁺ ([M + H]⁺) 257.11, found: 257.00.

Methyl 4-[(3,5-dimethoxyphenyl)methyl]benzoate (29)

The titled compound was synthesized following the general procedure using potassium trifluoro(3,5-dimethoxybenzyl)borate (193.5 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 136 mg (95% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.77 (s, 6H), 3.92 (s, 3H), 3.98 (s, 2H), 6.35 (s, 3H), 7.29 (d, *J* = 5.0 Hz, 2H), 7.98 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 42.13, 52.02, 55.27, 98.19, 107.15, 128.16, 128.91, 129.81, 142.37, 146.13, 160.93.

APCI-MS *m/z* calcd for C₁₇H₁₉O₄⁺ ([M + H]⁺) 286.12, found: 268.85.

Methyl 4-[(4-methoxycarbonylphenyl)methyl]benzoate (30)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (192 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 125 mg (88% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.92 (s, 6H), 4.10 (s, 2H), 7.26 (d, *J* = 10.0 Hz, 4H), 7.99 (d, *J* = 10.0 Hz, 4H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.86, 52.06, 128.42, 128.97, 129.95, 145.43, 166.93.

APCI-MS *m/z* calcd for C₁₇H₁₇O₄⁺ ([M + H]⁺) 285.10, found: 285.00.

Methyl 4-(4-(trifluoromethyl)benzyl)benzoate (31)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-(trifluoromethyl)benzyl)borate (199 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 109 mg (74% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.93 (s, 3H), 4.11 (s, 2H), 7.27 (d, *J* = 10.0 Hz, 2H), 7.31 (d, *J* = 10.0 Hz, 2H), 7.58 (d, *J* = 5.0 Hz, 2H), 8.01 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 41.64, 52.07, 125.50, 125.53, 125.56, 125.59, 128.52, 128.96, 129.23, 130.00, 144.18, 145.24, 166.90. ¹⁹F NMR (CDCl₃, 470 MHz, ppm): δ -62.43 (s, 3F).

APCI-MS *m/z* calcd for C₁₆H₁₄F₃O₂⁺ ([M + H]⁺) 295.09, found: 295.00.

Methyl 4-(naphthalen-2-ylmethyl)benzoate (32)

The titled compound was synthesized following the general procedure using potassium trifluoro(naphthalen-2-ylmethyl)borate (186 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 99 mg (72% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.94 (s, 3H), 4.22 (s, 2H), 7.31 ~ 7.37 (m, 3H), 7.45 ~ 7.53 (m, 2H), 7.66 (s, 1H), 7.78 ~ 7.84 (m, 2H), 7.84 ~ 7.88 (m, 1H), 8.02 (d, *J* = 5.0 Hz, 2H).
¹³C NMR (CDCl₃, 125 MHz, ppm): δ 42.10, 52.04, 125.58, 126.16, 127.29, 127.57, 127.68, 127.92, 128.21, 128.31, 129.07, 129.88, 132.19, 133.66, 137.61, 146.38, 167.07.

APCI-MS *m/z* calcd for C₁₉H₁₆O₂⁺ ([M]⁺) 276.12, found: 276.05.

Methyl 4-[(benzyloxy)methyl]benzoate (33)

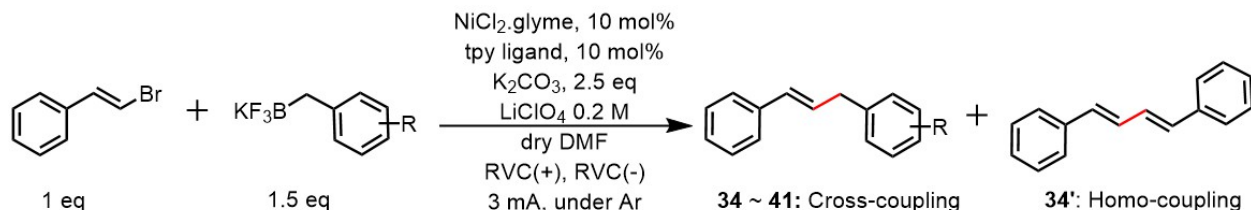
The titled compound was synthesized following the general procedure using potassium benzyloxymethyltrifluoroborate (171 mg) and methyl 4-bromobenzoate (108 mg) as the starting material. The titled compound was obtained as colorless oil, 60 mg (47% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.94 (s, 3H), 4.61 (s, 2H), 4.64 (s, 2H), 7.32 ~ 7.36 (m, 1H), 7.37 ~ 7.42 (m, 4H), 7.47 (d, *J* = 5.0 Hz, 2H), 8.06 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 52.10, 71.47, 72.51, 127.28, 127.80, 128.48, 128.68, 129.73, 137.91, 143.61, 166.97.

APCI-MS *m/z* calcd for C₁₆H₁₆O₃⁺ ([M]⁺) 256.11, found: 256.05.

4. C-C cross-coupling reaction between β-bromostyrene and benzylic trifluoroborates

4.1 General procedure



In an Ar filled glovebox, a microwave reaction tube was charged with the β-bromostyrene (92 mg, 0.5 mmol, 1.0 eq.), potassium benzylic trifluoroborate (0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), tpy ligand (11.7 mg, 50 μmol, 10 mol%), K₂CO₃ (173 mg, 1.25 mmol, 3.0 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL). Two RVC electrodes were immersed into the reaction mixture as anode and cathode. The electrolysis was performed at room temperature with a constant current of 3.0 mA maintained for 20 ~ 36 h. The RVC anode was washed with EtOAc (2 × 5 mL) in an ultrasonic bath, and combined with the reaction mixture. The reaction mixture was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO₄. Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel).

4.2 Reaction scope

3-(4-Methoxycarbonylphenyl)-1-phenylpropene (34)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (192 mg) as the starting material. The titled compound was obtained as white solid, 105 mg (83% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.63 (d, J = 5.0 Hz, 2H), 3.94 (s, 3H), 6.31 ~ 6.42 (m, 1H), 6.43 ~ 6.54 (m, 1H), 7.22 ~ 7.27 (m, 1H), 7.31 ~ 7.35 (m, 4H), 7.39 (d, J = 5.0 Hz, 2H), 8.02 (d, J = 5.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 39.29, 52.03, 126.16, 127.33, 128.04, 128.22, 128.56, 128.69, 129.85, 131.82, 137.19, 145.62, 167.00.

APCI-MS m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2^+$ ($[\text{M}]^+$) 252.12, found: 252.05.

1,4-Diphenylbutadiyne (34')

^1H NMR (MeCN-d_3 , 500 MHz, ppm): δ 6.71 ~ 6.81 (m, 2H), 7.04 ~ 7.12 (m, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 4H), 7.52 (d, J = 8.0 Hz, 4H). ^{13}C NMR (MeCN-d_3 , 125 MHz, ppm): 126.35, 127.64, 128.74, 129.34, 132.74, 137.42.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{14}^+$ ($[\text{M}]^+$) 206.11, found: 206.05.

(3-Phenylprop-1-en-1-yl)benzene (35)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) as the starting material. The titled compound was obtained as white solid, 71 mg (73% yield).

^1H NMR (MeCN-d_3 , 500 MHz, ppm): δ 3.57 (d, J = 5.0 Hz, 2H), 6.39 ~ 6.47 (m, 1H), 6.49 ~ 6.55 (m, 1H), 7.22 ~ 7.26 (m, 2H), 7.27 ~ 7.32 (m, 3H), 7.32 ~ 7.36 (m, 3H), 7.38 ~ 7.42 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 38.85, 126.02, 126.13, 127.15, 128.53, 128.58, 128.59, 129.54, 130.70, 137.56, 140.45.

APCI-MS m/z calcd for $\text{C}_{15}\text{H}_{14}^+$ ($[\text{M}]^+$) 194.11, found: 194.05.

1-methyl-3-(3-phenyl-2-propenyl)benzene (36)

The titled compound was synthesized following the general procedure using potassium trifluoro(3-methylbenzyl)borate (159 mg) as the starting material. The titled compound was obtained as white solid, 95 mg (92% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 2.38 (s, 3H), 3.56 (d, J = 10.0 Hz, 1.55H), 3.70 (d, J = 5.0 Hz, 0.29 H), 6.35 ~ 6.45 (m, 0.75H), 6.46 ~ 6.54 (m, 0.77H), 6.59 ~ 6.75 (m, 0.46H), 7.03 ~ 7.12 (m, 3H), 7.21 ~ 7.27 (m, 1.79H), 7.31 ~ 7.36 (m, 1.7H), 7.36 ~ 7.48 (m, 2.57H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 21.43, 39.34, 125.70, 126.15, 126.94, 127.09, 128.41, 128.51, 129.38, 129.45, 130.96, 132.84, 137.54, 140.12.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{16}^+$ ($[\text{M}]^+$) 208.13, found: 208.05.

1-Methoxy-2-(3-phenyl-2-propen-1-yl)benzene (37)

The titled compound was synthesized following the general procedure using potassium trifluoro(2-methoxybenzyl)borate (171 mg) as the starting material. The titled compound was obtained as white solid, 101 mg (90% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.59 (d, J = 10.0 Hz, 2H), 3.89 (s, 3H), 6.38 ~ 6.54 (m, 2H), 6.88 ~ 6.97 (m, 2H), 7.19 ~ 7.27 (m, 3H), 7.30 ~ 7.34 (m, 2H), 7.36 ~ 7.43 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 33.43, 55.41, 110.38, 120.55, 126.09, 126.90, 127.43, 128.45, 128.94, 129.87, 130.70, 137.80, 157.31.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}^+$ ($[\text{M}]^+$) 224.12, found: 224.05.

4-Methoxy-2-(3-phenyl-2-propen-1-yl)benzene (38)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-methoxybenzyl)borate (171 mg) as the starting material. The titled compound was obtained as colorless oil, 71 mg (63% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.52 (d, J = 5.0 Hz, 2H), 3.82 (s, 3H), 6.31 ~ 6.40 (m, 1H), 6.41 ~ 6.51 (m, 1H), 6.89 (d, J = 10.0 Hz, 2H), 7.19 (d, J = 5.0 Hz, 2H), 7.22 (t, J = 10.0 Hz, 1H), 7.31 (t, J = 10.0 Hz, 2H), 7.38 (d, J = 10.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 38.46, 55.30, 113.91, 126.10, 127.04, 128.48, 129.59, 129.67, 130.73, 132.18, 137.53, 158.07.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{16}\text{O}^+$ ($[\text{M}]^+$) 224.12, found: 224.05.

3,5-Dimethoxy-2-(3-phenyl-2-propen-1-yl)benzene (39)

The titled compound was synthesized following the general procedure using potassium trifluoro(3,5-dimethoxybenzyl)borate (193.5 mg) as the starting material. The titled compound was obtained as colorless oil, 91 mg (72% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.53 (d, J = 5.0 Hz, 2H), 3.82 (s, 6H), 6.29 ~ 6.54 (m, 5H), 7.24 (t, J = Hz, 1H), 7.33 (t, J = 10.0 Hz, 2H), 7.41 (d, J = 10.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 39.63, 55.31, 98.20, 106.71, 126.17, 127.14, 128.51, 128.84, 131.24, 137.46, 142.62, 160.91.

APCI-MS m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2^+$ ($[\text{M} + \text{H}]^+$) 255.14, found: 255.10.

5-(3-Phenyl-2-propen-1-yl)-1,3-benzodioxole (40)

The titled compound was synthesized following the general procedure using potassium (1,3-benzodioxol-5-ylmethyl)trifluoroborate (181.5 mg) as the starting material. The titled compound was obtained as white solid, 102 mg (86% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.51 (d, *J* = 5.0 Hz, 2H), 5.97 (s, 2H), 6.30 ~ 6.41 (m, 1H), 6.43 ~ 6.51 (m, 1H), 6.71 ~ 6.81 (m, 3H), 6.22 ~ 6.28 (m, 1H), 6.29 ~ 6.36 (m, 2H), 6.38 ~ 6.42 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 39.06, 100.87, 108.25, 109.20, 121.42, 126.15, 127.15, 128.53, 129.37, 130.99, 133.98, 137.46, 145.96, 147.74.

APCI-MS *m/z* calcd for C₁₆H₁₄O₂⁺ ([M]⁺) 238.10, found: 238.05.

1-cinnamyl-2-naphthalene (41)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-(trifluoromethyl)benzyl)borate (199 mg) as the starting material. The titled compound was obtained as colorless oil, 81 mg (67% yield).

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.78 (d, *J* = 5.0 Hz, 2H), 6.43 ~ 6.60 (m, 2H), 7.26 ~ 7.31 (m, 1H), 7.35 ~ 7.40 (m, 2H), 7.42 ~ 7.46 (m, 3H), 7.50 ~ 7.55 (m, 2H), 7.75 (s, 1H), 7.85 ~ 7.89 (m, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 39.53, 125.40, 126.22, 126.45, 126.81, 127.22, 127.52, 127.57, 127.70, 128.10, 128.59, 129.12, 131.38, 132.88, 133.74, 137.52, 137.71.

APCI-MS *m/z* calcd for C₁₉H₁₆⁺ ([M]⁺) 244.13, found: 244.05.

5. Late-stage functionalization of pharmaceuticals

Fenofibrate derivative (42)

The titled compound was synthesized following the general procedure using potassium trifluoro(2-methoxybenzyl)borate (171 mg) and Fenofibrate (180 mg) as the starting material. The titled compound was obtained as white powder, 161 mg (72% yield).

¹H NMR (MeCN-d₃, 500 MHz, ppm): δ 1.21 (d, *J* = 5.0 Hz, 6H), 1.64 (s, 6H), 3.82 (s, 3H), 4.05 (s, 2H), 5.02 ~ 5.09 (m, 1H), 6.90 (d, *J* = 10.0 Hz, 2H), 6.93 (t, *J* = 10.0 Hz, 1H), 6.99 (d, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 7.26 (t, *J* = 5.0 Hz, 1H), 7.37 (d, *J* = 10.0 Hz, 2H), 7.65 (d, *J* = 5.0 Hz, 2H), 7.73 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (MeCN-d₃, 125 MHz, ppm): δ 20.75, 24.71, 35.56, 55.07, 69.21, 79.31, 110.89, 120.57, 127.97, 128.54, 129.73, 130.38, 131.76, 146.16, 157.38, 159.30, 172.72, 194.55.

APCI-MS *m/z* calcd for C₂₈H₃₀O₅⁺ ([M]⁺) 446.21, found: 446.85.

Fenofibrate derivative (43)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-trifluoromethoxybenzyl)borate (211 mg) and Fenofibrate (180 mg) as the starting material. The titled compound was obtained as white powder, 197 mg (79% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 1.23 (d, J = 10.0 Hz, 6H), 1.68 (s, 6H), 4.07 (s, 2H), 5.08 ~ 5.13 (m, 1H), 6.88 (d, J = 10.0 Hz, 2H), 7.18 (d, J = 5.0 Hz, 2H), 7.24 (d, J = 10.0 Hz, 2H), 7.29 (d, J = 10.0 Hz, 2H), 7.73 (d, J = 5.0 Hz, 2H), 7.76 (d, J = 5.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 21.51, 25.37, 41.15, 69.30, 79.37, 117.17, 121.15, 128.72, 130.22, 130.24, 130.68, 131.96, 136.32, 138.94, 144.80, 147.79, 147.81, 159.50, 173.15, 195.00. ^{19}F NMR (CDCl_3 , 470 MHz, ppm): δ -57.91 (s, 3F).

APCI-MS m/z calcd for $\text{C}_{28}\text{H}_{28}\text{F}_3\text{O}_5^+$ ($[\text{M} + \text{H}]^+$) 501.18, found: 501.65.

Fenofibrate derivative (44)

The titled compound was synthesized following the general procedure using potassium benzyloxymethyltrifluoroborate (171 mg) and Fenofibrate (180 mg) as the starting material. The titled compound was obtained as white powder, 91 mg (41% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 1.23 (d, J = 5.0 Hz, 6H), 1.68 (s, 6H), 4.63 (s, 2H), 4.66 (s, 2H), 5.07 ~ 5.15 (m, 1H), 6.88 (d, J = 5.0 Hz, 2H), 7.34 (s, 1H), 7.38 ~ 7.42 (m, 4H), 7.50 (d, J = 5.0 Hz, 2H), 7.78 (t, J = 10.0 Hz, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 21.53, 25.39, 69.32, 71.56, 72.53, 79.39, 117.19, 127.22, 127.82, 128.50, 129.98, 130.70, 132.03, 137.42, 142.62, 159.55, 173.18, 195.25.

APCI-MS m/z calcd for $\text{C}_{28}\text{H}_{31}\text{O}_5^+$ ($[\text{M} + \text{H}]^+$) 447.21, found: 447.00.

Fenofibrate derivative (45)

The titled compound was synthesized following the general procedure using potassium trifluoro(4-trifluoromethylbenzyl)borate (200 mg) and Fenofibrate (180 mg) as the starting material. The titled compound was obtained as white powder, 210 mg (86% yield).

A 2.5 mmol scale reaction was conducted in a 150 mL bottle as shown in Figure S1. 1.0 g potassium trifluoro(4-trifluoromethylbenzyl)borate, 0.9 g Fenofibrate, 0.875 g K_2CO_3 , 55 mg $\text{NiCl}_2\cdot\text{glyme}$, 0.1 g dtbbpy ligand, and 0.53 g LiClO_4 were dissolved in 30 mL dry DMF. The electrocatalysis was performed at room temperature with a constant current of 20 mA. 0.93 g product was obtained (77 % yield)

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.23 (d, *J* = 10.0 Hz, 6H), 1.68 (s, 6H), 4.13 (s, 2H), 5.10 ~ 5.13 (m, 1H), 6.88 (d, *J* = 10.0 Hz, 2H), 7.30 (d, *J* = 5.0 Hz, 2H), 7.34 (d, *J* = 10.0 Hz, 2H), 7.58 (d, *J* = 5.0 Hz, 2H), 7.73 (d, *J* = 5.0 Hz, 2H), 7.78 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 21.52, 25.37, 41.65, 69.31, 79.39, 117.19, 125.52, 125.55, 125.58, 125.61, 128.77, 129.29, 130.29, 130.65, 131.98, 136.45, 144.29, 144.33, 159.54, 173.16, 195.07. ¹⁹F NMR (CDCl₃, 470 MHz, ppm): δ -62.39 (s, 3F).

APCI-MS *m/z* calcd for C₂₈H₂₇F₃O₄⁺ ([M]⁺) 484.19, found: 484.80.

Fenofibrate derivative (46)

The titled compound was synthesized following the general procedure using potassium trifluoro(3,5-dimethoxybenzyl)borate (193.5 mg) and Fenofibrate (180 mg) as the starting material. The titled compound was obtained as white powder, 193 mg (81% yield).

¹H NMR (MeCN-d₃, 500 MHz, ppm): δ 1.21 (d, *J* = 5.0 Hz, 6H), 1.64 (s, 6H), 3.75 (s, 6H), 3.98 (s, 2H), 4.98 ~ 5.11 (m, 1H), 6.37 (s, 1H), 6.45 (s, 2H), 6.90 (d, *J* = 5.0 Hz, 2H), 7.38 (d, *J* = 10.0 Hz, 2H), 7.67 (d, *J* = 5.0 Hz, 2H), 7.72 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (MeCN-d₃, 125 MHz, ppm): δ 20.77, 24.73, 26.54, 41.49, 54.93, 69.21, 79.33, 97.86, 107.00, 117.17, 117.30, 128.60, 129.90, 130.69, 131.79, 135.93, 143.07, 145.95, 159.34, 161.11, 172.71, 194.50.

APCI-MS *m/z* calcd for C₂₉H₃₂O₆⁺ ([M]⁺) 476.22, found: 476.90.

Clofibrate derivative (47)

The titled compound was synthesized following the general procedure using potassium trifluoro(3,5-dimethoxybenzyl)borate (193.5 mg) and Clofibrate derivative (143 mg) as the starting material. The titled compound was obtained as white powder, 193 mg (63% yield).

¹H NMR (MeCN-d₃, 500 MHz, ppm): δ 1.23 (t, *J* = 5.0 Hz, 3H), 1.54 (s, 3H), 1.57 (s, 3H), 3.77 (s, 3H), 3.85 (s, 2H), 4.18 ~ 4.22 (m, 2H), 6.77 (d, *J* = 10.0 Hz, 2H), 6.86 (d, *J* = 10.0 Hz, 2H), 7.11 (d, *J* = 10.0 Hz, 2H), 7.14 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (MeCN-d₃, 125 MHz, ppm): δ 13.37, 24.69, 39.61, 54.83, 61.17, 78.95, 113.82, 119.22, 121.02, 129.34, 129.62, 132.07, 133.82, 135.86, 153.69, 158.06, 173.74.

APCI-MS *m/z* calcd for C₂₀H₂₄O₄⁺ ([M]⁺) 328.17, found: 328.10.

Methyl (S)-3-(4-benzylphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (48)

The titled compound was synthesized following the general procedure using potassium benzyltrifluoroborate (150 mg) and methyl (S)-3-(4-bromophenyl)-2-((tert-butoxycarbonyl)amino)propanoate (200 mg) as the starting material. The titled compound was obtained as colorless oil, 170 g (83 % yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 1.42 (s, 9H), 1.45 (s, 9H), 3.05 (d, J = 5.0 Hz, 2H), 3.98 (s, 2H), 4.44 ~ 4.50 (m, 1H), 5.04 (d, J = 10.0 Hz, 1H), 7.09 ~ 7.17 (m, 4H), 7.21 (t, J = 5.0 Hz, 2H), 7.30 (t, J = 5.0 Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 27.96, 28.35, 38.19, 41.59, 54.89, 79.62, 81.96, 126.07, 128.45, 128.92, 129.57, 129.66, 134.12, 139.67, 141.16, 155.11, 171.04.

APCI-MS m/z calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3^+$ ($[\text{M} - \text{tBuO}]^+$) 338.18, found: 338.30.

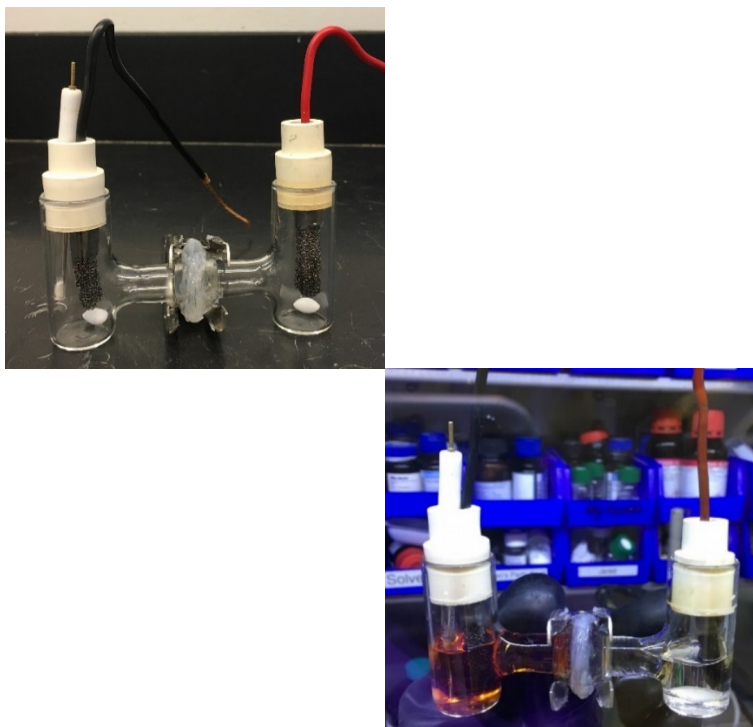
6. Flow cell synthesis of 46

As shown in Figure S2, the flow reactor was constructed with two home-made graphite electrolyte chambers, two graphite felt electrodes (SGL Carbon Group, Germany), a piece of home-made separator (0.6 mm Daramic membrane) sandwiched between graphite felts, and two copper current collectors. The carbon chambers were connected with an electrolyte reservoir using a piece of Viton tubing. The electrolyte reservoir is a home designed plastic tube. The active area of the cell was 10 cm^2 . A Masterflex L/S peristaltic pump (Cole-Parmer, Vernon Hills, IL) was used to press the Viton tubing to circulate the electrolytes through the electrodes at a flow rate of 60 mL/min. The reservoir and reaction mixture were purged with Ar to remove O_2 and then sealed before electrolysis.

Fenofibrate derivative (46)

A 8 mmol scale reaction was conducted in the flow reactor. 3.0 g potassium trifluoro(3,5-dimethoxybenzyl)borate, 2.88 g Fenofibrate, 2.8 g K_2CO_3 , 176 mg $\text{NiCl}_2\cdot\text{glyme}$, 0.32 g dtbbpy ligand, and 2.1 g LiClO_4 were dissolved in 80 mL dry DMF. The electrocatalysis was performed at room temperature with a constant current of 35 mA. 3.2 g product was obtained (84 % yield). The NMR and MS data are identical as previously described.

7. Carbon free radical trapping experiment



In an Ar filled glovebox, a glass H cell was divided by a 0.16 mm Daramic membrane. The anode side was charged with TEMPO free radical (234 mg, 1.5 mmol, 3 eq.), potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (128 mg, 0.5 mmol, 1 eq.), LiClO₄ (106 mg, 0.2 M), and DMF (5 mL). The cathode side was charged with LiClO₄ (106 mg, 0.2 M) and DMF (5 mL). A RVC electrode and Ag/Ag⁺ electrode were immersed into the anolyte as anode and reference electrode, respectively. A RVC electrode was immersed into the catholyte as cathode. The electrolysis was performed at room temperature with CPE at 1.2 V (vs. Fc⁺⁰) until the overall charge reach 140 C. The RVC anode was washed with EtOAc (2 × 5 mL) in an ultrasonic bath and mixed with the reaction solution. The solution in both side was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO₄. Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel). 131 mg compound **49** (86% yield) was obtained.

Methyl 4-[(2,2,6,6-tetramethyl-1-piperidinyl)oxy]methyl] benzoate (49)

¹H NMR (CDCl₃, 500 MHz, ppm): δ 1.19 (s, 6H), 1.25 (s, 6H), 1.33 ~ 1.42 (m, 1H), 1.46 ~ 1.58 (m, 4H), 1.58 ~ 1.65 (m, 1H), 3.94 (s, 3H), 4.91 (s, 2H), 7.44 (d, *J* = 10.0 Hz, 2H), 8.03 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 17.10, 20.30, 33.05, 39.71, 52.05, 60.07, 78.18, 126.87, 128.97, 129.57, 143.67, 167.04.

APCI-MS *m/z* calcd for C₁₈H₂₈NO₃⁺ ([M + H]⁺) 306.20, found: 306.10.

8. C-C coupling reactions between other substrates

In an Ar filled glovebox, a microwave reaction tube was charged with the methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq.), phenylacetic acid (102 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy ligand (20 mg, 75 μmol, 15 mol%), Cs₂CO₃ (488 mg, 1.5 mmol, 3.0 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL). Two RVC electrodes were immersed into the reaction mixture as anode and cathode. The electrolysis was performed at room temperature with a constant current of 3.0 mA maintained for 30 h. The RVC anode was washed with EtOAc (2 × 5 mL) in an ultrasonic bath and combined with the reaction solution. The reaction mixture was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO₄. Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel). Obtained 20 mg compound **1** (17% yield) and 82 mg compound **1'** (61% yield).

In an Ar filled glovebox, a microwave reaction tube was charged with the methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq.), potassium phenyltrifluoroborate (138 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy ligand (20 mg, 75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL). Two RVC electrodes were immersed into the reaction mixture as anode and cathode. The electrocatalysis was performed at room temperature with a constant current of 3.0 mA maintained for 30 h. The RVC anode was washed with EtOAc (2 × 5 mL) in an ultrasonic bath and combined with the reaction mixture. The reaction mixture was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO₄. Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel). Only obtained 75 mg compound **1'** (56% yield).

In an Ar filled glovebox, a microwave reaction tube was charged with 1-chlorobutane (46 mg, 0.5 mmol, 1.0 eq.), potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (192 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy ligand (20 mg, 75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL). Two RVC electrodes were immersed into the reaction mixture as anode and cathode. The electrolysis was performed at room temperature with a constant current of 3.0 mA maintained for 30 h. The RVC anode was washed with EtOAc (2 × 5 mL) in an ultrasonic bath and combined with the reaction mixture. The reaction mixture was diluted with EtOAc, washed with saturated NaCl solution and dried over MgSO₄. Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel). Only obtained 46 mg compound **50** (62% yield).

Methyl 4-[2-(4-methoxycarbonylphenyl)ethyl]benzoate (50)

¹H NMR (CDCl₃, 500 MHz, ppm): δ 3.01(s, 4H), 3.93 (s, 6H), 7.22, (d, *J* = 5.0 Hz, 4H), 7.96 (d, *J* = 5.0 Hz, 4H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 37.42, 52.02, 128.12, 128.53, 129.74, 146.49, 167.06.

APCI-MS *m/z* calcd for C₁₈H₁₉O₄⁺ ([M + H]⁺) 299.12, found: 299.05.

9. Electrochemical Studies

9.1 Electrochemical CV measurement

CV measurements were performed on a Gamry Instruments 1000 electrochemical workstation with a three-electrode cell system, in which a glassy carbon electrode (GC) was used as the working electrode, a carbon rod as counter electrode, and an Ag/Ag⁺ electrode as reference electrode with ferrocenium-ferrocene (Fc⁺⁰) as an internal standard. CV measurements were carried out in DMF containing 0.2 M LiClO₄ as a supporting electrolyte. All potentials were referenced to the internal standard Fc⁺⁰. CV scans were recorded at a rate of 100 mV/s. Before the CV testing, the working electrode was polished using Al₂O₃ (BAS CF-1050) suspended in deionized H₂O, then rinsed with deionized H₂O and dried with an air flow. The reference electrode consisted of a silver wire suspended in a solution of 0.2 M LiClO₄ and 0.01 M AgNO₃ in dry DMF.

9.2 Electrochemical kinetics study

The exchange current *i*₀ can be expressed as following equation (eq. 1):

$$\begin{aligned} E \\ -\alpha f (E_{eq} - E^0) \\ i_0 = F k^0 C_o^i e^{\frac{i}{i_0}} \end{aligned} \quad (1)$$

where $f = F/RT$.

Together with Nernst Equation (eq. 2):

$$E_{eq} = E^0 + \frac{RT}{F} \ln \frac{C_o^i}{C_R^i} \quad (2)$$

Substitution of eq. 2 into eq.1 gives eq. 3,

$$i_0 = F k^0 C_o^{i(1-\alpha)} C_R^{i\alpha} \quad (3)$$

At equilibrium potential, $C_o = C_o^* = C_R^*$.

$$\text{Then, } i_0 = F k^0 C_o \quad (4)$$

The X-intercept of the fitted Tafel plot (η vs $\log i$, Tafel Equation, eq. 5) gives the log of the exchange current i_0 . And according to eq. 4, electron transfer rate constant k^0 can be figured out. Meanwhile, the Tafel slope (b in eq. 5) with unit of volts per decade of current represents the increment of overpotential needed to increase the reaction rate tenfold.

$$\eta = a + b \log i \quad (5)$$

$$\text{where, } a = \frac{-2.303 RT}{(1-\alpha)F} \log i_0, \quad b = \frac{2.303 RT}{(1-\alpha)F}.$$

Corresponding parameters in eq. 1– 5 are defined as follows: F is Faraday constant (96,485 C/mol), C_o is the concentration of the substrates, i is the electrode current density (mA/cm²), i_0 is the exchange current density (mA/cm²), η is the overpotential (V), α is the ionic transference number, and k^0 is the electron transfer rate constant (cm/s).

10. Control experiments and optimization studies

Table S1. Control experiments for the C(sp²)-C(sp³) cross-coupling reaction

Entry	Variation from standard conditions ^a	Conversion (%) ^b	Yield (%) ^c	Selectivity (%) ^b
1	None	100	93	95
2	No dtbbpy ligand	0	0	---
3	No Ni(DME) ₂ Cl ₂	0	0	---
4	Na ₂ CO ₃ instead of K ₂ CO ₃	100 (48 h)	78	81

5	KOAc instead of K ₂ CO ₃	100	0	0 ^d
7	No K ₂ CO ₃	100	47	55
8	TBAPF ₆ instead of LiClO ₄	100 (20 h)	74	82
9	KPF ₆ instead of LiClO ₄	100 (22 h)	89	91
10	NaBF ₄ instead of LiClO ₄	100 (20 h)	75	79
9	No current	0	0	---
6	1.0 mA current electrolysis	100 (48 h)	48	64
7	5.0 mA current electrolysis	100	76	77

^aStandard conditions: methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq.), potassium benzyltrifluoroborate (149 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy (20 mg, 75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL), RVC as anode and cathode, 3.0 mA current under Ar at room temperature for 28 h. ^bConversion and selectivity were measured by ¹H-NMR using 4-bromobenzaldehyde as internal standard, and the byproduct is the dimethyl 4,4'-biphenyldicarboxylate (**1'**). ^cIsolated yield. ^d**1'** as the only product (86% yield).

Table S2. Screening of solvent for the C(sp²)-C(sp³) cross-coupling reaction^a

Entry	Solvent	Conversion (%) ^b	Yield (%) ^c	Selectivity (%) ^b
1	DMF	100	93	95
2	DMSO	20	15	70
3	MeCN	0	0	---
4	CH ₂ Cl ₂	0	0	---
5	MeOH	0	0	---

^aStandard conditions: methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq.), potassium benzyltrifluoroborate (149 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), dtbbpy ligand (20 mg, 75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), solvent (5 mL), RVC as anode and cathode, 3.0 mA current under Ar at room temperature for 28 h. ^bConversion and selectivity were measured by ¹H-NMR using 4-

bromobenzaldehyde as internal standard, and the byproduct is the dimethyl 4,4'-biphenyldicarboxylate (**1'**). ^cIsolated yield.

Table S3. Screening of polypy ligands for the C-C cross-coupling reaction.^a

Entry	Ligand	Conversion (%) ^b	Yield (%) ^c	Selectivity (%) ^b
1	dtbbpy	100	93	95
2	dmbpy	0	0	---
3	2,2'-bpy	100	87	88
4	dmcbpy	0	0	---
5	1,10-Phen	100	77	81
6	bip	0	0	---
7	tpy ^d	100	73	96

^aMethyl 4-bromobenzoate (108 mg, 0.5 mmol, 1 eq.), potassium benzyltrifluoroborate (149 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μmol, 10 mol%), ligand (75 μmol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL), RVC as anode and cathode, 3.0 mA current under Ar at room temperature for 28 h. ^bConversion was measured by ¹H-NMR using 4-bromobenzaldehyde as internal standard, and the byproduct is the dimethyl 4,4'-biphenyldicarboxylate (**1'**). ^cIsolated yield. ^d50 μmol, 10 mol% tpy was used.

Table S4. Screening of ligand in C-C cross-coupling reaction between β-bromostyrene and potassium trifluoro(4-(methoxycarbonyl)benzyl)borate^a

Entry	Ligand	Conversion (%) ^b	Yield (%) ^c	Selectivity (%) ^b
1	dtbbpy	100	48	52
2	2,2'-bpy	100	26	35
3	1,10-Phen	100	64	81
4	tpy ^d	100	83	90

^aStandard conditions: β -Bromostyrene (92 mg, 0.5 mmol, 1.0 eq.), potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (192 mg, 0.75 mmol, 1.5 eq.), $\text{NiCl}_2\cdot\text{glyme}$ (11 mg, 50 μmol , 10 mol%), ligand (75 μmol , 15 mol%), K_2CO_3 (173 mg, 1.25 mmol, 2.5 eq.), LiClO_4 (106 mg, 0.2 M), DMF (5 mL), RVC as anode and cathode, 3 mA current under Ar at room temperature for 28 h. ^bConversion was measured by ^1H -NMR using 4-bromobenzaldehyde as internal standard, and the byproduct is 1,4-diphenylbutadiyne (**34'**). ^cIsolated yield. ^d50 μmol , 10 mol% tpy was used.

11. Supporting Figures

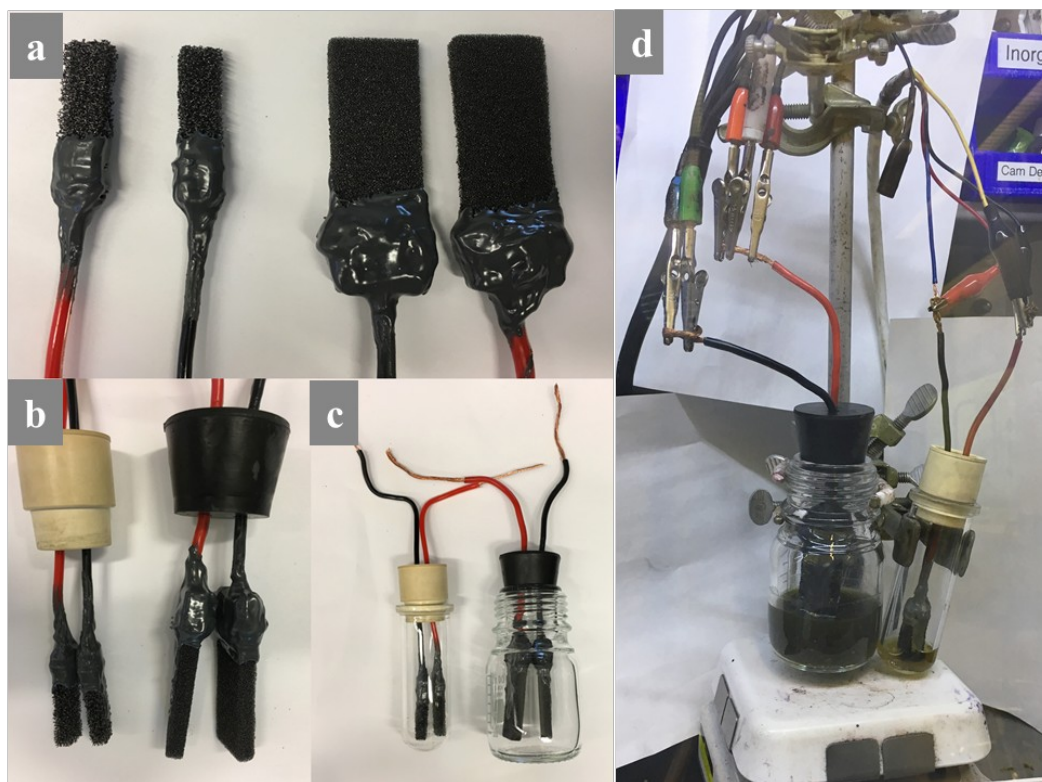


Figure S1. Electrodes (a and b) and reaction setups (c and d) for 0.5 mmol and 2.5 mmol scale reactions in a vial and a bottle.

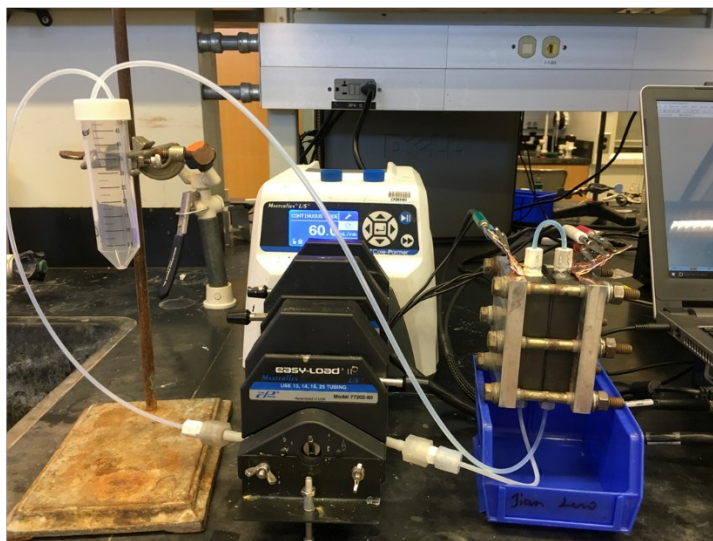


Figure S2. Reaction setup for the follow-cell synthesis.

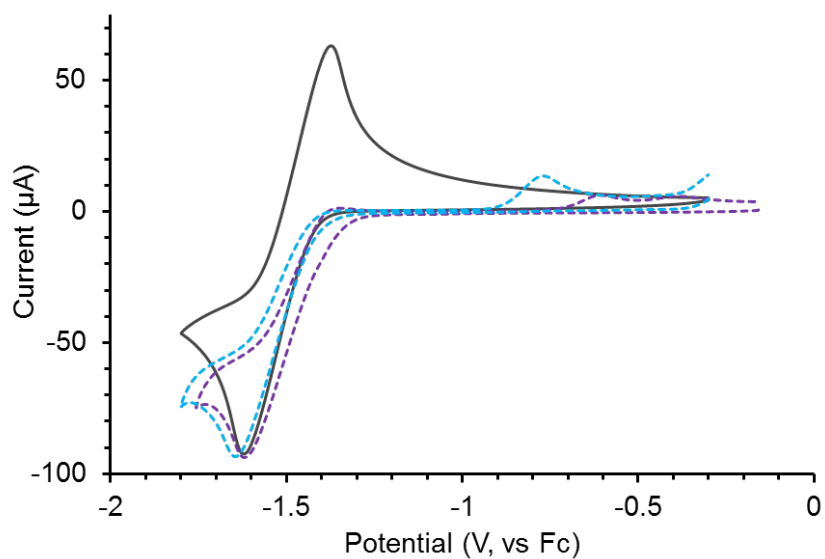


Figure S3. CV curve of 5 mM $\text{NiCl}_2 \cdot \text{glyme}$ and 15 mM 2,2'-bpy (gray) and after addition of 50 mM n-butyl bromide (light blue) or t-butyl bromide (purple). DMF solvent, 0.2 M LiClO_4 supporting electrolyte, GC working electrode, 100 mV/s scan rate.

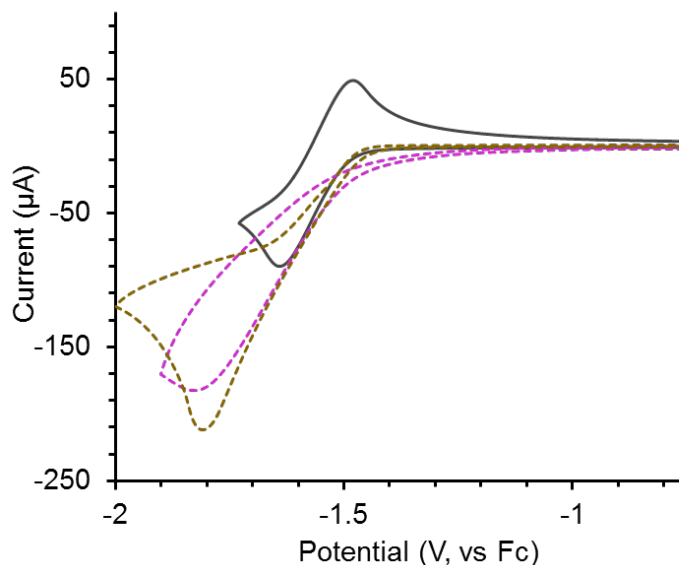


Figure S4. CV curve of 5 mM $\text{NiCl}_2 \cdot \text{glyme}$ and 15 mM 2,2'-bpy (gray) and after addition of 50 mM β -bromostyrene (yellow) and methyl 3-bromopropiolate (purple). DMF solvent, 0.2 M LiClO_4 supporting electrolyte, GC working electrode, 100 mV/s scan rate.

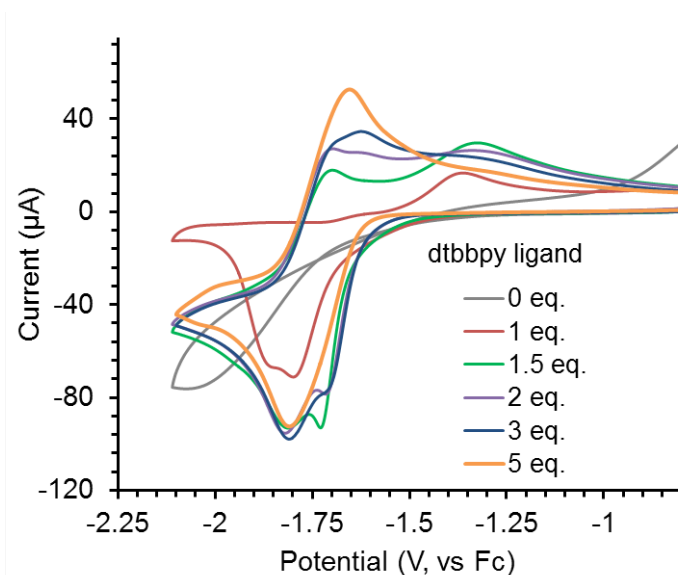


Figure S5. CV curves of 5 mM $\text{NiCl}_2 \cdot \text{glyme}$ in the presence of different ratio of dtbbpy ligand. The CV curves were recorded in DMF solvent with 0.2 M LiClO_4 supporting electrolyte. GC working electrode, 100 mV/s scan rate.

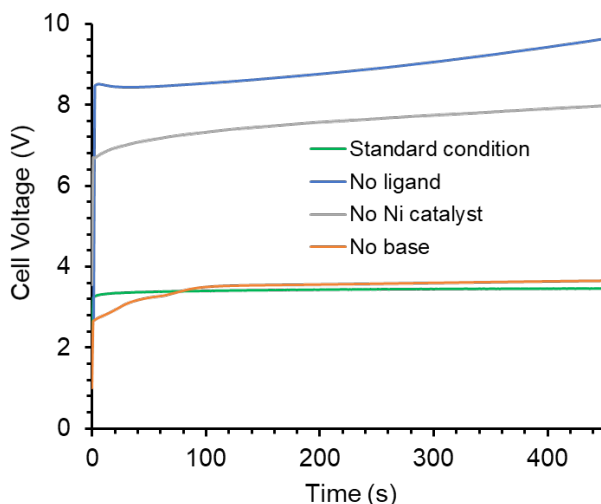


Figure S6. Cell voltage changes at the initial stage of Chronopotentiometry electrolysis under different reaction conditions. Standard conditions: methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq.), potassium benzyltrifluoroborate (149 mg, 0.75 mmol, 1.5 eq.), NiCl₂.glyme (11 mg, 50 μ mol, 10 mol%), dtbbpy (20 mg, 75 μ mol, 15 mol%), K₂CO₃ (173 mg, 1.25 mmol, 2.5 eq.), LiClO₄ (106 mg, 0.2 M), DMF (5 mL), RVC as anode and cathode, 3 mA current under Ar at room temperature for 28 h.

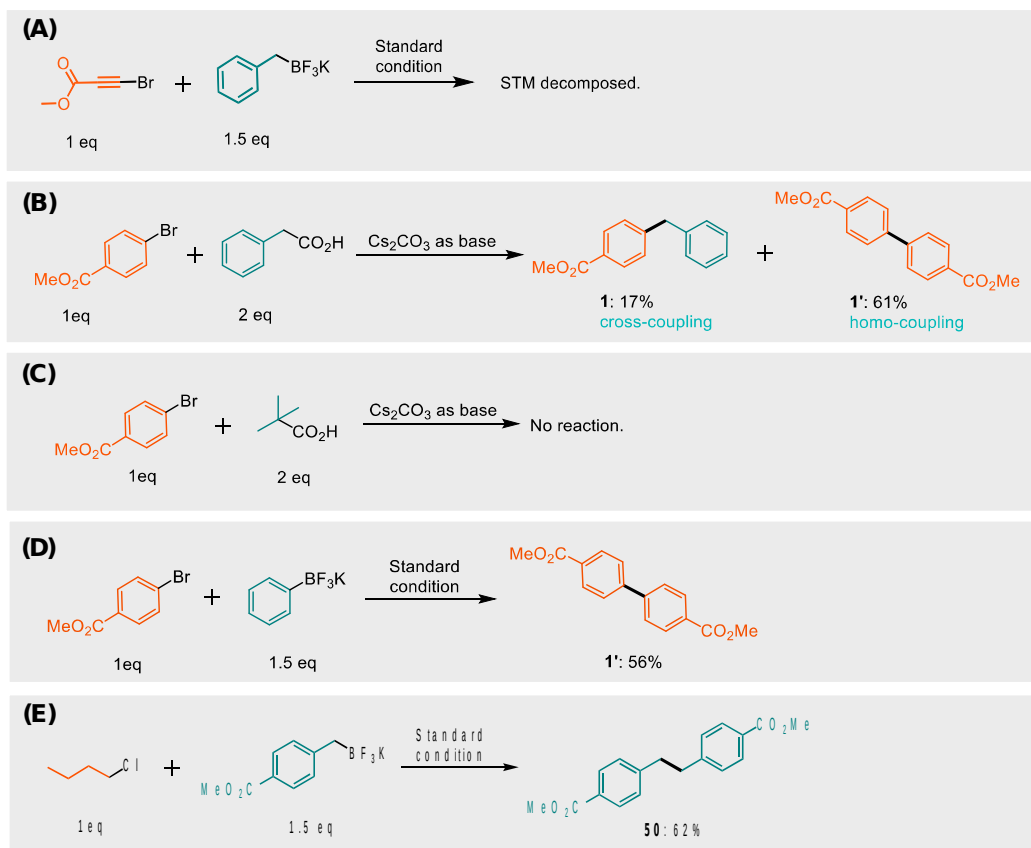


Figure S7. Electrolysis of other substrates under the standard conditions. **(A)** Reaction between potassium benzyltrifluoroborate and methyl 3-bromopropynoate. **(B)** Reaction between

phenylacetic acid and methyl 4-bromobenzoate (3.0 eq. of Cs_2CO_3 was used to replace K_2CO_3 in the standard condition). (C) Reaction between pivalic acid and methyl 4-bromobenzoate (3.0 eq. of Cs_2CO_3 was used to replace K_2CO_3 in the standard condition). (D) Reaction between potassium phenyltrifluoroborate and methyl 4-bromobenzoate. (E) Reaction between potassium benzyltrifluoroborate and 1-chlorobutane. Yields refer to isolated yields of products after chromatography on silica gel.

Note for Figure S7. When methyl 3-bromopropiolate was used as electrophile (Figure S7A), no desired product was observed, it is due to the instability of methyl 3-bromopropiolate at room temperature. Potassium phenylacetate showed irreversible oxidation behavior with peak potential of 0.94 V vs $\text{Fc}^{+/0}$ (Figure 2B(ii)). When phenylacetic acid was used as anodic half-reaction substrate and Cs_2CO_3 was used as base, only 17% yield of desired $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ cross-coupling product **1** was isolated while 61% yield of undesired homo-coupling product **1'** was obtained (Figure S7B). Despite the oxidation reactivity of potassium pivalate in the anodic half-cell reaction (Figure 2B(ii)), no reaction happened between pivalic acid and methyl 4-bromobenzoate under the standard conditions (Figure S7C). It was found that the poor solubility of Cesium pivalate in DMF impedes the electrochemical reaction. In addition, when potassium phenyltrifluoroborate was used as nucleophile (Figure S7D) or 1-chlorobutane was used as electrophile (Figure S7E), homo-coupling products **1'** or **50** were obtained as the only product, respectively, instead of cross-coupling product, which is consistent with the early electrochemical screening studies where phenyl trifluoroborates and alkyl halides are not effective nucleophiles and electrophiles, respectively.

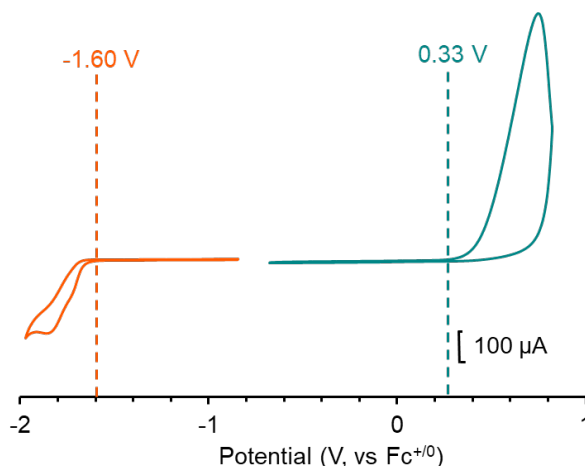


Figure S8. CV curves of a solution with 5 mM $\text{NiCl}_2\cdot\text{glyme}$, 7.5 mM dtbbpy, 50 mM methyl 4-bromobenzoate, and 75 mM potassium benzyltrifluoroborate in DMF with 0.2 M LiClO_4 at the negative range (orange) and positive range (blue). The half-reactions displayed onset potentials at -1.60V and 0.33V vs $\text{Fc}^{+/0}$, respectively.

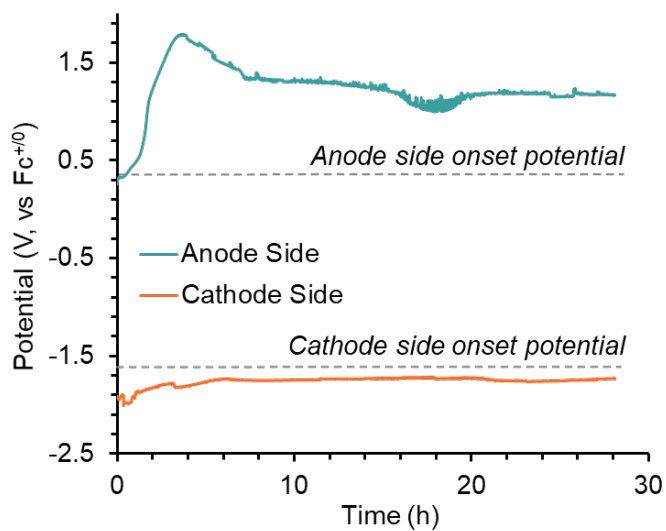
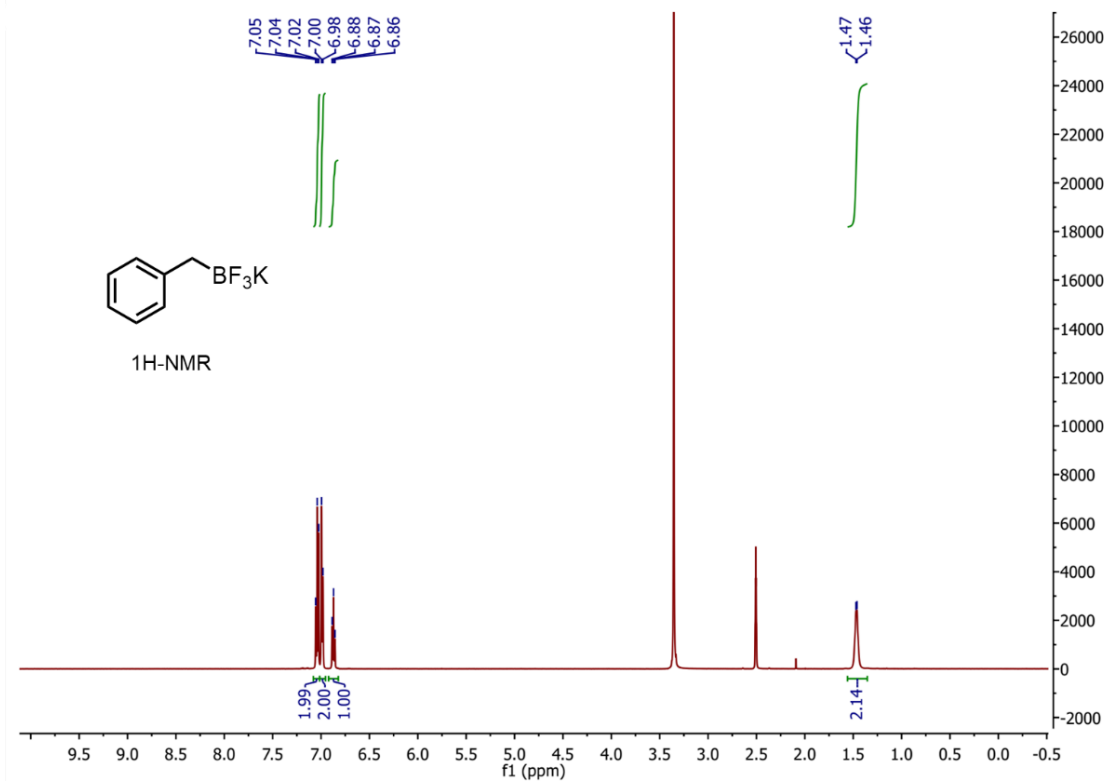


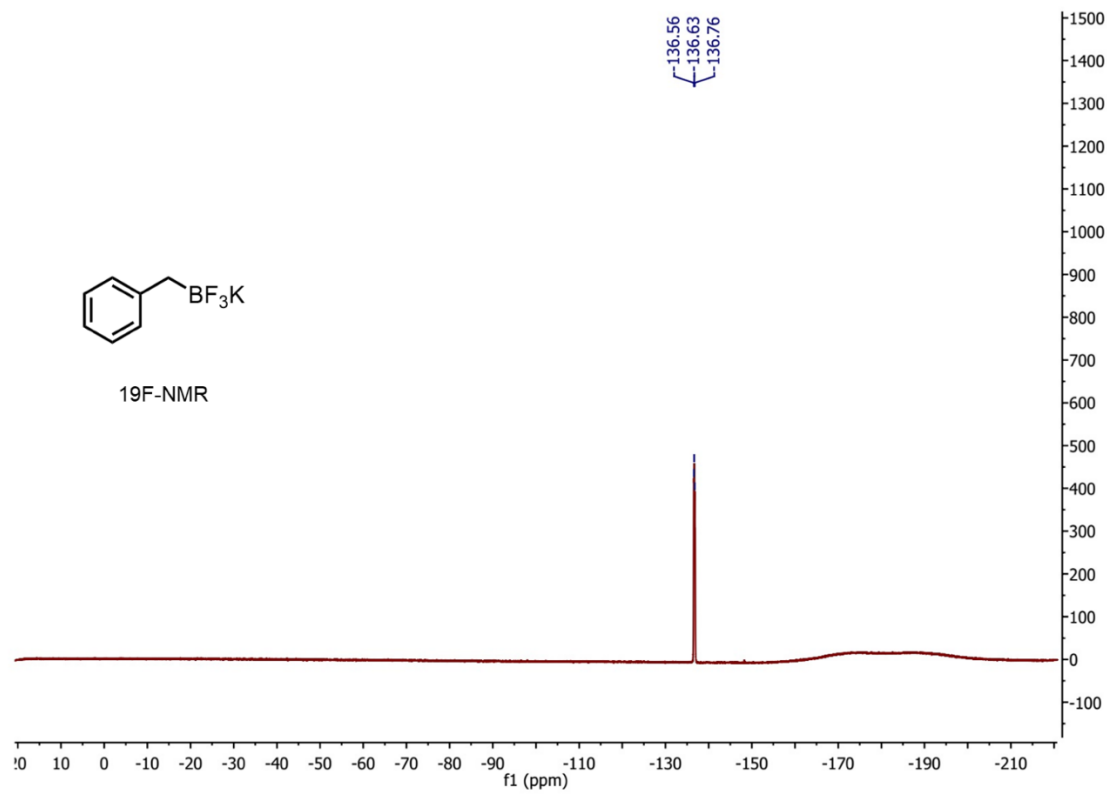
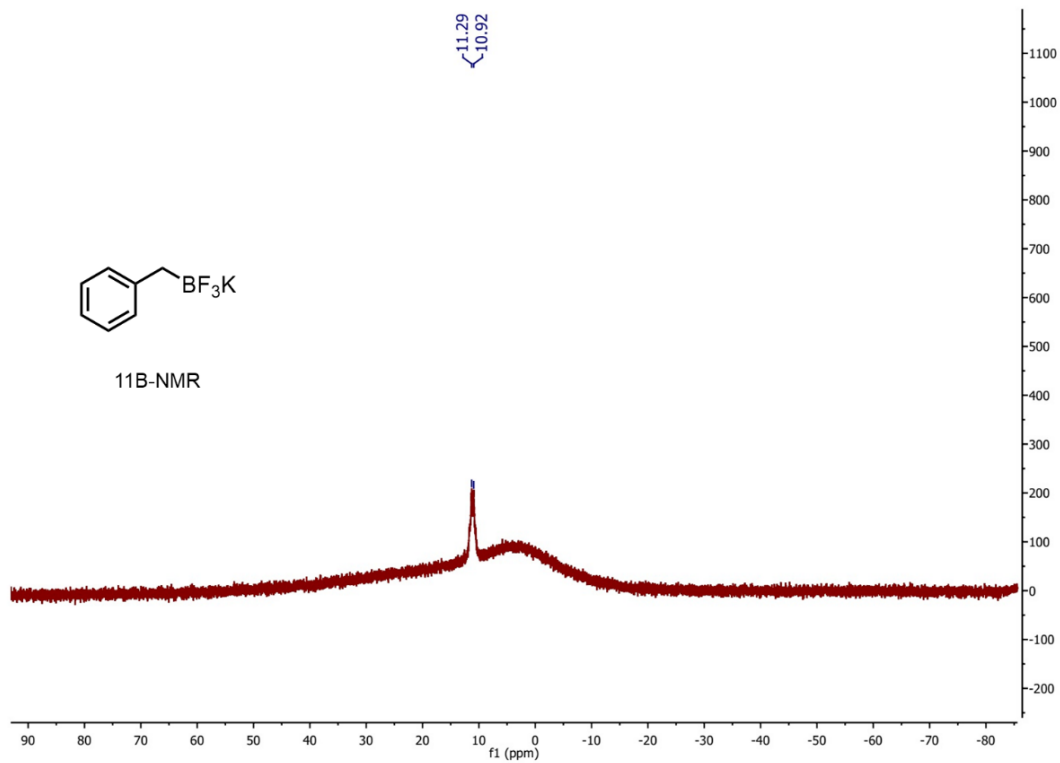
Figure S9. Potential changes of cathode and anode during the electrolysis.

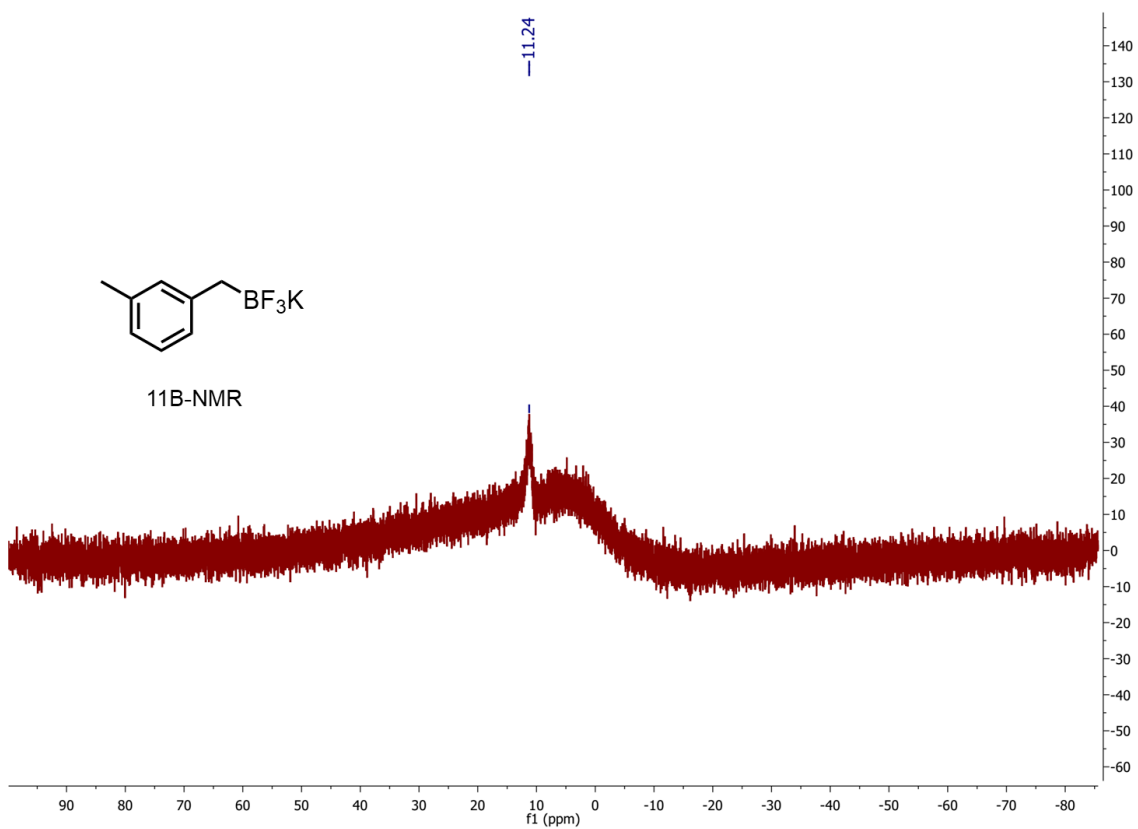
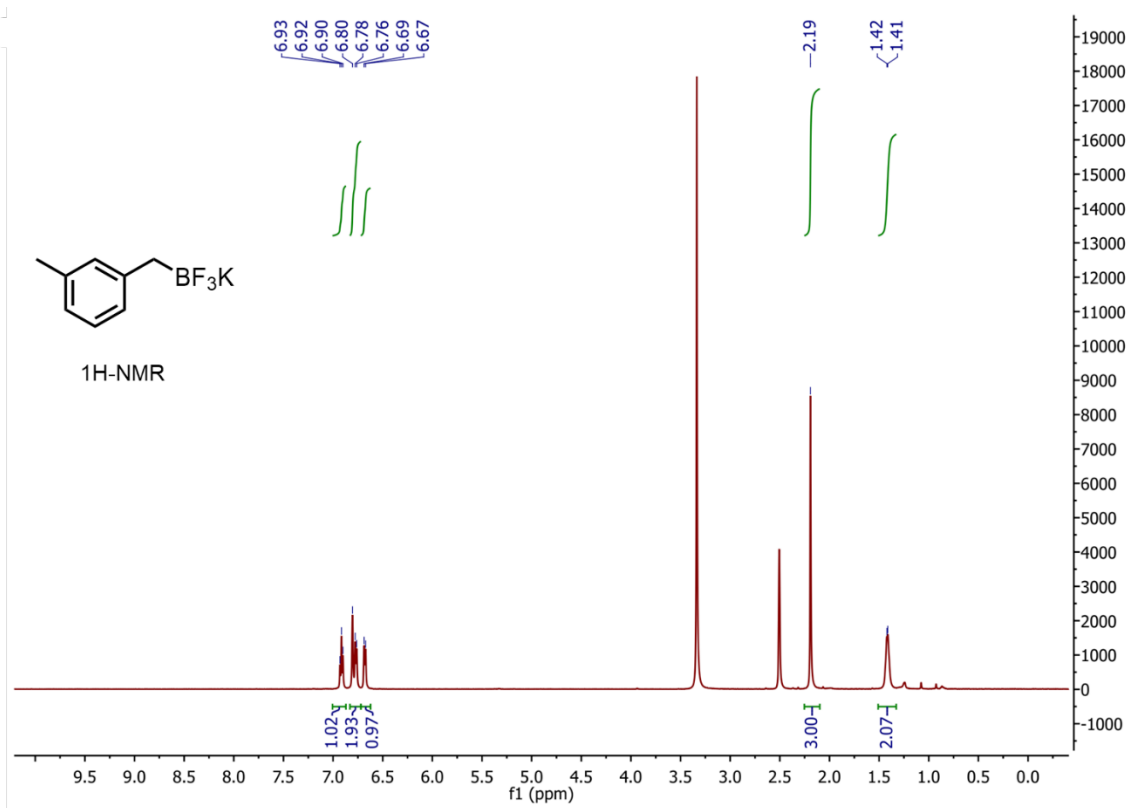
12. References

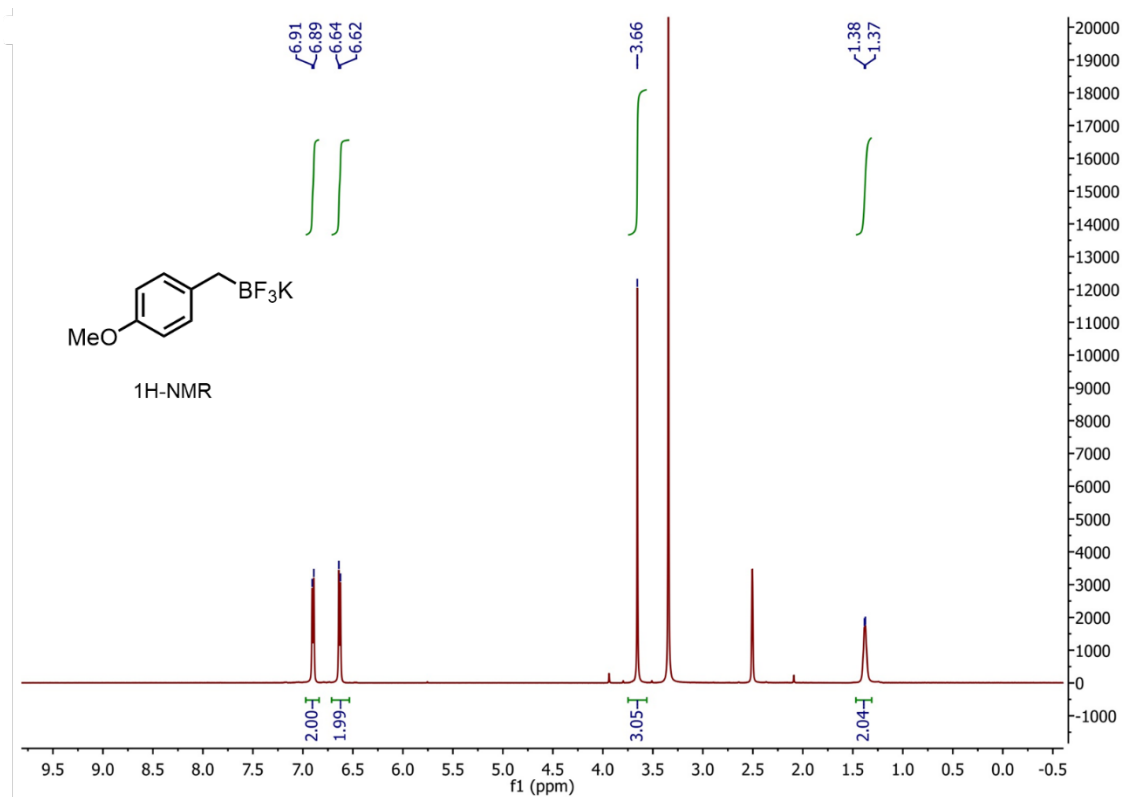
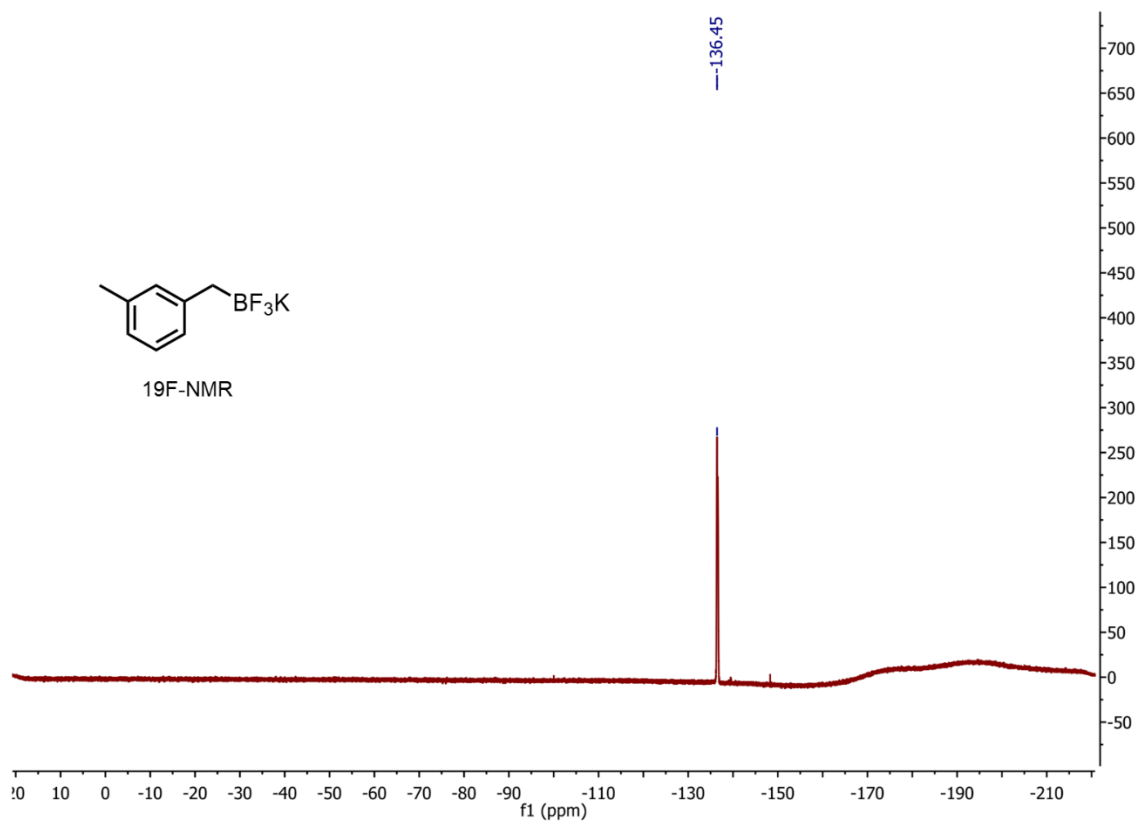
[1] Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433–436.

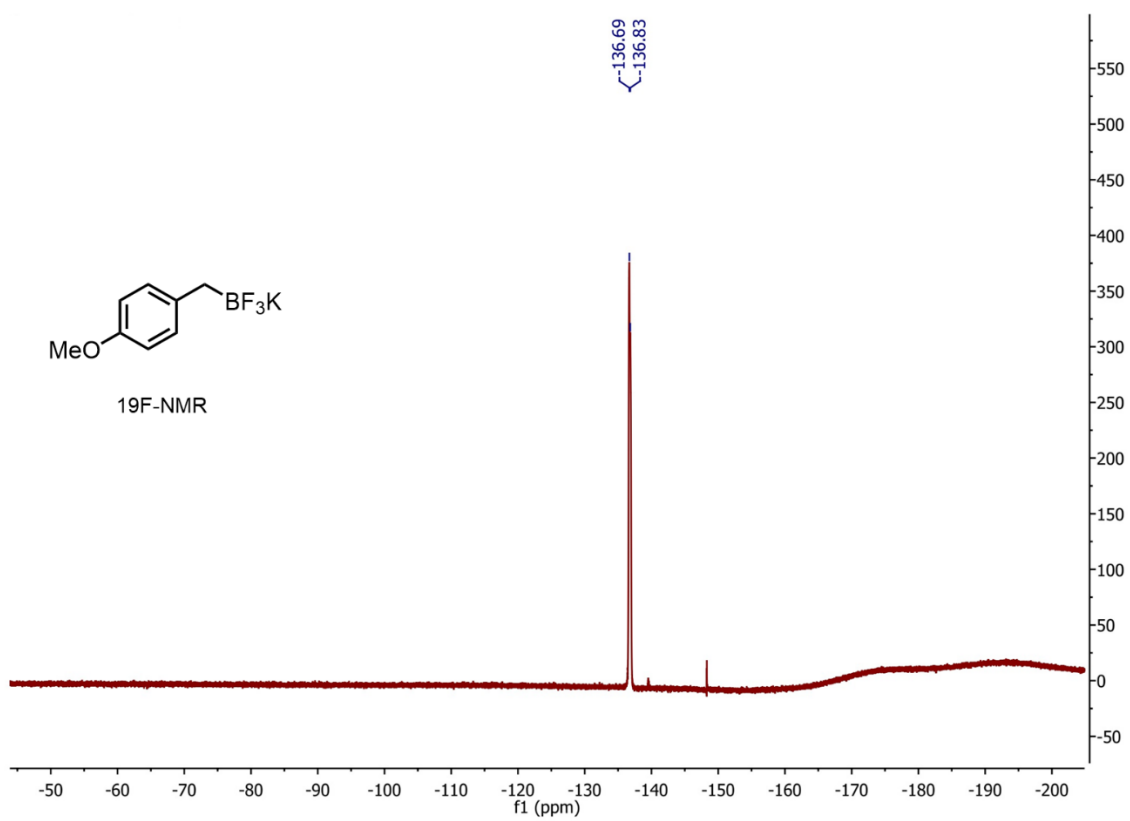
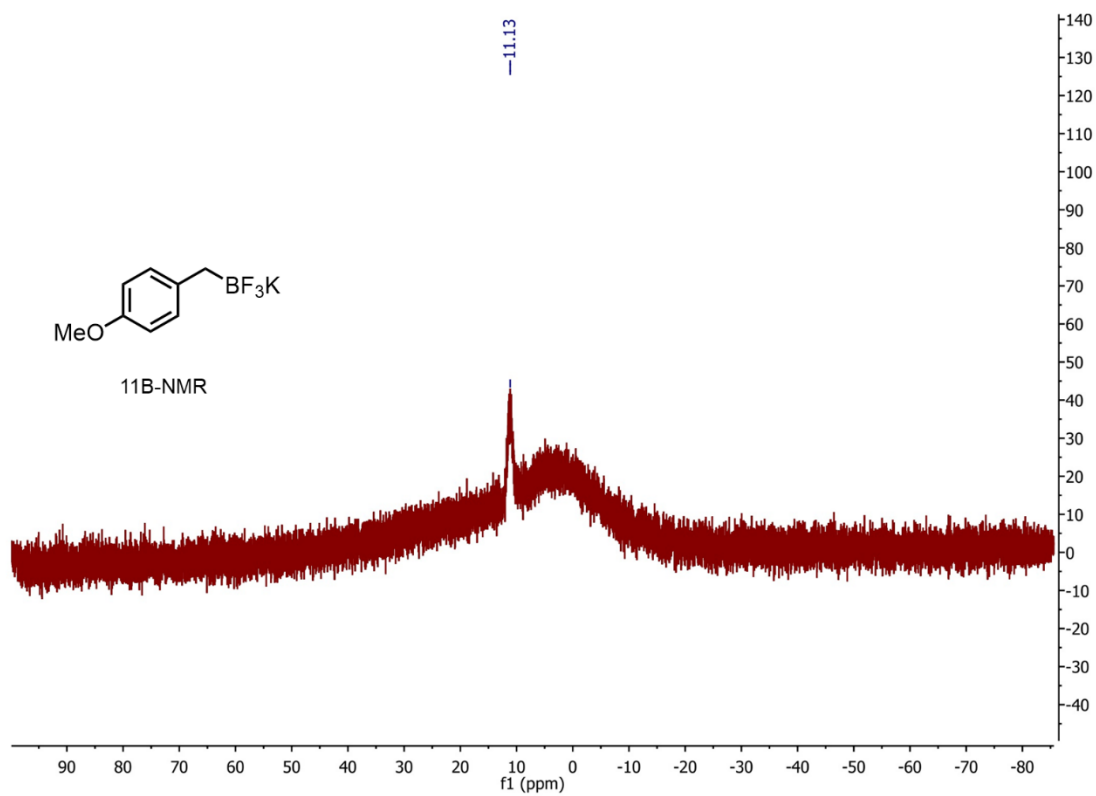
13. NMR spectra

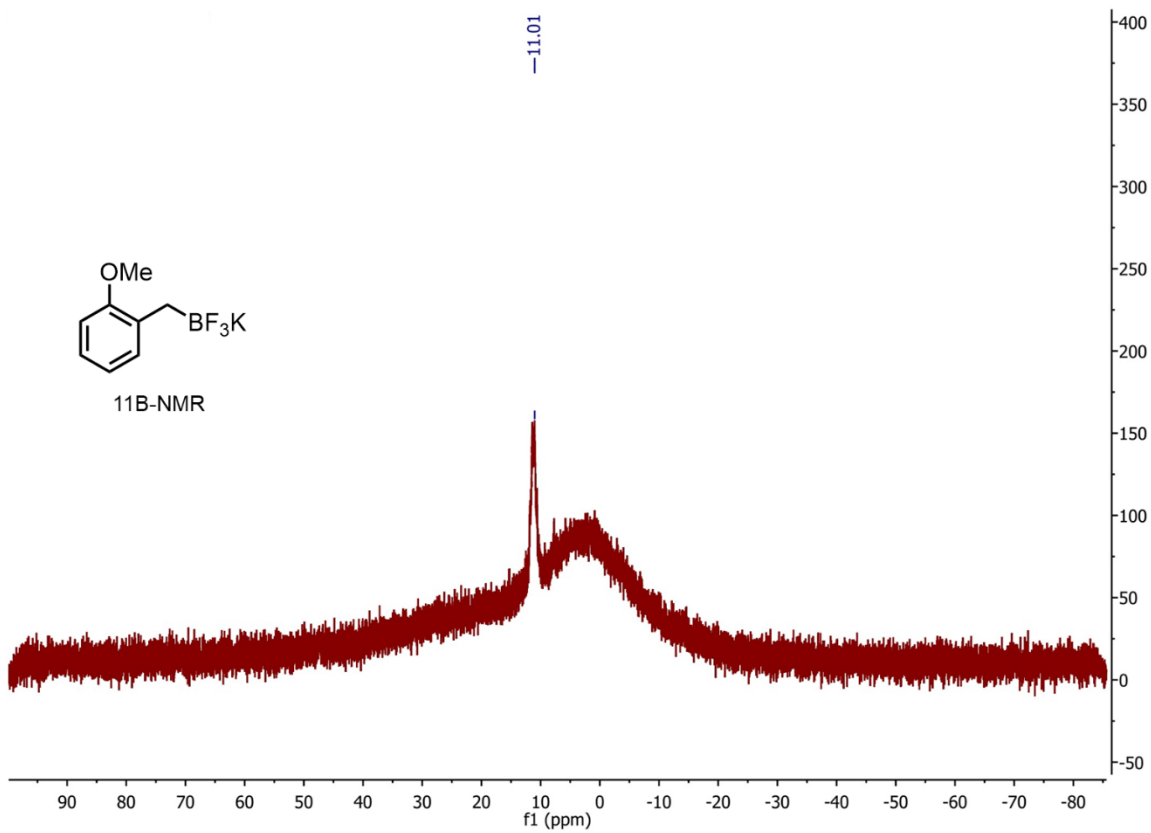
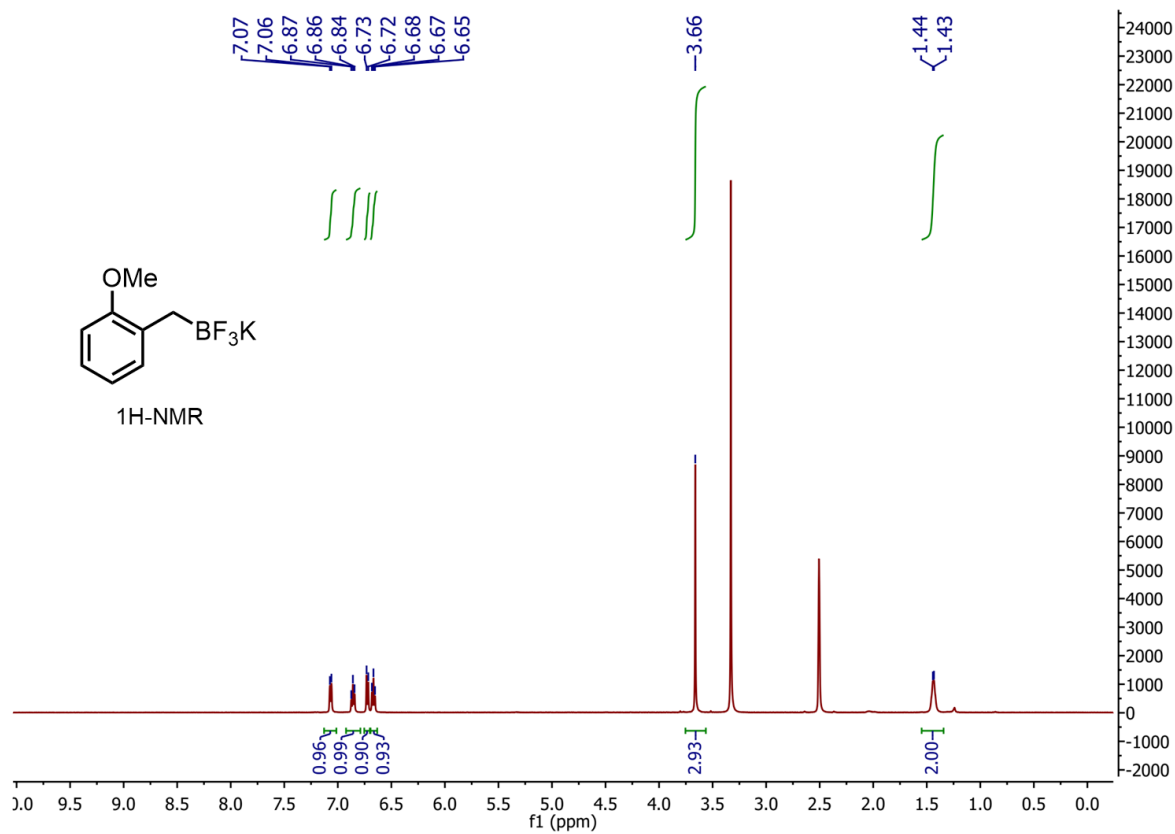


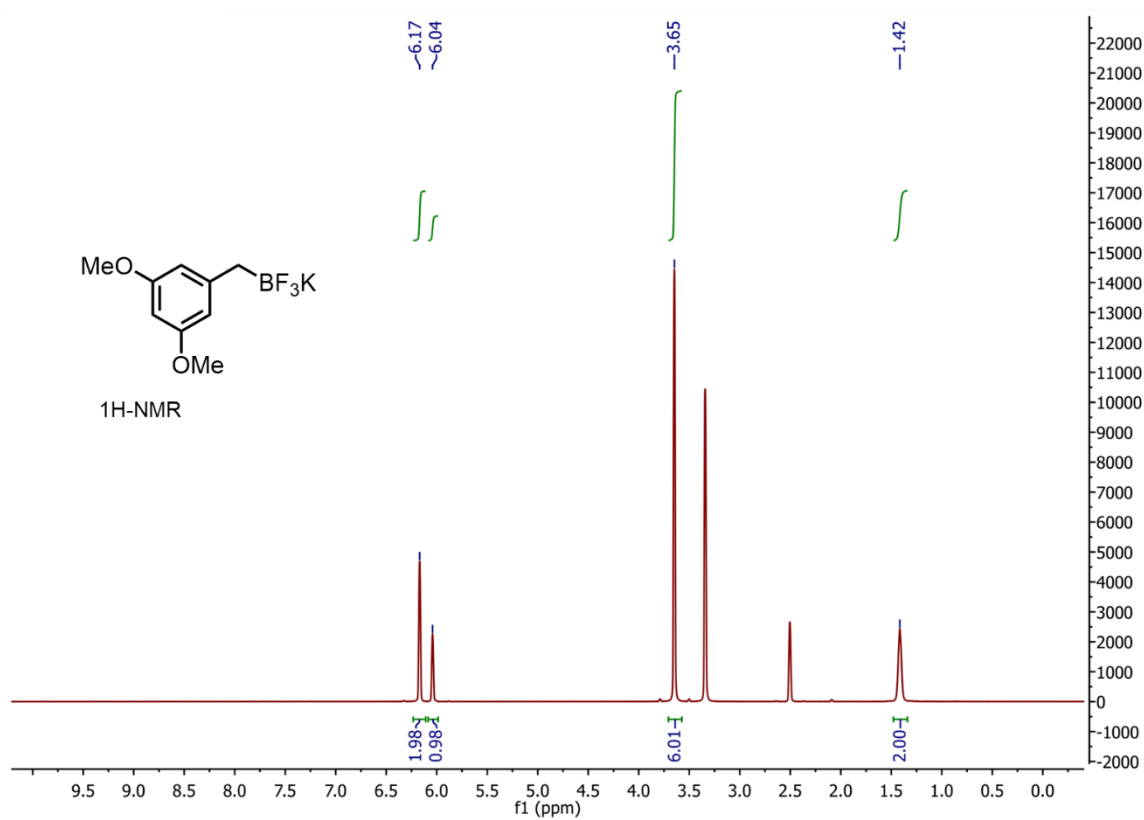
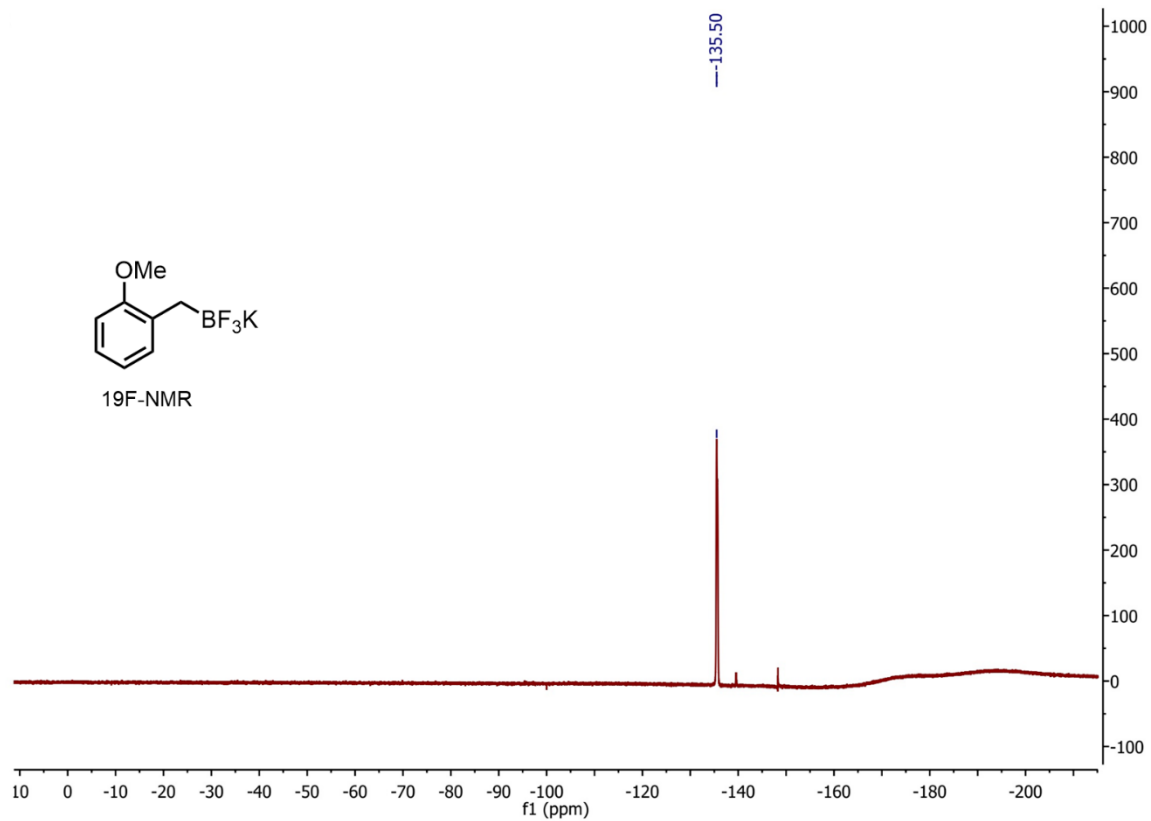


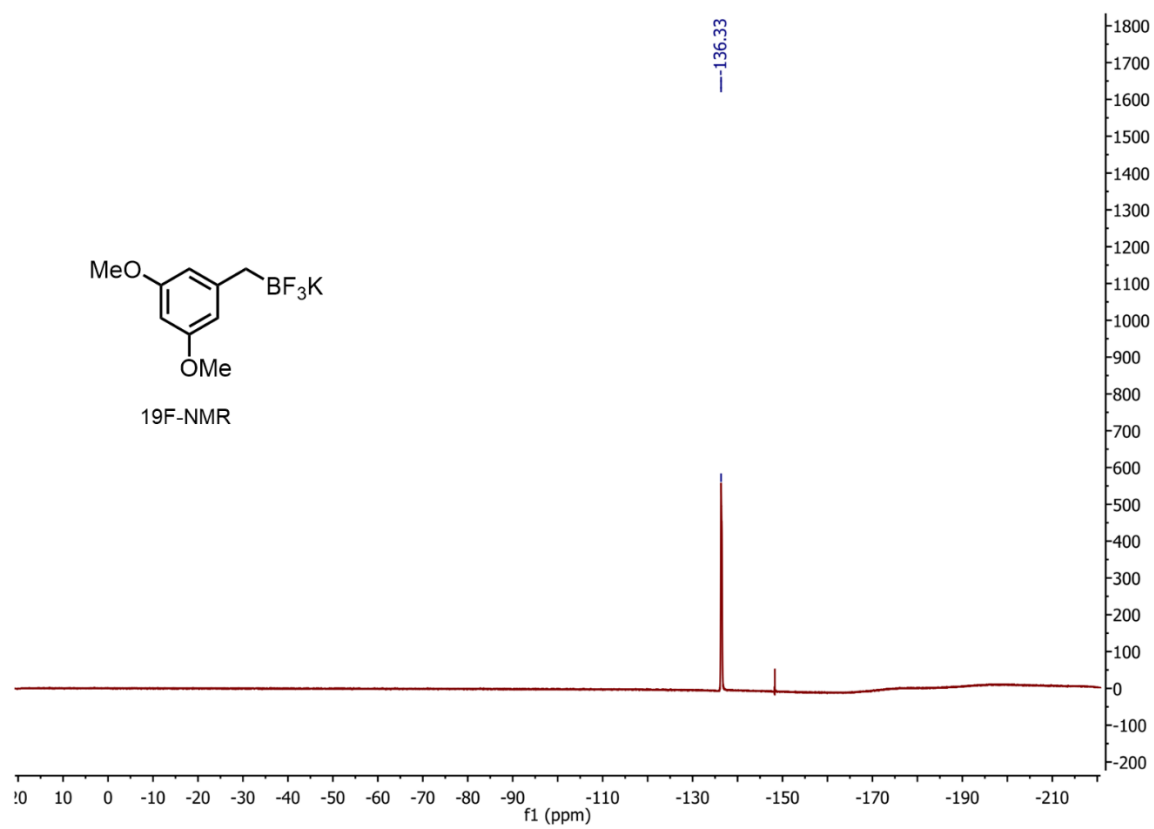
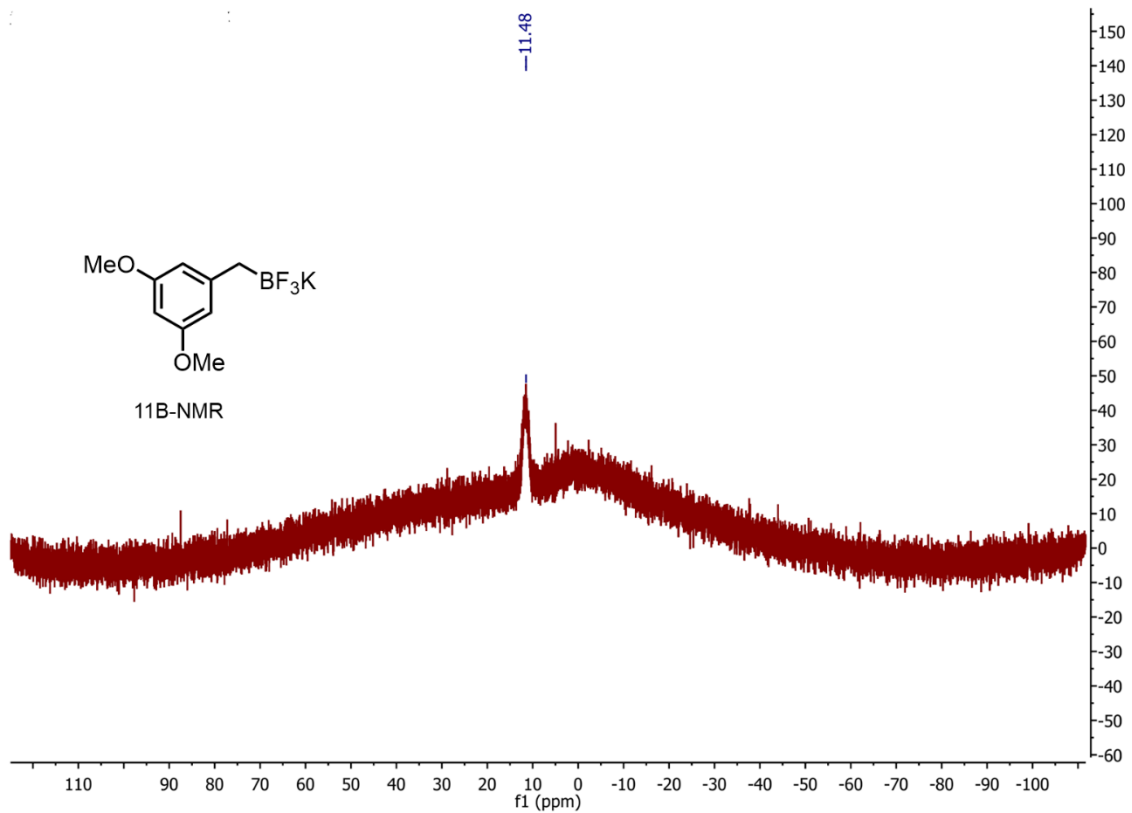


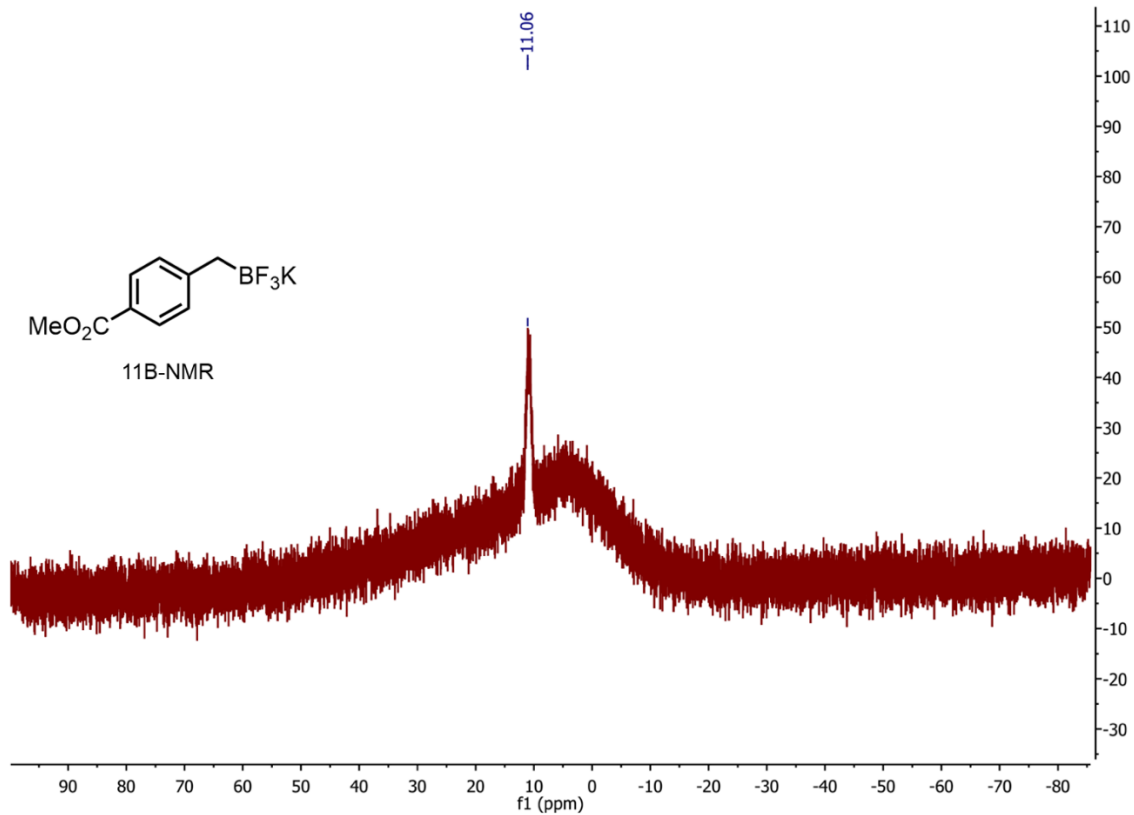
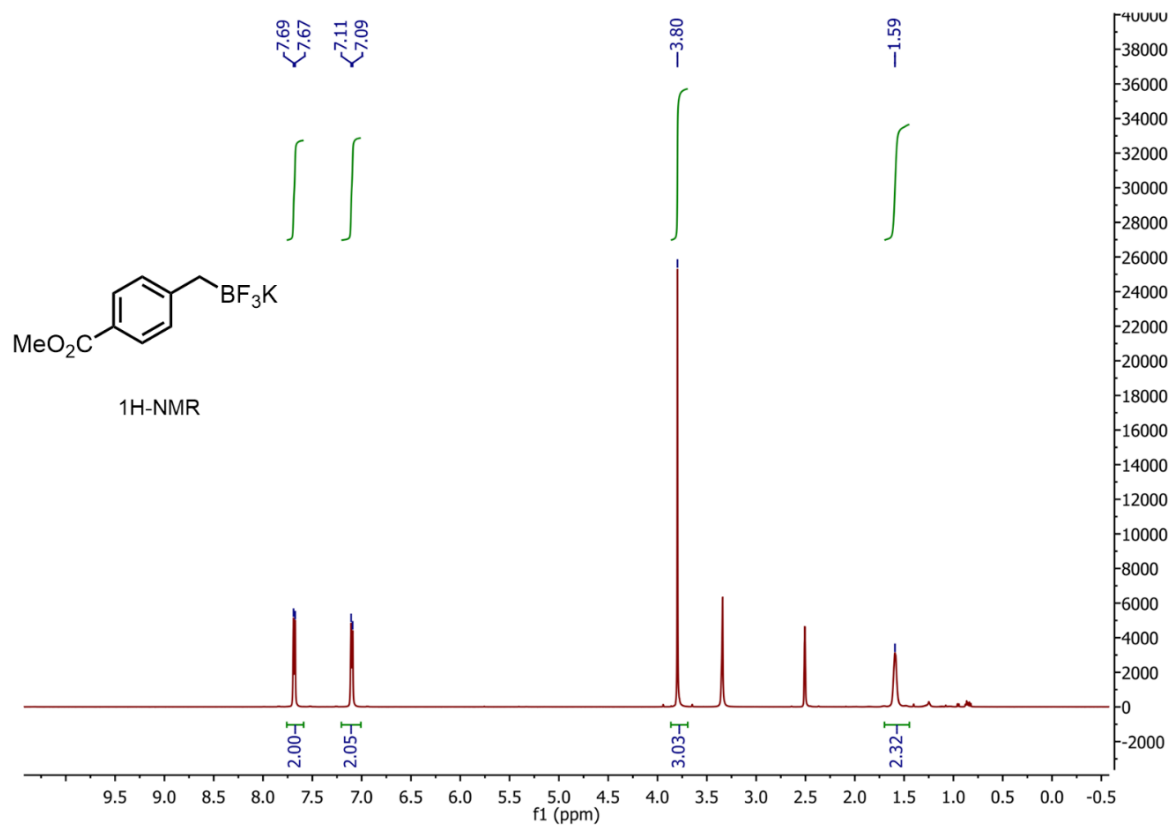


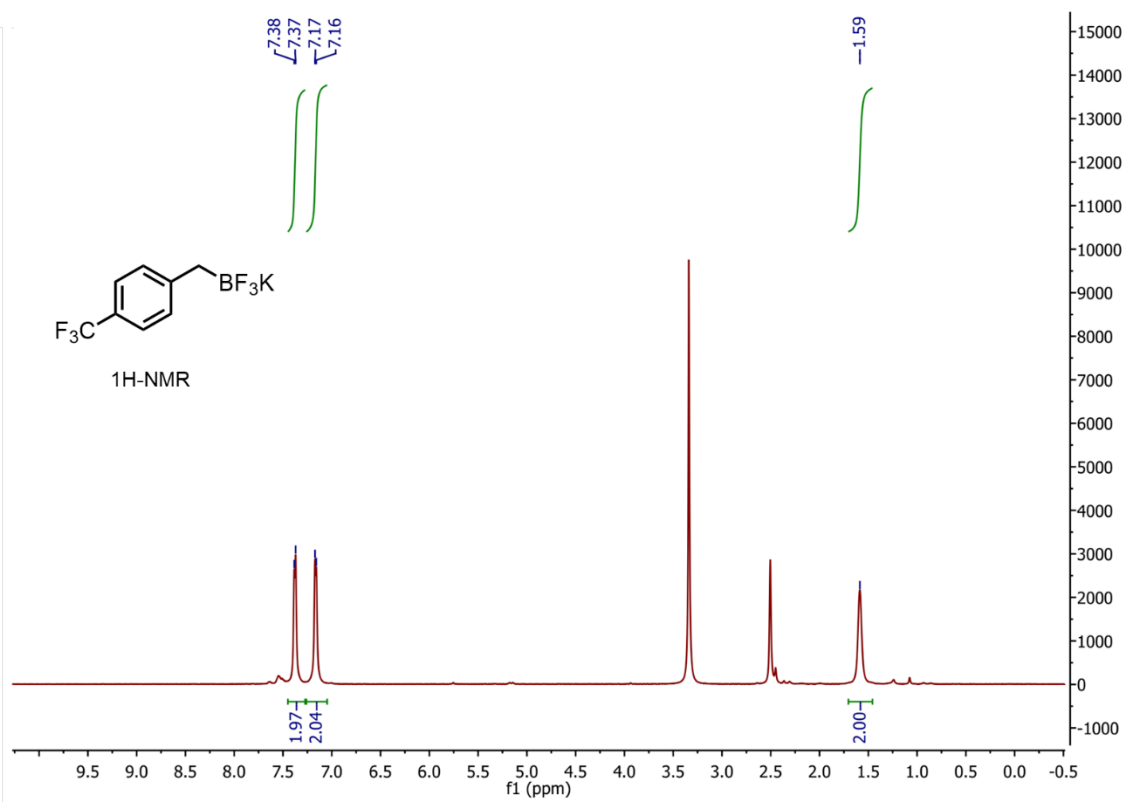
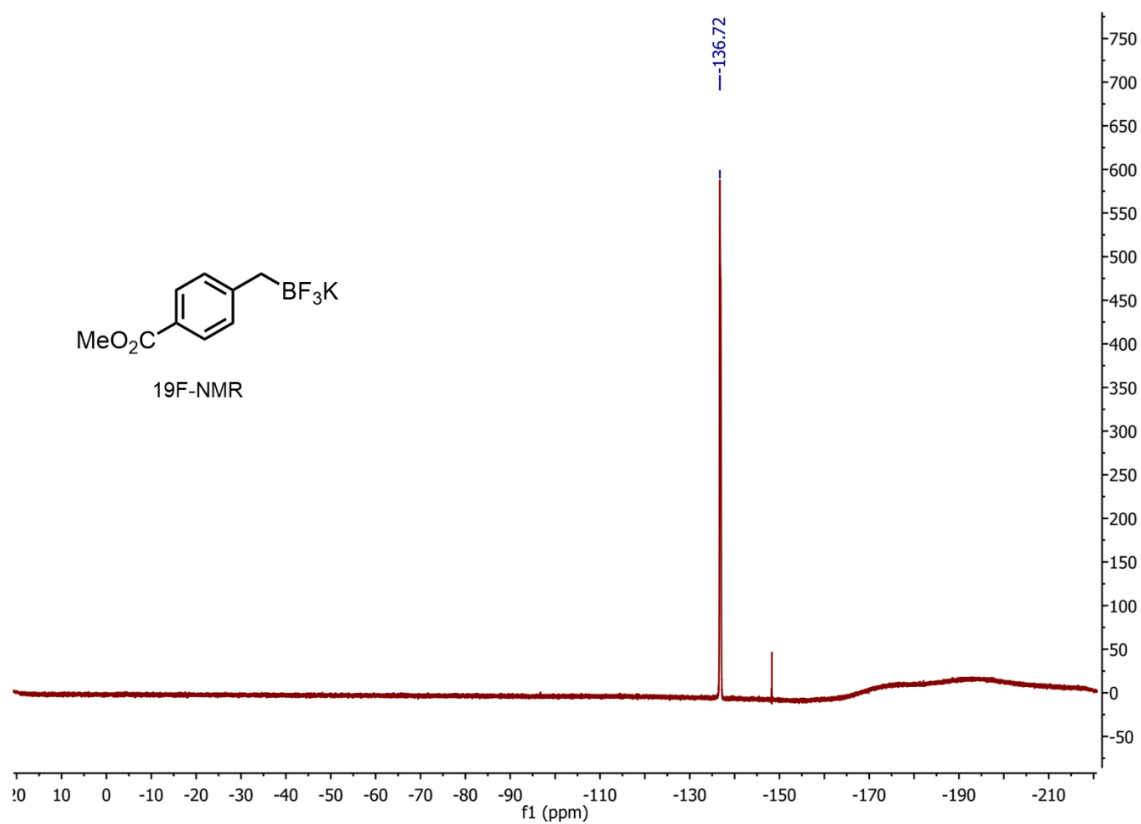


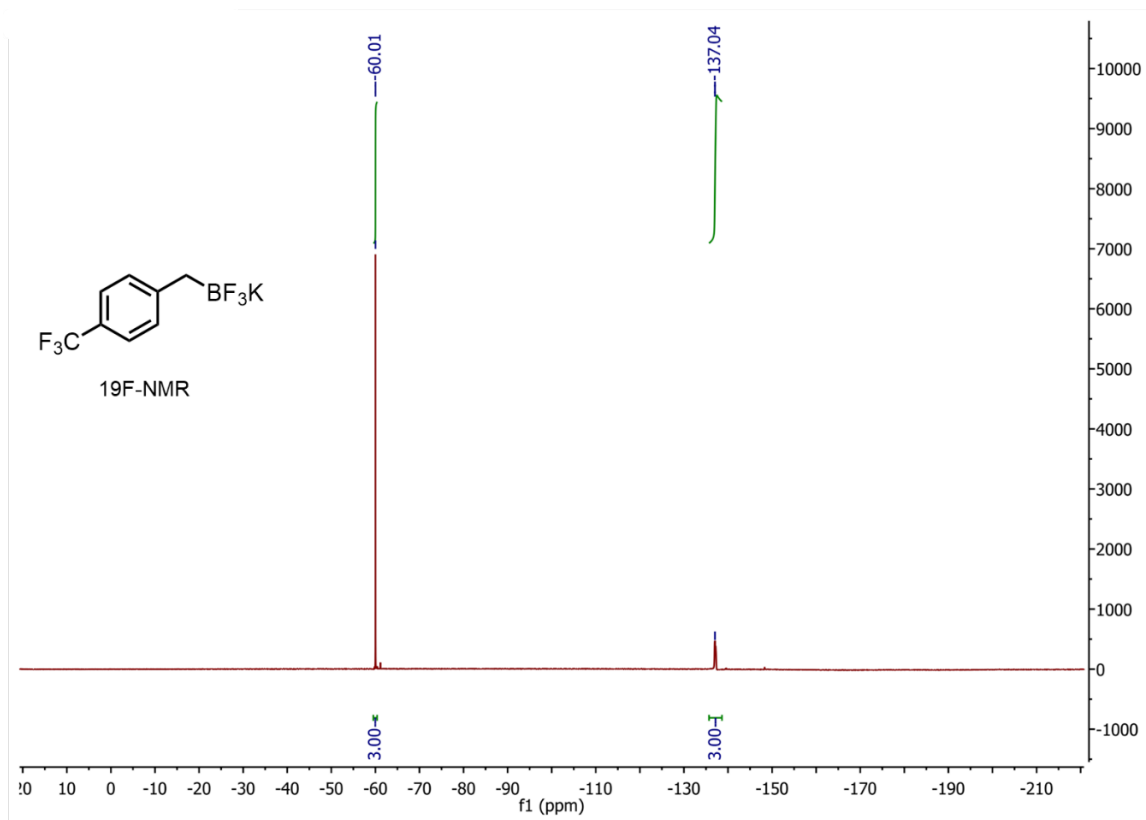
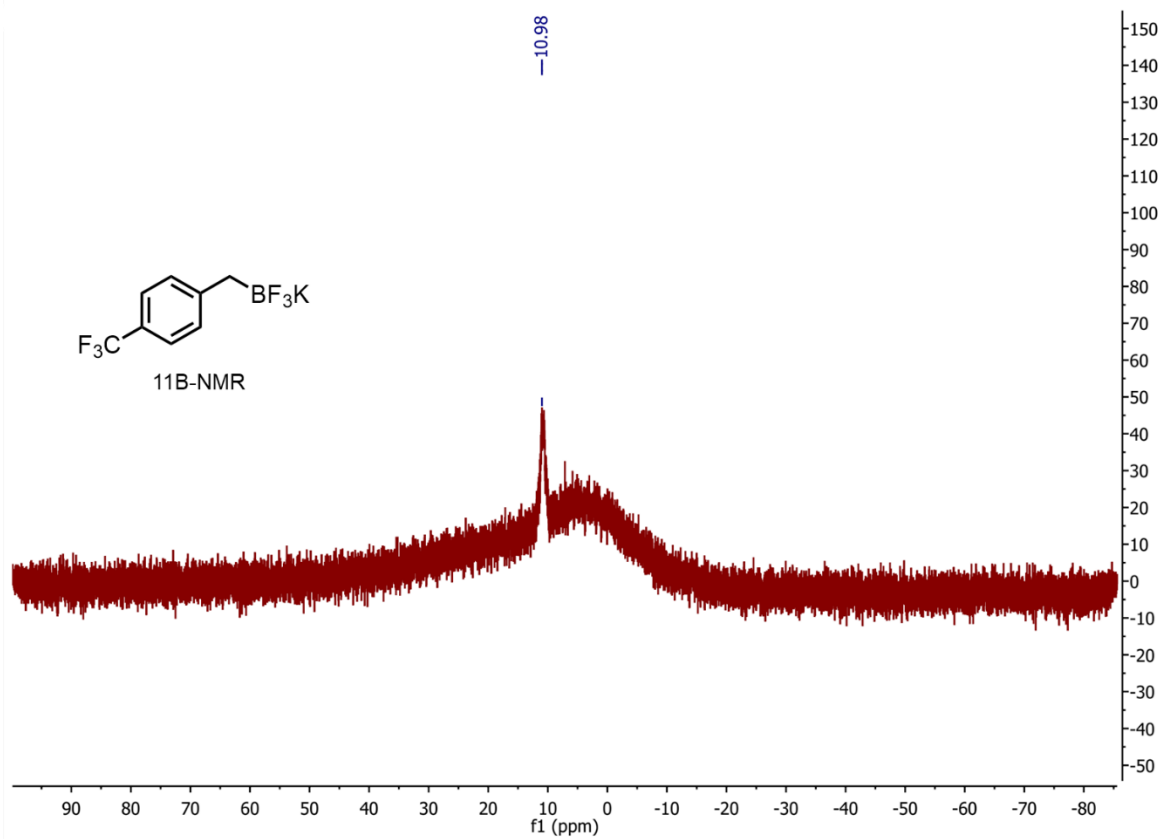


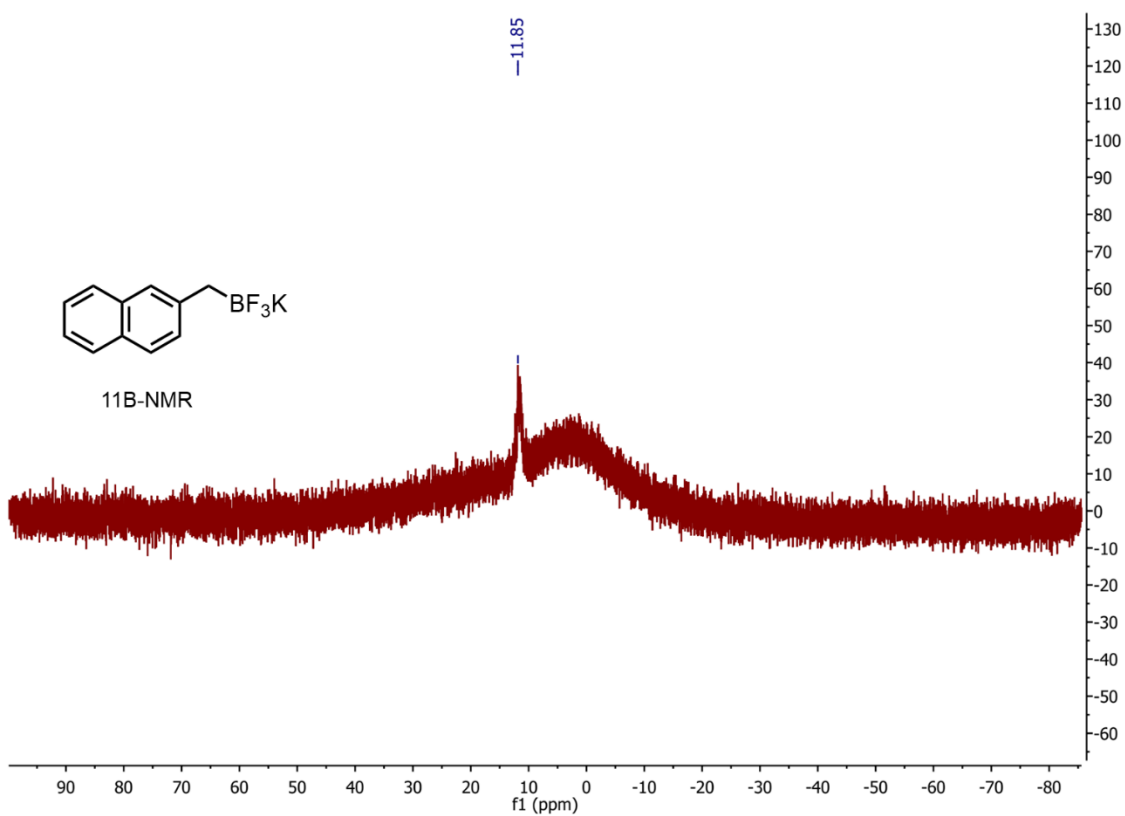
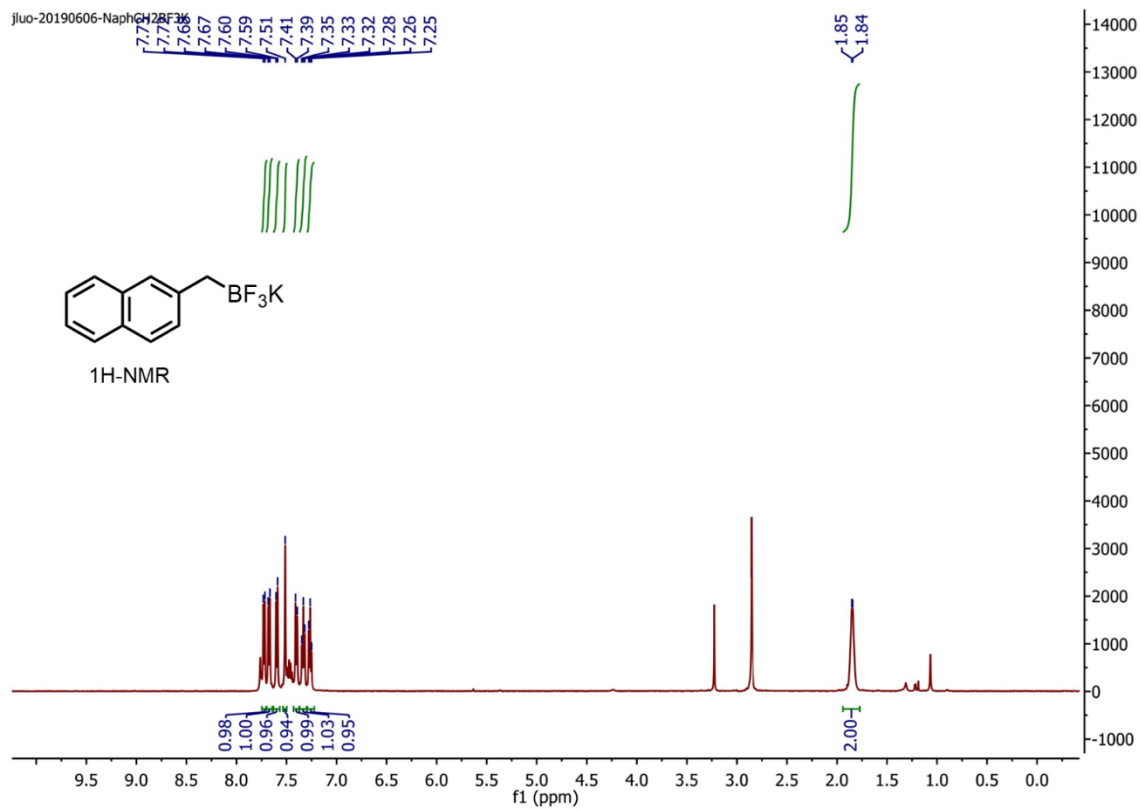


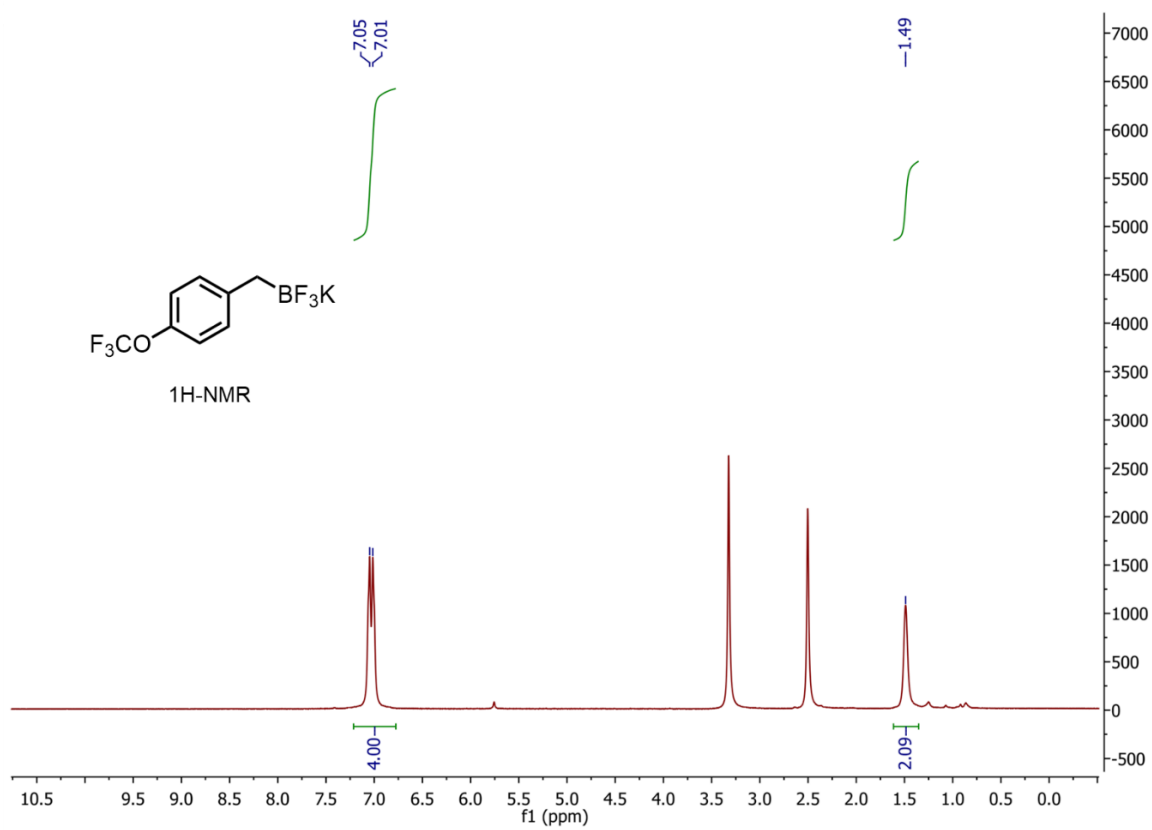
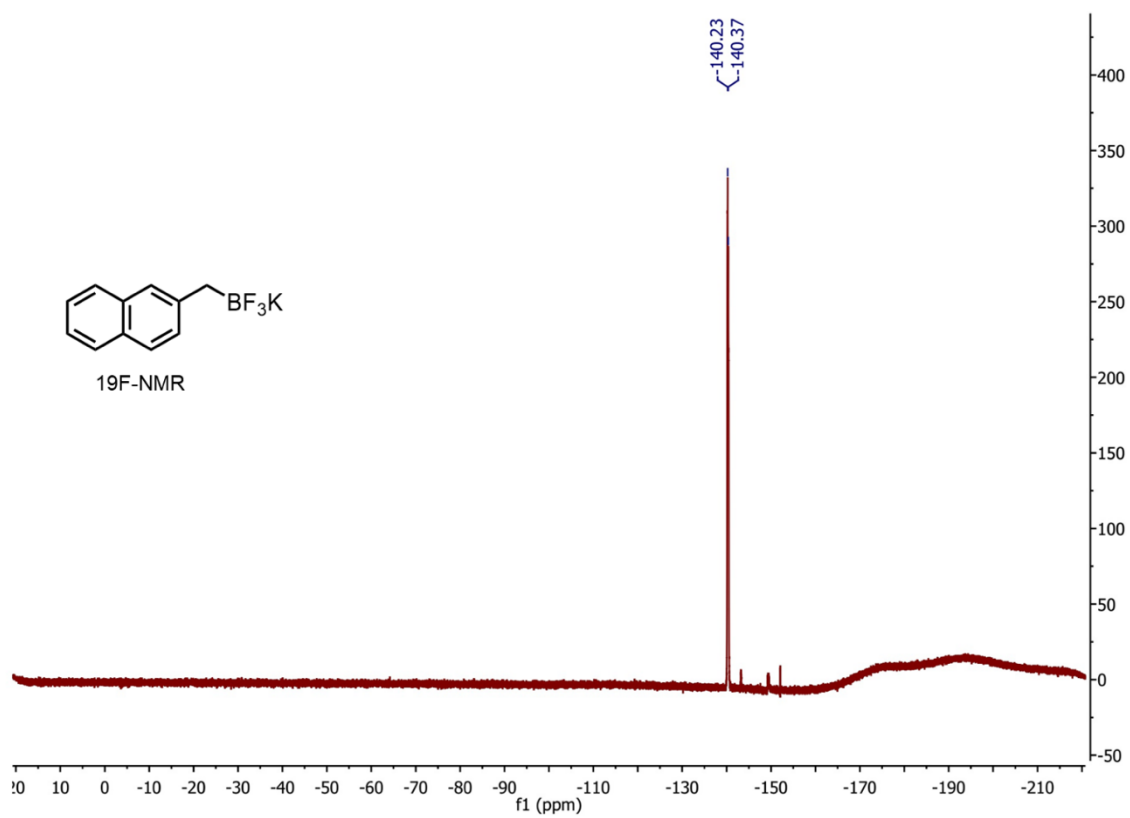


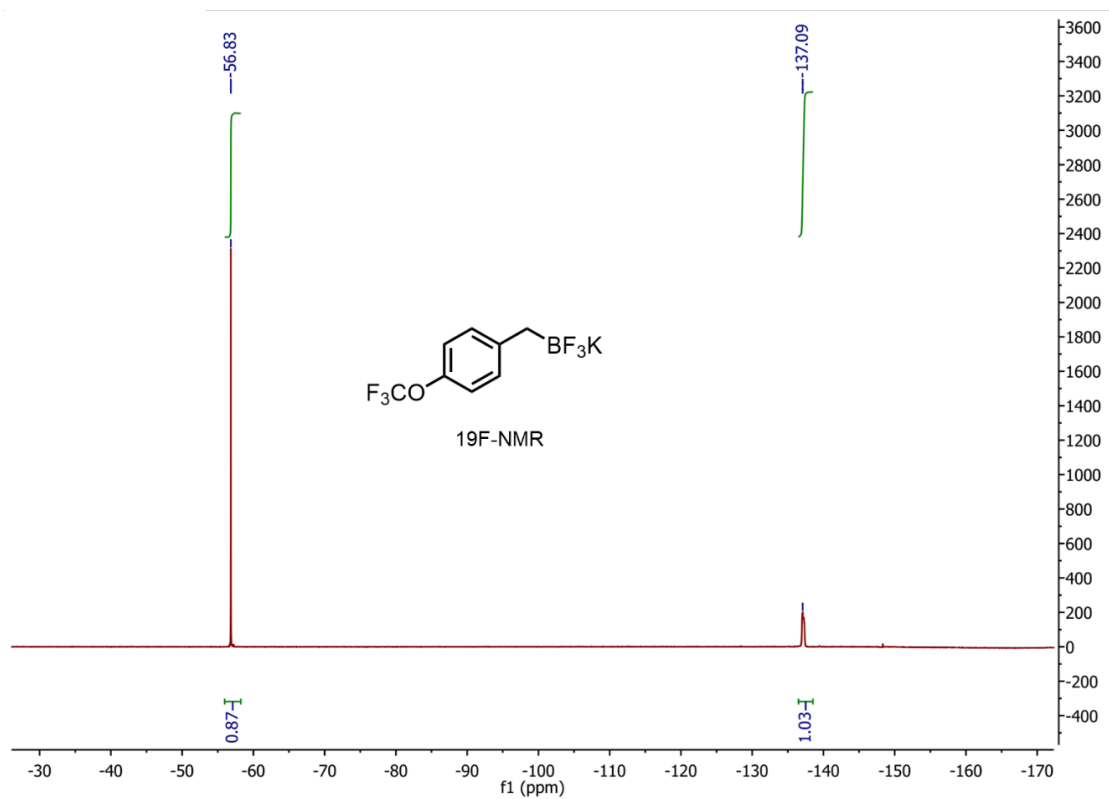
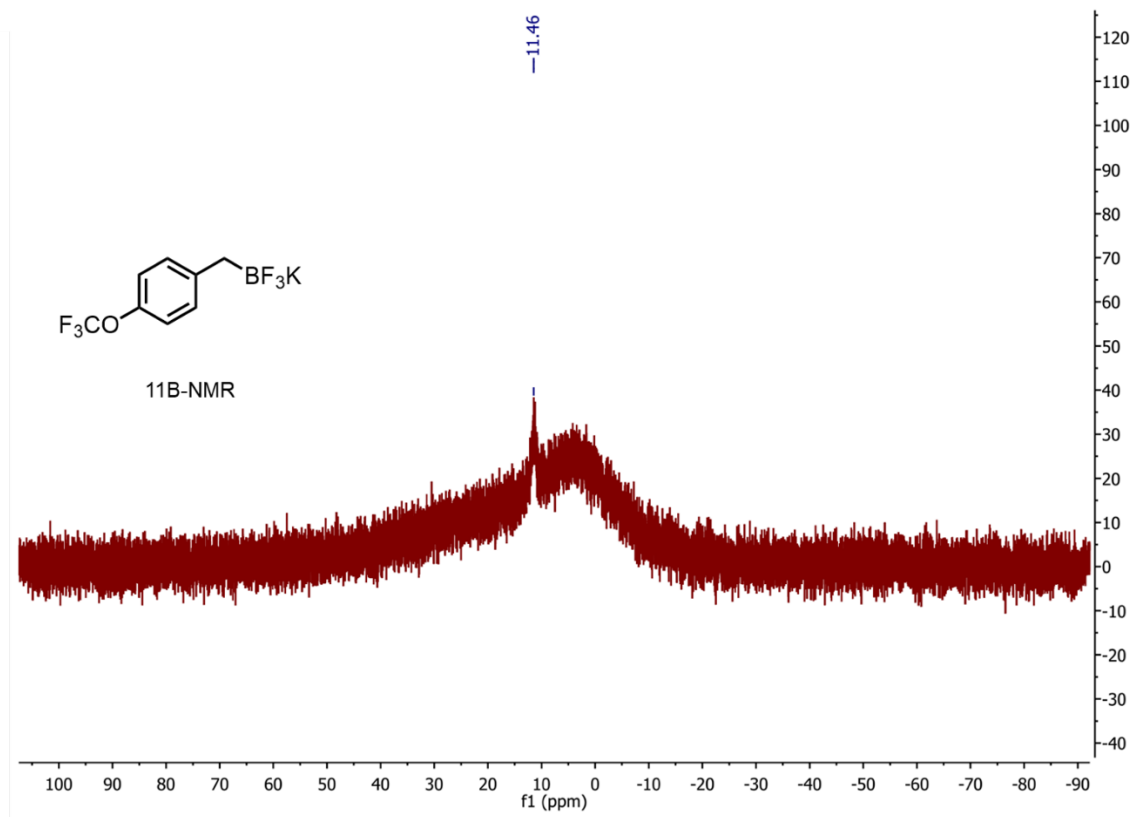


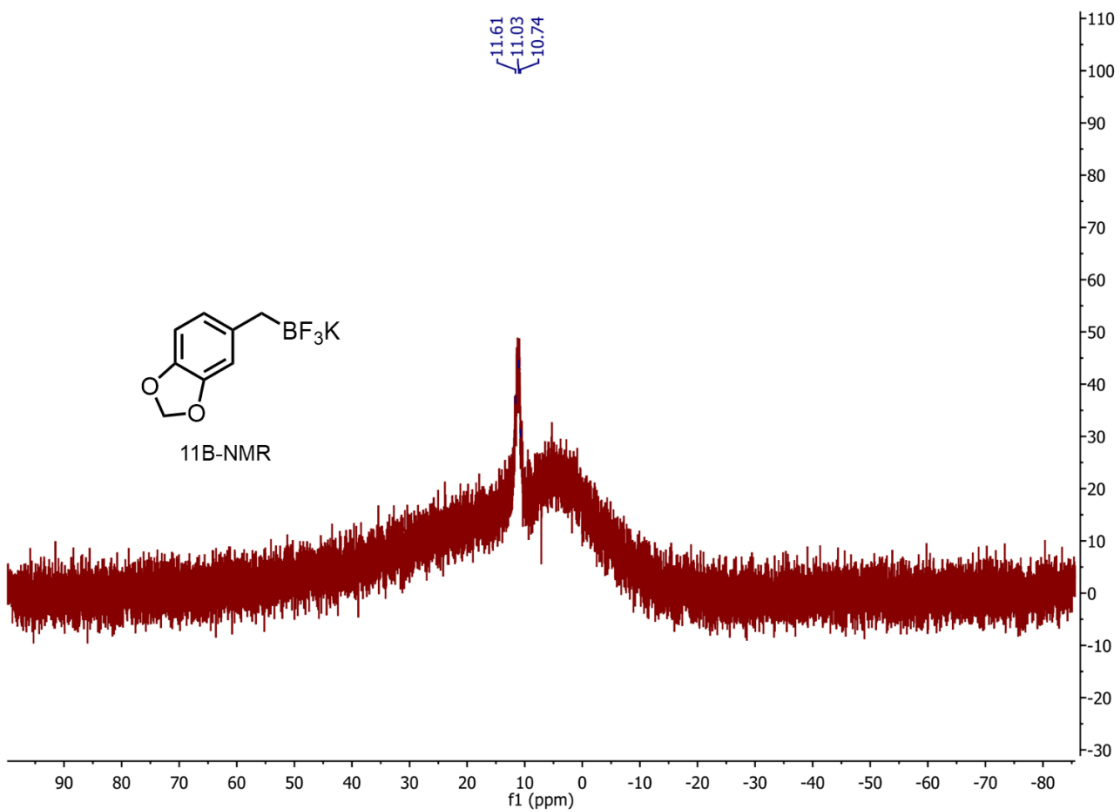
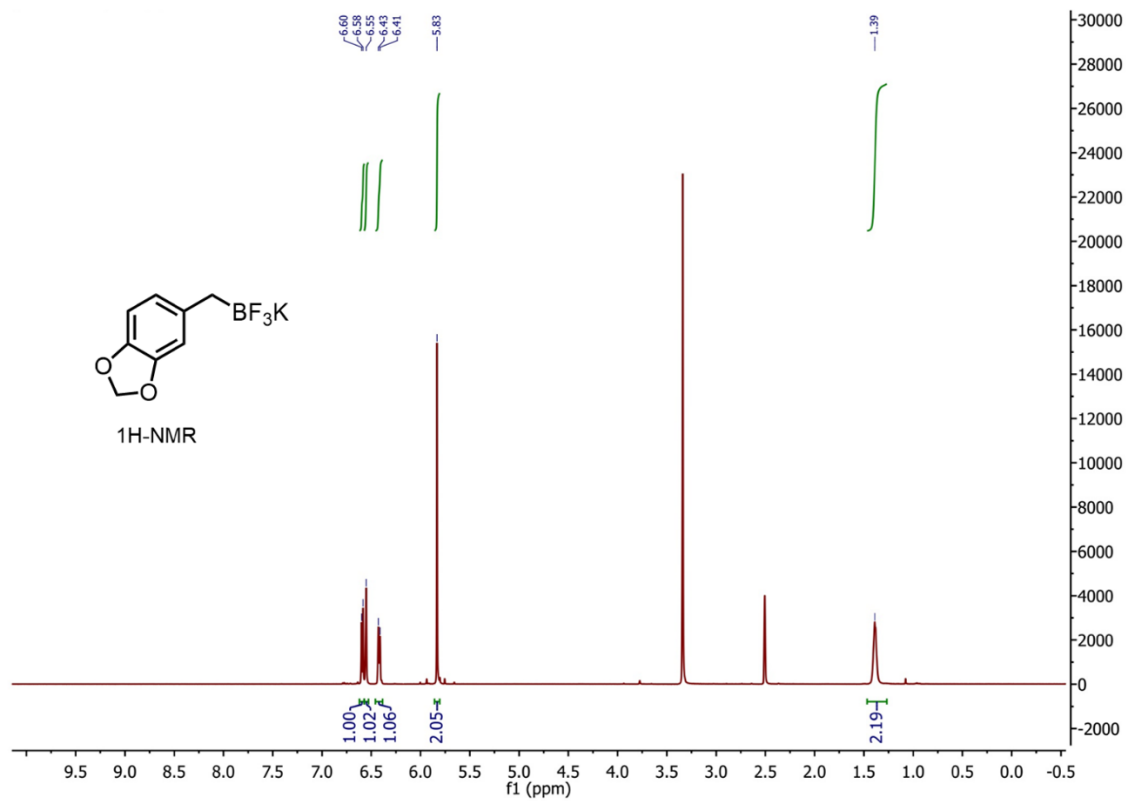


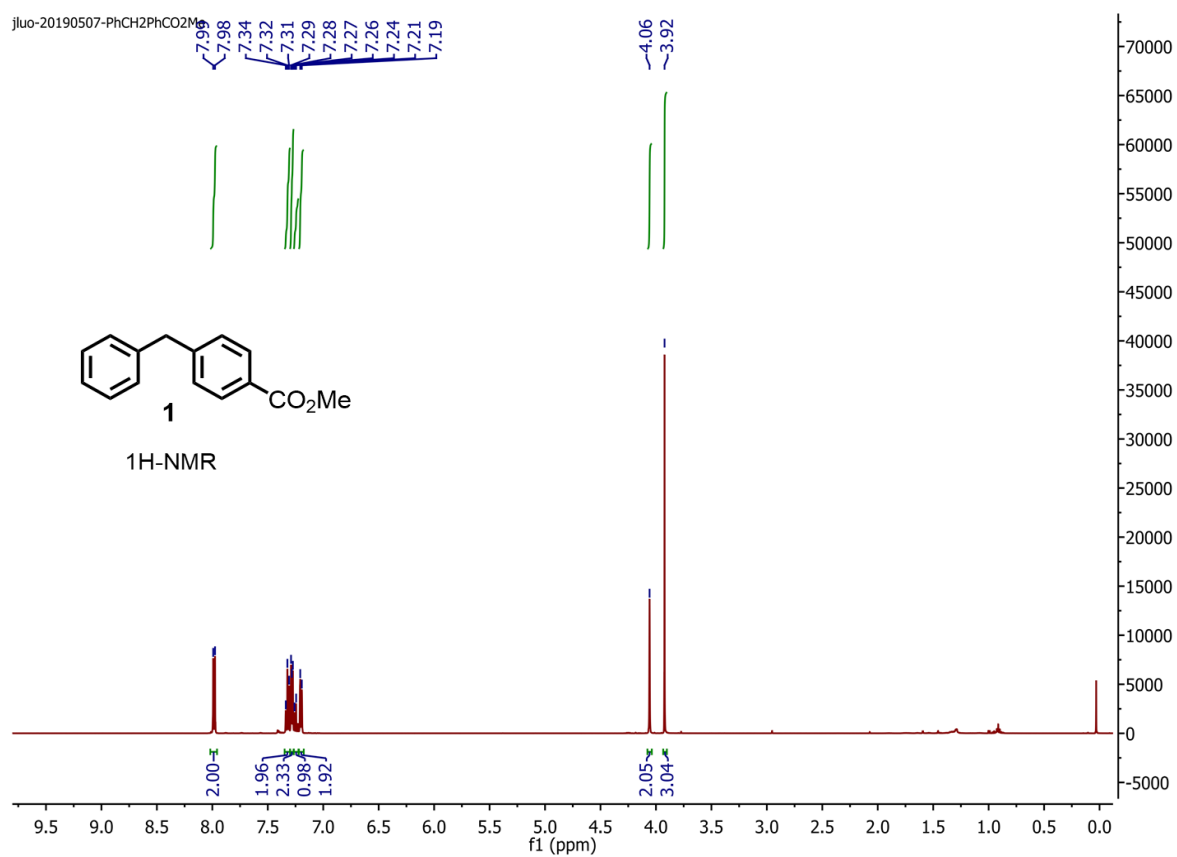
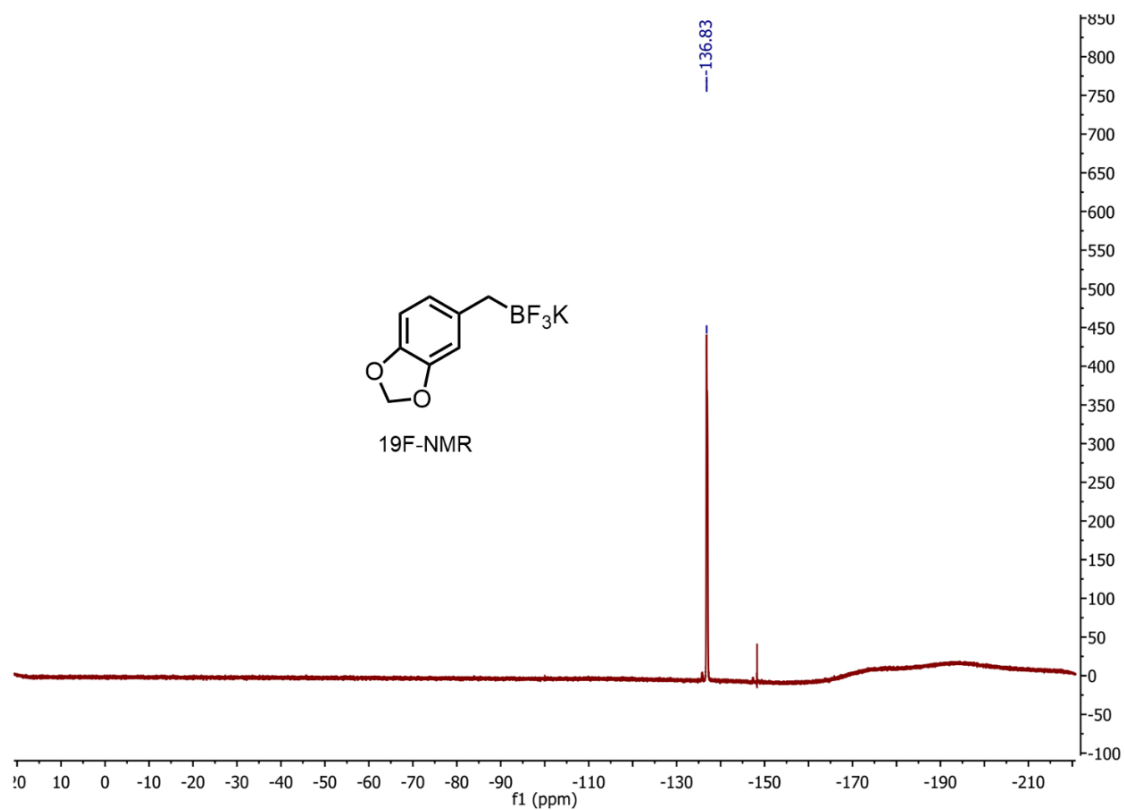


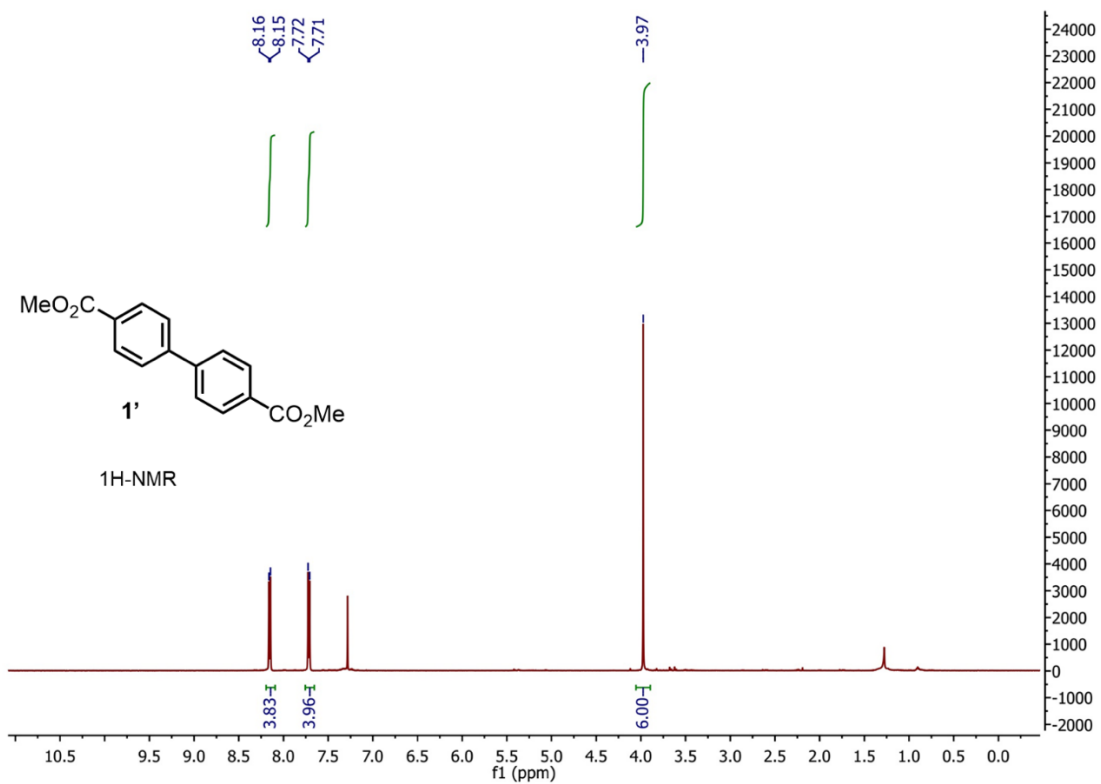
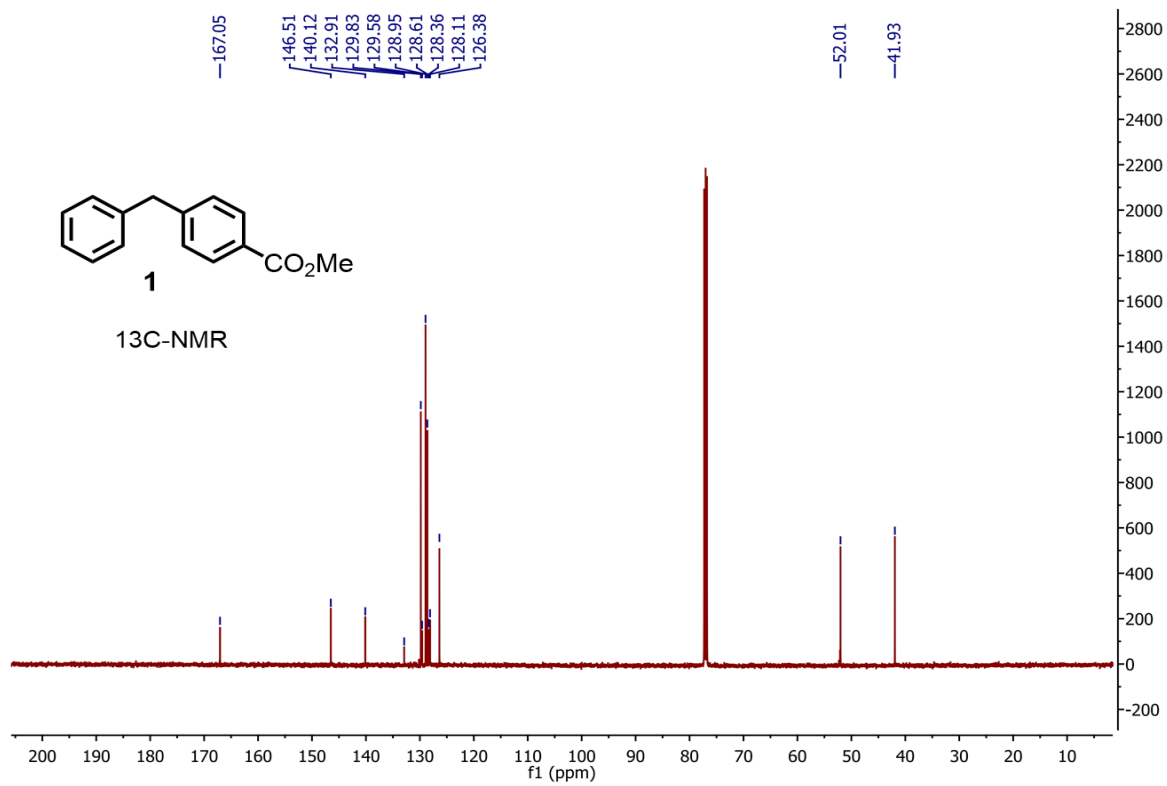


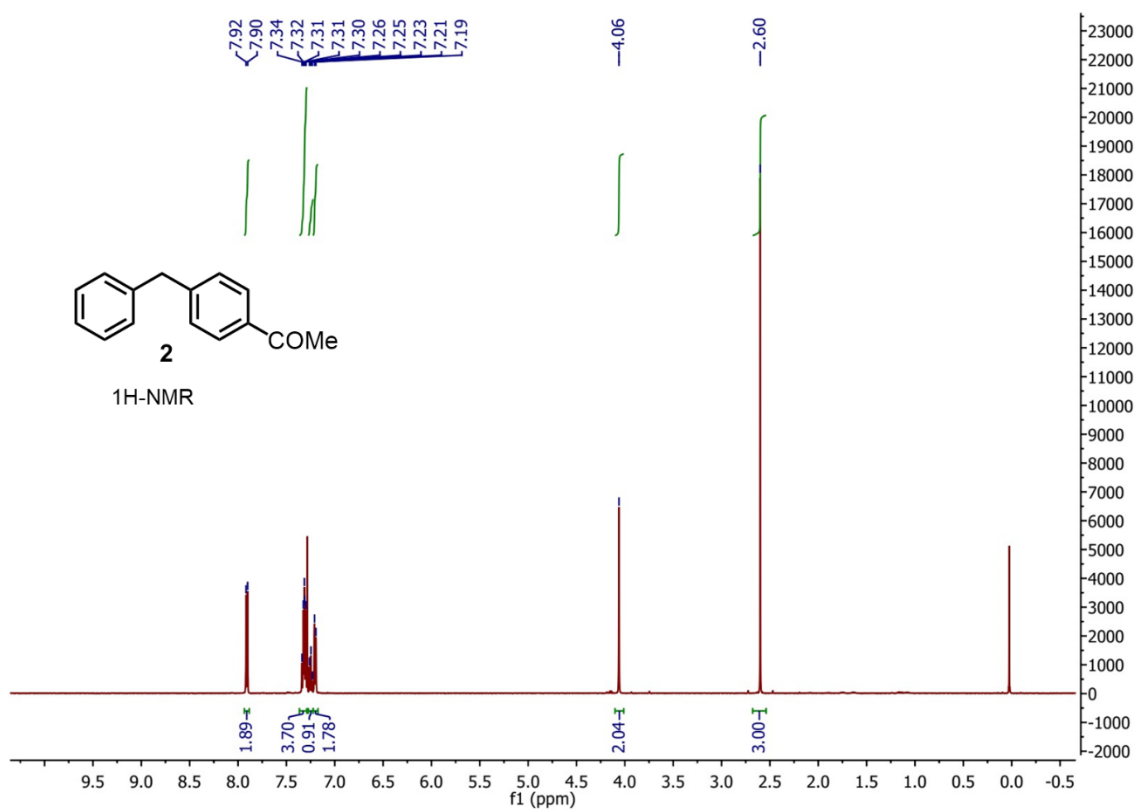
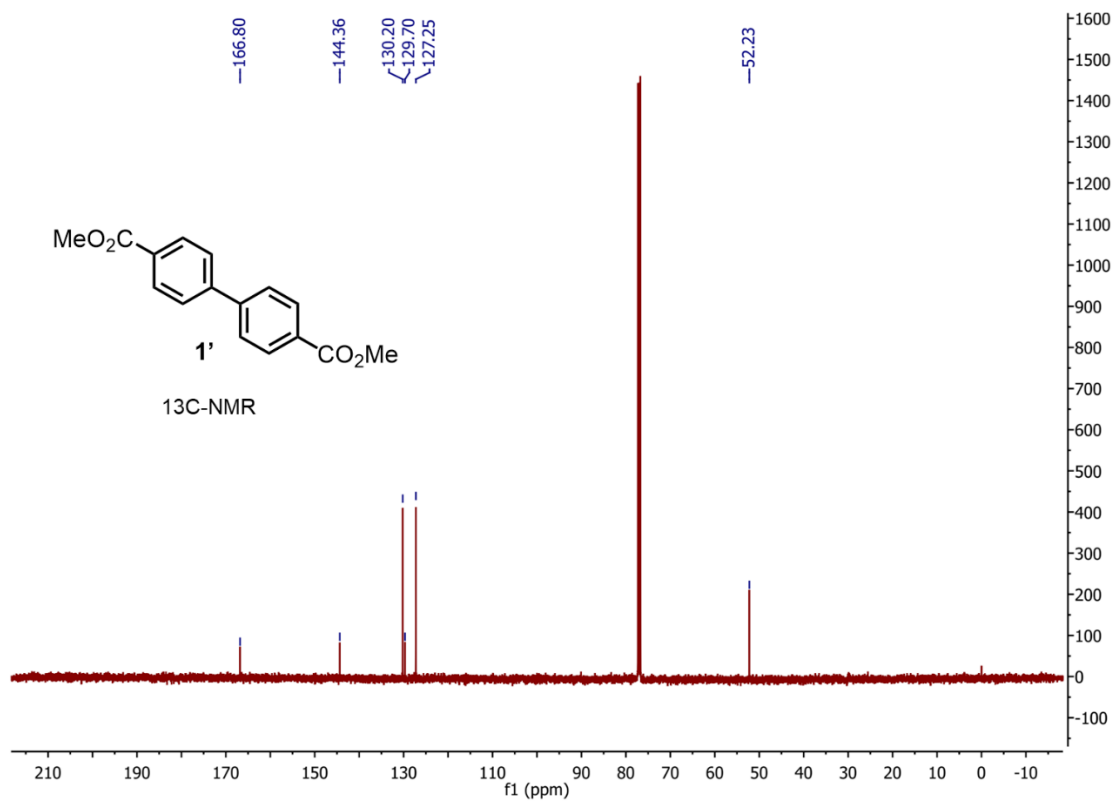


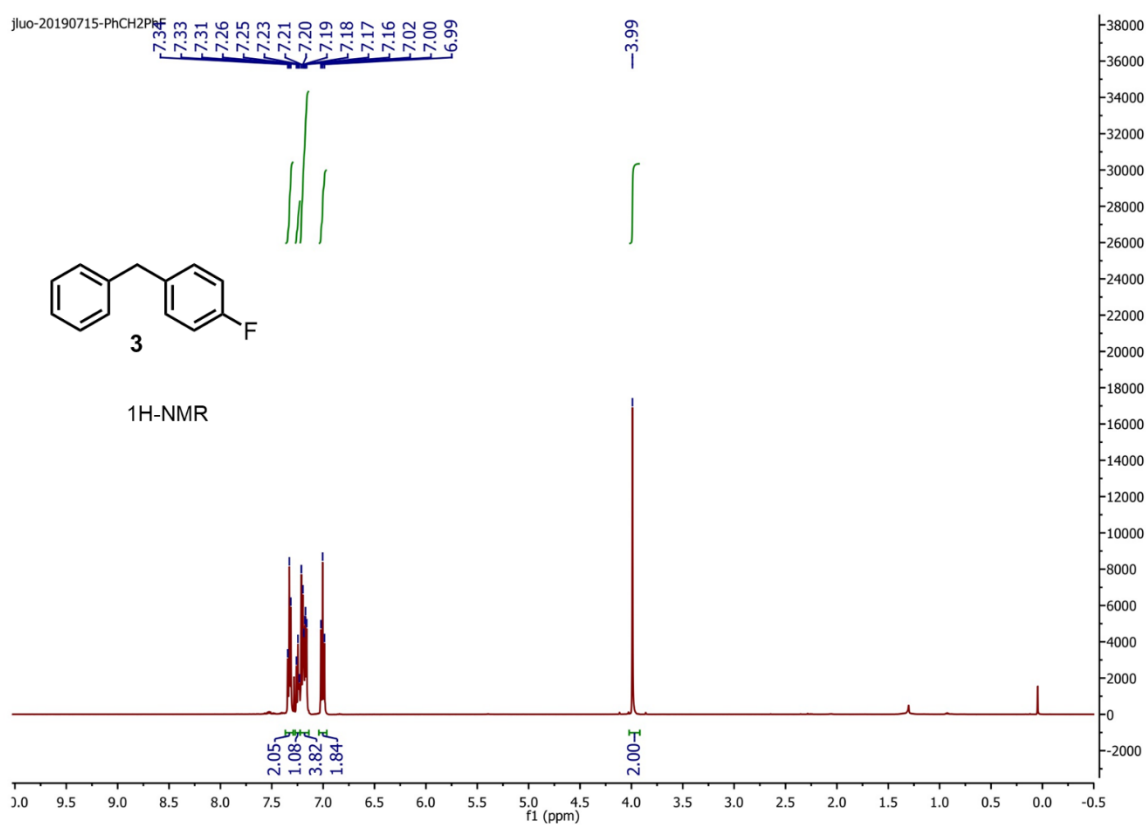
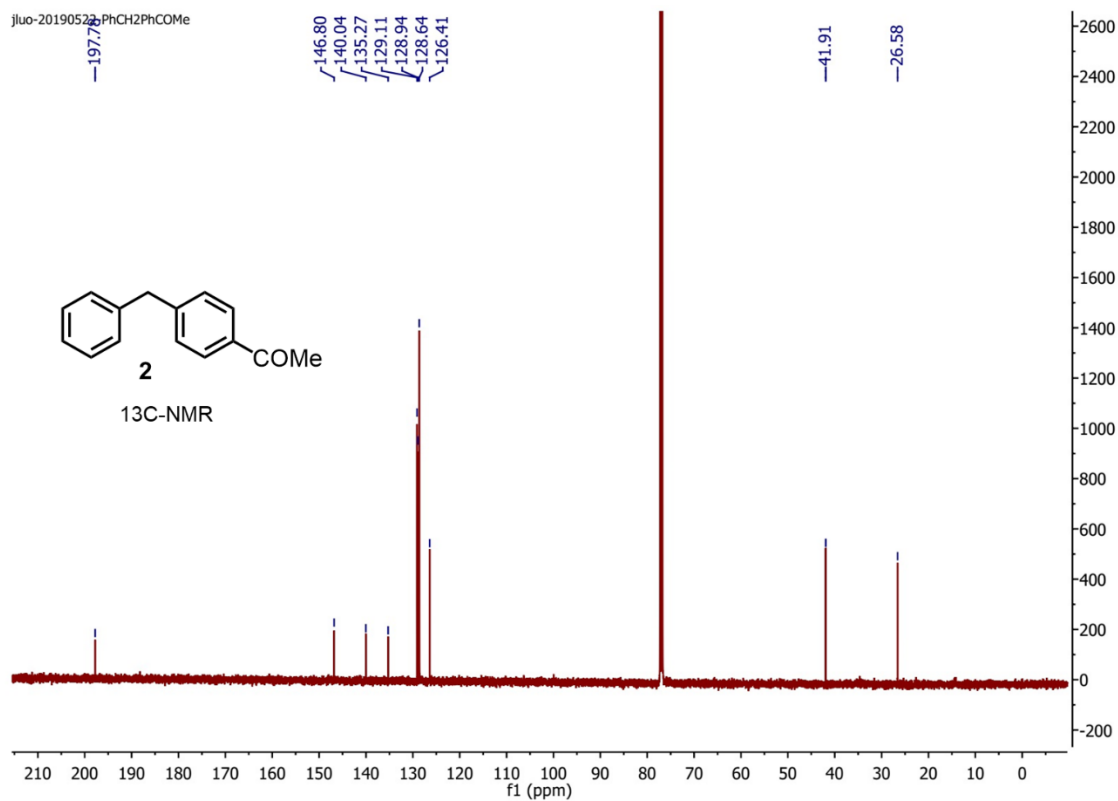


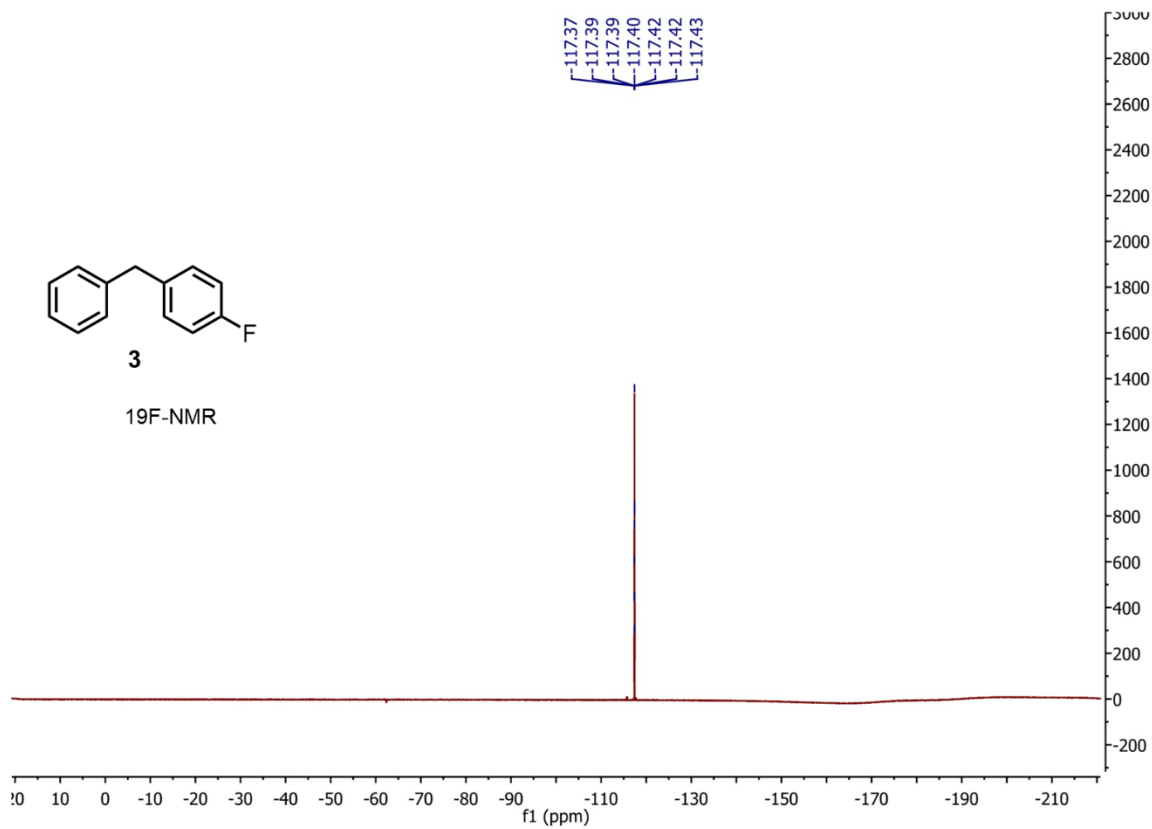
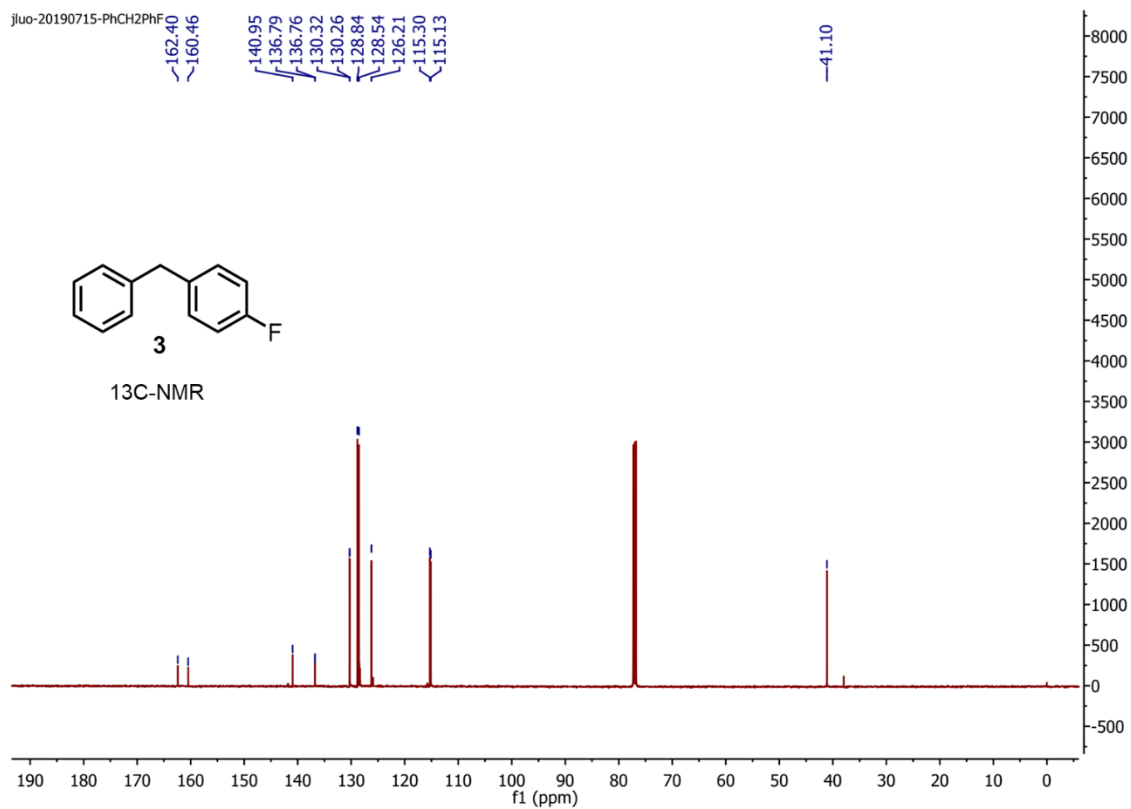


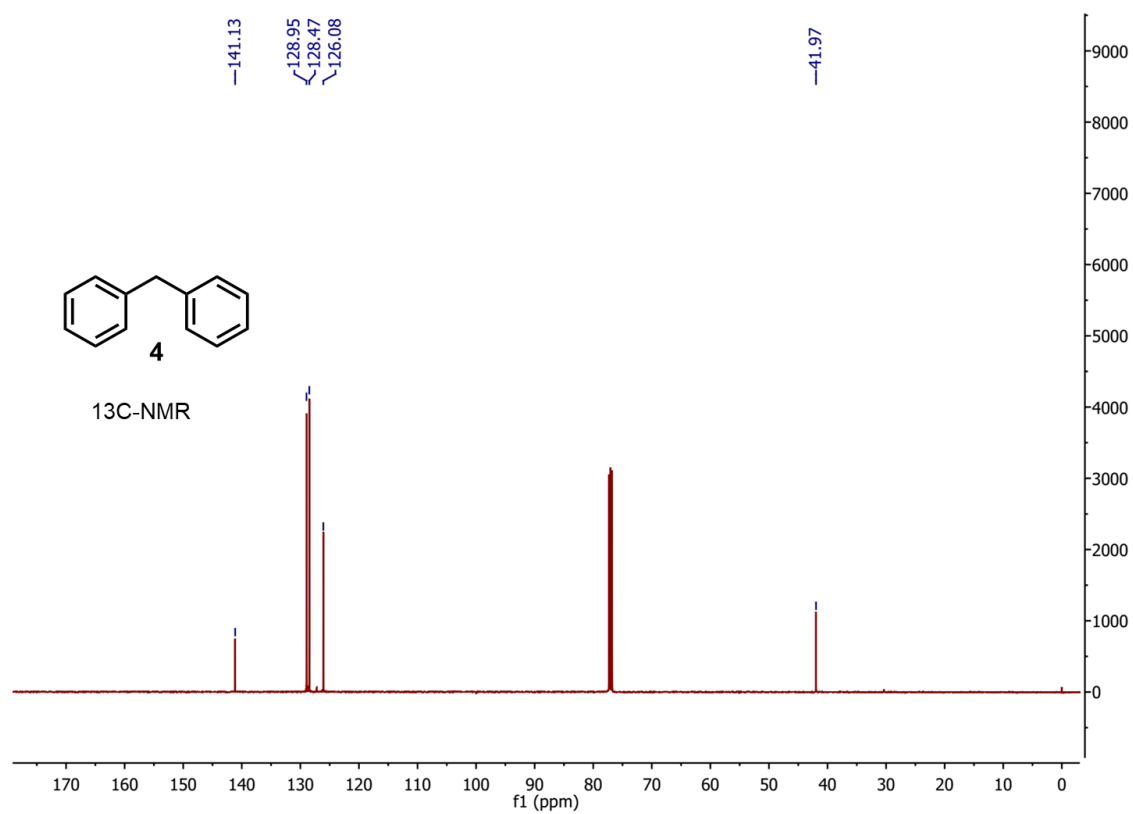
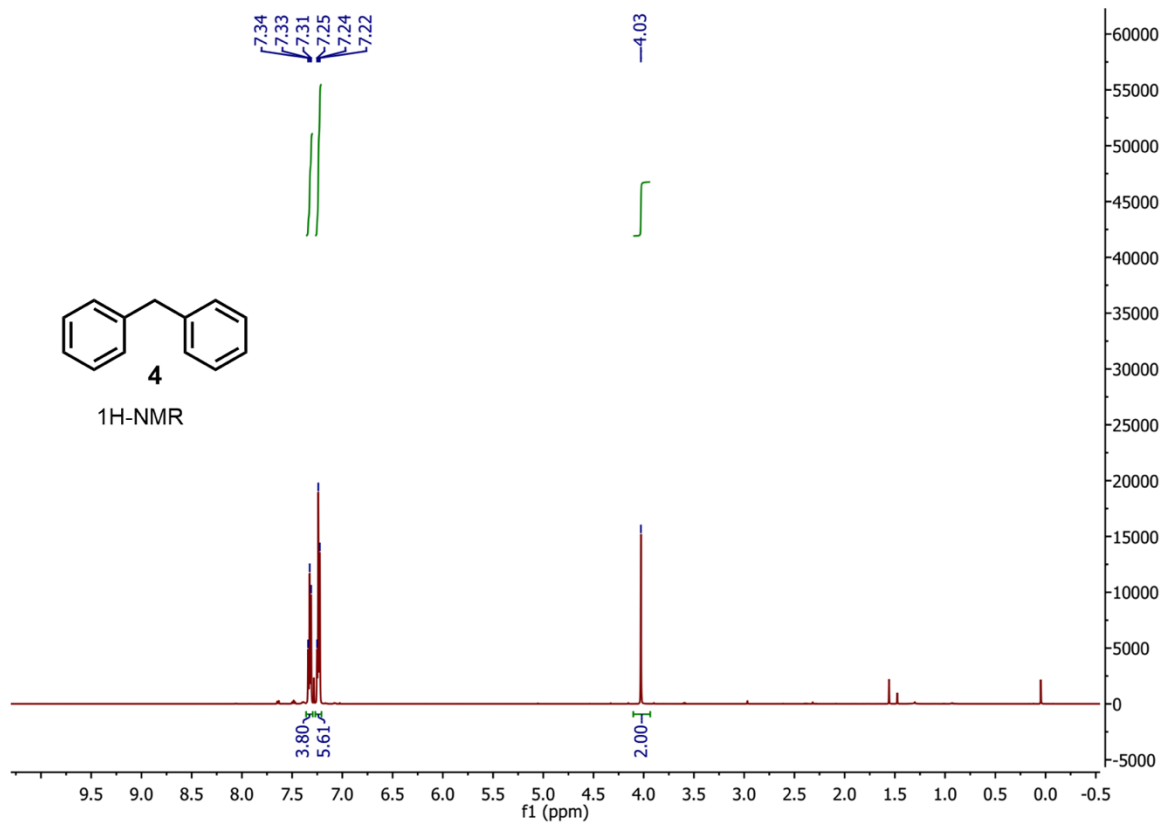


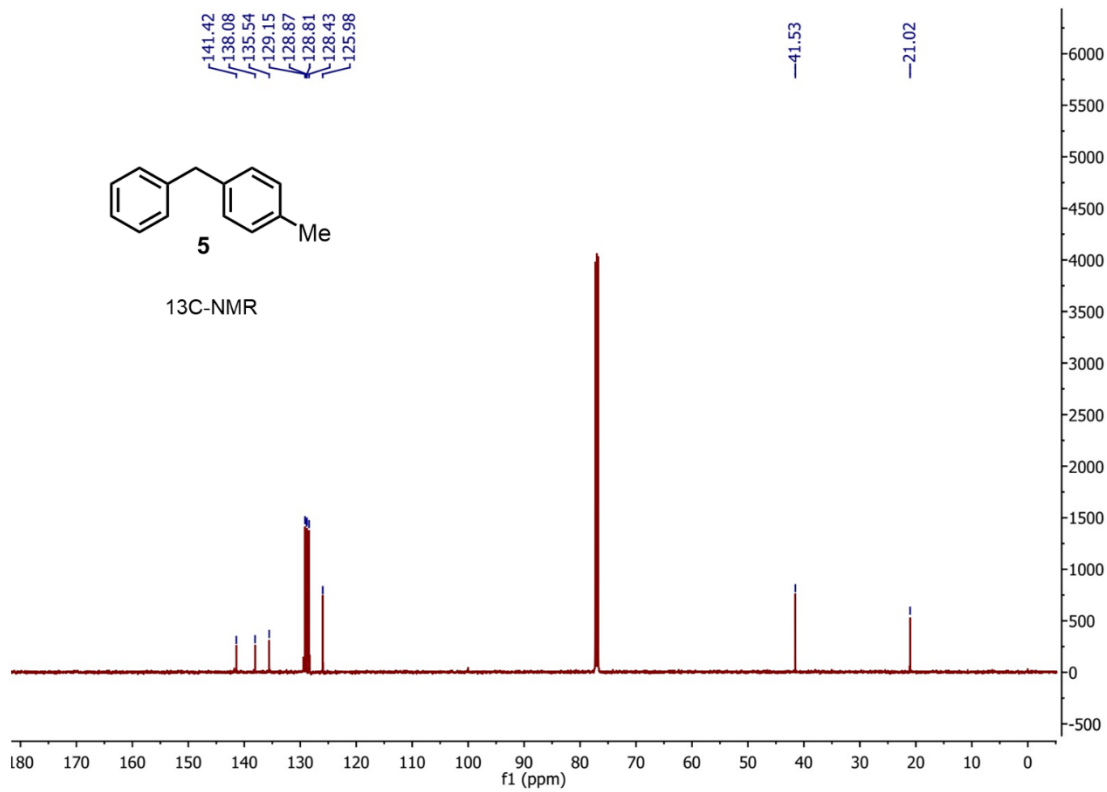
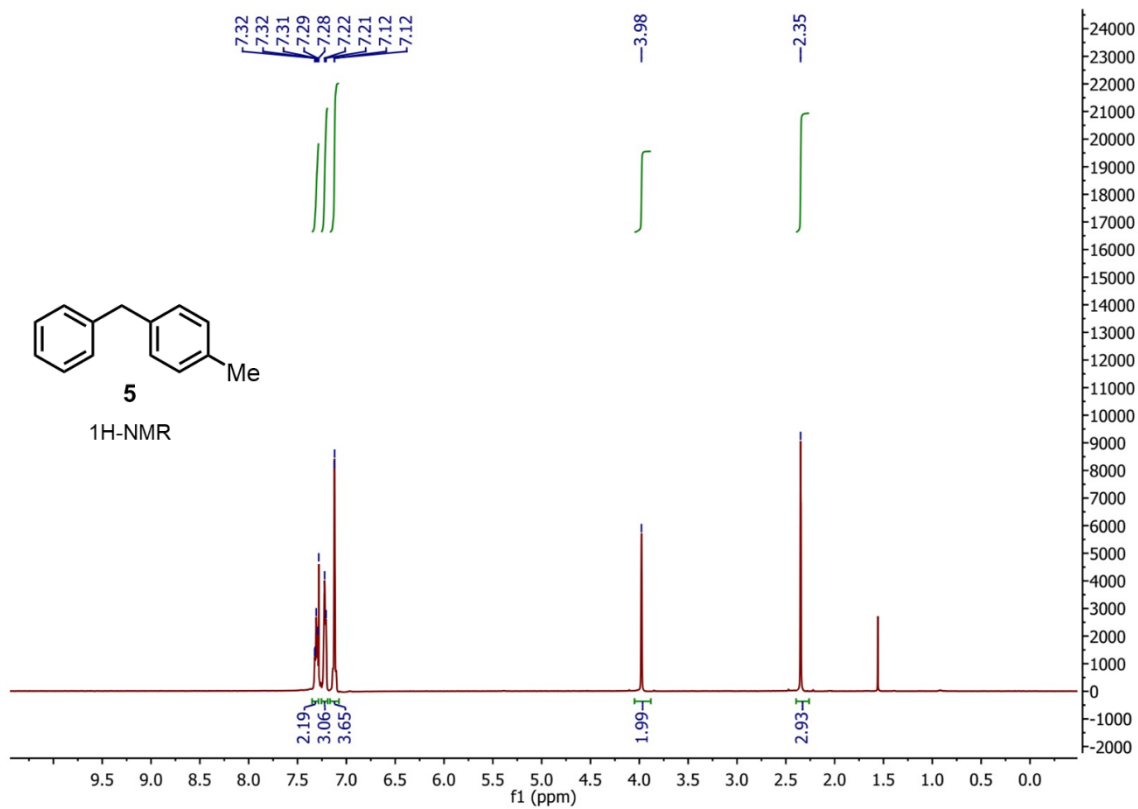


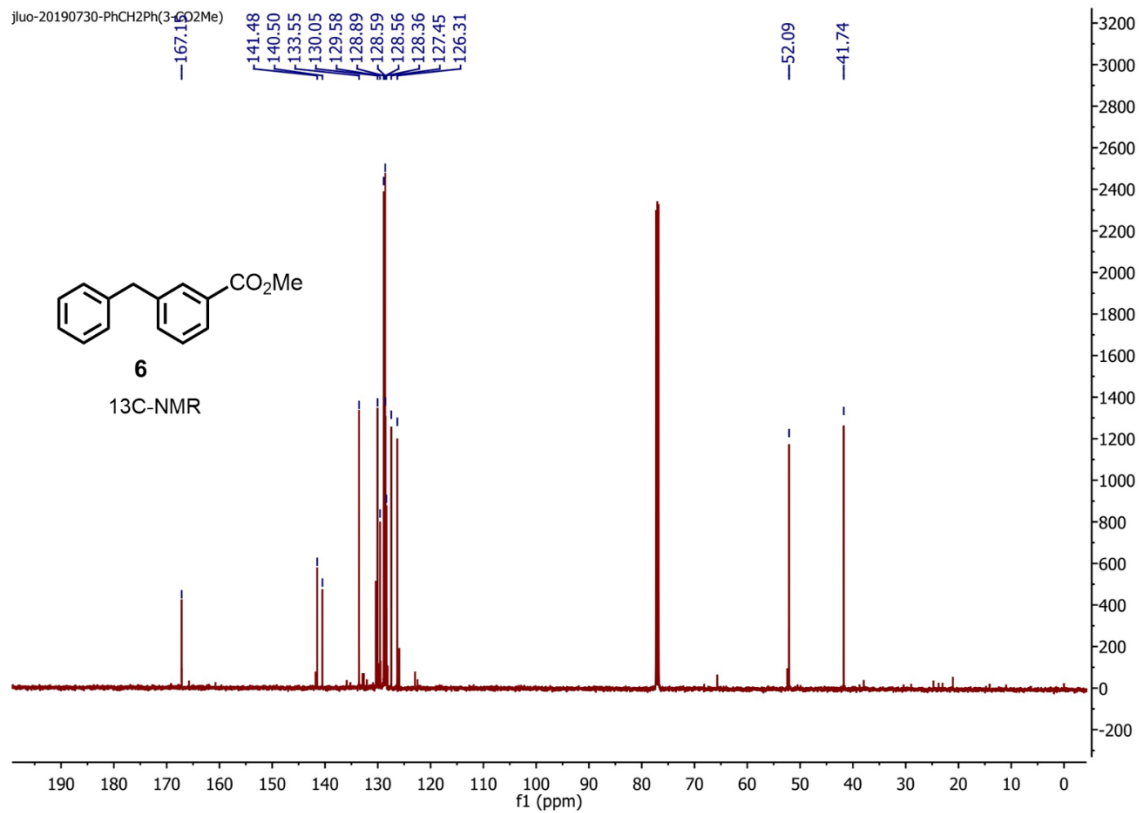
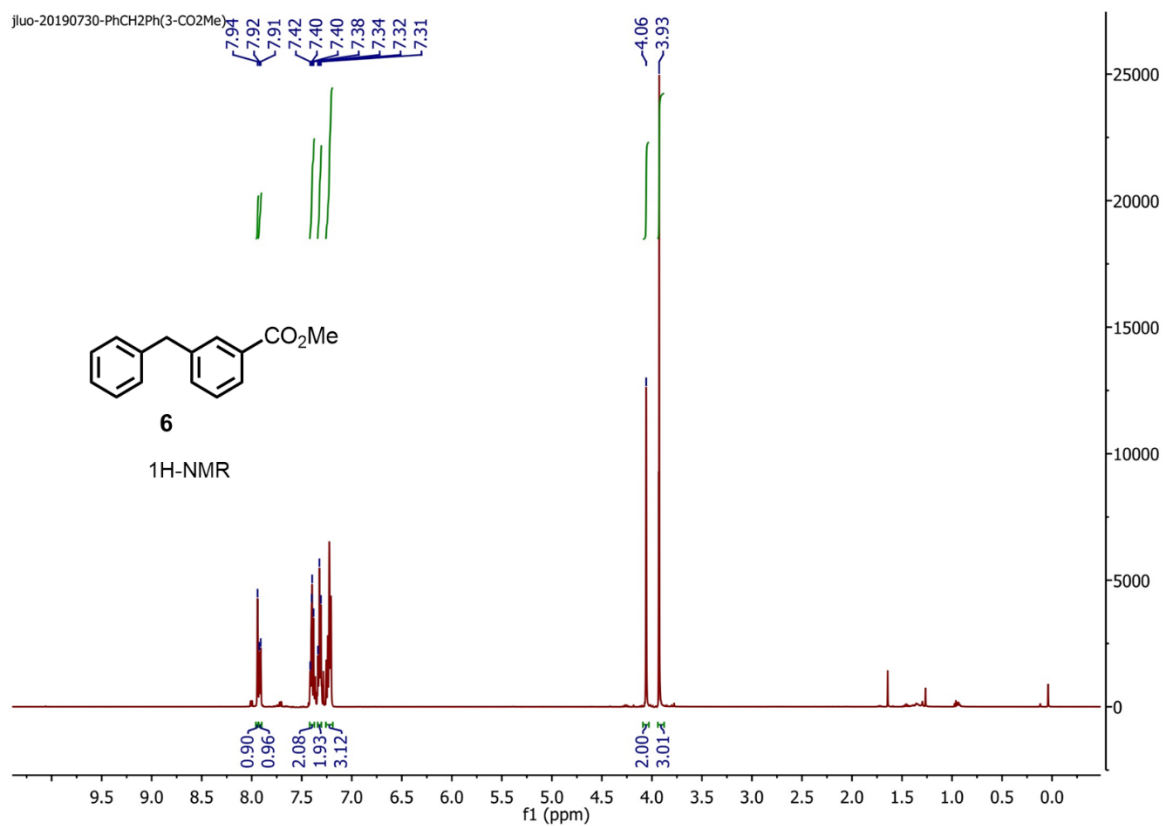


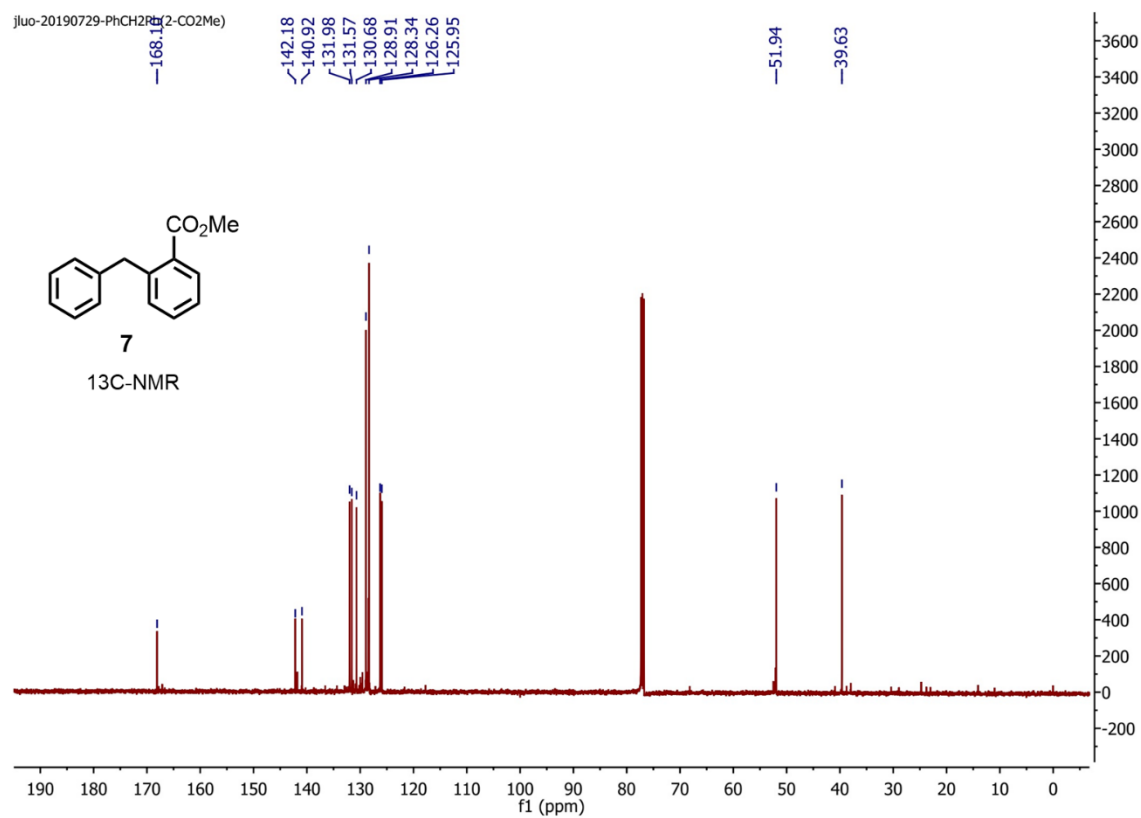
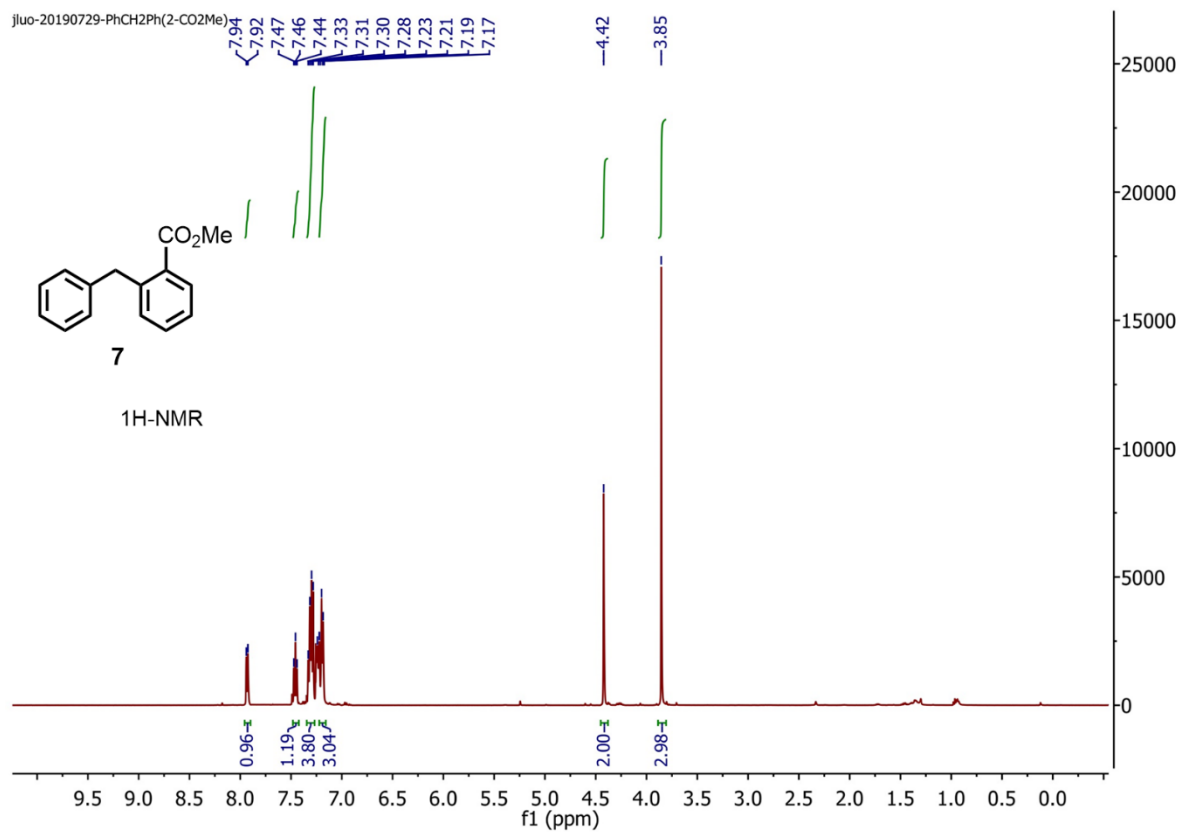


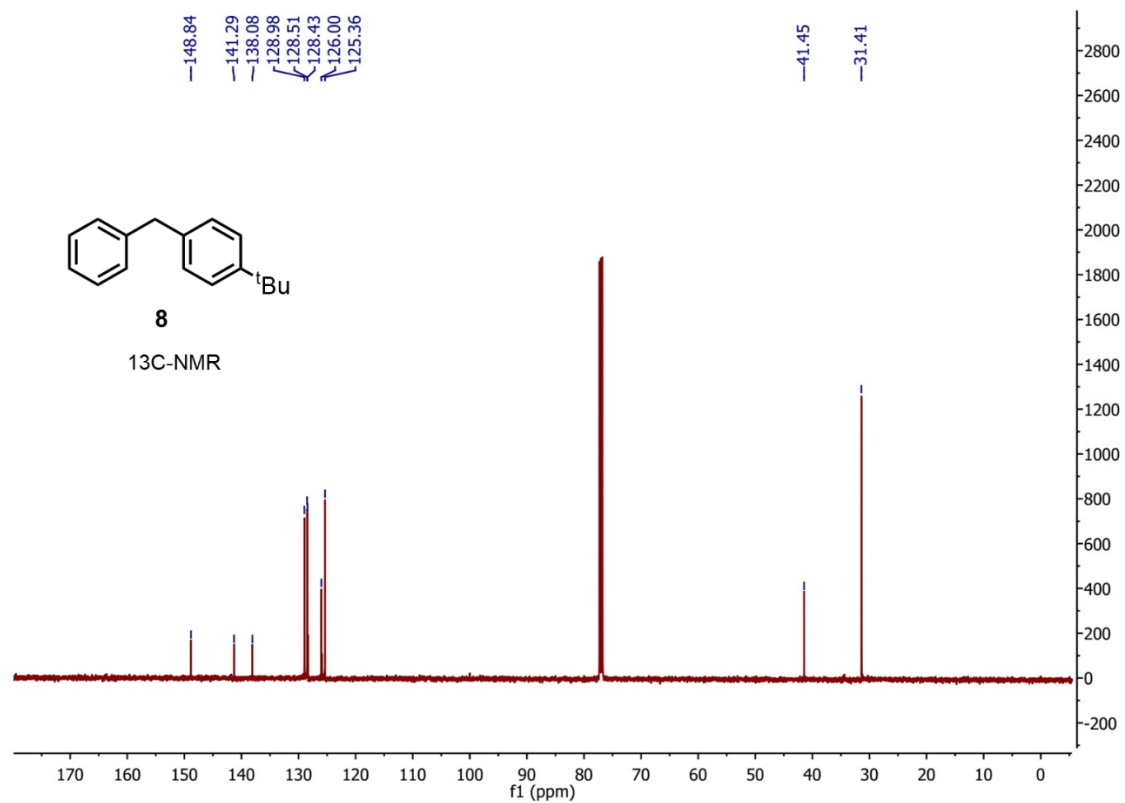
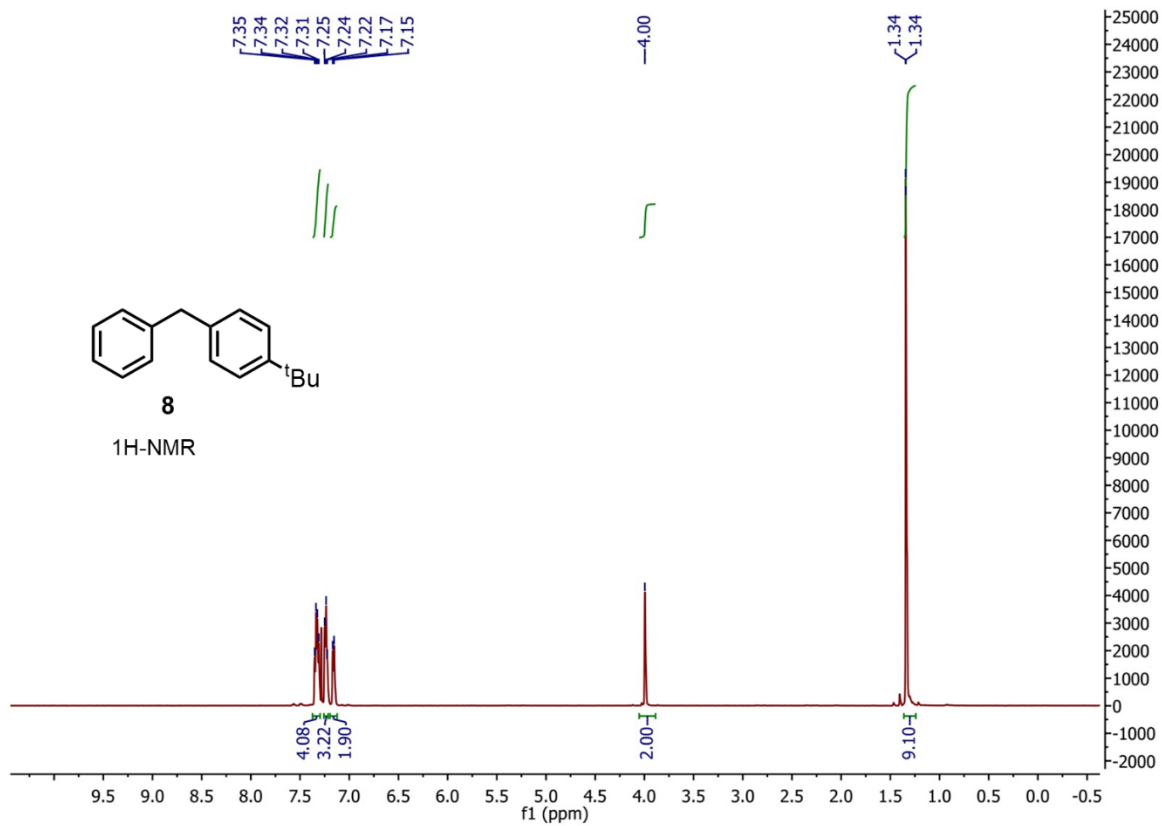


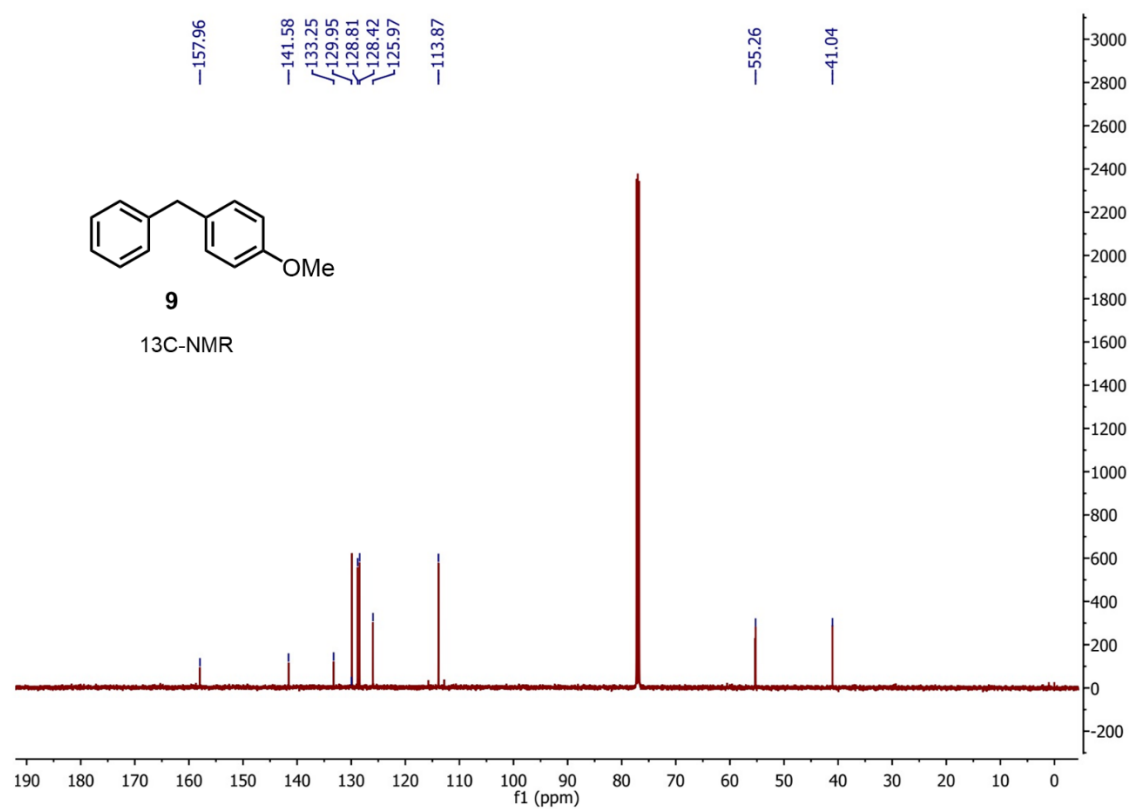
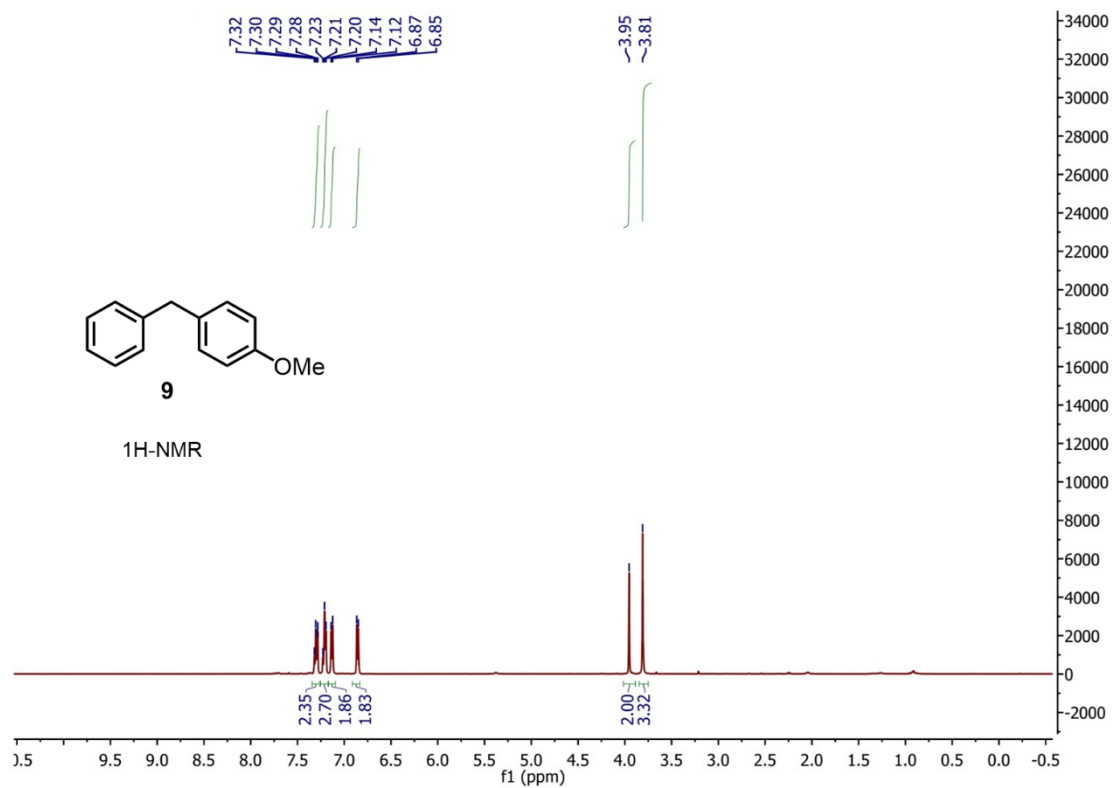


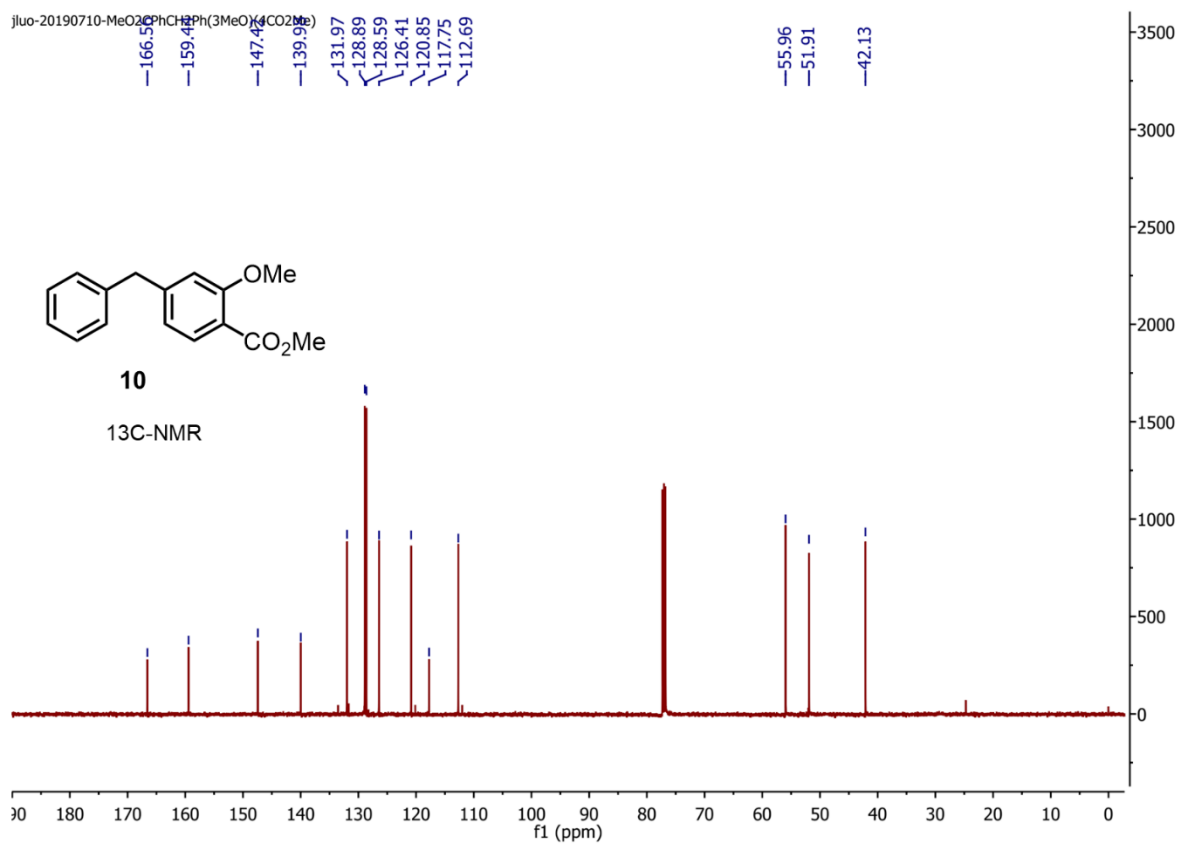
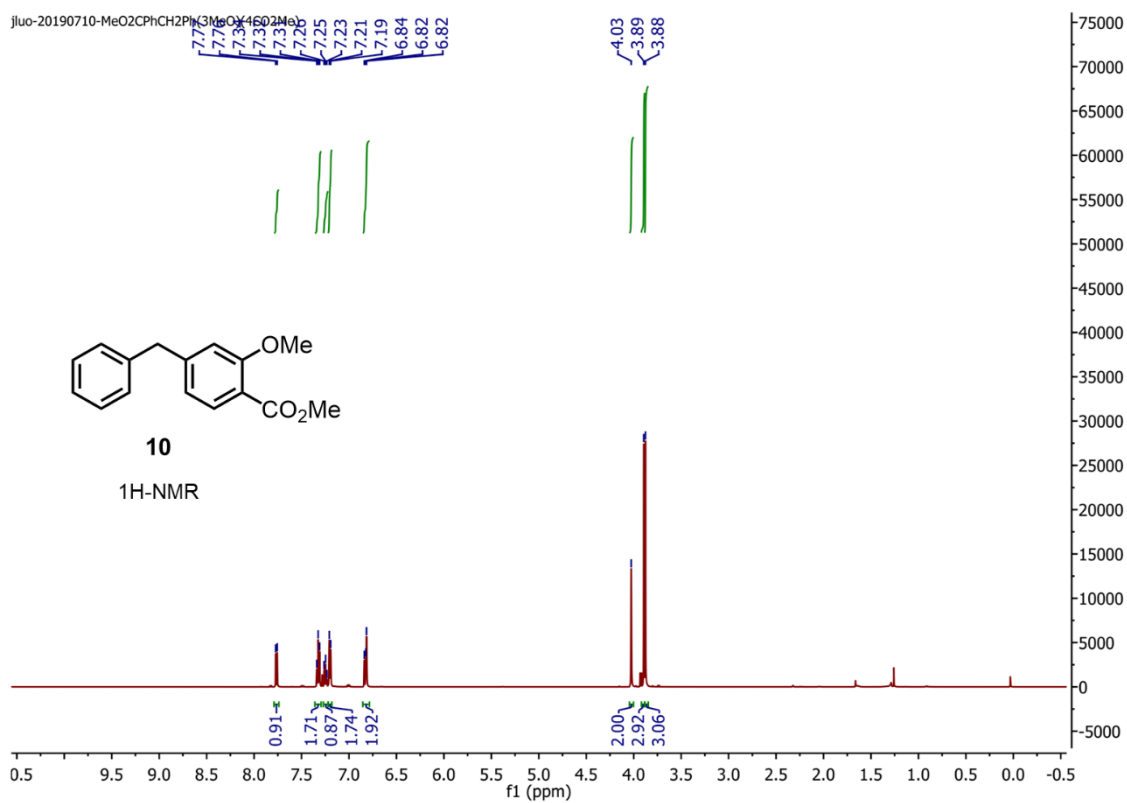


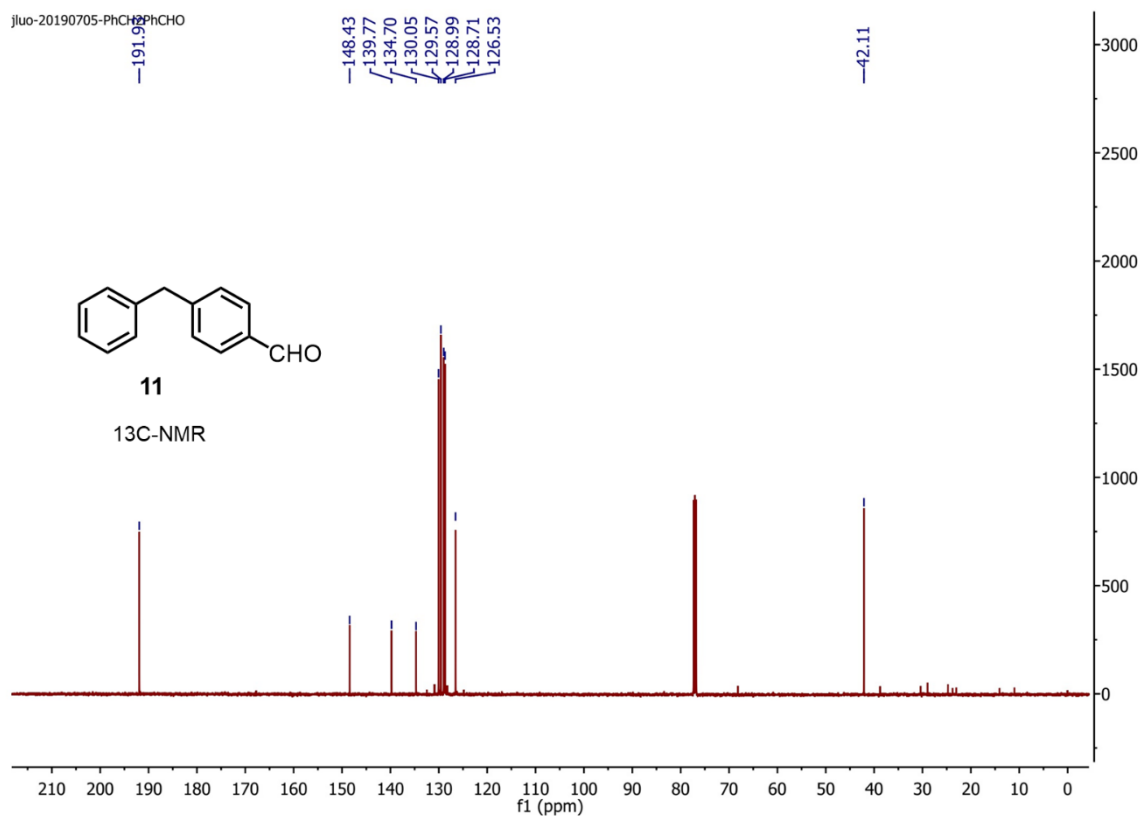
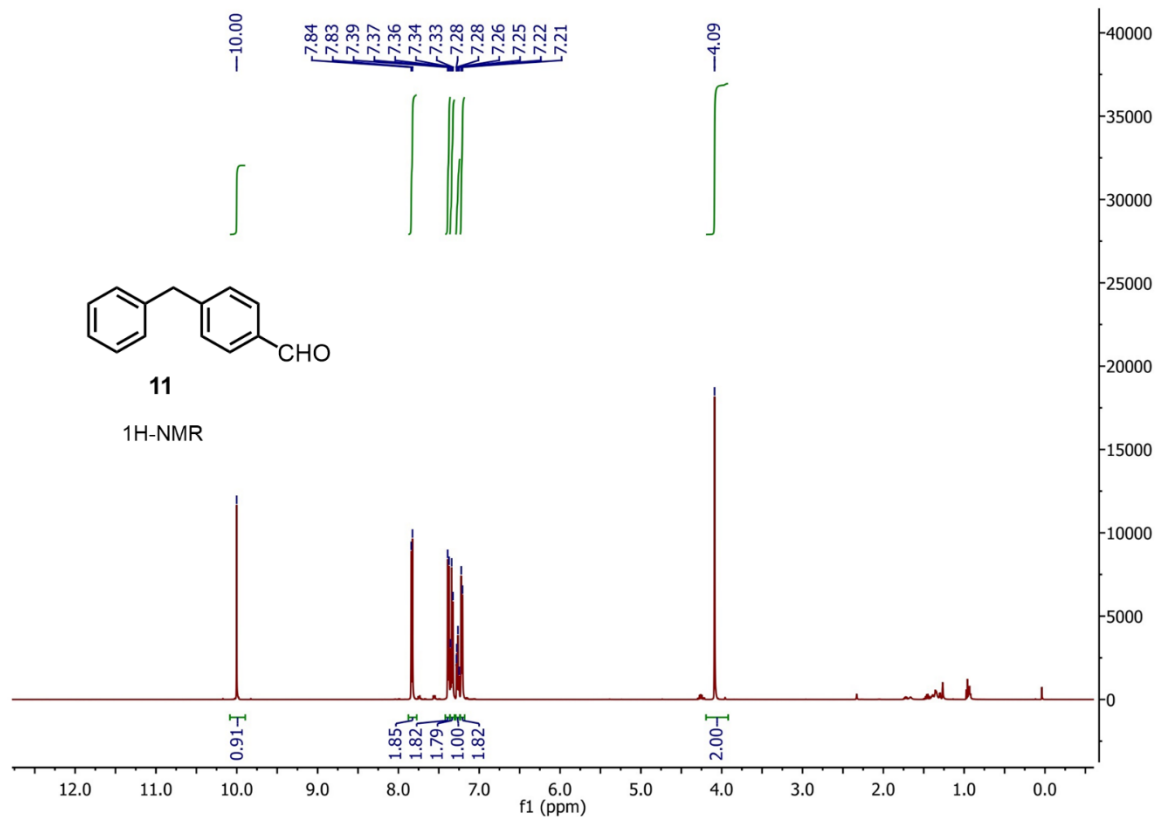


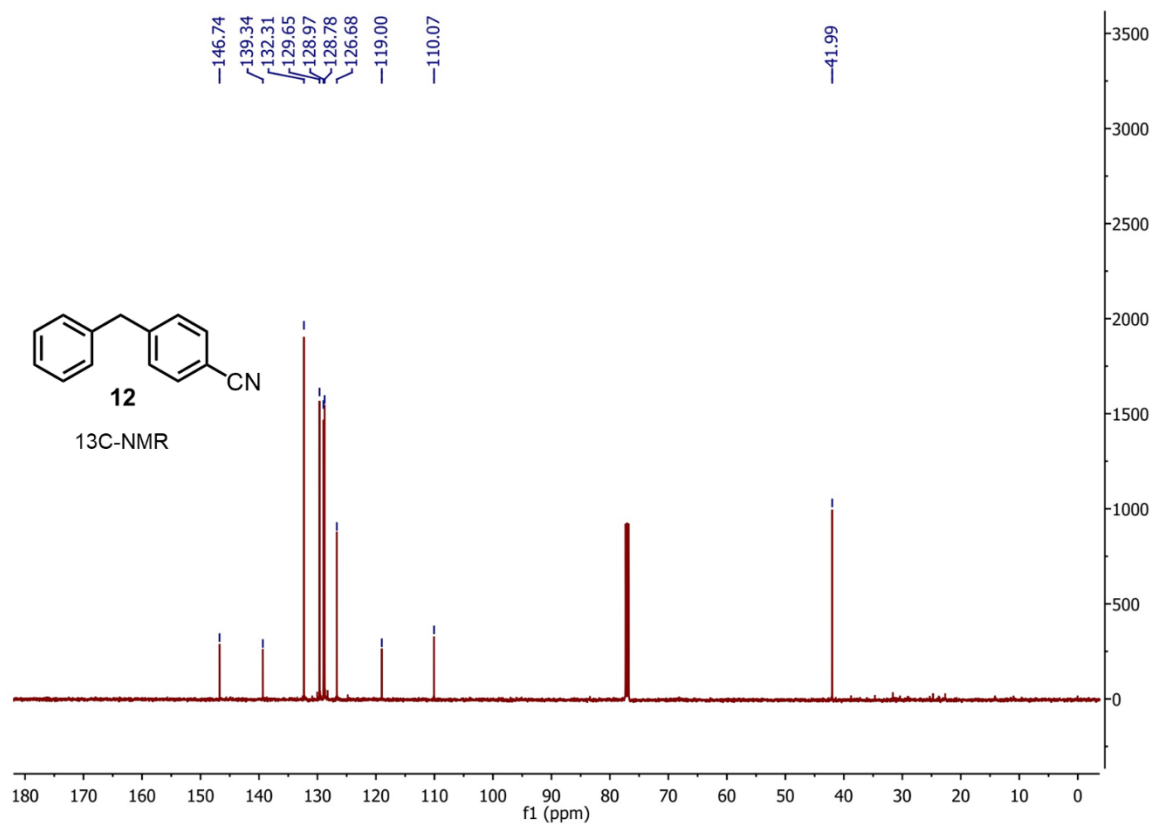
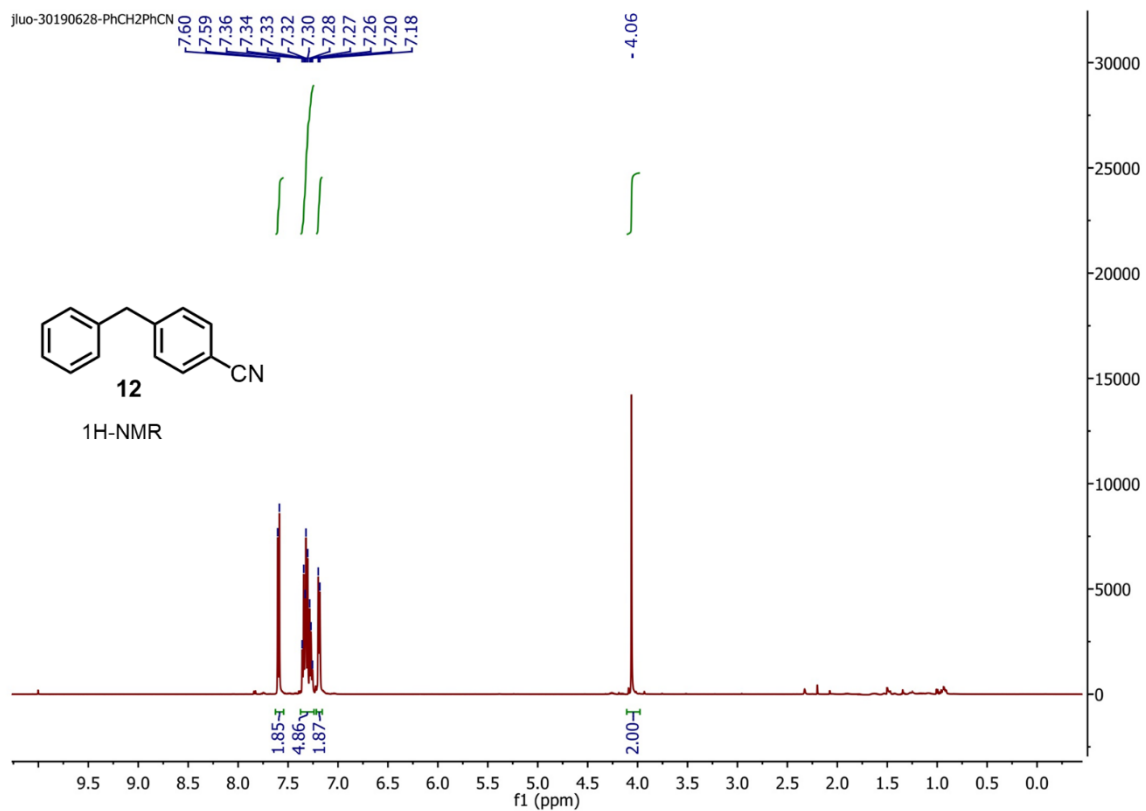


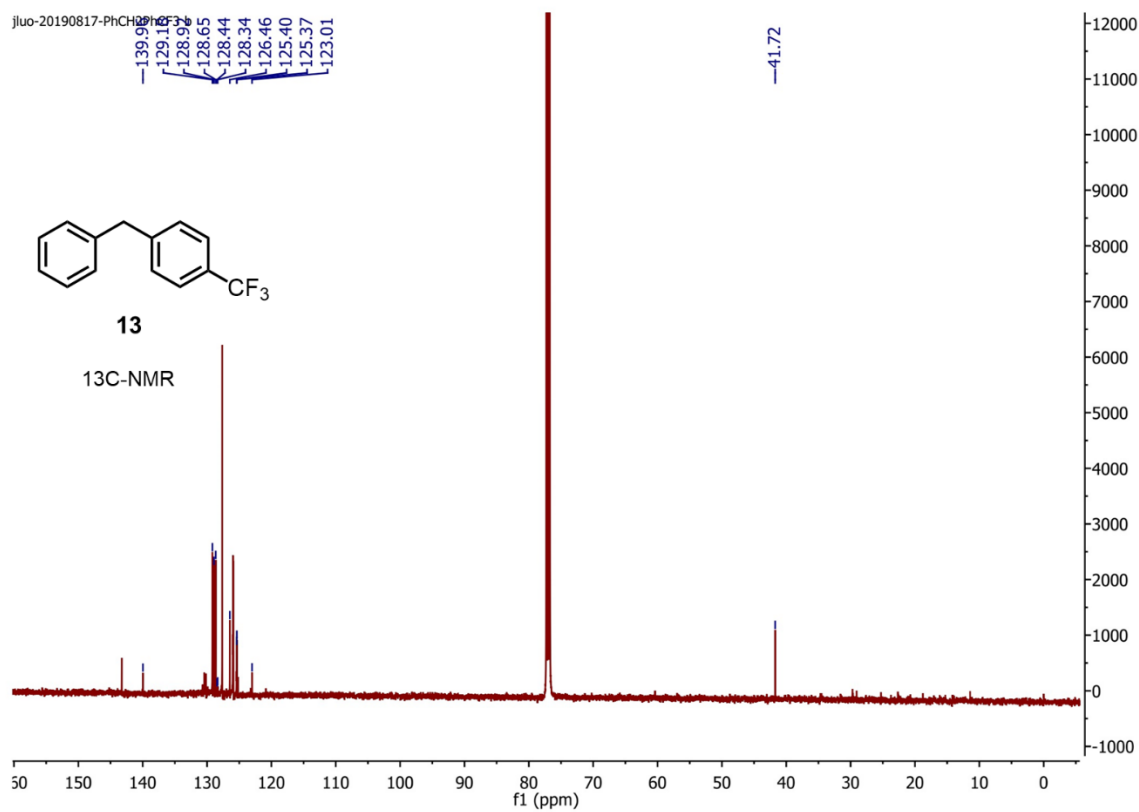
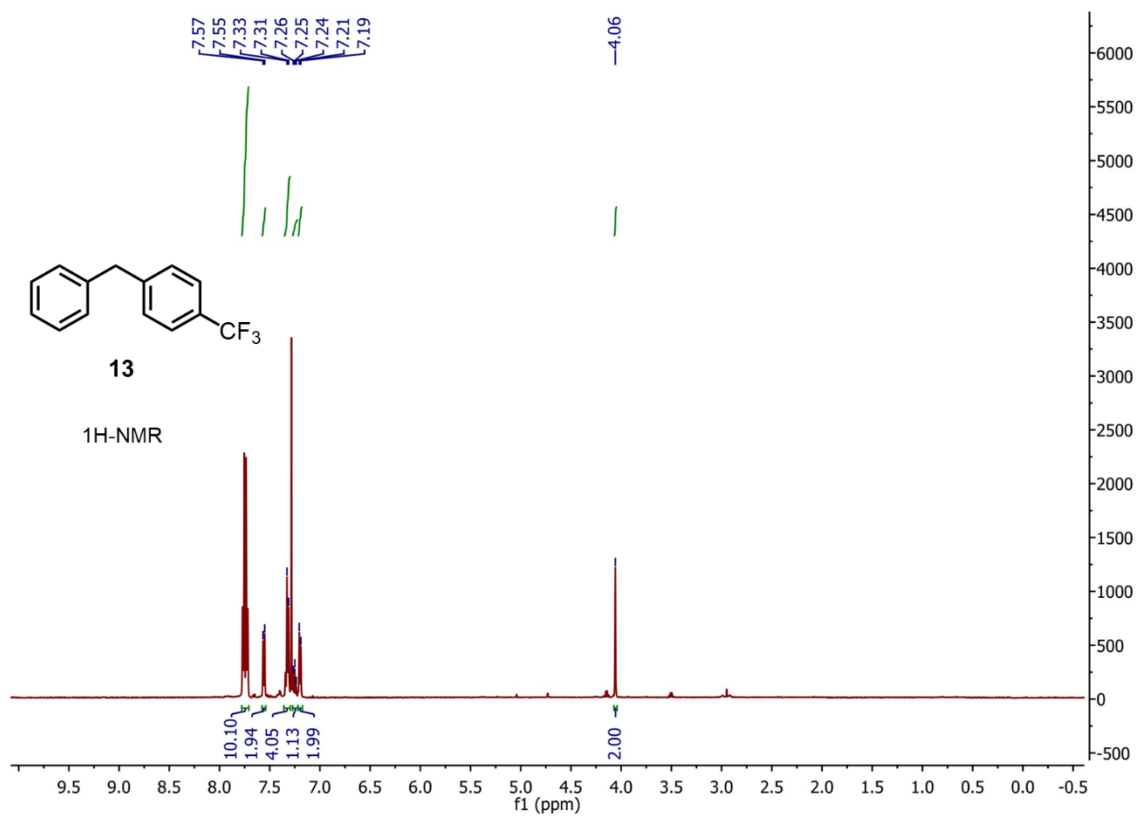


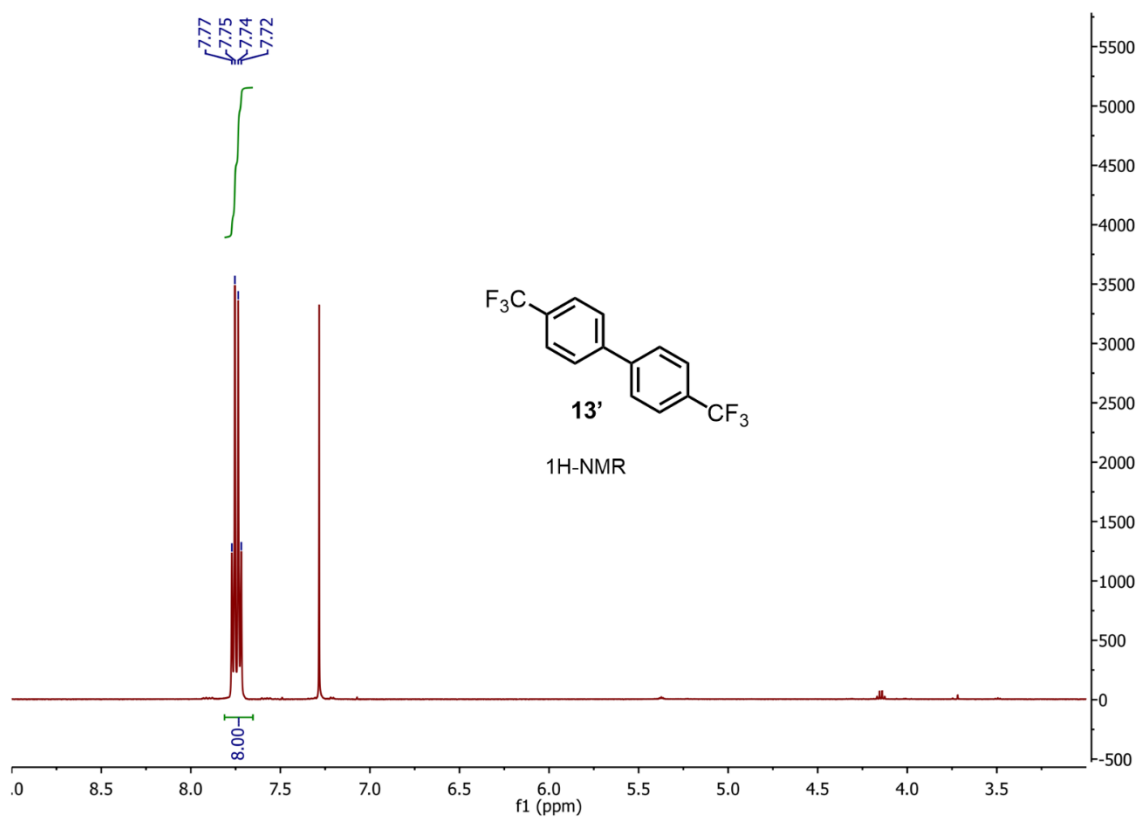
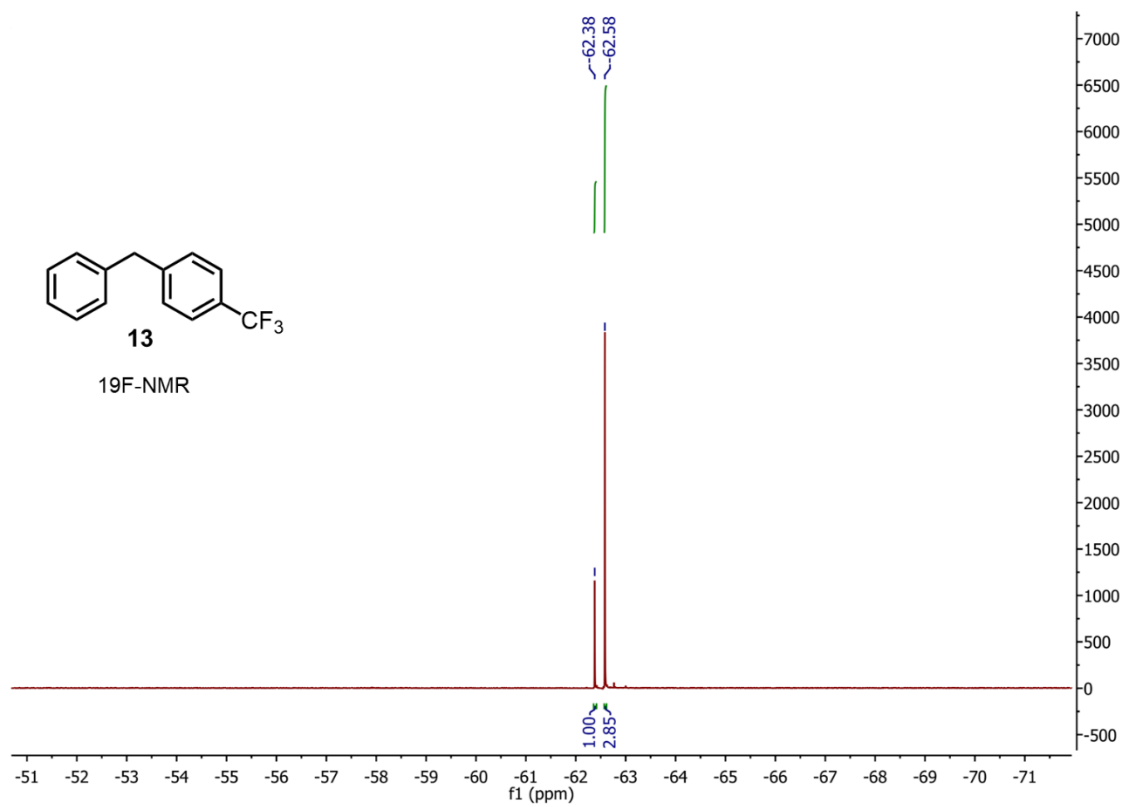


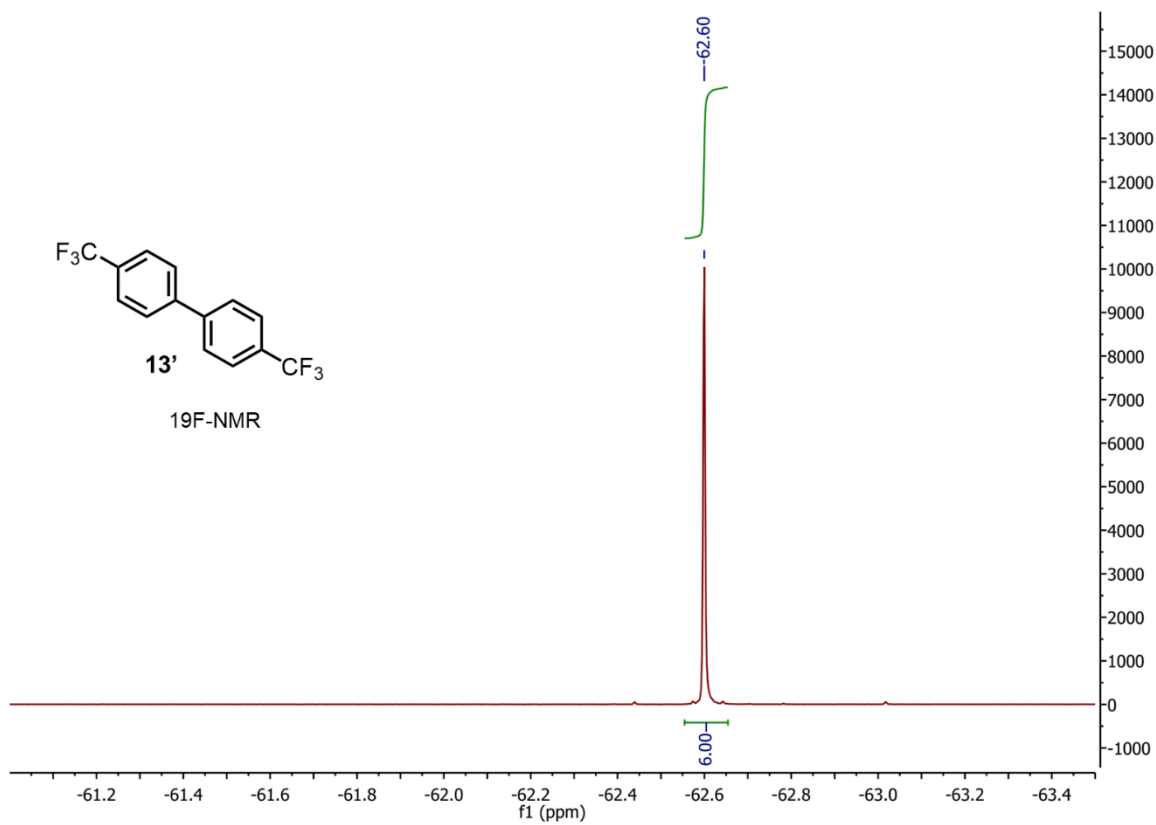
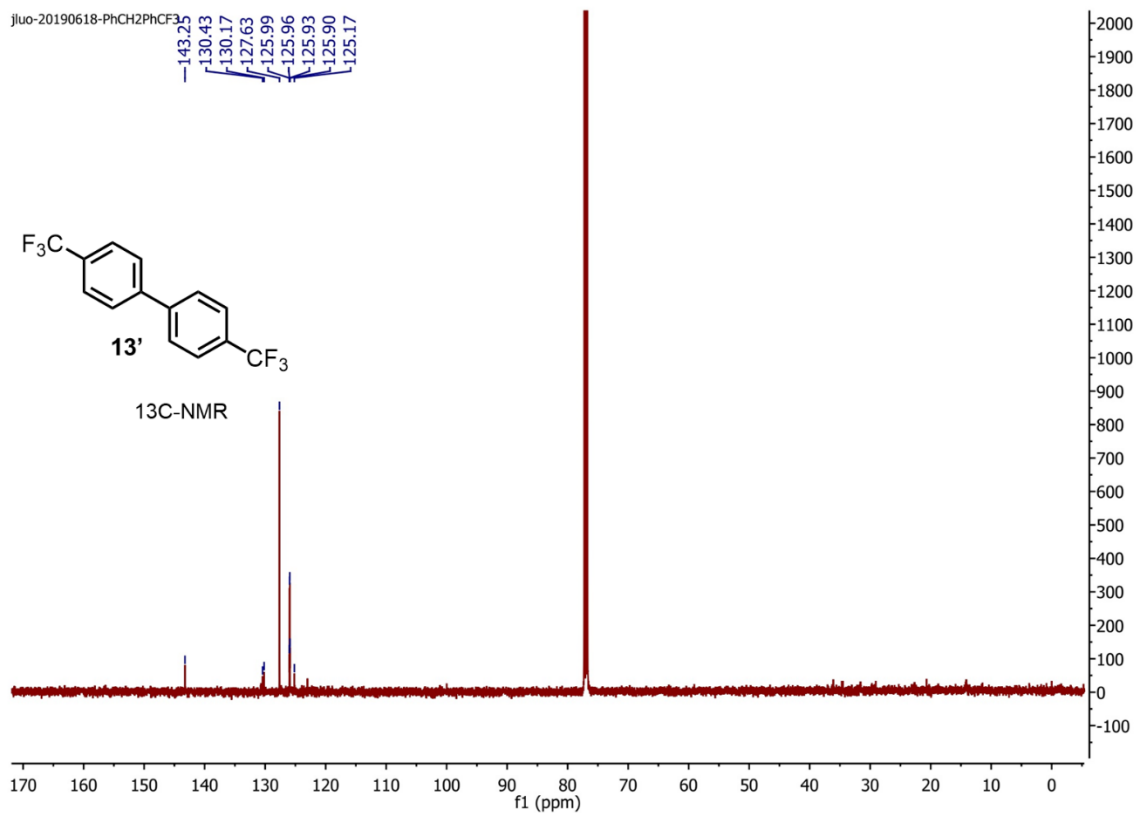


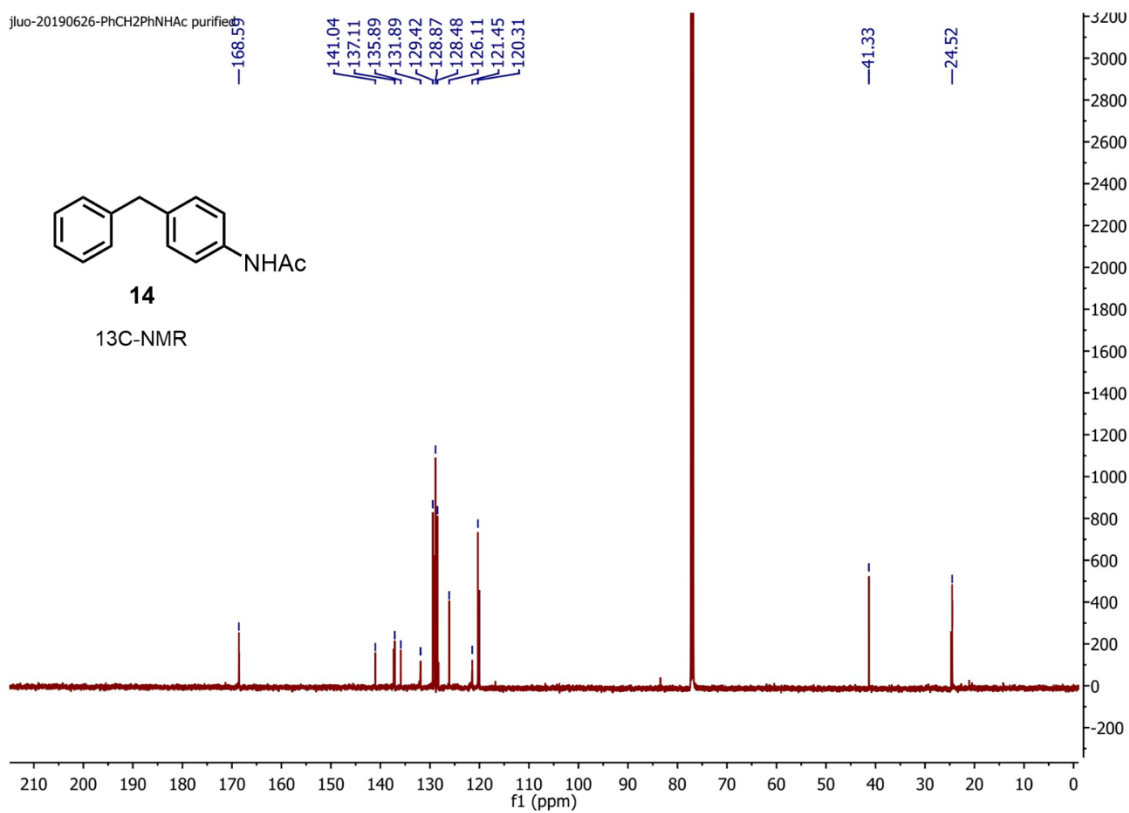
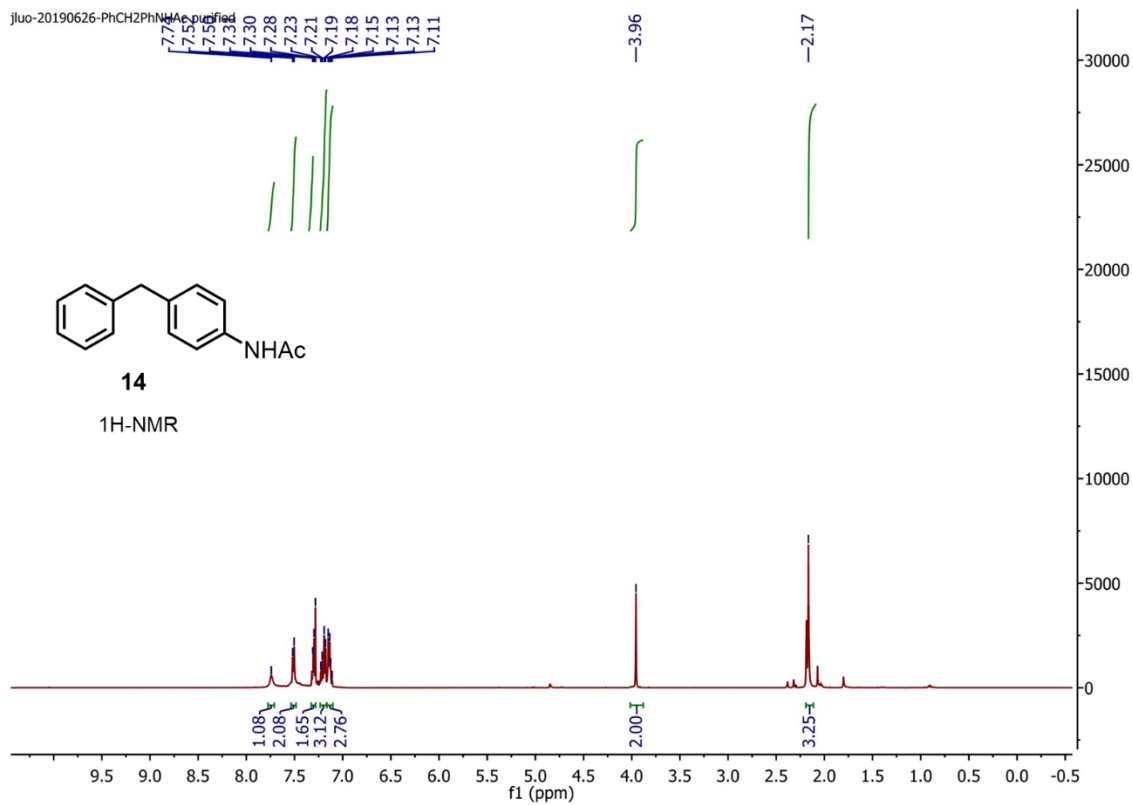


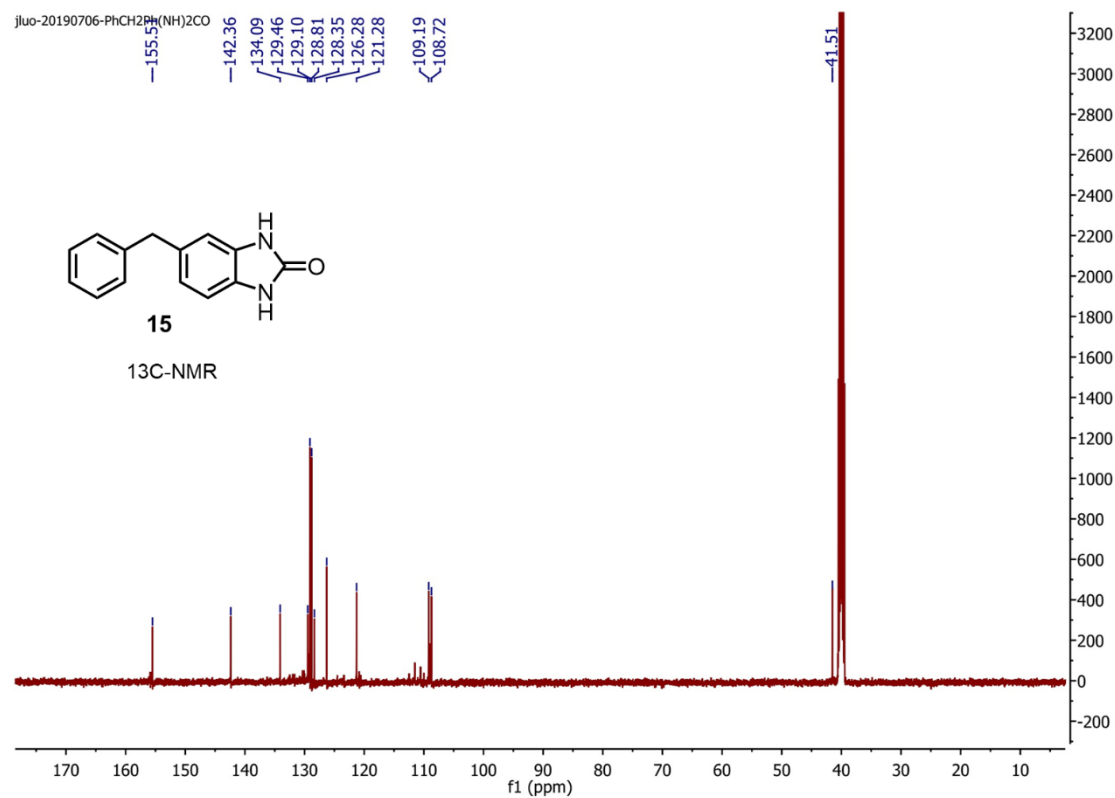
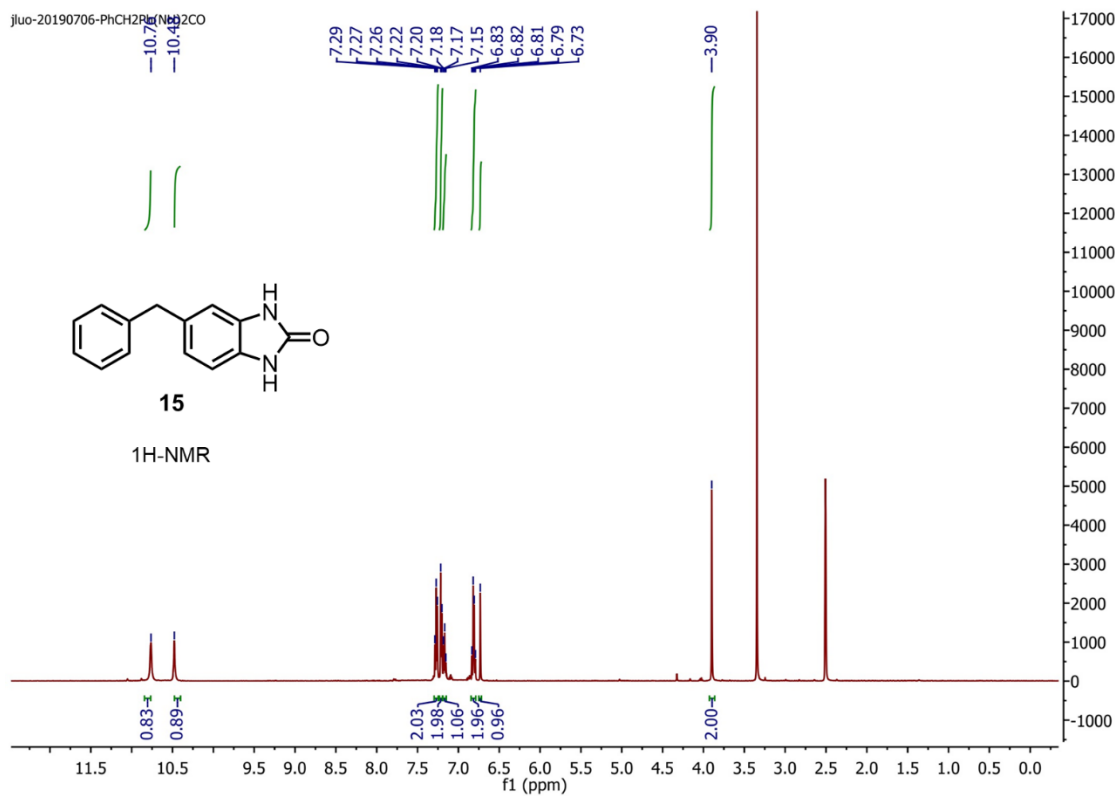


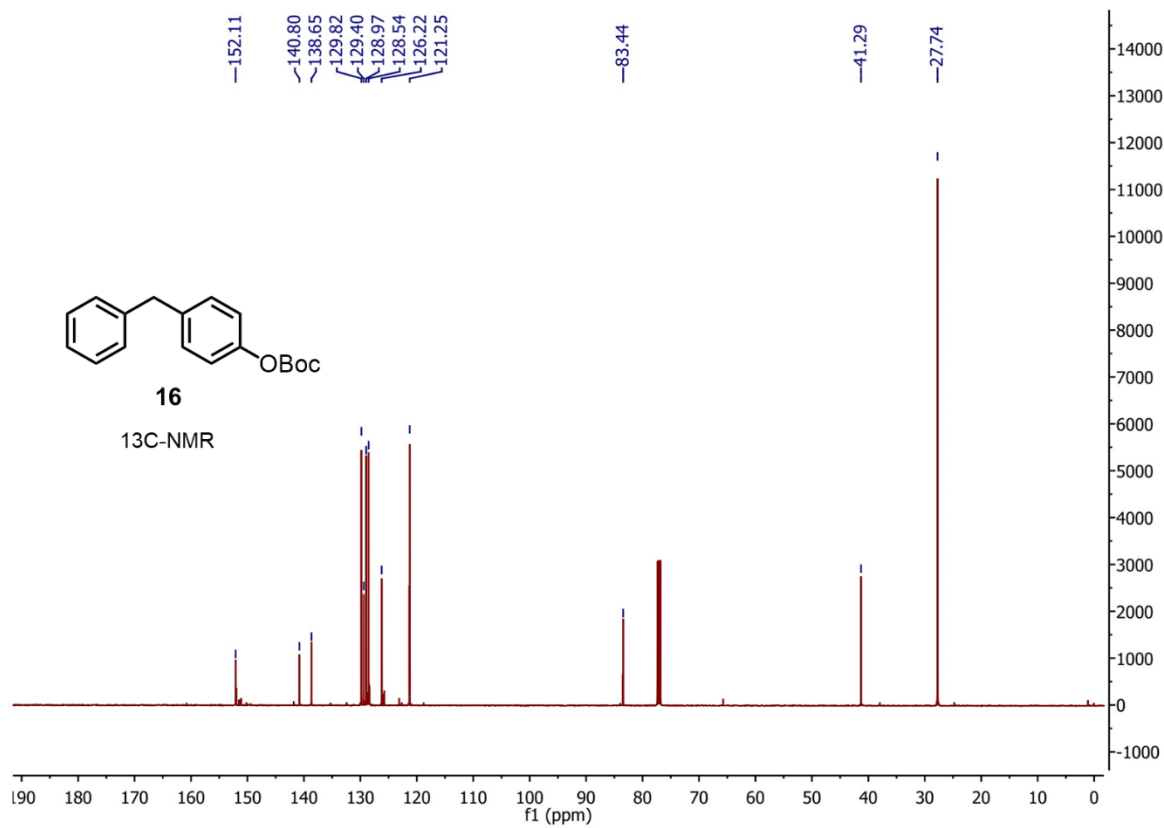
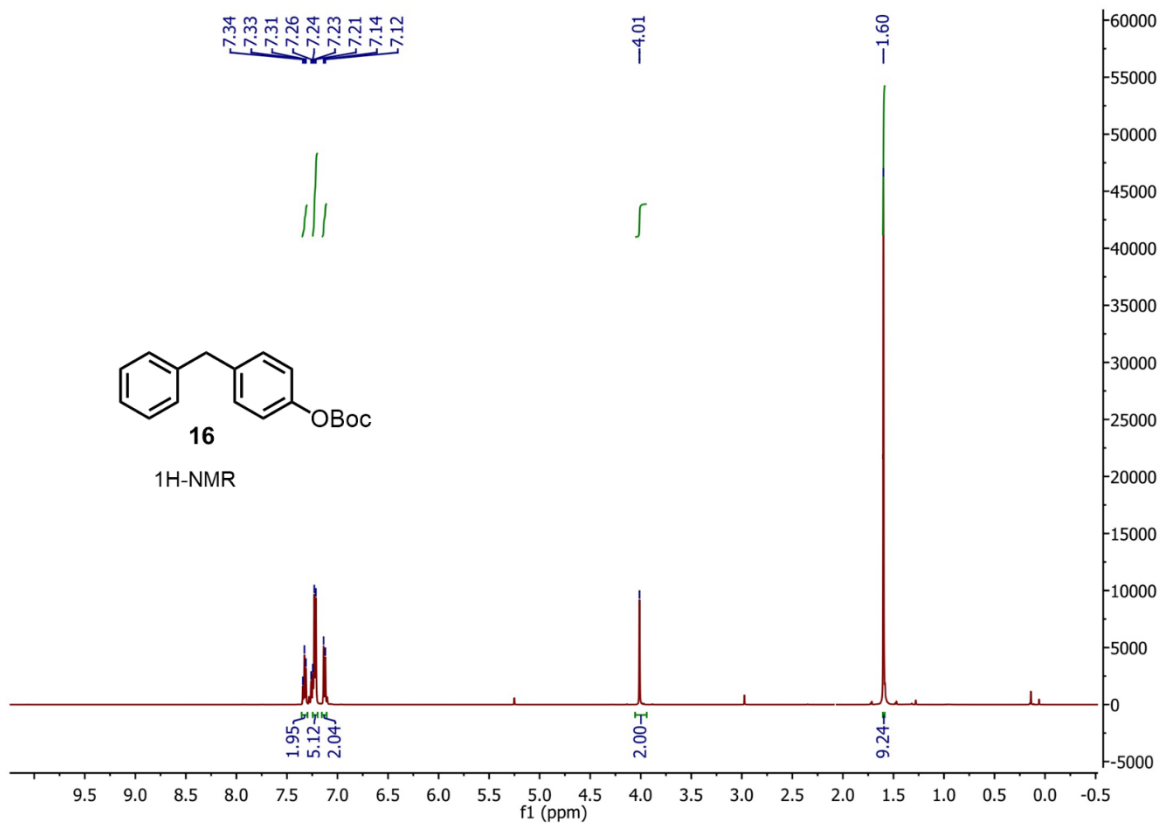


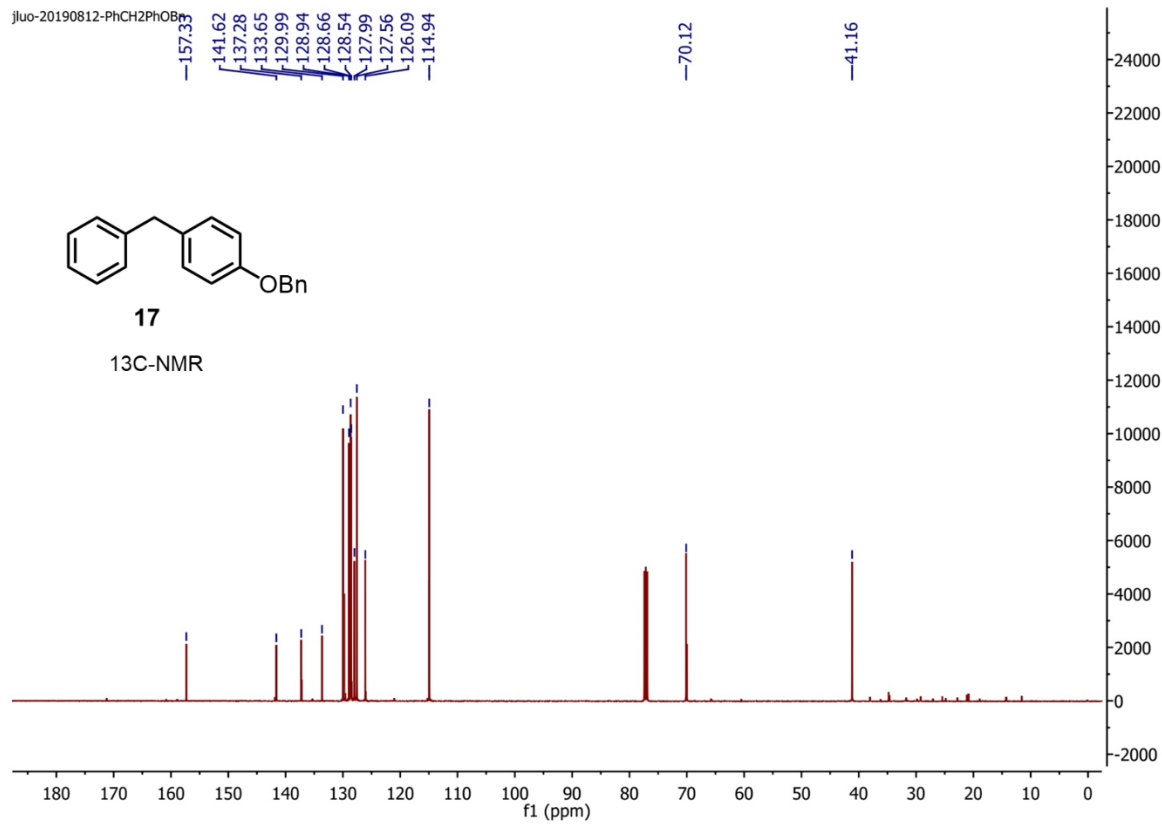
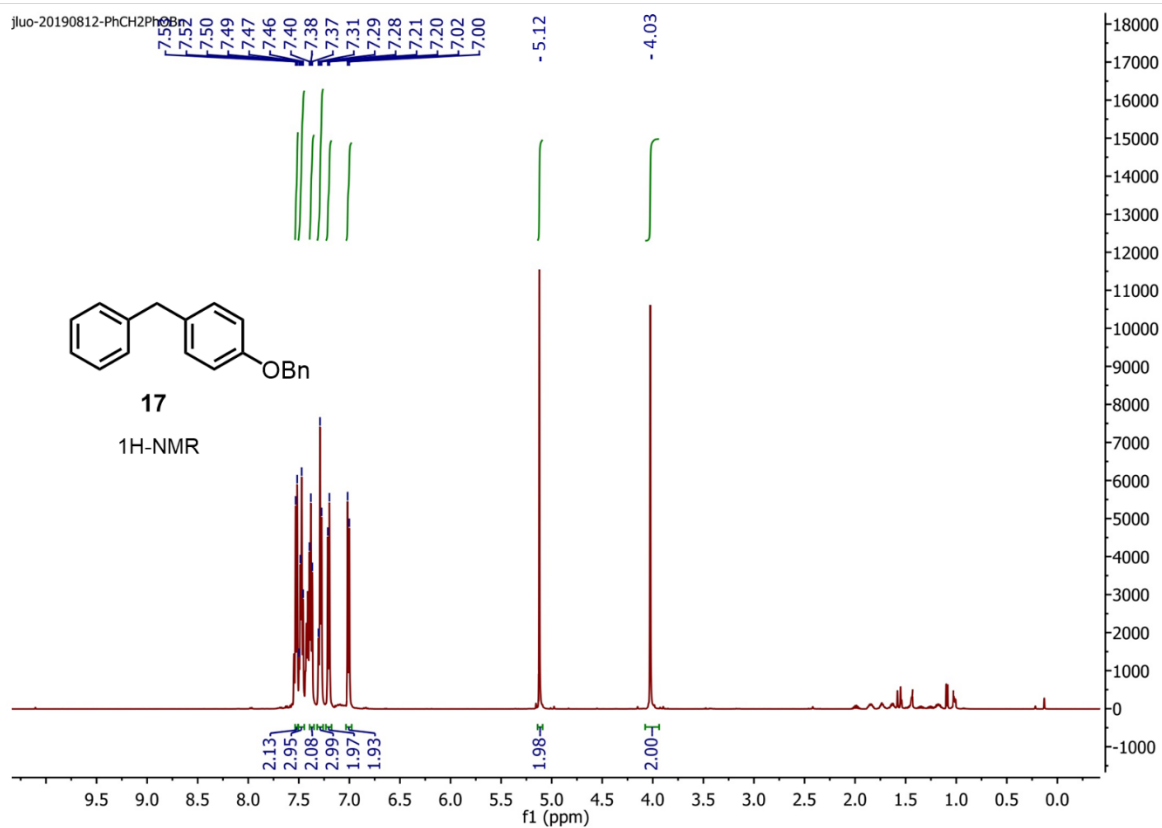


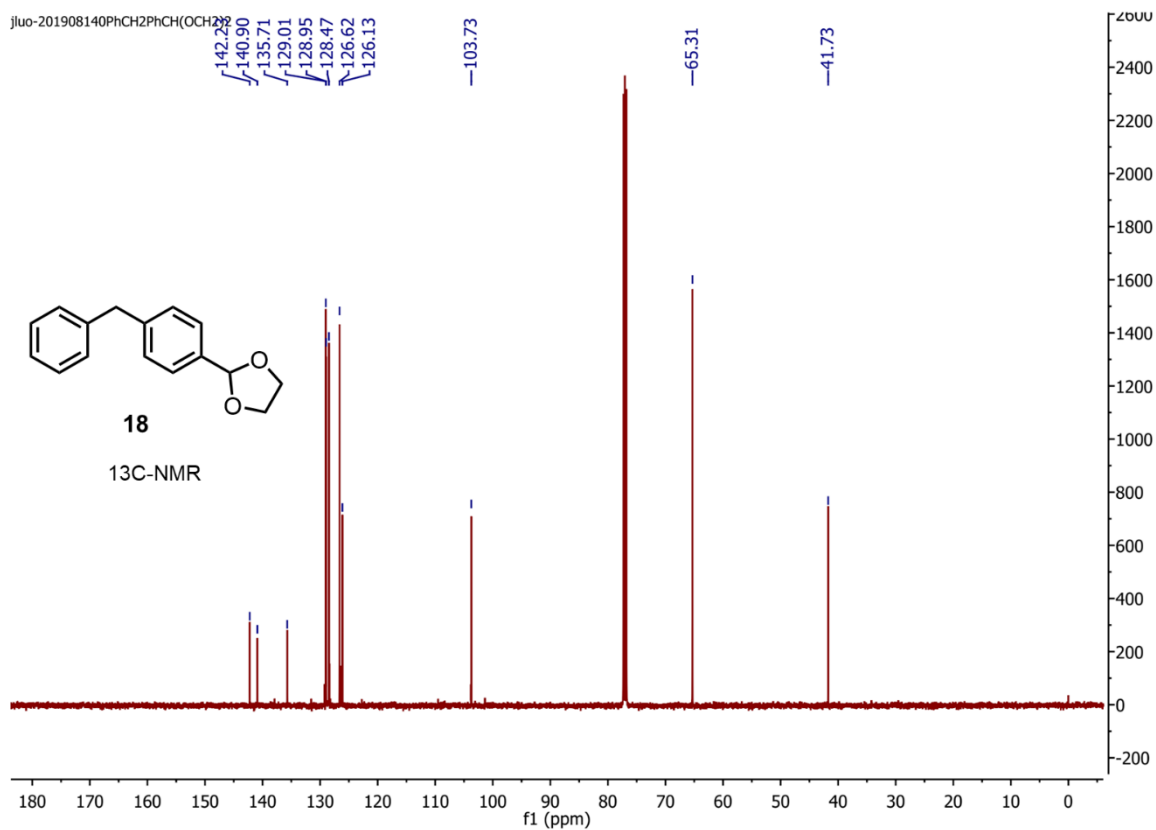
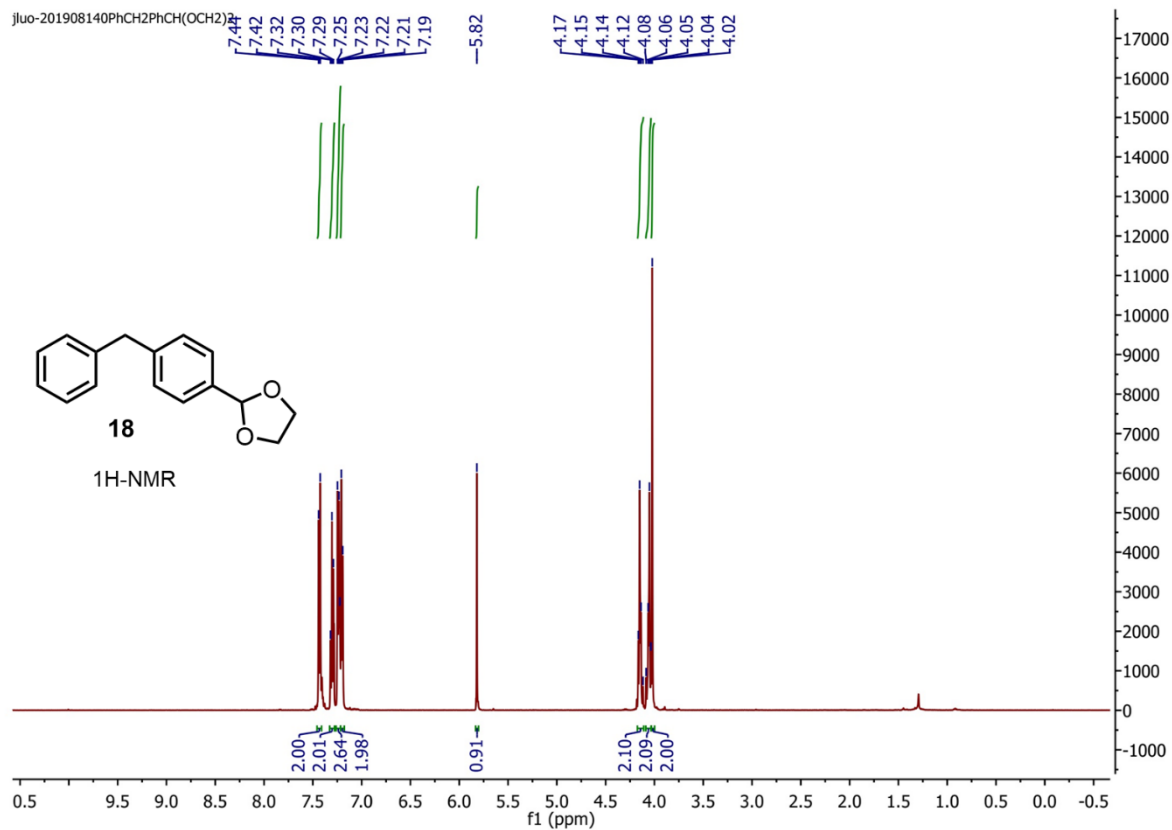


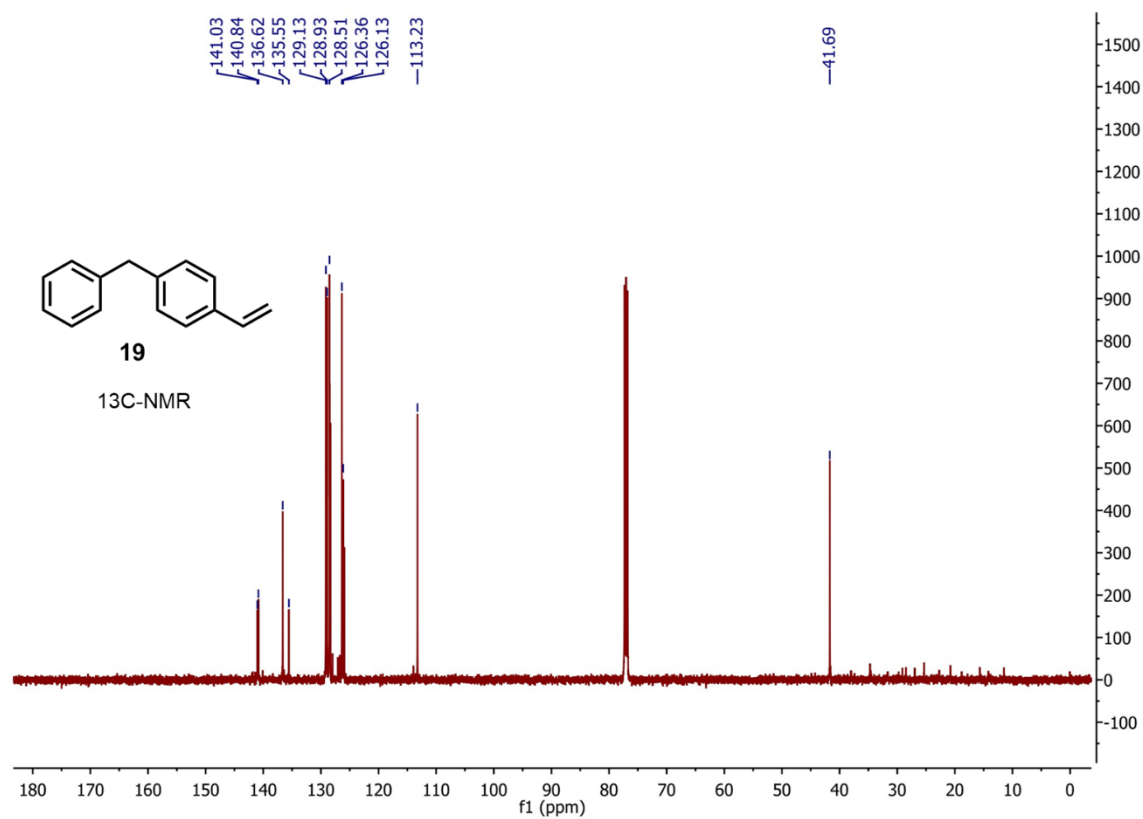
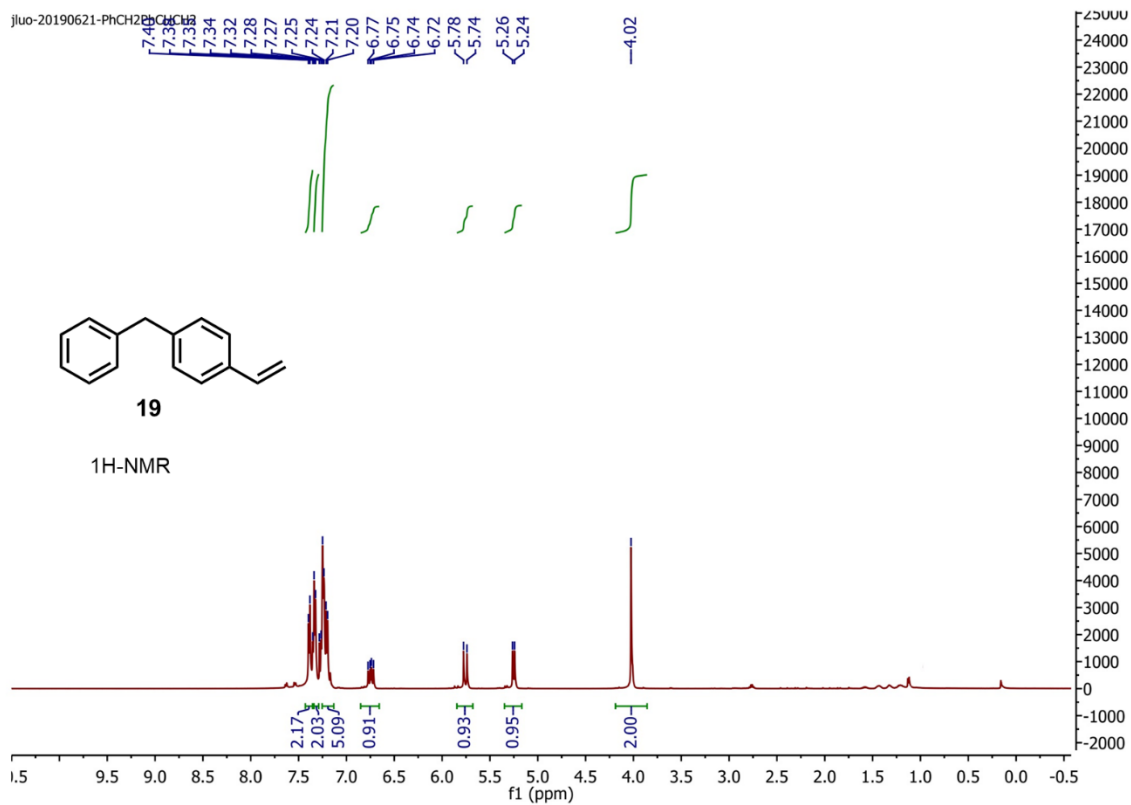


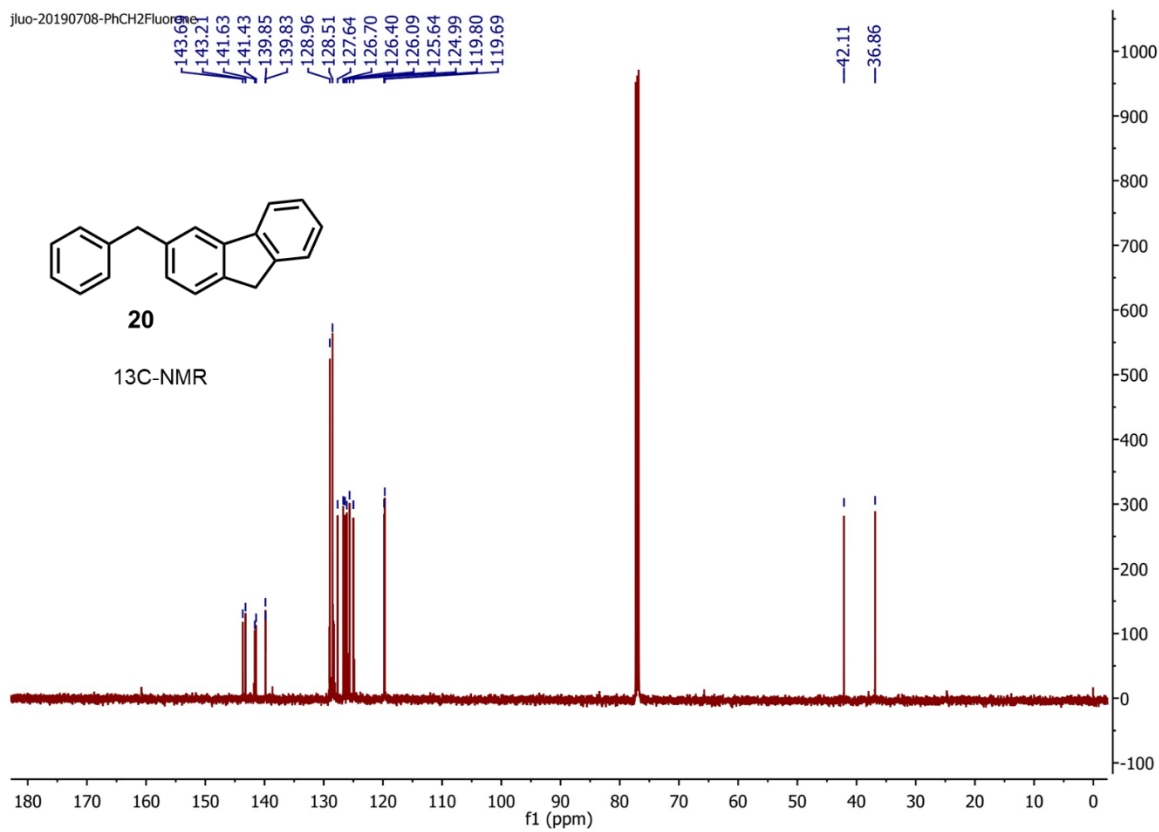
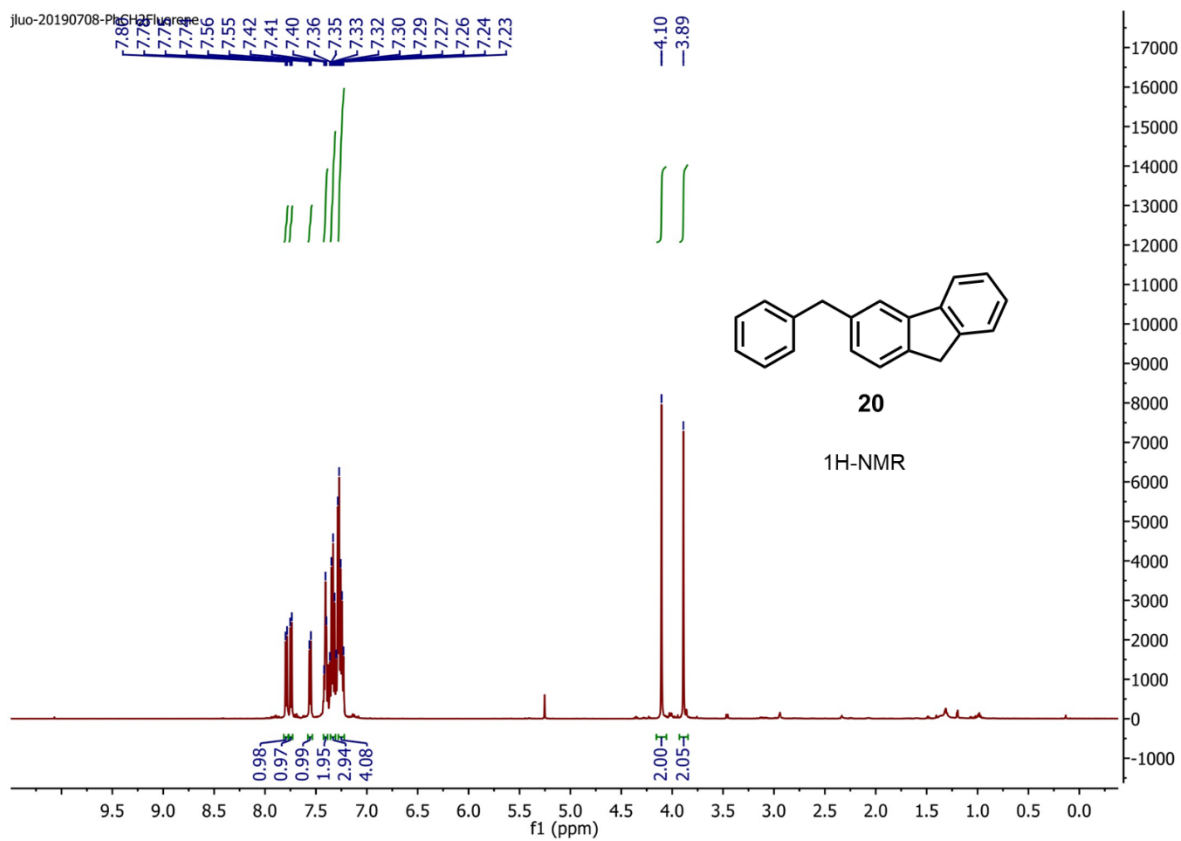


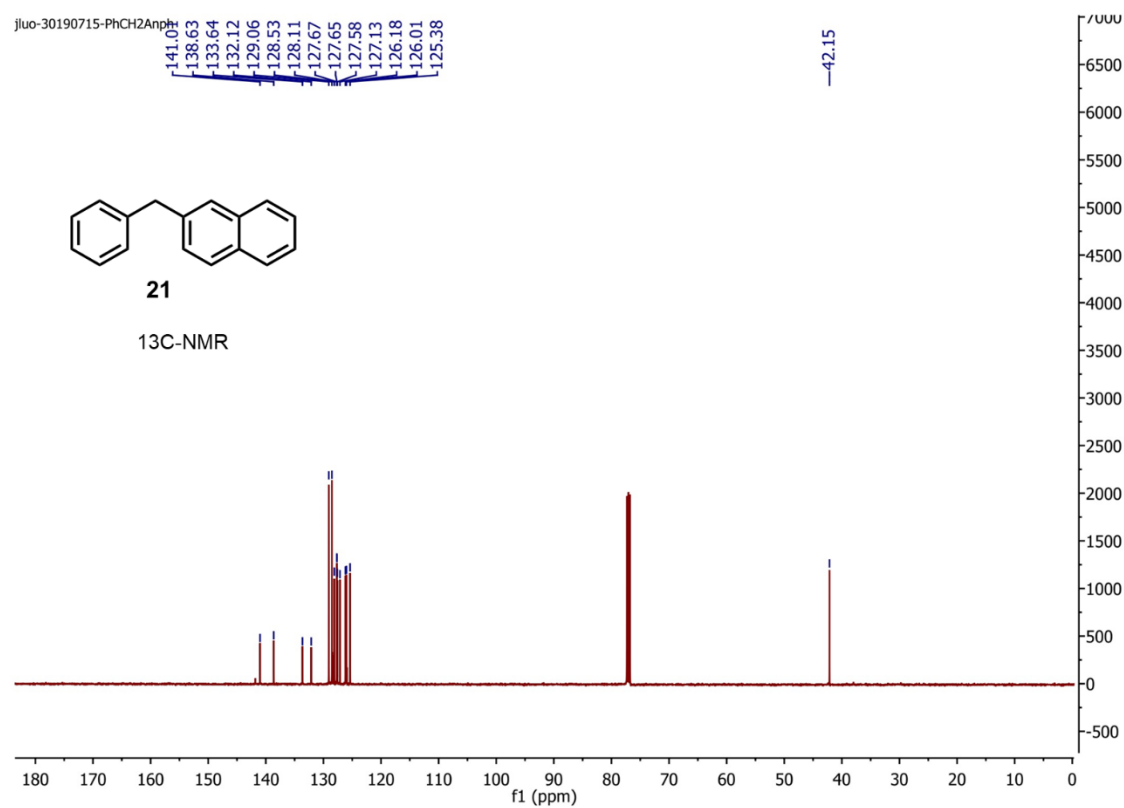
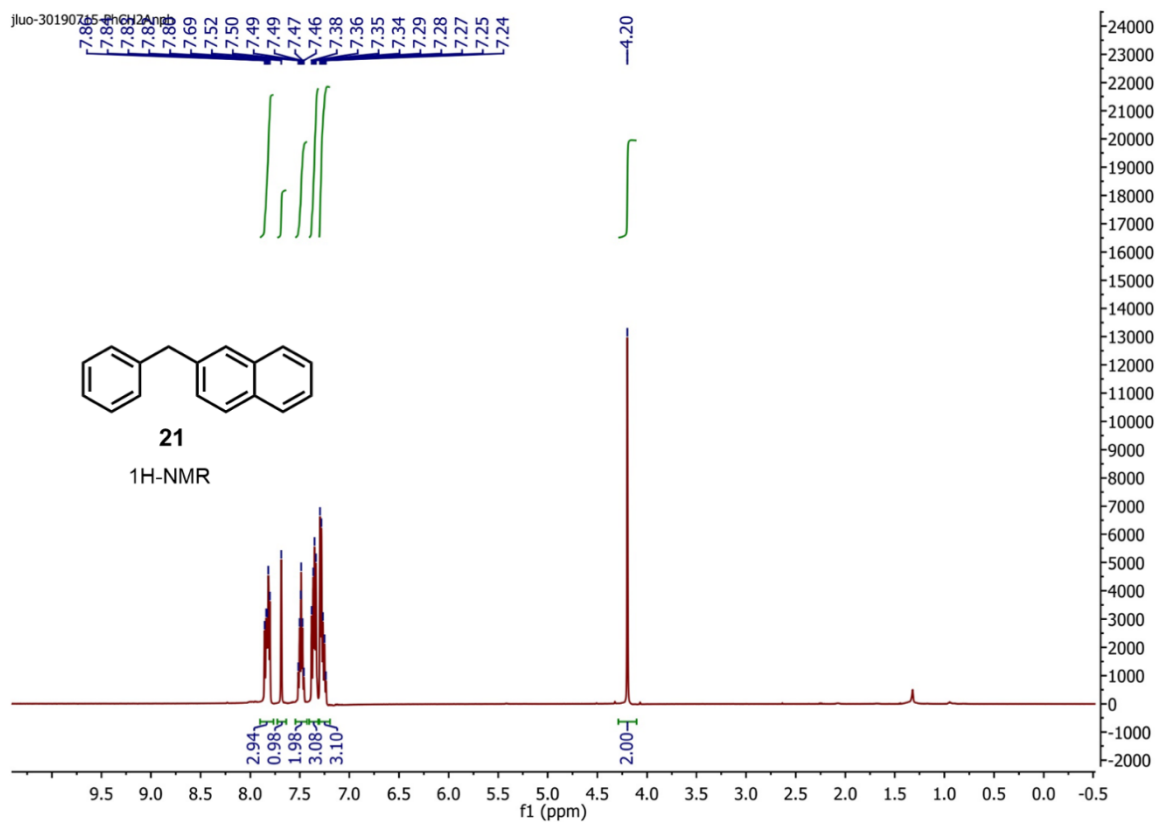


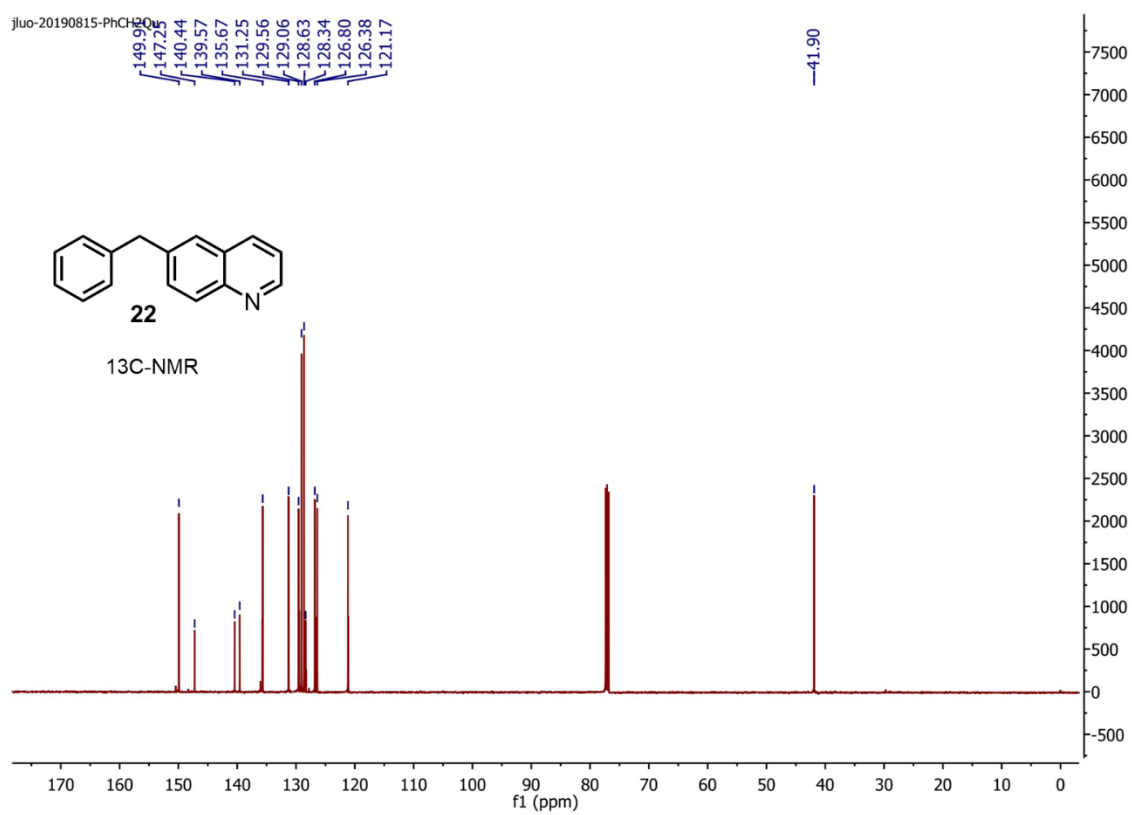
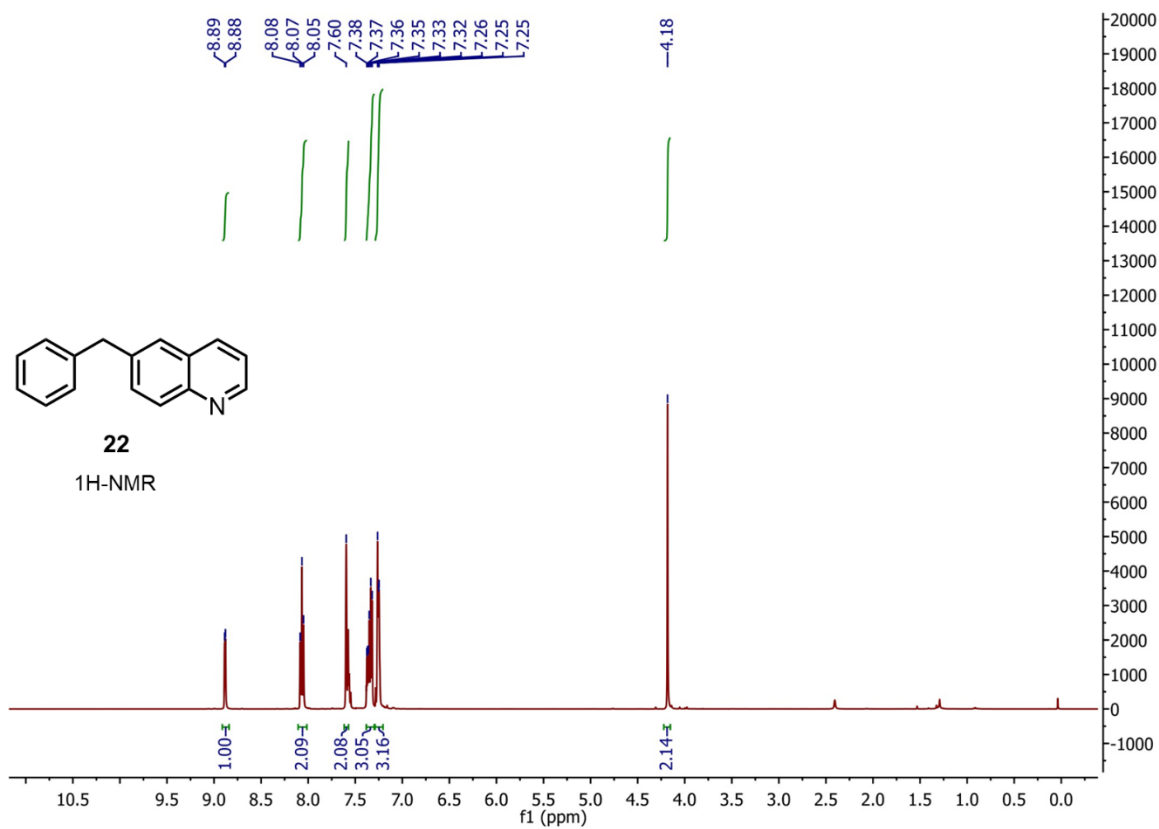


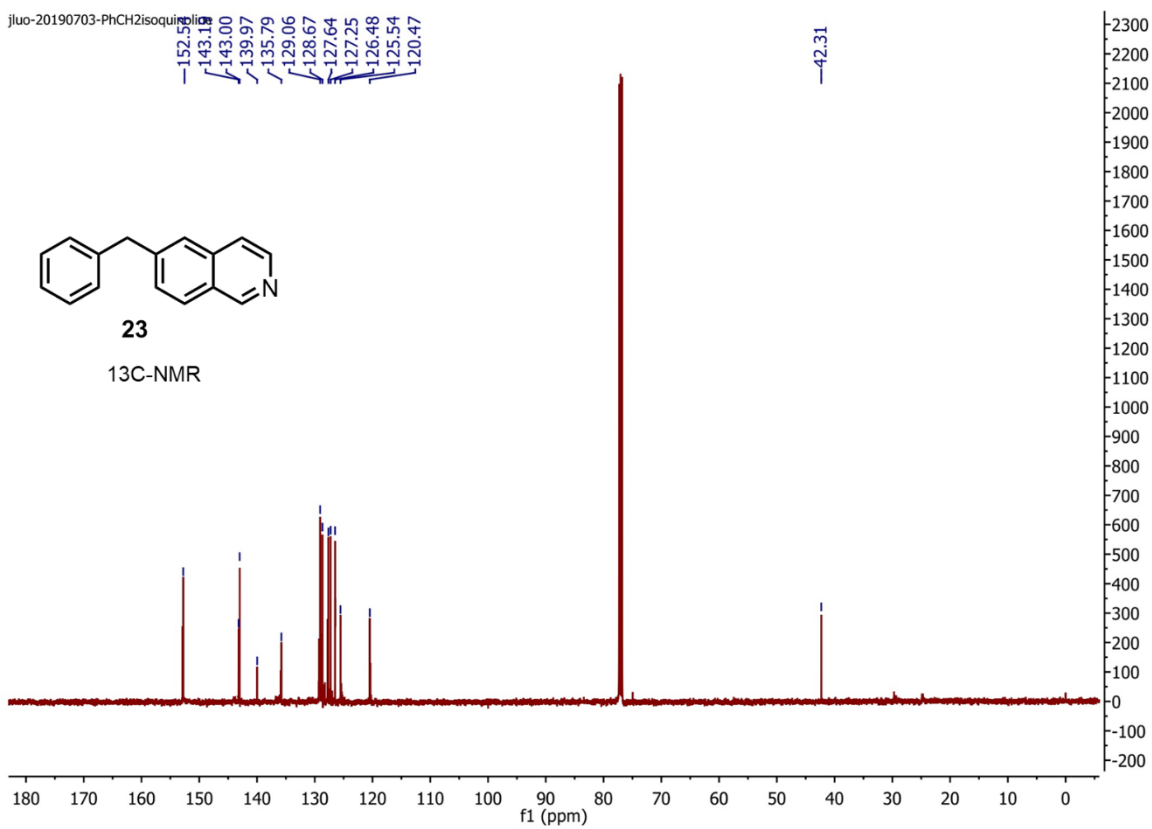
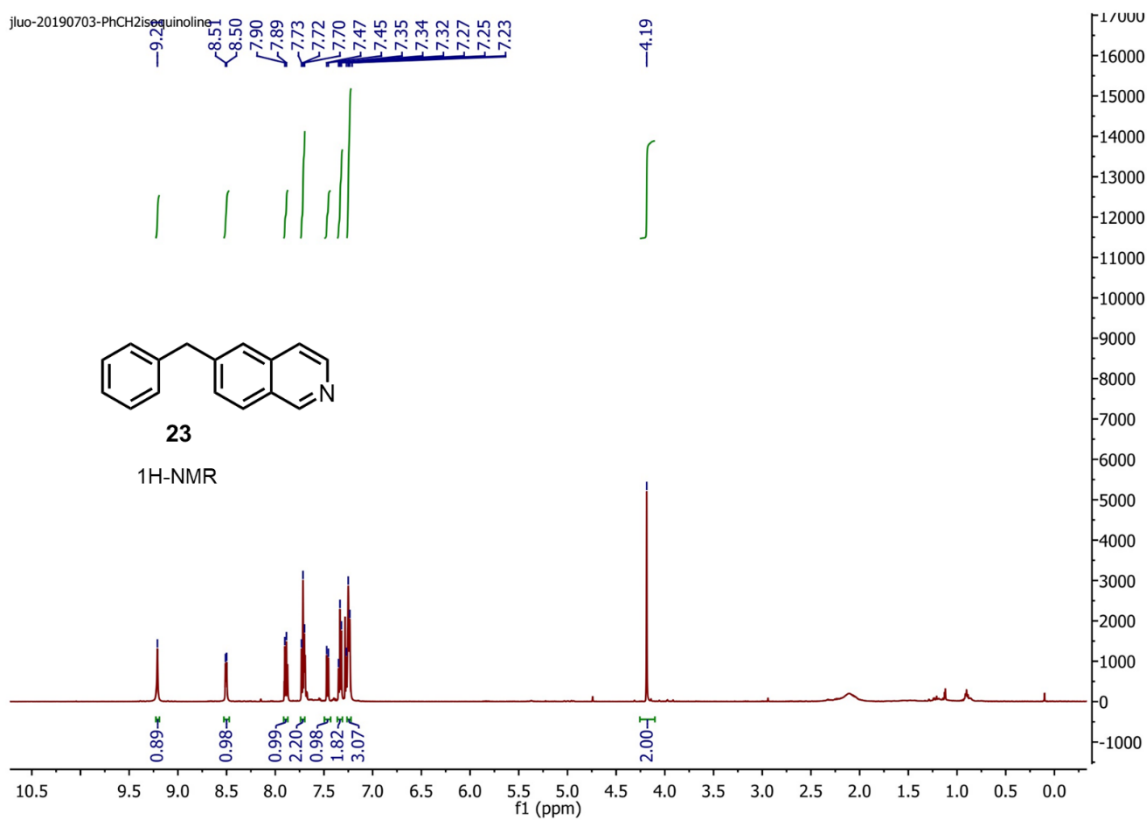


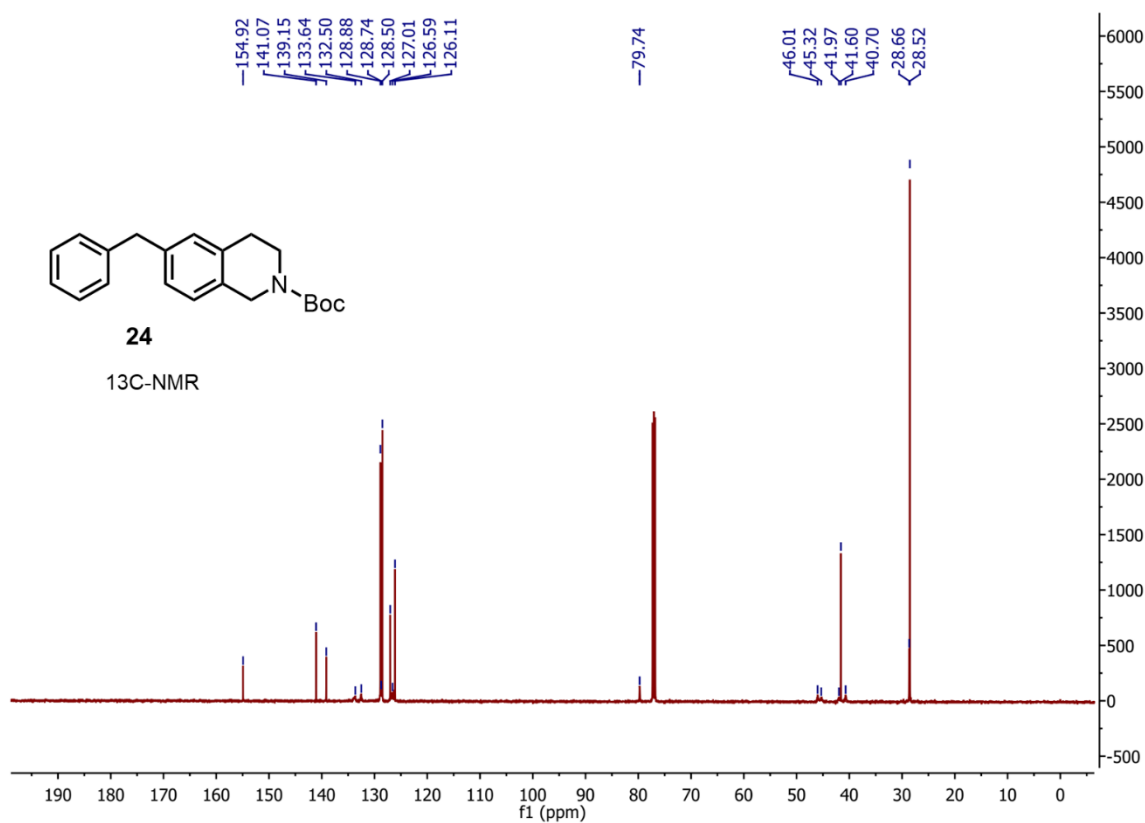
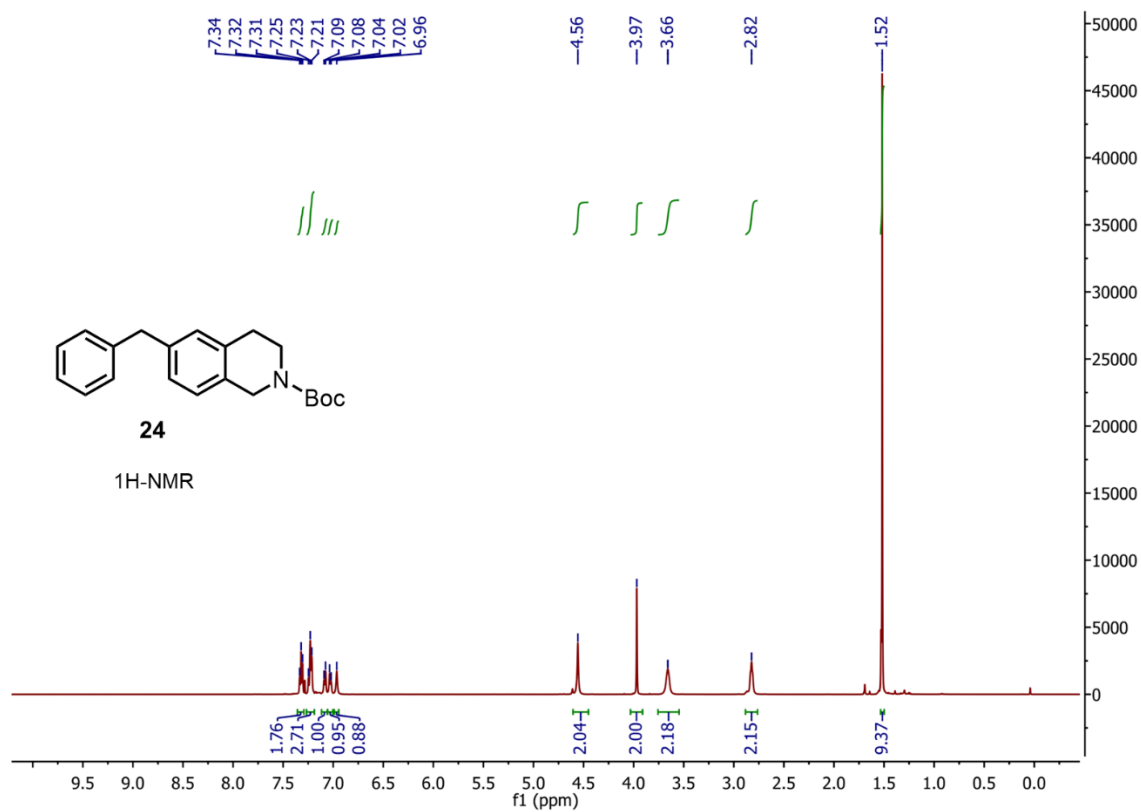


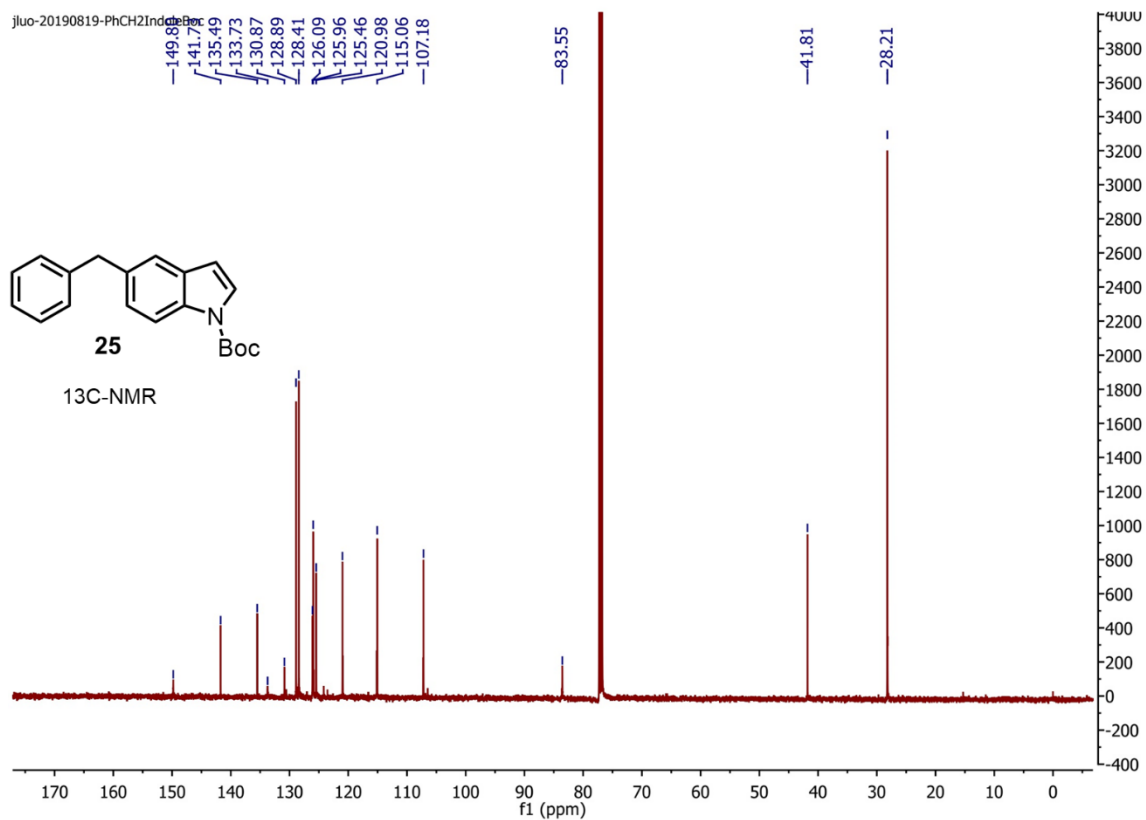
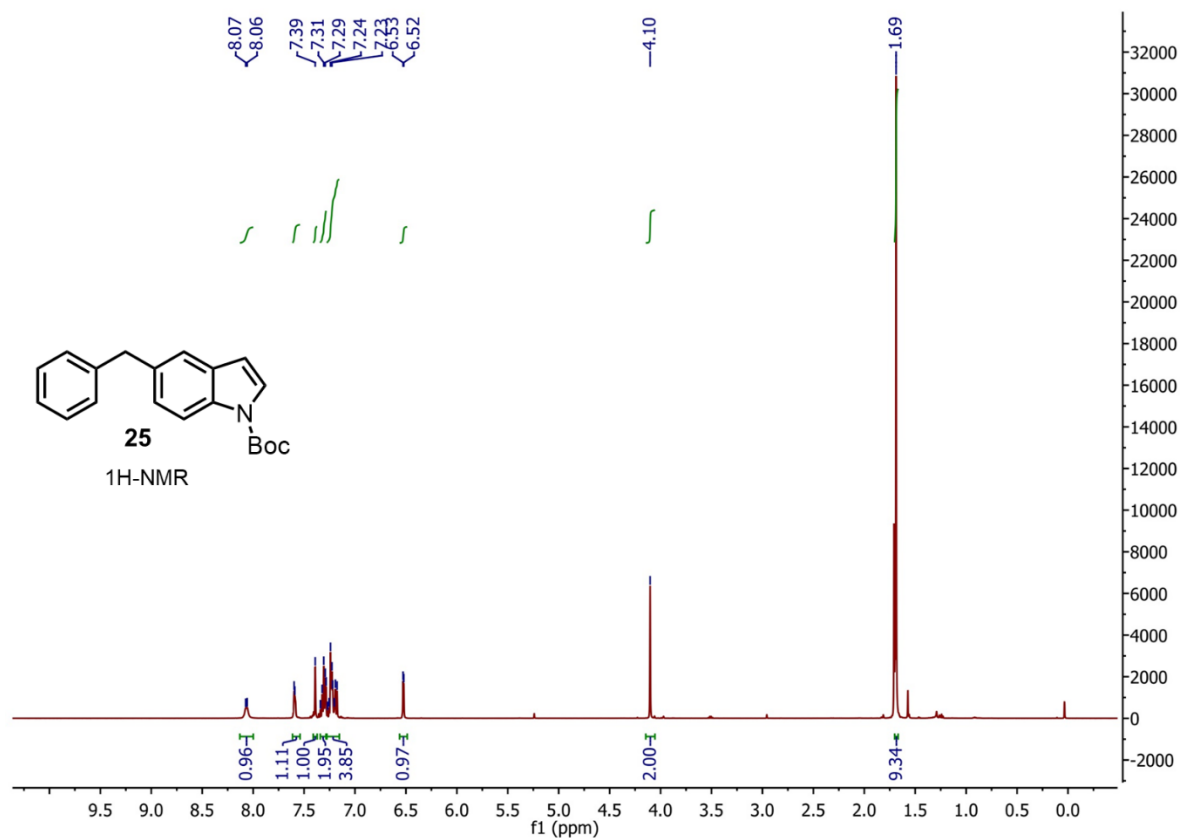


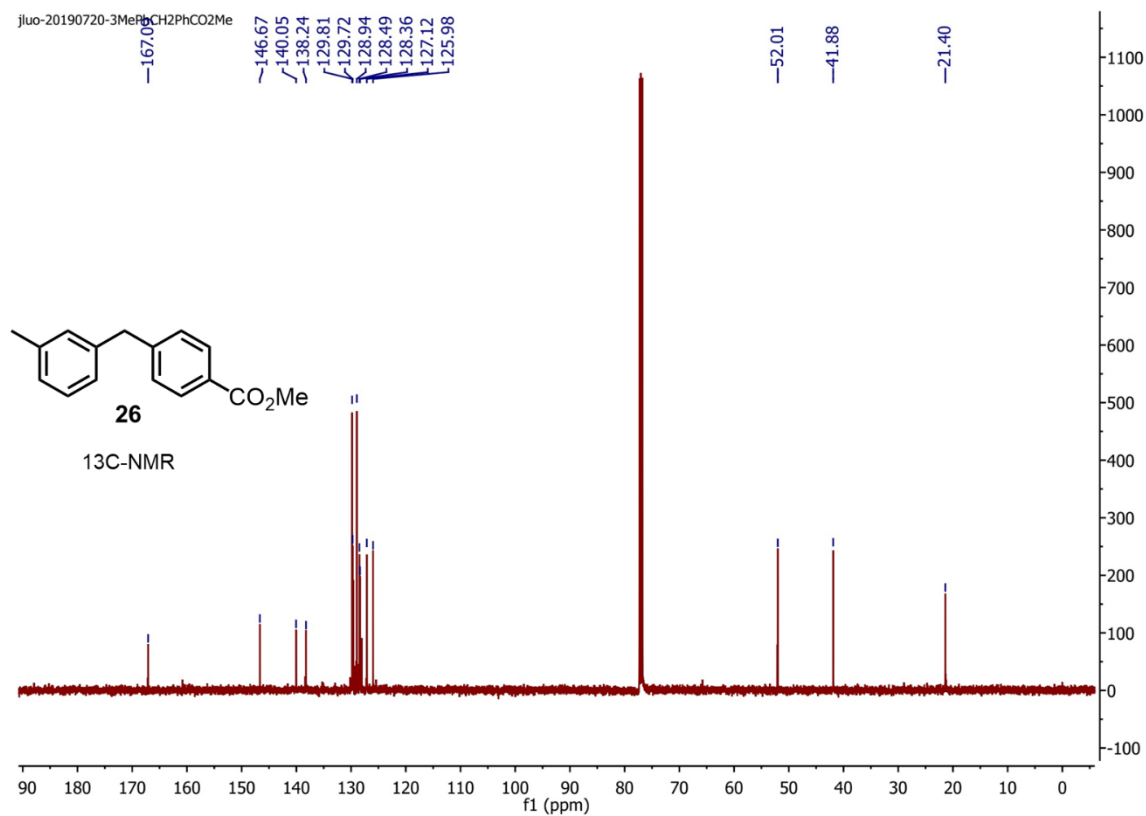
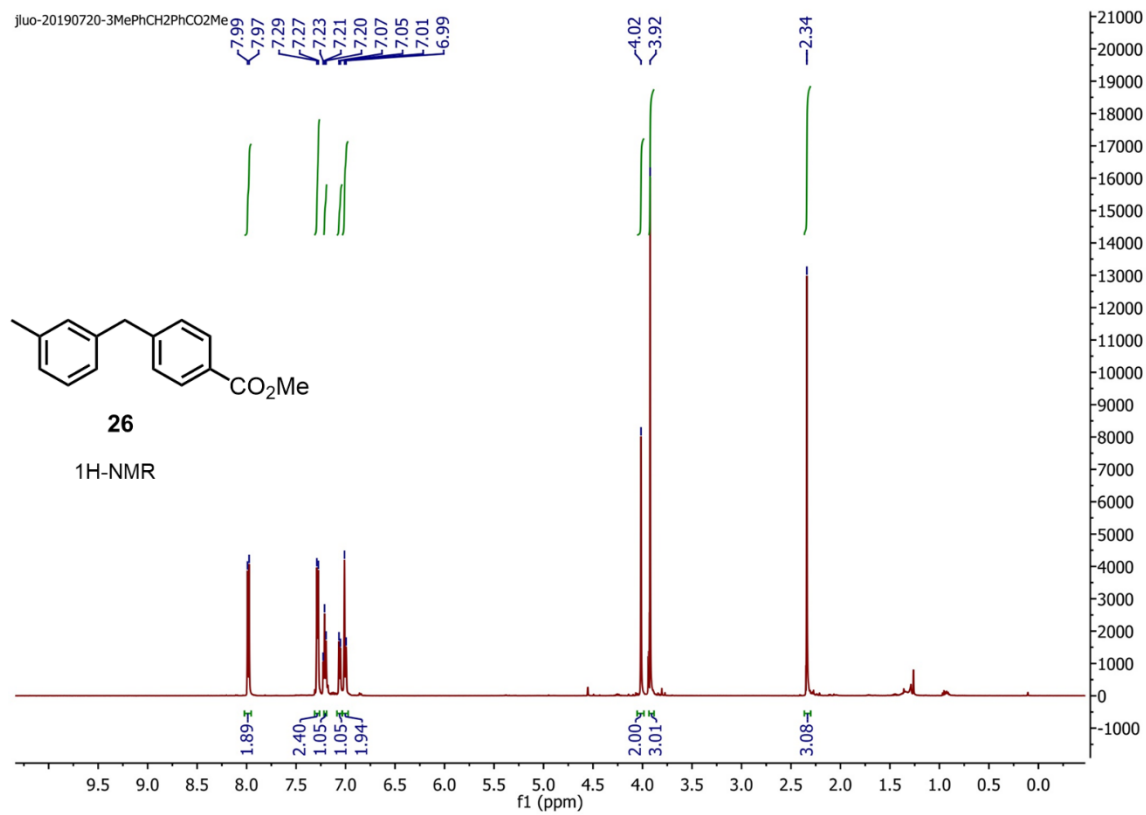


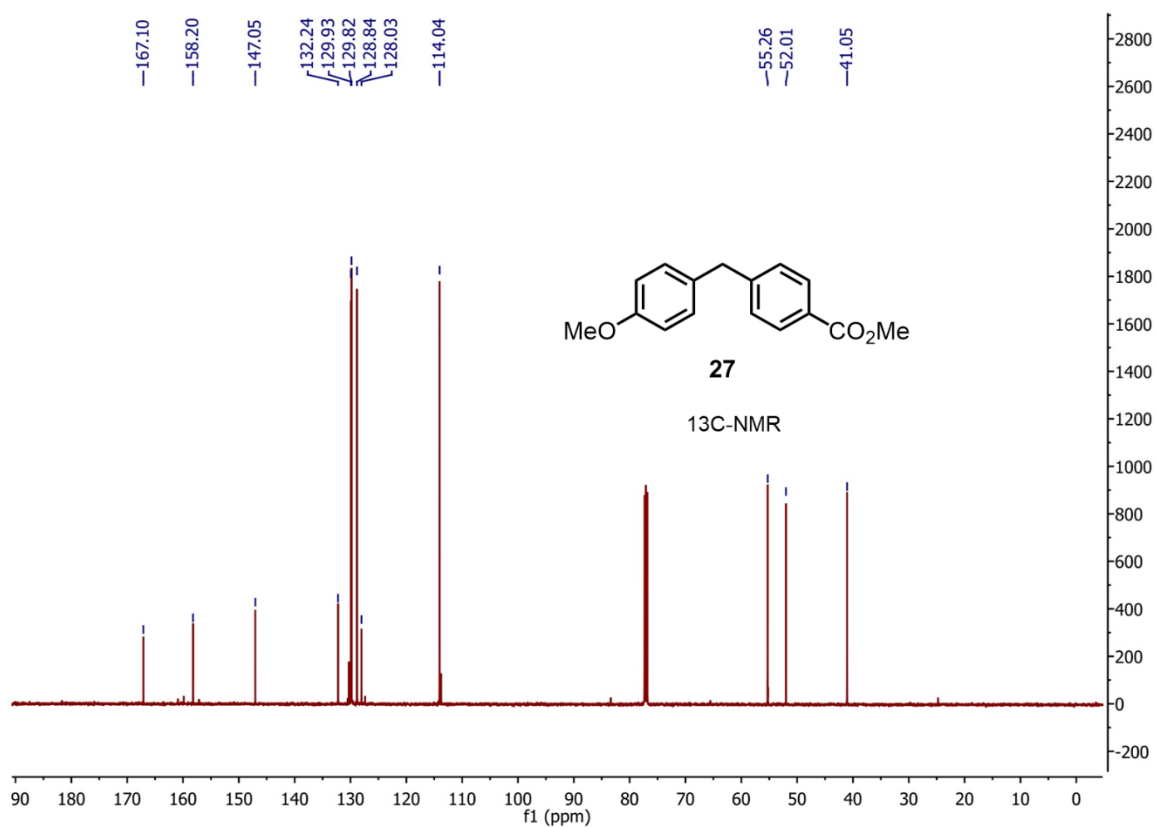
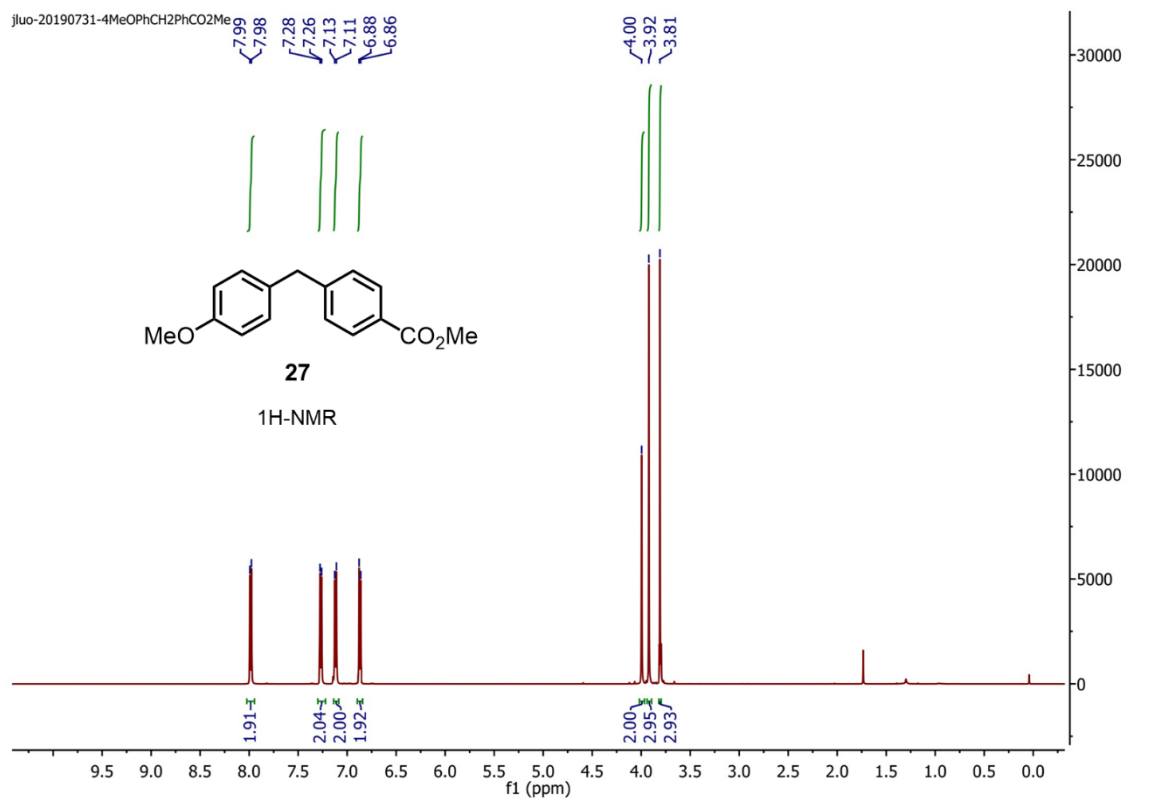


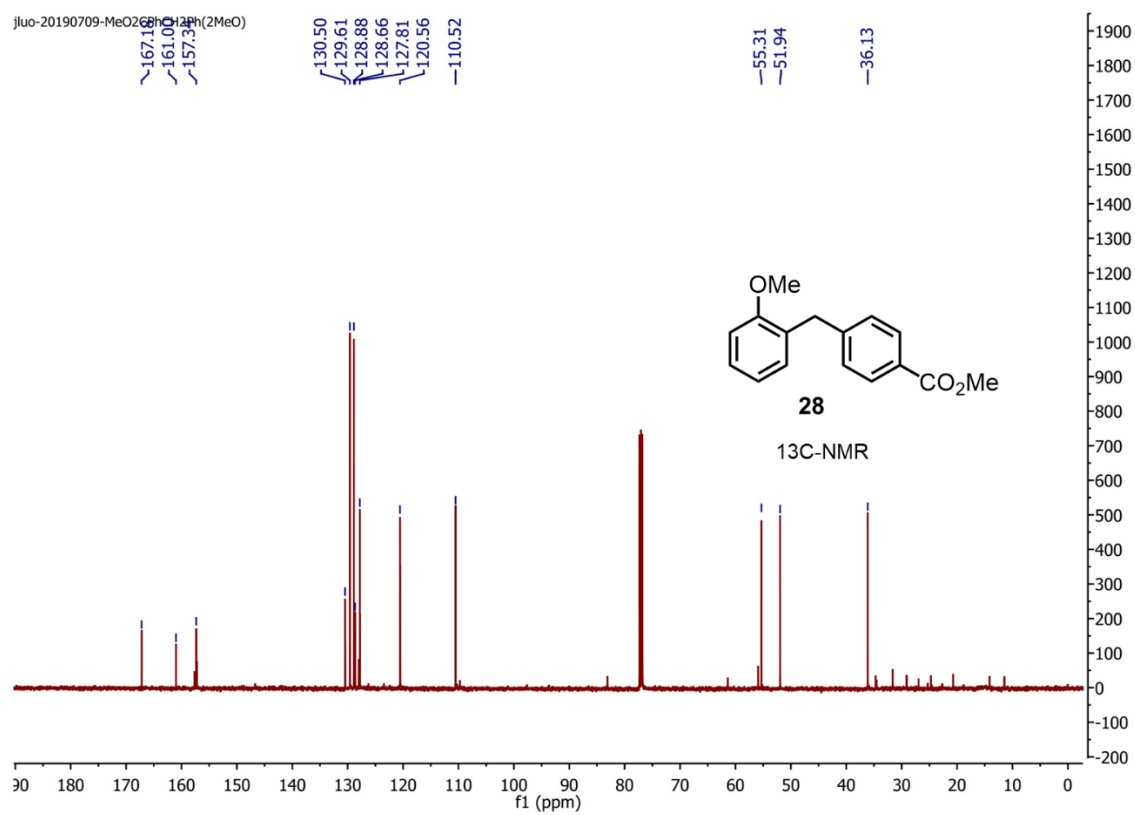
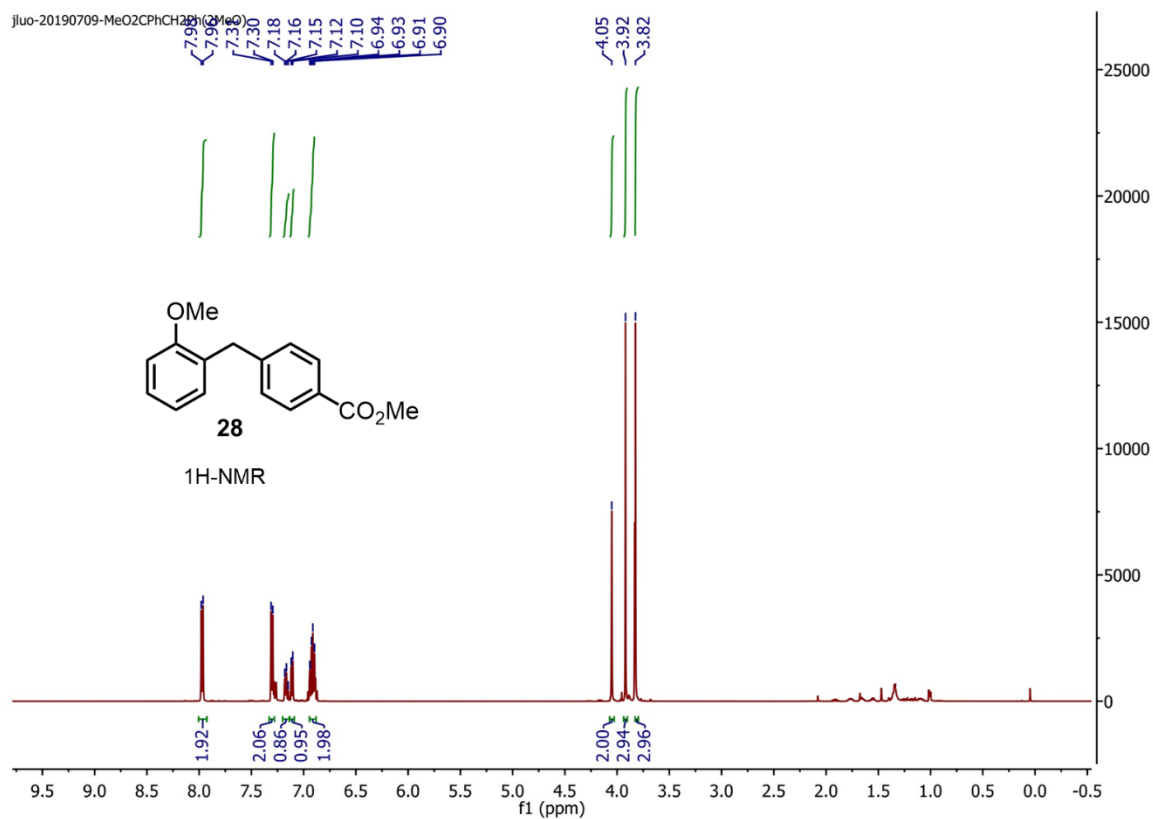


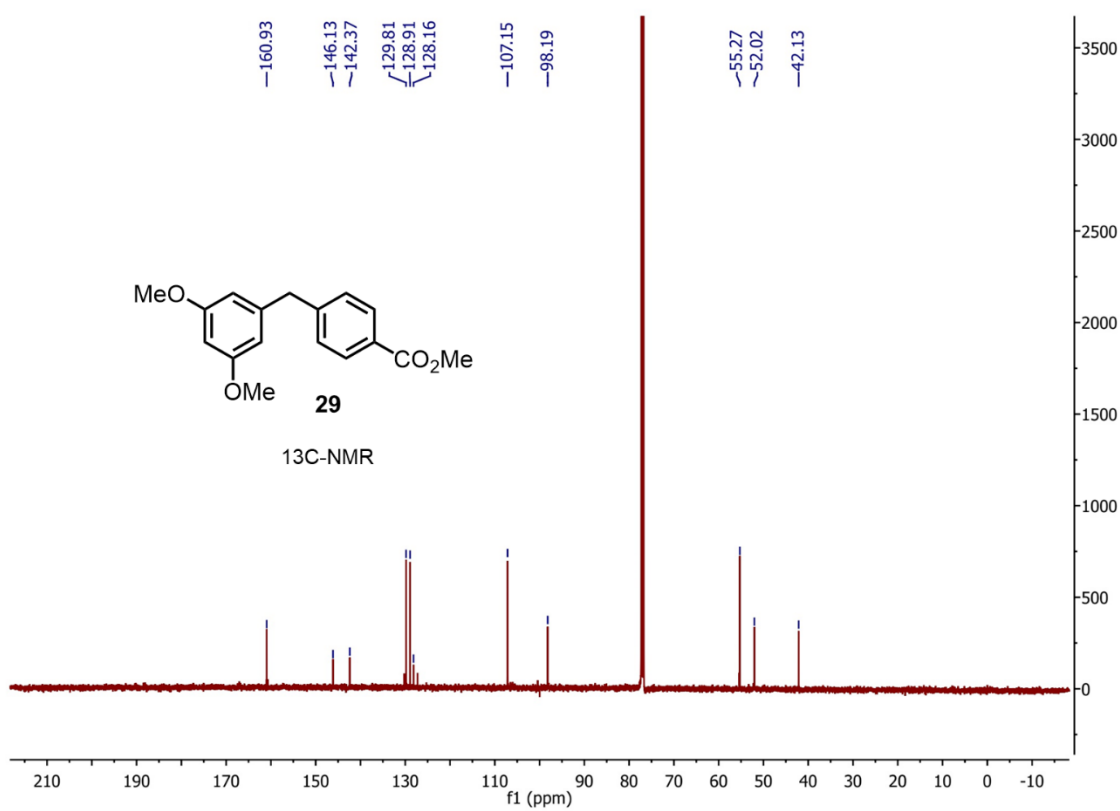
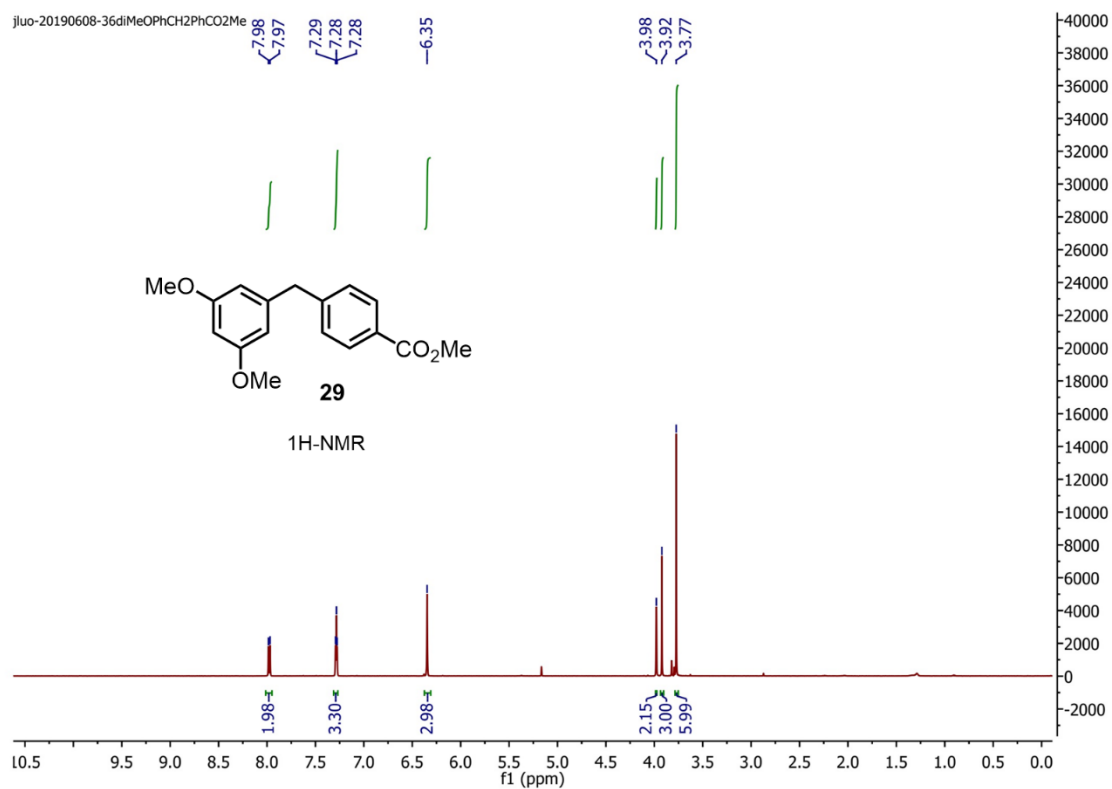


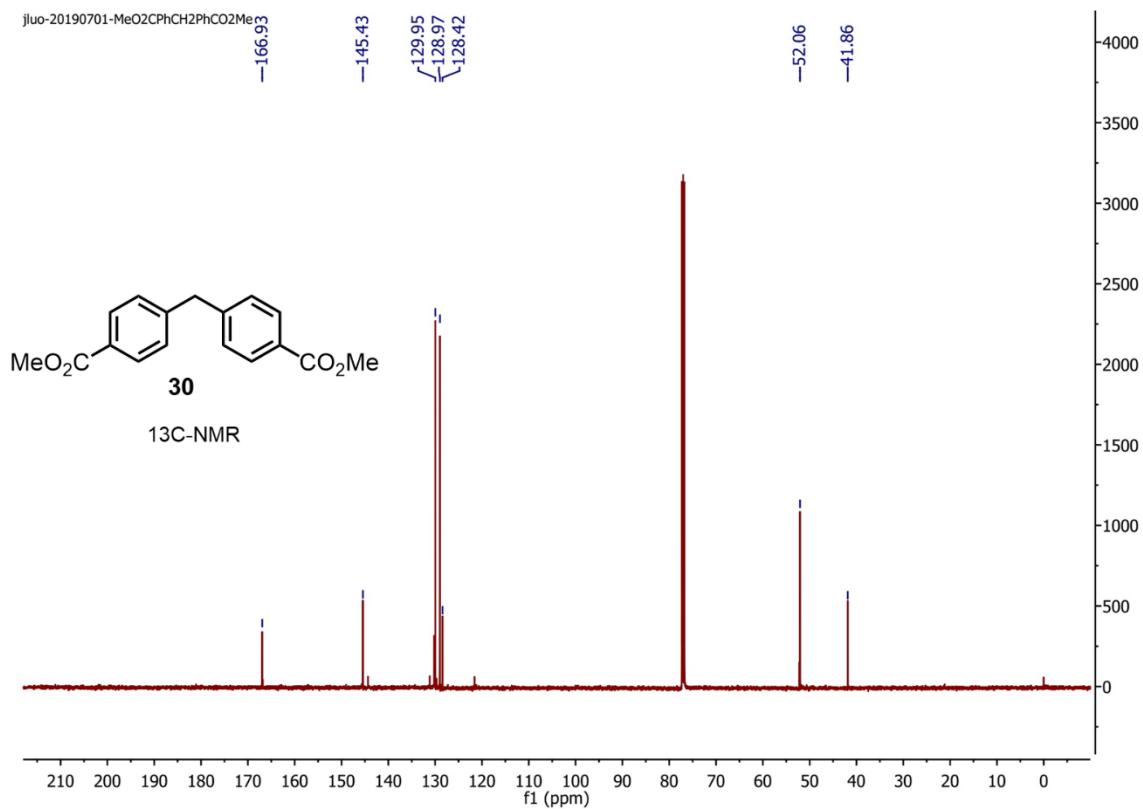
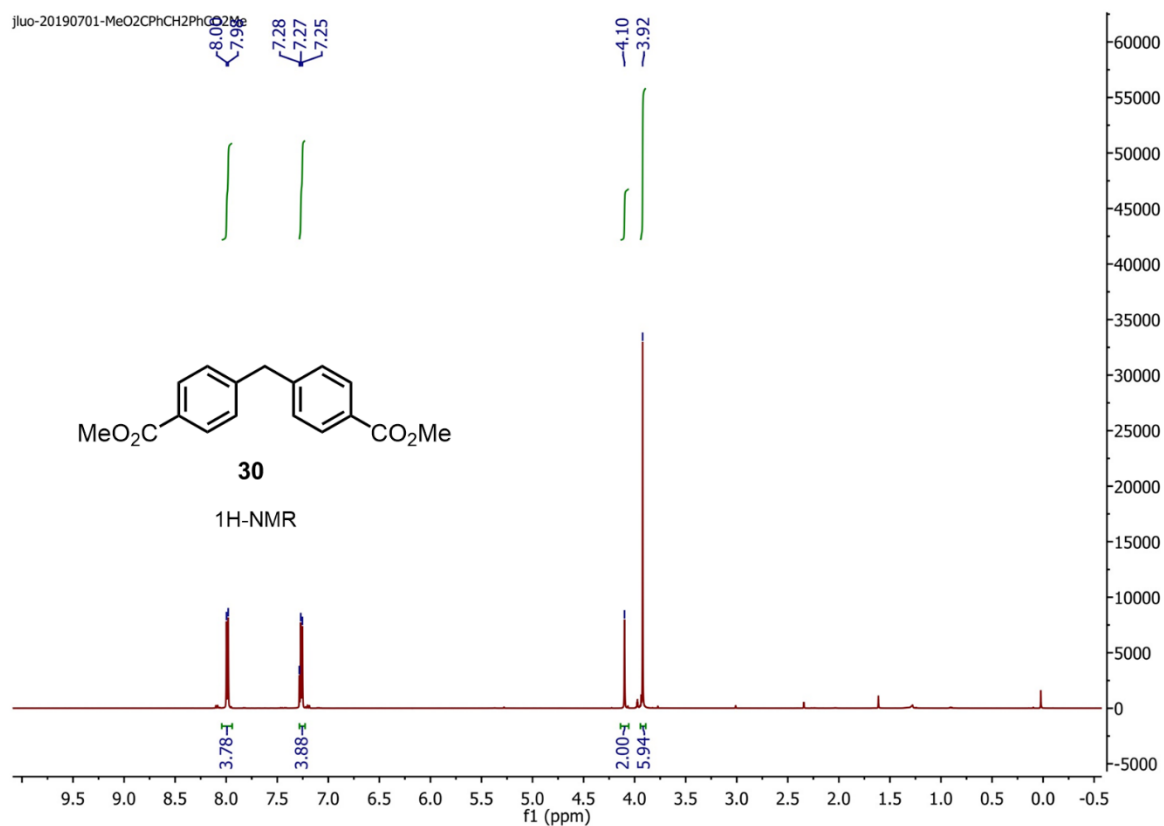


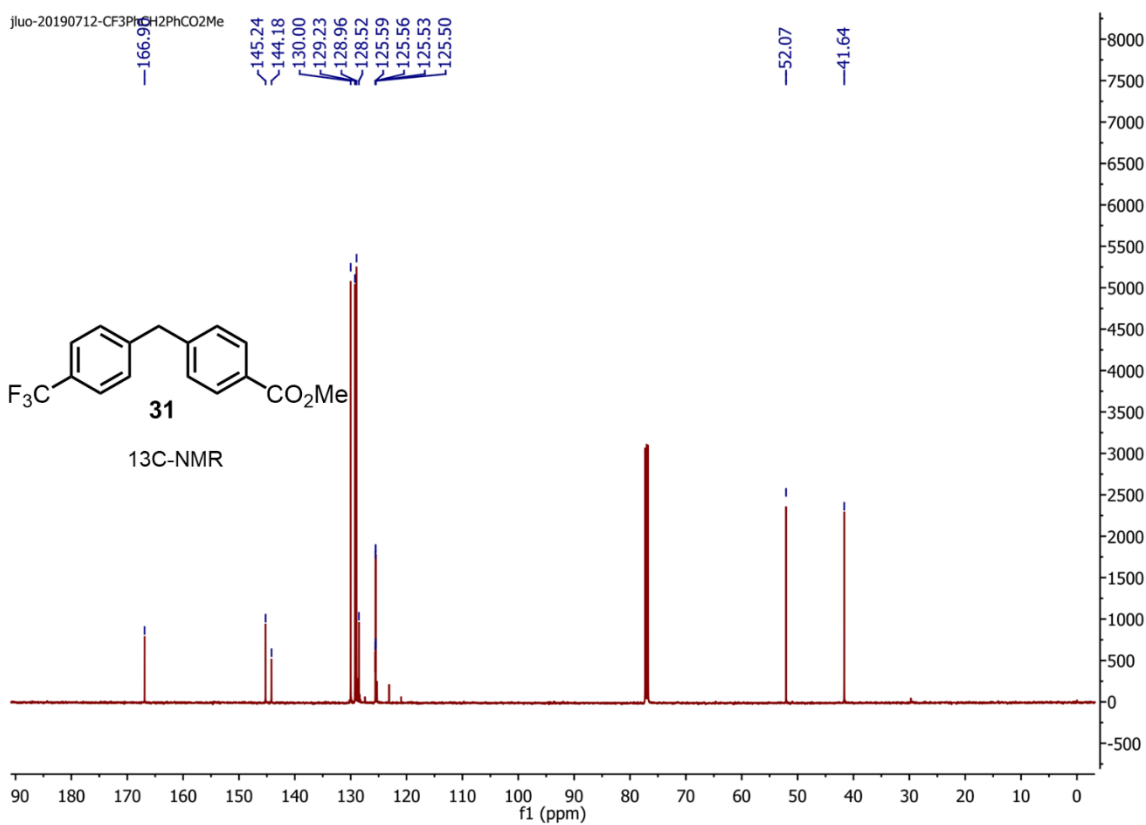
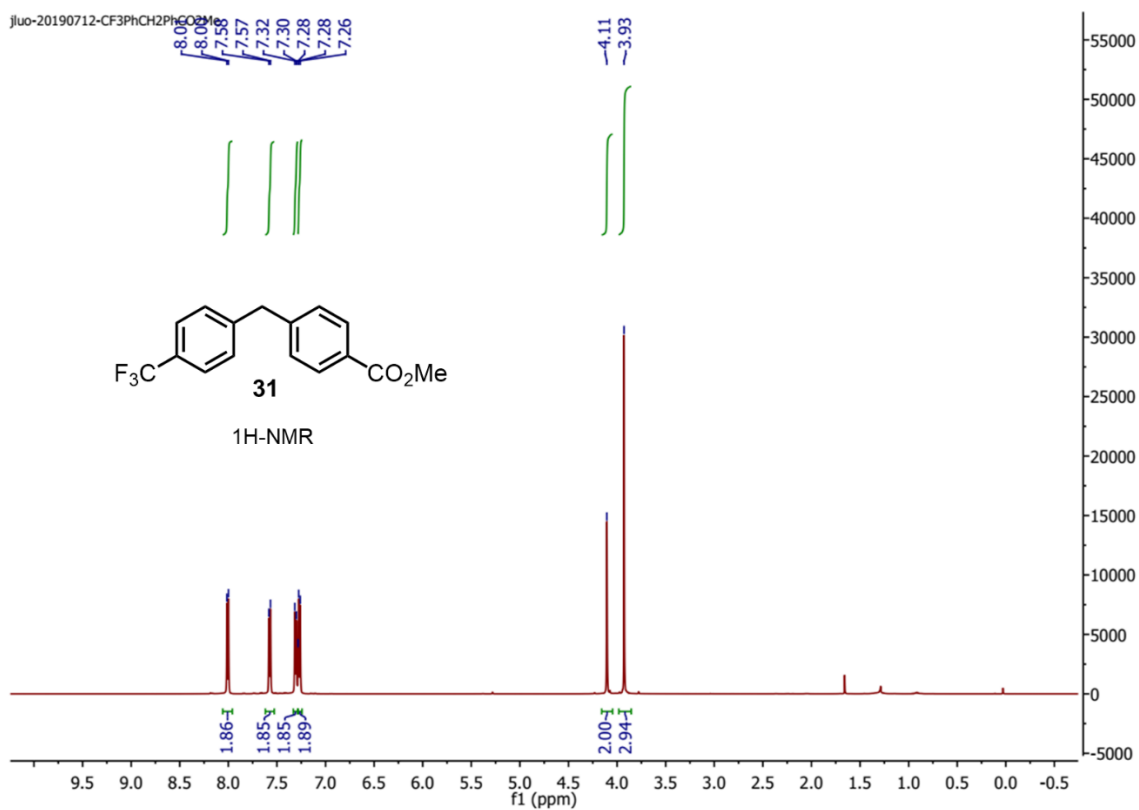


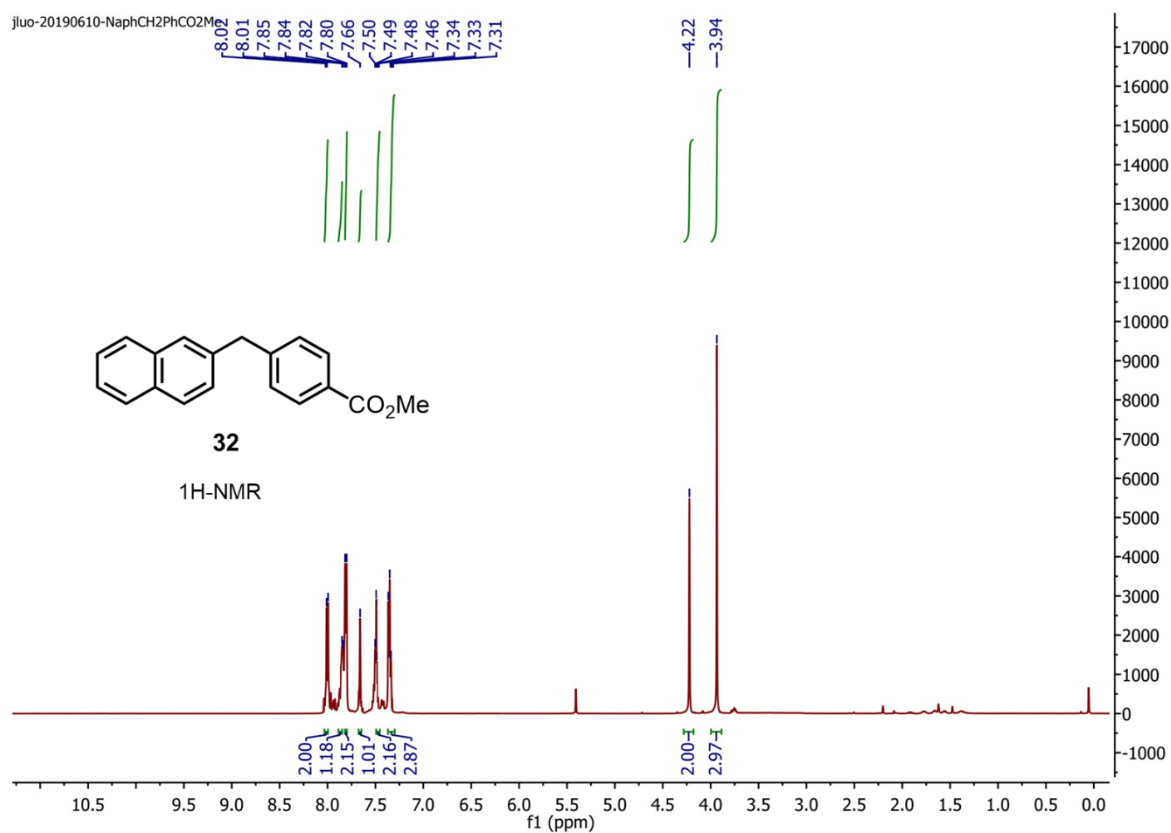
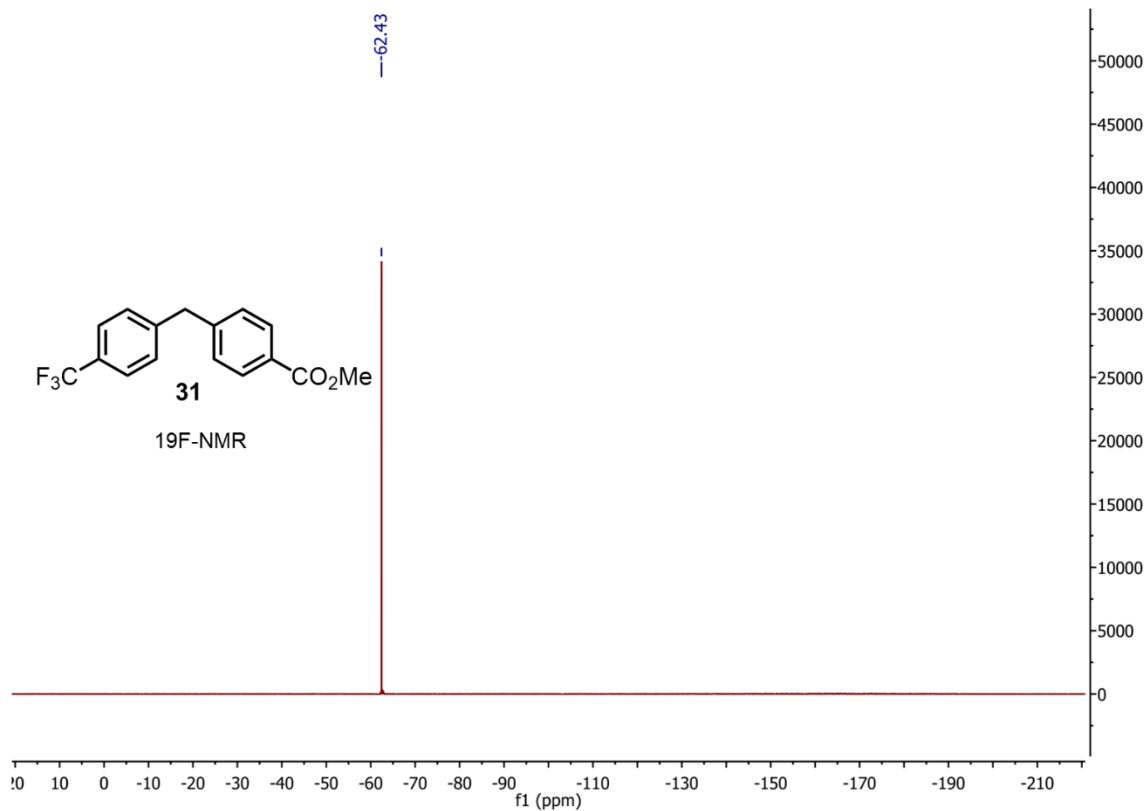


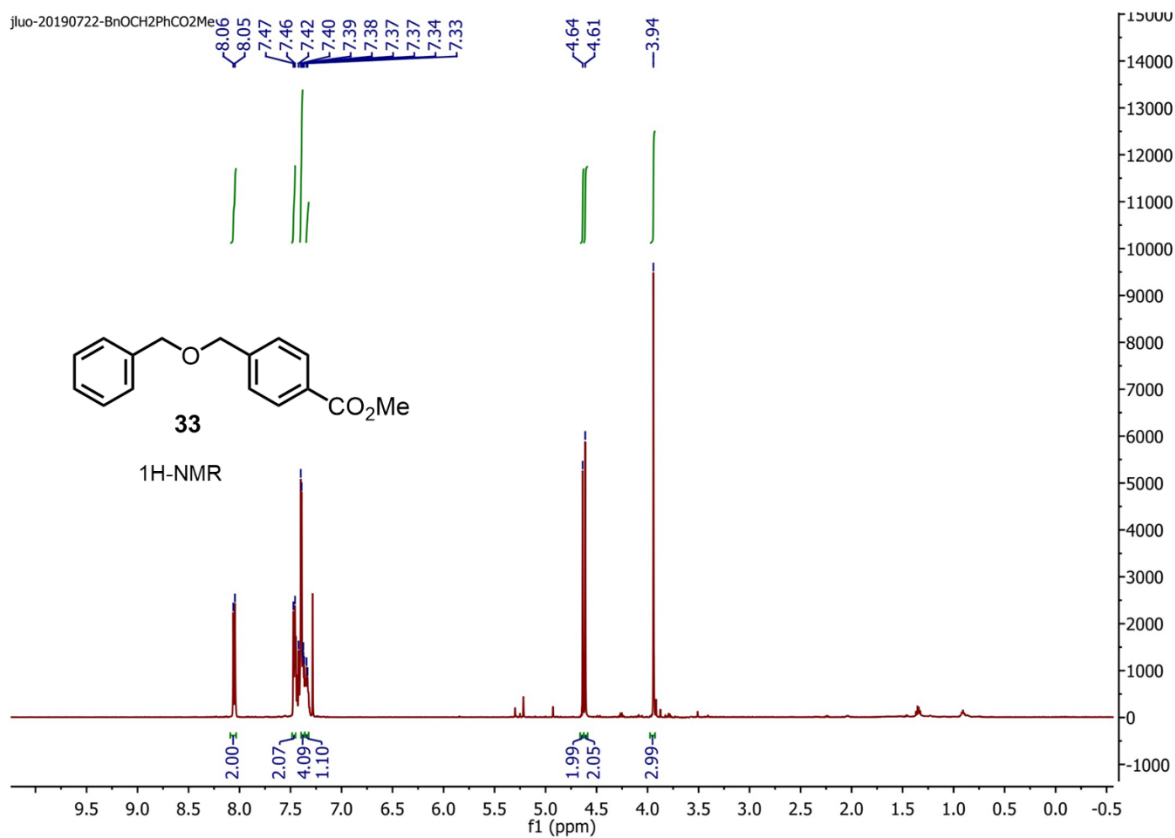
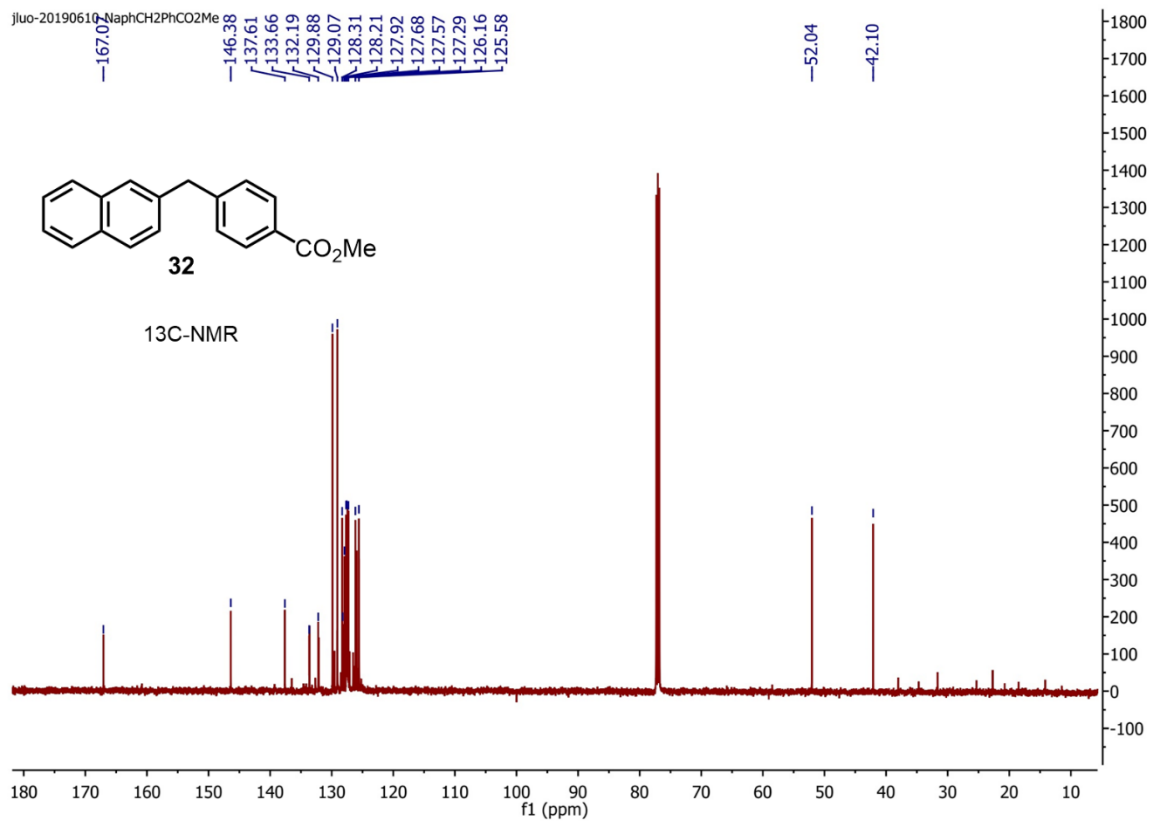


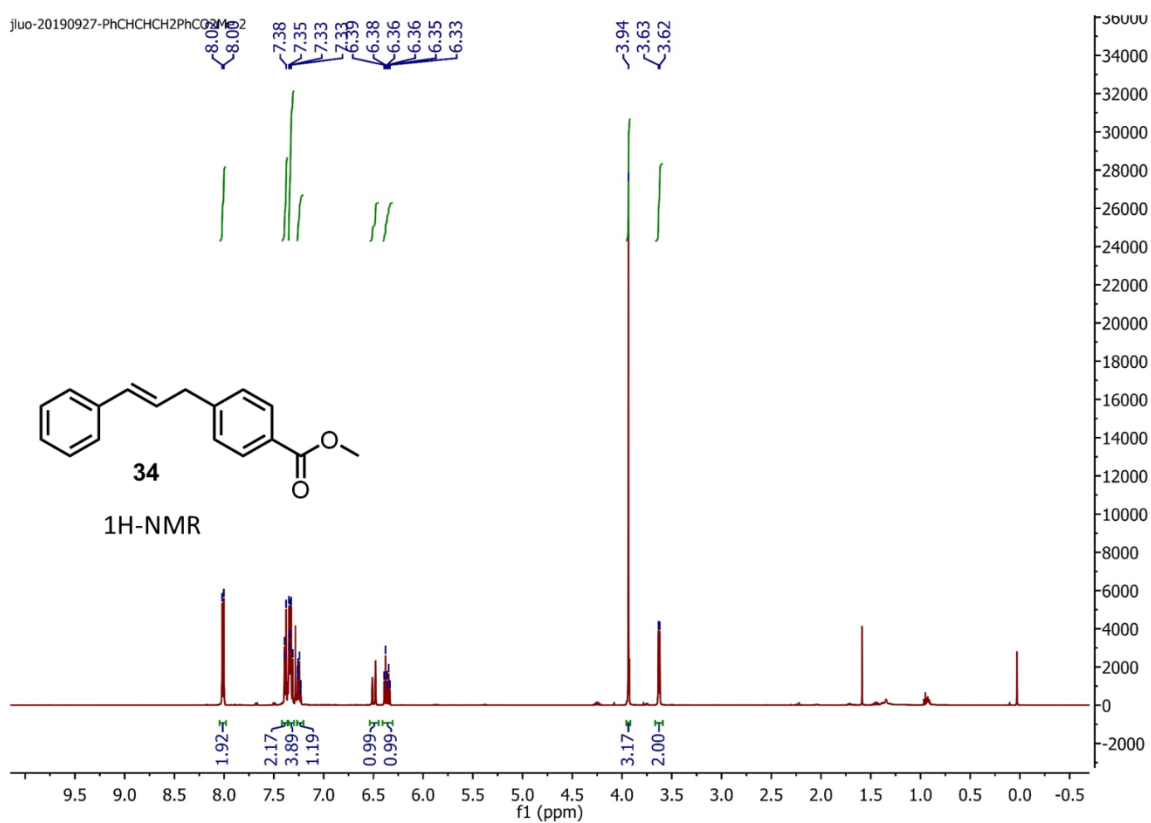
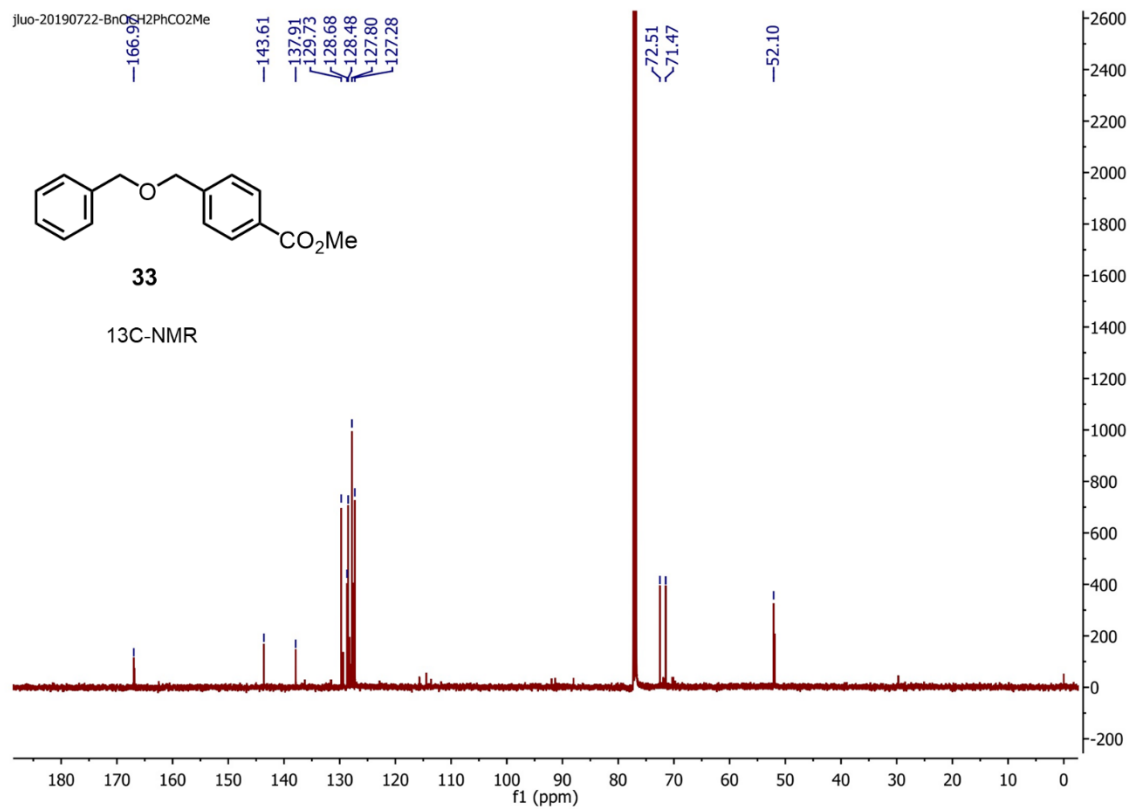


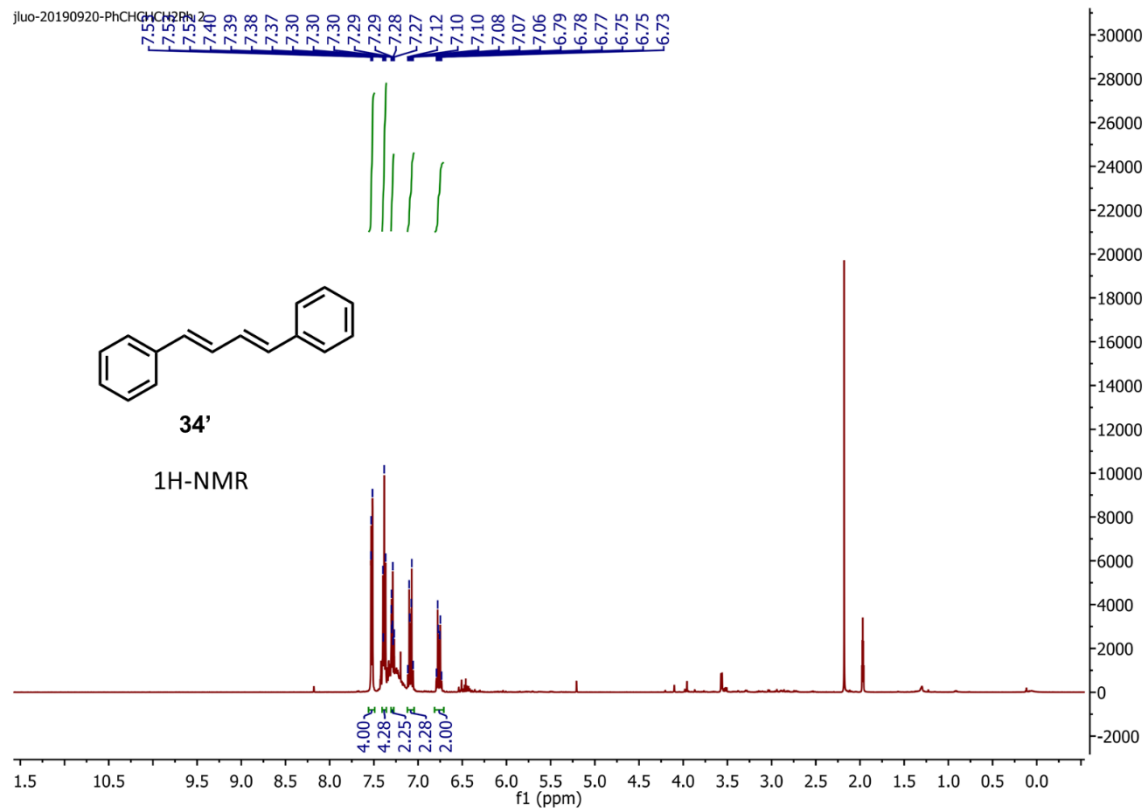
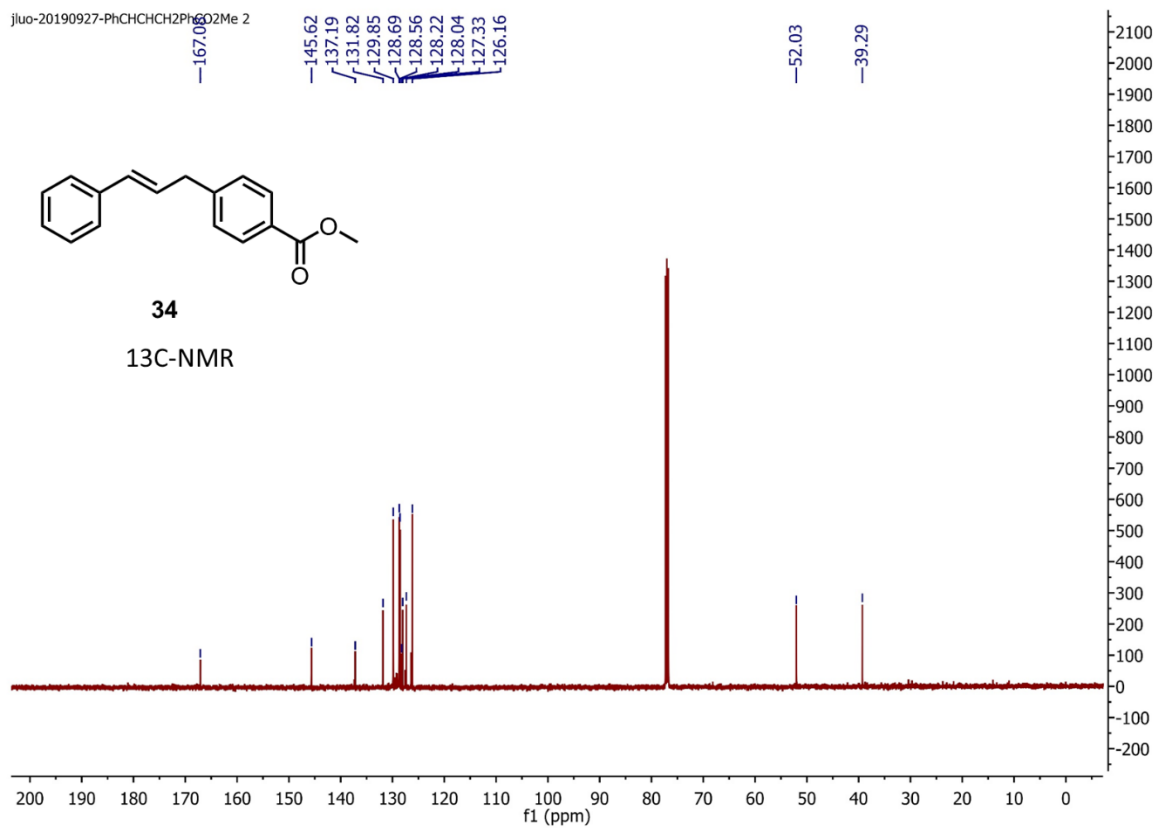


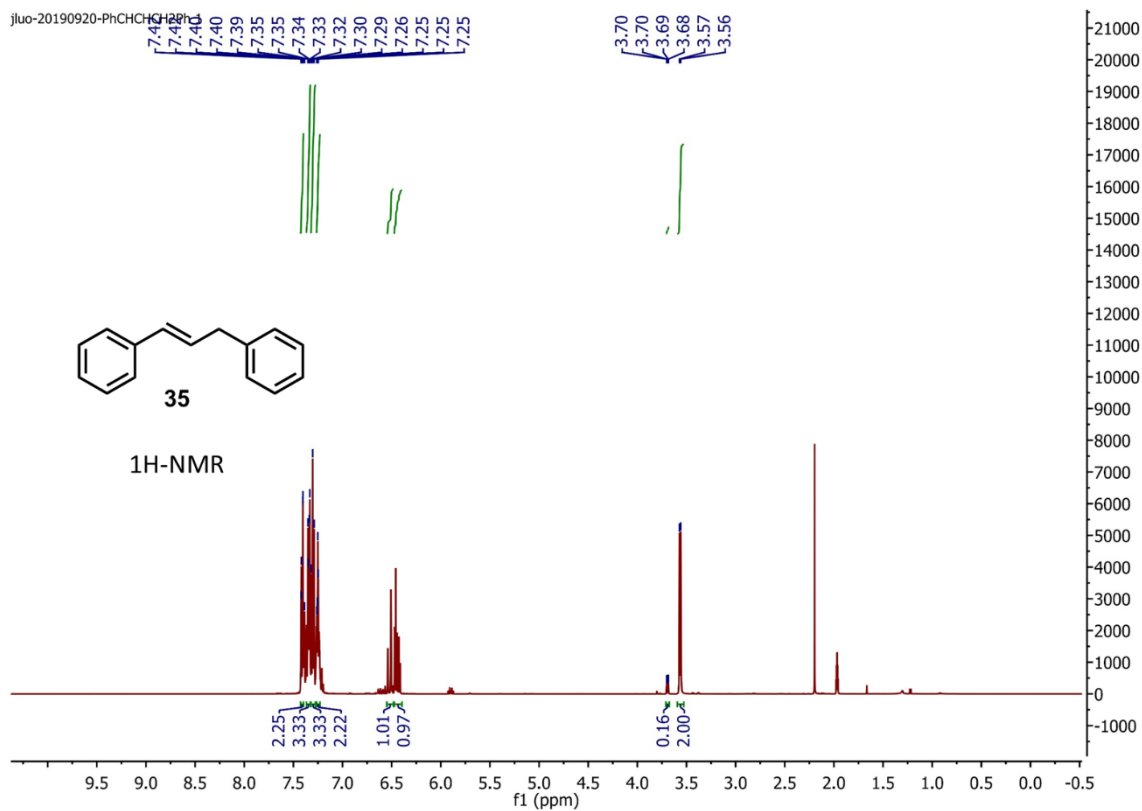
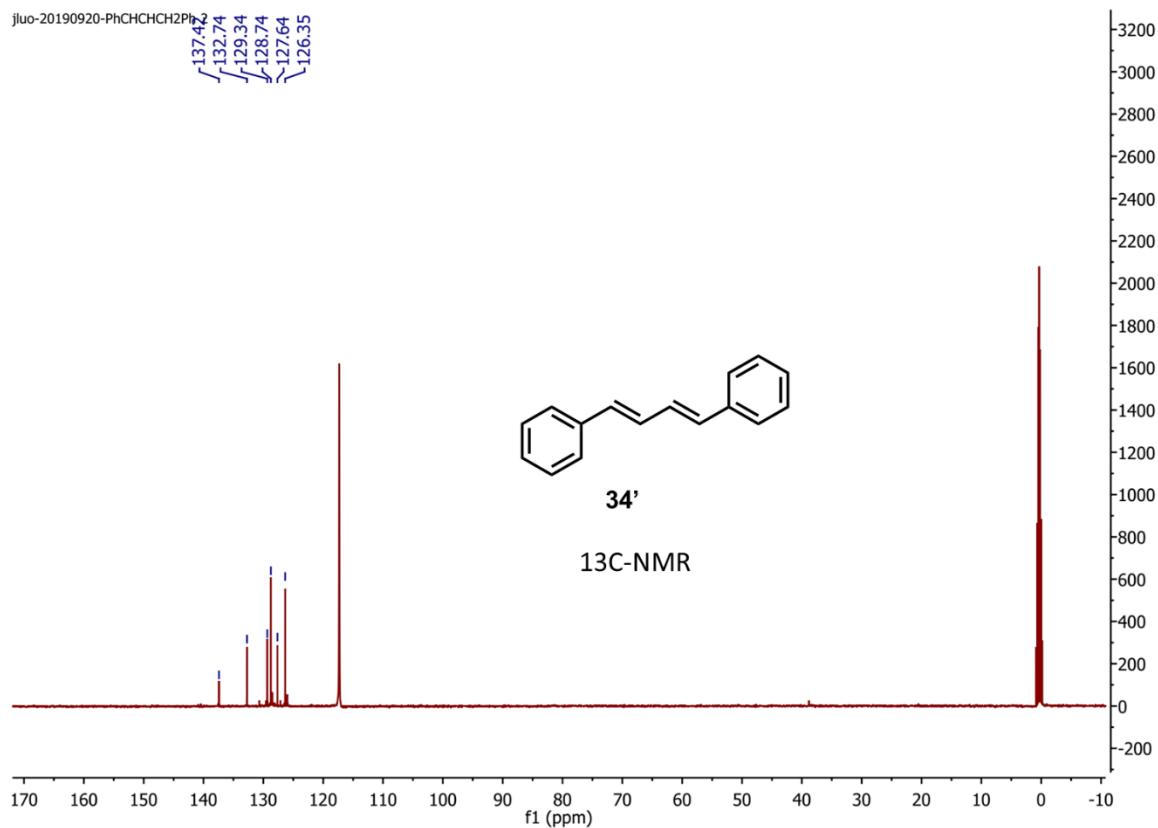


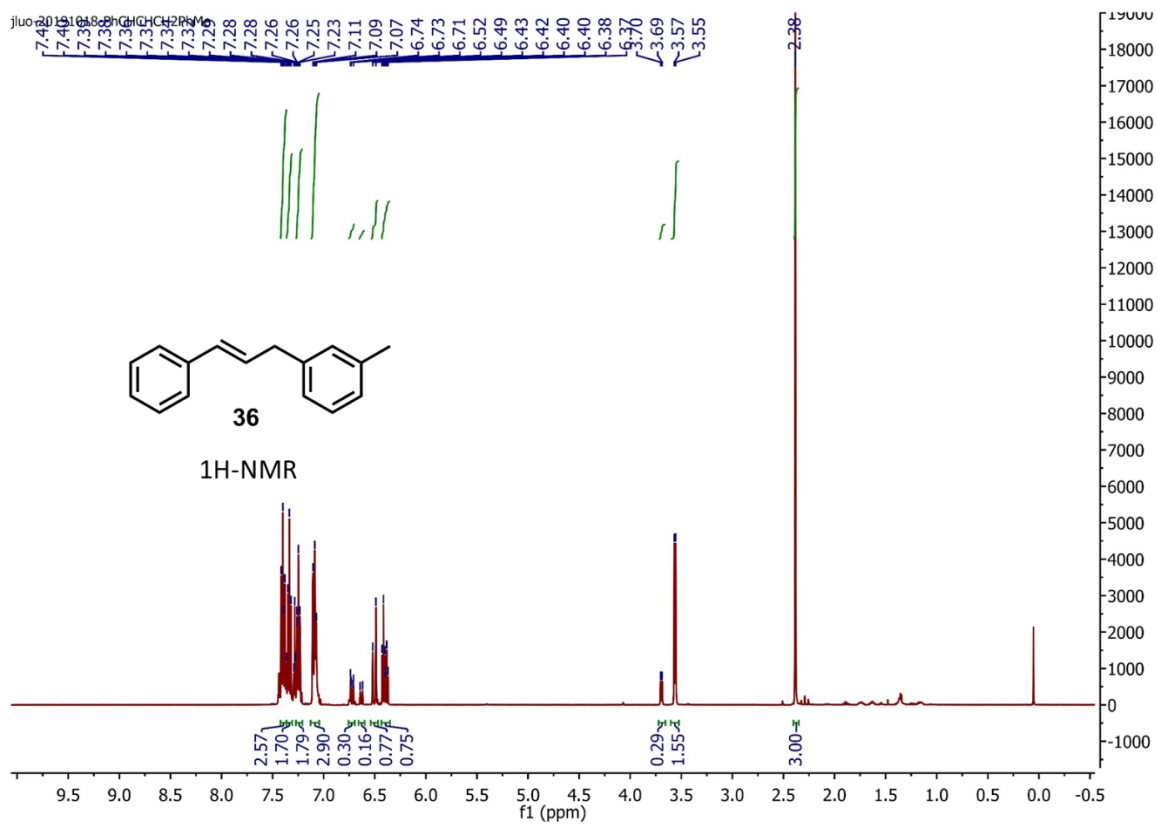
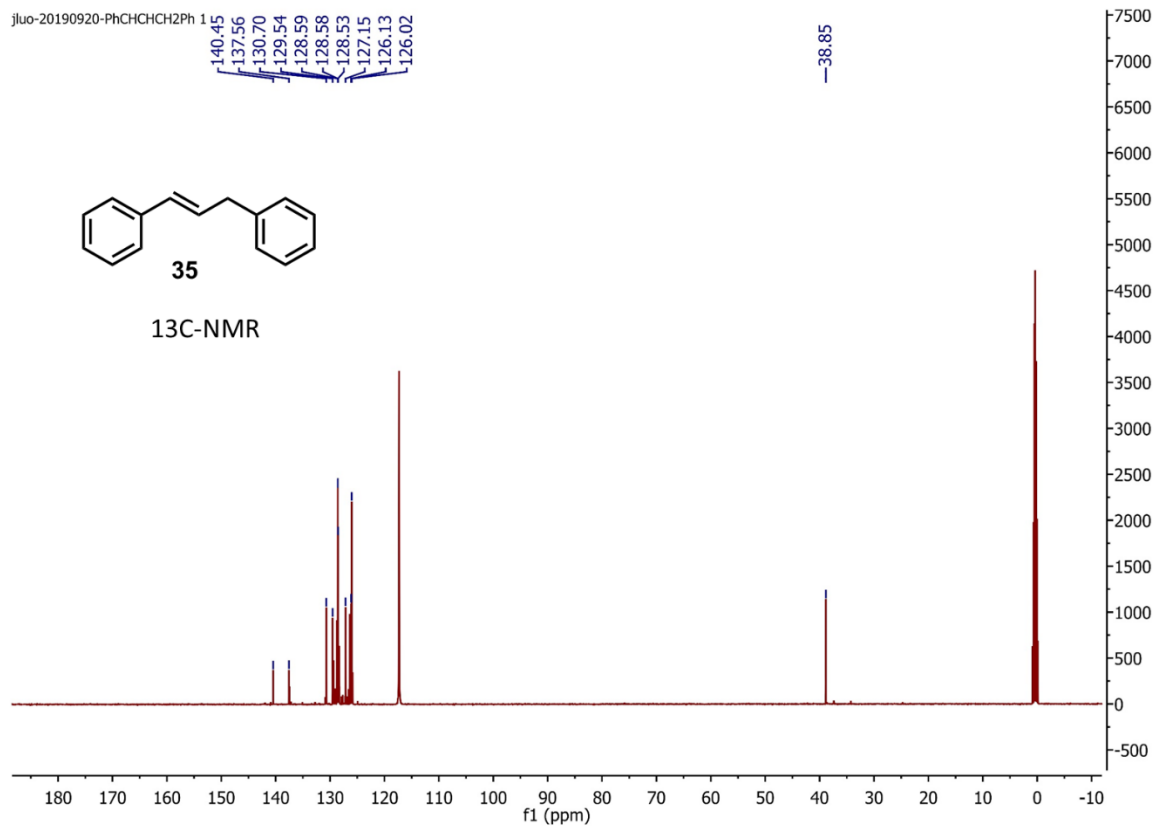


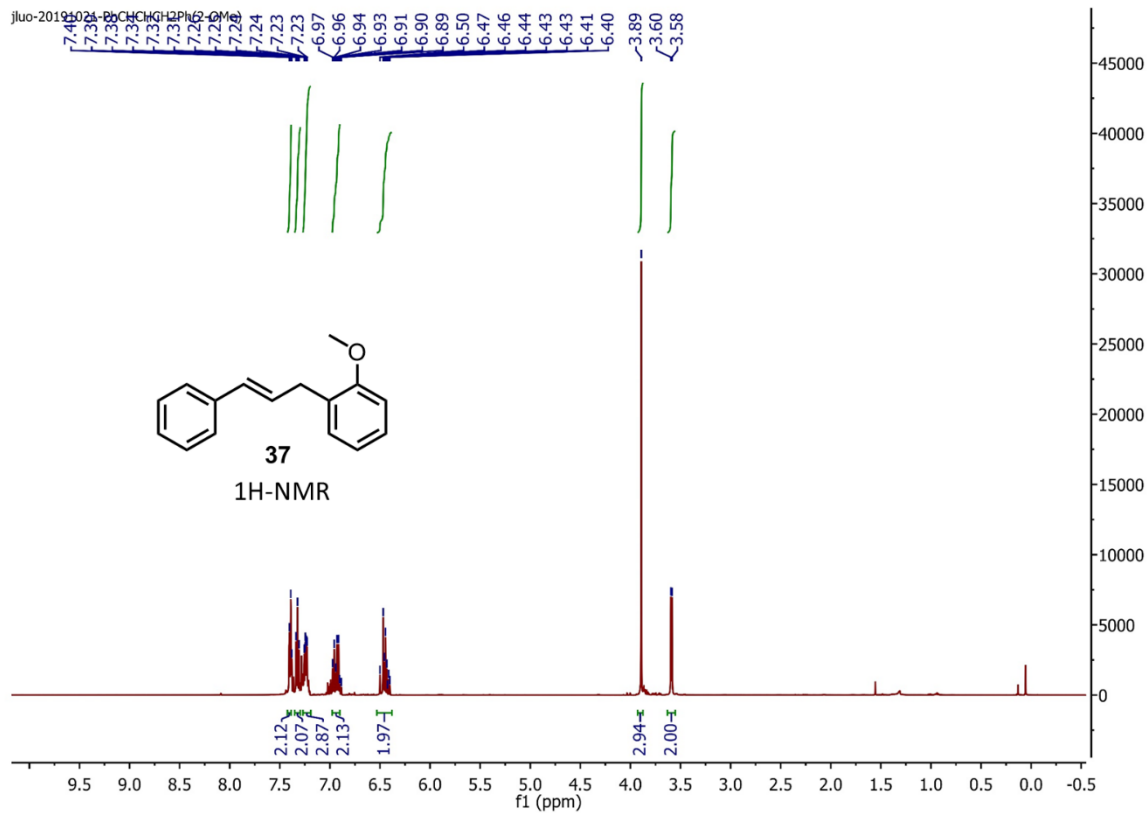
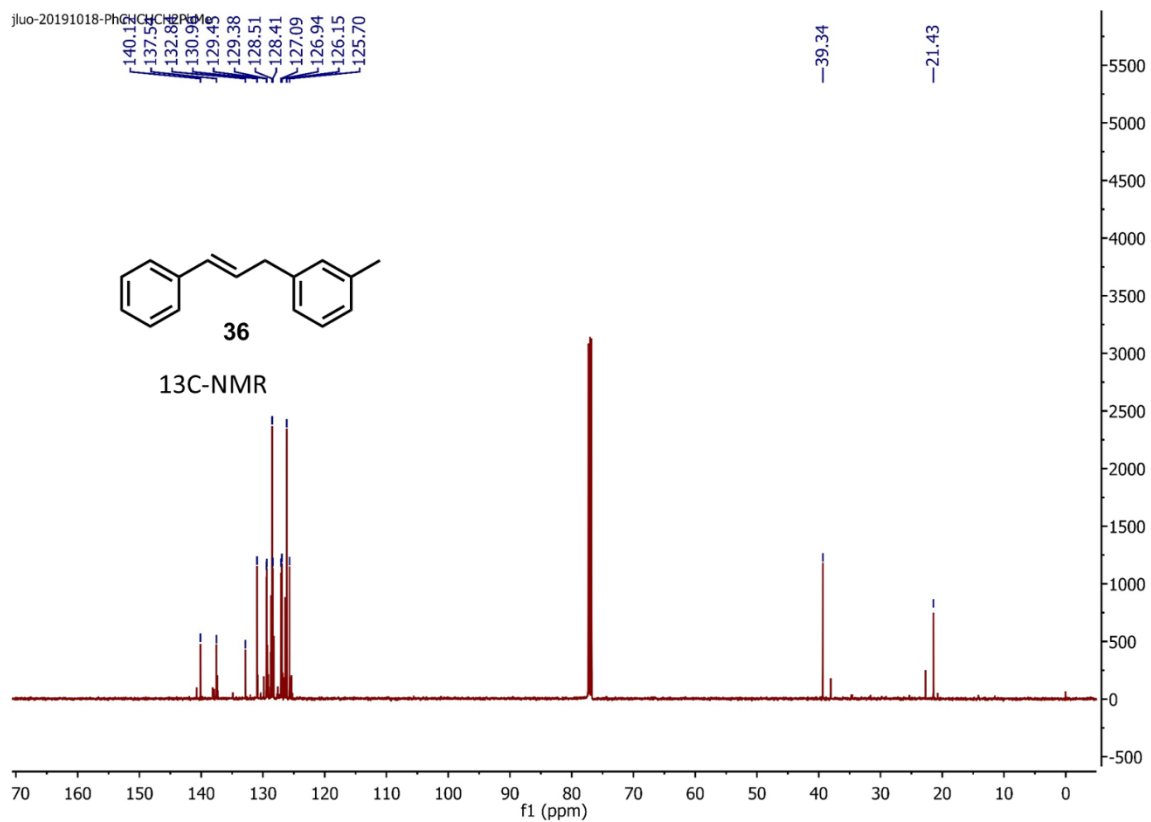


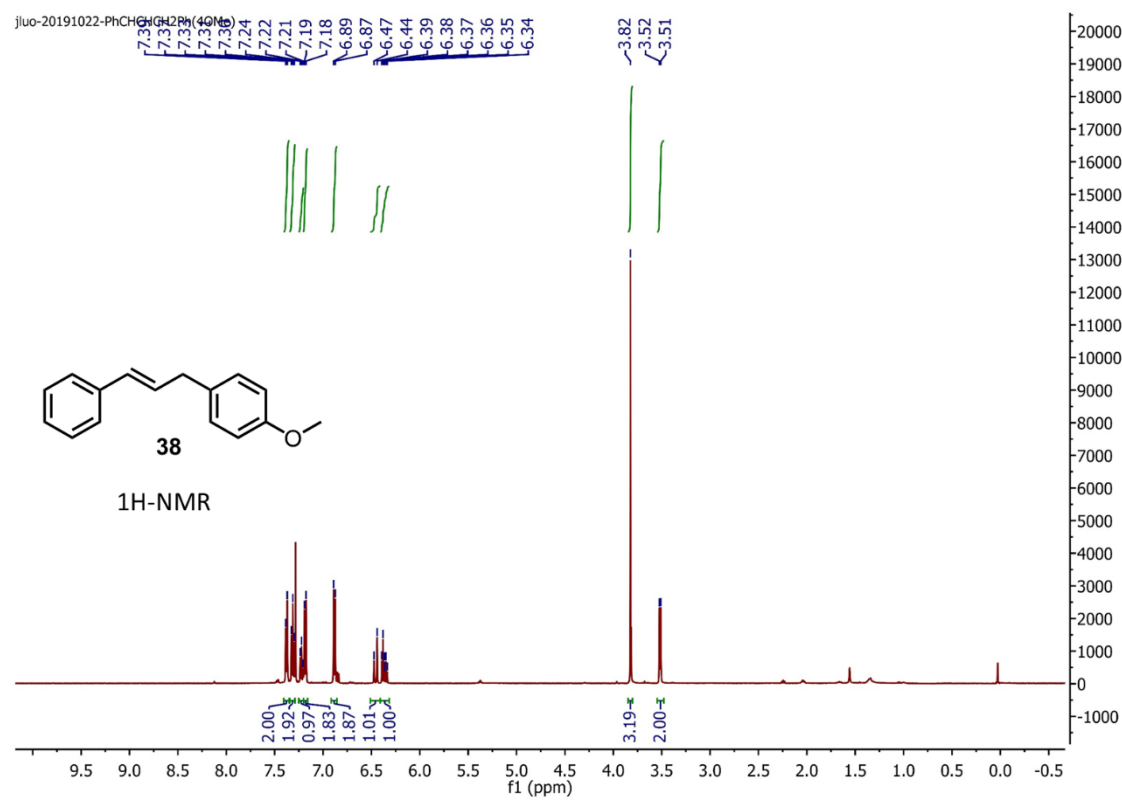
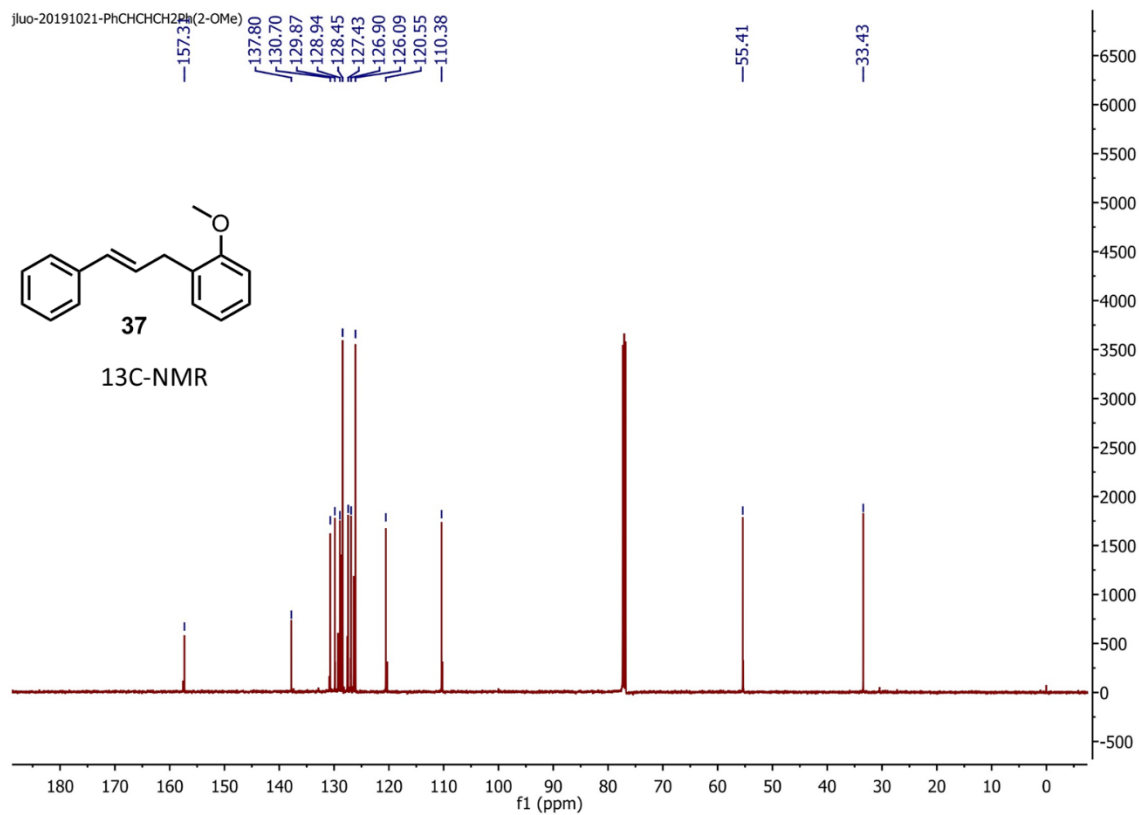


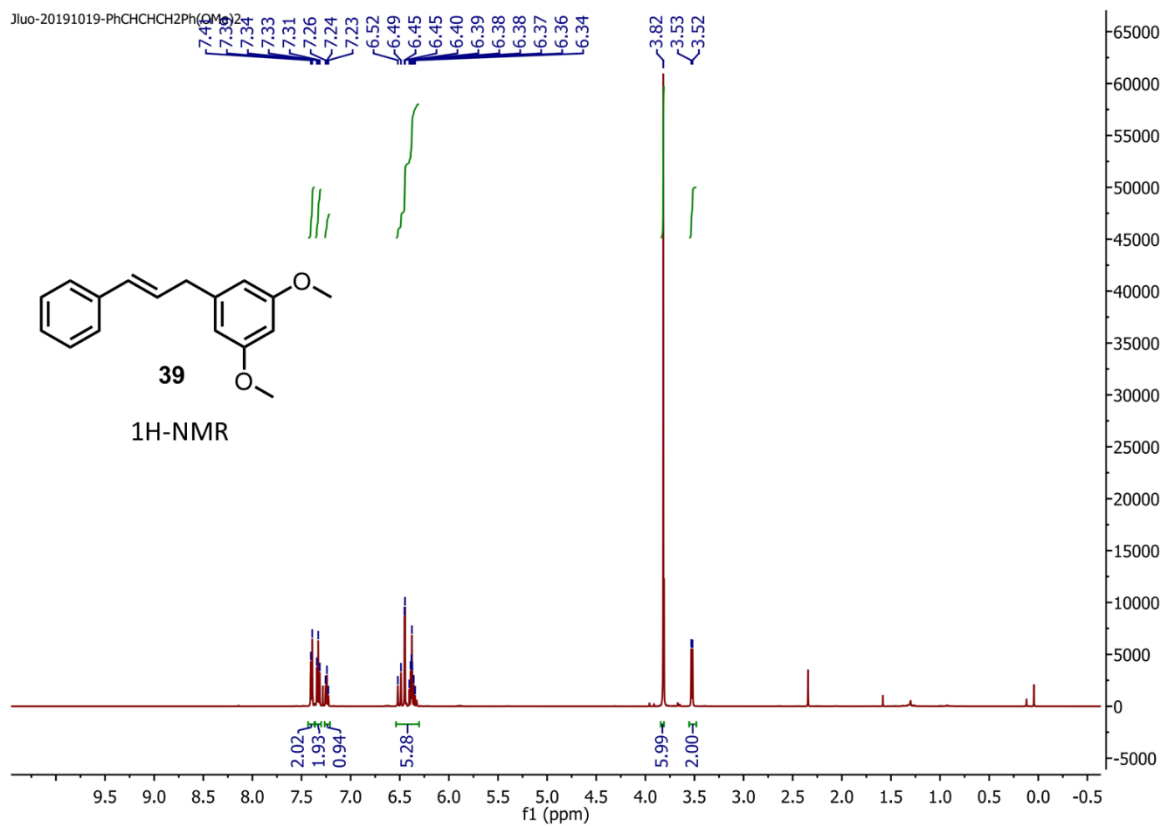
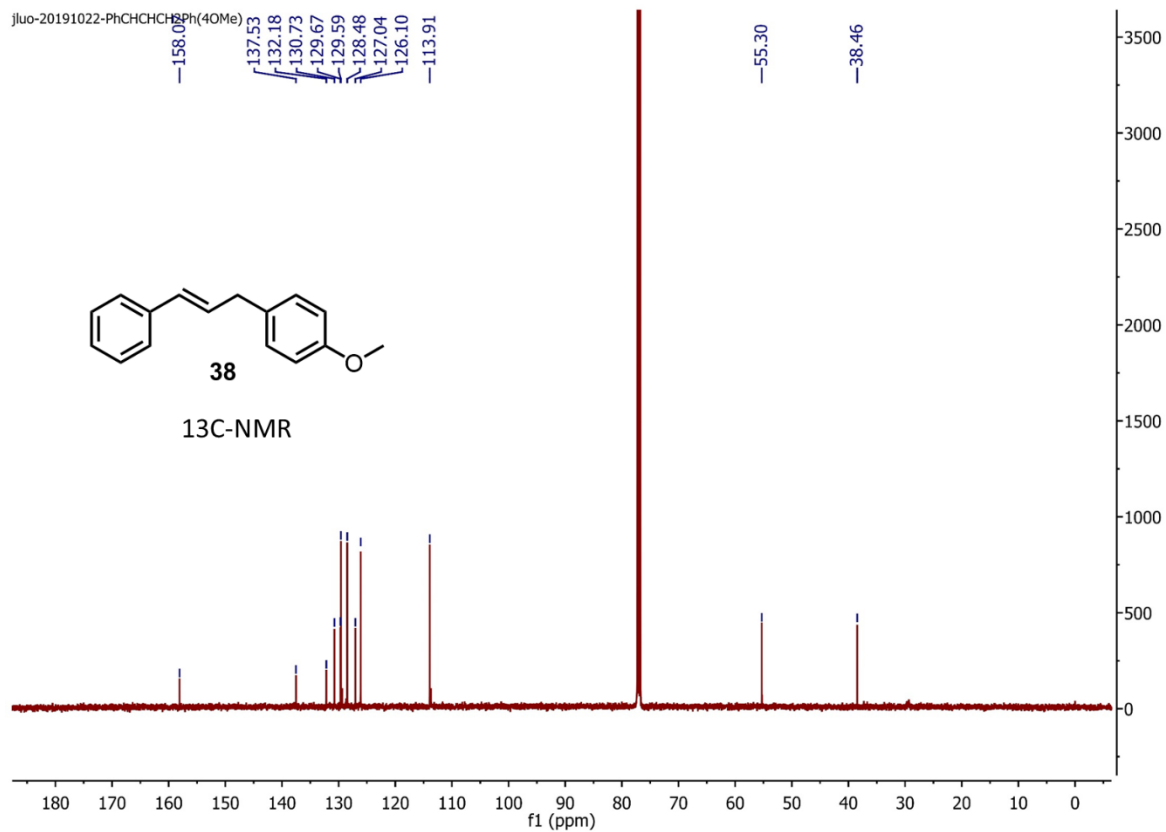


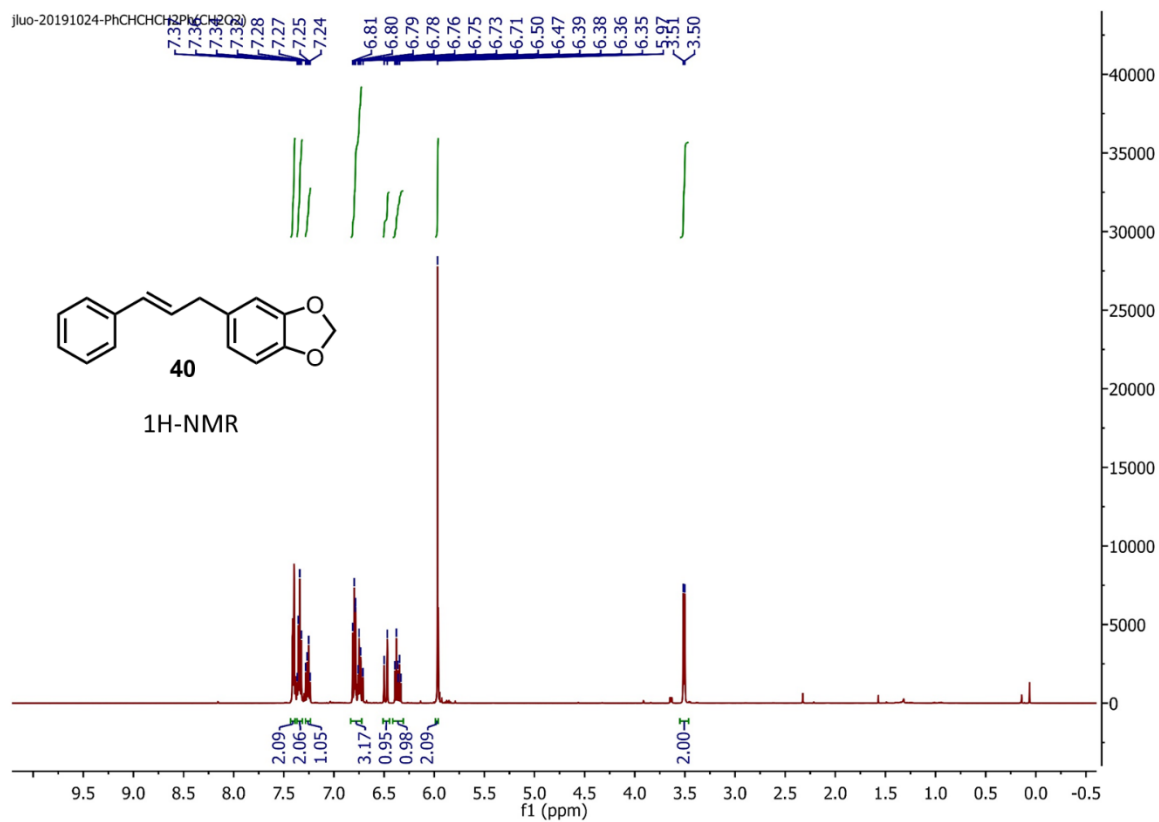
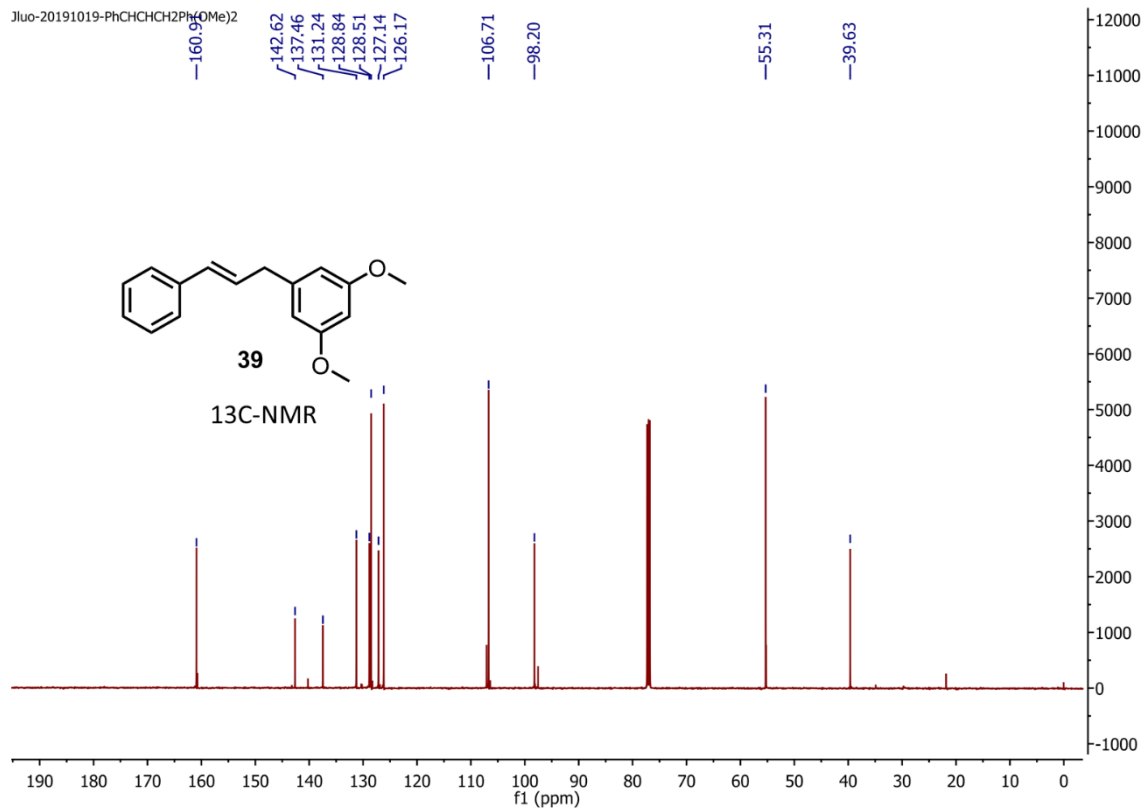


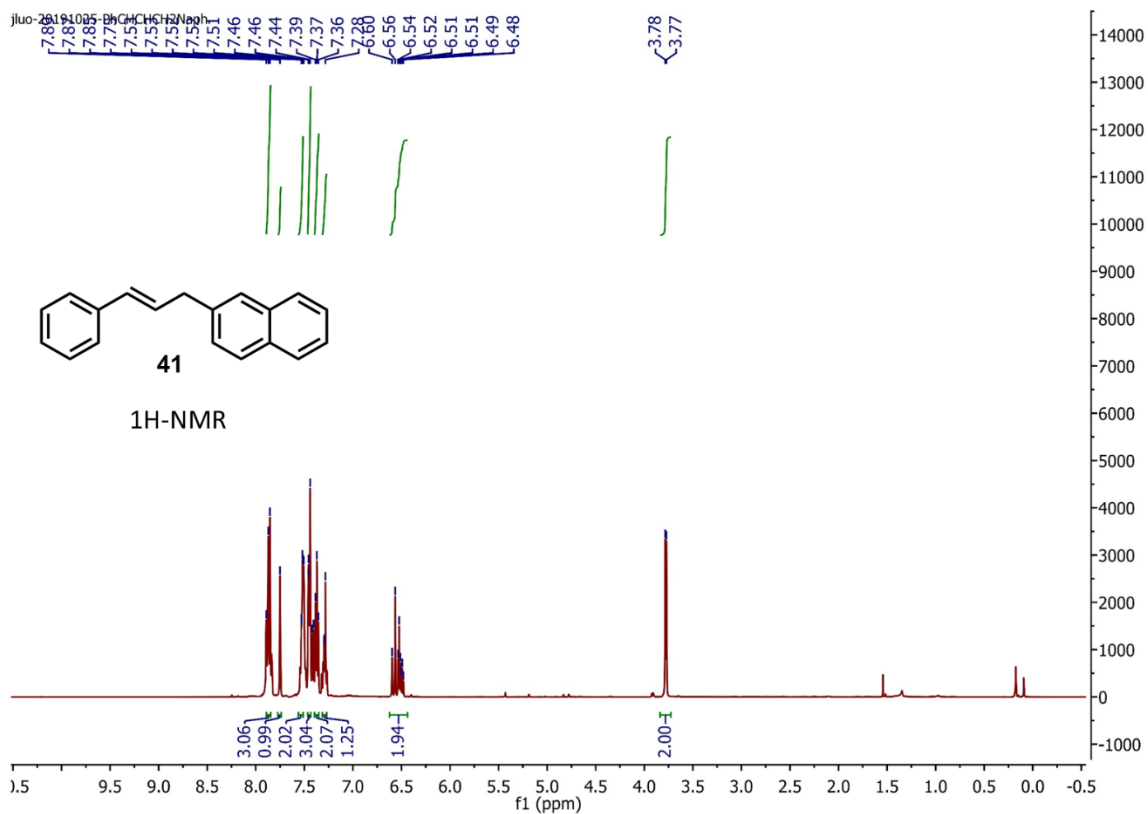
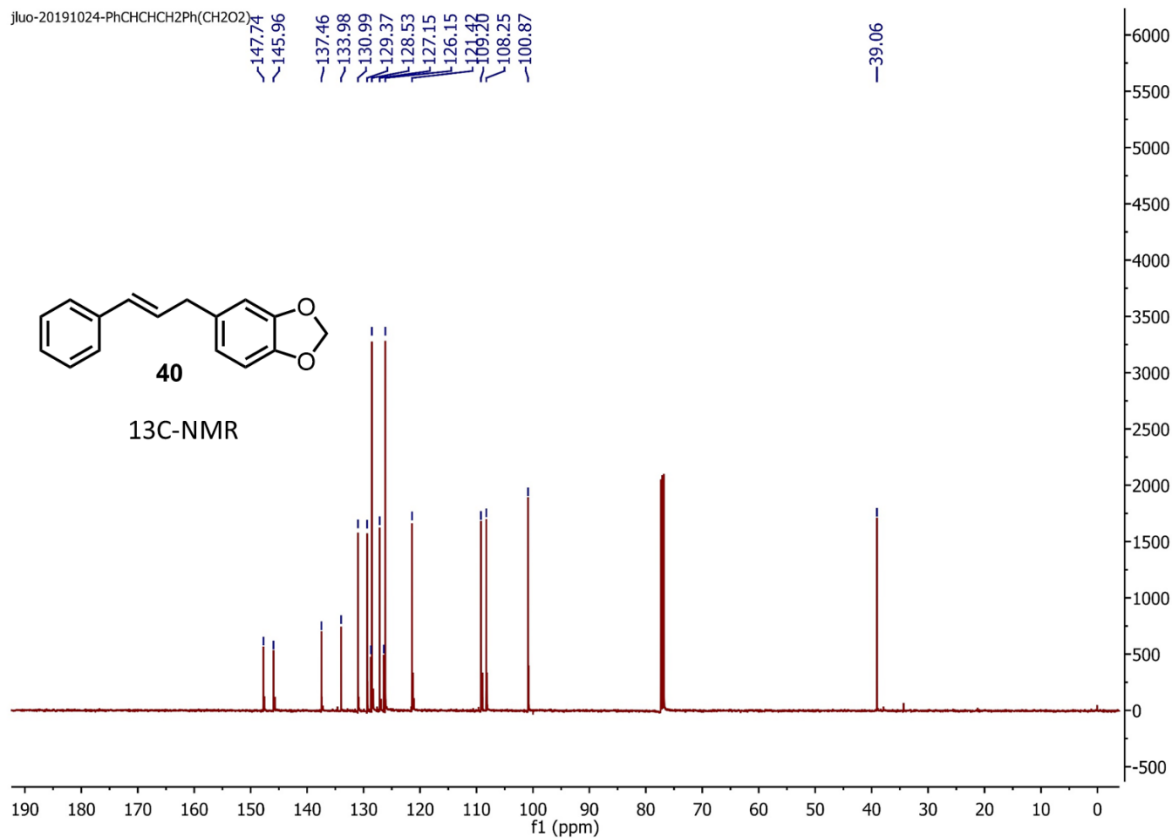


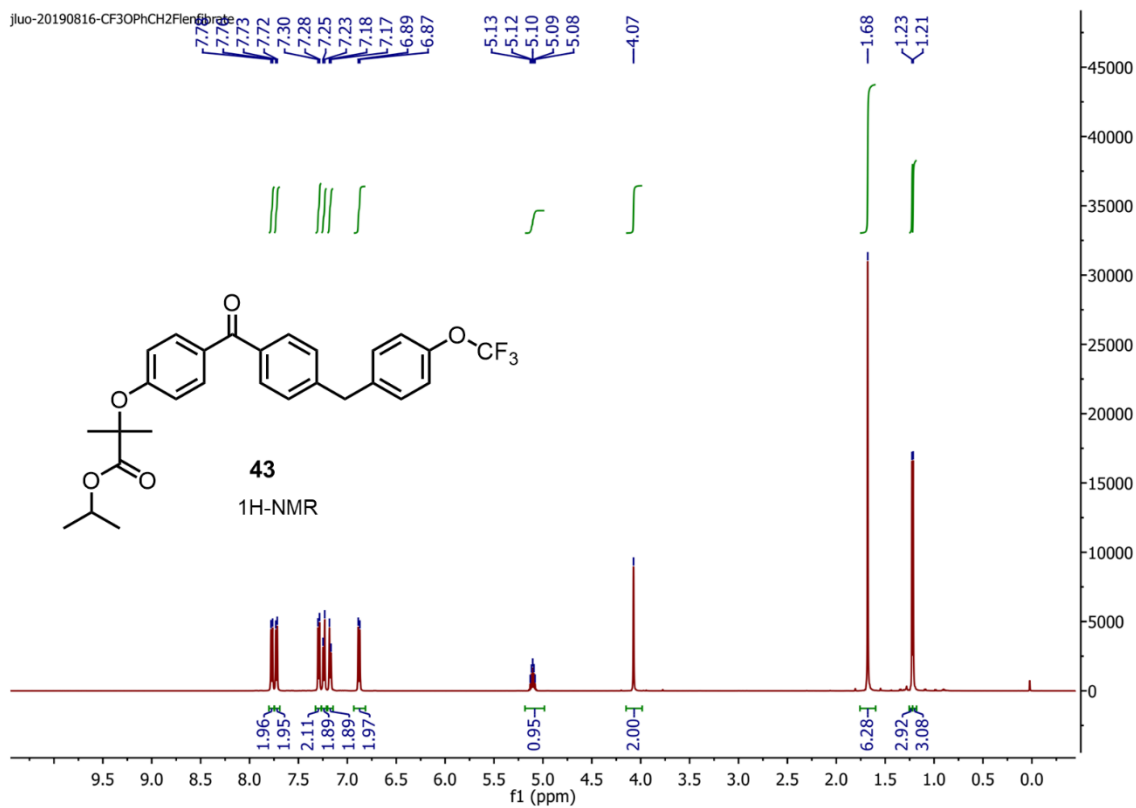
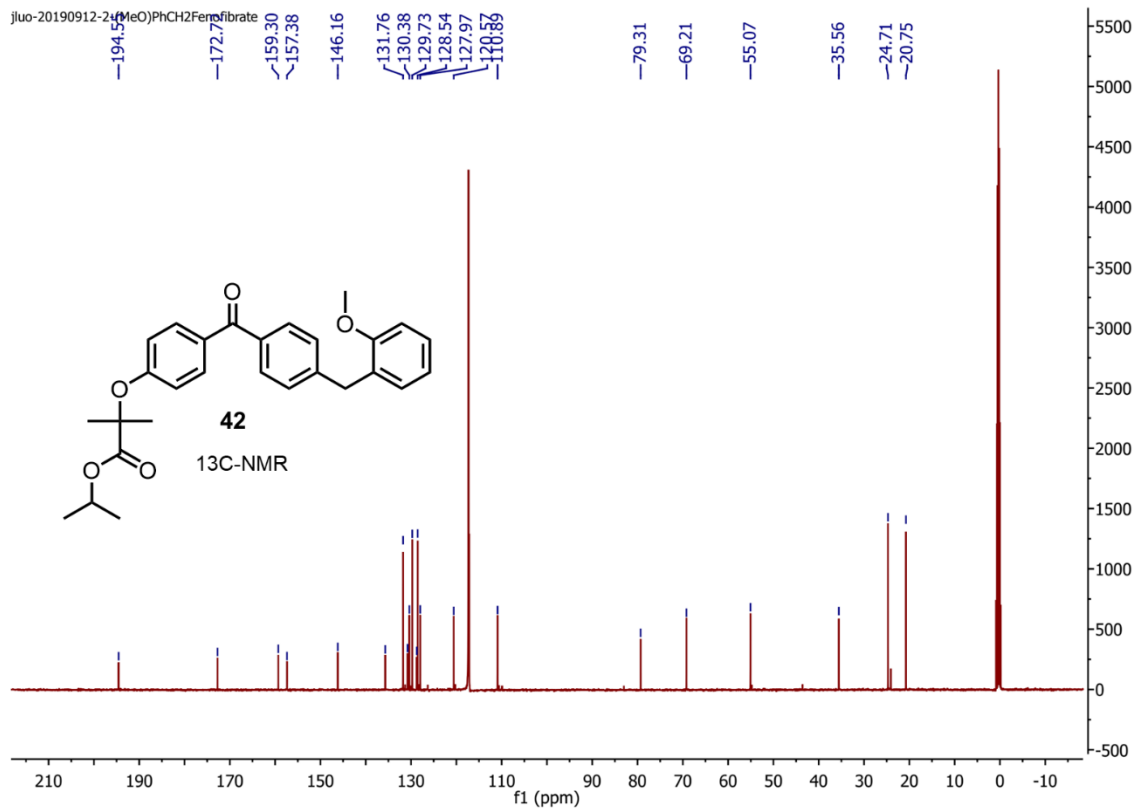


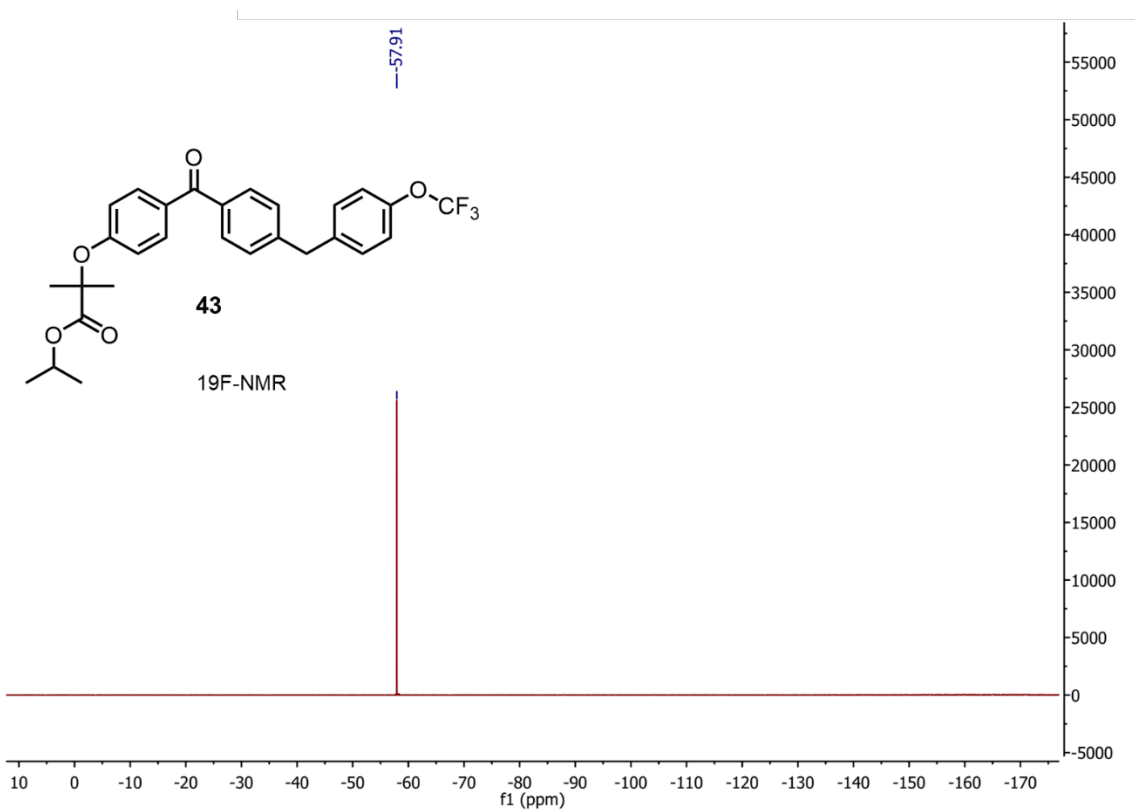
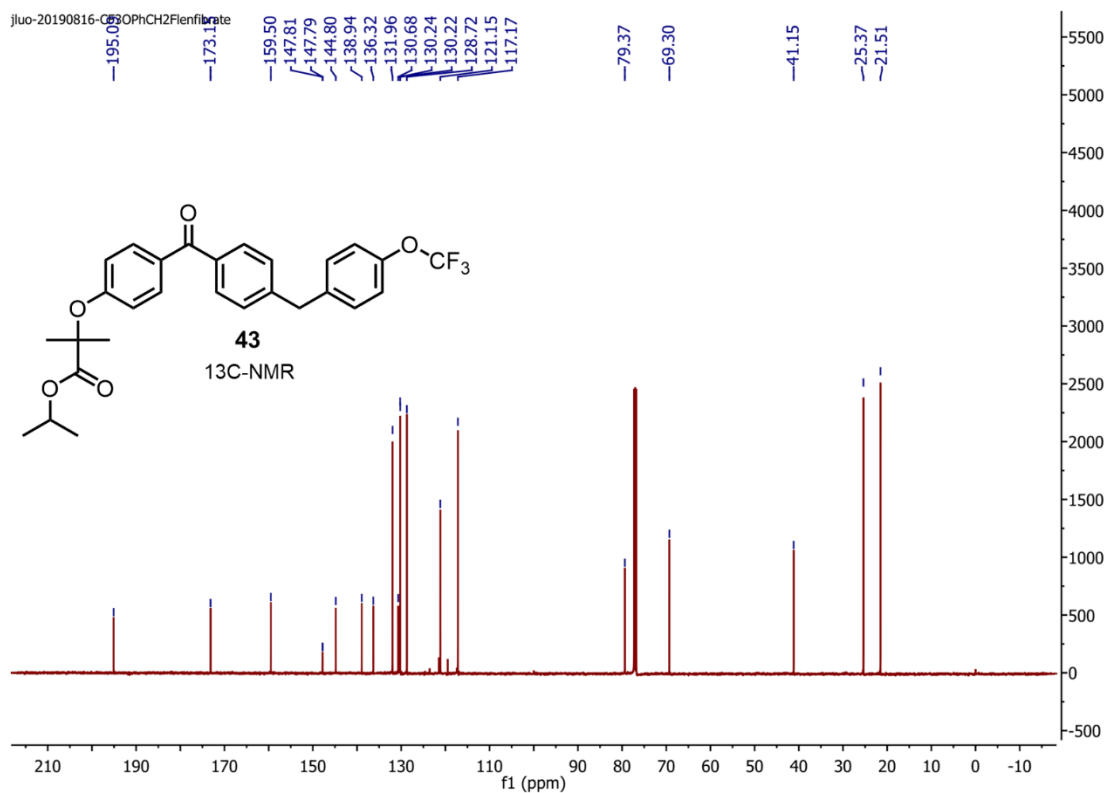


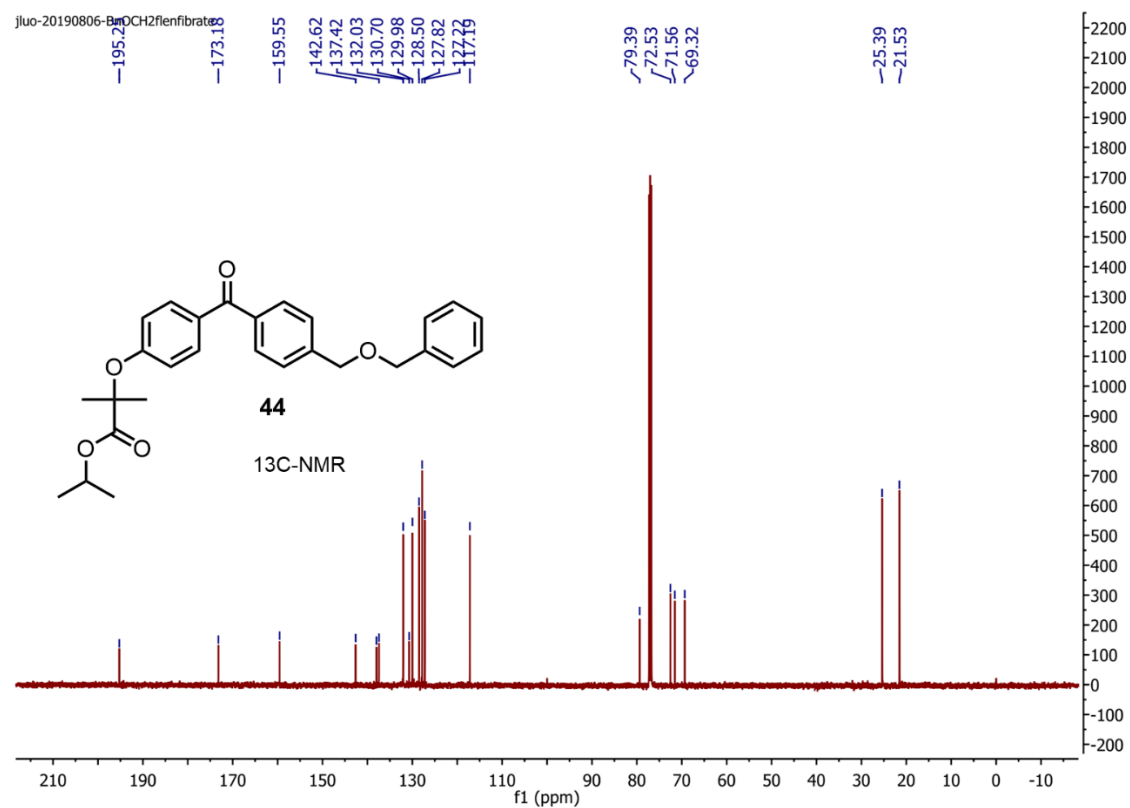
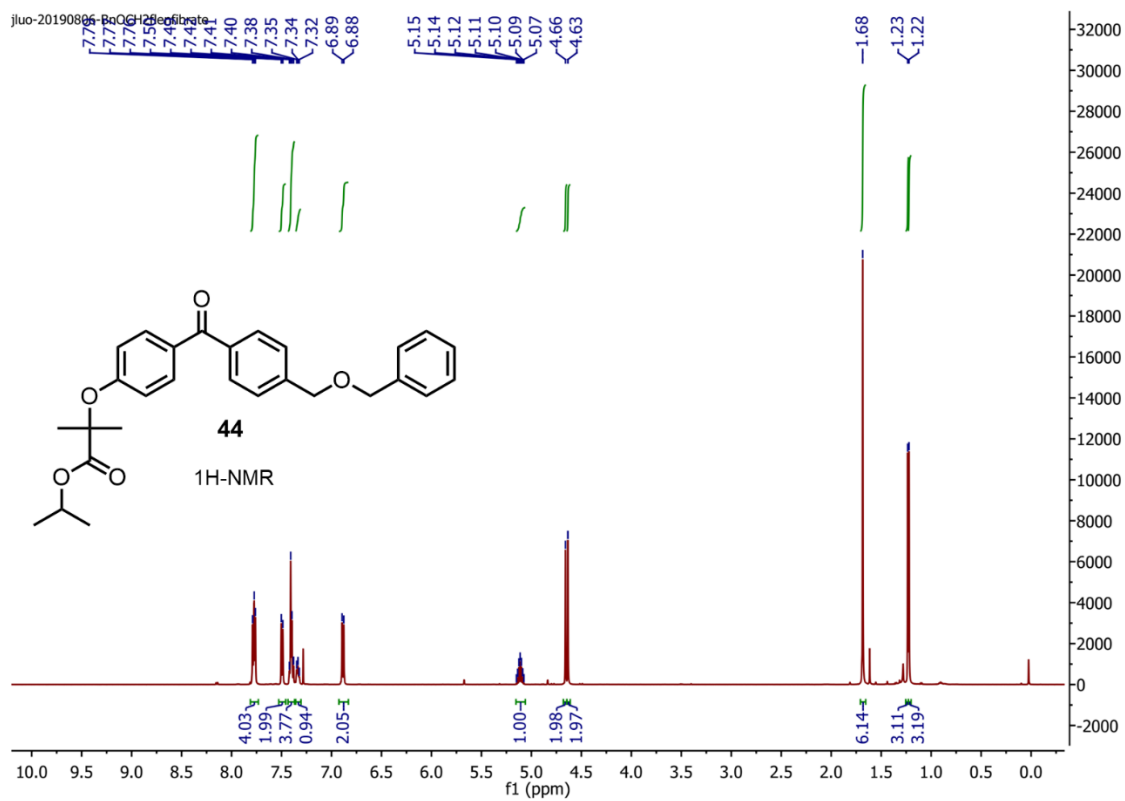


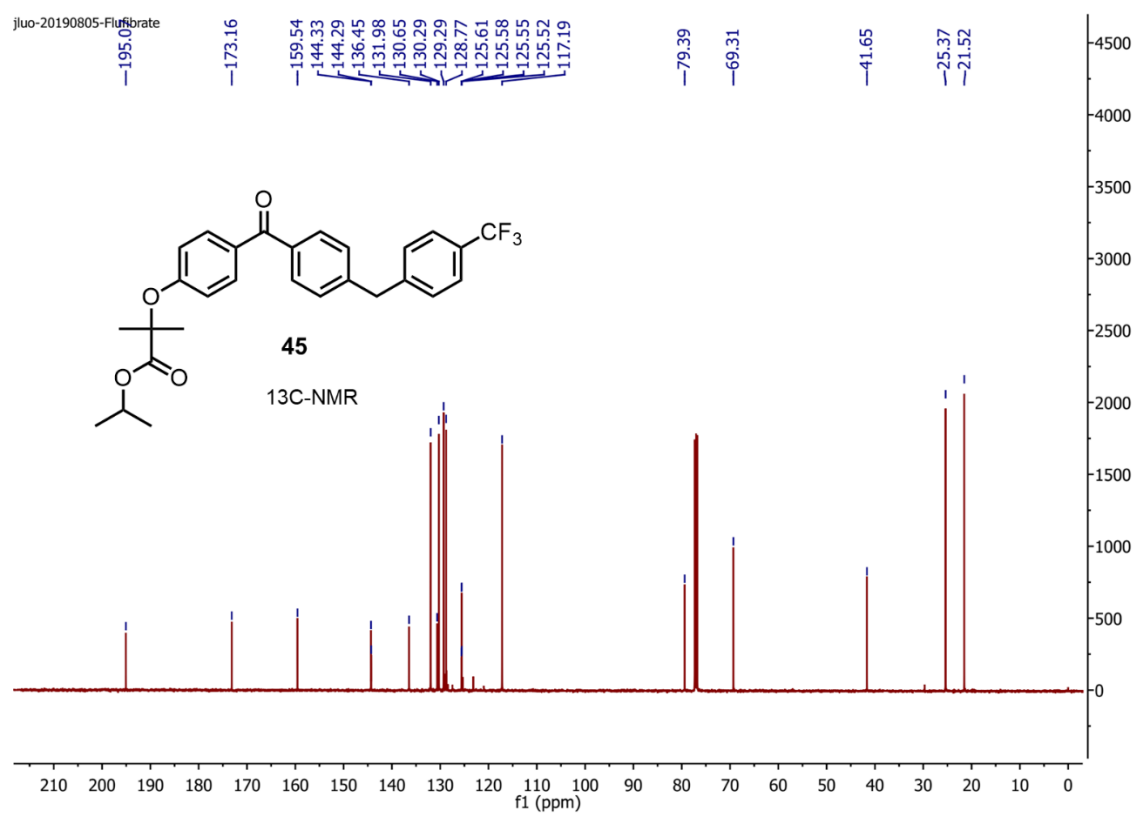
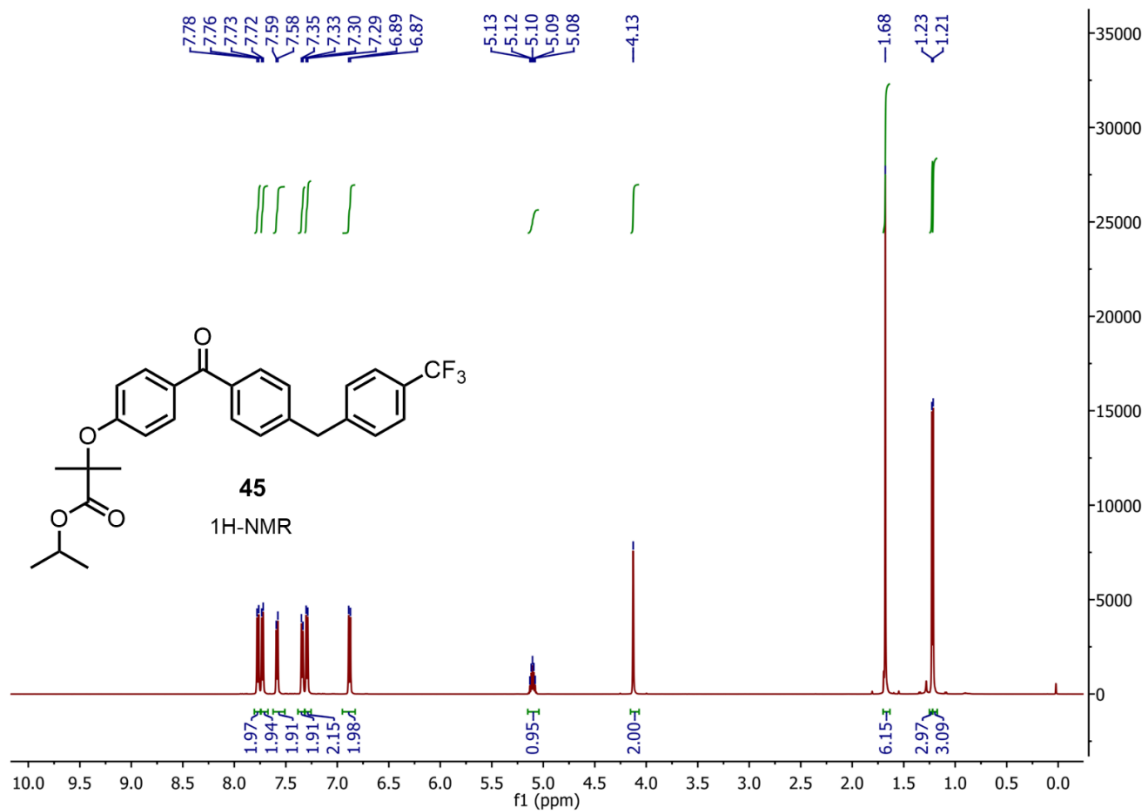


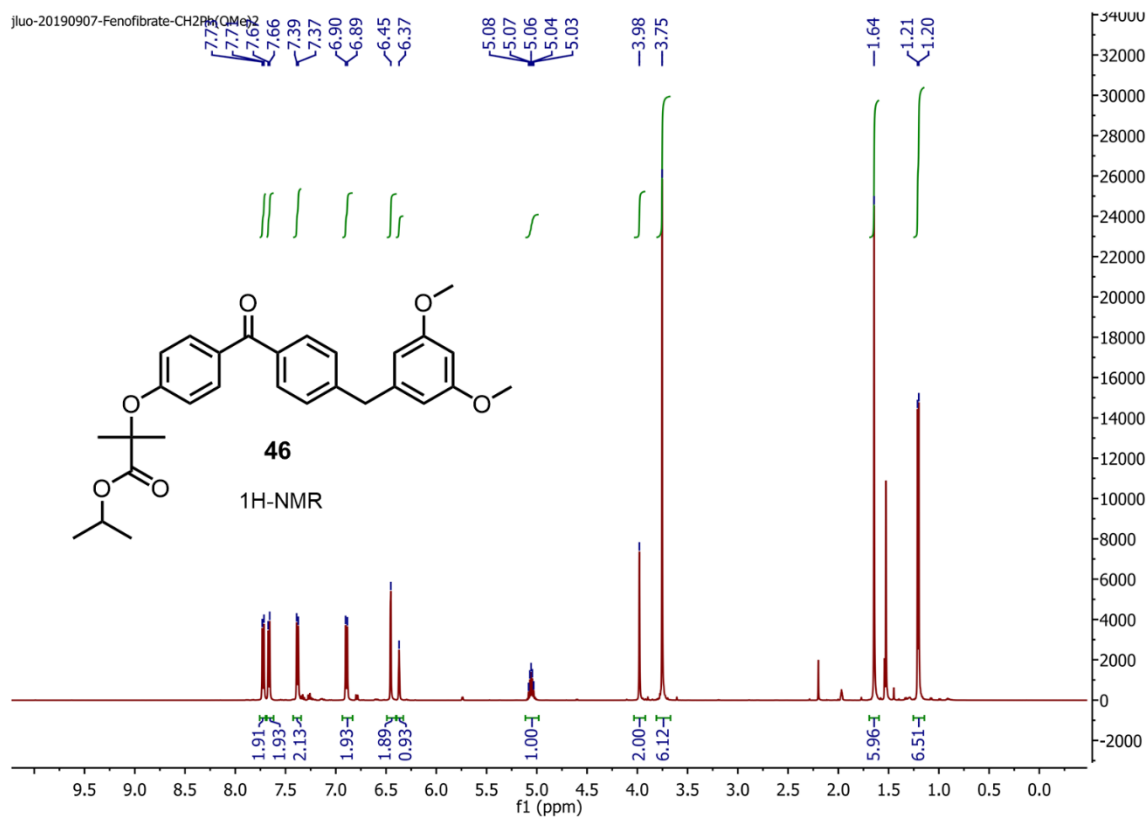
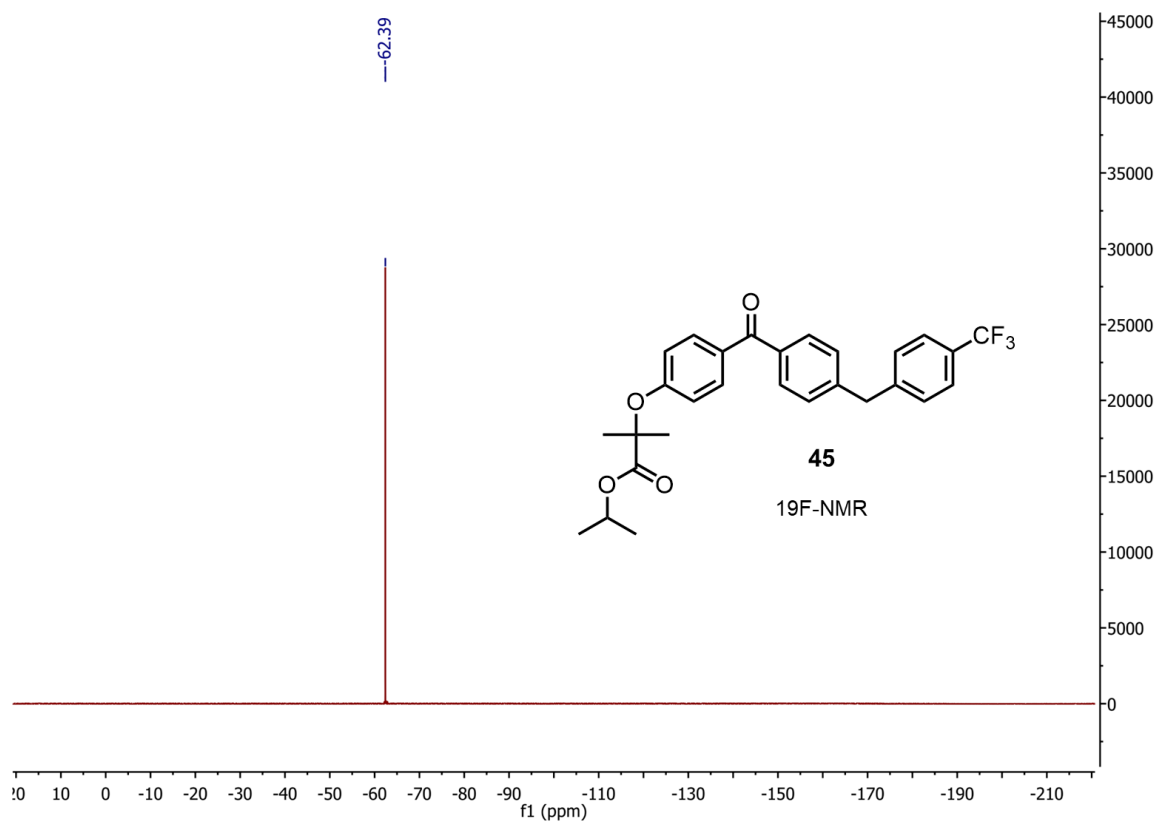


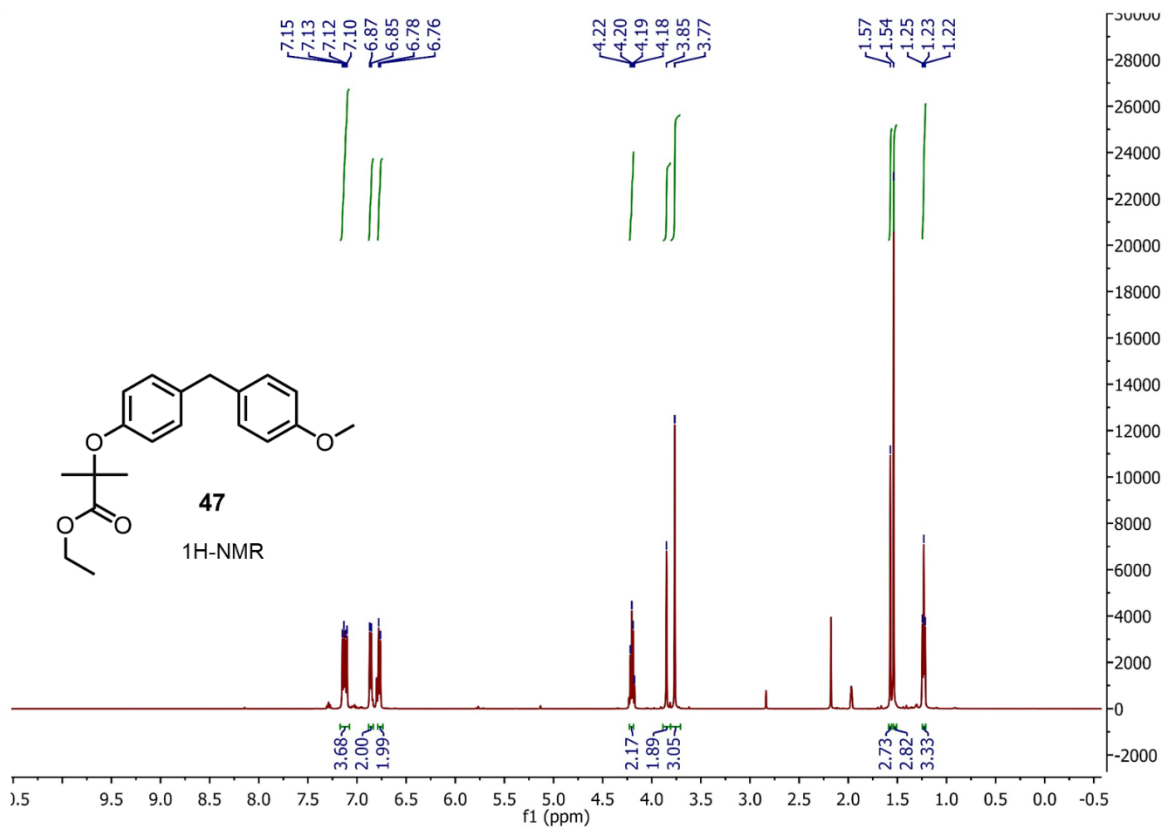
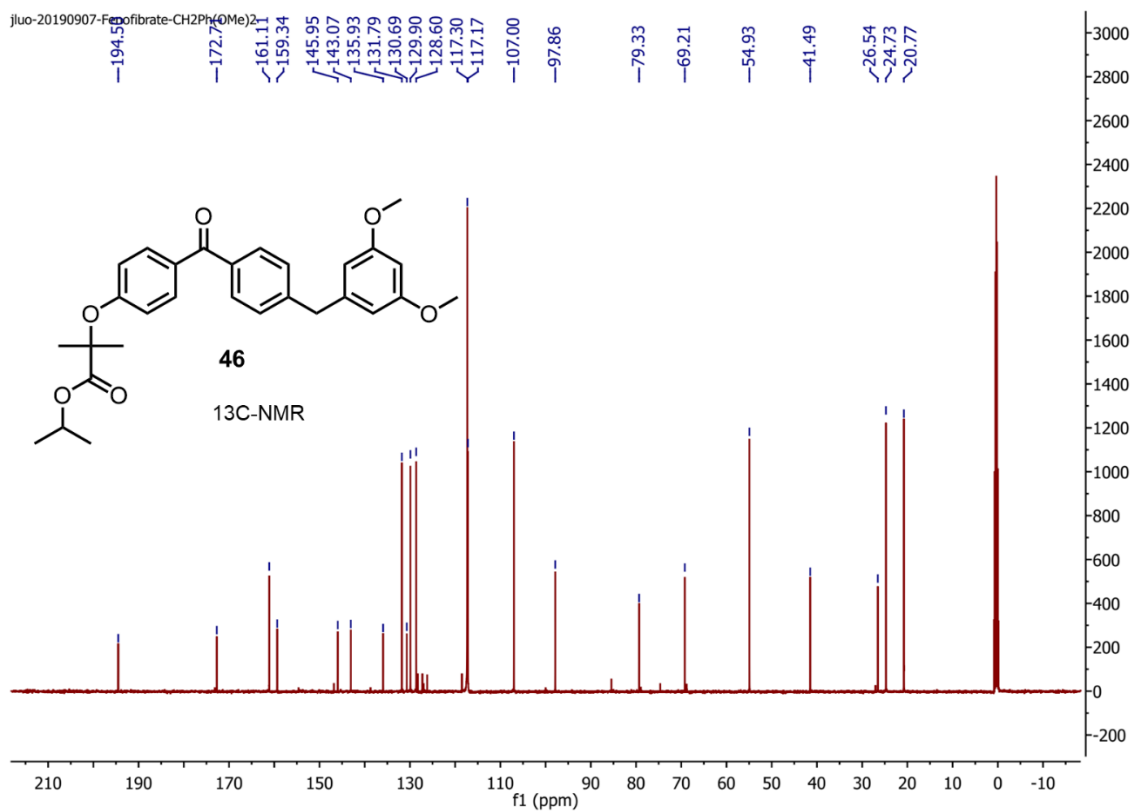


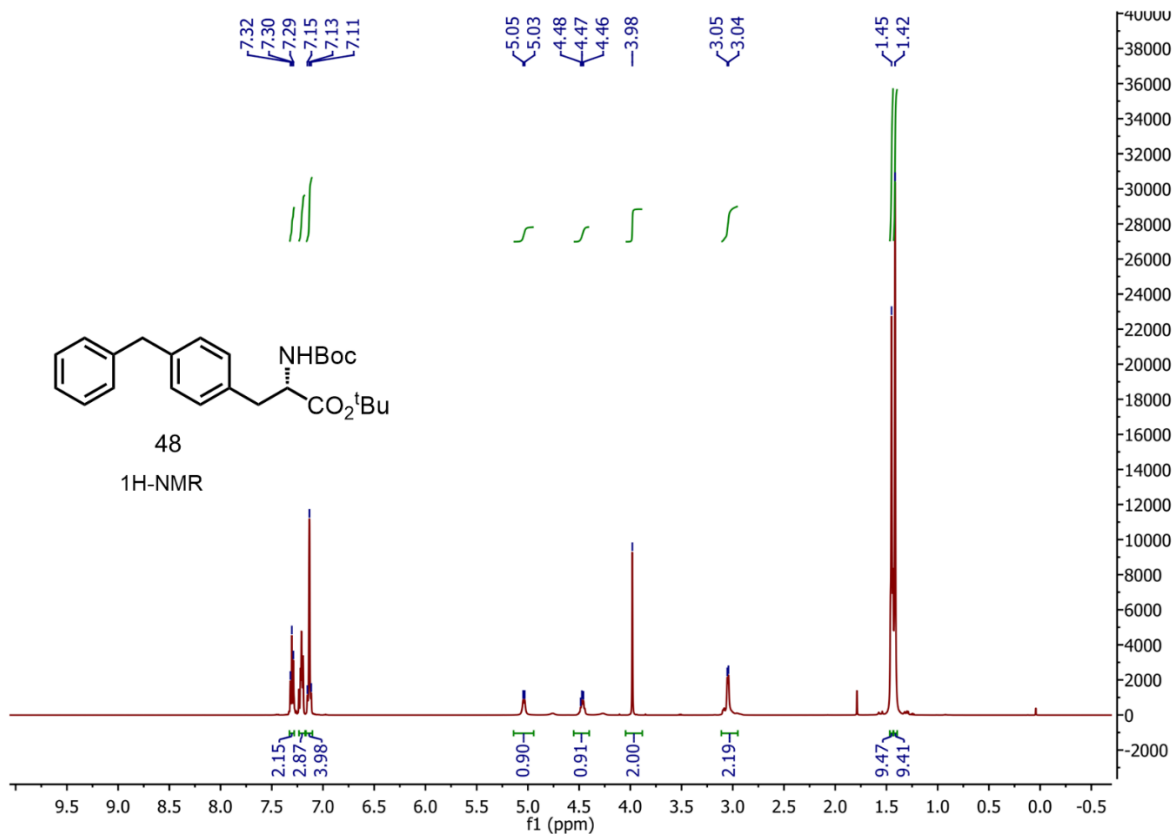
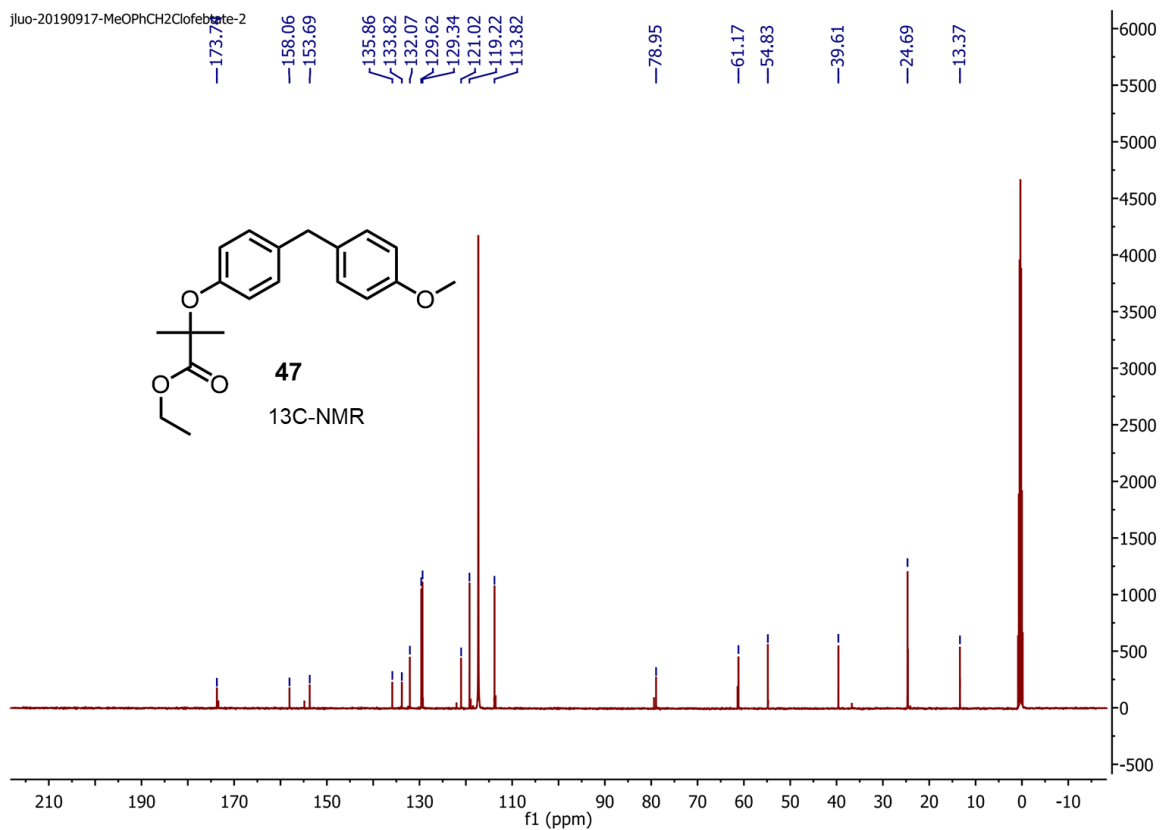


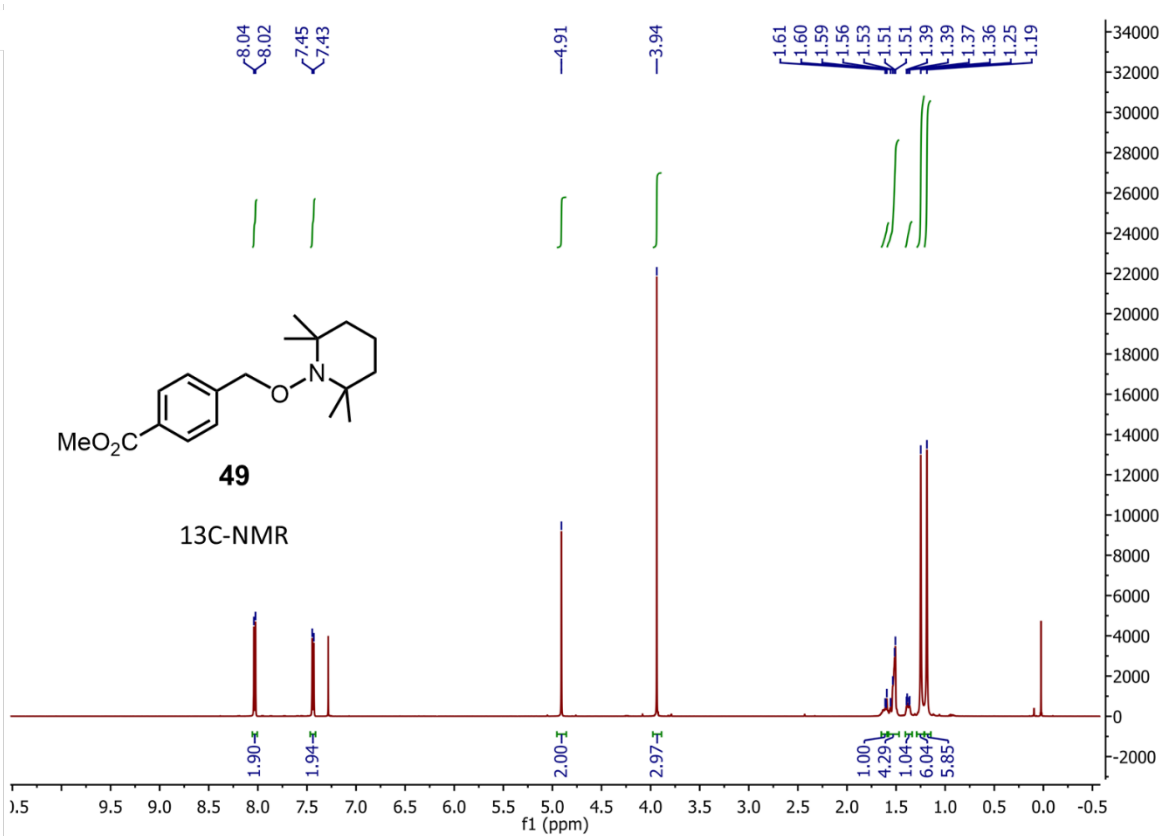
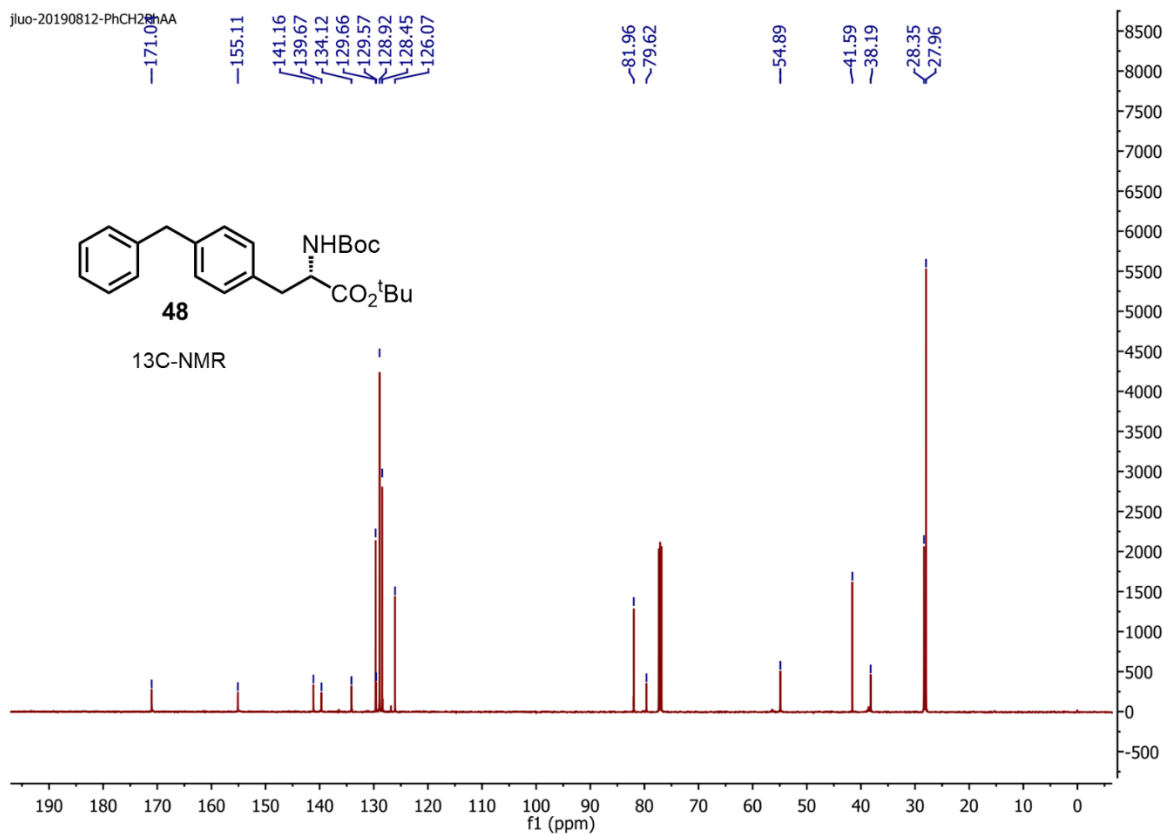


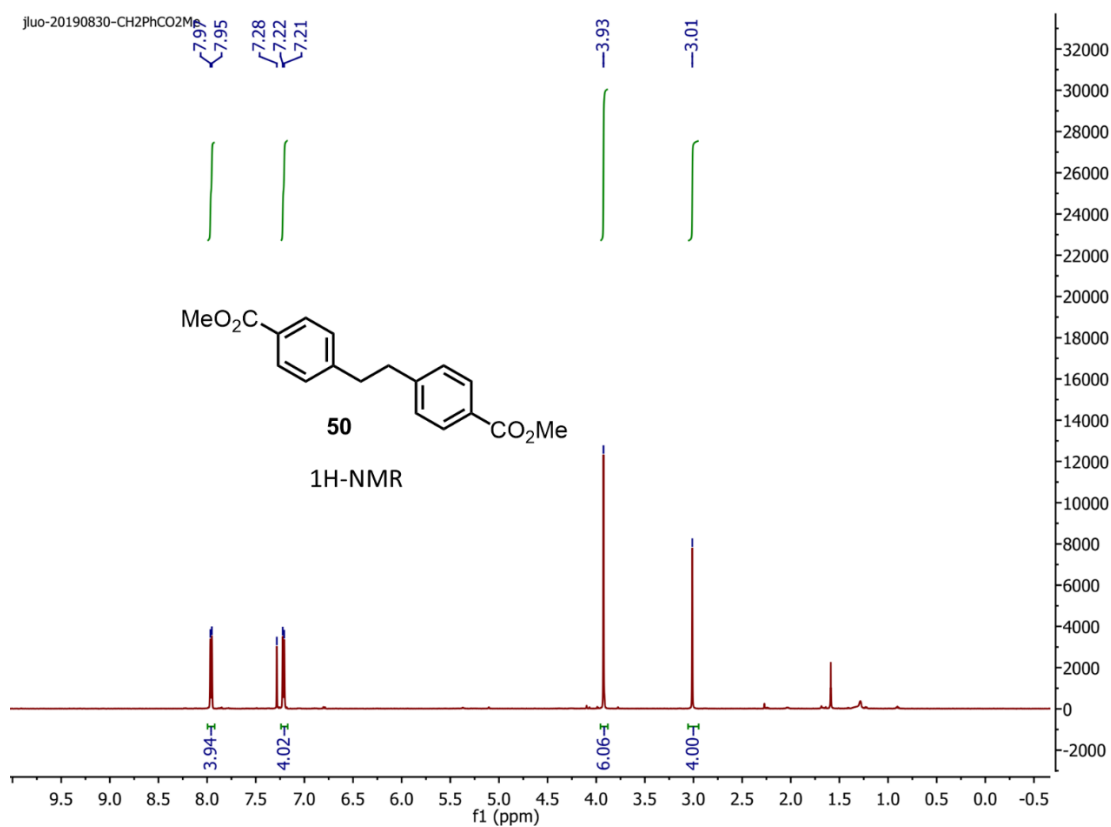
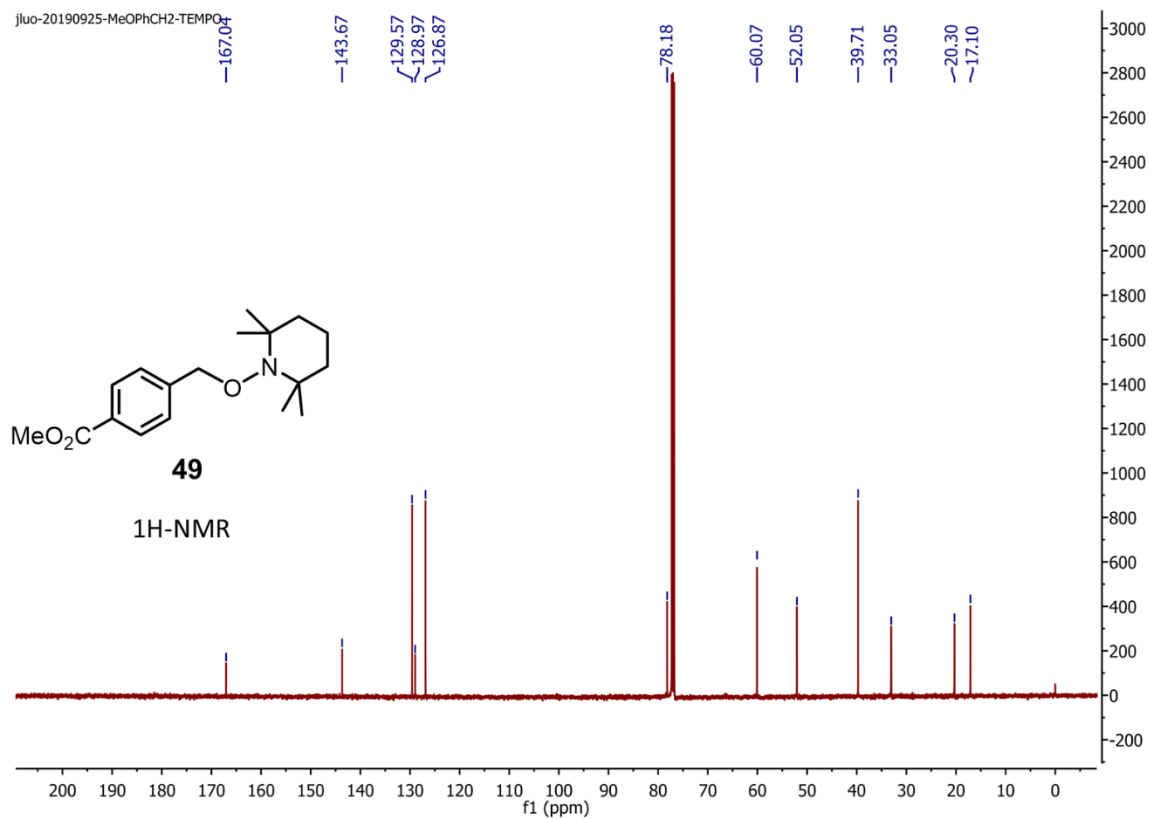


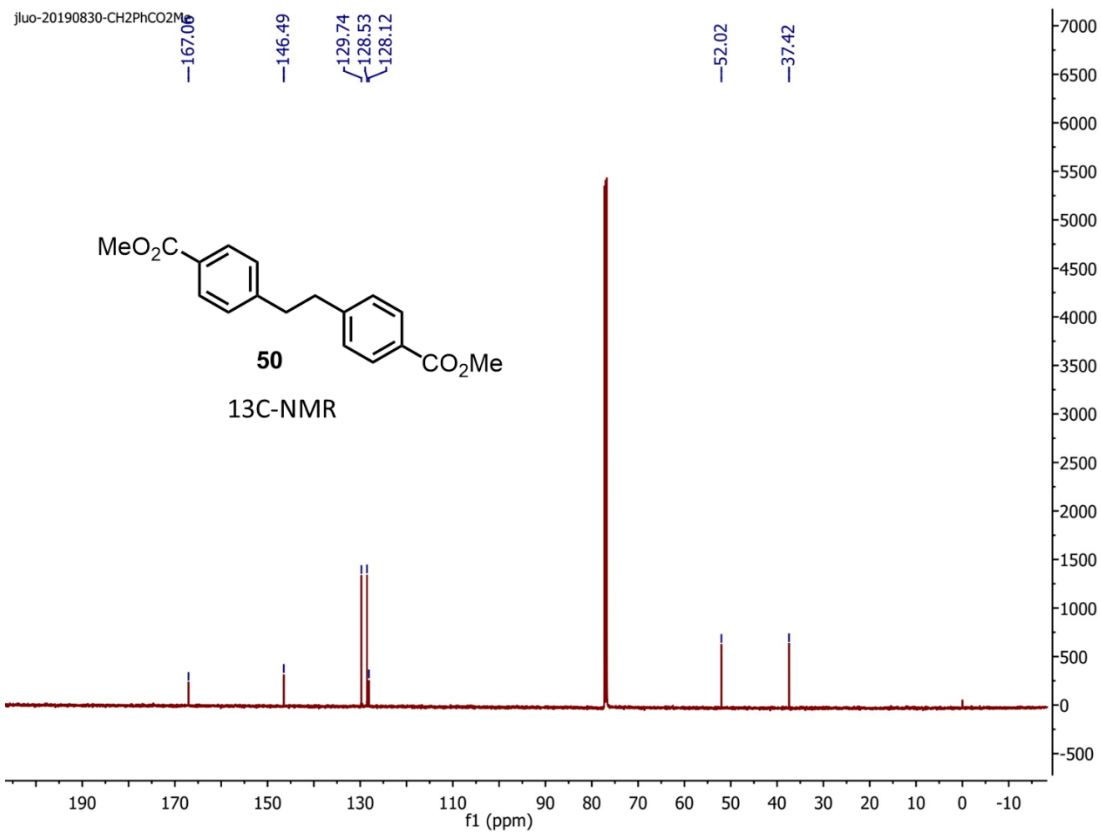












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