

Supporting Information

Visible-light-induced halocyclization of 2-alkynylthioanisoles with simple alkyl halides towards 3-halobenzo[*b*]thiophenes without an external photocatalyst

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1. General considerations

All materials were obtained from commercial suppliers or prepared according to standard procedure unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (b.p. 60-90°C) are used. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz, 150 MHz or 564 MHz, respectively). For ^1H NMR, tetramethylsilane (TMS, $\delta = 0$ ppm) serves as the internal standard; For ^{13}C NMR, Chloroform-d ($\delta = 77.00$ ppm) serves as the internal standard. All chemical shifts of ^1H NMR are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), and br (broad). The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on a Thermo Scientific Q Exactive and Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). All the visible-light-induced halocyclizations were carried out under a blue LED (425 nm, 10 W) irradiation (Figure S1, left), and the gram-scale synthesis reactions were carried out under a Kessil (PR160L-427 nm, 20 W) lamp irradiation (Figure S1, right).

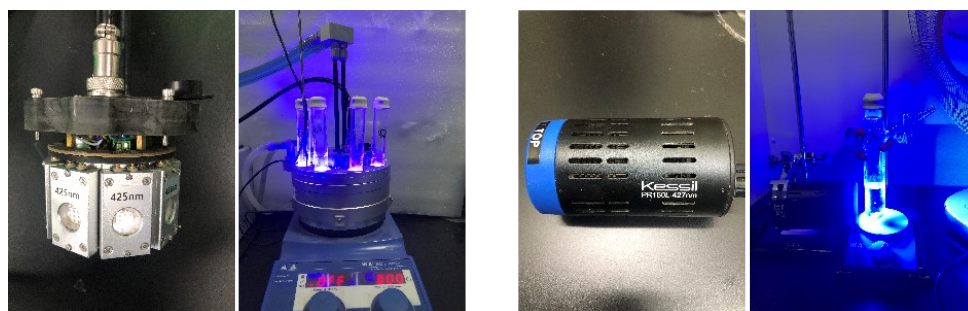
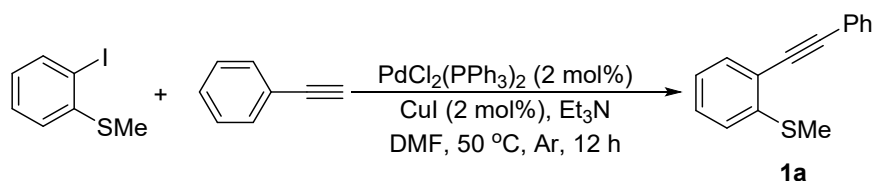


Figure S1. Reaction setup

2. Experimental Section

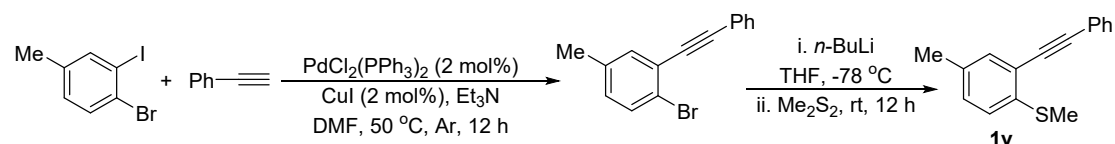
2.1 General procedure for the preparation of substrates

2.1.1 Typical procedure for the preparation of methyl(2-(phenylethynyl)phenyl)sulfane (1a)^[1]



To a solution of (2-iodophenyl)(methyl)sulfane (2.5010 g, 10.0 mmol) and phenylacetylene (1.2256 g, 12.0 mmol, 1.2 equiv) in DMF (5 mL), PdCl₂(PPh₃)₂ (140.4 mg, 2 mol%), CuI (38.1 mg, 2 mol%) and Et₃N (20 mL) were added. The reaction mixture was stirred vigorously at 50 °C for 12 h under an Ar atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (200:1, V/V) as the eluent to afford the corresponding product **1a** as a yellow oil (2.0189 g, 90% yield).

2.1.2 Typical procedure for the preparation of (1v)^[1]

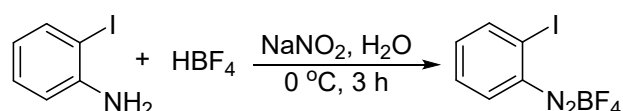


To a solution of 1-bromo-2-iodo-4-methylbenzene (2.9693g, 10.0 mmol) and phenylacetylene (1.2256 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), PdCl₂(PPh₃)₂ (140.4 mg, 2 mol%), CuI (38.1 mg, 2 mol%) and Et₃N (20 mL) were added. The reaction mixture was stirred vigorously at 50 °C for 12 h under an Ar atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (200:1, V/V) as the eluent to afford the corresponding product 1-bromo-4-methyl-2-(phenylethynyl)benzene as a yellow oil (2.3862 g, 88% yield).

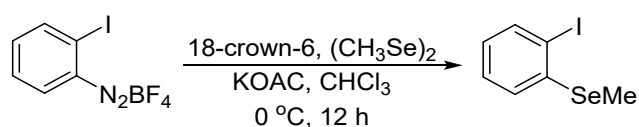
The 1-bromo-4-methyl-2-(phenylethynyl)benzene (2.1693g, 8.0 mmol) was dissolved in dry THF (80 mL) under an Ar atmosphere and cooled to -78 °C for 0.5 h.

Then, 2.0 equiv. of *n*-BuLi (2.0 M solution in cyclohexane, 16.0 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction was stirred at -78 °C for 1 h. Dimethyl disulfide (0.9042 g, 9.6 mmol, 1.2 equiv.) was then added and the reaction mixture was stirred at this temperature under an Ar atmosphere before being allowed to warm to room temperature for 18 h. After completion, THF was evaporated under reduced pressure, then the mixture was diluted with ethyl acetate (50 mL) and water (50 mL), and then extracted with ethyl acetate (2*50 mL), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (200:1, V/V) as the eluent to afford the corresponding product **1v** as a yellow oil (1.4301 g, 75% yield).

2.1.3 Typical procedure for the preparation of (**1ad**)^[1, 2, 3]

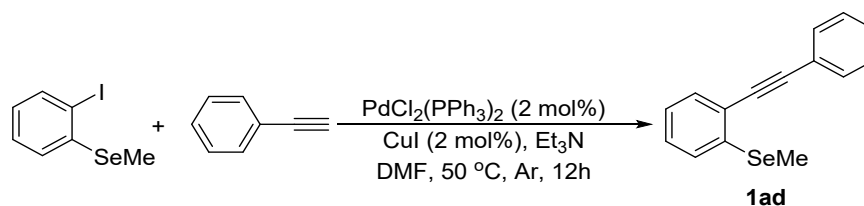


In a 100 mL round-bottom flask, 2-iodoaniline (2.1902g, 10 mmol) was dissolved in a mixture of H₂O (2.0 mL) and an aqueous solution of HBF₄ (48%, 4.0 mL), followed by dropwise addition of aqueous solution of NaNO₂ (1.3804 g, 20 mmol, 2 equiv in 3.0 mL H₂O). The reaction mixture was stirred at 0 °C for 3 h. Then the reaction mixture was worked up by filtration, washing successively with a small amount of ice water, alcohol and diethyl ether, The diazonium salt was dried under vacuum and used for the next step without purification. The product was obtained as a white solid (2.7650 g, 87% yield).



To a flame-dried round-bottom flask, crude diazonium salt (3.1782 g, 10.0 mmol), 18-crown-6 (1.3215 g, 5 mmol, 0.5 equiv), dimethyl diselenide (2.0678g, 11 mmol, 1.1 equiv) and CHCl₃ (40 mL) were added, the mixture was stirred at 0 °C. To this mixture, KOAc (1.9628 g, 20 mmol, 2 equiv) was added in small portions over a

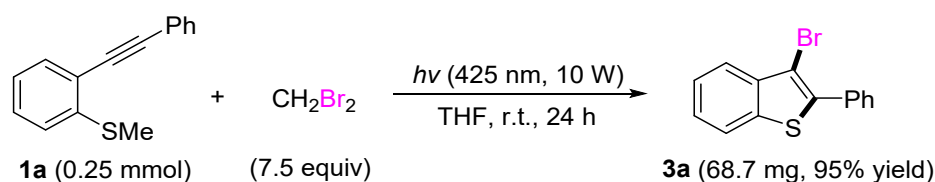
period of 20 min and the resulting solution was allowed to stir for 12 h and then filtered. The solid residue was washed with chloroform and the resulting filtrate was washed with water, dried over anhydrous Na_2SO_4 , and concentrated under vacuum. The obtained crude product was then purified by flash chromatography on silica gel using petroleum ether as the eluent. The product was obtained as a yellow oil (2.1384g, 72% yield).



To a solution of (2-iodophenyl)(methyl)sulfane (2.9701 g, 10.0 mmol) and phenylacetylene (1.2256 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), $\text{PdCl}_2(\text{PPh}_3)_2$ (140.4 mg, 2 mol%), CuI (38.1 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorously at 50 °C for 12 h under an Ar atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 , filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (200:1, V/V) as the eluent to afford the corresponding product **1ad** as a yellow oil (2.3326 g, 86% yield).

2.2 Typical procedure for the halocyclization reactions

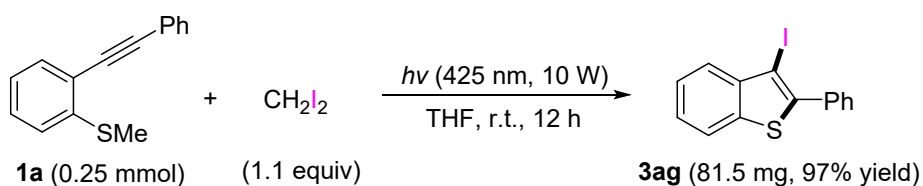
2.2.1 Typical procedure for the bromocyclization of **1a**



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 56.1 mg, 0.25 mmol), CH_2Br_2 (325.9 mg, 1.875 mmol, 7.5 equiv), and THF (2.0 mL). The reaction mixture

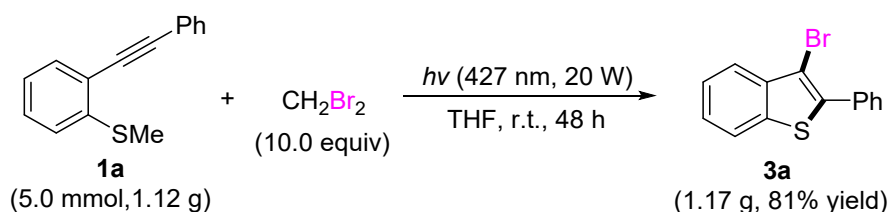
was exposed to blue LED (425 nm, 10 W) irradiation at room temperature in a sealed tube with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3a** as a white solid (68.7 mg, 95% yield).

2.2.2 Typical procedure for the iodocyclization of **1a**



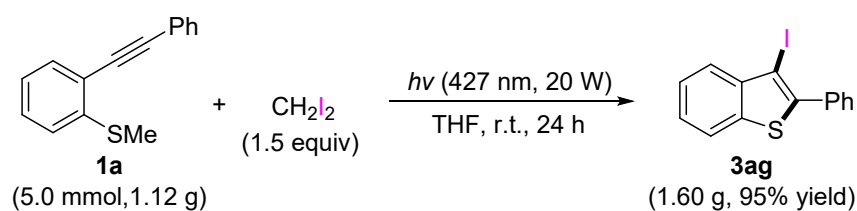
A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 56.1 mg, 0.25 mmol), CH_2I_2 (73.7 mg, 0.275 mmol, 1.1 equiv), and THF (2.0 mL). The reaction mixture was exposed to blue LED (425 nm, 10 W) irradiation at room temperature in a sealed tube with stirring for 12 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3ag** as a white solid (81.5 mg, 97% yield).

2.2.3 Gram-scale synthesis of **3a**



A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 1.12 g, 5.0 mmol), CH_2Br_2 (8.70 g, 50.0 mmol, 10 equiv), and THF (30.0 mL). The reaction mixture was exposed to blue LED (427 nm, 20 W) irradiation at room temperature in a sealed tube with stirring for 48 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3a** as a white solid (1.17 g, 81% yield).

2.2.4 Gram-scale synthesis of 3ag



A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 1.12 g, 5.0 mmol), CH_2I_2 (2.01 g, 7.5 mmol, 1.5 equiv), and THF (30.0 mL). The reaction mixture was exposed to blue LED (427 nm, 20 W) irradiation at room temperature in a sealed tube with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3ag** as a white solid (1.60 g, 95% yield).

2.3 Preliminary mechanistic study

2.3.1 UV-visible absorption spectra

The ultraviolet/visible absorption spectra were recorded on a UV-Visible U-4100 spectrophotometer, as shown in **Figure S2**. The absorption spectrum of **1a** and **3a** have a wide absorption range from 300 nm to 450 nm, which is consistent with the wavelength of the LED used in the experiment (425 nm).

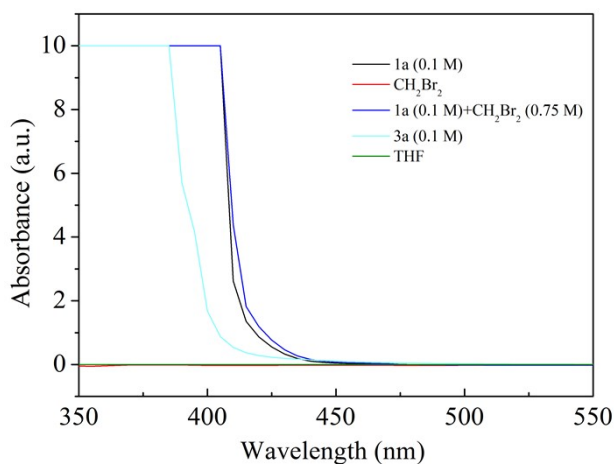


Figure S2. Absorption spectra with different substance

2.3.2 Fluorescence quenching experiment

(1) Fluorescence quenching studies of **1a** with CH₂Br₂ in THF

Increasing amounts of CH₂Br₂ were added to the solution of **1a** in THF. Emission spectrum were recorded after each addition. The results in **Figure S3** (left) shows a weak change in the emission intensity of **1a** with a calculated K_{sv} of 0.0389 mM⁻¹ [**Figure S3** (right)].

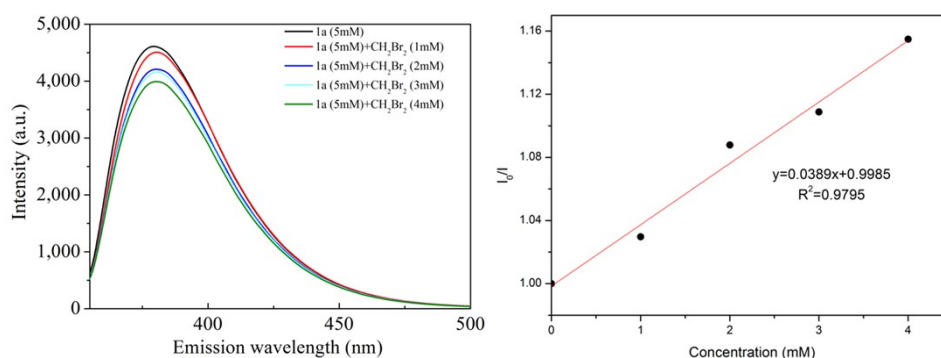


Figure S3. (a) Fluorescence quenching of **1a** by CH₂Br₂ in THF (left); (b) Stern-Volmer plots of **1a** quenching with CH₂Br₂ (right).

(2) Fluorescence quenching studies of **3a** with CH₂Br₂ in THF

Increasing amounts of CH₂Br₂ were added to the solution of **3a** in THF. Emission spectrum were recorded after each addition. The results in **Figure S4** (left) shows an obvious change in the emission intensity of **3a** with a calculated K_{sv} of 0.0982 mM⁻¹ [**Figure S4** (right)].

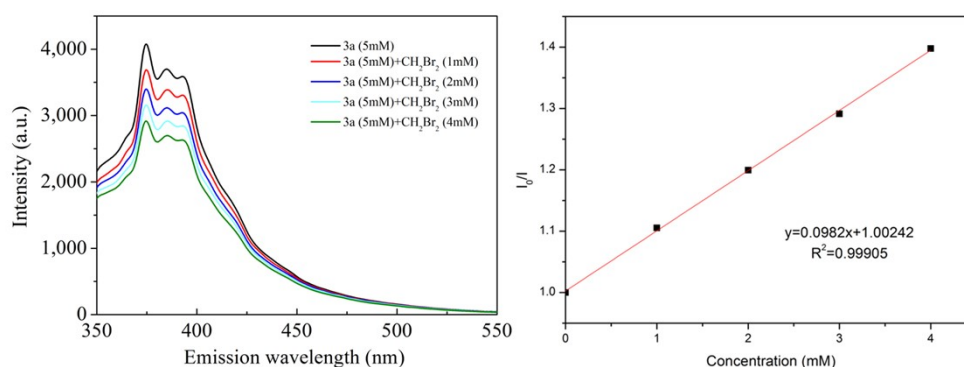
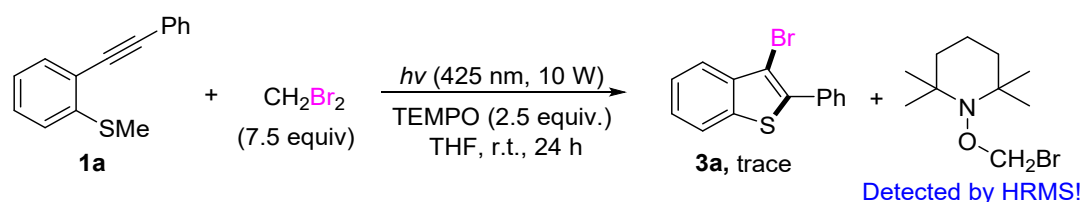


Figure S4. (a) Fluorescence quenching of **2a** by CH₂Br₂ in THF (left); (b) Stern-Volmer plots of **2a** quenching with CH₂Br₂ (right).

The results of Stern–Volmer quenching experiments of the effect of CH_2Br_2 on the fluorescence emission of excited **1a** and **3a** reveal apparent quenching effects with CH_2Br_2 , which indicated that an energy-transfer quenching of excited **1a*** and **3a*** by CH_2Br_2 were involved in the mechanism, and **3a*** shows a stronger quenching effect with CH_2Br_2 . The results are also consistent with the On/Off experiments, the reaction is accelerated with increase of the concentration of **3a**.

2.3.2 Radical inhibition experiment

(1) The reaction of **1a** and CH_2Br_2 inhibited by TEMPO



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 56.1 mg, 0.25 mmol), CH_2Br_2 (325.9 mg, 1.875 mmol, 7.5 equiv), TEMPO (97.7 mg, 0.625 mmol, 2.5 equiv), and THF (2.0 mL). The reaction mixture was exposed to blue LED (425 nm, 10 W) irradiation at room temperature in a sealed tube with stirring for 24 h. After completion, only trace amount of **3a** was detected in the reaction mixture, and the corresponding adduct of bromomethyl radical and TEMPO was detected by HRMS analysis, and the related results were shown in **Figure S5**.

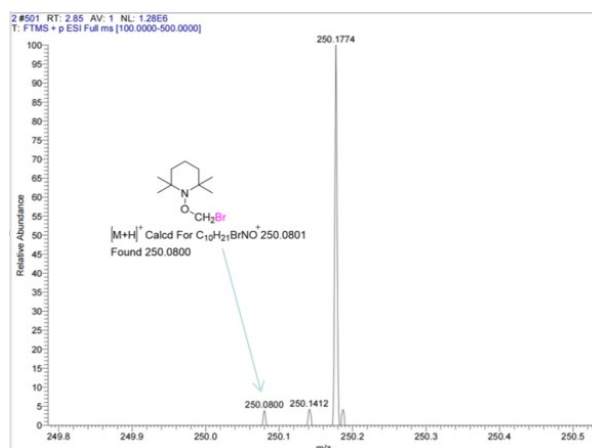
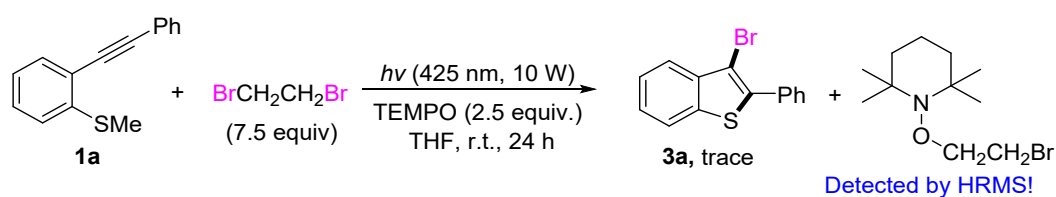


Figure S5. Analysis of reaction mixture by HRMS for the adduct of bromomethyl radical

(2) The reaction of **1a** and BrCH₂CH₂Br inhibited by TEMPO



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 56.1 mg, 0.25 mmol), BrCH₂CH₂Br (352.2 mg, 1.875 mmol, 7.5 equiv), TEMPO (97.7 mg, 0.625 mmol, 2.5 equiv), and THF (2.0 mL). The reaction mixture was exposed to blue LED (425 nm, 10 W) irradiation at room temperature in a sealed tube with stirring for 24 h. After completion, only trace amount of **3a** was detected in the reaction mixture, and the corresponding adduct of bromoethyl radical and TEMPO was detected by HRMS analysis, and the related results were shown in **Figure S6**.

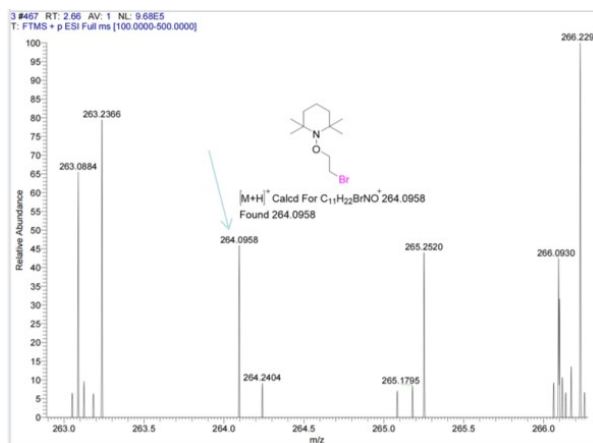


Figure S6. Analysis of reaction mixture by HRMS for the adduct of bromoethyl radical

2.3.4 Light/dark experiments

In order to illustrate the radical addition/cyclization by self-sustaining in an autocatalytic manner, the light/dark experiments were conducted, as shown in **Figure S7**. A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 56.1 mg, 0.25 mmol), CH₂Br₂ (325.9 mg, 1.875 mmol, 7.5 equiv.), and THF (2.0 mL). The reaction mixture was exposed to blue LED (425 nm, 10 W) irradiation at room temperature in a sealed

tube with stirring for 2 h, then stirring for 2 h without irradiation. The following product yields based on the irradiation with LED (425 nm, 10 W) at room temperature for a certain time, and without irradiation for a certain time were also presented in the **Figure S7**.

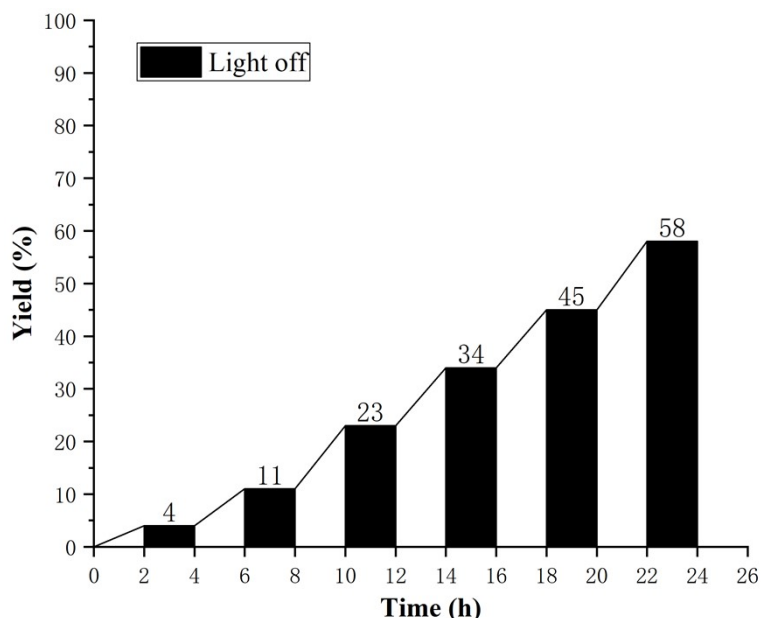
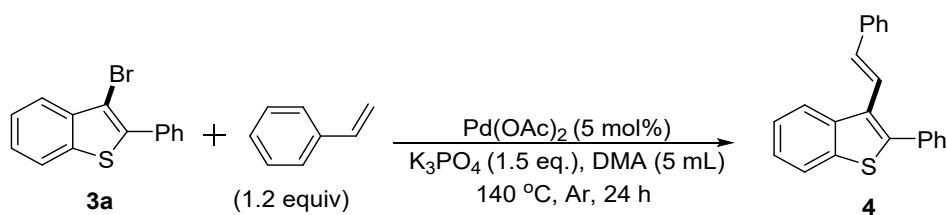


Figure S7. Light/dark experiments

2.4 Synthetic applications of **3a** and **3ag**

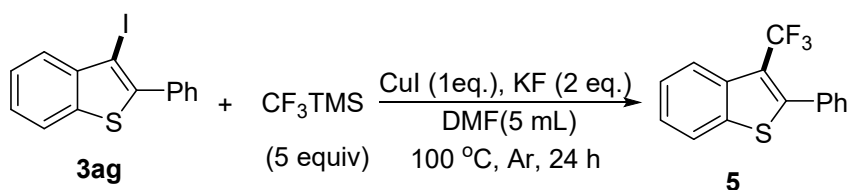
2.4.1 The coupling reaction of **3a** with styrene^[4]



3-Bromo-2-phenylbenzo[*b*]thiophene (**3a**, 289.2 mg, 1.0 mmol), styrene (125.0 mg, 1.2 mmol, 1.2 equiv), Pd(OAc)₂ (11.2 mg, 5 mol%), K₃PO₄ (318.4 mg, 1.5 mmol, 1.5 equiv) and DMA (5 mL) were added to a 20 mL oven-dried reaction vessel equipped with a magnetic stirrer bar. The reaction mixture was stirred vigorously at 140 °C for 24 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2*50 mL). The separated organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the

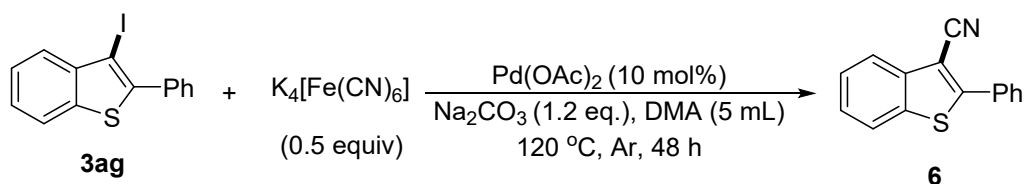
4 as a yellow solid (249.9 mg, 80% yield).

2.4.2 The trifluoromethylation of **3a** with CF_3TMS ^[5]



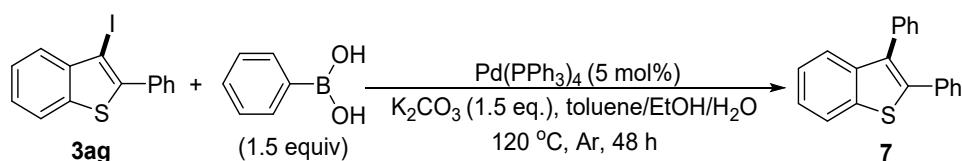
3-Iodo-2-phenylbenzo[*b*]thiophene (**3ag**, 336.2 mg, 1.0 mmol), CF_3TMS (711.0 mg, 5.0 mmol, 5 equiv), KF (116.2 mg, 2 mmol, 2 equiv), CuI (190.5 mg, 1.0 mmol, 1.0 equiv), DMF (5 mL), were added to a 30 mL oven-dried reaction vessel equipped with a magnetic stirrer bar. The reaction mixture was stirred vigorously at 100 °C for 24 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2*50 mL). The separated organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the **5** as a white solid (264.4 mg, 95% yield).

2.4.3 The cyanidation of **3a** with $\text{K}_4[\text{Fe}(\text{CN})_6]$ ^[6]



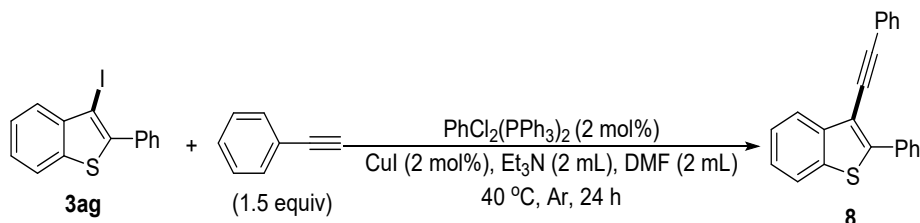
3-Iodo-2-phenylbenzo[*b*]thiophene (**3ag**, 336.2 mg, 1.0 mmol), $\text{K}_4[\text{Fe}(\text{CN})_6]$ (184.2 mg, 0.5 mmol, 0.5 equiv), Na_2CO_3 (127.2 mg, 1.2 mmol, 1.2 equiv), $\text{Pd}(\text{OAc})_2$ (22.5 mg, 0.1 mmol, 10 mol%), DMA (5 mL), were added to a 30 mL oven-dried reaction vessel equipped with a magnetic stirrer bar. The reaction mixture was stirred vigorously at 120 °C for 48 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2*50 mL). The separated organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using 2% ethyl acetate/petroleum ether as the eluent to afford the **6** as a white solid (197.7 mg, 84% yield).

2.4.4 The coupling reaction of **3ag** with phenylboronic acid^[1]



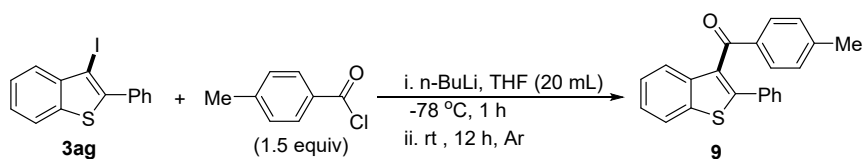
3-Iodo-2-phenylbenzo[*b*]thiophene (**3ag**, 336.2 mg, 1.0 mmol), PhB(OH)₂ (182.9 mg, 1.5 mmol, 1.5 equiv), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol, 5 mol%), K₂CO₃ (207.3 mg, 1.5 mmol, 1.5 equiv), toluene (10 mL), ethyl alcohol (2 mL) and H₂O (0.5 mL), were added to a 50 mL oven-dried reaction vessel equipped with a magnetic stirrer bar. The reaction mixture was stirred vigorously at 80 °C for 12 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2*50 mL). The separated organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the **7** as a white solid (260.6 mg, 91% yield).

2.4.5 The coupling reaction of **3ag** with phenylacetylene^[1]



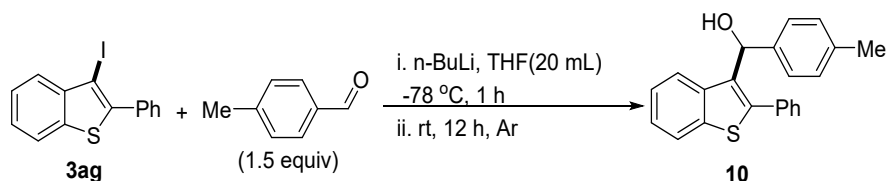
3-Iodo-2-phenylbenzo[*b*]thiophene (**3ag**, 336.2 mg, 1.0 mmol), ethynylbenzene (153.2 mg, 1.5 mmol, 1.5 equiv), PdCl₂(PPh₃)₂ (35.1 mg, 2 mol%), CuI (3.8 mg, 2 mol%), Et₃N (2 mL), DMF (2 mL), were added to a 30 mL oven-dried reaction vessel equipped with a magnetic stirrer bar. The reaction mixture was stirred vigorously at 40 °C for 24 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2*50 mL). The separated organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the **8** as a white solid (260.7 mg, 84% yield).

2.4.6 The coupling reaction of **3ag** with 4-chlorobenzoyl chloride^[7]



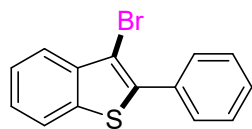
3-Iodo-2-phenylbenzo[*b*]thiophene (**3ag**, 336.2 mg, 1.0 mmol) and 4-methylbenzoyl chloride (231.9 mg, 1.5 mmol, 1.5 equiv) was dissolved in dry THF (20 mL) under an Ar atmosphere and cooled to -78 °C for 0.5 h. Then, 2.0 equiv of *n*-BuLi (2.0 M solution in cyclohexane, 2.0 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction was stirred at -78 °C for 1 h. the reaction mixture was stirred at this temperature under an Ar atmosphere before being allowed to warm to room temperature for 12 h. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using 5% ethyl acetate/petroleum ether as the eluent to afford the **9** as a white solid (239.8 mg, 73% yield).

2.4.7 The coupling reaction of **3ag** with with 4-chlorobenzaldehyde^[7]

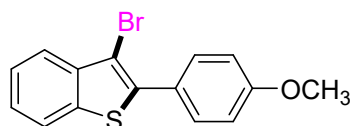


The **3ag** (336.2 mg, 1.0 mmol) and 4-methylbenzaldehyde (180.2 mg, 1.5 mmol, 1.5 equiv) was dissolved in dry THF (20 mL) under an Ar atmosphere and cooled to -78 °C for 0.5 h. Then, 2.0 equiv of *n*-BuLi (2.0 M solution in cyclohexane, 2.0 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction was stirred for 1 h at -78 °C. the reaction mixture was stirred further at this temperature under an Ar atmosphere before being allowed to warm to room temperature for 12 h. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using 10% ethyl acetate/petroleum ether as the eluent to afford the **10** as a yellow oil (224.7 mg, 68% yield).

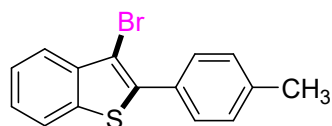
3. Characterization data for the products



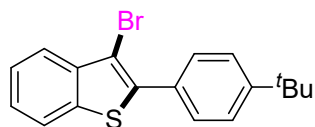
3-Bromo-2-phenylbenzo[*b*]thiophene (3a)⁸. White solid; mp 62-64 °C; 95% yield (68.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.83 (d, *J* = 7.8 Hz, 1H), 7.74–7.72 (m, 3H), 7.43–7.40 (m, 3H), 7.38–7.36 (m, 1H), 7.35–7.32 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.1, 138.2, 137.6, 133.0, 129.6, 128.7, 128.5, 125.4, 125.2, 123.6, 122.1, 104.9.



3-Bromo-2-(4-methoxyphenyl)benzo[*b*]thiophene (3b)⁸. White solid; mp 86-88 °C; 92% yield (73.4 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.48–7.46 (m, 1H), 7.40–7.38 (m, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 160.0, 139.2, 138.2, 137.4, 130.9, 125.4, 125.2, 125.1, 123.4, 122.1, 114.0, 104.2, 55.4.

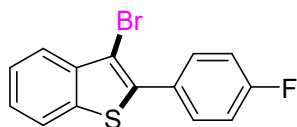


3-Bromo-2-(*p*-tolyl)benzo[*b*]thiophene (3c)⁸. White solid; mp 62-64 °C; 96% yield (72.8 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.51–7.48 (m, 1H), 7.43–7.40 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.2, 138.8, 138.4, 137.6, 130.1, 129.4, 129.3, 125.3, 125.1, 123.5, 122.1, 104.5, 21.3.

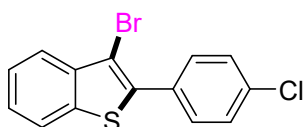


3-Bromo-2-(4-(*tert*-butyl)phenyl)benzo[*b*]thiophene (3d). White solid; mp 57-58 °C; 90% yield (77.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.51–7.48 (m,

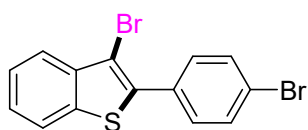
1H), 7.43–7.40 (m, 1H), 1.42 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 151.9, 139.2, 138.3, 137.6, 130.1, 129.2, 125.6, 125.3, 125.1, 123.5, 122.1, 104.4, 34.7, 31.2; IR (cm⁻¹): 2953, 1624, 1434, 1381, 1357, 1246, 1107, 1065, 1017, 893, 830, 785, 753, 719; HRMS (ESI) m/z: [M+H]⁺ Calcd For C₁₈H₁₈BrS⁺ 345.0307; Found 345.0309.



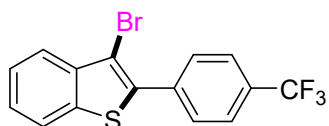
3-Bromo-2-(4-fluorophenyl)benzo[b]thiophene (3e)⁸. White solid; mp 63-65 °C; 93% yield (71.4 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.87 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.75–7.72 (m, 2H), 7.50–7.48 (m, 1H), 7.43–7.41 (m, 1H), 7.18 (t, *J* = 8.4 Hz, 2H); ¹⁹F NMR (564 MHz, CDCl₃): δ = -112.04; ¹³C NMR (150 MHz, CDCl₃): δ = 162.9 (d, *J* = 250.0 Hz), 139.0, 137.6, 137.1, 131.5 (d, *J* = 8.4 Hz), 129.1 (d, *J* = 3.2 Hz), 125.6, 125.3, 123.7, 122.2, 115.6 (d, *J* = 21.8 Hz), 105.2.



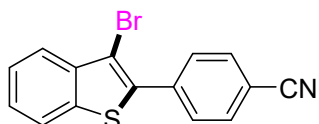
3-Bromo-2-(4-chlorophenyl)benzo[b]thiophene (3f)⁸. White solid; mp 78-80 °C; 94% yield (76.1 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.88 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.50–7.48 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.44–7.41 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.0, 137.6, 136.8, 134.9, 131.5, 130.9, 128.9, 125.7, 125.4, 123.7, 122.2, 105.4.



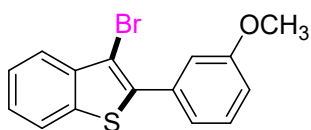
3-Bromo-2-(4-bromophenyl)benzo[b]thiophene (3g)⁸. White solid; mp 81-83 °C; 92% yield (84.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.62 (q, *J* = 8.4 Hz, 4H), 7.50–7.48 (m, 1H), 7.44–7.41 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.0, 137.6, 136.8, 132.0, 131.8, 131.1, 125.7, 125.4, 123.8, 123.2, 122.2, 105.4.



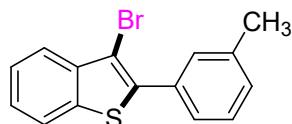
3-Bromo-2-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (3h). White solid; mp 78-79 °C; 85% yield (75.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.91–7.88 (m, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.52–7.50 (m, 1H), 7.46–7.44 (m, 1H); ¹⁹F NMR (564 MHz, CDCl₃): δ = -62.70; ¹³C NMR (150 MHz, CDCl₃): δ = 139.0, 137.8, 136.7, 136.3, 130.6 (q, *J* = 32.8 Hz), 130.0, 126.0, 125.6 (q, *J* = 4.1 Hz), 125.5, 124.0 (CF₃) (q, *J* = 272.4 Hz), 123.9, 122.3, 106.2; IR (cm⁻¹): 2929, 1635, 1434, 1406, 1378, 1322, 1243, 1163, 1114, 1062, 1010, 893, 840, 788, 753, 722, 670; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₅H₉BrF₃S⁺ 356.9555; Found 356.9555.



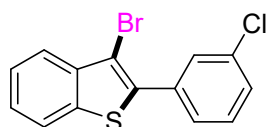
4-(3-Bromobenzo[b]thiophen-2-yl)benzonitrile (3i)⁸. White solid; mp 117-118 °C; 84% yield (66.0 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.91–7.88 (m, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.78–7.76 (m, 2H), 7.53–7.50 (m, 1H), 7.47–7.45 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.0, 137.9, 137.7, 135.7, 132.3, 130.2, 126.3, 125.6, 124.1, 122.3, 118.5, 112.2, 106.7; IR (cm⁻¹): 3106, 2918, 2230, 1635, 1594, 1493, 1454, 1420, 1357, 1232, 1163, 1083, 1024, 879, 837, 767, 743, 726, 698.



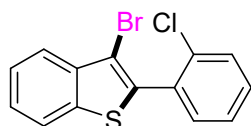
3-Bromo-2-(3-methoxyphenyl)benzo[b]thiophene (3j). Colorless oil; 94% yield (75.0 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.51–7.48 (m, 1H), 7.43–7.42 (m, 1H), 7.41–7.40 (m, 1H), 7.37–7.35 (m, 2H), 7.01–6.99 (m, 1H), 3.89 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 159.5, 139.1, 138.0, 137.6, 134.2, 129.6, 125.5, 125.2, 123.6, 122.1, 122.0, 115.1, 114.5, 105.0, 55.3; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₅H₁₂BrOS⁺ 318.9787; Found 318.9789.



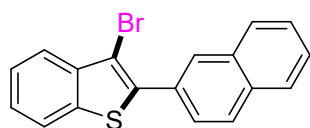
3-Bromo-2-(*m*-tolyl)benzo[*b*]thiophene (3k)⁸. Colorless oil; 92% yield (69.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.50–7.47 (m, 1H), 7.43–7.37 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 2.46 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.1, 138.4, 138.3, 137.6, 132.9, 130.2, 129.6, 128.5, 126.7, 125.4, 125.2, 123.6, 122.1, 104.8, 21.4.



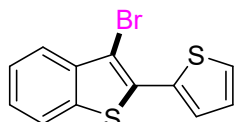
3-Bromo-2-(3-chlorophenyl)benzo[*b*]thiophene (3l). White solid; mp 77-79 °C; 95% yield (76.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 0.6 Hz, 1H), 7.66–7.63 (m, 1H), 7.51–7.48 (m, 1H), 7.44–7.43 (m, 1H), 7.42–7.41 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.0, 137.7, 136.4, 134.8, 134.5, 129.8, 129.5, 128.8, 127.8, 125.8, 125.4, 123.8, 122.2, 105.7; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₄H₉BrClS⁺ 322.9291; Found 322.9293.



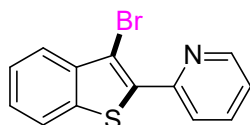
3-Bromo-2-(2-chlorophenyl)benzo[*b*]thiophene (3m). Colorless oil; 95% yield (76.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53–7.51 (m, 1H), 7.49 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.47–7.44 (m, 1H), 7.43 (td, *J* = 7.8, 1.8 Hz, 1H), 7.38 (td, *J* = 7.2, 1.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 138.5, 137.9, 135.5, 134.5, 132.6, 132.0, 130.5, 129.9, 126.6, 125.7, 125.2, 123.6, 122.2, 108.6; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₄H₉BrClS⁺ 322.9291; Found 322.9293.



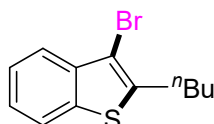
3-Bromo-2-(naphthalen-2-yl)benzo[*b*]thiophene (3n)⁸. White solid; mp 82-84 °C; 86% yield (72.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.26 (s, 1H), 7.96–7.92 (m, 3H), 7.91–7.89 (m, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 2H), 7.53–7.50 (m, 1H), 7.45–7.42 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.2, 138.3, 137.8, 133.1 (133.10, 133.07), 130.5, 129.2, 128.3, 128.2, 127.8, 126.9, 126.8, 126.6, 125.5, 125.3, 123.7, 122.2, 105.2.



3-Bromo-2-(thiophen-2-yl)benzo[*b*]thiophene (3o)¹¹. White solid; mp 102-104 °C; 90% yield (66.4 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61–7.60 (m, 1H), 7.47–7.44 (m, 2H), 7.40–7.37 (m, 1H), 7.15 (dd, *J* = 4.8, 3.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.2, 136.7, 134.6, 132.1, 127.9, 127.2, 127.1, 125.7, 125.3, 123.4, 121.9, 104.8.

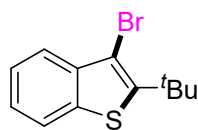


2-(3-Bromobenzo[*b*]thiophen-2-yl)pyridine (3p). White solid; mp 102-104 °C; 85% yield (61.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.65 (d, *J* = 4.8 Hz, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.43–7.40 (m, 1H), 7.39–7.36 (m, 1H), 7.22 (dd, *J* = 7.8, 4.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 151.3, 149.5, 139.6, 139.1, 138.2, 136.3, 126.0, 125.0, 123.8, 123.0, 122.3, 122.2, 105.1; IR (cm⁻¹): 3050, 2918, 1656, 1635, 1576, 1520, 1461, 1423, 1246, 1149, 989, 878, 809, 774, 753, 733, 677; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₃H₉BrNS⁺ 289.9634; Found 289.9636.

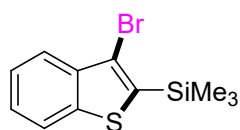


3-Bromo-2-butylbenzo[*b*]thiophene (3q)⁹. Colorless oil; 92% yield (61.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.76–7.74 (m, 2H), 7.44–7.41 (m, 1H), 7.35–7.32 (m, 1H), 2.97 (t, *J* = 7.8 Hz, 2H), 1.76–1.71 (m, 2H), 1.48–1.44 (m, 2H), 0.98 (t, *J* = 7.2

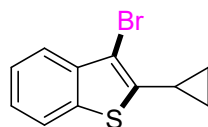
Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 140.9, 138.4, 137.1, 124.8, 124.6, 122.6, 122.2, 105.7, 32.4, 29.6, 22.2, 13.8$.



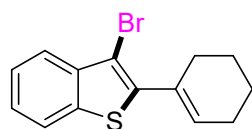
3-Bromo-2-(*tert*-butyl)benzo[*b*]thiophene (3r)⁸. Colorless oil; 90% yield (60.6 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.81$ (d, $J = 7.8$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.41 (m, 1H), 7.36 – 7.33 (m, 1H), 1.61 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 148.8, 139.9, 135.4, 124.8, 124.6, 122.5, 121.8, 102.7, 35.5, 29.9$.



(3-Bromobenzo[*b*]thiophen-2-yl)trimethylsilane (3s)⁹. Colorless oil; 87% yield (62.0 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.89$ (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.48 – 7.46 (m, 1H), 7.42 – 7.39 (m, 1H), 0.53 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 141.3, 139.8, 136.0, 125.1, 124.8, 122.9, 122.1, 114.7, -0.8$.

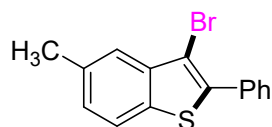


3-Bromo-2-cyclopropylbenzo[*b*]thiophene (3t)¹⁰. Colorless oil; 94% yield (59.5 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.72$ (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.42 – 7.40 (m, 1H), 7.32 – 7.30 (m, 1H), 2.39 – 2.34 (m, 1H), 1.19 – 1.15 (m, 2H), 0.90 – 0.87 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 143.5, 138.8, 135.6, 124.9, 124.6, 122.3, 122.1, 106.2, 11.9, 10.1$.

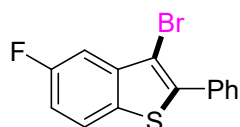


3-Bromo-2-(cyclohex-1-en-1-yl)benzo[*b*]thiophene (3u)⁹. Colorless oil; 60% yield (44.0 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.80$ (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.42 (m, 1H), 7.36 – 7.34 (m, 1H), 6.34 – 6.33 (m, 1H), 2.55 – 2.53 (m, 2H), 2.29 – 2.26 (m, 2H), 1.84 – 1.80 (m, 2H), 1.74 – 1.70 (m, 2H); ^{13}C NMR (150 MHz,

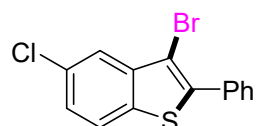
CDCl₃): δ = 141.1, 139.0, 136.6, 132.1, 130.7, 124.9 (2), 123.1, 122.0, 103.1, 29.4, 25.7, 22.8, 21.7.



3-Bromo-5-methyl-2-phenylbenzo[b]thiophene (3v). White solid; mp 71-73 °C; 97% yield (73.5 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.74–7.73 (m, 2H), 7.66–7.64 (m, 2H), 7.46–7.43 (m, 2H), 7.40–7.38 (m, 1H), 6.21–6.19 (m, 1H), 2.50 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 139.3, 138.3, 135.1, 134.8, 133.2, 129.6, 128.7, 128.5, 127.2, 123.5, 121.8, 104.5, 21.5; IR (cm⁻¹): 3064, 2911, 2852, 1951, 1871, 1732, 1652, 1600, 1482, 1444, 1294, 1246, 1284, 1243, 1149, 1069, 1031, 923, 871, 820, 795, 736, 684; HRMS (ESI) m/z: [M+H]⁺ HRMS (ESI) m/z: [M+H]⁺ Calcd For C₁₅H₁₂BrS⁺ 302.9838; Found 302.9840.

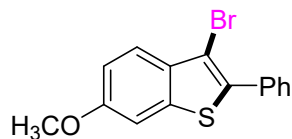


3-Bromo-5-fluoro-2-phenylbenzo[b]thiophene (3w). White solid; mp 65-66 °C; 96% yield (73.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.77–7.75 (m, 2H), 7.73 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.57 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.51–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.16 (td, *J* = 9.0, 2.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 161.4 (d, *J* = 243 Hz), 140.8, 140.5 (d, *J* = 9.8 Hz), 133.0, 132.7, 129.5, 129.0, 128.6, 123.5 (d, *J* = 9.0 Hz), 114.3 (d, *J* = 25.2 Hz), 190.4 (d, *J* = 24.4 Hz), 104.2 (d, *J* = 4.4 Hz); IR (cm⁻¹): 3023, 2924, 2848, 1653, 1631, 1602, 1560, 1438, 1278, 1166, 987, 856, 836, 795, 743, 686; HRMS (ESI) m/z: [M+H]⁺ Calcd For C₁₄H₉BrFS⁺ 306.9587; Found 306.9587.

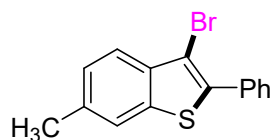


3-Bromo-5-chloro-2-phenylbenzo[b]thiophene (3x)¹². White solid; mp 101-103 °C; 94% yield (76.1 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.86 (d, *J* = 1.8 Hz, 1H), 7.76–7.74 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.51–7.48 (m, 2H), 7.47–7.44 (m, 1H),

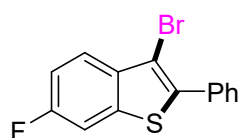
7.37 (dd, $J = 8.4, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 140.4, 140.3, 135.8, 132.6, 131.7, 129.5, 129.1, 128.7, 125.9, 123.3, 123.2, 104.0$.



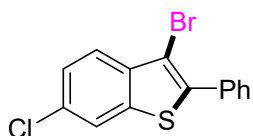
3-Bromo-6-methoxy-2-phenylbenzo[*b*]thiophene (3y)¹³. White solid; mp 97-99 °C; 95% yield (75.8 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.77\text{--}7.75$ (m, 3H), 7.49–7.47 (m, 2H), 7.43–7.40 (m, 1H), 7.29 (d, $J = 2.4$ Hz, 1H), 7.10 (dd, $J = 9.0, 2.4$ Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 158.3, 138.9, 135.3, 133.2, 129.5, 128.52, 128.45, 124.3, 115.2, 104.6, 104.3, 55.7$.



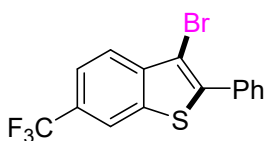
3-Bromo-6-methyl-2-phenylbenzo[*b*]thiophene (3z)¹⁰. Colorless oil; 94% yield (71.3 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.79$ (s, 1H), 7.78–7.76 (m, 2H), 7.61 (s, 1H), 7.51–7.48 (m, 2H), 7.45–7.42 (m, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 137.8, 137.0, 136.9, 135.6, 133.2, 129.5, 128.6, 128.5, 126.9, 123.2, 121.9, 104.6, 21.5$.



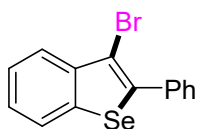
3-Bromo-6-fluoro-2-phenylbenzo[*b*]thiophene (3aa). White solid; mp 60-61 °C; 95% yield (73.0 mg). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.82$ (dd, $J = 9.0, 4.8$ Hz, 1H), 7.76–7.75 (m, 2H), 7.52–7.48 (m, 3H), 7.46–7.44 (m, 1H), 7.23 (td, $J = 9.0, 2.4$ Hz, 1H); ^{19}F NMR (564 MHz, CDCl_3): $\delta = -115.63$; ^{13}C NMR (150 MHz, CDCl_3): $\delta = 161.1$ (d, $J = 246$ Hz), 138.4 (d, $J = 10.5$ Hz), 137.8 (d, $J = 3.6$ Hz), 135.6, 132.8, 129.5, 128.8, 128.6, 124.9 (d, $J = 9.4$ Hz), 114.2 (d, $J = 24.6$ Hz), 108.3 (d, $J = 25.7$ Hz), 104.3; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd For $\text{C}_{14}\text{H}_9\text{BrFS}^+$ 306.9587; Found 306.9584.



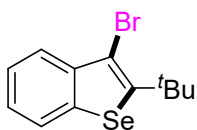
3-Bromo-6-chloro-2-phenylbenzo[*b*]thiophene (3ab). White solid; mp 107-109 °C; 91% yield (73.6 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.80 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.76–7.75 (m, 1H), 7.74–7.73 (m, 1H), 7.50–7.48 (m, 2H), 7.46–7.43 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 138.7, 138.5, 137.7, 132.6, 131.6, 129.5, 129.0, 128.7, 126.1, 124.5, 121.7, 104.5; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₄H₉BrClS⁺ 322.9291; Found 322.9289.



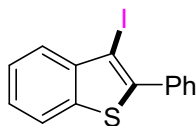
3-Bromo-2-phenyl-6-(trifluoromethyl)benzo[*b*]thiophene (3ac). White solid; mp 80-82 °C; 93% yield (83.0 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.17 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.78–7.77 (m, 2H), 7.64–7.63 (m, 1H), 7.53–7.46 (m, 3H); ¹⁹F NMR (564 MHz, CDCl₃): δ = -61.56; ¹³C NMR (150 MHz, CDCl₃): δ = 140.8, 140.5, 139.0, 132.3, 129.6, 129.2, 128.7, 127.9 (q, *J* = 32.3 Hz), 125.3, 124.4 (q, *J* = 272.0 Hz), 122.8, 121.6 (q, *J* = 3.3 Hz), 120.9 (q, *J* = 4.0 Hz), 105.1; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₅H₉BrF₃S⁺ 356.9555; Found 356.9557.



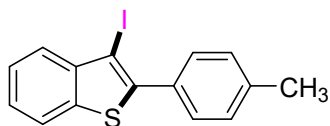
3-Bromo-2-phenylbenzo[*b*]selenophene (3ad)¹⁴. White solid; mp 91-93 °C; 91% yield (76.5 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.99–7.98 (m, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.74–7.72 (m, 2H), 7.53–7.48 (m, 3H), 7.46–7.43 (m, 1H), 7.39–7.37 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 140.9, 140.7, 138.9, 134.9, 129.8, 128.6, 128.5, 126.1, 125.7, 125.5, 125.1, 106.6.



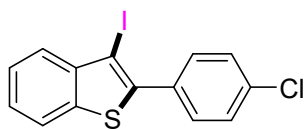
3-Bromo-2-(*tert*-butyl)benzo[*b*]selenophene (3ae). White solid; mp 82-84 °C; 80% yield (63.2 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.89 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.45–7.42 (m, 1H), 7.32–7.29 (m, 1H), 1.62 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 153.2, 142.0, 136.3, 125.1, 124.9, 124.7, 104.1, 37.1, 30.3.



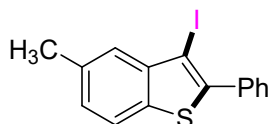
3-Iodo-2-phenylbenzo[*b*]thiophene (3ag)⁸. White solid; mp 54-56 °C; 97% yield (81.5 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.86 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.72–7.70 (m, 2H), 7.52–7.45 (m, 4H), 7.43–7.40 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 142.1, 141.9, 138.9, 134.6, 130.0, 128.9, 128.5, 126.3, 125.5, 125.4, 122.1, 79.4.



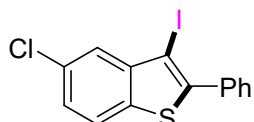
3-Iodo-2-(*p*-tolyl)benzo[*b*]thiophene (3ah)⁸. White solid; mp 97-99 °C; 97% yield (84.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.51–7.48 (m, 1H), 7.42–7.39 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 142.3, 141.9, 138.9, 138.8, 131.6, 129.8, 129.2, 126.1, 125.3 (125.35, 125.32), 122.0, 79.0, 21.4.



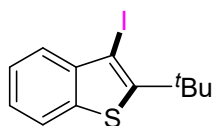
2-(4-Chlorophenyl)-3-iodobenzo[*b*]thiophene (3ai)⁸. White solid; mp 102-104 °C; 95% yield (88.0 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.84 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.50–7.45 (m, 3H), 7.43–7.40 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 141.8, 140.7, 138.8, 135.0, 133.0, 131.3, 128.8, 126.4, 125.7, 125.6, 122.1, 79.9.



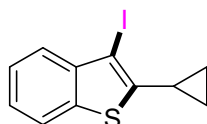
3-Iodo-5-methyl-2-phenylbenzo[*b*]thiophene (3aj). White solid; mp 101-103 °C; 96% yield (84.1 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.72–7.70 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.51–7.49 (m, 2H), 7.47–7.45 (m, 1H), 7.24 (dd, *J* = 7.8, 2.4 Hz, 1H), 2.57 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 142.2, 142.0, 136.0, 135.3, 134.7, 130.0, 128.8, 128.4, 127.2, 126.2, 121.8, 79.1, 21.5; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₅H₁₂IS⁺ 350.9699; Found 350.9699.



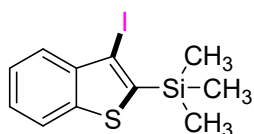
5-Chloro-3-iodo-2-phenylbenzo[*b*]thiophene (3ak). White solid; mp 101-102 °C; 94% yield (87.1 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.79 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68–7.67 (m, 2H), 7.51–7.46 (m, 3H), 7.43 (dd, *J* = 8.4, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 142.6, 140.5, 139.6, 134.1, 131.6, 129.9, 129.1, 128.6, 127.1, 126.2, 121.5, 78.6; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₄H₉ClISe⁺ 370.9153; Found 370.9157.



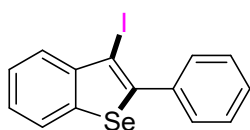
2-(*tert*-Butyl)-3-iodobenzo[*b*]thiophene (3al)⁸. White solid; mp 96-98 °C; 93% yield (73.5 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.85–7.82 (m, 1H), 7.75–7.73 (m, 1H), 7.45–7.41 (m, 1H), 7.36–7.32 (m, 1H), 1.67 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 151.7, 142.8, 136.1, 125.2, 125.0, 124.7, 121.6, 74.7, 35.8, 30.3.



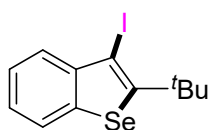
2-Cyclopropyl-3-iodobenzo[*b*]thiophene (3am)¹⁰. Colorless oil; 91% yield (68.3 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.73–7.70 (m, 2H), 7.44–7.41 (m, 1H), 7.33–7.31 (m, 1H), 2.38–2.33 (m, 1H), 1.22–1.19 (m, 2H), 0.94–0.92 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 147.2, 141.4, 136.2, 125.1, 124.6, 124.3, 122.2, 80.2, 15.0, 10.3.



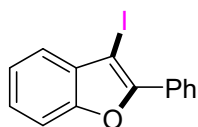
(3-Iodobenzo[*b*]thiophen-2-yl)trimethylsilane (3an)⁸. Colorless oil; 90% yield (74.8 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.87–7.84 (m, 2H), 7.48–7.46 (m, 1H), 7.41–7.38 (m, 1H), 0.56 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 142.9, 141.2, 140.6, 125.2, 125.1, 125.0, 121.8, 87.1, -0.7.



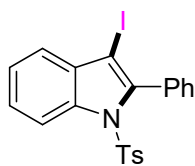
3-Iodo-2-phenylbenzo[*b*]selenophene (3ao)⁸. White solid; mp 112–115 °C; 95% yield (91.0 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.95 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.64–7.63 (m, 2H), 7.51–7.43 (m, 4H), 7.36–7.34 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 144.5, 143.6, 140.5, 136.9, 130.0, 128.9, 128.7, 128.4, 125.8, 125.7, 125.1, 82.7.



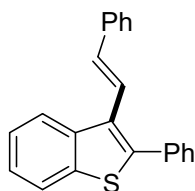
2-(*tert*-Butyl)-3-iodobenzo[*b*]selenophene (3ap). White solid; mp 108–110 °C; 90% yield (81.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.95 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.45–7.42 (m, 1H), 7.30–7.27 (m, 1H), 1.66 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 156.1, 144.9, 137.2, 125.8, 125.3, 125.0, 124.5, 77.5, 37.6, 30.7; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₁₂H₁₄ISE⁺ 364.9300; Found 364.9302.



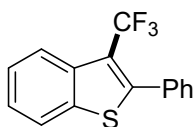
3-Iodo-2-phenylbenzofuran (3aq)¹⁰. Colorless oil; 78% yield (62.4 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.16–8.15 (m, 2H), 7.47–7.44 (m, 3H), 7.43–7.41 (m, 1H), 7.40–7.37 (m, 1H), 7.32 (td, *J* = 7.2, 1.2 Hz, 1H), 7.29–7.26 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 153.8, 153.0, 132.4, 129.4, 129.2, 128.5, 127.4, 125.6, 123.5, 121.8, 111.1, 61.1.



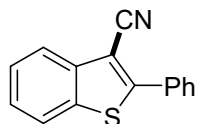
3-Iodo-2-phenyl-1-tosyl-1H-indole (3ar)¹⁶. White solid; mp 110-115 °C; 76% yield (86.0 mg, mixture of **3ar** and **3ar'**). ¹H NMR (600 MHz, CDCl₃): δ = 8.30 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.45–7.43 (m, 3H), 7.41 (d, *J* = 4.8 Hz, 1H), 7.36–7.35 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H) ; ¹³C NMR (150 MHz, CDCl₃): δ = 145.0, 141.0, 136.9, 135.0, 132.2, 131.7, 131.5, 129.4, 129.2, 127.4, 126.8, 126.0, 124.6, 122.1, 115.9, 75.8, 21.5.



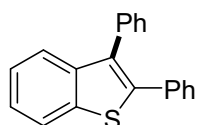
(E)-2-Phenyl-3-styrylbenzo[b]thiophene (4). White solid; mp 62-64 °C; 80% yield (249.9 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.09 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.39–7.36 (m, 3H), 7.33–7.28 (m, 4H), 7.21–7.18 (m, 2H), 7.12–7.09 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 140.8, 139.2, 139.0, 137.6, 134.5, 132.2, 129.9, 129.3, 128.7, 128.6, 128.1, 127.6, 126.3, 124.6, 124.5, 123.3, 122.3, 122.2; HRMS (ESI) *m/z*: [M+H]⁺ Calcd For C₂₂H₁₇S⁺ 313.1045; Found 313.1047.



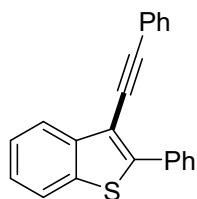
2-Phenyl-3-(trifluoromethyl)benzo[b]thiophene (5)⁸. Colorless oil; 95% yield (264.4 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.51–7.50 (m, 2H), 7.47–7.39 (m, 5H); ¹⁹F NMR (564 MHz, CDCl₃): δ = –54.85; ¹³C NMR (150 MHz, CDCl₃): δ = 147.6 (q, *J* = 3.6 Hz), 138.8, 136.5, 132.5, 129.7, 129.2, 128.2, 125.4, 125.2, 123.2 (q, *J* = 2.2 Hz), 122.8 (q, *J* = 272.5 Hz), 121.9, 120.4 (q, *J* = 33.4 Hz).



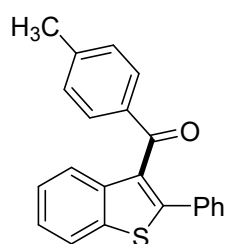
2-Phenylbenzo[*b*]thiophene-3-carbonitrile (6)¹⁸. White solid; mp 109-110 °C; 84% yield (197.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.96 (d, *J* = 7.8 Hz, 1H), 7.89–7.87 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.53–7.48 (m, 4H), 7.45–7.43 (m, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 155.0, 139.1, 137.3, 131.4, 130.4, 129.3, 128.2, 126.1(126.08, 126.06), 122.5, 122.3, 115.1, 102.0.



2,3-Diphenylbenzo[*b*]thiophene (7)¹⁹. White solid; mp 115-117 °C; 91% yield (260.6 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.86–7.85 (m, 1H), 7.59–7.58 (m, 1H), 7.39–7.37 (m, 2H), 7.35–7.30 (m, 7H), 7.23–7.21 (m, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 140.9, 139.5, 138.8, 135.5, 134.2, 133.2, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.3, 122.0.

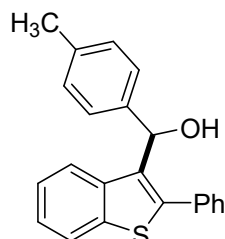


2-Phenyl-3-(phenylethynyl)benzo[*b*]thiophene (8)²⁰. White solid; mp 70-72 °C; 84% yield (260.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 8.12–8.10 (m, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.62–7.60 (m, 2H), 7.53–7.49 (m, 3H), 7.45–7.38 (m, 5H); ¹³C NMR (150 MHz, CDCl₃): δ = 146.2, 141.0, 137.5, 133.9, 131.5, 128.8, 128.7, 128.4, 128.3, 125.2, 124.9, 123.3 (123.34, 123.31), 122.1, 113.6, 94.6, 84.1.



(2-Phenylbenzo[*b*]thiophen-3-yl)(*p*-tolyl)methanone (9)¹⁵. White solid; mp 126-128

°C; 73% yield (239.8 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.87–7.85 (m, 1H), 7.69–7.66 (m, 3H), 7.44–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.23–7.20 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 194.0, 145.4, 144.3, 139.7, 138.9, 134.8, 133.3, 131.8, 130.0, 129.1 (129.14, 129.08), 128.7, 128.6, 125.0 (125.01, 124.96), 123.5, 121.9, 21.6.



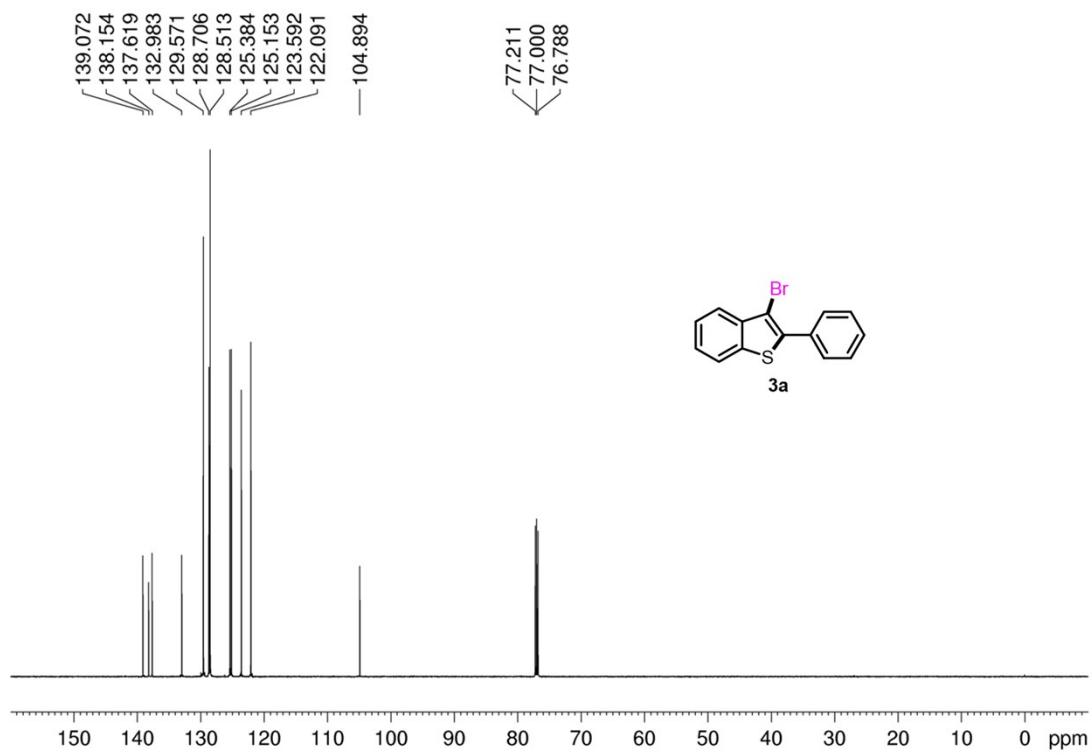
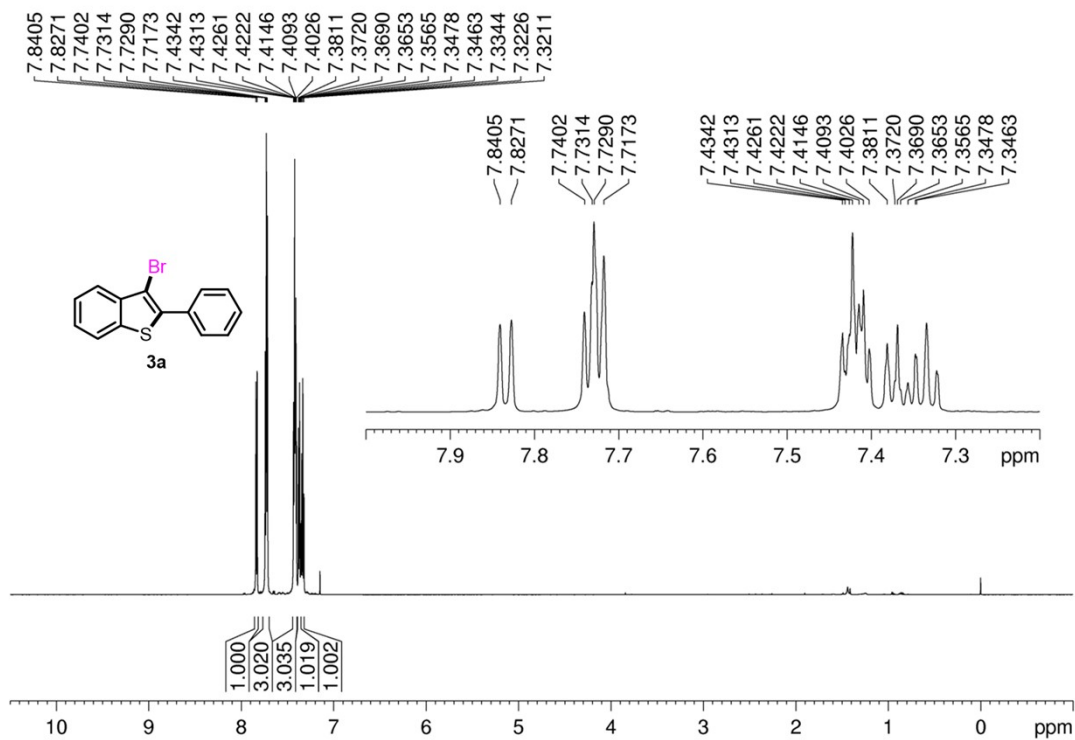
(2-Phenylbenzo[*b*]thiophen-3-yl)(*p*-tolyl)methanol (10). Yellow oil; 68% yield (224.7 mg). ¹H NMR (600 MHz, CDCl₃): δ = 7.77 (d, *J* = 7.8 Hz, 1H), 7.68–7.66 (m, 1H), 7.49–7.47 (m, 2H), 7.38–7.34 (m, 3H), 7.27–7.26 (m, 2H), 7.25–7.22 (m, 1H), 7.17–7.14 (m, 1H), 7.09–7.08 (m, 2H), 6.19 (s, 1H), 2.42 (br, 1H), 2.29 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 194.0, 145.4, 144.3, 139.7, 138.9, 134.8, 133.3, 131.8, 130.0, 129.1 (129.14, 129.08), 128.7, 128.6, 125.0 (125.01, 124.96), 123.5, 121.9, 21.6.

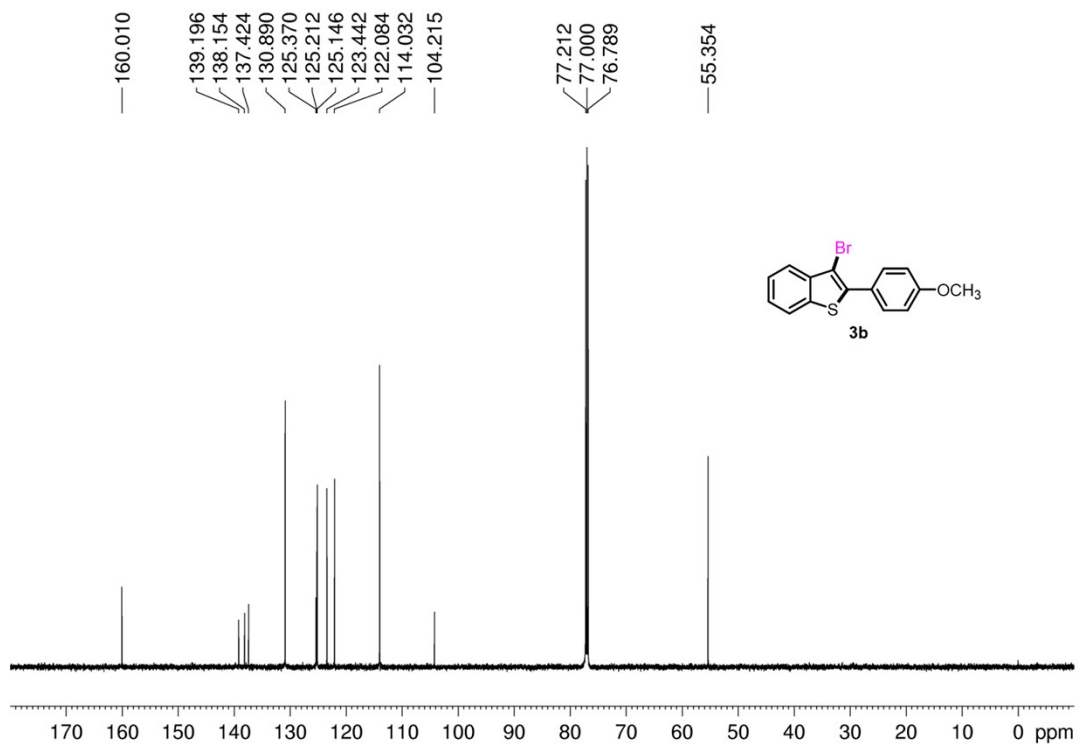
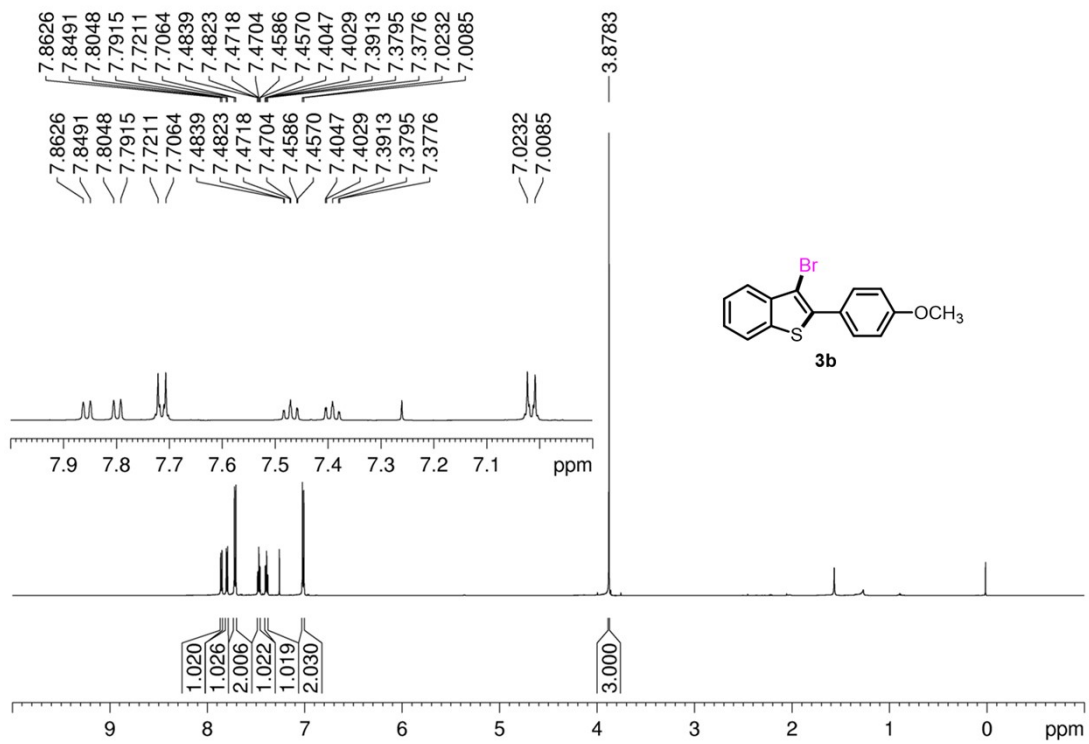
4. References

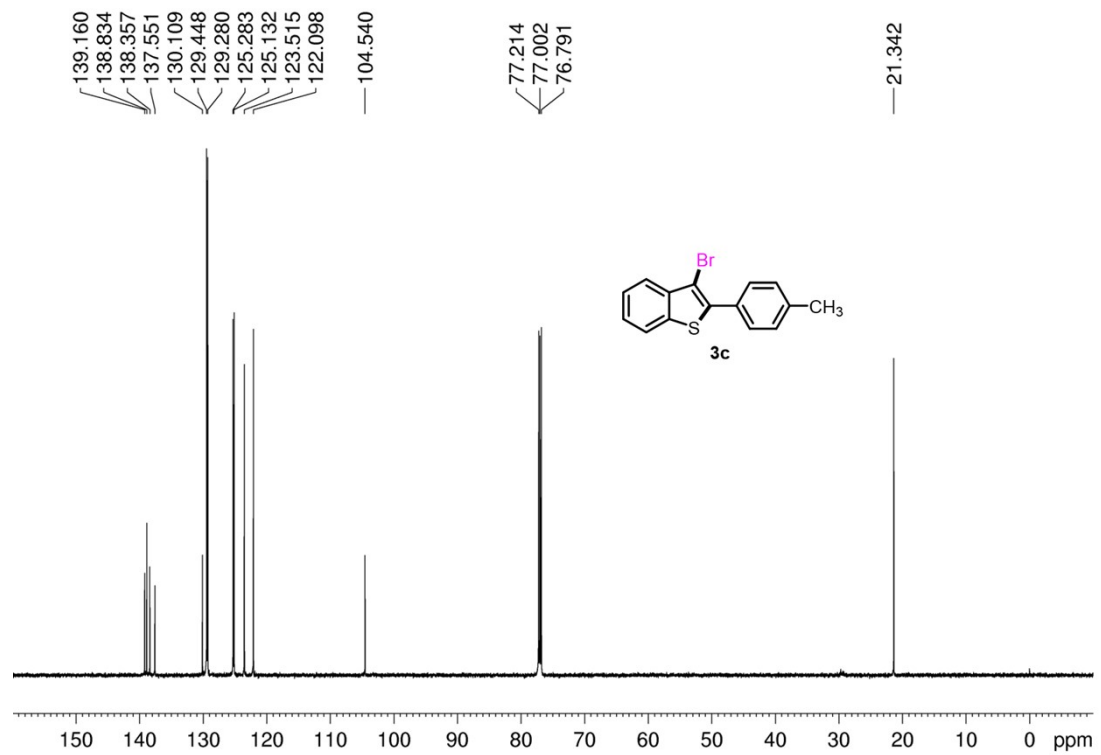
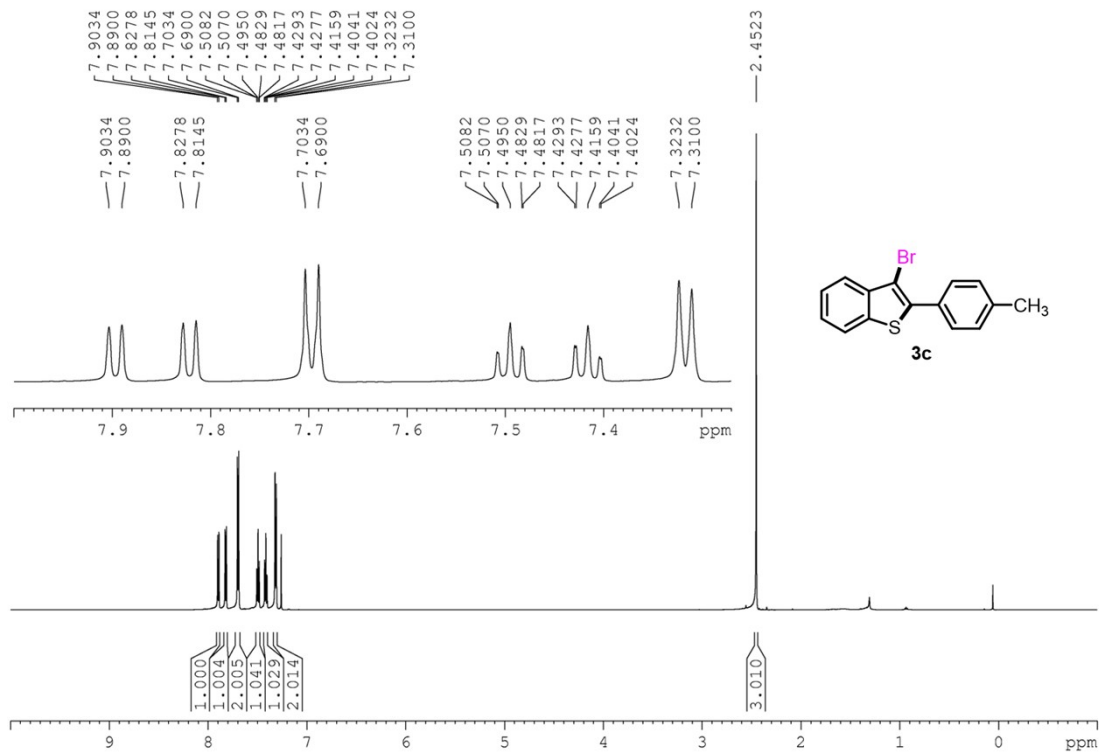
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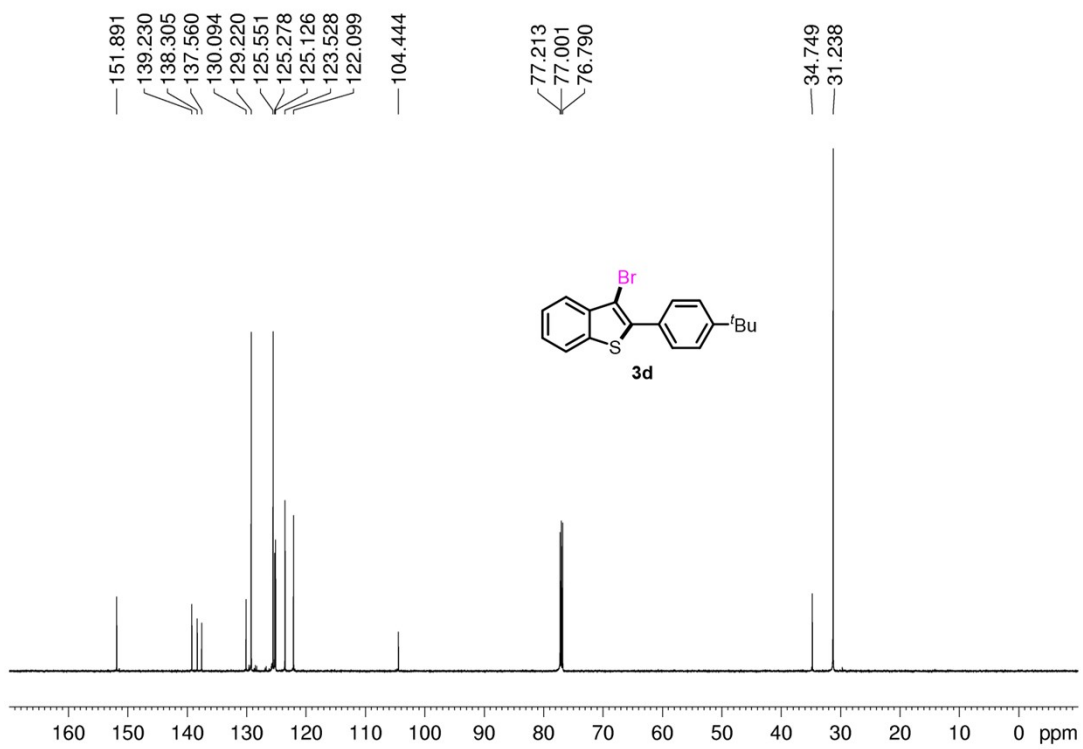
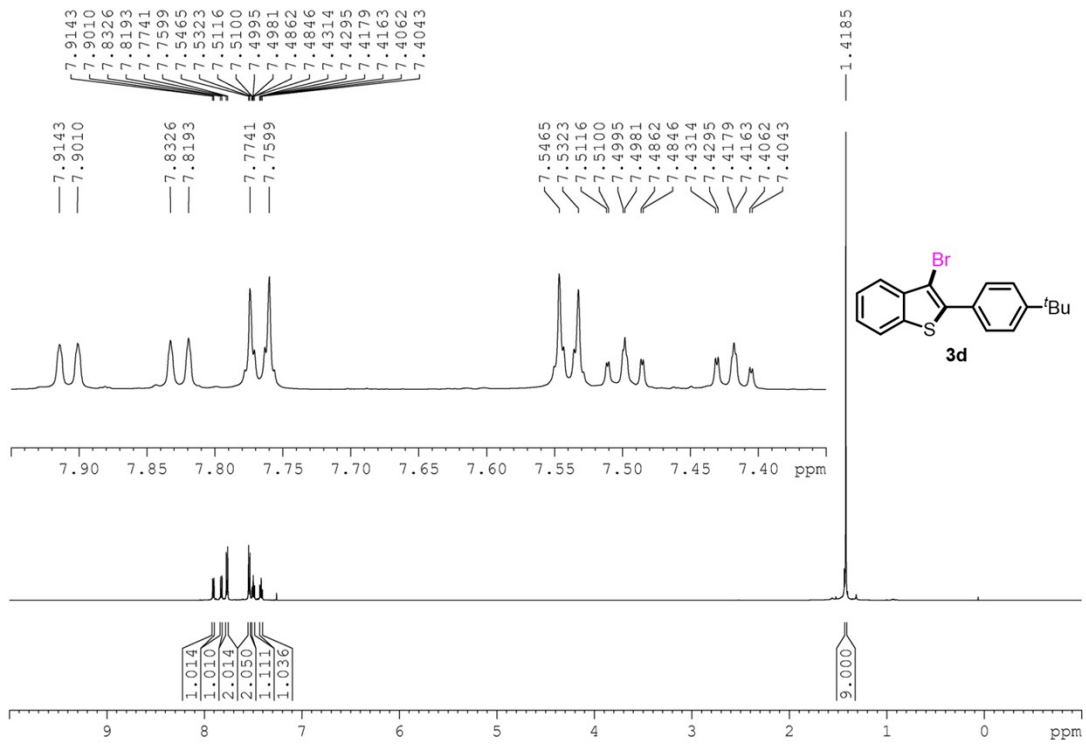
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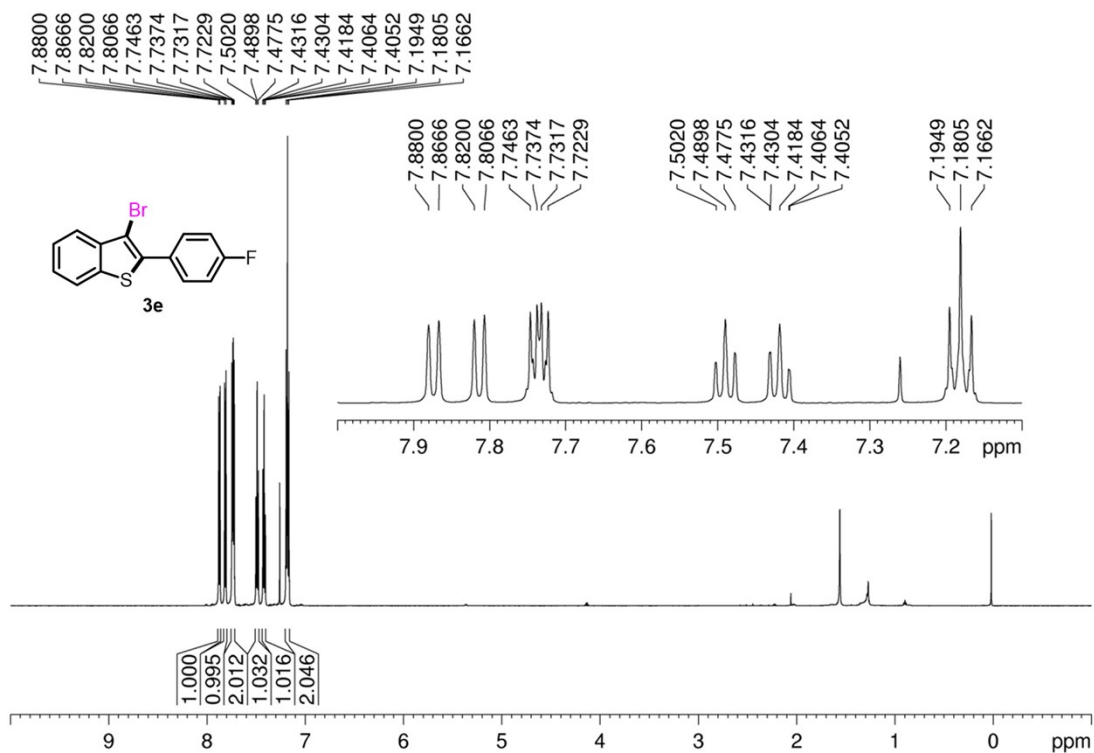
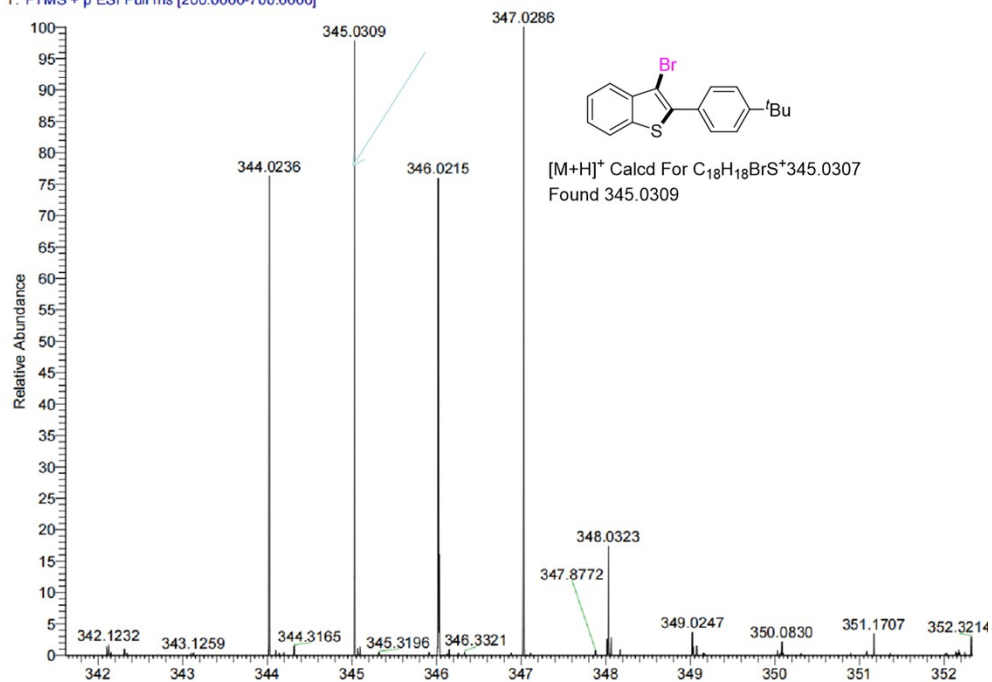
5. ^1H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectra of the products

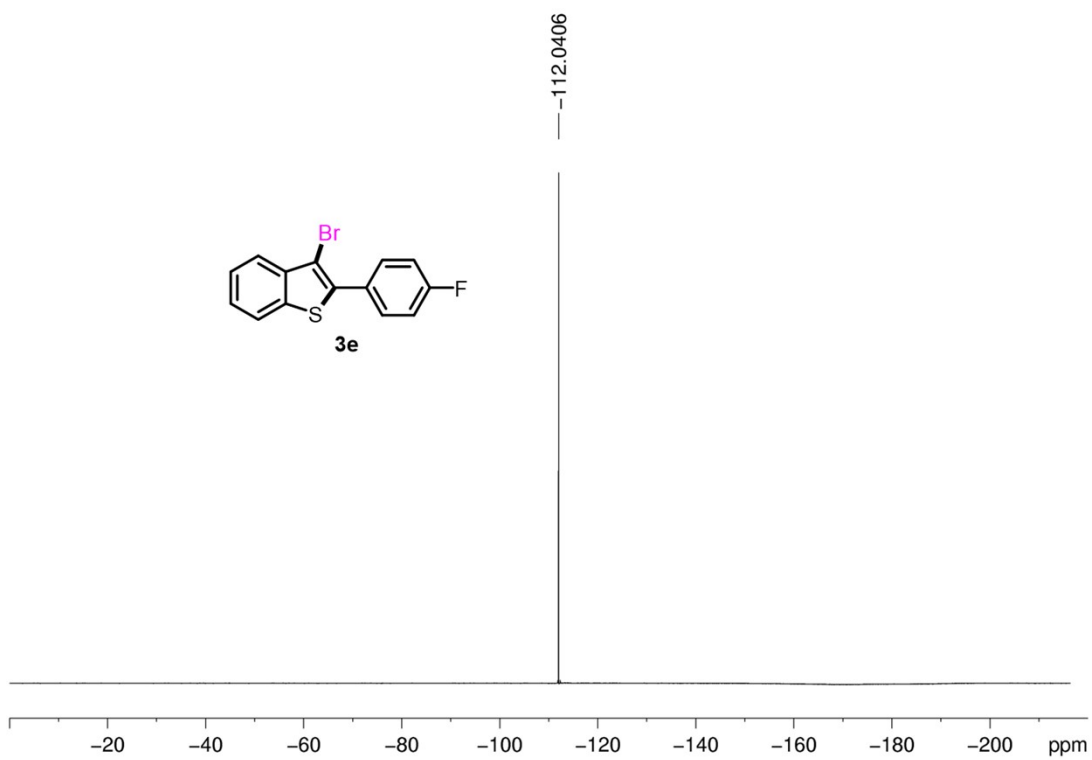
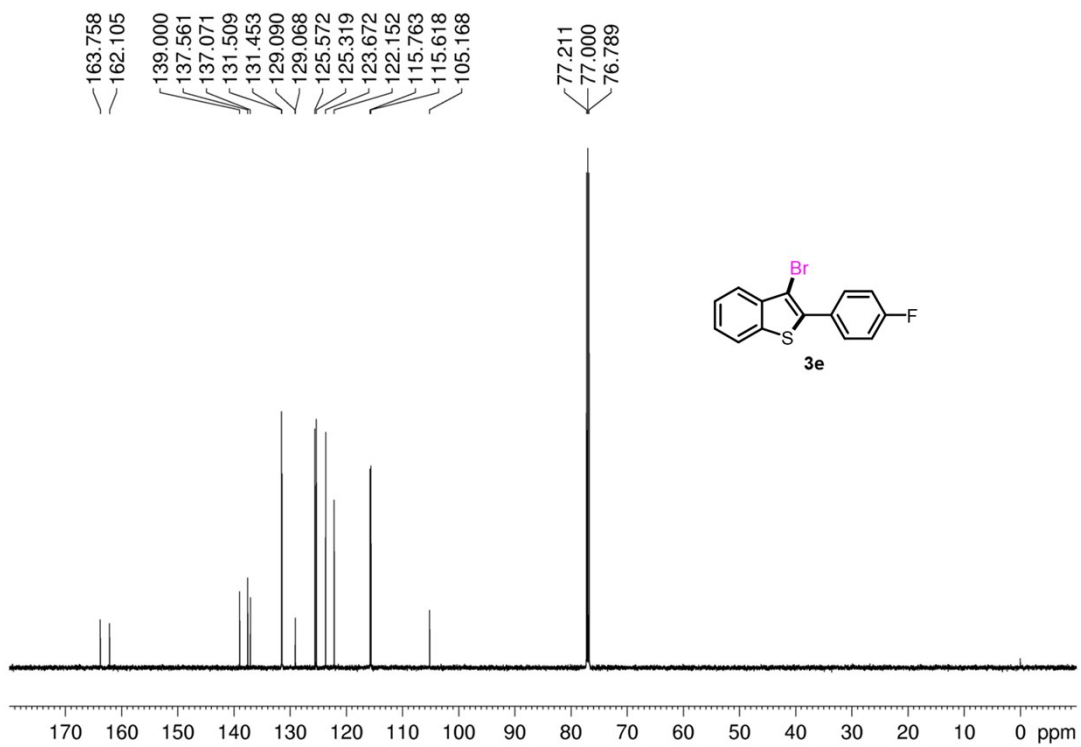


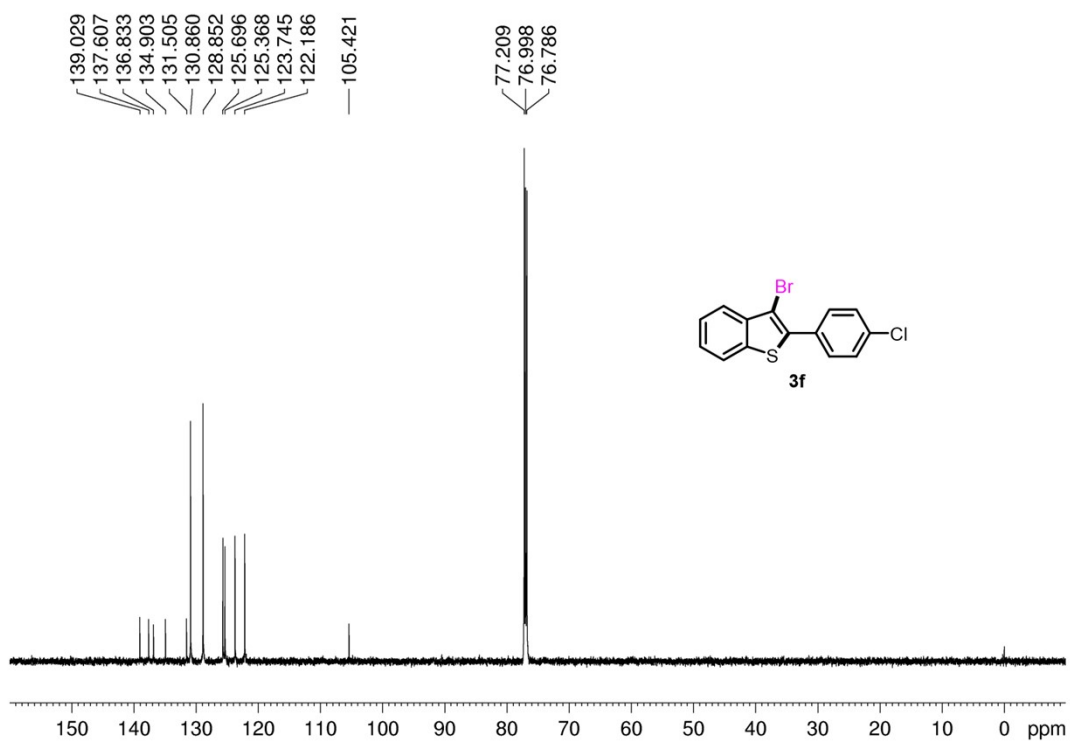
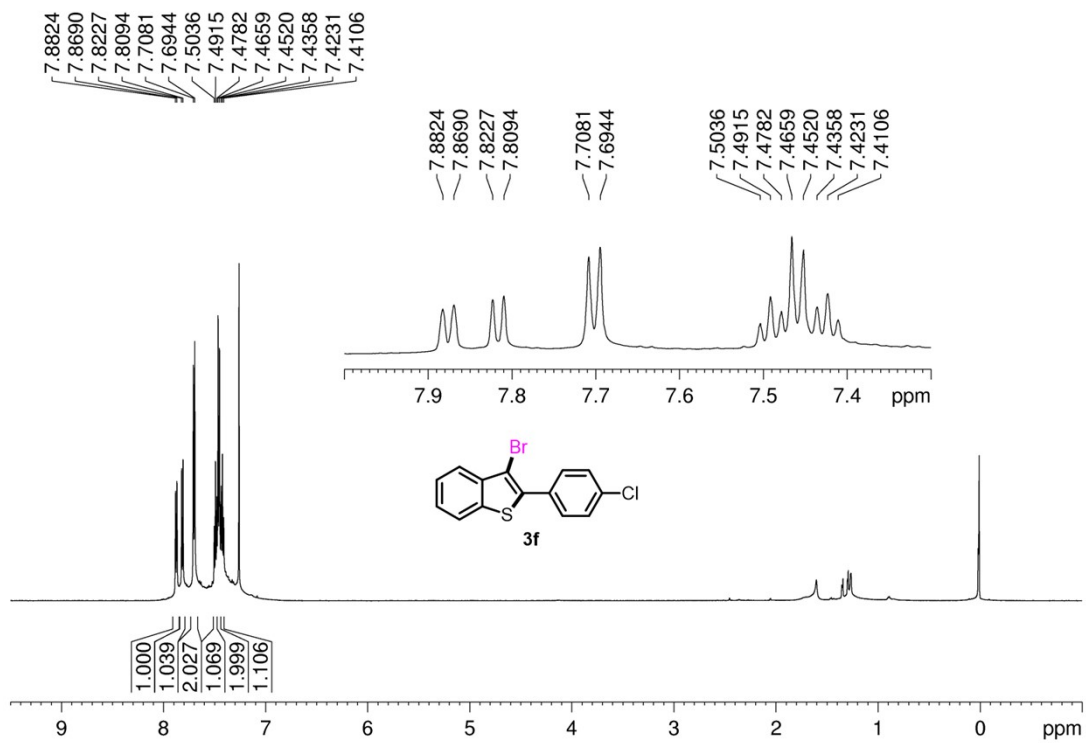


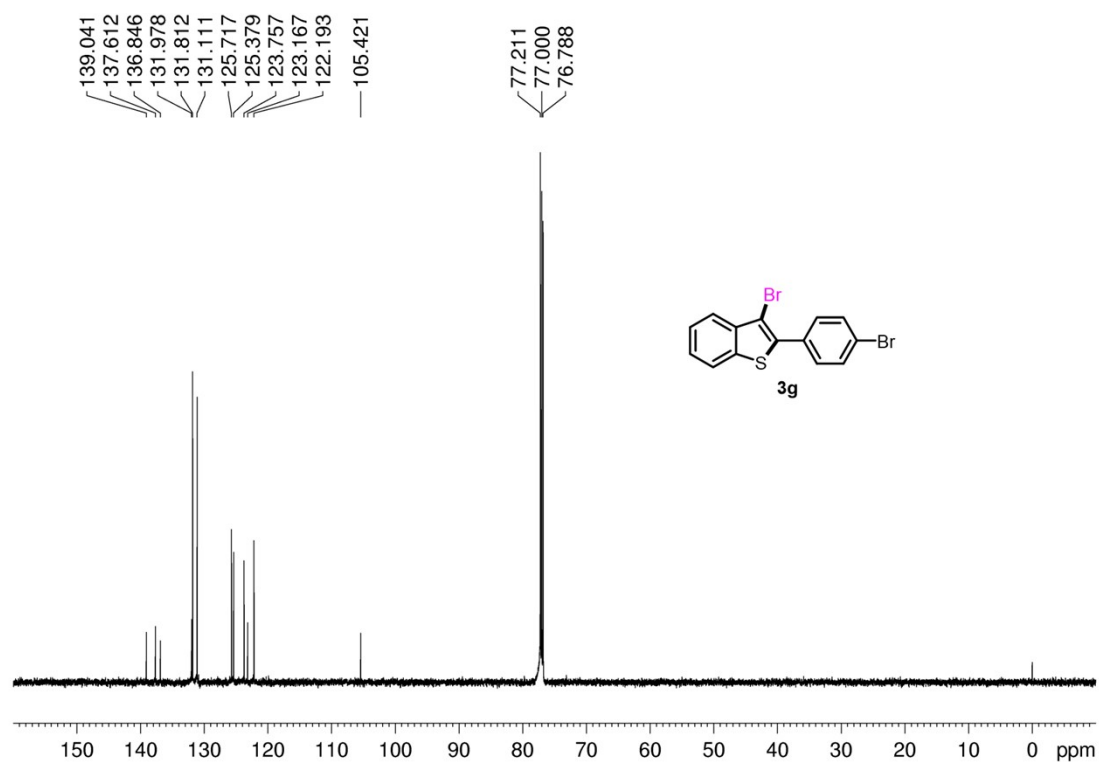
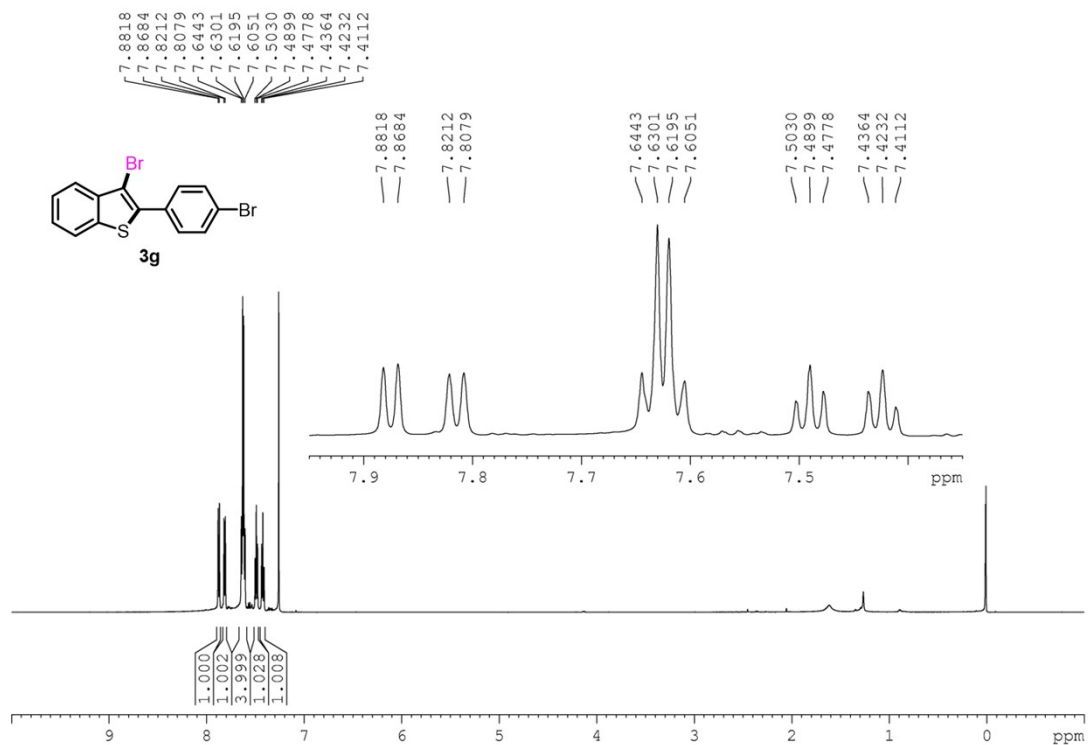


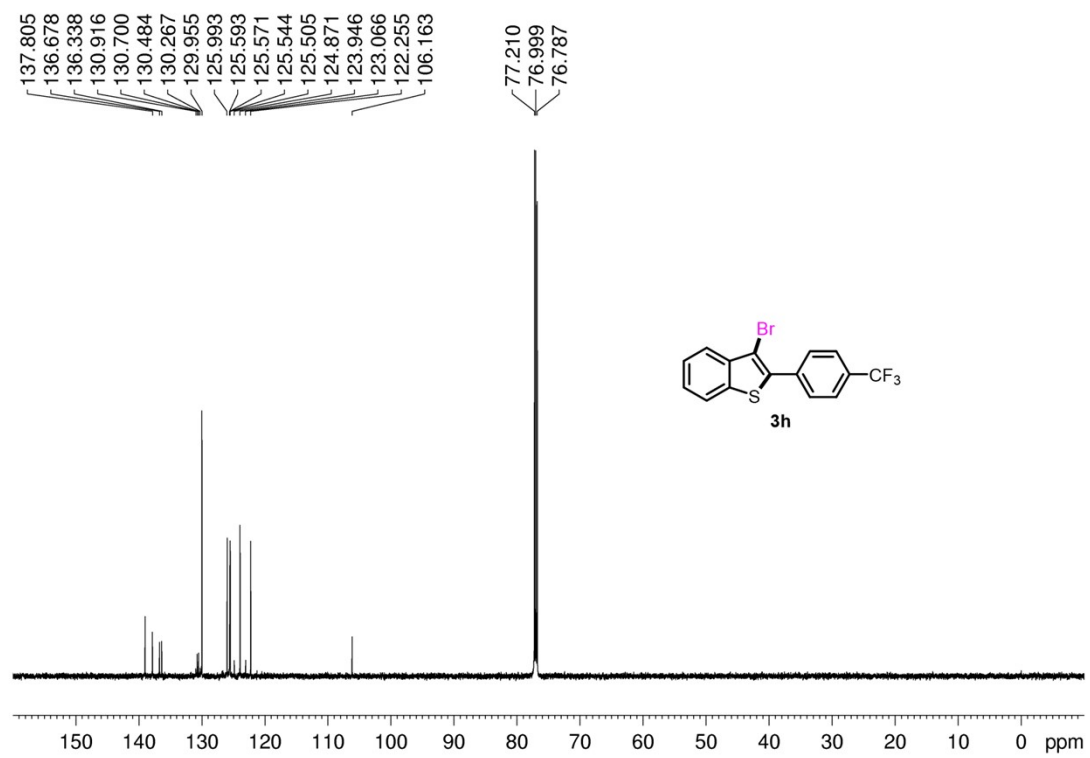
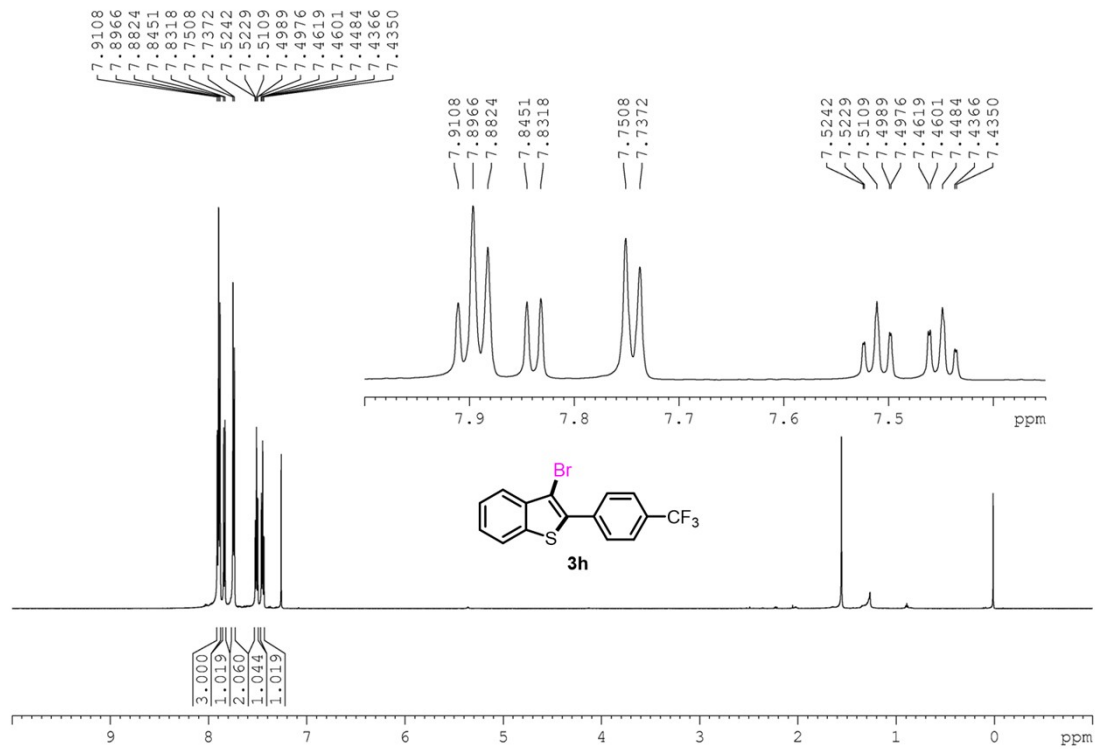


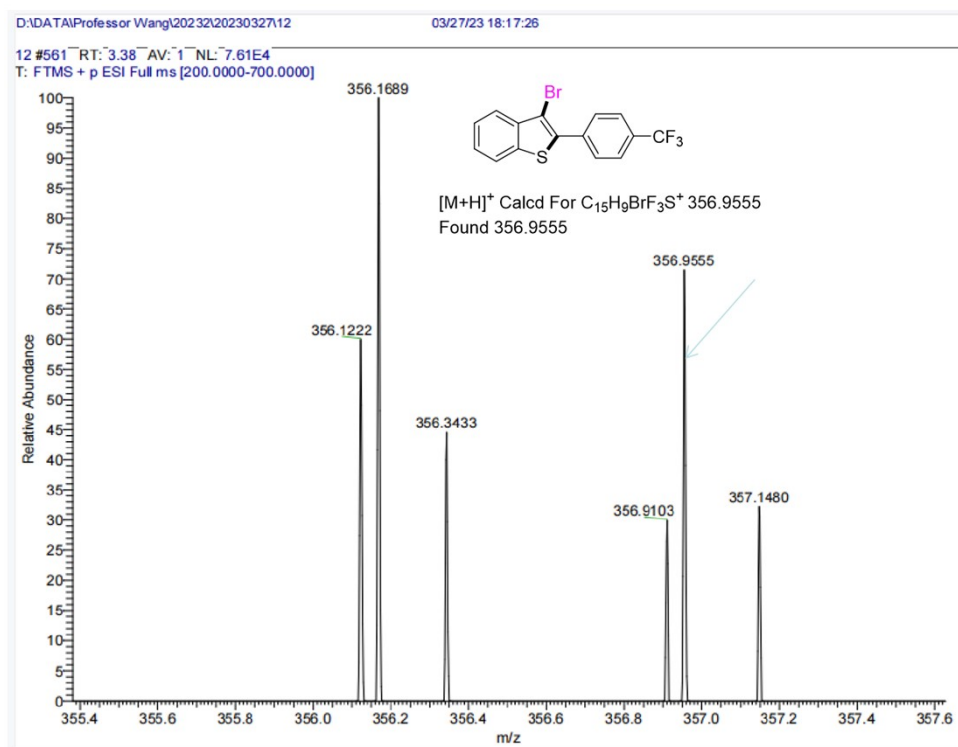
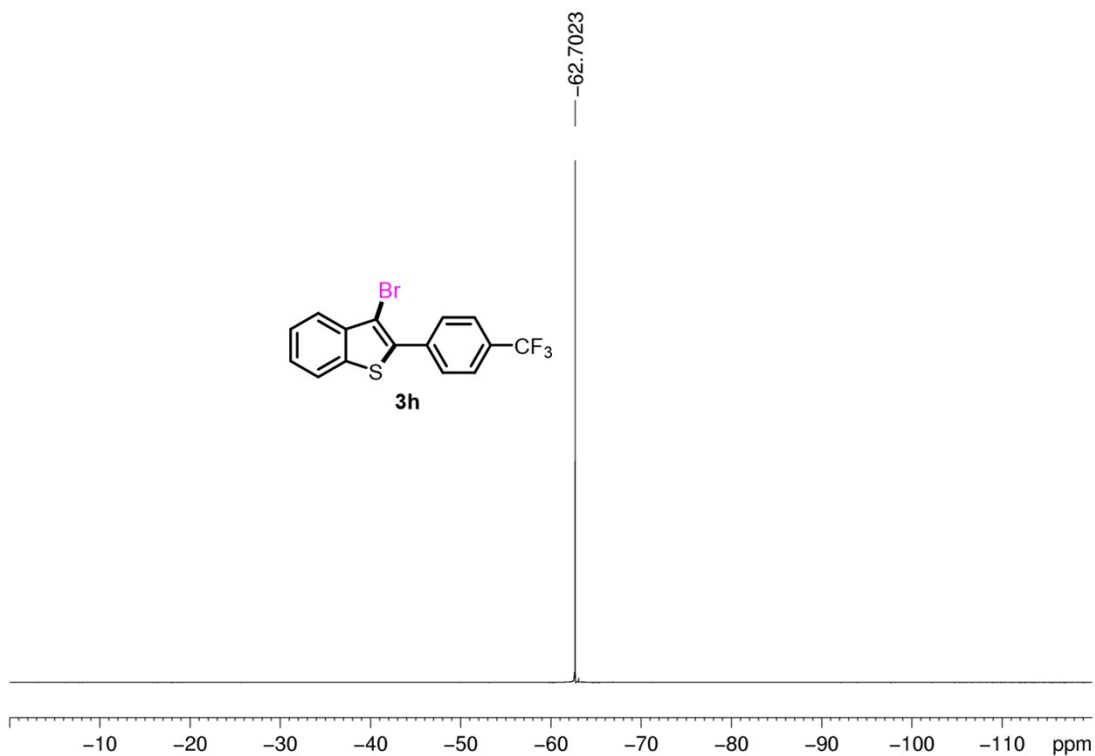
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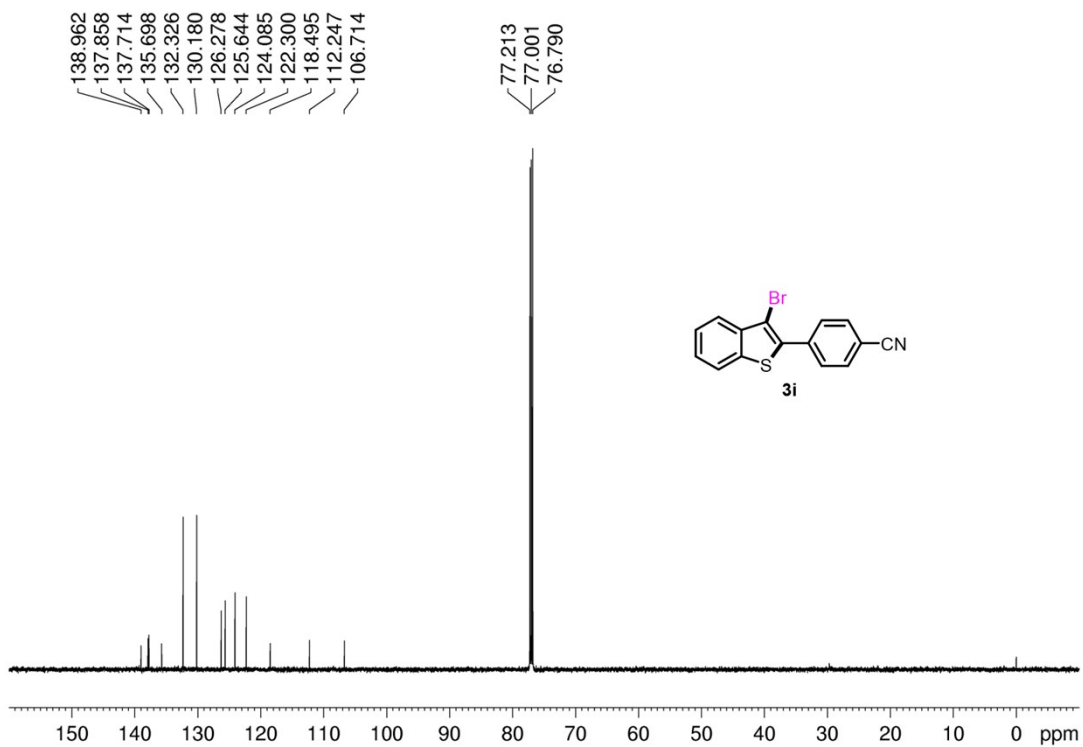
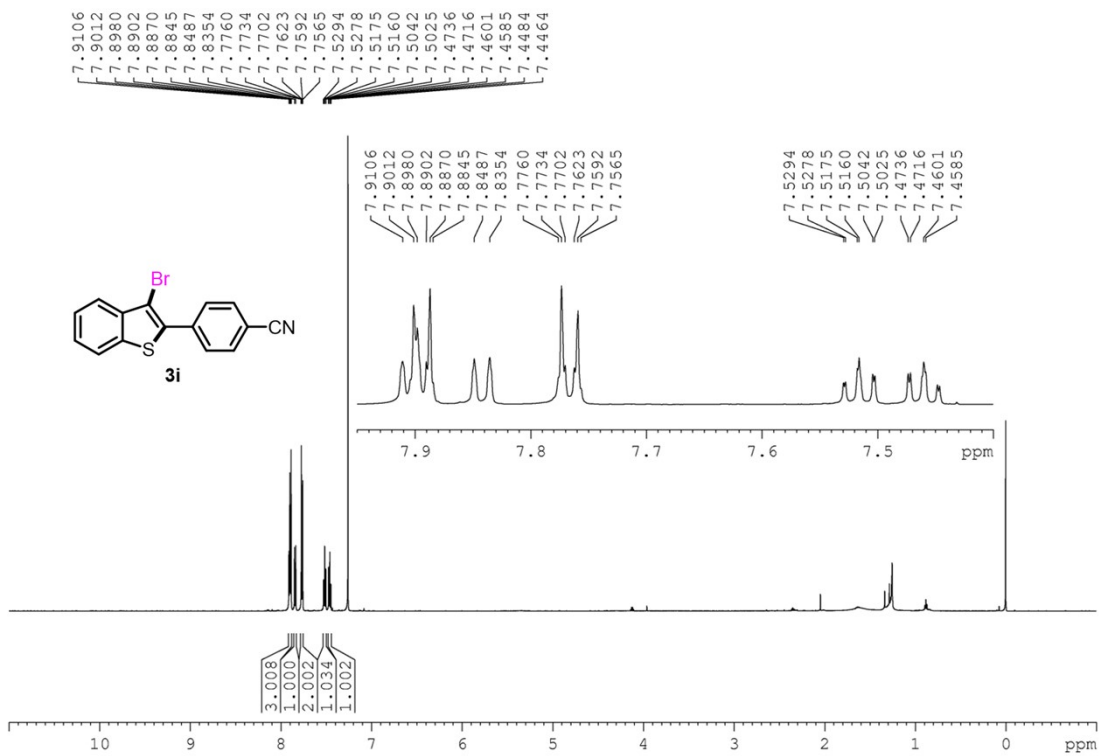


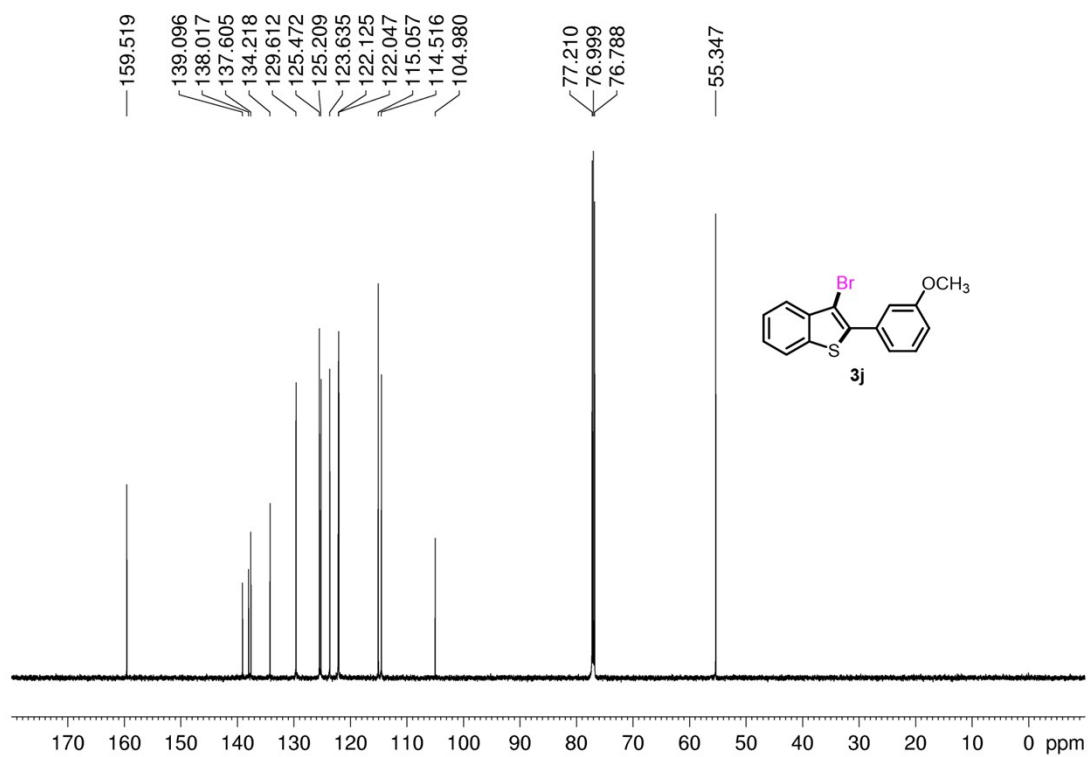
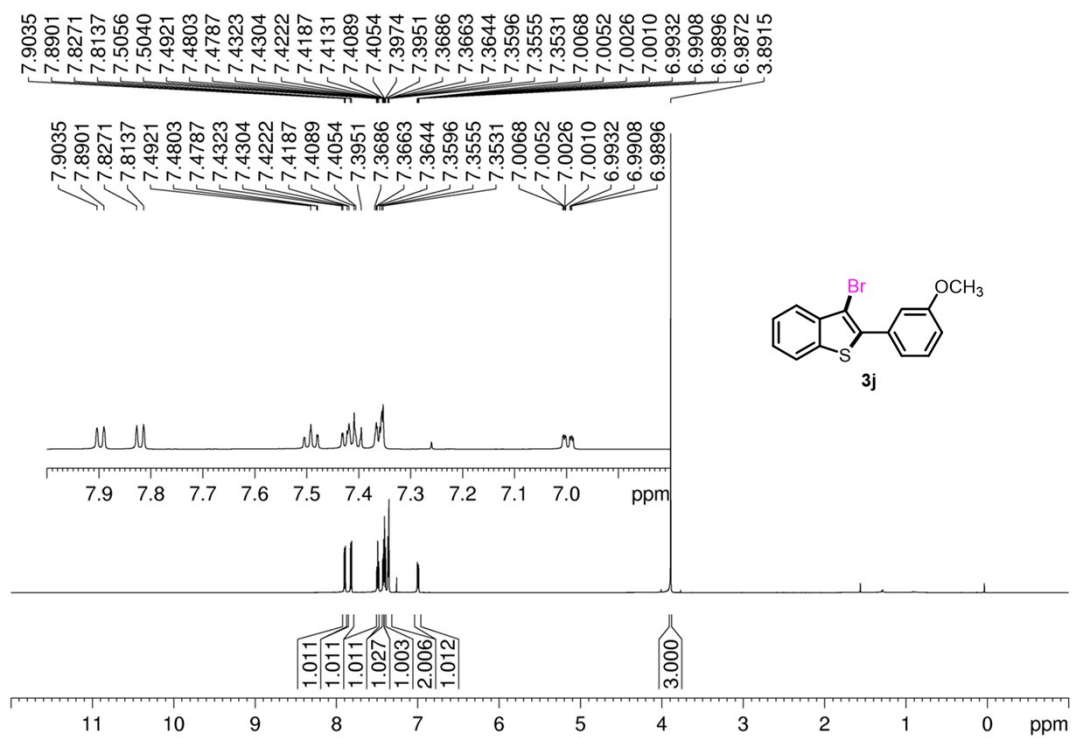




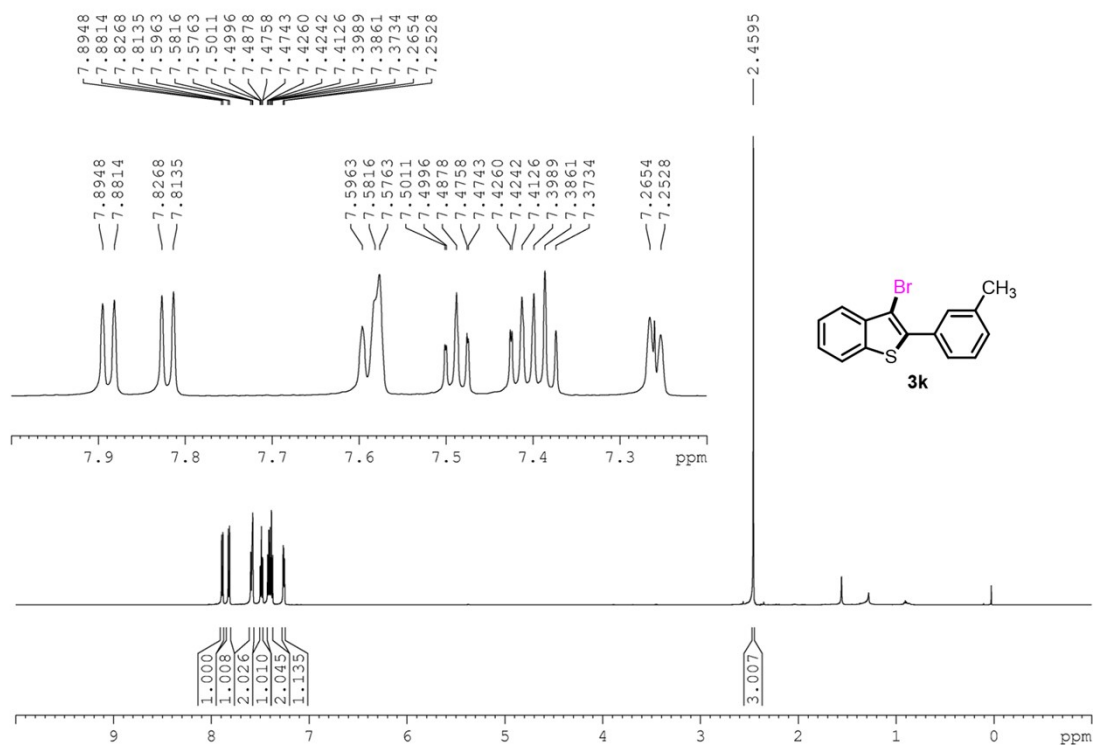
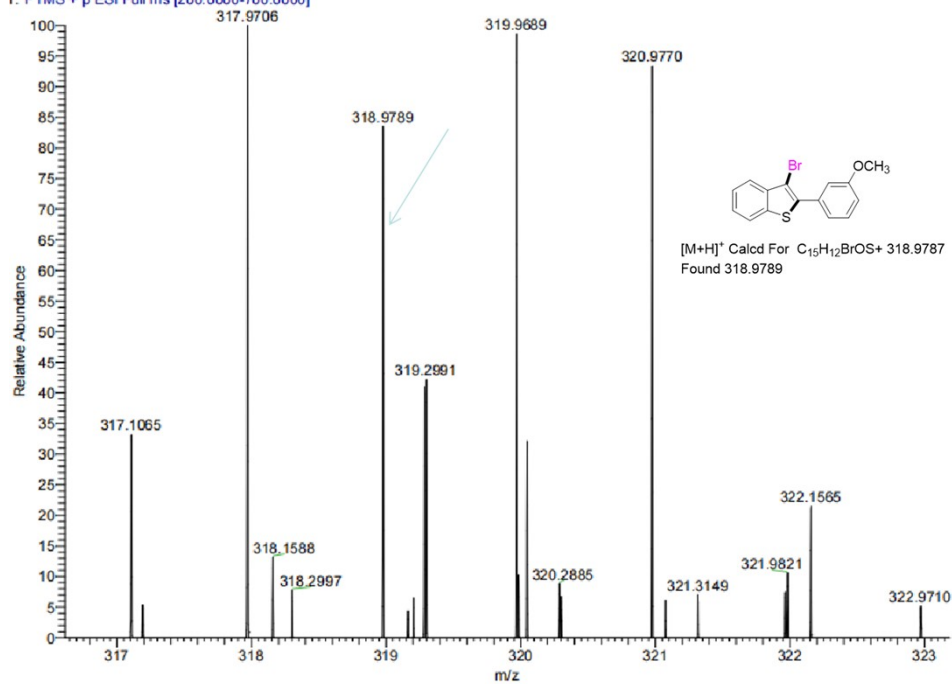


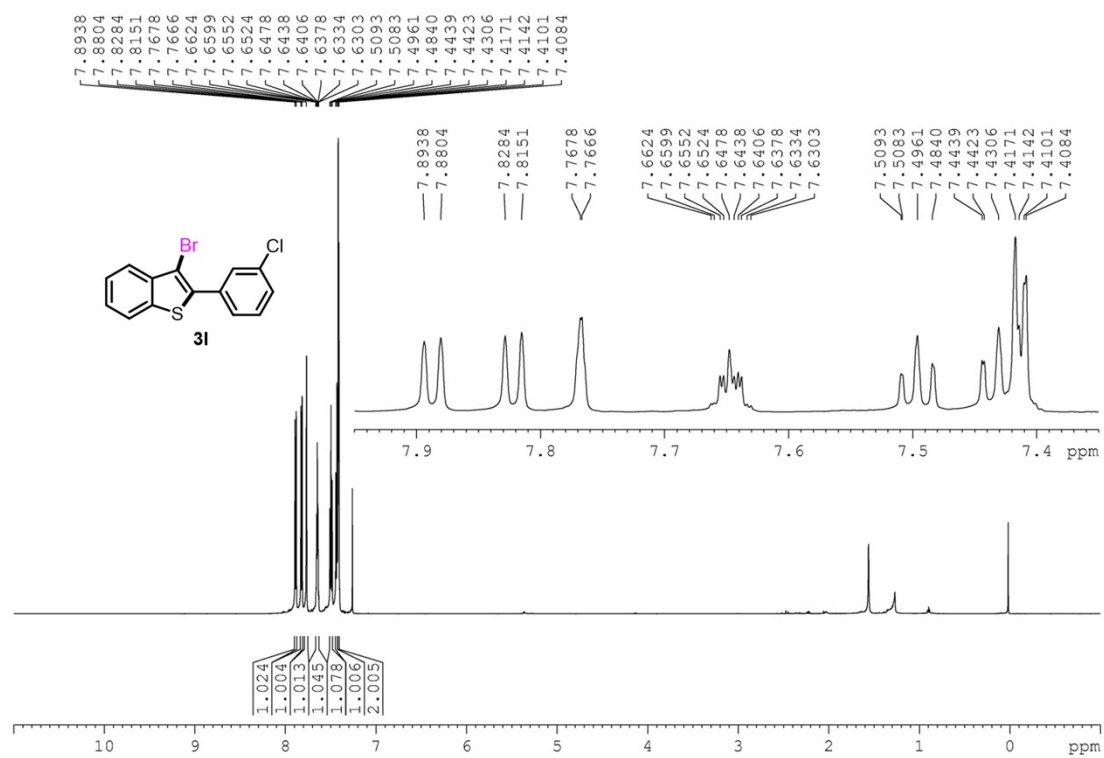
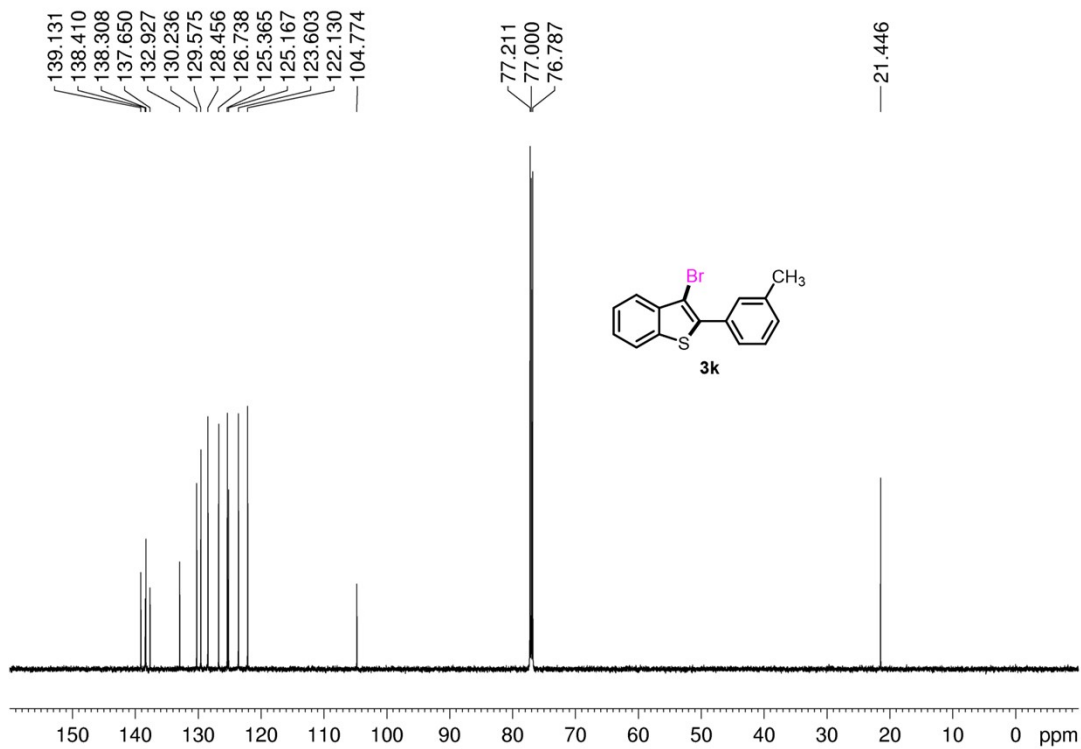


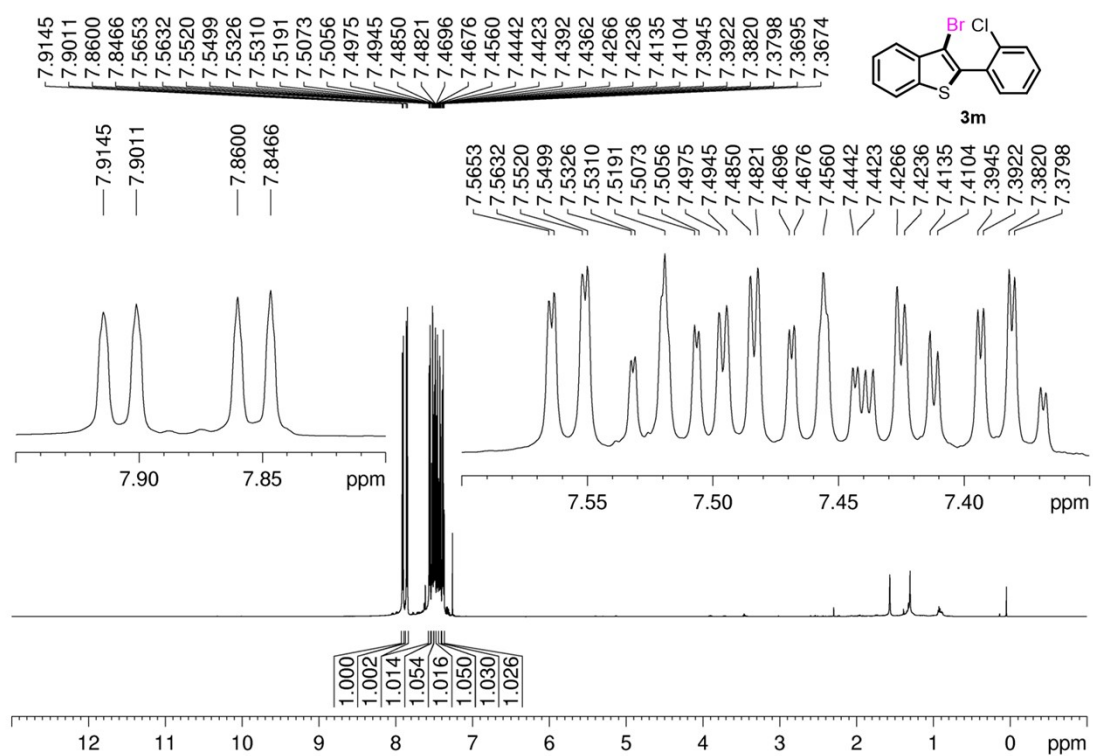
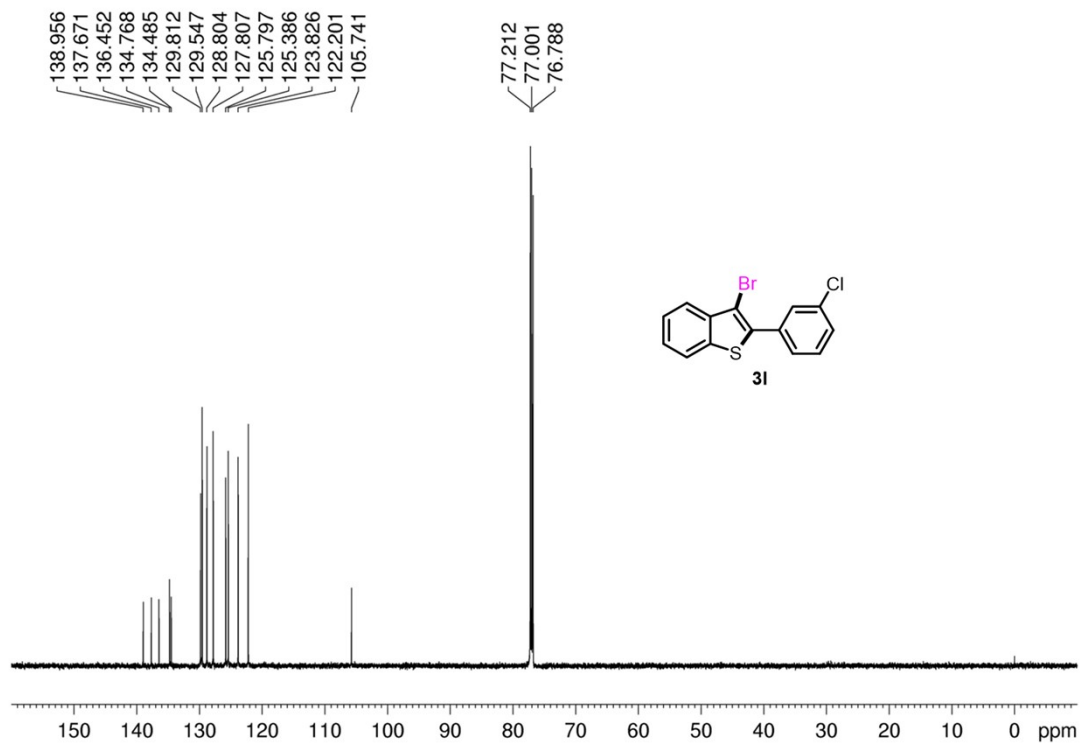


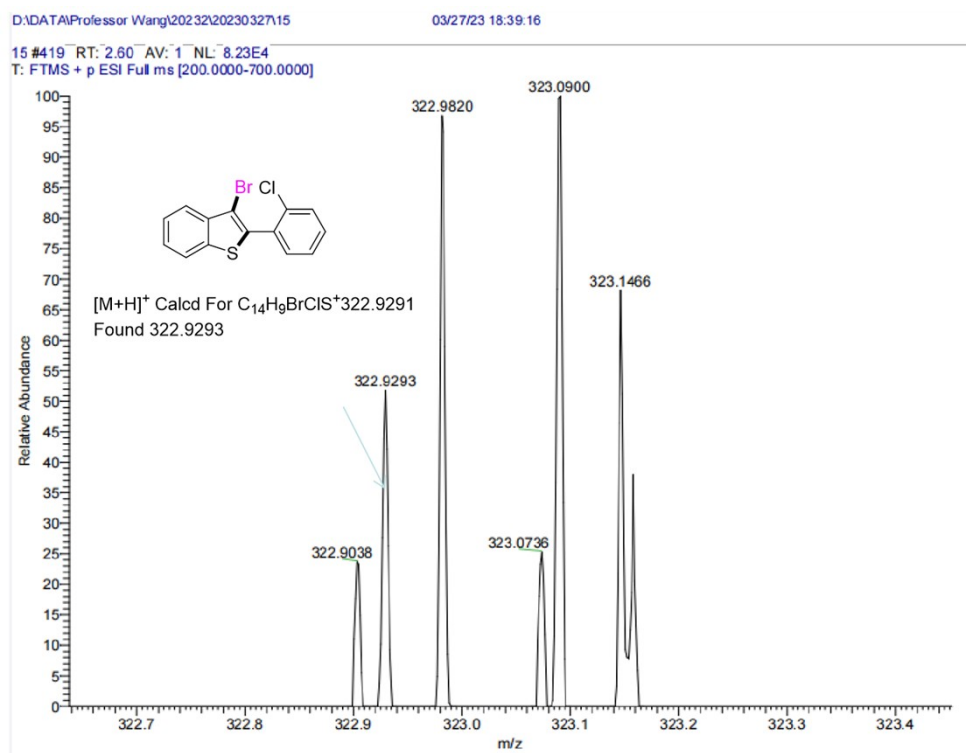
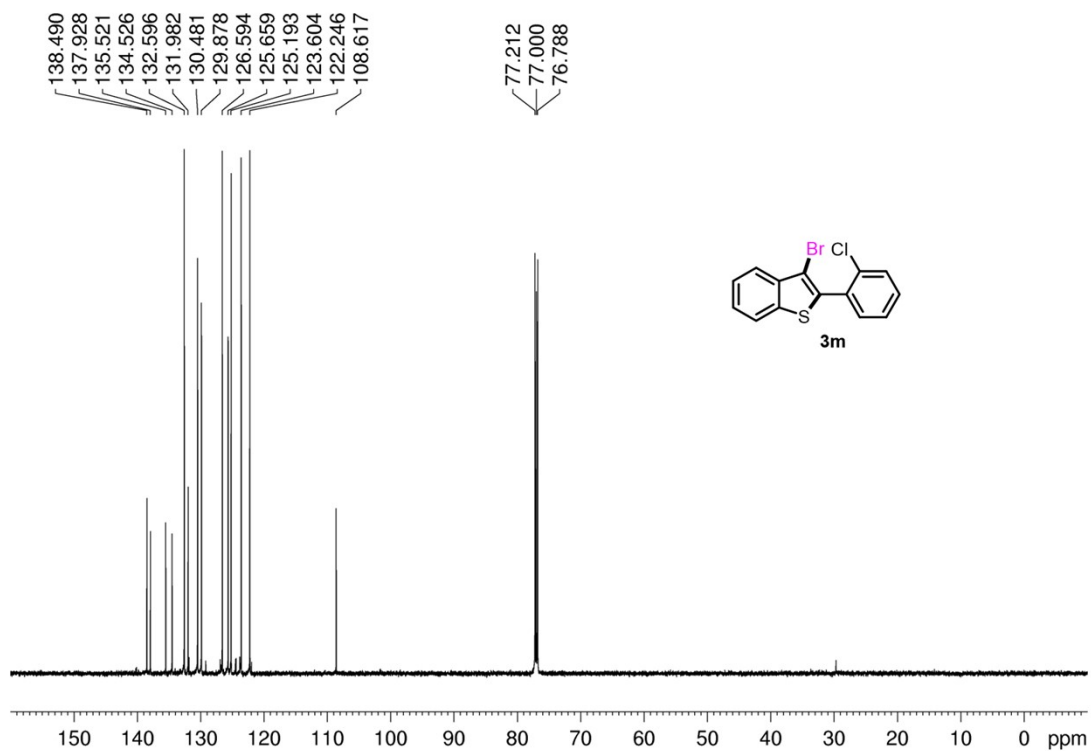


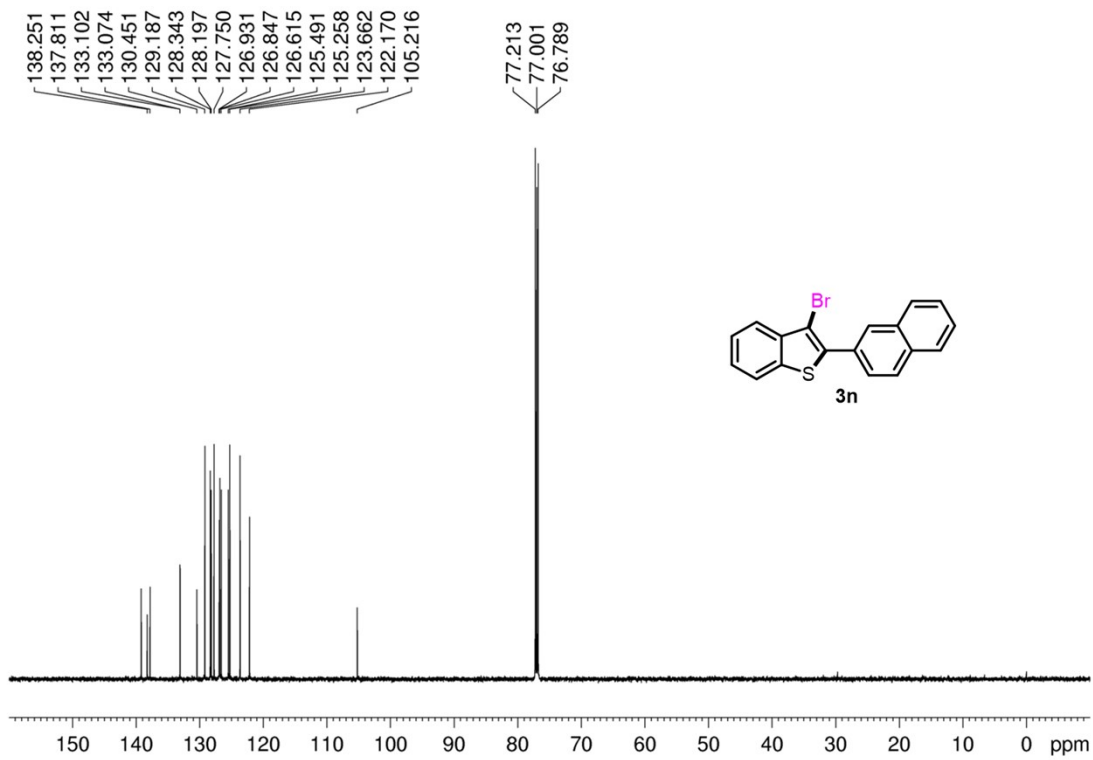
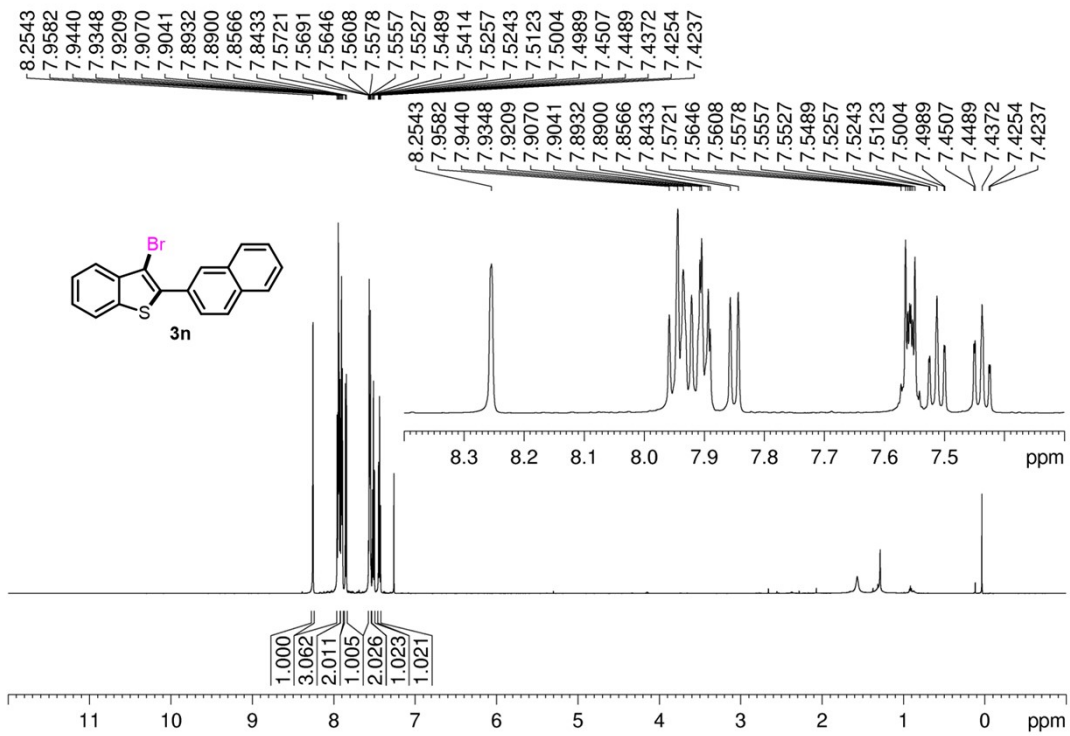
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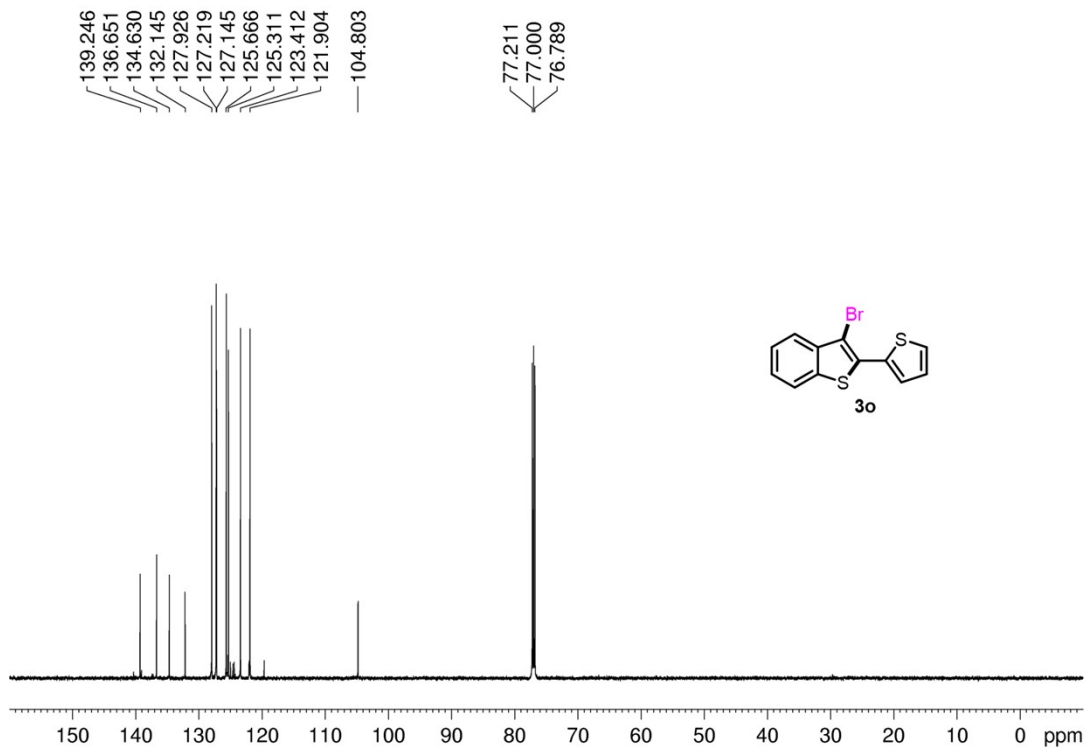
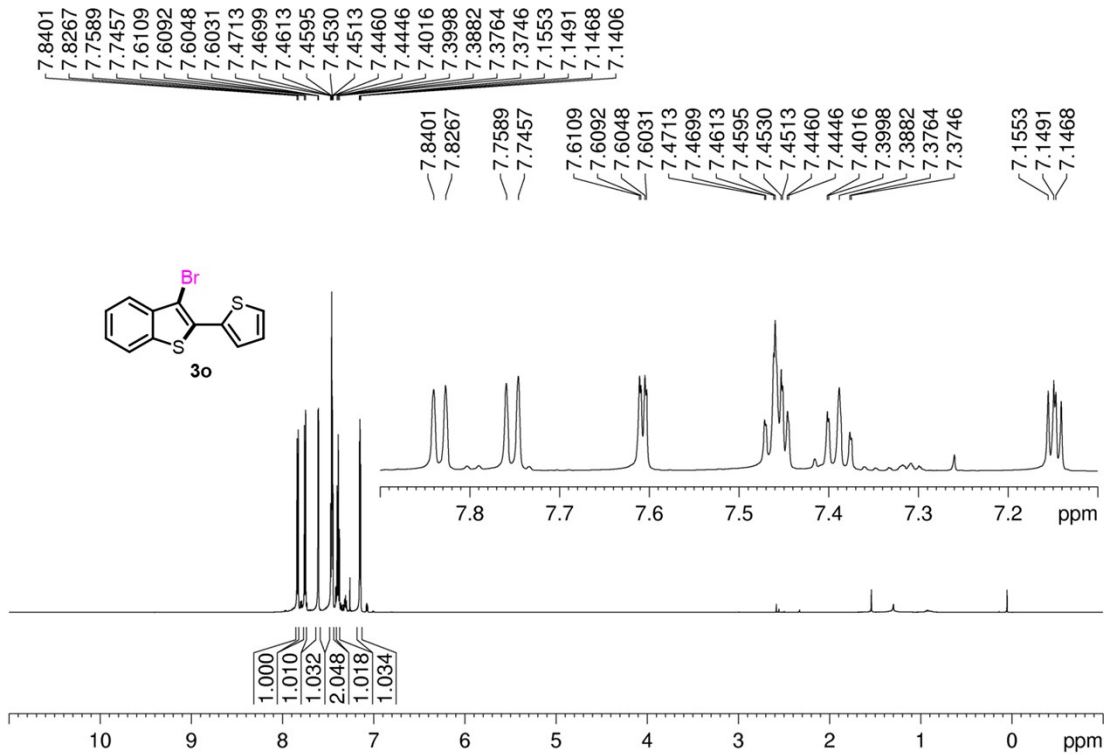


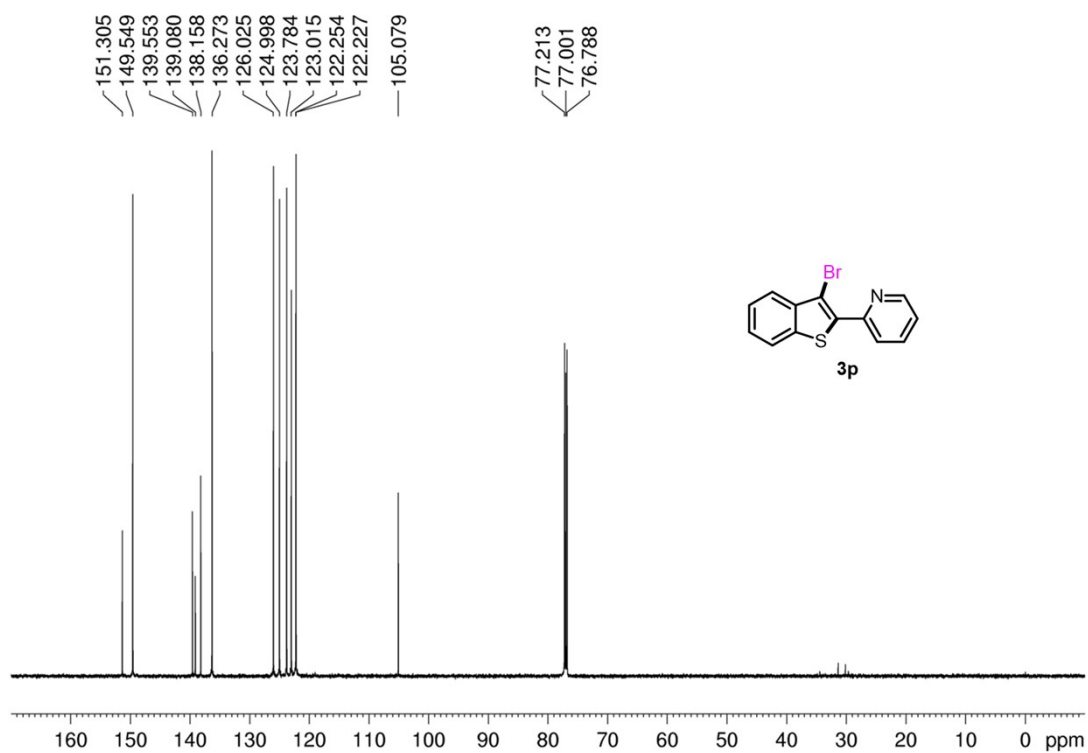
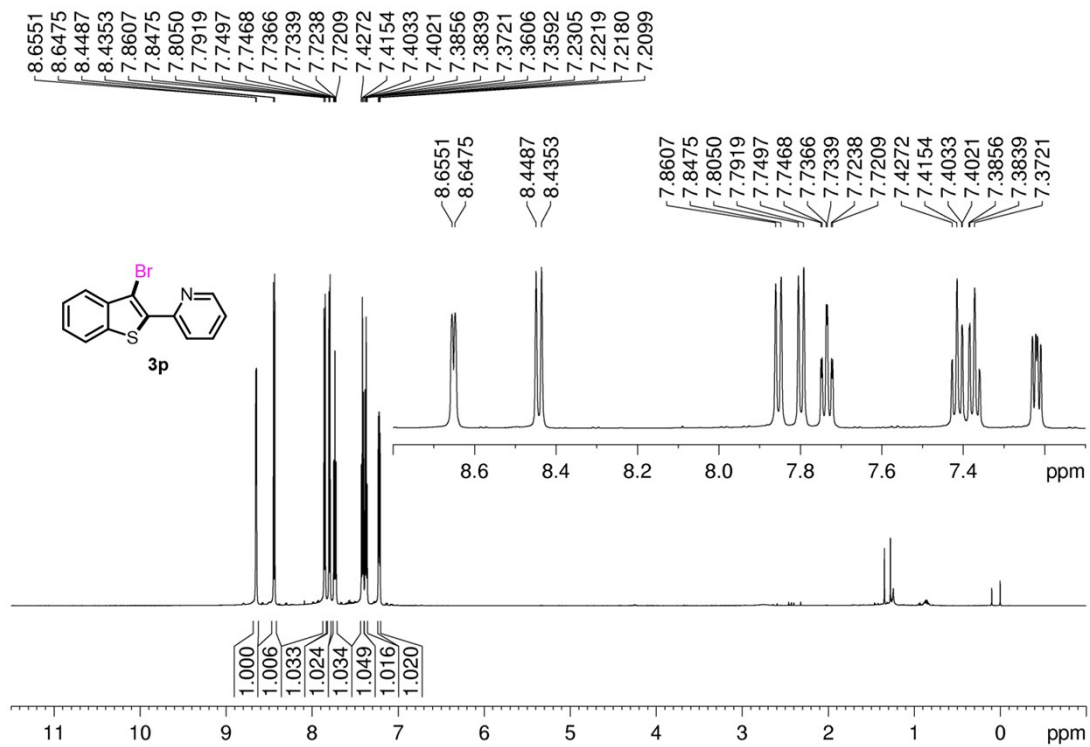




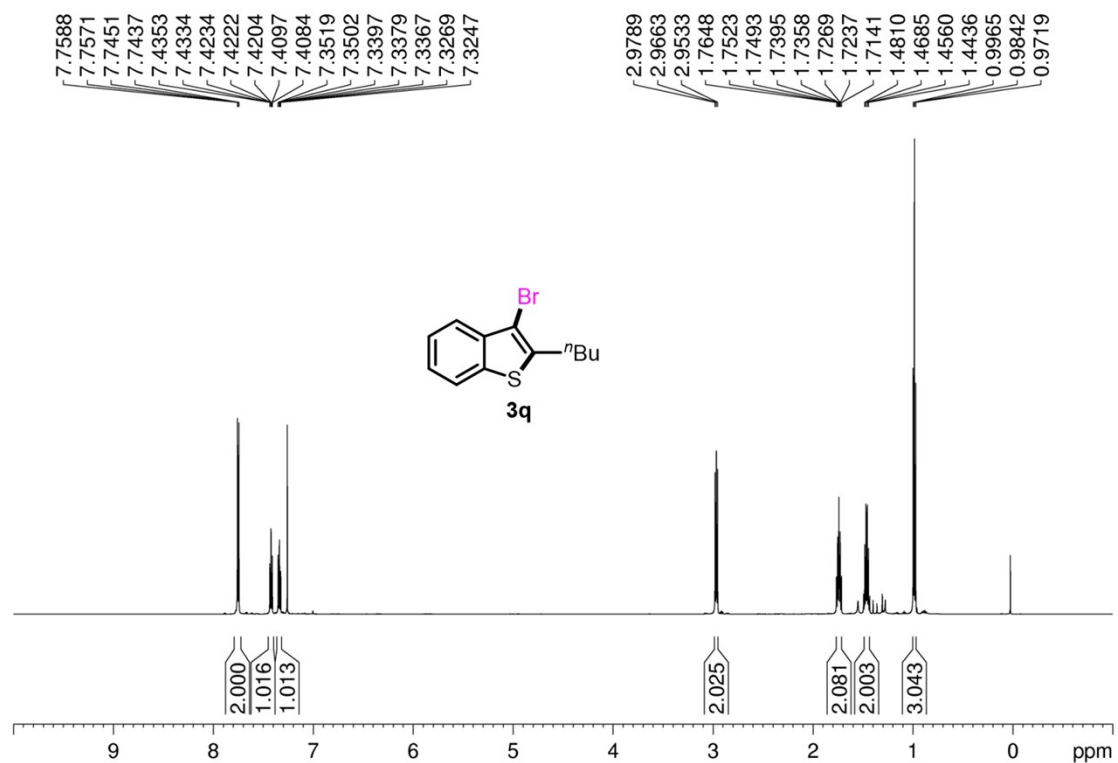
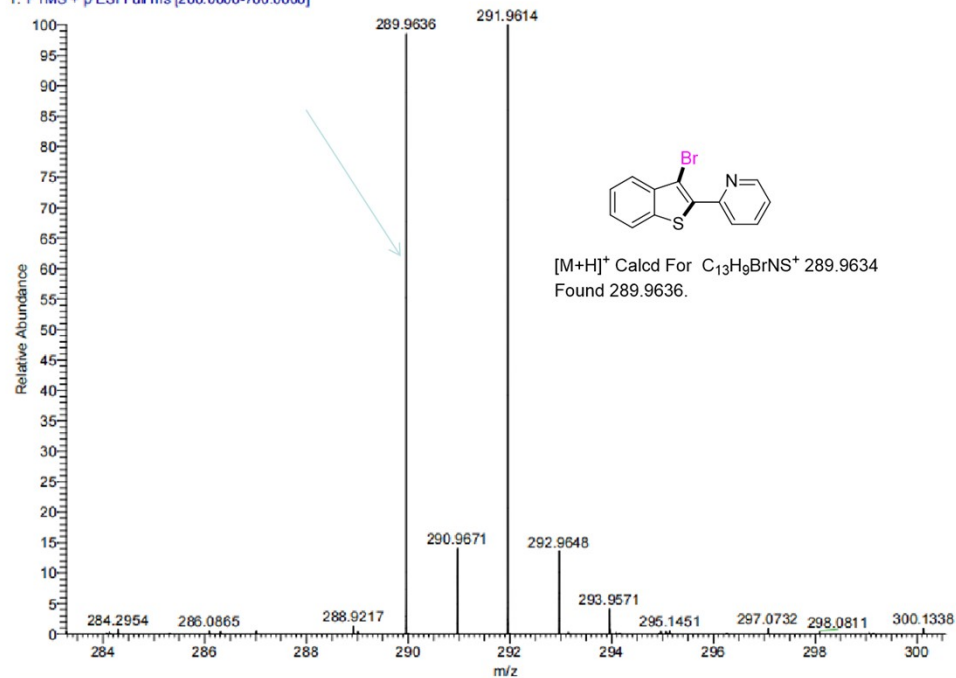


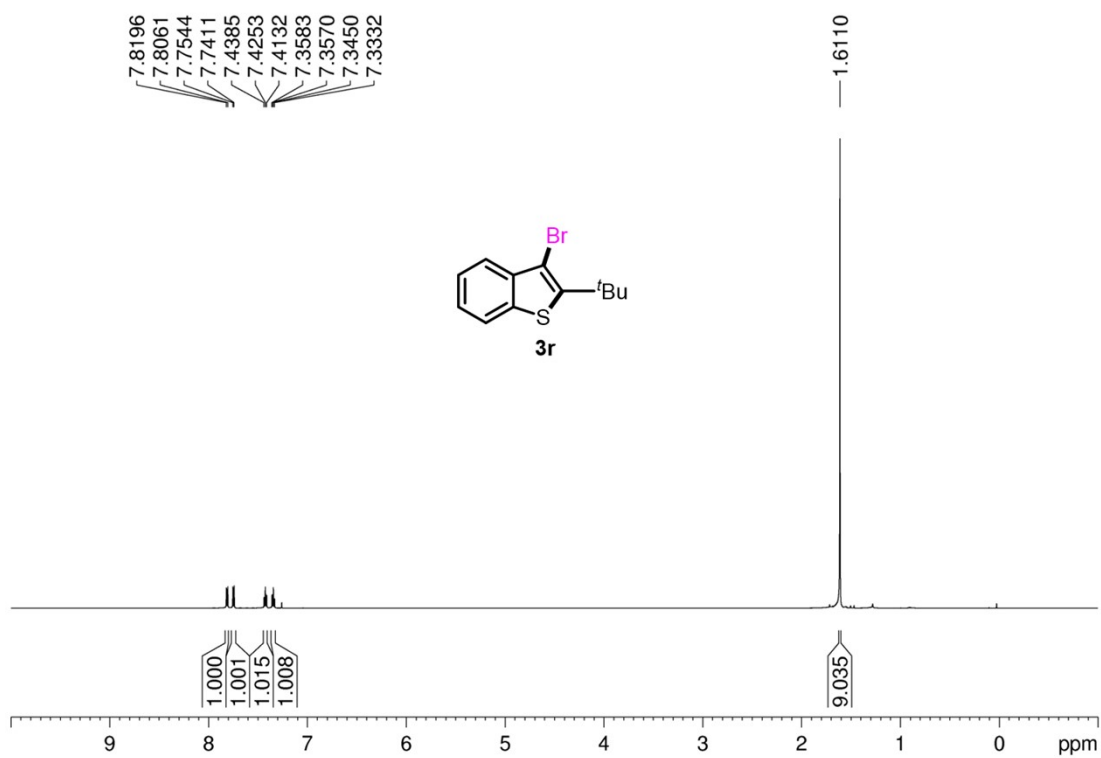
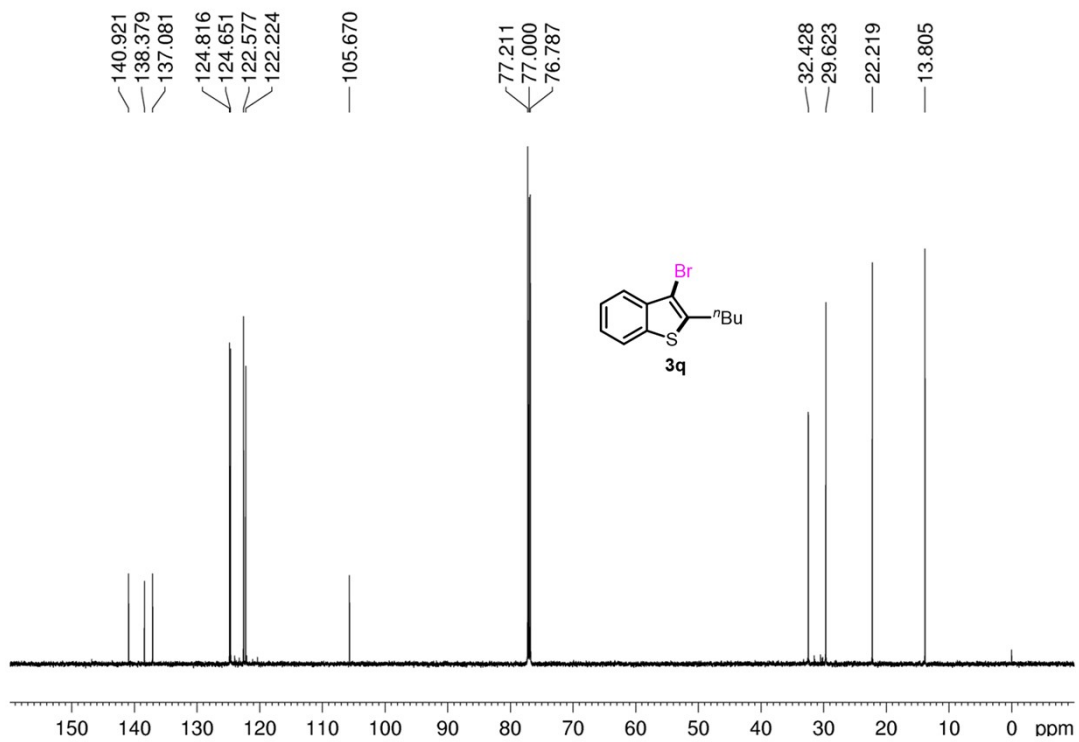


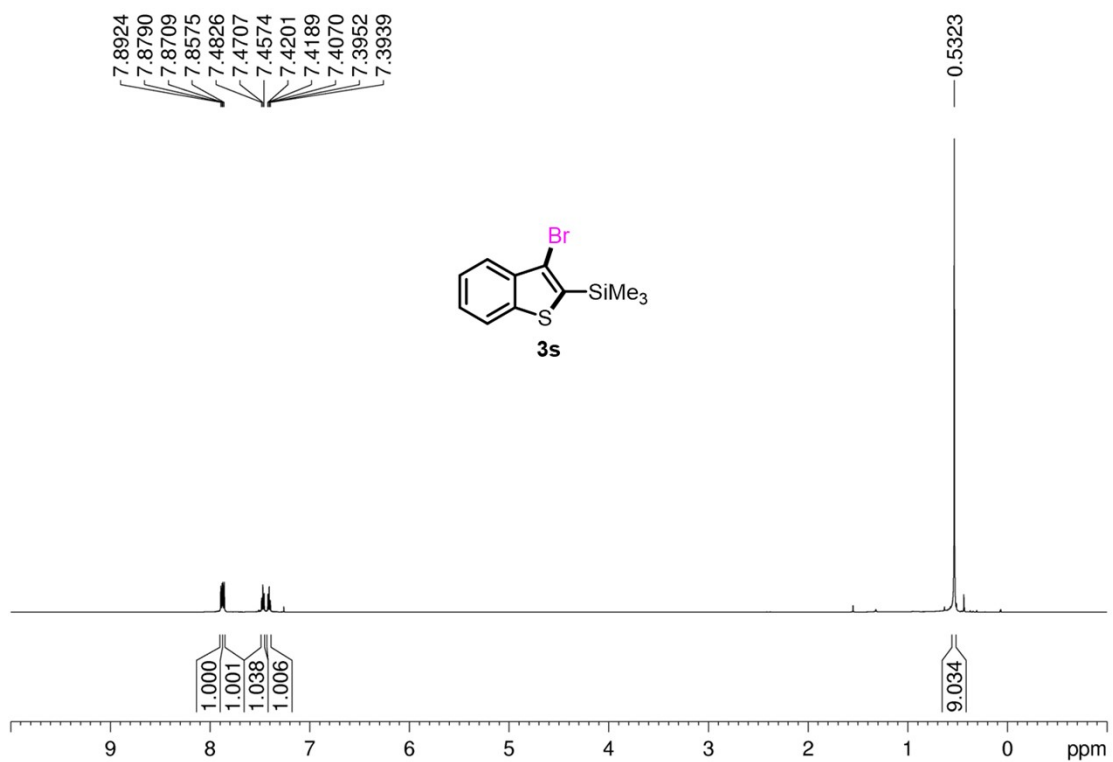
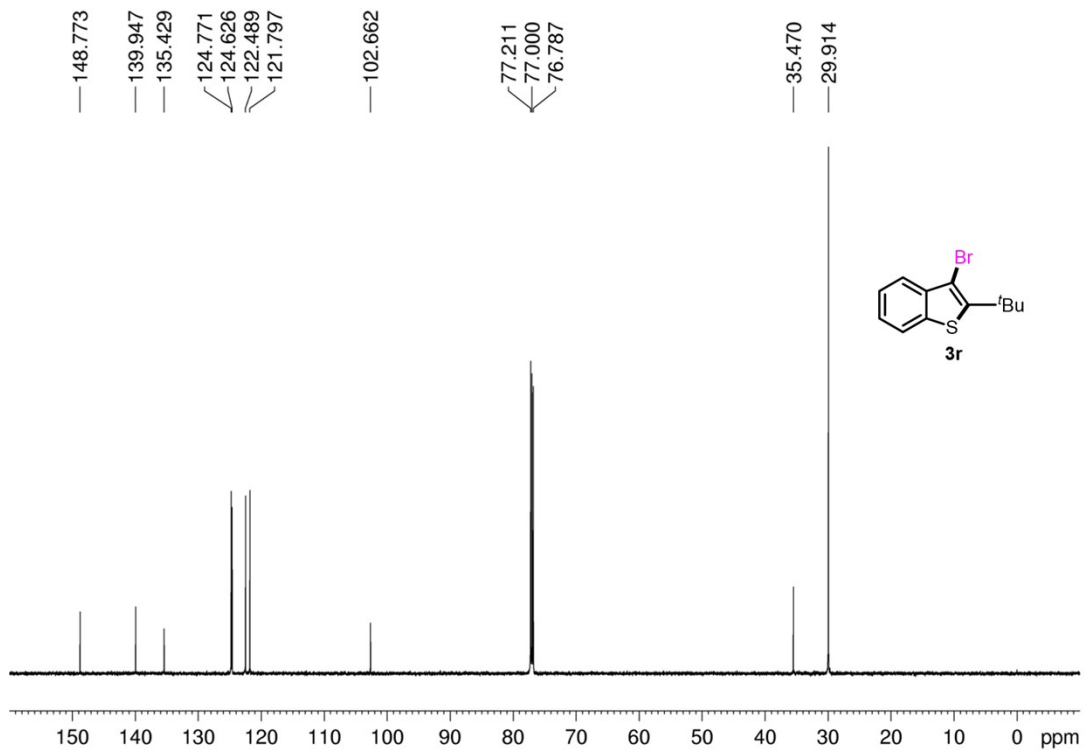


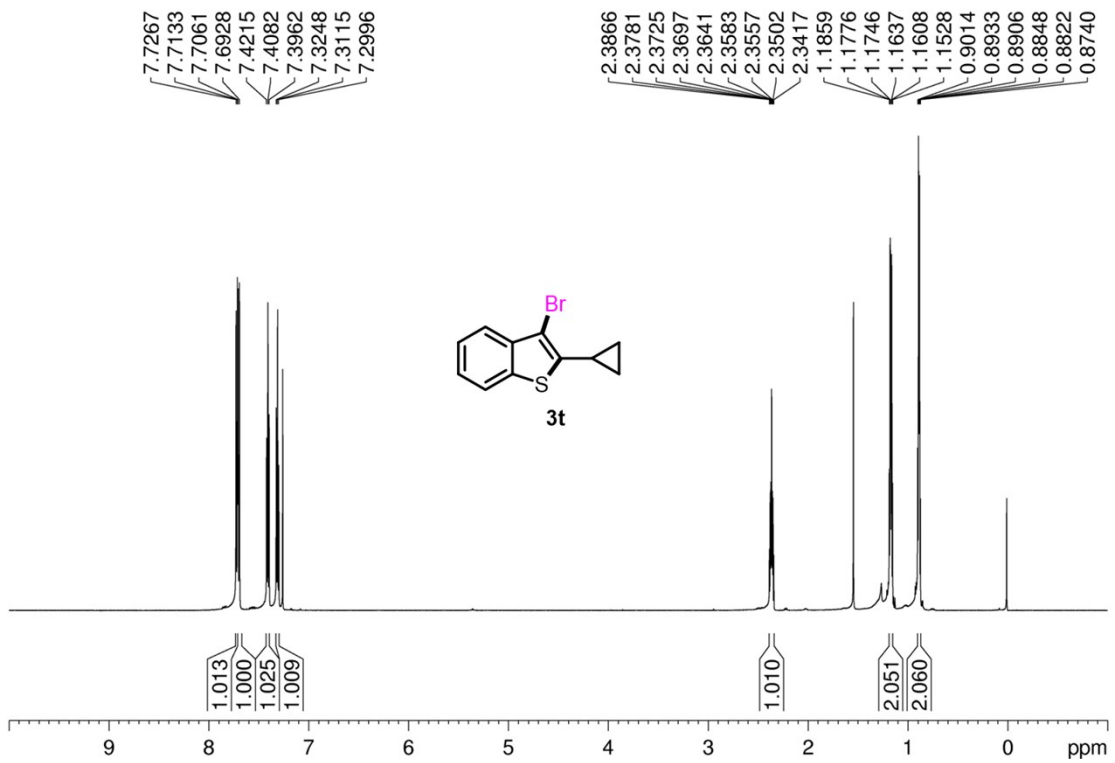
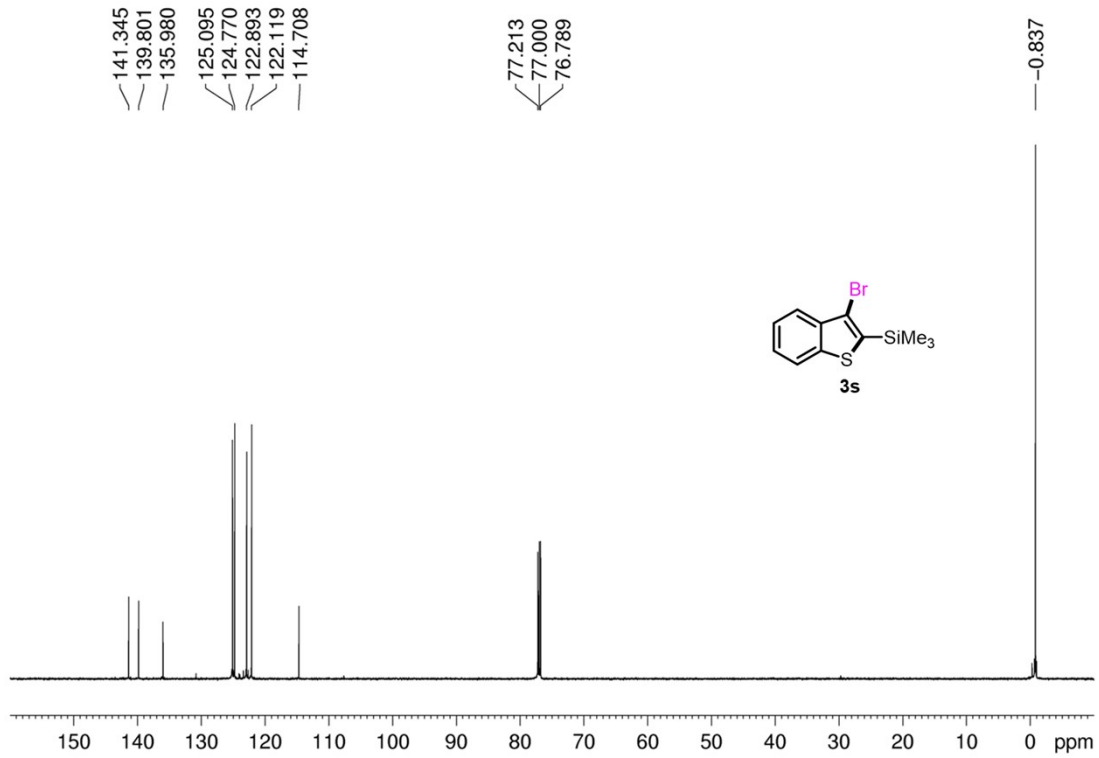


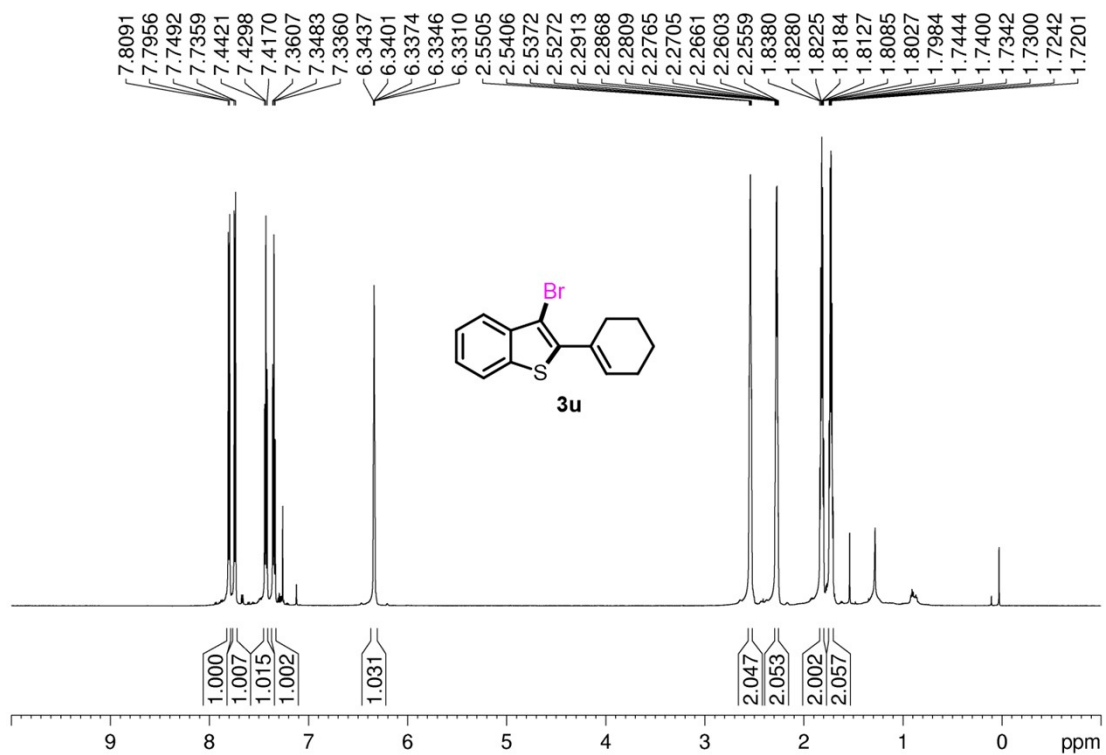
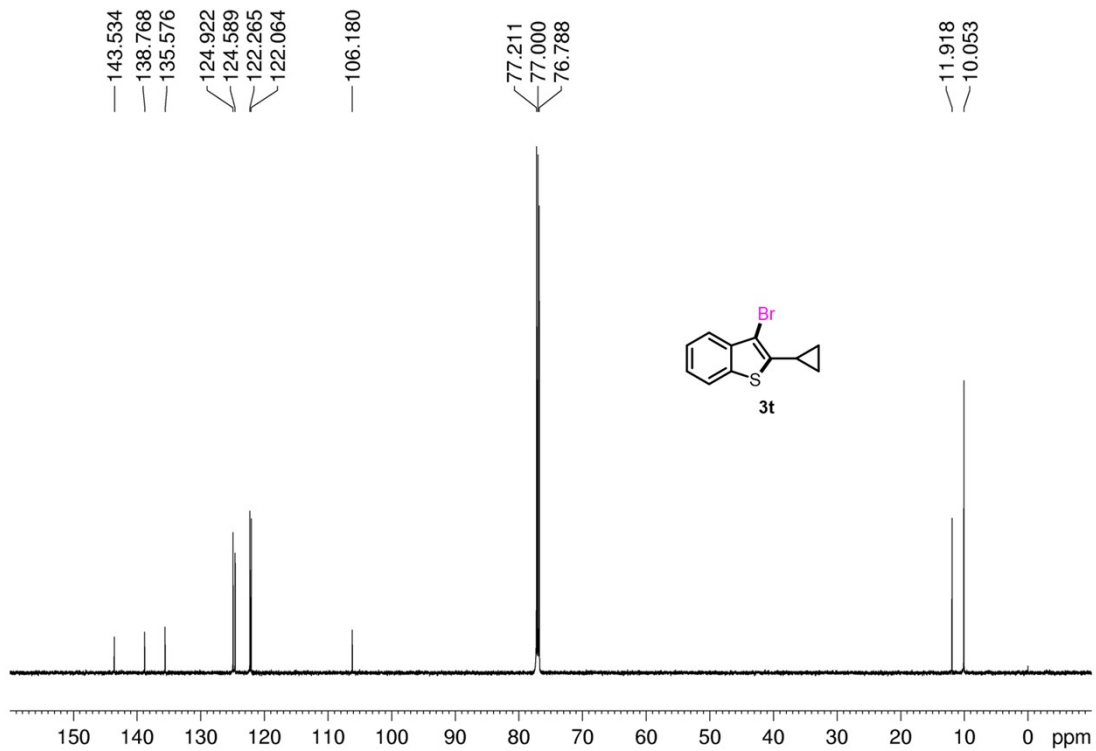
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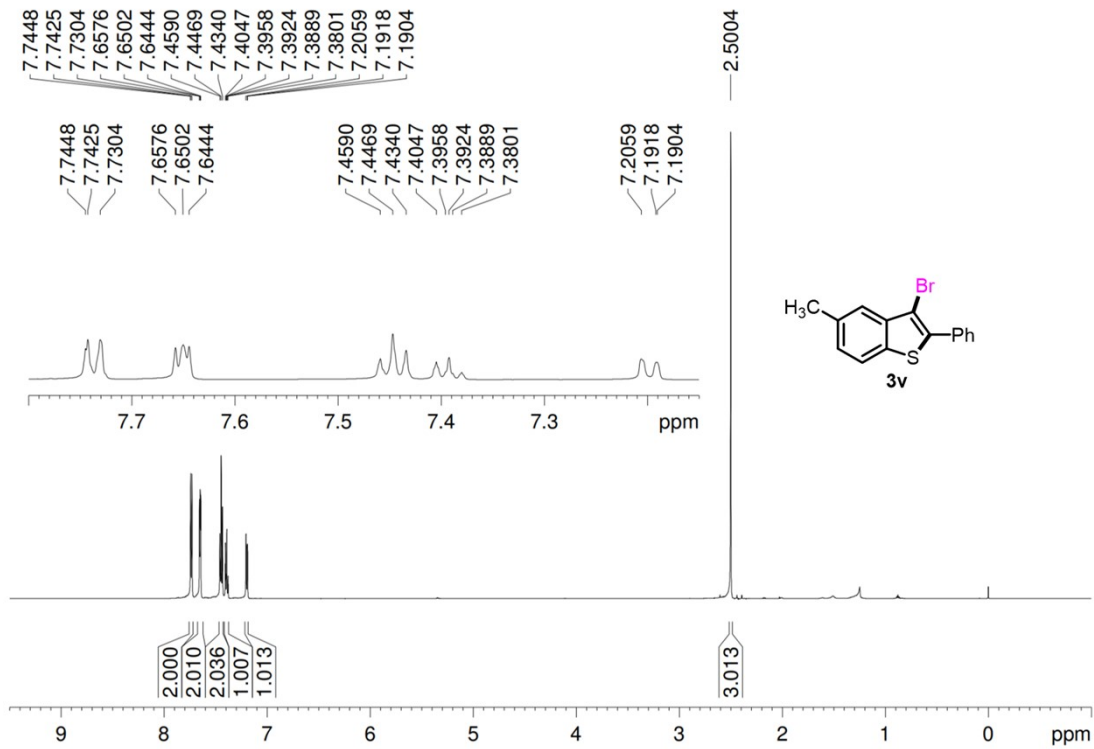
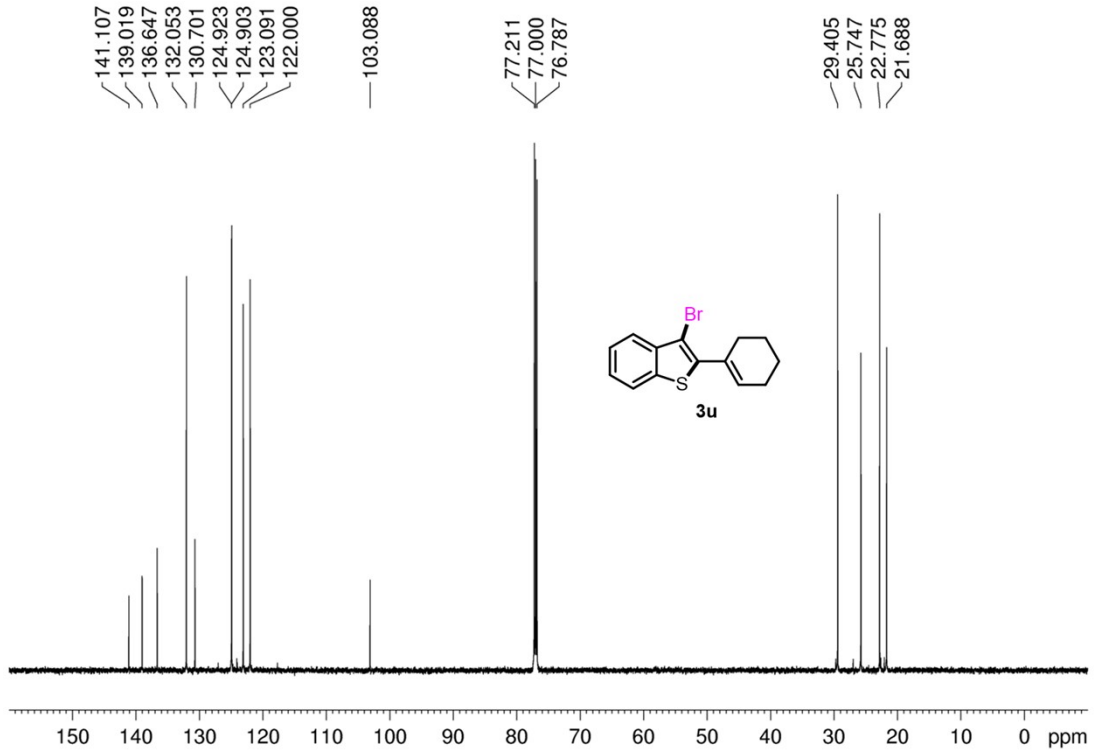


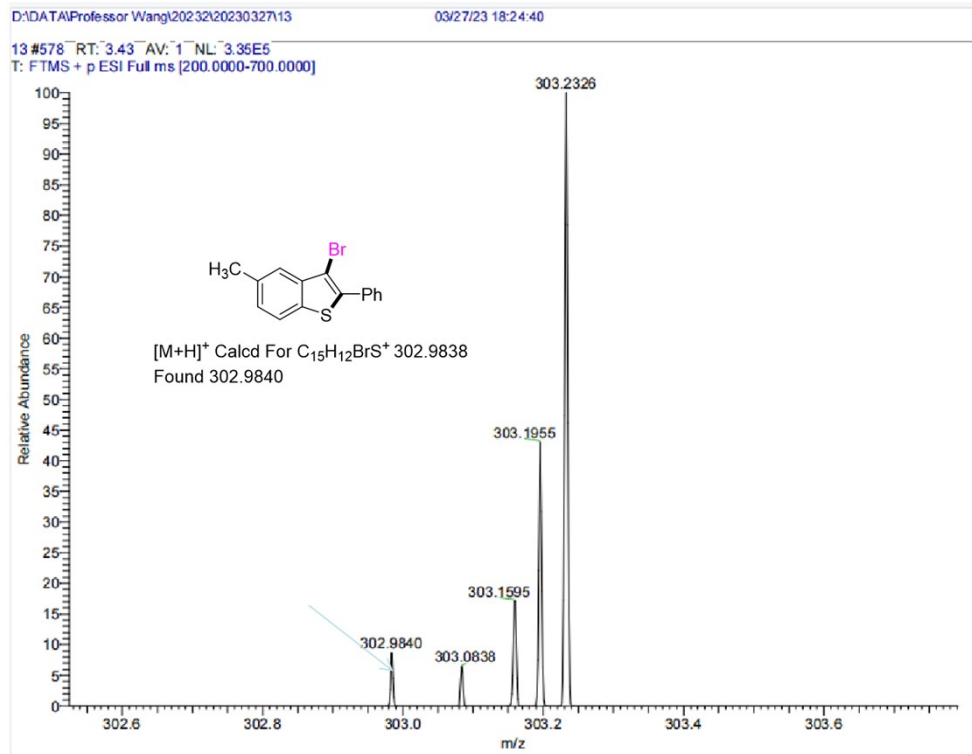
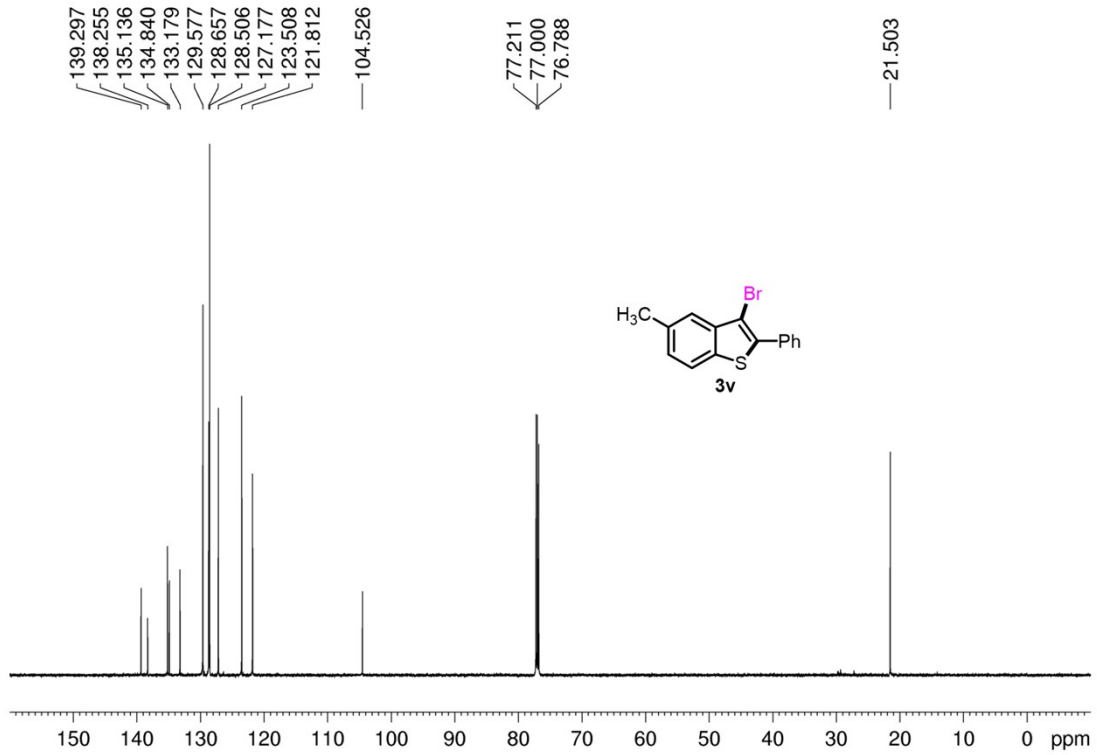


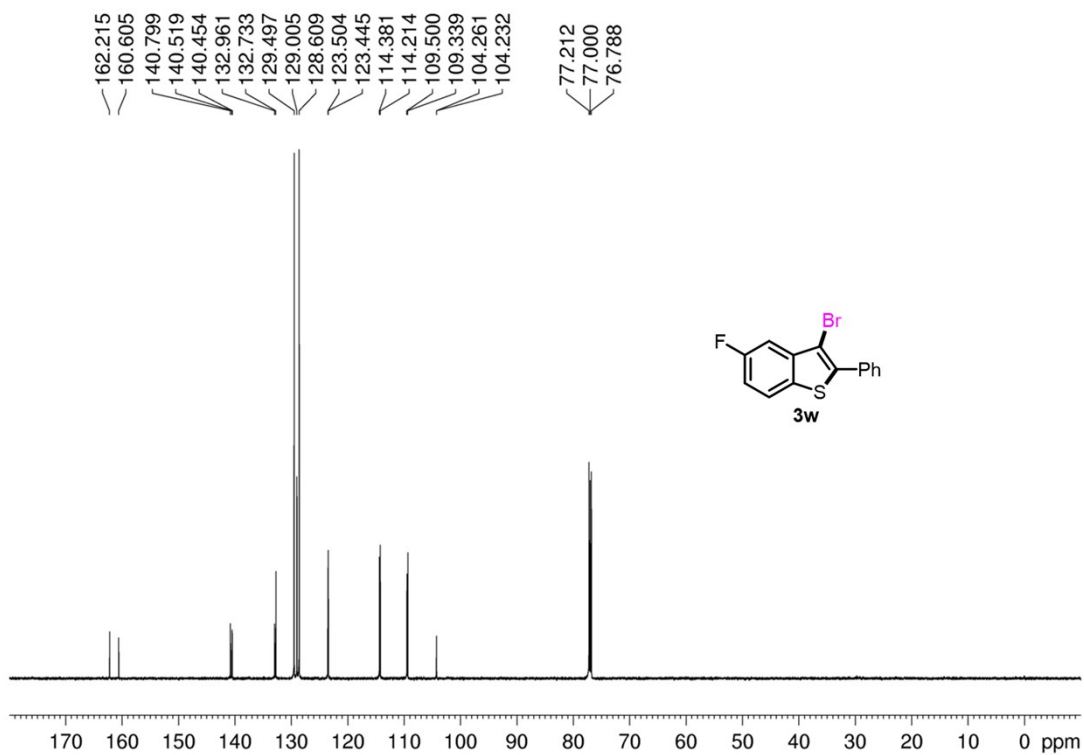
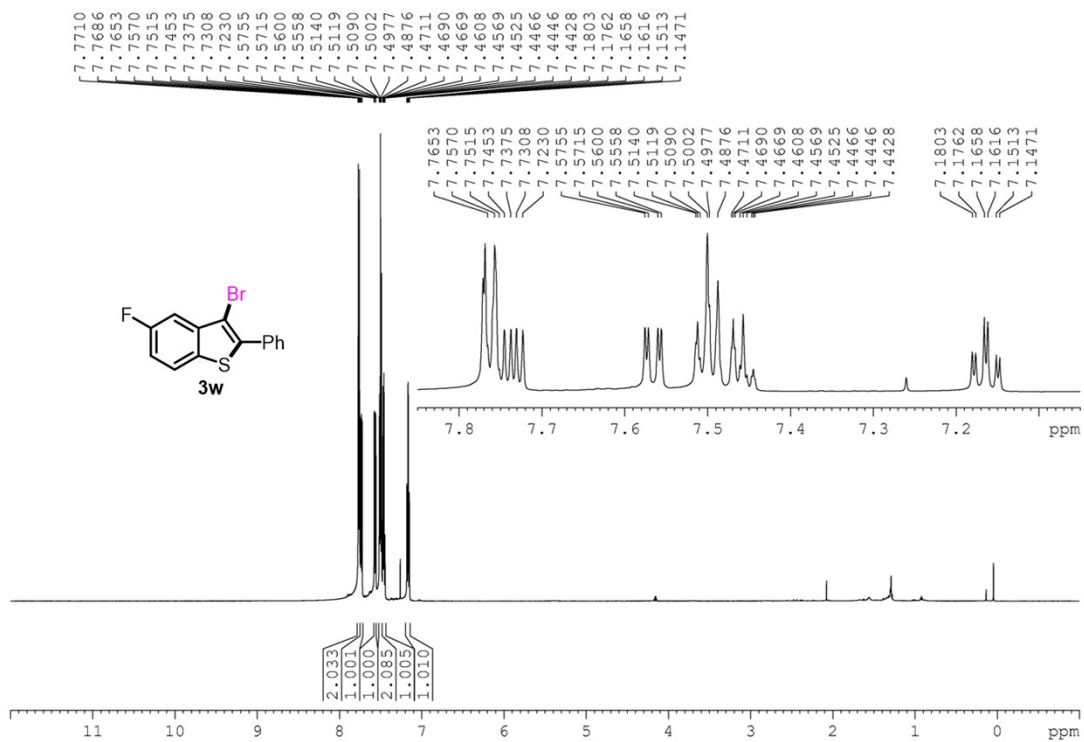




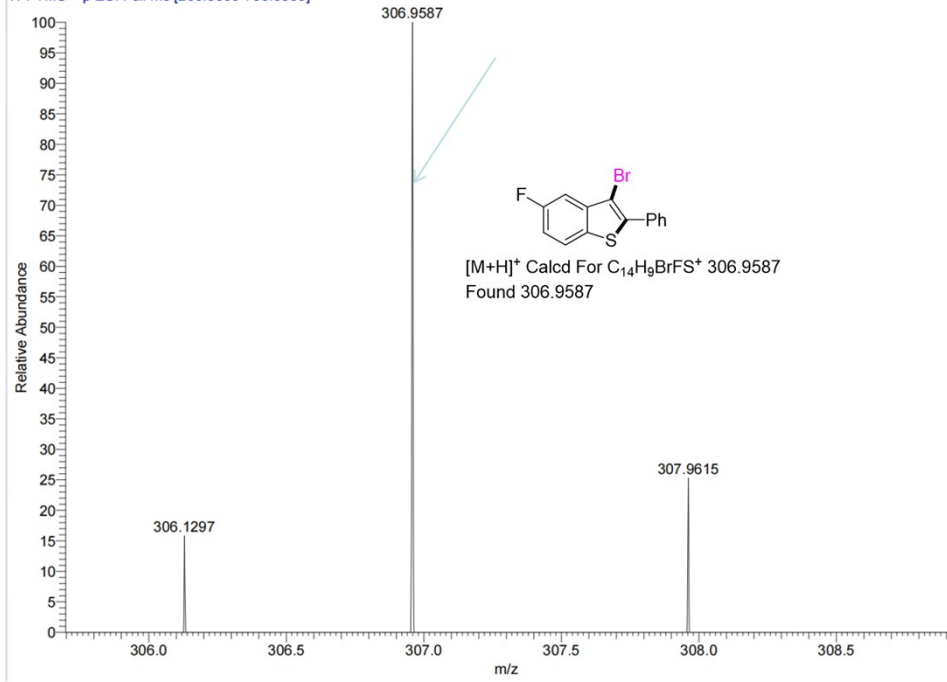






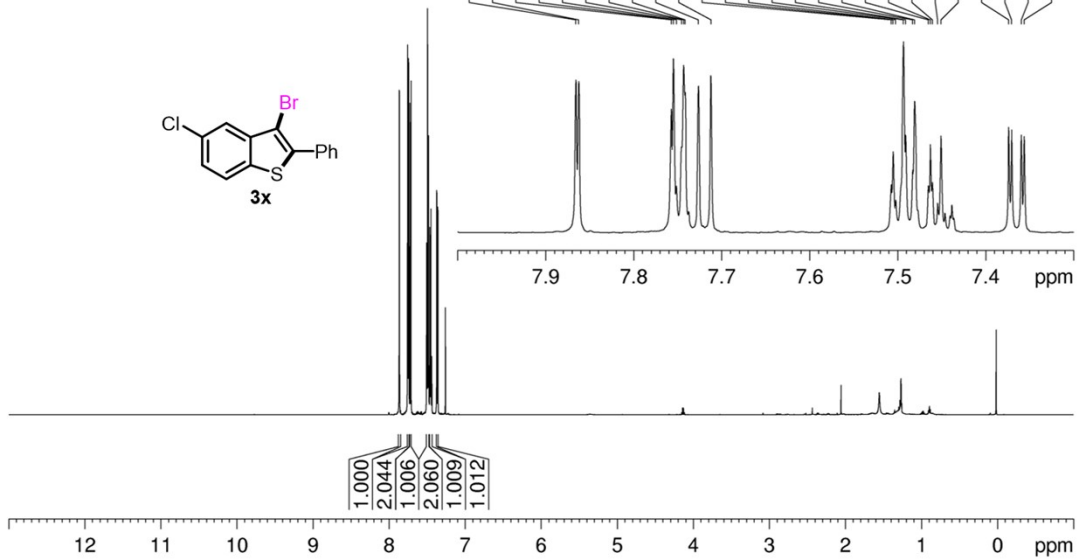
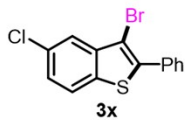


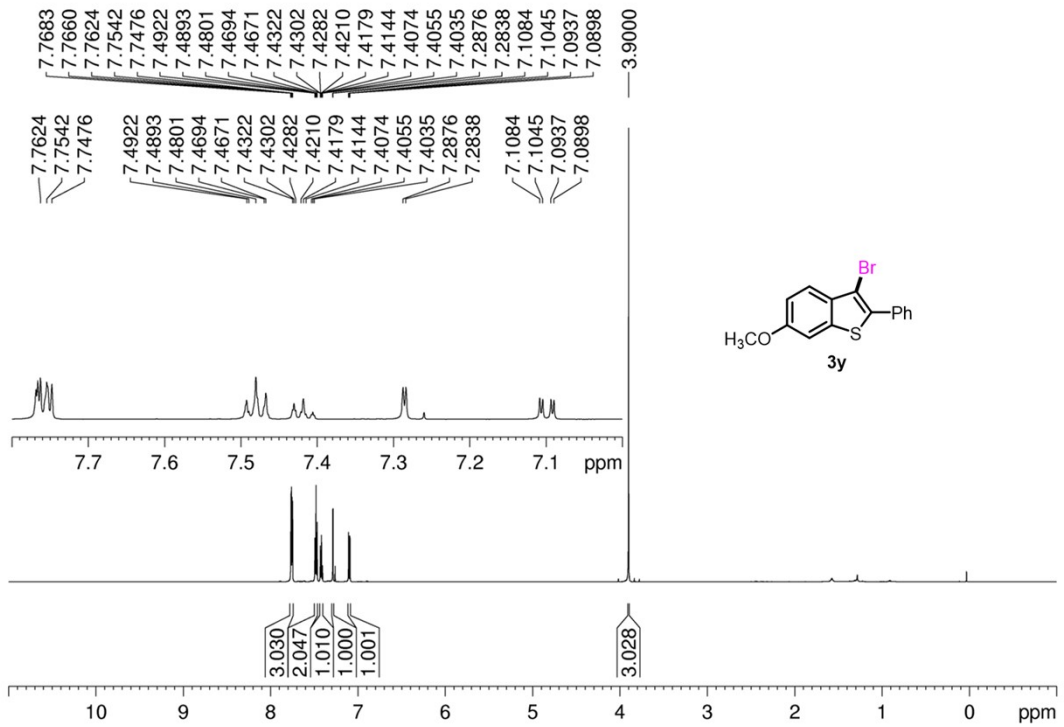
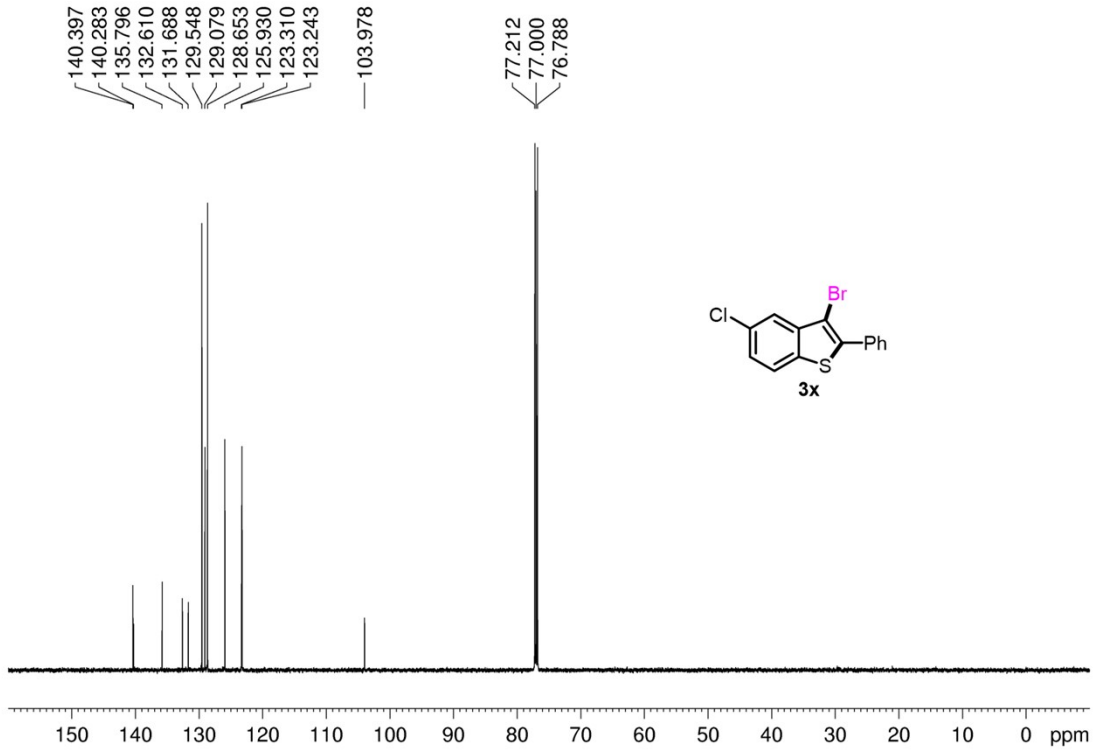
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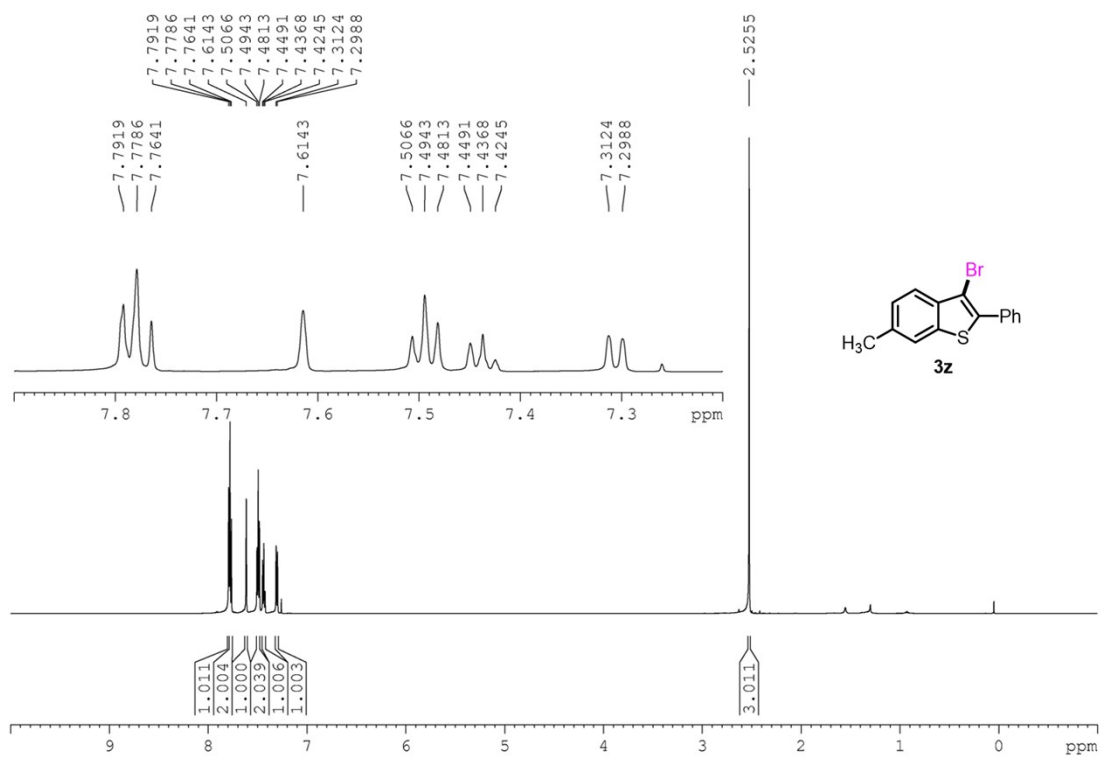
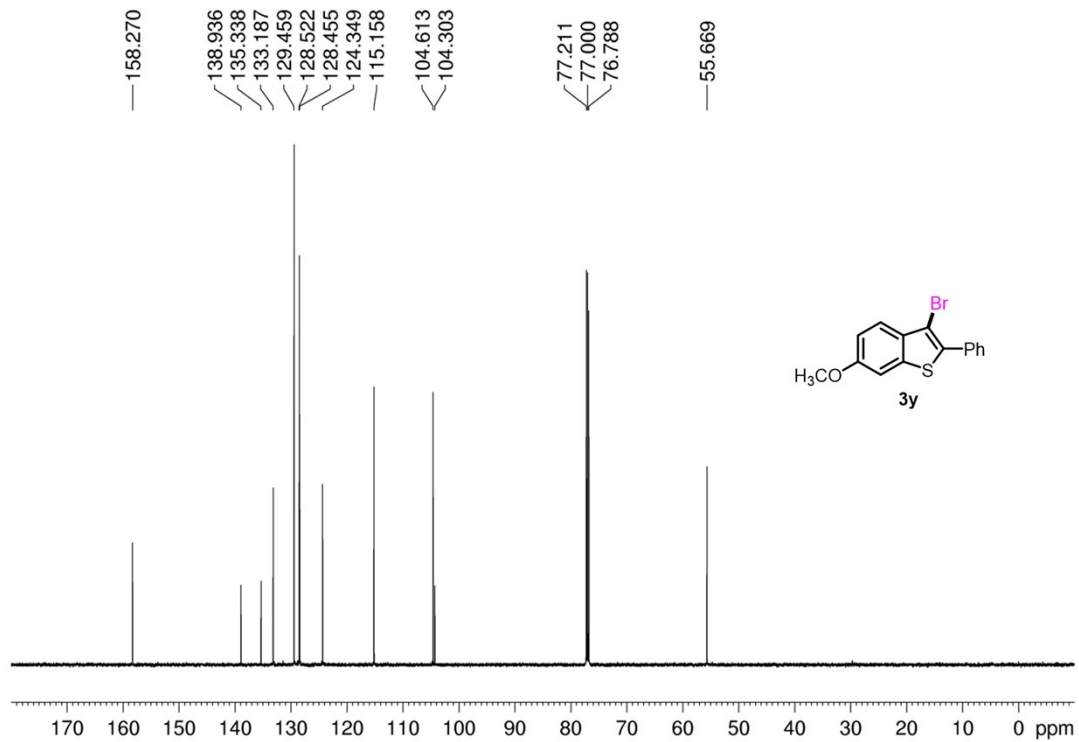


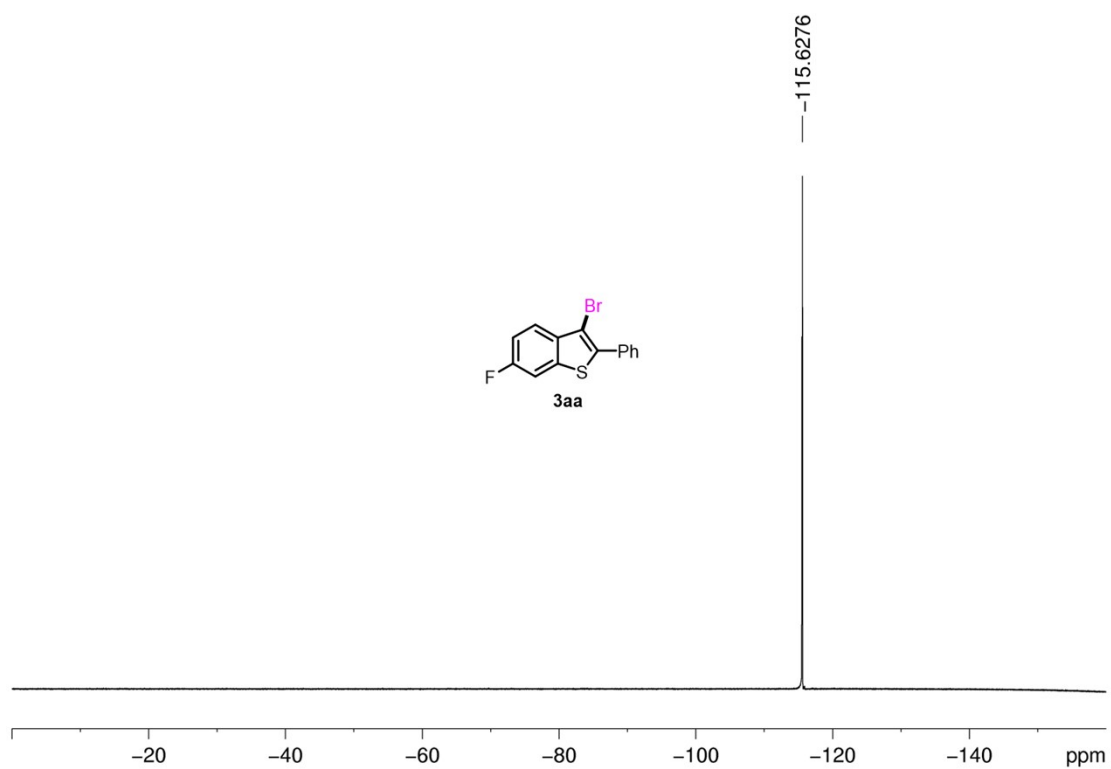
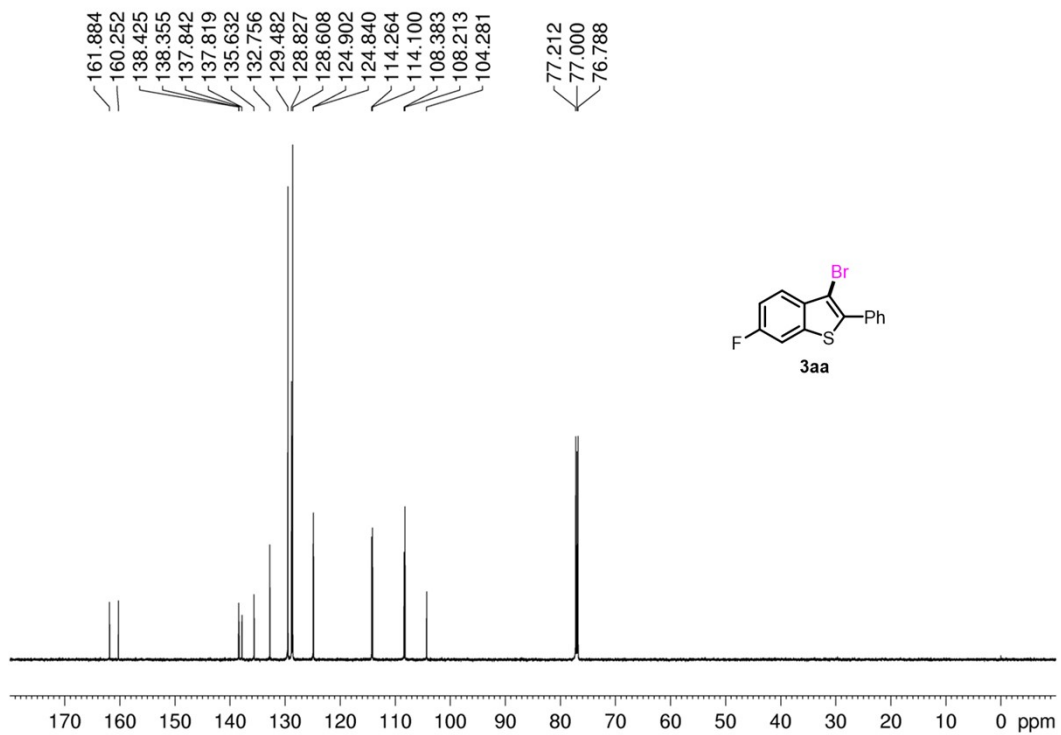
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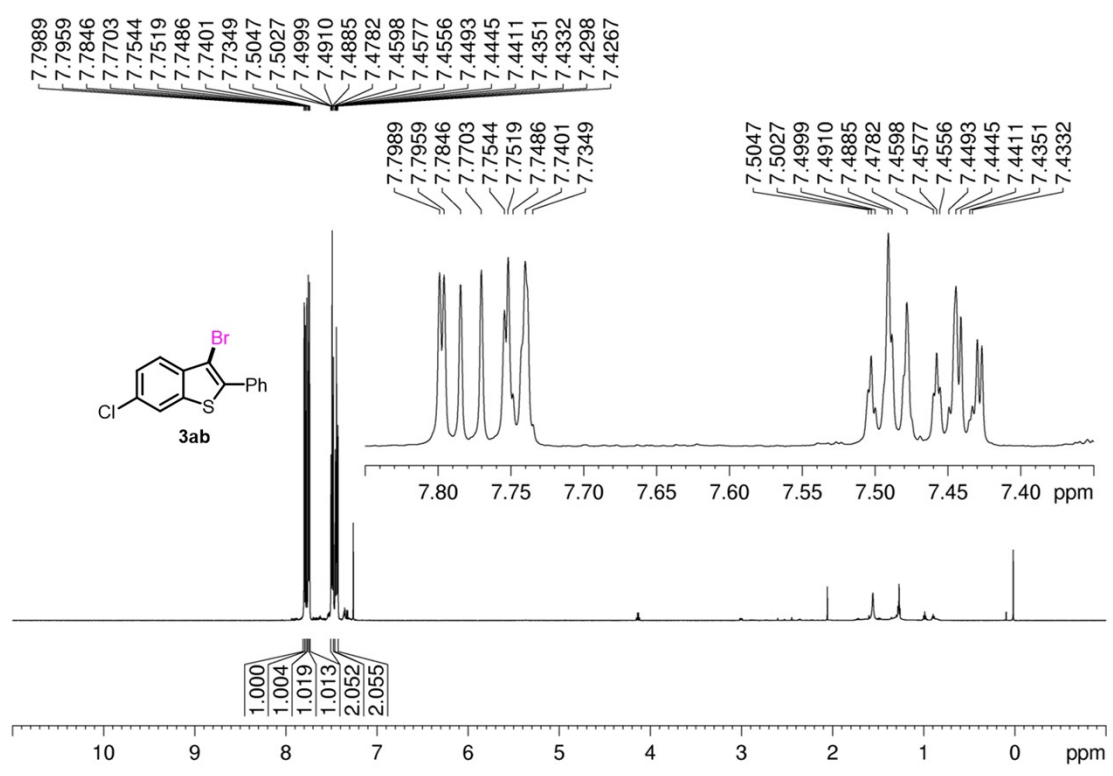
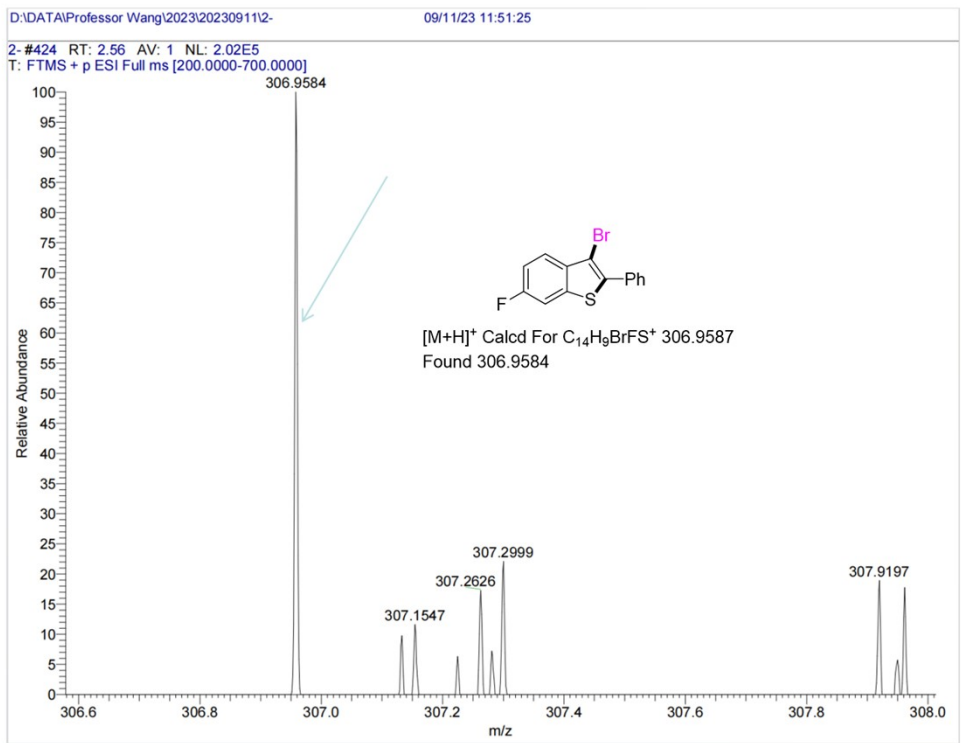
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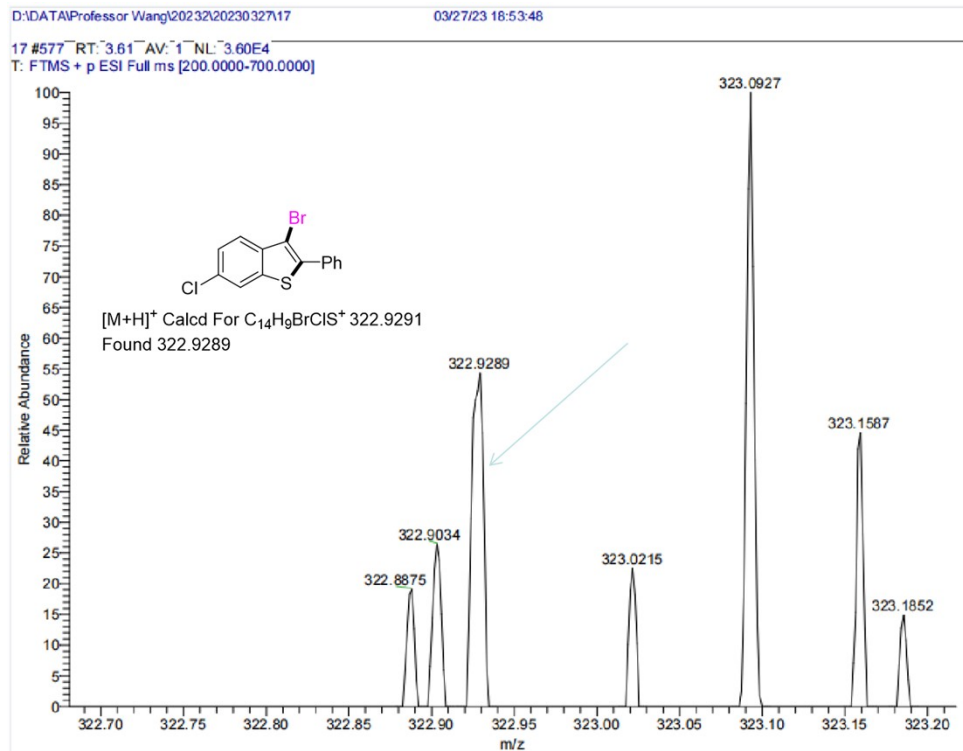
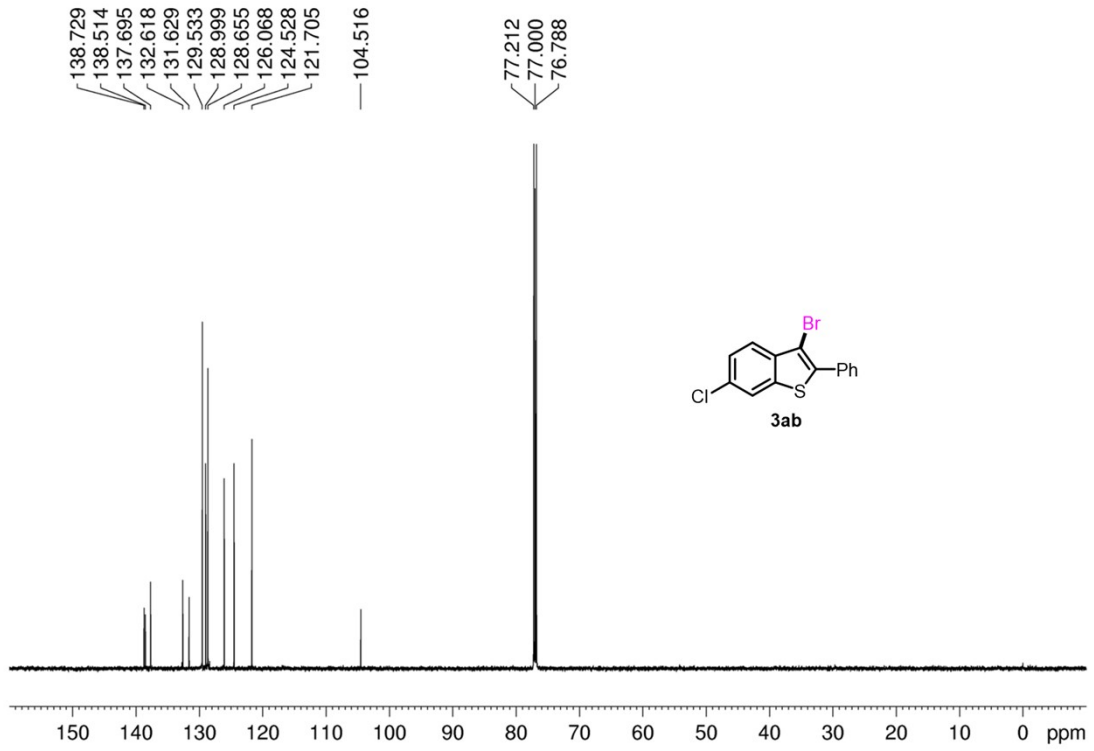


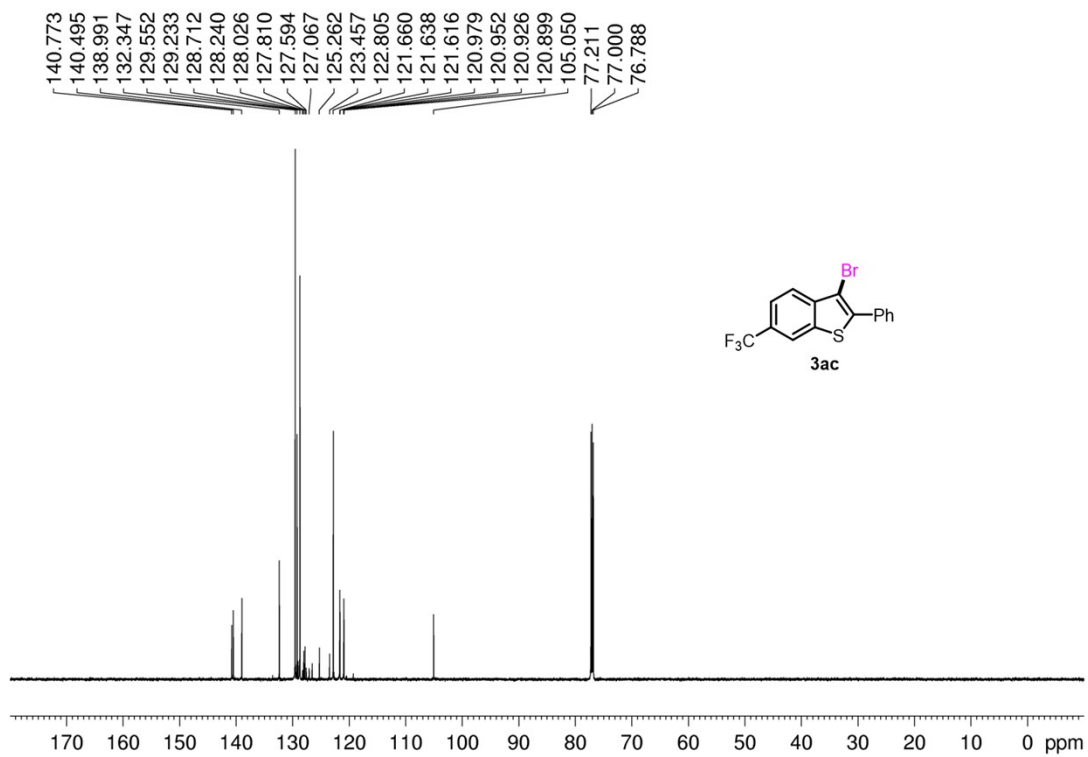
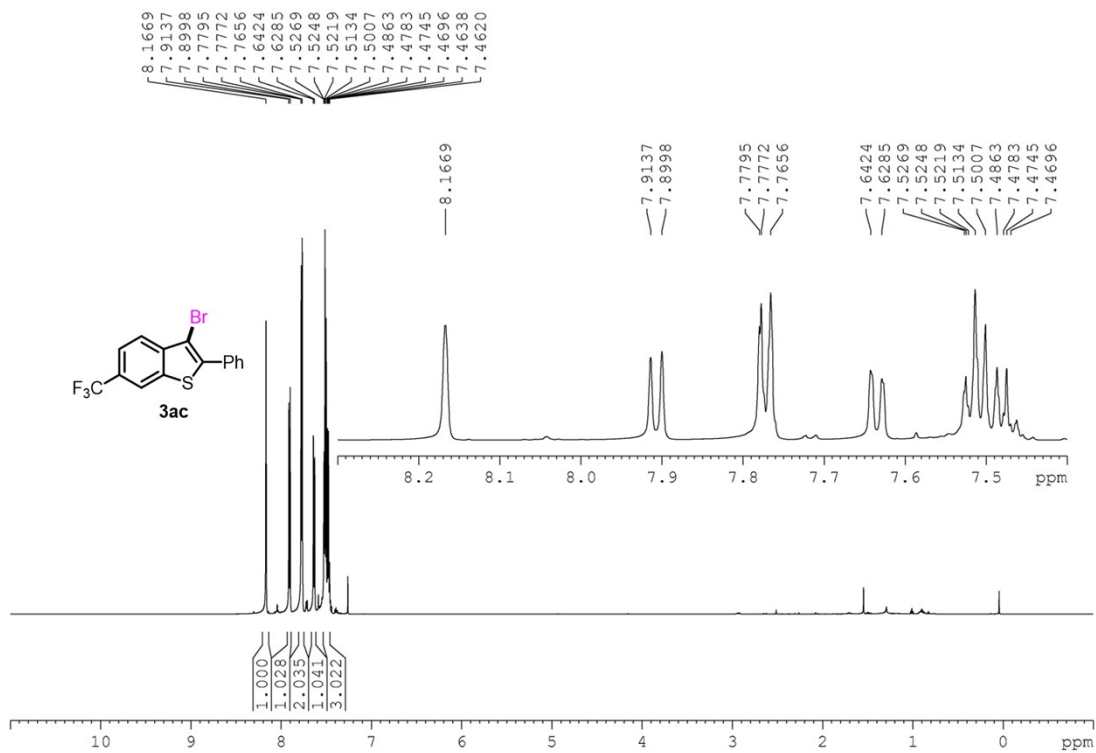


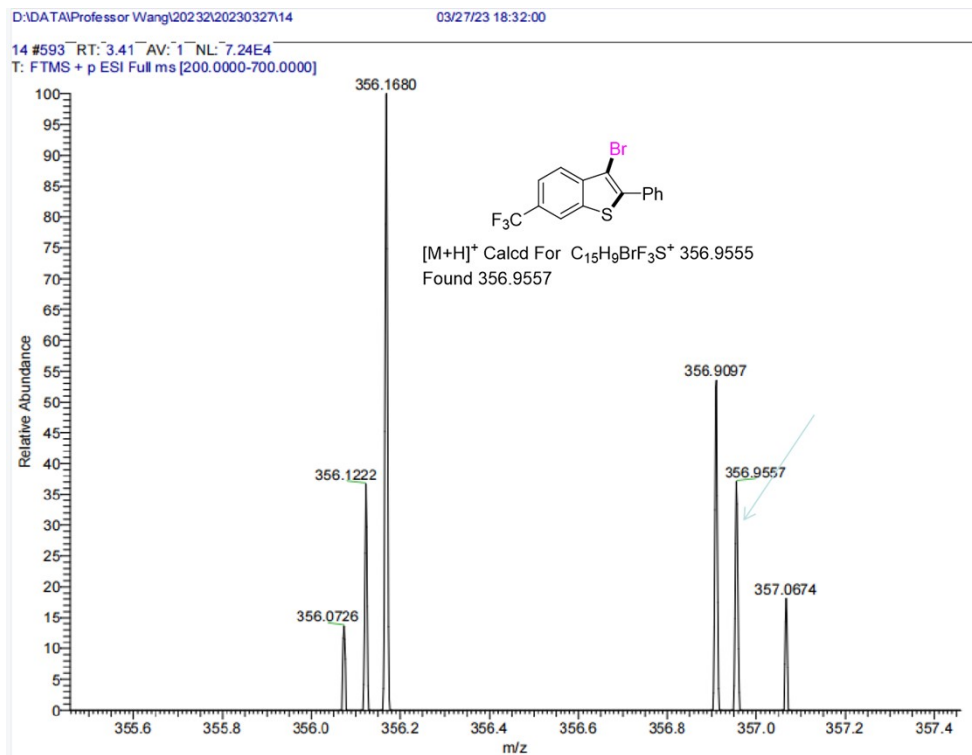


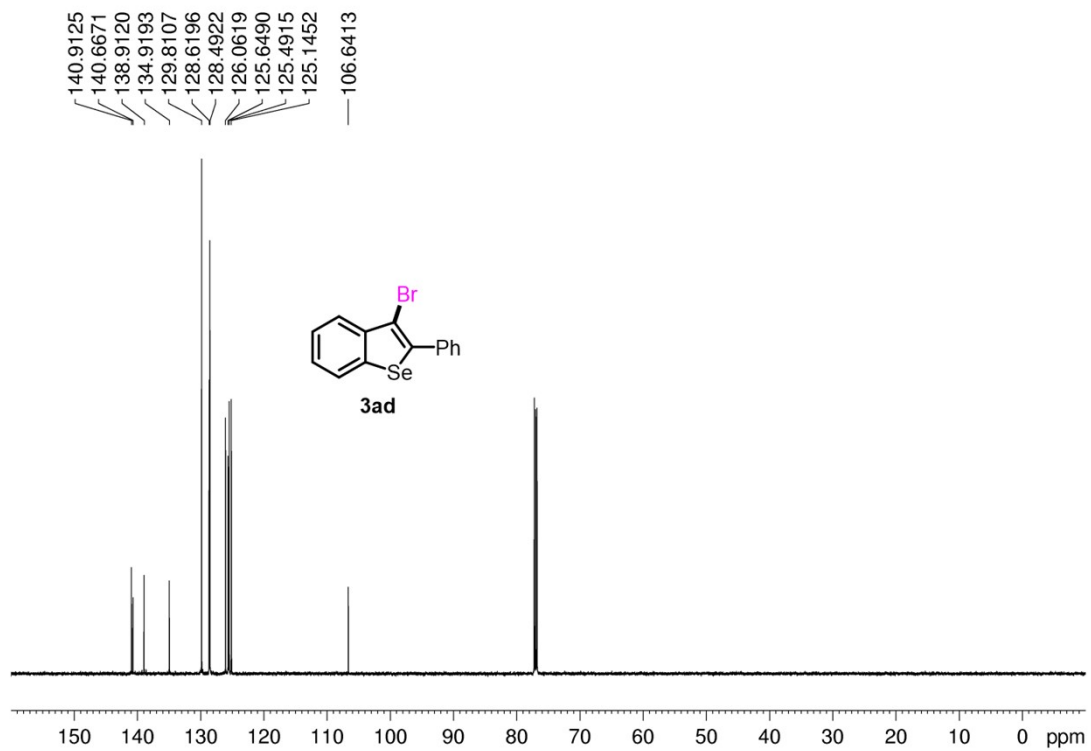
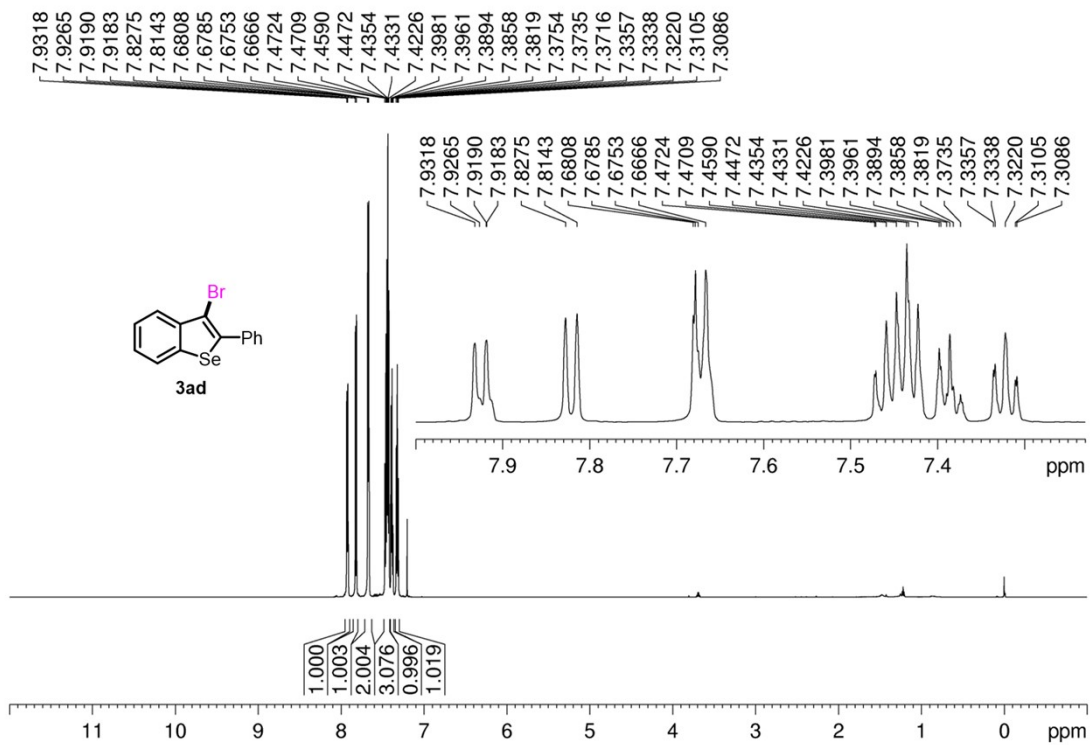


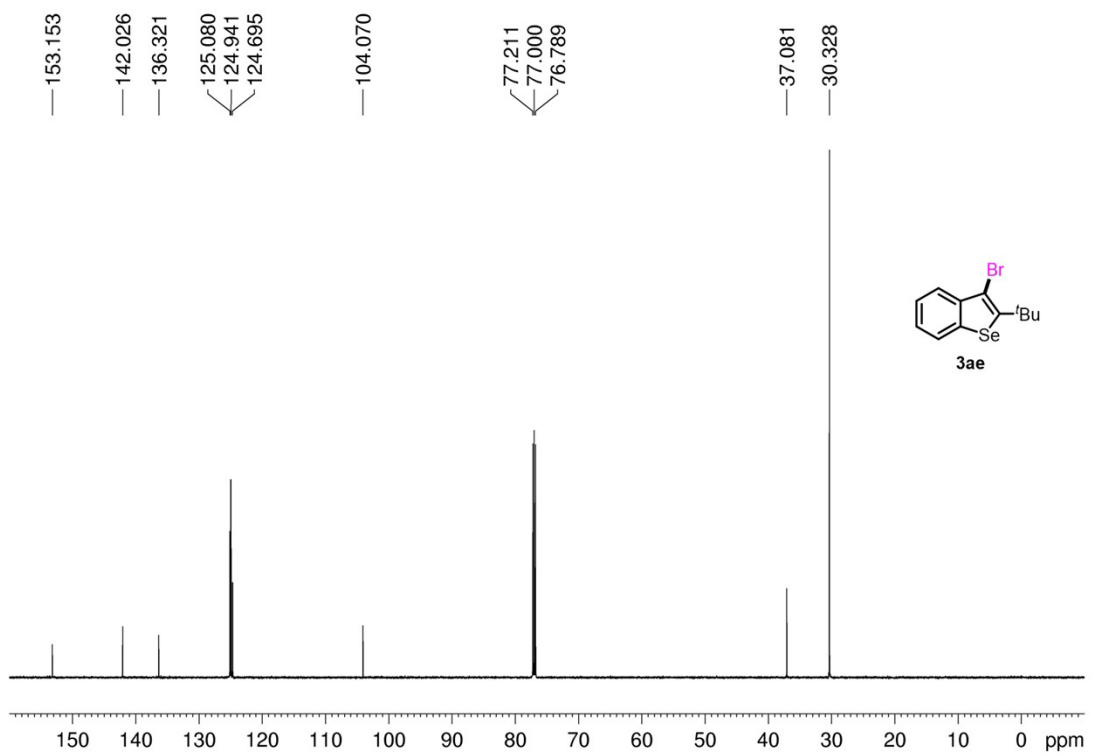
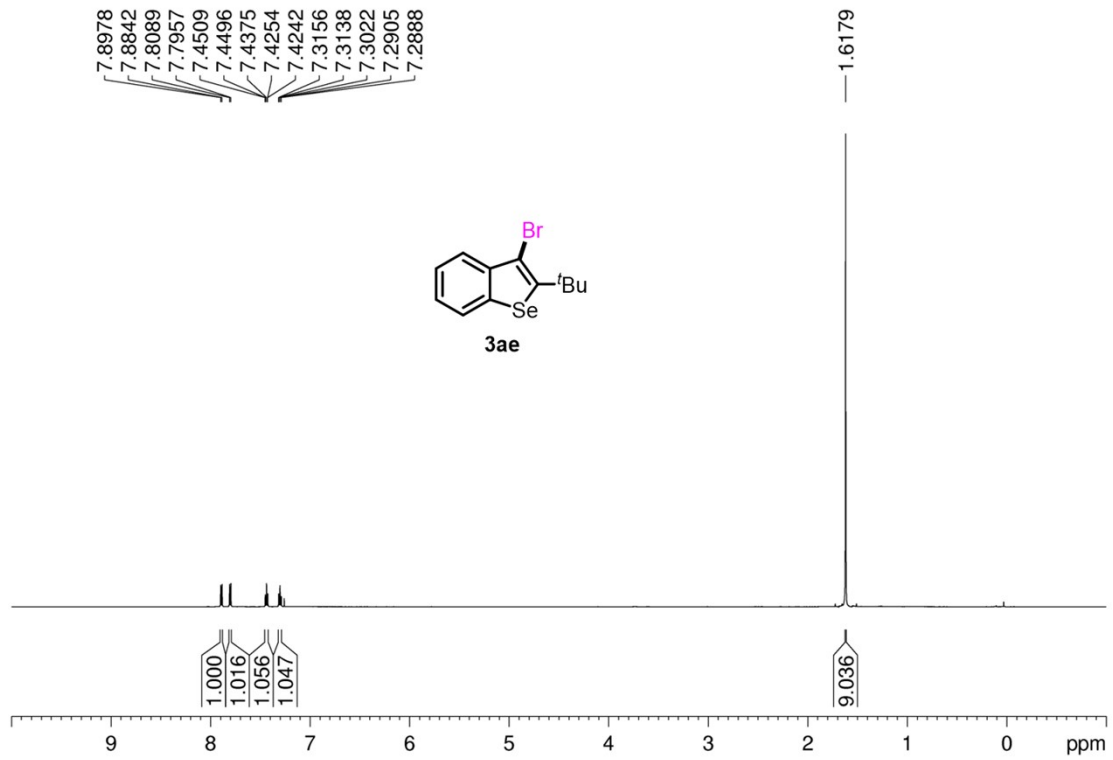


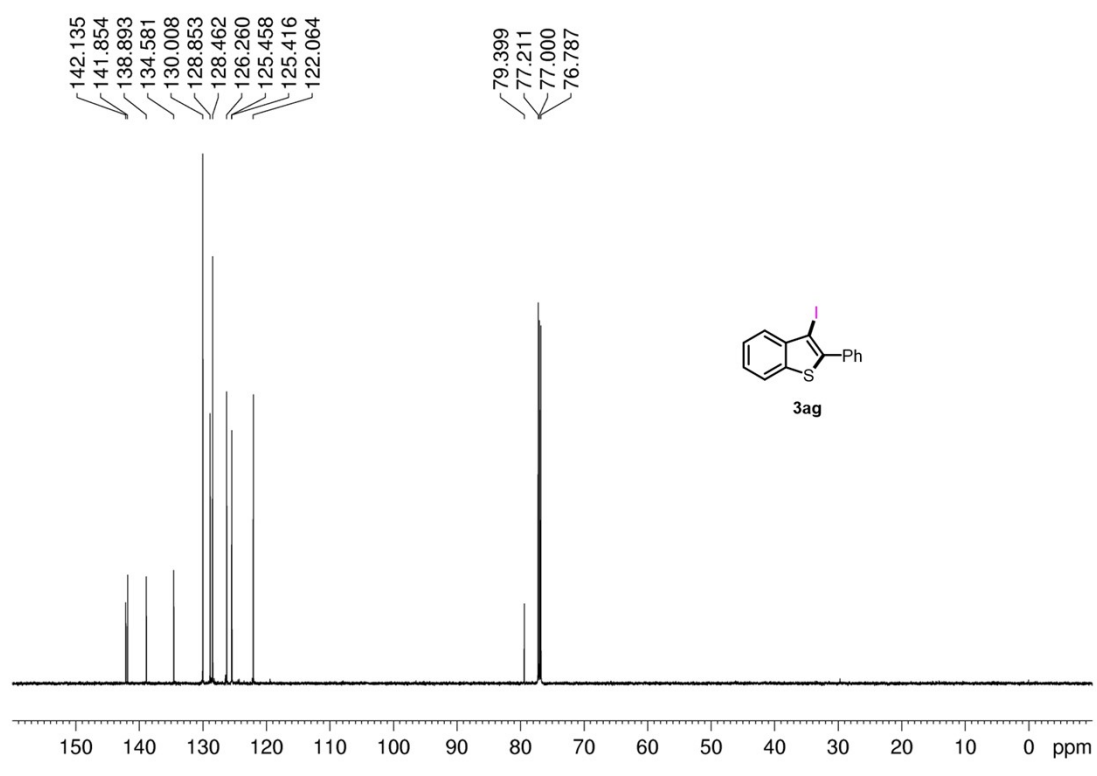
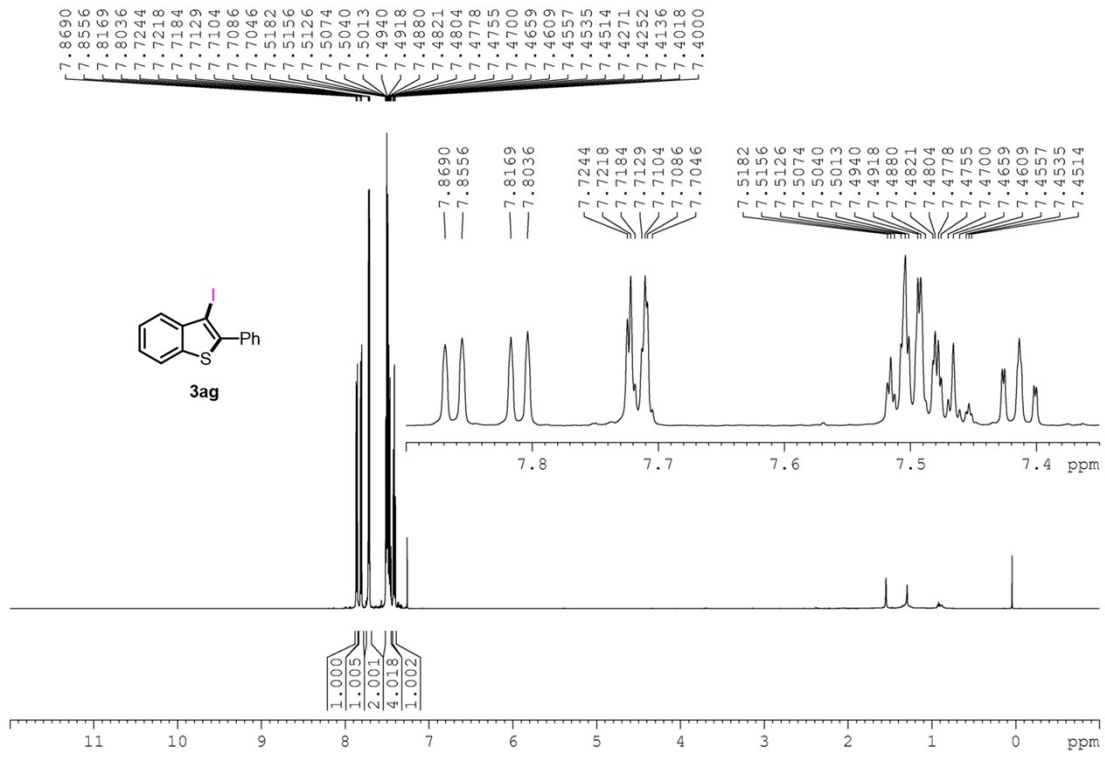


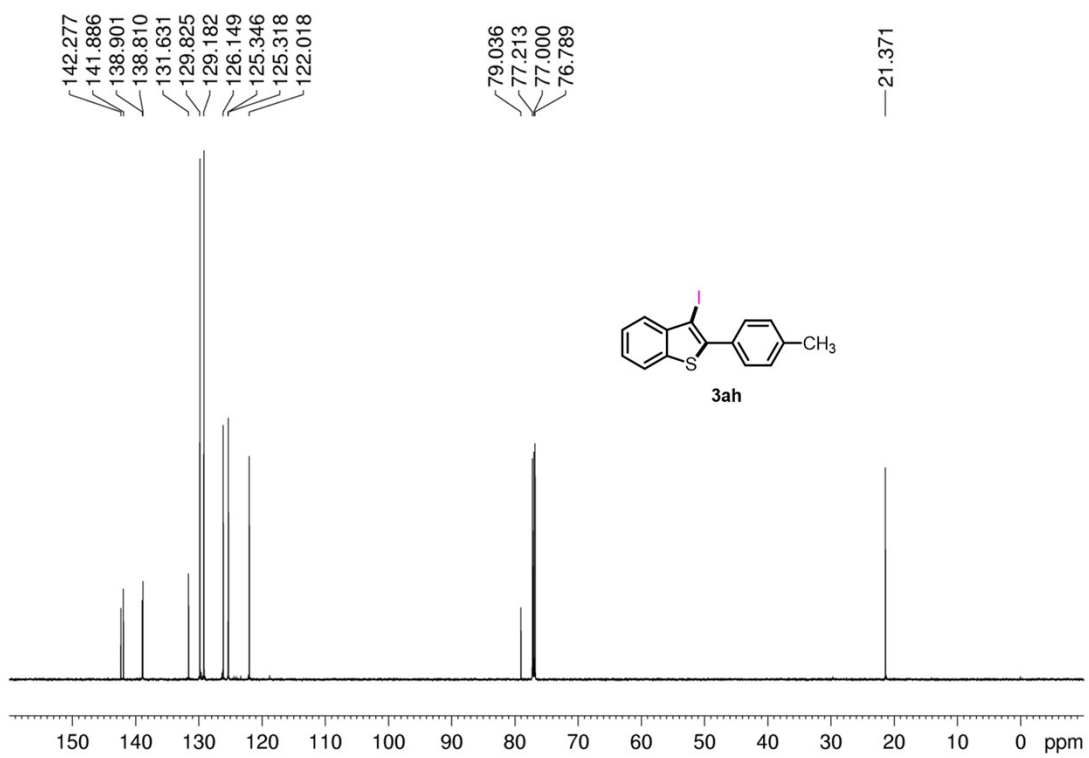
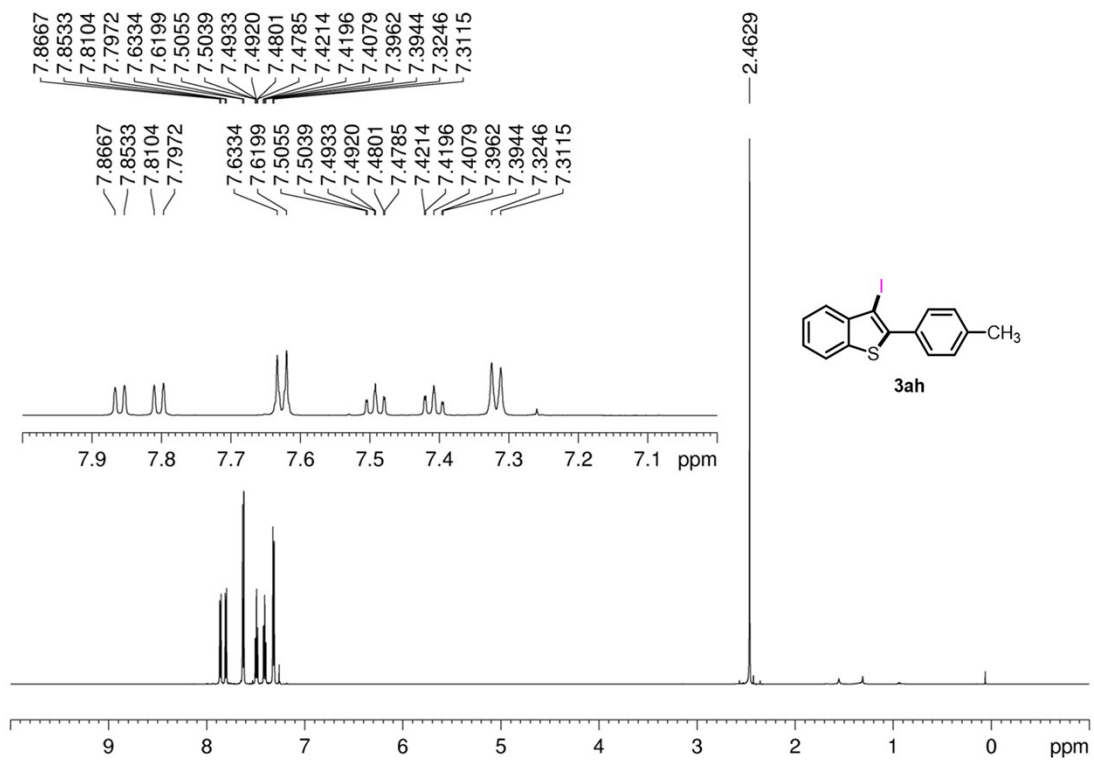


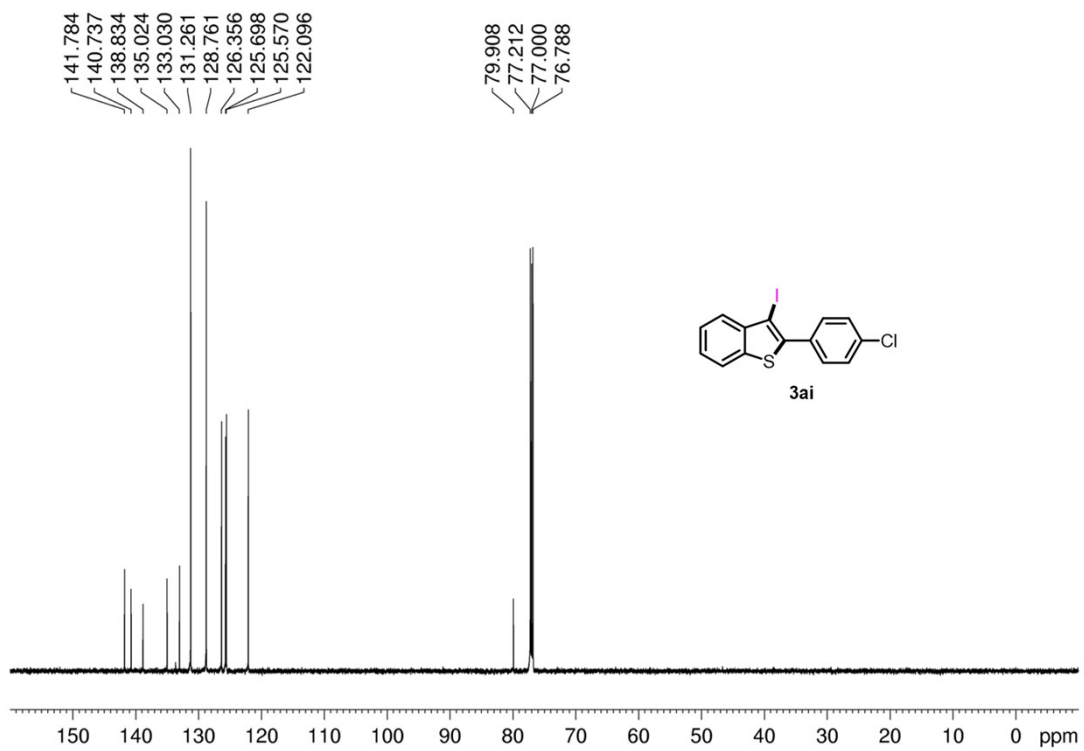
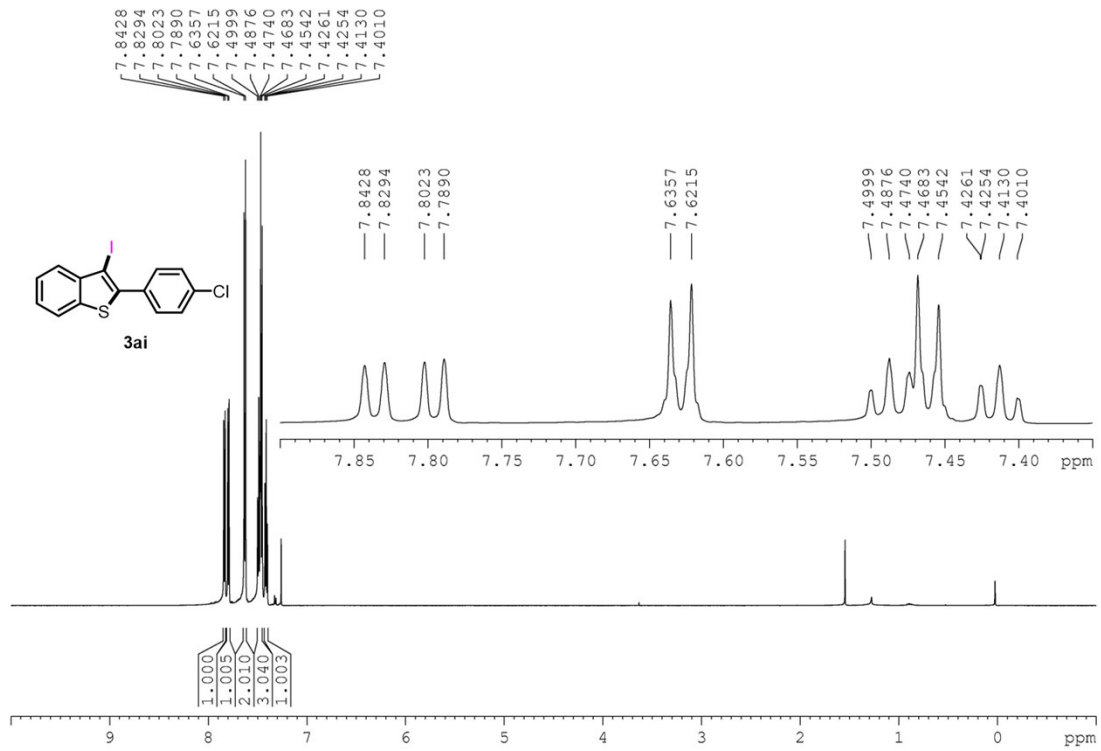


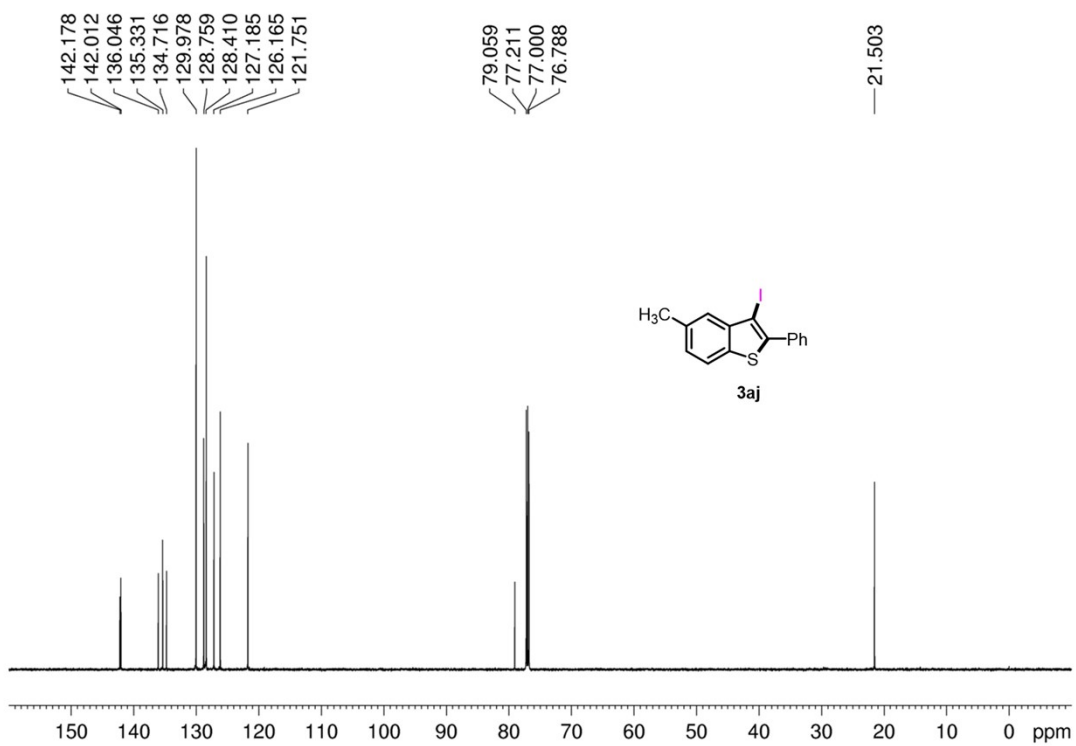
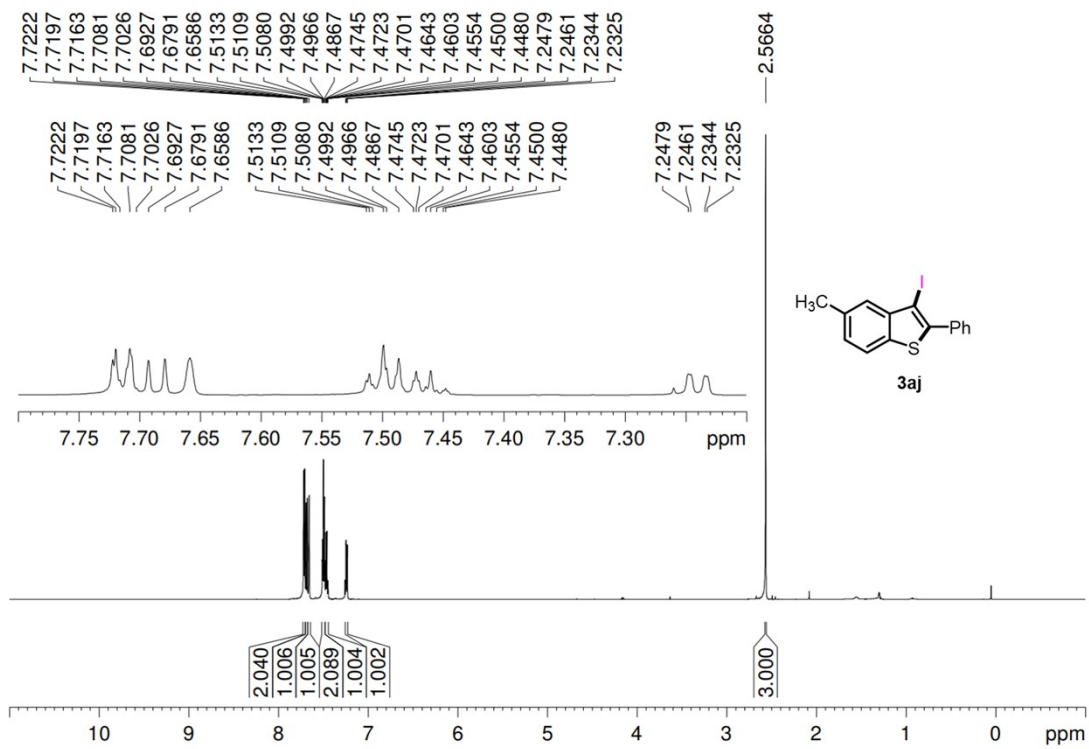




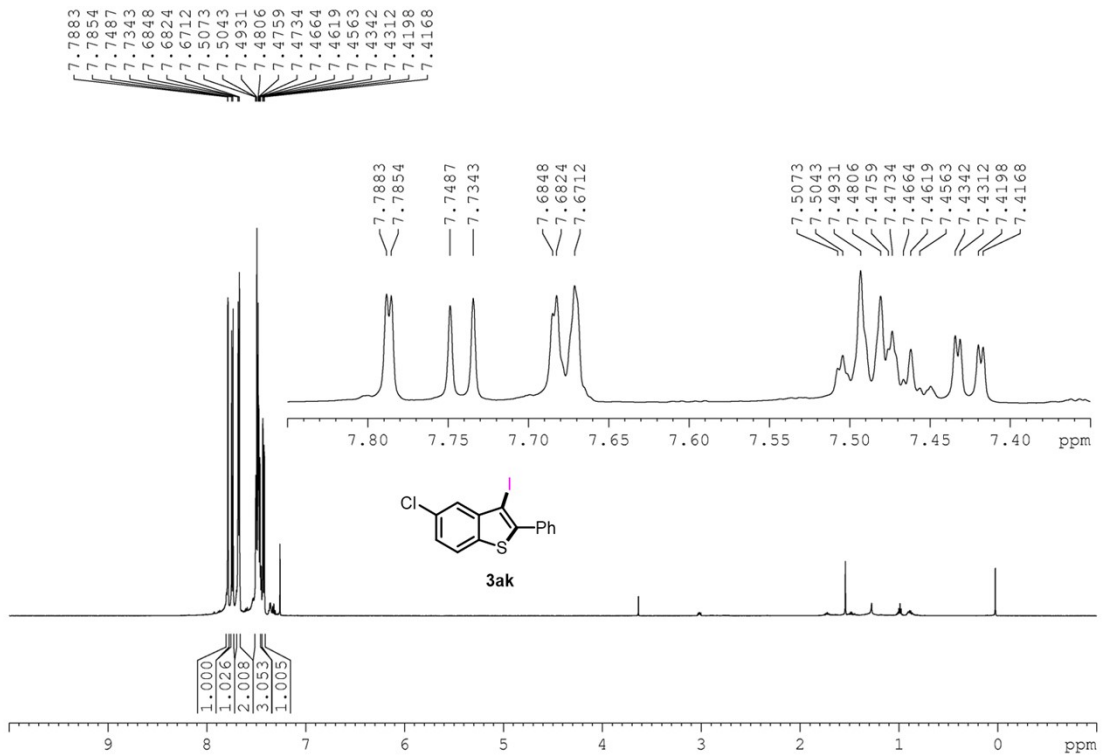
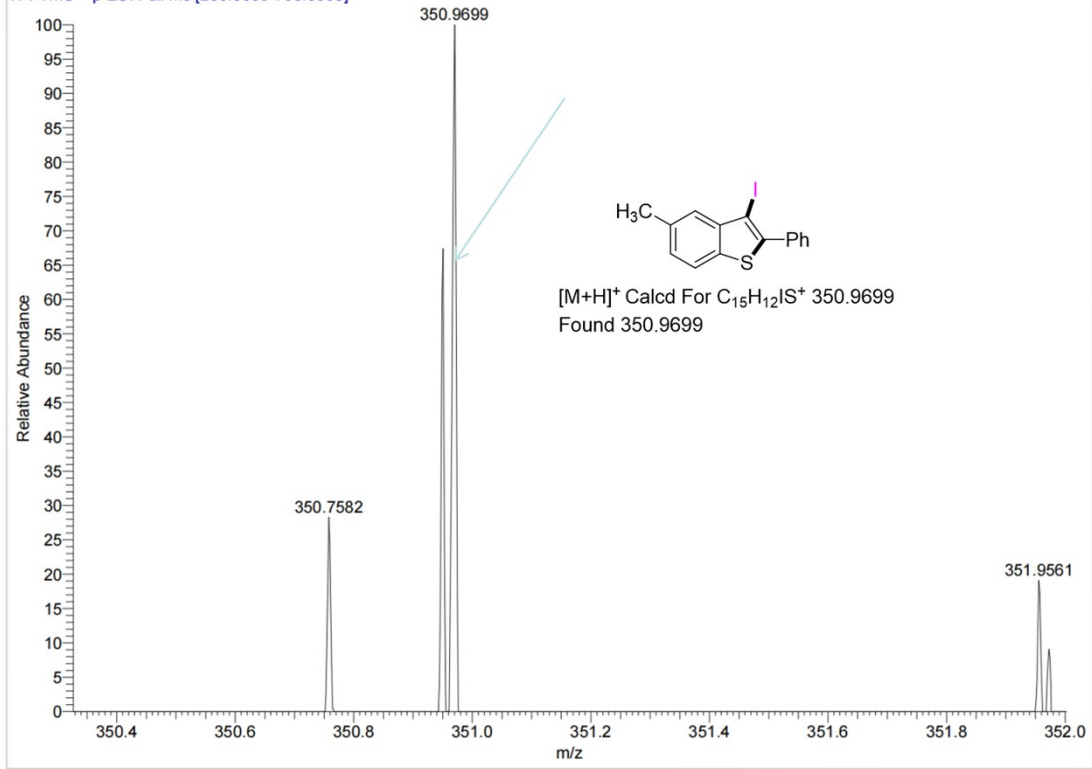


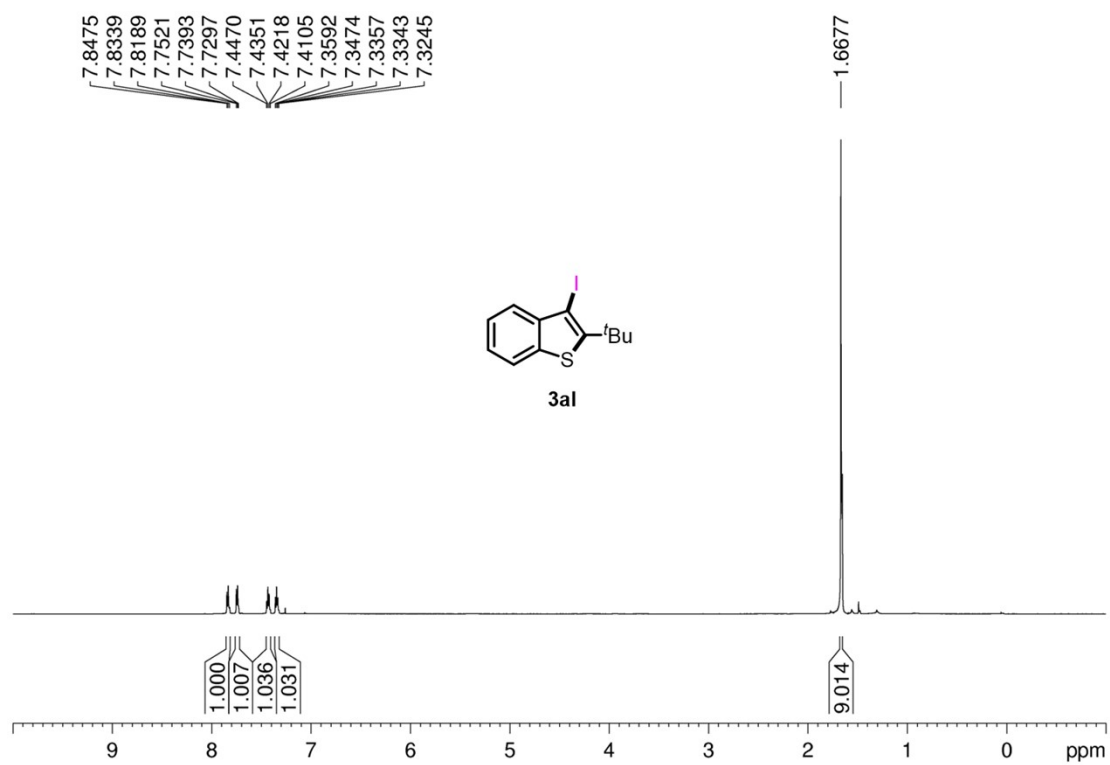
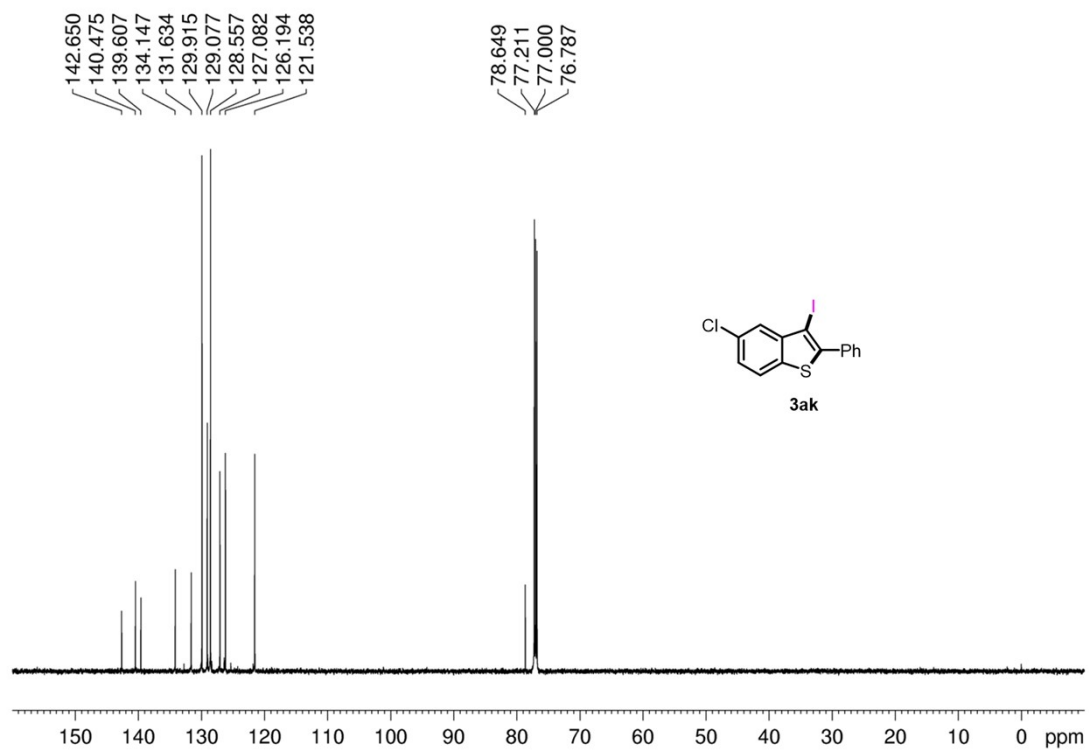


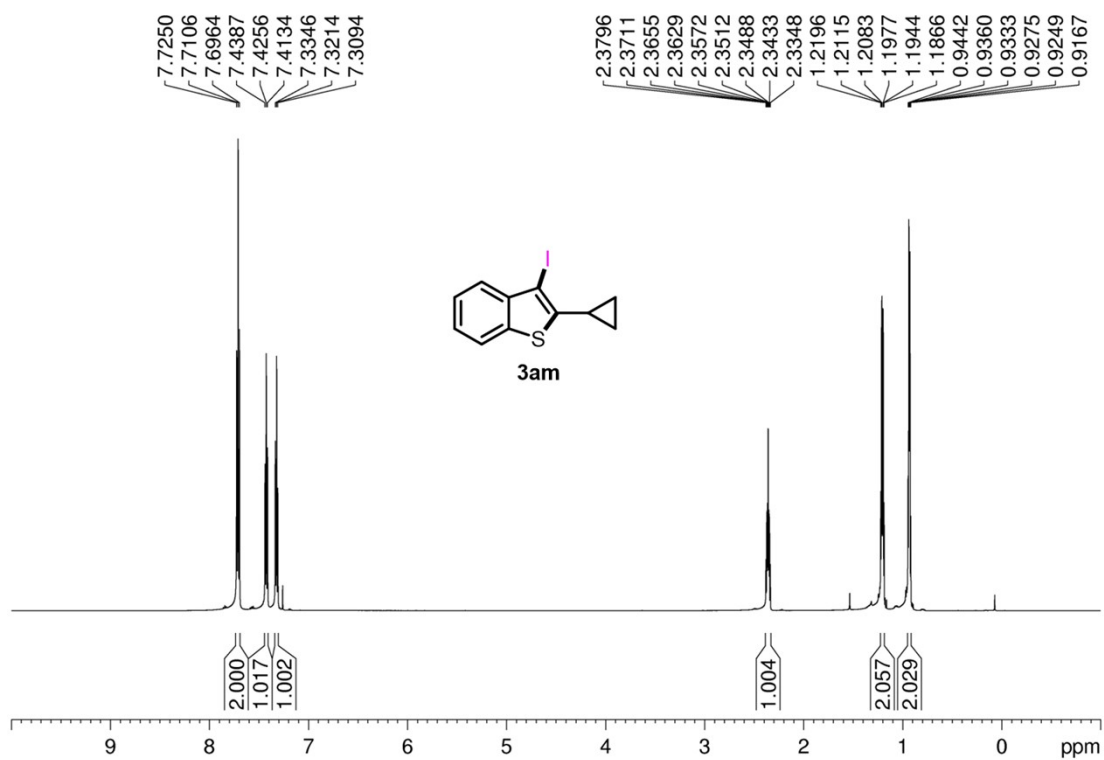
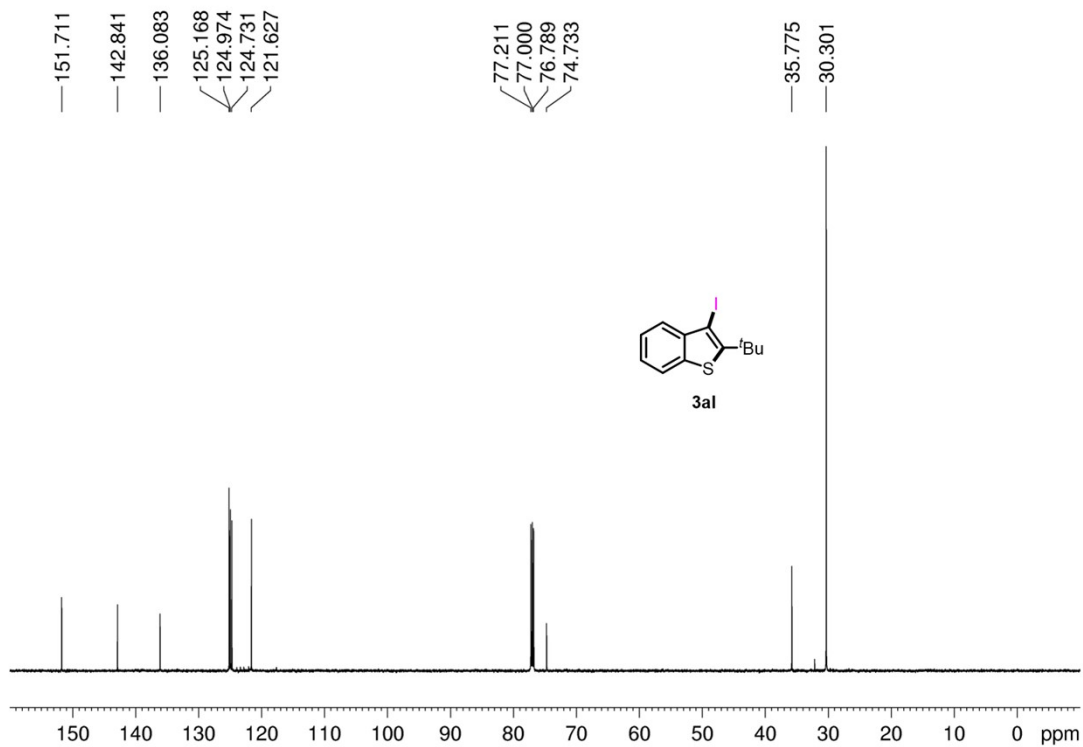


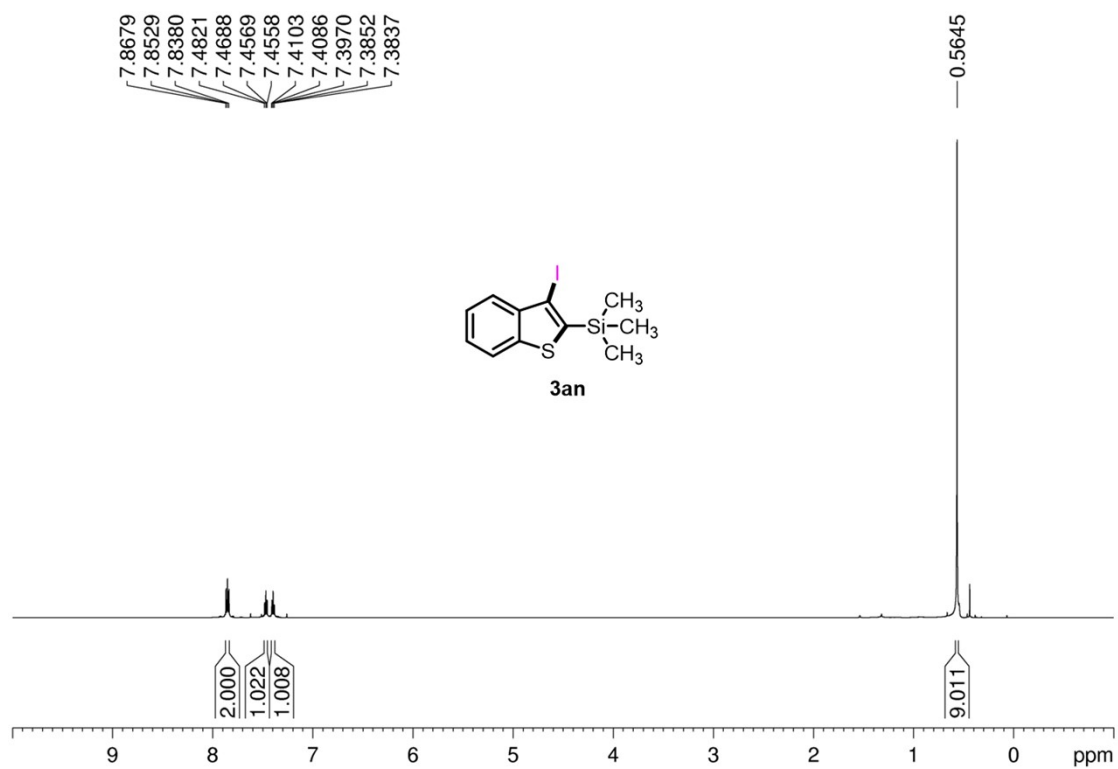
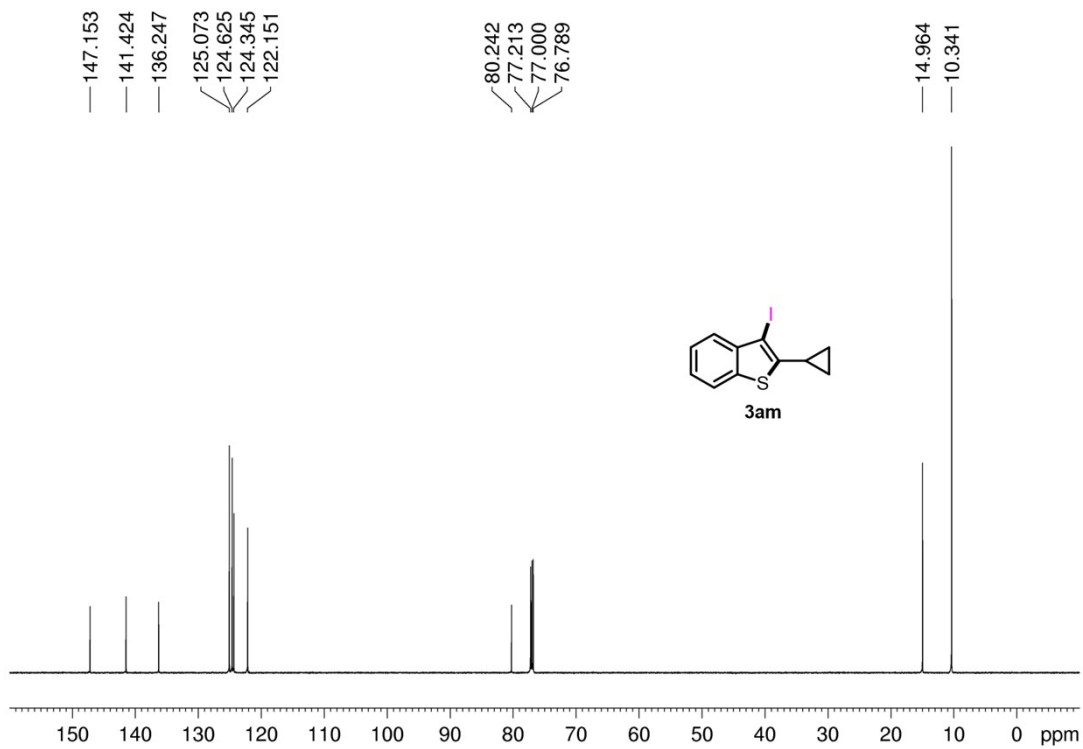


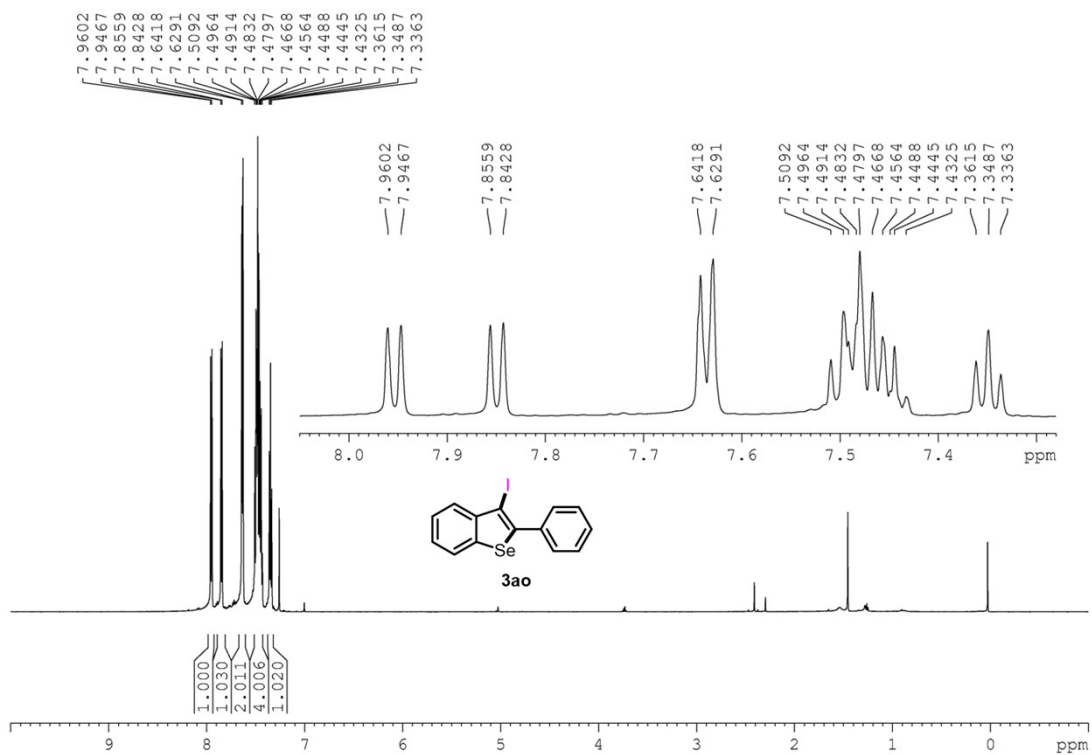
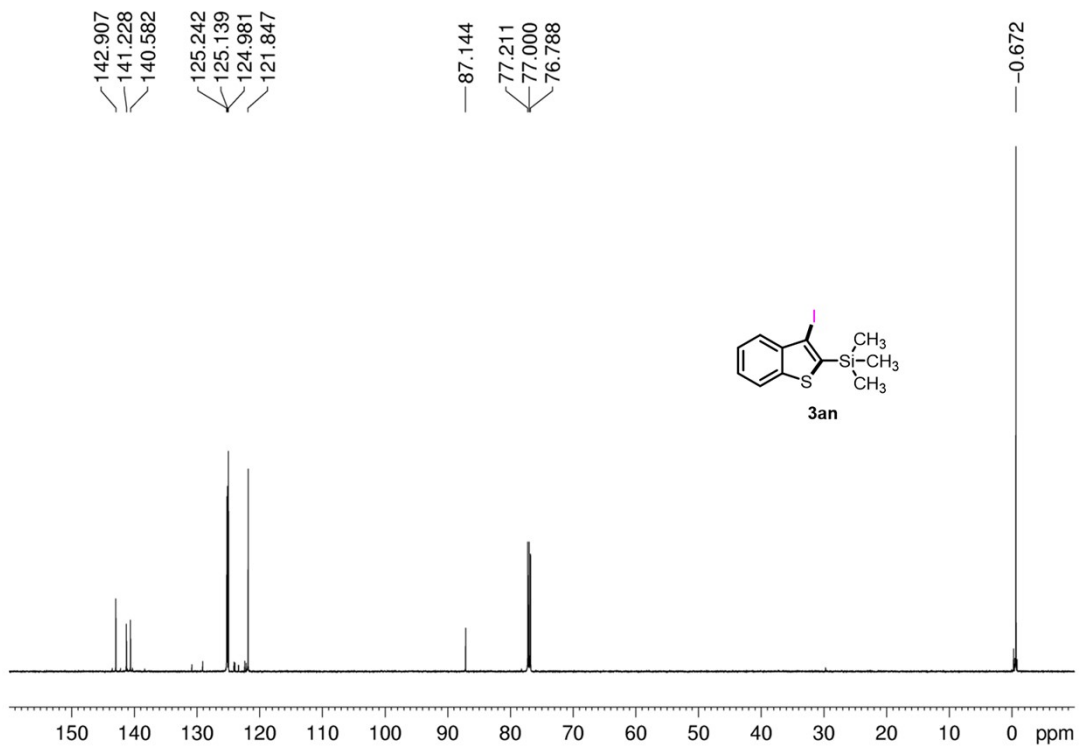
2- #525 RT: 3.09 AV: 1 NL: 2.38E5
T: FTMS + p ESI Full ms [200.0000-700.0000]

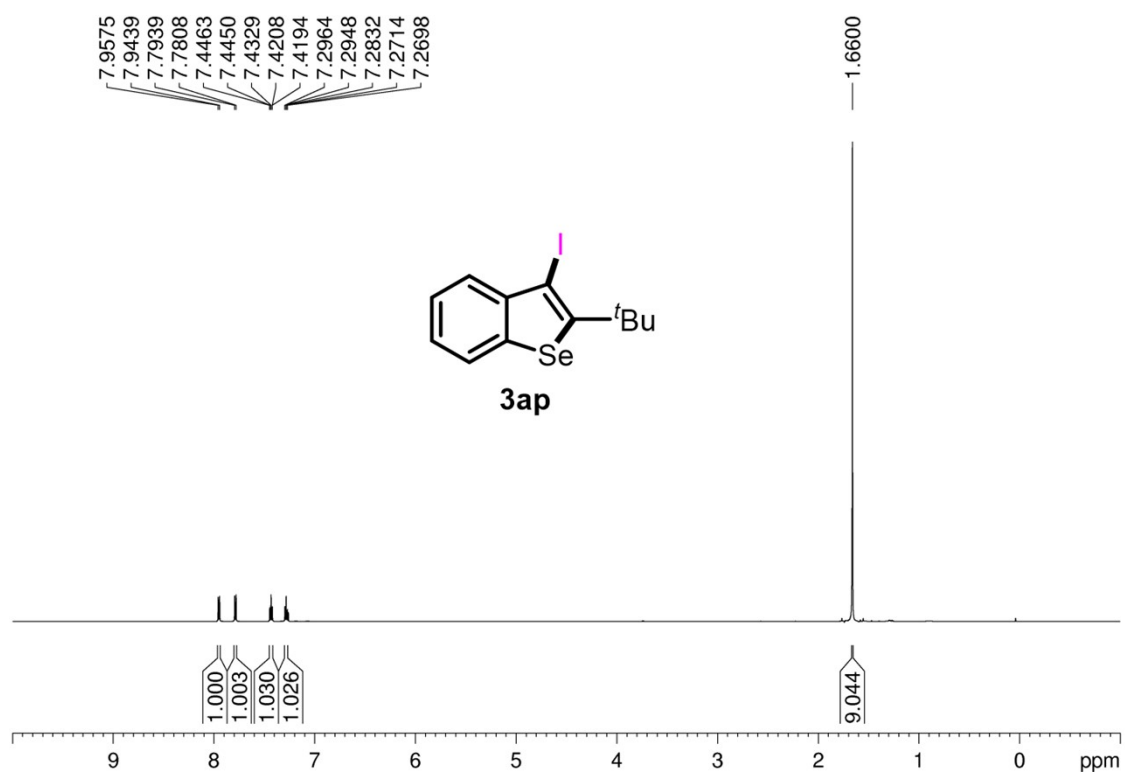
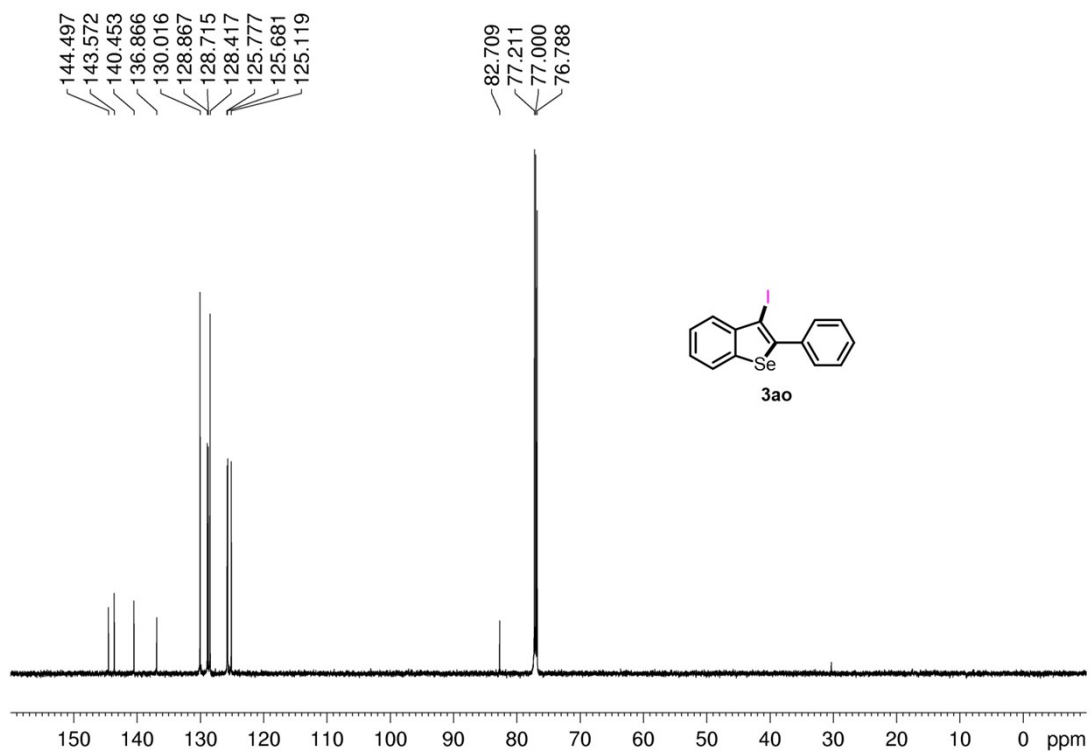


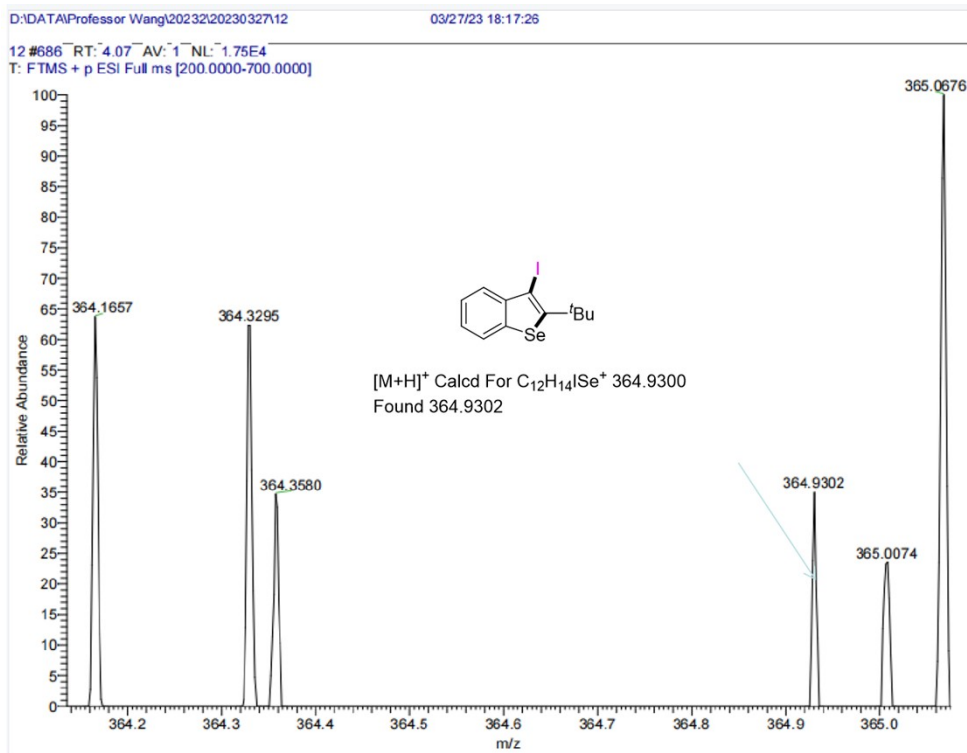
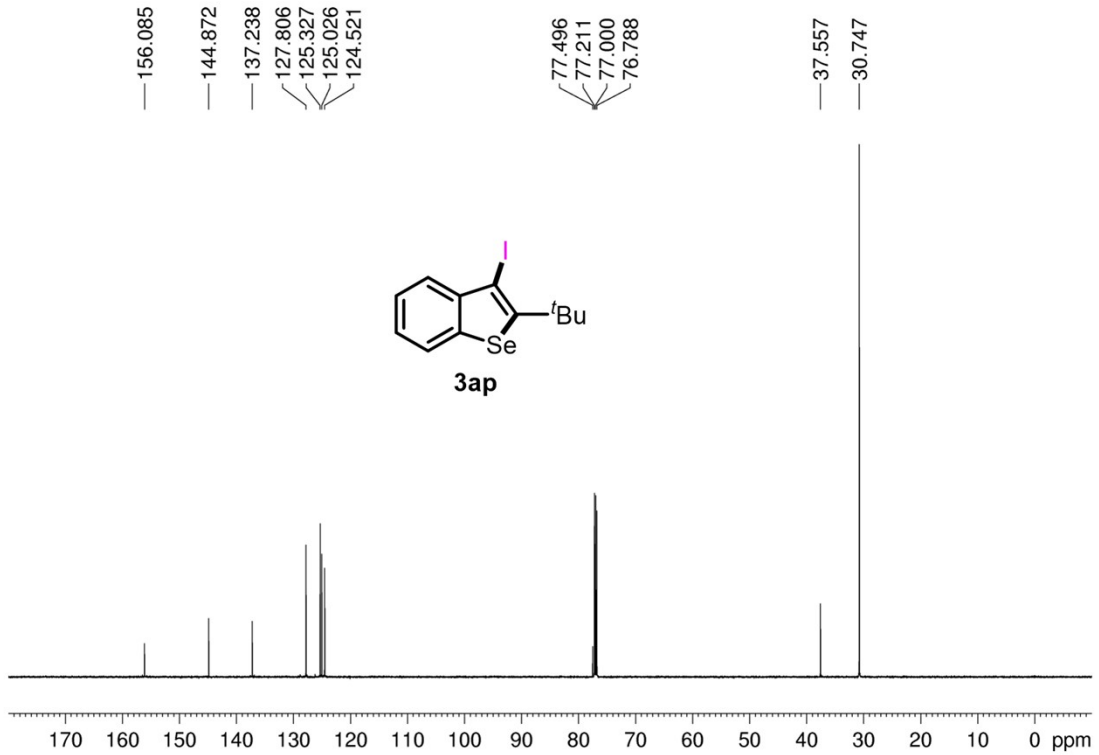


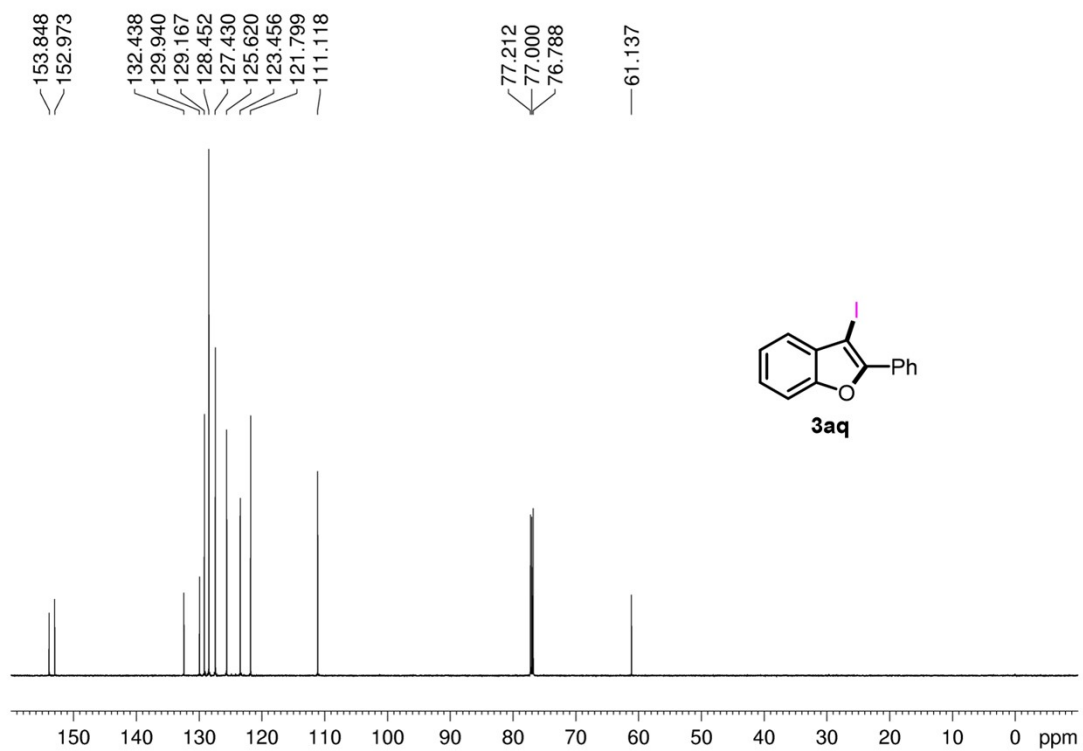
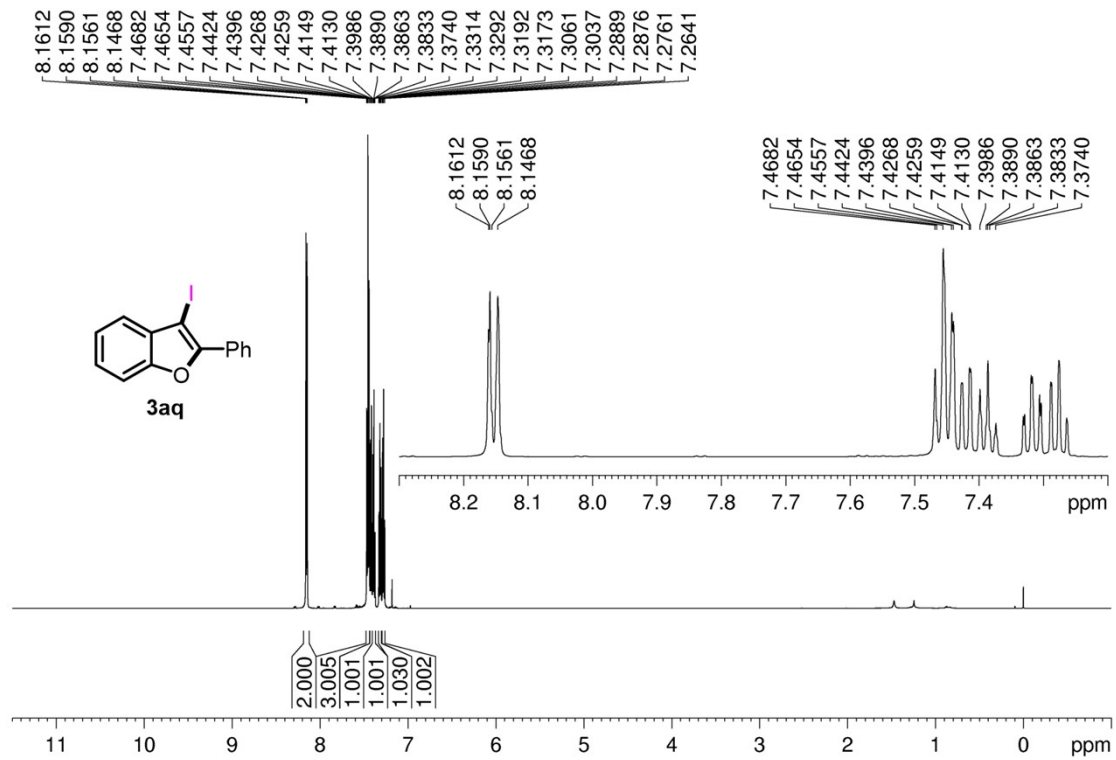


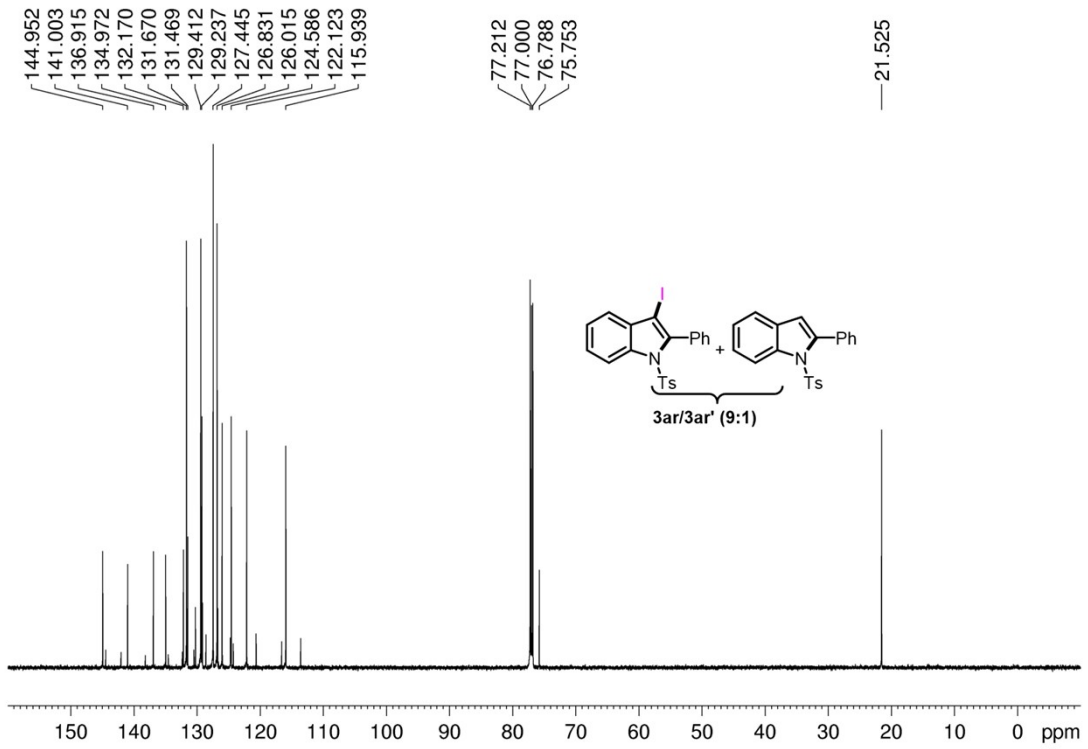
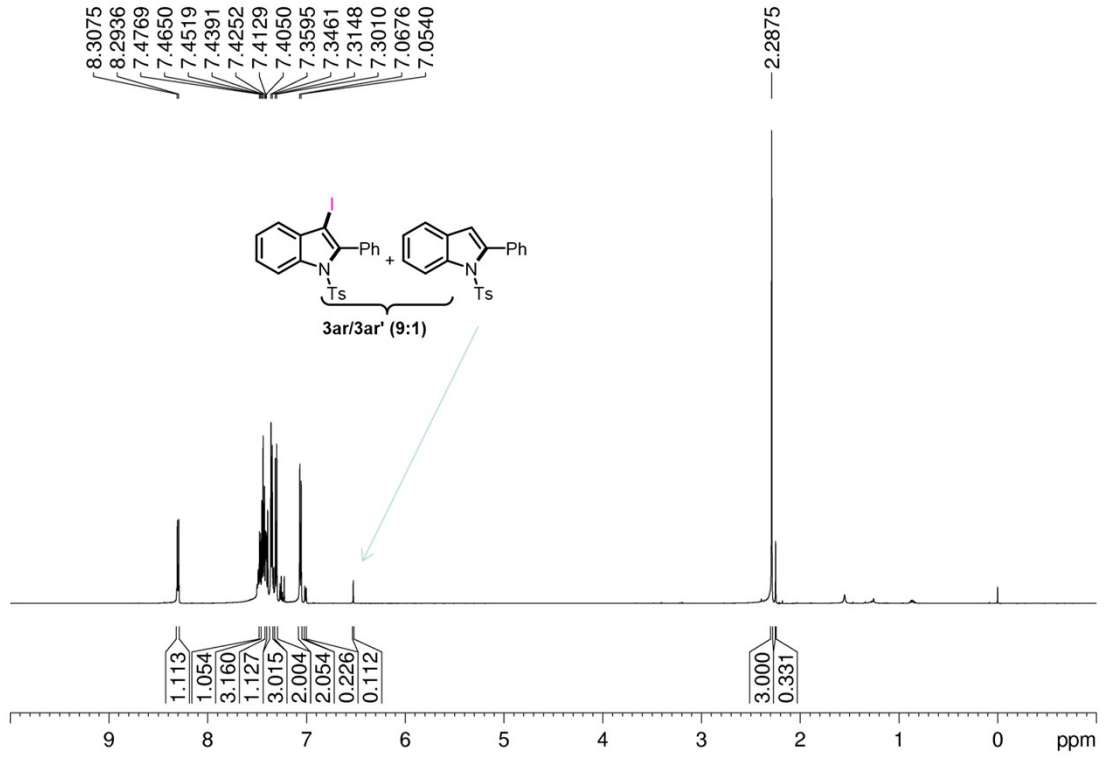


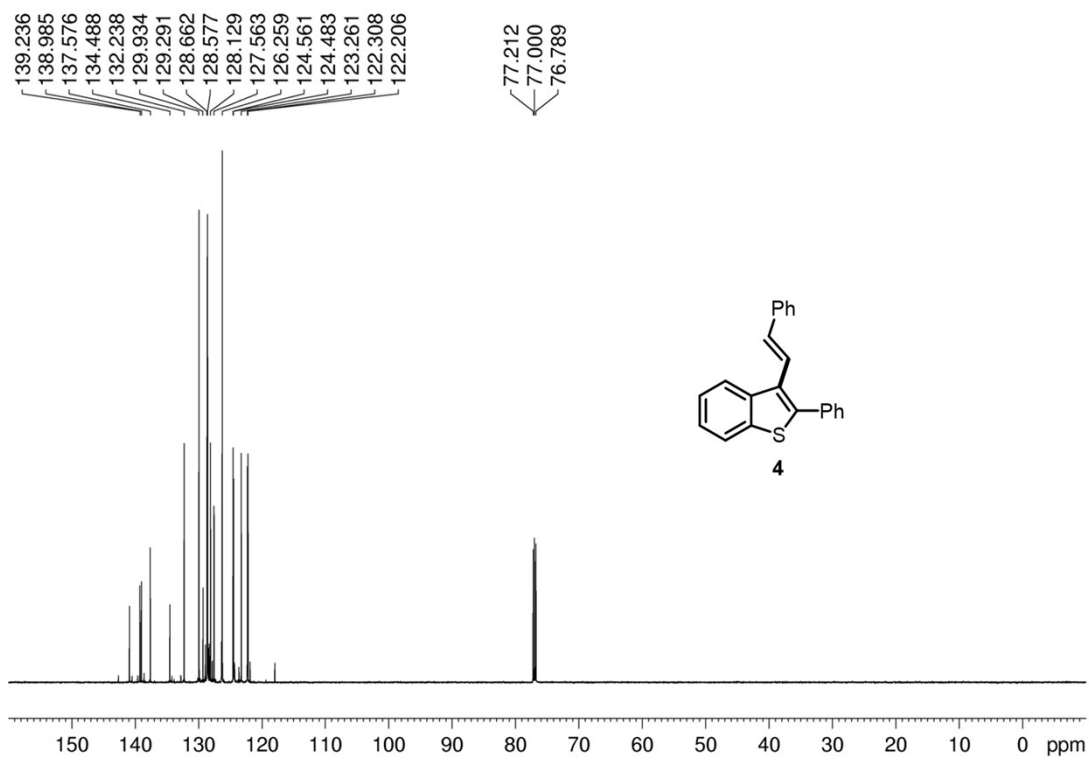
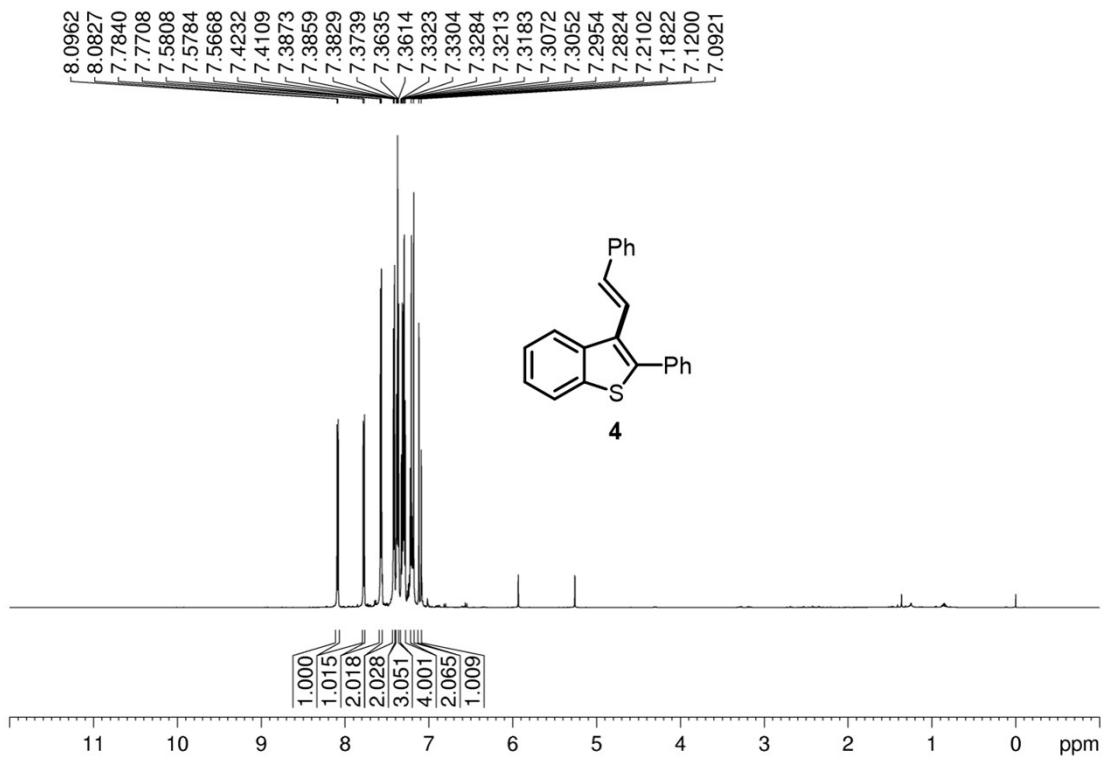












7 #447 RT: 2.80 AV: 1 NL: 2.60E5
T: FTMS + p ESI Full ms [200.0000-700.0000]