Supporting Information

Photoinduced borylation of *N*-tosylhydrazones and application into the drug derivation

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1. Materials and methods

Commercial reagents were used without purification. All solvents can be used directly without further drying and deoxygenation.

Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath.

Kessil lamps were purchased from Tansoole, with precise wavelengths (390 nm).

Chromatographic purification of products was accomplished using flash column chromatography (FC) on silica gel (200-300 mesh).

Thin layer chromatography (TLC) was performed using MilliporeSigma glass TLC plates (silica gel 60 coated with F_{254}, 250 μm) and spots were visualized using UV light (254 nm).

NMR-spectra were recorded on Bruker DRX-500 (500 MHz) spectrometer and calibrated by using residual undeuterated chloroform (δ = 7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C) and DMSO (δ = 2.50 ppm for ^{1}H, 39.52 ppm for ^{13}C) as internal references. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, td = triplet of doublets, ddd = doublet of doublet of doublets.

High-resolution mass spectra (HRMS) were recorded on an Agilent MSD-Trap-XCT or Q-Tof micro mass spectrometer.

Ultraviolet-visible absorption experiments were performed using a UV-8000S(T) spectrophotometer.

Cell viability assay

The RKO cell lines were plated into 96-well plates (1 × 104 cells/ml) containing different concentrations of **24d**, **25d**, **25e**, **25f**, **25g** and **25h**. After treatment for 24 h, the effect of these compounds on cell viability was measured via a Cell Counting Kit-8 (Yeasen, Shanghai, China) according to the manufacturer's instructions.

2. Setup for photochemical reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of 4 commercially available Kessil lamps which were purchased from Tansoole, with precise wavelengths (390 nm), cooling of the setup was performed by two commercially available fans to keep the temperature around 30 ℃. The distance between the lamp and the schlenk tube was set 3 cm. Magnetic stirring was performed at 500 rpm.

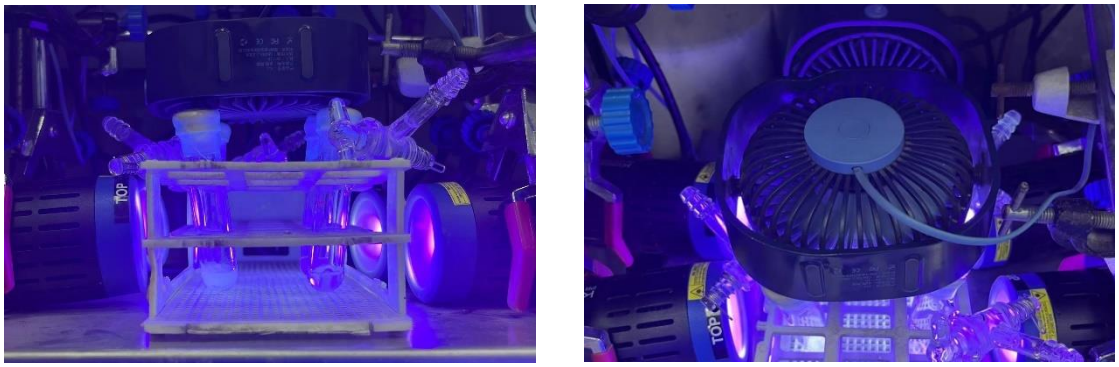


Figure S1. Photochemical set-up for regular-scale reactions.

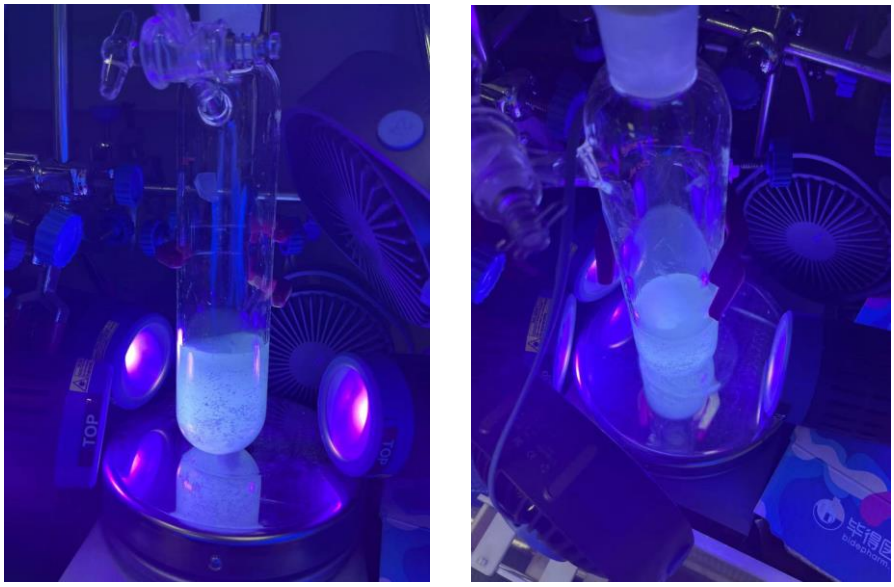
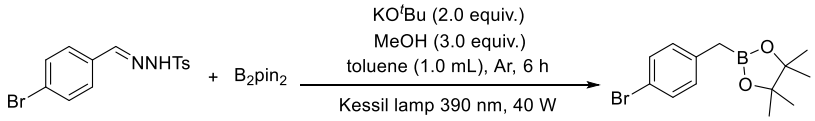


Figure S2. Photochemical set-up for large-scale reactions.

3. Optimization details for the reaction conditions

3.1 Control experiments[a,b]

Table S1:



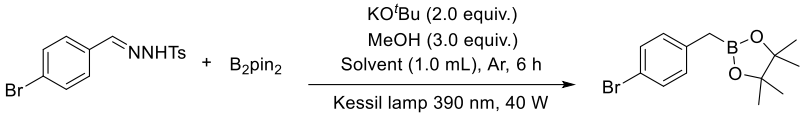
13a 1b 13d

Entry	Controlled parameter	Yield [%][b]
1	without light	trace
2	without MeOH	14
3	without KO^{t}Bu	trace

[a]Standard conditions: **13a** (0.2 mmol, 1.0 equiv.), **1b** (0.3 mmol, 1.5 equiv.), KO^{t}Bu (0.4 mmol, 2.0 equiv.), MeOH (0.6 mmol, 3.0 equiv.), toluene (1 mL), irradiation with 40 W Kessil lamps (390 nm) at room temperature (around 30 °C) with cooling fan under air for 6 h. [b]Yields were determined by ^{1}H NMR analysis using dibromomethane as an internal standard.

3.2 Screening of solvents[a,b]

Table S2:



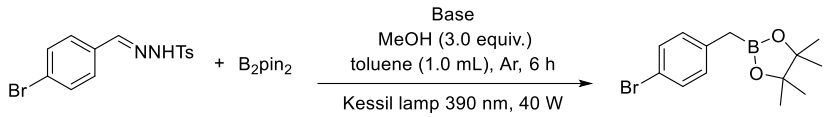
13a 1b 13d

Entry	Solvent (0.2 M)	Yield [%][b]
1	1,4-Dioxane	trace
2	DCM	16
3	DCE	trace
4	MeCN	n.d.
5	2-Me-THF	n.d.

[a]Reaction conditions: **13a** (0.2 mmol, 1.0 equiv.), **1b** (0.3 mmol, 1.5 equiv.), KO^{t}Bu (0.4 mmol, 2.0 equiv.), MeOH (0.6 mmol, 3.0 equiv.), solvent, irradiation with 40 W Kessil lamps (390 nm) at room temperature (around 30 °C) with cooling fan under air for 6 h. [b]Yields were determined by ^{1}H NMR analysis using dibromomethane as an internal standard.

3.3 Screening of bases[a,b]

Table S3:



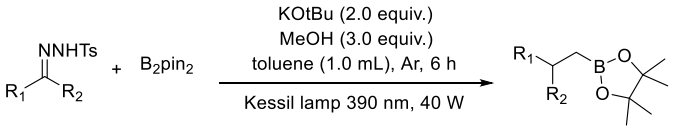
13a **1b** **13d**

Entry	Base	Yield [%][b]
1	KO^{t}Bu (2.0 equiv.)	83
2	DBU (2.0 equiv.)	n.d.
3	K_2CO_3 (2.0 equiv.)	trace
4	Cs_2CO_3 (2.0 equiv.)	30
5	NaOMe (2.0 equiv.)	52

[a]Standard conditions: **13a** (0.2 mmol, 1.0 equiv.), **1b** (0.3 mmol, 1.5 equiv.), base, MeOH (0.6 mmol, 3.0 equiv.), toluene (1 mL), irradiation with 40 W Kessil lamps (390 nm) at room temperature (around 30 °C) with cooling fan under air for 6 h. [b]Yields were determined by ^{1}H NMR analysis using dibromomethane as an internal standard.

3.4 Screening of *N*-tosylhydrazones [a,b]

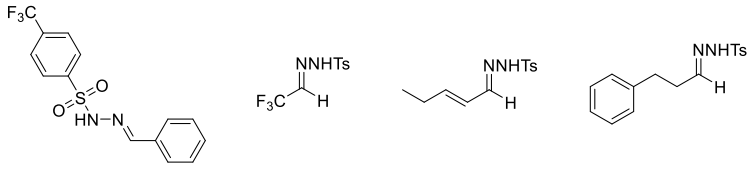
Table S4:



13a' **1b** **13d'**

Entry	Reagent 1	Yield [%][b]
1	13ab	55
2	13ac	n.d.
3	13ad	trace
4	13ae	trace

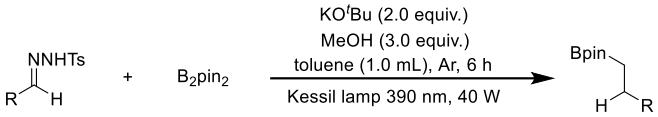
[a]Standard conditions: **13a'** (0.2 mmol, 1.0 equiv.), **1b** (0.3 mmol, 1.5 equiv.), KO^{t}Bu (0.4 mmol, 2.0 equiv.), MeOH (0.6 mmol, 3.0 equiv.), toluene (1 mL), irradiation with 40 W Kessil lamps (390 nm) at room temperature (around 30 °C) with cooling fan under air for 6 h. [b]Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.



13ab **13ac** **13ad** **13ae**

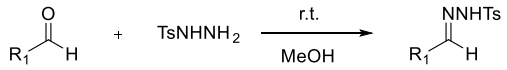
4. General procedures

4.1 General procedure A to afford benzyl boronates



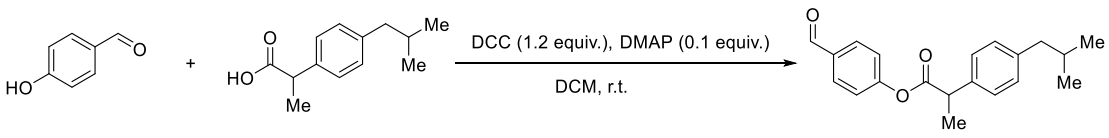
A 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone, B_2pin_2 (1.5 equiv., 0.3 mmol, 76.2 mg), KO^{t}Bu (2.0 equiv., 0.4 mmol, 44.9 mg), MeOH (3.0 equiv., 0.6 mmol, 23.6 μL), toluene (1 mL) was added. The reaction was kept for 6 h under 390 nm Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Products were purified by column chromatography with ethyl acetate and hexane as solvents.

4.2 General procedure B to afford *N*-tosylhydrazones



N-tosylhydrazones were prepared according a reported procedure.[1] To a stirred solution of tosylhydrazide (10 mmol) in MeOH (10 mL) at room temperature, aldehyde (1.0 equiv.) was added dropwise (or portionwise if solid). The reaction was completed within 0.1-3 h. After that, the solvent was removed directly under reduced pressure, and further purified by recrystallization or *via* silica gel chromatography (hexane : EtOAc, 2:1).[1]

4.3 General procedure C to afford 24-25



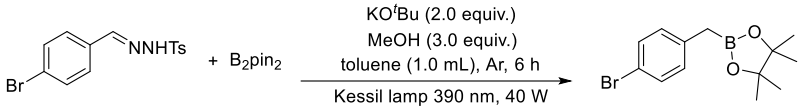
To a 0°C solution of 4-hydroxybenzaldehyde (1.78 g, 14.5 mmol) in dichloromethane (30 mL) Ibuprofen (3.0 g, 2.9 mL, 14.5 mmol) was added followed by DCC (3.6 g, 17.4 mmol) and DMAP (0.18 g, 1.45 mmol), purging the flask for three times under vacuum and three times argon, Then, the homogeneous solution was removed from the ice bath and stirred at room temperature for 12 h. The reaction mixture was saturated aqueous NaCl (2x) and finally with brine. The combined organic layers were dried over

$MgSO_4$, filtered, and concentrated under reduced pressure to obtain the product as a clear oil (3.6 g.11.6 mmol, 81%).[2]

5. The application of the reaction

5.1 Gram-scale synthesis of 13d

Synthesis of 13d in gram scale:

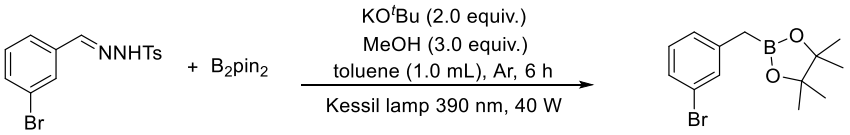


13a, 5 mmol **1b** **13d,** 68%, 1.01 g

Following the general procedure A, to a glass vial, containing the **13a** (1.76 g, 5.0 mmol), **1b** (1.91 g, 7.5 mmol, 1.5 equiv.), KO^{t}Bu (1.12 g, 10.0 mmol, 2.0 equiv.), MeOH (480.6 mg, 15.0 mmol, 3.0 equiv.) was added toluene (25 mL). The vial was placed in the 390 nm irradiation setup as shown on **Figure S2**. The reaction was stirred for 10 h (the progress can be monitored *via* TLC), then the solvent was evaporated, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel with petroleum ether and ethyl acetate (v/v = 60/1) as solvents afforded product **13d** as a yellow solid (1.01 g, 68% yield).

5.2 Gram-scale synthesis of 15d

Synthesis of 15d in gram scale:

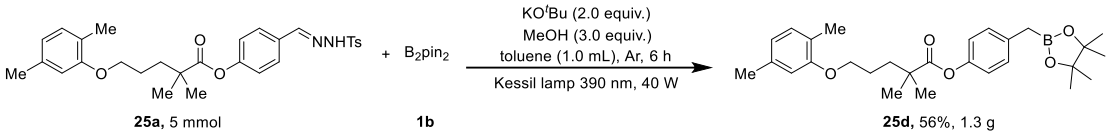


15a, 8.5 mmol **1b** **15d,** 59%, 1.48 g

Following the general procedure A, to a glass vial, containing the **15a** (3.00 g, 8.5 mmol), **1b** (3.24 g, 12.75 mmol, 1.5 equiv.), KO^{t}Bu (1.91 g, 17.0 mmol, 2.0 equiv.), MeOH (817.02 mg, 25.5 mmol, 3.0 equi) was added toluene (43 mL). The vial was placed in the 390 nm irradiation setup as shown on **Figure S2**. The reaction was stirred for 10 h (the progress can be monitored *via* TLC), then the solvent was evaporated, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel with petroleum ether and ethyl acetate (v/v = 60/1) as solvents afforded product **15d** as a yellow oli (1.48 g, 59% yield).

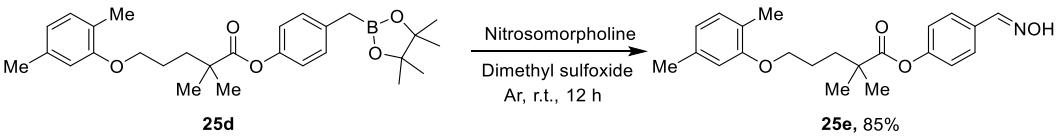
5.3 Gram-scale synthesis of 25d

Synthesis of 25d in gram scale:



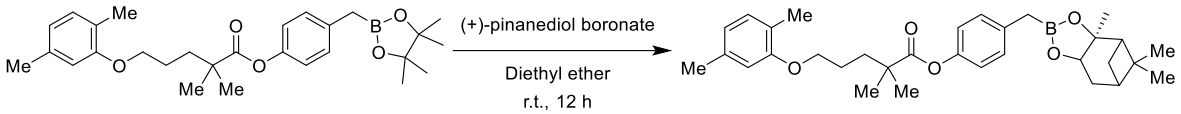
Following the general procedure A, to a glass vial, containing the **25a** (2.61 g, 5.0 mmol), **1b** (1.91 g, 7.5 mmol, 1.5 equiv.), KO^{t}Bu (1.12 g, 10.0 mmol, 2 equiv.), MeOH (480.6 mg, 15.0 mmol, 3.0 equiv.) was added toluene (25 mL). The vial was placed in the 390 nm irradiation setup as shown on **Figure S2**. The reaction was stirred for 10 h (the progress can be monitored *via* TLC), then the solvent was evaporated, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel with petroleum ether and ethyl acetate (v/v = 30/1) as solvents afforded product **25d** as a white oil (1.30 g, 56% yield).

5.4 Further transformation of compound 25d



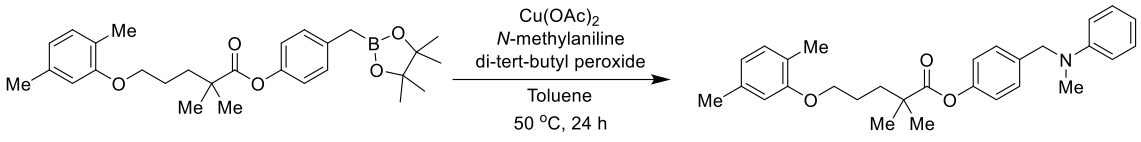
25d **25e**, 85%

Procedure D: The title compound was prepared following a literature protocol.[3] To a stirred solution of **25d** (46.6 mg, 0.1 mmol) in DMSO (1.0 mL), was added N-nitrosomorpholine. and (23.0 mg, 0.2 mmol, 2.0 equiv). At Ar atmosphere, the mixture was stirred at room temperature for 12 hours. (the progress can be monitored *via* TLC). Then, place the reaction quench with water (2 mL) and extract with ethyl acetate (3 x 15 mL). Filter the mixture and concentrate the solvent. Products were purified *via* column chromatography with petroleum ether/ethyl acetate (10/1, v/v) as solvents, to obtain **25e** (31.4 mg, 85%) as a colorless oil.



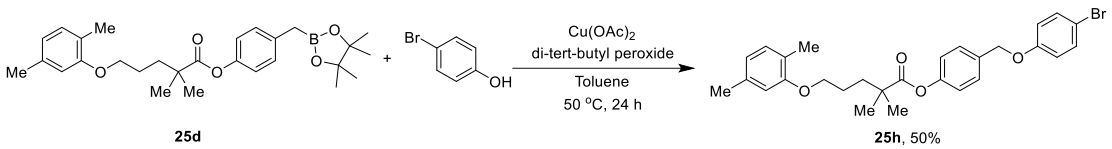
25d **25f**, 88%

Procedure E: The title compound was prepared following a literature protocol.[4] To a stirred solution of **25d** (233 mg, 0.5 mmol) in Et_2O (1.0 mL), was added (+)-pinanediol (110.65 mg, 0.65 mmol, 1.3 equiv). The mixture was stirred at room temperature for 24 hours. (the progress can be monitored *via* TLC). Then, place the reaction quench with water (2 mL) and extract with ethyl acetate (3 x 15 mL). Filter the mixture and concentrate the solvent. Products were purified *via* column chromatography with petroleum ether/ethyl acetate (30/1, v/v) as solvents, to obtain **25f** (228 mg, 88%) as a colorless oil.



25d **25g**, 63%

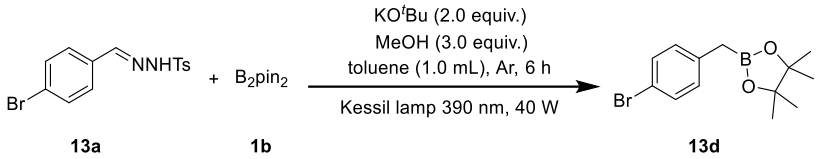
Procedure F: The title compound was prepared following a literature protocol.[5] A mixture of benzyl pinacol boronic acid ester **25d** (58.3 mg, 0.125 mmol), *N*-methylaniline (14.7 mg, 0.138 mmol), di-tert-butyl peroxide (36.6 mg, 0.25 mmol), $Cu(OAc)_2$ (1.1 mg, 6.3 μmol), and toluene (0.50 mL) was stirred at 50 °C for 24 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give *N*-benzyl-*N*-methylaniline **25g** (35.8 mg, 63% yield).



Procedure G: The title compound was prepared following a literature protocol.[5] A mixture of benzyl pinacol boronic acid ester **25d** (116.6 mg, 0. 25 mmol), 4-bromophenol (47.6 mg, 0.275 mmol), di-tert-butyl peroxide (73.2 mg, 0.5 mmol), $Cu(OAc)_2$ (2.2 mg, 12.6 μmol), and toluene (1.0 mL) was stirred at 50 °C for 24 h in a sealed tube. Then, the solvent was removed in vacuo and the product was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give *N*-benzyl-*N*-methylaniline **25h** (63.8 mg, 50% yield).

6. Mechanistic investigations

6.1 Time course



13a **1b** **13d**

N-tosylhydrazone **13a** (0.4 mmol, 140.8 mg), **1b** (152.4 mg, 0.6 mmol, 1.5 equiv.), KO^{t}Bu (89.8 mg, 0.4 mmol, 2.0 equiv.), MeOH (480.6 mg, 15.0 mmol, 3.0 equiv.), and internal standard (1,3,5-trimethoxybenzene, 0.1 mmol, 16.8 mg) were added into a dry 10 mL Schlenk tube equipped with a stirring bar, followed by the addition of toluene (2 mL). Then the reaction mixture was irradiated by a 390 nm Kessil lamps (40 W) at room temperature. An aliquot of the reaction mixture then taken at the indicated times and the yields were determined by ^{1}H NMR spectroscopy.

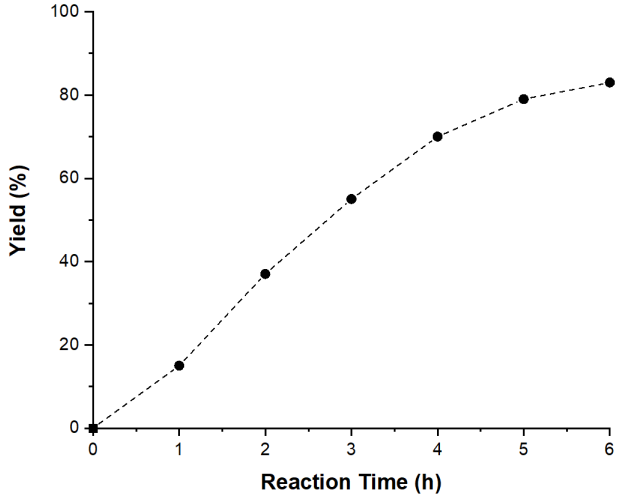
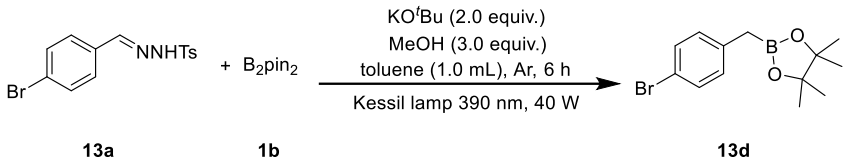


Figure S3. Time course experiment, yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard.

6.2 On-off experiments



13a **1b** **13d**

A dry 10 mL Schlenk tube containing a stirring bar was charged with *N*-tosylhydrazone **13a** (0.4 mmol, 140.8 mg), **1b** (152.4 mg, 0.6 mmol, 1.5 equiv.), KO^{t}Bu (89.8 mg, 0.4 mmol, 2 equiv.), MeOH (480.6 mg, 15.0 mmol, 3.0 equiv.), and 1,3,5-trimethoxybenzene (0.2 mmol, as the internal standard). After purging the flask three times under vacuum and three times under argon, it was charged with 2.0 mL of toluene. Then the mixture was irradiated by 40 W 390 nm Kessil lamps reaction setup at room temperature. After 1 h, the Kessil lamps were turned off, and 0.2 ml of reaction solvent was taken for NMR analysis. Then the tube was reacted in the absence of light for an additional 1 h, and 0.2 ml of reaction solvent was removed for analysis, and the Kessil lamps were turned back on to irradiate the analyzed mixtures. So repeatedly, the yields were determined by ^{1}H NMR spectroscopy.

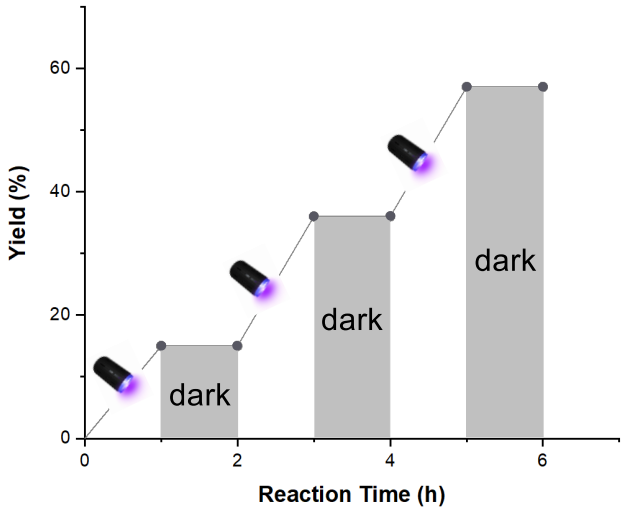


Figure S4. The comparison of On-off experiment yields determined by hydrogen spectrometry.

6.3 Ultraviolet visible absorption experiments

Ultraviolet-visible absorption experiments were performed using a UV-8000S(T) spectrophotometer. In each experiment, the varying samples were combined in the solvent toluene in screw-top 1.0 cm quartz cuvettes.

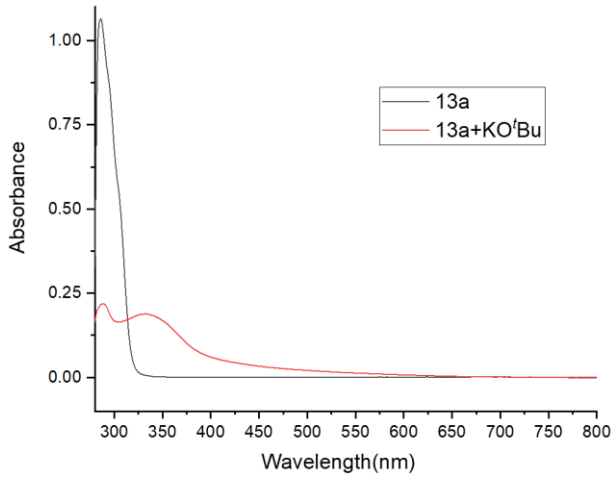
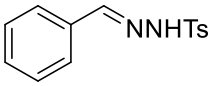


Figure S5. UV/vis absorption spectra of individual reaction components and a combination thereof. Ultraviolet-visible absorption experiments:**13a** (2.0×10^{-4} M) in toluene, [**13a** + KO^{t}Bu] (2.0×10^{-4} M) in toluene. The right picture is a partial enlargement of the left picture.

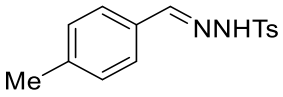
7. Characterization data of products and synthesized substrates.



***N*'-benzylidene-4-methylbenzenesulfonohydrazide (1a)**: Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 86%). **1a** was known in the published literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.81 (s, 1H), 7.59 – 7.52 (m, 2H), 7.37 – 7.27 (m, 5H), 2.38 (s, 3H).

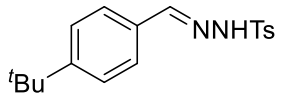
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{14}H_{14}N_2O_2SH$: 275.0849, found: 275.0873.



4-methyl-*N*'-(4-methylbenzylidene)benzenesulfonohydrazide (2a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 75%). **2a** was known in the published literature.[7]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.86 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.41 (dd, J = 18.8, 8.2 Hz, 4H), 7.19 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 3H).

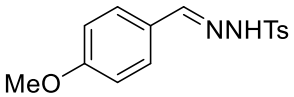
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{15}H_{16}N_2O_2SH$: 289.1005, found: 289.0089.



***N*'-(4-(*tert*-butyl)benzylidene)-4-methylbenzenesulfonohydrazide (3a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 72%). **3a** was known in the published literature.[8]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.34 (s, 1H), 7.87 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.40 (dd, J = 8.1, 3.0 Hz, 4H), 2.35 (s, 3H), 1.25 (s, 9H).

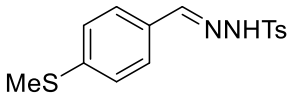
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}N_2O_2SH$ 331.1475; Found 331.1490.



***N*'-(4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (4a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 88%). **4a** was known in the published literature.[9]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.24 (s, 1H), 7.84 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.43 – 7.37 (m, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.35 (s, 3H).

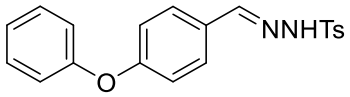
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}N_2O_3SH$ 305.0954; Found 305.0980.



4-methyl-*N'*-(4-(methylthio)benzylidene)benzenesulfonohydrazide (5a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 94%). **5a** was known in the published literature.[10]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.39 (s, 1H), 7.86 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 2.46 (s, 3H), 2.34 (s, 3H).

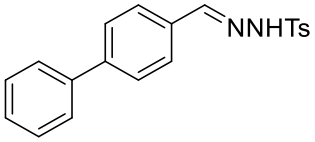
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}N_2O_2S_2H$ 321.0726; Found 321.0745.



4-methyl-*N'*-(4-phenoxybenzylidene)benzenesulfonohydrazide (6a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 82%). **6a** was known in the published literature.[10]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.38 (s, 1H), 7.89 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.18 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H).

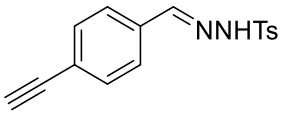
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}N_2O_3SH$ 367.1111; Found 367.1132.



***N'*-([1,1'-biphenyl]-4-ylmethylene)-4-methylbenzenesulfonohydrazide (7a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 86%). **7a** was known in the published literature.[11]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.50 (s, 1H), 7.95 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.69 – 7.66 (m, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.40 – 7.35 (m, 1H), 2.35 (s, 3H).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_2SNa$ 373.0981; Found 373.0998

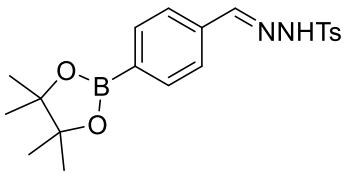


***N'*-(4-ethynylbenzylidene)-4-methylbenzenesulfonohydrazide (8a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 88%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.58 (s, 1H), 7.90 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.44 – 7.33 (m, 2H), 4.33 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 145.9, 143.5, 136.1, 134.0, 132.1, 129.7, 127.2, 126.9, 123.0, 83.1, 82.6, 21.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2O_2SNa$ 321.0668; Found 321.0687.

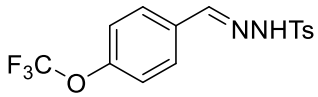


4-methyl-*N'*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)benzenesulfonohydrazide (9a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 90%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.56 (s, 1H), 7.91 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.43 – 7.34 (m, 2H), 2.35 (s, 3H), 1.28 (s, 12H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 146.6, 143.5, 136.3, 136.1, 134.8, 129.7, 127.2, 126.1, 83.8, 24.7, 21.0

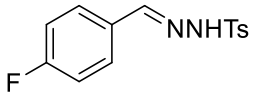
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}BN_2O_4SH$ 401.1701; Found 401.1732.



4-methyl-*N'*-(4-(trifluoromethoxy)benzylidene)benzenesulfonohydrazide (10a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 88%). **10a** was known in the published literature.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.75 (s, 1H), 7.60 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.25 – 7.11 (m, 2H), 2.41 (s, 3H).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}F_3N_2O_3SNa$ 381.0491; Found 381.0513.

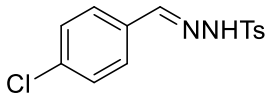


***N'*-(4-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (11a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 86%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.48 (s, 1H), 7.92 (s, 1H), 7.83 – 7.76 (m, 2H), 7.61 (dd, J = 8.7, 5.7 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.21 (t, J = 8.8 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 164.1, 162.1, 145.9, 143.5, 136.1, 130.3 (d, $J_{C\text{-}F}$ = 1.26 Hz), 129.7, 128.9 (d, $J_{C\text{-}F}$ = 8.82 Hz), 127.3, 115.9 (d, $J_{C\text{-}F}$ = 22.68 Hz), 21.0.

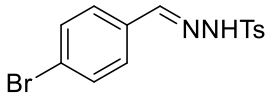
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}N_2O_2SNa$ 315.0574; Found 315.0599.



***N'*-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (12a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 93%). **12a** was known in the published literature.[14]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.56 (s, 1H), 7.90 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H).

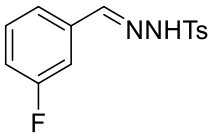
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}ClN_2O_2SH$ 309.0459; Found 309.0476.



***N'*-(4-bromobenzylidene)-4-methylbenzenesulfonohydrazide (13a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 89%). **13a** was known in the published literature.[14]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.56 (s, 1H), 7.89 (s, 1H), 7.79 – 7.73 (m, 2H), 7.61 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.43 – 7.36 (m, 2H), 2.35 (s, 3H).

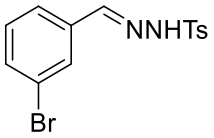
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}BrN_2O_2SH$ 352.9954; Found 352.9968.



***N'*-(3-fluorobenzylidene)-4-methylbenzenesulfonohydrazide (14a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 90%). **14a** was known in the published literature.[13]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.60 (s, 1H), 7.90 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.35 (m, 1H), 7.23 (m, 1H), 2.36 (s, 3H).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}FN_2O_2SH$ 293.0755; Found 293.0784.

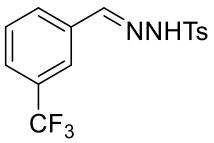


***N'*-(3-bromobenzylidene)-4-methylbenzenesulfonohydrazide (15a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 90%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.66 (s, 1H), 7.89 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.72 (s, 1H), 7.58 – 7.52 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.33 (t, J = 7.9 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 145.2, 143.6, 136.1, 132.6, 130.9, 129.7, 129.1, 127.2, 125.7, 122.1, 21.0.

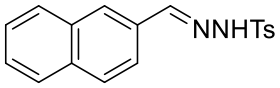
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}BrN_2O_2SH$ 352.9954; Found 352.9971.



4-methyl-*N'*-(3-(trifluoromethyl)benzylidene)benzenesulfonohydrazide (16a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 93%). **16a** was known in the published literature.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.82 – 7.74 (m, 3H), 7.65 – 7.58 (m, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H).

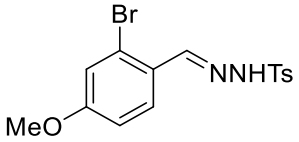
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}F_3N_2O_2SNa$ 365.0542; Found 365.0566.



4-methyl-*N*'-(naphthalen-2-ylmethylene)benzenesulfonohydrazide (17a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 92%). **17a** was known in the published literature.[14]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.56 (s, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.50 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 6.0 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.43 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}N_2O_2SH$ 325.1005; Found: 325.1021.

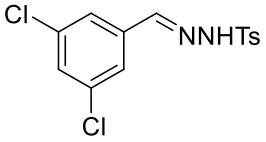


***N*'-(2-bromo-4-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (18a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 73%). **18a** was known in the published literature.[14]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.55 (s, 1H), 8.15 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 2.6 Hz, 1H), 6.98 (dd, J = 8.8, 2.5 Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 161.6, 145.5, 144.0, 136.5, 130.2, 128.2, 127.7, 125.3, 124.5, 117.9, 115.5, 56.3, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}BrN_2O_3SH$ 383.0060; Found: 383.0042.

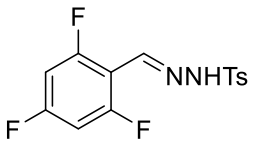


***N*'-(3,5-dichlorobenzylidene)-4-methylbenzenesulfonohydrazide (19a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.82 (s, 1H), 7.87 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.60 (t, J = 1.9 Hz, 1H), 7.57 (d, J = 2.0 Hz, 2H), 7.44 – 7.38 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 143.7, 143.7, 137.3, 136.0, 134.6, 129.8, 129.1, 127.2, 125.0, 21.0.

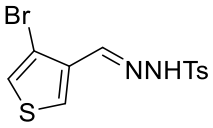
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}Cl_2N_2O_2SH$ 343.0069; Found 343.0083.



4-methyl-*N*'-(2,4,6-trifluorobenzylidene)benzenesulfonohydrazide (20a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 66%). **21a** was known in the published literature.[14]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.72 (s, 1H), 7.91 (s, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.25 (t, J = 9.1 Hz, 2H), 2.36 (s, 3H).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}F_3N_2O_2SH$ 329.0566; Found: 329.0581.

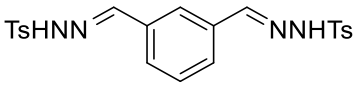


***N*'-((4-bromothiophen-3-yl)methylene)-4-methylbenzenesulfonohydrazide (21a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 74%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.54 (s, 1H), 7.90 (d, J = 2.9 Hz, 2H), 7.80 – 7.72 (m, 3H), 7.39 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 143.6, 140.7, 136.1, 133.3, 129.7, 127.3, 126.2, 125.6, 109.6, 21.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}BrN_2O_2S_2H$ 358.9518; Found: 358.9531.

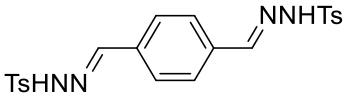


***N'*, *N'''*-1,3-phenylenebis(methanylylidene))bis(4-methylbenzenesulfonohydrazide) (22a):** Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 88%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.55 (s, 2H), 7.92 (s, 2H), 7.77 (d, J = 8.3 Hz, 4H), 7.74 (d, J = 1.7 Hz, 1H), 7.55 (dd, J = 7.7, 1.7 Hz, 2H), 7.39 (d, J = 8.0 Hz, 5H), 2.34 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 146.3, 143.5, 136.1, 134.2, 129.7, 129.3, 128.3, 127.2, 124.5, 21.0.

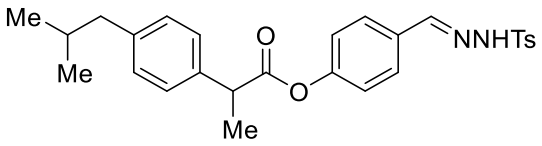
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}N_4O_4S_2H$ 471.1115; Found 471.1134.



***N'*, *N'''*--1,4-phenylenebis(methanylylidene))bis(4-methylbenzenesulfonohydrazide) (23a)**: Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 93%). **23a** was known in the published literature.[15]

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.54 (s, 2H), 7.88 (s, 2H), 7.80 – 7.69 (m, 4H), 7.56 (s, 4H), 7.40 (d, J = 8.1 Hz, 4H), 2.35 (s, 6H).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}N_4O_4S_2H$ 471.1115; Found 471.1129.

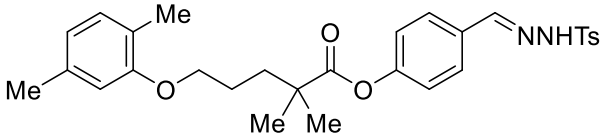


4-((2-tosylhydrazono)methyl)phenyl 2-(4-isobutylphenyl)propanoate (24a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.62 (s, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.1 Hz, 4H), 7.15 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.93 (q, J = 7.1 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.86 (dp, J = 13.6, 6.8 Hz, 1H), 1.60 (d, J = 7.1 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 152.3, 146.6, 144.3, 141.0, 136.9, 135.2, 130.8, 129.7, 129.6, 128.4, 127.9, 127.2, 121.8, 45.2, 45.0, 30.2, 22.4, 21.6, 18.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{30}N_2O_4SH$ 479.1999; Found: 479.2011.

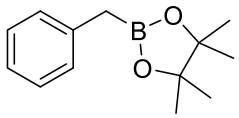


4-((2-tosylhydrazono)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25a): Following the general procedure B, it was obtained as a white solid by recrystallization (isolated yield: 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H), 7.52 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.02 – 6.99 (m, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 6.6 Hz, 1H), 6.63 (s, 1H), 3.98 (t, J = 5.4 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H), 1.88 (s, 4H), 1.37 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 156.8, 152.4, 146.6, 144.3, 136.5, 135.2, 130.8, 130.3, 129.7, 128.4, 127.9, 123.5, 121.9, 120.8, 111.9, 67.6, 42.5, 37.0, 25.2, 25.1, 21.6, 21.4, 15.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{34}N_2O_5SH$ 535.2261; Found: 535.2283.



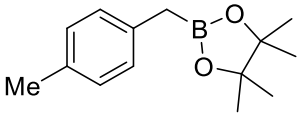
2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 64%). **1d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.20 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 2.30 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 129.2, 128.5, 125.1, 83.6, 25.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{19}BO_2H$ 219.1551; Found: 219.1568.



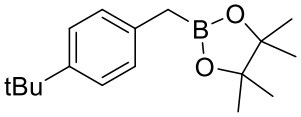
4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (2d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 53%). **2d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.03 (m, 4H), 2.30 (s, 3H), 2.26 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.2, 129.1, 129.0, 83.5, 24.9, 21.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}BO_2H$ 233.1707; Found: 233.1721.



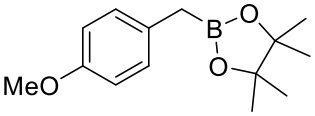
2-(4-(*tert*-butyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 63%). **3d** was known in the published literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (d, 2H), 7.14 – 7.09 (d, 2H), 2.27 (s, 2H), 1.30 (s, 9H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 135.5, 128.8, 125.3, 83.5, 34.4, 31.6, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{27}BO_2H$ 275.2177; Found: 275.2190.



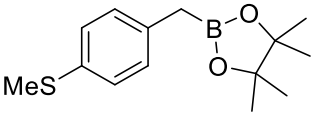
2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 50/1) to give the title compound as a colorless liquid (isolated yield: 46%). **4d** was known in the published literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 2.23 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 130.6, 129.9, 113.9, 83.5, 55.3, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}BO_3H$ 249.1657; Found: 249.1666.



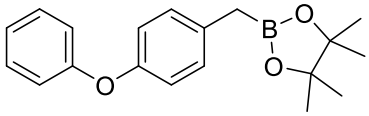
4,4,5,5-tetramethyl-2-(4-(methylthio)benzyl)-1,3,2-dioxaborolane (5d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 70%). **5d** was known in the published literature.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 134.1, 129.6, 127.5, 83.6, 24.9, 16.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}BO_2SH$ 265.1428; Found: 265.1439.



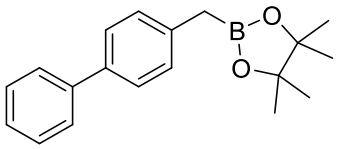
4,4,5,5-tetramethyl-2-(4-phenoxybenzyl)-1,3,2-dioxaborolane (6d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 60%). **6d** was known in the published literature.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.06 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 2.28 (s, 2H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 154.5, 133.7, 130.3, 129.7, 122.8, 119.2, 118.5, 83.6, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}BO_3H$ 311.1813; Found: 311.1831.



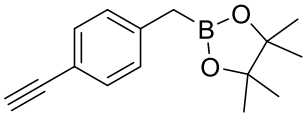
2-([1,1'-biphenyl]-4-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 80%). **7d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.3 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.31 (s, 2H), 1.22 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 138.0, 137.9, 129.5, 128.8, 127.1, 127.0, 127.0, 83.6, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}BO_2H$ 295.1864; Found: 295.1877.



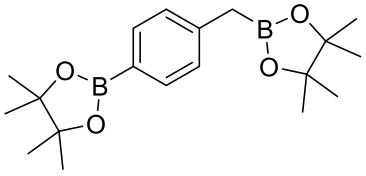
2-(4-ethynylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 53%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 2H), 7.16 – 7.07 (m, 2H), 3.01 (s, 1H), 2.29 (s, 2H), 1.22 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 132.2, 129.1, 118.6, 84.2, 83.7, 76.4, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}BO_2H$ 243.1551; Found: 243.1567.



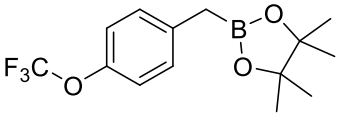
4,4,5,5-tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1,3,2-dioxaborolane (9d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a colorless liquid (isolated yield: 42%). **9d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 2.30 (s, 2H), 1.33 (s, 12H), 1.21 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 135.0, 128.6, 83.7, 83.6, 25.0, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{30}B_2O_4H$ 345.2403; Found: 345.2422.



4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)benzyl)-1,3,2-dioxaborolane (10d)

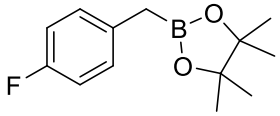
Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 50%). **10d** was known in the published literature.[19]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.11 – 7.00 (m, 2H), 2.29 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 137.6, 130.2, 123.5, 121.7(q, $J_{C\text{-}F}$ = 257.04 Hz), 83.7, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.93.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}BF_3O_3H$ 303.1374; Found: 303.1399.



2-(4-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11d)

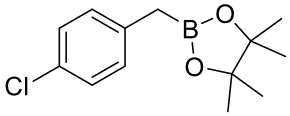
Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 55%). **11d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 6.96 – 6.83 (m, 2H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 160.0, 134.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 130.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.4 Hz), 83.6, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.37.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}BFO_2H$ 237.1457; Found: 237.1477.



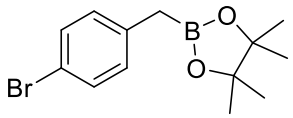
2-(4-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 75%). **12d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.25 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 130.7, 130.4, 128.4, 83.7, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}BClO_2H$ 253.1161; Found: 253.1189.



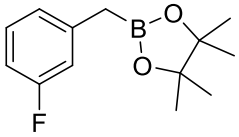
2-(4-bromobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 82%). **13d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 2.23 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 131.4, 130.9, 118.7, 83.7, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}BBrO_2H$ 297.0656; Found: 297.0677.



2-(3-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14d)

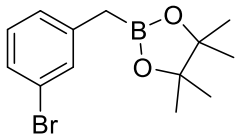
Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 65%). **14d** was known in the published literature.[19]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (td, J = 7.9, 6.2 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.90 (dt, J = 10.3, 2.1 Hz, 1H), 6.85 – 6.78 (m, 1H), 2.29 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 245.7 Hz), 141.4 (d, $J_{C\text{-}F}$ = 7.6 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 124.8 (d, $J_{C\text{-}F}$ = 2.5 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.4 Hz), 111.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 83.7, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.28.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}BFO_2H$ 237.1457; Found: 237.1485.



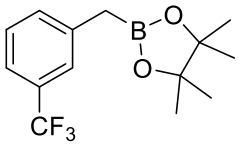
2-(3-bromobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 68%). **15d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dq, J = 1.3, 0.8 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.10 (d, J = 1.0 Hz, 1H), 7.09 (dd, J = 2.2, 1.0 Hz, 1H), 2.26 (s, 2H), 1.23 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 132.1, 129.9, 128.1, 127.8, 122.4, 83.8, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}BBrO_2H$ 297.0656; Found: 297.0684.



4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (16d)

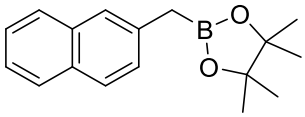
Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 75%). **16d** was known in the published literature.[20]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dt, J = 1.8, 0.9 Hz, 1H), 7.39 – 7.32 (m, 3H), 2.35 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 132.4, 130.4 (q, $J_{C\text{-}F}$ = 31.9 Hz), 128.6, 125.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 272.9 Hz), 121.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 83.7, 24.7

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.61.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}BF_3O_2H$ 287.1425; Found: 287.1459.



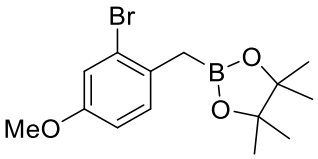
4,4,5,5-tetramethyl-2-(naphthalen-2-ylmethyl)-1,3,2-dioxaborolane (17d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 20/1) to give the title compound as a white solid (isolated yield: 65%). **17d** was known in the published literature.[16]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 3H), 7.65 – 7.61 (m, 1H), 7.41 (m, 2H), 7.35 (dd, J = 8.4, 1.8 Hz, 1H), 2.47 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 133.9, 131.6, 128.4, 127.8, 127.7, 127.4, 126.7, 125.8, 124.8, 83.6, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}BO_2H$ 269.1707; Found: 269.1745.



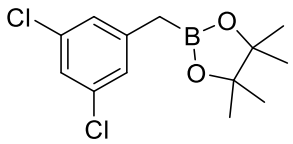
2-(2-bromo-4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a colorless crystal (isolated yield: 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 2.7 Hz, 1H), 6.76 (dd, J = 8.4, 2.7 Hz, 1H), 3.76 (s, 3H), 2.33 (s, 2H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 131.3, 131.0, 124.7, 117.7, 113.7, 83.7, 55.6, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}BBrO_3H$ 327.0762, Found: 327,0799.



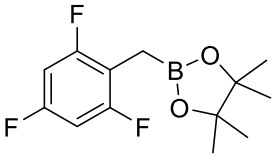
2-(3,5-dichlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, J = 1.9 Hz, 1H), 7.06 (t, J = 1.3 Hz, 2H), 2.24 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 134.6, 127.6, 125.3, 83.9, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}BCl_2O_2H$ 287.0771, Found: 287.0799.



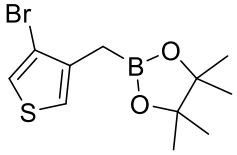
4,4,5,5-tetramethyl-2-(2,4,6-trifluorobenzyl)-1,3,2-dioxaborolane (20d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (dd, J = 8.9, 7.4 Hz, 2H), 2.16 (s, 2H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.16 (q, $J_{C\text{-}F}$ = 2.5 Hz), 161.3, 160.2 (q, $J_{C\text{-}F}$ = 2.5 Hz), 159.4, 111.1 (td, $J_{C\text{-}F}$ = 21.4 Hz, 3.8 Hz), 99.8 (q, $J_{C\text{-}F}$ = 25.2 Hz, 7.6 Hz), 83.9, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}BF_3O_2H$ 273.1268, Found: 273.1303.



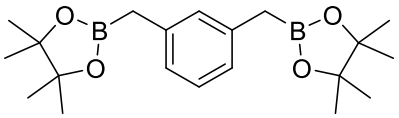
2-((4-bromothiophen-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 60/1) to give the title compound as a colorless liquid (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 3.4 Hz, 1H), 7.05 (dt, J = 3.4, 1.0 Hz, 1H), 2.25 (s, 2H), 1.27 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 122.4, 120.8, 113.8, 83.8, 25.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}BBrO_2SH$ 303.0220, Found: 303.0255.



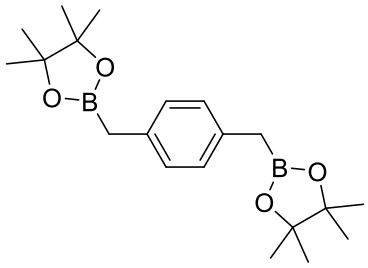
1,3-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene (22d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 40/1) to give the title compound as a colorless liquid (isolated yield: 65%). **22d** was known in the published literature.[21]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 1.8 Hz, 1H), 6.93 (dd, J = 7.6, 1.7 Hz, 2H), 2.23 (s, 4H), 1.22 (s, 24H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 129.9, 128.3, 125.7, 83.5, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{32}B_2O_4H$ 359.2559, Found: 359.2587.



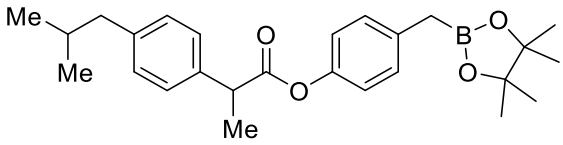
1,4-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene (23d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 40/1) to give the title compound as a colorless liquid (isolated yield: 72%). **23d** was known in the published literature.[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 4H), 2.23 (s, 4H), 1.22 (s, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 129.1, 83.5, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{32}B_2O_4H$ 359.2559, Found: 359.2592.



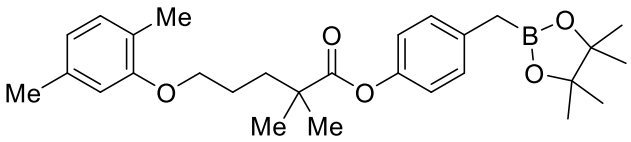
4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl-2-(4-isobutylphenyl)propanoate (24d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a yellow solid (isolated yield: 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 4H), 6.86 (d, J = 8.5 Hz, 2H), 3.92 (q, J = 7.1 Hz, 1H), 2.47 (d, J = 7.1 Hz, 2H), 2.26 (s, 2H), 1.87 (m, 1H), 1.59 (d, J = 7.1 Hz, 3H), 1.22 (d, J = 0.9 Hz, 12H), 0.91 (d, J = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 148.4, 140.8, 137.5, 136.2, 129.8, 129.6, 129.6, 127.3, 121.1, 83.6, 45.4, 45.2, 30.3, 24.8, 22.5, 18.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{35}BO_4H$ 423.2701, Found: 423.2738.



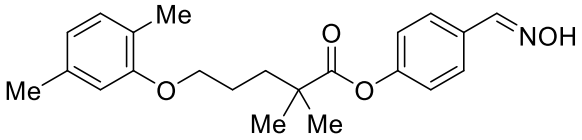
4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25d)

Prepared according to the general procedure A. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a yellow solid (isolated yield: 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 2H), 7.05 – 6.98 (m, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.69 – 6.66 (m, 1H), 6.64 (d, J = 1.6 Hz, 1H), 3.99 (m, 2H), 2.32 (s, 3H), 2.29 (s, 2H), 2.19 (s, 3H), 1.88 (m, 4H), 1.37 (s, 6H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 157.0, 148.5, 136.6, 136.1, 130.4, 129.9, 128.1, 123.7, 121.7, 121.3, 120.8, 112.1, 83.6, 67.9, 42.5, 37.3, 25.4, 25.3, 24.9, 21.5, 15.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{39}BO_5H$ 467.2963, Found: 467.2999.



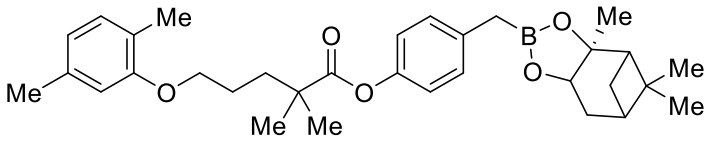
4-((hydroxyimino)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25e)

Prepared according to the general procedure D. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give the title compound as a yellow solid (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.00 (s, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 7.4 Hz, 1H), 6.67 (dd, J = 7.5, 1.5 Hz, 1H), 6.63 (d, J = 1.5 Hz, 1H), 3.99 (t, J = 5.3 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.92 – 1.78 (m, 4H), 1.38 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 156.9, 152.4, 149.6, 136.6, 130.5, 129.7, 128.2, 123.7, 122.2, 120.9, 112.1, 67.8, 42.7, 37.3, 25.4, 25.3, 21.6, 15.9.

HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{27}NO_4H$ 370.2013; Found 370.2045.



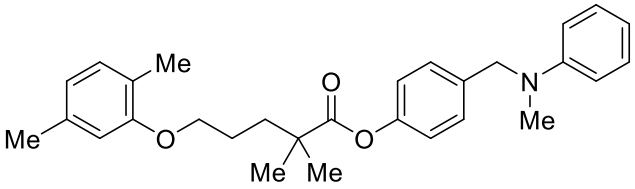
4-(((3aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25f)

Prepared according to the general procedure E. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a yellow solid (isolated yield: 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.04 – 6.99 (m, 1H), 6.96 – 6.85 (m, 2H), 6.67 (dd, J = 7.2, 1.4 Hz, 1H), 6.64 (d, J = 1.5 Hz, 1H), 4.28 (dd, J = 8.7, 2.0 Hz, 1H), 3.98 (m, 2H), 2.32 (d, J = 8.6 Hz, 2H), 2.29 (t, J = 2.4 Hz, 4H), 2.19 (s, 4H), 2.05 (dd, J = 6.0, 5.1 Hz, 1H), 1.92 – 1.87 (m, 6H), 1.39 (s, 3H), 1.36 (s, 6H), 1.28 (s, 3H), 1.05 (d, J = 10.9 Hz, 1H), 0.83 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 157.0, 148.5, 136.6, 136.2, 130.4, 129.9, 123.7, 121.3, 120.8, 112.0, 86.0, 78.1, 77.4, 67.9, 51.4, 51.0, 42.5, 39.7, 39.5, 38.2, 38.0, 37.3, 35.5, 35.1, 28.7, 27.2, 26.7, 26.5, 25.4, 25.3, 24.1, 21.5, 15.9.

HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{32}H_{43}BO_5H$ 519.3276; Found 519.3287.



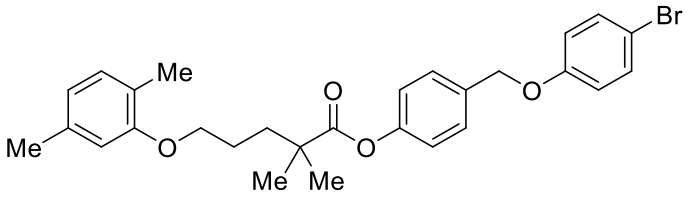
4-((methyl(phenyl)amino)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25g)

Prepared according to the general procedure F. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 30/1) to give the title compound as a yellow solid (isolated yield: 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dt, J = 8.8, 3.8 Hz, 4H), 7.01 (d, J = 7.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 6.76 (dd, J = 8.8, 1.1 Hz, 2H), 6.74 – 6.71 (m, 1H), 6.67 (dd, J = 7.6, 1.5 Hz, 1H), 6.63 (d, J = 1.5 Hz, 1H), 4.52 (s, 2H), 3.98 (q, J = 3.2 Hz, 2H), 3.01 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.88 (d, J = 2.9 Hz, 4H), 1.37 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 157.0, 150.0, 149.8, 136.6, 136.5, 130.5, 129.3, 127.8, 123.7, 121.7, 120.9, 116.8, 112.6, 112.1, 67.9, 56.3, 42.6, 38.6, 37.3, 25.4, 25.3, 21.6, 16.0.

HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{29}H_{35}NO_3H$ 446.2690; Found 446.2723.



4-((4-bromophenoxy)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (25h)

Prepared according to the general procedure G. Following workup, the product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10/1) to give the title compound as a yellow solid (isolated yield: 50%).

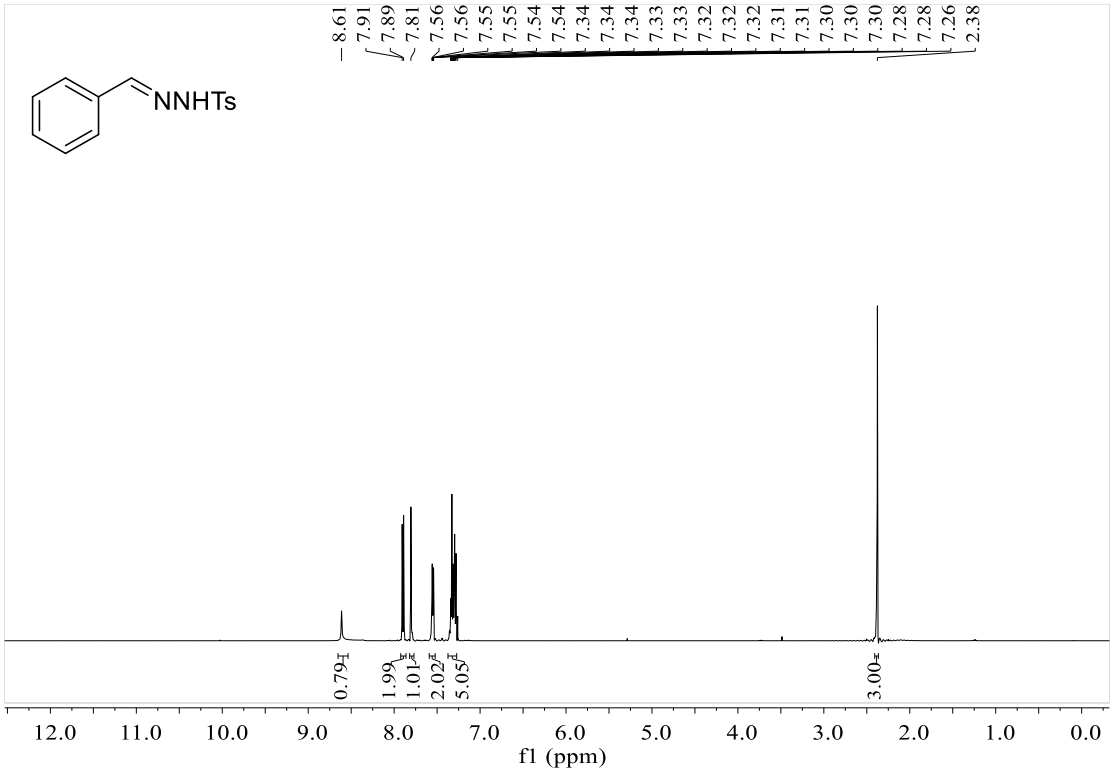
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 15.1, 8.8 Hz, 4H), 7.11 – 7.03 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.67 (d, J = 7.4 Hz, 1H), 6.65 – 6.61 (m, 1H), 5.02 (s, 2H), 4.00 – 3.92 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.88 (dd, J = 3.2, 1.7 Hz, 4H), 1.37 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 157.8, 157.0, 150.9, 136.6, 134.1, 132.5, 130.5, 128.6, 123.7, 121.9, 120.9, 116.8, 113.4, 112.1, 69.8, 67.9, 42.6, 37.3, 25.4, 25.3, 21.6, 16.0.

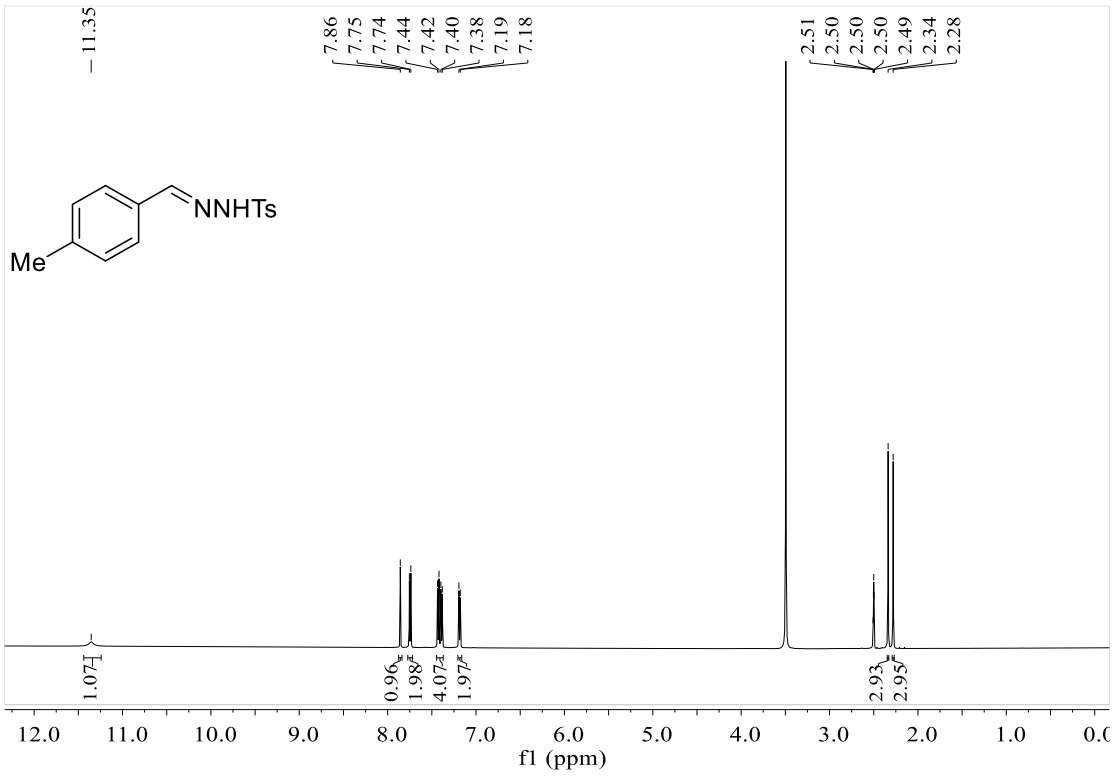
HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{28}H_{31}BrO_4H$ 511.1478, Found 511.1507.

8 NMR spectra of products and synthesized substrates

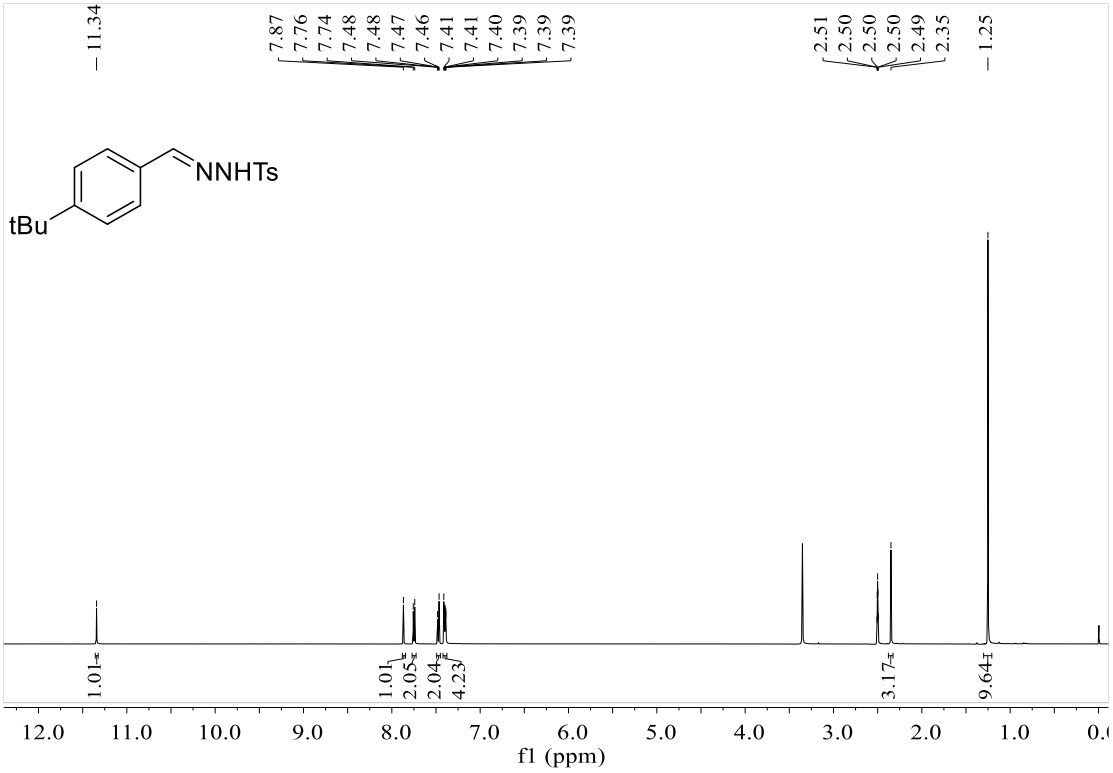
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 1a



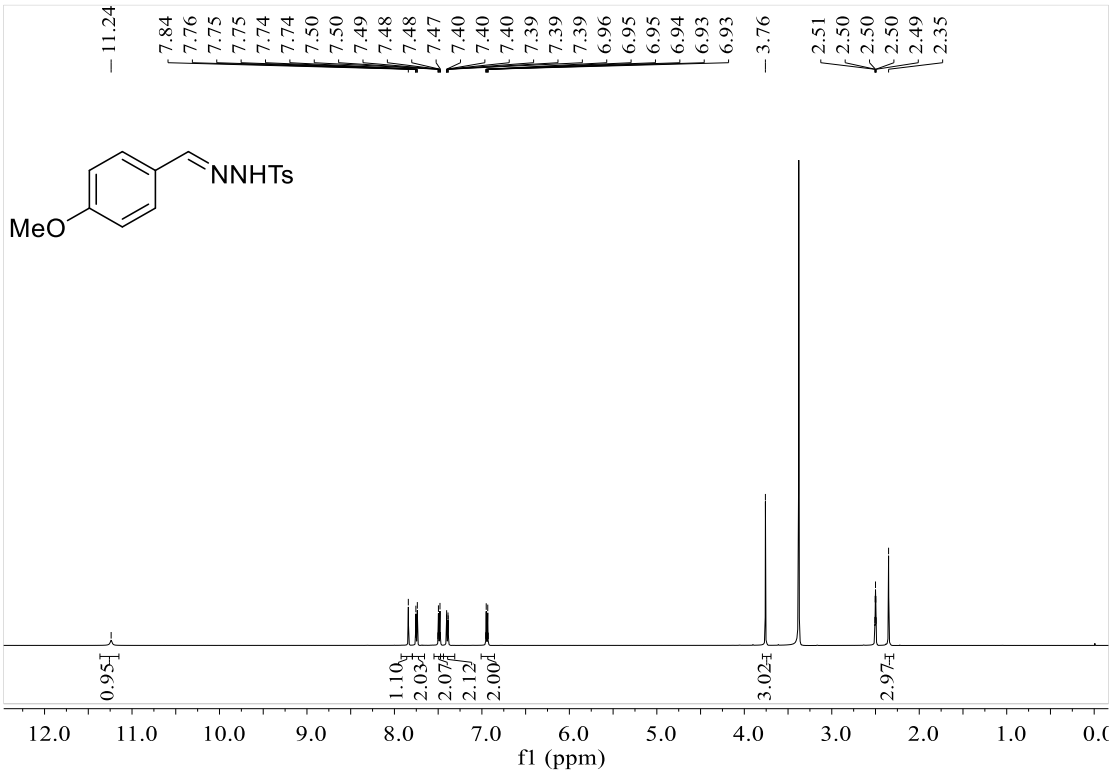
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 2a



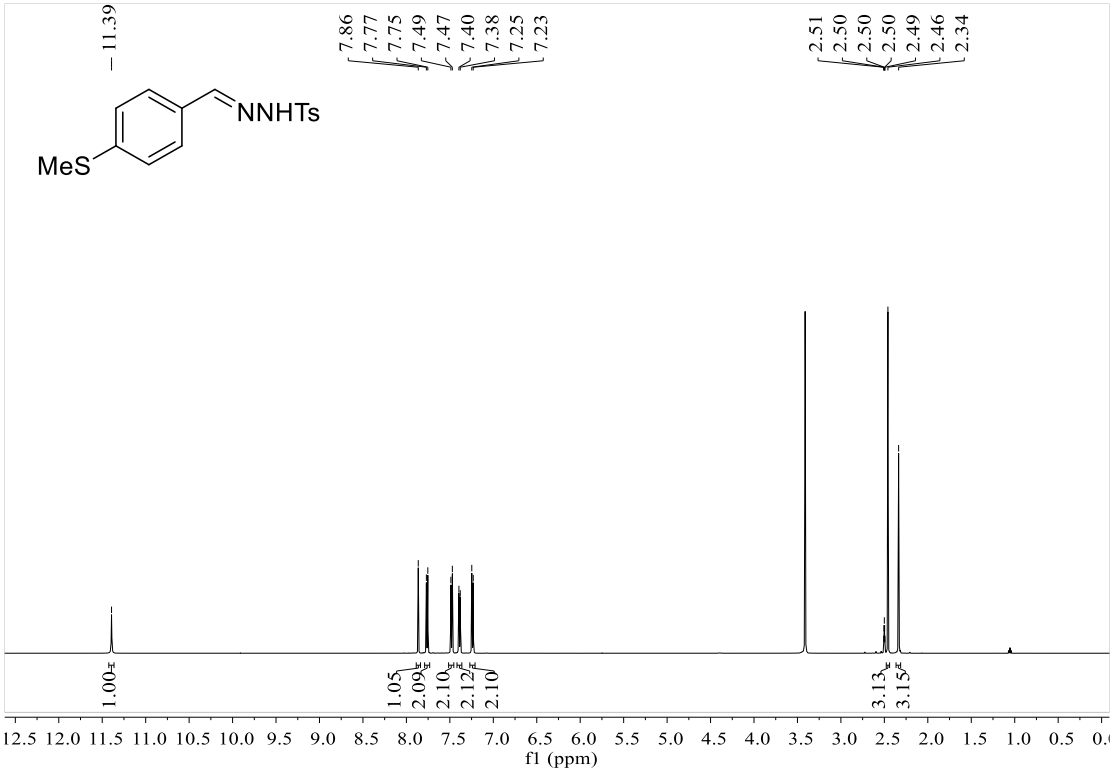
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 3a



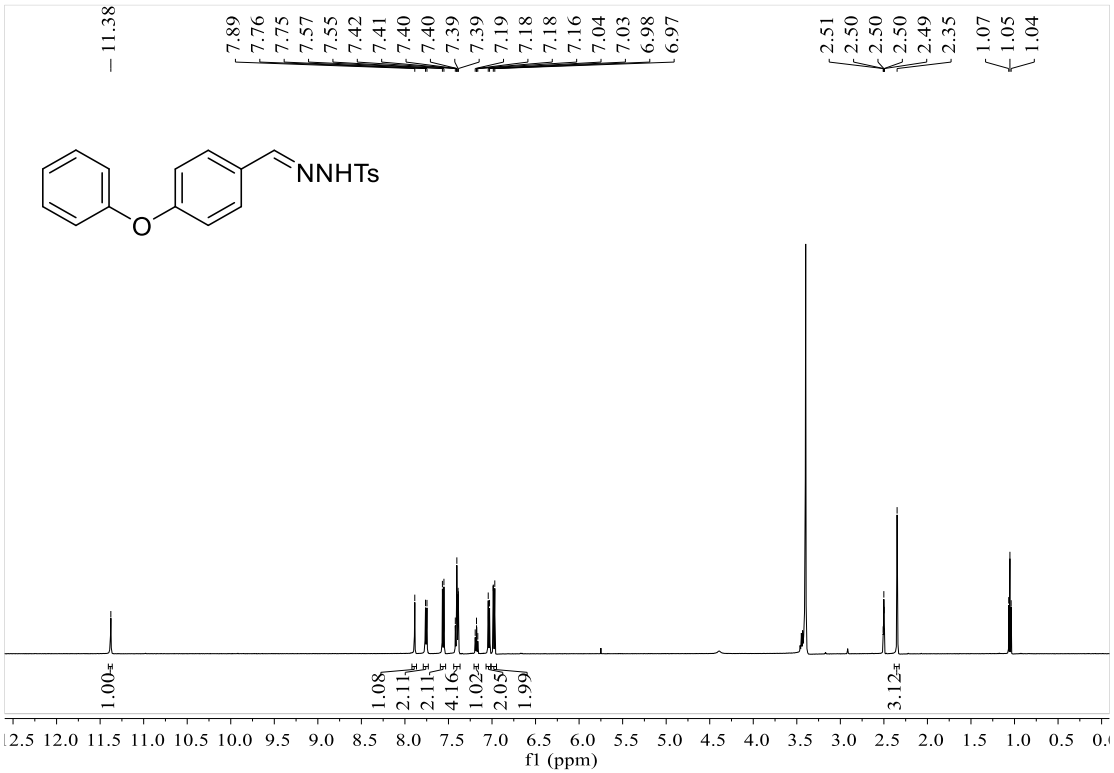
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 4a



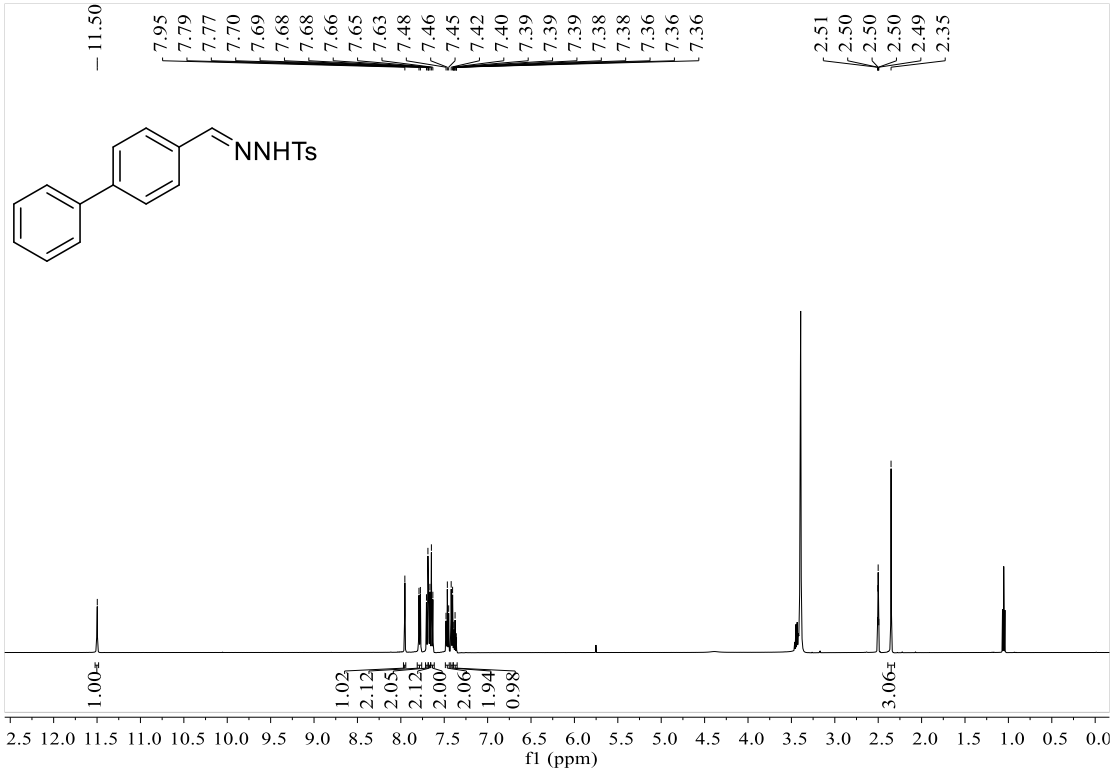
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 5a



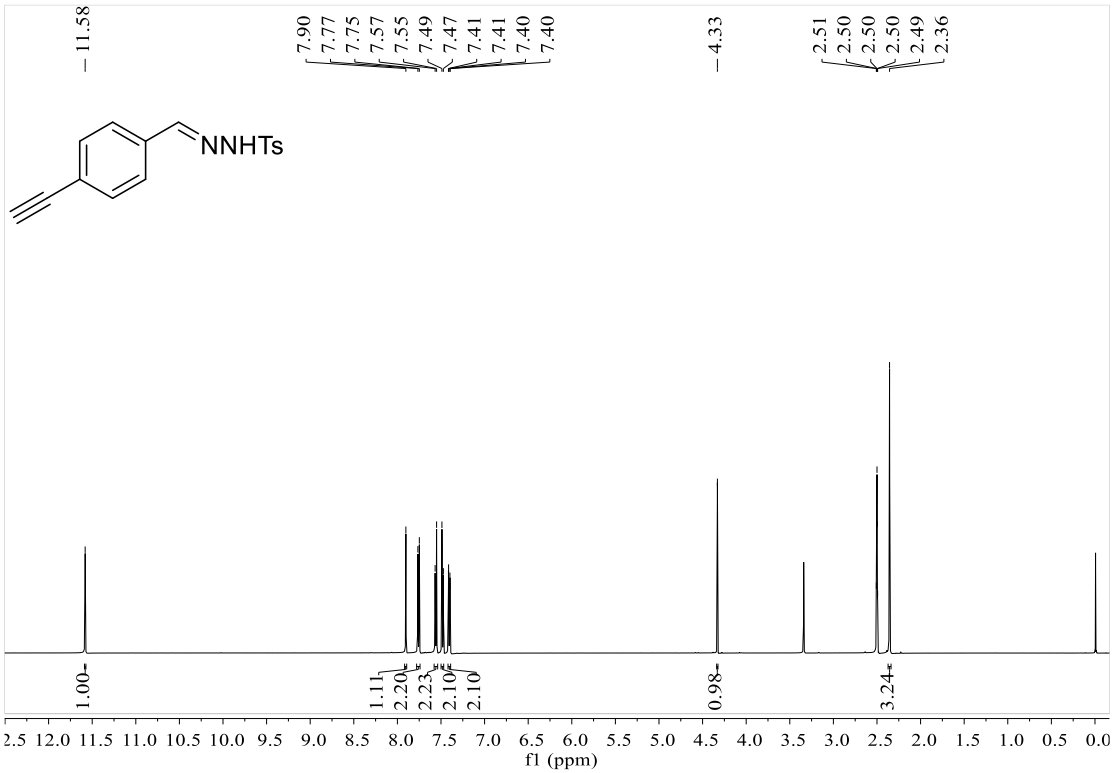
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 6a



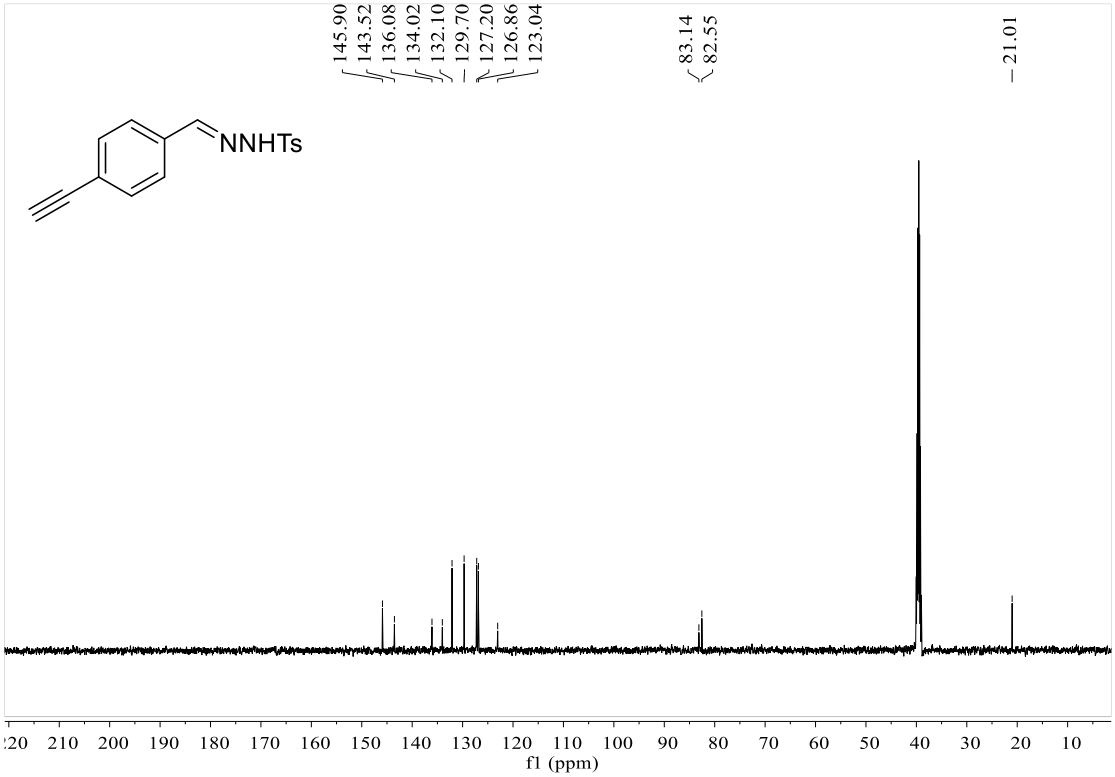
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 7a



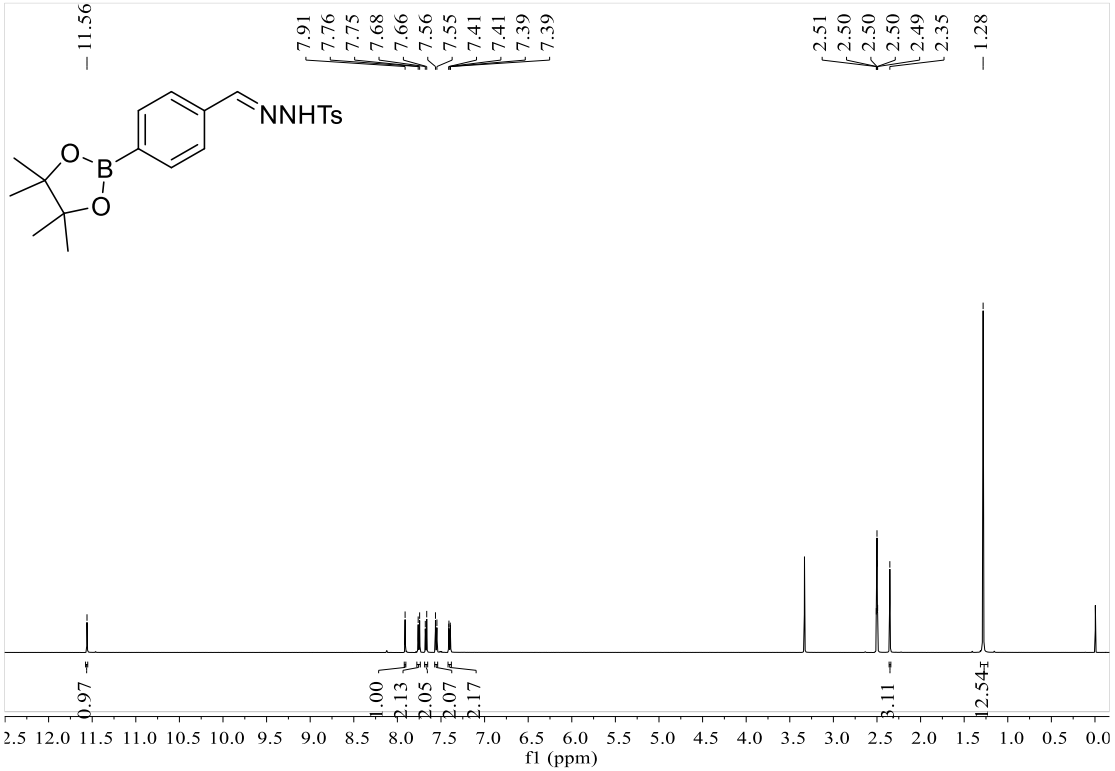
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 8a



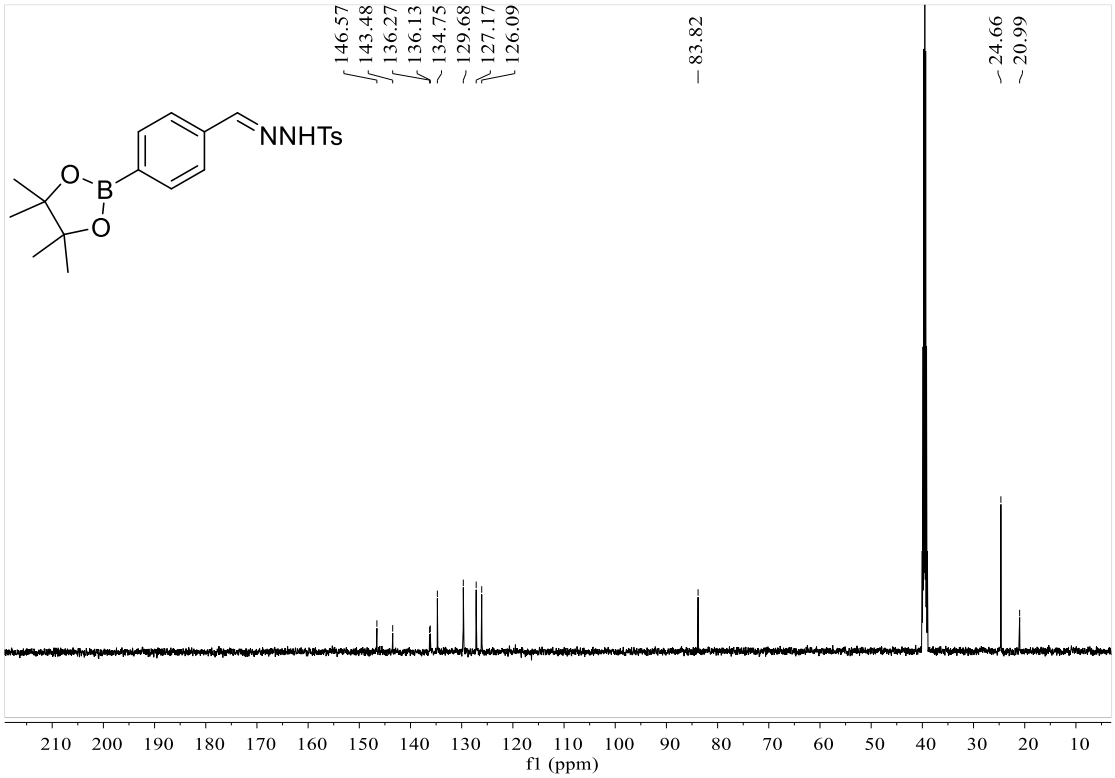
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 8a



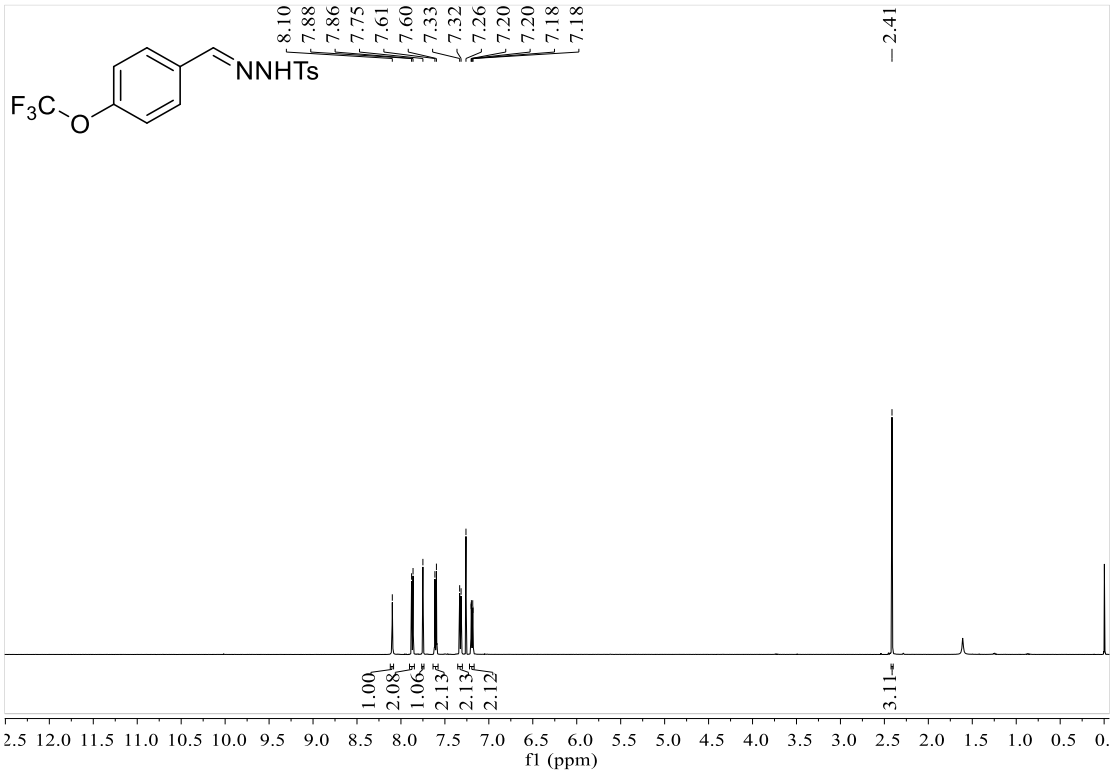
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 9a



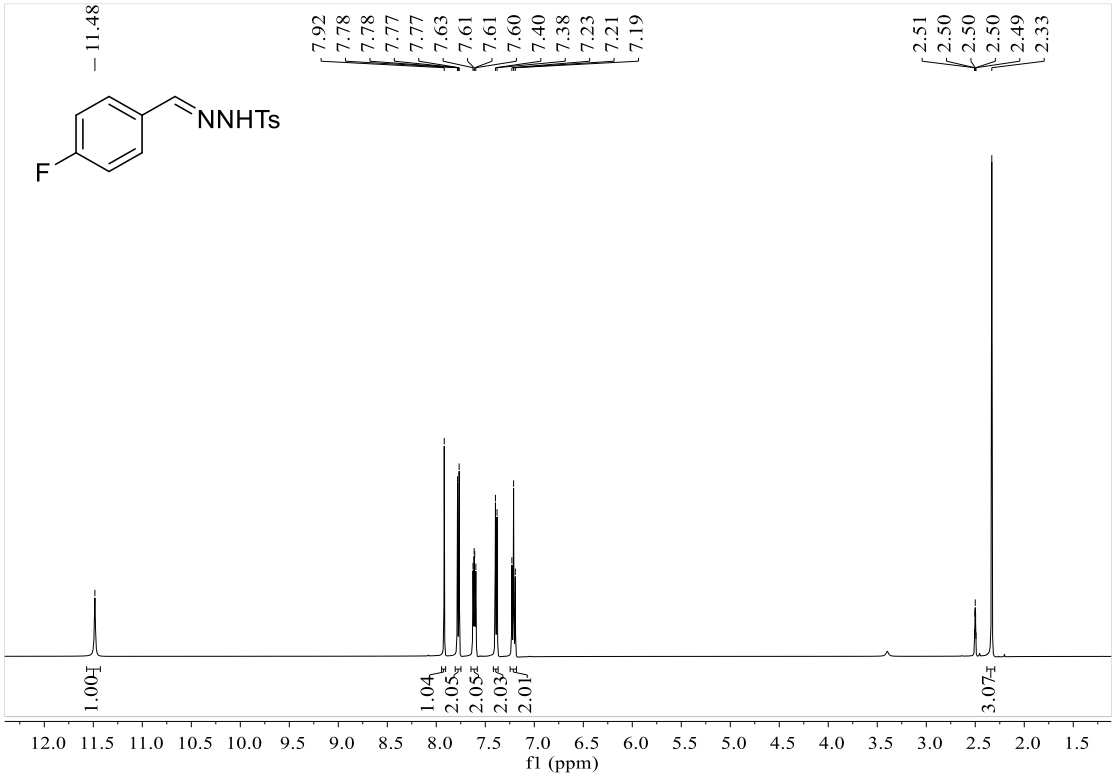
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 9a

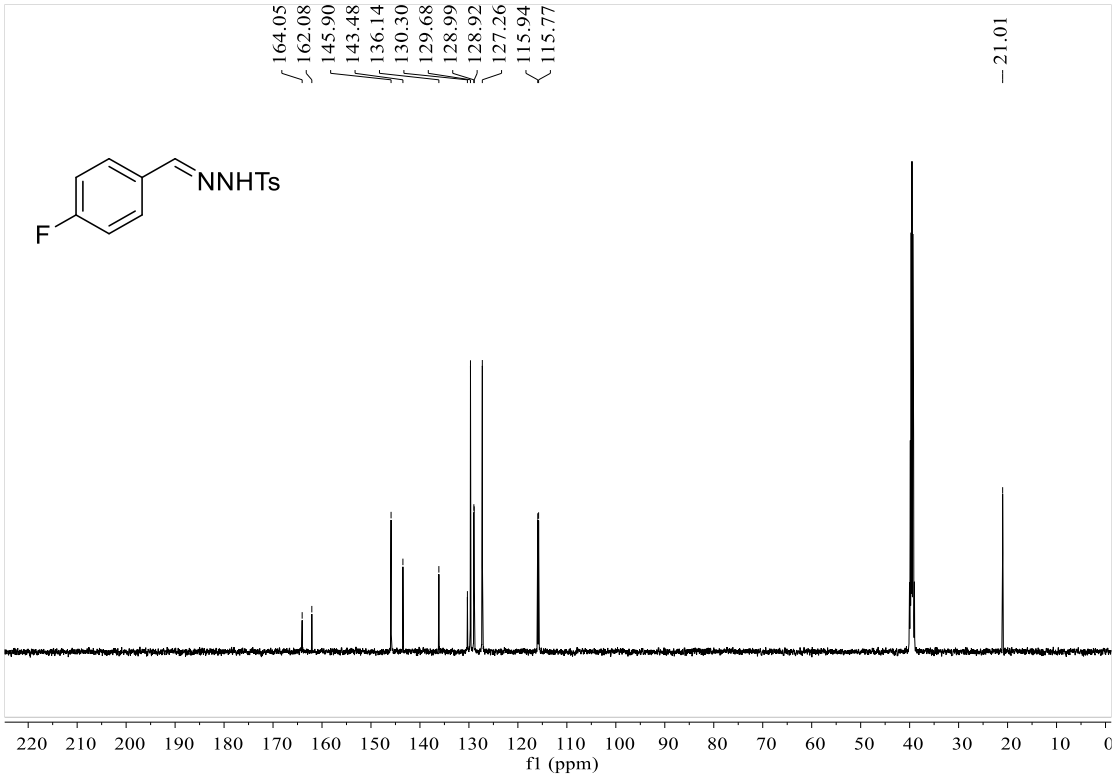


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 10a

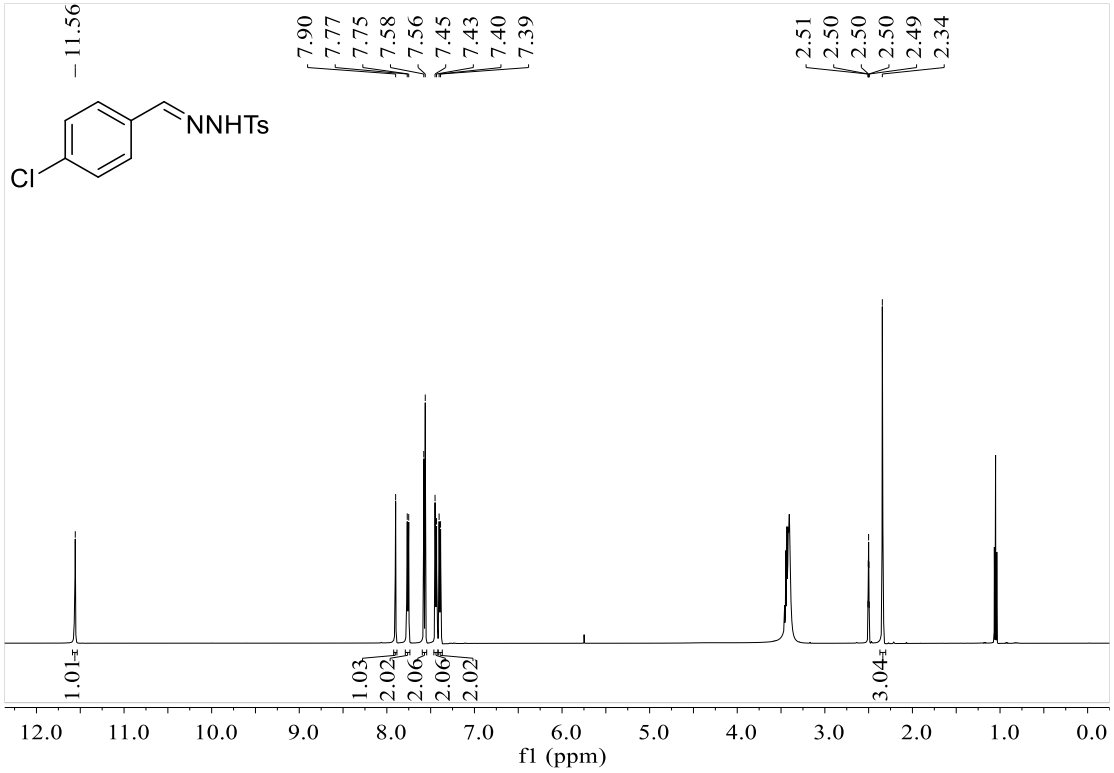


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 11a

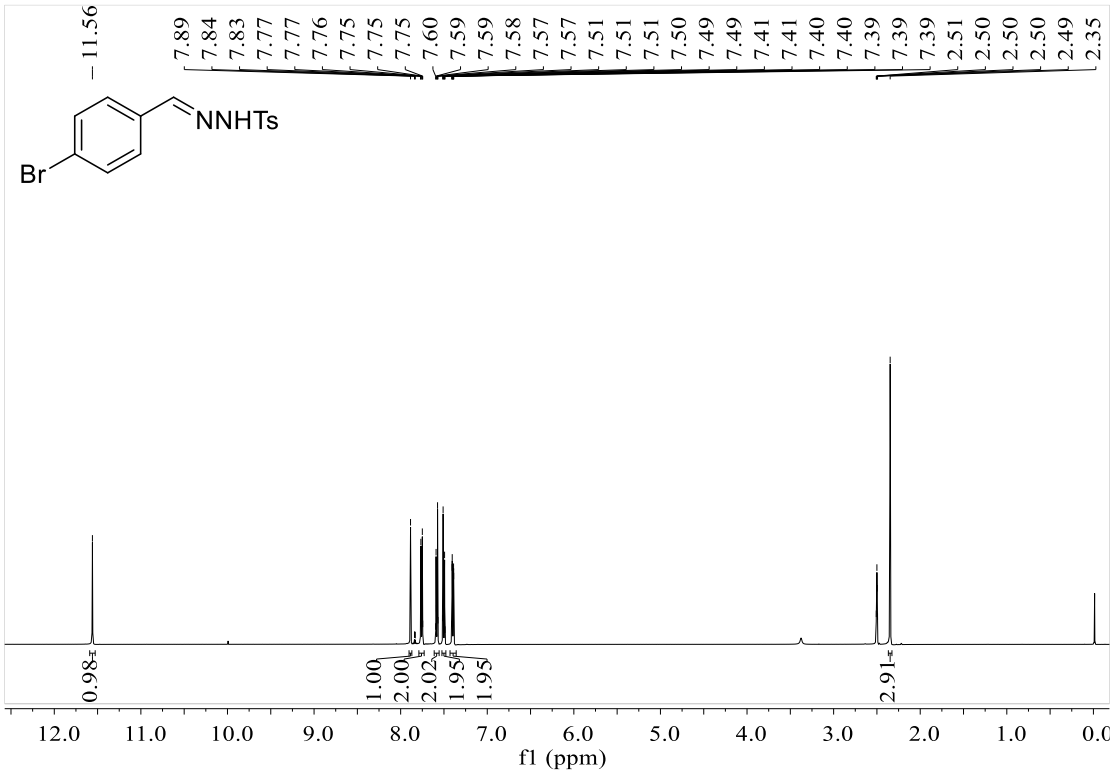




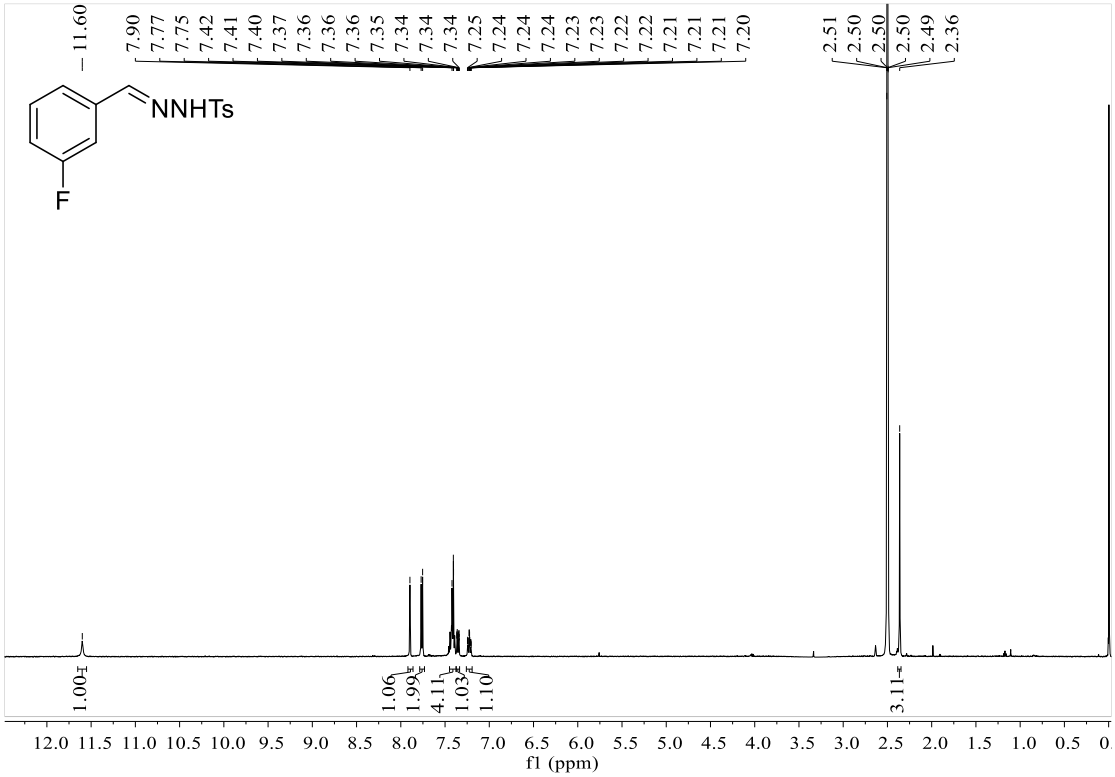
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 12a



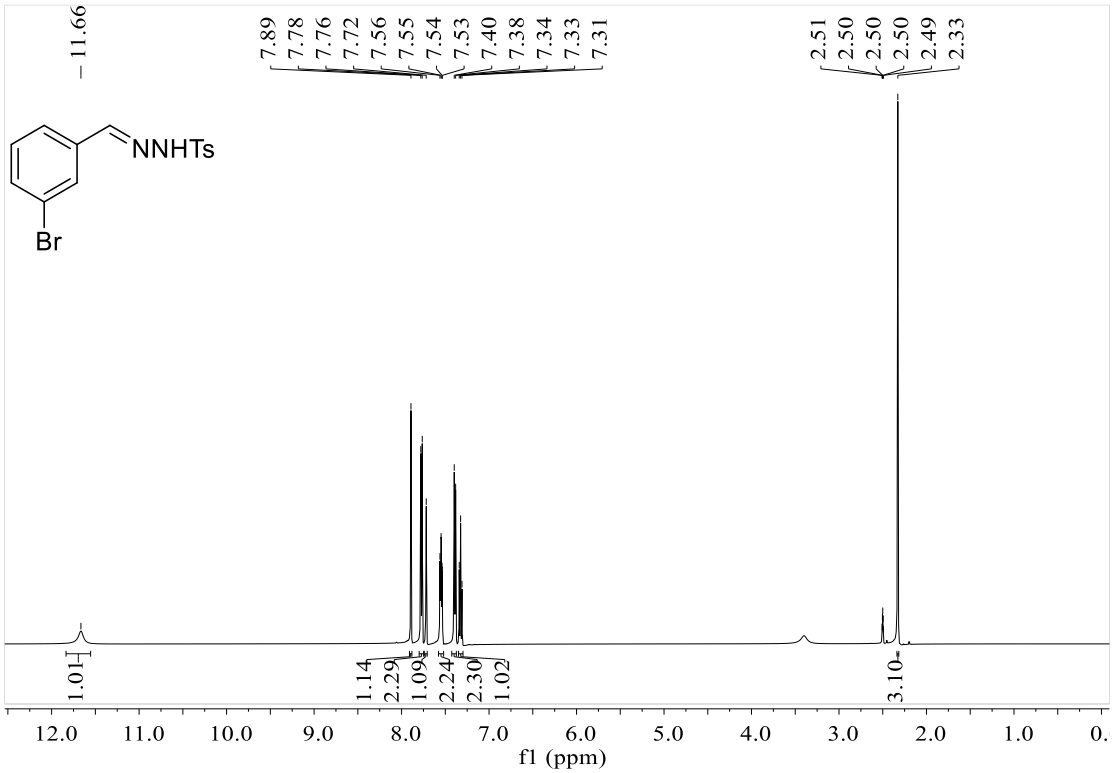
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 13a



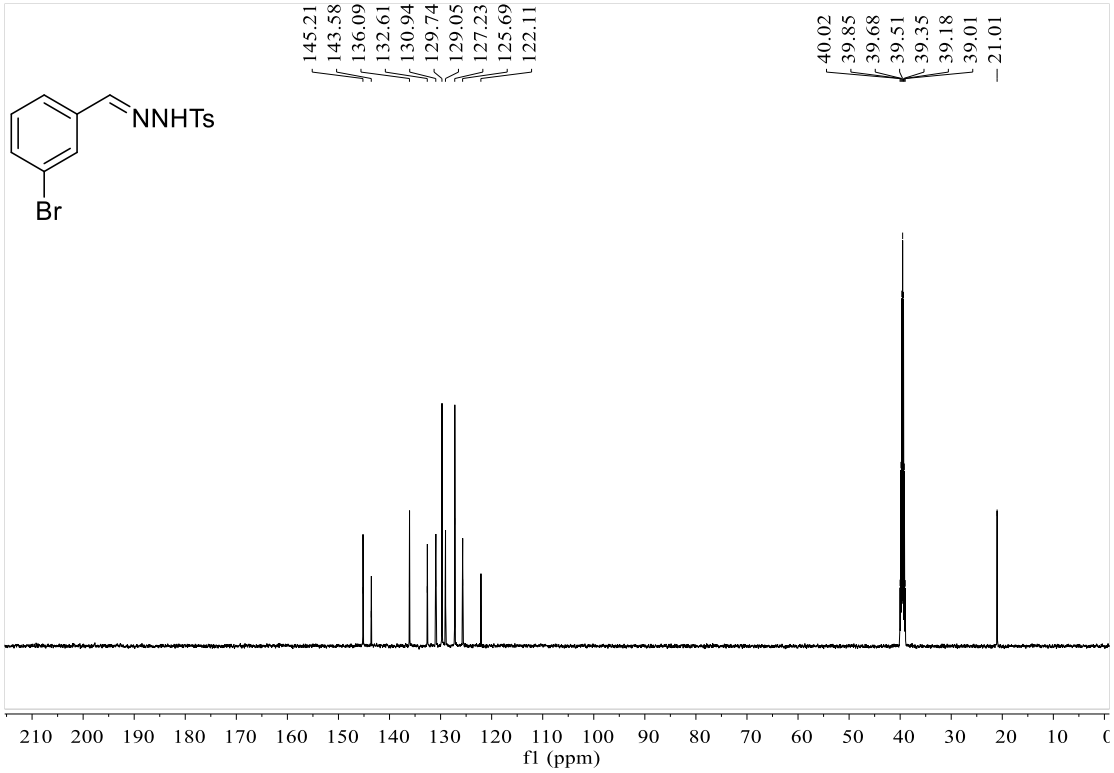
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 14a



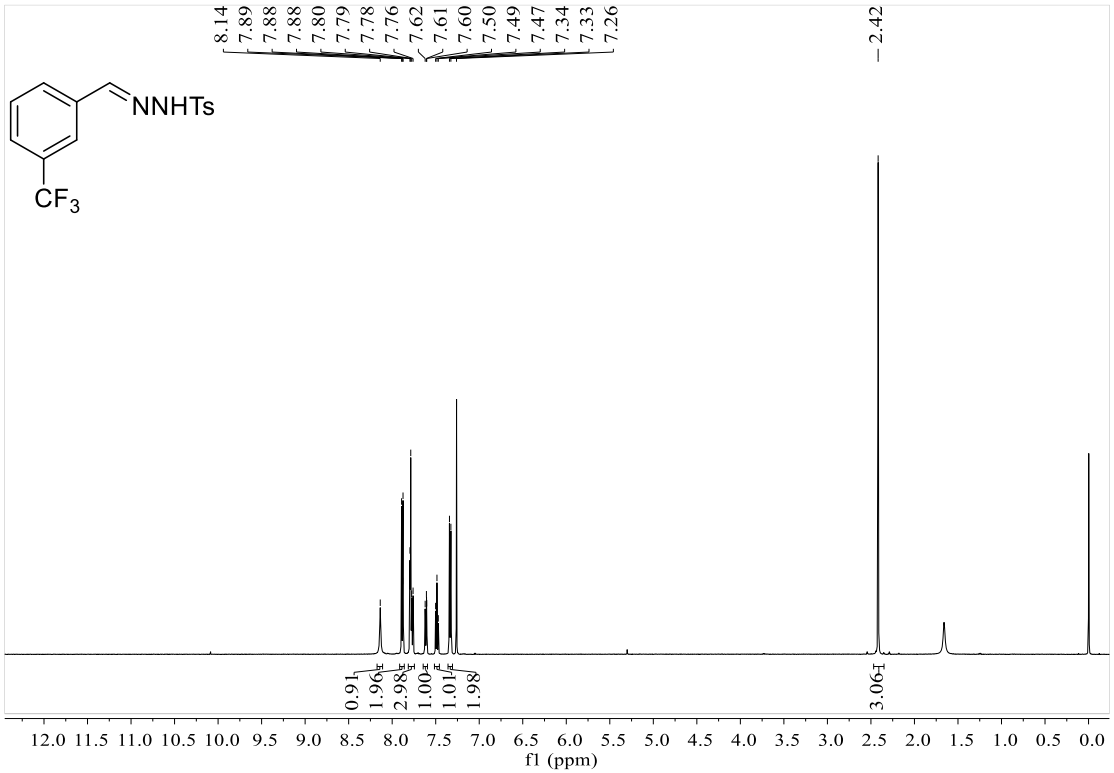
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 15a



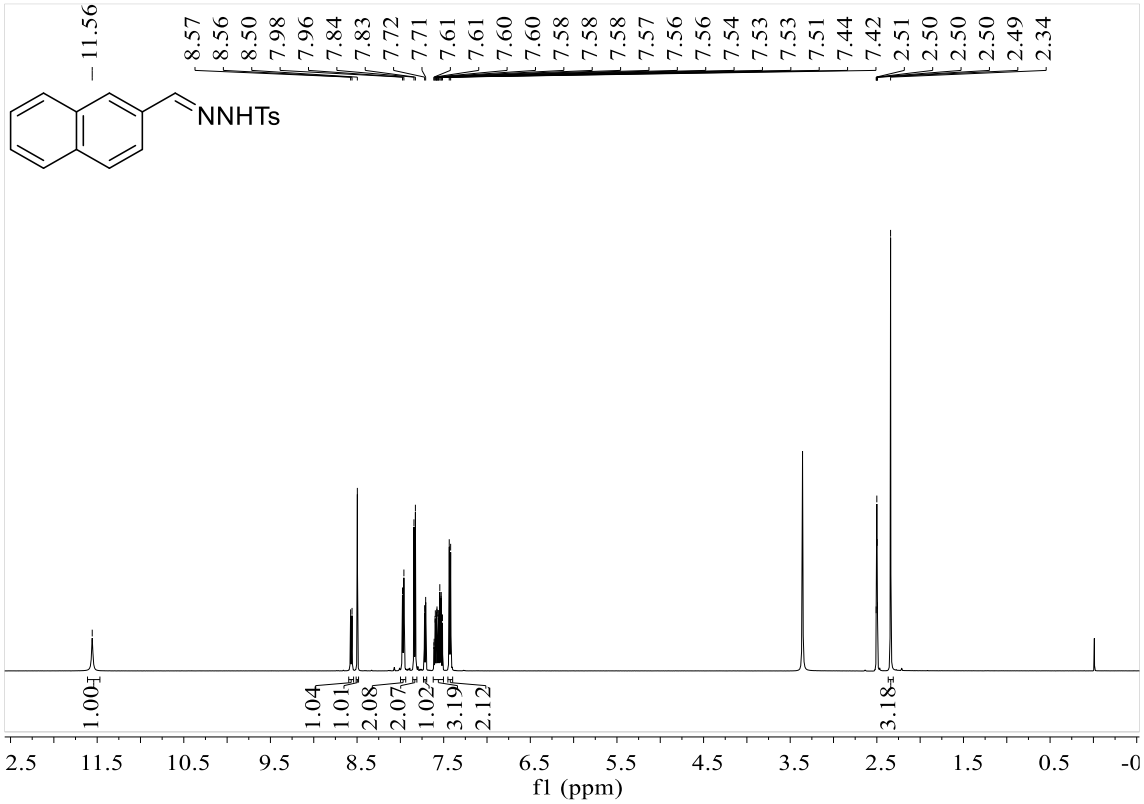
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 15a



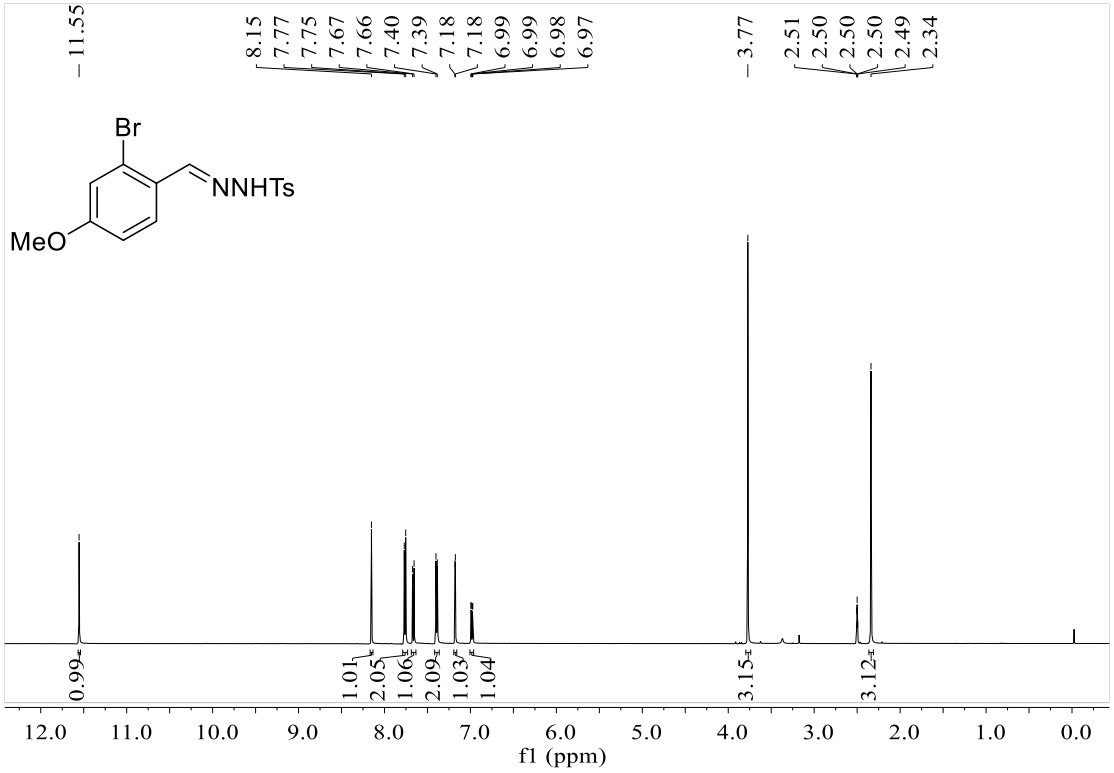
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 16a



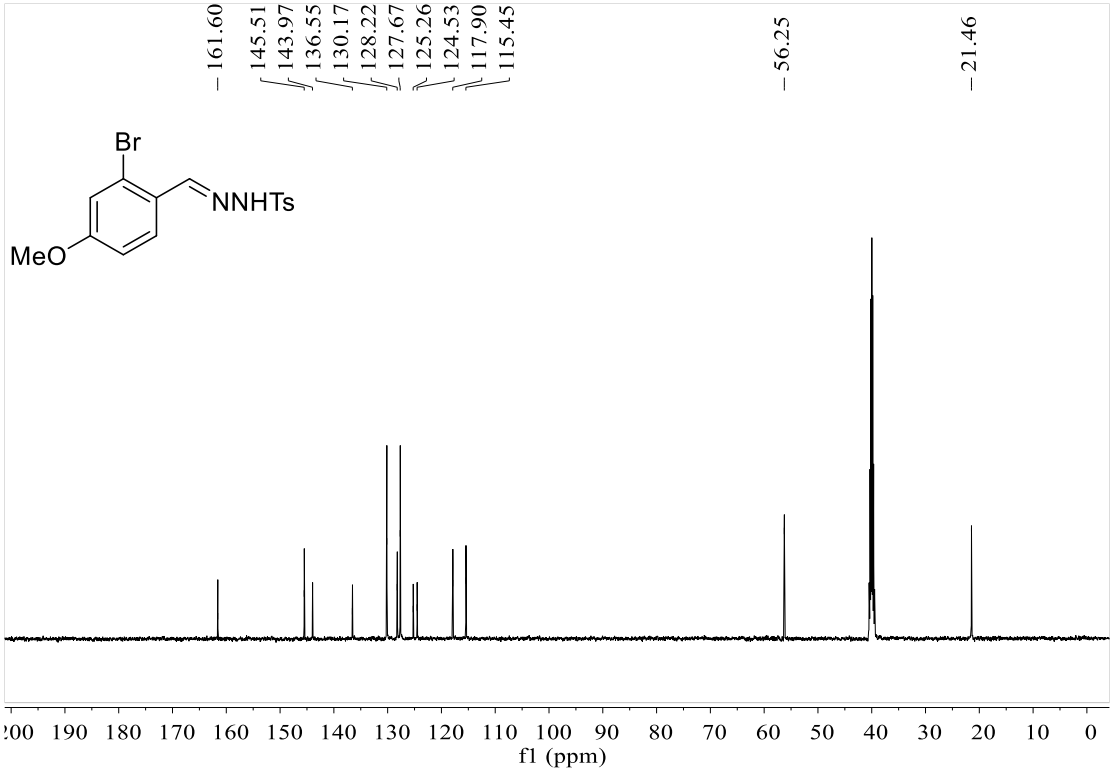
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 17a



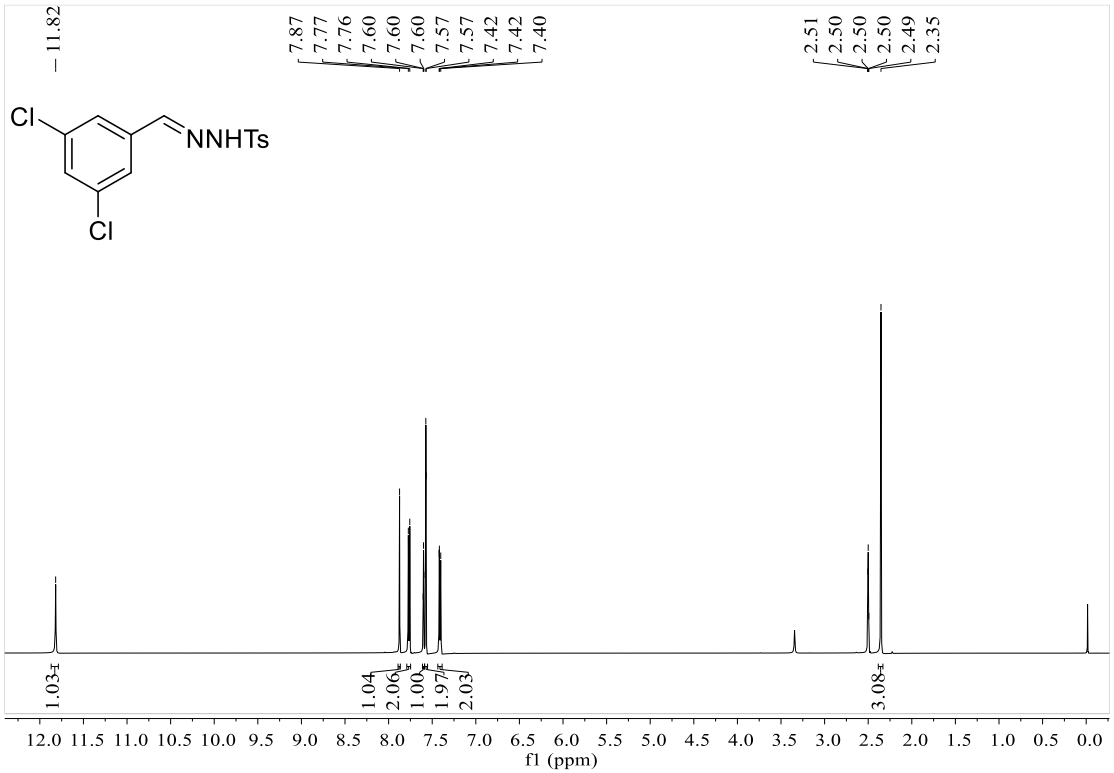
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 18a



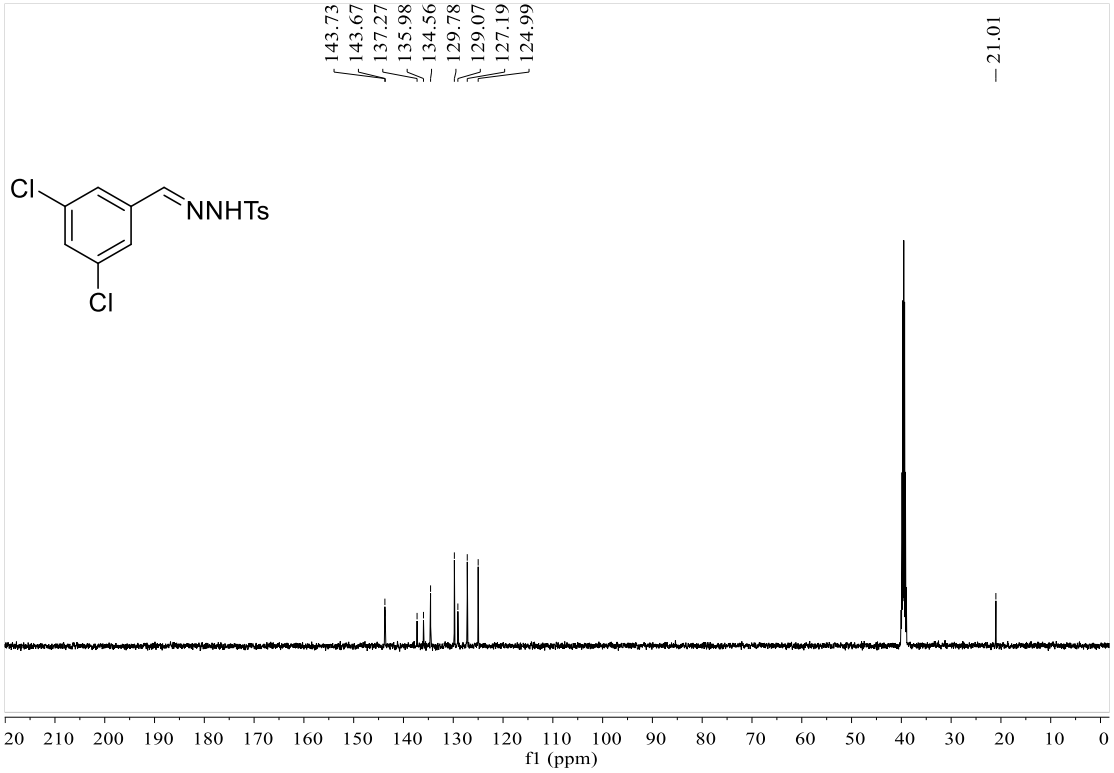
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 18a.



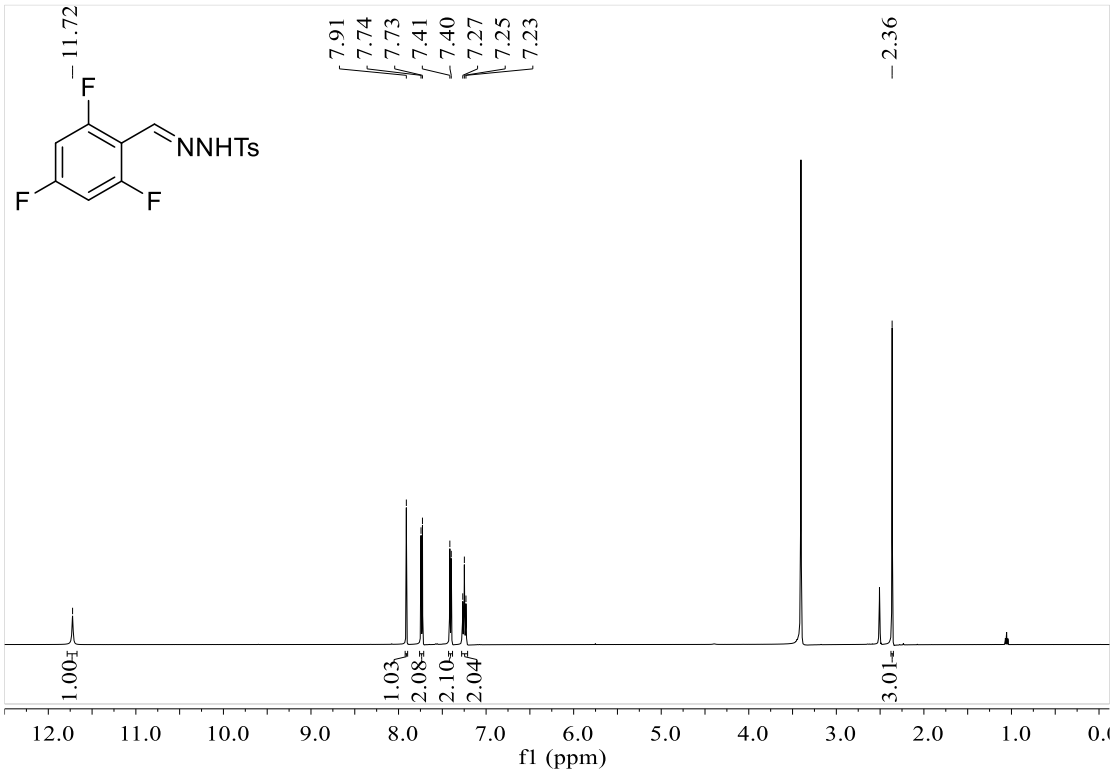
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 19a



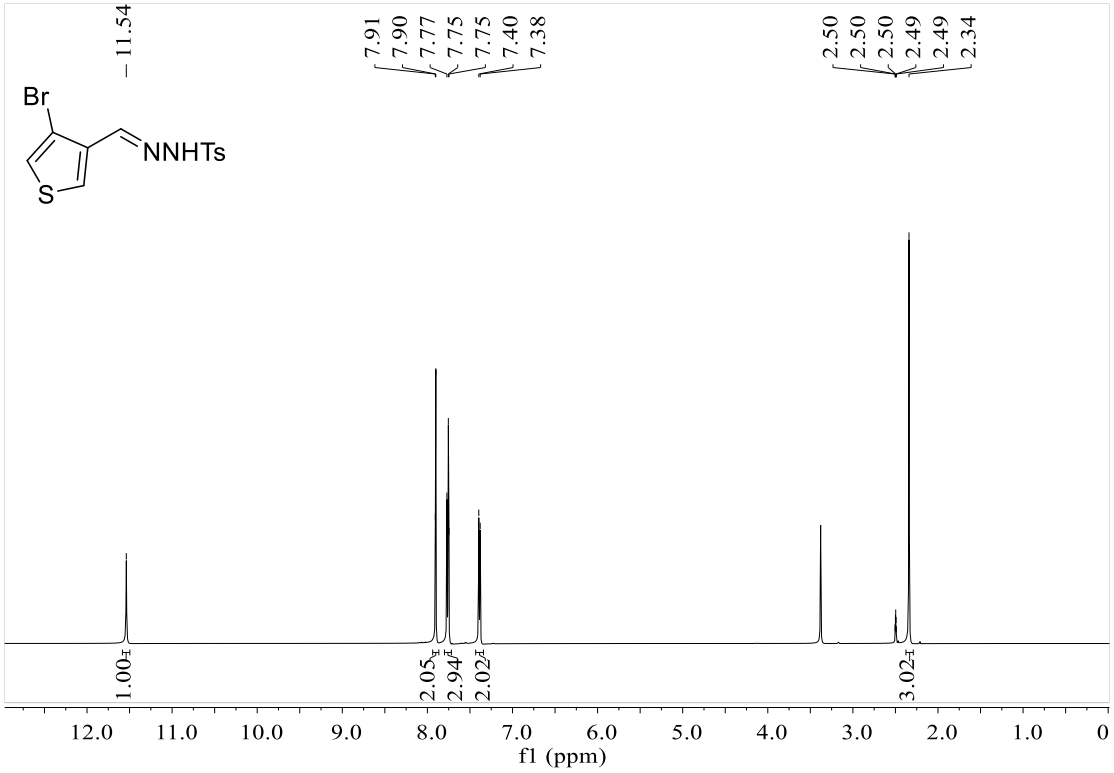
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 19a



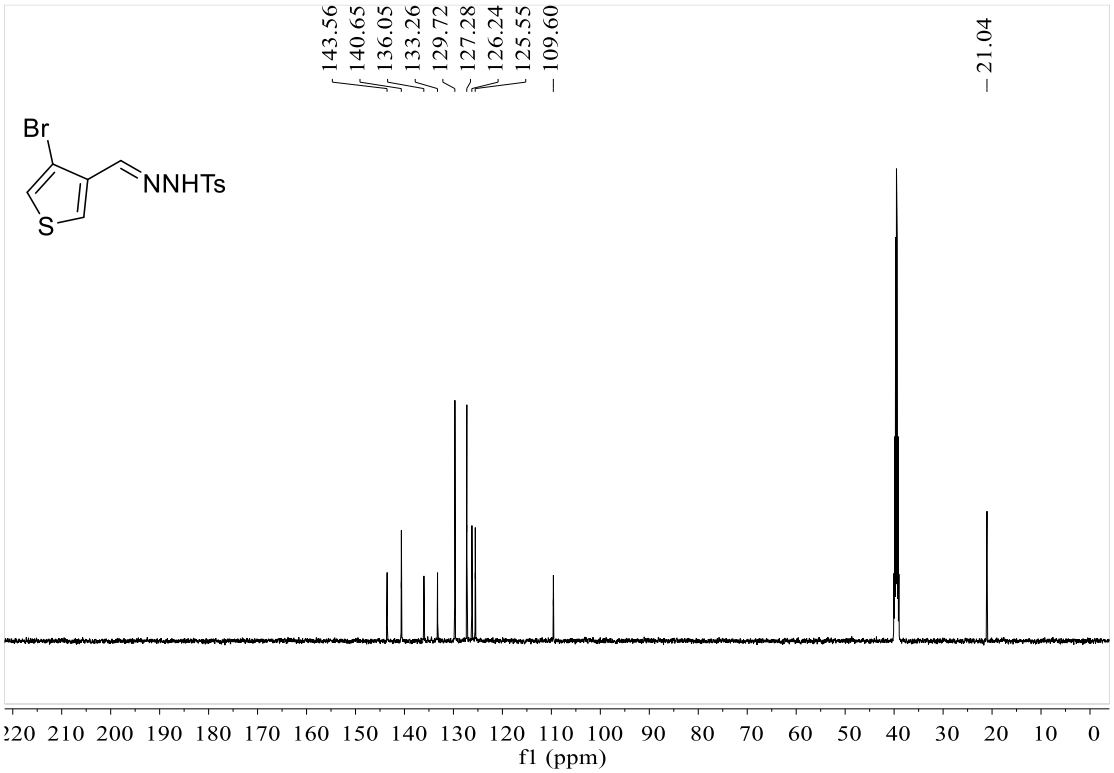
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 20a



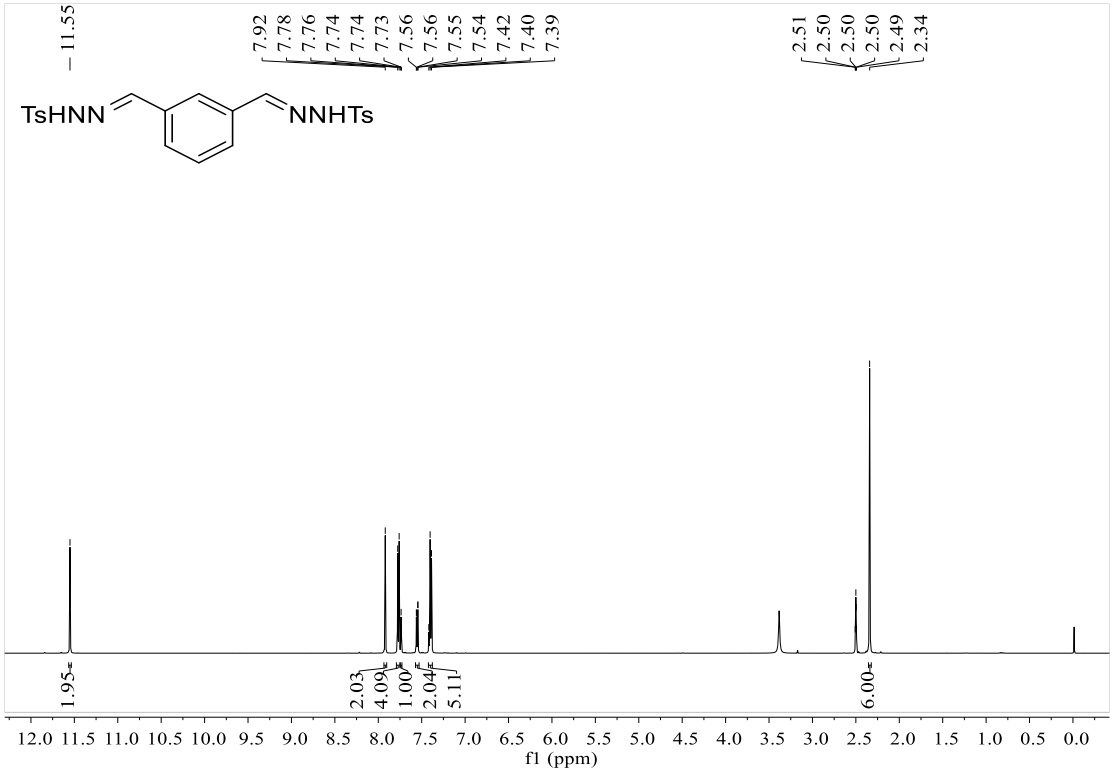
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 21a



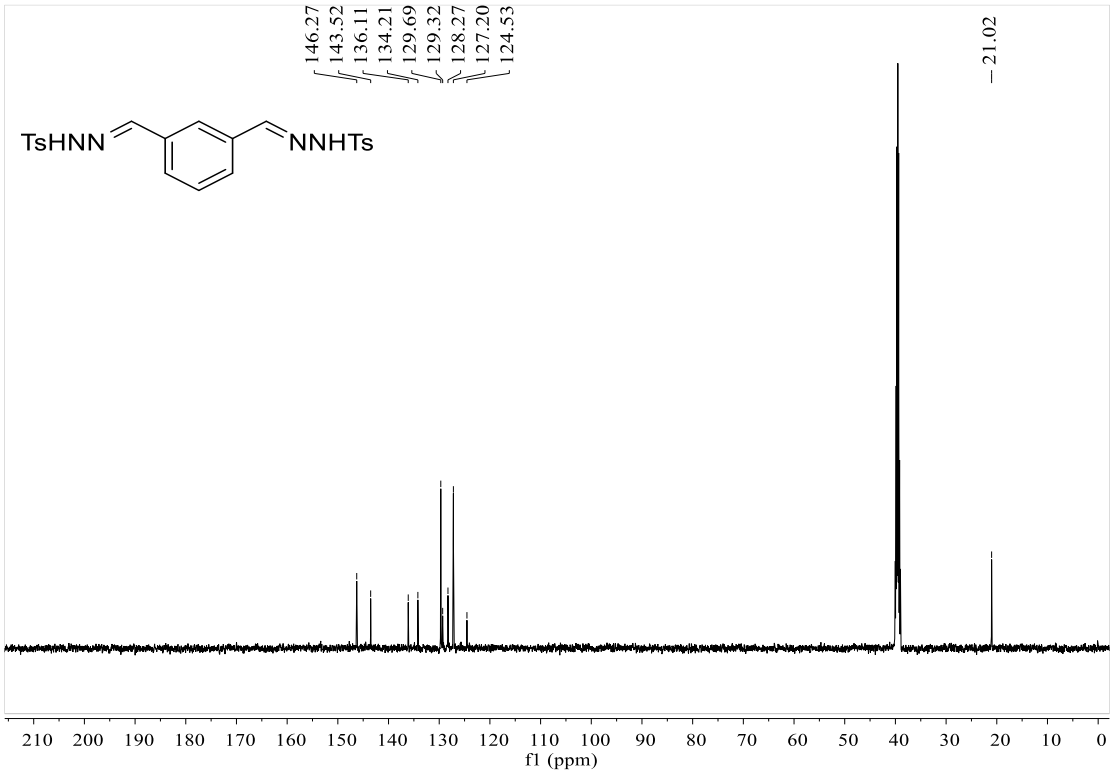
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 21a



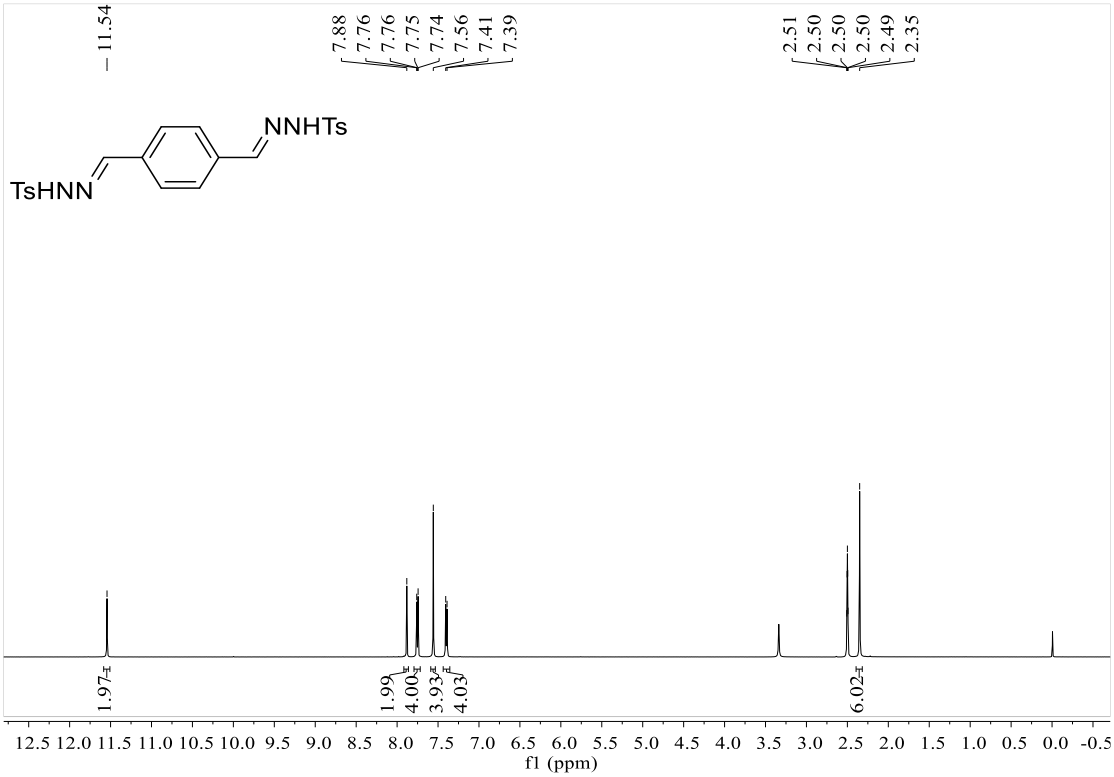
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 22a



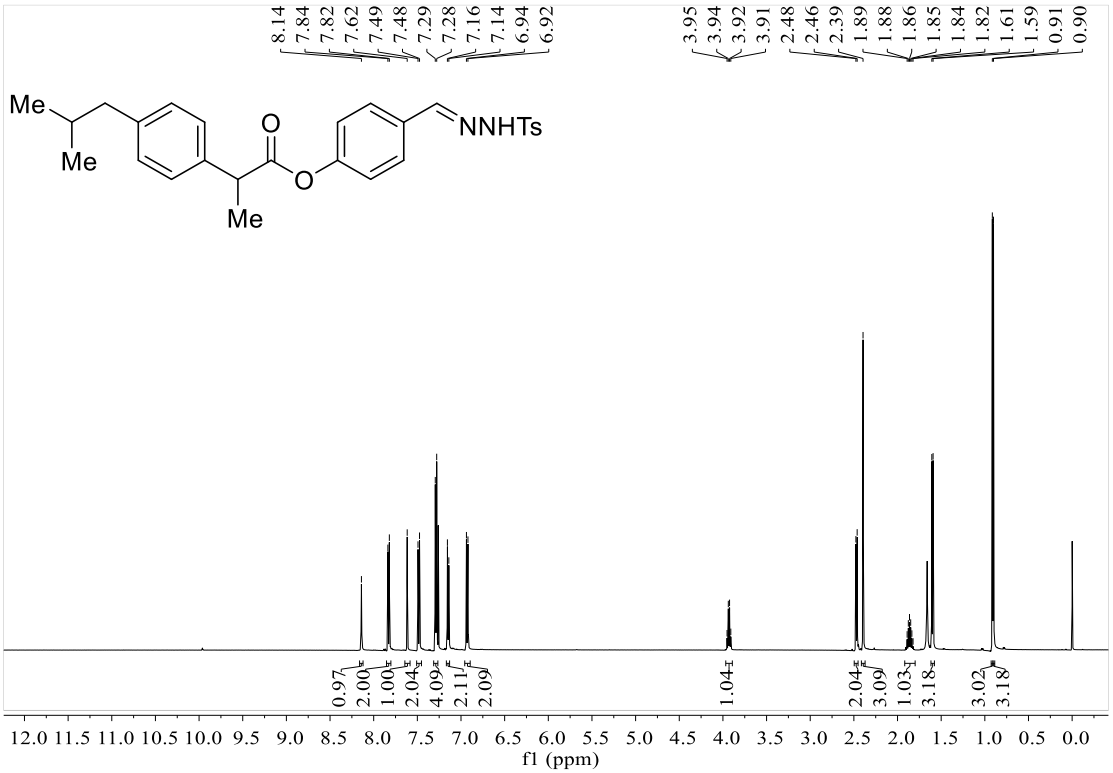
^{13}C NMR (126 MHz, DMSO-d_6) spectra for 22a



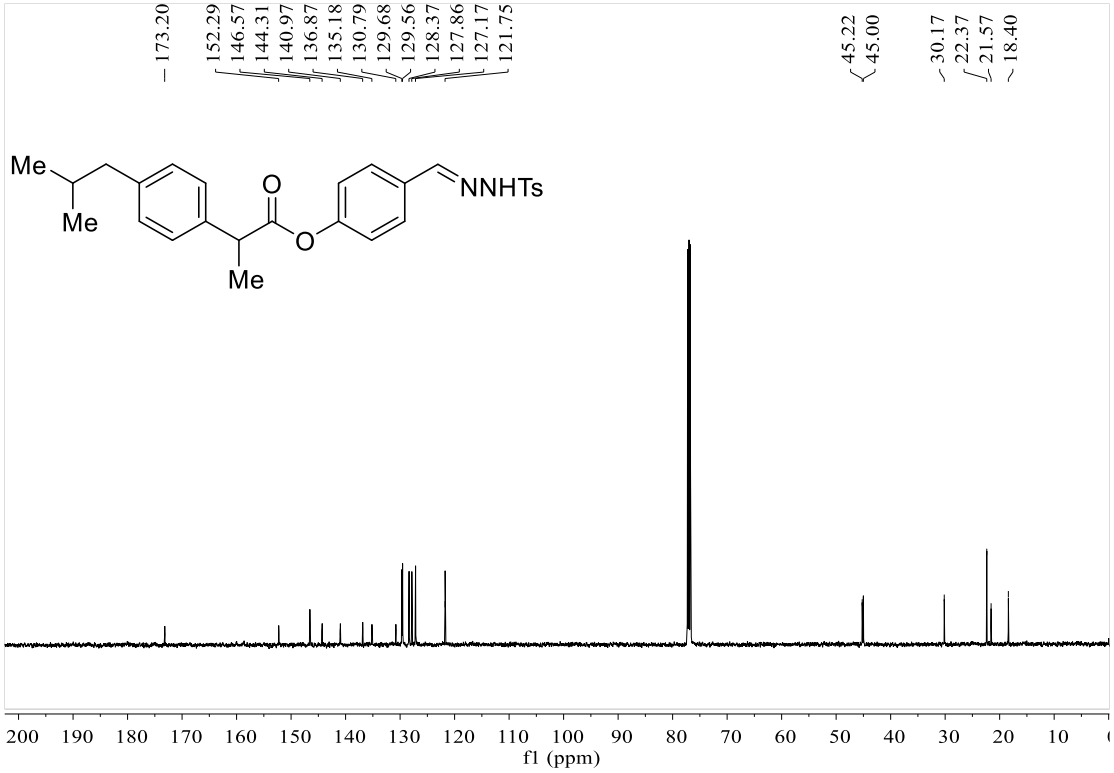
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 23a



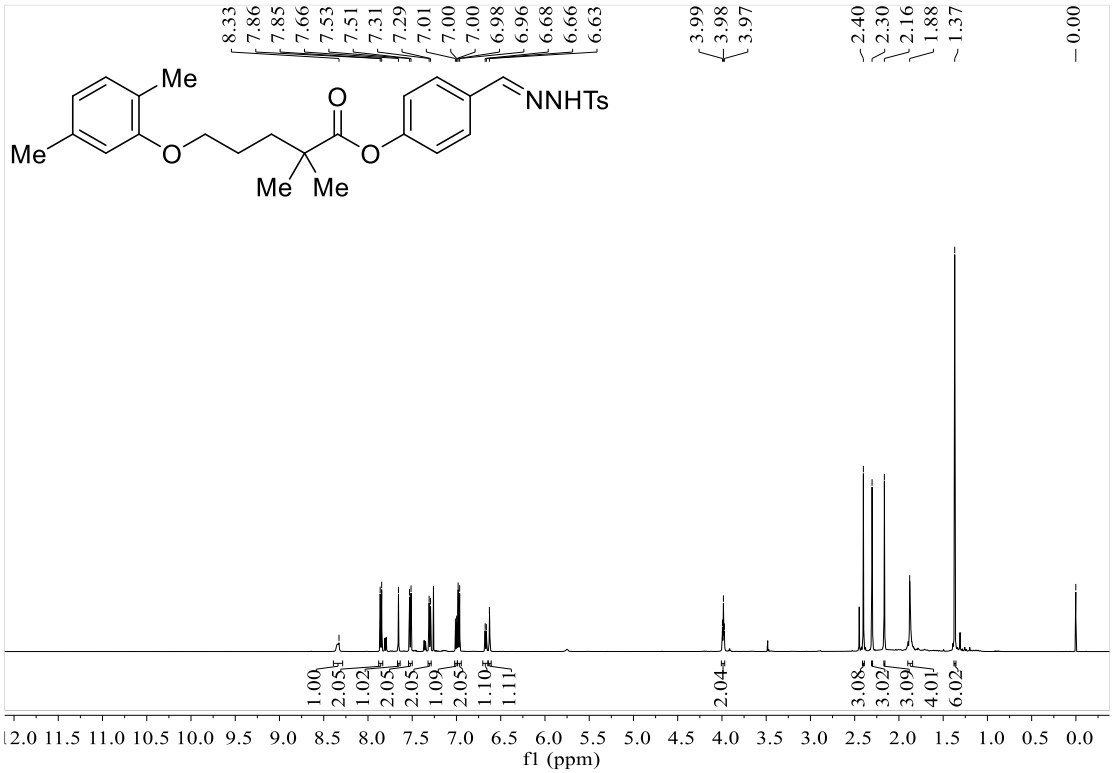
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 24a



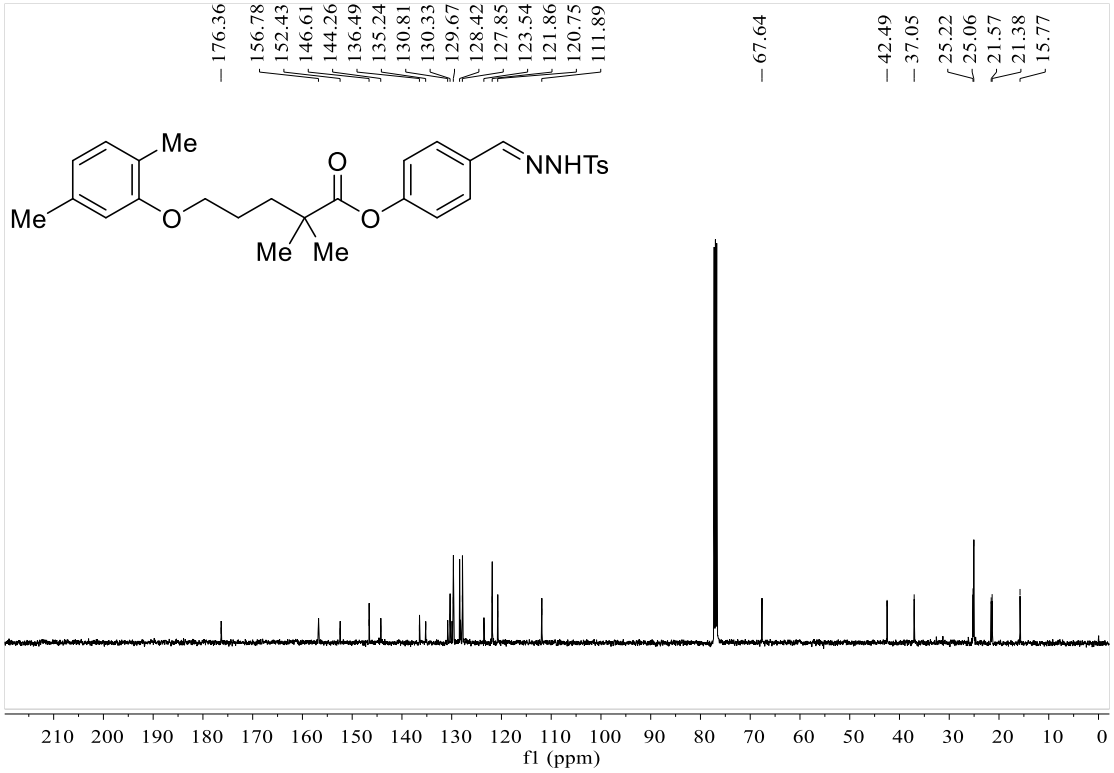
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 24a



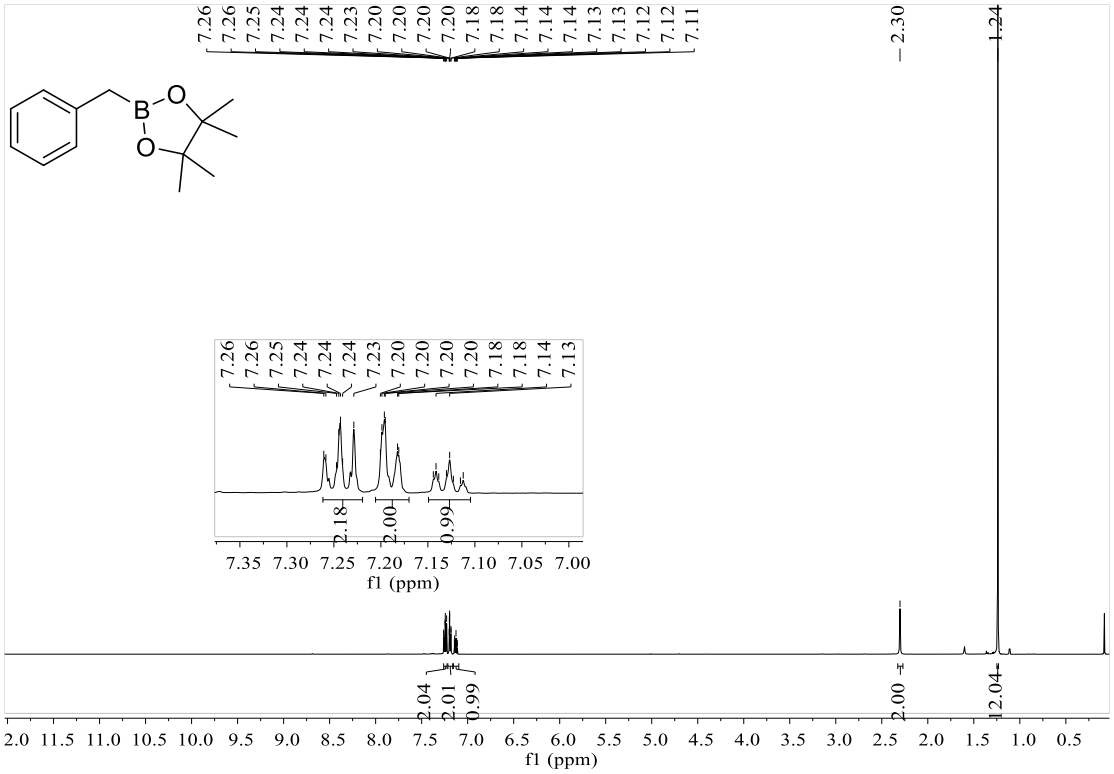
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 25a

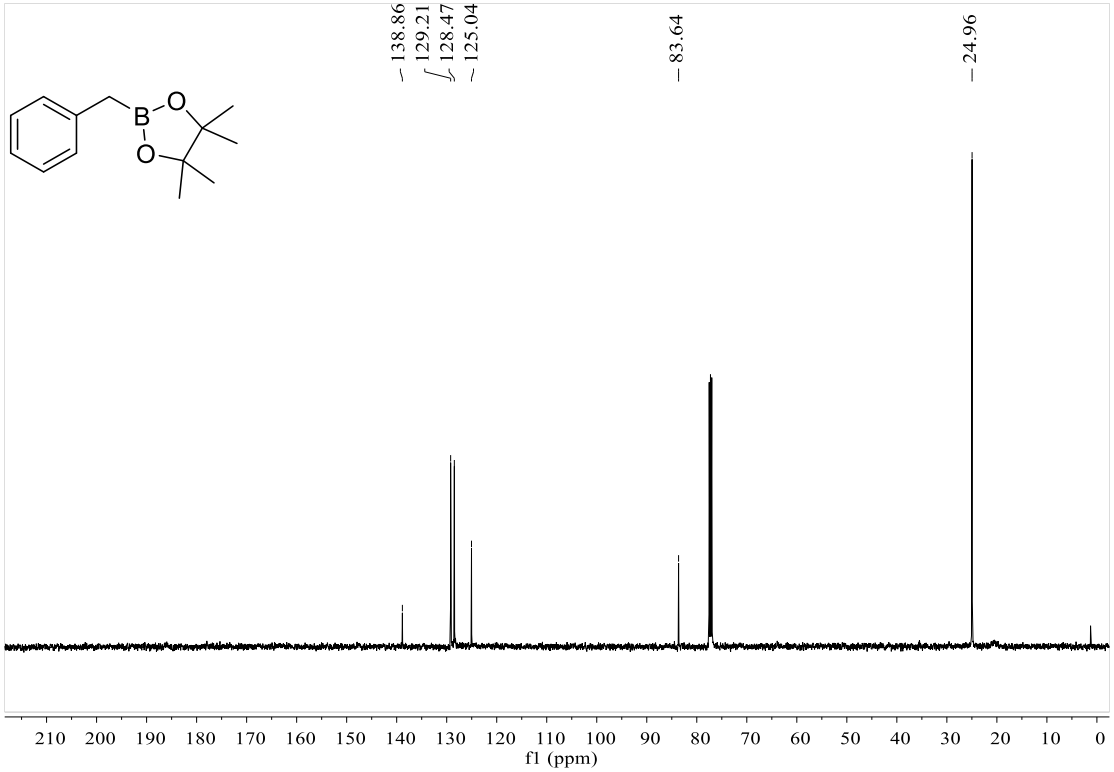


^{13}C NMR (126 MHz, $CDCl_3$) spectra for 25a

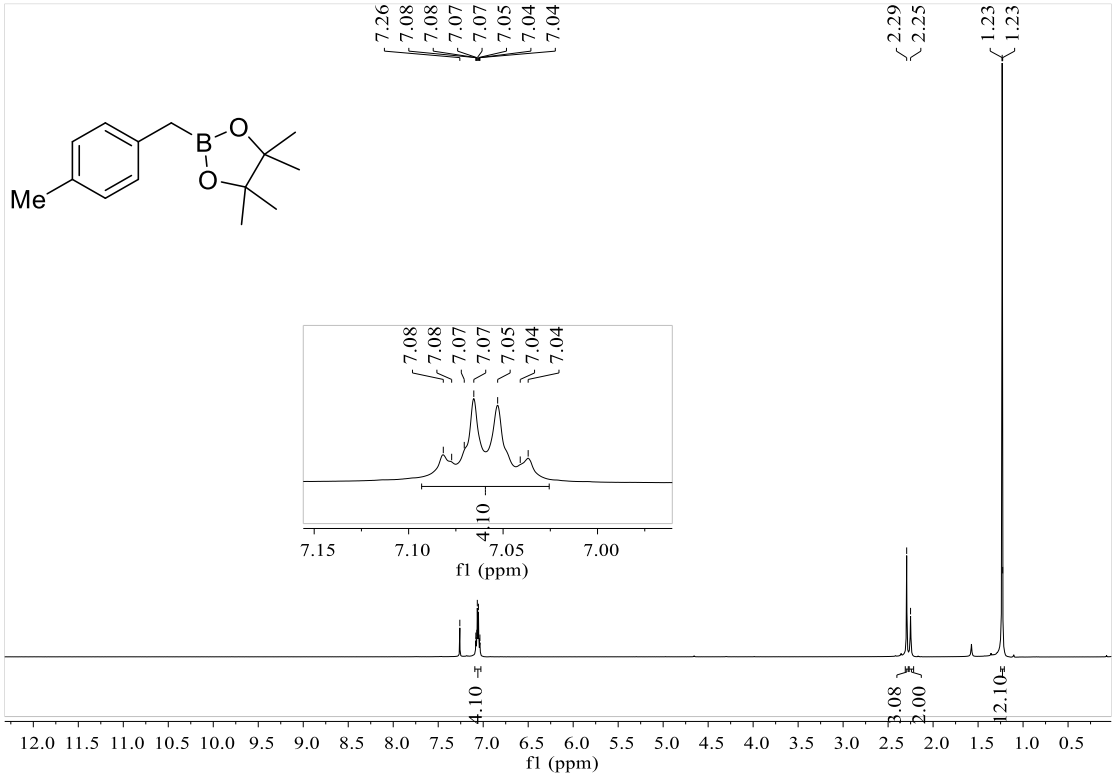


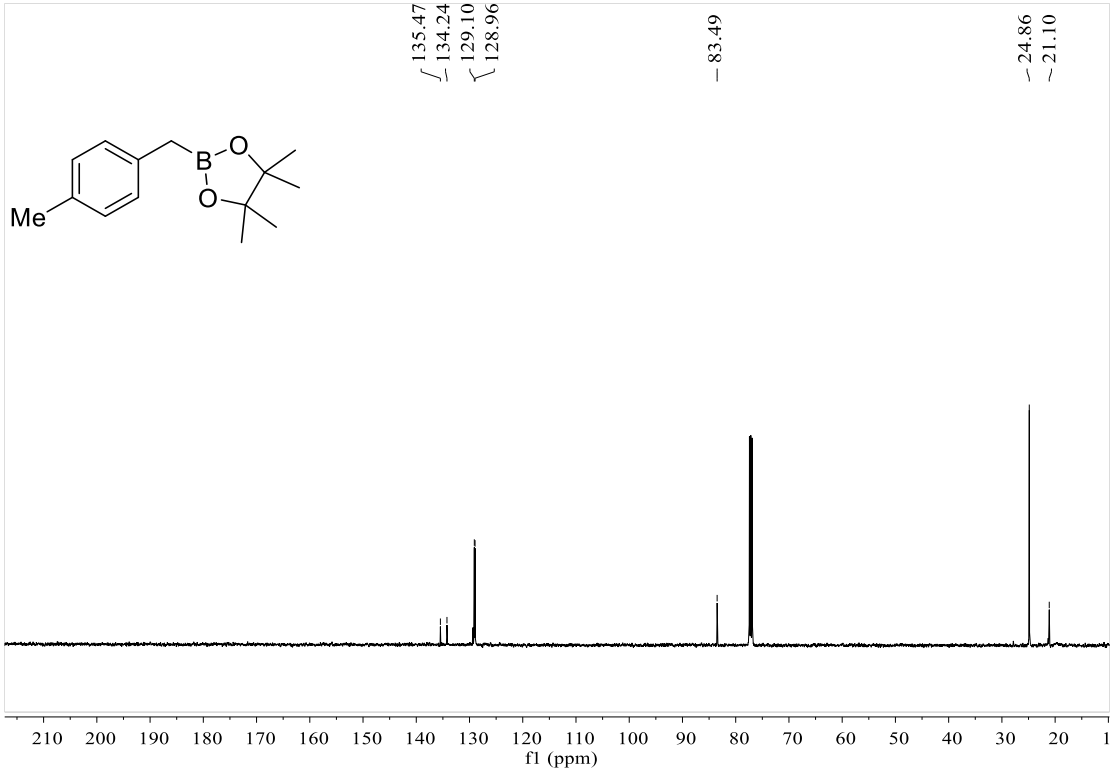
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1d



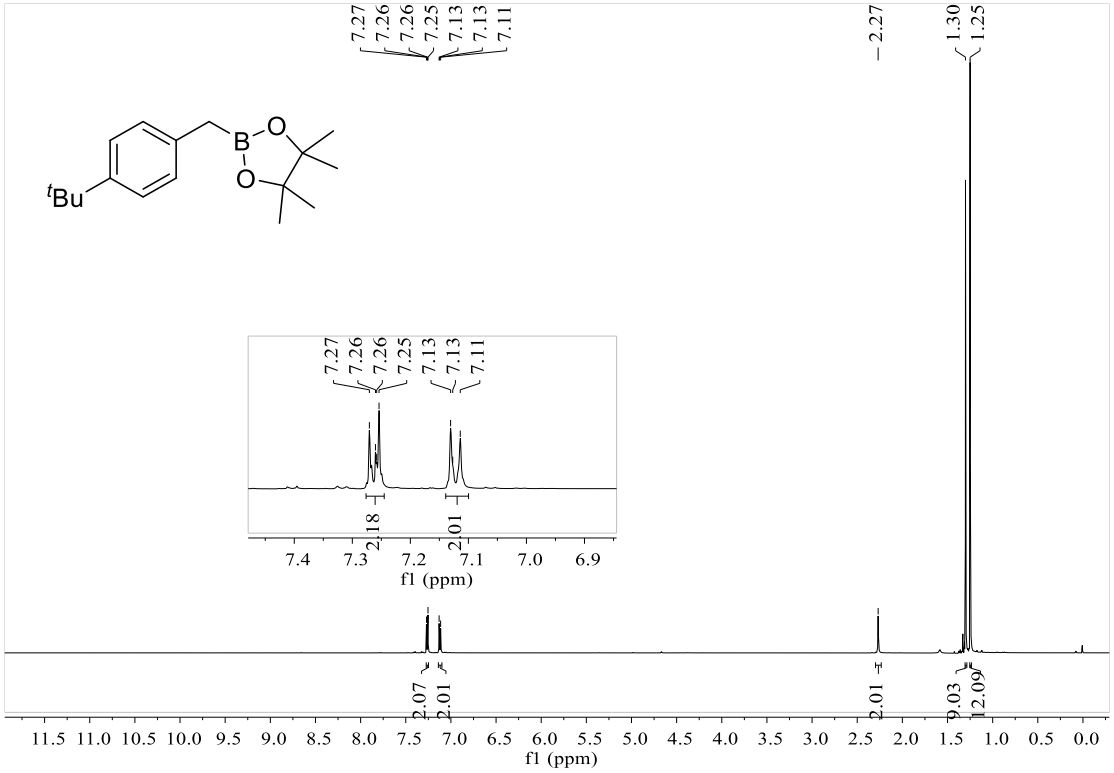


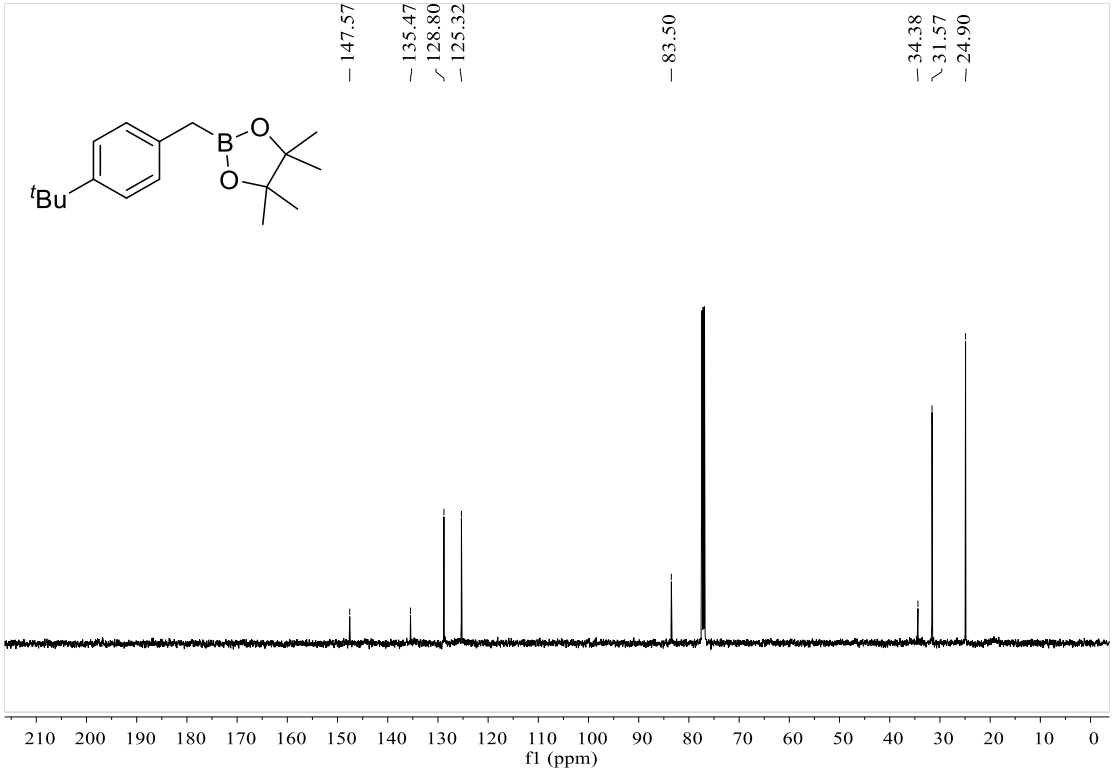
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 2d



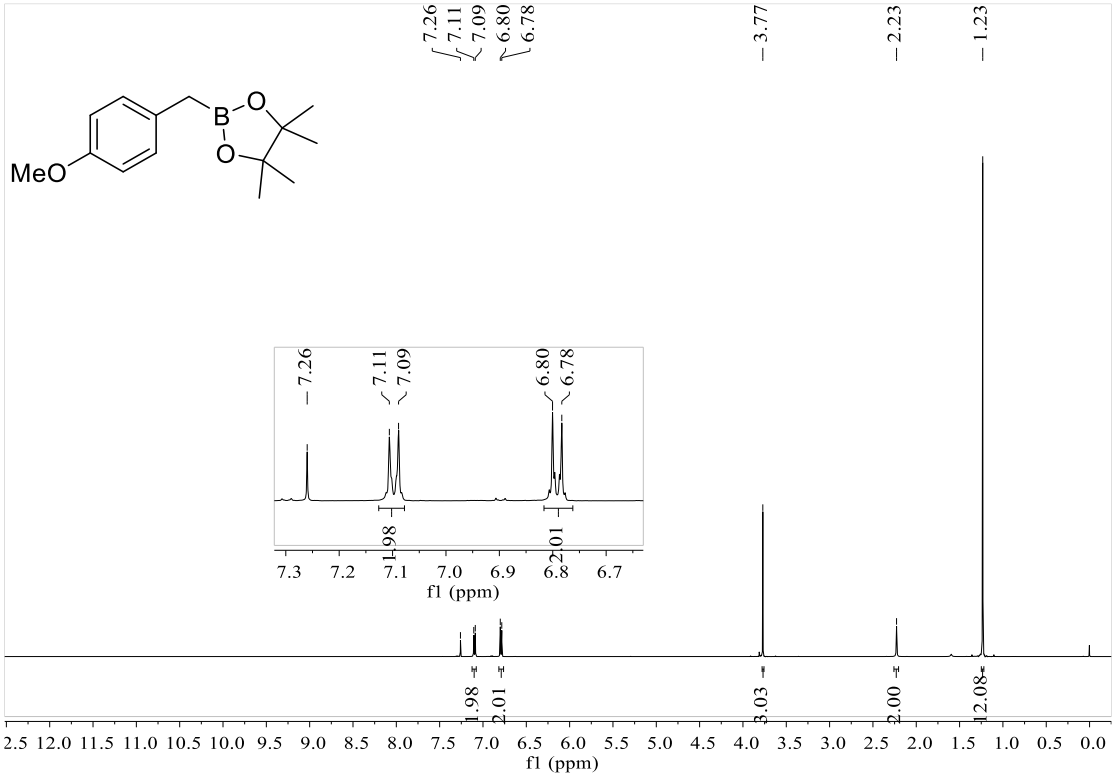


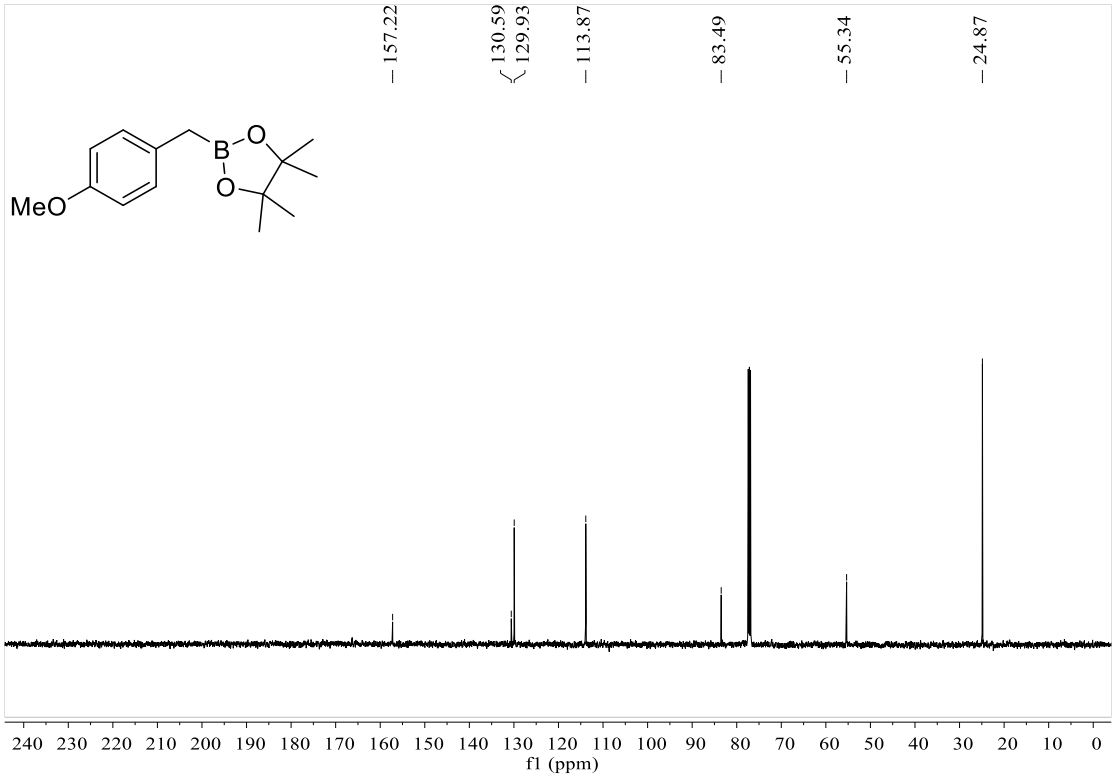
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 3d



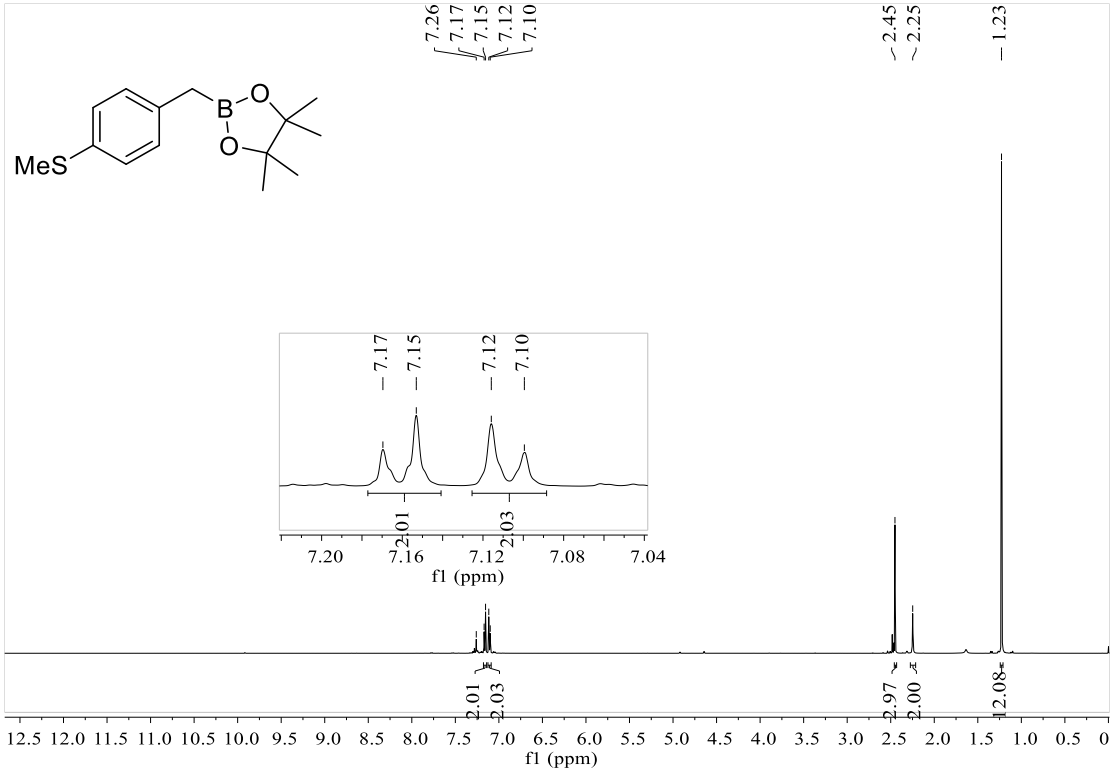


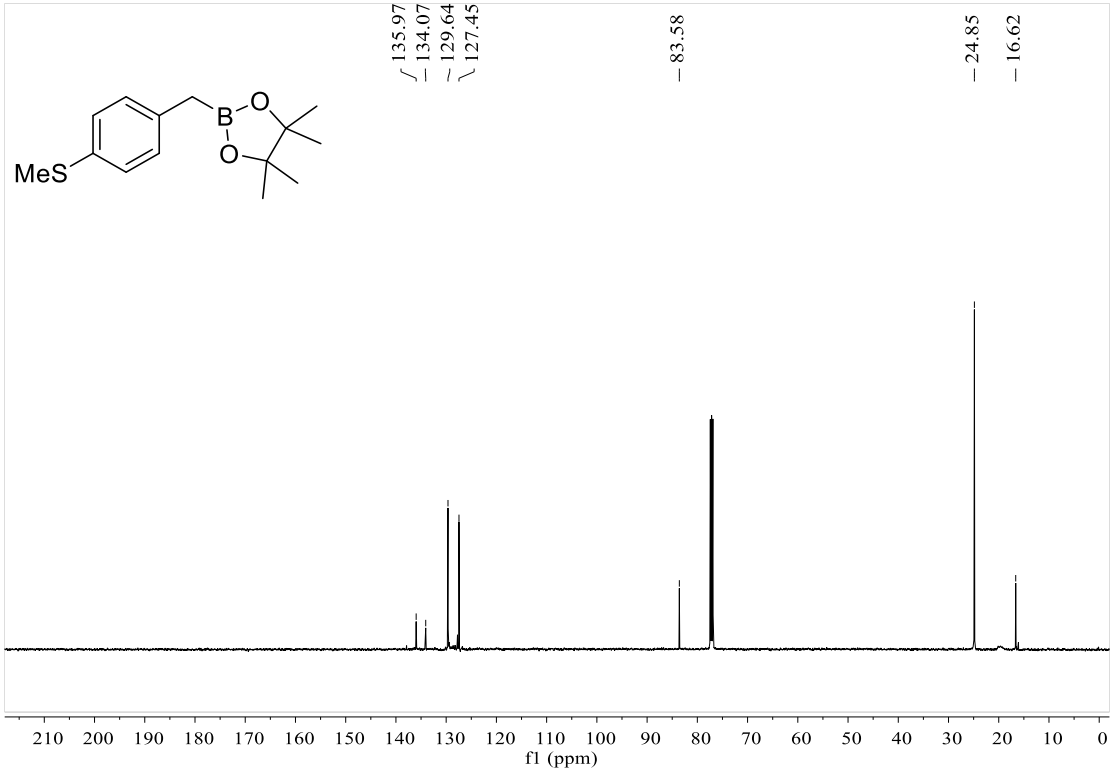
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 4d



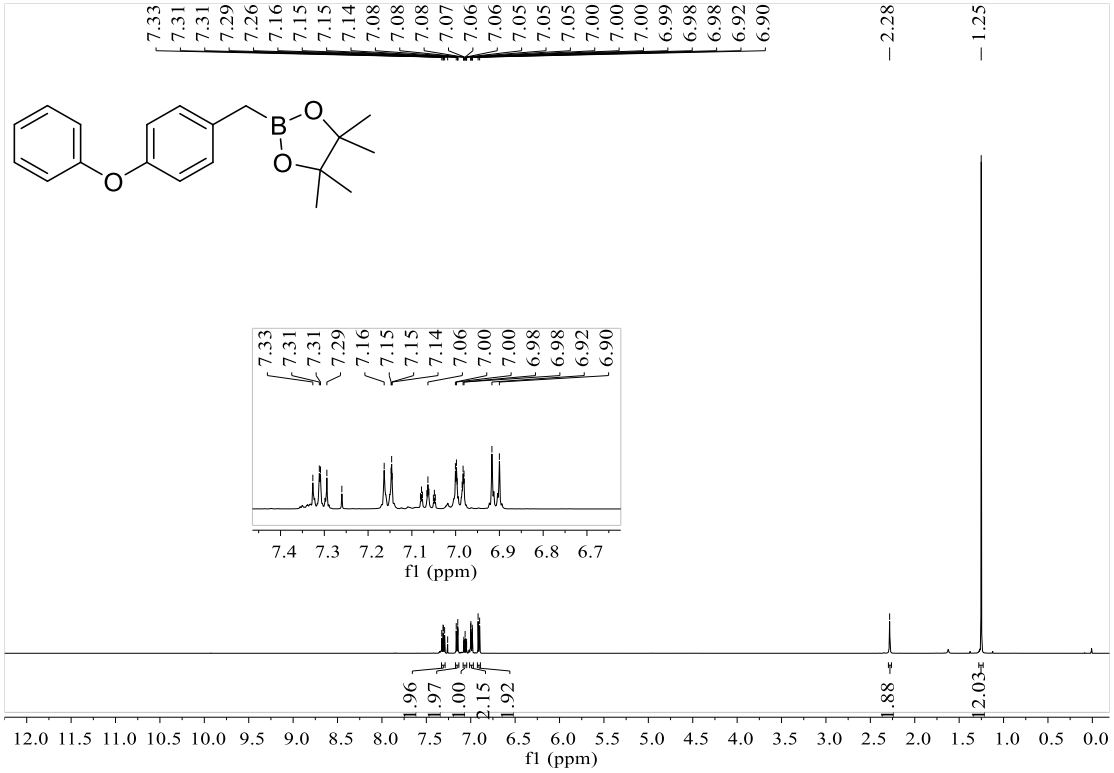


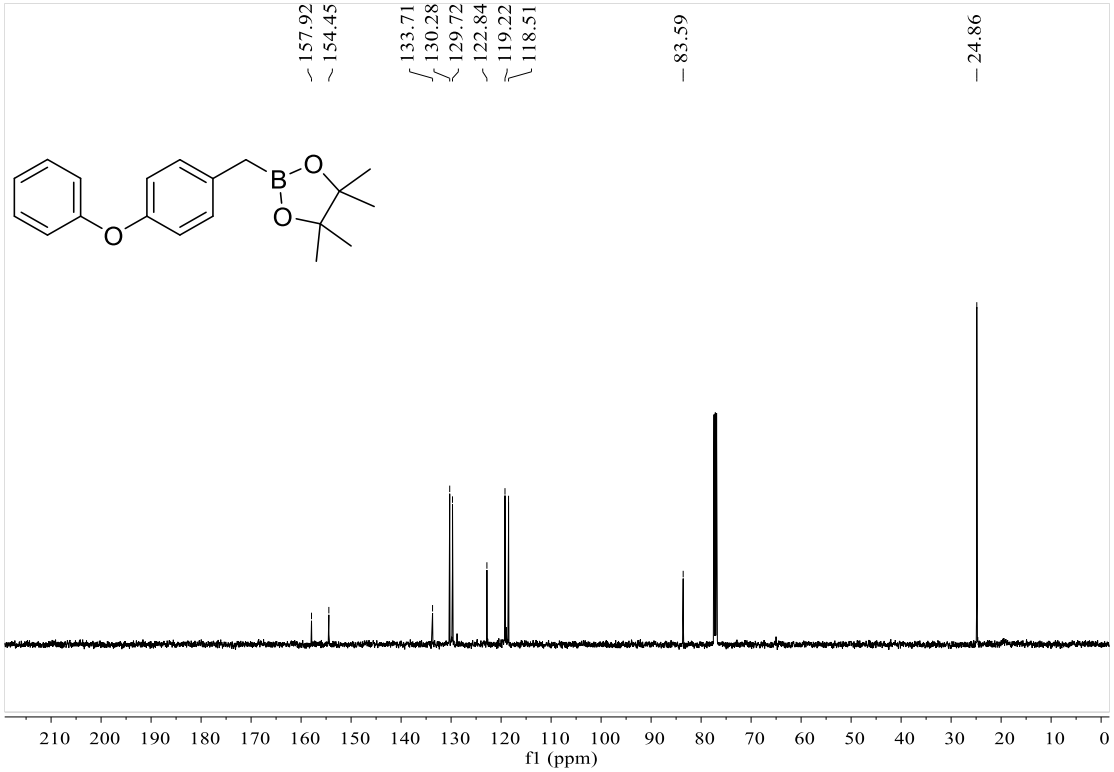
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 5d



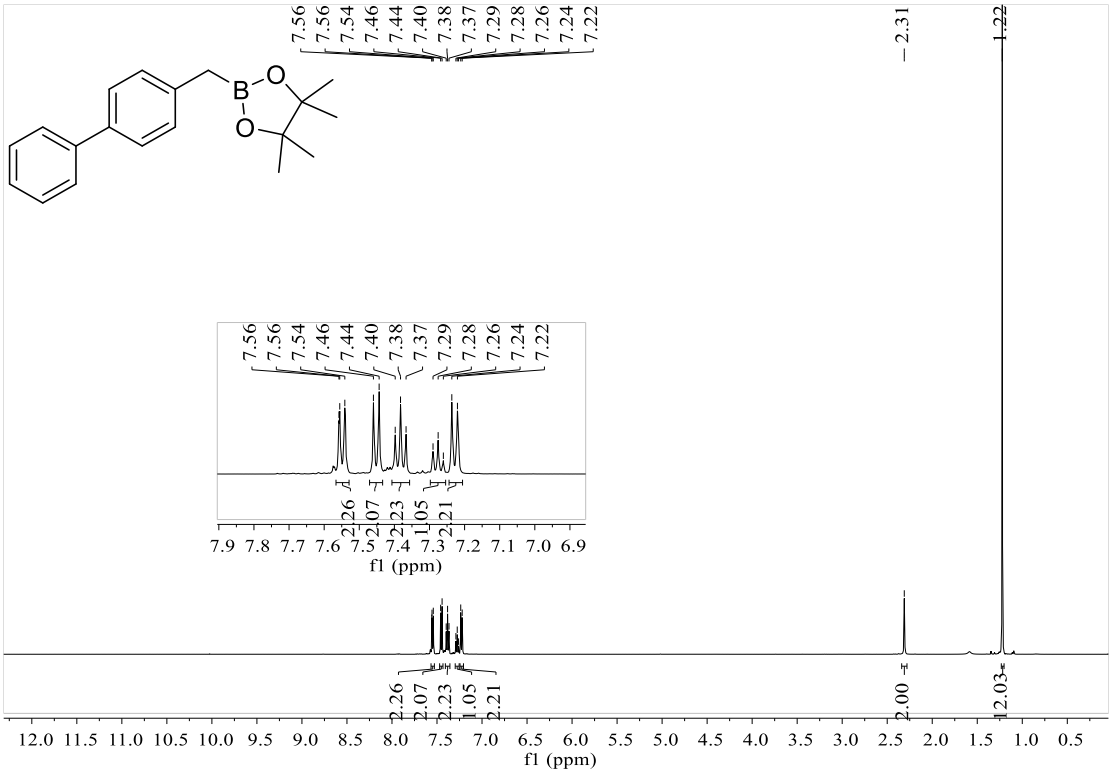


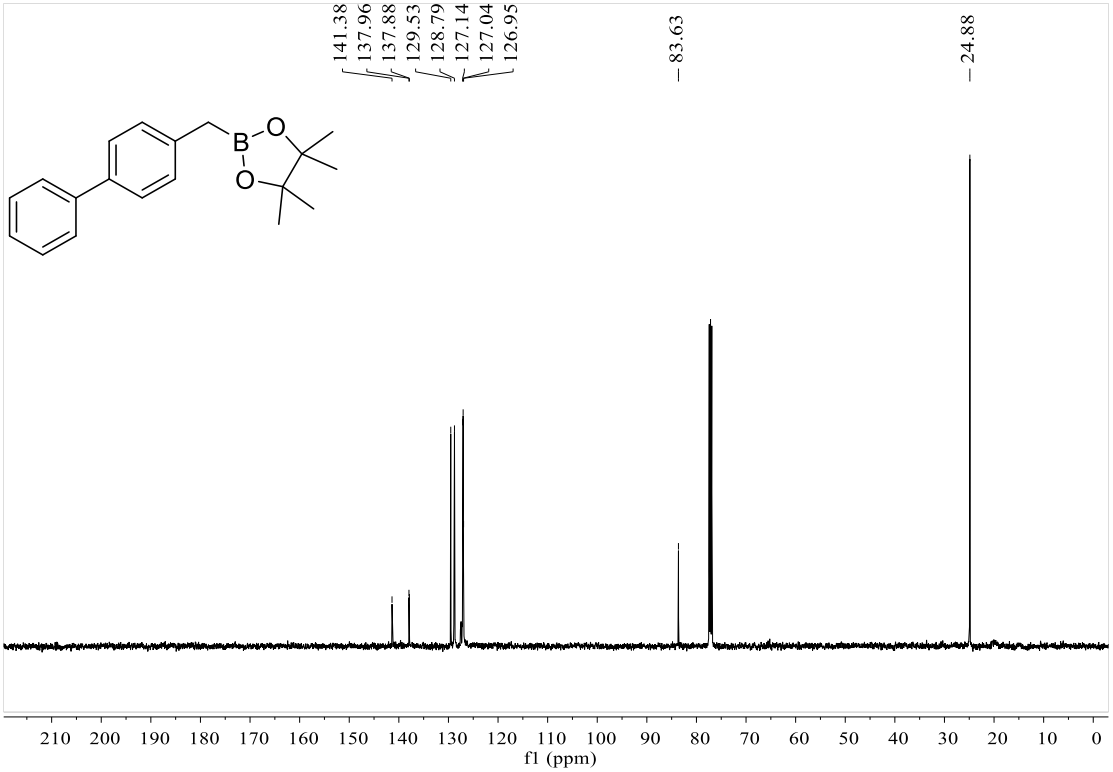
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 6d



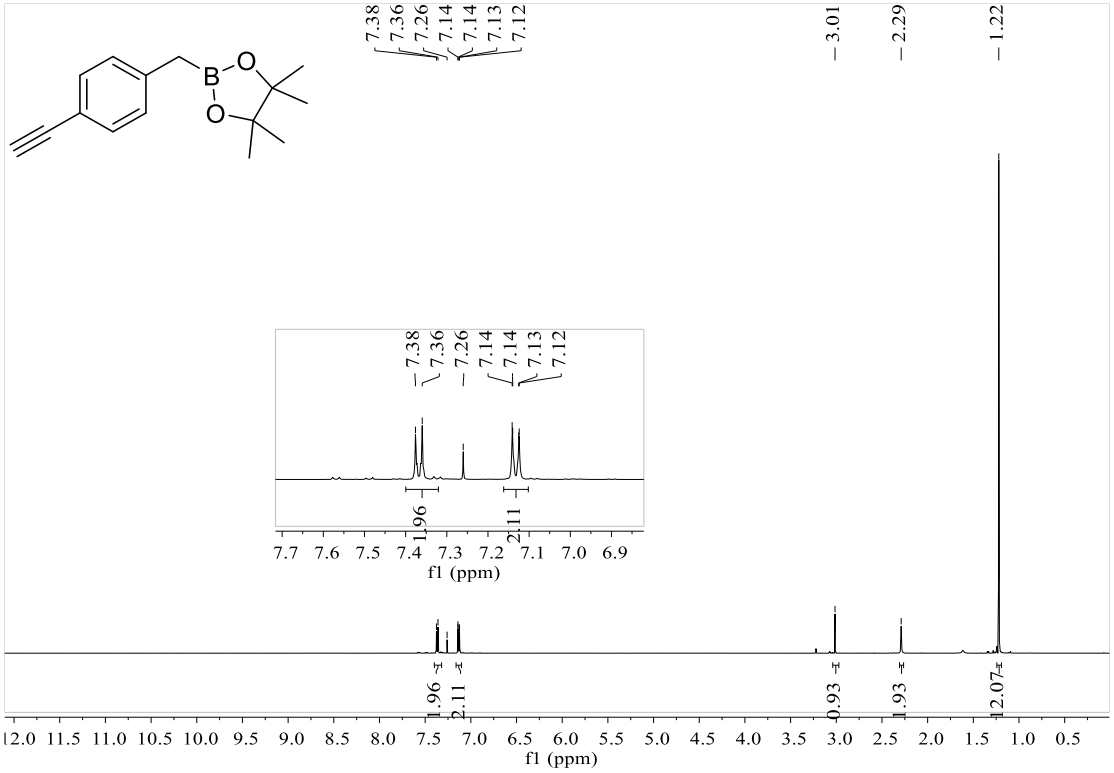


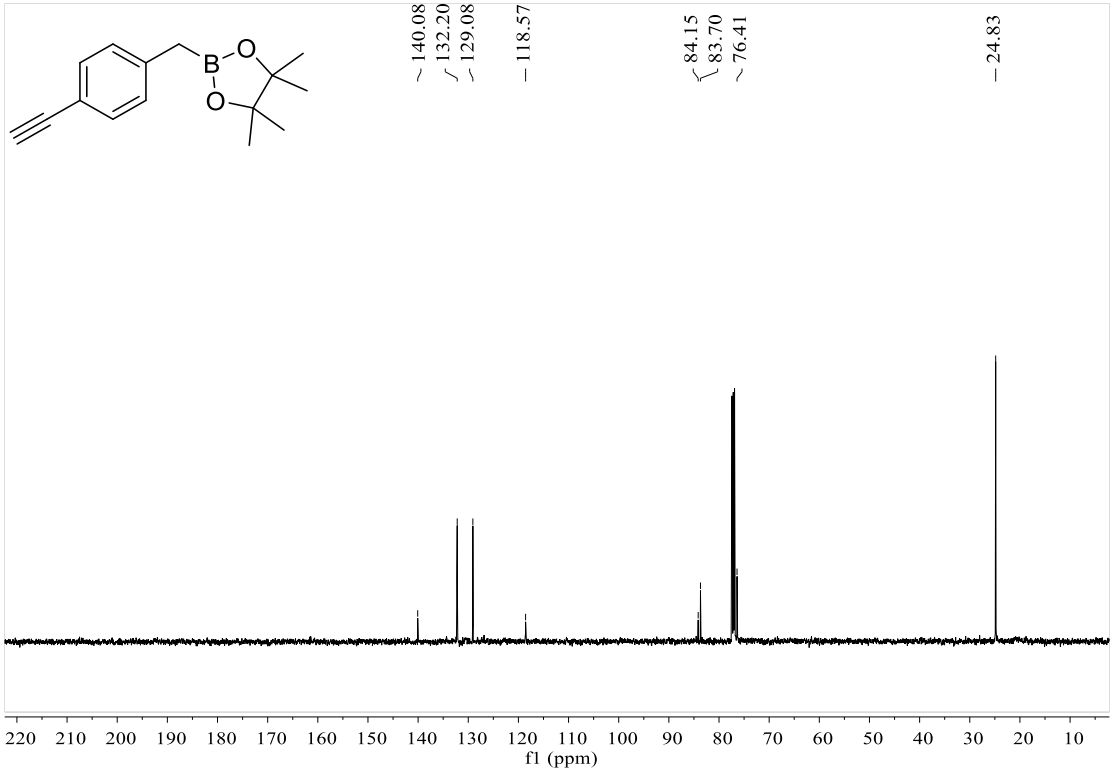
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 7d



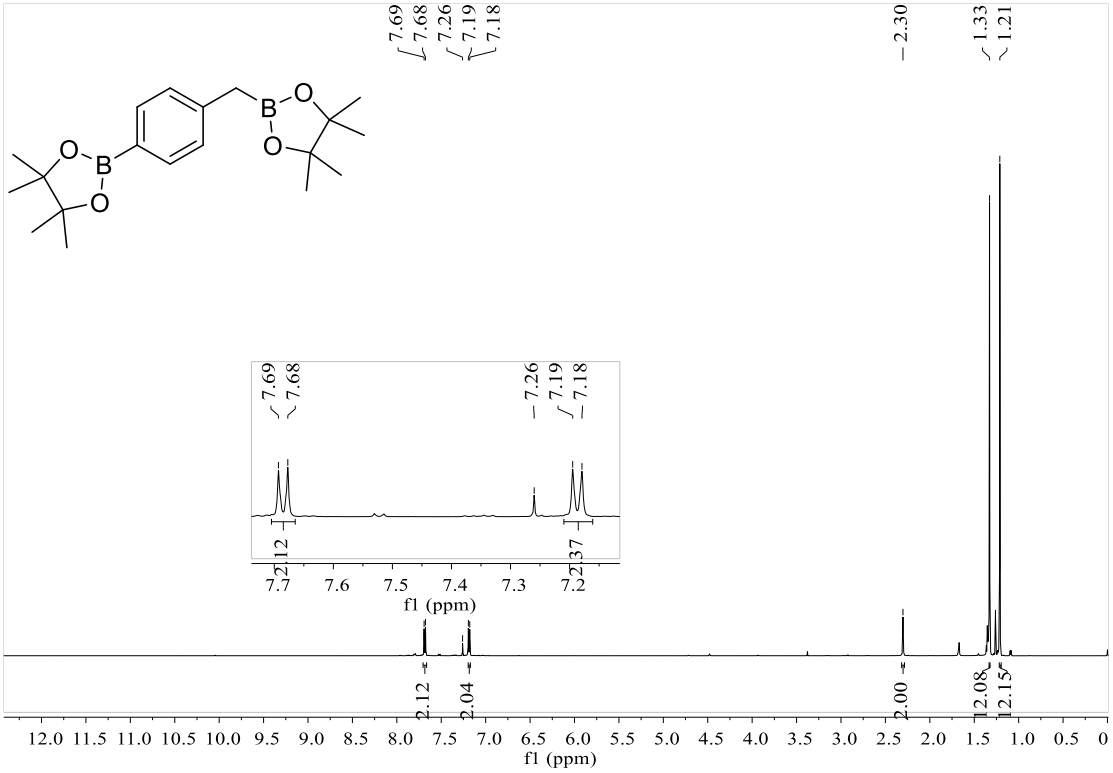


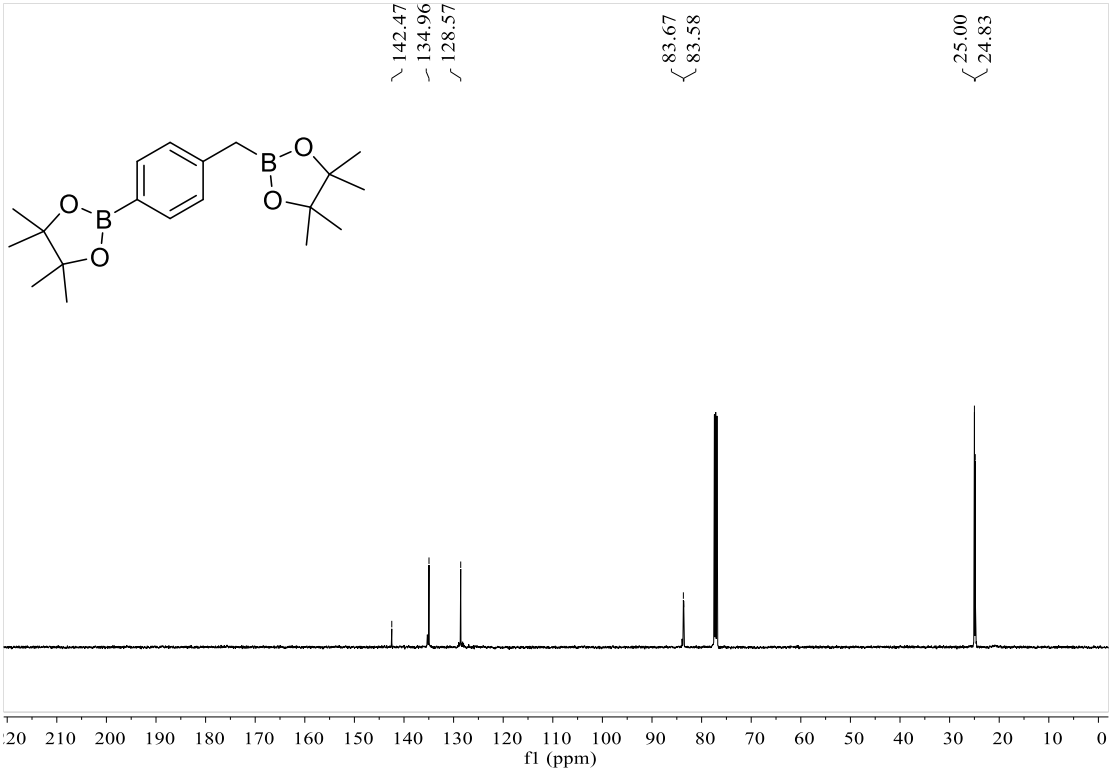
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 8d



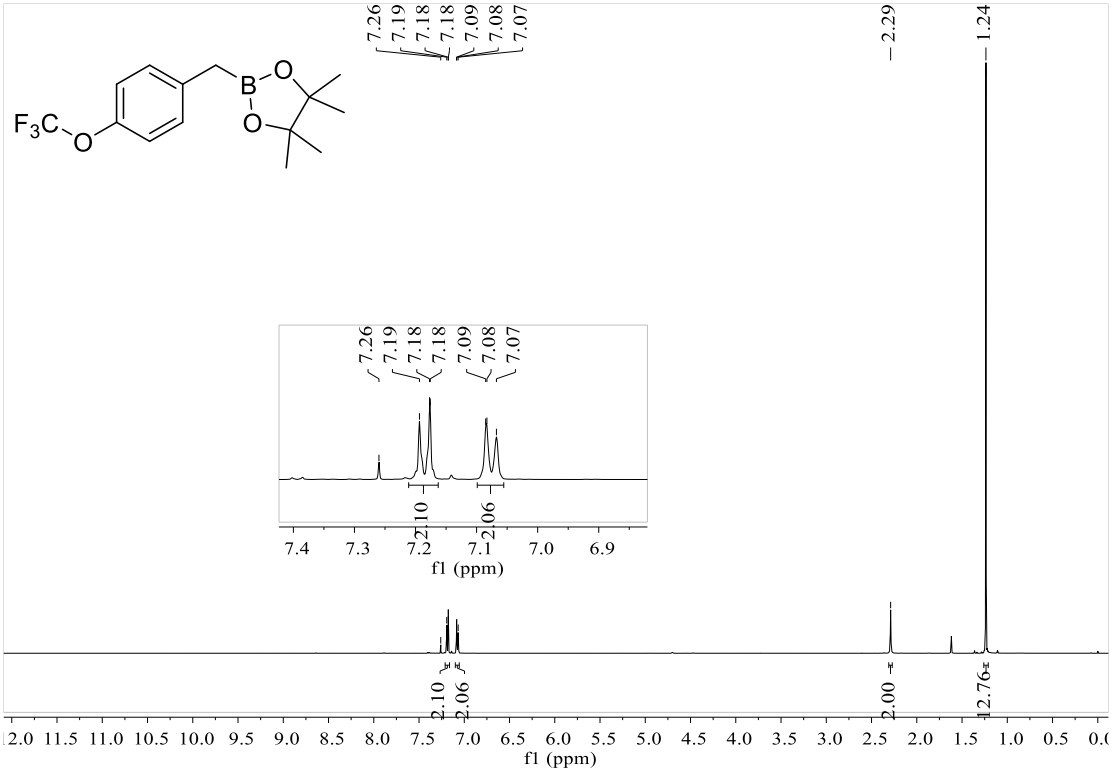


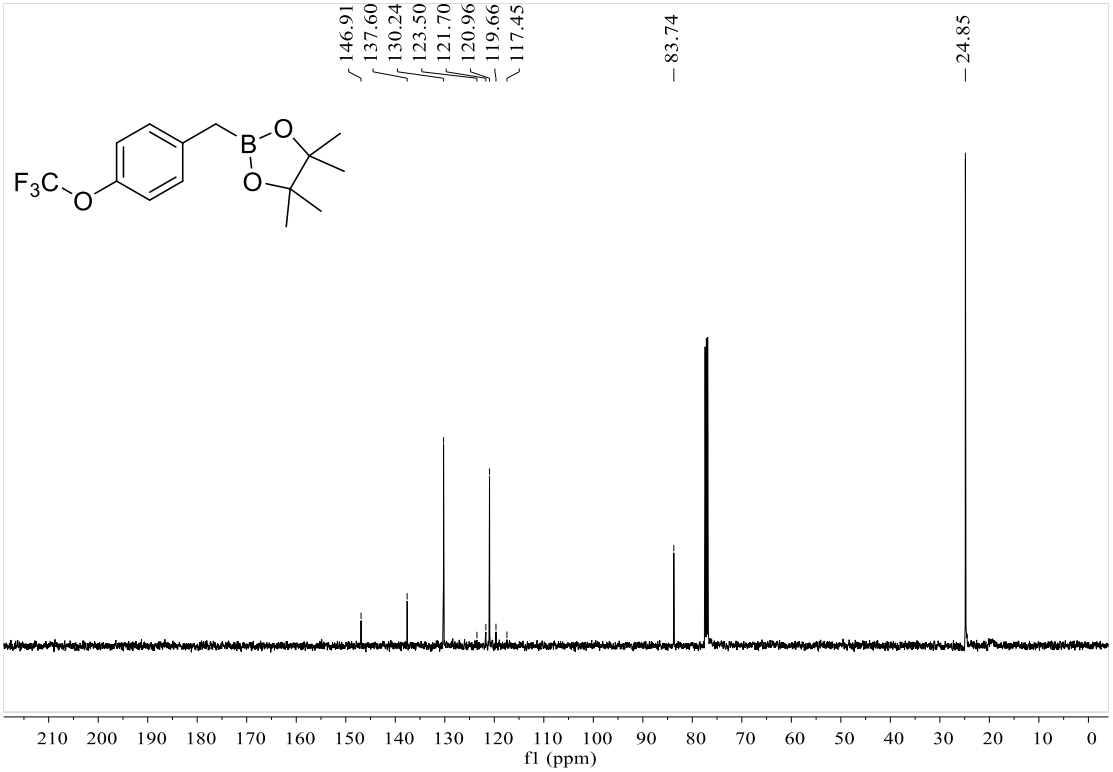
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 9d



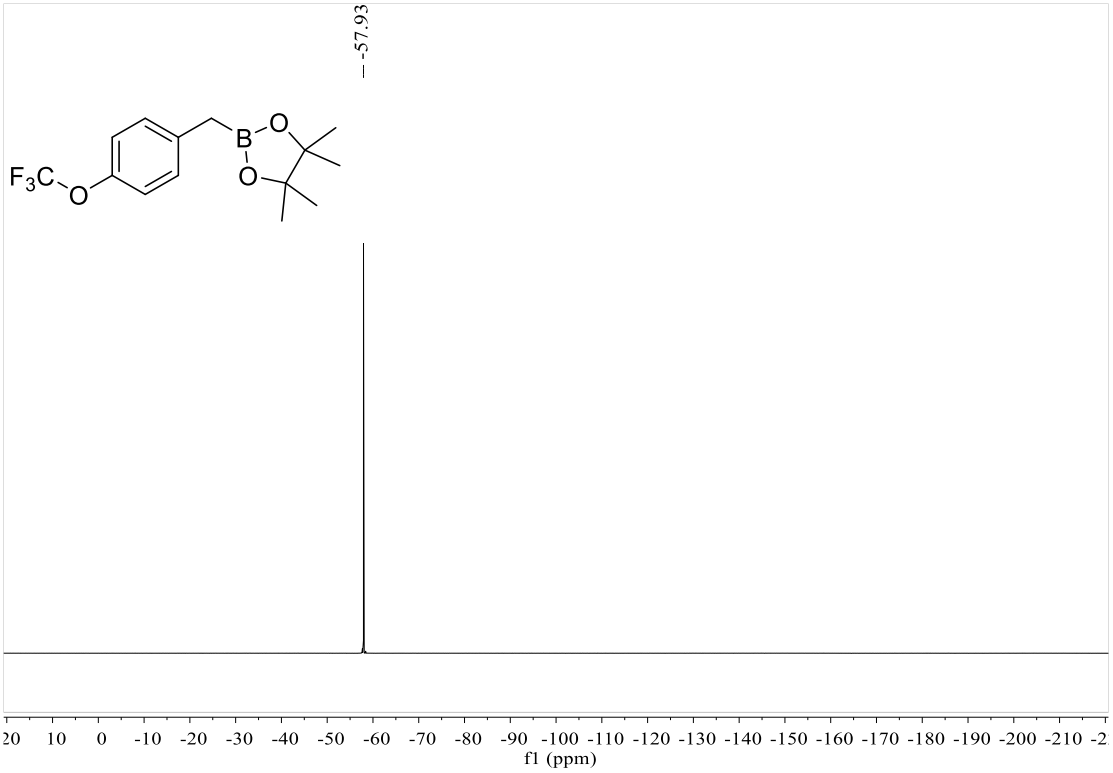


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 10d

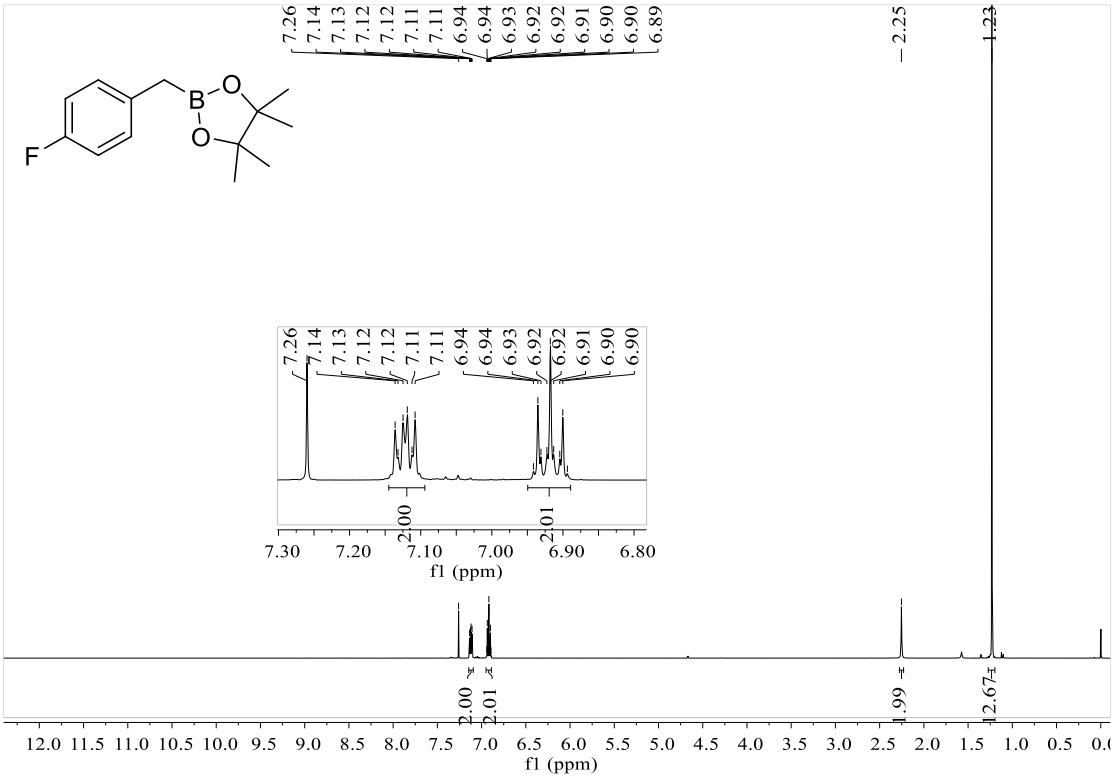


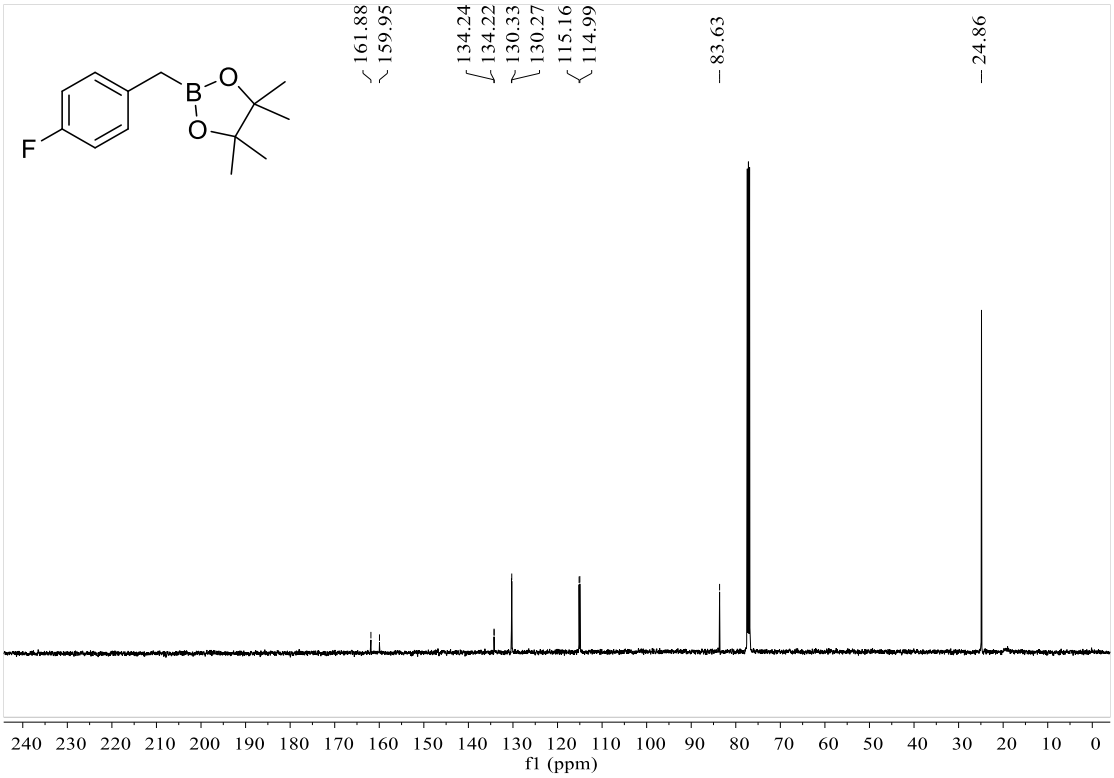


^{19}F NMR (376 MHz, $CDCl_3$)

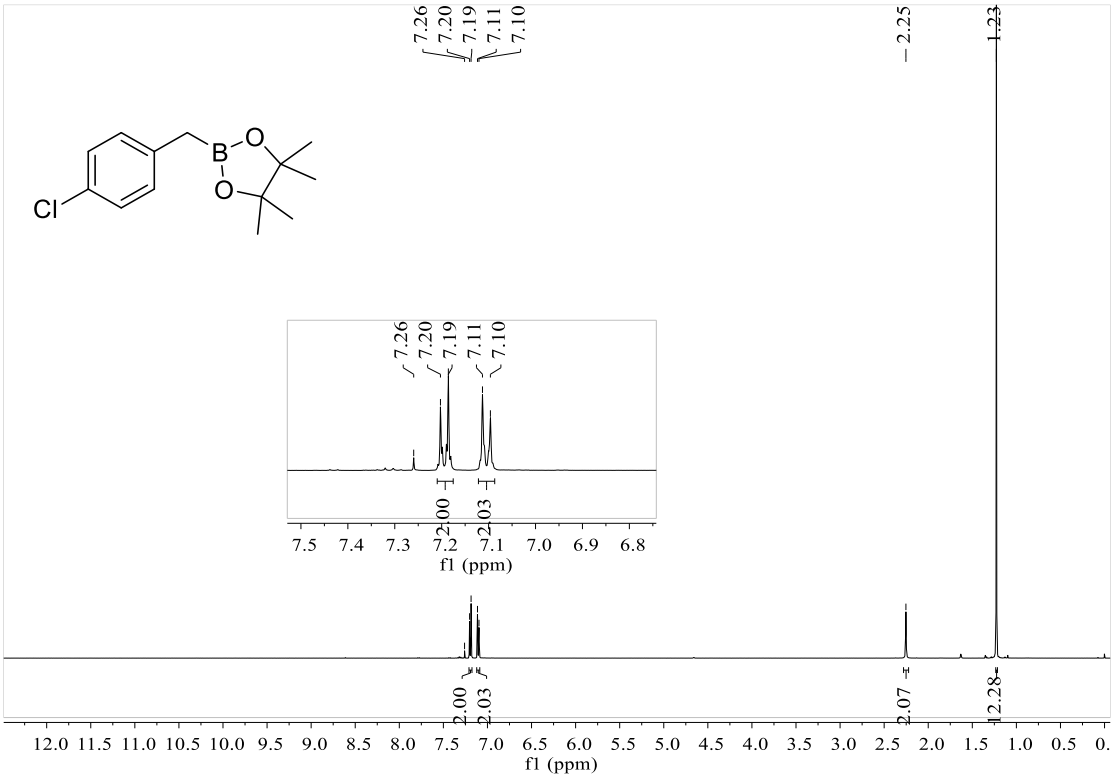


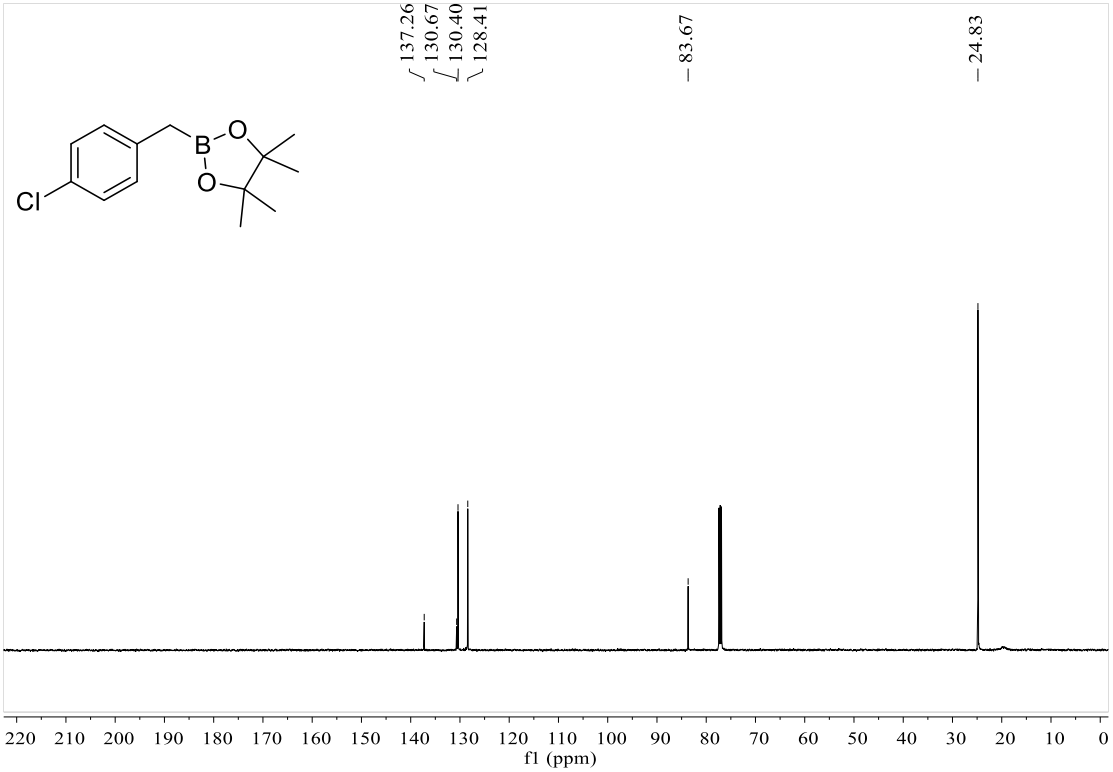
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 11d



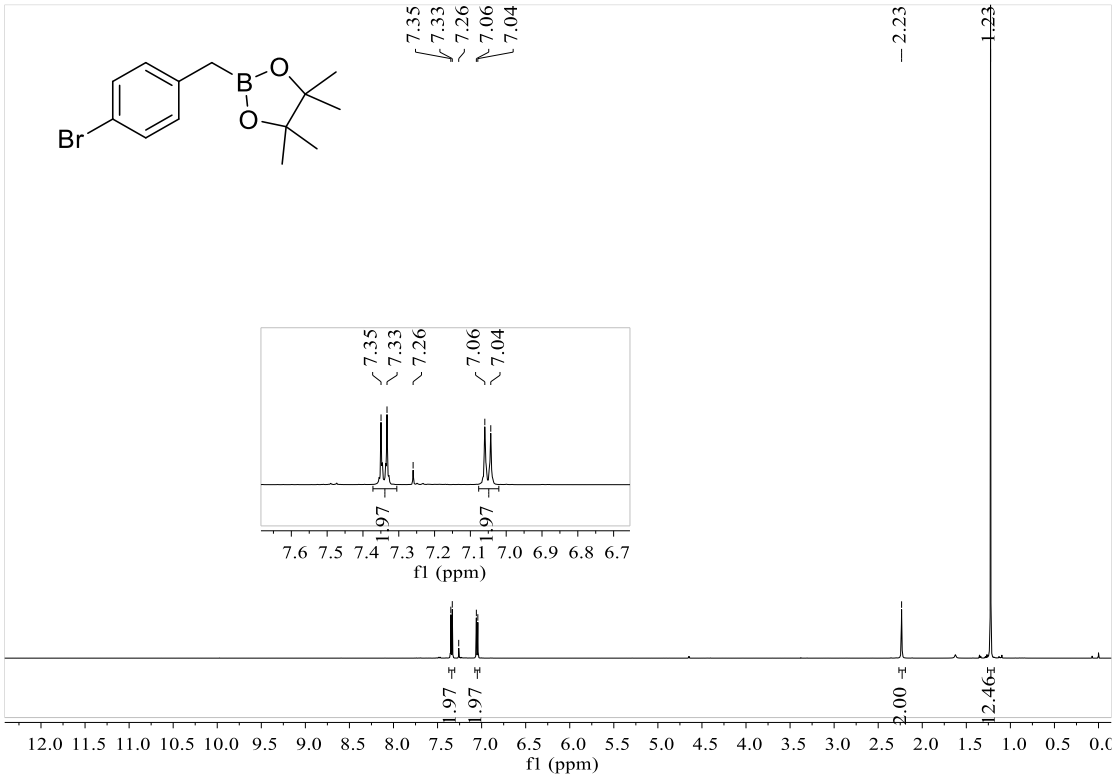


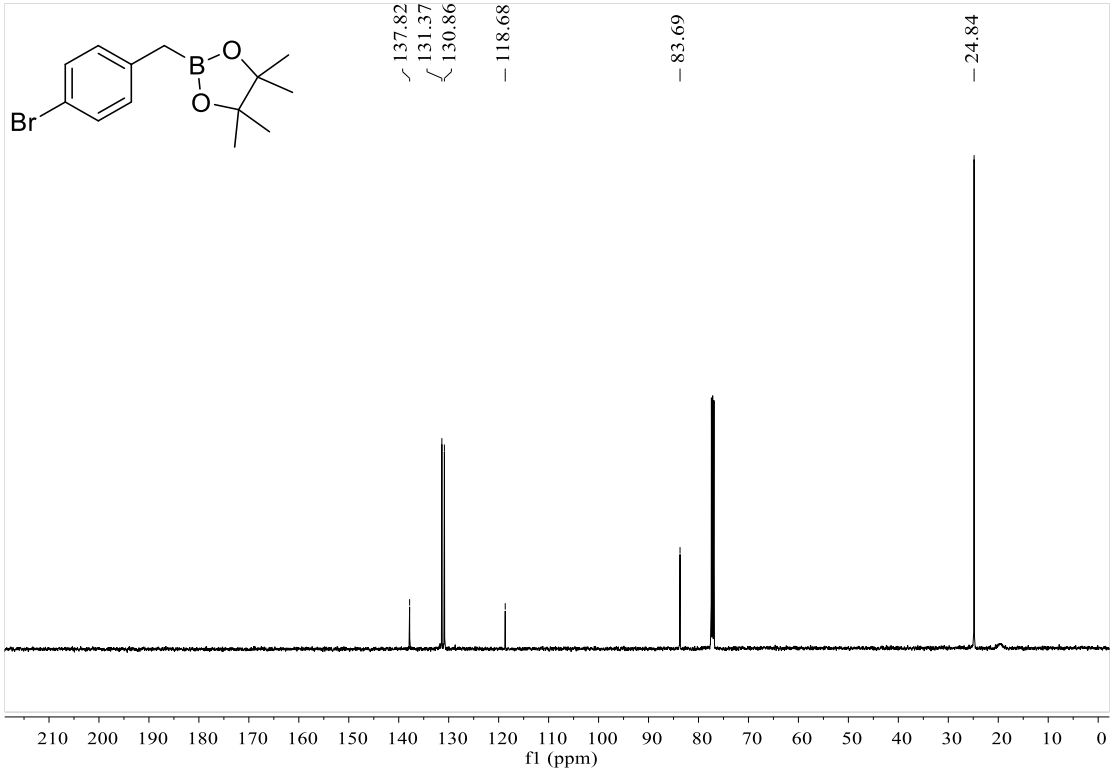
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 12d





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 13d





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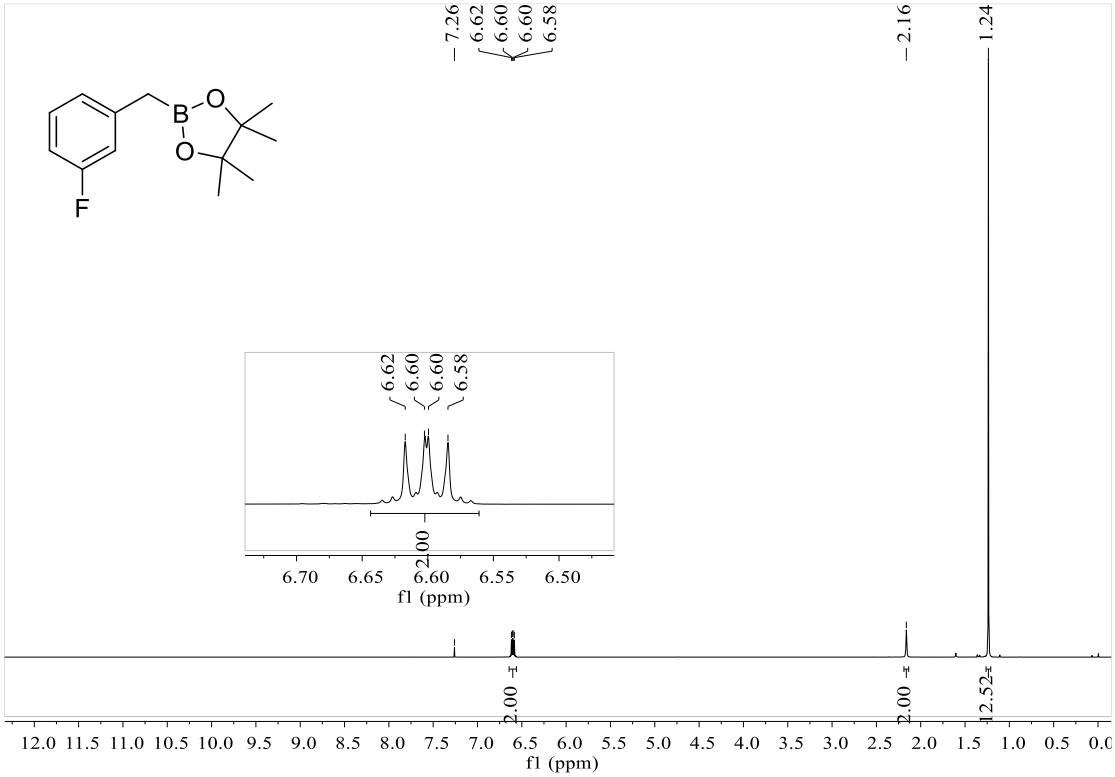
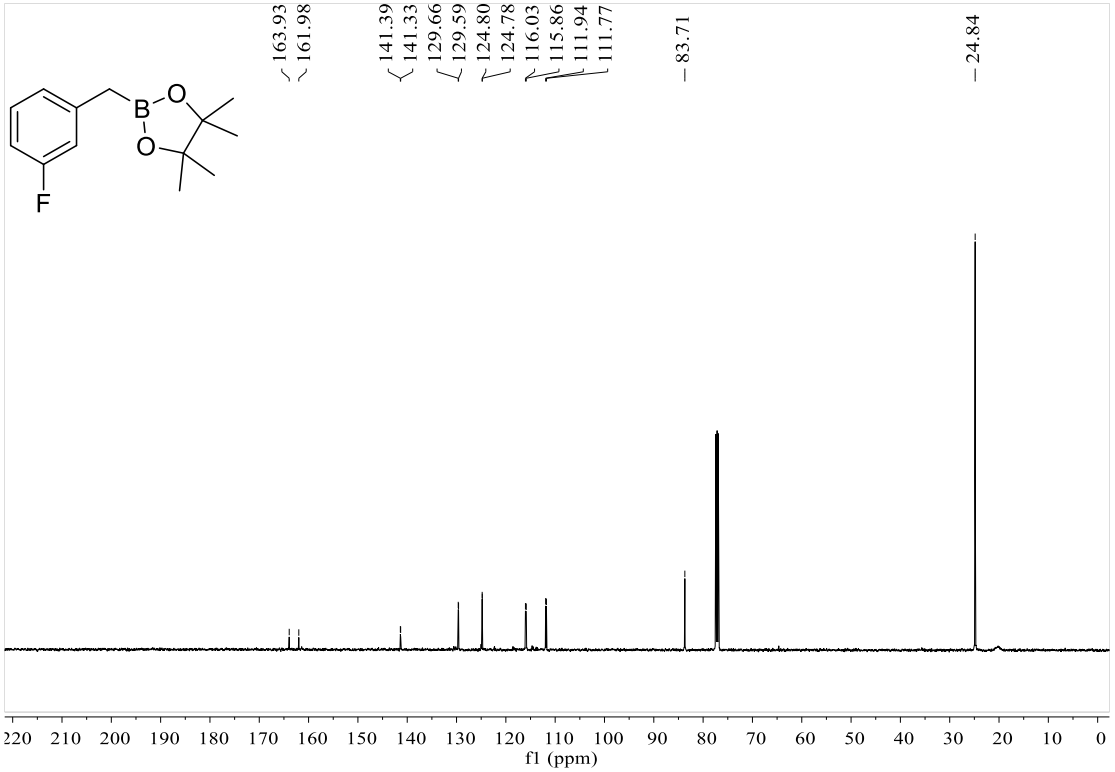
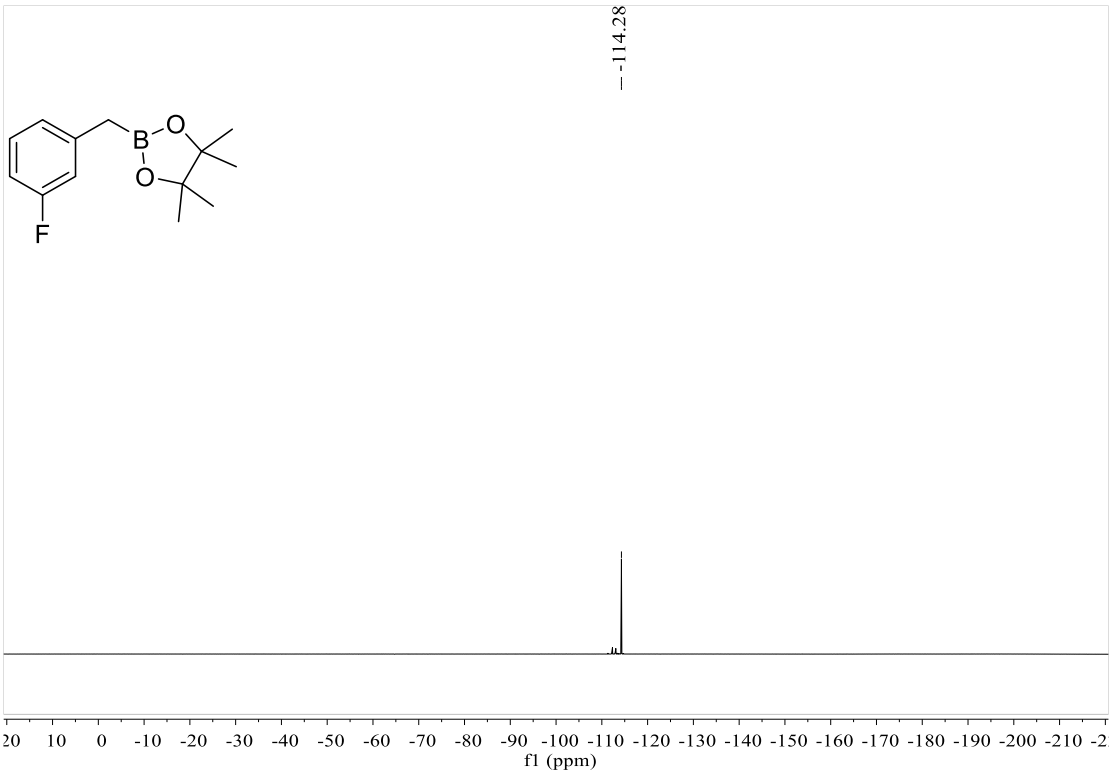
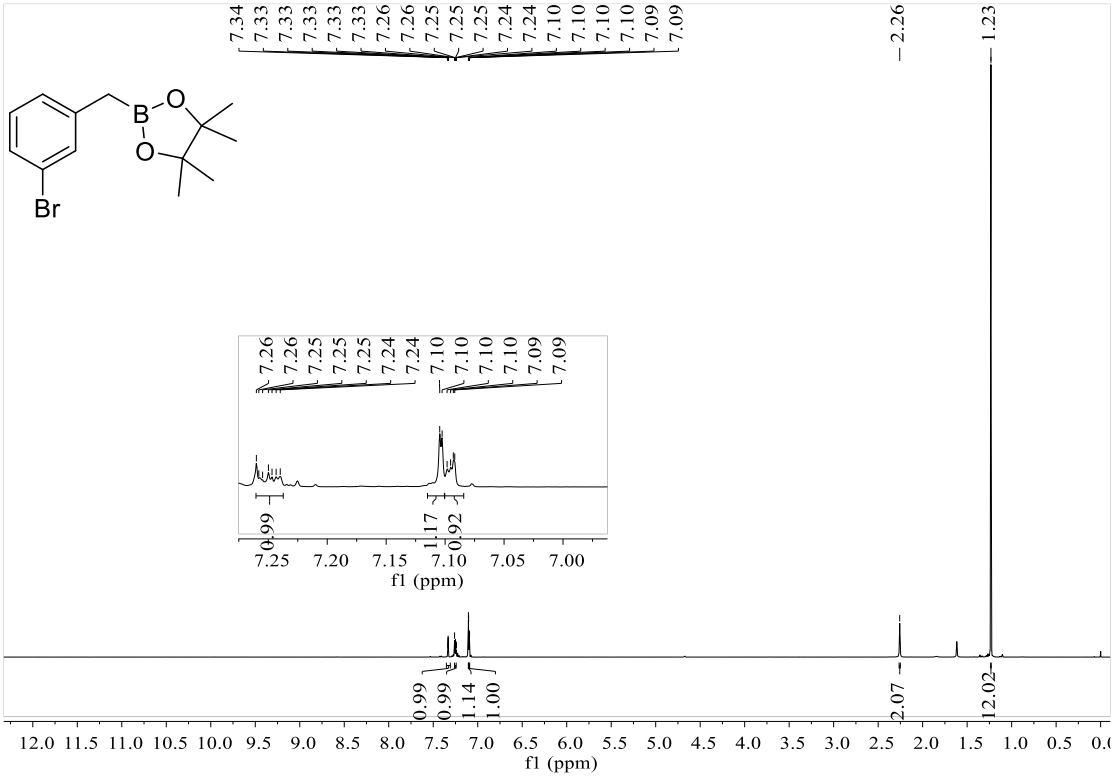


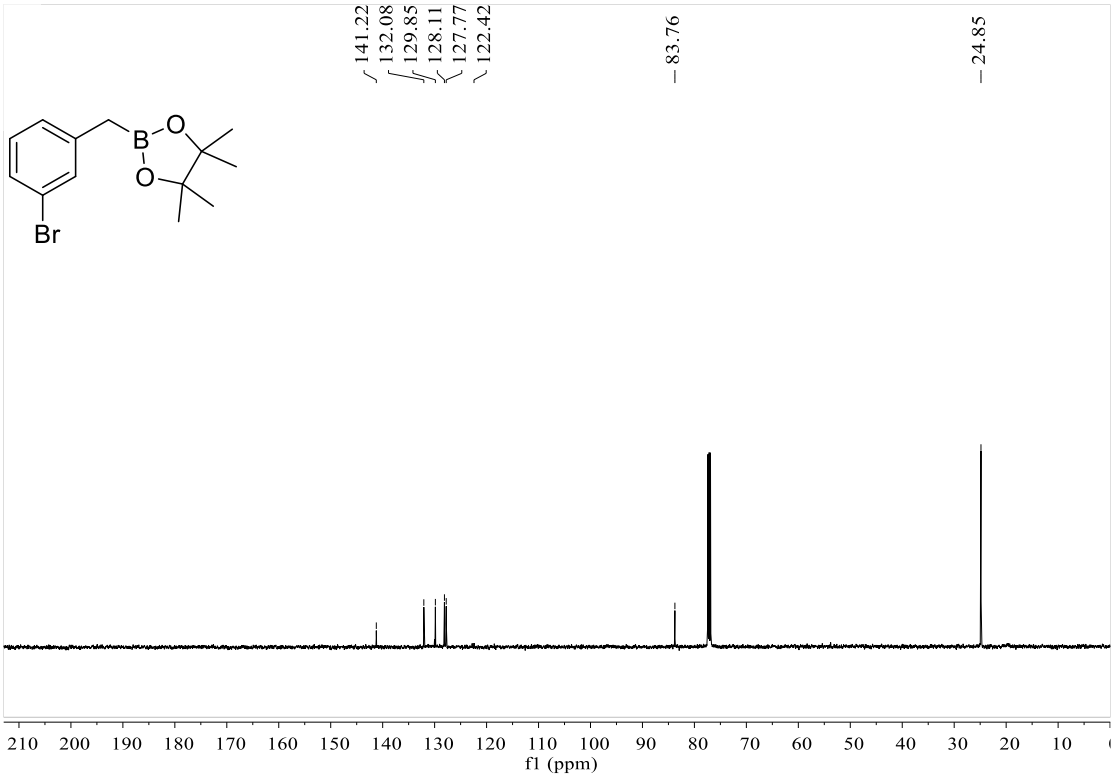


^{19}F NMR (376 MHz, $CDCl_3$)

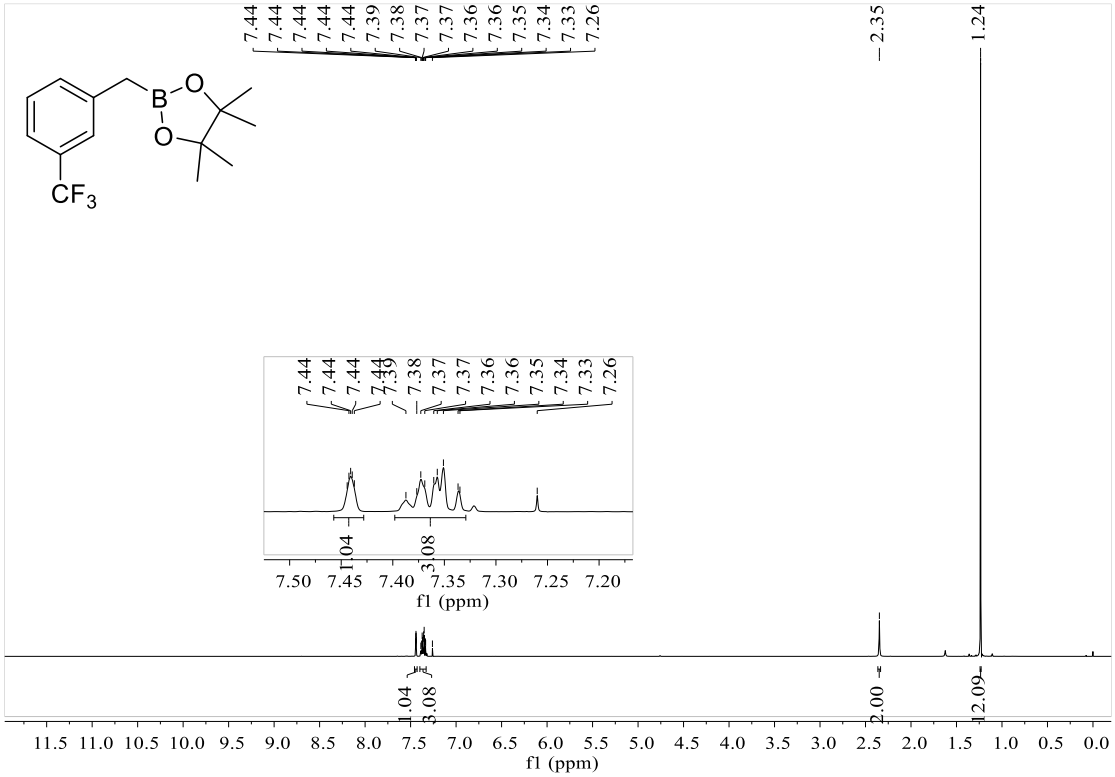


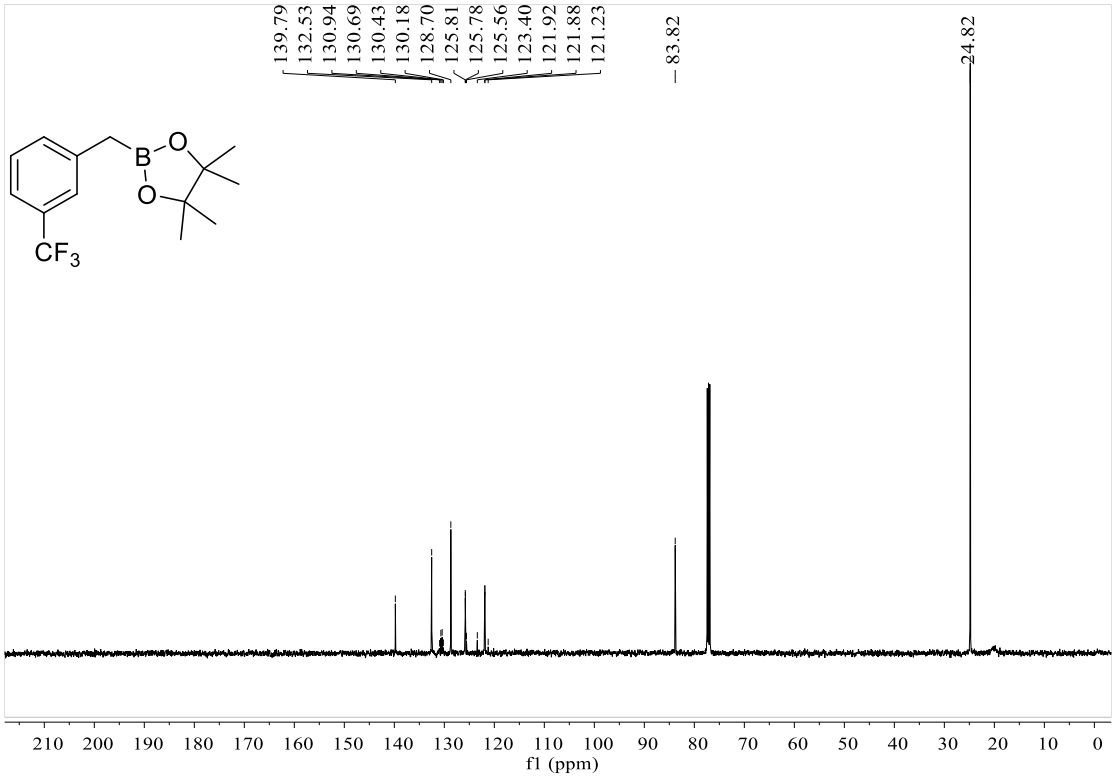
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 15d



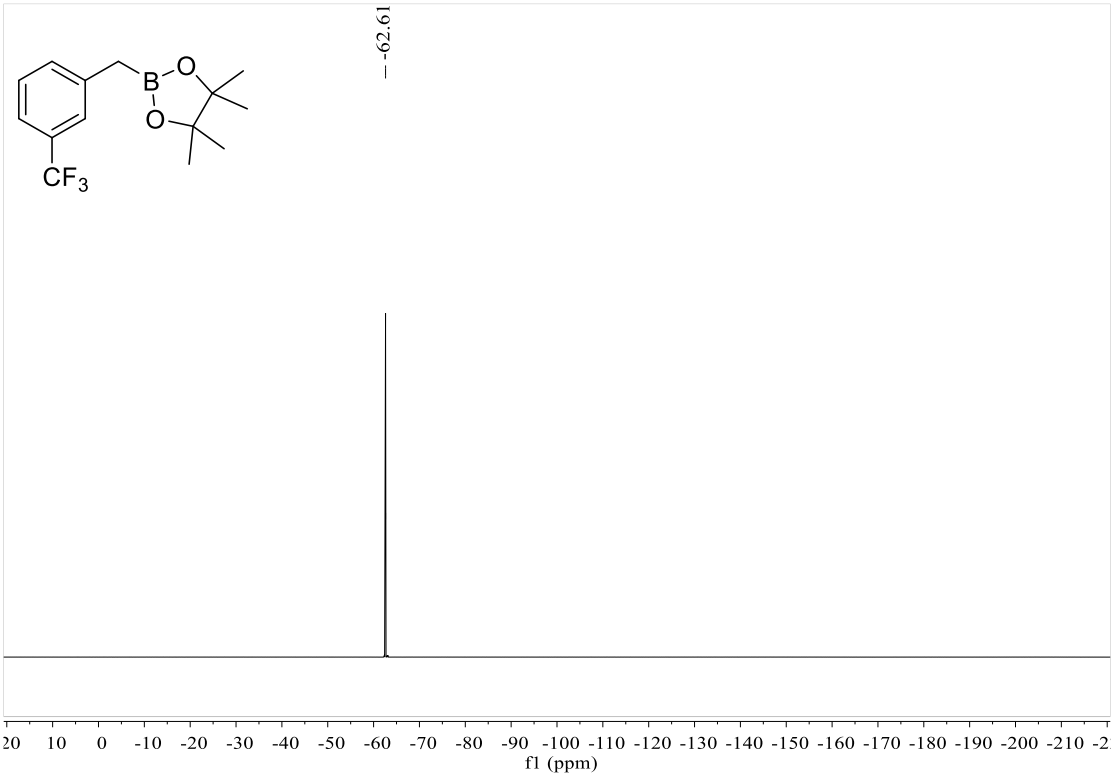


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 16d

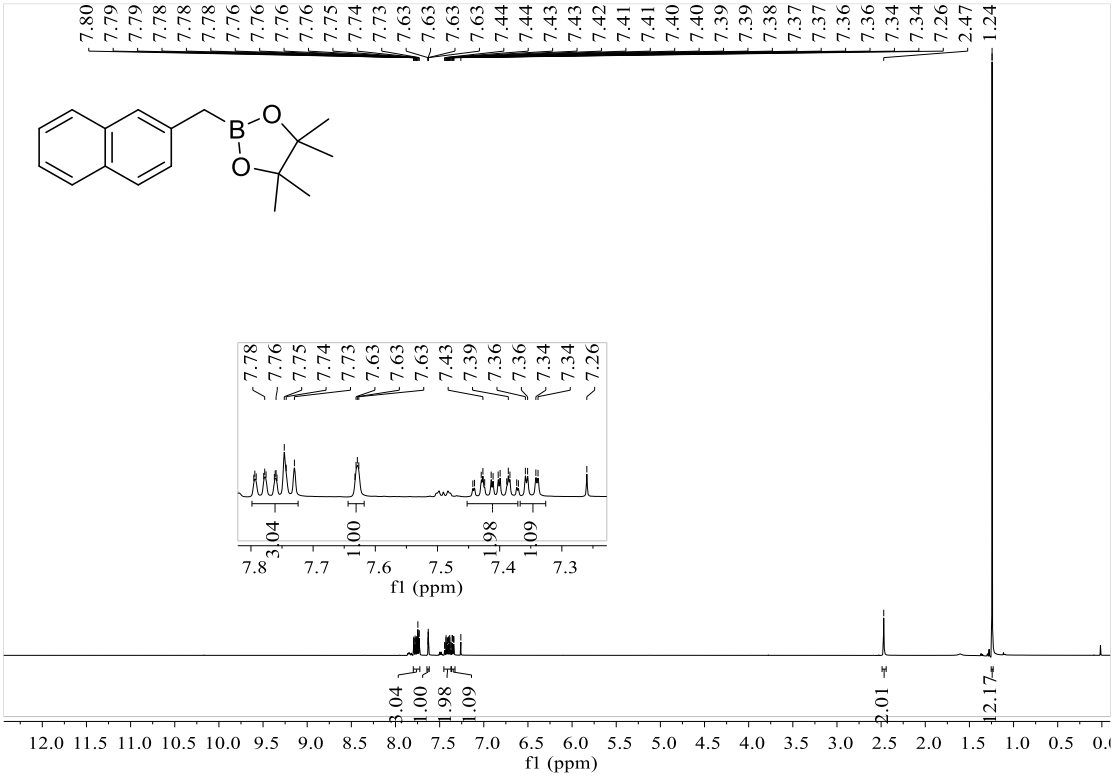


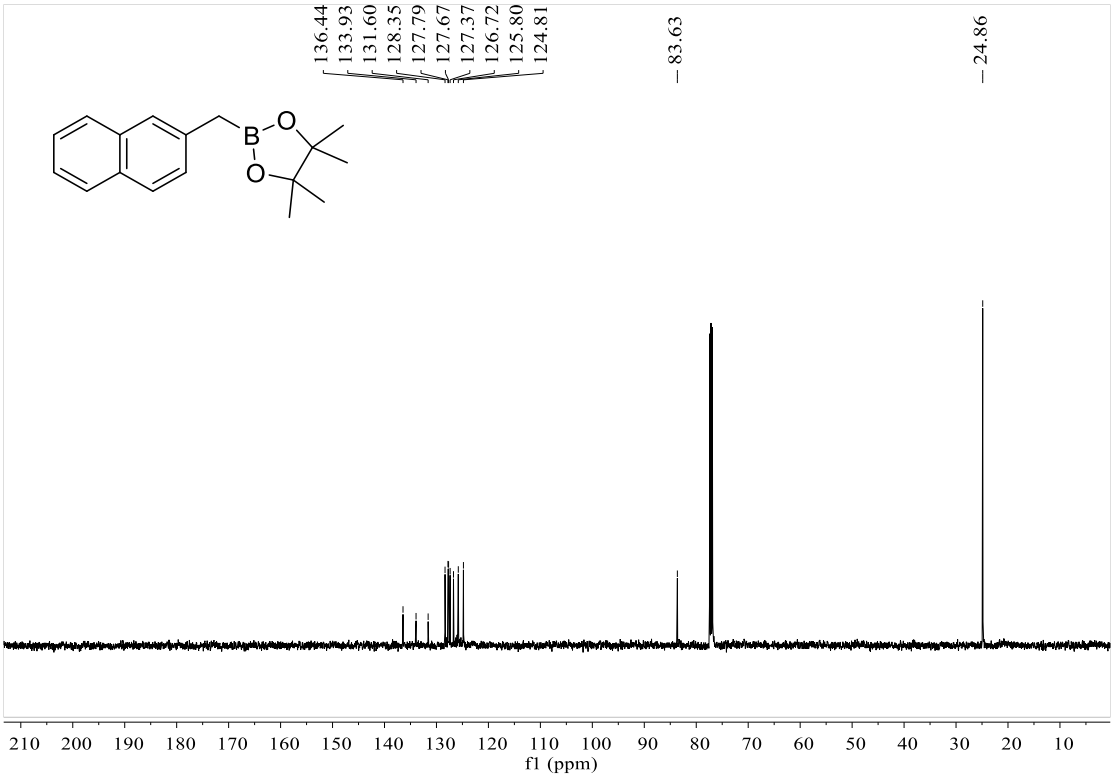


^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 17d





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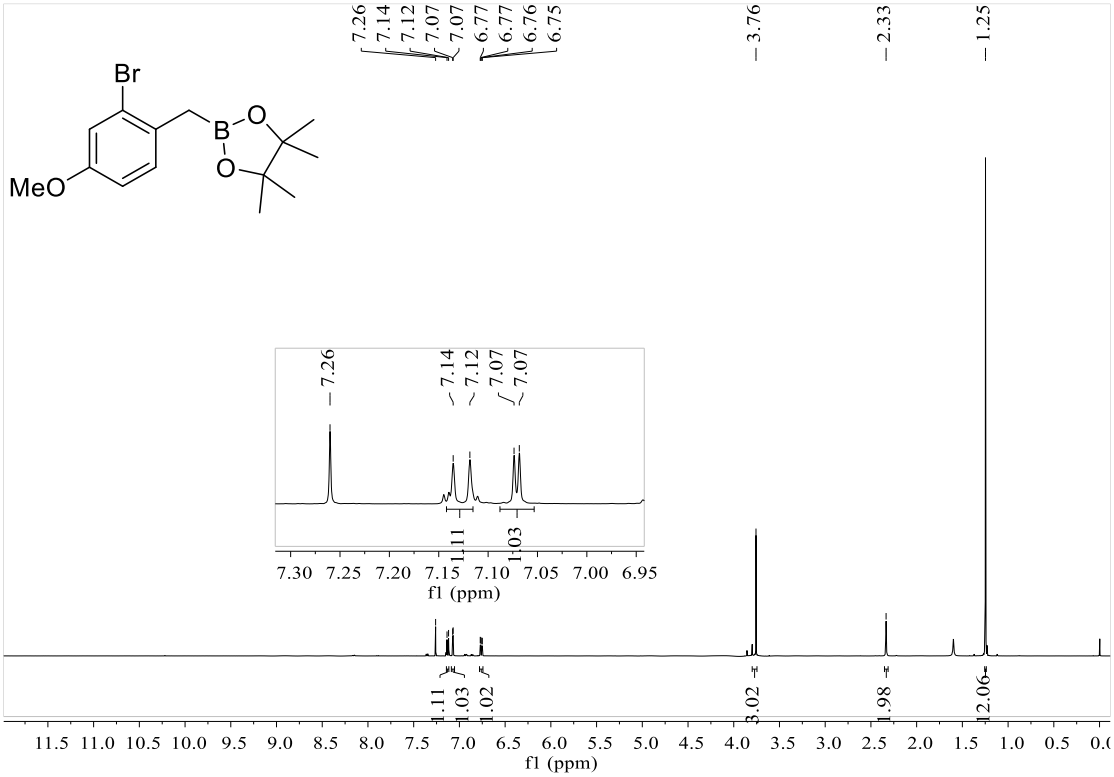
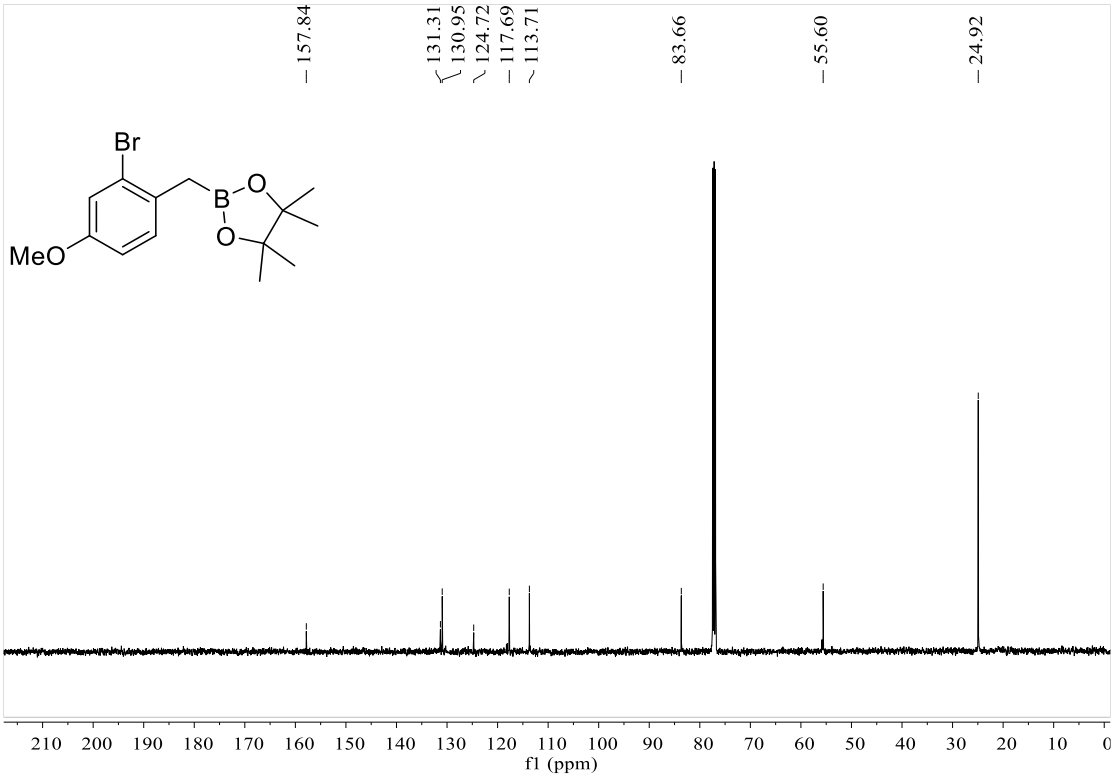
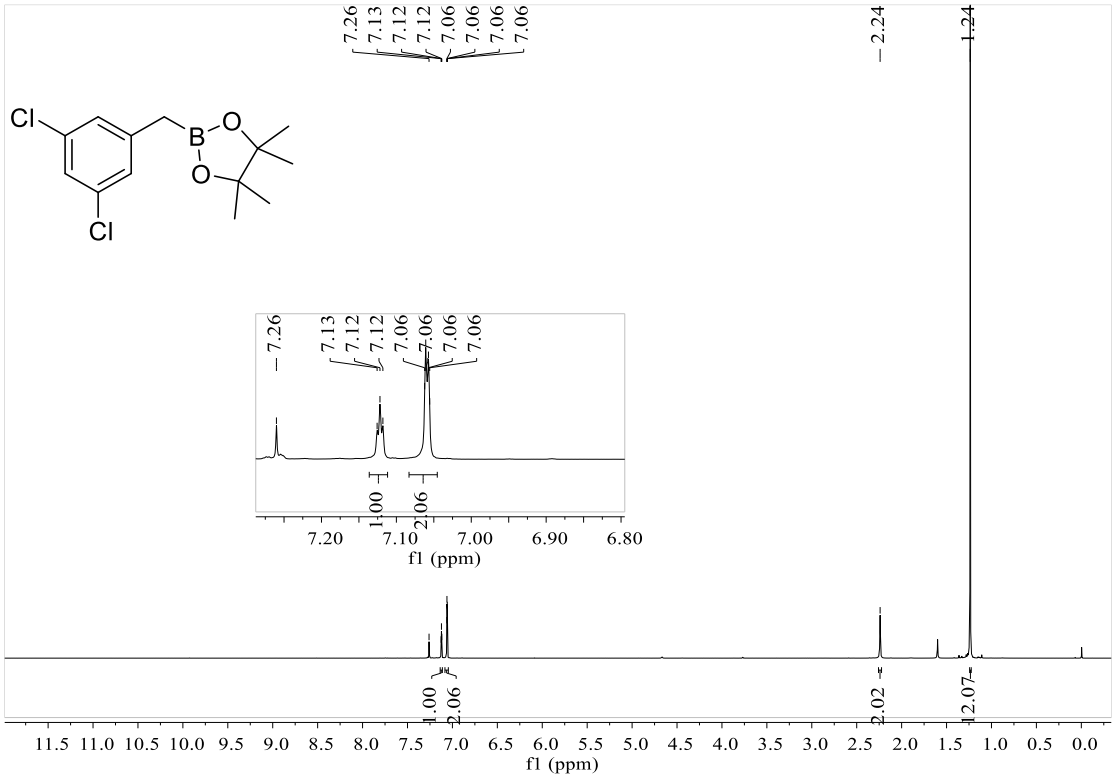
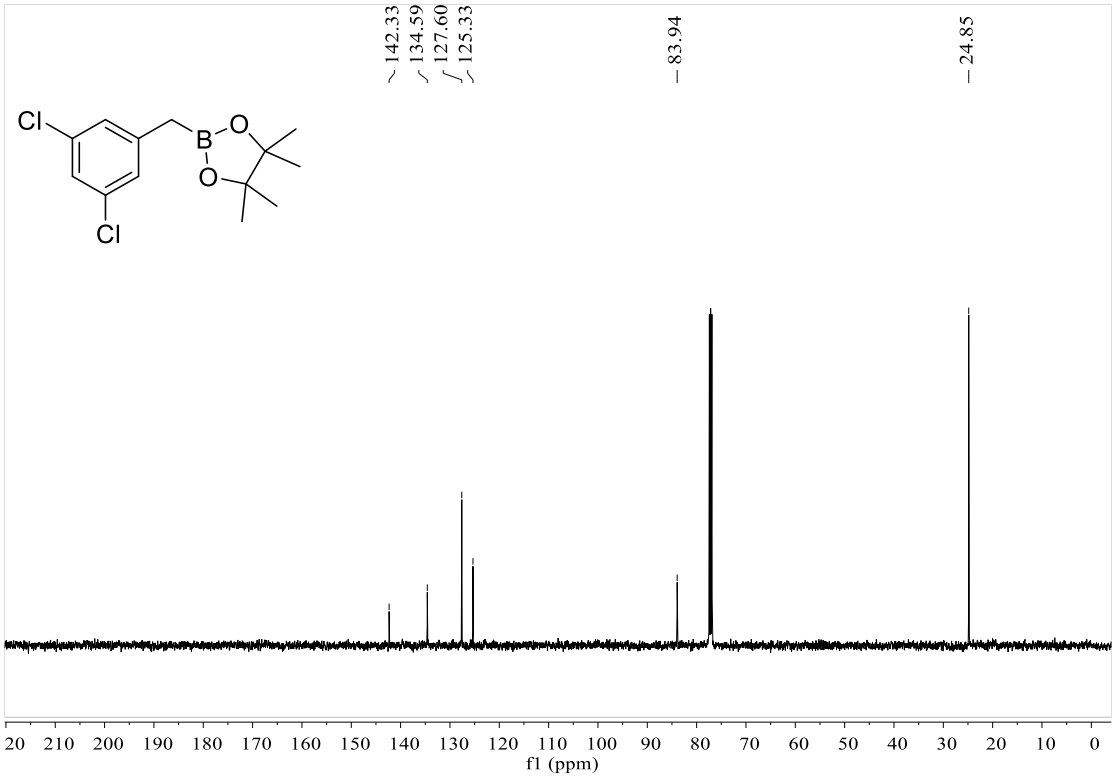




^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 19d





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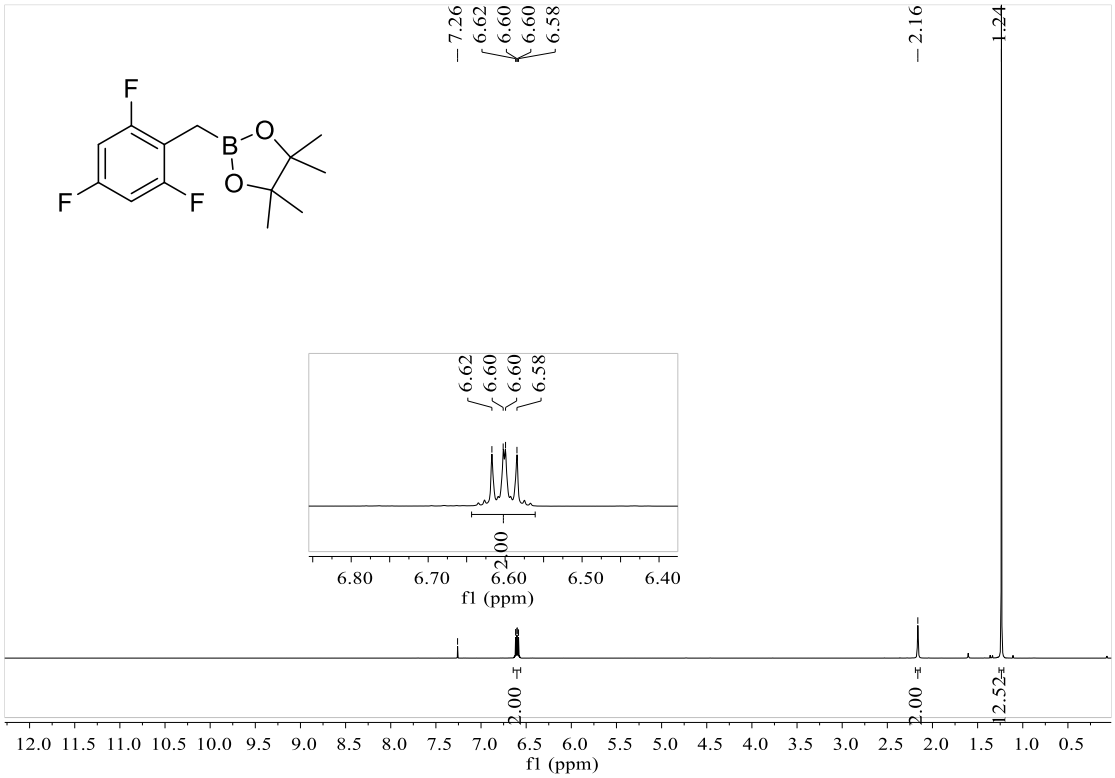
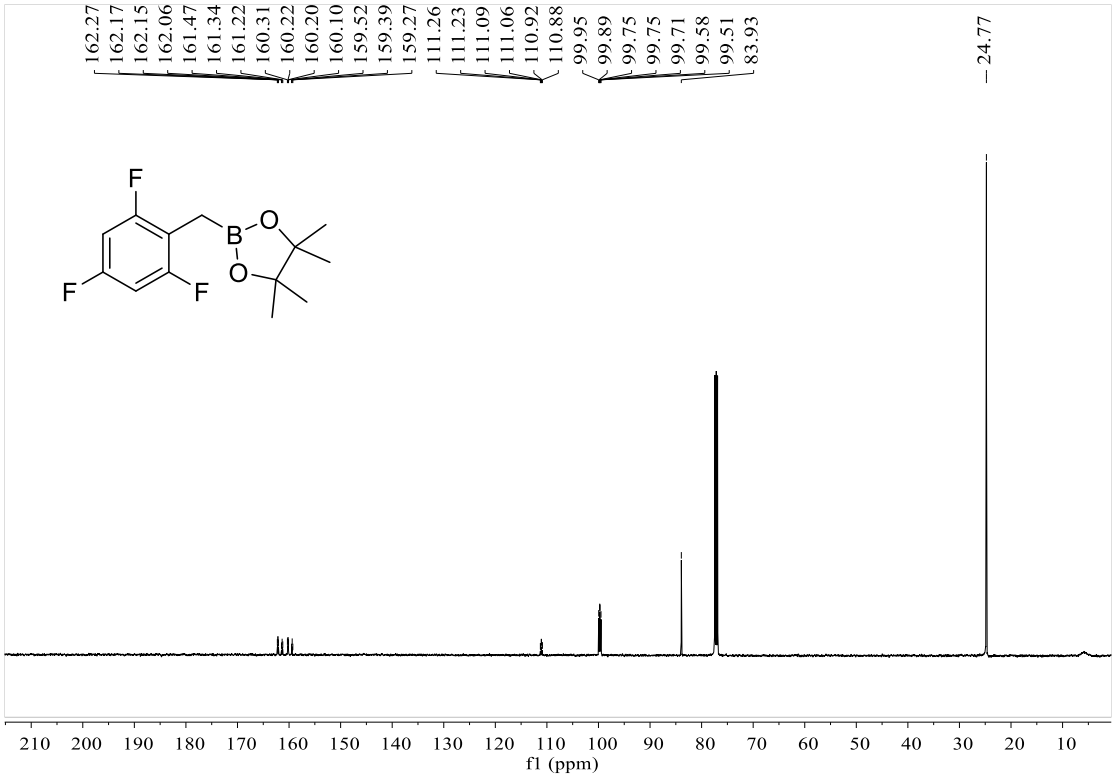
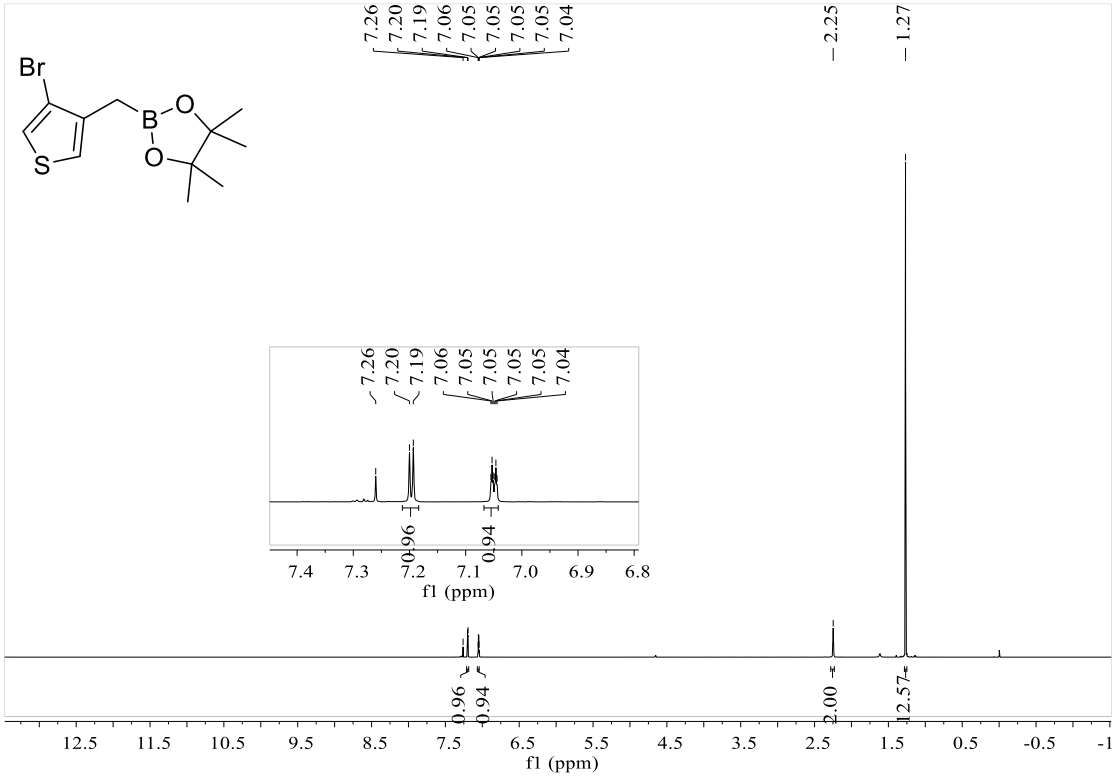
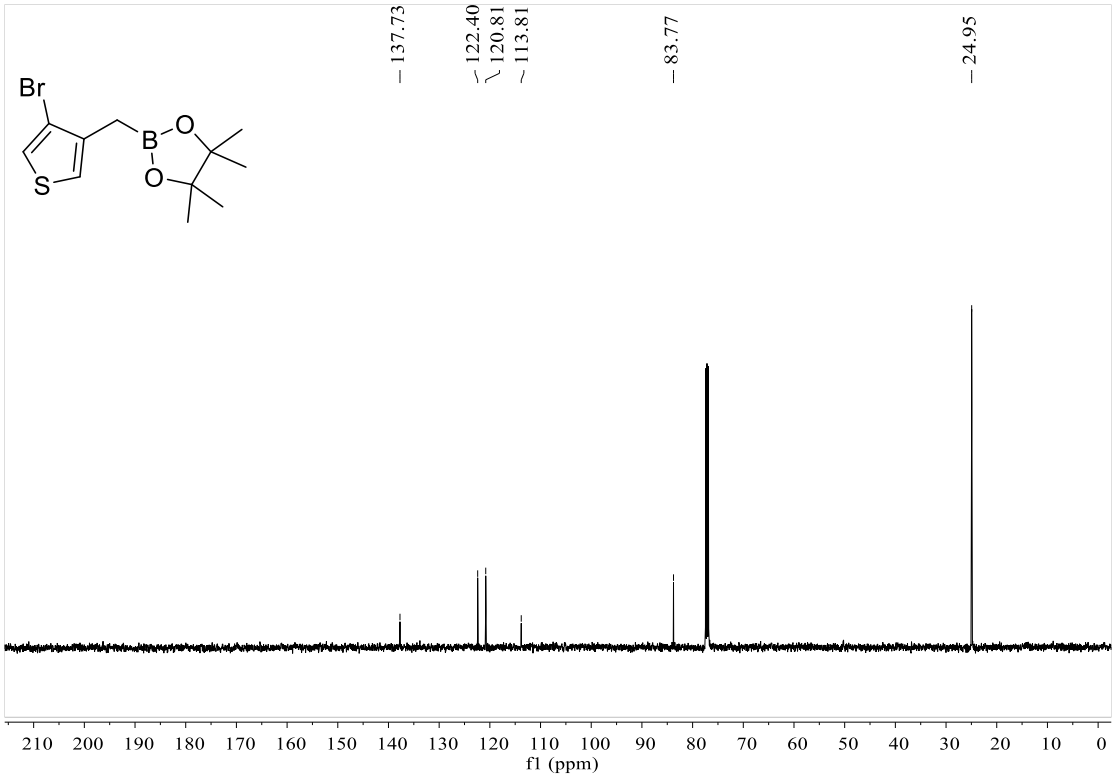


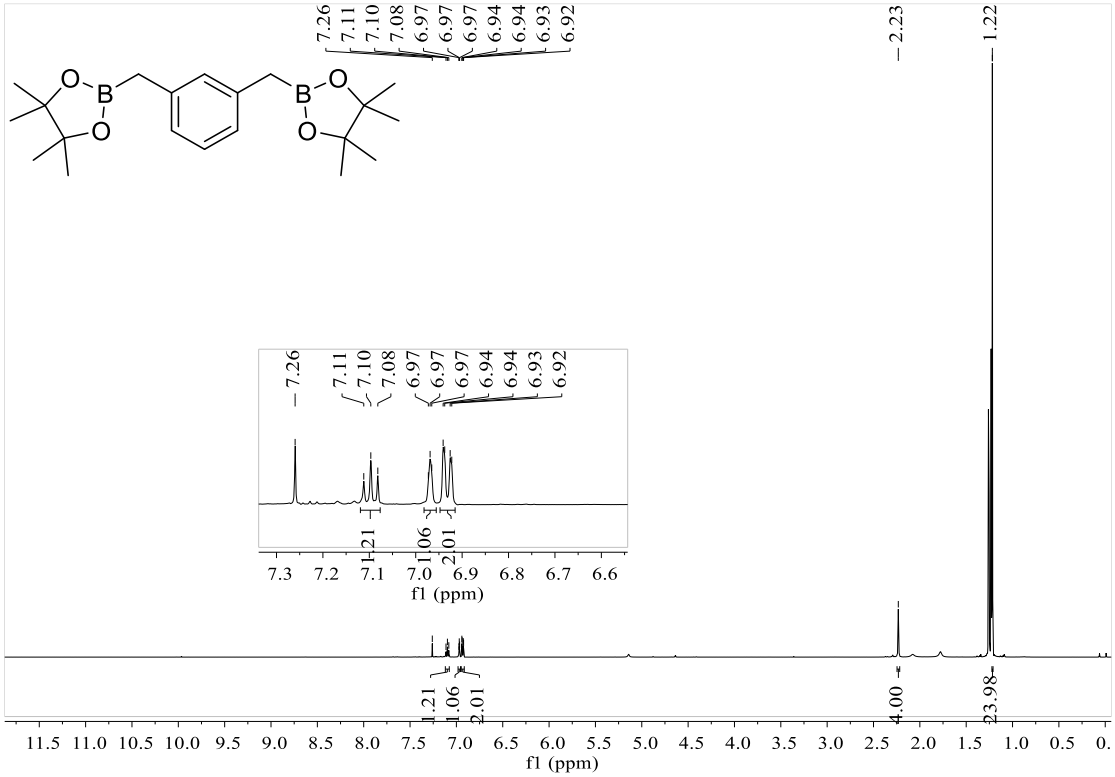


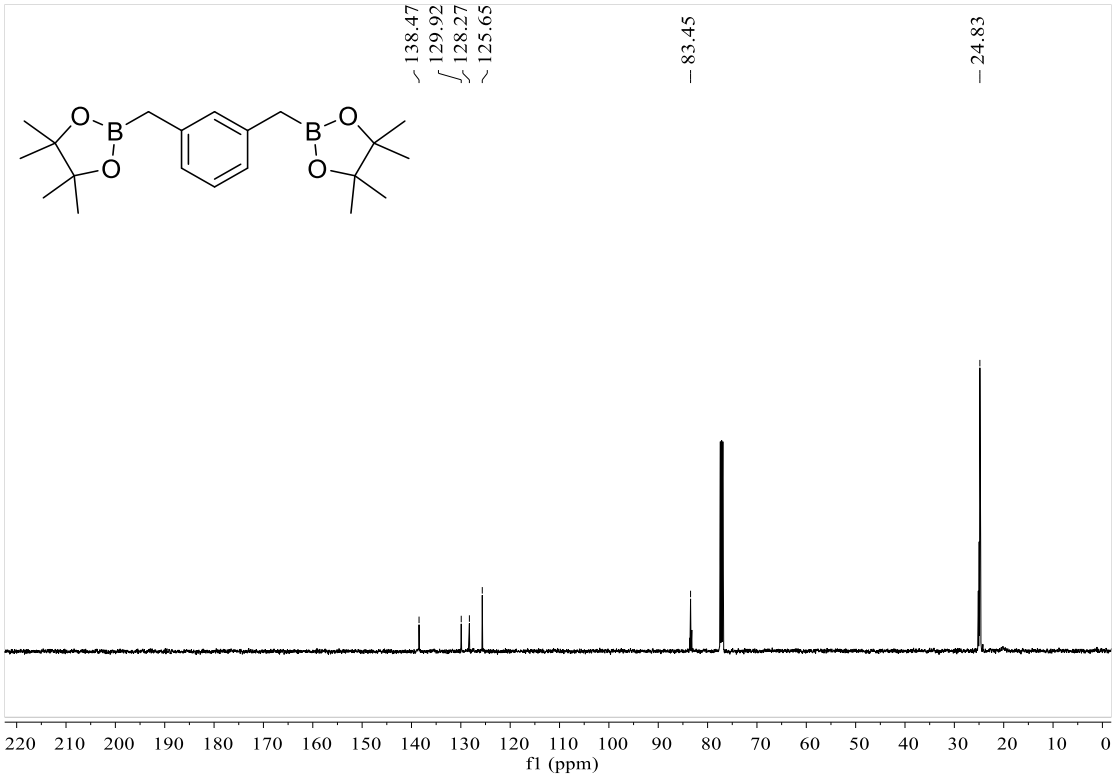
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 21d





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 22d





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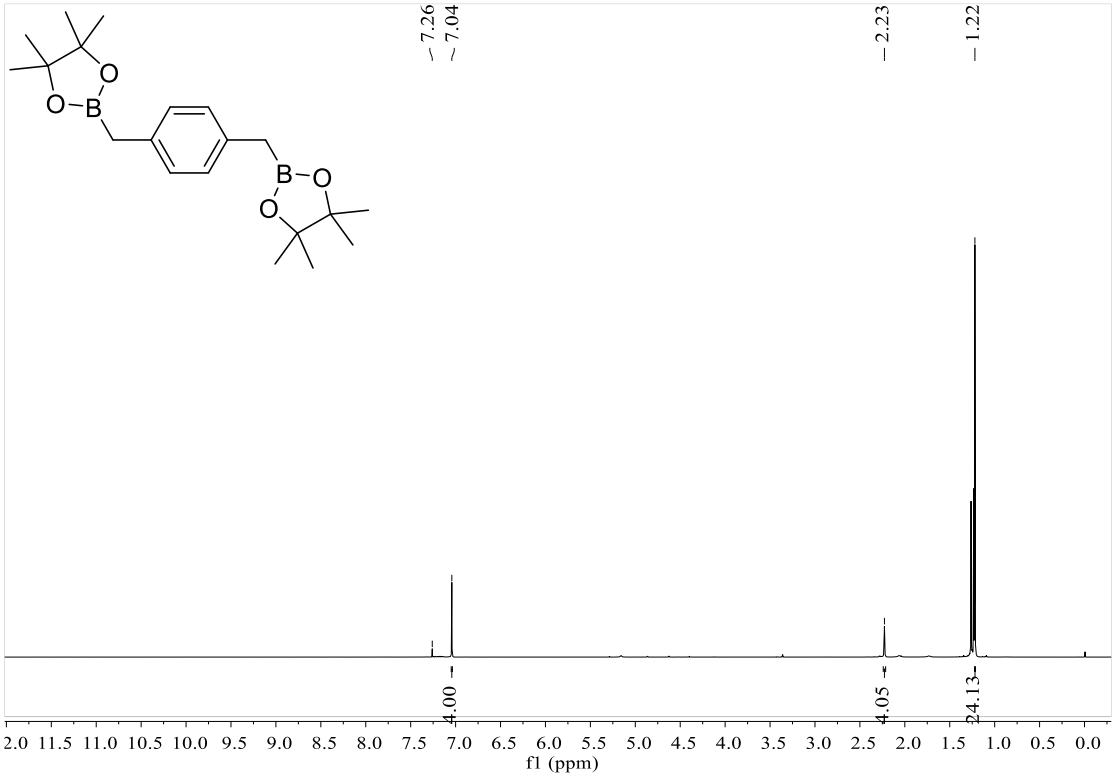
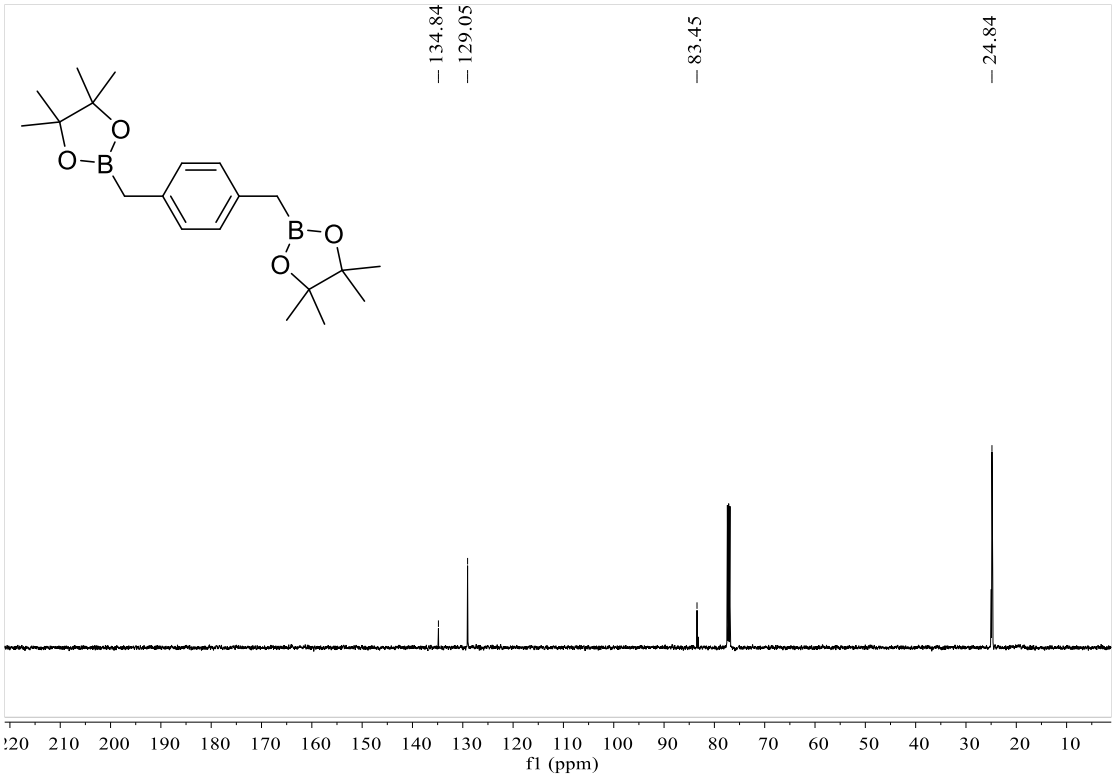
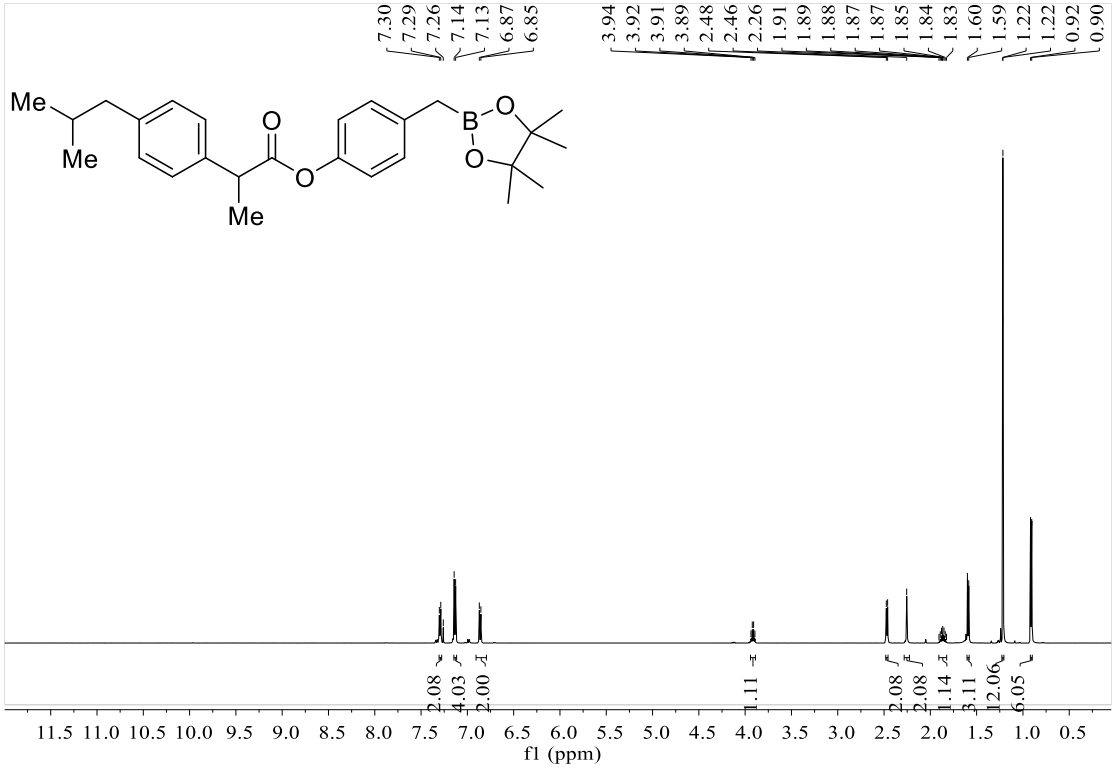
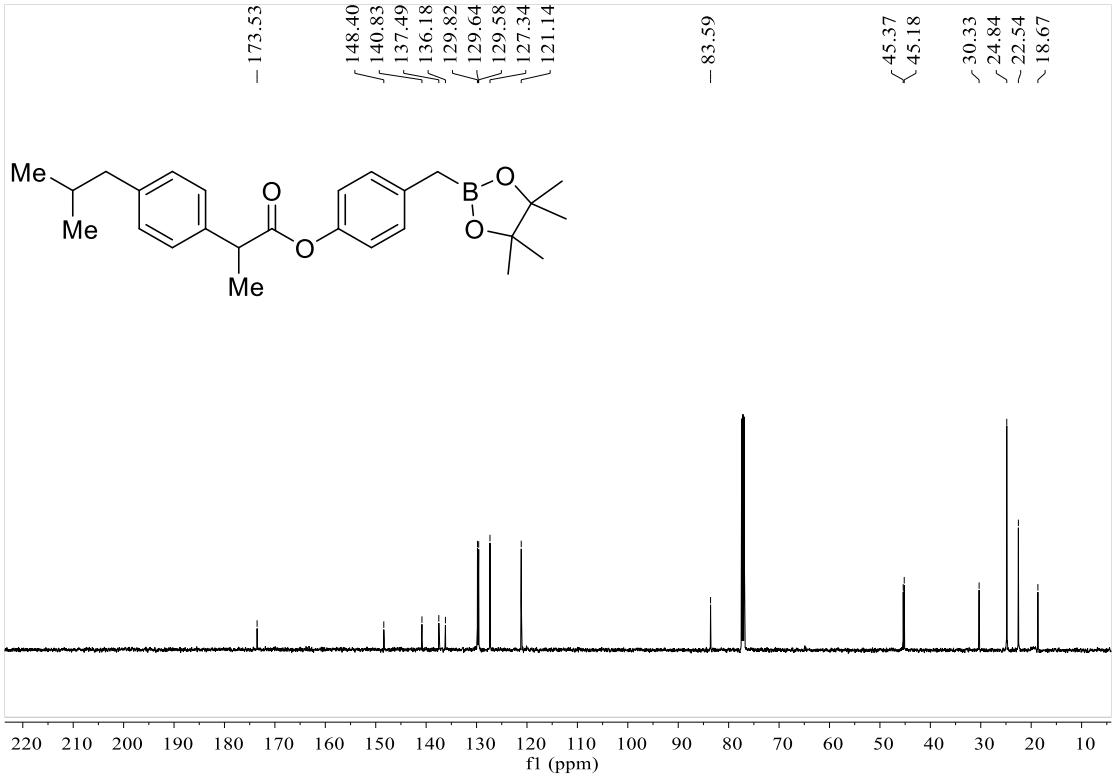


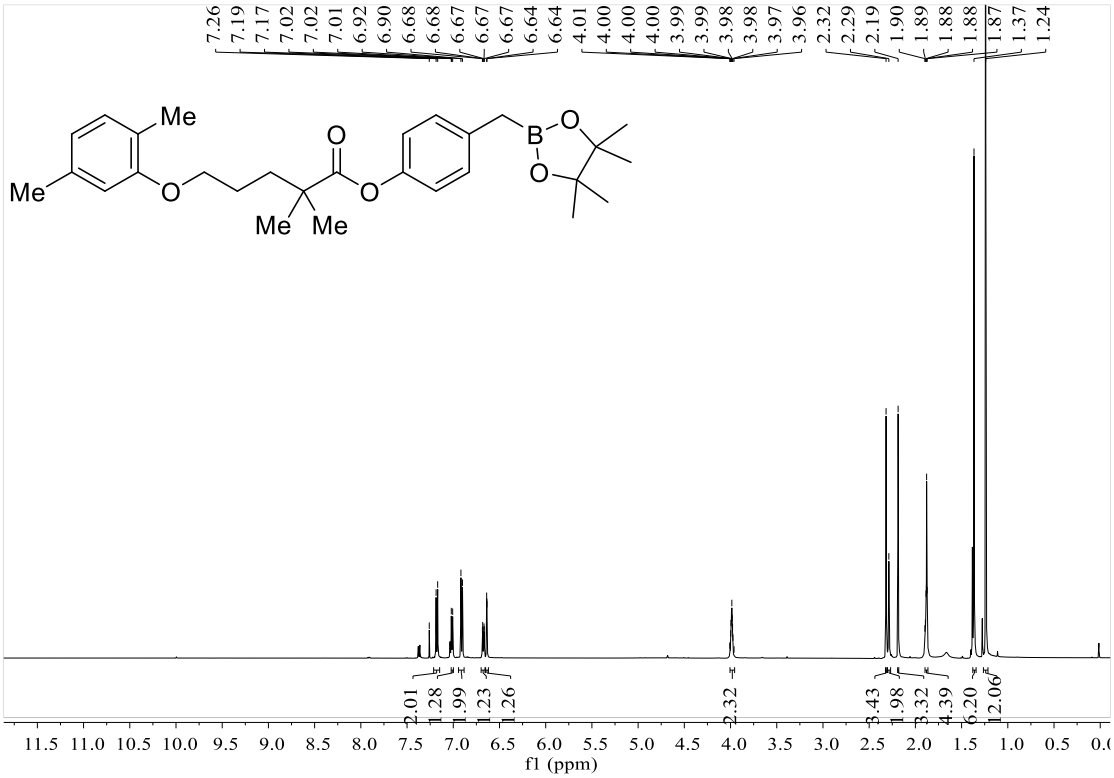


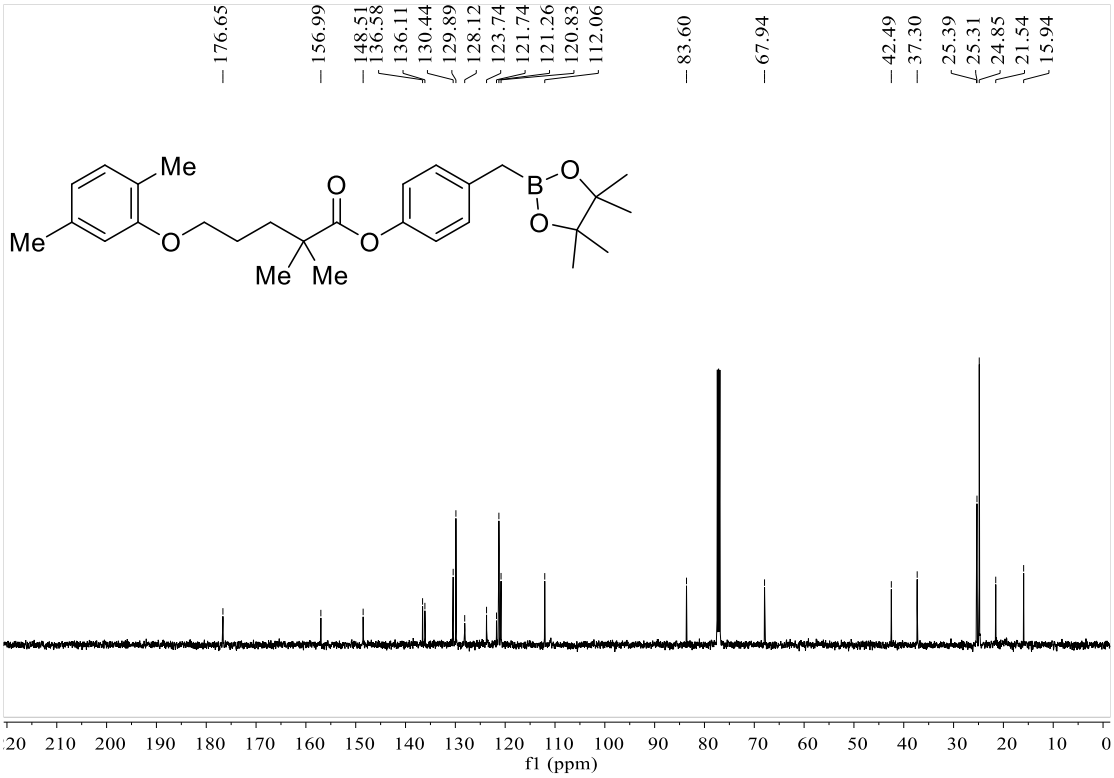
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 24d





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 25d





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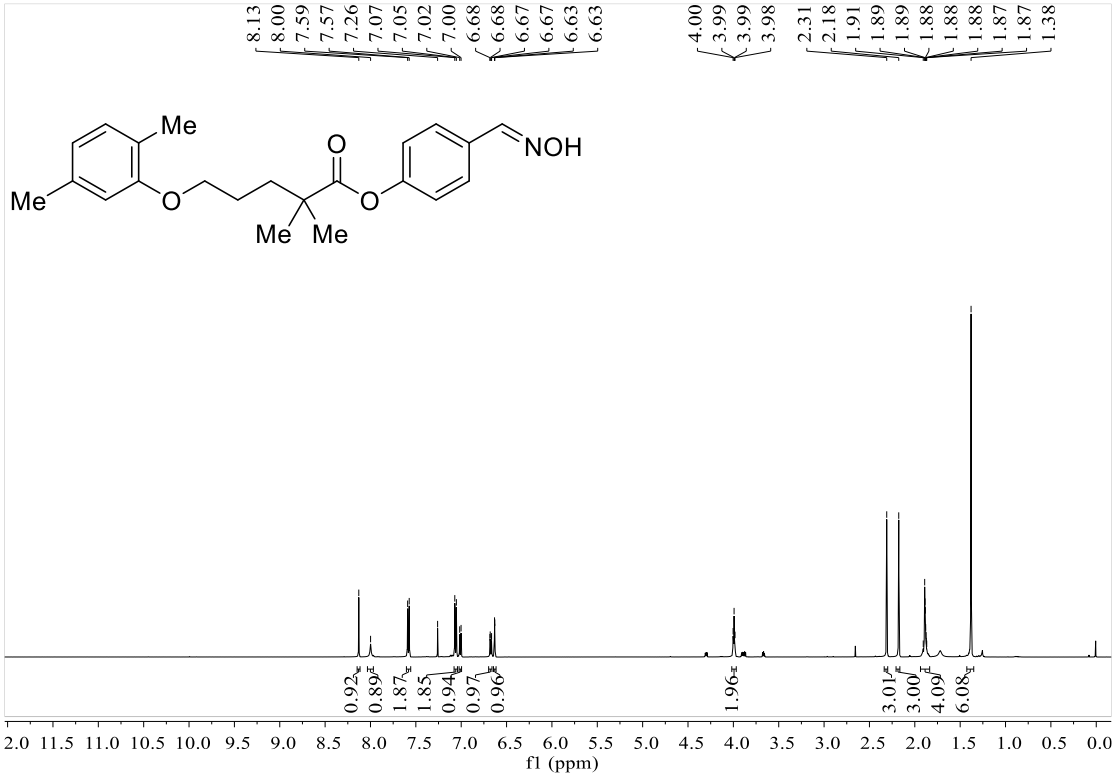

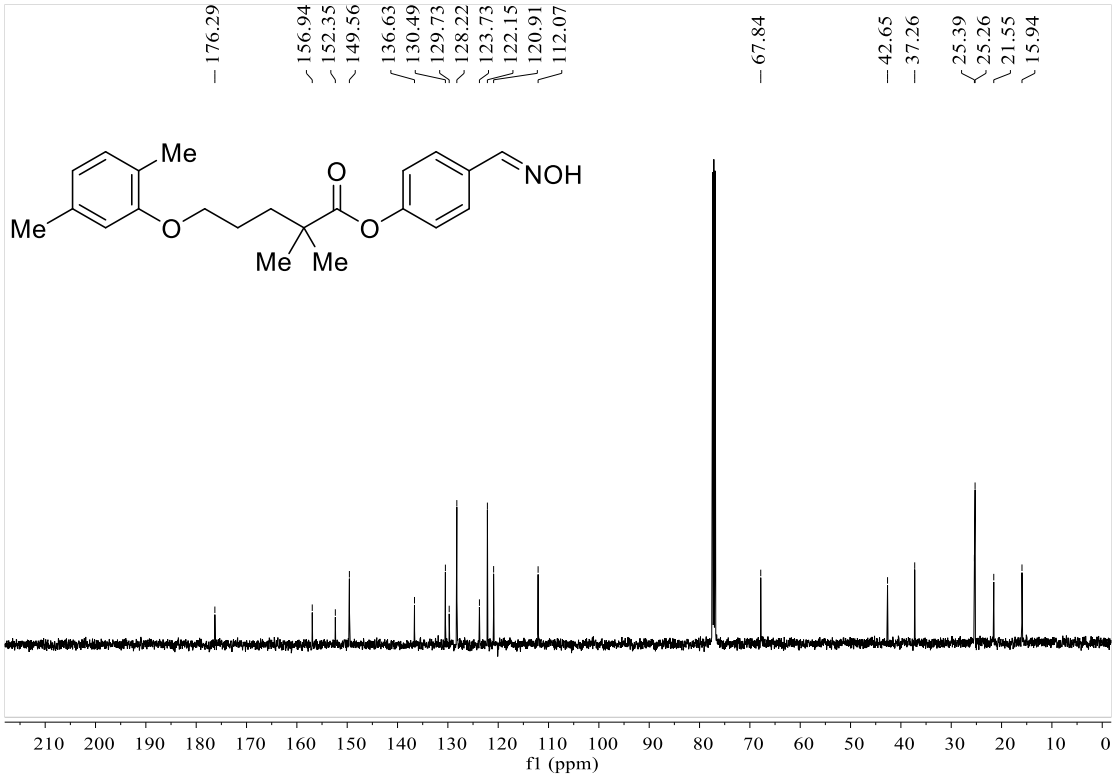

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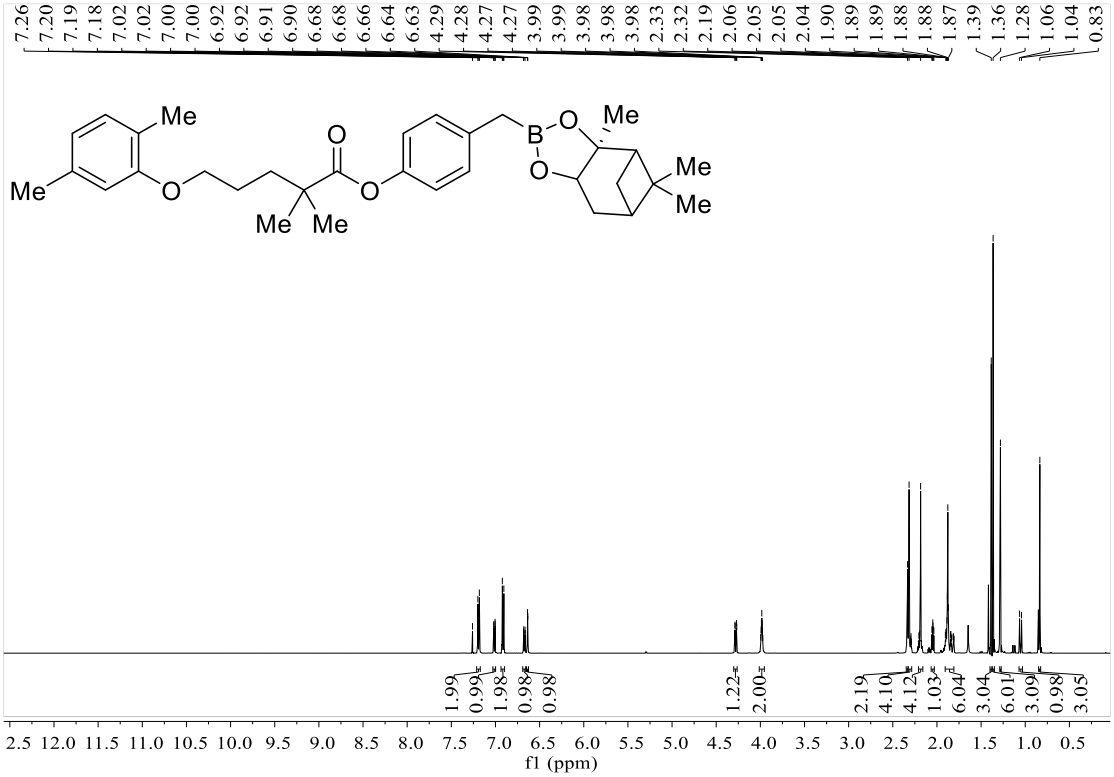

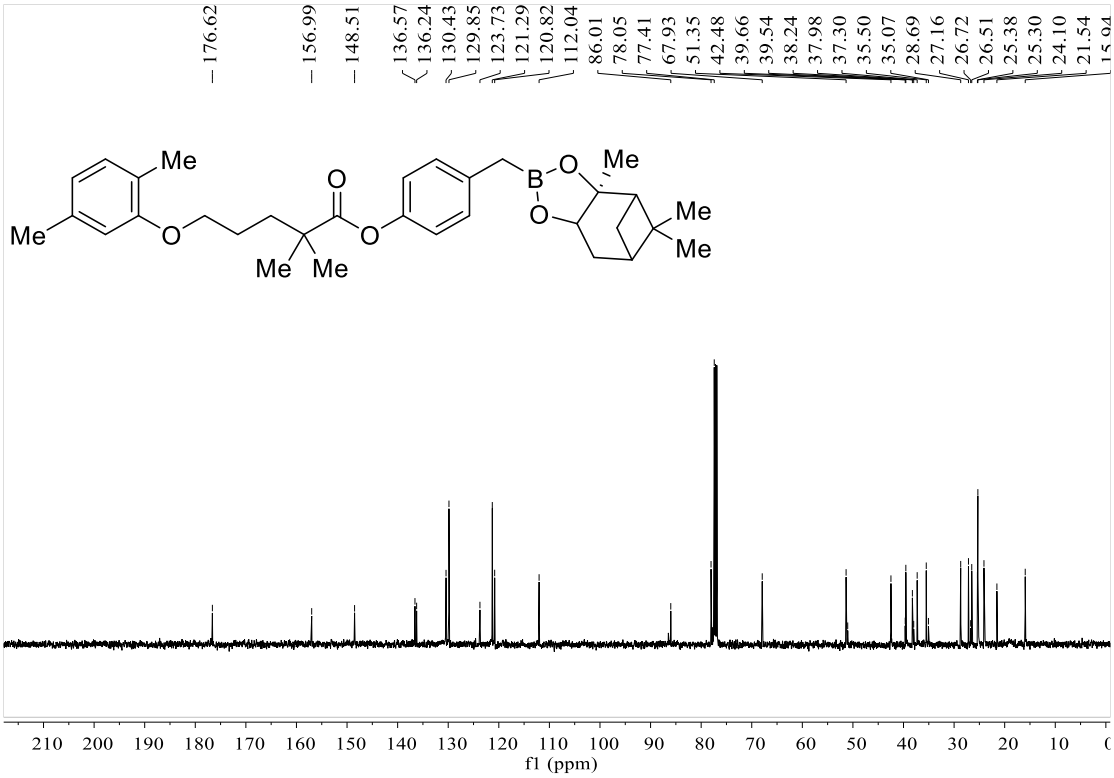

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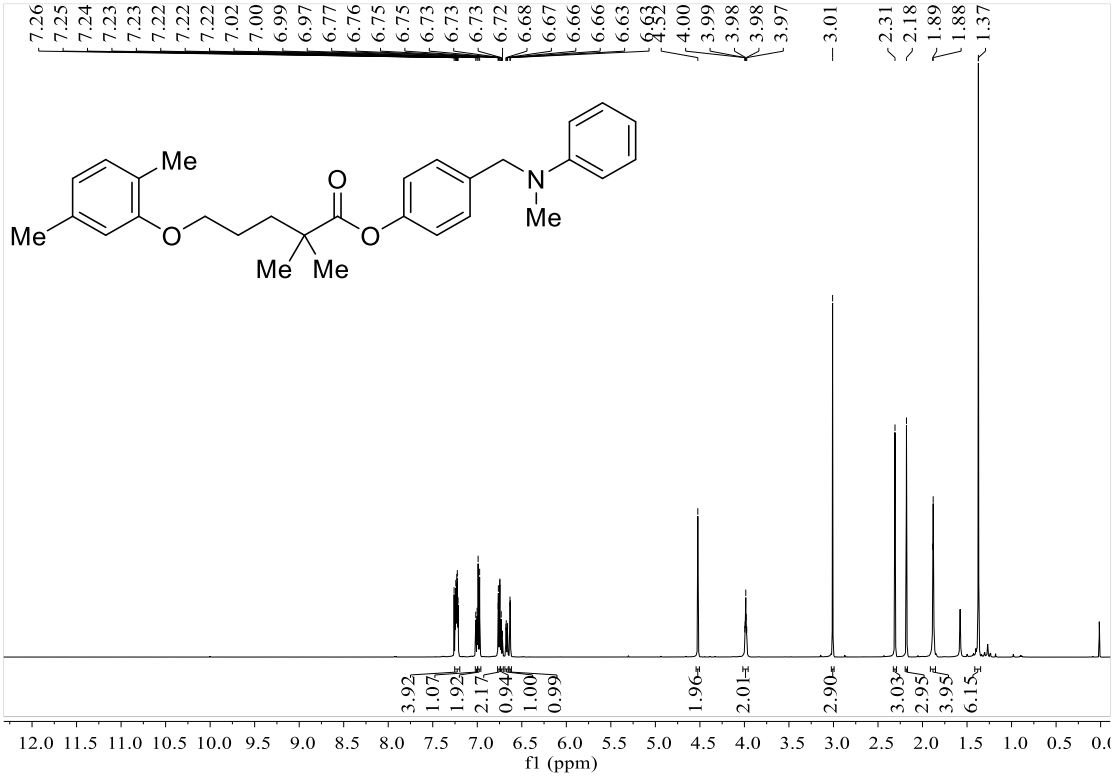

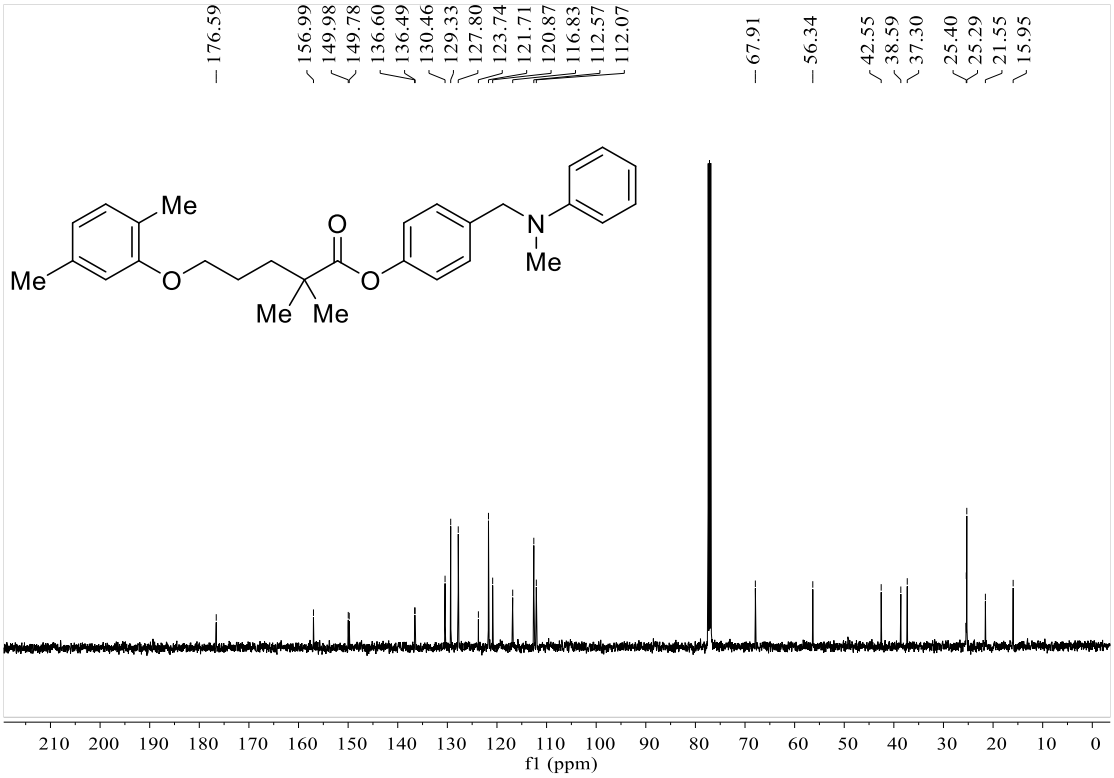

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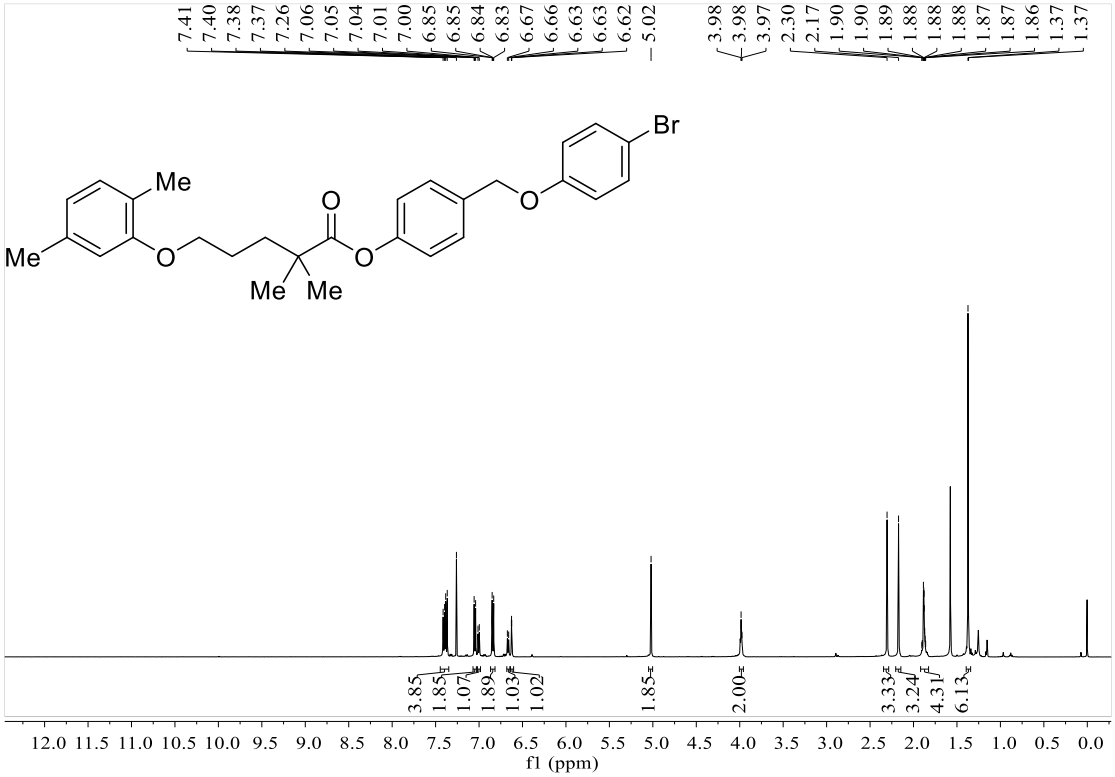

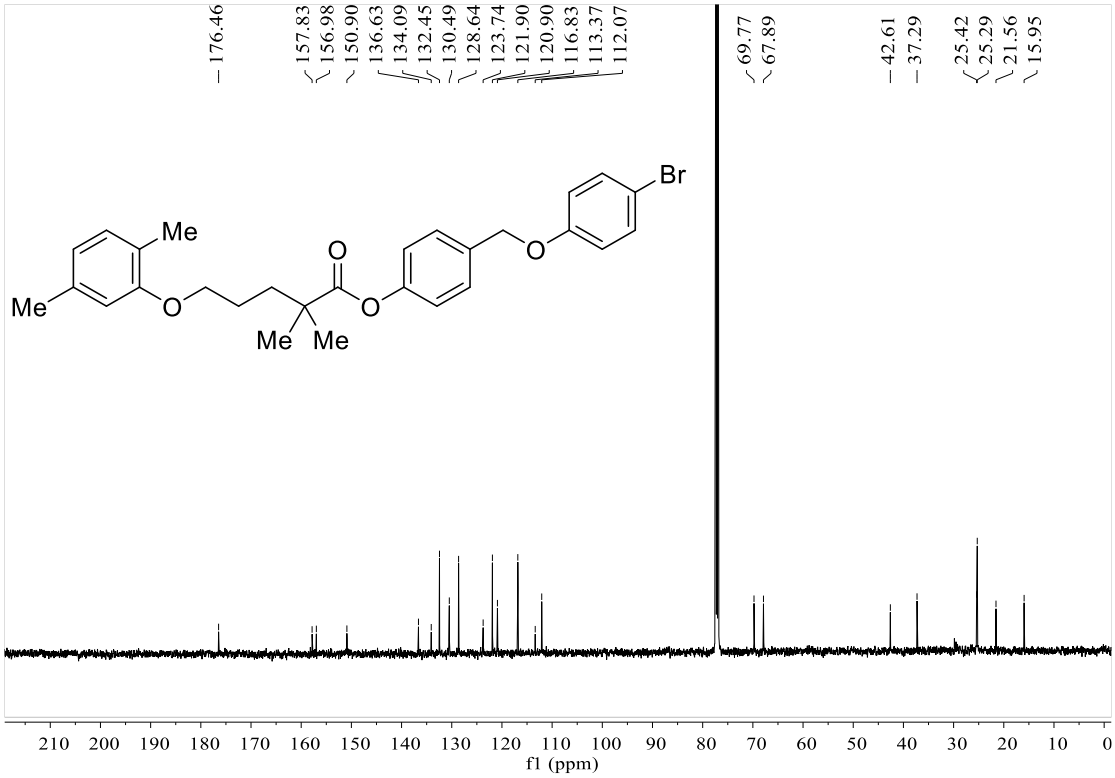

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