Supporting Information

Photoinduced Intramolecular S-α-C(sp^3)−H Functionalization Enabled by an Electron Donor−Acceptor Complex−Mediated Radical Relay

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1. General considerations

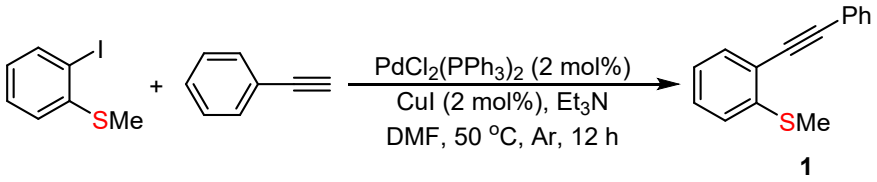
All materials were obtained from commercial suppliers or prepared according to standard procedure unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh), light petroleum ether and AcOEt are used. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz, 150 MHz or 564 MHz, respectively). For ^{1}H NMR, tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; For ^{13}C NMR, Chloroform-d (δ = 77.16 ppm) serves as the internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), tt (triplet of triplet), qd (quartet of doublet). The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on a Thermo Scientific Q Exactive and Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). All the visible-light-induced cyclization reactions were carried out under Kessil PR160L 390, 427nm, 440nm (40W) LED lamps irradiation (Figure S1).

Figure S1. Reaction setup

2. Experimental Section

2.1 General procedure for the preparation of substrate

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



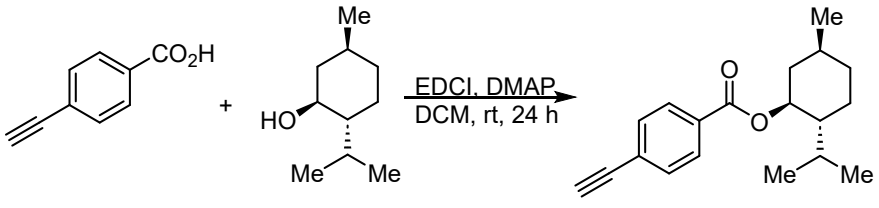
1

To a solution of 2-iodophenylmethylsulfane (2.50 g, 10.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (140.4 mg, 2 mol%), CuI (38.1 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 ℃ for 12 h under an argon atmosphere. After completion, the mixture was diluted with water, and then extracted with ethyl acetate, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the corresponding product **1** as a yellow oil (1.95 g, 87% yield).

Unless otherwise noted, all other *o*-alkynyl aryl sulphides were prepared according to the methods reported in the literature. [1,2]

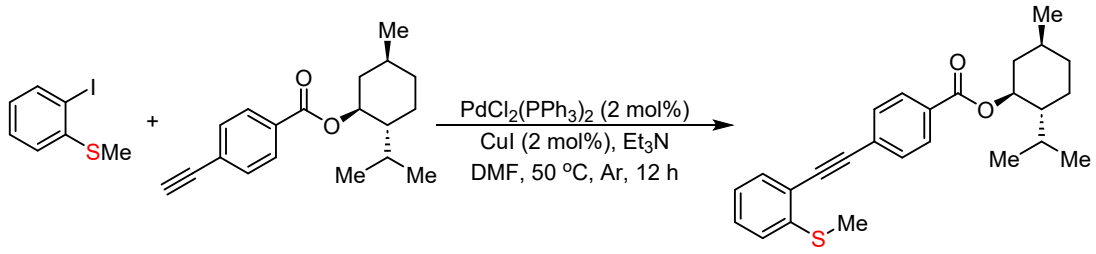
2.1.2 Typical procedure for the preparation of bioactive molecule contained substrates

I. Preparation of menthol fragments contained methyl(2-(phenylethynyl)-phenyl)sulfane [2, 3]



To a stirred solution of 4-ethynylbenzoic acid (876.2 mg, 6 mmol, 1 equiv.) and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (3.45 g，18 mmol, 3.0 equiv.) in DCM (25 mL) were added 4-dimethylaminepyridine (DMAP) (146.6 mg, 1.2 mmol, 0.2 equiv.) and (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexan-1-ol

(936.9 mg, 6 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (TLC), the reaction was quenched with water and the mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography afforded the product (1*S*,2*R*,5*S*)-2-isopropyl-5- methylcyclohexyl 4-ethynylbenzoate as a colourless oil (1.60 g, 94% yield).



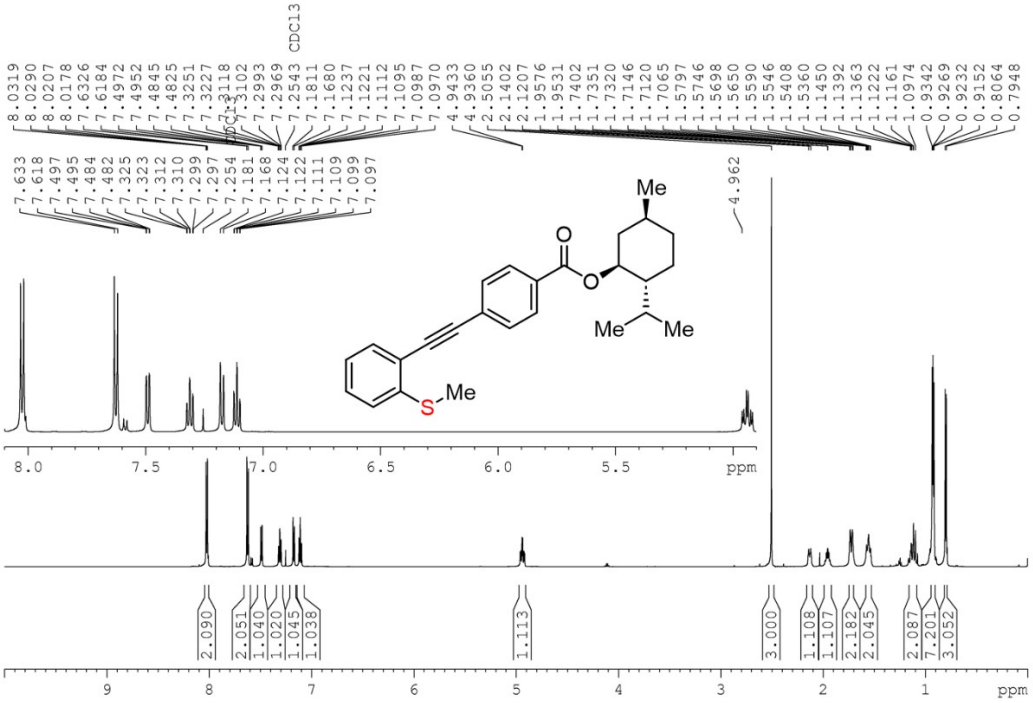
To a solution of (2-iodophenyl)(methyl)sulfane (1.00 g, 4.0 mmol) and (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-ethynylbenzoate (1.36 g, 4.8 mmol, 1.2 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (56.2 mg, 2 mol%), CuI (15.2 mg, 2 mol%) and Et_3N (10 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 °C for 12 h under an argon atmosphere. After completion, the mixture was diluted with water, and then extracted with ethyl acetate, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the corresponding product (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-4-((2-(methylthio)phenyl)ethynyl)benzoate as a yellow oil (1.28 g, 79% yield).

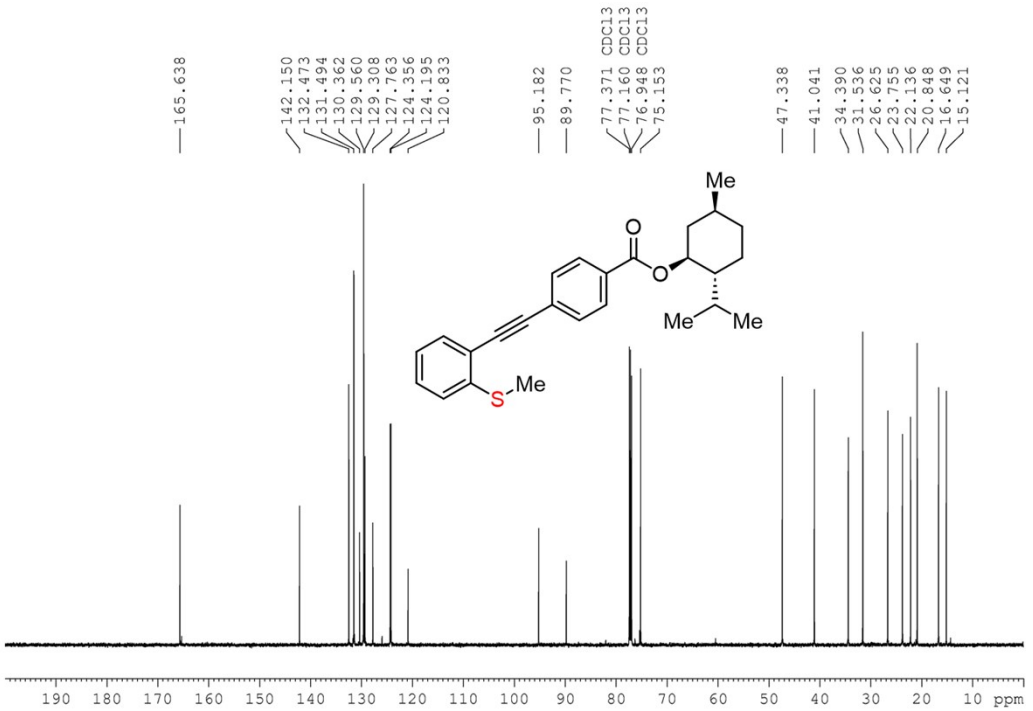
Characterization data for the compound:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03–8.02 (m, 2H), 7.63–7.62 (m, 2H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.33–7.30 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 2.51 (s, 3H), 2.14–2.12 (m, 1H), 1.98–1.93 (m, 1H), 1.74–1.71 (m, 2H), 1.59–1.53 (m, 2H), 1.17–1.08 (m, 2H), 0.93–0.92 (m, 7H), 0.80 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.6, 142.2, 132.5, 131.5, 130.4, 129.6, 129.3, 127.8, 124.4, 124.2, 120.8, 95.2, 89.8, 75.2, 47.3, 41.0, 34.4, 31.5,

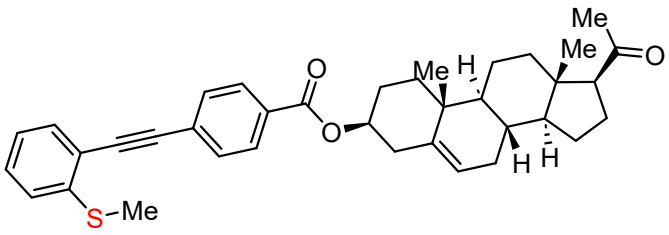
26.6, 23.8, 22.8, 20.9, 16.6, 15.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{26}H_{31}O_2S^+$ 407.2039; Found 407.2036.

^{1}H NMR and **^{13}C NMR** {1H} **spectra of the desired compound**





II. Preparation of Pregnenolone fragments contained methyl(2-(phenylethynyl)phenyl)sulfane [2, 3]

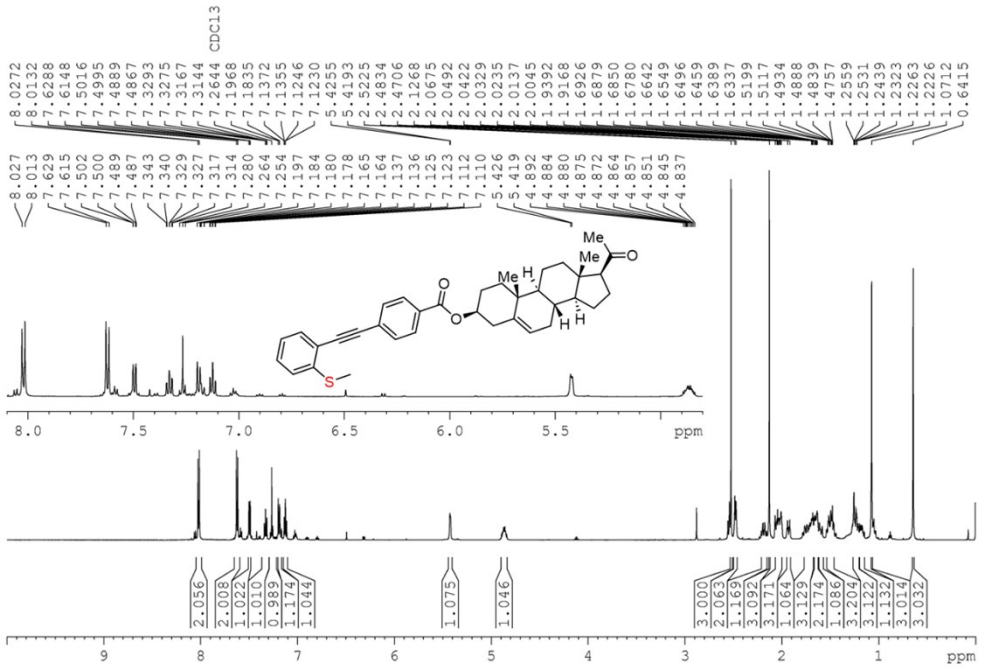


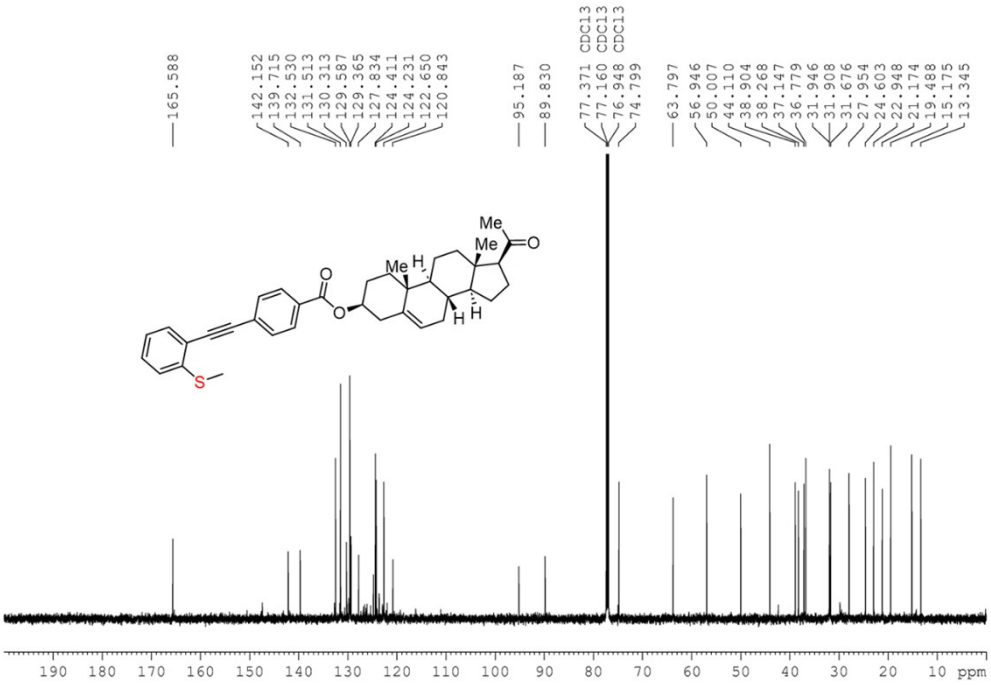
The compound was prepared according to the above method in 66% total yield.

Characterization data for the compound:

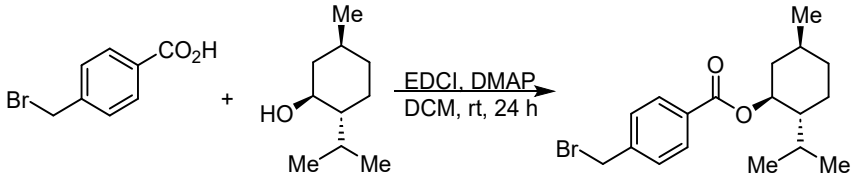
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 2H), δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.50–7.49 (m, 1H), 7.34–7.31 (m, 1H), 7.28–7.23 (m, 1H), 7.20–7.16 (m, 1H), 7.14–7.11 (m, 1H), 5.42 (d, *J* = 3.7, 1H), 4.89–4.84 (m, 1H), 2.52 (s, 3H), 2.48 (d, *J* = 7.7 Hz, 2H), 2.23–2.15 (m, 1H), 2.13 (s, 3H), 2.07–2.00 (m, 3H), 1.94–1.92 (m, 1H), 1.78–1.68 (m, 3H), 1.66–1.63 (m, 2H), 1.61–1.58 (m, 1H), 1.54–1.46 (m, 3H), 1.27–1.21 (m, 3H), 1.19–1.15 (m, 1H), 1.07 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 209.7, 165.6, 142.2, 139.7, 132.5, 131.5, 130.3, 129.6, 129.4, 127.8, 124.4, 124.2, 122.6, 120.8, 95.2, 89.8, 74.8, 63.8, 56.9, 50.0, 44.1, 38.9, 38.3, 37.1, 36.8, 31.94, 31.91, 31.7, 28.0, 24.6, 22.9, 21.2, 19.5, 15.2, 13.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{37}H_{43}O_3S^+$ 567.2927; Found 567.2928.

^{1}H NMR and **^{13}C NMR** {1H} **spectra of the desired compound**

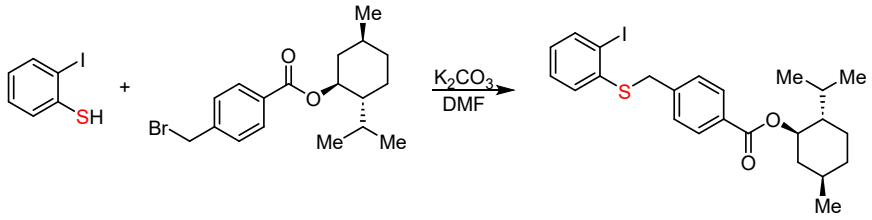




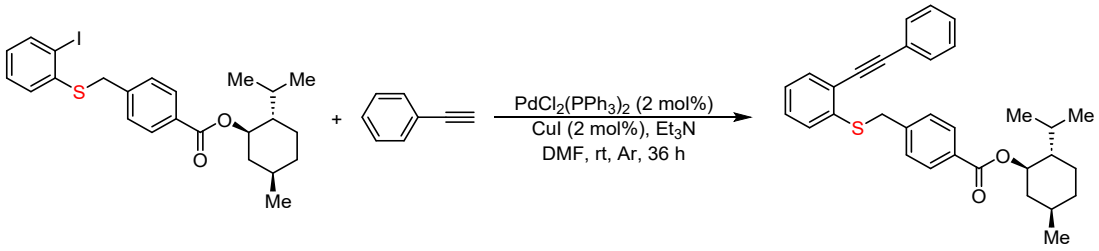
III. Preparation of menthol fragments contained benzyl(2-(phenylethynyl)-phenyl)sulfane [3-5]



To a stirred solution of 4-(bromomethyl)benzoic acid (1.28 g, 6 mmol, 1 equiv.) and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI) (3.45 g，18 mmol, 3.0 equiv.) in DCM (25 mL) were added DMAP (4-dimethylaminepyridine) (146.6 mg, 1.2 mmol, 0.2 equiv.) and (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexan-1-ol (936.9 mg, 6 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (TLC), the reaction was quenched with water and the mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography afforded the product (1*S*,2*R*,5*S*)-2-isopropyl-5- methylcyclohexyl 4-(bromomethyl)benzoate as a colourless oil (1.92 g, 91% yield).



To a solution of 2-iodothiophenol (1.42 g, 6 mmol, 1.2 equiv.) in dry DMF (10 mL) was added K_2CO_3 (1.04 g, 7.5 mmol), after being stirred at room temperature for 30 min, to which a solution of (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-(bromomethyl)benzoate (1.76 g, 5 mmol, 1.0 equiv.) in dry DMF (5 mL) was added, and the resulting mixture was stirred at room temperature for another 12 h, After completion of the reaction (TLC), the reaction was quenched with water and the mixture was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography afforded the product (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(((2-iodophenyl)thio)methyl)benzoate as a colourless oil (2.11 g, 83% yield).



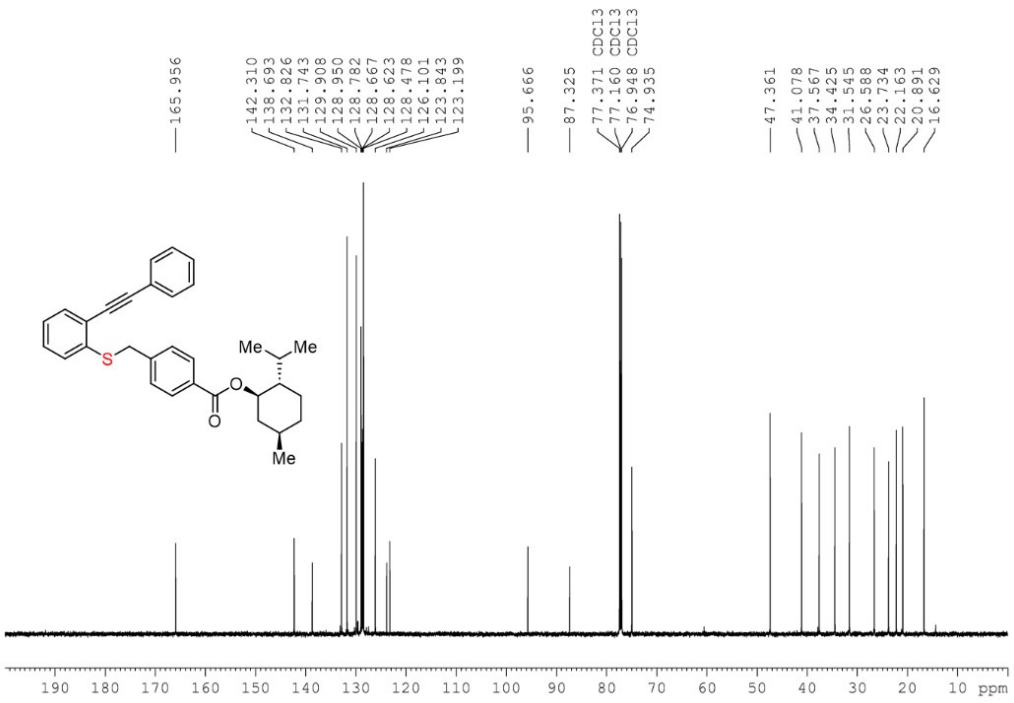
To a solution of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(((2-iodophenyl)thio)methyl)benzoate (2.03 g, 4.0 mmol) and phenylacetylene (612.8 mg, 6.0 mmol, 1.5 equiv.) in DMF (3 mL), $PdCl_2(PPh_3)_2$ (56.2 mg, 2 mol%), CuI (15.2 mg, 2 mol%) and Et_3N (10 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 ℃ for 24 h under an argon atmosphere. After completion, the mixture was diluted with water, and then extracted with ethyl acetate, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the corresponding product (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-(((2-(phenylethynyl)phenyl)thio)-methyl)benzoate as

a yellow solid (1.23 g, 64% yield).

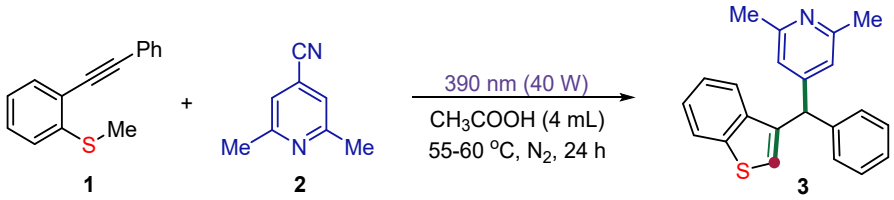
Characterization data for the compound:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.3 Hz, 2H), 7.57–7.56 (m, 2H), 7.52–7.51 (m, 1H), δ = 7.40 (d, *J* = 8.3 Hz, 2H), 7.36–7.33 (m, 3H), 7.23–7.14 (m, 3H), 4.91 (dt, *J* = 10.9, 4.38 Hz, 1H), 4.24 (s, 2H), 2.12–2.09 (m, 1H), 1.97–1.92 (m, 1H), 1.73–1.71 (m, 2H), 1.56–1.51 (m, 2H), 1.15–1.05 (m, 2H), δ = 0.91 (t, *J* = 6.8 Hz, 7H), δ = 0.78 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.0, 142.3, 138.7, 132.8, 131.7, 129.9, 128.9, 128.8, 128.7, 128.6, 128.5, 126.1, 123.8, 123.2, 95.7, 87.3, 74.9, 47.4, 41.1, 37.6, 34.4, 31.5, 26.6, 23.7, 22.2, 20.9, 16.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{32}H_{35}O_2S^+$ 483.2352; Found 483.2352.

^{1}H NMR and **^{13}C NMR** {1H} **spectra of the desired compound**

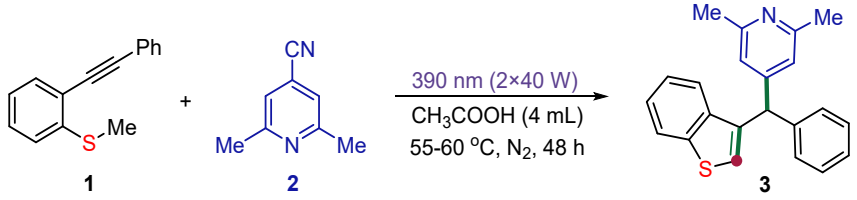


2.2 Typical procedure for the cyclization reactions of 1 and 2



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the desired product **3** as a yellow oil (51.3 mg, 78% yield).

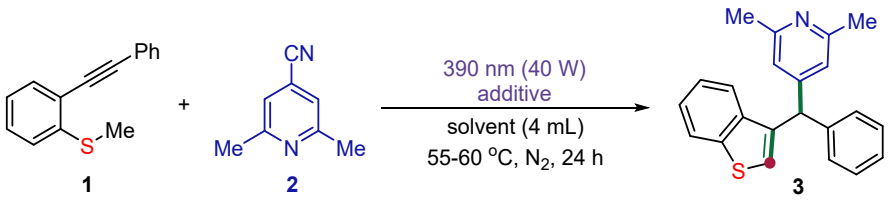
2.3 Typical procedure for gram-scale synthesis



A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 1.08 g, 4.8 mmol), 4-cyano-2,6-lutidine (**2**, 0.53 g, 4.0 mmol), and CH_3COOH (80.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (2×40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 48 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the desired product **3** as a yellow solid (0.79 g, 60% yield).

2.4 Optimization of the reaction conditions of the model reaction

Table S1. Optimization of Reaction Conditions[a]



Entry	Solvent	Deviation	Yield (%)[b]
1	CH_3CN	-	n.d.
2	DCE	-	n.d.
3	1,4-Dioxane	-	n.d.
4	CH_3CN	20 % mol TFA	11
5	CH_3CN	20 % mol TsOH	17
6	CH_3CN	20 % mol BNDHP	51
7	CH_3CN	20 % mol H_2SO_4	trace
8	CH_3CN/ CH_3COOH (1:1)	-	<5%
9	CH_3CN/ CH_3COOH (1:2)	-	23
10	CH_3COOH	-	65(78[c], 78[d])
11	CH_3COOH (2 mL)		32[d]
12	CH_3COOH (6 mL)	-	69[d]
13	CH_3COOH	12 h or 36 h	48[d], 76[d]
14	CH_3COOH	With fan	53[d]
15	CH_3COOH	427 nm (40 W)	51[d]

16	CH_3COOH	370 nm (40 W)	38[d]
17	CH_3COOH	dark	n.d.[d]
18	CH_3COOH	80 °C in the dark	n.d.[d]

[a]Reaction conditions: **1** (0.20 mmol) and **2** (4-cyano-2,6-lutidine, 0.24 mmol) in solvent were irradiated with 390 nm Kessil LED (40 W) in a reaction tube Under N_2 atmosphere at 55-60 °C for 24 h unless otherwise stated. [b]Isolated yield. [c]**1** (0.24 mmol) and **2** (0.20 mmol) was used. [d]**1** (0.22 mmol) and **2** (0.20 mmol) was used, BNDHP = 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (racemic), n.d. = not detected.

3. Preliminary mechanistic study

3.1 UV-visible absorption spectra

The UV-vis absorption spectra of **1** (5×10^{-2} M), 4-cyano-2,6-dimethylpyridine (**2**, 5×10^{-2} M), and a mixture of **1** and **2** in acetic acid (CH_3COOH) were separately recorded on a UV-Vis spectrophotometer. As shown in Figure S2, the absorption spectrum of the mixture (blue curve) exhibited a red shift compared to the spectra of the individual components **1** and **2**. This shift became more pronounced after 10 minutes of irradiation with a 390 nm Kessil LED (40 W).

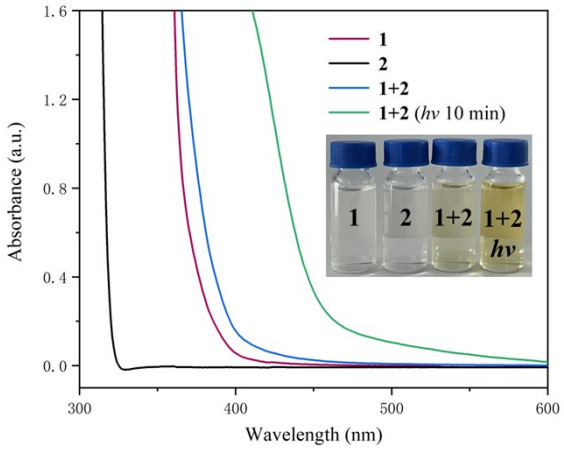


Figure S2. UV/Vis absorption spectra of the reaction components and their mixture in CH_3COOH

3.2 Quantum yield measurements[6,7]

Determination of the light intensity of single Kessil PR160-390 nm LEDs

Standard ferrioxalate actinometry[8,9] was used to determine the photon flux of Kessil PR160-390 nm LEDs. A solution of ferrioxalate (0.15 M) was prepared by dissolving potassium ferrioxalate trihydrate (737 mg, 1.50 mmol) in 10.0 mL of 0.20 M aqueous H_2SO_4. A buffered solution of 1,10-phenanthroline (0.15 M) was prepared

by dissolving NaOAc (1.23 g, 15.0 mmol) and 1,10-phenanthroline (541 mg, 3.00 mmol) in 20 mL of 0.20 M aqueous H_2SO_4.

To a 10 mL oven-dried reaction vessel equipped with a stir bar was added 4.0 mL of the ferrioxalate solution. The vessel was sealed with a septum-cap and placed 2 cm away from a Kessil PR160-390 nm LEDs. After being irradiated for 60 seconds, 1.0 mL of 0.20 M aqueous H_2SO_4 and 5.0 mL of the buffered solution were immediately added into the above 4.0 mL of the ferrioxalate solution which has been irradiated. The resulting mixture was then allowed to rest for 1 hour to allow the formed ferrous ions to react completely with 1,10 phenanthroline. An aliquot (50 μL) of the resulting solution was diluted with 3.0 mL of 0.20 M aqueous H_2SO_4, and the absorbance in a cuvette (l=1.0 cm) at 510 nm was measured by UV-Vis spectrometer. The above procedure was repeated with three times, and the average absorption was used for the calculation of photon flux. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

entry	absorbance	ΔA	mol Fe^{2+} (mol)	photon flux (Einstein/s)
non-irradiation	0.035	-	-	-
1	0.356	0.321	3.47×10^{-6}	5.12×10^{-8}
2	0.328	0.293	3.17×10^{-6}	4.68×10^{-8}
3	0.330	0.295	3.19×10^{-6}	4.71×10^{-8}

The photon flux was calculated as follows:

$$mol\ Fe^{2+} = \frac{V \times \Delta A\ (510\ nm)}{l \times \varepsilon}$$

where V is the total volume (0.120 L) of the solution that was analyzed, ΔA is the difference between the average absorption of irradiated and non-irradiated solutions at 510 nm, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}).

The photon flux was calculated as follows:

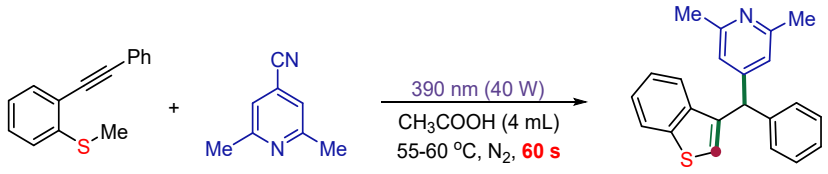
$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \times t \times f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 1.13[10], which was reported at λ=392 nm), t is the irradiation time (60 s), and f is the fraction of light absorbed at λ=390 nm by the ferrioxalate actinometer. This value is calculated using the following equation where A (390 nm) is the absorption of the ferrioxalate solution at 390 nm. An absorption spectrum gave an A (390 nm) value of > 3, indicating that the fraction of absorbed light (f) is >0.999.

$$f = 1 - 10^{-A(390\ nm)}$$

The average photon flux was thus calculated to be 4.84×10^{-6} einsteins s^{-1}.

Determination of quantum yield



1 **2** **3, yield 8%**

A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 60 s. After completion, the product yield was quantified by gas chromatography (GC) after the reaction reached completion.

The quantum yield was calculated as follows:

$$\Phi = \frac{mol\ (product)}{(photon\ flux)\ \times\ t\ \times\ f}$$

Where mol (product) is the amount of product **3** (1.6×10^{-5} mol), photon flux is determined by above ferrioxalate actinometry (4.84×10^{-6} einsteins s^{-1}), t is the reaction time (60 s), and f is the fraction of light absorbed by the reaction mixture at 390 nm. This value is calculated using the following equation where A (390 nm) is the absorption of the non-irradiated reaction mixture (0.863) at 390 nm. The fraction of light absorbed at 390 nm was calculated:

$$f = 1 - 10^{-A(390\,nm)} = 1 - 10^{-0.863} = 0.863$$

Thus, the quantum yield was calculated as Φ =0.06. Therefore, the reaction mechanism does not involve a radical chain reaction.

3.3 Fluorescence quenching experiment

To further elucidate the possible reaction pathway, the related fluorescence quenching experiments were performed and the results were shown in Figure S3. In each experiment, the fluorescence quenching of methyl (2-(phenylethynyl)phenyl) sulfide (**1**) (1.0×10^{-4} M) was observed by increasing the concentration of 4-cyano-2,6-dimethylpyridine (**2**), with an excitation wavelength of 284 nm. Emission spectrum was recorded after each addition. The results in Figure S3 (left) shows an obvious change in the emission intensity of **1** with a calculated Ksv of 5.22×10^{-3} M^{-1} [Figure S3 (right)].

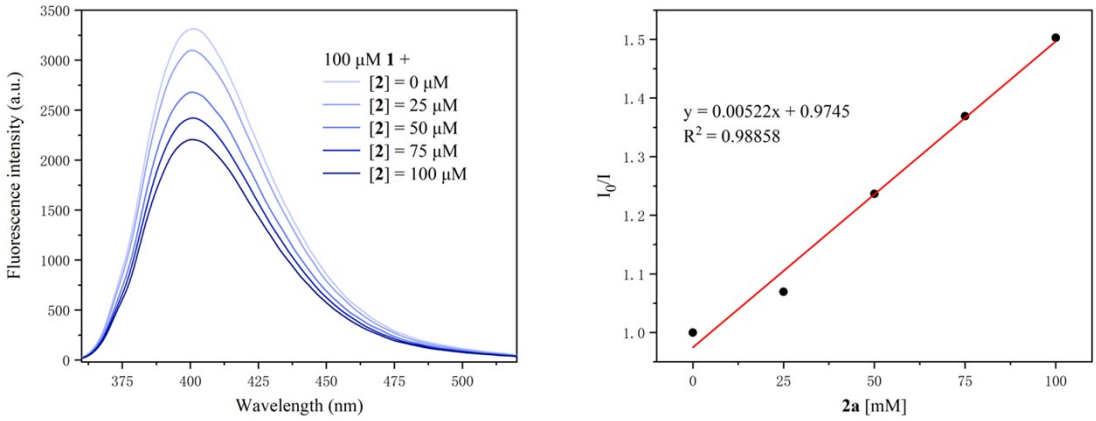


Figure S3. (a) Fluorescence quenching of **1** by **2** in CH_3COOH (left); (b) Stern-Volmer plots of **1** quenching with **2** (right)

Time-correlated single-photon counting decays of **1** in CH_3COOH in the presence of different concentrations of **2**, the fluorescence lifetime of **1** (τ**1**~ 0.8 ns) is not affected by the increasing concentration of **2** which shows the static character of the quenching, indicative of a static quenching process (Figure S4).

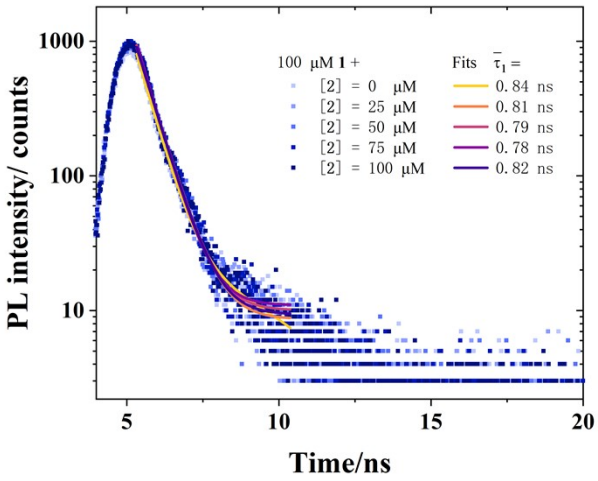


Figure S4. Time-correlated single-photon counting spectra

3.4 Switched light on/off experiment

In order to illustrate the cyclization reaction by self-sustaining in an autocatalytic manner, the light/dark experiments were conducted, as shown in Figure S5. A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (**2**, 26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The reaction mixture was exposed to a 390 nm LED (40 W) irradiation at 55-60℃ in N_2 with stirring for 2 h, then stirring for 2 h without irradiation. The following product yields based on the irradiation with LED (390 nm, 40 W) for a certain time, and without irradiation for a certain time were also presented in the Figure S5.

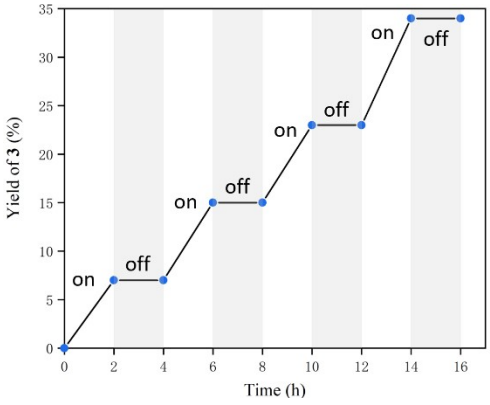
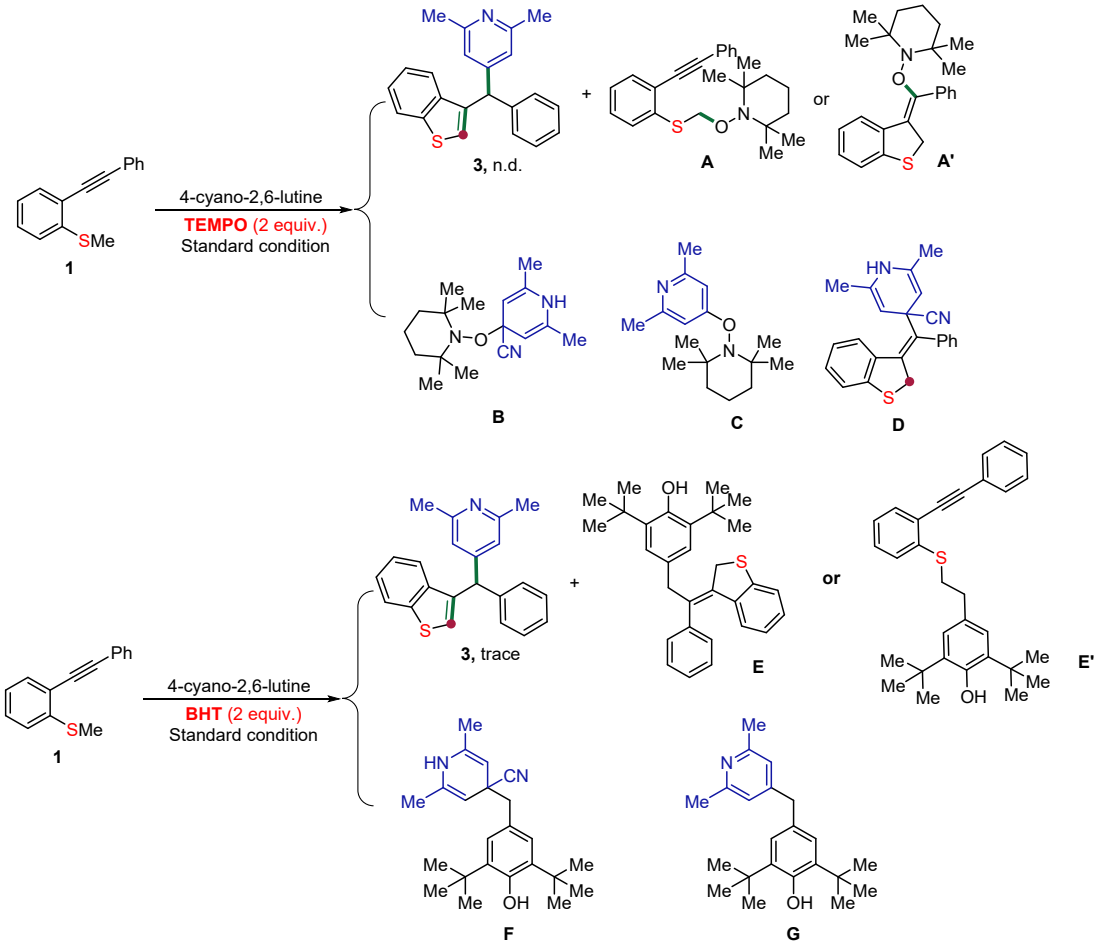


Figure S5. Light/dark experiments

3.5 Radical inhibition experiment

A 25 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was

charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (**2**, 26.4 mg, 0.2 mmol), TEMPO (or BHT) (62.5 mg, 0.40 mmol, 2.0 equiv.), with the standard condition. The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 50 °C in a reaction tube with an N_2 balloon with stirring for 24 h. After completion, **3** was not detected in the reaction mixture, and the corresponding adducts (**A**-**G** or **A'** and E') of free radical with TEMPO (or BHT) and corresponding reaction the reaction intermediate **D** were detected by HRMS analysis of the reaction mixture, and the results are shown in the figure below (Figure S6-12).



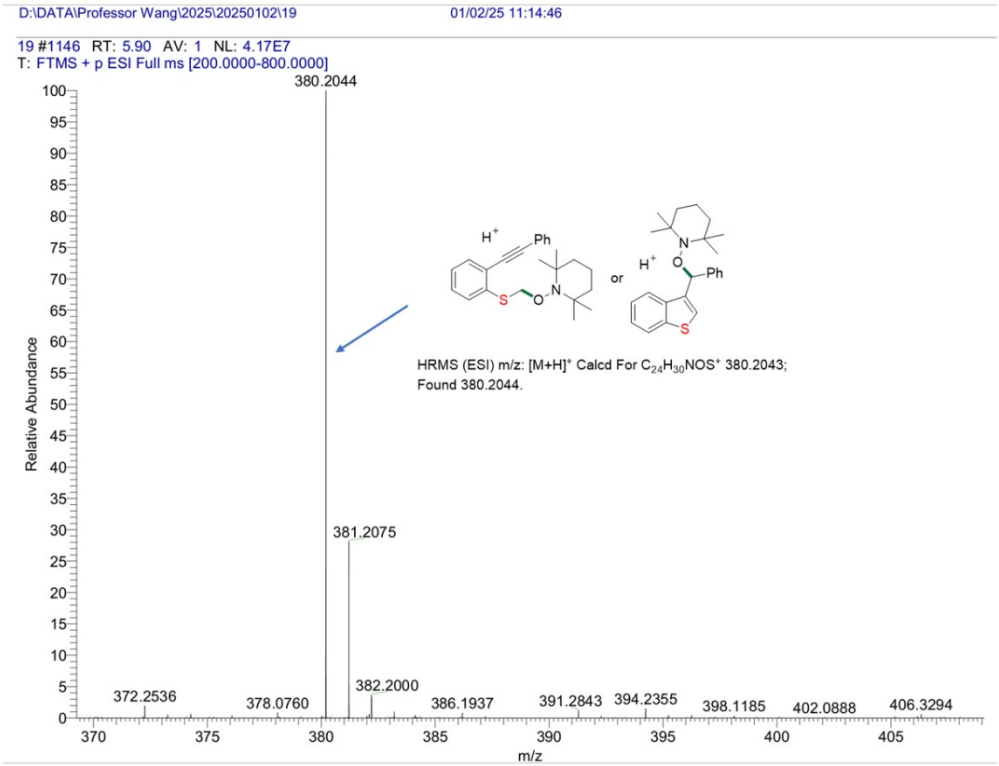


Figure S6. Analysis of reaction mixture by HRMS for the adduct of **A** and **A'**

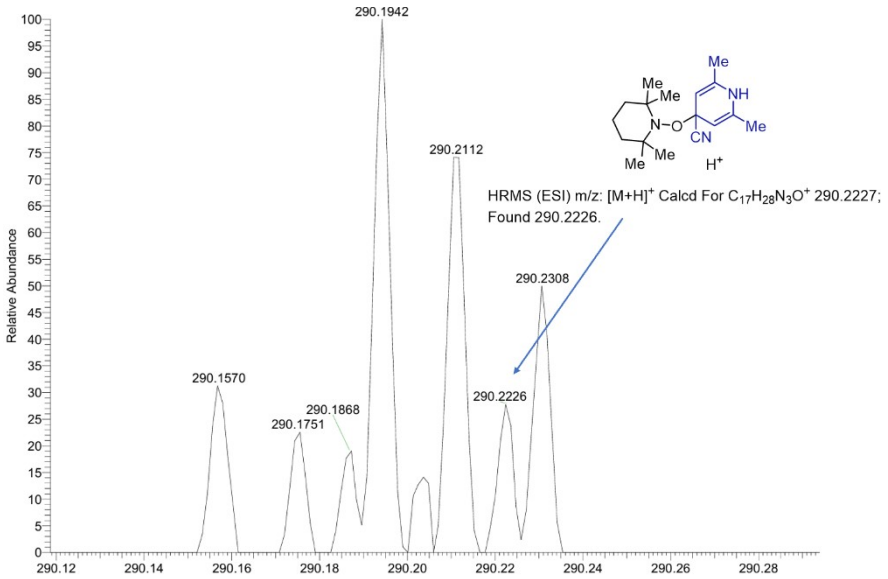


Figure S7. Analysis of reaction mixture by HRMS for the adduct of **B**

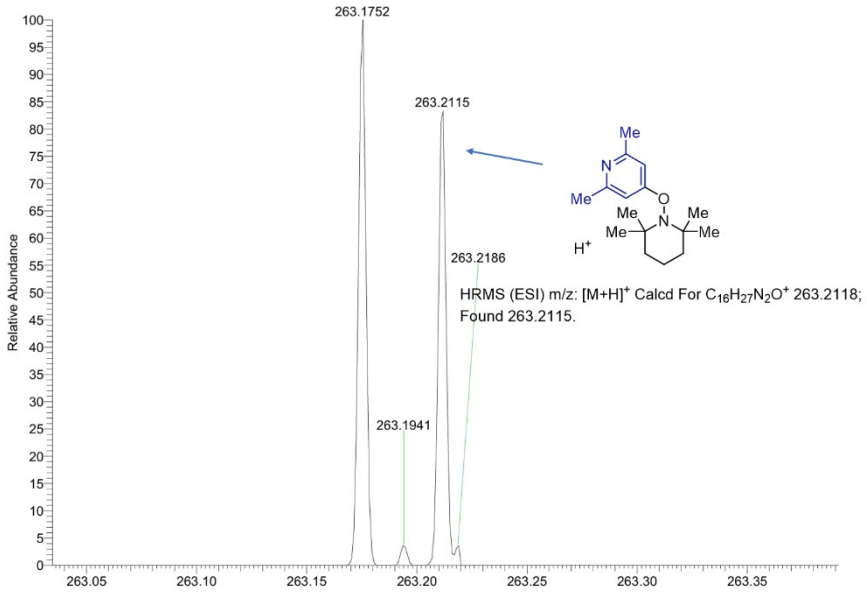


Figure S8. Analysis of reaction mixture by HRMS for the adduct of **C**

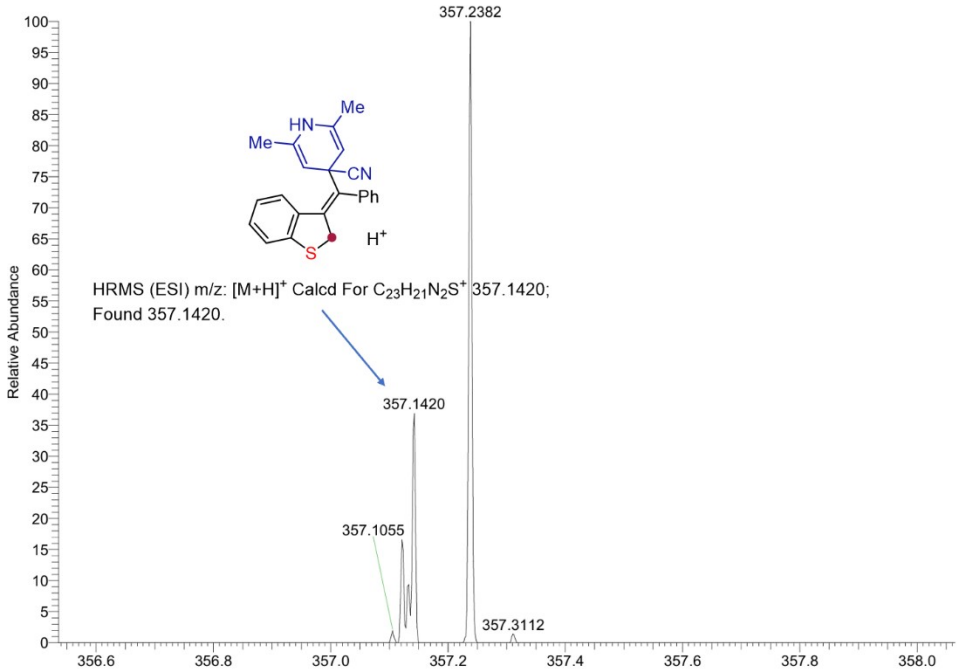


Figure S9. Analysis of reaction mixture by HRMS for the reaction intermediate **D**

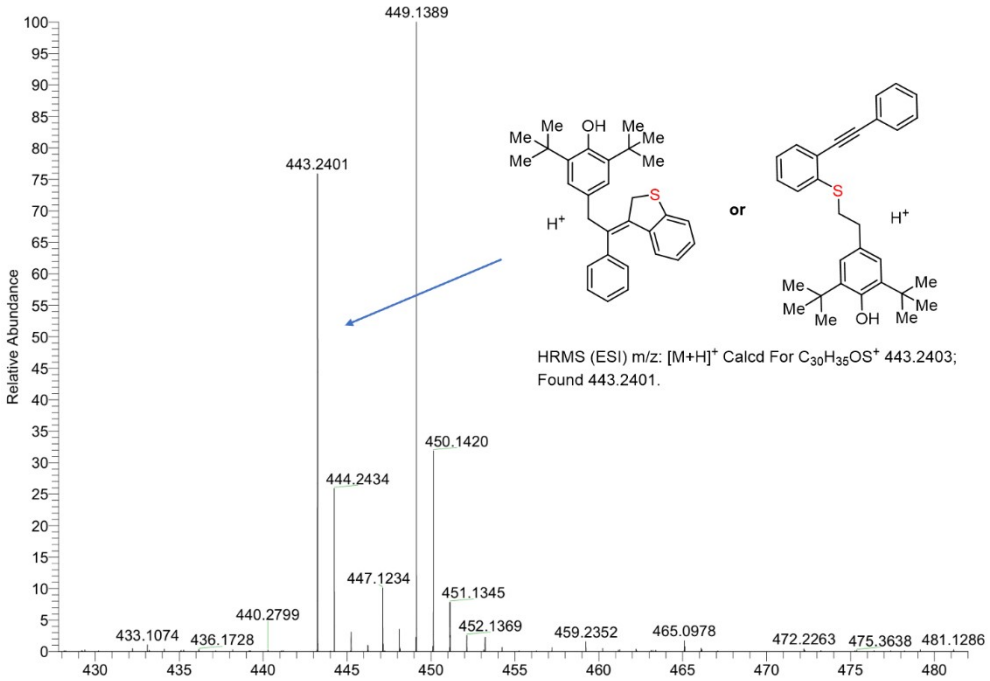


Figure S10. Analysis of reaction mixture by HRMS for the adduct of **E** and **E'**

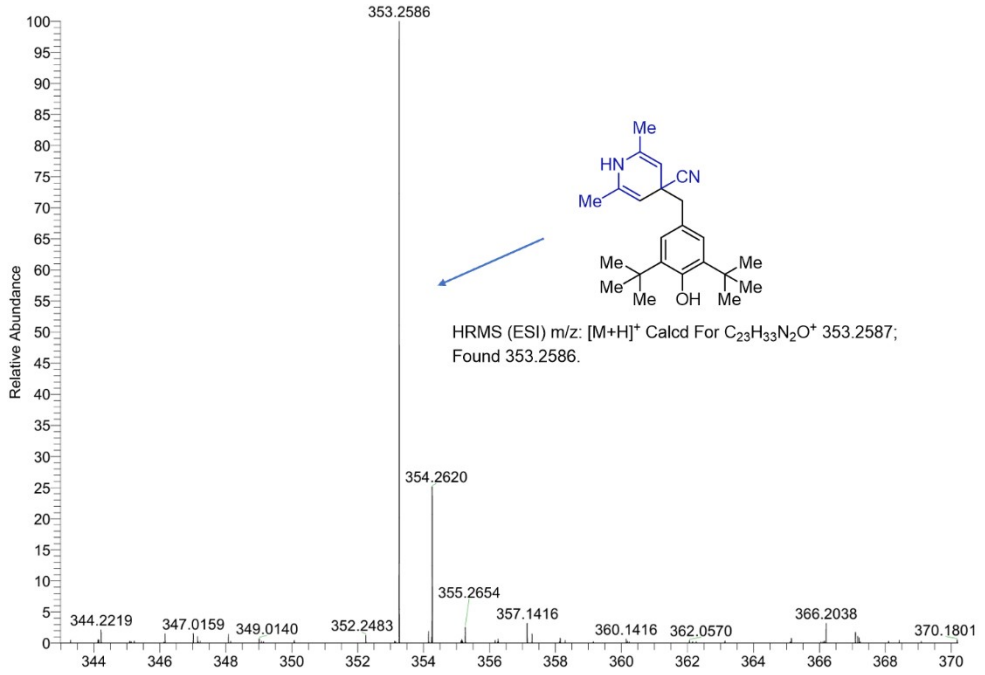


Figure S11. Analysis of reaction mixture by HRMS for the adduct of **F**

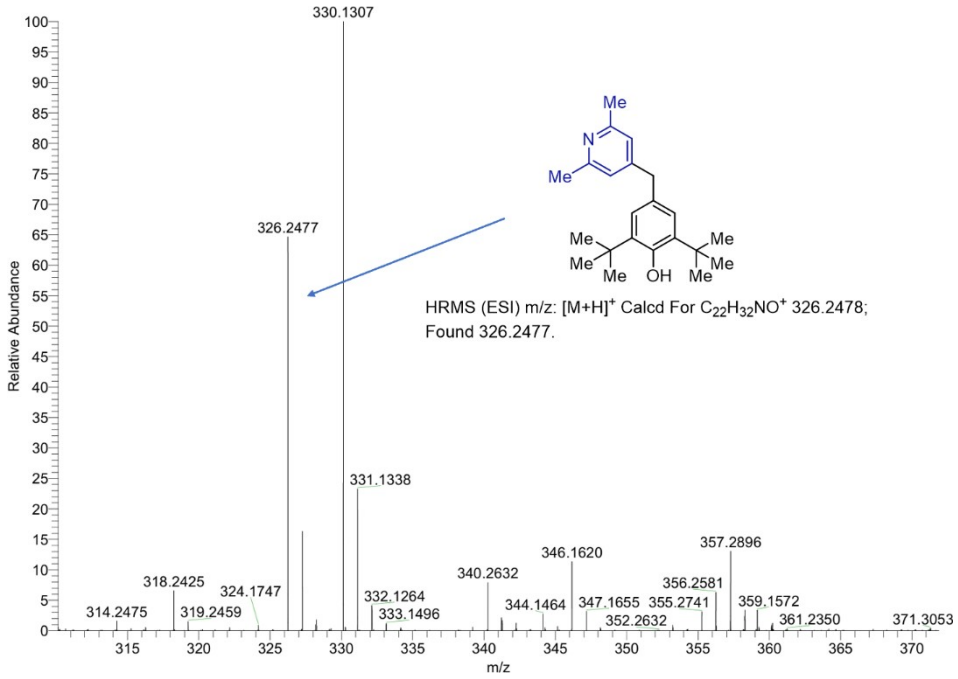
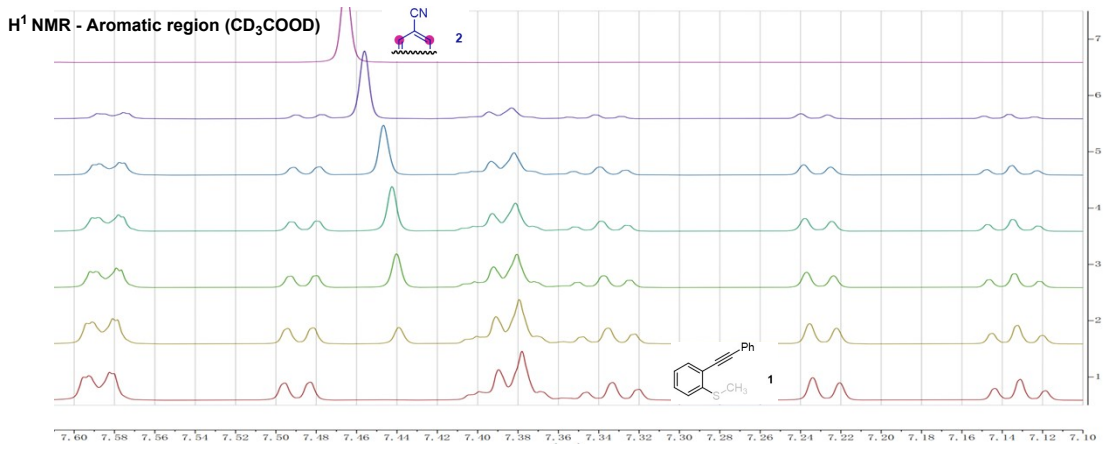


Figure S12. Analysis of reaction mixture by HRMS for the adduct of **G**

3.6 Determination of Binding Stoichiometry

I. NMR titration experiments

The ^{1}H NMR spectra of seven mixtures of **1** and **2** in CD_3COOD were recorded at 298 K under a nitrogen atmosphere. CH_3COOH was employed as an internal standard. The total volume of each mixture was 1 mL, with the combined amount of **1** and **2** kept constant at 0.2 mmol (0.2 M), while the amount of **1** was varied from 0 to 0.2 mmol (0 - 0.2 M). NMR titration experiments revealed that upon complexation, acceptor **2** displayed upfield shifts in its aliphatic and aromatic regions, accompanied by downfield shifts in donor **1** (Figure S13).



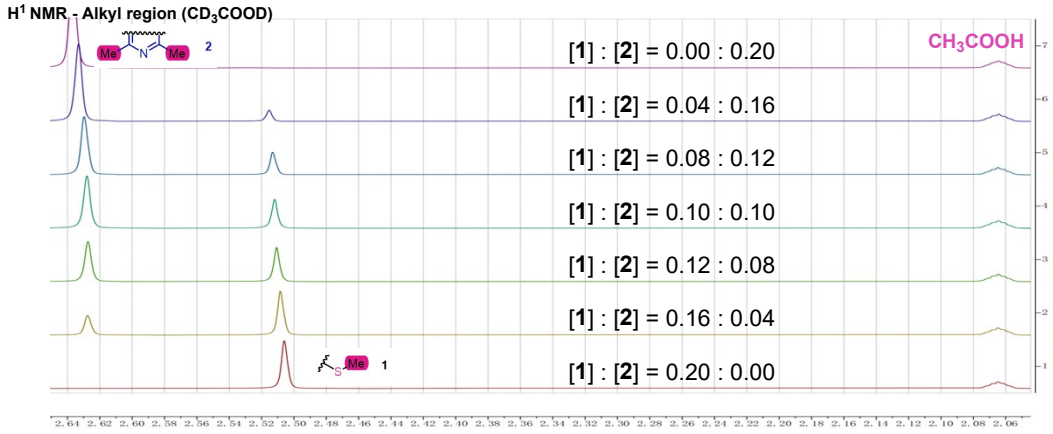


Figure S13. ^{1}H NMR spectra of **1**, **2** and their mixture

II. Job's Method Experiment

The stoichiometry of the EDA complexes was calculated using the Job´s plot method. The Job's plot of the EDA complex between **1** and **2** was calculated measuring the absorption of MeCN solutions at 390 nm with different donor/acceptor ratios with constant concentration (0.20 M) of the two components. The absorbance values were plotted against the molar fraction of **2**. Job's plot analysis for the EDA complex between **1** and **2** exhibited a maximum absorbance at a mole fraction of [**2**]/ ([**1**] + [**2**]) ≈ 0.5, which suggests the formation of a complex with a 1:1 stoichiometric ratio in solution (Figure S14).

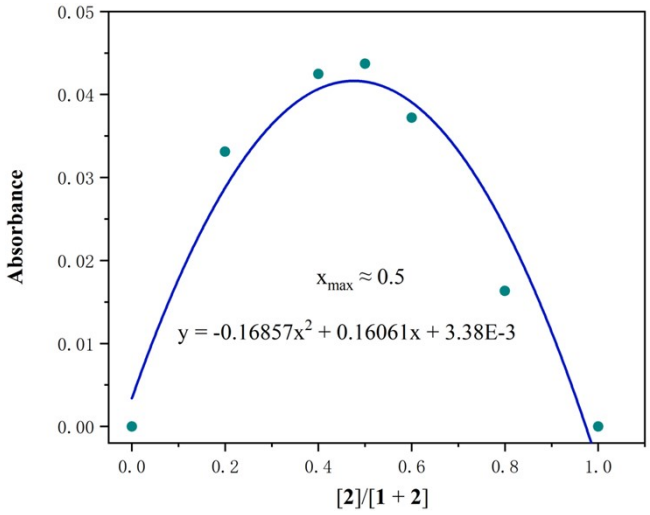


Figure S14. Association constant determination

3.7 Determination of the association constant (Ka)

In an NMR tube, a CD_3COOD solution of **2** (50 mM, 0.6 mL, 0.03 mmol) was added at 298 K. To the tube, **1** was added from 0.1 to 0.3 mmol. ^{1}H NMR for each

sample was recorded to measure the change in chemical shift for the (-Me) of **2** CD_3COOD was used as internal standard and δ = 2.10 ppm.

	[**1**] (M)	1/ [**2**]	Δδ (ppm)	1/Δδ
1	0.1	10.00	0.0169	59.17
2	0.15	6.67	0.0235	42.55
3	0.20	5.00	0.0290	34.48
4	0.25	4.00	0.0344	29.07
5	0.30	3.33	0.0397	25.19

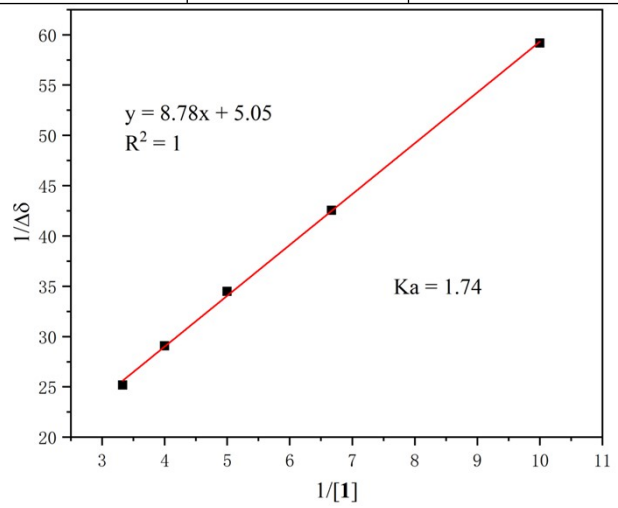


Figure S15. Association constant determination.

3.8 Deuteration experiment

The line 1: A 25 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the desired product **3** as a yellow oil (51.3 mg, 78% yield).

The line 2: A 25 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with (methyl-d_3)(2-(phenylethynyl)phenyl)sulfane (**d-1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The

reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the desired product **d-3**.

The line 3: A 25 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 49.3 mg, 0.22 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CD_3COOD (4.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in a reaction tube with nitrogen atmosphere with stirring for 24 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the desired product **d-3'** as a yellow oil.

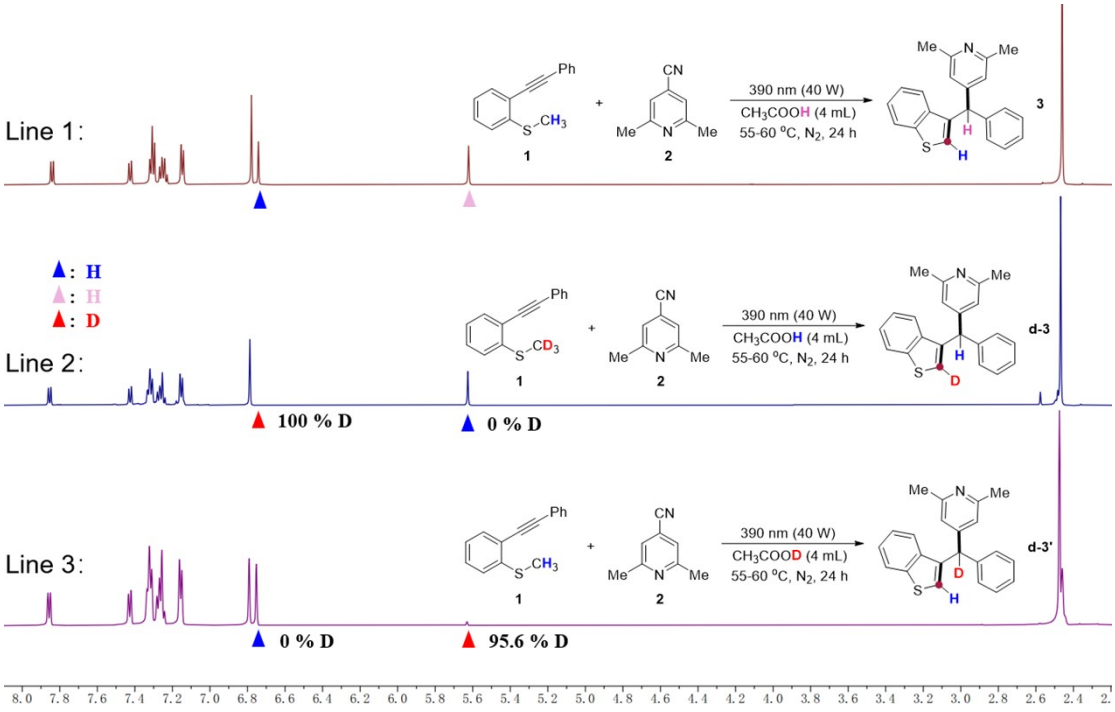
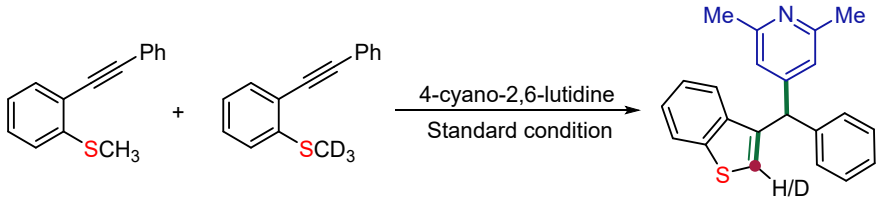


Figure S16. Deuteration experiment.

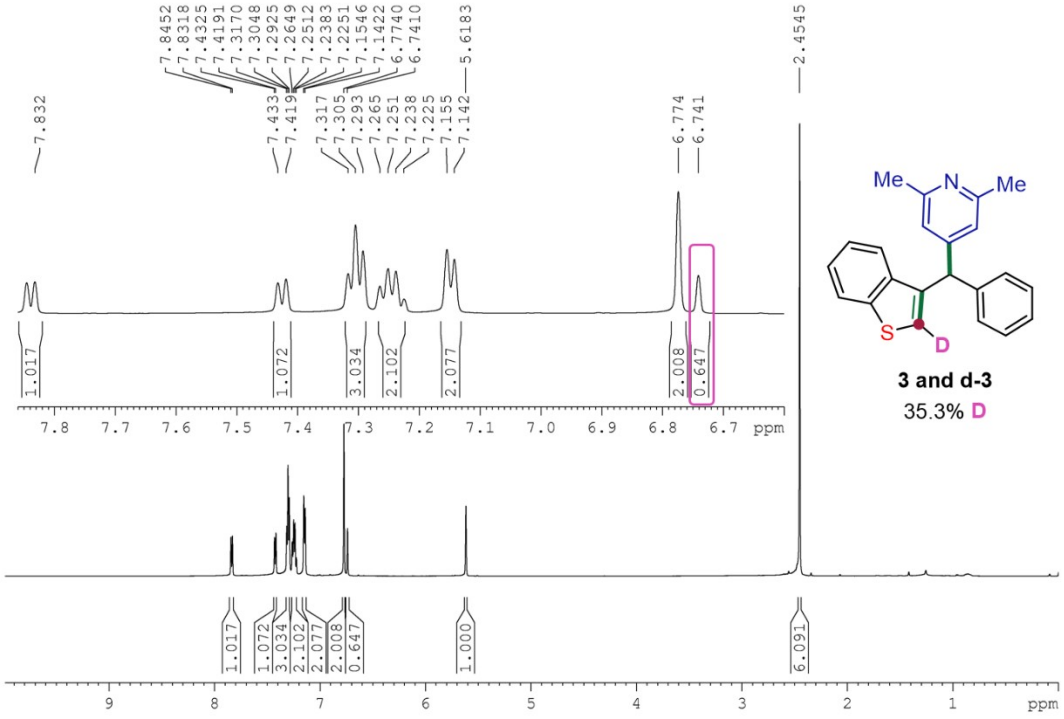
3.9 Intermolecular competition experiment



1:d-1 = 1:1 **3 and d-3**

A 25 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1**, 24.6 mg, 0.11 mmol), (methyl-d_3)(2-(phenylethynyl)phenyl)sulfane (**d-1**, 25.0 mg, 0.11 mmol), 4-cyano-2,6-lutidine (26.4 mg, 0.2 mmol) and CH_3COOH (4.0 mL). The reaction mixture was exposed to 390 nm Kessil LED (40 W) irradiation at 55-60 °C in in a reaction tube with nitrogen atmosphere with stirring for 8 h. After completion, the solvent was removed directly by rotary evaporation and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:9, V/V) as the eluent to afford the mixed product **3** and **d-3** as a yellow oil (11.2 mg, 17% yield).

4-((benzo[b]thiophen-3-yl-2-d)(phenyl)methyl)-2,6-dimethylpyridine (d-3/3 = 35.3/64.7). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 3H), 7.26–7.23 (m, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.77 (s, 2H), 6.74 (s, 0.647H), 5.62 (s, 1H), 2.45 (s, 6H).



3.10 Computational studies

To elucidate the reaction mechanism, density functional theory (DFT) calculations were performed to investigate the reaction process. Analyses were conducted from structural, energetic, and non-covalent interaction perspectives to uncover the theoretical basis behind the experimental observations. Geometry optimizations were carried out at the M062X/def2TZVP level, with converged structures confirmed to exhibit no imaginary frequencies. Subsequent chemical information analyses were based on the obtained wave functions. The DFT calculations and wave function analyses were conducted using Gaussian 16[11] and Multiwfn[12], respectively, while molecular visualization was performed with VMD[13].

The molecular surface electrostatics significantly influence the reaction process and can be used to infer molecular orientation and kinetic behavior. Based on the wave functions obtained from DFT calculations, we analyzed the distribution of the electrostatic potential (ESP) on the van der Waals surface. The results show that protonation of molecule **a** leads to a predominantly positive ESP over its surface, with extremum positions coinciding with the protonation sites. The projected region at the center of its benzene ring also exhibits notable positive potential. Molecules **b** and **c**, which are two conformers of the same compound, display pronounced polarization in their ESP distributions. The negative ESP regions are localized around the sulfur atoms in both conformers. The ESP results suggest that protonation sites, benzene rings, and the lone-pair electrons on sulfur atoms are likely to be reactive regions.

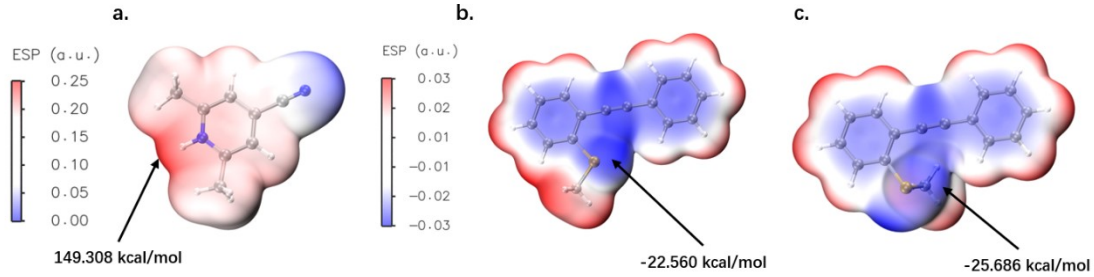


Figure S17. Molecular surface electrostatic potential map.

Table S2. Influence of Initial Structures on the Conformations of Reaction Precursors

NO.	Initial Structure	Stationary Point Structure

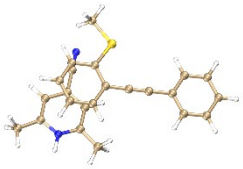
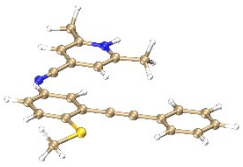
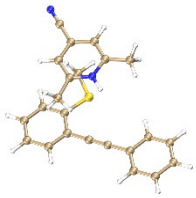
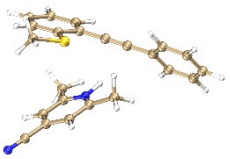
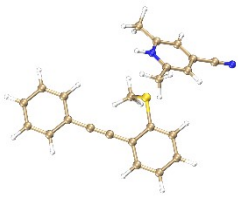
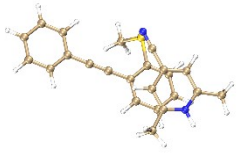
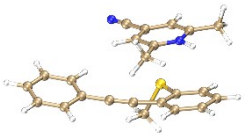
1		
2		
3		
4		

Table S3. Energy Comparison of Reaction Precursors (kcal/mol)

NO.	Energy	ΔEnergy
1	-876291.997	0.000
2	-876292.517	-0.520
3	-876290.754	1.243
4	-876289.088	2.909

To thoroughly investigate the influence of initial configurations on the dimeric structures, we selected the four most chemically intuitive stable structures as starting points to examine effects such as π-π and lone-pair–π interactions. The energies of the optimized conformers were calculated, and the Boltzmann populations were derived using $P_i = \frac{\exp\left(-\frac{E_i}{kT}\right)}{Z}$, $Z = \Sigma_{j=1}^{n} exp(-E_j/kT)$. The results indicate that under standard ambient conditions (298 K), the distribution probabilities of these four conformers are 28.27 %, 68.03 %, 3.47 %, and 0.21 %, respectively. Weak-interaction analysis of the highest-population conformer reveals a pronounced interaction between

the lone-pair electrons on the sulfur atom and the pyridinium (Figure S18).

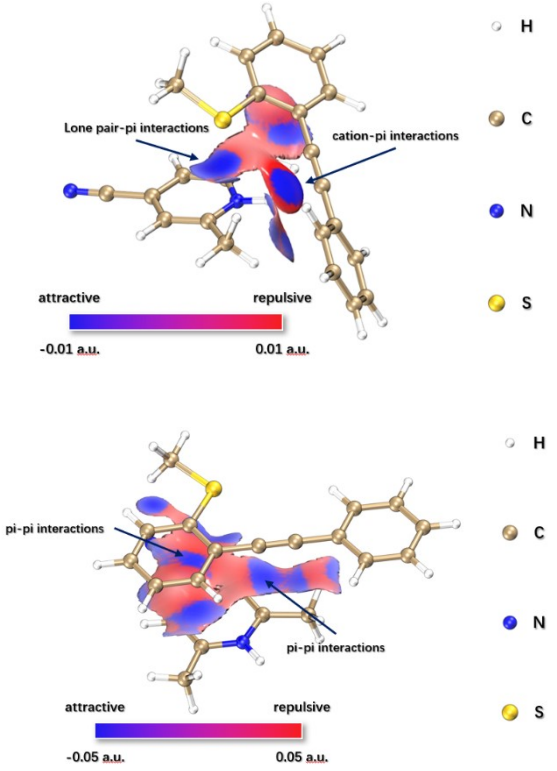


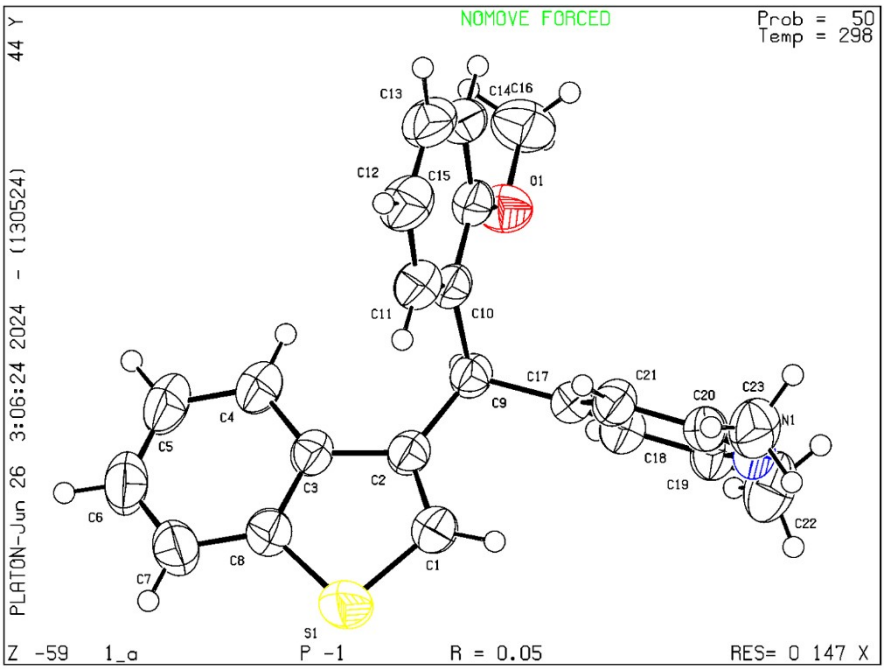
Figure S18. Weak interactions between **a** and **b**.

4. X-Ray Crystallographic Data of 18

Diffraction was performed on a Bruker D8 VENTURE area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for all complexes at 298(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvents were squeezed by using PLATON. All crystal structural pictures drawn by *OLEX* 2 program.

Single crystals of **18** were grown from slow evaporation of dichloromethane solution at room temperature. The data of the crystal structure **18** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number:

CCDC 2286087.



Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=9.1818(4) b=10.1332(4) c=11.5335(5)
alpha=106.943(1) beta=106.269(2) gamma=97.756(1)
Temperature: 298 K

	Calculated	Reported
Volume	957.60(7)	957.60(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C23 H21 N O S	C23 H21 N O S
Sum formula	C23 H21 N O S	C23 H21 N O S
Mr	359.47	359.47
Dx,g cm-3	1.247	1.247
Z	2	2
Mu (mm-1)	0.180	0.180
F000	380.0	380.0
F000'	380.38	
h,k,lmax	11,13,14	11,13,14
Nref	4384	4243
Tmin,Tmax	0.974,0.982	0.720,0.746
Tmin'	0.965	

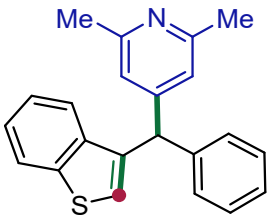
Correction method= # Reported T Limits: Tmin=0.720 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.968 Theta(max)= 27.468

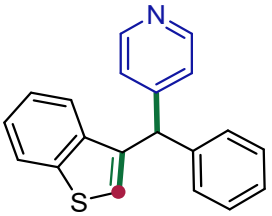
R(reflections)= 0.0465(3731) wR2(reflections)= 0.1289(4243)

S = 1.023 Npar= 238

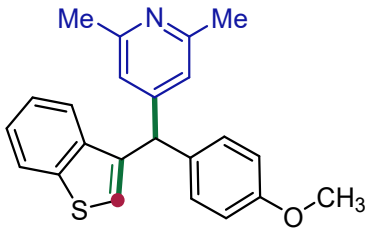
5. Characterization data for the products



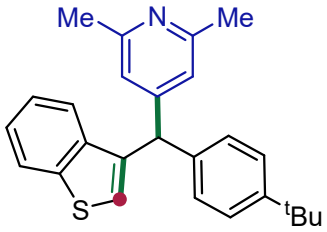
4-(benzo[b]thiophen-3-yl(phenyl)methyl)-2,6-dimethylpyridine (3). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 78% yield (51.3 mg), m.p. 112.0–113.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 3H), 7.27–7.23 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.78 (s, 2H), 6.74 (s, 1H), 5.62 (s, 1H), 2.46 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 152.4, 141.2, 140.8, 138.3, 137.5, 129.1, 128.8, 127.1, 125.5, 124.6, 124.2, 123.0, 122.5, 121.1, 50.8, 24.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{20}NS^+$ 330.1311; Found 330.1312.



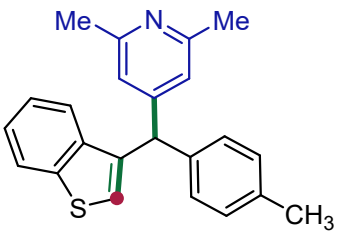
4-(benzo[b]thiophen-3-yl(phenyl)methyl)pyridine (4). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 66% yield (39.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.54 (s, 2H), 7.85 (d, *J* = 9.7 Hz, 1H), 7.42 (d, *J* = 9.7 Hz, 1H), 7.32 (t, *J* = 8.52 Hz, 3H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.24–7.23 (m, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 5.3 Hz, 2H), 6.74 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.0, 149.9, 140.9, 140.8, 138.2, 137.3, 129.2, 128.9, 127.4, 125.7, 124.7, 124.3, 123.1, 122.5, 50.9; HRMS (ESI) m/z: [M+H]+ Calcd For $C_{20}H_{16}NS^+$ 302.0998; Found 302.0998.



4-(benzo[b]thiophen-3-yl(4-methoxyphenyl)methyl)-2,6-dimethylpyridine (5). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 54% yield (38.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.26–7.23 (m, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.77 (s, 2H), 6.74 (s, 1H), 5.57 (s, 1H), 3.78 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.7, 158.0, 152.6, 140.8, 138.3, 138.0, 133.4, 130.1, 125.3, 124.6, 124.2, 123.0, 122.6, 120.9, 114.2, 55.3, 50.1, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NOS^+$ 360.1417; Found 360.1418.

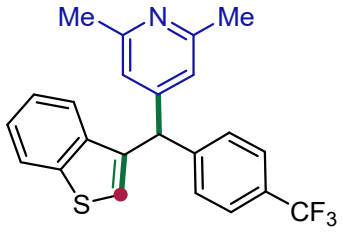


4-(benzo[b]thiophen-3-yl(4-(tert-butyl)phenyl)methyl)-2,6-dimethylpyridine (6). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 75% yield (57.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.32–7.29 (m, 3H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.78–6.76 (m, 3H), 5.59 (s, 1H), 2.45 (s, 6H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 152.4, 149.9, 140.8, 138.3, 138.2, 137.9, 128.7, 125.7, 125.4, 124.5, 124.1, 122.9, 122.6, 121.0, 50.4, 34.6, 31.5, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{26}H_{28}NS^+$ 386.1937; Found 386.1938.

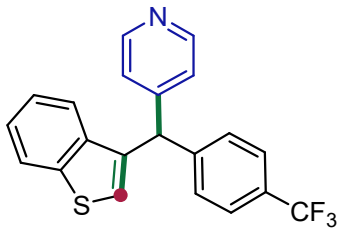


4-(benzo[b]thiophen-3-yl(p-tolyl)methyl)-2,6-dimethylpyridine (7). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 71%

yield (48.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.26–7.24 (m, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.79 (s, 2H), 6.75 (s, 1H), 5.59 (s, 1H), 2.47 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.9, 140.8, 138.3, 138.2, 137.7, 136.9, 129.5, 129.0, 125.4, 124.6, 124.2, 123.0, 122.6, 121.8, 121.1, 50.5, 24.5, 21.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1470.

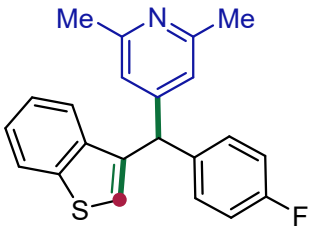


4-(benzo[b]thiophen-3-yl(4-(trifluoromethyl)phenyl)methyl-2,6-dimethylpyridine (8). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 58% yield (46.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28–7.6 (m, 3H), 6.77 (s, 2H), 6.75 (s, 1H), 5.69 (s, 1H), 2.49 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 151.6, 145.3, 140.8, 138.0, 136.5, 129.5, 125.87 (q, *J* = 2.9 Hz), 124.9, 124.4, 123.3, 123.1, 122.3, 121.0, 50.6, 24.5; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{19}F_3NS^+$ 398.1185; Found 398.1186.

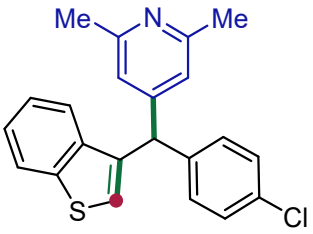


4-(benzo[b]thiophen-3-yl(4-(trifluoromethyl)phenyl)methyl)pyridine (9). Yellow oil; 54% yield (39.9 mg). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 5.5 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29–7.26 (m, 3H), 7.09 (d, *J* = 5.5 Hz, 2H), 6.74 (s, 1H), 5.78 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.8, 150.3, 144.5, 140.9, 137.9, 136.3, 129.8 (q, *J* = 32.5 Hz), 129.5, 126.0, 125.9 (q, *J* = 3.9 Hz), 124.9, 124.5, 124.4, 124.1 (q, *J* = 270.8

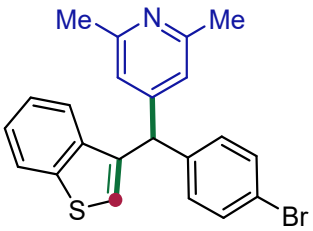
Hz), 123.2, 122.3, 50.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{15}F_3NS^+$ 370.0872; Found 370.0874.



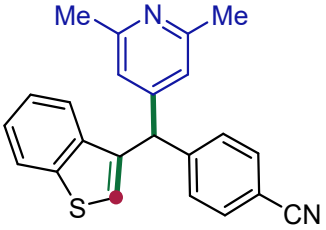
4-(benzo[b]thiophen-3-yl(4-fluorophenyl)methyl)-2,6-dimethylpyridine (10). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 77% yield (53.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.12–7.09 (m, 2H), 7.00 (t, J = 8.5 Hz, 2H), 6.75 (s, 2H), 6.73 (s, 1H), 5.61 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.7, 161.1, 158.2, 152.0, 140.8, 138.1, 137.4, 137.0 (d, J = 3.1 Hz), 130.6 (d, J = 8.2 Hz), 125.5, 124.7, 124.3, 123.0, 122.5, 120.9, 115.7 (d, J = 21.0 Hz), 50.0, 24.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –115.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}FNS^+$ 348.1217; Found 348.1217.



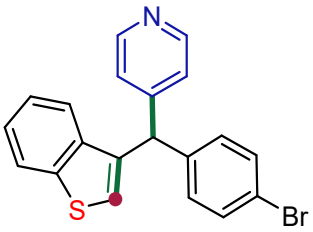
4-(benzo[b]thiophen-3-yl(4-chlorophenyl)methyl)-2,6-dimethylpyridine (11). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 69% yield (50.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29–7.25 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.75 (s, 2H), 6.74 (s, 1H), 6.60 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.2, 151.9, 140.8, 139.8, 138.1, 137.0, 133.1, 130.5, 129.0, 125.7, 124.7, 124.3, 123.1, 122.4, 120.9, 50.2, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}ClNS^+$ 364.0921; Found 364.0922.



4-(benzo[b]thiophen-3-yl(4-bromophenyl)methyl)-2,6-dimethylpyridine (12). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 68% yield (55.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27–7.25 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 2H), 6.74 (s, 1H), 5.58 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.2, 151.8, 140.8, 140.3, 138.1, 136.9, 132.0, 130.8, 125.7, 124.7, 124.3, 123.1, 122.4, 121.2, 120.9, 50.2, 24.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}BrNS^+$ 408.0416; Found 408.0417.

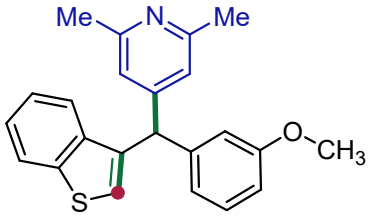


4-(benzo[b]thiophen-3-yl(2,6-dimethylpyridin-4-yl)methyl)benzonitrile (13). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 51% yield (36.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38–7.34 (m, 2H), 7.29–7.26 (m, 3H), 6.74 (s, 3H), 5.68 (s, 1H), 2.48 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.5, 150.9, 146.7, 140.8, 137.9, 136.0, 132.7, 130.0, 126.0, 124.9, 124.5, 123.2, 122.2, 120.9, 118.7, 111.3, 50.7, 24.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{19}N_2S^+$ 355.1263; Found 355.1263.

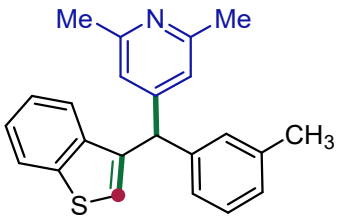


4-(benzo[b]thiophen-3-yl(4-bromophenyl)methyl)pyridine (14). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 52% yield

(38.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.54 (s, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27–7.25 (m, 1H), 7.09 (d, *J* = 4.6 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.73 (s, 1H), 5.68 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.5, 149.9, 140.8, 139.9, 137.9, 136.6, 132.1, 130.8, 125.9, 124.8, 124.44, 124.40, 123.1, 122.4, 121.4, 50.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}BrNS^+$ 380.0103; Found 380.0103.

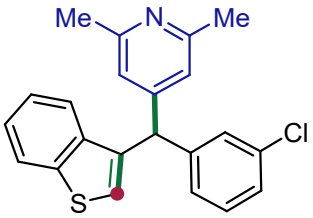


4-(benzo[b]thiophen-3-yl(3-methoxyphenyl)methyl)-2,6-dimethylpyridine (15). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 59% yield (42.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.26–7.22 (m, 2H), 6.81–6.78 (m, 4H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 5.59 (s, 1H), 3.74 (s, 3H), 2.46 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 158.0, 152.1, 142.9, 140.8, 138.3, 137.4, 129.8, 125.5, 124.6, 124.2, 123.0, 122.5, 121.6, 121.0, 115.4, 112.0, 55.3, 50.8, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NOS^+$ 360.1417; Found 360.1418.

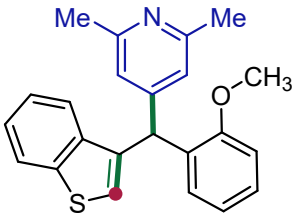


4-(benzo[b]thiophen-3-yl(m-tolyl)methyl)-2,6-dimethylpyridine (16). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 80% yield (54.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 2H), 6.75 (s, 1H), 5.58 (s, 1H), 2.45 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0,

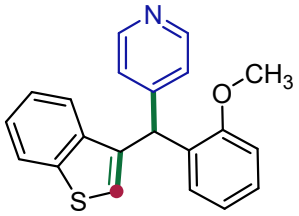
152.4, 141.2, 140.7, 138.4, 138.3, 137.6, 129.8, 128.6, 128.0, 126.2, 125.5, 124.5, 124.2, 122.9, 122.5, 121.0, 50.8, 24.5, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1469.



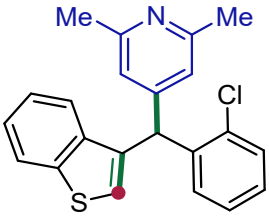
4-(benzo[b]thiophen-3-yl(3-chlorophenyl)methyl)-2,6-dimethylpyridine (17). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 70% yield (50.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34–7.32 (m, 1H), 7.27–7.24 (m, 3H), 7.15 (s, 1H), 7.03 (d, *J* = 5.7 Hz, 1H), 6.76 (s, 3H), 5.59 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 151.4, 143.4, 140.8, 138.1, 136.8, 134.8, 130.1, 129.2, 127.5, 127.3, 125.8, 124.7, 124.3, 123.1, 122.4, 120.9, 50.5, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}ClNS^+$ 364.0921; Found 364.0923.



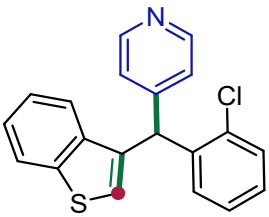
4-(benzo[b]thiophen-3-yl(2-methoxyphenyl)methyl)-2,6-dimethylpyridine (18). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), White solid; 58% yield (41.7 mg), m.p. 151.2–152.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27–7.24 (m, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.86–6.84 (m, 2H), 6.78 (s, 2H), 6.71 (s, 1H), 6.05 (s, 1H), 3.77 (s, 3H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.7, 156.9, 152.9, 140.7, 138.5, 137.7, 129.9, 129.6, 128.4, 124.9, 124.5, 124.1, 122.9, 122.6, 121.2, 120.7, 110.8, 55.8, 43.4, 24.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NOS^+$ 360.1417; Found 360.1418.



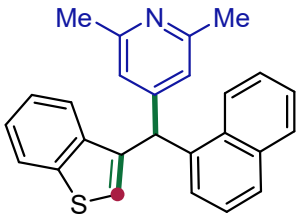
4-(benzo[b]thiophen-3-yl(2-methoxyphenyl)methyl)pyridine (19). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 52% yield (34.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 5.5 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.27–7.23 (m, 2H), 7.10 (d, *J* = 5.6 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 4.4 Hz, 2H), 6.71 (s, 1H), 6.12 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.9, 152.3, 149.7, 140.8, 138.4, 137.3, 129.8, 129.3, 128.6, 125.1, 124.58, 124.55, 124.2, 123.0, 122.6, 120.7, 110.9, 55.7, 43.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NOS^+$ 360.1417; Found 360.1418.



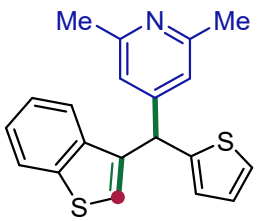
4-(benzo[b]thiophen-3-yl(2-chlorophenyl)methyl)-2,6-dimethylpyridine (20). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 51% yield (37.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27–7.25 (m, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.77 (s, 2H), 6.71 (s, 1H), 6.07 (s, 1H), 2.48 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.1, 151.0, 140.7, 138.7, 138.1, 136.6, 134.4, 130.5, 130.0, 128.6, 127.1, 125.6, 124.7, 124.4, 123.0, 122.4, 121.2, 47.3, 24.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}ClNS^+$ 364.0921; Found 364.0921.



4-(benzo[b]thiophen-3-yl(2-chlorophenyl)methyl)pyridine (21). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 50% yield (33.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (s, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 4.4 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.16 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.9, 140.8, 138.4, 138.0, 136.3, 134.4, 130.5, 130.1, 128.8, 127.2, 125.7, 125.4, 124.8, 124.7, 124.4, 123.1, 122.3, 47.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}ClNS^+$ 336.0608; Found 336.0606.

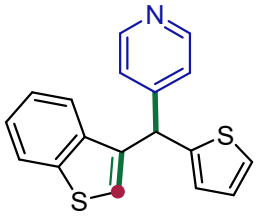


4-(benzo[b]thiophen-3-yl(naphthalen-1-yl)methyl)-2,6-dimethylpyridine (22). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 53% yield (40.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1H), 7.83–7.81 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.72–7.71 (m, 1H), 7.52 (s, 1H), 7.47–7.45 (m, 3H), 7.32–7.31 (m, 2H), 7.24–7.22 (m, 1H), 6.82 (s, 2H), 6.78 (s, 1H), 5.79 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.1, 152.2, 140.8, 138.8, 138.4, 137.4, 133.5, 132.6, 128.5, 128.0, 127.8, 127.7, 127.5, 126.4, 126.1, 125.7, 124.6, 124.3, 123.0, 122.6, 121.2, 50.9, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{26}H_{22}NS^+$ 380.1467; Found 380.1466.

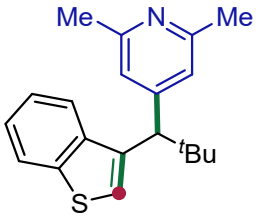


4-(benzo[b]thiophen-3-yl(thiophen-2-yl)methyl)-2,6-dimethylpyridine (23). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 49% yield (32.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* =

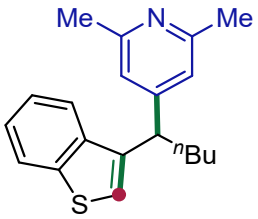
5.1 Hz, 1H), 6.96–6.95 (m, 2H), 6.87 (s, 2H), 6.76 (d, J = 3.1 Hz, 1H), 5.85 (s, 1H), 2.49 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.2, 152.1, 144.6, 140.8, 138.0, 137.3, 127.0, 126.7, 125.3, 125.1, 124.7, 124.3, 123.1, 122.3, 120.5, 45.8, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{17}NS_2^+$ 336.0875; Found 336.0874.



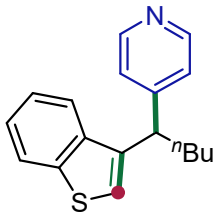
4-(benzo[b]thiophen-3-yl(thiophen-2-yl)methyl)pyridine (24). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 45% yield (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (d, J = 5.5 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.26–7.25 (m, 1H), 7.20 (d, J = 5.5 Hz, 2H), 6.97–6.95 (m, 2H), 6.77 (d, J = 3.1 Hz, 1H), 5.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.8, 150.0, 144.1, 140.8, 137.8, 137.0, 127.1, 126.9, 125.5, 125.4, 124.8, 124.4, 123.9, 123.1, 122.2, 45.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{14}NS_2^+$ 308.0562; Found 308.0564.



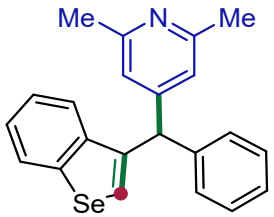
4-(1-(benzo[b]thiophen-3-yl)-2,2-dimethylpropyl)-2,6-dimethylpyridine (25). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 67% yield (41.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.35–7.29 (m, 2H), 6.97 (s, 2H), 4.18 (s, 1H), 2.48 (s, 6H), 1.09 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.1, 151.1, 140.1, 139.4, 135.9, 124.4, 124.0, 122.8, 122.1, 122.0, 121.8, 55.1, 35.3, 29.1, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{24}NS^+$ 310.1624; Found 310.1624.



4-(1-(benzo[b]thiophen-3-yl)pentyl)-2,6-dimethylpyridine (26). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 69% yield (42.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.2 Hz, 1H), 7.60–7.58 (m, 1H), 7.31–7.27 (m, 2H), 7.25 (s, 1H), 6.85 (s, 2H), 4.14 (t, *J* = 7.5 Hz, 1H), 2.47 (s, 6H), 2.19–2.14 (m, 1H), 2.03–1.97 (m, 1H), 1.37–1.26 (m, 4H), 0.90–0.87 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.8, 153.8, 140.6, 138.6, 138.2, 124.5, 124.1, 123.0, 122.0, 121.9, 120.0, 44.7, 35.4, 30.2, 24.6, 22.8, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{24}NS^+$ 310.1624; Found 310.1624.

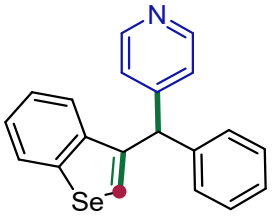


4-(1-(benzo[b]thiophen-3-yl)pentyl)pyridine (27). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 63% yield (35.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 5.0 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.31–7.25 (m, 3H), 7.18 (d, *J* = 5.2 Hz, 2H), 4.23 (t, *J* = 7.4 Hz, 1H), 2.24–2.18 (m, 1H), 2.07–2.01 (m, 1H), 1.38–1.36 (m, 2H), 1.33–1.26 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.3, 149.9, 140.7, 138.4, 137.8, 124.6, 124.1, 123.4, 123.0, 122.1, 122.0, 44.8, 35.2, 30.1, 22.8, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{20}NS^+$ 282.1311; Found 282.1312.

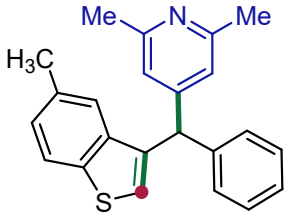


4-(benzo[b]selenophen-3-yl(phenyl)methyl)-2,6-dimethylpyridine (28). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 40%

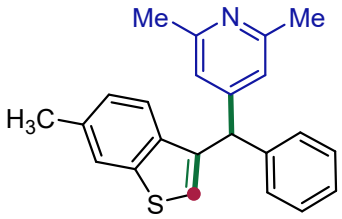
yield (30.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91–7.90 (m, 1H), 7.46–7.44 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.27–7.25 (m, 4H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.78 (s, 2H), 5.59 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 152.4, 141.9, 141.1, 140.6, 140.3, 129.2, 128.8, 127.9, 127.2, 126.2, 124.8, 124.6, 124.4, 121.2, 52.3, 24.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{20}NSe^+$ 378.0755; Found 378.0755.



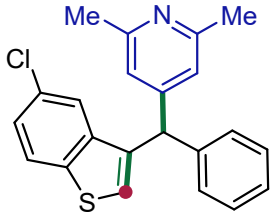
4-(benzo[b]selenophen-3-yl(phenyl)methyl)pyridine (29). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 30% yield (20.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 5.3 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.45–7.44 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29–7.25 (m, 4H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 5.5 Hz, 2H), 5.69 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.2, 149.7, 142.0, 140.7, 140.4, 140.0, 129.3, 128.9, 128.2, 127.4, 126.2, 124.9, 124.7, 124.6, 124.4, 52.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{16}NSe^+$ 350.0442; Found 350.0441.



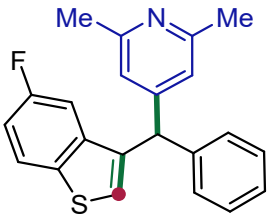
2,6-dimethyl-4-((5-methylbenzo[b]thiophen-3-yl)(phenyl)methyl)pyridine (30). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 71% yield (48.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 3H), 6.77 (s, 2H), 6.71 (s, 1H), 5.60 (s, 1H), 2.46 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 152.4, 141.4, 138.6, 137.9, 137.1, 134.0, 129.1, 128.8, 127.1, 126.4, 125.7, 122.6, 122.3, 121.0, 50.7, 24.5, 21.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1467.



2,6-dimethyl-4-((6-methylbenzo[b]thiophen-3-yl)(phenyl)methyl)pyridine (31). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 56% yield (38.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 3H), 7.27–7.24 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.78 (s, 2H), 6.64 (s, 1H), 5.59 (s, 1H), 2.46 (s, 6H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 152.4, 141.4, 141.1, 137.3, 136.2, 134.6, 129.1, 128.8, 127.1, 126.0, 124.4, 122.8, 122.2, 121.0, 50.9, 24.6, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1468.

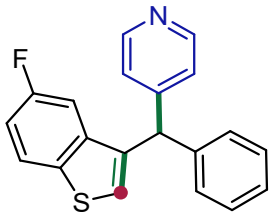


4-((5-chlorobenzo[b]thiophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (32). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 50% yield (36.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.6 Hz, 1H), 7.40 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29–7.26 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.81 (s, 1H), 6.75 (s, 2H), 5.56 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.2, 151.9, 140.9, 139.6, 138.9, 137.1, 130.7, 129.1, 128.9, 127.43, 127.38, 125.2, 124.0, 122.1, 120.9, 50.6, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}ClNS^+$ 364.0921; Found 364.0921.

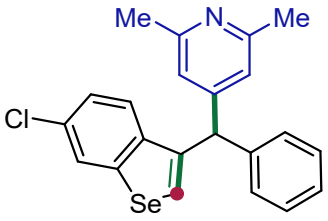


4-((5-fluorobenzo[b]thiophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (33). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow

oil; 52% yield (36.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78–7.76 (m, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29–7.27 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.09–7.06 (m, 2H), 6.83 (s, 1H), 6.77 (s, 2H), 5.53 (s, 1H), 2.47 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.6, 160.0, 158.2, 151.9, 140.8, 139.5 (d, *J* = 8.8 Hz), 137.4 (d, *J* = 4.3 Hz), 136.1, 129.1, 128.9, 127.9, 127.4, 124.1 (d, *J* = 9.1 Hz), 121.8, 120.9, 113.5 (d, *J* = 25.2 Hz), 108.3 (d, *J* = 23.4 Hz), 50.9, 24.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –118.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}FNS^+$ 348.1217; Found 348.1218.

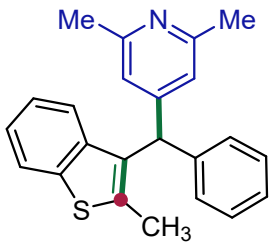


4-((5-fluorobenzo[b]thiophen-3-yl)(phenyl)methyl)pyridine (34). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 48% yield (30.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.6 Hz, 2H), 7.78–7.76 (m, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.30–7.27 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.10–7.06 (m, 4H), 6.83 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.8 (d, *J* = 240.6 Hz), 151.4, 150.1, 140.5, 139.4 (d, *J* = 8.9 Hz), 137.1 (d, *J* = 4.3 Hz), 136.1, 129.1 (d, *J* = 8.8 Hz), 128.0, 127.5, 124.4, 124.2 (d, *J* = 9.4 Hz), 113.6 (d, *J* = 25.0 Hz), 108.2 (d, *J* = 23.0 Hz), 50.8; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –117.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}FNS^+$ 320.0904; Found 320.0902.

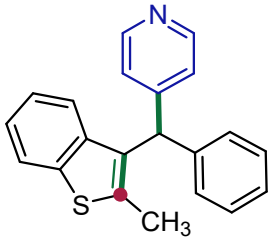


4-((6-chlorobenzo[b]selenophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (35). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 43% yield (35.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.39–7.38 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.31–7.28 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.76 (s, 2H), 5.54 (s, 1H), 2.49 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 142.4, 140.6, 140.5, 139.6, 129.9, 129.4, 129.1, 129.0, 127.9, 127.5, 127.4,

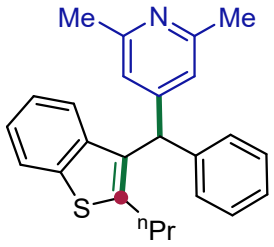
127.1, 121.2, 119.0, 52.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{19}ClNSe^+$ 412.0366; Found 412.0363.



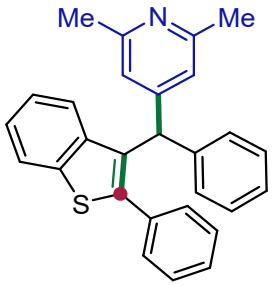
2,6-dimethyl-4-((2-methylbenzo[b]thiophen-3-yl)(phenyl)methyl)pyridine (36). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 66% yield (45.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.9 Hz, 1H), 7.31–7.28 (m, 3H), 7.25–7.21 (m, 2H), 7.17–7.14 (m, 3H), 6.76 (s, 2H), 5.81 (s, 1H), 2.45 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.9, 152.1, 140.5, 140.2, 138.2, 137.6, 131.0, 129.2, 128.7, 127.0, 124.0, 123.6, 122.5, 122.1, 121.1, 48.9, 24.5, 15.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1468.



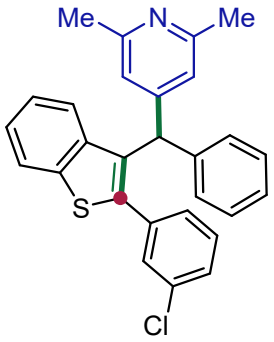
4-((2-methylbenzo[b]thiophen-3-yl)(phenyl)methyl)pyridine (37). Purified by flash column chromatography (petroleum ether/AcOEt = 6:1, v/v), Yellow oil; 55% yield (34.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 3.8 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.28–7.21 (m, 4H), 7.17–7.14 (m, 3H), 7.11 (d, *J* = 5.0 Hz, 2H), 5.90 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9, 149.7, 140.1, 139.9, 138.3, 137.9, 130.8, 129.1, 128.9, 127.2, 124.5, 124.1, 123.7, 122.5, 122.3, 48.9, 15.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{18}NS^+$ 316.1154; Found 316.1156.



2,6-dimethyl-4-(phenyl(2-propylbenzo[b]thiophen-3-yl)methyl)pyridine (38). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 54% yield (40.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.26–7.20 (m, 4H), 7.15–7.11 (m, 3H), 6.78 (s, 2H), 5.83 (s, 1H), 2.71–2.69 (m, 2H), 2.46 (s, 6H), 1.62–1.56 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.8, 144.0, 140.7, 139.9, 138.5, 130.6, 129.2, 128.7, 127.0, 124.0, 123.5, 123.0, 122.3, 121.1, 48.8, 31.4, 24.7, 24.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{25}H_{26}NS^+$ 372.1780; Found 372.1781.

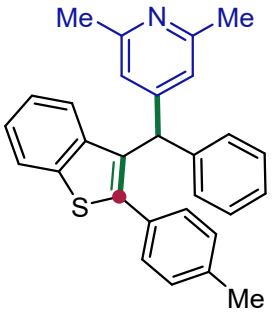


2,6-dimethyl-4-(phenyl(2-phenylbenzo[b]thiophen-3-yl)methyl)pyridine (39). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 70% yield (56.7 mg), m.p. 168.2–169.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.371–7.365 (m, 5H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.28–7.23 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.14–7.12 (m, 2H), 6.71 (s, 2H), 5.81 (s, 1H), 2.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.8, 142.0, 140.9, 139.5, 139.3, 134.2, 131.6, 130.0, 129.2, 129.1, 128.8, 128.7, 128.6, 126.9, 124.7, 124.2, 122.4, 121.1, 121.0, 49.1, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{24}NS^+$ 406.1624; Found 406.1627.

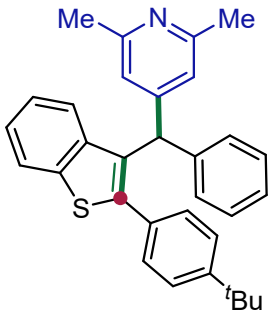


4-((2-(3-chlorophenyl)benzo[b]thiophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (40). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 72% yield (63.2 mg), m.p. 149.2–151.1 °C. ^{1}H

NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.34–7.32 (m, 2H), 7.30–7.26 (m, 4H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.70 (s, 2H), 5.76 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.9, 152.0, 140.7, 140.1, 139.5, 139.3, 136.0, 134.5, 132.3, 130.1, 129.7, 129.1, 128.74, 128.68, 128.2, 127.0, 124.8, 124.5, 124.4, 122.4, 121.0, 49.3, 24.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{23}ClNS^+$ 440.1234; Found 440.1234.

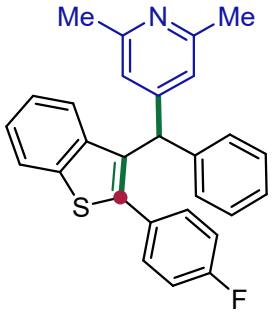


2,6-dimethyl-4-(phenyl(2-(p-tolyl)benzo[b]thiophen-3-yl)methyl)pyridine (41). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 62% yield (52.0 mg), m.p. 175.6–176.9 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.28–7.21 (m, 7H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.13–7.12 (m, 3H), 6.71 (s, 2H), 5.81 (s, 1H), 2.41 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.7, 152.5, 142.2, 141.0, 139.5, 139.4, 138.6, 131.30, 131.29, 129.9, 129.9, 129.4, 129.2, 128.6, 126.8, 124.6, 124.1, 124.0, 122.3, 121.1, 49.1, 24.5, 21.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{29}H_{26}NS^+$ 420.1780; Found 420.1783.

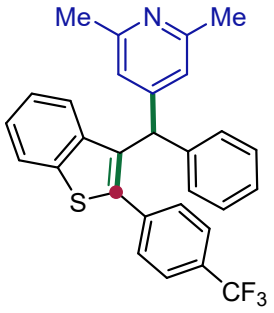


4-((2-(4-(tert-butyl)phenyl)benzo[b]thiophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (42). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 69% yield (63.6 mg), m.p. 177.7–178.4 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.30–7.23 (m, 7H), 7.14–7.11 (m, 3H), 6.72 (s, 2H), 5.85 (s, 1H), 2.41 (s, 6H), 1.35 (s, 9H);

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.7, 152.4, 151.7, 142.2, 141.0, 139.5, 131.3, 131.2, 129.7, 129.3, 128.6, 126.8, 125.6, 124.7, 124.1, 124.0, 122.3, 121.1, 49.1, 34.9, 31.4, 24.6; HRMS (ESI) m/z: $[M+H]^+$ $C_{32}H_{32}NS^+$ 462.2250; Found 462.2251.

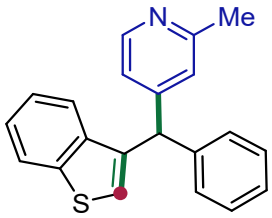


4-((2-(4-fluorophenyl)benzo[b]thiophen-3-yl)(phenyl)methyl)-2,6-dimethylpyridine (43). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow solid; 67% yield (56.7 mg), m.p. 178.9–180.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.32–7.22 (m, 7H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 6.69 (s, 2H), 5.74 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 162.1, 157.8, 152.2, 140.8 (d, *J* = 3.5 Hz), 139.4, 138.2, 131.9, 131.83, 131.78, 130.2 (d, *J* = 3.2 Hz), 129.2, 128.7, 127.0, 124.7, 124.3 (d, *J* = 3.5 Hz), 122.4, 121.0, 115.8, 115.6, 49.2, 24.5; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –112.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{23}FNS^+$ 424.1530; Found 424.1531.

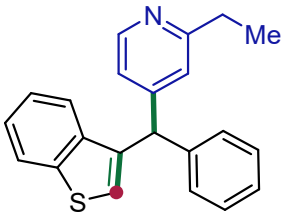


2,6-dimethyl-4-(phenyl(2-(4-(trifluoromethyl)phenyl)benzo[b]thiophen-3-yl)methyl)pyridine (44). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 70% yield (66.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.31–7.23 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.69 (s, 2H), 5.77 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.9, 152.0,

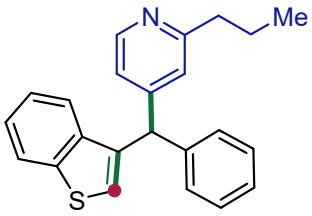
140.5, 140.0, 139.6, 139.2, 138.0, 132.6, 130.6 (q, J = 32.5 Hz), 130.4, 129.2, 128.8, 127.1, 125.5 (q, J = 3.8 Hz), 124.8, 124.7, 124.5, 124.1 (q, J = 270.8 Hz), 122.4, 121.0, 49.2, 24.5; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{28}H_{23}F_3NS^+$ 474.1498; Found 474.1498.



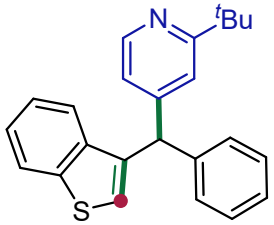
4-(benzo[b]thiophen-3-yl(phenyl)methyl)-2-methylpyridine (45). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 51% yield (32.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.40 (d, J = 5.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.3 Hz, 3H), 7.28–7.26 (m, 1H), 7.15 (d, J = 7.7 Hz, 2H), 6.98 (s, 1H), 6.91 (d, J = 5.0 Hz, 1H), 6.74 (s, 1H), 5.67 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.7, 152.3, 149.2, 141.1, 140.8, 138.2, 137.4, 129.1, 128.9, 127.3, 125.6, 124.7, 124.3, 124.0, 123.0, 122.5, 121.7, 50.9, 24.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{18}NS^+$ 316.1154; Found 316.1156.



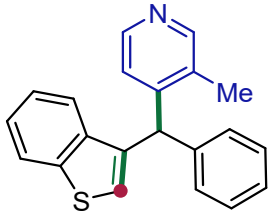
4-(benzo[b]thiophen-3-yl(phenyl)methyl)-2-ethylpyridine (46). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 53% yield (34.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, J = 6.7 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 3H), 7.28–7.23 (m, 2H), 7.16 (d, J = 7.6 Hz, 2H), 6.99 (s, 1H), 6.90 (d, J = 5.0 Hz, 1H), 6.74 (s, 1H), 5.69 (s, 1H), 2.77 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H),; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8, 152.3, 149.3, 141.1, 140.8, 138.3, 137.5, 129.1, 128.9, 127.3, 125.6, 124.6, 124.2, 123.0, 122.8, 122.5, 121.8, 51.0, 31.3, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{22}H_{20}NS^+$ 330.1311; Found 330.1310.



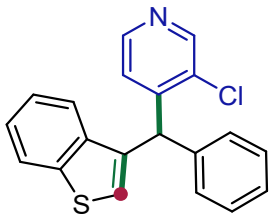
4-(benzo[b]thiophen-3-yl(phenyl)methyl)-2-propylpyridine (47). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 50% yield (34.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 5.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 3H), 7.28–7.23 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.97 (s, 1H), 6.90 (d, *J* = 5.1 Hz, 1H), 6.74 (s, 1H), 5.68 (s, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.73–1.67 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.6, 152.1, 149.4, 141.1, 140.8, 138.3, 137.5, 129.1, 128.9, 127.3, 125.5, 124.6, 124.2, 123.5, 123.0, 122.5, 121.8, 50.9, 40.3, 23.2, 13.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{23}H_{22}NS^+$ 344.1467; Found 344.1469.



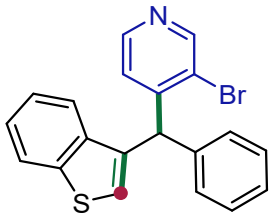
4-(benzo[b]thiophen-3-yl(phenyl)methyl)-2-(tert-butyl)pyridine (48). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 56% yield (40.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 5.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 3H), 7.25 (q, *J* = 7.5 Hz, 2H), 7.19 (s, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 4.7 Hz, 1H), 6.73 (s, 1H), 5.70 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.8, 151.8, 148.9, 141.3, 140.8, 138.3, 137.7, 129.1, 128.8, 127.2, 125.5, 124.6, 124.2, 123.0, 122.6, 121.4, 119.9, 51.2, 37.5, 30.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{24}H_{24}NS^+$ 358.1624; Found 358.1625



4-(benzo[b]thiophen-3-yl(phenyl)methyl)-3-methylpyridine (49). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 70% yield (44.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.31 (d, *J* = 5.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.25–7.23 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 6.76 (d, *J* = 5.0 Hz, 1H), 6.66 (s, 1H), 5.79 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.1, 149.9, 147.9, 140.8, 140.1, 138.1, 137.1, 132.0, 129.3, 128.9, 127.3, 125.7, 124.7, 124.3, 123.5, 123.1, 122.3, 47.6, 16.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{21}H_{18}NS^+$ 316.1154; Found 316.1156.

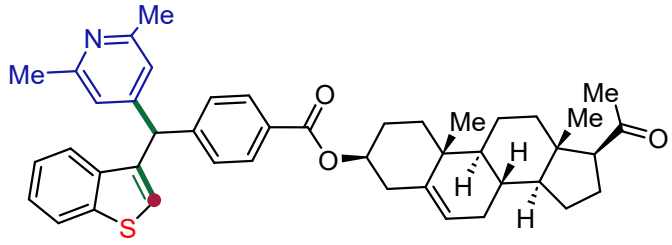


4-(benzo[b]thiophen-3-yl(phenyl)methyl)-3-chloropyridine (50). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 58% yield (38.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.76 (s, 1H), 8.38–8.37 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.40–7.38 (m, 1H), 7.34 (t, *J* = 6.8 Hz, 3H), 7.31–7.25 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 4.7 Hz, 1H), 6.71 (s, 1H), 6.05 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.4, 150.8, 148.5, 140.8, 139.3, 138.0, 136.4, 129.4, 129.0, 127.5, 125.9, 125.5, 124.8, 124.4, 123.1, 122.3, 50.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}ClNS^+$ 336.0608; Found 336.0608.

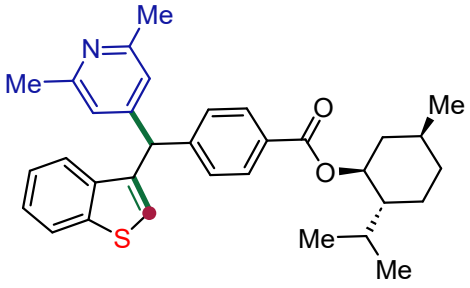


4-(benzo[b]thiophen-3-yl(phenyl)methyl)-3-bromopyridine (51). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 60% yield (45.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 8.34 (d, *J* = 5.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.34–7.32 (m, 3H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.27–7.24 (m, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 5.0 Hz, 1H), 6.72 (s, 1H),

6.08 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.8, 149.1, 148.0, 140.8, 139.3, 137.9, 136.3, 132.4, 129.3, 128.9, 127.5, 125.8, 125.0, 124.8, 124.4, 123.1, 122.3, 47.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{15}BrNS^+$ 380.0103; Found 380.0101.

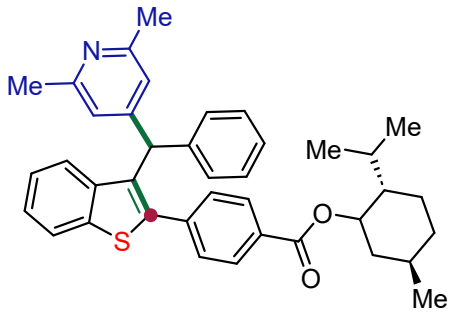


(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(benzo[b]thiophen-3-yl(2,6-dimethylpyridin-4-yl)methyl)benzoate (52). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 33% yield (44.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.27–7.22 (m, 3H), 6.77 (s, 2H), 6.75 (s, 1H), 5.68 (s, 1H), 5.42 (s, 1H), 4.88–4.83 (m, 1H), 2.54 (t, *J* = 8.9 Hz, 1H), 2.48 (s, 6H), 2.46 (s, 2H), 2.21–2.16 (m, 1H), 2.13 (s, 3H), 2.07–2.03 (m, 2H), 1.78–1.58 (m, 7H), 1.51–1.47 (m, 3H), 1.42 (s, 2H), 1.25–1.20 (m, 3H), 1.06 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 209.6, 165.8, 158.2, 146.2, 140.8, 139.7, 138.1, 136.7, 130.1, 129.9, 129.1, 125.7, 124.8, 124.3, 123.1, 122.7, 121.4, 121.0, 74.6, 63.8, 57.0, 50.8, 50.0, 44.1, 38.9, 38.3, 37.1, 36.8, 32.0, 31.9, 31.7, 28.0, 27.0, 24.6, 24.5, 23.0, 21.2, 19.5, 13.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{44}H_{50}NO_3S^+$ 672.3506; Found 672.3510.



(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(benzo[b]thiophen-3-yl(2,6-dimethylpyridin-4-yl)methyl)benzoate (53). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 48% yield (49.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H),

7.41 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.27–7.22 (m, 3H), 6.77–6.75 (m, 3H), 5.68 (s, 1H), 4.92 (td, J = 10.8 Hz, 4.1 Hz, 1H), 2.48 (s, 6H), 2.12 (d, J = 11.6 Hz, 1H), 1.97–1.94 (m, 1H), 1.72 (d, J = 11.4 Hz, 2H), 1.55–1.51 (m, 2H), 1.42 (s, 1H), 1.16–1.05 (m, 2H), 0.92–0.90 (m, 6H), 0.79 (t, J = 5.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.9, 158.2, 151.6, 146.2, 140.8, 138.1, 136.7, 130.1, 129.9, 129.1, 125.7, 124.8, 124.3, 123.1, 122.4, 121.0, 75.0, 50.8, 47.4, 41.1, 34.4, 31.6, 26.6, 24.5, 23.7, 22.2, 20.9, 16.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{33}H_{38}NO_2S^+$ 512.2618; Found 512.2621.



(2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(3-((2,6-dimethylpyridin-4-yl)(phenyl)methyl)benzo[b]thiophen-2-yl)benzoate (54). Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v), Yellow oil; 51% yield (59.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (d, J = 7.9 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 6.4 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.29–7.27 (m, 2H), 7.26–7.24 (m, 1H), 7.19 (s, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.3 Hz, 2H), 6.71 (d, J = 13.3 Hz, 2H), 5.80 (s, 1H), 4.97–4.94 (m, 1H), 2.58 (s, 2H), 2.42 (d, J = 5.7 Hz, 6H), 2.14 (d, J = 11.9 Hz, 1H), 1.97–1.96 (m, 1H), 1.74 (d, J = 11.6 Hz, 1H), 1.58–1.55 (m, 2H), 1.17–1.09 (m, 2H), 0.94–0.93 (m, 6H), 0.81 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.7, 159.5, 157.8, 140.7, 139.7, 139.2, 138.7, 132.3, 130.9, 130.0, 129.8, 129.2, 128.7, 127.0, 124.8, 124.5, 124.4, 122.4, 121.8, 121.1, 75.3, 49.2, 47.4, 41.1, 34.4, 31.6, 26.7, 24.6, 23.7, 22.2, 20.9, 16.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{39}H_{42}NO_2S^+$ 588.2931; Found 588.2932.

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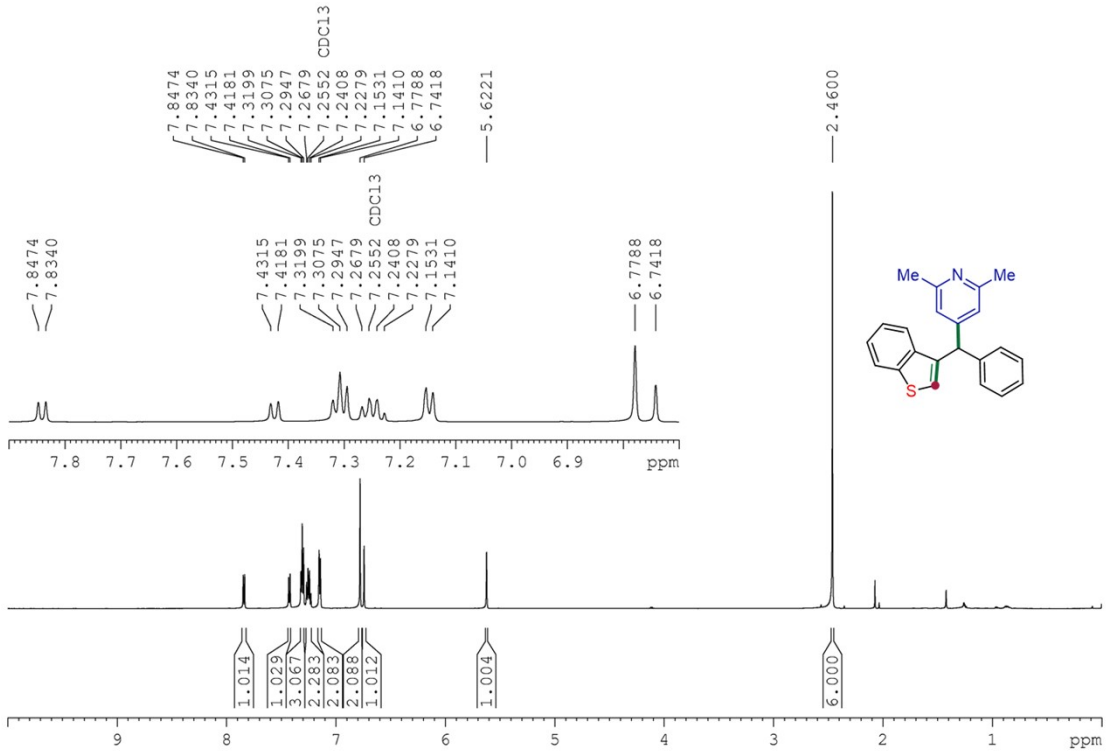
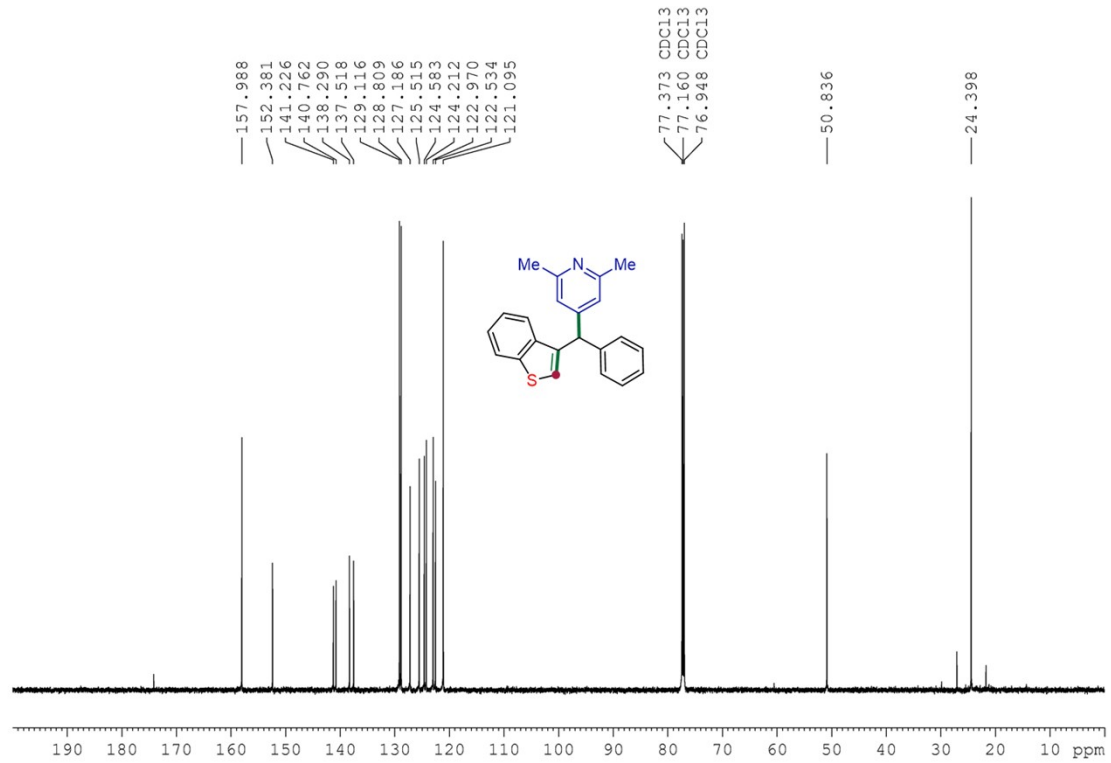
7. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectra of the products

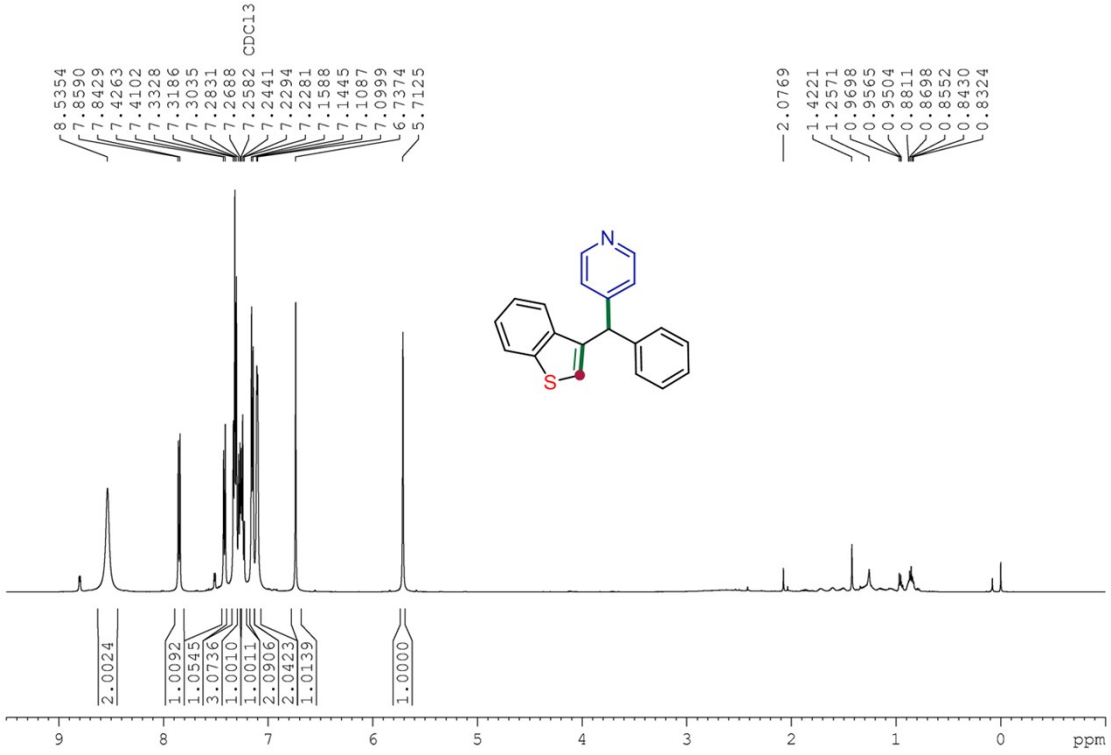
^{1}H NMR (600 MHz, $CDCl_3$) of **3**



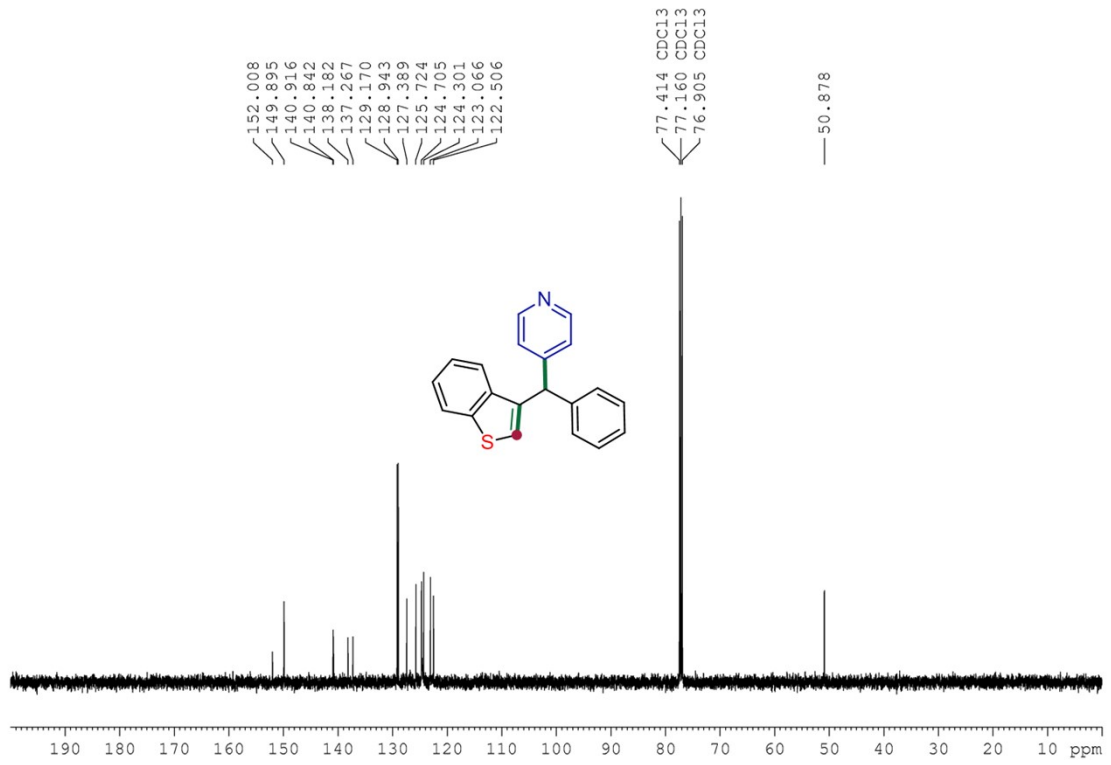
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3**



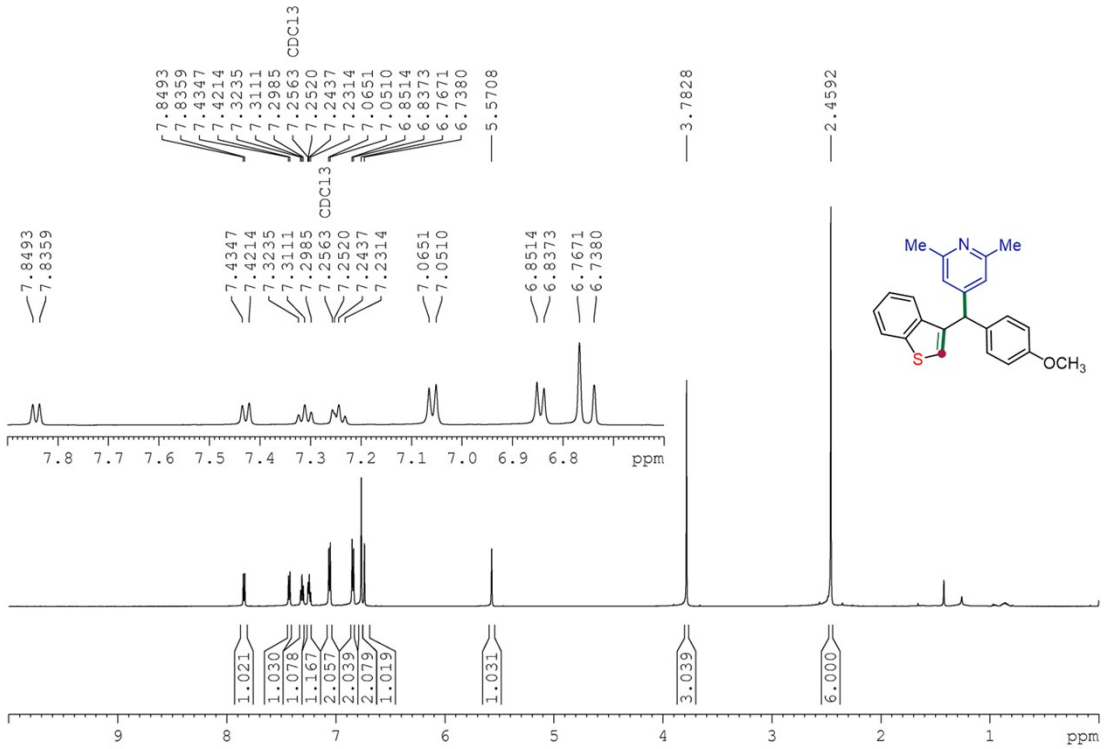
^{1}H NMR (600 MHz, $CDCl_3$) of **4**



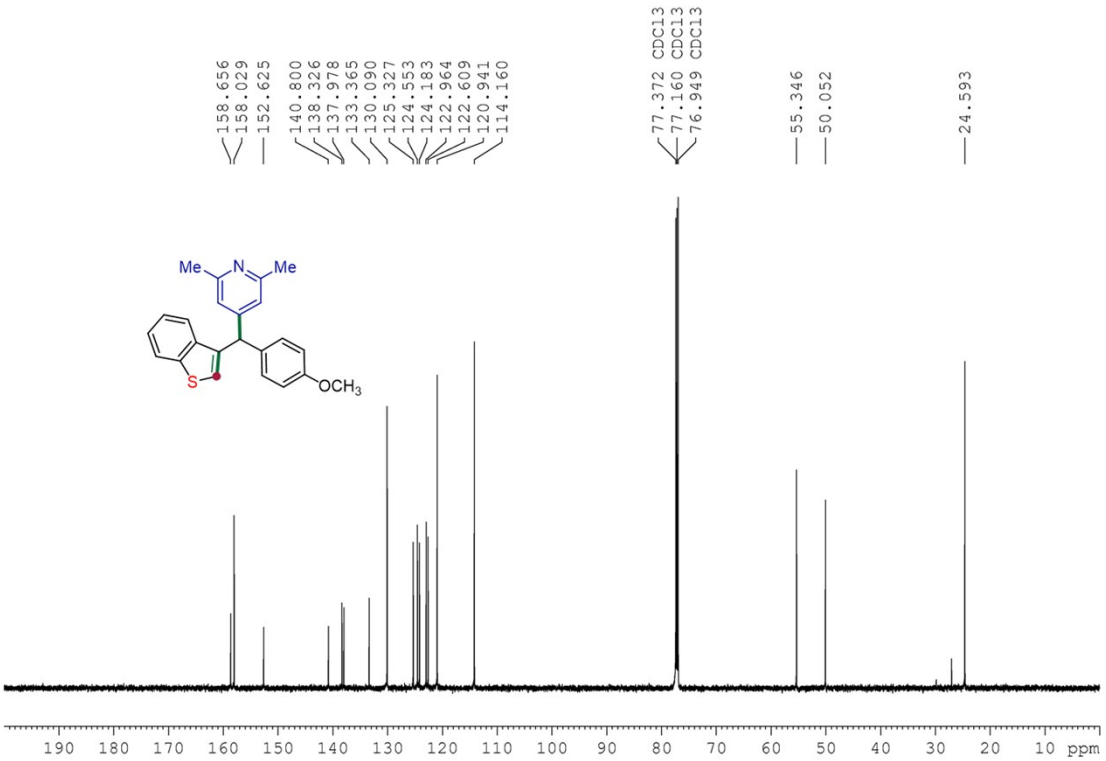
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **4**



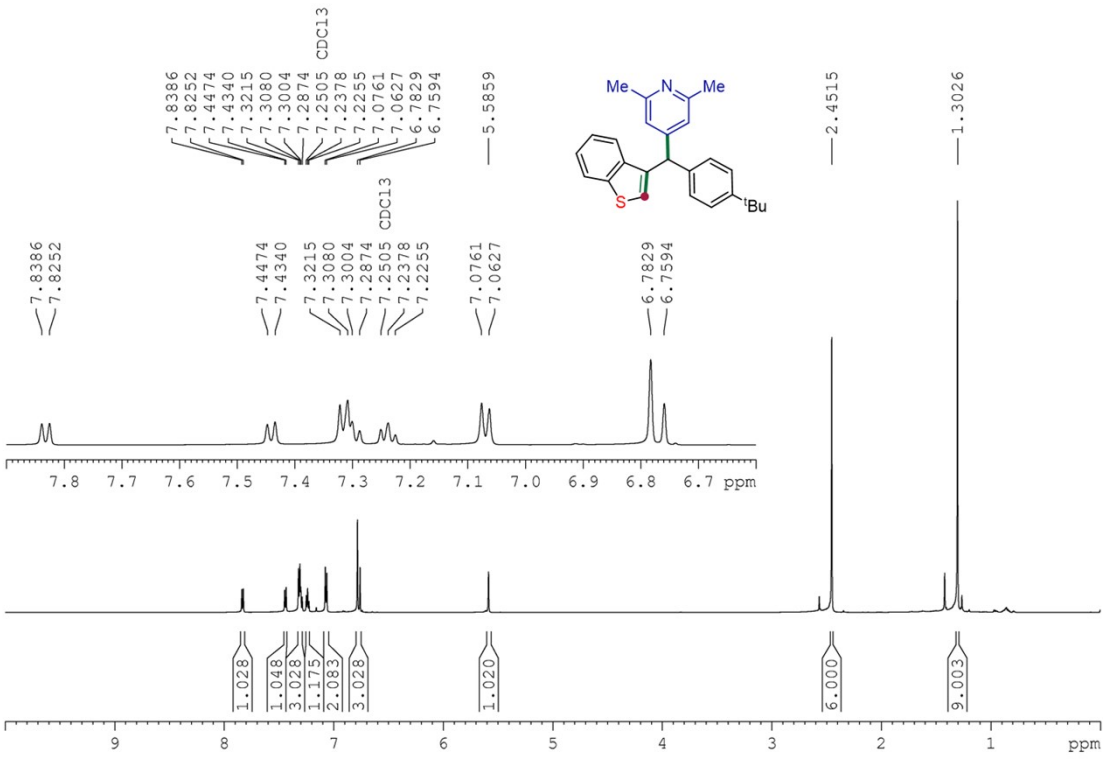
^{1}H NMR (600 MHz, $CDCl_3$) of **5**



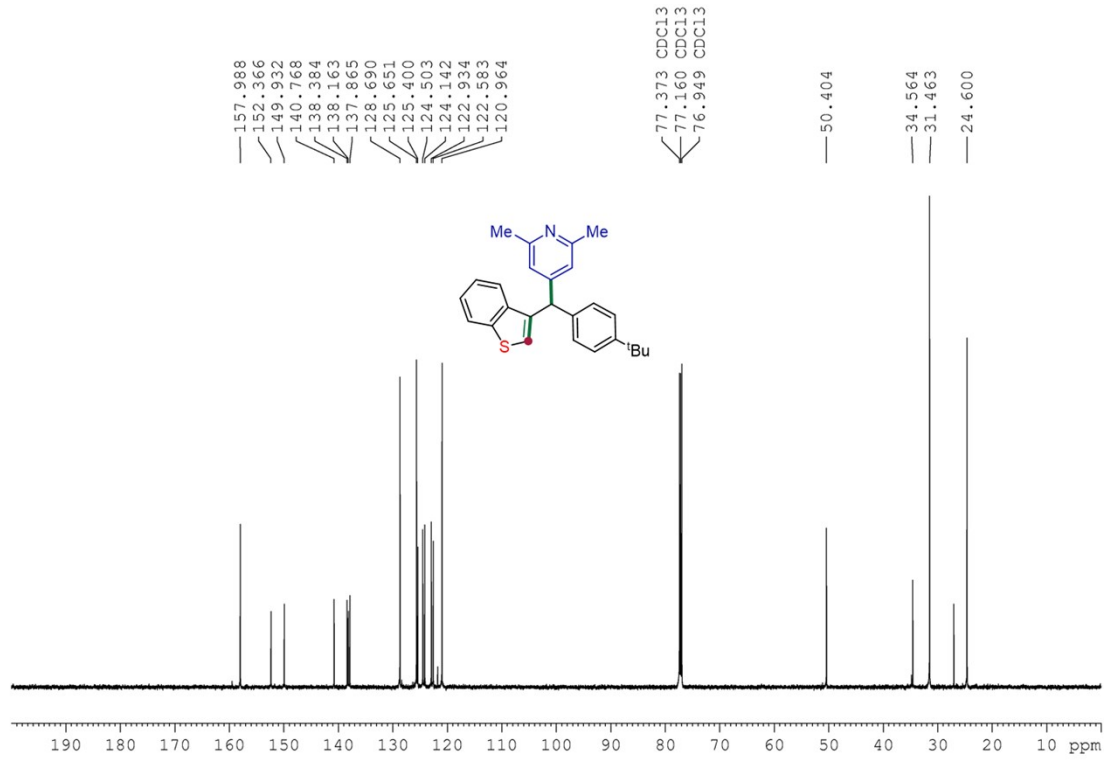
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **5**



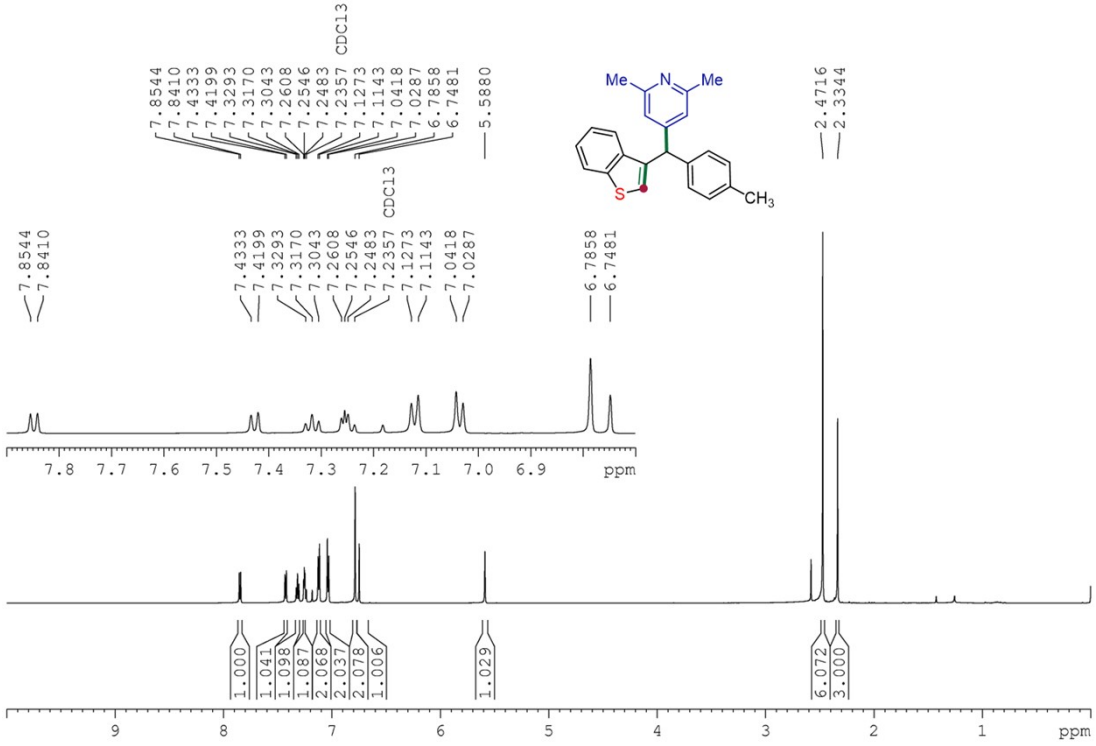
^{1}H NMR (600 MHz, $CDCl_3$) of **6**



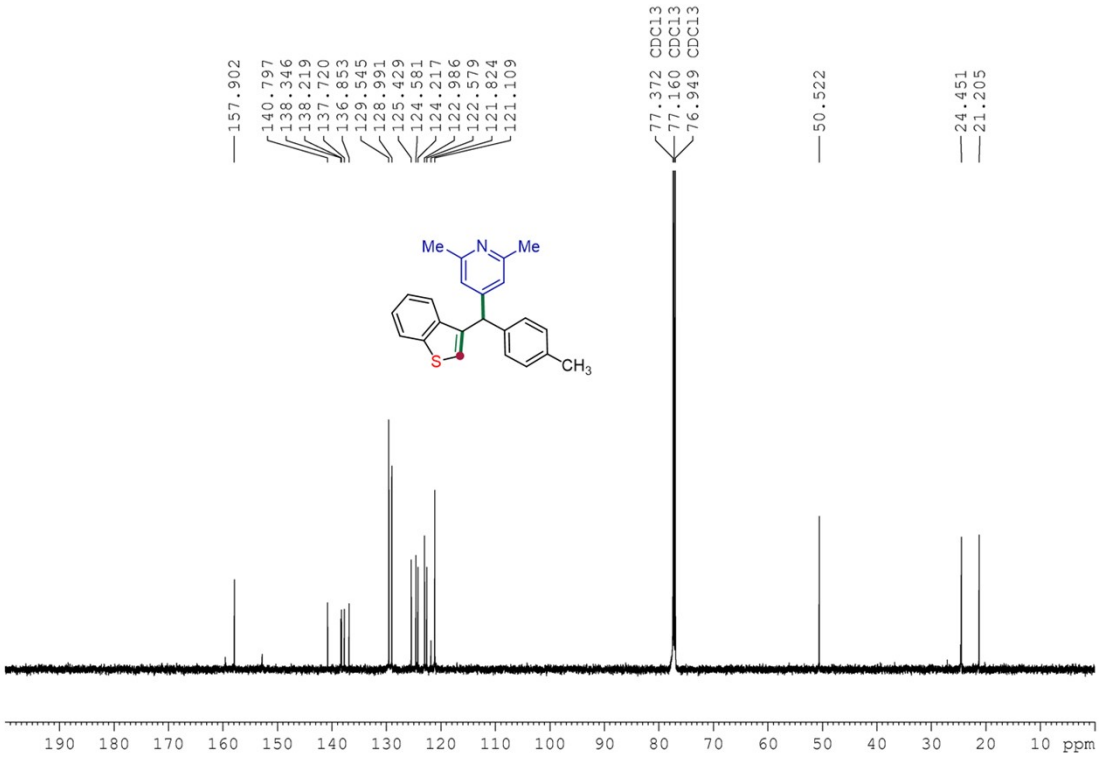
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **6**



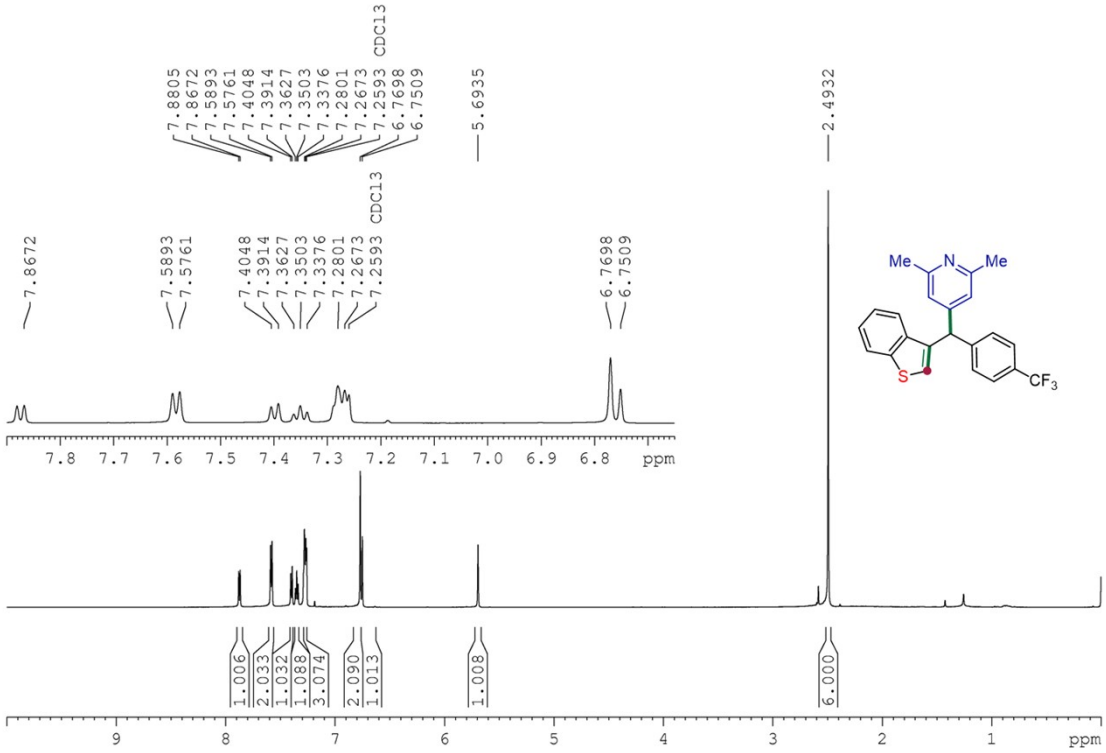
^{1}H NMR (600 MHz, $CDCl_3$) of **7**



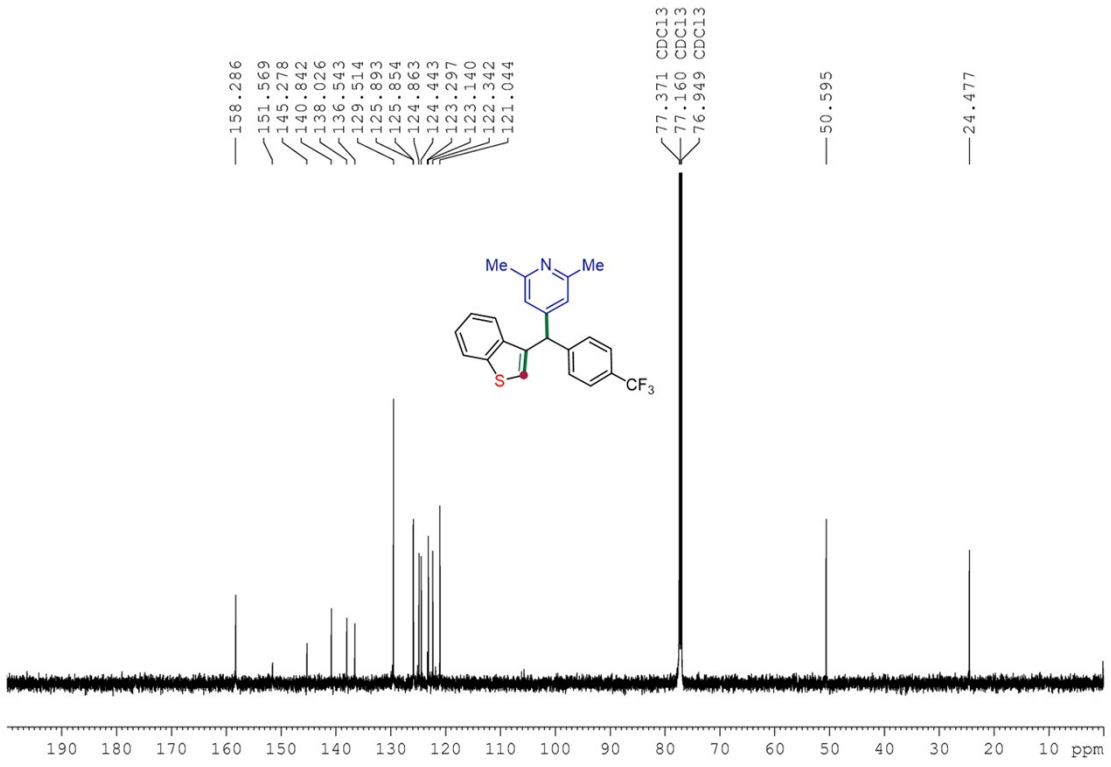
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **7**



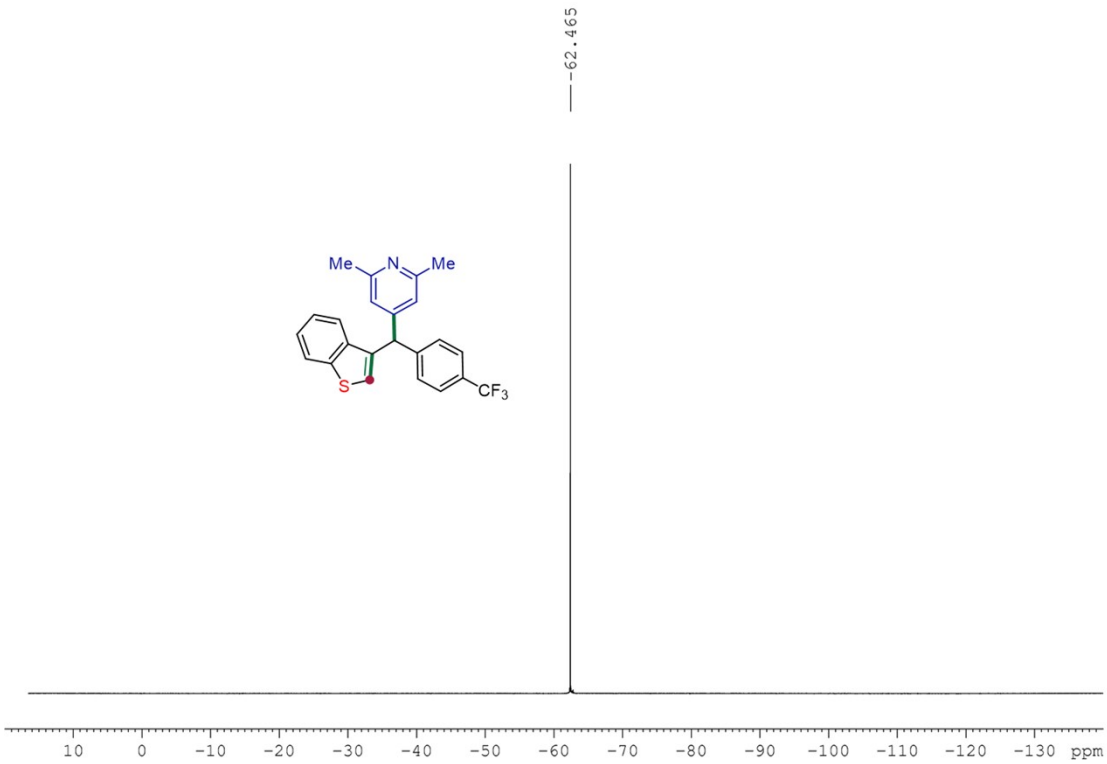
^{1}H NMR (600 MHz, $CDCl_3$) of **8**



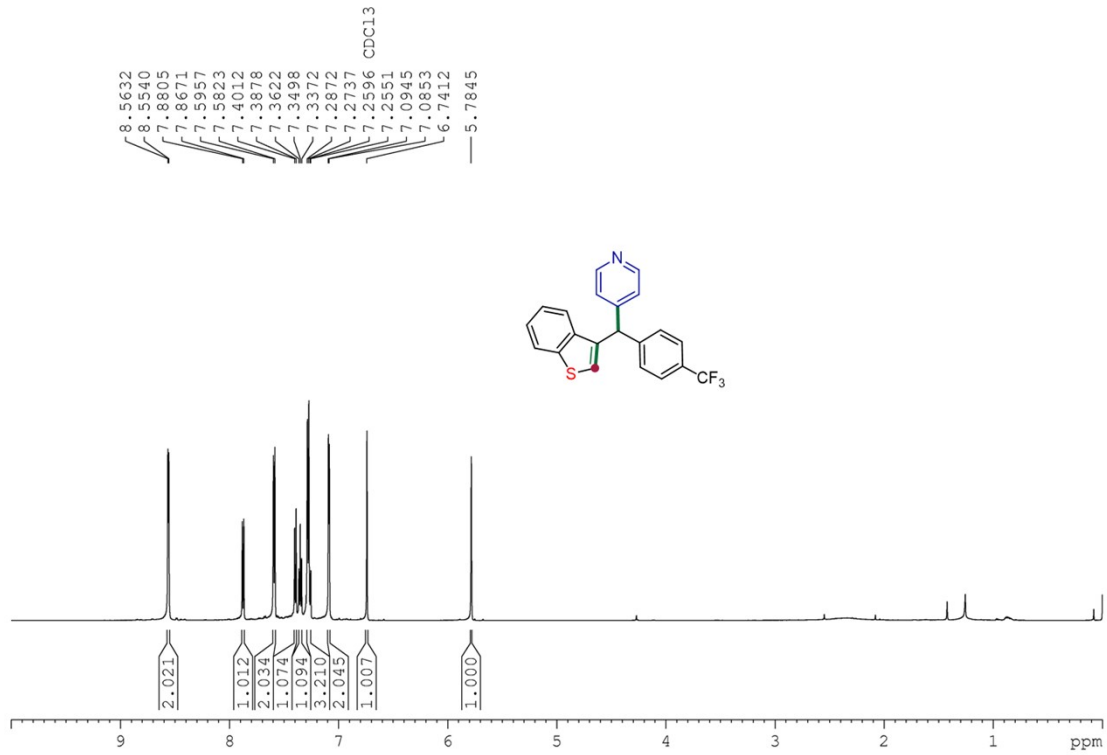
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **8**



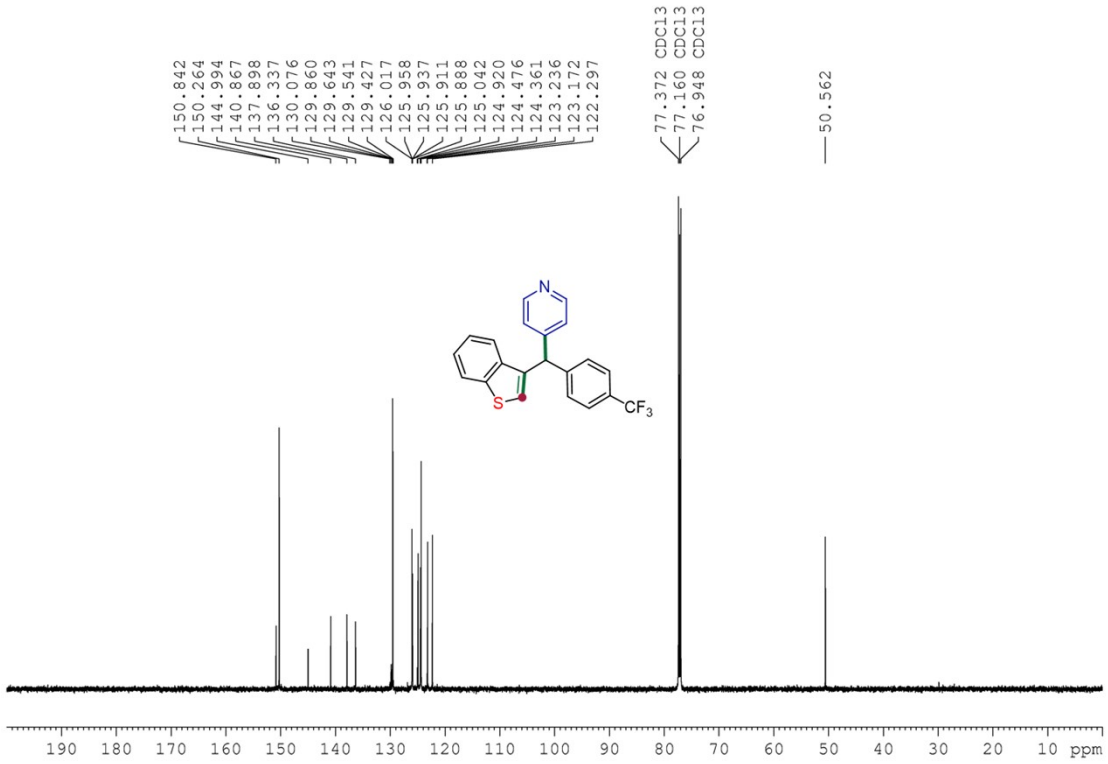
^{19}F NMR (564 MHz, $CDCl_3$) of **8**



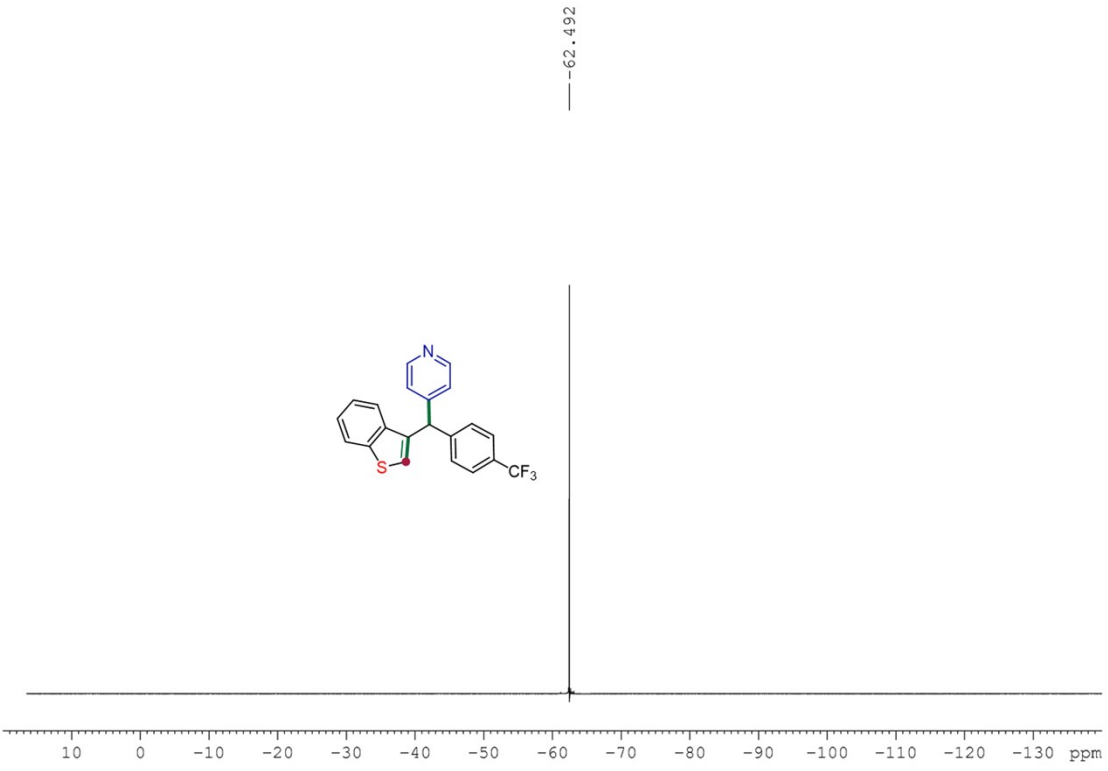
^{1}H NMR (600 MHz, $CDCl_3$) of **9**



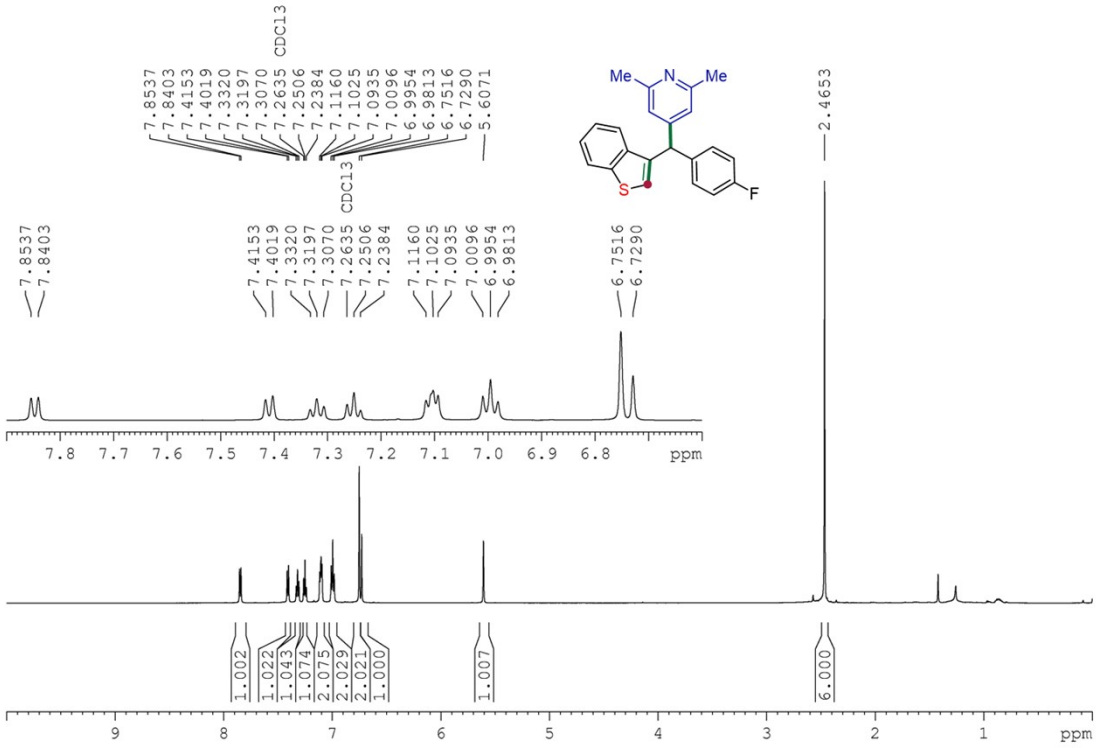
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **9**



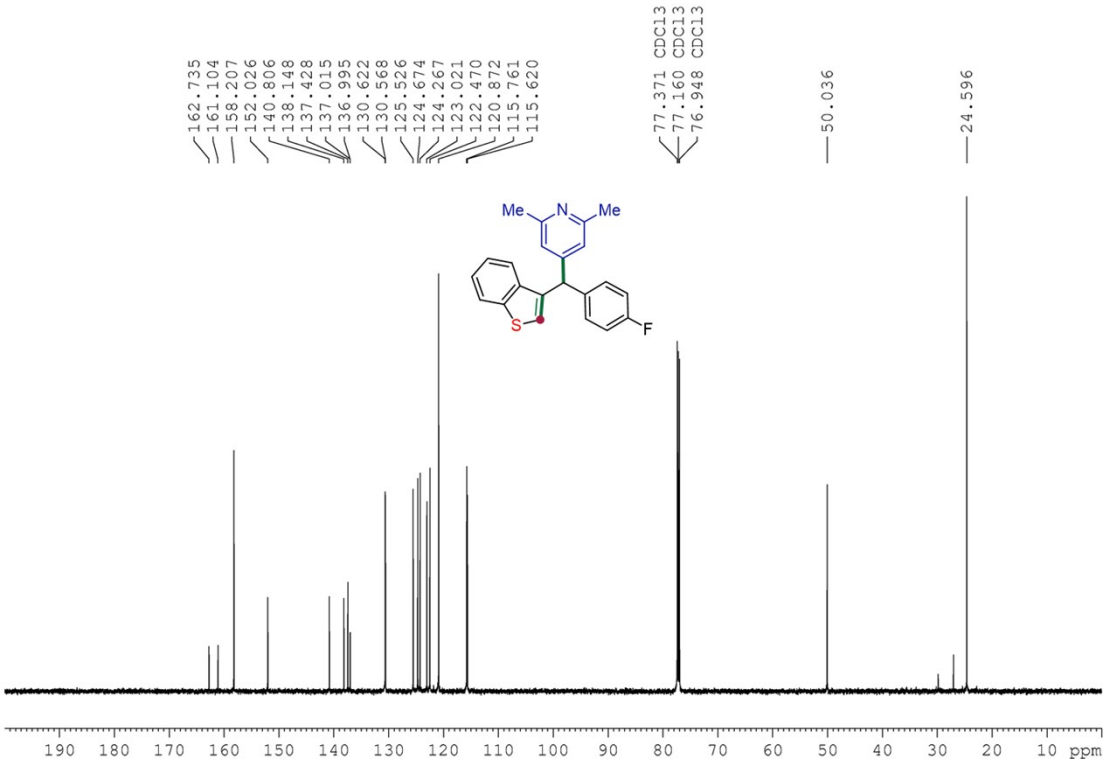
^{19}F NMR (564 MHz, $CDCl_3$) of **9**



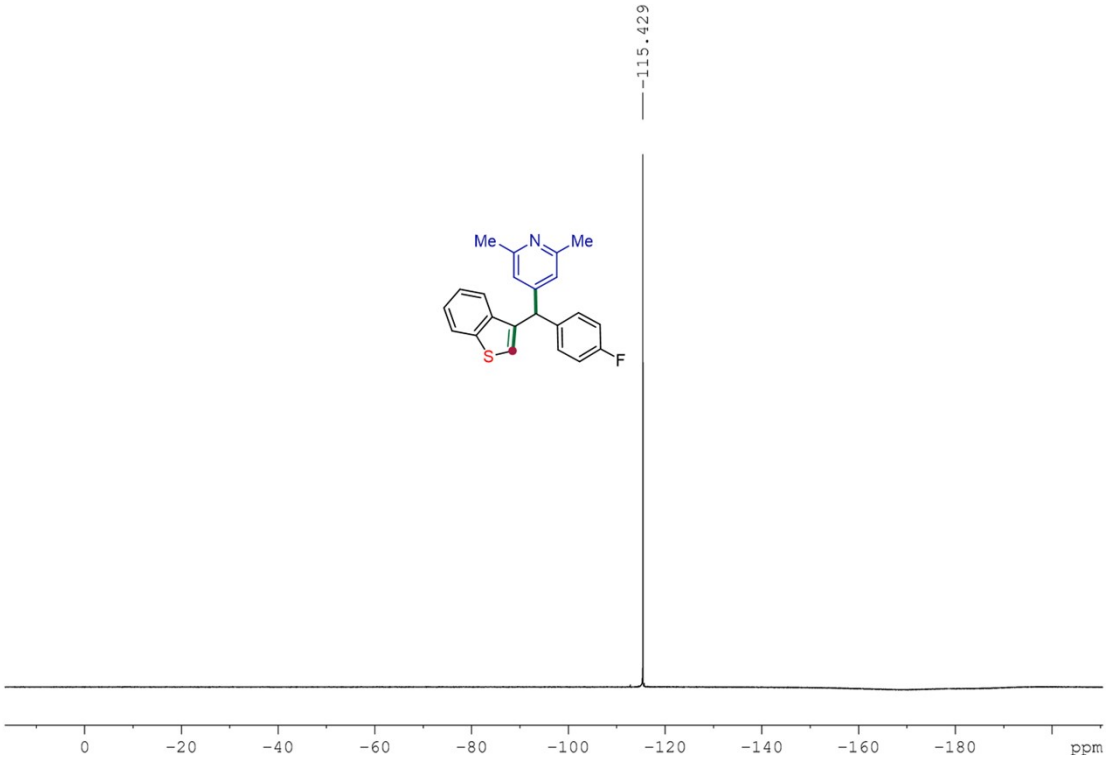
^{1}H NMR (600 MHz, $CDCl_3$) of **10**



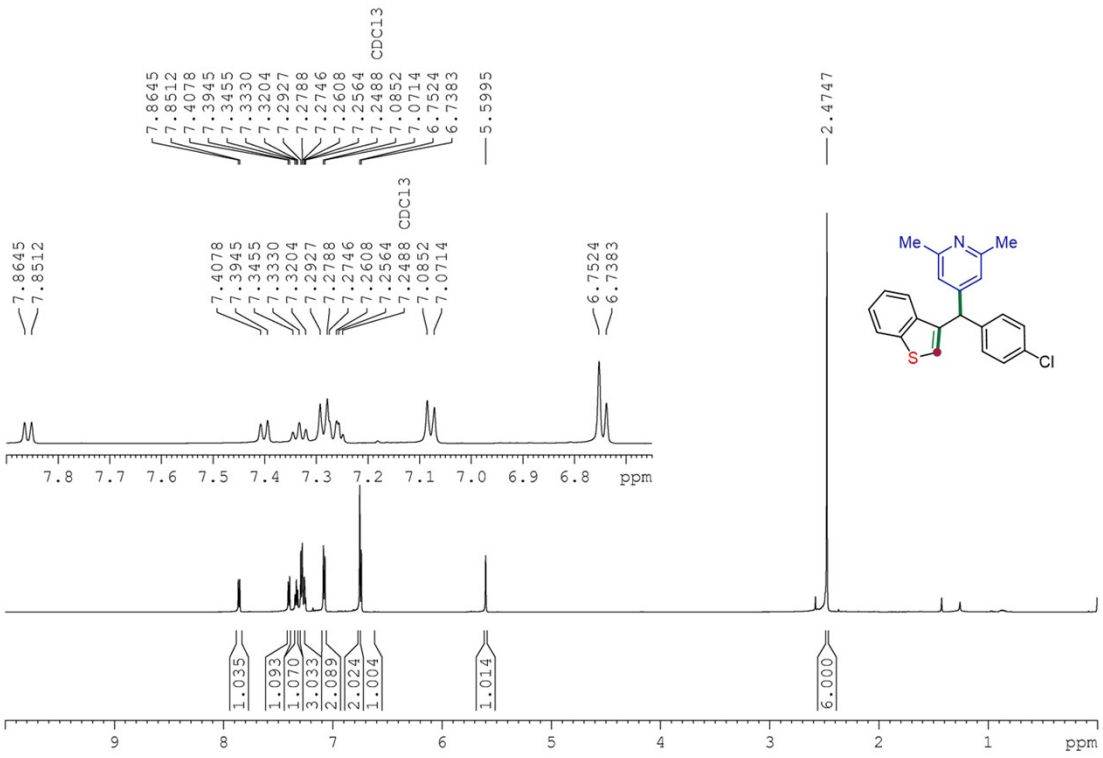
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **10**



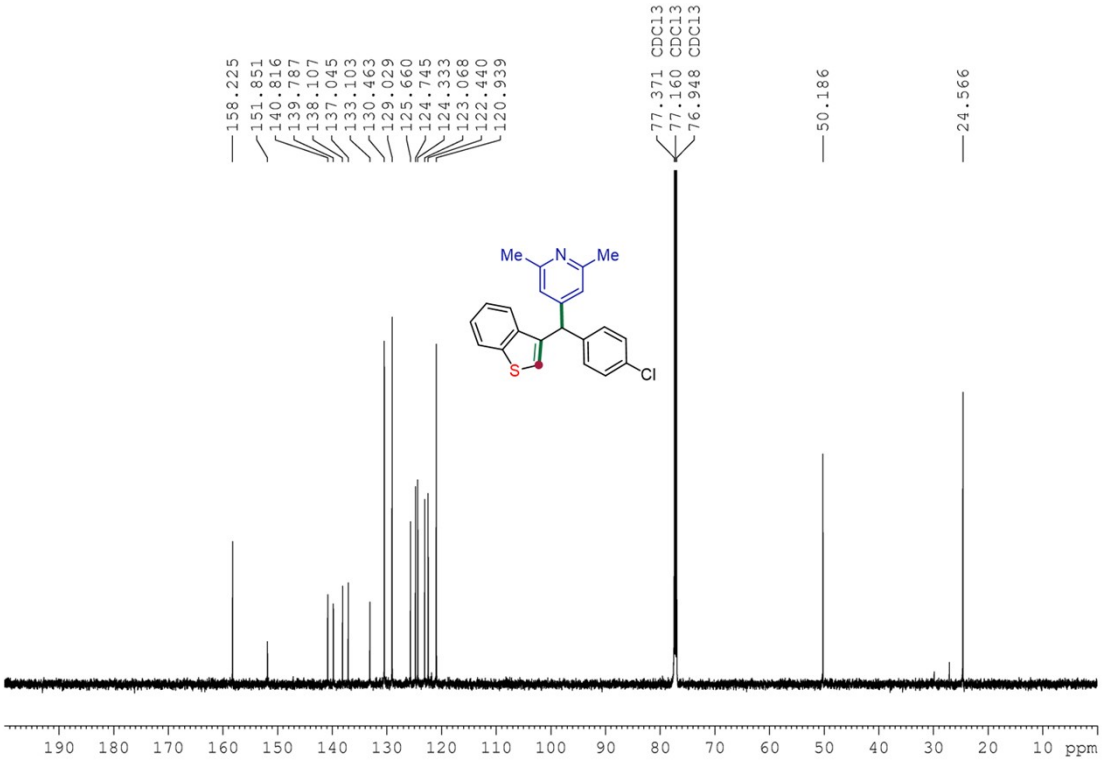
^{19}F NMR (564 MHz, $CDCl_3$) of **10**



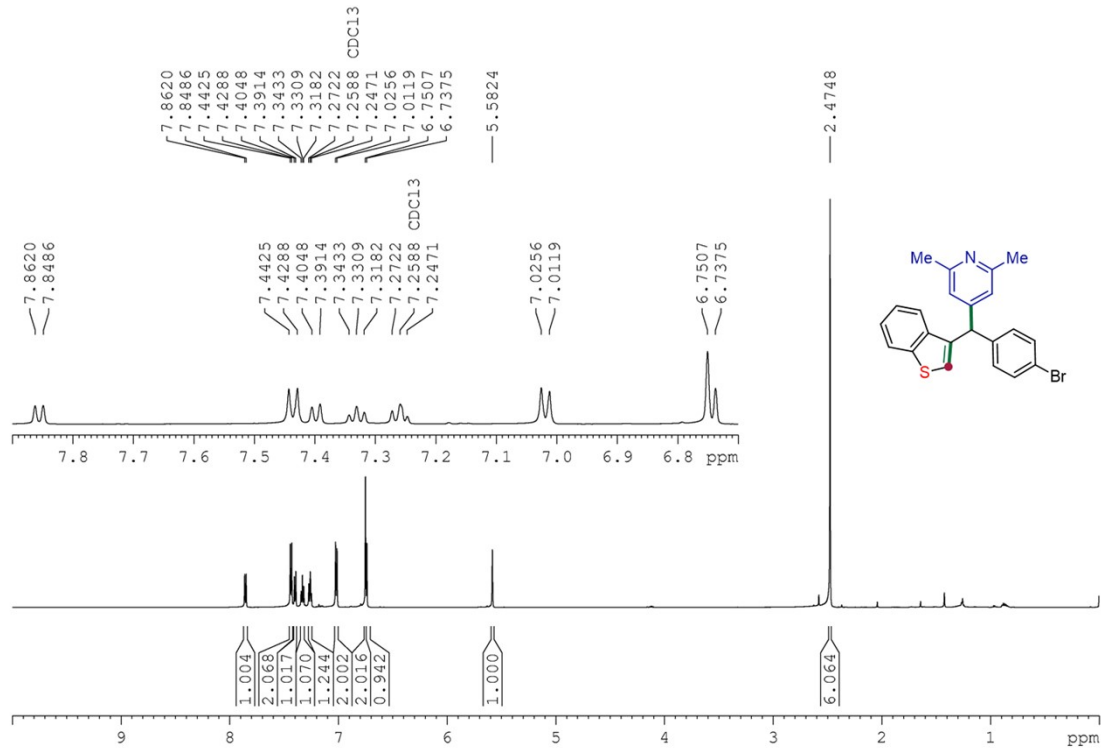
^{1}H NMR (600 MHz, $CDCl_3$) of **11**



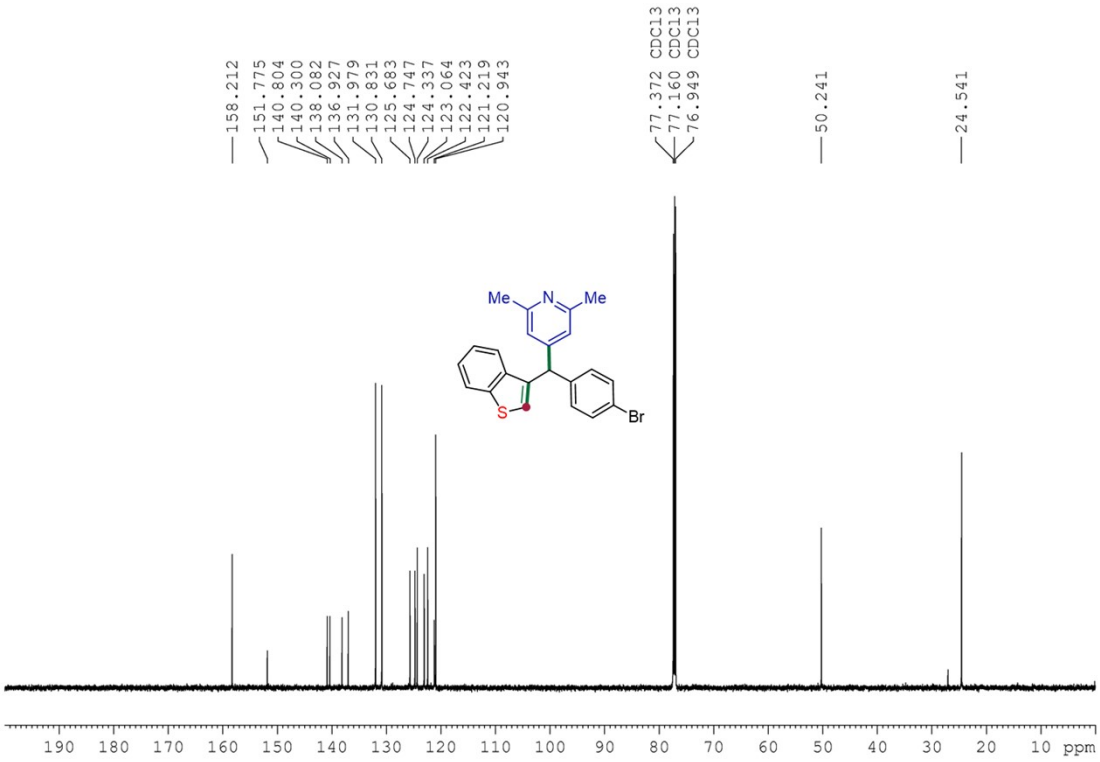
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **11**



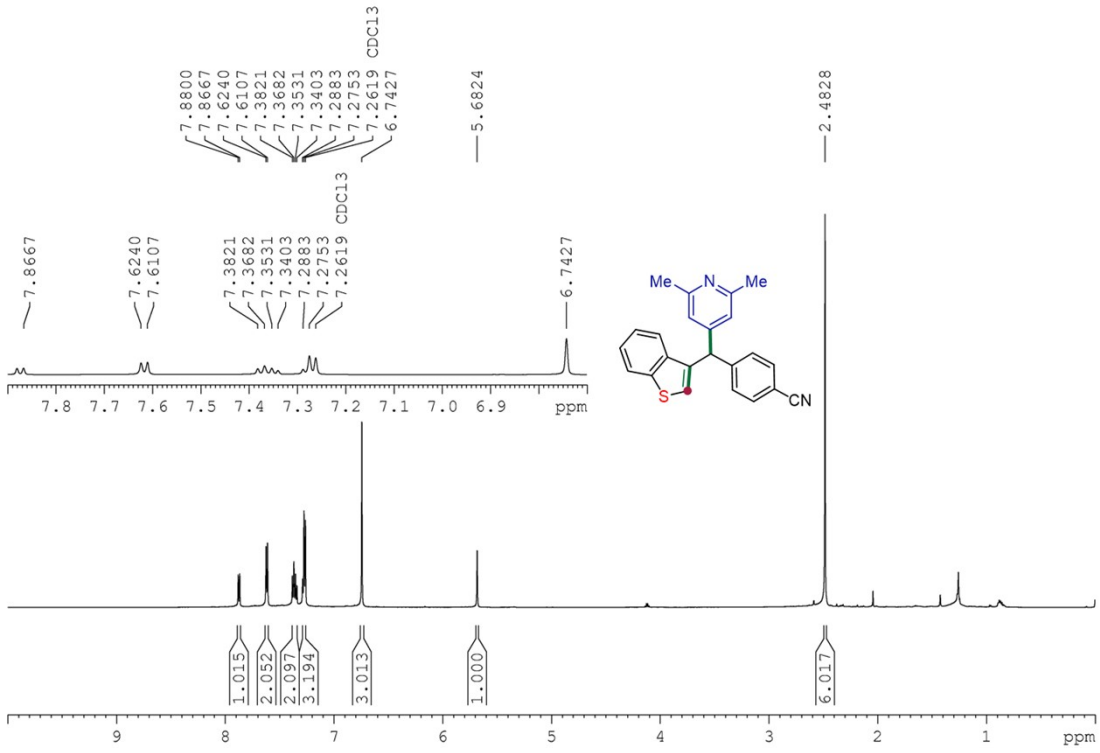
^{1}H NMR (600 MHz, $CDCl_3$) of **12**



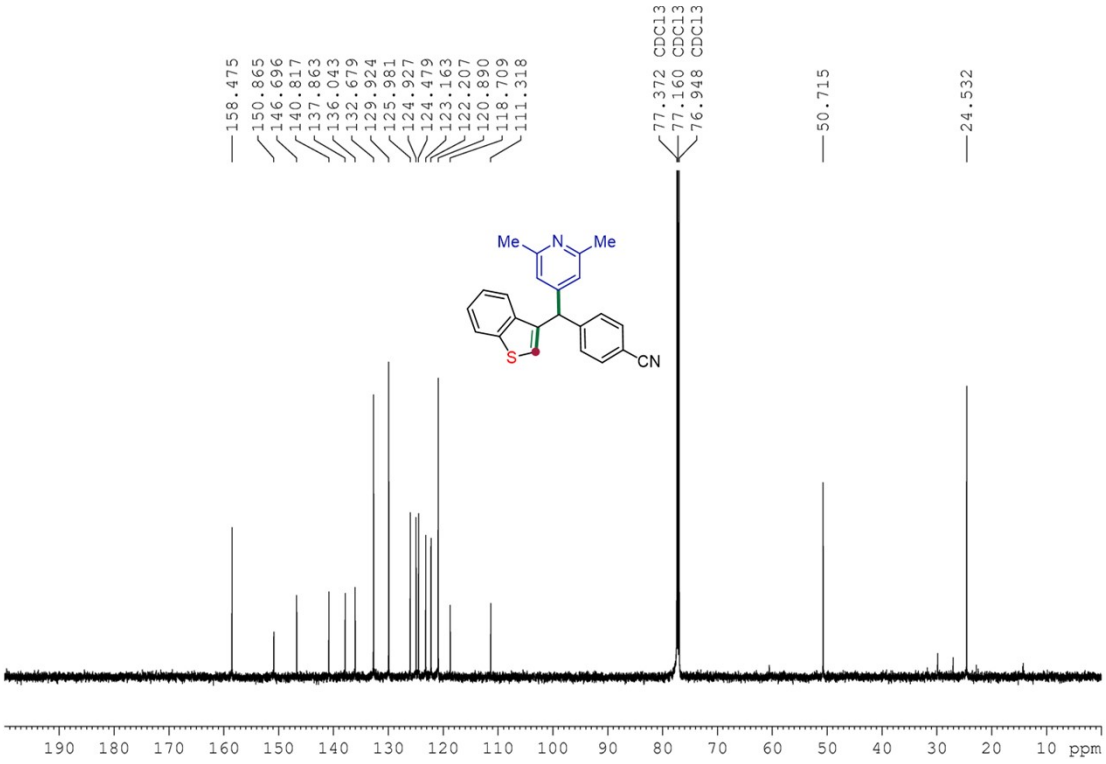
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **12**



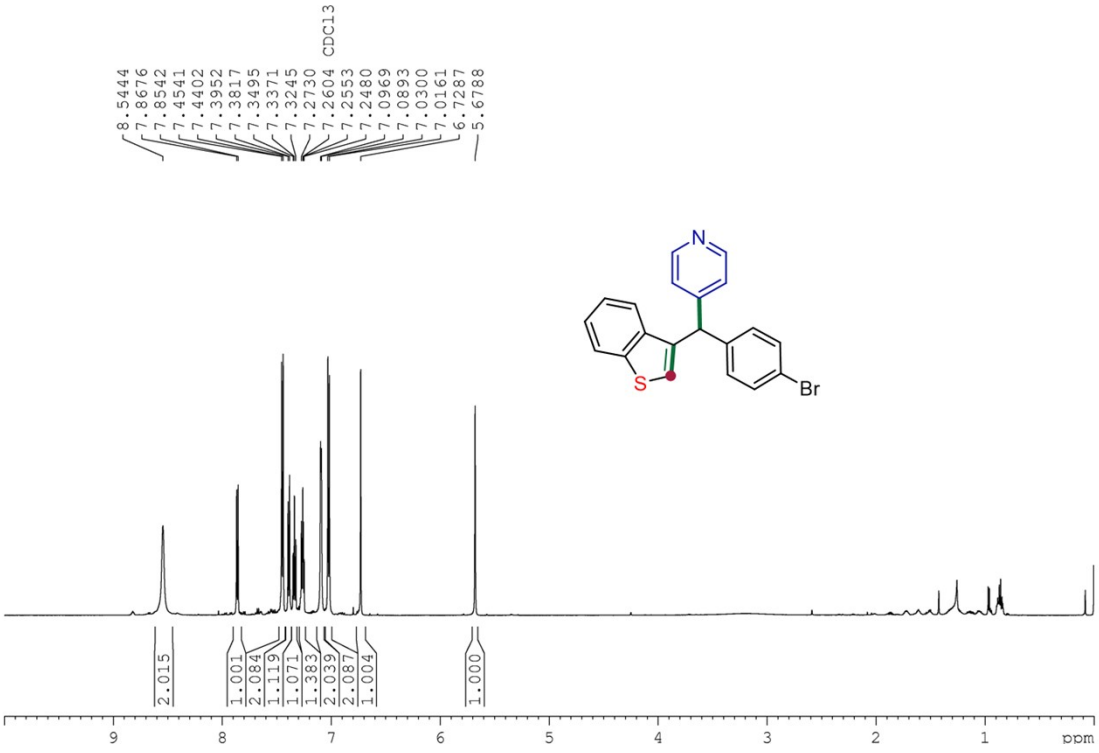
^{1}H NMR (600 MHz, $CDCl_3$) of **13**



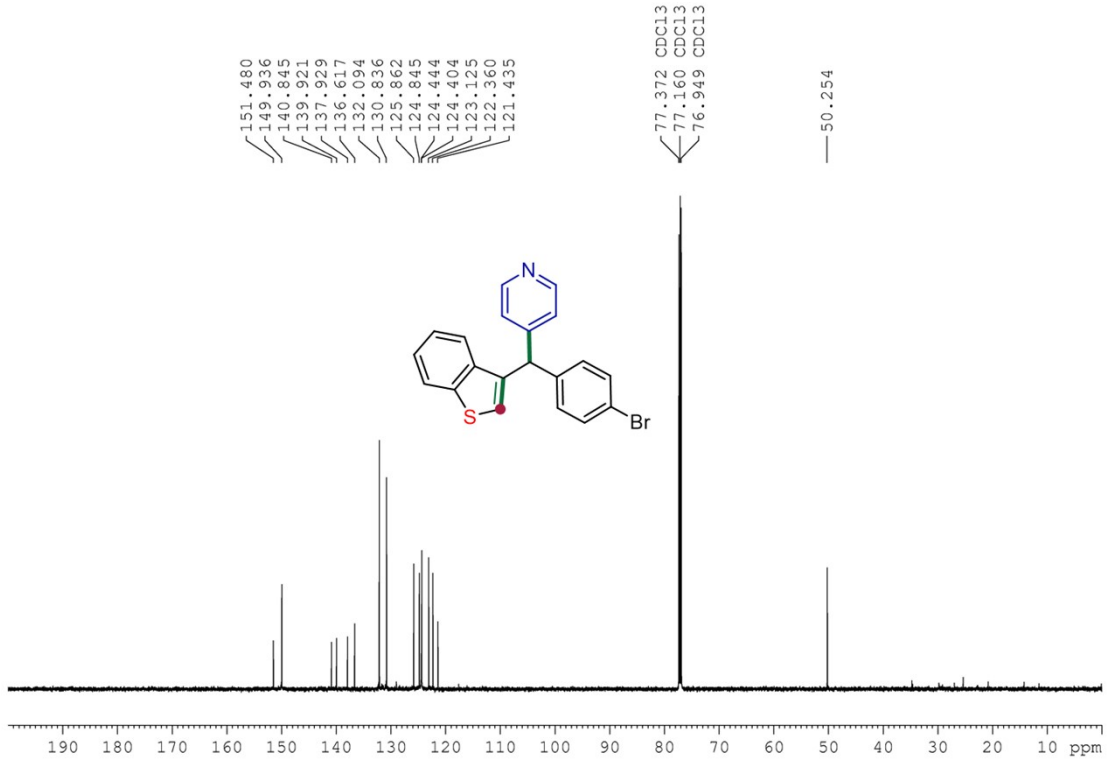
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **13**



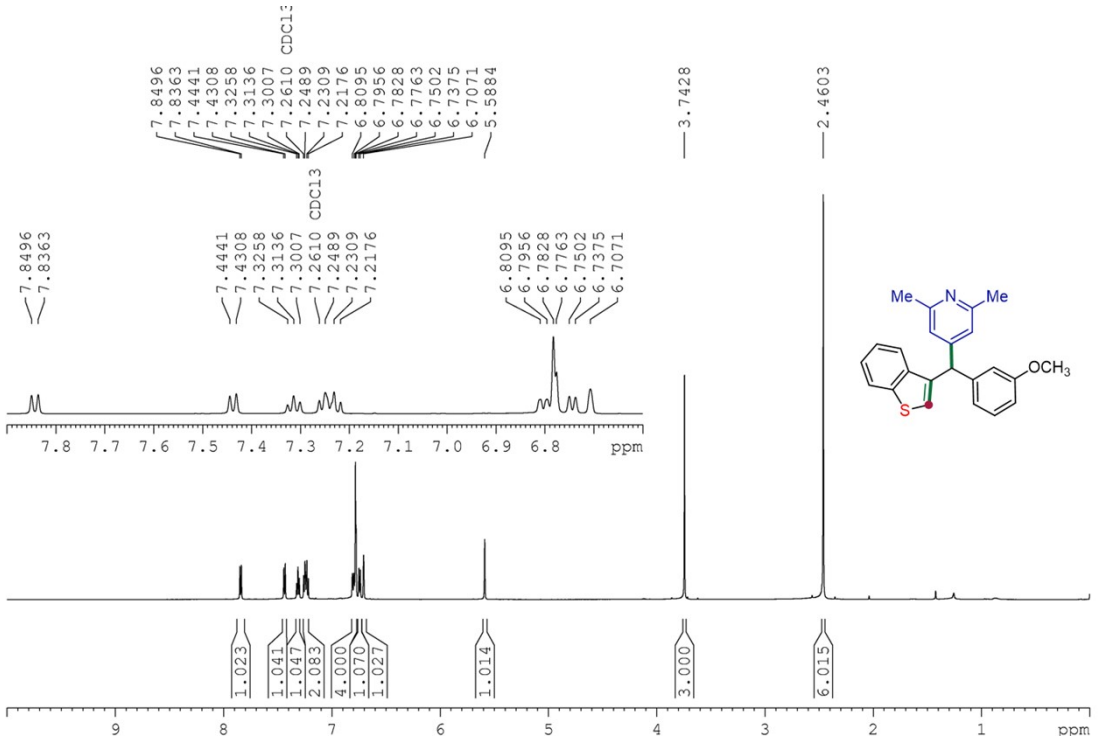
^{1}H NMR (600 MHz, $CDCl_3$) of **14**



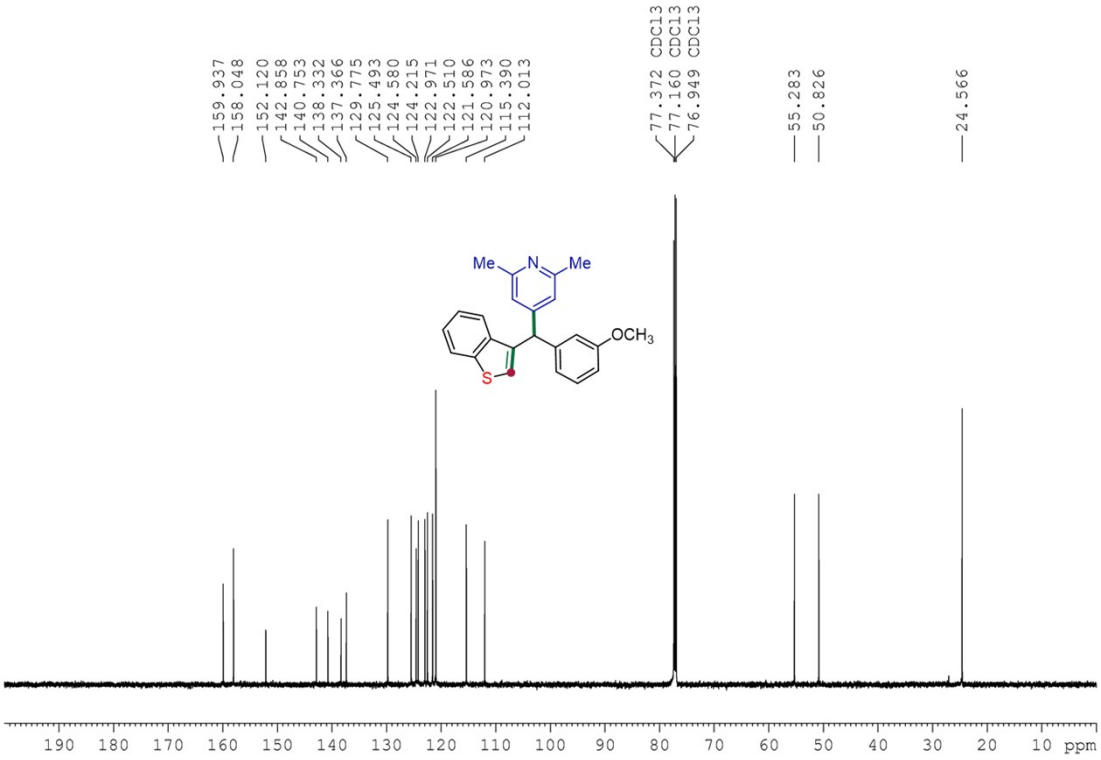
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **14**



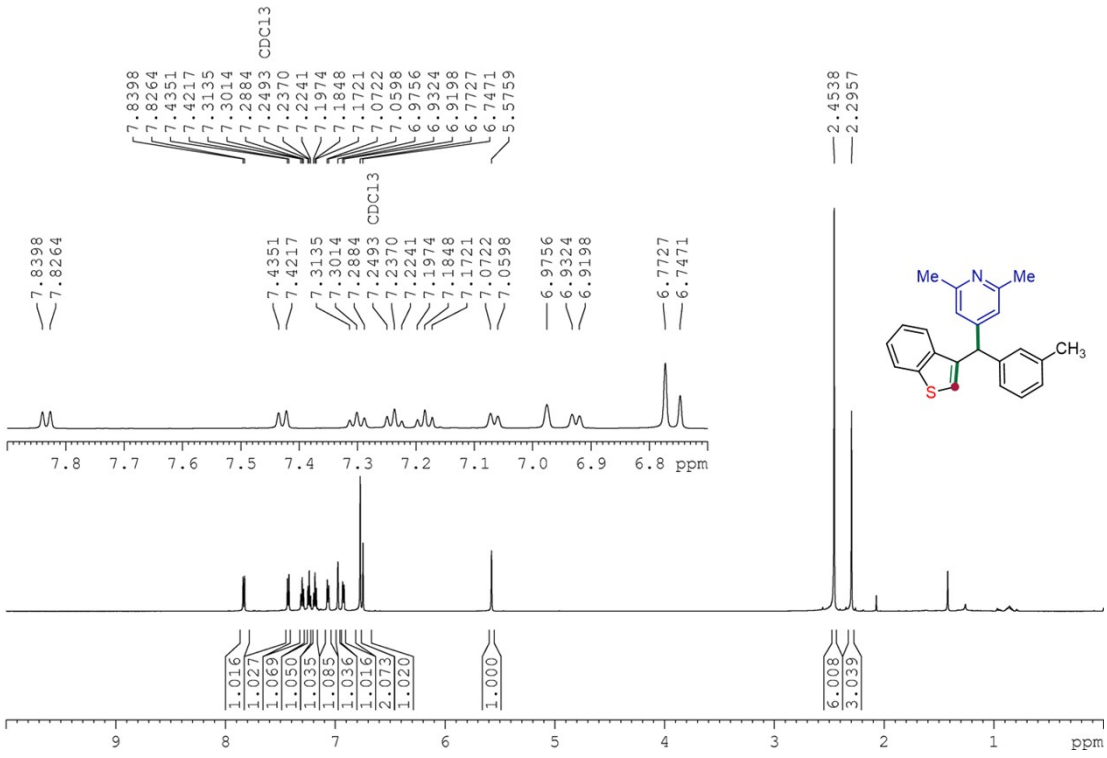
^{1}H NMR (600 MHz, $CDCl_3$) of **15**



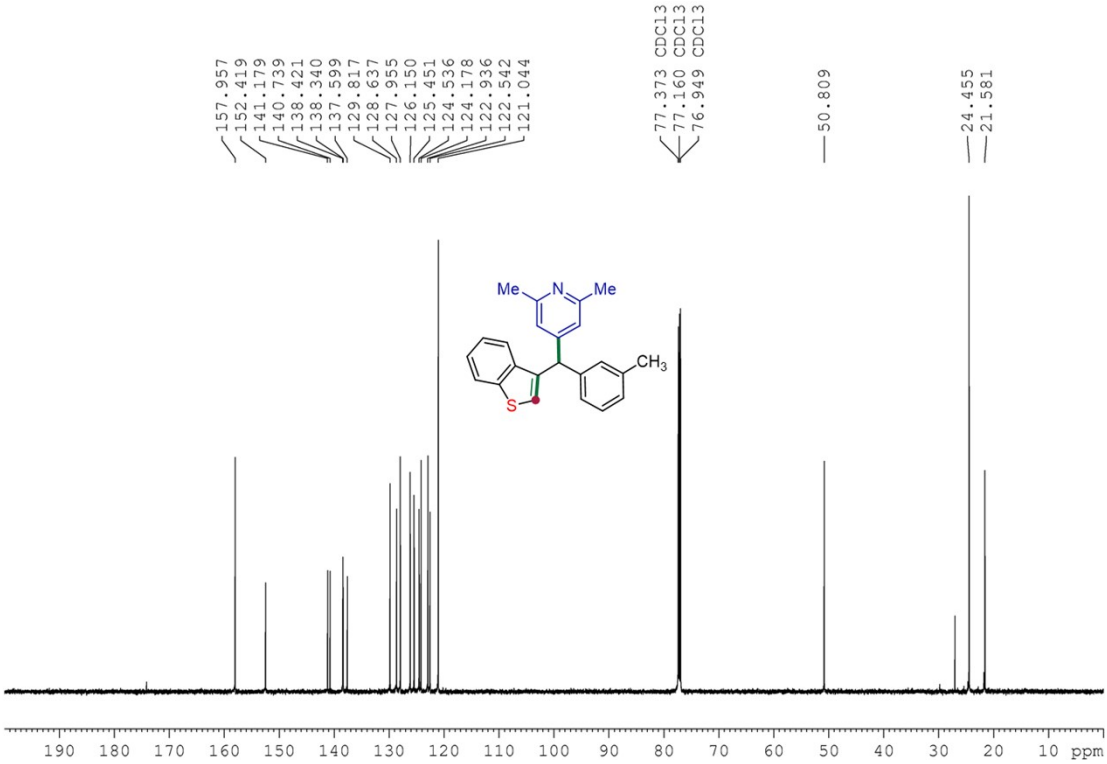
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **15**



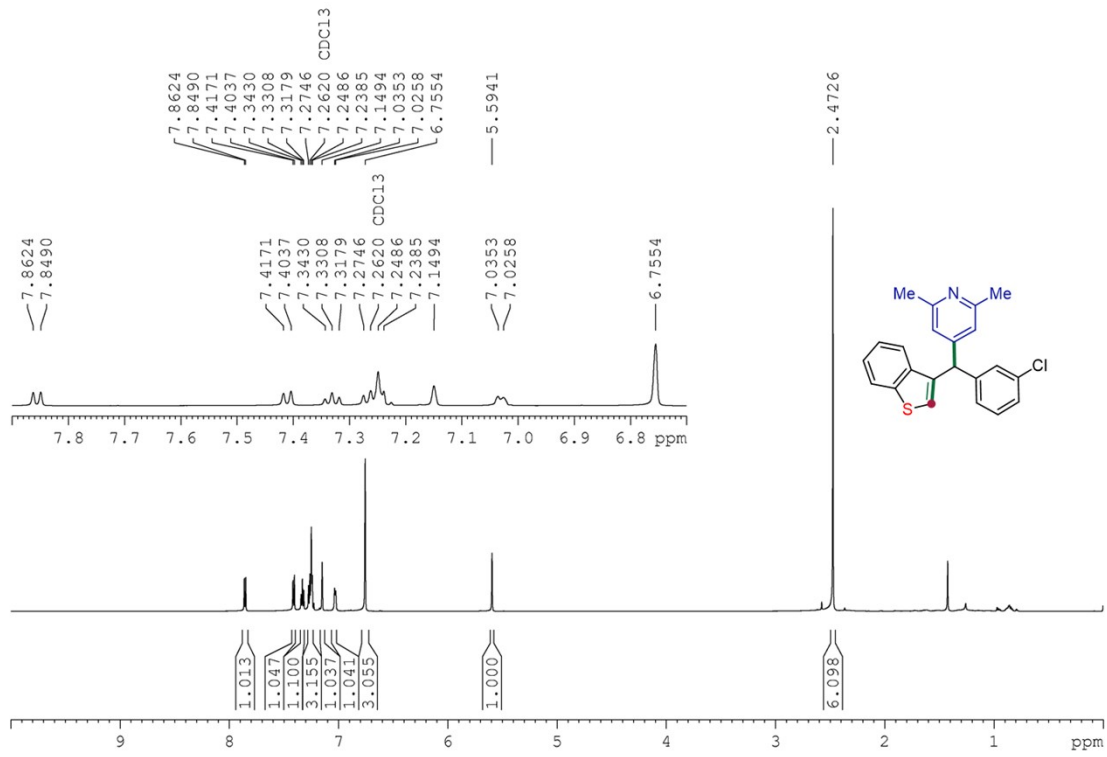
^{1}H NMR (600 MHz, $CDCl_3$) of **16**



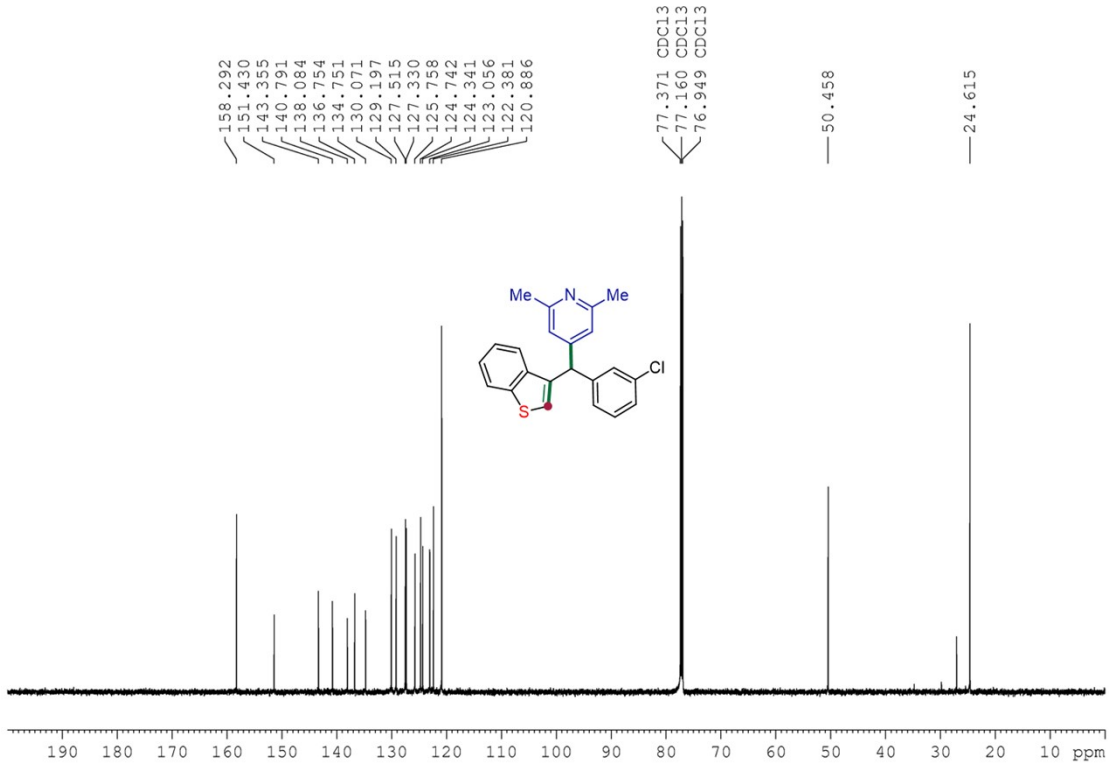
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **16**



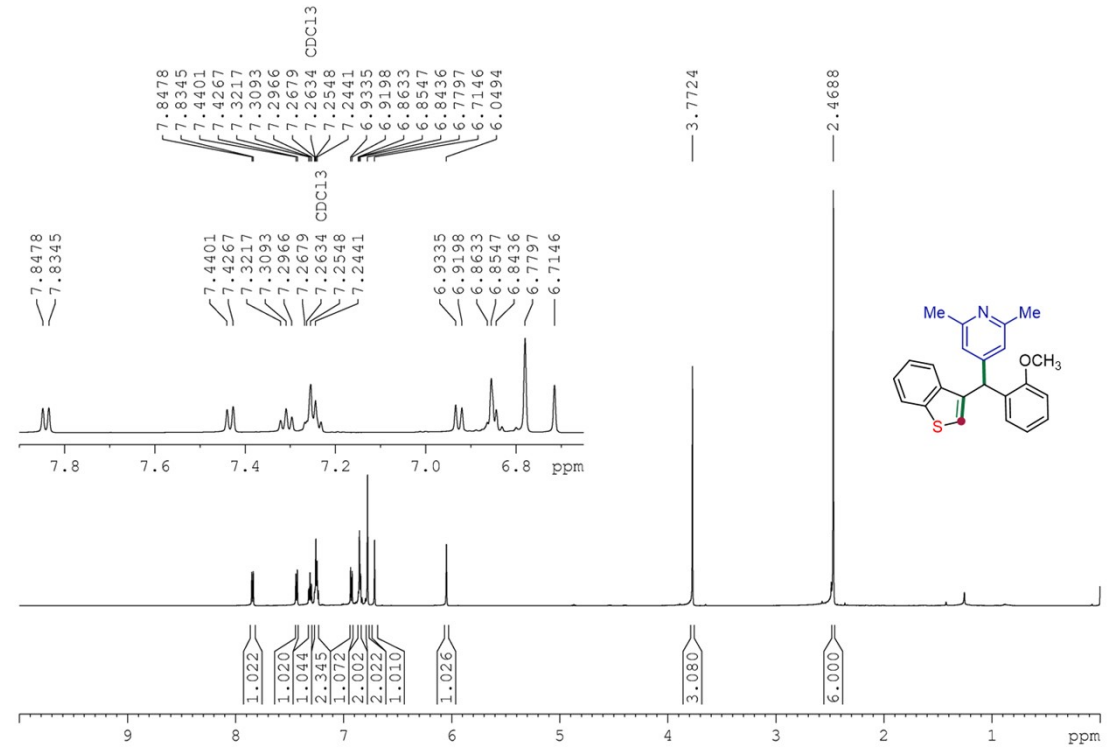
^{1}H NMR (600 MHz, $CDCl_3$) of **17**



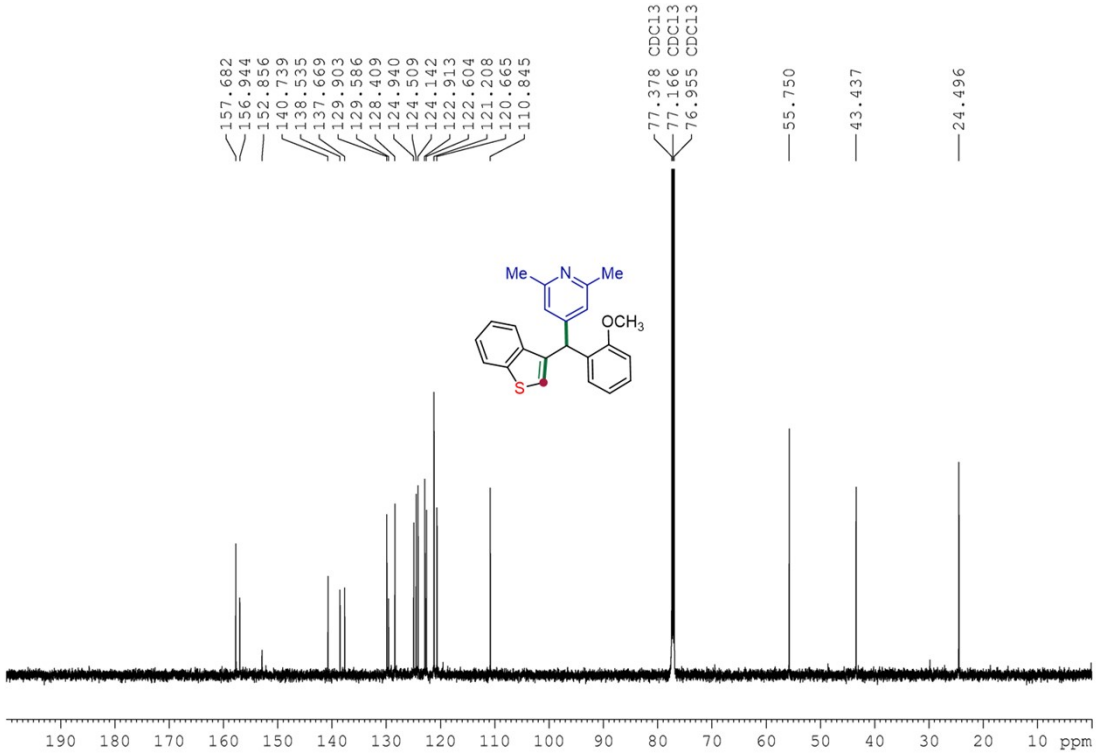
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **17**



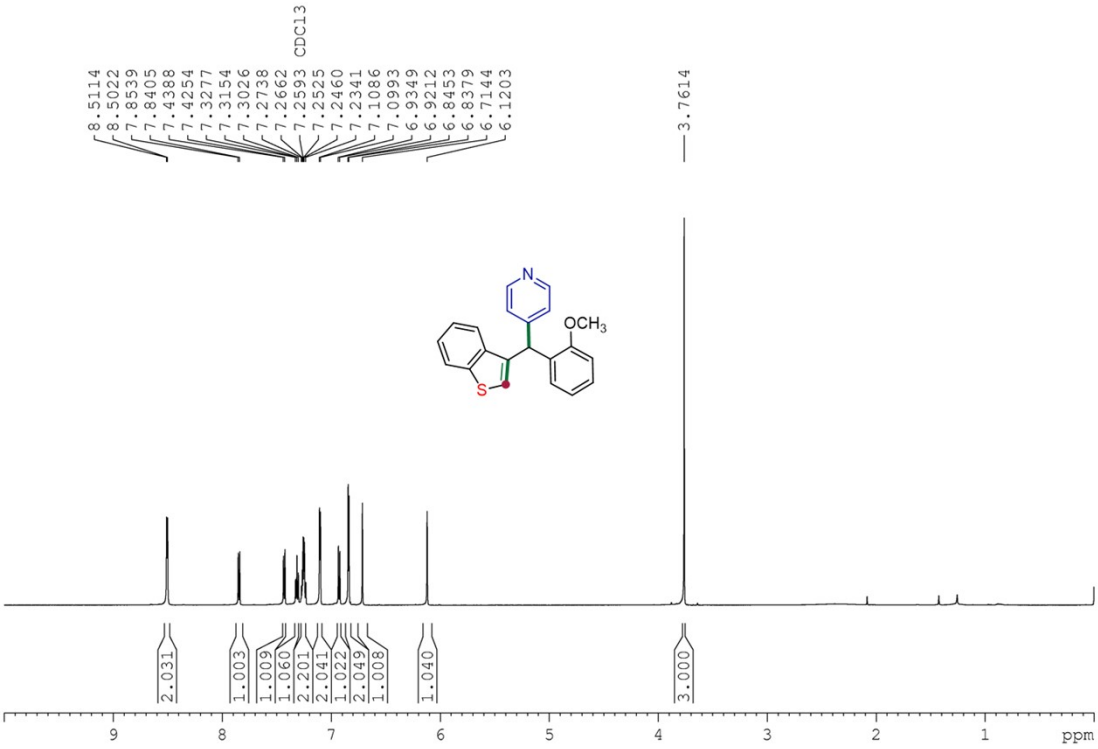
^{1}H NMR (600 MHz, $CDCl_3$) of **18**



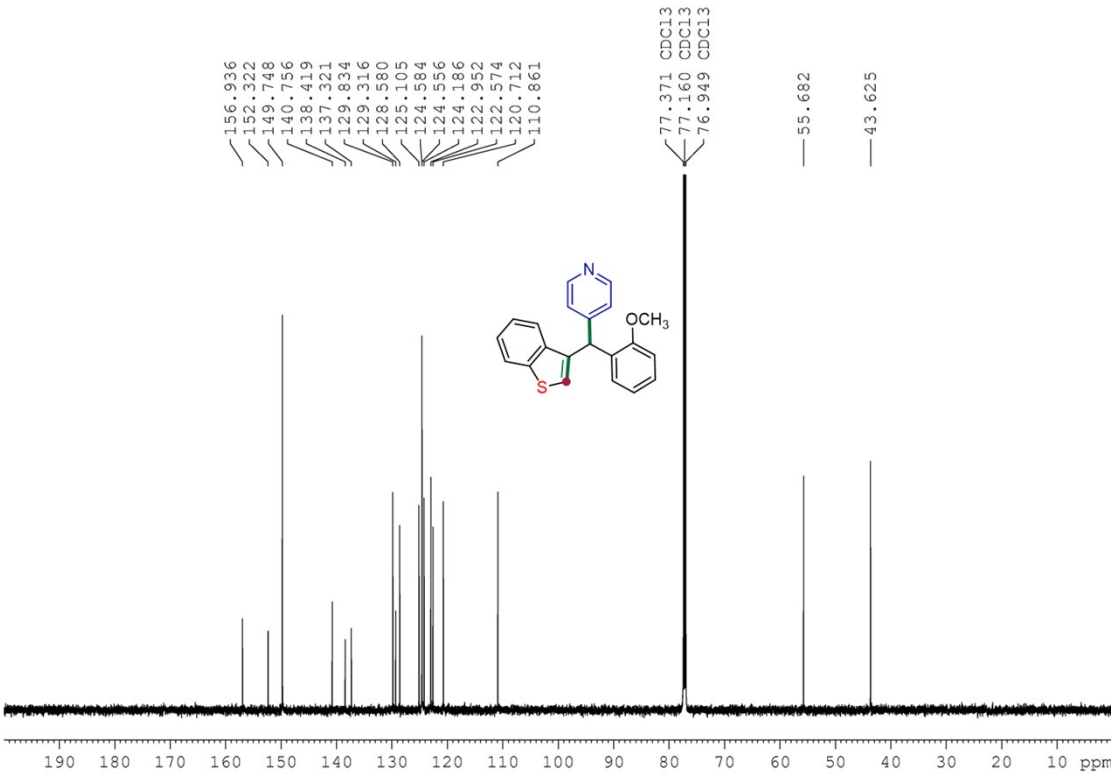
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **18**



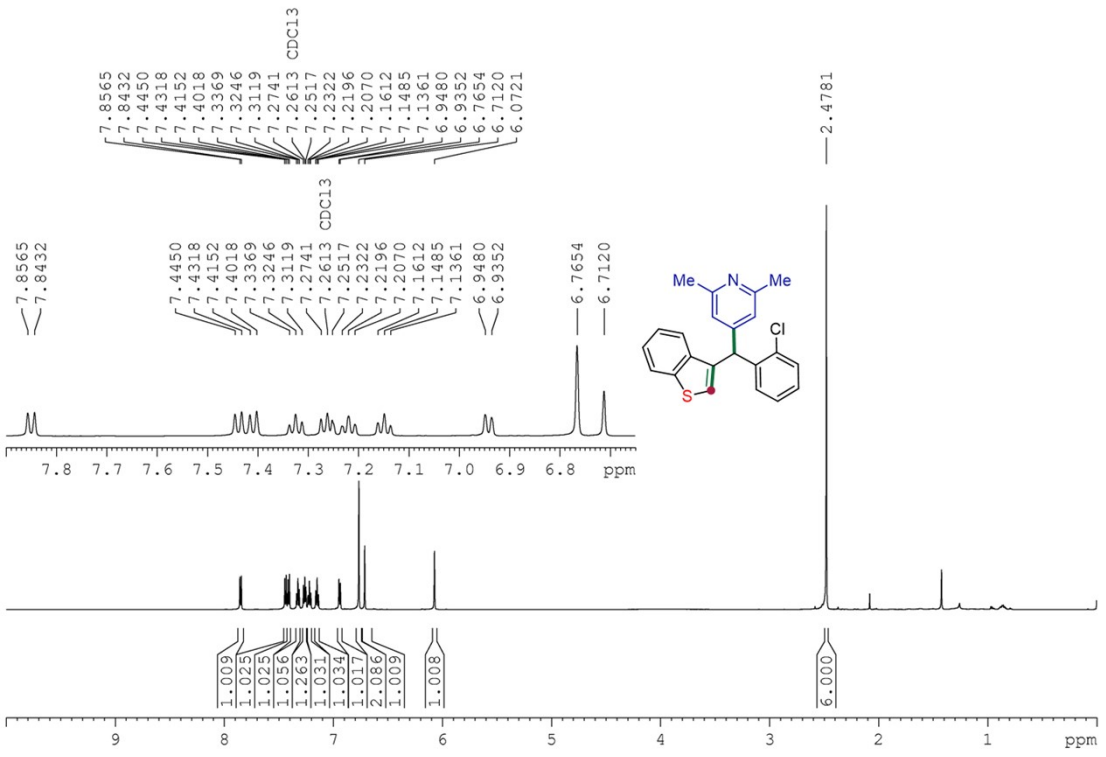
^{1}H NMR (600 MHz, $CDCl_3$) of **19**



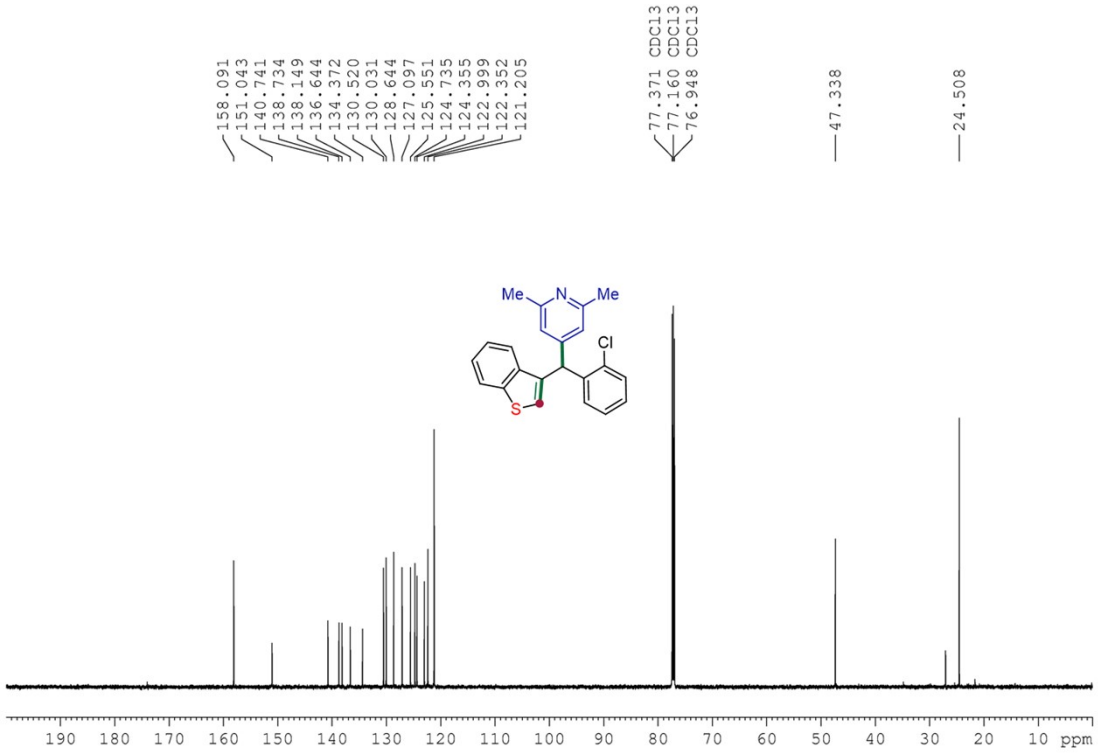
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **19**



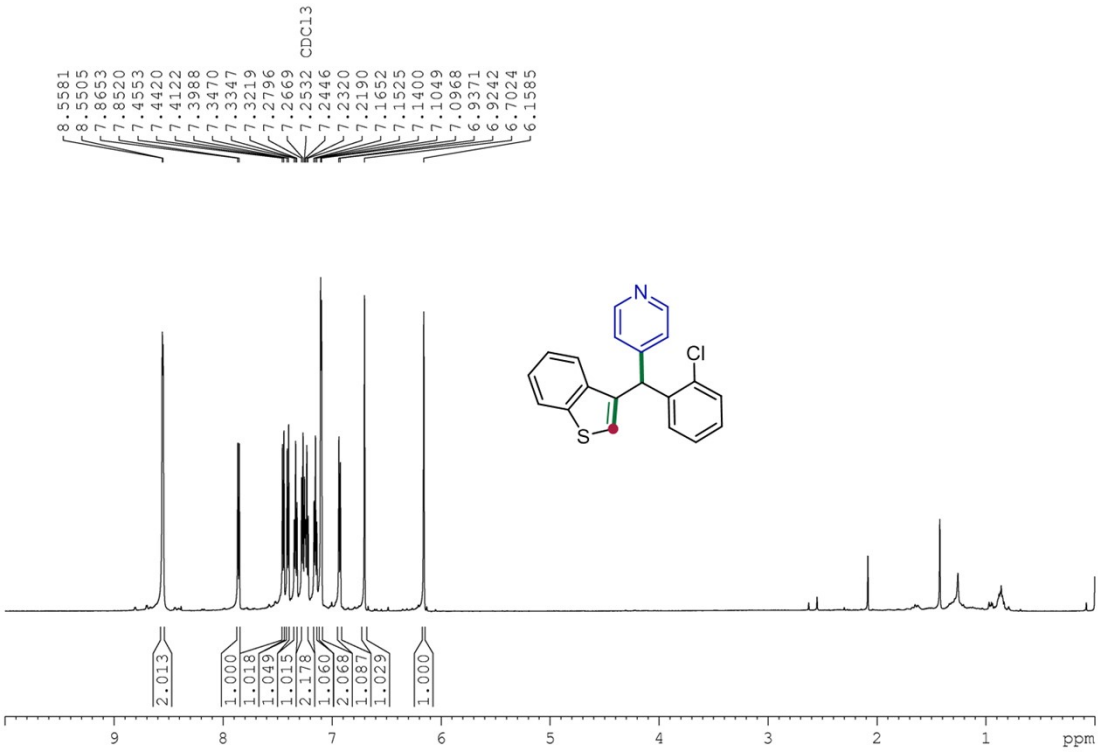
^{1}H NMR (600 MHz, $CDCl_3$) of **20**



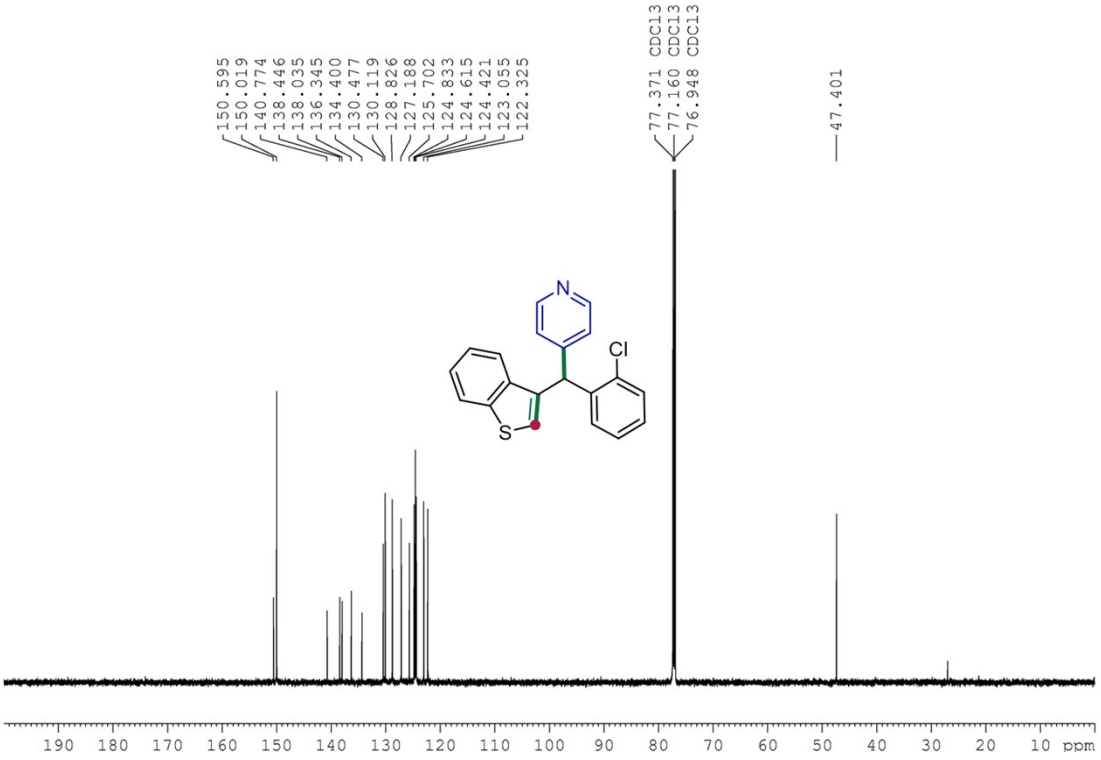
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **20**



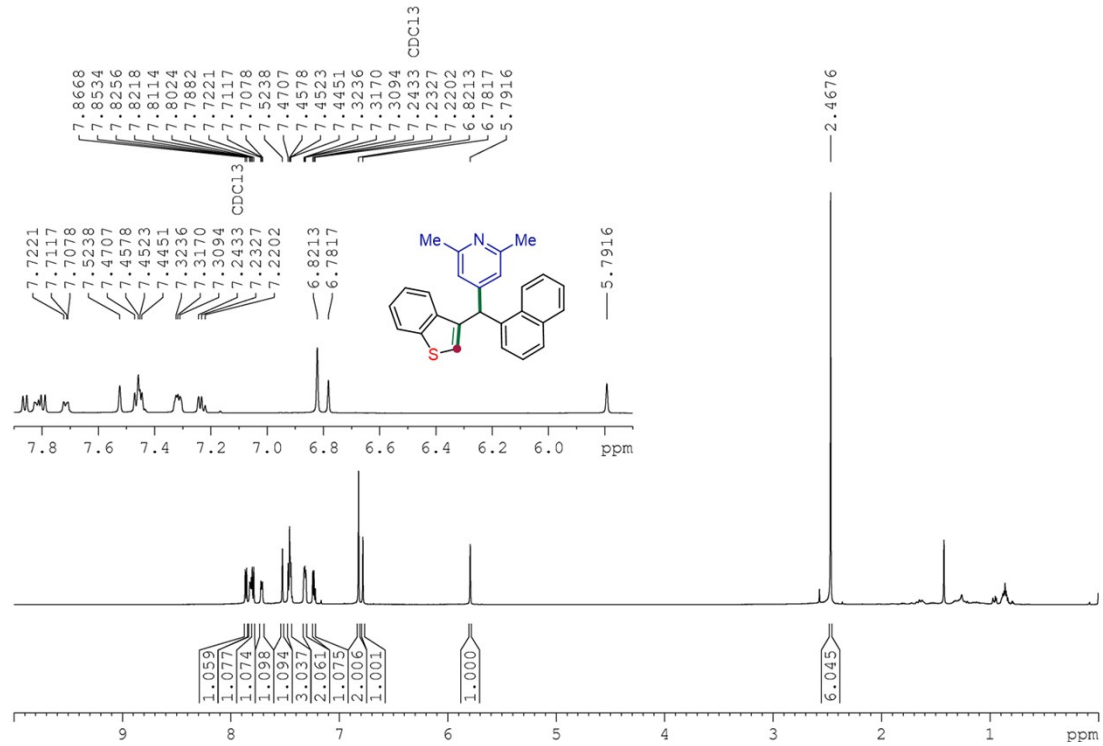
^{1}H NMR (600 MHz, $CDCl_3$) of **21**



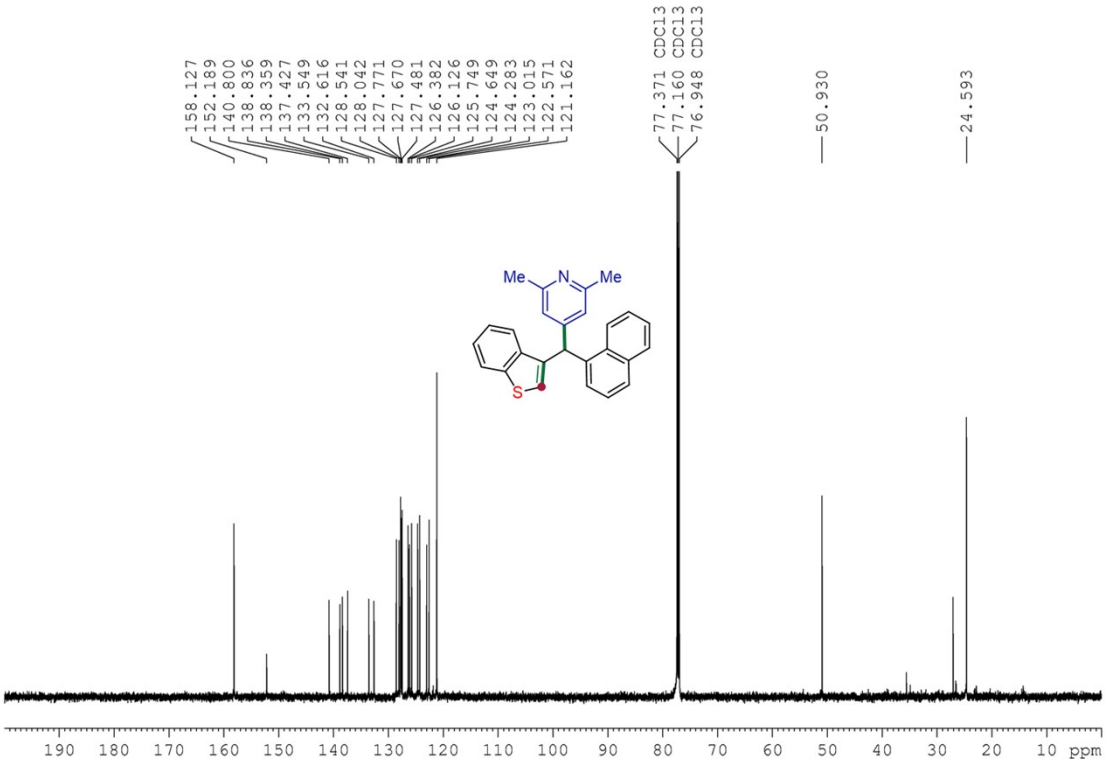
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **21**



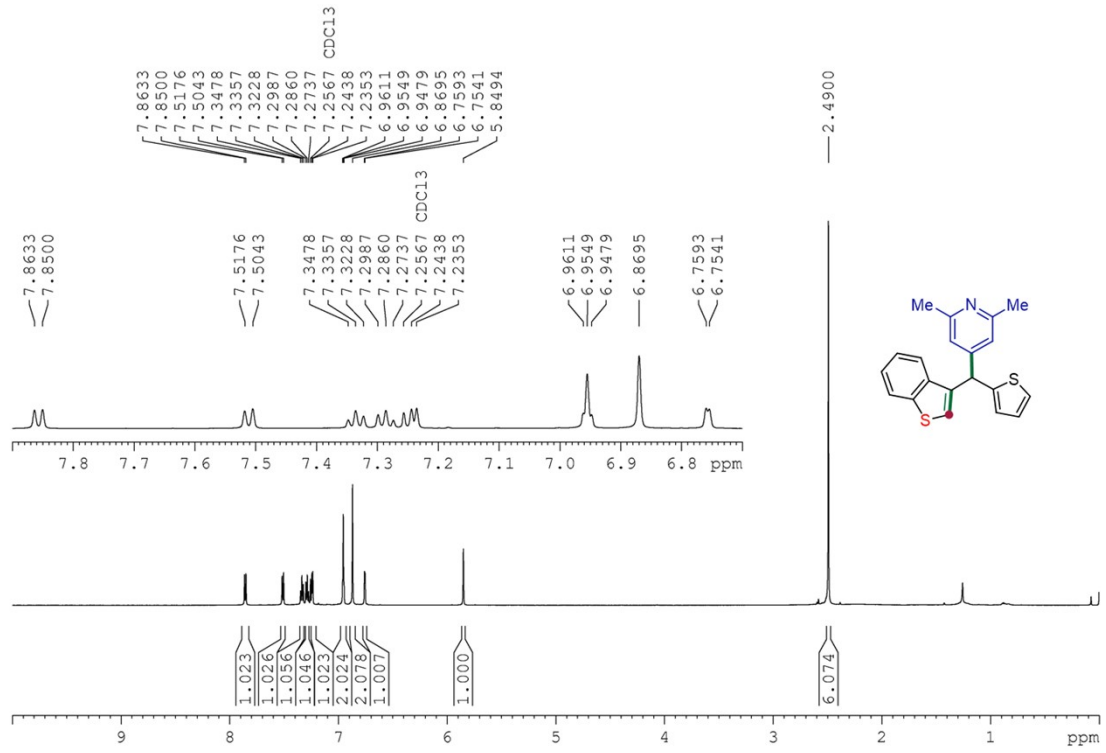
^{1}H NMR (600 MHz, $CDCl_3$) of **22**



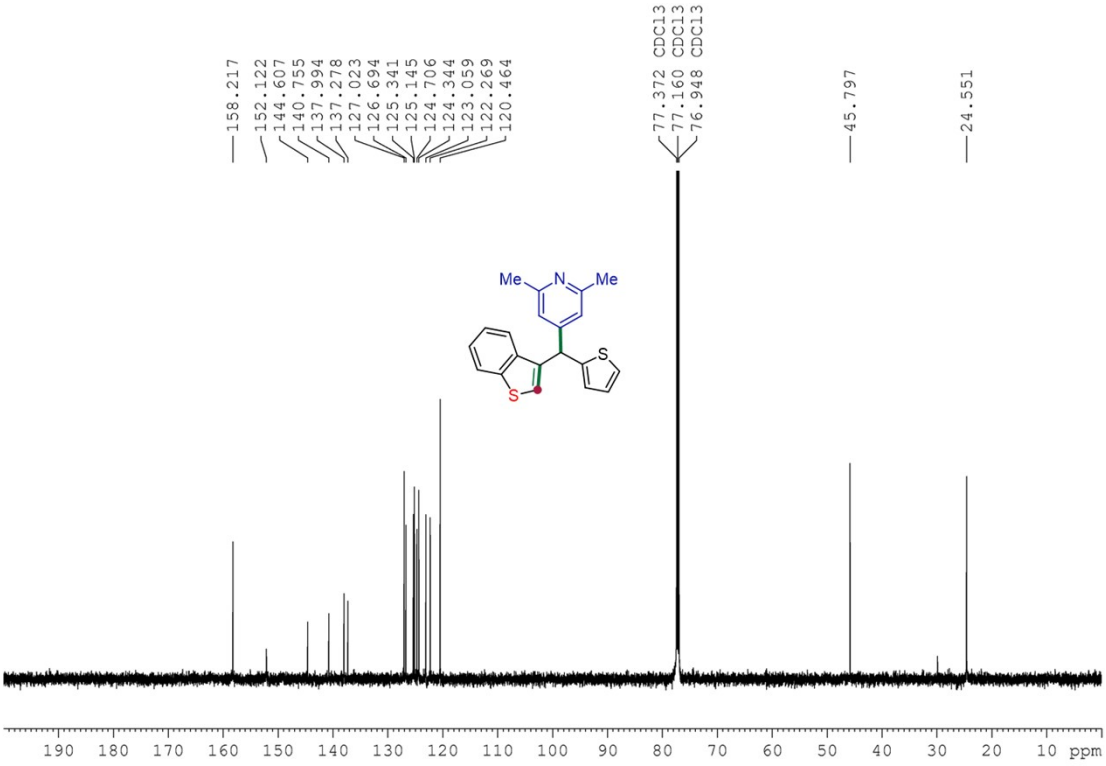
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **22**



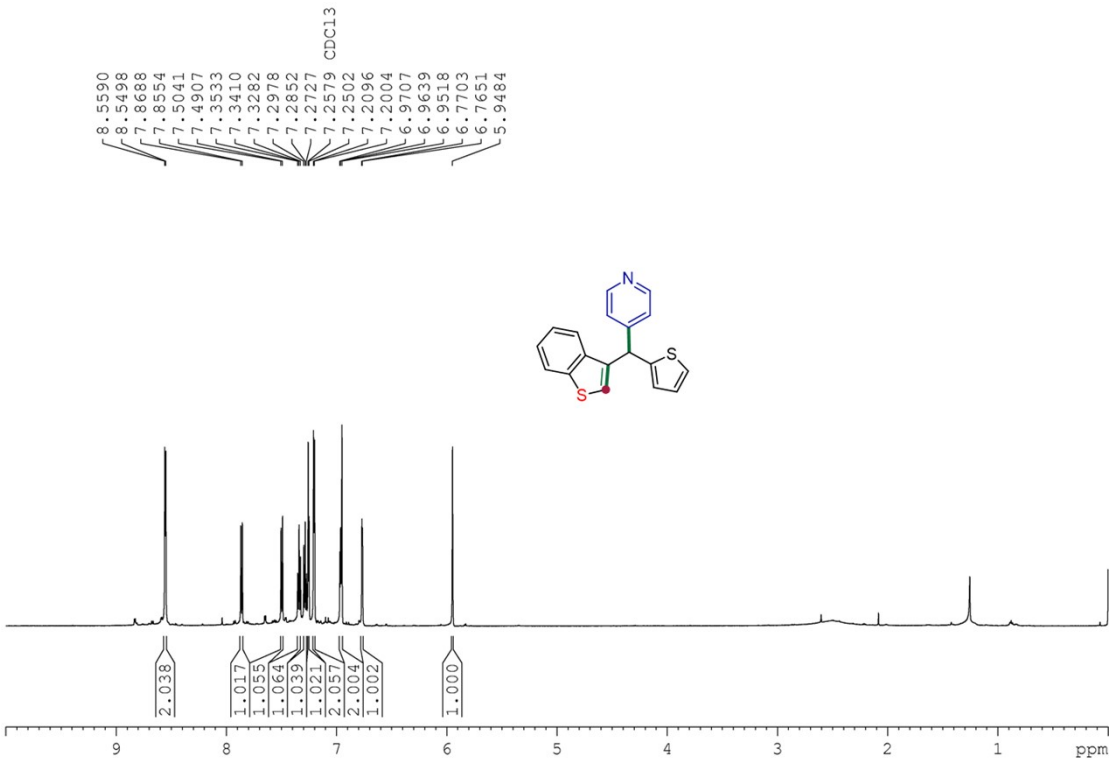
^{1}H NMR (600 MHz, $CDCl_3$) of **23**



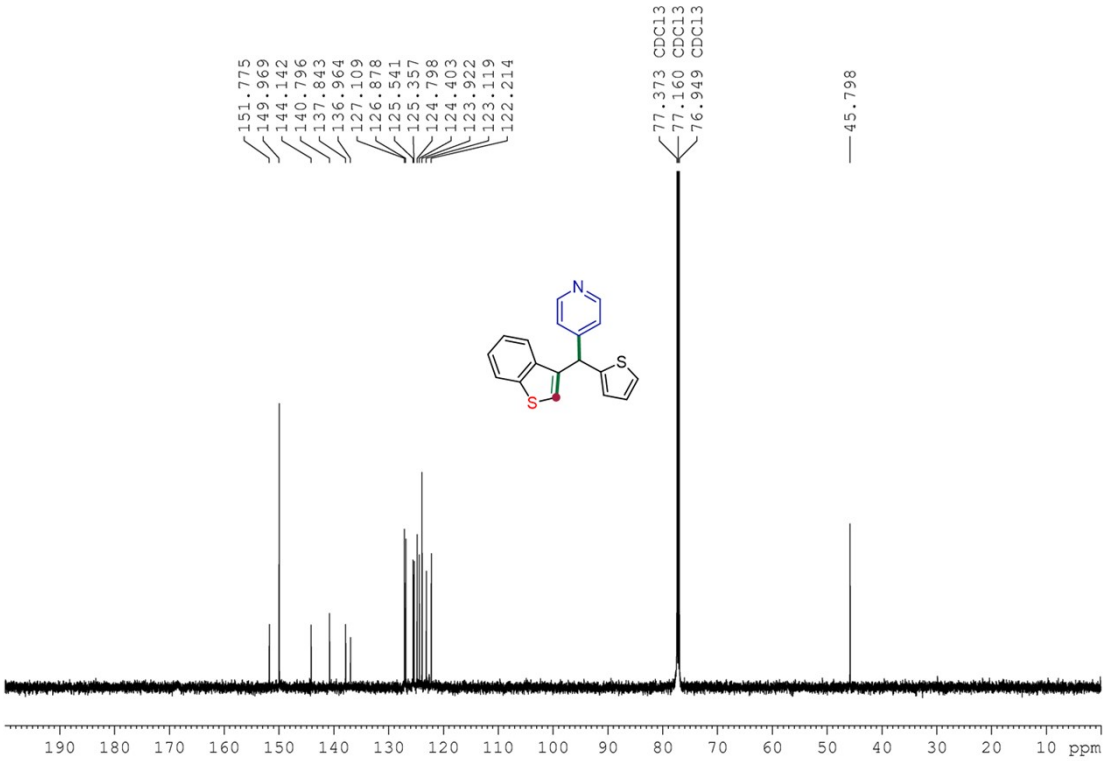
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **23**



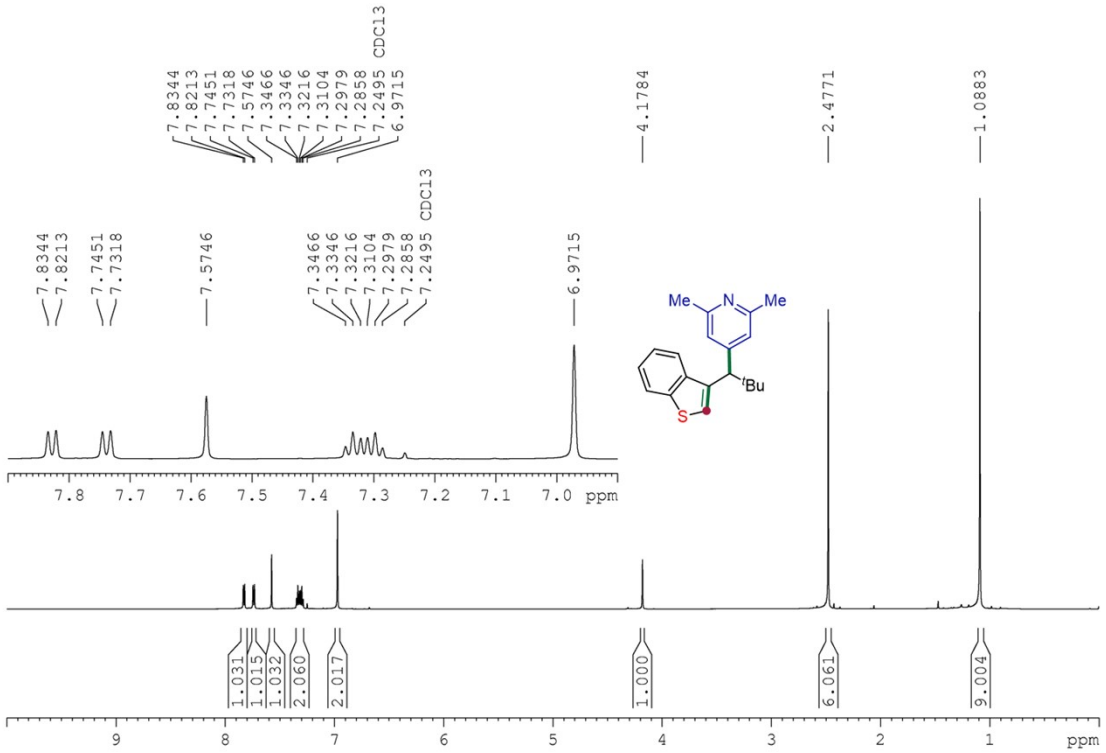
^{1}H NMR (600 MHz, $CDCl_3$) of **24**



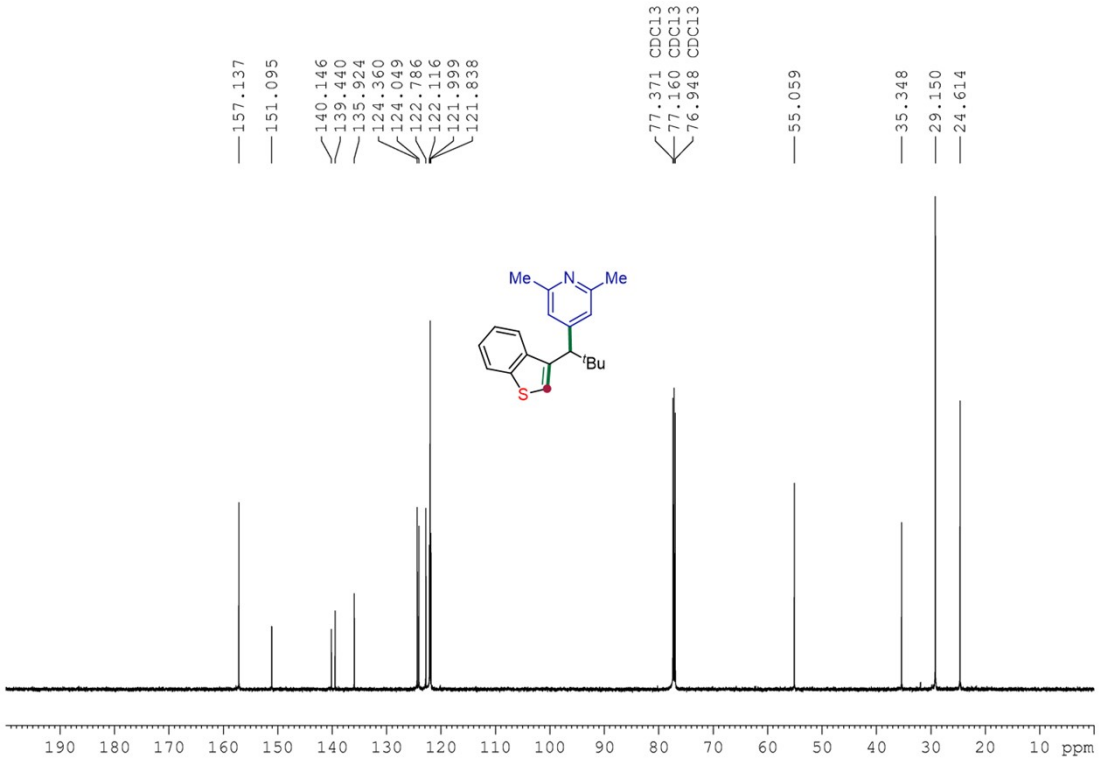
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **24**



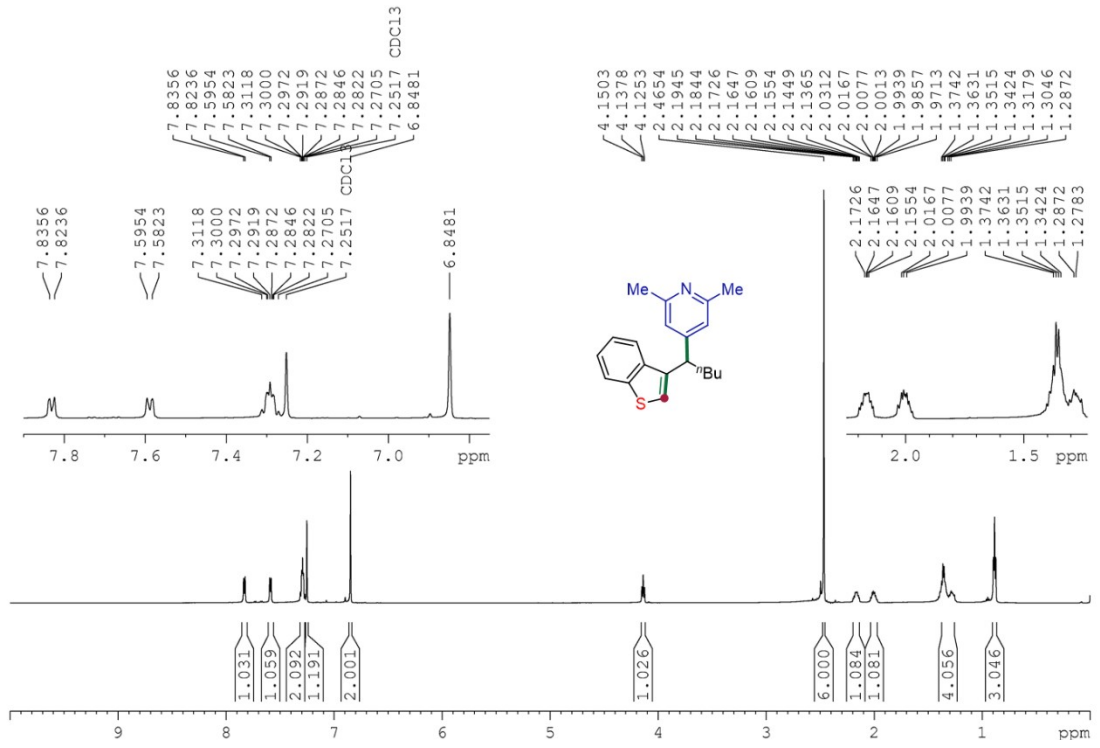
^{1}H NMR (600 MHz, $CDCl_3$) of **25**



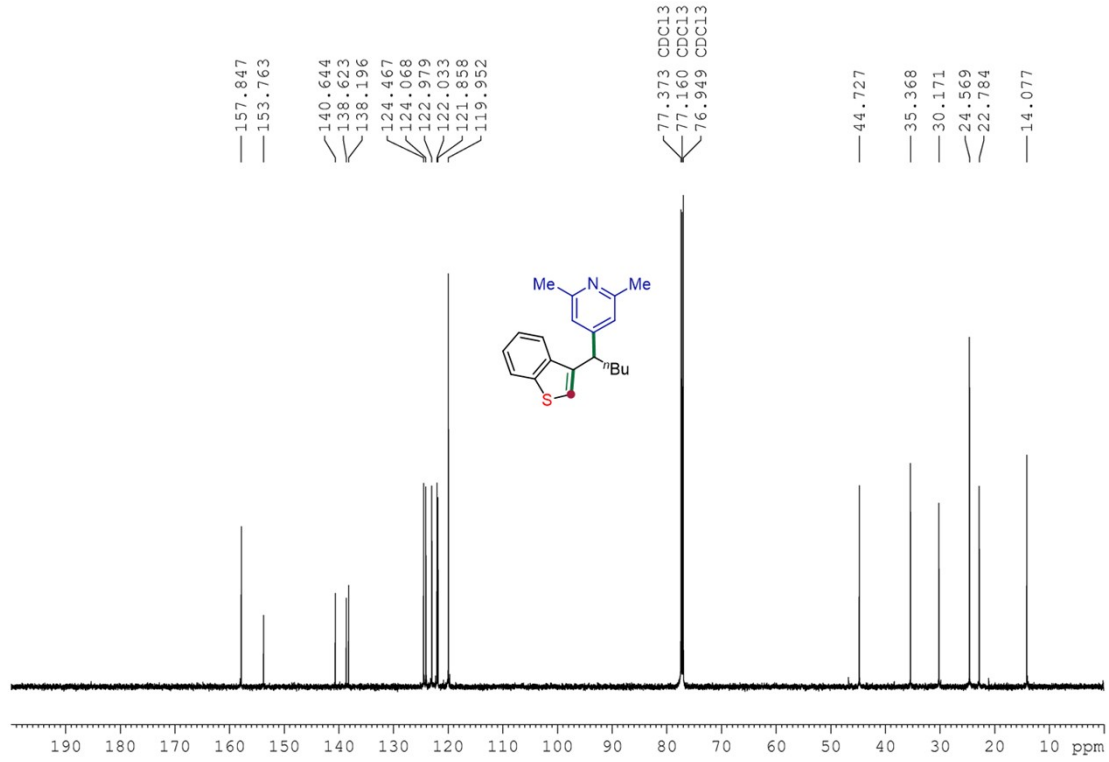
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **25**



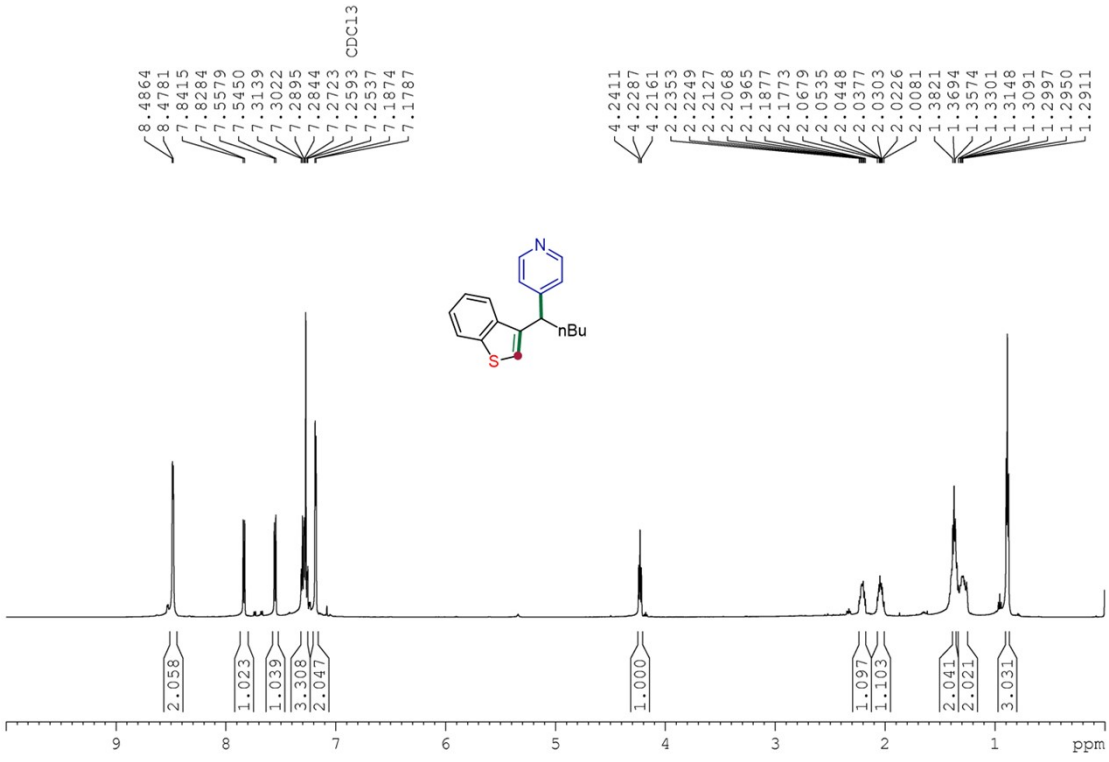
^{1}H NMR (600 MHz, $CDCl_3$) of **26**



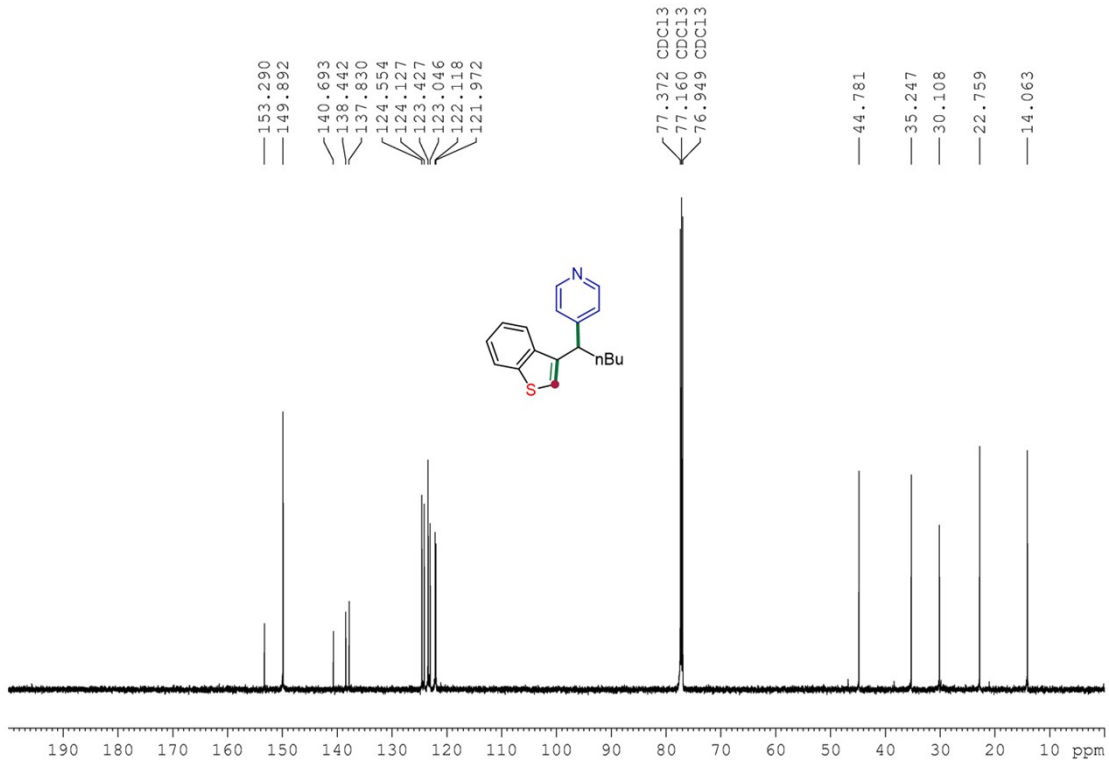
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **26**



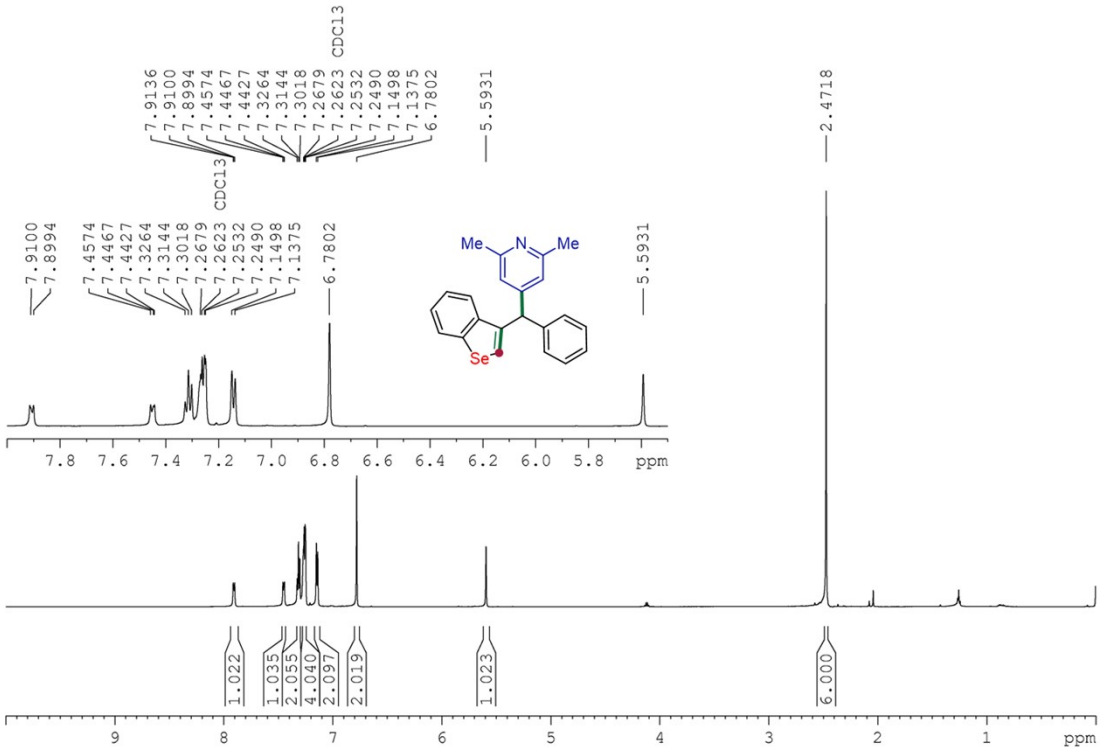
^{1}H NMR (600 MHz, $CDCl_3$) of **27**



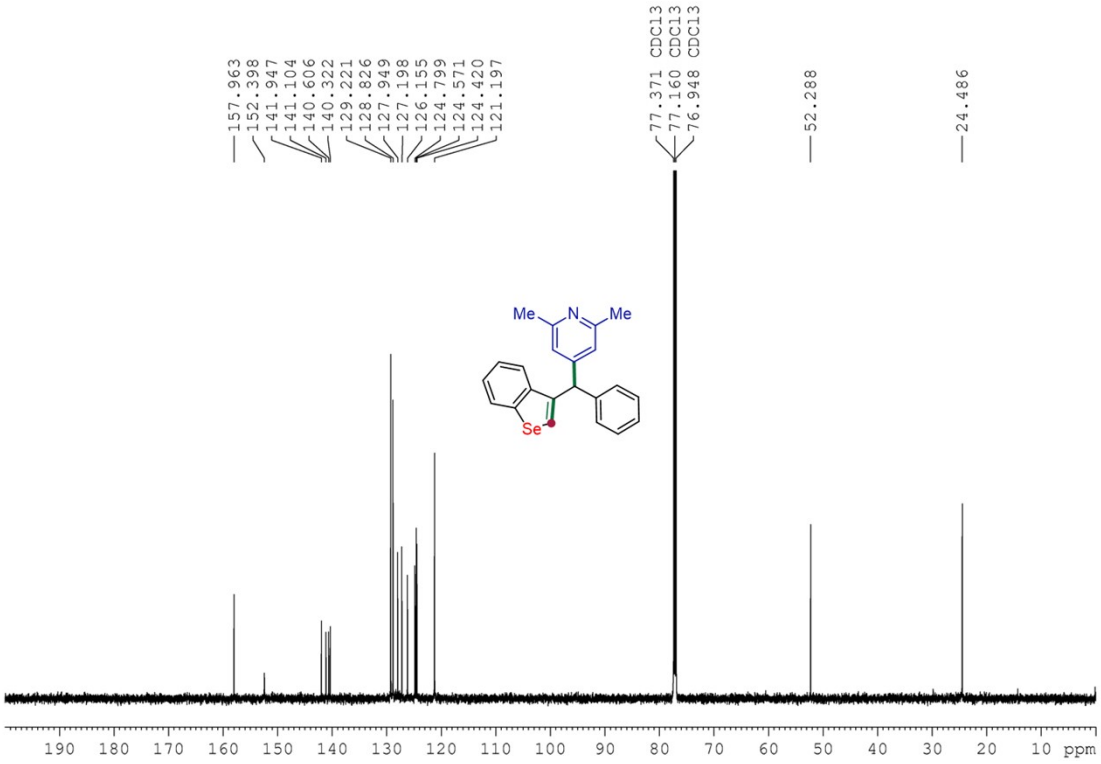
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **27**



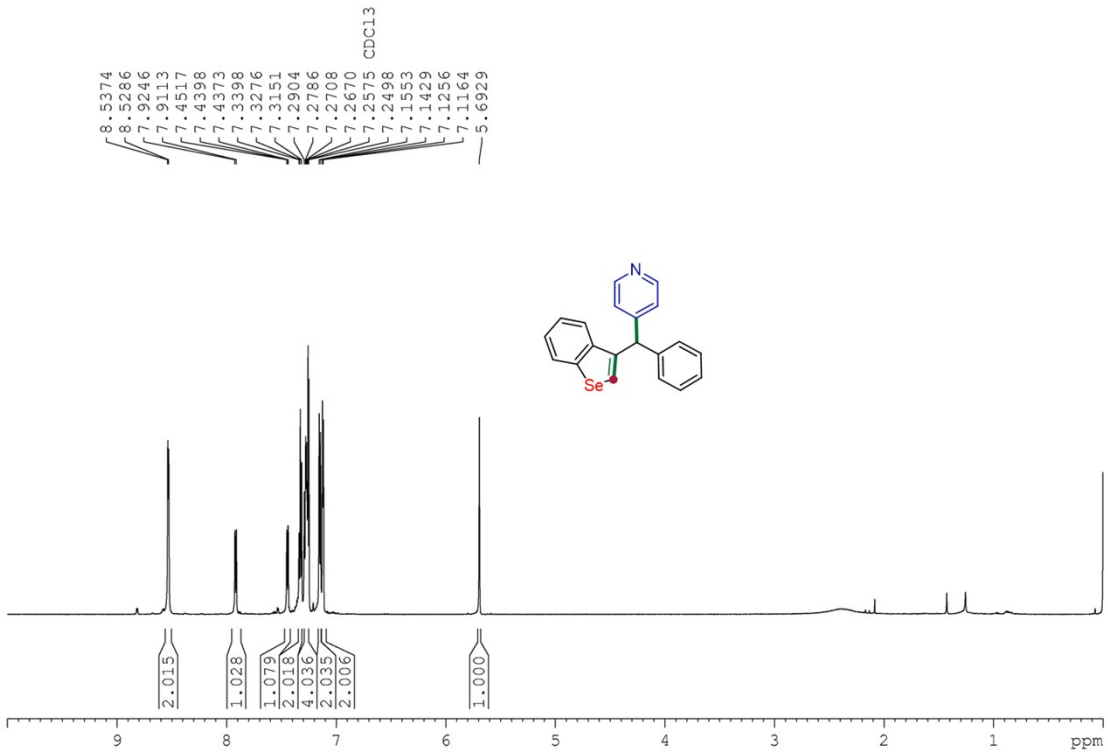
^{1}H NMR (600 MHz, $CDCl_3$) of **28**



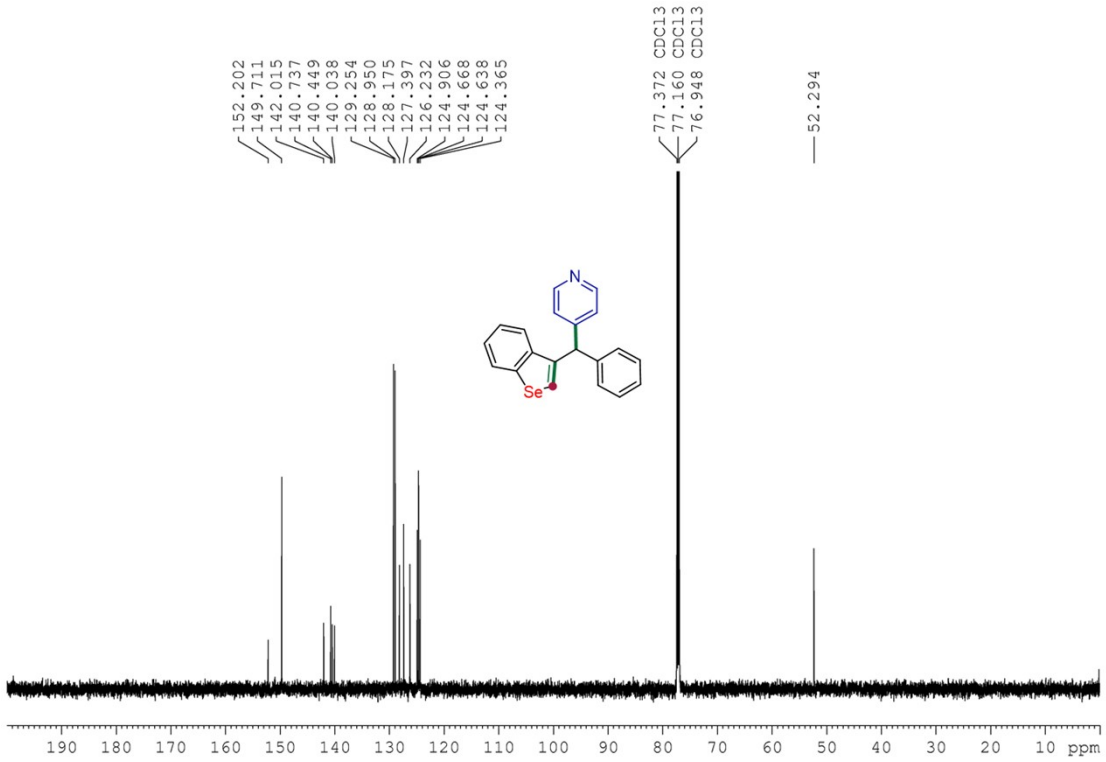
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **28**



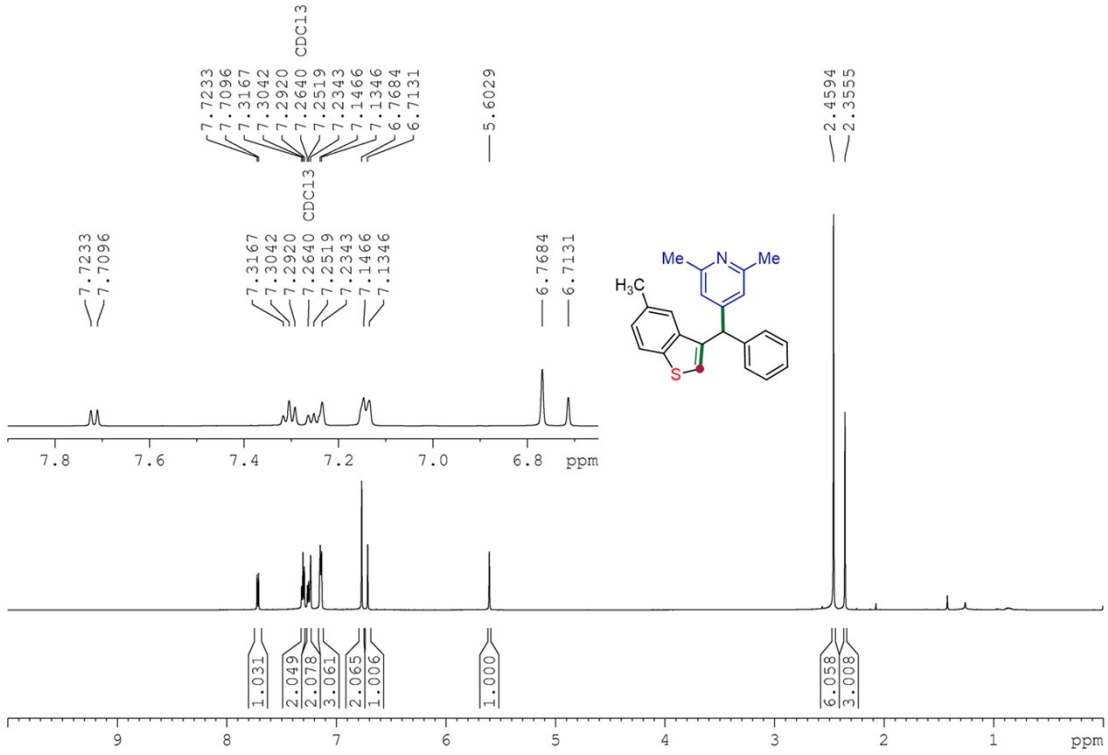
^{1}H NMR (600 MHz, $CDCl_3$) of **29**



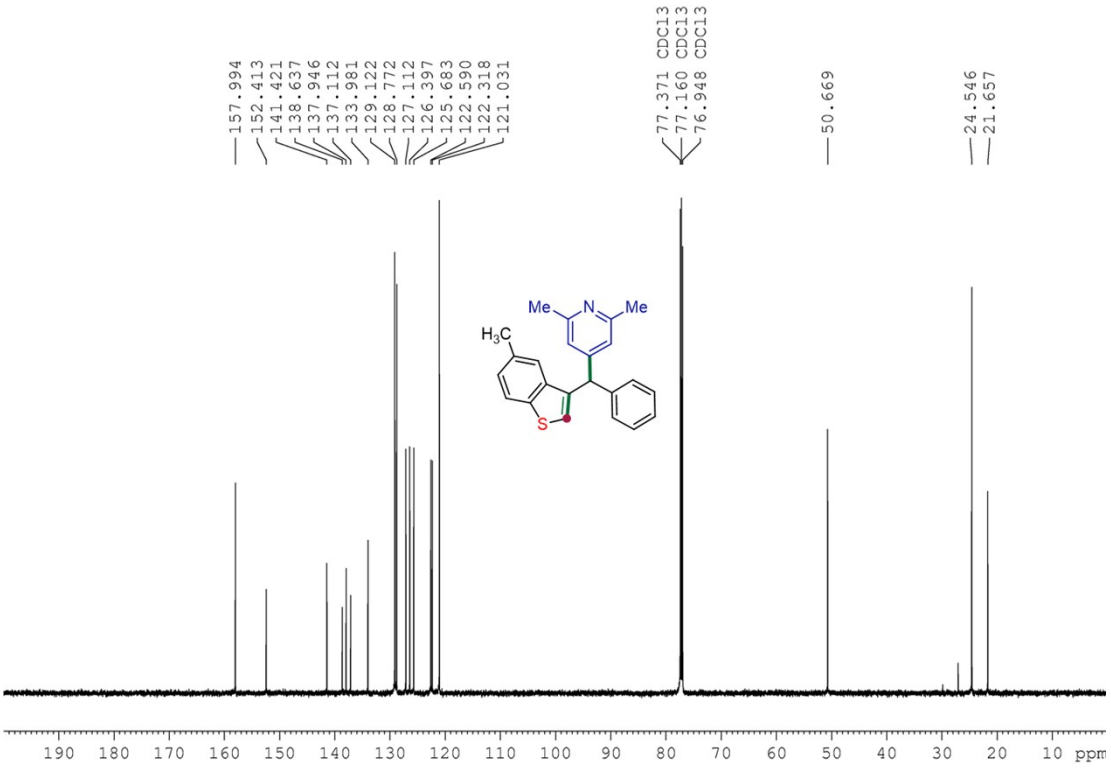
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **29**



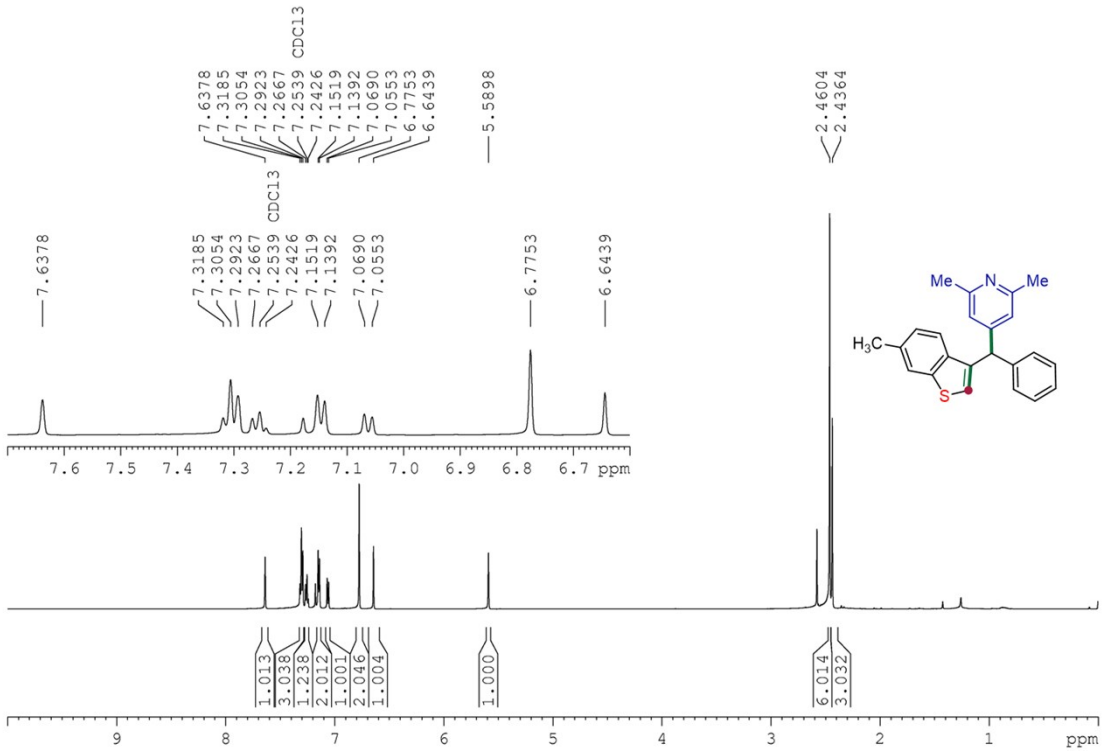
^{1}H NMR (600 MHz, $CDCl_3$) of **30**



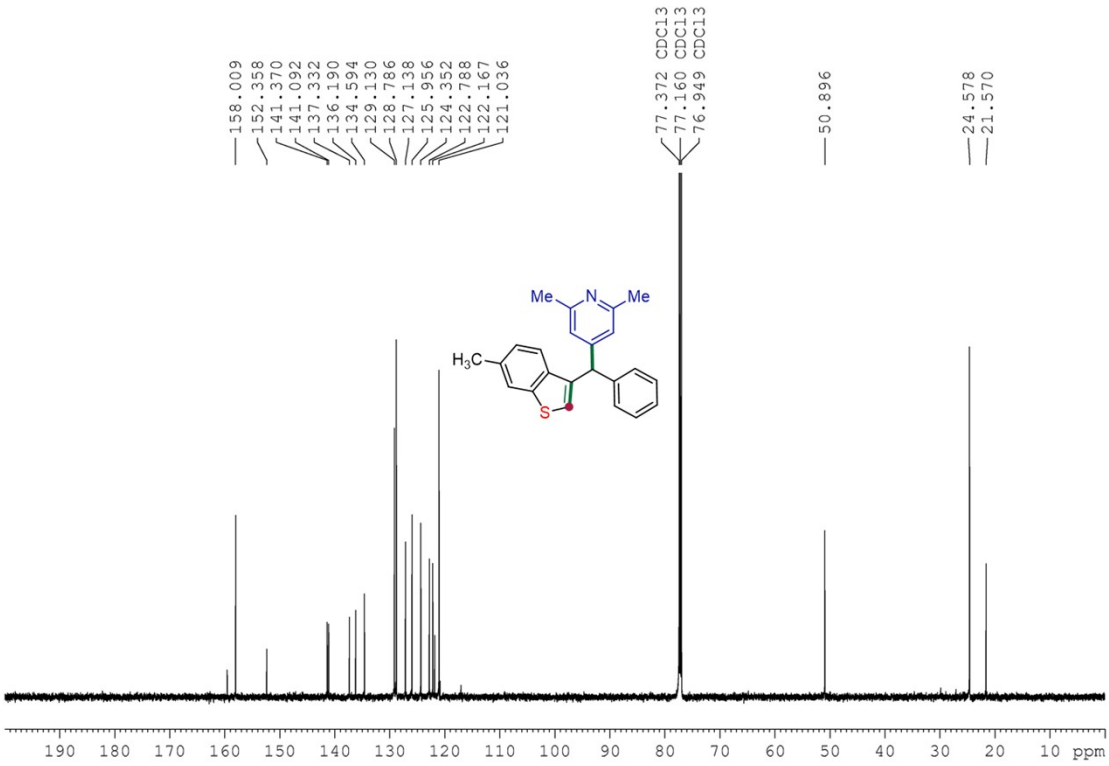
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **30**



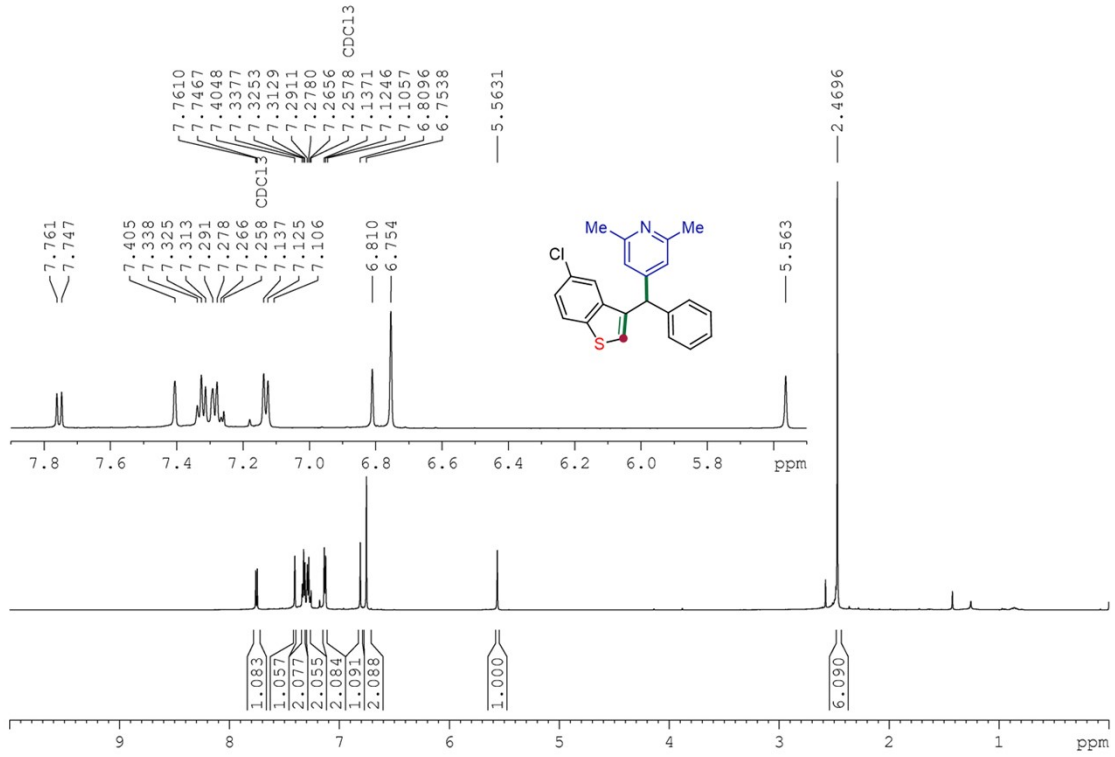
^{1}H NMR (600 MHz, $CDCl_3$) of **31**



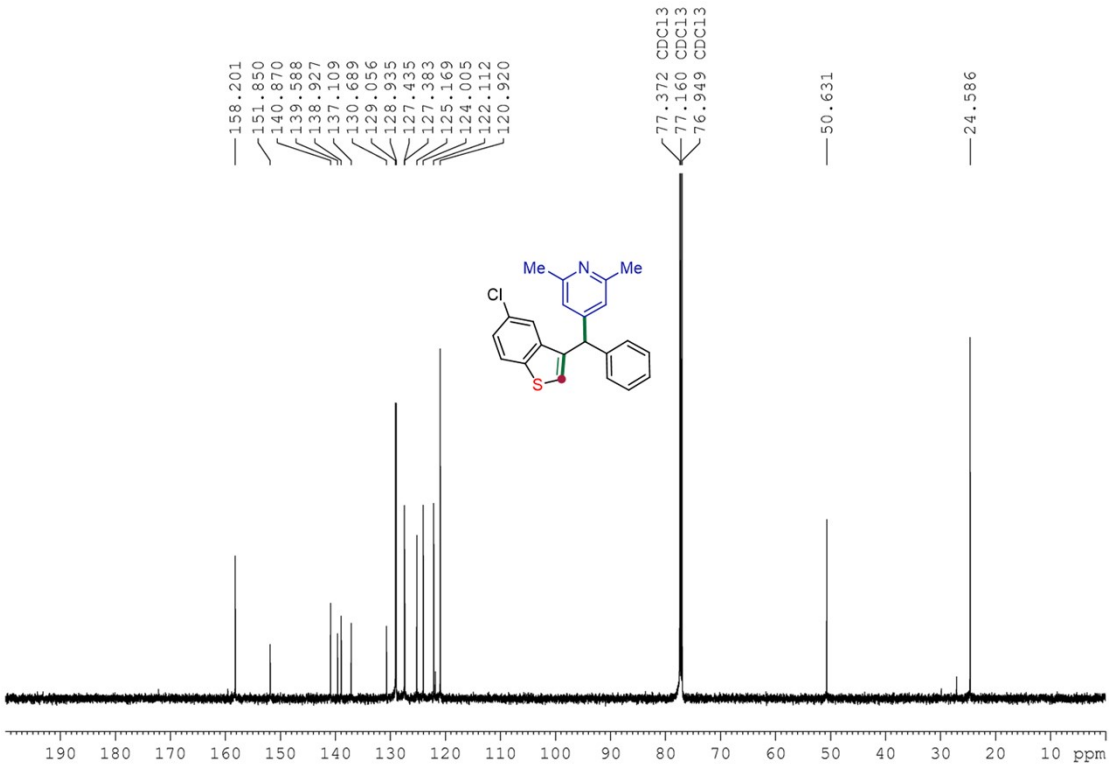
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **31**



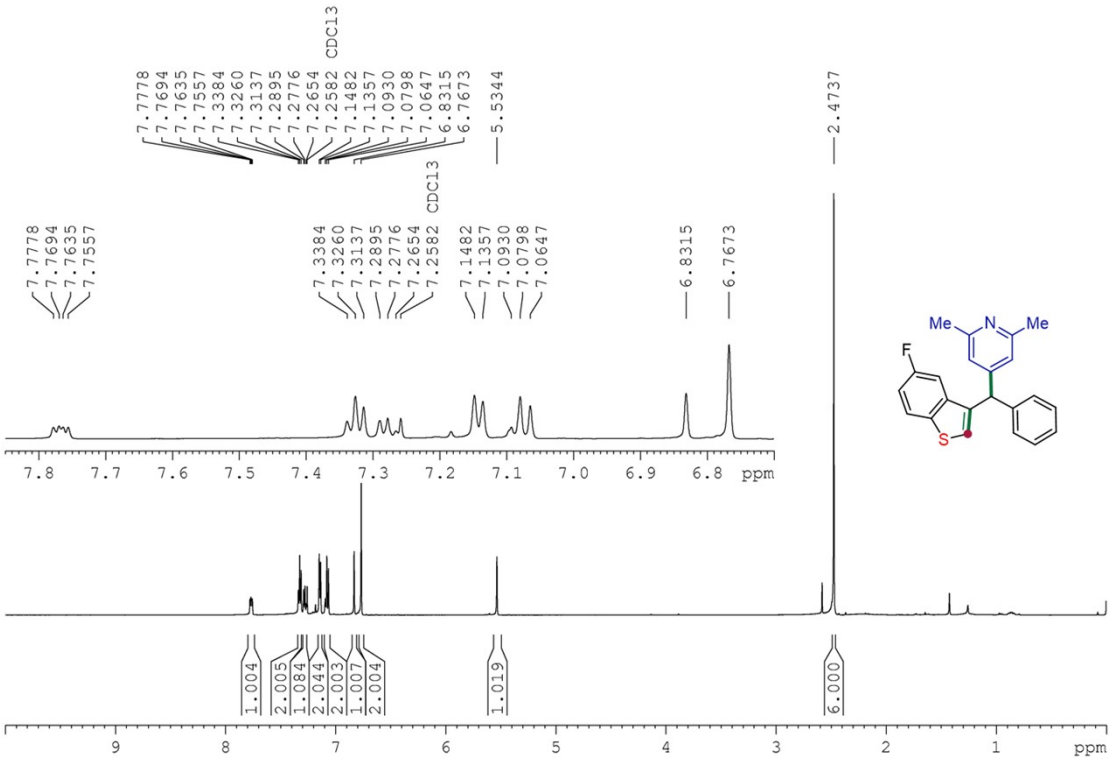
^{1}H NMR (600 MHz, $CDCl_3$) of **32**



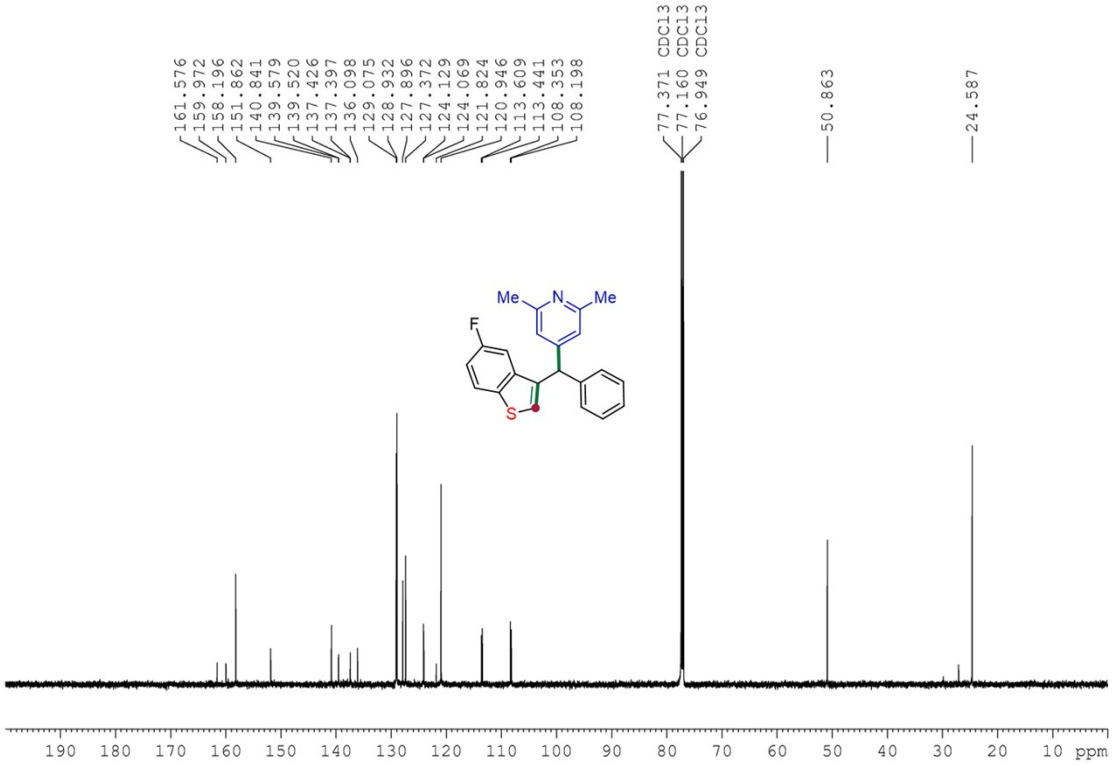
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **32**



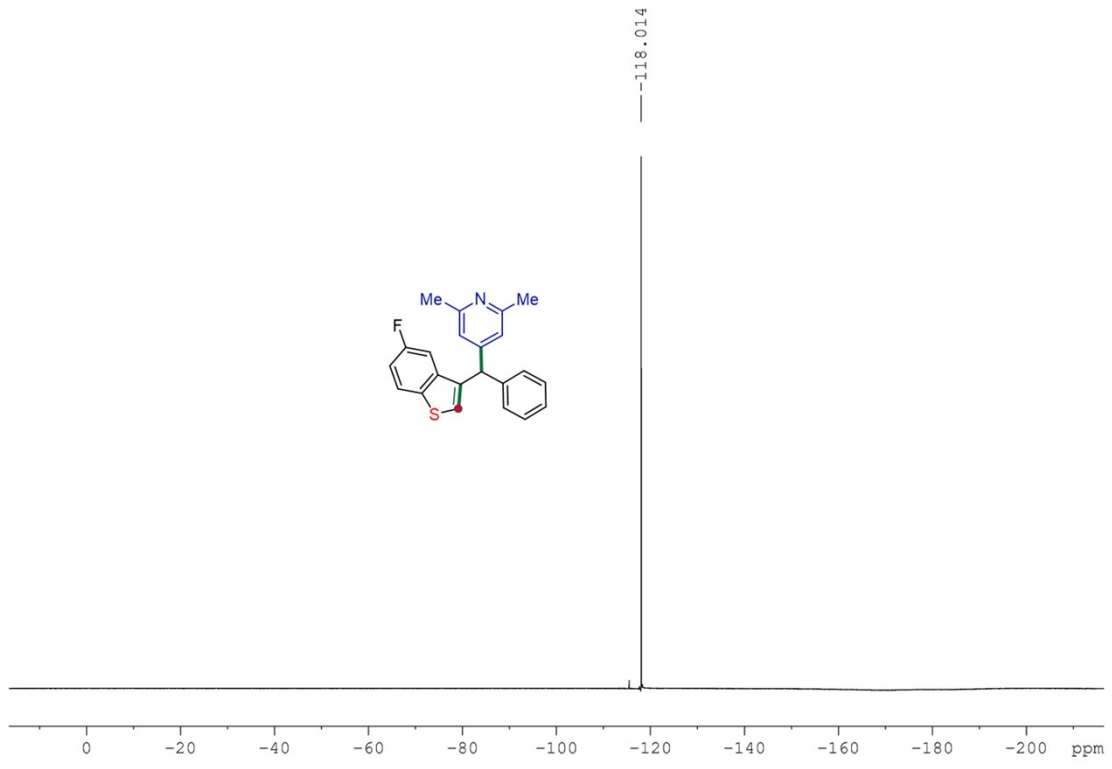
^{1}H NMR (600 MHz, $CDCl_3$) of **33**



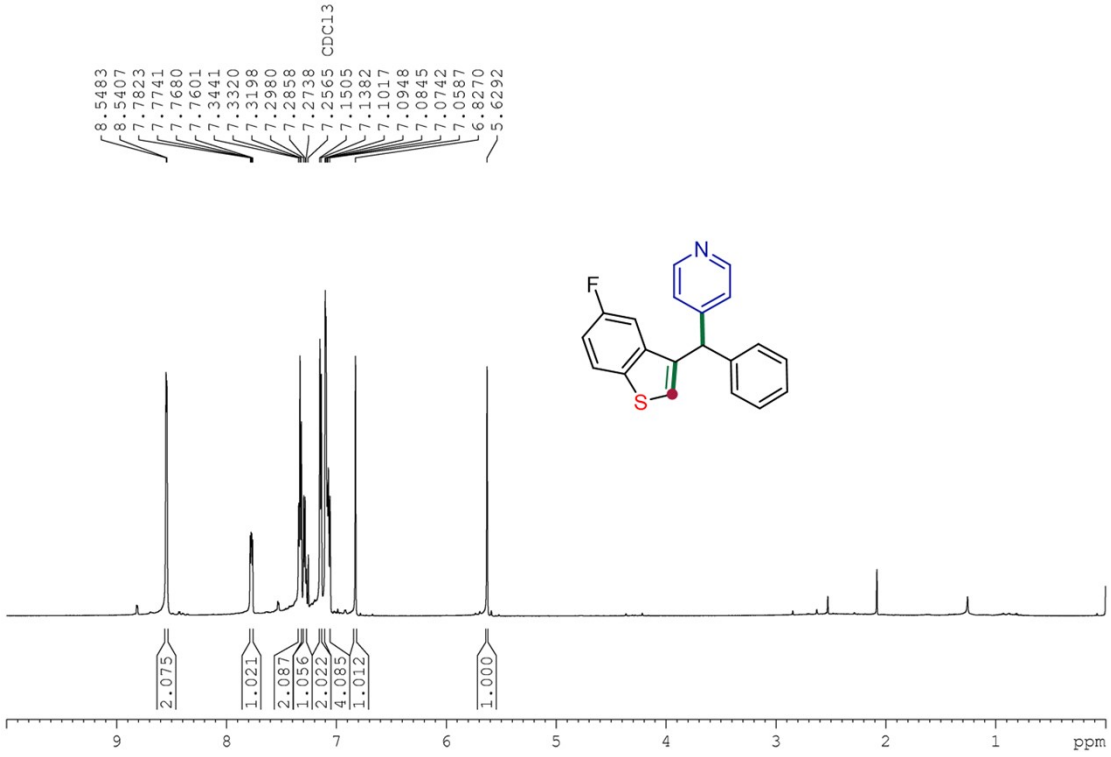
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **33**



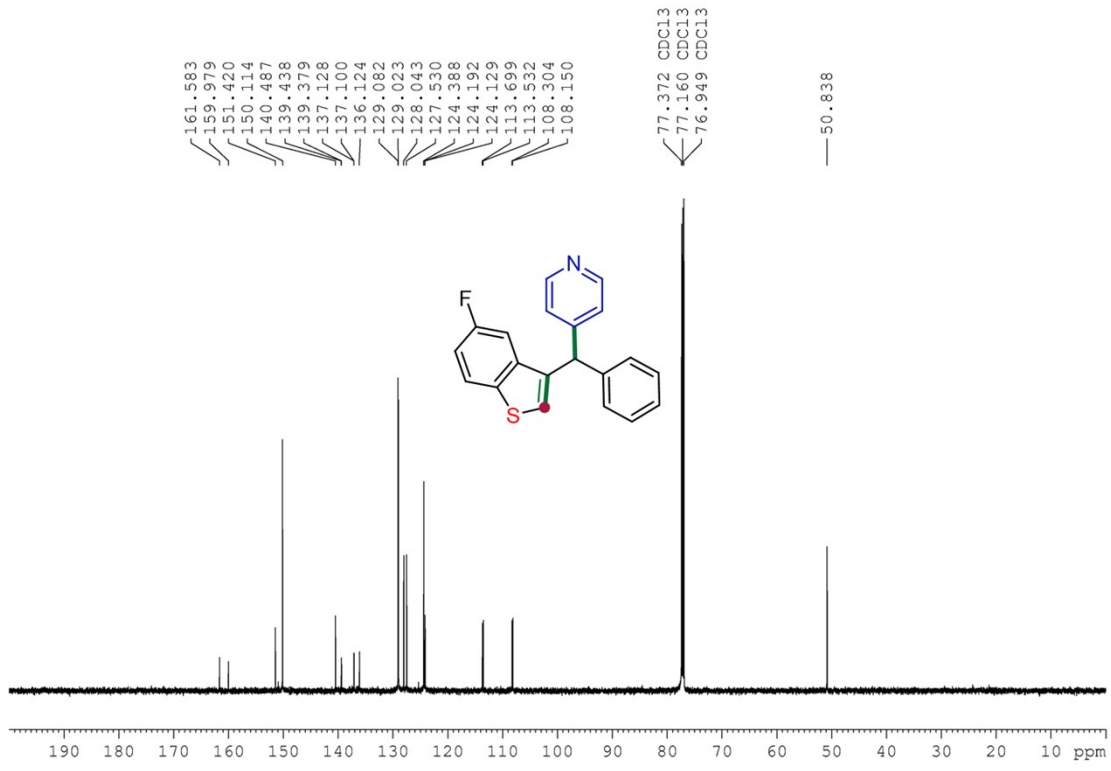
^{19}F NMR (564 MHz, $CDCl_3$) of **33**



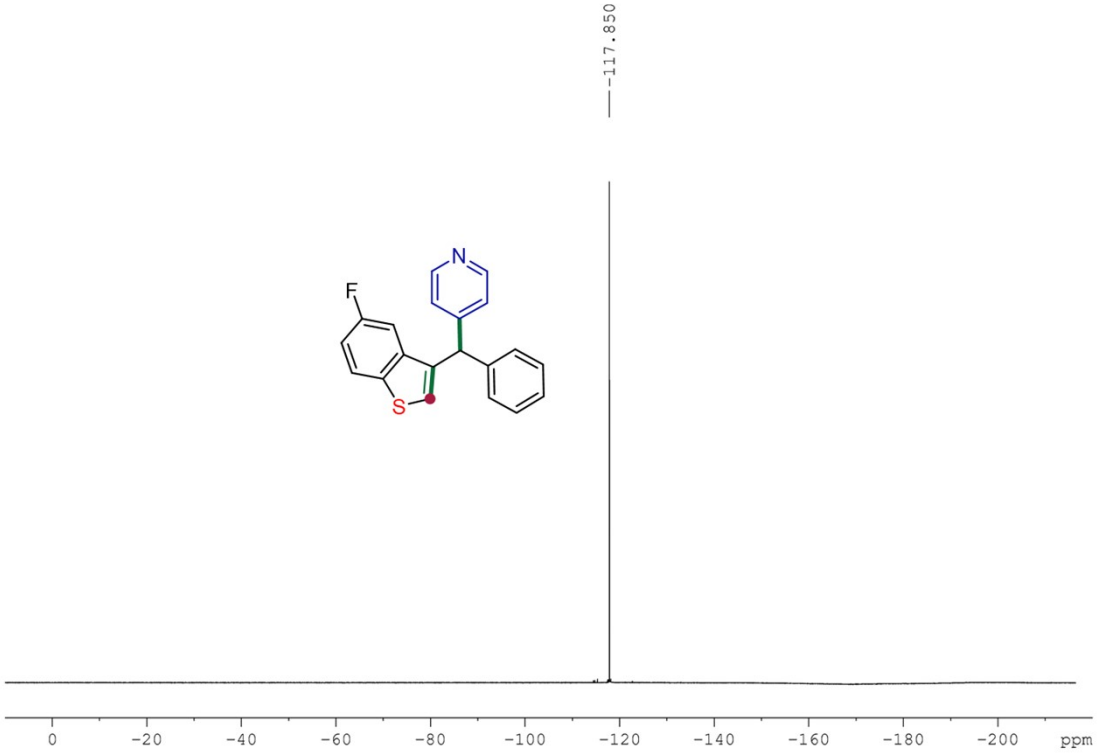
^{1}H NMR (600 MHz, $CDCl_3$) of **34**



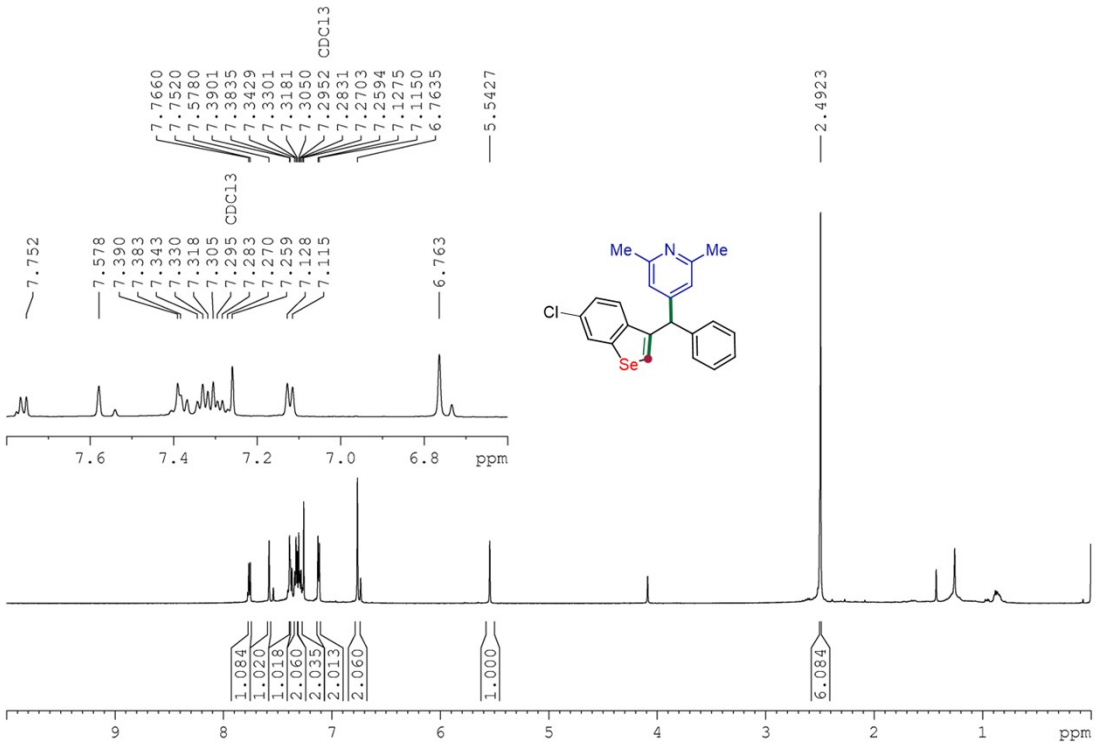
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **34**



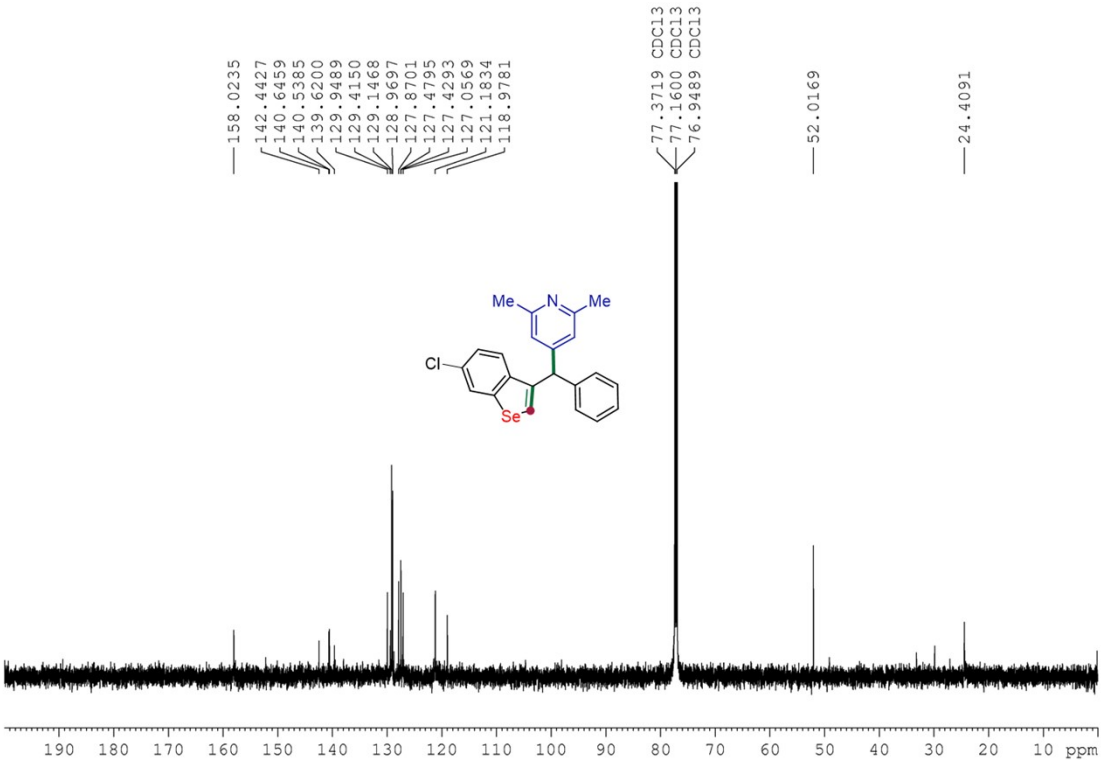
^{19}F NMR (564 MHz, $CDCl_3$) of **34**



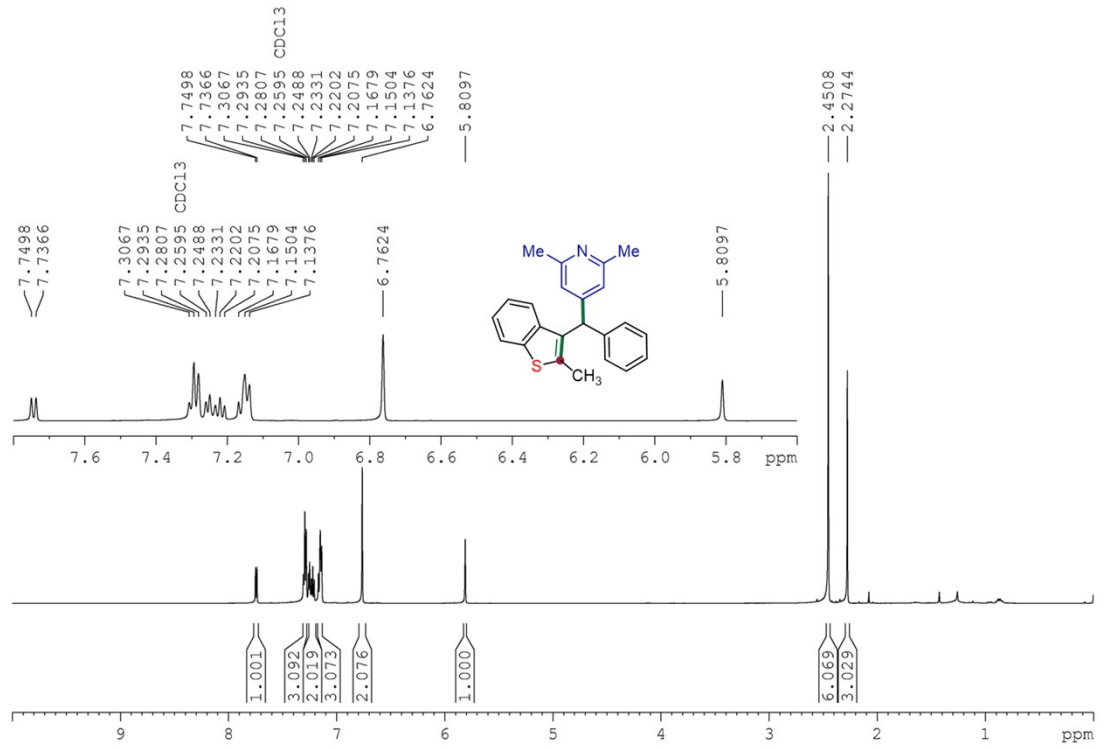
^{1}H NMR (600 MHz, $CDCl_3$) of **35**



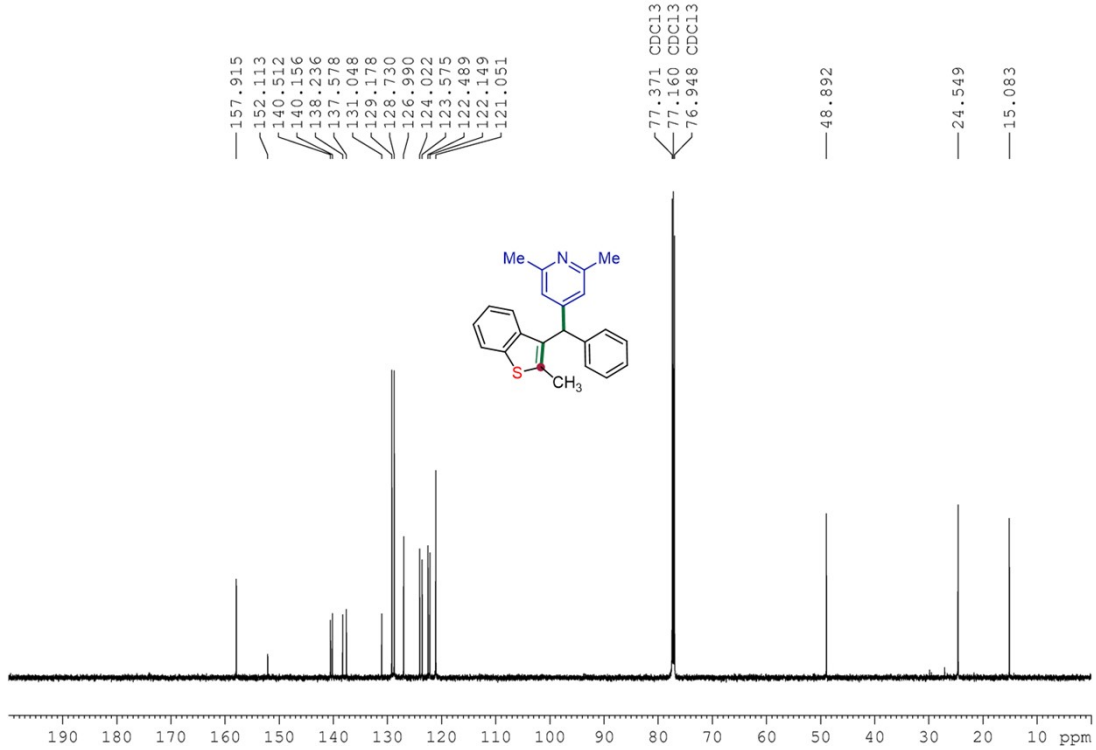
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **35**



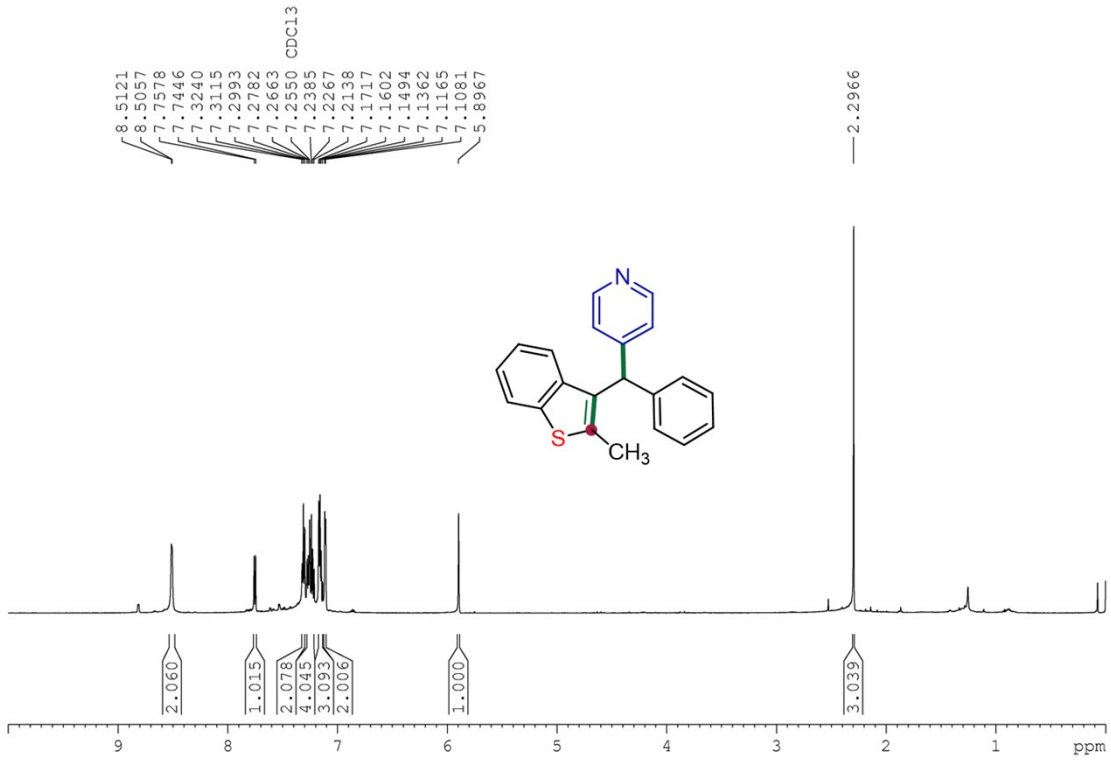
^{1}H NMR (600 MHz, $CDCl_3$) of **36**



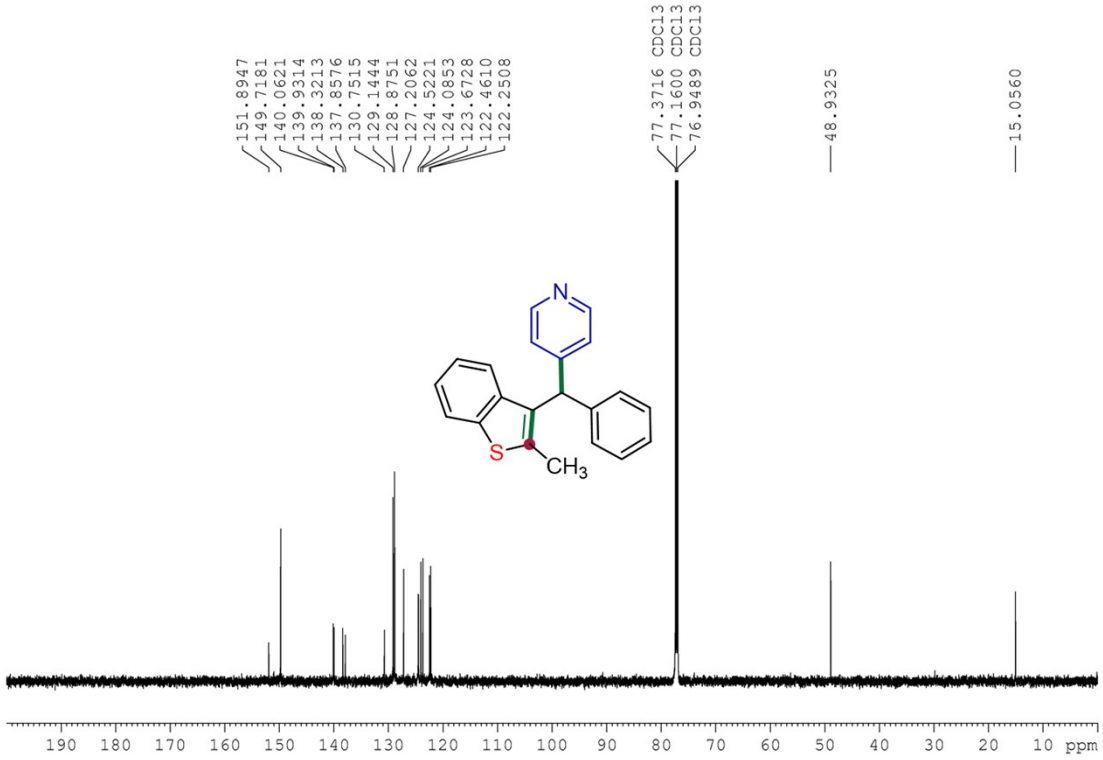
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **36**



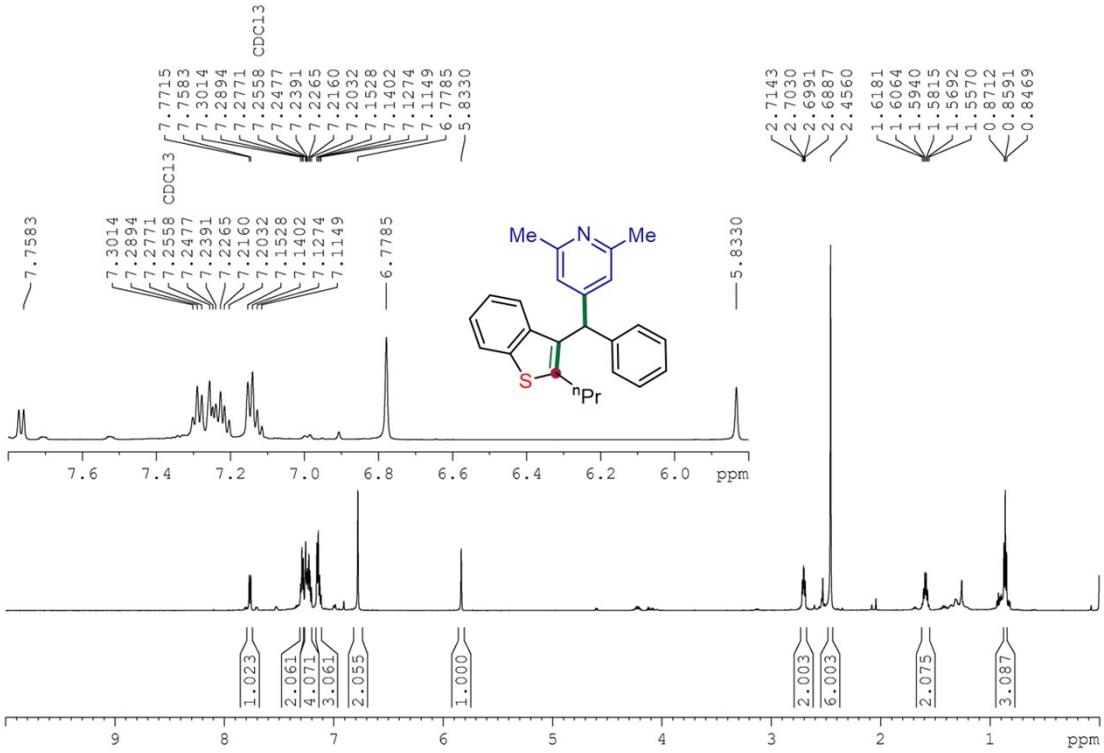
^{1}H NMR (600 MHz, $CDCl_3$) of **37**



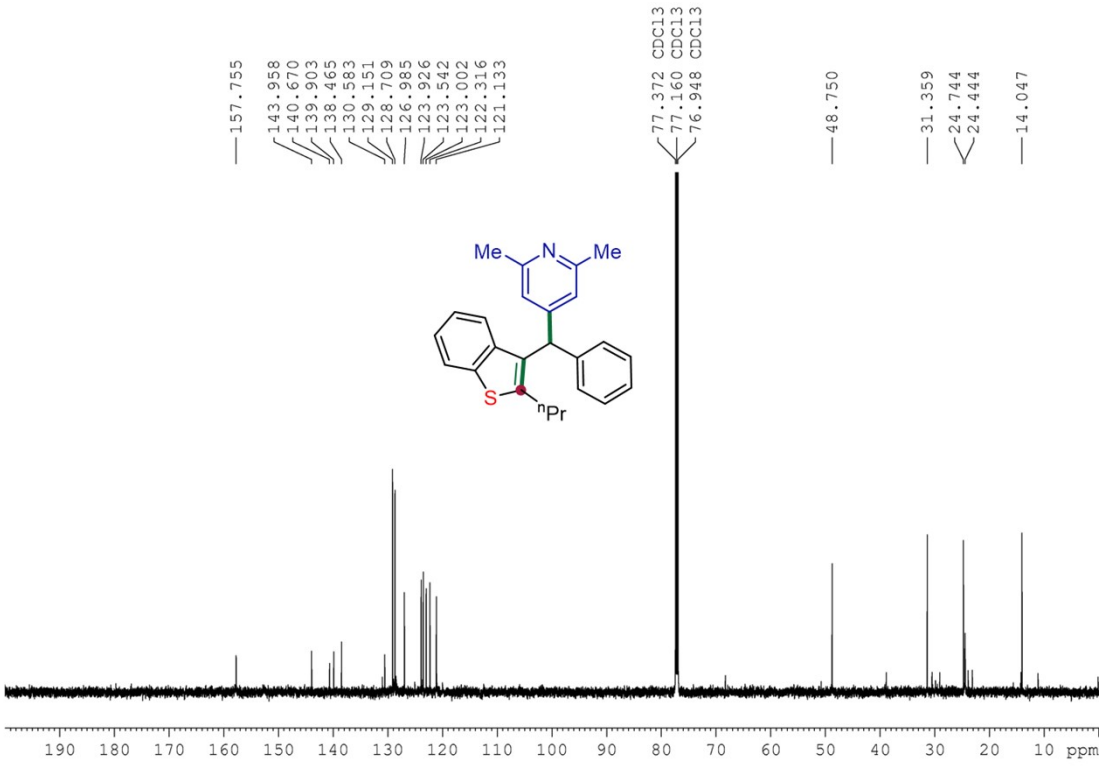
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **37**



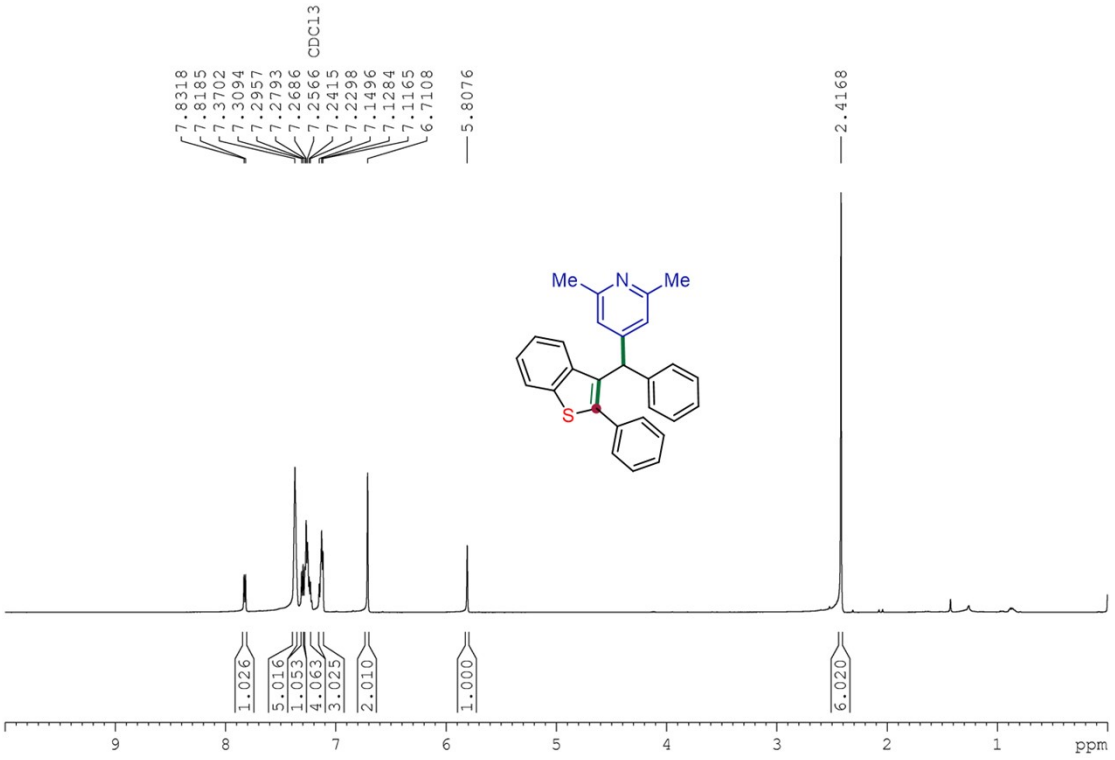
^{1}H NMR (600 MHz, $CDCl_3$) of **38**



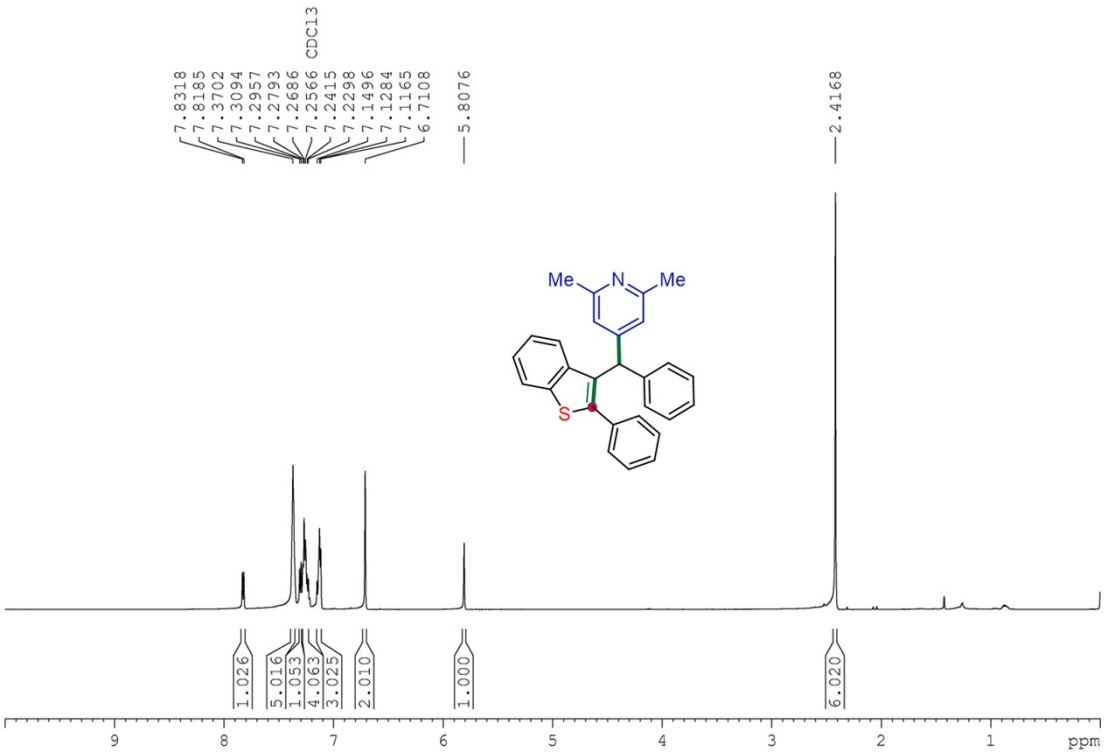
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **38**



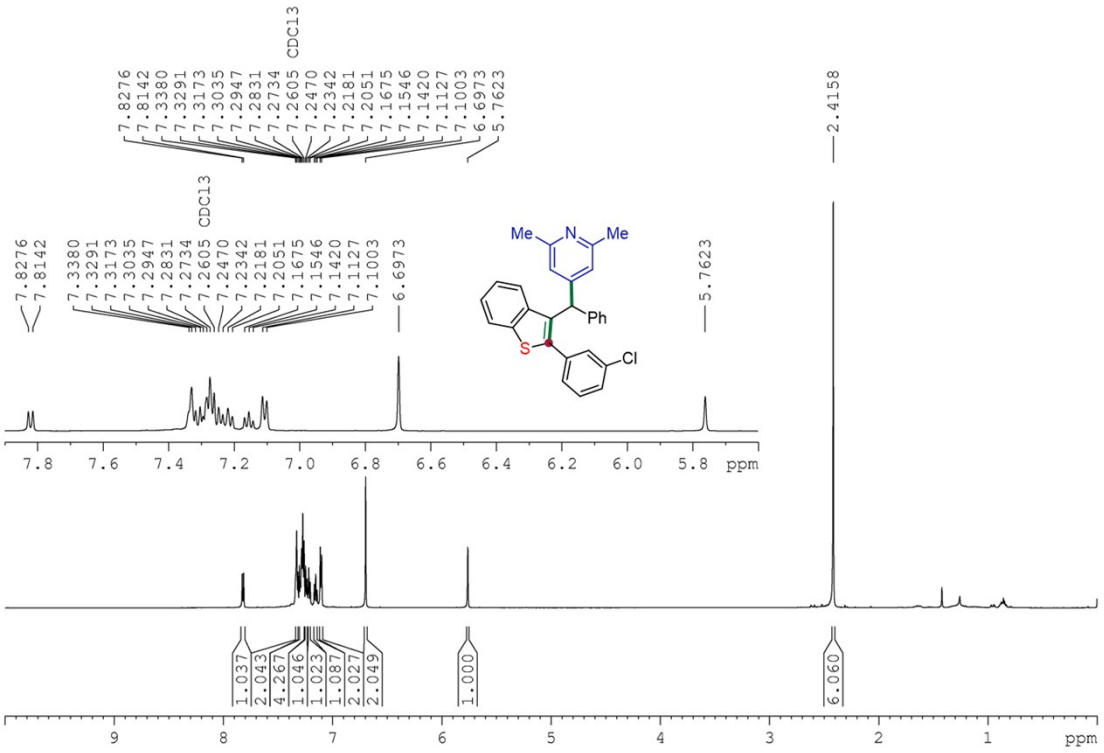
^{1}H NMR (600 MHz, $CDCl_3$) of **39**



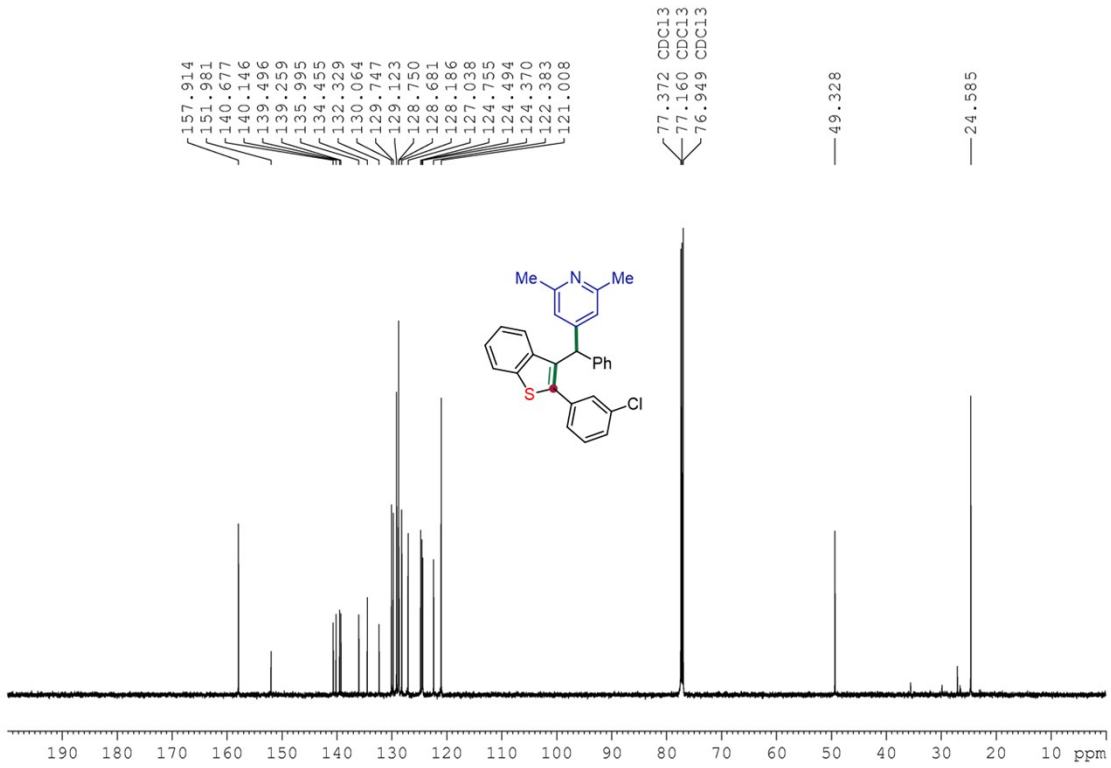
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **39**



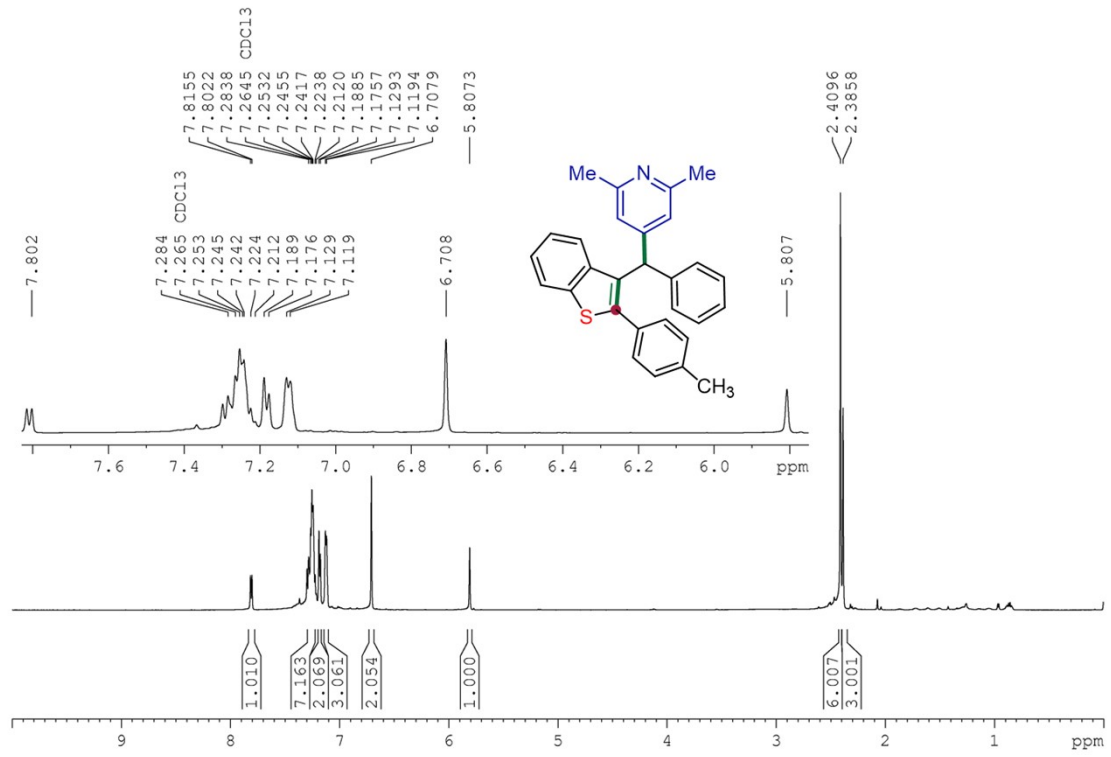
^{1}H NMR (600 MHz, $CDCl_3$) of **40**



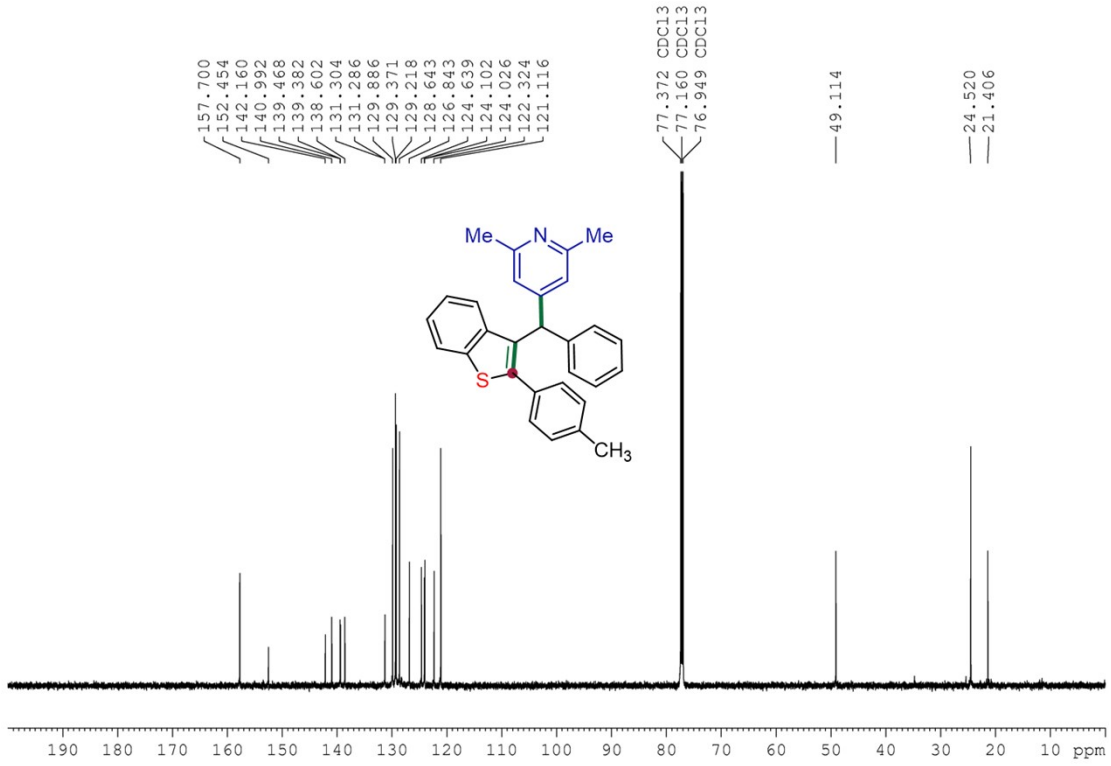
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **40**



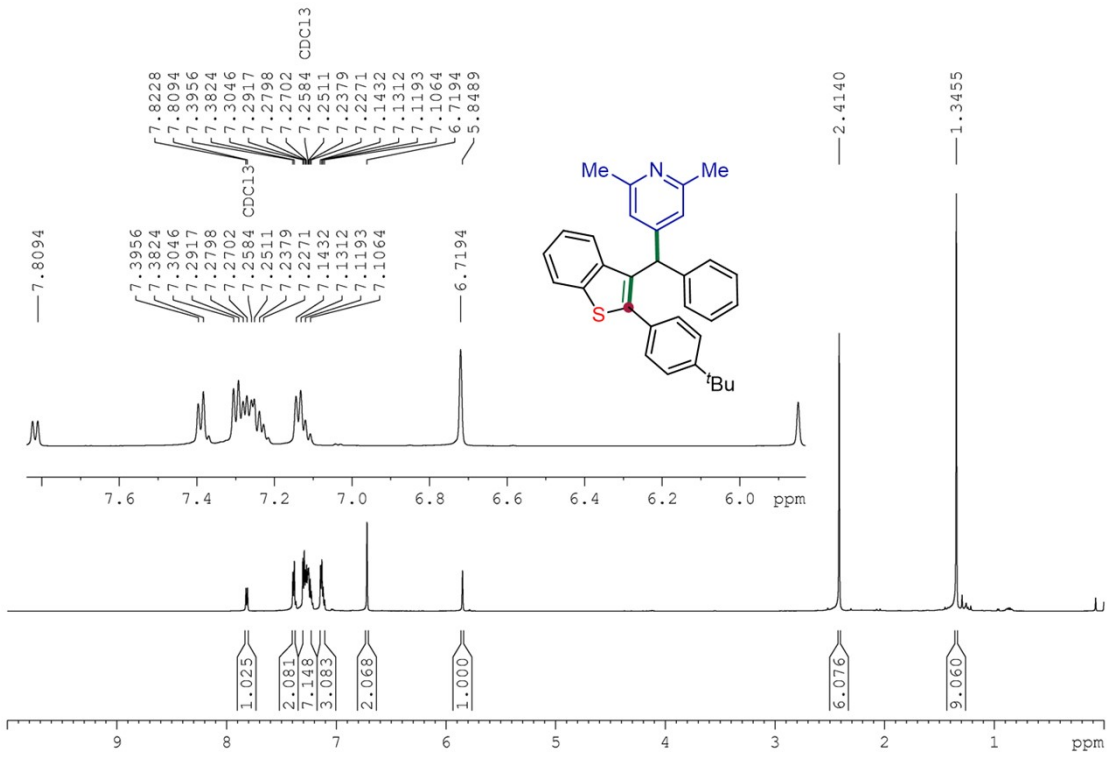
^{1}H NMR (600 MHz, $CDCl_3$) of **41**



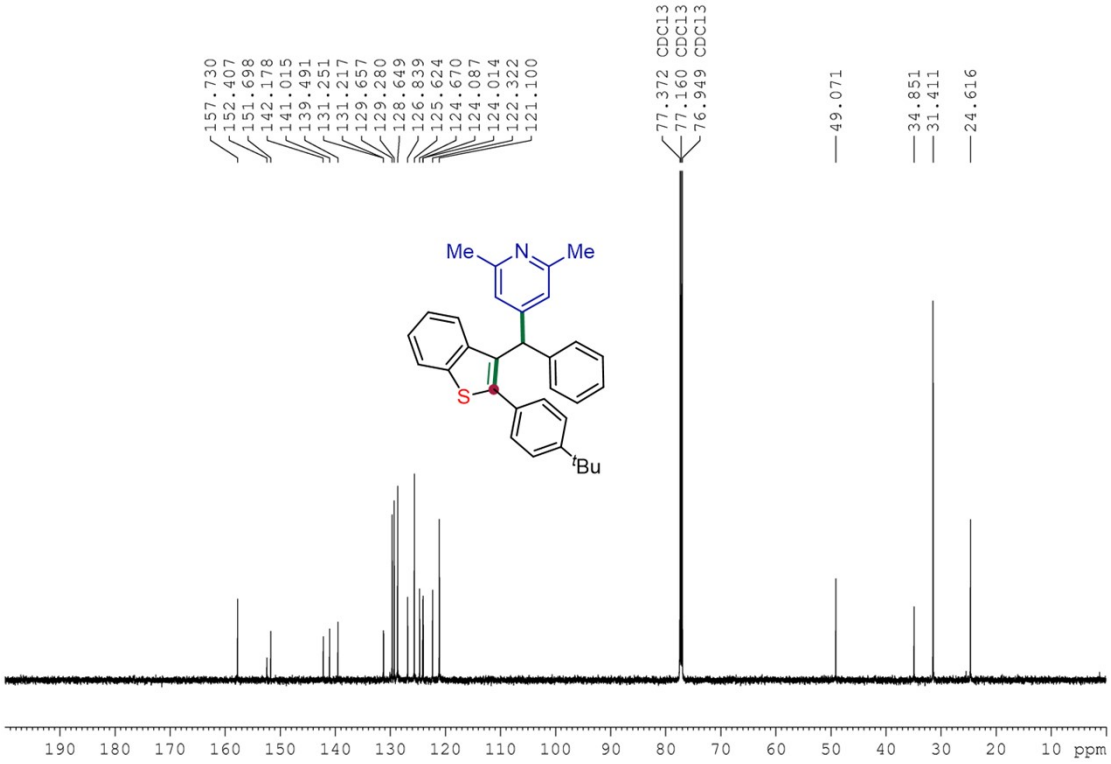
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **41**



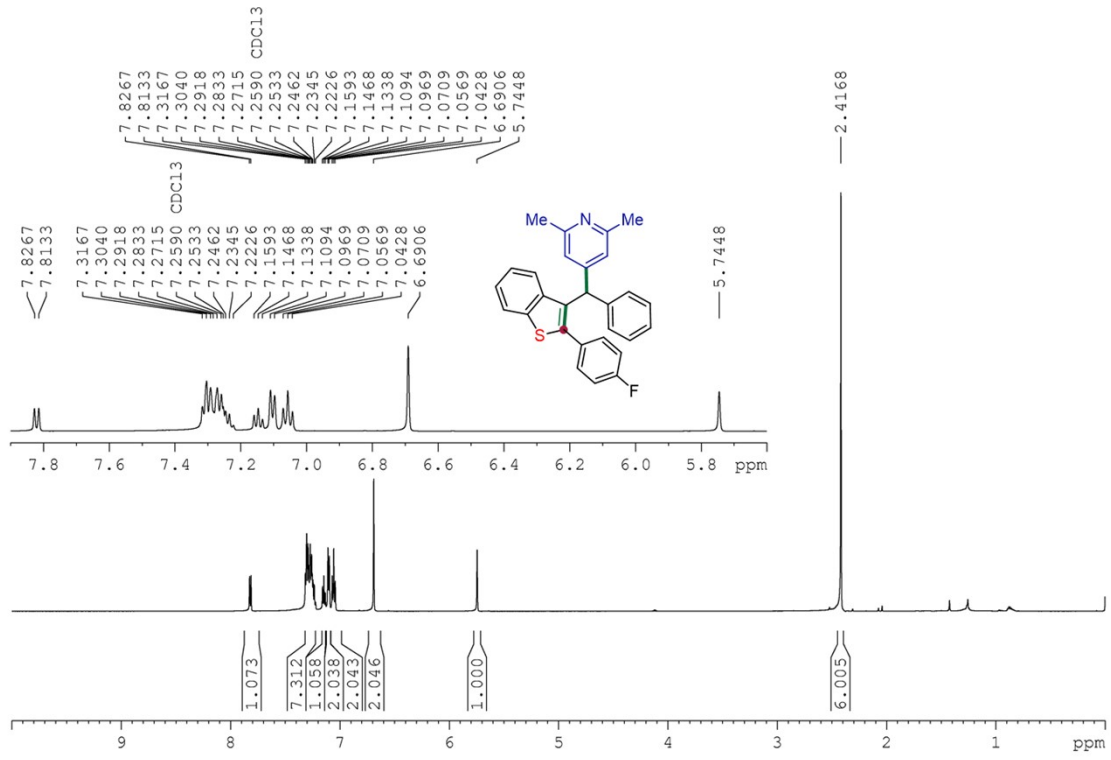
^{1}H NMR (600 MHz, $CDCl_3$) of **42**



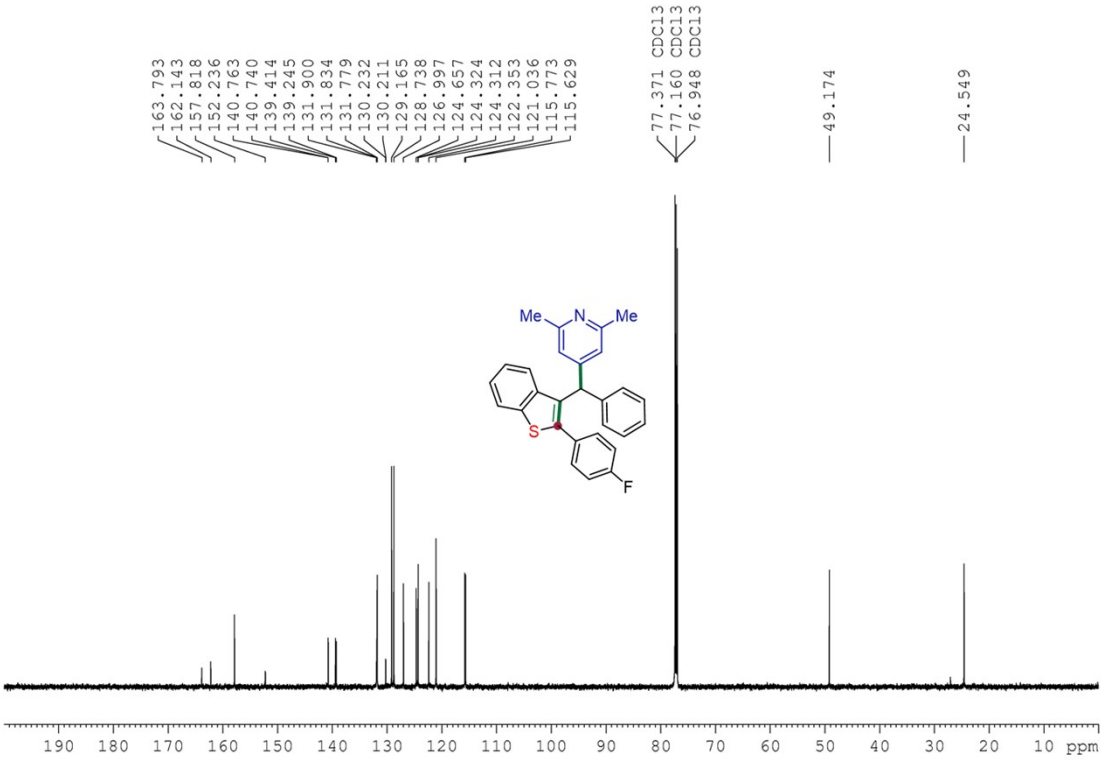
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **42**



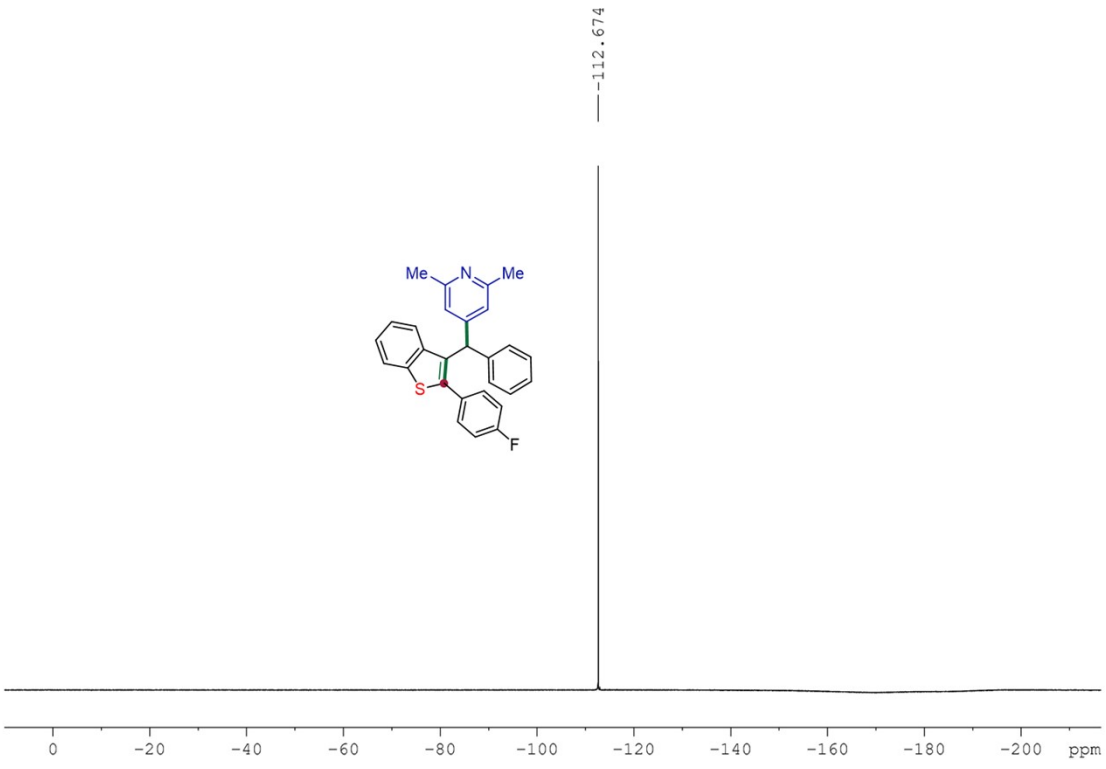
^{1}H NMR (600 MHz, $CDCl_3$) of **43**



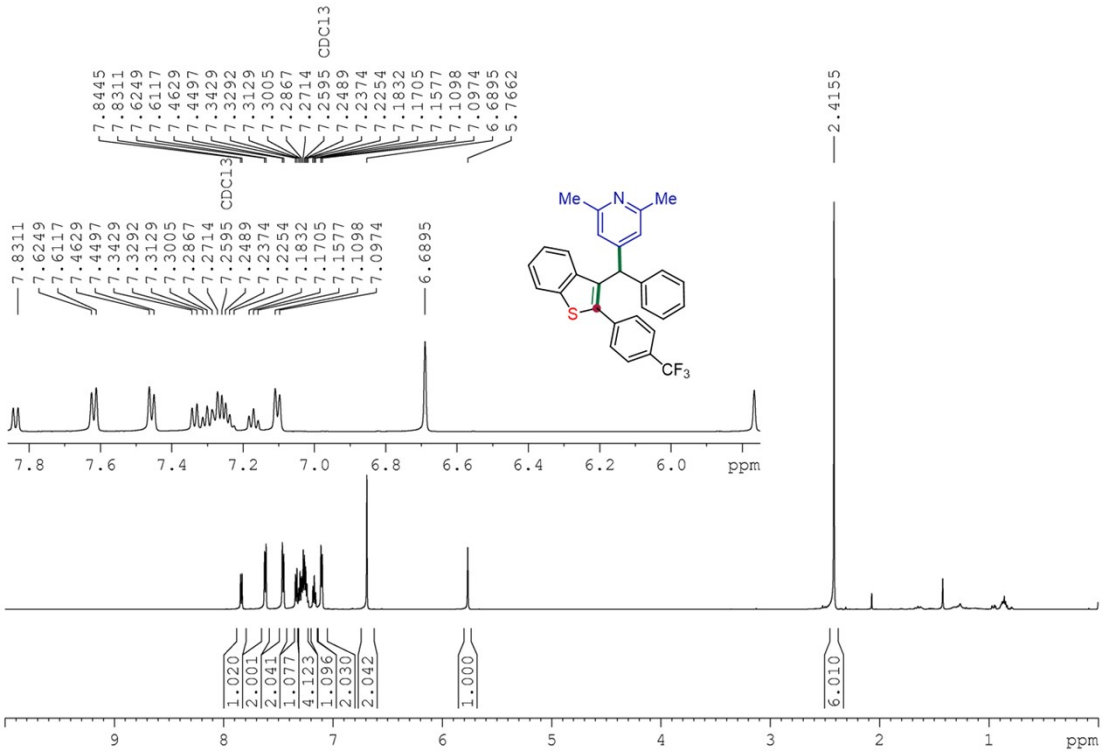
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **43**



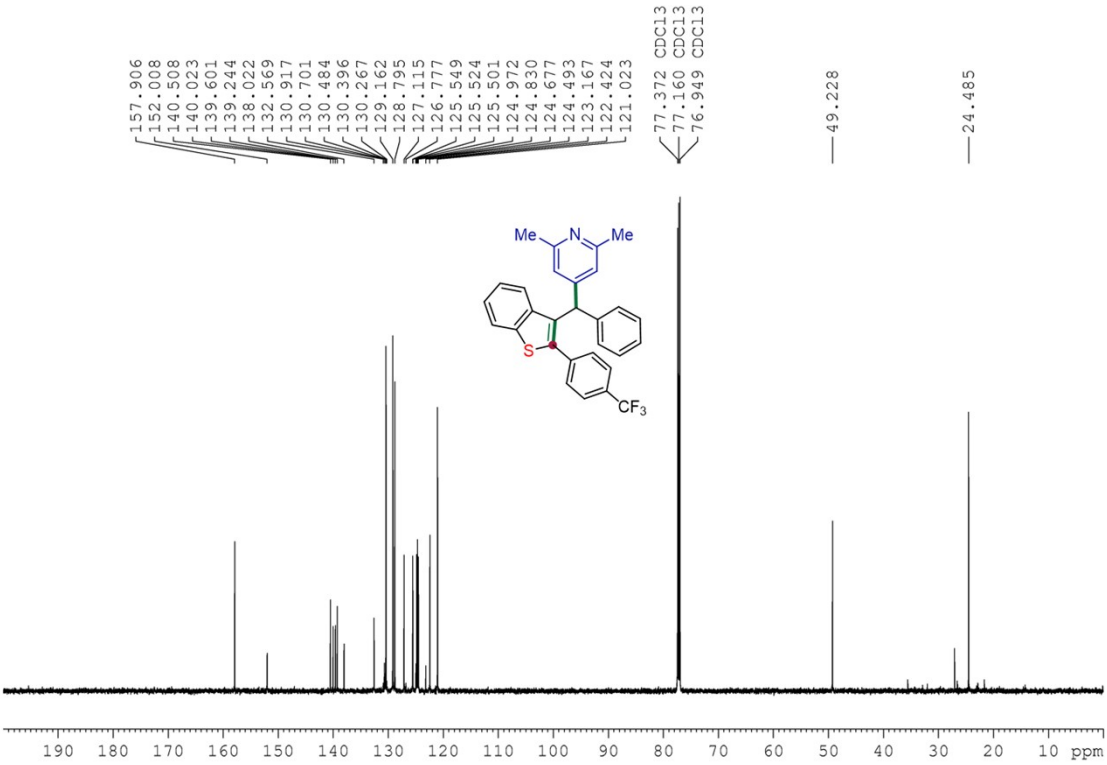
^{19}F NMR (564 MHz, $CDCl_3$) of **43**



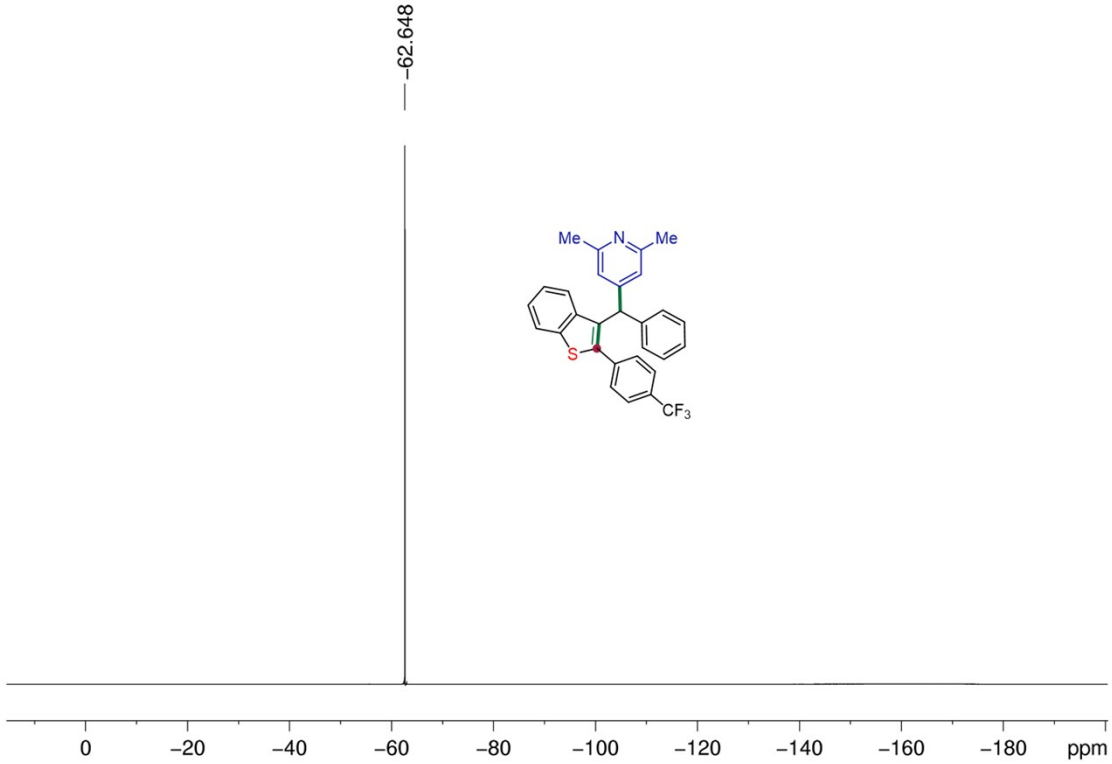
^{1}H NMR (600 MHz, $CDCl_3$) of **44**



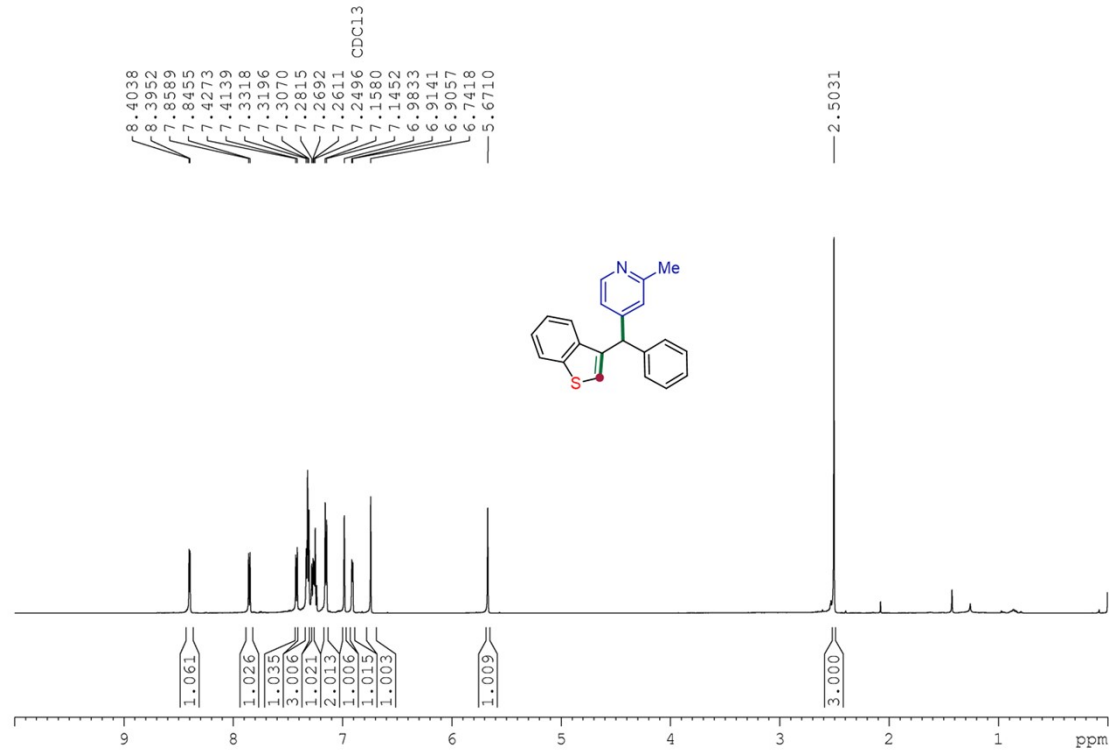
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **44**



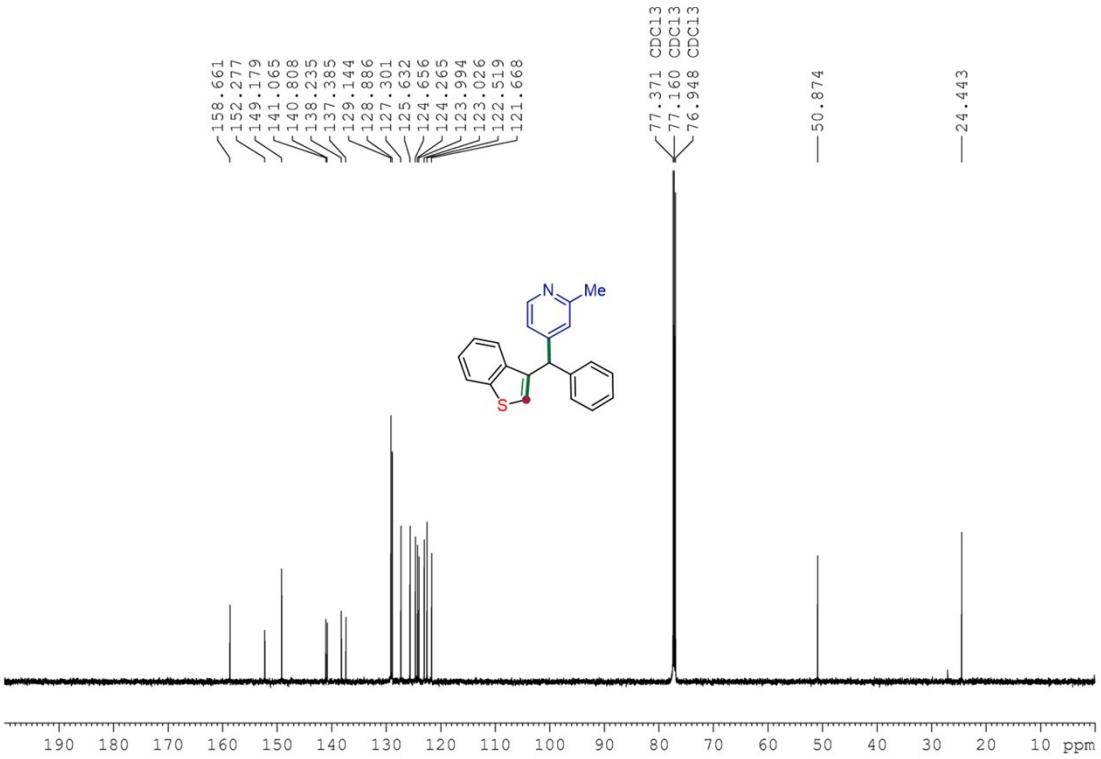
^{19}F NMR (564 MHz, $CDCl_3$) of **44**



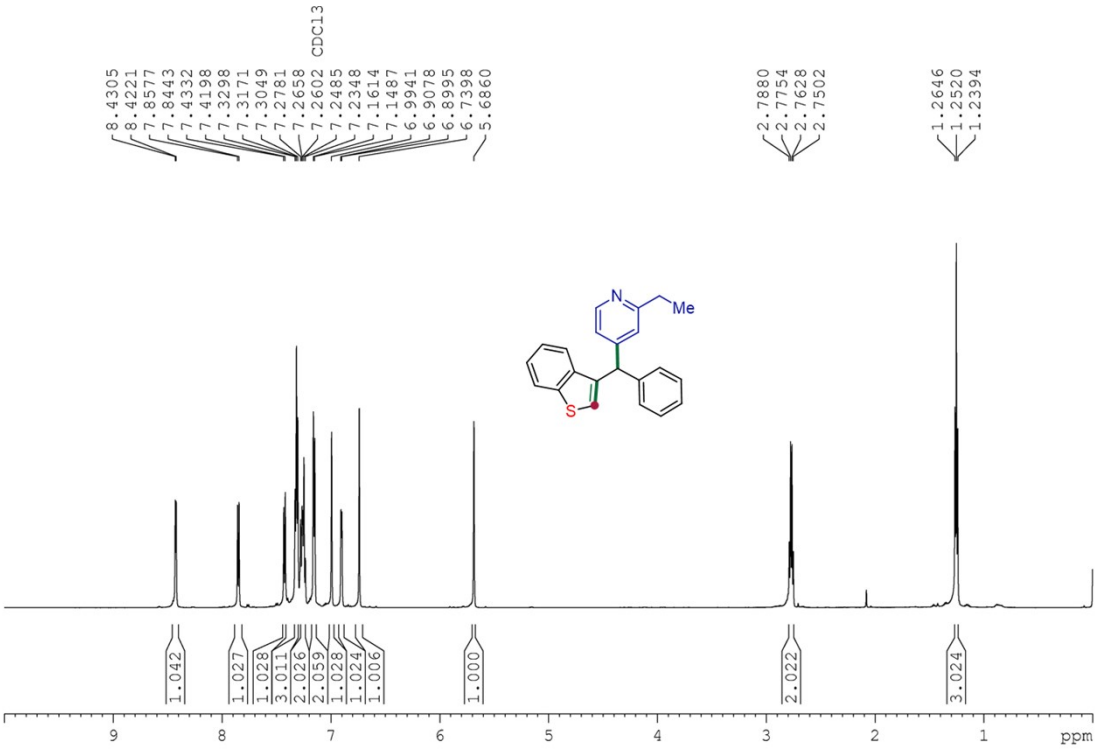
^{1}H NMR (600 MHz, $CDCl_3$) of **45**



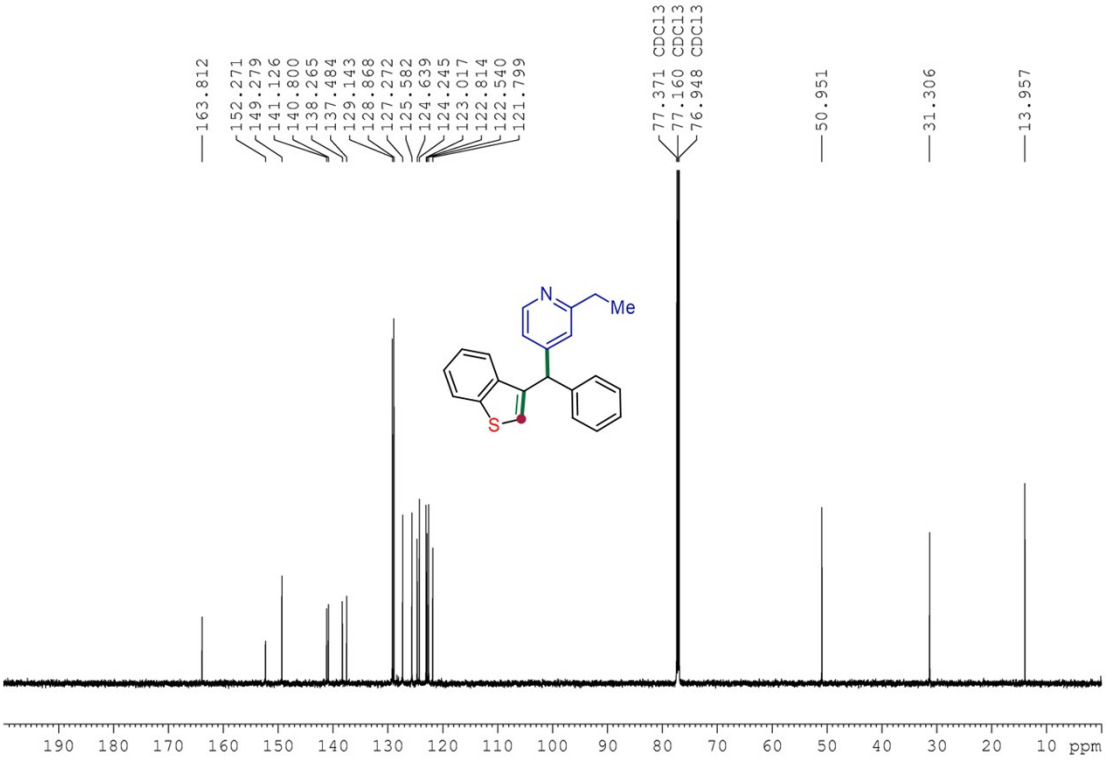
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **45**



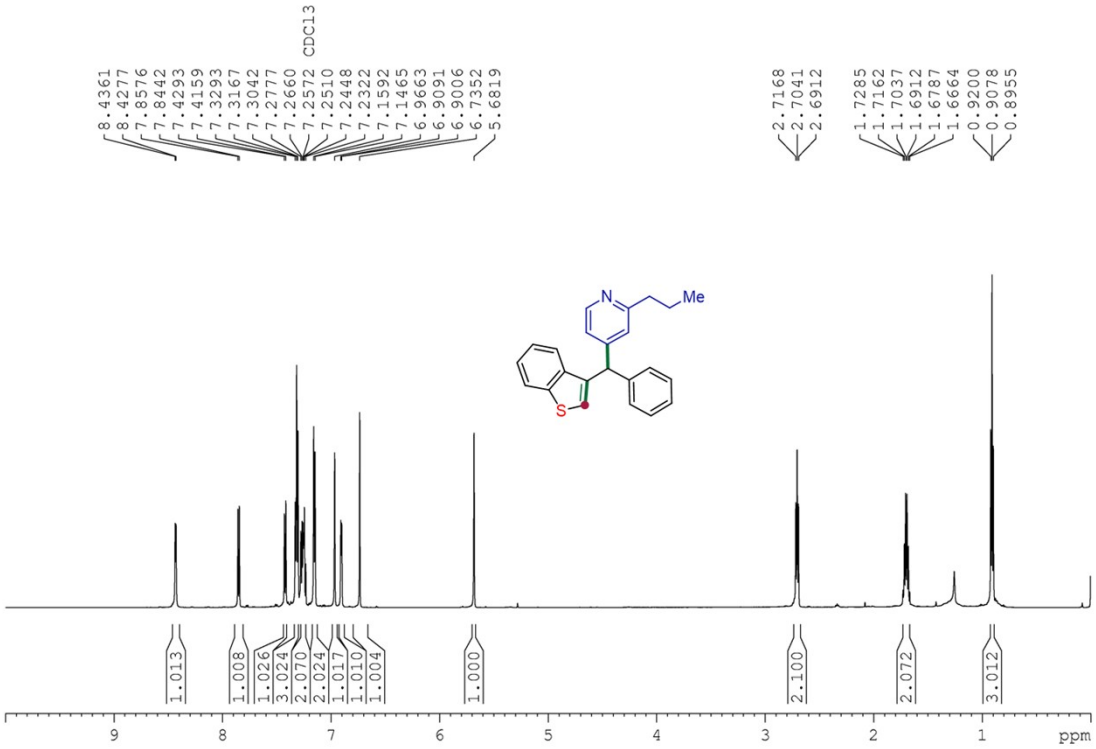
^{1}H NMR (600 MHz, $CDCl_3$) of **46**



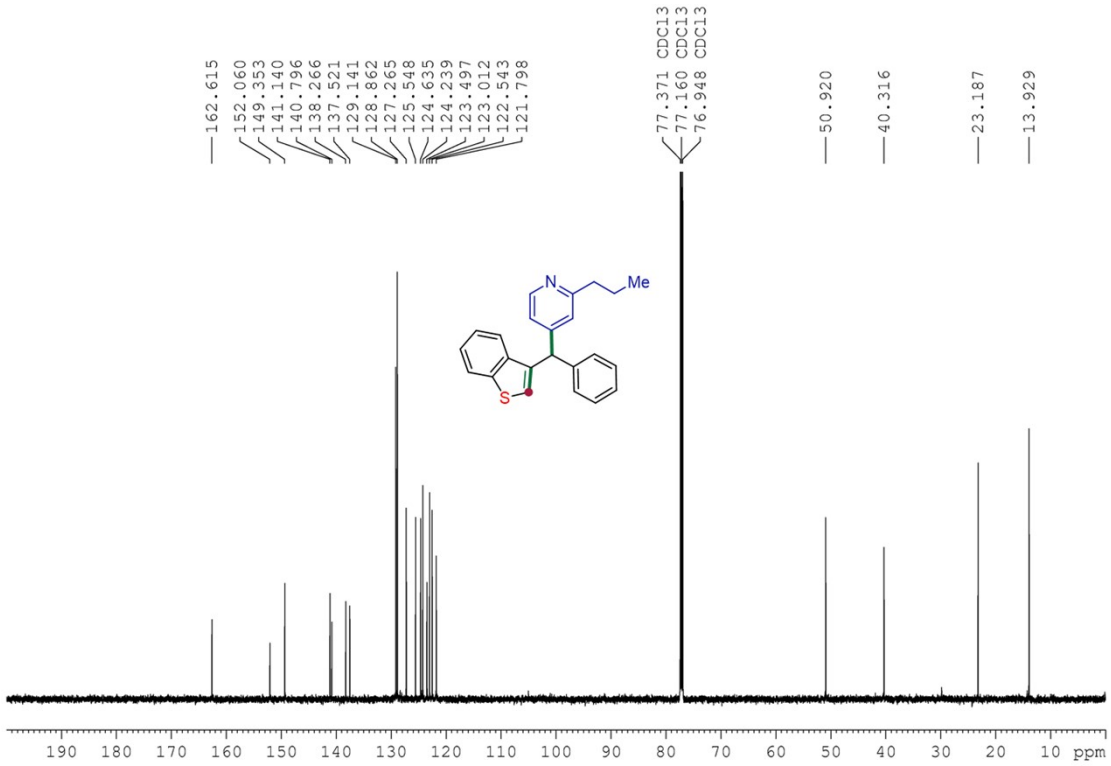
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **46**



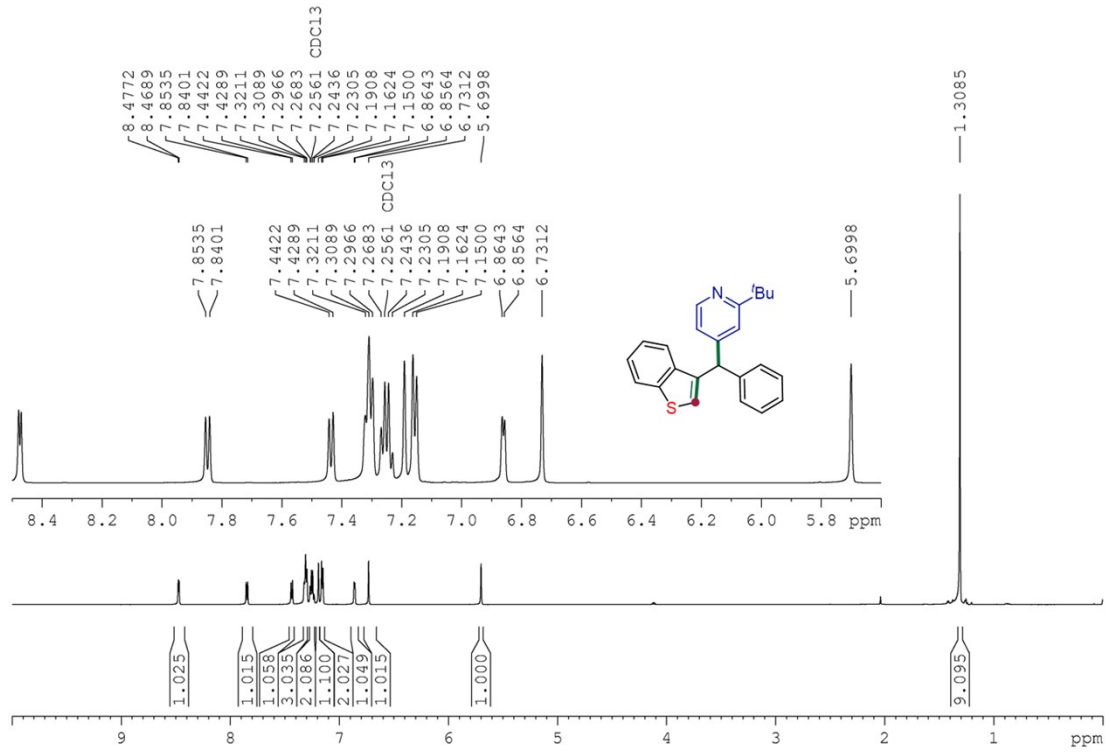
^{1}H NMR (600 MHz, $CDCl_3$) of **47**



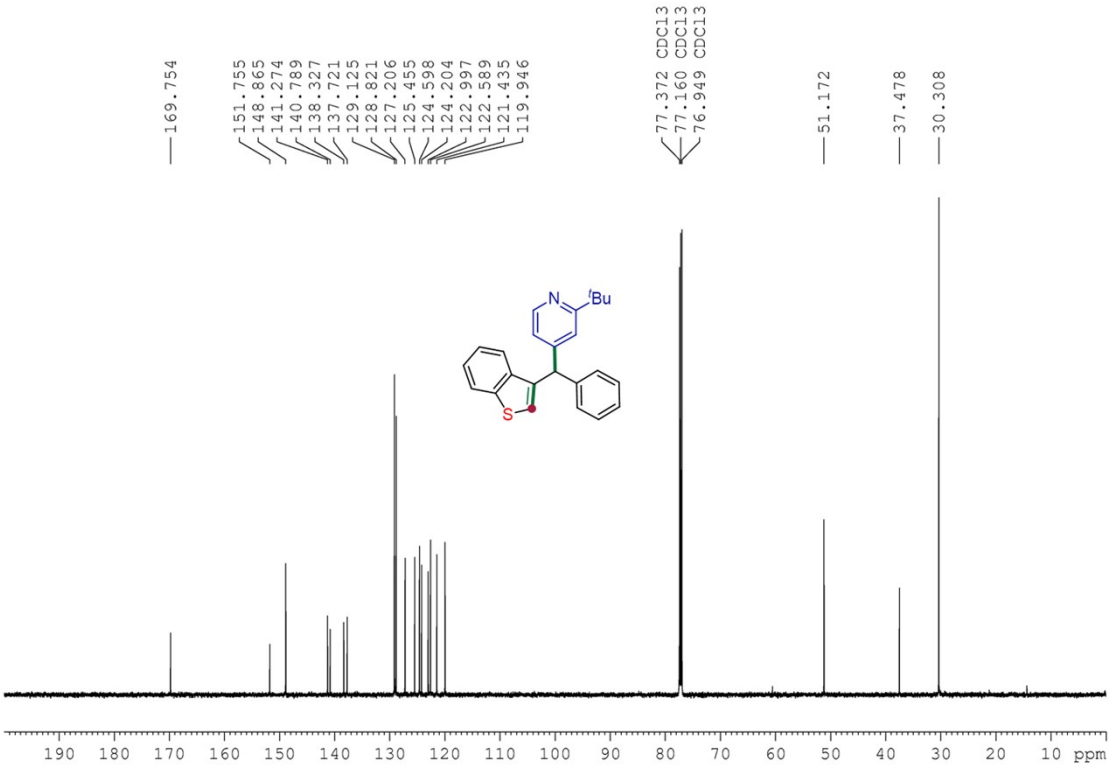
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **47**



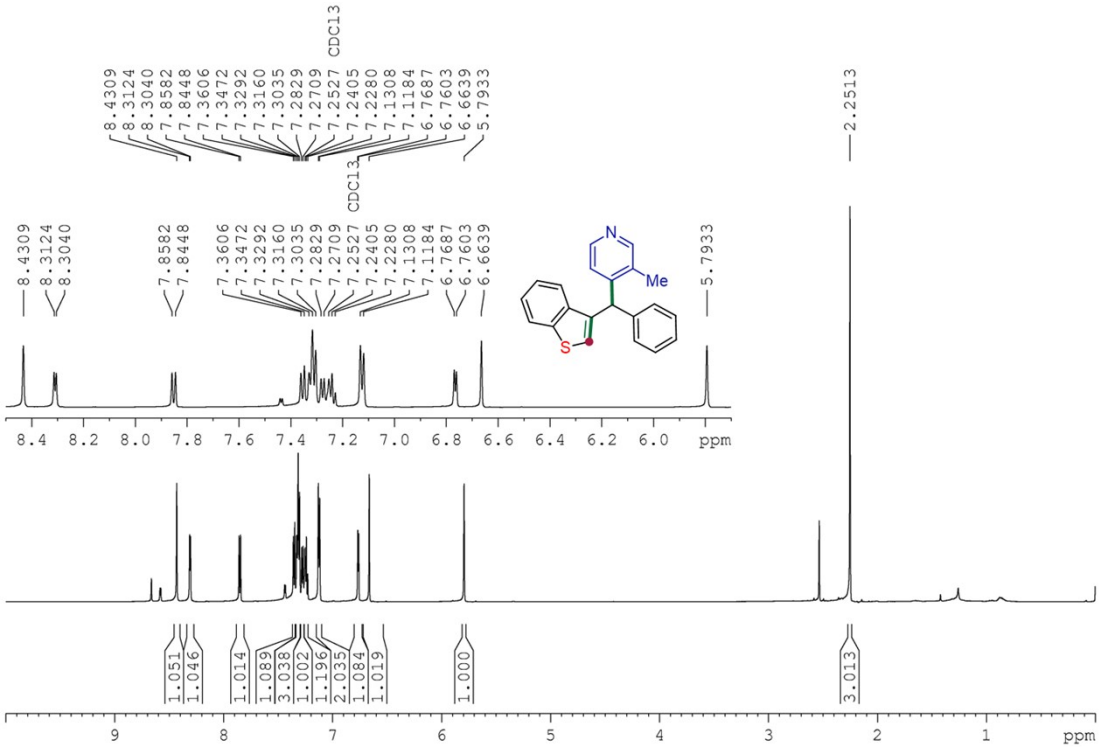
^{1}H NMR (600 MHz, $CDCl_3$) of **48**



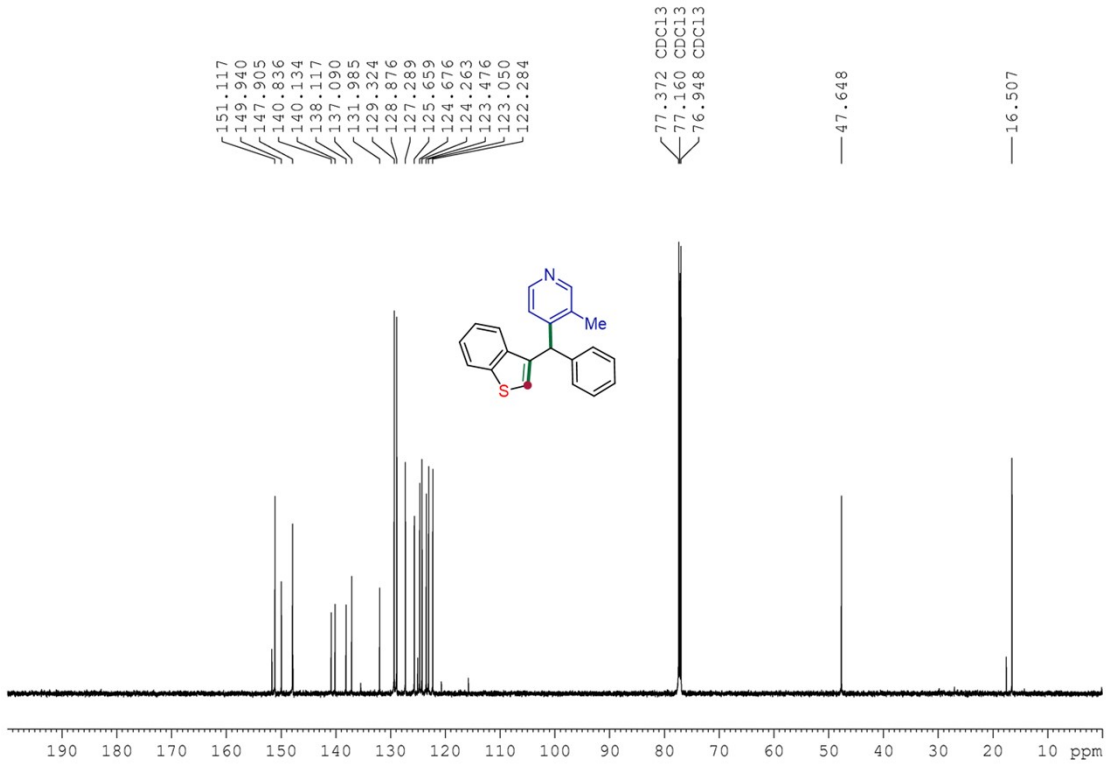
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **48**



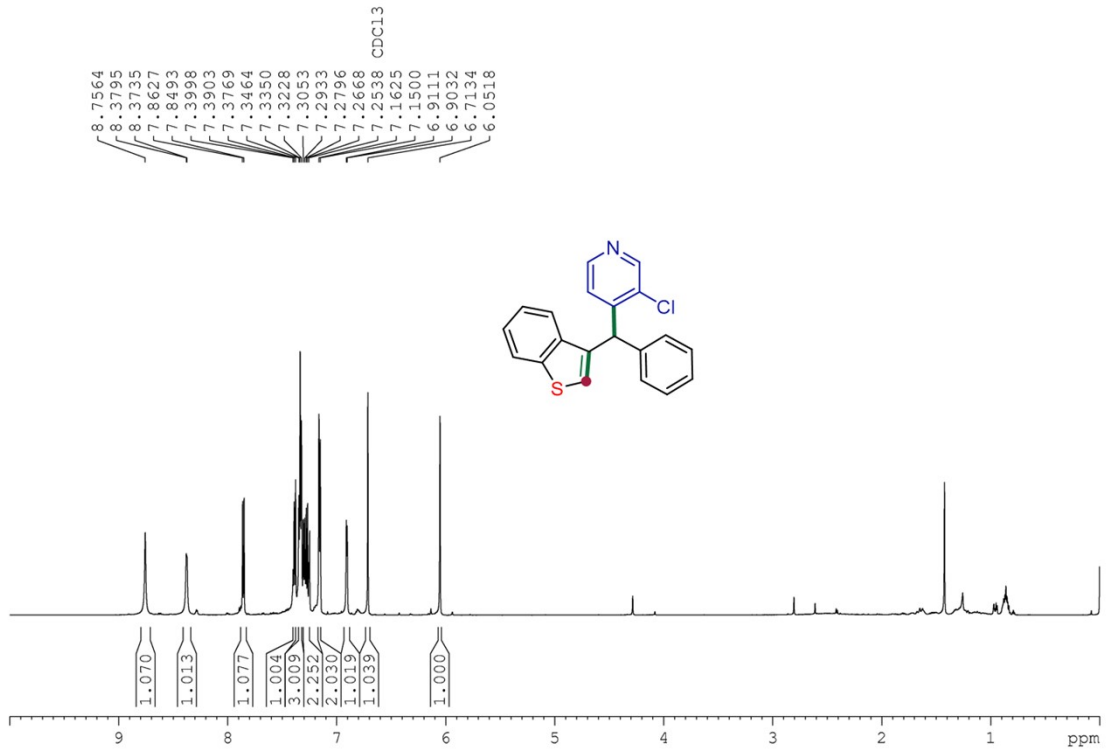
^{1}H NMR (600 MHz, $CDCl_3$) of **49**



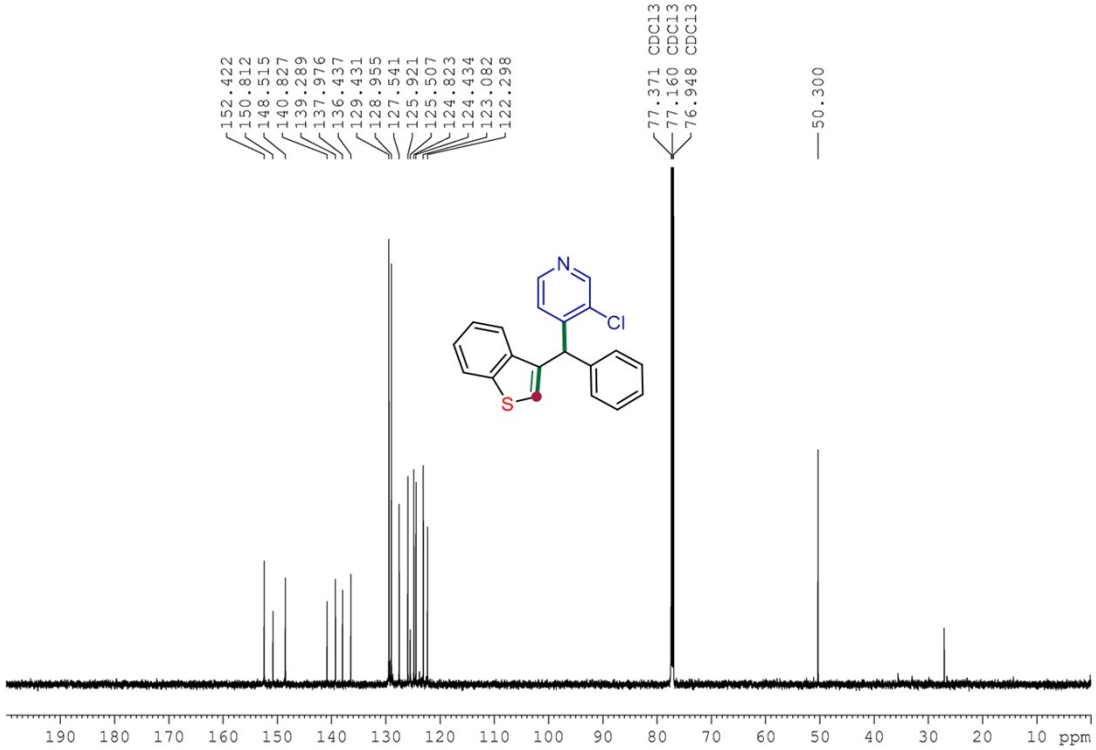
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **49**



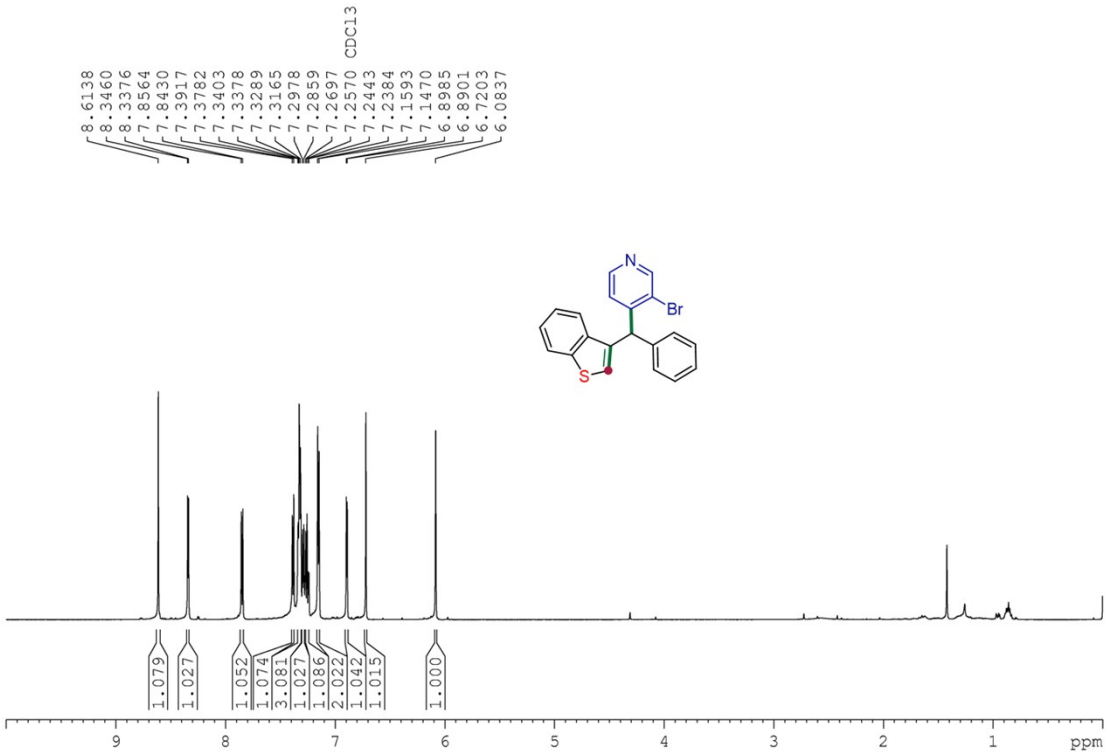
^{1}H NMR (600 MHz, $CDCl_3$) of **50**



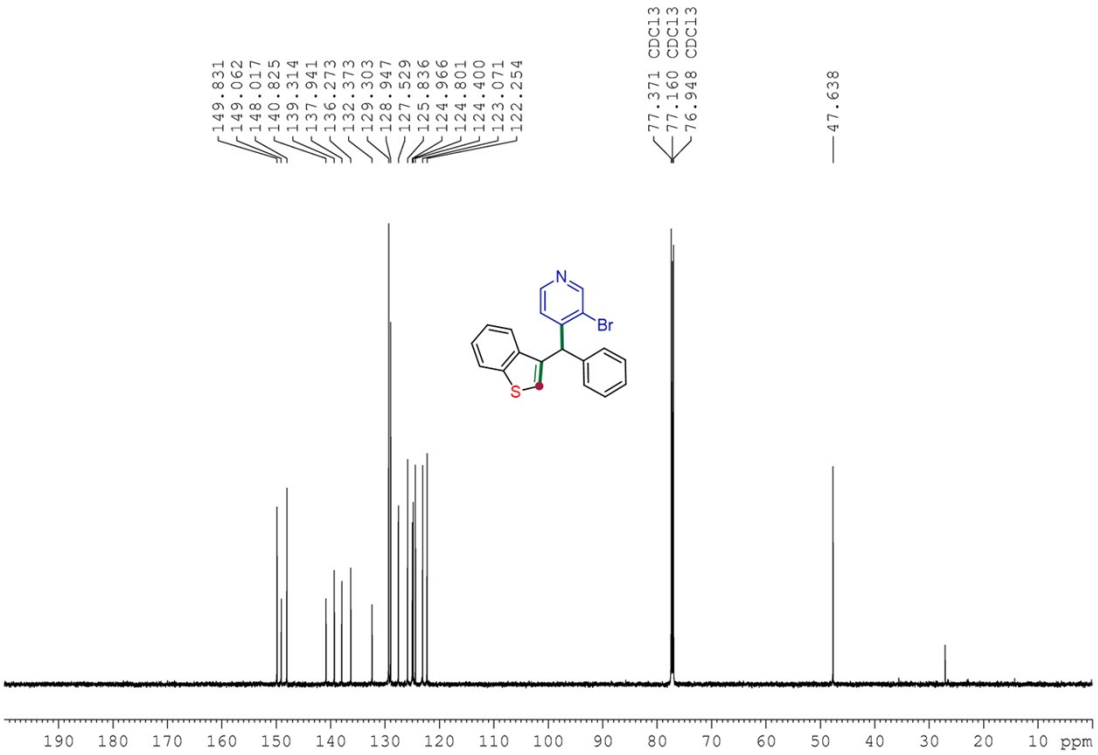
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **50**



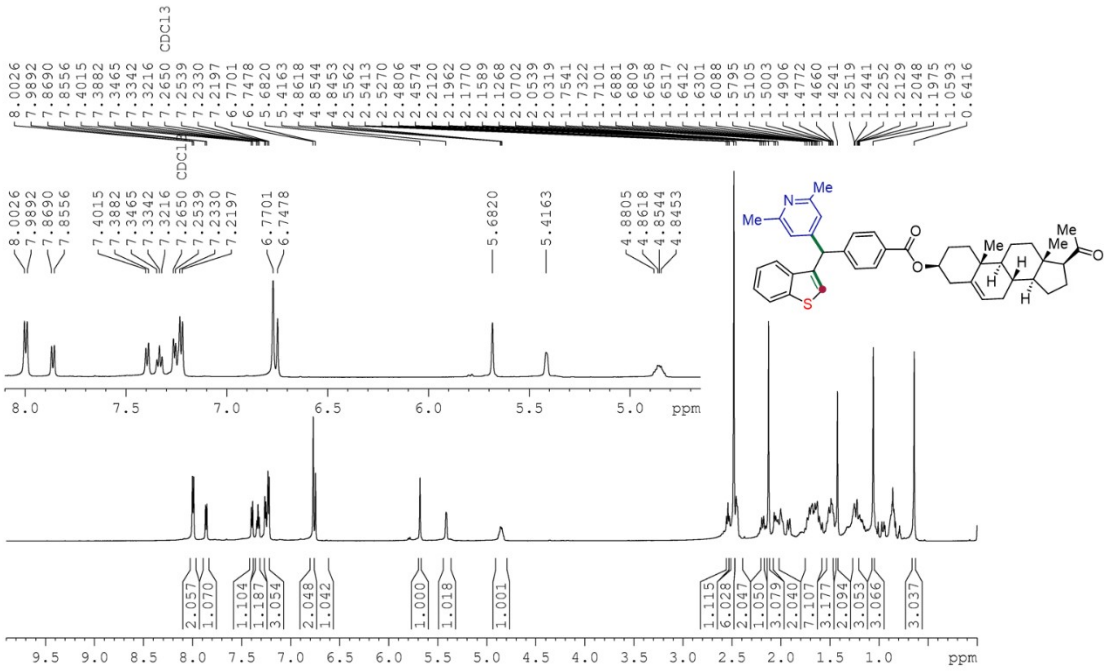
^{1}H NMR (600 MHz, $CDCl_3$) of **51**



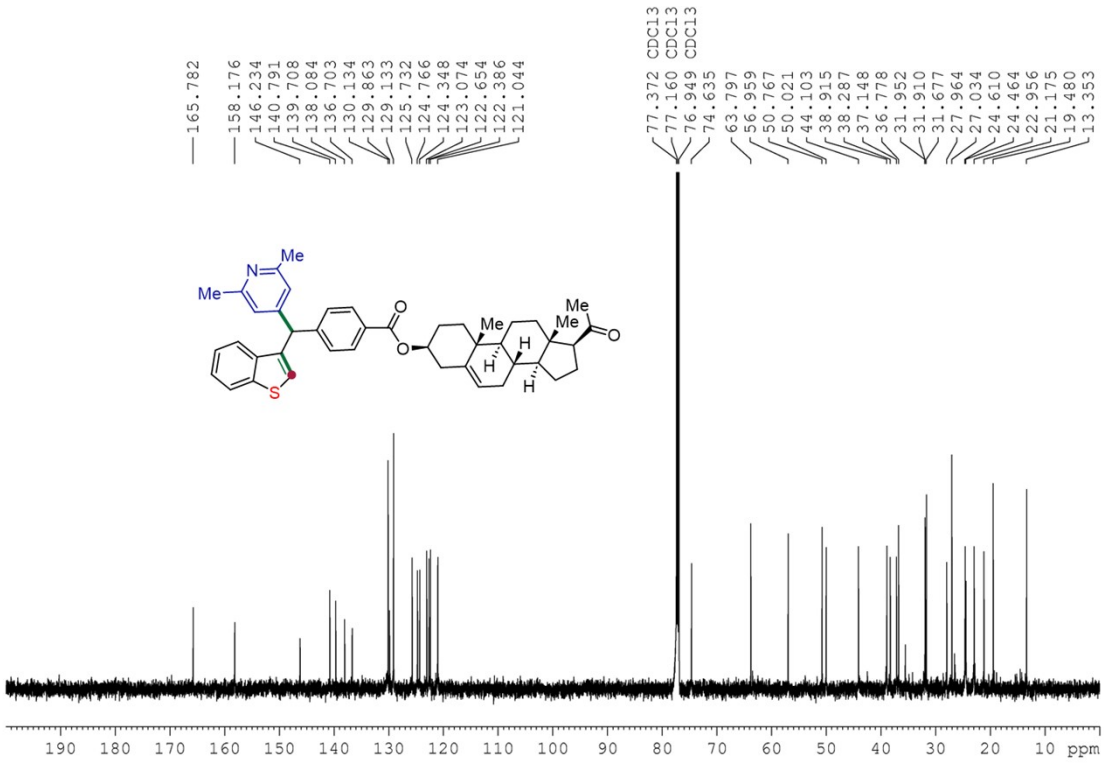
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **51**



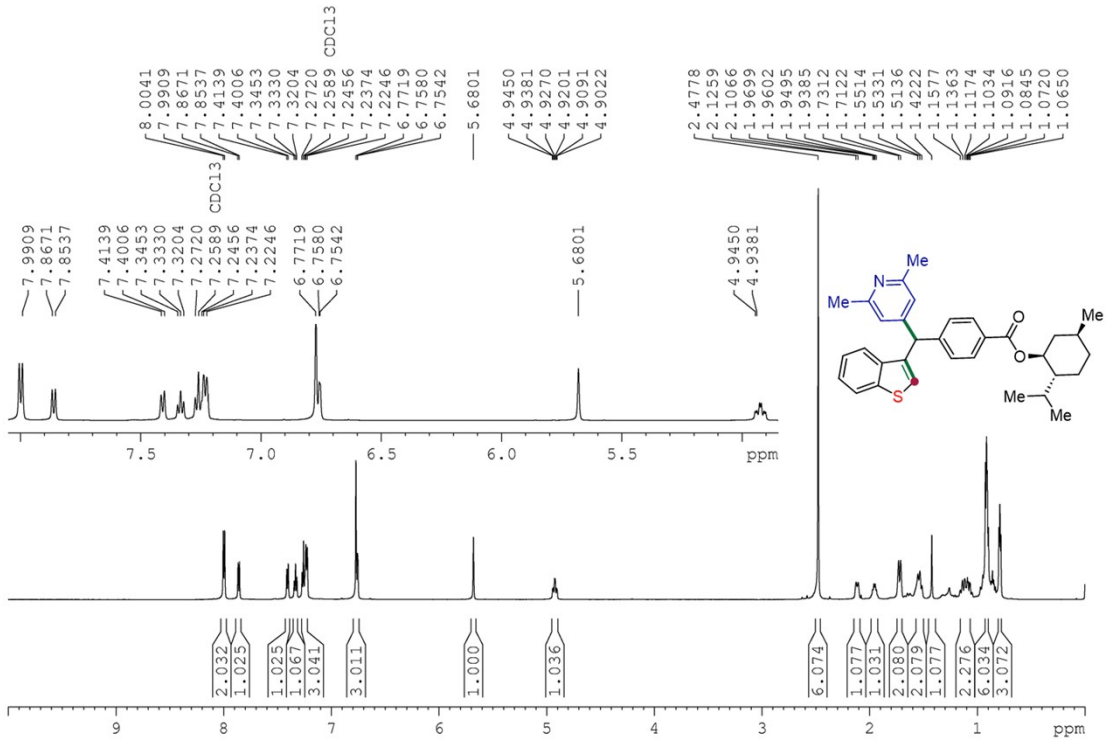
^{1}H NMR (600 MHz, $CDCl_3$) of **52**



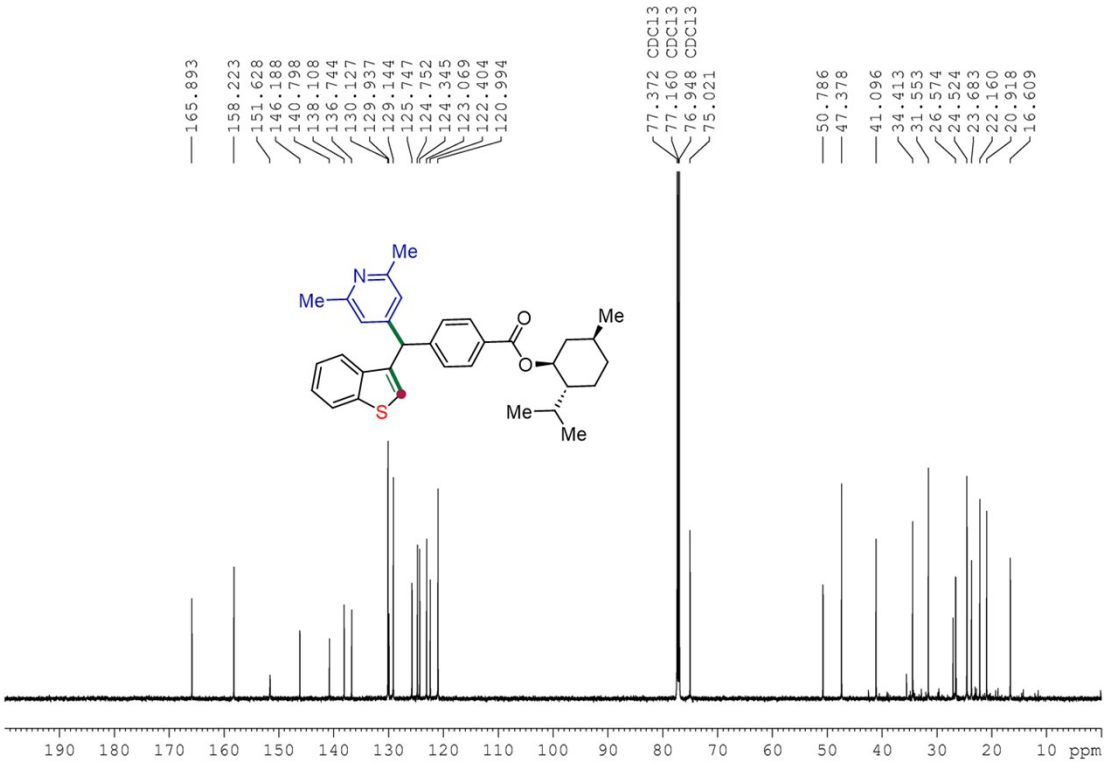
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **52**



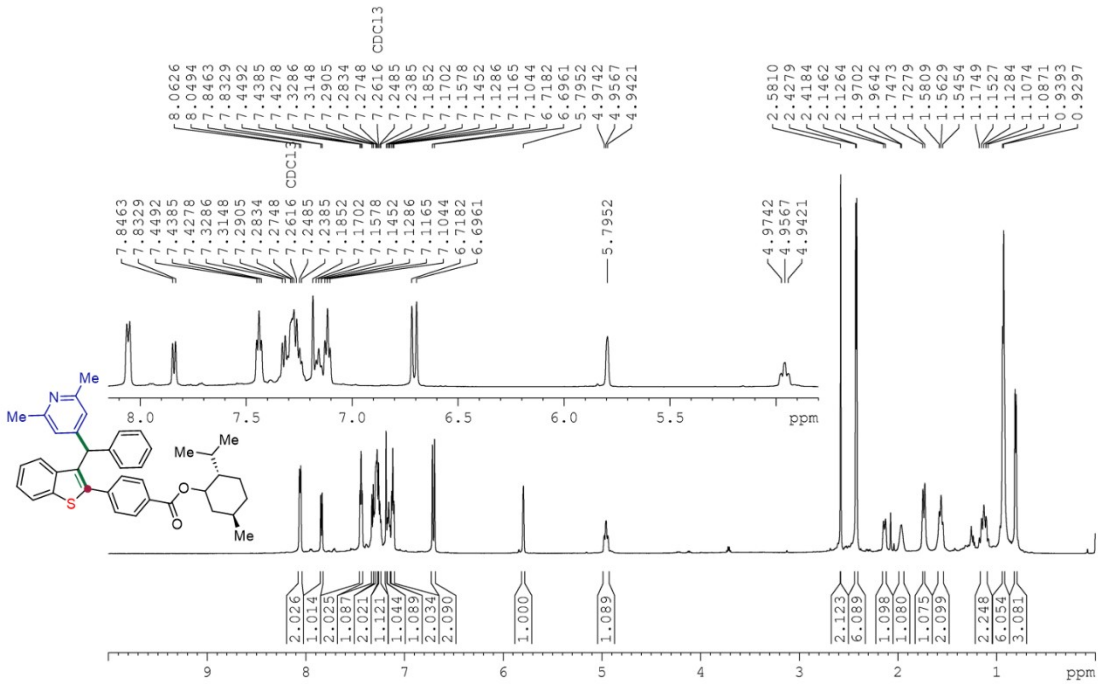
^{1}H NMR (600 MHz, $CDCl_3$) of **53**



^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **53**



^{1}H NMR (600 MHz, $CDCl_3$) of **54**



^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **54**