Supplementary Information (SI) for Organic & Biomolecular Chemistry.

# *Supporting Information*

# $H_3PO_3$ promoted reactions of thioamides with 2-substituted benzyl alcohols

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## A. General considerations:

$^1$H and $^{13}$C NMR spectra were recorded with a 300, 400 MHz spectrometer as solutions in CDCl$_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to CHCl$_3$ (δ = 7.28 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, t = triplet, q =quadrate, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq =doublet of quadrates, td = triplet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublet, and brs. = broad singlet. $^{13}$C NMR spectra were recorded as solutions in CDCl$_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, *δ*) and are referenced to CDCl$_3$ (δ =77.16 ppm) as an internal standard. The molecular fragments in High Resolution Mass Spectra (HRMS) are quoted as the relation between mass and charge (m/z). The routine monitoring of reactions was performed with silica gel GF$_{254}$ pre-coated Al plate, which was analysed with iodine and/or UV light. All reactions were executed with oven-dried glassware under nitrogen atmosphere.

## B. List of thioamides and alcohols used in this study:

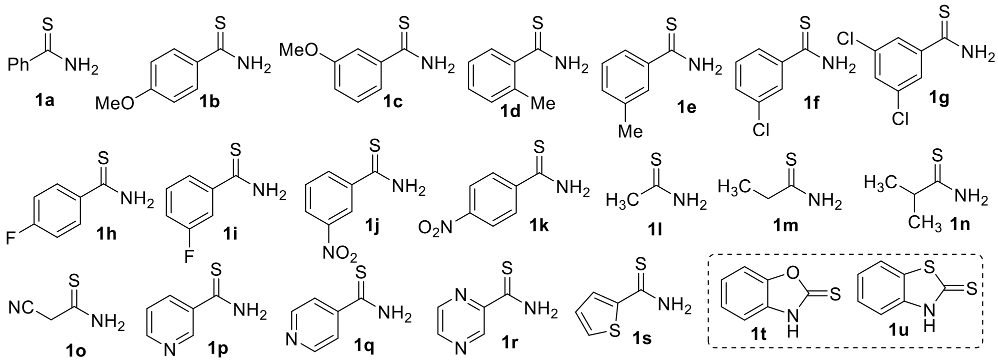


Figure S1: List of thioamides and heterocycles

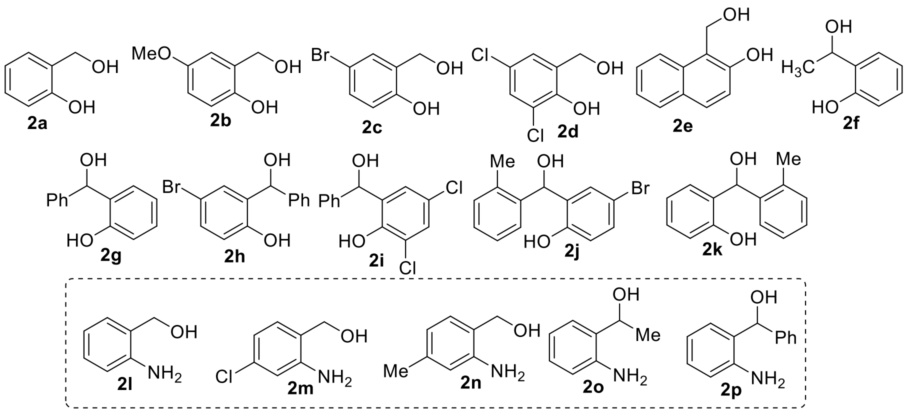


Figure S2: List of alcohols

## C. List of electrophiles/alcohols used in controlled experiments:

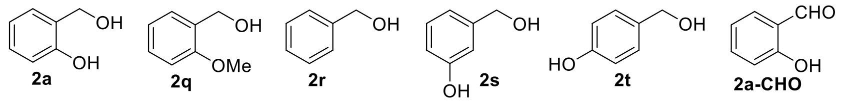
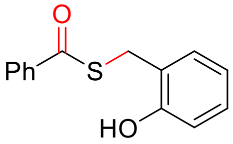


Figure S3: Electrophiles/alcohols used for mechanistic study

## D. General synthetic method A and characterisation data of compounds 3 and 4:

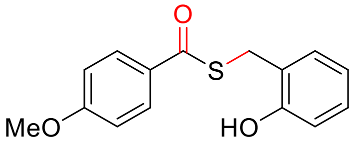
Unless otherwise noted, thioamides (**1a–1s**) / heterocycles (**1t–1u**) (0.5 mmol, 1 equiv.), alcohols (**2a–2k)** (0.65 mmol, 1.3 equiv.), $H_3PO_3$ (20.5 mg, 0.25 mmol, 0.5 equiv.), and 1.6 mL DCE were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere. The vial was capped and allowed to heat at 80 °C for 14 h with continuous stirring on a preheated dry Al- block. After completion of the reaction, the reaction mixture was cooled to room temperature and TLC was checked. After that, DCE was evaporated under reduced pressure and the crude reaction mixture was directly utilised to isolate the product by silica gel (100–200 mess) column chromatography using ethyl acetate / hexane solution as eluent to obtain the desired product titled as **3** and **4**.

### ***S*-(2-Hydroxybenzyl) benzothioate (3aa):**



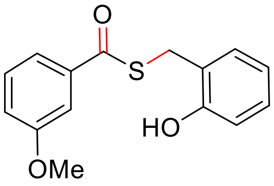
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3aa**, which was purified by silica gel flash column chromatography (using 5-10 % ethyl acetate/hexane as eluent) to give the titled compound as a brownish solid (98.0 mg, 0.40 mmol, 80 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.4 Hz, 2H), 7.66 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.96 – 6.88 (m, 2H), 4.33 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 195.74, 154.53, 136.18, 134.13, 130.97, 129.49, 128.75, 127.59, 123.89, 120.79, 117.53, 28.88 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{13}O_2S$ 245.0631; found 245.0629.

### ***S*-(2-Hydroxybenzyl) 4-methoxybenzothioate (3ba):**



Following the general synthetic method A, reaction between 4-methoxybenzothioamide **1b** (83.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ba**, which was purified by silica gel flash column chromatography (using 5-10 % ethyl acetate/hexane as eluent) to give the titled compound as a reddish crystalline solid (107.2 mg, 0.39 mmol, 78 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 8.00 – 7.94 (m, 3H), 7.22 – 7.17(m, 2H), 6.97 – 6.86 (m, 4H), 4.30 (s, 2H), 3.88 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 194.30, 164.41, 154.63, 130.92, 129.92, 129.43, 128.93, 124.17, 120.68, 117.59, 113.93, 55.59, 28.80 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_3S$ 275.0736; found 275.0731.

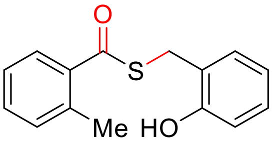
### ***S*-(2-Hydroxybenzyl) 3-methoxybenzothioate (3ca):**



Following the general synthetic method A, reaction between 3-methoxybenzothioamide **1c** (83.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ca**, which was purified by silica gel flash column chromatography (using 4–6

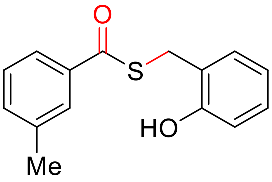
% ethyl acetate/hexane as eluent) to give the titled compound as a light pink sticky liquid (101.6 mg, 0.37 mmol, 74 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.63 – 7.59 (m, 2H), 7.50 – 7.49 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.14 (m, 3H), 6.96 – 6.88 (m, 2H), 4.32 (s, 2H), 3.87 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 195.57, 159.79, 154.51, 137.50, 130.99, 129.76, 129.48, 123.88, 120.82, 120.65, 120.22, 117.46, 111.65, 55.53, 28.96 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_3S$ 275.0736; found 275.0733.

***S*-(2-Hydroxybenzyl) 2-methylbenzothioate (3da):**



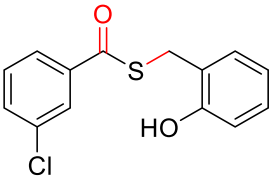
Following the general synthetic method A, reaction between 2-methylbenzothioamide **1d** (75.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3da**, which was purified by silica gel flash column chromatography (using 6-9 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (108.8 mg, 0.42 mmol, 84 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.7 Hz, 1H), 7.51 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.19 (m, 4H), 6.96 – 6.89 (m, 2H), 4.30 (s, 2H), 2.53 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 198.10, 154.53, 137.48, 136.34, 132.42, 131.82, 130.94, 129.42, 128.95, 125.87, 123.93, 120.74, 117.41, 29.58, 20.88 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_2S$ 259.0787; found 259.0784.

***S*-(2-Hydroxybenzyl) 3-methylbenzothioate (3ea):**



Following the general synthetic method A, reaction between 2-methylbenzothioamide **1e** (75.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ea**, which was purified by silica gel flash column chromatography (using 5 % ethyl acetate/hexane as eluent) to give the titled compound as a transparent white liquid (99.7 mg, 0.38 mmol, 77 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.96 – 6.88 (m, 2H), 4.32 (s, 2H), 2.42 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 195.96, 154.53, 138.69, 136.18, 134.92, 130.96, 129.46, 128.63, 128.03, 124.83, 123.98, 120.78, 117.53, 28.87, 21.31 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_2S$ 259.0787; found 259.0782.

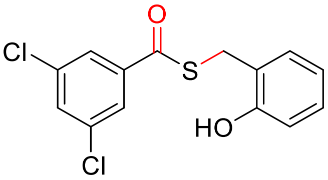
***S*-(2-Hydroxybenzyl) 3-chlorobenzothioate (3fa):**



Following the general synthetic method A, reaction between 3-chlorobenzothioamide **1f** (75.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3fa**, which was purified by silica gel flash column chromatography (using 10 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky white liquid (101.8 mg, 0.36

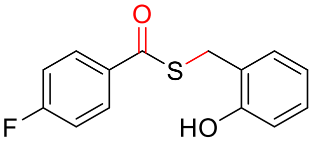
mmol, 73 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.26 – 7.18 (m, 2H), 6.95 – 6.89 (m, 2H), 4.34 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ = 194.18, 154.39, 137.75, 135.05, 133.89, 131.00, 130.04, 129.57, 127.54, 125.65, 123.54, 120.92, 117.38, 29.00 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}ClO_2S$ 279.0241; found 279.0235.

***S*-(2-Hydroxybenzyl) 3,5-dichlorobenzothioate (3ga):**



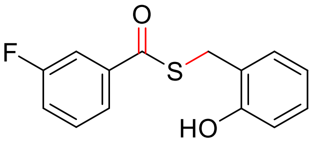
Following the general synthetic method A, reaction between 3,5-dichlorobenzothioamide **1g** (103.0 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ga**, which was purified by silica gel flash column chromatography (using 10 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (104.9 mg, 0.33 mmol, 67 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.75 (s, 2H), 7.48 (s, 1H), 7.19 – 7.09 (m, 2H), 6.92 (s, 1H), 6.83 – 6.81 (m, 2H), 4.25 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 192.72, 154.26, 138.68, 135.74, 133.48, 131.02, 129.64, 125.86, 123.20, 121.03, 117.23, 29.14 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{11}Cl_2O_2S$ 312.9851; found 312.9840.

***S*-(2-Hydroxybenzyl) 4-fluorobenzothioate (3ha):**



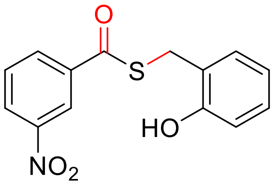
Following the general synthetic method A, reaction between 4-fluorobenzothioamide **1h** (77.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ha**, which was purified by silica gel flash column chromatography (using 7-10 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (81.5 mg, 0.31 mmol, 62 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 8.04 – 8.00 (m, 2H), 7.60 (s, 1H), 7.26 – 7.11 (m, 4H), 6.96 – 6.86 (m, 2H), 4.33 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 194.05, 166.32 (d, $J_{C\text{–}F}$ = 256.3 Hz), 154.44, 132.57 (d, $J_{C\text{–}F}$ = 3.0 Hz), 131.00, 130.22 (d, $J_{C\text{–}F}$ = 9.5 Hz), 129.55, 123.77, 120.89, 117.43, 115.97 (d, $J_{C\text{–}F}$ = 22.2 Hz), 28.97 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}FO_2S$ 263.0537; found 263.0531.

***S*-(2-Hydroxybenzyl) 3-fluorobenzothioate (3ia):**



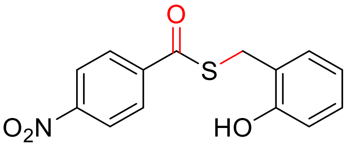
Following the general synthetic method A, reaction between 3-fluorobenzothioamide **1i** (77.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ia**, which was purified by silica gel flash column chromatography (using 5 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (90.4 mg, 0.34 mmol, 69 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.9 Hz, 1H), 7.68 (ddd, *J* = 9.2, 2.6, 1.6 Hz, 1H), 7.45 (td, *J* = 8.0, 5.5 Hz, 1H), 7.40 (s, 1H), 7.34 – 7.18 (m, 3H), 6.96 – 6.89 (m, 2H), 4.34 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 194.25 (d, $J_{C\text{–}F}$ = 2.6 Hz), 162.64 (d, $J_{C\text{–}F}$ = 248.8 Hz), 154.40, 138.18 (d, $J_{C–F}$ = 6.7 Hz), 131.02, 130.45 (d, $J_{C–F}$ = 7.8 Hz), 129.57, 123.58, 123.35 (d, $J_{C–F}$ = 3.1 Hz), 121.00 (d, $J_{C–F}$ = 21.4 Hz), 120.93, 117.38, 114.37 (d, $J_{C–F}$ = 23.3 Hz), 29.00 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}FO_2S$ 263.0537; found 263.0527.

***S*-(2-Hydroxybenzyl) 3-nitrobenzothioate (3ja):**



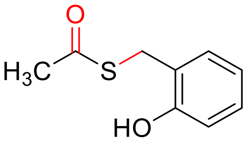
Following the general synthetic method A, reaction between 3-nitrobenzothioamide **1j** (91.1 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ja**, which was purified by silica gel flash column chromatography (using 10 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless oily liquid (127.6 mg, 0.44 mmol, 88 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.79 (s, 1H), 8.43 (d, $J$ = 9.0 Hz, 1H), 8.27 (d, $J$ = 7.1 Hz, 1H), 7.66 (t, $J$ = 8.0 Hz, 1H), 7.30 (d, $J$ = 7.4 Hz, 1H), 7.20 (t, $J$ = 7.7 Hz, 2H), 6.93 – 6.90 (m, 2H), 4.40 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 192.76, 154.23, 148.29, 137.67, 132.95, 131.10, 130.07, 129.65, 128.00, 123.16, 122.40, 121.06, 116.98, 29.17 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NO_4S$ 290.0482; found 290.0480.

***S*-(2-Hydroxybenzyl) 4-nitrobenzothioate (3ka):**



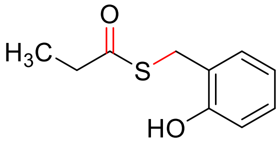
Following the general synthetic method A, reaction between 4-nitrobenzothioamide **1k** (91.1 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ka**, which was purified by silica gel flash column chromatography (using 7-10 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow liquid (103.0 mg, 0.35 mmol, 71 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.32 (d, $J$ = 8.5 Hz, 2H), 8.14 (d, $J$ = 8.6 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.22 (t, $J$ = 7.7, 1H), 6.95 – 6.91 (m, 2H), 4.39 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 193.32, 154.26, 150.76, 140.95, 131.07, 129.69, 128.53, 123.97, 123.08, 121.07, 117.15, 29.27 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NO_4S$ 290.0482; found 290.0477.

***S*-(2-Hydroxybenzyl) ethanethioate (3la):**



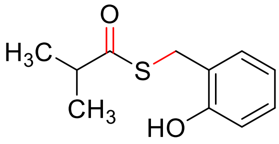
Following the general synthetic method A, reaction between ethanethioamide **1l** (37.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3la**, which was purified by silica gel flash column chromatography (using 3-4 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (69.5 mg, 0.38 mmol, 76 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.31 (s, 1H), 7.21 – 7.15 (m, 2H), 6.93 – 6.86 (m, 2H), 4.12 (s, 2H), 2.41 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 200.29, 154.32, 130.80, 129.42, 123.85, 120.81, 117.34, 30.23, 29.10 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_9H_{11}O_2S$ 183.0474; found 183.0471.

### *S*-(2-Hydroxybenzyl) propanethioate (3ma):



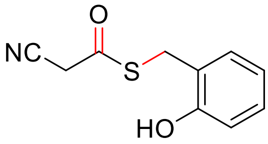
Following the general synthetic method A, reaction between propanethioamide **1m** (44.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ma**, which was purified by silica gel flash column chromatography (using 4 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (67.4 mg, 0.34 mmol, 69 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (s, 1H), 7.21 – 7.14 (m, 2H), 6.93 – 6.86 (m, 2H), 4.12 (s, 2H), 2.65 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 204.94, 154.34, 130.81, 129.41, 123.96, 120.78, 117.39, 37.07, 28.75, 9.64 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{13}O_2S$ 197.0631; found 197.0619.

### S-(2-Hydroxybenzyl) 2-methylpropanethioate (3na):



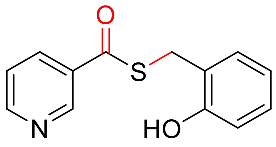
Following the general synthetic method A, reaction between 2-methylpropanethioamide **1n** (51.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3na**, which was purified by silica gel flash column chromatography (using 3 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (69.0 mg, 0.33 mmol, 66 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.45 (s, 1H), 7.21 – 7.13 (m, 2H), 6.93 – 6.85 (m, 2H), 4.10 (s, 2H), 2.82 (hept, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 208.91, 154.44, 130.80, 129.38, 123.93, 120.69, 117.39, 42.89, 28.64, 19.43 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{15}O_2S$ 211.0787; found 211.0777.

### *S*-(2-Hydroxybenzyl) 2-cyanoethanethioate (3oa):



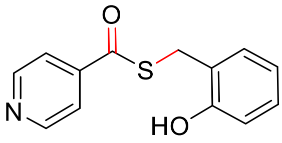
Following the general synthetic method A, reaction between 2-cyanoethanethioamide **1o** (50.0 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3oa**, which was purified by silica gel flash column chromatography (using 15–22 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (64.2 mg, 0.31 mmol, 62 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.19 (td, *J* = 8.0, 1.7 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.31 (s, 1H), 4.25 (s, 2H), 3.64 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 189.21, 154.00, 131.03, 129.69, 122.42, 121.06, 116.39, 112.78, 32.21, 29.60 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{10}NO_2S$ 208.0427; found 208.0424.

### *S*-(2-Hydroxybenzyl) pyridine-3-carbothioate (3pa):



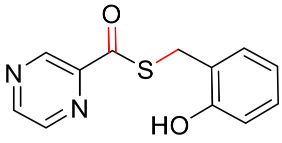
Following the general synthetic method A, reaction between pyridine-3-carbothioamide **1p** (69.0 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3pa**, which was purified by silica gel flash column chromatography (using 15-25 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (71.4 mg, 0.29 mmol, 58 %). **$^1$H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 9.03 (s, 1H), 8.66 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.76 – 6.64 (m, 2H), 4.25 (s, 2H). **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 190.68, 155.38, 153.10, 147.84, 134.87, 132.75, 130.59, 128.86, 123.74, 123.01, 119.44, 115.53, 28.53 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{12}NO_2S$ 246.0583; found 246.0580.

***S*-(2-Hydroxybenzyl) pyridine-4-carbothioate (3qa):**



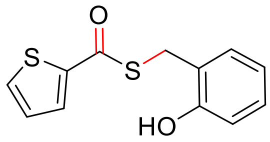
Following the general synthetic method A, reaction between pyridine-4-carbothioamide **1q** (69.0 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3qa**, which was purified by silica gel flash column chromatography (using 20-25 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (61.4 mg, 0.25 mmol, 50 %). **$^1$H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 8.98 (d, *J* = 8.2 Hz, 1H), 8.66 – 8.64 (m, 2H), 7.65 – 7.63 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.7, 1.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 4.27 (s, 2H). **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 191.58, 155.38, 150.60, 143.21, 130.62, 128.94, 122.84, 120.29, 119.49, 115.53, 28.72 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{12}NO_2S$ 246.0583; found 246.0577.

***S*-(2-Hydroxybenzyl) pyrazine-2-carbothioate (3ra):**



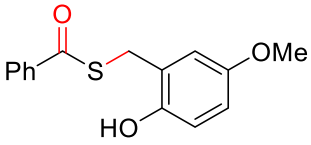
Following the general synthetic method A, reaction between pyrazine-2-carbothioamide **1r** (69.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ra**, which was purified by silica gel flash column chromatography (using 15–30 % ethyl acetate/hexane as eluent) to give the titled compound as a light yellow solid (77.1 mg, 0.31 mmol, 63 %). **$^1$H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 8.99 (s, 1H), 8.93 (s, 1H), 8.63 (d, *J* = 2.4 Hz, 1H), 8.47 (s, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 4.16 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 192.32, 155.03, 148.29, 146.18, 143.39, 141.21, 130.19, 128.34, 122.86, 118.99, 115.09, 27.73 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{11}N_2O_2S$ 247.0536; found 247.0531.

***S*-(2-Hydroxybenzyl) thiophene-2-carbothioate (3sa):**



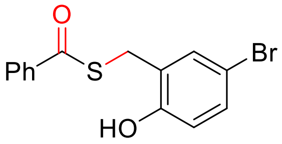
Following the general synthetic method A, reaction between thiophene-2-carbothioamide **1s** (71.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3sa**, which was purified by silica gel flash column chromatography (using 4–7 % ethyl acetate/hexane as eluent) to give the titled compound as a brownish yellow solid (74.9 mg, 0.30 mmol, 60 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 3.8 Hz, 1H), 7.69 (d, *J* = 5.0 Hz, 1H), 7.58 (s, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.12 (m, 1H), 6.96 – 6.86 (m, 2H), 4.32 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 187.42, 154.51, 140.97, 133.98, 132.24, 130.94, 129.58, 128.20, 123.80, 120.82, 117.58, 29.07 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{11}O_2S_2$ 251.0195; found 251.0192.

***S*-(2-Hydroxy-5-methoxybenzyl) benzothioate (3ab):**



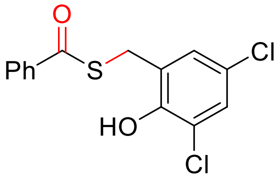
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)-4-methoxyphenol **2b** (97.1 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ab**, which was purified by silica gel flash column chromatography (using 5-8 % ethyl acetate/hexane as eluent) to give the titled compound as a brownish liquid (116.9 mg, 0.42 mmol, 85 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (s, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.80 – 6.75 (m, 2H), 4.29 (s, 2H), 3.78 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 195.29, 153.58, 148.31, 136.22, 134.07, 128.74, 127.56, 124.81, 118.35, 115.67, 114.96, 55.78, 28.95 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_3S$ 275.0736; found 275.0732.

***S*-(5-Bromo-2-hydroxybenzyl) benzothioate (3ac):**



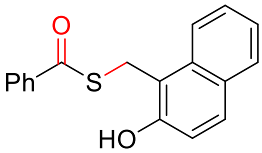
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 4-bromo-2-(hydroxymethyl)phenol **2c** (127.9 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ac**, which was purified by silica gel flash column chromatography (using 5-8 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (132.9 mg, 0.41 mmol, 82 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.85 (s, 1H), 7.65 – 7.61 (m, 1H), 7.50 – 7.46 (m, 2H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.29 – 7.27 (m, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.25 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 195.71, 153.75, 135.93, 134.35, 133.34, 132.23, 128.83, 127.63, 126.19, 119.43, 112.43, 28.42 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}BrO_2S$ 322.9736; found 322.9729.

***S*-(3,5-Dichloro-2-hydroxybenzyl) benzothioate (3ad):**



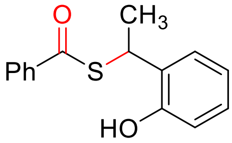
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2,4-dichloro-6-(hydroxymethyl)phenol **2d** (121.6 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ad**, which was purified by silica gel flash column chromatography (using 2-3 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow solid (109.9 mg, 0.35 mmol, 70 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 8.01 – 7.97 (m, 2H), 7.65 – 7.59 (m, 1H), 7.50 – 7.45 (m, 2H), 7.28 (s, 1H), 6.84 (s, 1H), 4.31 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 192.96, 148.76, 136.27, 133.98, 129.33, 128.76, 128.29, 127.49, 126.80, 125.15, 121.48, 28.14 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{11}Cl_2O_2S$ 312.9851; found 312.9848.

***S*-((2-Hydroxynaphthalen-1-yl)methyl) benzothioate (3ae):**



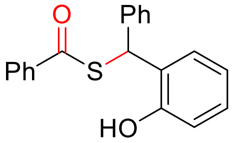
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 1-(hydroxymethyl)naphthalen-2-ol **2e** (109.7 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3ae**, which was purified by silica gel flash column chromatography (using 2 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (103.3 mg, 0.35 mmol, 70 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 8.73 (s, 1H), 8.01 – 7.98 (m, 2H), 7.84 – 7.80 (m, 2H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.48 – 7.37(m, 3H), 7.28 – 7.22 (m, 1H), 4.73 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 196.45, 152.96, 136.12, 134.20, 132.56, 130.12, 129.37, 128.97, 128.74, 127.65, 126.97, 123.44, 121.83, 119.95, 115.33, 24.90 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{15}O_2S$ 295.0787; found 295.0780.

***S*-(1-(2-Hydroxyphenyl)ethyl) benzothioate (3af):**



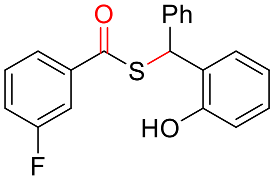
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2-(1-hydroxyethyl)phenol **2f** (87.0 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3af**, which was purified by silica gel flash column chromatography (using 5-8 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky white liquid (98.4 mg, 0.38 mmol, 76 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H), 7.62 – 7.56 (m, 1H), 7.47 – 7.42 (m, 3H), 7.35 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 6.99 – 6.94 (m, 2H), 5.21 (q, *J* = 7.3 Hz, 1H), 1.82 (d, *J* = 7.3 Hz, 3H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 195.07, 153.47, 136.34, 133.92, 129.65, 128.79, 128.68, 127.51, 127.20, 121.23, 117.88, 36.42, 20.91 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{15}O_2S$ 259.0787; found 259.0783.

***S*-((2-Hydroxyphenyl)(phenyl)methyl) benzothioate (3ag):**



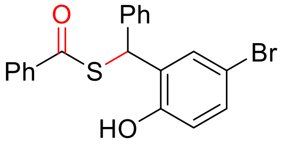
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxy(phenyl)methyl)phenol **2g** (126.1 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3ag**, which was purified by silica gel flash column chromatography (using 7-11 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky white liquid (113.9 mg, 0.35 mmol, 70 %). **$^1$H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 8.77 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (q, *J* = 7.8, 7.4 Hz, 4H), 7.28 – 7.20 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.45 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 190.79, 154.41, 141.16, 136.76, 133.36, 129.45, 128.56, 128.49, 128.33, 128.32, 128.25, 128.24, 127.26, 127.14, 126.83, 119.54, 116.02, 46.24 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{17}O_2S$ 321.0944; found 321.0940.

***S*-((2-Hydroxyphenyl)(phenyl)methyl) 3-fluorobenzothioate (3ig):**



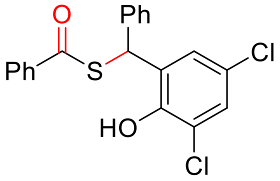
Following the general synthetic method A, reaction between 3-fluorobenzothioamide **1i** (77.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxy(phenyl)methyl)phenol **2g** (126.1 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3ig**, which was purified by silica gel flash column chromatography (using 10-15 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky yellow liquid (120.3 mg, 0.35 mmol, 71 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.48 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.44 (dd, *J* = 8.0, 5.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (dt, *J* = 8.0, 2.5 Hz, 3H), 7.20 – 7.18 (m, 1H), 6.95 – 6.88 (m, 2H), 6.46 (s, 1H), 6.14 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 190.93, 162.66 (d, $J_{C–F}$ = 248.7 Hz), 153.24, 139.52, 138.40 (d, $J_{C–F}$ = 6.7 Hz )130.37 (d, $J_{C–F}$ = 7.9 Hz), 129.80, 128.97, 128.67, 128.35, 127.59, 127.52, 123.30 (d, $J_{C–F}$ = 3.1 Hz), 121.24, 120.73 (d, $J_{C–F}$ = 21.5 Hz), 117.02, 114.37 (d, $J_{C–F}$ = 23.1 Hz), 46.42 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{16}FO_2S$ 339.0850; found 339.0847.

***S*-((5-Bromo-2-hydroxyphenyl)(phenyl)methyl) benzothioate (3ah):**



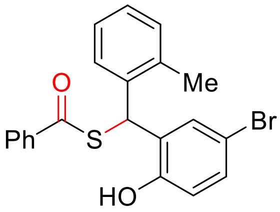
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 4-bromo-2-(hydroxy(phenyl)methyl)phenol **2h** (175.8 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3ah**, which was purified by silica gel flash column chromatography (using 4-5 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky white liquid (156.0 mg, 0.39 mmol, 78 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.02 – 8.00 (m, 2H), 7.62 (dd, *J* = 8.3, 6.6 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.38 (dd, *J* = 8.4, 6.6 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.24 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.67 (s, 1H), 6.38 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 192.43, 152.64, 138.87, 136.17, 134.08, 132.21, 131.65, 130.42, 128.84, 128.79, 128.36, 127.75, 127.60, 118.98, 113.12, 45.76 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{16}BrO_2S$ 399.0049; found 399.0045.

***S*-((3,5-Dichloro-2-hydroxyphenyl)(phenyl)methyl) benzothioate (3ai):**



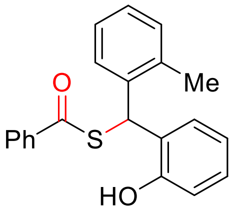
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2,4-dichloro-6-(hydroxy(phenyl)methyl)phenol **2i** (169.5 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3ai**, which was purified by silica gel flash column chromatography (using 2 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (150.5 mg, 0.38 mmol, 77 %). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta = 8.01$ (s, 1H), 7.99 (s, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.49 – 7.43 (m, 4H), 7.39 – 7.34 (m, 3H), 7.31 (d, $J = 7.1$ Hz, 1H), 7.29 (d, $J = 1.5$ Hz, 1H), 6.44 (s, 1H), 6.10 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) $\delta = 190.32$, 147.77, 138.93, 136.27, 133.84, 130.42, 128.75, 128.33, 128.16, 127.74, 127.71, 127.49, 125.42, 121.15, 46.20 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{15}Cl_2O_2S$ 389.0164; found 389.0161.

***S*-((5-Bromo-2-hydroxyphenyl)(*o*-tolyl)methyl) benzothioate (3aj):**



Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 4-bromo-2-(hydroxy(*o*-tolyl)methyl)phenol **2j** (184.7 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3aj**, which was purified by silica gel flash column chromatography (using 5 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (143.0 mg, 0.34 mmol, 69 %). **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta = 8.03 – 7.99$ (m, 2H), 7.65 – 7.59 (m, 1H), 7.51 – 7.45 (m, 3H), 7.31 (d, $J = 2.4$ Hz, 1H), 7.27 – 7.21 (m, 3H), 7.09 (s, 1H), 6.78 (d, $J = 8.6$ Hz, 1H), 6.46 (s, 1H), 2.38 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) $\delta = 193.17$, 152.71, 137.12, 136.24, 136.05, 134.18, 132.02, 131.63, 130.98, 129.83, 128.81, 128.29, 127.94, 127.65, 126.41, 119.07, 113.12, 42.86, 19.43 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}BrO_2S$ 413.0205; found 413.0202.

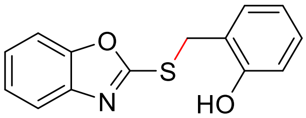
***S*-((2-Hydroxyphenyl)(*o*-tolyl)methyl) benzothioate (3ak):**



Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxy(*o*-tolyl)methyl)phenol **2k** (135.0 mg, 0.63 mmol, 1.3 equiv.) by using $H_3PO_3$

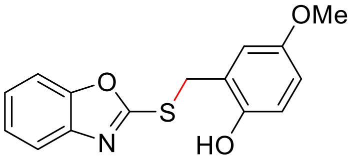
(41.0 mg, 0.5 mmol, 1.0 equiv.) instead of 0.5 equiv. $H_3PO_3$ afforded the corresponding product **3ak**, which was purified by silica gel flash column chromatography (using 4-8 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky yellow liquid (115.2 mg, 0.36 mmol, 73 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.87 – 6.84 (m, 1H), 6.56 (s, 1H), 2.39 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 193.02, 153.48, 137.96, 136.33, 136.31, 133.93, 130.84, 129.50, 128.76, 128.72, 128.38, 127.62, 127.60, 127.26, 126.14, 121.07, 117.16, 43.21, 19.46 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{19}O_2S$ 335.1100; found 335.1094.

**2-((Benzo[*d*]oxazol-2-ylthio)methyl)phenol (4ta):**



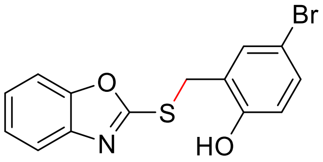
Following the general synthetic method A, reaction between benzo[*d*]oxazole-2(3*H*)-thione **1t** (75.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4ta**, which was purified by silica gel flash column chromatography (using 1-4 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (103.2 mg, 0.40 mmol, 80 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 10.36 (s, 1H), 7.68 – 7.66 (m, 1H), 7.45 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.34 (td, *J* = 7.7, 1.1 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.22 (td, *J* = 8.1, 1.6 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 4.51 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 167.59, 155.17, 152.20, 140.02, 131.14, 129.78, 124.83, 124.50, 121.14, 119.44, 117.92, 110.22, 32.00 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NO_2S$ 258.0583; found 258.0580.

**2-((Benzo[*d*]oxazol-2-ylthio)methyl)-4-methoxyphenol (4tb):**



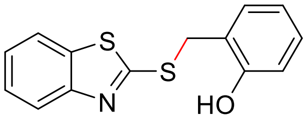
Following the general synthetic method A, reaction between benzo[*d*]oxazole-2(3*H*)-thione **1t** (75.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)-4-methoxyphenol **2b** (97.1 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4tb**, which was purified by silica gel flash column chromatography (using 4-10 % ethyl acetate/hexane as eluent) to give the titled compound as a white sticky liquid (110.9 mg, 0.38 mmol, 77 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 9.94 (s, 1H), 7.66 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.45 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.35 – 7.28 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.83 – 6.78 (m, 2H), 4.46 (s, 2H), 3.79 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 167.30, 153.87, 152.18, 148.82, 140.06, 125.63, 124.81, 124.49, 120.41, 117.94, 115.62, 115.38, 110.20, 55.77, 31.89 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}NO_3S$ 288.0689; found 288.0678.

**2-((Benzo[*d*]oxazol-2-ylthio)methyl)-4-bromophenol (4tc):**



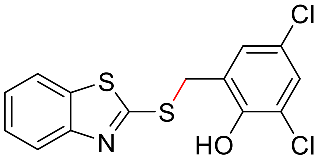
Following the general synthetic method A, reaction between benzo[*d*]oxazole-2(3*H*)-thione **1t** (75.6 mg, 0.5 mmol, 1 equiv.) and 4-bromo-2-(hydroxymethyl)phenol **2c** (127.9 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4tc**, which was purified by silica gel flash column chromatography (using 4-10 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (131.4 mg, 0.39 mmol, 78 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.67 – 7.64 (m, 1H), 7.47 – 7.45 (m, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.34 (td, *J* = 7.6, 1.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 4.43 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 167.25, 154.48, 152.21, 139.83, 133.51, 132.59, 127.04, 124.94, 124.67, 121.34, 117.89, 112.76, 110.32, 31.50 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{11}BrNO_2S$ 335.9688; found 335.9685.

**2-((Benzo[*d*]thiazol-2-ylthio)methyl)phenol (4ua):**



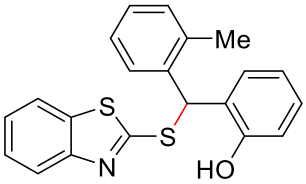
Following the general synthetic method A, reaction between benzo[*d*]thiaazole-2(3*H*)-thione **1u** (83.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxymethyl)phenol **2a** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4ua**, which was purified by silica gel flash column chromatography (using 1-5 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (103.0 mg, 0.37 mmol, 75 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 10.43 (s, 1H), 7.97 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.35 (td, *J* = 7.7, 1.2 Hz, 1H), 7.27 – 7.20 (m, 2H), 6.99 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.93 (td, *J* = 7.4, 1.3 Hz, 1H), 4.55 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 169.61, 155.28, 151.26, 134.93, 131.04, 129.73, 126.54, 124.89, 124.84, 121.23, 120.85, 120.71, 119.10, 33.09 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NOS_2$ 274.0355; found 274.0351.

**2-((Benzo[*d*]thiazol-2-ylthio)methyl)-4,6-dichlorophenol (4ud):**



Following the general synthetic method A, reaction between benzo[*d*]thiaazole-2(3*H*)-thione **1u** (83.6 mg, 0.5 mmol, 1 equiv.) and 2,4-dichloro-6-(hydroxymethyl)phenol **2d** (121.6 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4ud**, which was purified by silica gel flash column chromatography (using 2-3 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (122.1 mg, 0.35 mmol, 71 %). **$^1$H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 9.93 (s, 1H), 7.61 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.48 (dd, *J* = 8.5, 4.4 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.07 – 7.00 (m, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 4.28 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 167.10, 151.23, 149.62, 134.28, 128.48, 128.22, 126.78, 125.75, 124.07, 123.52, 122.31, 120.63, 120.28, 31.86 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{10}Cl_2NOS_2$ 341.9575; found 341.9582.

**2-((Benzo[*d*]thiazol-2-ylthio)(*o*-tolyl)methyl)phenol (4uk):**

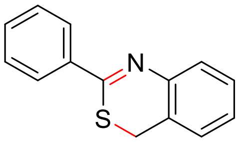


Following the general synthetic method A, reaction between benzo[*d*]thiaazole-2(3*H*)-thione **1u** (83.6 mg, 0.5 mmol, 1 equiv.) and 2-(hydroxy(*o*-tolyl)methyl)phenol **2k** (135.0 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **4uk**, which was purified by silica gel flash column chromatography (using 5-7 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (116.5 mg, 0.32 mmol, 64 %). **$^1$H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 9.27 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.19 – 7.13 (m, 2H), 7.06 – 6.87 (m, 5H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 2.25 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) δ = 167.28, 154.63, 152.66, 137.62, 136.48, 130.41, 129.10, 128.71, 127.84, 127.37, 125.97, 125.93, 125.31, 124.07, 121.32, 120.84, 119.51, 115.90, 46.89, 19.24 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{18}NOS_2$ 364.0824; found 364.0817.

### E. General synthetic method B and characterisation data of compounds 5al–5ip:

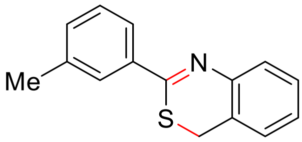
Unless otherwise noted, thioamides (**1a–1s**) (0.5 mmol, 1 equiv.), alcohol (**2l–2p**) (0.55 mmol, 1.1 equiv.), $H_3PO_3$ (41.0 mg, 0.5 mmol, 1.0 equiv.), 0.5 mL MeOH as co-solvent and 2.5 mL DCE solvent were taken in a 5 mL screw capped reaction vial under nitrogen atmosphere. The vial was capped and allowed to heat at 80 °C for 14 h with continuous stirring on a preheated dry Al- block. After completion of the reaction, the reaction mixture was cooled to room temperature and TLC was checked. After that, solvent was evaporated under reduced pressure and the crude reaction mixture was directly utilised to isolate the product by silica gel (100–200 mess) column chromatography using ethyl acetate / hexane solution as eluent to obtain the desired product titled as **5**.

**2-Phenyl-4*H*-benzo[*d*][1,3]thiazine (5al):**



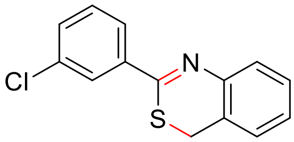
Following the general synthetic method B, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5al**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow oil (89.3 mg, 0.39 mmol, 79 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.17 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.50 – 7.46 (m, 2H), 7.40 (td, *J* = 7.6, 1.6 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.20 (d, *J* = 6.9 Hz, 1H), 4.04 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 161.18, 144.42, 137.96, 131.55, 128.50, 128.24, 127.63, 127.05, 126.90, 119.65, 114.08, 29.72 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}NS$ 226.0685; found 226.0682.

**2-(*m*-Tolyl)-4*H*-benzo[*d*][1,3]thiazine (5dl):**



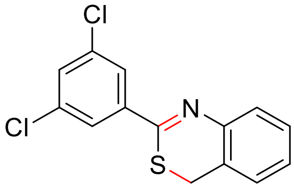
Following the general synthetic method B, reaction between 2-methylbenzothioamide **1d** (75.6 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5dl**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky colourless liquid (96.8 mg, 0.40 mmol, 81 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.32 – 7.26 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 4.03 (s, 2H), 2.47 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 161.42, 144.46, 138.26, 137.94, 132.40, 128.68, 128.46, 128.39, 127.56, 127.01, 126.90, 125.60, 119.71, 28.64, 21.45 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}NS$ 240.0841; found 240.0836.

**2-(3-Chlorophenyl)-4*H*-benzo[*d*][1,3]thiazine (5fl):**



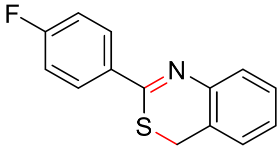
Following the general synthetic method B, reaction between 3-chlorobenzothioamide **1f** (75.6 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5fl**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky white liquid (98.4 mg, 0.38 mmol, 76 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.18 (t, *J* = 1.9 Hz, 1H), 8.04 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.52 – 7.39 (m, 4H), 7.31 (td, *J* = 7.4, 1.5 Hz, 1H), 7.20 (dd, *J* = 7.5, 1.4 Hz, 1H), 4.04 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 159.57, 144.15, 139.64, 134.69, 131.41, 129.69, 128.61, 128.09, 128.03, 127.17, 126.96, 126.36, 119.43, 28.55 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{14}H_{11}ClNS$ 260.0295; found 260.0292.

**2-(3,5-Dichlorophenyl)-4*H*-benzo[*d*][1,3]thiazine (5gl):**



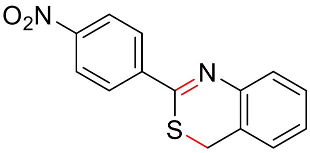
Following the general synthetic method B, reaction between 3,5-dichlorobenzothioamide **1g** (103.0 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5gl**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow solid (104.0 mg, 0.35 mmol, 70 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 1.9 Hz, 2H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (td, *J* = 7.3, 1.5 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 4.04 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 158.07, 143.90, 140.66, 135.24, 131.06, 128.72, 128.41, 127.31, 127.01, 126.47, 119.23, 28.49 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{14}H_{10}Cl_2NS$ 293.9906; found 293.9912.

**2-(4-Fluorophenyl)-4*H*-benzo[*d*][1,3]thiazine (5hl):**[1]



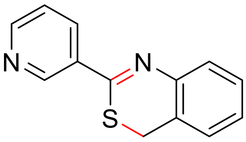
Following the general synthetic method B, reaction between 4-fluorobenzothioamide **1h** (77.6 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5hl**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a white solid (84.3 mg, 0.34 mmol, 69 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.20 – 8.16 (m, 2H), 7.46 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.21 – 7.15 (m, 3H), 4.04 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 165.01 (d, $J_{C-F}$ = 252.2 Hz), 159.81, 144.34, 134.16 (d, $J_{C-F}$ = 3.0 Hz), 130.34 (d, $J_{C-F}$ = 8.8 Hz), 128.54, 127.69, 126.97, 126.93, 119.50, 115.55 (d, $J_{C-F}$ = 21.9 Hz), 28.65 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{14}H_{11}FNS$ 244.0591; found 244.0588.

**2-(4-Nitrophenyl)-4*H*-benzo[*d*][1,3]thiazine (5kl):**



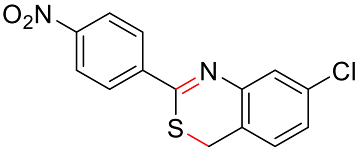
Following the general synthetic method B, reaction between 4-nitrobenzothioamide **1k** (91.1 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5kl**, which was purified by silica gel flash column chromatography (using 2 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow solid (97.6 mg, 0.36 mmol, 72 %). **$^1$H NMR** (300 MHz, CDCl$_3$) δ = 8.34 (s, 4H), 7.51 – 7.41 (m, 2H), 7.35 (td, *J* = 7.3, 1.7 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 1H), 4.09 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, CDCl$_3$) δ = 158.41, 149.45, 143.95, 143.28, 128.80, 128.73, 127.49, 127.08, 123.64, 119.00, 28.45 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{14}H_{11}N_2O_2S$ 271.0536; found 271.0534.

**2-(Pyridin-3-yl)-4*H*-benzo[*d*][1,3]thiazine (5pl):**[1]



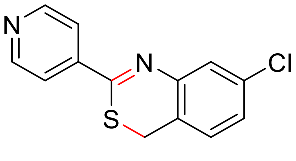
Following the general synthetic method B, reaction between pyridine-3-carbothioamide **1p** (69.0 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)methanol **2l** (67.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5pl**, which was purified by silica gel flash column chromatography (using 10-20 % ethyl acetate/hexane as eluent) to give the titled compound as a yellowish semi-solid (73.8 mg, 0.32 mmol, 65 %). **$^1$H NMR** (300 MHz, CDCl$_3$) δ = 9.35 – 9.34 (m, 1H), 8.74 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.41 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.34 – 7.28 (m, 1H), 7.20 (dd, *J* = 7.5, 1.5 Hz, 1H), 4.06 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, CDCl$_3$) δ = 158.44, 152.08, 149.46, 144.02, 135.39, 133.57, 128.68, 128.19, 127.20, 127.04, 123.36, 119.31, 28.45 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{13}H_{11}N_2S$ 227.0637; found 227.0631.

**7-Chloro-2-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]thiazine (5km):**



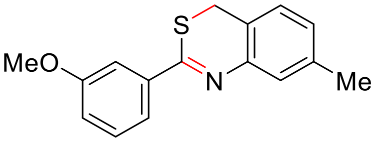
Following the general synthetic method B, reaction between 4-nitrobenzothioamide **1k** (91.1 mg, 0.5 mmol, 1 equiv.) and (2-amino-4-chlorophenyl)methanol **2m** (86.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5km**, which was purified by silica gel flash column chromatography (using 0–1 % ethyl acetate/hexane as eluent) to give the titled compound as a yellow solid (129.5 mg, 0.42 mmol, 85 %). $^1$H NMR (400 MHz, CDCl$_3$) δ = 8.33 (d, *J* = 2.3 Hz, 4H), 7.50 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) δ = 160.14, 149.66, 144.97, 142.84, 134.18, 128.93, 128.41, 128.01, 127.32, 123.69, 117.45, 28.02 ppm. **HRMS** (ESI) m/z: [M + H]$^+$ calculated for $C_{14}H_{10}ClN_2O_2S$ 305.0146; found 305.0138.

**7-Chloro-2-(pyridin-4-yl)-4*H*-benzo[*d*][1,3]thiazine (5qm):**



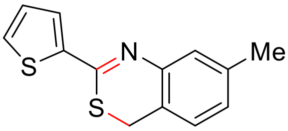
Following the general synthetic method B, reaction between pyridine-4-carbothioamide **1q** (69.0 mg, 0.5 mmol, 1 equiv.) and (2-amino-4-chlorophenyl)methanol **2m** (86.7 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5qm**, which was purified by silica gel flash column chromatography (using 10–18 % ethyl acetate/hexane as eluent) to give the titled compound as a yellowish white solid (65.6 mg, 0.25 mmol, 50 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.78 – 8.77 (m, 2H), 7.98 – 7.96 (m, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 4.02 (s, 2H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 160.54, 150.42, 144.84, 144.32, 134.11, 128.39, 128.02, 127.32, 121.50, 117.61, 27.79 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{10}ClN_2S$ 261.0248; found 261.0240.

**2-(3-Methoxyphenyl)-7-methyl-4*H*-benzo[*d*][1,3]thiazine (5cn):**



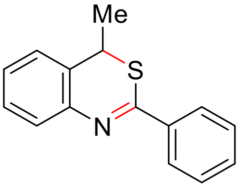
Following the general synthetic method B, reaction between 3-methoxybenzothioamide **1c** (83.6 mg, 0.5 mmol, 1 equiv.) and (2-amino-4-methylphenyl)methanol **2n** (75.4 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5cn**, which was purified by silica gel flash column chromatography (using 2–3 % ethyl acetate/hexane as eluent) to give the titled compound as a light yellowish liquid (113.0 mg, 0.42 mmol, 84 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.78 – 7.75(m, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.33 (s, 1H), 7.13 – 7.06 (m, 3H), 4.00 (s, 2H), 3.93 (s, 3H), 2.44 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 160.79, 159.73, 144.21, 139.50, 138.30, 129.43, 128.40, 127.68, 126.68, 120.93, 117.87, 116.69, 112.64, 55.47, 28.41, 21.13 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{16}NOS$ 270.0947; found 270.0942.

**7-Methyl-2-(thiophen-2-yl)-4*H*-benzo[*d*][1,3]thiazine (5sn):**



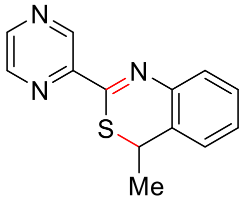
Following the general synthetic method B, reaction between thiophene-2-carbothioamide **1s** (71.6 mg, 0.5 mmol, 1 equiv.) and (2-amino-4-methylphenyl)methanol **2n** (75.4 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5sn**, which was purified by silica gel flash column chromatography (using 0–1 % ethyl acetate/hexane as eluent) to give the titled compound as a yellowish white solid (86.0 mg, 0.35 mmol, 70 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.26 (s, 1H), 7.15 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.09 – 7.05 (m, 2H), 3.97 (s, 2H), 2.41 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 154.05, 144.12, 143.70, 138.38, 130.56, 129.69, 128.10, 127.66, 127.37, 126.68, 116.87, 28.55, 21.08 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{12}NS_2$ 246.0406; found 246.0400.

**4-Methyl-2-phenyl-4*H*-benzo[*d*][1,3]thiazine (5ao):**



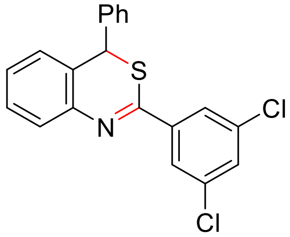
Following the general synthetic method B, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 1-(2-aminophenyl)ethan-1-ol **2o** (75.4 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5ao**, which was purified by silica gel flash column chromatography (using 0–1 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless oil (101.9 mg, 0.42 mmol, 85 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 8.19 – 8.16 (m, 2H), 7.55 – 7.47 (m, 4H), 7.41 (td, *J* = 7.6, 1.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.6 Hz, 1H), 7.21 (dd, *J* = 7.5, 1.6 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 1H), 1.53 (d, *J* = 7.0 Hz, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 159.32, 143.22, 138.49, 131.43, 128.49, 128.24, 128.12, 127.80, 127.61, 125.69, 125.56, 37.30, 23.41 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}NS$ 240.0841; found 240.0829.

**4-Methyl-2-(pyrazin-2-yl)-4*H*-benzo[*d*][1,3]thiazine (5ro):**



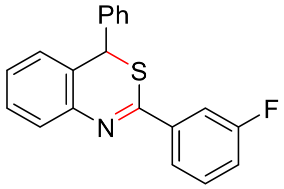
Following the general synthetic method B, reaction between pyrazine-2-carbothioamide **1r** (69.6 mg, 0.5 mmol, 1 equiv.) and 1-(2-aminophenyl)ethan-1-ol **2o** (75.5 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5ro**, which was purified by silica gel flash column chromatography (using 3–6 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky yellow liquid (103.7 mg, 0.43 mmol, 86 %). **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 9.59 (s, 1H), 8.64 (d, *J* = 3.2 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.43 – 7.33 (m, 2H), 7.22 – 7.19 (m, 1H), 4.26 (q, *J* = 7.0 Hz, 1H), 1.51 (d, *J* = 7.0 Hz, 3H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 158.40, 149.91, 145.77, 143.22, 142.93, 142.33, 129.22, 128.32, 128.18, 125.93, 125.34, 36.48, 24.14 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{12}N_3S$ 242.0476; found 242.0472.

**2-(3,5-Dichlorophenyl)-4-phenyl-4*H*-benzo[*d*][1,3]thiazine (5gp):**



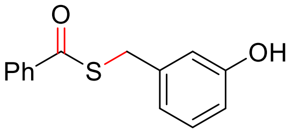
Following the general synthetic method B, reaction between 3,5-dichlorobenzothioamide **1g** (103.0 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)(phenyl)methanol **2p**(109.6 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5gp**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky yellow liquid (170.0 mg, 0.46 mmol, 92 %). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.85 (t, *J* = 1.8 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.18 – 7.10 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.0 Hz, 1H), 5.24 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 156.28, 143.73, 140.91, 140.73, 135.26, 131.07, 128.97, 128.88, 128.75, 128.10, 128.07, 127.65, 127.45, 126.45, 122.40, 45.63 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{14}Cl_2NS$ 370.0219; found 370.0216.

**2-(3-Fluorophenyl)-4-phenyl-4*H*-benzo[*d*][1,3]thiazine (5ip):**



Following the general synthetic method B, reaction between 3-fluorobenzothioamide **1i** (77.6 mg, 0.5 mmol, 1 equiv.) and (2-aminophenyl)(phenyl)methanol **2p** (109.6 mg, 0.55 mmol, 1.1 equiv.) afforded the corresponding product **5ip**, which was purified by silica gel flash column chromatography (using 1 % ethyl acetate/hexane as eluent) to give the titled compound as a sticky yellow liquid (134.4 mg, 0.42 mmol, 84 %). $^1$**H NMR** (400 MHz, $CDCl_3$) δ = 7.74 (t, $J$ = 8.5 Hz, 2H), 7.50 (d, $J$ = 7.9 Hz, 1H), 7.33 (td, $J$ = 7.6, 1.5 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.12 (m, 4H), 7.10 – 7.04 (m, 3H), 6.96 (dd, $J$ = 7.7, 1.5 Hz, 1H), 5.27 (s, 1H) ppm. $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 162.84 (d, $J_{C–F}$ = 246.6 Hz), 157.87, 157.83, 143.96, 141.16, 140.28 (d, $J_{C–F}$ = 7.4 Hz), 129.98 (d, $J_{C–F}$ = 8.1 Hz), 128.88, 128.76, 128.34, 127.95, 127.65, 127.41, 123.95 (d, $J_{C–F}$ = 2.9 Hz), 122.58, 118.37 (d, $J_{C–F}$ = 21.5 Hz), 114.91 (d, $J_{C–F}$ = 23.4 Hz) 45.61 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{15}FNS$ 320.0904; found 320.0899.

***S*-(3-hydroxybenzyl) benzothioate (3as):**



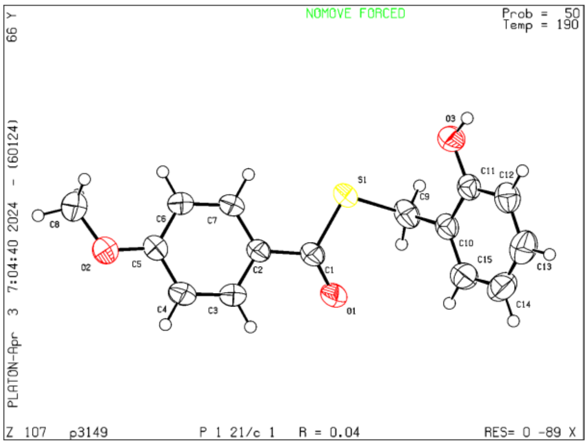
Following the general synthetic method A, reaction between benzothioamide **1a** (68.6 mg, 0.5 mmol, 1 equiv.) and 3-(hydroxymethyl)phenol **2s** (78.2 mg, 0.63 mmol, 1.3 equiv.) afforded the corresponding product **3as**, which was purified by silica gel flash column chromatography (using 5-10 % ethyl acetate/hexane as eluent) to give the titled compound as a colourless sticky liquid (12.2 mg, 0.05 mmol, 10 %). $^1$**H NMR** (300 MHz, $CDCl_3$) δ = 8.00 – 7.97 (m, 2H), 7.60 (t, $J$ = 7.4 Hz, 1H), 7.47 (dd, $J$ = 8.3, 6.9 Hz, 2H), 7.20 (t, $J$ = 7.8 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.89 (t, $J$ = 2.1 Hz, 1H), 6.77 – 6.74 (m, 1H), 5.15 (s, 1H), 4.29 (s, 2H) ppm. $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) δ = 191.55, 155.83, 139.26, 136.74, 133.55, 129.92, 128.68, 127.33, 121.32, 115.87, 114.45, 33.11 ppm. **HRMS** (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{13}O_2S$ 245.0631; found 245.0627.

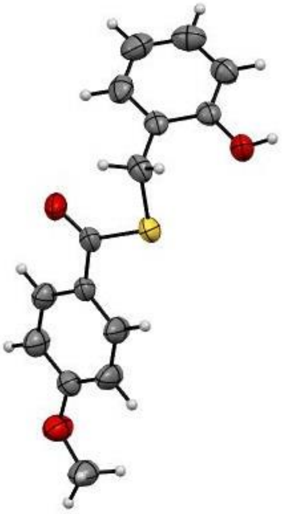
## F. X-ray Crystallography:

Single-crystal X-ray data of compound **3ba** was collected on a Bruker SMART Apex-II CCD diffractometer in the presence of graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 190.0 K. The Bruker Apex-II suite program was used to perform data processing, structure solution, and refinement. Reflections available in $2\Theta_{max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.[2] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS.[3] The structures were solved using direct methods and refined by means of full-matrix least-squares techniques based on $F^2$ with with SHELX2017/1 software package.[4] Non-hydrogen atoms present in the structures were refined with anisotropic thermal parameters. C−H hydrogen atoms were introduced at geometrical positions with $U_{iso} = 1/2U_{eq}$ to those of the atoms to which they are attached.

**Crystallisation process of compound 3ba:**

70 mg solid compound of **3ba** was taken in a 10 mL conical flask. Then the compound was dissolved in 0.8 mL EtOAc solvent and then 0.8 mL hexane was added. The conical flask was kept at 3-5 °C temperature inside a fridge. The slow evaporation of solvent for 10 days at that temperature grows clear yellow crystals in plate shaped.





ORTEP view of **3ba**
(Ellipsoids are drawn at 50% probability)

**Table S1: Crystal data and structure refinement for 3b.**

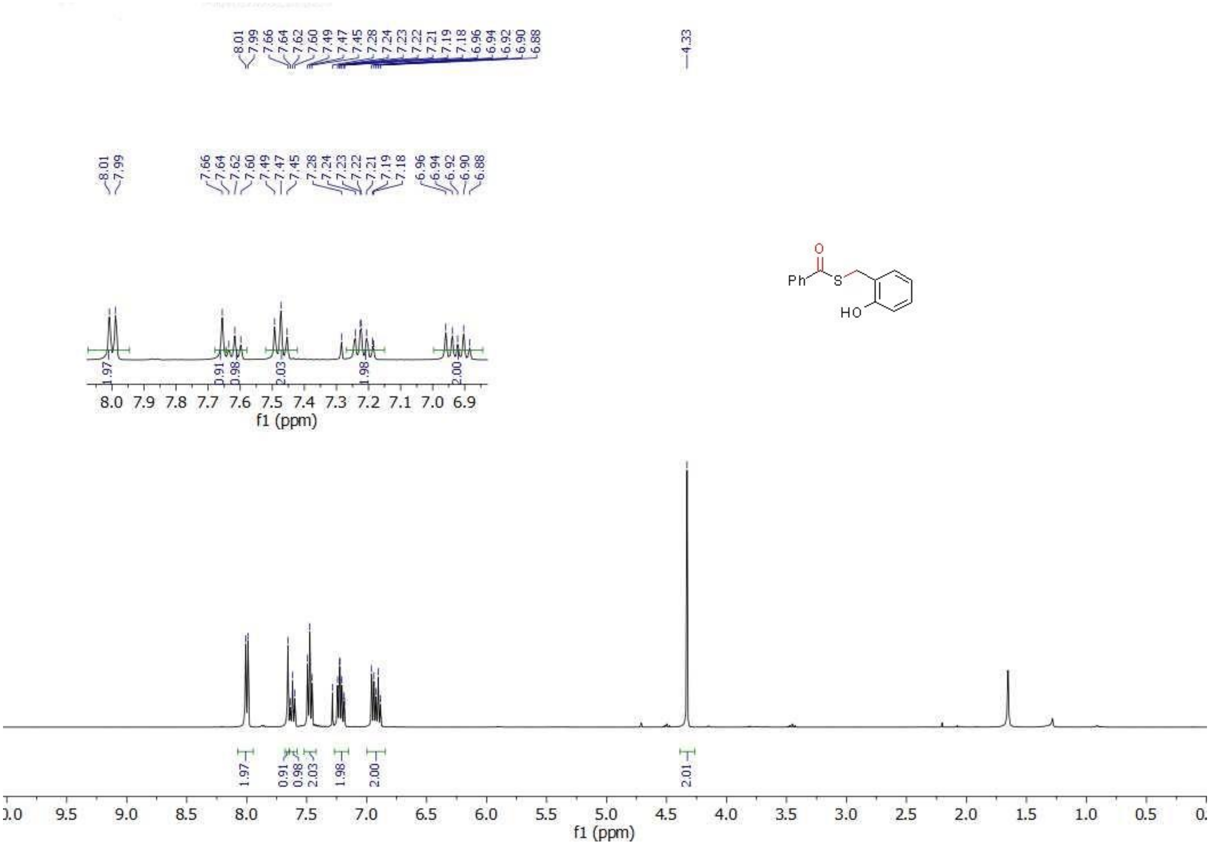
| | |
|---|---|
| Identification code | **3ba** |
| Empirical formula | $C_{15}H_{14}O_3S$ |
| Formula weight | 274.32 |
| Temperature/K | 189.68 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 4.4993(14) |
| b/Å | 15.165(4) |
| c/Å | 19.844(6) |
| α/° | 90 |
| β/° | 96.395(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 1345.6(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.354 |
| μ/mm$^{-1}$ | 0.241 |
| F(000) | 576.0 |
| Crystal size/mm$^3$ | 0.15 × 0.1 × 0.02 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.928 to 54.146 |
| Index ranges | $-5 \leq h \leq 5$, $-19 \leq k \leq 19$, $-25 \leq l \leq 25$ |
| Reflections collected | 15607 |
| Independent reflections | 2926 [$R_{int}$ = 0.0433, $R_{sigma}$ = 0.0322] |
| Data/restraints/parameters | 2926/0/175 |
| Goodness-of-fit on F$^2$ | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0411, $wR_2$ = 0.0933 |
| Final R indexes [all data] | $R_1$ = 0.0518, $wR_2$ = 0.1009 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.19/-0.21 |
| CCDC Number | 2370262 |

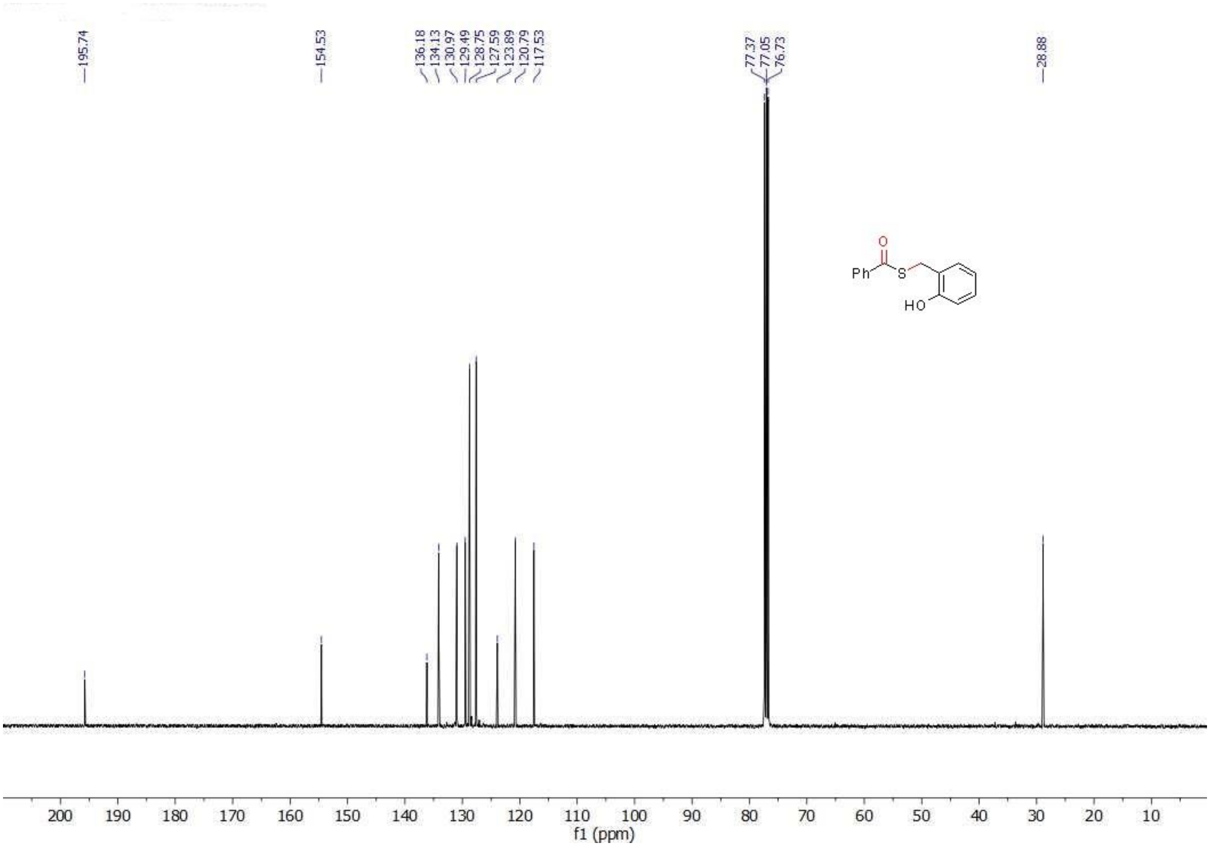
## G. References:

1. V. P. R. K. Putta, R. Gujjarappa, U. Tyagi, P. P. Pujar and C. C. Malakar, *Org. Biomol. Chem.*, 2019, **17**, 2516.
2. G. M. Sheldrick, SADABS, software for empirical absorption correction, Universitat: Göttingen, Germany, **1999**.
3. G. M. Sheldrick*, SHELXS-2013 and SHELXL-2013, Program for Refinement of Crystal Structures; University of Göttigen: Göttigen, Germany*, **2013.**
4. M. Steinmetz. Grimme, Effects of London dispersion correction in density functional theory on the structures of organic molecules in the gas phase. *Phys. Chem. Chem. Phys.* 2013, **15**, 16031.

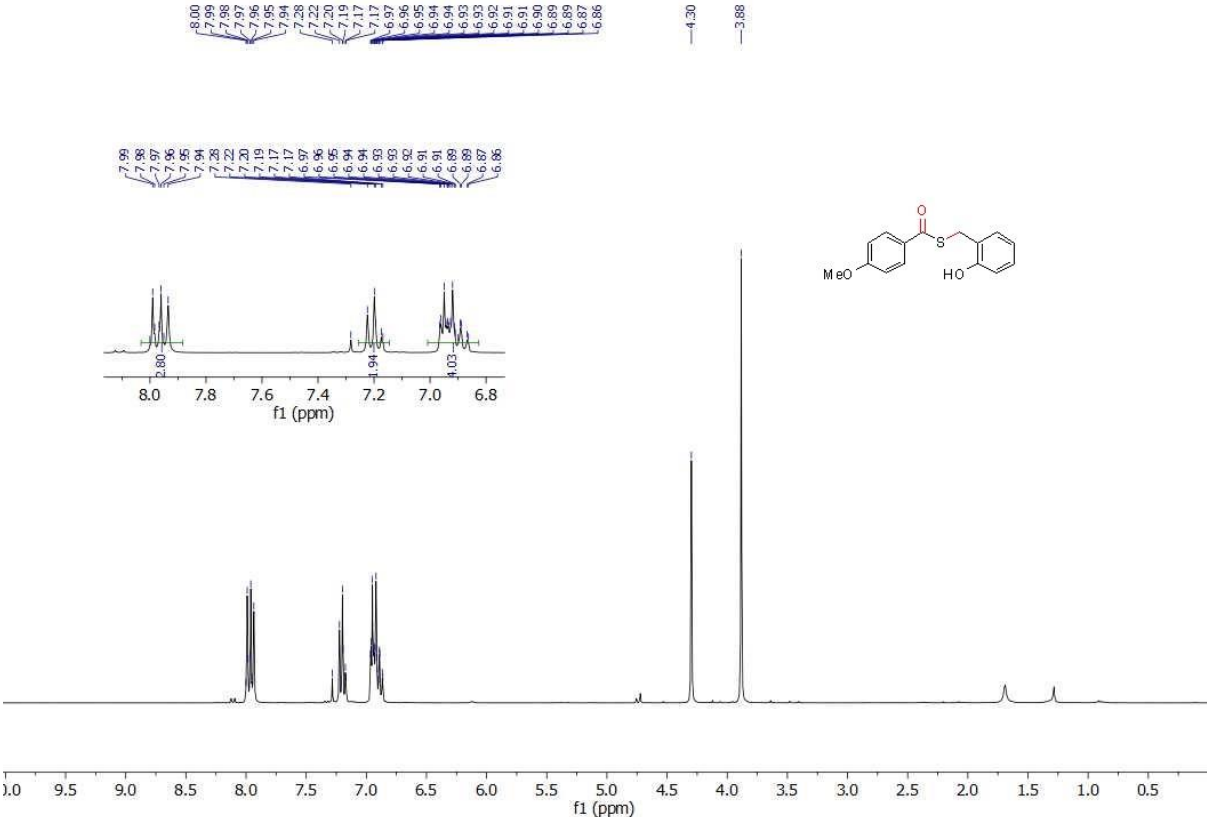
## H. Copies of $^1$H and $^{13}$C{$^1$H} NMR Spectra of all products:

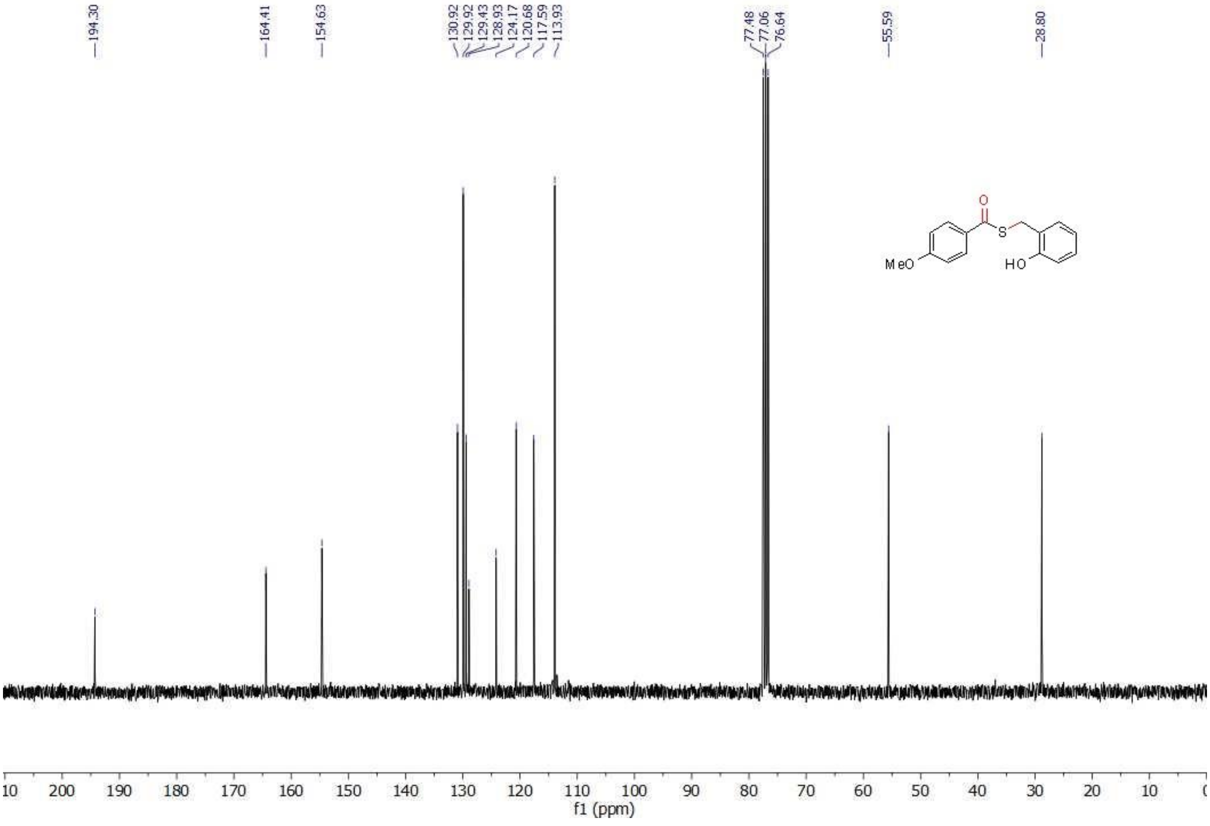
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3aa**:



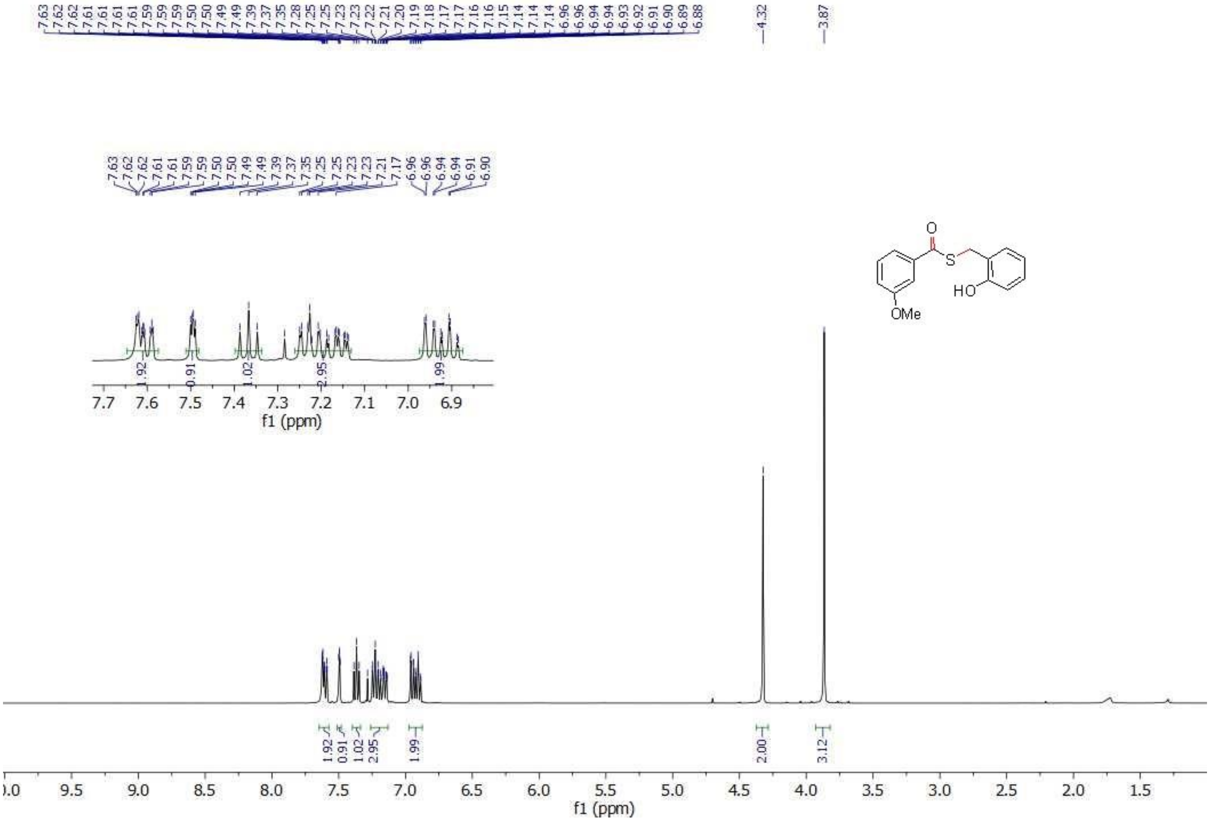


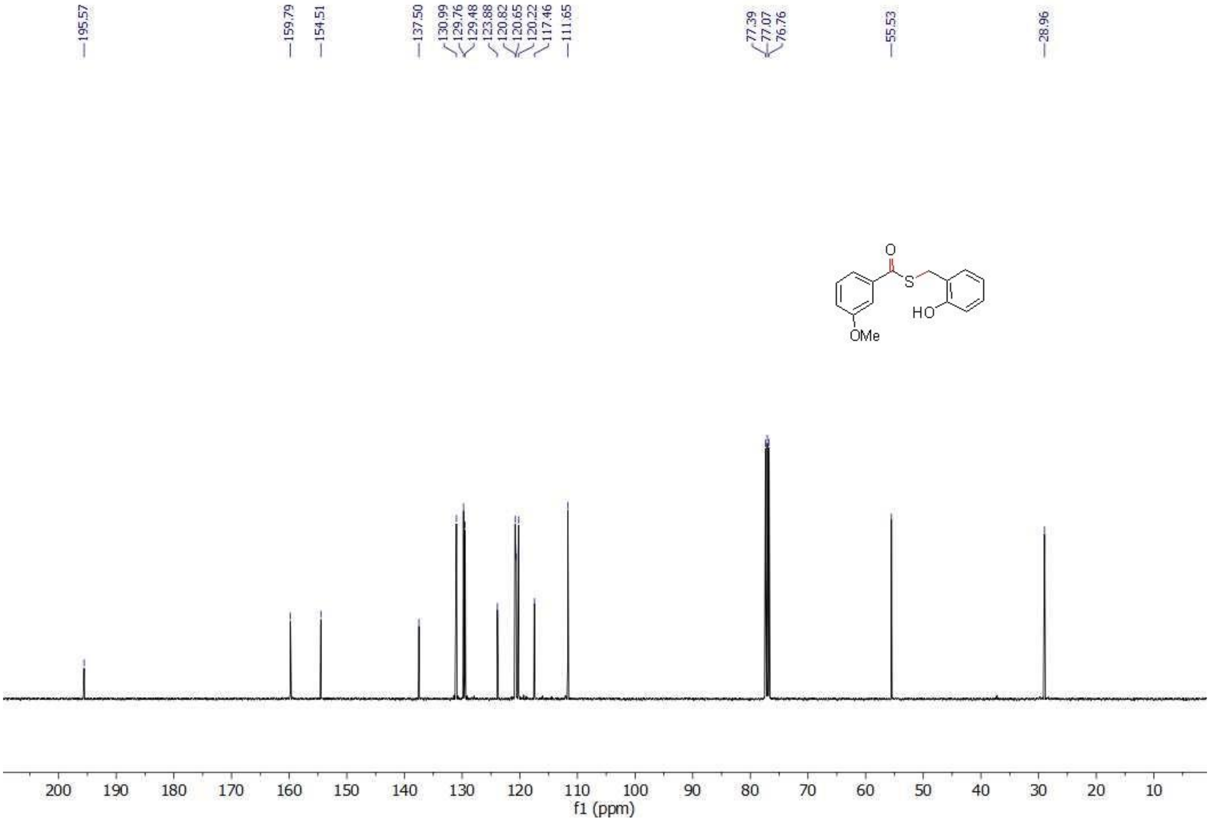
$^1$**H NMR** (300 MHz, $CDCl_3$) and $^{13}$**C{$^1$H} NMR** (75 MHz, $CDCl_3$) spectra of **3ba**:



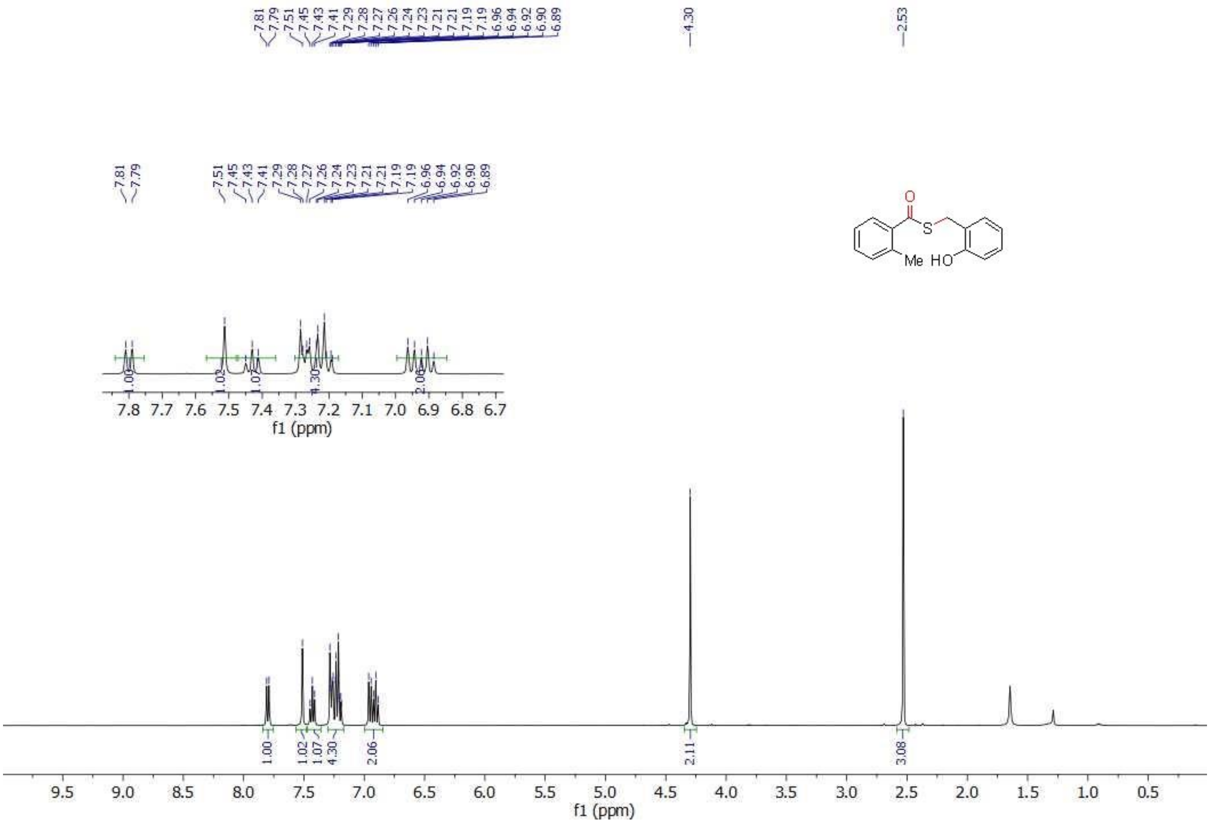


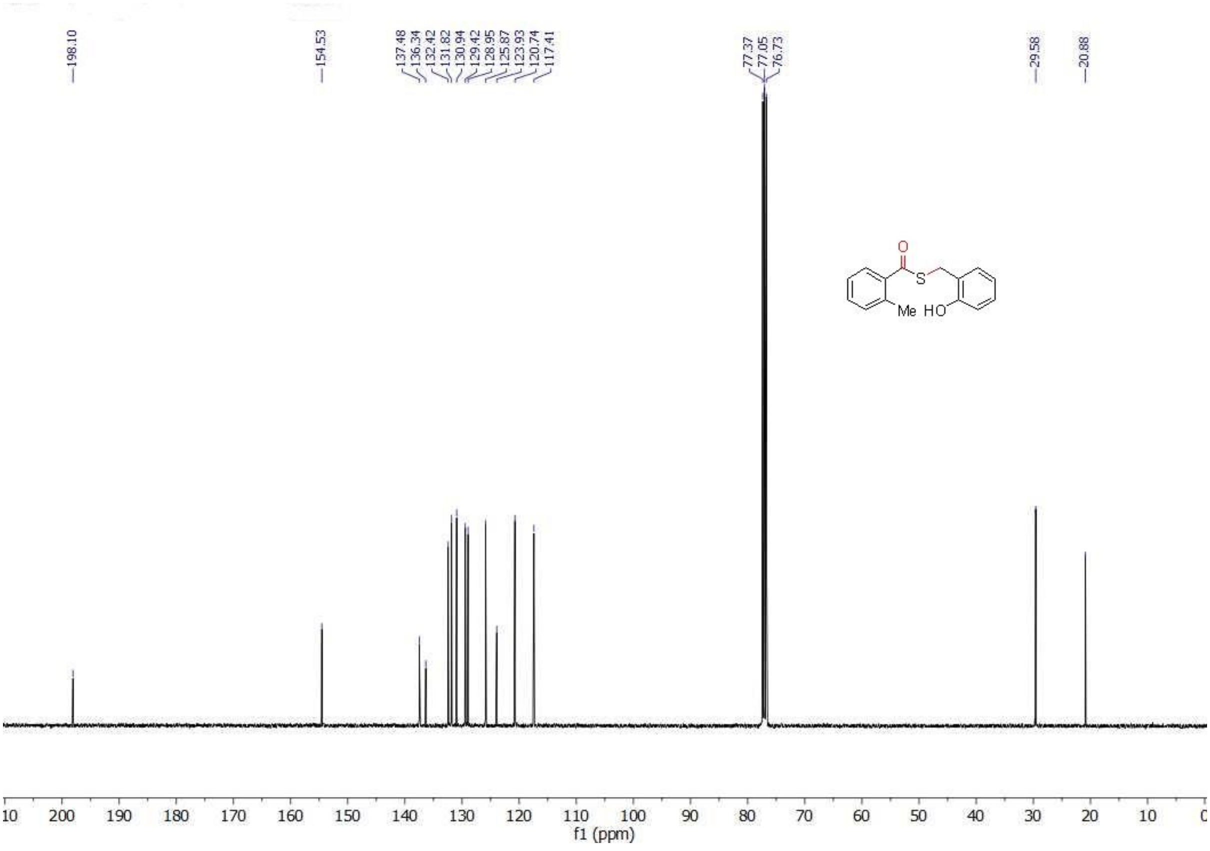
$^{1}$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) spectra of **3ca**:



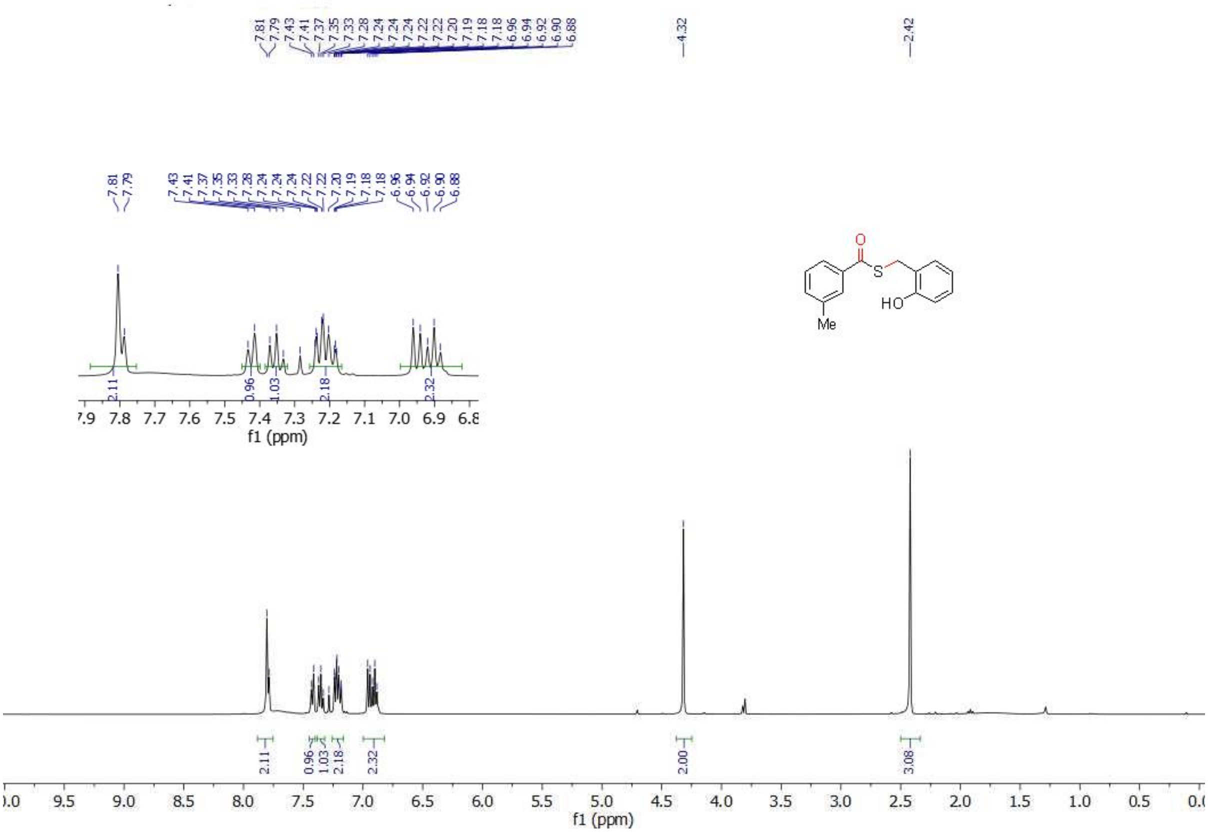


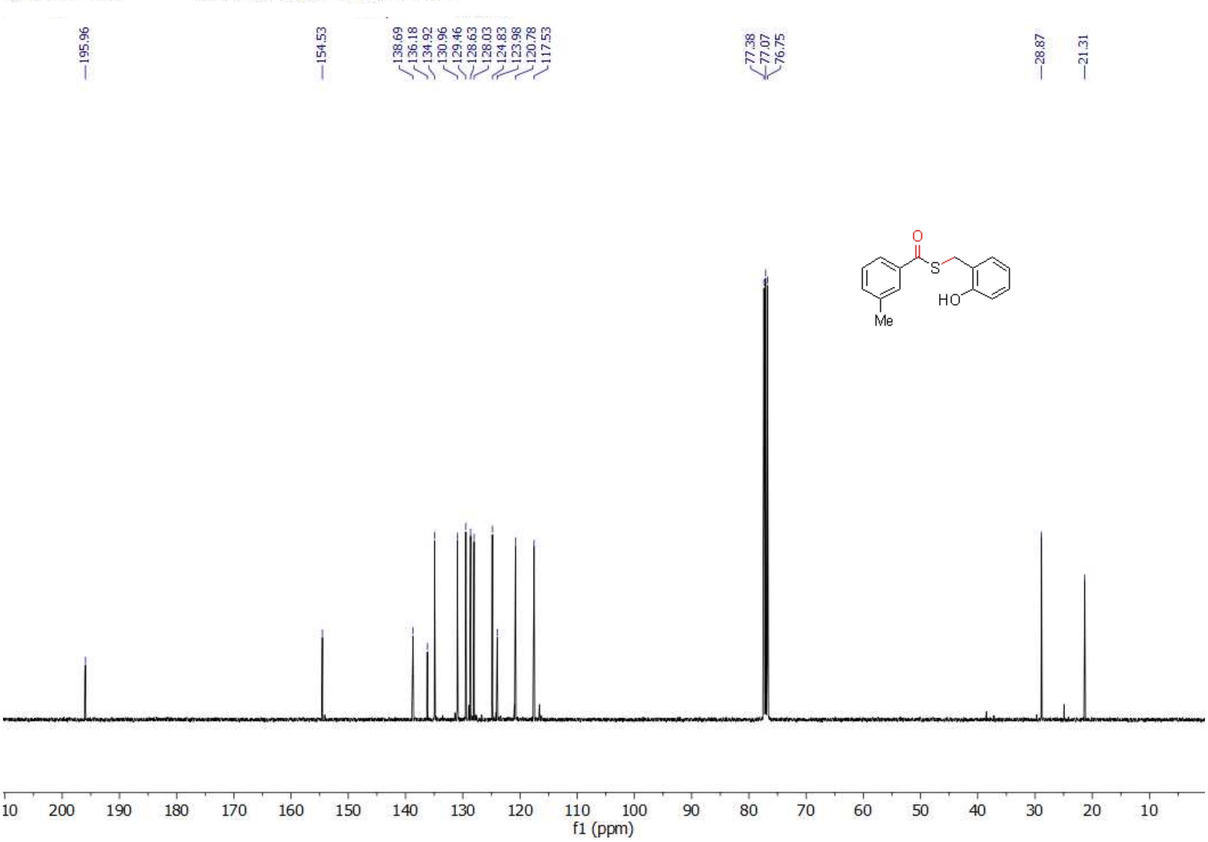
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3da**:



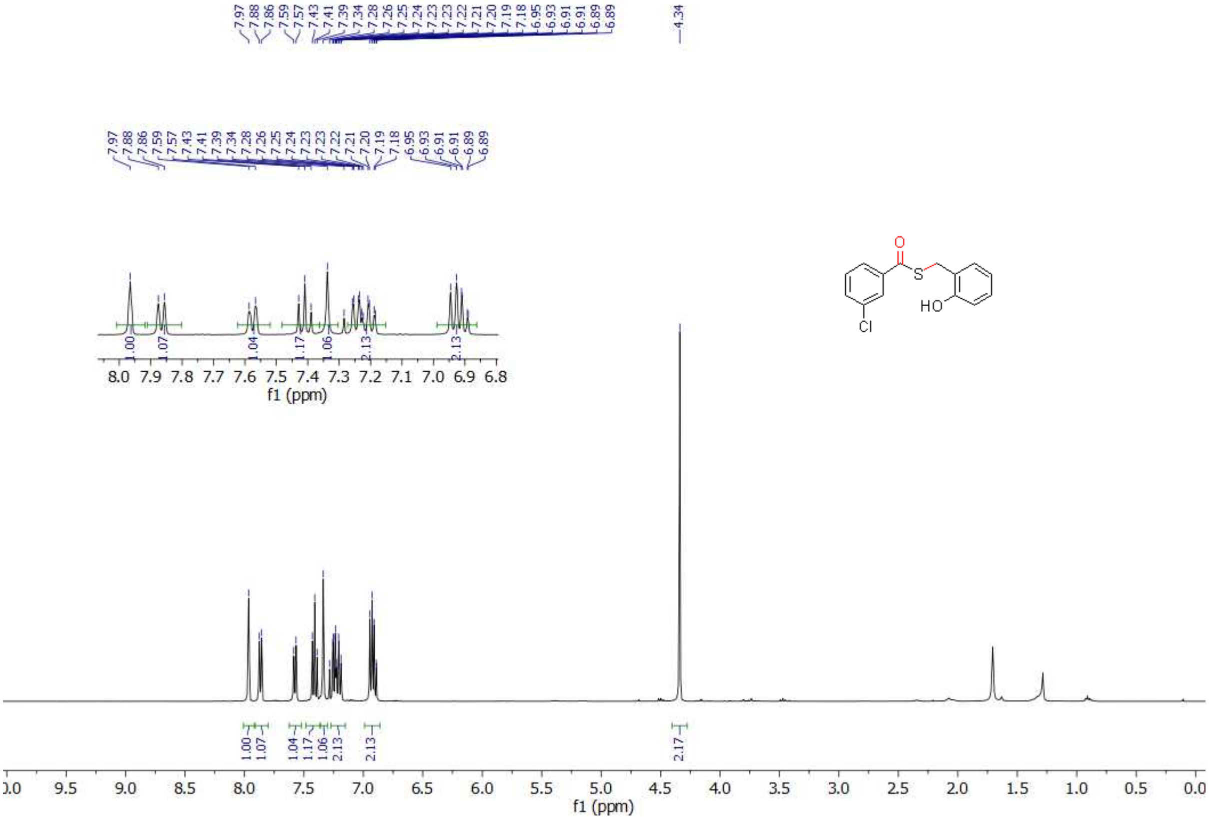


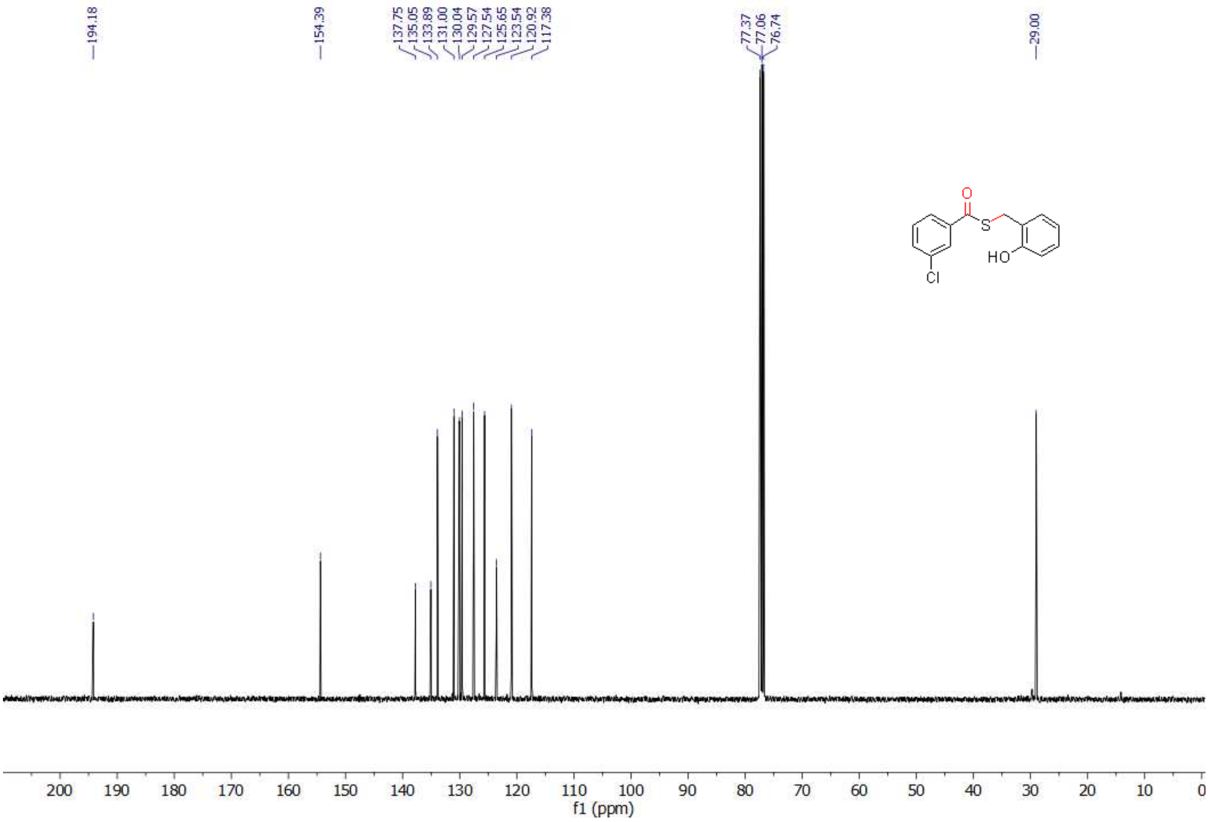
$^1$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ea**:



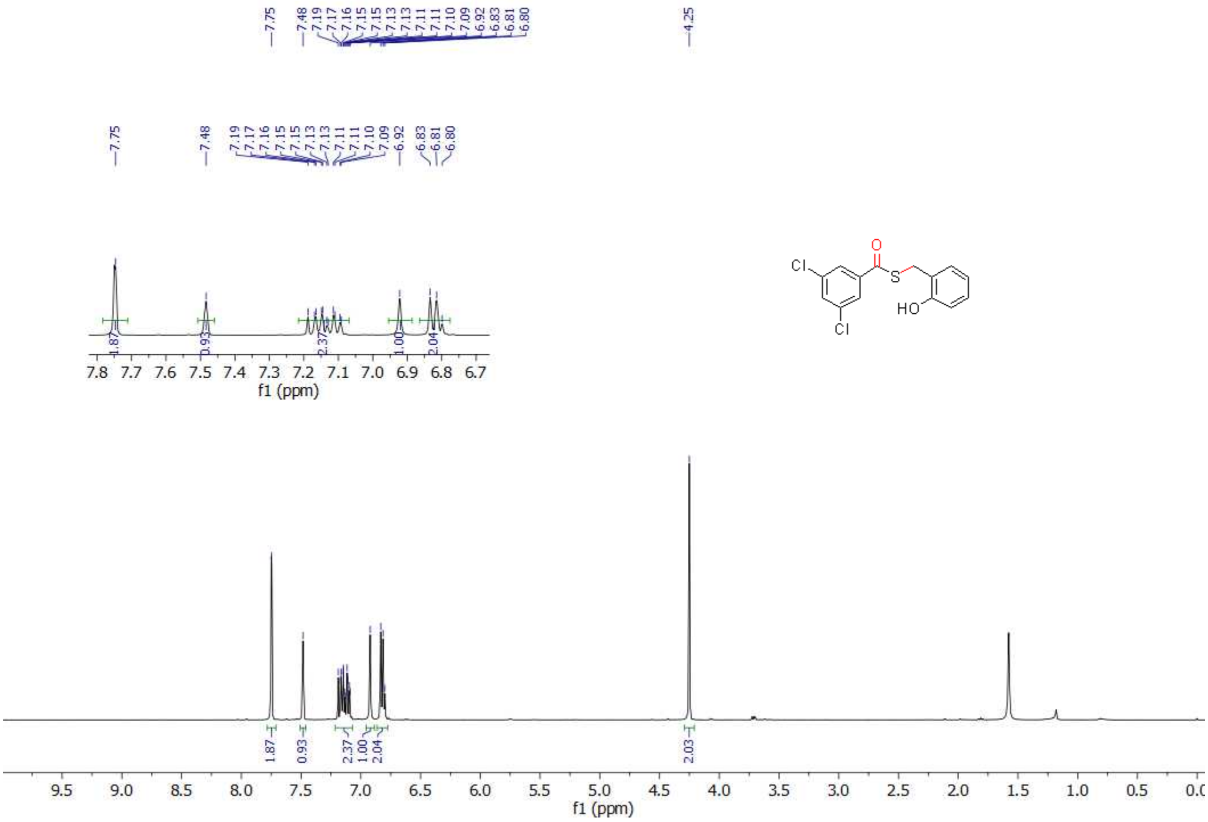


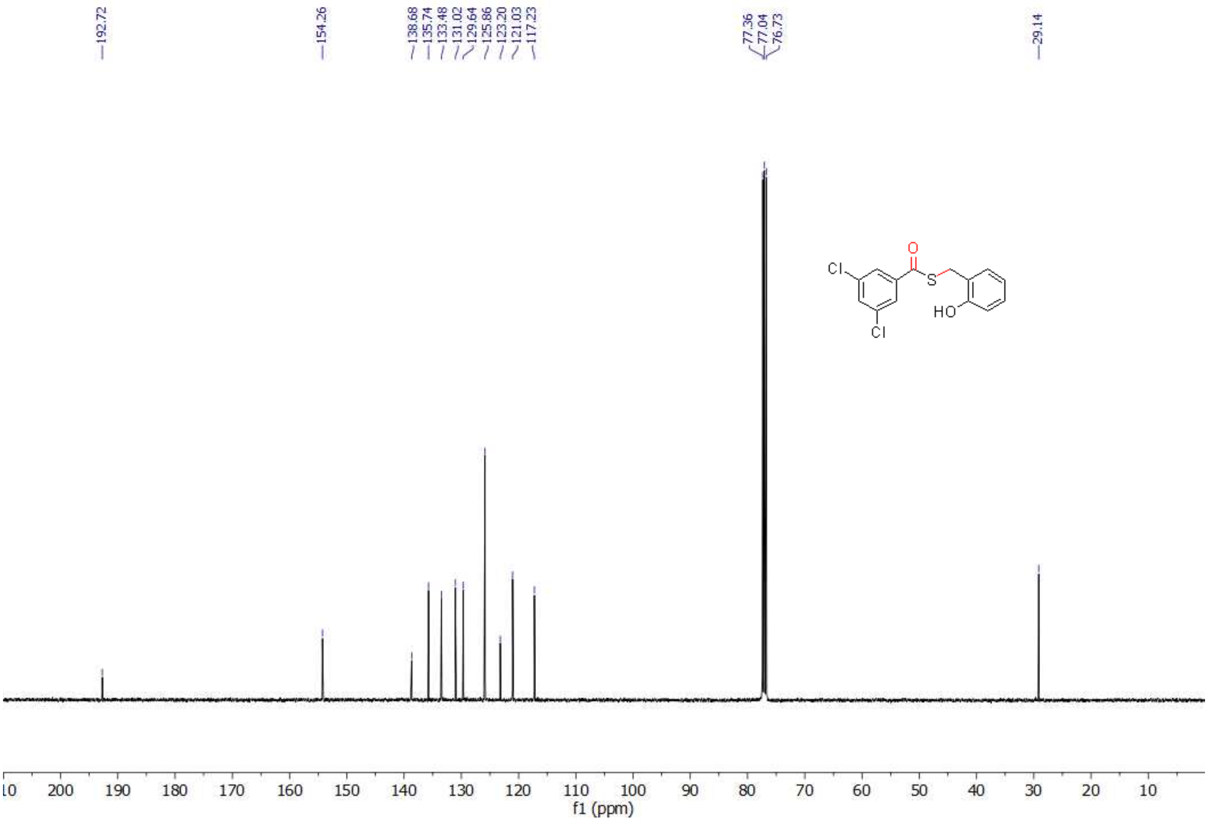
**$^{1}$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3fa**:



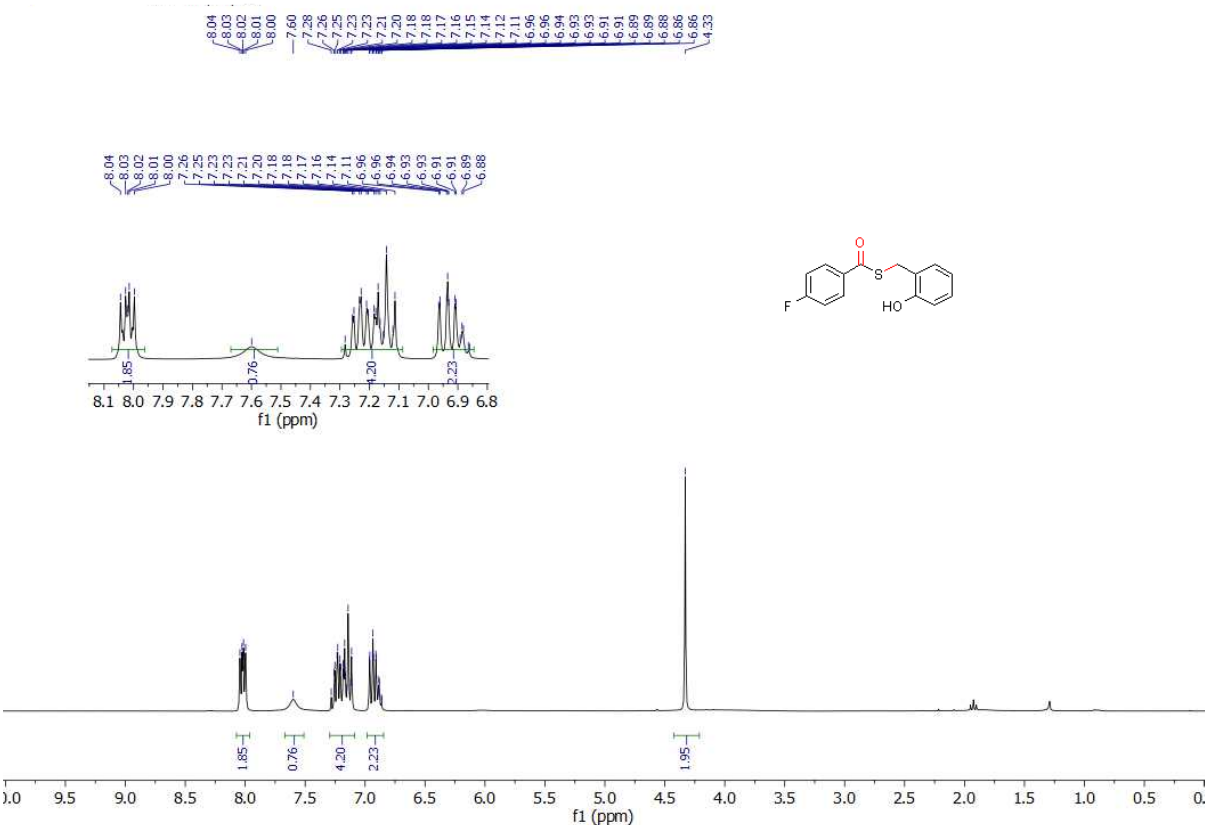


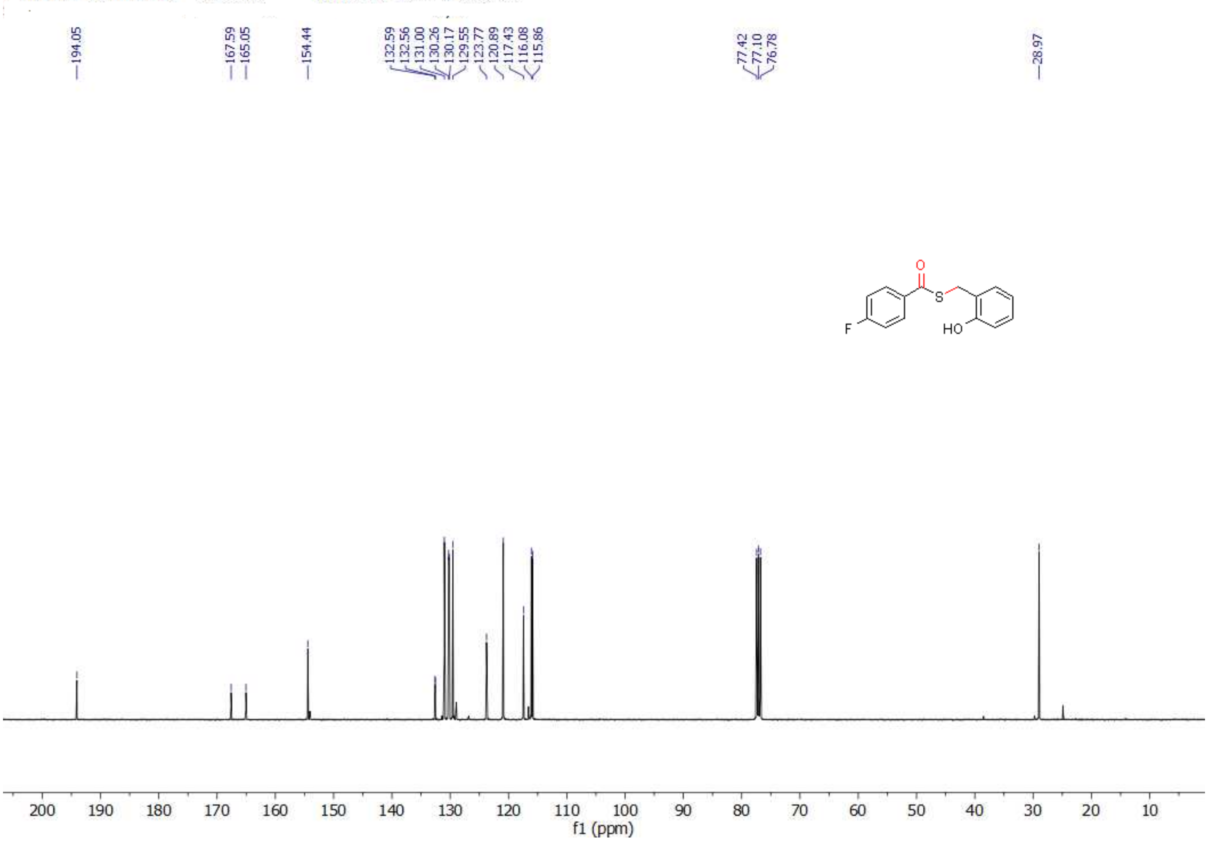
**$^1$H NMR** (400 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) spectra of **3ga**:



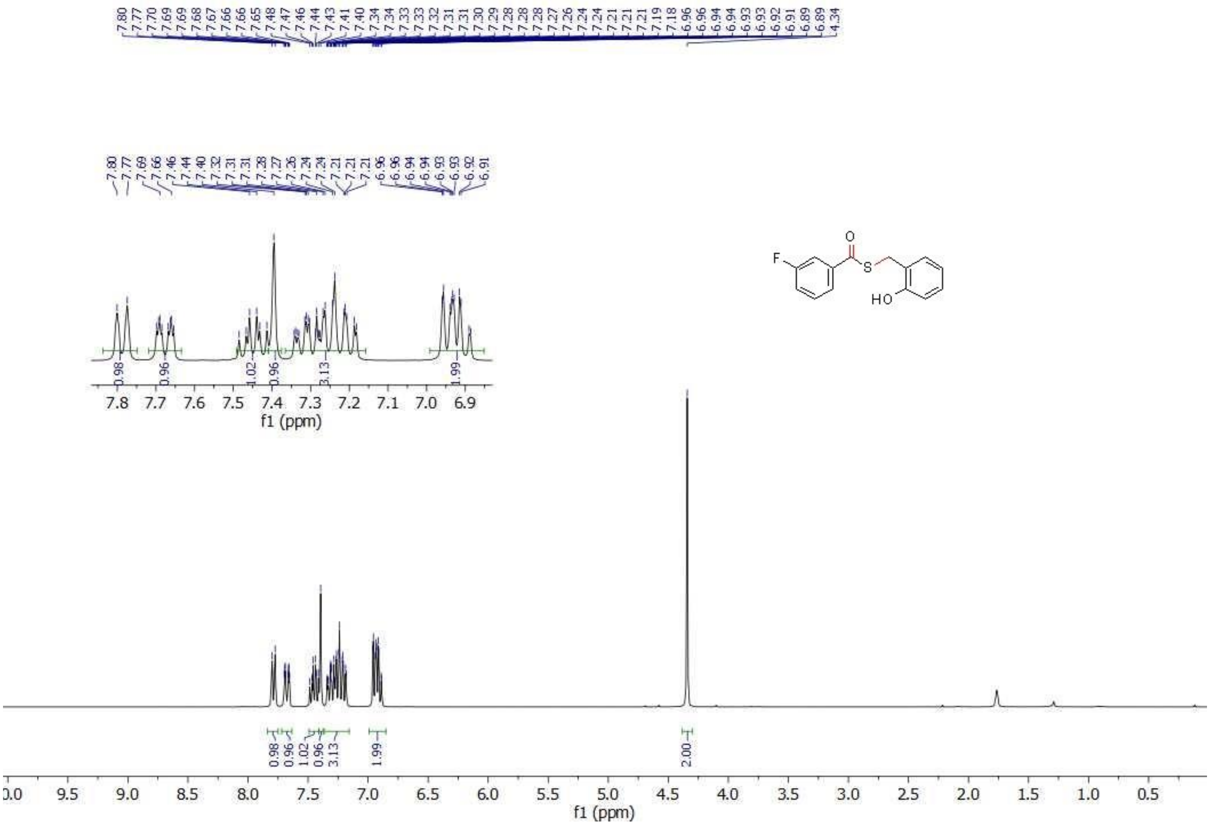


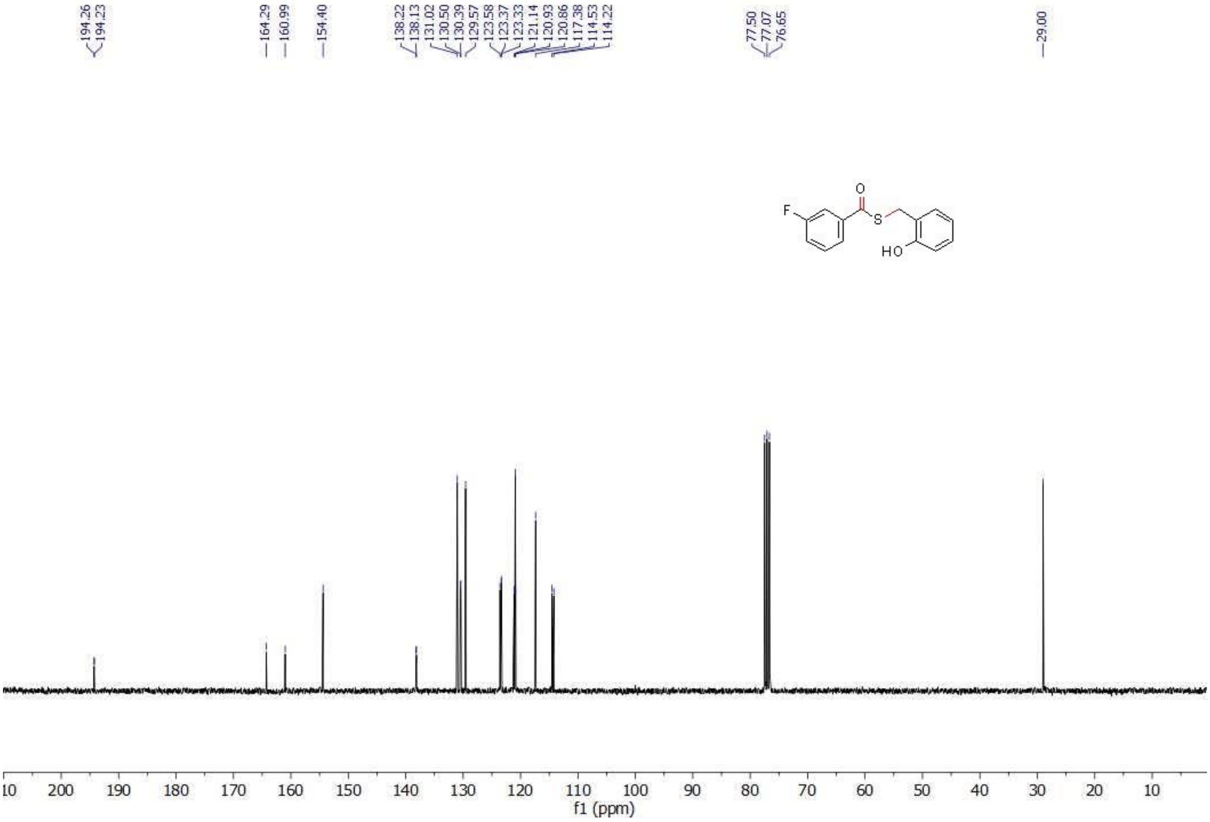
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ha**:



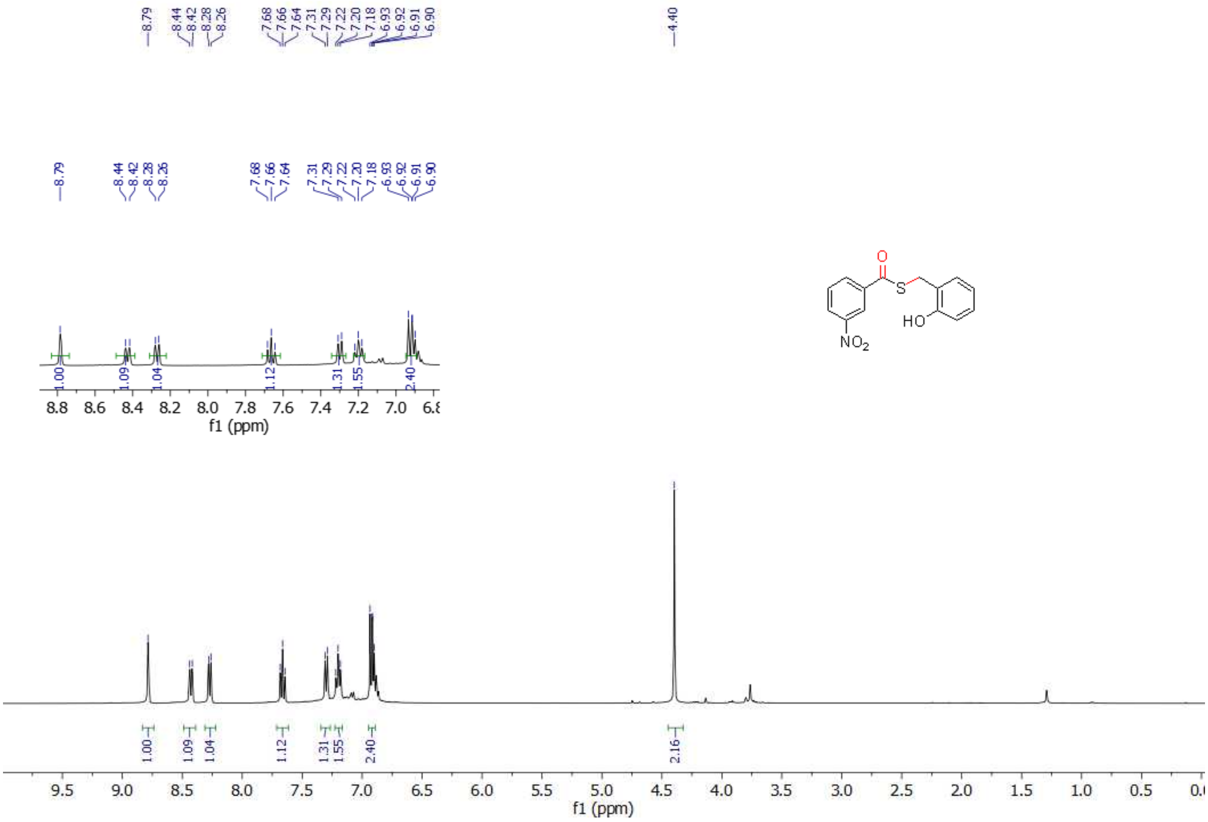


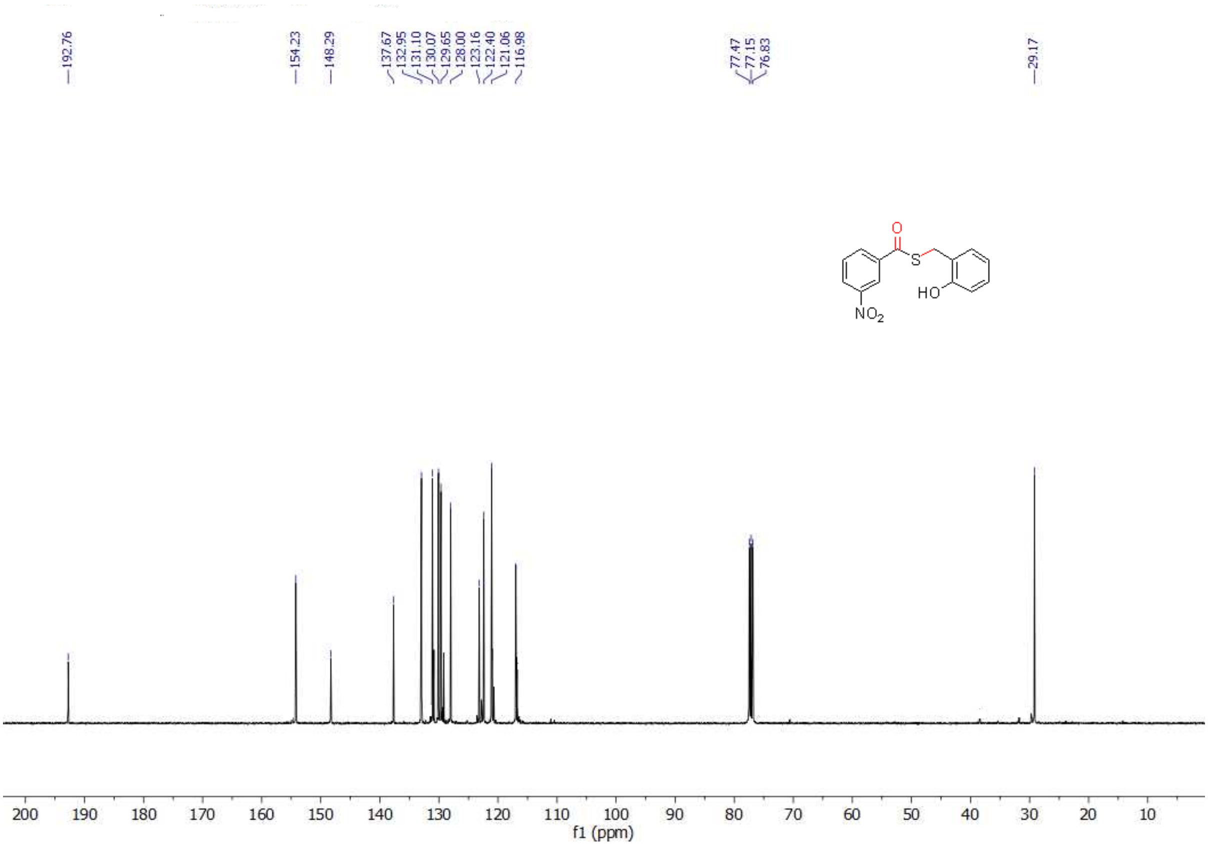
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (75 MHz, CDCl$_3$) spectra of **3ia**:



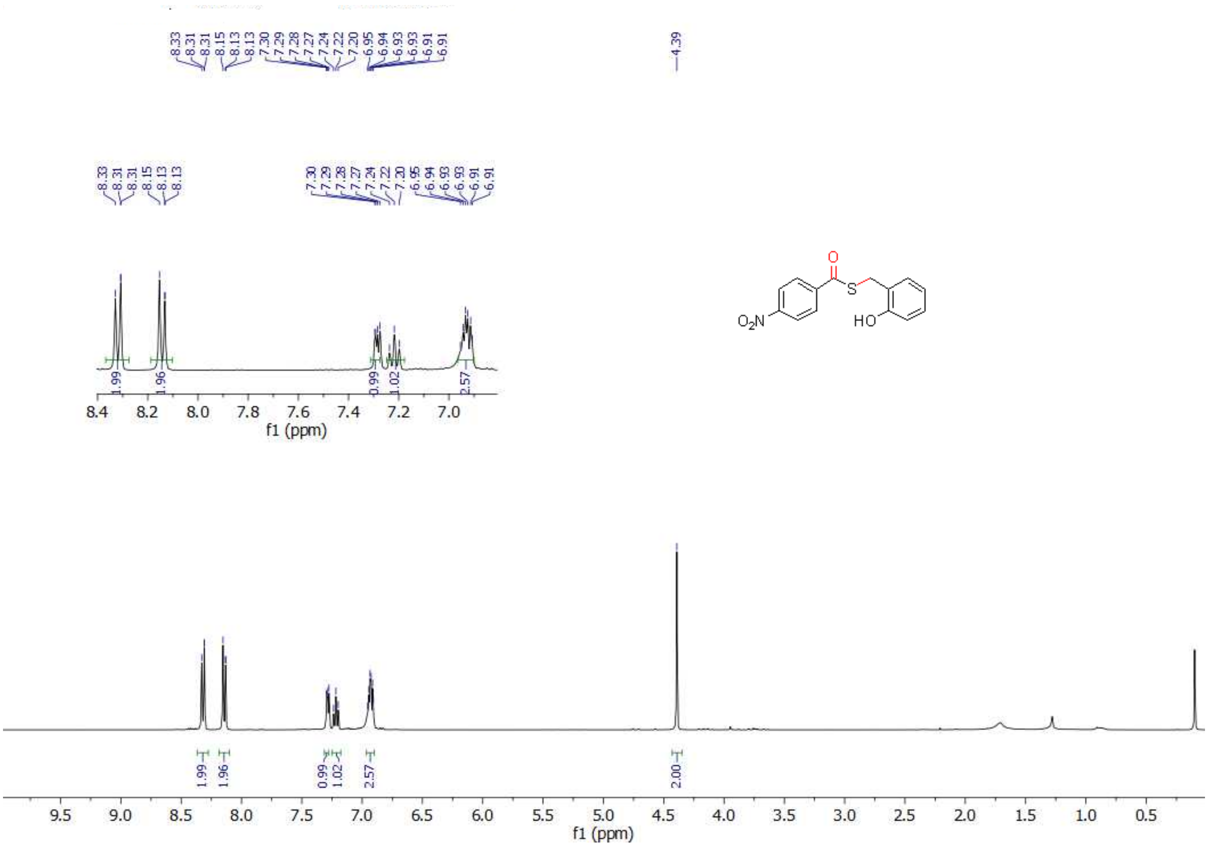


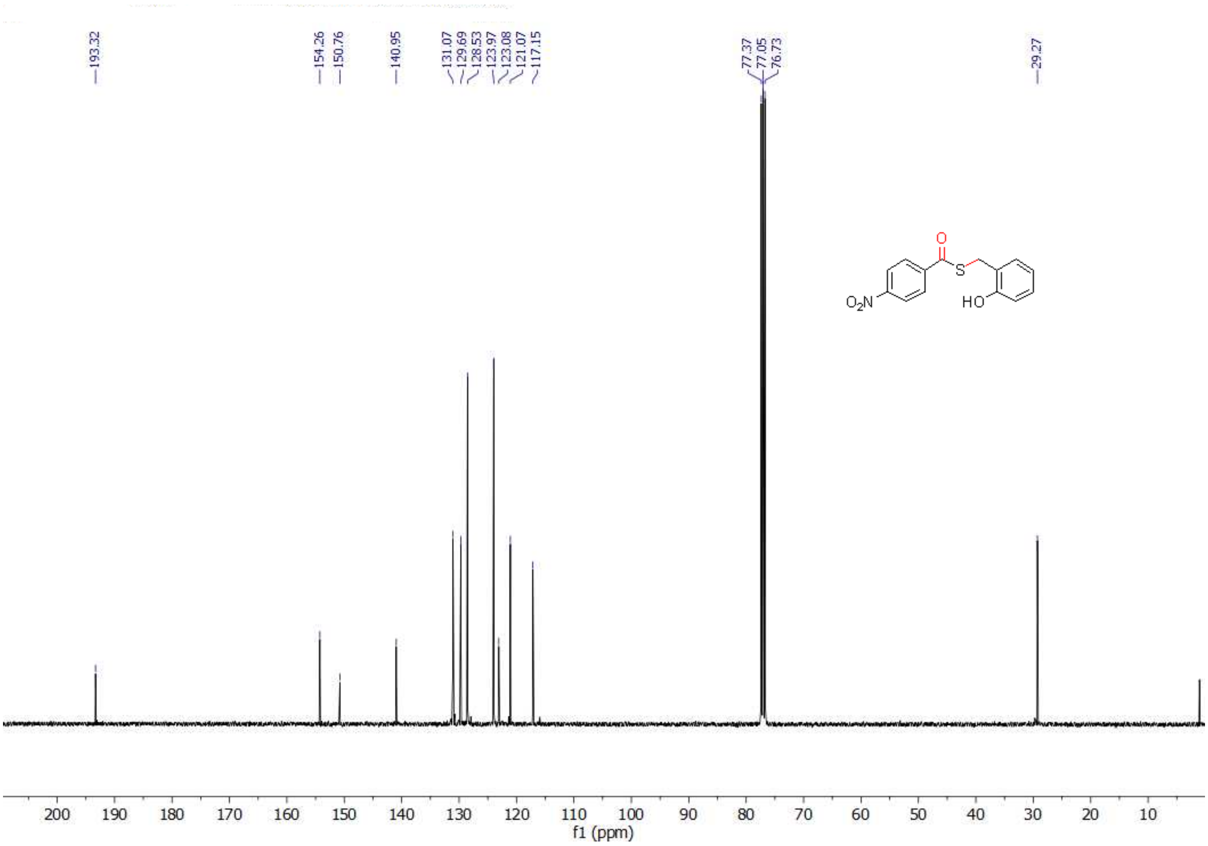
$^1$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) spectra of **3ja**:



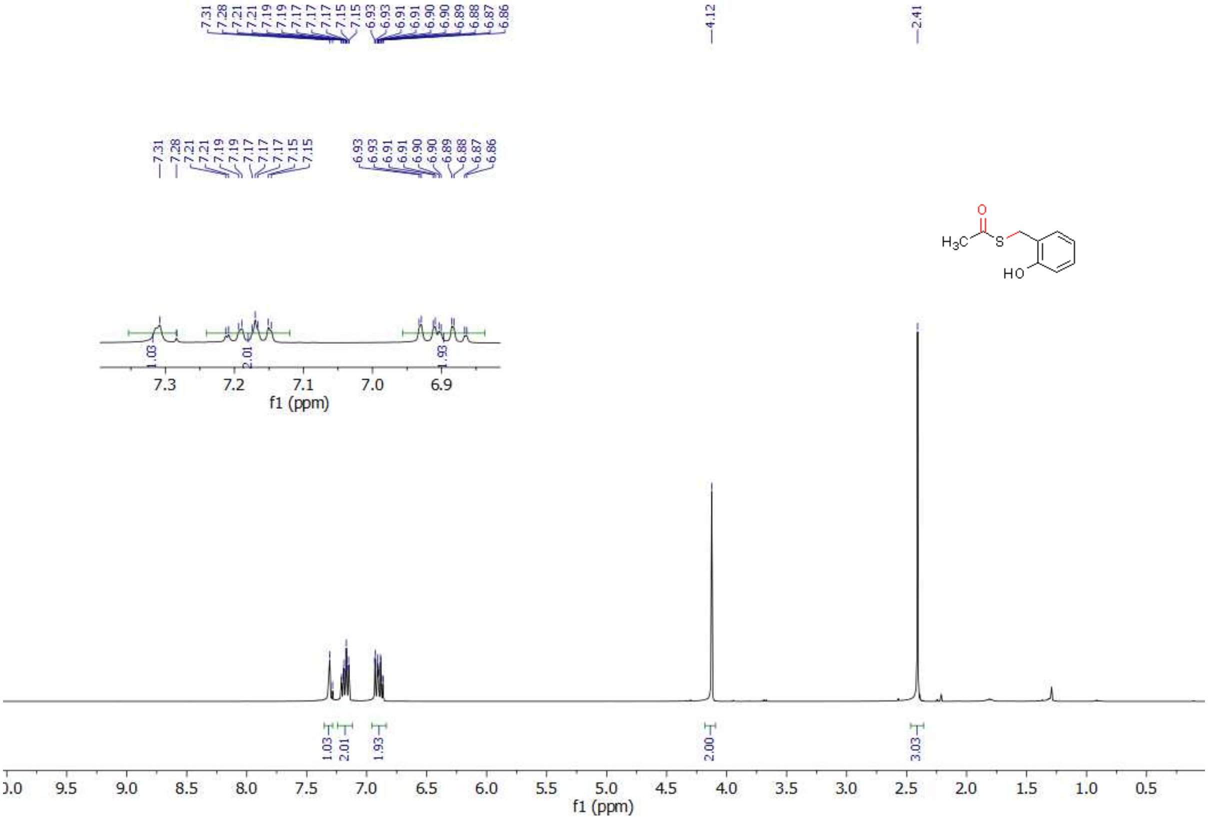


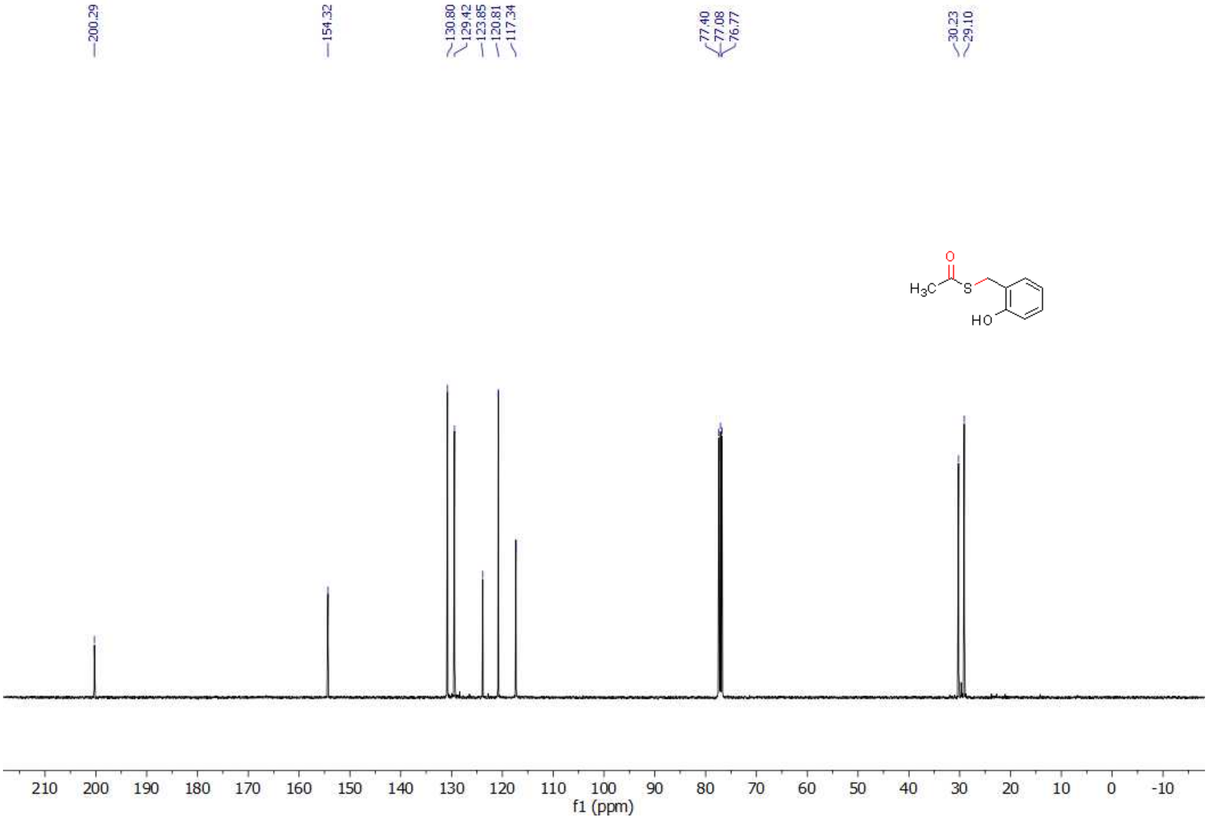
$^1$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) spectra of **3ka**:



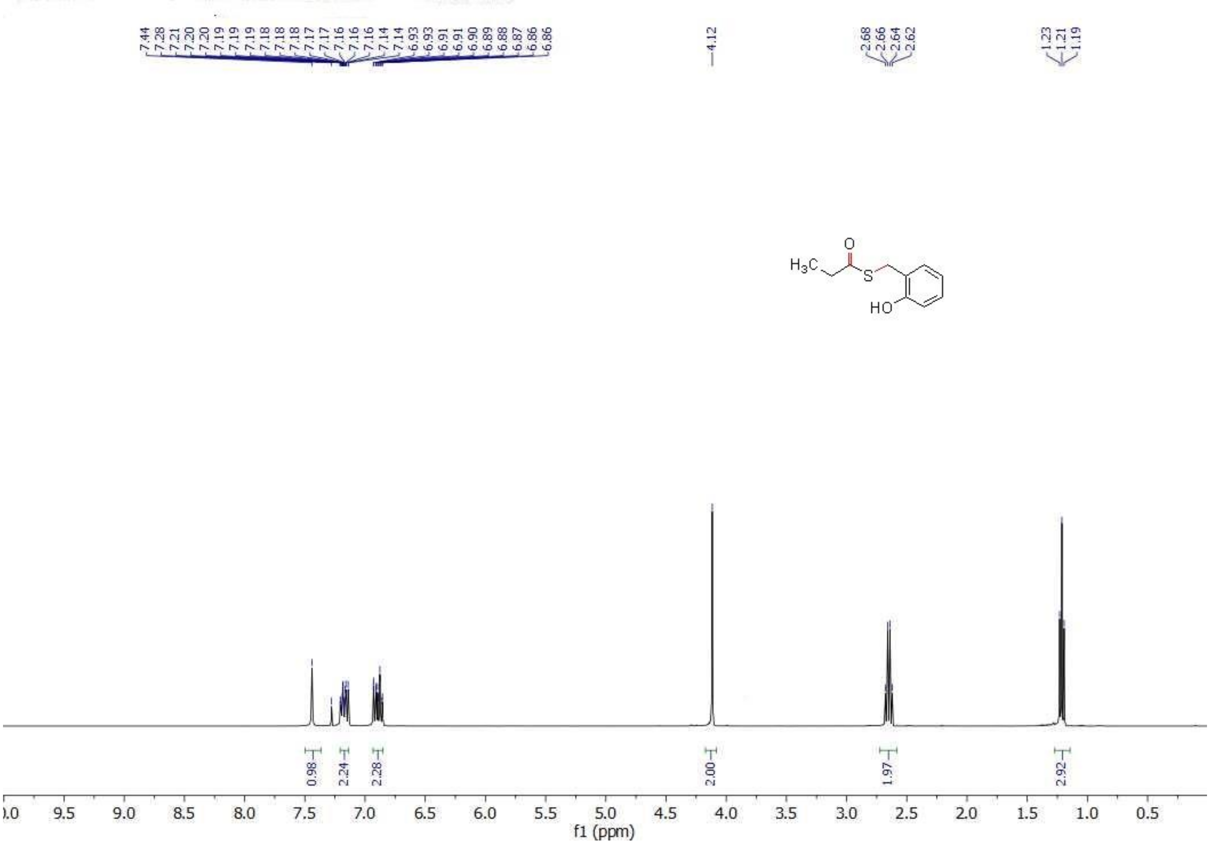


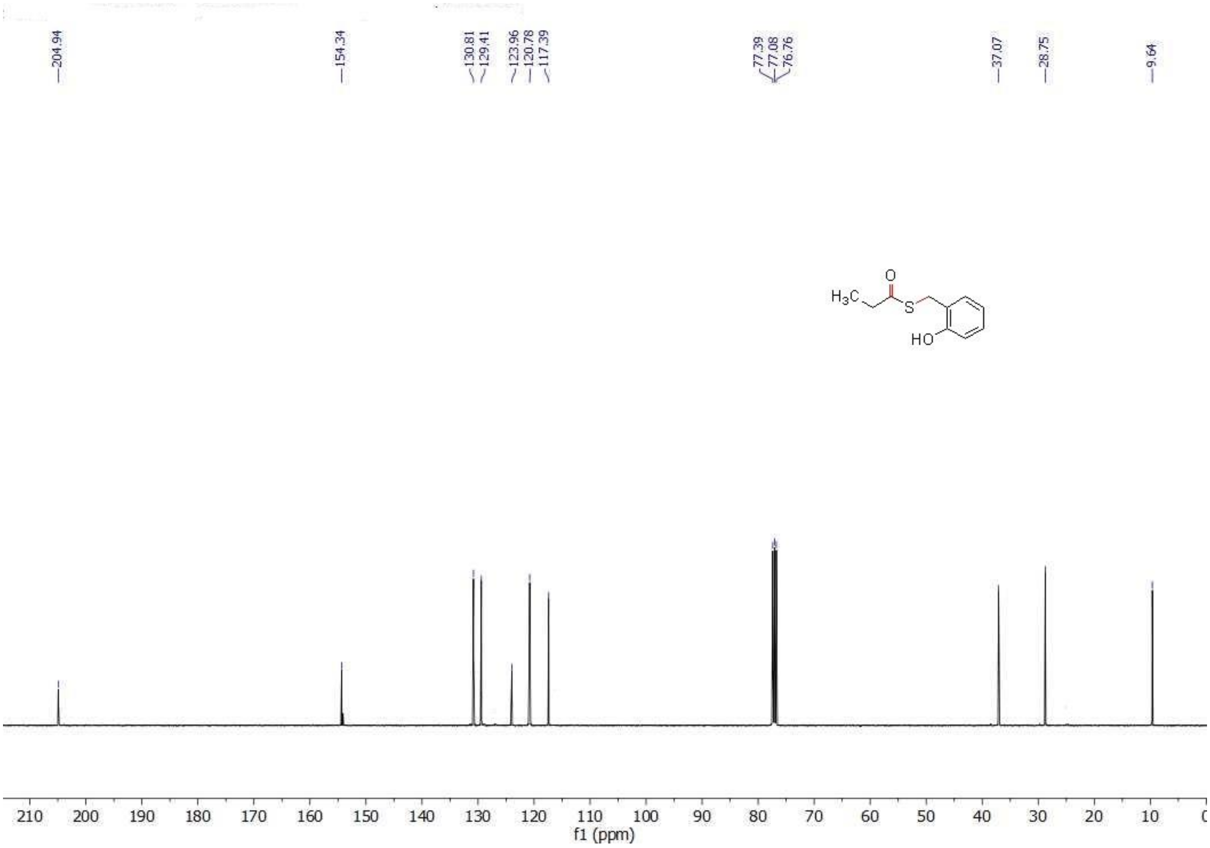
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3la**:



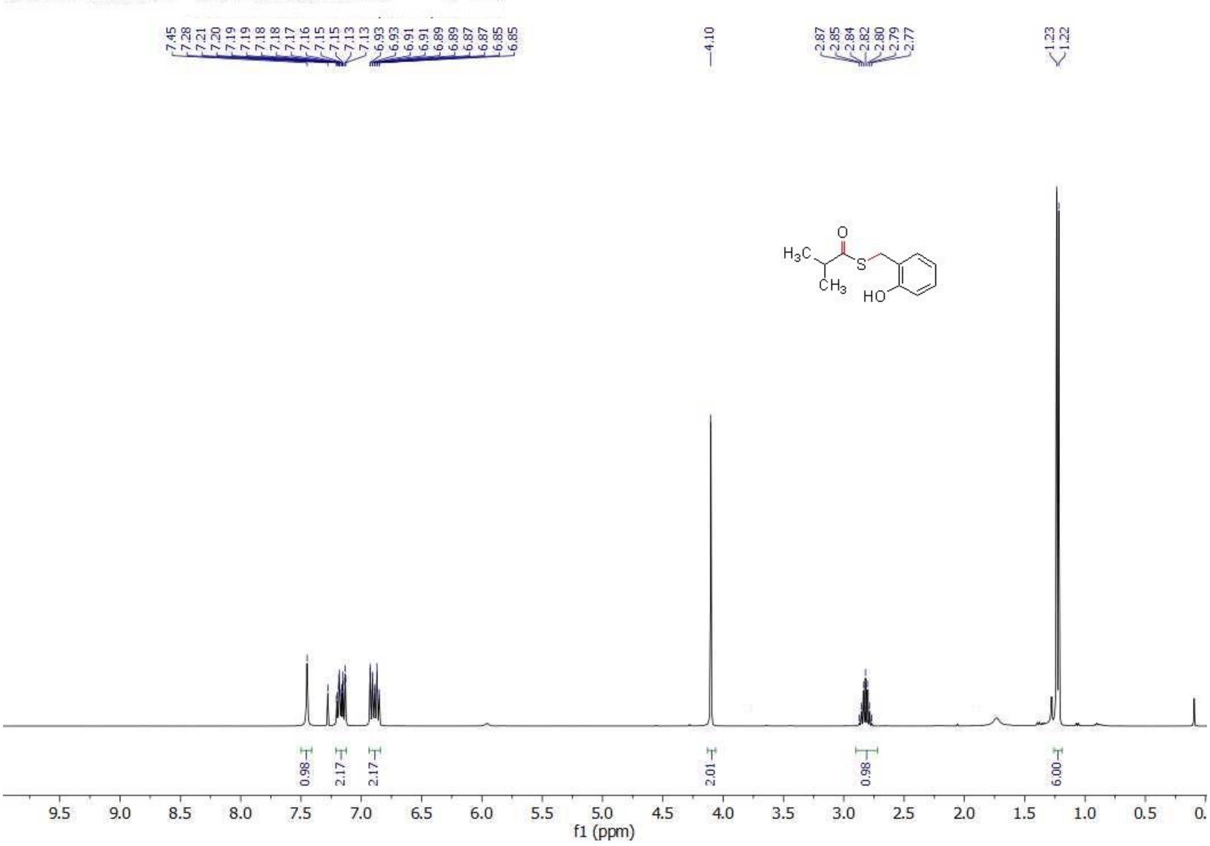


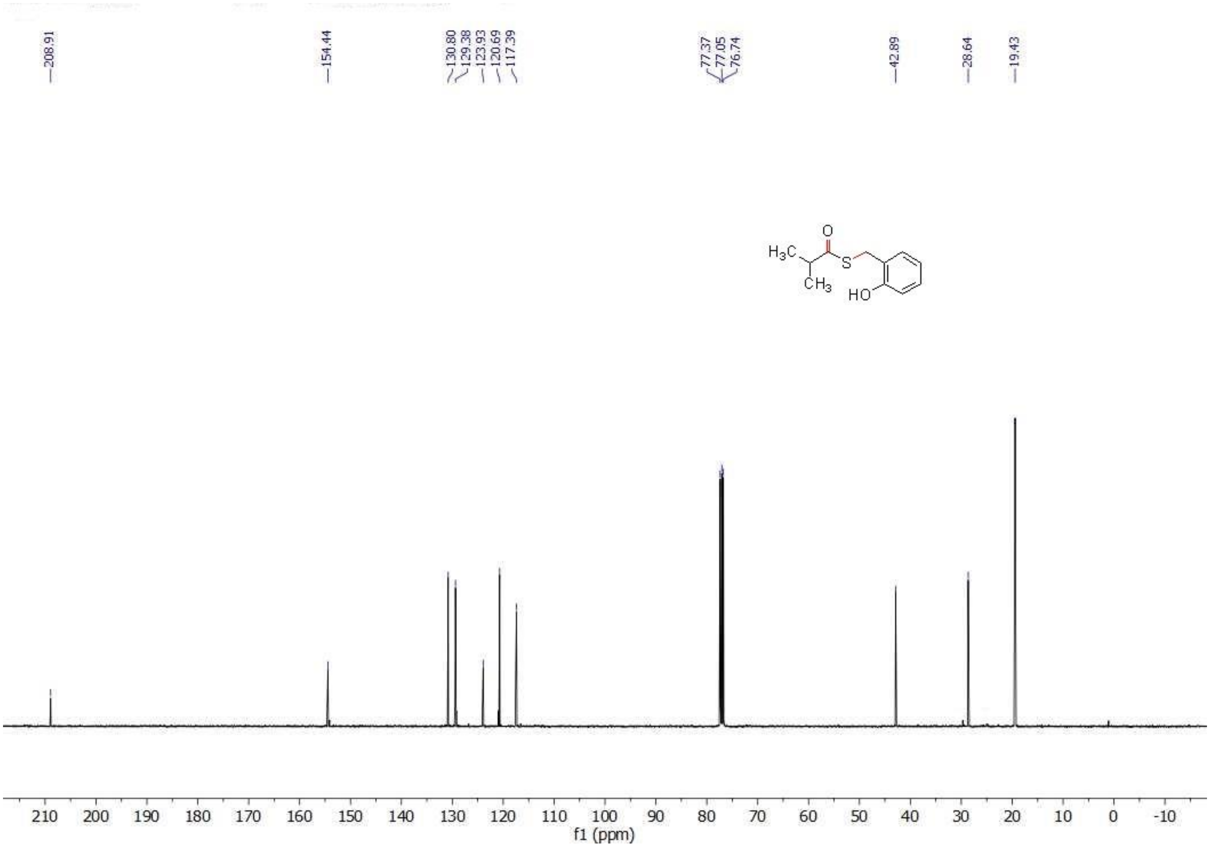
$^1$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ma**:



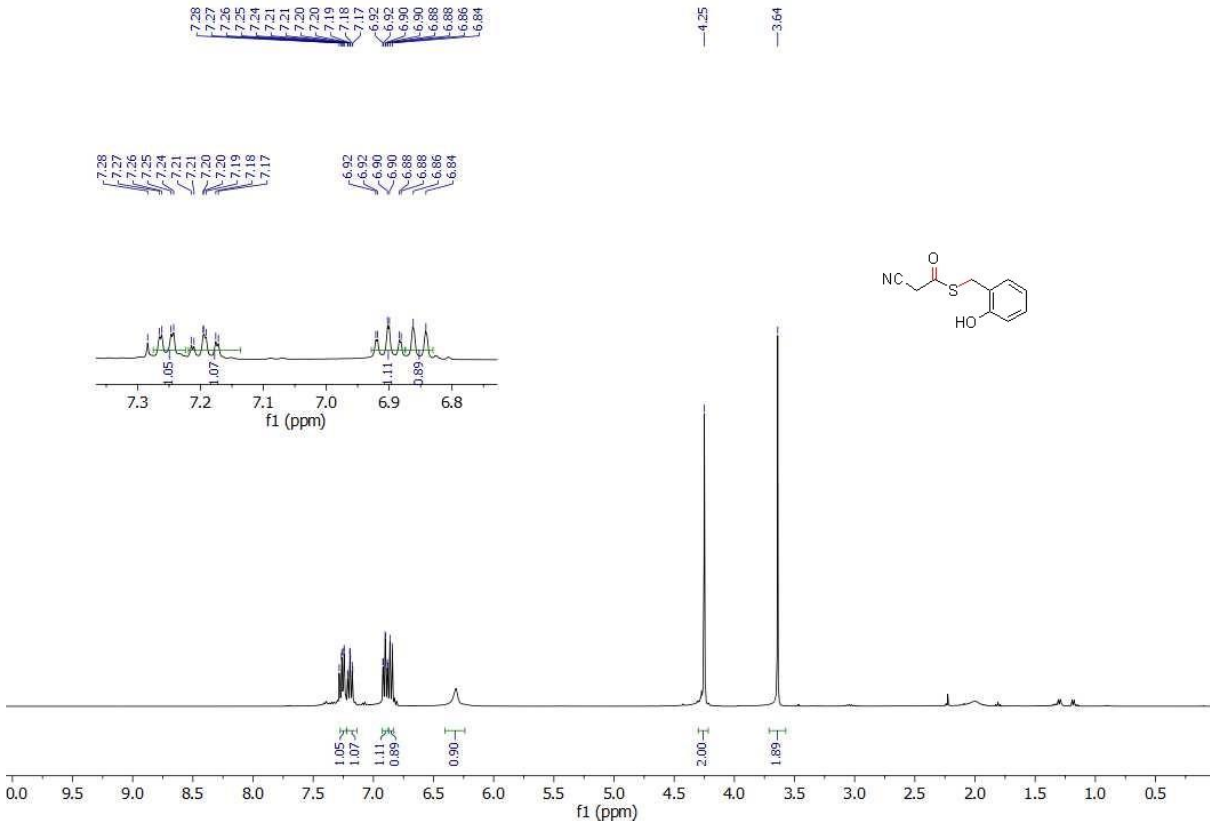


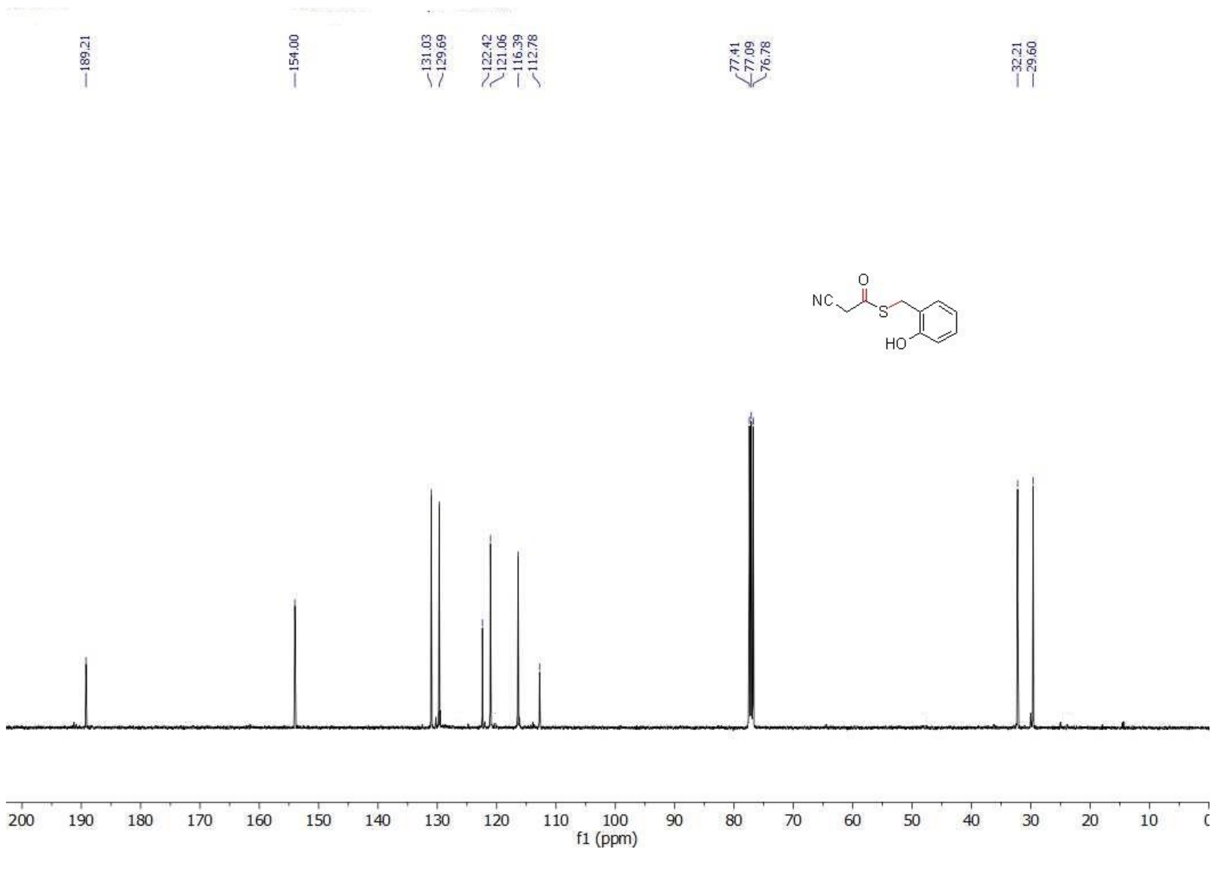
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3na**:



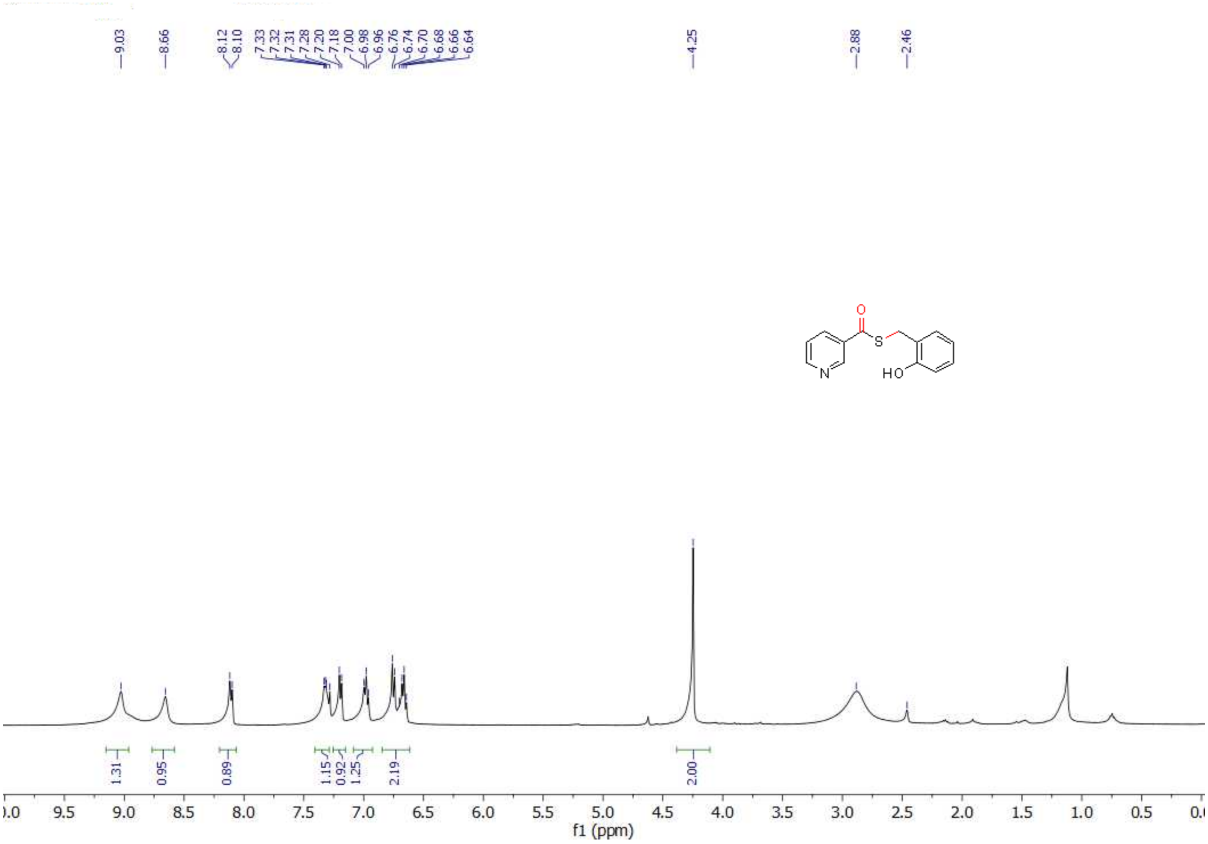


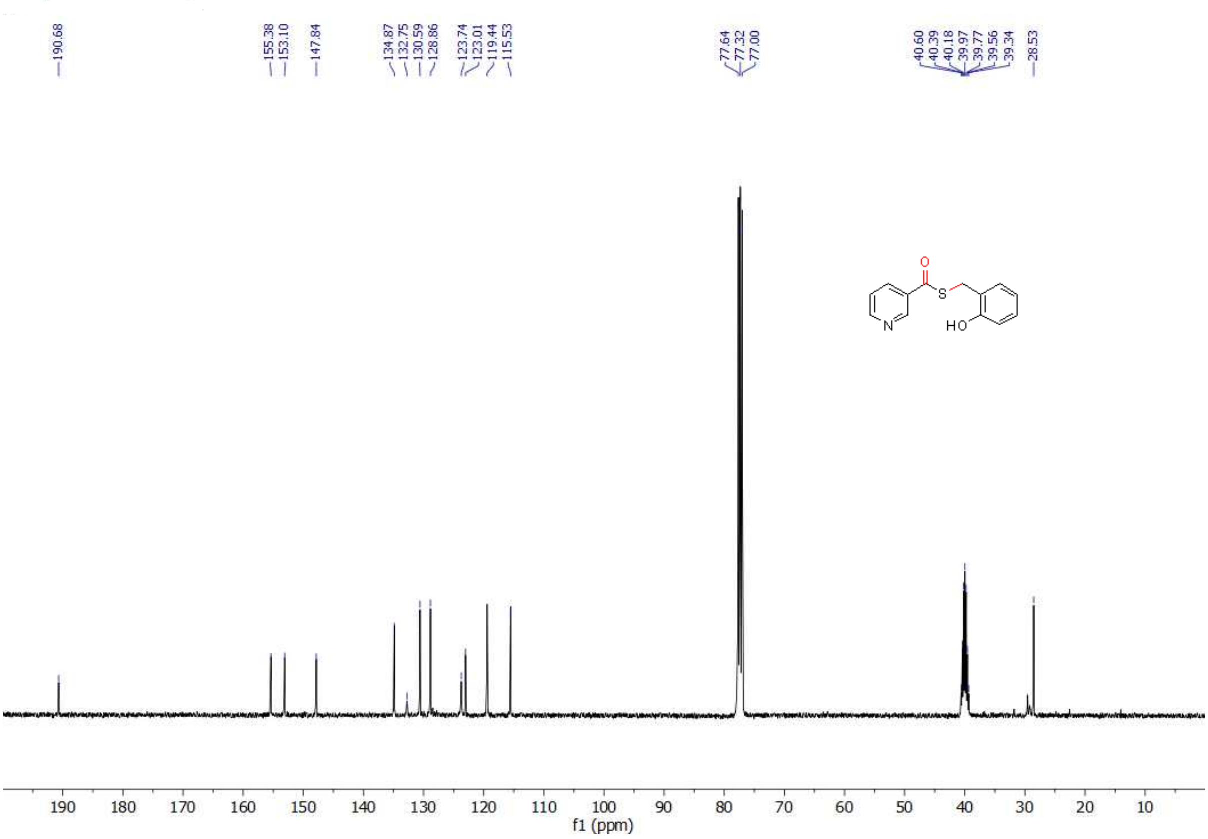
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3oa**:



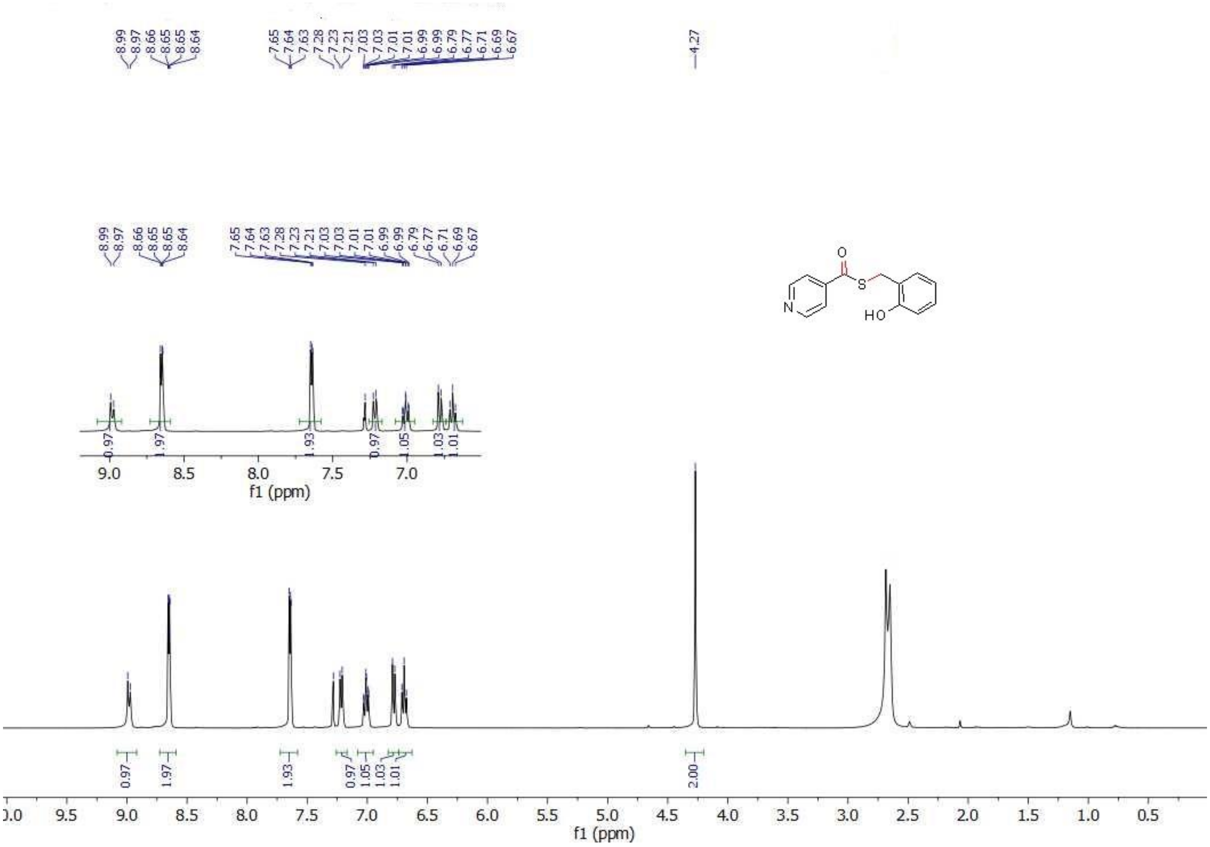


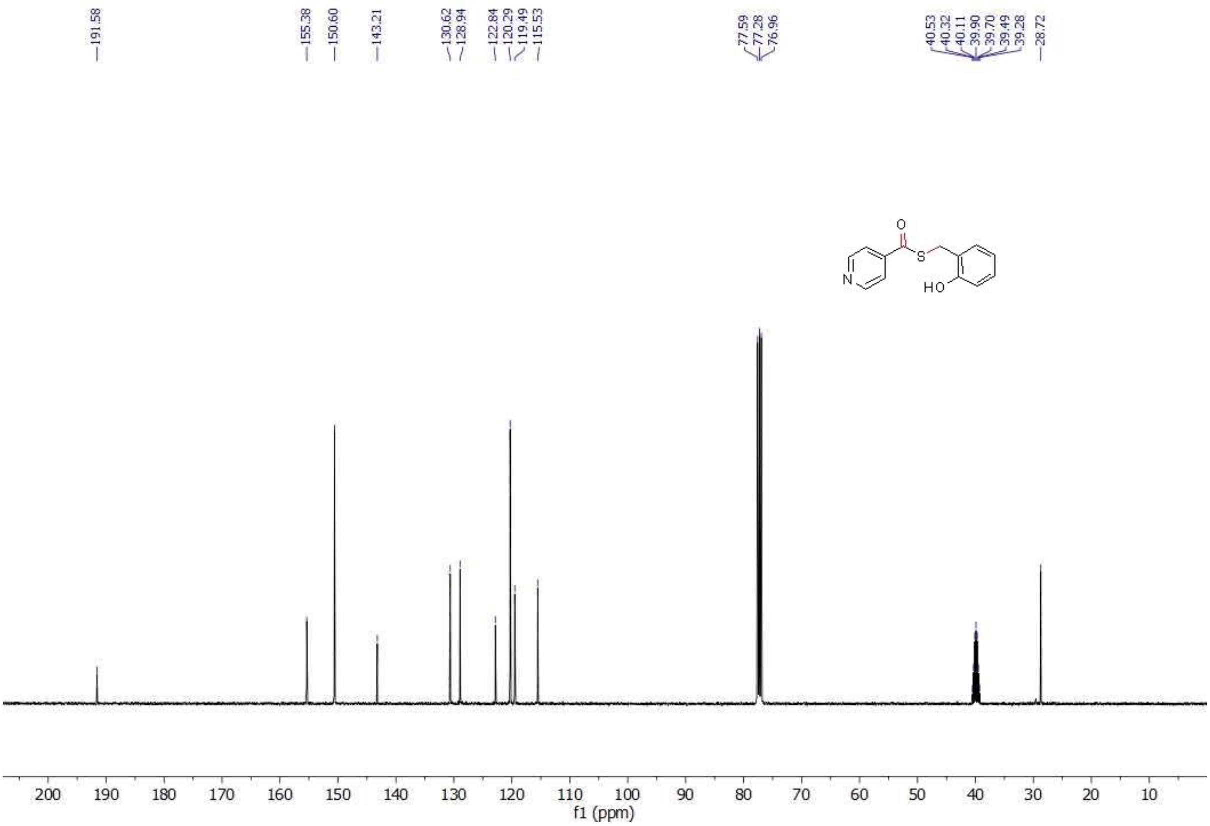
**$^1$H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) and **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **3pa**:



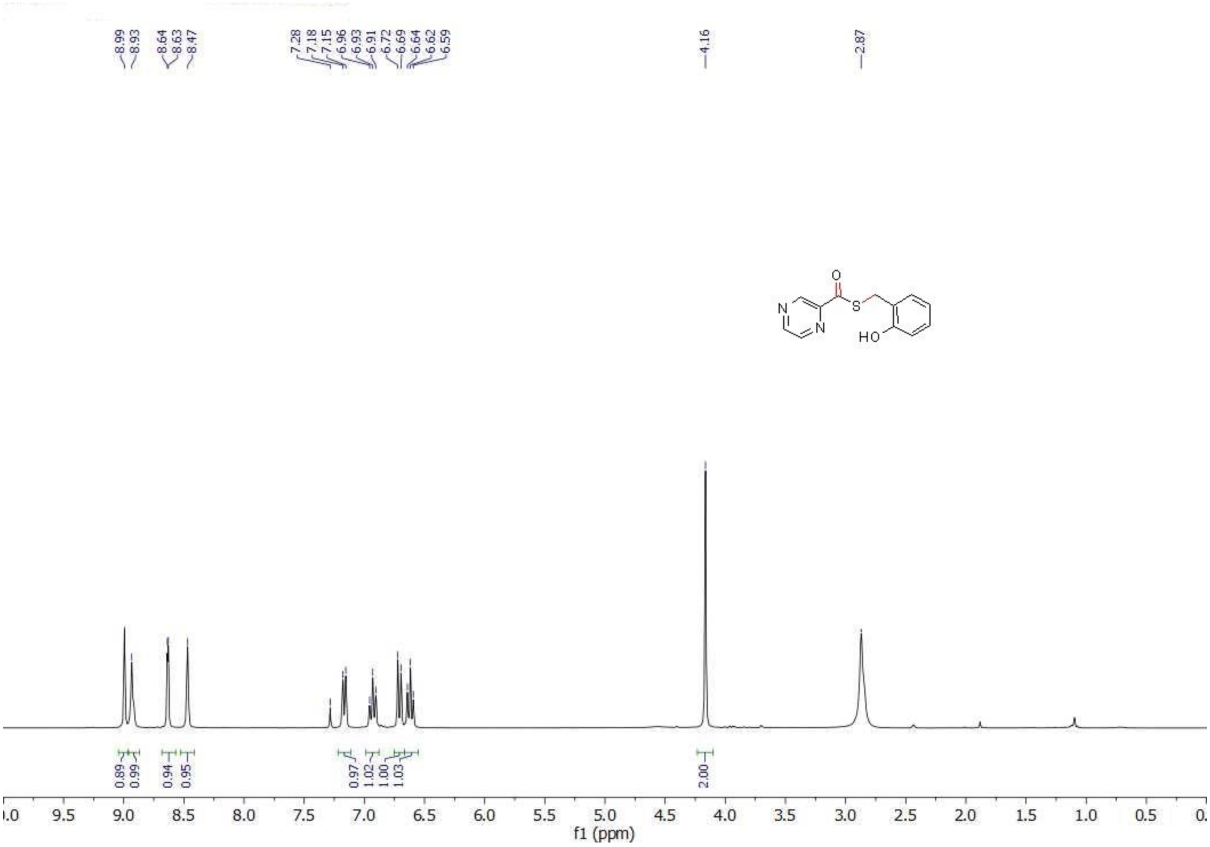


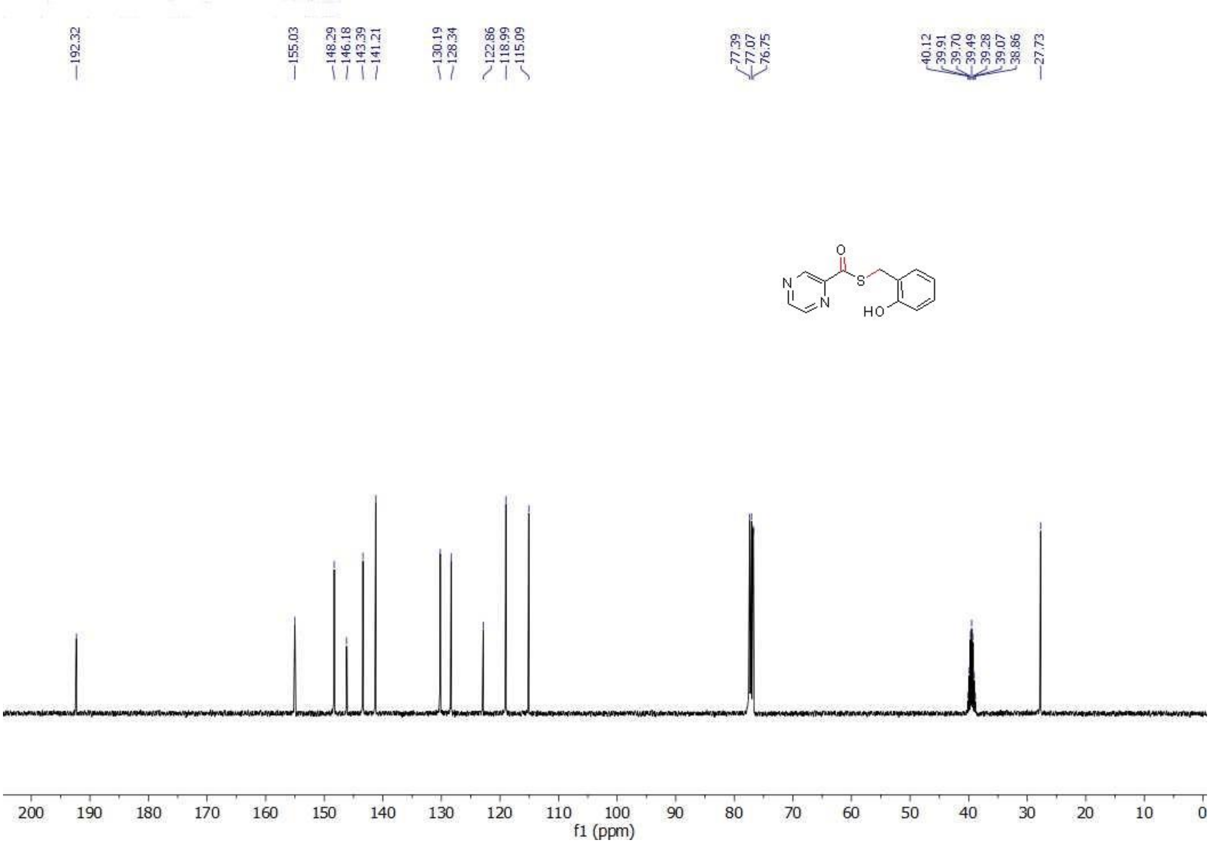
$^{1}$**H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **3qa**:



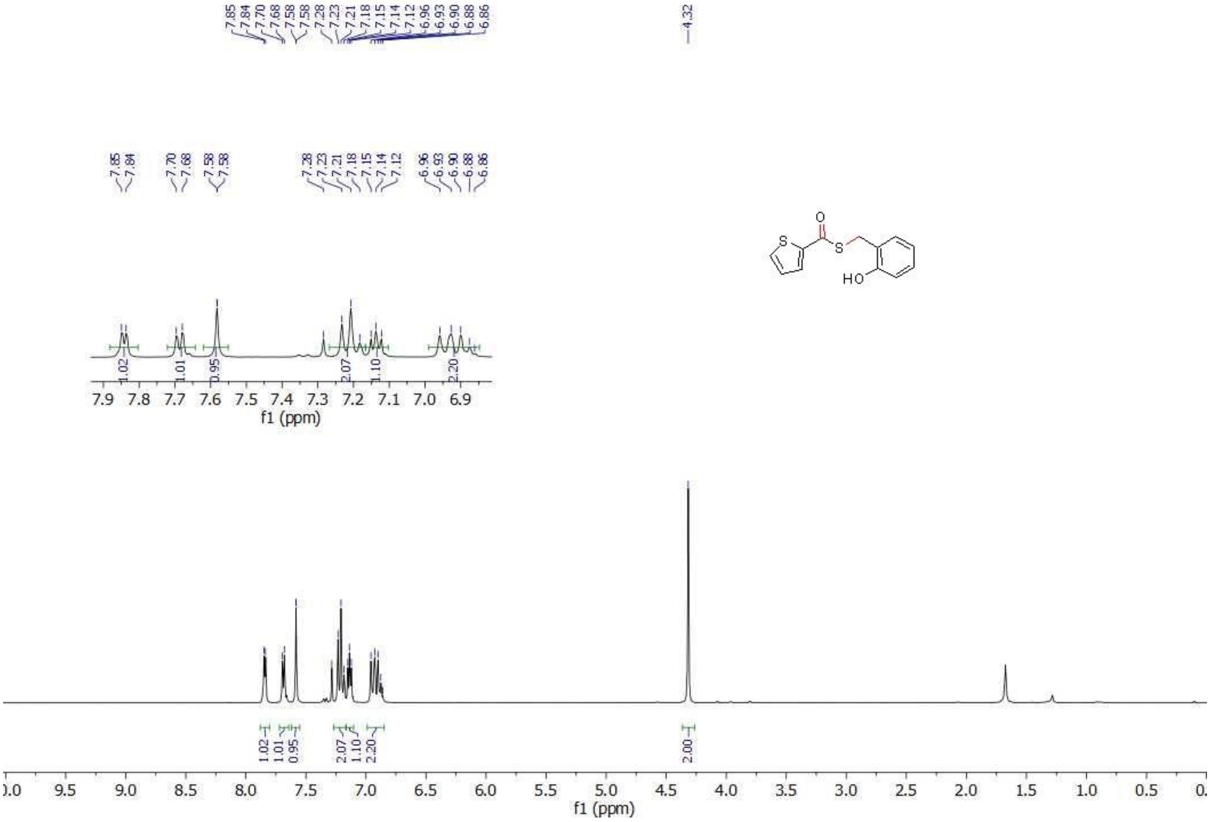


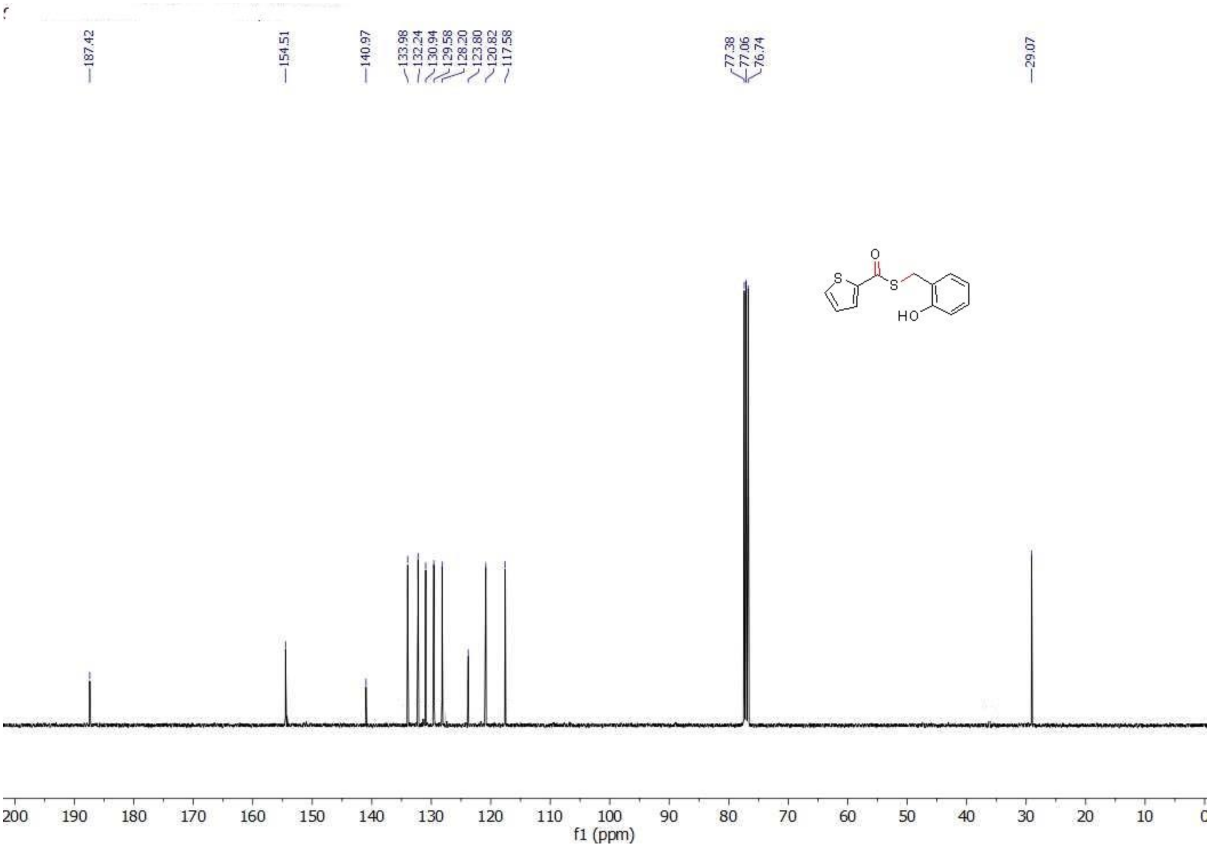
**$^1$H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) and **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **3ra**:



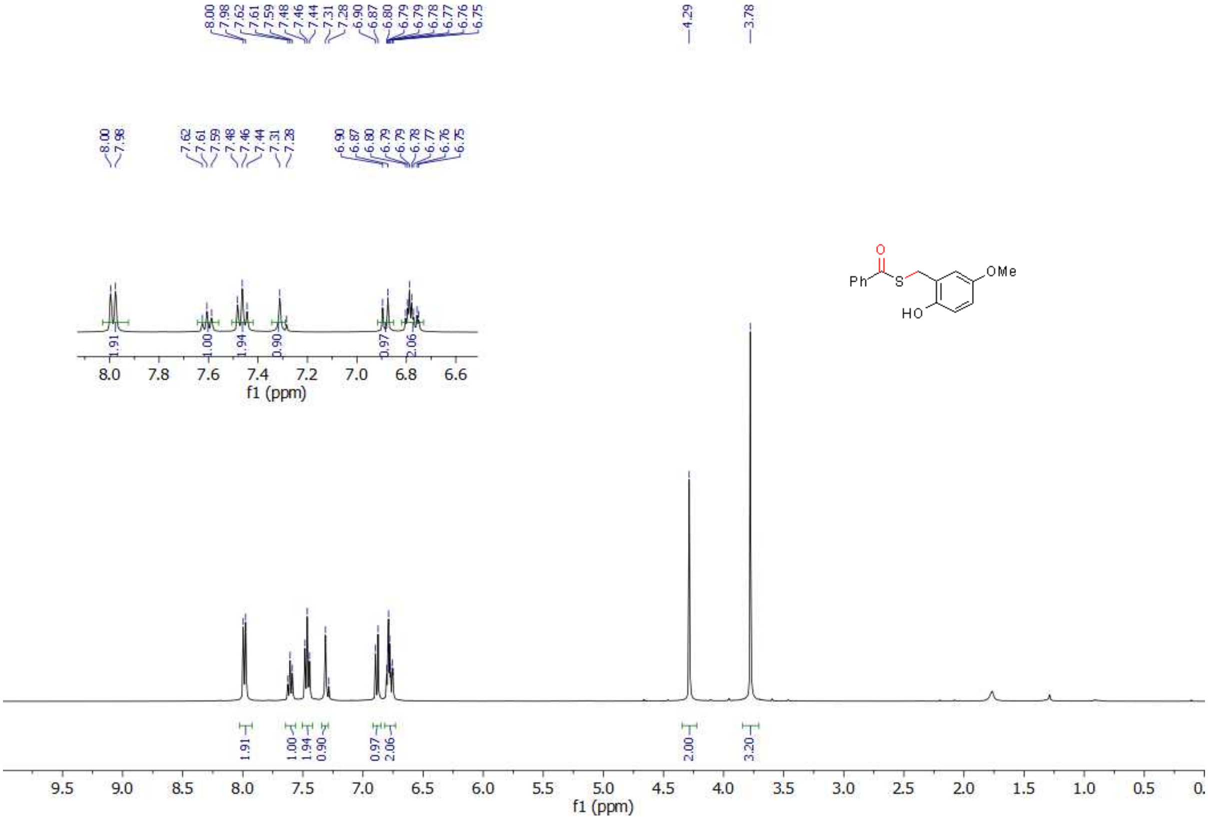


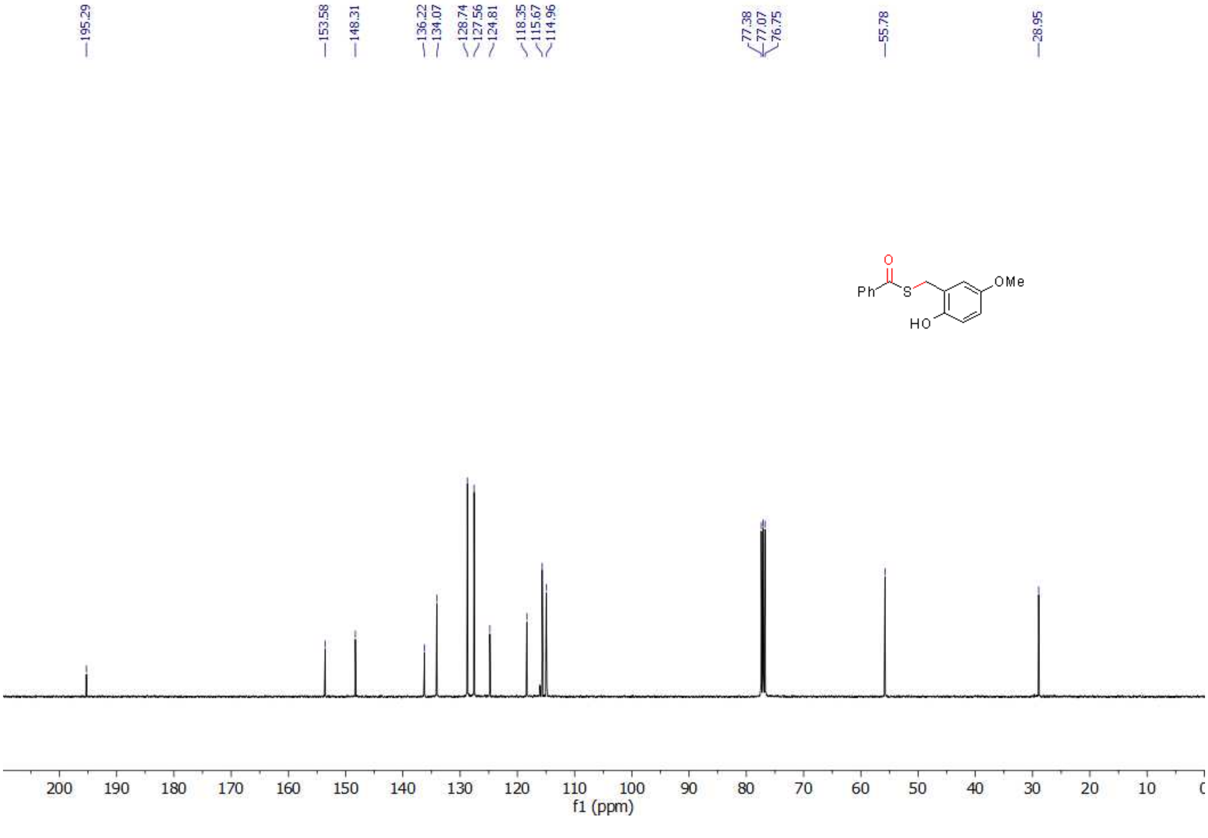
**$^1$H NMR** (300 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$) spectra of **3sa**:



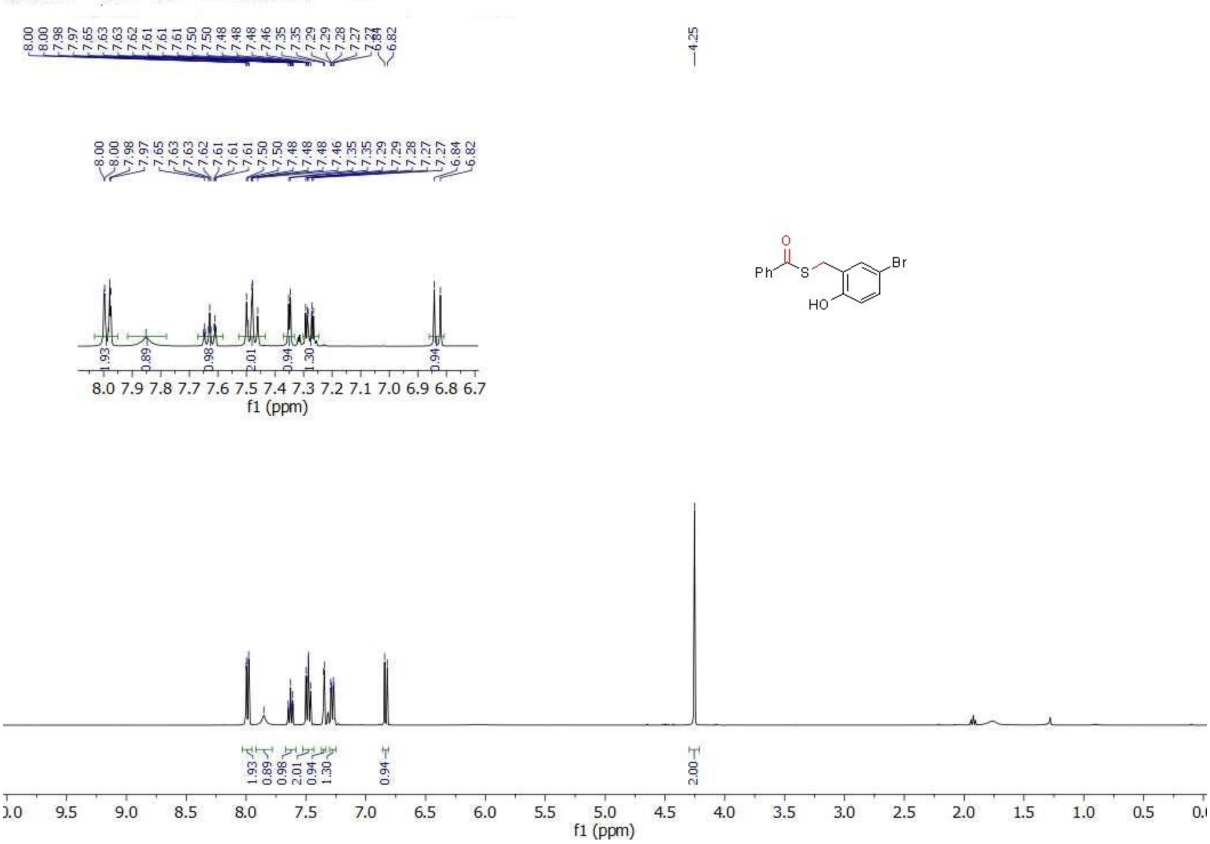


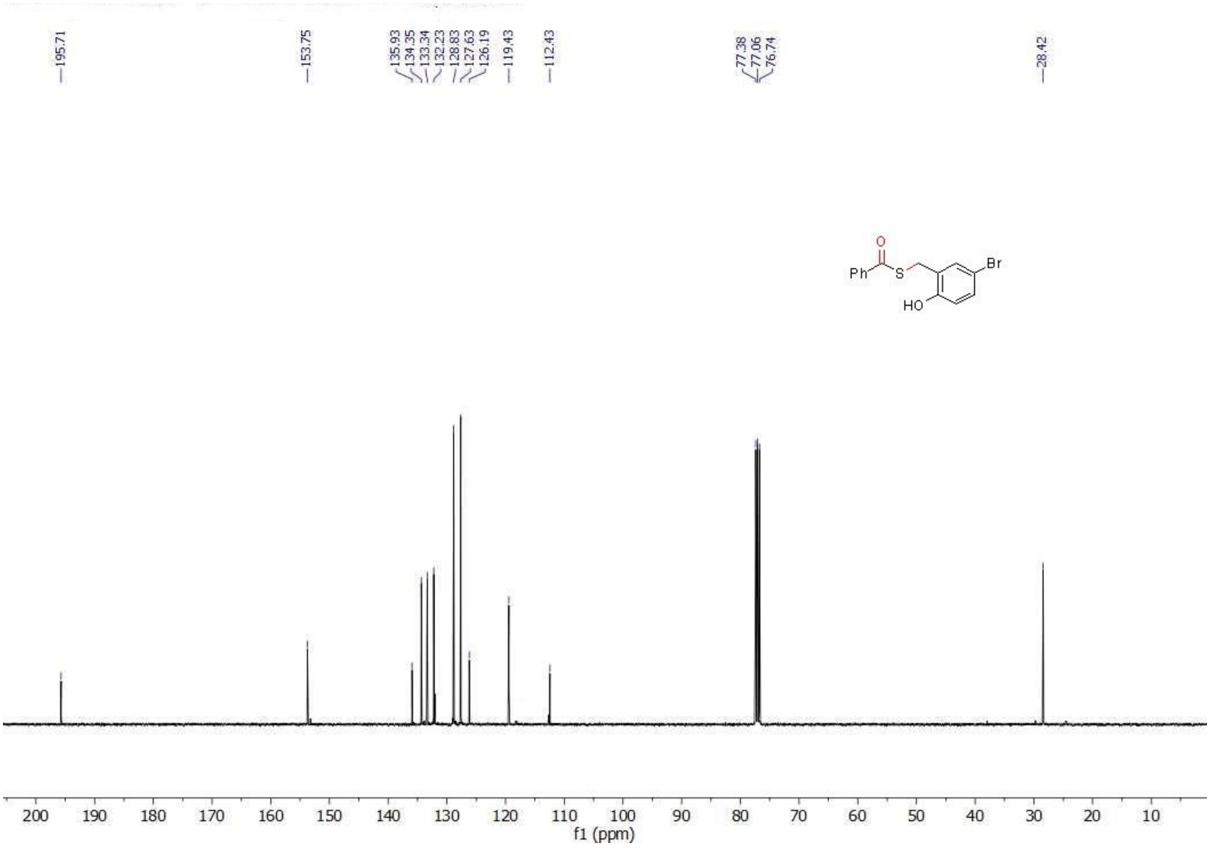
**$^{1}$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ab**:



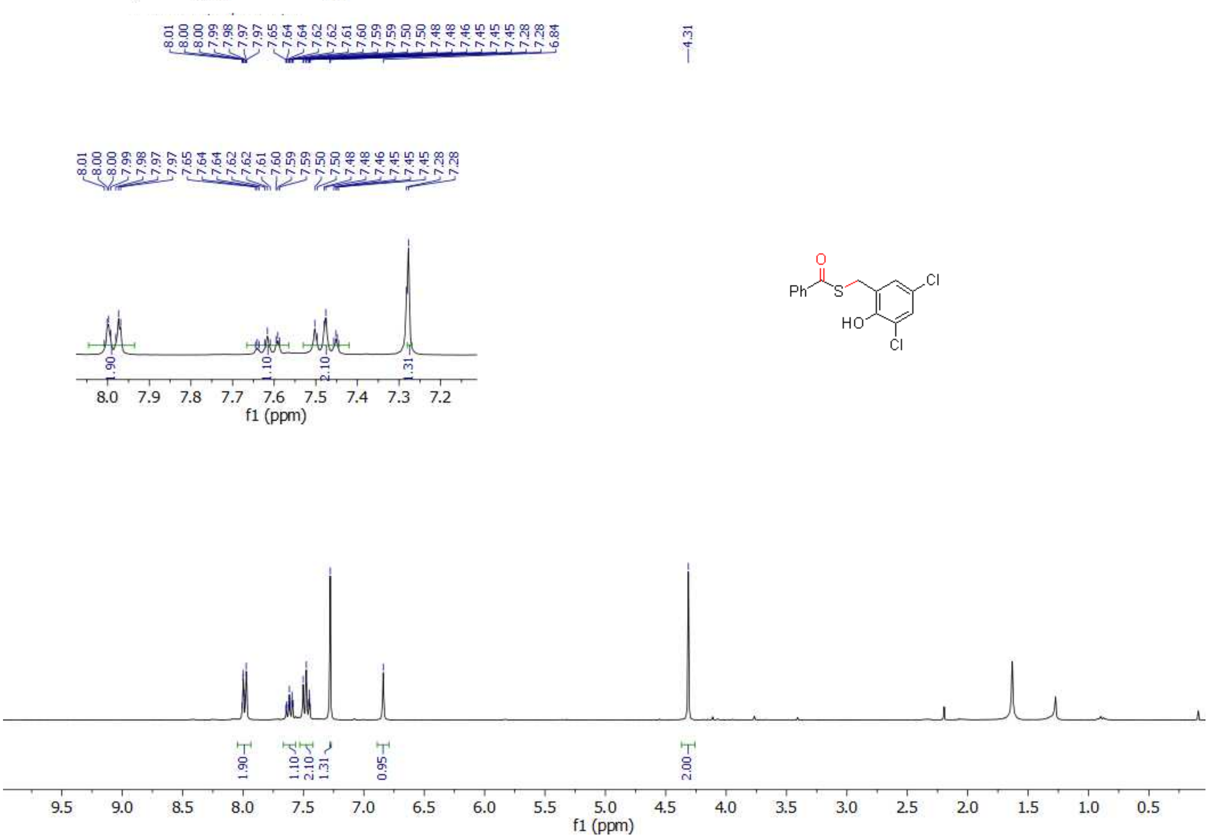


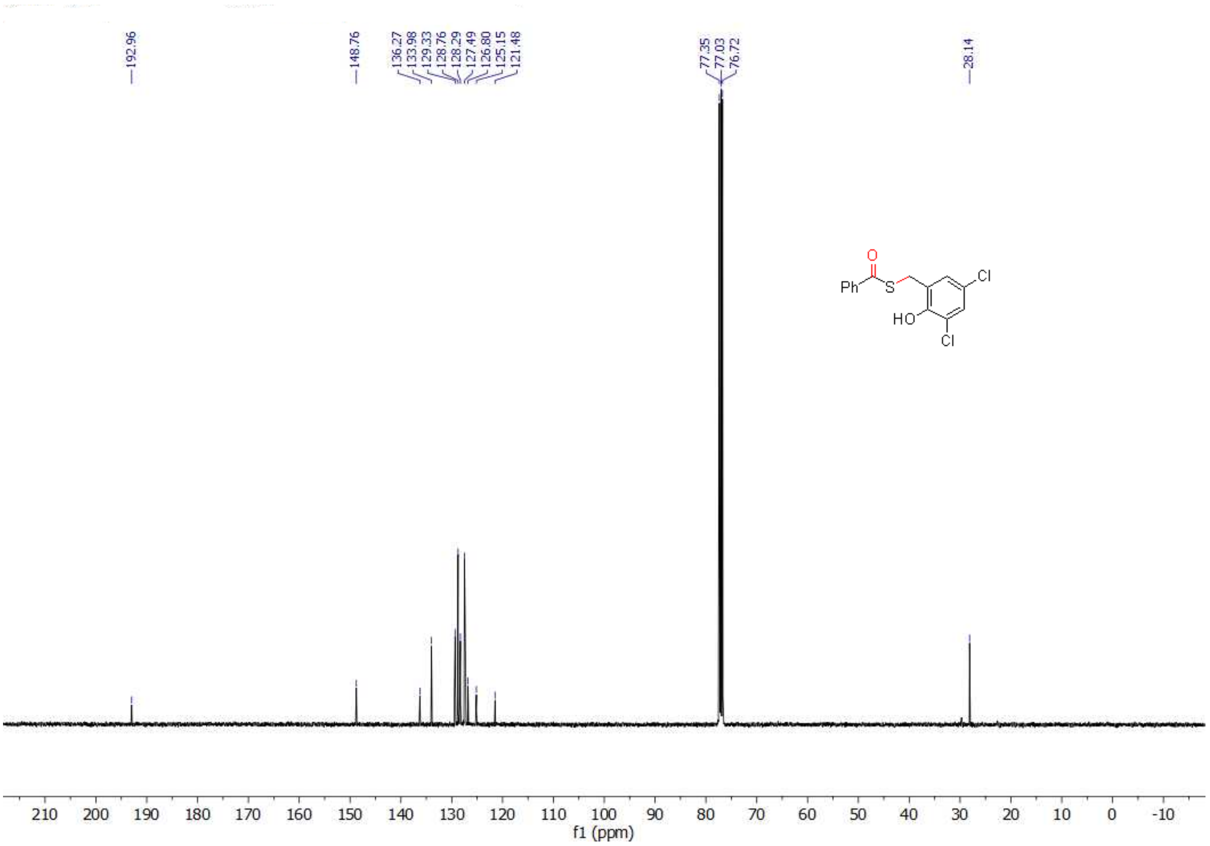
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ac**:



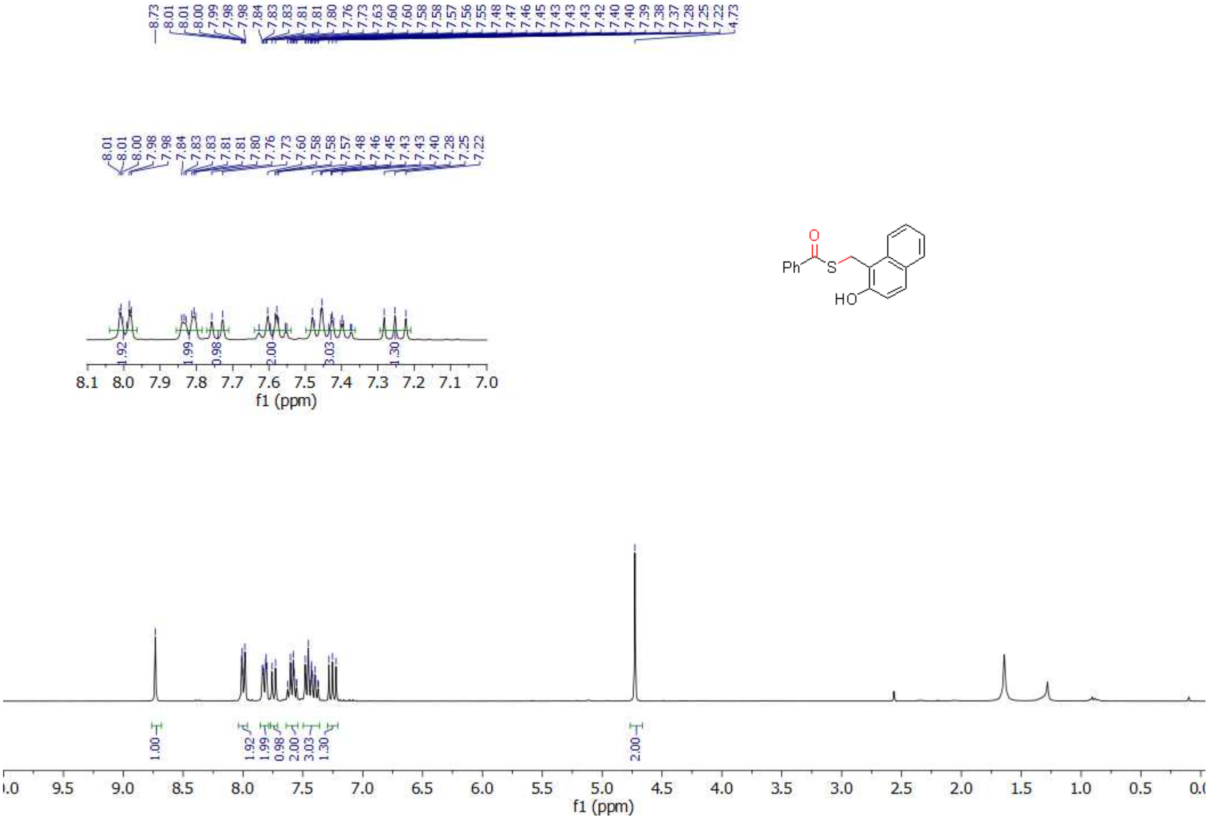


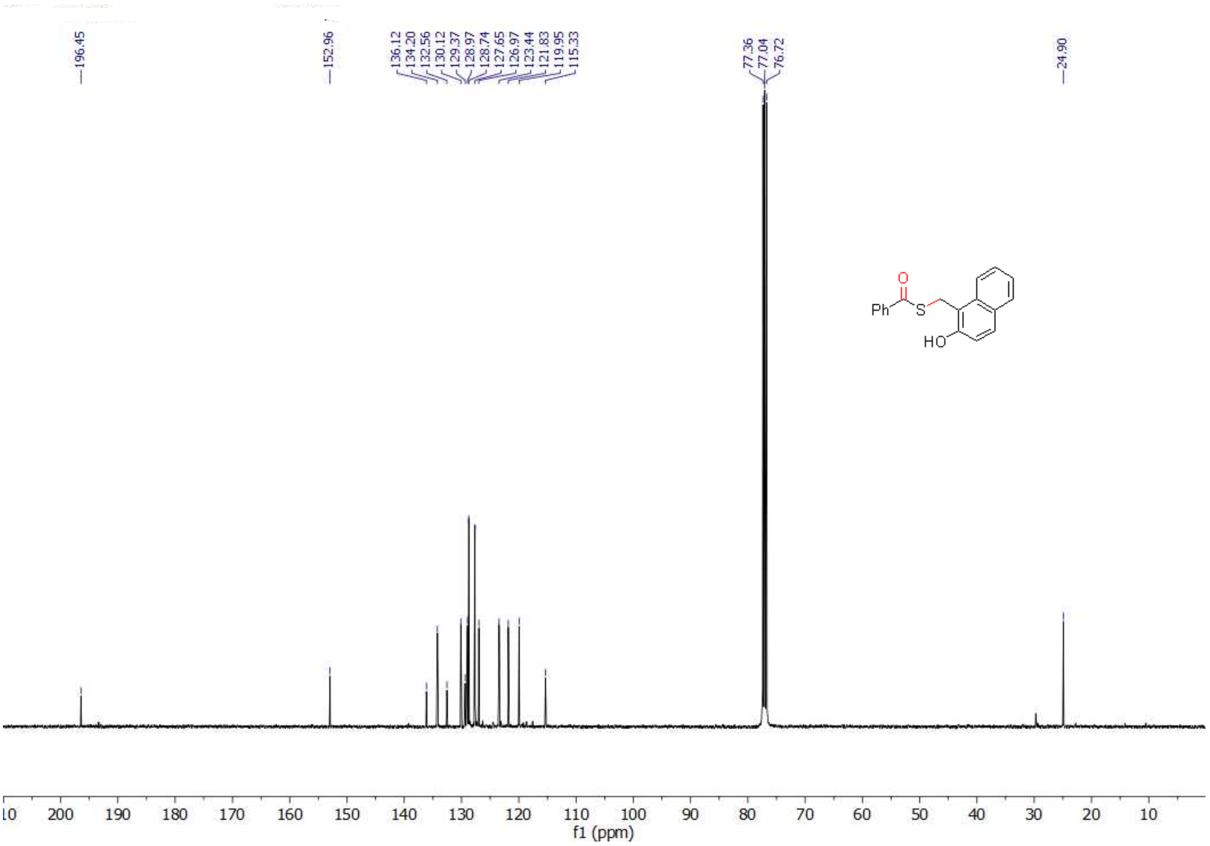
**$^1$H NMR** (300 MHz, $CDCl_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) spectra of **3ad**:



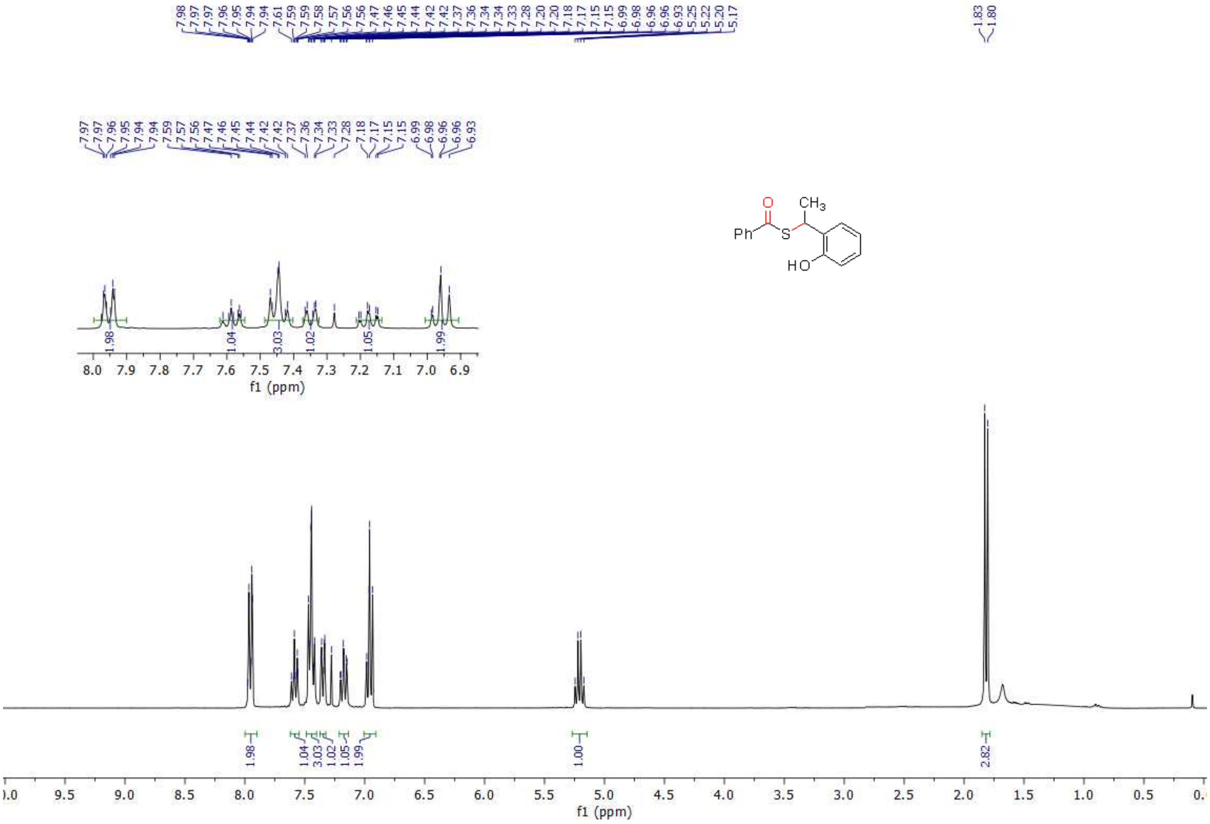


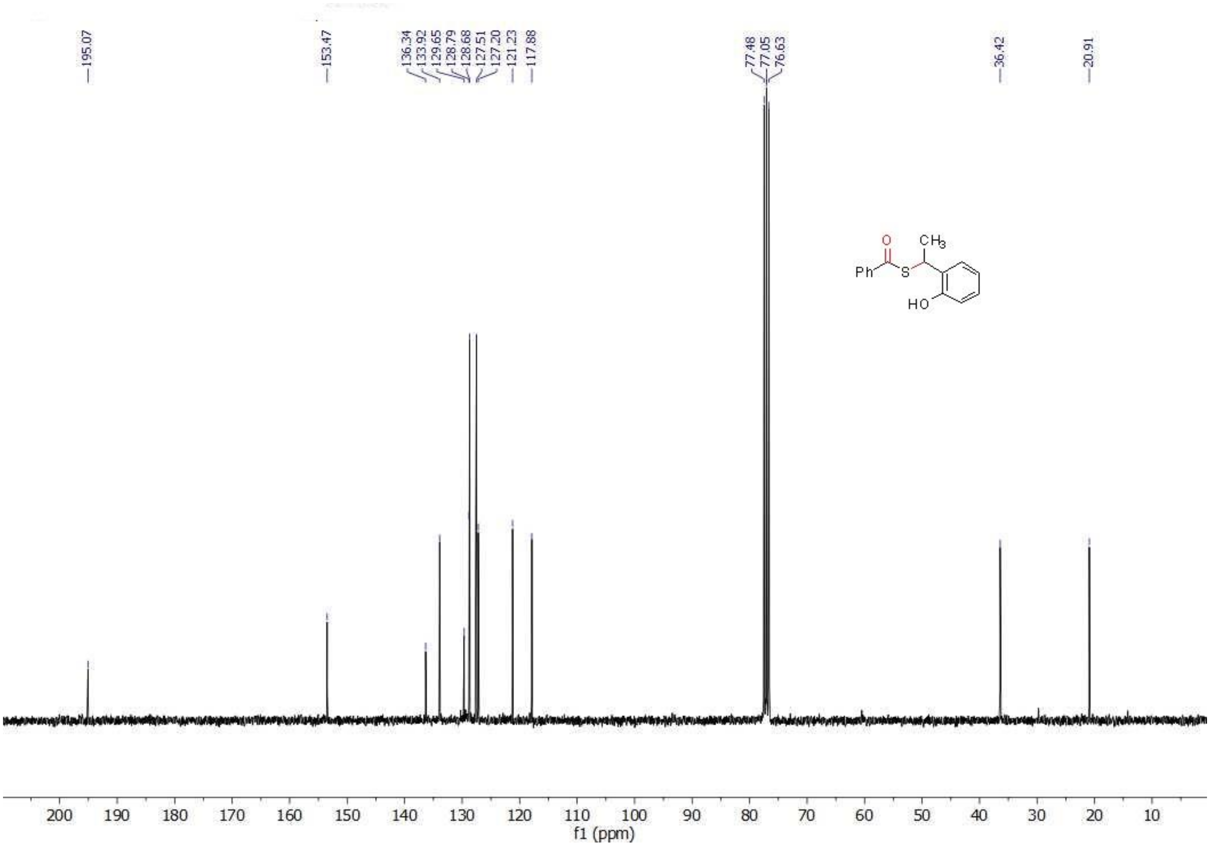
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ae**:



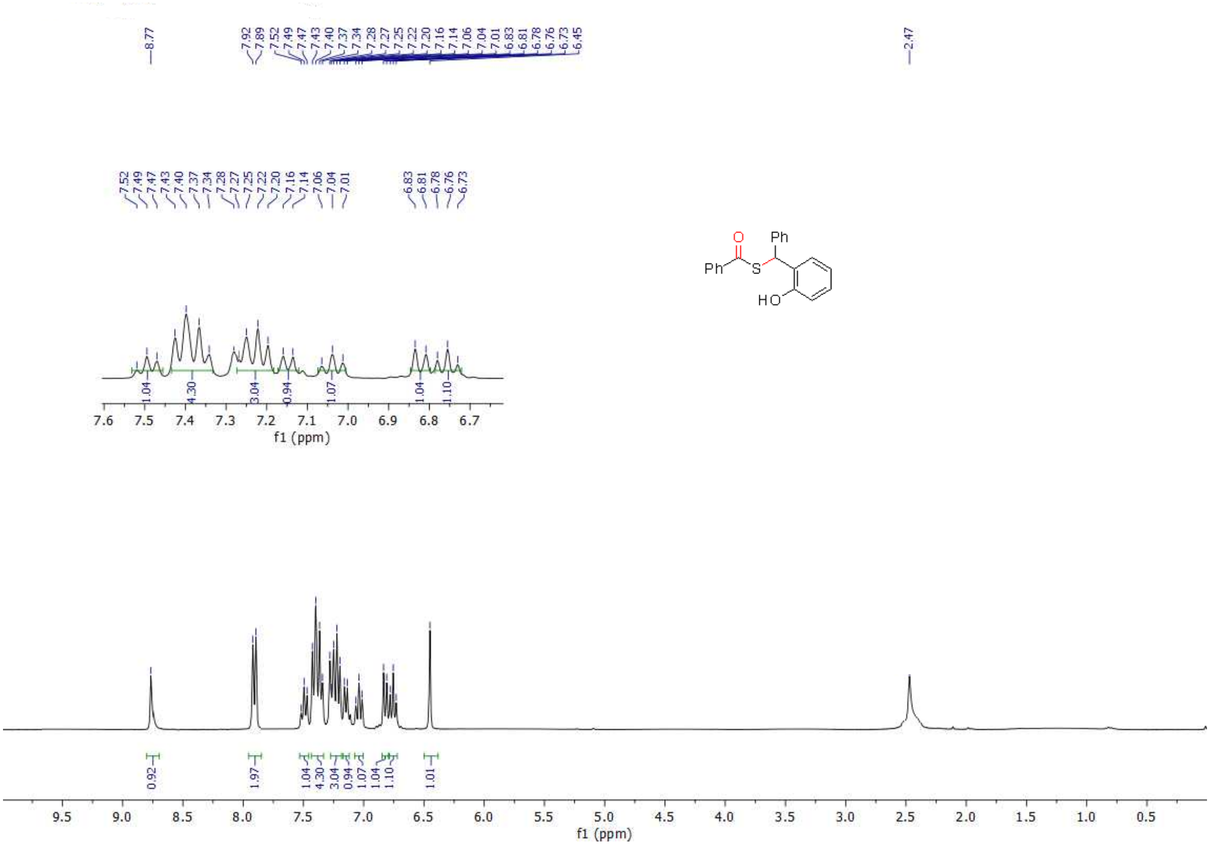


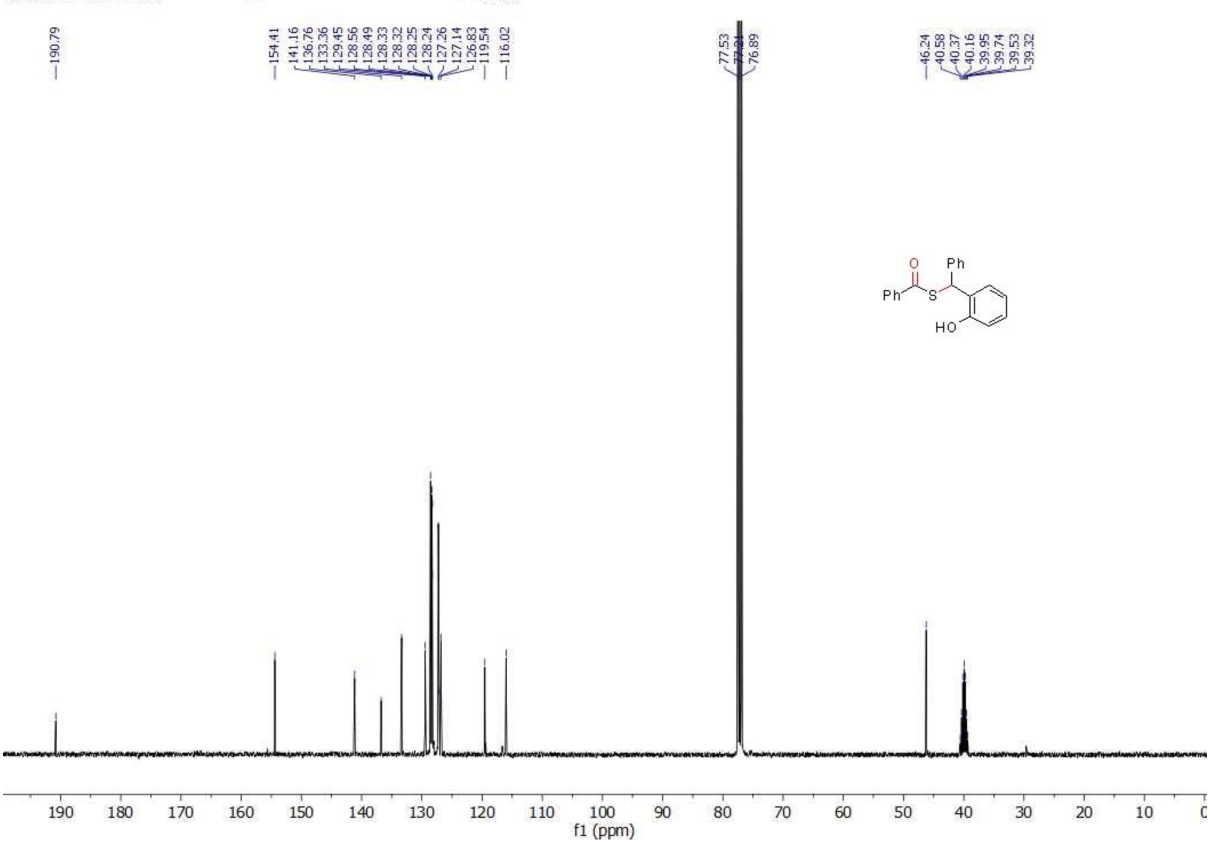
$^{1}$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (75 MHz, CDCl$_3$) spectra of **3af**:



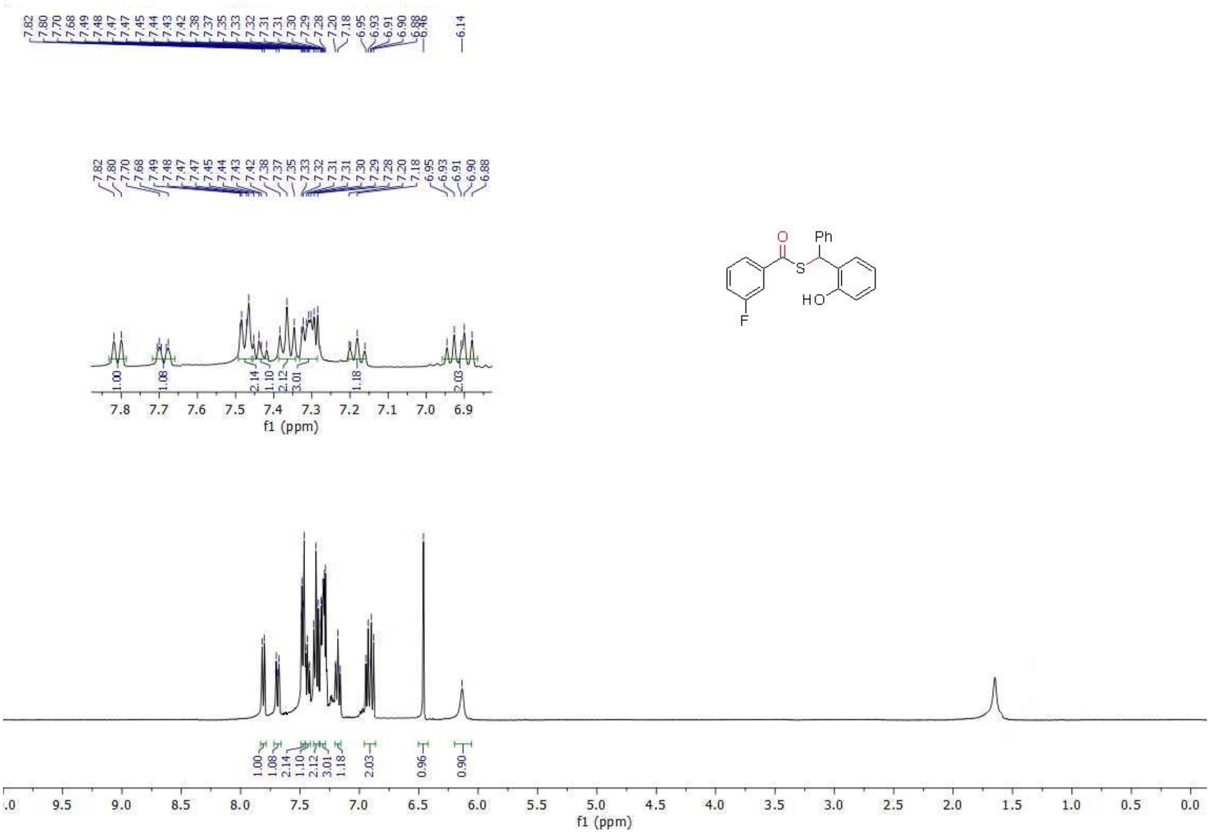


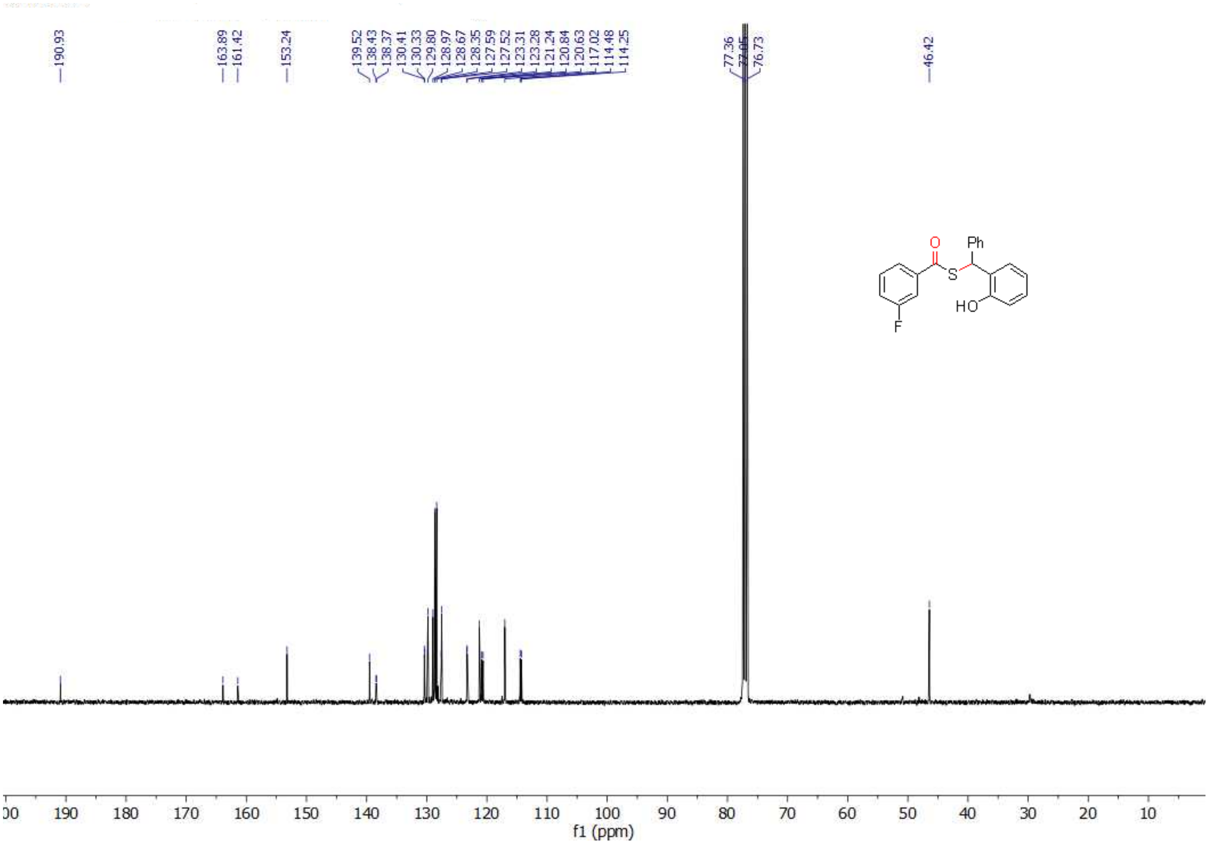
**$^{1}$H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) and **$^{13}$C{$^{1}$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **3ag**:



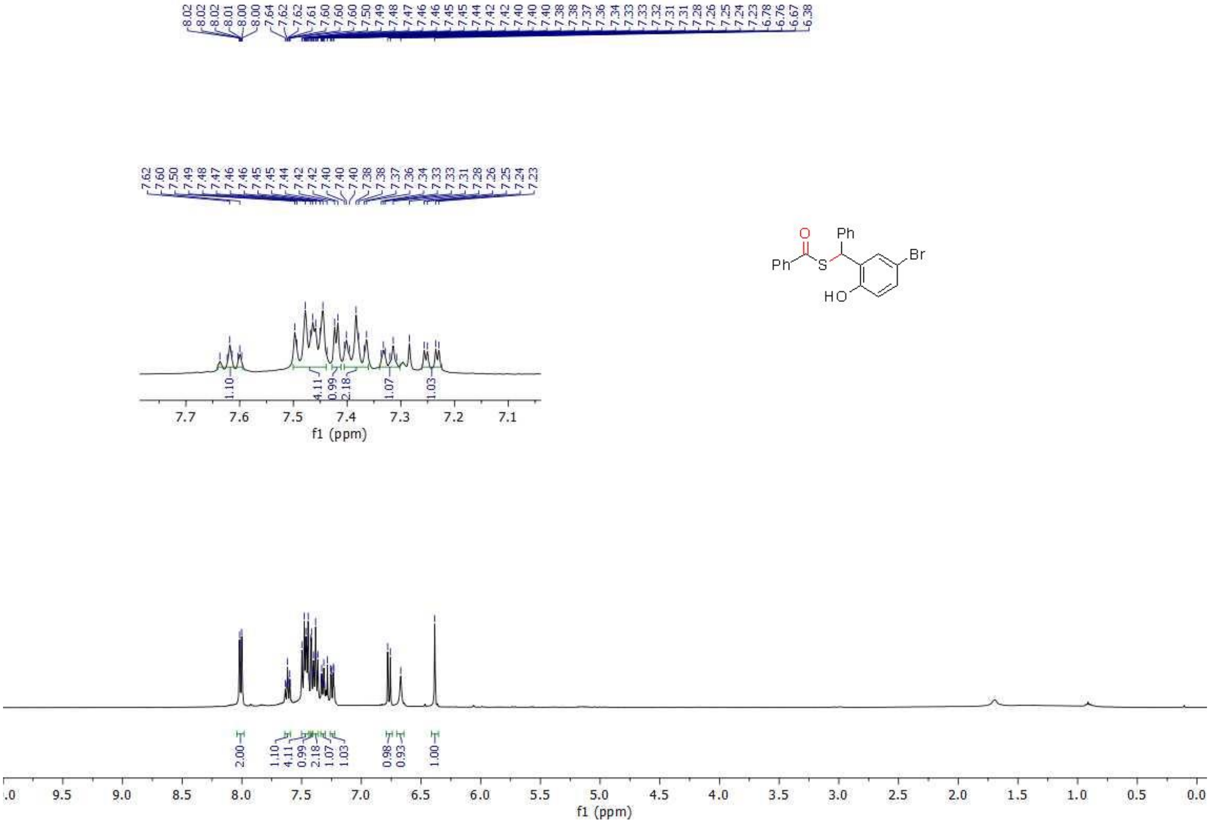


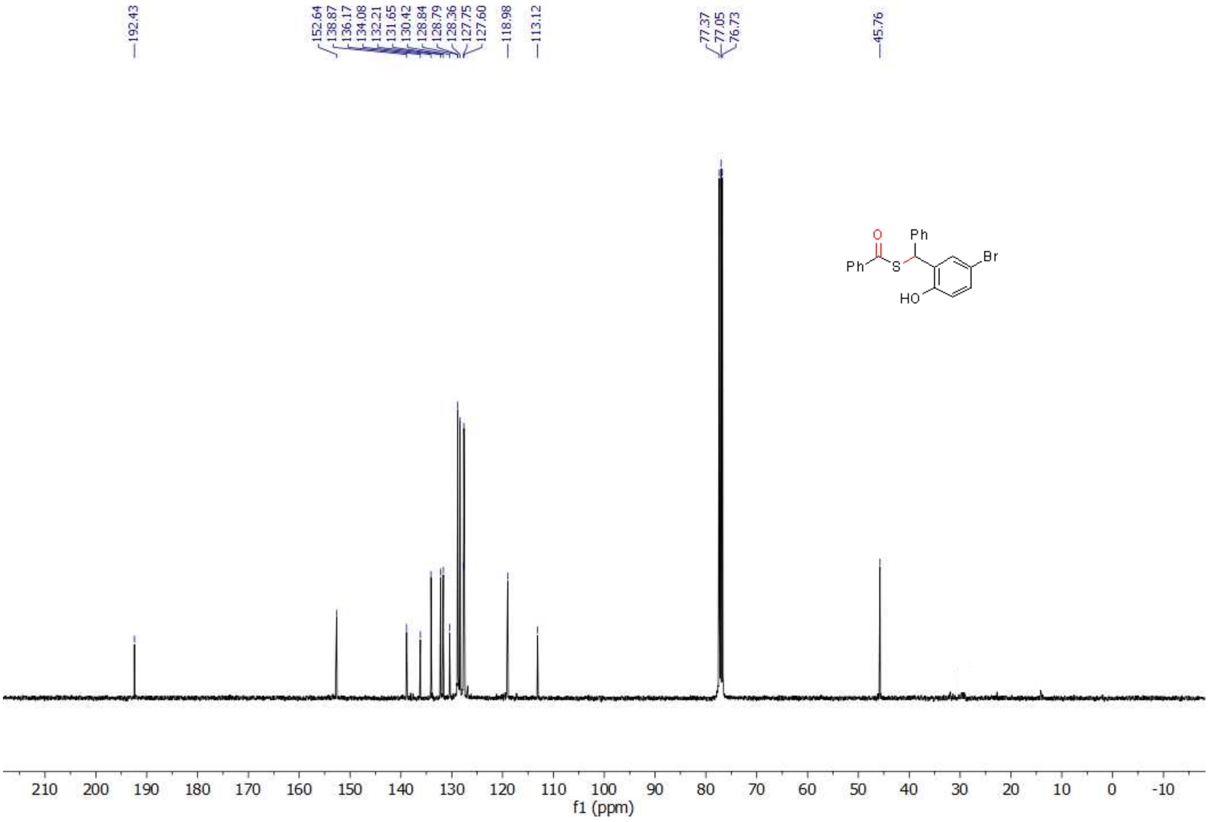
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ig**:



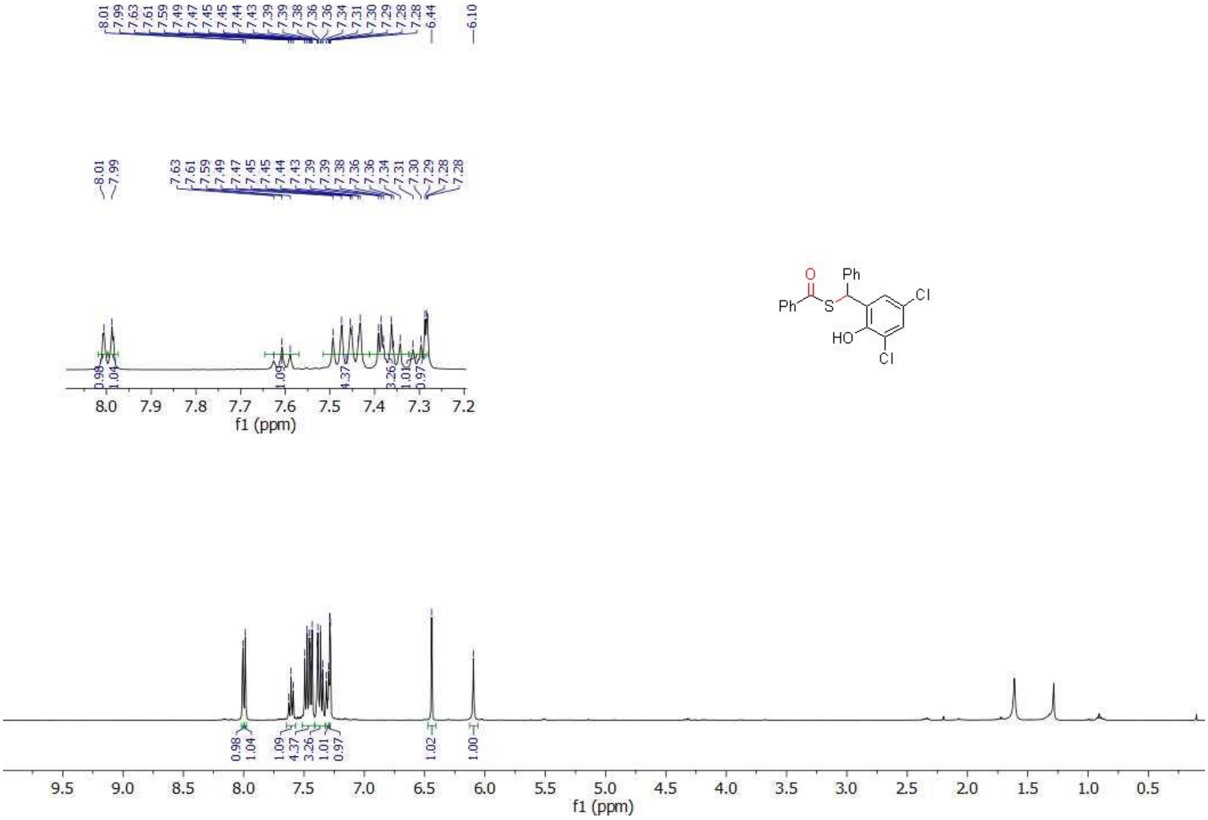


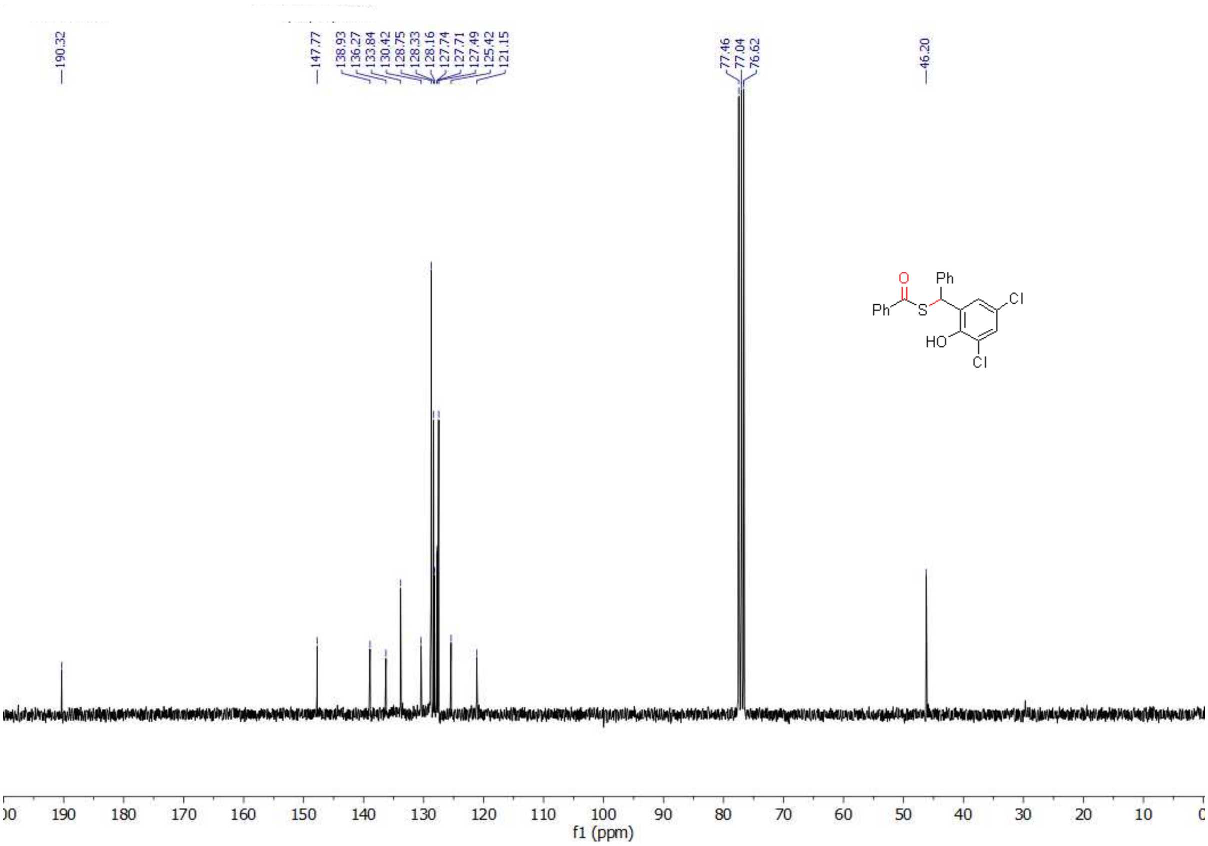
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ah**:



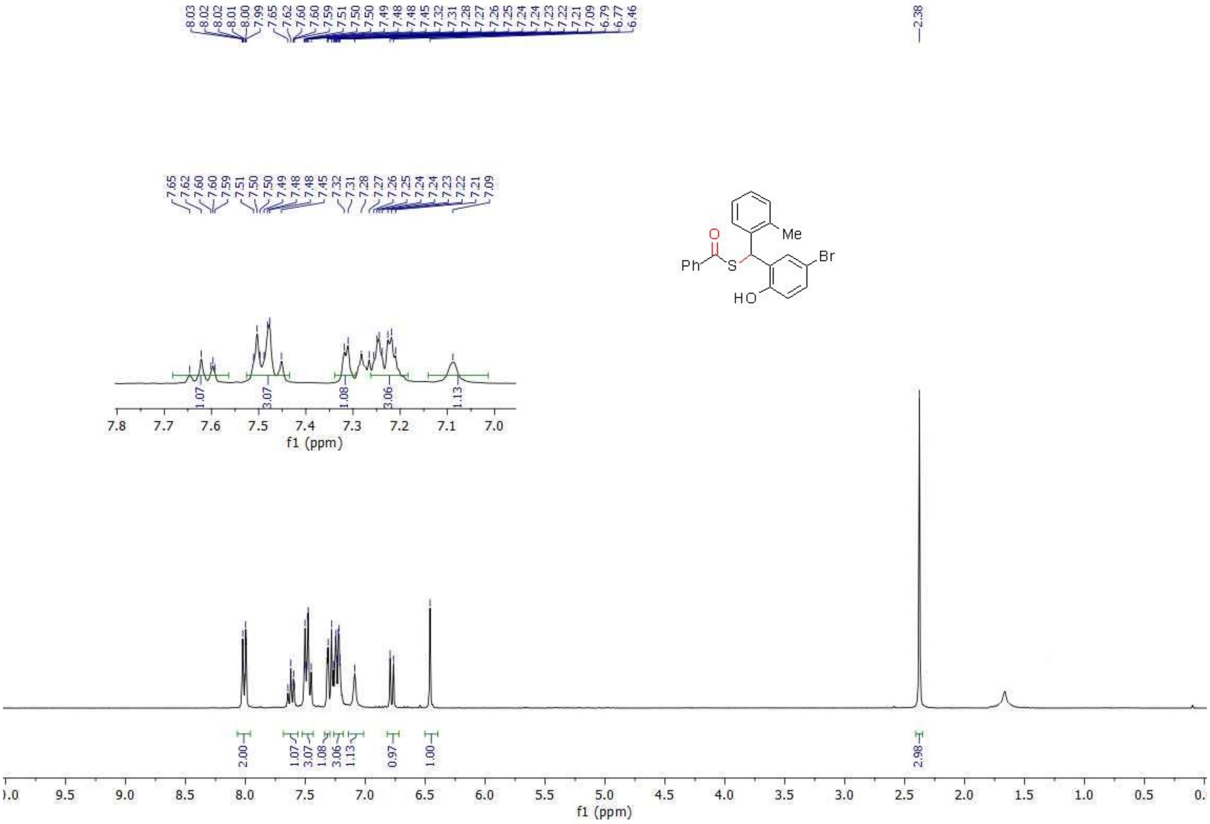


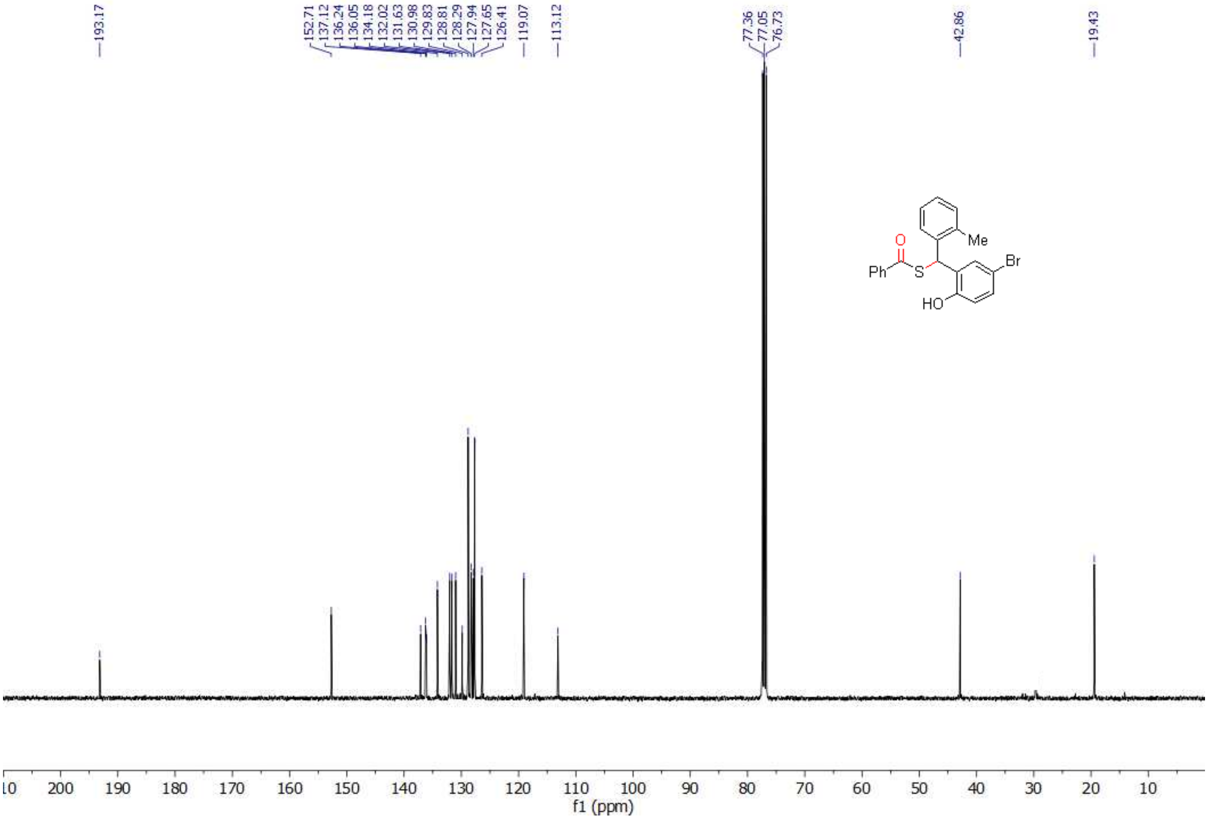
$^1$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (75 MHz, CDCl$_3$) spectra of **3ai**:



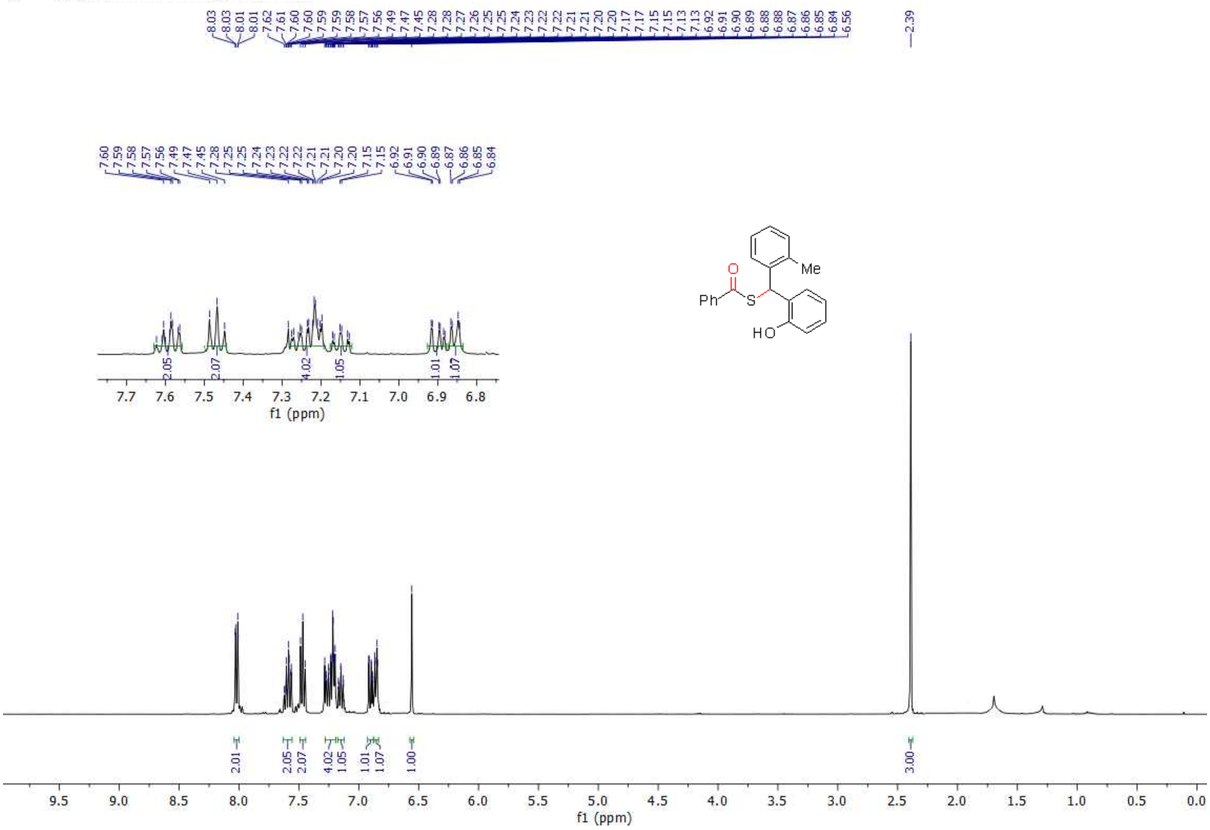


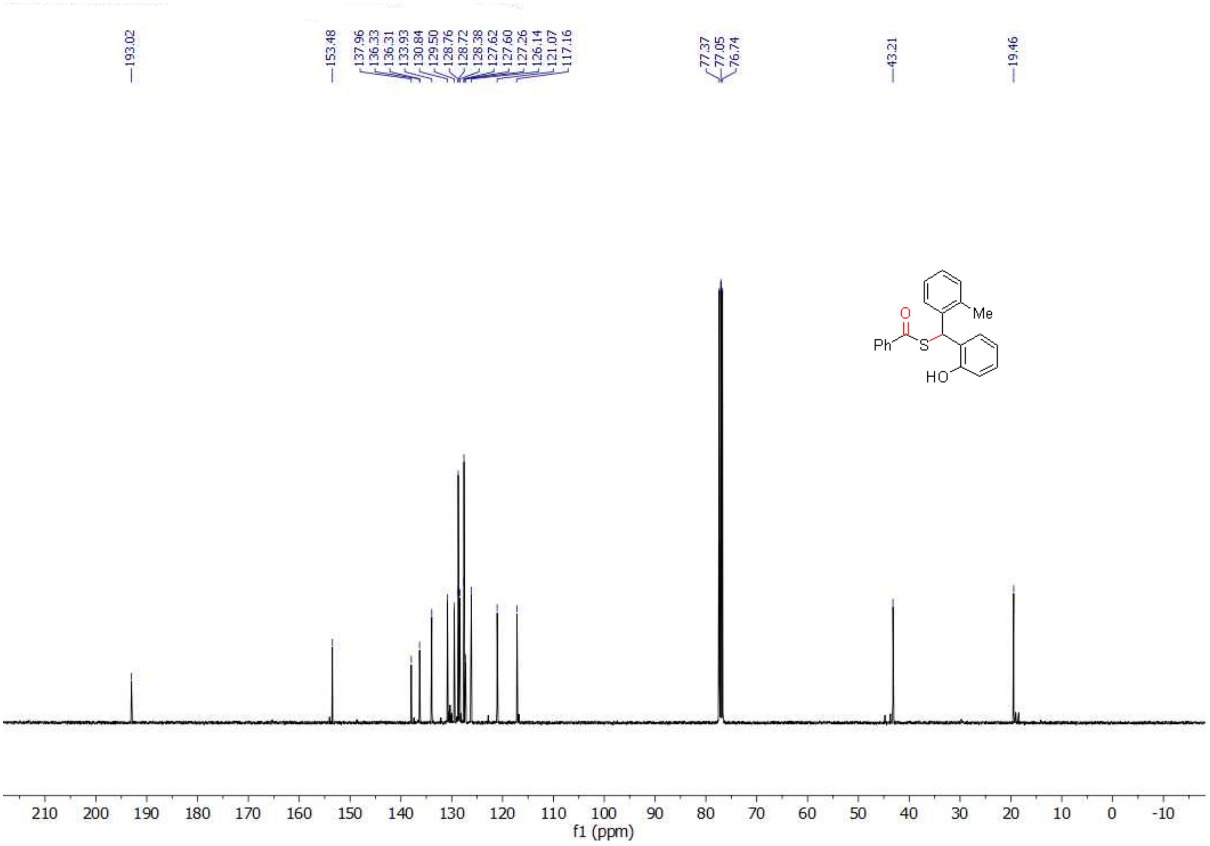
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3aj**:



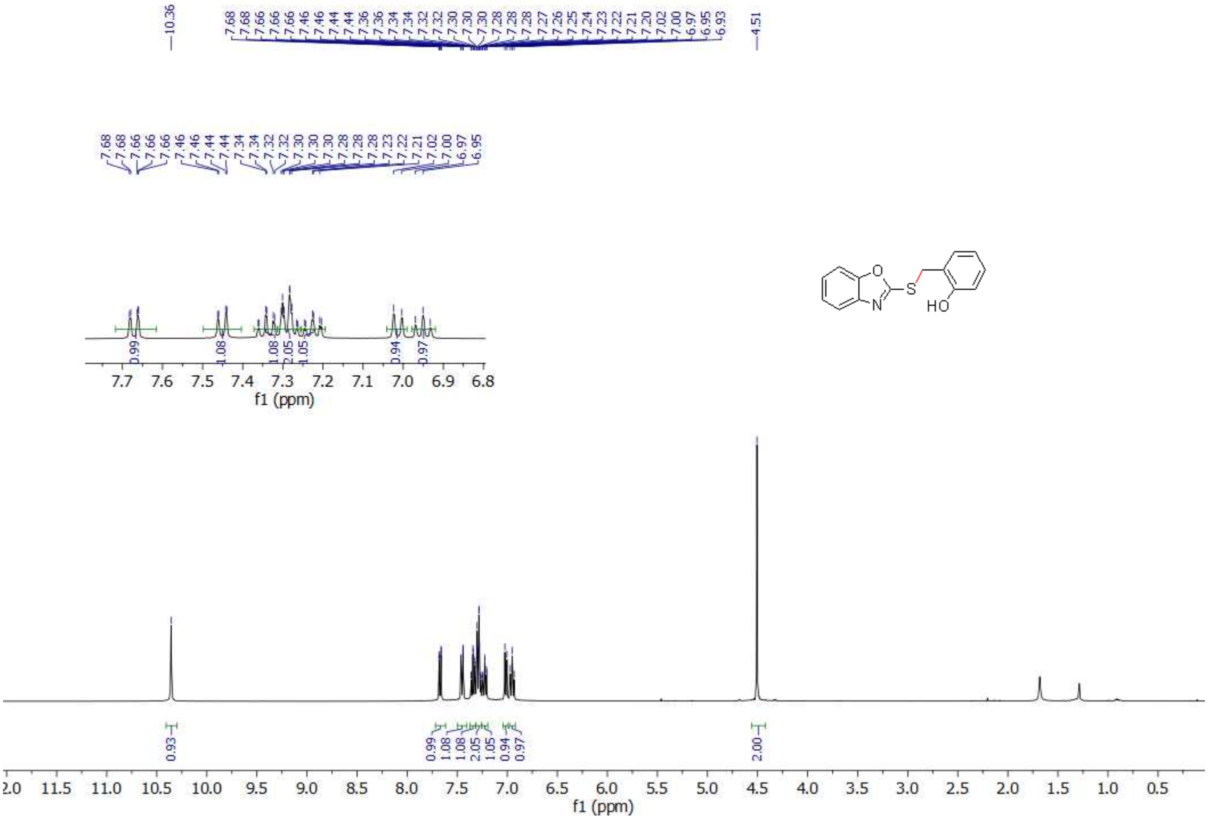


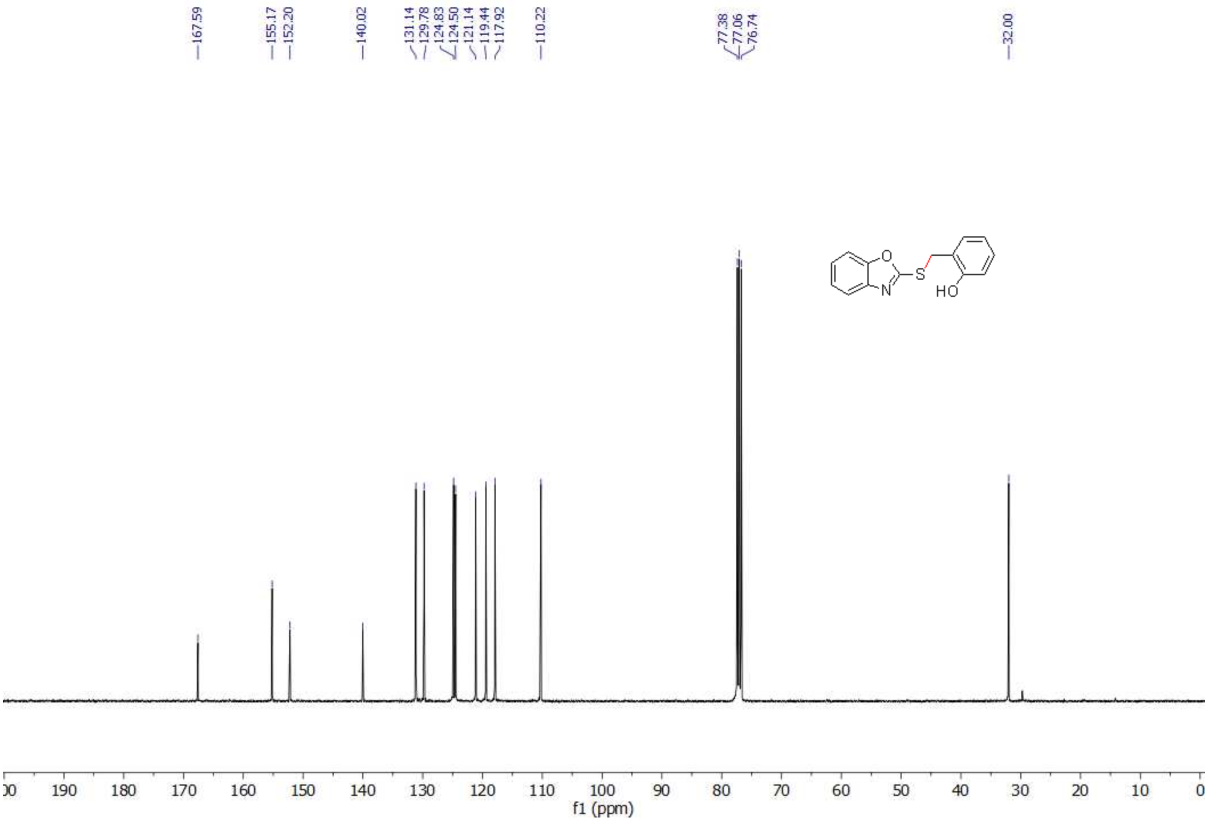
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **3ak**:



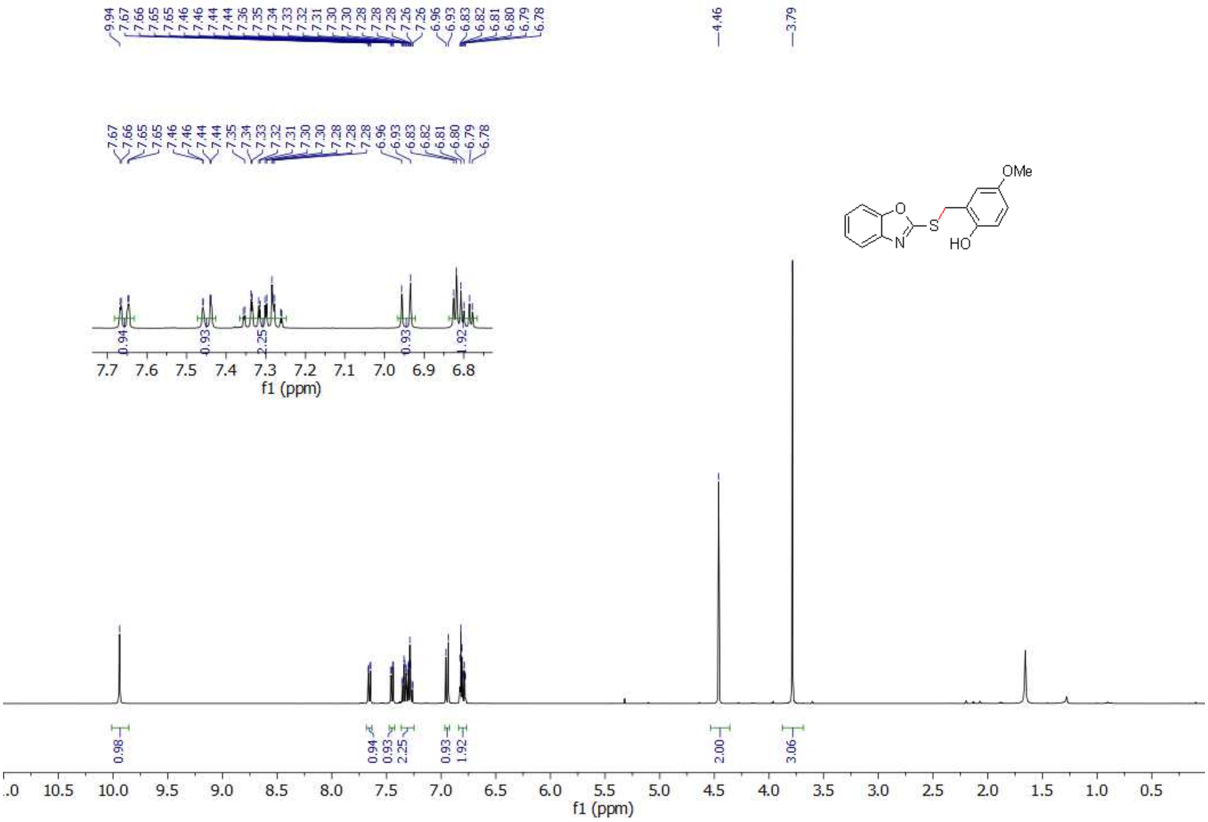


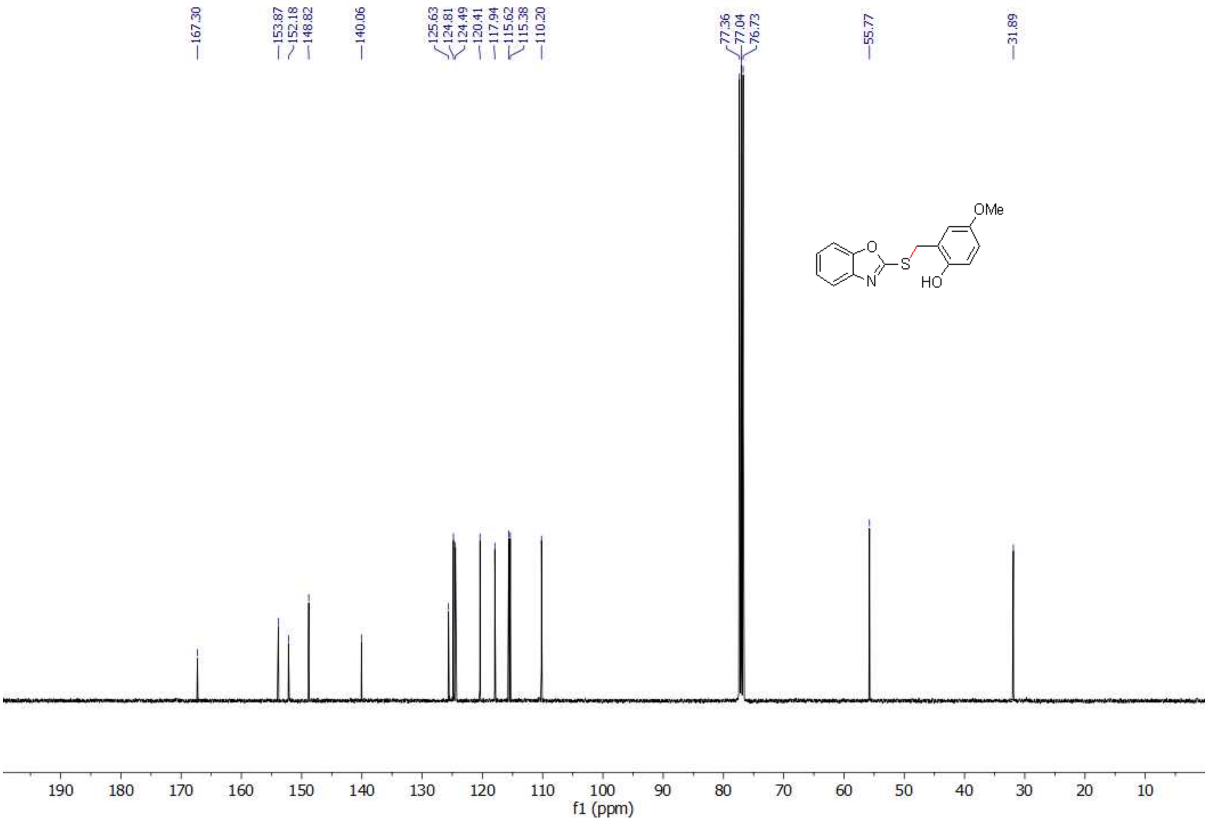
**$^{1}$H NMR** (400 MHz, $CDCl_3$) and **$^{13}$C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) spectra of **4ta**:



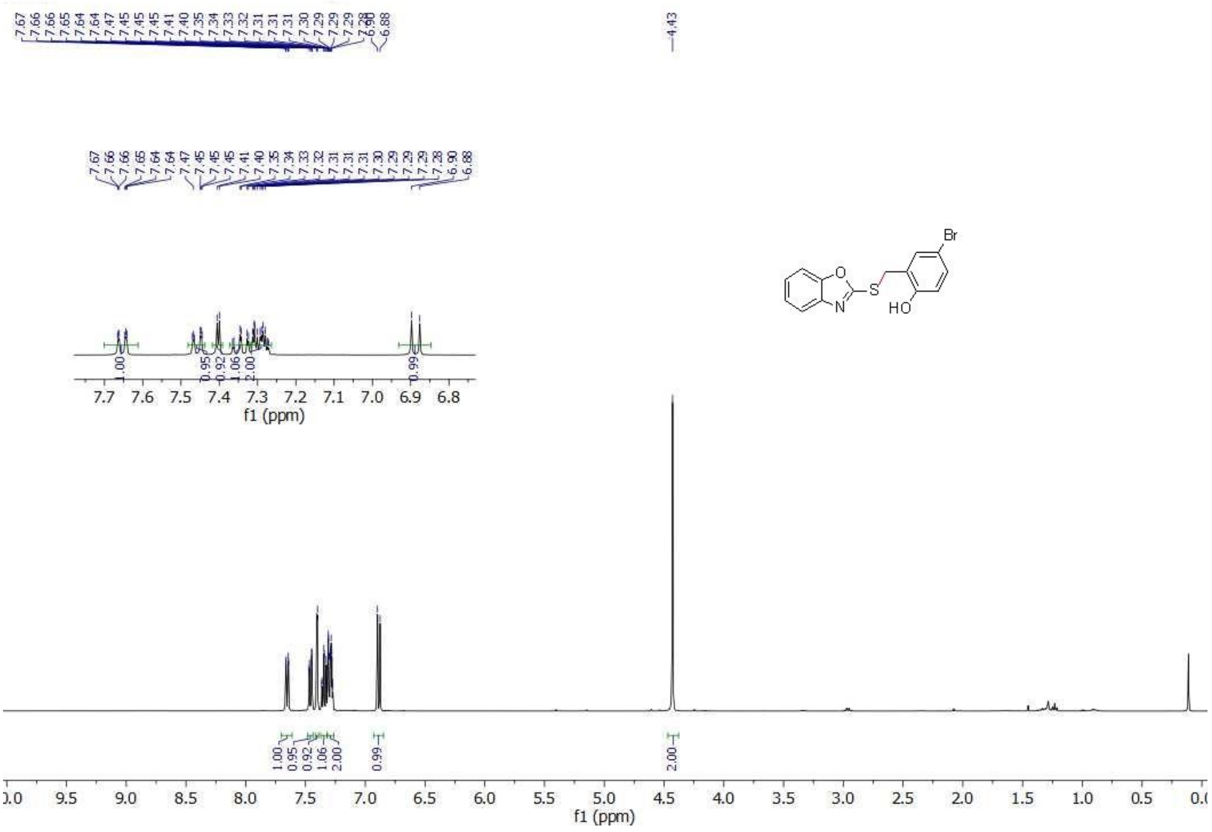


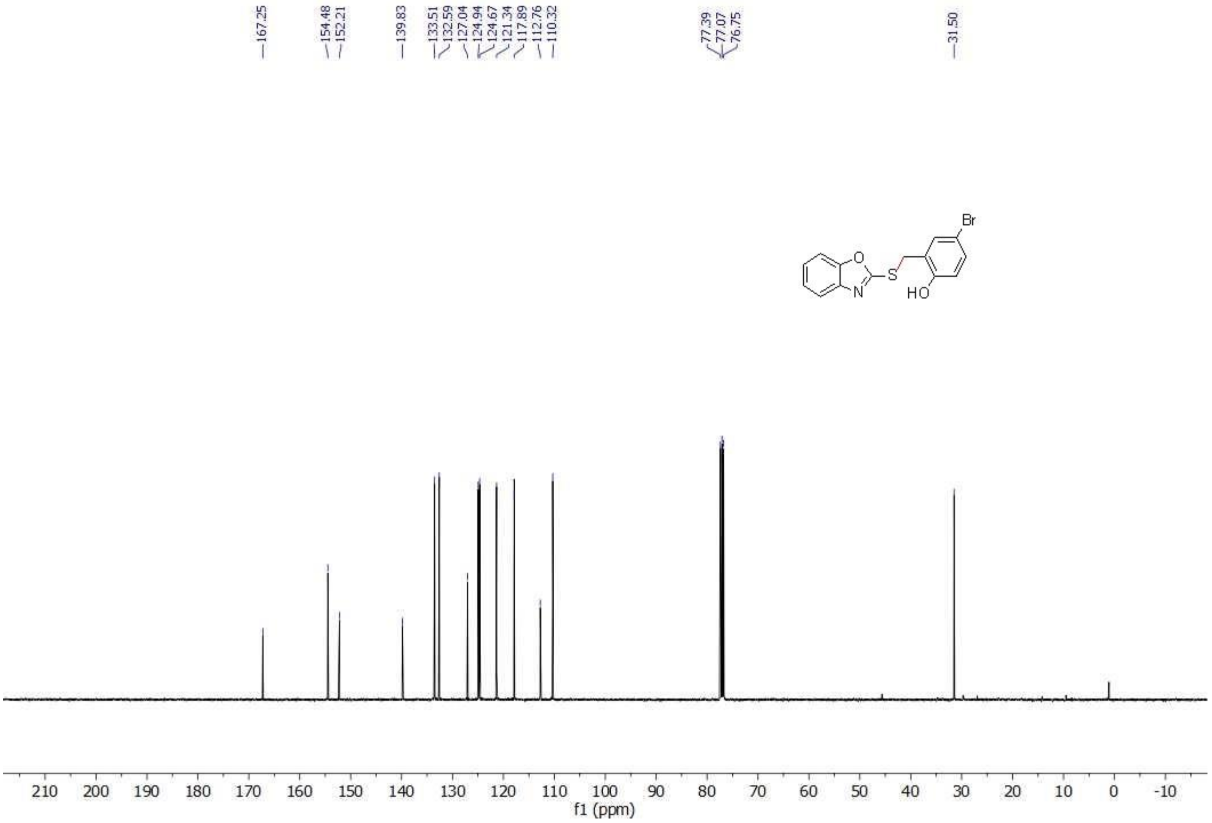
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **4tb**:



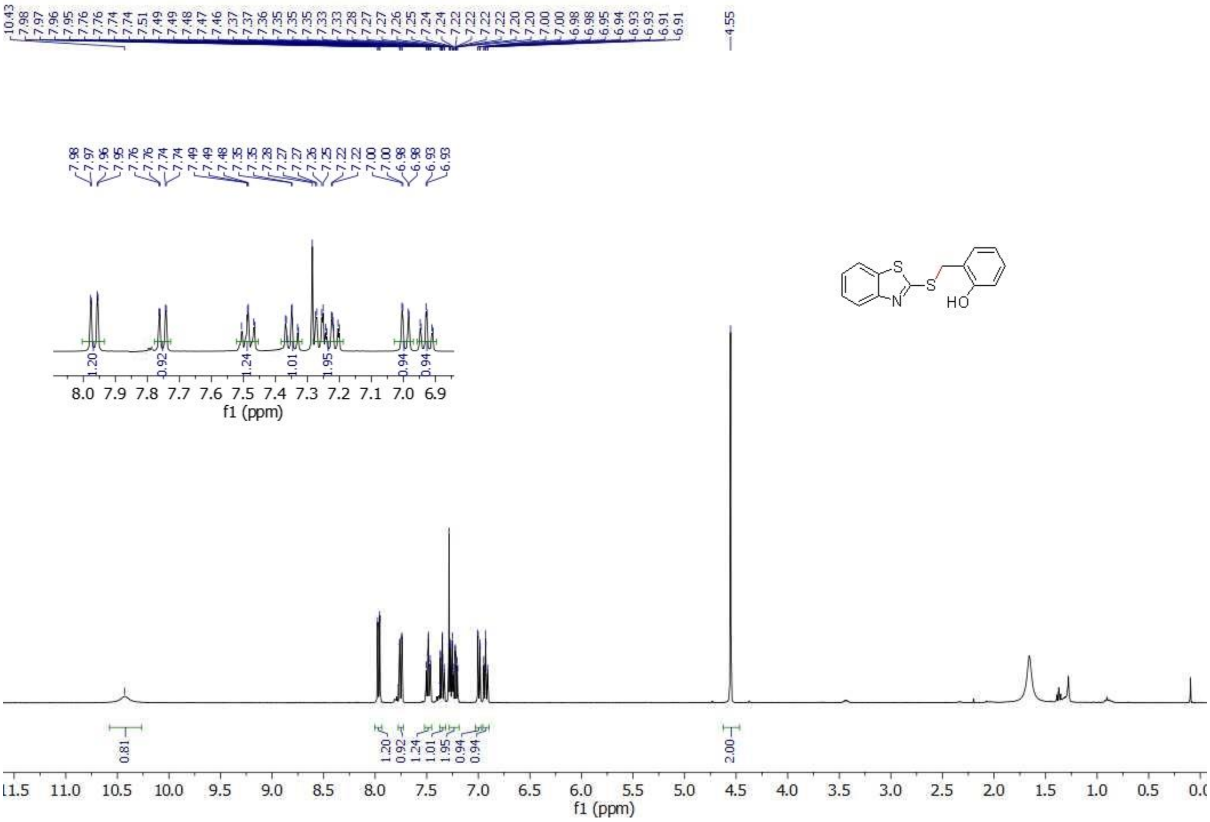


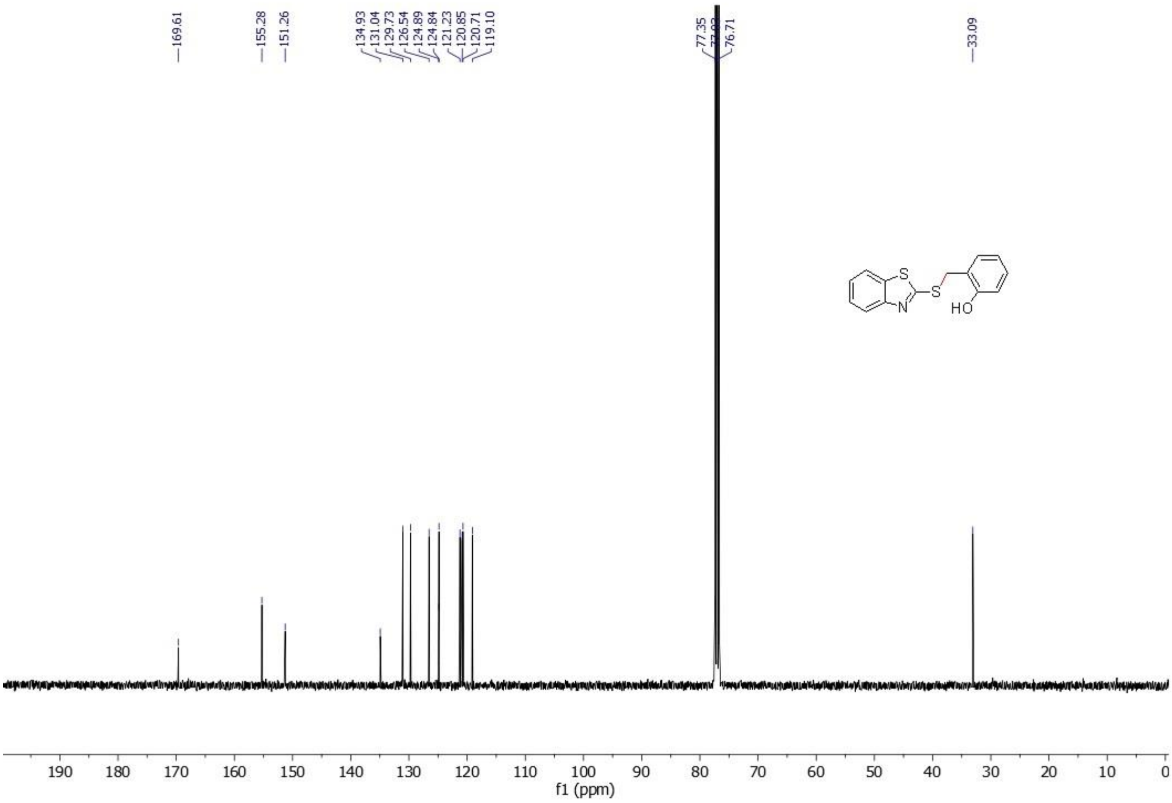
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **4tc**:



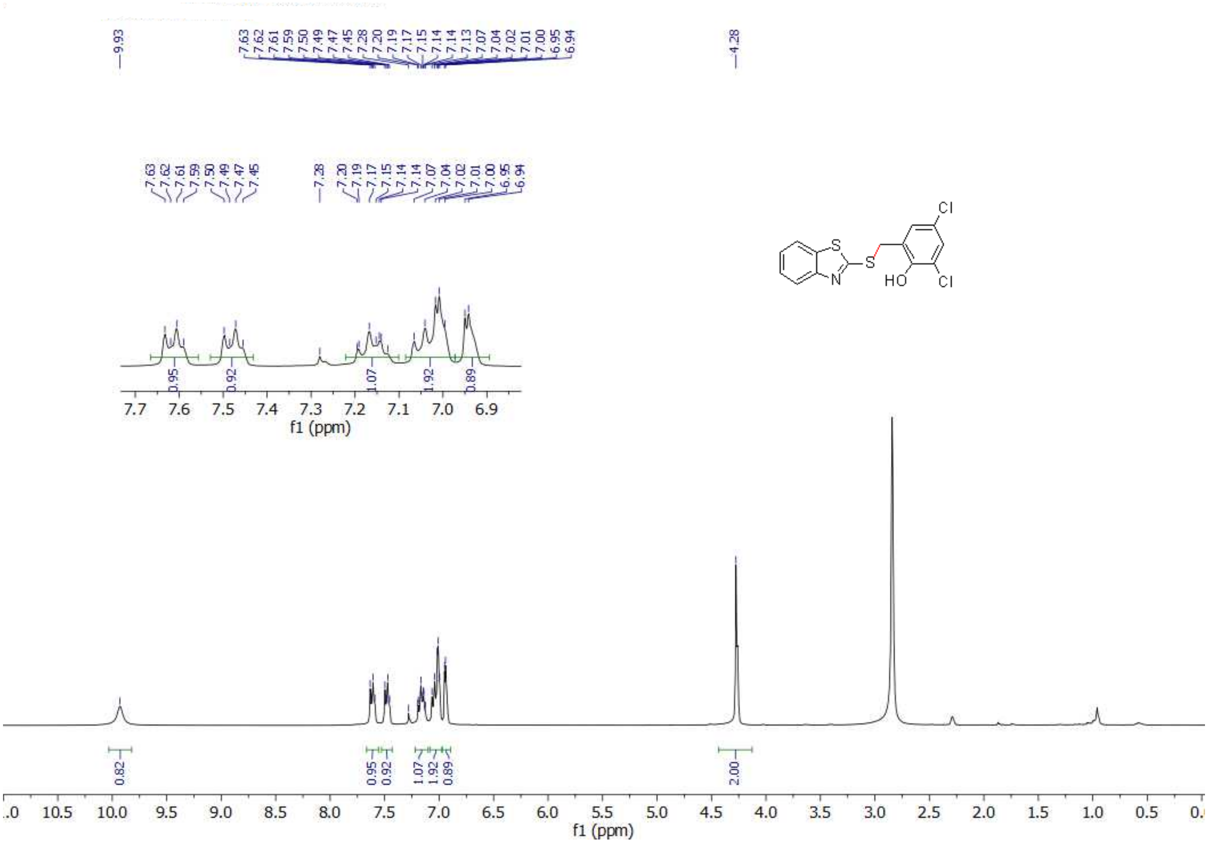


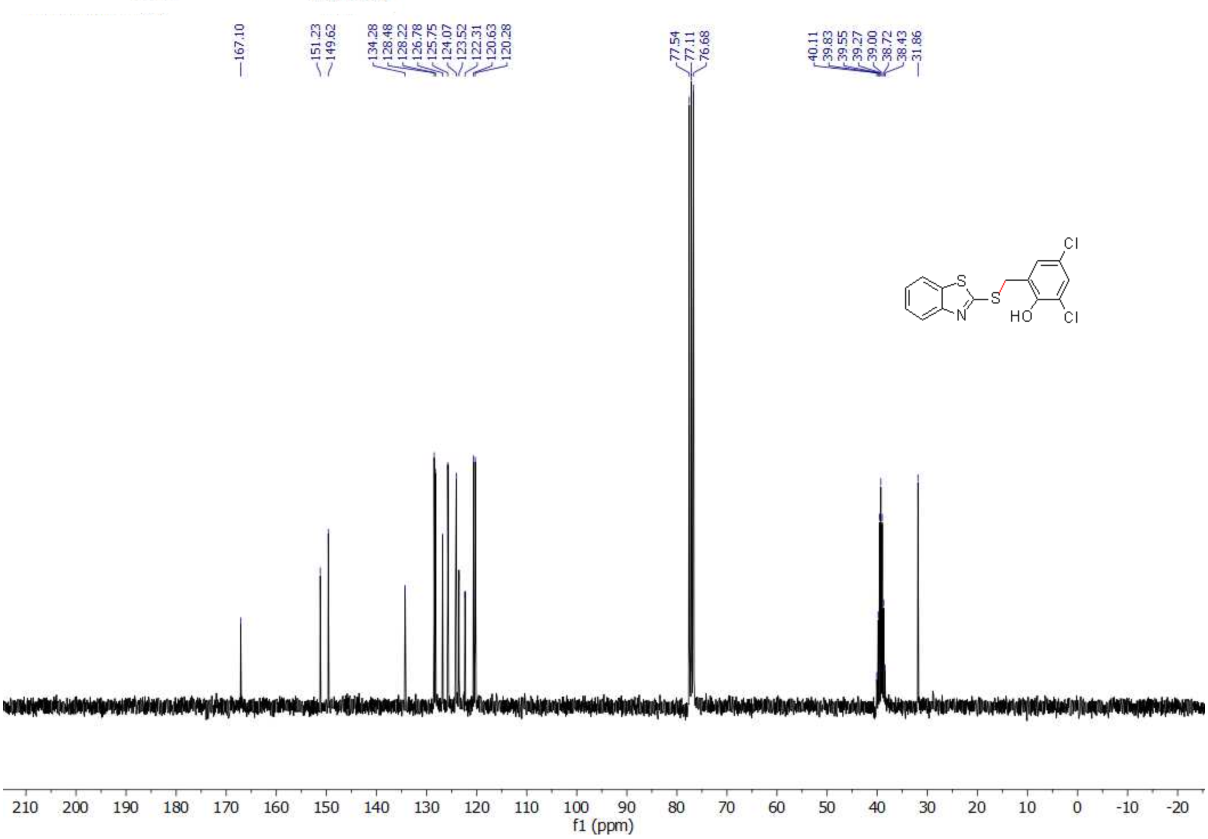
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **4ua**:



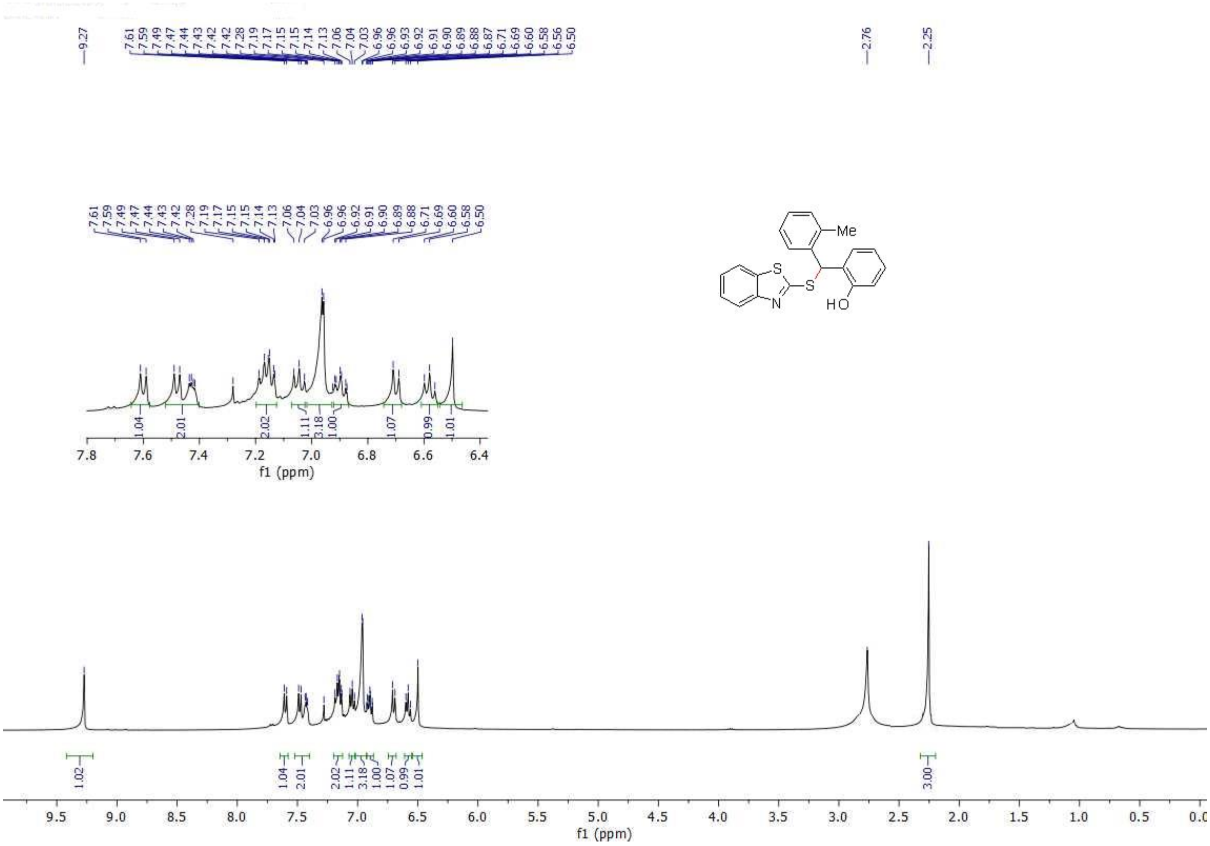


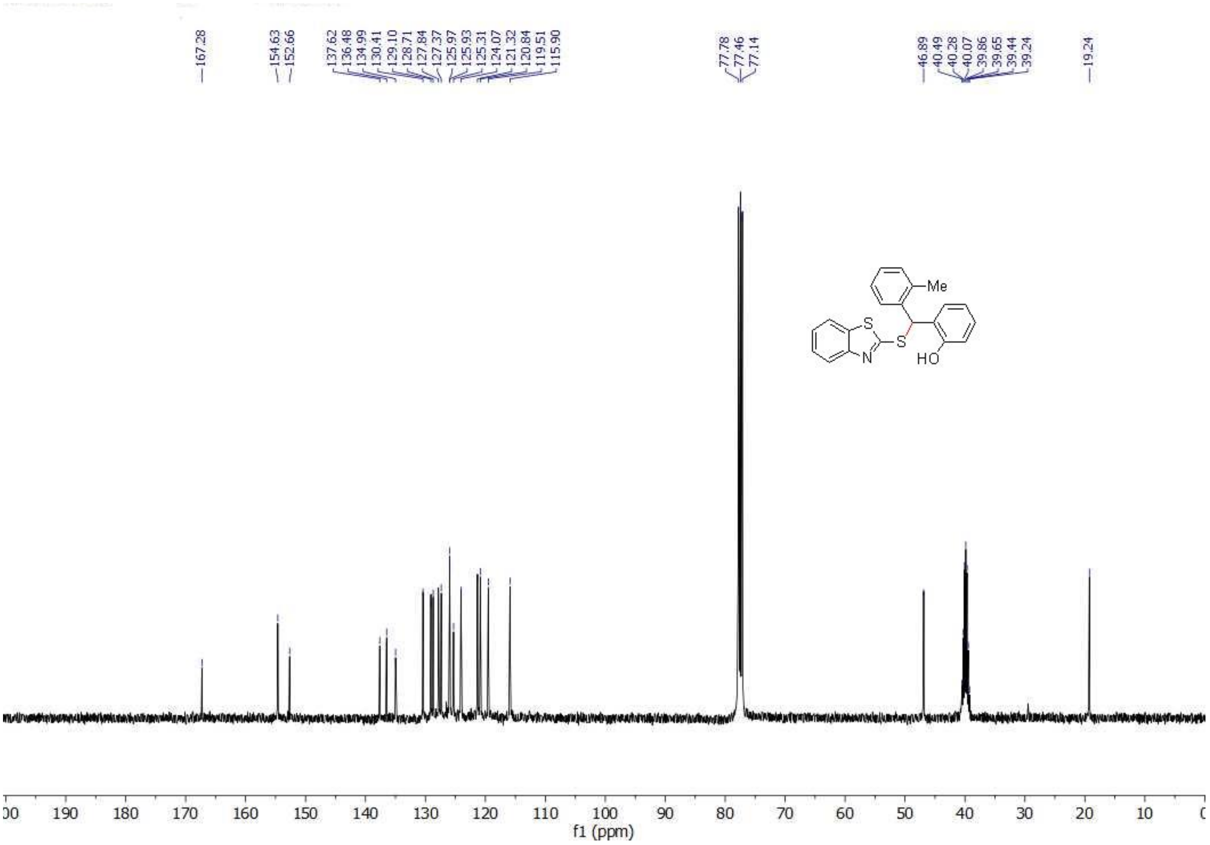
$^{1}$**H NMR** (300 MHz, $CDCl_3$ + 2 drops DMSO-d6) and $^{13}$**C{$^{1}$H} NMR** (75 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **4ud**:



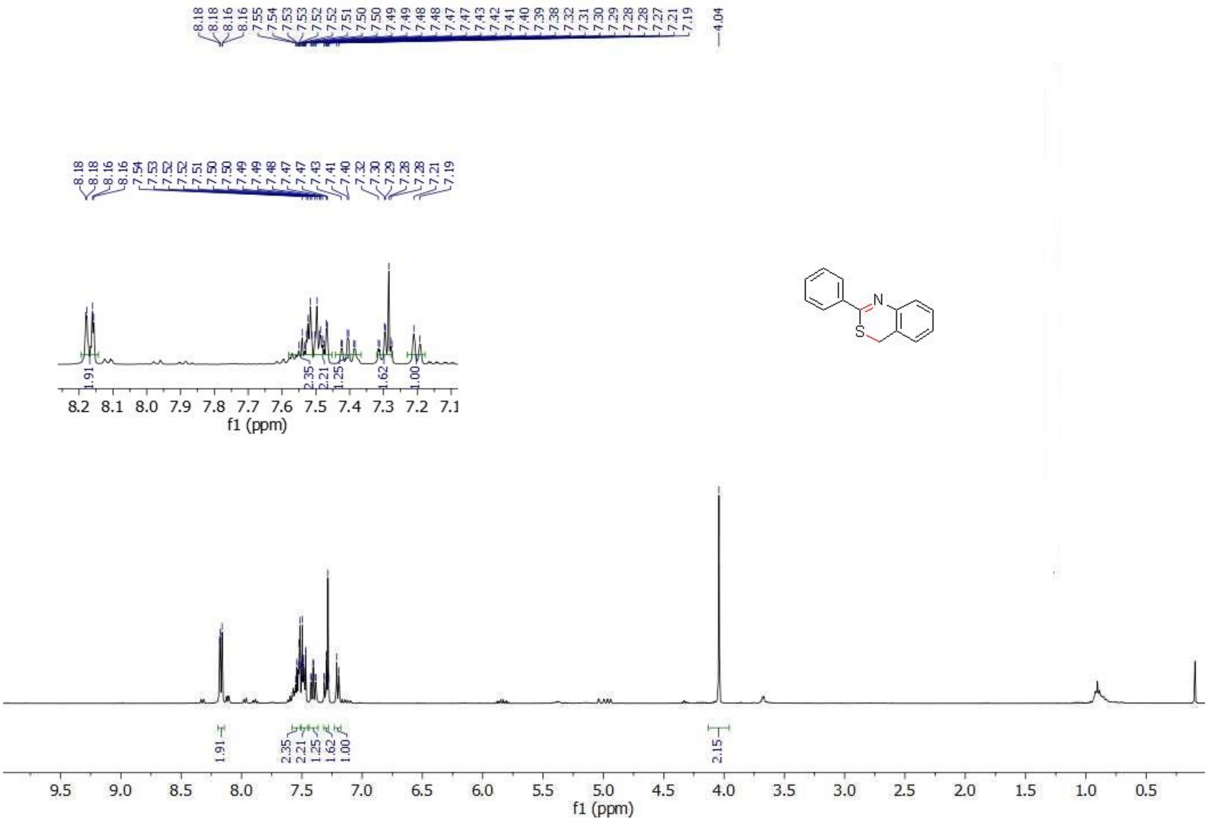


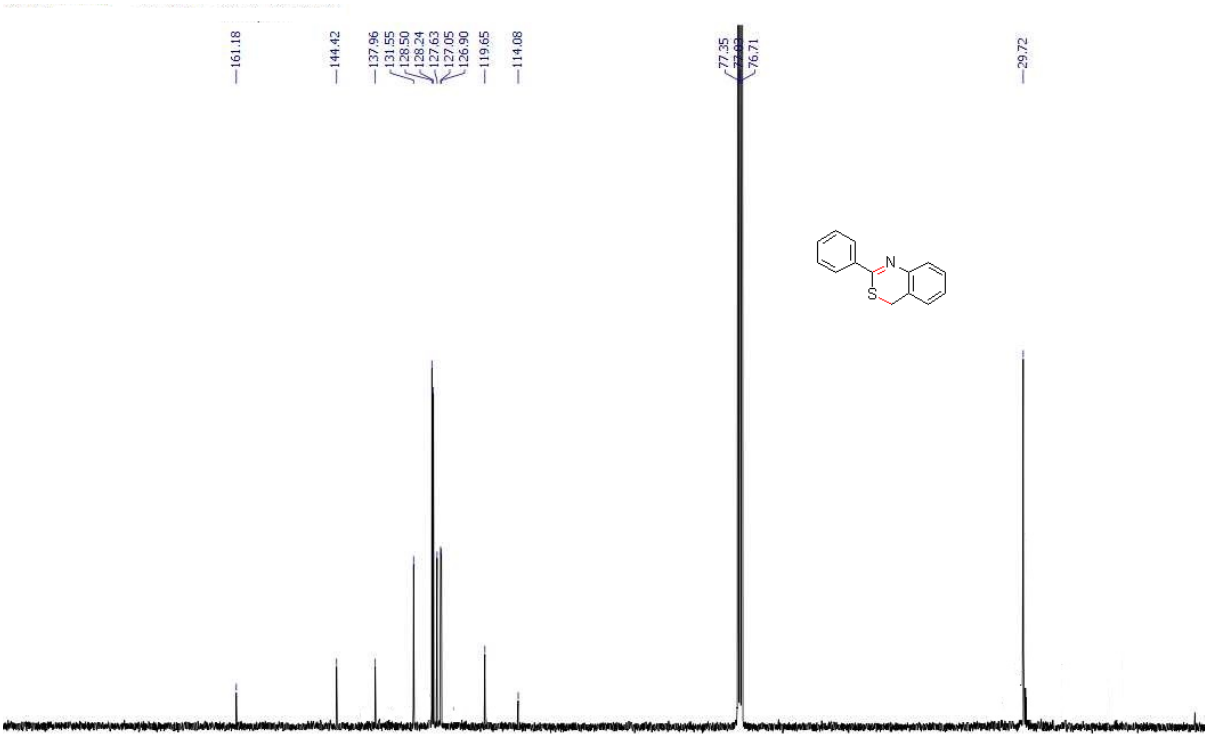
$^1$**H NMR** (400 MHz, $CDCl_3$ + 2 drops DMSO-d6) and $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$ + 2 drops DMSO-d6) spectra of **4uk**:



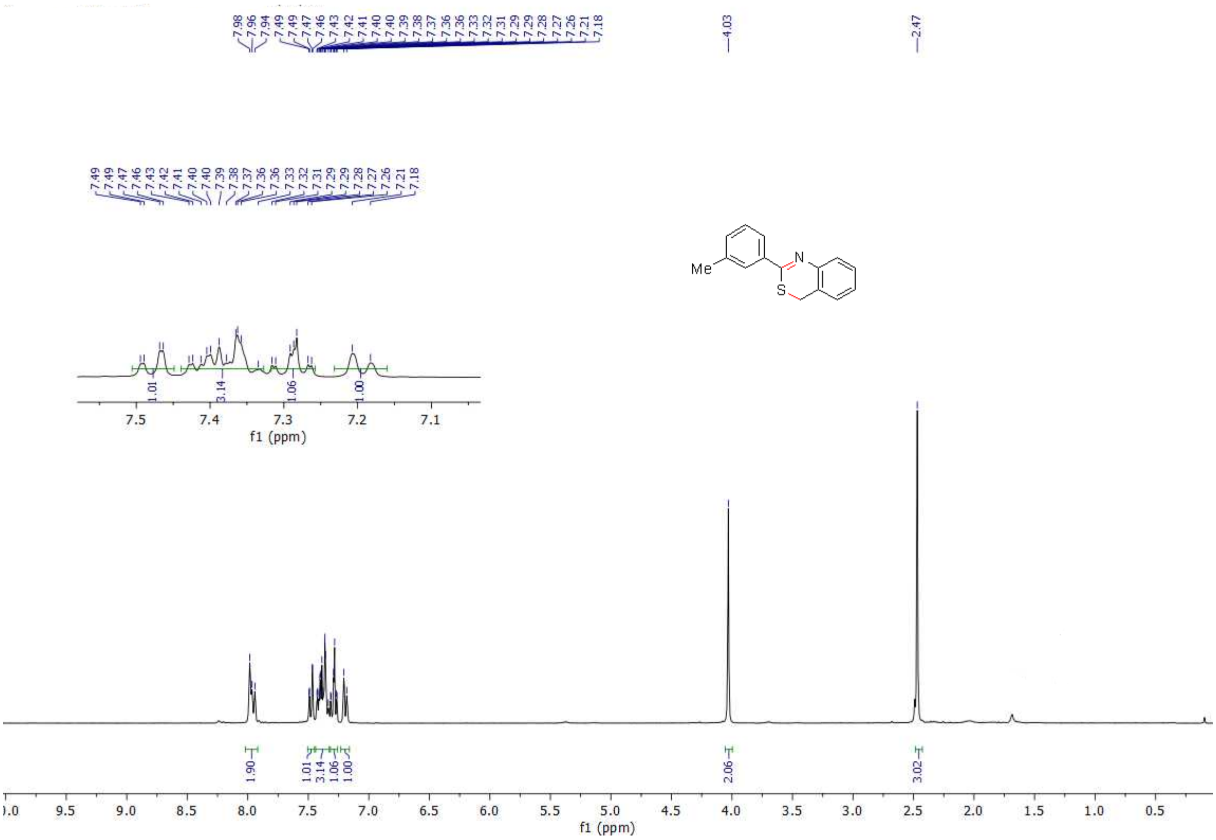


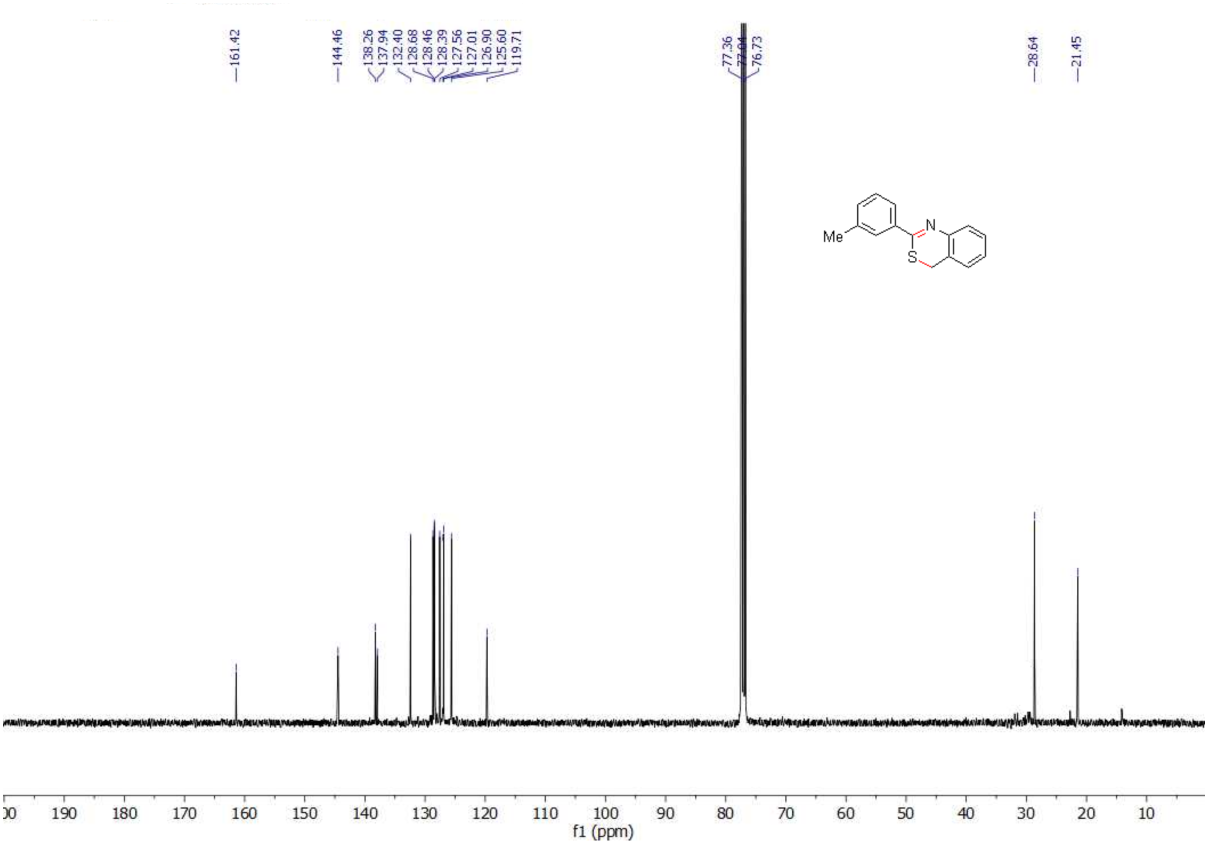
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **5al**:



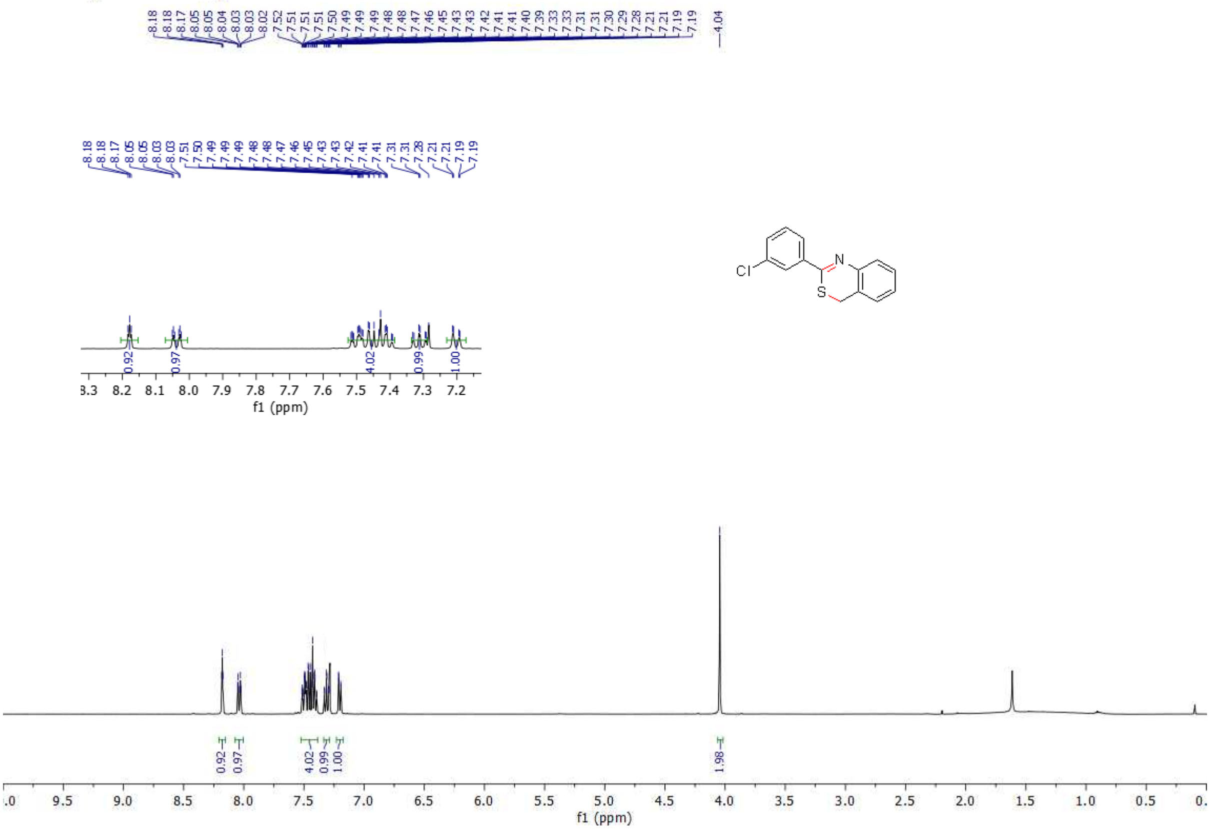


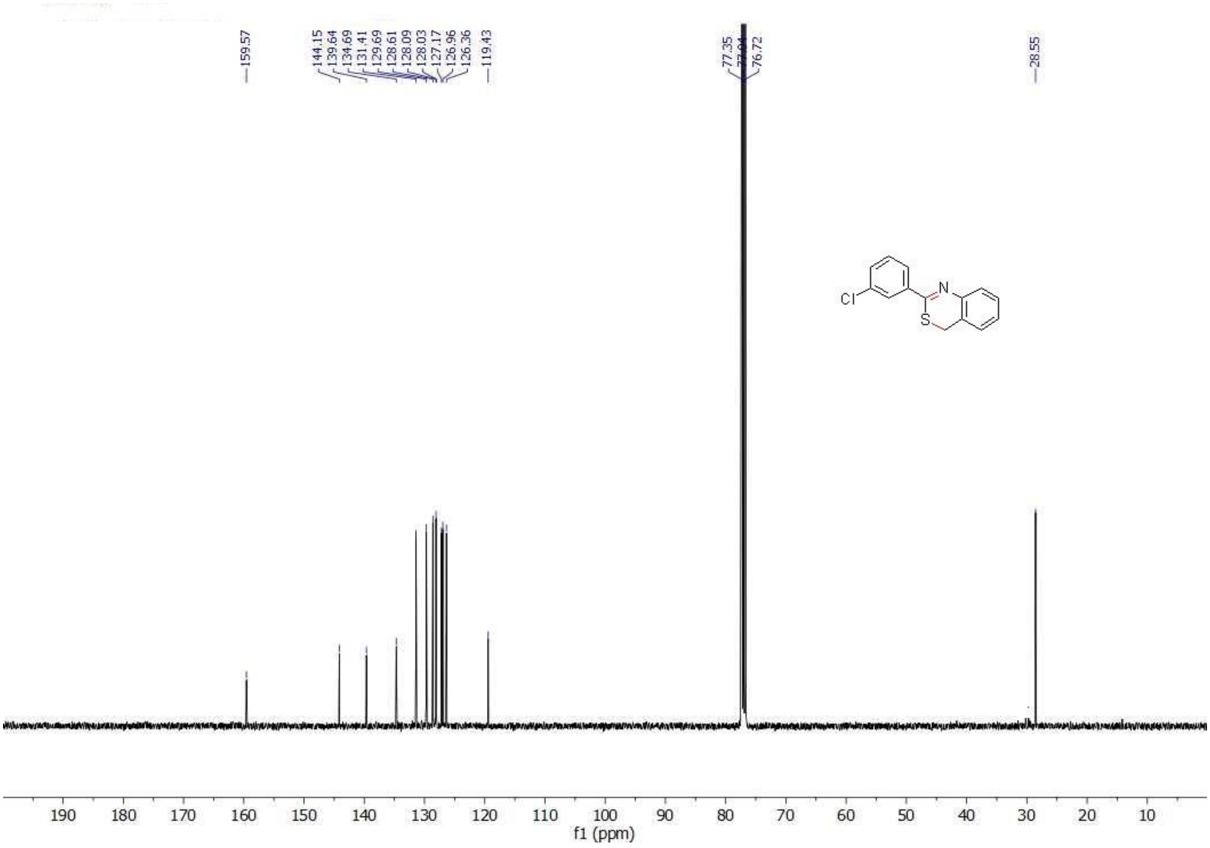
$^{1}$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{**$^{1}$**H} NMR** (100 MHz, CDCl$_3$) spectra of **5dl**:



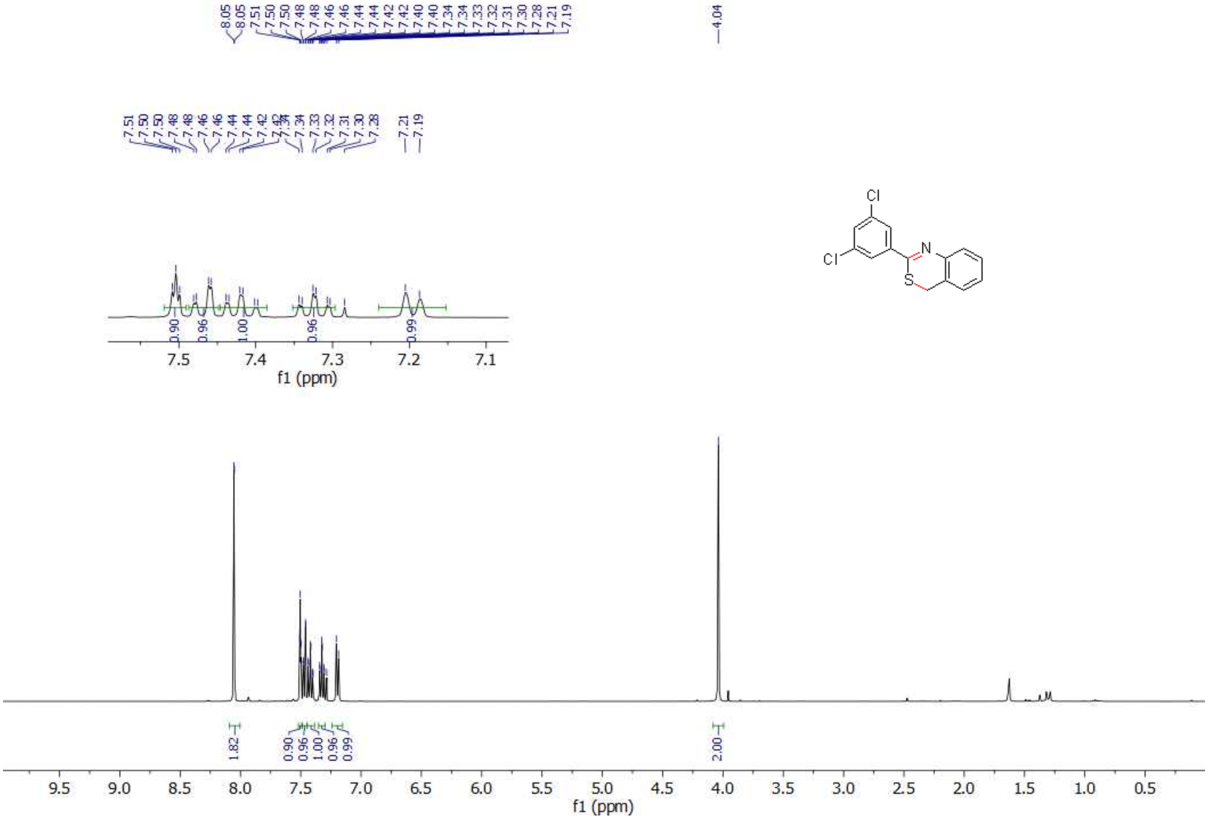


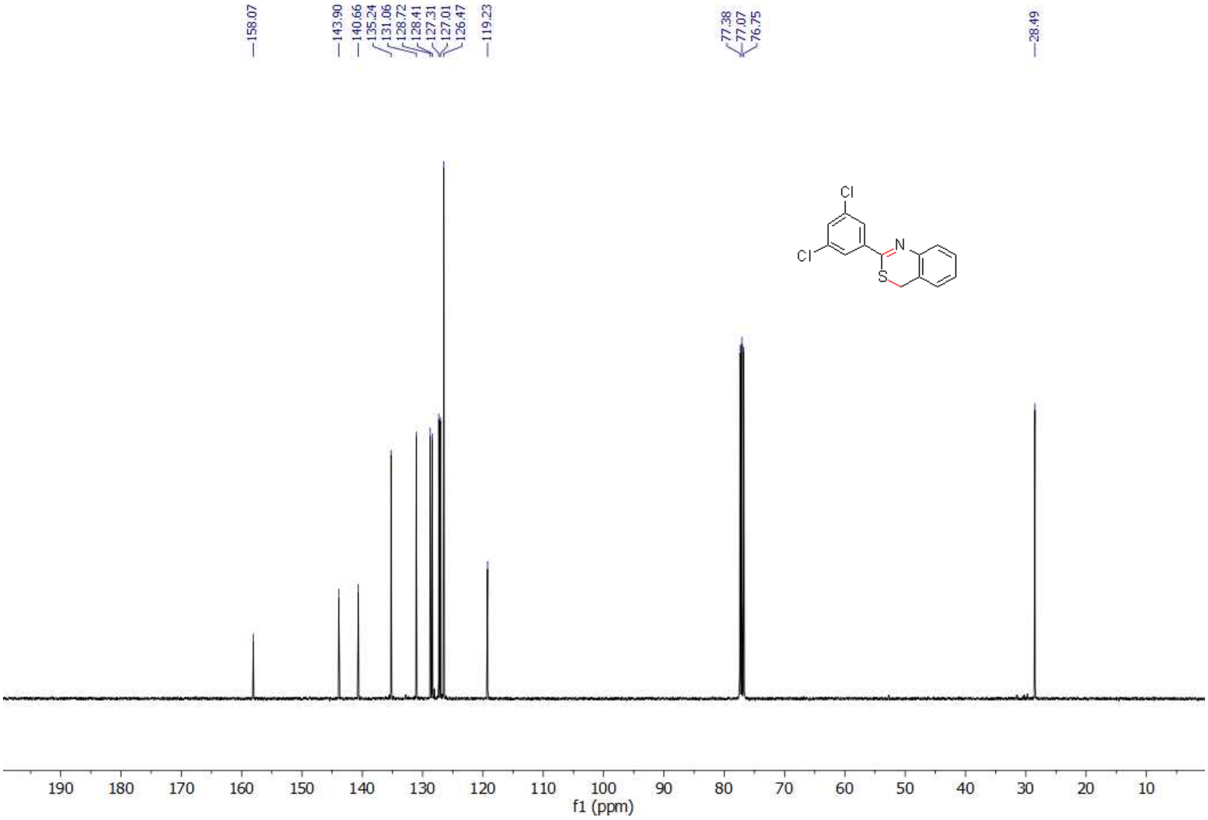
$^{1}$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) spectra of **5fl**:



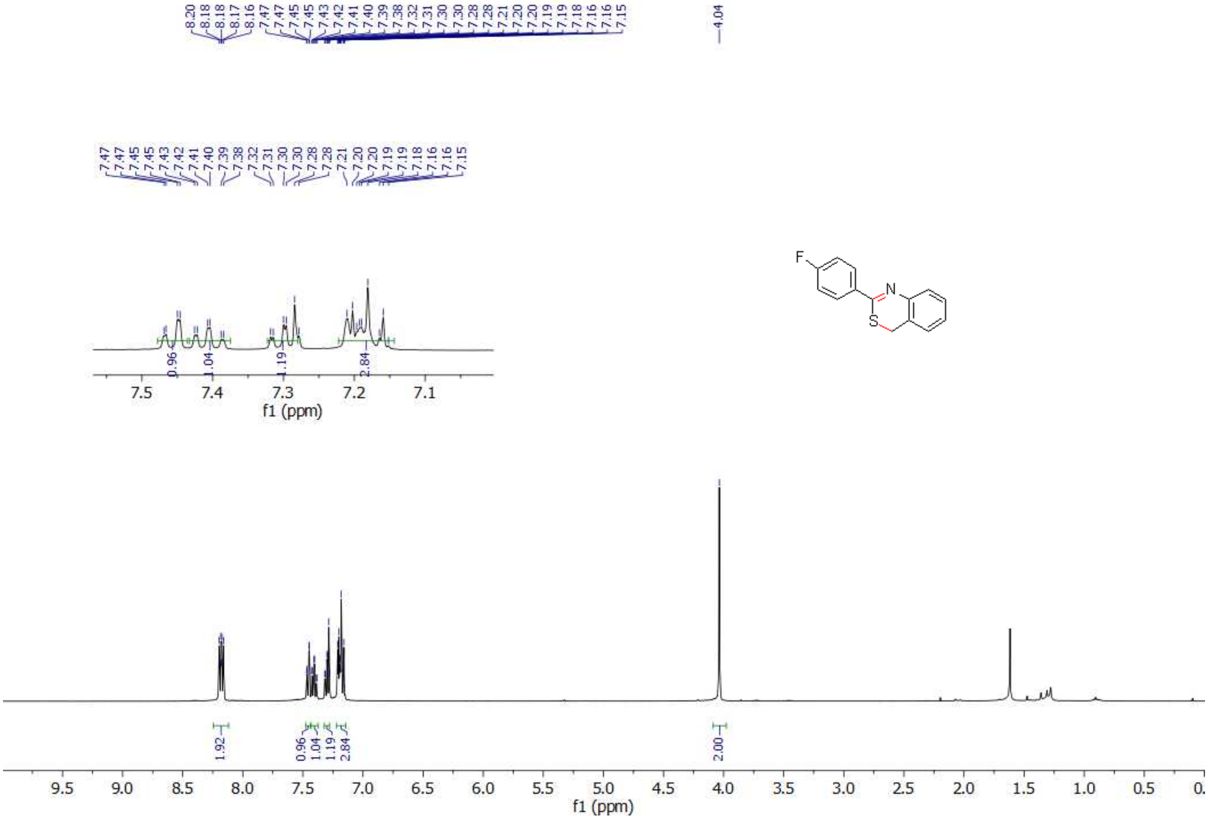


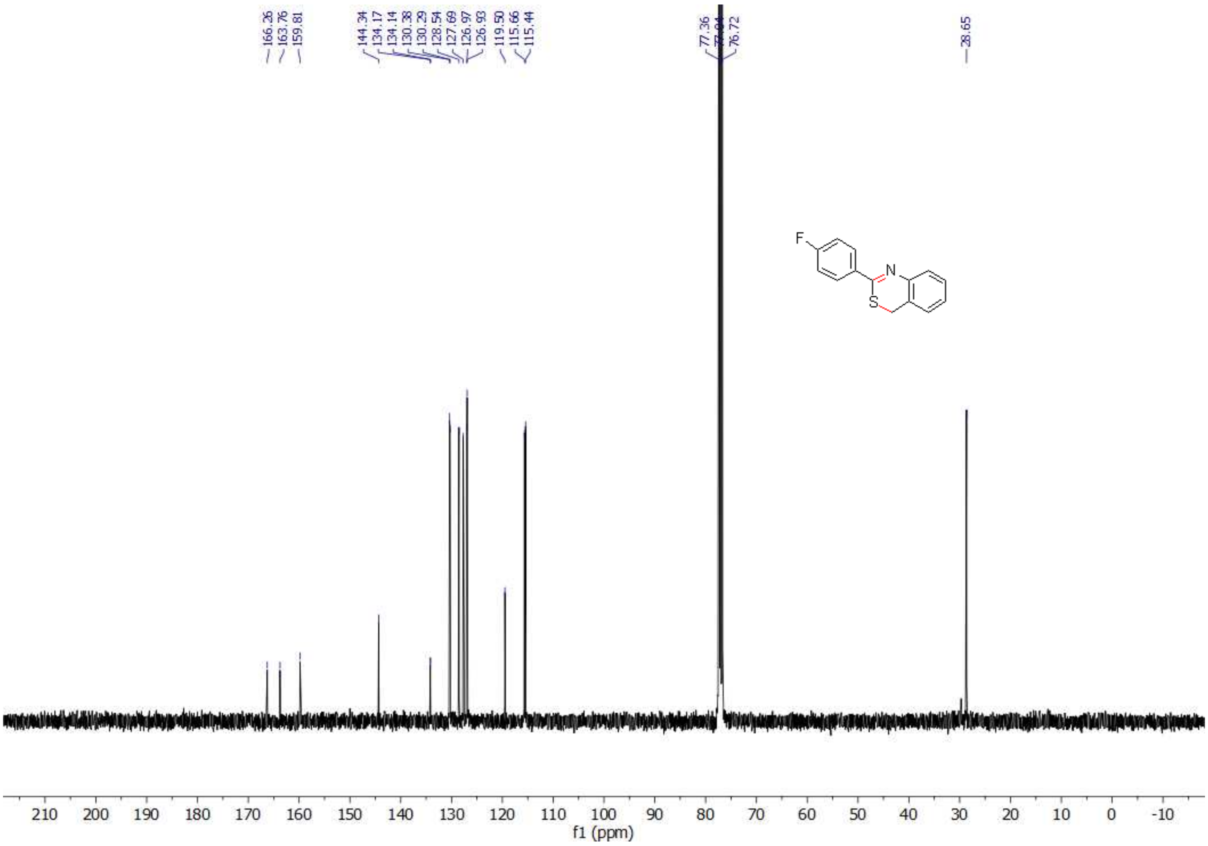
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **5gl**:



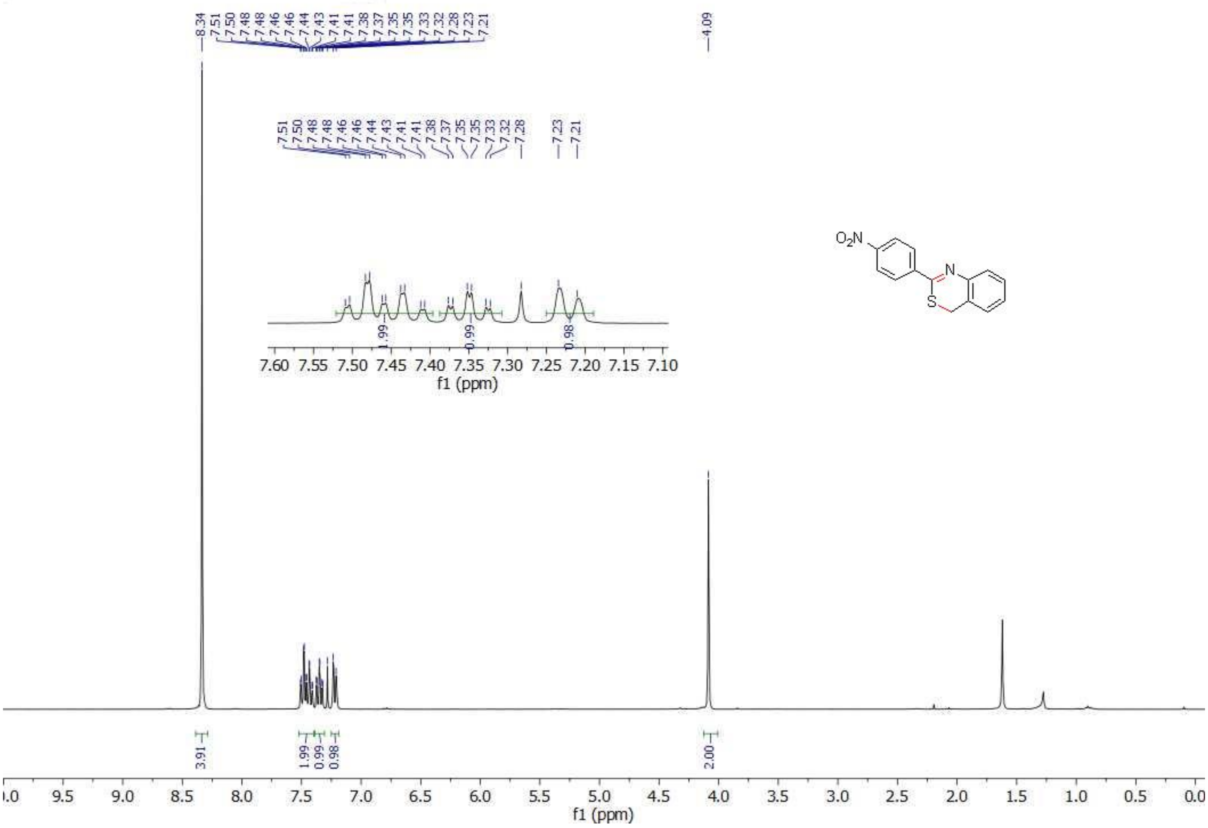


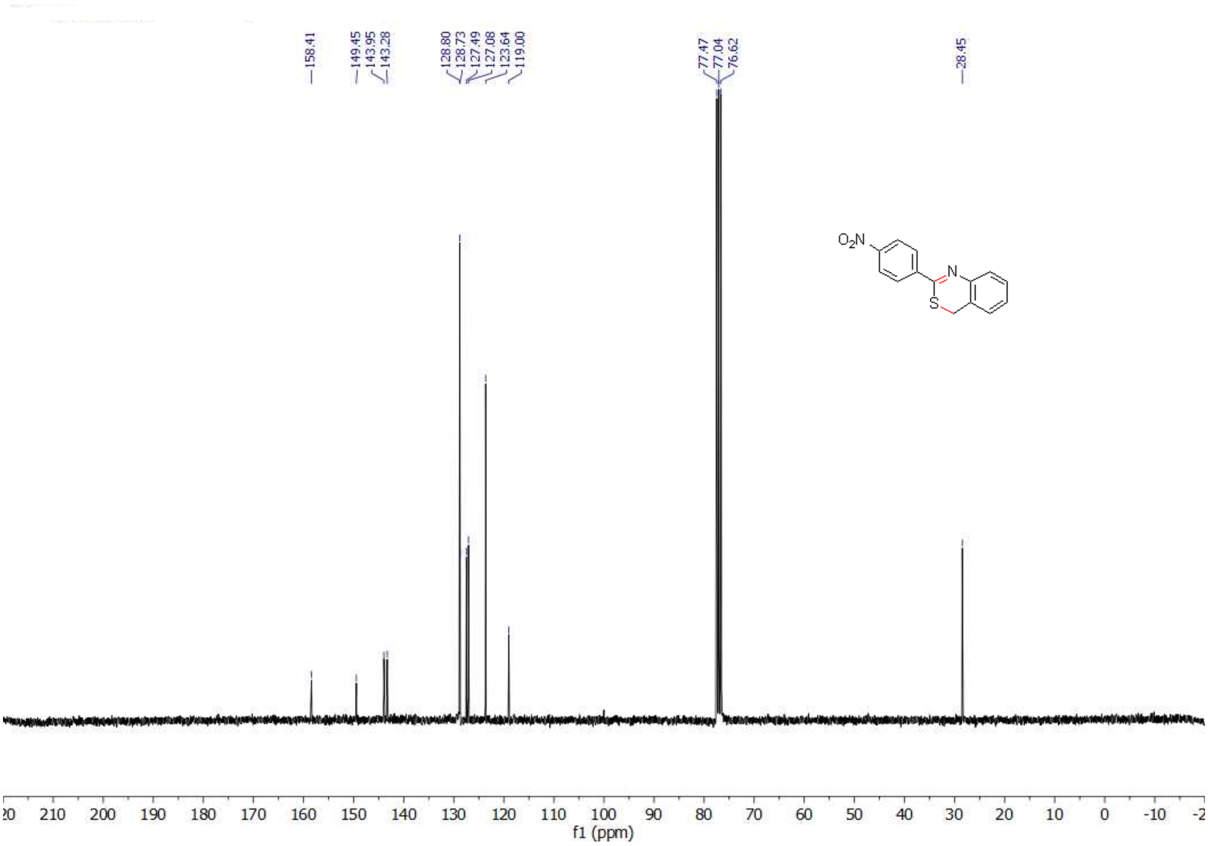
$^{1}$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **5hl**:



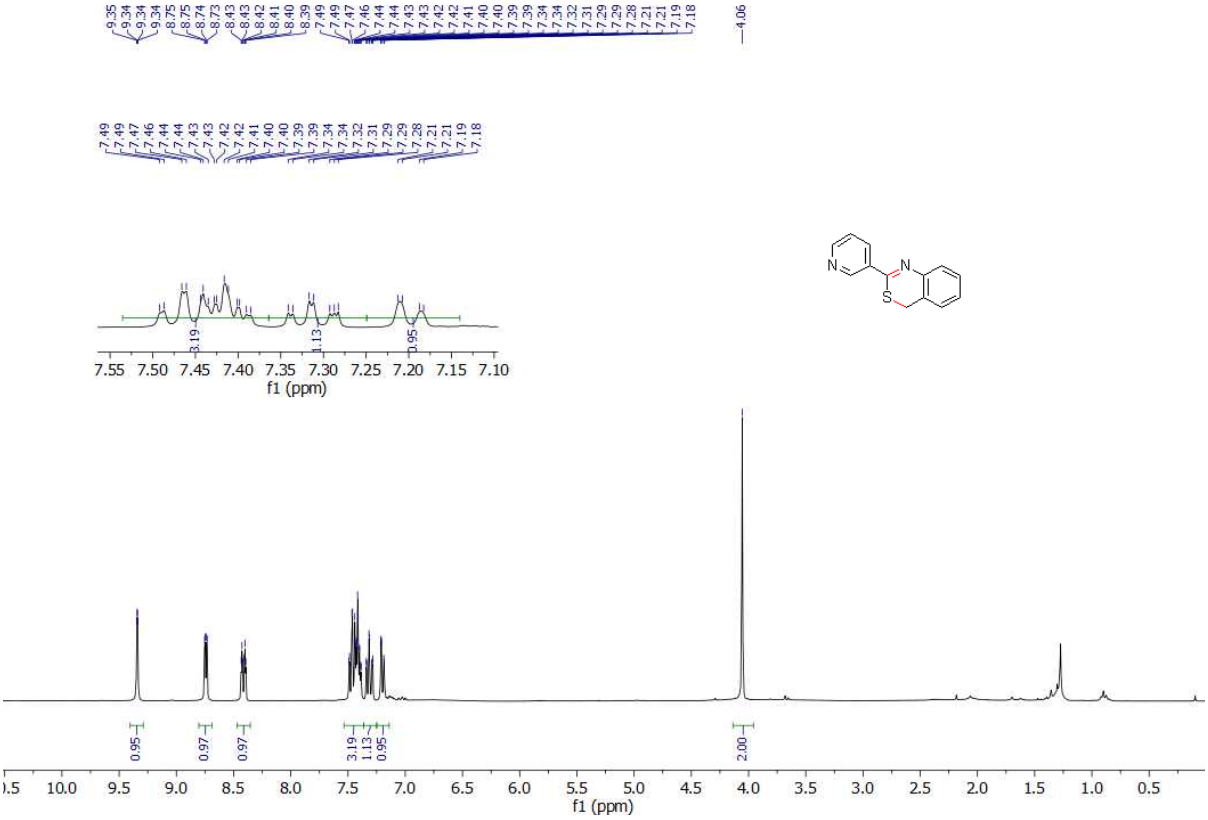


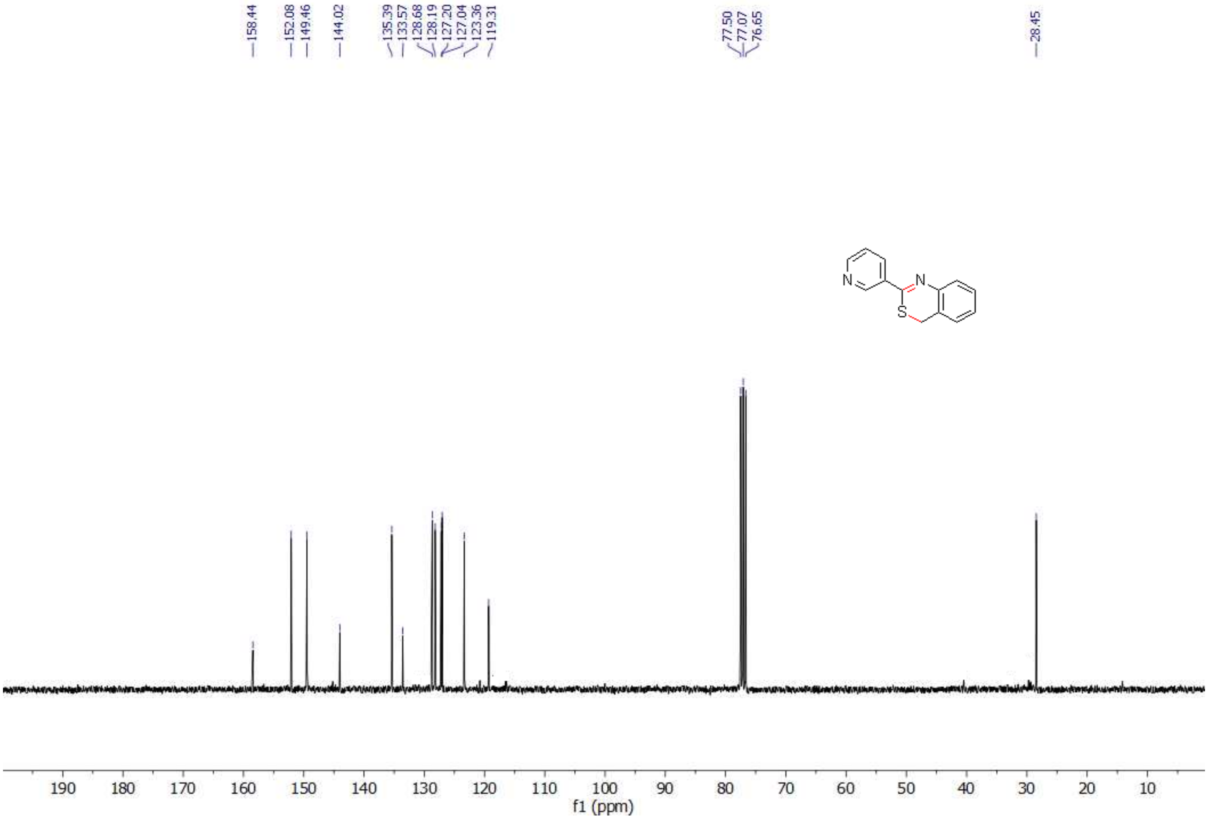
$^{1}$**H NMR** (300 MHz, $CDCl_3$) and $^{13}$**C{$^{1}$H} NMR** (75 MHz, $CDCl_3$) spectra of **5kl**:



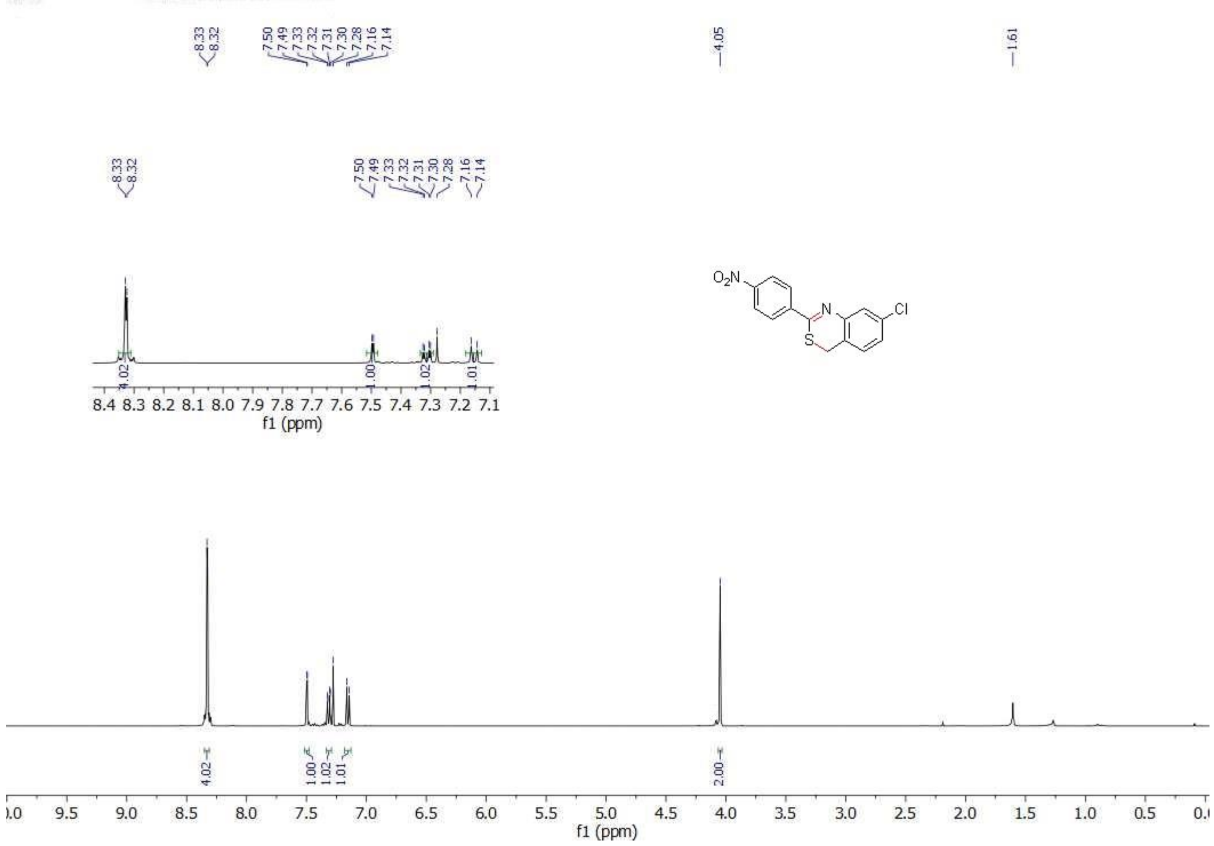


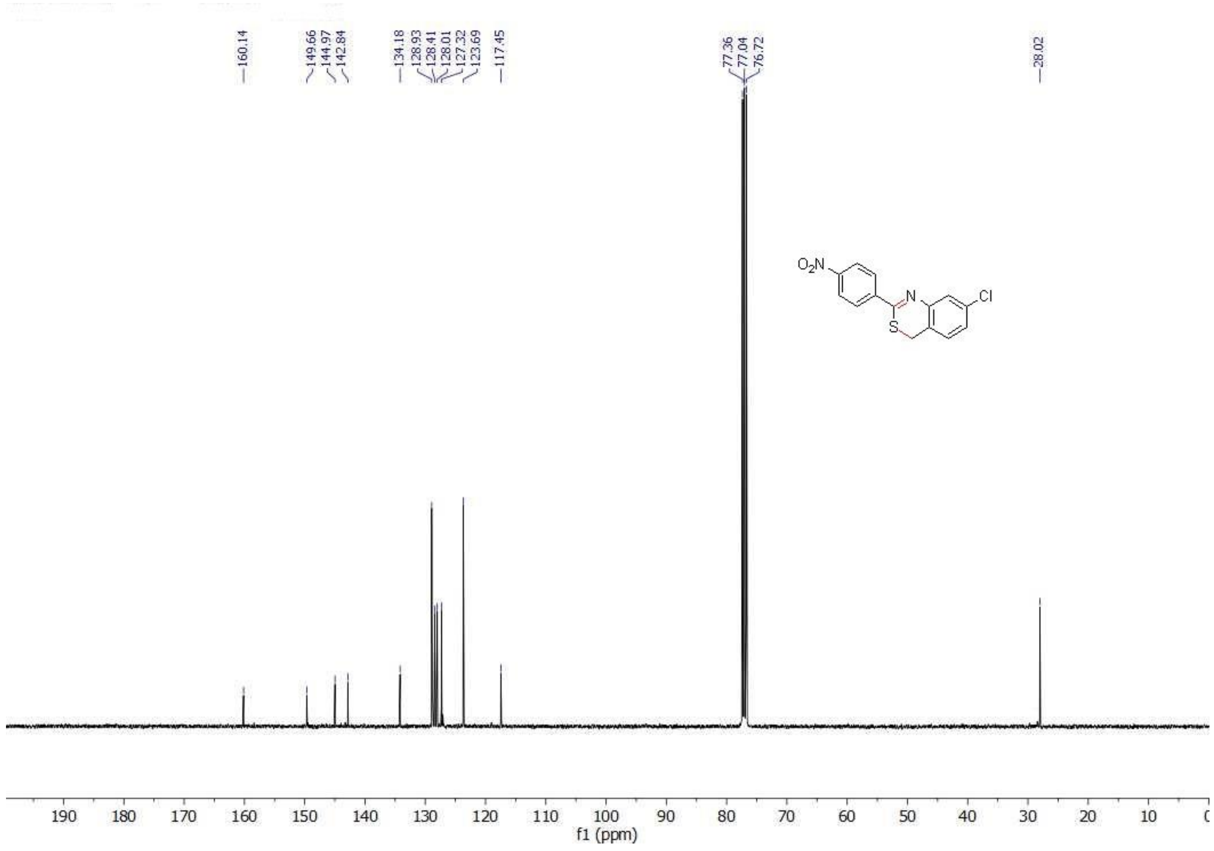
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (75 MHz, CDCl$_3$) spectra of **5pl**:



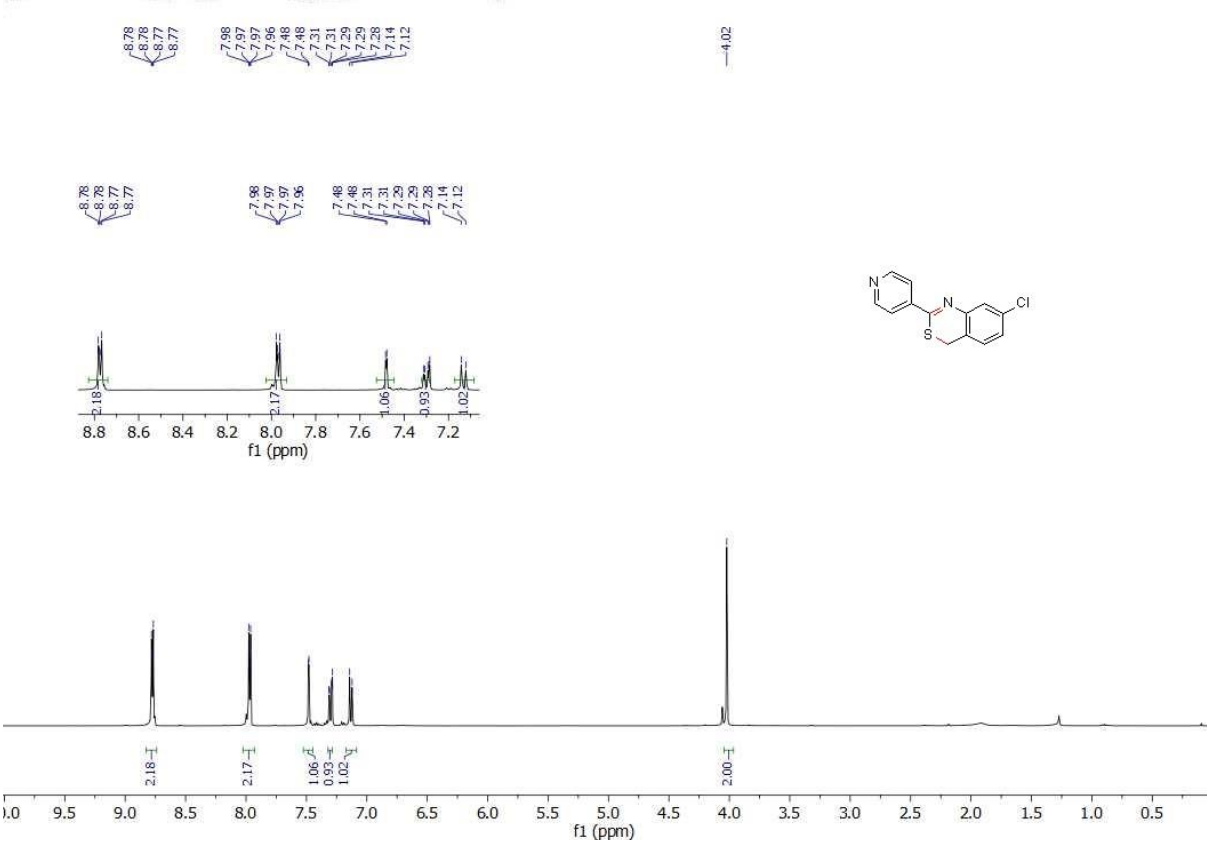


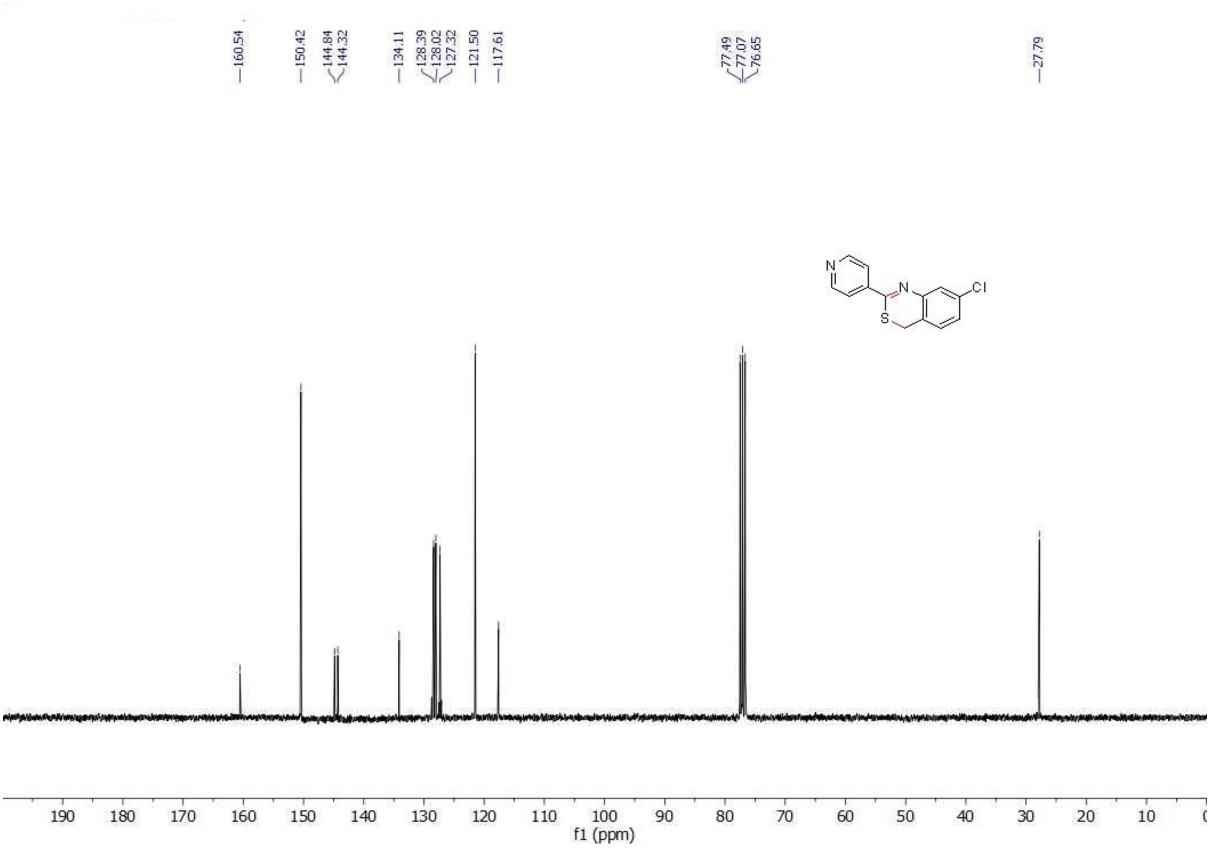
$^1$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) spectra of **5km**:



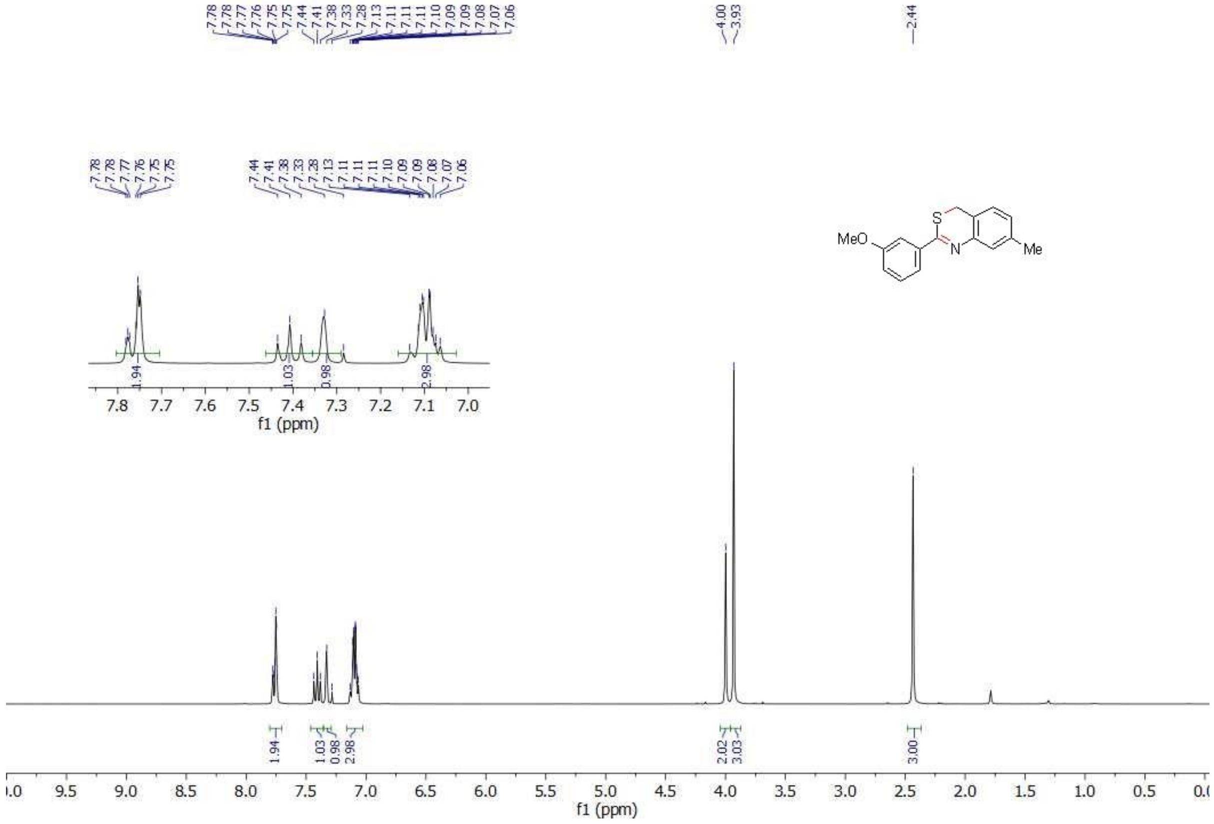


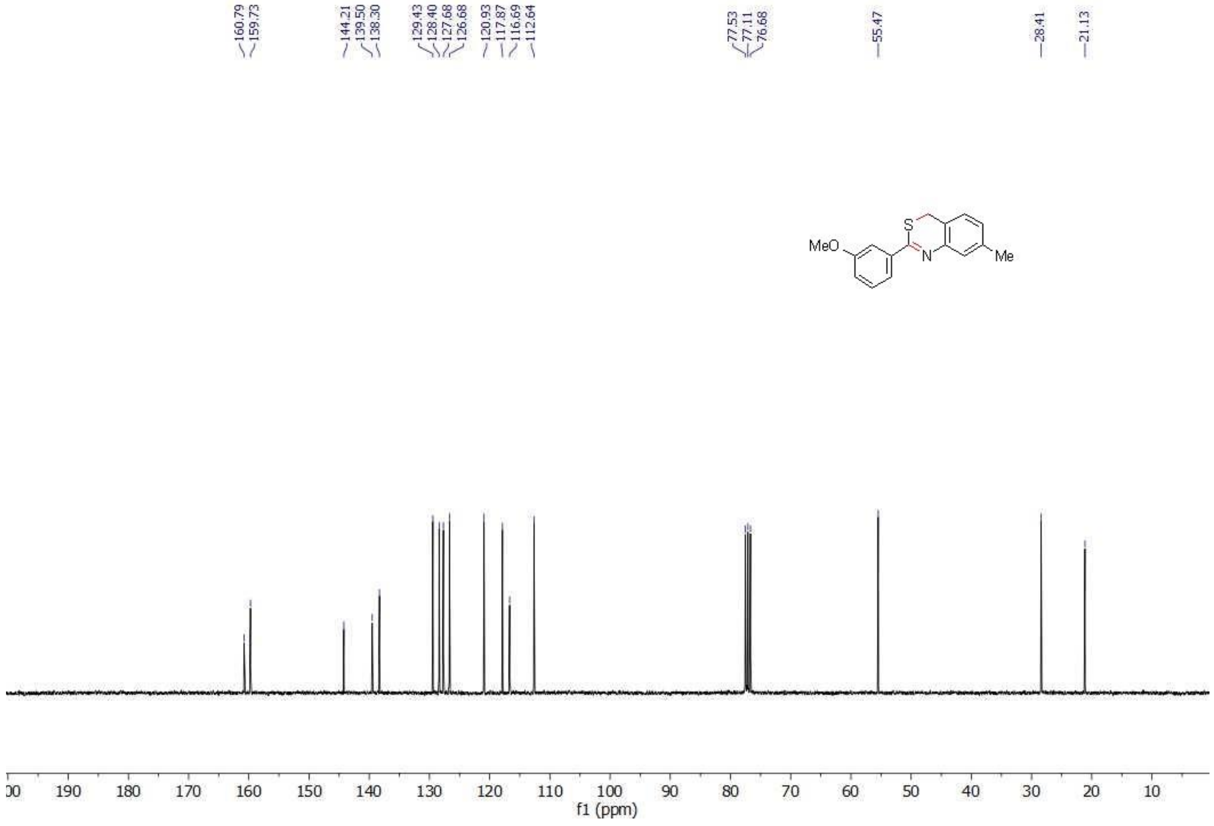
**$^1$H NMR** (400 MHz, $CDCl_3$) and **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) spectra of **5qm**:



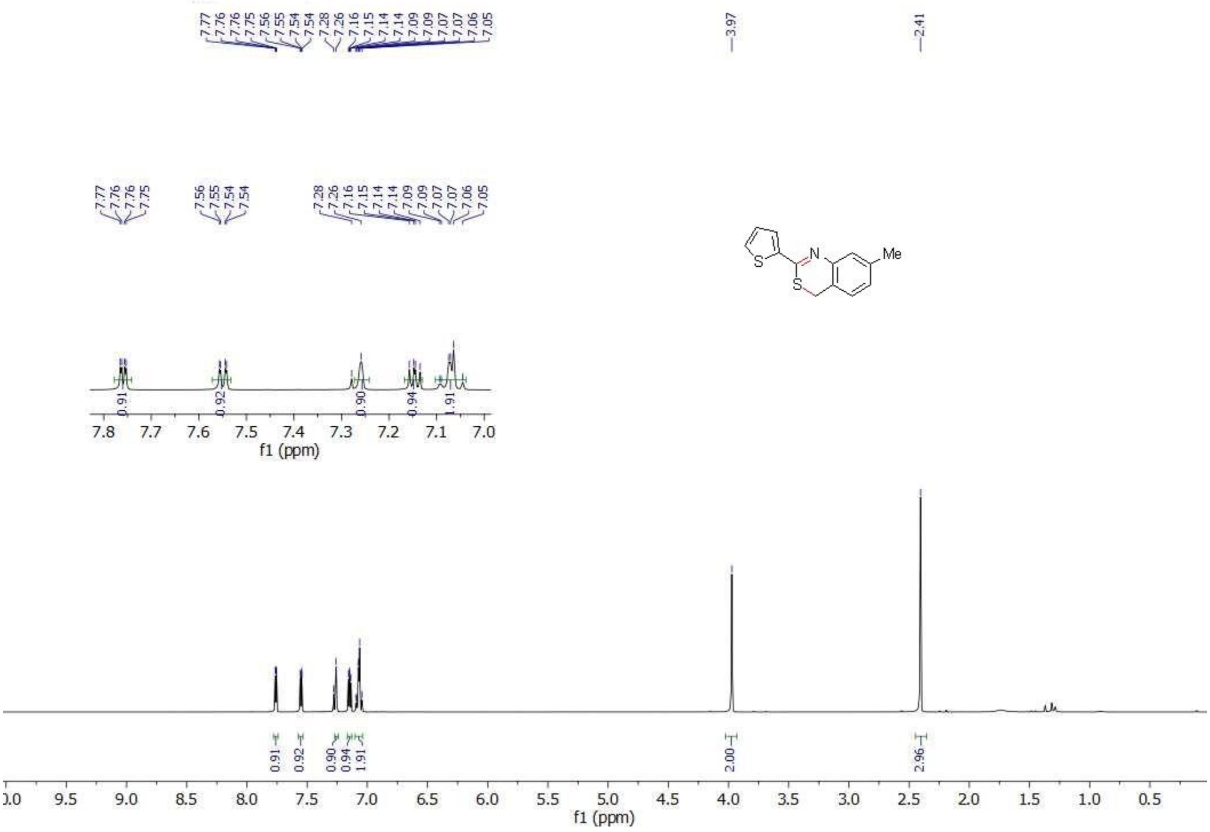


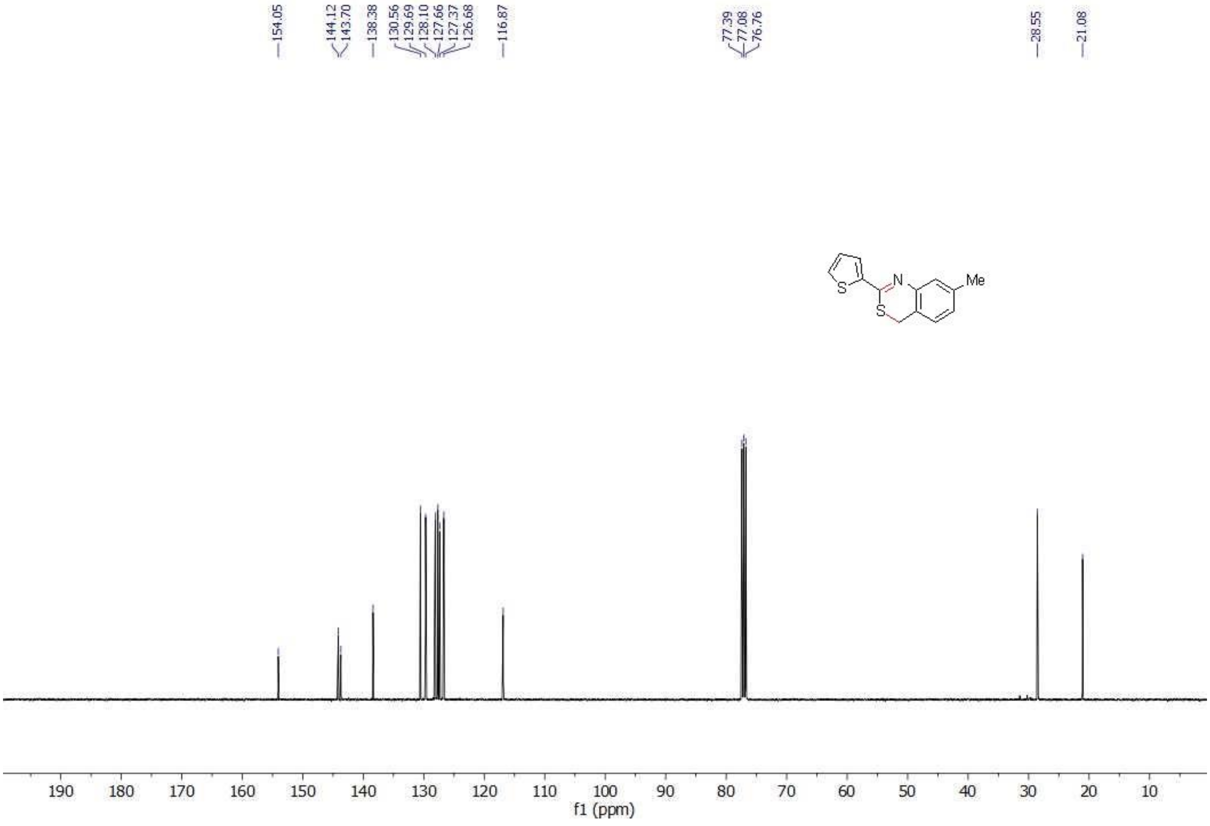
$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (75 MHz, CDCl$_3$) spectra of 5**cn**:



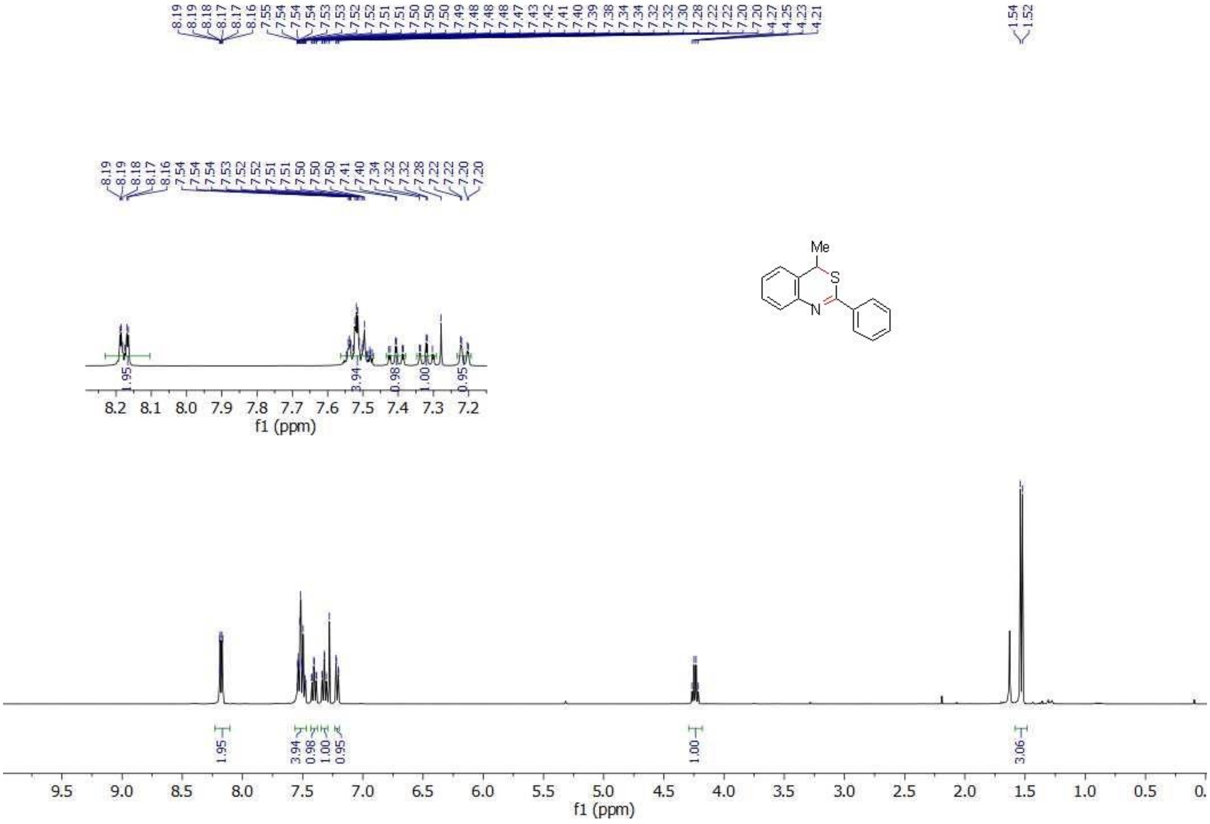


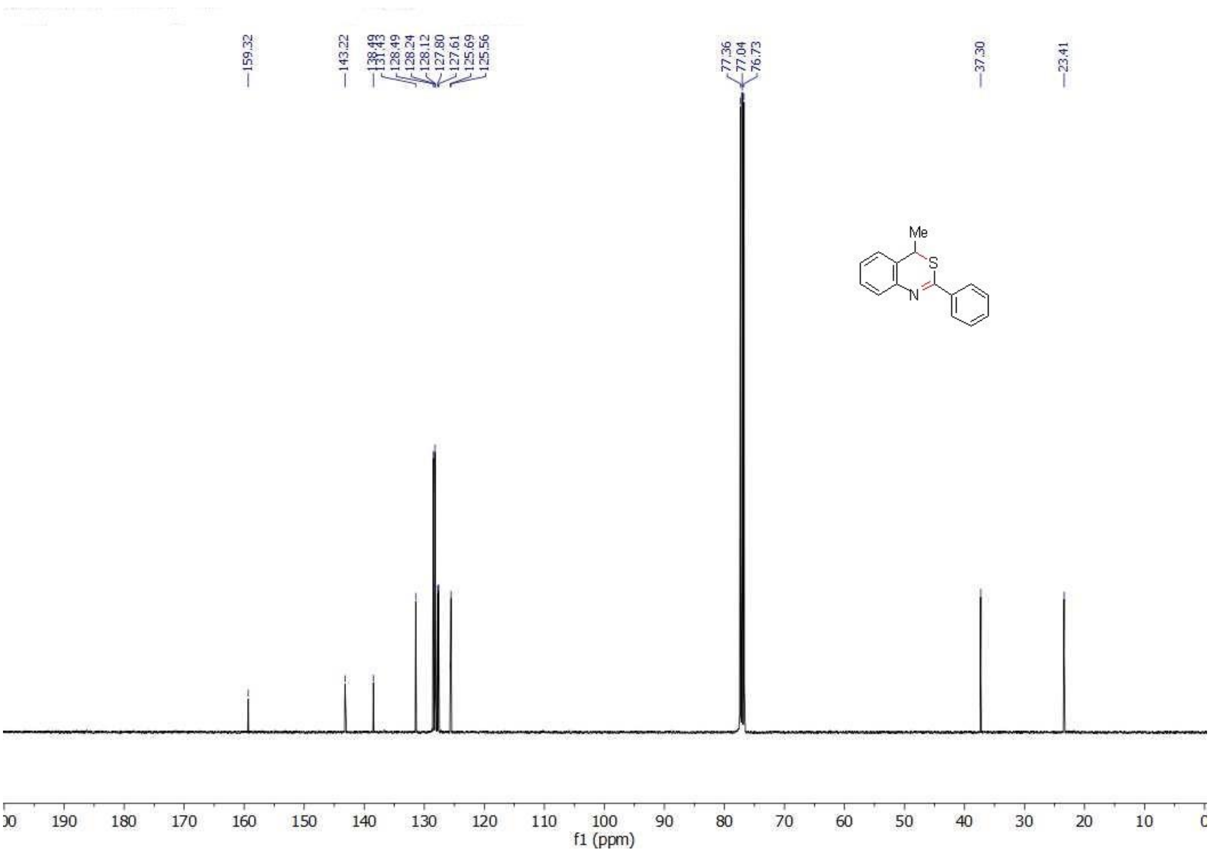
$^{1}$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, $CDCl_3$) spectra of 5**sn**:



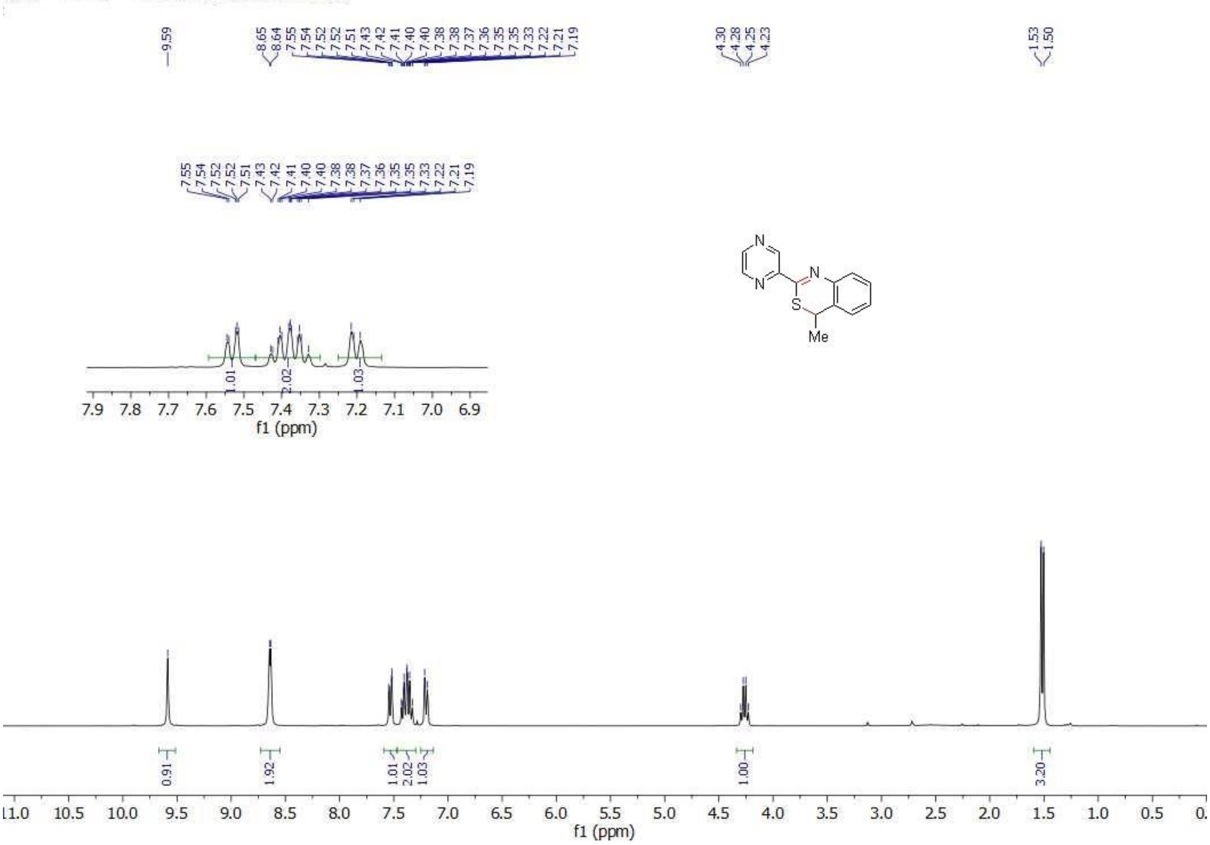


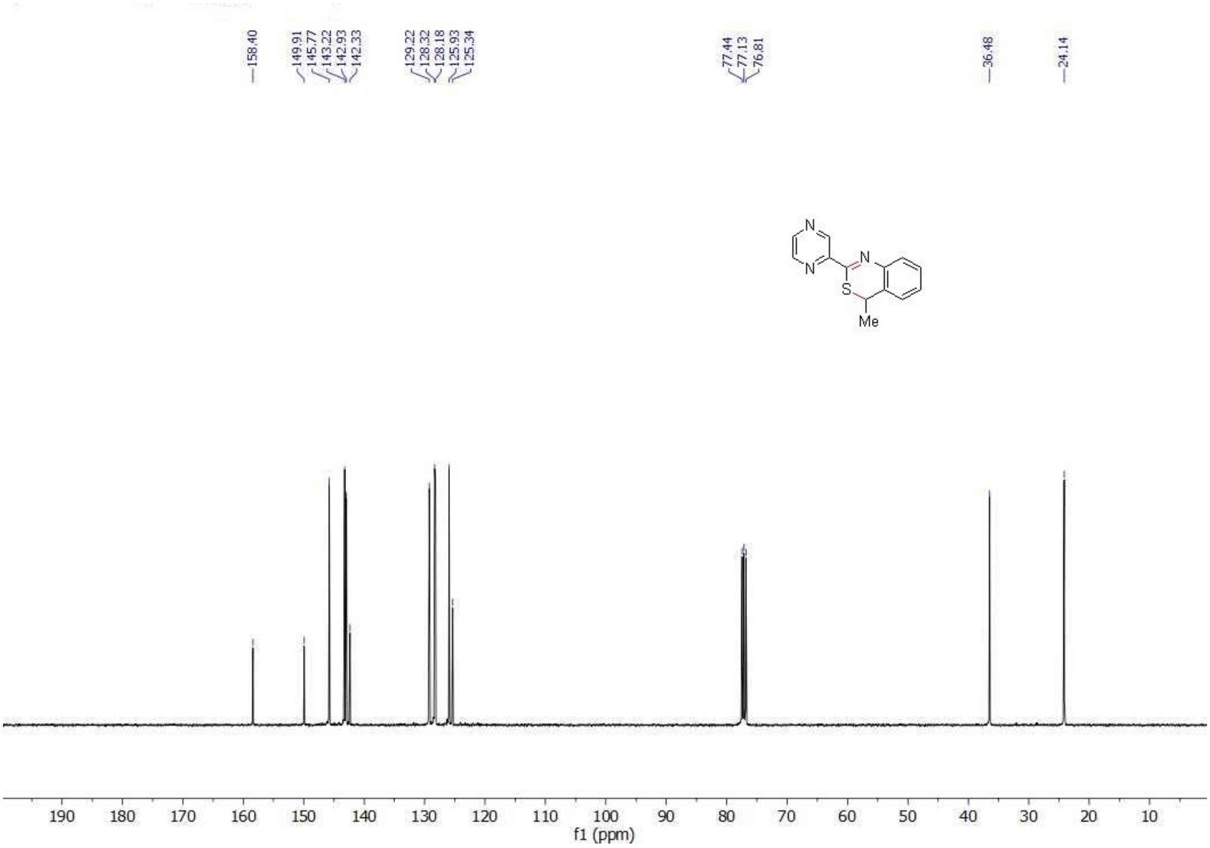
**$^1$H NMR** (400 MHz, CDCl$_3$) and **$^{13}$C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of 5**ao**:



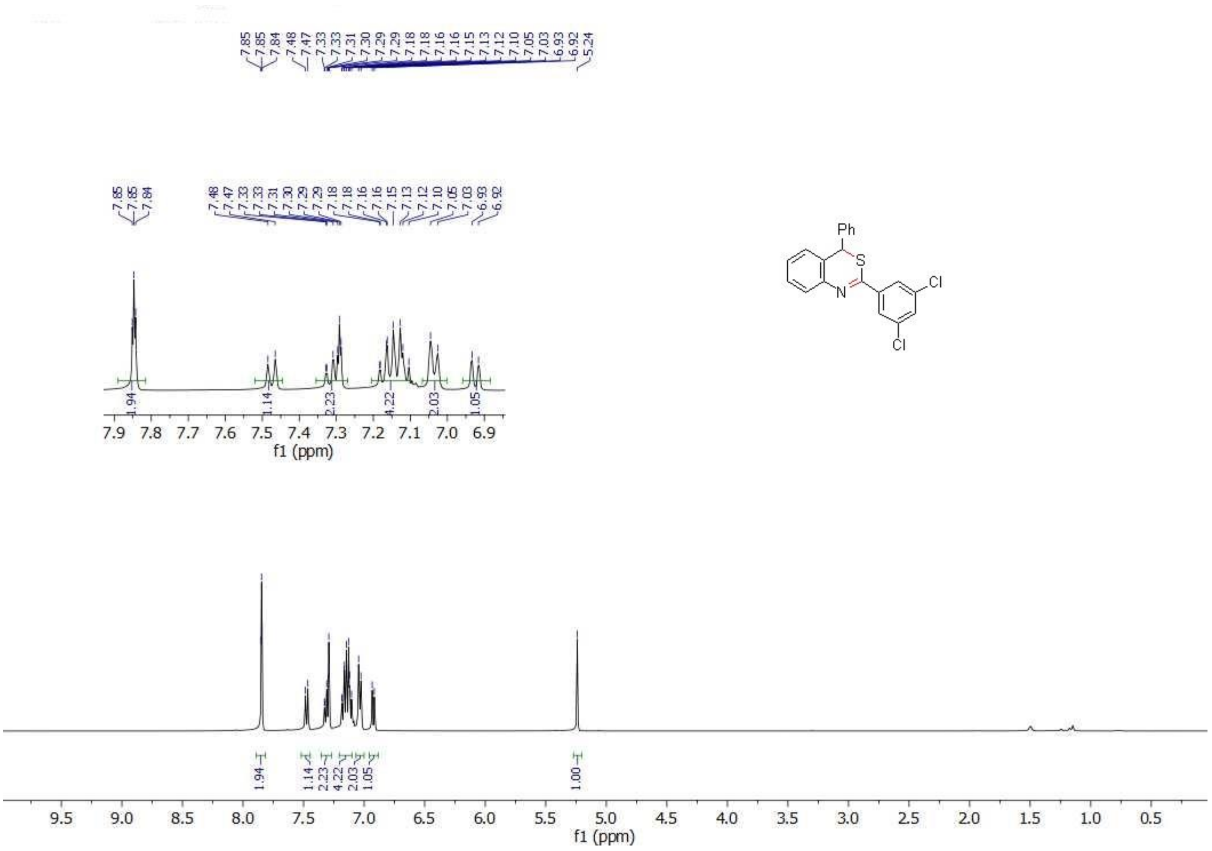


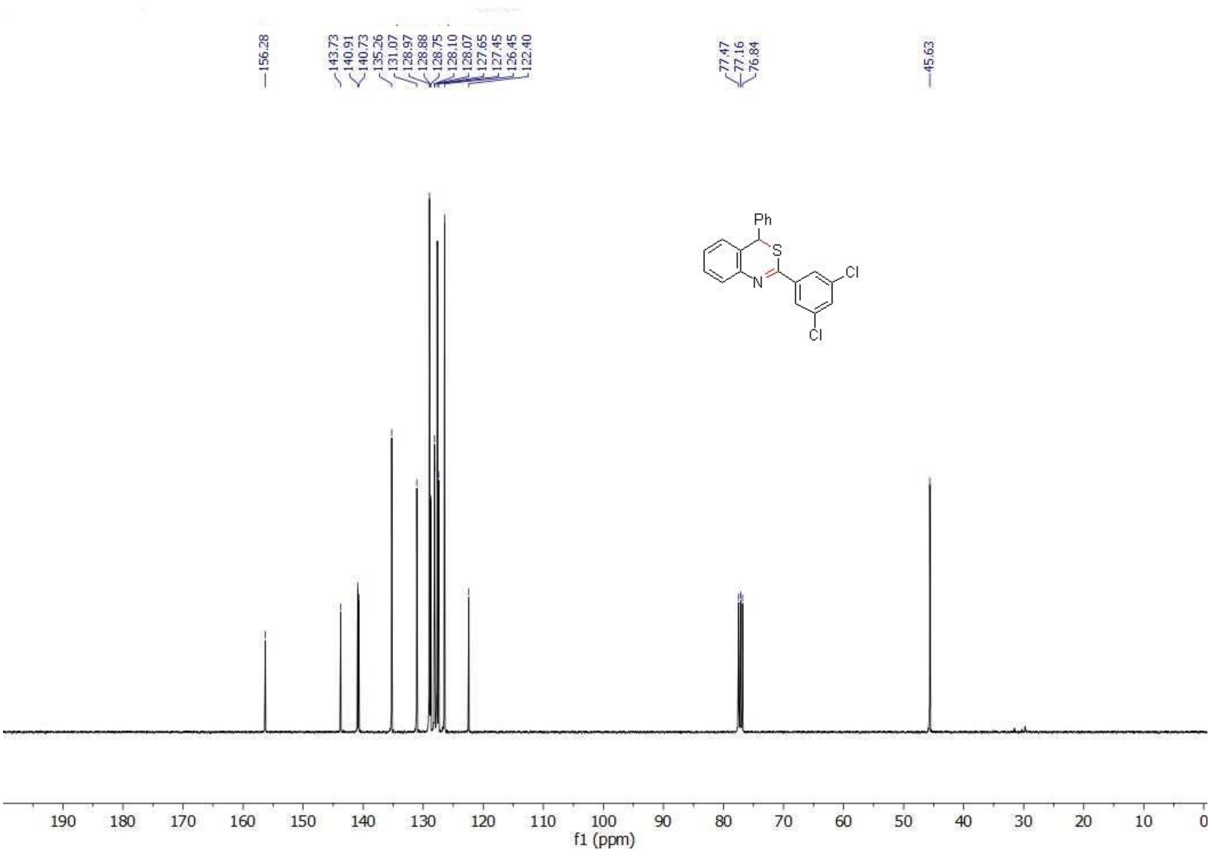
$^{1}$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^{1}$H} NMR** (100 MHz, CDCl$_3$) spectra of **5ro**:



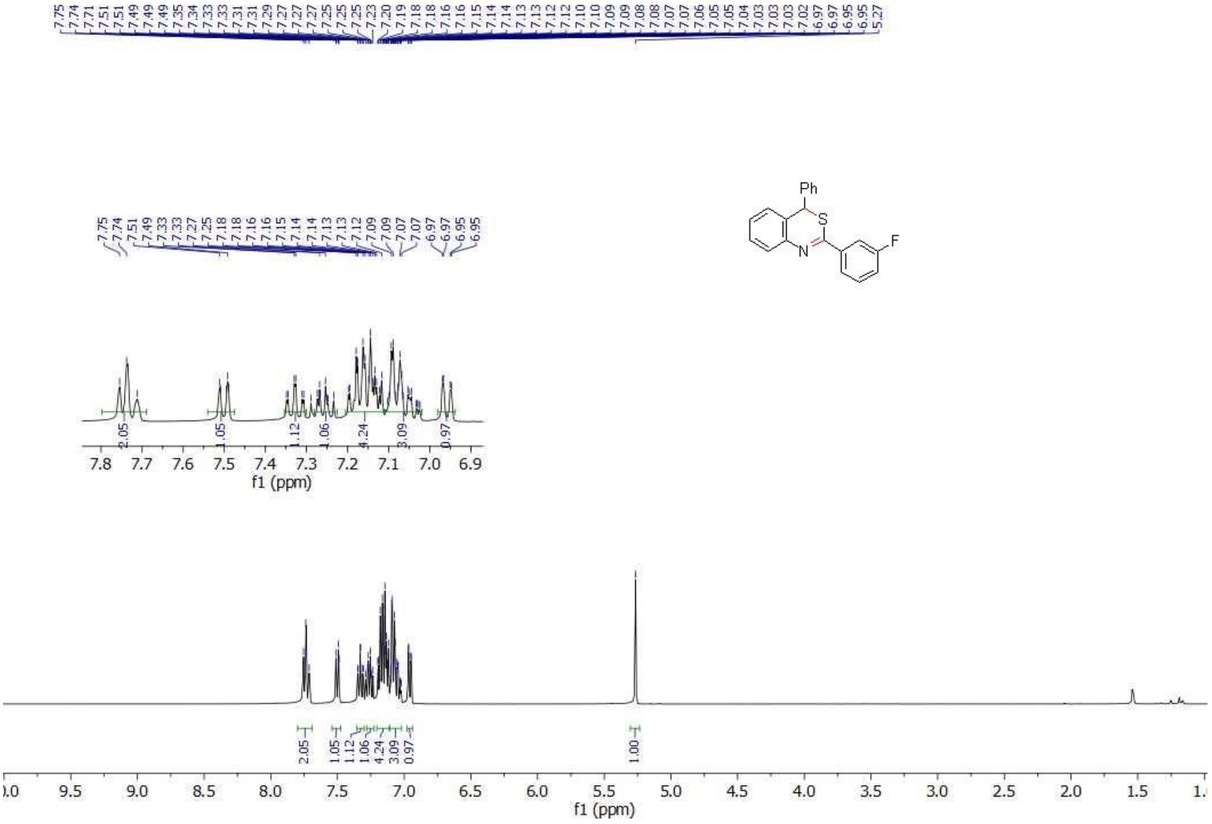


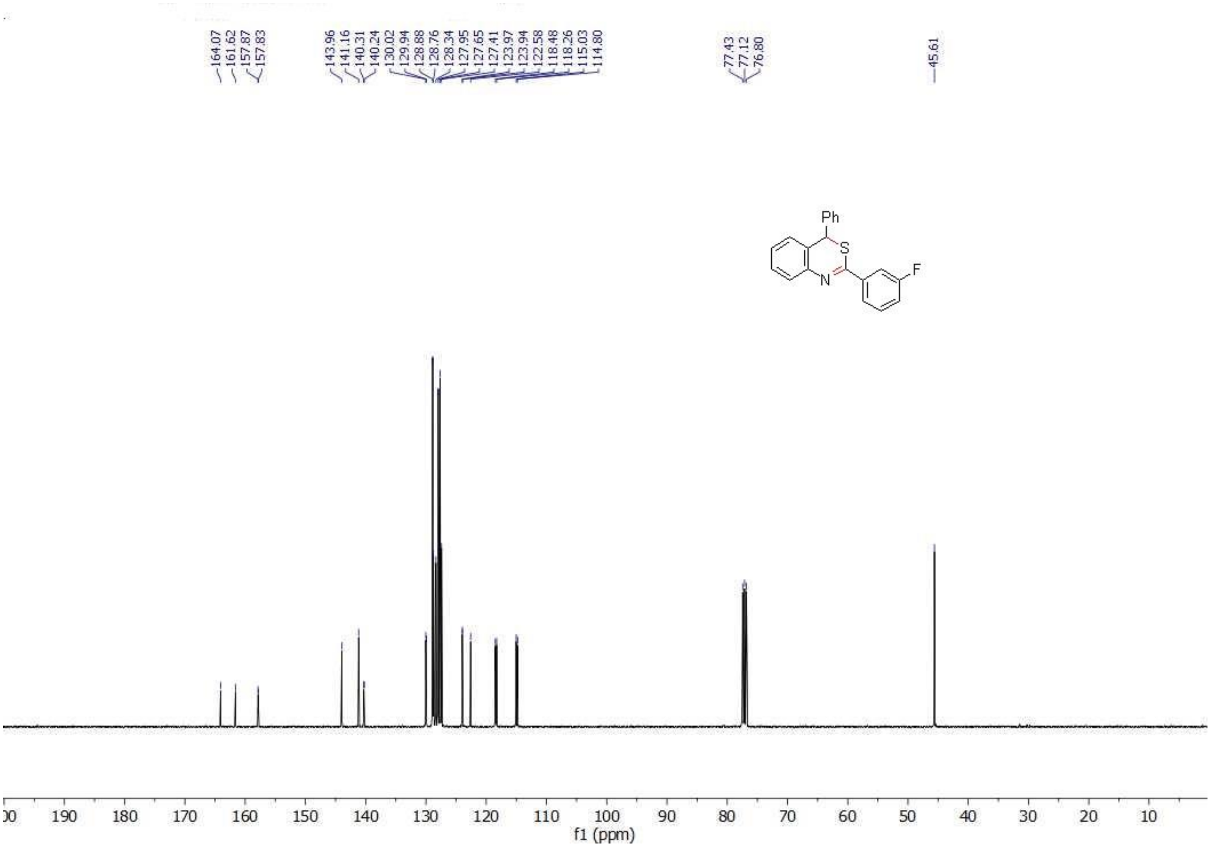
$^1$**H NMR** (400 MHz, $CDCl_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, $CDCl_3$) spectra of **5gp**:





$^1$**H NMR** (400 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **5ip**:





$^1$**H NMR** (300 MHz, CDCl$_3$) and $^{13}$**C{$^1$H} NMR** (100 MHz, CDCl$_3$) spectra of **3as**: