Supporting information

for

Copper-Catalyzed Double C-S Bond Formation for the Synthesis of 2-Acyldihydrobenzo[*b*]thiophenes and 2-Acylbenzo[*b*]thiophenes

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1. General information

All the reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra Synthesis Pvt. Ltd. and used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the reactions were carried out in temperature controlled IKA magnetic stirrers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz (100 MHz and 125 MHz for ^{13}C) instrument. ^{1}H NMR spectra were reported relative to residual TMS (δ 0 ppm) and DMSO-d_6 (δ 2.50 ppm). ^{13}C NMR spectral data were reported relative to $CDCl_3$ (δ 77.16 ppm) and DMSO-d_6 (δ 39.51 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and are corrected with benzoic acid as reference. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using dry KBr pellet. The wave numbers of recorded IR signals are quoted in cm^{-1}. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. X-ray photoelectron spectroscopy analysis was done with the Omicron ESCA Probe Spectrometer equipped with monochromatic Mg Kα 1253.6 eV.

Solvents used for extraction and column chromatography were laboratory grade and used as received. Solvents for reactions were obtained from Fischer Scientific, India Pvt. Ltd. Various acetophenones were purchased from Alfa-aesar, Sigma-Aldrich Company, Avra synthesis and Spectrochem Pvt Ltd. $Cu(acac)_2$ purchased from Sigma Aldrich and CuI from Alfa-aesar. The potassium ethyl xanthogenate was obtained from Sigma-Aldrich and used directly as received.

2. Experimental data

2.1. General procedure for synthesis of 2-acyl-2,3-dihydrobenzo[*b*]thiophene derivatives (2)

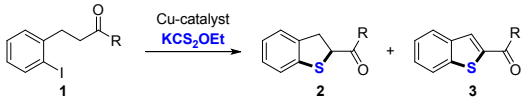
Under open atmosphere, (*E*)-2-iodoketone (1.0 mmol), potassium ethyl xanthate (2.0 mmol) and $Cu(acac)_2$ (0.1 mmol) were successively added to an oven dried reaction tube. Then, DMF (4 mL) was added and closed with glass-stopper. The reaction tube was then immersed in a 100 ºC pre-heated oil bath. Then the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was brought to room temperature; water was added and extracted with ethyl acetate (3×10 mL). Brine wash (1×20 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and silica gel column separation of crude reaction mixture using hexanes and ethyl acetate mixture (19:1) afforded the corresponding 2-acyl-2,3-dihydrobenzo[*b*]thiophenes (**2**).

2.2. General procedure for synthesis of 2-acylbenzo[*b*]thiophene derivatives (3)

In an oven dried reaction tube, (*E*)-2-iodoketone (1.0 mmol), potassium ethyl xanthate (2.0 mmol) and CuI (0.1 mmol) were successively added. Then, DMSO (4 mL) was added and closed with glass-stopper. After completion of the domino reaction, the reaction mixture was brought to room temperature and H_2SO_4 (1 equivalent) was added in the same pot. Next, it was allowed to heat with stirring at 100 ^oC until all the 2-acyldihydrobenzothiophenes consumption. The reaction mixture was monitored by TLC. Then, reaction mixture was cooled to room temperature. The water (3 mL) was added in the reaction mixture and it was extracted using ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated using rota evaporator. Eventually, the crude reaction mixture was purified using hexanes:ethyl acetate (9:1) to get pure 2-acylbenthiophenes (**3**).

Same procedure was followed for the preparation of other 2-acyl-2,3-dihydrobenzo[*b*]thiophenes and 2-acylbenzothiophenes.

2.3. Table 1. Optimization of reaction conditions



entry	Cu salt	xanthate (equiv)	solvent	temp (^oC)	time (h)	yield (%)[b] (**2a**/**3a**)
1	$Cu(OAc)_2$	1+1	DMSO	100	4	69/4[c]
2	$Cu(acac)_2$	1+1	DMSO	100	4	73/7
3	$CuBr_2$	1+1	DMSO	100	4	53/9
4	Cu(OTf)-toluene	1+1	DMSO	100	4	68/10
5	CuI	1+1	DMSO	100	4	43/18
6	CuBr	1+1	DMSO	100	5	59/6
7	$CuCl_2$	1+1	DMSO	100	4	57/8
8	$Cu(acac)_2$	1+1	DMSO	100	4	42/5[d]
9	$Cu(acac)_2$	1+1	DMSO	100	5	73/8[e]
10	$Cu(acac)_2$	1+1	DMF	100	4	82/3
11	$Cu(acac)_2$	1+1	PEG-400	100	4	76/6
12	$Cu(acac)_2$	2	DMF	100	4	87(85)/4[f]
13	$Cu(acac)_2$	3	DMF	100	4	74/5
14	$Cu(acac)_2$	2	DMF	110	3	77/8
15	$Cu(acac)_2$	2	DMF	120	2	70/8
16	-	2	DMF	100	5	0[g]

[a]Standard reaction conditions: **1a** (0.5 mmol), xanthate, Cu-catalyst (10 mol%) in 2 mL solvent. [b]Yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Trace amount **6a** was detected in TLC. [d]5 mol% of catalyst was used. [e]15 mol% of catalyst was used. [f]Isolated yield in parenthesis. [g]Only starting material remained.

The initial screening was examined with various copper salts and the copper-(II) acetylacetonate gave the highest yield of desired product **2a**. (Entries 3-7 vs 2). When 5 mol% of $Cu(acac)_2$, the yield of **2a** was decreased to 43% (entry 8). The yield of product was not changed while increasing the quantity of $Cu(acac)_2$ (entry 9). In solvent study, DMF was found to be the suitable solvent to carry out this reaction as it gave 82% yield of **2a** (entries 2 and 11 vs 10). Increase in the yield of **2a** was observed while adding 2 equivalents of xanthate at once (entry 12). Then, the temperature study revealed that 100 ^{o}C was the optimum temperature for this reaction (entries 14 and 15 vs 12). More importantly, when the reaction was carried out without catalyst, the reaction did not take place (entry 16).

2.4. Determination of reduction of copper(II)-Cu(I) using X-ray photoelectron Spectroscopy

To test our hypothesis, the black carbon was stirred at room temperature to the already reacted mixture of 1 equivalent of $Cu(acac)_2$ and 1 equivalent of xanthate at 100 ^{o}C for 6h in DMSO solvent. Then the reaction mixture was brought to room temperature. Then black carbon was added into the reaction mixture and stirred for 1 h at room temperature. The ethanol solvent (3 mL) was added in the reaction and centrifuged. The centrifuge process was repeated again using ethanol (3 mL) followed by acetone (3 mL). The black carbon containing copper was dried and used for X-ray photoelectron spectroscopy.

Figure 1a demonstrates the survey spectrum of copper, which implies the presence of the elements such as copper, oxygen and carbon. Two peaks appeared at 932.7 eV and 952.4 eV in copper core level peak-fitting spectrum are attributed by the core levels of Cu 2p3/2 and Cu 2p1/2, which clearly indicates the presence of copper as Cu(I) oxidation state in the sample (figure 1b).[1] In addition to this, the shakeup satellite peak at 943.2 eV was also appeared. If the xanthate plays as a reducing agent for Cu(II)salt, it should give the disulfide product via the self-oxidization process. Hence, a small portion in the combined organic layer was also tested for HRMS analysis to confirm the formation of disulfide in the reaction mixture. However, the characteristic peak was not observed. This might be due to the cleavage of disulfide by DMSO solvent during the course of the reaction.

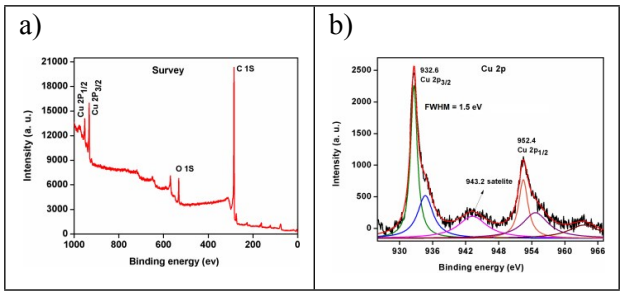


Figure 1: a) Survey and b) high resolution XPS spectrum of Cu-salt

2.5. Preparation of (*E*)-4-(2-iodophenyl)but-3-en-2-one (1)[2]

To an oven dried round bottom flask, 2-iodochalcone[3] (1 mmol), tosylhydrazone (1.1 mmol) and anhydrous potassium carbonate (1.5 mmol) in 1,4-dioxane (2 mL) were refluxed under nitrogen atmosphere for 24 h. The completion of reaction was monitored by thin layer chromatography. After completion, the reaction mixture was diluted with water (5 mL) and extracted using diethylether solvent (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of solvent, the crude reaction mixture was purified using column chromatography (**1b**): 73% yield; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14-3.21 (m, 2H), 3.26-3.33 (m, 2H), 6.91 (ddd, *J* = 8.5 Hz, 6.4 Hz, 0.8 Hz, 1H), 7.27-7.34 (m, 2H), 7.43-7.49 (m, 2H), 7.57 (tt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.83 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.96-8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3, 39.1, 77.2, 100.4, 128.2, 128.7, 128.8, 130.0, 133.3, 136.9, 139.7, 144.0, 198.9; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{15}H_{13}NaIO$:358.9883; found: 358.9893.

Same procedure was followed for the preparation of other 2'-iodoketones.

2.6. Preparation of (*O*-ethyl S-(2-(3-oxo-3-phenylpropyl)phenyl)carbonodithioate (4b)

The 2-iodochalcone (1 mmol), xanthate (1 mmol) and $Cu(OAc)_2$ (0.1 mmol) in chlobenzene (4 mL) were added and closed with stopper in an oven dried reaction tube. Then it was heated at 120 ^{o}C using the preheated oil bath for 12 h. Then, the reaction mixture was monitored by TLC. After completing the reaction, the solvent was removed under reduced pressure. Further, water (4 mL) was added into the reaction mixture and extracted using ethyl acetate (15 mL×2). The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated using rota evaporator. The crude reaction mixture was purified using hexanes:ethyl acetate (9:1) as colourless liquid. 81% yield (134 mg); R_f 0.44 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.20 (t, *J* = 8.0 Hz, 2H), 3.27 (t, *J* = 8.4 Hz, 2H), 4.59 (q, *J* = 7.2 Hz, 2H), 7.27-7.33 (m, 1H), 7.41-7.58 (m, 6H), 7.95 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 29.2, 40.1, 70.6, 127.5, 128.2 (2C), 128.8 (2C), 129.6, 130.6, 131.2, 133.3, 136.8, 137.5, 145.5, 199.1, 213.4; FTIR (KBr) 2930, 1601, 1033, 757 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{18}H_{18}NaO_2S_2$: 353.0622; found: 353.0631.

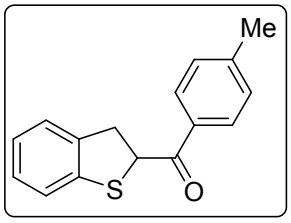
3. References

1. (a) S. Poulston, P. M. Parlett, P. Stone, M. Bowker, *Surf. Interface Anal.* 1996, **24**, 811-820. (b) H. Sun, O. A. Zelekew, X. Chen, Y. Guo, D. H. Kuo, Q. Lu, J. Lin, *RSC Adv*. 2019, **9**, 31828-31839.

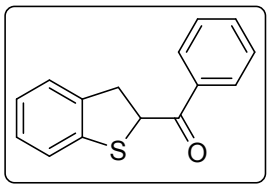
2. X. Zhou, X. Li, W. Zhang, J. Chen, *Tetrahedron Lett.* 2014, **55**, 5137-5140.

3. S. Sangeetha, G. Sekar, *Org. Lett.* 2017, **19**, 1670-1673.

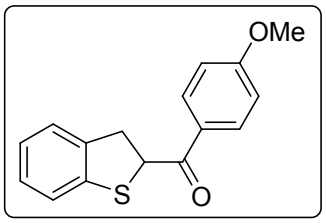
4. ^{1}H and ^{13}C NMR data for all compounds



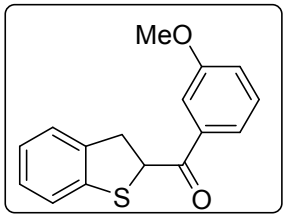
(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(*p*-tolyl)methanone (2a): 85% yield (108 mg); Off white solid; mp 92-94 ^{o}C; R_f 0.45 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 2.41 (s, 3H), 3.44 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.98 (dd, *J* = 16.0 Hz, 4.4 Hz, 1H), 5.19 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.02-7.14 (m, 3H), 7.23-7.29 (m, 3H), 7.84 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 36.4, 50.1, 121.8, 124.8, 125.1, 127.6, 128.9 (2C), 129.6 (2C), 132.6, 138.7, 139.4, 144.5, 193.6; FTIR (KBr) 3055, 2987, 1678, 1264, 747 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^{+}$calcd for $C_{16}H_{15}OS$: 255.0843; found: 255.0844.



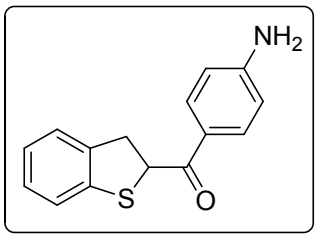
2,3-Dihydrobenzo[*b*]thiophen-2-yl(phenyl)methanone (2b): 82% yield (99 mg); Off white solid; mp 88-92 ^{o}C ; R_f 0.47 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.46 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.98 (dd, *J* = 16.0 Hz, 4.4 Hz, 1H), 5.21 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.01- 7.16 (m, 3H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.5, 50.1, 121.8, 124.9, 125.2, 127.6, 128.8 (2C), 128.9 (2C), 133.5, 135.1, 138.5, 139.4, 193.8; FTIR (KBr) 3056, 2985, 1685, 1265,743 cm^{-1}; HRMS (*m*/*z*): $[M+H]^{+}$calcd for $C_{15}H_{13}OS$:241.0687; found: 241.0683.



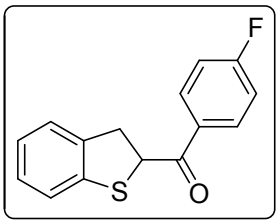
(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(4-methoxyphenyl)methanone (2c): 81% yield (109 mg); Off white solid; mp 106-108 ^{o}C; R_f 0.42 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.44 (dd, *J* = 16.0 Hz, 8.8 Hz, 1H), 3.88 (s, 3H), 3.99 (dd, *J* = 16.0 Hz, 5.2 Hz, 1H), 5.20 (dd, *J* = 8.4 Hz, 4.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.04-7.11 (m, 3H), 7.24-7.26 (m, 1H), 7.94 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.6, 50.1, 55.7, 114.1 (2C), 121.8, 124.8, 125.1, 127.6, 128.1, 131.1 (2C), 138.8, 139.5, 163.9, 192.8; FTIR (KBr) 3055, 2986, 1675, 1264, 749 cm^{-1}; HRMS (*m*/*z*): $[M+H]^{+}$calcd for $C_{16}H_{15}O_2S$: 271.0792; found: 271.0792.



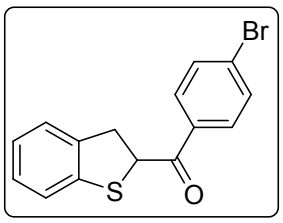
(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(2-methoxyphenyl)methanone (2d): 72% yield (97 mg); Off white solid; mp 94-96 ^{o}C; R_f 0.40 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H) 3.83 (s, 3H), 3.97 (dd, *J* = 15.6 Hz, 4.4 Hz, 1H), 5.19 (dd, *J* = 8.8 Hz, 4.4 Hz, 1H), 7.03-7.14 (m, 4H), 7.23-7.28 (m, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.46-7.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.5, 50.2, 55.5, 113.1, 120.1, 121.1, 121.9, 124.8, 125.1, 127.6, 129.8, 136.6, 138.5, 139.3, 160.1, 193.6; FTIR (KBr) 3055, 2986, 1684, 1424, 1265, 748 cm^{-1}; HRMS (*m*/*z*): $[M+H]^{+}$calcd for $C_{16}H_{15}O_2S$: 271.0792; found: 271.0794.



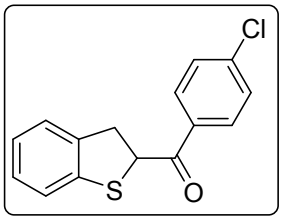
(4-Aminophenyl)(2,3-dihydrobenzo[*b*]thiophen-2-yl)methanone (2e): 64% yield (82 mg); Pale yellow solid; mp 150-152 ^{o}C; R_f 0.45 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.99 (dd, *J* = 15.6 Hz, 5.2 Hz, 1H), 4.17 (br s, 2H), 5.20 (dd, *J* = 8.4 Hz, 5.6 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 7.02-7.18 (m, 1H), 7.10 (d, *J* = 4.0 Hz, 2H), 7.23 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.7, 50.1, 114.0 (2C), 121.7, 124.8, 125.0, 127.5, 130.7, 131.3 (2C), 139.1, 139.6, 151.6, 192.6; FTIR (KBr) 3356, 2922, 1647, 1589, 1228, 778 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{14}NOS$: 256.0791; found: 256.0791.



(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(4-fluorophenyl)methanone (2f): 70% yield (90 mg); Off white solid; mp 119-120 ^{o}C; R_f 0.45 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.98 (dd, *J* = 15.6 Hz, 4.4 Hz, 1H), 5.17 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.06-7.19 (m, 5H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.5, 50.1, 116.1 (d, *J* = 21.8 Hz), 121.9, 124.9, 125.3, 127.7 (2C), 131.4 (d, *J* = 9.4 Hz), 138.4, 139.3, 167.8 (d, *J* = 281.3 Hz), 192.4; FTIR (KBr) 3065, 2922, 1679, 1218, 1019, 826 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{12}FOS$:259.0589; found: 259.0586.

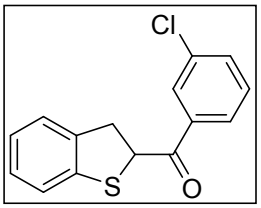


(4-Bromophenyl)(2,3-dihydrobenzo[*b*]thiophen-2-yl)methanone (2g): 68% yield (109 mg); Off white solid; mp 95-97 ^{o}C; R_f 0.52 (15 % ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.46 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.97 (dd, *J* = 16.0 Hz, 3.6 Hz, 1H), 5.13 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.04-7.16 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.4, 50.0, 121.9, 124.9, 125.3, 127.7, 128.8, 130.3 (2C), 132.2 (2C), 134.0, 138.3, 139.2, 192.8; FTIR (KBr) 3055, 2986, 1685, 1265, 744; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{12}OSBr$:318.9792; found: 318.9780.

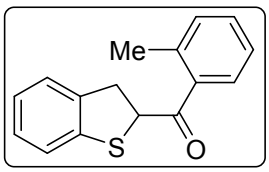


(4-Chlorophenyl)(2,3-dihydrobenzo[*b*]thiophen-2-yl)methanone (2h): 72% yield (99 mg); Off white solid; mp 114-116 ^{o}C; R_f 0.54 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.97 (dd, *J* = 16.0 Hz, 3.2 Hz, 1H), 5.15 (dd, *J* = 8.4 Hz, 3.2 Hz, 1H), 7.04-7.16 (m, 3H), 7.23-7.29 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.4, 50.1, 121.9, 124.9, 125.3, 127.7, 129.2

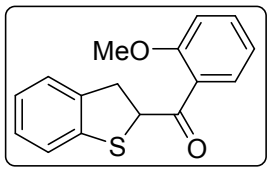
(2C), 130.2 (2C), 133.5, 138.3, 139.3, 140.0, 192.6; FTIR (KBr) 3054, 2987, 1683, 1264, 749 cm^{-1}; HRMS (*m*/*z*):[M+H]$^+$calcd for $C_{15}H_{12}OSCl$: 275.0297; found: 275.0289.



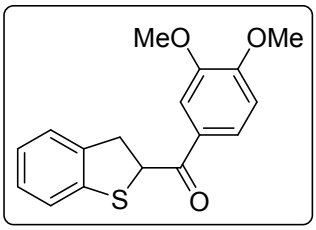
(3-Chlorophenyl)(2,3-dihydrobenzo[*b*]thiophen-2-yl)methanone (2i): 66% yield (91 mg); Off white solid; mp 119-121 ^oC; R_f 0.51 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.47 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.92 (dd, *J* = 15.6 Hz, 3.2 Hz, 1H), 5.21 (dd, *J* = 8.4 Hz, 3.2 Hz, 1H), 7.03-7.14 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.30-7.34 (m, 1H), 7.38-7.41 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.5, 54.5, 122.0, 124.8, 125.2, 127.0, 127.7, 130.3, 130.5, 131.3, 132.0, 137.6, 138.0, 139.2, 197.3; FTIR (KBr) 3055, 2986, 1685, 1265, 744 cm^{-1}; HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{15}H_{12}OSCl$:275.0297; found: 275.0289.



(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(*o*-tolyl)methanone (2j): 82% yield (104 mg); Off white solid; mp 84-86 ^oC; R_f 0.54 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 3.44 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.94 (dd, *J* = 15.6 Hz, 4.4 Hz, 1H), 5.17 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.03-7.14 (m, 3H), 7.23-7.29 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 36.5, 53.0, 121.8, 124.9, 125.1, 125.8, 127.6, 128.0, 131.7, 132.2, 136.5, 138.5, 139.4, 139.6, 197.3; FTIR (KBr) 3945, 2985, 1687, 1428, 746; HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{16}H_{15}OS$: 255.0843; found: 255.0840.

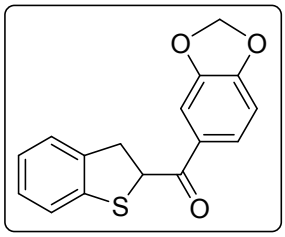


(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(2-methoxyphenyl)methanone (2k): 88% yield (119 mg); Off white solid; mp 72-74 ^oC; R_f 0.45 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.39 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.91-3.97 (m, 4H), 5.25 (d, *J* = 8.4 Hz, 1H), 6.96-7.07 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.1, 55.7, 55.8, 111.6, 121.2, 121.9, 124.6, 124.8, 125.3, 127.4, 130.4, 134.3, 138.5, 140.3, 158.7, 195.0; FTIR (KBr) 3055, 2986, 1669, 1265, 747 cm^{-1}; HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{16}H_{15}OS$: 271.0792; found: 271.0790.

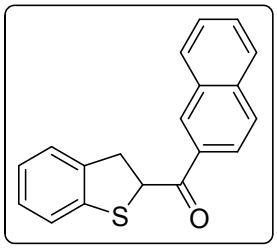


(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(3,4-dimethoxyphenyl)methanone (2l): 78% yield (117 mg); Off white solid; mp 124-126 ^oC; R_f 0.43 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.92 (s, 3H), 3.94-4.03 (m, 4H), 5.23 (dd, *J* = 8.0 Hz, 5.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.00-7.20 (m, 3H), 7.22-7.29 (m, 1H), 7.51-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.2, 50.0, 56.1, 56.2, 110.2, 111.0, 121.7, 123.1, 124.8, 125.1, 127.6, 128.3, 138.8, 139.4, 149.4,

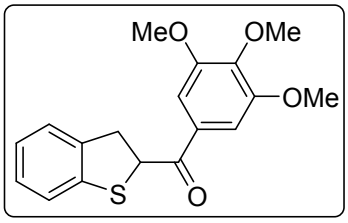
153.7, 192.9; FTIR (KBr) 3064, 3003, 2934, 1629, 1267, 765 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{17}H_{14}O_3NaS$:321.0561; found: 321.0590.



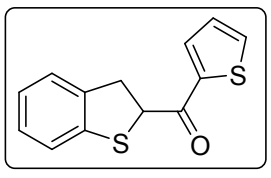
Benzo[*d*][1,3]dioxol-5-yl(2,3-dihydrobenzo[*b*]thiophen-2-yl)methanone (2m): 76% yield (108 mg); Off white solid; mp 104-106 ^oC; R_f 0.49 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.97 (dd, *J* = 15.6 Hz, 4.8 Hz, 1H), 5.15 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 6.05 (s, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 7.05 -7.10 (m, 3H), 7.24-7.26 (m, 1H), 7.44 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.7, 50.1, 102.1, 108.2, 108.6, 121.8, 124.8, 125.0, 125.1, 127.6, 130.0, 138.7, 139.4, 148.5, 152.3, 192.3; FTIR (KBr) 3057, 2986, 1676, 1262, 743 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{13}O_3S$:285.0585; found: 285.0584.



(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(naphthalen-2-yl)methanone (2n): 69 % yield (100 mg); Off white solid; mp 108-110 ^oC; R_f 0.51 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.50 (dd, *J* = 15.8 Hz, 8.8 Hz, 1H), 4.04 (dd, *J* = 16.0 Hz, 4.4 Hz, 1H), 5.38 (dd, *J* = 8.4 Hz, 4.8 Hz, 1H), 7.02-7.17 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.53-7.63 (m, 2H), 7.87-8.02 (m, 4H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.6, 50.3, 121.8, 124.4, 124.9, 125.2, 127.0, 127.7, 127.9, 128.7, 128.8, 129.8, 130.4, 132.5, 132.6, 135.9, 138.6, 139.4, 193.9; FTIR (KBr) 3056, 2986, 1681, 1266, 748 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{19}H_{15}OS$:291.0843; found: 291.0839.

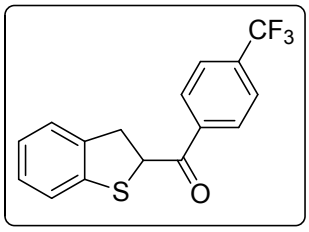


(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(3,4,5-trimethoxyphenyl)methanone (2o): 62% yield (102 mg); Off white solid; mp 99-101 ^oC; R_f 0.42 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.46 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.91 (s, 6H), 3.93 (s, 3H), 3.99 (dd, *J* = 16.0 Hz, 4.8 Hz, 1H), 5.21 (dd, *J* = 8.4 Hz, 5.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.19-7.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.6, 50.2, 56.4 (2C), 61.1, 106.3 (2C), 121.8, 124.9, 125.2, 127.7, 130.3, 138.6, 139.3, 143.1, 153.3 (2C), 192.9; FTIR (KBr) 3058, 2986, 1663, 1265, 745 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{18}H_{19}O_4S$: 331.1004; found: 331.1001.

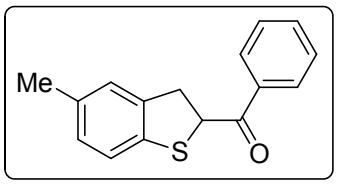


(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (2p): 75 % yield (92 mg); Off white solid; mp 110-112 ^oC; R_f 0.48 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.46 (dd, *J* = 16.0 Hz, 8.8 Hz, 1H), 3.96 (dd, *J* = 16.0 Hz, 4.8 Hz, 1H), 5.09 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 7.04-7.10 (m, 1H), 7.11-7.14 (m, 2H), 7.16 (t, *J* = 4.4 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* =

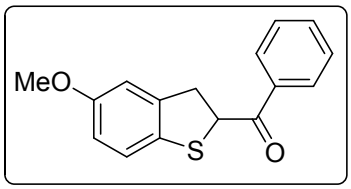
4.8 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.8, 51.5, 121.8, 124.8, 125.2, 127.7, 128.4, 132.5, 134.4, 138.7, 139.0, 142.3, 187.7; FTIR (KBr) 3055, 2986, 1679, 1265, 743 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{13}H_{11}OS_2$: 247.0251; found: 247.0250.



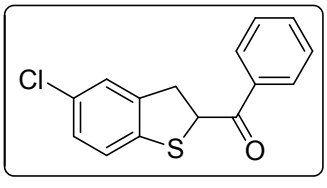
(2,3-Dihydrobenzo[*b*]thiophen-2-yl)(4-(trifluoromethyl)phenyl)methanone (2q): 57% yield (88 mg); Off white solid; mp 110-112 °C; R_f 0.51 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.51 (dd, *J* = 15.8 Hz, 8.5 Hz, 1H), 3.99 (dd, *J* = 15.5 Hz, 3.5 Hz, 1H), 5.17 (dd, *J* = 8.5 Hz, 3.5 Hz, 1H), 7.07-7.16 (m, 3H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.3, 50.1, 122.0, 123.7 (q, *J* = 271.1 Hz), 125.0, 125.5, 126.0 (q, *J* = 3.6 Hz), 127.8 (2C), 129.1 (2C), 134.8 (q, *J* = 32.6 Hz), 137.9, 138.0, 139.2, 192.5; FTIR (KBr) 2953, 2921, 1685, 1132, 1074, 863 cm^{-1}. HRMS (*m*/*z*): $[M+NH_4]^+$calcd for $C_{16}H_{15}F_3NOS$:326.0772; found: 326.0795.



(5-Methyl-2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2r): 81% yield (88 mg); Off white solid; mp 122-124 °C; R_f 0.53 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.42 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.92 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 5.18 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 36.4, 50.2, 121.6, 125.7, 128.4, 128.7 (2C), 128.8 (2C), 133.5, 134.9, 135.0, 135.1, 139.5, 193.8; FTIR (KBr) 3056, 2917, 1680, 1210, 1051, 852, 717 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{15}OS$: 255.0854; found: 255.0846.

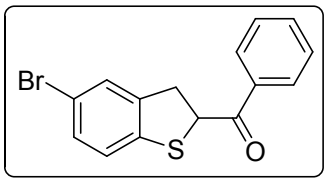


(5-Methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2s): 83% yield (112 mg); Off white solid; mp 107-109 °C; R_f 0.44 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.43 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.77 (s, 3H), 3.92 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 5.20 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 6.68 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 6.86 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.7, 50.5, 55.6, 111.2, 113.5, 122.3, 128.7 (2C), 128.9 (2C), 129.3, 133.5, 135.1, 141.1, 158.2, 193.7; FTIR (KBr) 3059, 2998, 1681, 1248, 1027, 852 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{15}O_2S$:271.0785; found: 271.0787.

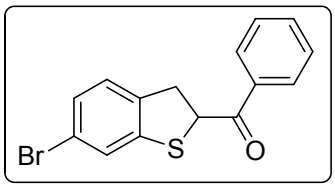


(5-Chloro-2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2t): 67% yield (92 mg); Off white solid; mp 124-125 °C; R_f0.49 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (dd, *J* =

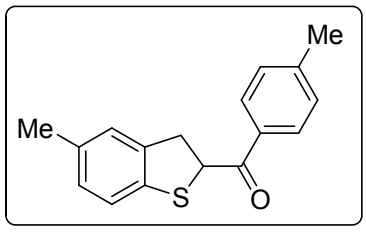
16.0 Hz, 8.8 Hz, 1H), 3.96 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 5.23 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.23-7.27 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.4, 50.4, 122.7, 125.1, 127.7, 128.8 (2C), 129.0 (2C), 131.0, 133.7, 134.9, 137.1, 141.4, 193.5; FTIR (KBr) 3058, 2967, 1678, 1213, 871, 725 cm^{-1}. HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{15}H_{12}ClOS$:275.0293; found: 275.0289.



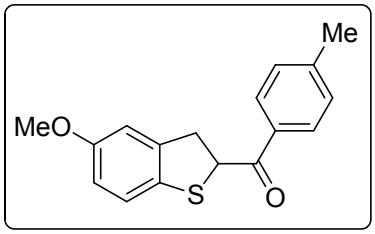
(5-Bromo-2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2u): 73% yield (116 mg); Off white solid; mp 127-129 °C; R_f 0.51 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.96 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 5.21 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.39 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.3, 50.4, 118.6, 123.1, 128.0, 128.8 (2C), 129.0 (2C), 130.6, 133.7, 134.9, 137.8, 141.8, 193.4; FTIR (KBr) 3058, 2923, 1680, 1215, 1063, 867 cm^{-1}. HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{15}H_{12}BrOS$:318.9787; found: 318.9788.



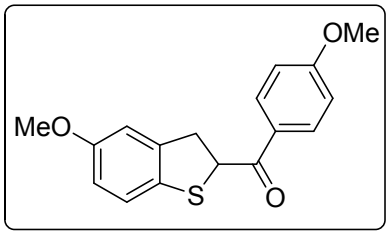
(6-Bromo-2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2v): 77% yield (123 mg); Off white solid; mp 129-131 °C; R_f 0.46 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.91 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 5.21 (dd, *J* = 8.8 Hz, 4.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.14-7.23 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.0, 50.5, 121.0, 124.6, 126.0, 128.2, 128.7 (2C), 128.9 (2C), 133.7, 134.9, 138.5, 141.0, 193.5; FTIR (KBr) 2923, 2856, 1672, 1254, 1073, 850, 728 cm^{-1}. HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{15}H_{12}BrOS$:318.9772; found: 318.9780.



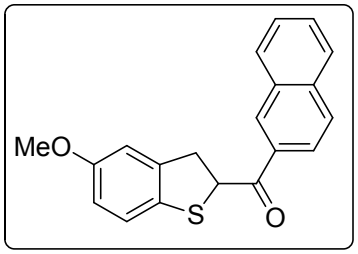
(5-Methyl-2,3-dihydrobenzo[*b*]thiophen-2-yl)(*p*-tolyl)methanone (2w): 84% yield (100 mg); Off white solid; mp 155-157 °C; R_f 0.49 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.42 (s, 3H), 3.41 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.93 (dd, *J* = 15.6 Hz, 4.0 Hz, 1H), 5.18 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 21.8, 36.4, 50.3, 121.5, 125.7, 128.4, 128.9 (2C), 129.6 (2C), 132.7, 134.9, 135.1, 139.6, 144.4, 193.7; FTIR (KBr) 2966, 2907, 1666, 1216, 800 cm^{-1}. HRMS (*m*/*z*): [M+H]$^+$calcd for $C_{17}H_{17}OS$:269.1009; found: 269.1003.



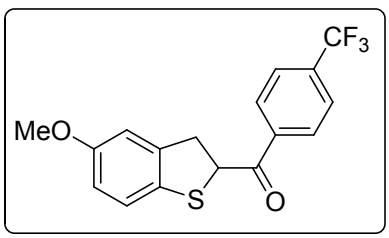
(5-methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(*p*-tolyl)methanone (2x): 85% yield (120 mg); Off white solid; mp 134-136 °C; R_f 0.42 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 3.41 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.77 (s, 3H), 3.92 (dd, *J* = 15.6 Hz, 3.6 Hz, 1H), 5.19 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 36.7, 50.5, 55.6, 111.1, 113.4, 122.3, 128.8 (2C), 129.4, 129.6 (2C), 132.6, 141.1, 144.4, 158.2, 193.5; FTIR (KBr) 2930, 2836, 1666, 1028, 846 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{17}H_{17}O_2S$: 285.0943; found: 285.0944.



(5-Methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(4-methoxyphenyl)methanone (2y): 80% yield (120 mg); Off white solid; mp 117-119 °C; R_f 0.46 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.40 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 3.77 (s, 3H), 3.87 (s, 3H), 3.93 (dd, *J* = 18.0 Hz, 4.4 Hz, 1H), 5.19 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 6.68 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.86 (s, 1H), 6.96 (t, *J* = 9.2 Hz, 3H), 7.93 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.9, 50.5, 55.7 (2C), 111.2, 113.4, 114.1 (2C), 122.2, 128.1,129.5, 131.0 (2C), 141.2, 158.2, 163.9, 192.7; FTIR (KBr) 3002, 2937, 1671, 1250, 847 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{17}H_{17}O_3S$:301.0891; found: 301.0892.

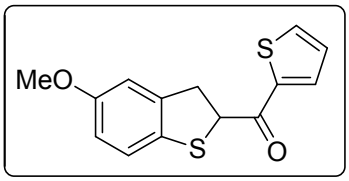


(5-Methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(naphthalen-2-yl)methanone (2z): 65% yield (104 mg); Off white solid; mp 128-130 °C; R_f 0.43 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (dd, *J* = 15.6 Hz, 8.0 Hz, 1H), 3.77 (s, 3H), 3.98 (dd, *J* = 16.0 Hz, 3.6 Hz, 1H), 5.36 (dd, *J* = 8.0 Hz, 4.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.48-7.68 (m, 2H), 7.88 (t, *J* = 9.6 Hz, 2H), 7.98 (dd, *J* = 17.6 Hz, 8.4 Hz, 2H), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.8, 50.6, 55.9, 111.2, 113.5, 122.3, 124.4, 127.0, 127.9, 128.7, 128.8, 129.4, 129.8, 130.4, 132.5, 132.6, 135.8, 141.1, 158.2, 193.7; FTIR (KBr) 3055, 2999, 1673, 1465, 1250, 803, 745 cm^{-1}. HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{20}H_{17}O_2S$:321.0944; found: 321.0945.

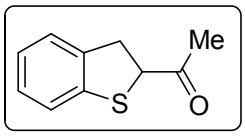


(5-Methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(4-(trifluoromethyl)phenyl)methanone (2aa): 63 % yield (106 mg); Off white solid; mp 131-133 °C; R_f 0.45 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.47 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 3.78 (s, 3H), 3.92 (dd, *J* = 16.0 Hz, 3.5 Hz, 1H), 5.15 (dd, *J* = 8.0 Hz, 3.5 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 36.5, 50.4, 55.6, 111.2, 113.2,

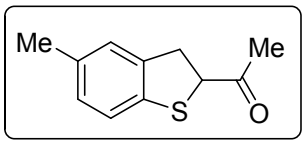
122.5, 123.7 (q, J = 270.8 Hz), 125.9 (q, J = 3.6 Hz), 128.6 (2C), 129.1 (2C), 134.6 (q, J = 32.6 Hz), 138.0, 140.9, 158.4, 192.3; FTIR (KBr) 2922, 2845, 1685, 1132, 1062, 862 cm^{-1}. HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{14}F_3O_2S$:339.0661; found: 339.0662.



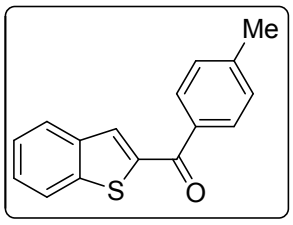
(5-Methoxy-2,3-dihydrobenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (2ab): 84% yield (115 mg); Off white solid; mp 92-94 ^oC; R_f 0.46 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.42 (dd, J = 16.0 Hz, 8.4 Hz, 1H), 3.77 (s, 3H), 3.89 (dd, J = 16.0 Hz, 4.4 Hz, 1H), 5.07 (dd, J = 8.0 Hz, 4.4 Hz, 1H), 6.69 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 4.0 Hz, 1H), 7.69 (dd, J = 16.0 Hz, 4.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.0, 51.8, 55.7, 111.2, 113.5, 122.2, 128.4, 129.4, 132.5, 134.3, 140.7, 142.3, 158.2, 187.7; FTIR (KBr) 3091, 2997, 1655, 1240, 1022, 852, 723 cm^{-1}. HRMS (m/z): $[M+H]^+$calcd for $C_{14}H_{13}O_2S_2$:277.0363; found: 277.0358.



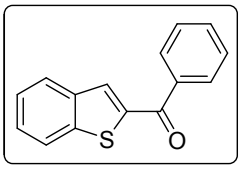
(1-(2,3-Dihydrobenzo[*b*]thiophen-2-yl)ethanone (2ac): 81% yield (72 mg); Colorless liquid; R_f 0.56 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.19 (s, 3H), 3.28 (dd, J = 16.0 Hz, 8.8 Hz, 1H), 3.61 (dd, J = 16.0 Hz, 3.6 Hz, 1H), 4.24 (dd, J = 8.8 Hz, 3.6 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 7.02-7.14 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.9, 36.7, 55.8, 122.0, 124.8, 125.1, 127.7, 138.5, 138.8, 203.4; FTIR (KBr) 3059, 2960, 1709, 1274, 744 cm^{-1}. HRMS (m/z): $[M+H]^+$calcd for $C_{10}H_{11}OS$:178.9542; found: 178.9543.



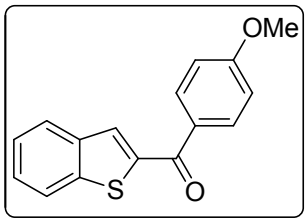
(1-(5-Methyl-2,3-dihydrobenzo[*b*]thiophen-2-yl)ethanone (2ad): 78% yield (75 mg); Colorless liquid; R_f 0.49 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 2.28 (s, 3H), 3.33 (dd, J = 15.6 Hz, 8.4 Hz, 1H), 3.63 (dd, J = 15.6 Hz, 3.2 Hz, 1H), 4.30 (dd, J = 8.4 Hz, 3.2 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.01-7.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 26.9, 36.7, 56.0, 121.7, 125.7, 128.5, 134.9, 134.9, 139.0, 203.6; FTIR (KBr) 3010, 2918, 1709, 1159, 807 cm^{-1}. HRMS (m/z): $[M+H]^+$calcd for $C_{11}H_{13}OS$:193.0644; found: 193.0660.



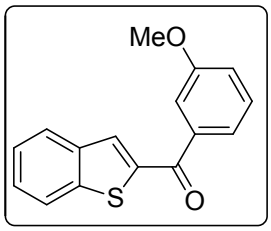
(Benzo[*b*]thiophen-2-yl(*p*-tolyl)methanone (3a): 90% yield (113 mg); ^1H NMR ($CDCl_3$, 400 MHz,) δ 2.46 (s, 3H), 7.33 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.80-7.94 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 123.0, 125.1, 126.1, 127.4, 129.3 (2C), 129.6 (2C), 131.9, 135.3, 139.2, 142.7, 143.5 (2C), 189.4; HRMS (m/z): $[M+H]^+$calcd for $C_{16}H_{13}OS$:253.0680; found: 253.0681.



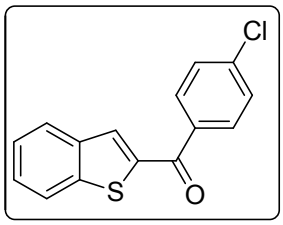
(Benzo[*b*]thiophen-2-yl(phenyl)methanone (3b): 89% yield (106 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.41 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.82-7.89 (m, 2H), 7.92 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.0, 125.2, 126.2, 127.6, 128.7, 129.4, 132.4 (2C), 132.6 (2C), 138.0, 139.2, 142.8, 143.2, 189.8; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{11}OS$: 239.0527; found: 239.0526.



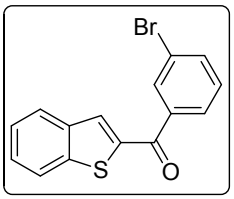
(Benzo[*b*]thiophen-2-yl(4-methoxyphenyl)methanone (3c): 92% yield (123 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.91 (s, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.82-7.93 (m, 3H), 7.96 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 114.0 (2C), 123.0, 125.1, 126.0, 127.3, 130.6, 131.3, 131.9 (2C), 139.2, 142.5, 143.5, 163.5, 188.3; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{13}O_2S$: 269.0633; found: 269.0632.



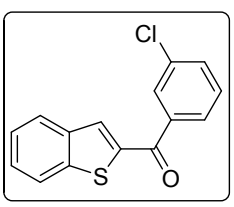
(Benzo[*b*]thiophen-2-yl(3-methoxyphenyl)methanone (3d): 93% yield (125 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.87 (s, 3H), 7.15 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.38-7.51 (m, 5H), 7.83-7.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 114.0, 118.8, 121.9, 123.0, 125.1, 126.2, 127.6, 129.6, 132.4, 139.1, 139.2, 142.8, 143.1, 159.8, 189.5; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{13}O_2S$: 269.0640; found: 269.0635.



(Benzo[*b*]thiophen-2-yl(4-chlorophenyl)methanone (3e): 82% yield (113 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.43 (t, *J* = 7.6 Hz, 1H), 7.47-7.56 (m, 3H), 7.80-7.97 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.1, 125.3, 126.3, 127.8, 129.0 (2C), 130.8 (2C), 132.3, 136.3, 139.1 (2C), 142.8, 142.9, 188.5; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{15}H_9NaClOS$: 294.9947; found: 294.9951.

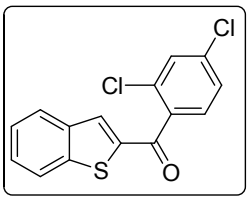


(Benzo[*b*]thiophen-2-yl(3-bromophenyl)methanone (3f): 82% yield (131 mg); White solid; mp 80-82 ^{o}C; R_f 0.52 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.43 (q, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.79-7.84 (m, 2H), 7.89 (dd, *J* = 8.2 Hz, 3.6 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 123.0, 125.3, 126.3, 127.9 (2C), 130.2, 132.1, 132.6, 135.4, 139.0, 139.7, 142.5, 142.9, 188.1; FTIR (KBr) 2938, 2922, 1680, 1218, 743 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{10}BrOS$: 316.9633; found: 316.9632.

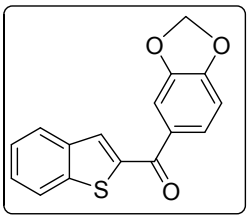


(Benzo[*b*]thiophen-2-yl(3-chlorophenyl)methanone (3g): 80% yield (109 mg); White solid; mp 84-86 ^{o}C; R_f 0.47 (15% ethyl acetate in hexanes); ^{1}H

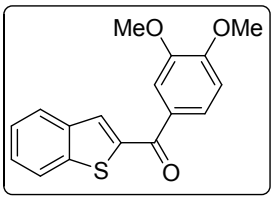
NMR ($CDCl_3$, 400 MHz,) δ 7.36-7.41 (m, 2H), 7.44-7.53 (m, 4H), 7.61 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.2, 125.3, 126.4, 126.7, 128.0, 129.1, 130.4, 131.4, 131.5, 133.7, 138.1, 139.0, 143.2, 143.5, 188.8; FTIR (KBr) 3005, 2922, 2819, 1672, 1285, 762 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{10}ClOS$: 273.0134; found: 273.0135.



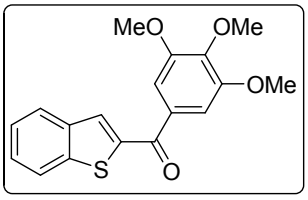
(Benzo[*b*]thiophen-2-yl(2,4-dichlorophenyl)methanone (3h): 76% yield (117 mg); White solid; mp 92-94 °C; R_f 0.45 (15% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz,) δ 7.38-7.54 (m, 5H), 7.62 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.2, 125.4, 126.5, 127.2, 128.2, 130.1, 130.4, 132.6, 133.7, 136.5, 137.1, 139.0, 142.9, 143.6, 187.8; FTIR (KBr) 3005, 2932, 2837, 1681, 1245, 727 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_9Cl_2OS$: 306.9740; found: 306.9743.



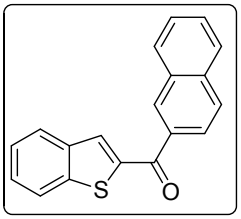
(Benzo[*b*]thiophen-2-yl(benzo[*d*][1,3]dioxol-5-yl)methanone (3i): 86% yield (121 mg); ^1H NMR ($CDCl_3$, 400 MHz,) δ 6.09 (s, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.39-7.51 (m, 3H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.82-7.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 102.1, 108.1, 109.6, 123.0, 125.2, 125.9, 126.1, 127.4, 131.4, 132.2, 139.1, 142.6, 143.2, 148.2, 151.8, 187.9; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{11}O_3S$:283.0432; found: 283.0428.



(Benzo[*b*]thiophen-2-yl(3,4-dimethoxyphenyl)methanone (3j): 90% yield (134 mg); ^1H NMR ($CDCl_3$, 400 MHz,) δ 3.97 (s, 3H), 3.99 (s, 3H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.40-7.54 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.83-7.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.2, 56.3, 110.1, 111.9, 122.9, 124.3, 125.1, 126.0, 127.3, 130.6, 131.3, 139.1, 142.5, 143.2, 149.3, 153.2, 188.2; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{17}H_{14}NaO_3S$: 321.0547; found: 321.0552.

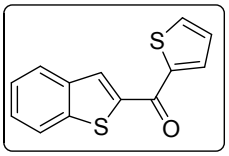


(Benzo[*b*]thiophen-2-yl(3,4,5-trimethoxyphenyl)methanone (3k): 92% yield (151 mg); ^1H NMR ($CDCl_3$, 400 MHz,) δ 3.93 (s, 6H), 3.96 (s, 3H), 7.20 (s, 2H), 7.39-7.46 (m, 1H), 7.47-7.56 (m, 1H), 7.83-7.97 (3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.5 (2C), 61.2, 107.2 (2C), 123.0, 125.2, 126.1, 127.5, 131.8, 133.1, 139.1, 142.3, 142.7, 143.0, 153.2 (2C), 188.7; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{18}H_{17}O_4S$: 329.0843; found: 329.0842.

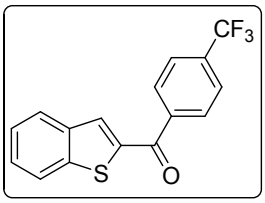


(Benzo[*b*]thiophen-2-yl(naphthalen-2-yl)methanone (3l): 84% yield (121 mg); ^1H NMR ($CDCl_3$, 400 MHz,) δ 7.42 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.55-7.67 (m, 2H), 7.87-8.01 (m, 7H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.1, 125.2, 125.4, 126.2, 127.1, 127.6, 128.0, 128.5,

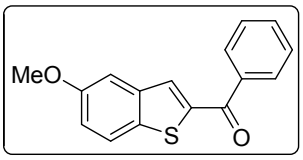
128.7, 129.5, 130.9, 132.4, 132.5, 135.3, 135.5, 139.2, 142.8, 143.4, 189.7; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{19}H_{13}OS$: 289.0683; found: 289.0682.



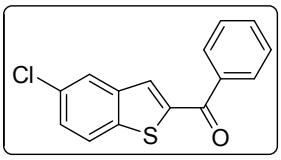
(Benzo[*b*]thiophen-2-yl(thiophen-2-yl)methanone (3m): 85% yield (104 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.23 (t, *J* = 3.6 Hz, 1H), 7.41-7.52 (m, 2H), 7.75 (d, *J* = 4.4 Hz, 1H), 7.92 (t, *J* = 6.8 Hz, 2H), 7.98 (d, *J* = 2.8 Hz, 1H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.9, 125.2, 126.1, 127.5, 128.2, 130.4, 133.7, 134.0, 139.1, 142.4, 142.6, 142.8, 180.2; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{13}H_9OS_2$: 245.0095; found: 245.0093.



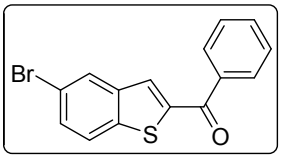
(Benzo[*b*]thiophen-2-yl(4-(trifluoromethyl)phenyl)methanone (3n): 68% yield (104 mg); ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 7.41-7.46 (m, 1H), 7.51 (td, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.84 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.7, 123.1, 123.8 (q, *J* = 270.9 Hz), 125.4, 125.7 (q, *J* = 3.6 Hz), 126.4, 128.1, 129.6 (2C), 133.0, 134.0 (q, *J* = 32.6 Hz), 139.1, 141.0, 142.6, 143.1, 188.7;



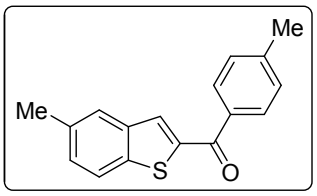
(5-Methoxybenzo[*b*]thiophen-2-yl)(phenyl)methanone (3o): 89% yield (119 mg); White solid; mp 107-109 ^{o}C; R_f 0.43 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.86 (s, 3H), 7.14 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.73-7.80 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 107.0, 118.7, 123.7 (2C), 128.6, 129.4, 132.0, 132.6, 135.7, 138.0, 140.2, 144.2, 158.0, 189.7; FTIR (KBr) 3045, 2923, 1628, 1215, 753 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{16}H_{13}O_2S$: 269.0637; found: 269.0634.



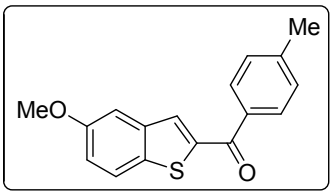
(5-Chlorobenzo[*b*]thiophen-2-yl)(phenyl)methanone (3p): 78% yield (107 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.78 (s, 1H), 7.81-7.88 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 124.2, 125.4, 128.1, 128.8 (2C), 129.4 (2C), 131.1, 131.5, 132.9, 137.7, 140.2, 140.8, 145.1, 189.5;



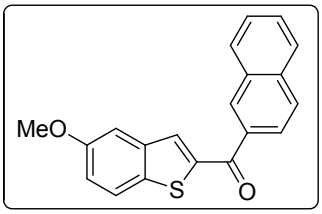
(5-Bromobenzo[*b*]thiophen-2-yl)(phenyl)methanone (3q): 81% yield (129 mg); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.55 (q, *J* = 7.6 Hz, 3H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.74-7.81 (m, 2H), 7.91 (d, *J* = 7.2 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 119.1, 124.4, 128.6, 128.8 (2C), 129.4 (2C), 130.6, 130.9, 132.9, 137.6, 140.7, 141.2, 144.9, 189.4; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{15}H_{10}BrOS$: 316.9633; found: 316.9632.



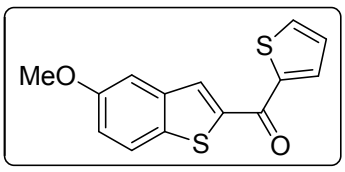
(5-Methylbenzo[*b*]thiophen-2-yl)(*p*-tolyl)methanone (3r): 91% yield (120 mg); White solid; mp 94-96 ^{o}C; R_f 0.52 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 2.44-2.47 (m, 6H), 7.26-7.34 (m, 3H), 7.64 (s, 1H), 7.76 (t, *J* = 4.8 Hz, 2H), 7.82 (dd, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.8, 122.6, 125.7, 129.3 (2C), 129.4 (2C), 129.6, 131.7, 134.9, 135.4, 139.5, 140.0, 143.3, 143.4, 189.4; FTIR (KBr) 3010, 2980, 1631, 1456, 730 cm^{-1}; HRMS (*m*/*z*): [M+Na]$^{+}$calcd for $C_{17}H_{14}NaOS$: 289.0639; found: 289.0648.



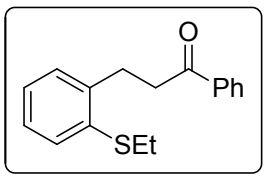
(5-Methoxybenzo[*b*]thiophen-2-yl)(*p*-tolyl)methanone (3s): 93% yield (131 mg); White solid; mp 82-84 ^{o}C; R_f 0.46 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 2.46 (s, 3H), 3.86 (s, 3H), 7.13 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 7.27 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.73-7.79 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 55.7, 107.0, 118.6, 123.7, 129.3 (2C), 129.6 (2C), 131.6, 135.3, 135.5, 140.2, 143.4, 144.4, 158.0, 189.4; FTIR (KBr) 3052, 3091, 2917, 1626, 1256, 723 cm^{-1}.



(5-Methoxybenzo[*b*]thiophen-2-yl)(naphthalen-2-yl)methanone (3t): 89% yield (141 mg); White solid; mp 132-134 ^{o}C; R_f 0.49 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.88 (s, 3H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.30 (s, 1H), 7.54-7.70 (m, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.86 (s, 1H), 7.92-8.01 (m, 4H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 107.0, 118.8, 123.8, 125.5, 127.1, 128.0, 128.5, 128.7, 129.5, 130.8, 132.0, 132.5, 135.3, 135.4, 135.7, 140.2, 144.4, 158.1. 189.7; HRMS (*m*/*z*): FTIR (KBr) 2992, 2843, 1685, 1230, 727 cm^{-1}; [M+Na]$^{+}$calcd for $C_{20}H_{14}NaO_2S$: 341.0603; found: 341.0603.

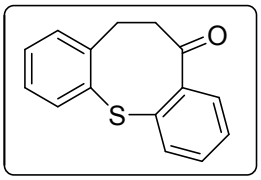


(5-Methoxybenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (3u): 93% yield (128 mg); Pale yellow solid; mp 97-99 ^{o}C; R_f 0.47 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.89 (s, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.21 (t, *J* = 4.0 Hz, 1H), 7.32 (s, 1H), 7.70-7.80 (m, 2H), 7.97 (d, *J* = 3.6 Hz, 1H), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 106.9, 118.7, 123.7, 128.2, 130.1, 133.7, 134.0, 135.2, 140.1, 142.9, 143.5, 158.1, 180.2; FTIR (KBr) 3065, 2932, 2839, 1633, 1587, 1290, 785 cm^{-1}; HRMS (*m*/*z*): [M+H]$^{+}$calcd for $C_{14}H_{11}O_2S_2$: 275.0206; found: 275.0199.



(3-(2-(Ethylthio)phenyl)-1-phenylpropan-1-one (5b): 23% yield (31 mg); colorless liquid; R_f 0.49 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 1.32 (t, *J* = 7.2 Hz, 3H), 2.95 (q, *J* = 7.2 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H),

7.19 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 27.6, 28.9, 39.3, 126.0, 127.0, 128.2 (2C), 128.6 (3C), 129.8, 133.1, 135.7, 136.9, 140.7, 199.5; FTIR (KBr) 2998, 1635, 1021,763 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{17}H_{18}NaOS$: 293.0960; found: 293.0965.



(5-Methoxybenzo[*b*]thiophen-2-yl)(thiophen-2-yl)methanone (6b): 31% yield (50 mg); colorless liquid; R_f 0.46 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 3.17-3.27 (m, 4H), 7.12-7.26 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.52-7.58 (m, 1H), 7.91 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.4, 39.7, 127.5, 128.1, 128.2, 128.4, 128.7 (2C), 130.1, 130.9, 133.2, 135.6, 136.8, 141.5, 199.0; FTIR (KBr) 2938, 1620, 1149, 745 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{15}H_{12}NaOS$: 263.0490; found: 263.0496.

5. ^{1}H and ^{13}C NMR spectra for all compounds

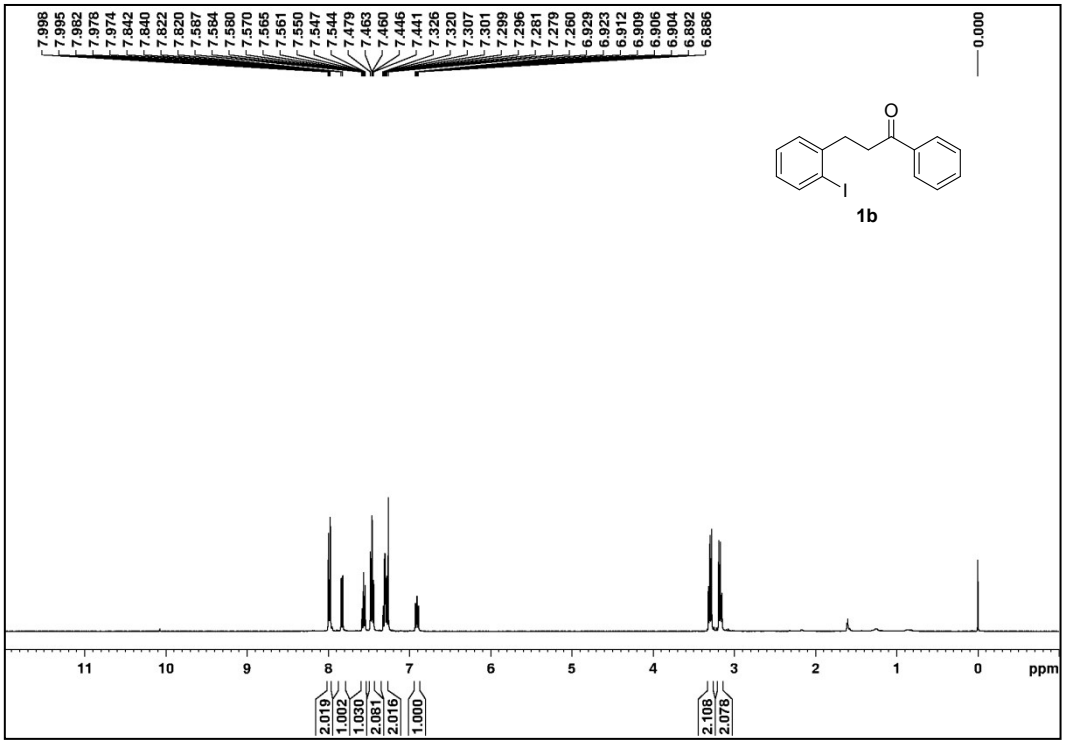


Figure 1:400 MHz ^{1}HNMR spectrum of **1b** in $CDCl_3$

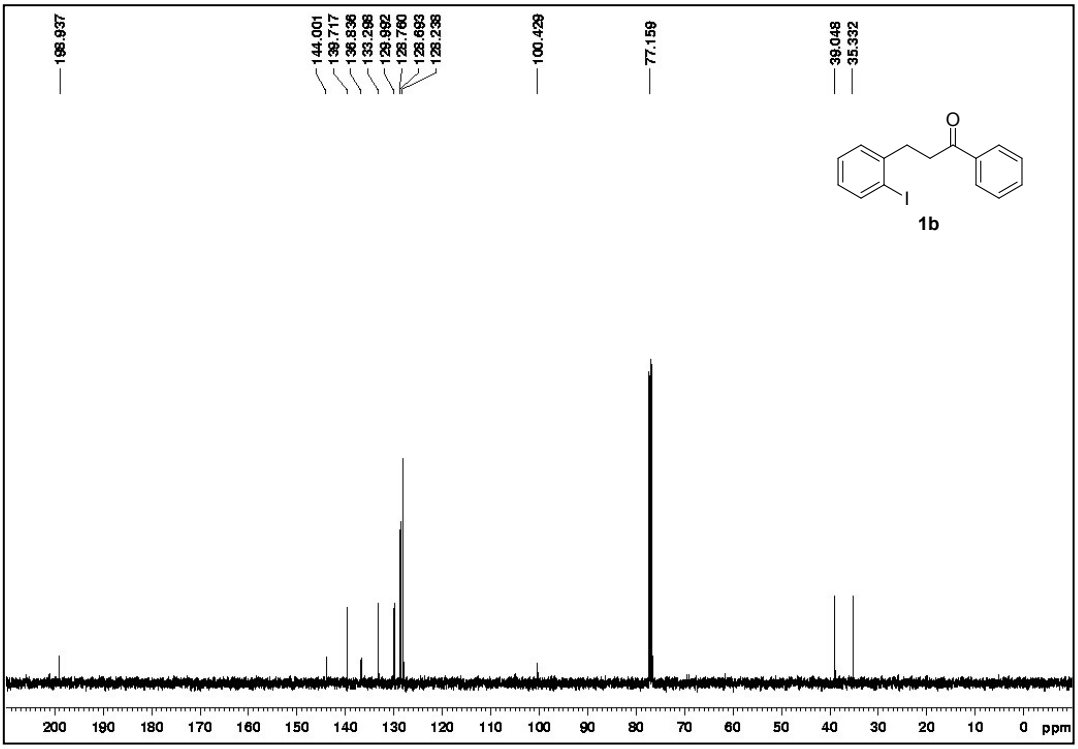


Figure 2:100 MHz ^{13}CNMR spectrum of **1b** in $CDCl_3$

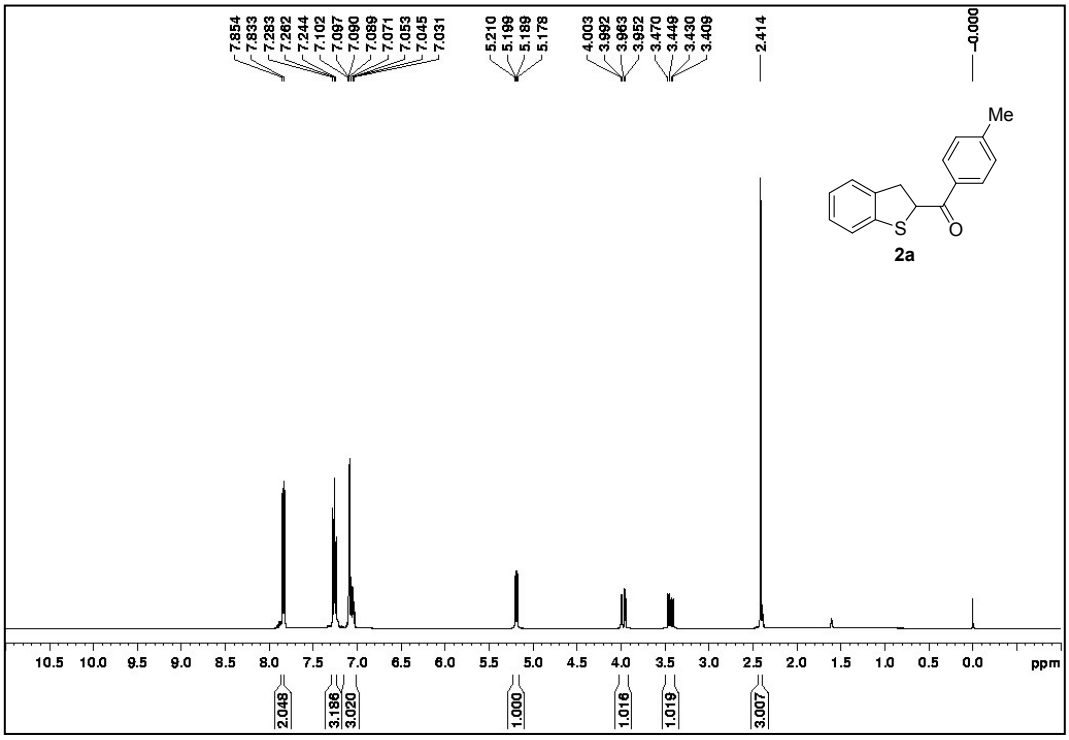


Figure 3: 400 MHz ^{1}HNMR spectrum of **2a** in $CDCl_3$

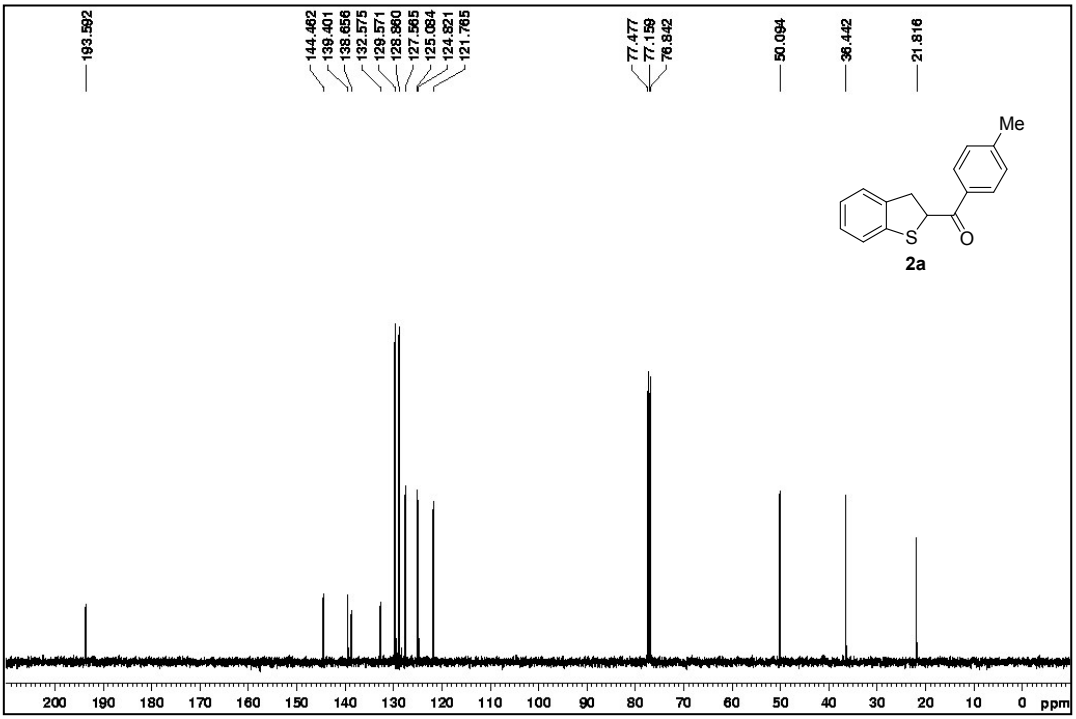


Figure 4: 100 MHz ^{13}CNMR spectrum of **2a** in $CDCl_3$

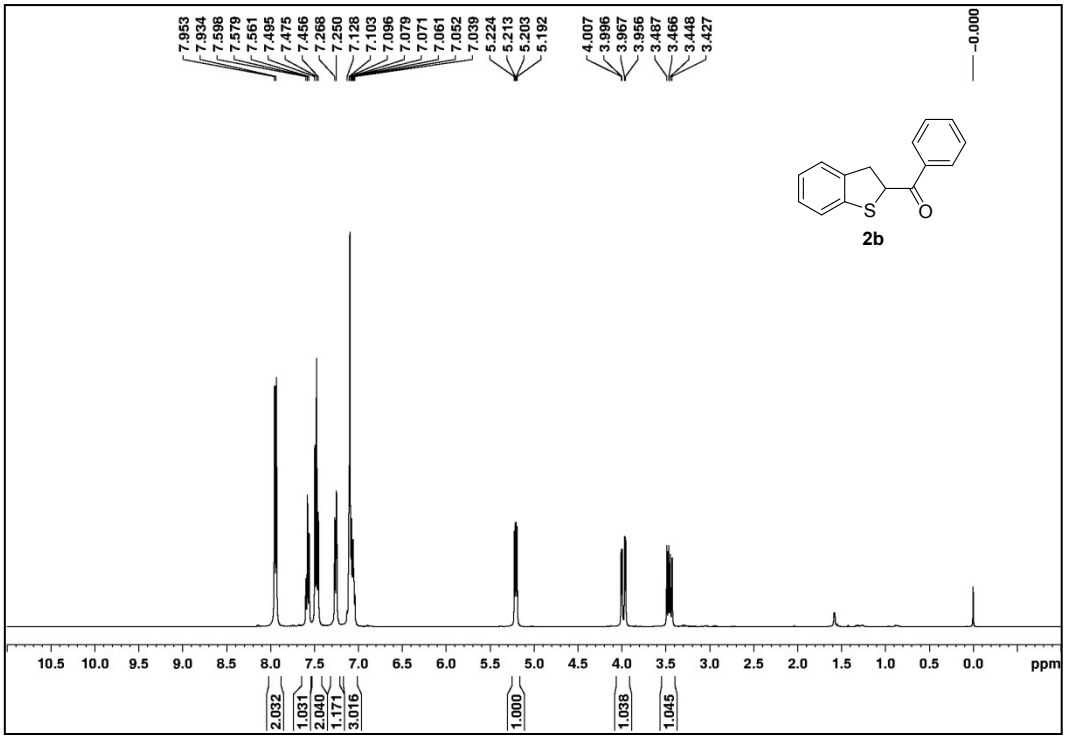


Figure 5:400 MHz ^{1}HNMR spectrum of **2b** in $CDCl_3$

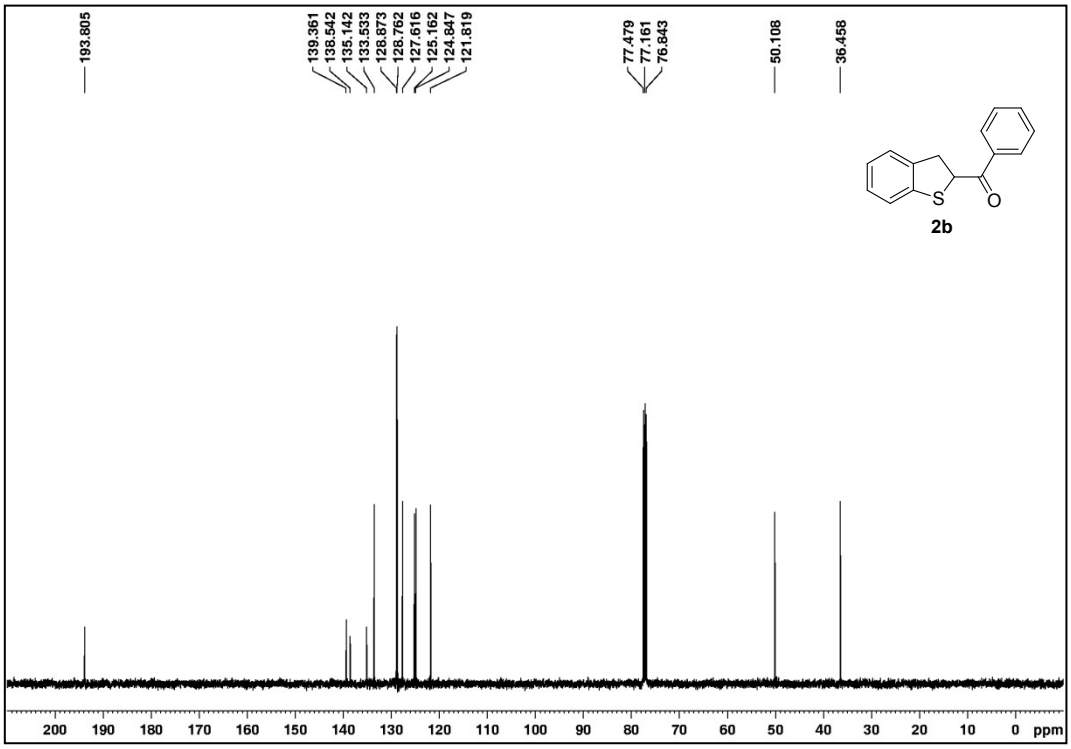


Figure 6:100 MHz ^{13}CNMR spectrum of **2b** in $CDCl_3$

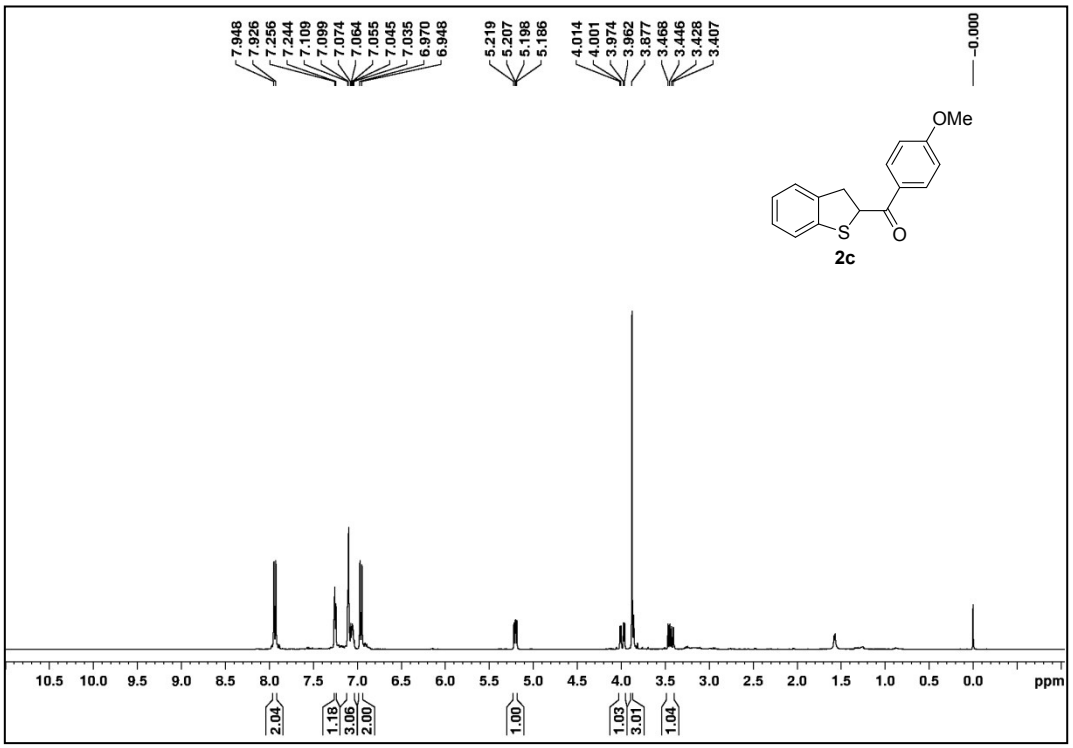


Figure 7: 400 MHz ^{1}HNMR spectrum of **2c** in $CDCl_3$

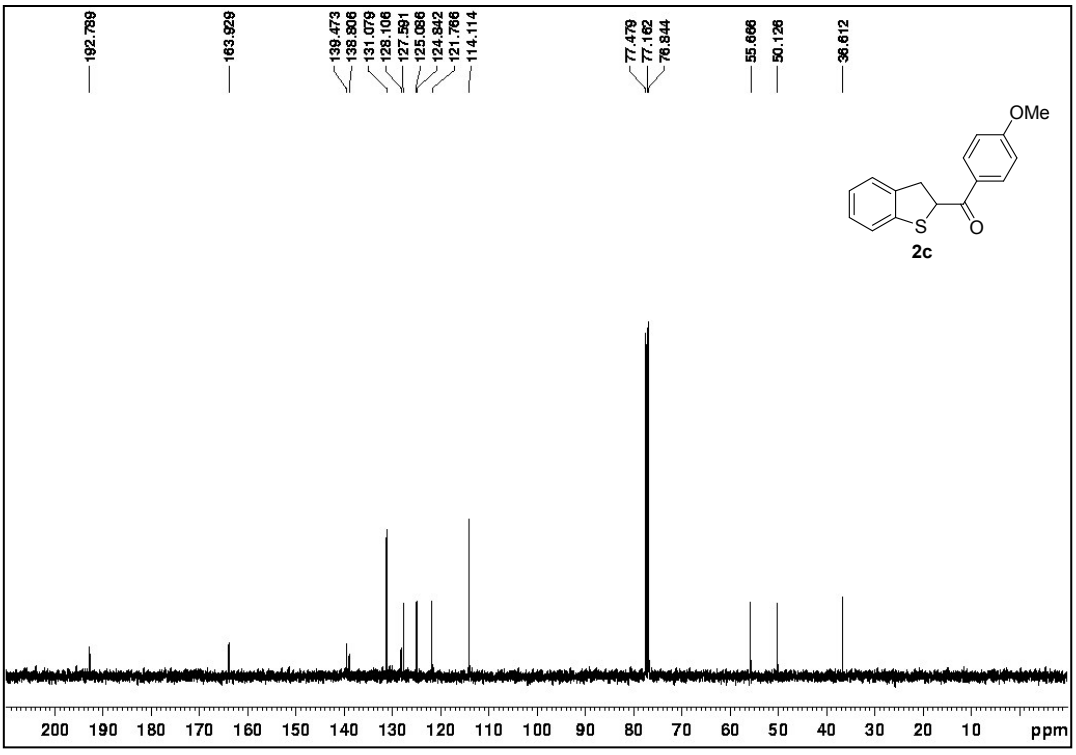


Figure 8: 100 MHz ^{13}CNMR spectrum of **2c** in $CDCl_3$

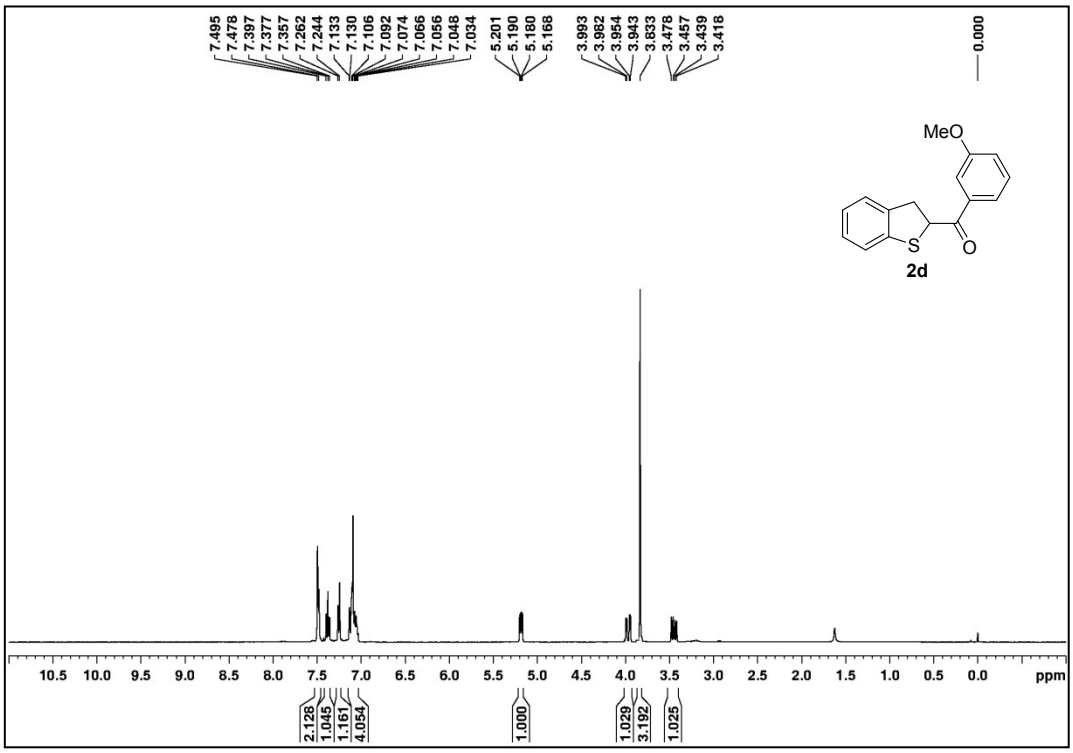


Figure 9: 400 MHz ^{1}HNMR spectrum of **2d** in $CDCl_3$

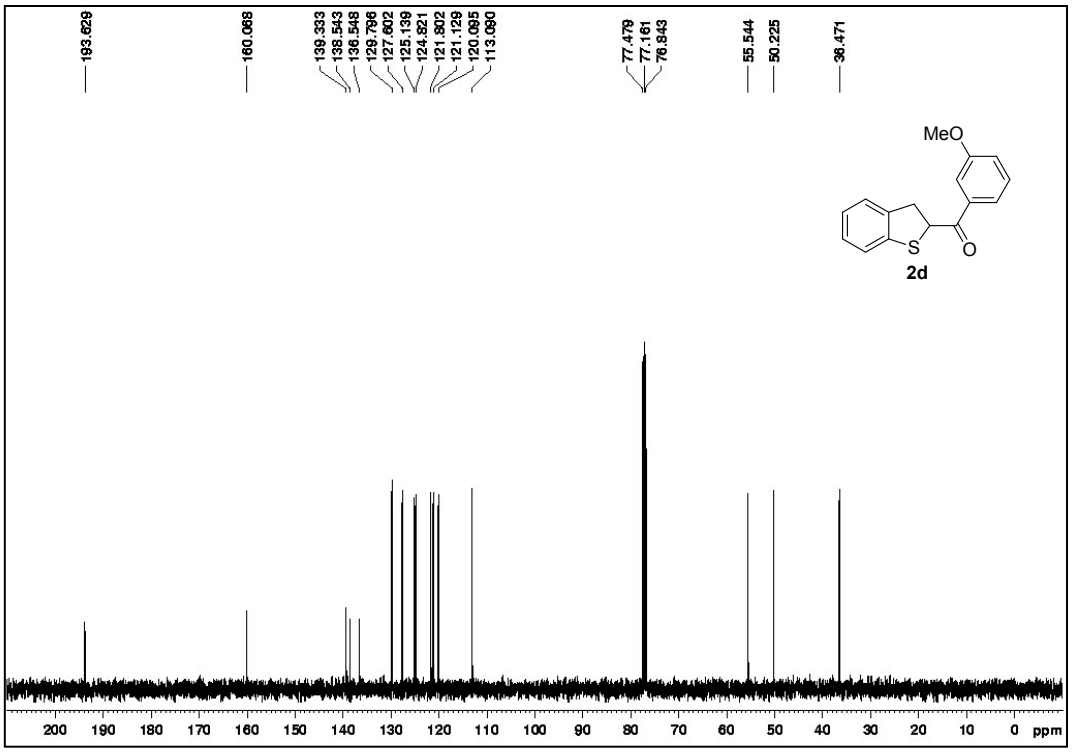


Figure 10: 100 MHz ^{13}CNMR spectrum of **2d** in $CDCl_3$

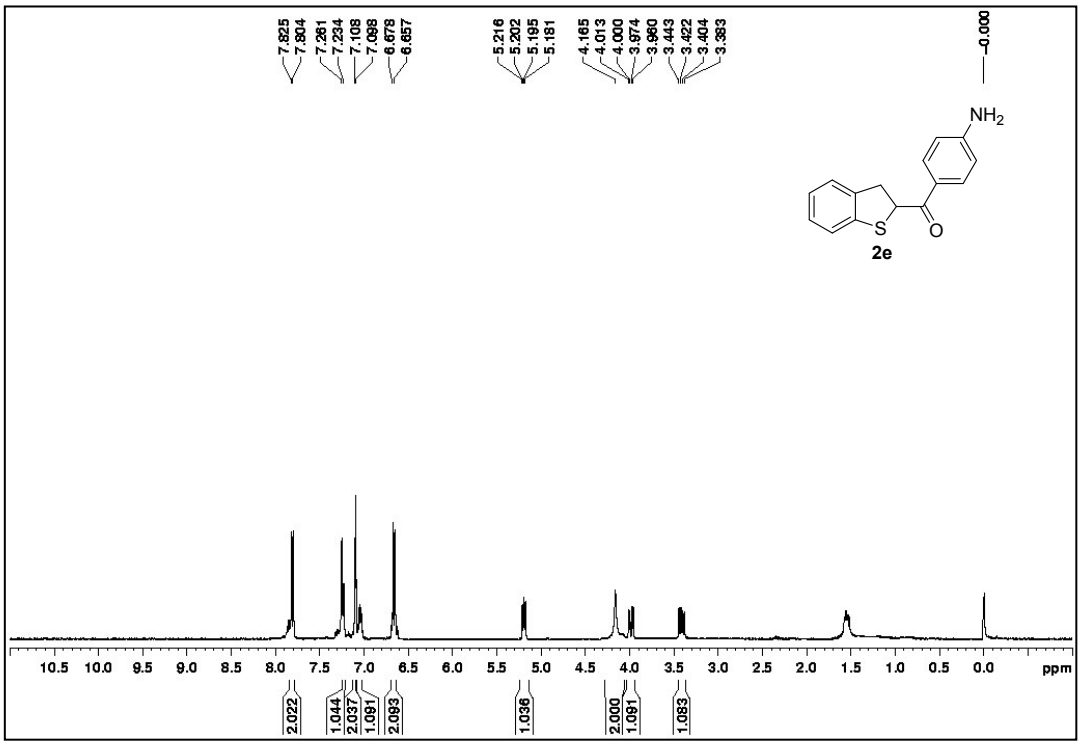


Figure 11: 400 MHz ^{1}HNMR spectrum of **2e** in $CDCl_3$

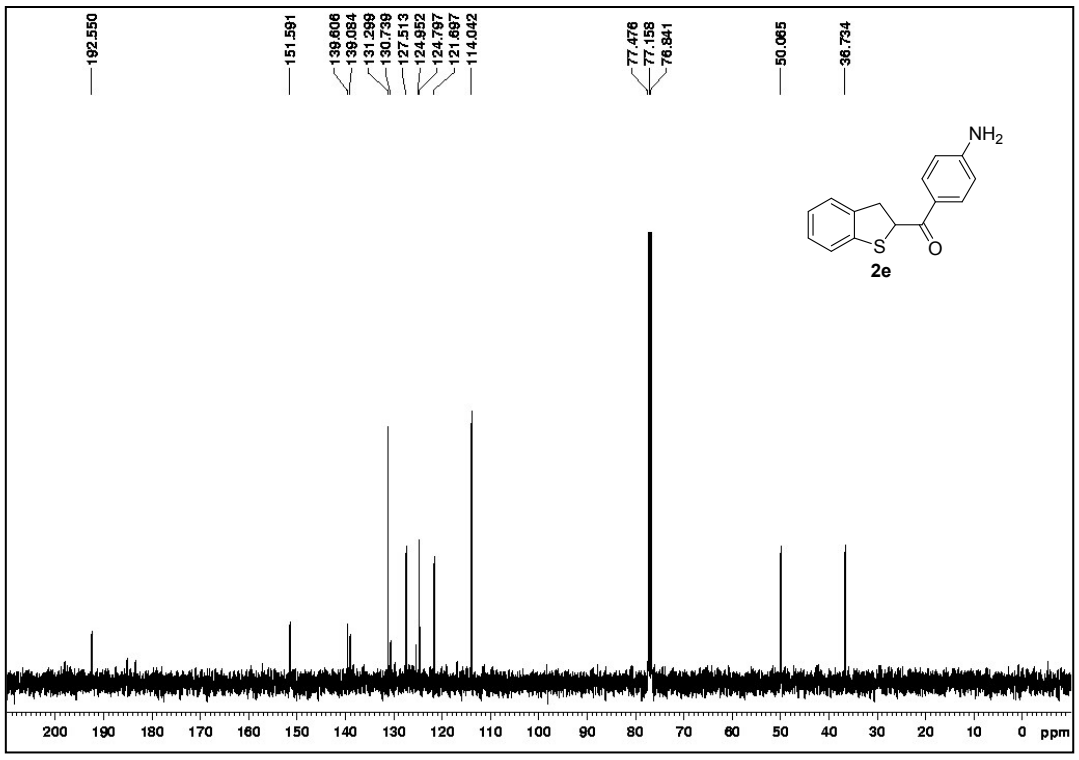


Figure 12: 100 MHz ^{13}CNMR spectrum of **2e** in $CDCl_3$

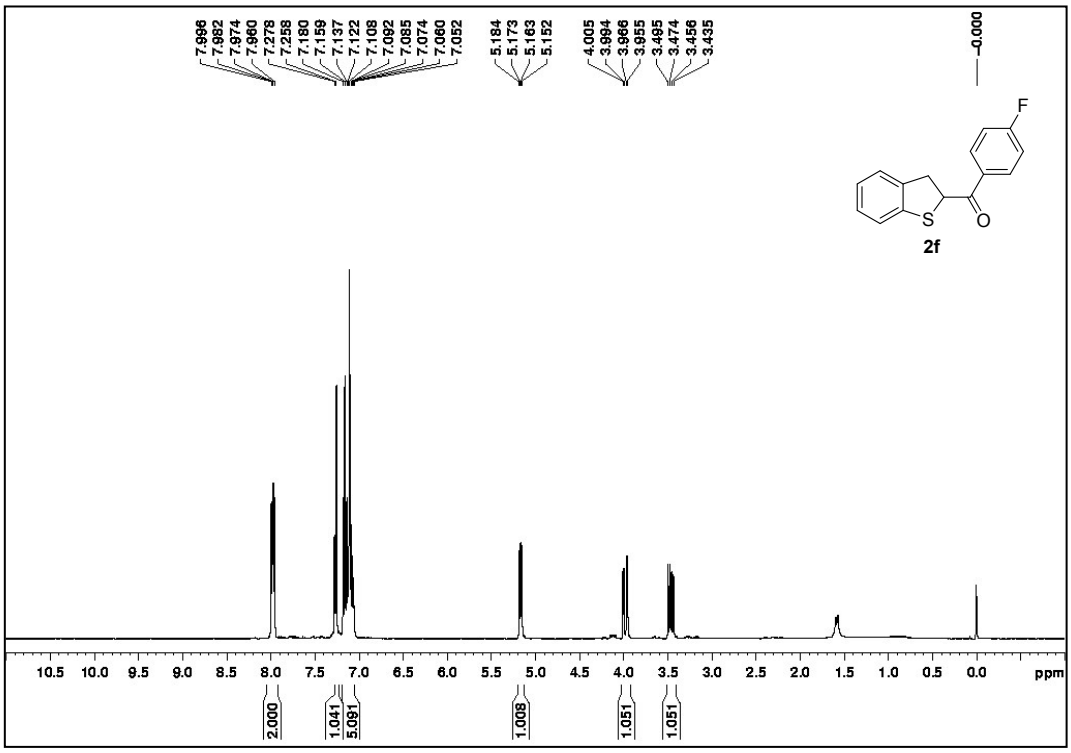


Figure 13: 400 MHz ^{1}HNMR spectrum of **2f** in $CDCl_3$

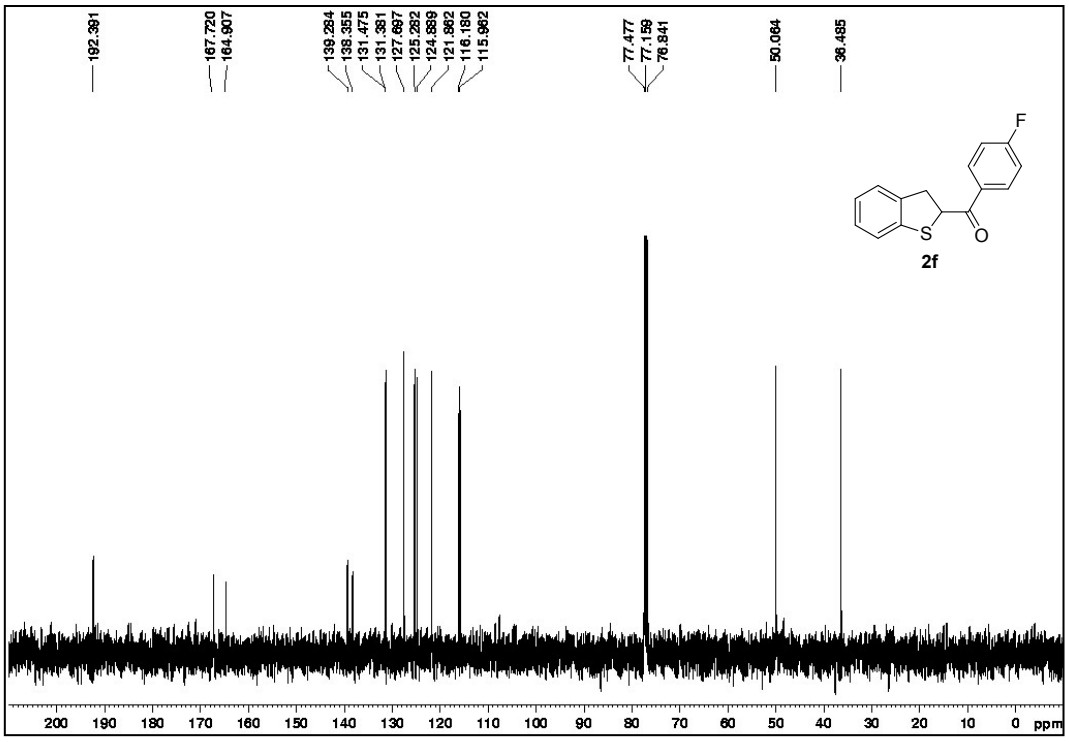


Figure 14: 100 MHz ^{13}CNMR spectrum of **2f** in $CDCl_3$

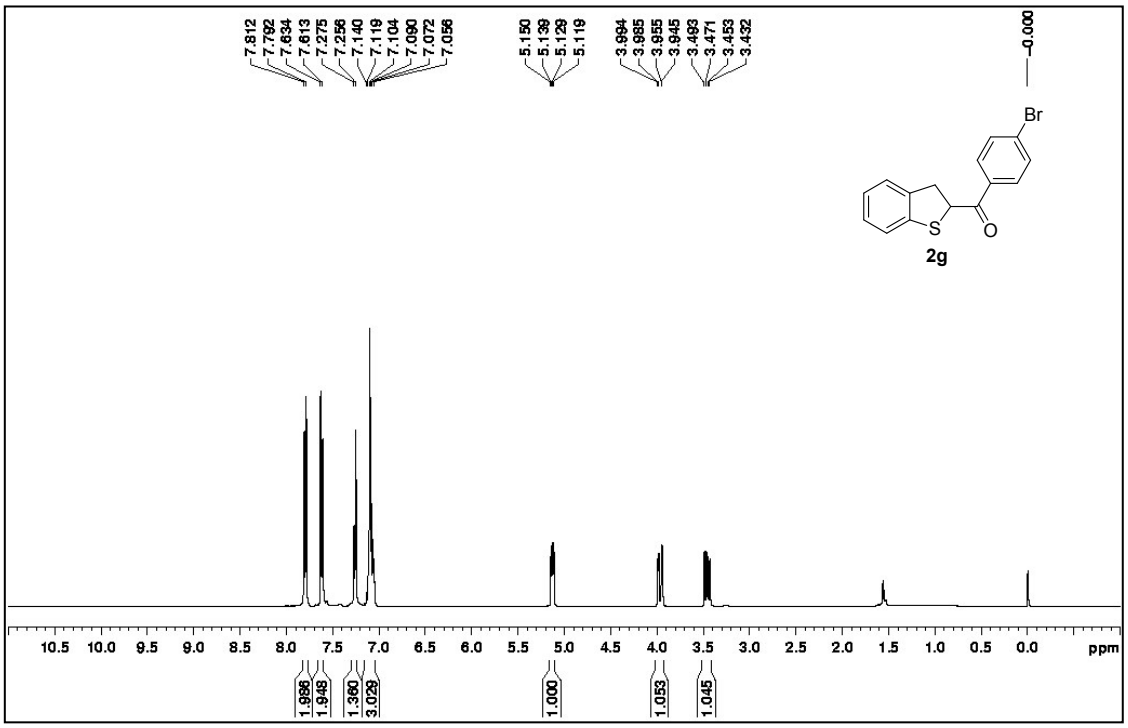


Figure 15: 400 MHz ^{1}HNMR spectrum of **2g** in $CDCl_3$

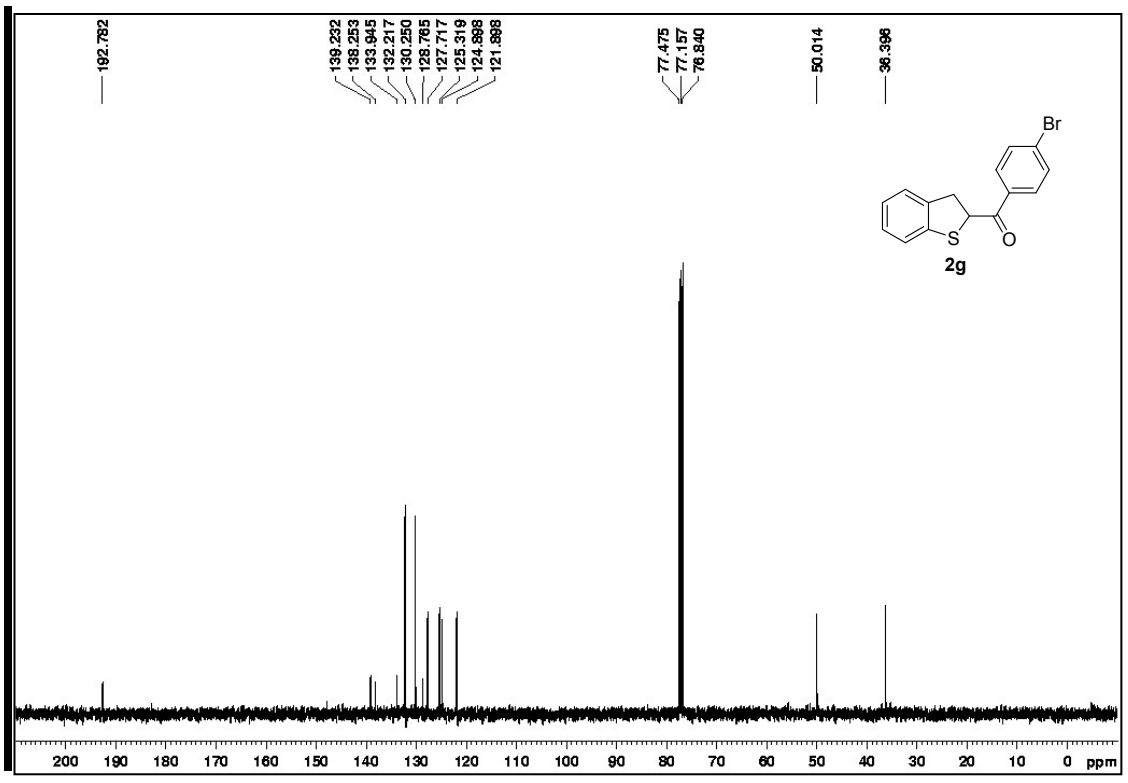


Figure 16: 100 MHz ^{13}CNMR spectrum of **2g** in $CDCl_3$

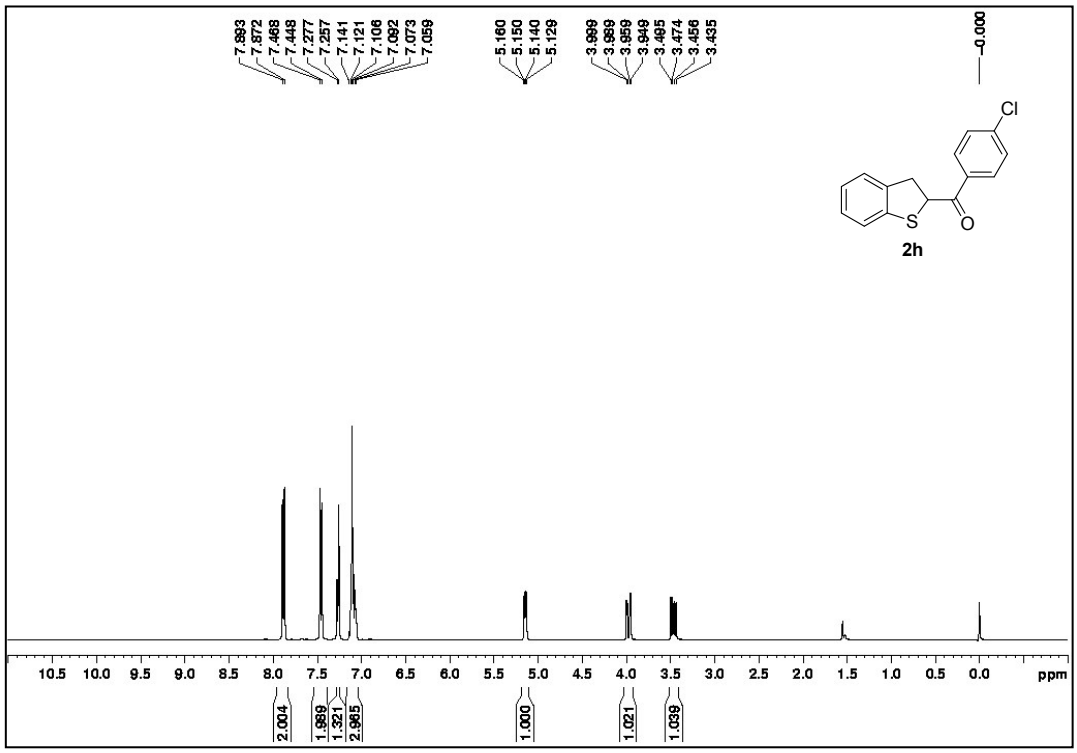


Figure 17: 400 MHz ^{1}HNMR spectrum of **2h** in $CDCl_3$

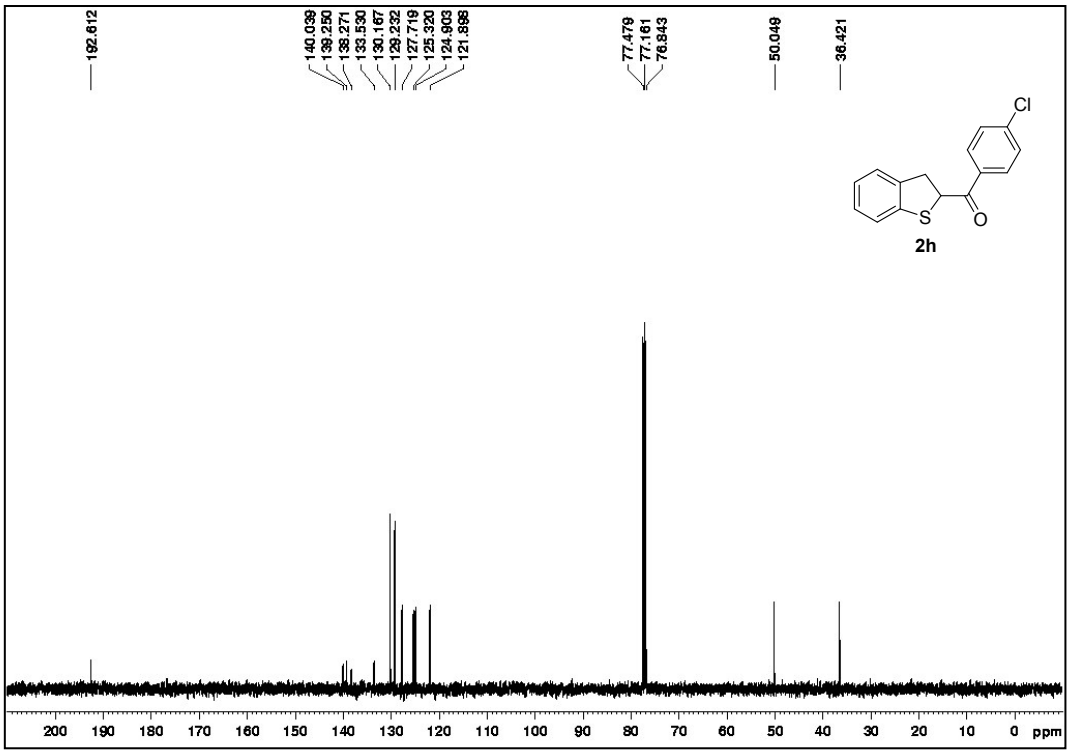


Figure 18: 100 MHz ^{13}CNMR spectrum of **2h** in $CDCl_3$

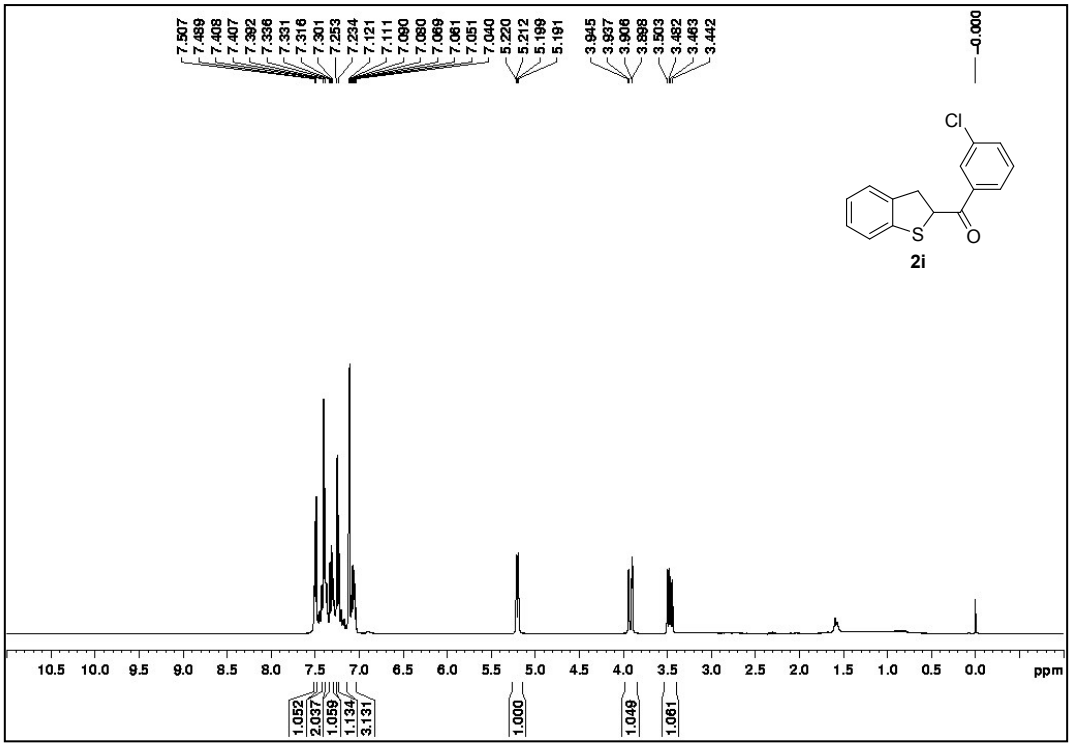


Figure 19: 400 MHz ^{1}HNMR spectrum of **2i** in $CDCl_3$

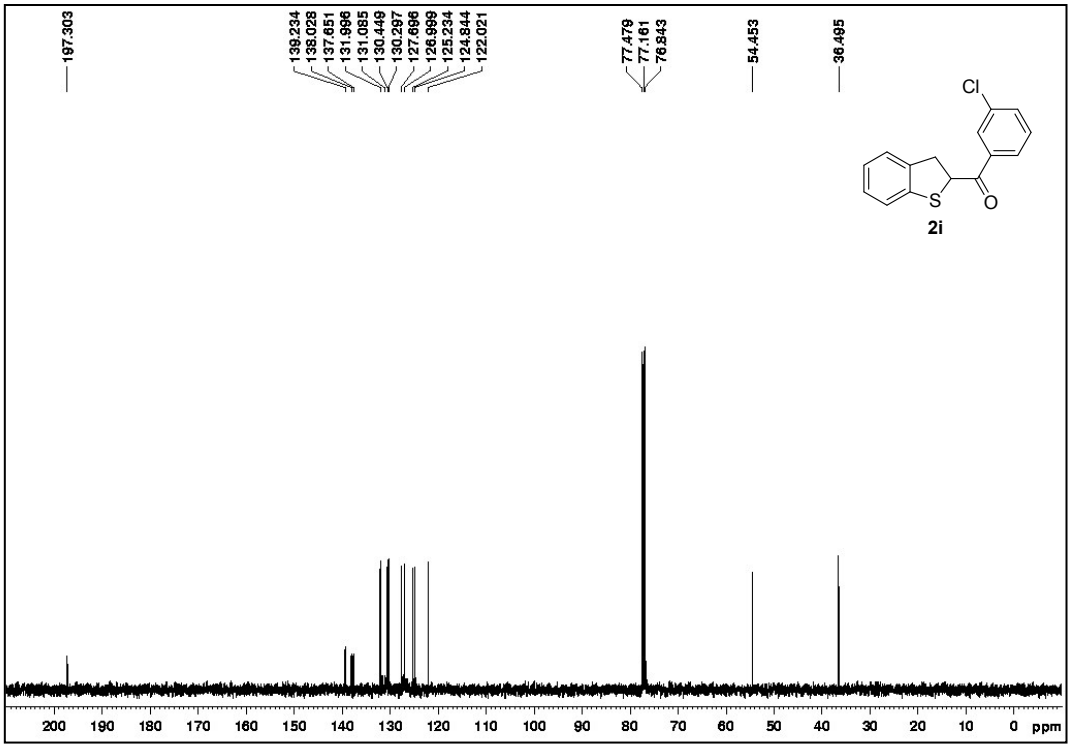


Figure 20: 100 MHz ^{13}CNMR spectrum of **2i** in $CDCl_3$

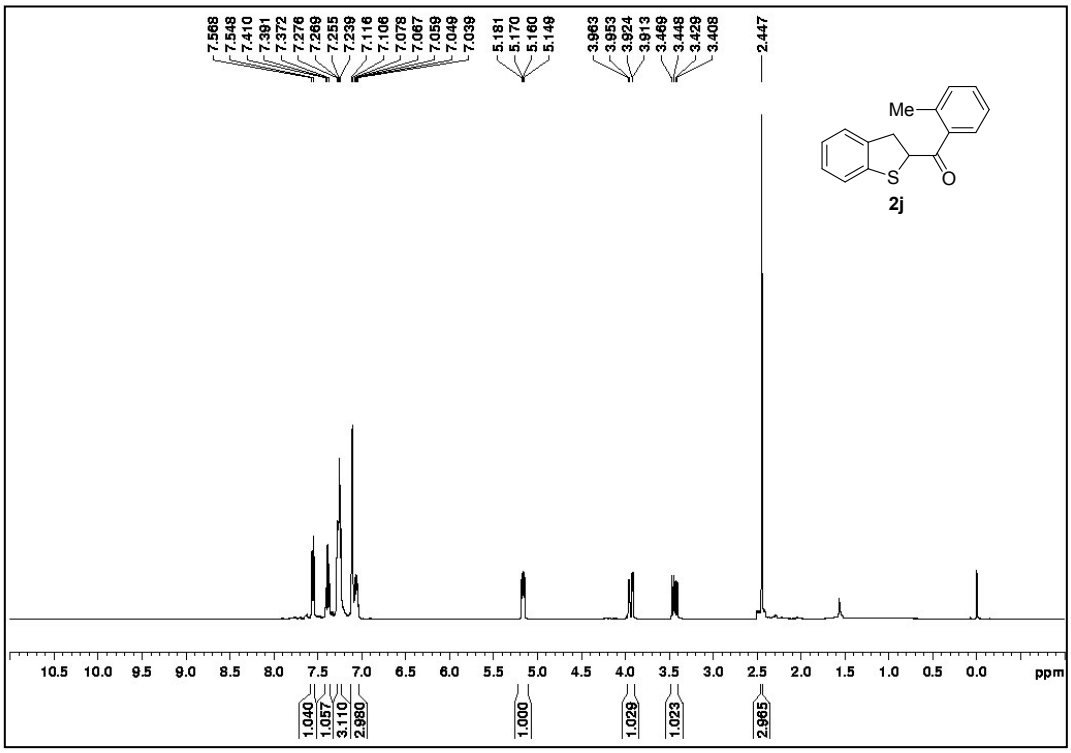


Figure 21: 400 MHz ^{1}HNMR spectrum of **2j** in $CDCl_3$

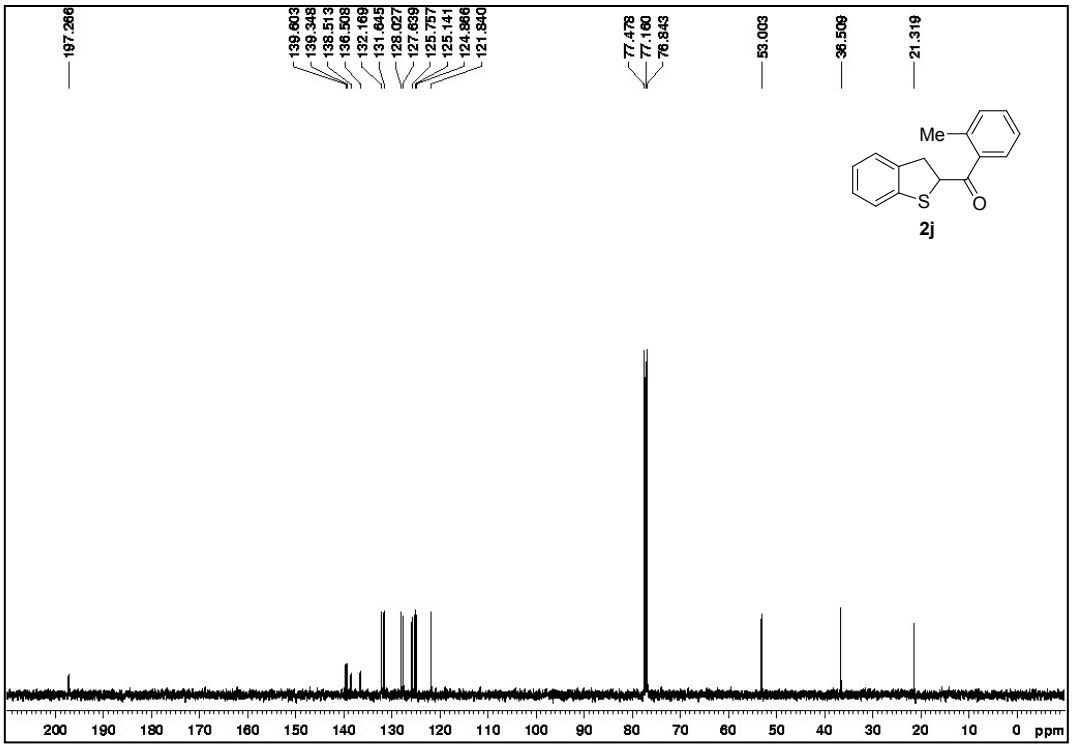


Figure 22: 100 MHz ^{13}CNMR spectrum of **2j** in $CDCl_3$

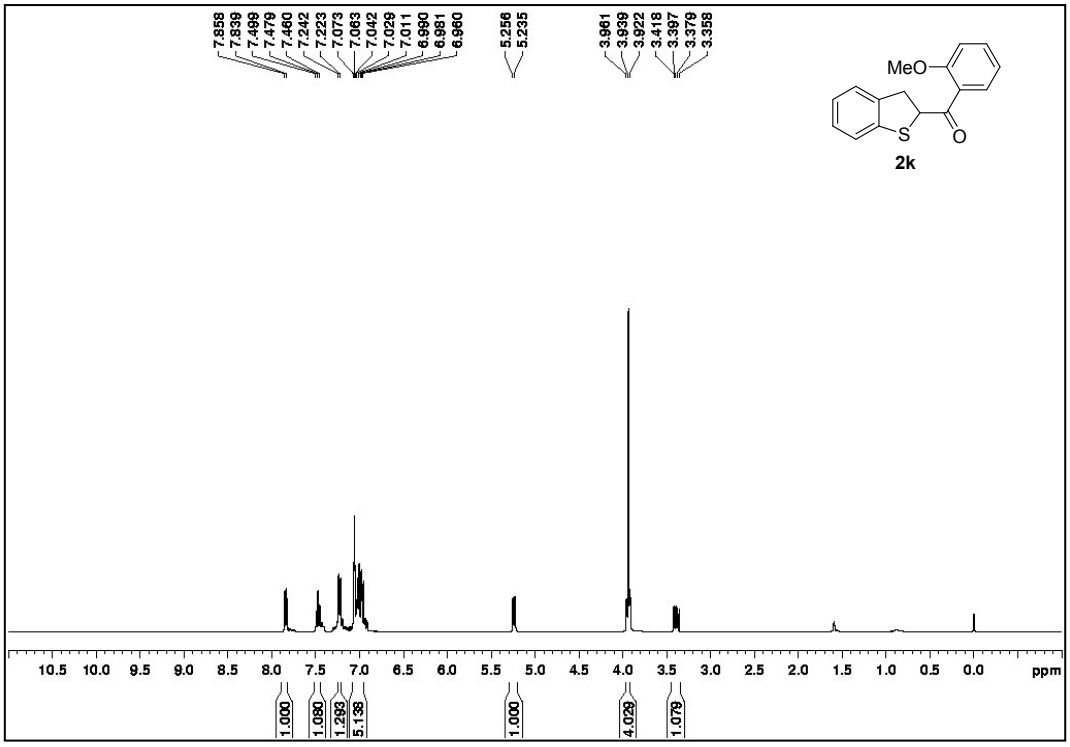


Figure 23: 400 MHz ^{1}HNMR spectrum of **2k** in $CDCl_3$

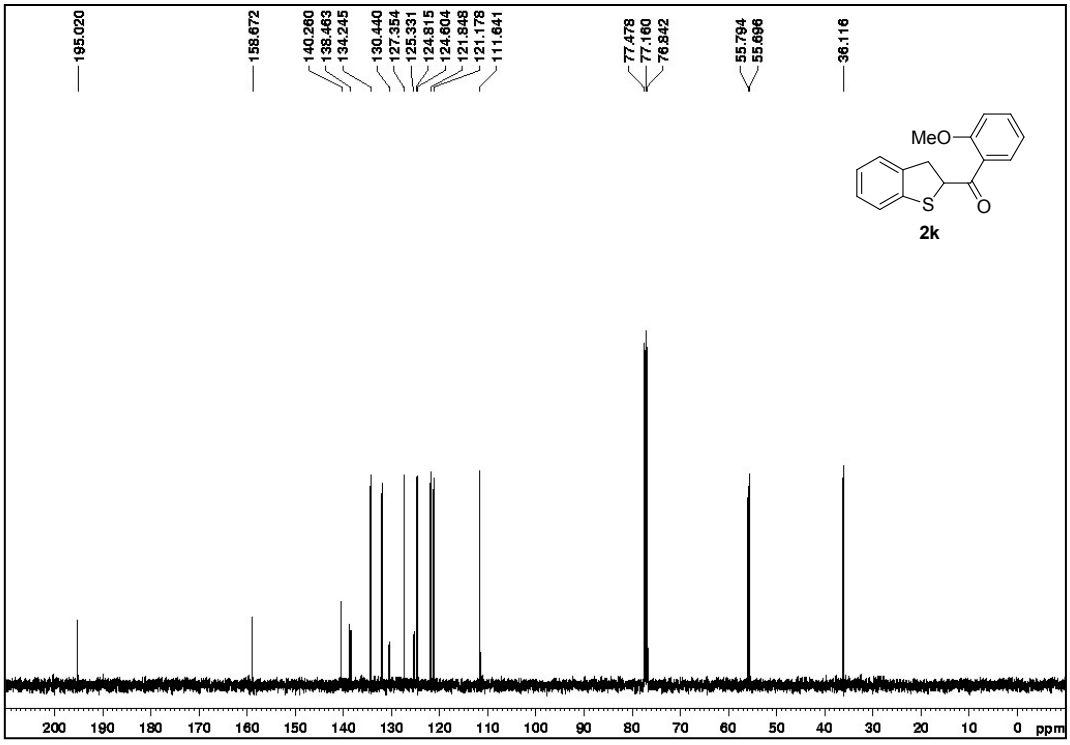


Figure 24: 100 MHz ^{13}CNMR spectrum of **2k** in $CDCl_3$

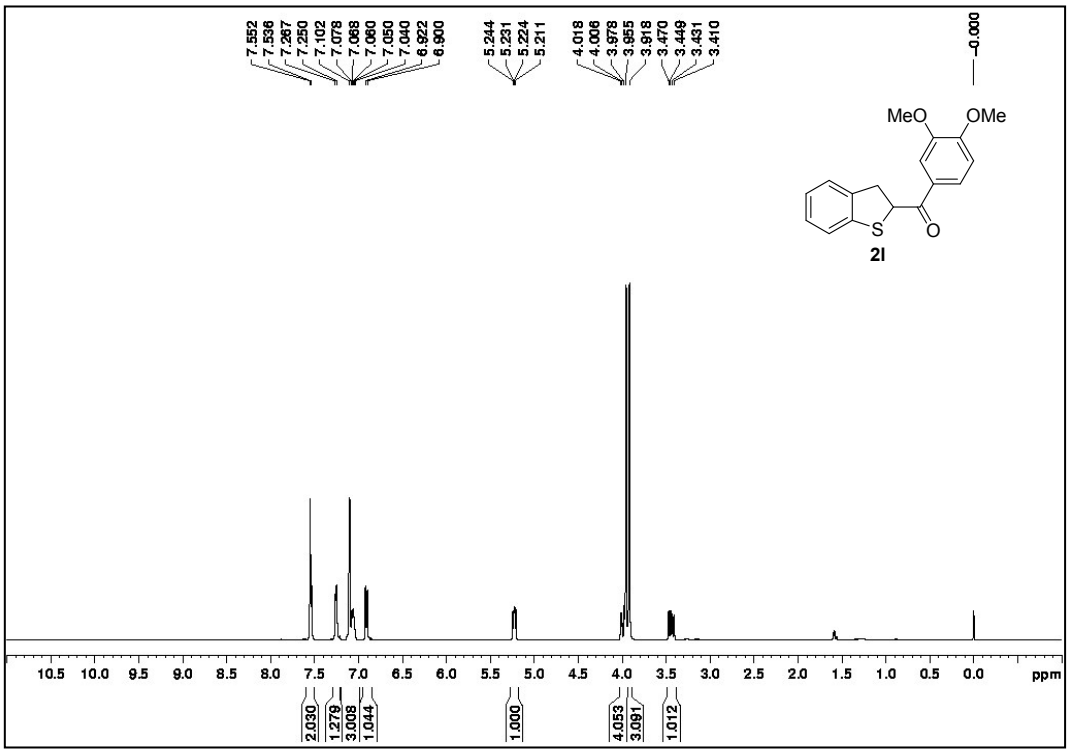


Figure 25: 400 MHz ^{1}HNMR spectrum of **2l** in $CDCl_3$

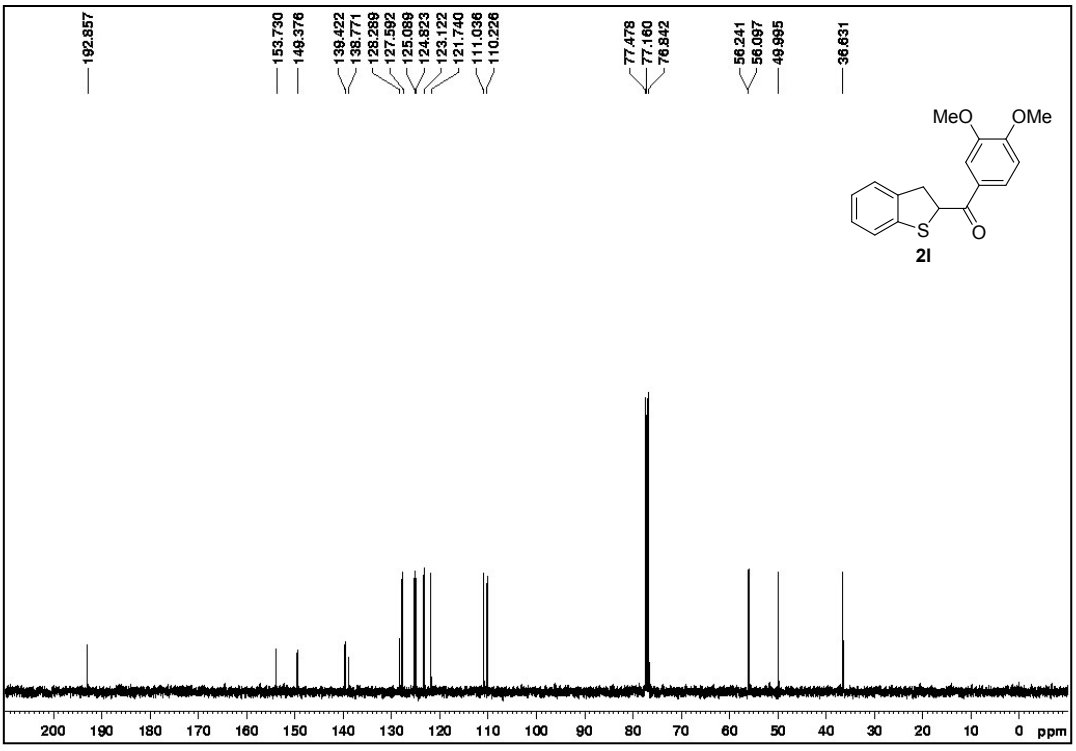


Figure 26: 100 MHz ^{13}CNMR spectrum of **2l** in $CDCl_3$

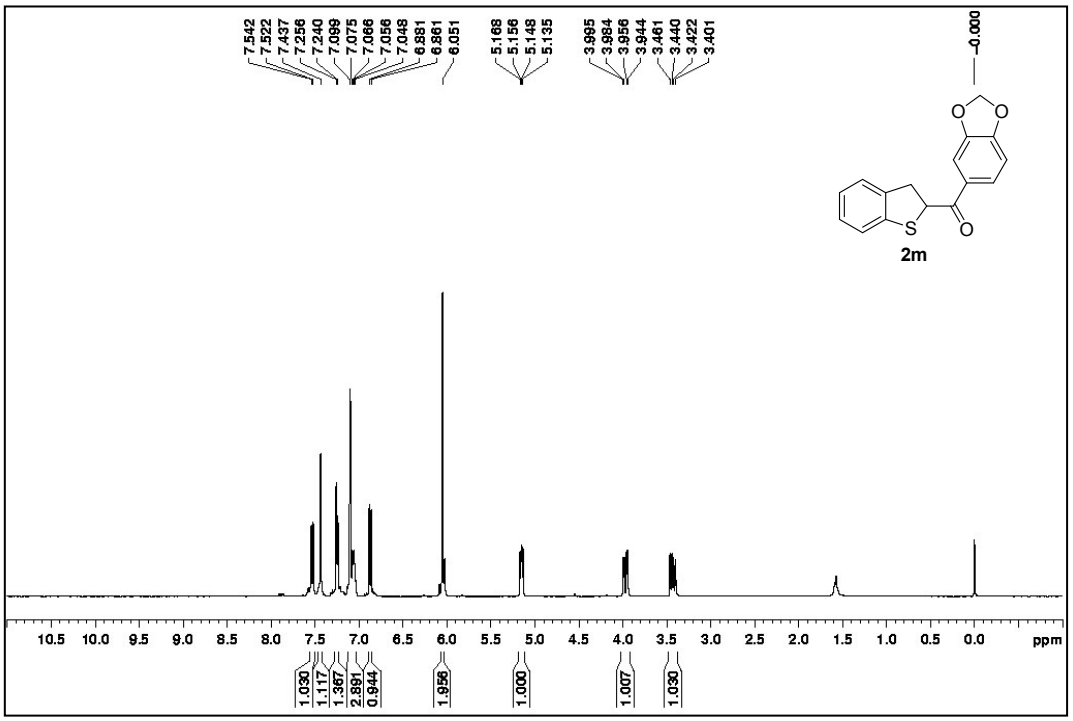


Figure 27: 400 MHz ^{1}HNMR spectrum of **2m** in $CDCl_3$

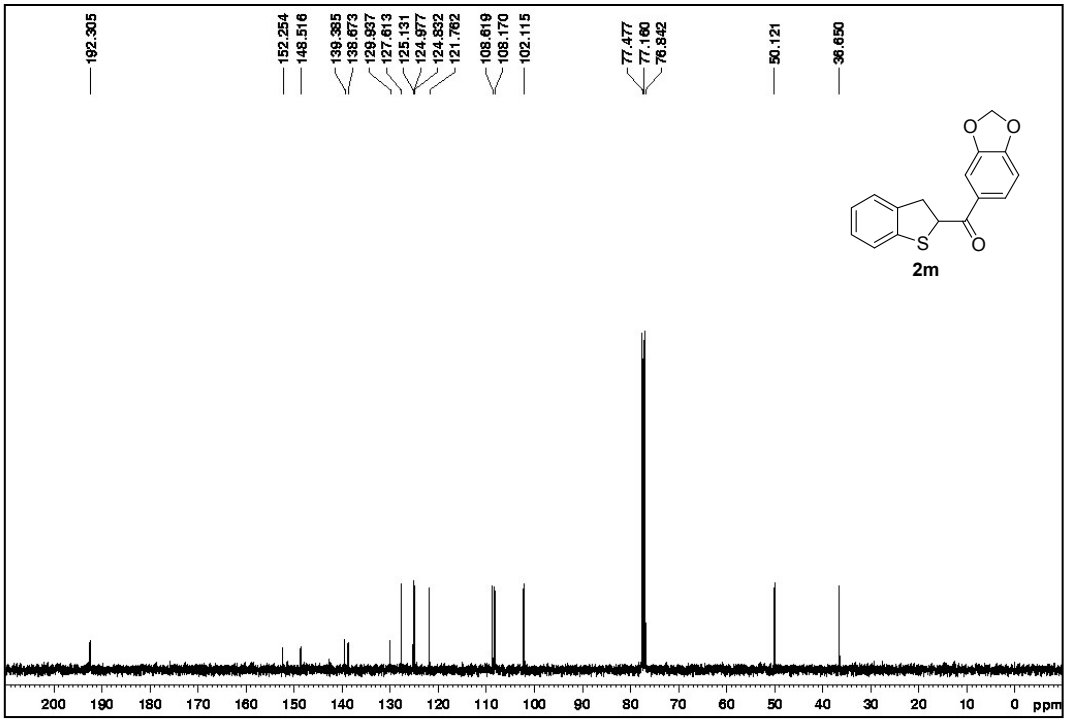


Figure 28: 100 MHz ^{13}CNMR spectrum of **2m** in $CDCl_3$

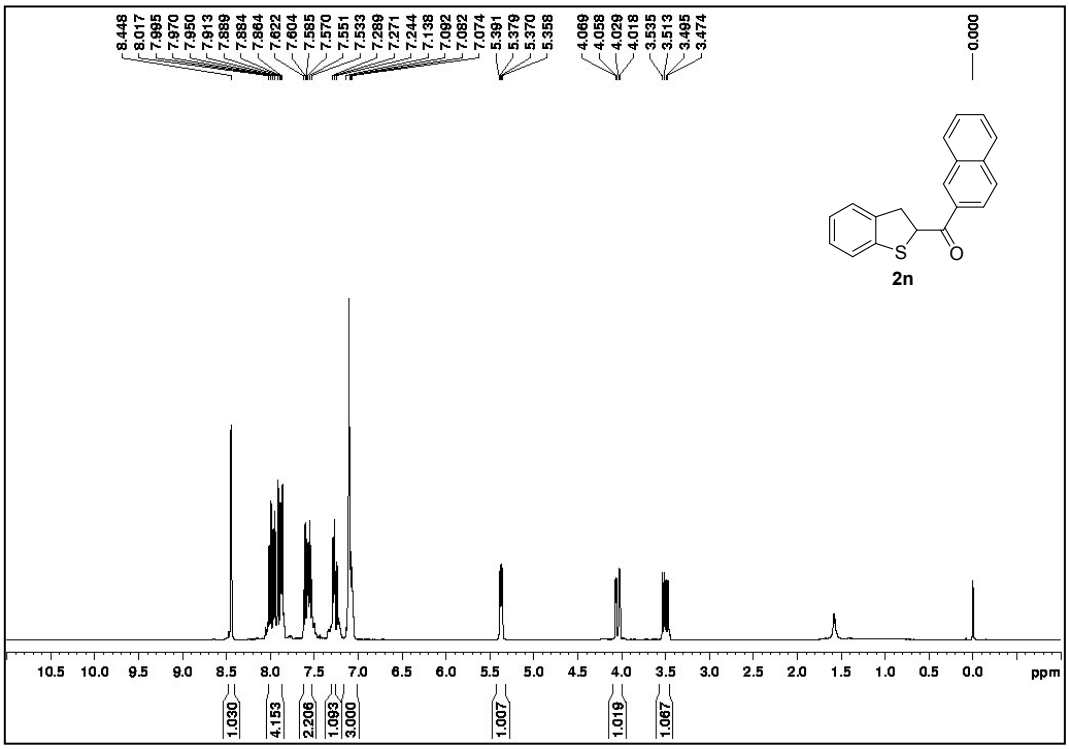


Figure 29: 400 MHz ^{1}HNMR spectrum of **2n** in $CDCl_3$

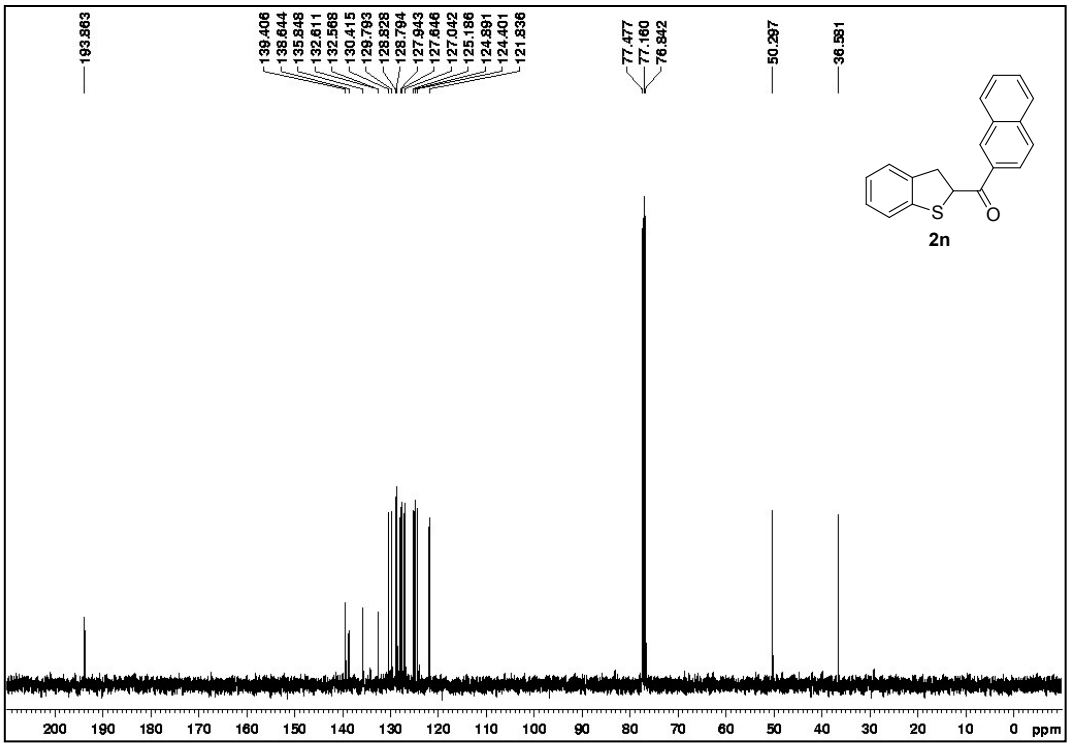


Figure 30: 100 MHz ^{13}CNMR spectrum of **2n** in $CDCl_3$

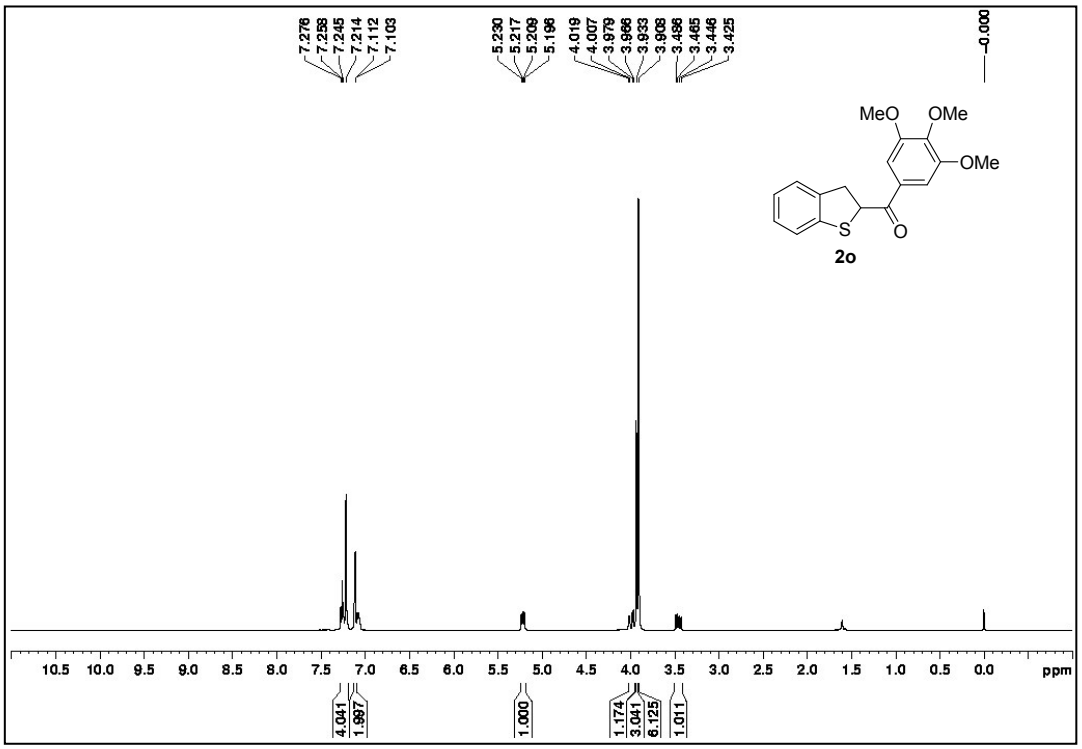


Figure 31: 400 MHz ^{1}HNMR spectrum of **2o** in $CDCl_3$

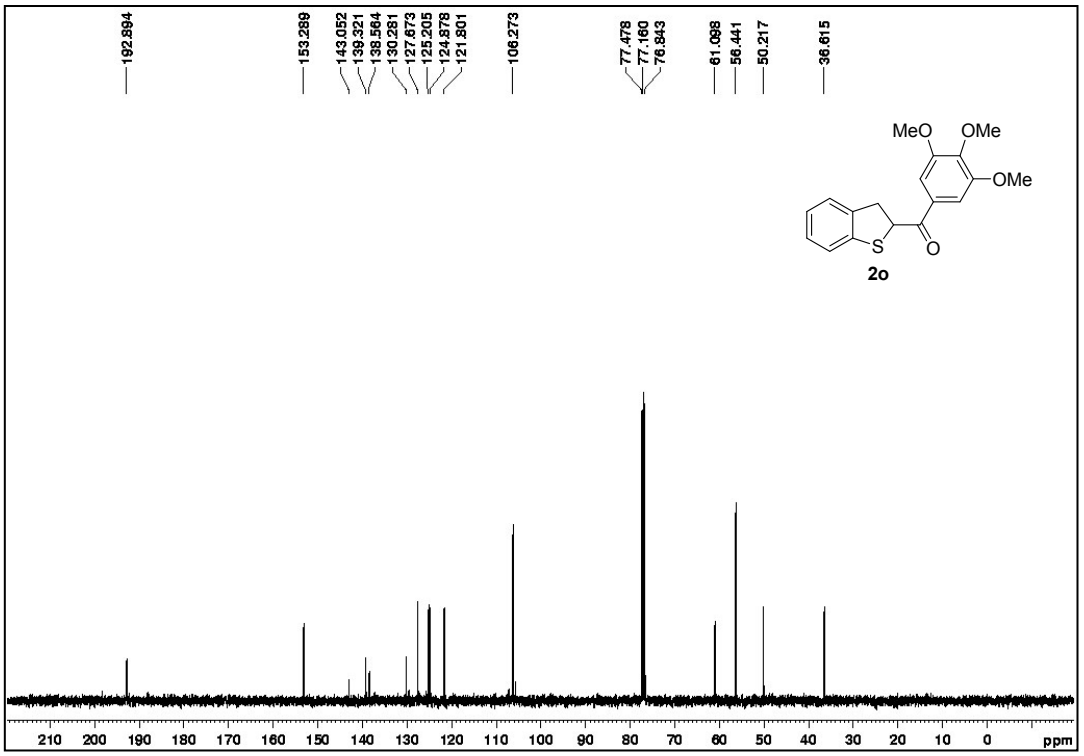


Figure 32: 100 MHz ^{13}CNMR spectrum of **2o** in $CDCl_3$

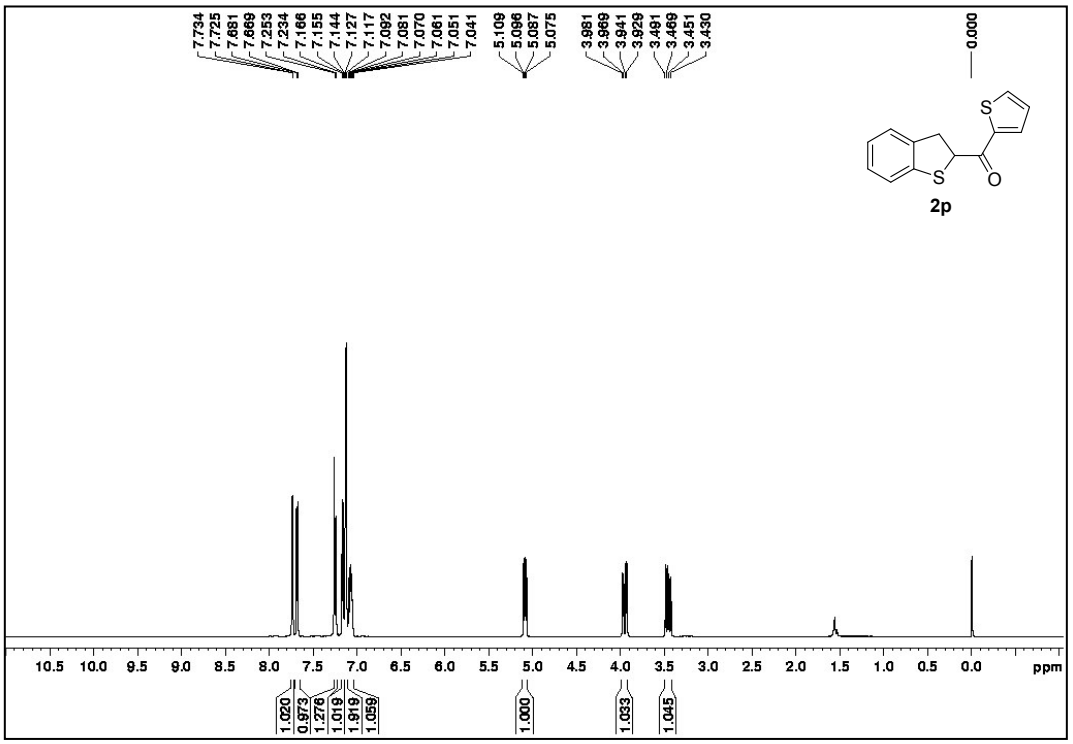


Figure 33: 400 MHz ^{1}HNMR spectrum of **2p** in $CDCl_3$

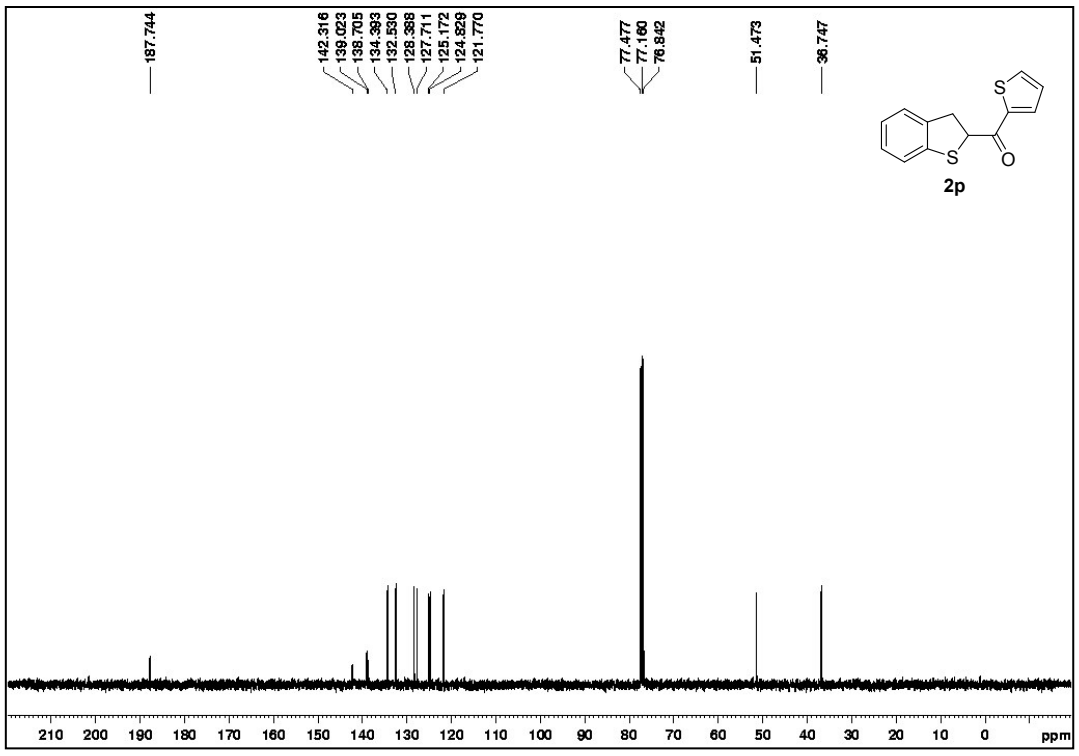


Figure 34: 100 MHz ^{13}CNMR spectrum of **2p** in $CDCl_3$

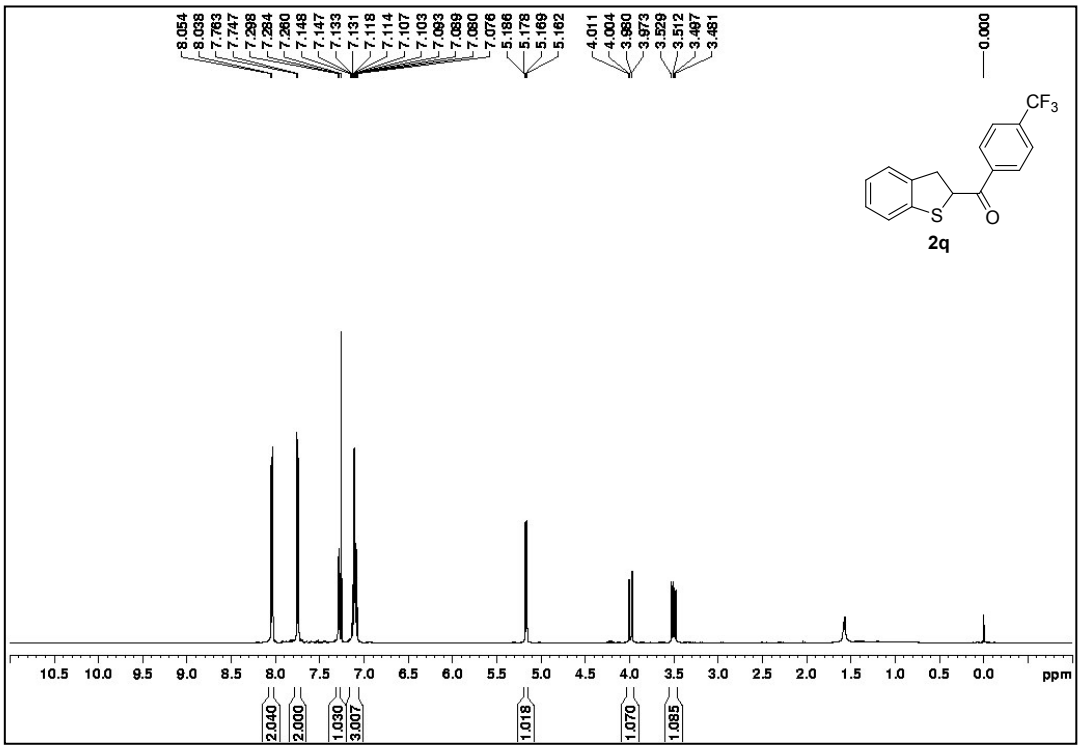


Figure 35: 500 MHz ^{1}HNMR spectrum of **2q** in $CDCl_3$

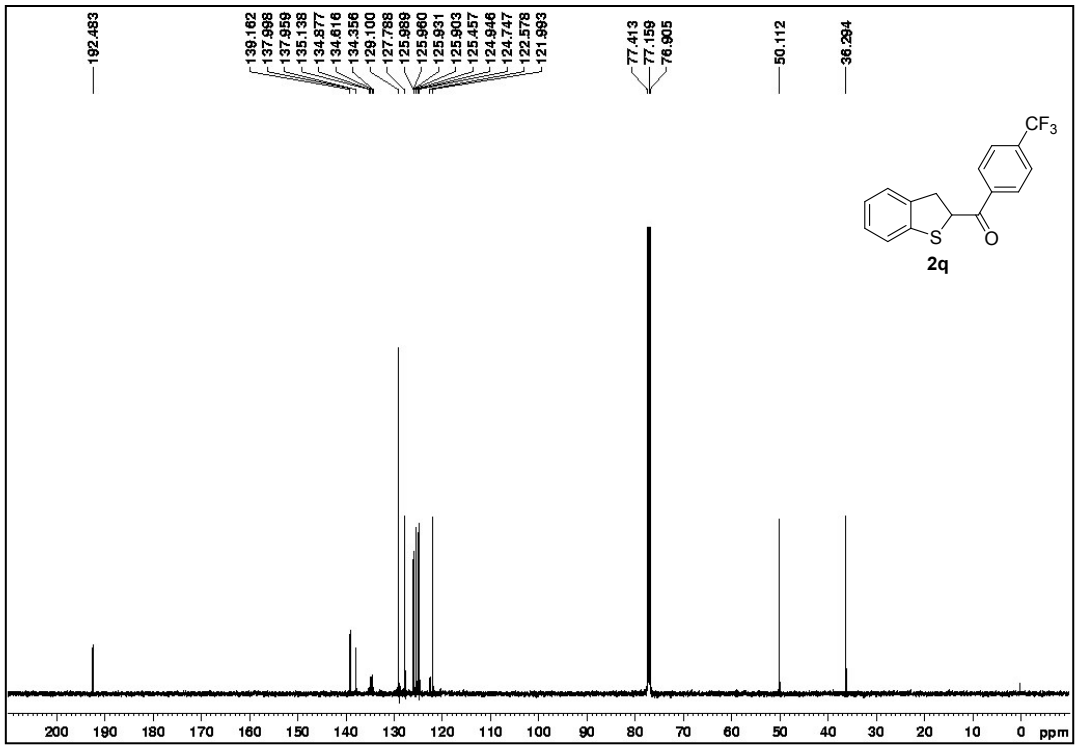


Figure 36: 125 MHz ^{13}CNMR spectrum of **2q** in $CDCl_3$

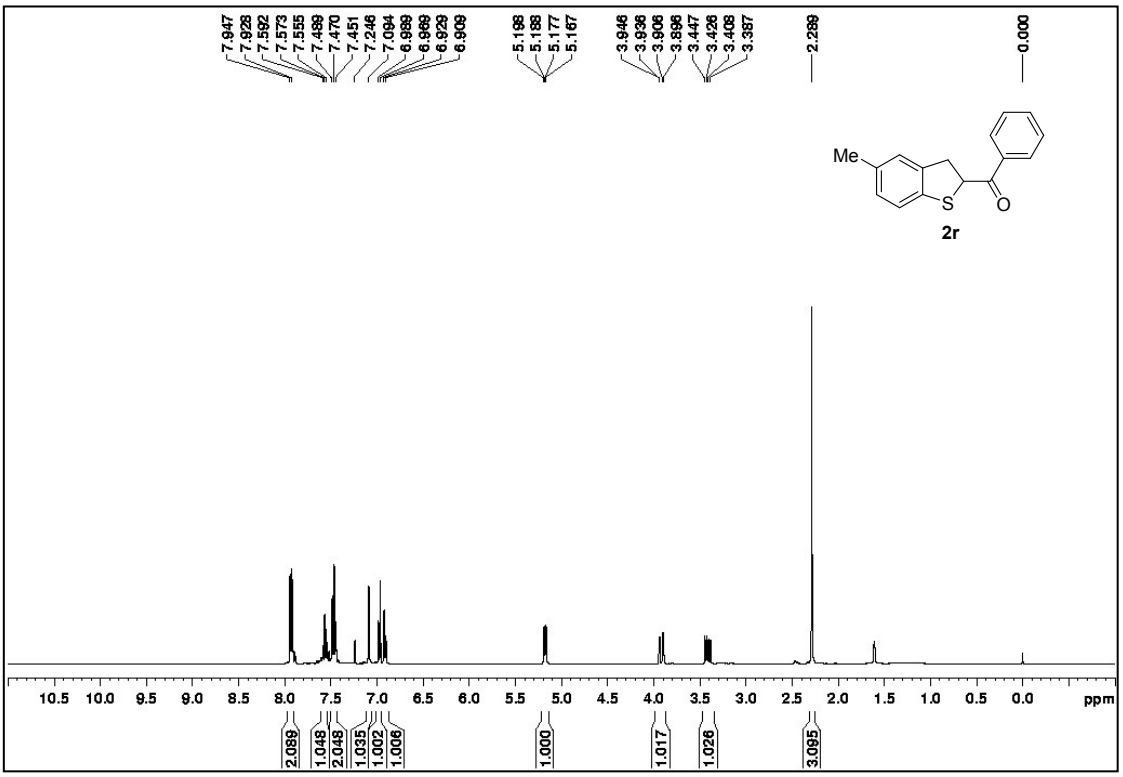


Figure 37: 400 MHz ^{1}HNMR spectrum of **2r** in $CDCl_3$

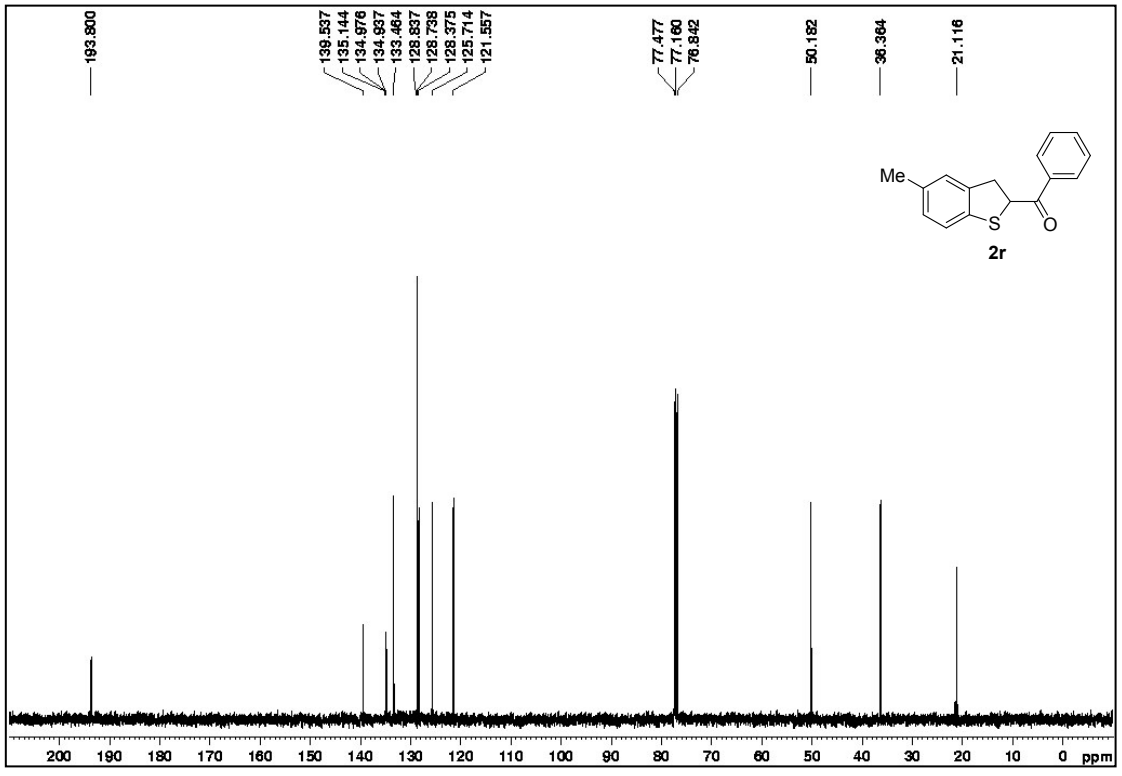


Figure 38: 100 MHz ^{13}CNMR spectrum of **2r** in $CDCl_3$

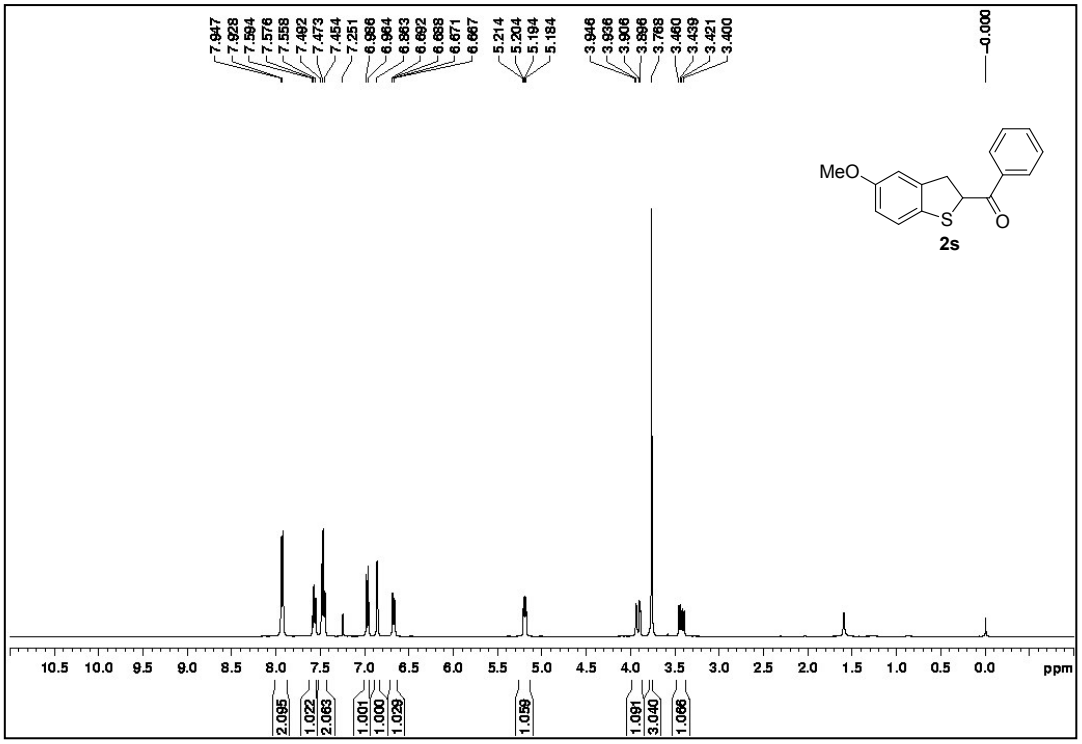


Figure 39: 400 MHz ^{1}HNMR spectrum of **2s** in $CDCl_3$

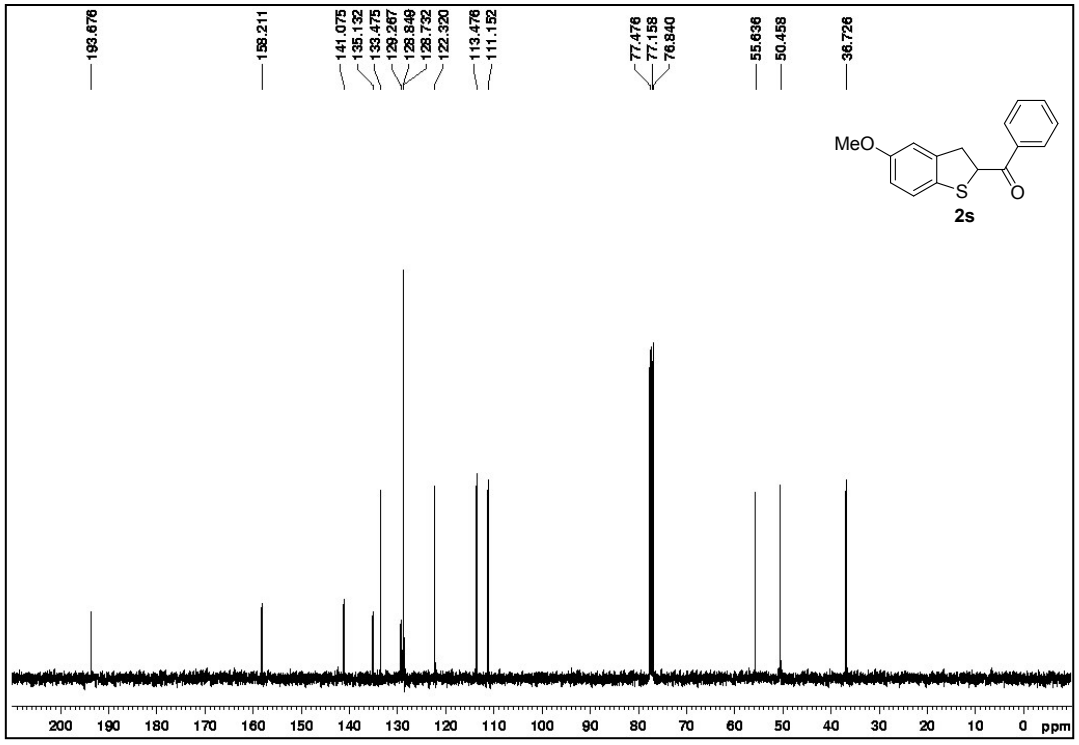


Figure 40: 100 MHz ^{13}CNMR spectrum of **2s** in $CDCl_3$

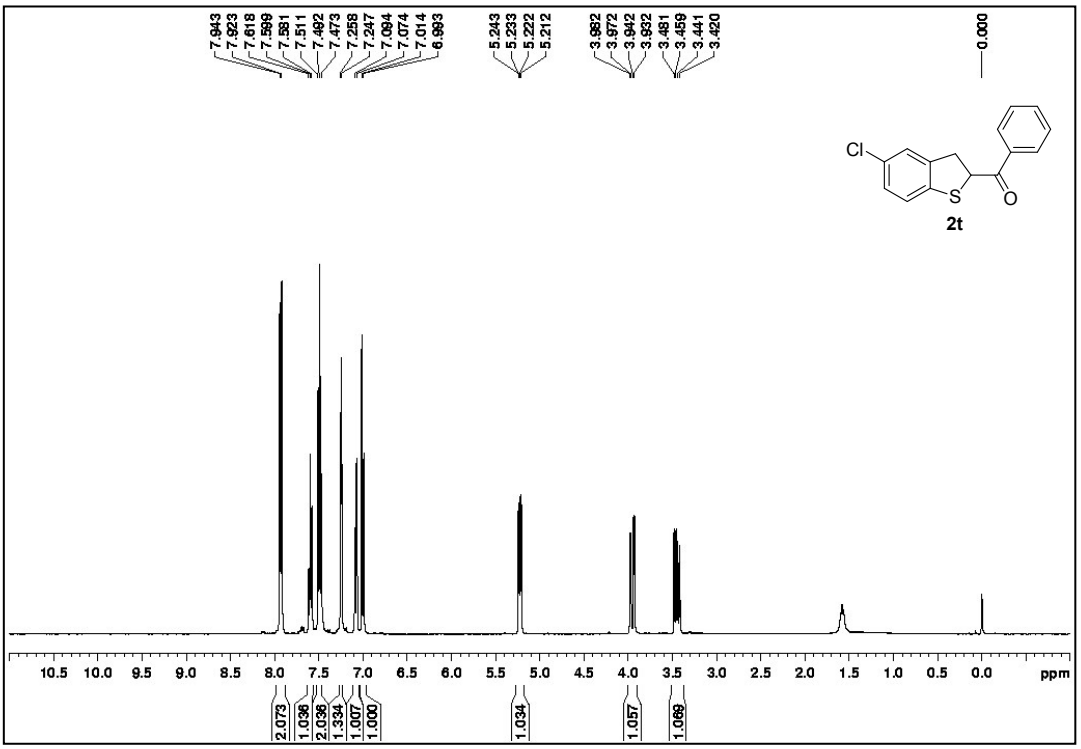


Figure 41: 400 MHz ^{1}HNMR spectrum of **2t** in $CDCl_3$

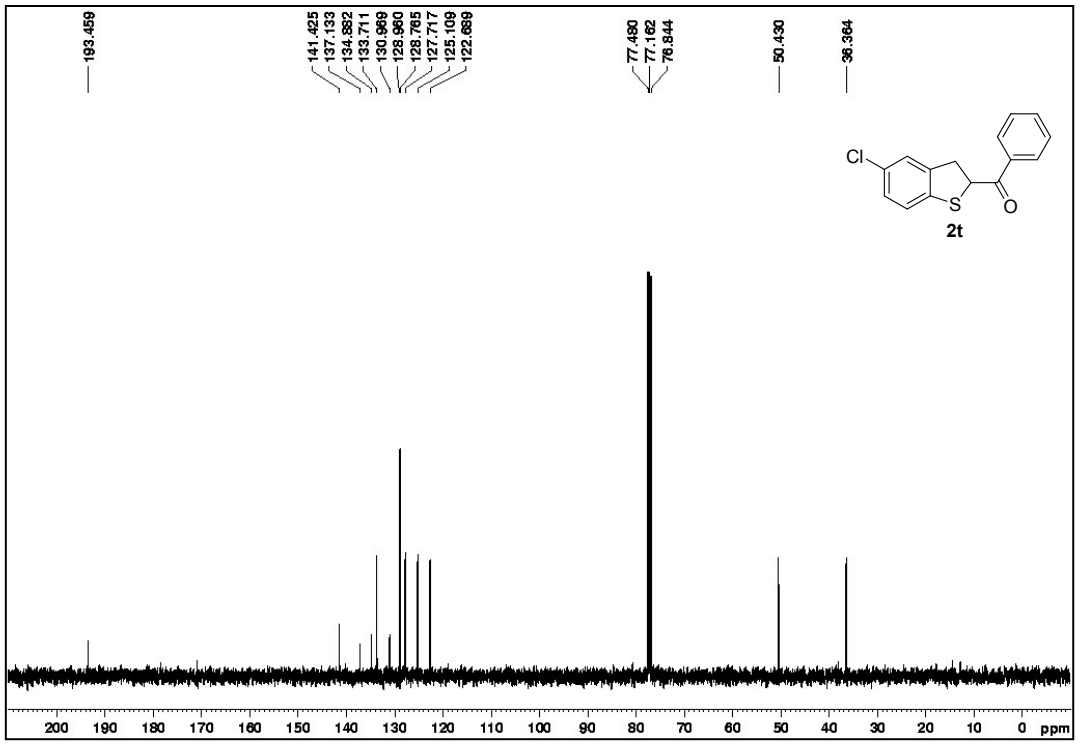


Figure 42: 100 MHz ^{13}CNMR spectrum of **2t** in $CDCl_3$

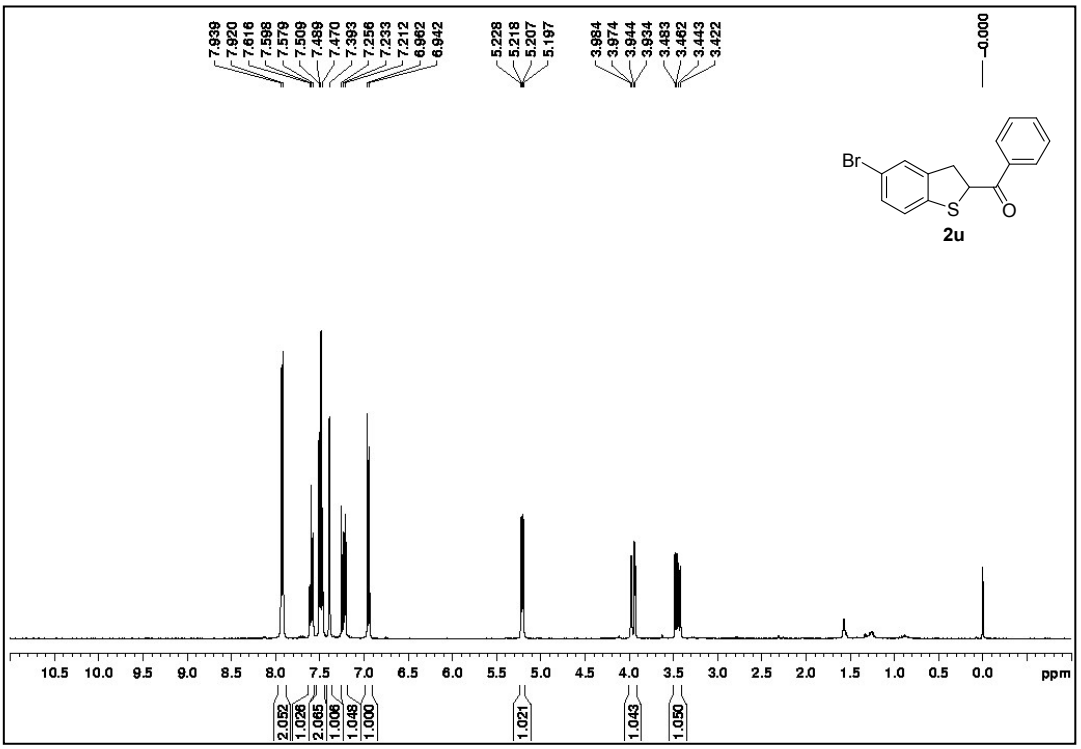


Figure 43: 400 MHz ^{1}HNMR spectrum of **2u** in $CDCl_3$

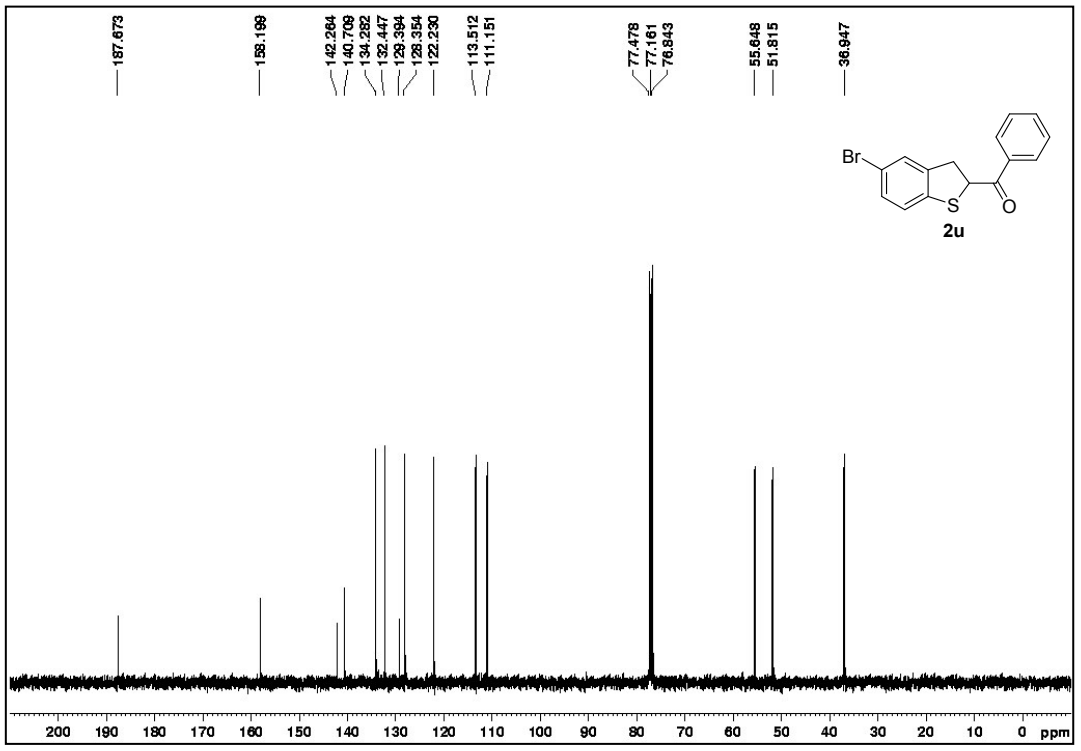


Figure 44: 100 MHz ^{13}CNMR spectrum of **2u** in $CDCl_3$

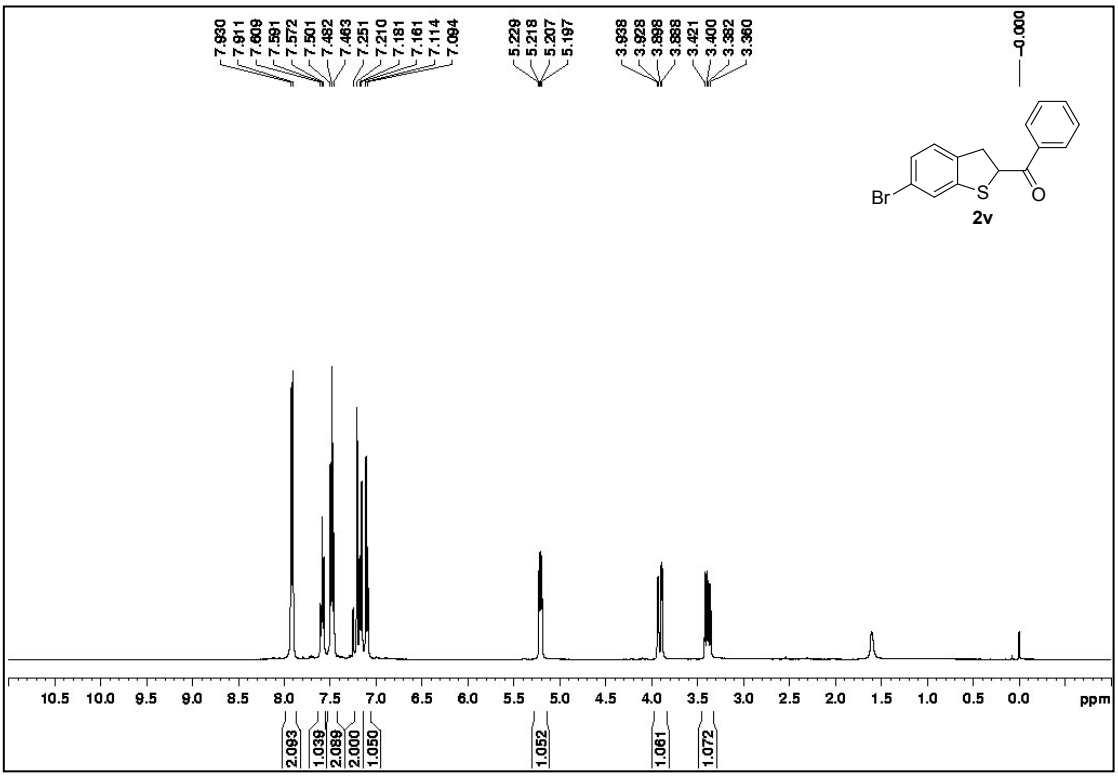


Figure 45: 400 MHz ^{1}HNMR spectrum of **2v** in $CDCl_3$

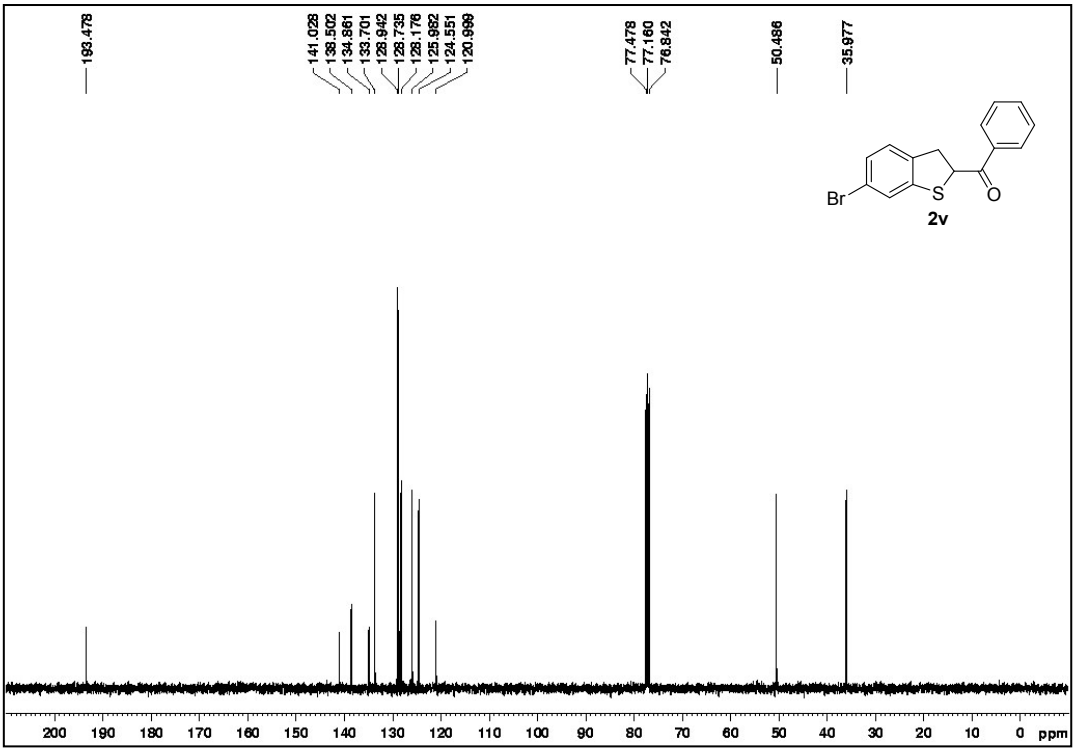


Figure 46: 100 MHz ^{13}CNMR spectrum of **2v** in $CDCl_3$

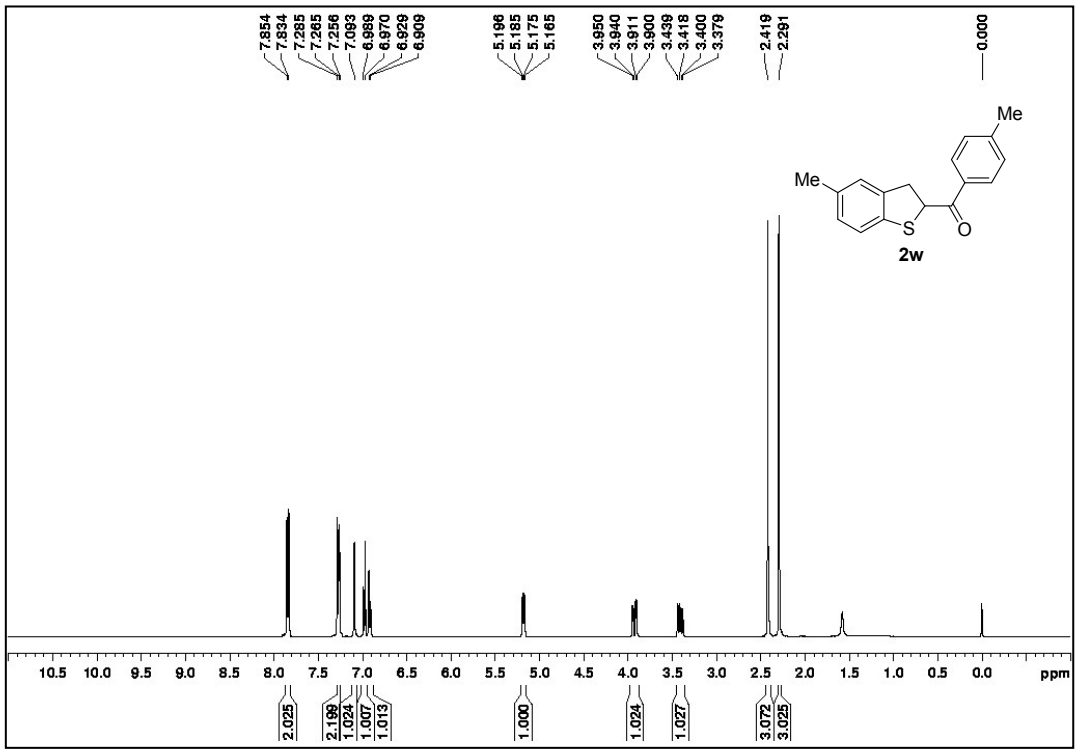


Figure 47: 400 MHz ^{1}HNMR spectrum of **2w** in $CDCl_3$

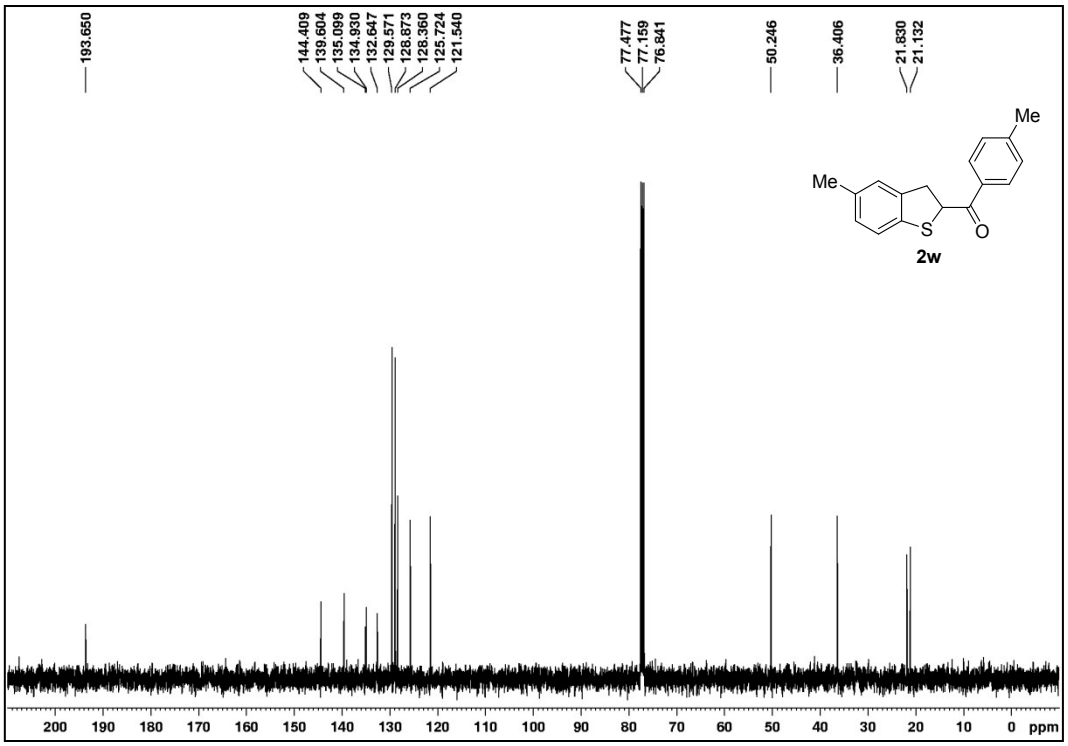


Figure 48: 100 MHz ^{13}CNMR spectrum of **2w** in $CDCl_3$

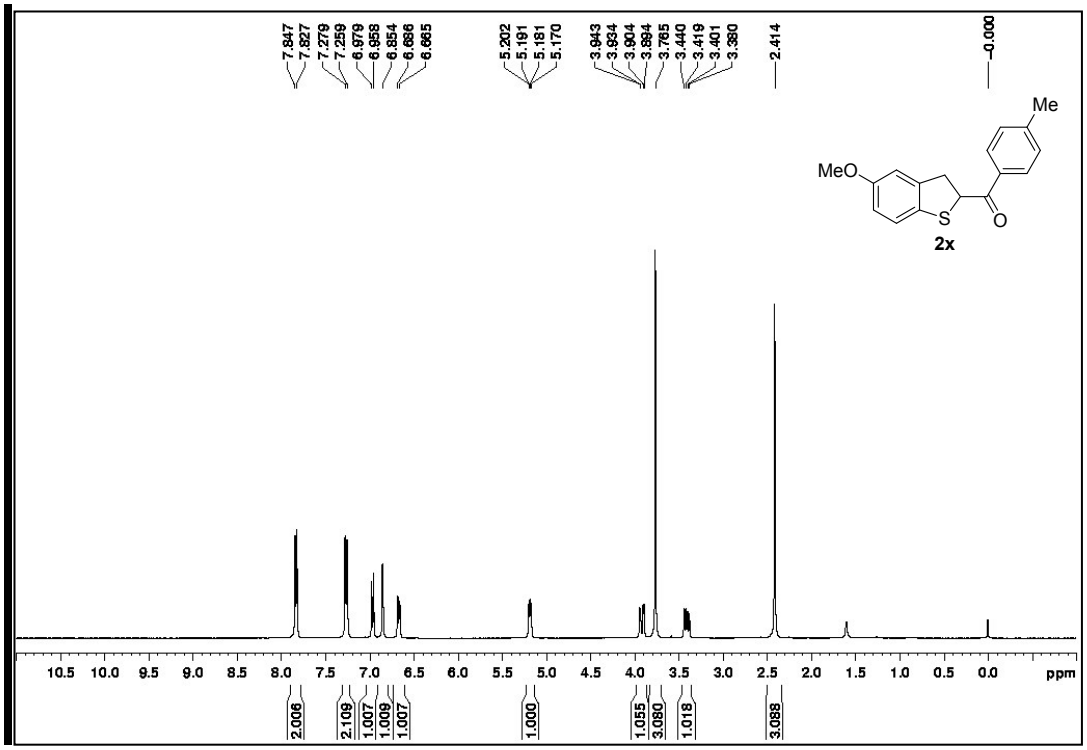


Figure 49: 400 MHz ^{1}HNMR spectrum of **2x** in $CDCl_3$

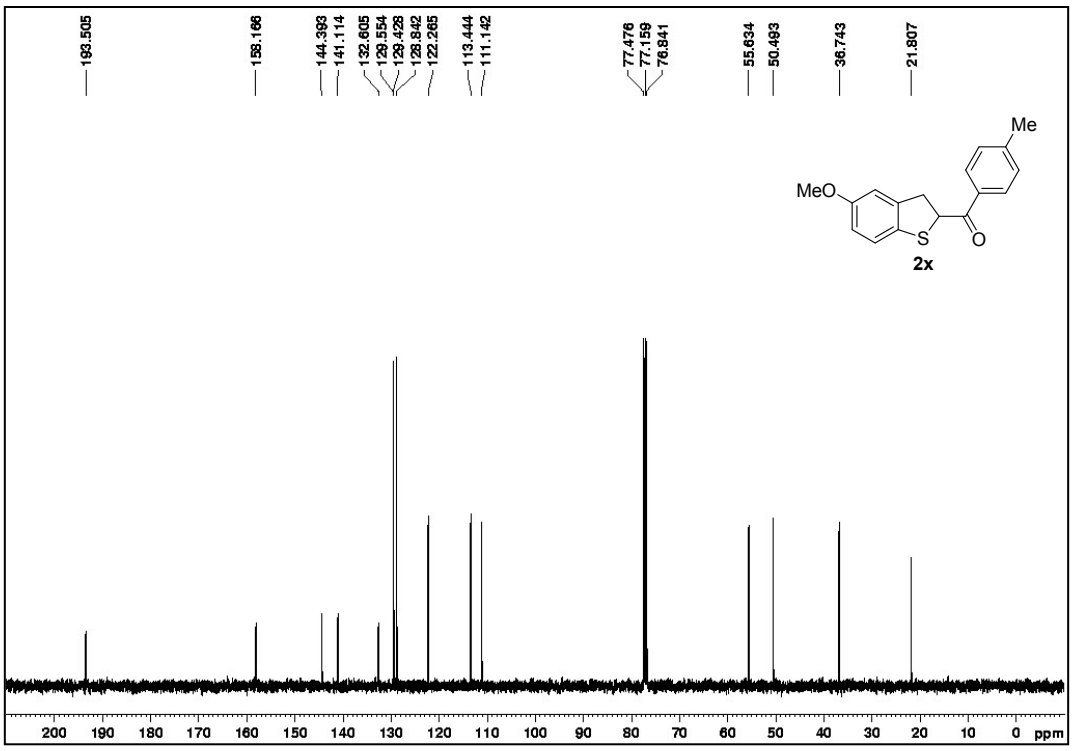


Figure 50: 100 MHz ^{13}CNMR spectrum of **2x** in $CDCl_3$

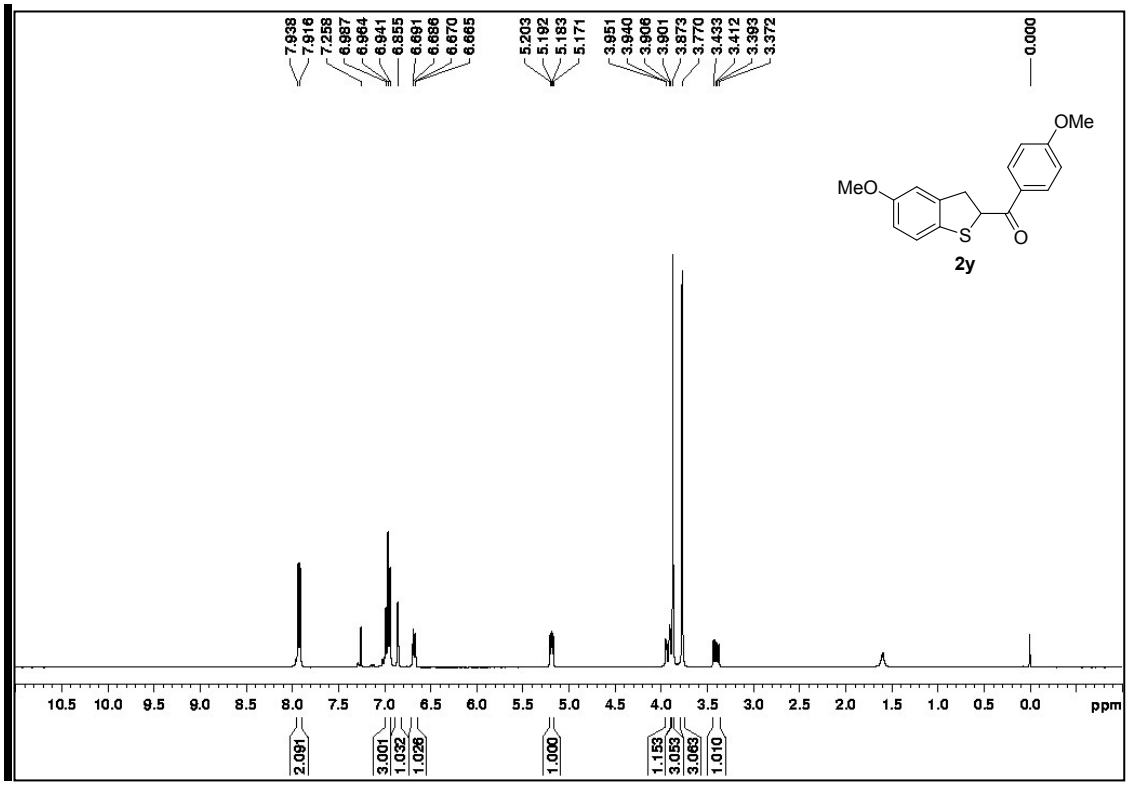


Figure 51: 400 MHz ^{1}HNMR spectrum of **2y** in $CDCl_3$

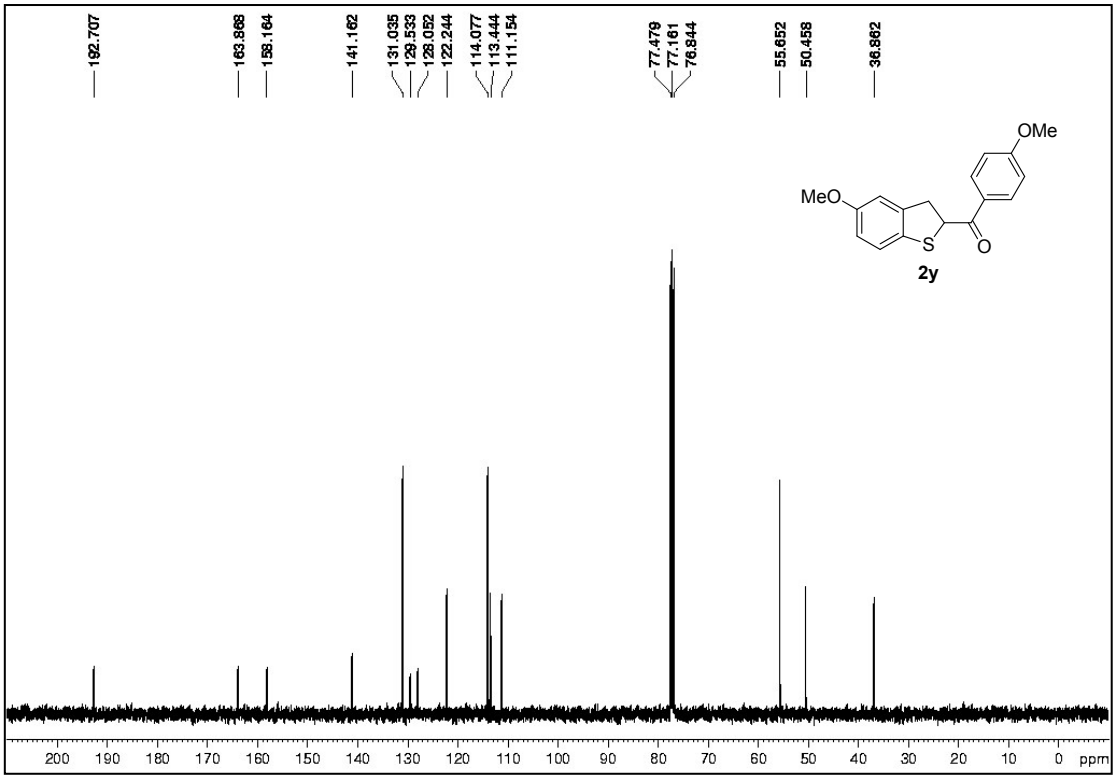


Figure 52: 100 MHz ^{13}CNMR spectrum of **2y** in $CDCl_3$

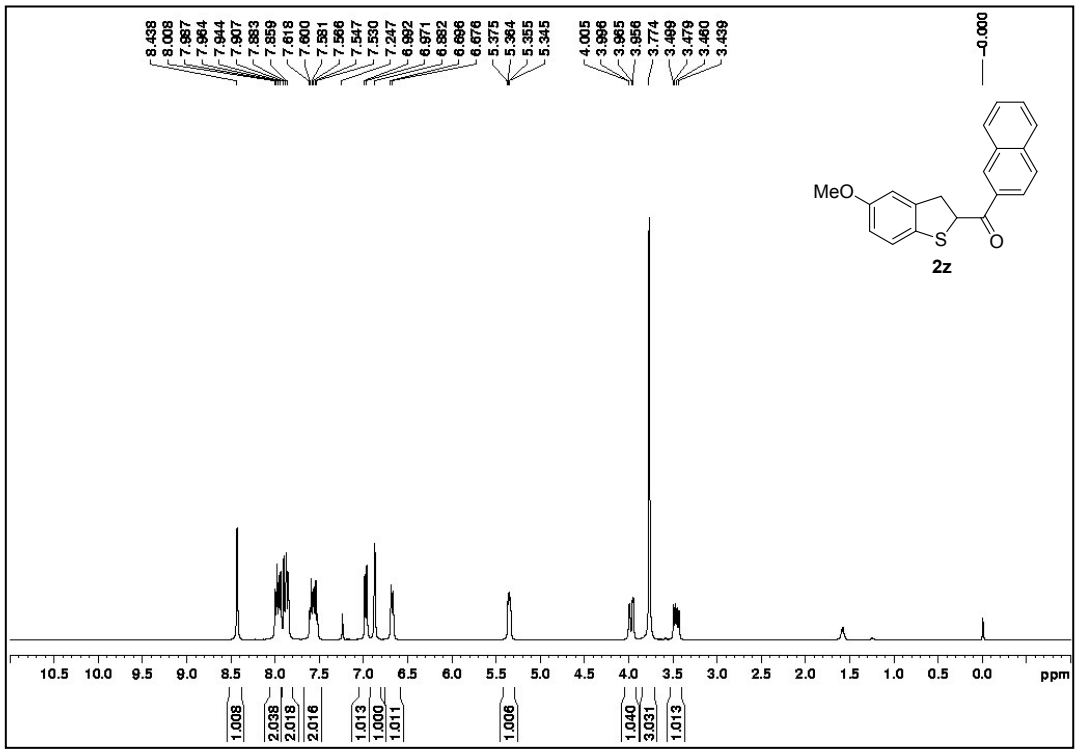


Figure 53: 400 MHz ^{1}HNMR spectrum of **2z** in $CDCl_3$

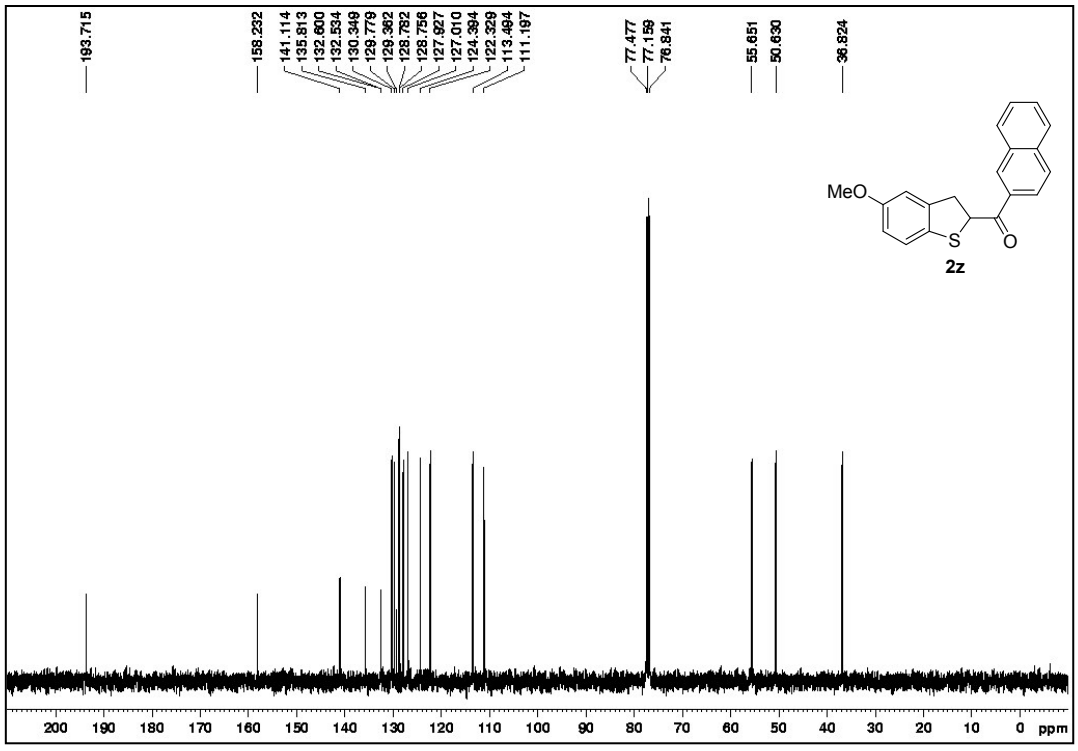


Figure 54: 100 MHz ^{13}CNMR spectrum of **2z** in $CDCl_3$

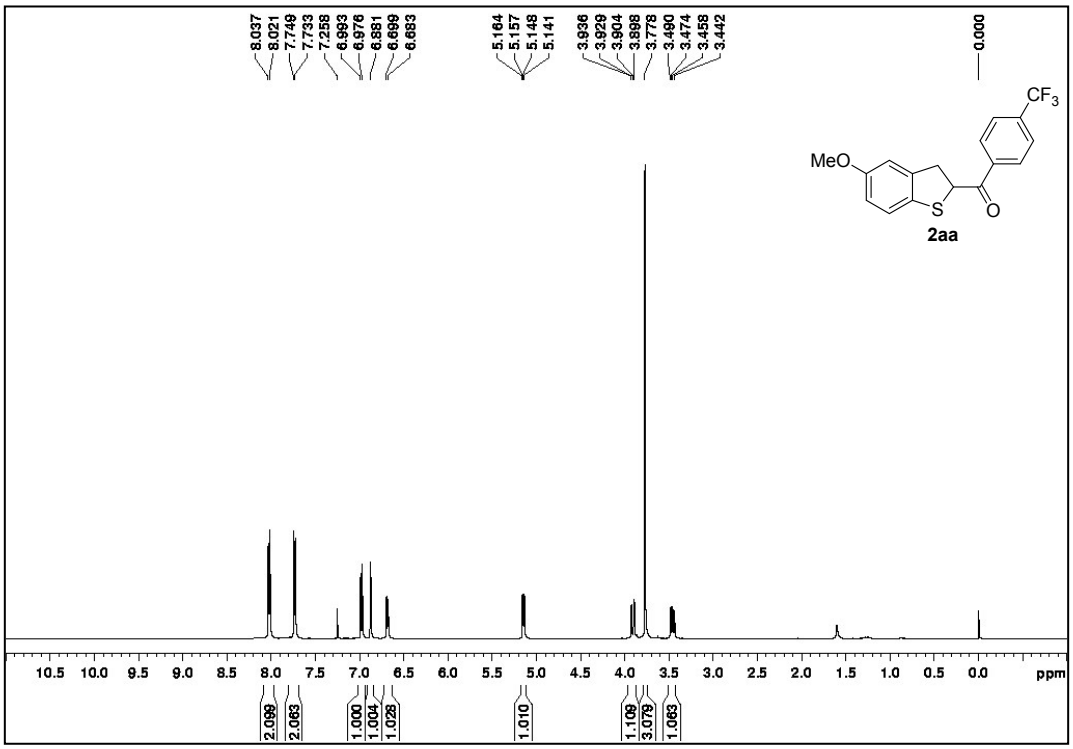


Figure 55: 500 MHz ^{1}HNMR spectrum of **2aa** in $CDCl_3$

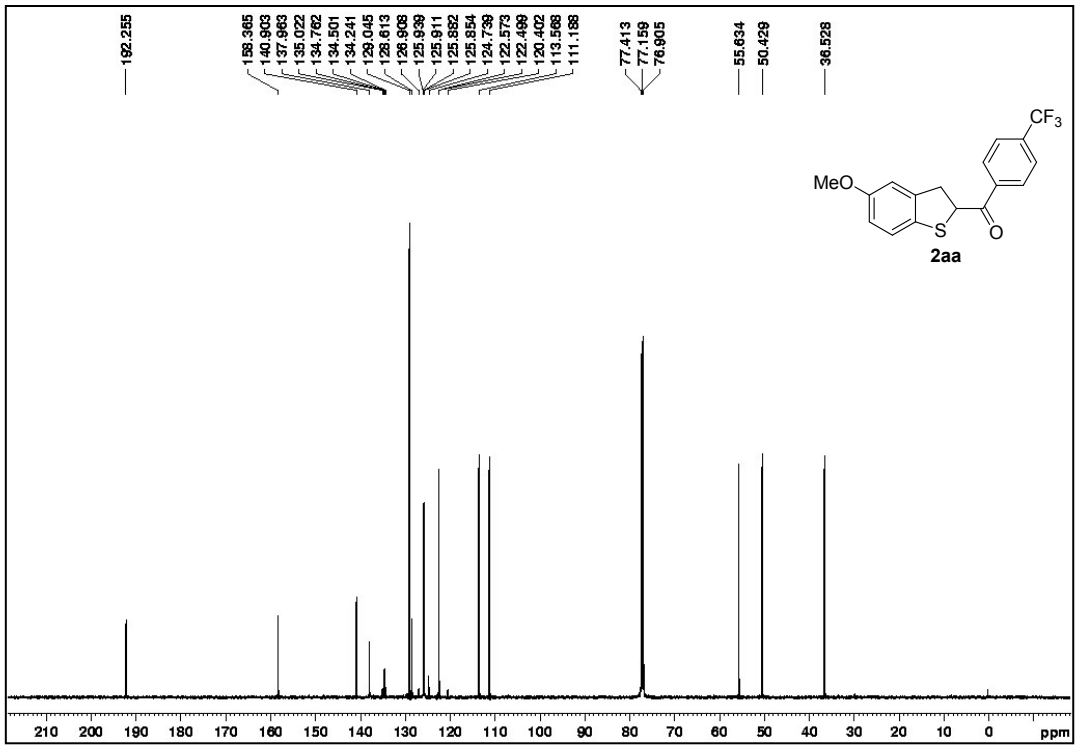


Figure 56: 125 MHz ^{13}CNMR spectrum of **2aa** in $CDCl_3$

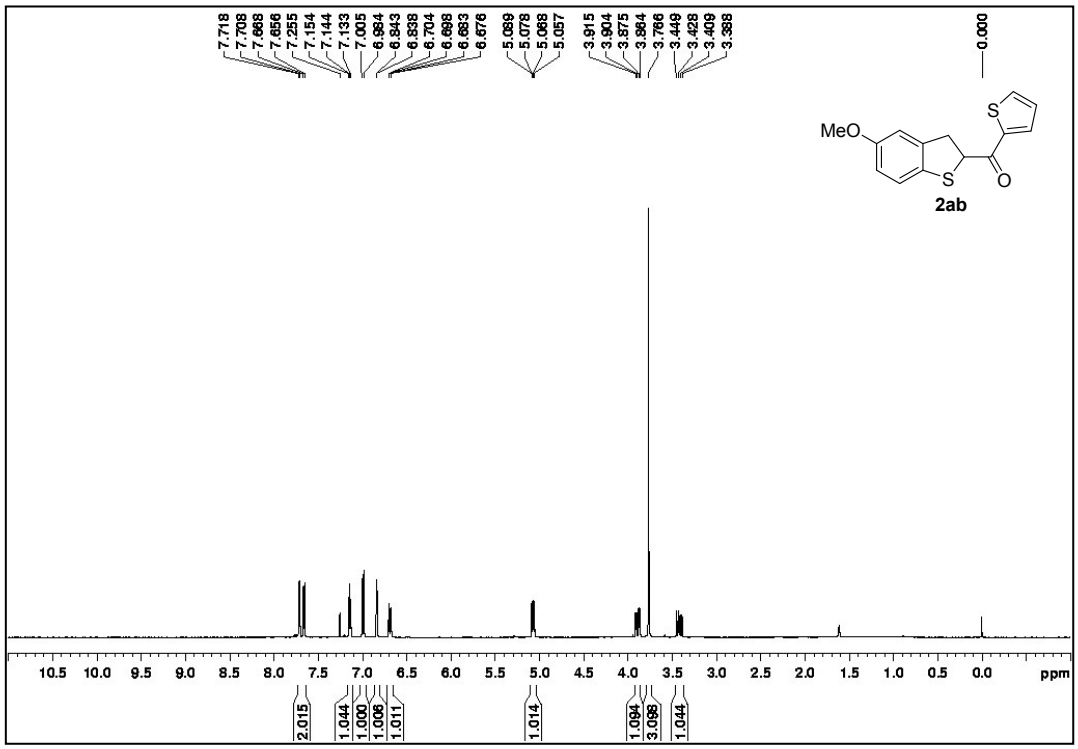


Figure 57: 400 MHz ^{1}HNMR spectrum of **2ab** in $CDCl_3$

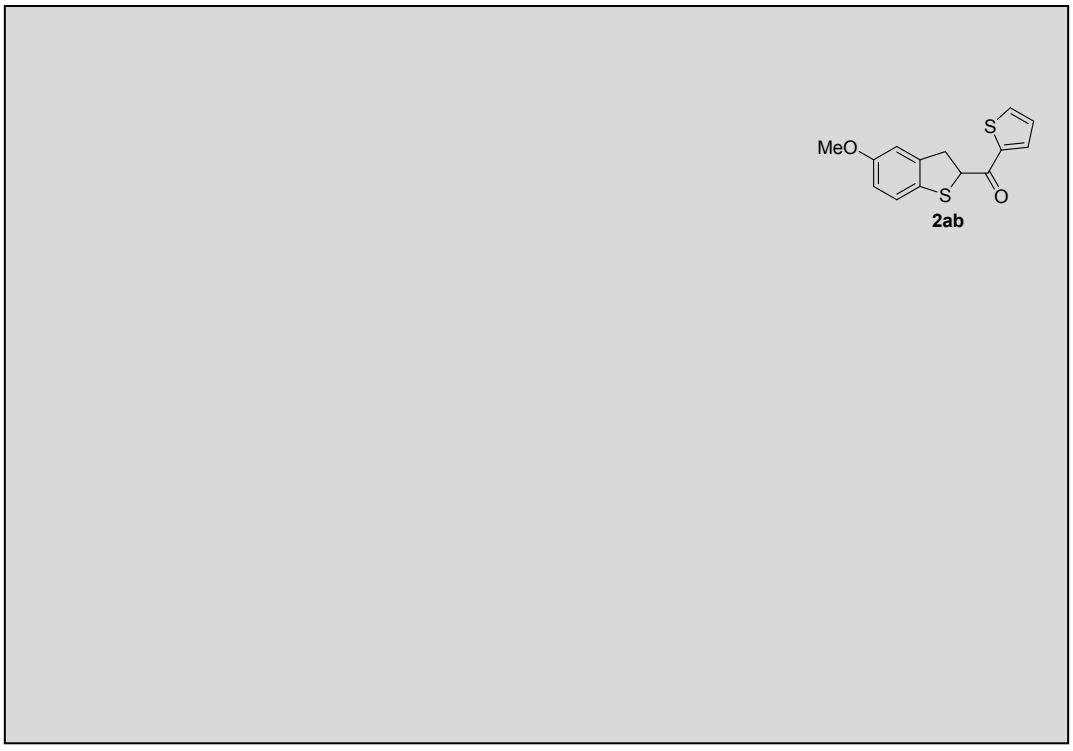


Figure 58: 100 MHz ^{13}CNMR spectrum of **2ab** in $CDCl_3$

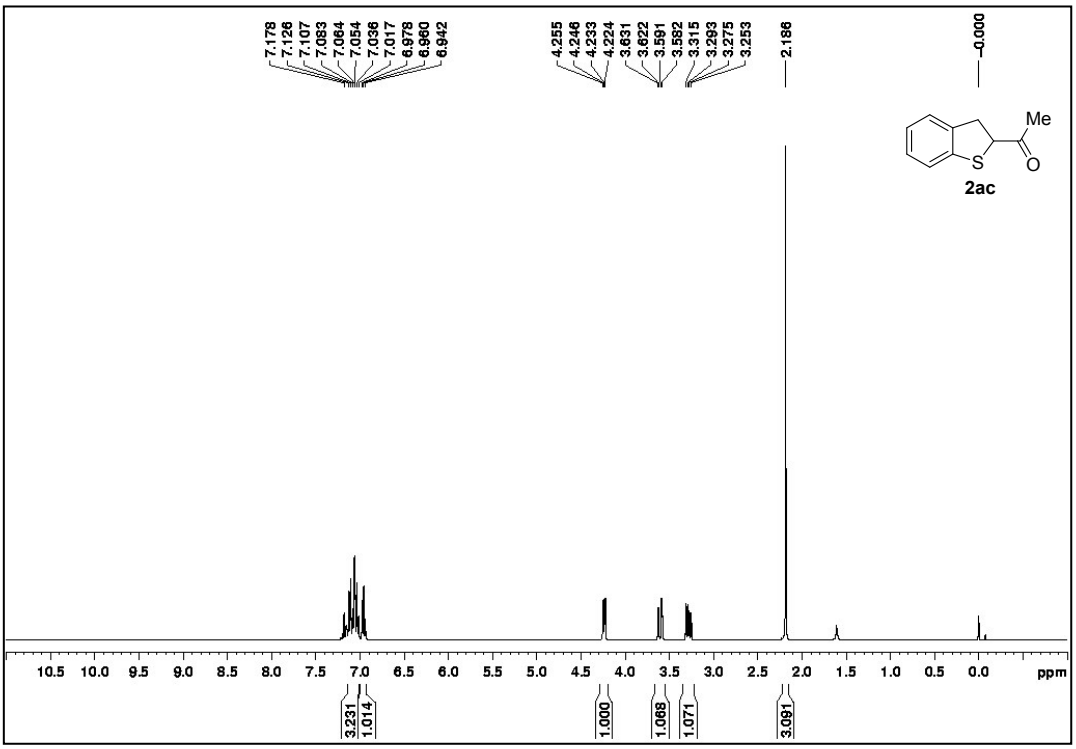


Figure 59: 400 MHz ^{1}HNMR spectrum of **2ac** in $CDCl_3$

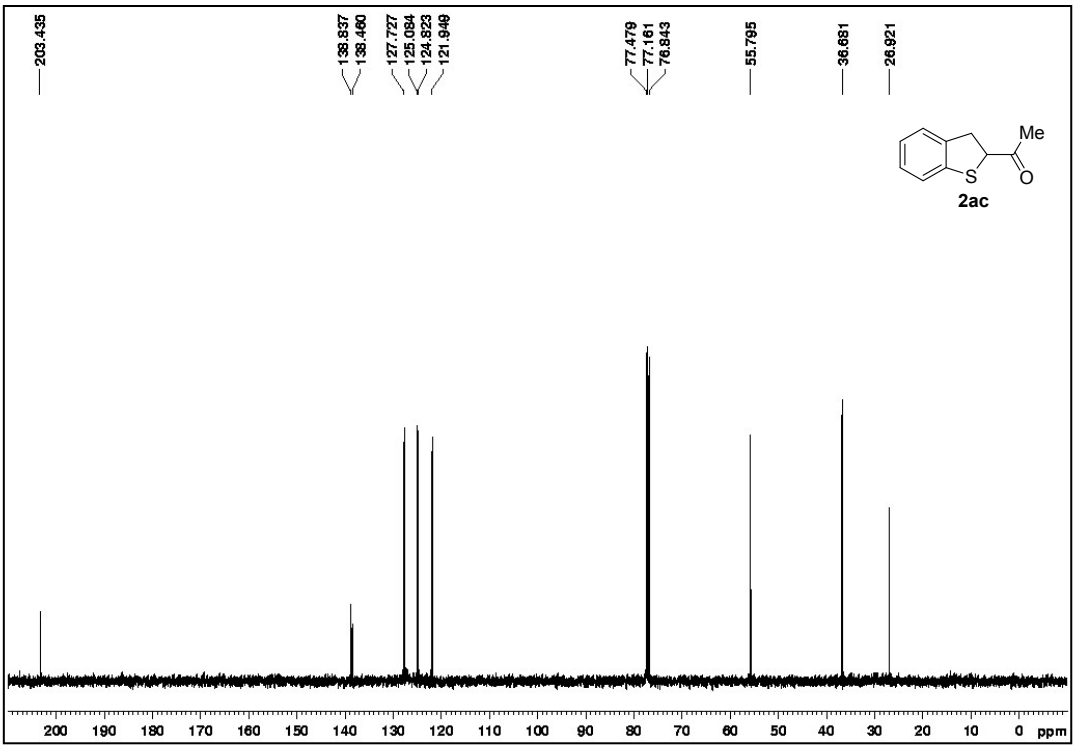


Figure 60: 100 MHz ^{13}CNMR spectrum of **2ac** in $CDCl_3$

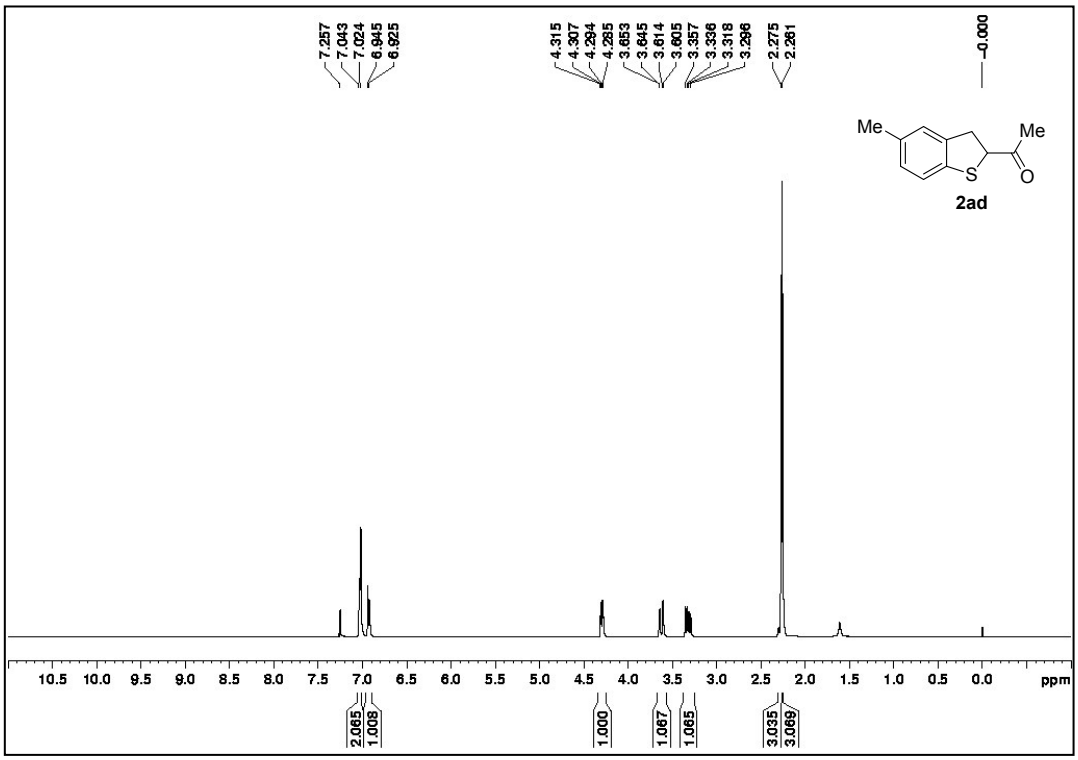


Figure 61:400 MHz ^{1}HNMR spectrum of **2ad** in $CDCl_3$

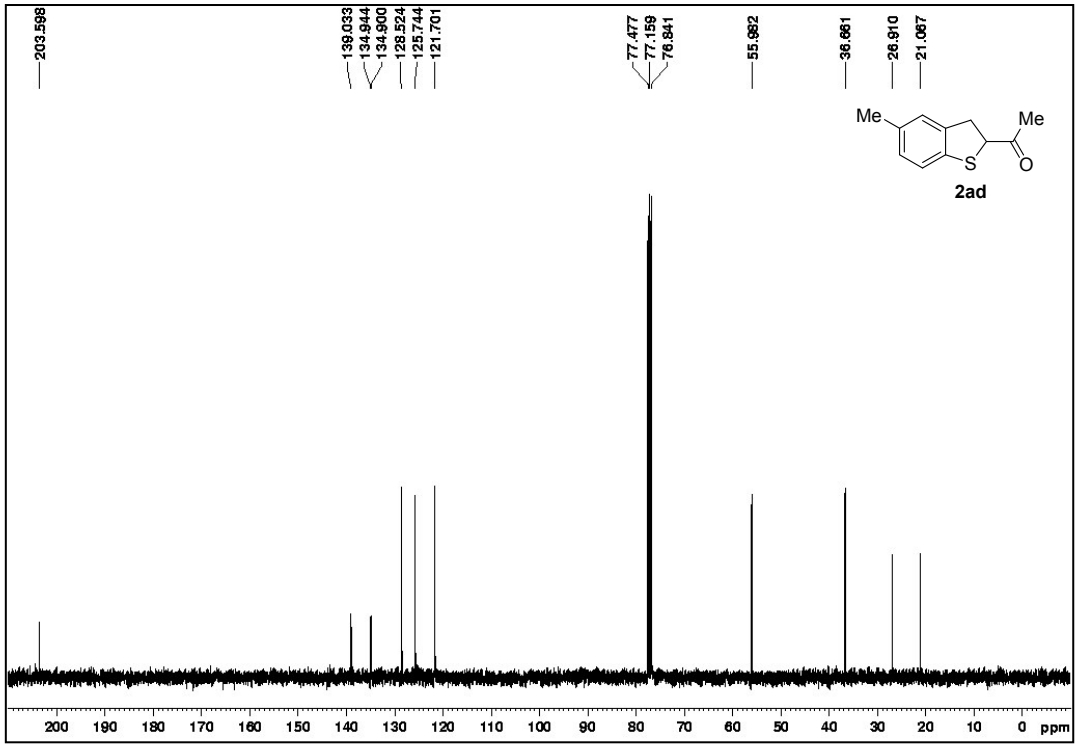


Figure 62:100 MHz ^{13}CNMR spectrum of **2ad** in $CDCl_3$

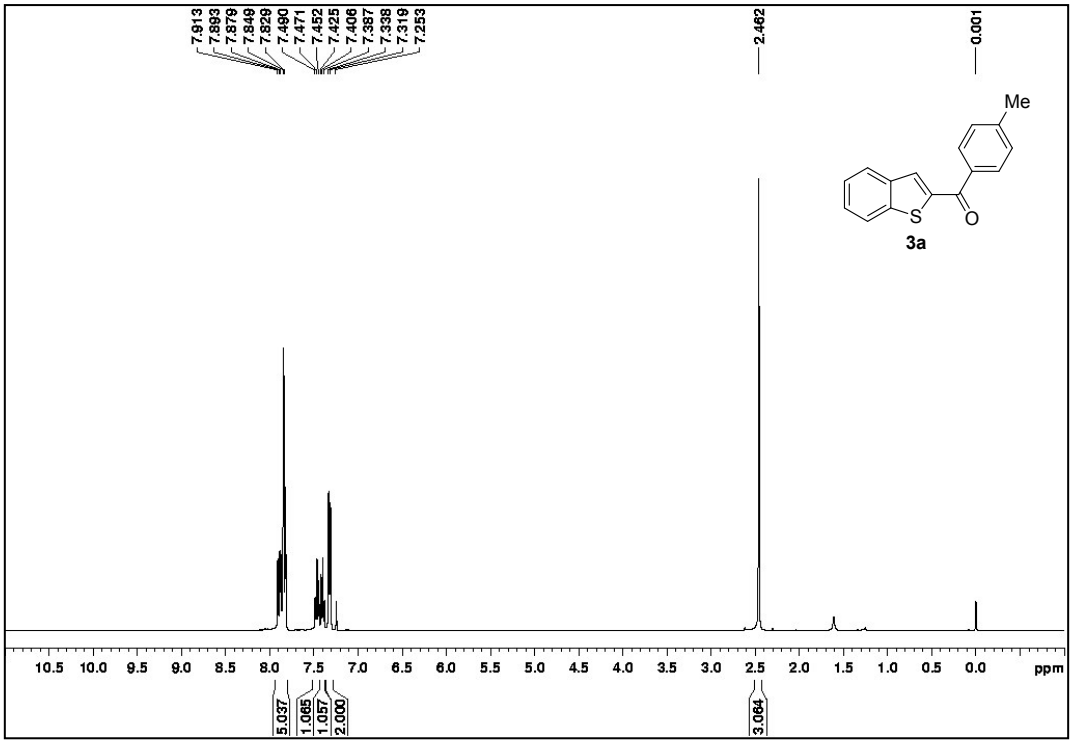


Figure 63:400 MHz ^{1}HNMR spectrum of **3a** in $CDCl_3$

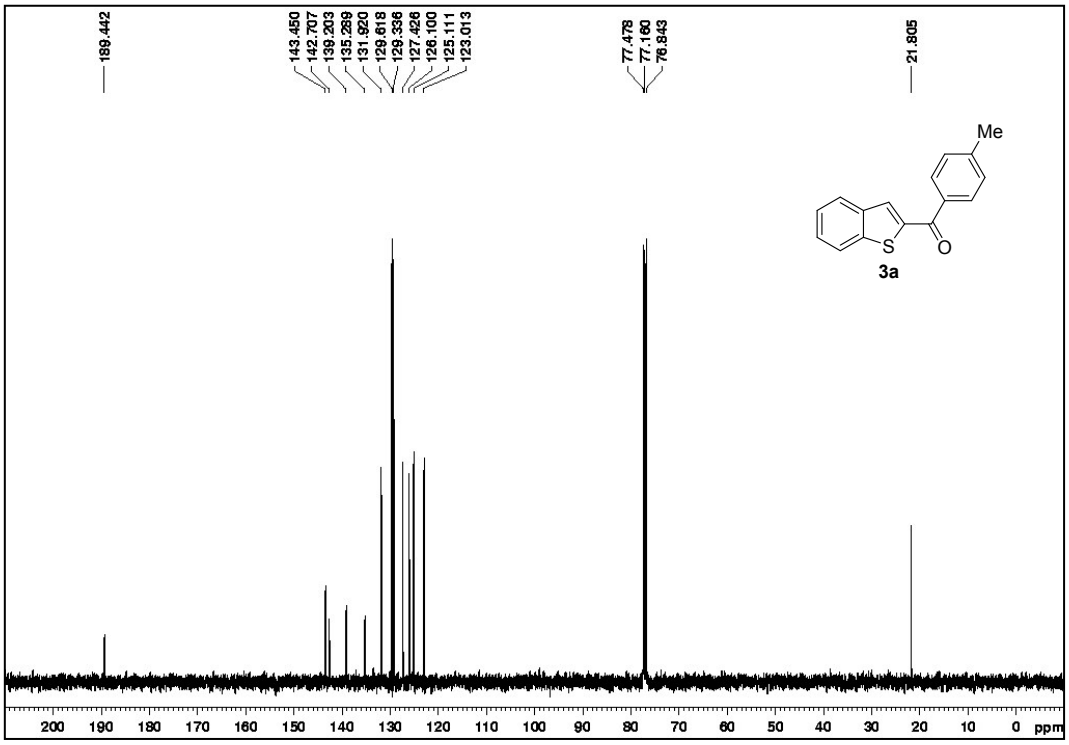


Figure 64:100 MHz ^{13}CNMR spectrum of **3a** in $CDCl_3$

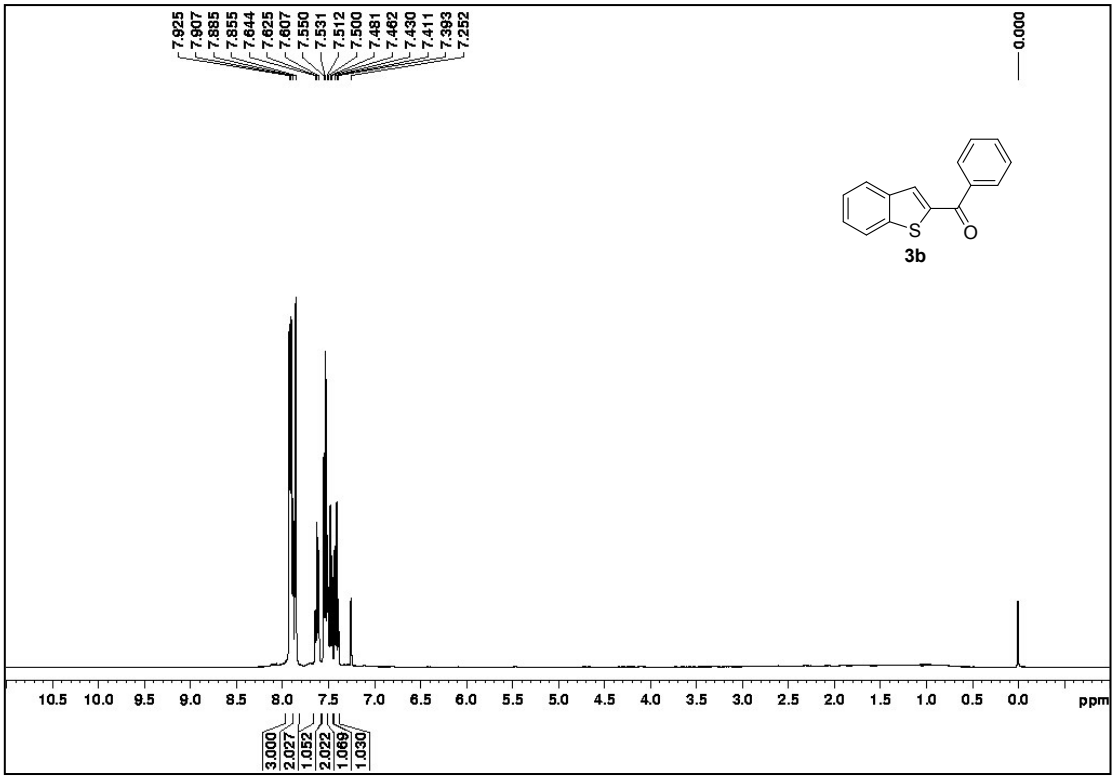


Figure 65:400 MHz ^{1}HNMR spectrum of **3b** in $CDCl_3$

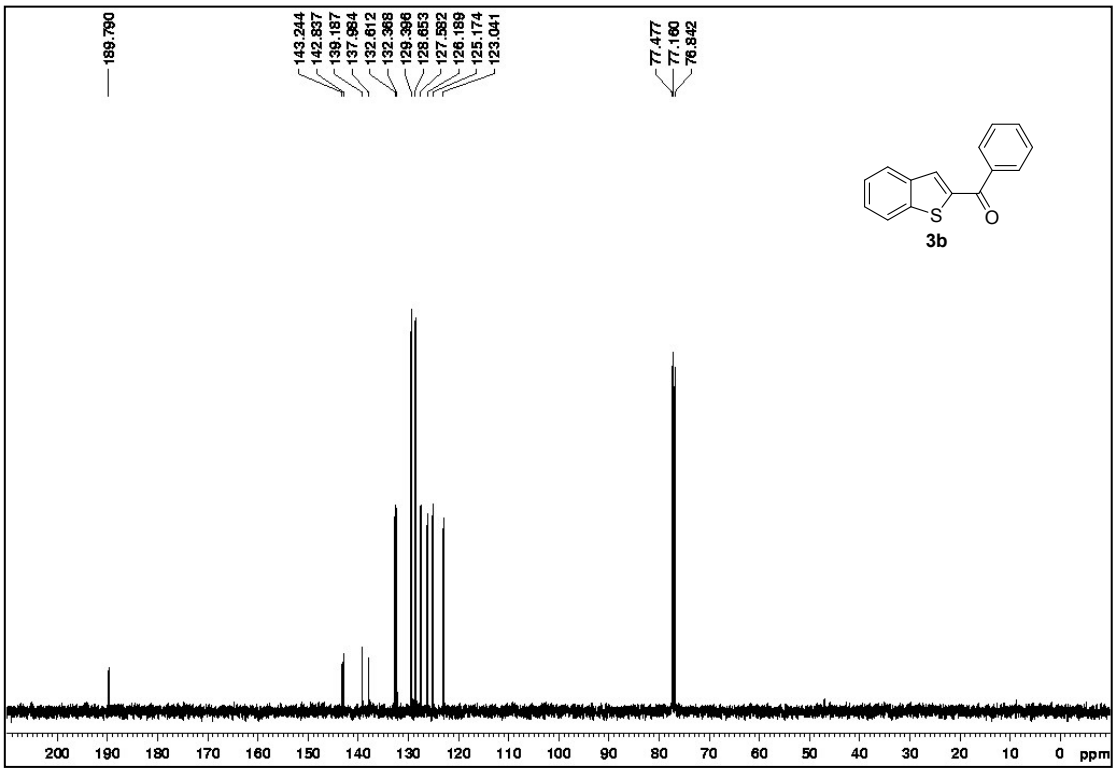


Figure 66:100 MHz ^{13}CNMR spectrum of **3b** in $CDCl_3$

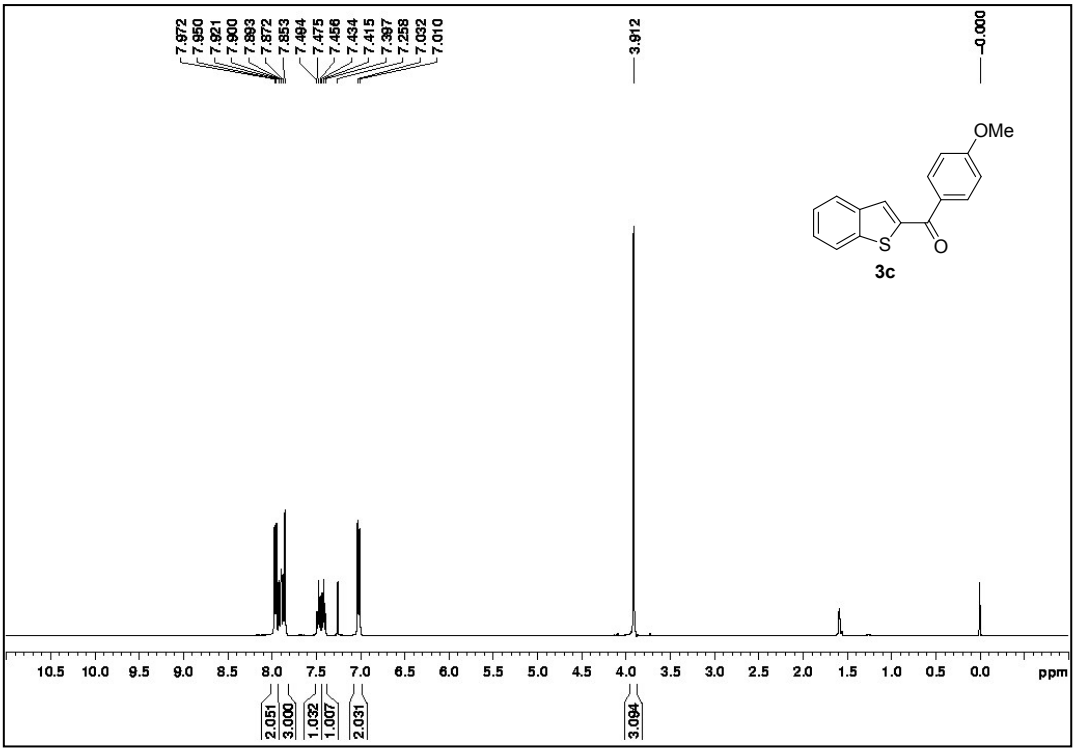


Figure 67:400 MHz ^{1}HNMR spectrum of **3c** in $CDCl_3$

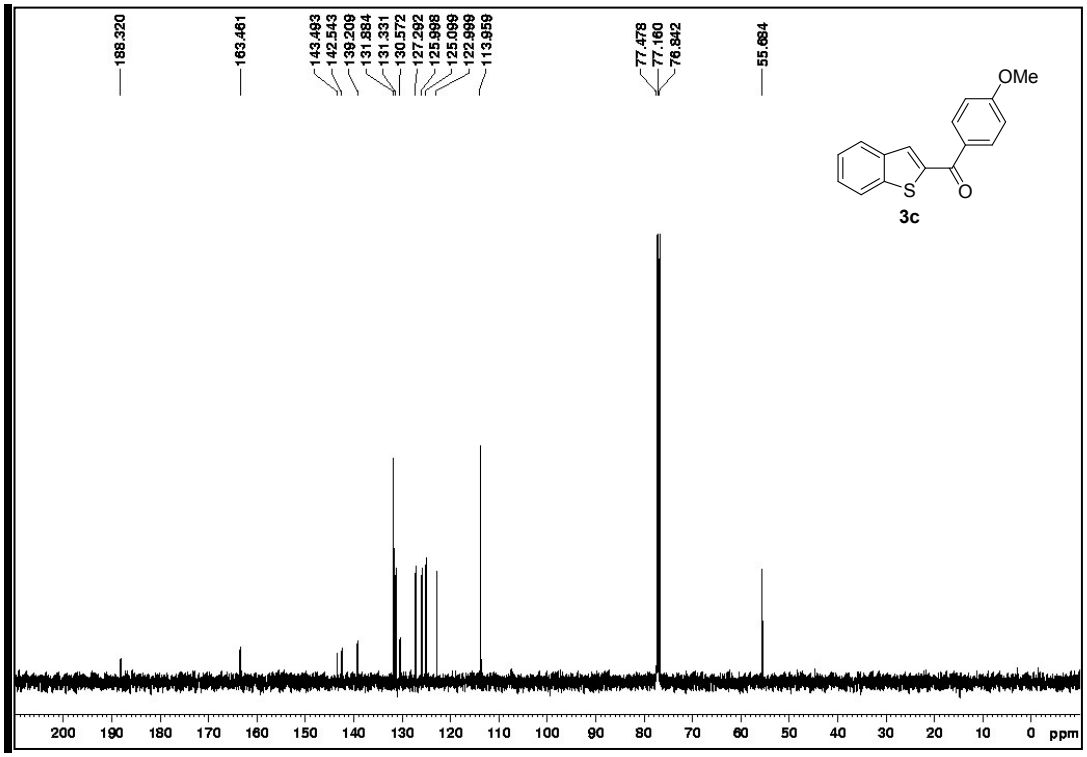


Figure 68:100 MHz ^{13}CNMR spectrum of **3c** in $CDCl_3$

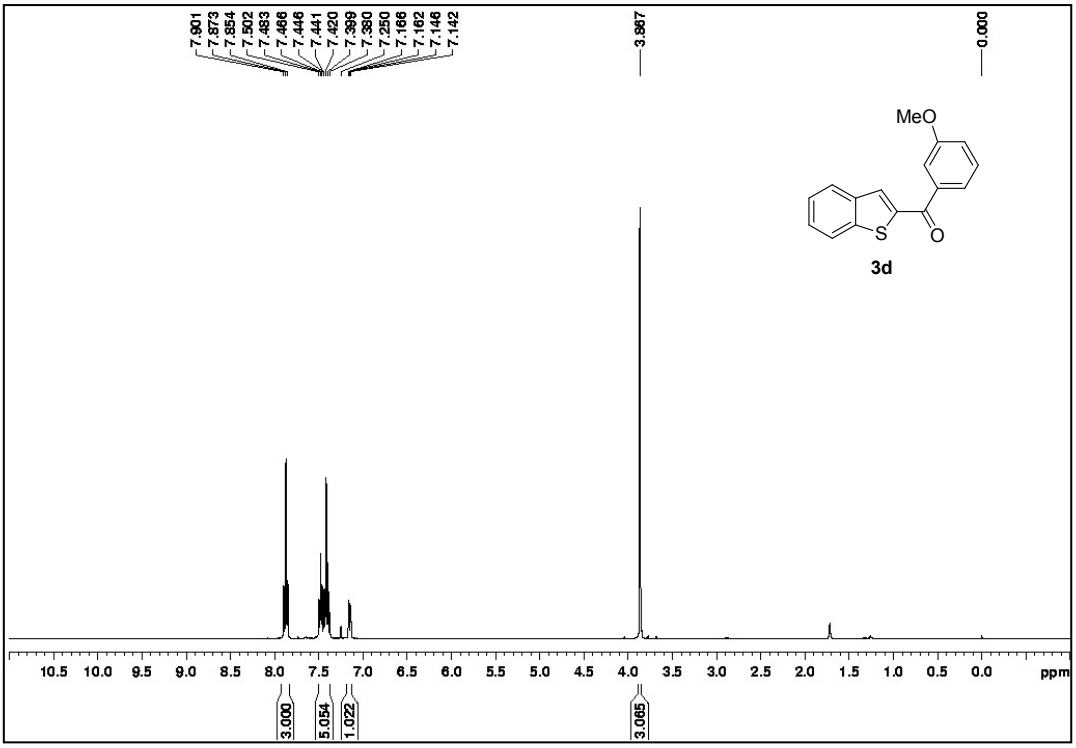


Figure 69:400 MHz ^{1}HNMR spectrum of **3d** in $CDCl_3$

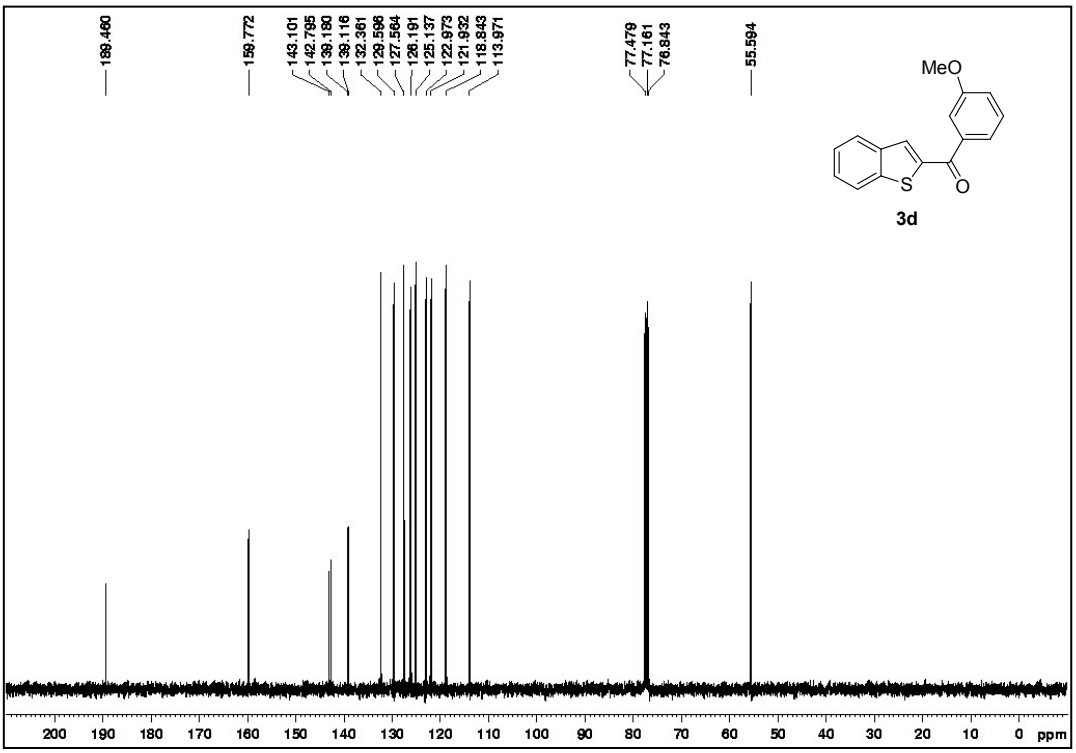


Figure 70:100 MHz ^{13}CNMR spectrum of **3d** in $CDCl_3$

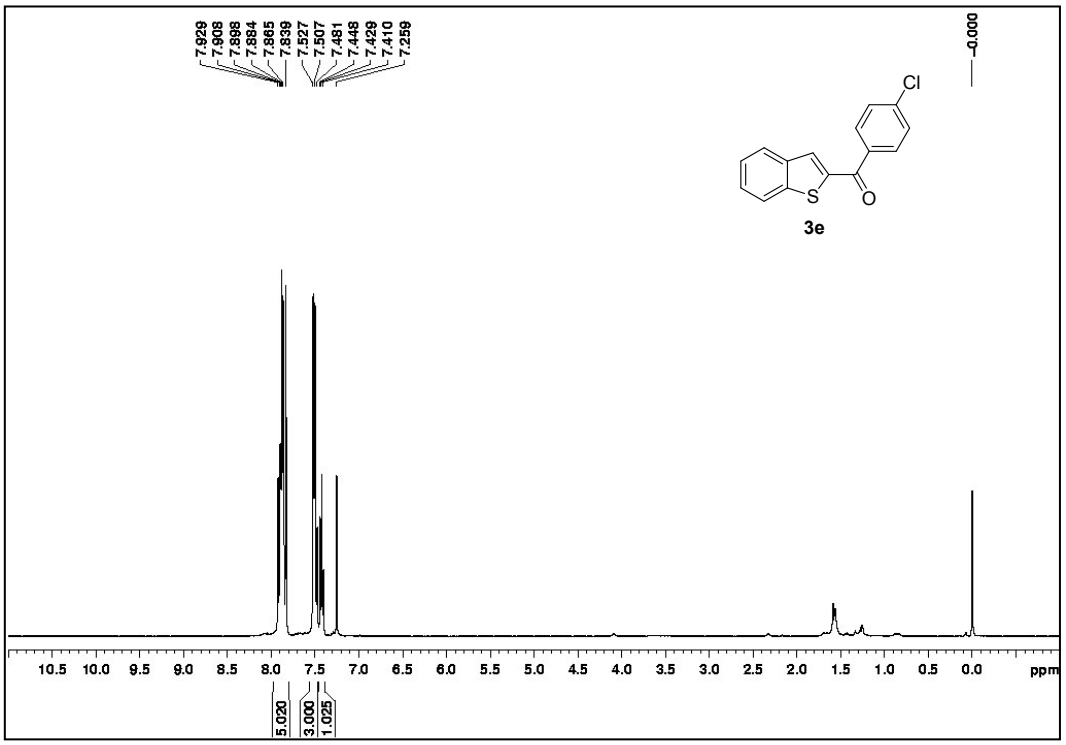


Figure 71:400 MHz ^{1}HNMR spectrum of **3e** in $CDCl_3$

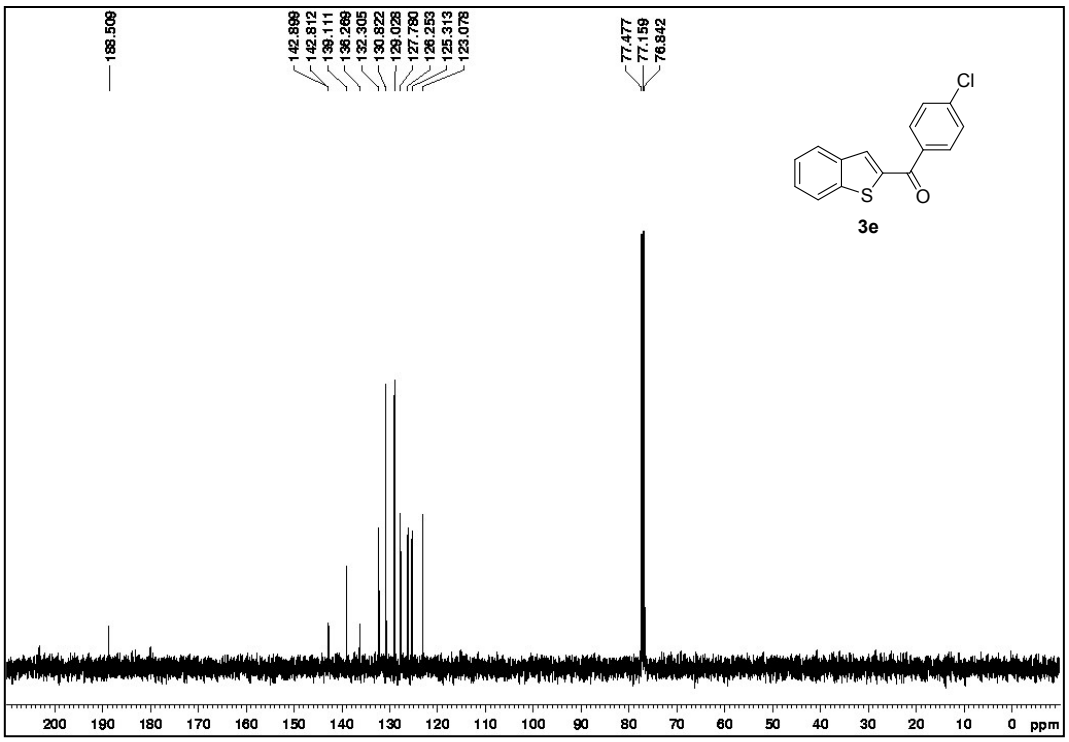


Figure 72:100 MHz ^{13}CNMR spectrum of **3e** in $CDCl_3$

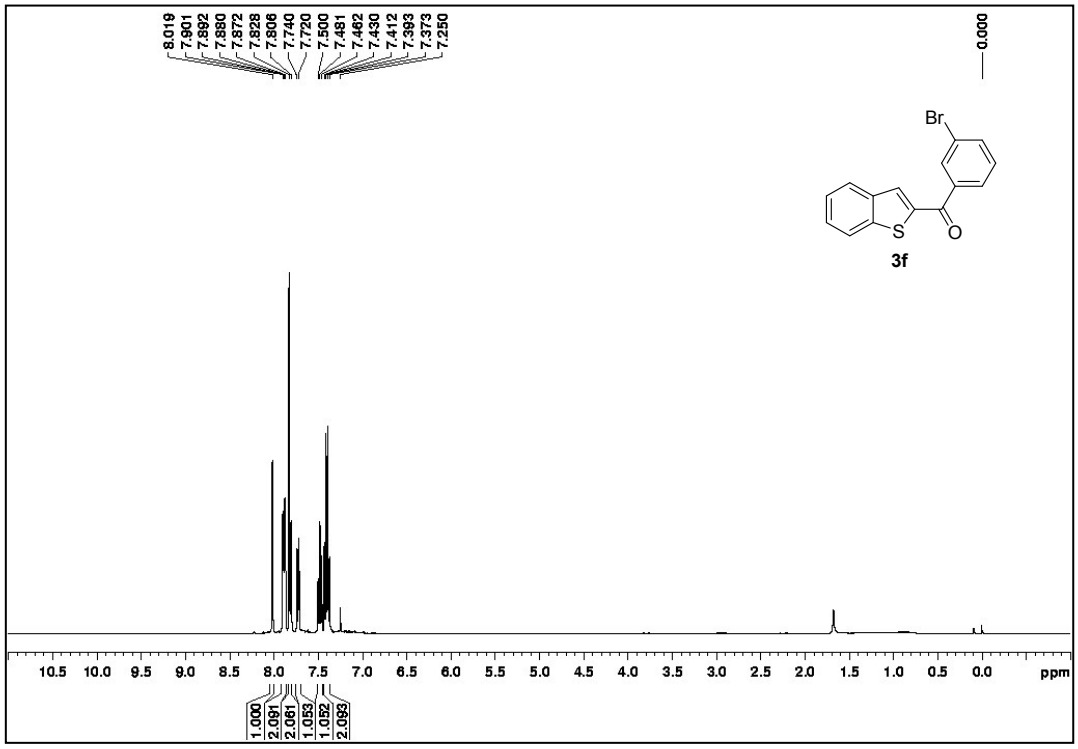


Figure 73:400 MHz ^{1}HNMR spectrum of **3f** in $CDCl_3$

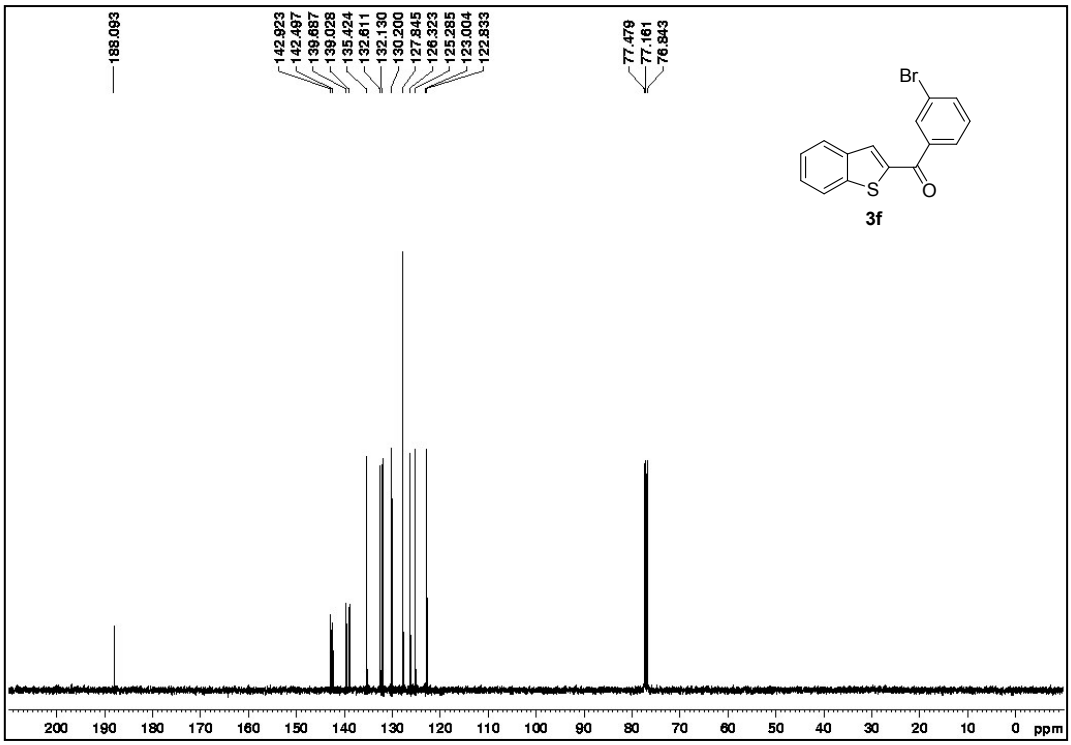


Figure 74:100 MHz ^{13}CNMR spectrum of **3f** in $CDCl_3$

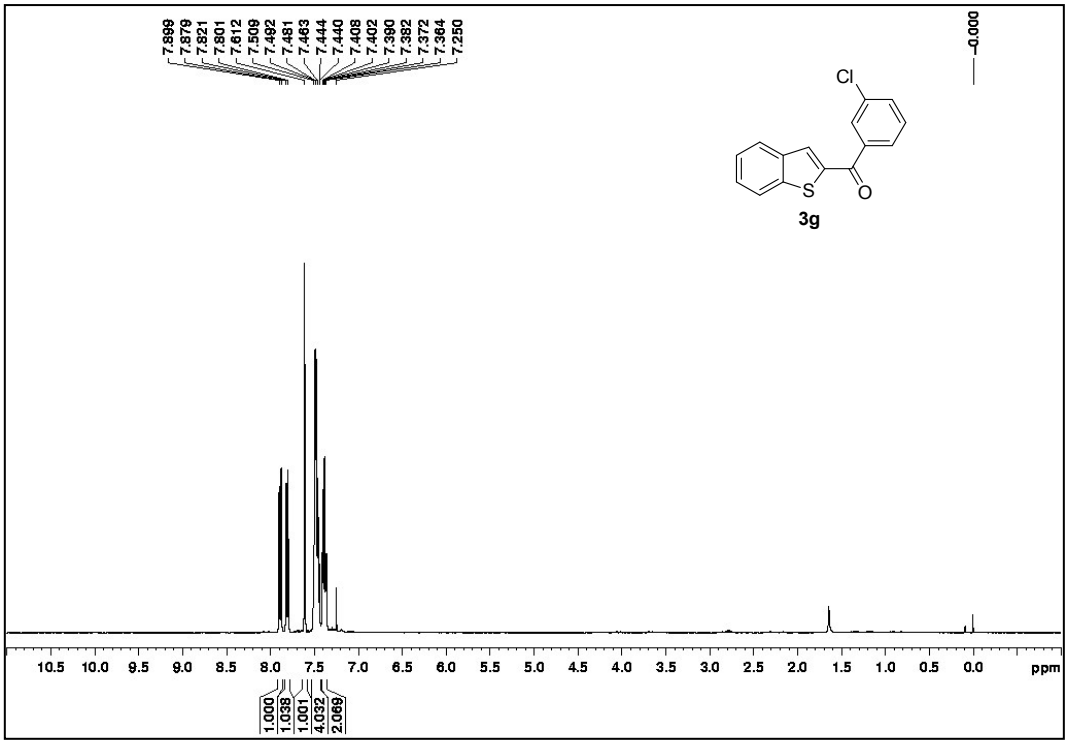


Figure 75:400 MHz ^{1}HNMR spectrum of **3g** in $CDCl_3$

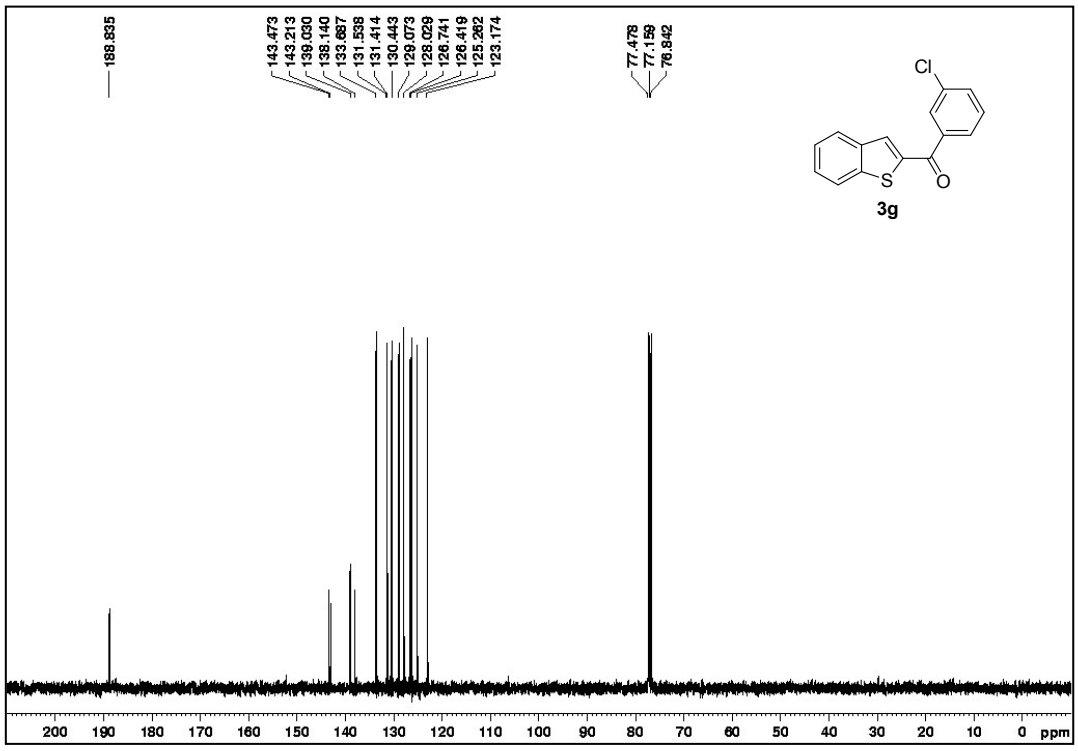


Figure 76:100 MHz ^{13}CNMR spectrum of **3g** in $CDCl_3$

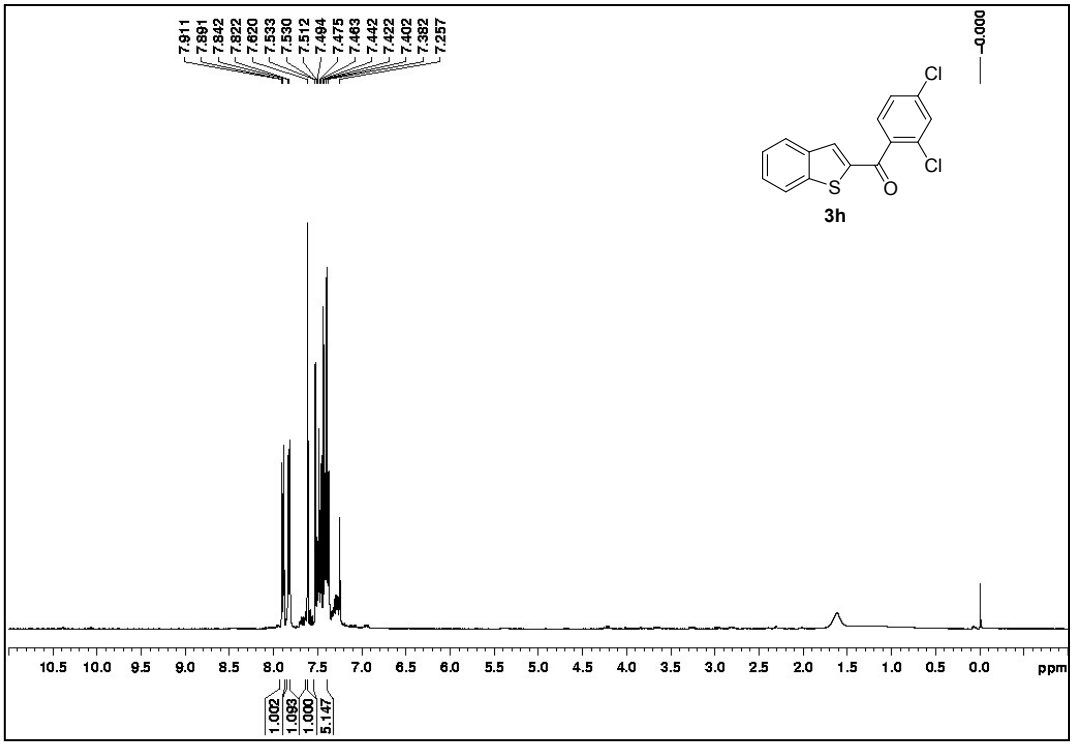


Figure 77:400 MHz ^{1}HNMR spectrum of **3h** in $CDCl_3$

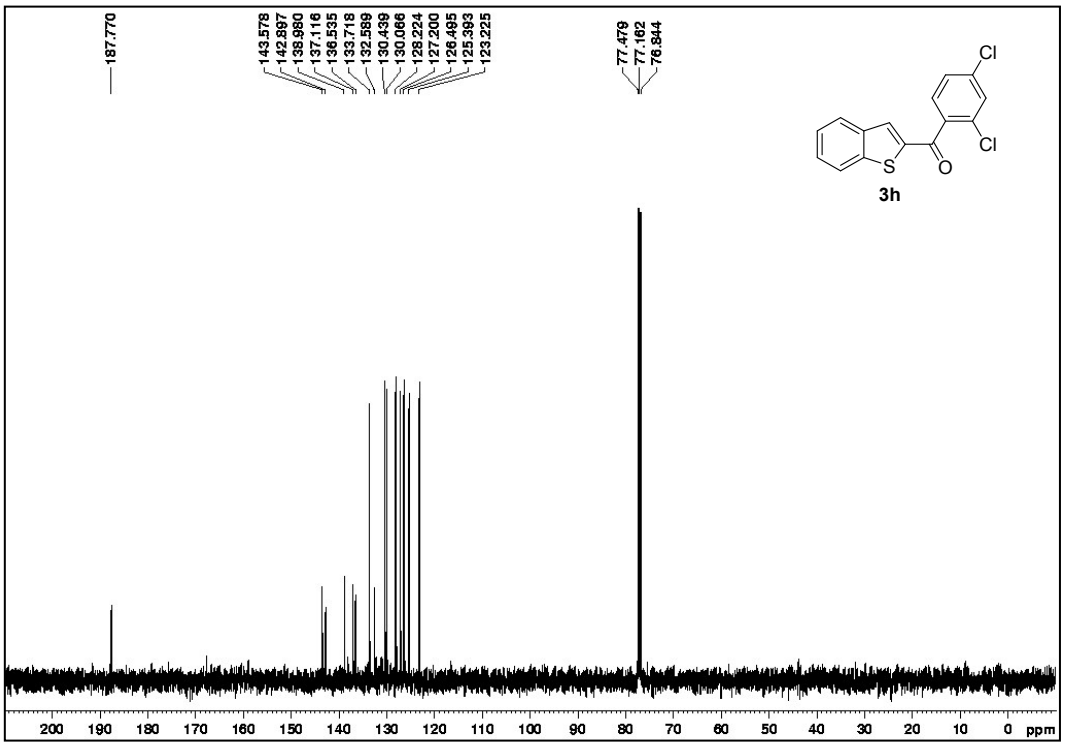


Figure 78:100 MHz ^{13}CNMR spectrum of **3h** in $CDCl_3$

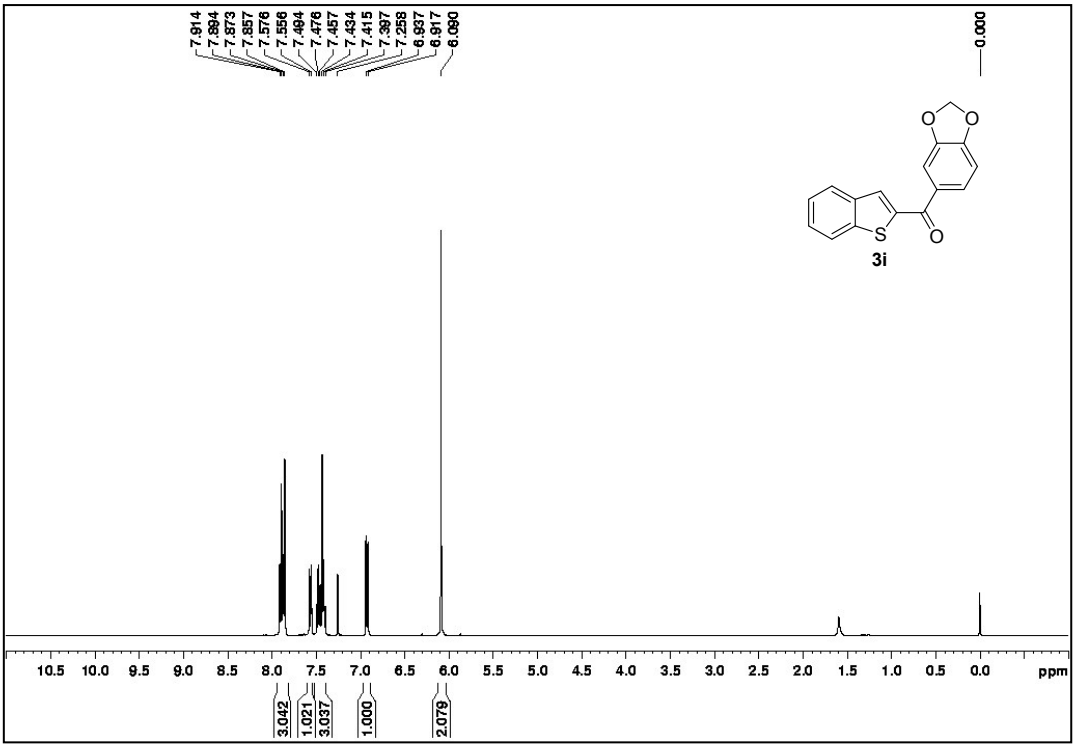


Figure 79:400 MHz ^{1}HNMR spectrum of **3i** in $CDCl_3$

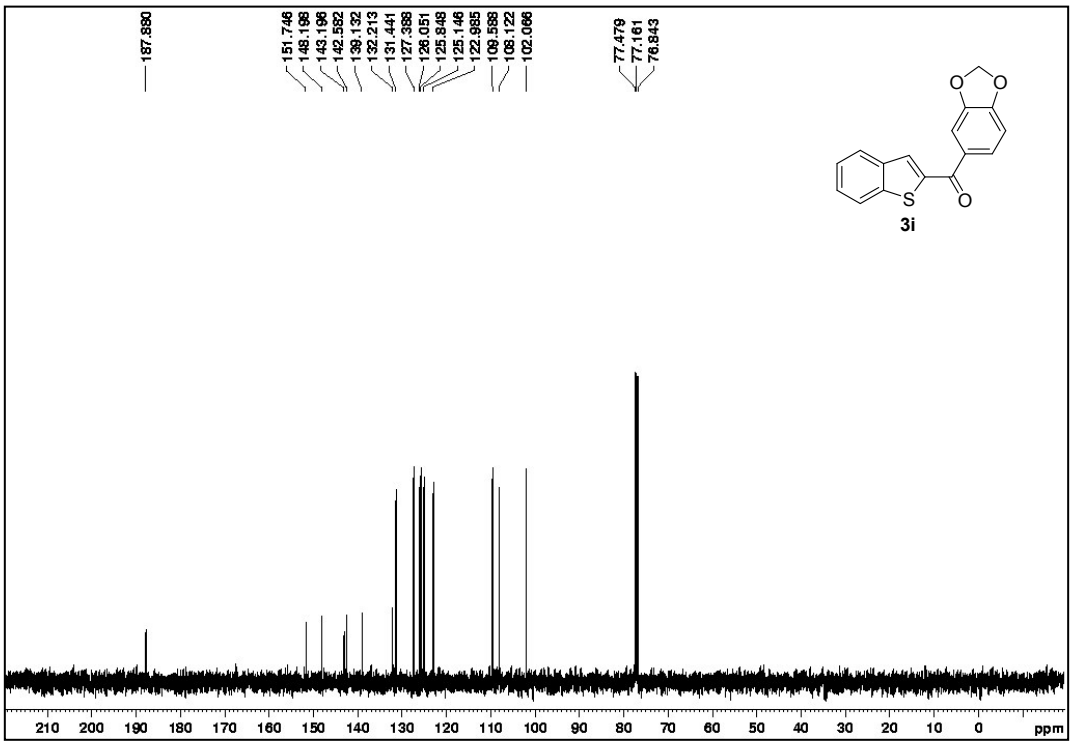


Figure 80:100 MHz ^{13}CNMR spectrum of **3i** in $CDCl_3$

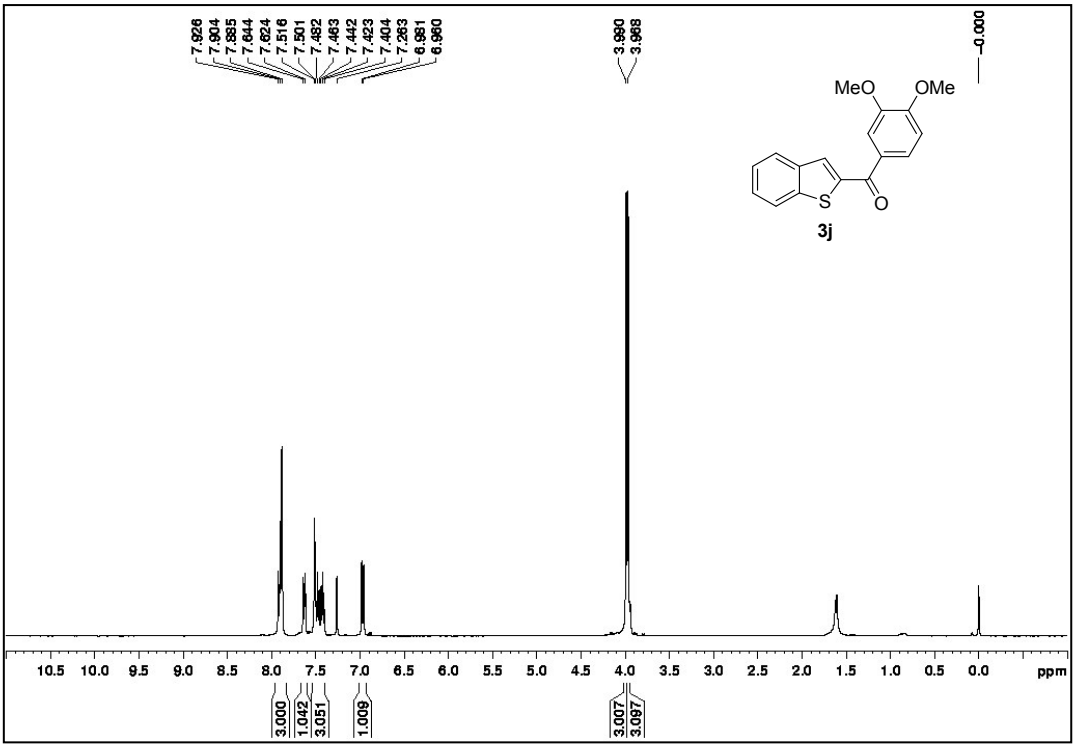


Figure 81:400 MHz ^{1}HNMR spectrum of **3j** in $CDCl_3$

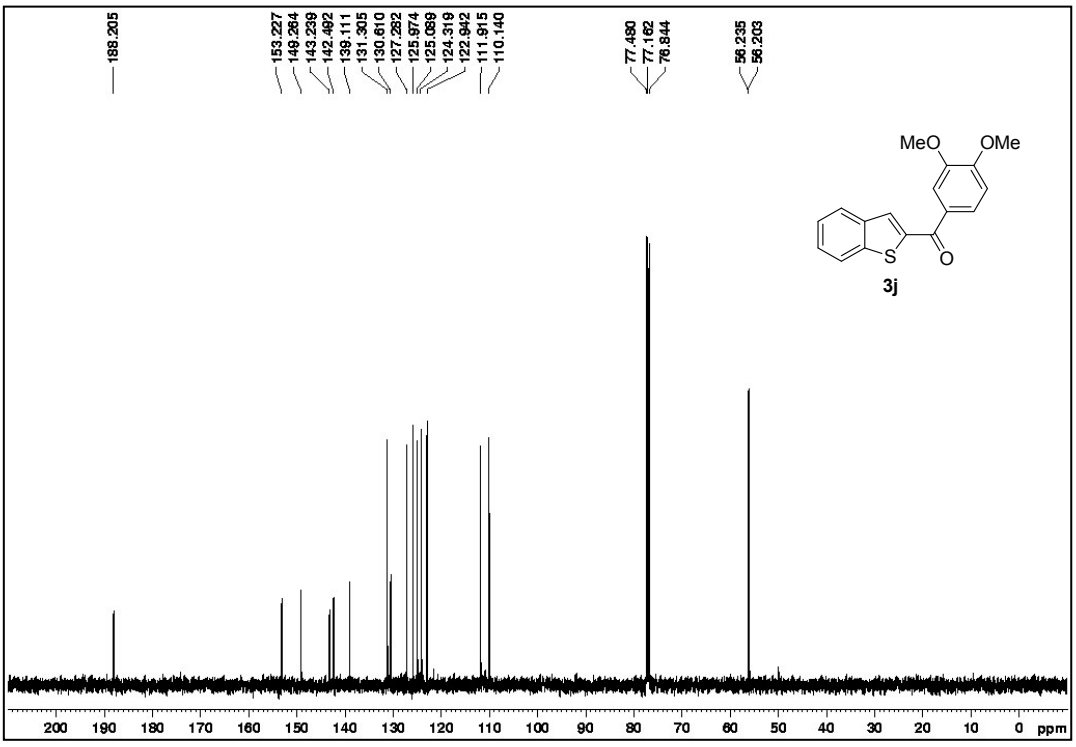


Figure 82:100 MHz ^{13}CNMR spectrum of **3j** in $CDCl_3$

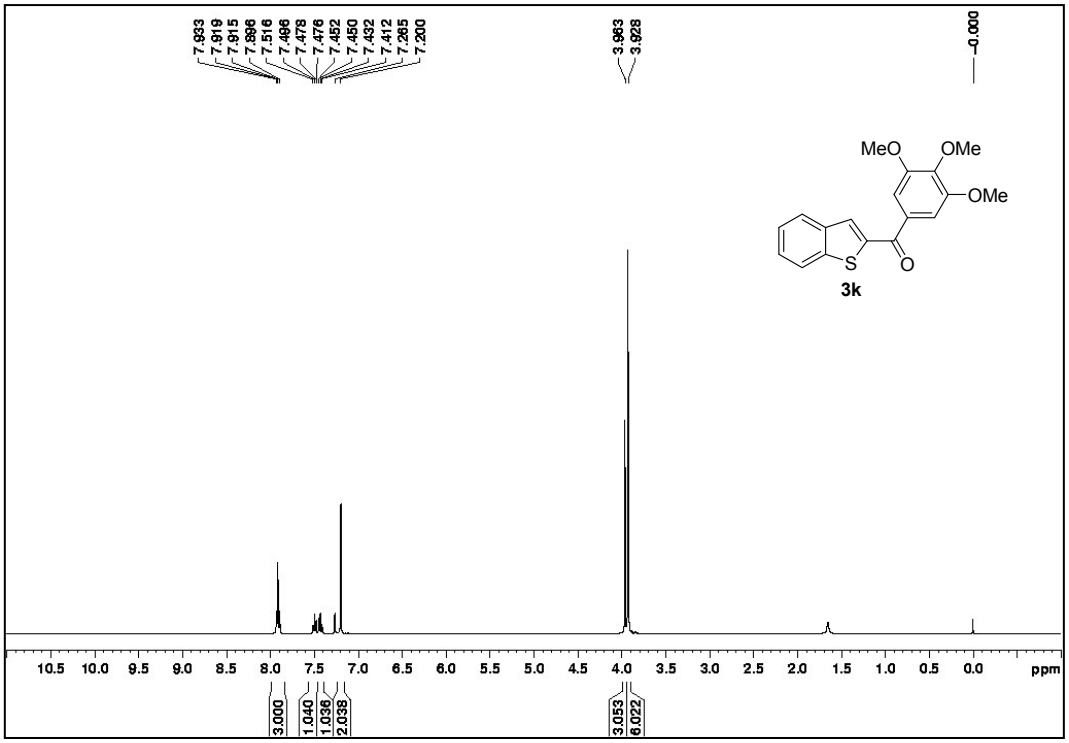


Figure 83:400 MHz ^{1}HNMR spectrum of **3k** in $CDCl_3$

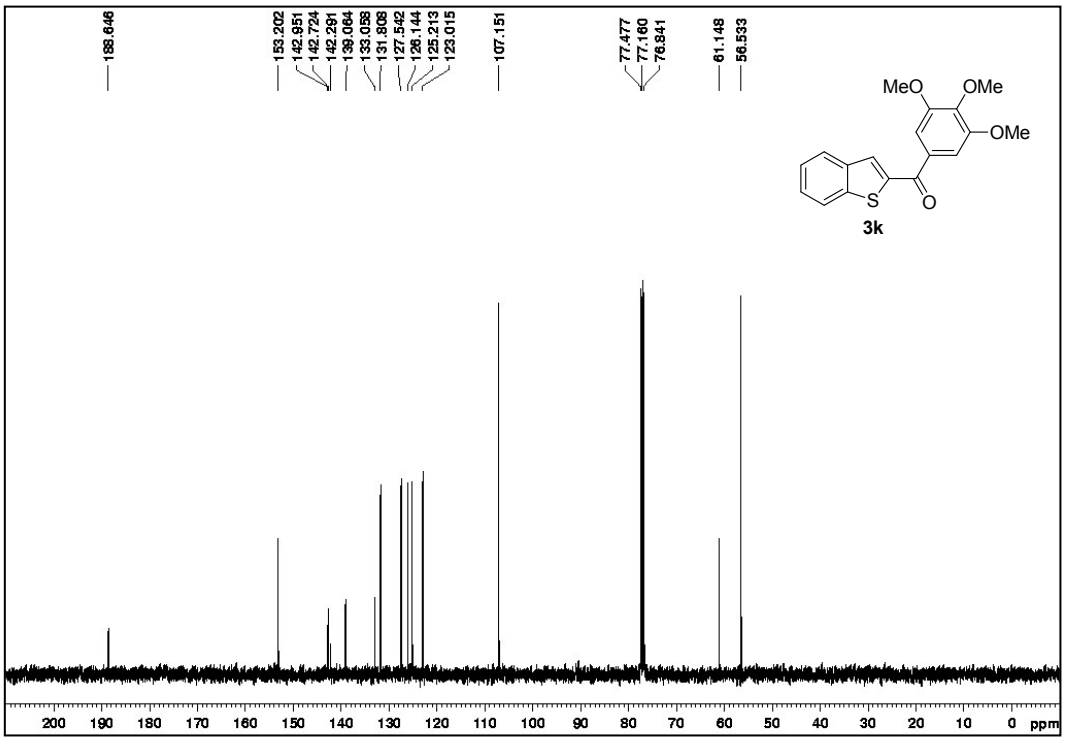


Figure 84:100 MHz ^{13}CNMR spectrum of **3k** in $CDCl_3$

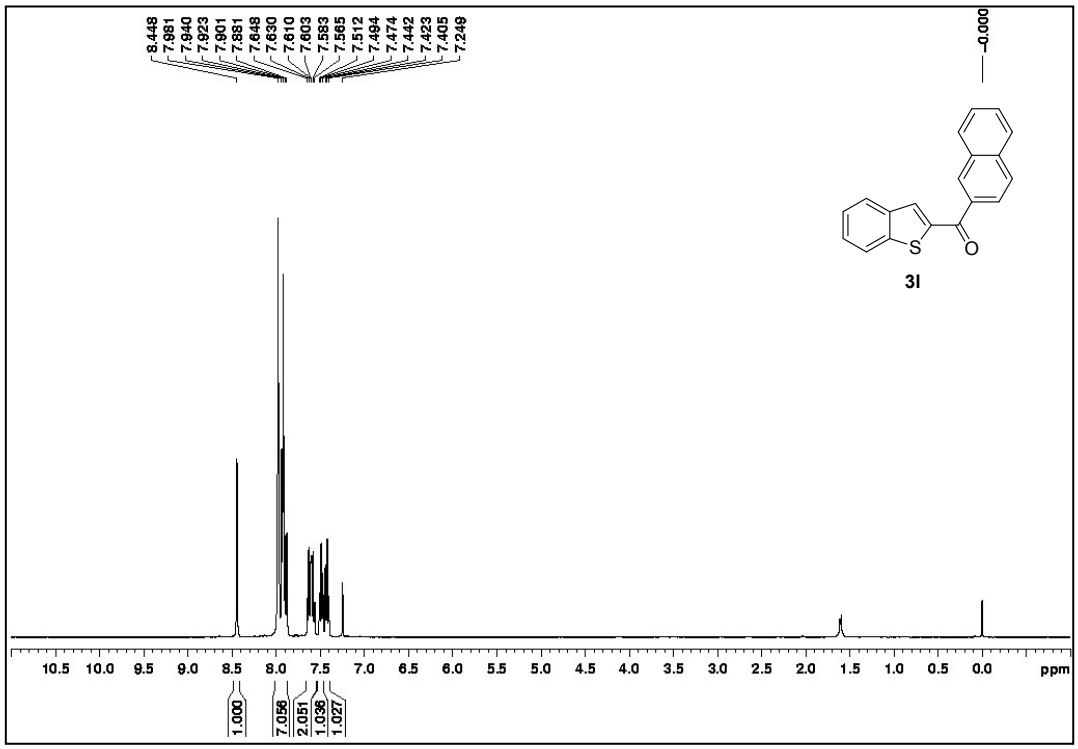


Figure 85:400 MHz ^{1}HNMR spectrum of **3l** in $CDCl_3$

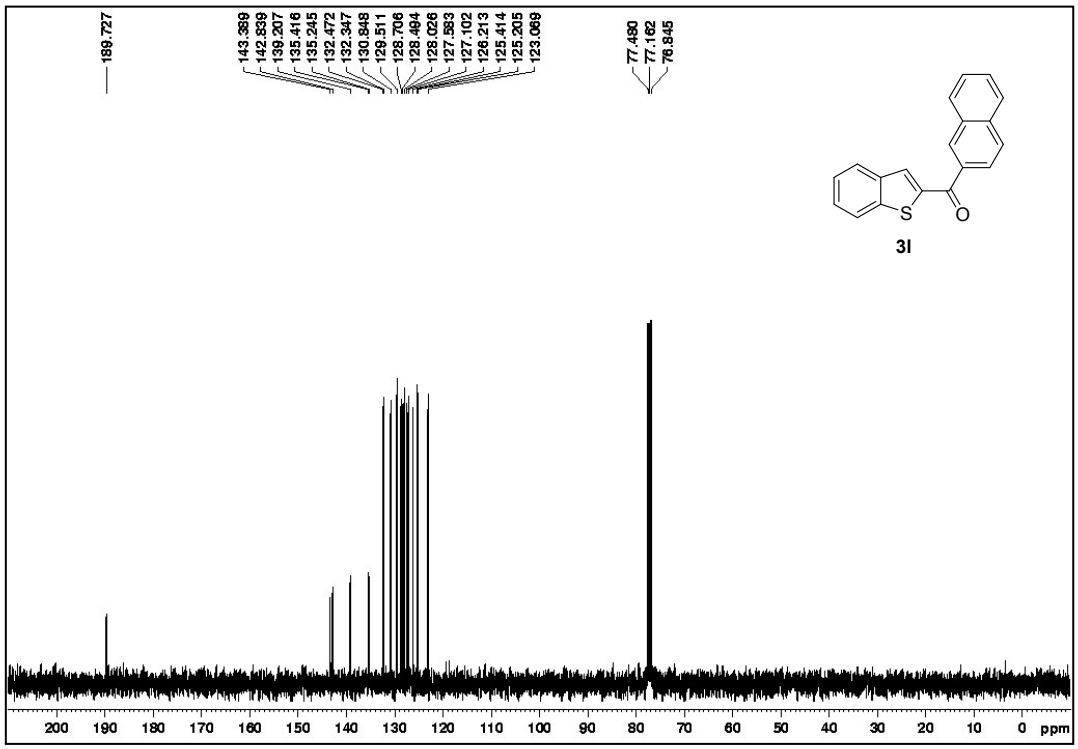


Figure 86:100 MHz ^{13}C NMR spectrum of **3l** in $CDCl_3$

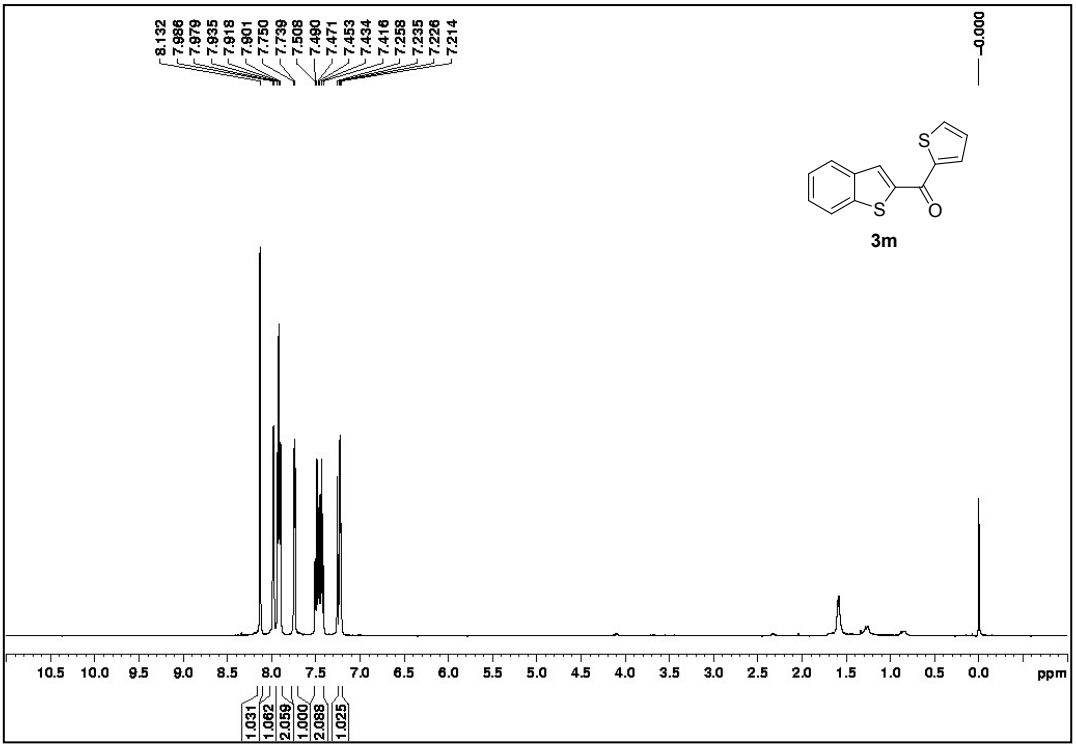


Figure 87:400 MHz ^{1}HNMR spectrum of **3m** in $CDCl_3$

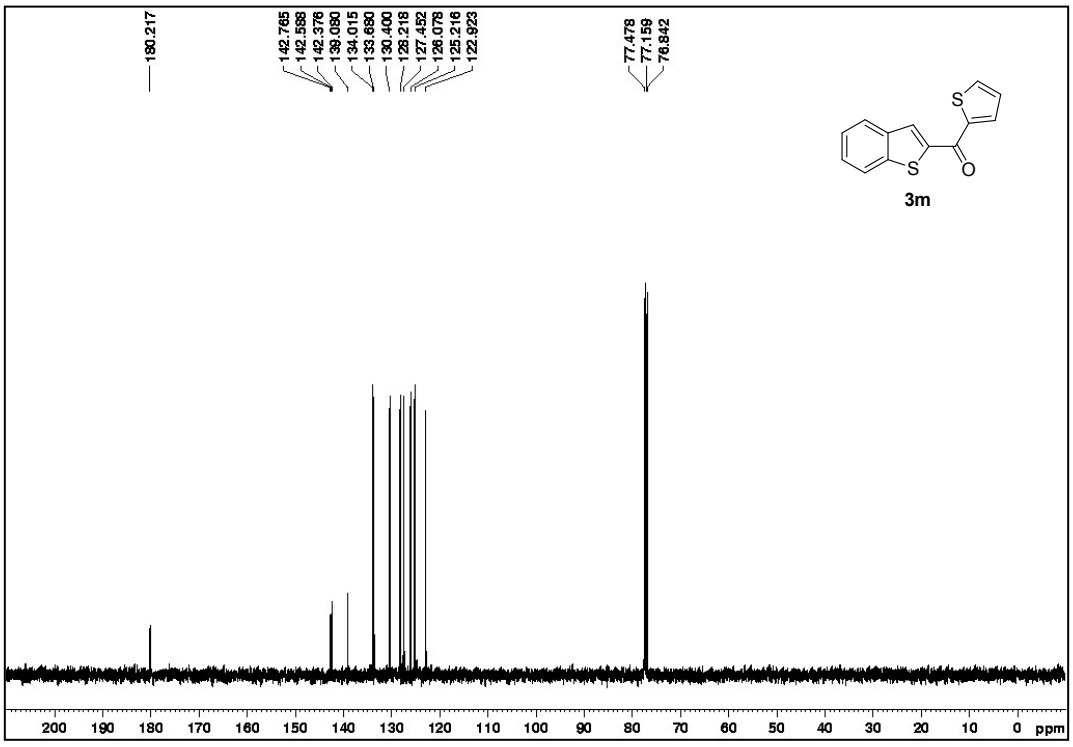


Figure 88:100 MHz ^{13}CNMR spectrum of **3m** in $CDCl_3$

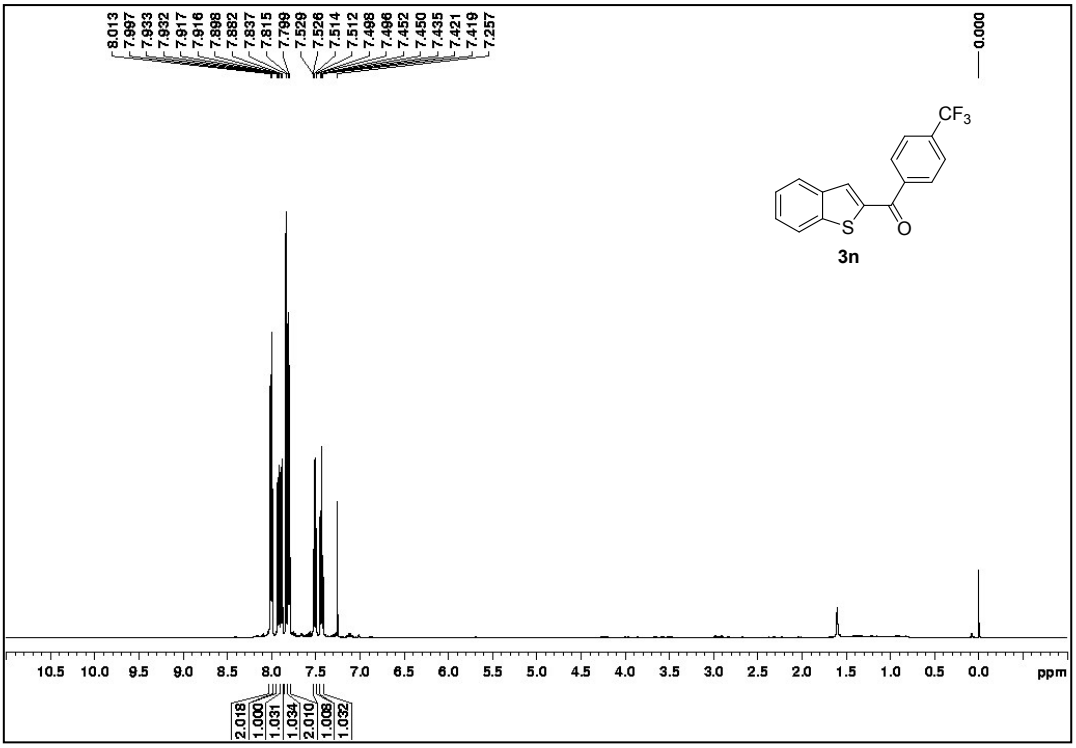


Figure 89:500 MHz ^{1}HNMR spectrum of **3n** in $CDCl_3$

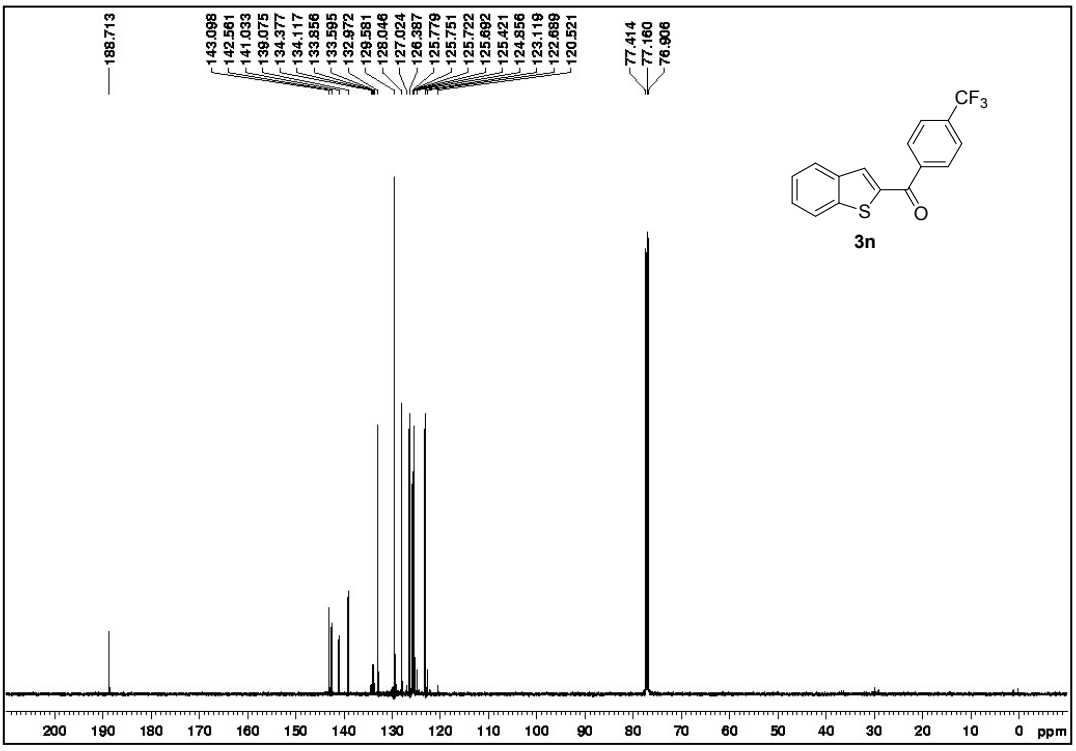


Figure 90:125 MHz ^{13}CNMR spectrum of **3n** in $CDCl_3$

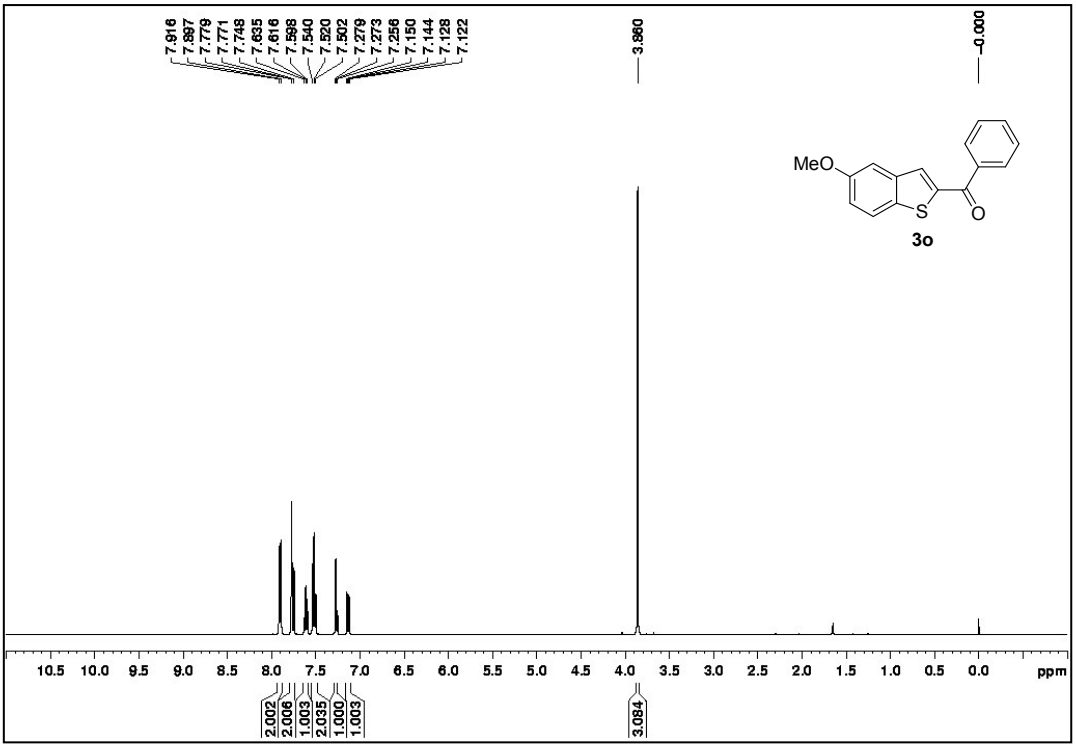


Figure 91:400 MHz ^{1}HNMR spectrum of **3o** in $CDCl_3$

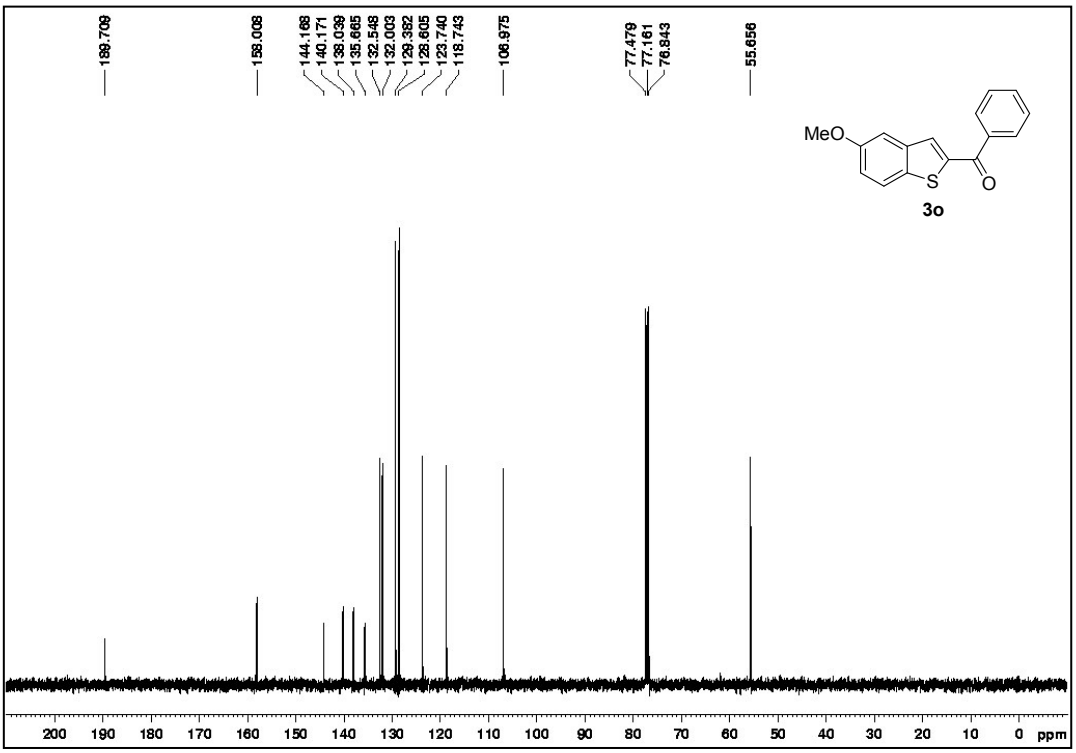


Figure 92:100 MHz ^{13}CNMR spectrum of **3o** in $CDCl_3$

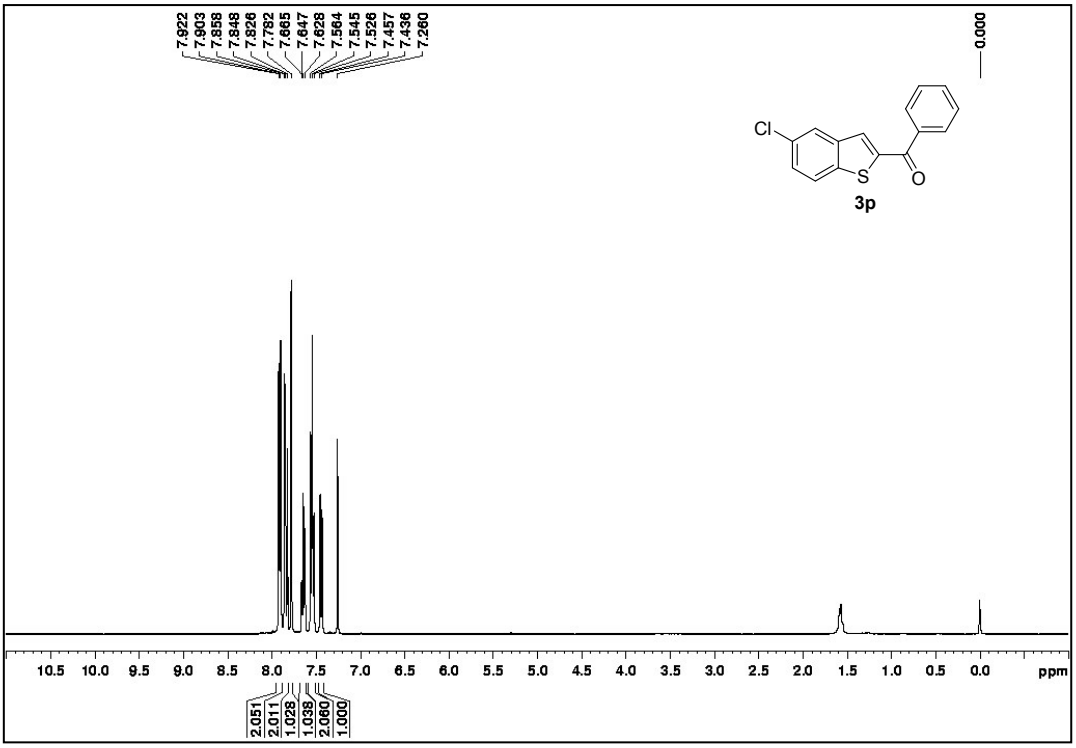


Figure 93:400 MHz ^{1}HNMR spectrum of **3p** in $CDCl_3$

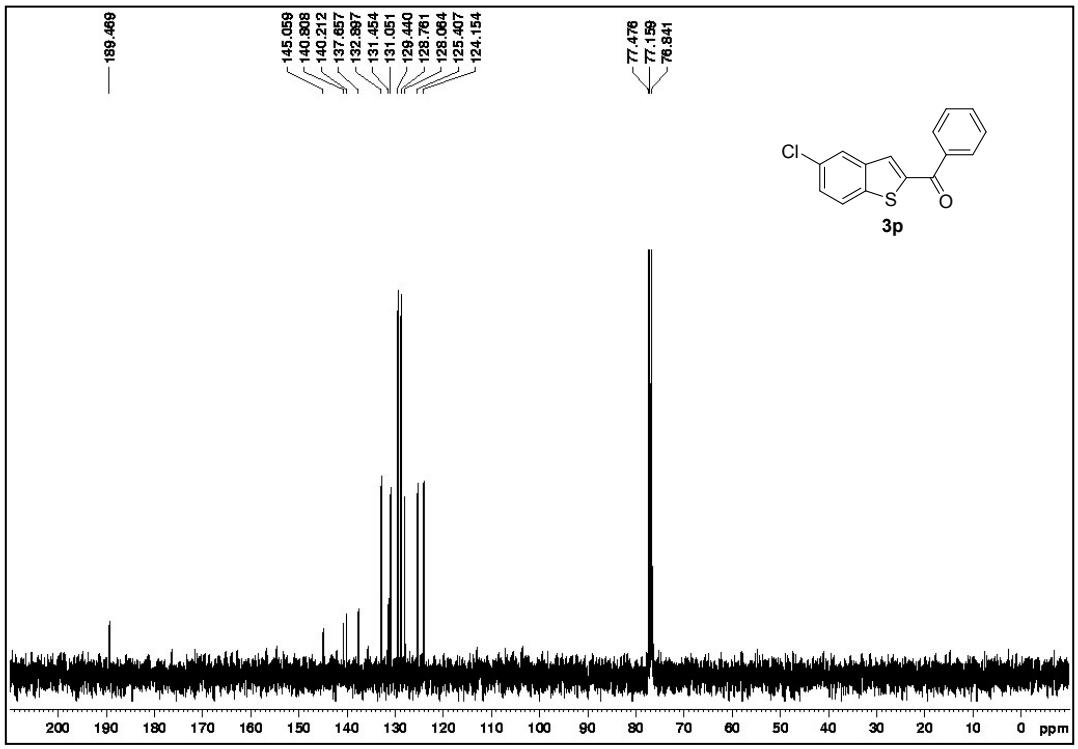


Figure 94:100 MHz ^{13}CNMR spectrum of **3p** in $CDCl_3$

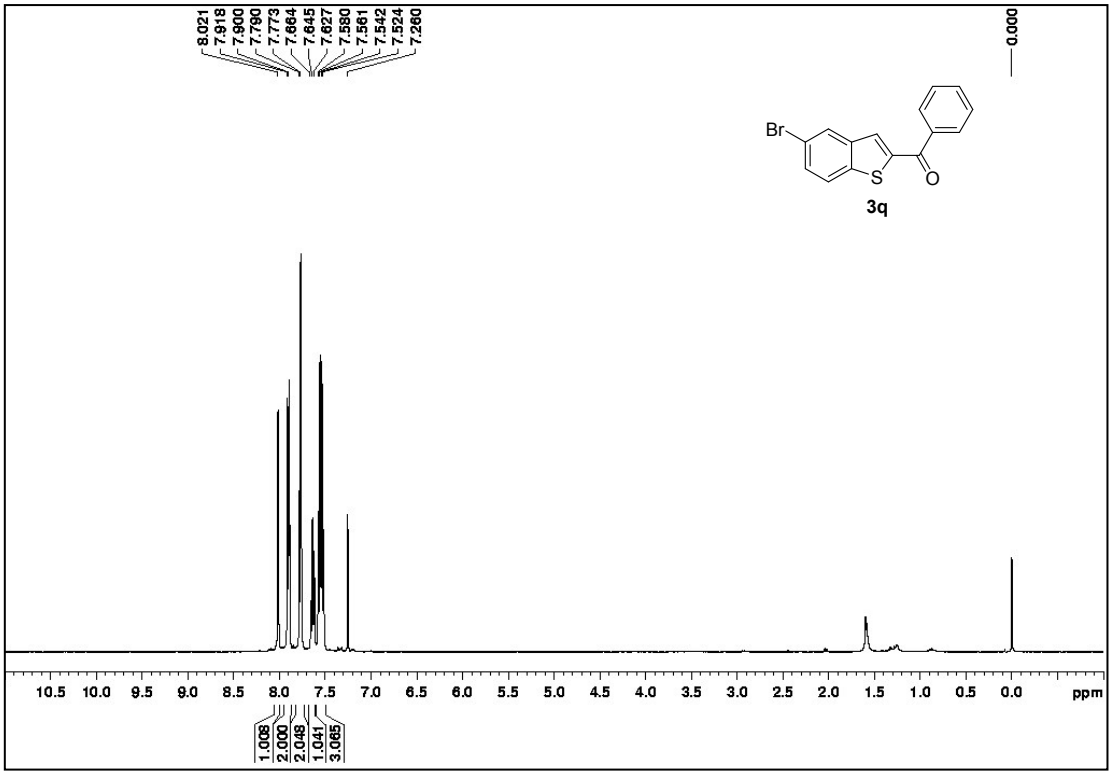


Figure 95:400 MHz ^{1}HNMR spectrum of **3q** in $CDCl_3$

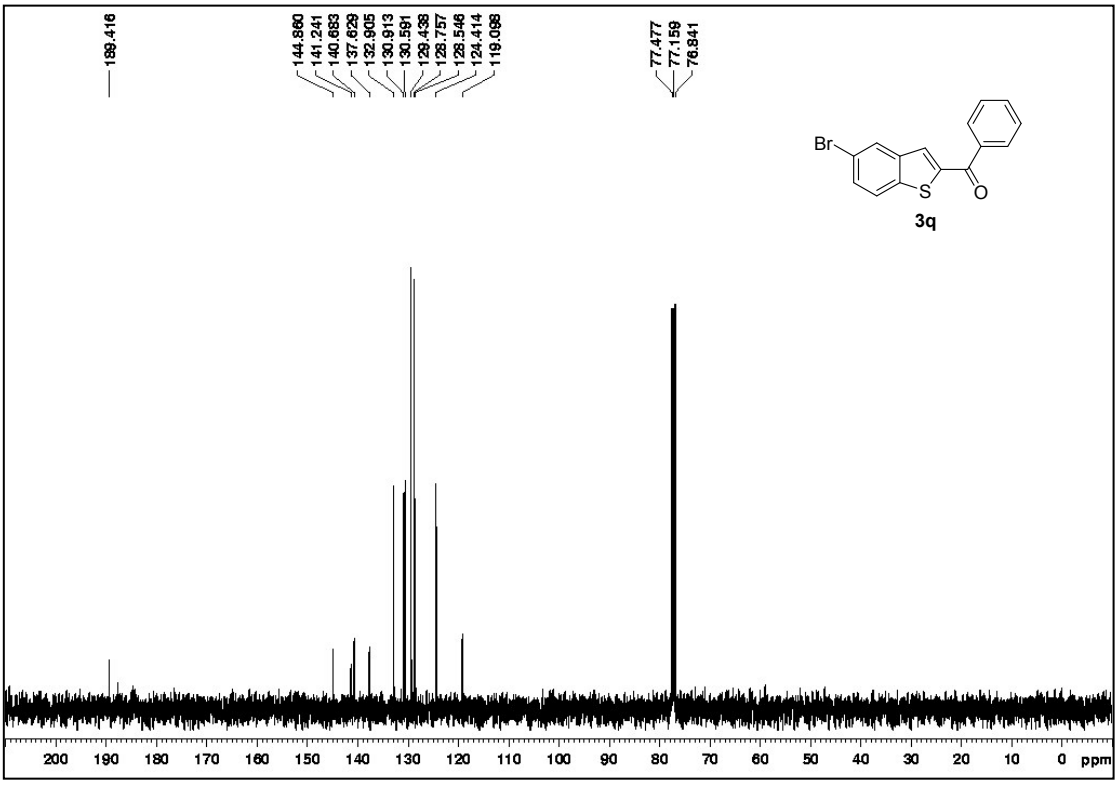


Figure 96:100 MHz ^{13}CNMR spectrum of **3q** in $CDCl_3$

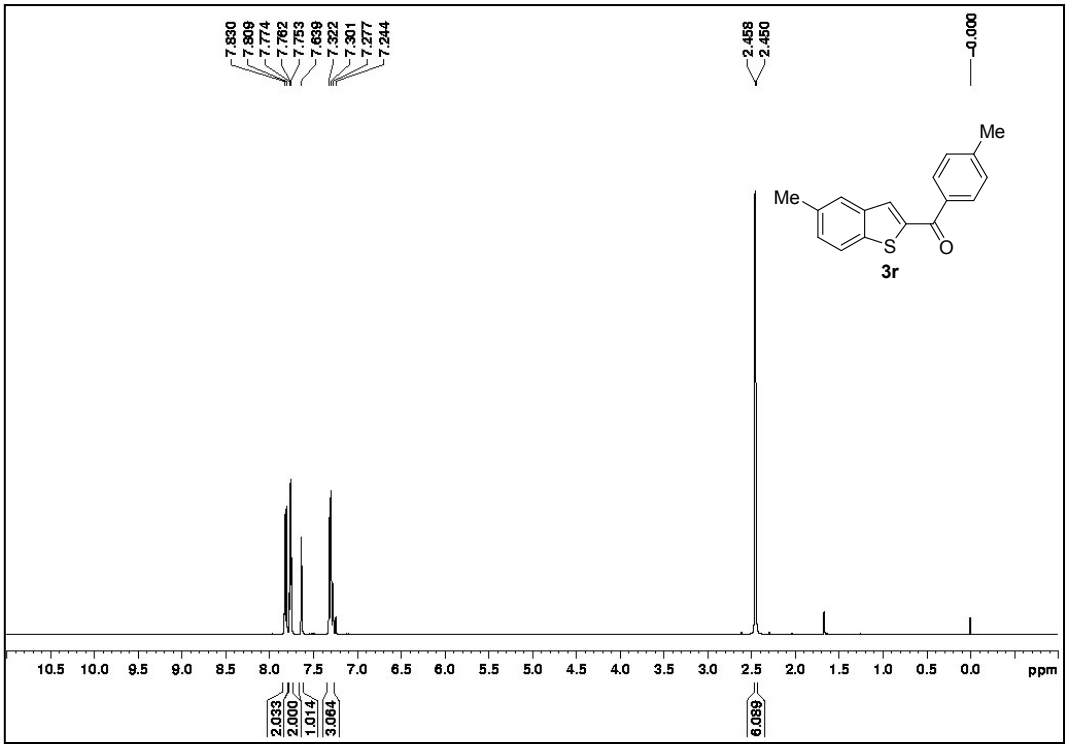


Figure 97:400 MHz ^{1}HNMR spectrum of **3r** in $CDCl_3$

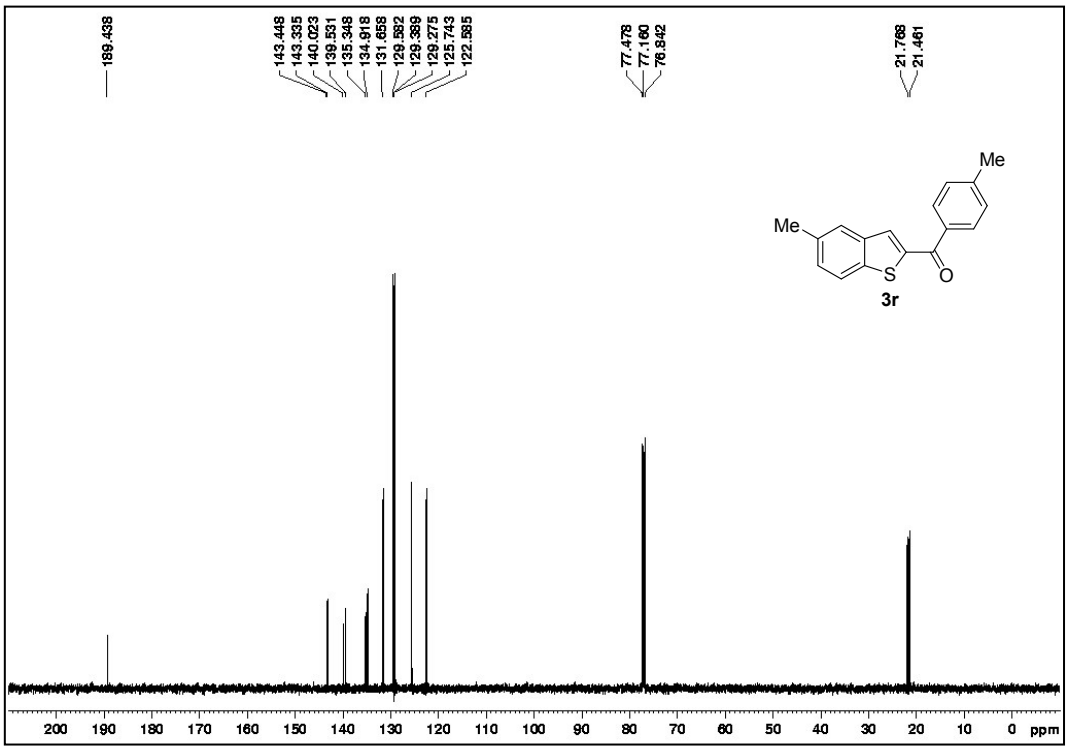


Figure 98:100 MHz ^{13}CNMR spectrum of **3r** in $CDCl_3$

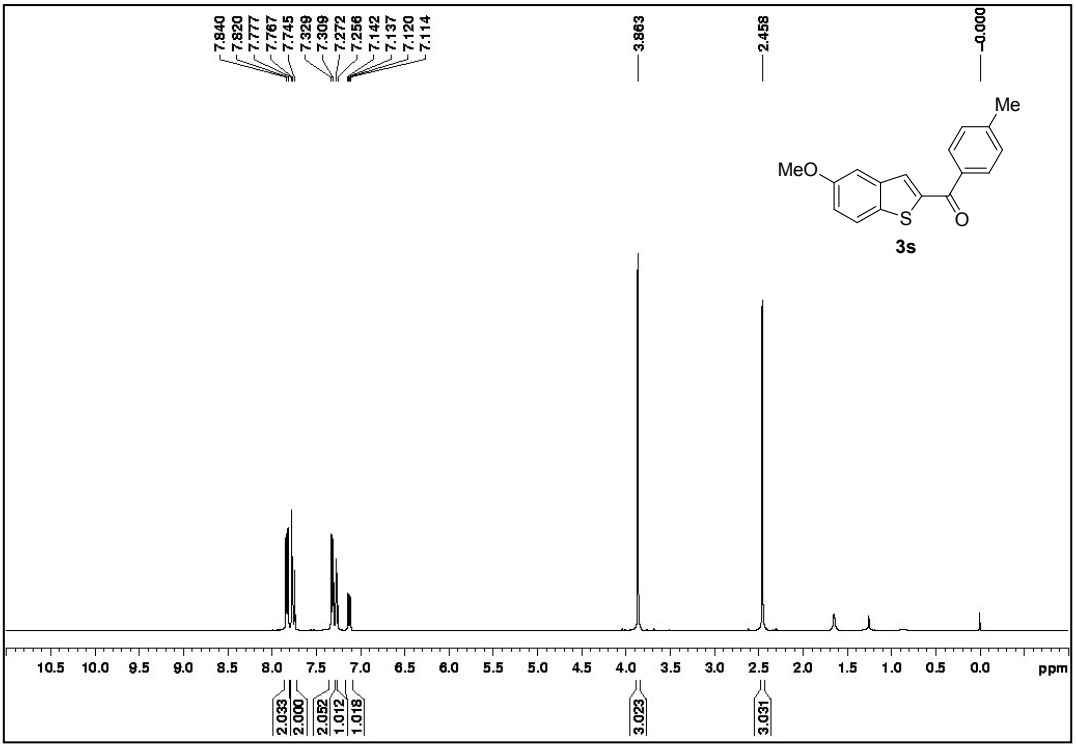


Figure 99:400 MHz ^{1}HNMR spectrum of **3s** in $CDCl_3$

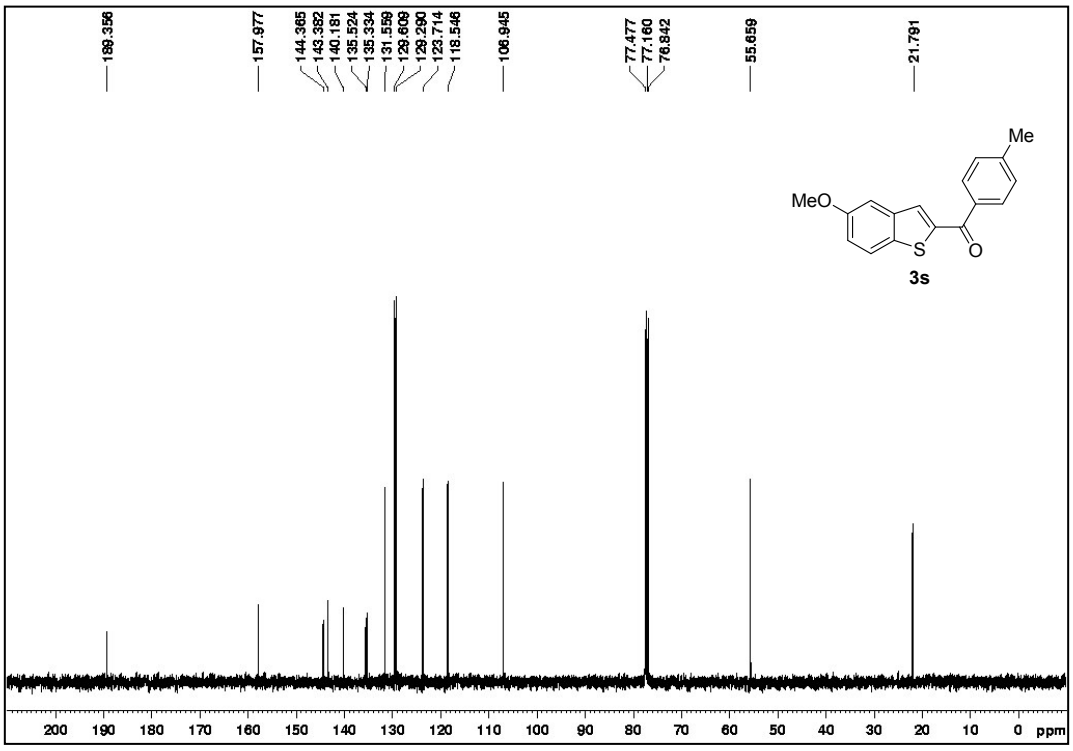


Figure 100:100 MHz ^{13}CNMR spectrum of **3s** in $CDCl_3$

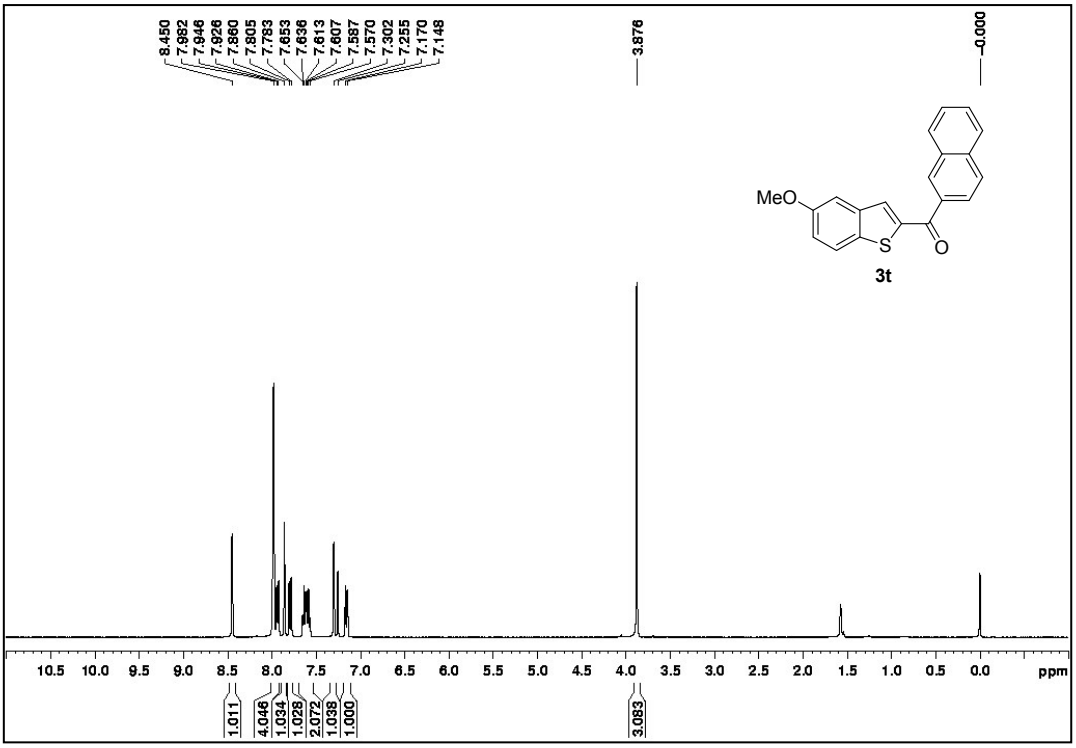


Figure 101:400 MHz ^{1}HNMR spectrum of **3t** in $CDCl_3$

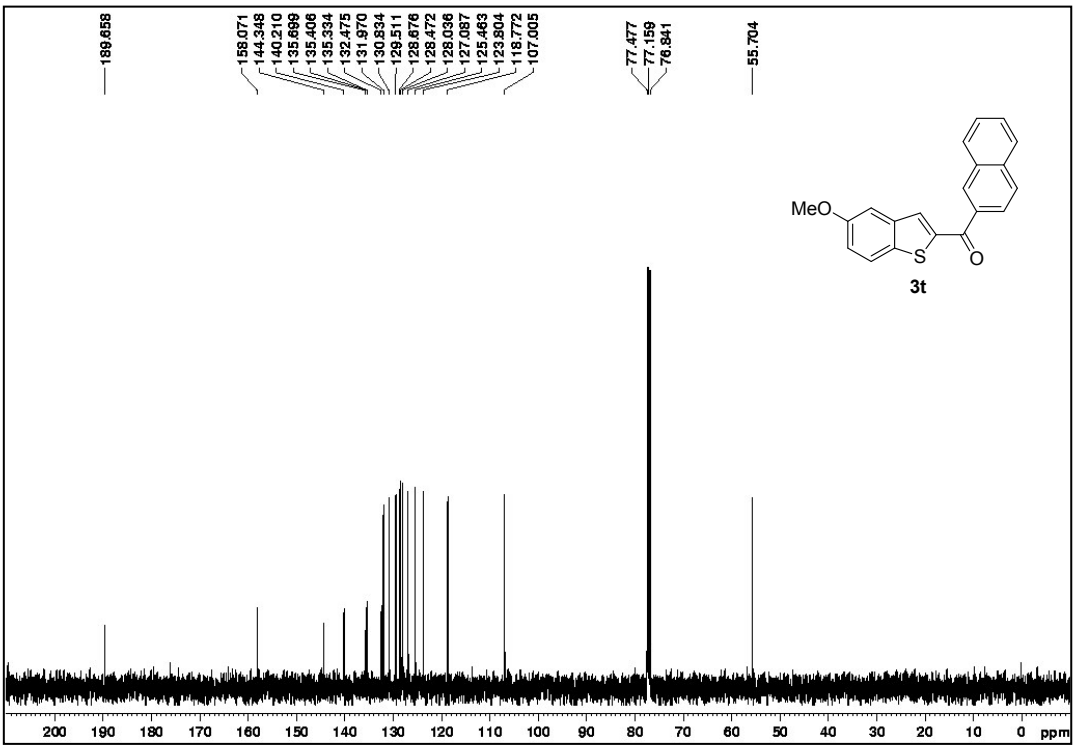


Figure 102:100 MHz ^{13}CNMR spectrum of **3t** in $CDCl_3$

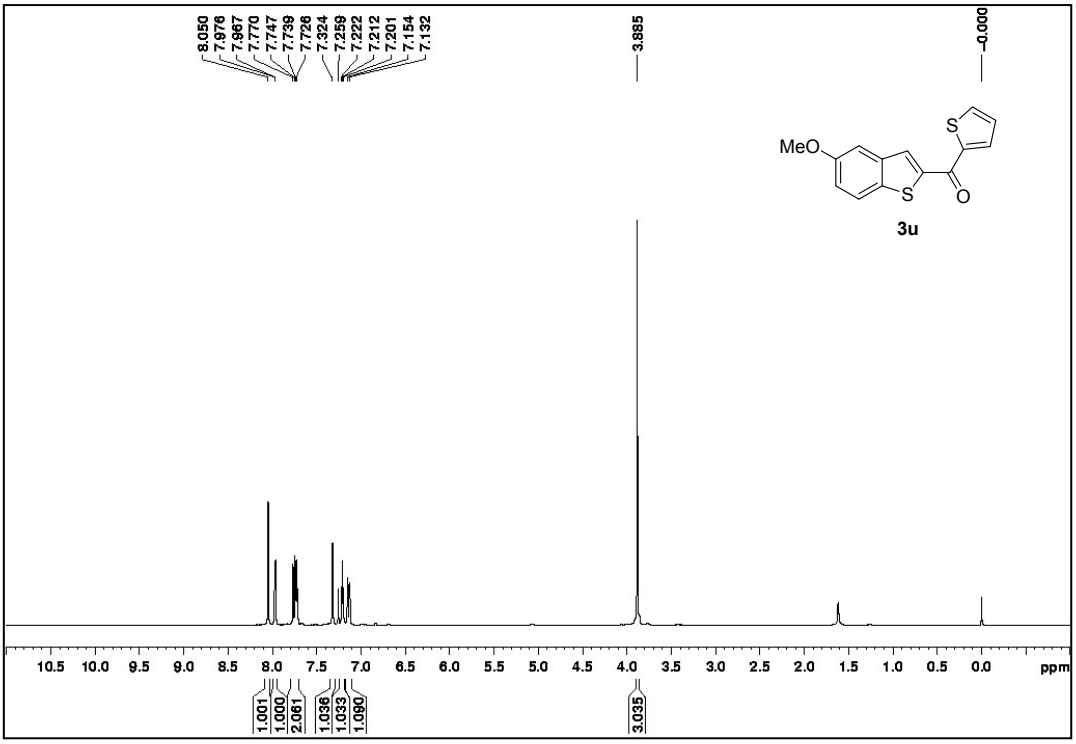


Figure 103:400 MHz ^{1}HNMR spectrum of **3u** in $CDCl_3$

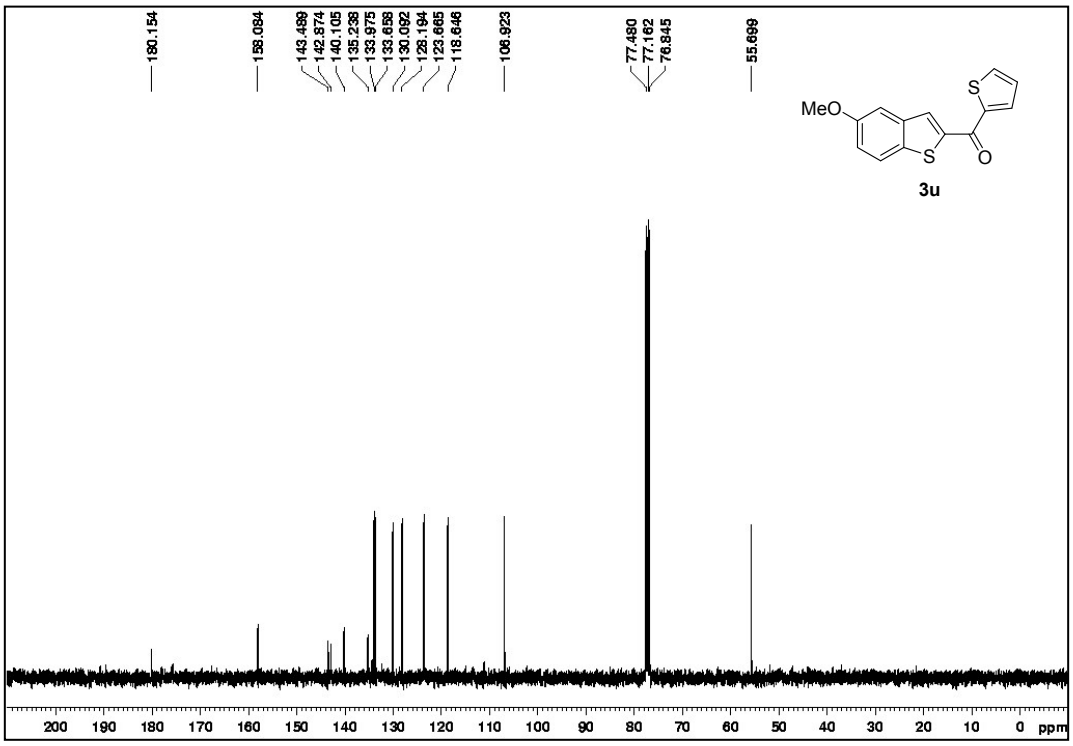


Figure 104:100 MHz ^{13}CNMR spectrum of **3u** in $CDCl_3$

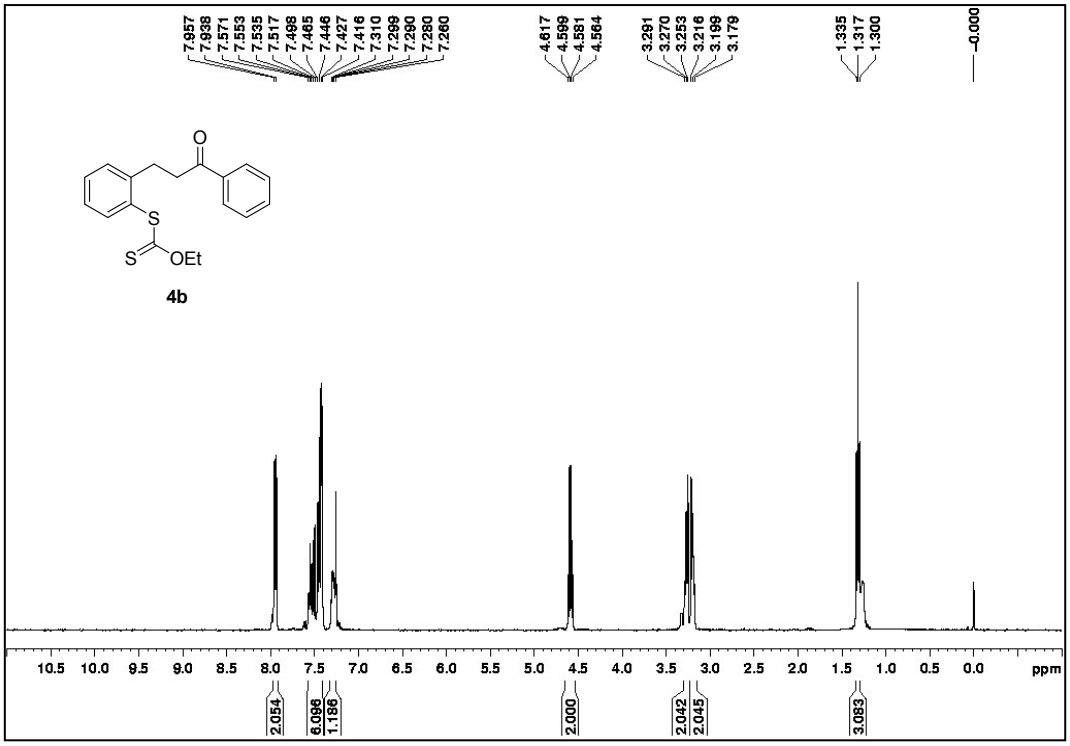


Figure 105:400 MHz ^{1}HNMR spectrum of **4b** in $CDCl_3$

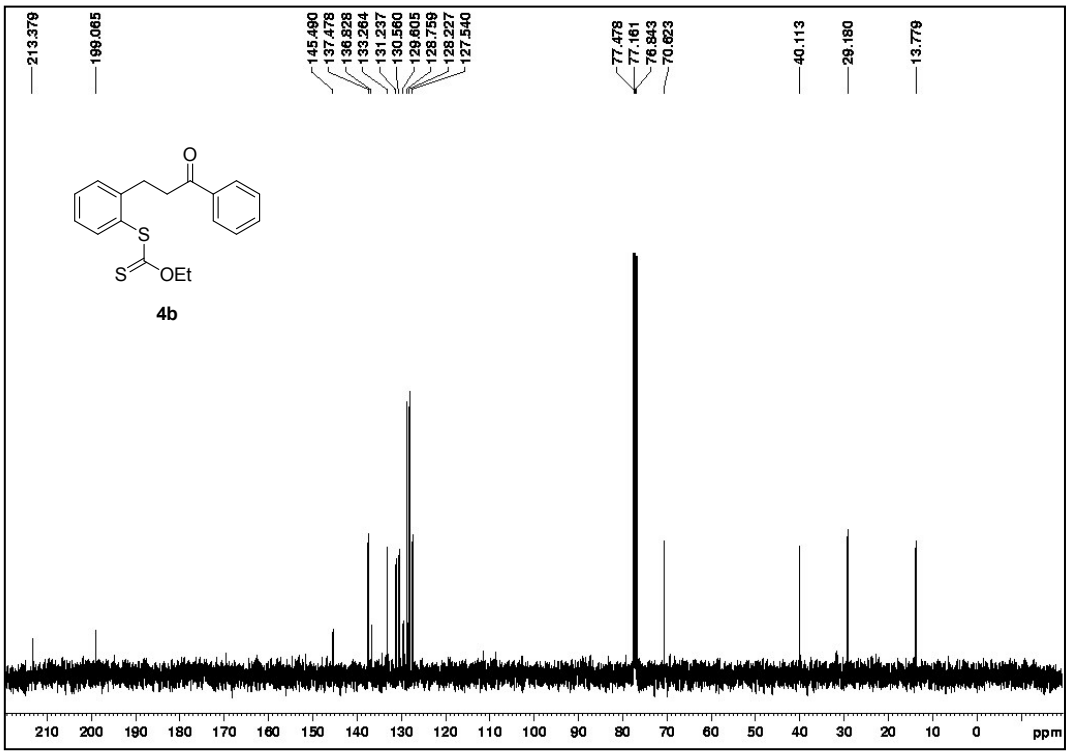


Figure 106:100 MHz ^{13}CNMR spectrum of **4b** in $CDCl_3$

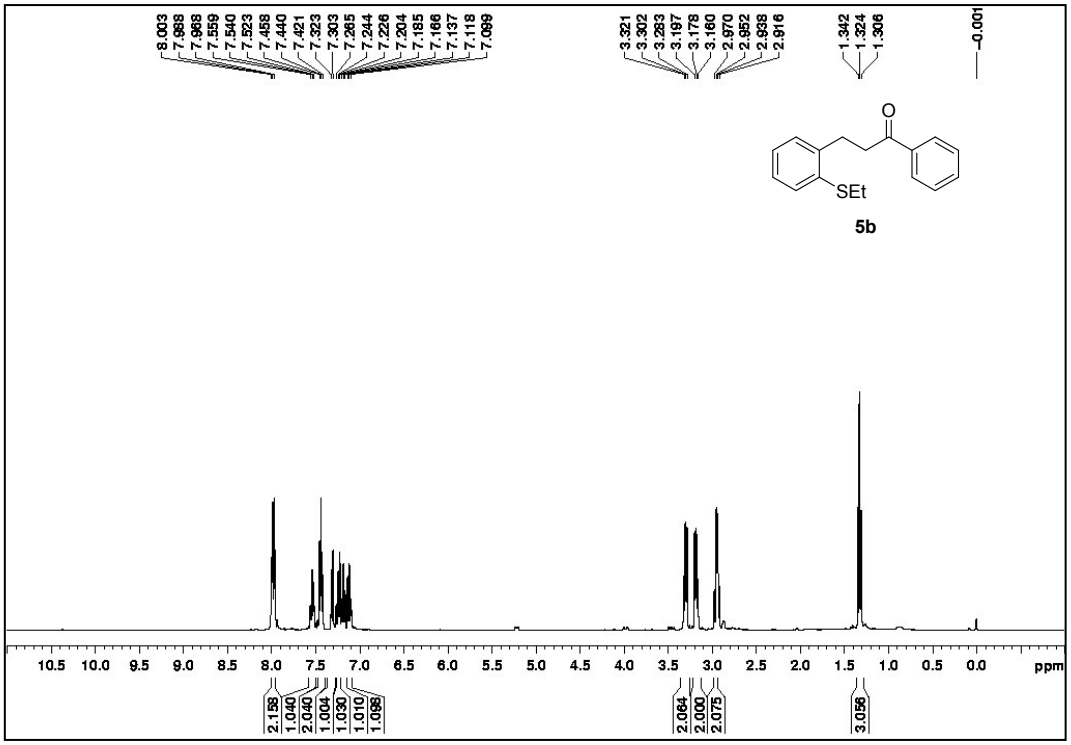


Figure 107:400 MHz ^{1}HNMR spectrum of **5b** in $CDCl_3$

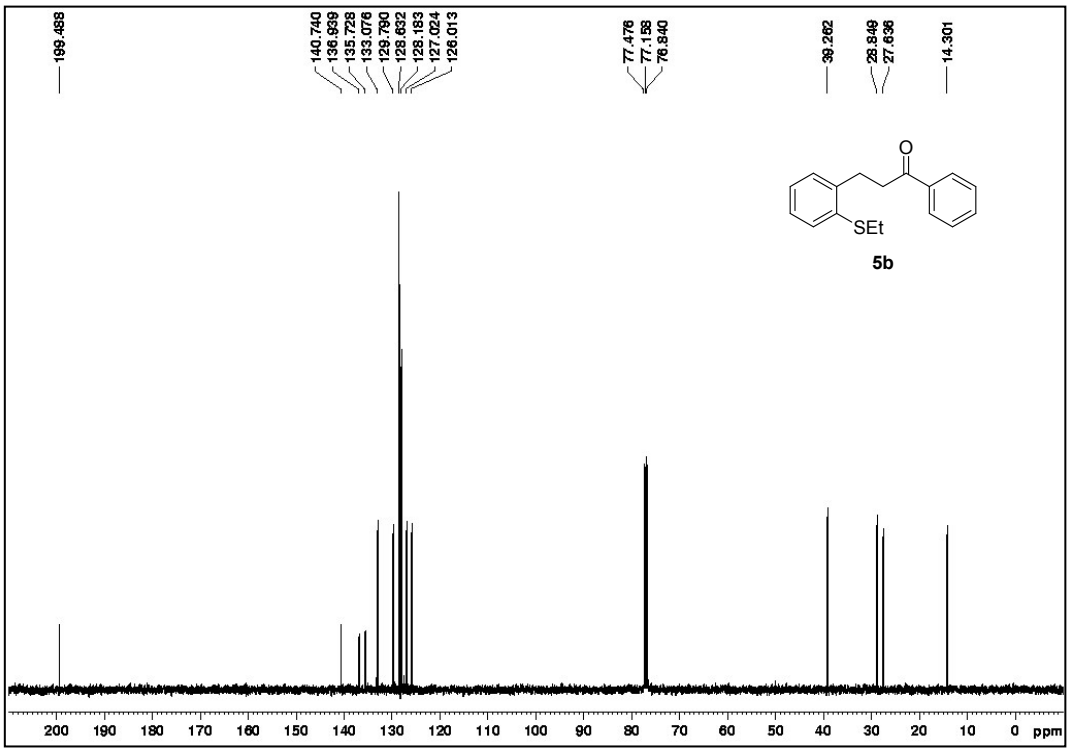


Figure 108:100 MHz ^{13}CNMR spectrum of **5b** in $CDCl_3$

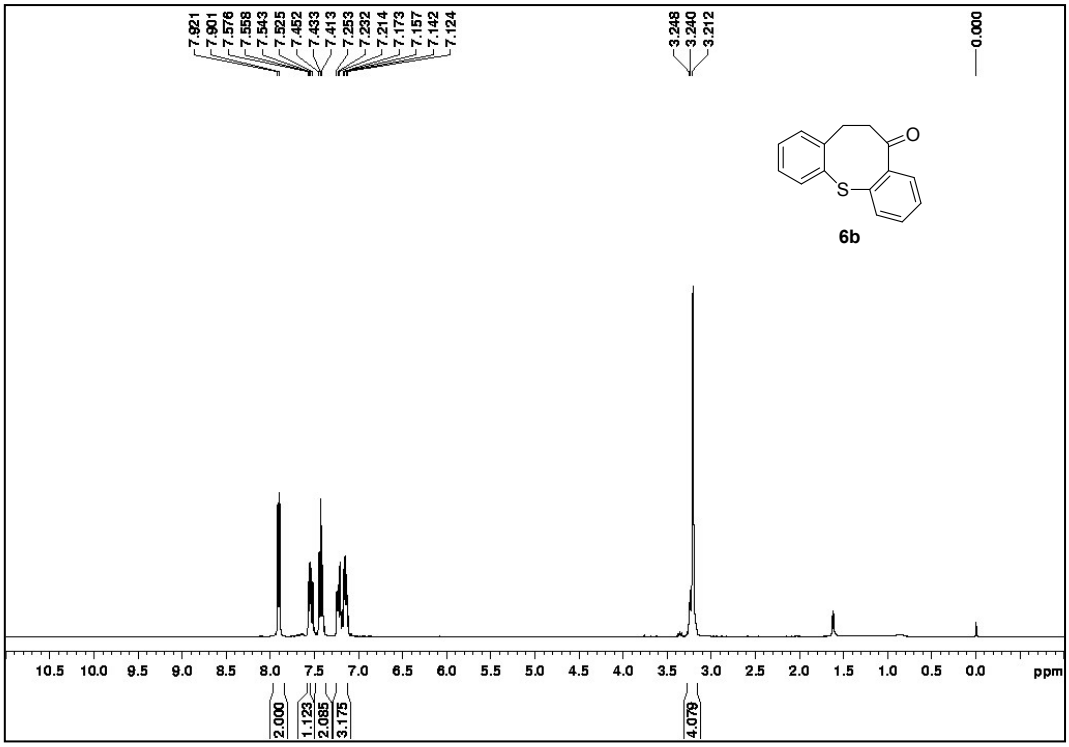


Figure 109:400 MHz ^{1}HNMR spectrum of **6b** in $CDCl_3$

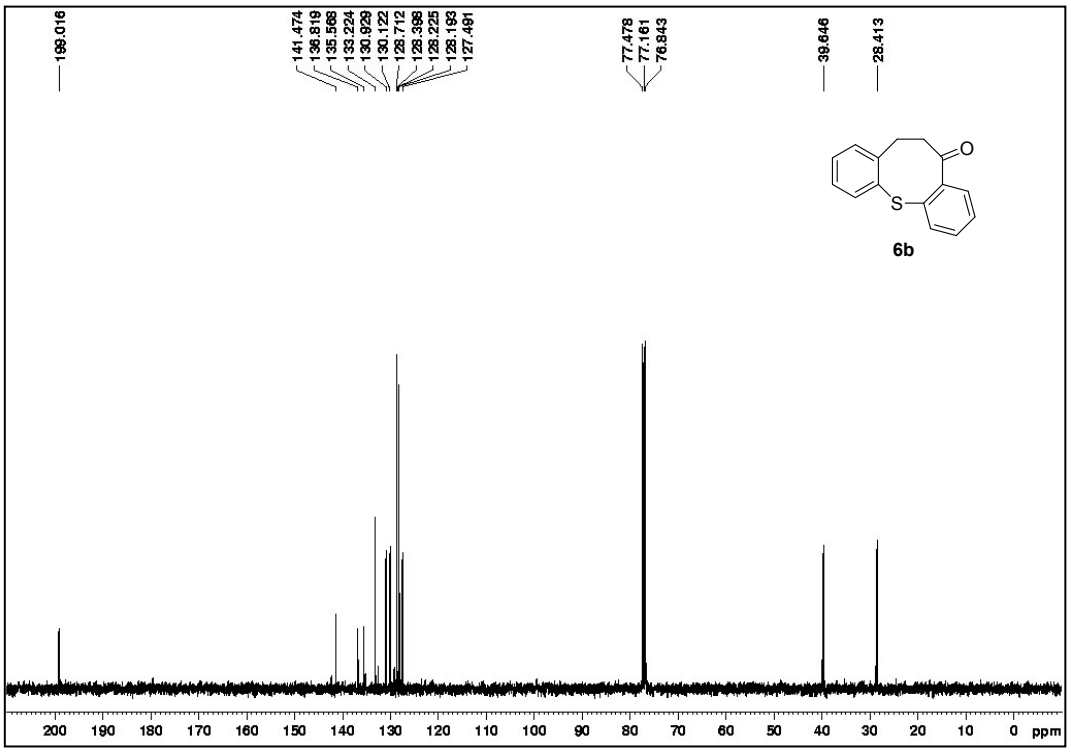


Figure 110:100 MHz ^{13}CNMR spectrum of **6b** in $CDCl_3$

6. Crystal data

XRD data for Compound 2a (CCTC No. 1889041)

Empirical formula	$C_{16}H_{14}OS$
Formula weight	254.33
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 4.7107(12) Å α = 90 deg. b = 10.021(2) Å β = 94.105(11) deg. c = 27.643(6) Å γ = 90 deg.
Volume	1301.6(5) $Å^3$
Z, Calculated density	4, 1.298 Mg/m^3
Absorption coefficient	0.233 mm^{-1}
F(000)	536
Crystal size	0.290 x 0.220 x 0.170 mm
Theta range for data collection	2.162 to 24.994 deg.
Limiting indices	-5<=h<=4, -11<=k<=11, -32<=l<=32
Reflections collected / unique	7581 / 7581
Completeness to theta = 24.994	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7581 / 0 / 166
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0694, wR2 = 0.1849
R indices (all data)	R1 = 0.1021, wR2 = 0.2109
Extinction coefficient	0.013(4)
Largest diff. peak and hole	0.394 and -0.246 $eÅ^3$

XRD data for Compound 3u (CCTC No. 1998140)

Empirical formula	$C_{14}H_{10}O_2S_2$
Formula weight	274.34
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.9604(9) Å alpha = 90 deg. b = 5.9708(3) Å beta = 113.6217(18) deg. c = 16.2069(9) Å gamma = 90 deg.
Volume	1237.73(12) $Å^3$
Z, Calculated density	4, 1.472 Mg/m^3
Absorption coefficient	0.419 mm^{-1}
F(000)	568
Crystal size	0.220 x 0.160 x 0.120 mm
Theta range for data collection	2.483 to 24.998 deg.
Limiting indices	-16<=h<=16, -7<=k<=6, -19<=l<=19
Reflections collected / unique	15195 / 2167 [R(int) = 0.0767]
Completeness to theta = 24.994	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2167 / 0 / 164
Goodness-of-fit on F^2	1.148
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1248
R indices (all data)	R1 = 0.0564, wR2 = 0.1328
Extinction coefficient	n/a
Largest diff. peak and hole	0.304 and -0.294 $eÅ^{-3}$