Supporting Information

Facile Access to Thieno[2,3-b]thiophenes and Poly-substituted thiophenes through Divergent Annulation of Ketene 1,3-Dithietanes

You Wu,[a] Shuqi Wang, [a] Bo Peng, [a] Jie Cen, [a] Yongping Yu, * [a,b] Wenteng Chen * [a,b]

a. College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, Zhejiang, China, 310058

b. Jinhua Institute of Zhejiang University, Jinhua, 321299, China.

*Corresponding authors. wentengchen@zju.edu.cn (for W. Chen), yyu@zju.edu.cn (for Y. Yu)

Table of Contents

I. General Information

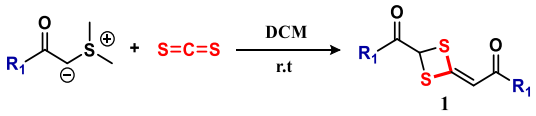
Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used without purification. Purifications of reaction products were carried out by chromatography using silica gel (200-300 mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS ($\delta = 0$) or Chloroform-*d* (δ = 77.26) was used as internal standard and spectra were obtained with complete proton decoupling. HPLC analysis and the HRMS of all final products were confirmed on a Agilent 1290 HPLC-6224 Time of Fight Mass Spectrometer using PhenomenexLuna 5 µ C18, 100 Å, 150 × 4.60 mm 5 µm column at a flow rate of 0.5 mL/min using liner gradients buffer B in A (B: CH_3OH containing 0.1% formic acid, A: H_2O containing 0.1% formic acid). Mobile phase B was increased linearly from 5% to 95% over 7 min and 95% over the next 2 min, after which the column was equilibrated to 5% for 1 min. Sulfur ylides and substituted phenylacetaldehydes were synthesized according to literature procedure. [1,2]

References:

1. Sabounchei, S. J.; Ahmadianpoor, M.; Yousefi, A.; Bayat, M.; Sedghi, A.; Bagherjeri, F. A.; Gable, R. W. *RSC Adv.* **2016**, 6, 28308
2. Al-Smadi, D.; Enugala, T. R.; Norberg, T.; Kihlberg, J.; Widersten, M. *Synlett* **2018,** 29, 1187-1190.

II. Synthesis and Characterization Data of Starting Materials and Final Products

1) Synthesis and characterization of 1,3-dithietanes 1



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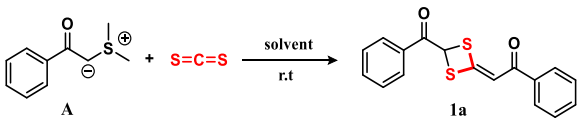
Typical procedure: To a 25 mL flask were added sulfur ylides (180 mg, 1.0 equiv), CS_2 (1 mL, 16 equiv.) and DCM (4 mL). The mixture was stirred at room temperature for 30 min. After the completion of the reaction *via* TLC, the organic phase was removed under vacuum. Then the residue was purified by silica gel flash column chromatography (PE/DCM = 1/1) to afford product 1.

Table S1. Reaction Optimization for the Synthesis of 1, 3-Dithietanes 1



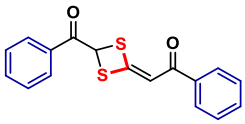
A 1a

entry	A: CS_2	solvent	Concentration (A)	yield (%)[b]
1	1:1.5	$CHCl_3$	1 M	44
2	1:1.5	DCM	1 M	46
3	1:1.5	CH_3CN	1 M	18
4	1:1.5	EtOH	1 M	33
5	1:1.5	THF	1 M	39
6	1:1.5	CH_3COOH	1 M	trace
7	1:1.5	Toluene	1 M	36

8	1:1.5	DMF	1 M	14
9	1:1.5	DCE	1 M	46
10	1:1.5	CH_3COCH_3	1 M	28
11	1:1.5	MTBE	1 M	31
12	1:1.5	CS_2	1 M	36
13	1:1.5	H_2O	1 M	24
14	1:2.5	DCM	1 M	47
15	1:10	DCM	1 M	56
16	1:15	DCM	1 M	63
17	1:25	DCM	1 M	62
18	1:15	DCM	2 M	31
19	1:15	DCM	0.5M	68
20	**1:15**	**DCM**	**0.25M**	**86**

[a] Reaction conditions: A (1mmol), CS_2, and solvent at room temperature for 30 min.

[b] Isolated yield; yields were calculated based on A.



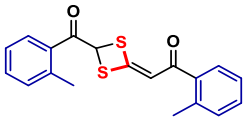
2-(4-benzoyl-1,3-dithietan-2-ylidene)-1-phenylethan-1-one(1a)

yellow solid; 134 mg (86% yield); m.p. 146.7-147.4 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89-7.81 (m, 4H), 7.67-7.62 (m, 1H), 7.55-7.49 (m, 3H), 7.46-7.43 (m, 2H), 7.06 (s, 1H), 6.08 (s, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ191.3, 189.2, 162.7, 137.4, 134.6, 132.8, 132.9, 129.4, 128.8, 128.5, 127.9, 107.6, 48.3.

HRMS (ESI): m/z calcd for $(C_{17}H_{12}O_2S_2+H)^+$: 313.0351; found: 313.0346.



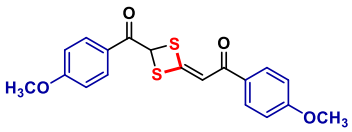
2-(4-(2-methylbenzoyl)-1,3-dithietan-2-ylidene)-1-(*o*-tolyl)ethan-1-one(1b)

yellow solid; 130 mg (77% yield); m.p. 93.5-93.9 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50-7.48 (m, 1H), 7.48-7.41 (m, 2H), 7.35-7.26 (m, 3H), 7.24-7.20 (m, 2H), 6.78 (s, 1H), 6.06 (s, 1H), 2.61 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.1, 193.0, 161.4, 140.5, 138.4, 138.0, 133.1, 133.1, 132.5, 131.8, 131.1, 128.5, 128.2, 126.2, 125.8, 110.8, 49.5, 21.7, 20.9.

HRMS (ESI): m/z calcd for $(C_{19}H_{16}O_2S_2$ +H)$^+$:341.0664; found: 341.0668.



2-(4-(4-methoxybenzoyl)-1,3-dithietan-2-ylidene)-1-(4-methoxyphenyl)ethan-1-one (1c)

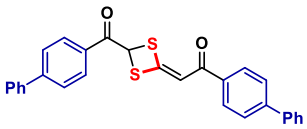
yellow solid; 134 mg (72% yield); m.p. 140.3-141.1 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86-7.80(m, 4H), 7.01 (s, 1H), 6.98-6.91 (m, 4H), 6.03 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 189.7, 187.8, 164.5, 163.2, 161.5, 130.8, 130.2, 129.9, 125.7,

114.5, 113.9, 107.1, 55.7, 55.5, 48.0.

HRMS (ESI): m/z calcd for $(C_{19}H_{16}O_4S_2+H)^+$:373.0563; found: 373.0556.



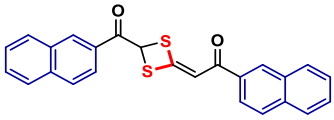
2-(4-([1,1'-biphenyl]-4-carbonyl)-1,3-dithietan-2-ylidene)-1-([1,1'-biphenyl]-4-yl)ethan-1-one(1d)

yellow solid; 190 mg (82% yield); m.p. 191.3-191.8 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07-7.97 (m, 4H), 7.94-7.89 (m, 2H), 7.84-7.78 (m, 4H), 7.76-7.73 (m, 2H), 7.57 (s, 1H), 7.54-7.48 (m, 4H), 7.46-7.39 (m, 2H), 6.78 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 191.3, 187.3, 163.3, 145.7, 144.2, 138.9, 138.6, 135.8, 131.6, 129.2, 129.1, 128.7, 128.3, 127.5, 127.1, 127.0, 127.0, 107.9, 47.5.

HRMS (ESI): m/z calcd for $(C_{29}H_{20}O_2S_2+H)^+$:465.0977; found: 465.0978.



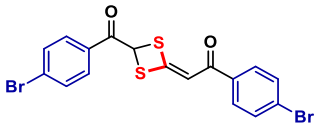
2-(4-(2-naphthoyl)-1,3-dithietan-2-ylidene)-1-(naphthalen-2-yl)ethan-1-one(1e)

yellow solid; 175 mg (85% yield); m.p. 189.4-189.7 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 1H), 8.62 (s, 1H), 8.18-8.17 (m, 1H), 8.13-8.11 (m, 1H), 8.09-8.04 (m, 2H), 8.01-7.96 (m, 4H), 7.75-7.72 (m, 1H), 7.70-7.60 (m, 4H), 6.89 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 192.1, 188.1, 135.9, 135.3, 134.8, 132.8, 132.6, 131.0, 130.7, 130.2, 129.8, 129.9, 129.6, 129,5, 129.0, 128.3, 128.2, 127.9, 127.4, 124.0, 108.5, 47.9.

HRMS (ESI): m/z calcd for $(C_{25}H_{16}O_2S_2+H)^+$:413.0670; found: 413.0673.



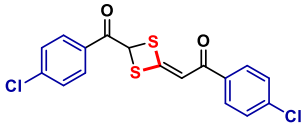
2-(4-(4-bromobenzoyl)-1,3-dithietan-2-ylidene)-1-(4-bromophenyl)ethan-1-one(1f)

yellow solid; 163 mg (70% yield); m.p. 183.3-183.6 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.90-7.85 (m, 2H), 7.85-7.79 (m, 4H), 7.73-7.71 (m, 2H), 7.50 (s, 1H), 6.69 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 191.5, 187.2, 164.7, 136.4, 132.9, 132.4 ,132.4, 130.8, 130.1,129.1, 127.3, 108.2, 47.7.

HRMS (ESI): m/z calcd for $(C_{17}H_{10}Br_2O_2S_2+Na)^+$: 490.8381; found: 490.8376.



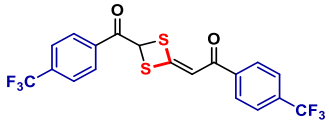
2-(4-(4-chlorobenzoyl)-1,3-dithietan-2-ylidene)-1-(4-chlorophenyl)ethan-1-one(1g)

yellow solid; 161 mg (85% yield); m.p. 195.7-196.5 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99-7.94 (m, 2H), 7.94-7.89 (m, 2H), 7.71-7.65 (m, 2H), 7.62-7.55 (m, 2H), 7.50 (s, 1H), 6.70 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 190.8, 186.5, 164.2, 139.4, 137.7, 135.6, 131.7, 130.3, 129.5, 129.5, 129.0 107.7, 47.2.

HRMS (ESI): m/z calcd for $(C_{17}H1_0Cl_2O_2S_2 +H)^+$:380.9572; found: 380.9573.



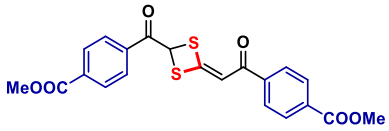
2-(4-(4-(trifluoromethyl)benzoyl)-1,3-dithietan-2-ylidene)-1-(4-(trifluoromethyl)phenyl) ethan-1-one(1h)

yellow solid; 202 mg (90% yield); m.p. 175.6-175.9 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17-8.15 ((m, 2H), 8.10-8.09 (m, 2H), 7.99-7.98 (m, 2H), 7.89 - 7.88 (m, 2H), 7.58 (s, 1H), 6.78 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 191.2, 186.6, 165.4, 140.2, 136.4, 133.4 (q, J = 32 Hz), 132.2 (q, J = 32 Hz), 129.3, 128.4, 126.3 (q, J = 7.0, 3.6 Hz), 125.9 (q, J = 3.6 Hz), 124.8 (d, J = 27 Hz), 122.6 (d, J = 27 Hz), 108.0, 47.3.

HRMS (ESI): m/z calcd for $(C_{19}H_{10}F_6O_2S_2 +Na)^+$:470.9919; found: 470.9907.



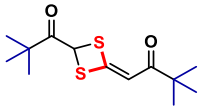
methyl 4-(2-(4-(4-(methoxycarbonyl)benzoyl)-1,3-dithietan-2-ylidene)acetyl)benzoate(1i)

yellow solid; 152 mg (71% yield); m.p. 198.7-199.6 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.16-8.12 (m, 2H), 8.09-8.05 (m, 4H), 8.04-8.01 (m, 2H), 7.56 (s, 1H), 6.75 (s, 1H), 3.91 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 191.5, 187.0, 165.6, 165.4, 165.1, 140.5, 136.4, 134.2, 132.9, 129.9, 129.6, 128.8, 127.9, 108.1, 52.7, 52.5, 47.4.

HRMS (ESI): m/z calcd for $(C_{21}H_{16}O_6S_2 +H)^+$:429.0461; found: 429.0463.



3,3-dimethyl-1-(4-pivaloyl-1,3-dithietan-2-ylidene)butan-2-one(1j)

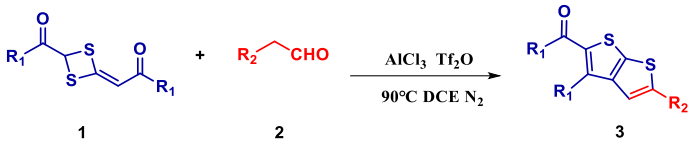
yellow solid; 120 mg (88% yield); m.p. 86.4-87.0 ℃.

^{1}H NMR (500 MHz, Chloroform-d) δ 6.49 (s, 1H), 5.62 (s, 1H), 1.21 (s, 9H), 1.12 (s, 9H).

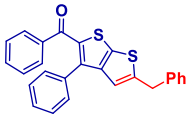
^{13}C NMR (125 MHz, Chloroform-d) δ 206.4, 205.3, 160.8, 107.1, 47.0, 44.7, 42.7, 26.9, 26.7.

HRMS (ESI): m/z calcd for $(C_{13}H_{20}O_2S_2+H)^+$:295.0802; found: 295.0798.

2) Synthesis and characterization data of thieno[2,3-b]thiophenes 3



Typical procedure (with 3m as an example): To a 25 mL of dried schlenk tube equipped with a magnetic stir bar was charged with 1,3-dithietane 1a (100 mg, 1.0 equiv), hexanal (80 μL, 2.0 equiv), $AlCl_3$ (9 mg, 20 mol%), Tf_2O (10 μL, 20 mol%) and 2 mL DCE under N_2 atmosphere. The mixture was then stirred at 90 °C for 12 h. After the reaction, the mixture was cooled to room temperature, and the organic phase was removed under vacuum. Purification of the crude product by silica-gel chromatography using PE/DCM affords thieno[2,3-b]thiophenes **3m**.



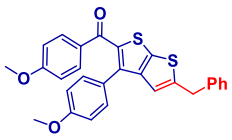
(5-benzyl-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone(3a)

yellow solid; 96 mg (60% yield); m.p. 157.8-158.3 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 -7.51 (m, 2H), 7.35-7.30 (m, 2H), 7.29-7.26 (m, 3H), 7.26-7.22 (m, 3H), 7.17-7.14 (m, 3H), 7.13-7.09 (m, 2H), 6.96 (s, 1H), 4.20 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 149.1, 147.5, 141.2, 140.2, 139.6, 139.5, 137.8, 135.2, 132.0, 129.8, 129.6, 128.9, 128.7, 128.3, 128.0, 127.8, 127.0, 118.7, 37.5.

HRMS (ESI): m/z calcd for $(C_{26}H_{18}OS_2+H)^+$: 411.0872; found: 411.0881.



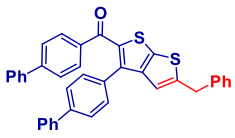
(5-benzyl-3-(4-methoxyphenyl)thieno[2,3-b]thiophen-2-yl)(4-methoxyphenyl)methanone (3b)

brown solid; 80 mg (53% yield); m.p. 70.4-70.9 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62-7.57 (m, 2H), 7.35-7.30 (m, 2H), 7.30-7.25 (m, 3H), 7.23-7.19 (m, 2H), 6.98 (t, *J* = 1.0 Hz, 1H), 6.76 – 6.71 (m, 2H), 6.67-6.62 (m, 2H), 4.20 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.9, 162.8, 159.5, 148.8, 147.3, 140.2, 139.5, 139.4, 138.5, 132.2, 131.0, 130.4, 128.8, 128.7, 127.8, 127.0, 118.7, 113.9, 113.2, 55.5, 55.4, 37.5.

HRMS (ESI): m/z calcd for $(C_{28}H_{22}O_3S_2+H)^+$: 471.1083; found: 471.1078.



[1,1'-biphenyl]-4-yl(3-([1,1'-biphenyl]-4-yl)-5-benzylthieno[2,3-b]thiophen-2-yl)methanone (3c)

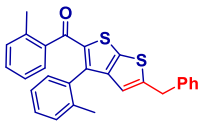
yellow solid; 90 mg (50% yield); m.p. 81.5-82.0 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.42-7.24 (m, 21H), 7.01 (s, 1H),

4.21 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 189.7, 149.1, 147.4, 144.7, 141.4, 140.9, 140.4, 140.4, 140.1, 139.3, 139.2, 136.5, 134.1, 130.2, 130.1, 128.8, 128.7, 128.7, 128.6, 127.9, 127.5, 127.3, 127.2, 126.9, 126.9, 126.4, 118.6, 37.4.

HRMS (ESI): m/z calcd for $(C_{38}H_{26}OS_2+H)^+$: 563.1498; found: 563.1491.



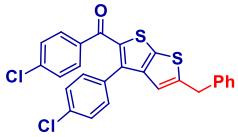
(5-benzyl-3-(o-tolyl)thieno[2,3-b]thiophen-2-yl)(o-tolyl)methanone (3d)

white solid; 84 mg (60% yield); m.p. 132.9-133.2 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33-7.28 (m, 2H), 7.26-7.21 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.09-7.04 (m, 2H), 7.04-6.95 (m, 4H), 6.86 (t, *J* = 7.0 Hz, 1H), 6.60 (s, 1H), 4.14 (s, 2H), 2.31 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 191.5, 148.9, 148.4, 142.1, 134.0, 139.3, 138.8, 135.9, 135.8, 134.6, 130.3, 129.9, 129.8, 129.6, 128.7, 128.6, 128.0, 127.7, 126.9, 125.2, 124.5, 118.7, 37.4, 20.1, 19.7.

HRMS (ESI): m/z calcd for $(C_{28}H_{22}OS_2+H)^+$: 439.1185; found: 439.1180.



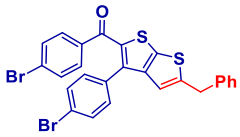
(5-benzyl-3-(4-chlorophenyl)thieno[2,3-b]thiophen-2-yl)(4-chlorophenyl)methanone (3e)

yellow solid; 111 mg (73% yield); m.p. 135.3-135.7 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51-7.47 (m, 2H), 7.35-7.30 (m, 2H), 7.26 (m 3H), 7.21-7.13 (m, 6H), 6.90 (s, 1H), 4.20 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.5, 149.7, 147.1, 141.4, 139.6, 139.2, 138.6, 138.2, 136.0, 134.3, 133.4, 130.9, 128.8, 128.6, 128.6, 128.2, 127.0, 118.1, 37.4.

HRMS (ESI): m/z calcd for $(C_{26}H_{16}Cl_2OS_2+H)^+$: 479.0092; found: 479.0093.



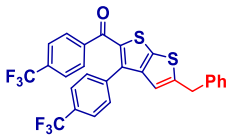
(5-benzyl-3-(4-bromophenyl)thieno[2,3-b]thiophen-2-yl)(4-bromophenyl)methanone (3f)

yellow solid; 157 mg (87% yield); m.p. 148.1-149.0 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43-7.38 (m, 2H), 7.38-7.30 (m, 6H), 7.28-7.25 (m, 3H), 7.13-7.08 (m, 2H), 6.90 (t, *J* = 1.0 Hz, 1H), 4.20 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.8, 149.9, 147.2, 141.6, 139.7, 139.2, 138.4, 136.6, 134.0, 131.6, 131.3, 131.2, 131.1, 128.9, 128.7, 127.3, 127.1, 122.7, 118.1, 37.5.

HRMS (ESI): m/z calcd for $(C_{26}H_{16}Br_2OS_2+H)^+$: 566.9082; found: 566.9083.



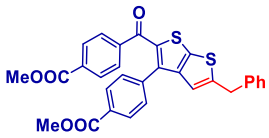
(5-benzyl-3-(4-(trifluoromethyl)phenyl)thieno[2,3-b]thiophen-2-yl)(4-(trifluoromethyl)phenyl)methanone (3g)

white solid; 126 mg (72% yield); m.p. 123.5-123.8 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.36-7.29 (m, 4H), 7.29-7.26 (m, 3H), 6.88 (s, 1H), 4.20 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.7, 150.4, 147.4, 142.6, 141.0, 140.5, 1391, 138.6, 138.6, 133.5 (d, *J* = 33 Hz), 130.5 (q, *J* = 33Hz), 130.1, 129.5, 129.0, 128.7, 127.2, 125.2 (q, *J* = 3.5 Hz), 124.9 (q, *J* = 3.5 Hz), 122.7, 122.3, 118.0, 37.5.

HRMS (ESI): m/z calcd for $(C_{28}H_{16}F_6OS_2+H)^+$: 547.0620; found: 547.0611.



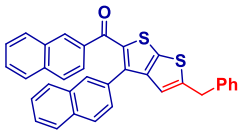
methyl 4-(5-benzyl-2-(4-(methoxycarbonyl)benzoyl)thieno[2,3-b]thiophen-3-yl)benzoate (3h)

yellow solid; 112 mg (67% yield); m.p. 140.3-141.1 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.34-7.30 (m, 4H), 7.27-7.24 (m, 4H), 6.90 (s, 1H), 4.20 (s, 2H), 3.89 (s, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 189.2, 166.6, 166.2, 150.0, 147.3, 142.0, 141.5, 140.2, 139.6, 139.2, 138.7, 132.9, 129.8, 129.7, 129.6, 129.4, 129.2, 128.9, 128.7, 127.1, 118.2, 52.5, 52.3, 37.5.

HRMS (ESI): m/z calcd for $(C_{30}H_{22}O_5S_2+H)^+$: 527.0981; found:527.0975.



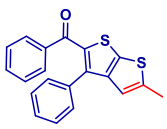
(5-benzyl-3-(naphthalen-2-yl)thieno[2,3-b]thiophen-2-yl)(naphthalen-2-yl)methanone(3i)

white solid; 113 mg (69% yield); m.p. 164.2-165.1 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.78 (s, 1H), 7.70-7.68 (m, 1H), 7.65-7.61 (m, 1H), 7.58-7.55 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.39-7.25 (m, 10H), 7.03 (s, 1H), 4.22 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 189.9, 149.2, 147.6, 141.1, 140.1, 139.6, 139.4, 135.0, 134.8, 132.9, 132.7, 132.5, 131.8, 131.4, 128.9, 128.8, 128.6, 127.9, 127.8, 127.8, 127.7, 127.4, 127.1, 126.9, 126.3, 126.2, 126.1, 125.0, 118.6, 37.4.

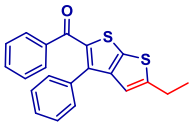
HRMS (ESI): m/z calcd for $(C_{34}H_{22}OS_2+H)^+$: 511.1185; found: 511.1181.



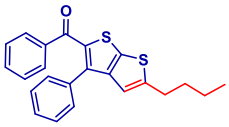
(5-methyl-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3k)

yellow solid; 53 mg (50% yield); m.p. 153.7-153.9 ℃.

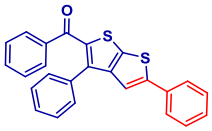
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55-7.53 (m, 2H), 7.28-7.22 (m, 3H), 7.17-7.13 (m, 3H), 7.13-7.09 (m, 2H), 6.87 (q, *J* = 1.0 Hz, 1H), 2.56 (d, *J* = 1.0 Hz, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.4, 147.8, 144.6, 140.4, 140.1, 139.4, 137.8, 135.3, 131.9, 129.8, 129.6, 128.2, 127.9, 127.8, 118.7, 16.6.
HRMS (ESI): m/z calcd for $(C_{20}H_{14}OS_2+H)^+$: 335.0559; found: 335.0559.



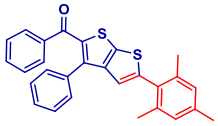
(5-ethyl-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3l)
yellow solid; 66 mg (59% yield); m.p. 150.9-151.4 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57-7.52 (m, 2H), 7.28-7.24 (m, 3H), 7.18-7.15 (m, 3H), 7.13-7.10 (m, 2H), 6.89 (s, 1H), 2.93-2.88 (m, 2H), 1.35 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.4, 152.4, 147.7, 140.18, 140.1, 139.6, 137.9, 135.4, 131.9, 129.9, 129.6, 128.2, 127.9, 127.8, 116.9, 24.7, 15.9.
HRMS (ESI): m/z calcd for $(C_{20}H_{14}OS_2+H)^+$: 349.0715; found: 349.0715.



(5-butyl-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3m)
white solid; 66 mg (59% yield); m.p. 93.0-93.2 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*)) δ 7.56-7.52 (m, 2H), 7.29-7.23 (m, 3H), 7.18-7.14 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.88 (s, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.74-1.66 (m, 2H), 1.45-1.37 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*)) δ 190.4, 150. 9, 147.6, 140.2, 140.1, 139.5, 137.9, 135.4, 131.9, 129.9, 129, 128.2, 127.9, 127.8, 117.5, 33.8, 31.1, 22.3, 13.9.
HRMS (ESI): m/z calcd for $(C_{23}H_{20}OS_2+H)^+$: 377.1028; found: 377.1020.



(3,5-diphenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3n)
yellow solid; 89 mg (70% yield); m.p. 198.0-198.7 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61-7.56 (m, 4H), 7.43-7.37 (m, 3H), 7.35-7.27 (m, 4H), 7.21-7.18 (m, 3H), 7.13 (t, *J* = 8.0 Hz, 2H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.3, 148.7, 148.5, 141.5, 140.6, 139.8, 137.7, 135.1, 134.3, 132.1, 129.9, 129.7, 129.2, 128.4, 128.4, 128.2, 127.9, 126.1, 116.5.
HRMS (ESI): m/z calcd for $(C_{25}H_{16}OS_2+H)^+$: 397.0715; found:397.0713.



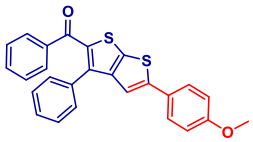
(5-mesityl-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone(3o)

yellow solid; 133 mg (95% yield); m.p. 209.1-209.9 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61-7.59 (m, 2H), 7.31-7.27 (m, 3H), 7.16-7.11 (m, 5H), 6.94-6.93 (m, 3H), 2.32 (s, 3H), 2.20 (s, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.5, 147.8, 146.3, 142.1, 140.1, 139.8, 138.8, 138.4, 137.8, 135.2, 132.1, 130.5, 129.9, 129.8, 128.3, 128.3, 128.1, 127.8, 120.1, 21.3, 20.9.

HRMS (ESI): m/z calcd for $(C_{28}H_{22}OS_2+H)^+$: 439.1185; found: 439.1177.



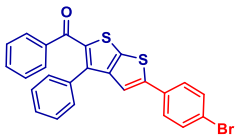
(5-(4-methoxyphenyl)-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3p)

yellow solid; 133 mg (95% yield); m.p. 160.5-161.4 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59-7.55 (m, 2H), 7.54-7.51 (m, 2H), 7.31-7.26 (m, 4H), 7.21-7.16 (m, 3H), 7.15-7.11 (m, 2H), 6.95-6.90 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.3, 159.9, 148.7, 148.6, 140.8, 140.5, 139.8, 137.8, 135.2, 132.0, 129.9, 129.7, 128.4, 128.1, 127.8, 127.5, 127.1, 115.3, 114.6, 55.5.

HRMS (ESI): m/z calcd for $(C_{26}H_{18}O_2S_2+H)^+$: 427.0821; found: 427.0817.



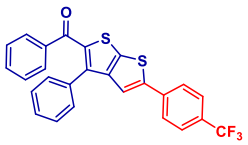
(5-(4-bromophenyl)-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3q)

yellow solid; 107 mg (71% yield); m.p. 208.6-209.0 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*)) δ 7.57-7.54 (m, 2H), 7.53-7.50 (m, 2H), 7.47-7.44 (m, 2H), 7.37 (s, 1H), 7.29-7.27 (m, 3H), 7.21-7.17 (m, 3H), 7.14-7.11 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*)) δ 190.2, 148.5, 147.3, 141.6, 140.8, 139.8, 137.6, 135.0, 133.3, 132.3, 132.2, 129.8, 129.7, 128.4, 128.2, 127.9, 127.5, 122.3, 116.9.

HRMS (ESI): m/z calcd for $(C_{25}H_{15}BrOS_2+H)^+$: 474.9820; found: 474.9819.



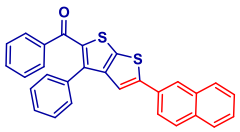
phenyl(3-phenyl-5-(4-(trifluoromethyl)phenyl)thieno[2,3-b]thiophen-2-yl)methanone (3r)

white solid; 122 mg (82% yield); m.p. 133.2-133.9 ℃.

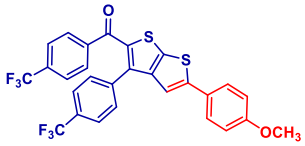
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71-7.70 (m, 2H), 7.66-7.64 (m, 2H), 7.59-7.55 (m, 2H), 7.47 (s, 1H), 7.32-7.27 (m, 3H), 7.22-7.19 (m, 3H), 7.16 – 7.11 (m, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.3, 148.4, 146.7, 142.2, 141.1, 139.8, 137.6, 137.5, 134.9,

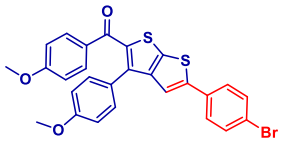
132.2, 129.8, 129.7, 128.5, 128.3, 127.9, 126.2(q, J = 3.75Hz), 126.2, 118.0.
HRMS (ESI): m/z calcd for $(C_{26}H_{15}F_3OS_2+H)^+$: 465.0589; found: 465.0588.



(5-(naphthalen-2-yl)-3-phenylthieno[2,3-b]thiophen-2-yl)(phenyl)methanone (3s)
yellow solid; 131 mg (92% yield); m.p. 92.9-93.2 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.25-8.19 (m, 1H), 7.94-7.86 (m, 2H), 7.65-7.57 (m, 3H), 7.55-7.49 (m, 3H), 7.35 (s, 1H), 7.34-7.27 (m, 3H), 7.21-7.10 (m, 5H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.5, 147.9, 146.1, 142.1, 140.6, 139.9, 137.8, 135.1, 133.9, 132.1, 132.1, 131.9, 129.9, 129.7, 129.4, 128.8, 128.6, 128.4, 128.2, 127.9, 127.0, 126.4, 125.63 125.3, 121.0.
HRMS (ESI): m/z calcd for $(C_{29}H_{18}OS_2+H)^+$: 447.0872; found: 447.0880.

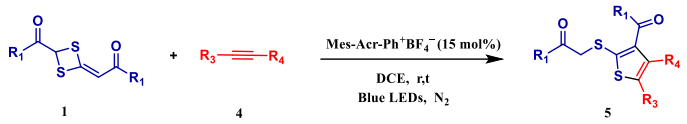


(5-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)thieno[2,3-b]thiophen-2-yl)(4-(trifluoromethyl)phenyl)methanone (3t)
yellow solid; 109 mg (61% yield); m.p. 201.5-201.8 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62-7.57 (m, 2H), 7.54-7.49 (m, 2H), 7.46-7.44 (m, 2H), 7.41-7.39 (m, 2H), 7.37-7.35 (m, 2H), 7.18 (s, 1H), 6.96-6.91 (m, 2H), 3.84 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.6, 160.2, 149.8, 148.4, 142.2, 141.0, 140.7, 138.8, 138.6, 133.5 (q, J = 33Hz), 130.7, 130.5 (q, J = 33Hz), 129.6, 127.6, 126.6, 125.3 (q, J = 3.6Hz), 125.0 (q, J = 3.6Hz), 114.7, 114.6, 55.6.
HRMS (ESI): m/z calcd for $(C_{28}H_{16}F_6O_2S_2+H)^+$: 563.0569; found: 563.0572.



(5-(4-bromophenyl)-3-(4-methoxyphenyl)thieno[2,3-b]thiophen-2-yl)(4-methoxyphenyl)methanone(3u)
yellow solid; 124 mg (73% yield); m.p. 144.5-144.9 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65-7.59 (m, 2H), 7.54-7.44 (m, 4H), 7.39 (s, 1H), 7.27-7.23 (m, 2H), 6.79-6.75 (m, 2H), 6.70-6.63 (m, 2H), 3.77-3.76 (m, 6H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 188.9, 163.0, 159.6, 148.3, 146.9, 140.7, 140.1, 138.6, 133.4, 132.3, 132.3, 131.0, 130.2, 127.6, 127.5, 122.2, 116.9, 114.0, 113.3, 55.5, 55.4.
HRMS (ESI): m/z calcd for $(C_{27}H_{19}BrO_3S_2+H)^+$: 535.0032; found: 535.0026.

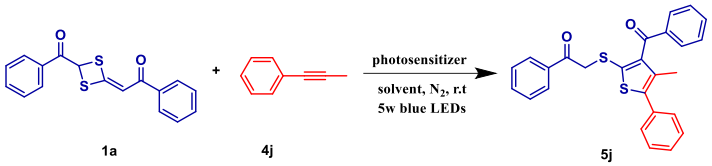
3) Synthesis and characterization of poly-substituted thiophenes 5



1 4 5

Typical procedure (with 5j as an example): The oven-dried schlenk tube (25 mL) was charged with 1,3-dithietanes **1a** (100 mg, 1.0 equiv), Mes-Acr-Ph$^+$BF$_4^-$ (20 mg, 0.2 equiv), 1-phenyl-1-propyne (74 mg, 2.0 equiv) and 2 mL DCE under N_2 atmosphere. The reaction mixture was stirred for 48 h under irradiation using 5 W blue LEDs at room temperature. After the completion of the reaction as indicated by TLC, the organic phase was removed under vacuum. The crude product was purified by silica gel chromatography (PE/EA=75/1) to afford compound **5j**.

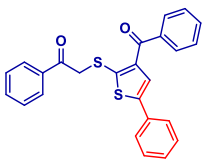
Table S2. Reaction Optimization for the Synthesis of poly-substituted thiophenes 5 [a]



1a 4j 5j

entry	1a:4j	photosensitizer (mol %)	solvent	time(h)	yield (%)[b]
1	1:1.2	Mes-Acr-Ph$^+$BF$_4^-$(5)	DCE	48	43
2	1:2	Mes-Acr-Ph$^+$BF$_4^-$(5)	DCE	48	47
3	1:3	Mes-Acr-Ph$^+$BF$_4^-$(5)	DCE	48	48
4	1:2	Mes-Acr-Ph$^+$BF$_4^-$(5)	DMF	48	0
5	1:2	Mes-Acr-Ph$^+$BF$_4^-$(5)	CH_3CN	48	0
6	1:2	Mes-Acr-Ph$^+$BF$_4^-$(5)	EtOH	48	0
7	1:2	Mes-Acr-Ph$^+$BF$_4^-$(5)	THF	48	19
8	1:2	Mes-Acr-Ph$^+$BF$_4^-$(10)	DCE	48	56
9	**1:2**	**Mes-Acr-Ph$^+$BF$_4^-$(15)**	**DCE**	**48**	**62**
10	1:2	Mes-Acr$^+$ClO$_4^-$(10)	DCE	48	42
11	1:2	Ru(bpy)$_3$(PF$_6$)$_2$(10)	DCE	48	0
12	1:2	Ir(ppy)$_2$(bpy)]PF$_6$(10)	DCE	48	0
13	1:2	Rose Bengal (10)	DCE	48	0
14 [c]	1:2	Mes-Acr-Ph$^+$BF$_4^-$(10)	DCE	48	0
15	1:2	–	DCE	48	0

[a] Reaction conditions: 1,3-dithietane 1a (0.32 mmol), alkynes 4j, and photocatalyst in solvent (2.0 mL) under irradiation using 5 W blue LEDs at room temperature under a N_2 atmosphere.
[b] Isolated yield; yields were calculated based on 1a.
[c] Under air.



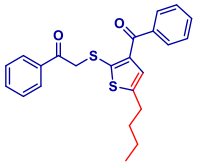
2-((3-benzoyl-5-phenylthiophen-2-yl)thio)-1-phenylethan-1-one (5a)

brown oil; 80 mg (60% yield);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99-7.97 (m, 2H), 7.84-7.81 (m, 2H), 7.60-7.56 (m, 2H), 7.51-7.46 (m, 6H), 7.39-7.36 (m, 3H), 7.32-7.30 (m, 1H), 4.52 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.4, 190.6, 143.6, 143.3, 140.5, 138.6, 135.5, 133.9, 133.1, 132.7, 129.6, 129.2, 128.9, 128.8, 128.6, 128.4, 125.9, 125.4, 44.2.

HRMS (ESI): m/z calcd for ($C_{25}H_{18}O_2S_2$+H)$^+$: 415.0821; found: 415.0818.



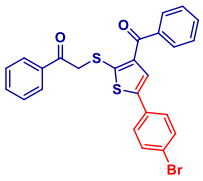
2-((3-benzoyl-5-butylthiophen-2-yl)thio)-1-phenylethan-1-one (5b)

brown oil; 61 mg (48% yield);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.79-7.73 (m, 2H), 7.58-7.51 (m, 2H), 7.46-7.40 (m, 4H), 6.87 (s, 1H), 4.41 (s, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.63-1.57 (m, 2H), 1.41-1.32 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.6, 190.6, 146.0, 140.4, 139.9, 138.6, 135.5, 133.7, 132.4, 129.5, 128.7, 128.8, 128.4, 126.8, 44.1, 33.4, 29.9, 22.1, 13.8

HRMS (ESI): m/z calcd for $(C_{23}H_{22}O_2S_2+H)^+$: 395.1134; found: 395.1137.



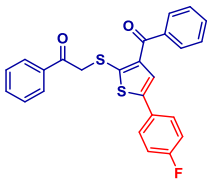
2-((3-benzoyl-5-(4-bromophenyl)thiophen-2-yl)thio)-1-phenylethan-1-one (5c)

yellow solid; 103 mg (66% yield); m.p. 131.6-132.4 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00-7.95 (m, 2H), 7.82-7.79 (m, 2H), 7.61-7.57 (m, 2H), 7.51-7.47 (m, 6H), 7.38-7.35 (m, 3H), 4.51 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 190.5, 144.1, 142.0, 140.4, 138.5, 135.4, 134.0, 132.8, 132.3, 132.1, 129.6, 128.9, 128.8, 128.6, 127.3, 125.8, 122.3, 44.1.

HRMS (ESI): m/z calcd for $(C_{25}H_{17}BrO_2S_2+H)^+$: 492.9926; found: 492.9928.



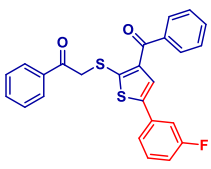
2-((3-benzoyl-5-(4-fluorophenyl)thiophen-2-yl)thio)-1-phenylethan-1-one (5d)

yellow solid; 91 mg (66% yield); m.p. 118.4-118.9 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.81 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.61-7.55 (m, 2H), 7.51-7.44 (m, 6H), 7.31 (s, 1H), 7.09-7.03 (m, 2H), 4.50 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.3, 190.6, 162.8 (d, *J* = 247.1 Hz), 143.1, 142.5, 140.6, 138.5, 135.4, 133.9, 132.7, 129.6, 129.4 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 15.4 Hz), 128.6, 127.7 (d, *J* = 8.1 Hz), 125.4, 116.3, 116.1, 44.1.

HRMS (ESI): m/z calcd for $(C_{25}H_{17}FO_2S_2+Na)^+$: 455.0546; found: 455.0551.



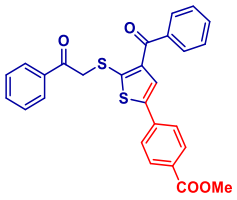
2-((3-benzoyl-5-(3-fluorophenyl)thiophen-2-yl)thio)-1-phenylethan-1-one (5e)

yellow solid; 87 mg (63% yield); m.p. 107.3-108.1 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03-7.95 (m, 2H), 7.84-7.78 (m, 2H), 7.62-7.56 (m, 2H), 7.51-7.46 (m, 4H), 7.35-7.31(m, 1H), 7.29-7.27 (m, 1H), 7.21-7.17 (m, 1H), 7.02-6.98 (m, 1H), 4.53 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 190.4, 163.2(d, J = 245.2 Hz), 144.6, 141.7, 140.1, 138.5, 135.4, 135.2 (d, J = 8.2 Hz), 133.9, 132.7, 130.8 (d, J = 8.7 Hz), 129.6, 128.9 (d, J = 19.5 Hz), 128.6, 126.1, 121.5 (d, J = 2.6 Hz), 115.3(d, J = 21.1Hz), 112.8, 112.6, 44.1.

HRMS (ESI): m/z calcd for $(C_{25}H_{17}FO_2S_2+H)^+$: 455.0546; found: 455.0551.



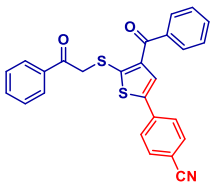
methyl 4-(4-benzoyl-5-((2-oxo-2-phenylethyl)thio)thiophen-2-yl)benzoate (5g)

yellow solid; 94 mg (63% yield); m.p. 128.1-128.9 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.90 (m, 2H), 7.73-7.66 (m, 2H), 7.58-7.53 (m, 1H), 7.45-7.39 (m, 3H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 3H), 7.18-7.15 (m, 2H), 7.08-7.01 (m, 5H), 4.32 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.5, 194.0, 148.1, 144.2, 137.9, 137.3, 135.5, 134.6, 133.7, 133.5, 133.0, 130.7, 130.0, 129.9, 129.3, 128.8, 128.8, 128.6, 128.4, 128.4, 128.1, 127.5, 45.6.

HRMS (ESI): m/z calcd for $(C_{27}H_{20}O_4S_2+H)^+$: 473.0876; found: 473.0873.



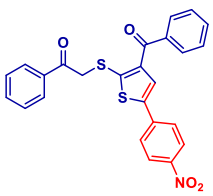
4-(4-benzoyl-5-((2-oxo-2-phenylethyl)thio)thiophen-2-yl)benzonitrile (5h)

yellow solid; 70 mg (50% yield); m.p. 143.2-144.4 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00-7.98 (m, 2H), 7.80-7.79 (m, 2H), 7.65-7.57 (m, 6H), 7.52-7.48 (m, 4H), 7.47 (s, 1H), 4.54 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.8, 190.1, 147.0, 140.1, 139.6, 138.3, 137.2, 135.2, 134.0, 132.9, 132.7, 129.37, 128.90, 128.7, 128.6, 127.3, 125.9, 118.6, 111.3, 43.8.

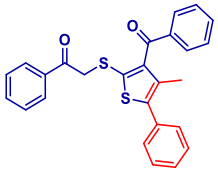
HRMS (ESI): m/z calcd for $(C_{26}H_{17}NO_2S_2+H)^+$: 440.0773; found: 440.0772.



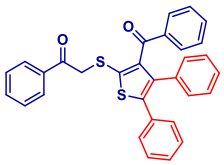
2-((3-benzoyl-5-(4-nitrophenyl)thiophen-2-yl)thio)-1-phenylethan-1-one (5i)

yellow solid; 31 mg (21% yield); m.p. 85.5-86.7 ℃.

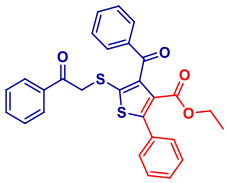
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23-8.21 (m, 2H), 8.00-7.99 (m, 2H), 7.81.7.80 (m, 2H), 7.64-7.59 (m, 4H), 7.56 (s, 1H), 7.51-7.49 (m, 4H), 4.56 (s, 2H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.8, 190.2, 148.1, 147.1, 139.6, 139.5, 139.2, 138.4, 135.3, 134.1, 132.9, 129.5, 129.0, 128.8, 128.7, 127.9, 126.0, 124.7, 43.8.
HRMS (ESI): m/z calcd for $(C_{25}H_{17}NO_4S_2+H)^+$: 460.0672; found: 460.0676.



2-((3-benzoyl-4-methyl-5-phenylthiophen-2-yl)thio)-1-phenylethan-1-one (5j)
brown oil; 78 mg (57% yield);
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90-7.83 (m, 4H), 7.62-7.58 (m, 1H), 7.56-7.53 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.40 (m, 6H), 7.38-7.35 (m, 1H), 4.23 (s, 2H), 2.07 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.8, 193.8, 147.8, 143.4, 137.5, 135.5, 133.9, 133.7, 133.36, 132.5, 130.4, 130.0, 129.4, 128.9, 128.8, 128.8, 128.7, 128.2, 45.7, 14.3.
HRMS (ESI): m/z calcd for $(C_{26}H_{20}O_2S_2+Na)^+$: 451.0797; found: 451.0797.



2-((3-benzoyl-4,5-diphenylthiophen-2-yl)thio)-1-phenylethan-1-one (5k)
yellow solid; 50 mg (32% yield); m.p. 61.2-61.7 ℃.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.90 (m, 2H), 7.73-7.66 (m, 2H), 7.58-7.53 (m, 1H), 7.45-7.39 (m, 3H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 3H), 7.18-7.15 (m, 2H), 7.08-7.01 (m, 5H), 4.32 (s, 2H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.5, 194.0, 148.1, 144.2, 137.9, 137.3, 135.5, 134.6, 133.7, 133.5, 133.0, 130.7, 130.0, 129.9, 129.3, 128.8, 128.8, 128.6, 128.4, 128.4, 128.1, 127.5, 45.6.
HRMS (ESI): m/z calcd for $(C_{31}H_{22}O_2S_2+H)^+$: 491.1134; found: 491.1133.



2-((3-benzoyl-5-(4-nitrophenyl)thiophen-2-yl)thio)-1-phenylethan-1-one (5l)
yellow oil; 44 mg (30% yield);
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90-7.84 (m, 4H), 7.58-7.54 (m, 2H), 7.47-7.44 (m, 5H), 7.42-7.40 (m, 5H), 4.32 (s, 2H), 3.84 (d, J = 7.0 Hz, 2H), 0.81 (t, J = 7.0 Hz, 3H).
^{13}C NMR (125MHz, Chloroform-*d*) δ 193.7, 192.7, 162.0, 154.2, 147.8, 137.4, 135.4, 133.8 133.6, 132.1, 131.4, 129.7, 129.5, 129.3, 128.8, 128.7 ,128.7, 128.3, 61.2, 45.6, 13.3.
HRMS (ESI): m/z calcd for $(C_{28}H_{22}O_4S_2+H)^+$: 487.1032; found: 487.1032.

III. X-ray Crystallography Data of 1a (CCDC No. 2284367)

Single crystals of compound **1a** was measured on a Bruker APEX-II CCD single-crystal diffractom eter. The recrystallization solvent of **1a** was MeOH.

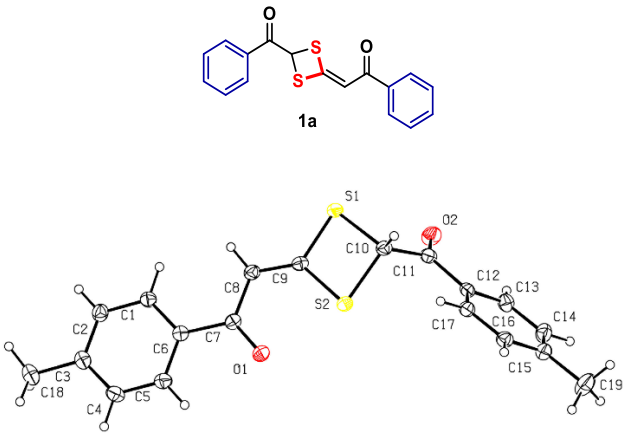


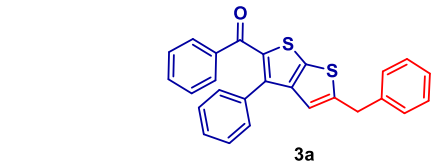
Figure S1 X-ray crystallography of 1a

Table S3 X-ray crystallography data of 1a.

Empirical formula	$C_{19}H_{16}O_2S_2$
Formula weight	340.44
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.302(5)
b/Å	10.967(3)
c/Å	13.148(4)
α/°	90
β/°	111.025(12)
γ/°	90
Volume/Å^3	1655.8(9)
Z	4
ρ_{calc}g/cm^3	1.366
μ/mm^{-1}	0.328
F(000)	712.0
Crystal size/mm^3	0.42 × 0.08 × 0.035
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.982 to 54.228
Index ranges	-15 ≤ h ≤ 15, -12 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	12981
Independent reflections	3649 [R_{int} = 0.0327, R_{sigma} = 0.0324]
Data/restraints/parameters	3649/0/210
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0856
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.0903
Largest diff. peak/hole / e Å^{-3}	0.29/-0.25

IV. X-ray Crystallography Data of 3a (CCDC No. 2284471)

Single crystals of compound **3a** was measured on a Bruker APEX-II CCD single-crystal diffractom eter. The recrystallization solvent of **3a** was DCM.



3a

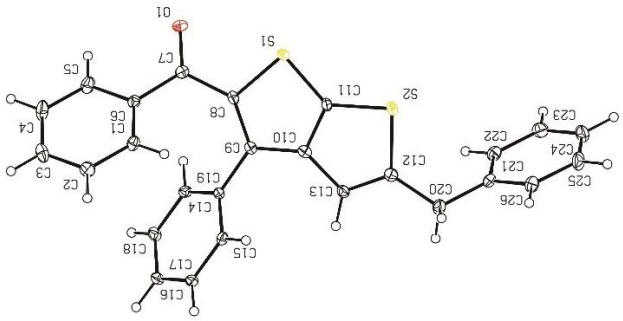


Figure S2 X-ray crystallography of 3a

Table S4 X-ray crystallography data of 3a.

Empirical formula	$C_{26}H_{18}OS_2$
Formula weight	410.52
Temperature/K	170.00
Crystal system	monoclinic
Space group	C2/c
a/Å	18.529(4)
b/Å	6.3197(16)
c/Å	33.942(8)
α/°	90
β/°	99.181(9)
γ/°	90
Volume/Å^3	3923.6(17)
Z	8
ρ_{calc}g/cm^3	1.390
μ/mm^{-1}	1.688
F(000)	1712.0
Crystal size/mm^3	0.07 × 0.02 × 0.02
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.588 to 118.536
Index ranges	-23 ≤ h ≤ 16, -7 ≤ k ≤ 8, -42 ≤ l ≤ 43
Reflections collected	16777
Independent reflections	4286 [R_{int} = 0.0963, R_{sigma} = 0.0827]
Data/restraints/parameters	4286/0/262
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1209
Final R indexes [all data]	R_1 = 0.0855, wR_2 = 0.1294
Largest diff. peak/hole / e Å^{-3}	0.33/-0.34

V. X-ray Crystallography Data of 5e (CCDC No. 2284470)

Single crystals of compound **5e** was measured on a Bruker APEX-II CCD single-crystal diffractom eter. The recrystallization solvent of **5e** was DCM.

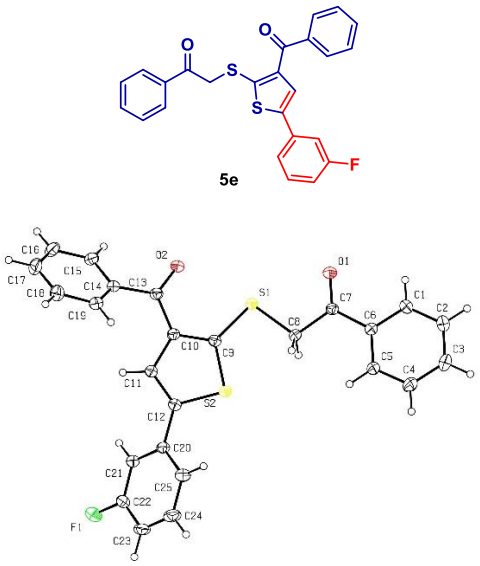
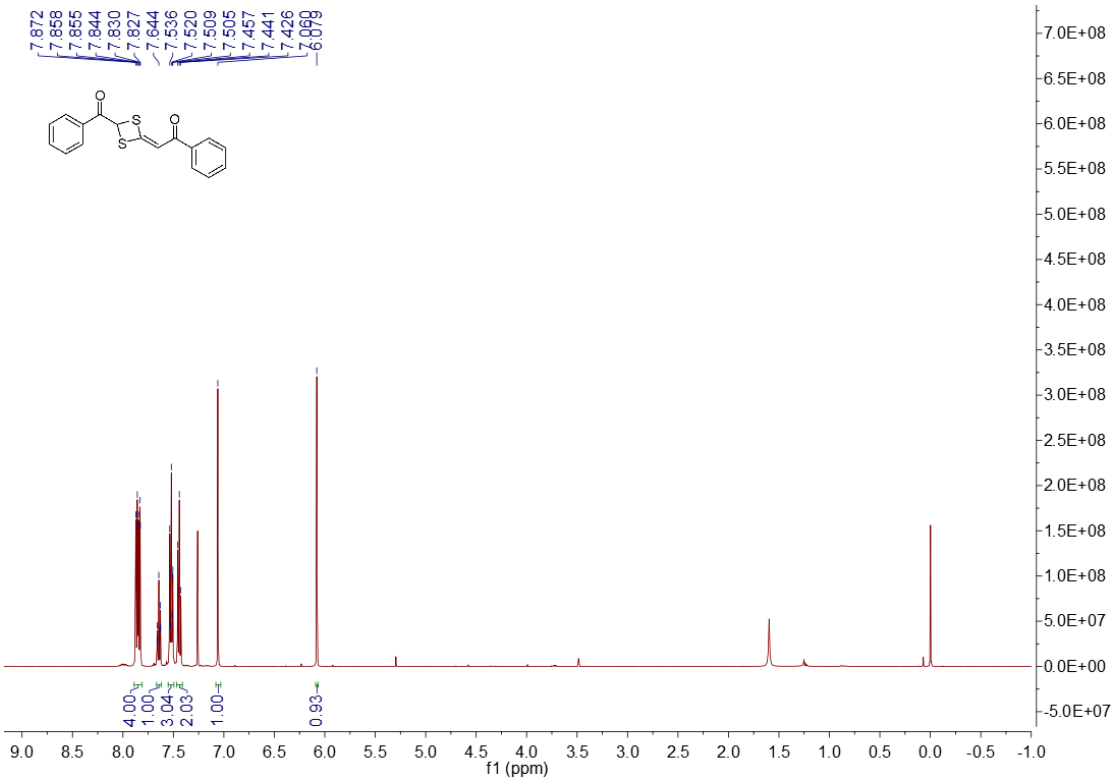


Figure S3 X-ray crystallography of 5e

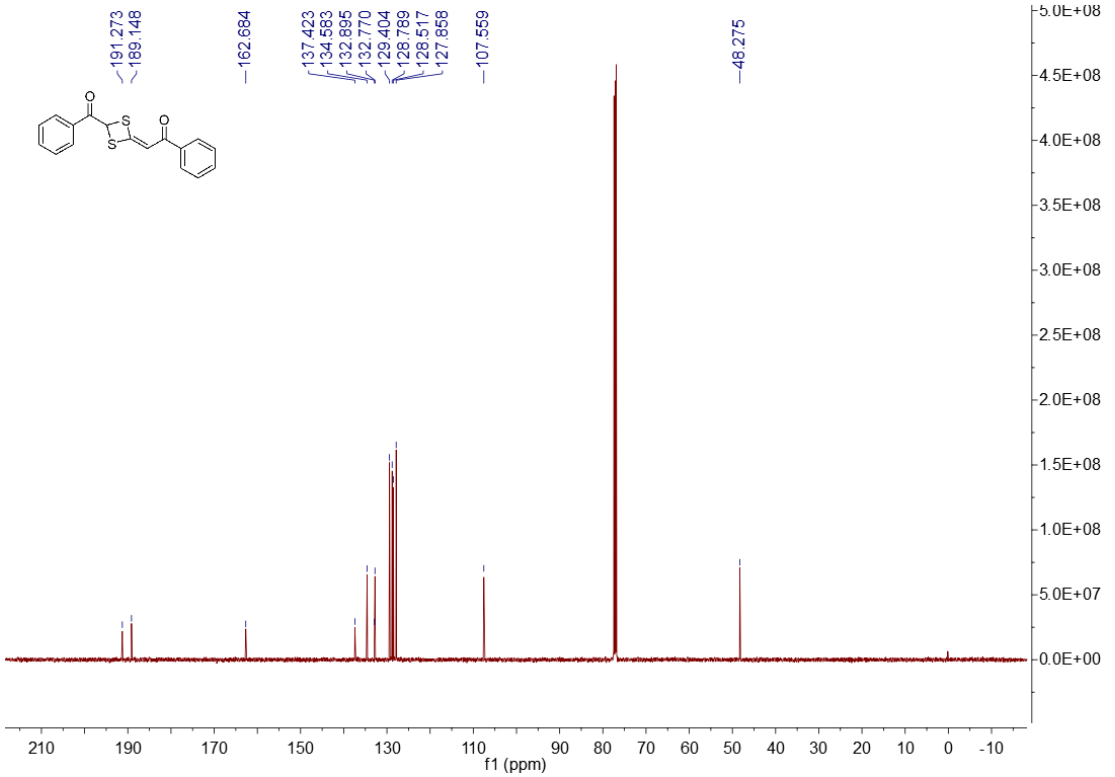
Table S5 X-ray crystallography data of 5e.

Empirical formula	$C_{25}H_{17}FO_2S_2$
Formula weight	432.50
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	8.1146(11)
b/Å	13.3076(16)
c/Å	19.949(2)
α/°	79.440(4)
β/°	82.471(5)
γ/°	81.303(5)
Volume/Å^3	2081.5(4)
Z	4
ρ_{calc}g/cm^3	1.380
μ/mm^{-1}	0.284
F(000)	896.0
Crystal size/mm^3	0.48 × 0.35 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.052 to 53.606
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -25 ≤ l ≤ 24
Reflections collected	38993
Independent reflections	8852 [R_{int} = 0.0572, R_{sigma} = 0.0460]
Data/restraints/parameters	8852/0/541
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	0.42/-0.33

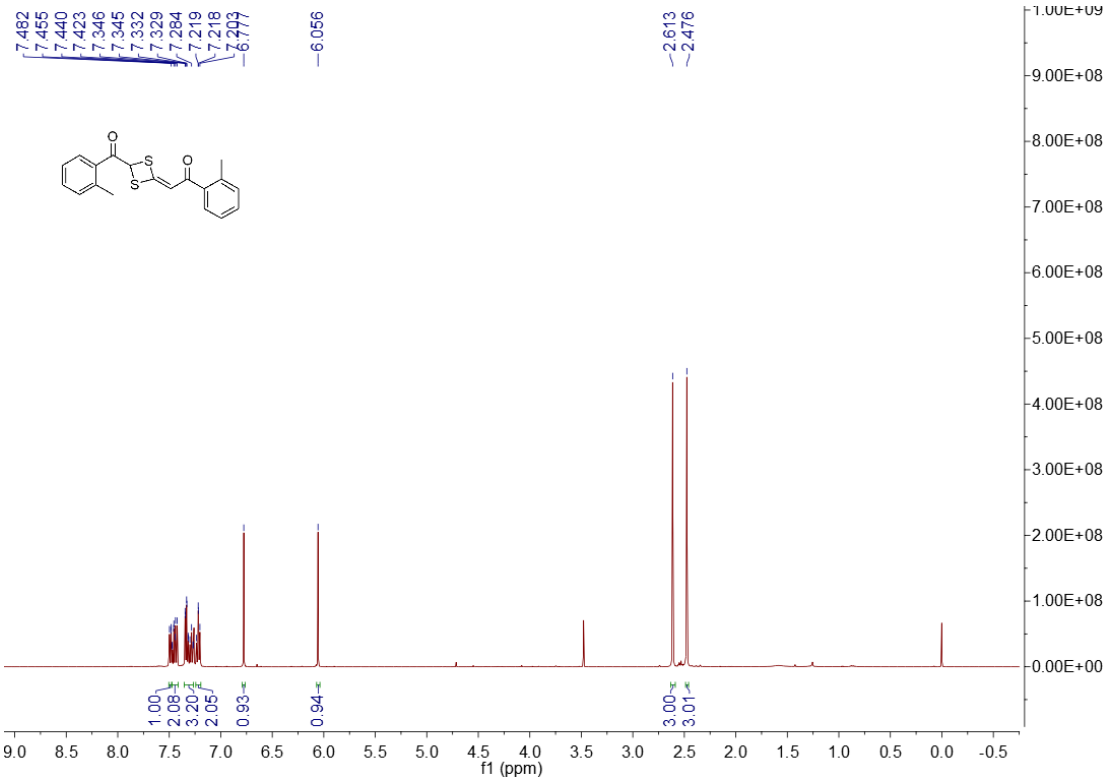
VI. ^{1}H NMR and ^{13}C NMR Spectra of Starting Material



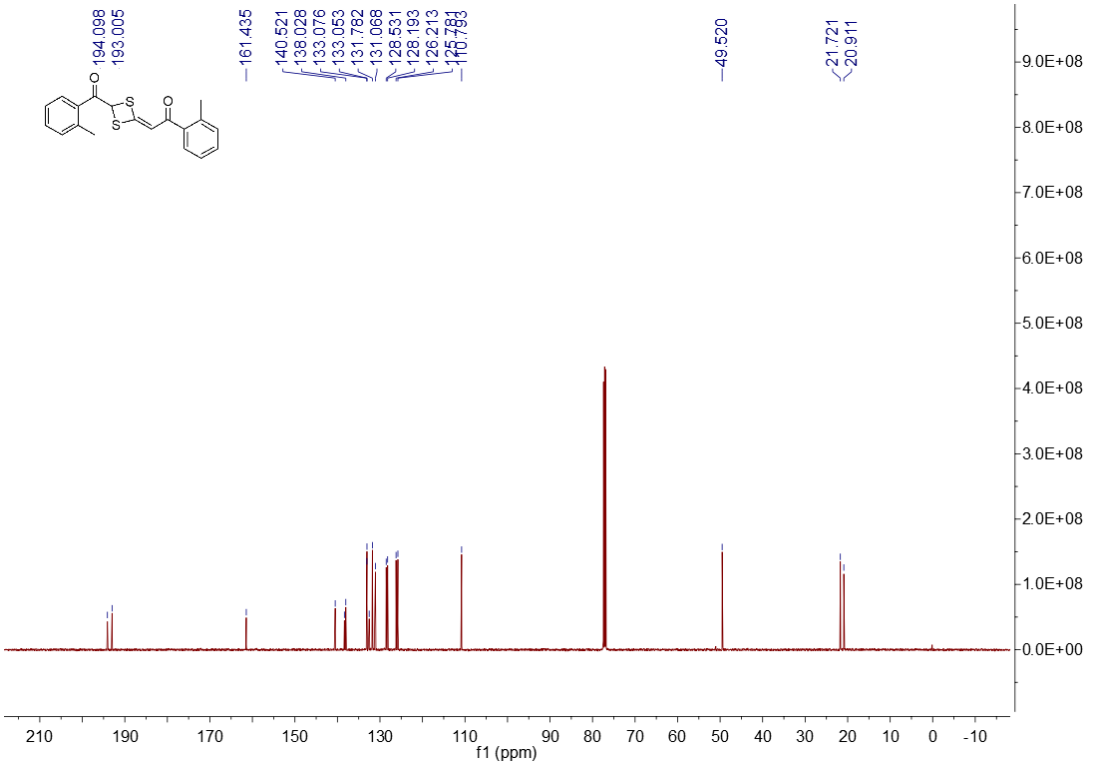
^{1}H NMR Spectrum of 1a ($CDCl_3$, 500 MHz)



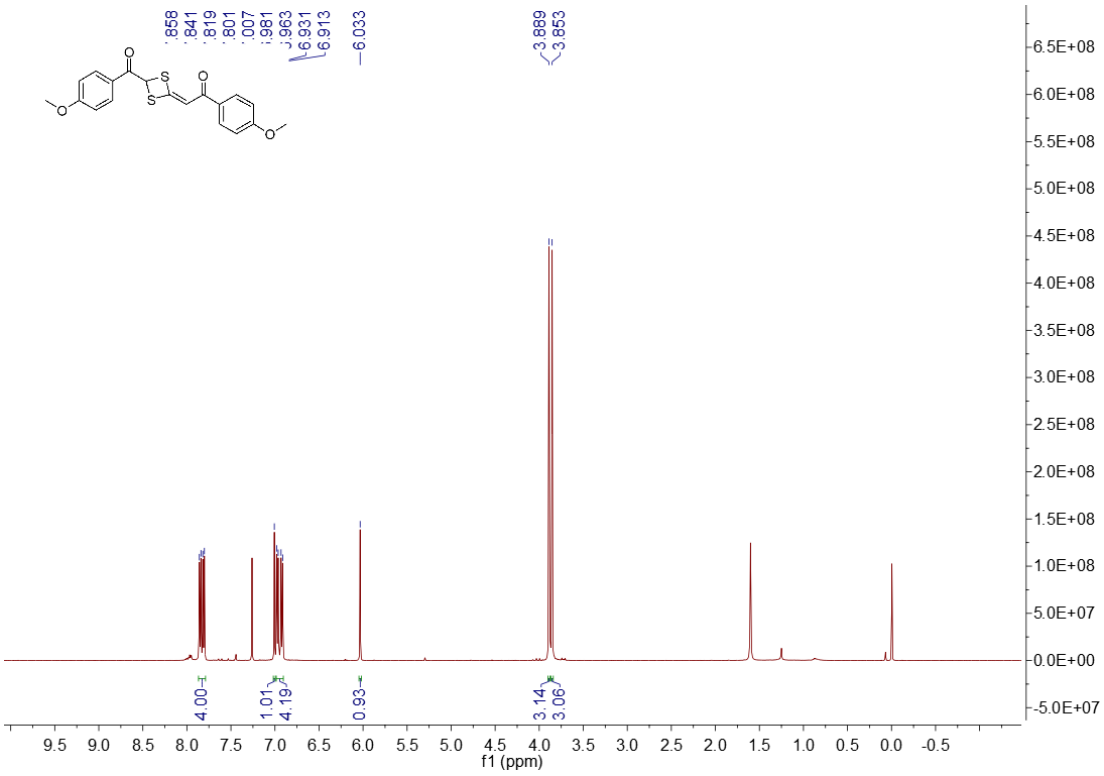
^{13}C NMR Spectrum of 1a ($CDCl_3$, 125 MHz)



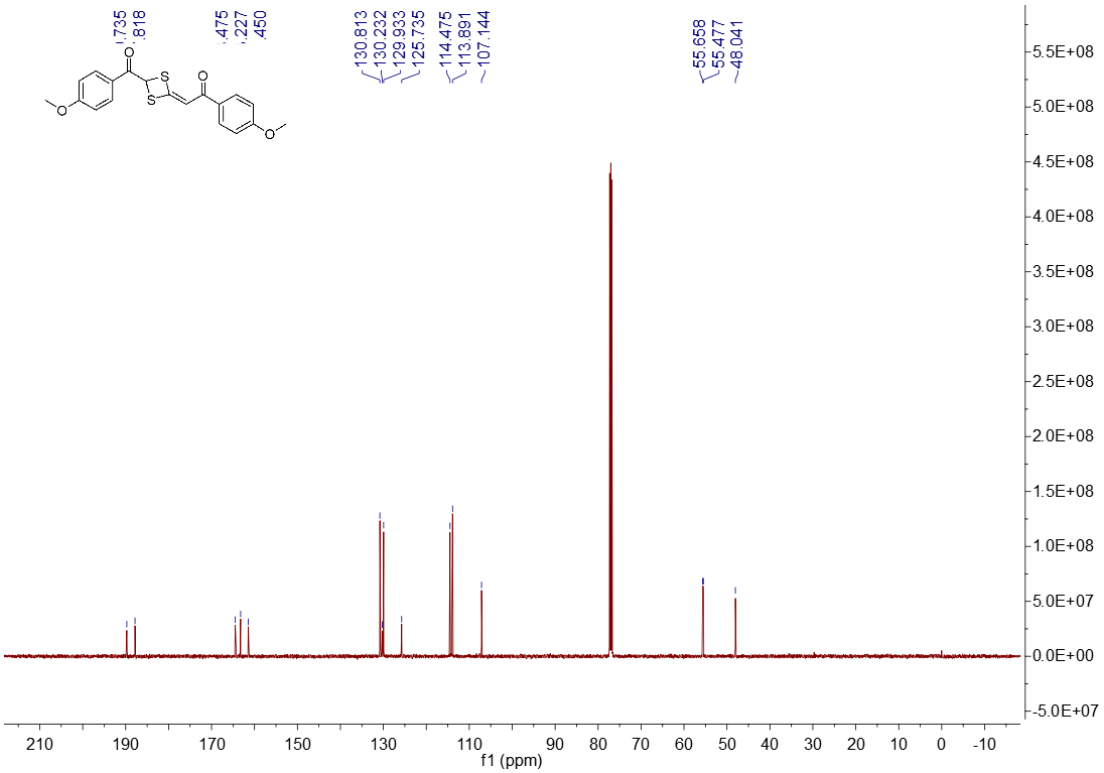
^{1}H NMR Spectrum of 1b ($CDCl_3$, 500 MHz)



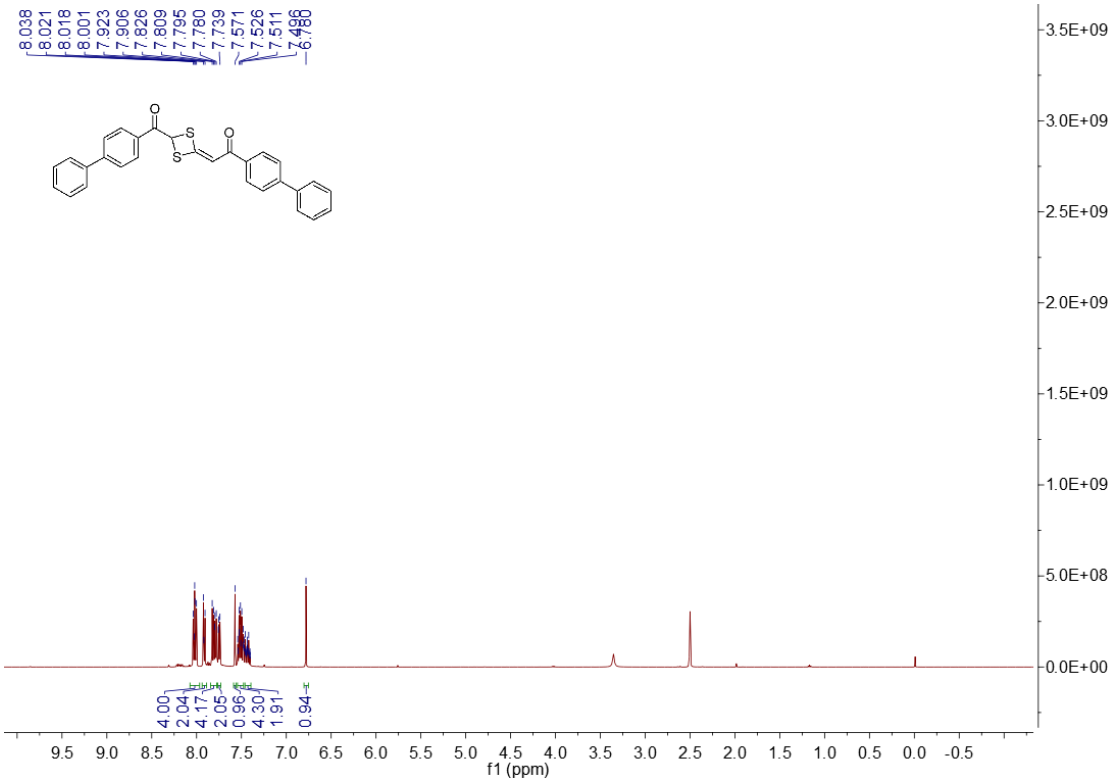
^{13}C NMR Spectrum of 1b ($CDCl_3$, 125 MHz)



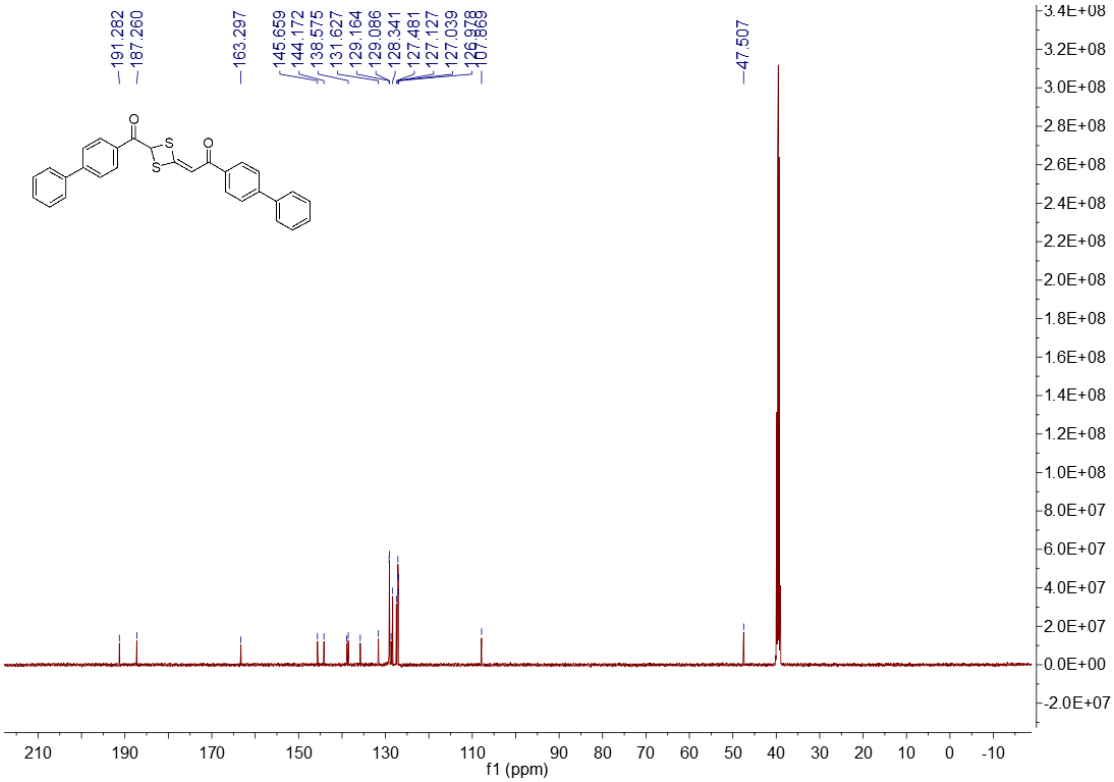
^{1}H NMR Spectrum of 1c ($CDCl_3$, 500 MHz)



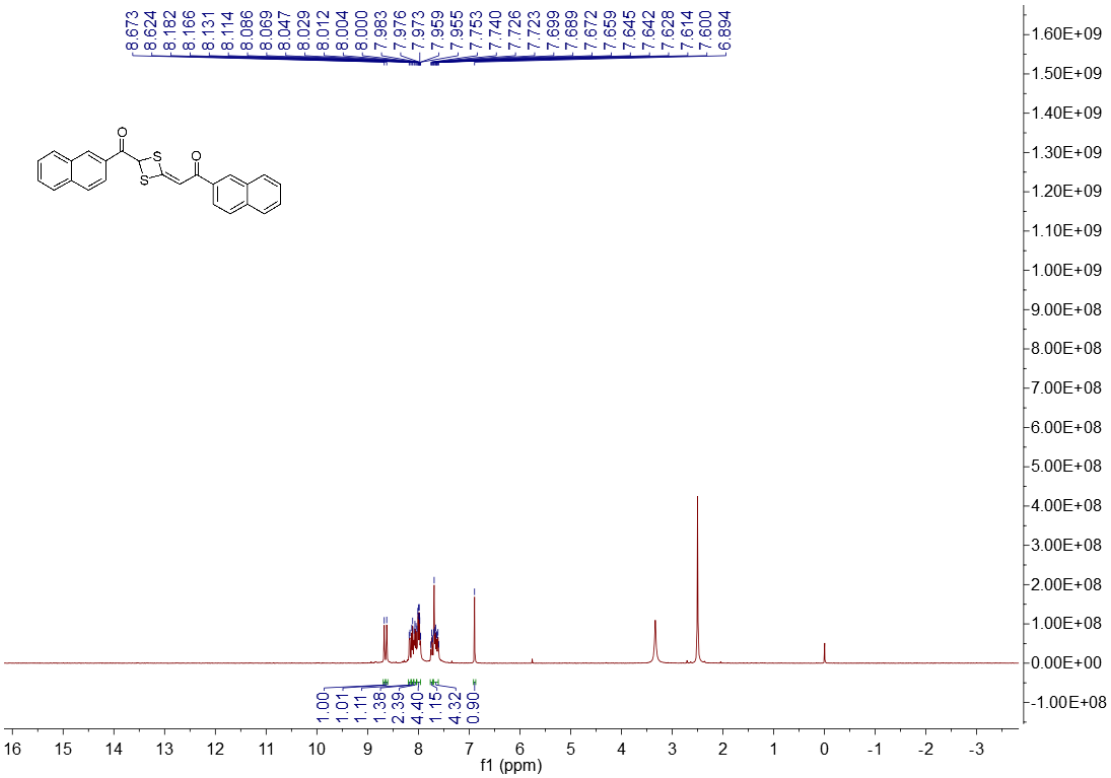
^{13}C NMR Spectrum of 1c ($CDCl_3$, 125 MHz)



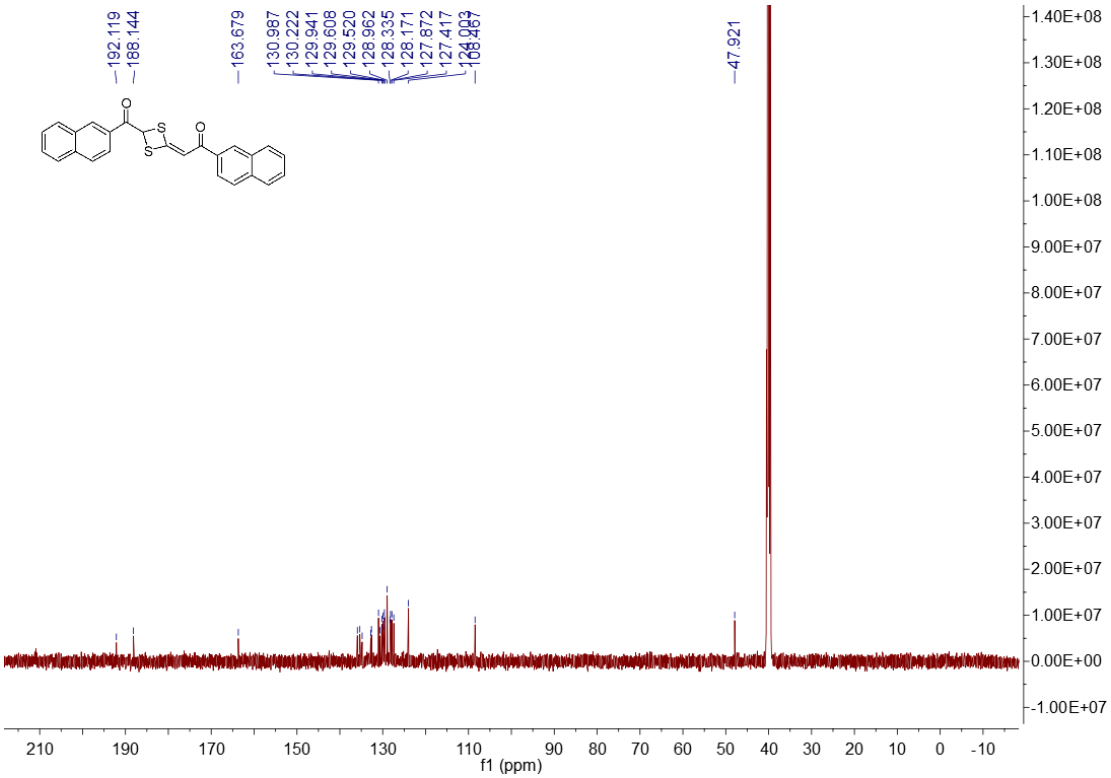
^{1}H NMR Spectrum of 1d (DMSO-d_6), 500 MHz)



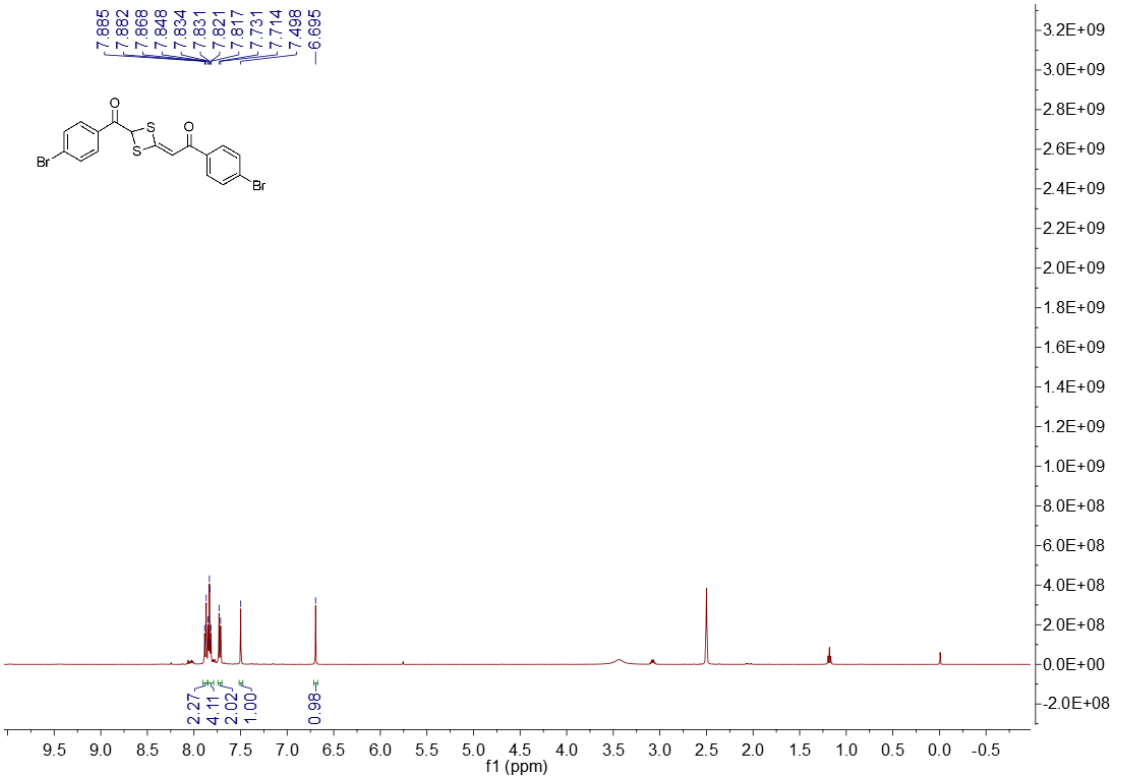
^{13}C NMR Spectrum of 1d (DMSO-d_6, 125 MHz)



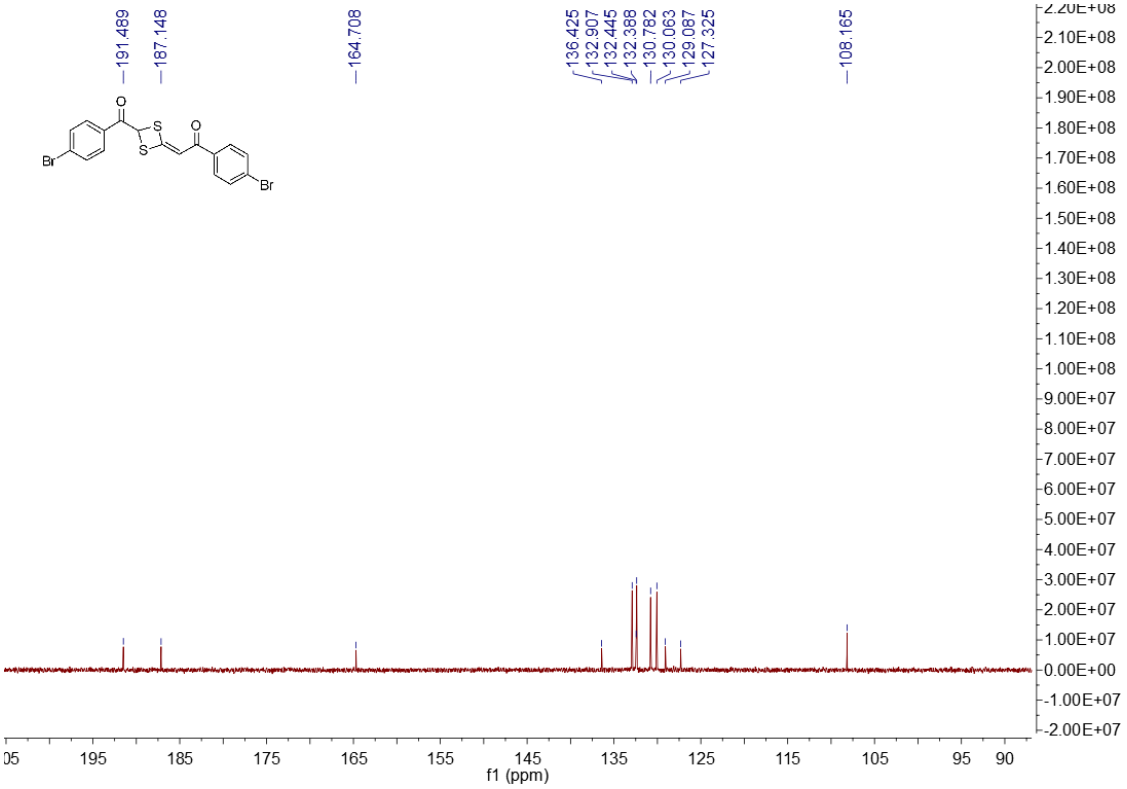
^{1}H NMR Spectrum of 1e (DMSO-d_6), 500 MHz)



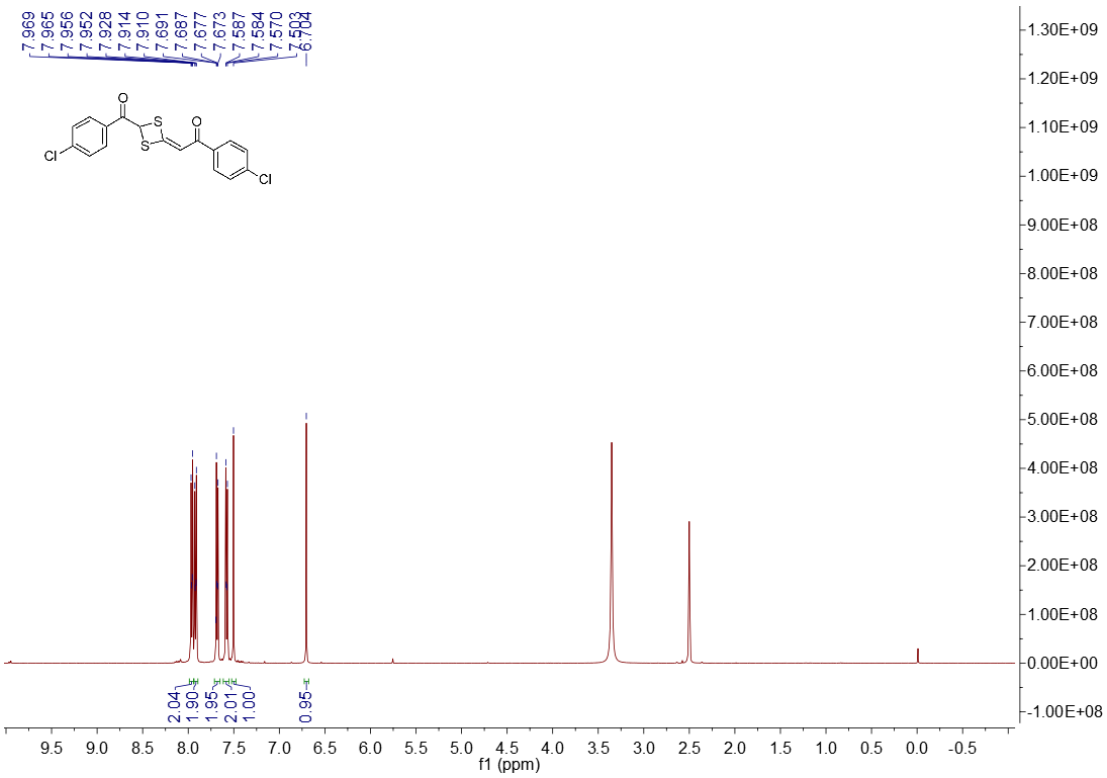
^{13}C NMR Spectrum of 1e (DMSO-d_6, 125 MHz)



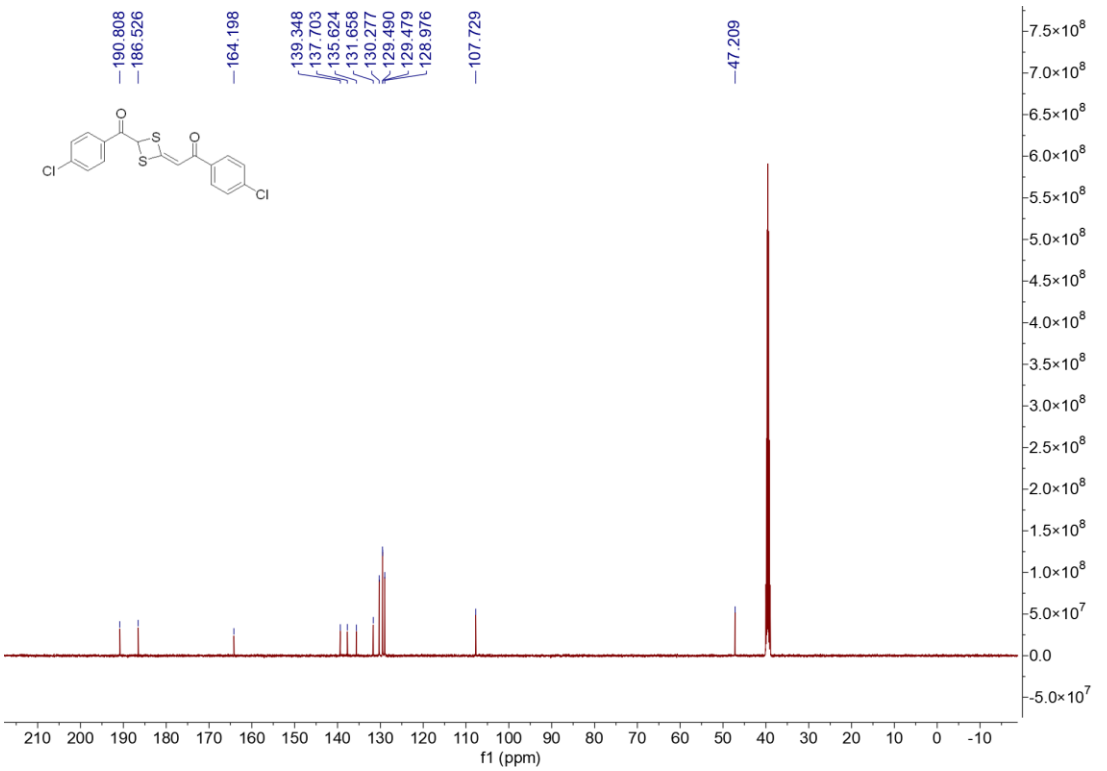
^{1}H NMR Spectrum of 1f (DMSO-d_6), 500 MHz)



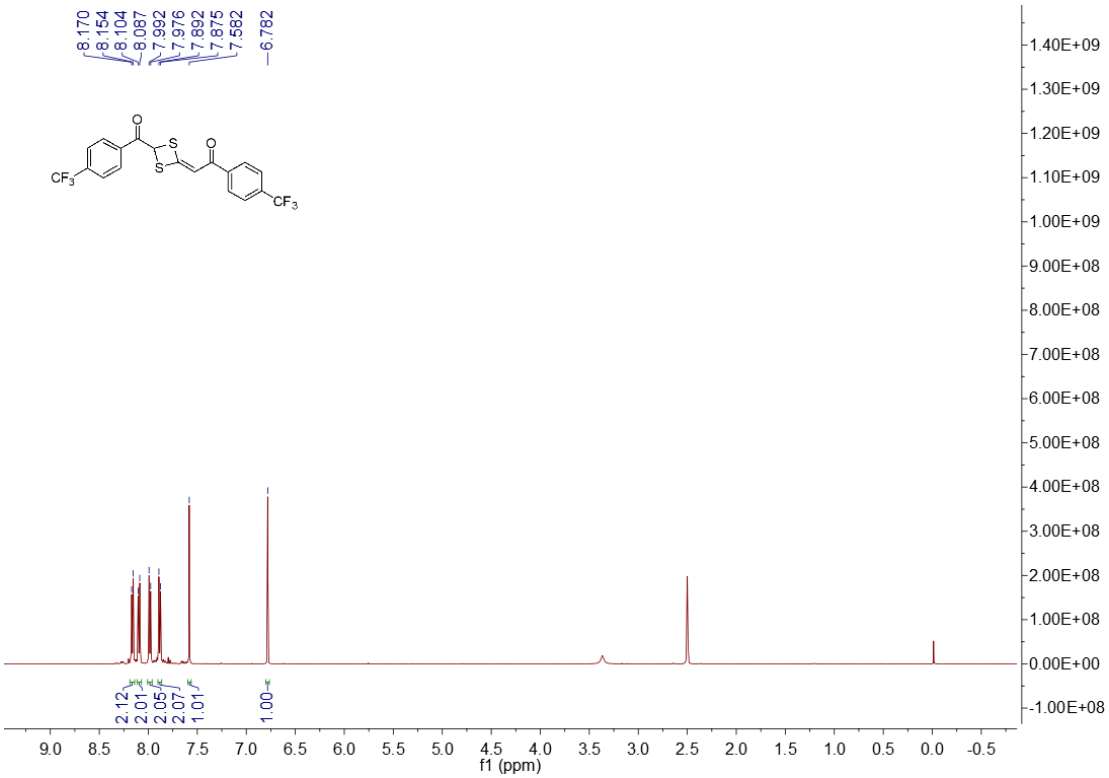
^{13}C NMR Spectrum of 1f (DMSO-d_6, 125 MHz)



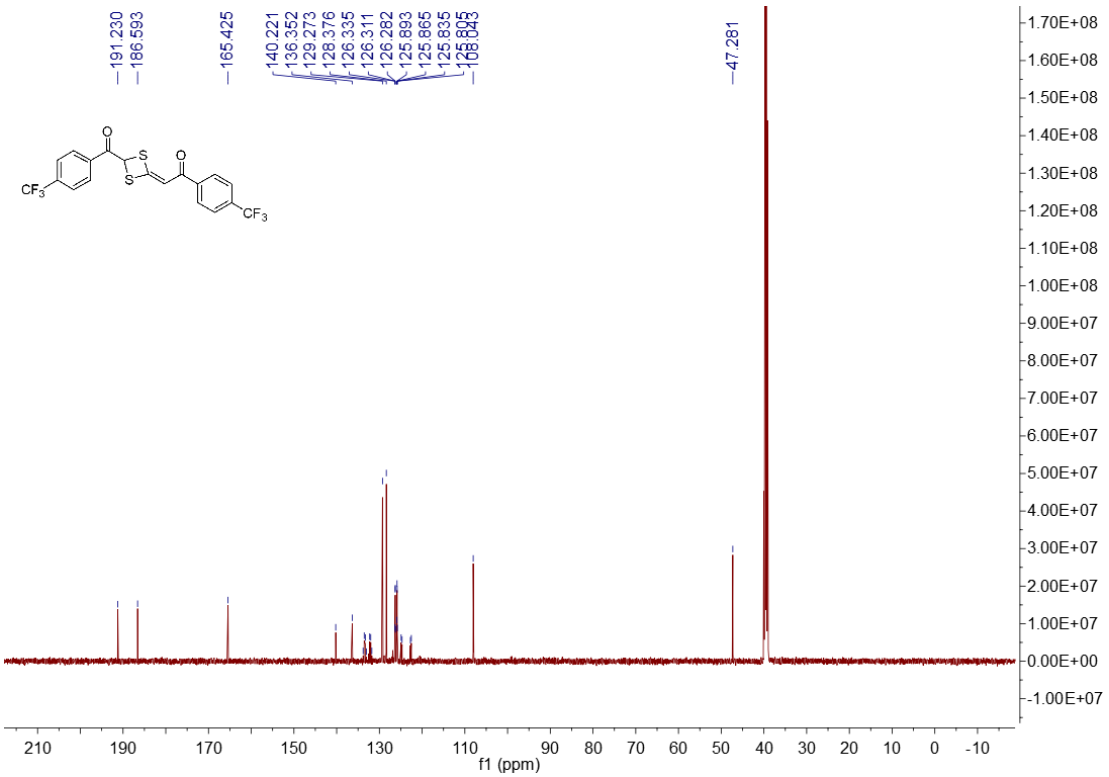
^{1}H NMR Spectrum of 1g (DMSO-d_6), 500 MHz)



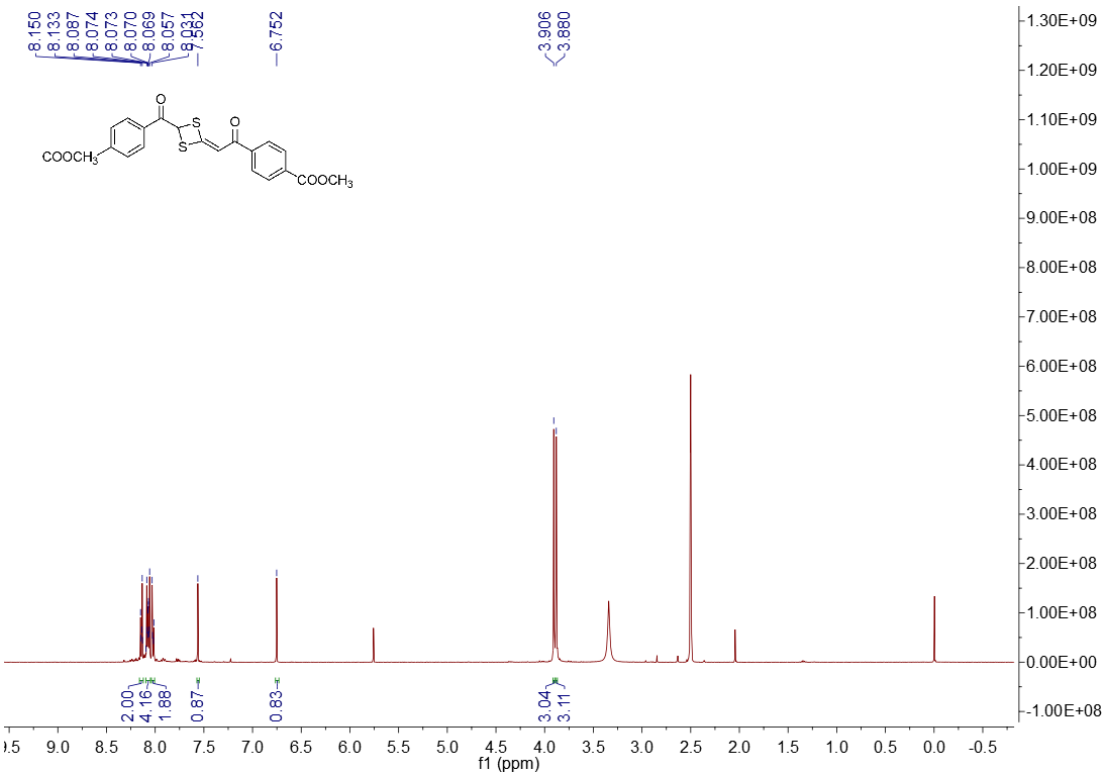
^{13}C NMR Spectrum of 1g (DMSO-d_6, 125 MHz)



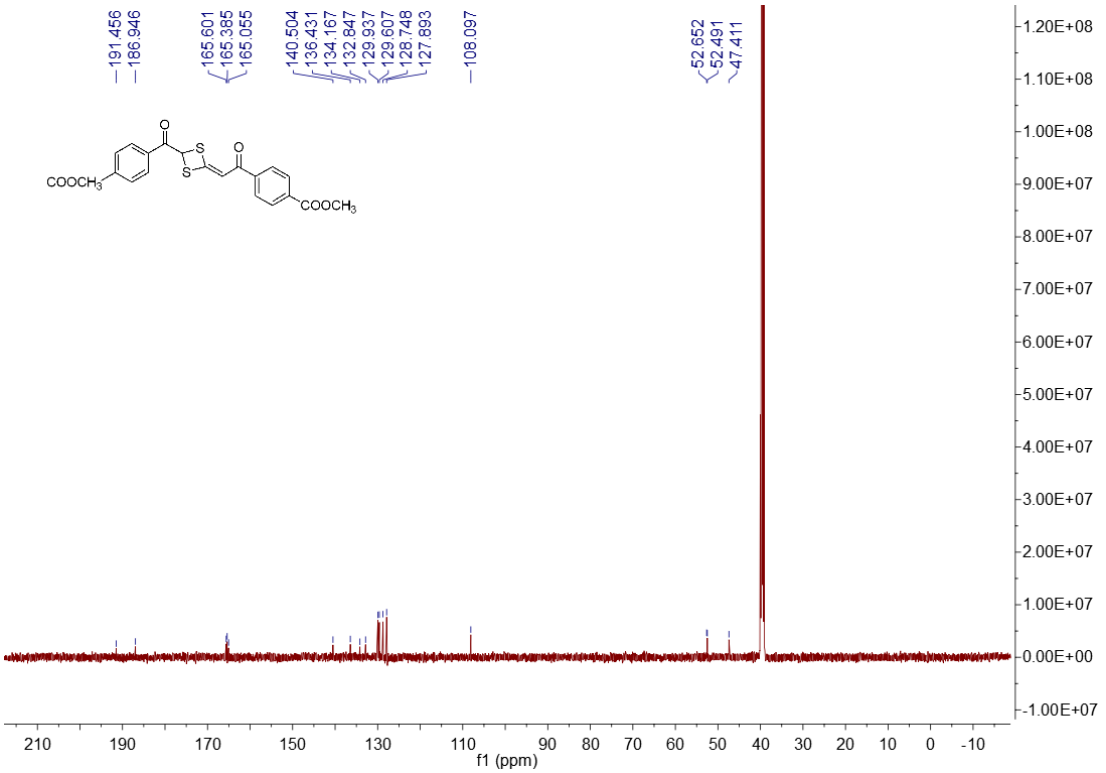
^{1}H NMR Spectrum of 1h (DMSO-d_6), 500 MHz)



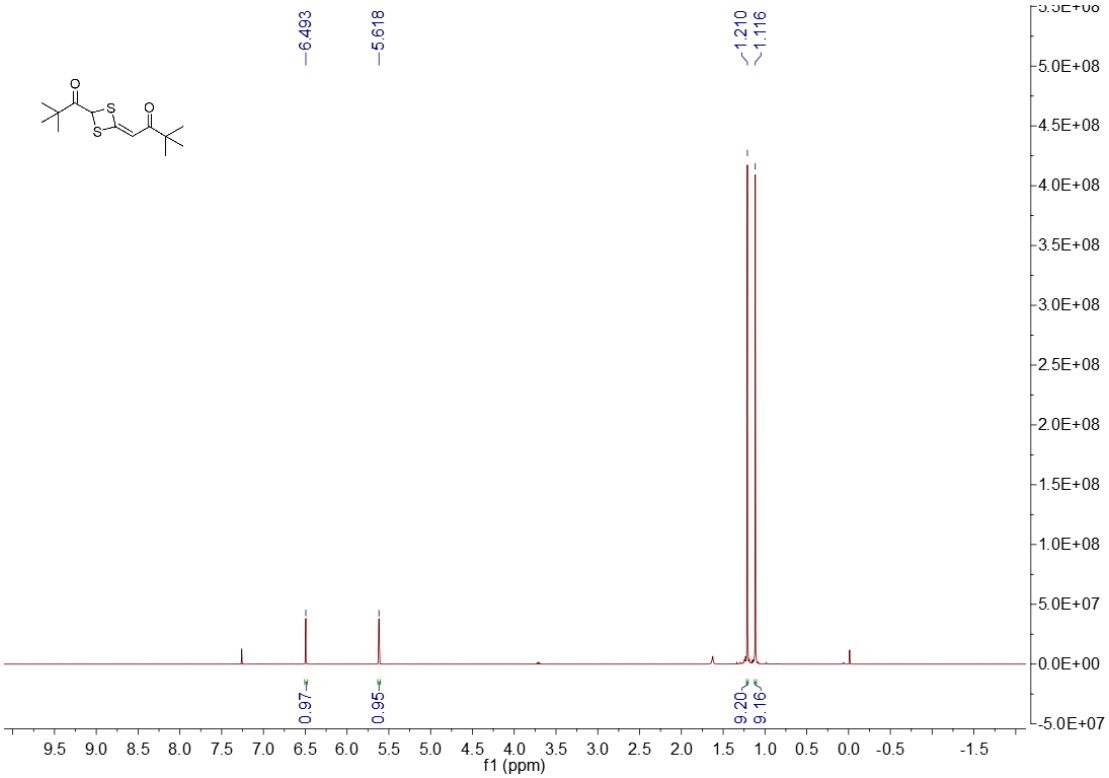
^{13}C NMR Spectrum of 1h (DMSO-d_6, 125 MHz)



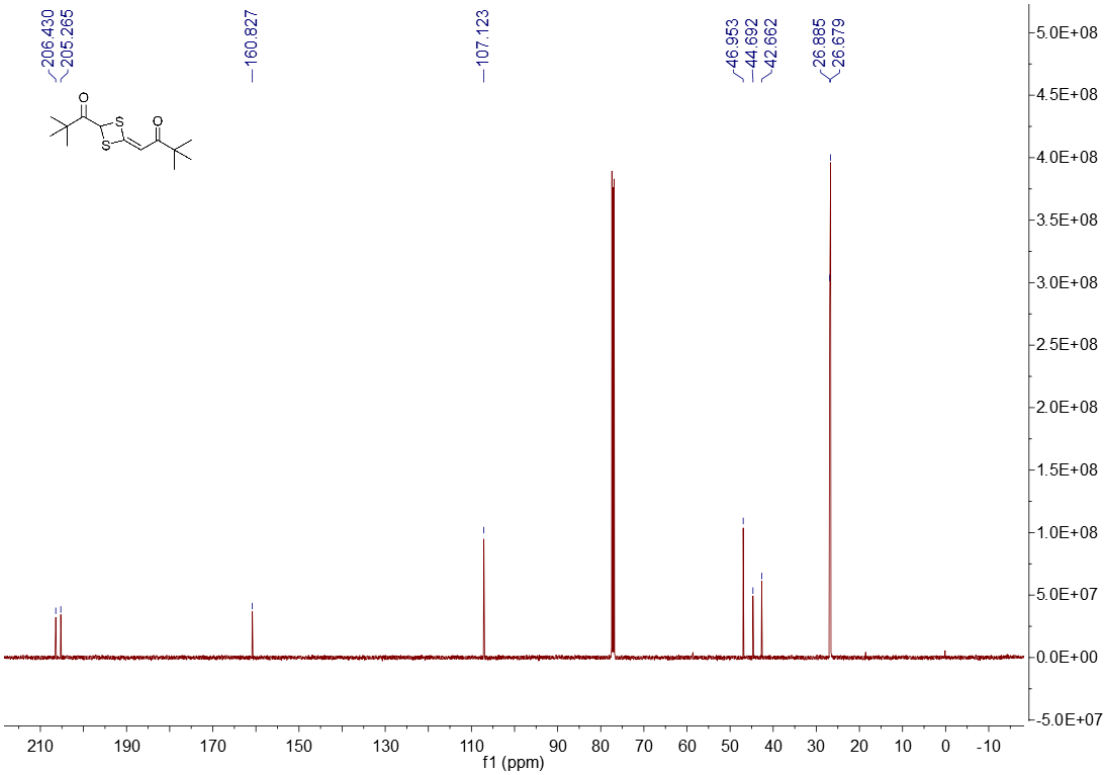
^{1}H NMR Spectrum of 1i (DMSO-d_6), 500 MHz)



^{13}C NMR Spectrum of 1i (DMSO-d_6, 125 MHz)

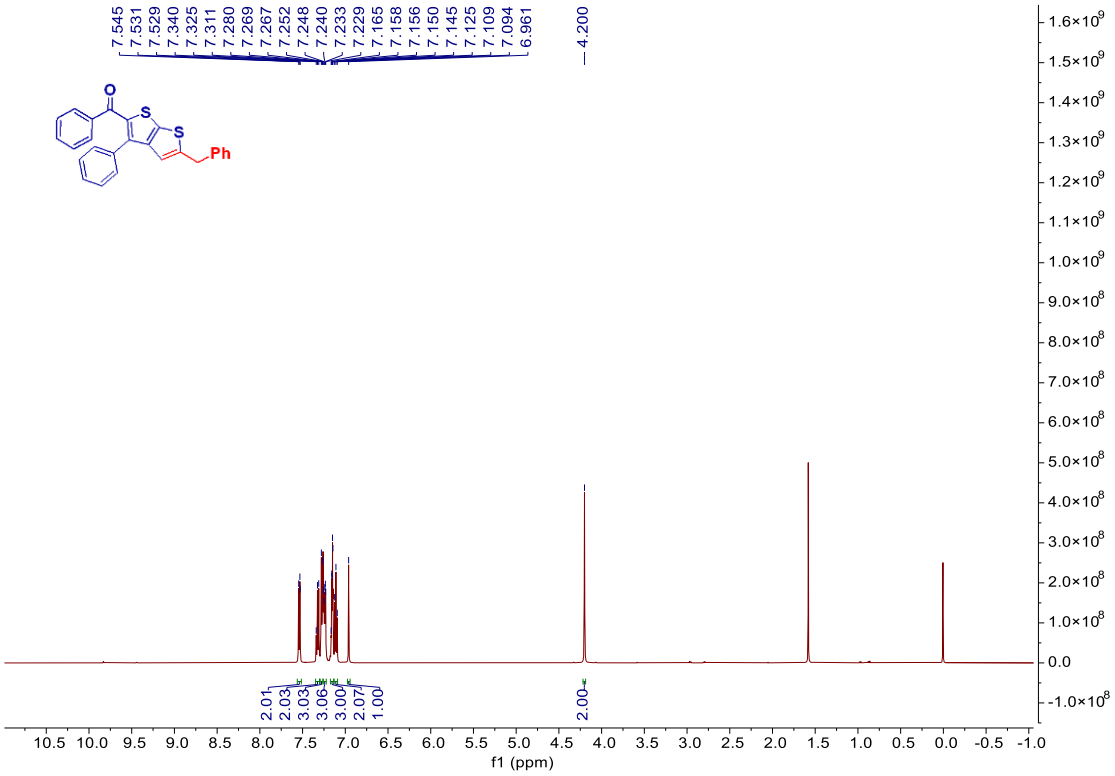


^{1}H NMR Spectrum of 1j ($CDCl_3$, 500 MHz)

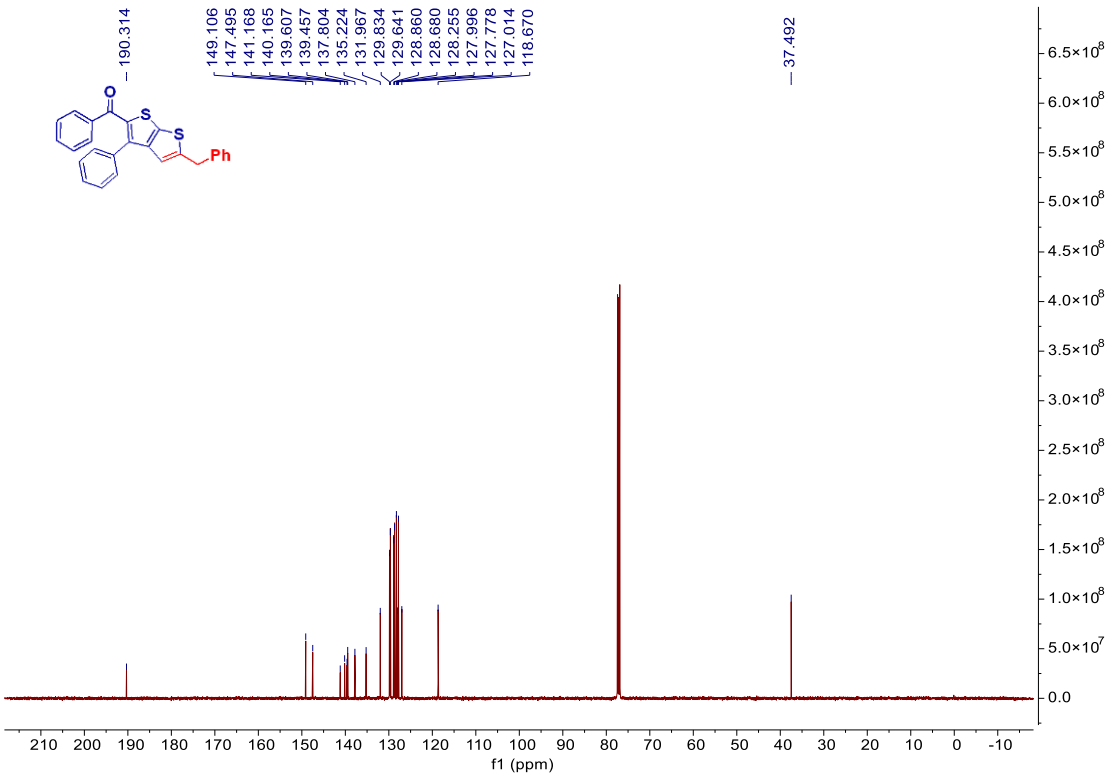


^{13}C NMR Spectrum of 1j ($CDCl_3$, 125 MHz)

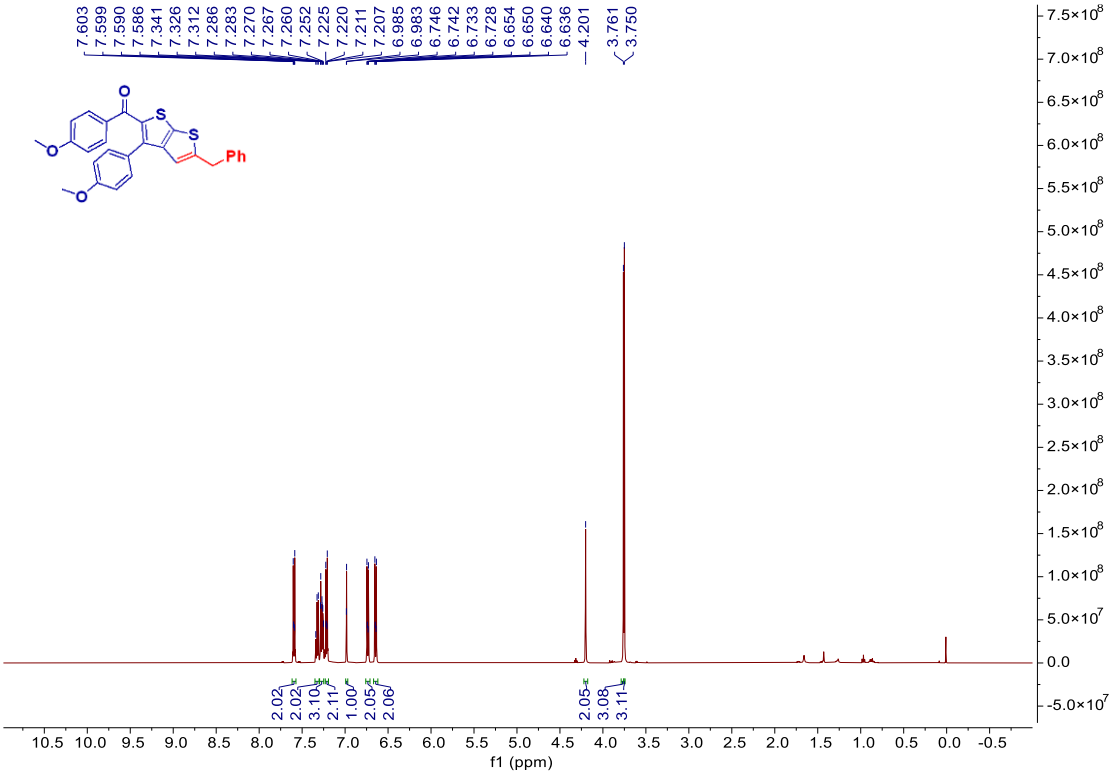
VII. ^{1}H NMR and ^{13}C NMR Spectra of Final Products 3 and 5



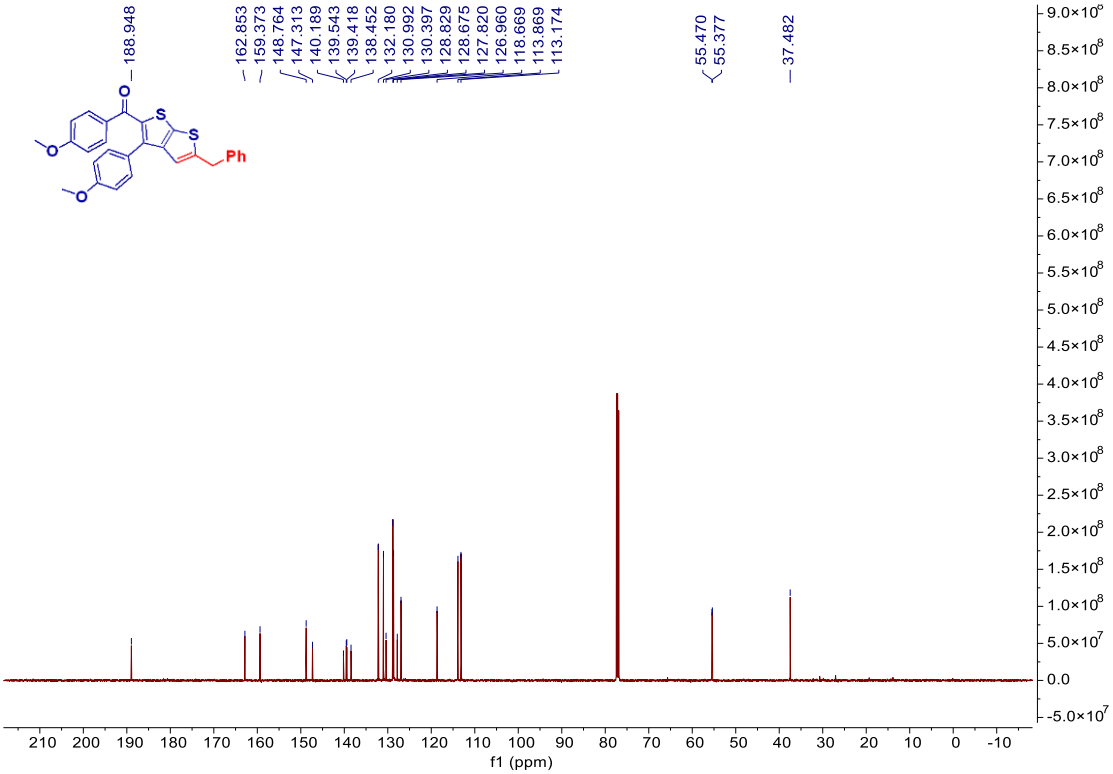
^{1}H NMR Spectrum of 3a ($CDCl_3$, 500 MHz)



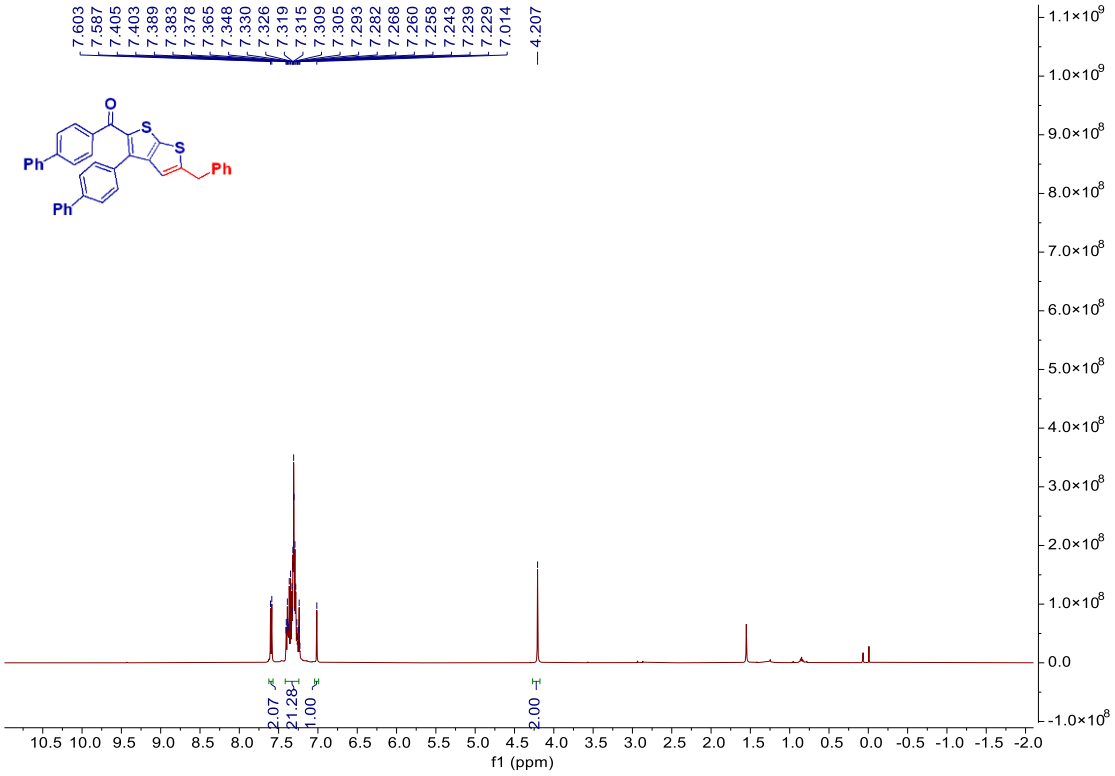
^{13}C NMR Spectrum of 3a ($CDCl_3$, 125 MHz)



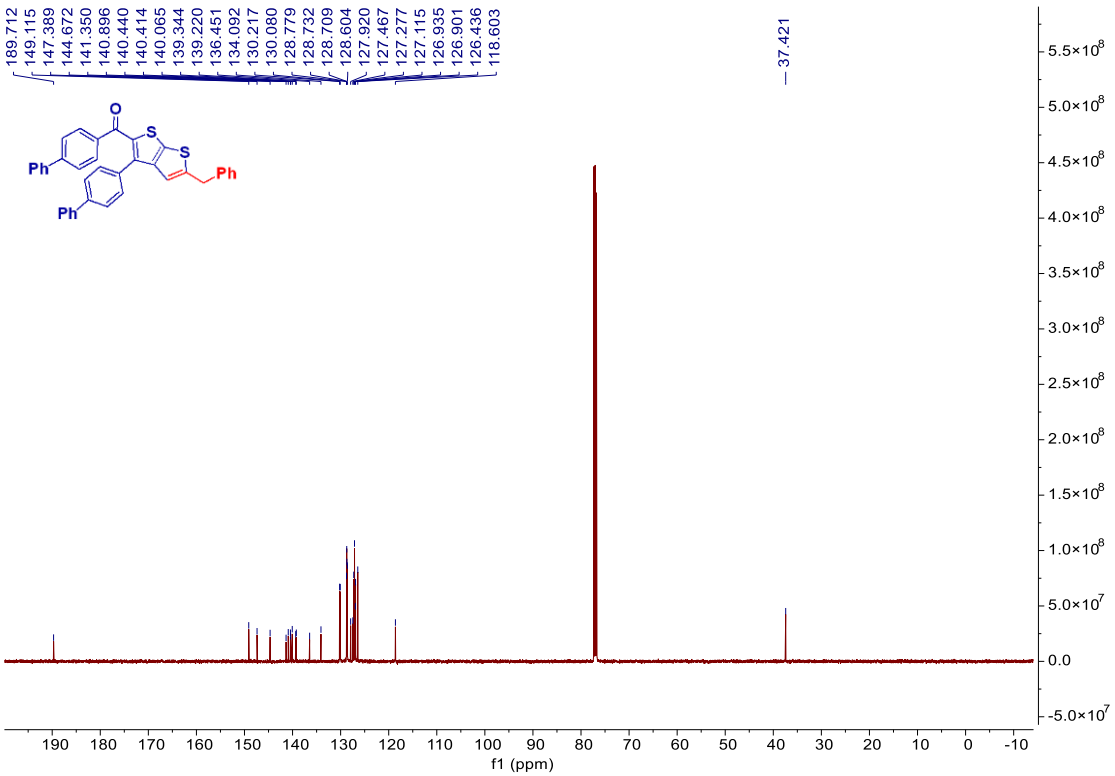
^{1}H NMR Spectrum of 3b ($CDCl_3$, 500 MHz)



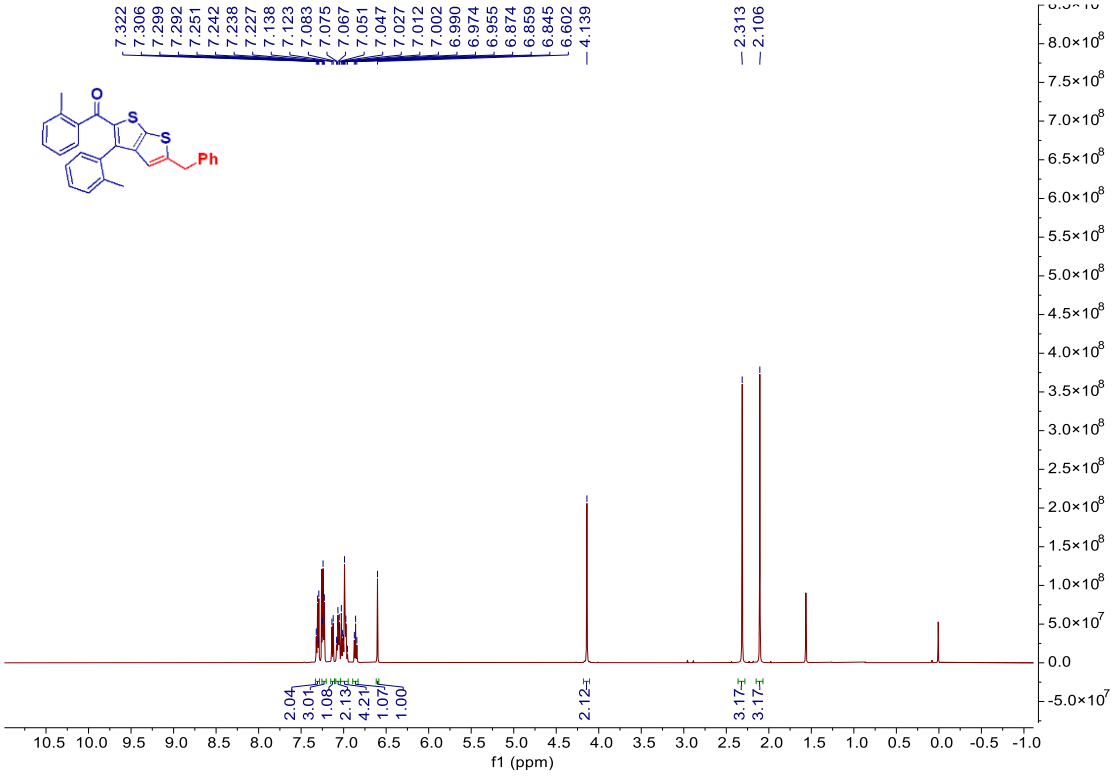
^{13}C NMR Spectrum of 3b ($CDCl_3$, 125 MHz)



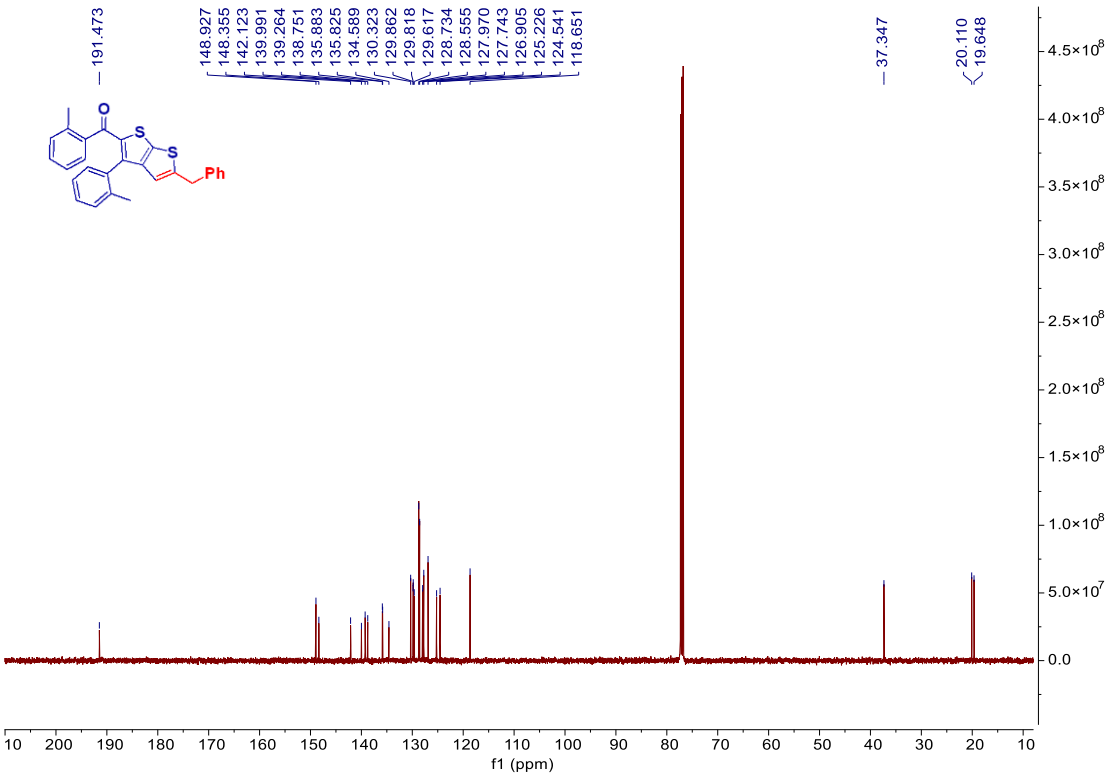
^{1}H NMR Spectrum of 3c ($CDCl_3$, 500 MHz)



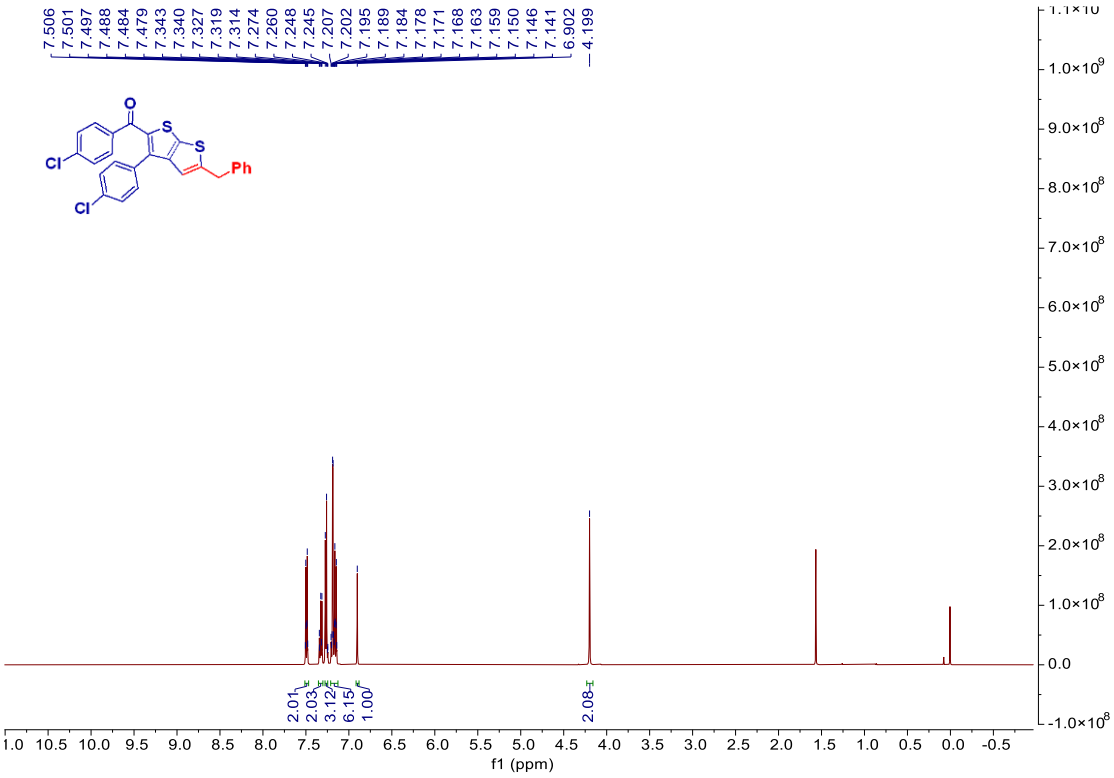
^{13}C NMR Spectrum of 3c ($CDCl_3$, 125 MHz)



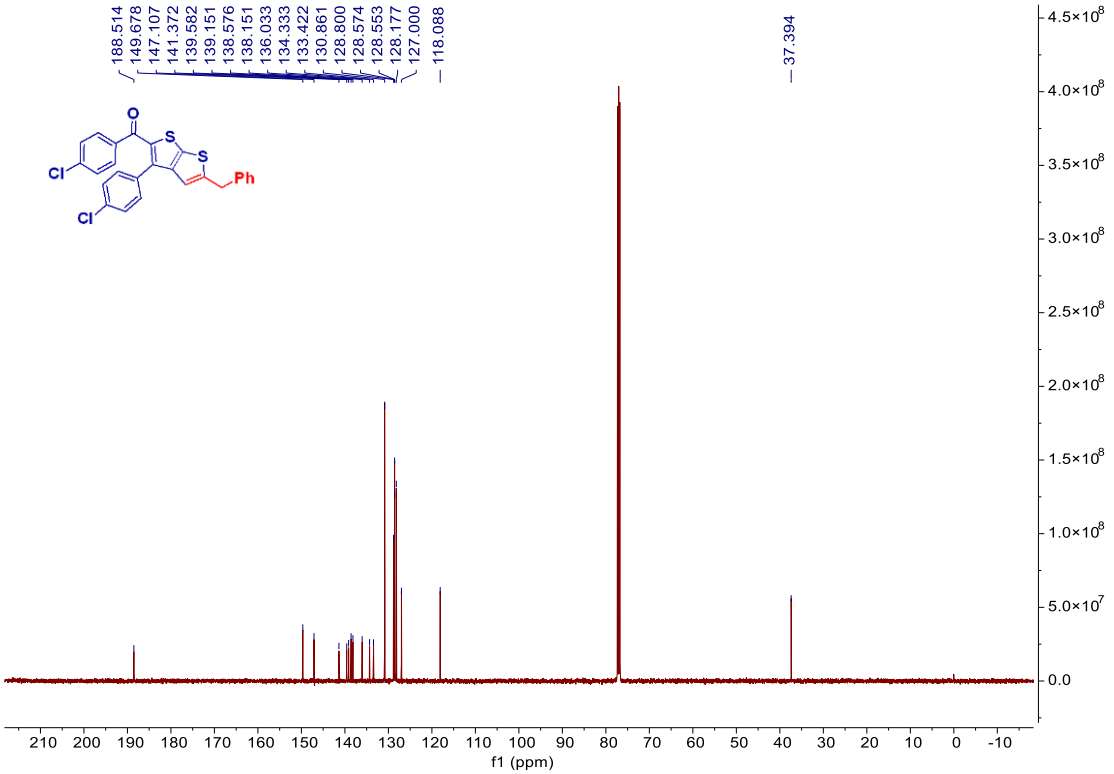
^{1}H NMR Spectrum of 3d ($CDCl_3$, 500 MHz)



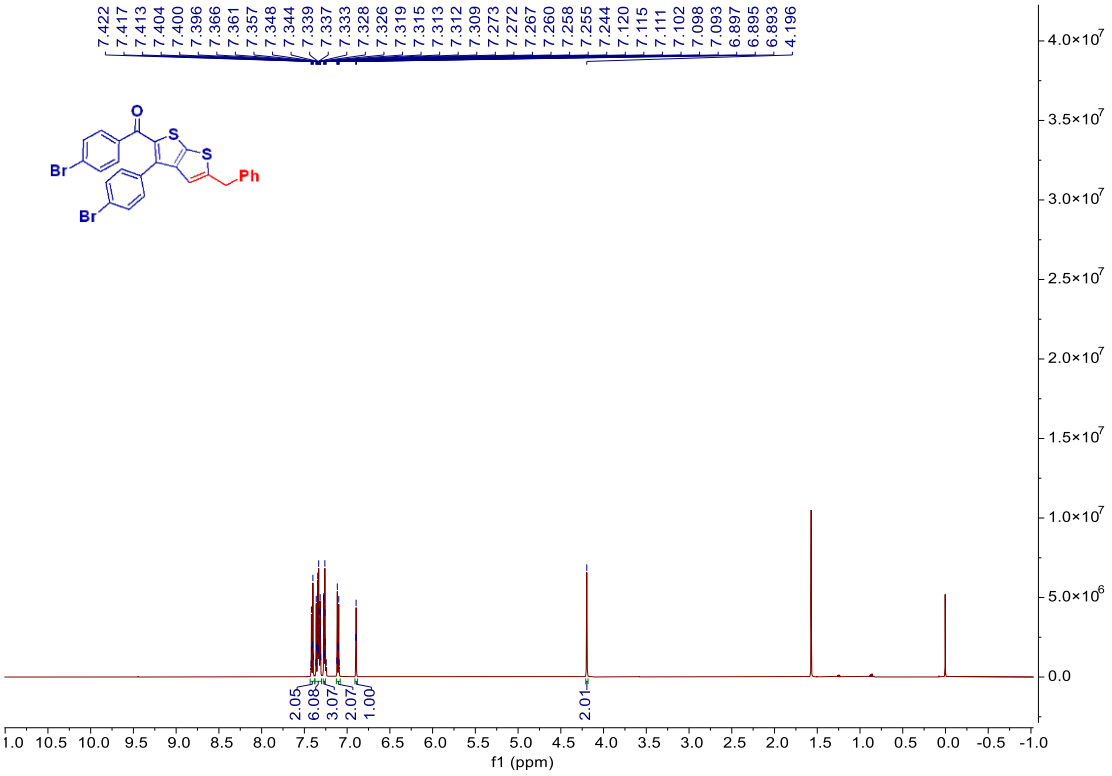
^{13}C NMR Spectrum of 3d ($CDCl_3$, 125 MHz)



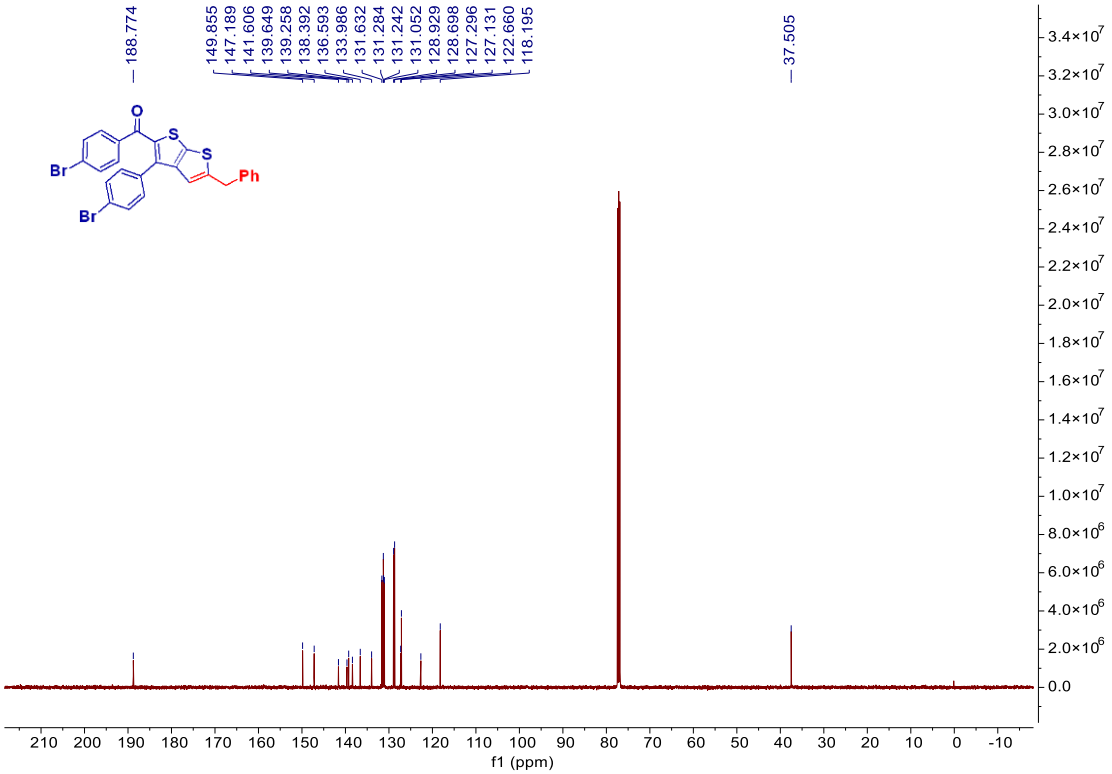
^{1}H NMR Spectrum of 3e ($CDCl_3$, 500 MHz)



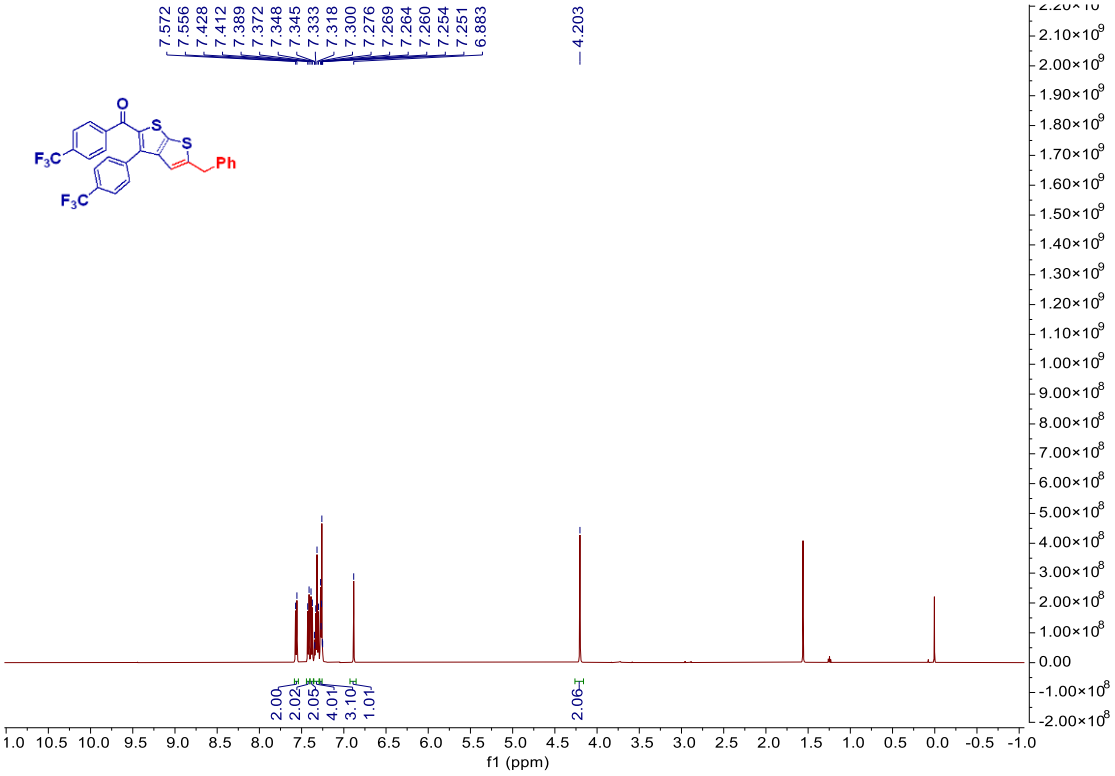
^{13}C NMR Spectrum of 3e ($CDCl_3$, 125 MHz)



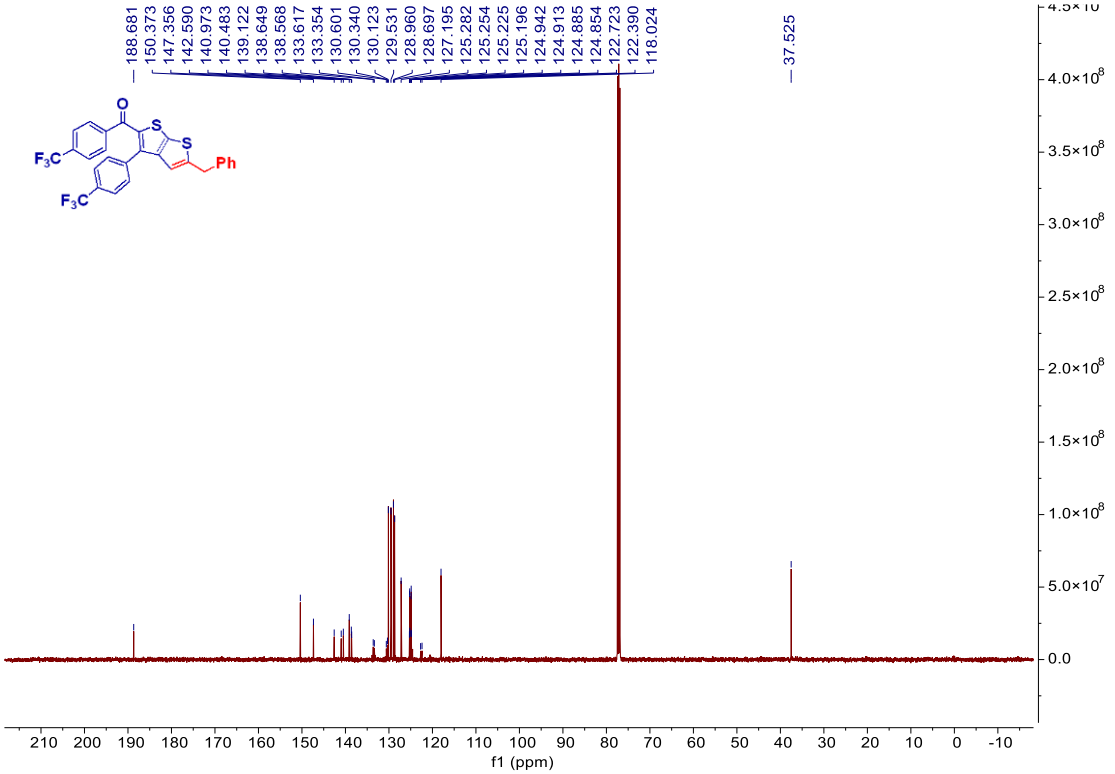
^{1}H NMR Spectrum of 3f ($CDCl_3$, 500 MHz)



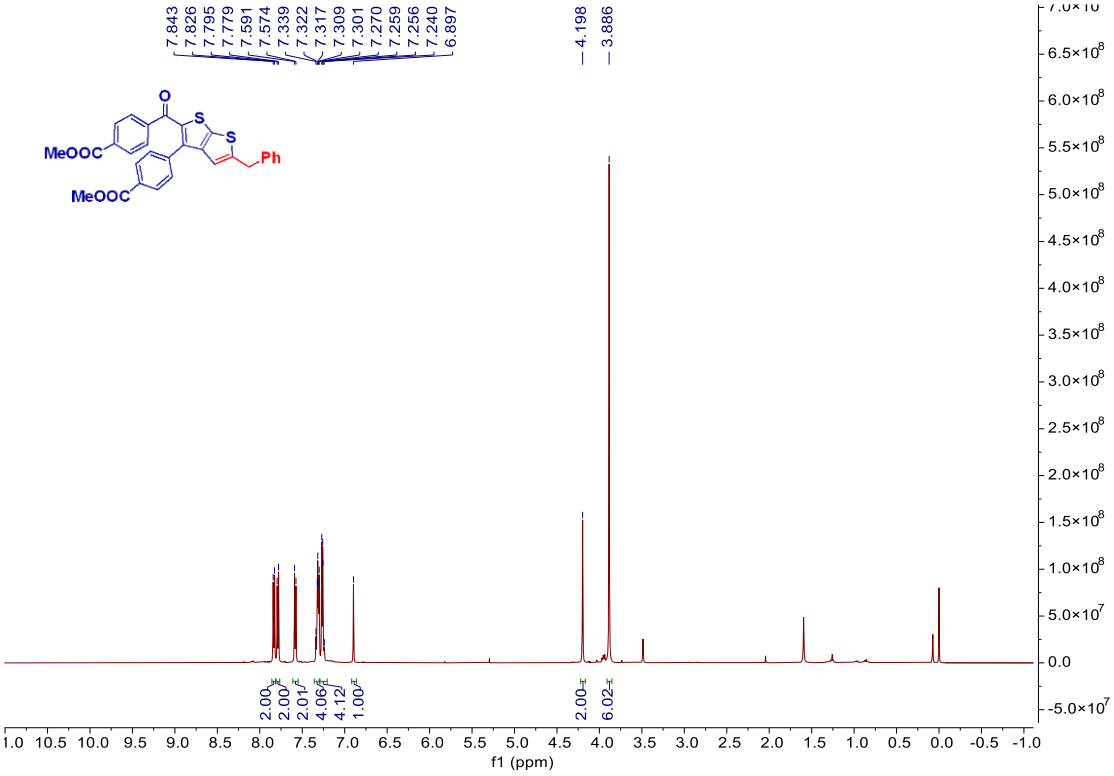
^{13}C NMR Spectrum of 3f ($CDCl_3$, 125 MHz)



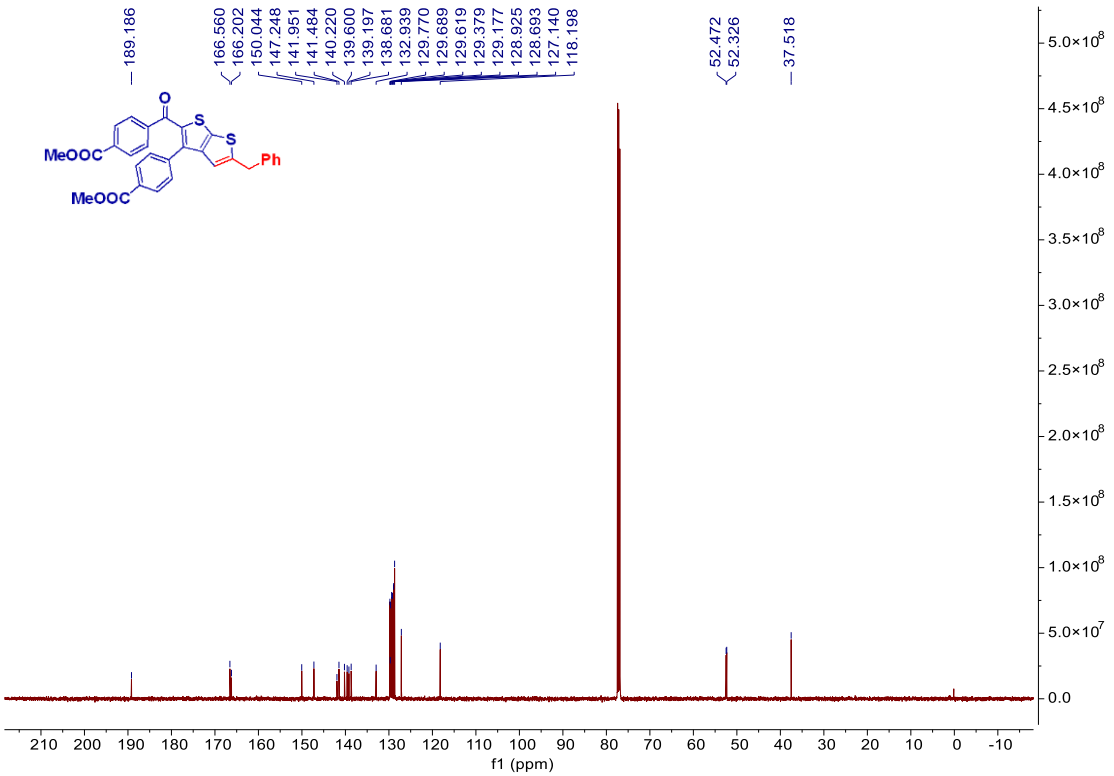
^{1}H NMR Spectrum of 3g ($CDCl_3$, 500 MHz)



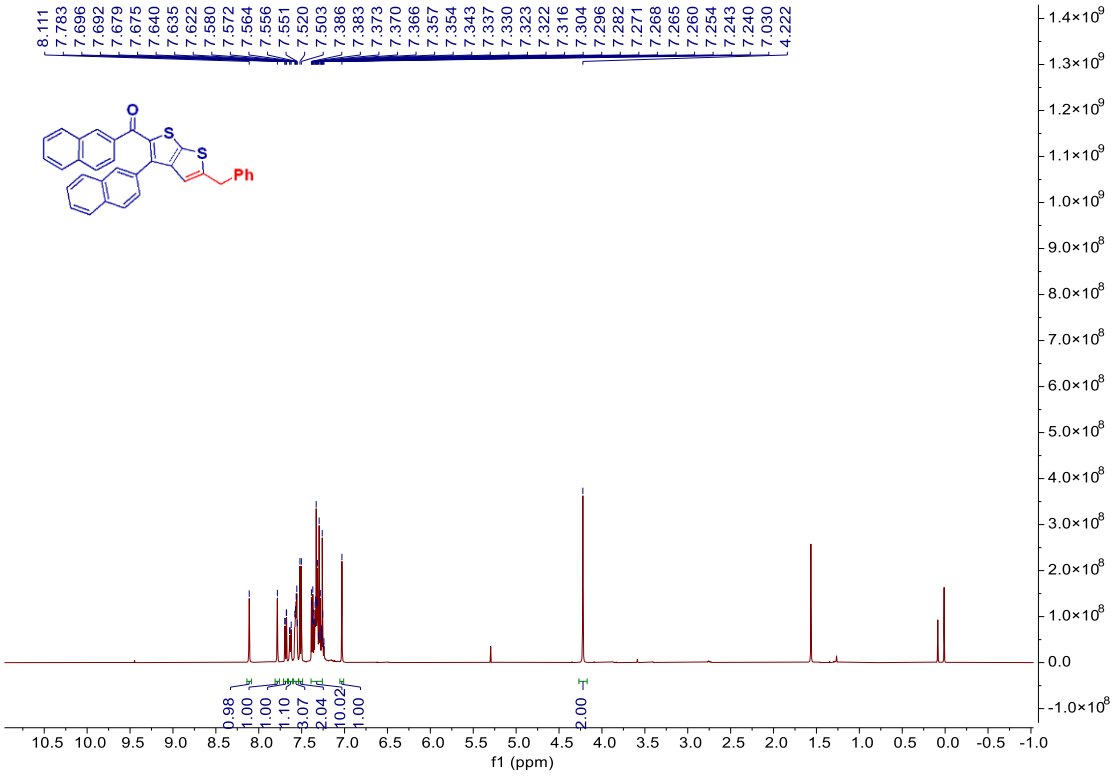
^{13}C NMR Spectrum of 3g ($CDCl_3$, 125 MHz)



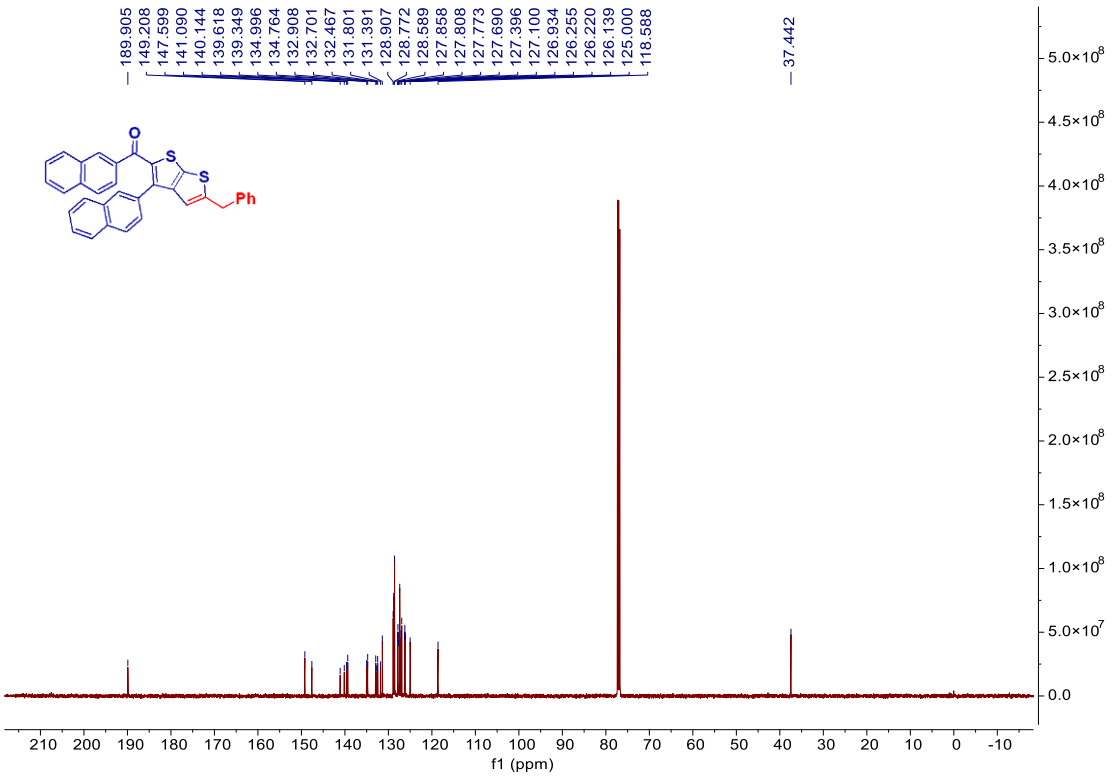
^{1}H NMR Spectrum of 3h ($CDCl_3$, 500 MHz)



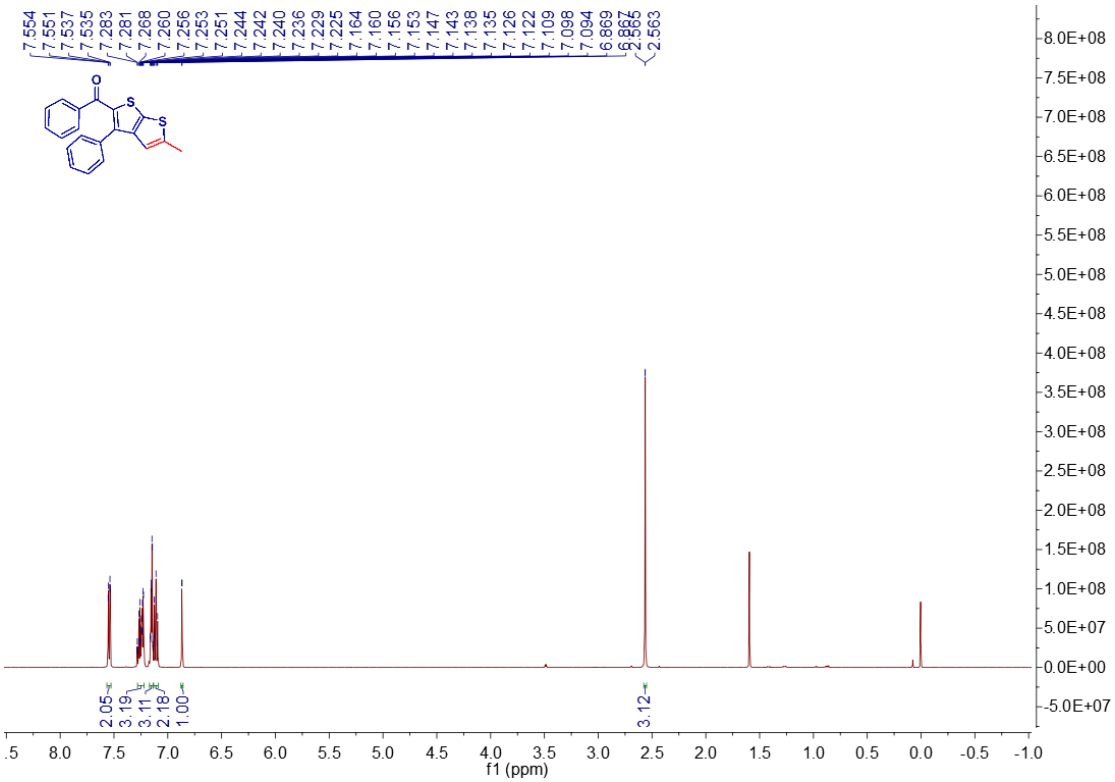
^{13}C NMR Spectrum of 3h ($CDCl_3$, 125 MHz)



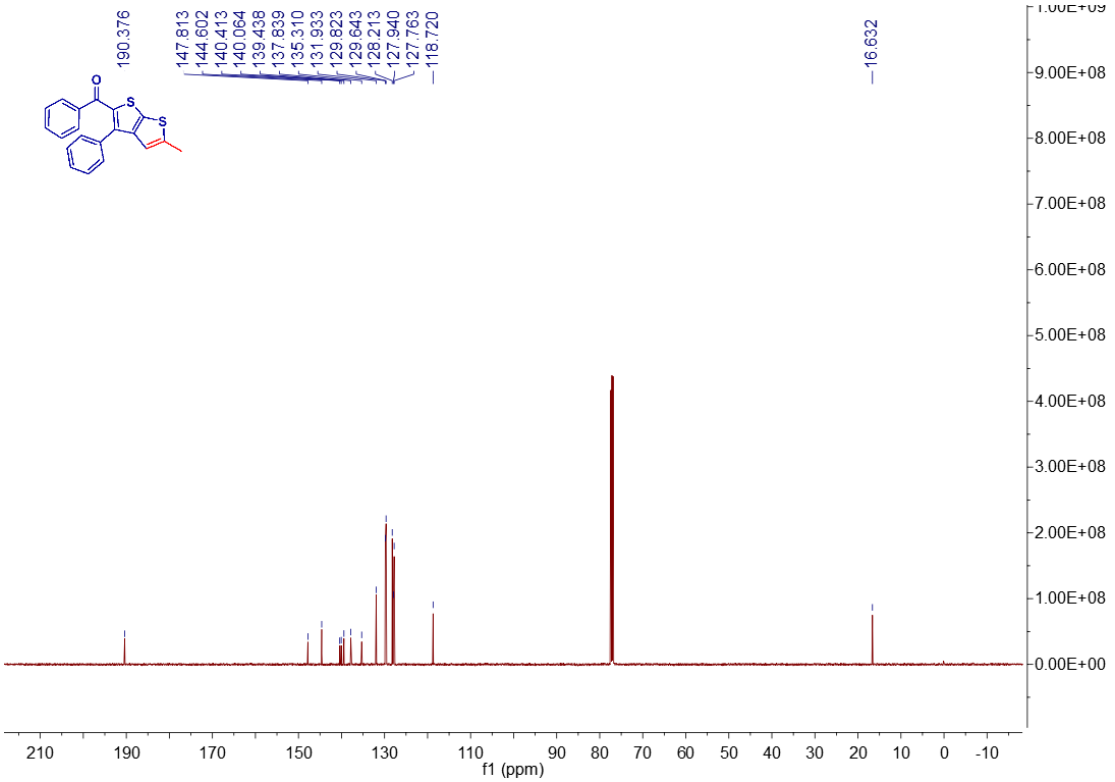
^{1}H NMR Spectrum of 3i ($CDCl_3$, 500 MHz)



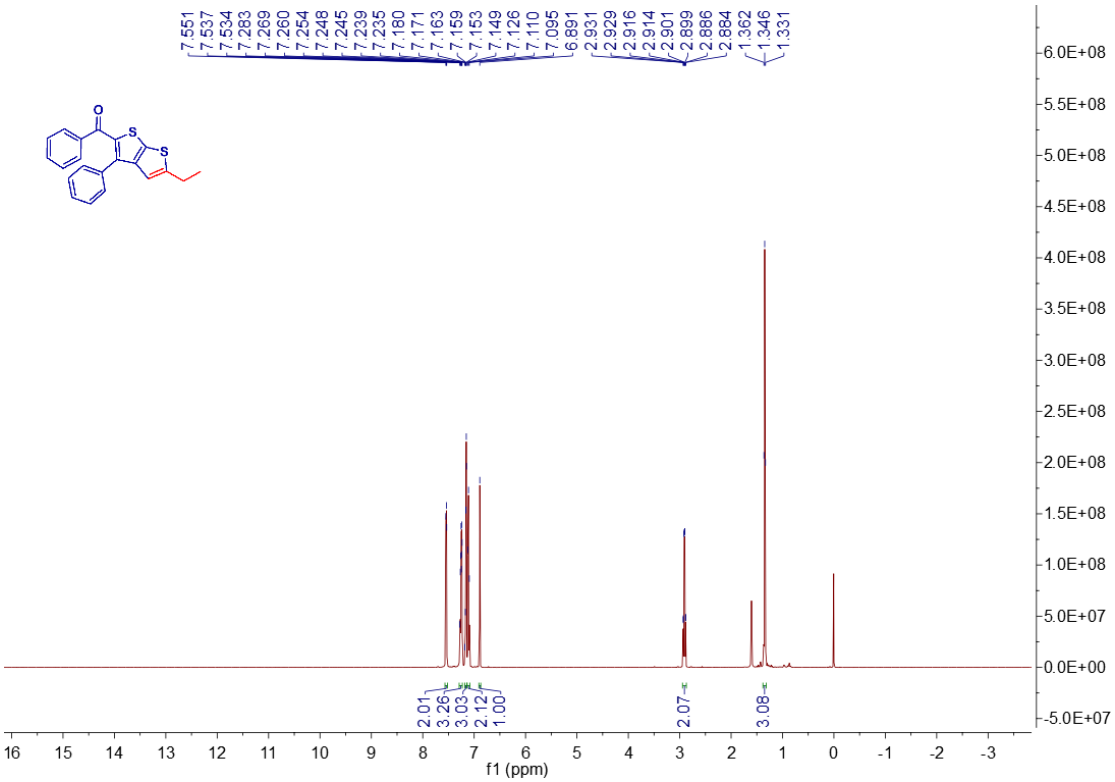
^{13}C NMR Spectrum of 3i ($CDCl_3$, 125 MHz)



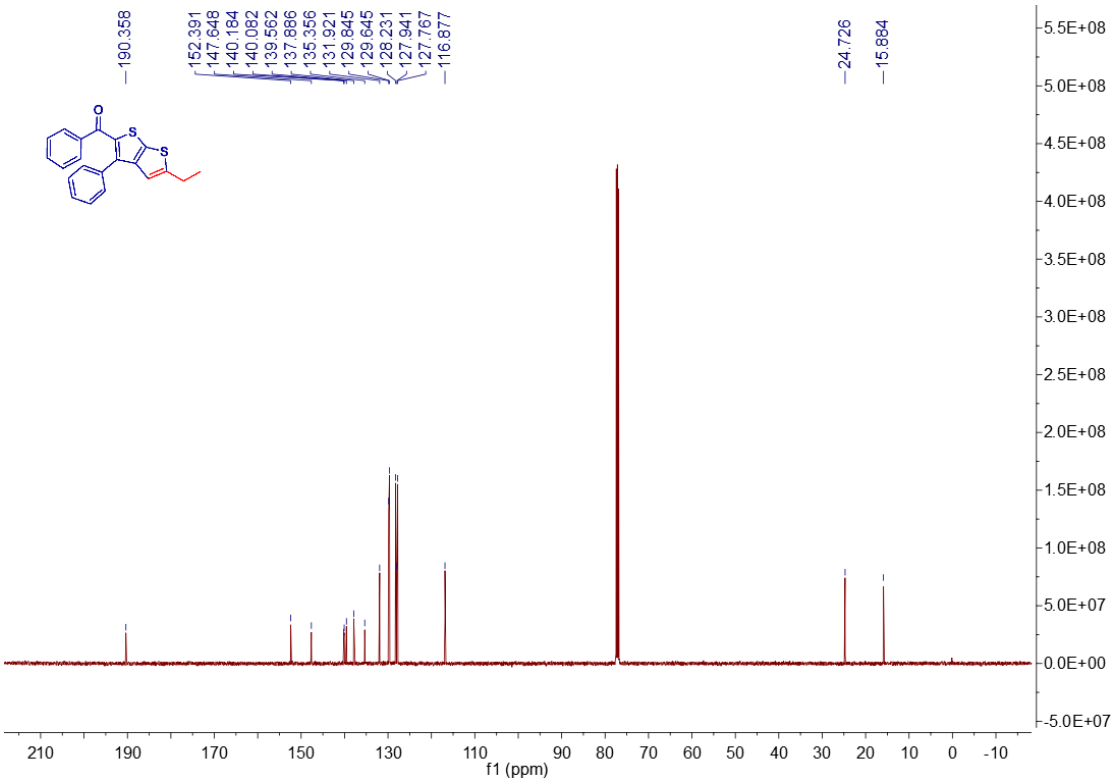
^{1}H NMR Spectrum of 3k ($CDCl_3$, 500 MHz)



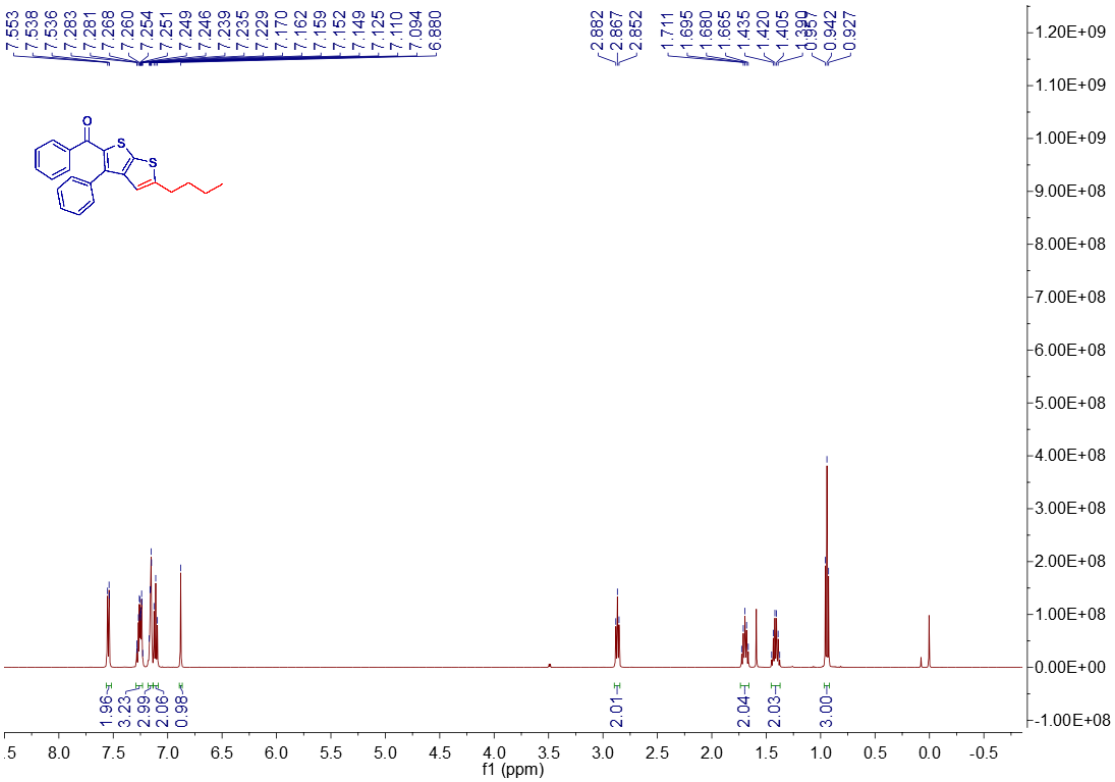
^{13}C NMR Spectrum of 3k ($CDCl_3$, 125 MHz)



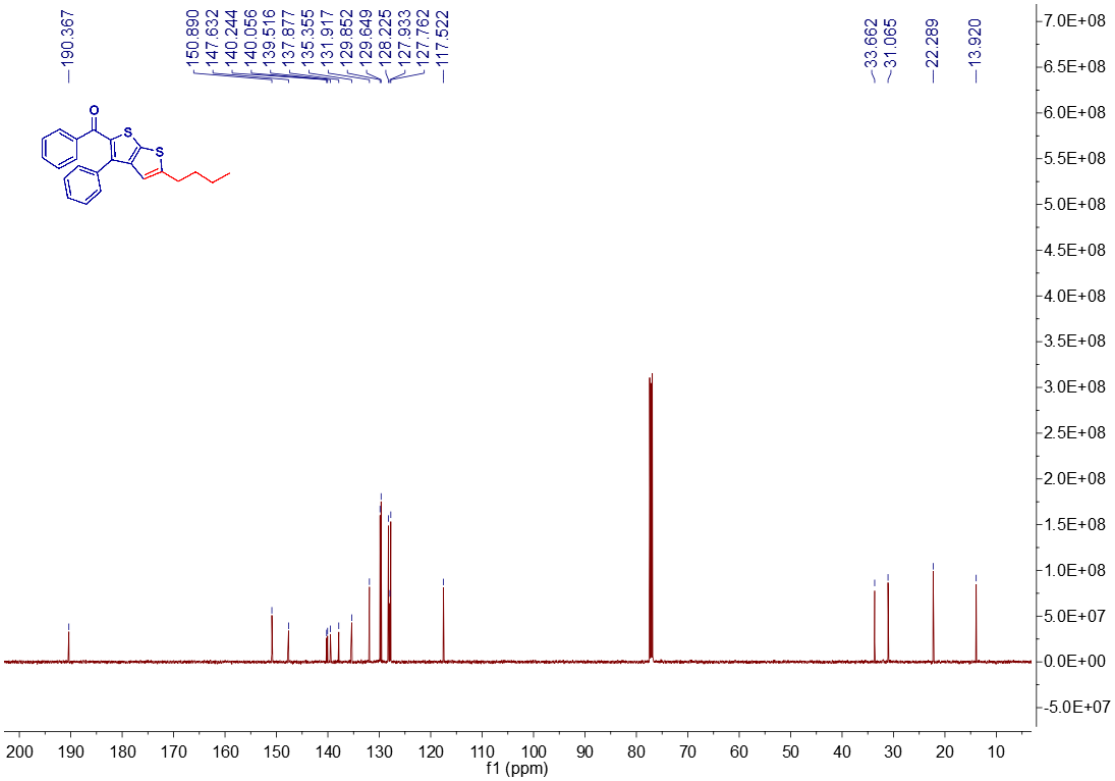
^{1}H NMR Spectrum of 3l ($CDCl_3$, 500 MHz)



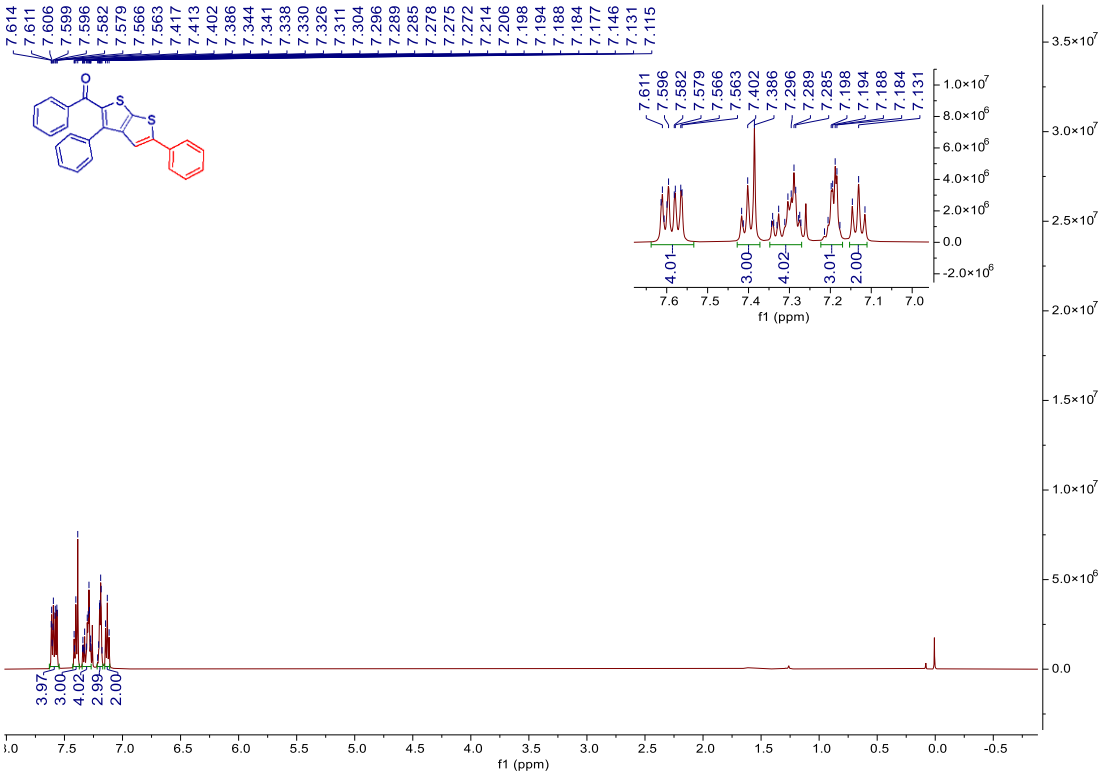
^{13}C NMR Spectrum of 3l ($CDCl_3$, 125 MHz)



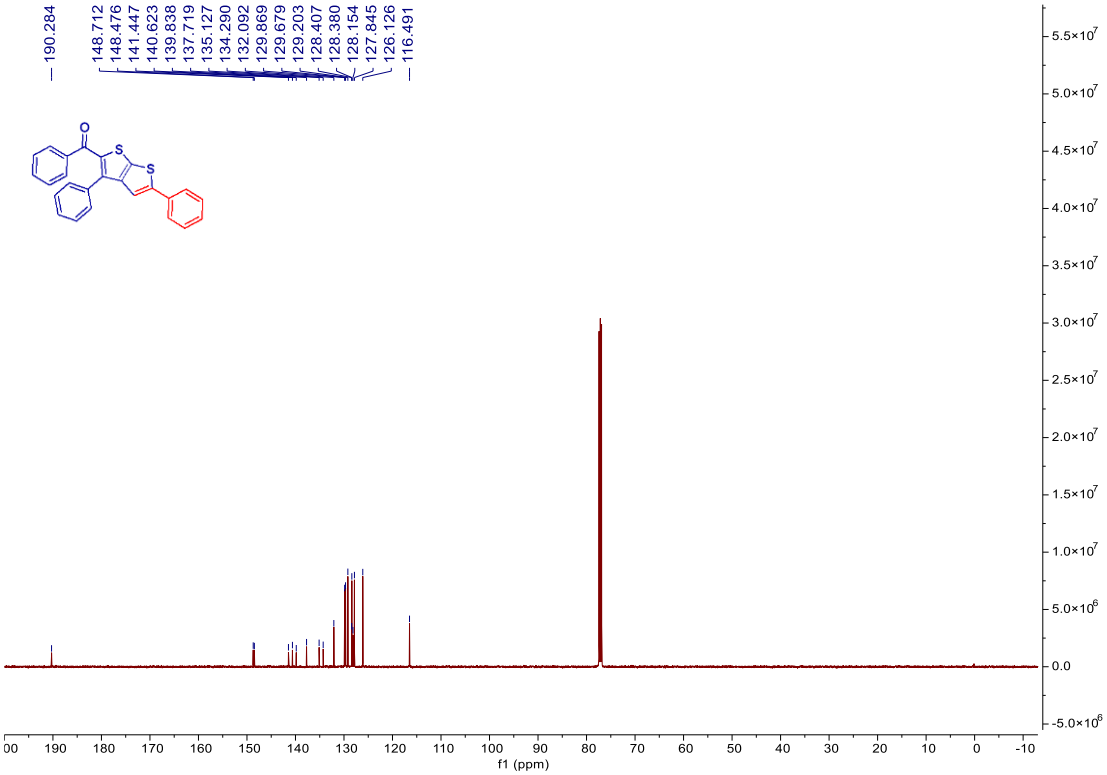
^{1}H NMR Spectrum of 3m ($CDCl_3$, 500 MHz)



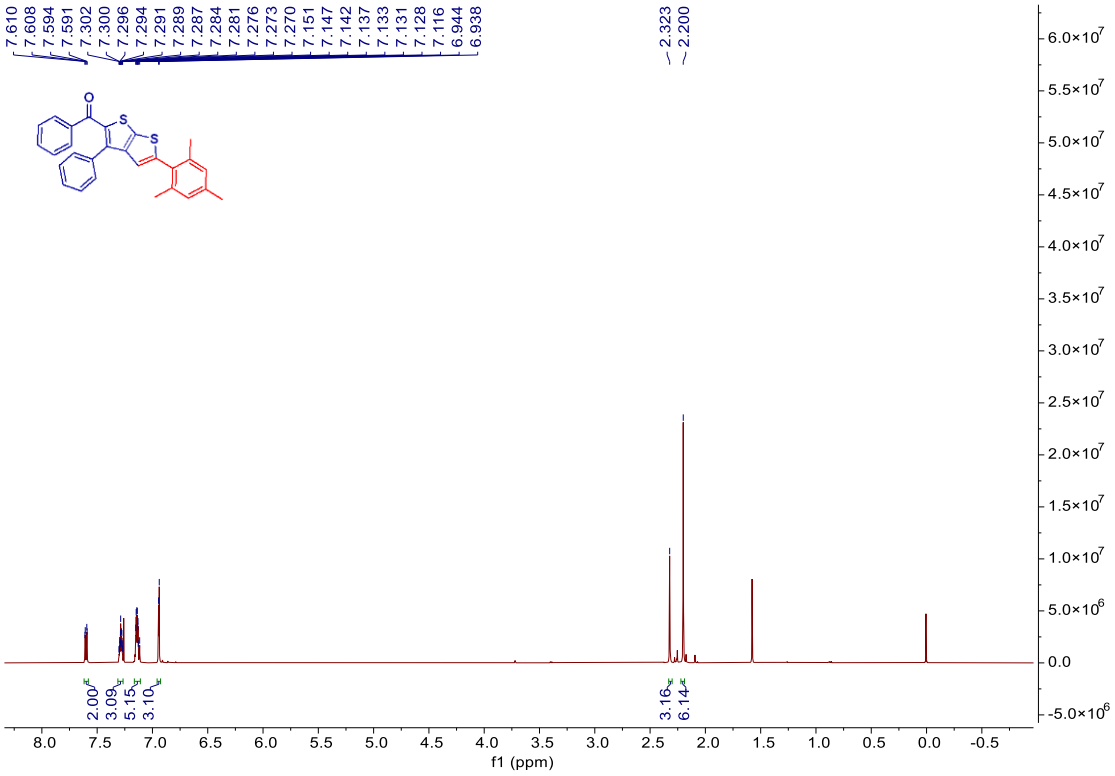
^{13}C NMR Spectrum of 3m ($CDCl_3$, 125 MHz)



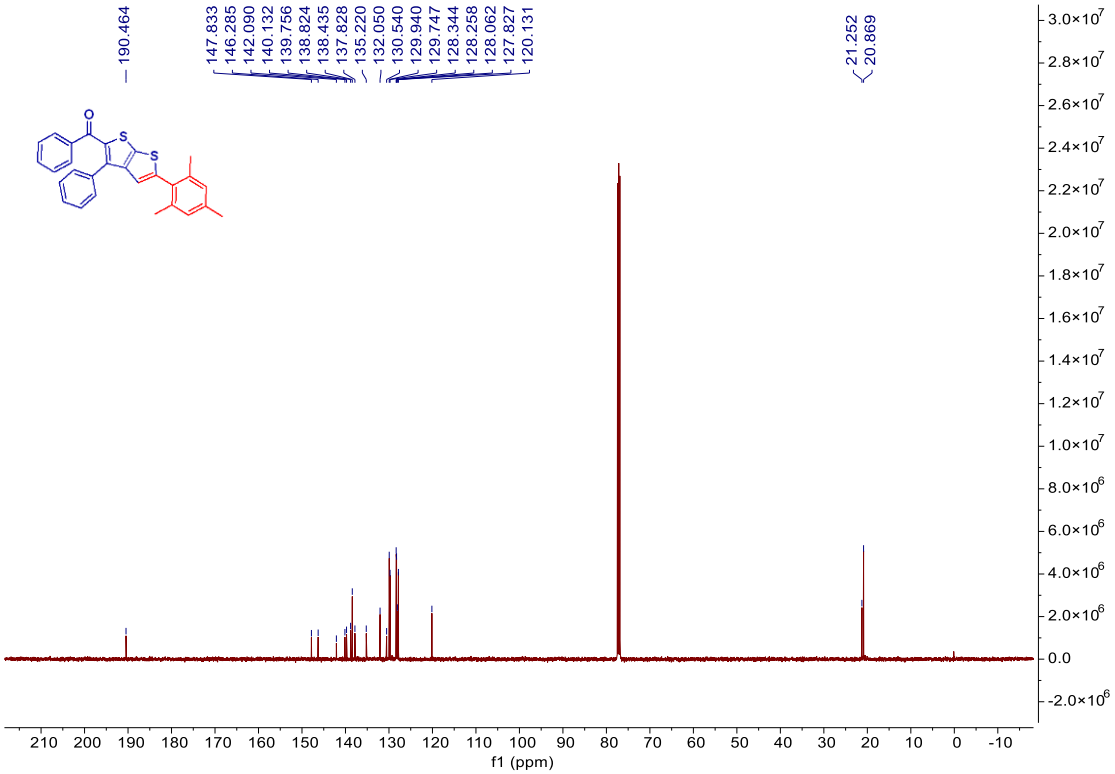
^{1}H NMR Spectrum of 3n ($CDCl_3$, 500 MHz)



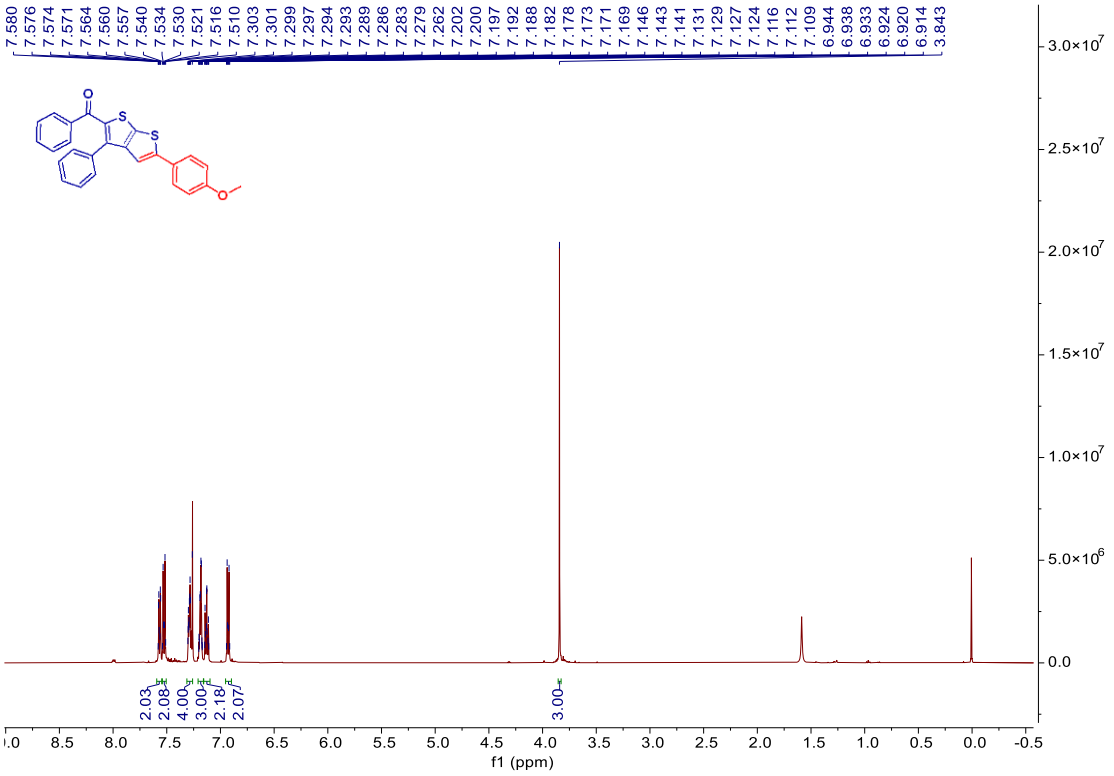
^{13}C NMR Spectrum of 3n ($CDCl_3$, 125 MHz)



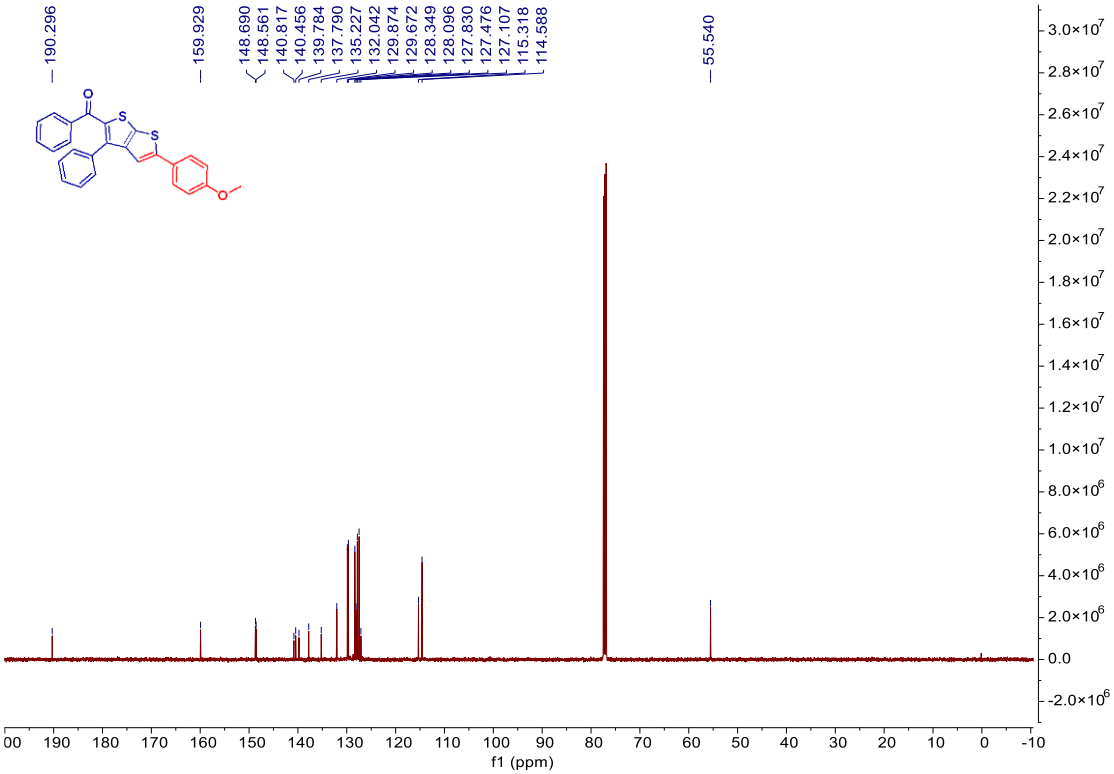
^{1}H NMR Spectrum of 3o ($CDCl_3$, 500 MHz)



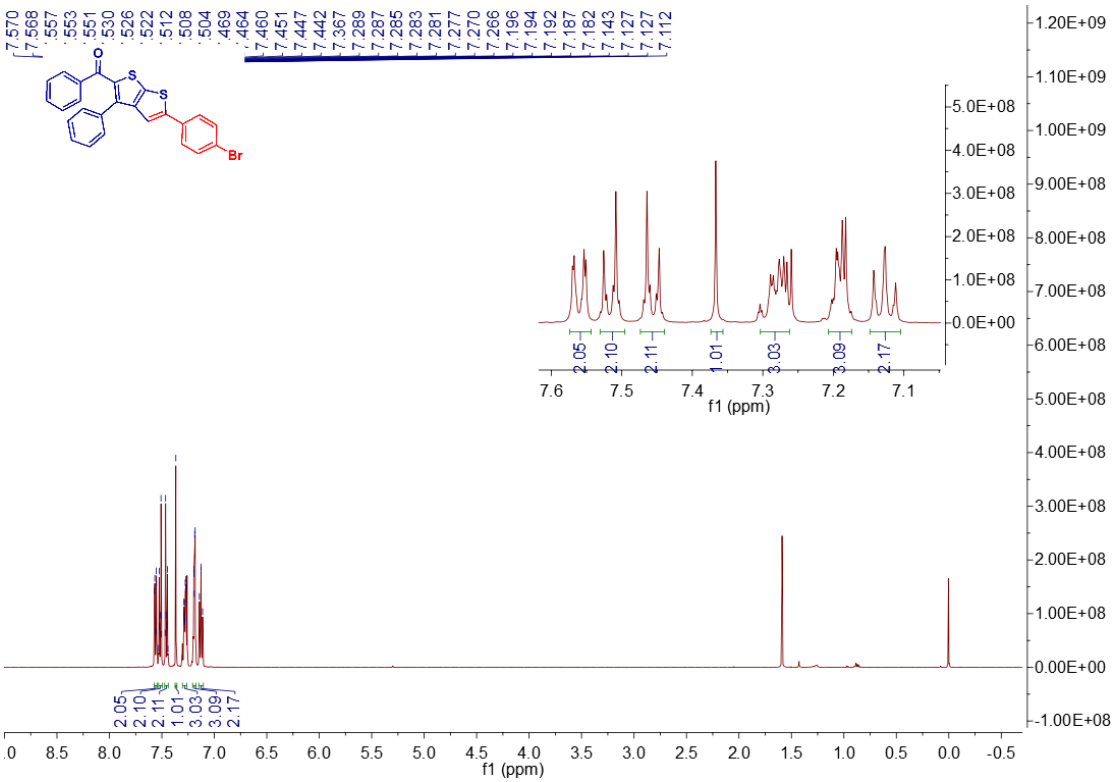
^{13}C NMR Spectrum of 3o ($CDCl_3$, 125 MHz)



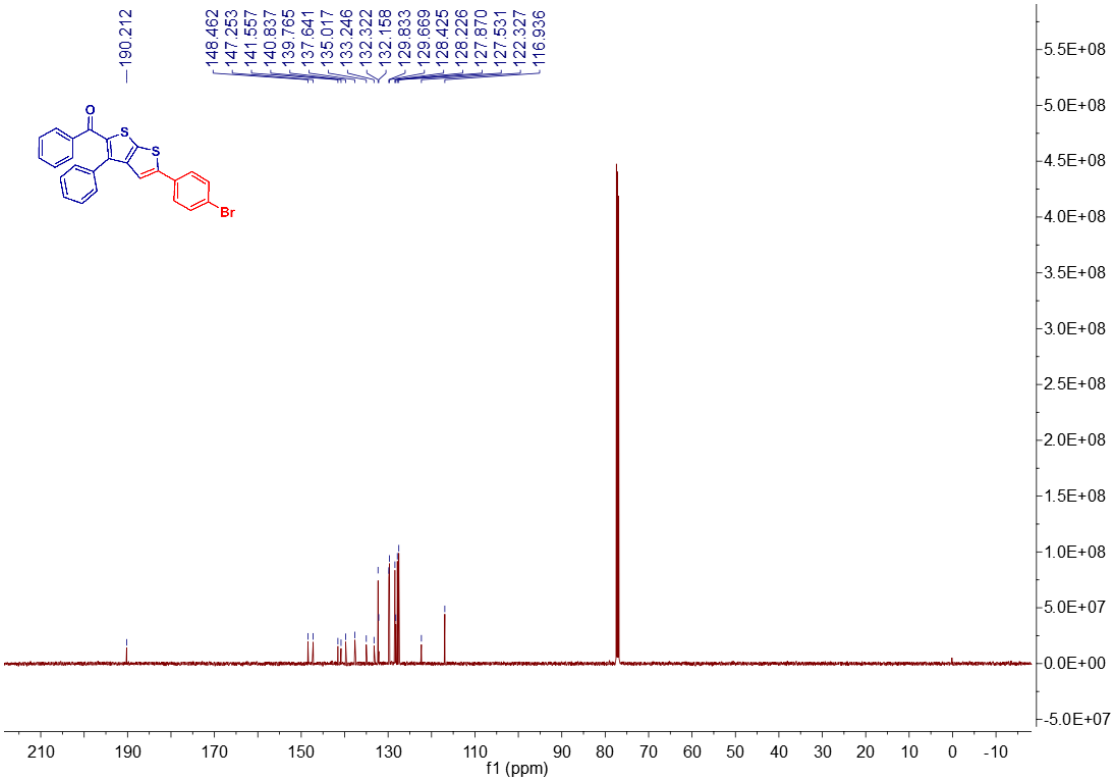
^{1}H NMR Spectrum of 3p ($CDCl_3$, 500 MHz)



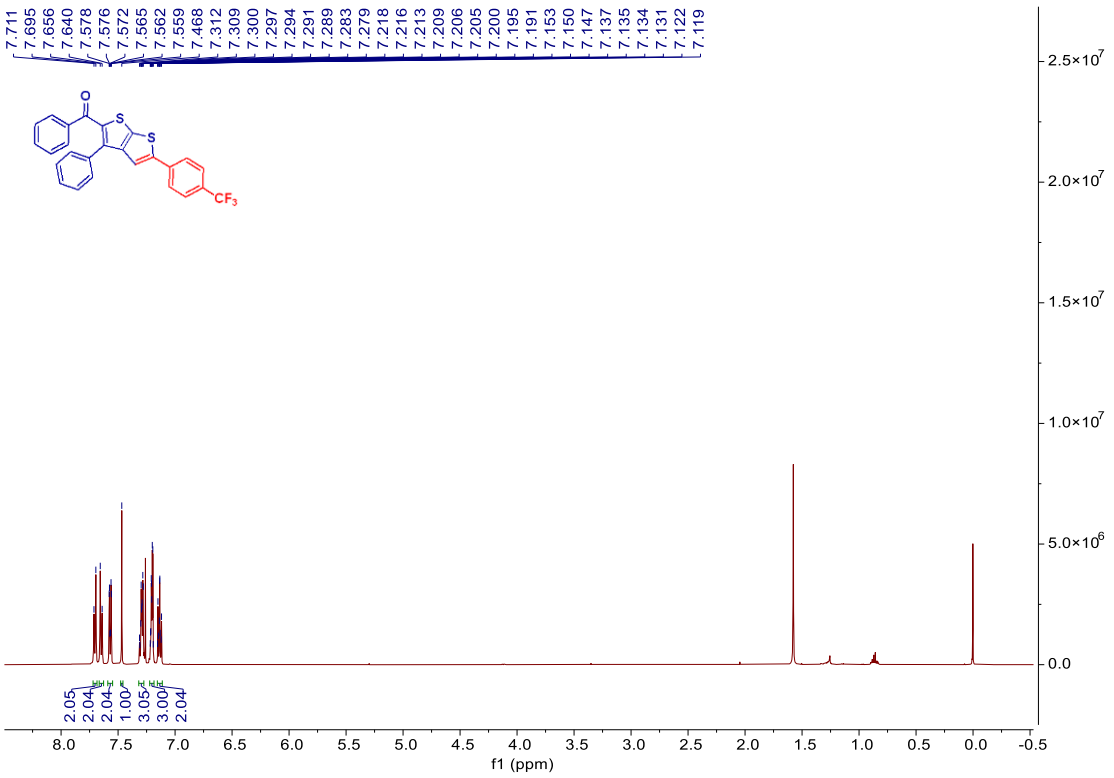
^{13}C NMR Spectrum of 3p ($CDCl_3$, 125 MHz)



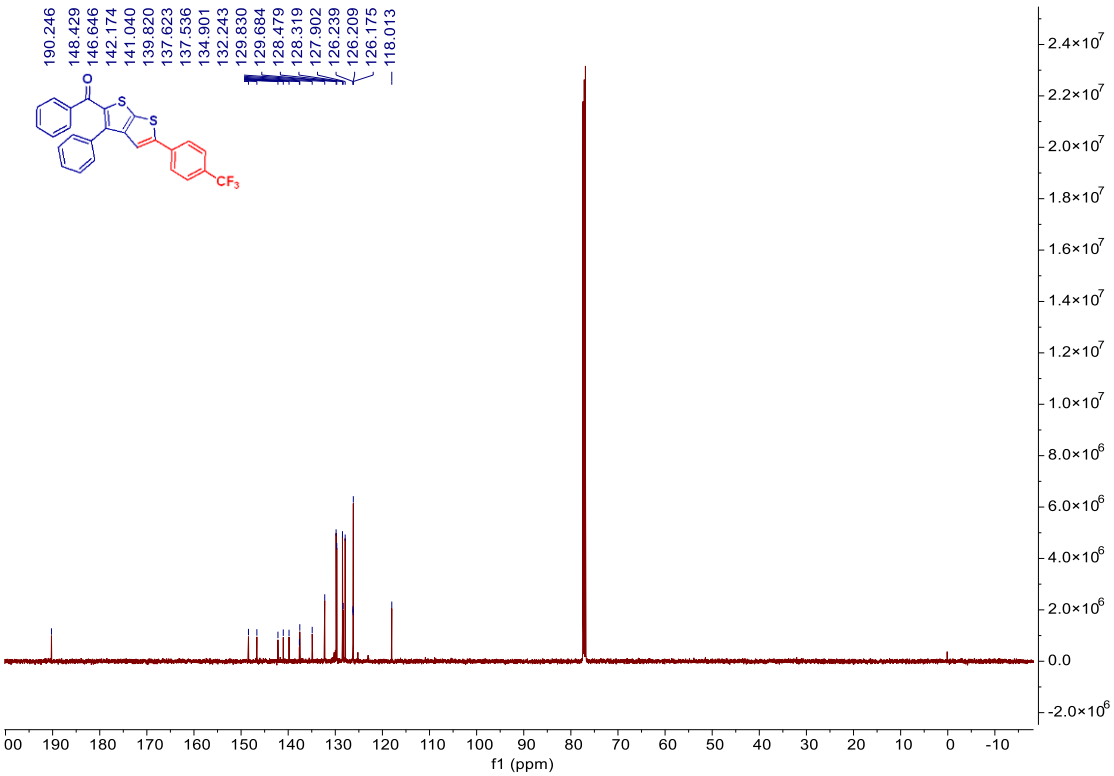
^{1}H NMR Spectrum of 3q ($CDCl_3$, 500 MHz)



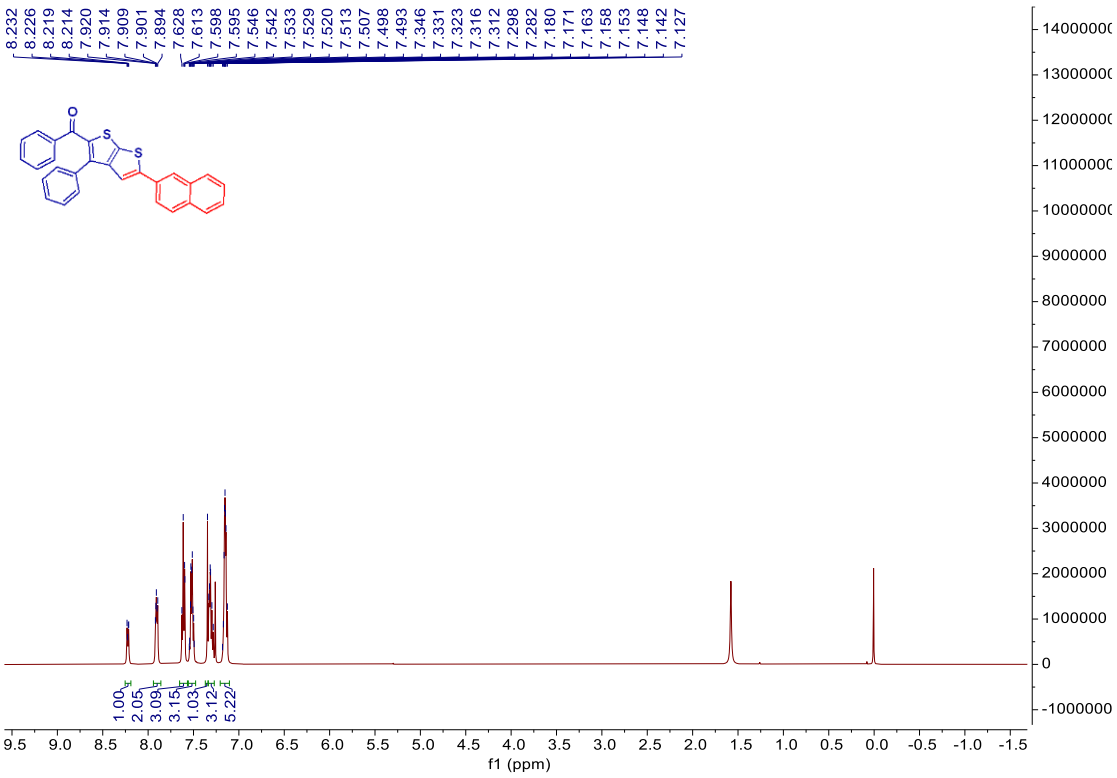
^{13}C NMR Spectrum of 3q ($CDCl_3$, 125 MHz)



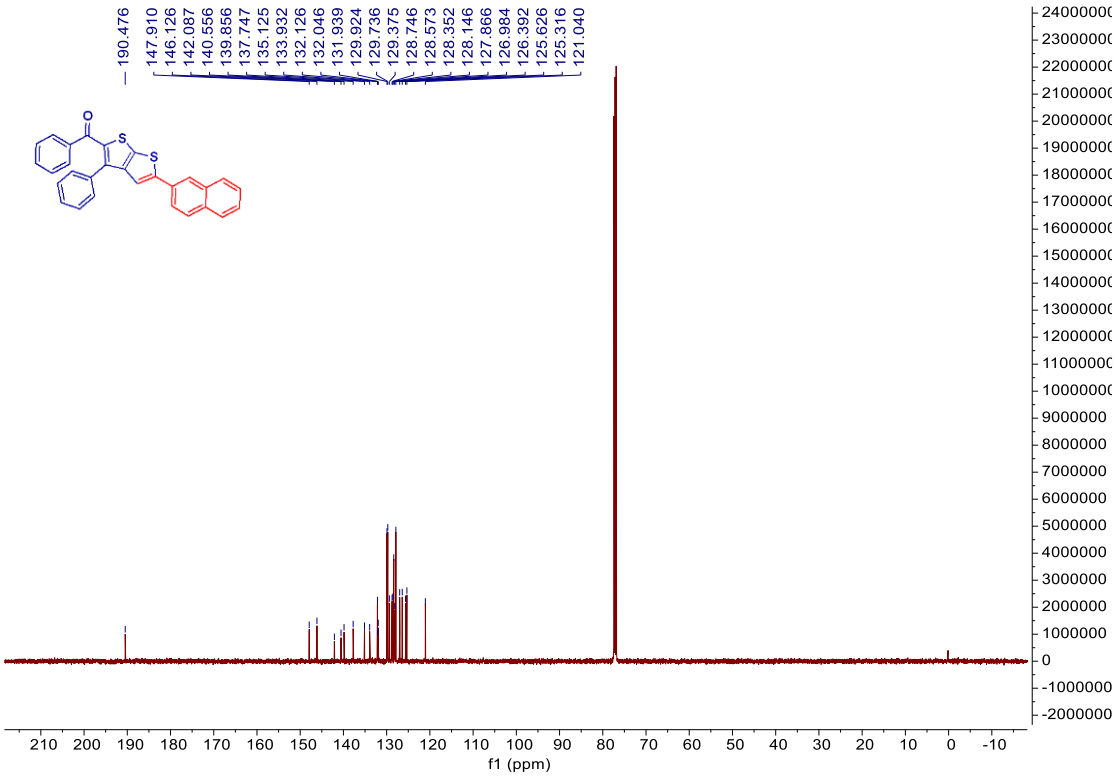
^{1}H NMR Spectrum of 3r ($CDCl_3$, 500 MHz)



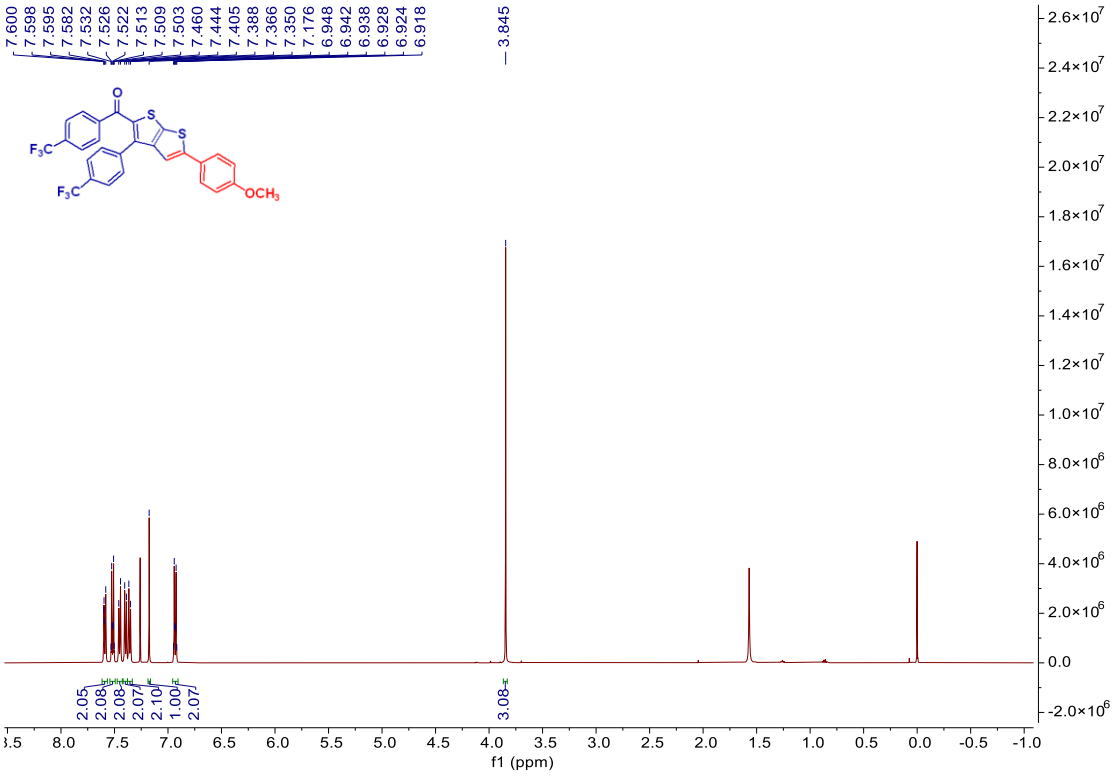
^{13}C NMR Spectrum of 3r ($CDCl_3$, 125 MHz)



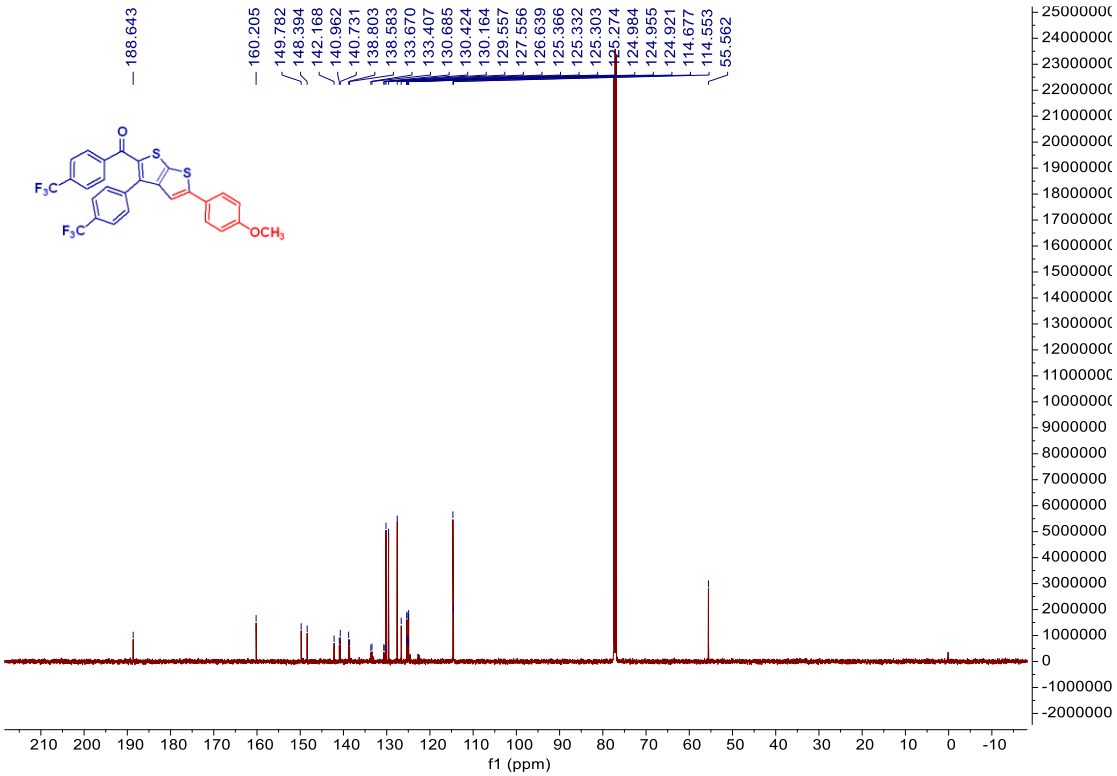
^{1}H NMR Spectrum of 3s ($CDCl_3$, 500 MHz)



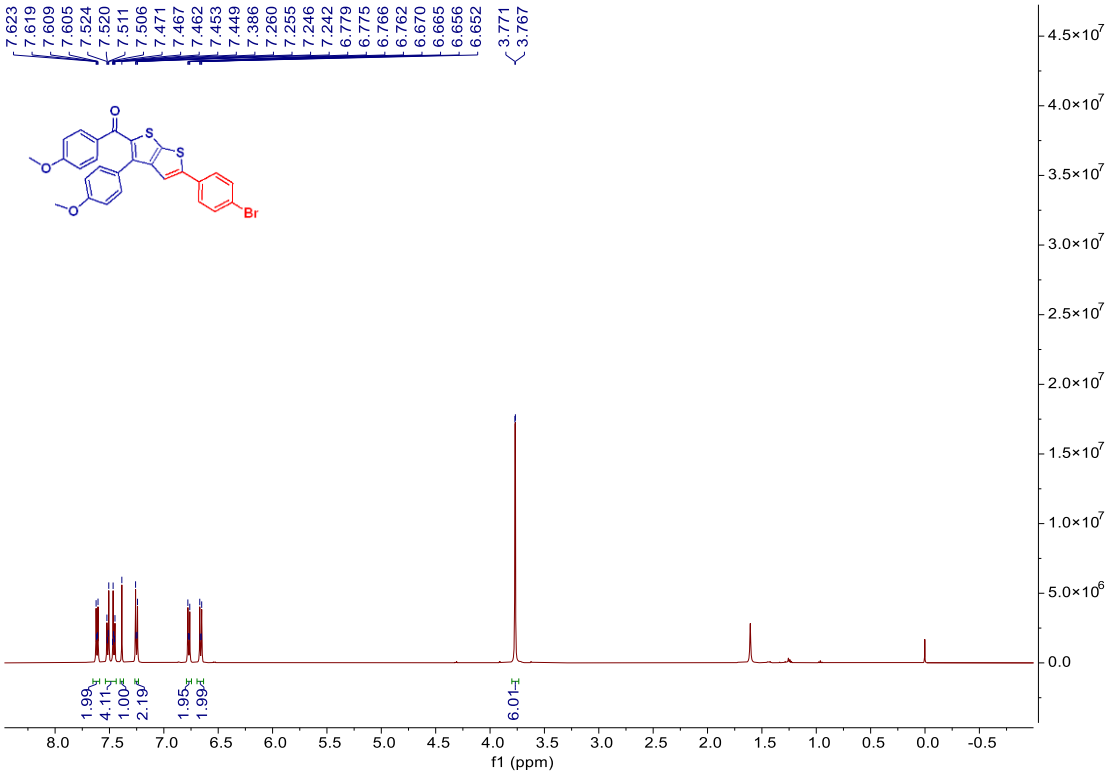
^{13}C NMR Spectrum of 3s ($CDCl_3$, 125 MHz)



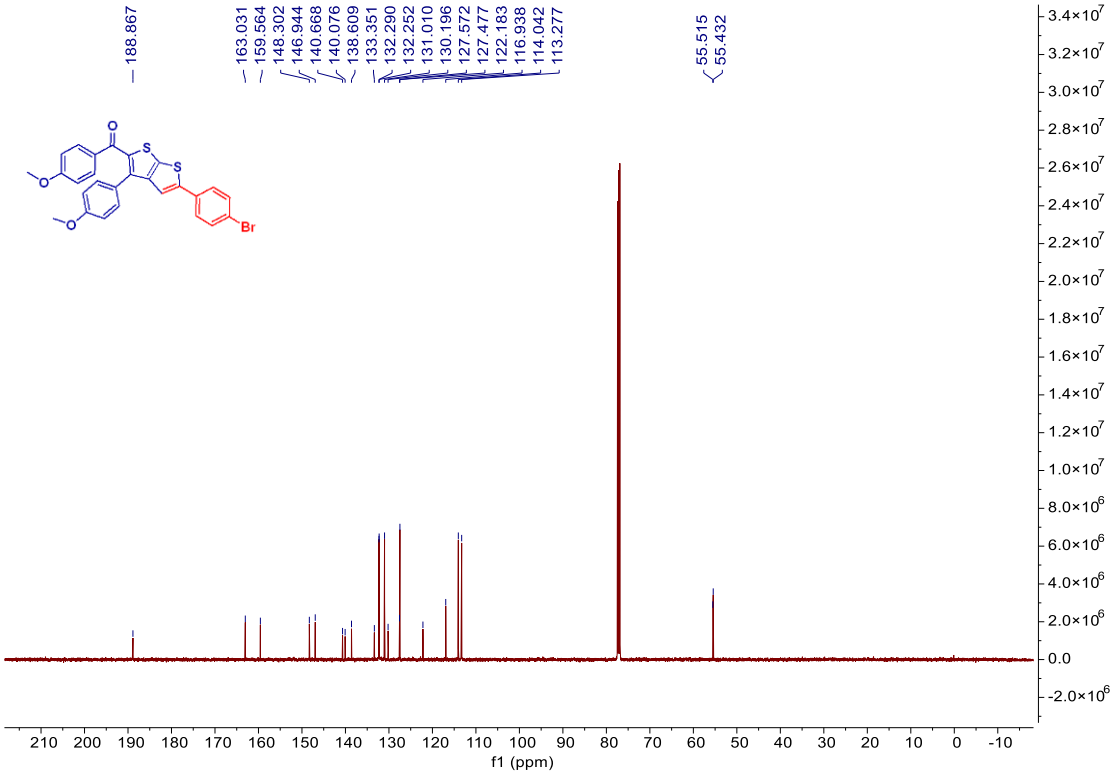
^{1}H NMR Spectrum of 3t ($CDCl_3$, 500 MHz)



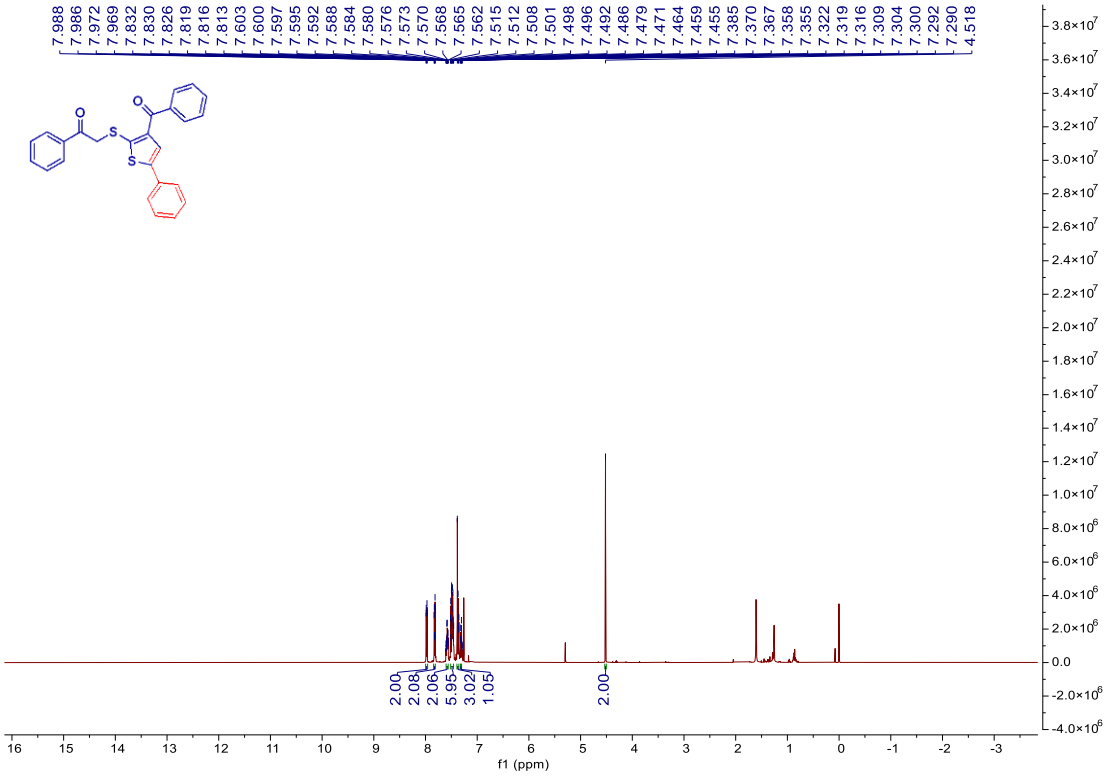
^{13}C NMR Spectrum of 3t ($CDCl_3$, 125 MHz)



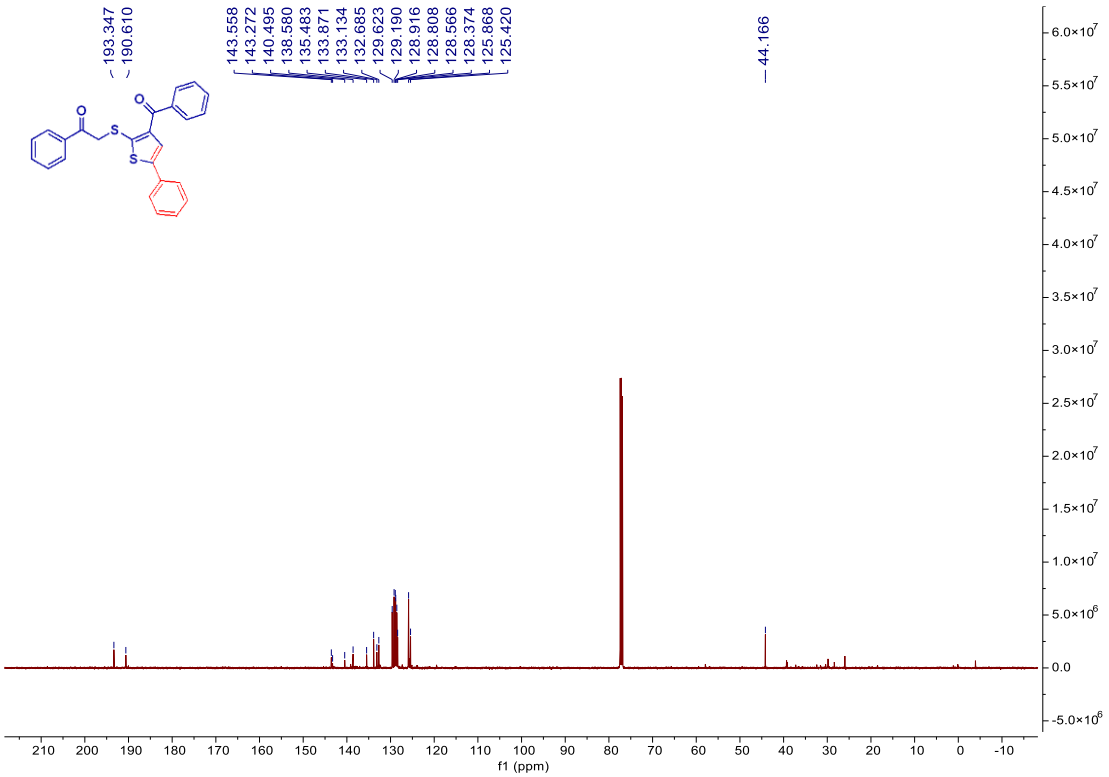
^{1}H NMR Spectrum of 3u ($CDCl_3$, 500 MHz)



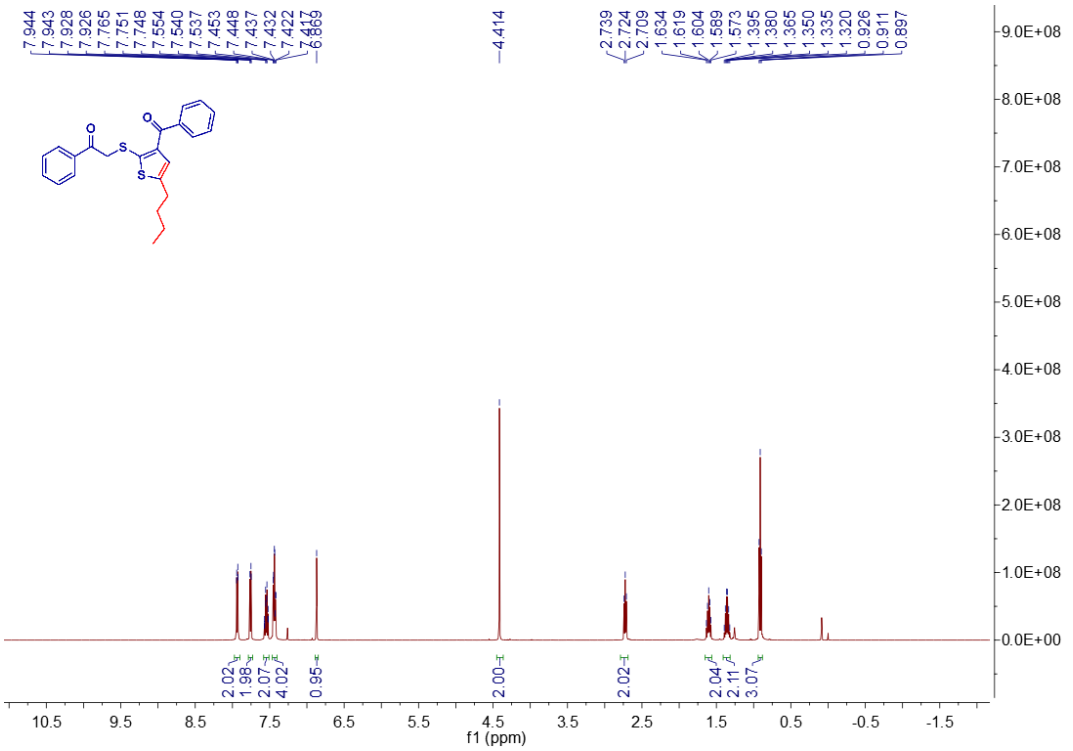
^{13}C NMR Spectrum of 3u ($CDCl_3$, 125 MHz)



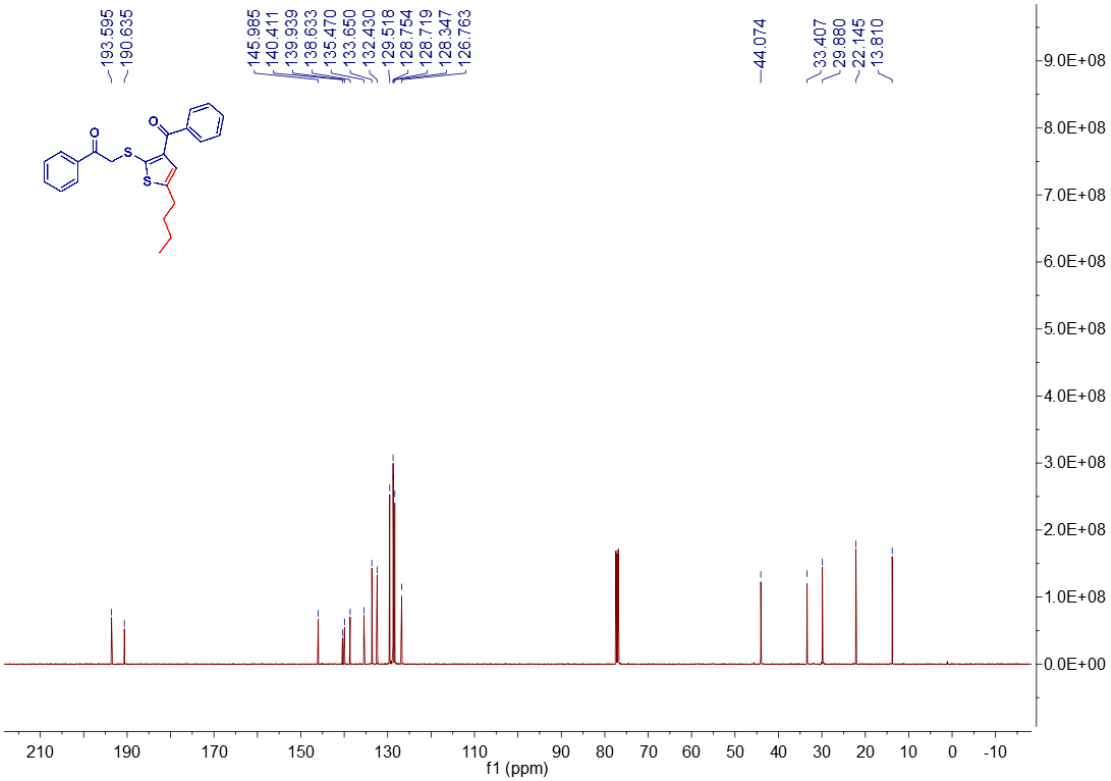
^{1}H NMR Spectrum of 5a ($CDCl_3$, 500 MHz)



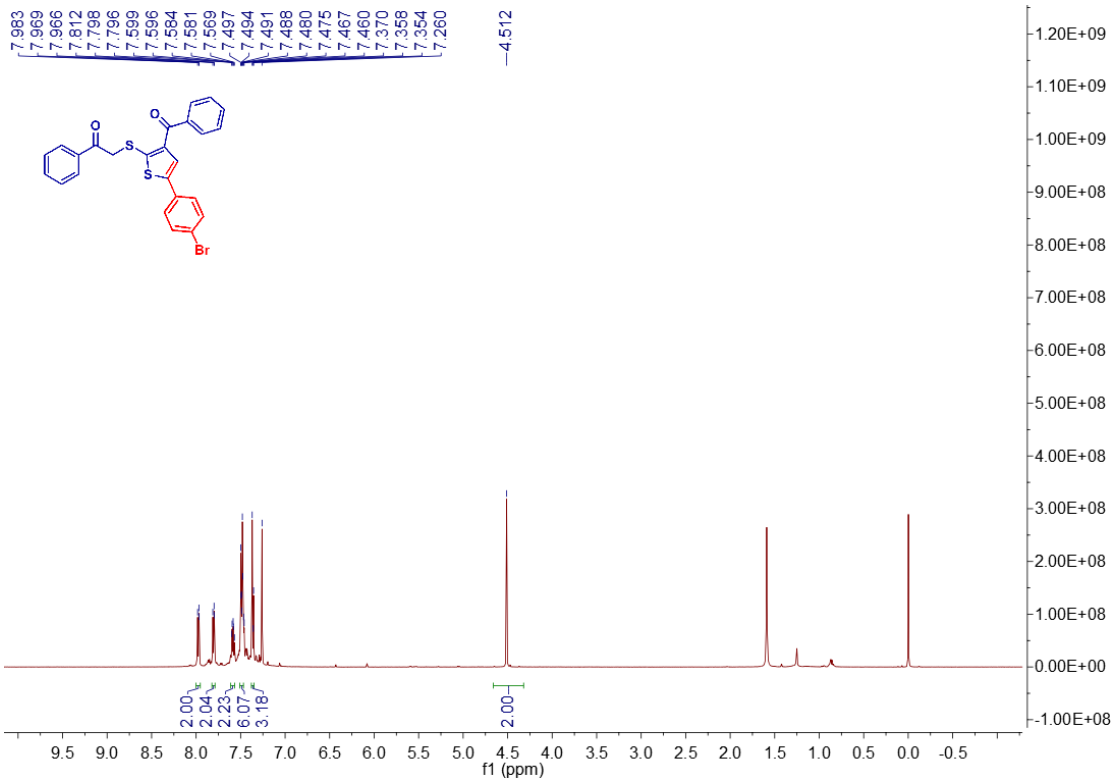
^{13}C NMR Spectrum of 5a ($CDCl_3$, 125 MHz)



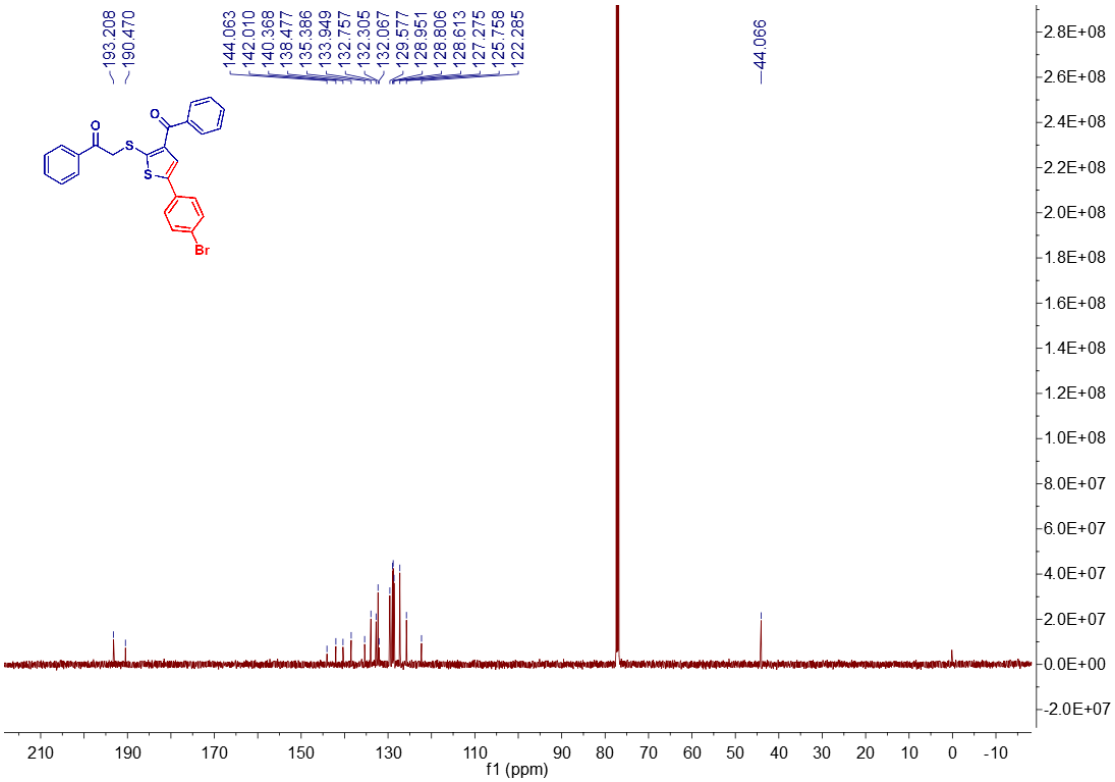
^{1}H NMR Spectrum of 5b ($CDCl_3$, 500 MHz)



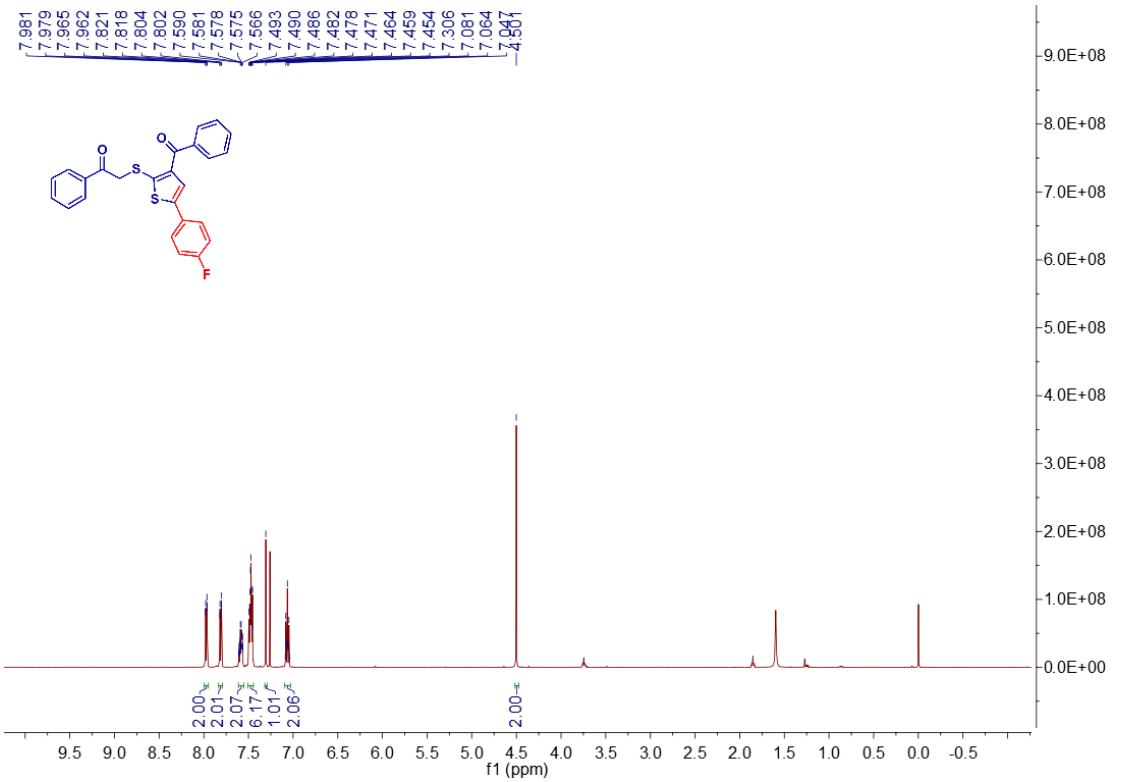
^{13}C NMR Spectrum of 5b ($CDCl_3$, 125 MHz)



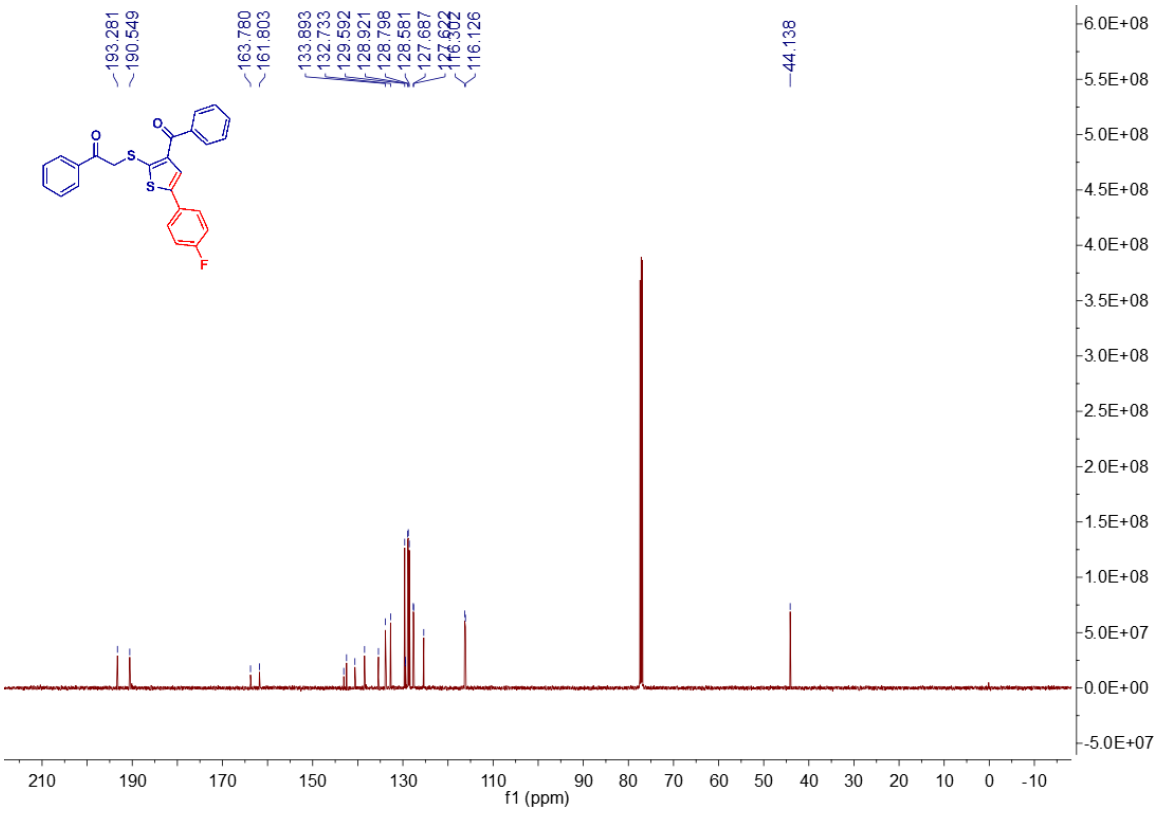
^{1}H NMR Spectrum of 5c ($CDCl_3$, 500 MHz)



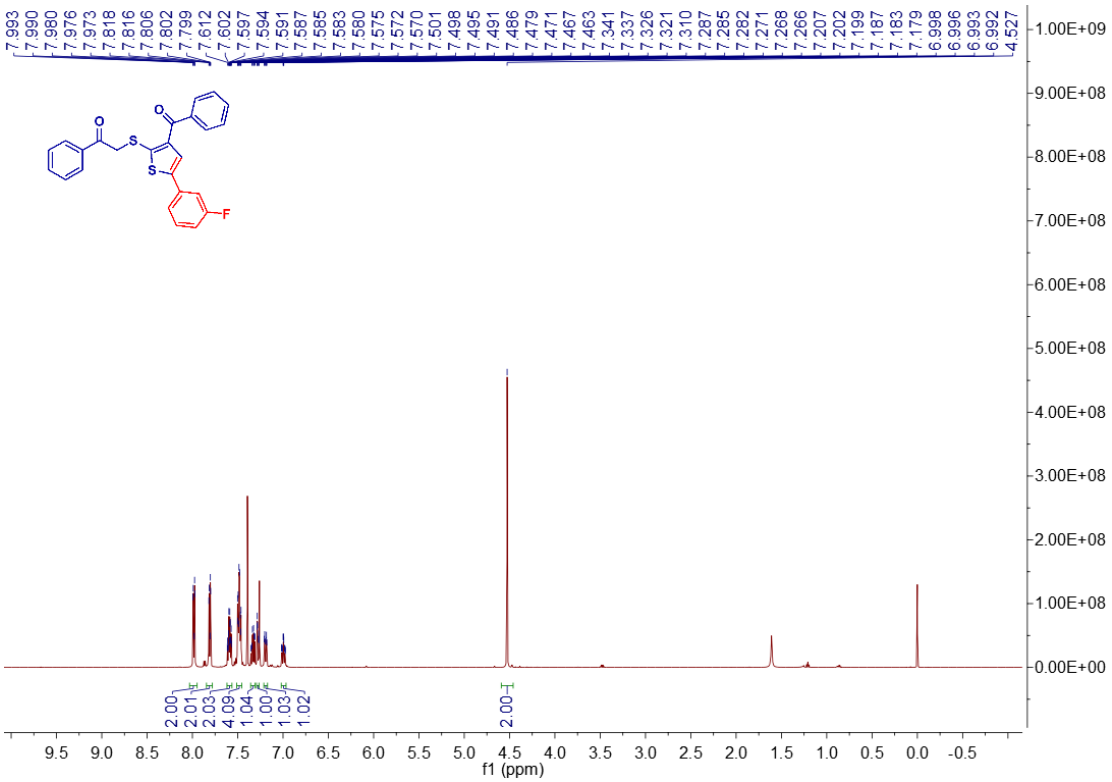
^{13}C NMR Spectrum of 5c ($CDCl_3$, 125 MHz)



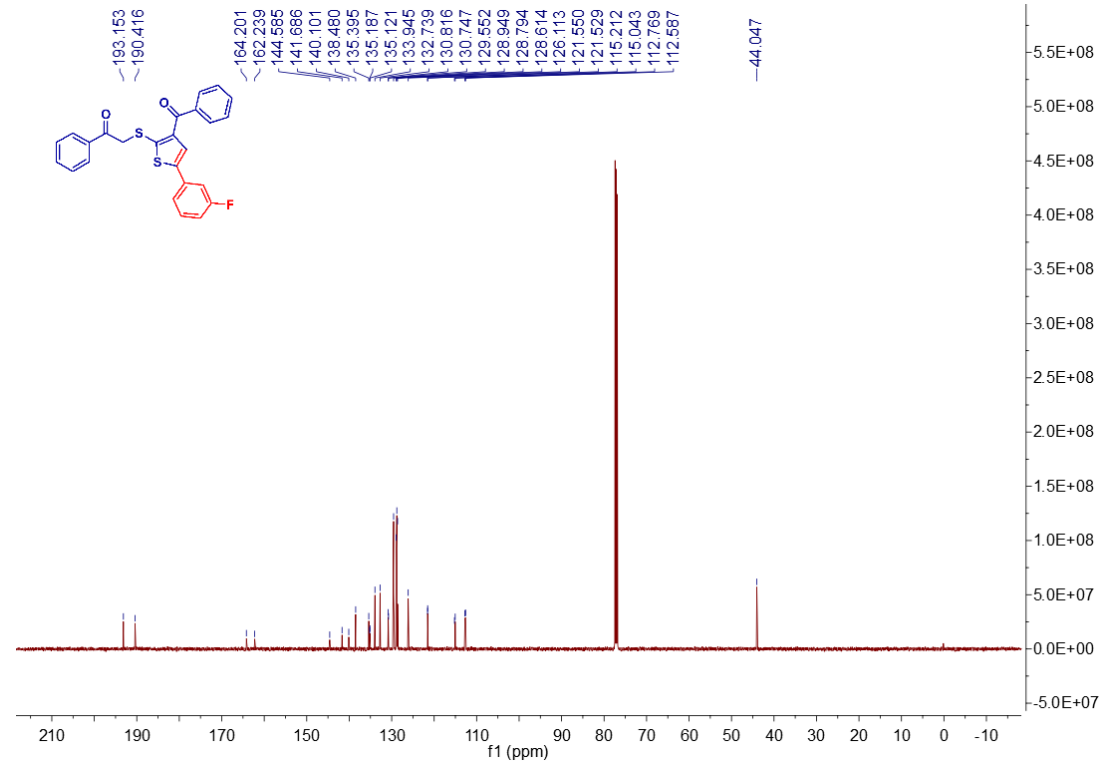
^{1}H NMR Spectrum of 5d ($CDCl_3$, 500 MHz)



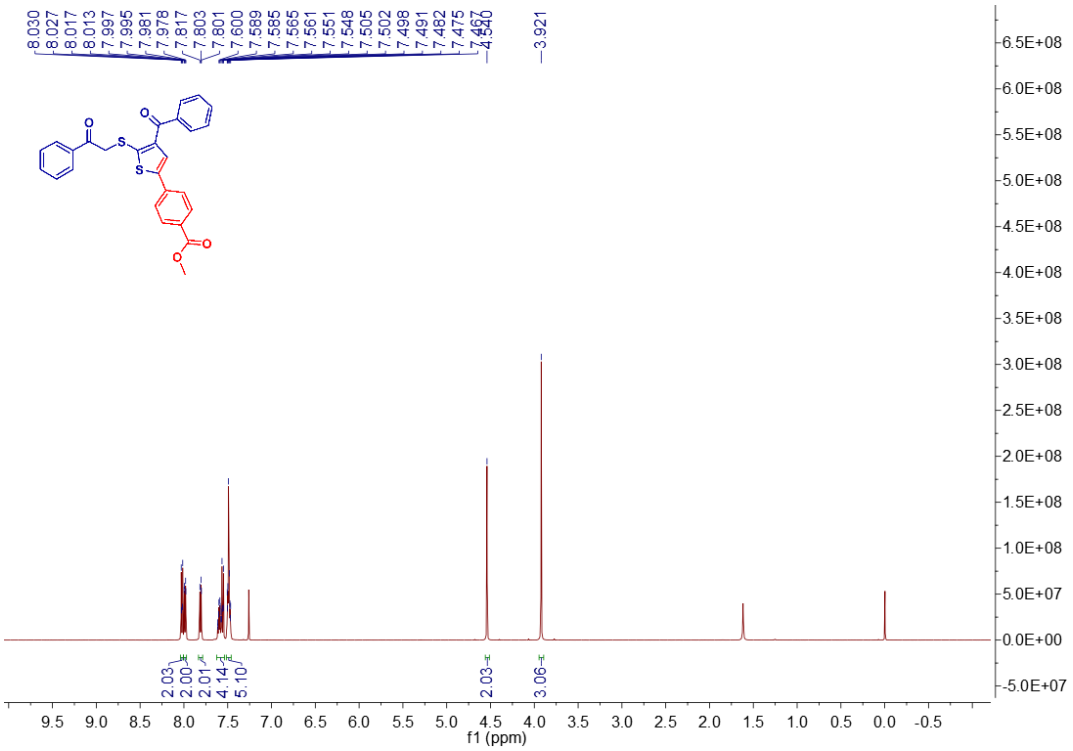
^{13}C NMR Spectrum of 5d ($CDCl_3$, 125 MHz)



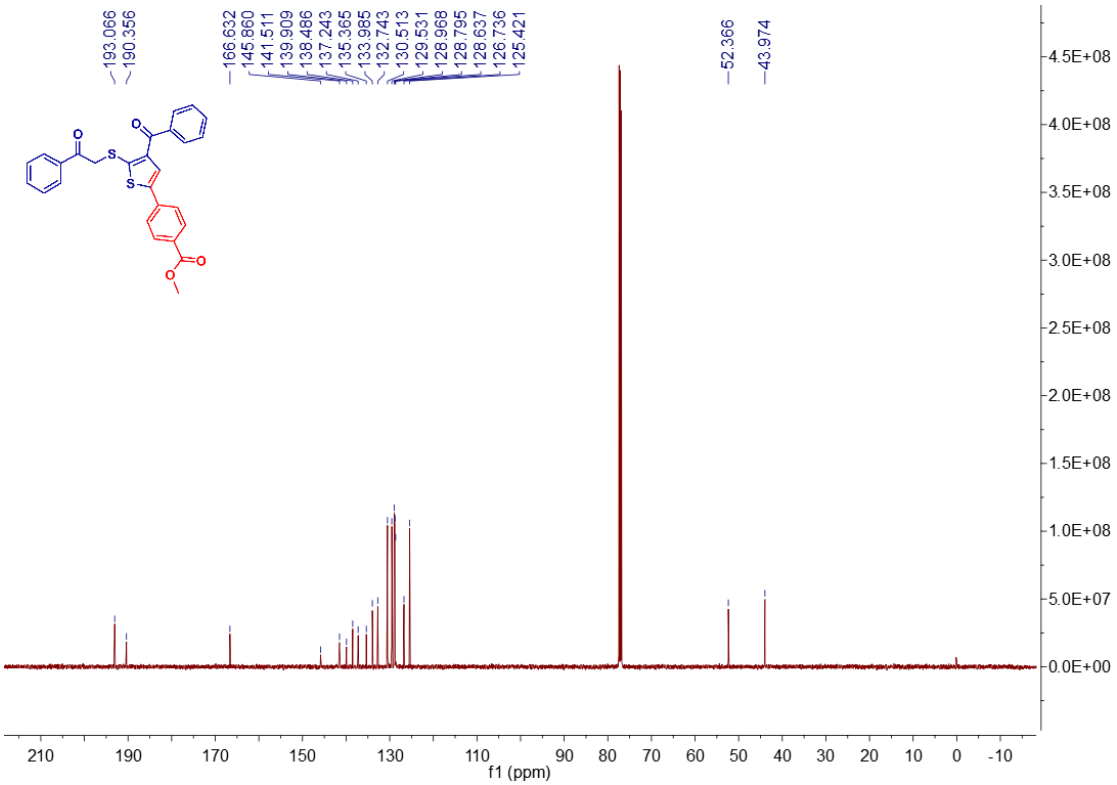
^{1}H NMR Spectrum of 5e ($CDCl_3$, 500 MHz)



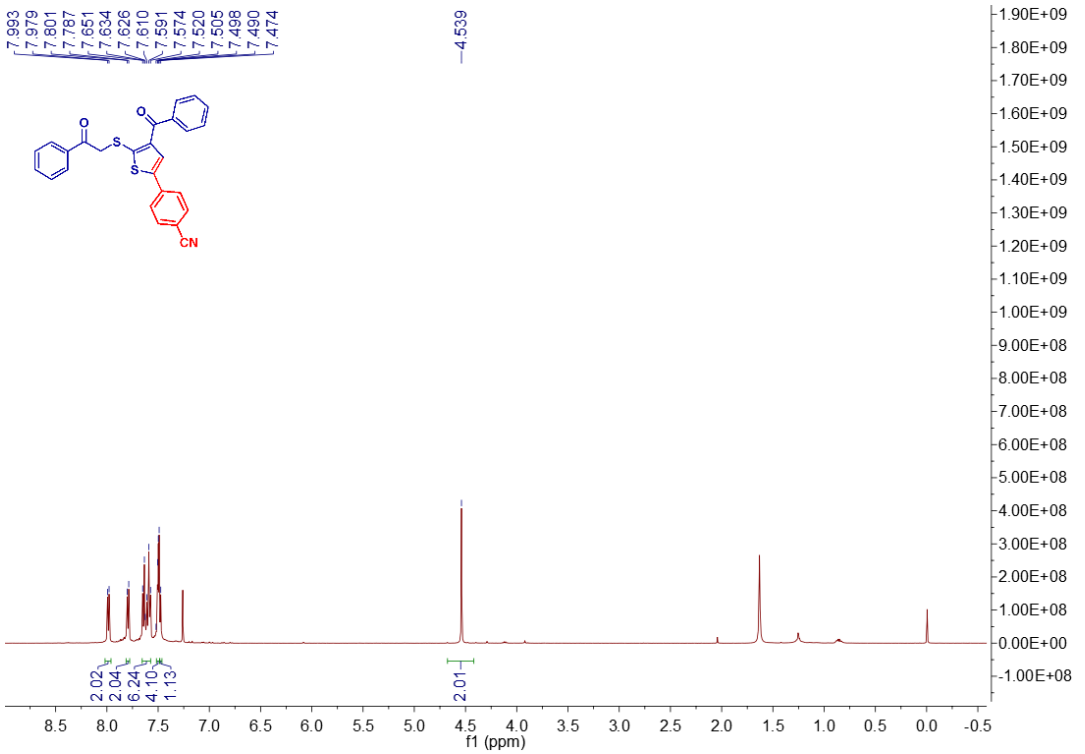
^{13}C NMR Spectrum of 5e ($CDCl_3$, 125 MHz)



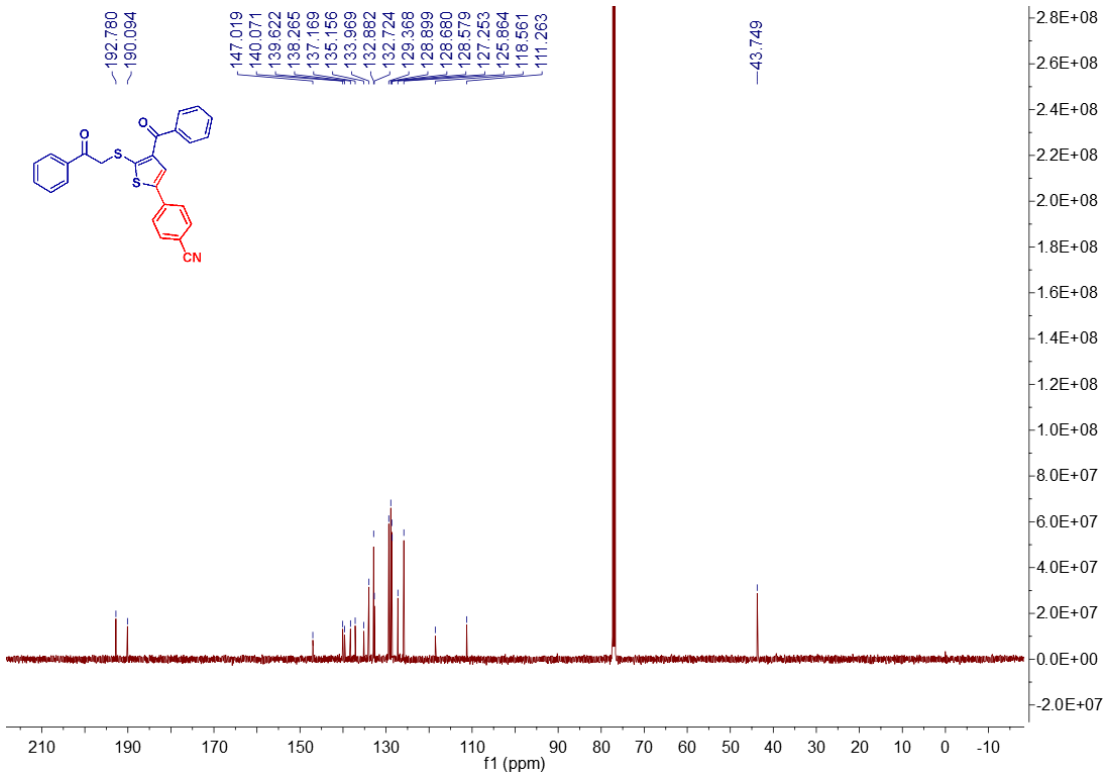
^{1}H NMR Spectrum of 5g ($CDCl_3$, 500 MHz)



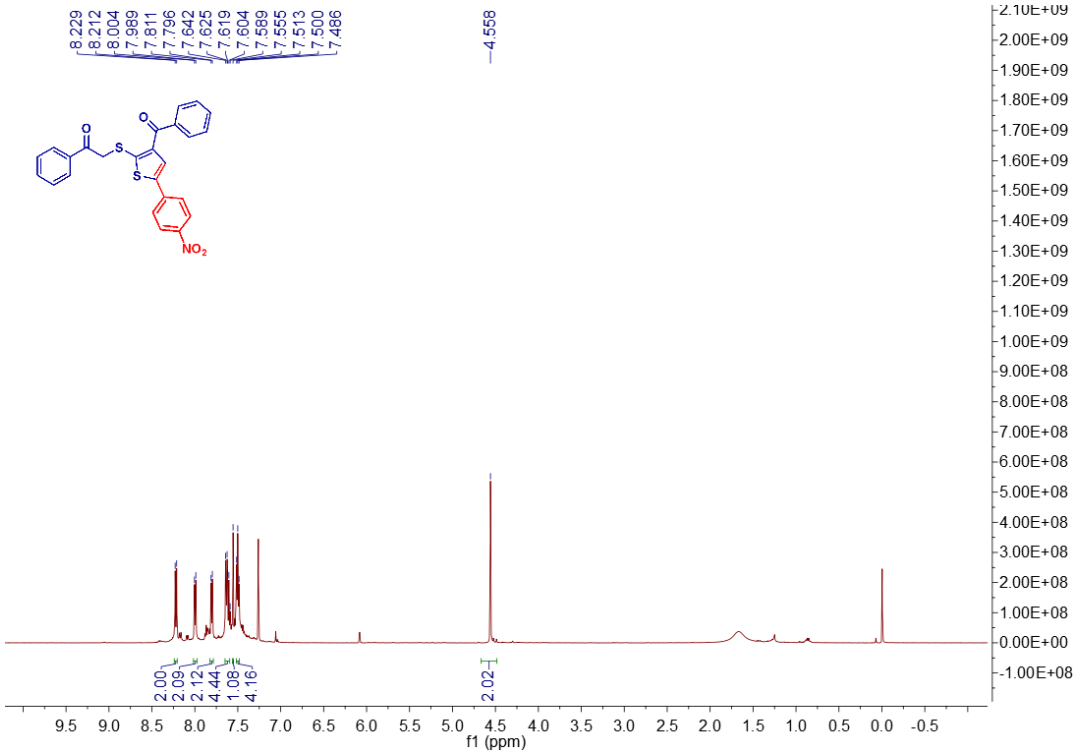
^{13}C NMR Spectrum of 5g ($CDCl_3$, 125 MHz)



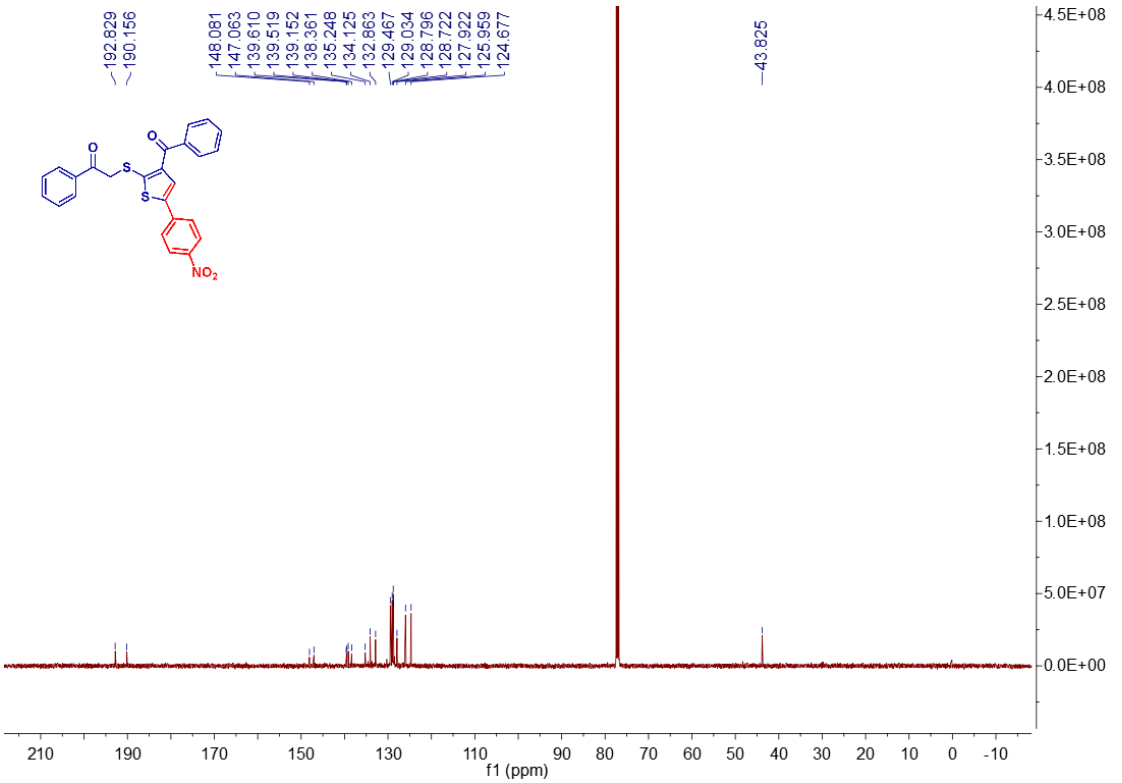
^{1}H NMR Spectrum of 5h ($CDCl_3$, 500 MHz)



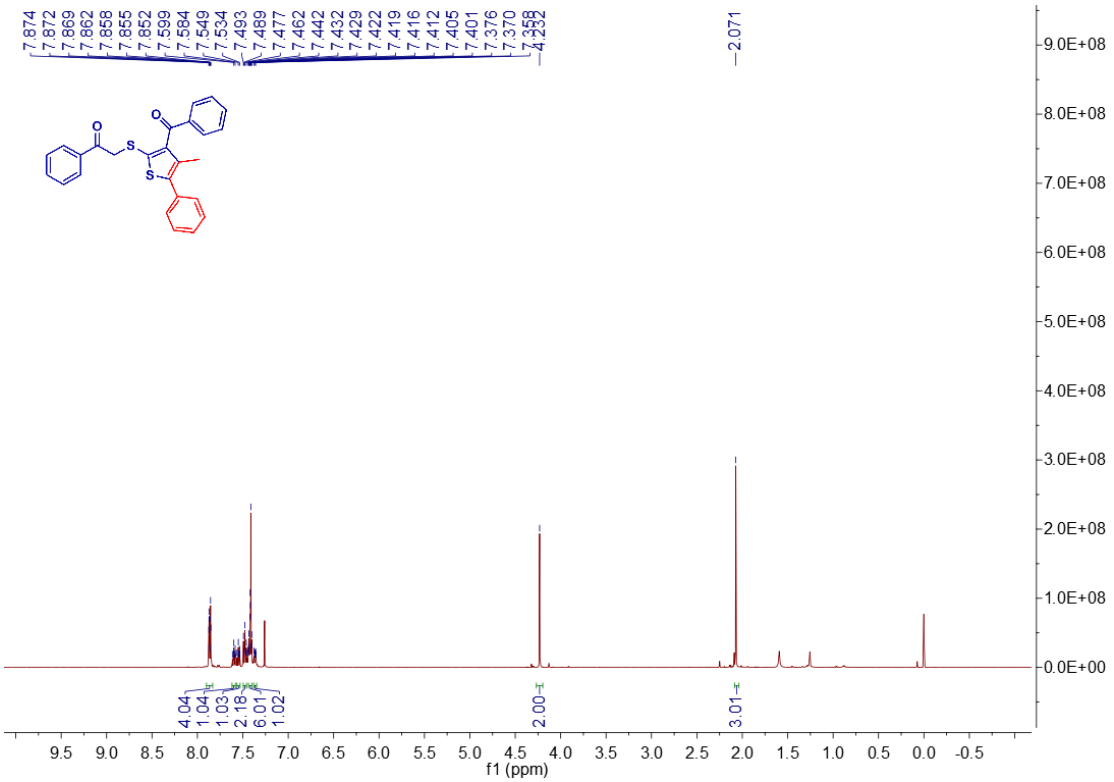
^{13}C NMR Spectrum of 5h ($CDCl_3$, 125 MHz)



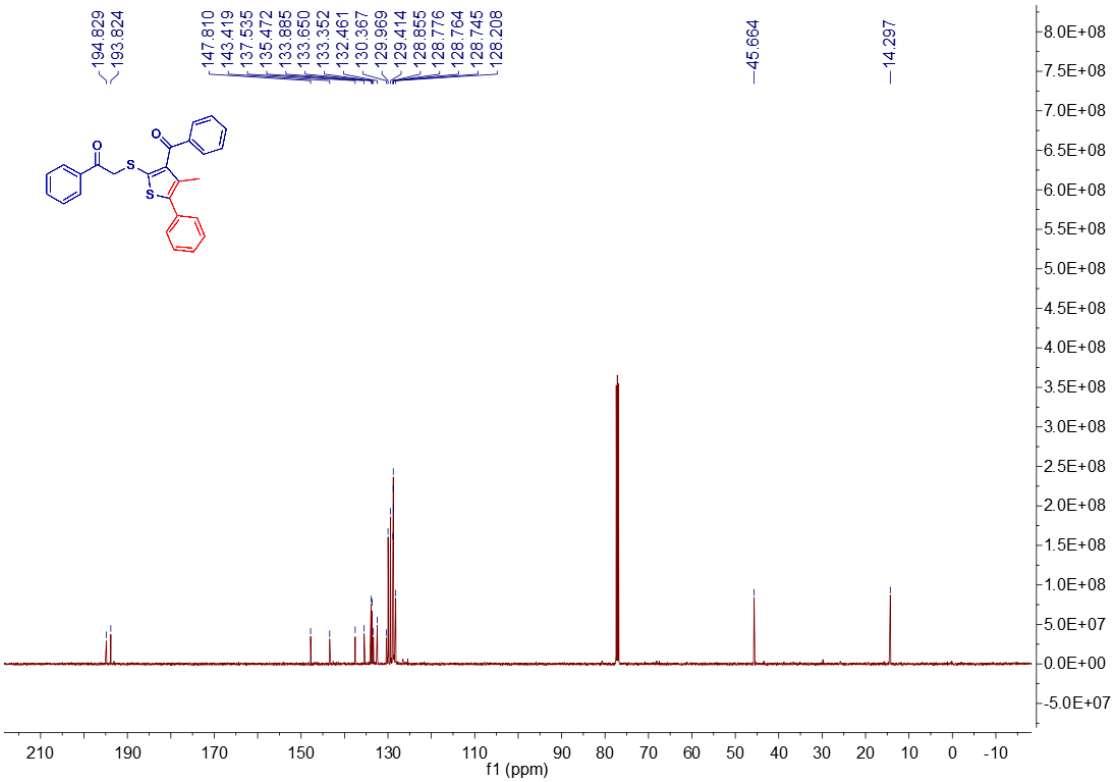
^{1}H NMR Spectrum of 5i ($CDCl_3$, 500 MHz)



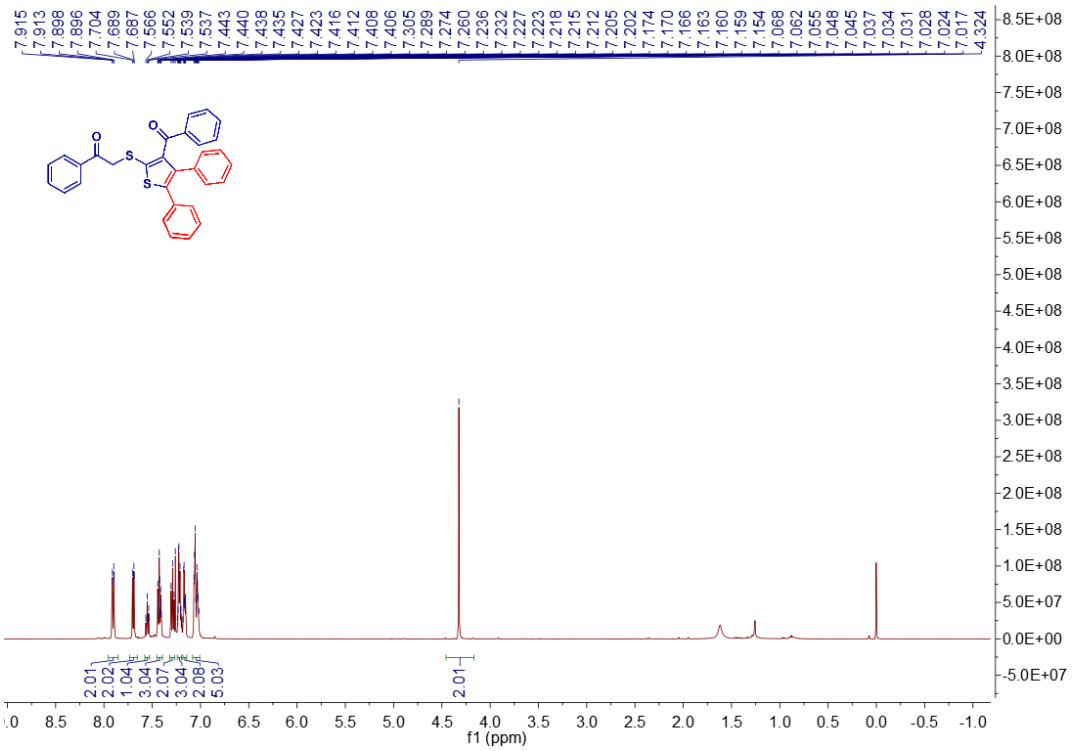
^{13}C NMR Spectrum of 5i ($CDCl_3$, 125 MHz)



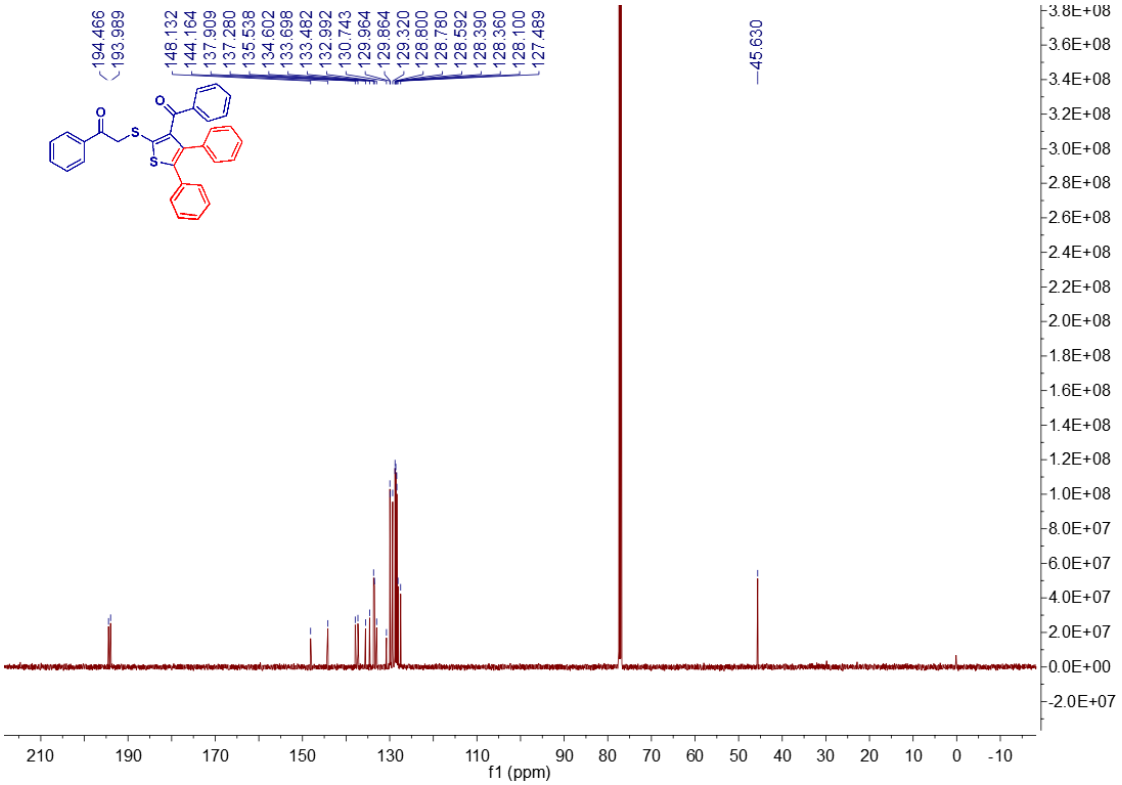
^{1}H NMR Spectrum of 5j ($CDCl_3$, 500 MHz)



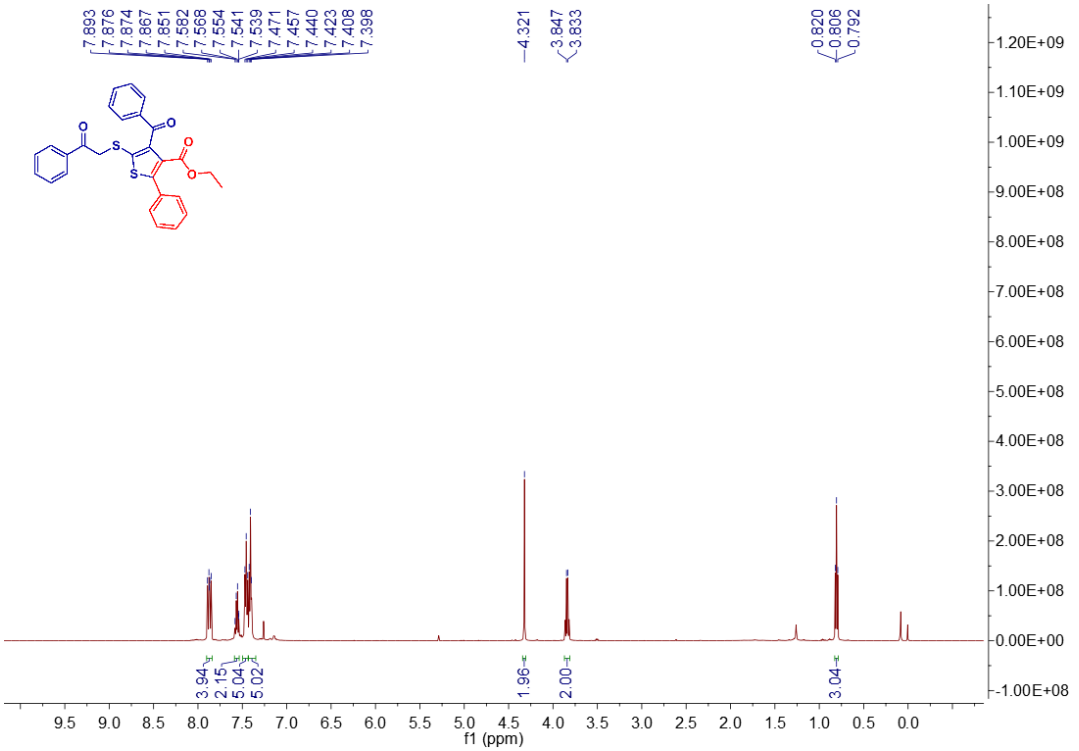
^{13}C NMR Spectrum of 5j ($CDCl_3$, 125 MHz)



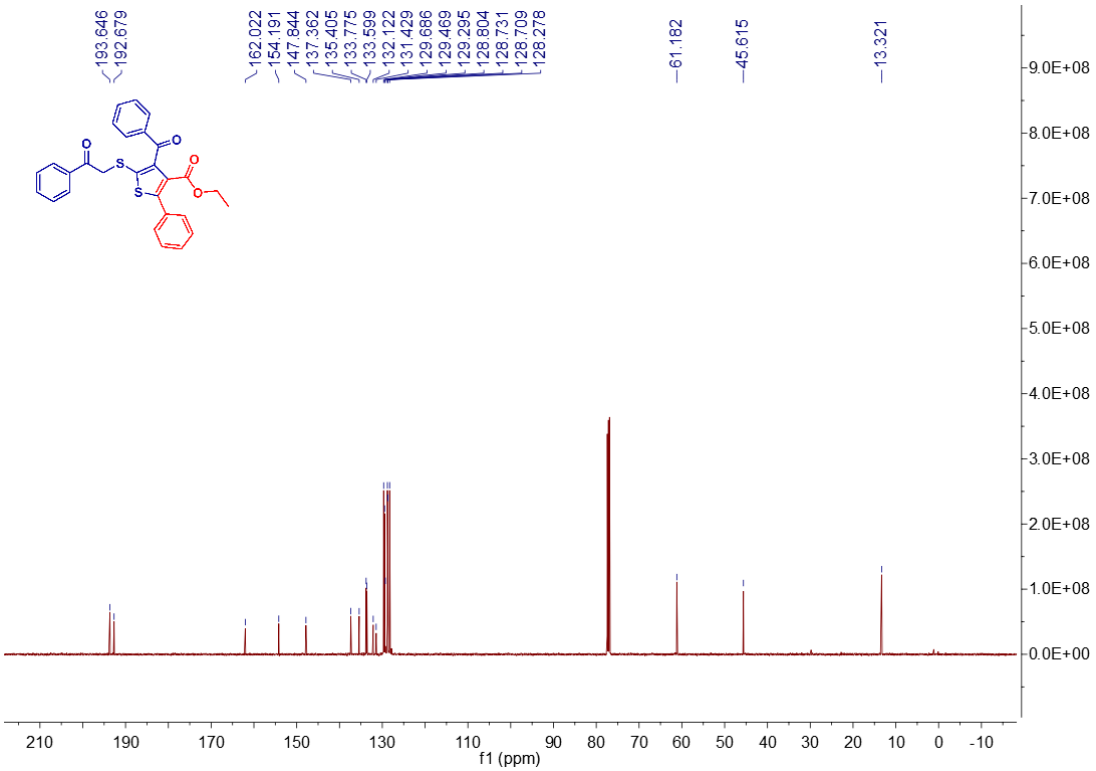
^{1}H NMR Spectrum of 5k ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of 5k ($CDCl_3$, 125 MHz)



^{1}H NMR Spectrum of 5l ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of 5l ($CDCl_3$, 125 MHz)

VIII. ^{1}H NMR Spectra of Detected Intermediate e

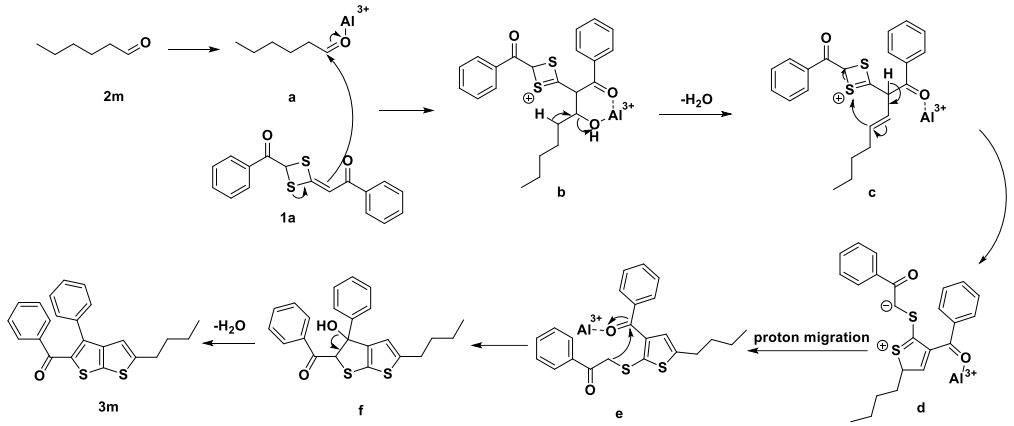
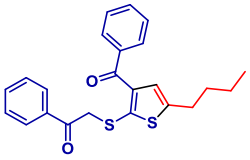


Figure S4 Proposed Mechanism of product 3 (with 3m as an example)



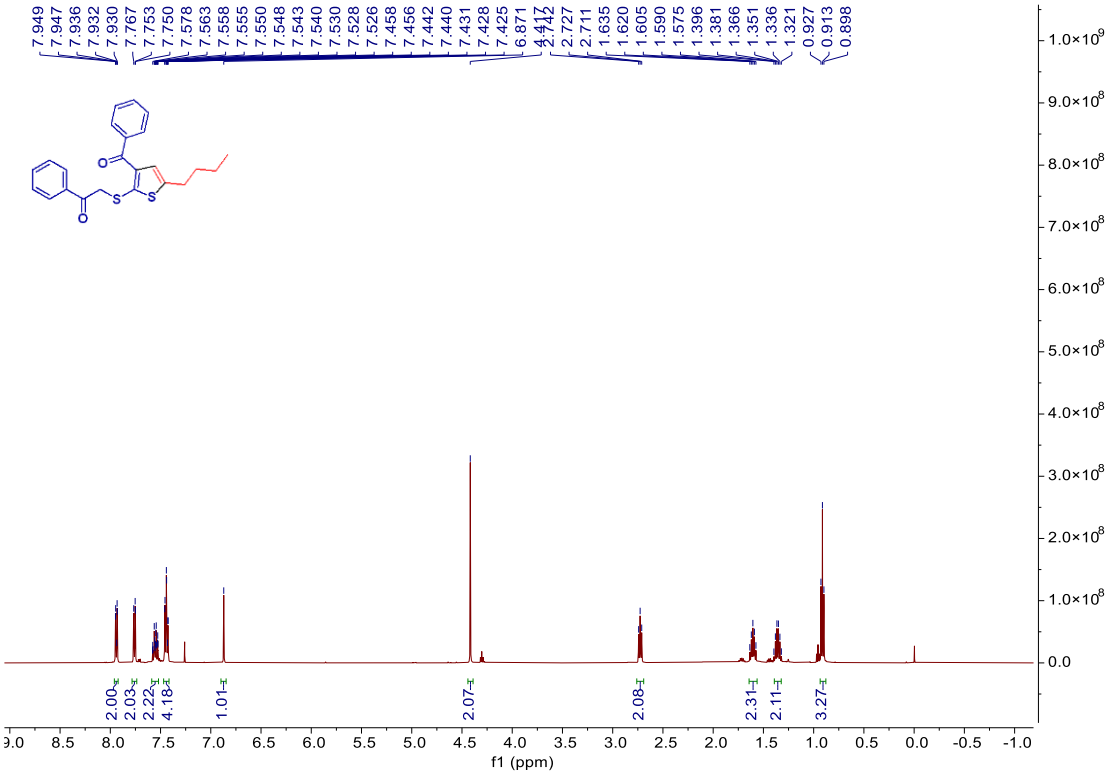
2-((3-benzoyl-5-butylthiophen-2-yl)thio)-1-phenylethan-1-one (intermediate e with 3m as an example)

yellow solid;

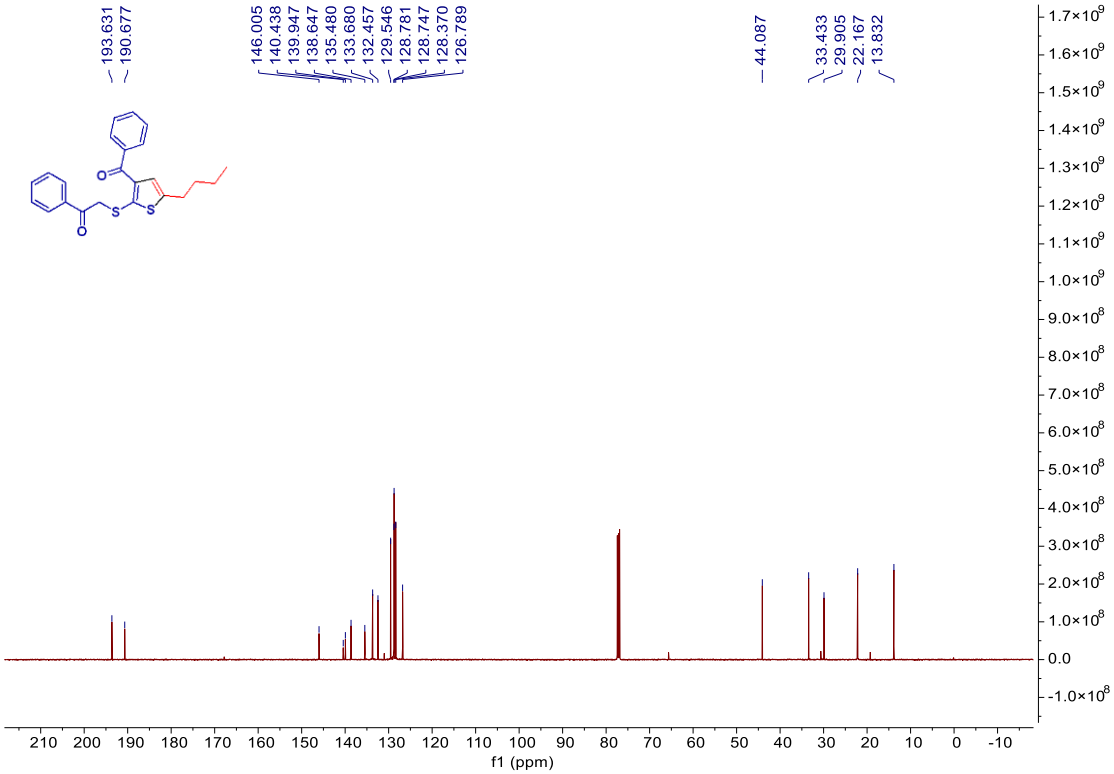
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95-7.93 (m, 2H), 7.78 – 7.74 (m, 2H), 7.59 – 7.52 (m, 2H), 7.46-7.42 (m, 4H), 6.87 (s, 1H), 4.42 (s, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.60 (p, *J* =7.5 Hz, 2H), 1.39 – 1.32 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.6, 190.7, 146.0, 140.4, 134.0, 138.7, 135.5, 133.7, 132.5, 129.6, 128.8, 128.8, 128.4, 126.8, 44.1, 33.4, 29.9, 22.2, 13.8.

HRMS (ESI): m/z calcd for $(C_{23}H_{22}O_2S_2+H)^+$: 395.1134; found: 395.1140



^{1}H NMR Spectrum of Intermediate e (with 3m as an example) ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of Intermediate e (with 3m as an example) ($CDCl_3$, 125 MHz)