Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Four-component thiazole formation from simple chemicals under metal-free conditions

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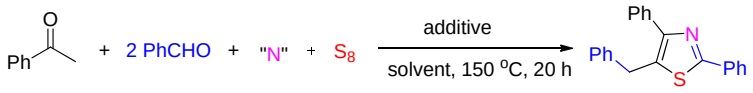
General information

All reactions were carried out under air atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded with the Thermo Scientific LTQ Orbitrap XL mass spectrometer (ESI). The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Ketoxime acetates were prepared according previously reported method. All other reagents were obtained from commercial suppliers and used without further purification. The molecular weight of S_8 is determined to be 32 g/mol unless otherwise noted.

Optimization of reaction conditions

Table S1.[a]

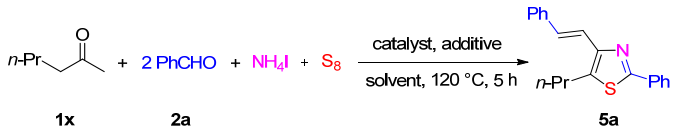


1a **2a** **3a**

entry	"N" source	additive (x equiv)	solvent	yield(%)[b]
1	$(NH_4)_2S_2O_8$	—	pyridine	32
2	NH_4Cl	—	pyridine	17
3	NH_4PF_6	—	pyridine	37
4	NH_4OAc	—	pyridine	trace
5	NH_4I	—	pyridine	47
6	NH_4I	—	DMF	20
7	NH_4I	—	DMSO	trace
8	NH_4I	—	*o*-DCB	trace
9	NH_4I	—	mesitylene	trace
10	NH_4I	—	1,4-dioxane	10
11	NH_4I	H_2O (3)	pyridine	60
12	NH_4I	H_2O (6)	pyridine	77
13	NH_4I	H_2O (9)	pyridine	75
14[c]	NH_4I	H_2O (6)	pyridine	65
15[d]	NH_4I	—	pyridine	n.d
16[e]	NH_4I	H_2O (6)	pyridine	65

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), S_8 (0.4 mmol, 32 g/mol), NH_4I (0.4 mmol), pyridine (0.6 mL), under air at 150 °C for 20 h. [b] Isolated yields. [c] 120 °C, [d] Na_2S replace S_8, [e] 5 mmol gram-scale (1.063g).

Table S2.[a]



entry	catalyst	additive (x mol%)	[O]	yield(%)[b]
1	Cu	—	—	35
2	CuBr	—	—	43
3	$CuCl_2$	—	—	36
4	$FeCl_3$	—	—	33
5	$La(OTf)_3$	—	—	34
6	$Sc(OTf)_3$	—	—	17
7	CuBr	BzOH	—	54 (50)[c]
8	CuBr	AcOH	—	31
9[d]	CuBr	HCl (aq)	—	36
10	—	BzOH		44
11	—	BzOH (60)		54 (51)[c]
12	—	BzOH (70)		40 (36)[c]
13[e]	—	—	H_2O_2	22
14	—	—	TBHP	22
15	—	—	O_2	34
16	—	—	Ar	32
17	—	—	—	37

[a] Reaction conditions: **1x** (0.2 mmol), **2a** (0.6 mmol), NH_4I (0.4 mmol), S_8 (0.8 mmol, 32 g/mol), catalyst (50 mol%), additive (30 mol%), pyridine (0.6 mL), under air at 120 °C for 5 h. [b] GC yields. [c] Isolated yields, [d] HCl (12 mol/L), [e] H_2O_2 (30%, 9.8 mol/L).

General procedure for the synthesis of thiazoles

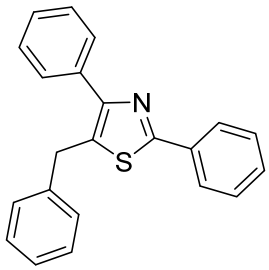
General procedure A: Aromatic ketone **1a-1p** (0.2 mmol), aromatic aldehyde **2** (0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol), H_2O (6 equiv) and pyridine (0.6 mL) were added successfully to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 150 °C for 20 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **3**.

General procedure B: Alphatic ketone **1q-1w** (0.2 mmol), aromatic aldehyde **2** (0.3 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol), H_2O (6 equiv) and pyridine (0.6 mL) were added successfully to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 150 °C for 15-20 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **4**.

General procedure C: Alphatic ketone **1x-1ac** (0.2 mmol), aromatic aldehyde **2** (0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (25.6 mg, 0.8 mmol), PhCOOH (60 mol%) and pyridine (0.6 mL) were added successfully to a 10 mL oven-dried reaction vessel. The sealed reaction vessel was stirred at 120 °C for 5 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/DCM) to yield the desired product **5**.

5 mmol-scale reaction: Acetophenone **1a** (0.6 mL, 5 mmol), benzaldehyde **2a** (1.5 mL, 15 mmol), S_8 (0.32 g, 10 mmol), NH_4I (1.45 g, 10 mmol), H_2O (0.54 mL, 30 mmol) and pyridine (6 mL) were added successfully to a 100 mL round-bottom flask. The sealed round-bottom flask was stirred at 150 °C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (30 mL) and filtered through a short column of silica gel with additional ethyl acetate (30 mL) as the eluent. The filtrate was washed with brine (90 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc: 200/1) to afford **3a** as a white solid (1.063 g, 65%).

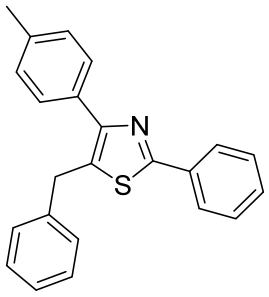
Characterization data of products



5-Benzyl-2,4-diphenylthiazole (3a)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3a** (50.4 mg, 77%) as a white solid. mp: 123-124 ^oC.

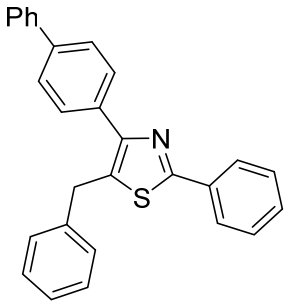
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.8, 2.5 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.48 – 7.30 (m, 8H), 7.28 – 7.21 (m, 3H), 4.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 152.5, 140.0, 134.9, 133.6, 133.0, 129.8, 128.8, 128.7, 128.5, 128.3, 127.9, 126.8, 126.3, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3059, 1600, 1483, 982, 758, 696, 518. HRMS (ESI) m/z calcd for $C_{22}H_{18}NS^+$ $(M+H)^+$ 328.1155, found 328.1158.



5-Benzyl-2-phenyl-4-(*p*-tolyl)thiazole (3b)

The general procedure A was followed using 1-(*p*-tolyl)ethan-1-one (**1b**, 28 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3b** (45.0 mg, 66%) as a white solid. mp: 147-148 ^oC.

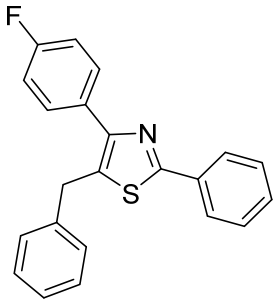
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.9, 2.6 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.33 (t, J = 7.2 Hz, 2H), 7.29 – 7.22 (m, 5H), 4.30 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.4, 152.3, 140.1, 133.8, 131.8, 130.0, 129.7, 128.8, 128.7, 128.3, 127.6, 126.7, 126.3, 113.9, 55.3, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 1489, 1242, 978, 823, 768, 694, 520. HRMS (ESI) m/z calcd for $C_{23}H_{20}NS^+$ $(M+H)^+$ 342.1311, found 342.1313.



4-([1,1'-Biphenyl]-4-yl)-5-benzyl-2-phenylthiazole (3c)

The general procedure A was followed using 1-([1,1'-biphenyl]-4-yl)ethan-1-one (**1c**, 40 mg, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3c** (52.4 mg, 65%) as a white solid. mp: 149-150 ^{o}C.

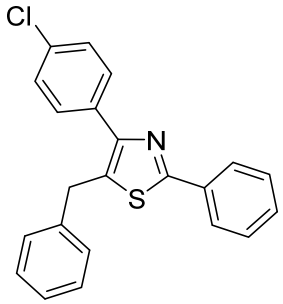
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.9, 2.0 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.48 – 7.31 (m, 8H), 7.29 – 7.24 (m, 3H), 4.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 152.2, 140.7, 140.6, 140.0, 134.0, 133.7, 133.1, 129.8, 129.1, 128.8, 128.8, 128.4, 127.4, 127.2, 127.1, 126.8, 126.3, 33.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3029, 2917, 1601, 1481, 978, 847, 767, 694. HRMS (ESI) m/z calcd for $C_{28}H_{22}NS^+$ $(M+H)^+$ 404.1468, found 404.1471.



5-Benzyl-4-(4-fluorophenyl)-2-phenylthiazole (3d)

The general procedure A was followed using 1-(4-fluorophenyl)ethan-1-one (**1d**, 22 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3d** (44.9 mg, 65%) as a colorless solid. mp: 119-120 ^oC.

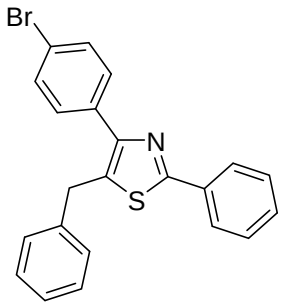
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.6, 4.0 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.43 – 7.37 (m, 3H), 7.34 (t, J = 7.3 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.14 (t, J = 8.7 Hz, 2H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 162.5 (d, J = 246.0 Hz), 151.5, 139.8, 133.5, 132.8, 131.0 (d, J = 3.2 Hz), 130.5 (d, J = 8.8 Hz), 129.9, 128.8, 128.8, 128.3, 126.9, 126.3, 115.4 (d, J = 21.4 Hz), 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 1602, 1489, 1223, 841, 760, 696. HRMS (ESI) m/z calcd for $C_{22}H_{17}FNS^+$ $(M+H)^+$ 346.1060, found 346.1065.



5-Benzyl-4-(4-chlorophenyl)-2-phenylthiazole (3e)

The general procedure A was followed using 1-(4-chlorophenyl)ethan-1-one (**1e**, 27 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3e** (52.7 mg, 73%) as a white solid. mp: 159-160 ^oC.

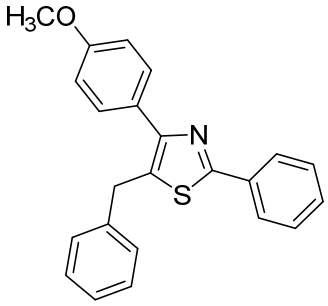
^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.44 – 7.37 (m, 5H), 7.33 (t, J = 7.2 Hz, 2H), 7.29 – 7.21 (m, 3H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 151.3, 139.7, 133.8, 133.5, 133.4, 133.3, 130.0, 129.9, 128.8, 128.8, 128.7, 128.3, 126.9, 126.3, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3059, 1601, 1481, 1089, 978, 835, 760, 702. HRMS (ESI) m/z calcd for $C_{22}H_{17}ClNS^+$ $(M+H)^+$ 362.0765, found 362.0768.



5-Benzyl-4-(4-bromophenyl)-2-phenylthiazole (3f)

The general procedure A was followed using 1-(4-bromophenyl)ethan-1-one (**1f**, 41 mg, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3f** (56.0 mg, 69%) as a white solid. mp: 167-168 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.63 – 7.53 (m, 4H), 7.45 – 7.37 (m, 3H), 7.33 (t, J = 7.3 Hz, 2H), 7.29 – 7.20 (m, 3H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 151.2, 139.7, 133.9, 133.5, 133.3, 131.6, 130.3, 129.9, 128.8, 128.8, 128.3, 126.9, 126.3, 122.0, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 1600, 1477, 1070, 978, 833, 758, 694, 519. HRMS (ESI) m/z calcd for $C_{22}H_{17}BrNS^+$ $(M+H)^+$ 406.0260, found 406.0254.

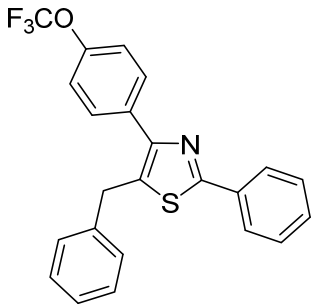


5-Benzyl-4-(4-methoxyphenyl)-2-phenylthiazole (3g)

The general procedure A was followed using 1-(4-methoxyphenyl)ethan-1-one (**1g**, 31 mg, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3g** (39.3 mg, 55%) as a white solid. mp: 91-92 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.8, 2.2 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.25 (t, J = 6.6 Hz, 3H), 7.01 – 6.94 (m, 2H), 4.27 (s, 2H), 3.83 (s,

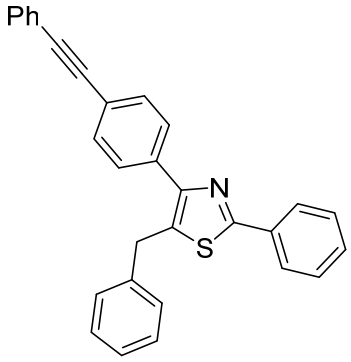
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.4, 152.3, 140.1, 133.8, 131.8, 130.0, 129.7, 128.8, 128.7, 128.3, 127.6, 126.7, 126.3, 113.9, 55.3, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3020, 2933, 1606, 1486, 1254, 1173, 1037, 835, 771, 696. HRMS (ESI) m/z calcd for $C_{23}H_{20}NOS^+$ $(M+H)^+$ 358.1260, found 358.1262.



5-Benzyl-2-phenyl-4-(4-(trifluoromethoxy)phenyl)thiazole (3h)

The general procedure A was followed using 1-(4-(trifluoromethoxy)phenyl)ethan-1-one (**1h**, 33 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **3h** (61.7 mg, 75%) as a white solid. mp: 72-73 ^{o}C.

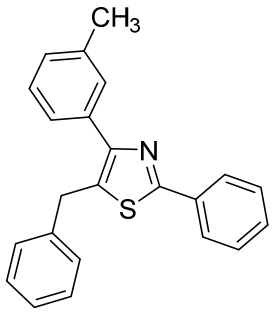
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.7, 3.2 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.36 – 7.22 (m, 7H), 4.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.0, 148.8, 139.6, 133.6, 133.5, 133.4, 130.2, 130.0, 128.9, 128.8, 128.3, 127.0, 126.3, 120.5 (q, J = 255.8 Hz), 116.6, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3064, 1604, 1489, 1265, 1167, 762, 688. HRMS (ESI) m/z calcd for $C_{23}H_{17}F_3NOS^+$ $(M+H)^+$ 412.0977, found 412.0978.



5-Benzyl-2-phenyl-4-(4-(phenylethynyl)phenyl)thiazole (3i)

The general procedure A was followed using 1-(4-(phenylethynyl)phenyl)ethan-1-one (**1i**, 46 mg, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3i** (64 mg, 75%) as a white solid. mp: 153-154 ^oC.

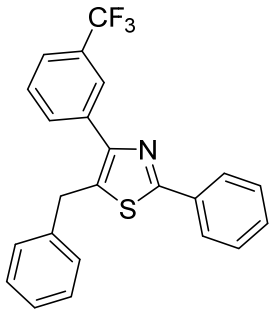
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.8, 2.8 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.55 (dd, J = 7.8, 2.4 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.38 – 7.32 (m, 5H), 7.30 – 7.24 (m, 3H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 151.6, 139.8, 134.7, 133.6, 133.5, 131.7, 131.6, 129.9, 128.8, 128.8, 128.6, 128.3, 128.3, 126.9, 126.3, 123.2, 122.7, 90.2, 89.3, 33.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 3022, 1600, 1492, 1452, 840, 760, 692. HRMS (ESI) m/z calcd for $C_{30}H_{22}NS^+$ $(M+H)^+$ 428.1468, found 428.1464.



5-Benzyl-2-phenyl-4-(*m*-tolyl)thiazole (3j)

The general procedure A was followed using 1-(*m*-tolyl)ethan-1-one (**1j**, 28 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3j** (49.8 mg, 73%) as a colorless liquid.

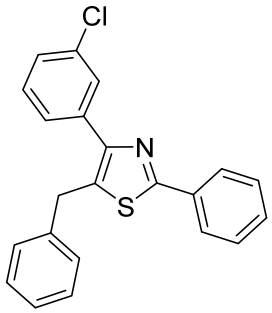
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.4, 2.0 Hz, 2H), 7.56 (s, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.33 (t, J = 7.2 Hz, 3H), 7.26 (t, J = 5.6 Hz, 3H), 7.19 (d, J = 7.6 Hz, 1H), 4.29 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 152.7, 140.2, 138.1, 134.9, 133.8, 133.0, 129.7, 129.6, 128.8, 128.7, 128.7, 128.4, 128.3, 126.8, 126.4, 125.8, 33.3, 21.5. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3025, 2921, 1602, 1495, 1250, 793, 760, 690. HRMS (ESI) m/z calcd for $C_{23}H_{20}NS^+$ $(M+H)^+$ 342.1311, found 342.1310.



5-Benzyl-2-phenyl-4-(3-(trifluoromethyl)phenyl)thiazole (3k)

The general procedure A was followed using 1-(3-(trifluoromethyl)phenyl)ethan-1-one (**1k**, 31 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3k** (55.3 mg, 70%) as a white solid. mp: 82-83 ^oC.

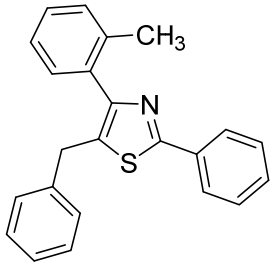
^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.98 – 7.91 (m, 2H), 7.88 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.34 (t, J = 7.2 Hz, 2H), 7.29 – 7.22 (m, 3H), 4.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 150.8, 139.5, 135.7, 134.1, 133.5, 131.8, 130.9 (q, J = 32.2 Hz), 130.0, 128.9, 128.9, 128.9, 128.3, 127.0, 126.3, 125.7 (q, J = 3.8 Hz), 124.6 (q, J = 3.7 Hz), 124.1 (q, J = 270.8 Hz), 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 3035, 1600, 1342, 1308, 1163, 1122, 1074, 760, 698. HRMS (ESI) m/z calcd for $C_{23}H_{17}F_3NS^+$ $(M+H)^+$ 396.1028, found 396.1032.



5-Benzyl-4-(3-chlorophenyl)-2-phenylthiazole (3l)

The general procedure A was followed using 1-(3-chlorophenyl)ethan-1-one (**1l**, 27 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3l** (45.5 mg, 63%) as a white solid. mp: 83-84 ^oC.

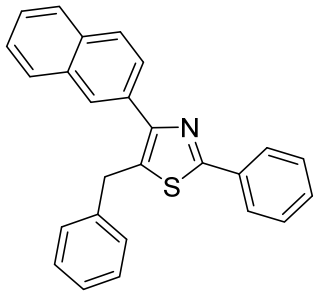
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.75 (s, 1H), 7.58 – 7.53 (m, 1H), 7.42 – 7.38 (m, 3H), 7.36 – 7.30 (m, 4H), 7.29 – 7.22 (m, 3H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 150.8, 139.6, 136.6, 134.4, 134.0, 133.4, 130.0, 129.7, 128.9, 128.8, 128.8, 128.3, 128.0, 126.9, 126.7, 126.3, 33.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3064, 3026, 1595, 1564, 1477, 1263, 1078, 756, 696. HRMS (ESI) m/z calcd for $C_{22}H_{17}ClNS^+$ $(M+H)^+$ 362.0765, found 362.0769.



5-Benzyl-2-phenyl-4-(*o*-tolyl)thiazole (3m)

The general procedure A was followed using 1-(*o*-tolyl)ethan-1-one (**1m**, 27 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **3m** (28.7 mg, 42%) as a yellow liquid.

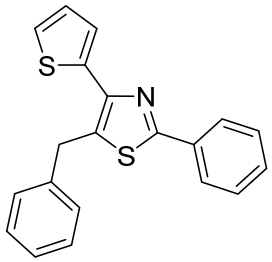
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 5.5 Hz, 2H), 7.38 (d, J = 5.3 Hz, 3H), 7.35 – 7.19 (m, 7H), 7.14 (d, J = 7.4 Hz, 2H), 4.02 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 152.9, 140.0, 137.8, 134.3, 134.2, 133.7, 130.5, 130.2, 129.7, 128.8, 128.6, 128.5, 128.3, 126.6, 126.3, 125.6, 32.9, 20.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3061, 2924, 1681, 1600, 1479, 1248, 979, 761, 688. HRMS (ESI) m/z calcd for $C_{23}H_{20}NS^+$ $(M+H)^+$ 342.1311, found 342.1313.



5-Benzyl-4-(naphthalen-2-yl)-2-phenylthiazole (3n)

The general procedure A was followed using 1-(naphthalen-2-yl)ethan-1-one (**1n**, 35 mg, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3n** (52.8 mg, 70%) as a white solid. mp: 88-89 ^oC.

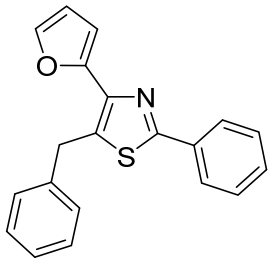
^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.97 (dd, J = 8.0, 2.1 Hz, 2H), 7.91 – 7.81 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 3H), 4.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 152.4, 140.0, 133.7, 133.4, 133.2, 132.8, 132.3, 129.8, 128.8, 128.8, 128.4, 128.2, 128.1, 127.7, 127.6, 126.8, 126.8, 126.3, 126.2, 33.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3055, 1601, 1493, 1454, 822, 756, 711, 698, 683. HRMS (ESI) m/z calcd for $C_{26}H_{20}NS^+$ $(M+H)^+$ 378.1311, found 378.1314.



5-Benzyl-2-phenyl-4-(thiophen-2-yl)thiazole (3o)

The general procedure A was followed using 1-(thiophen-2-yl)ethan-1-one (**1o**, 22 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3o** (40.6 mg, 61%) as a gray solid. mp: 101-102 ^oC.

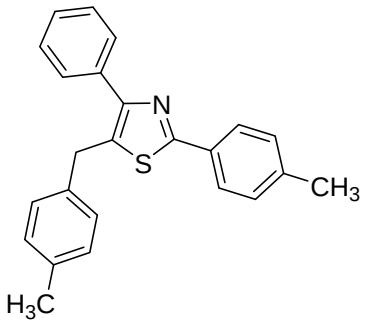
^1H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.42 – 7.31 (m, 7H), 7.30 – 7.25 (m, 3H), 7.11 – 7.06 (m, 1H), 4.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 145.9, 139.2, 137.9, 133.3, 131.9, 129.9, 128.8, 128.4, 127.5, 126.9, 126.4, 125.7, 125.5, 33.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3104, 1602, 1493, 1211, 970, 762, 708. HRMS (ESI) m/z calcd for $C_{20}H_{16}NS_2^+$ $(M+H)^+$ 334.0719, found 334.0721.



5-Benzyl-4-(furan-2-yl)-2-phenylthiazole (3p)

The general procedure A was followed using 1-(furan-2-yl)ethan-1-one (**1p**, 21 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3p** (25.4 mg, 40%) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.5, 3.9 Hz, 2H), 7.52 (s, 1H), 7.42 – 7.38 (m, 3H), 7.34 – 7.25 (m, 5H), 6.88 (d, J = 3.3 Hz, 1H), 6.55 – 6.51 (m, 1H), 4.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 150.4, 142.6, 142.1, 139.9, 133.3, 133.0, 130.0, 128.8, 128.7, 128.5, 126.8, 126.4, 111.3, 108.8, 32.9. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 2927, 1682, 1495, 1248, 762, 688. HRMS (ESI) m/z calcd for $C_{20}H_{16}NOS^+$ $(M+H)^+$ 318.0947, found 318.0948.

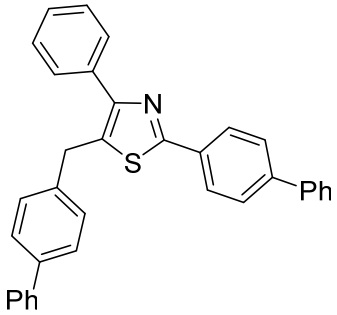


5-(4-Methylbenzyl)-4-phenyl-2-(*p*-tolyl)thiazole (3q)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-methylbenzaldehyde (**2b**, 73 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **4a** (48.3 mg, 68%) as a white solid. mp: 110-111 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (s, 4H), 4.25 (s, 2H), 2.37 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 152.1, 140.0, 137.1, 136.4, 135.0, 133.0, 131.1,

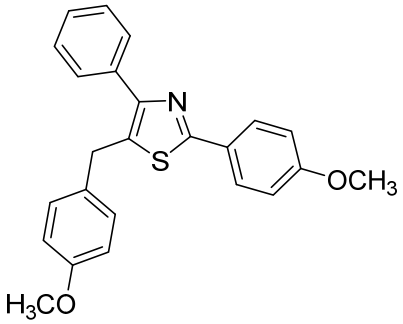
129.5, 129.4, 128.8, 128.4, 128.2, 127.8, 126.3, 32.9, 21.4, 21.0. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3022, 1600, 1511, 1483, 978, 823, 771, 696, 482. HRMS (ESI) m/z calcd for $C_{24}H_{22}NS^+$ $(M+H)^+$ 356.1468, found 356.1469.



2-([1,1'-Biphenyl]-4-yl)-5-([1,1'-biphenyl]-4-ylmethyl)-4-phenylthiazole (3r)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), [1,1'-biphenyl]-4-carbaldehyde (**2c**, 113 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3r** (67.1 mg, 70%) as a white solid. mp: 147-148 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 7.4 Hz, 2H), 7.69 – 7.54 (m, 8H), 7.52 – 7.29 (m, 11H), 4.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 152.8, 142.5, 140.7, 140.3, 139.8, 139.1, 135.0, 132.9, 132.7, 128.9, 128.8, 128.8, 128.8, 128.5, 128.0, 127.7, 127.5, 127.4, 127.3, 127.0, 127.0, 126.8, 33.0. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3030, 1600, 1487, 1261, 843, 766, 696. HRMS (ESI) m/z calcd for $C_{34}H_{26}NS^+$ $(M+H)^+$ 480.1781, found 480.1783.

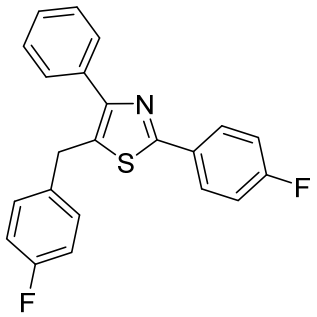


5-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4-phenylthiazole (3s)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-methoxybenzaldehyde (**2d**, 75 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4

mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **3s** (55.0 mg, 71%) as a white solid. mp: 122-123 ^{o}C.

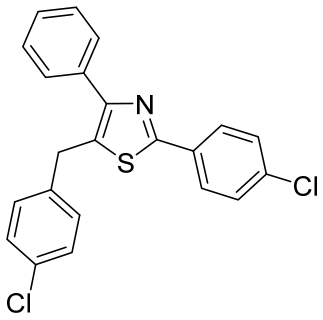
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 7.73 – 7.68 (m, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.22 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 161.0, 158.4, 151.8, 135.0, 132.8, 132.3, 129.4, 128.8, 128.4, 127.8, 126.7, 114.1, 114.1, 55.3, 55.2, 32.4. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3070, 2833, 1608, 1510, 1251, 1171, 1034, 825, 698. HRMS (ESI) m/z calcd for $C_{24}H_{22}NO_2S^+$ $(M+H)^+$ 388.1366, found 388.1365.



5-(4-Fluorobenzyl)-2-(4-fluorophenyl)-4-phenylthiazole (3t)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-fluorobenzaldehyde (**2e**, 66 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3t** (45.0 mg, 62%) as a white solid. mp: 108-109 ^{o}C.

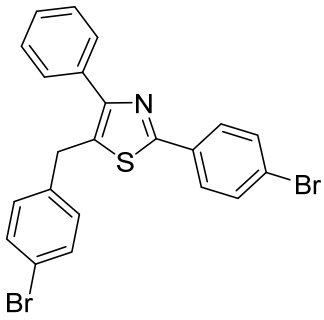
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.22 – 7.16 (m, 2H), 7.12 – 7.06 (m, 2H), 7.04 – 6.98 (m, 2H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.8 (d, J = 248.6 Hz), 161.7 (d, J = 243.8 Hz), 152.5, 135.6 (d, J = 3.1 Hz), 134.6, 132.9, 129.9, 129.8 (d, J = 8.0 Hz), 128.7, 128.5, 128.3 (d, J = 8.4 Hz), 128.1, 115.9 (d, J = 21.9 Hz), 115.6 (d, J = 21.3 Hz), 32.4. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 1599, 1504, 1223, 1155, 982, 839, 771, 696, 542. HRMS (ESI) m/z calcd for $C_{22}H_{16}F_2NS^+$ $(M+H)^+$ 364.0966, found 364.0968.



5-(4-Chlorobenzyl)-2-(4-chlorophenyl)-4-phenylthiazole (3u)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-chlorobenzaldehyde (**2f**, 86 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3u** (56.1 mg, 71%) as a white solid. mp: 91-92 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 8.5 Hz, 3H), 7.29 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 152.8, 138.3, 135.8, 134.5, 132.7, 132.7, 132.0, 129.7, 129.1, 128.9, 128.7, 128.6, 128.2, 127.5, 32.6. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3057, 1599, 1479, 1092, 984, 825, 771, 696. HRMS (ESI) m/z calcd for $C_{22}H_{16}Cl_2NS^+$ $(M+H)^+$ 396.0375, found 396.0378.

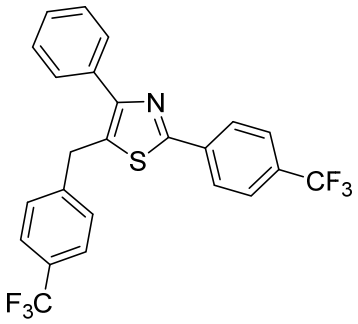


5-(4-Bromobenzyl)-2-(4-bromophenyl)-4-phenylthiazole (3v)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-bromobenzaldehyde (**2g**, 112 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3v** (73.6 mg, 76%) as a white solid. mp: 87-88 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.70 – 7.65 (m, 2H), 7.56 – 7.52 (m, 2H), 7.48 – 7.37 (m, 5H), 7.10 (d, J = 8.3 Hz, 2H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 152.9,

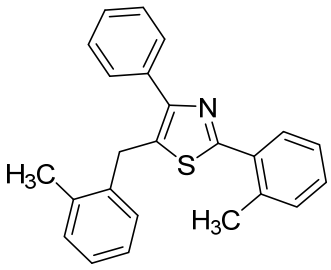
138.8, 133.4, 132.6, 132.6, 132.0, 131.9, 130.0, 128.7, 128.6, 128.2, 127.8, 124.1, 120.8, 32.7. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3051, 2910, 1485, 1068, 1008, 978, 827, 771, 698. HRMS (ESI) m/z calcd for $C_{22}H_{16}Br_2NS^+$ $(M+H)^+$ 483.9365, found 483.9367.



4-Phenyl-5-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)thiazole (3w)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 4-(trifluoromethyl)benzaldehyde (**2h**, 84 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **3w** (37 mg, 40%) as a white solid. mp: 158-159 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.71 – 7.64 (m, 4H), 7.59 (d, J = 8.1 Hz, 2H), 7.50 – 7.32 (m, 5H), 4.37 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 153.7, 143.7, 136.7, 134.4, 132.8, 131.6 (q, J = 32.4 Hz), 129.4 (q, J = 32.4 Hz), 128.7, 128.7, 128.4, 126.6, 126.0, 125.9 (q, J = 3.7 Hz), 125.8 (q, J = 3.7 Hz), 124.1 (q, J = 270.4 Hz), 123.9 (q, J = 270.5 Hz), 33.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3070, 1616, 1490, 1331, 1130, 843, 700. HRMS (ESI) m/z calcd for $C_{24}H_{16}F_6NS^+$ $(M+H)^+$ 464.0902, found 464.0904.

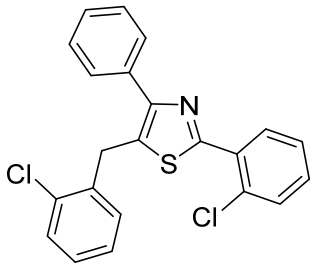


5-(2-Methylbenzyl)-4-phenyl-2-(*o*-tolyl)thiazole (3x)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 2-methylbenzaldehyde (**2i**, 71 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4

mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3x** (51.8 mg, 73%) as a colorless liquid.

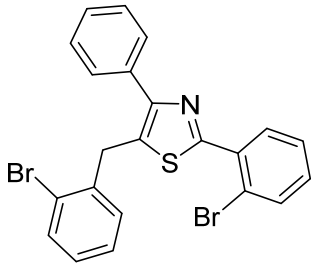
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 3H), 7.44 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.28 – 7.17 (m, 7H), 4.28 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 151.4, 138.5, 136.5, 136.1, 135.1, 133.3, 132.9, 131.4, 130.4, 129.7, 129.1, 128.7, 128.6, 128.4, 127.8, 127.1, 126.3, 125.9, 31.3, 21.7, 19.4. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2925, 1602, 1489, 1230, 972, 763, 696, 445. HRMS (ESI) m/z calcd for $C_{24}H_{22}NS^+$ $(M+H)^+$ 356.1468, found 356.1469.



5-(2-Chlorobenzyl)-2-(2-chlorophenyl)-4-phenylthiazole (3y)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 2-chlorobenzaldehyde (**2j**, 69 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3y** (66.4 mg, 84%) as a white solid. mp: 123-124 ^{o}C.

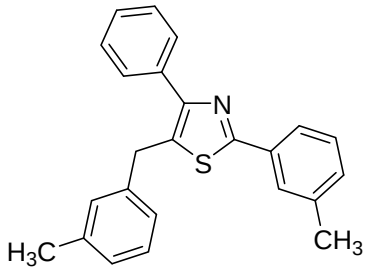
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.29 (m, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.47 – 7.27 (m, 7H), 7.23 – 7.15 (m, 3H), 4.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.8, 137.5, 134.8, 133.8, 132.7, 132.0, 131.8, 130.6, 130.5, 130.1, 130.0, 129.6, 128.6, 128.5, 128.3, 127.9, 127.1, 126.9, 30.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3068, 1564, 1468, 1446, 1273, 1036, 978, 752, 700. HRMS (ESI) m/z calcd for $C_{22}H_{16}Cl_2NS^+$ $(M+H)^+$ 396.0375, found 396.0379.



5-(2-Bromobenzyl)-2-(2-bromophenyl)-4-phenylthiazole (3z)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 2-bromobenzaldehyde (**2k**, 70 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3z** (77.4 mg, 80%) as a white solid. mp: 116-117 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.9, 1.7 Hz, 1H), 7.78 – 7.64 (m, 3H), 7.60 (dd, J = 8.0, 1.0 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.31 – 7.10 (m, 4H), 4.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 152.0, 139.2, 139.2, 134.7, 134.1, 134.0, 133.0, 132.8, 131.4, 130.3, 130.1, 128.6, 128.5, 128.0, 127.8, 127.4, 124.3, 121.5, 33.6. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 1485, 1461, 1413, 1022, 760, 700. HRMS (ESI) m/z calcd for $C_{22}H_{16}Br_2NS^+$ $(M+H)^+$ 483.9365, found 483.9369.

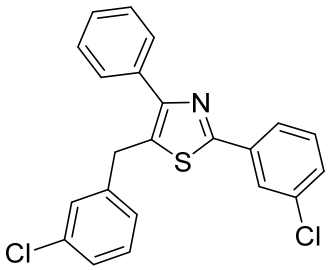


5-(3-Methylbenzyl)-4-phenyl-2-(*m*-tolyl)thiazole (3aa)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 3-methylbenzaldehyde (**2l**, 73 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3aa** (49.7 mg, 70%) as a colorless liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.75 – 7.69 (m, 3H), 7.45 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.06 (t, J = 8.3 Hz, 3H), 4.26 (s, 2H),

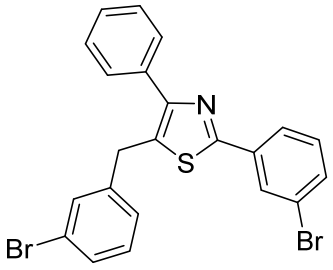
2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 152.3, 140.0, 138.5, 138.4, 135.0, 133.6, 133.1, 130.6, 129.1, 128.8, 128.7, 128.6, 128.5 127.9, 127.5, 126.9, 125.4, 123.6, 33.2, 21.4, 21.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3055, 2917, 1740, 1605, 1483, 787, 769, 692. HRMS (ESI) m/z calcd for $C_{24}H_{22}NS^+$ $(M+H)^+$ 356.1468, found 356.1471.



5-(3-Chlorobenzyl)-2-(3-chlorophenyl)-4-phenylthiazole (3ab)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 3-chlorobenzaldehyde (**2m**, 70 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **3ab** (45.8 mg, 58%) as a colorless liquid.

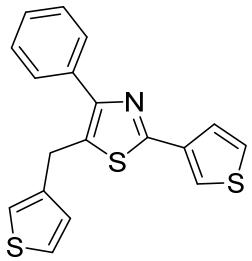
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.78 (d, J = 7.1 Hz, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.42 – 7.30 (m, 3H), 7.28 – 7.19 (m, 3H), 7.10 (t, J = 6.2 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 153.1, 141.7, 135.2, 134.9, 134.6, 134.5, 132.6, 130.1, 130.0, 129.8, 128.7, 128.6, 128.5, 128.2, 127.1, 126.5, 126.2, 124.5, 32.9. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2925, 1595, 1475, 1246, 1076, 777, 698. HRMS (ESI) m/z calcd for $C_{22}H_{15}Cl_2NS^+$ $(M+H)^+$ 396.0375, found 396.0380.



5-(3-Bromobenzyl)-2-(3-bromophenyl)-4-phenylthiazole (3ac)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 3-bromobenzaldehyde (**2n**, 72 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether) yielded **3ac** (55.2 mg, 57%) as a colorless liquid.

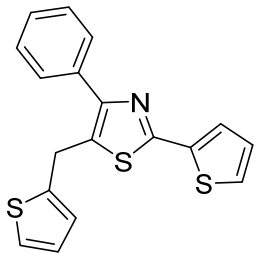
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.53 – 7.36 (m, 6H), 7.27 (t, J = 8.1 Hz, 1H), 7.21 – 7.12 (m, 2H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 153.2, 142.1, 135.5, 134.5, 132.7, 132.6, 131.4, 130.3, 130.1, 129.1, 128.7, 128.6, 128.2, 128.0, 127.0, 125.0, 123.0, 122.9, 32.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 2927, 1591, 1477, 1240, 1070, 993, 773, 698. HRMS (ESI) m/z calcd for $C_{22}H_{16}Br_2NS^+$ $(M+H)^+$ 483.9365, found 483.9370.



4-Phenyl-2-(thiophen-3-yl)-5-(thiophen-3-ylmethyl)thiazole (3ad)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), thiophene-3-carbaldehyde (**2o**, 54 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3ad** (30.5 mg, 45%) as a brown solid. mp: 104-105 ^{o}C.

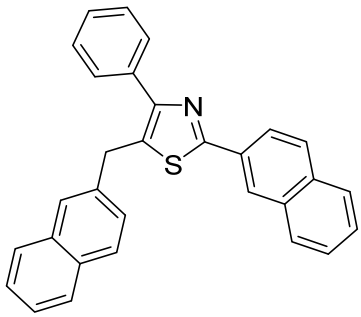
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 2.8, 0.9 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.56 (dd, J = 5.0, 1.1 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.29 (m, 1H), 7.07 – 7.03 (m, 1H), 6.97 (dd, J = 5.0, 1.2 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 151.9, 140.3, 135.9, 134.8, 131.8, 128.7, 128.5, 128.0, 127.8, 126.5, 126.2, 126.2, 123.5, 121.7, 28.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3089, 1481, 1248, 860, 781, 696, 648. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS_3^+$ $(M+H)^+$ 340.0283, found 340.0287.



4-Phenyl-2-(thiophen-2-yl)-5-(thiophen-2-ylmethyl)thiazole (3ae)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), thiophene-2-carbaldehyde (**2p**, 57 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3ae** (24.4 mg, 36%) as a brown solid. mp: 122-123 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.47 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.20 (dd, J = 5.1, 1.0 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.98 – 6.94 (m, 1H), 6.90 (d, J = 2.5 Hz, 1H), 4.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 152.0, 142.6, 137.4, 134.4, 131.6, 128.8, 128.5, 128.1, 127.7, 127.5, 127.0, 126.4, 125.5, 124.5, 27.7. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3077, 2925, 1483, 1413, 1259, 843, 775, 708. HRMS (ESI) m/z calcd for $C_{18}H_{14}NS_3^+$ $(M+H)^+$ 340.0283, found 340.0289.

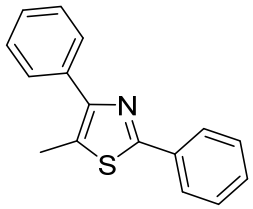


2-(Naphthalen-2-yl)-5-(naphthalen-2-ylmethyl)-4-phenylthiazole (3af)

The general procedure A was followed using acetophenone (**1a**, 24 μL, 0.2 mmol), 2-naphthaldehyde (**2q**, 94 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **3af** (64.1 mg, 75%) as a white solid. mp: 145-146 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 0.8 Hz, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 7.88 – 7.77 (m, 8H), 7.70 (s, 1H), 7.50 – 7.44 (m, 6H), 7.41 – 7.22 (m, 2H), 4.48 (s, 2H). ^{13}C NMR (100 MHz,

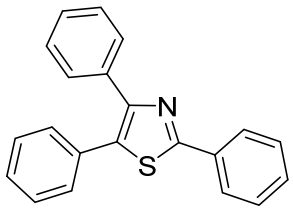
$CDCl_3$) δ 165.4, 152.8, 137.6, 134.9, 134.0, 133.6, 133.3, 133.2, 132.4, 131.1, 128.8, 128.6, 128.5, 128.0, 127.8, 127.7, 127.7, 126.8, 126.7, 126.6, 126.3, 125.8, 125.7, 123.9, 33.5. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3055, 1595, 1493, 856, 812, 748, 698, 472. HRMS (ESI) m/z calcd for $C_{30}H_{22}NS^+$ $(M+H)^+$ 428.1468, found 428.1466.



5-Methyl-2,4-diphenylthiazole (4a)

The general procedure B was followed using propiophenone (**1q**, 27 μL, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **4a** (25.1 mg, 50%) as a yellow liquid.

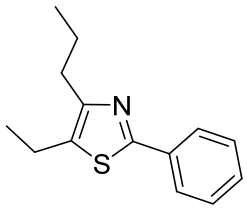
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.1, 1.8 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.49 – 7.38 (m, 6H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 163.8, 151.8, 134.8, 133.6, 129.7, 128.8, 128.7, 128.4, 127.7, 126.4, 12.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3060, 2925, 1666, 1483, 1248, 764, 698. HRMS (ESI) m/z calcd for $C_{16}H_{14}NS^+$ $(M+H)^+$ 252.0842, found 252.0843.



2,4,5-Triphenylthiazole (4b)

The general procedure B was followed using 1,2-diphenylethan-1-one (**1r**, 40 mg, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **4b** (32.6 mg, 52%) as a yellow liquid.

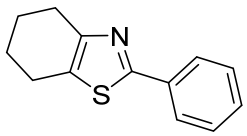
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.8, 1.9 Hz, 2H), 7.60 (dd, J = 7.8, 2.2 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.41 – 7.37 (m, 2H), 7.35 – 7.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.7, 134.9, 133.6, 133.1, 132.0, 130.0, 129.6, 129.1, 128.9, 128.7, 128.3, 128.2, 127.8, 126.4. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3050, 1599, 1477, 978, 764, 692. HRMS (ESI) m/z calcd for $C_{21}H_{16}NS^+$ $(M+H)^+$ 314.0998, found 314.0998.



5-Ethyl-2-phenyl-4-propylthiazole (4c)

The general procedure B was followed using heptan-4-one (**1s**, 28 μL, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 200/1) yielded **4c** (22.7 mg, 49%) as a yellow liquid.

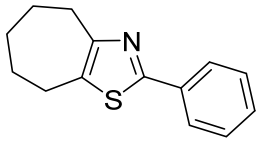
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.41 – 7.36 (m, 3H), 2.80 (q, J = 7.5 Hz, 2H), 2.69 (t, 2H), 1.75 (q, J = 15.0, 7.5 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 152.7, 134.7, 134.1, 129.3, 128.8, 126.2, 31.1, 23.1, 19.9, 16.7, 13.9. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3064, 2960, 1684, 1458, 760, 688. HRMS (ESI) m/z calcd for $C_{14}H_{18}NS^+$ $(M+H)^+$ 232.1155, found 232.1151.



2-Phenyl-4,5,6,7-tetrahydrobenzo[*d*]thiazole (4d)

The general procedure B was followed using cyclohexanone (**1t**, 21 μL, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4d** (18.9 mg, 44%) as a yellow liquid.

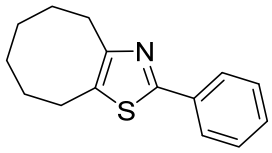
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.80 (m, 2H), 7.41 – 7.29 (m, 3H), 2.86 – 2.72 (m, 4H), 1.90 – 1.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.2, 133.9, 129.2, 129.0, 128.6, 126.0, 26.7, 23.5, 23.2, 22.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2937, 1541, 1458, 974, 760, 688. HRMS (ESI) m/z calcd for $C_{13}H_{14}NS^+$ $(M+H)^+$ 216.0842, found 216.0846.



2-Phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[*d*]thiazole (4e)

The general procedure B was followed using cycloheptanone (**1u**, 24 μL, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4e** (28.9 mg, 63%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.41 – 7.34 (m, 3H), 3.03 – 2.99 (m, 2H), 2.86 – 2.81 (m, 2H), 1.90 – 1.84 (m, 2H), 1.78 – 1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 156.4, 133.9, 133.0, 129.2, 128.7, 126.0, 31.9, 31.6, 28.0, 26.6. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2924, 1599, 1537, 1500, 1458, 1234, 760, 688. HRMS (ESI) m/z calcd for $C_{14}H_{16}NS^+$ $(M+H)^+$ 230.0998, found 230.1001.

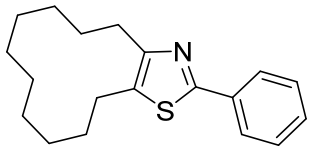


2-Phenyl-4,5,6,7,8,9-hexahydrocycloocta[*d*]thiazole (4f)

The general procedure B was followed using cyclooctanone (**1v**, 26 mg, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4f** (33.0 mg, 68%) as a brown solid. mp: 61-62 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.43 – 7.34 (m, 3H), 2.95 – 2.87 (m, 4H), 1.80 – 1.69 (m, 4H), 1.49 – 1.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 154.4, 134.1, 131.6, 129.2, 128.7, 126.1, 31.5, 29.8, 28.3, 26.0, 25.4, 24.7. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2927,

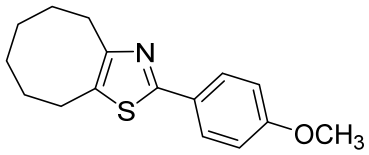
1539, 1458, 1238, 987, 758, 685. HRMS (ESI) m/z calcd for $C_{15}H_{18}NS^+$ $(M+H)^+$ 244.1155, found 244.1159.



2-Phenyl-4,5,6,7,8,9,10,11,12,13-decahydrocyclododeca[*d*]thiazole (4g)

The general procedure B was followed using cyclododecanone (**1w**, 37 mg, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4g** (38.3 mg, 64%) as a yellow liquid.

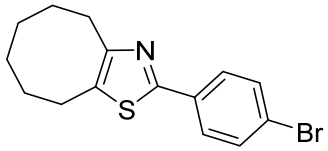
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 6.8 Hz, 2H), 7.43 – 7.33 (m, 3H), 2.82 (t, J = 6.9 Hz, 2H), 2.74 (t, J = 6.7 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.79 – 1.72 (m, 2H), 1.46 – 1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 153.4, 134.1, 134.0, 129.4, 128.7, 126.2, 30.1, 27.4, 25.8, 24.8, 24.6, 24.4, 24.1, 23.5, 22.6, 22.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 2929, 2856, 1664, 1468, 1250, 1051, 760, 687. HRMS (ESI) m/z calcd for $C_{19}H_{26}NS^+$ $(M+H)^+$ 300.1781, found 300.1788.



2-(4-Methoxyphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[*d*]thiazole (4h)

The general procedure B was followed using cyclooctanone (**1v**, 26 mg, 0.2 mmol), 4-methoxybenzaldehyde (**2d**, 38 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4h** (43.7 mg, 80%) as a white solid. mp: 66-67 ^{o}C.

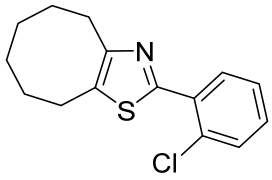
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 2.93 – 2.84 (m, 4H), 1.73 (d, J = 24.6 Hz, 4H), 1.49 – 1.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.5, 154.0, 130.5, 127.5, 127.1, 114.0, 55.3, 31.4, 29.8, 28.2, 26.0, 25.4, 24.6. IR spectrum (ν_{max}(KBr)/cm^{-1}) 2927, 1608, 1517, 1450, 1248, 1026, 820, 594. HRMS (ESI) m/z calcd for $C_{16}H_{20}NOS^+$ $(M+H)^+$ 274.1260, found 274.1263.



2-(4-Bromophenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[*d*]thiazole (4i)

The general procedure B was followed using cyclooctanone (**1v**, 26 mg, 0.2 mmol), 4-bromobenzaldehyde (**2g**, 56 mg, 0.3 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4i** (38.0 mg, 59%) as a yellow solid. mp: 89-90 ^oC.

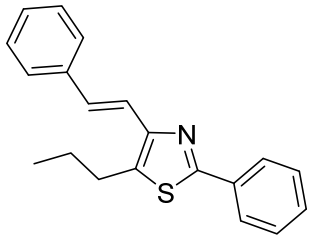
^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 2.95 – 2.86 (m, 4H), 1.74 (d, J = 19.7 Hz, 4H), 1.49 – 1.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 154.7, 133.0, 132.2, 131.9, 127.5, 123.3, 31.4, 29.8, 28.3, 26.0, 25.4, 24.7. IR spectrum (ν_{max}(KBr)/cm^{-1}) 2920, 1537, 1493, 1440, 1240, 1068, 987, 829. HRMS (ESI) m/z calcd for $C_{15}H_{17}BrNS^+$ $(M+H)^+$ 322.0260, found 322.0259.



2-(2-Chlorophenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[*d*]thiazole (4j)

The general procedure B was followed using cycloheptanone (**1v**, 26 mg, 0.2 mmol), 2-chlorobenzaldehyde (**2j**, 35 μL, 0.4 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (12.8 mg, 0.4 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4j** (36.1 mg, 65%) as a brown liquid.

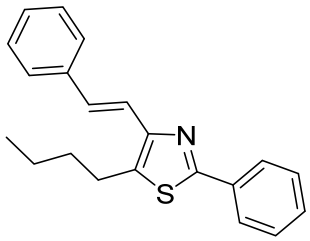
^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.35 – 7.25 (m, 2H), 2.97 – 2.91 (m, 4H), 1.80 – 1.71 (m, 4H), 1.49 – 1.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 153.2, 133.7, 132.4, 131.5, 130.5, 129.5, 126.9, 31.5, 29.8, 28.1, 25.9, 25.4, 24.5. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3066, 2929, 1703, 1539, 1479, 1271, 1065, 985, 754. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClNS^+$ $(M+H)^+$ 278.0765, found 278.0767.



(*E*)-2-Phenyl-5-propyl-4-styrylthiazole (5a)

The general procedure C was followed using hexan-2-one (**1x**, 26 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5a** (31.1 mg, 51%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.1, 1.6 Hz, 2H), 7.64 (d, J = 15.7 Hz, 1H), 7.57 (d, J = 7.5 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.29 – 7.24 (m, 1H), 7.08 (d, J = 15.7 Hz, 1H), 2.91 (t, J = 7.5 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.04 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.6, 137.6, 135.5, 133.8, 131.1, 129.8, 128.8, 128.6, 127.6, 126.6, 126.5, 119.1, 28.2, 25.2, 13.7. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3061, 2962, 2871, 1470, 960, 756, 692. HRMS (ESI) m/z calcd for $C_{20}H_{20}NS^+$ $(M+H)^+$ 306.1311, found 306.1314.

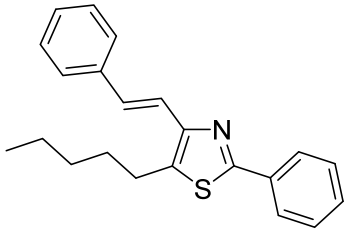


(*E*)-5-Butyl-2-phenyl-4-styrylthiazole (5b)

The general procedure C was followed using heptan-2-one (**1y**, 29 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5b** (35.7 mg, 56%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.9, 1.5 Hz, 2H), 7.64 (d, J = 15.7 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.46 – 7.34 (m, 5H), 7.29 – 7.24 (m, 1H), 7.08 (d, J = 15.7 Hz, 1H), 2.94 (t, J = 7.6 Hz, 2H), 1.75 – 1.66 (m, 2H), 1.51 – 1.40 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.5, 137.5, 135.8, 133.8, 131.1, 129.8, 128.8, 128.6, 127.6, 126.6, 126.5, 119.1,

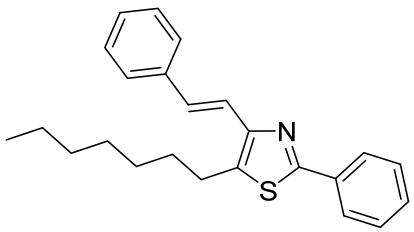
34.0, 25.9, 22.2, 13.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3059, 2954, 1466, 1250, 960, 754, 692. HRMS (ESI) m/z calcd for $C_{21}H_{22}NS^+$ $(M+H)^+$ 320.1468, found 320.1466.



(*E*)-5-Pentyl-2-phenyl-4-styrylthiazole (5c)

The general procedure C was followed using octan-2-one (**1z**, 32 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5c** (34.0 mg, 51%) as a yellow liquid.

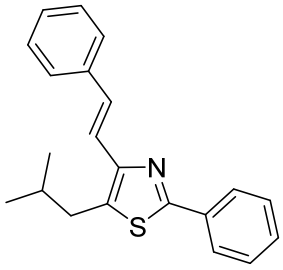
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.0, 1.5 Hz, 2H), 7.64 (d, J = 15.7 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.29 – 7.24 (m, 1H), 7.08 (d, J = 15.7 Hz, 1H), 2.93 (t, J = 7.6 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.44 – 1.34 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 149.5, 137.6, 135.9, 133.8, 131.0, 129.8, 128.8, 128.6, 127.6, 126.6, 126.5, 119.1, 31.6, 31.3, 26.2, 22.4, 14.0. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2926, 1470, 960, 754, 692. HRMS (ESI) m/z calcd for $C_{22}H_{24}NS^+$ $(M+H)^+$ 334.1624, found 334.1621.



(*E*)-5-Heptyl-2-phenyl-4-styrylthiazole (5d)

The general procedure C was followed using decan-2-one (**1aa**, 39 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5d** (43.3 mg, 60%) as a yellow liquid.

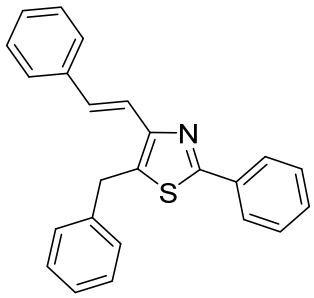
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.0, 1.6 Hz, 2H), 7.64 (d, J = 15.7 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.29 – 7.24 (m, 1H), 7.07 (d, J = 15.7 Hz, 1H), 2.92 (t, J = 7.6 Hz, 2H), 1.76 – 1.66 (m, 2H), 1.42 – 1.26 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 149.5, 137.6, 135.9, 133.8, 131.0, 129.8, 128.8, 128.6, 127.6, 126.6, 126.5, 119.1, 31.9, 31.7, 29.1, 29.0, 26.2, 22.6, 14.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2927, 1500, 1460, 960, 754, 688. HRMS (ESI) m/z calcd for $C_{24}H_{28}NS^+$ $(M+H)^+$ 362.1937, found 362.1938.



(*E*)-5-Isobutyl-2-phenyl-4-styrylthiazole (5e)

The general procedure C was followed using 5-methylhexan-2-one (**1ab**, 29 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5e** (35.7 mg, 56%) as a yellow liquid.

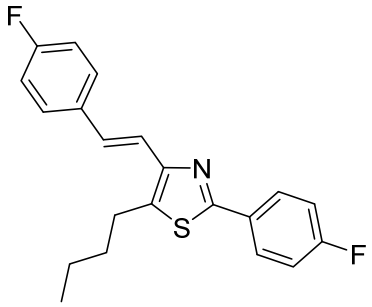
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 15.7 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.37 (t, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.07 (d, J = 15.7 Hz, 1H), 2.80 (d, J = 7.1 Hz, 2H), 2.01 – 1.90 (m, 1H), 1.02 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 150.2, 137.6, 134.4, 133.8, 131.0, 129.8, 128.8, 128.6, 127.6, 126.6, 126.4, 119.3, 35.2, 31.2, 22.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3062, 2958, 1693, 1466, 962, 760, 692. HRMS (ESI) m/z calcd for $C_{21}H_{22}NS^+$ $(M+H)^+$ 320.1468, found 320.1469.



(*E*)-5-Benzyl-2-phenyl-4-styrylthiazole (5f)

The general procedure C was followed using 4-phenylbutan-2-one (**1ac**, 32 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5f** (41.0 mg, 58%) as a yellow solid. mp: 114-115 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.70 (d, J = 15.7 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.44 – 7.31 (m, 7H), 7.30 – 7.25 (m, 4H), 7.17 (d, J = 15.7 Hz, 1H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 149.9, 139.4, 137.3, 133.8, 133.4, 132.1, 130.1, 128.8, 128.8, 128.7, 128.4, 127.8, 126.9, 126.7, 126.5, 118.7, 32.2. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3028, 1599, 1470, 960, 760, 706. HRMS (ESI) m/z calcd for $C_{24}H_{20}NS^+$ $(M+H)^+$ 354.1311, found 354.1315.

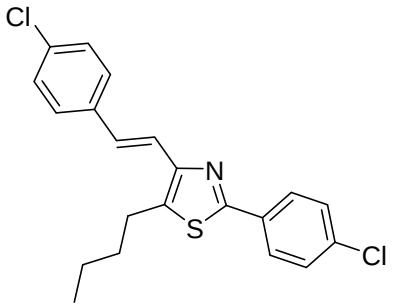


(*E*)-5-Butyl-2-(4-fluorophenyl)-4-(4-fluorostyryl)thiazole (5g)

The general procedure C was followed using heptan-2-one (**1y**, 29 μL, 0.2 mmol), 4-fluorobenzaldehyde (**2e**, 66 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5g** (36.9 mg, 52%) as a yellow solid. mp: 57-58 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.62 – 7.49 (m, 3H), 7.13 (t, J = 8.5 Hz, 2H), 7.06 (t, J = 8.5 Hz, 2H), 6.98 (d, J = 15.7 Hz, 1H), 2.92 (t, J = 7.5 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.49 – 1.42 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, J = 248.6 Hz), 163.2, 162.4 (d, J = 245.9 Hz), 149.2, 135.7, 133.6 (d, J = 3.3 Hz), 130.0 (d, J = 3.1 Hz), 129.9, 128.3 (d, J = 8.4 Hz), 128.1 (d, J = 7.9 Hz), 118.7 (d, J = 2.1 Hz), 115.9 (d, J = 21.9 Hz), 115.6 (d, J = 21.5 Hz), 34.0, 25.9, 22.2, 13.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3039, 2956, 1599,

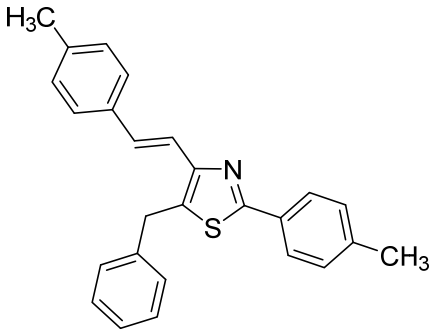
1512, 1230, 1155, 827, 494. HRMS (ESI) m/z calcd for $C_{21}H_{20}F_2NS^+$ $(M+H)^+$ 356.1279, found 356.1287.



(*E*)-5-Butyl-2-(4-chlorophenyl)-4-(4-chlorostyryl)thiazole (5h)

The general procedure C was followed using heptan-2-one (**1y**, 29 μL, 0.2 mmol), 4-chlorobenzaldehyde (**2f**, 86 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5h** (48.9 mg, 63%) as a yellow solid. mp: 53-54 ^oC.

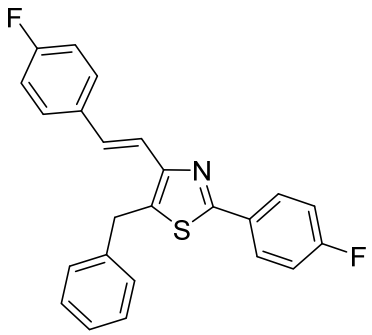
^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 15.7 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 15.7 Hz, 1H), 2.92 (t, J = 7.5 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.48 – 1.41 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 149.3, 136.6, 135.8, 135.7, 133.2, 132.1, 129.8, 129.0, 128.8, 127.8, 127.6, 119.3, 34.0, 25.9, 22.2, 13.8. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3045, 2929, 1593, 1490, 1462, 1090, 833. HRMS (ESI) m/z calcd for $C_{21}H_{20}Cl_2NS^+$ $(M+H)^+$ 388.0688, found 388.0691.



(*E*)-5-Benzyl-4-(4-methylstyryl)-2-(*p*-tolyl)thiazole (5i)

The general procedure C was followed using 4-phenylbutan-2-one (**1ac**, 32 μL, 0.2 mmol), 4-methylbenzaldehyde (**2b**, 73 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5i** (30.5 mg, 40%) as a yellow solid. mp: 153-154 ^oC.

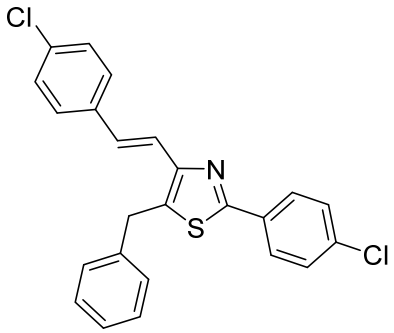
^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 15.7 Hz, 1H), 7.45 (d, J = 7.9 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.16 (m, 7H), 7.11 (d, J = 15.7 Hz, 1H), 4.25 (s, 2H), 2.37 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.0, 140.1, 139.6, 137.6, 134.5, 132.8, 131.7, 130.9, 129.5, 129.4, 128.7, 128.4, 126.8, 126.6, 126.3, 117.9, 32.1, 21.4, 21.3. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3020, 1600, 1520, 1468, 970, 800, 702, 584. HRMS (ESI) m/z calcd for $C_{26}H_{24}NS^+$ $(M+H)^+$ 382.1624, found 382.1630.



(*E*)-5-Benzyl-2-(4-fluorophenyl)-4-(4-fluorostyryl)thiazole (5j)

The general procedure C was followed using 4-phenylbutan-2-one (**1ac**, 32 μL, 0.2 mmol), 4-fluorobenzaldehyde (**2e**, 66 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5j** (28.8 mg, 37%) as a yellow solid. mp: 137-138 ^oC.

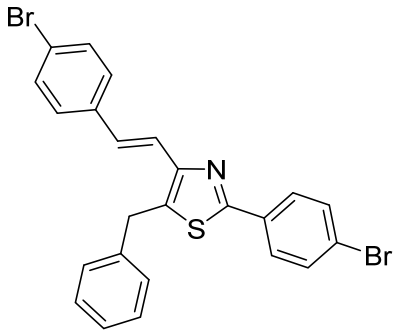
^1H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.63 (d, J = 15.7 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.36 – 7.32 (m, 2H), 7.26 (d, J = 7.0 Hz, 3H), 7.14 – 7.03 (m, 5H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.9 (d, J = 248.9 Hz), 162.5 (d, J = 246.0 Hz), 149.8, 139.3, 133.7, 133.4 (d, J = 3.3 Hz), 130.8, 129.8 (d, J = 3.0 Hz), 128.8, 128.4, 128.3, 128.2 (d, J = 8.0 Hz), 127.0, 118.4 (d, J = 2.1 Hz), 115.9 (d, J = 21.9 Hz), 115.6 (d, J = 21.5 Hz), 32.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3023, 1599, 1514, 1225, 965, 835, 694, 581, 497. HRMS (ESI) m/z calcd for $C_{24}H_{18}F_2NS^+$ $(M+H)^+$ 390.1123, found 390.1124.



(*E*)-5-Benzyl-2-(4-chlorophenyl)-4-(4-chlorostyryl)thiazole (5k)

The general procedure C was followed using 4-phenylbutan-2-one (**1ac**, 32 μL, 0.2 mmol), 4-chlorobenzaldehyde (**2f**, 86 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5k** (44.7 mg, 53%) as a yellow solid. mp: 156-157 ^oC.

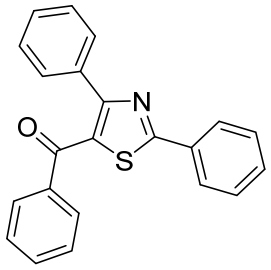
^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 15.7 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 4H), 7.25 (d, J = 7.1 Hz, 3H), 7.09 (d, J = 15.7 Hz, 1H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.09, 149.9, 139.2, 135.9, 135.7, 134.5, 133.4, 132.0, 130.7, 129.0, 128.8, 128.7, 128.3, 127.8, 127.6, 127.0, 119.1, 32.1. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3027, 1489, 1093, 1007, 966, 831, 808, 696. HRMS (ESI) m/z calcd for $C_{24}H_{18}Cl_2NS^+$ $(M+H)^+$ 422.0532, found 422.0530.



(*E*)-5-Benzyl-2-(4-bromophenyl)-4-(4-bromostyryl)thiazole (5l)

The general procedure C was followed using 4-phenylbutan-2-one (**1ac**, 32 μL, 0.2 mmol), 4-bromobenzaldehyde (**2g**, 112 mg, 0.6 mmol), NH_4I (58 mg, 0.4 mmol) and S_8 (25.6 mg, 0.8 mmol). Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **5l** (42.9 mg, 42%) as a yellow solid. mp: 126-127 ^oC.

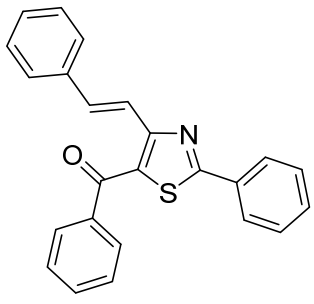
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.6, 1.8 Hz, 2H), 7.62 (d, J = 15.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.25 (m, 4H), 7.13 (dd, J = 15.8, 1.6 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.7, 139.1, 136.1, 134.7, 132.1, 131.9, 131.2, 131.2, 128.9, 128.4, 128.3, 128.0, 127.1, 124.6, 121.7, 119.0, 32.4. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3026, 1485, 1392, 1070, 966, 808, 698. HRMS (ESI) m/z calcd for $C_{24}H_{18}Br_2NS^+$ $(M+H)^+$ 509.9521, found 509.9522.



(2,4-Diphenylthiazol-5-yl)(phenyl)methanone (6a)

The mixture of 5-benzyl-2,4-diphenylthiazole (65.4 mg, 0.2 mmol), CuI (19.2 mg, 50 mol%), AcOH (40 μL, 3.5 equiv), TBHP (168 μL, 6 equiv) and DMSO (1.0 mL) was stirred at 100 °C under air for 12 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **6a** (49.8 mg, 73%) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.57 – 7.47 (m, 5H), 7.40 (t, J = 7.3 Hz, 1H), 7.27 – 7.18 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 170.0, 158.7, 137.0, 134.1, 132.9, 132.8, 131.4, 131.1, 129.7, 129.7, 129.1, 128.8, 128.1, 128.0, 127.0. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3064, 1736, 1637, 1475, 1335, 1257, 764, 690. HRMS (ESI) m/z calcd for $C_{22}H_{16}NOS^+$ $(M+H)^+$ 342.0947, found 342.0949.



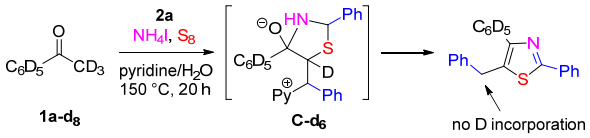
(*E*)-Phenyl(2-phenyl-4-styrylthiazol-5-yl)methanone (6b)

The mixture of (*E*)-5-benzyl-2-phenyl-4-styrylthiazole (70.6 mg, 0.2 mmol), CuI (19.2 mg, 50 mol%), AcOH (40 μL, 3.5 equiv), TBHP (168 μL, 6 equiv) and DMSO (1.0 mL) was stirred at 100 °C under air for 12 h. Purification by column chromatography on silica gel (petroleum ether/DCM: 4/3) yielded **6b** (38.9 mg, 53%) as a yellow liquid.

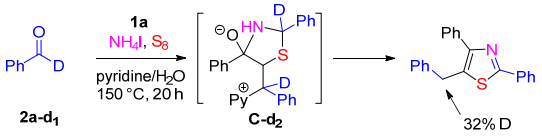
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.96 (d, J = 15.8 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.65 – 7.58 (m, 2H), 7.55 – 7.48 (m, 7H), 7.37 – 7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 170.3, 158.5, 140.1, 137.1, 136.6, 132.8, 132.8, 131.4, 129.5, 129.1, 129.1, 128.7, 128.7, 128.6, 127.4, 127.2, 121.0. IR spectrum (ν_{max}(KBr)/cm^{-1}) 3419, 2975, 1633, 1430, 1050, 758, 693. HRMS (ESI) m/z calcd for $C_{24}H_{18}NOS^{+}$ $(M+H)^{+}$ 368.1104, found 368.1104.

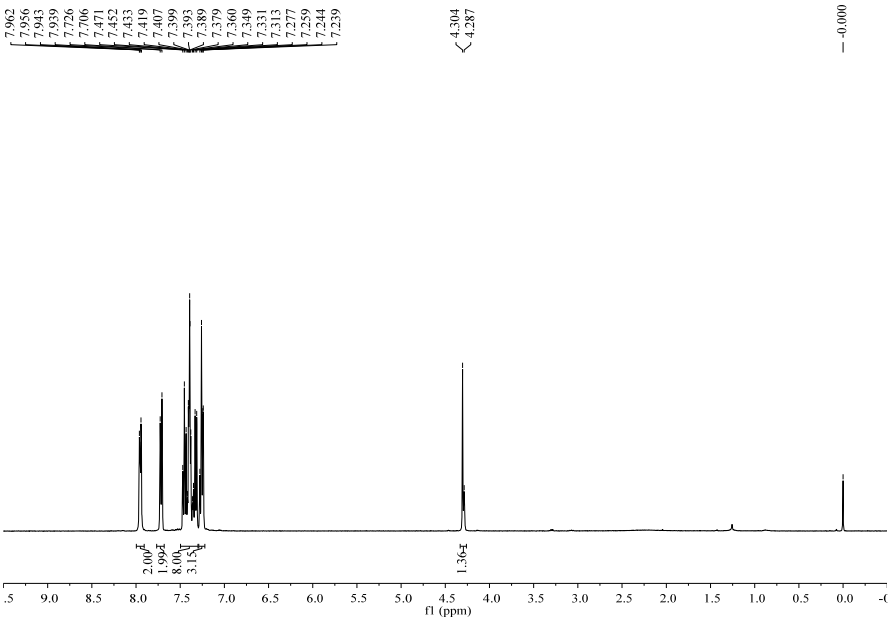
Mechanistic studies

(a) Treatment of ketone 1a-d_8: A mixture of ketone (**1a-d_8**, 24 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and H_2O (22 μL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. GC-MS analysis of the organic solvent revealed that no benzyl deuterated product formed.

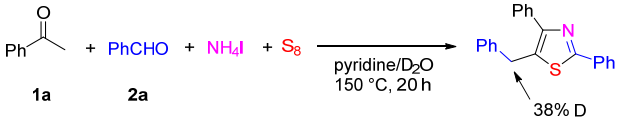


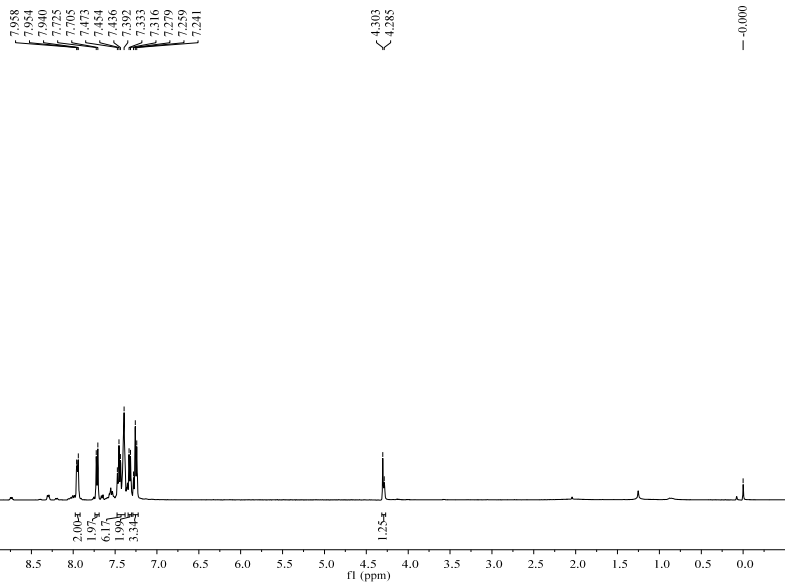
(b) Treatment of aldehyde 2a-d_1: A mixture of acetophenone (**1a**, 24 μL, 0.2 mmol), aldehyde (**2a-d_1**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and H_2O (22 μL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the benzene deuterated product. ^1H NMR analysis revealed that the benzyl deuterated product was formed in 32%.





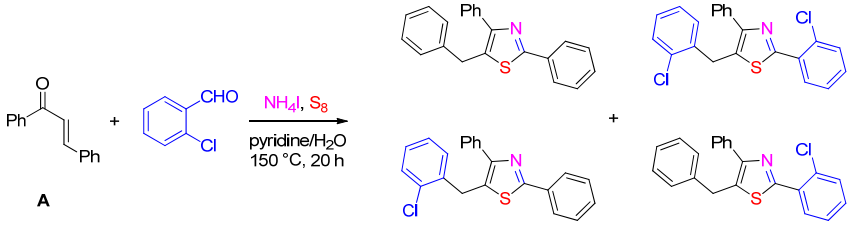
(c) Treatment of D_2O: A mixture of acetophenone (**1a**, 24 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and D_2O (22 μL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the benzene deuterated product. ^1H NMR analysis revealed that the benzyl deuterated product formed in 38%.



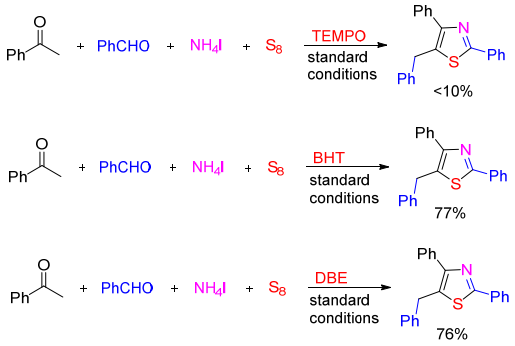


(d) Thiazole formation from *(E)*-chalcone: A mixture of *(E)*-chalcone (43 mg, 0.2 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and H_2O (22 µL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. After cooling to room temperature, the reaction was diluted with ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 200/1) to yield the product **3a** (17.0 mg, 52%).

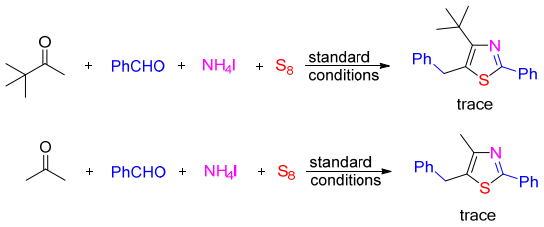
(e) Thiazole formation from *(E)*-chalcone and 2j: A mixture of *(E)*-chalcone (**1a'**) (43 mg, 0.2 mmol), 2-chlorobenzaldehyde (**2j)** (24 µL, 0.2 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and H_2O (22 µL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. GC-MS analysis of the organic solvent revealed that four thiazole products formed.



(f) Free radical trapping experiment with TEMPO, BHT, and DBE: Three reactions were performed under standard conditions with 2.0 equiv of radical trapping agent. After cooling to room temperature, the reaction was diluted with ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 200/1). Then the product of each reaction was isolated to provide the following conversions:

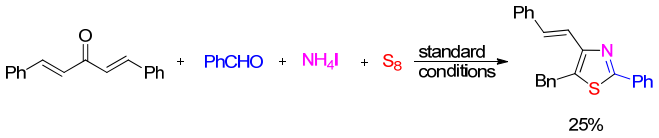


(g) Treatment of the following ketones: A mixture of 3,3-dimethylbutan-2-one (26 μL, 0.2 mmol) / propan-2-one (15 μL, 0.2 mmol), benzaldehyde (**2a**, 61 μL, 0.6 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol) and H_2O (22 μL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. Then, the mixture was flushed through a short column of silica gel with EtOAc, and the combined organic layer was dried over magnesium sulfate. With dodecane (46 μL, 0.2 mmol) as the internal standard, GC analysis of the organic solvent revealed that trace amounts of both 5-benzyl-4-(*tert*-butyl)-2-phenylthiazole and 5-benzyl-4-methyl-2-phenylthiazole formed.



(h) Reaction with dibenzylidene acetone (dba): A mixture of dibenzylidene acetone (48 mg, 0.2 mmol), benzaldehyde (**2a**, 30 μL, 0.3 mmol), NH_4I (58 mg, 0.4 mmol), S_8 (12.8 mg, 0.4 mmol)

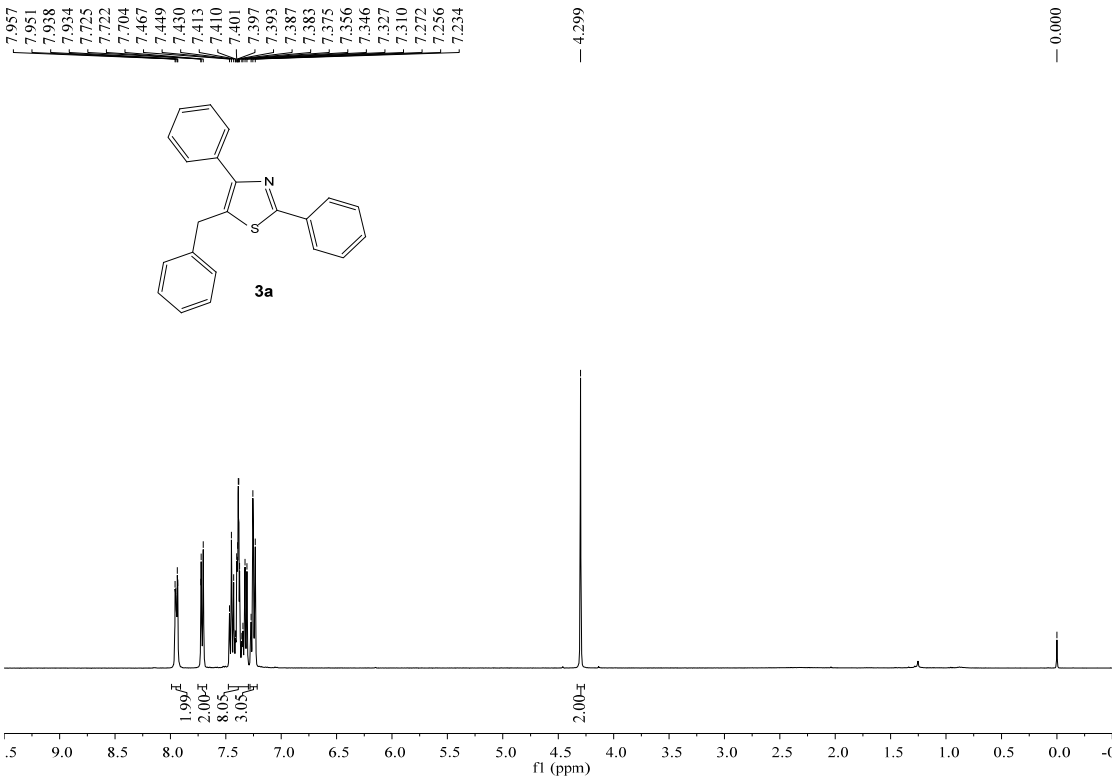
and H_2O (22 μL, 6 equiv) in pyridine (0.6 mL) was stirred under ambient air at 150 °C for 20 h. Then, the mixture was flushed through a short column of silica gel with EtOAc, and the combined organic layer was dried over magnesium sulfate. With dodecane (46 μL, 0.2 mmol) as the internal standard, GC-MS analysis revealed that the corresponding product formed in 25%.

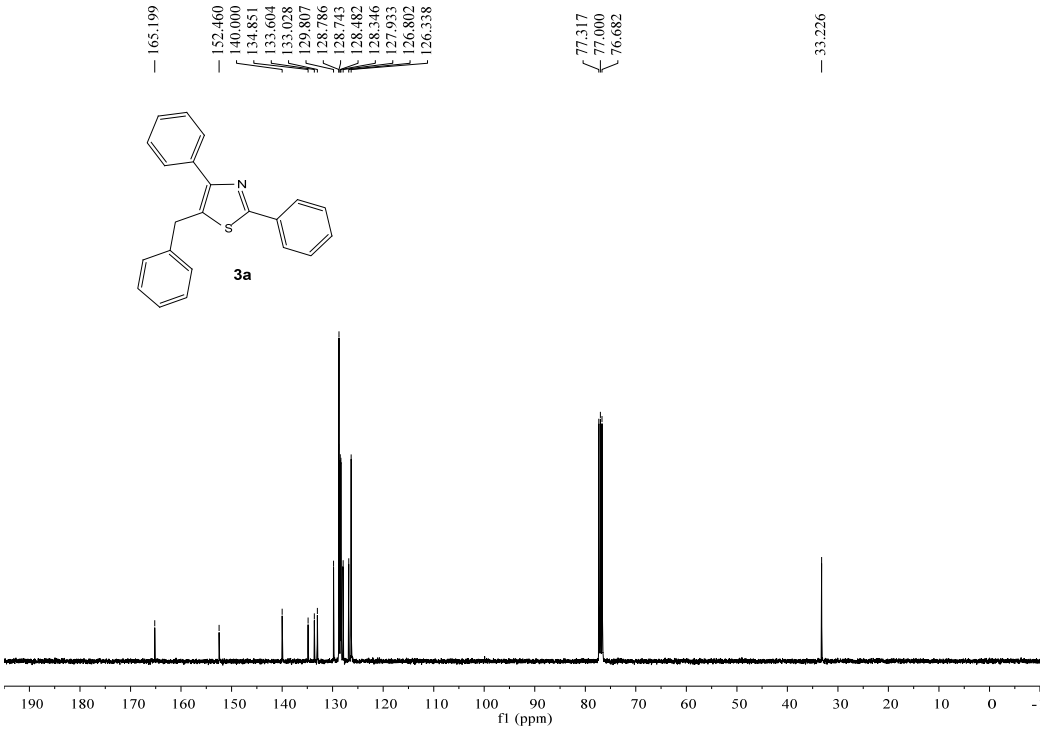


25%

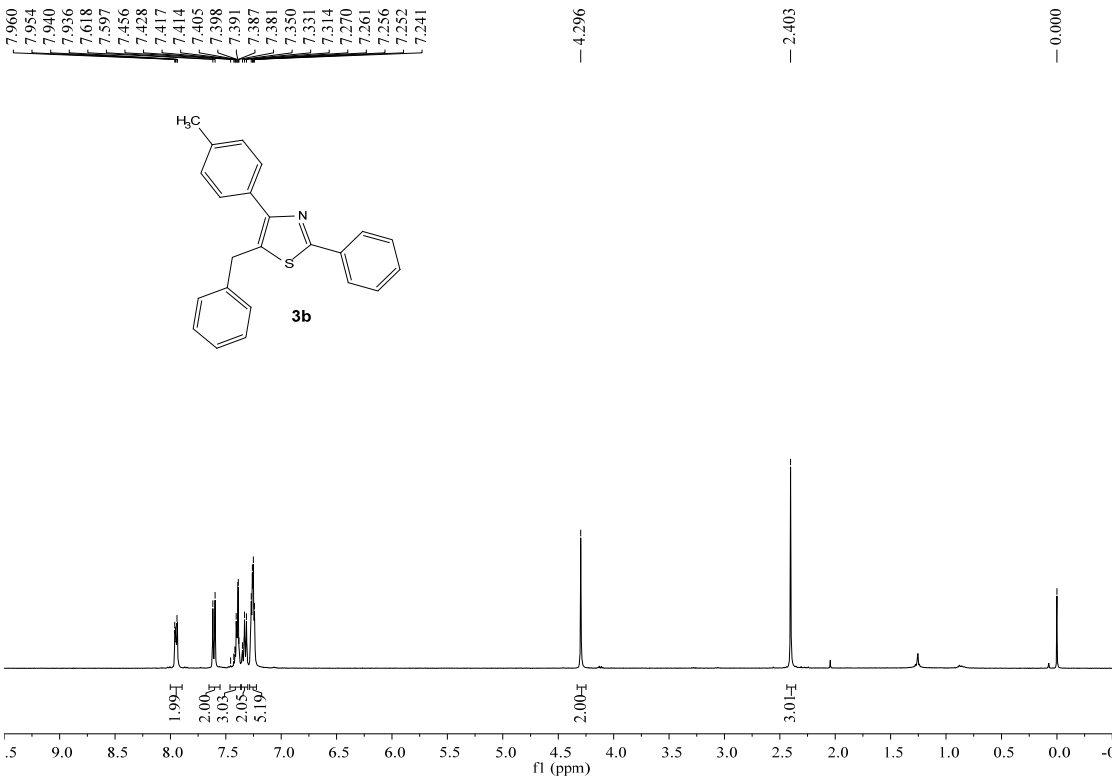
Copies of ^{1}H and ^{13}C NMR spectra of all products

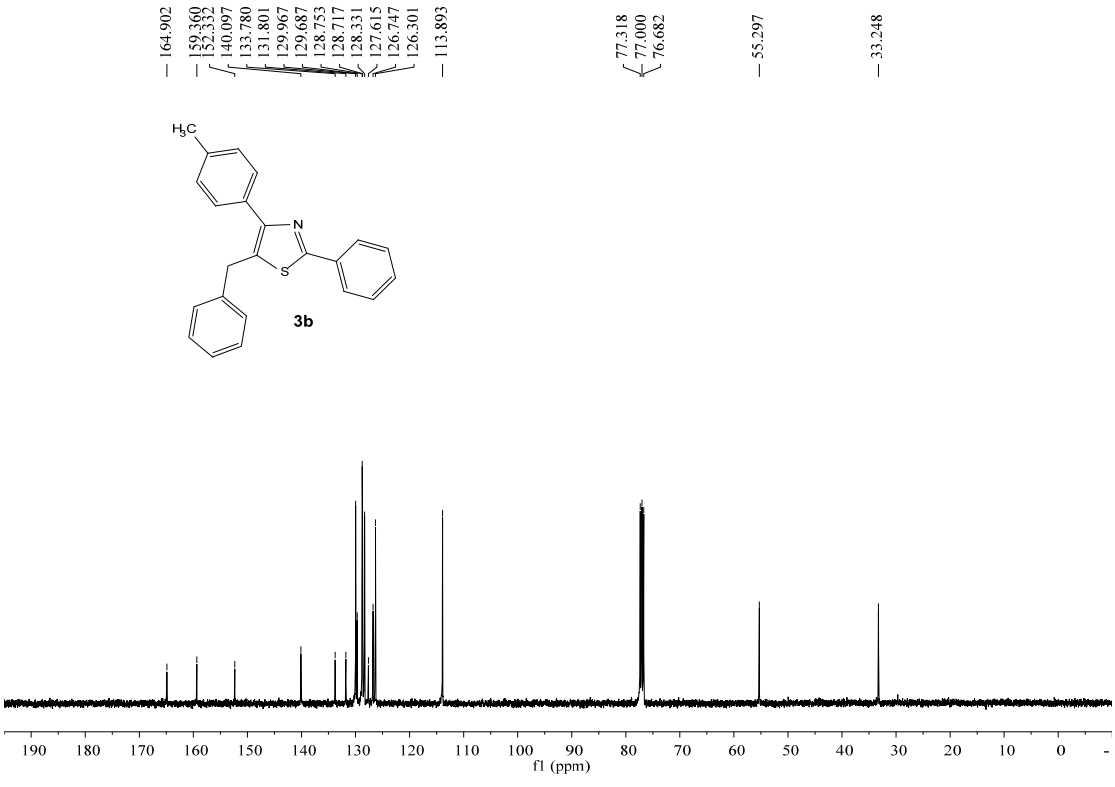
^{1}H and ^{13}C NMR spectra of 3a



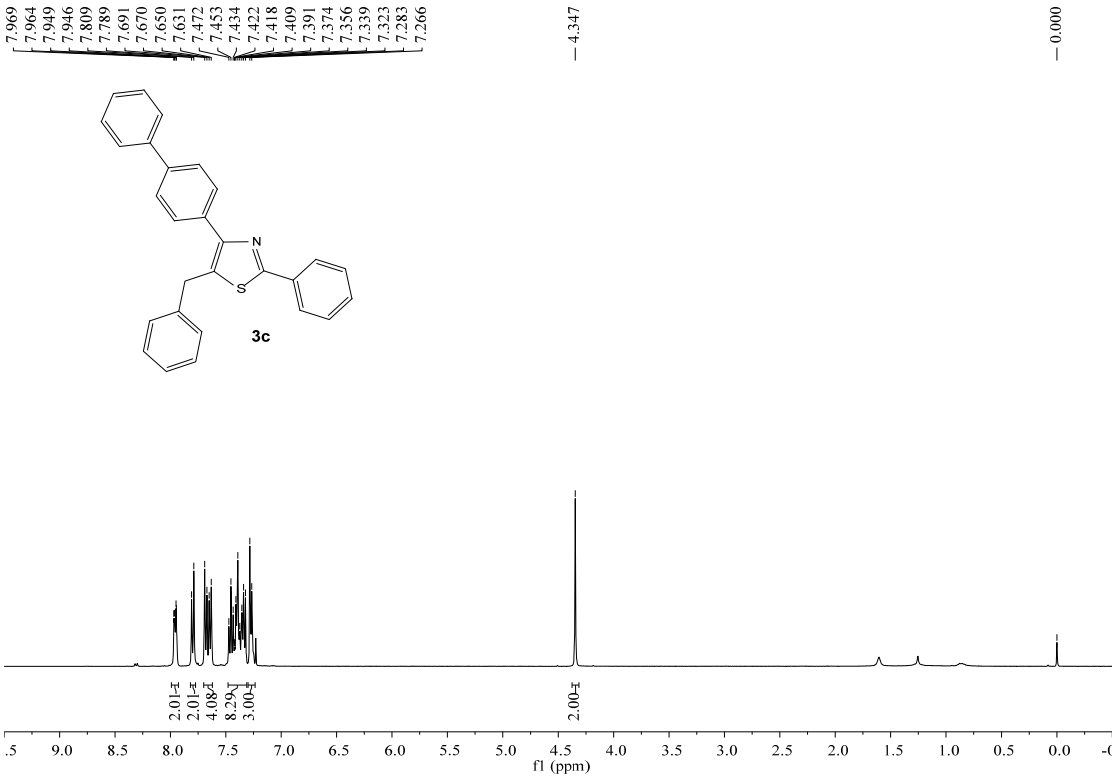


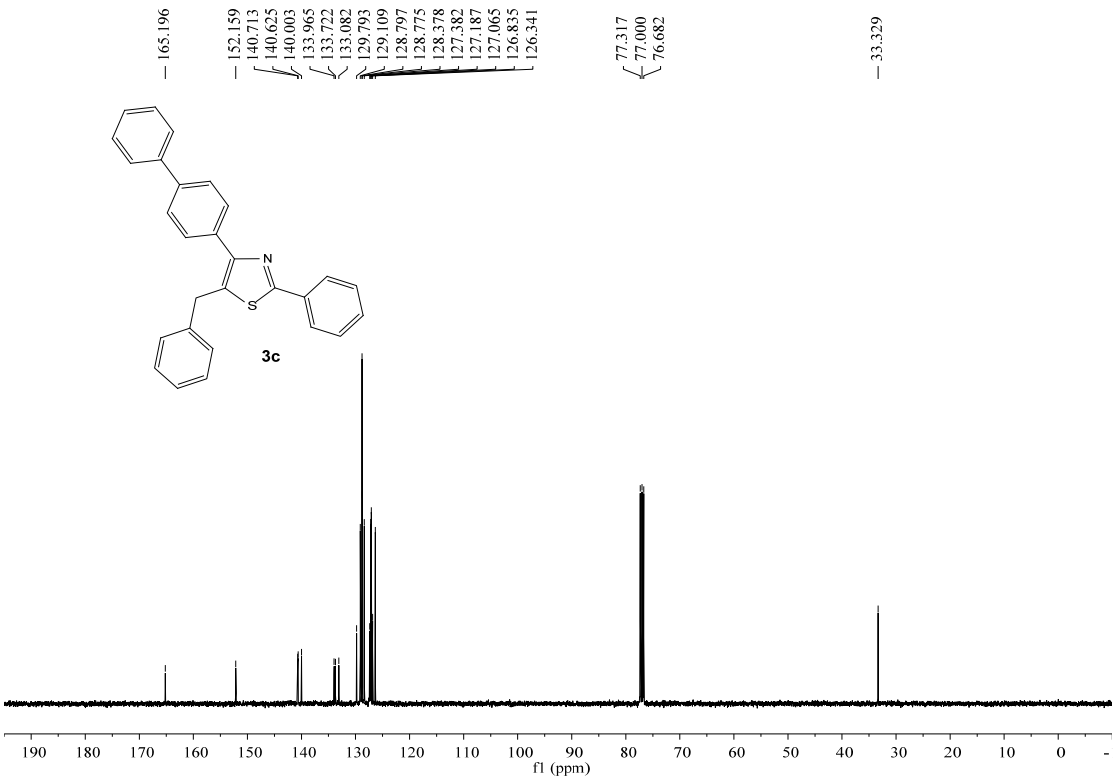
^{1}H and ^{13}C NMR spectra of 3b



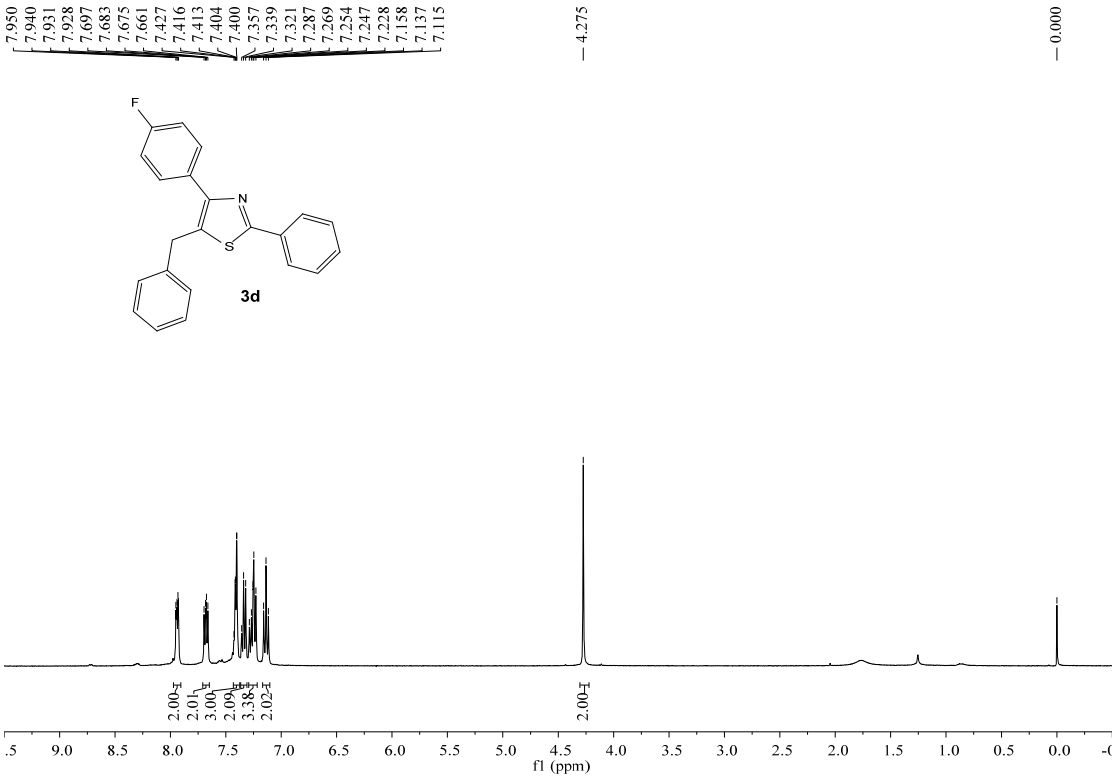


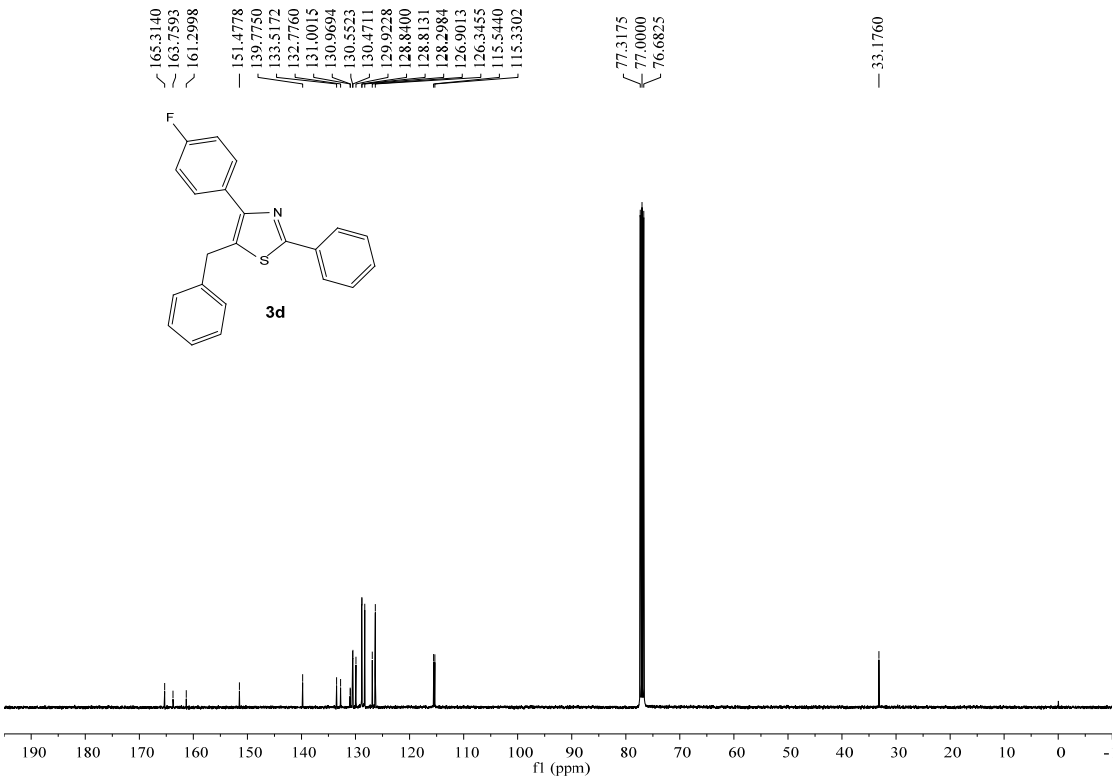
^{1}H and ^{13}C NMR spectra of 3c



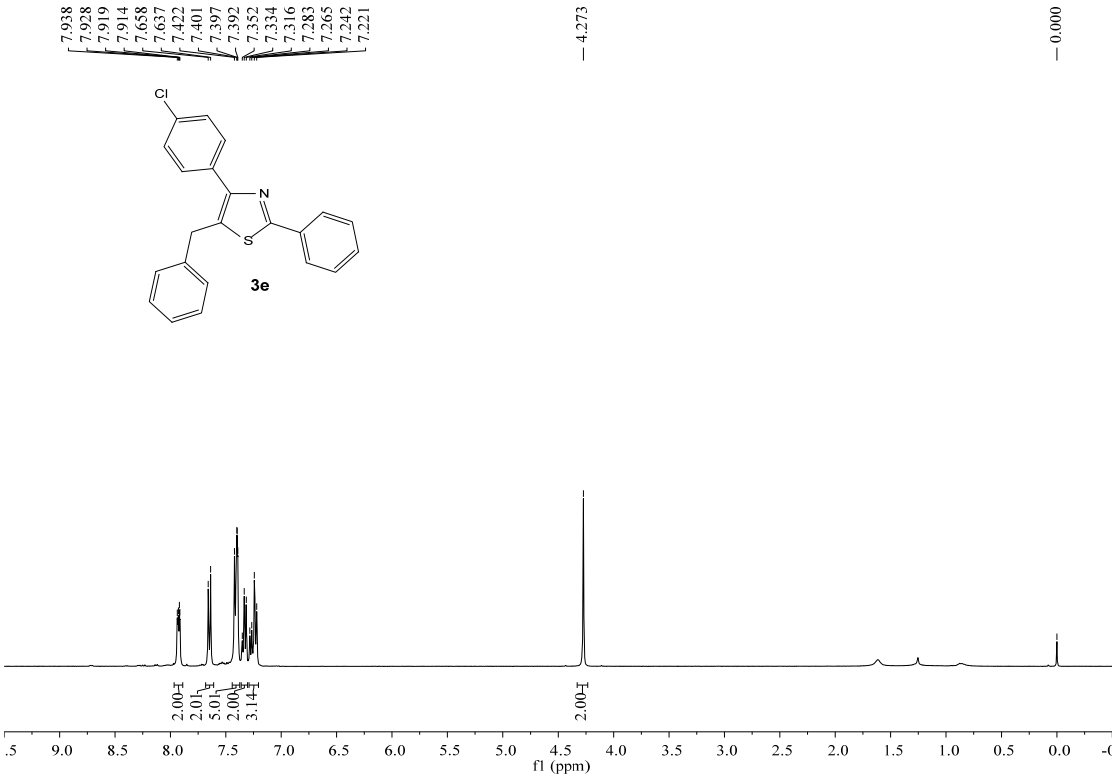


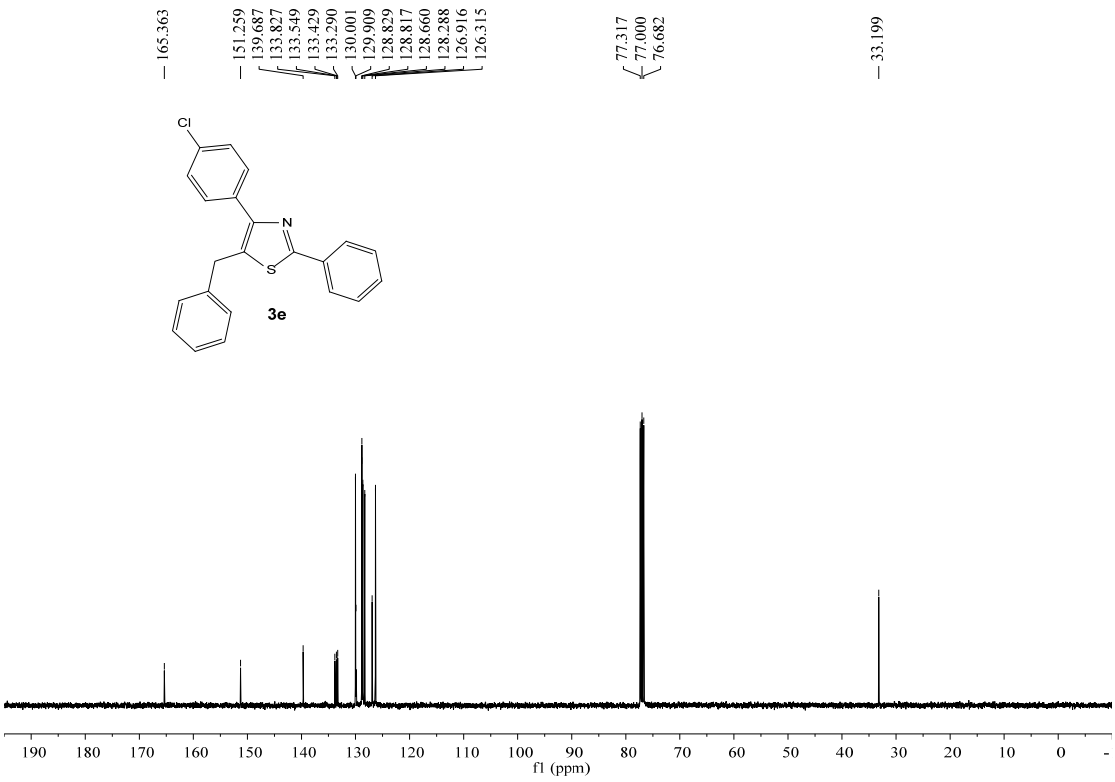
^{1}H and ^{13}C NMR spectra of 3d



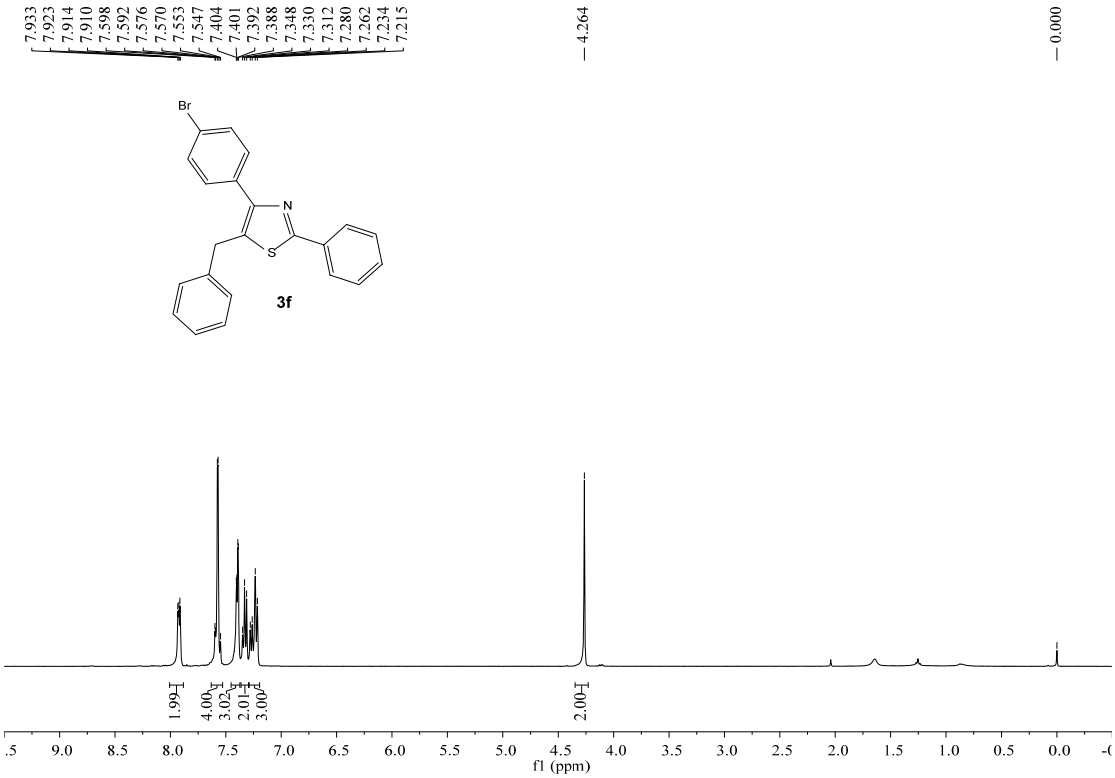


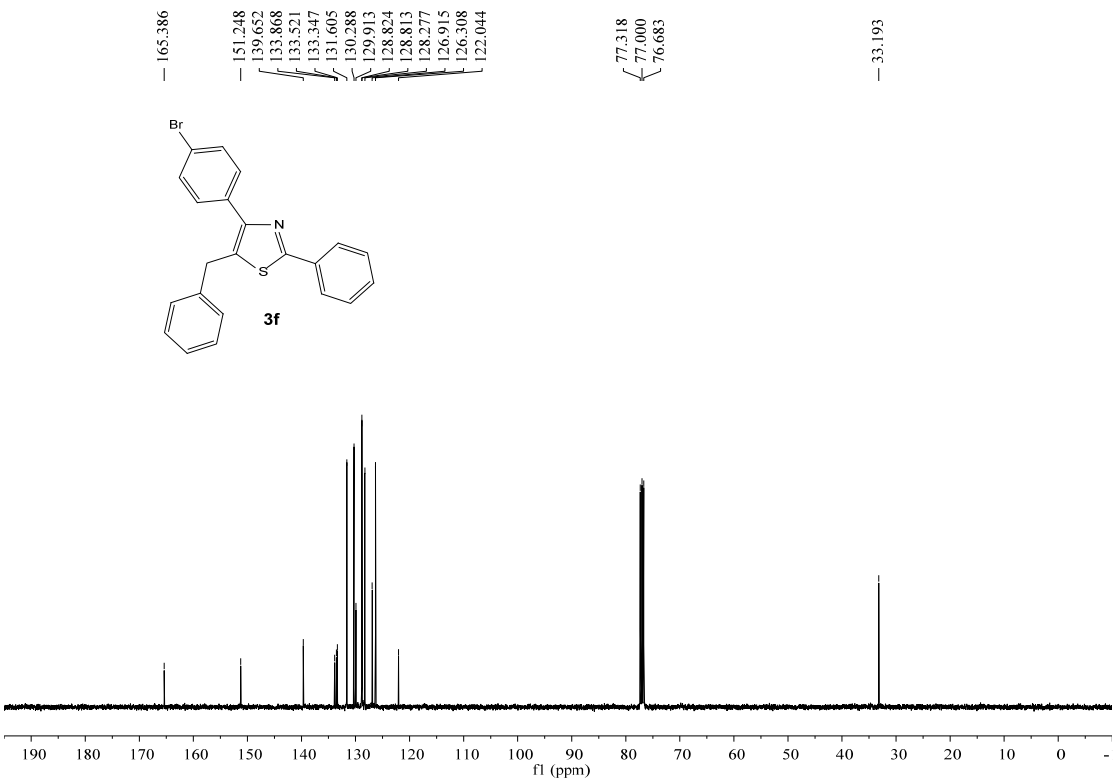
^{1}H and ^{13}C NMR spectra of 3e



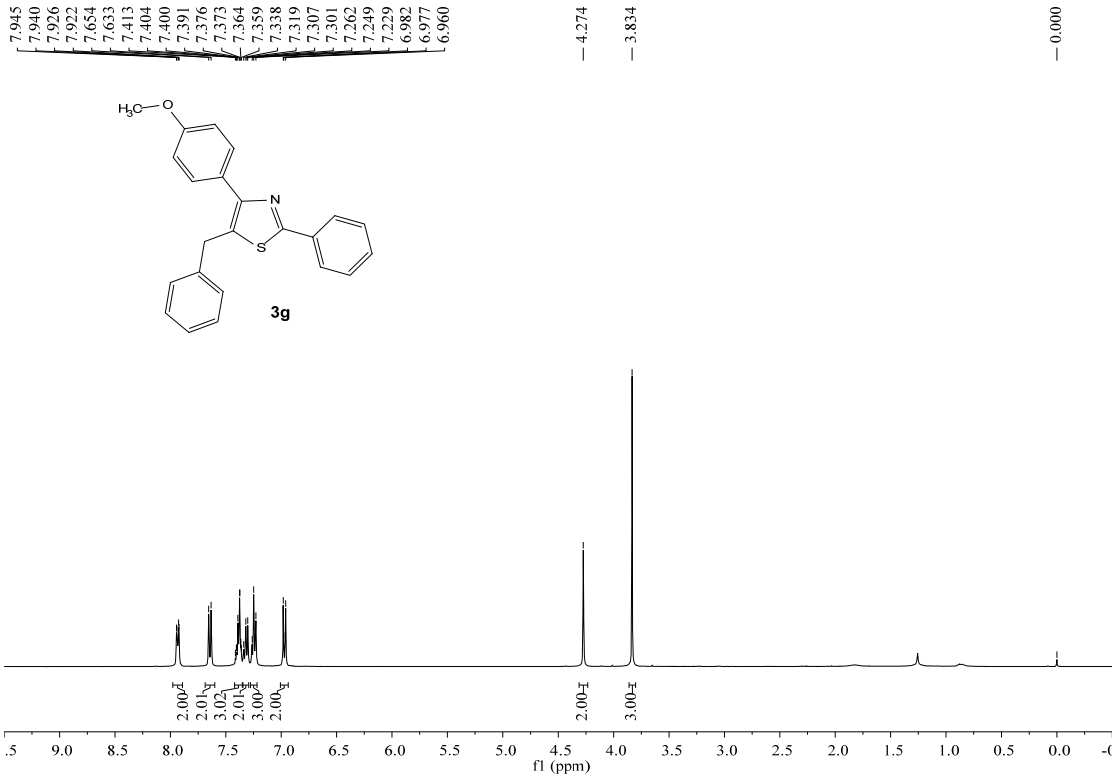


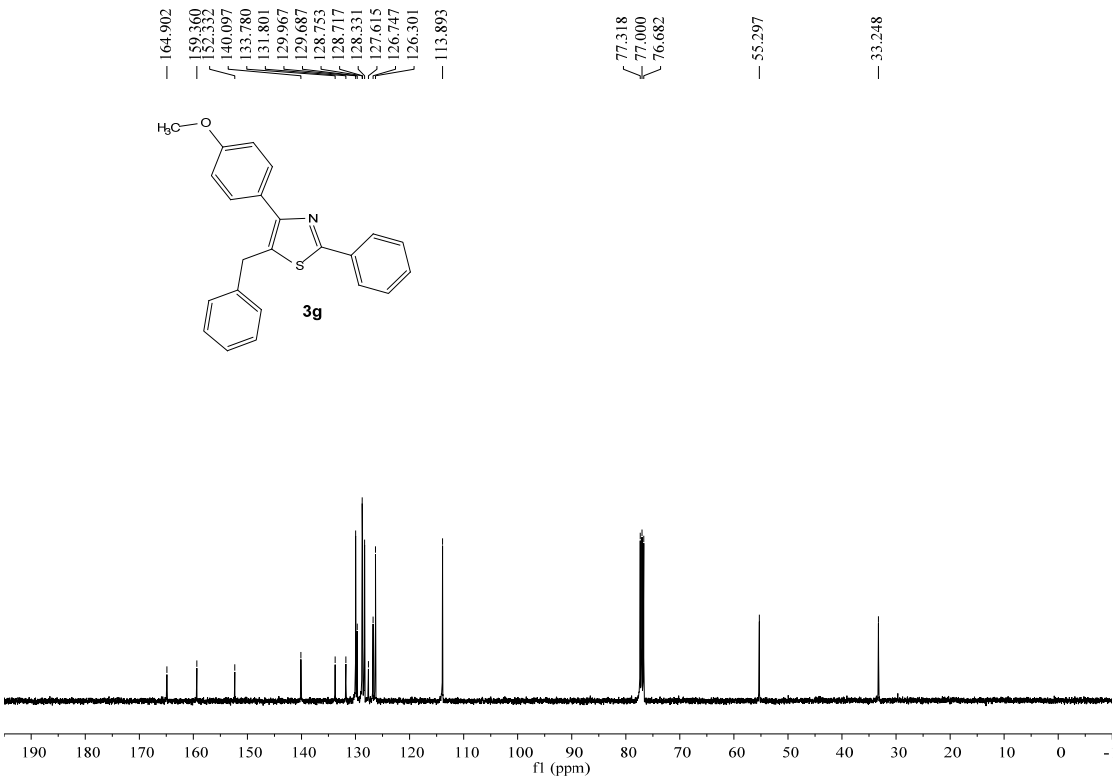
^{1}H and ^{13}C NMR spectra of 3f



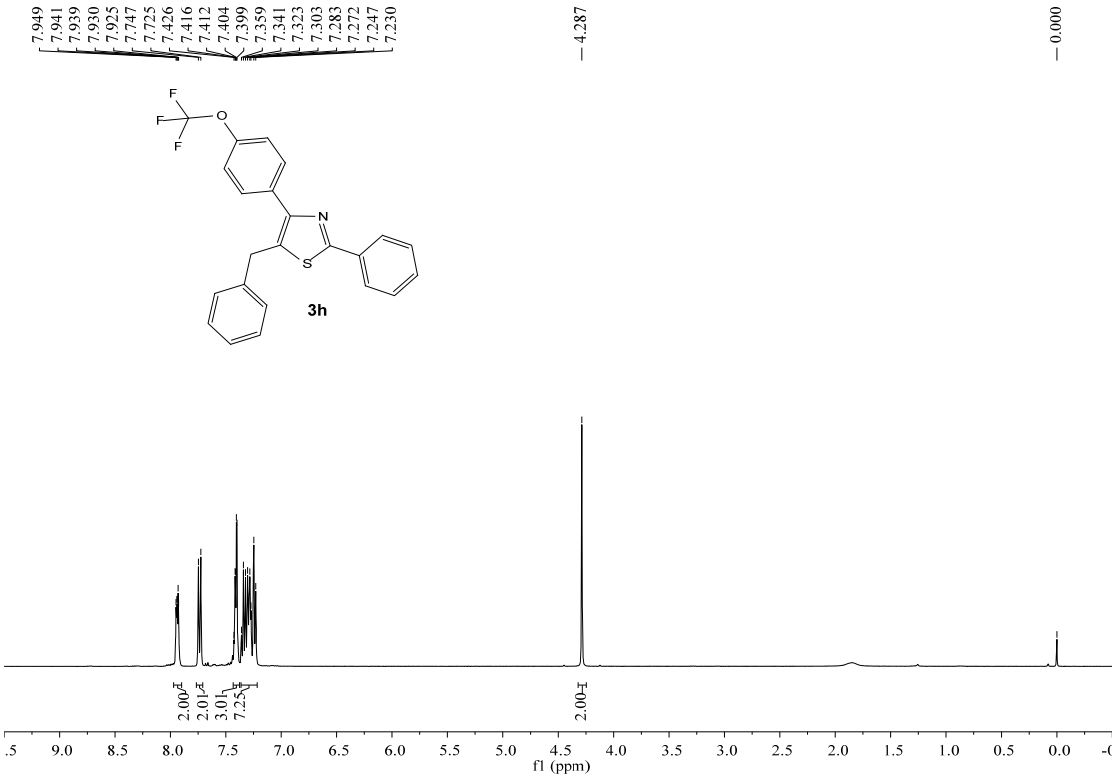


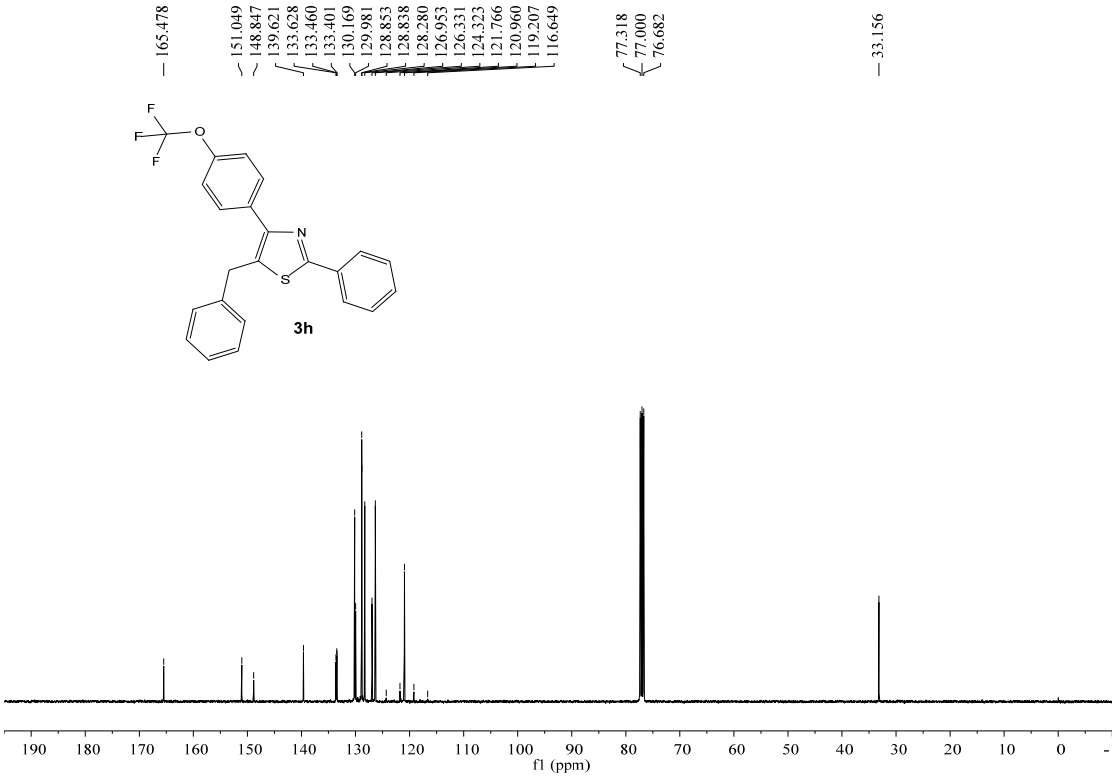
^{1}H and ^{13}C NMR spectra of 3g



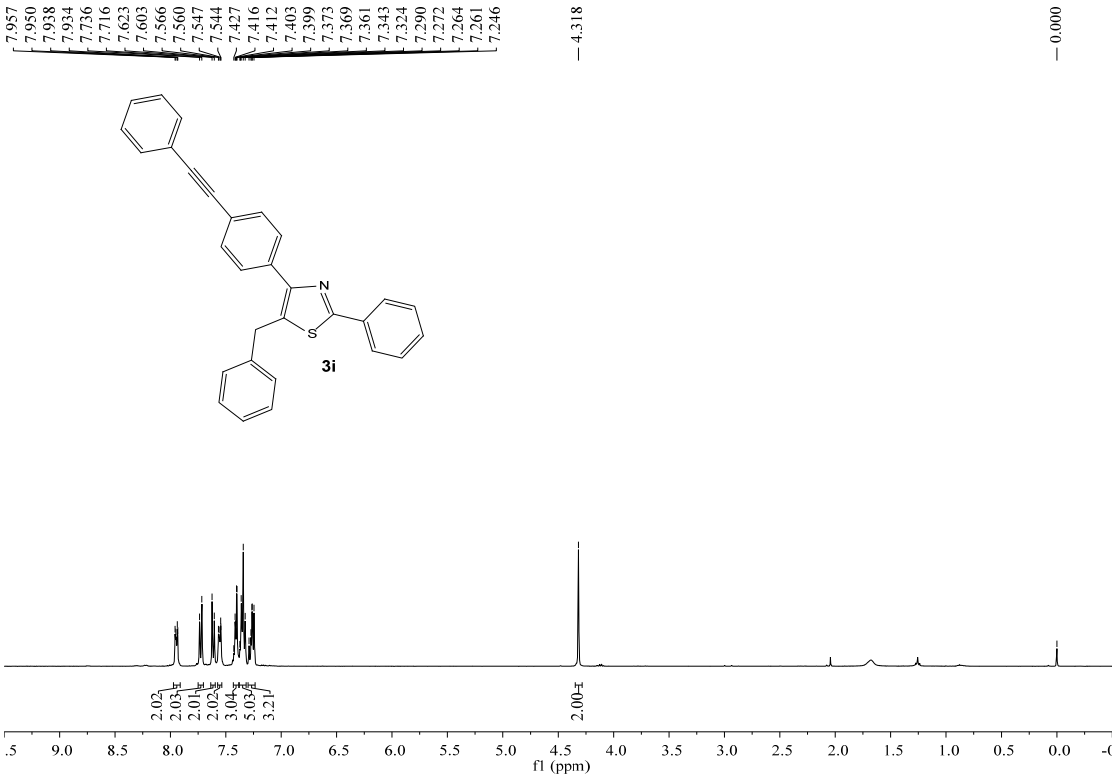


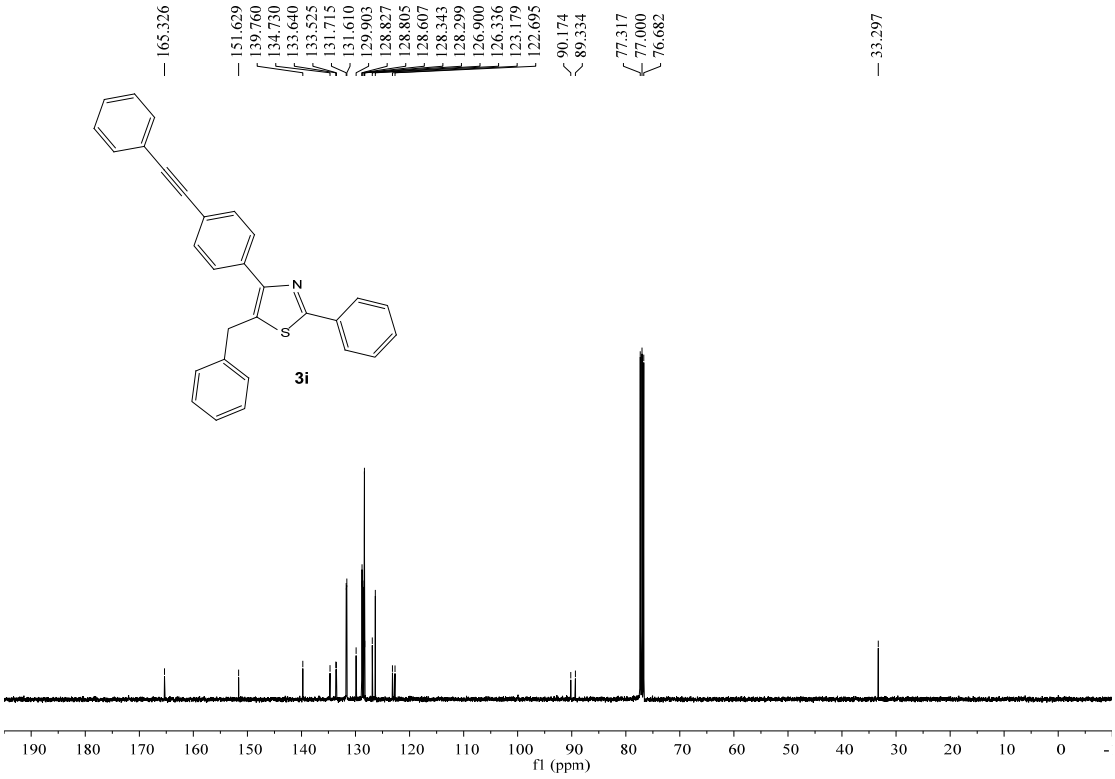
^{1}H and ^{13}C NMR spectra of 3h



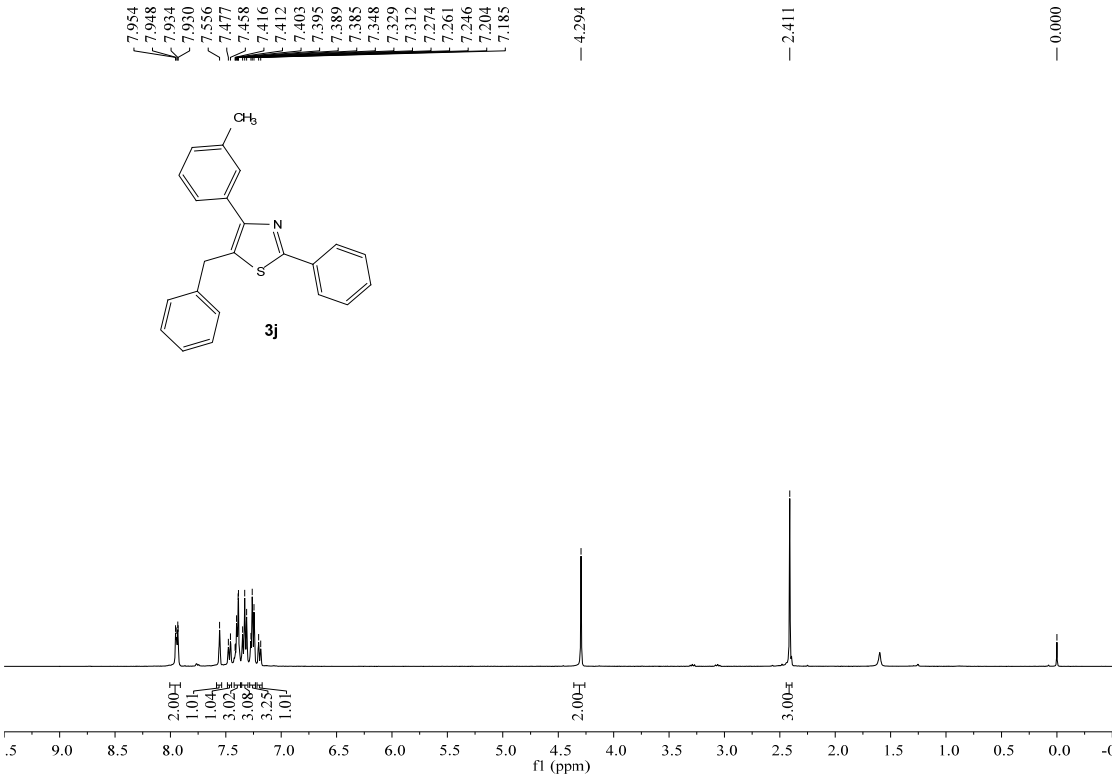


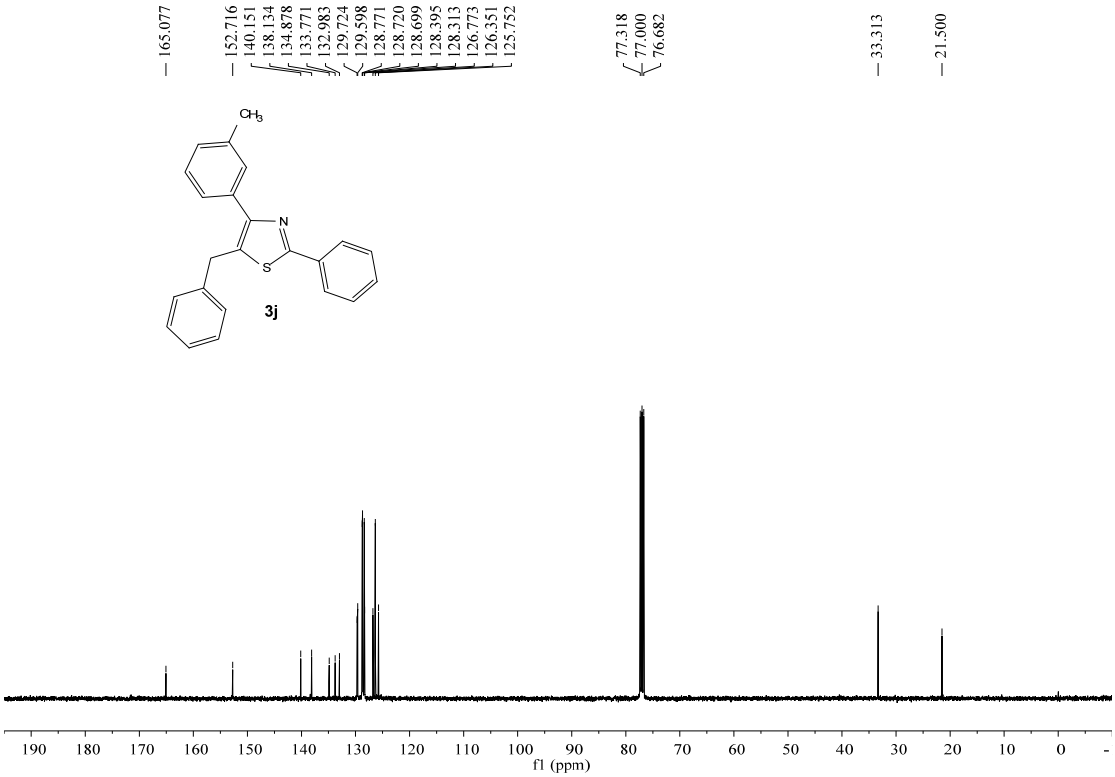
^{1}H and ^{13}C NMR spectra of 3i



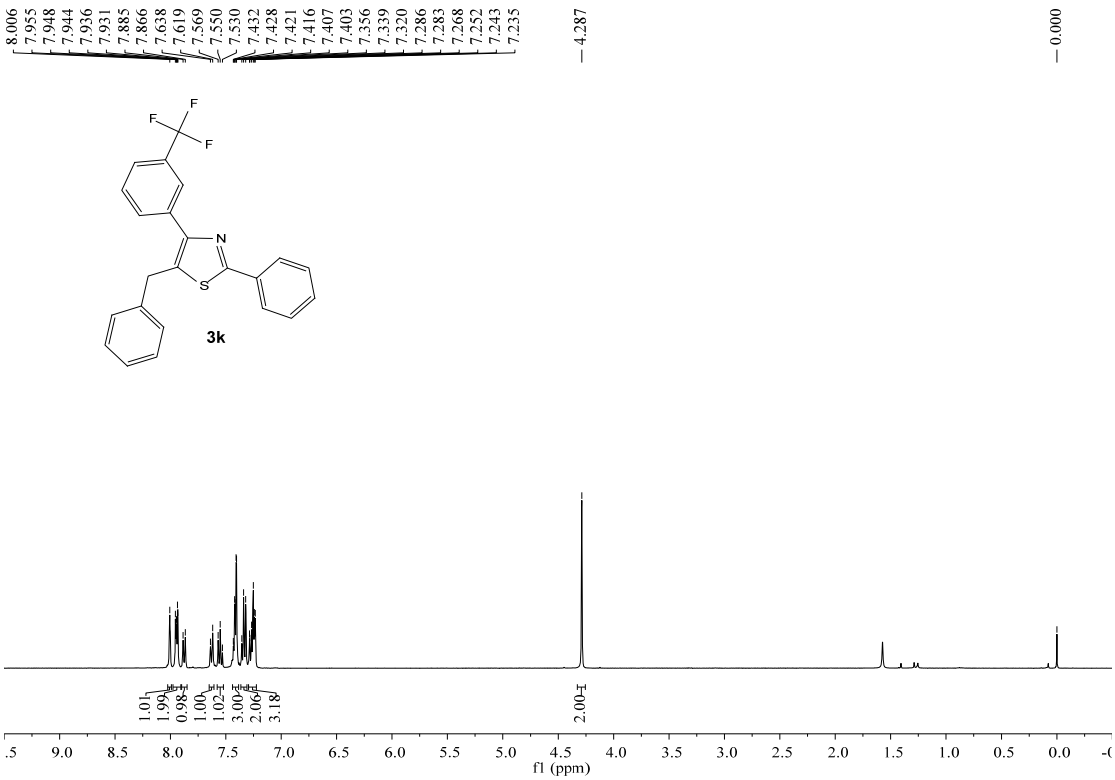


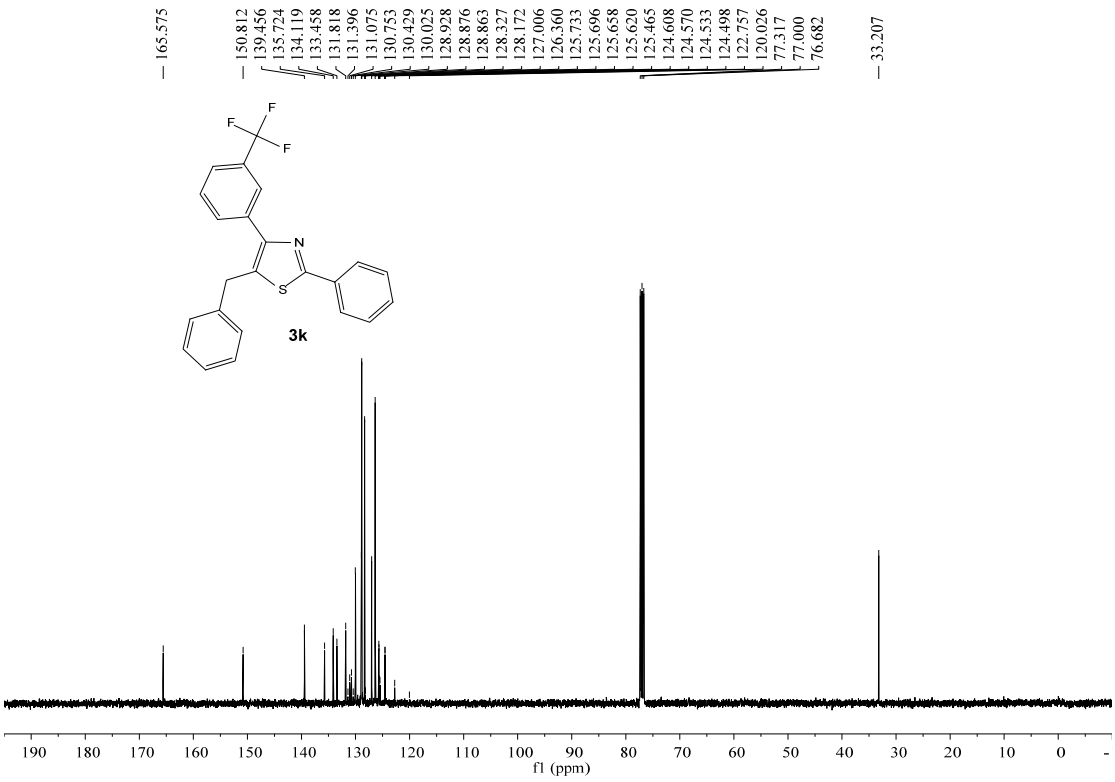
^{1}H and ^{13}C NMR spectra of 3j



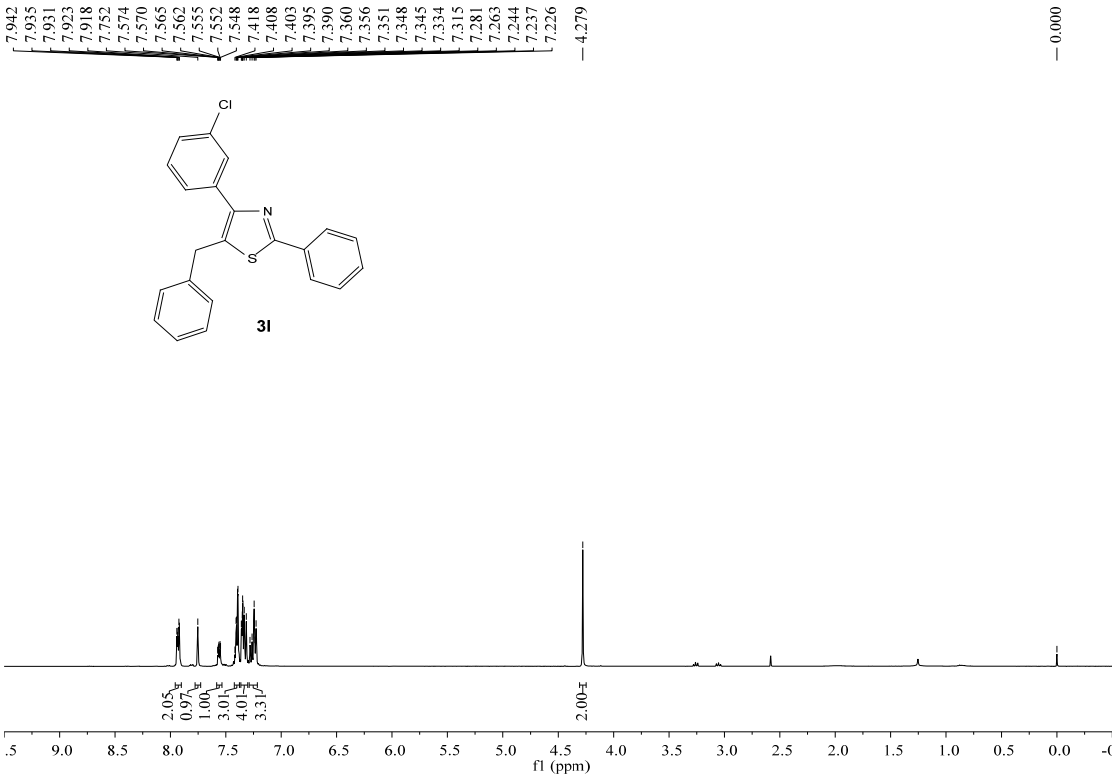


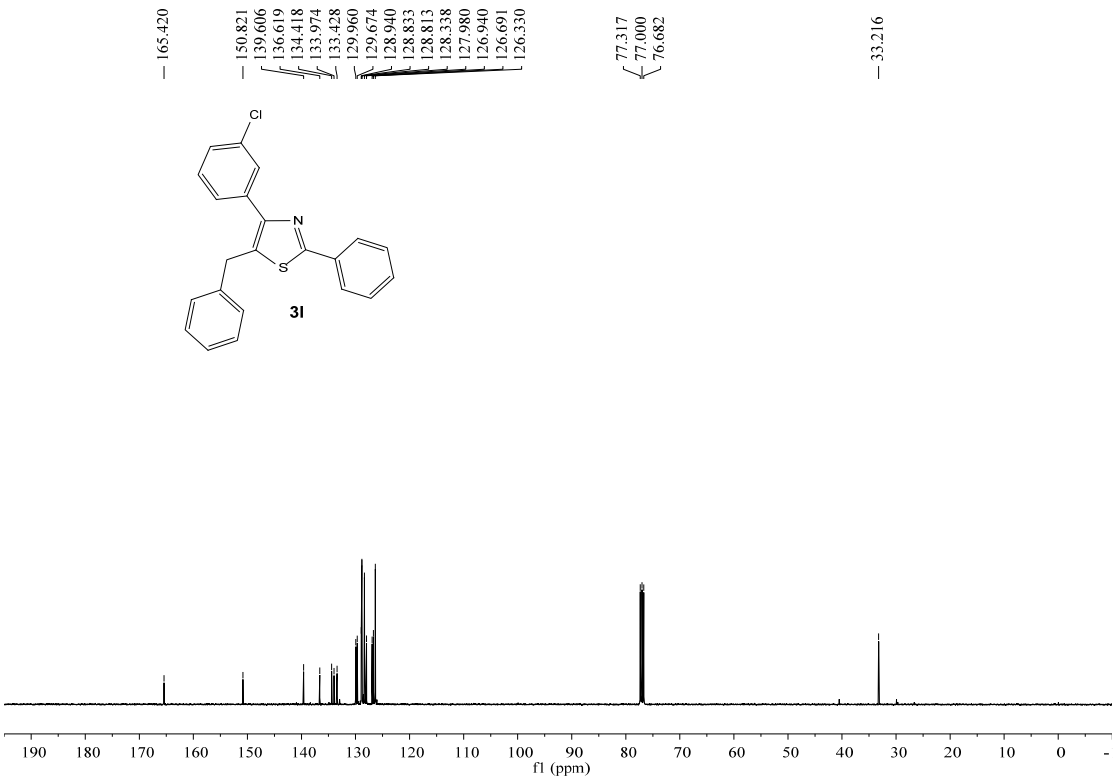
^{1}H and ^{13}C NMR spectra of 3k



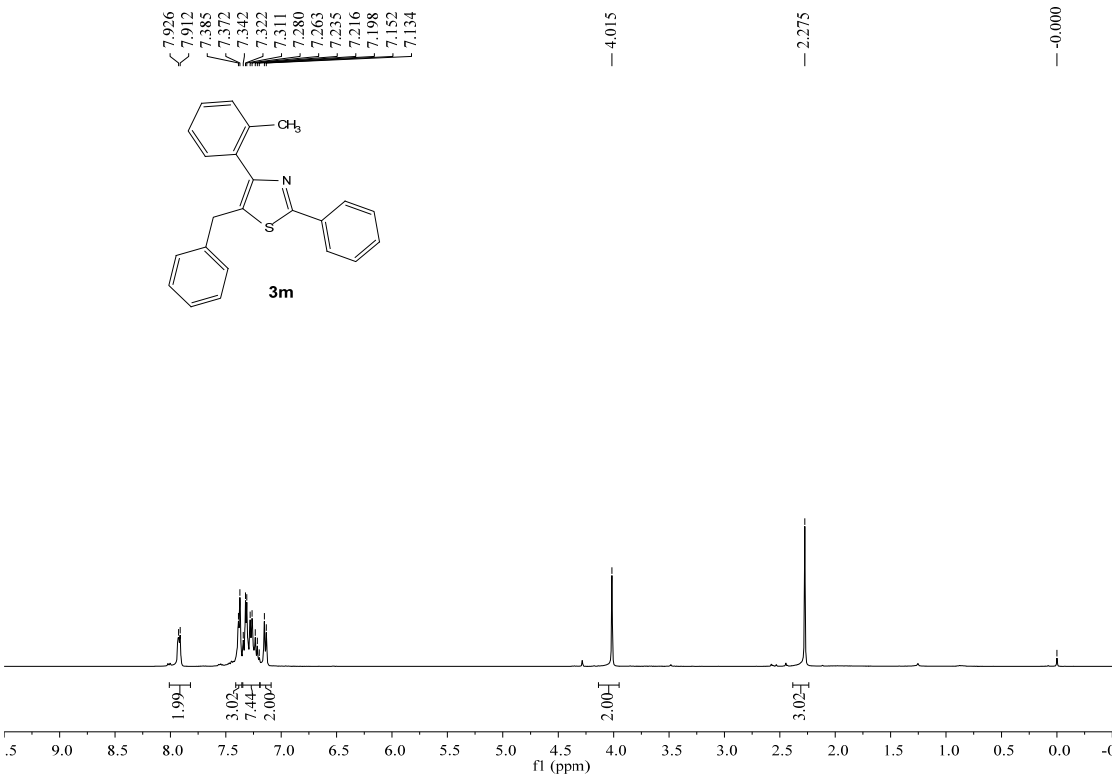


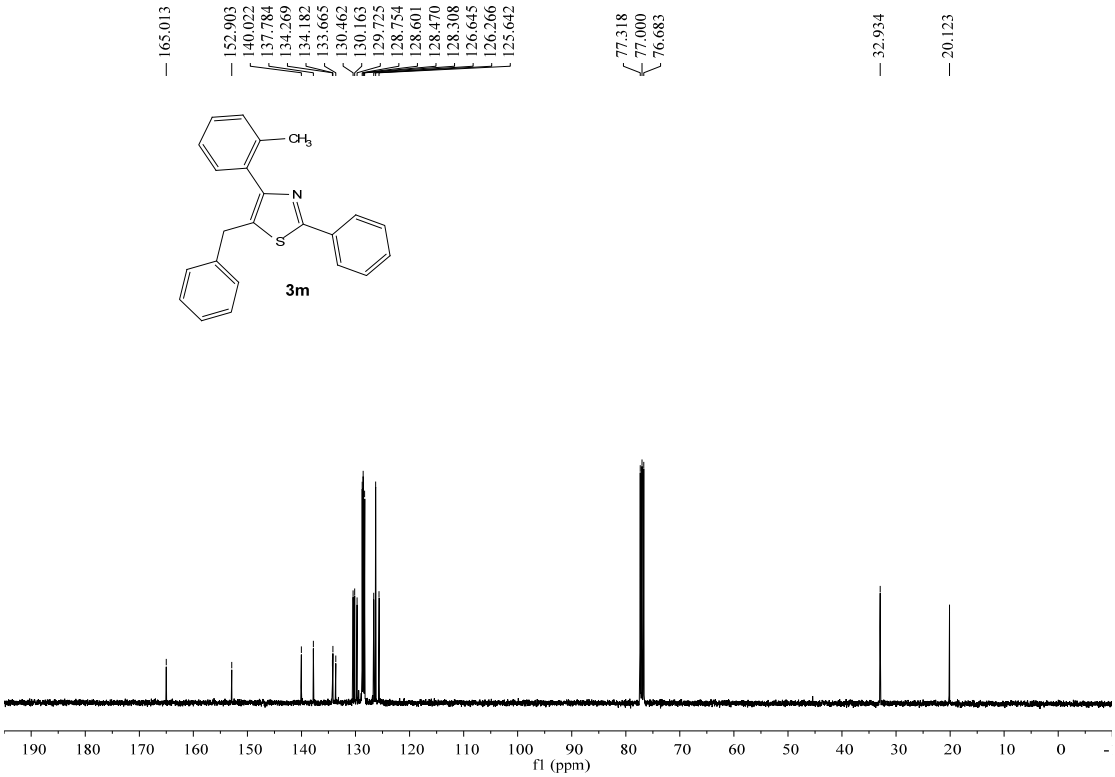
^{1}H and ^{13}C NMR spectra of 3l



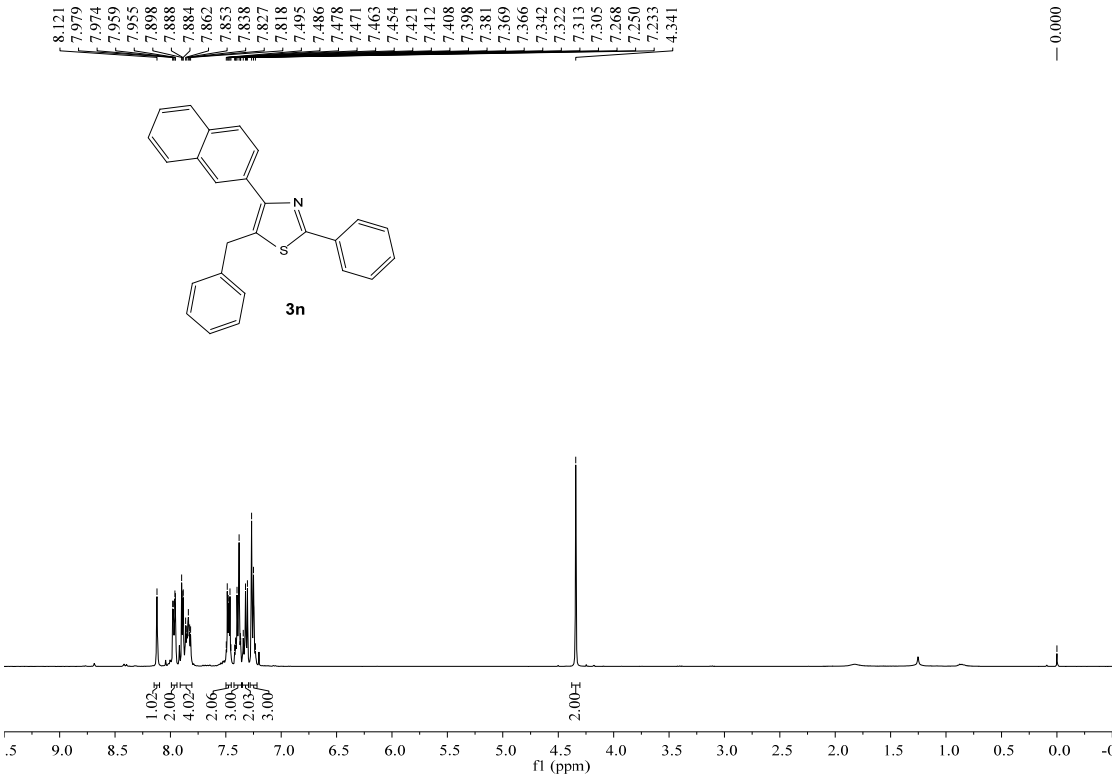


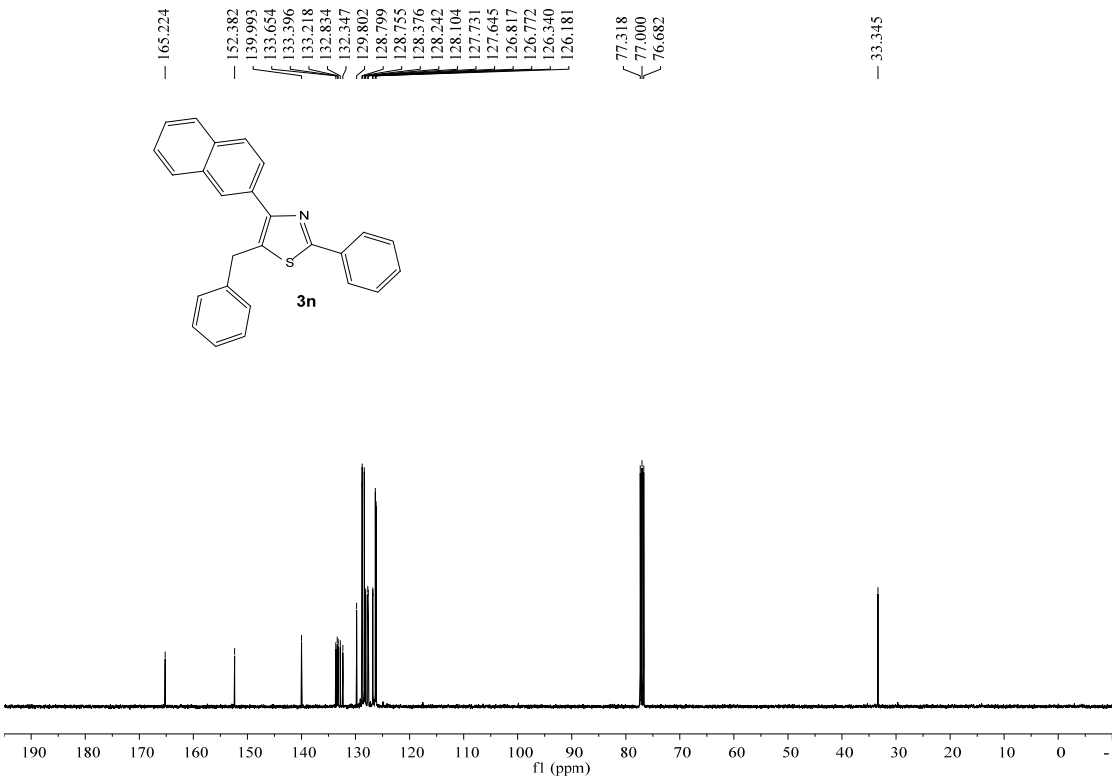
^{1}H and ^{13}C NMR spectra of 3m



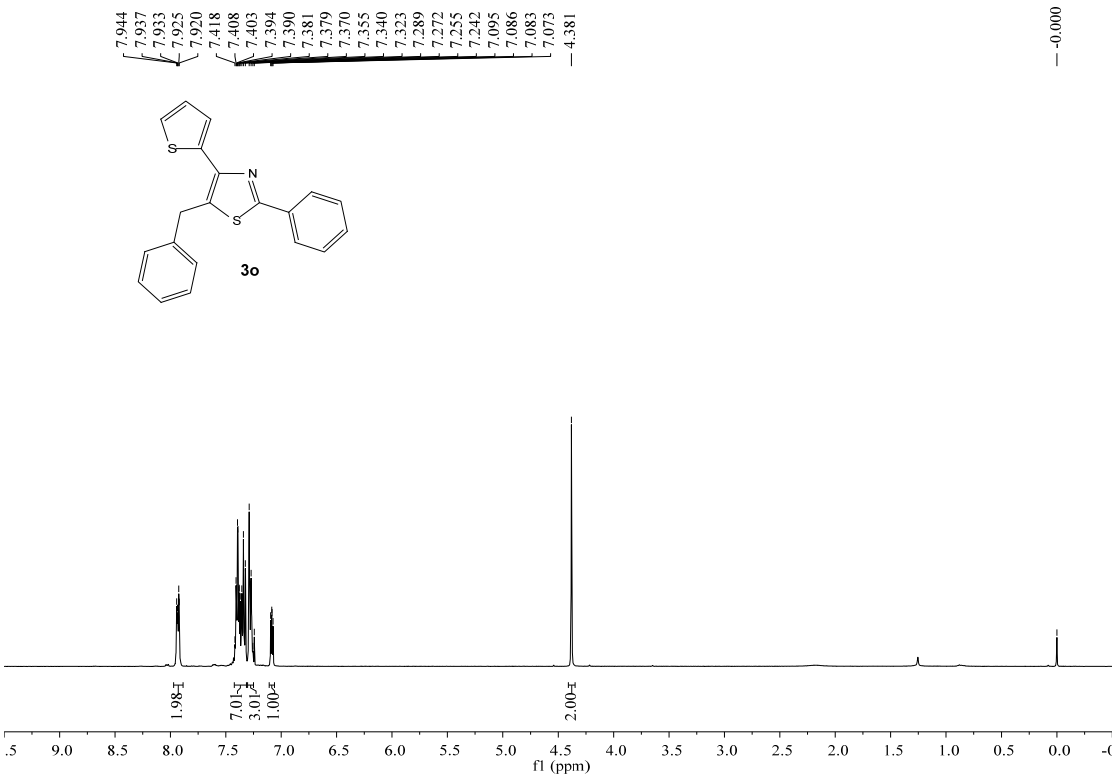


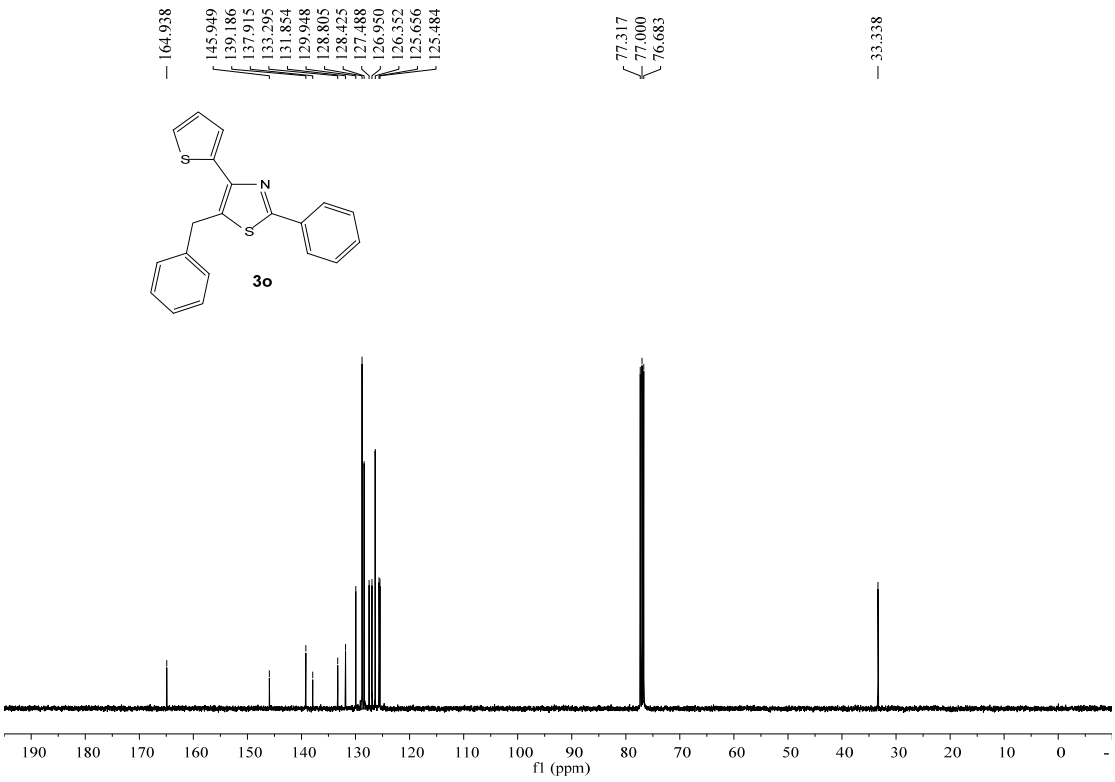
^{1}H and ^{13}C NMR spectra of 3n



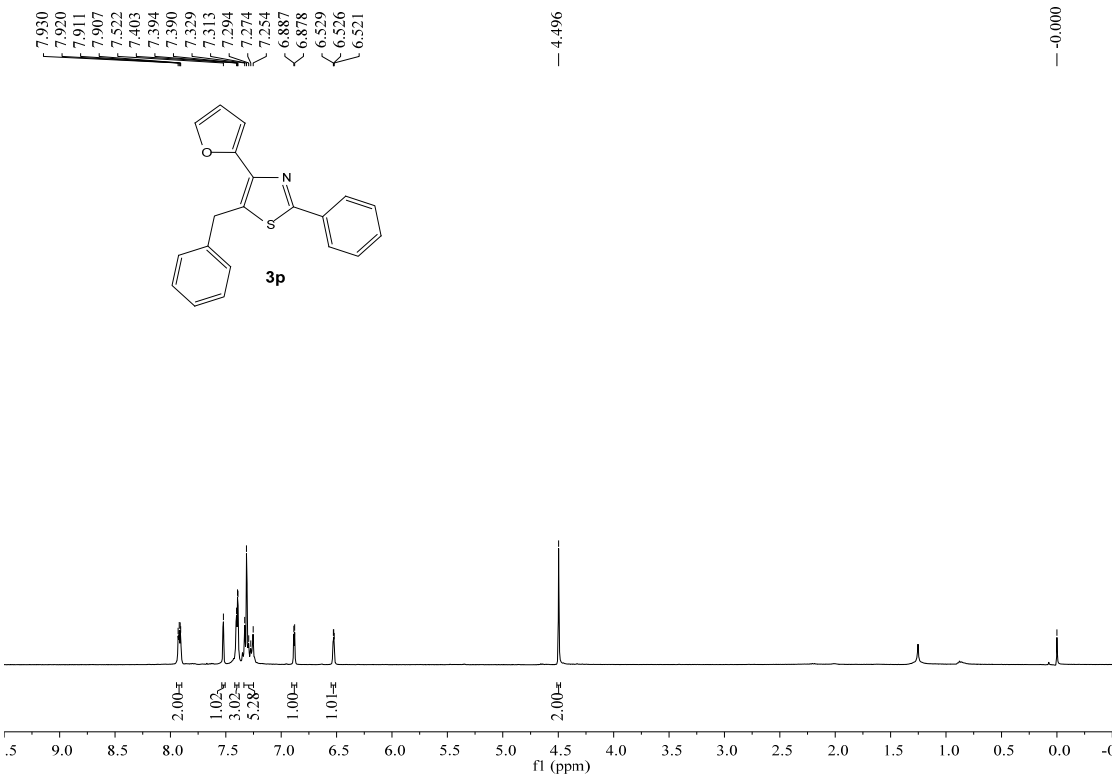


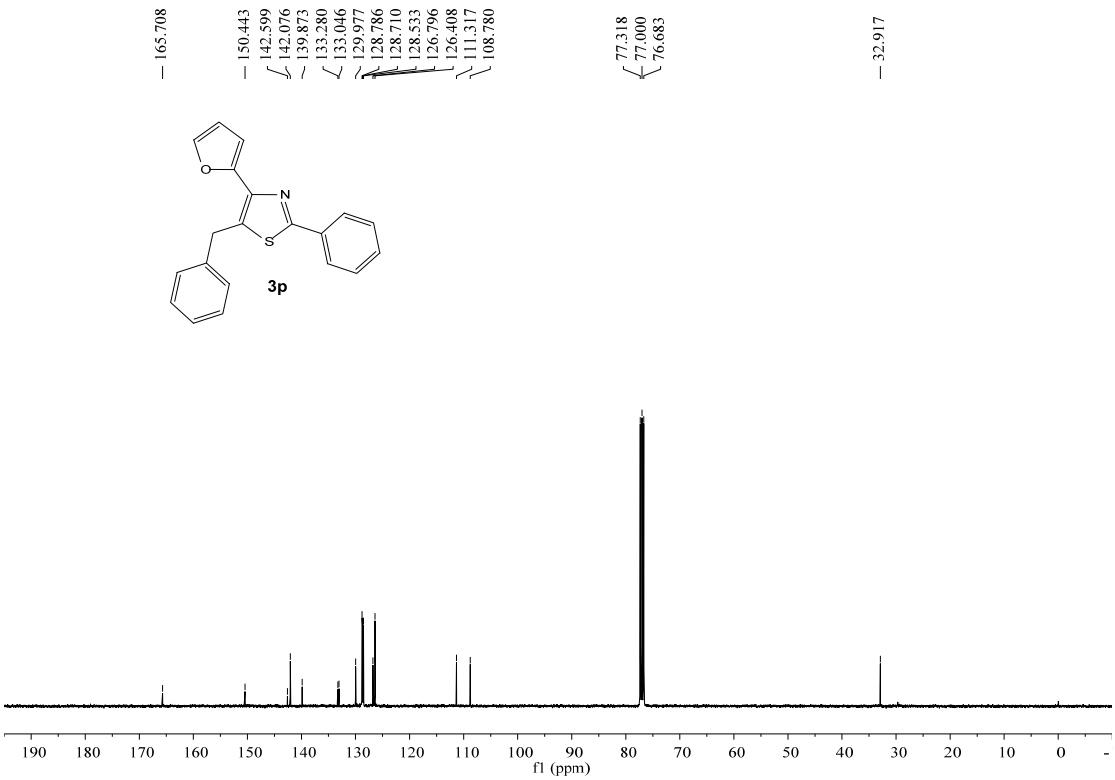
^{1}H and ^{13}C NMR spectra of 3o



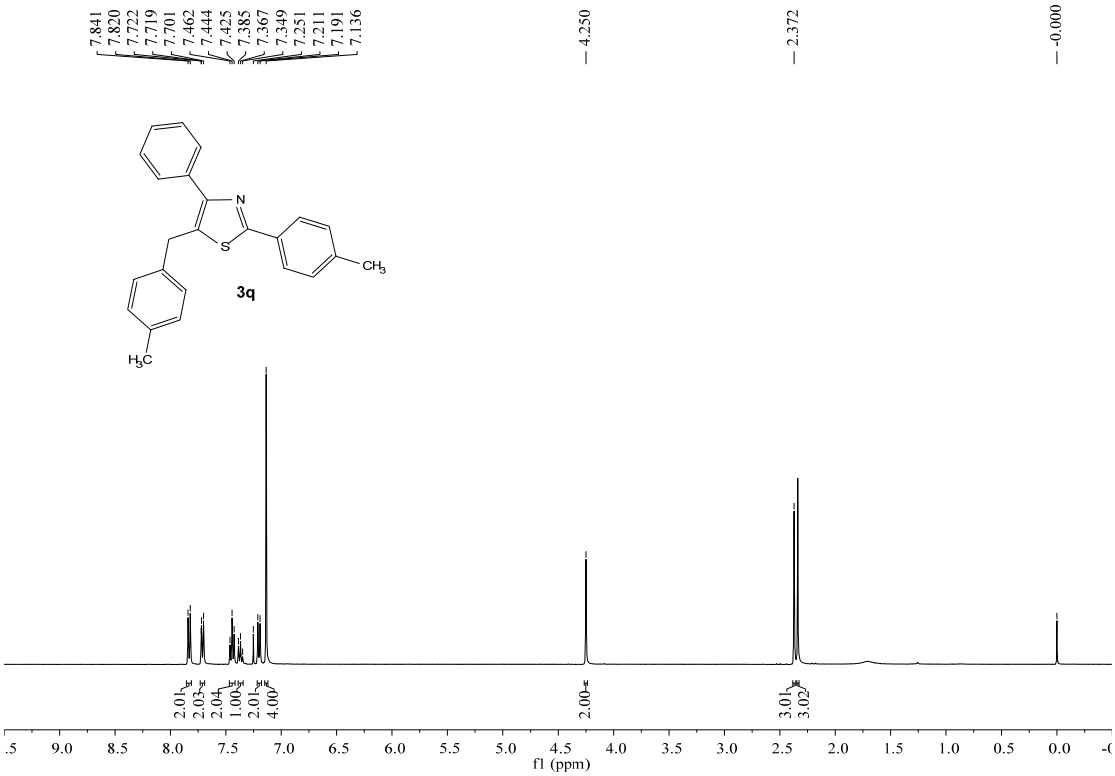


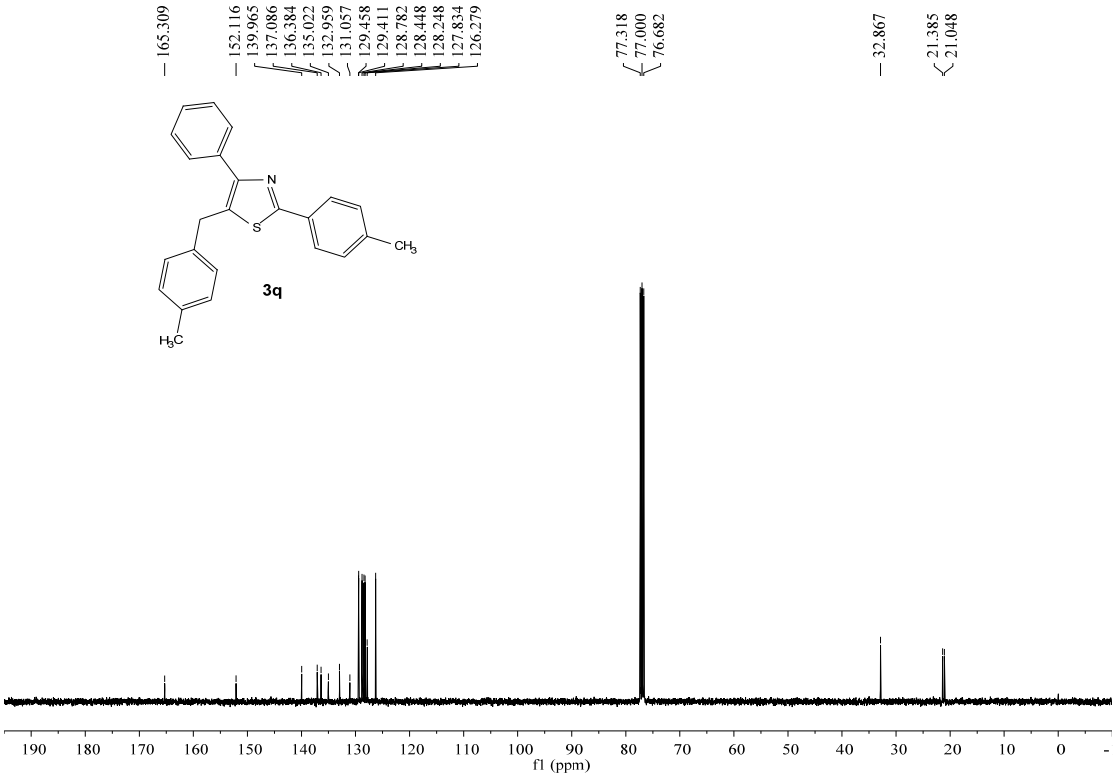
^{1}H and ^{13}C NMR spectra of 3p



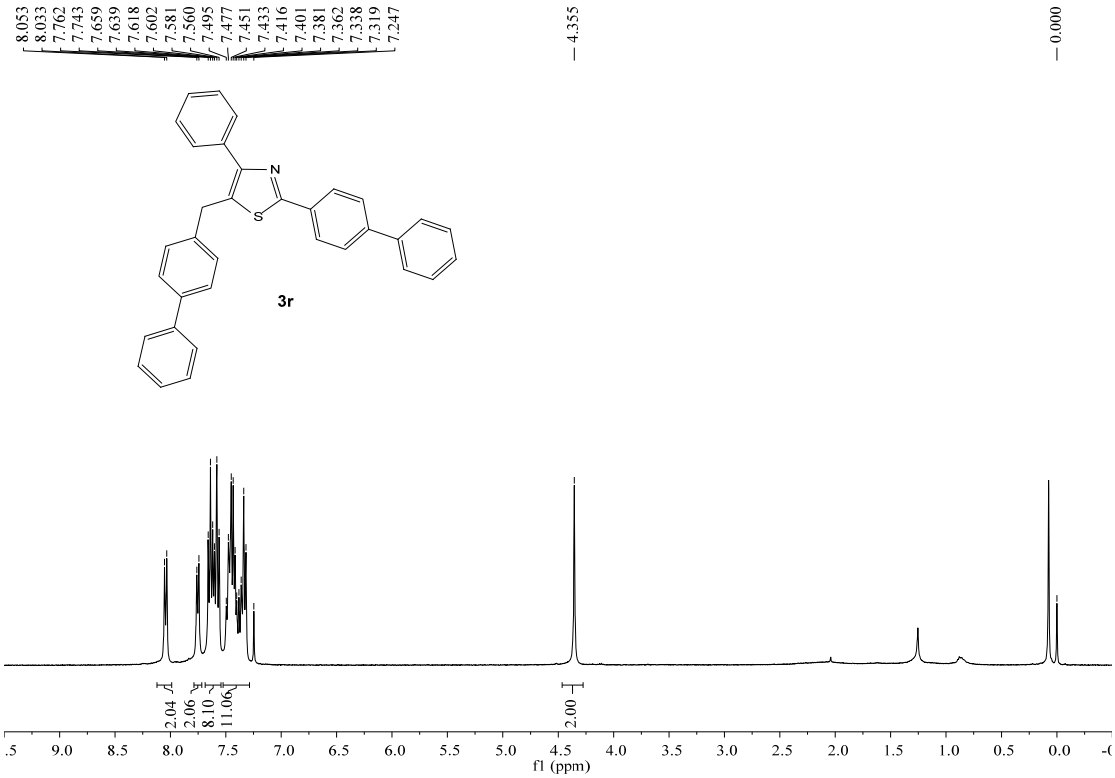


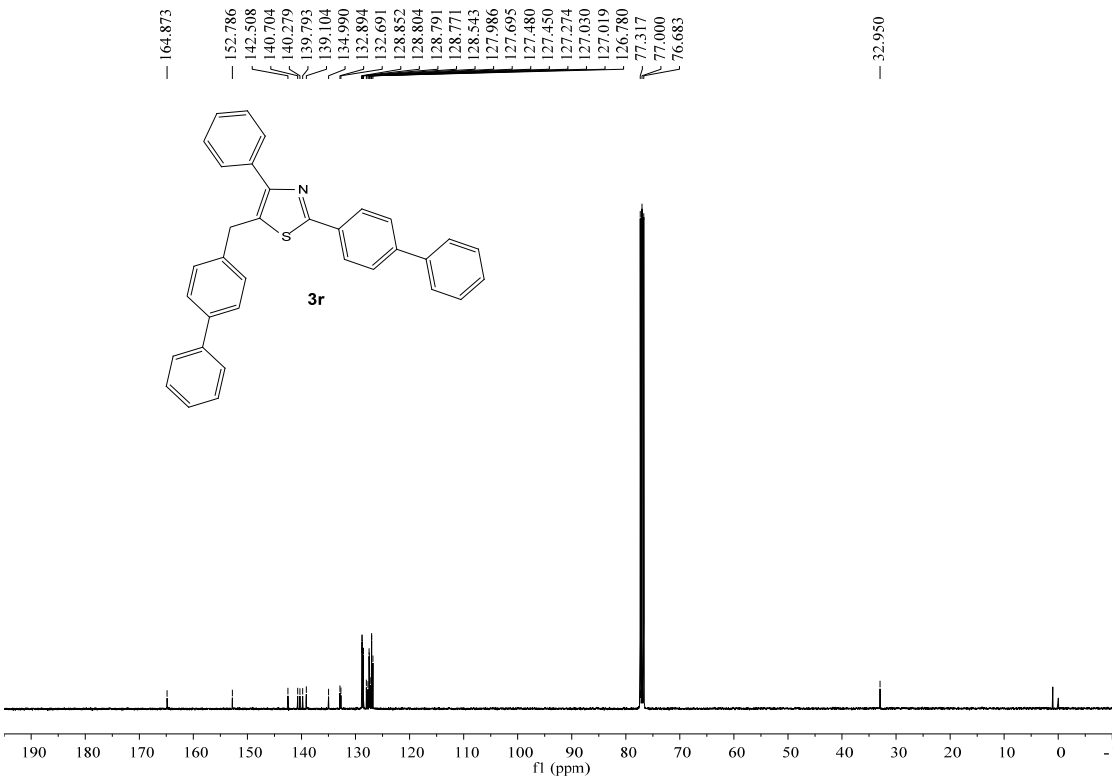
^{1}H and ^{13}C NMR spectra of 3q



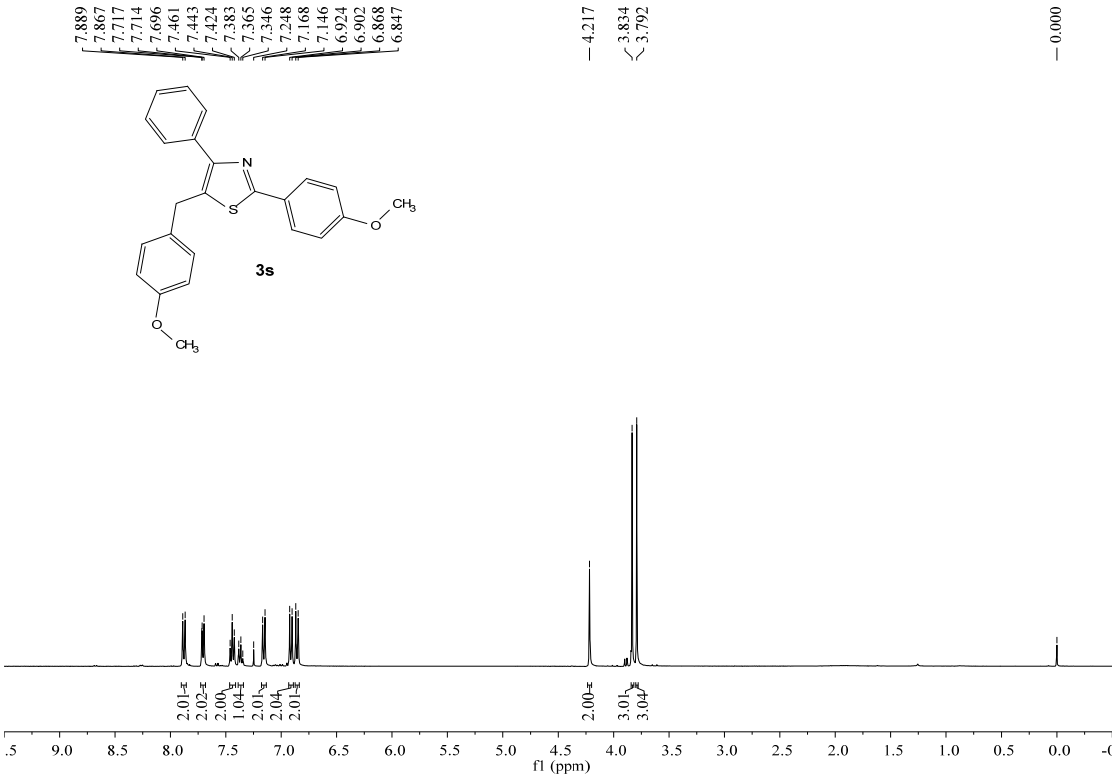


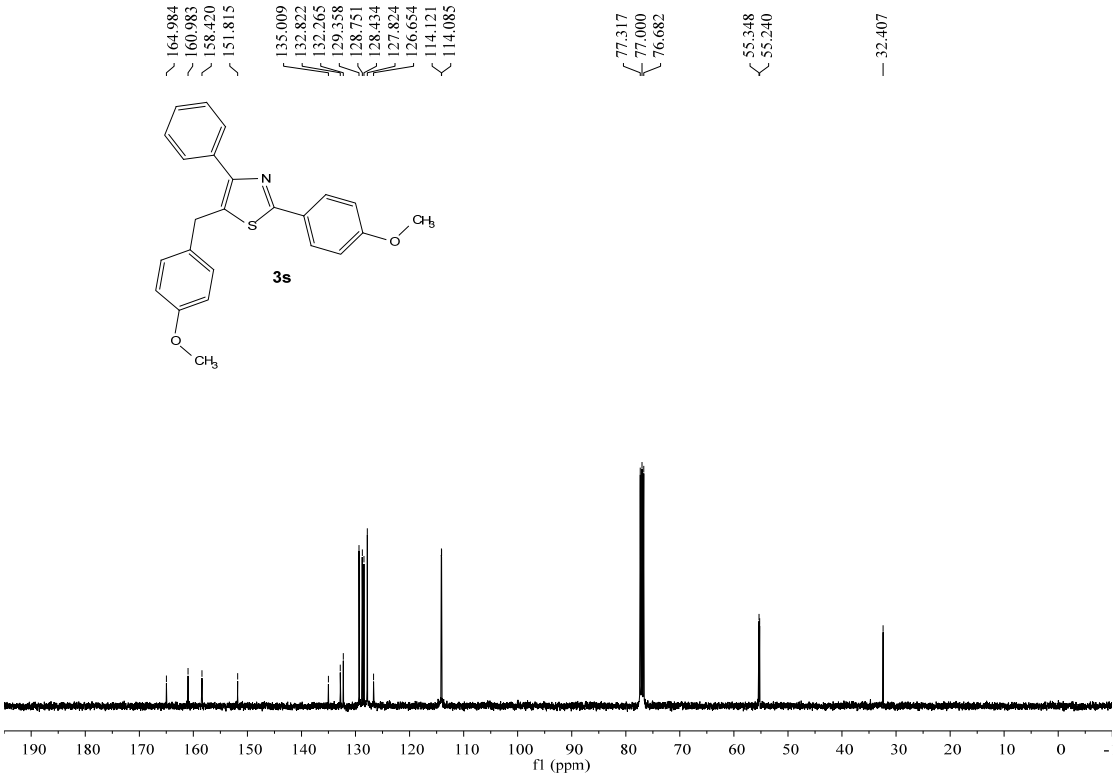
^{1}H and ^{13}C NMR spectra of 3r



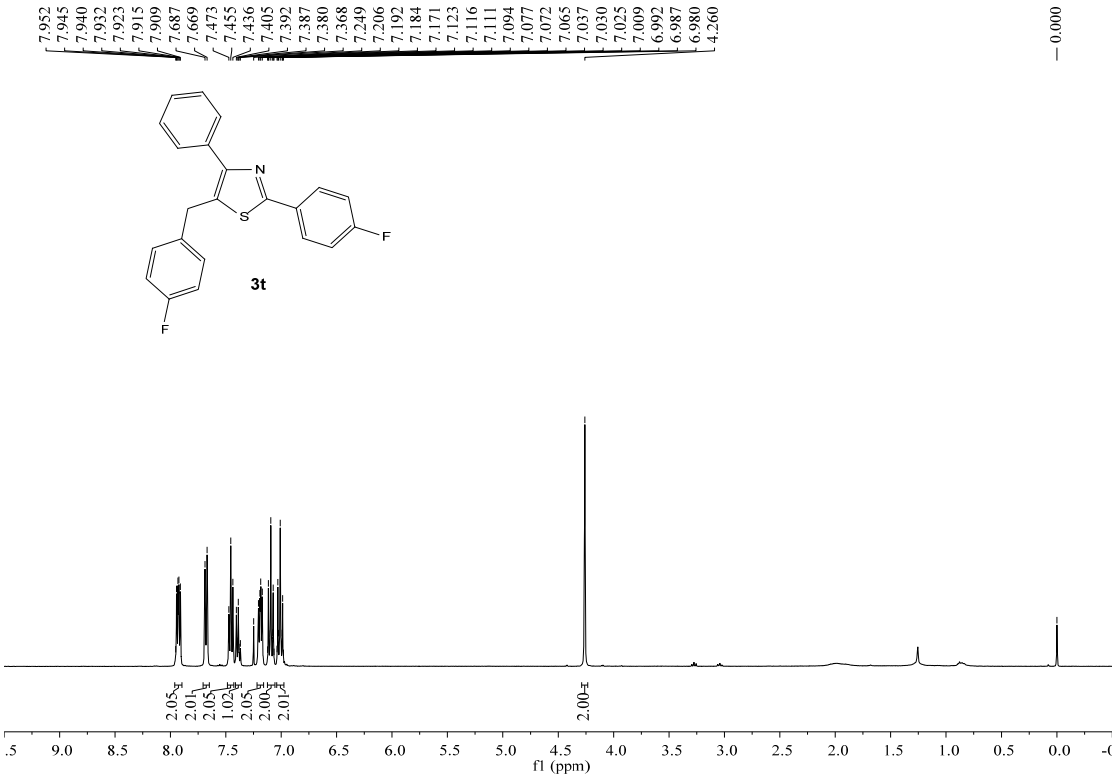


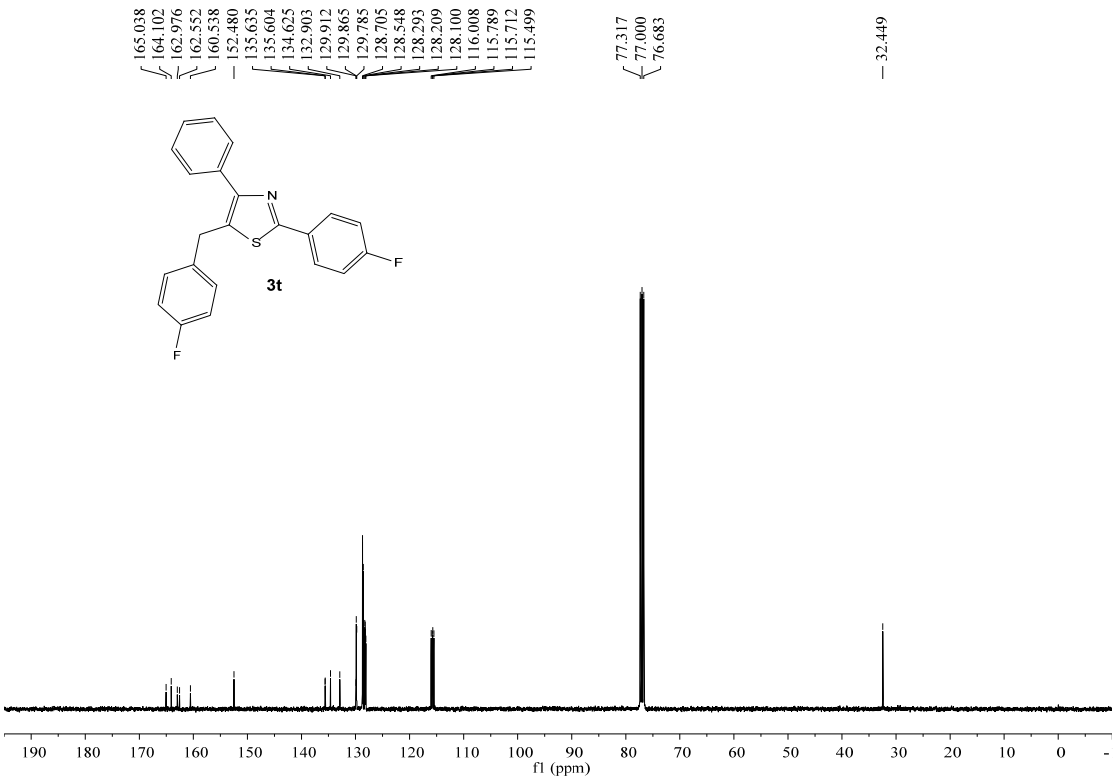
^{1}H and ^{13}C NMR spectra of 3s



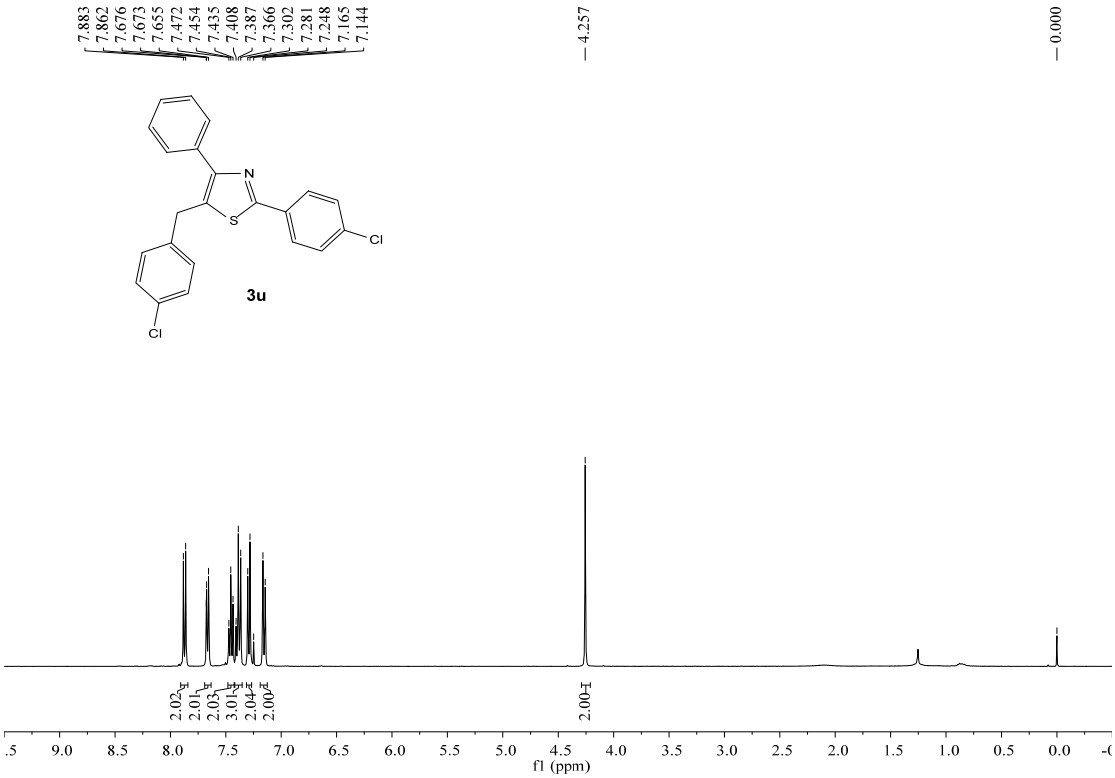


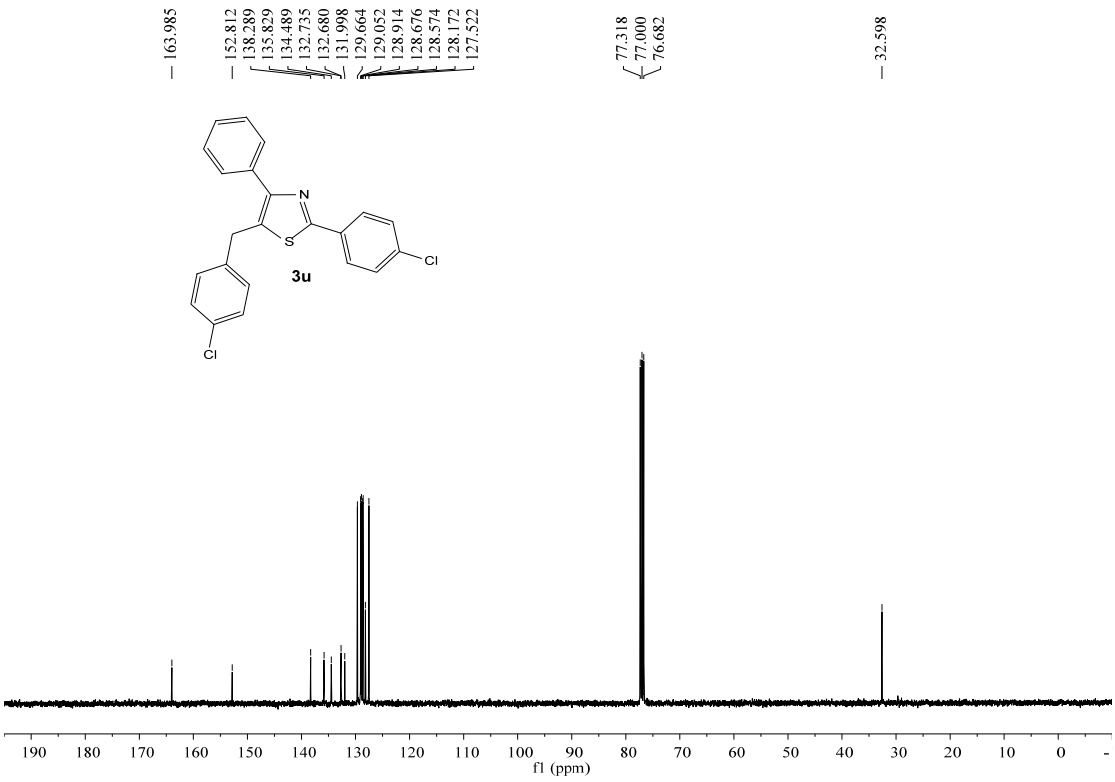
^{1}H and ^{13}C NMR spectra of 3t



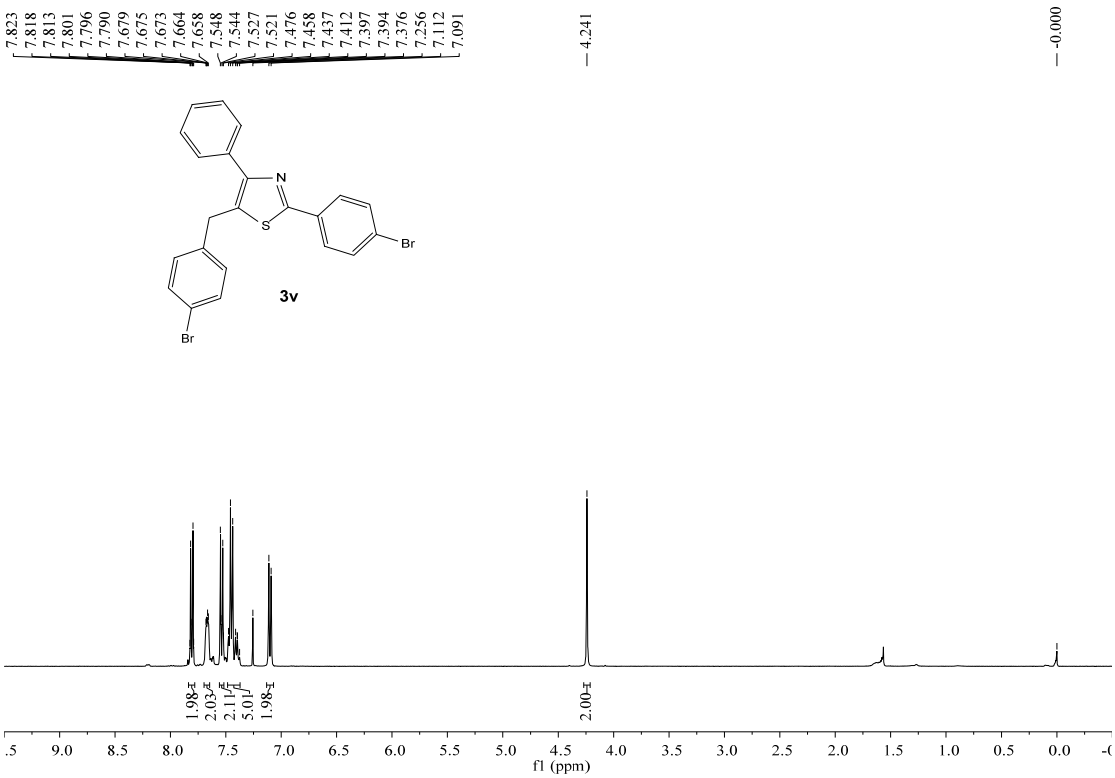


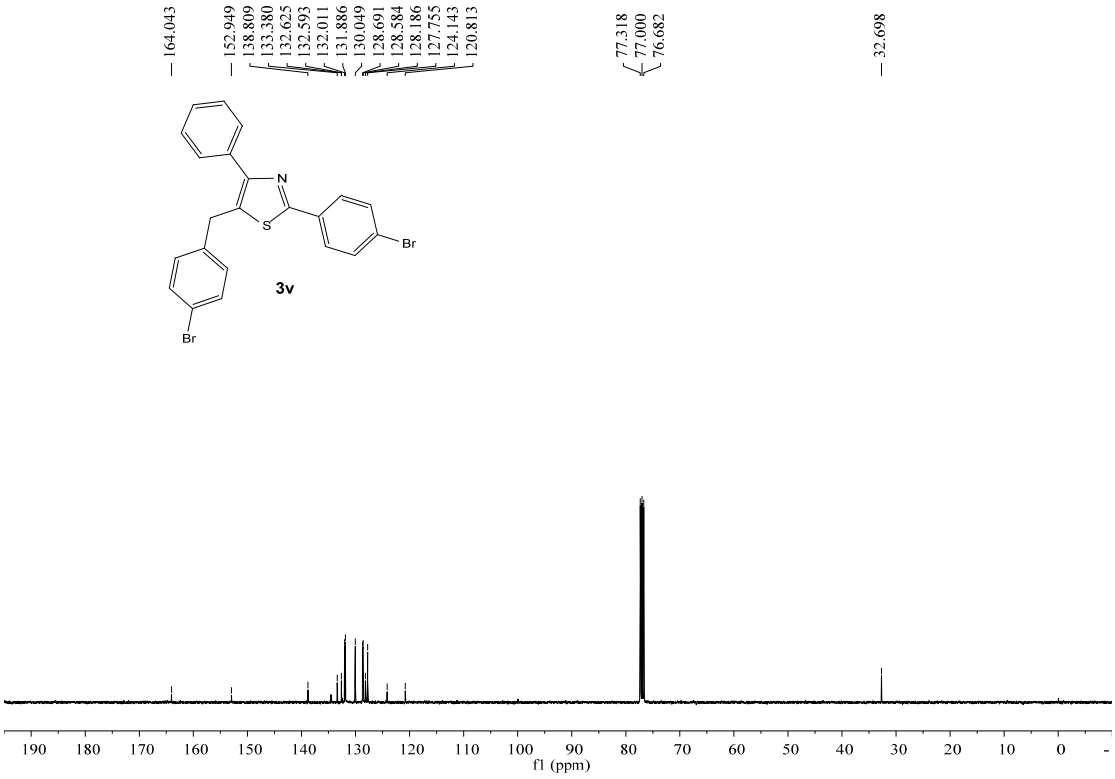
^{1}H and ^{13}C NMR spectra of 3u



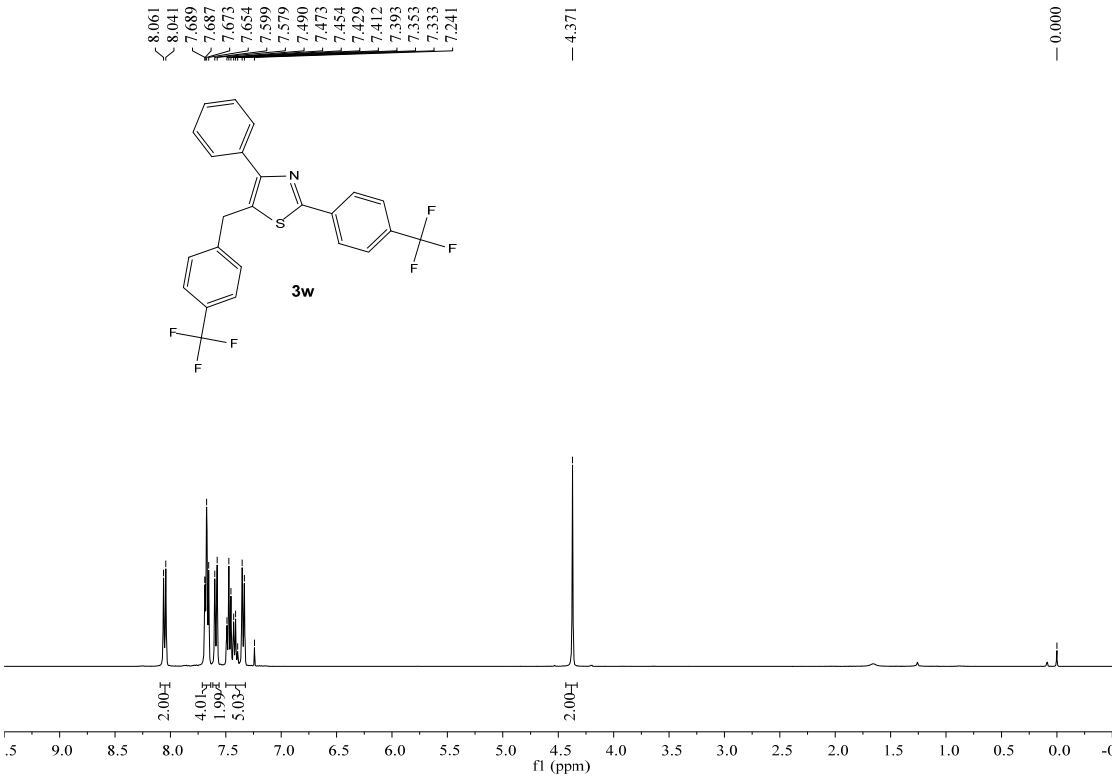


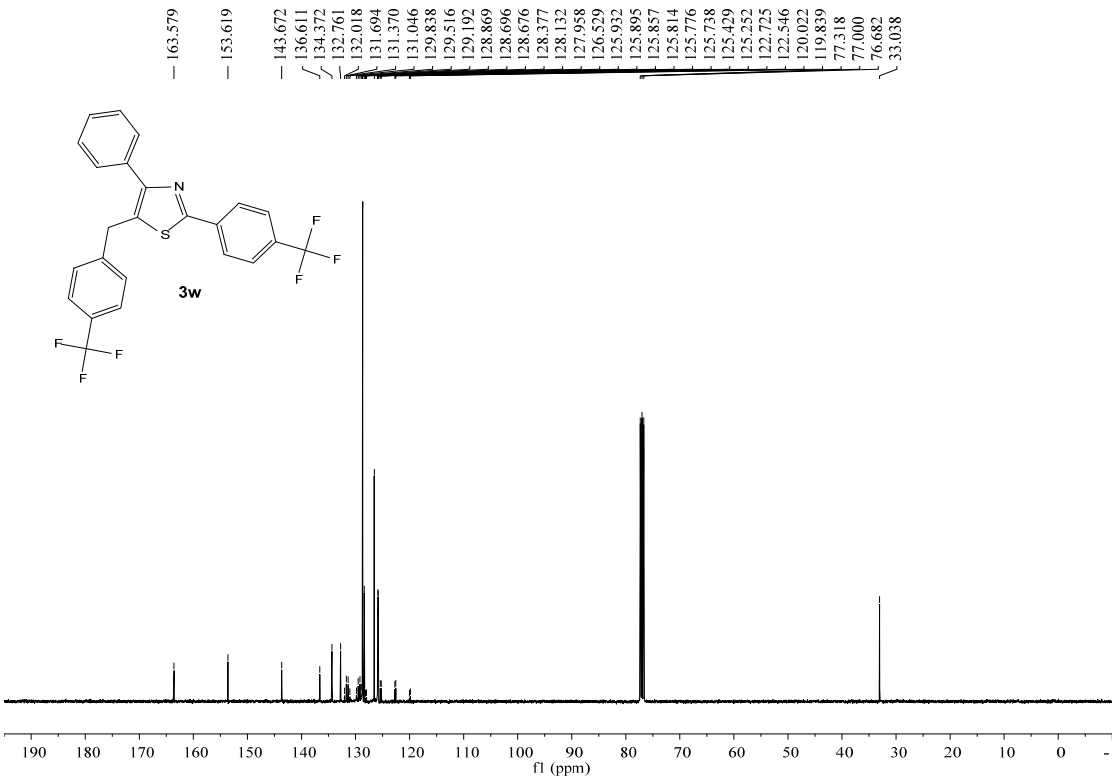
^{1}H and ^{13}C NMR spectra of 3v



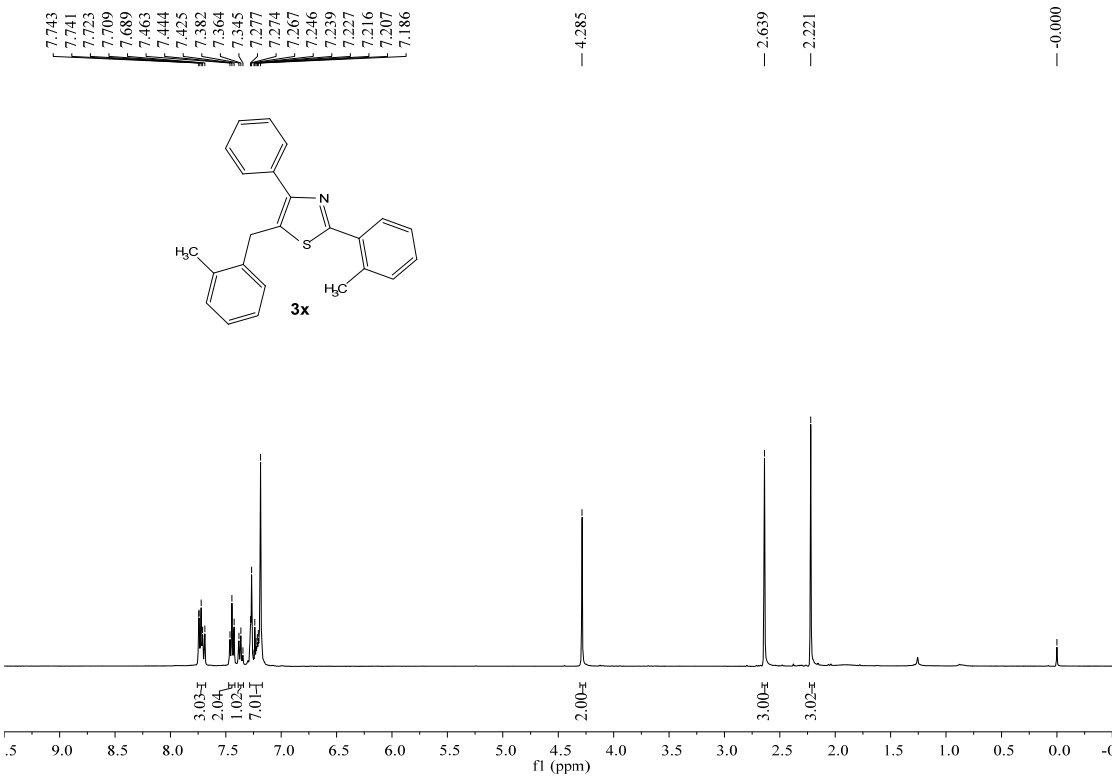


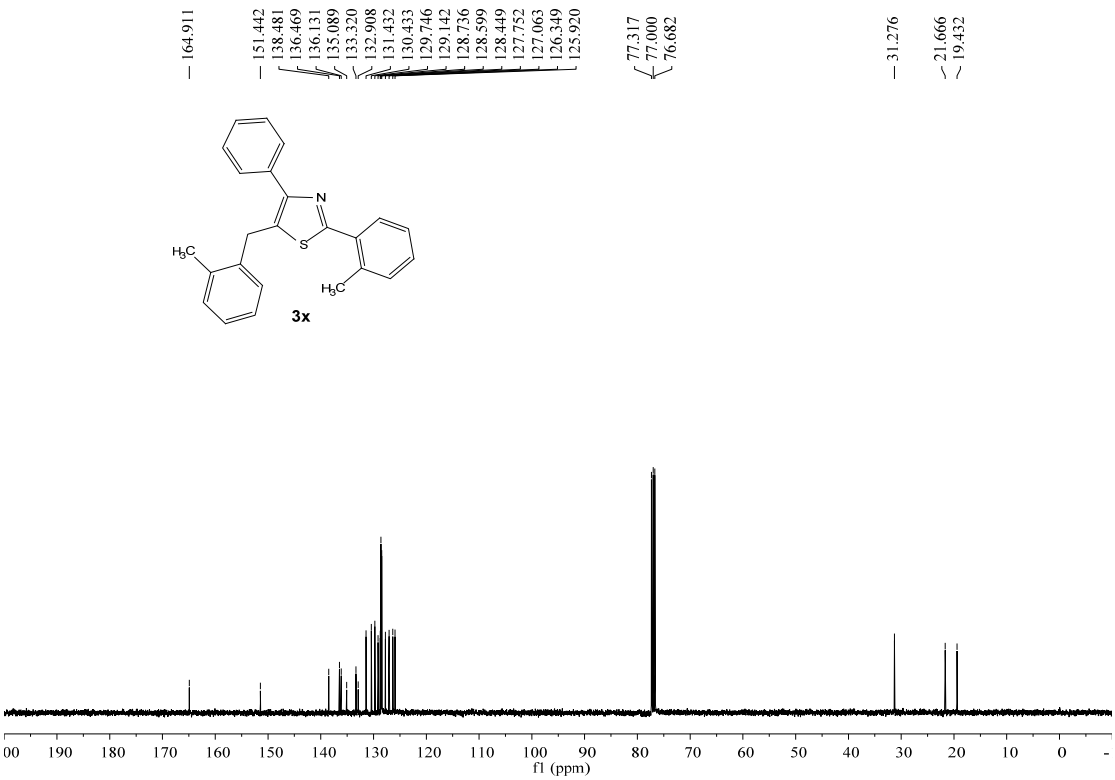
^{1}H and ^{13}C NMR spectra of 3w



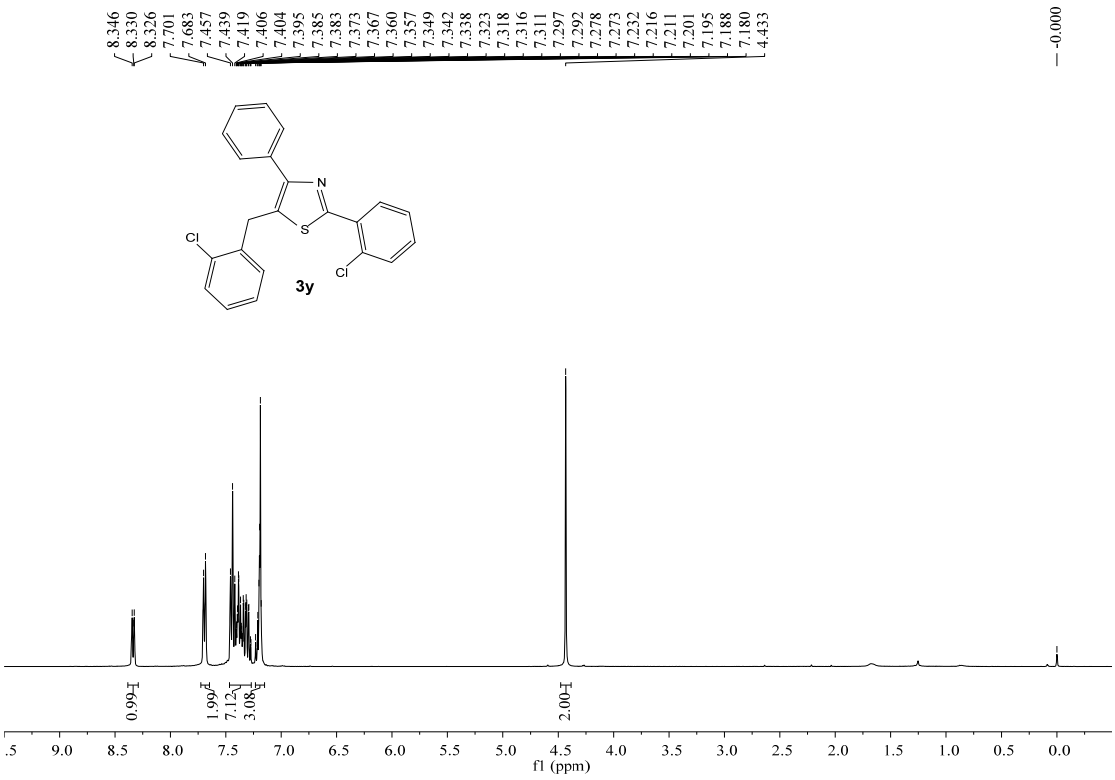


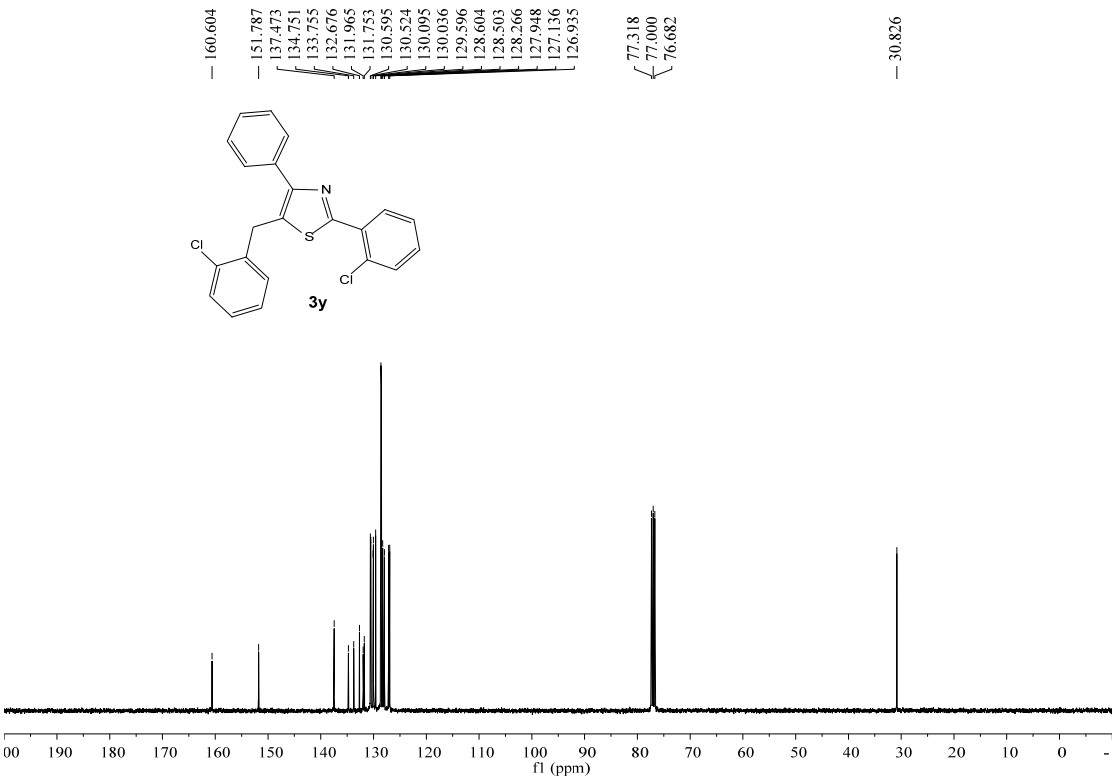
^{1}H and ^{13}C NMR spectra of 3x



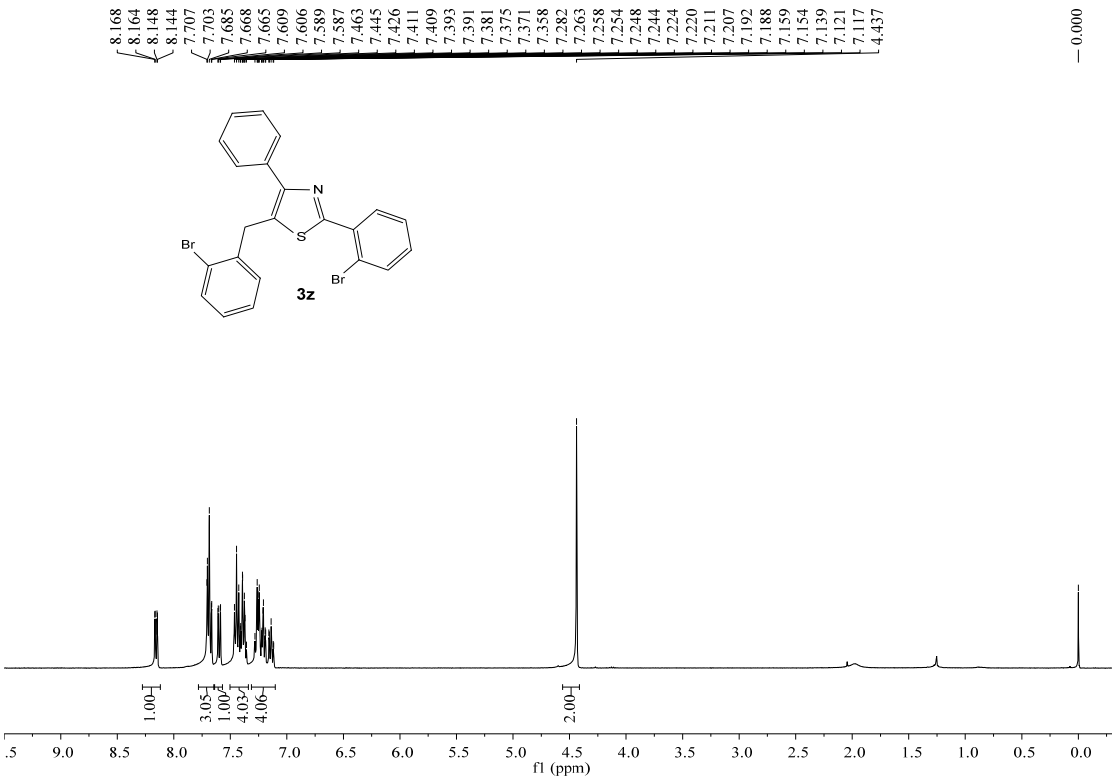


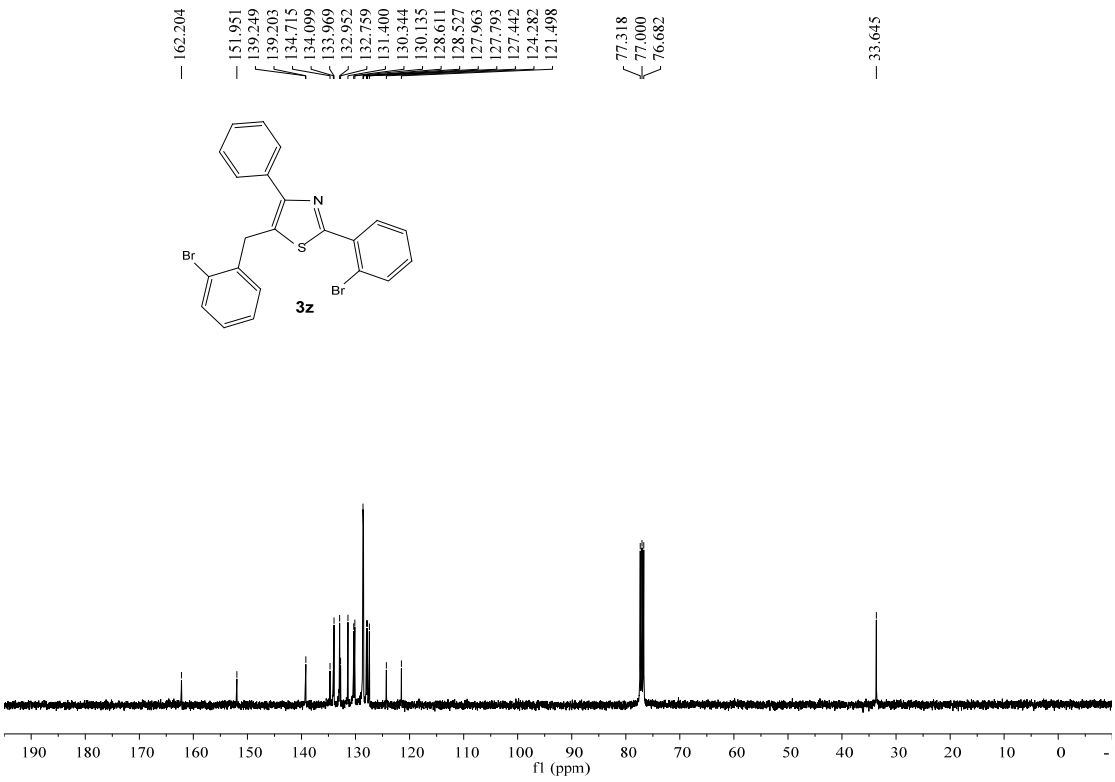
^{1}H and ^{13}C NMR spectra of 3y



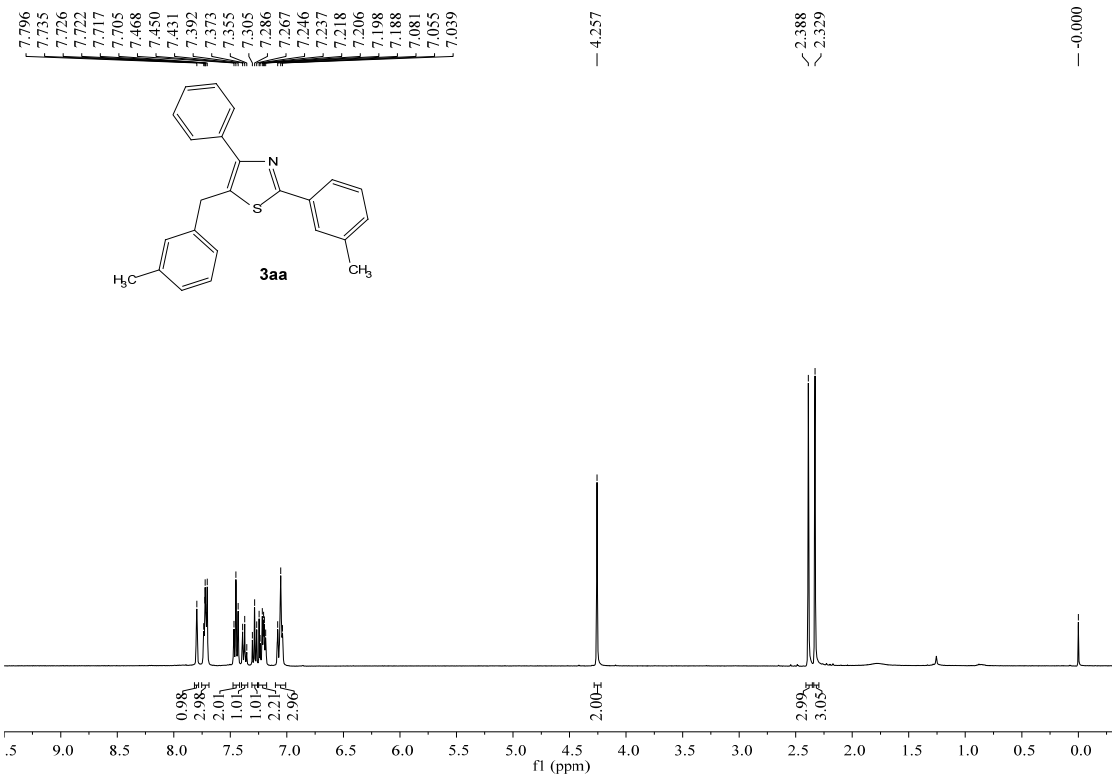


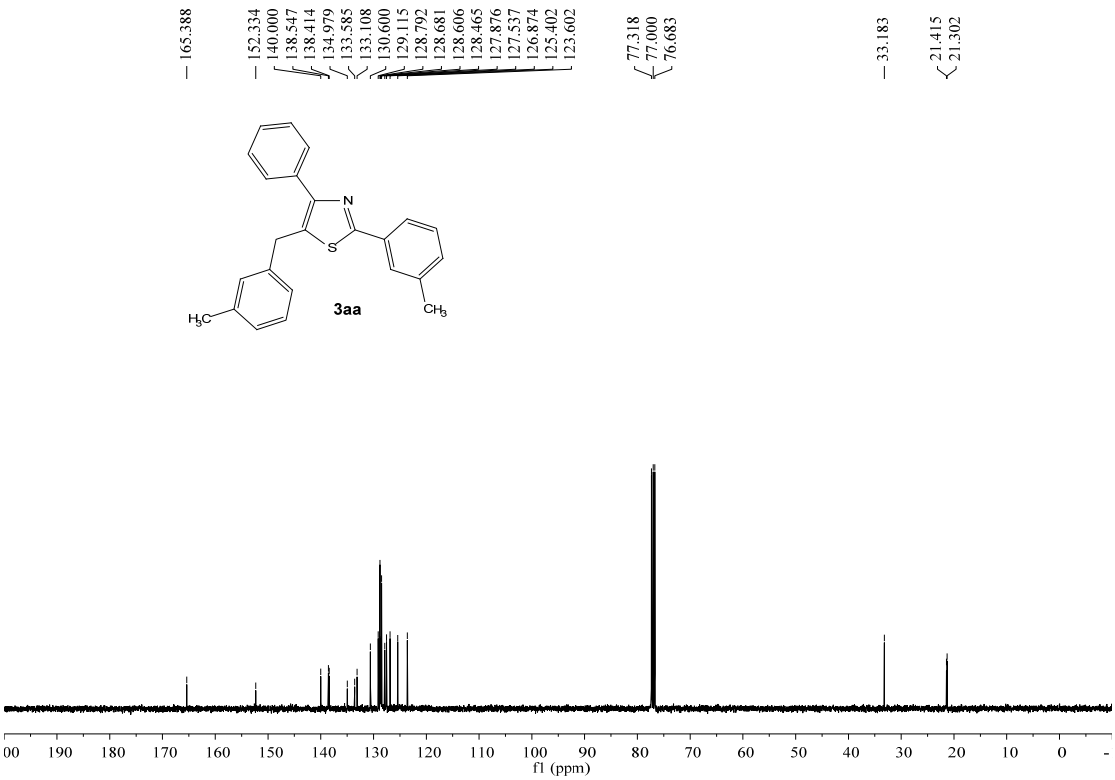
^{1}H and ^{13}C NMR spectra of 3z



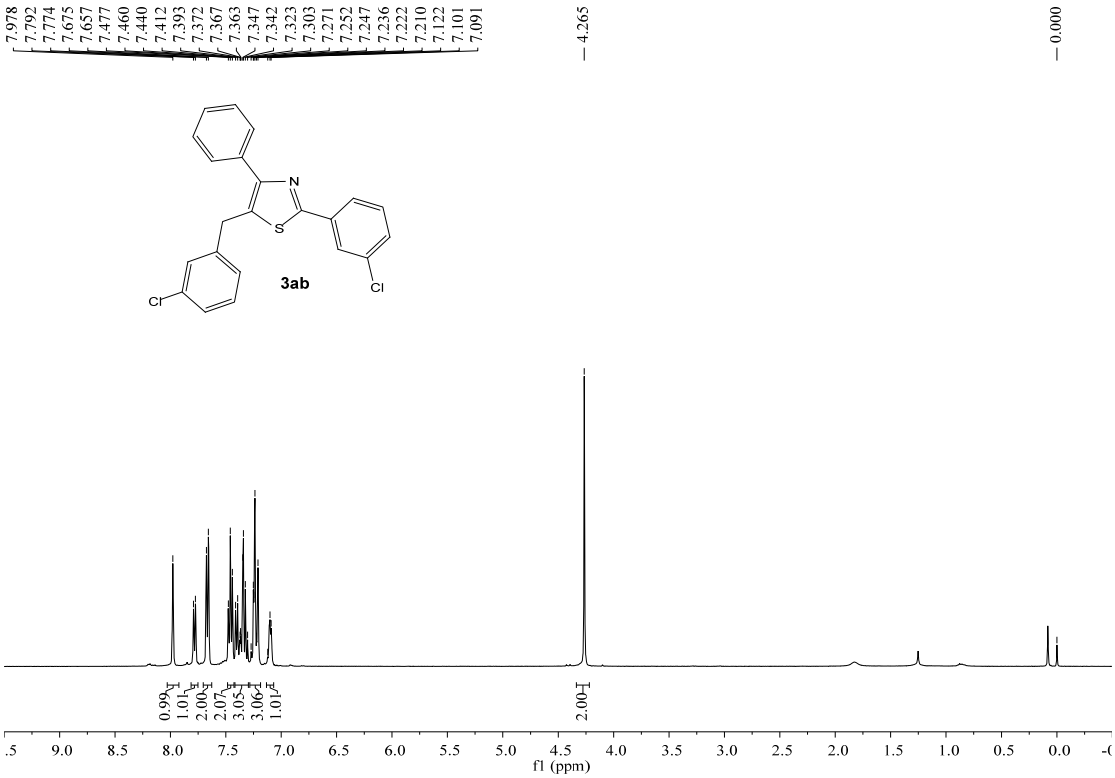


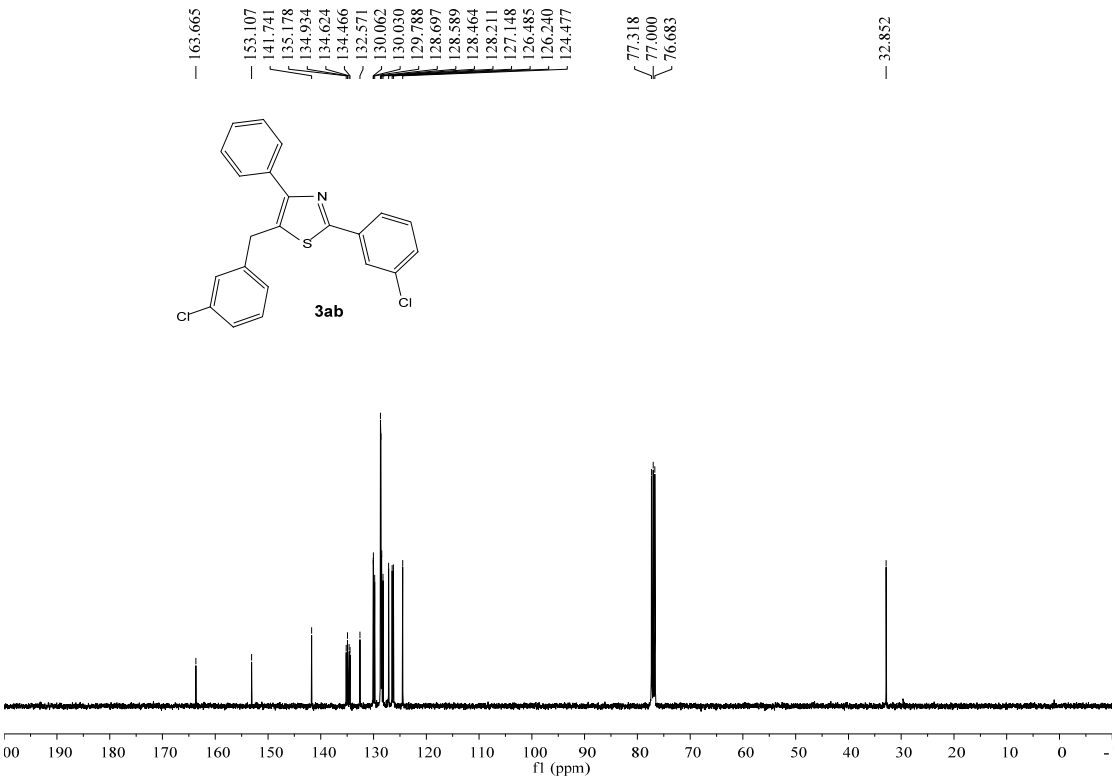
^{1}H and ^{13}C NMR spectra of 3aa



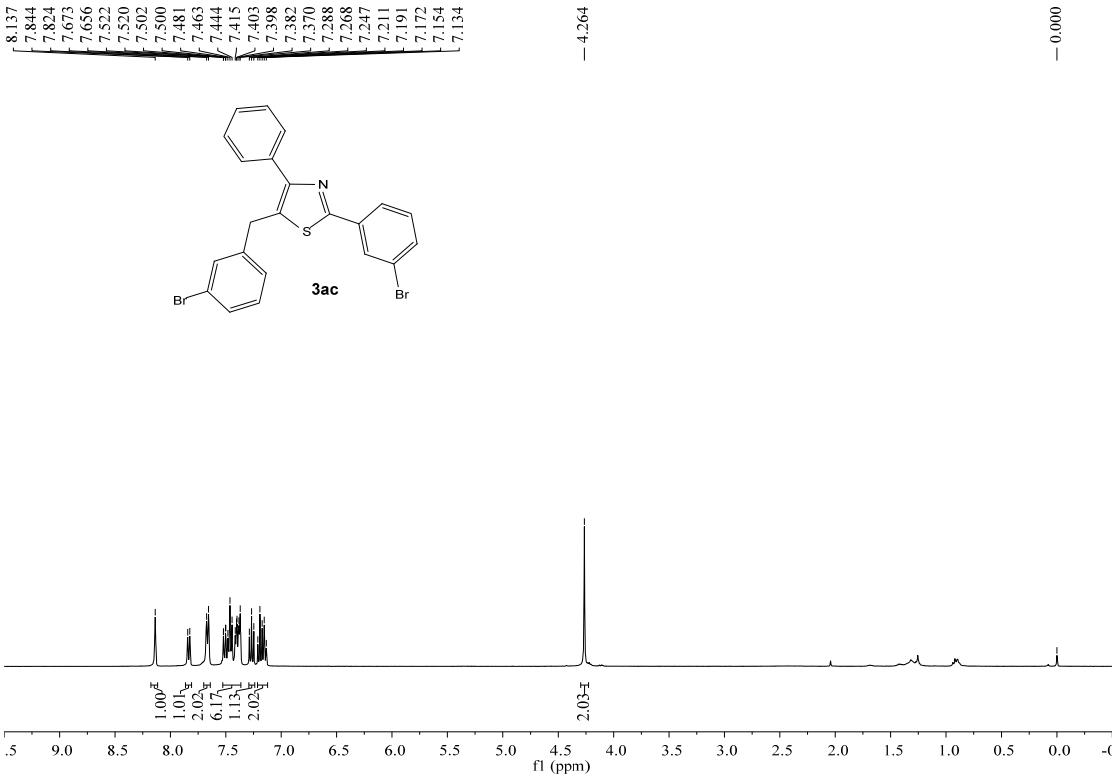


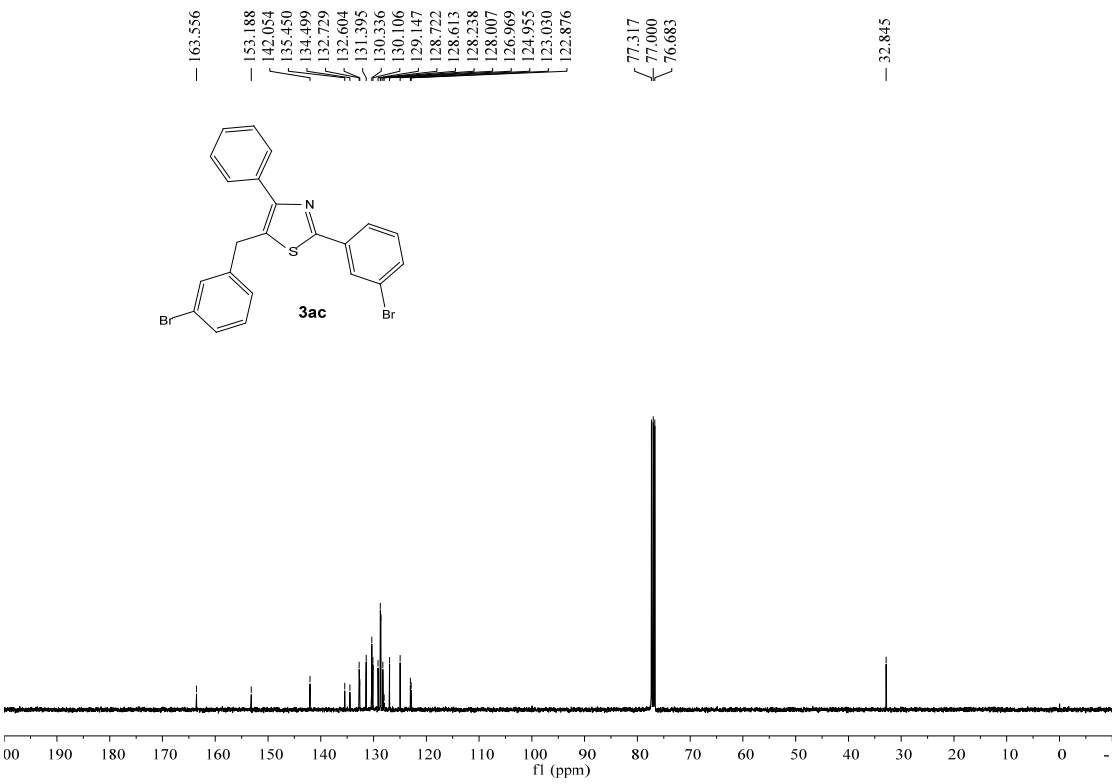
^{1}H and ^{13}C NMR spectra of 3ab



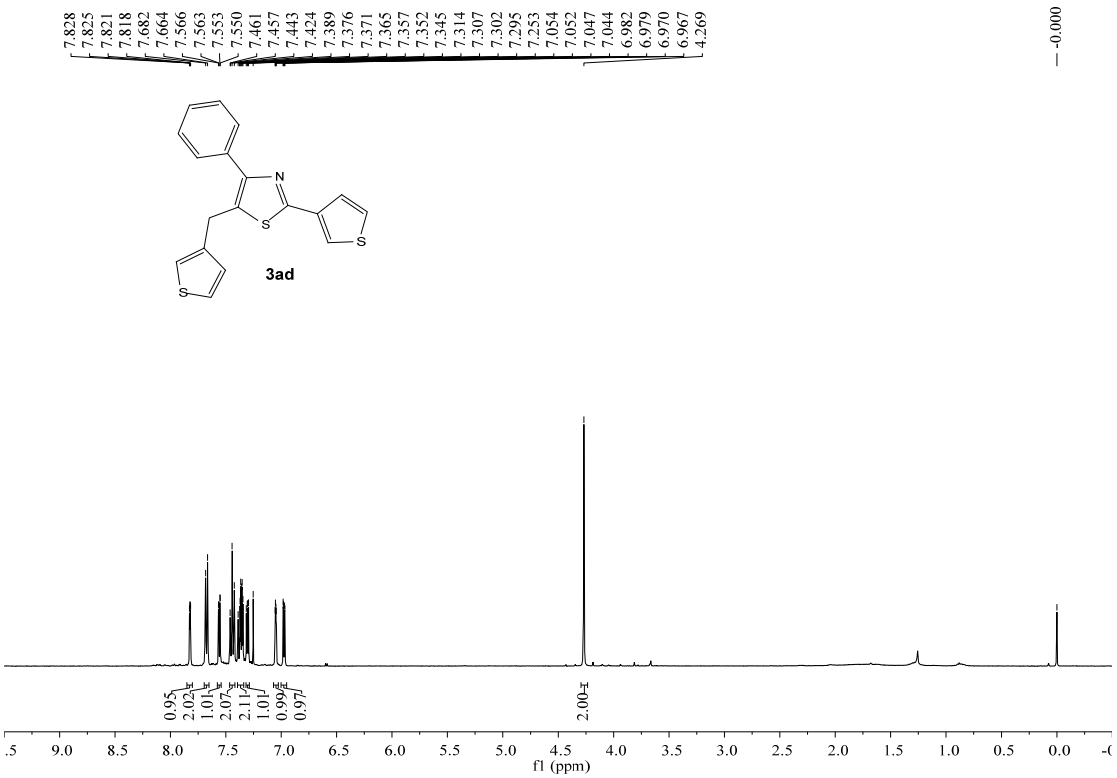


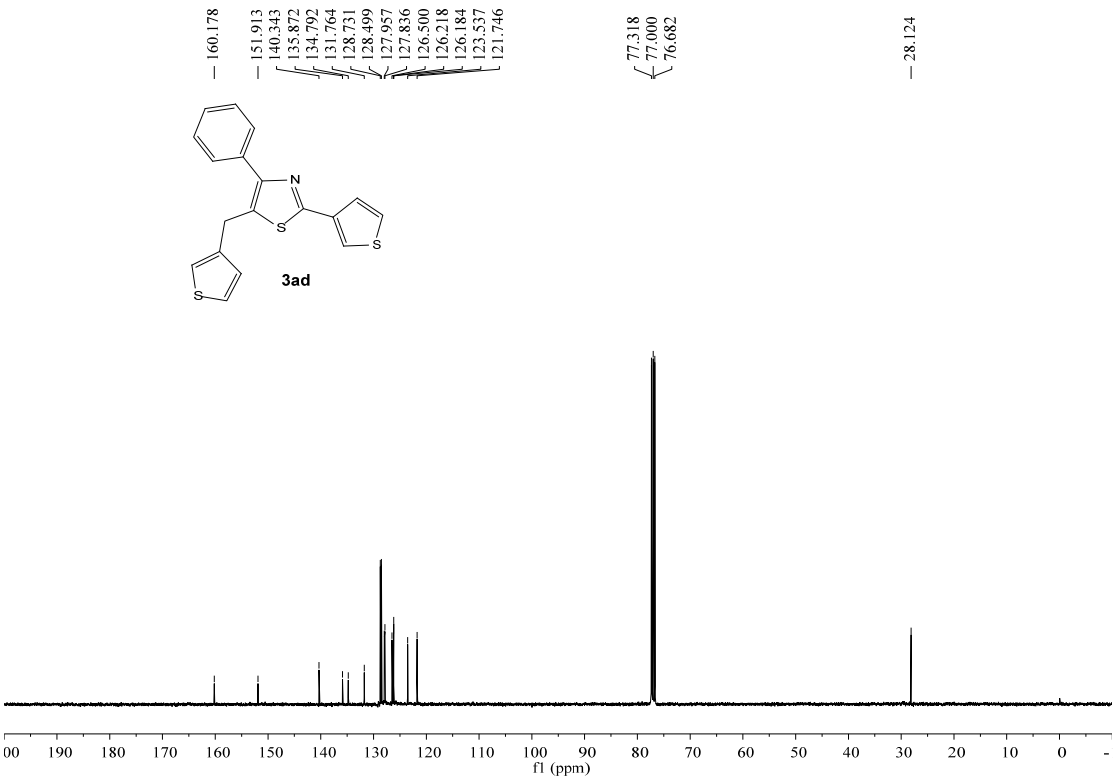
^{1}H and ^{13}C NMR spectra of 3ac



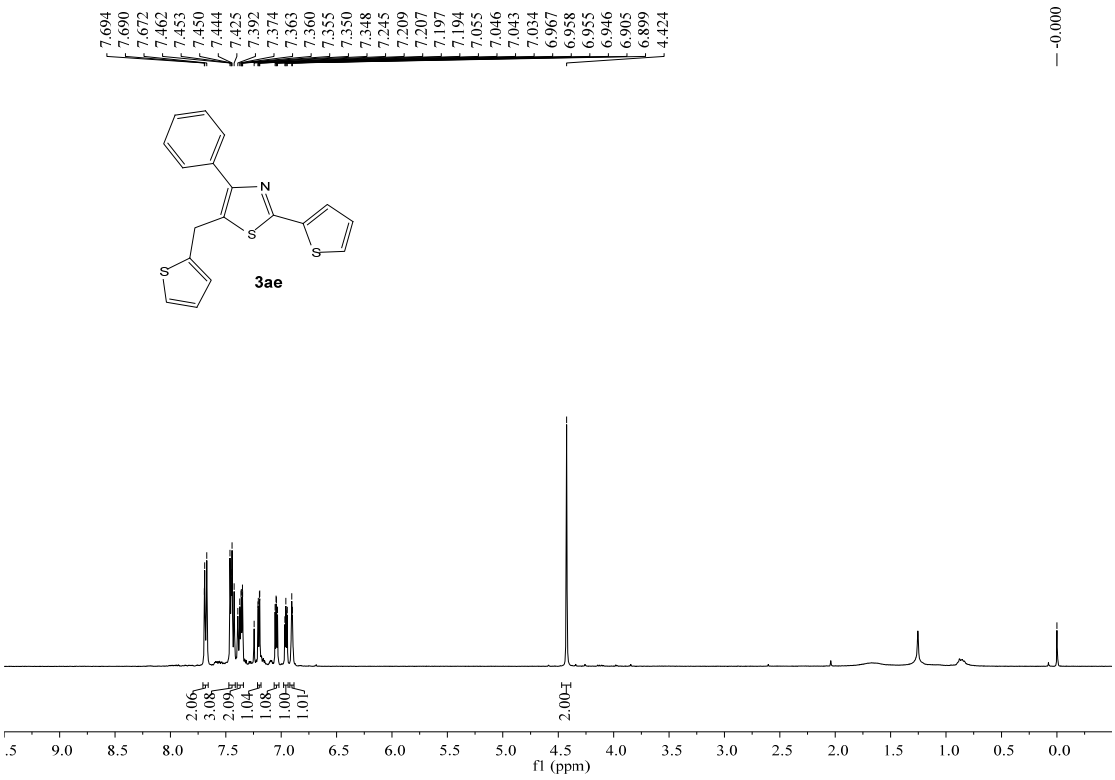


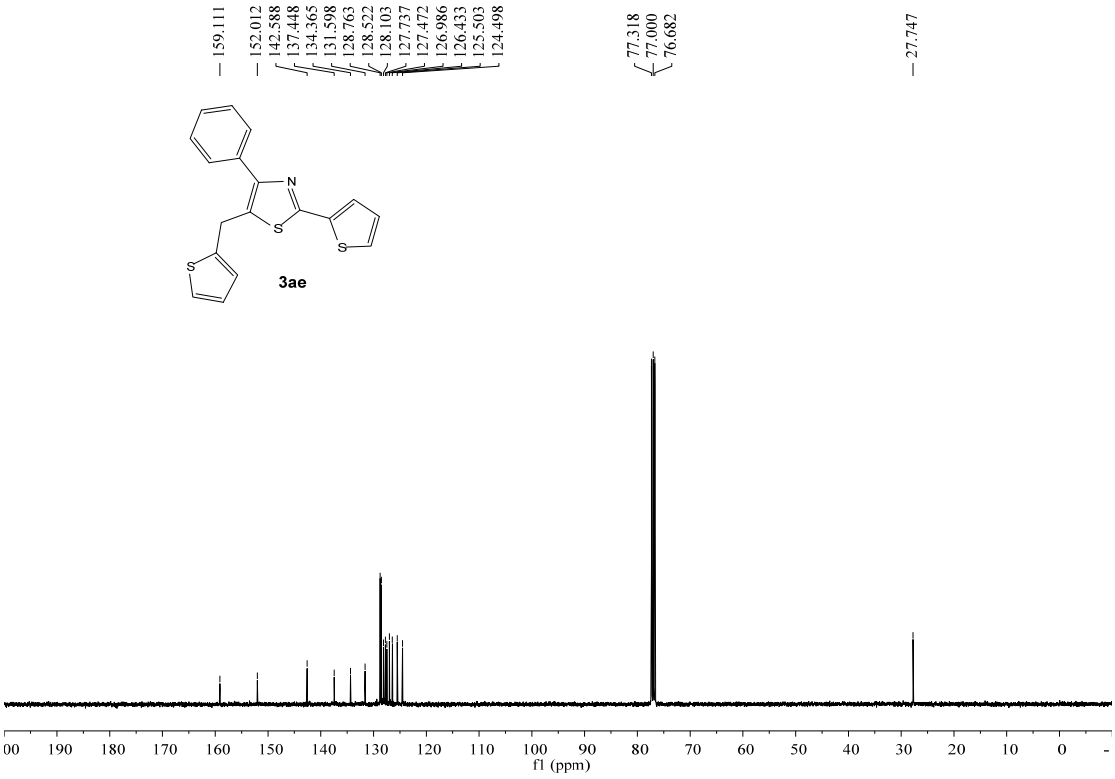
^{1}H and ^{13}C NMR spectra of 3ad



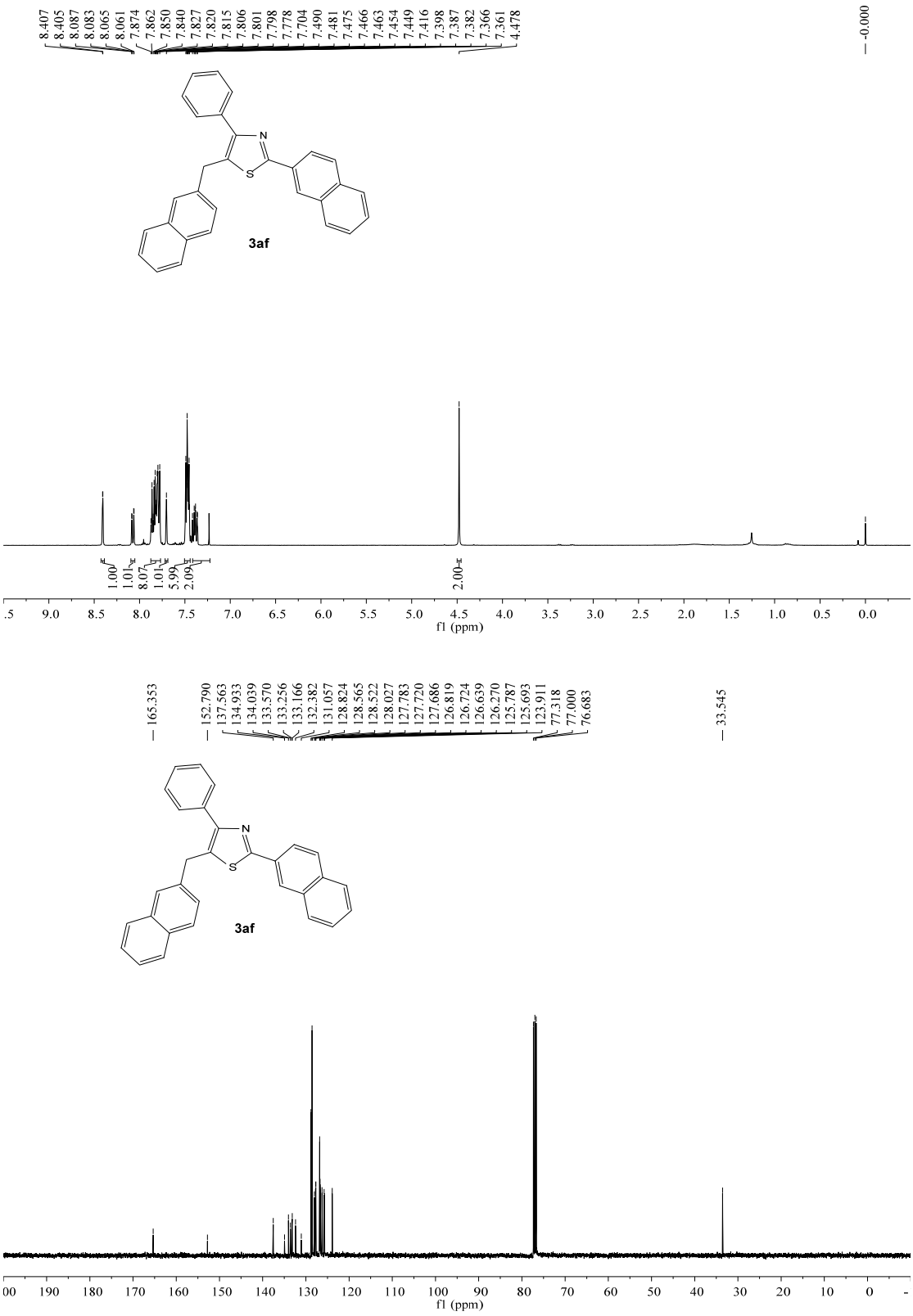


^{1}H and ^{13}C NMR spectra of 3ae

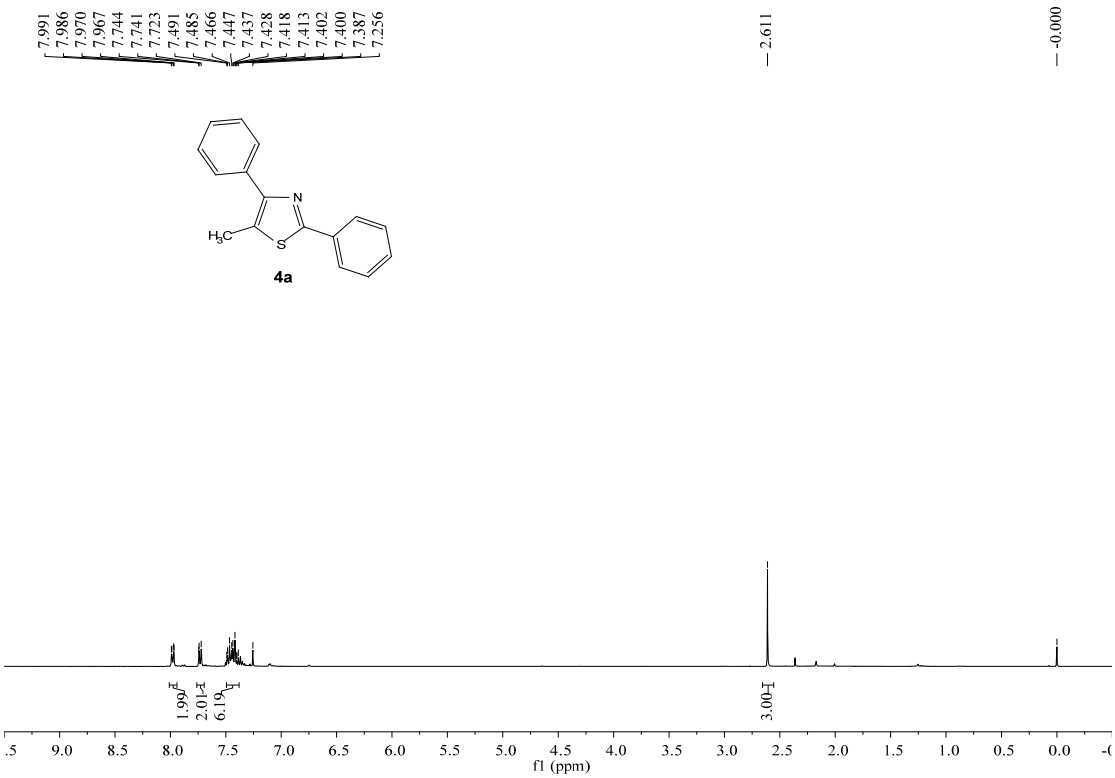


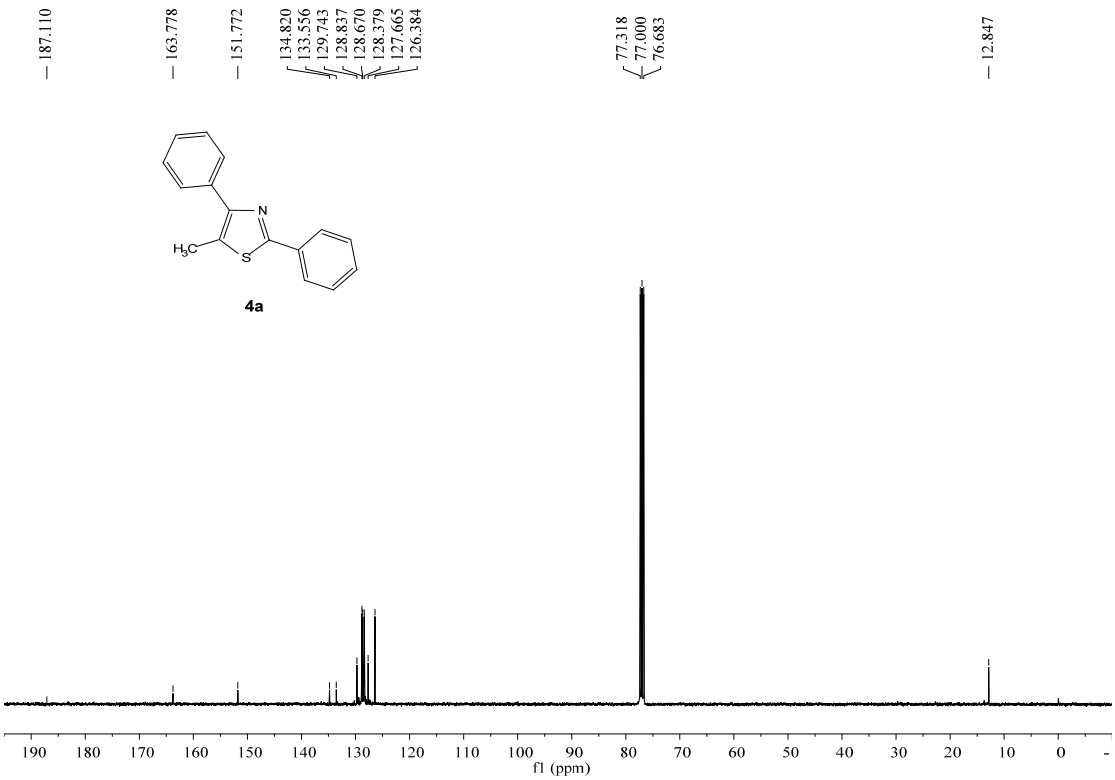


^{1}H and ^{13}C NMR spectra of 3af

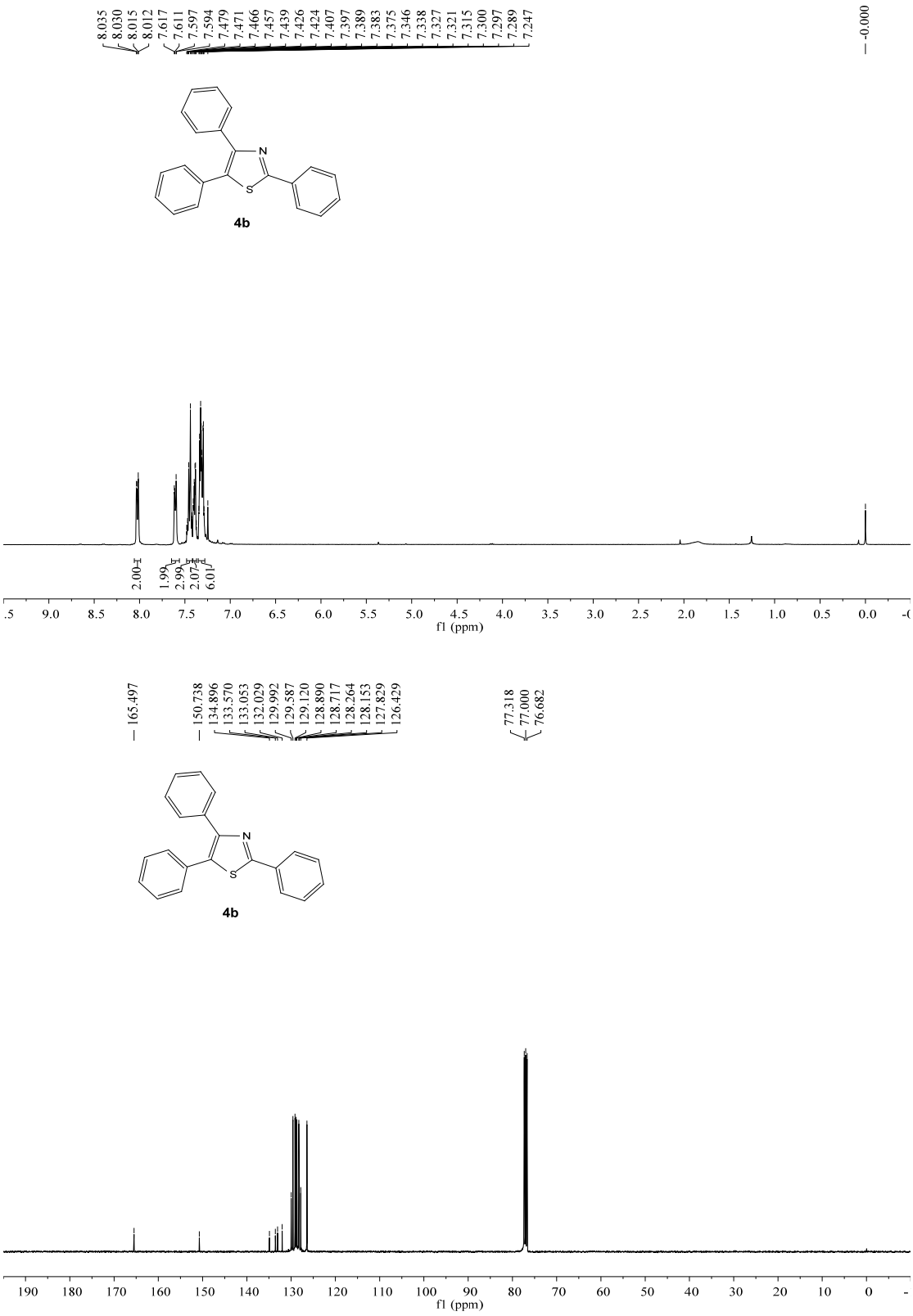


^{1}H and ^{13}C NMR spectra of 4a

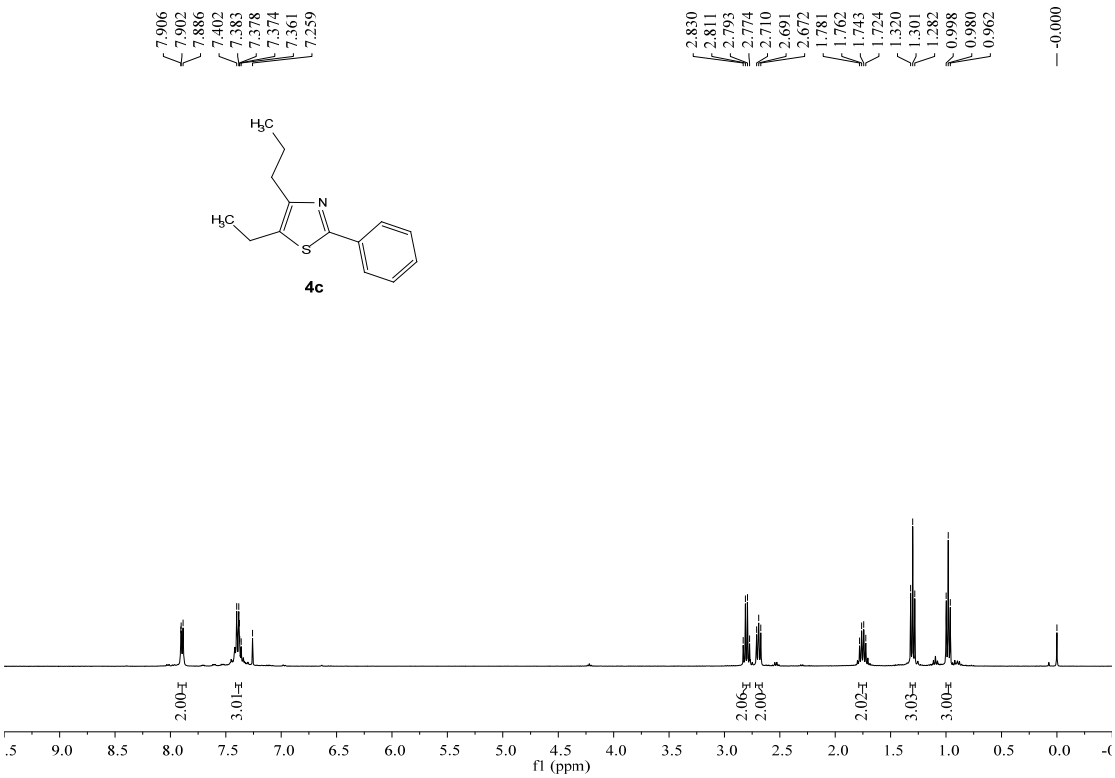


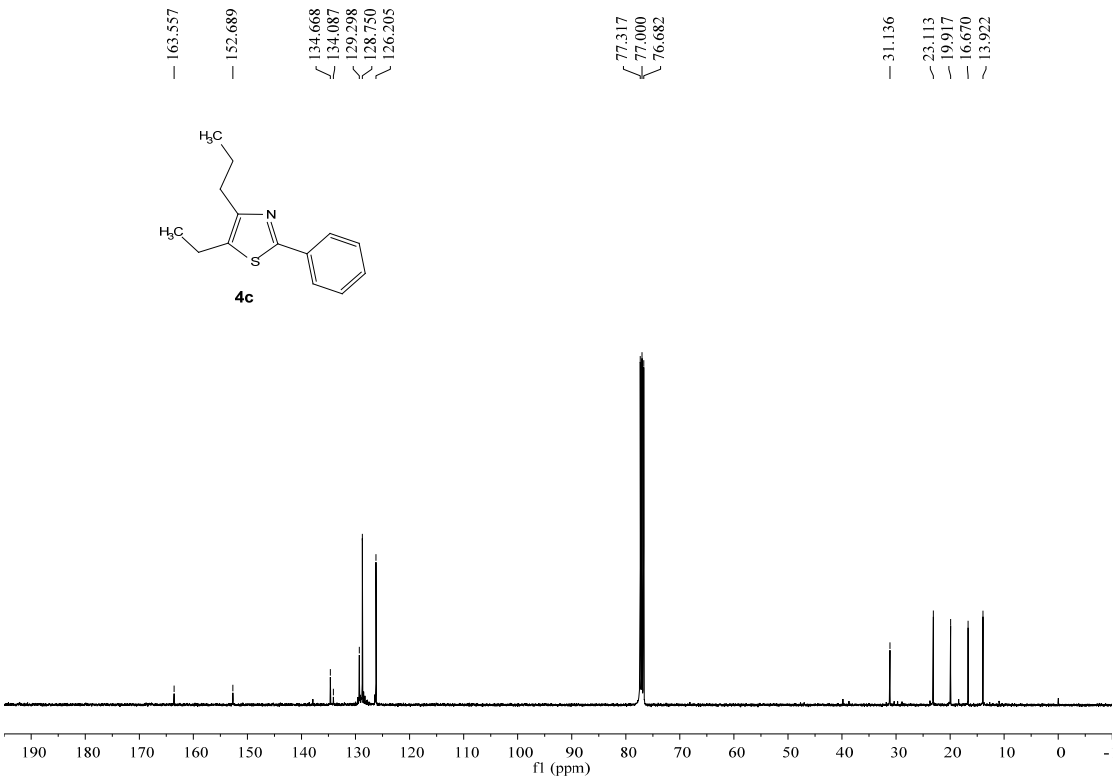


^{1}H and ^{13}C NMR spectra of 4b

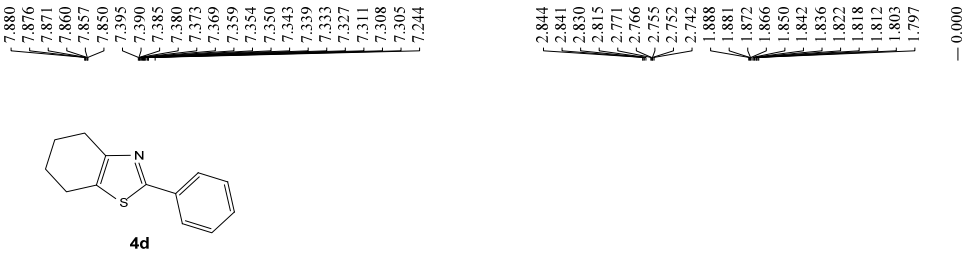


^{1}H and ^{13}C NMR spectra of 4c

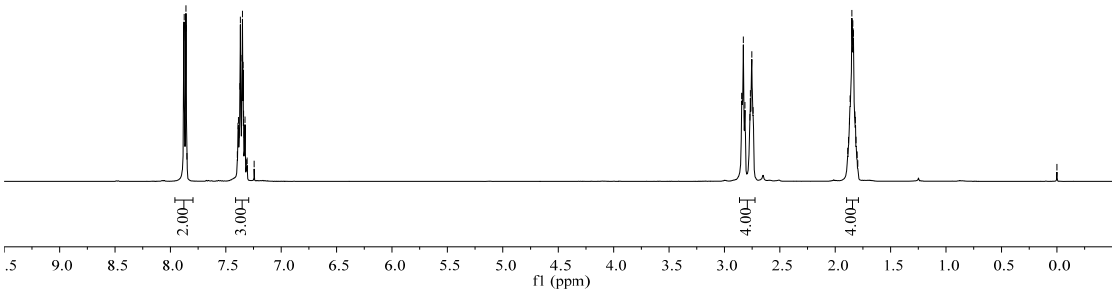


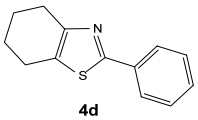


^{1}H and ^{13}C NMR spectra of 4d

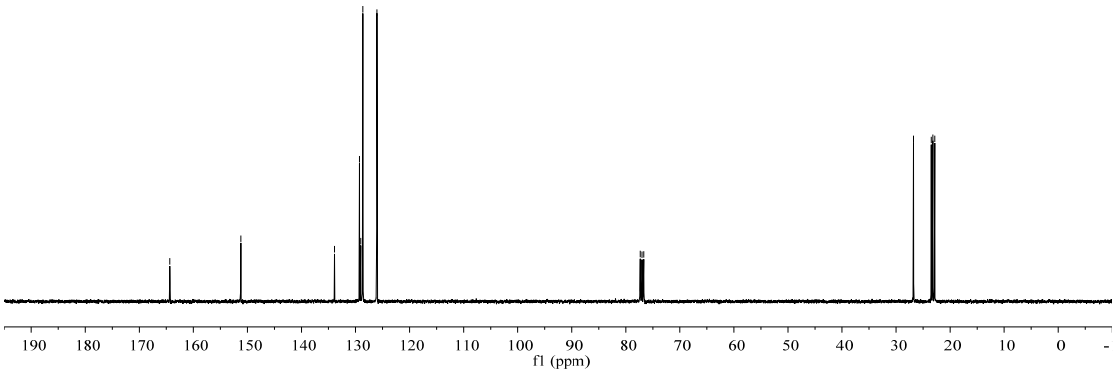


4d

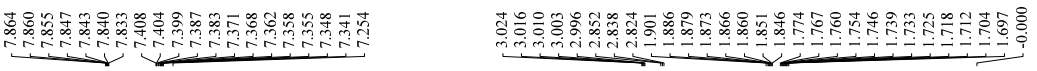


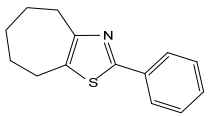


4d

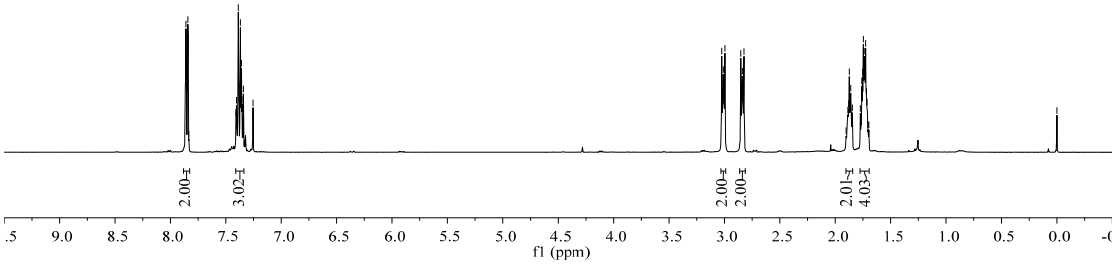


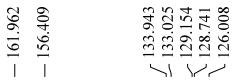
^{1}H and ^{13}C NMR spectra of 4e

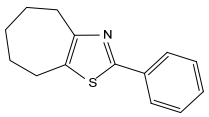




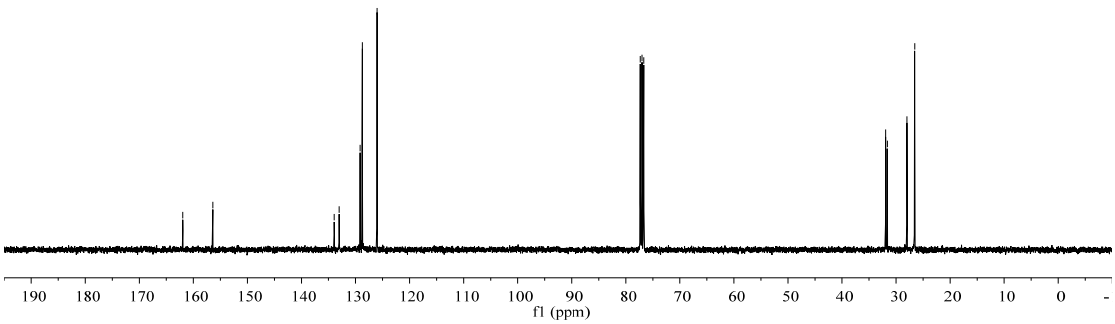
4e



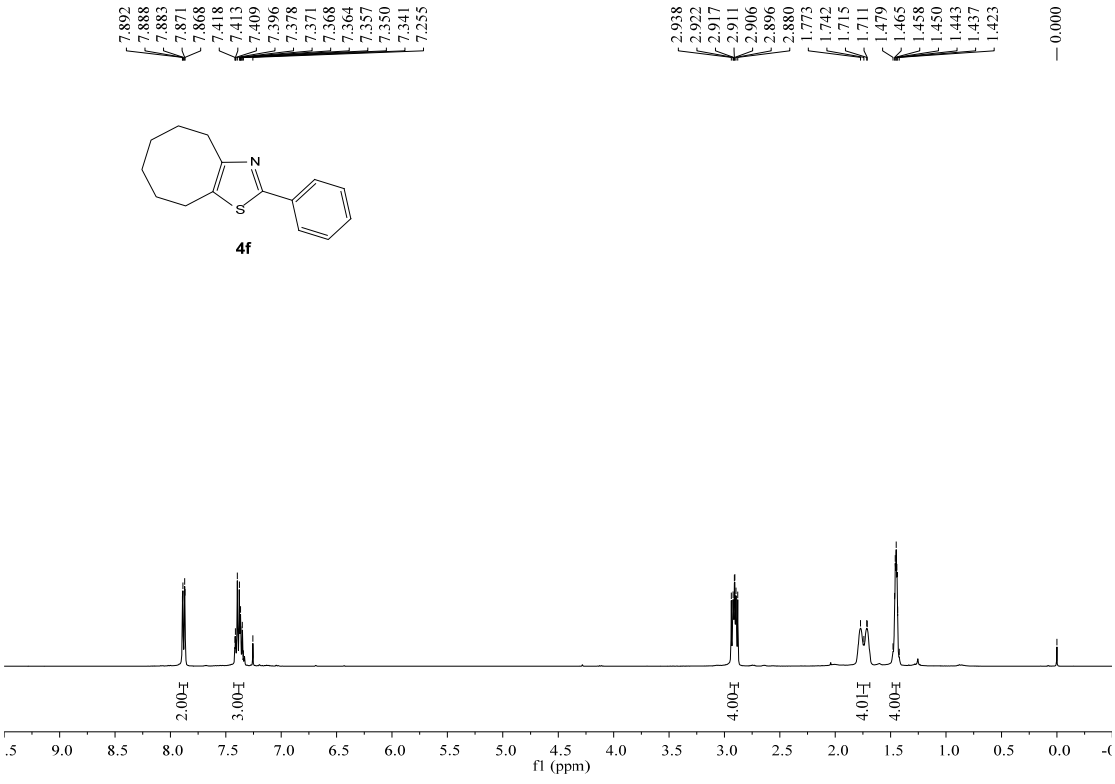


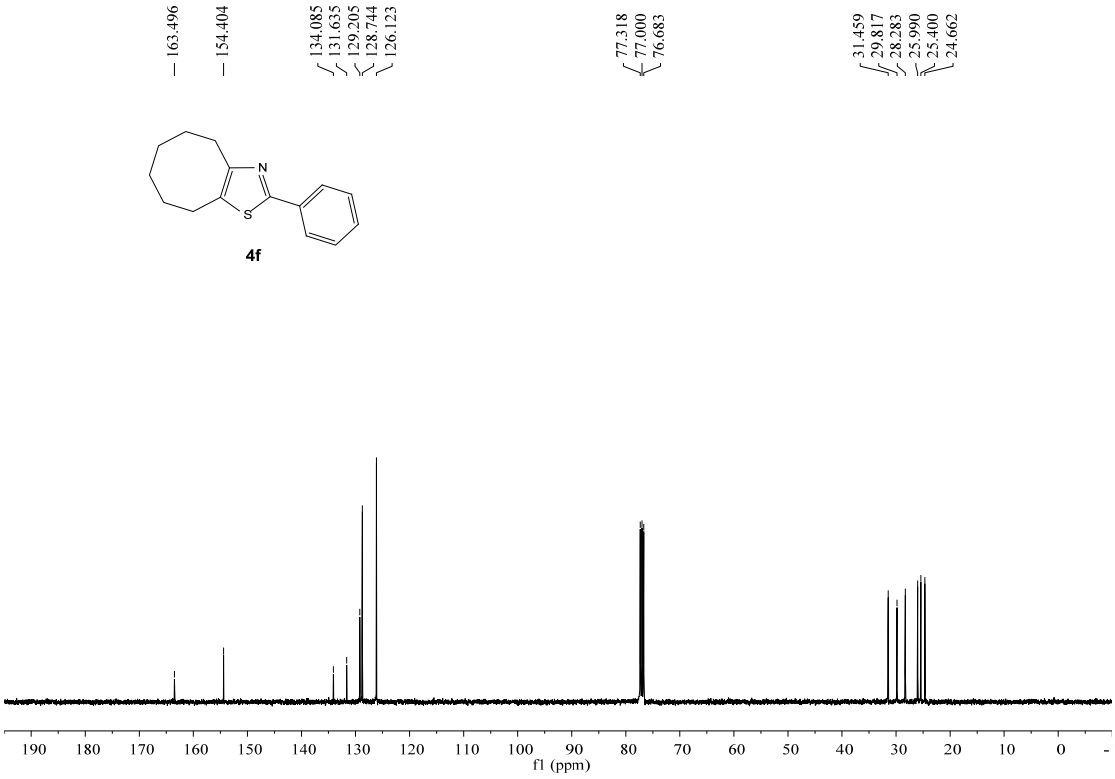


4e

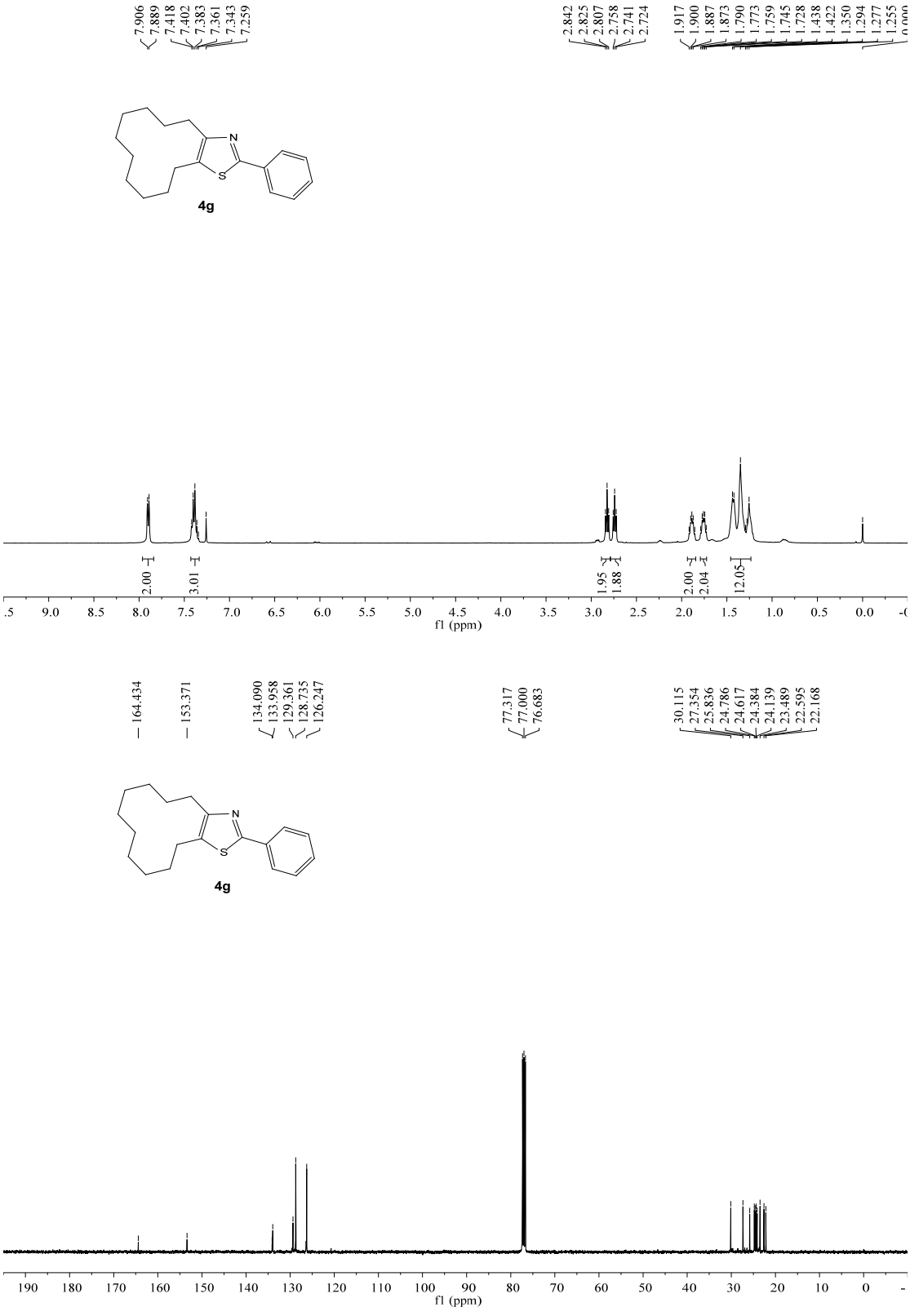


^{1}H and ^{13}C NMR spectra of 4f

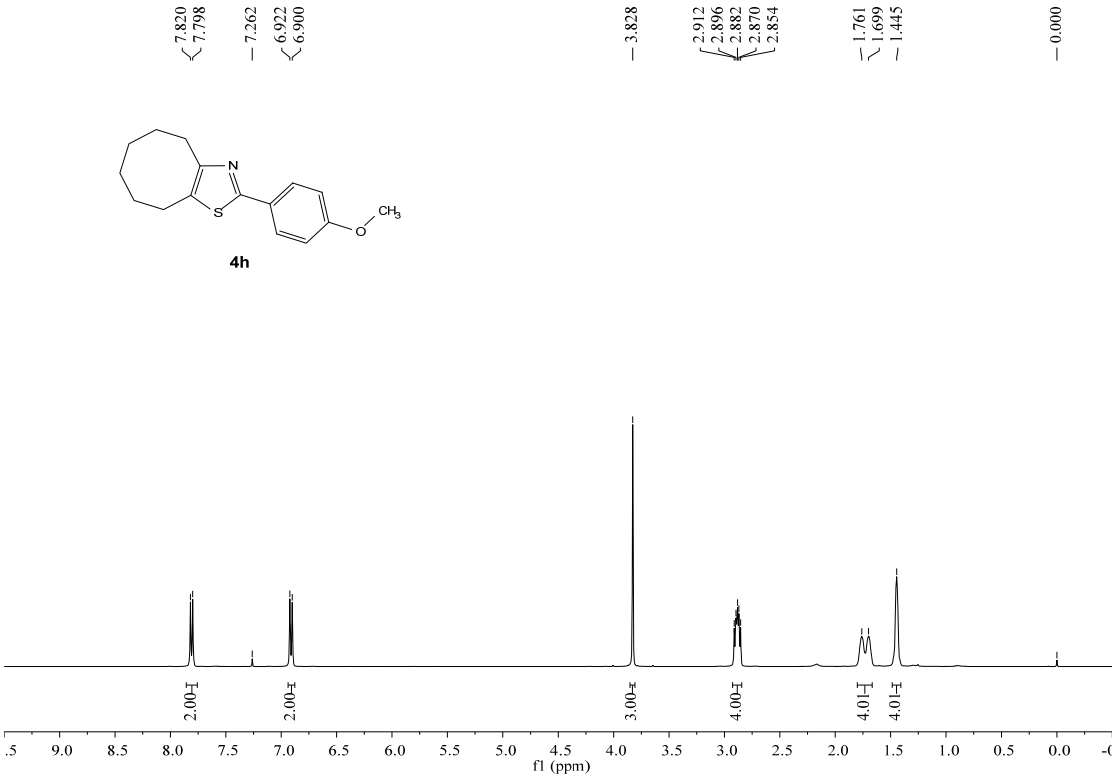


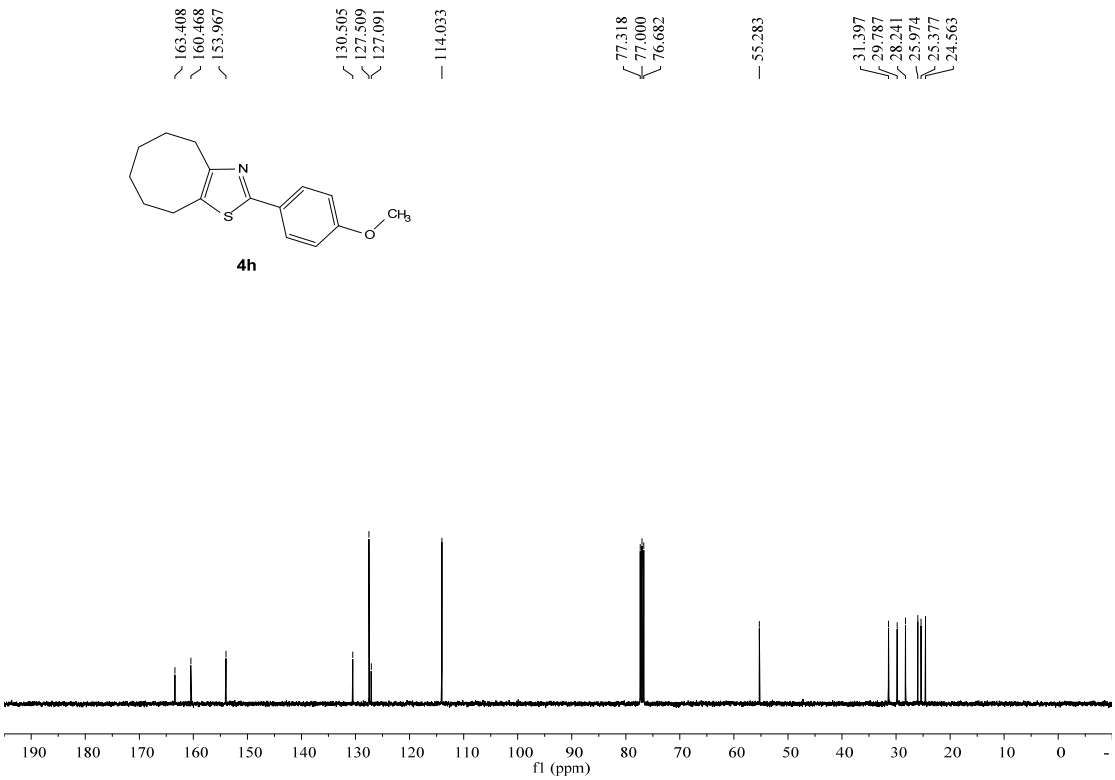


^{1}H and ^{13}C NMR spectra of 4g

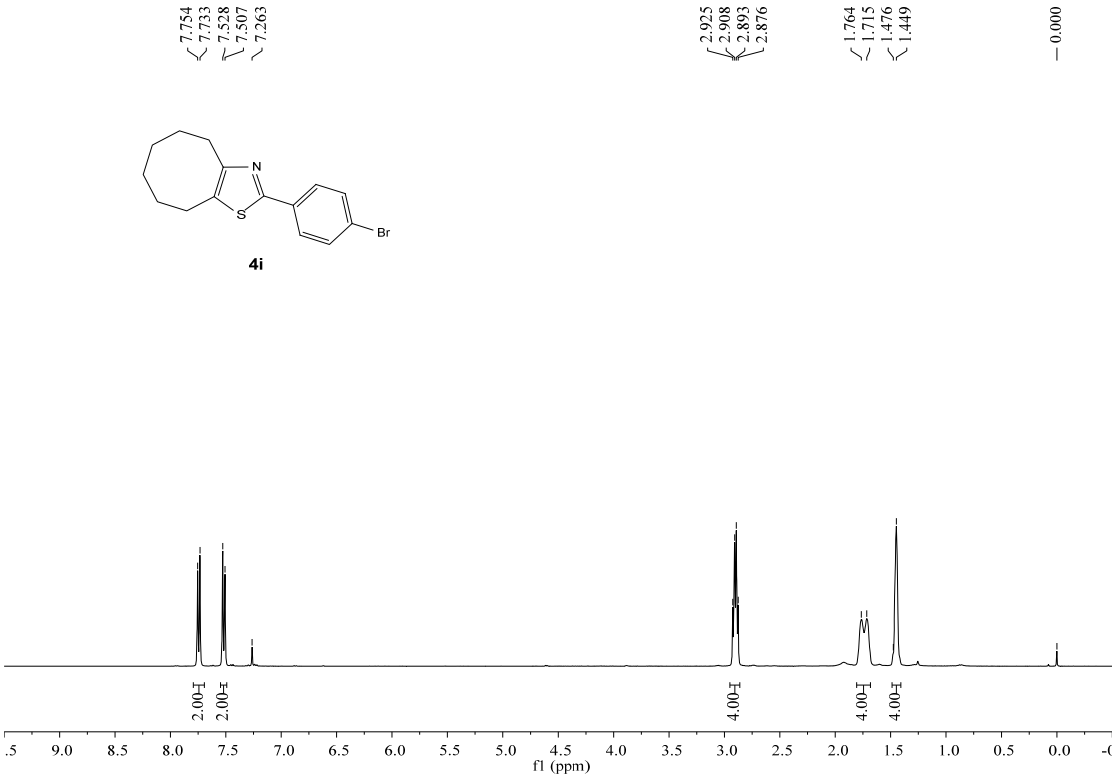


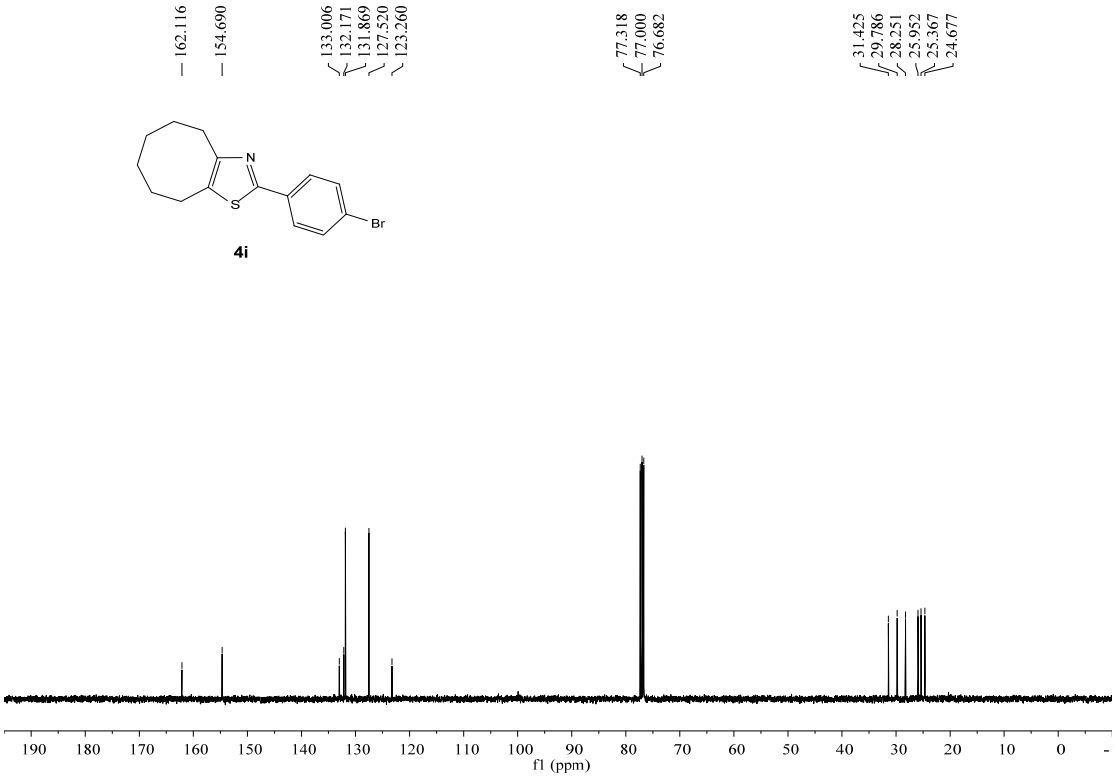
^{1}H and ^{13}C NMR spectra of 4h



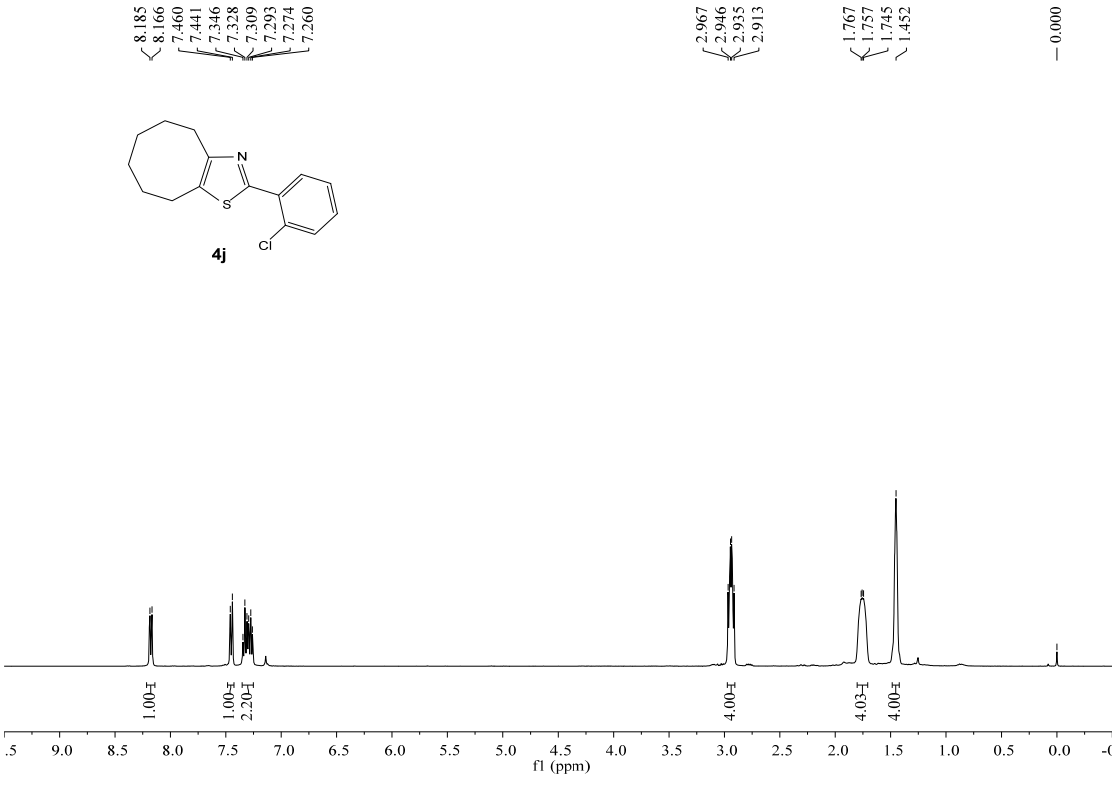


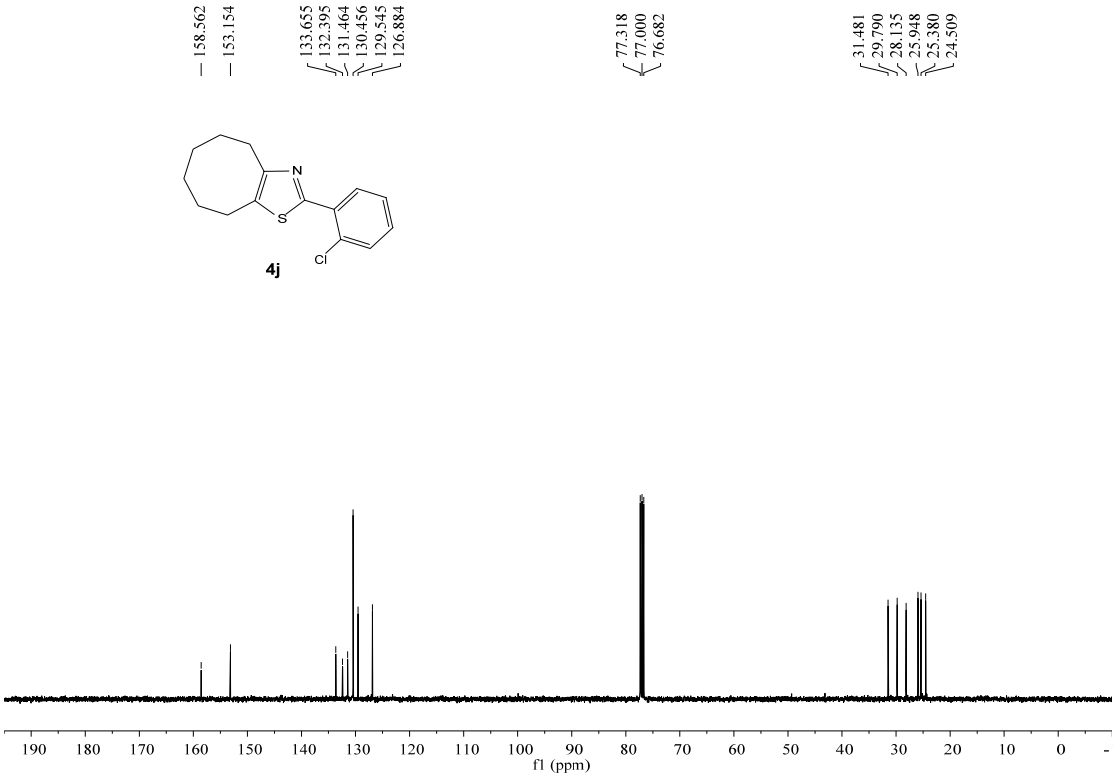
^{1}H and ^{13}C NMR spectra of 4i



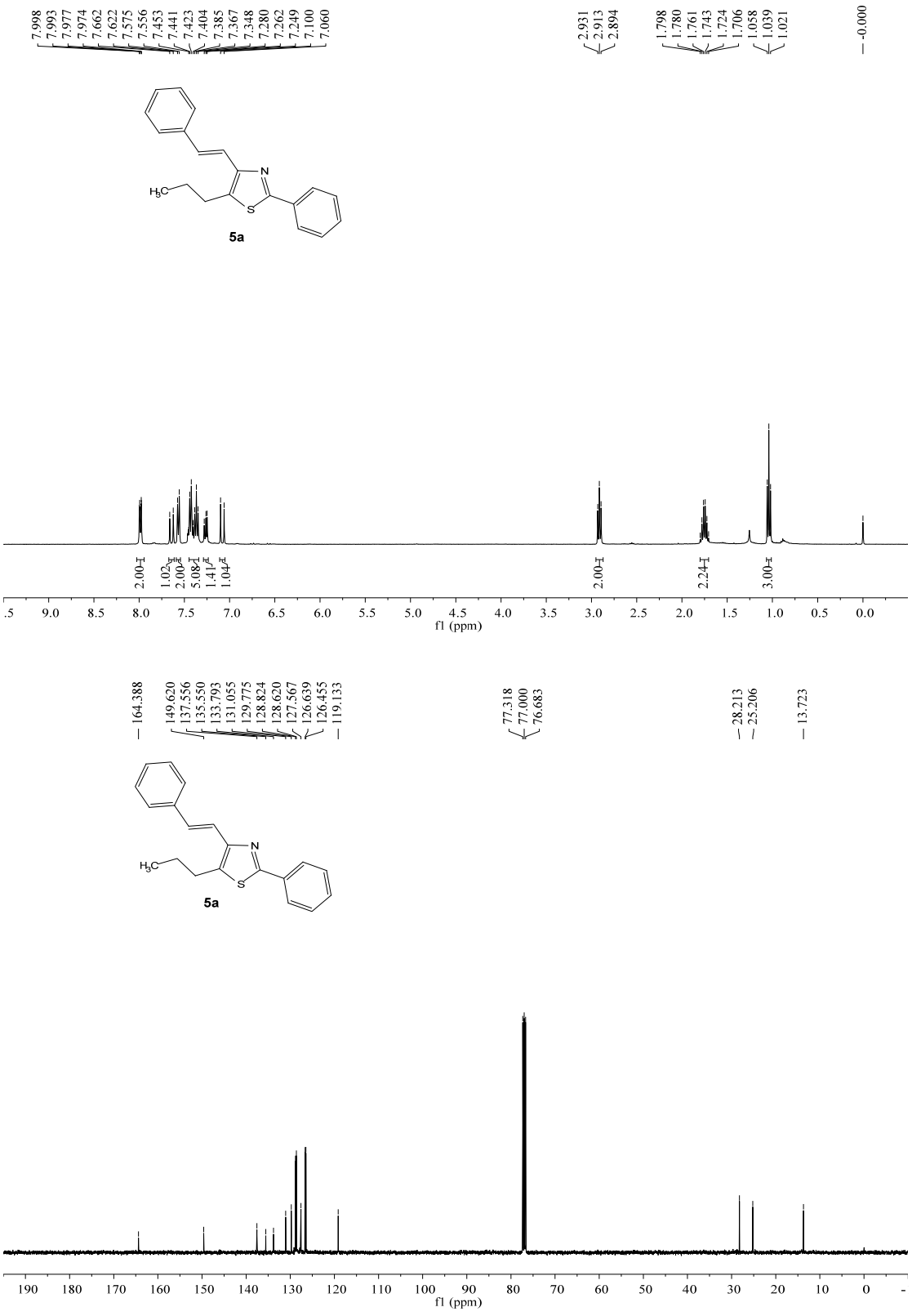


^{1}H and ^{13}C NMR spectra of 4j

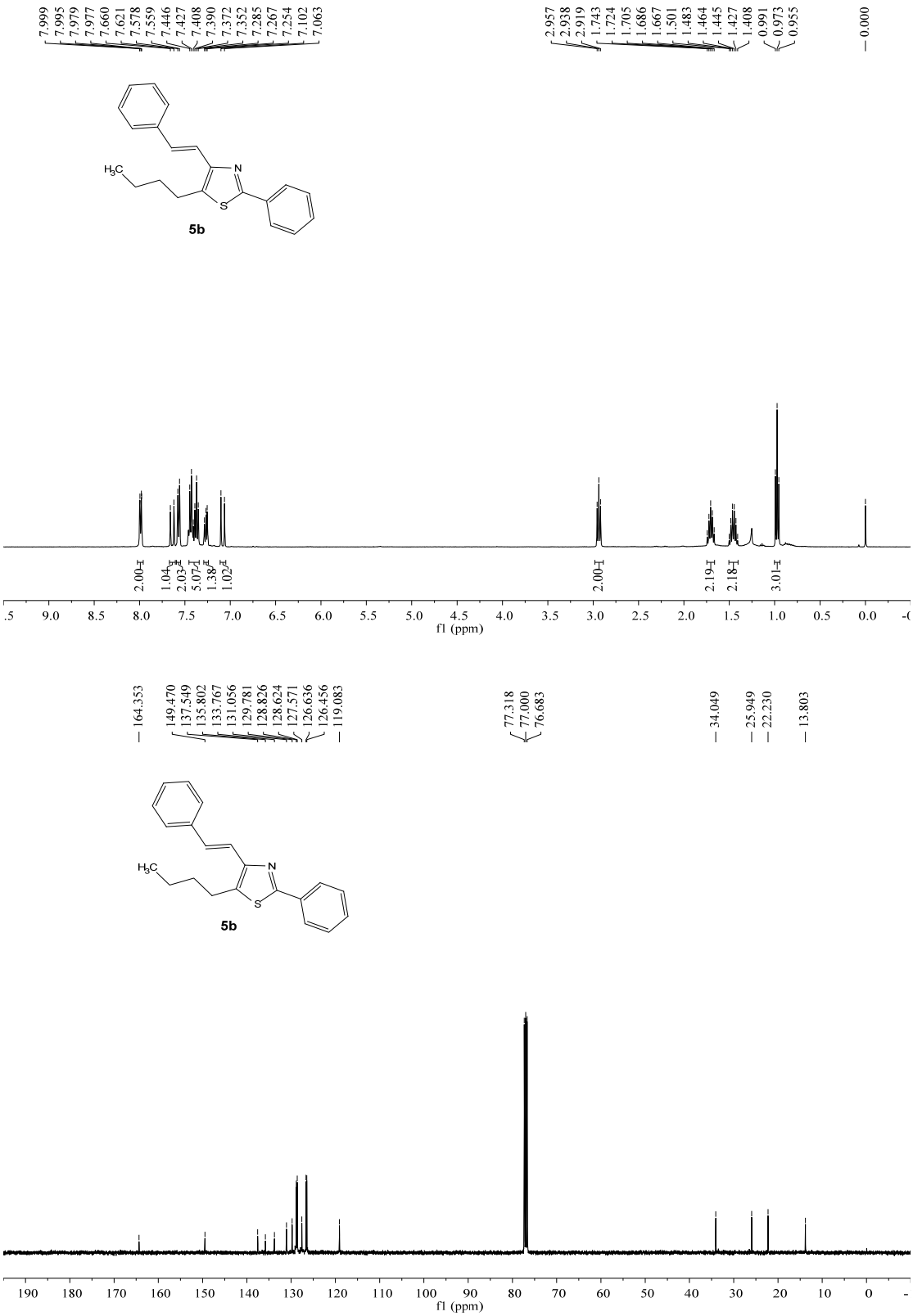




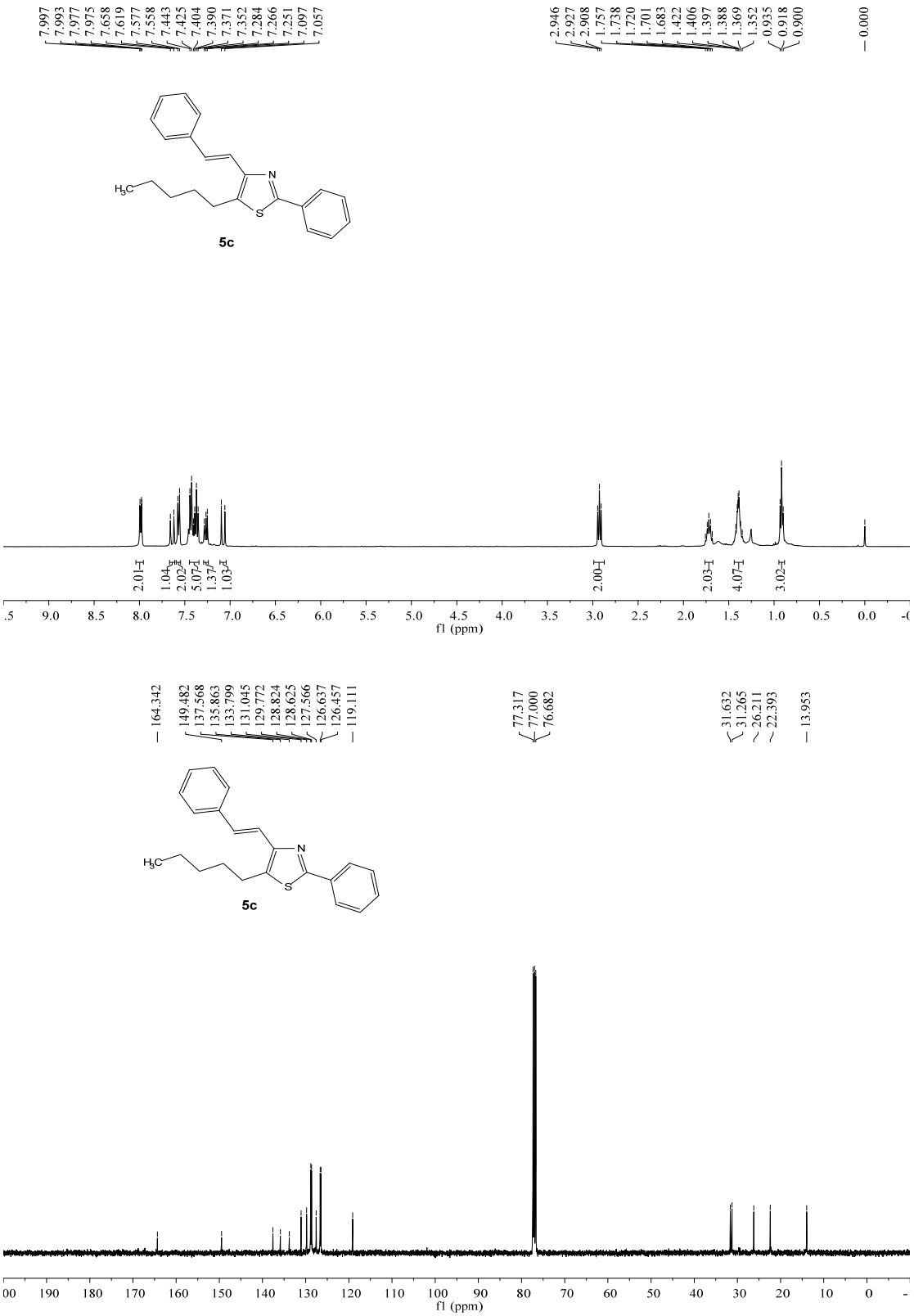
^{1}H and ^{13}C NMR spectra of 5a



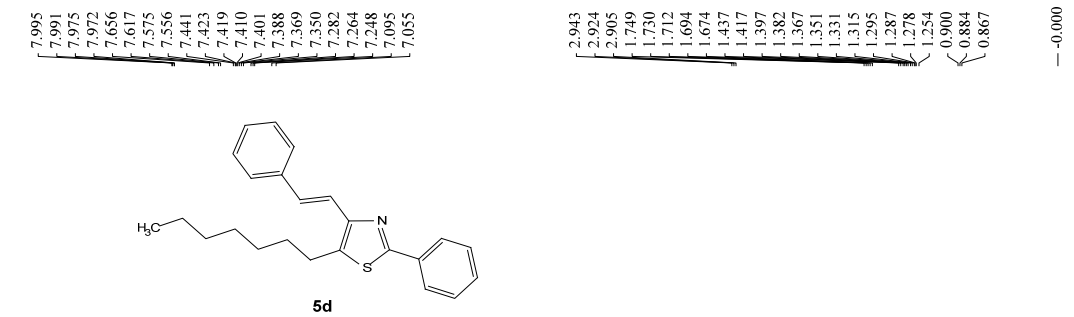
^{1}H and ^{13}C NMR spectra of 5b



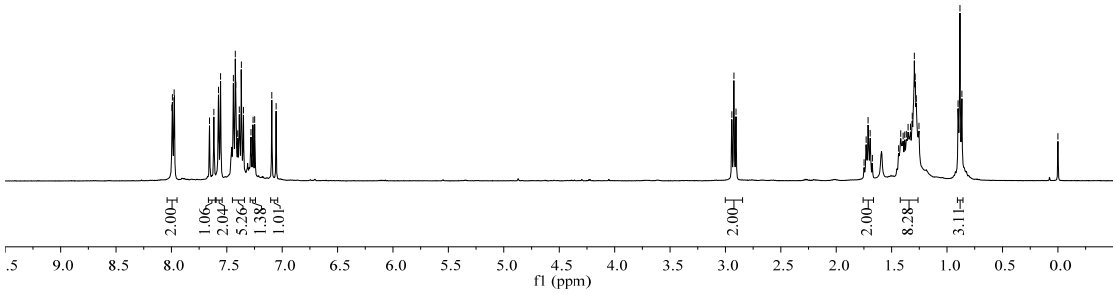
^{1}H and ^{13}C NMR spectra of 5c

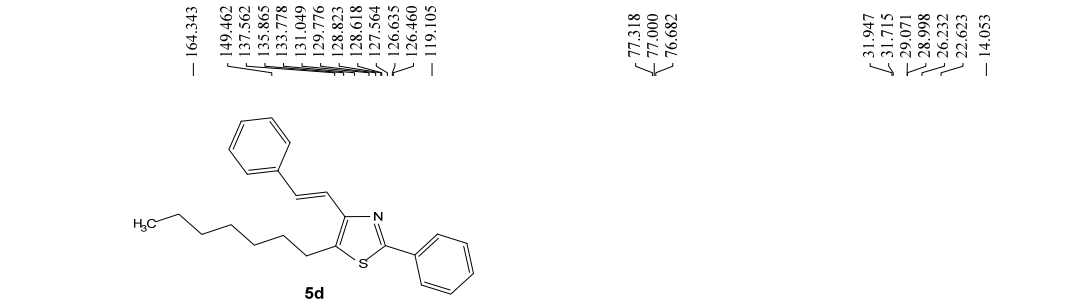


^{1}H and ^{13}C NMR spectra of 5d

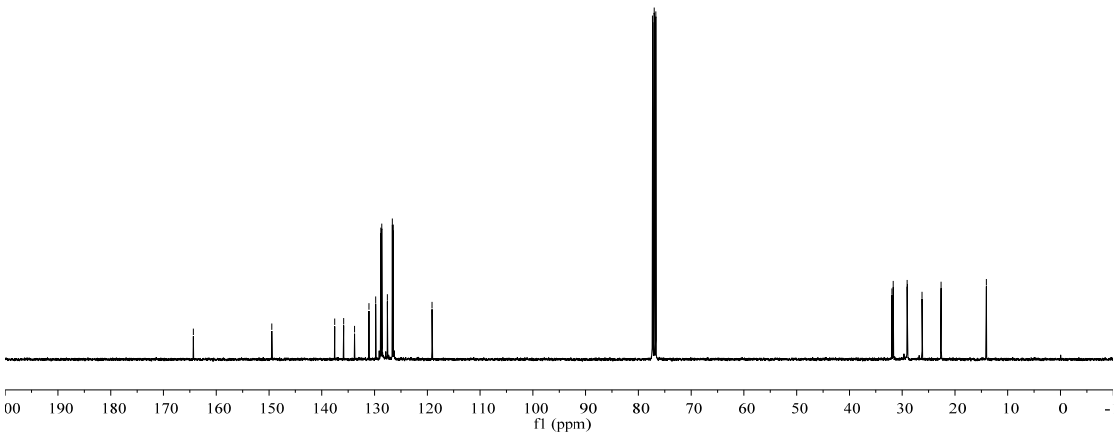


5d

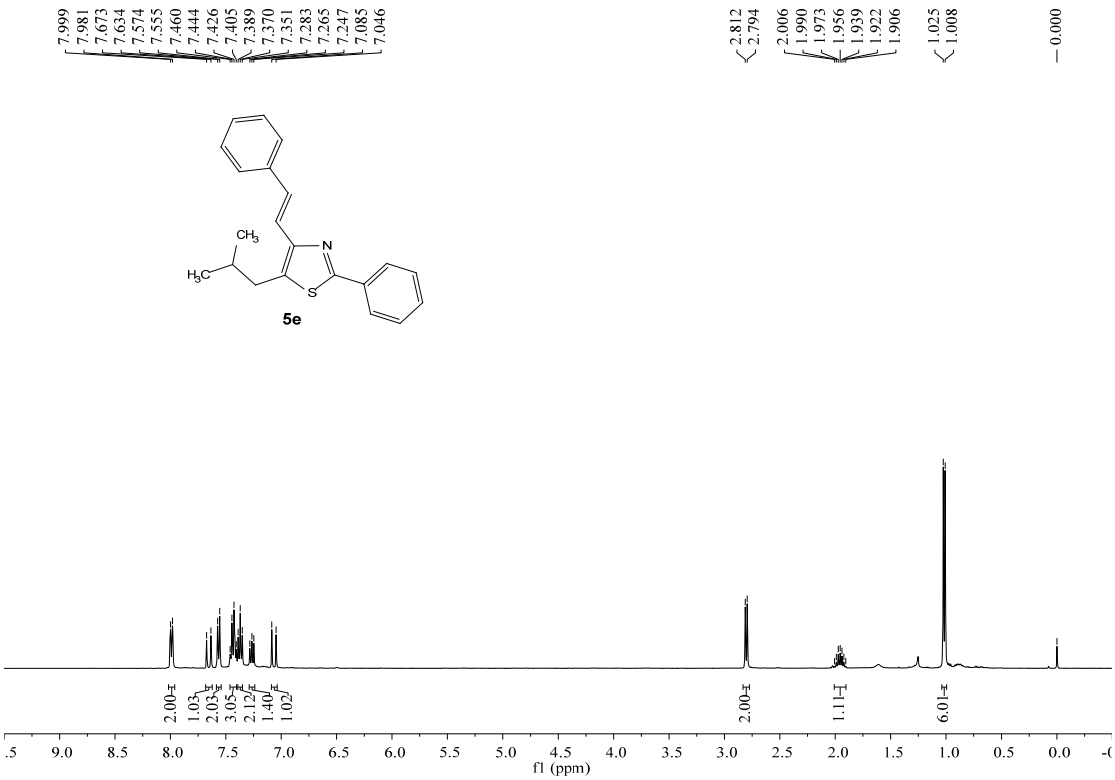


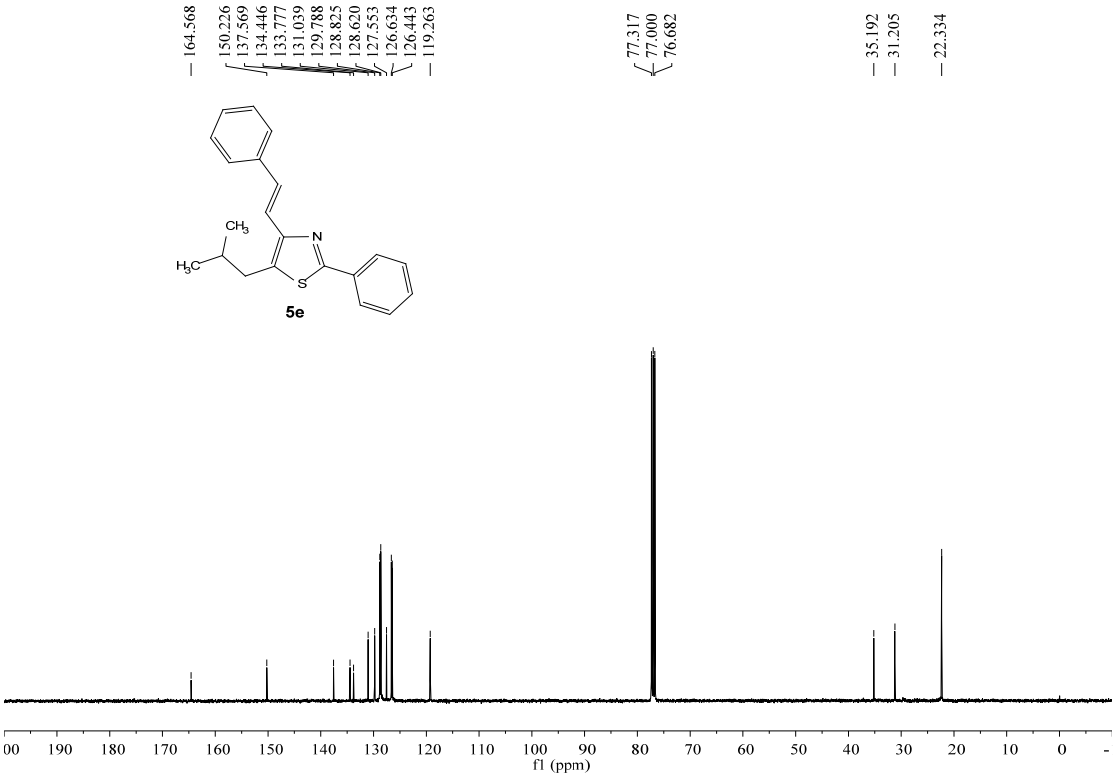


5d

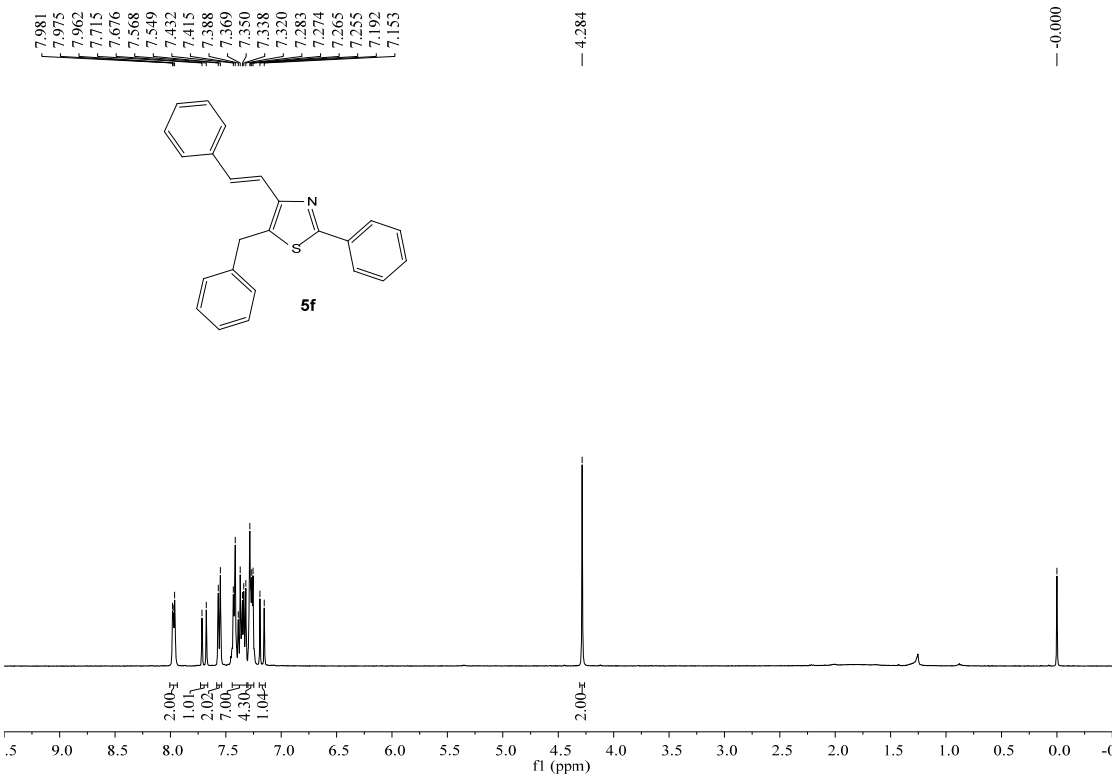


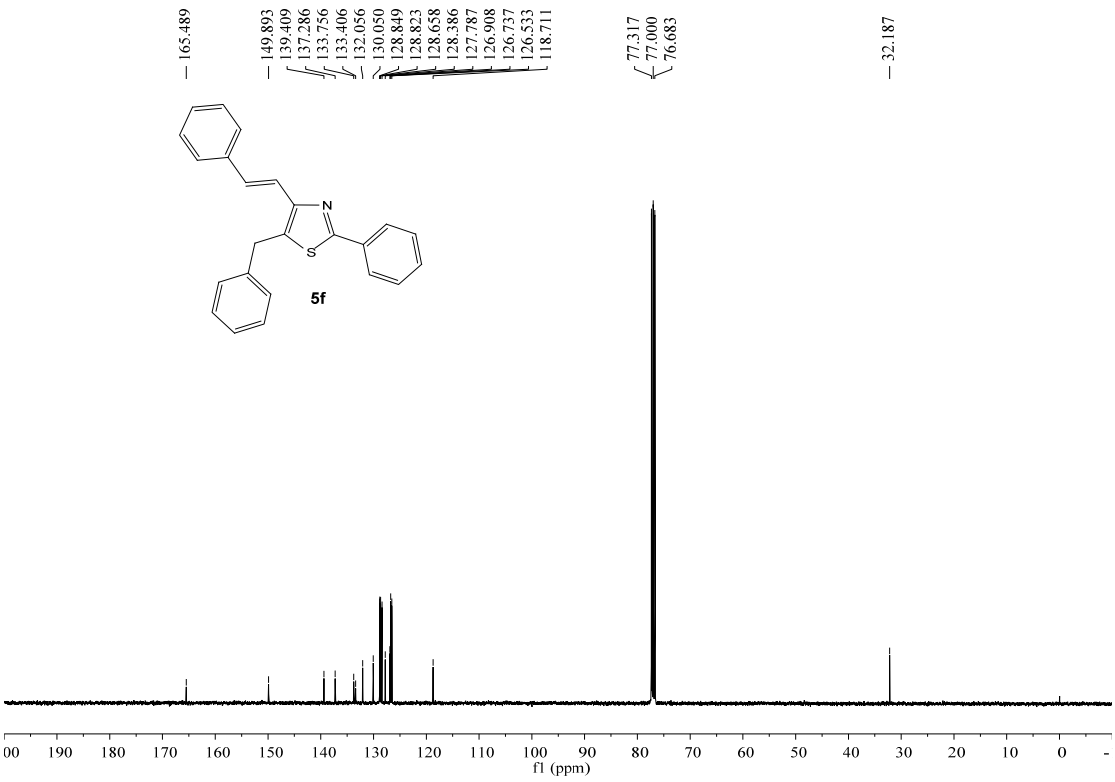
^{1}H and ^{13}C NMR spectra of 5e



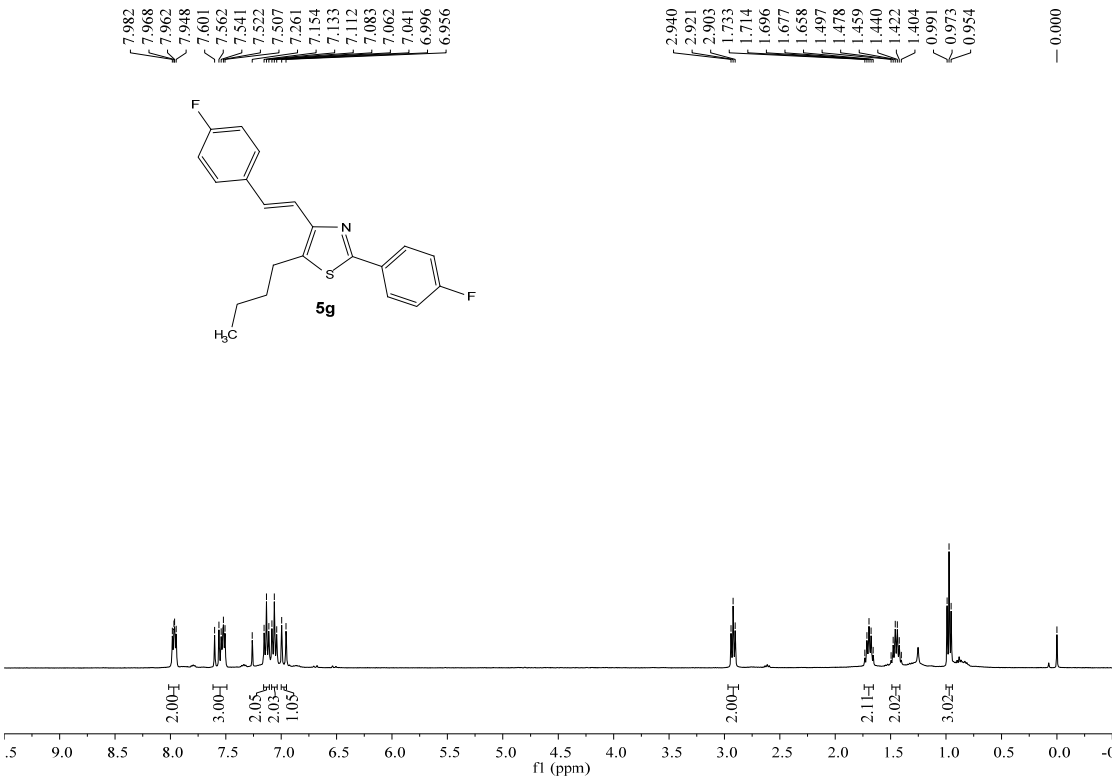


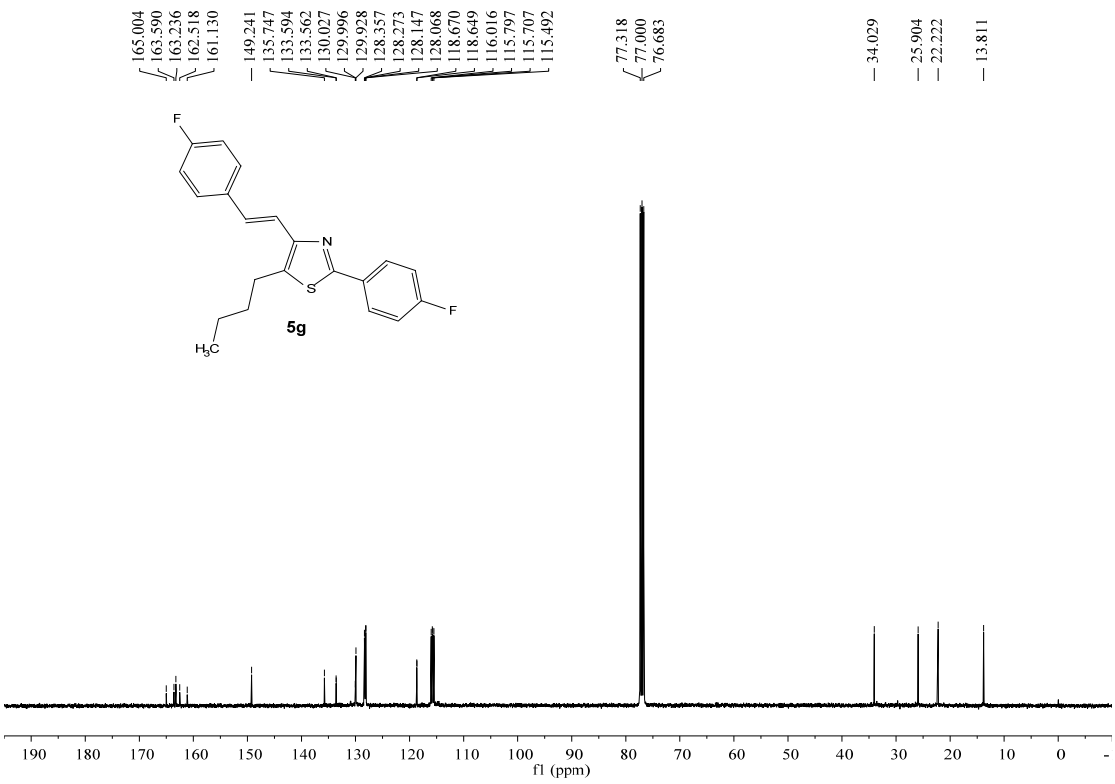
^{1}H and ^{13}C NMR spectra of 5f



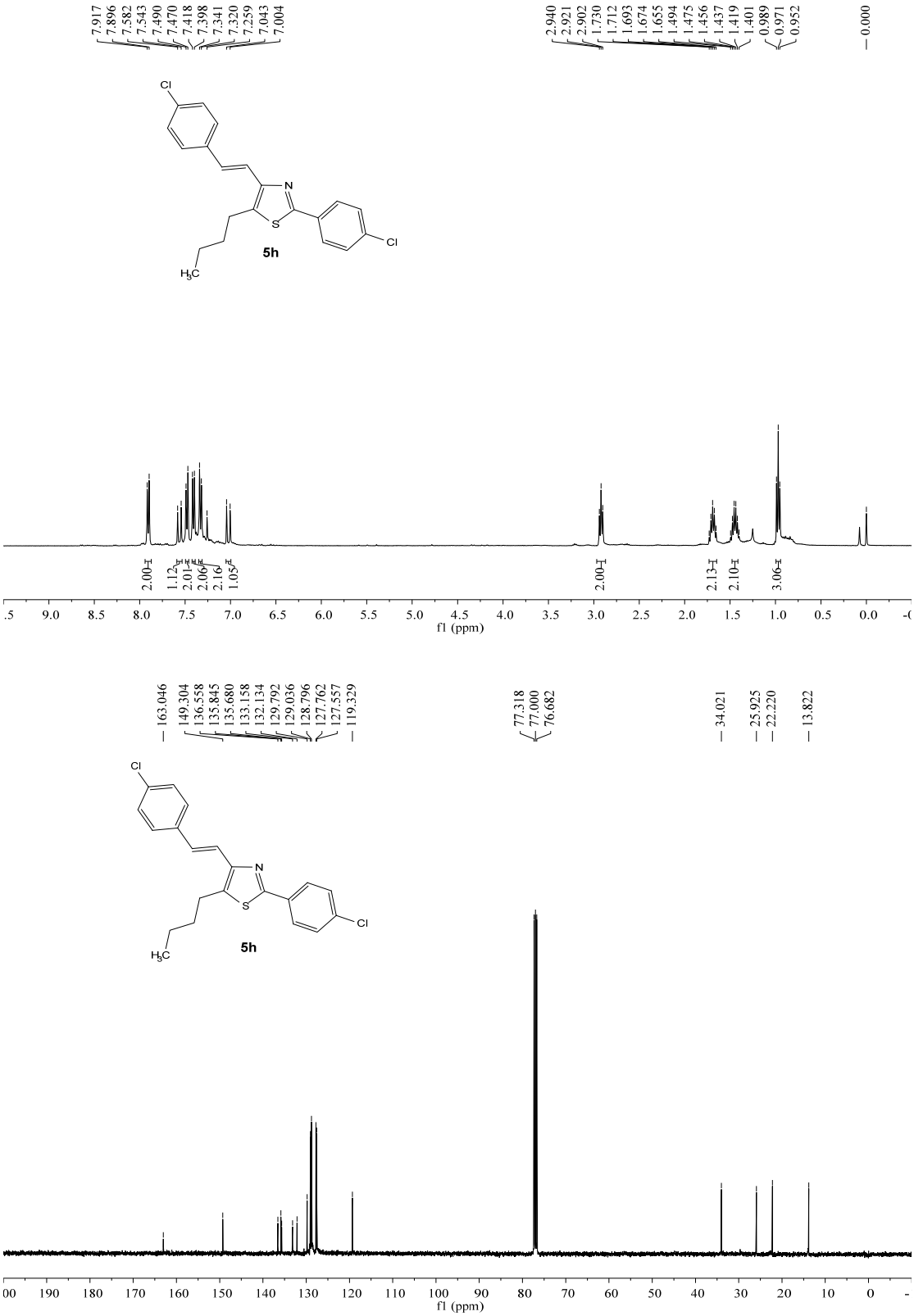


^{1}H and ^{13}C NMR spectra of 5g

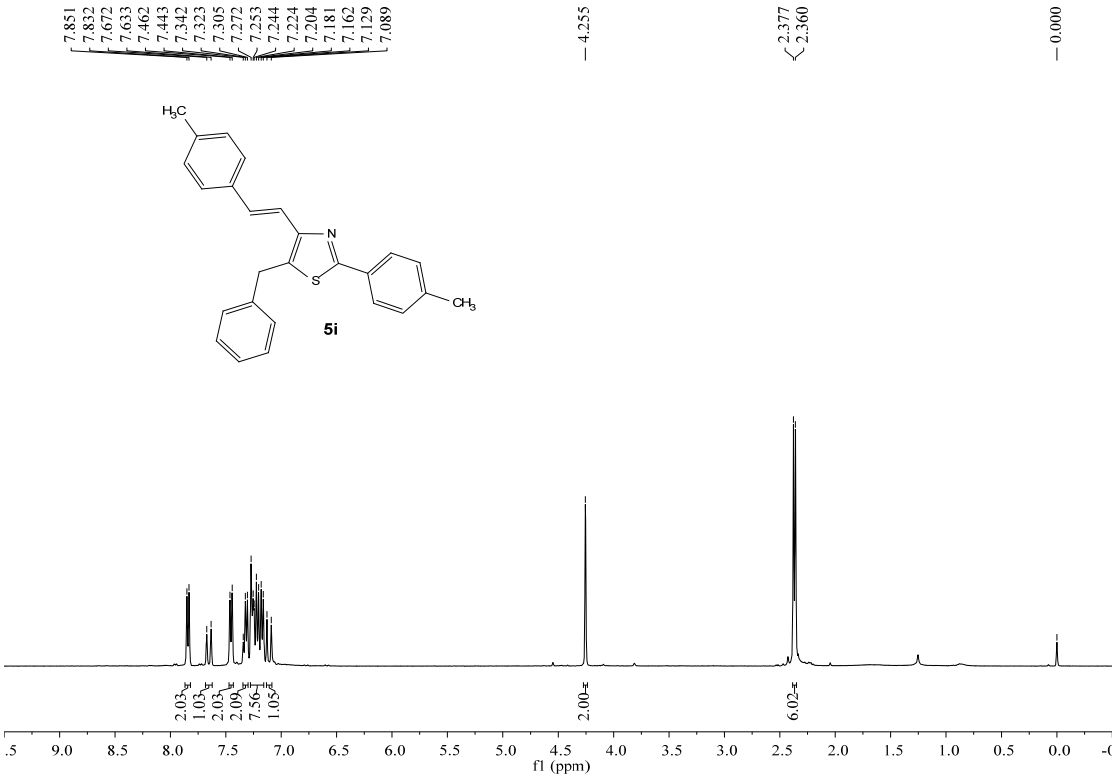


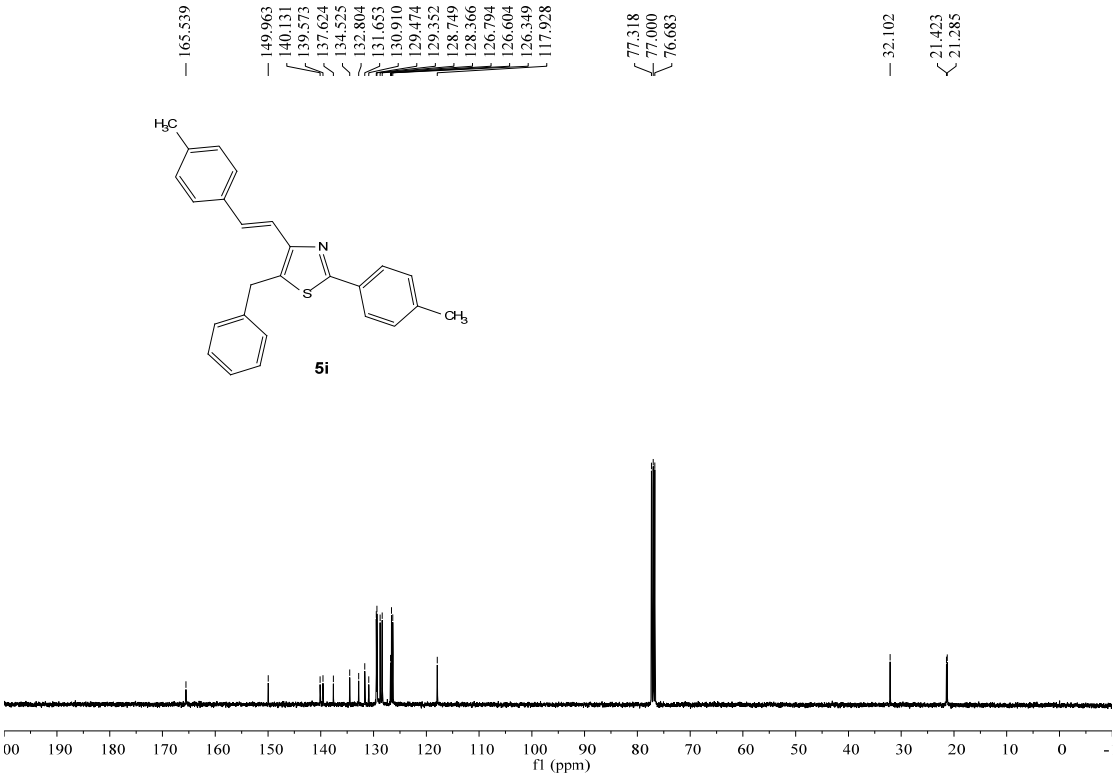


^{1}H and ^{13}C NMR spectra of 5h

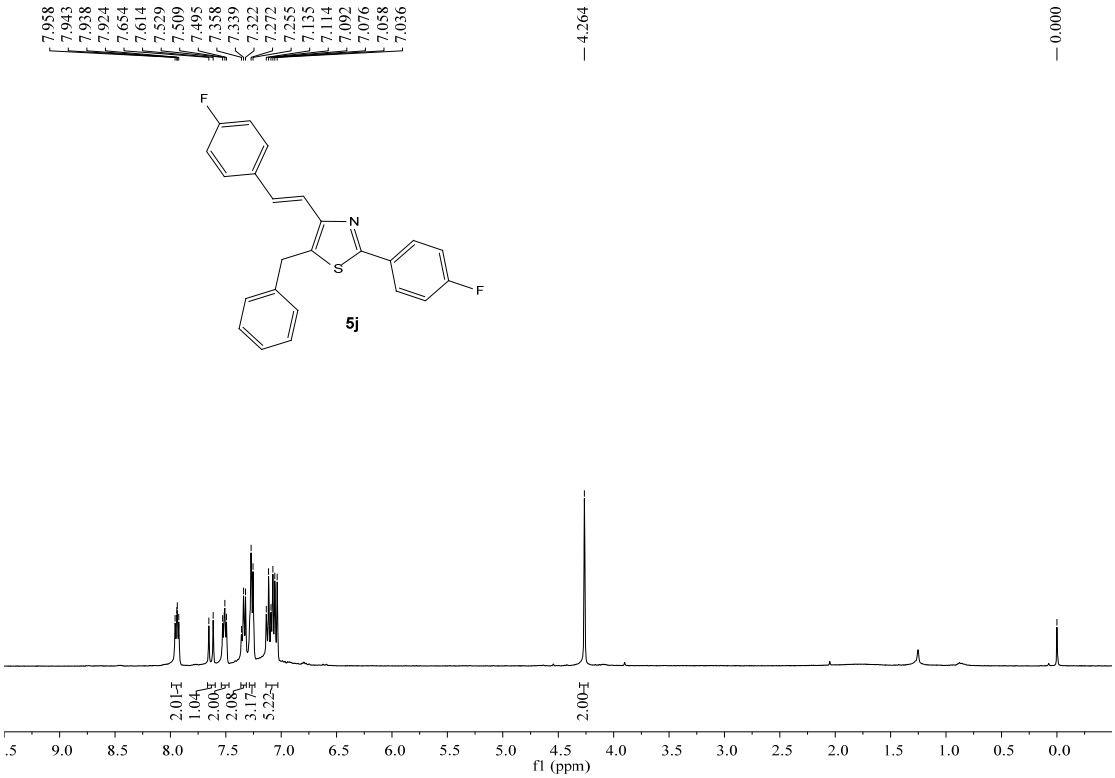


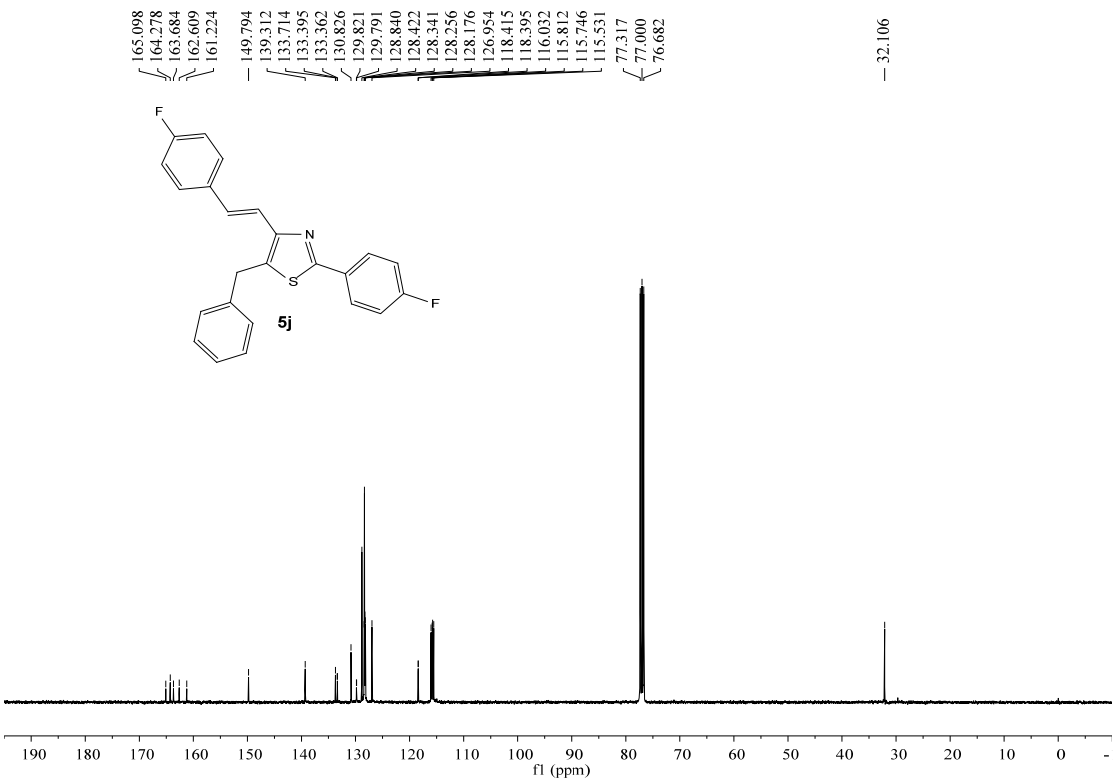
^{1}H and ^{13}C NMR spectra of 5i



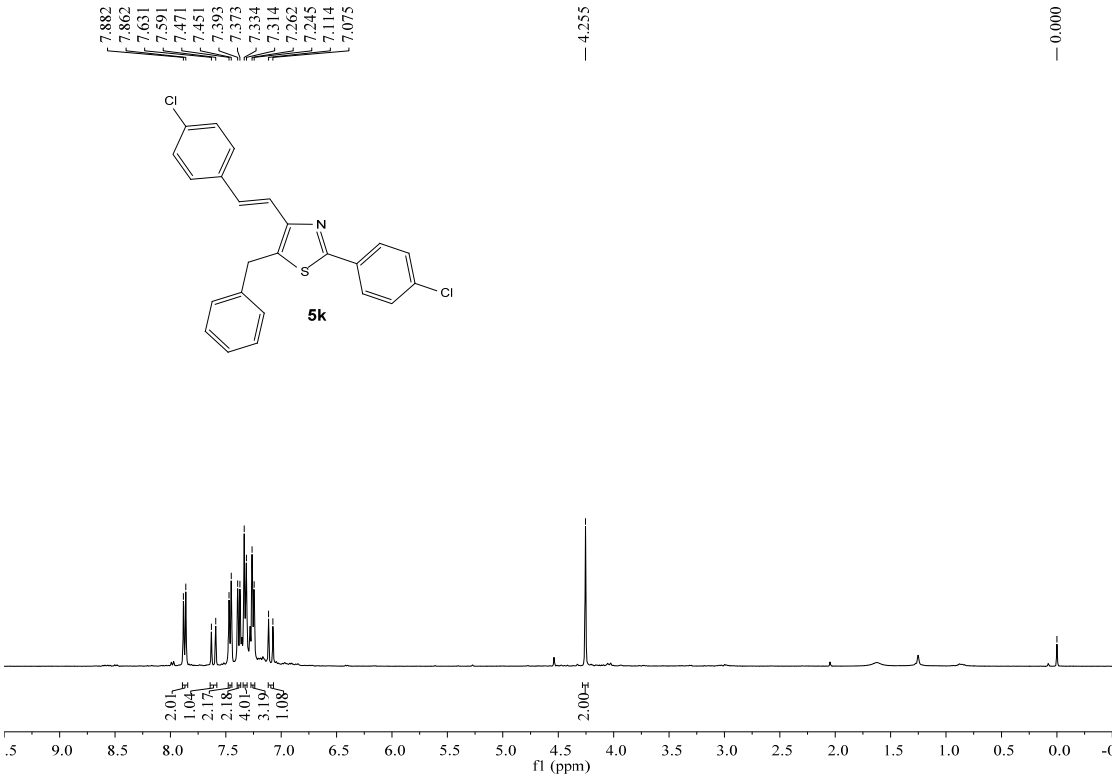


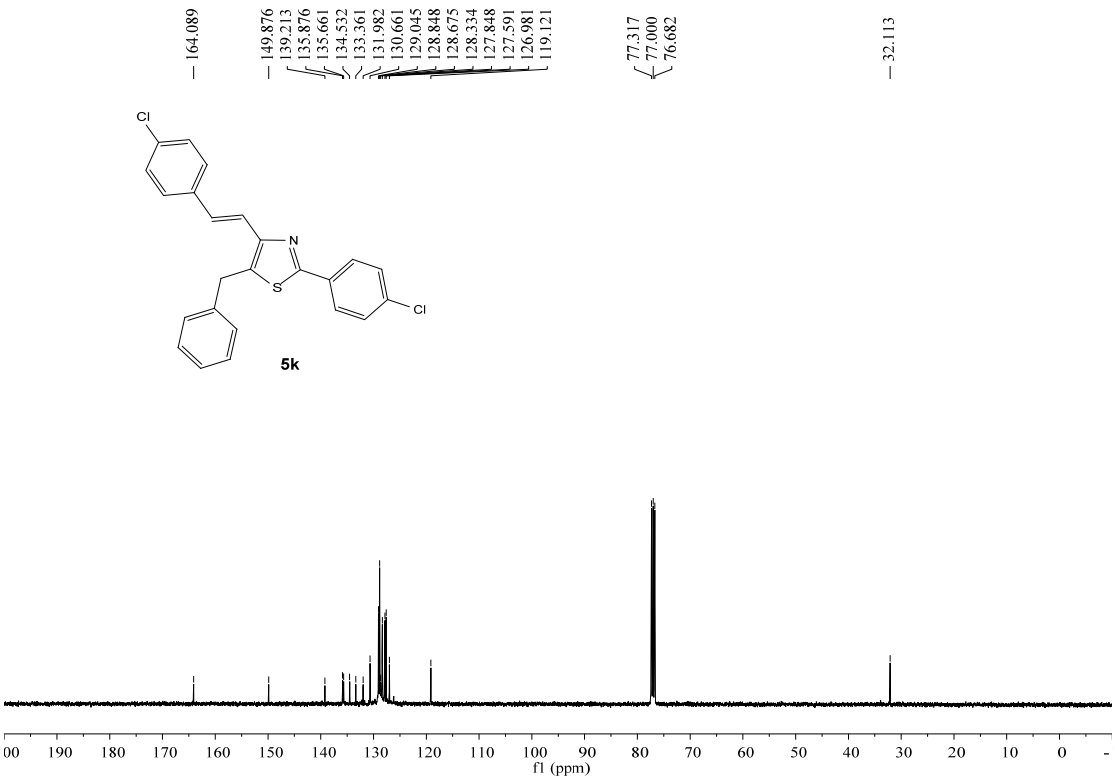
^{1}H and ^{13}C NMR spectra of 5j



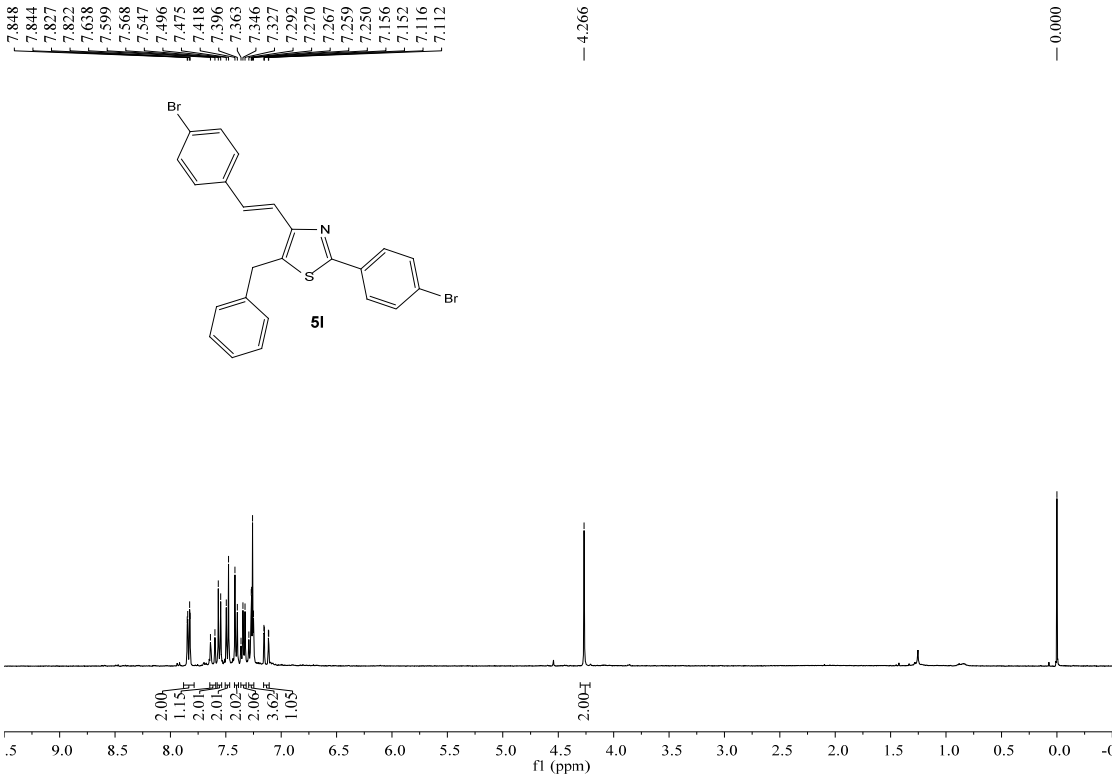


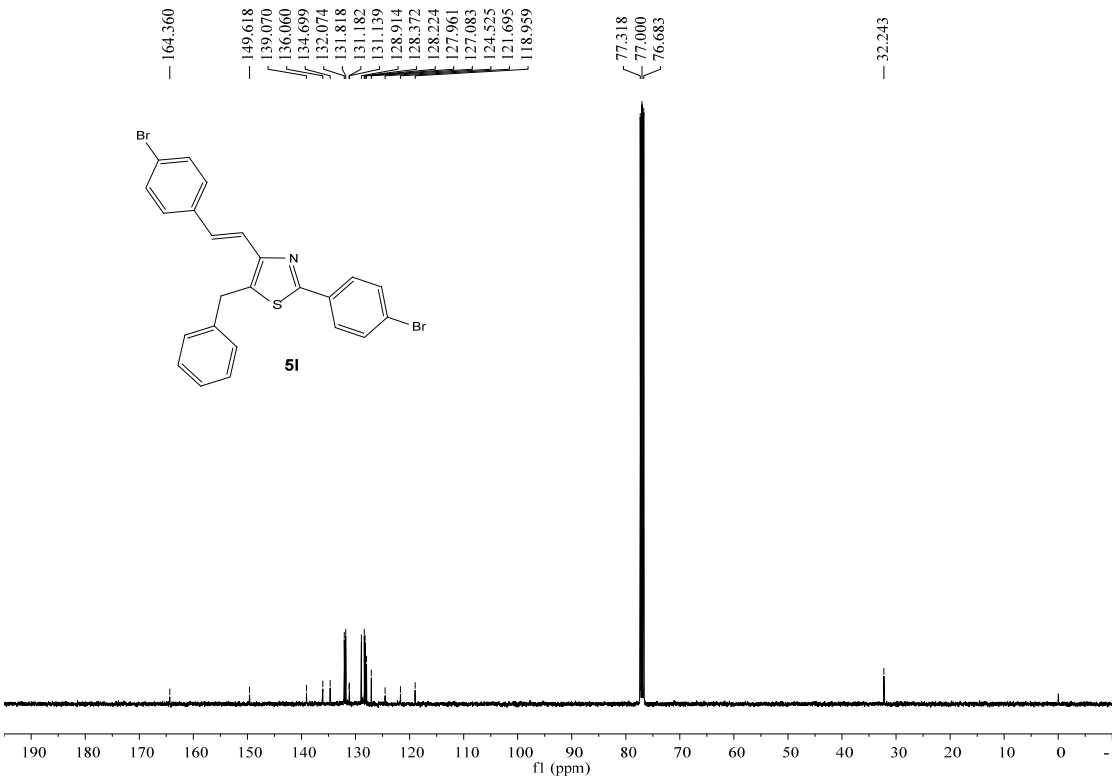
^{1}H and ^{13}C NMR spectra of 5k



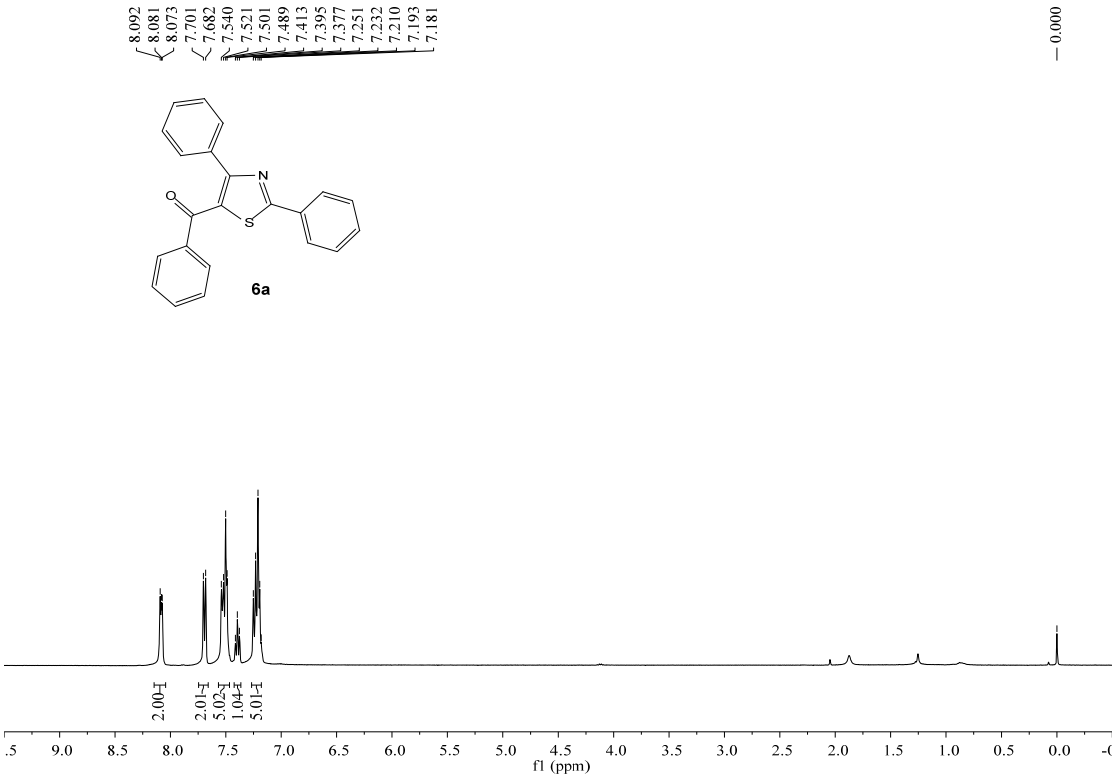


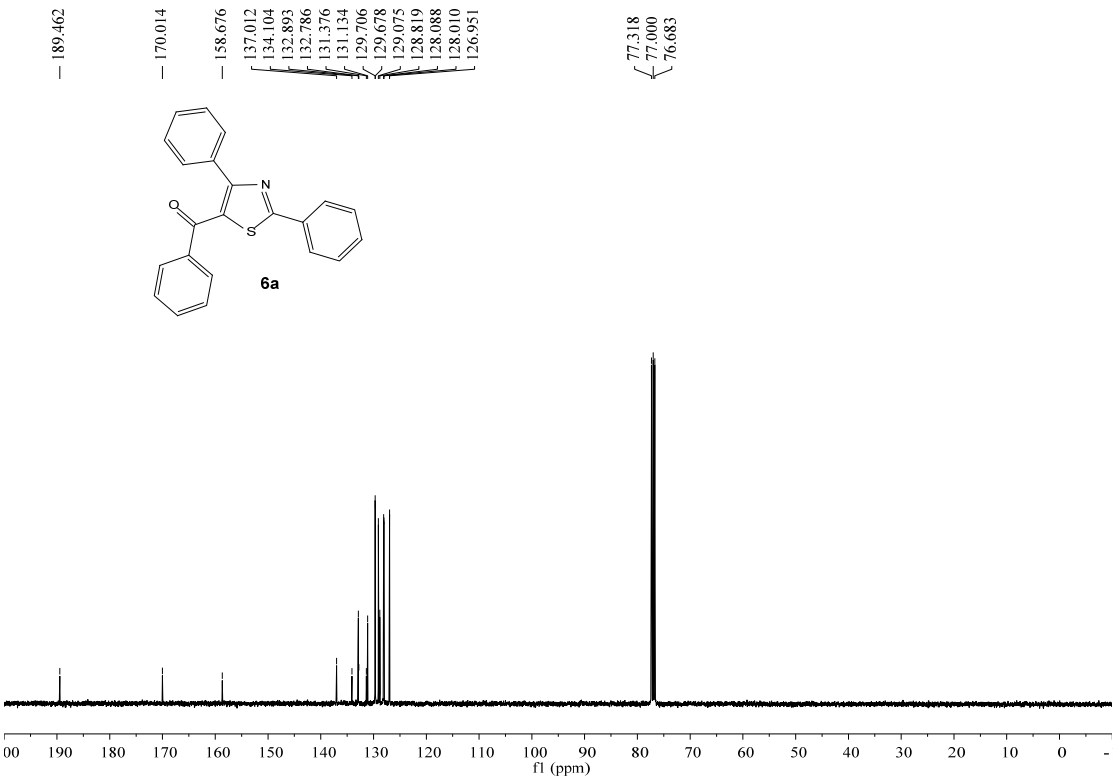
^{1}H and ^{13}C NMR spectra of 5l





^{1}H and ^{13}C NMR spectra of 6a





^{1}H and ^{13}C NMR spectra of 6b