Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One-Pot Synthesis of Hydrazono-Sulfonamide Adducts using Cu(BTC) MOF Catalyst and Their Remarkable AIEE Properties: Unprecedented Copper(II)-Catalyzed Generation of Ketenimine

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Contents

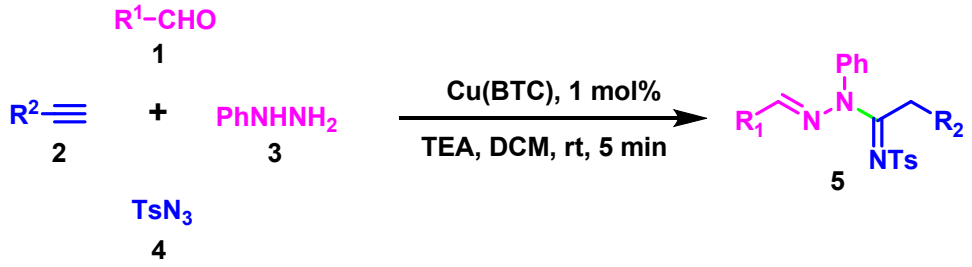
General Methods

All reactions were carried out under aerobic conditions. Unless stated otherwise, all solvents and chemicals were obtained from commercial sources and used without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel-G plates (Merck) using a mixture of petroleum ether (60-80 ˚C) and ethyl acetate (7:3) as eluent. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300 MHz instrument using TMS as an internal standard and $CDCl_3$ as solvent. Chemical shifts are expressed in parts per million (ppm) and the coupling constants (*J* values) are expressed in hertz (Hz). The following abbreviations are used to indicate spin multiplicities: s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet). The powder XRD pattern of the catalyst sample was performed on X'Pert PANalytical Diffractometer – Version 3.0 instrument using a Cu Kα radiation at room temperature with sample stage PW3071/60. FT-IR spectra were recorded on SHIMADZU FT-IR-8400S instrument using KBr pellet technique in the range of 4000–400 cm^{-1}. Elemental analyses were carried out with Perkin-Elmer 2400 series II analyzer. Melting points were determined in open capillaries and were uncorrected. Tosyl azide[1] was prepared by adopting reported method. Absorption measurements were carried out in Agilent single beam UV-Diode Array spectrophotometer. Fluorescence spectra were recorded in Agilent Cary Eclipse Fluorescence spectrophotometer. The slit width was 5 nm for both excitation and emission.

Procedure for synthesis of Cu(BTC) MOF

The Cu(BTC) MOF was prepared following the procedure reported by Yaghi et al.[2] A mixture of benzenetricarboxylic acid (BTC) (3 mmol) and $Cu(OAc)_2.H_2O$ (5.43 mmol) was stirred in a mixture of DMF/EtOH/H_2O (1:1:1, 30 mL) at room temperature. To the clear solution obtained was added triethylamine (3.57 mmol). The reaction mixture was stirred for 23 h. The product formed was collected by filtration and washed with DMF (2 × 32 mL). It was dispersed in DCM (HPLC grade, 63 mL) overnight. Next day, the solvent was decanted and the solid was washed with fresh DCM (3 × 63 mL). It was then dried under vacuum at 130 ˚C for 12 h. Cu(BTC) MOF was obtained as deep blue colored solid in 47% yield.

General procedure for Cu(BTC) MOF catalyzed four component coupling reactions



To the stirring mixture of aldehyde **1** (1 mmol) and phenylhydrazine **3** (1 mmol) in DCM (3 mL) was added alkyne **2** (1 mmol), azide **4** (1 mmol) and activated Cu(BTC) MOF (1 mol%). To the above mixture, triethylamine (1.1 mmol) was added slowly. The whole reaction mixture was allowed to agitated for 5 min at room temperature and then filtered to separate the catalyst from reaction mixture. To the filtrate was added petroleum ether and ethyl acetate mixture (1:1, 20 mL) and resulting mixture was stirred for 10 min. About 75% of solvent mixture was distilled off from filtrate under vacuum at 70 ˚C. The above crude product was cooled to 0 to 5 ˚C and triturated immediately in 5-8 min to afford white solid which was collected by filtration. The recovered catalyst was thoroughly washed with DCM and air dried for 10 min before using it for next reaction.

The crystal structure of compound **5a** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number **CCDC 1023738**

References

1**.** Lu, H.; Subbarayan, V.; Tao, J.; Zhang, X. P. *Organometallics* **2010**, *29,* 389-393.

2. Tranchemontagne, D. J.; Hunt, J. R.; Yaghi, O. M. *Tetrahedron* **2008**, *64,* 8553-8557.

Characterization Data for Cu(BTC) MOF

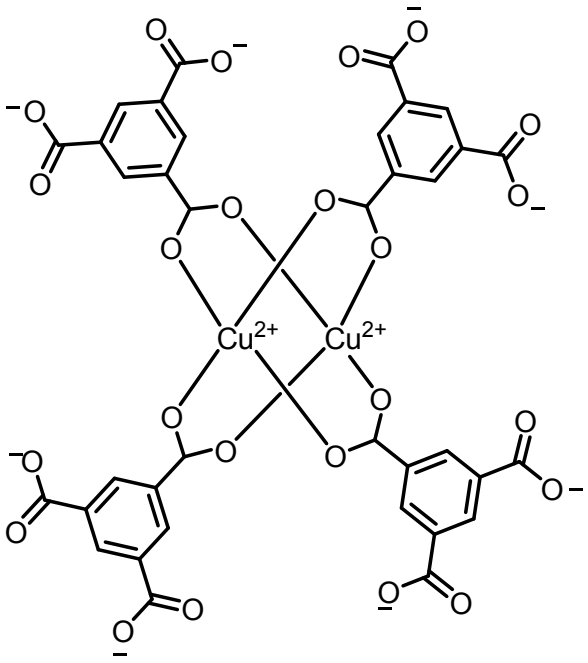


Figure 1. Structure of Cu(BTC)

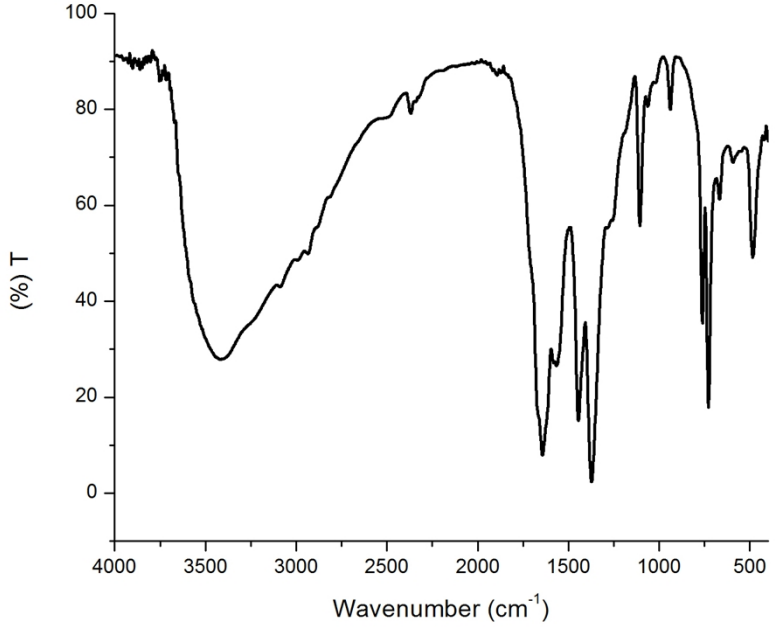


Figure 2. FT-IR spectra of Cu(BTC)

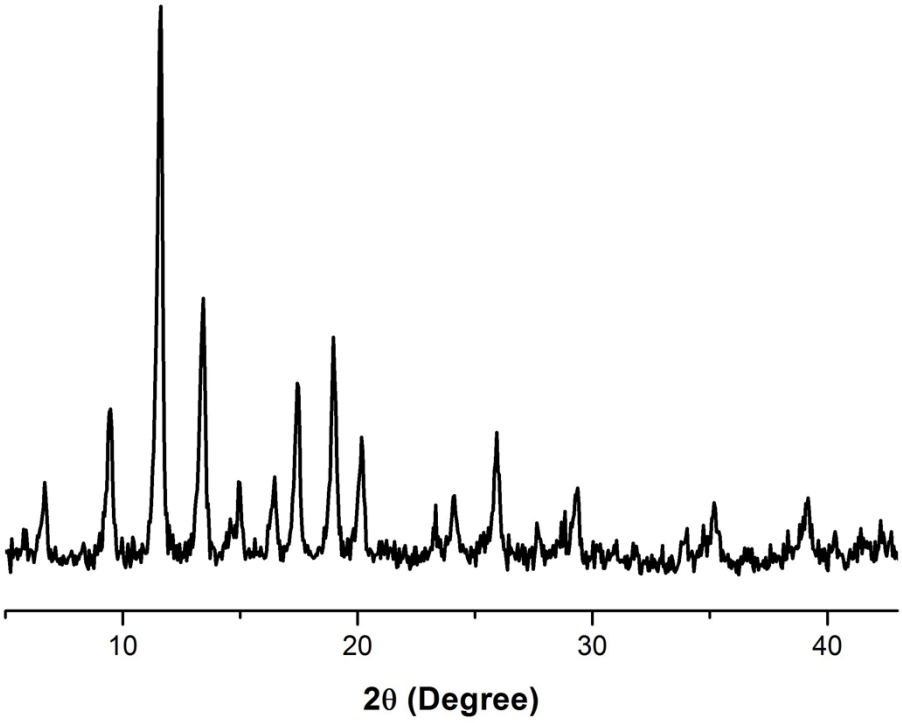


Figure 3. Powder XRD pattern of Cu(BTC)

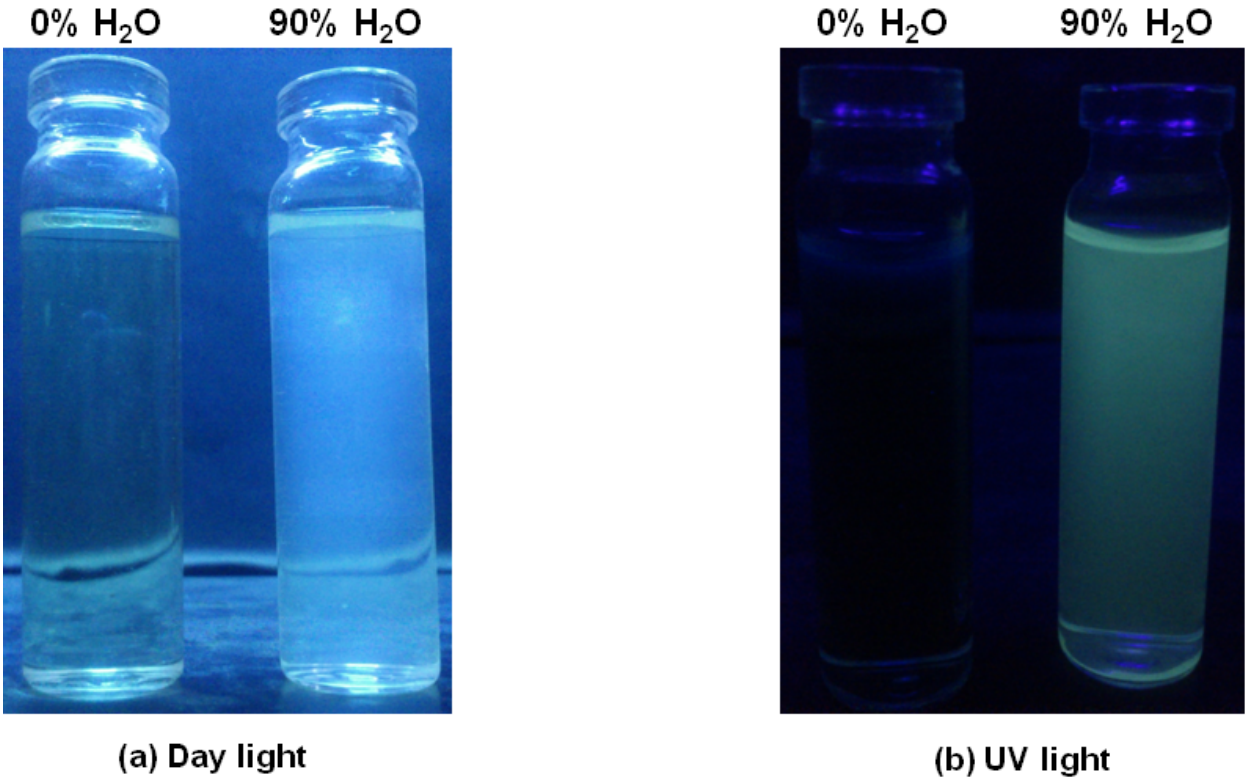
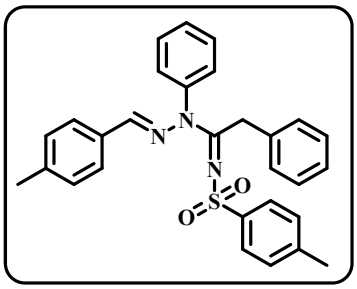
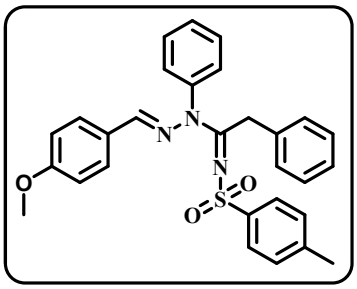
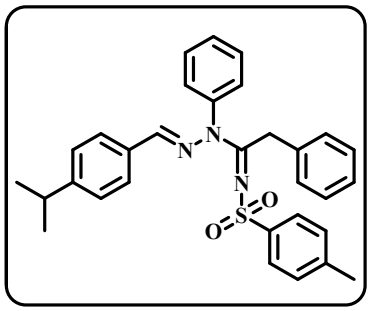
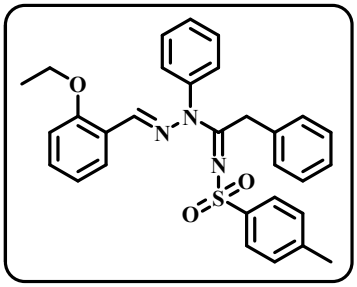
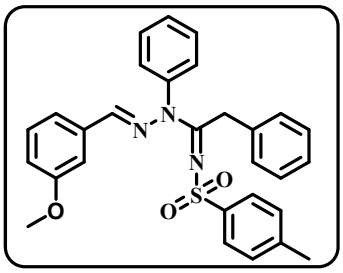
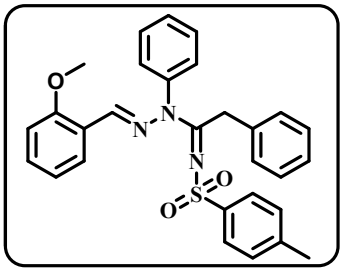
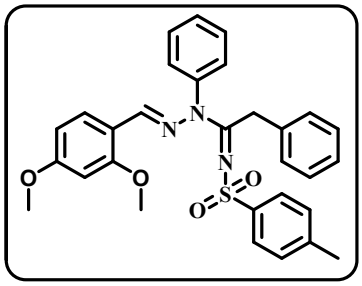
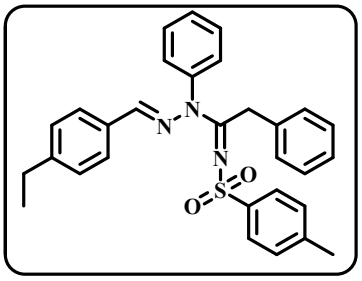
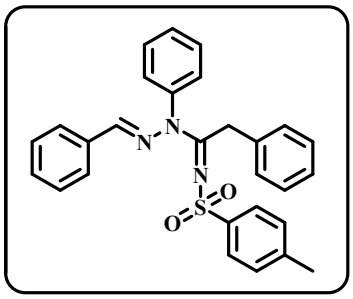


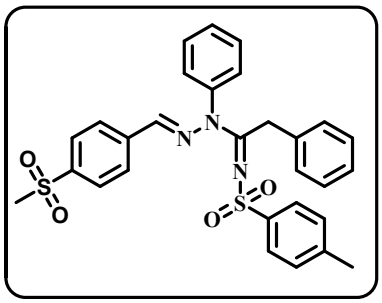
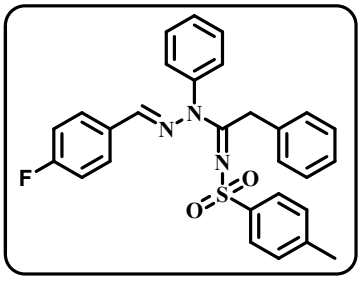
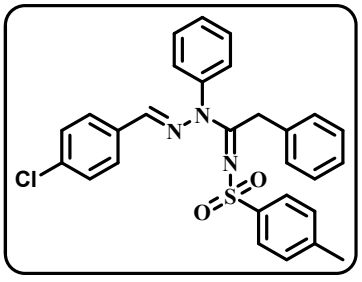
Figure 4. Color changes of **5r** under day light (a) and UV light (b) with Water:THF mixtures

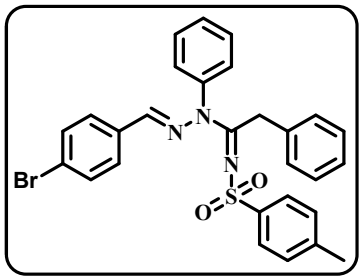
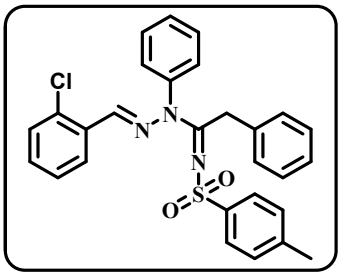
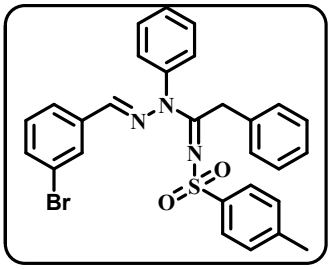
Characterization Data for all Products

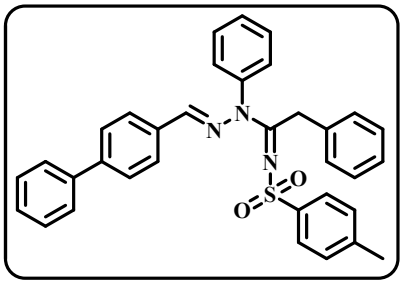
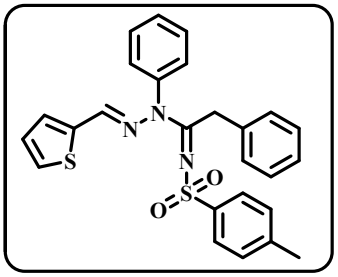
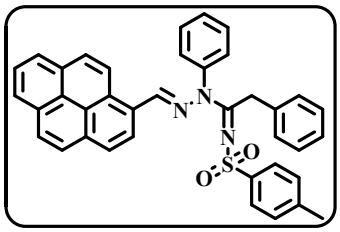
	**4-methyl-*N*-(1-((*E*)-2-(4-methylbenzylidene)-1 phenylhydrazinyl)-2 phenylethylidene)benzenesulfonamide (5a)** White solid; Isolated yield 95% (0.38g); mp 169-171 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.50 (m, 4H), 7.46 (d, *J* = 8.1 Hz ,2H), 7.35 (d, *J* = 8.1 Hz ,2H), 7.31 – 7.27 (m, 3H), 7.22 – 7.20 (m, 2H), 7.17 – 7.10 (m, 6H), 4.96 (s, 2H), 2.34 & 2.33 (2 s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 145.4, 141.8, 140.8, 140.7, 136.4, 135.8, 130.8, 130.1, 129.4, 129.3, 128.8, 128.8, 128.7, 128.5, 127.4, 126.5, 126.1, 37.0, 21.4, 21.3; MS (ESI) m/z $[M+H]^+$: 482.2; Anal. Calcd for: $C_{29}H_{27}N_3O_2S$: C, 72.32; H, 5.65; N, 8.72%. Found C, 72.36; H, 5.63; N, 8.76%.
	***N*-(1-((*E*)-2-(4-methoxybenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5b)** White solid; Isolated yield 93% (0.34g); mp 179-181 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 7H), 7.40 (d, *J* = 8.7 Hz ,2H), 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 2H), 7.10 – 7.11 (m, 4H), 6.84 (d, *J* = 8.7 Hz ,2H), 4.95 (s, 2H), 3.80 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 161.6, 145.2, 141.8, 140.8, 136.6, 135.9, 130.1, 129.3, 129.2, 128.8, 128.7, 128.5, 126.5, 126.3, 126.1, 114.2, 55.4, 37.0, 21.3; MS (ESI) m/z $[M+H]^+$: 498.2; Anal. Calcd for: $C_{29}H_{27}N_3O_3S$: C, 70.00; H, 5.47; N, 8.44%. Found C, 70.02; H, 5.44; N, 8.42%.
	***N*-(1-((*E*)-2-(4-isopropylbenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5c)** White solid; Isolated yield 93% (0.32g); mp 171-173 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 7H), 7.38 (d, *J* = 8.1 Hz ,2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 3H), 7.17 (s, 1H), 7.10 – 7.06 (m, 4H), 4.95 (s, 2H), 2.89 (sept, *J* = 6.9 Hz, 1H), 2.32 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 151.8, 145.4, 141.8, 140.7, 136.5, 135.8, 131.2, 130.1, 129.3, 128.8, 128.8, 128.7, 128.5, 127.7, 126.8, 126.5, 126.1, 36.9, 34.1, 23.7, 21.3; MS (ESI) m/z $[M+H]^+$: 510.3; Anal. Calcd for: $C_{31}H_{31}N_3O_2S$: C, 73.05; H, 6.13; N, 8.24%. Found C, 73.00; H, 6.17; N, 8.27%.

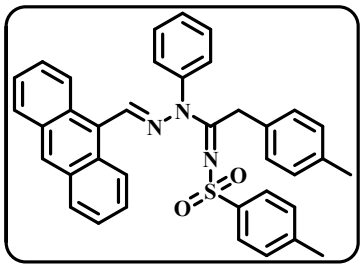
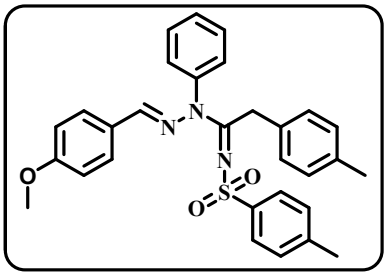
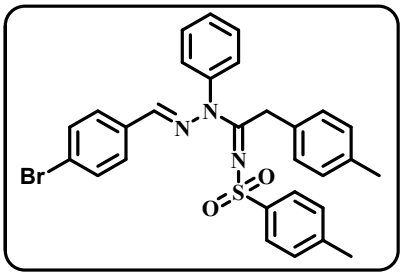
	***N*-(1-((*E*)-2-(2-ethoxybenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5d)** White solid; Isolated yield 91% (0.31g); mp 150-152 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ; 7.71 (d, *J* = 10.2 Hz, 2H), 7.55 – 7.44 (m, 7H), 7.32 – 7.27 (m, 3H), 7.22 – 7.17 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 4H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 2H), 3.85 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.29 (s, 3H), 1.12 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 157.8, 142.2, 141.7, 140.8, 136.7, 135.9, 131.7, 129.9, 129.1, 128.9, 128.7, 128.6, 128.4, 126.4, 126.3, 126.0, 122.3, 120.8, 112.4, 64.0, 37.0, 21.3, 14.3; MS (ESI) m/z $[M+H]^+$: 511.2; Anal. Calcd for: $C_{30}H_{29}N_3O_3S$: C, 70.43; H, 5.71; N, 8.21%. Found C, 70.41; H, 5.75; N, 8.24%.
	***N*-(1-((*E*)-2-(3-methoxybenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5e)** White solid; Isolated yield 90% (0.33g); mp 151-153 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.46 (m, 6H), 7.31 – 7.17 (m, 6H), 7.11 – 7.04 (m, 5H), 6.96 – 6.87 (m, 2H), 4.96 (s, 2H), 3.77 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 159.9, 145.1, 141.9, 140.6, 136.3, 135.7, 134.9, 130.1, 129.6, 129.4, 128.8, 128.7, 128.6, 128.5, 126.5, 126. 1, 120.9, 117.1, 111.3, 55.3, 37.1, 21.3; MS (ESI) m/z $[M+H]^+$: 498.2; Anal. Calcd for: $C_{29}H_{27}N_3O_3S$: C, 70.00; H, 5.47; N, 8.44%. Found C, 70.04; H, 5.49; N, 8.41%.
	***N*-(1-((*E*)-2-(2-methoxybenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5f)** White solid; Isolated yield 90% (0.33g); mp 180-182 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 6.0 Hz, 1H), 7.60 (s, 1H), 7.47 – 7.37 (m, 7H), 7.26 – 7.17 (m, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 4.90 (s, 2H), 3.55 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 158.1, 141.8, 141.6, 140.6, 136.4, 135.7, 131.7, 130.0, 129.3, 128.8, 128.6, 128.4, 126.5, 126.4, 126.0, 122.0, 120.7, 110.9, 55.3, 36.9, 21.3; MS (ESI) m/z $[M+H]^+$: 498.2; Anal. Calcd for: $C_{29}H_{27}N_3O_3S$: C, 70.00; H, 5.47; N, 8.44%. Found C, 70.04; H, 5.49; N, 8.47%.

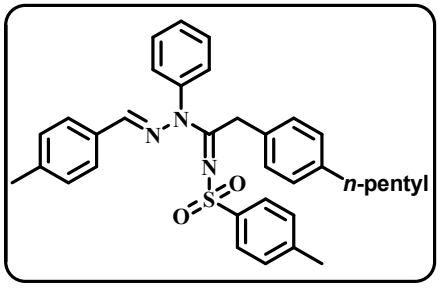
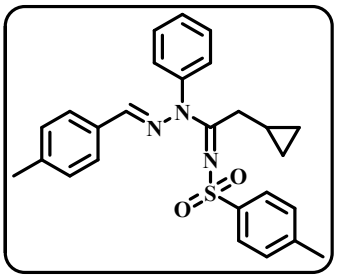
	***N*-(1-((*E*)-2-(2,4-dimethoxybenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5g)** White solid; Isolated yield 87% (0.27g); mp 173-175 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.55 – 7.44 (m, 7H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.08 (t, *J* = 8.1 Hz, 4H), 6.49 (dd, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 4.94 (s, 2H), 3.82 (s, 3H), 3.62 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 163.1, 159.7, 141.9, 141.6, 141.0, 136.8, 136.0, 129.9, 129.1, 128.9, 128.7, 128.4, 127.8, 126.4, 126.0, 115.3, 106.8, 98.1, 55.4 (2 carbons merged), 37.0, 21.3; MS (ESI) m/z $[M+H]^+$: 528.2; Anal. Calcd for: $C_{30}H_{29}N_3O_4S$: C, 68.29; H, 5.54; N, 7.96%. Found C, 68.34; H, 5.52; N, 7.99%.
	***N*-(1-((*E*)-2-(4-ethylbenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5h)** White solid; Isolated yield 94% (0.35g); mp 159-161 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 7H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 1H), 7.19 – 7.14 (m, 3H), 7.10 – 7. 06 (m, 4H), 4.97 (s, 2H), 2.63 (q, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 147.2, 145.4, 141.8, 140.7, 136.4, 135.8, 131.1, 130.1, 129.3, 128.8, 128.8, 128.7, 128.5, 128.2, 127.7, 126.5, 126.0, 36.9, 28.8, 21.3, 15.1; MS (ESI) m/z $[M+H]^+$: 496.2; Anal. Calcd for: $C_{30}H_{29}N_3O_2S$: C, 72.70; H, 5.90; N, 8.48%. Found C, 72.75; H, 5.87; N, 8.46%.
	***N*-(1-((*E*)-2-benzylidene-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5i)** White solid; Isolated yield 92% (0.40g); mp 169-171 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.44 (m, 9H), 7.34 – 7.25 (m, 5H), 7.22 – 7.17 (m, 2H), 7.11 – 7.06 (m, 3H), 4.97 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 145.2, 141.9, 140.6, 136.4, 135.7, 133.6, 130.4, 130.1, 129.4, 128.8, 128.7, 128.7, 128.5, 127.6, 126.5, 126.1, 37.0, 21.3; MS (ESI) m/z $[M+H]^+$: 468.02; Anal. Calcd for: $C_{28}H_{25}N_3O_2S$: C, 71.92; H, 5.39; N, 8.99%. Found C, 71.88; H, 5.42; N, 9.02%.

	**4-methyl-*N*-(1-((*E*)-2-(4-(methylsulfonyl)benzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)benzenesulfonamide (5j)** White solid; Isolated yield 88% (0.26g); mp 167-168 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.53 (m, 5H), 7.49 – 7.44 (m, 4H), 7.34 – 7.19 (m, 5H), 7.12 (d, *J* = 6.4 Hz, 4H), 4.96 (s, 2H), 3.03 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 142.2, 141.6, 140.2, 138.7, 135.9, 135.5, 130.3, 129.8, 128.9, 128.7, 128.5, 128.4, 128.1, 127.7, 126.7, 126.1, 44.3, 37.2, 21.3; MS (ESI) m/z $[M+H]^+$: 546.1; Anal. Calcd for: $C_{29}H_{27}N_3O_4S_2$: C, 63.83; H, 4.99; N, 7.70%. Found C, 63.87; H, 5.04; N, 7.67%.
	***N*-(1-((*E*)-2-(4-fluorobenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5k)** White solid; Isolated yield 91% (0.35g); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.40 (m, 9H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.10 – 7.06 (m, 4H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.95 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 165.6, 162.3, 143.9, 141.9, 140.6, 136.2, 135.7, 130.1, 129.9, 129.8, 129.5, 129.4, 128.8, 128.6, 129.5, 126.5, 126.0, 116.0, 115.7, 37.1, 21.3; MS (ESI) m/z $[M+H]^+$: 486.2Anal. Calcd for: $C_{28}H_{24}FN_3O_2S$: C, 69.26; H, 4.98; N, 8.65%. Found C, 69.24; H, 4.95; N, 8.68%.
	***N*-(1-((*E*)-2-(4-chlorobenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5l)** White solid; Isolated yield 88% (0.31g); mp 178-179 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.45 (m, 8H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 - 7.27 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 7.09 – 7.06 (m, 4H), 4.95 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 143.6, 142.0, 140.3, 136.2, 135.9, 135.6, 131.9, 130.1, 129.5, 128.9, 128.8, 128.6, 128.5, 128.5,126.5, 125.9, 37.0, 21.3. MS (ESI) m/z $[M+H]^+$: 502.1; Anal. Calcd for: $C_{28}H_{24}ClN_3O_2S$: C, 66.99; H, 4.82; N, 8.37%. Found C, 66.72; H, 4.80; N, 8.33%.

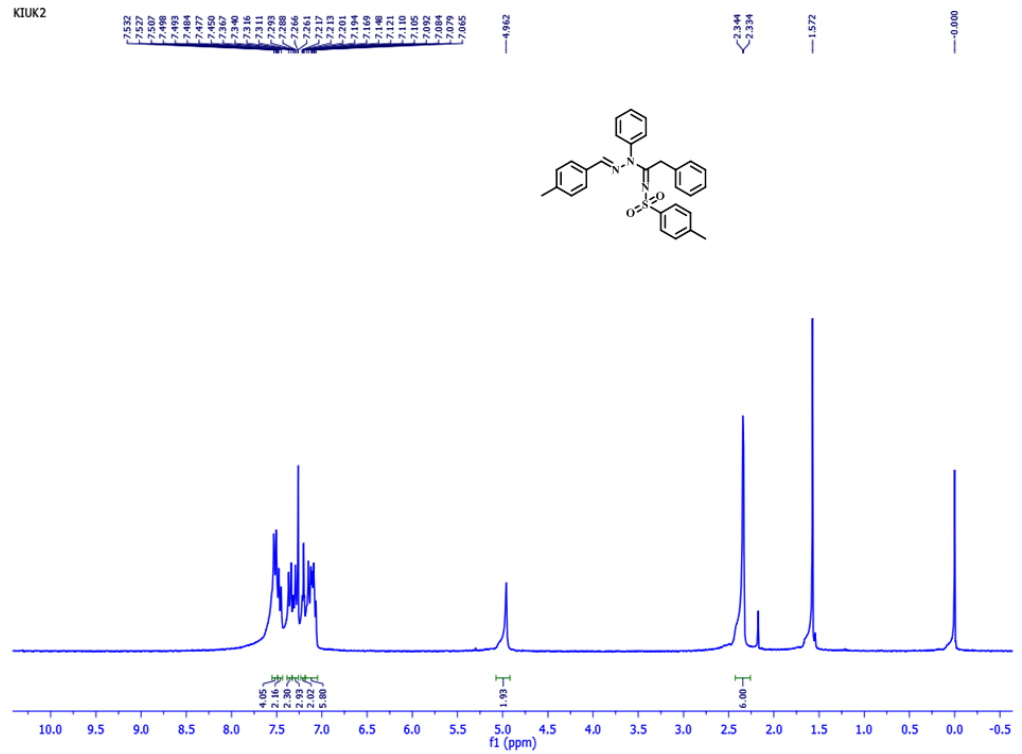
	***N*-(1-((*E*)-2-(4-bromobenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5m)** White solid; Isolated yield 88% (0.26g); mp 175-177 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.43 (m, 9H), 7.32 - 7.27 (m, 4H), 7.22 – 7.19 (m, 1H), 7.17 – 7.15 (m, 1H), 7.10 – 7.07 (m, 4H), 4.94 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 143.7, 142.0, 140.5, 136.2, 135.6, 132.5, 131.9, 130.2, 129.5, 128.9, 128.8, 128.6, 128.5, 126.6, 126.1, 124.7, 37.1, 21.3; MS (ESI) m/z $[M+H]^+$: 546.1; Anal. Calcd for: $C_{28}H_{24}BrN_3O_2S$: C, 61.54; H, 4.43; N, 7.69%. Found C, 61.51; H, 4.45; N, 7.73%.
	***N*-(1-((*E*)-2-(2-chlorobenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5n)** White solid; Isolated yield 86% (0.30g); mp 169-171 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 1H), 7.66 (s, 1H), 7.57 – 7.47 (m, 7H), 7.33 – 7.28 (m, 2H), 7.26 – 7.18 (m, 4H), 7.12 – 7.07 (m, 4H), 4.96 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 142.0, 141.9, 140.5, 136.2, 135.6, 134.6, 131.2, 131.1, 130.2, 129.8, 129.6, 128.8, 128.6, 128.5, 128.4, 127.3, 127.0, 126.6, 126.1, 37.1, 21.3; MS (ESI) m/z $[M+H]^+$: 502.1; Anal. Calcd for: $C_{28}H_{24}ClN_3O_2S$: C, 66.99; H, 4.82; N, 8.37%. Found C, 67.04; H, 4.80; N, 8.34%.
	***N*-(1-((*E*)-2-(3-bromobenzylidene)-1-phenylhydrazinyl)-2-phenylethylidene)-4-methylbenzenesulfonamide (5o)** White solid; Isolated yield 90% (0.26g); mp 188-190 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.55 – 7.43 (m, 8H), 7.35 – 7.30 (m, 3H), 7.25 – 7.16 (m, 2H), 7.14 – 7.04 (m, 5H), 4.94 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 143.1, 142.1, 140.0, 135.9, 135.6, 135.5, 133.1, 130.2, 130.1, 129.6, 128.8, 128.6, 128.5, 126.6, 126.2, 126.0, 122.8, 37.2, 21.3; MS (ESI) m/z $[M+H]^+$: 546.1; Anal. Calcd for: $C_{28}H_{24}BrN_3O_2S$: C, 61.54; H, 4.43; N, 7.69%. Found C, 61.58; H, 4.41; N, 7.71%.

	**_N_-(1-((_E_)-2-(biphenyl-4-ylmethylene)-1 phenylhydrazinyl)-2-phenylethylidene)-4 methylbenzenesulfonamide (5p)** White solid; Isolated yield 89% (0.26g); mp 179-181 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.51 (m, 11H), 7.50 – 7.41 (m, 4H), 7.38 – 7.18 (m, 6H), 7.12 – 7.07 (m, 4H), 4.99 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 144.8, 143.2, 141.9, 140.6, 140.1, 136.4, 135.8, 132.5, 130.1, 129.4, 128.8, 128.7, 128.5, 128.1, 127.8, 127.3, 127.0, 126.5, 126.1, 37.0, 21.3; MS (ESI) m/z $[M+H]^+$: 544.1; Anal. Calcd for: $C_{34}H_{29}N_3O_2S$: C, 75.11; H, 5.38; N, 7.73%. Found C, 75.07; H, 5.41; N, 7.77%.
	**4-methyl-_N_-(2-phenyl-1-((_E_)-1-phenyl-2-(thiophen-2-ylmethylene)hydrazinyl)ethylidene)benzenesulfonamide (5q)** White solid; Isolated yield 89% (0.37g); mp 148-150 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 7.2 Hz, 2H) 7.56 – 7.46 (m, 5H), 7.38 – 7.28 (m, 4H), 7.23 – 7.18 (m, 1H), 7.11 – 7.06 (m, 4H), 7.01 – 6.95 (m, 2H), 4.90 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 141.8, 140.6, 139.4, 138.5, 136.2, 135.5, 130.7, 130.1, 129.4, 129.2, 128.8, 128.8, 128.5, 128.4, 127.4, 126.5, 126.0, 36.9, 21.3; MS (ESI) m/z $[M+H]^+$: 473.9; Anal. Calcd for: $C_{26}H_{23}N_3O_2S_2$: C, 65.94; H, 4.89; N, 8.87%. Found C, 65.90; H, 4.92; N, 8.85%.
	**4-methyl-_N_-(2-phenyl-1-((_E_)-1-phenyl-2-(pyren-1-ylmethylene)hydrazinyl)ethylidene)benzenesulfonamide (5r)** Yellow solid; Isolated yield 80% (0.2g); mp 200-202 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J = 7.8 Hz, 2H), 8.21 – 8.08 (m, 5H), 8.04 – 7.94 (m, 3H), 7.67 – 7.51 (m, 7H), 7.35 – 7.19 (m, 6H), 7.11 (d, J = 7.8 Hz, 2H), 5.10 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 144.0, 141.9, 140.6, 137.0, 135.7, 132.7, 131.2, 130.4, 130.3, 129.6, 129.4, 128.8, 128.8, 128.7, 128.7, 128.6, 127.3, 126.6, 126.4, 126.2, 126.1, 126.1, 126.0, 125.7, 125.3, 124.9, 124.8, 124.5, 121.8, 37.1, 21.3; MS (ESI) m/z $[M+H]^+$: 592.2; Anal. Calcd for: $C_{38}H_{29}N_3O_2S$: C, 77.13; H, 4.94; N, 7.10%. Found C, 77.18.16; H, 4.91; N, 7.05%.

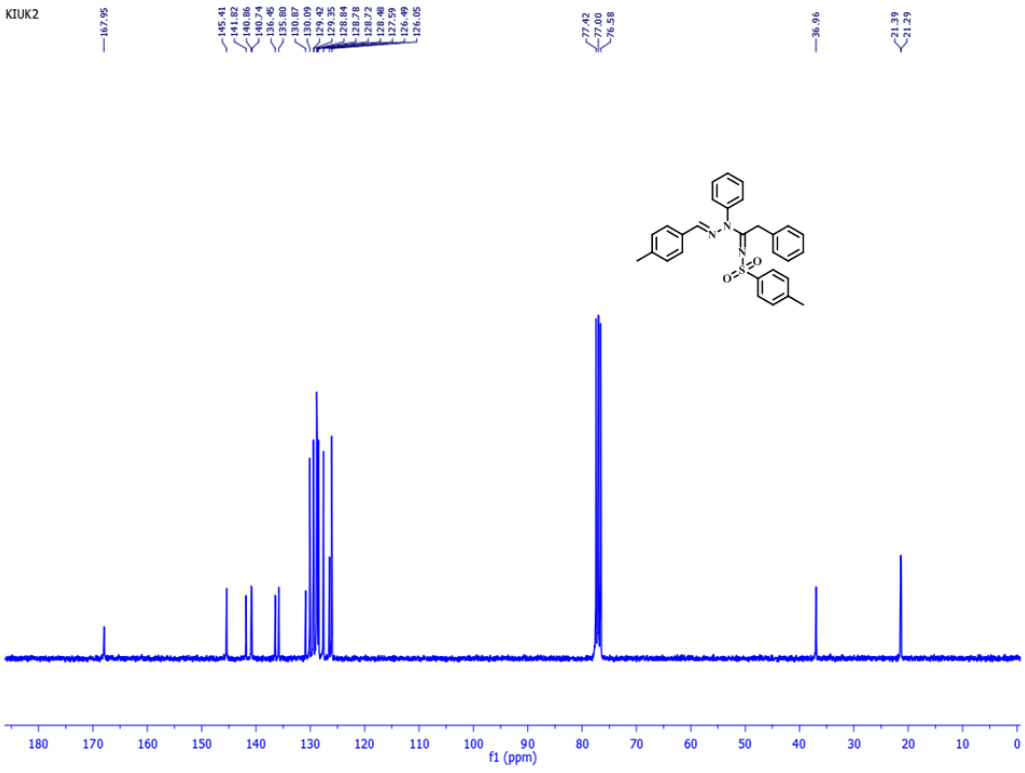
	***N*-(1-((*E*)-2-(anthracen-9-ylmethylene)-1-phenylhydrazinyl)-2-p-tolylethylidene)-4-methylbenzenesulfonamide (5s)** Yellow solid; Isolated yield 81% (0.22g); mp 193-195 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.46 – 7.28 (m, 11H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.01 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 145.0, 142.0, 140.6, 136.7, 135.4, 131.2, 130.5, 130.1, 130.0, 129.7, 128.9, 128.9, 128.8, 128.6, 128.6, 127.1, 126.5, 126.2, 125.3, 124.7, 124.3, 36.7, 21.3; MS (ESI) m/z $[M+H]^+$: 582.2; Anal. Calcd for: $C_{37}H_{31}N_3O_2S$: C, 76.39; H, 5.37; N, 7.22; O, 5.50; S, 5.51%. Found C, 76.46; H, 5.33; N, 7.26%.
	***N*-(1-((*E*)-2-(4-methoxybenzylidene)-1-phenylhydrazinyl)-2-p-tolylethylidene)-4-methylbenzenesulfonamide (5t)** White solid; Isolated yield 89% (0.33g); mp 182-184 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.39 (m, 10H), 7.18 (s, 1H), 7.11 – 7.07 (m, 6H), 6.85 (d, *J* = 8.7 Hz ,1H), 4.91 (s, 2H), 3.82 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 161.5, 145.0, 141.7, 140.7, 136.4, 136.0, 132.6, 130.1, 129.3, 129.2, 129.1, 128.7, 128.7, 126.2, 125.9, 114.1, 55.3, 36.5, 21.3, 21.0; MS (ESI) m/z $[M+H]^+$: 512.2; Anal. Calcd for: $C_{30}H_{29}N_3O_3S$: C, 70.43; H, 5.71; N, 8.21%. Found C, 70.46; H, 5.66; N, 8.26%.
	***N*-(1-((*E*)-2-(4-bromobenzylidene)-1-phenylhydrazinyl)-2-p-tolylethylidene)-4-methylbenzenesulfonamide (5u)** White solid; Isolated yield 87% (0.26g); mp 194-196 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.44 (m, 7H), 7.38 – 7.31 (m, 4H), 7.15 (s, 1H), 7.11 – 7.07 (m, 6H), 4.90 (s, 2H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 143.6, 141.9, 140.5, 136.2, 136.0, 132.6, 132.5, 131.9, 130.1, 129.5, 129.2, 128.9, 128.8, 128.6, 128.5, 126.0, 124.6, 36.5, 21.3, 21.0; MS (ESI) m/z $[M+H]^+$: 560.1; Anal. Calcd for: $C_{29}H_{26}BrN_3O_2S$: C, 62.14; H, 4.68; N, 7.50%. Found C, 62.16; H, 4.65; N, 7.53%.

	**4-methyl-*N*-(1-((*E*)-2-(4-methylbenzylidene)-1-phenylhydrazinyl)-2-(4-pentylphenyl)ethylidene)benzenesulfonamide (5v)** White solid; Isolated yield 90% (0.41g); mp 140-142 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 3H), 7.44 (t, *J* = 8.4 Hz ,5H), 7.37 (d, *J* = 8.1 Hz ,2H), 7.21 (s, 1H), 7.15 (s, 1H), 7.12 – 7.08 (m, 5H), 7.06 (s, 1H), 4.92 (s, 2H), 2.53 (t, *J* = 7.5 Hz ,2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.62 – 1.52 (m, 2H), 1.33 – 1.27 (m, 4H), 0.86 (t, *J* = 6.6 Hz ,3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.2, 145.3, 141.7, 141.1, 140.8, 136.5, 132.8, 130.9, 130.0, 129.4, 129.3, 128.7, 128.5, 127.6, 127.0, 36.4, 35.5, 31.5, 31.0, 22.5, 21.4, 21.3, 14.0; MS (ESI) m/z $[M+H]^+$: 552.2; Anal. Calcd for: $C_{34}H_{37}N_3O_2S$: C, 74.01; H, 6.76; N, 7.62%. Found C, 74.04; H, 6.72; N, 7.65%.
	***N*-(2-cyclopropyl-1-((*E*)-2-(4-methylbenzylidene)-1-phenylhydrazinyl)ethylidene)-4-methylbenzenesulfonamide (5w)** White solid; Isolated yield 87% (0.32g); mp 150-152 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 3H), 7.48 – 7.42 (m, 4H), 7.30 (s, 1H), 7.19 (s, 1H), 7.17 – 7.13 (m, 3H), 7.07 (d, *J* = 7.5 Hz ,2H), 3.53 (d, *J* = 7.2 Hz ,2H), 2.36 (s, 3H), 2.32 (s, 3H), 1.60 – 1.46 (m, 1H), 0.66 – 0.53(m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 144.8, 141.7, 140.9, 140.8, 136.4, 130.8, 130.0, 129.5, 129.3, 128.8, 128.7, 127.4, 125.8, 34.6, 21.4, 21.3, 9.2, 4.5; MS (ESI) m/z $[M+H]^+$: 446.1; Anal. Calcd for: $C_{26}H_{27}N_3O_2S$: C, 70.08; H, 6.11; N, 9.43%. Found C, 70.10; H, 6.14; N, 9.40%.

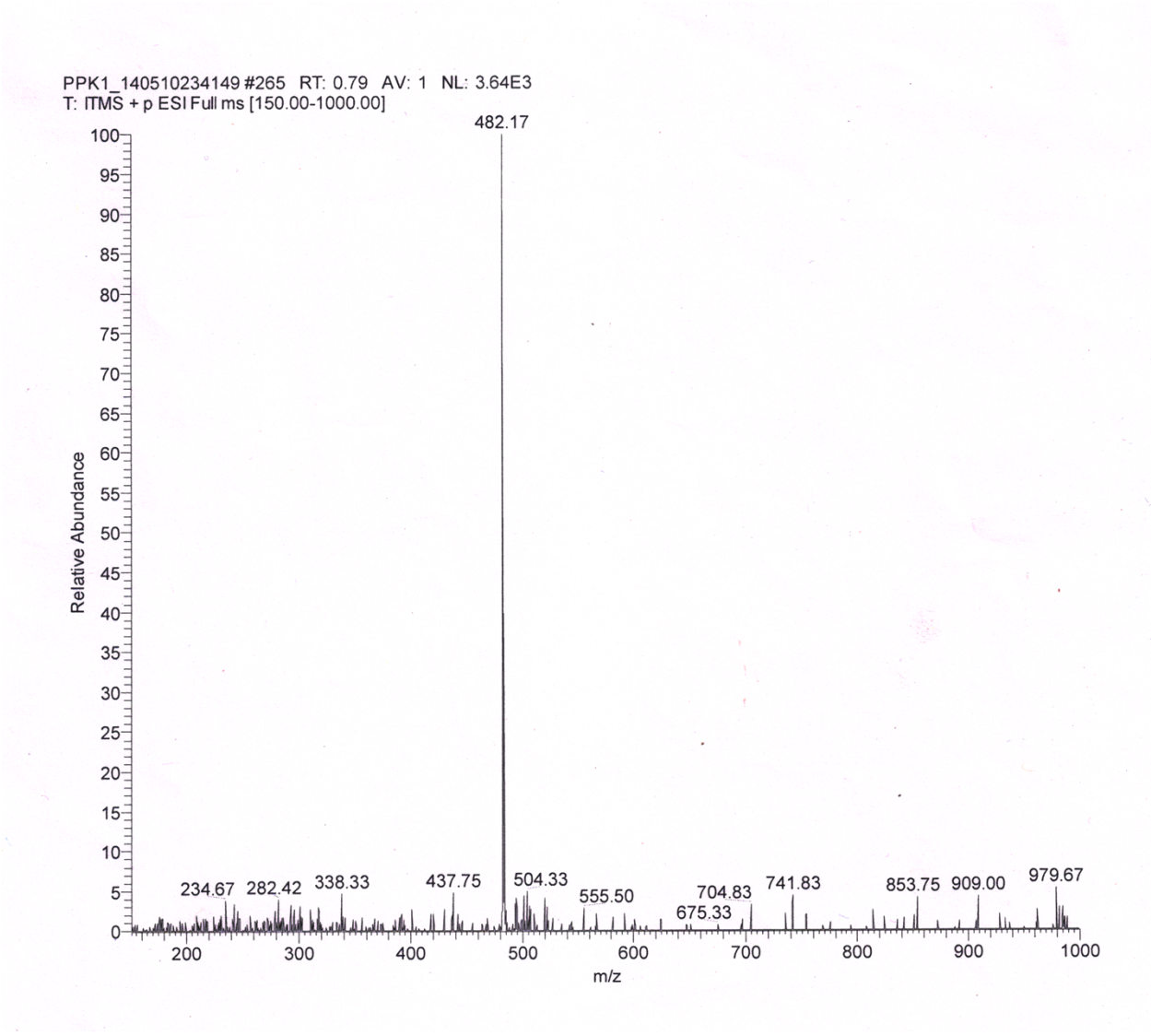
Copies of spectra for all Products



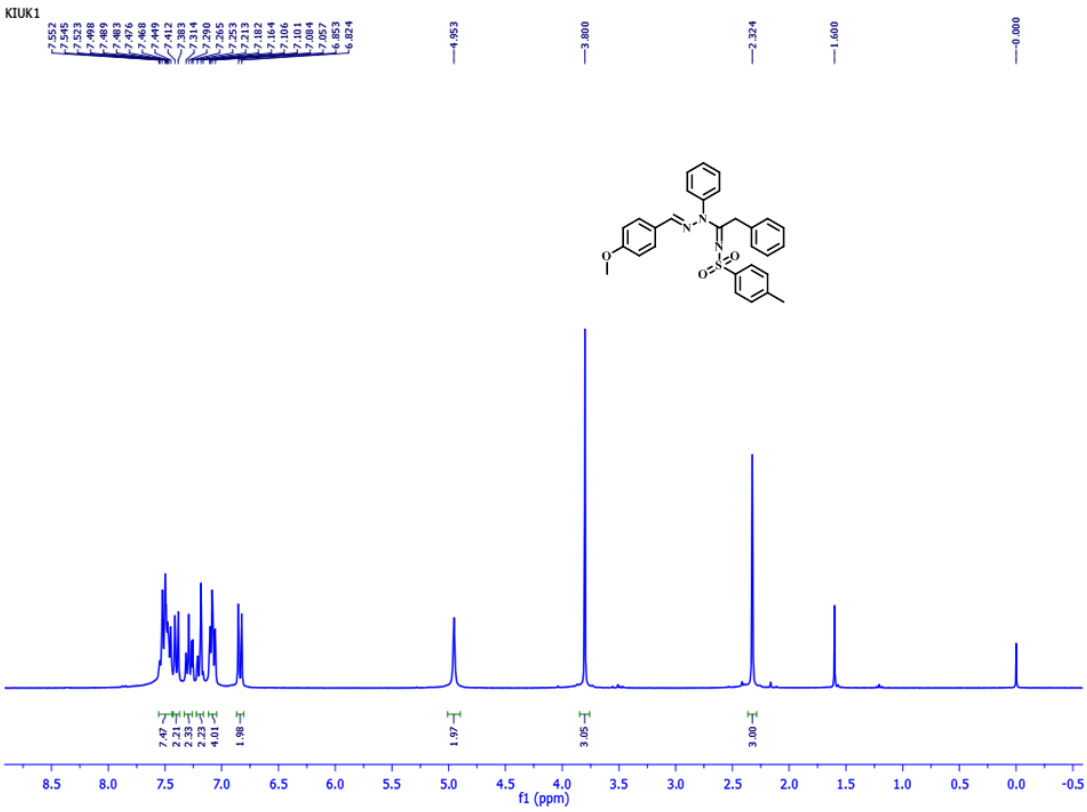
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5a**



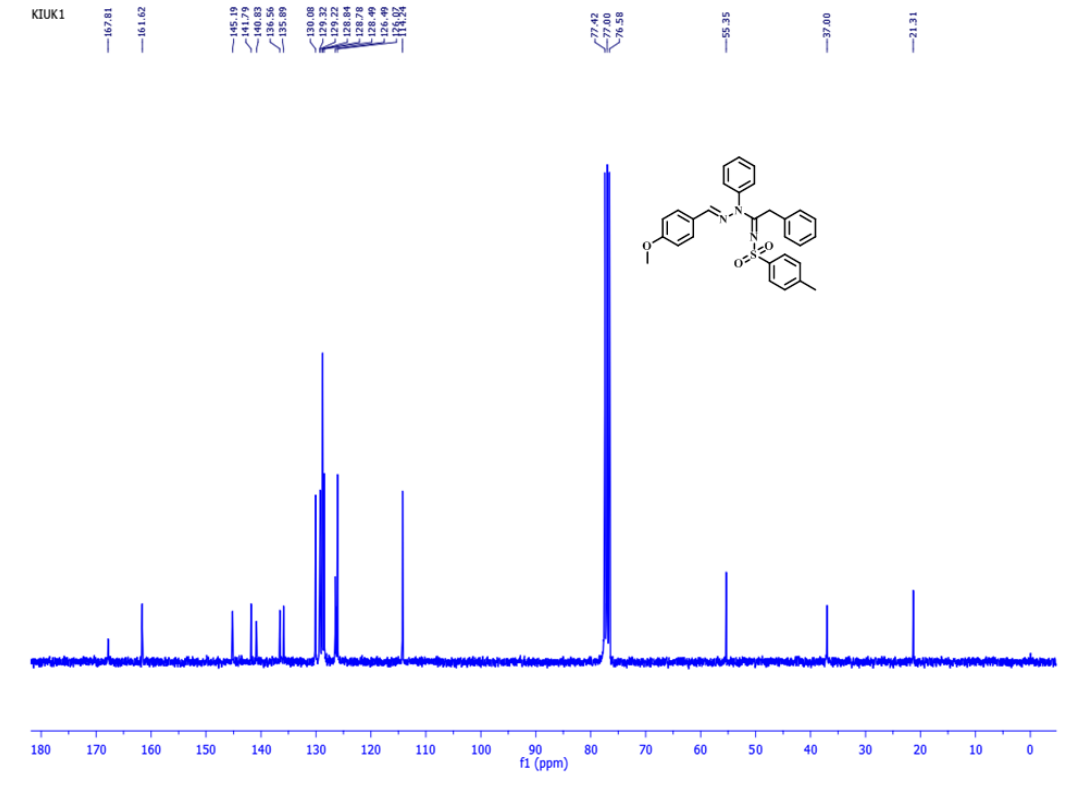
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5a**



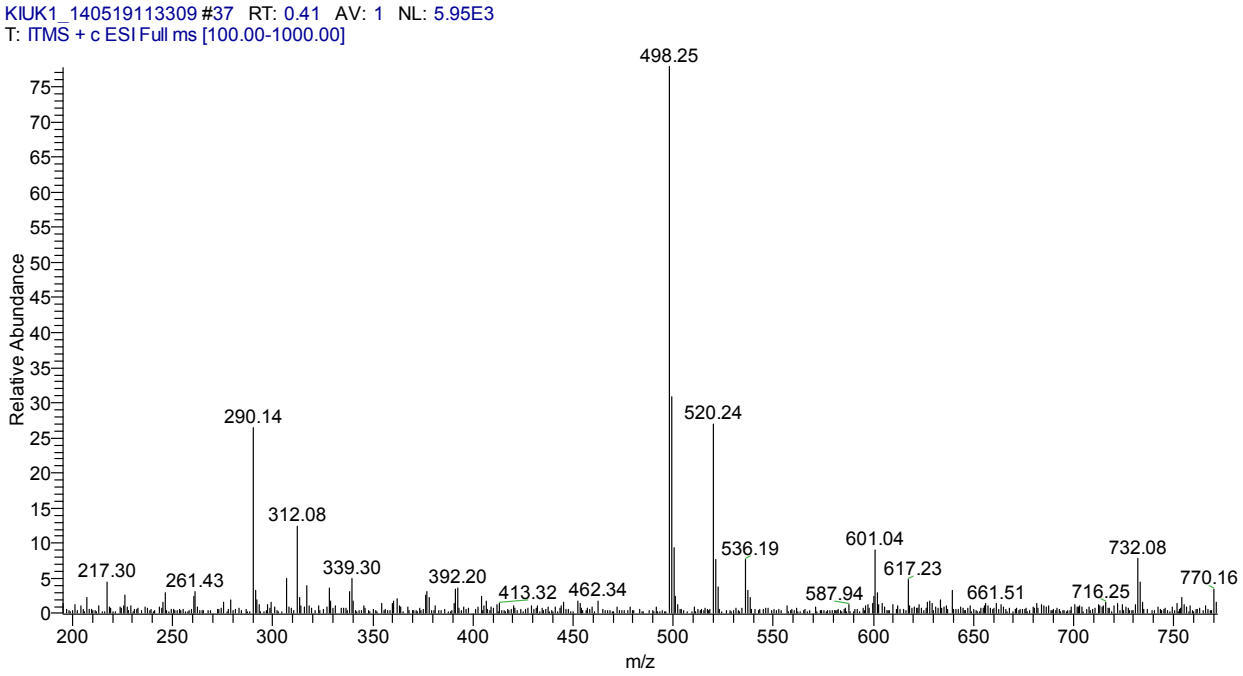
Mass spectrum of **5a**



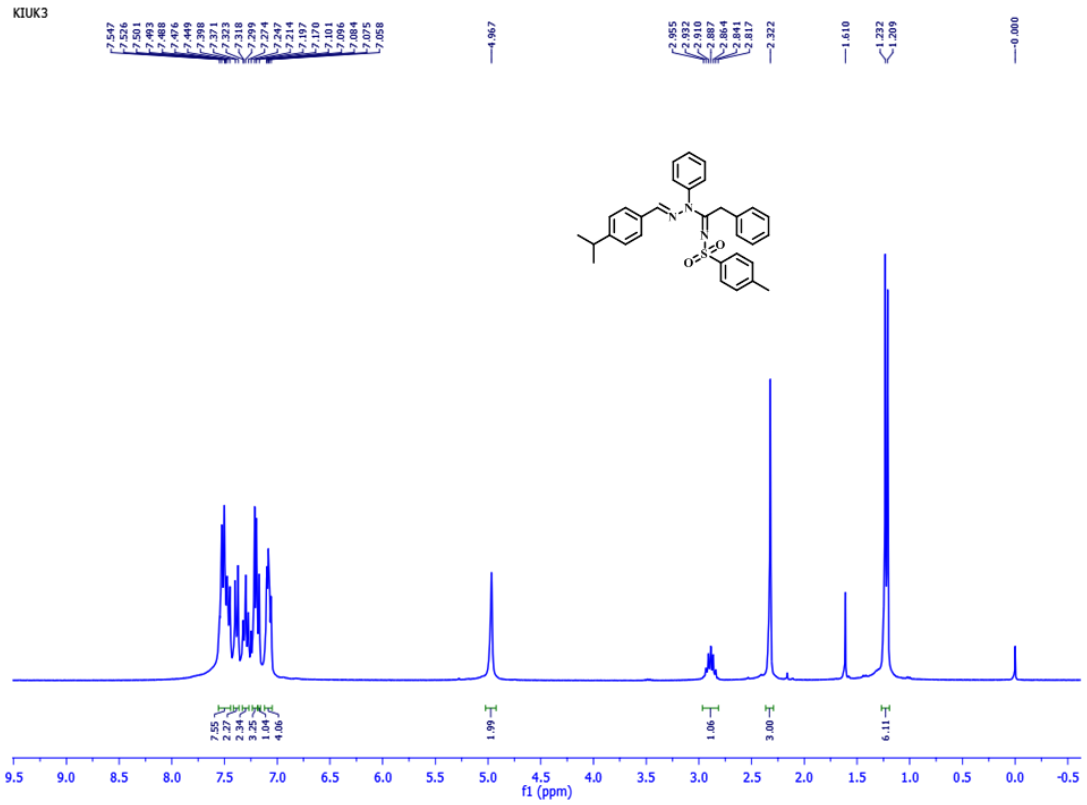
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5b**



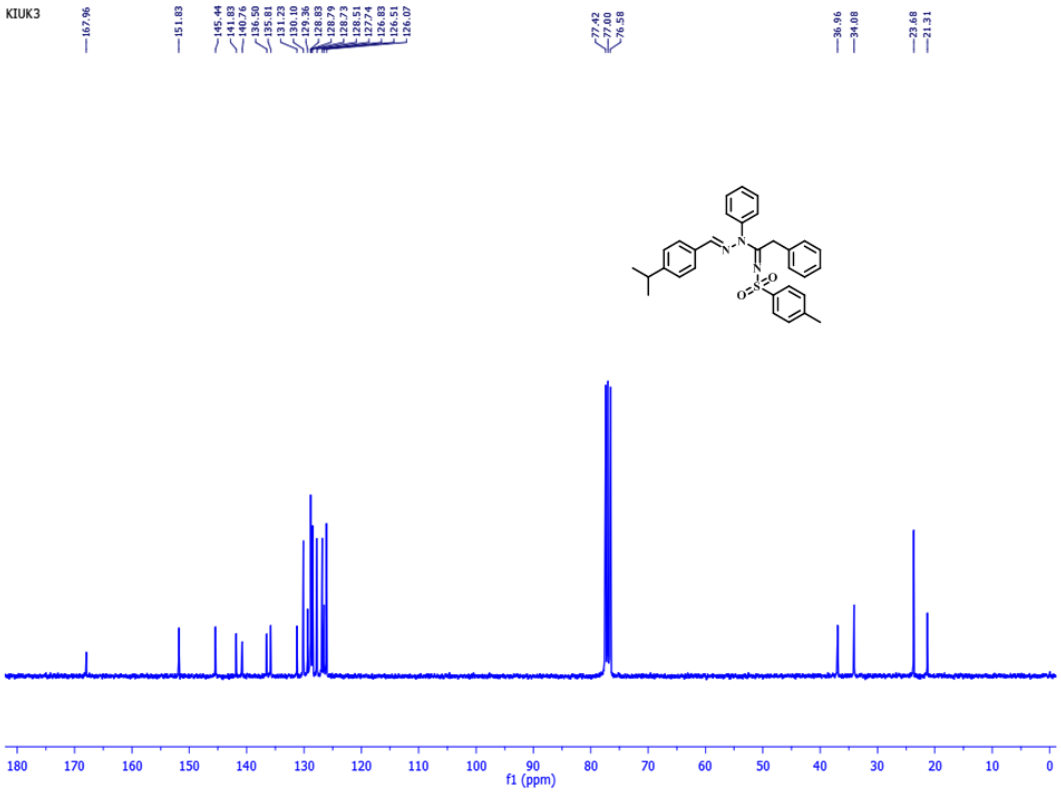
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5b**



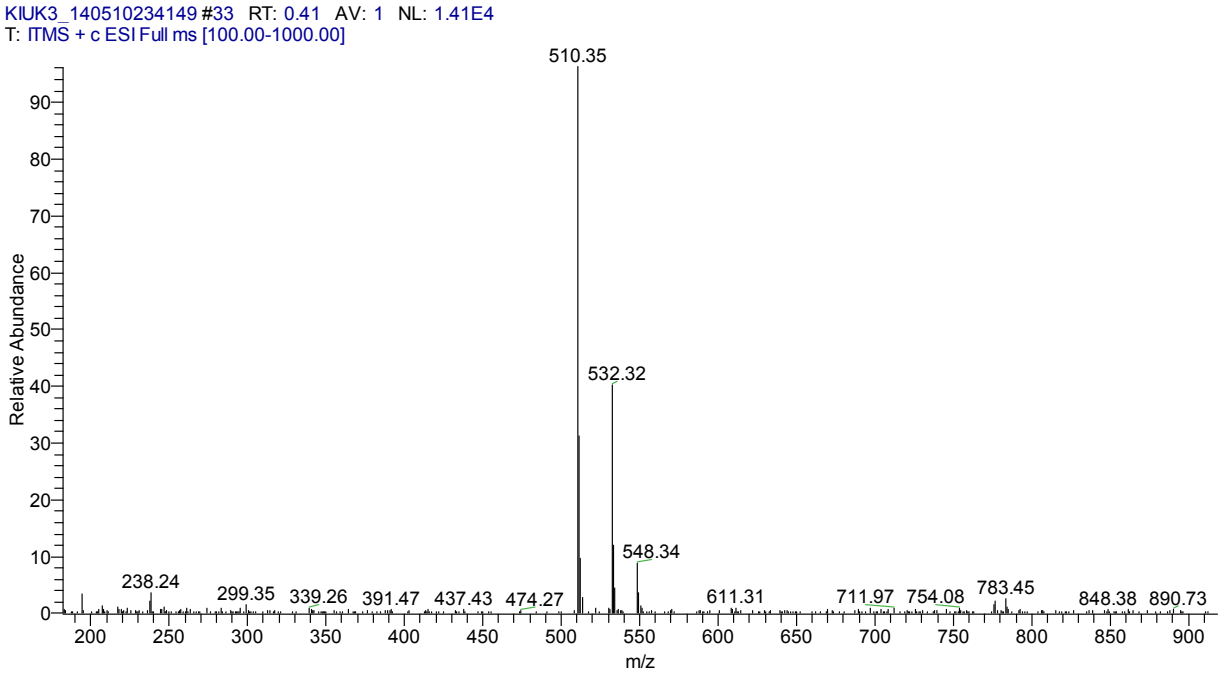
Mass spectrum of **5b**



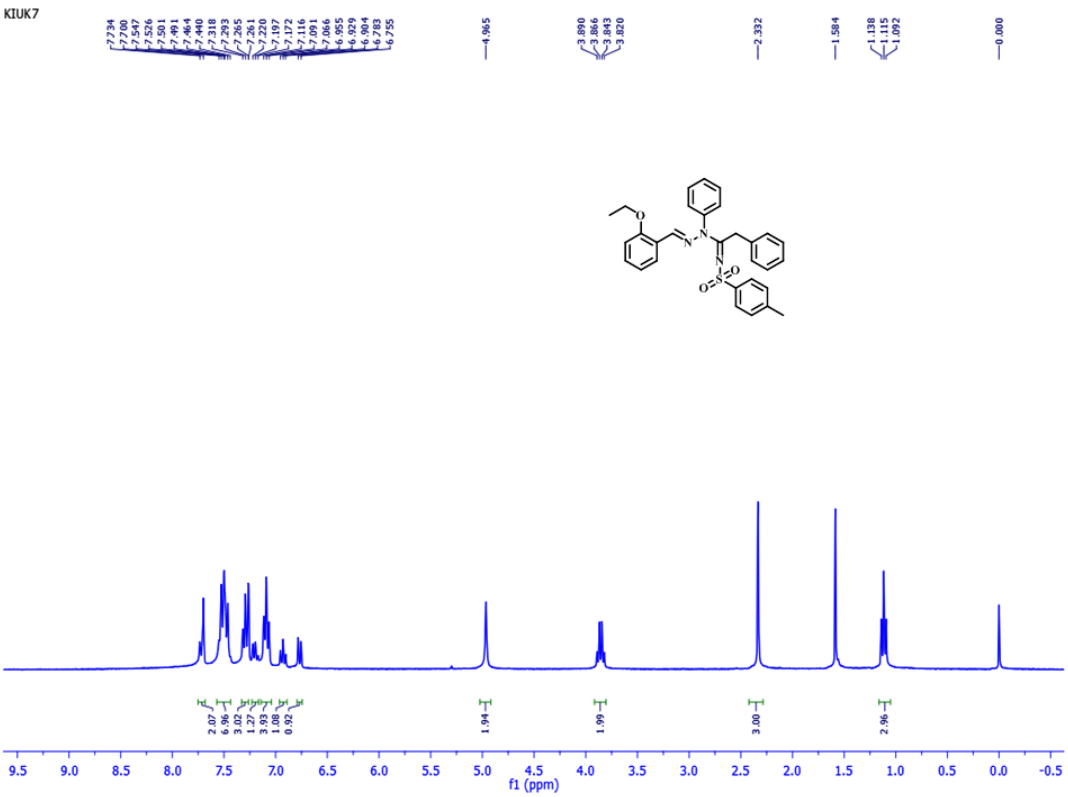
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5c**



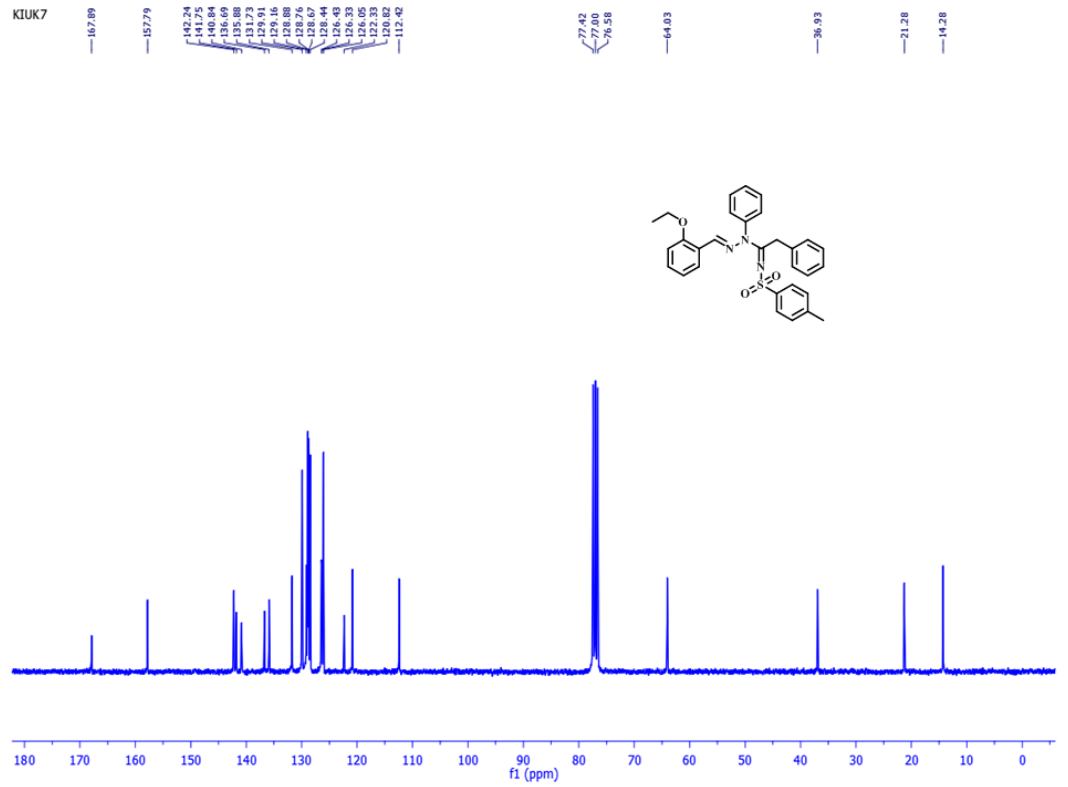
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5c**



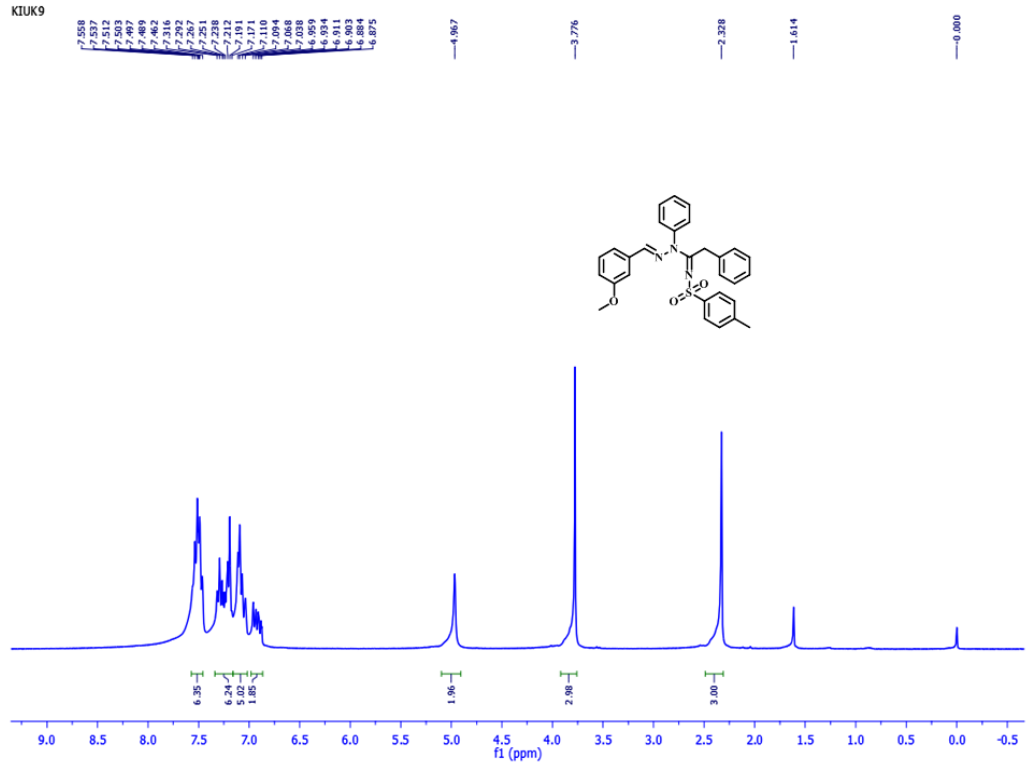
Mass spectrum of **5c**



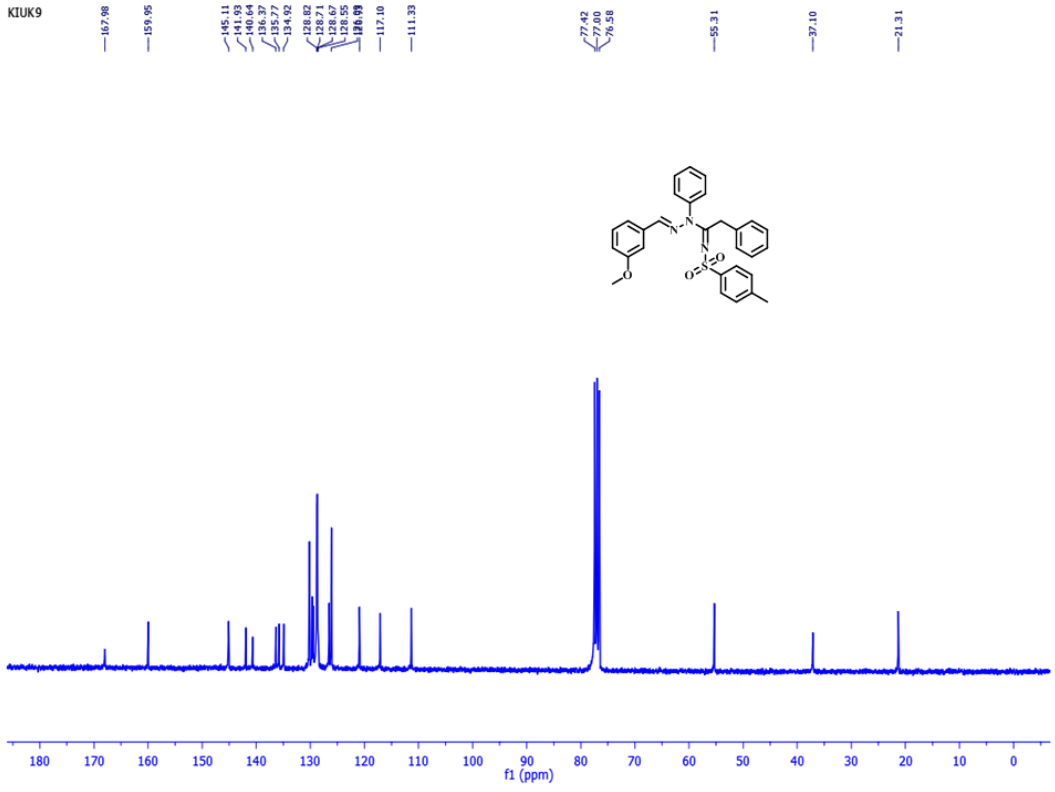
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5d**



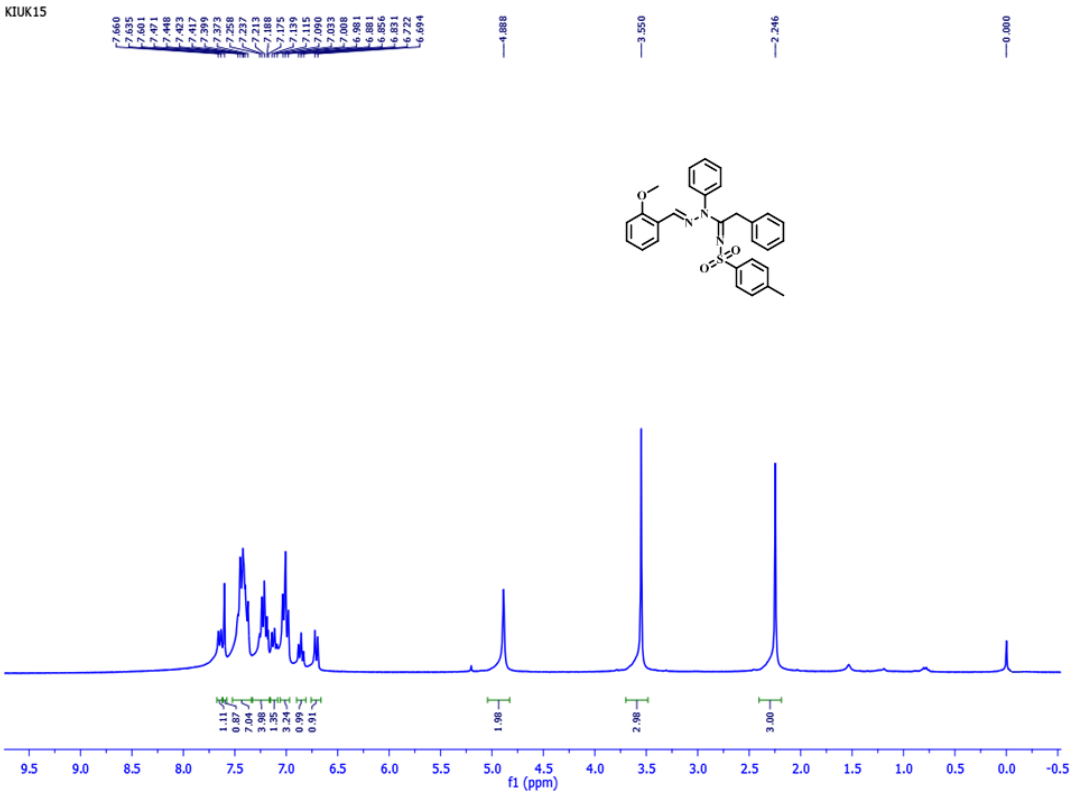
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5d**



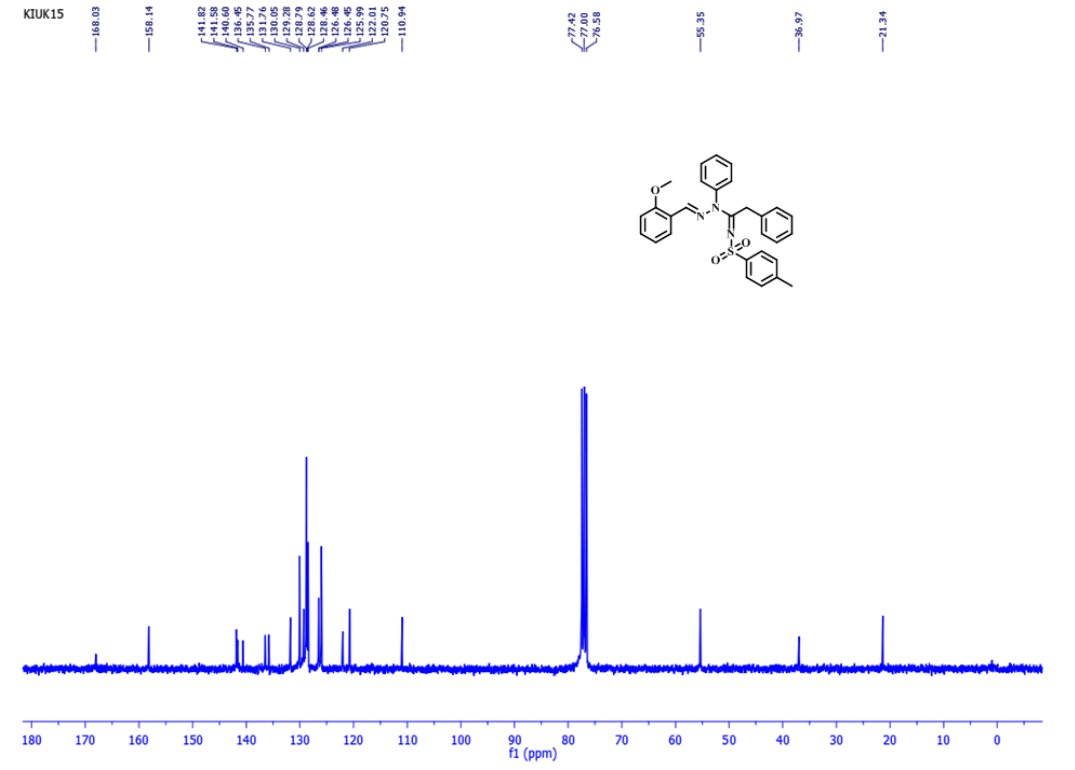
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5e**



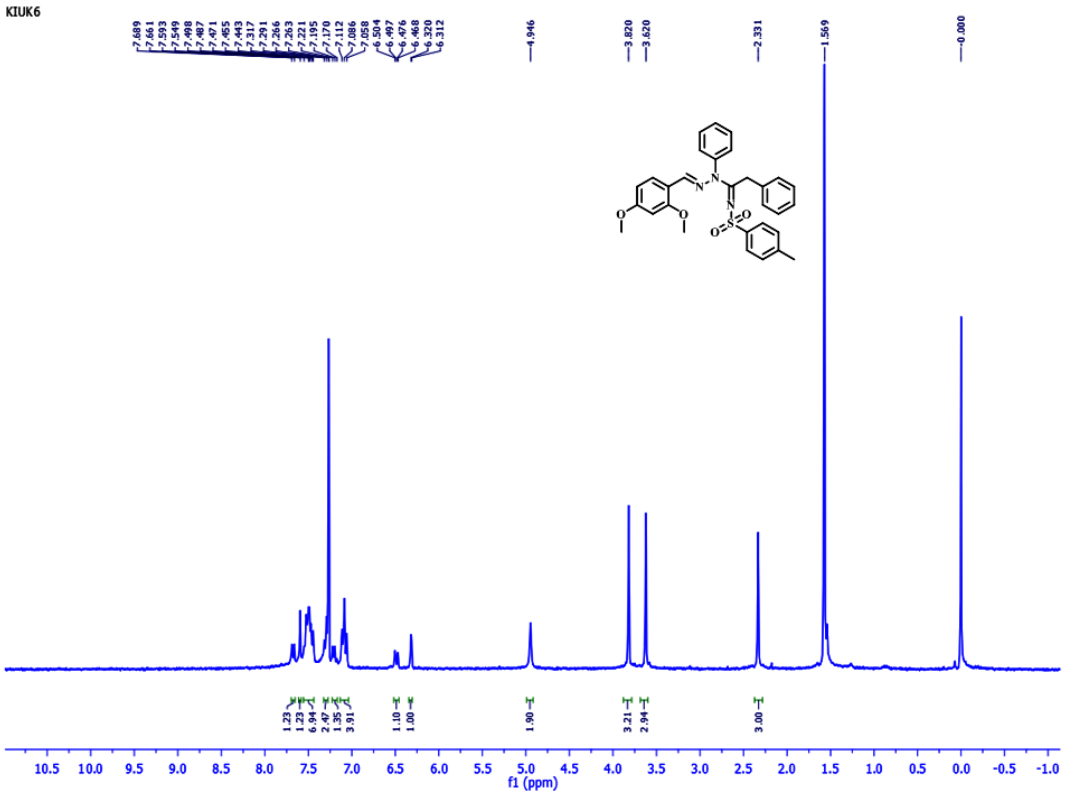
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5e**



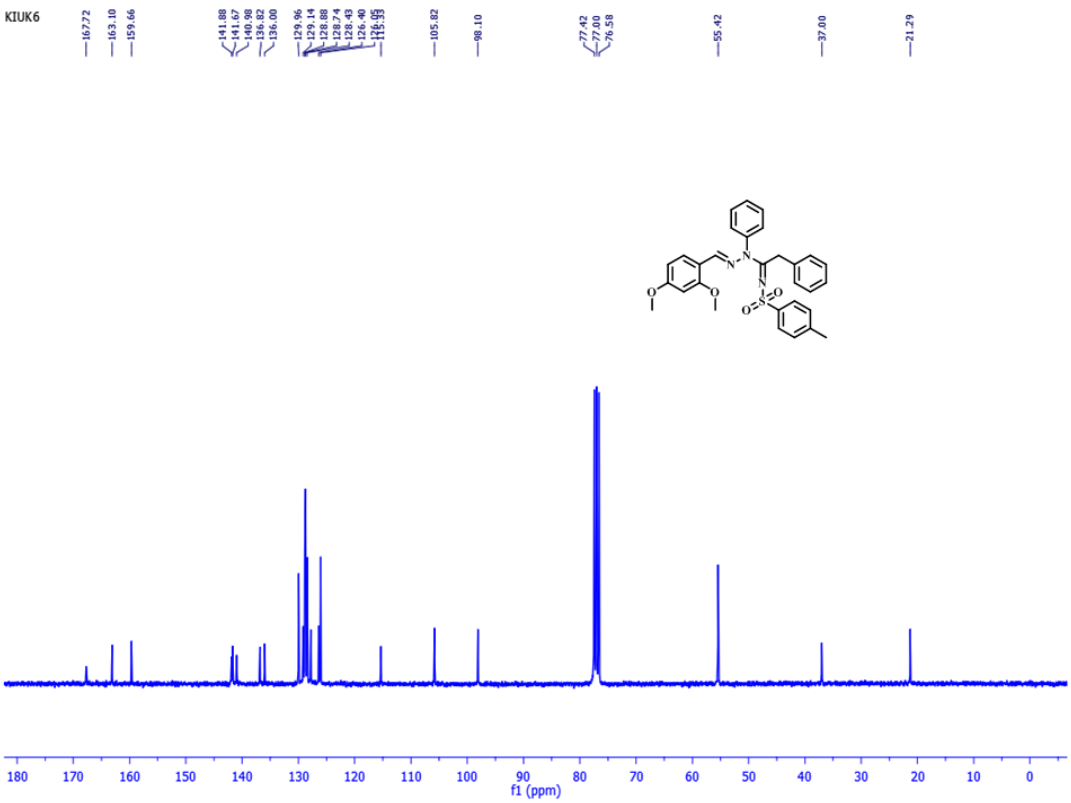
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5f**



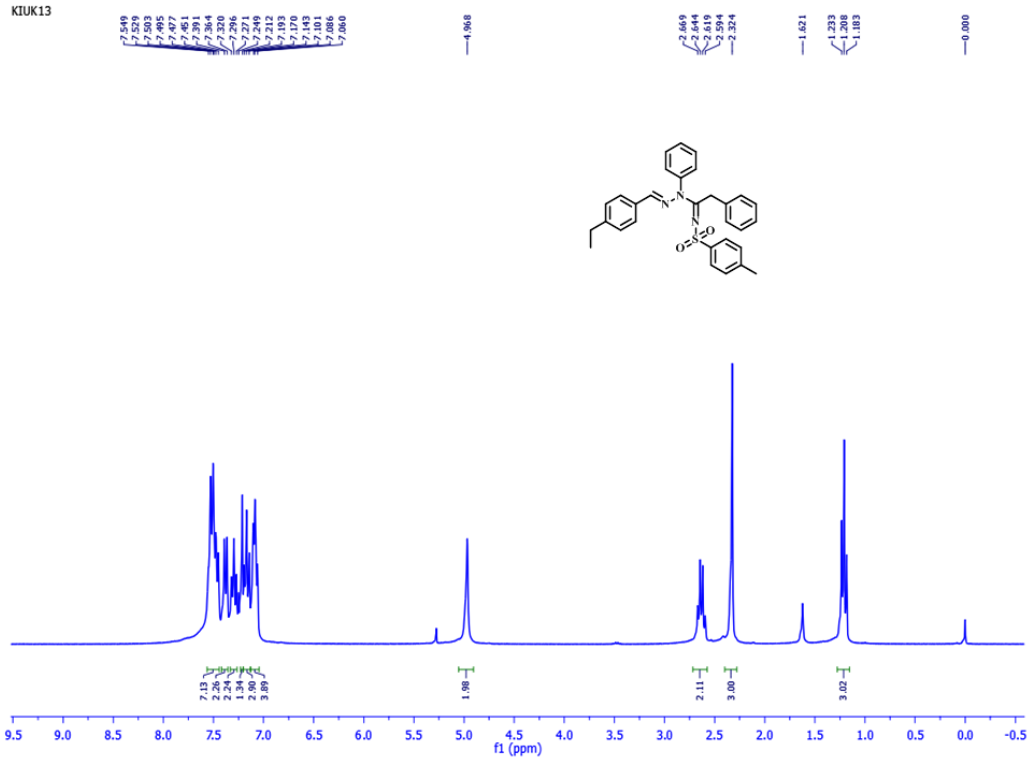
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5f**



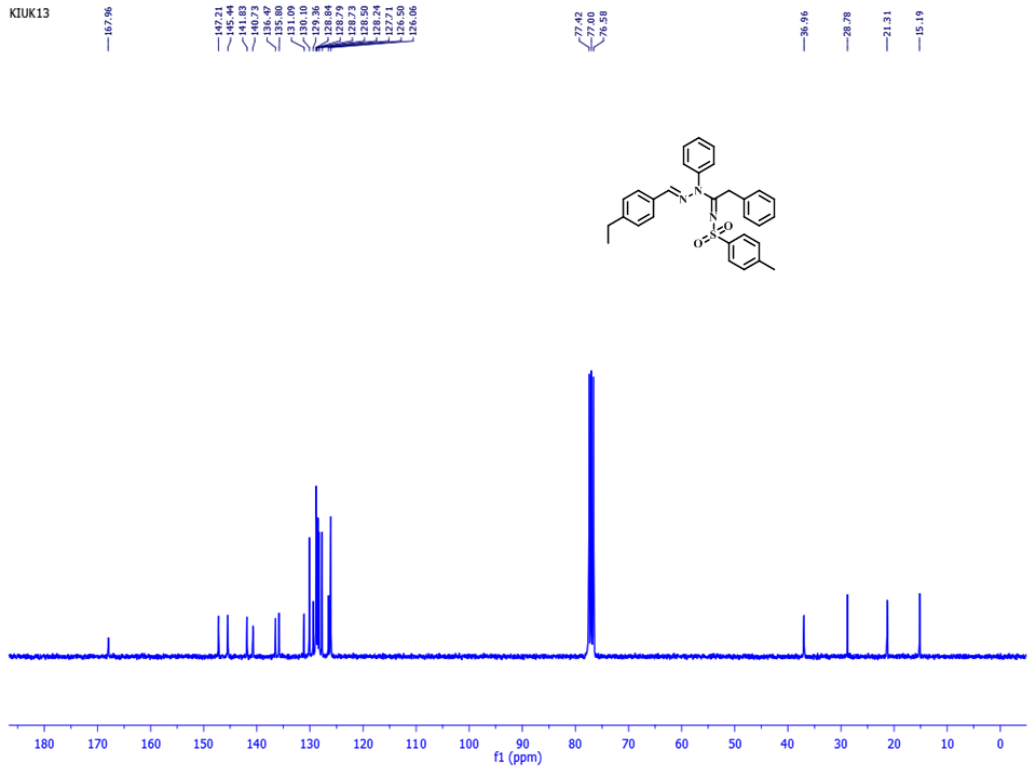
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5g**



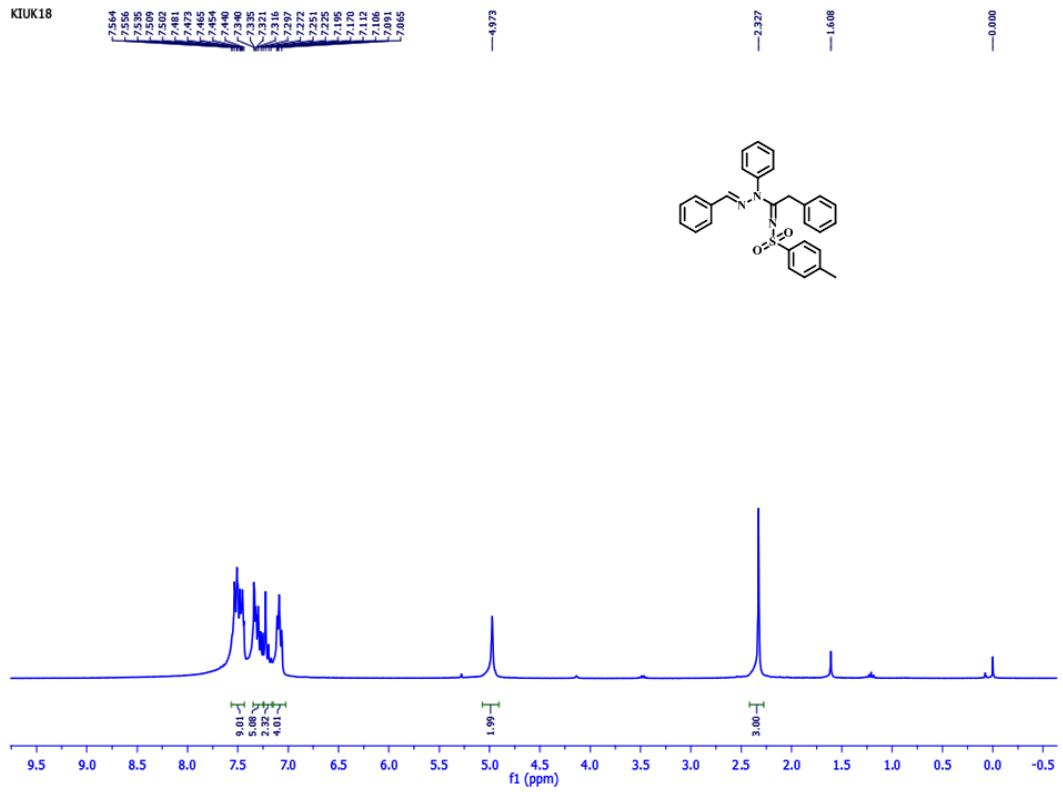
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5g**



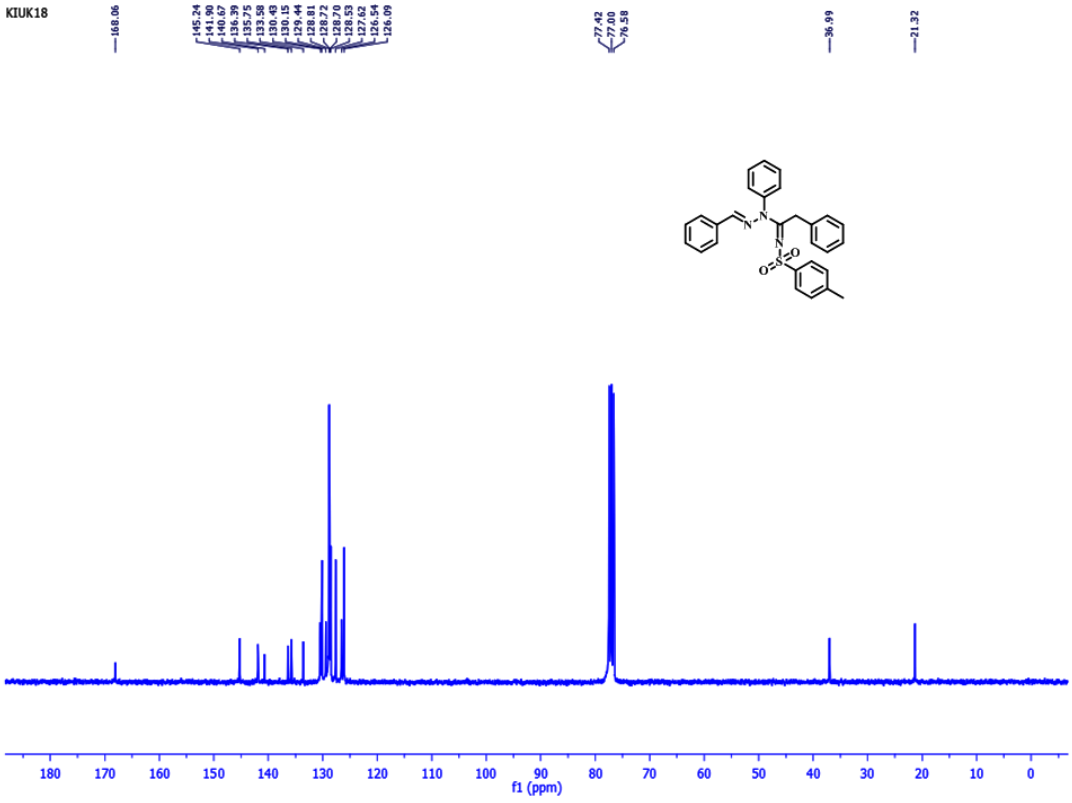
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5h**



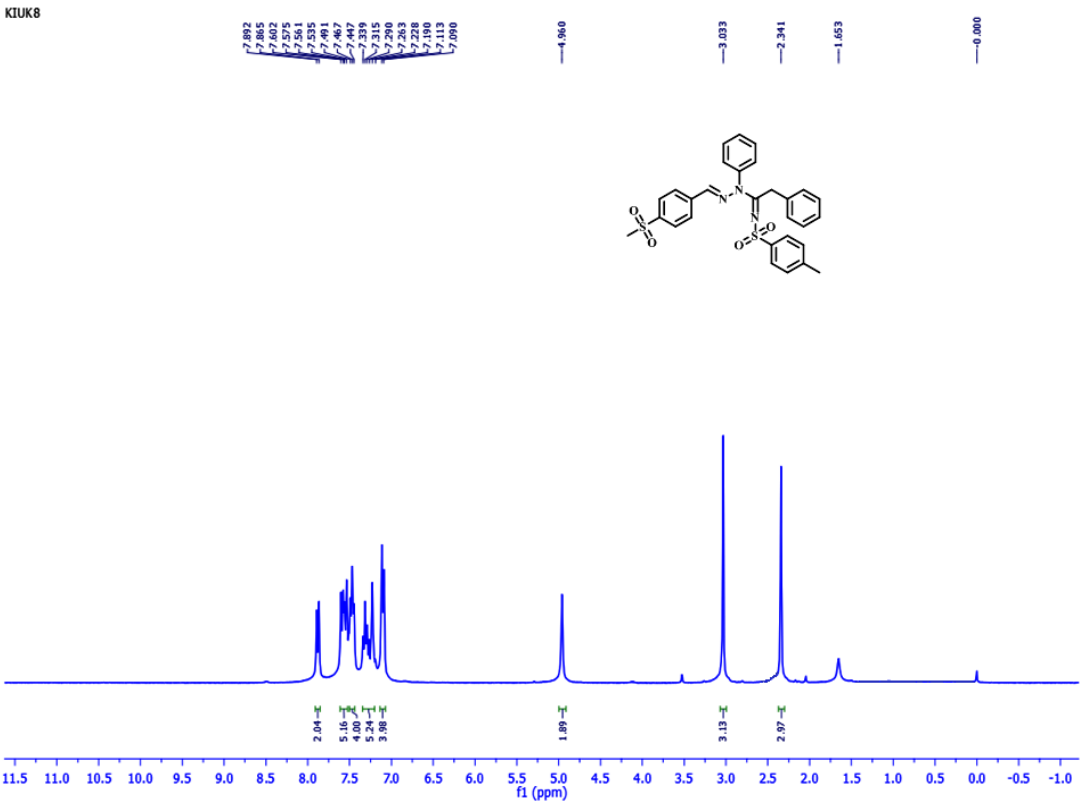
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5h**



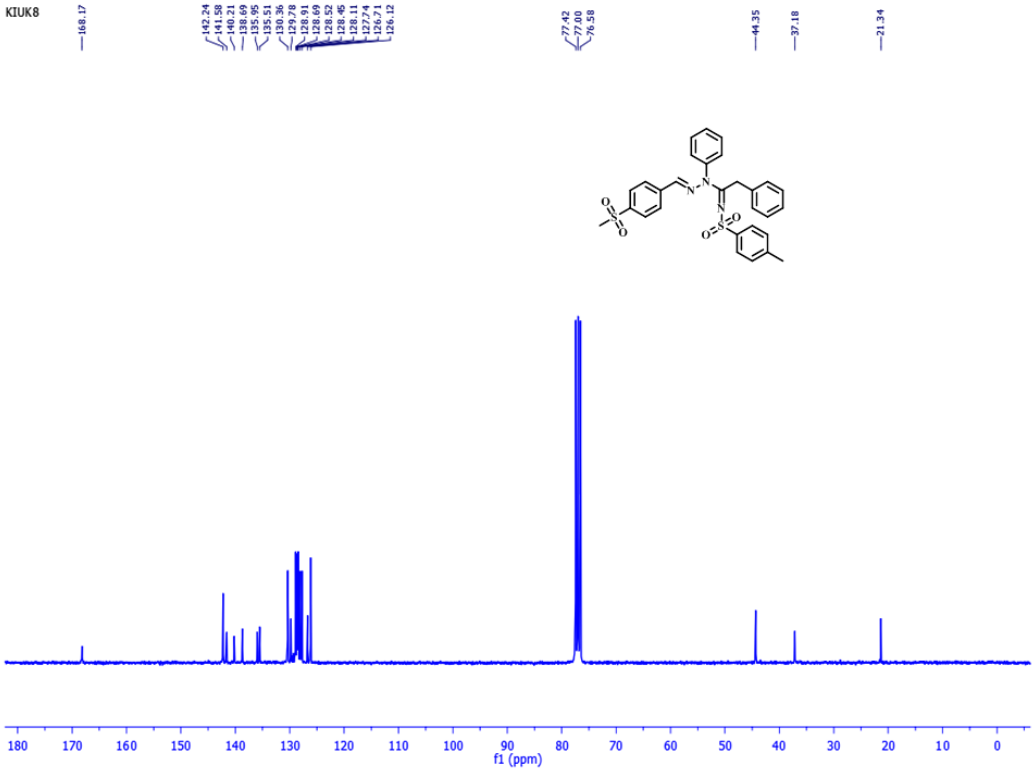
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5i**



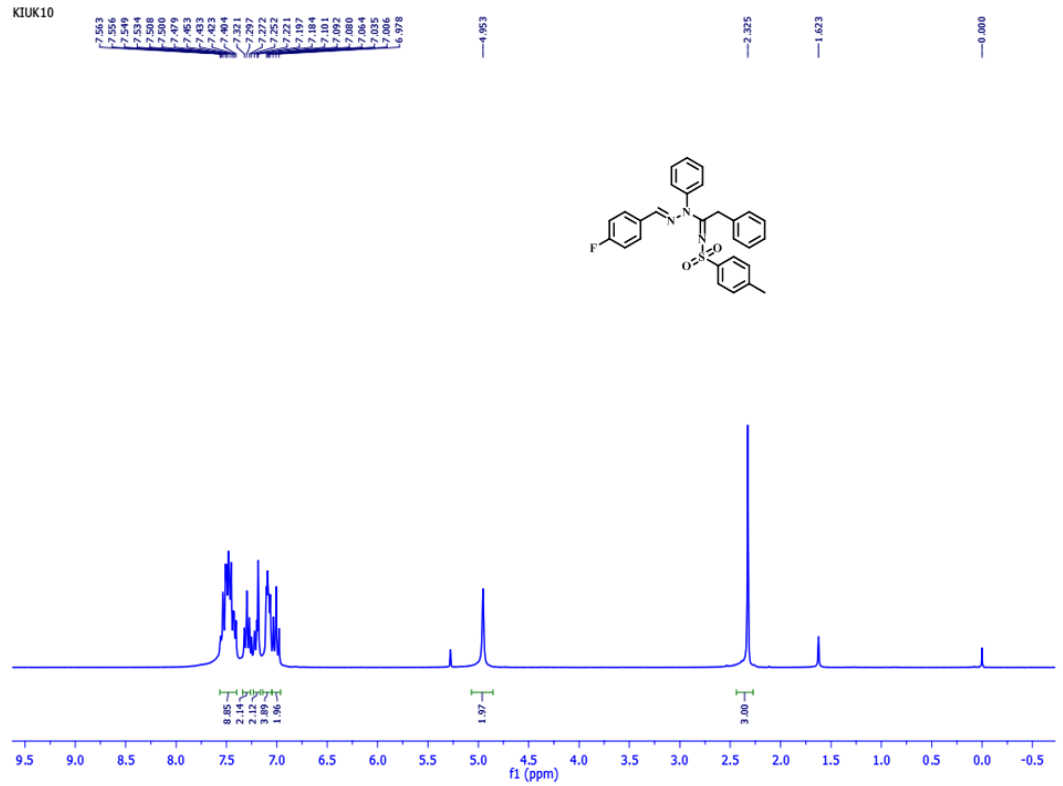
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5i**



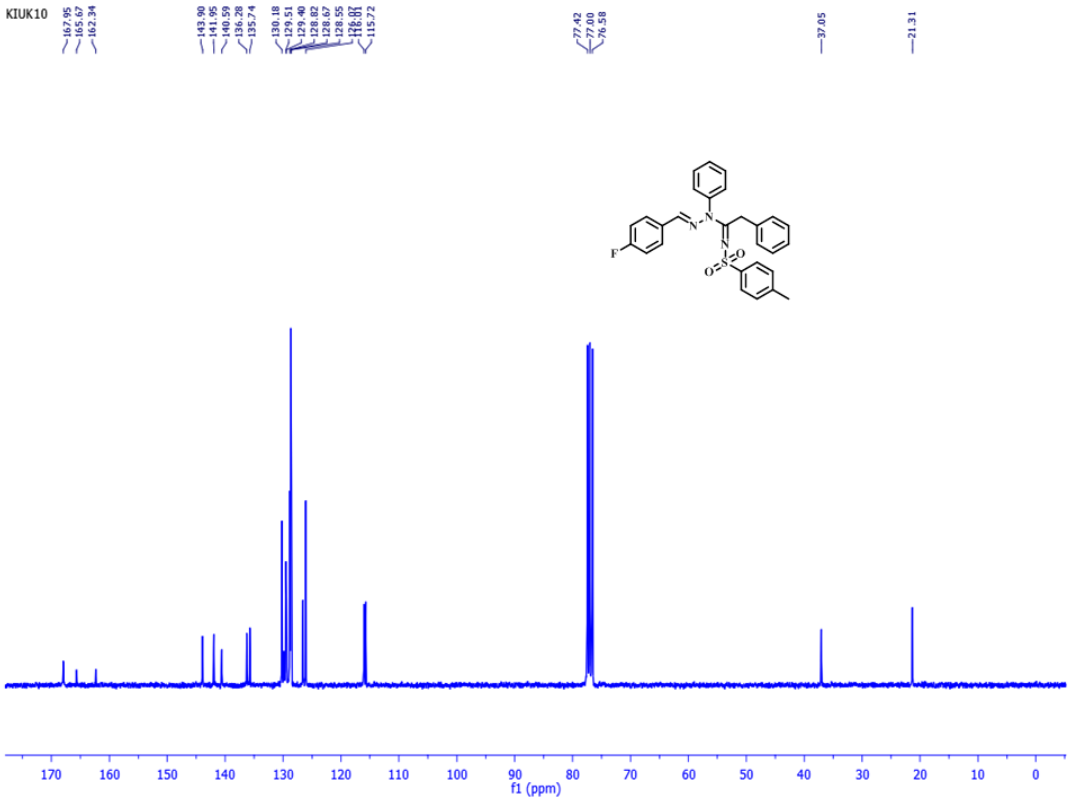
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5j**



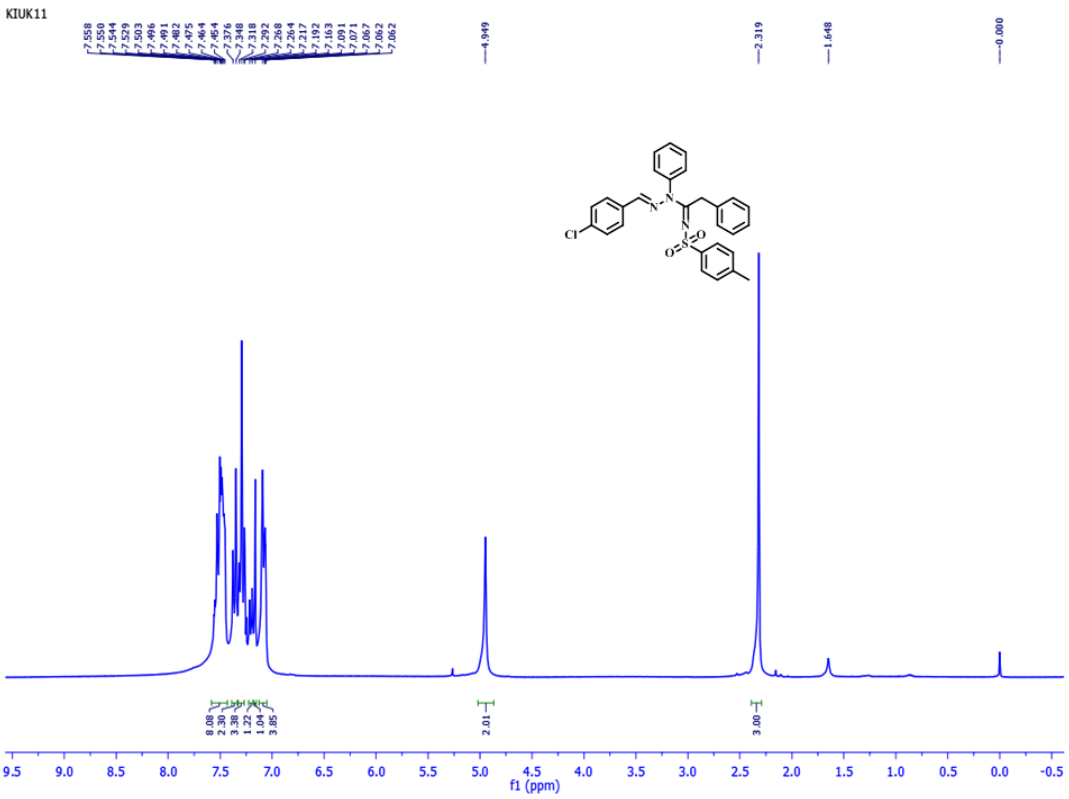
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5j**



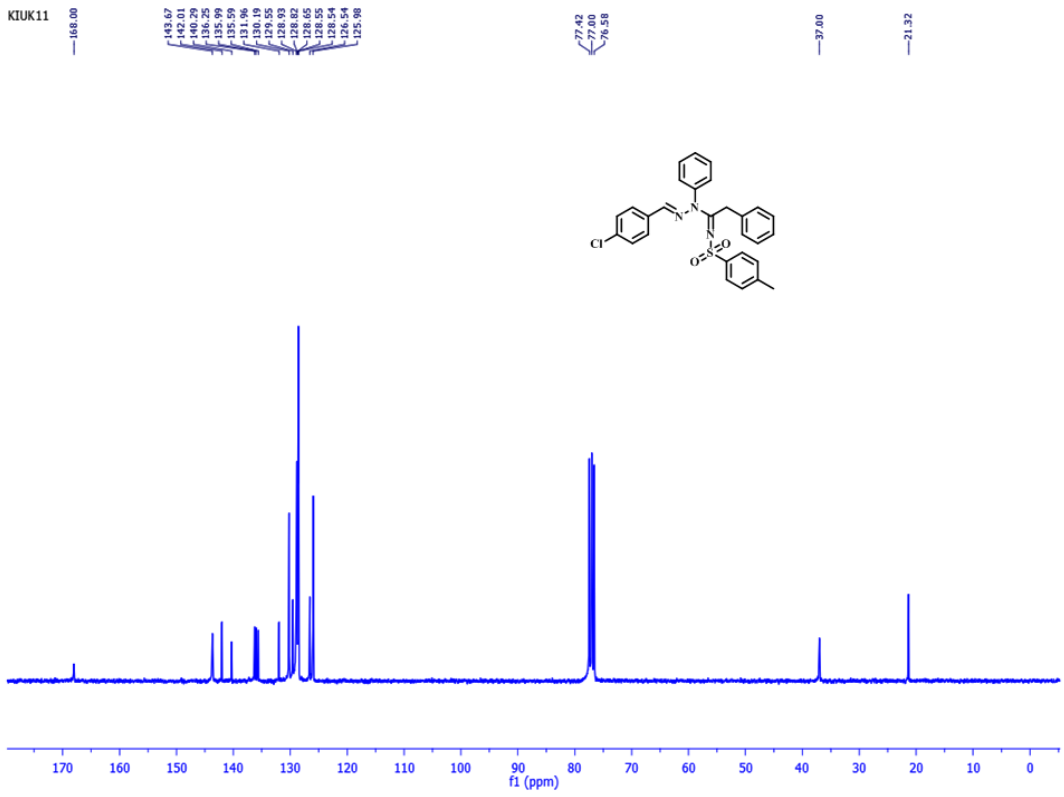
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5k**



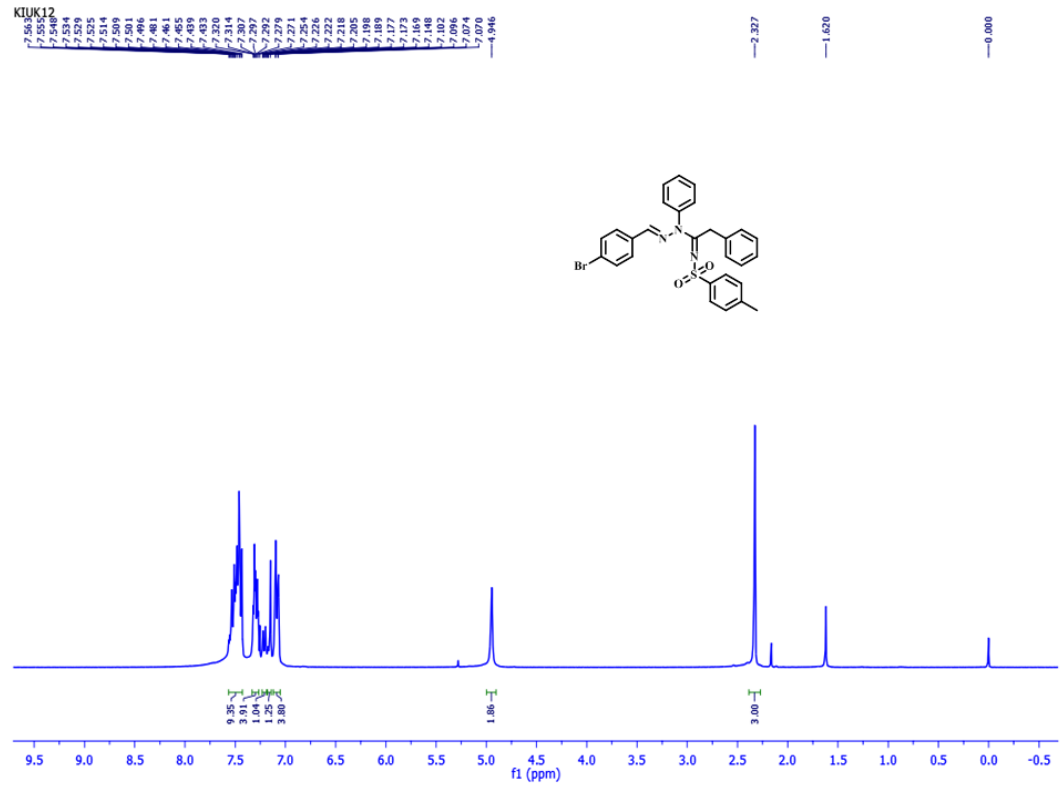
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5k**



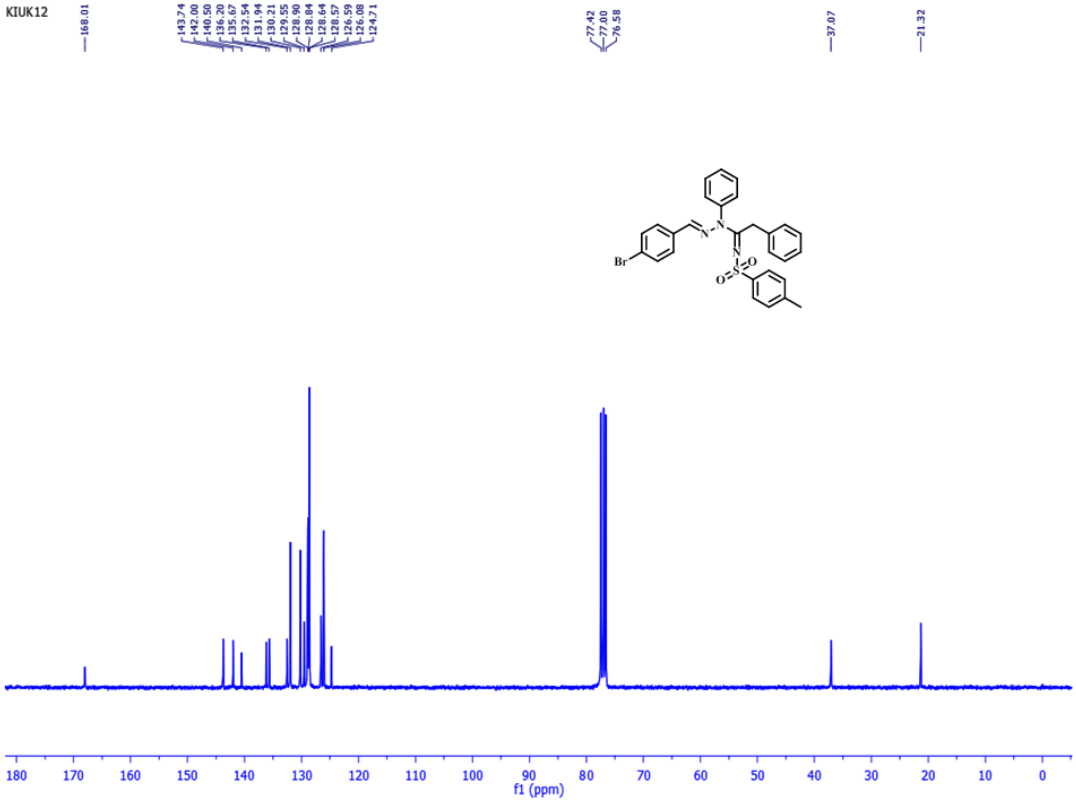
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5l**



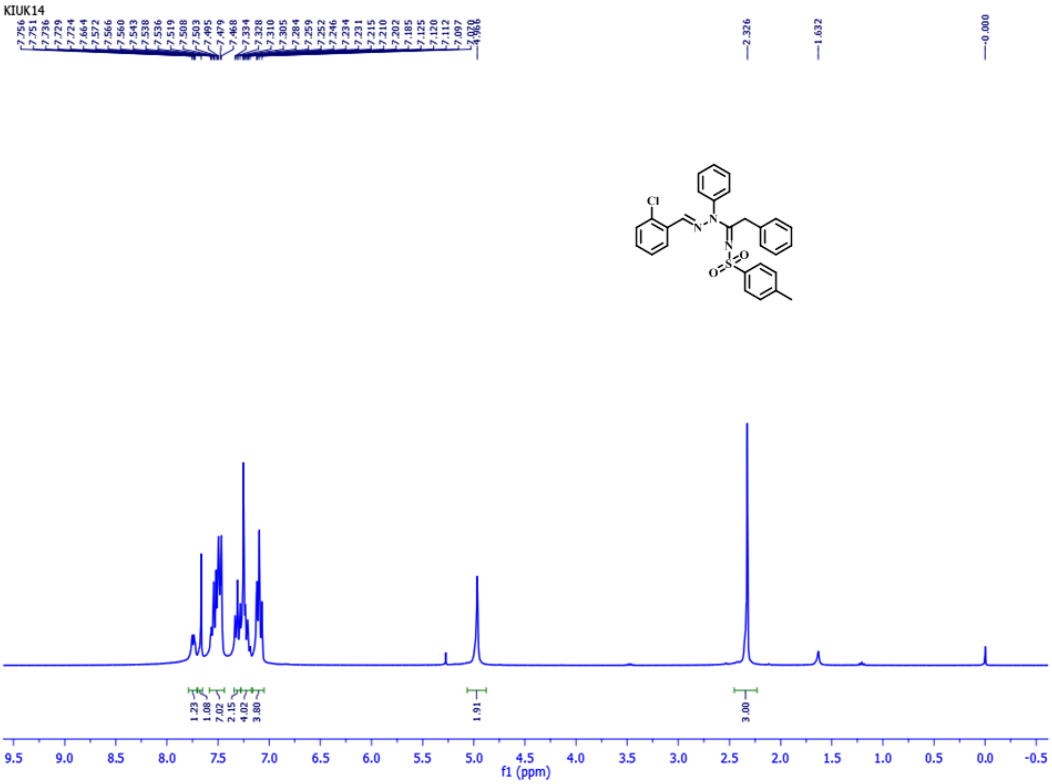
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5l**



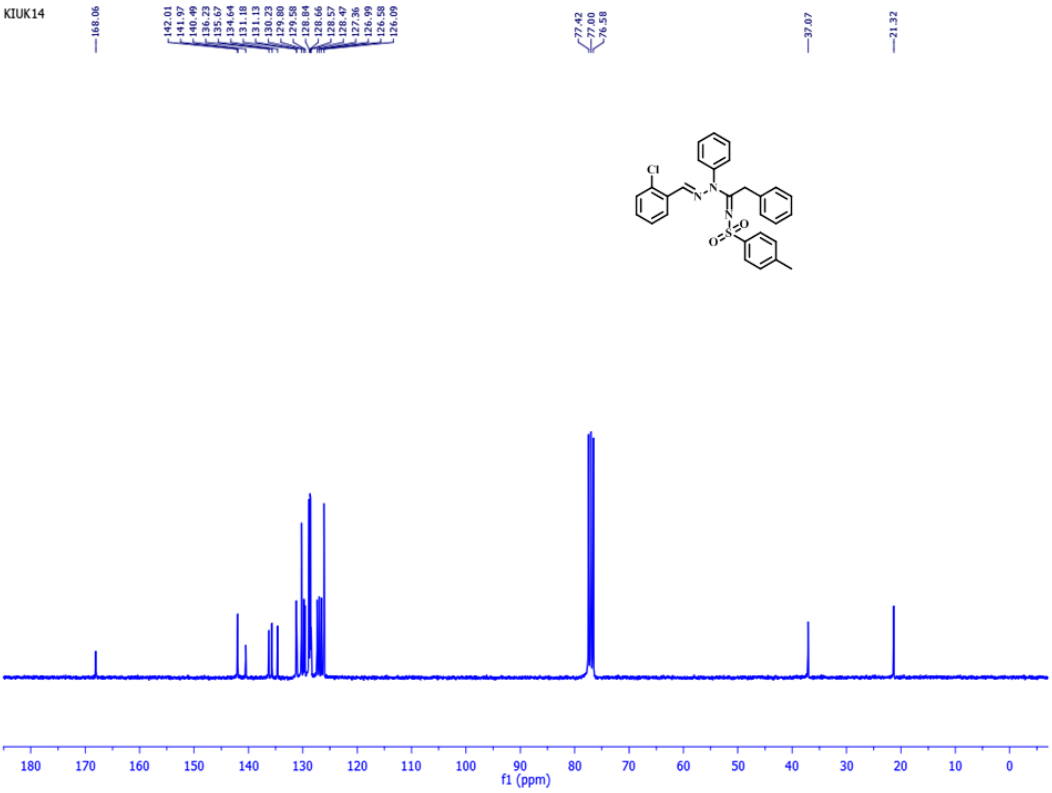
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5m**



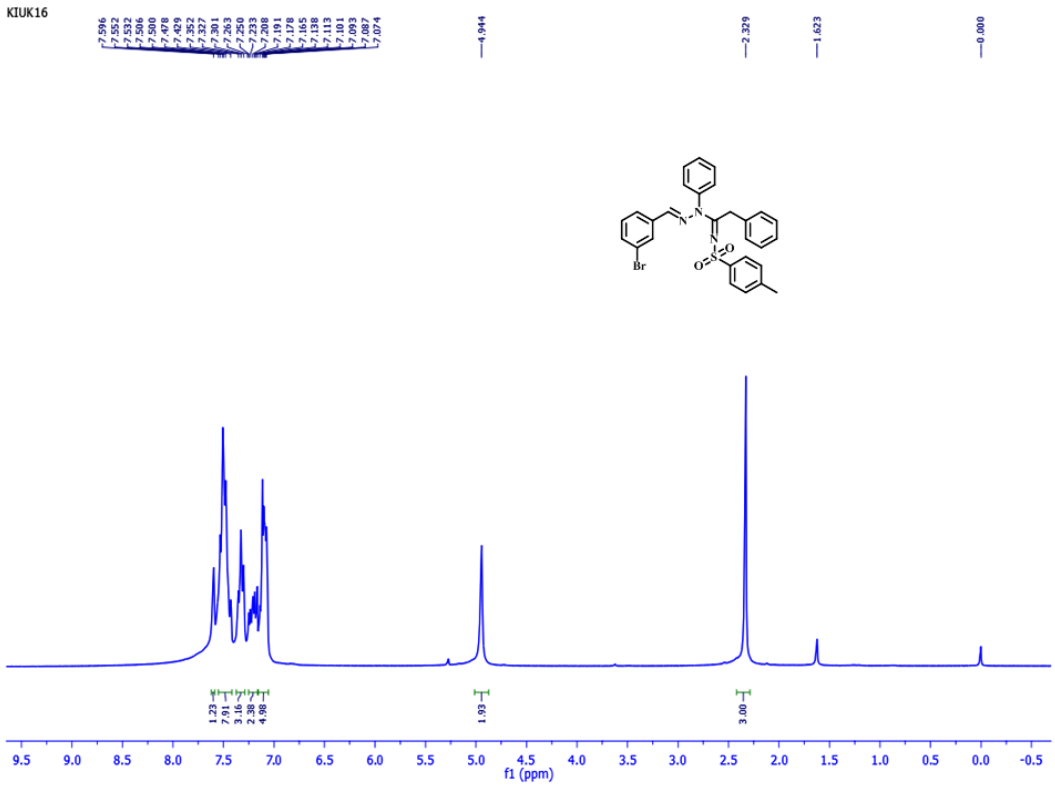
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5m**



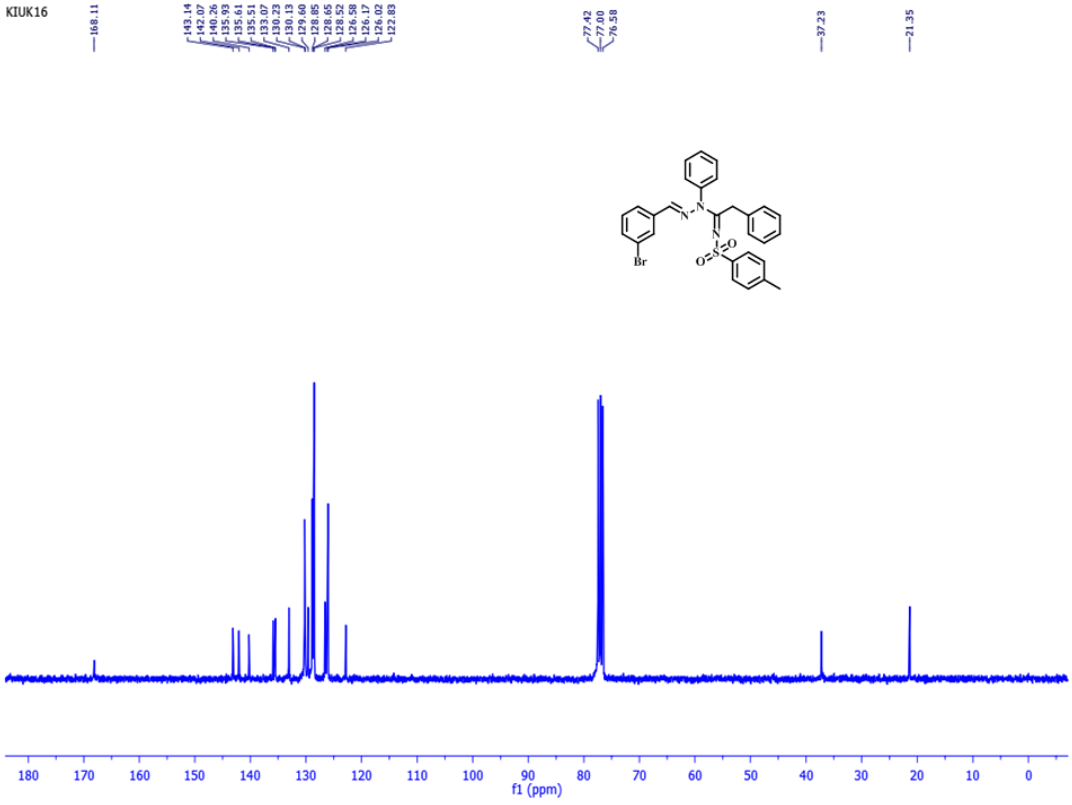
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5n**



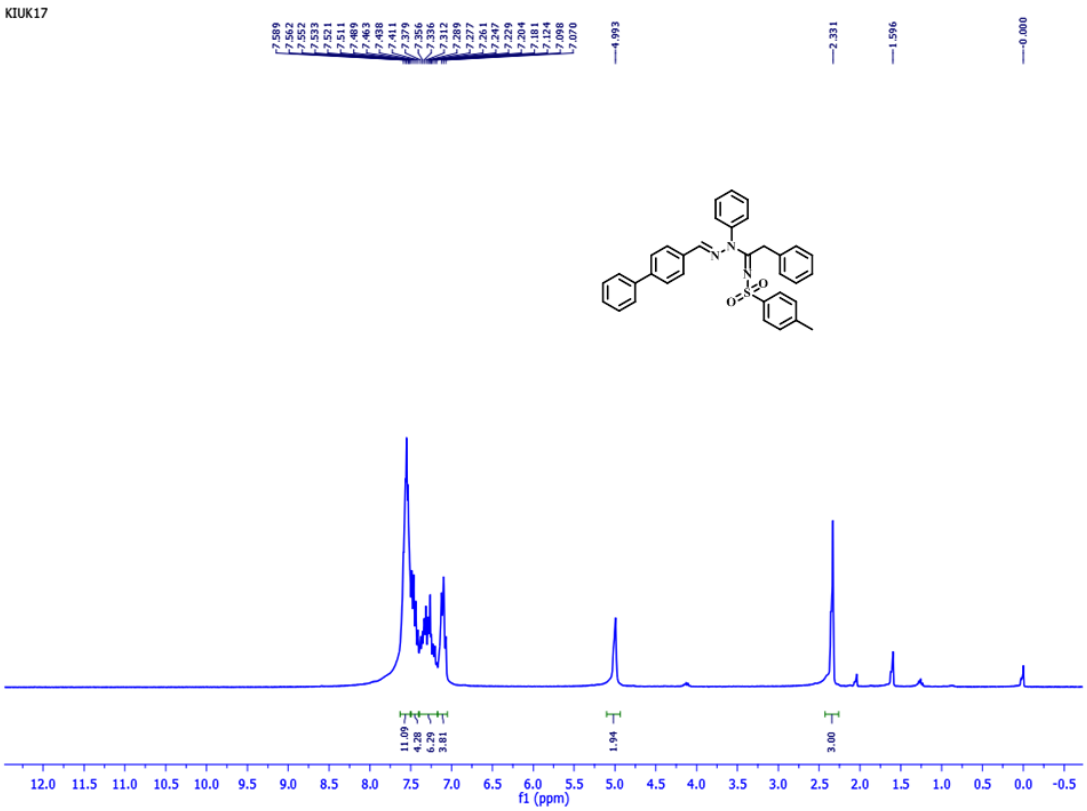
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5n**



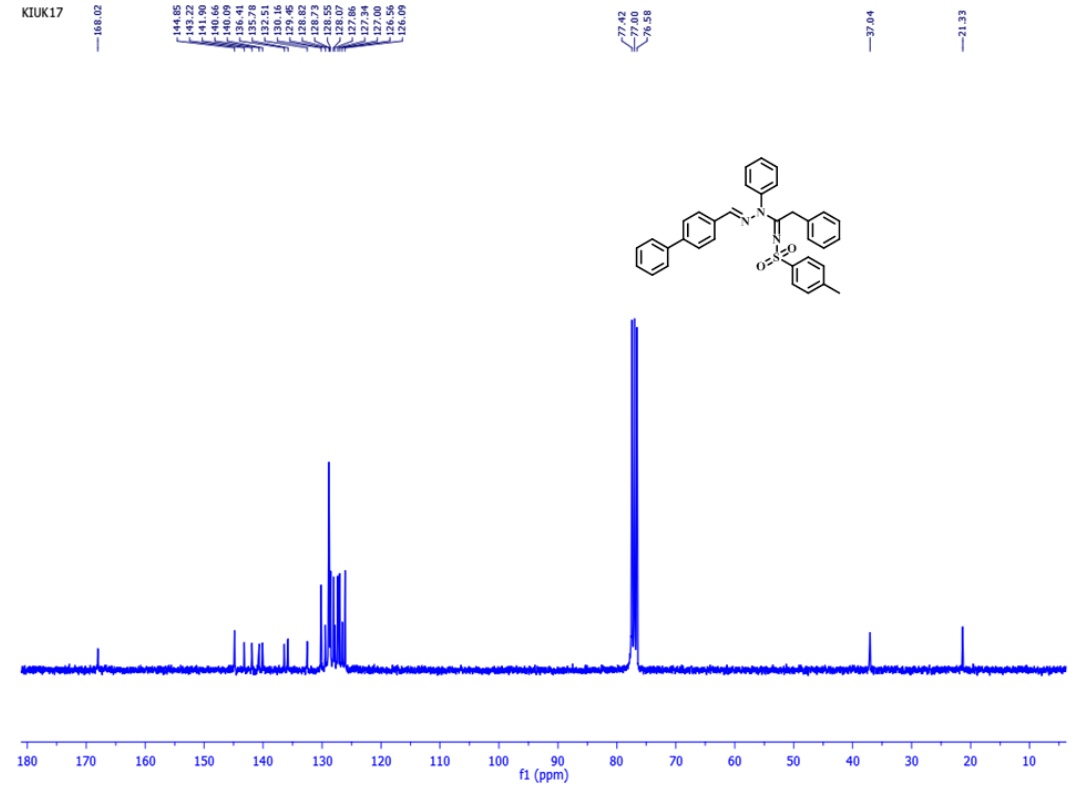
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5o**



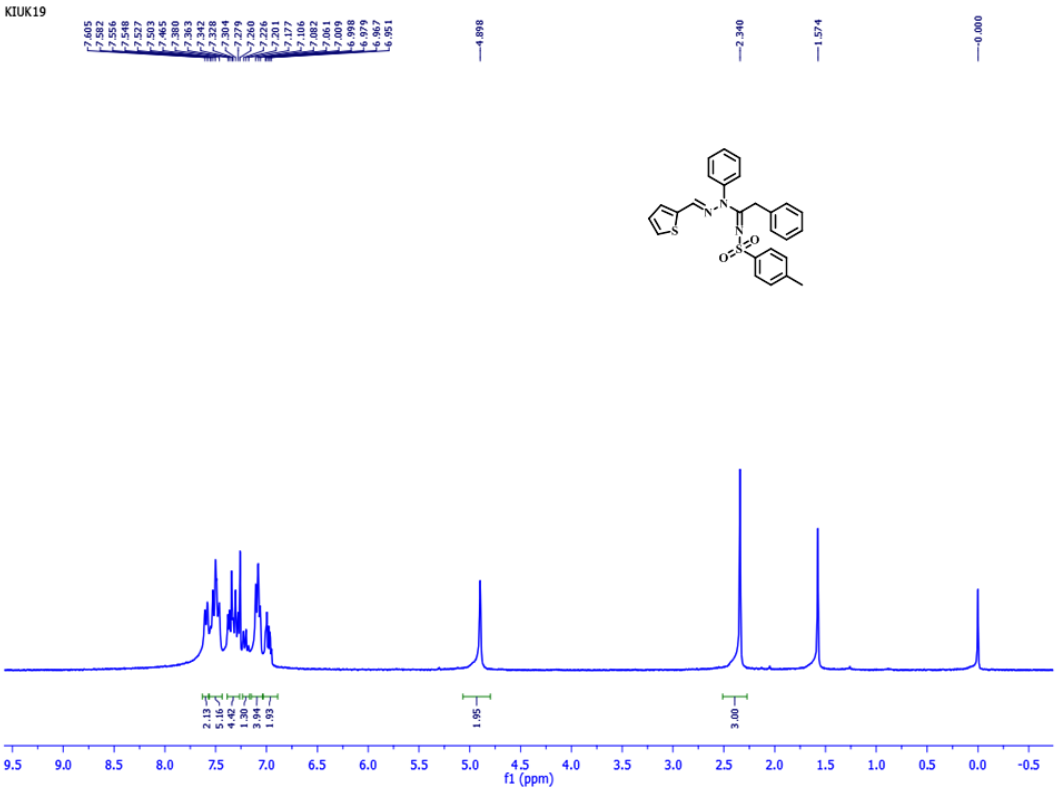
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5o**



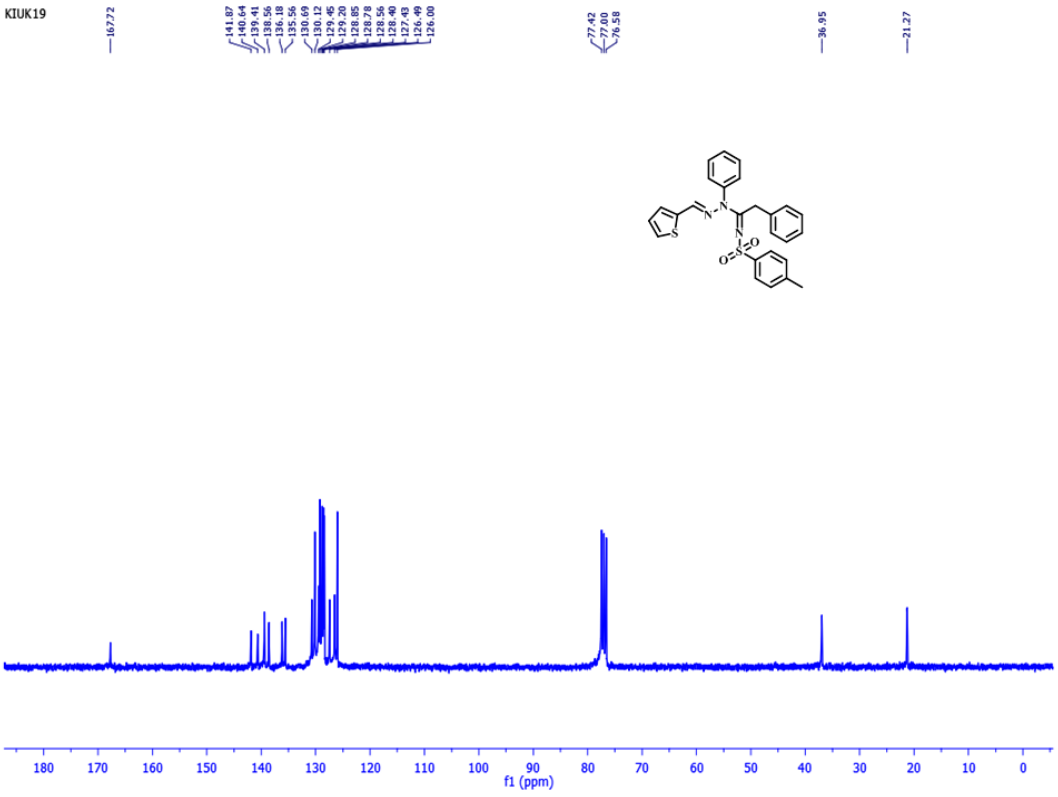
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5p**



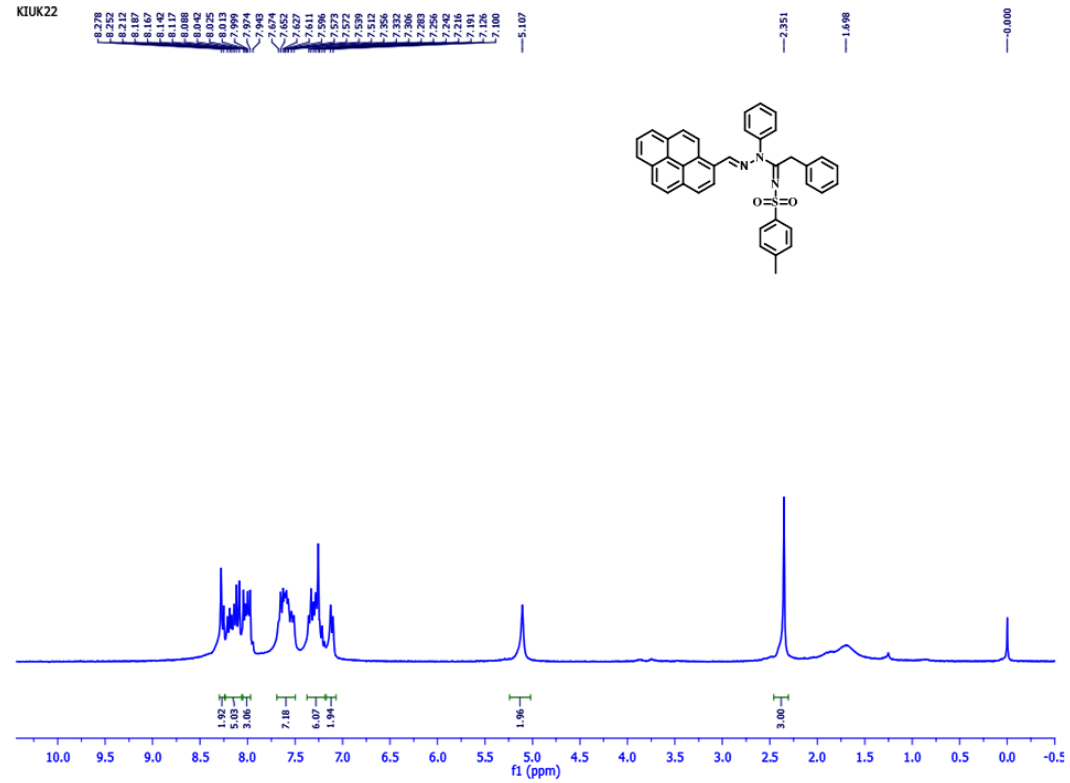
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5p**



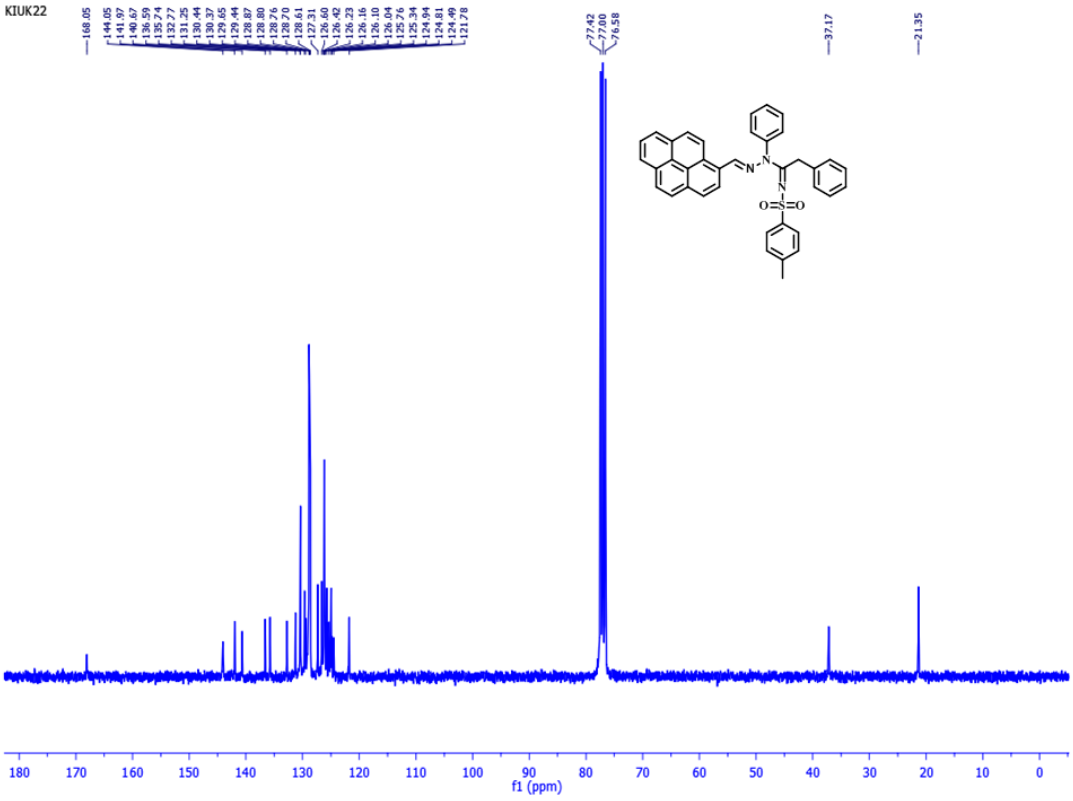
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5q**



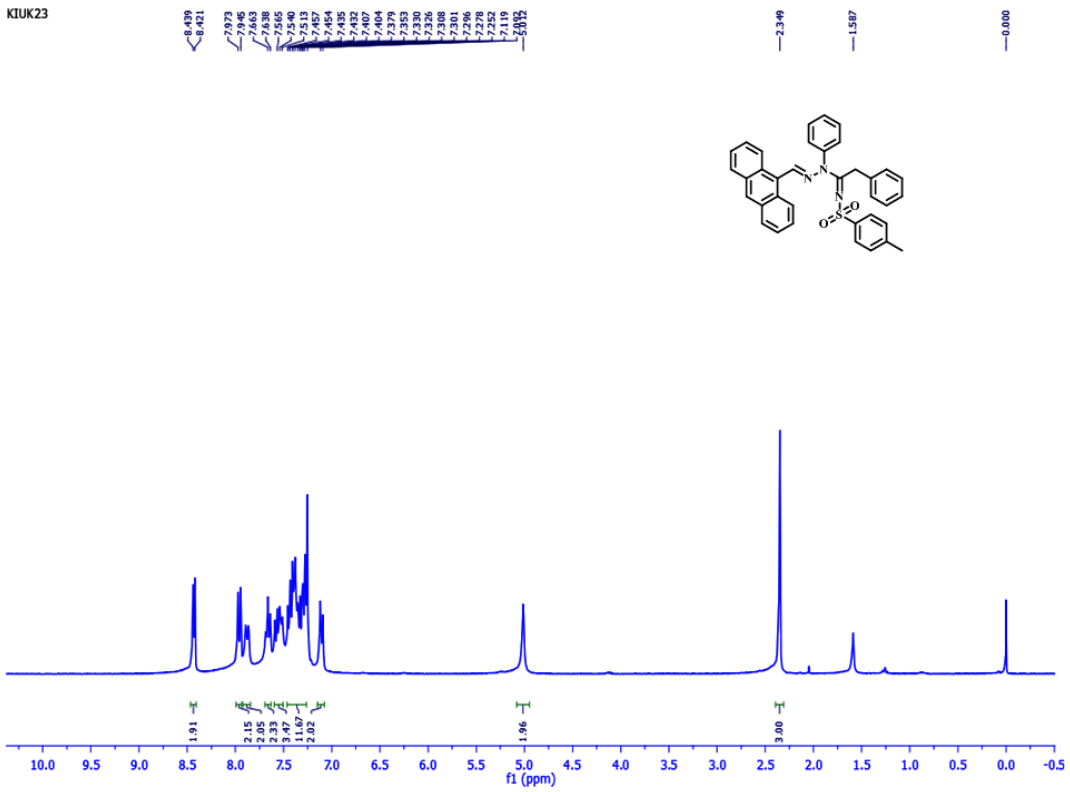
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5q**



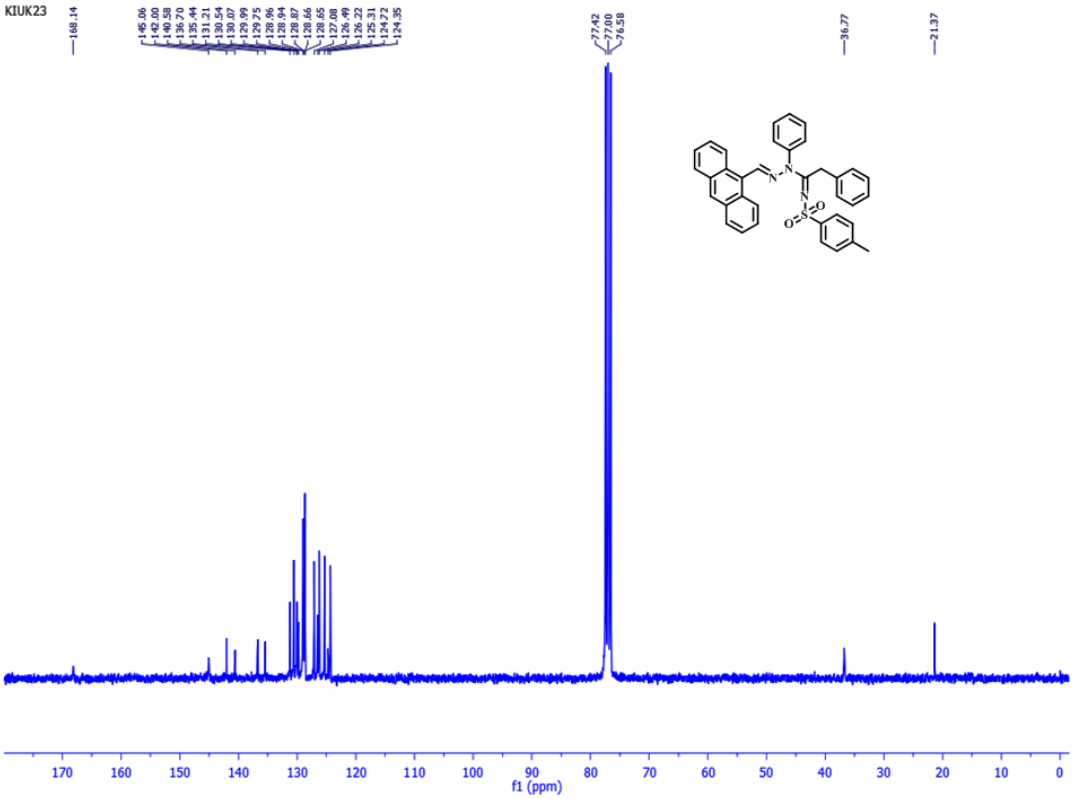
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5r**



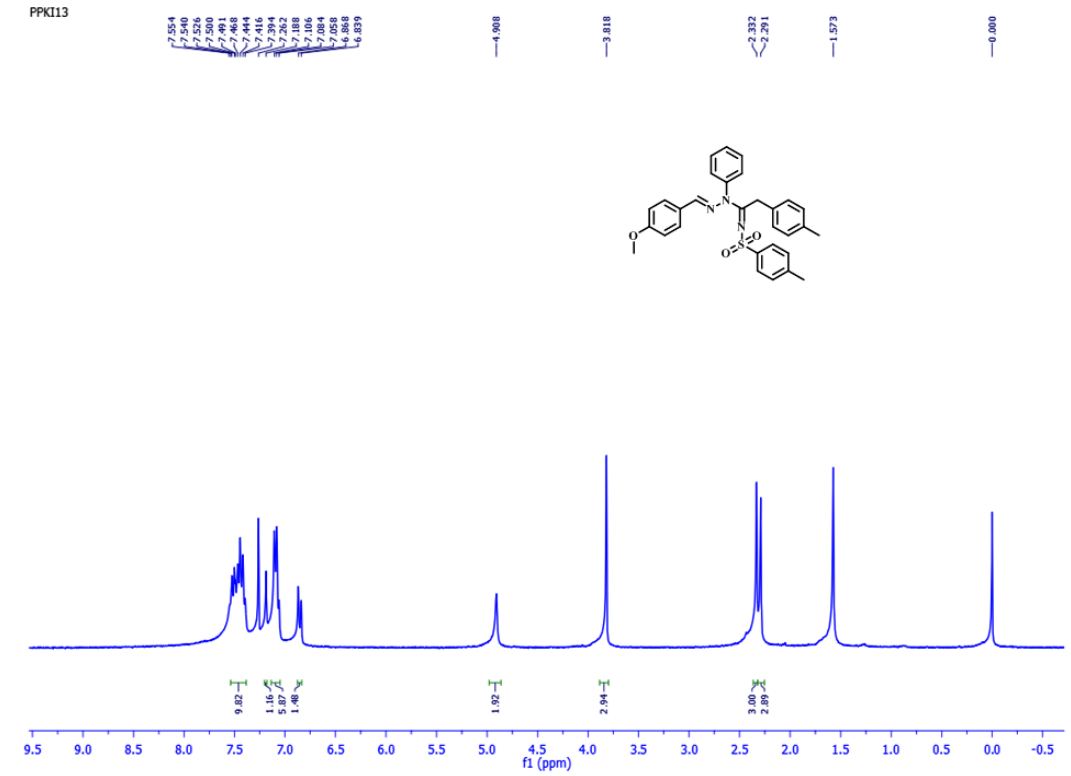
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5r**



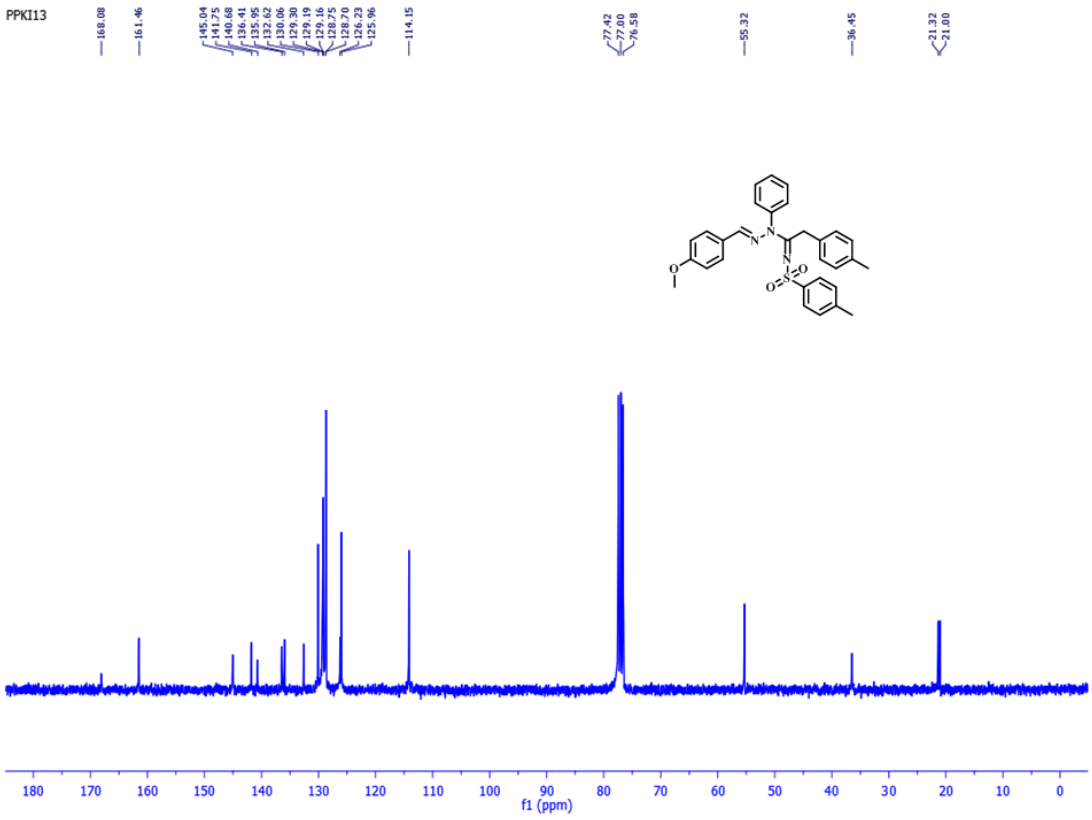
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5s**



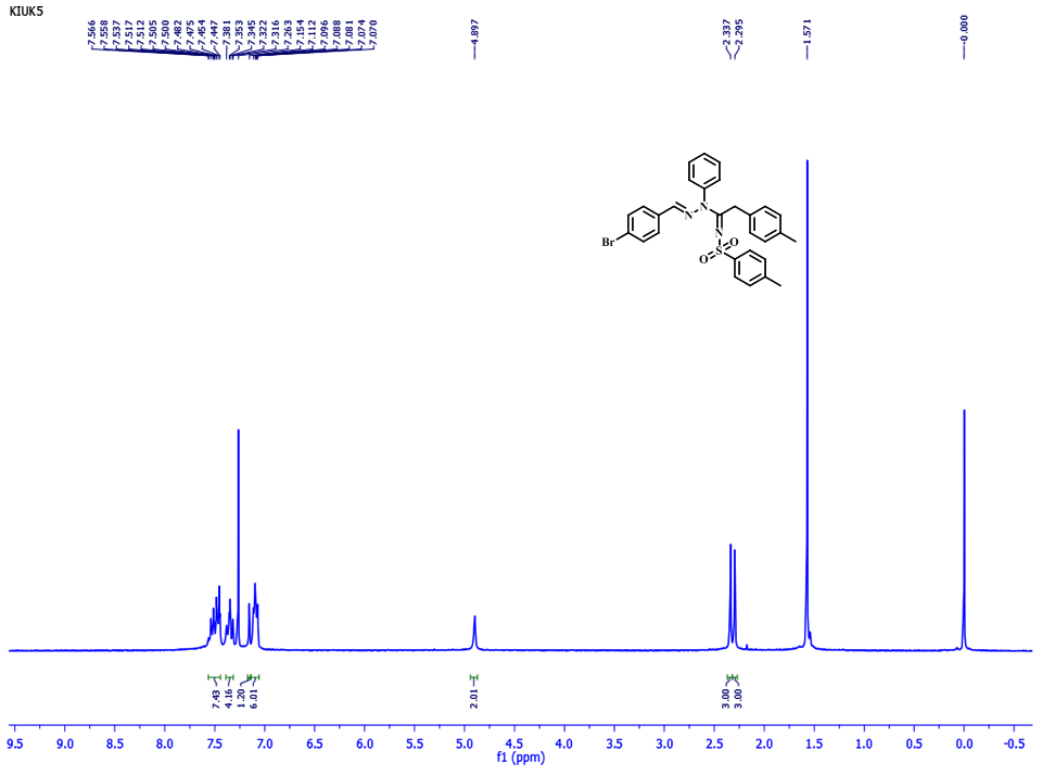
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5s**



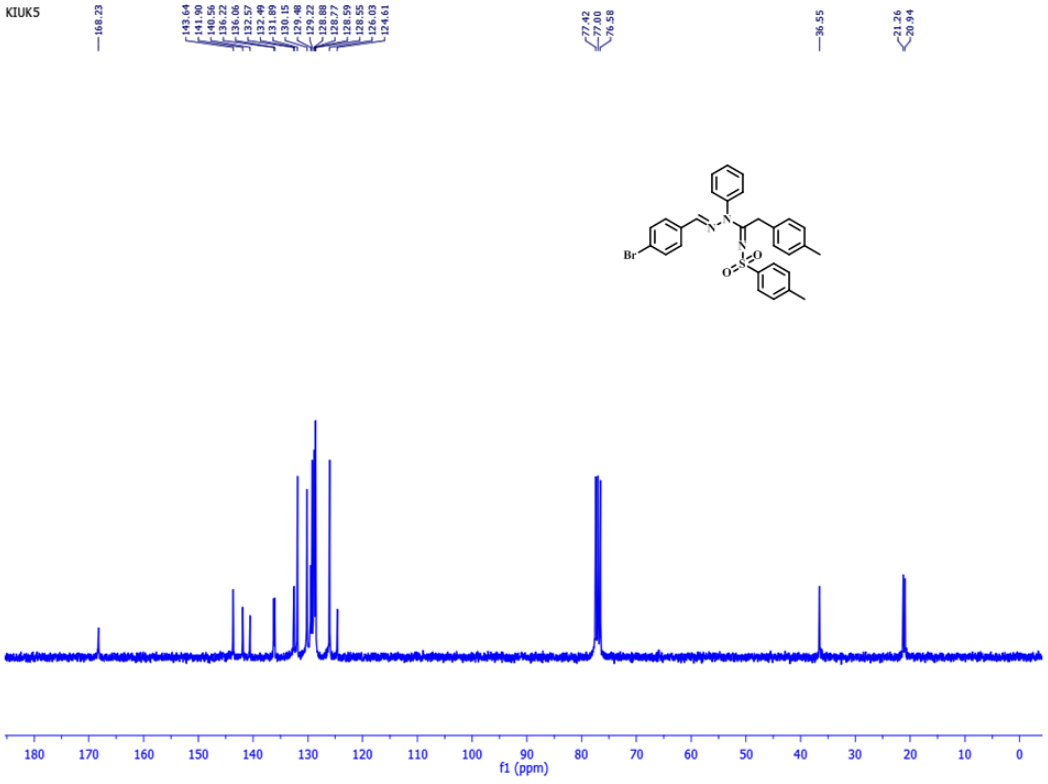
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5t**



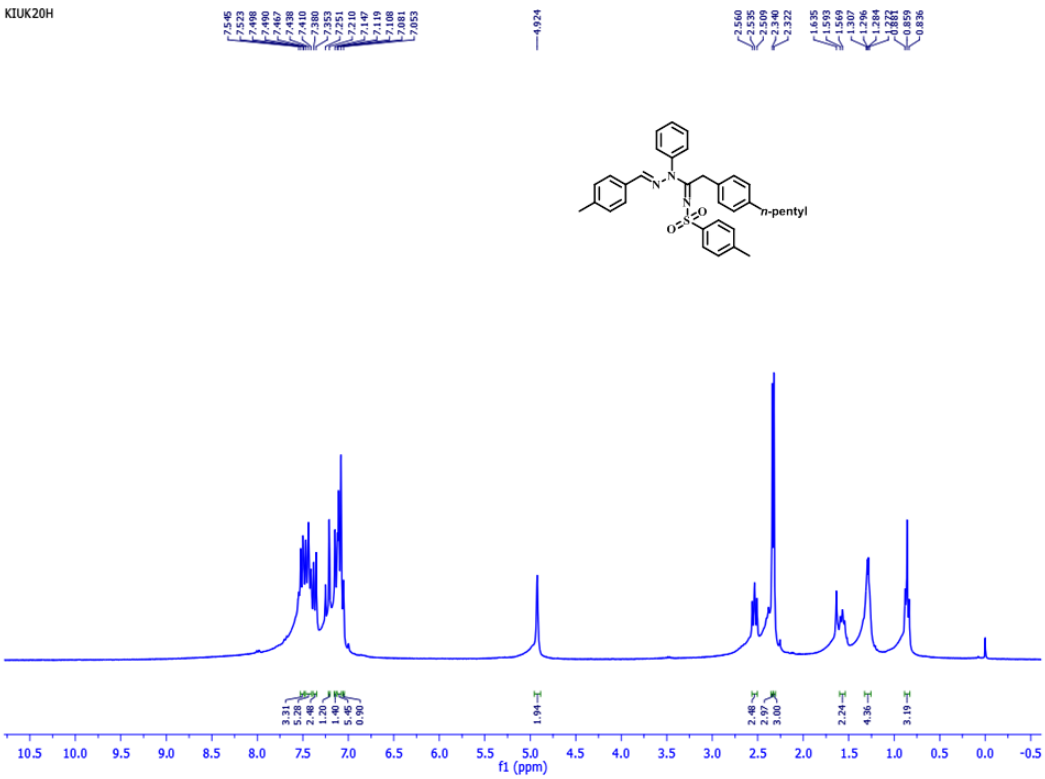
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5t**



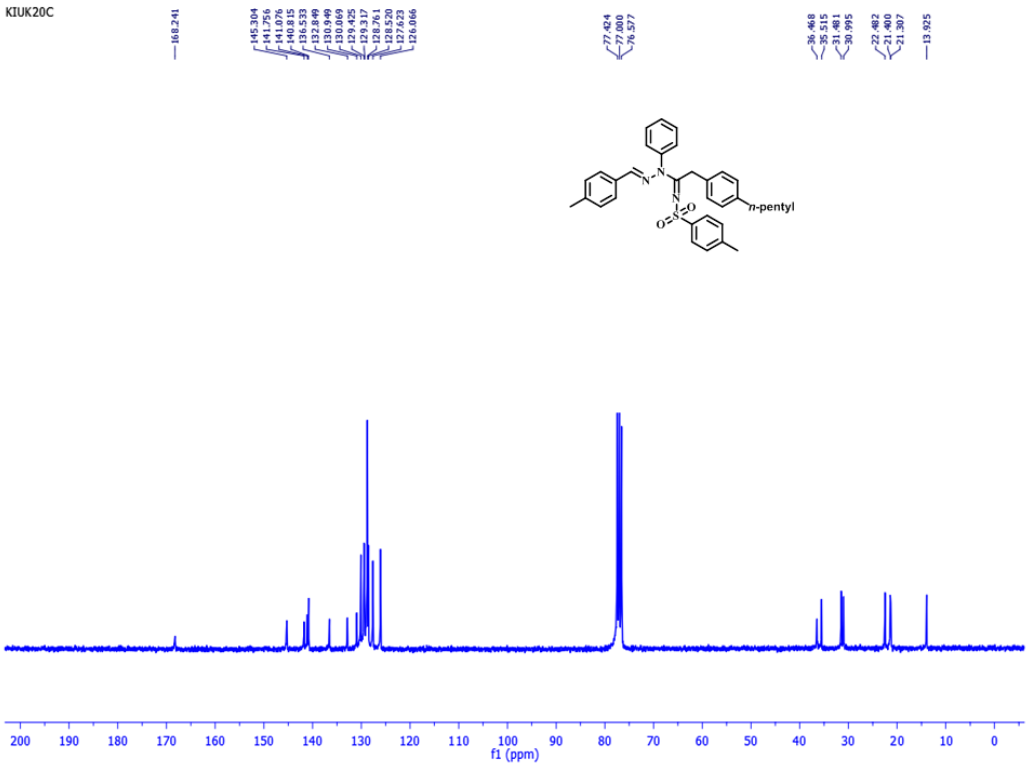
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5u**



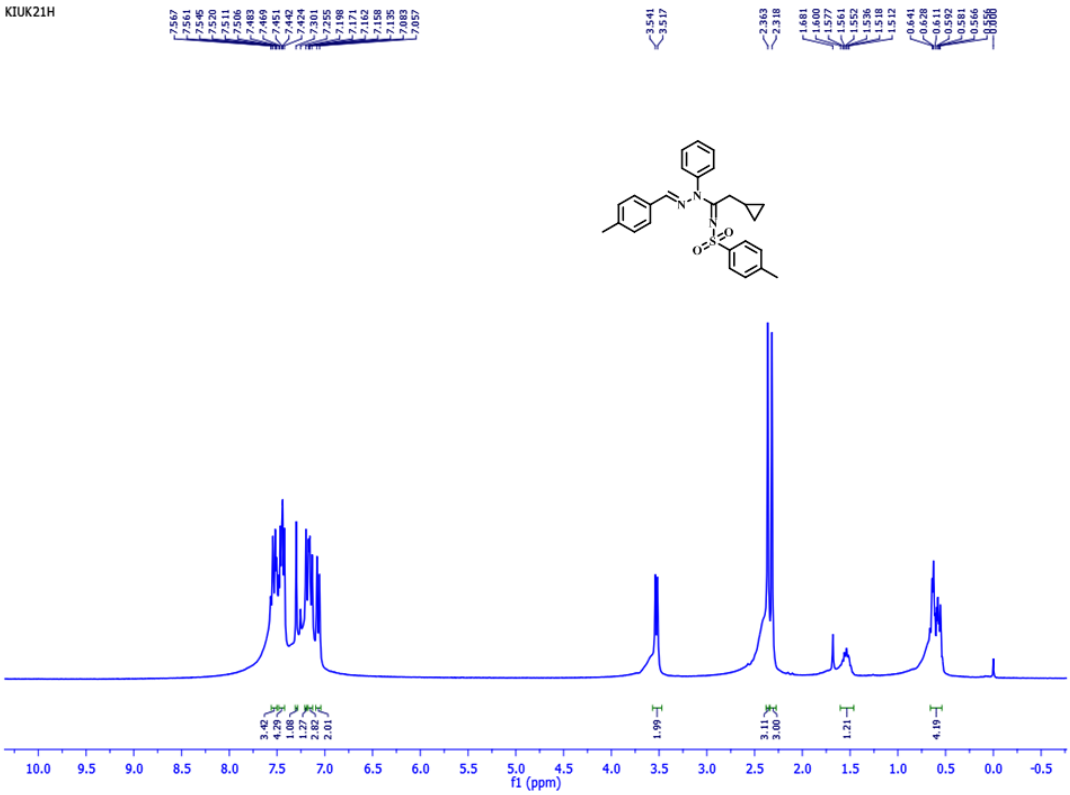
^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5u**



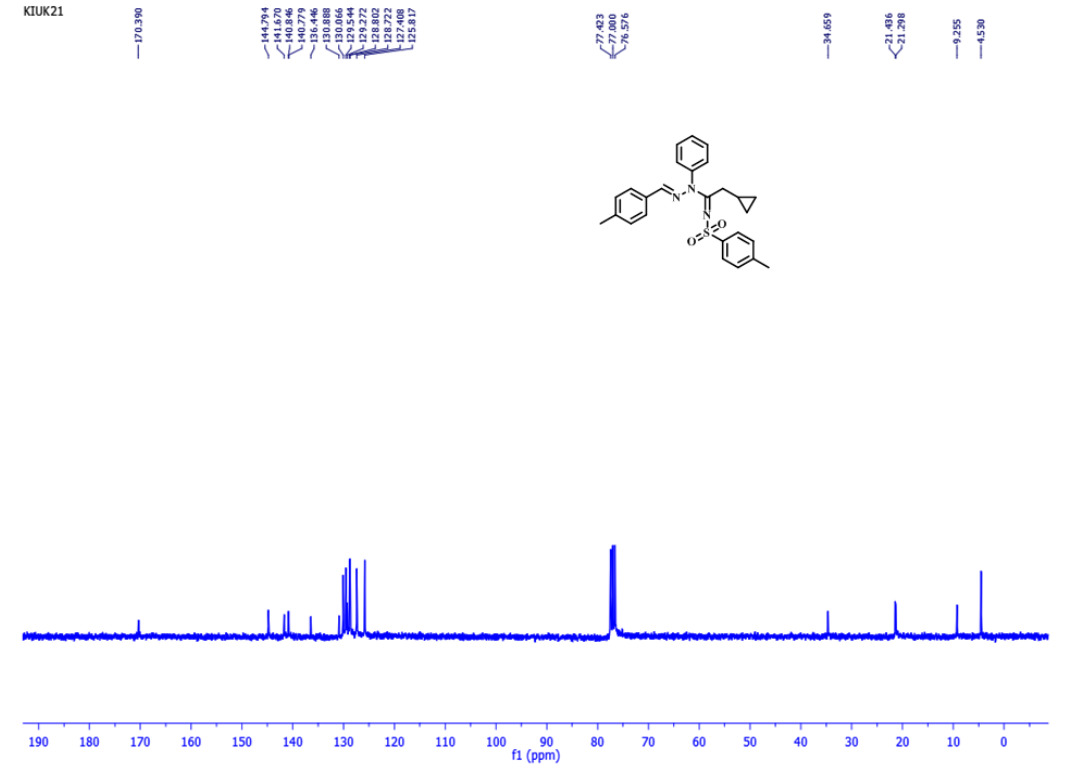
^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5v**



^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5v**



^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5w**



^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **5w**