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Supporting Information

An Improved One-Pot Multicomponent Strategy for the Preparation of Thiazoline, Thiazolidinone and Thiazolidinol Scaffolds

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1. X-ray structure of product (4j; Table 3; entry j)

X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5202 reflections. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms. H bound to N was located from the difference Fourier map.

Crystal data for 4j (table 3): $C_{20}H_{25}N_2O_2S_1^+$. Br^-, $M = 437.39$, brown plate, 0.35 x 0.20 x 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.7828(8)$, $b = 11.0859(7)$, $c = 16.1335(10)$ Å, $\beta = 93.1990(10)°$, $V = 2104.1(2)$ $Å^3$, $Z = 4$, $Dc = 1.381$ g/cm^3, $F_{000} = 904$, CCD area detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 293(2)$K, $2\theta_{max} = 50.0°$, 19639 reflections collected, 3696 unique ($R_{int} = 0.0202$), Final *GooF* = 1.040, $R_1 = 0.0293$, *wR2* = 0.0797, *R* indices based on 3291 reflections with $I > 2\sigma(I)$ (refinement on F^2), 241 parameters, $\mu = 2.069$ mm^{-1}. CCDC 1410087 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

References:

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

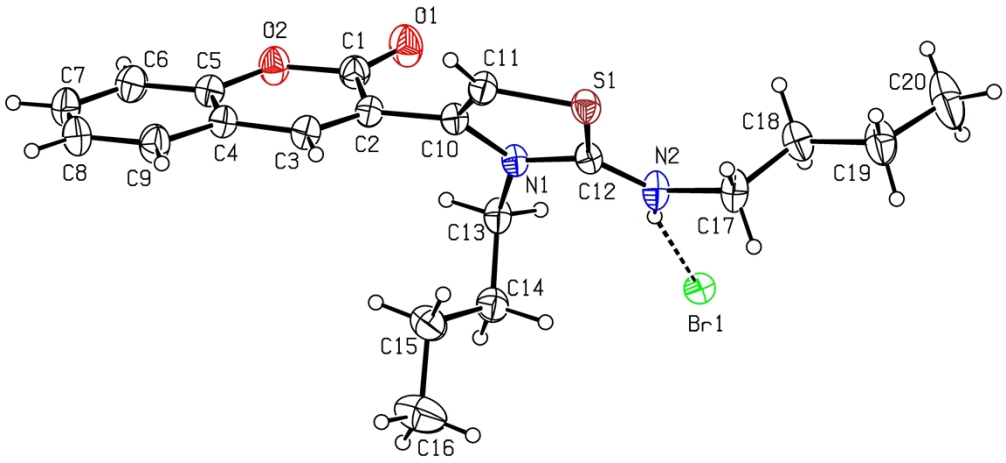


Fig. ORTEP molecular diagram of 4j

Figure caption: The molecular structure of 4j with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. The thiazoline derivative has crystallized in the form of a HBr salt. Dotted lines indicate hydrogen bonding between the protonated N2 atom and the bromide ion.

Experimental Section

All solvents were distilled before use. Dry reactions were conducted under a nitrogen atmosphere. Crude products were purified by column chromatography on silica gel (60–120 mesh). Thin-layer chromatography plates were visualized by exposure to ultraviolet light, exposure to iodine vapors. IR spectra were recorded with an FTIR spectrometer. ^{1}H, ^{19}F, and ^{13}C (proton decoupled) NMR spectra were recorded in $CDCl_3$ with 500 MHz NMR spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane, which was used as an internal standard. Coupling constants (J) are quoted in Hertz (Hz). High-resolution mass spectral (HRMS) were recorded using electro spray ionization (ESI) and an orbitrap mass analyser.

General procedure for synthesis of 2-aminothiazolin derivatives:

The mixture of and primary amine **1** (2 mmol) and carbon disulphide **2** (1 mmol) in DMF was allowed to microwave irradiation. The power was set at 160 W and the temperature was set at 100 ^{0}C. After 5 min, the mixture was allowed to room temperature and added Phenacyl bromide or 3-Bromoacylcoumarine (3a-b) and again allowed to micro wave irradiation for 5 min under the same conditions. After five minutes the reaction mixture allowed to room temperature. The resultant mixture was and poured in to crushed ice and filtered to afford HBr salt of thiazoline which is further neutralized with saturated sodium bicarbonate and organic layer extracted with ethyl acetate, dried with Na_2SO_4. Finally, the desired compounds (4a-j) table 3 achieved by solvent evaporation under reduced pressure in good to excellent yield listed in table 3.

(*Z*)-*N*-(3,4-diphenylthiazol-2(3H)-ylidene)aniline (4a): Solid, m.p. 188-190^{0}C. ^{1}H NMR ($CDCl_3$): δ = 5.96 (s, 1H), 7.01-7.06 (m, 3H), 7.09 (dd, J = 7.9 Hz, 2H), 7.17-7.24 (m, 3H), 7.25-7.28 (m, 3H), 7.29-7.34 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 97.24, 121.60, 123.21, 127.51, 128.14, 128.15, 128.25, 128.78, 128.83, 129.35, 131.54, 137.85, 139.90, 151.73, 16.22 ppm. IR (KBr): 1590, 1540, 1520, 1255, 1170, 1027 cm^{-1}. MS (ESI): m/z = 329 $[M + H]^{+}$. HRMS (ESI): calcd. For $C_{21}H_{17}N_2S$ 329.111245 $[M + H]^{+}$; found 329.11042.

(*Z*)-4-methoxy-*N*-(3-(4-methoxyphenyl)-4-phenylthiazol-2(3H)-ylidene)aniline (4b): Solid, m.p. 127-129^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.79-3.82 (m, 6H), 6.76 (s,

1H), 6.92 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.11-7.15 (m, 2H), 7.23-7.28 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H) ppm. ^{13}C NMR (DMSO- d^6, 75 MHz): δ = 54.53, 54.65, 104.16, 114.34, 114.65, 124.50, 125.55, 126.97, 127.51, 128.19, 128.89, 129.12, 141.61, 158.61, 159.99, 169.77 ppm. IR (KBr): 1607, 1557, 1510, 1251, 1175, 1022 cm^{-1}. MS (ESI): m/z = 389 $[M + H]^+$. HRMS (ESI): calcd. For $C_{23}H_{21}O_2N_2S$ 389.13183 $[M + H]^+$; found 389.13142.

(*Z*)-*N*-(3-benzyl-4-phenylthiazol-2(3H)-ylidene)-1-phenylmethanamine (4c): Solid, m.p. 165-167°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.64 (d, J = 5.2 Hz, 2H), 5.82 (s, 2H), 6.58 (s, 1H), 7.07-7.36 (m, 12H), 7.41-7.57 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 49.82, 50.85, 104.59, 127.08, 127.81, 127.82, 128.09, 128.21, 128.50, 128.65, 129.09, 129.20, 130.63, 132.63, 133.15, 143.06, 168.42 ppm. IR (KBr): 1595, 1447, 1348, 1128, 955 cm^{-1}. MS (ESI): m/z = 357 $[M + H]^+$. HRMS (ESI): calcd. For $C_{23}H_{21}N_2S$ 357.14200 $[M + H]^+$; found 357.14179.

(*Z*)-*N*-(3-cyclohexyl-4-phenylthiazol-2(3H)-ylidene)cyclohexanamine (4d): Solid, m.p. 210-212^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.78-0.98 (m,1H), 1.19-1.43(m, 3H), 1.47-1.95 (m, 12H), 1.99-2.14 (m, 2H), 2.22-2.42 (m, 2H), 3.19-3.37 (m, 1H), 5.09-5.27 (m, 1H), 6.51 (s, 1H), 7.32-7.42 (m, 2H), 7.42-7.61 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.43, 25.08, 25.32, 31.01, 31.21, 61.71, 62.01, 105.04, 128.33, 130.29, 130.42, 13.50, 143.00, 167.18 ppm. IR (KBr): 1563, 1446, 1342, 1117, 1004 cm^{-1}. MS (ESI): m/z = 341 $[M + H]^+$. HRMS (ESI): calcd. For $C_{21}H_{29}N_2S$ 341.20460 $[M + H]^+$; found 341.20407.

(*Z*)-1-(furan-2-yl)-*N*-(3-(furan-2-ylmethyl)-4-phenylthiazol-2(3H)-ylidene)methanamine (4e): Solid, m.p. 139-141°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.70 (d, J = 6.0 Hz, 2H), 5.69 (s, 2H), 6.15-6.49 (m, 3H), 6.58 (s, 1H), 6.98 (d, J = 3.8 Hz, 1H), 7.24-7.31 (m, 1H), 7.32-7.38 (m, 1H), 7.39-7.65 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 43.17, 44.47, 104.00, 110.30, 110.48, 110.58, 112.60, 127.83, 129.04, 129.77, 130.76, 142.93, 143.04, 143.19, 144.55, 146.80 ppm. IR (KBr): 1660, 1585, 1343, 1145, 1012, 740 cm^{-1}. MS (ESI): m/z = 337 $[M + H]^+$. HRMS (ESI): calcd. For $C_{19}H_{17}O_2N_2S$ 337.10053 $[M + H]^+$; found 337.09987.

(*Z*)-*N*-(3-butyl-4-phenylthiazol-2(3H)-ylidene)butan-1-amine (4f): Solid, m.p. 154-156^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.70 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3, 3H),

1.17-1.28 (m, 2H), 1.42-1.52 (m, 2H), 1.54-1.63 (m, 2H), 1.86-1.94 (m, 2H), 3.47-3.54 (m, 2H), 4.44 (t, J = 7.6 Hz, 2H), 6.54 (s, 1H), 7.30-7.40 (m, 2H), 7.48-7.61 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.19, 13.48, 18.92, 19.97, 29.39, 29.42, 47.61, 48.12, 103.42, 128.20, 129.07, 129.28, 130.61, 142.89, 167.44 ppm. IR (KBr): 1592, 1486, 1360, 1148, 1106, 982 cm^{-1}. MS (ESI): m/z = 289 $[M + H]^+$. HRMS (ESI): calcd. For $C_{17}H_{25}N_2S$ 289.17330 $[M + H]^+$; found 289.17354.

(*Z*)-3-(3-phenyl-2-(phenylimino)-2,3-dihydrothiazol-4-yl)-2H-chromen-2-one (4g): Solid, m.p. 307-310°C. ^{1}H NMR (DMSO- d^6, 500 MHz): δ = 7.27-7.45 (m, 6H), 7.46-7.70 (m, 9H), 8.17 (s, 1H) ppm. ^{13}C NMR (DMSO- d^6, 75 MHz): δ = 107.80, 116.26, 116.8, 117.89, 121.05, 124.25, 125.11, 127.66, 128.51, 129.34, 129.79, 130.13, 130.39, 133.47, 133.80, 135.54, 147.11, 153.43, 157.88, 167.49 ppm. IR (KBr): 1718, 1602, 1560, 1490, 1450, 1361, 1212, 1100, 1038 cm^{-1}. MS (ESI): m/z = 397 $[M + H]^+$. HRMS (ESI): calcd. For $C_{24}H_{17}O_2N_2S$ 397.10053 $[M + H]^+$; found 397.10031.6.

(*Z*)-3-(3-benzyl-2-(benzylimino)-2,3-dihydrothiazol-4-yl)-2H-chromen-2-one (4h): Solid, m.p. 198-200°C. ^{1}H NMR (DMSO-d^6, 500 MHz): δ = 4.64 (br. s, 2H), 5.83 (s, 2 H), 6.87 (s, 1H), 7.06-7.41 (m, 12H), 7.43-7.52 (m, 1H), 7.60-7.70 (m, 1H), 7.73 (s, 1H) ppm. ^{13}C NMR (DMSO-d^6, 75 MHz): δ = 48.99, 49.26, 108.15, 114.93, 114.98, 116.62, 123.66, 125.28, 126.27, 126.89, 127.39, 127.83, 131.73, 132.28, 135.23, 145.89, 152.59, 157.41, 167.20 ppm. IR (KBr): 1723, 1606, 1560, 1454, 1361, 1216, 1135, 1083 cm^{-1}. MS (ESI): m/z = 425 $[M + H]^+$. HRMS (ESI): calcd. For $C_{26}H_{21}O_2N_2S$ 425.13183 $[M + H]^+$; found 425.13185.

(*Z*)-3-(3-cyclohexyl-2-(cyclohexylimino)-2,3-dihydrothiazol-4-yl)-2H-chromen-2-one (4i): Solid, m.p. 245-247^{0}C. ^{1}H NMR (DMSO-d^6, 500 MHz): δ = 1.07-1.49 (m, 6H), 1.51-2.15 (m, 14H), 3.35-3.45 (m, 1H), 4.11-4.37 (m, 1H), 7.40-7.50 (m, 2H), 7.69-7.85 (m, 2H), 8.22- 8.32 (m, 1H), 8.77-9.08 (m, 1H) ppm. ^{13}C NMR (DMSO-d^6, 75 MHz): δ = 23.56, 24.59, 24.66, 24.93, 28.17, 30.87, 60.42, 60.84, 109.19, 116.46, 117.99, 118.43, 125.04, 129.46, 133.53, 136.61, 147.42, 153.94, 159.32, 166.96 ppm. IR (KBr): 1727, 1610, 1564, 1455, 1366, 1220, 1129, 1090 cm^{-1}. MS (ESI): m/z = 409 $[M + H]^+$. HRMS (ESI): calcd. For $C_{24}H_{29}O_2N_2S$ 409.19443 $[M + H]^+$; found 409.19345.

(*Z*)-3-(3-butyl-2-(butylimino)-2,3-dihydrothiazol-4-yl)-2H-chromen-2-one (4j): Solid, m.p. 166-168^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.81 (t, J = 7.3 Hz, 3H), 0.98 (t, J =

7.3, 3H), 1.30-1.39 (m, 2H), 1.40-1.50 (m, 2H), 1.67-1.77 (m, 2H), 1.82-1.91 (m, 2H), 3.45-3.53 (m, 2H), 4.37 (t, *J* = 7.8 Hz, 2H), 6.95-7.04 (m, 1H), 7.38-7.47 (m, 2H), 7.68-7.74 (m, 2H), 8.10-8.16 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.45, 19.19, 19.91, 29.39, 29.60, 48.07, 48.17, 108.31, 116.40, 116.68, 117.78, 125.33, 129.23, 133.91, 136.48, 147.41, 154.21, 158.76, 167.20 ppm. IR (KBr): 1722, 1615, 1574, 1446, 1359, 1226, 1132, 1085 cm^{-1}. MS (ESI): *m*/*z* = 357 $[M + H]^+$. HRMS (ESI): calcd. For $C_{20}H_{25}O_2N_2S$ 357.16313 $[M + H]^+$; found 357.16375.

General procedure for synthesis of 2-iminothiazolidin-4-one ester derivatives (6a-i): The mixture of and primary amine **1** (2 mmol) and carbon disulphide **2** (1 mmol) in DMF was allowed to microwave irradiation. The power was set at 160 W and the temperature was set at 100 ^{0}C. After 5 min, the mixture was allowed to room temperature and added DMAD or DEAD (5a-b) and the reaction mixture was stirred at room temperature for 10–15 min. After completion of the reaction, the resultant mixture was diluted with water and admixed with ethyl acetate (20 mL). The ethyl acetate layer was washed with brain solution (5 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified over a silica gel column (4% EtOAc/hexane) to give desired products (6a-i, table 4) in good yield.

(*Z*)-Ethyl 2-((*Z*)-4-oxo-3-phenyl-2-(phenylimino)thiazolidin-5-ylidene)acetate (6a): Solid, m.p. 76-78°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.32 (t, *J* = 7.2 Hz, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.40-7.59 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.10, 61.73, 116.94, 120.87, 125.17, 127.83, 129.11, 129.24, 129.29, 133.99, 141.09, 147.30, 151.68, 164.58, 165.91 ppm. IR (KBr): 1705, 1692, 1642, 1492, 1367, 1313, 1192, 1027 cm^{-1}. MS (ESI): *m*/*z* = 353 $[M + H]^+$. HRMS (ESI): calcd. For $C_{19}H_{17}O_3N_2S$ 353.09544 $[M + H]^+$; found 353.09595.

(*Z*)-ethyl 2-((*Z*)-3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-4-oxothiazolidin-5-ylidene)acetate (6b): Viscous liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.32 (t, *J* = 7.3 Hz, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 4.27 (q, *J* = 7.3 Hz, 2H), 6.84-6.91 (m, 4H), 6.97 (s, 1H), 7.01-7.06 (m, 2H), 7.31-7.36 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.09, 55.39, 55.44, 61.65, 114.42, 114.60, 116.57, 122.08, 126.49, 128.89, 140.55, 141.22, 151.78, 157.12, 159.75, 164.78, 165.94 ppm. IR (neat): 1712, 1697, 1630, 1627, 1509,

1460, 1373, 1237, 1187, 1036 cm^{-1}. MS (ESI): *m/z* = 413 $[M + H]^+$. HRMS (ESI): calcd. For $C_{21}H_{21}O_5N_2S$ 413.11657 $[M + H]^+$; found. 413.11619.

(*Z*)-ethyl 2-((*Z*)-3-benzyl-2-(benzylimino)-4-oxothiazolidin-5-ylidene)acetate (6c): Solid, m.p. 125-127°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.33 (t, *J* = 6.9 Hz, 3H), 4.29 (q, *J* = 6.9 Hz, 2H), 4.67 (s, 2H), 5.06 (s, 2H), 6.92 (s, 1H), 7.22-7.38 (m, 8H), 7.40-7.48 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.15, 46.01, 55.89, 61.62, 116.14, 127.02, 127.40, 127.86, 128.42, 128.88, 135.78, 138.60, 140.83, 149.55, 164.72, 165.90 ppm. IR (neat): 1724, 1686, 1625, 1635, 1512, 14702 1369, 1240, 1190, 1040 cm^{-1}. MS (ESI): *m/z* = 381 $[M + H]^+$. HRMS (ESI): calcd. For $C_{21}H_{21}O_3N_2S$ 381.12674 $[M + H]^+$; found. 381.12662.

(*Z*)-ethyl 2-((*Z*)-3-(furan-2-ylmethyl)-2-((furan-2-ylmethyl)imino)-4-oxothiazolidin-5-ylidene)acetate (6d): Solid, m.p. 89-91°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.34 (t, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.65 (s, 2H), 5.03 (s, 2H), 6.21-6.24 (m, 1H), 6.32-6.35 (m, 2H), 6.93 (s, 1H), 7.31-7.34 (m, 1H), 7.36-7.40 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.14, 38.66, 49.10, 61.70, 107.09, 109.52, 110.30, 110.37, 116.44, 140.41, 142.07, 142.32, 148.67, 150.46, 151.60, 164.30, 165.85 ppm. IR (KBr): 1721, 1651, 1613, 1381, 1316, 1195, 1026 cm^{-1}. MS (ESI): *m/z* = 361$[M + H]^+$, 383 $[M + Na]^+$. HRMS (ESI): calcd. For $C_{17}H_{16}O_5N_2NaS$ 383.06721 $[M + H]^+$; found. 383.06759**.**

(*Z*)-methyl 2-((*Z*)-4-oxo-3-phenyl-2-(phenylimino)thiazolidin-5-ylidene)acetate (6e): Solid, m.p. 128-130°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.82 (s, 3H), 6.90-6.97 (m, 2H), 7.00 (s, 1H), 7.15 (t, J = 7.4Hz, 1H), 7.33 (t, J = 7.7Hz, 2H), 7.41-7.59 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 52.52, 116.43, 120.84, 125.19, 127.79, 129.13, 129.24, 129.28, 133.93, 141.35, 147.26, 151.51, 164.50, 166.29 ppm. IR (KBr): 1711, 1690, 1607, 1387, 1316, 1191, 1022 cm^{-1}. MS (ESI): *m/z* = 339 $[M + H]^+$, 361 $[M + Na]^+$. HRMS (ESI): calcd. For $C_{18}H_{15}O_3N_2S$ 339.07979 $[M + H]^+$; found. 339.07990

(*Z*)-methyl 2-((*Z*)-3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-4-oxothiazolidin-5-ylidene)acetate (6f): Viscous liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.78-3.87 (m, 9H), 6.80-6.93 (m, 4H), 6.98 (s, 1H), 6.99-7.10 (m, 2H), 7.28-7.38 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.65, 55.36, 114.44, 114.63, 116.13, 122.02, 126.48, 128.90, 140.53, 141.53, 151.64, 157.17, 159.79, 164.75, 166.37 ppm. IR (KBr):

1722, 1680, 1617, 1377, 1326, 1181, 1020 cm^{-1}. MS (ESI): *m/z* = 399 $[M + H]^+$, 421 $[M + Na]^+$. HRMS (ESI): calcd. For $C_{20}H_{19}O_5N_2S$ 399.10092 $[M + H]^+$; found. 399.10195.

(*Z*)-methyl 2-((*Z*)-3-benzyl-2-(benzylimino)-4-oxothiazolidin-5-ylidene)acetate (6g): Solid, m.p. 130-132°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.84 (s, 3H), 4.67 (s, 2H), 5.06 (s, 2H), 6.92 (s, 1H), 7.25-7.35 (m, 8H), 7.41-7.45(m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 46.08, 52.48, 55.95, 115.67, 127.08, 127.43, 127.91, 128.46, 128.90, 135.77, 138.59, 141.18, 149.43, 164.70, 166.36 ppm. IR (KBr): 1718, 1692, 1620, 1380, 1330, 1190, 1025 cm^{-1}. MS (ESI): *m/z* = 367 $[M + H]^+$; 389 $[M + Na]^+$. HRMS (ESI): calcd. For $C_{20}H_{19}O_3N_2S$ 367.11109 $[M + H]^+$; found. 367.11193.

(*Z*)-methyl 2-((*Z*)-3-(furan-2-ylmethyl)-2-((furan-2-ylmethyl)imino)-4-oxothiazolidin-5-ylidene)acetate (6h): Solid, m.p. 123-125°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.85 (s, 3H), 4.65 (s, 2H), 5.04 (s, 2H), 6.22-6.24 (m, 1H), 6.28-6.30 (m, 1H), 6.33-6.35 (m, 2H), 6.94 (s, 1H), 7.31-7.33 (m, 1H), 7.37-7.39 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 38.70, 49.13, 52.53, 107.12, 109.55, 110.31, 110.38, 115.94, 140.74, 142.09, 142.34, 148.64, 150.31, 151.55, 164.25, 166.27 ppm. IR (KBr): 1721, 1651, 1613, 1419, 1384, 1318, 1194, 1024 cm^{-1}. MS (ESI): *m/z* = 347 $[M + H]^+$, 369 $[M + Na]^+$. HRMS (ESI): calcd. For $C_{16}H_{15}O_5N_2S$ 347.06962 $[M + H]^+$; found. 347.07009.

(*Z*)-methyl 2-((*Z*)-3-butyl-2-(butylimino)-4-oxothiazolidin-5-ylidene)acetate (6i): Solid, m.p. 78-80°C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.90-0.99 (m, 6H), 1.30-1.44 (m, 4H), 1.61-1.66 (m, 4H), 3.44 (t, *J* = 7.02 Hz, 2H), 3.78-3.88 (m, 5H), 6.88 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.67, 13.82, 19.93, 20.39, 29.44, 29.64, 32.74, 42.61, 52.56, 114.67, 141.73, 147.89, 164.80, 166.55 ppm. IR (KBr): 1715, 1645, 1613, 1432, 1392, 1325, 1208, 1008 cm^{-1}. MS (ESI): *m/z* = 299 $[M + H]^+$. HRMS (ESI): calcd. For $C_{14}H_{23}O_3N_2S$ 299.14239 $[M + H]^+$; found. 299.14258.

General procedure for synthesis of 2-imino-4-trifluoromethyl thiazolidinol derivatives(8a-h):

The mixture of and primary amine **1** (2 mmol) and carbon disulphide **2** (1 mmol) in DMF was allowed to microwave irradiation. The power was set at 160 W and the temperature was set at 100 ^0C. After 5 min, the mixture was allowed to room temperature and added 3-bromo-1,1,1-trifluoropropan-2-one **7** drop wise at room temperature and continued stirring for 10-15 min at room temperature. After completion of the reaction, the resultant

mixture was diluted with water and admixed with ethyl acetate (20 mL). The ethyl acetate layer was washed with sodium bicarbonate solution and then brain solution (5 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified over a silica gel column (6% EtOAc/hexane) to give desired products (8a-h, table 5) in good yield.

(*Z*)-3-phenyl-2-(phenylimino)-4-(trifluoromethyl)thiazolidin-4-ol (8a): Solid, m.p. 154-156^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.36 (d, J = 12.4 Hz, 1H), 3.60 (br. s, 1H), 3.73 (d, J = 12.4 Hz, 1H), 6.85-6.89 (m, 2H), 7.02-7.07 (m, 1H), 7.23-7.28 (m, 2H), 7.35-7.49 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.74, 91.09 (q, J = 31.0 Hz), 121.54, 123.99, 128.93, 129.11, 129.28, 129.56, 130.44, 136.73, 150.69, 158.52 ppm. IR (KBr): 3025, 1619, 1585, 1490, 1324, 1183 cm^{-1}. MS (ESI): m/z = 339 $[M + H]^+$. HRMS (ESI): calcd. For $C_{16}H_{14}ON_2F_3S$ 339.07734 $[M + H]^+$; found 339.07719.

(*Z*)-3-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)-4 (trifluoromethyl)thiazolidin-4-ol (8b): Solid, m.p. 142-144^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.33 (d, J = 12.2 Hz, 1H), 3.69 (d, J = 12.2 Hz, 1H), 3.76 (s, 3H), 3.81 (s, 3H), 6.80 (br. s, 4H), 6.94-6.98 (m, 2H), 7.25-7.29 (m, 2H) ppm.^{13}C NMR ($CDCl_3$, 75 MHz): 34.37, 55.32, 55.35, 90.93 (q, J = 31.7), 114.07, 114.65, 122.55, 122.84 (q, J = 287.5), 129.11, 131.44, 144.19, 156.13, 159.26, 159.58 ppm. IR (KBr): 3030, 1620, 1590, 1485, 1330, 1189 cm^{-1}. MS (ESI): m/z = 399 $[M + H]^+$. HRMS (ESI): calcd. For $C_{18}H_{18}O_3N_2F_3S$ 399.09847 $[M + H]^+$; found 399.09699.

(*Z*)-3-(2,4-dimethoxyphenyl)-2-((2,4-dimethoxyphenyl)imino)-4-(trifluoromethyl)thiazolidin-4-ol (8c): Solid, m.p. 128-130^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.32 (d, J = 12.1 Hz, 1H), 3.62 (d, J = 12.1 Hz, 1H), 3.72 (s, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 3.97 (s, 3H), 5.63 (br. s, 1H), 6.35-6.46 (m, 2H), 6.58-6.64 (m, 2H), 6.69-6.76 (m, 1H), 7.21-7.28 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 35.31, 55.33, 55.45, 55.77, 56.90, 91.73 (q, J = 30.7 Hz), 99.84, 100.9, 103.74, 106.53, 119.06, 122.15, 124.62, 133.36, 134.20, 152.06, 155.60, 157.06, 159.51, 160.98 ppm. IR (KBr): 1612, 1506, 1462, 1187, 1158, 1036 cm^{-1}. MS (ESI): m/z = 459 $[M + H]^+$. HRMS (ESI): calcd. For $C_{20}H_{22}O_5N_2F_3S$ 459.11960 $[M + H]^+$; found 459.11822.

(*Z*)-3-(3-chloro-4-fluorophenyl)-2-((3-chloro-4-fluorophenyl)imino)-4-(trifluoromethyl)thiazolidin-4-ol (8d): Solid, m.p. 146-148^{0}C. ^{1}H NMR ($CDCl_3$, 500

MHz): δ = 3.41 (d, J = 12.4 Hz, 1H), 3.55 (br. s, 1H), 3.79 (d, J = 12.4 Hz, 1H), 6.70-6.75 (m, 1H), 6.93 (dd, J = 6.6 Hz, 1H), 7.03 (t, J = 8.5 Hz, 1H), 7.21-7.29 (m, 2H), 7.44 (dd, J = 6.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 35.02, 91.32 (q, J = 32.2), 116.66 (d, J = 21.9 Hz), 117.27 (d, J = 21.9 Hz), 120.96 (d, J = 6.6 Hz), 123.35, 124.37, 130.34 (d, J = 6.6 Hz), 132.57, 132.80, 135.45, 146.73, 153.34, 156.56, 159.15, 160.00 ppm. IR (KBr): 1612, 1506, 1462, 1187, 1158, 1036 cm^{-1}. IR (KBr): 1581, 1494, 1259, 1184, 1014 cm^{-1}. MS (ESI): m/z = 443 [M + H]$^+$. HRMS (ESI): calcd. For $C_{16}H_{10}ON_2Cl_2F_5S$ 442.98056 [M + H]$^+$; found 442.98004.

(*Z*)-4-(trifluoromethyl)-3-(3-(trifluoromethyl)phenyl)-2-((3-(trifluoromethyl)phenyl)imino)thiazolidin-4-ol (8e): Solid, m.p. 106-108^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.41 (d, J = 12.5 Hz, 1H), 3.81 (d, J = 12.5 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.13 (br. s, 1H), 7.28-7.42 (m, 2H), 7.54-7.73 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 35.2, 91.1 (q, J = 32.4 Hz), 118.6, 120.7, 121.7, 124.4, 124.8, 125.3, 125.9, 127.3, 129.5, 129.9, 131.3 (q, J = 32.4 Hz), 131.4 (q, J = 32.4 Hz), 133.9, 137.2, 150.4, 159.0 ppm. IR (KBr): 3160, 2660, 1583, 1451, 1334, 1158 cm^{-1}. MS (ESI): m/z = 475 [M + H]$^+$. HRMS (ESI): calcd. for $C_{18}H_{12}ON_2F_9S$ 475.0498 [M + H]$^+$; found 475.0497.

(*Z*)-3-benzyl-2-(benzylimino)-4-(trifluoromethyl)thiazolidin-4-ol (8f): Solid, m.p. 108-110^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.80 (d, J = 12.9 Hz, 1H), 4.37-4.56 (m, 3H), 5.05 (d, J = 17.4 Hz, 1H), 5.20 (d, J = 17.4 Hz, 1H), 6.92-7.01 (m, 2H), 7.20-7.38 (m, 8H) ppm. ^{13}C NMR (DMSO- d^6, 75 MHz): δ = 33.00, 45.77, 49.33, 92.90 (q, J = 32.7 Hz), 125.38, 125.87, 125.94, 126.61, 126.98, 127.43, 131.92, 132.85, 169.47 ppm. IR (KBr): 3094, 1617, 1201, 1184, 1028 cm^{-1}. MS (ESI): m/z = 367 [M + H]$^+$. HRMS (ESI): calcd. For $C_{18}H_{18}ON_2F_3S$ 367.10865 [M + H]$^+$; found 367.10863.

(*Z*)-3-(furan-2-ylmethyl)-2-((furan-2-ylmethyl)imino)-4-(trifluoromethyl)thiazolidin-4-ol (8g): Solid, m.p. 150-152°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.85 (d, J = 12.8 Hz, 1H), 4.42 (d, J = 12.8 Hz, 1H), 4.58 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.93 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 17.1 Hz, 1H), 6.35-6.42 (m, 2H), 6.43-6.58 (m, 2H), 7.34-7.39 (m, 1H), 7.41-7.46 (m, 1H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.81, 39.86, 55.43, 91.00 (q, J = 32.5 Hz), 109.66, 110.91, 114.30, 122.64, 142.00, 142.83, 150.04, 156.39, 157.02 ppm. (KBr): 3076, 1626, 1414, 1176, 1018 cm^{-1}.

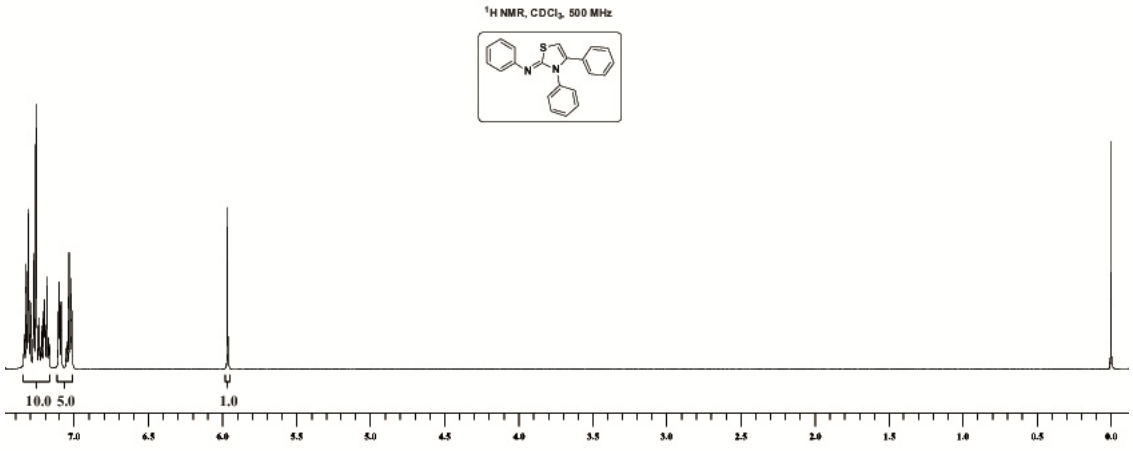
MS (ESI): *m*/*z* = 347 $[M + H]^+$. HRMS (ESI): calcd. For $C_{14}H_{14}O_3N_2F_3S$ 347.06717 $[M + H]^+$; found 347.06733.

(*Z*)-3-butyl-2-(butylimino)-4-(trifluoromethyl)thiazolidin-4-ol (8h): Solid, m.p. 98-100^{0}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.86-1.03 (m, 6H), 1.26-1.63 (m, 5H), 1.65-1.97 (m, 3H), 3.29-3.54 (m, 2H), 3.62-3.90 (m, 3H), 4.26-4.43 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.49, 19.63, 19.80, 28.59, 30.92, 33.61, 44.95, 47.87, 95.05 (q, *J* = 32.7 Hz), 122.45 (q, *J* = 287.6 Hz), 168.88 ppm. IR (KBr): 3064, 2966, 1627, 1264, 1179, 1094 cm^{-1}. MS (ESI): *m*/*z* = 299 $[M + H]^+$. HRMS (ESI): calcd. For $C_{12}H_{22}ON_2F_3S$ 299.13995 $[M + H]^+$; found 299.13999.

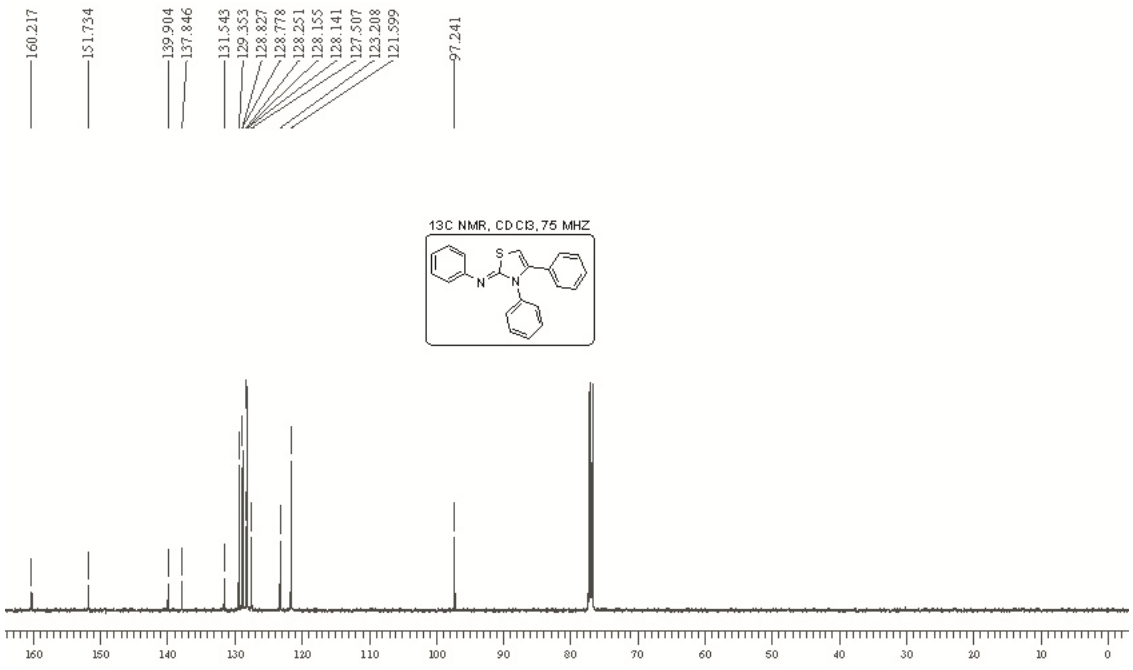
2. Copies of ^{1}H and ^{13}C NMR spectra of products 4a-j

^{1}H NMR spectra of 4a (Table 1, entry a)

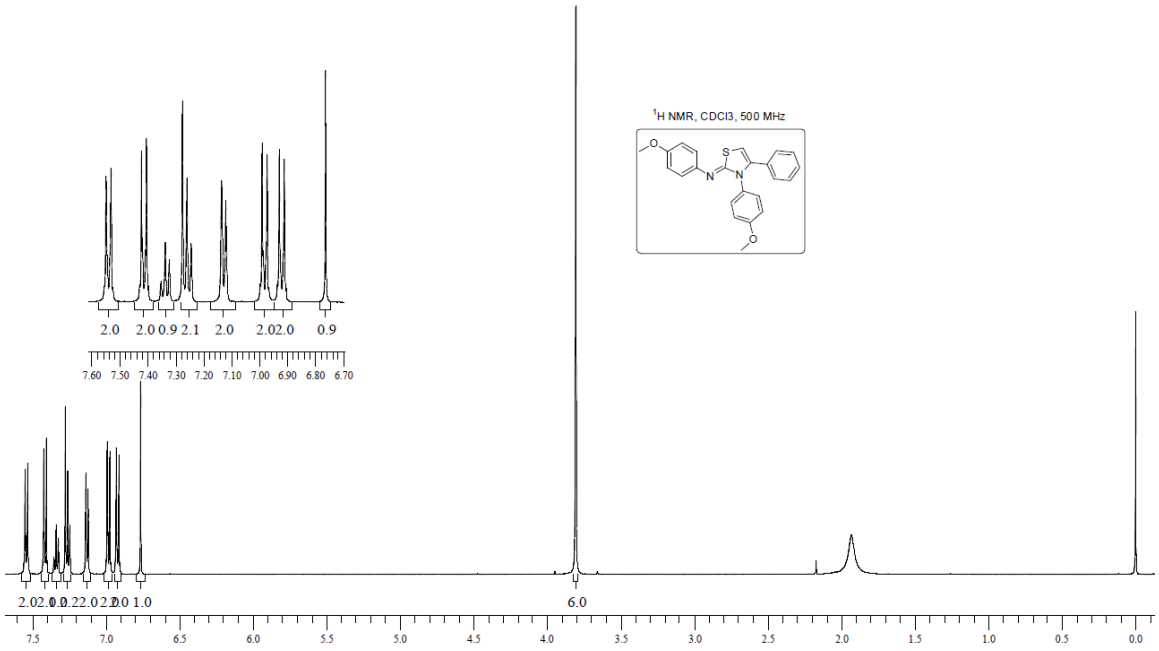
^{1}H NMR spectra of 4a



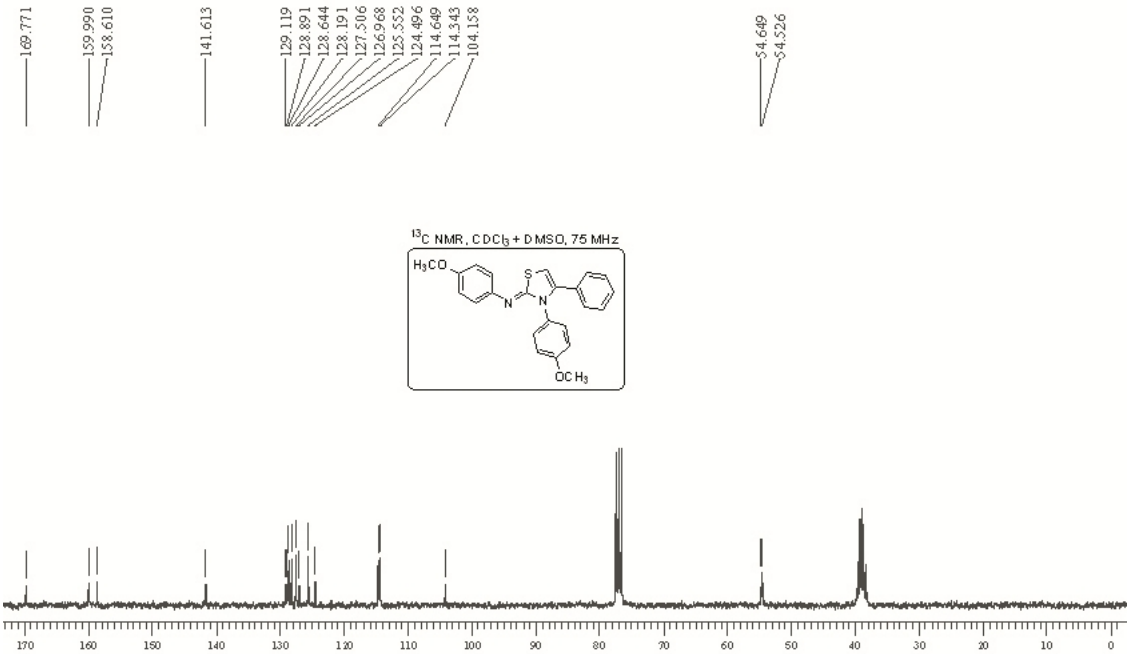
^{13}C NMR spectra of 4a



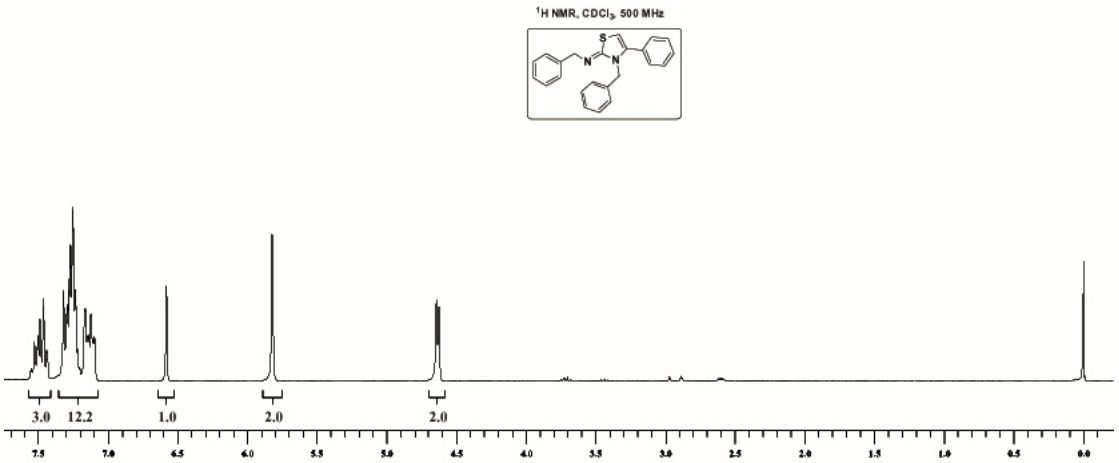
^{1}H NMR spectra of 4b



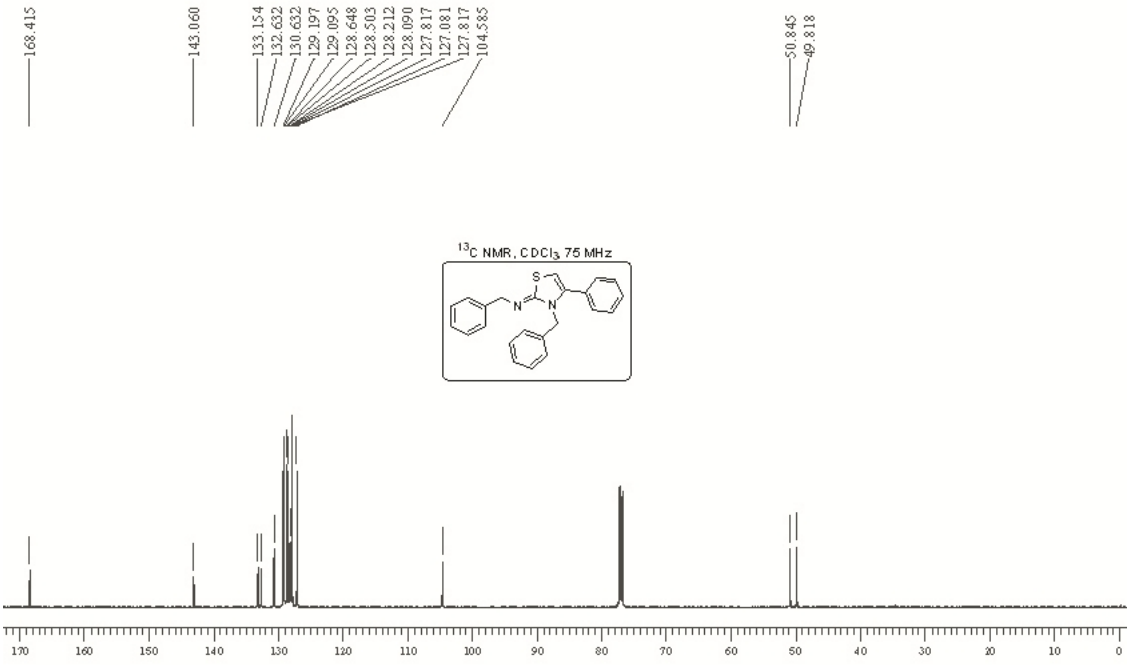
^{13}C NMR spectra of 4b



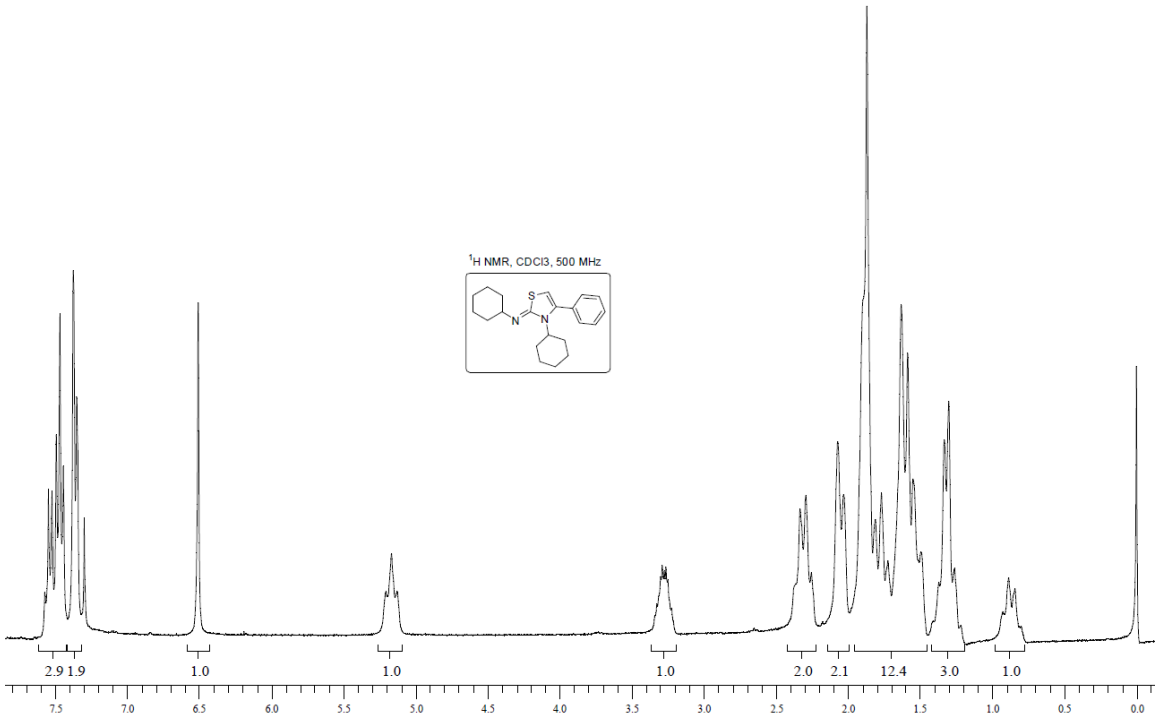
^{1}H NMR spectra of 4c



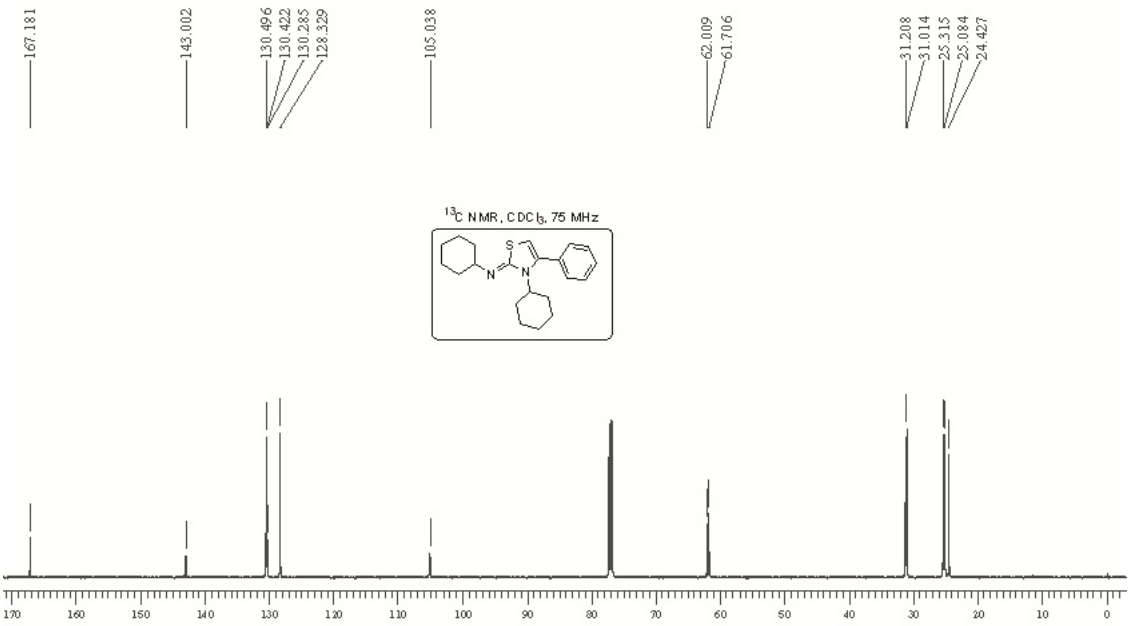
^{13}C NMR spectra of 4c



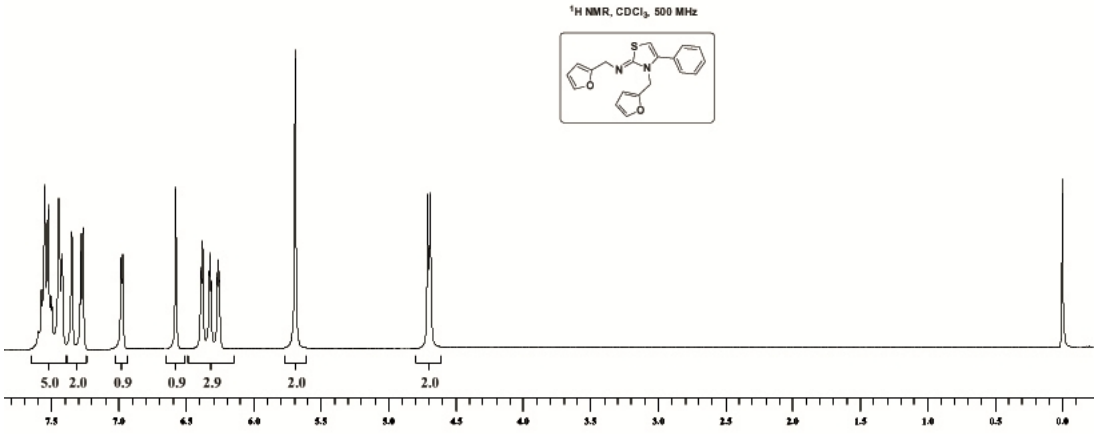
^{1}H NMR spectra of 4d



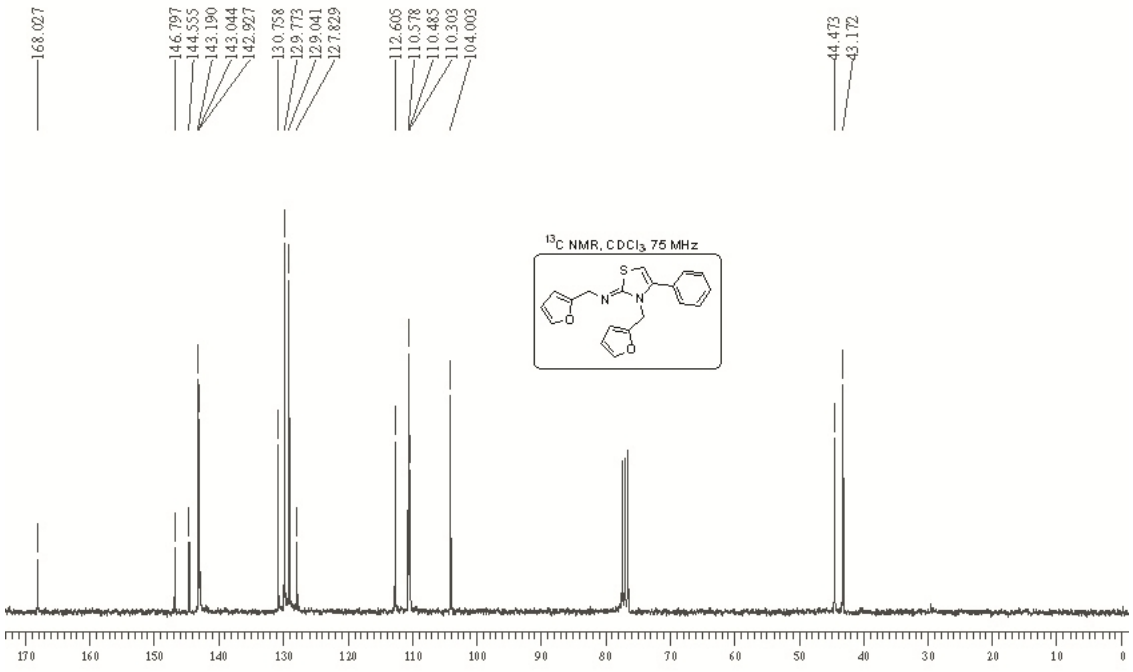
^{13}C NMR spectra of 4d



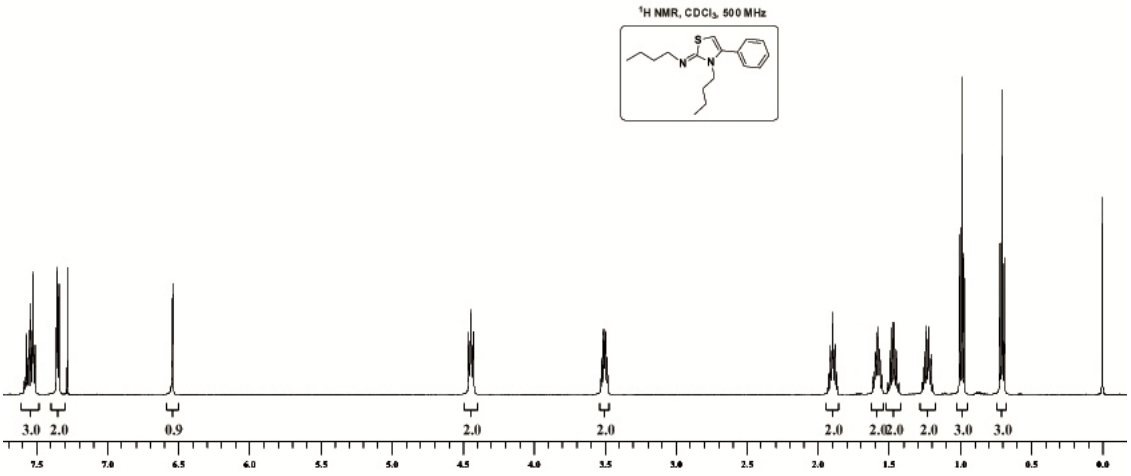
^{1}H NMR spectra of 4e



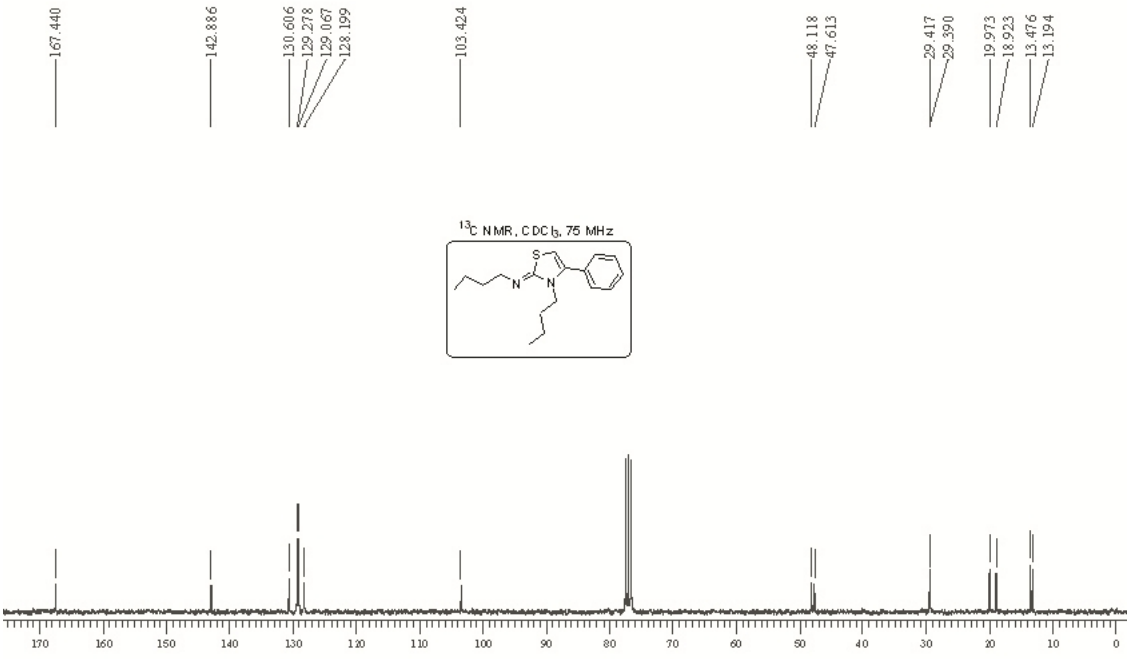
^{13}C NMR spectra of 4e



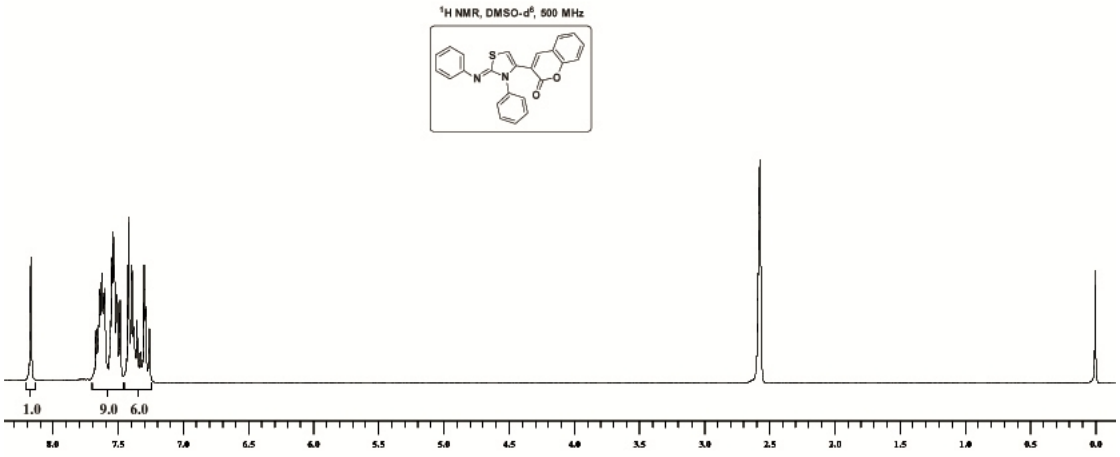
^{1}H NMR spectra of 4f



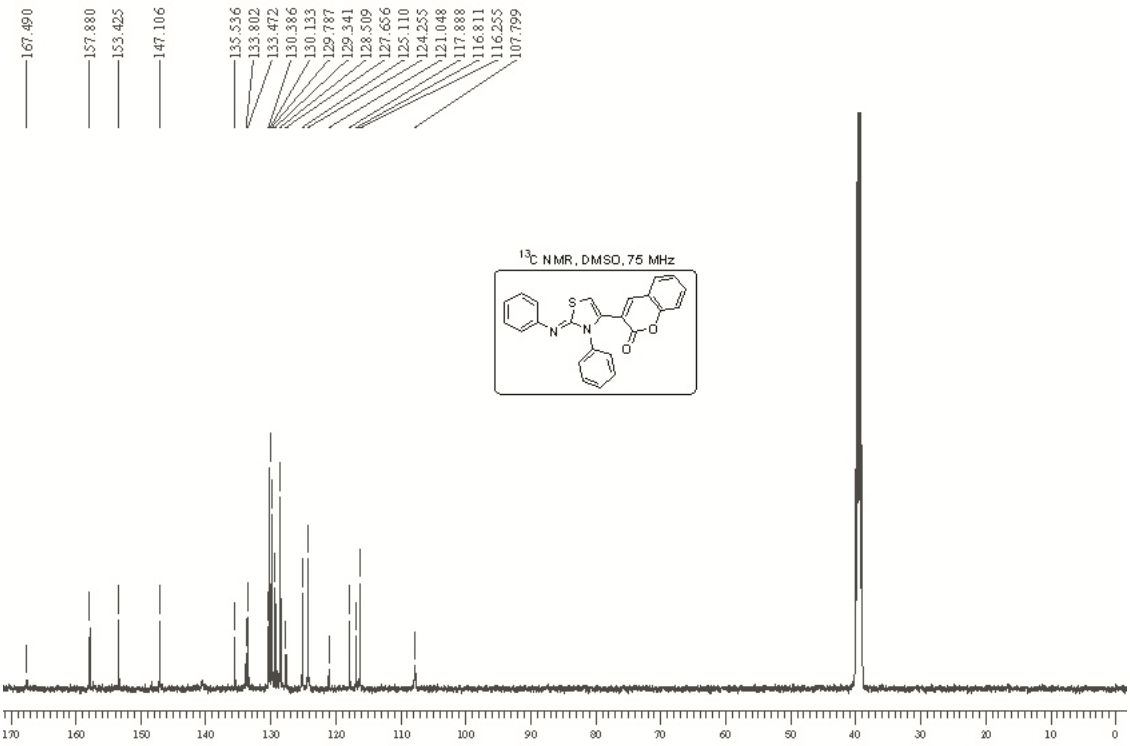
^{13}C NMR spectra of 4f



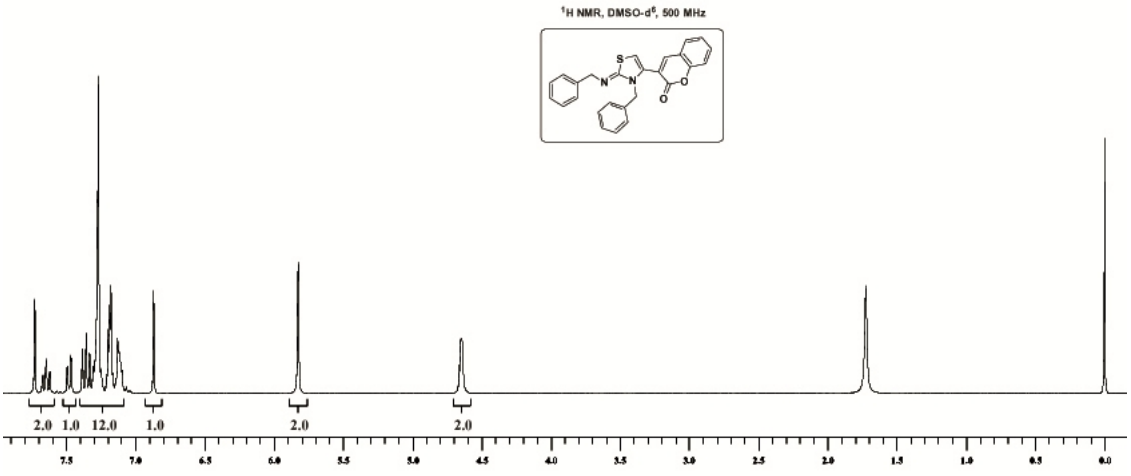
^{1}H NMR spectra of 4g



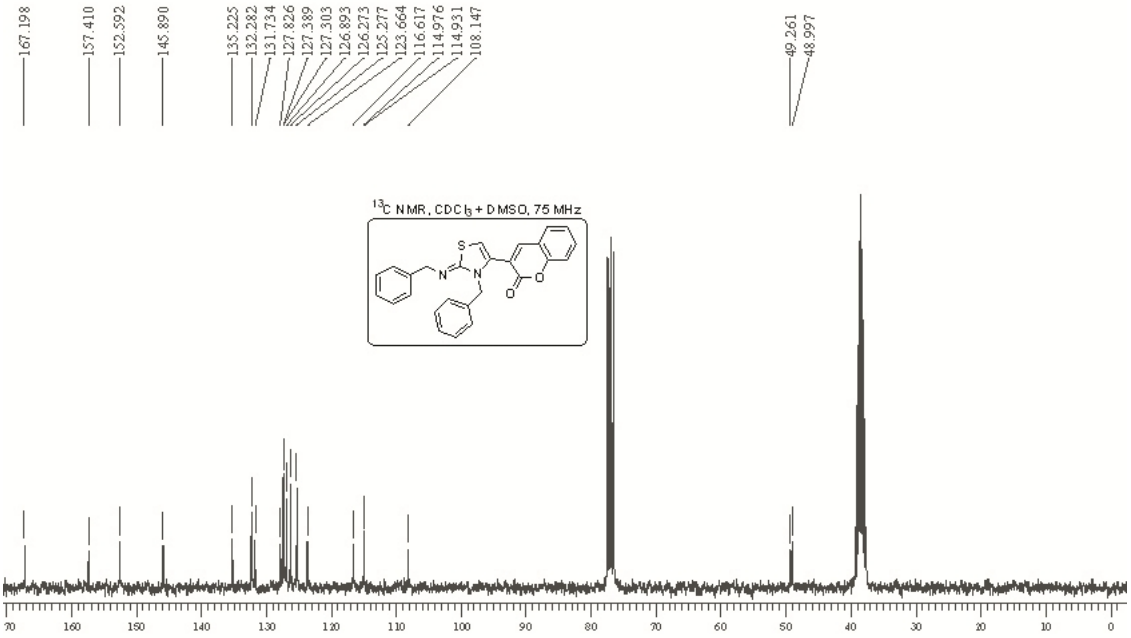
^{13}C NMR spectra of 4g



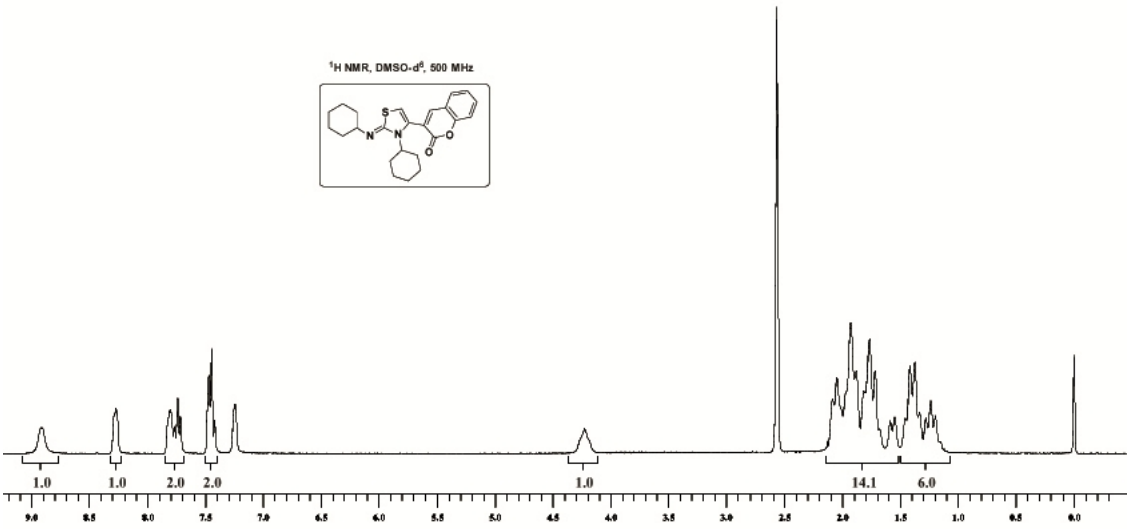
^{1}H NMR spectra of 4h



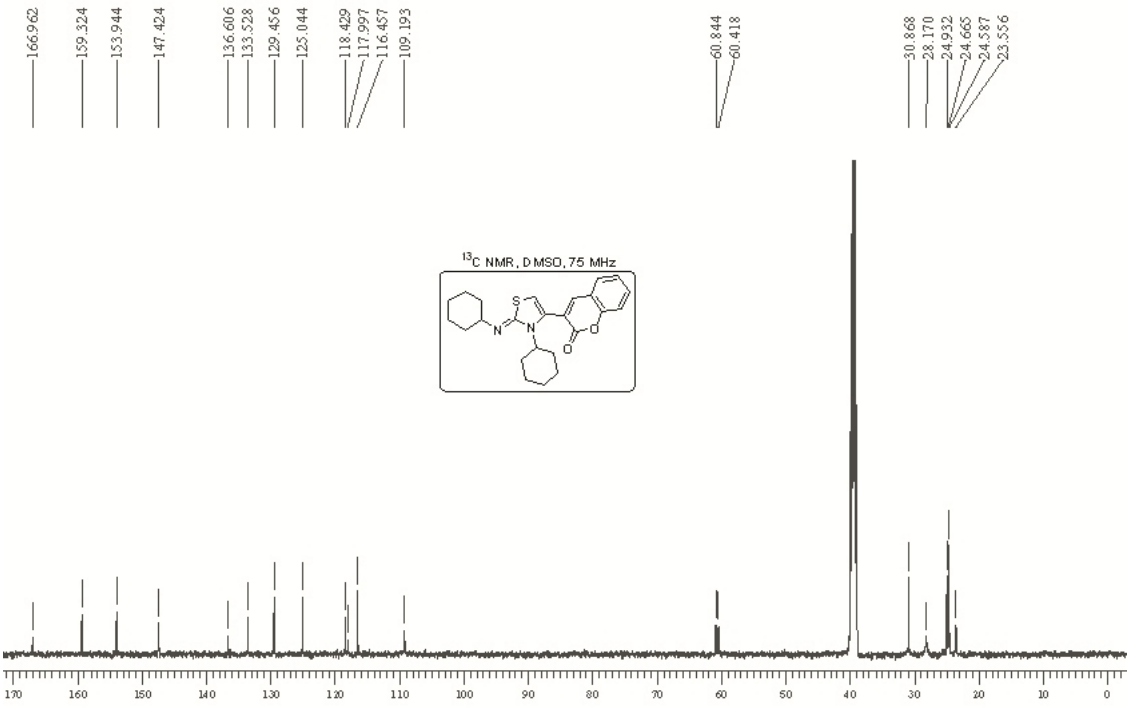
^{13}C NMR spectra of 4h



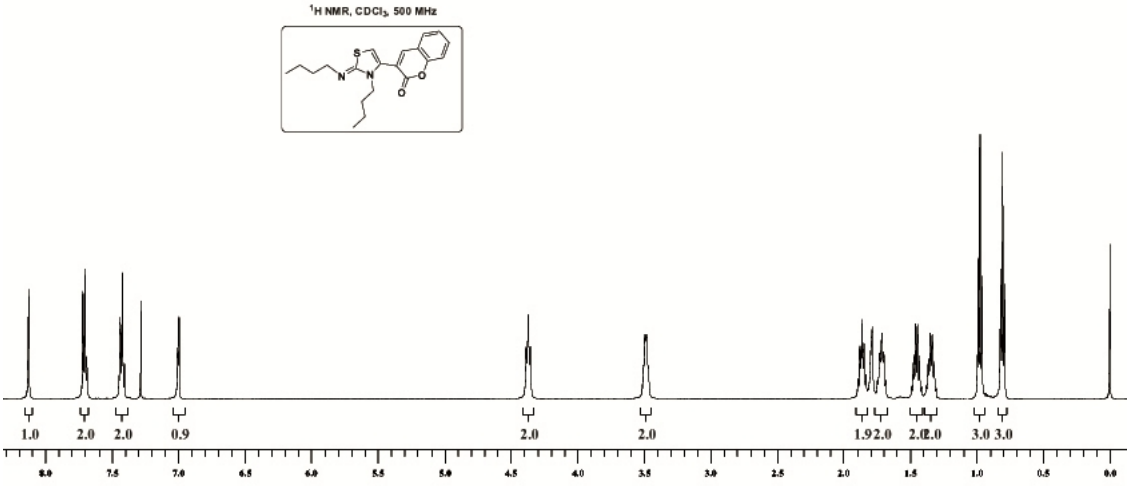
^{1}H NMR spectra of 4i



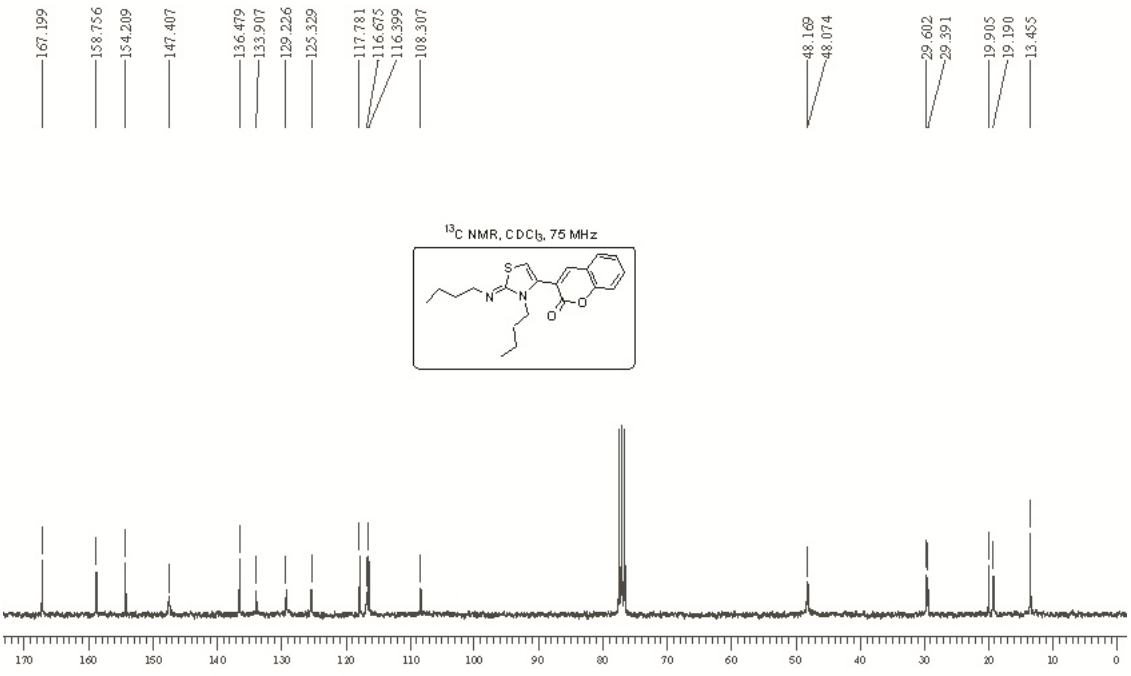
^{13}C NMR spectra of 4i



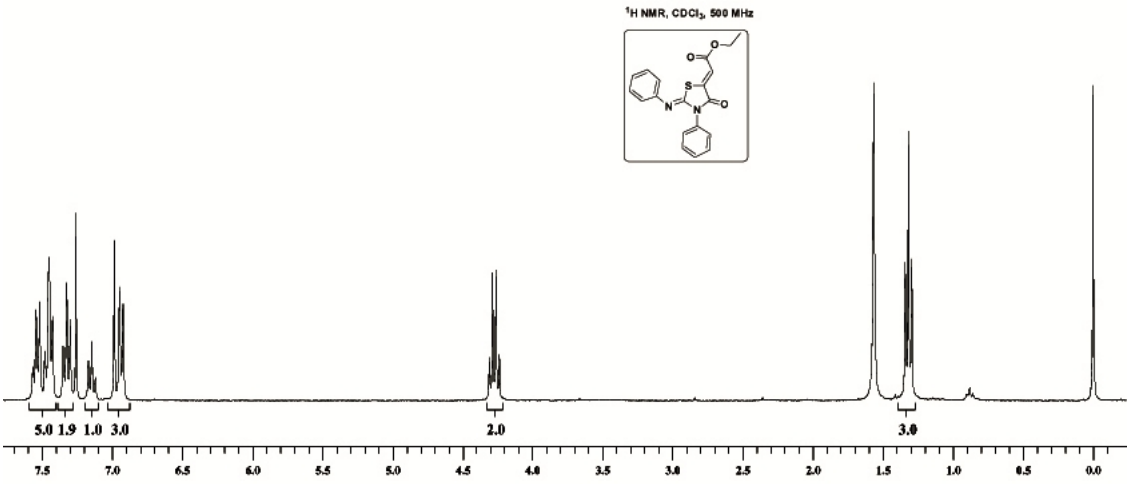
^{1}H NMR spectra of 4j



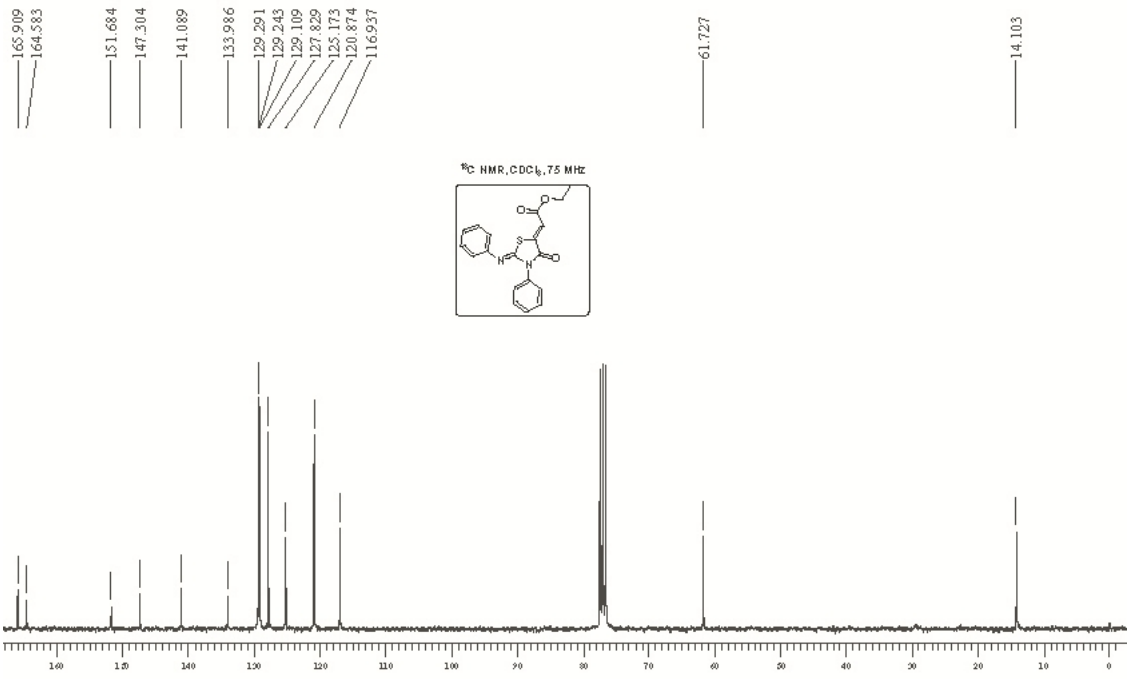
^{13}C NMR spectra of 4j



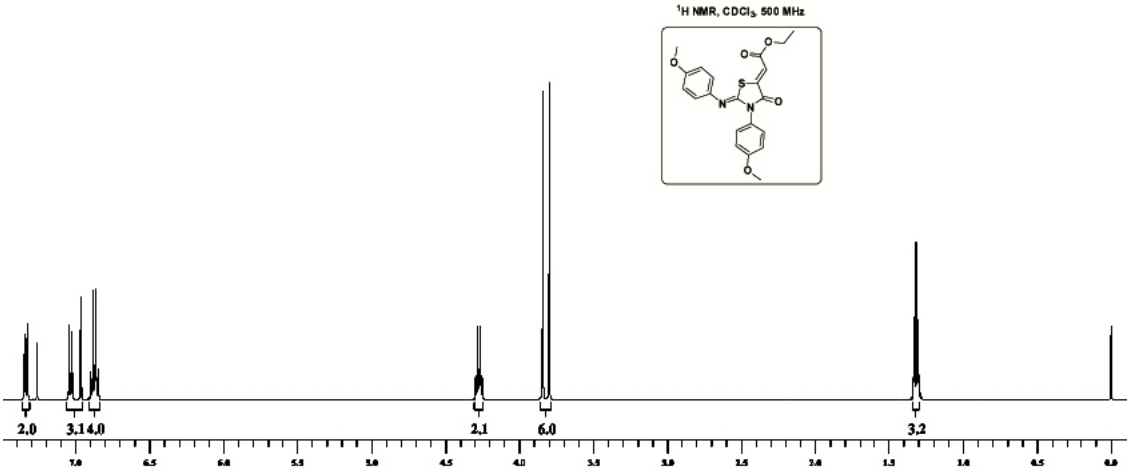
^{1}H NMR spectra of 6a



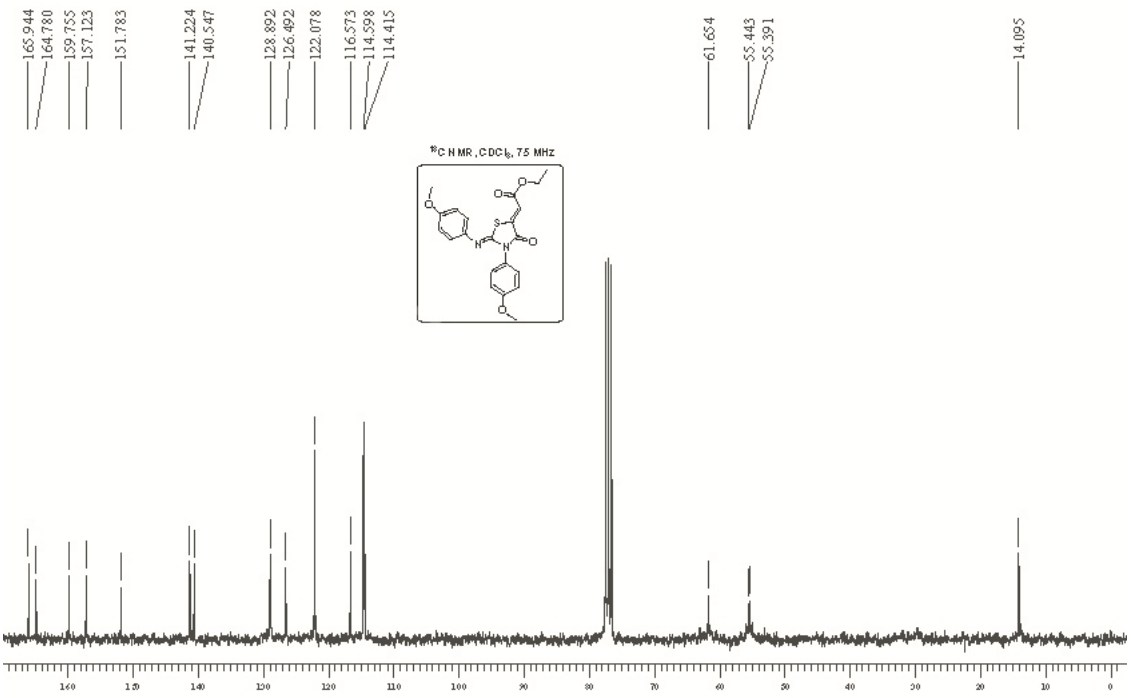
^{13}C NMR spectra of 6a



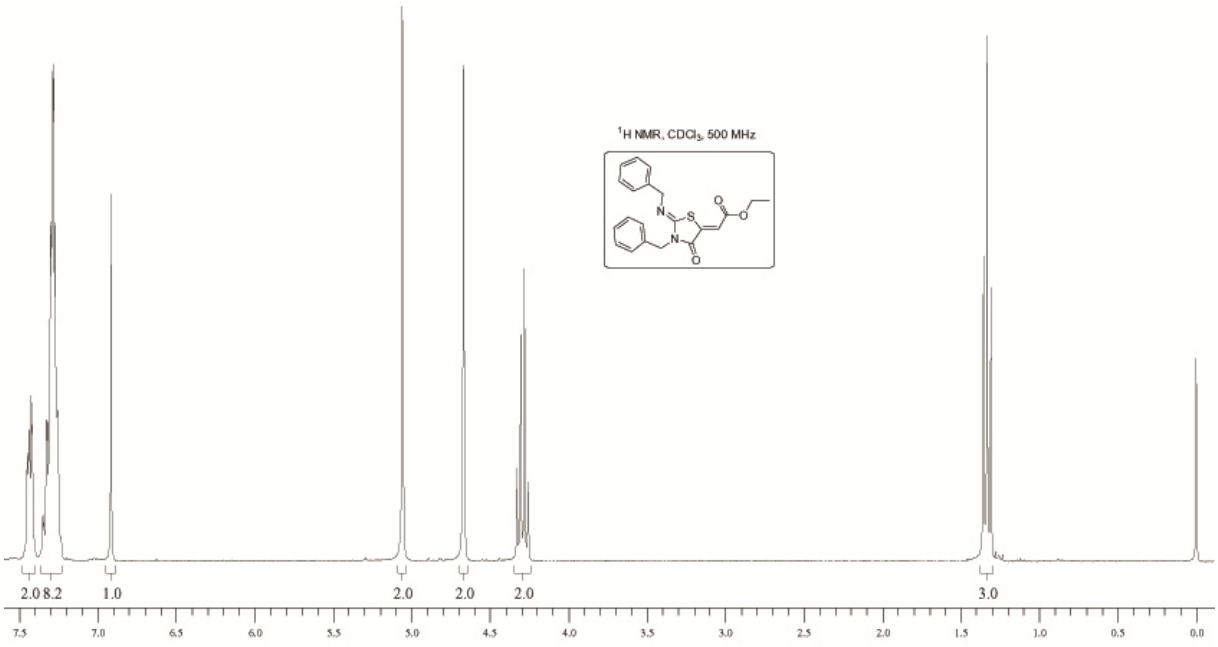
^{1}H NMR spectra of 6b



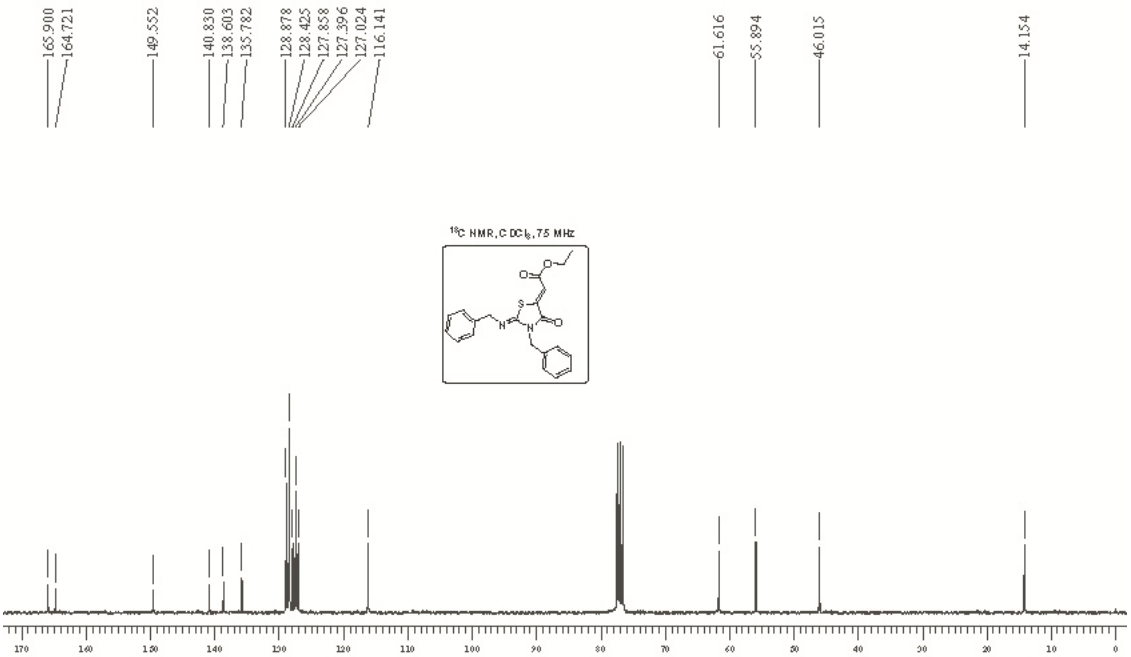
^{13}C NMR spectra of 6b



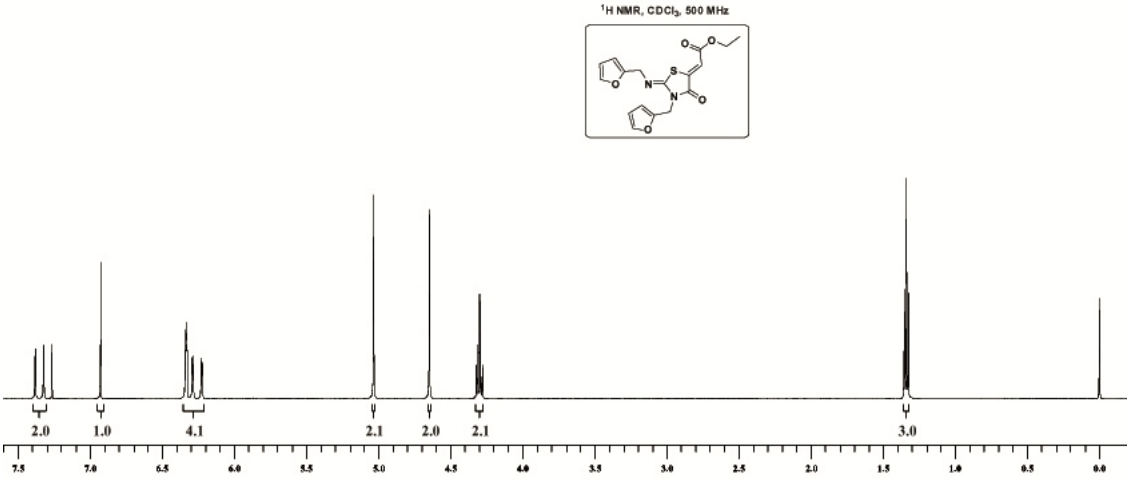
^{1}H NMR spectra of 6c



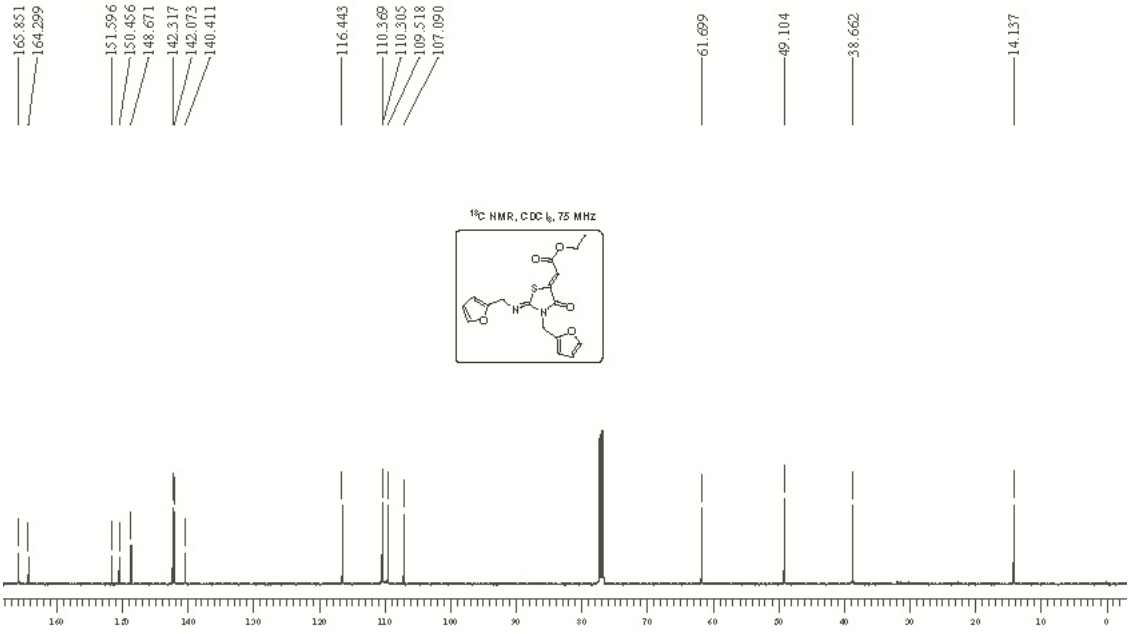
^{13}C NMR spectra of 6c



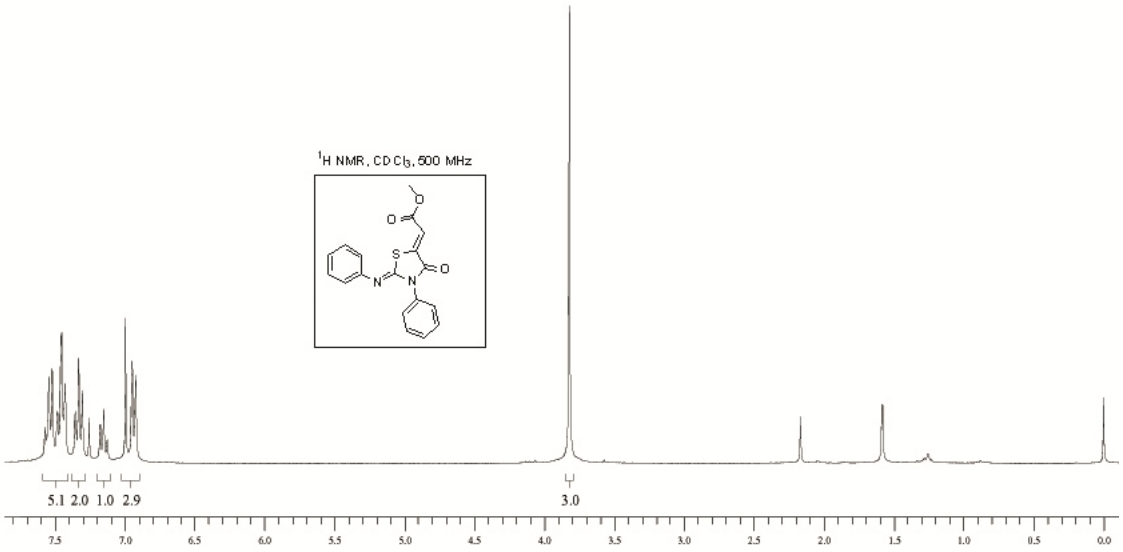
^{1}H NMR spectra of 6d



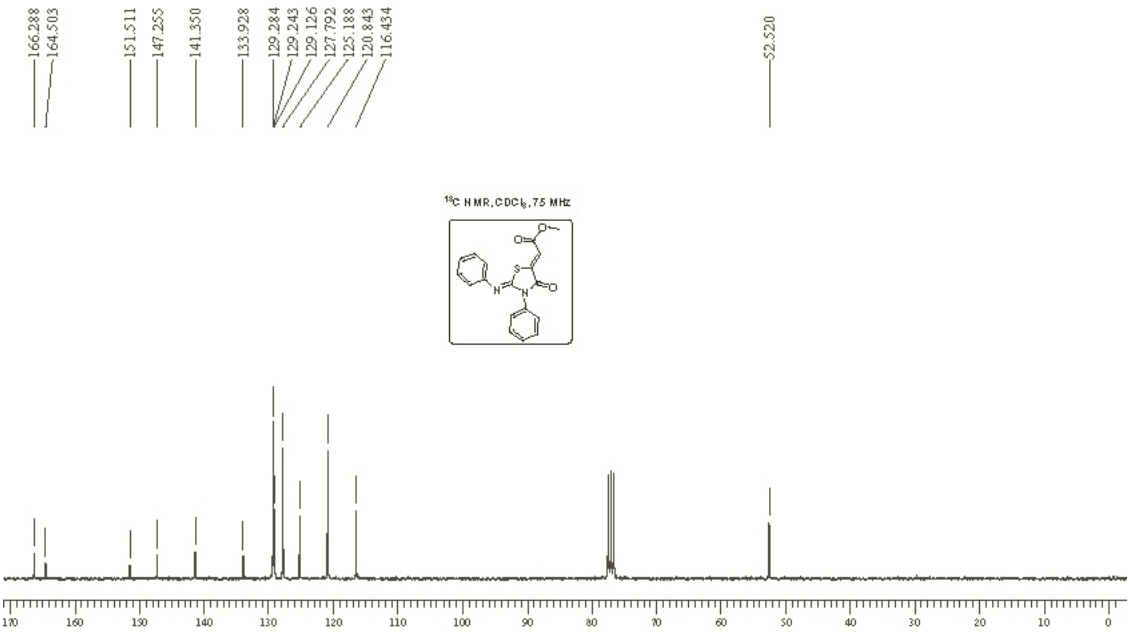
^{13}C NMR spectra of 6d



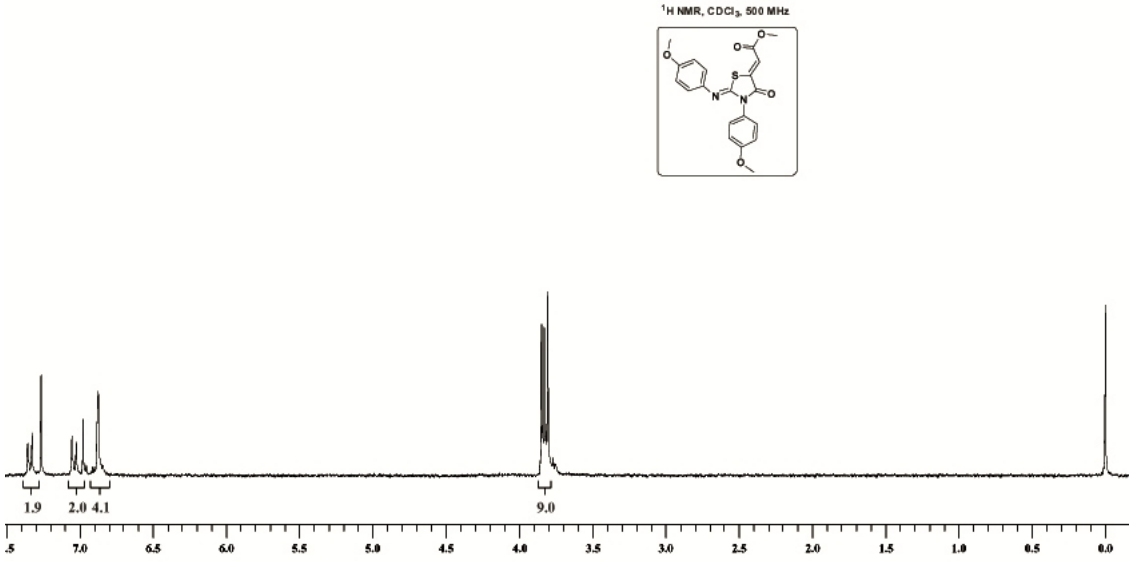
^{1}H NMR spectra of 6e



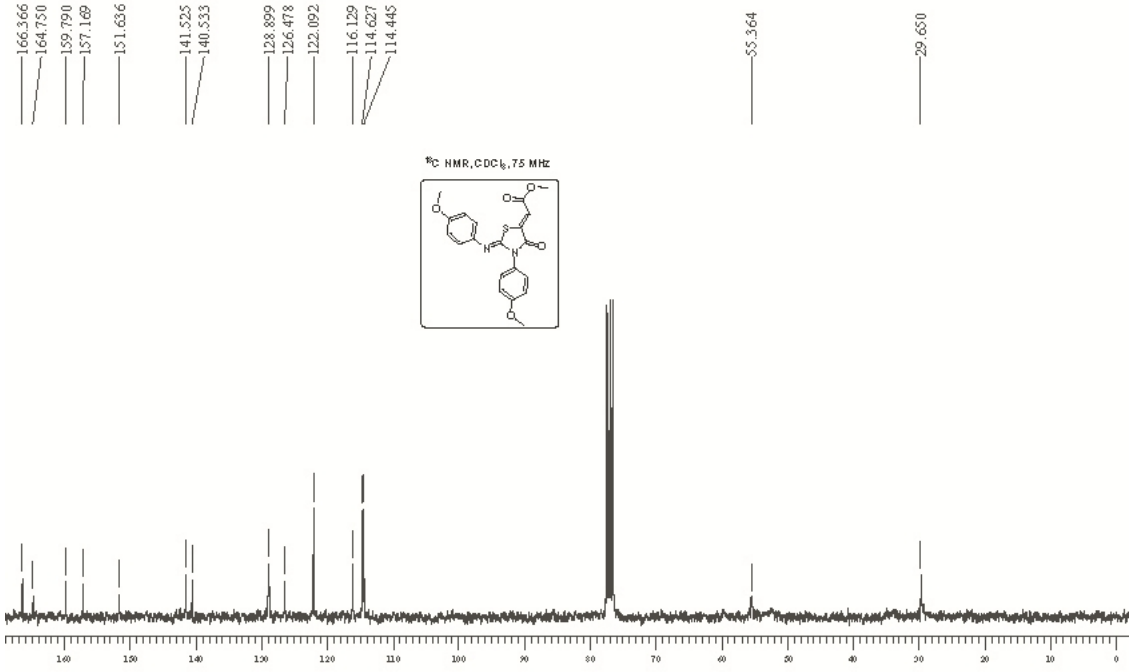
^{13}C NMR spectra of 6e



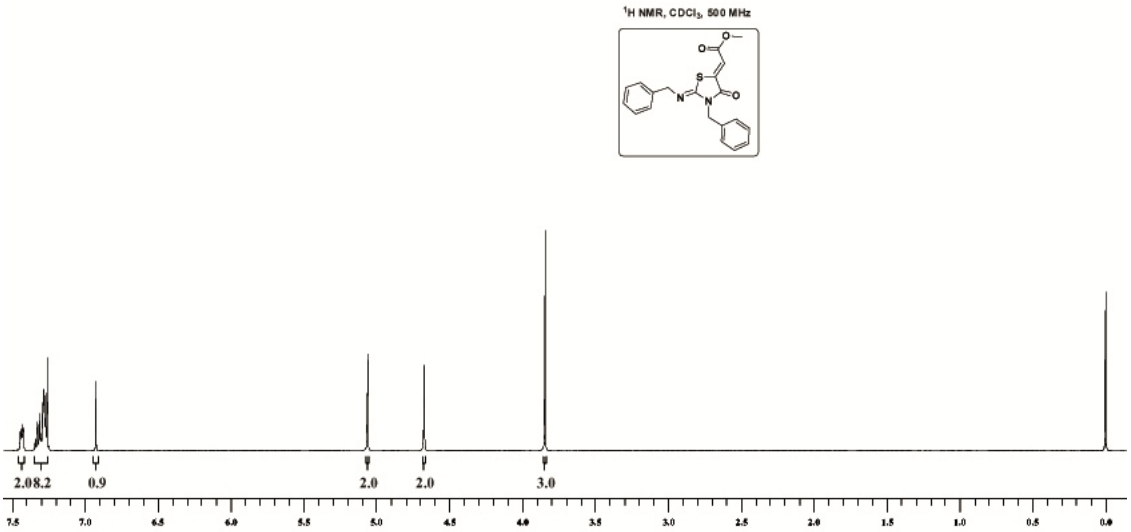
^{1}H NMR spectra of 6f



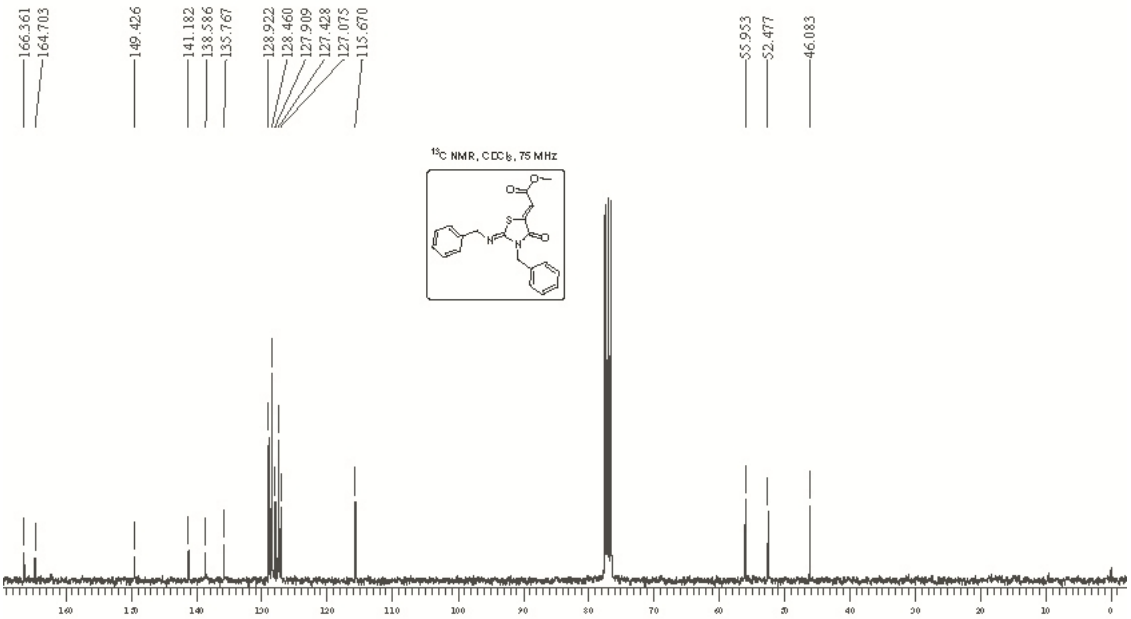
^{13}C NMR spectra of 6f



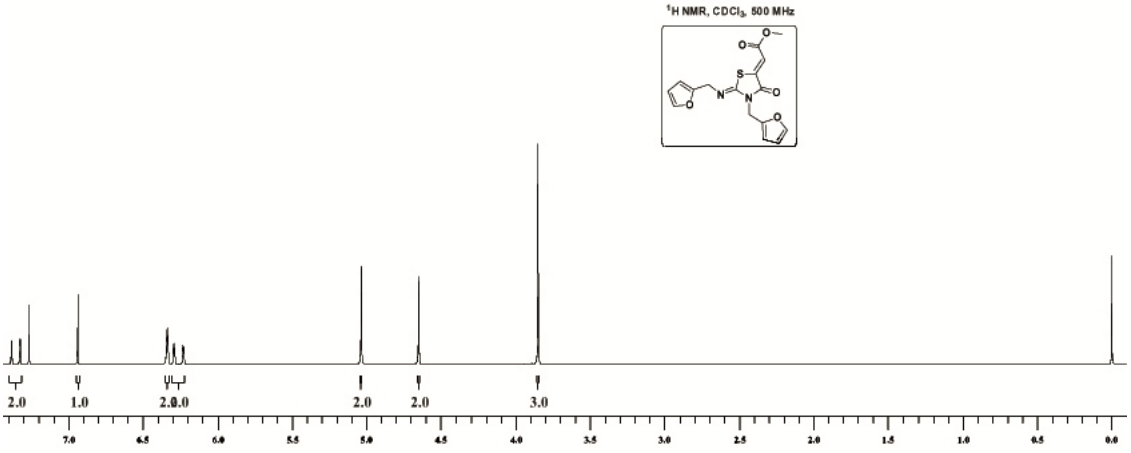
^{1}H NMR spectra of 6g



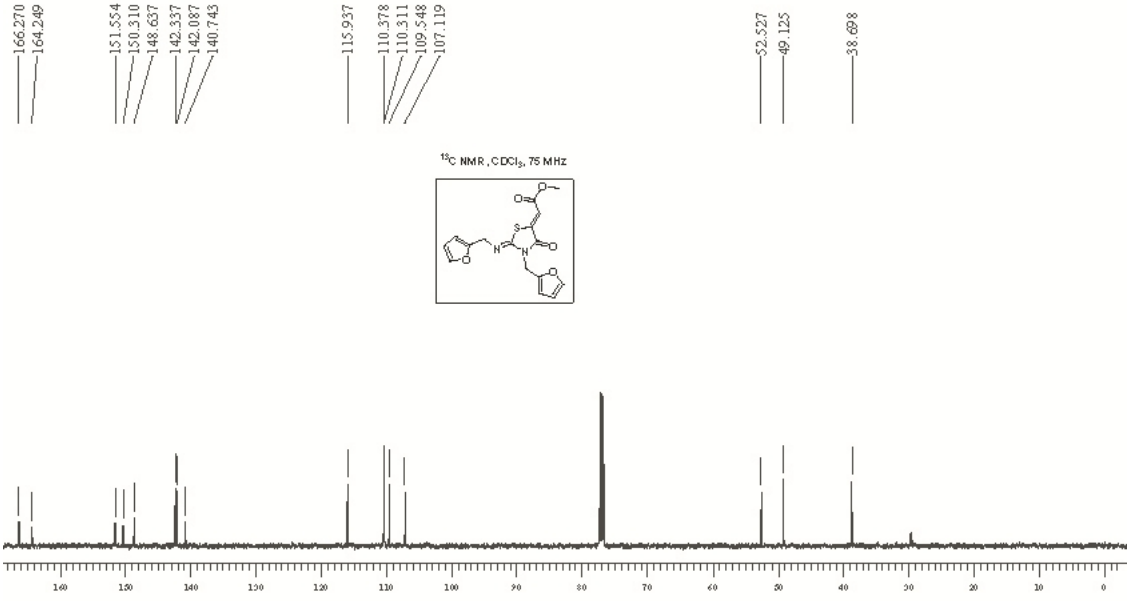
^{13}C NMR spectra of 6g



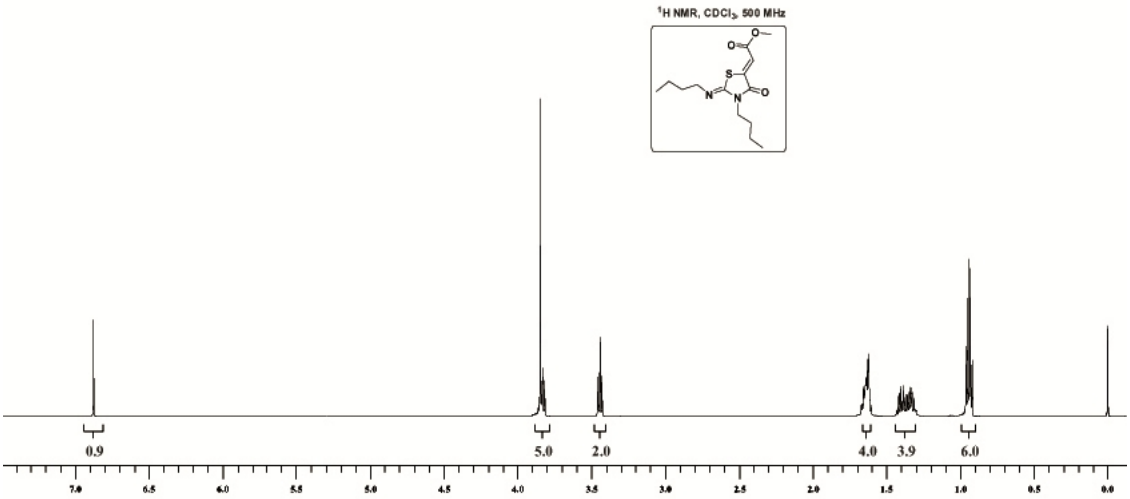
^{1}H NMR spectra of 6h



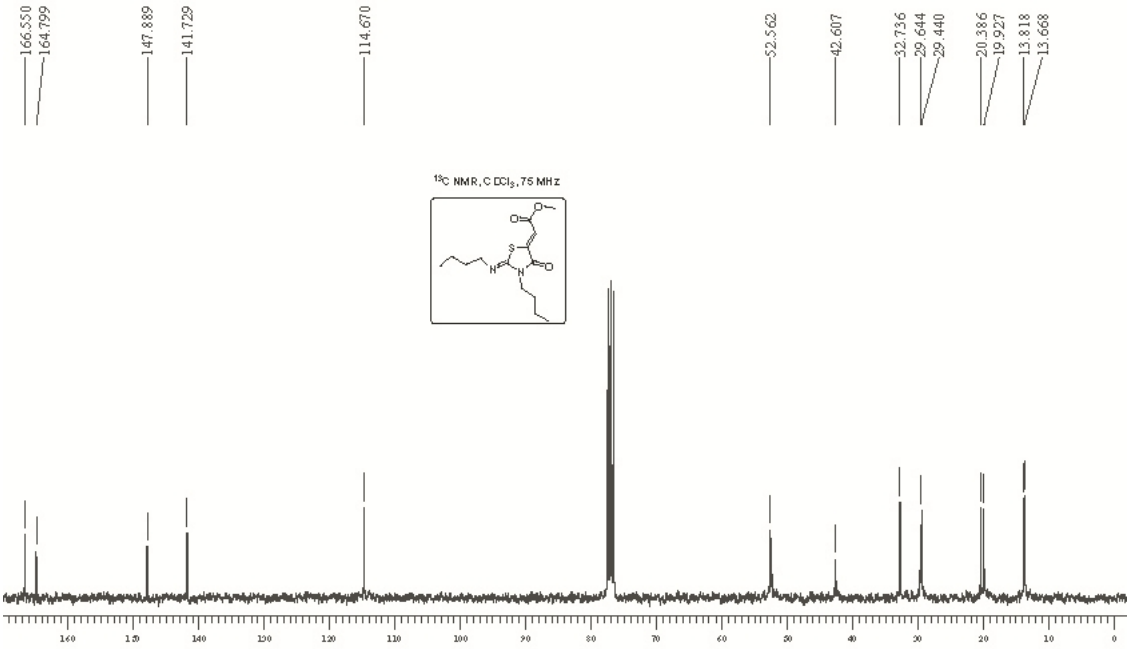
^{13}C NMR spectra of 6h



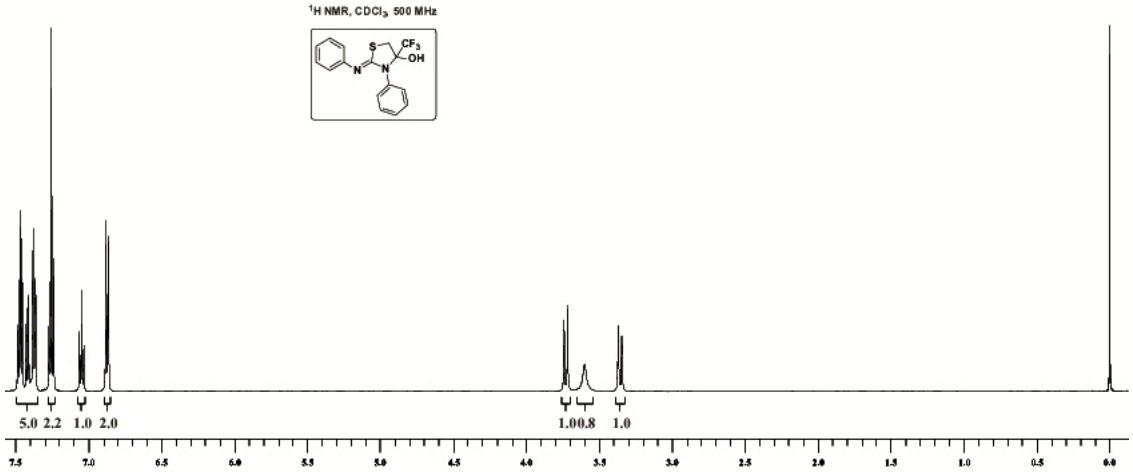
^{1}H NMR spectra of 6i



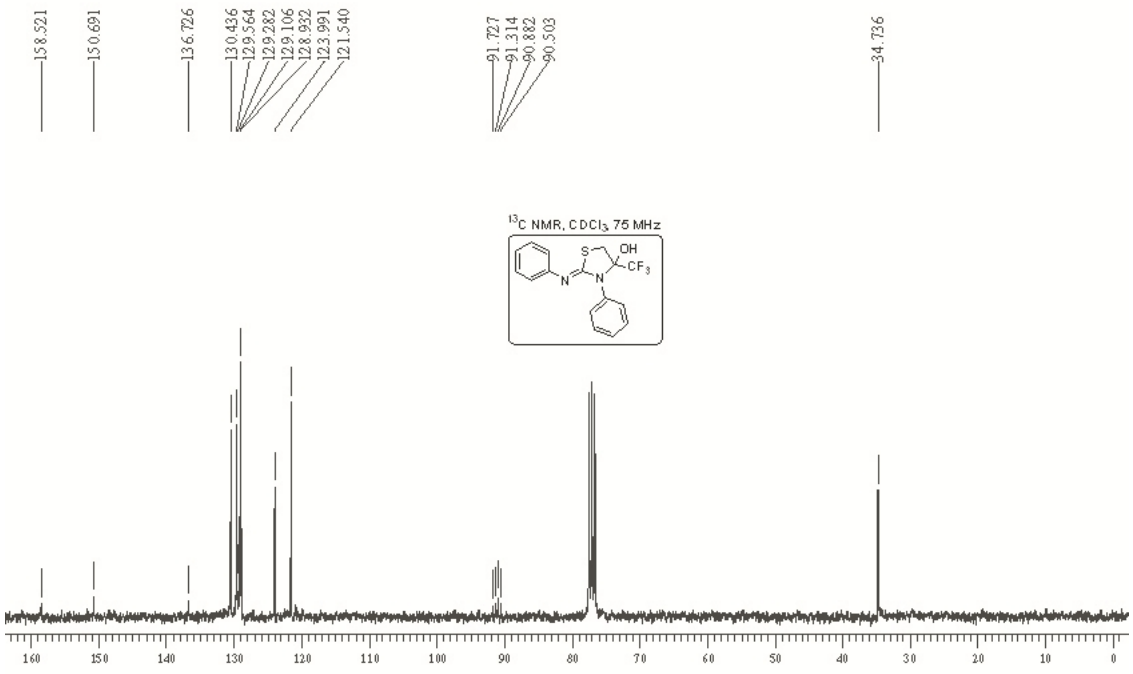
^{13}C NMR spectra of 6i



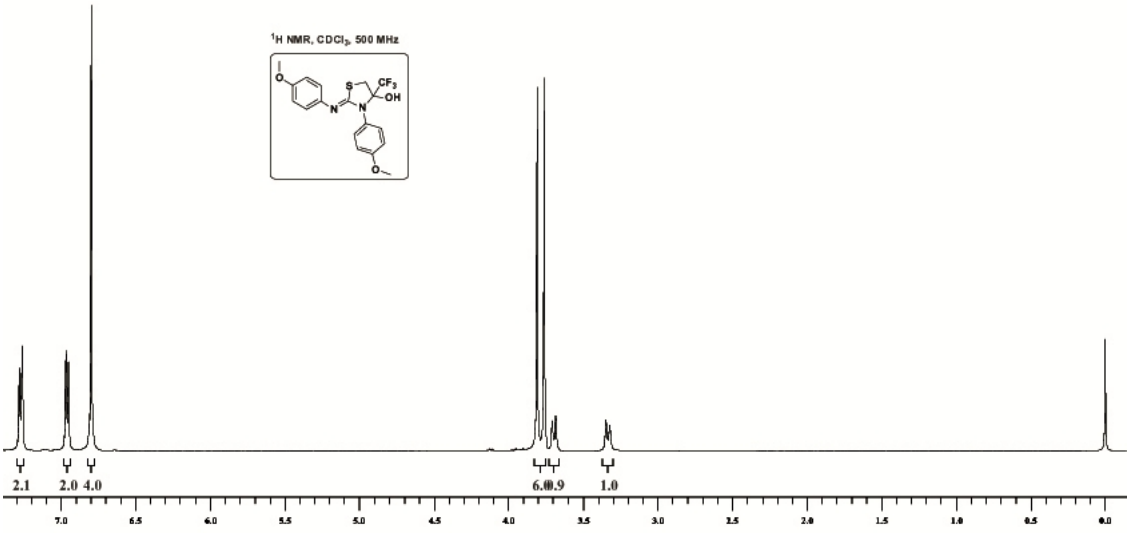
^{1}H NMR spectra of 8a



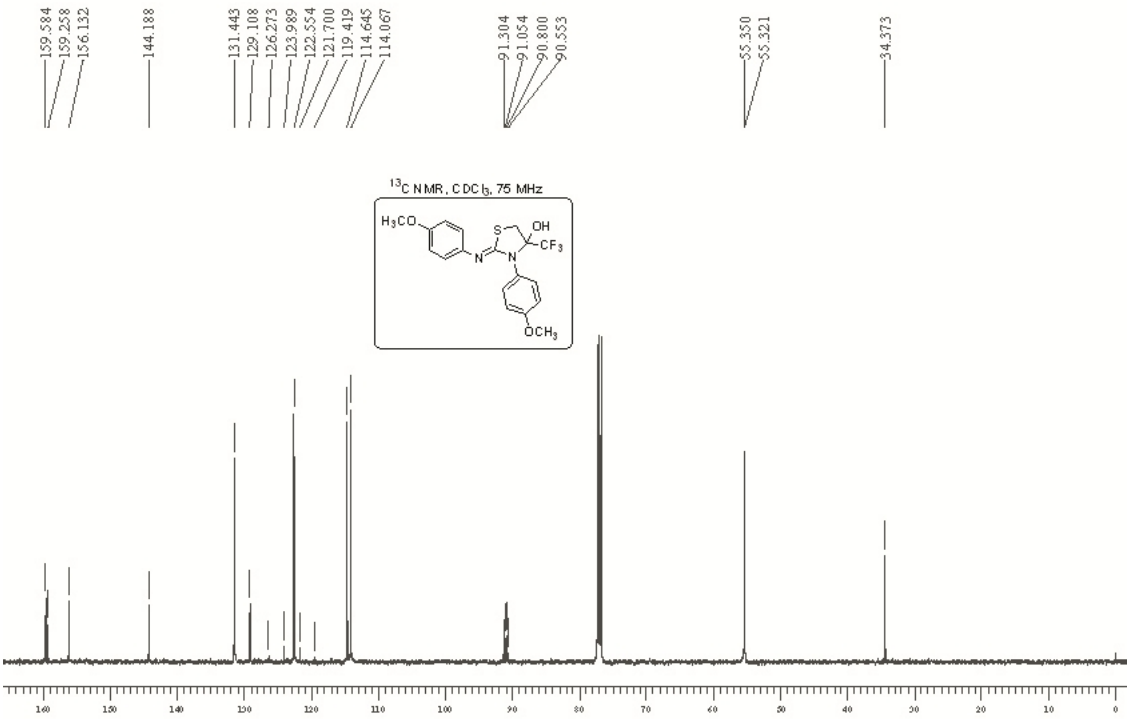
^{13}C NMR spectra of 8a



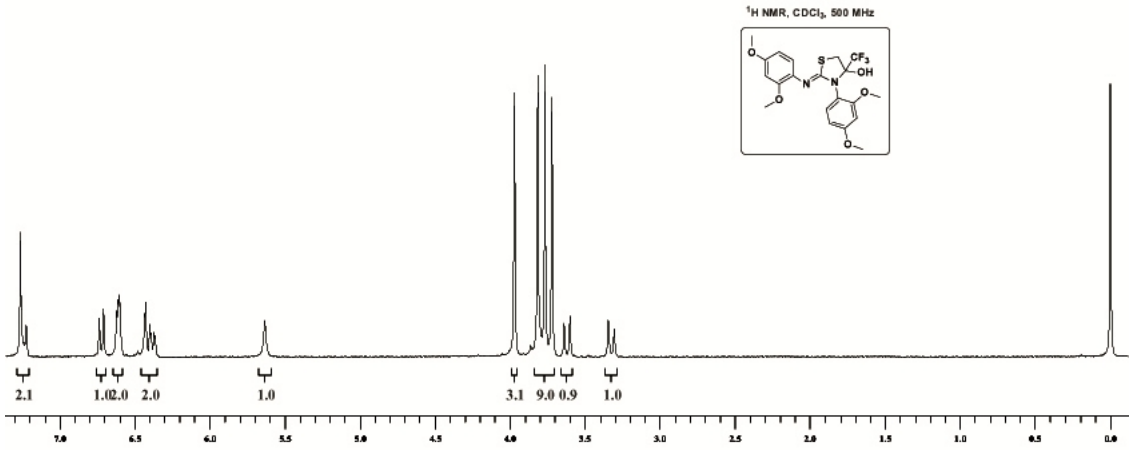
^{1}H NMR spectra of 8b



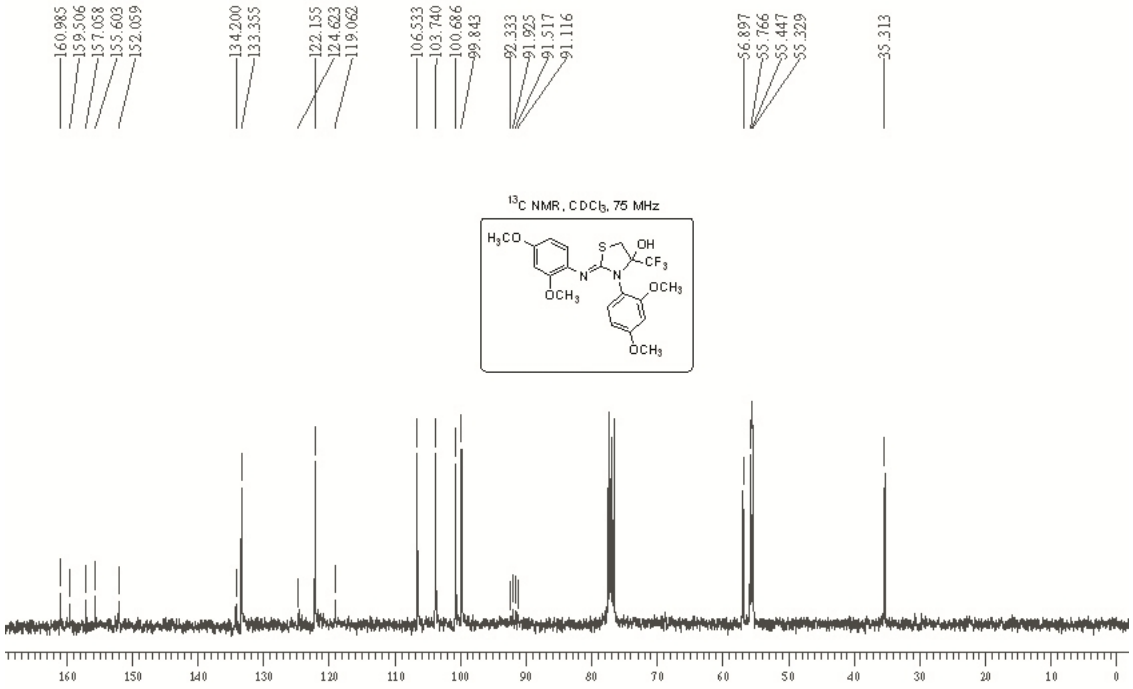
^{13}C NMR spectra of 8b



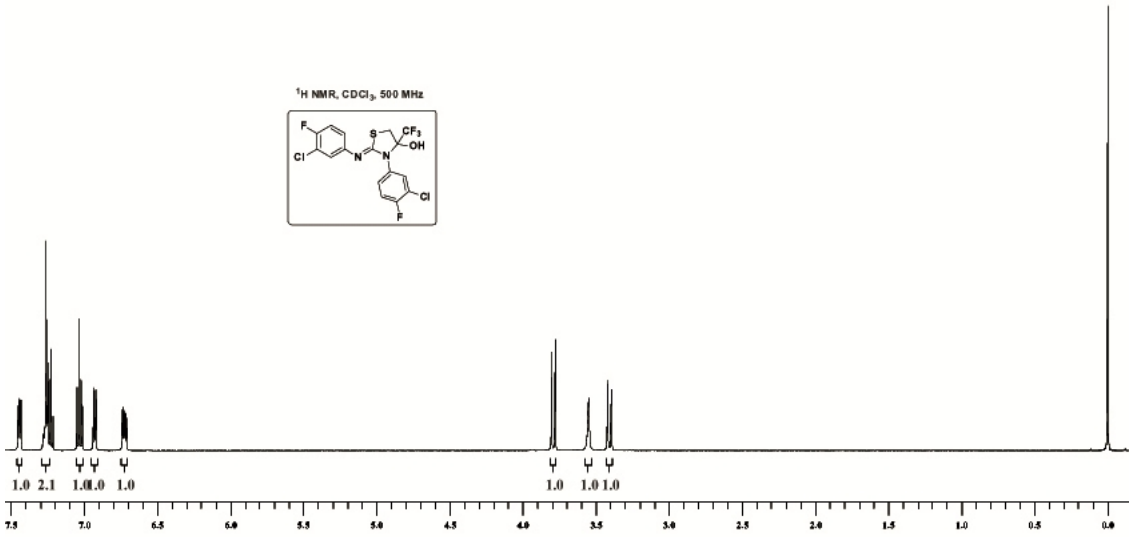
^{1}H NMR spectra of 8c



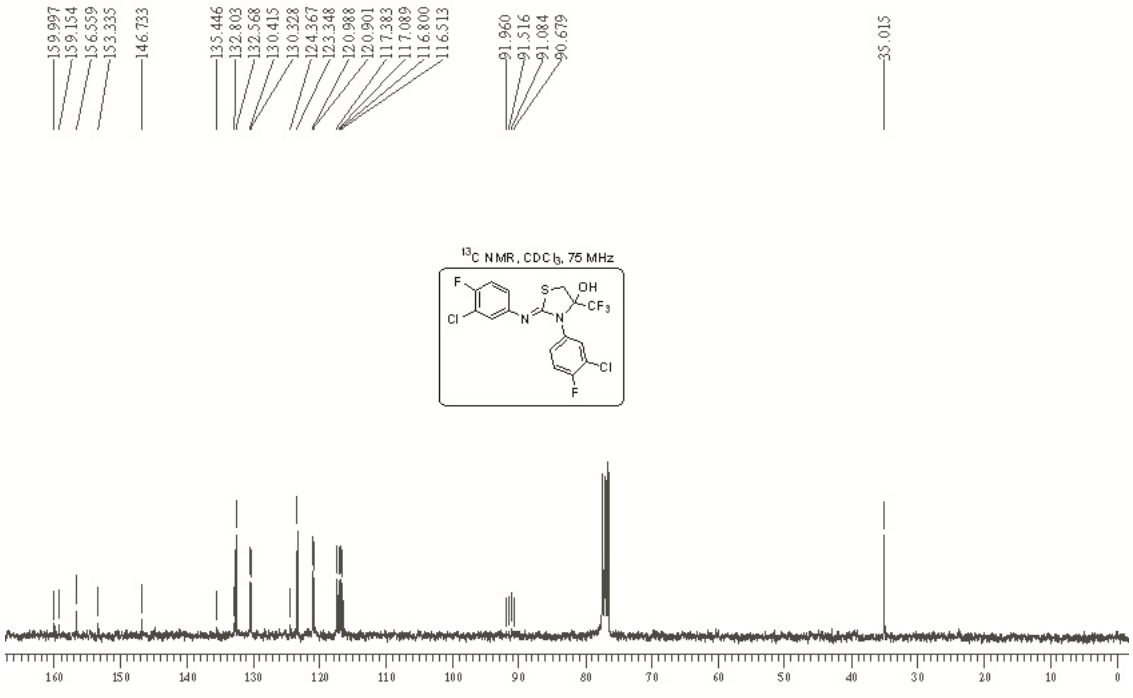
^{13}C NMR spectra of 8c



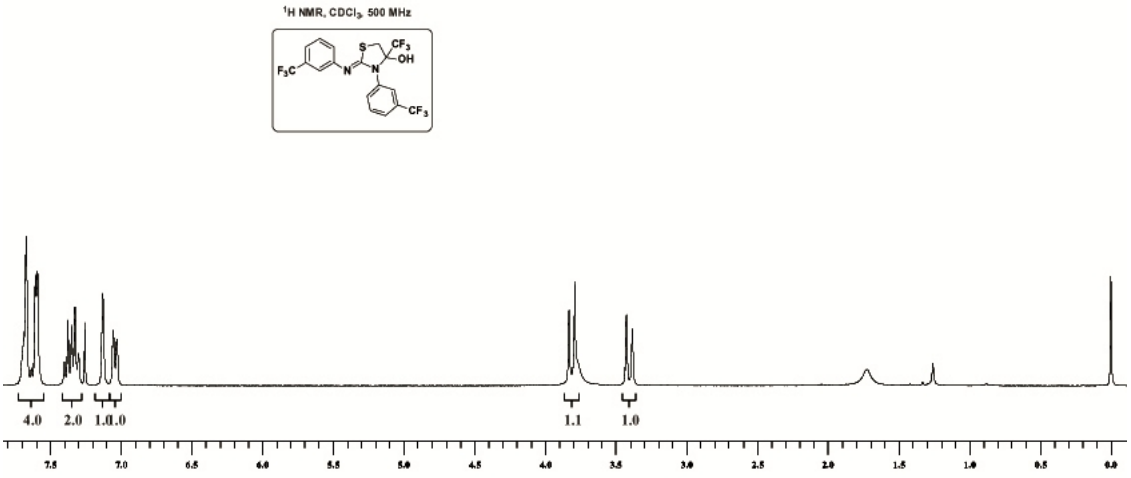
^{1}H NMR spectra of 8d



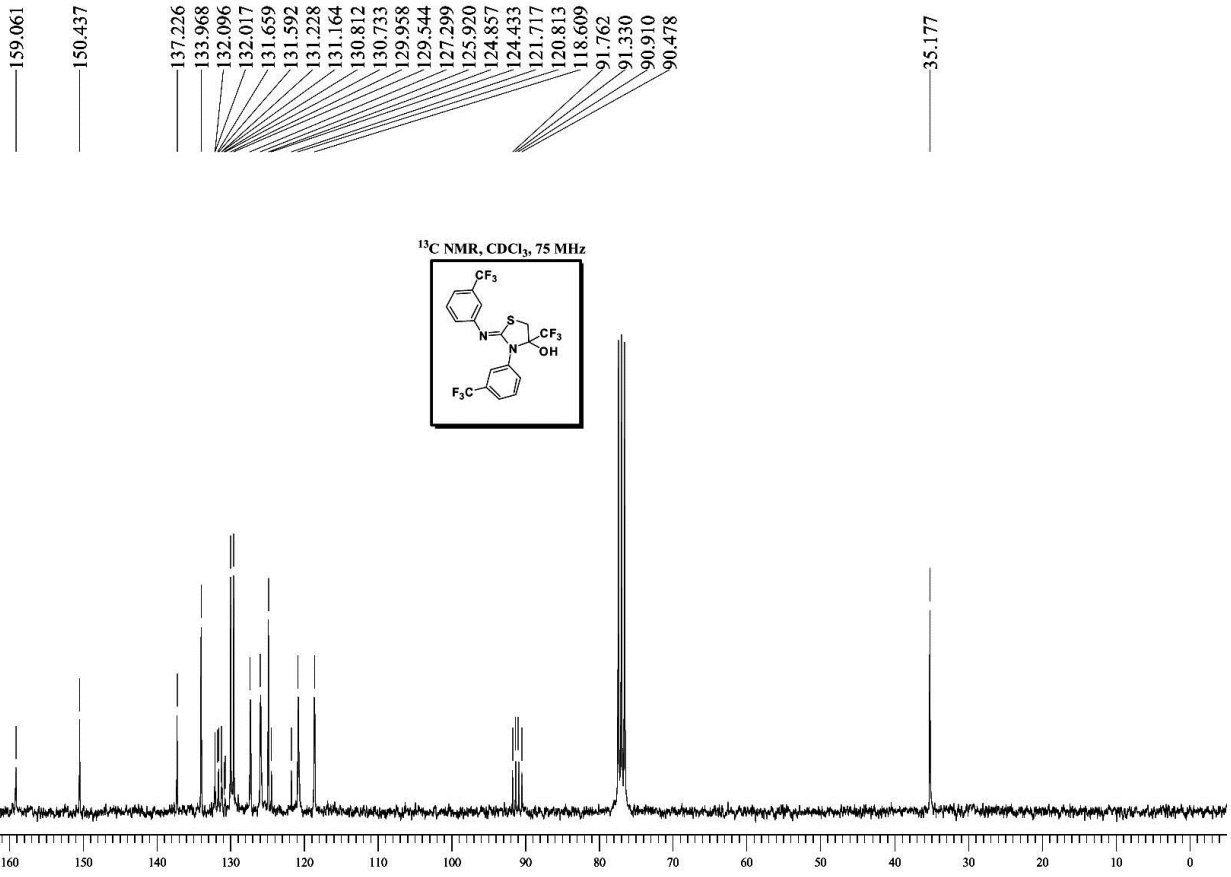
^{13}C NMR spectra of 8d



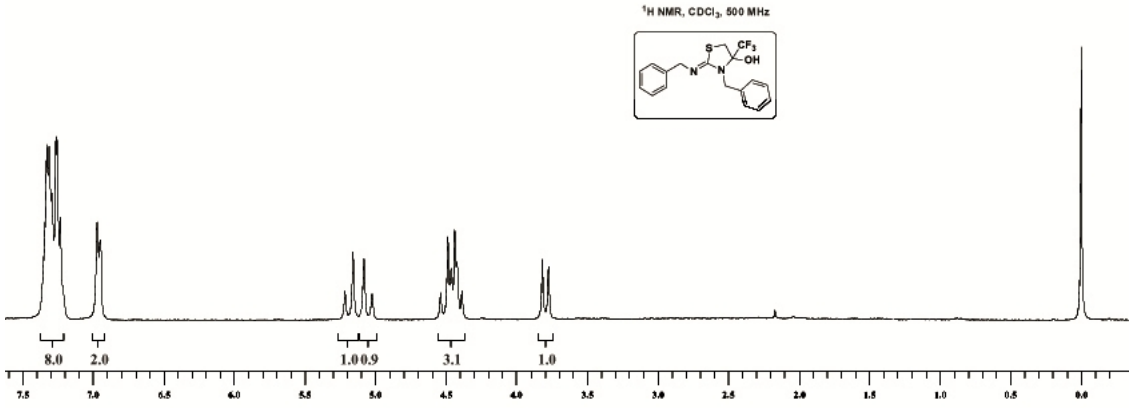
^{1}H NMR spectra of 8e



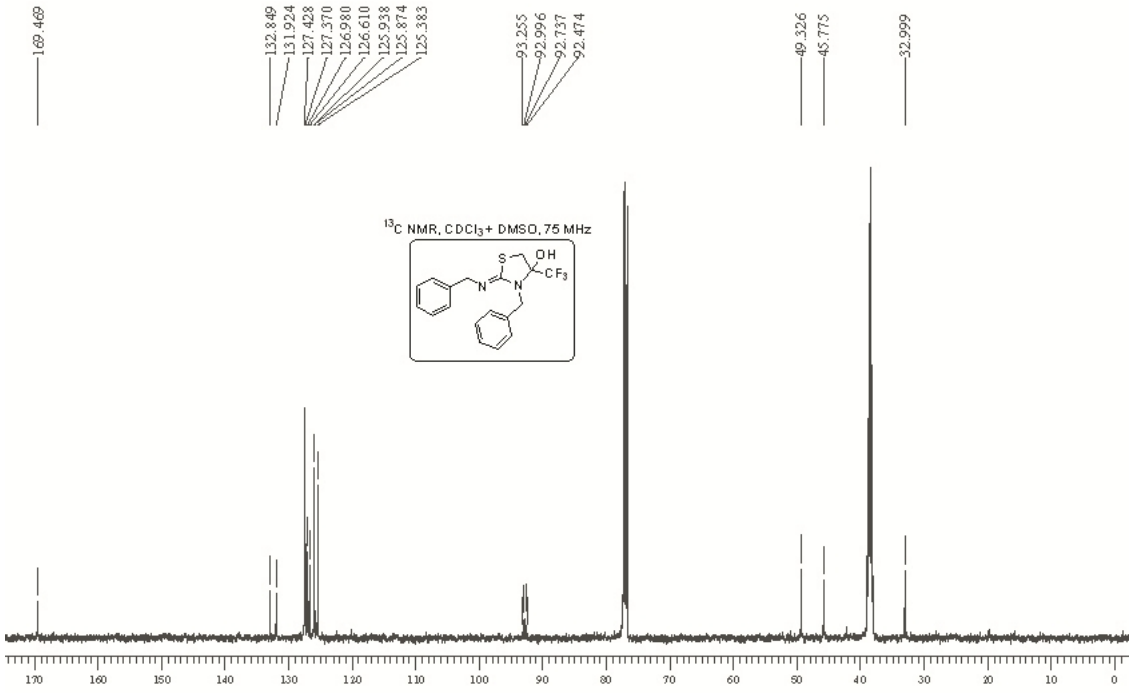
^{13}C NMR spectra of 8e



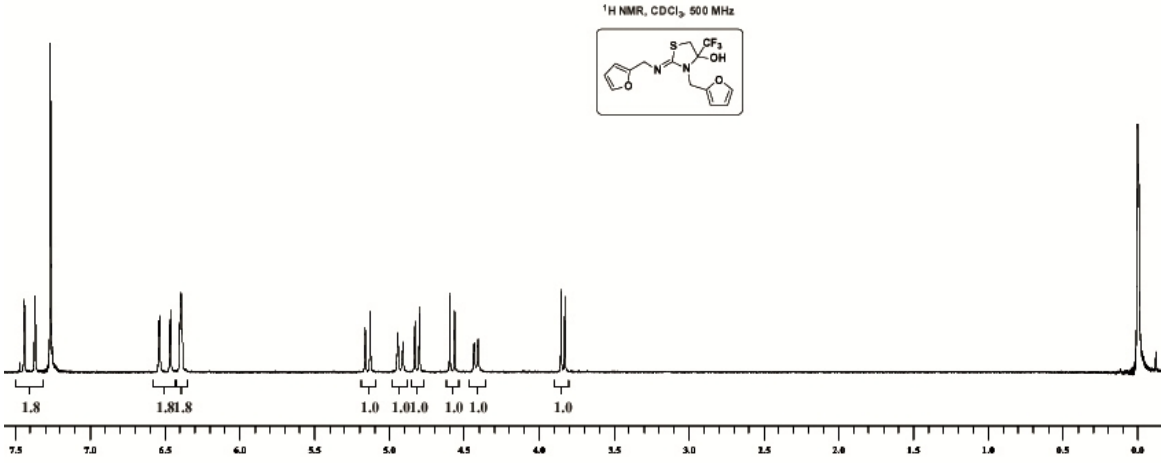
^{1}H NMR spectra of 8f



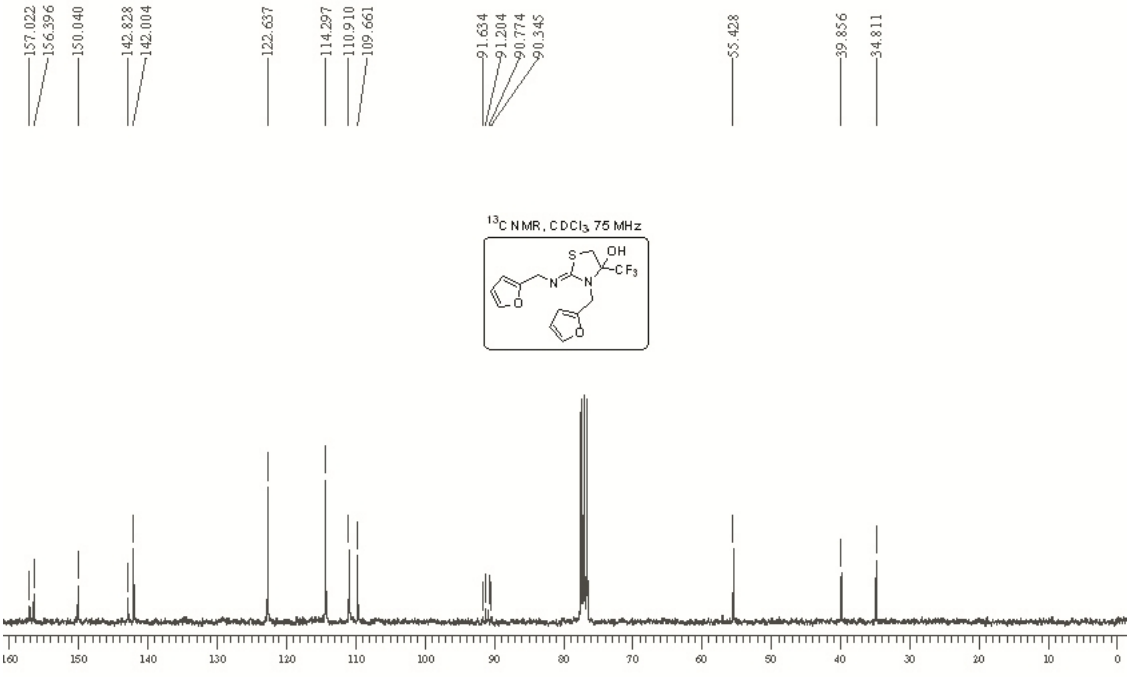
^{13}C NMR spectra of 8f



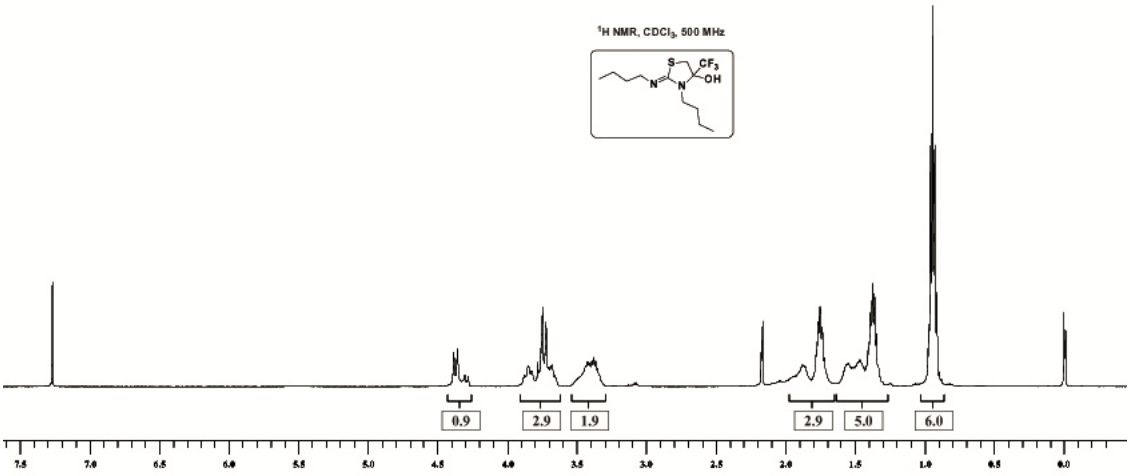
^{1}H NMR spectra of 8g



^{13}C NMR spectra of 8g



^{1}H NMR spectra of 8h



^{13}C NMR spectra of 8h