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Supporting Information

Synthesis of Spiro Oxazolidinedione Analogues Based on Tandem Multicyclizations of 1,3-Dimethylalloxan and Enaminones in Water

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Apparatus: Melting points were measured on a Büchi 535 apparatus and are uncorrected. Elemental analyses were performed using an elementar vario EL *III* instrument. FT-IR Spectra were recorded on a Bruker Equinox-55 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz, respectively, with $CDCl_3$ as solvent and calibrated using residual undeuterated solvent as an internal reference. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and visualized with UV light. All chemical reagents were obtained from Aldrich, Merck, Fluka or Acros and were used without further purification.

***Typical procedure for the synthesis of* 4** or **5**: A mixture of alkylamine **1** (1 mmol) and activated propyne **2** (1 mmol) in water (5 mL) were stirred at room temperature in a round-bottom flask for 3 h. Then, 1,3-dimethylalloxan (1 mmol) was added to the reaction mixture and the stirring was further continued up to 24 h at room temperature until the completion of the reaction as evidenced by TLC monitoring. After completion of the reaction, water was removed using a rotary evaporator. The residue was purified by column chromatography on silica gel with EtOAc/*n*-hexane (1:5) to afford the pure product **4** or **5** as a colorless solid.

Methyl (2*E*)-(3,7-dimethyl-2,4,6-trioxo-1-oxa-3,7-diazaspiro[4.4]non-8-ylidene)acetate (4a):

Colorless powder (0.196 g, 73%); m.p. 200-202 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.55; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3090 (=C-H), 1836, 1745, 1743 and 1699 (C=O), 1638 (C=C);^{1}H NMR ($CDCl_3$, 300.1 MHz):δ_H 3.13 (3 H, s, NCH_3), 3.16 (3 H, s, NCH_3), 3.73 (3 H, s, OCH_3), 3.55 and 3.90 (2 H, d of AB-system, $^{2}J_{HH}$ 19.3 Hz,$^{4}J_{HH}$ 1.8 Hz, CH_2), 5.43 (1 H, t, $^{4}J_{HH}$ 1.8 Hz, =CH); ^{13}C

NMR ($CDCl_3$, 75.5 MHz): δ_C 169.5, 166.8, 166.5, 153.9, 152.4, 95.4, 82.4, 51.5, 33.5, 28.3, 26.8; Anal. Calcd. for $C_{11}H_{12}N_2O_6$ (268.23): C 49.26, H 4.51, N 10.44%; Found: C 49.47, H 4.57, N 10.37%.

Ethyl (2*E*)-(3,7-dimethyl-2,4,6-trioxo-1-oxa-3,7-diazaspiro[4.4]non-8-ylidene)acetate (4b):

Colorless powder (0.195 g, 69%), m.p. 140-142 °C (dec.); R_f (25% EtOAc/*n*-hexane) 0.56; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3098 (=C-H), 1828, 1748, 1747 and 1698 (C=O), 1651 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.29 (3 H, t, $^3J_{HH}$ 7.1 Hz, $OCH_2\mathit{CH_3}$), 3.13 (3 H, s, NCH_3), 3.16 (3 H, s, NCH_3), 3.55 and 3.90 (2 H, d of AB-system, $^2J_{HH}$ 19.2 Hz, $^4J_{HH}$ 1.7 Hz, CH_2), 4.19 (2 H, q, $^3J_{HH}$ 7.1 Hz, $O\mathit{CH_2}CH_3$), 5.43 (1 H, t, $^4J_{HH}$ 1.7 Hz, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 169.5, 166.8, 166.1, 153.9, 152.1, 95.9, 82.5, 60.3, 33.5, 28.2, 26.8, 14.3; Anal. Calcd. for $C_{12}H_{14}N_2O_6$ (282.25): C 51.07, H 5.00, N 9.93%; Found: C 50.78, H 5.04, N 10.02%.

Methyl (2*E*)-(7-ethyl-3-methyl-2,4,6-trioxo-1-oxa-3,7-diazaspiro[4.4]non-8-ylidene)acetate (4c):

Colorless powder (0.217 g, 77%), m.p. 139-141 °C (dec.); R_f (25% EtOAc/*n*-hexane) 0.55; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1835, 1738 and 1708 (C=O), 1629 (C=C),^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.23 (3 H, t, $^3J_{HH}$ 7.2 Hz, $OCH_2\mathit{CH_3}$), 3.16 (3 H, s, NCH_3), 3.66 (2 H, ABX_3-system, $N\mathit{CH_2}CH_3$), 3.73 (3 H, s, OCH_3), 3.53 and 3.90 (2 H, d of AB-system, $^2J_{HH}$ 19.3 Hz, $^4J_{HH}$ 1.8 Hz, CH_2), 5.46 (1 H, t, $^4J_{HH}$ 1.8 Hz, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 169.5, 166.6, 153.9, 151.3, 95.0, 82.4, 51.4, 36.9, 33.7, 26.7, 11.6; Anal. Calcd. for $C_{12}H_{14}N_2O_6$ (282.25): C 51.07, H 5.00, N 9.93%; Found: C 50.79, H 4.94, N 9.88%.

Ethyl (2*E*)-(7-ethyl-3-methyl-2,4,6-trioxo-1-oxa-3,7-diazaspiro[4.4]non-8-ylidene)acetate (4d):

Colorless powder (0.222 g, 75%), m.p. 91-93 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.58; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3107 (=C-H), 1831, 1750, 1705 and 1691 (C=O), 1650 (C=C), ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.24 (3 H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2\mathit{CH_3}$), 1.29 (3 H, t, $^3J_{HH}$ 7.3 Hz, $OCH_2\mathit{CH_3}$), 3.17 (3 H, s, NCH_3), 3.59 and 3.86 (2 H, d of AB-system, $^2J_{HH}$ 19.2 Hz, $^4J_{HH}$ 1.8 Hz, CH_2), 3.62-3.71 (2 H, ABX_3-system, $N\mathit{CH_2}CH_3$), 4.18 (2 H, q, $^3J_{HH}$ 7.3 Hz, $O\mathit{CH_2}CH_3$), 5.45 (1 H, t, $^4J_{HH}$ 1.8 Hz, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 169.5, 166.6, 166.2, 153.9, 151.0, 95.4, 82.5, 60.3, 36.9, 33.6, 26.7, 14.3, 11.6; Anal. Calcd. for $C_{13}H_{16}N_2O_6$ (296.28): C 52.70, H 5.44, N 9.46%; Found: C 53.02, H 5.40, N 9.55%.

(8*E*)-3,7-Dimethyl-8-(2-oxopropylidene)-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4e):

Colorless powder (0.197 g, 78%), m.p. 133-135 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.65; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3071 (=C-H), 1853, 1735, 1703 and 1675 (C=O), 1598 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 2.26 (3 H, s, O=C-CH_3), 3.14 (3 H, s, NCH_3), 3.15 (3 H, s, NCH_3), 3.55 and 3.90 (2 H, d of AB-system, $^2J_{HH}$ 19.5 Hz, $^4J_{HH}$ 1.3 Hz, CH_2), 5.84 (1 H, t, $^4J_{HH}$ 1.3 Hz, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 196.6, 169.5, 167.1, 153.6, 151.7, 102.7, 82.4, 34.3, 31.7, 28.3, 26.8; Anal. Calcd. for $C_{11}H_{12}N_2O_5$ (252.22): C 52.38, H 4.80, N 11.11%; Found: C 52.51, H 4.68, N 11.02%.

(8*E*)-7-Ethyl-3-methyl-8-(2-oxopropylidene)-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4f):

Colorless powder (0.184 g, 69%), m.p. 137-139 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.61; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1834, 1747, 1734 and 1677 (C=O), 1591 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.27 (3 H, t, $^3J_{HH}$ 7.2 Hz, $NCH_2\mathit{CH_3}$), 2.29 (3 H, s, O=C-CH_3), 3.18 (3 H, s, NCH_3), 3.67-3.71 (2 H, ABX_3-system, $N\mathit{CH_2}CH_3$),, 3.57 and 3.92 (2 H, d of AB-system, $^2J_{HH}$ 19.5 Hz, $^4J_{HH}$ 1.3 Hz, CH_2), 5.89 (1 H, t, $^4J_{HH}$ 1.3 Hz, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 196.7, 169.5, 167.1, 153.9, 150.7, 102.3, 82.4, 36.9, 34.5, 31.8, 26.7, 11.7; Anal. Calcd. for $C_{12}H_{14}N_2O_5$ (266.25): C 54.13, H 5.30, N 10.52%; Found: C 53.85, H 5.25, N 10.54%.

(8*E*)-3-Methyl-8-(2-oxopropylidene)-7-propyl-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4g):

Colorless powder (0.179 g, 64%), m.p. 138-140 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.60; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3061 (=C-H), 1832, 1754, 1739 and 1678 (C=O), 1592 (C=C); ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ_H 0.82 (3 H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2\mathit{CH_3}$), 1.55 (2 H, m, $NCH_2\mathit{CH_2}CH_3$), 2.19 (3 H, s, O=C-CH_3), 2.95 (3 H, s, NCH_3), 3.57 (2 H, m, $N\mathit{CH_2}CH_2CH_3$), 3.42 and 3.82 (2 H, AB-system, $^2J_{HH}$ 19.5 Hz, CH_2), 6.17 (1 H, s, =CH); ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ_C 196.8, 170.1, 168.0, 154.6, 151.0, 102.9, 82.7, 42.5, 34.2, 31.5, 26.4, 19.4, 10.8; Anal. Calcd. for $C_{13}H_{16}N_2O_5$ (280.28): C 55.71, H 5.75, N 10.00%; Found: C 55.56, H 5.68, N 9.94%.

(8*E*)-7-isobutyl-3-methyl-8-(2-oxopropylidene)-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4h):

Colorless powder (0.177 g, 60%), m.p. 177-180 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.60; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1829, 1754, 1737 and 1680 (C=O), 1603 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 0.93 and 0.96 (6 H, 2 d, $^3J_{HH}$ 6.8 Hz, CH*(CH₃)₂*), 2.06-2.16 (1 H, m, C*H*(CH_3)$_2$), 2.26 (3 H, s, O=C-CH_3), 3.16 (3 H, s, NCH_3), 3.35-3.54 (2 H, m, NHC*H₂*), 3.55 and 3.92 (2 H, d of AB-system, $^2J_{HH}$ 19.5 Hz, $^4J_{HH}$ 1.6 Hz, CH_2), 5.84 (1 H, s, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 196.6, 169.6, 167.7, 154.0, 151.4, 102.7, 82.4, 49.0, 34.3, 31.8, 26.7, 26.1, 20.0, 19.8; Anal. Calcd. for $C_{14}H_{18}N_2O_5$ (294.31): C 57.14, H 6.16, N 9.52%; Found: C 56.98, H 6.13, N 9.45%.

(8*E*)-7-Allyl-3-methyl-8-(2-oxopropylidene)-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4i):

Colorless powder (0.181 g, 65%), m.p. 140-143 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.65; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1834, 1753, 1737, 1678 and 1660 (C=O), 1859 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz):δ_H 2.24 (3 H, s, O=C-CH_3), 3.16 (3 H, s, NCH_3), 3.56 and 3.93 (2 H, d of AB-system, $^2J_{HH}$ 19.5 Hz, $^4J_{HH}$ 1.5 Hz, CH_2), 4.22-4.27 (2 H, m, NH*CH₂*), 5.24 and 5.29 (2 H, 2 d, $^3J_{HH(trans)}$ 17.2 Hz, $^3J_{HH(cis)}$ 10.4 Hz, =CH_2), 5.67-5.80 (1 H, m, =CH), 5.83 (1 H, s, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 196.7, 169.6, 167.9, 153.8, 150.4, 128.4, 118.6, 103.3, 82.4, 43.9, 34.4, 31.8, 26.8; Anal. Calcd. for $C_{13}H_{14}N_2O_5$ (278.26): C 56.11, H 5.07, N 10.07%; Found: C 55.79, H 4.99, N 10.18%.

(8*E*)-3-Methyl-8-(2-oxopropylidene)-7-prop-2-yn-1-yl-1-oxa-3,7-diazaspiro[4.4]nonane-2,4,6-trione (4j):

Colorless powder (0.196 g, 71%), m.p. 134-137 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.67; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3315 (≡C-H), 1837, 1748 and 1684 (C=O), 1597 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 2.28 (3 H, s, O=C-CH_3), 2.35 (1 H, t, $^4J_{HH}$ 2.5 Hz, ≡CH), 3.15 (3 H, s, NCH_3), 3.58 and 3.92 (2 H, AB-system, $^2J_{HH}$ 19.6 Hz, CH_2), 4.32 and 4.45 (2 H, d of AB-system, $^2J_{HH}$ 17.6 Hz, $^4J_{HH}$ 2.5 Hz, ≡C-CH_2), 6.04 (1 H, s, =CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 196.6, 169.2, 166.4, 153.7, 149.1, 103.9, 82.2, 74.3, 74.1, 34.3, 31.8, 31.1, 26.8; Anal. Calcd. for $C_{13}H_{12}N_2O_5$ (276.25): C 56.52, H 4.38, N 10.14%; Found: C 56.35, H 4.40, N 10.17%.

Methyl 3-methyl-2,4,6-trioxo-8-piperidin-1-yl-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5a):

Colorless powder (0.200 g, 62%); m.p. 193-195 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.50; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1816, 1727, 1701 and 1667 (C=O), 1592 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.79 (6 H, m, $CH_2CH_2CH_2$), 3.01 and 3.24 (2 H, AB-system, $^2J_{HH}$ 16.6 Hz, CH_2), 3.12 (3 H, s, NCH_3), 3.54 (4 H, m, CH_2NCH_2), 3.82 (3 H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 185.7, 170.9, 170.3, 164.3, 154.4, 103.7, 85.4, 53.2, 51.5, 50.7, 35.7, 26.0, 25.9, 25.2, 23.0; Anal. Calcd. for $C_{15}H_{18}N_2O_6$ (322.32): C 55.90, H 5.63, N 8.69%; Found: C 56.17, H 5.60, N 8.76%.

Ethyl 3-methyl-2,4,6-trioxo-8-piperidin-1-yl-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5b):

Colorless powder (0.222 g, 66%); m.p. 115-117 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.53; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1820, 1742, 1711 and 1678 (C=O), 1568 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.32 (3 H, t, $^3J_{HH}$ 7.1 Hz, OCH_2CH_3), 1.76 (6 H, m, $CH_2CH_2CH_2$), 3.00 and 3.22 (2 H, AB-system, $^2J_{HH}$ 16.6 Hz, CH_2), 3.10 (3 H, s, NCH_3), 3.53 (4 H, m, CH_2NCH_2), 4.26 (2 H, q, $^3J_{HH}$ 7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 185.7, 170.7, 170.4, 164.2, 154.7, 103.2, 85.8, 60.9, 53.4, 51.0, 35.9, 26.4, 26.2, 25.6, 23.4, 14.2; Anal. Calcd. for $C_{16}H_{20}N_2O_6$ (336.34): C 57.14, H 5.99, N 8.33%; Found: C 56.88, H 6.08, N 8.28%.

Methyl 3-methyl-8-morpholin-4-yl-2,4,6-trioxo-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5c):

Colorless powder (0.204 g, 63%); m.p. 193-195 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.60; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1820, 1745, 1723 and 1662 (C=O), 1576 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 3.04 and 3.24 (2 H, AB-system, $^2J_{HH}$ 16.7 Hz, CH_2), 3.12 (3 H, s, NCH_3), 3.62-3.72 (4 H, m, CH_2NCH_2), 3.81 (3 H, s, OCH_3), 3.88 (4 H, m, CH_2OCH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_c 185.8, 171.4, 170.4, 163.8, 154.5, 103.1, 85.4, 66.4, 66.3, 52.4, 52.1, 50.0, 35.8, 26.5; Anal. Calcd. for $C_{14}H_{16}N_2O_7$ (324.29): C 51.85, H 4.97, N 8.64%; Found: C 51.67, H 5.05, N 8.53%.

Ethyl 3-methyl-8-morpholin-4-yl-2,4,6-trioxo-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5d)*:*

Colorless powder (0.230 g, 68%); m.p. 177-180 ˚C (dec.); R_f (25% EtOAc/*n*-hexane) 0.62; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1820, 1724, 1722 and 1663 (C=O), 1599 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz):

δ_H 1.32 (3 H, t, $^3J_{HH}$ 7.1 Hz, $OCH_2\mathit{CH_3}$), 3.03 and 3.22 (2 H, AB-system, $^2J_{HH}$ 16.7 Hz, CH_2), 3.10 (3 H, s, NCH_3), 3.61-3.70 (4 H, m, CH_2NCH_2), 3.86 (4 H, s,CH_2OCH_2), 4.25 (2 H, q, $^3J_{HH}$ 7.1 Hz, $O\mathit{CH_2}CH_3$); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_c 186.1, 171.1, 170.5, 163.9, 154.6, 103.7, 85.5, 66.3, 61.1, 52.2, 49.9, 35.7, 26.5, 14.2; Anal. Calcd. for $C_{15}H_{18}N_2O_7$ (338.32): C 53.25, H 5.36, N 8.28%; Found: C 52.97, H 5.32, N 8.25%.

Methyl 3-methyl-2,4,6-trioxo-8-thiomorpholin-4-yl-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5e):

Colorless powder (0.242 g, 71%); m.p. 197-199 °C (dec.); R_f (25% EtOAc/*n*-hexane) 0.65; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1814, 1751, 1704 and 1682 (C=O), 1578 (C=C); ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ_H 2.77 (4 H, m, CH_2SCH_2), 2.87 (2 H, m, CH_2), 2.95 (3 H, s, NCH_3), 3.55-3.95 (4 H, m, CH_2NCH_2), 3.67 (3 H, s, OCH_3); ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ_c 186.1, 171.3, 170.8, 164.5, 155.0, 102.6, 85.8, 54.1, 52.2, 51.7, 35.5, 26.9, 26.2, 26.1; Anal. Calcd. for $C_{14}H_{16}N_2O_6S$ (340.35): C 49.41, H 4.74, N 8.23%; Found: C 49.53, H 4.69, N 8.31%.

Ethyl 3-methyl-2,4,6-trioxo-8-thiomorpholin-4-yl-1-oxa-3-azaspiro[4.4]non-7-ene-7-carboxylate (5f):

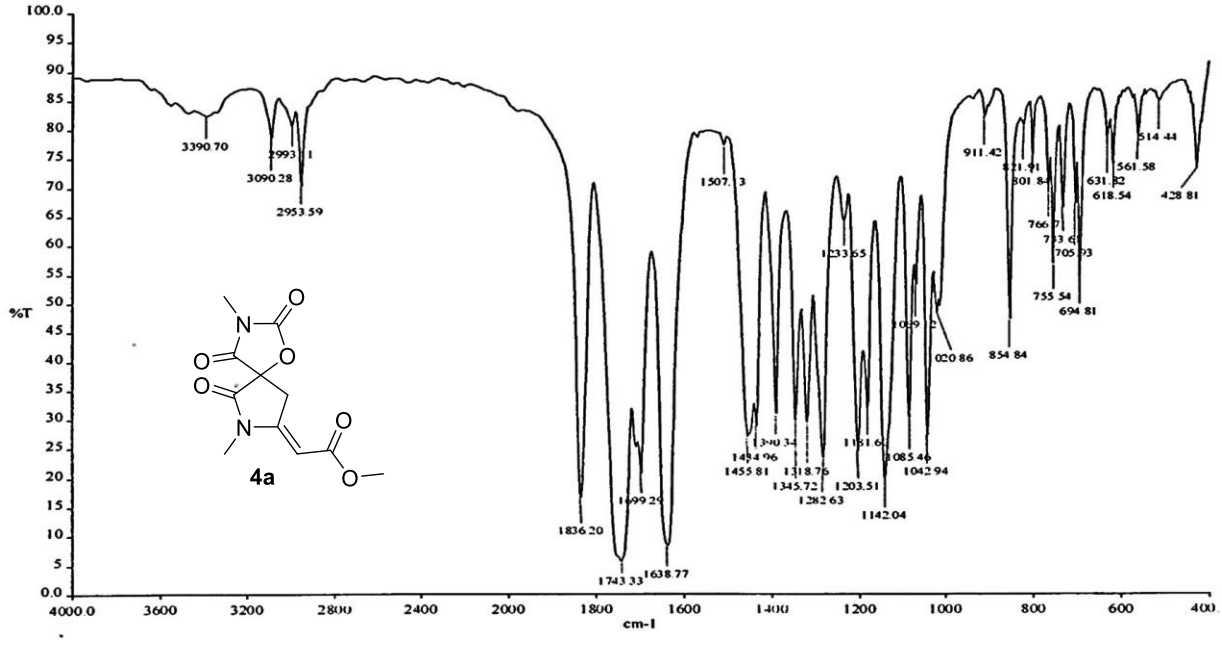
Colorless powder (0.241 g, 68%); m.p. 195-197 °C (dec.); R_f (25% EtOAc/*n*-hexane) 0.65; IR (KBr) ($\nu_{max,}$ cm^{-1}): 1820, 1743, 1725 and 1667 (C=O), 1591 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.31 (3 H, t, $^3J_{HH}$ 7.1 Hz, $OCH_2\mathit{CH_3}$), 2.82-2.96 (4 H, m, CH_2SCH_2), 3.02 and 3.20 (2 H, AB-system, $^2J_{HH}$ 16.7 Hz, CH_2), 3.09 (3 H, s, NCH_3), 3.79-3.86 (4 H, m, CH_2NCH_2), 4.25 (2 H, q, $^3J_{HH}$

7.1 Hz, O*CH*$_2$CH$_3$); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 186.1, 170.7, 170.5, 164.2, 154.6, 104.2, 85.4, 61.2, 55.0, 52.6, 35.8, 27.8 and 27.1, 26.5, 14.2; Anal. Calcd. for $C_{15}H_{18}N_2O_6S$ (354.38): C 50.84, H 5.12, N 7.91%; Found: C 51.05, H 5.18, N 8.01%.

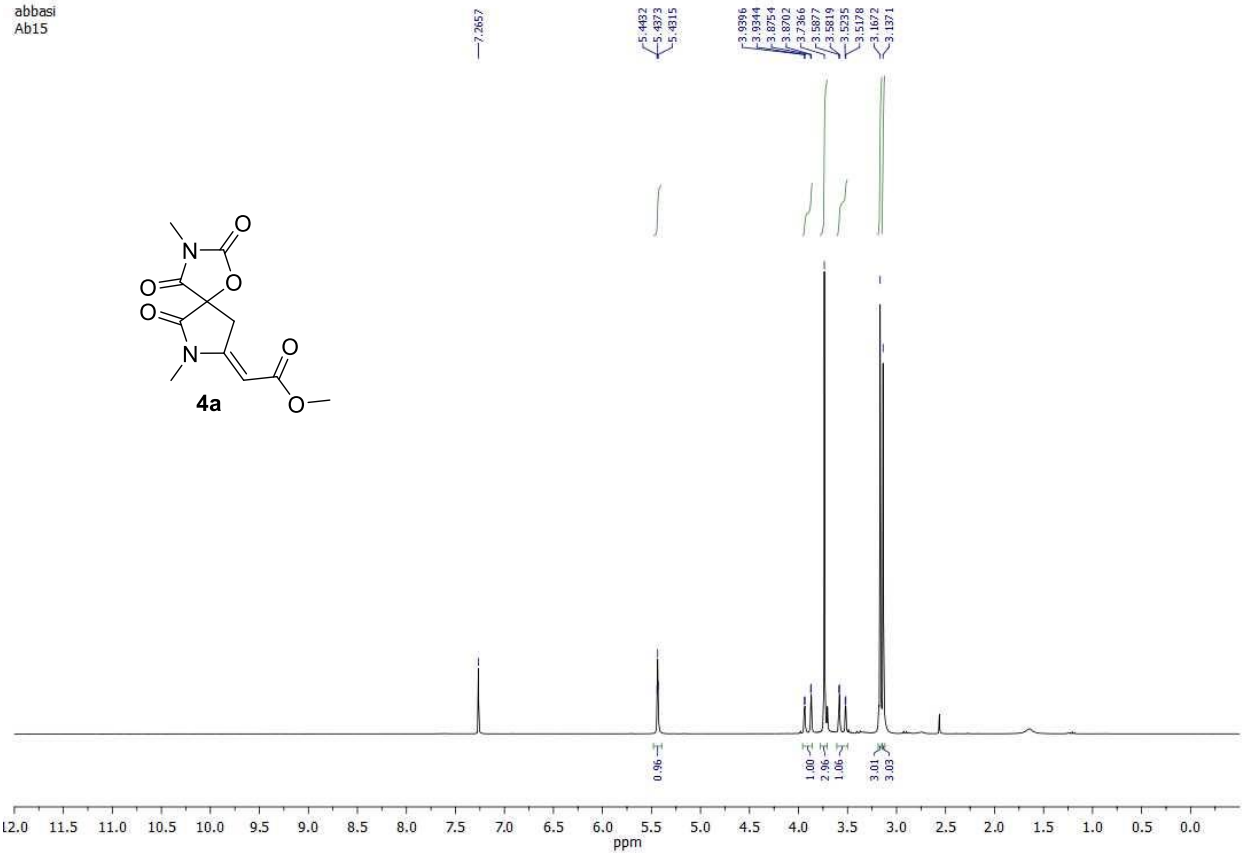
Ethyl (2*E*)-(7-isopropyl-3-methyl-2,4,6-trioxo-1-oxa-3,7-diazaspiro[4.4]non-8-ylidene)acetate (5g):

Colorless powder (0.208 g, 67%), m.p. 176-179 °C (dec.); R_f (25% EtOAc/*n*-hexane) 0.60; IR (KBr) ($\nu_{max,}$ cm^{-1}): 3248 (N-H), 1821, 1755, 1705 and 1660 (C=O), 1605 (C=C); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ_H 1.32-1.39 (9 H, m, 3 CH_3 overlapping), 3.12 (3 H, s, NCH_3), 3.02 and 3.33 (2 H, AB-system, $^2J_{HH}$ 17.9 Hz, CH_2), 3.79-3.82 (1 H, m, CH), 4.28 (2 H, q, $^3J_{HH}$ 7.1 Hz, O*CH*$_2$CH$_3$), 9.36 (1 H, br. d, $^3J_{HH}$ 7.7 Hz, NH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 184.1, 175.5, 170.9, 166.0, 154.7, 99.0, 85.4, 60.5, 47.5, 32.3, 26.5, 23.4, 23.3, 14.2; Anal. Calcd. for $C_{14}H_{18}N_2O_6$ (310.31): C 54.19, H 5.85, N 9.03%; Found: C 53.96, H 5.83, N 9.07%.

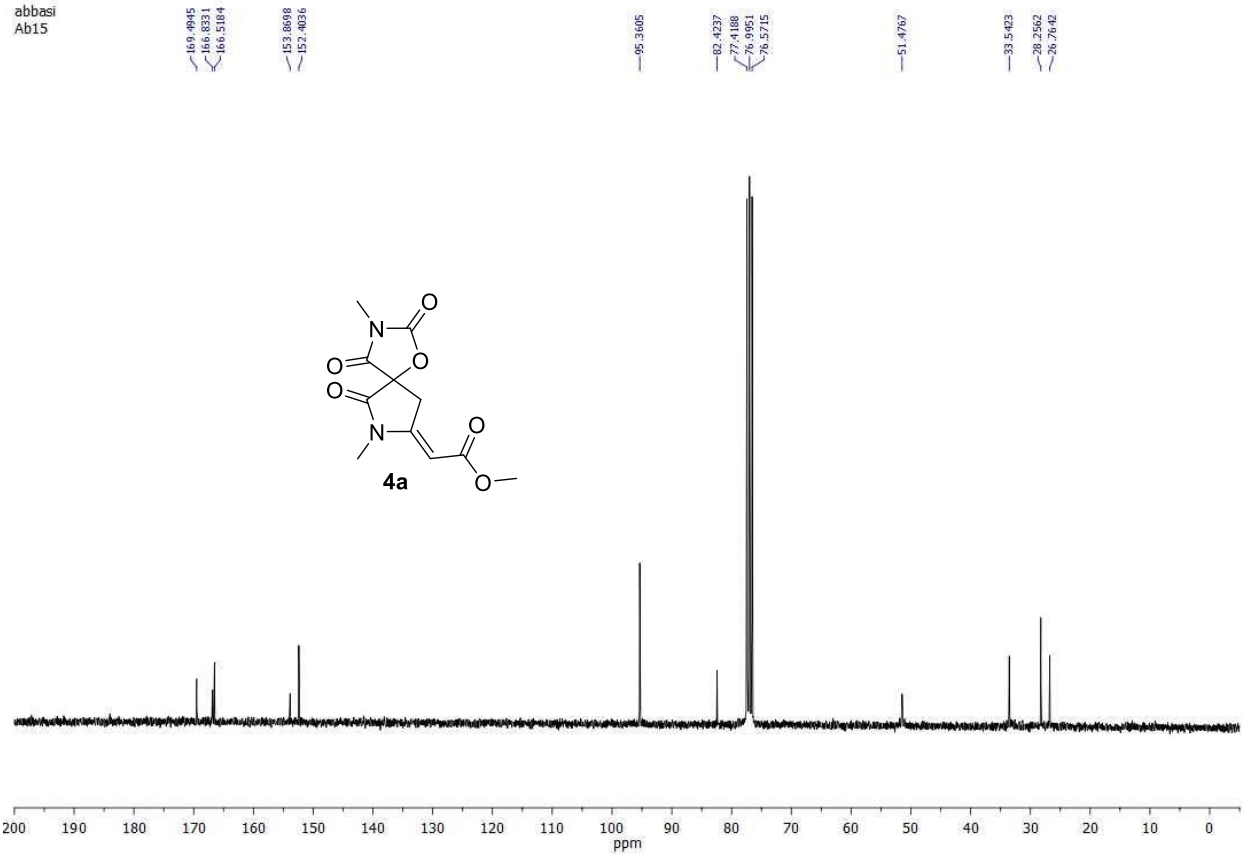
FT-IR of (4a):



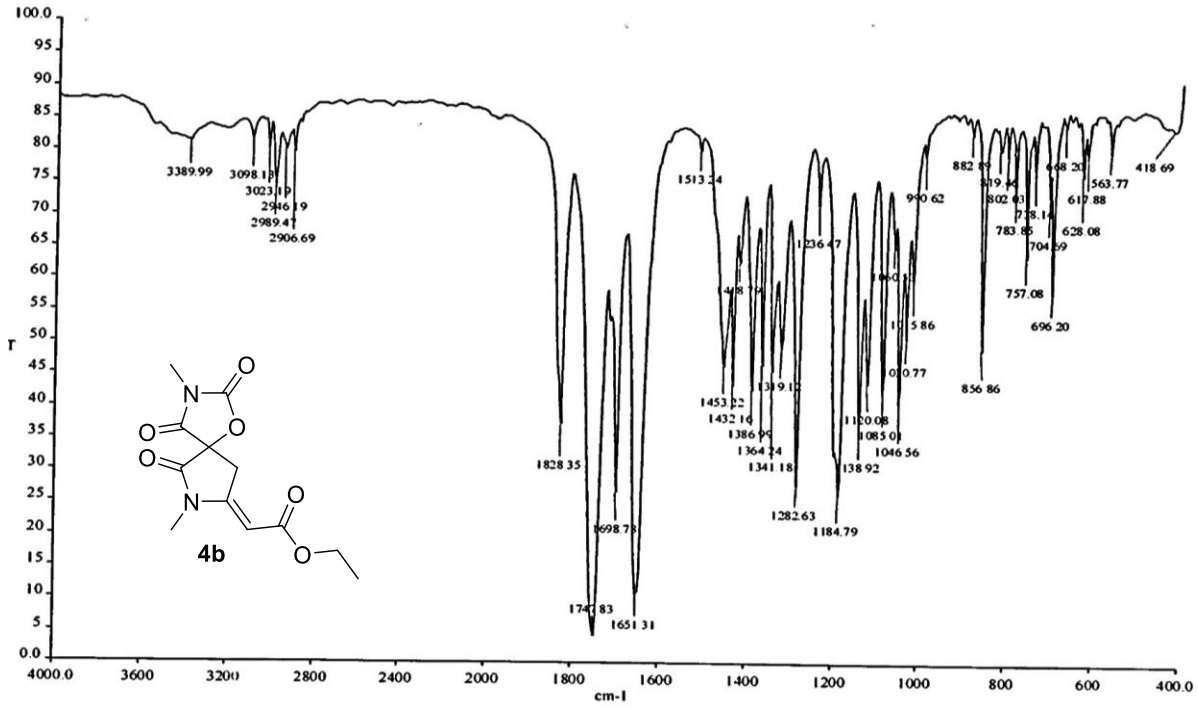
^{1}H NMR (300 MHz, $CDCl_3$) of (4a):



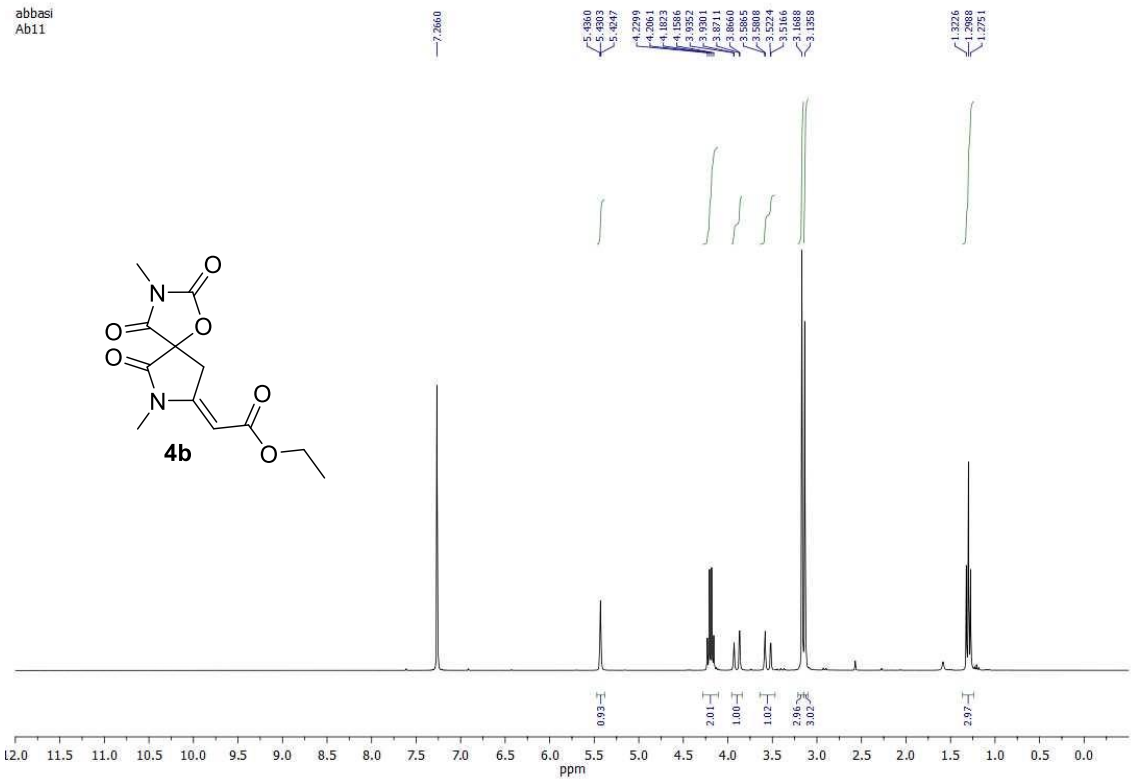
^{13}C NMR (75 MHz, $CDCl_3$) of (4a):



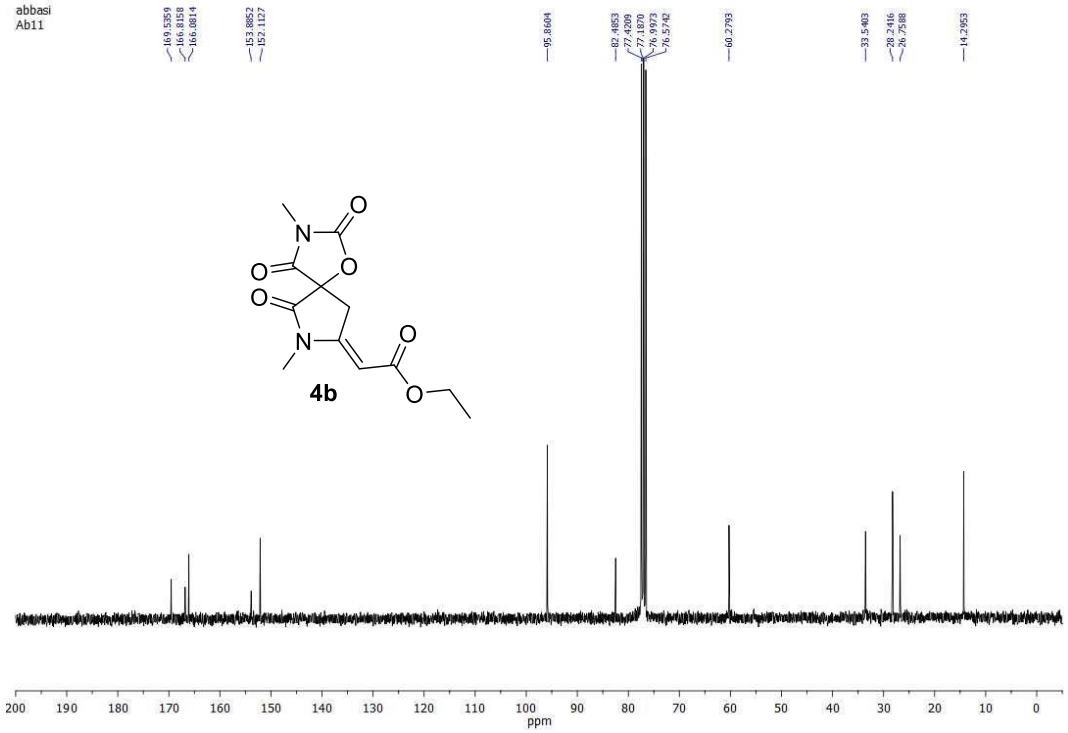
FT-IR of (4b):



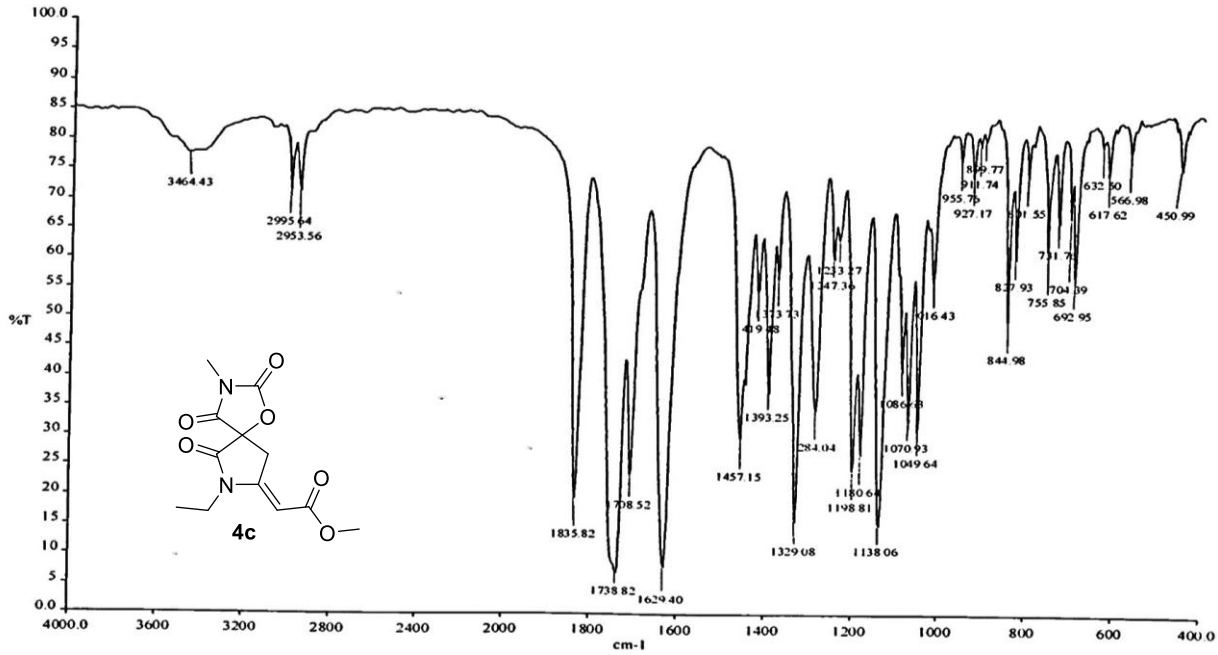
^{1}H NMR (300 MHz, $CDCl_3$) of (4b):



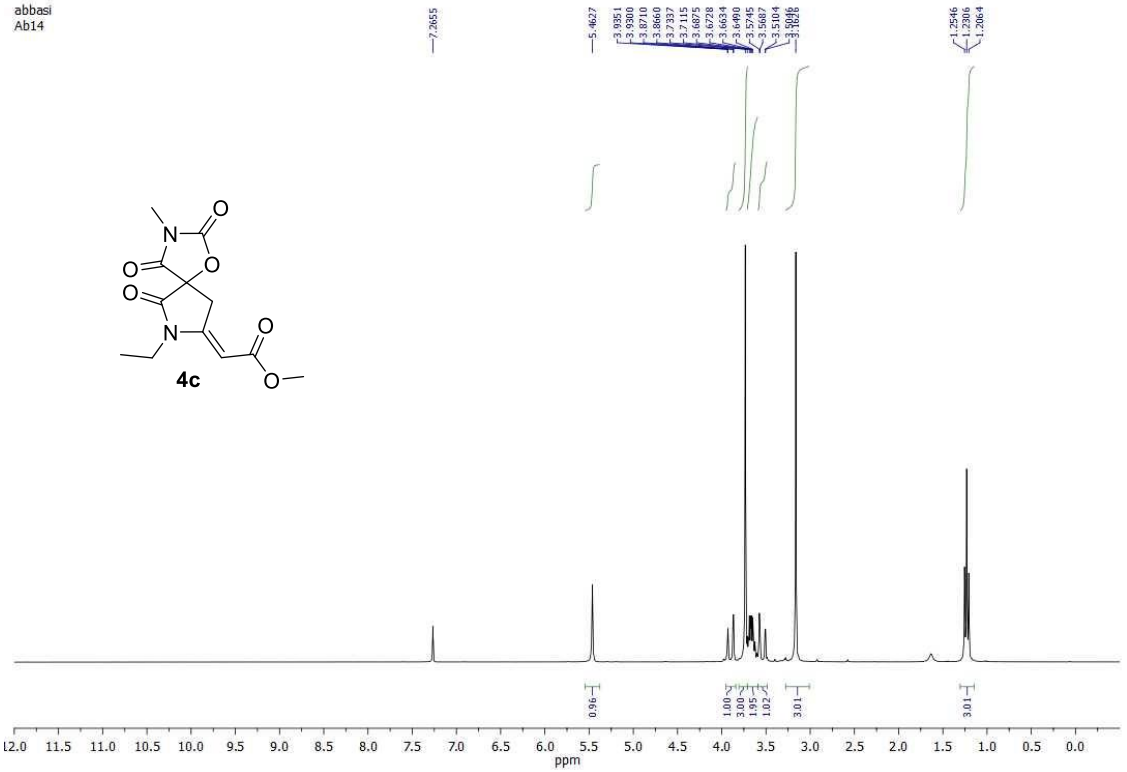
^{13}C NMR (75 MHz, $CDCl_3$) of (4b):



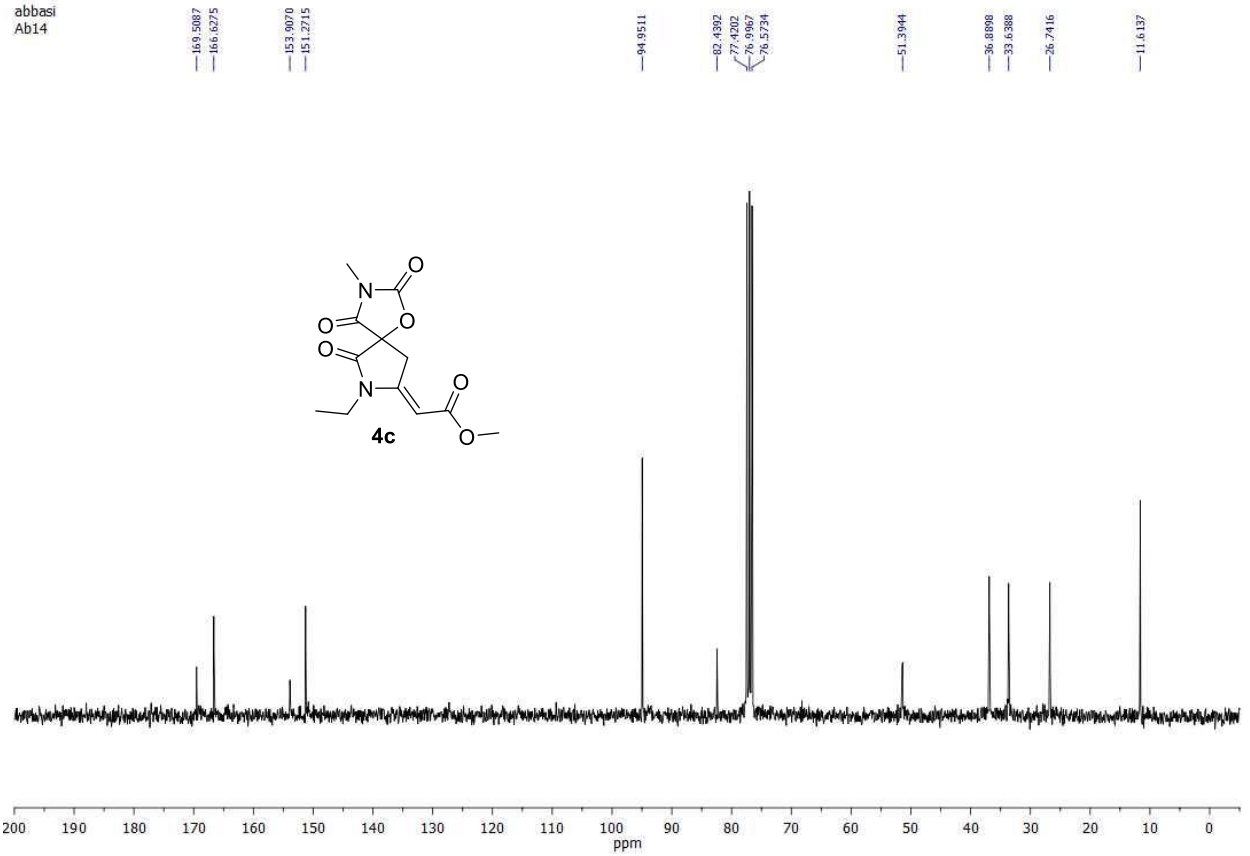
FT-IR of (4c):



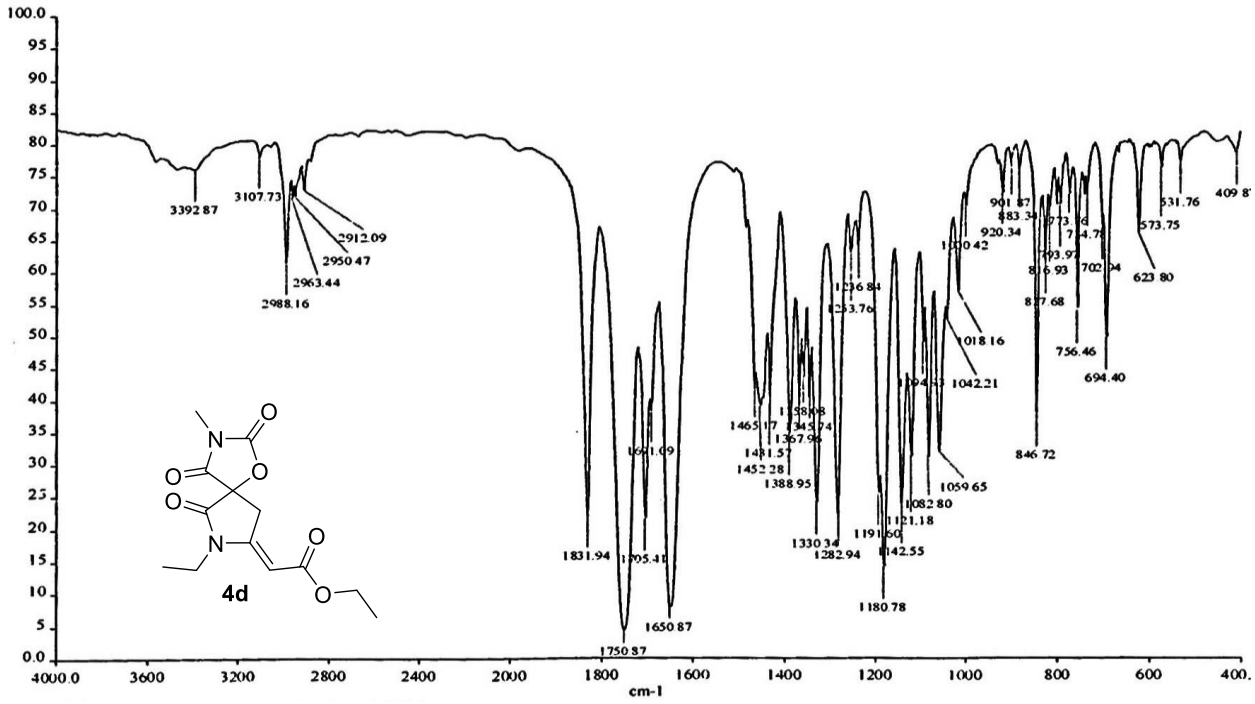
^{1}H NMR (300 MHz, $CDCl_3$) of (4c):



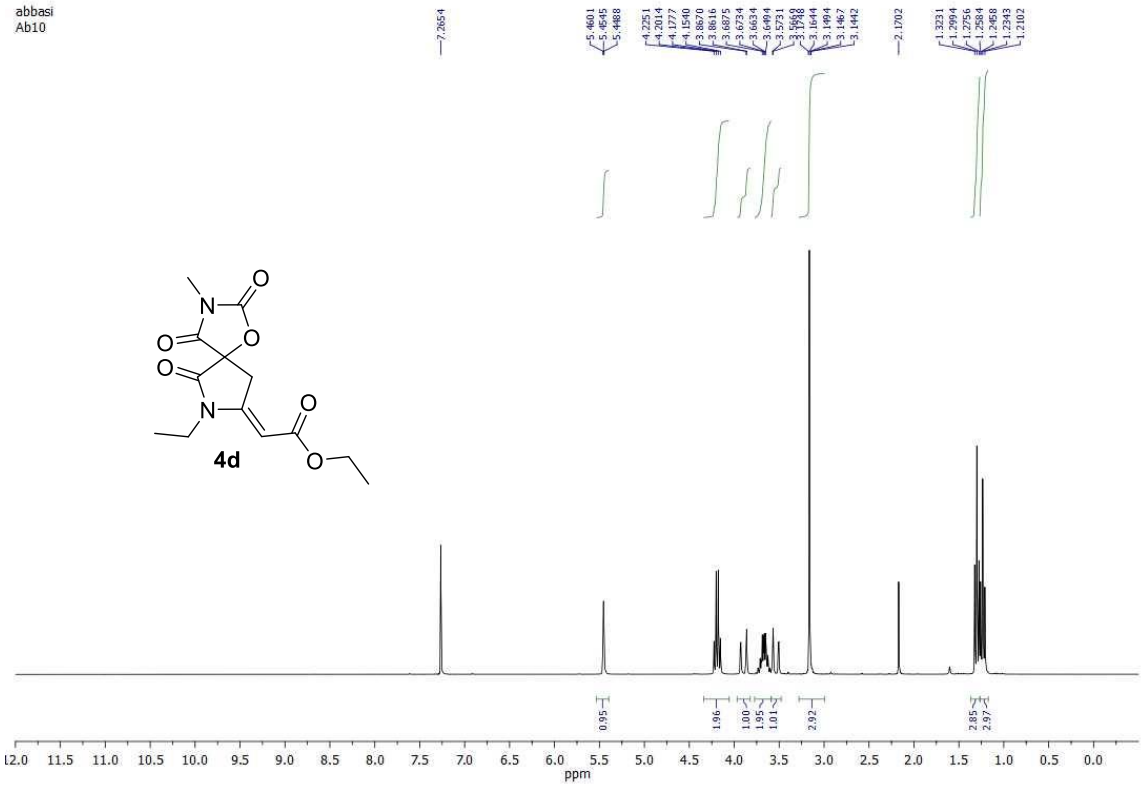
^{13}C NMR (75 MHz, $CDCl_3$) of (4c):



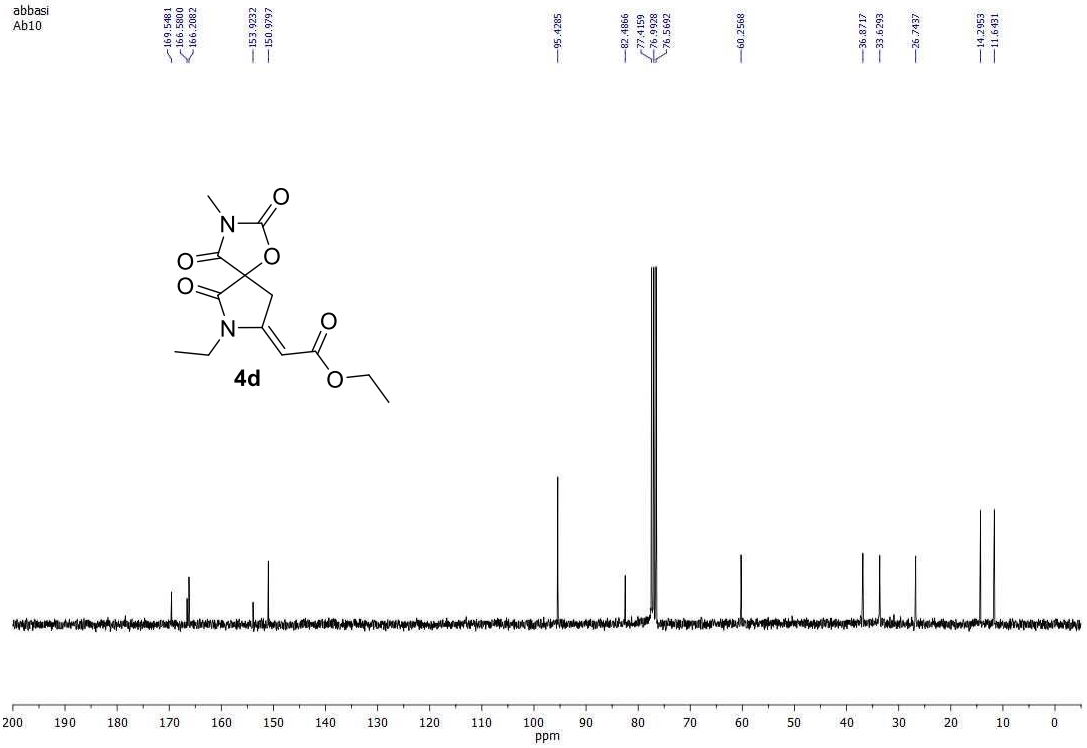
FT-IR of (4d):



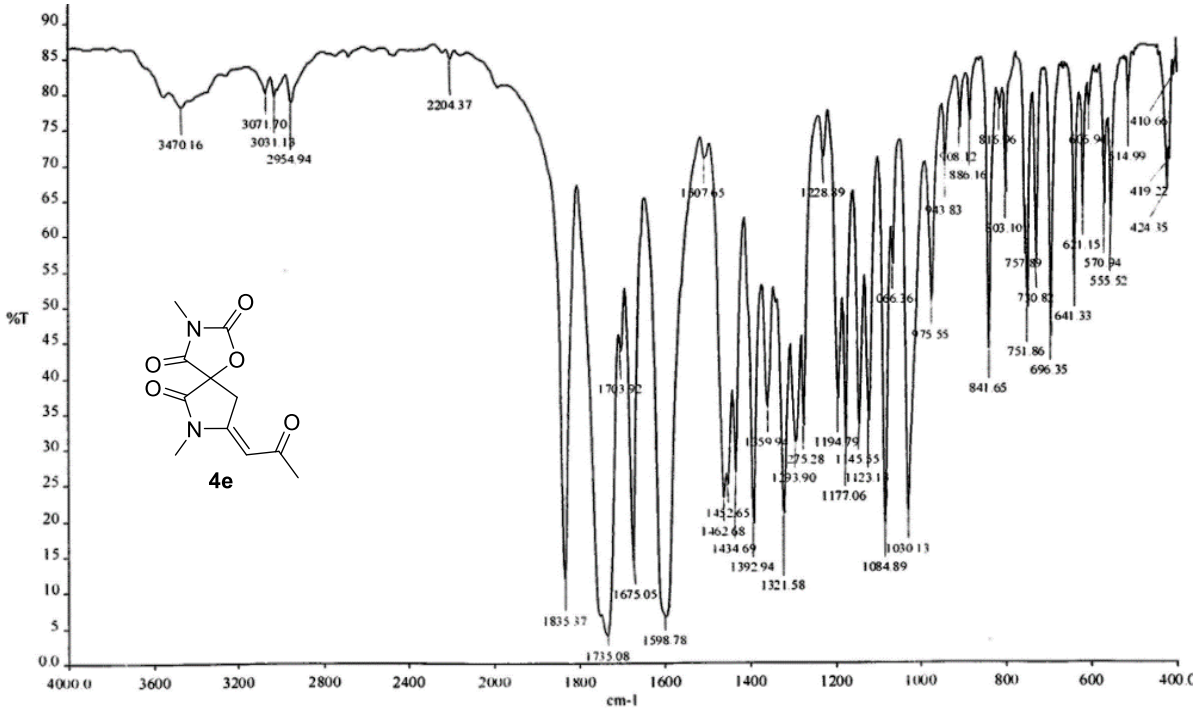
^{1}H NMR (300 MHz, $CDCl_3$) of (4d):



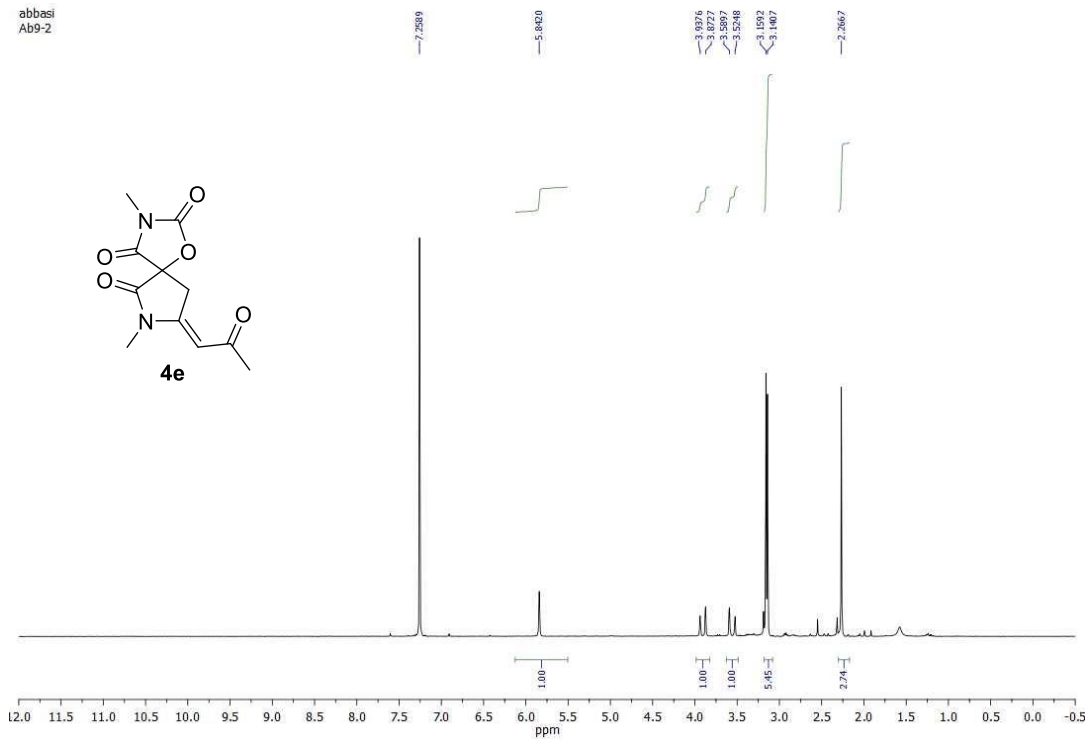
^{13}C NMR (75 MHz, $CDCl_3$) of (4d):



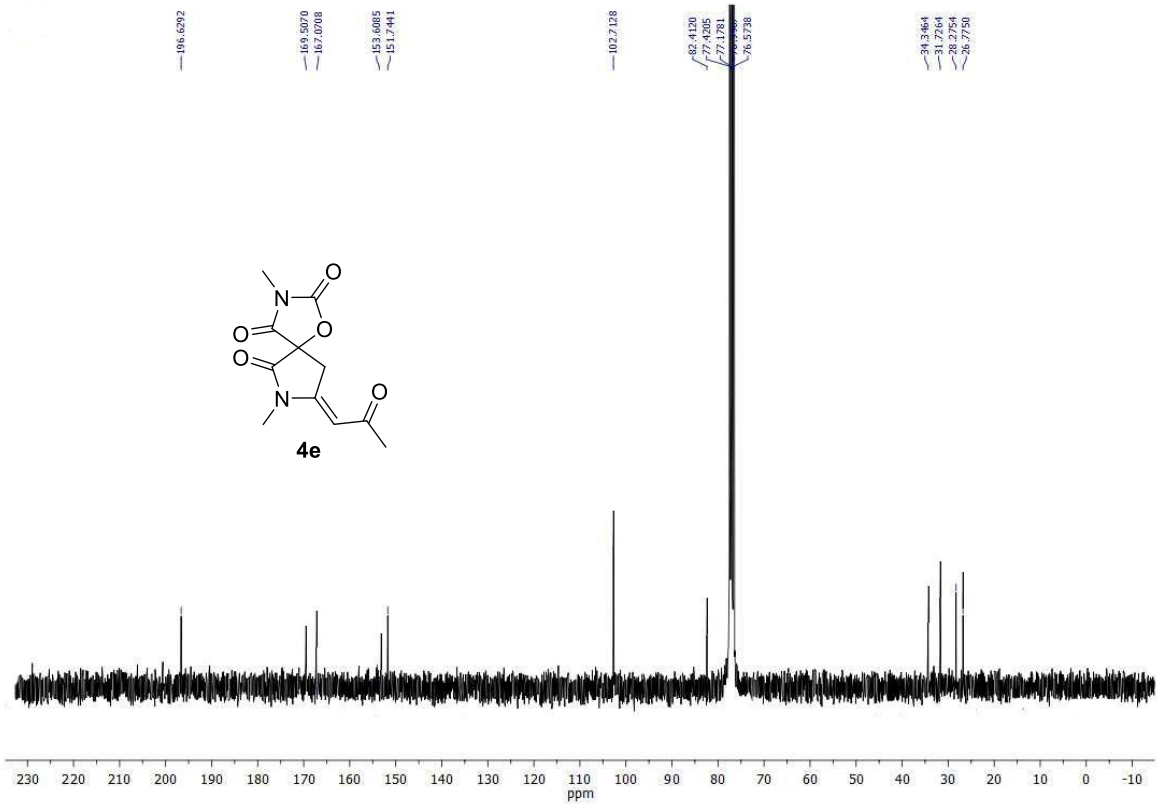
FT-IR of (4e):



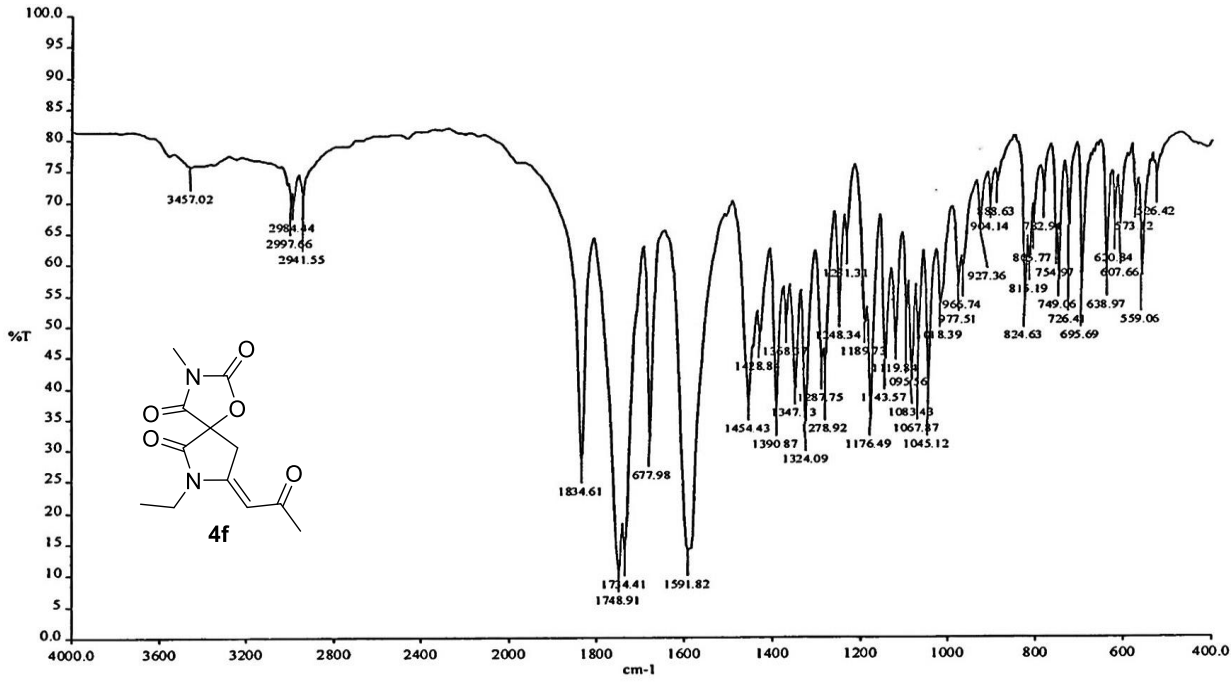
^{1}H NMR (300 MHz, $CDCl_3$) of (4e):



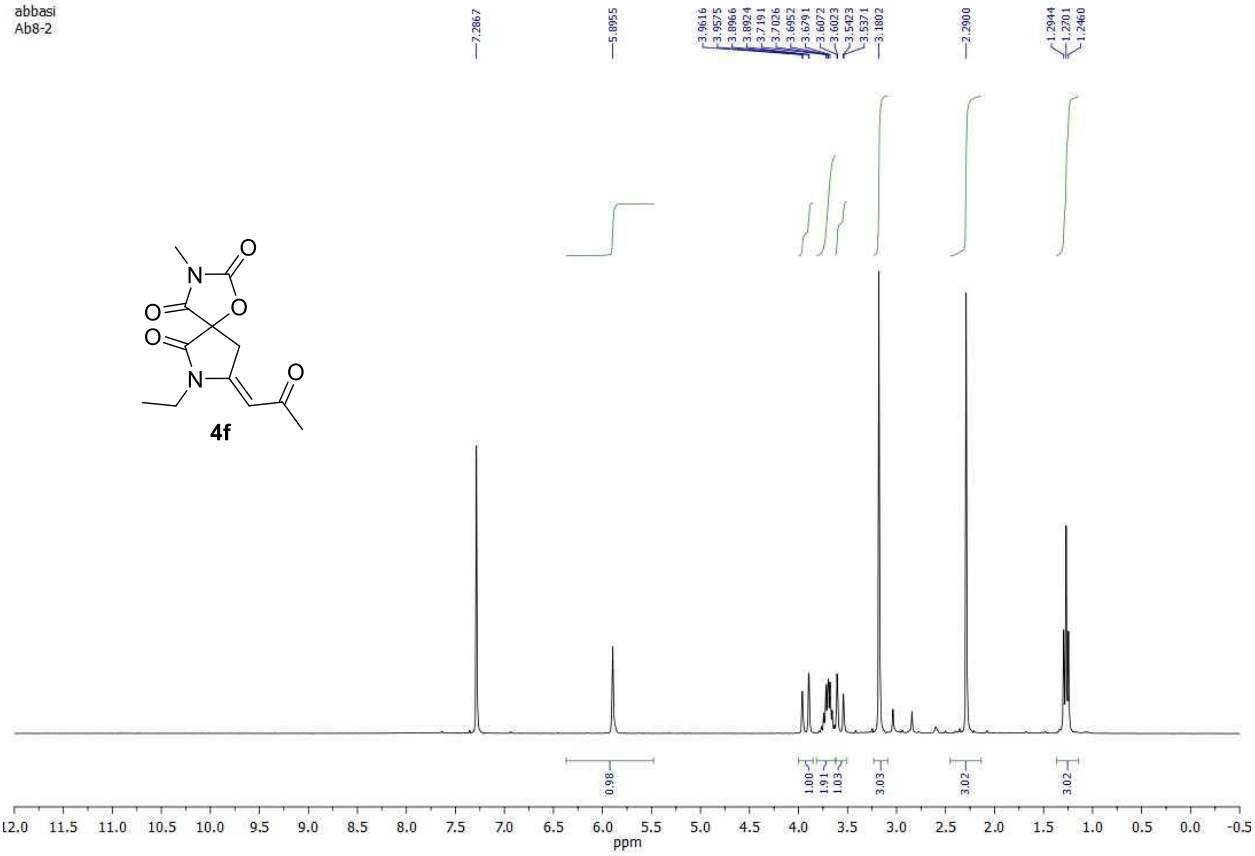
^{13}C NMR (75 MHz, $CDCl_3$) of (4e):



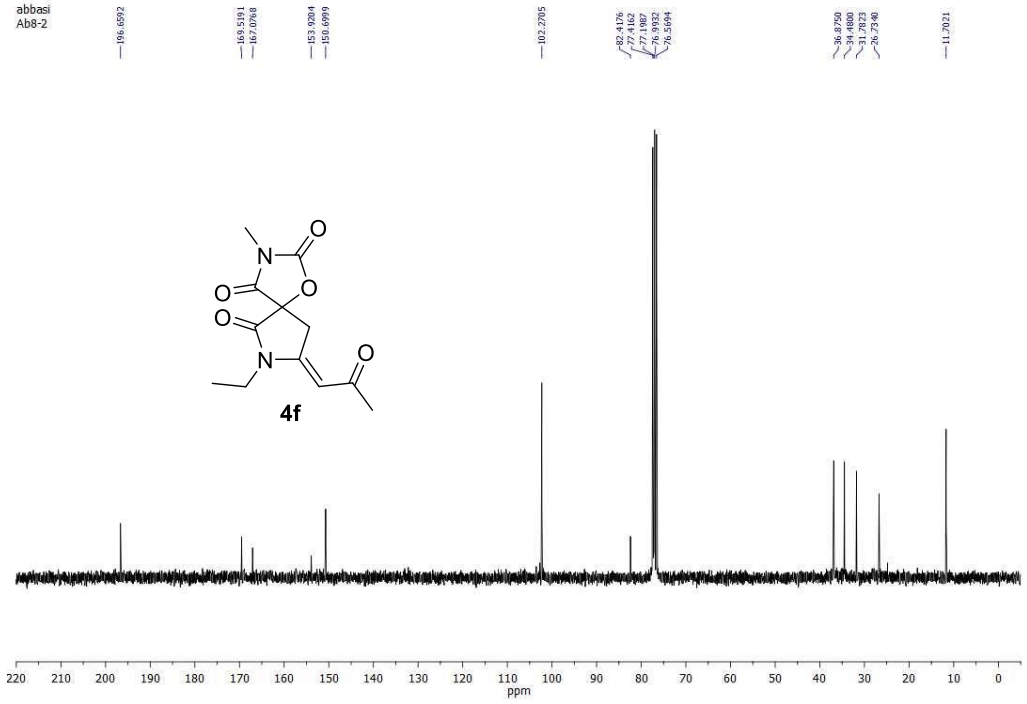
FT-IR of (4f):



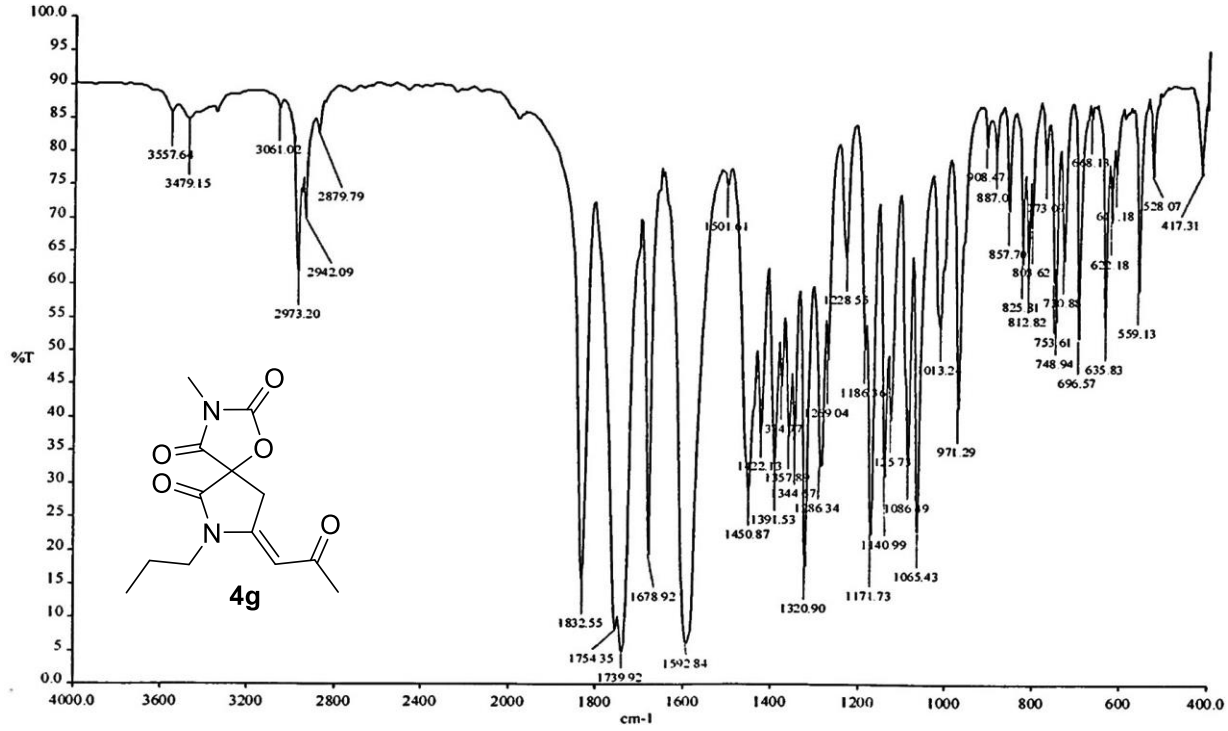
^{1}H NMR (300 MHz, $CDCl_3$) of (4f):



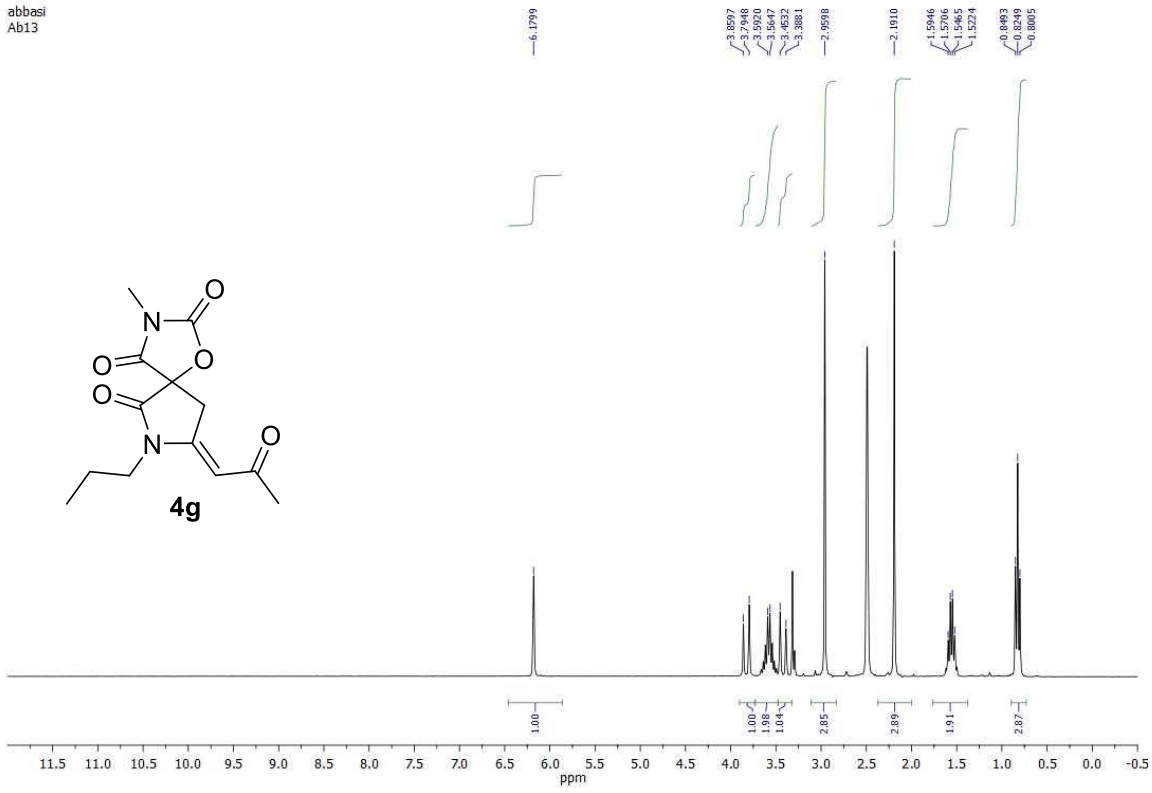
^{13}C NMR (75 MHz, $CDCl_3$) of (4f):



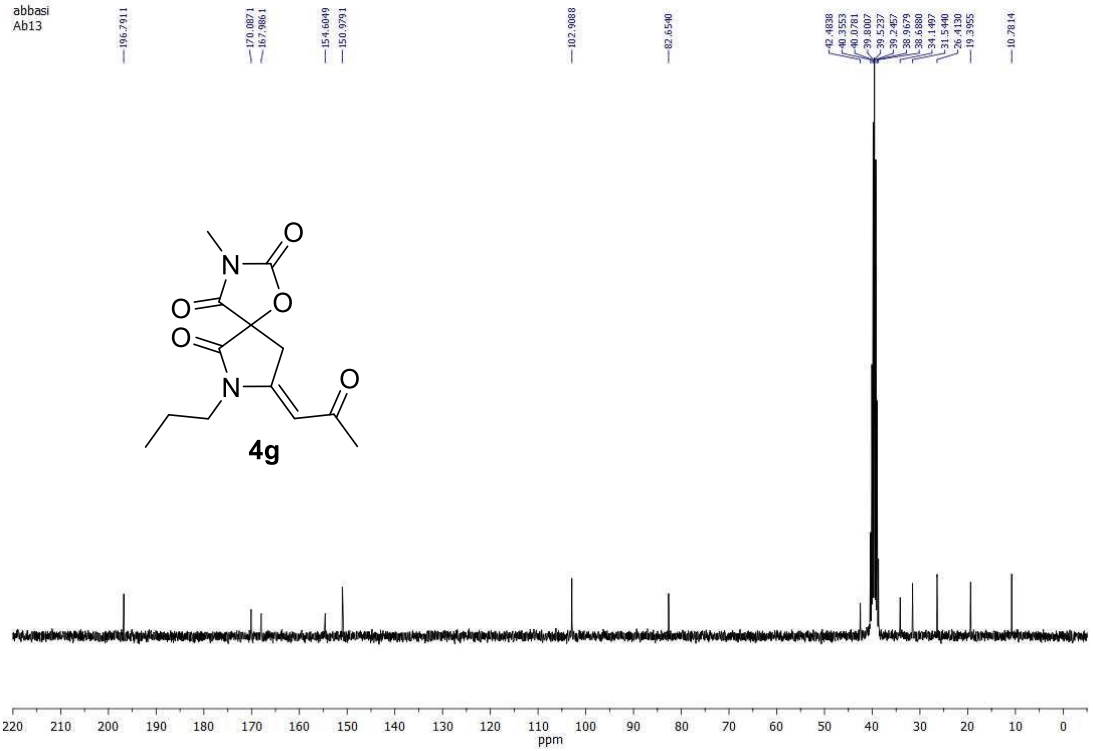
FT-IR of (4g):



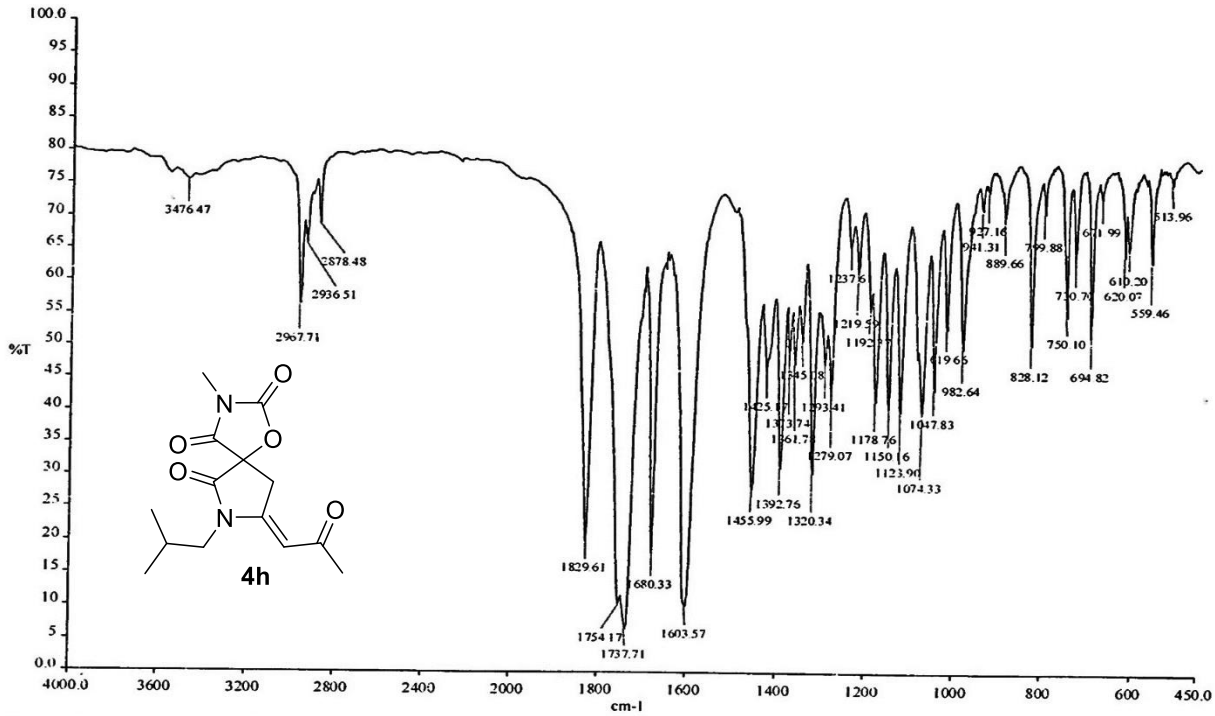
^{1}H NMR (300 MHz, DMSO-*d*$_6$) of (4g):



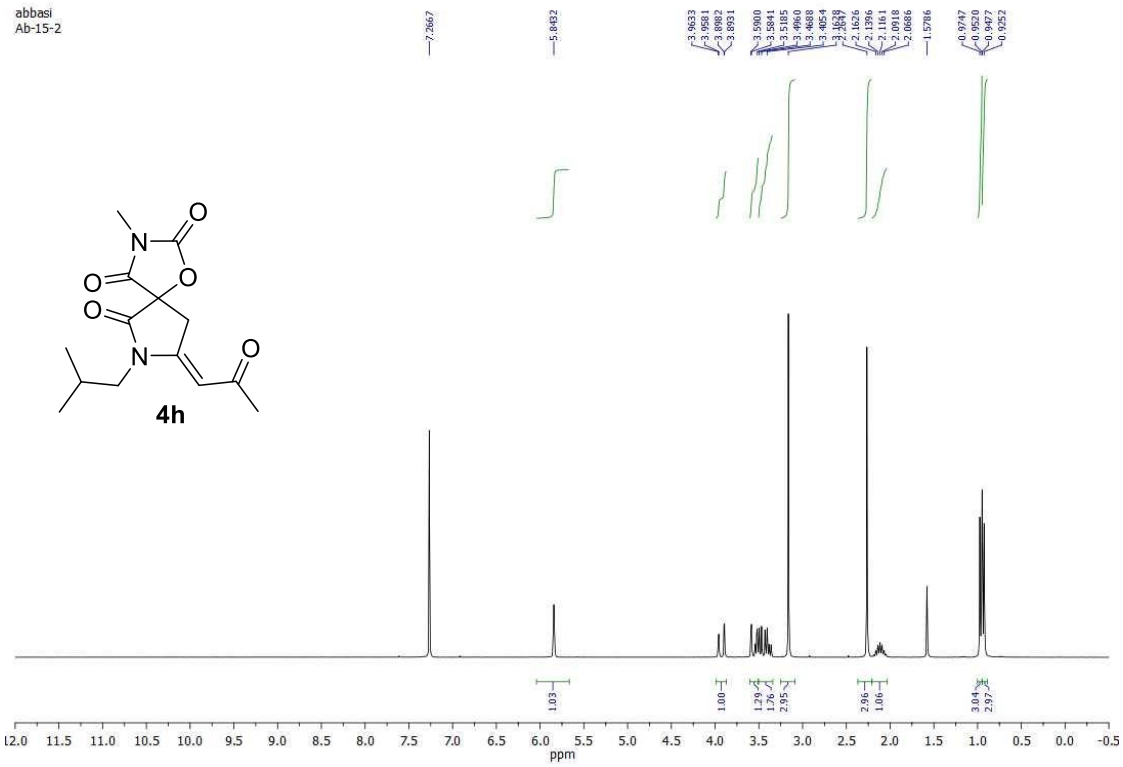
^{13}C NMR (75 MHz, DMSO-d_6) of (4g):



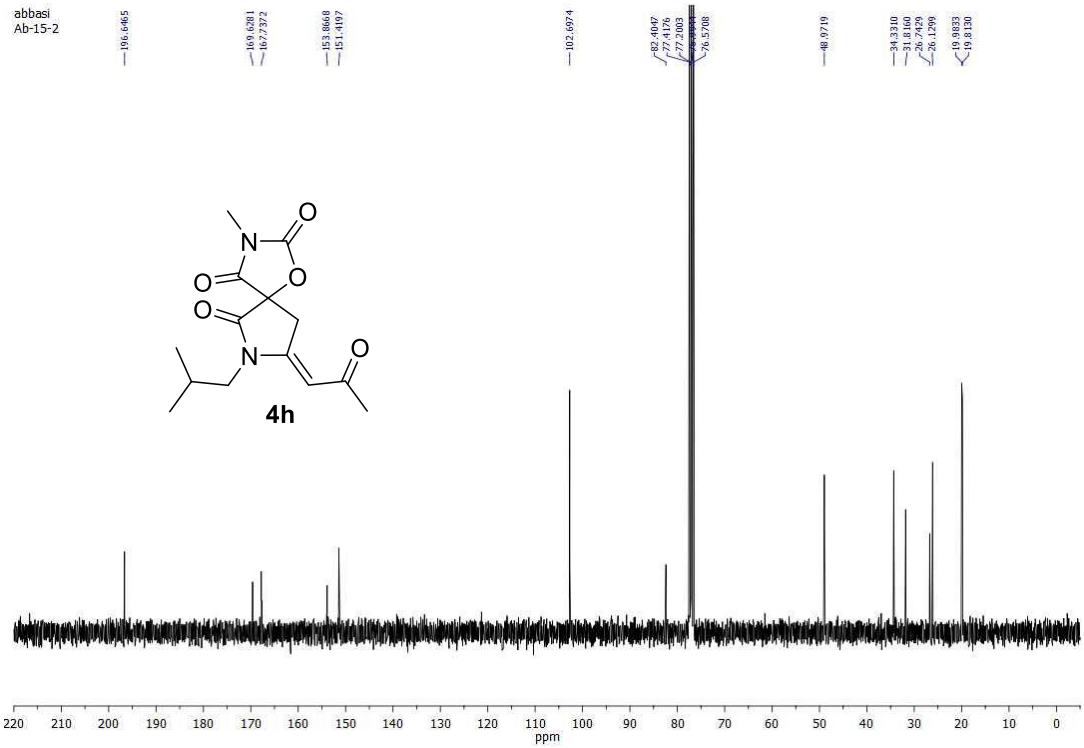
FT-IR of (4h):



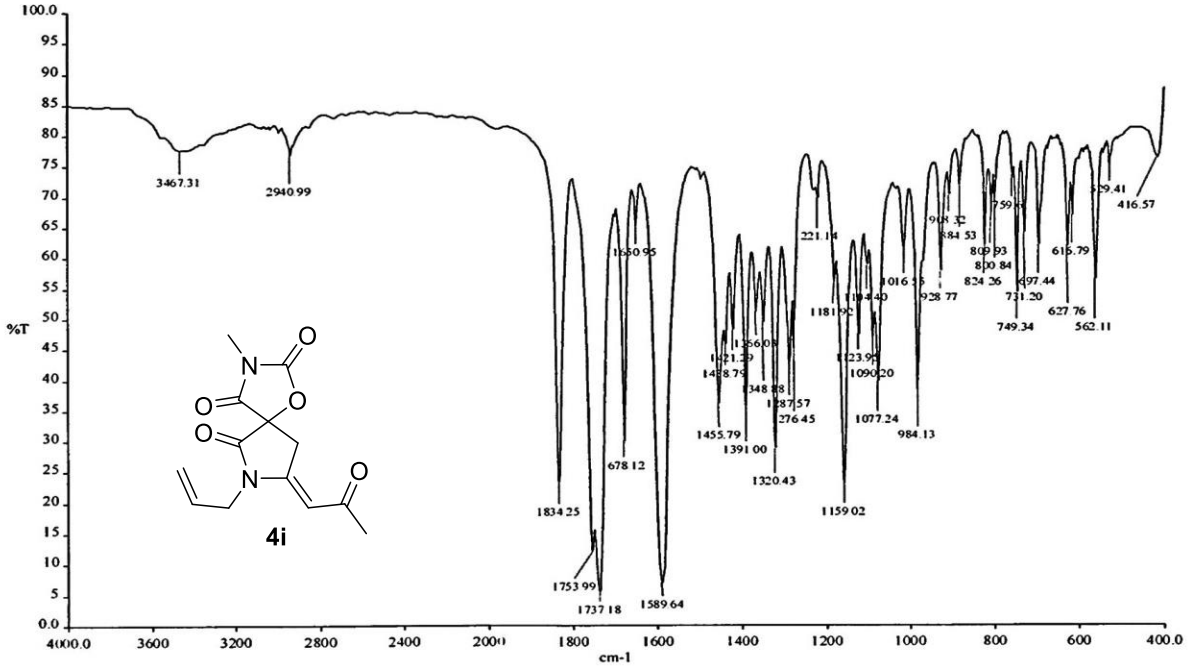
^{1}H NMR (300 MHz, $CDCl_3$) of (4h):



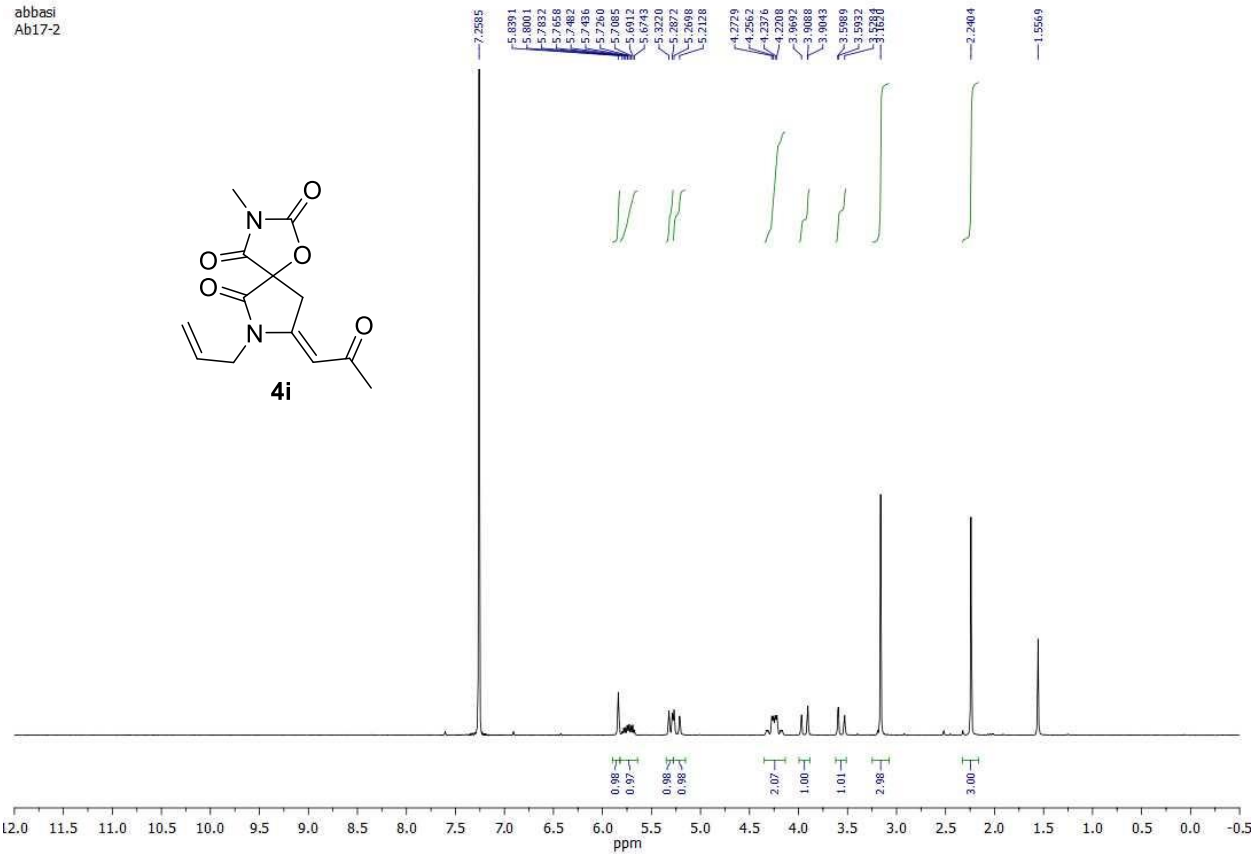
^{13}C NMR (75 MHz, $CDCl_3$) of (4h):



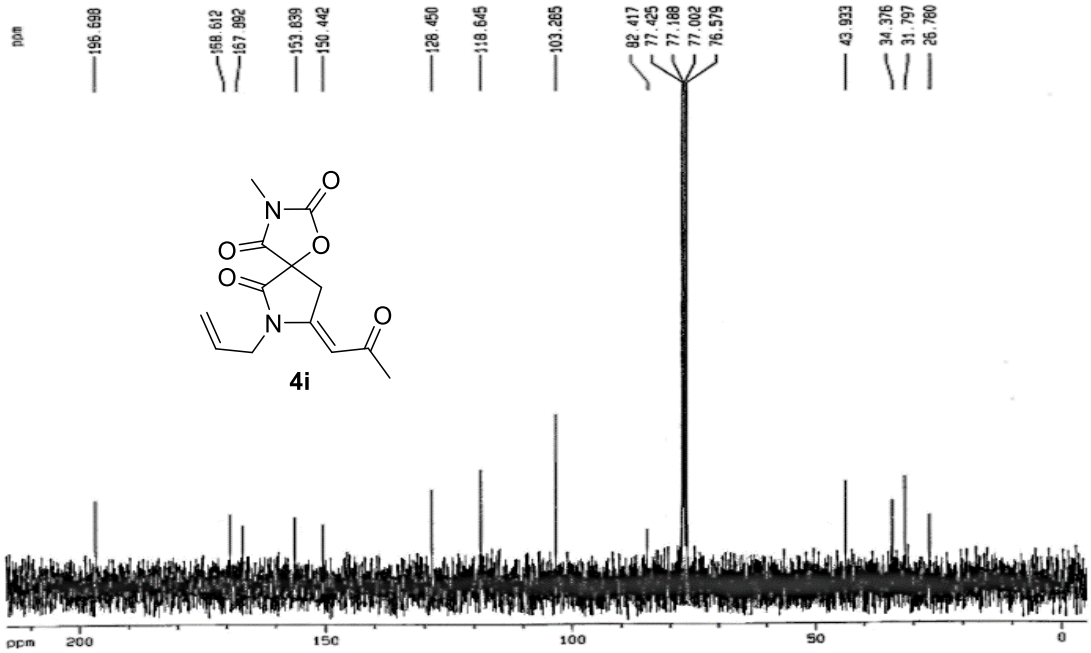
FT-IR of (4i):



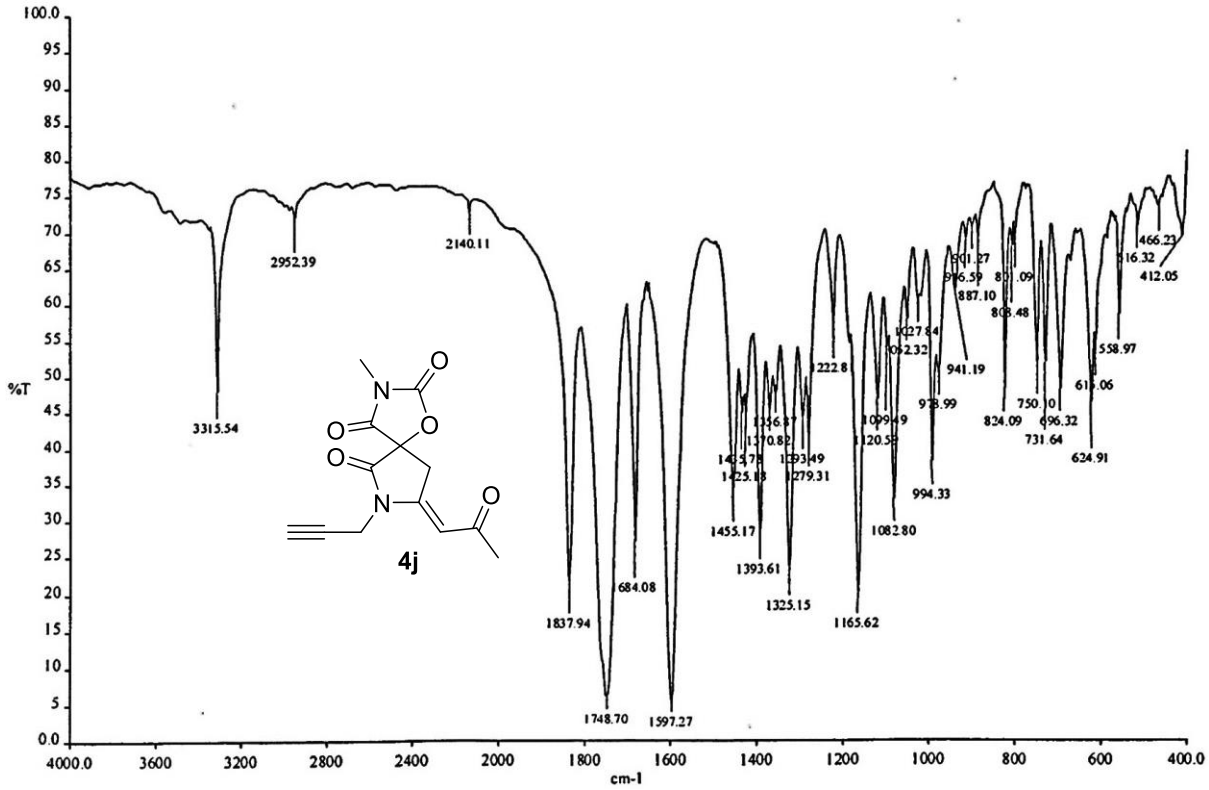
^{1}H NMR (300 MHz, $CDCl_3$) of (4i):



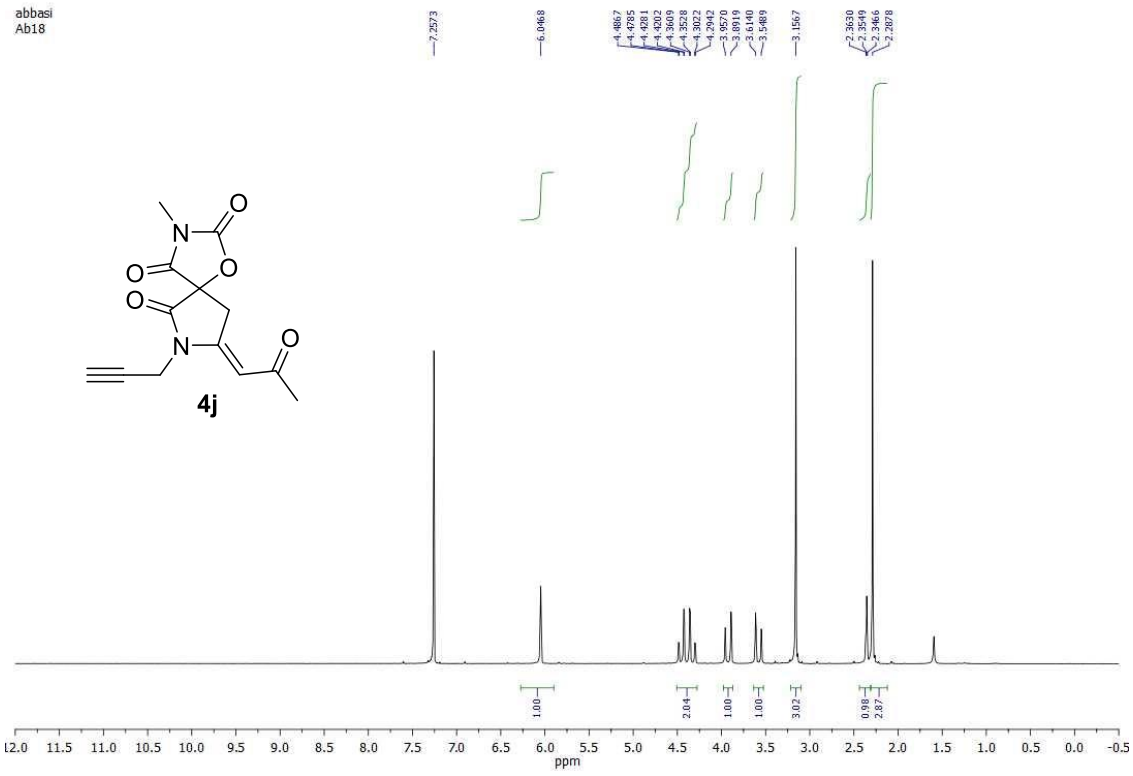
^{13}C NMR (75 MHz, $CDCl_3$) of (4i):



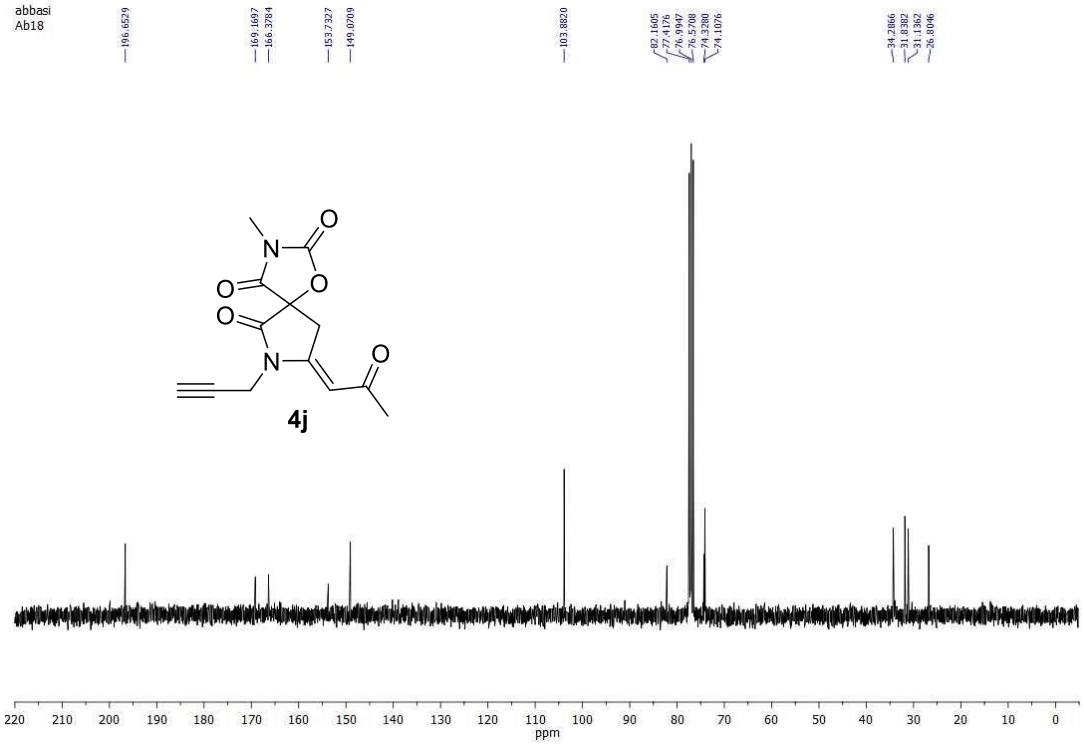
FT-IR of (4j):



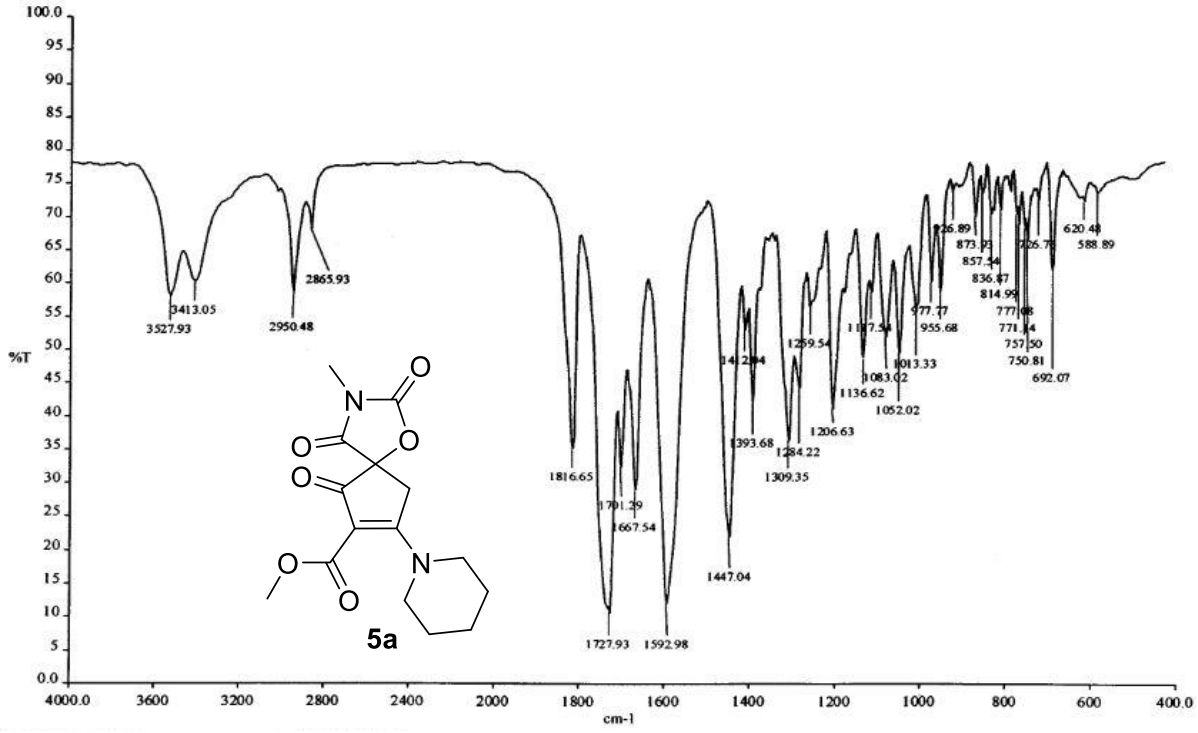
^{1}H NMR (300 MHz, $CDCl_3$) of (4j):



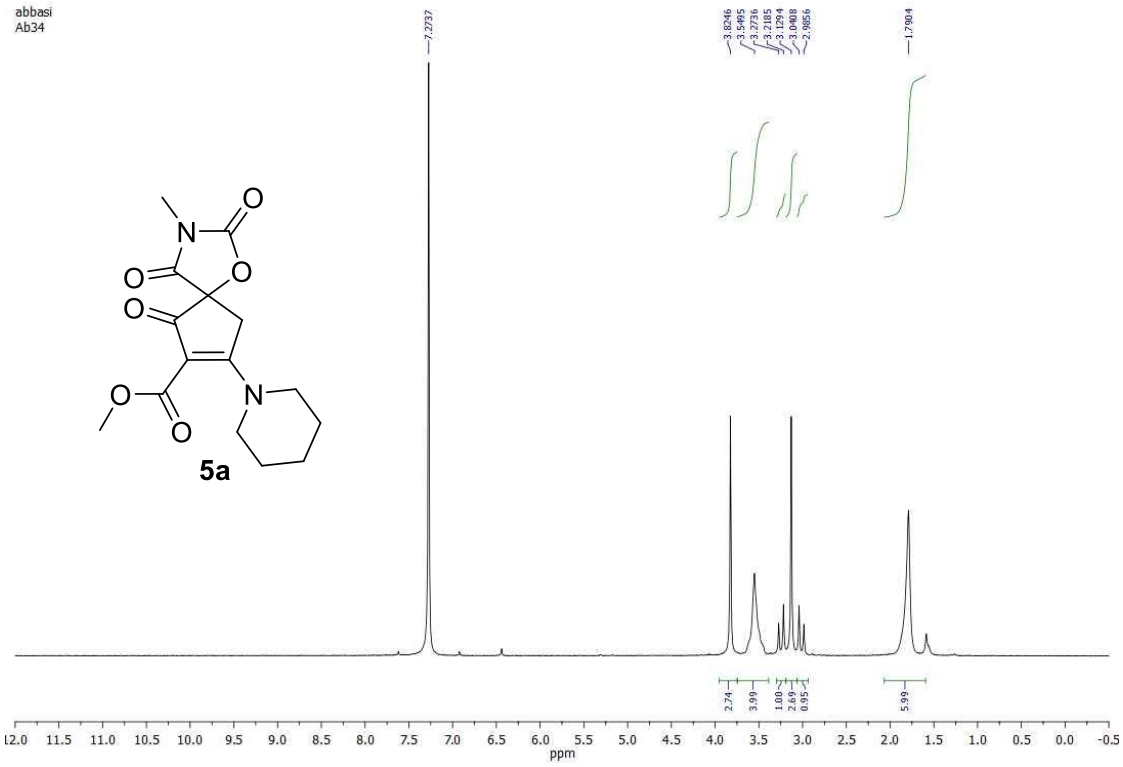
^{13}C NMR (75 MHz, $CDCl_3$) of (4j):



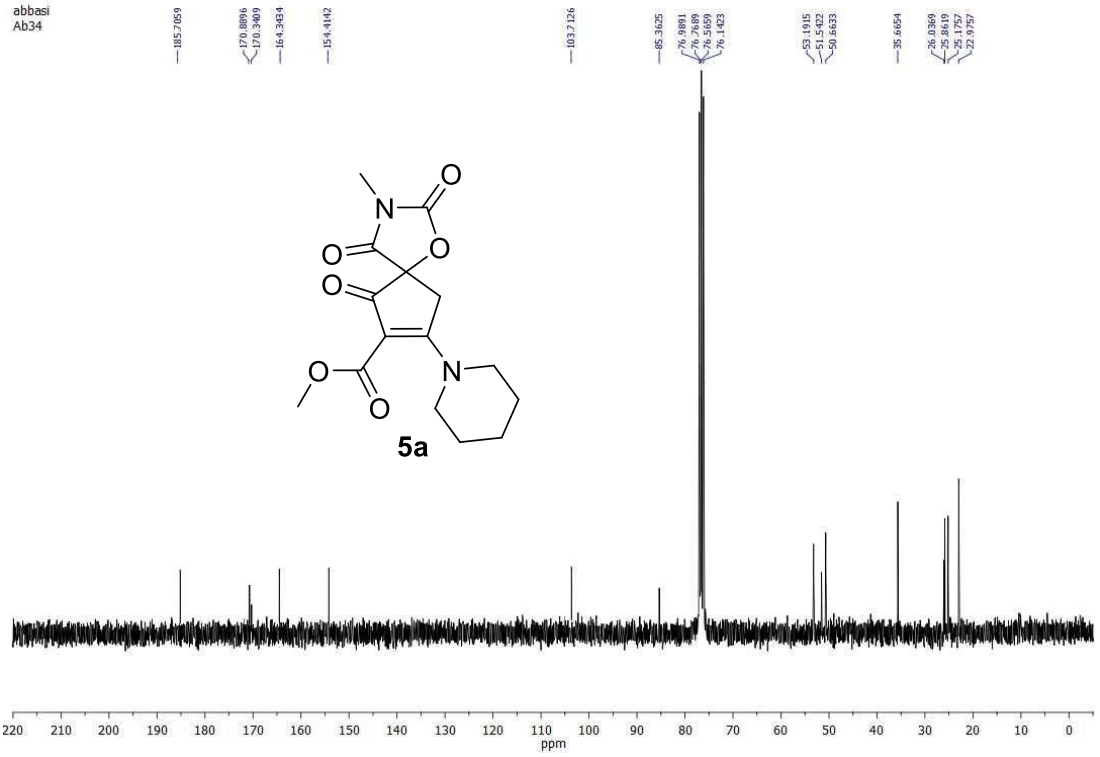
FT-IR of (5a):



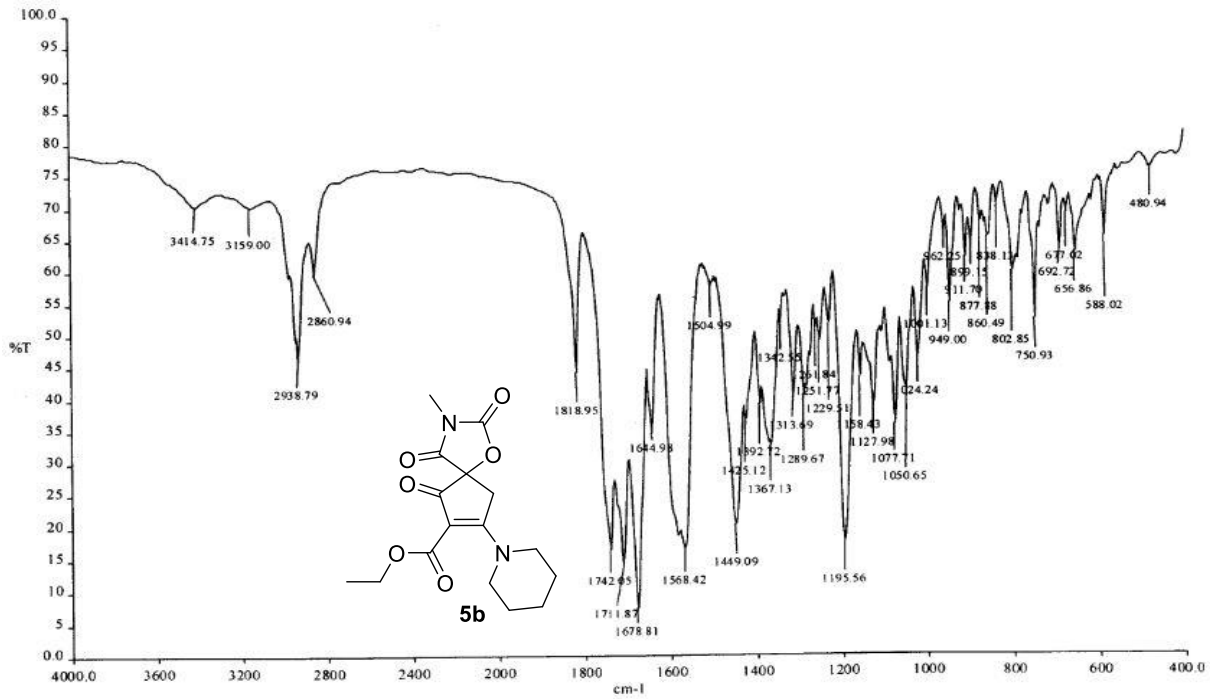
^{1}H NMR (300 MHz, $CDCl_3$) of (5a):



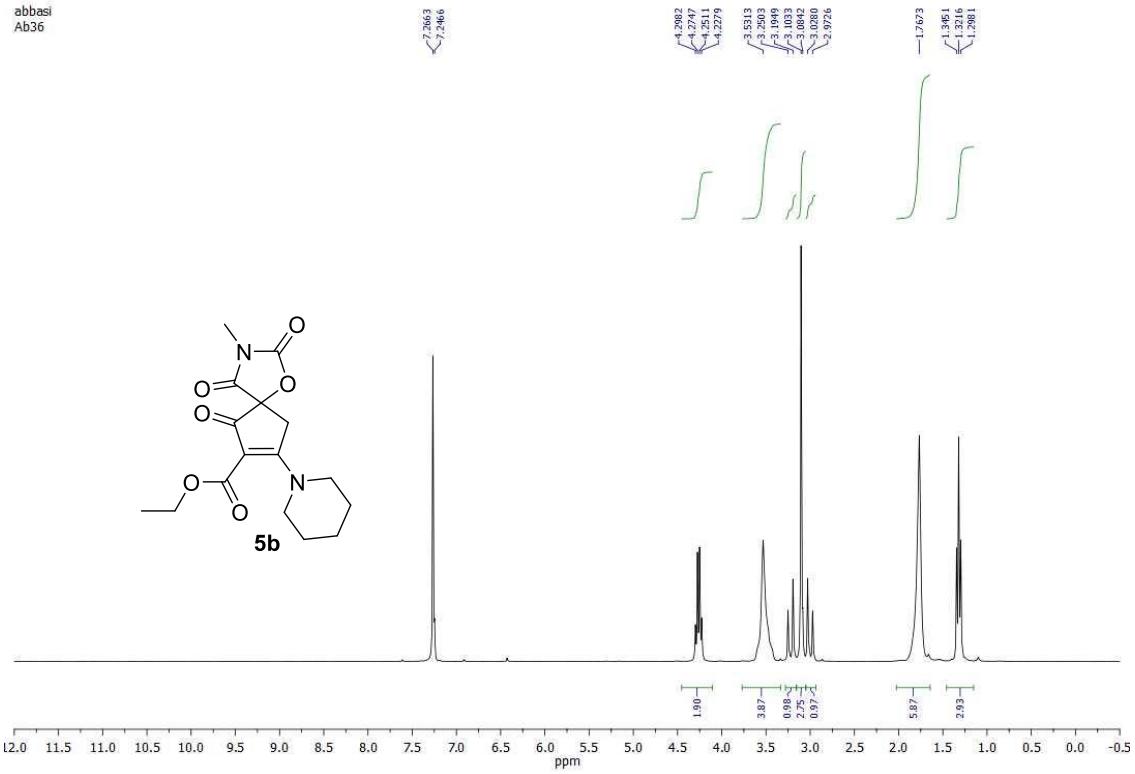
^{13}C NMR (75 MHz, $CDCl_3$) of (5a):



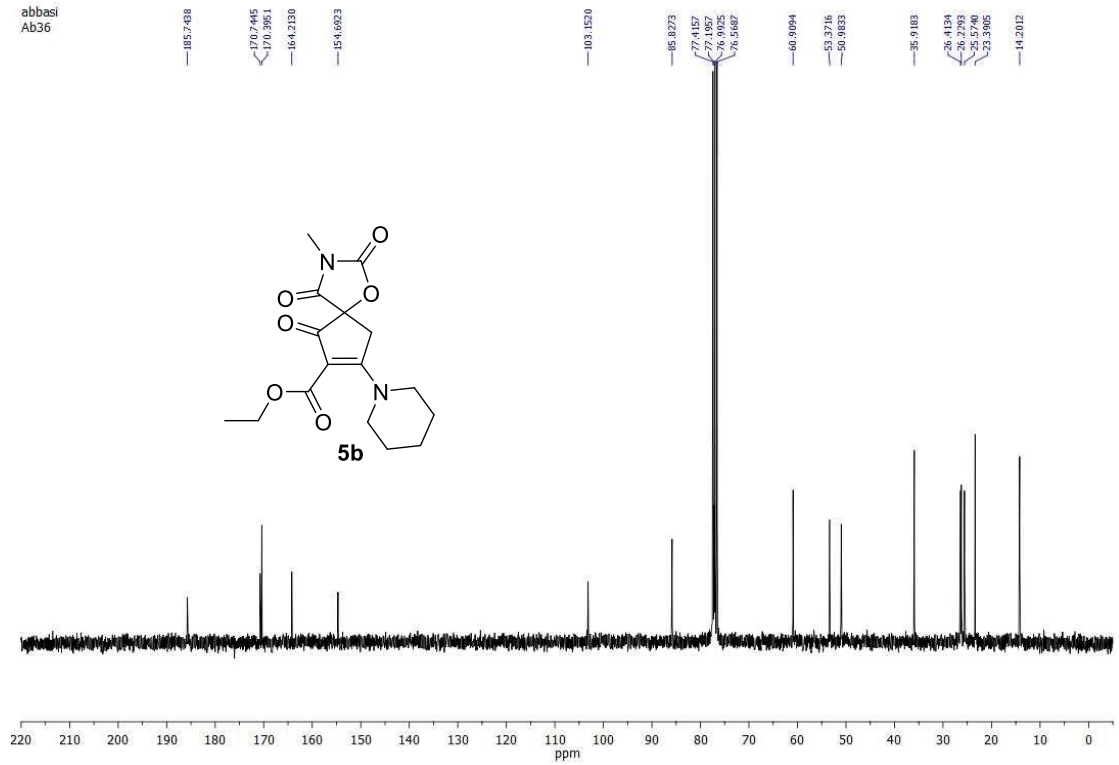
FT-IR of (5b):



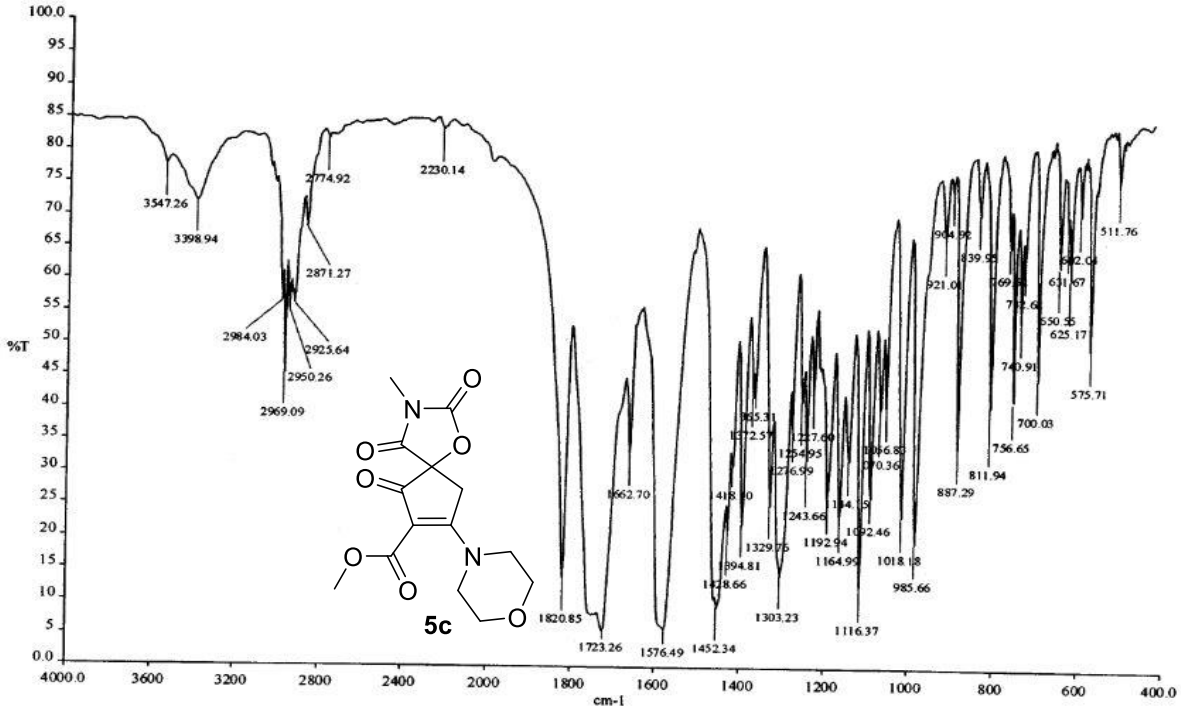
^{1}H NMR (300 MHz, $CDCl_3$) of (5b):



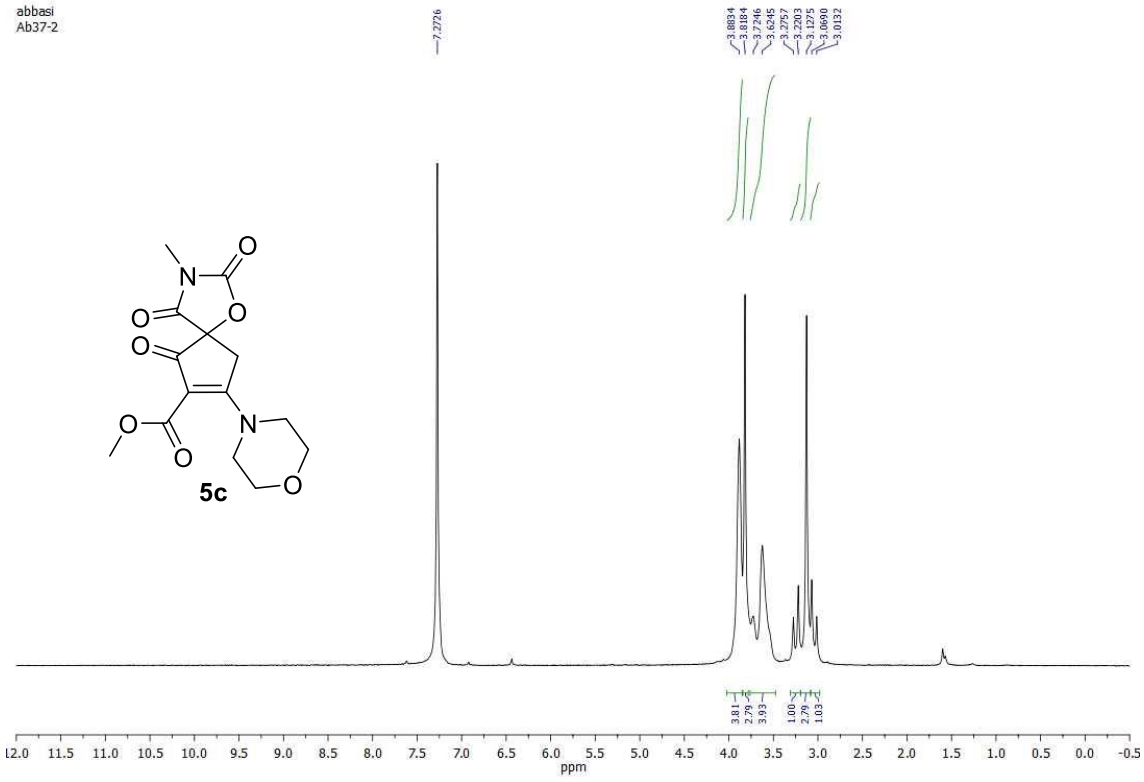
^{13}C NMR (75 MHz, $CDCl_3$) of (5b):



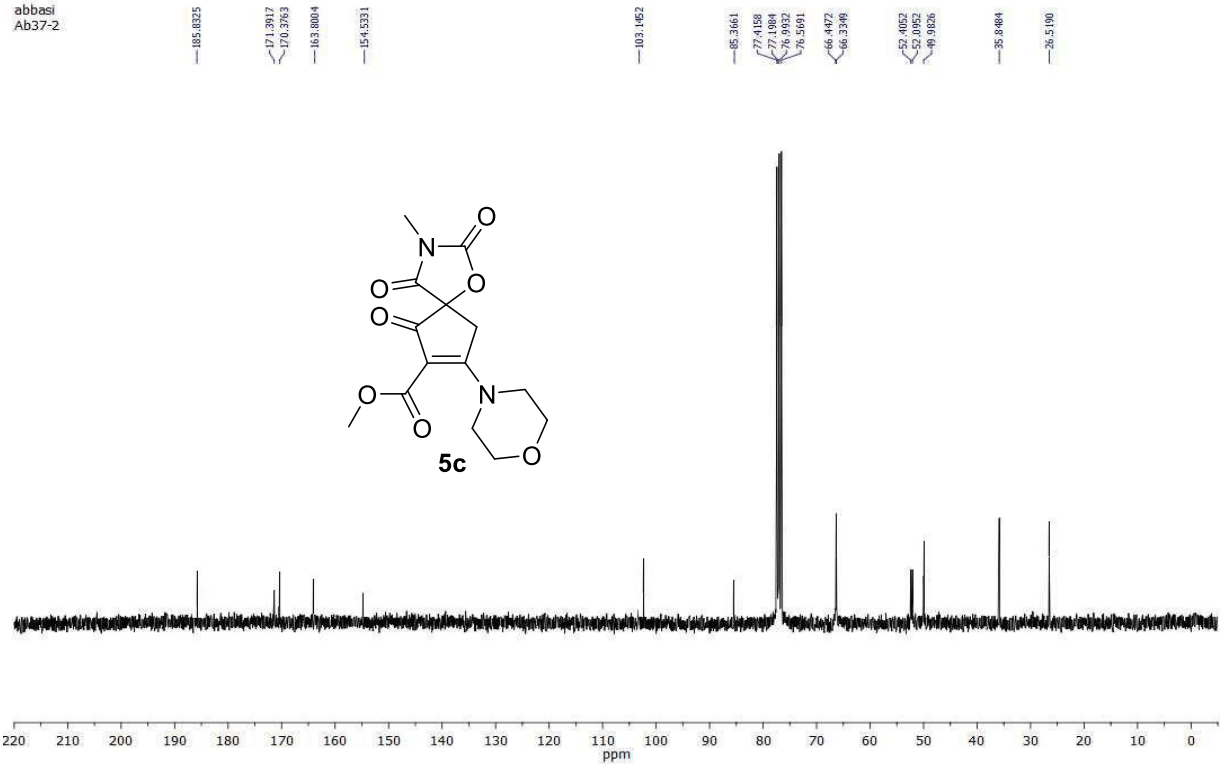
FT-IR of (5c):



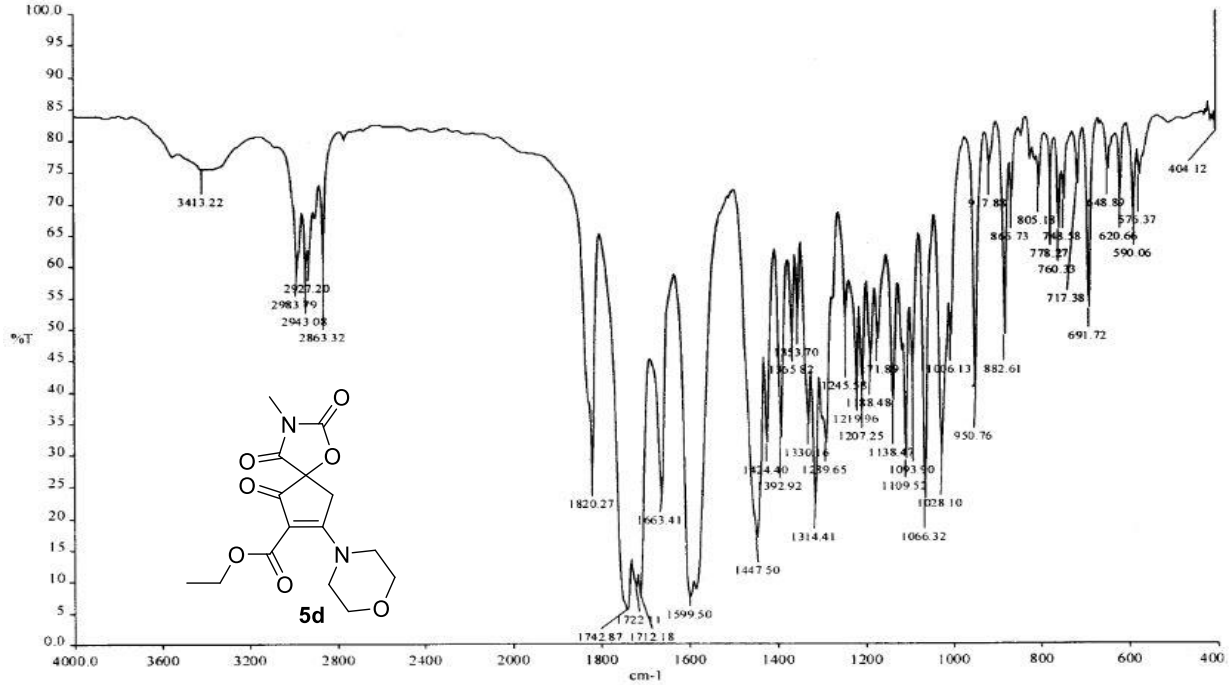
^{1}H NMR (300 MHz, $CDCl_3$) of (5c):



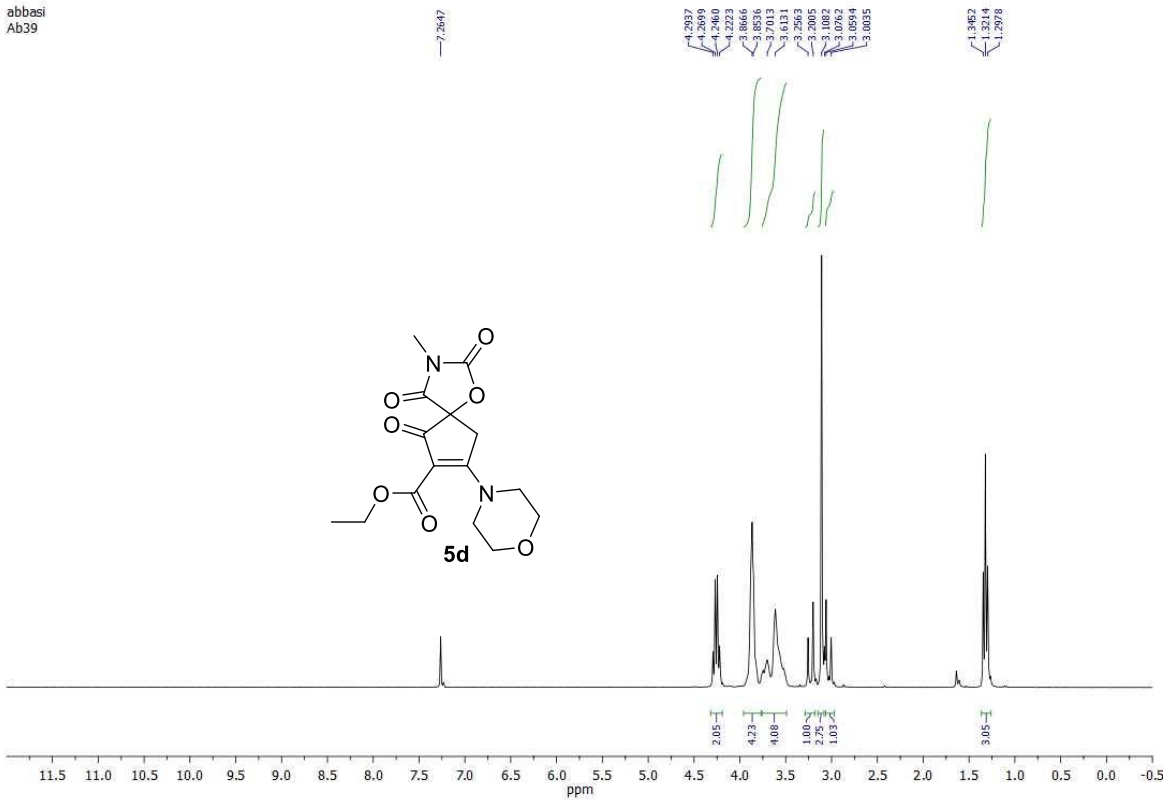
^{13}C NMR (75 MHz, $CDCl_3$) of (5c):



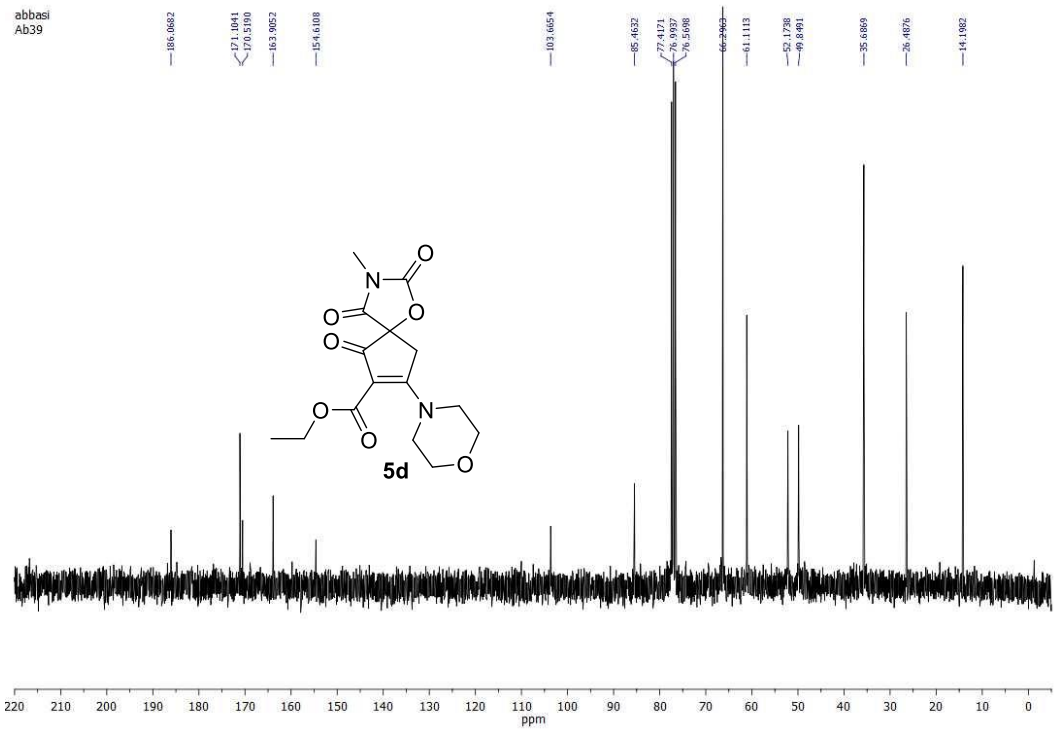
FT-IR of (5d):



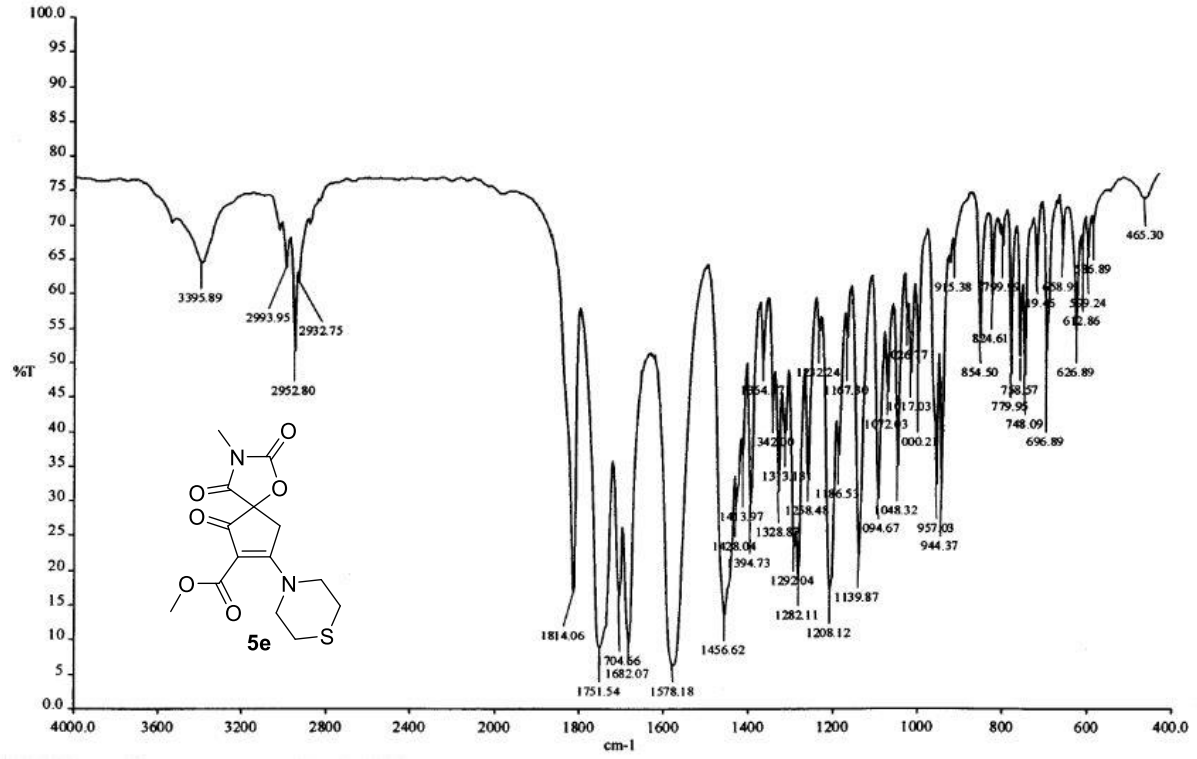
^{1}H NMR (300 MHz, $CDCl_3$) of (5d):



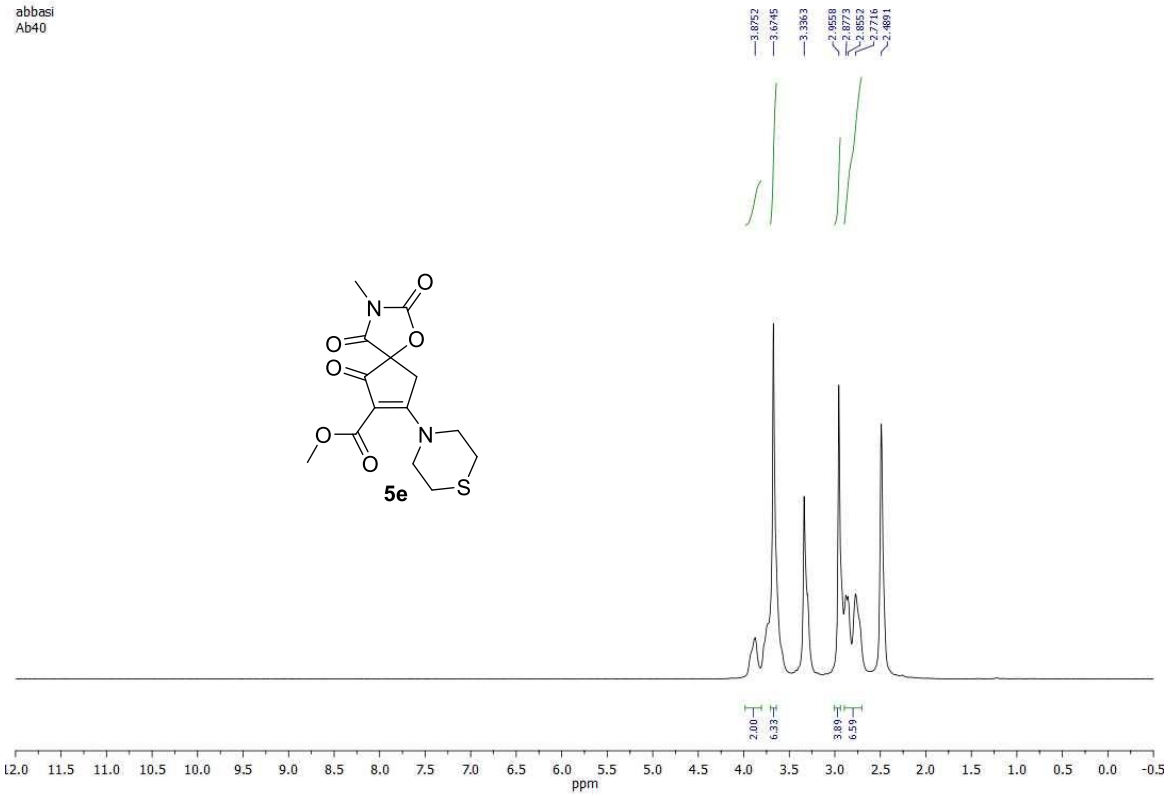
^{13}C NMR (75 MHz, $CDCl_3$) of (5d):



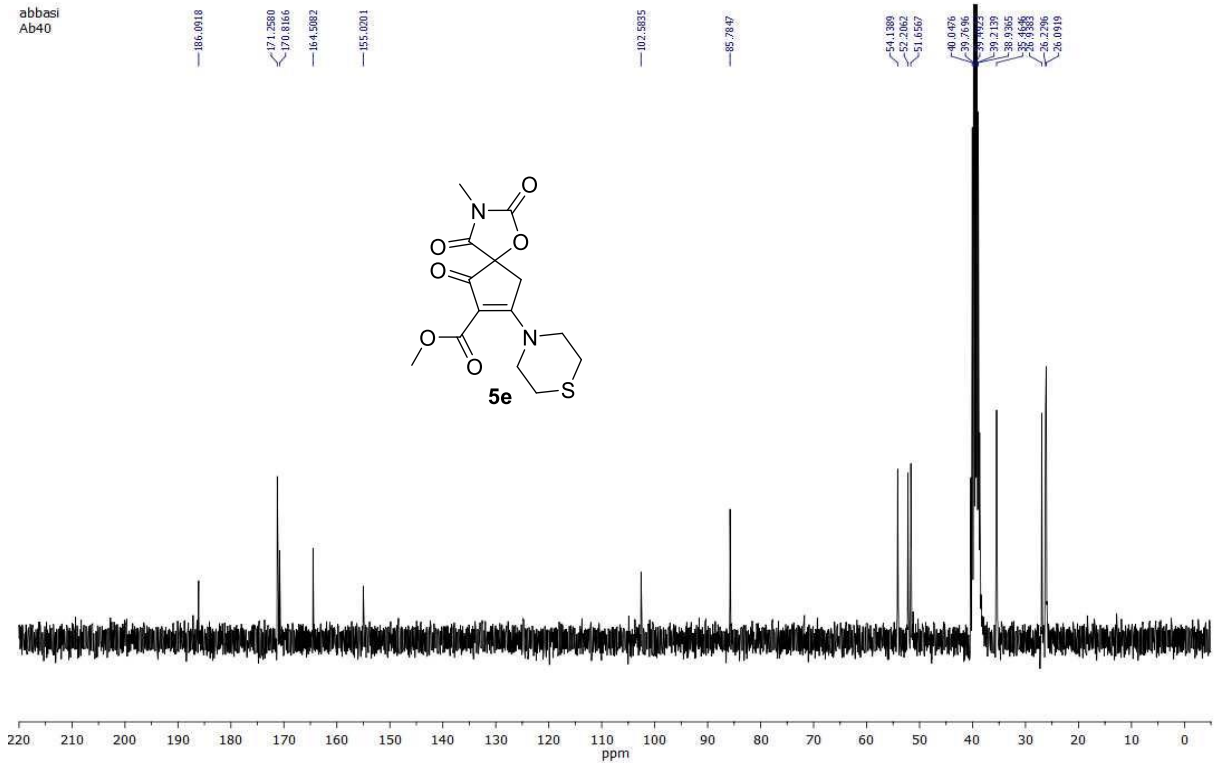
FT-IR of (5e):



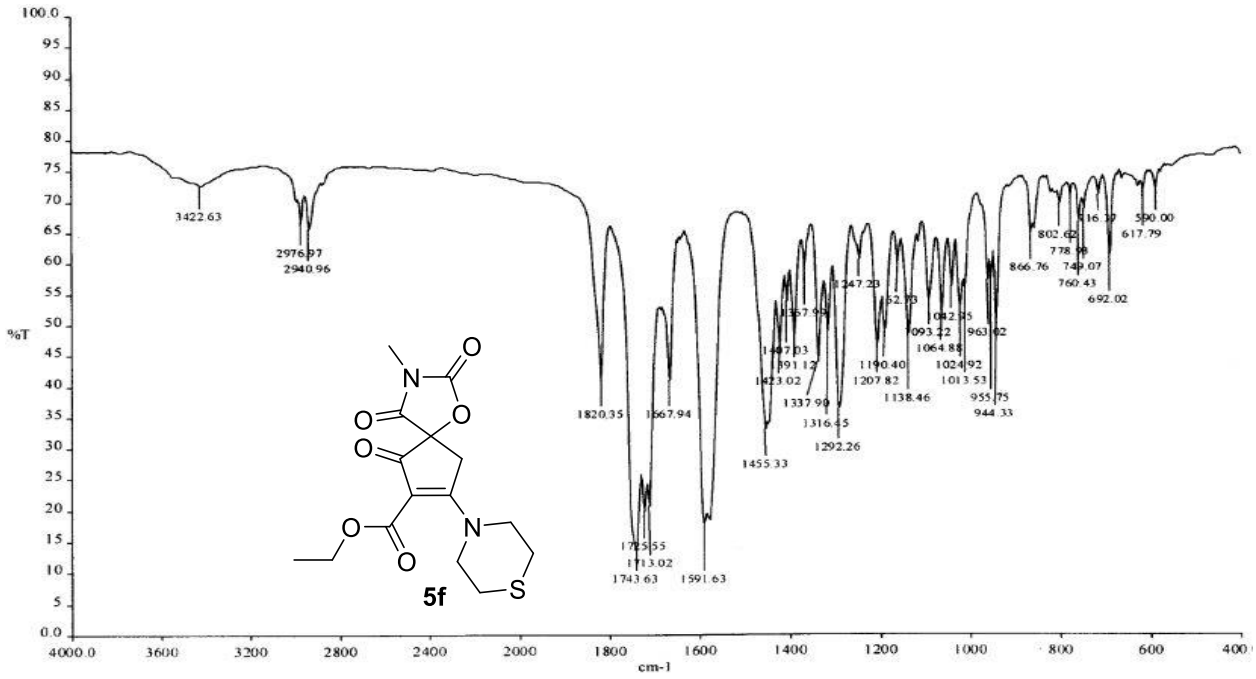
^{1}H NMR (300 MHz, DMSO-d_6) of (5e):



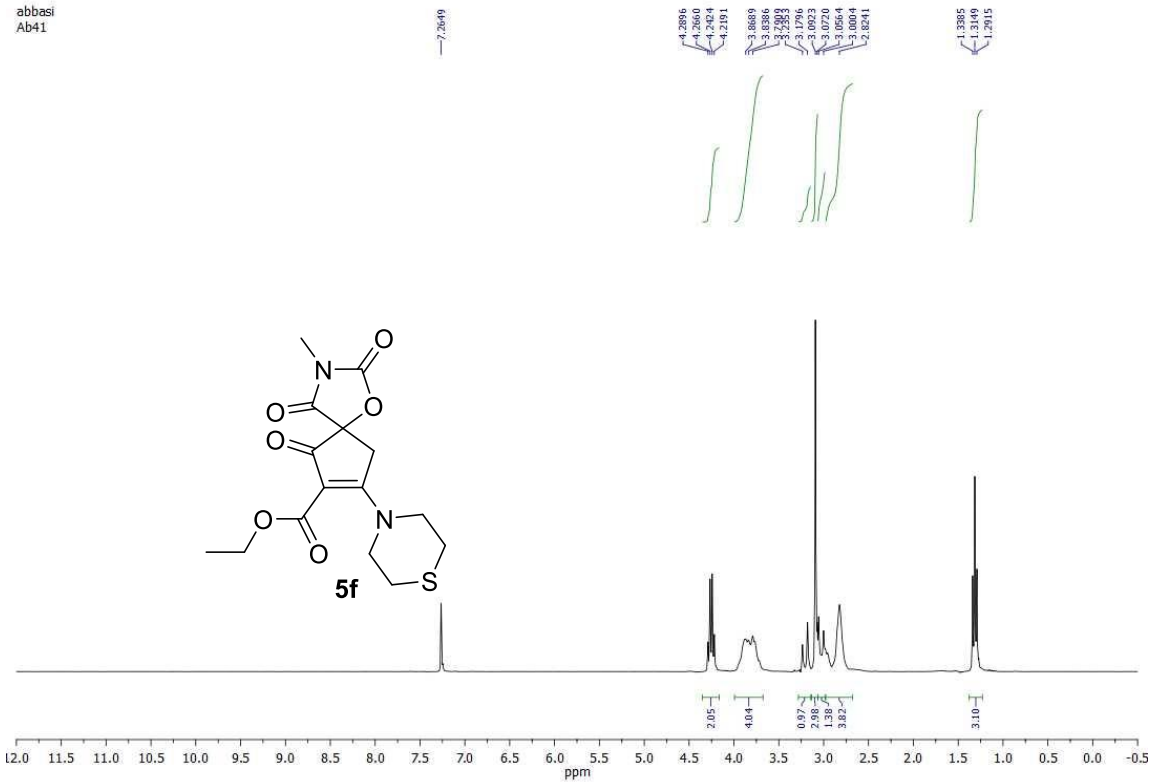
^{13}C NMR (75 MHz, DMSO-*d*$_6$) of (5e):



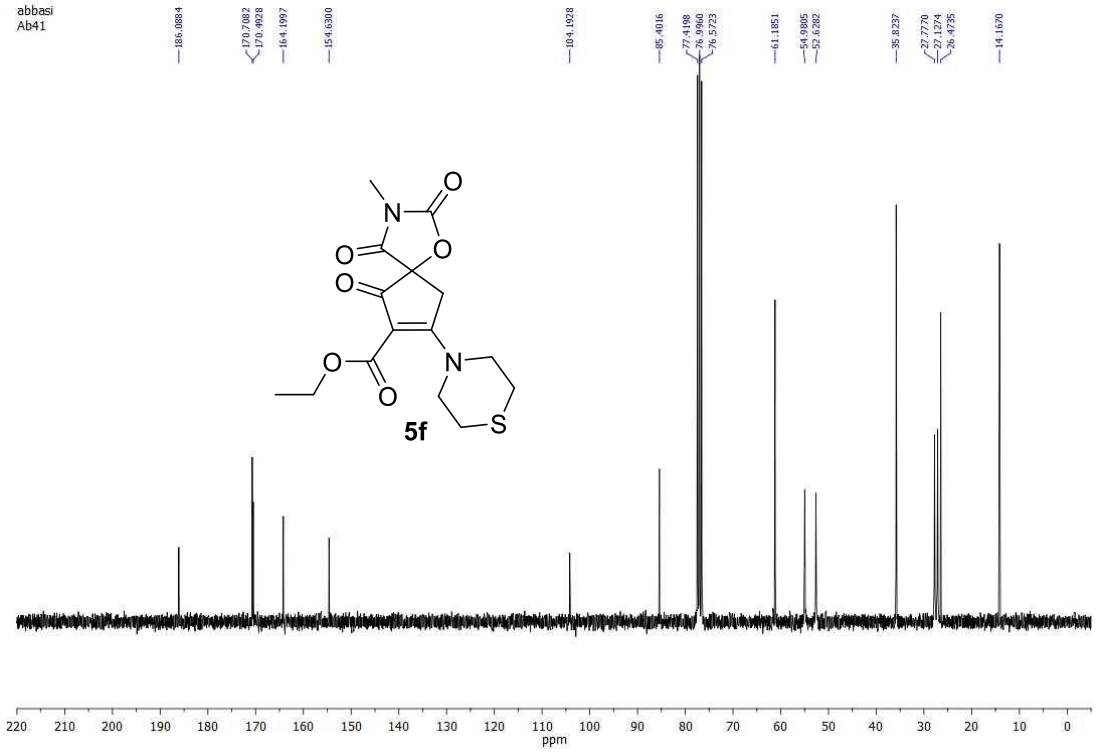
FT-IR of (5f):



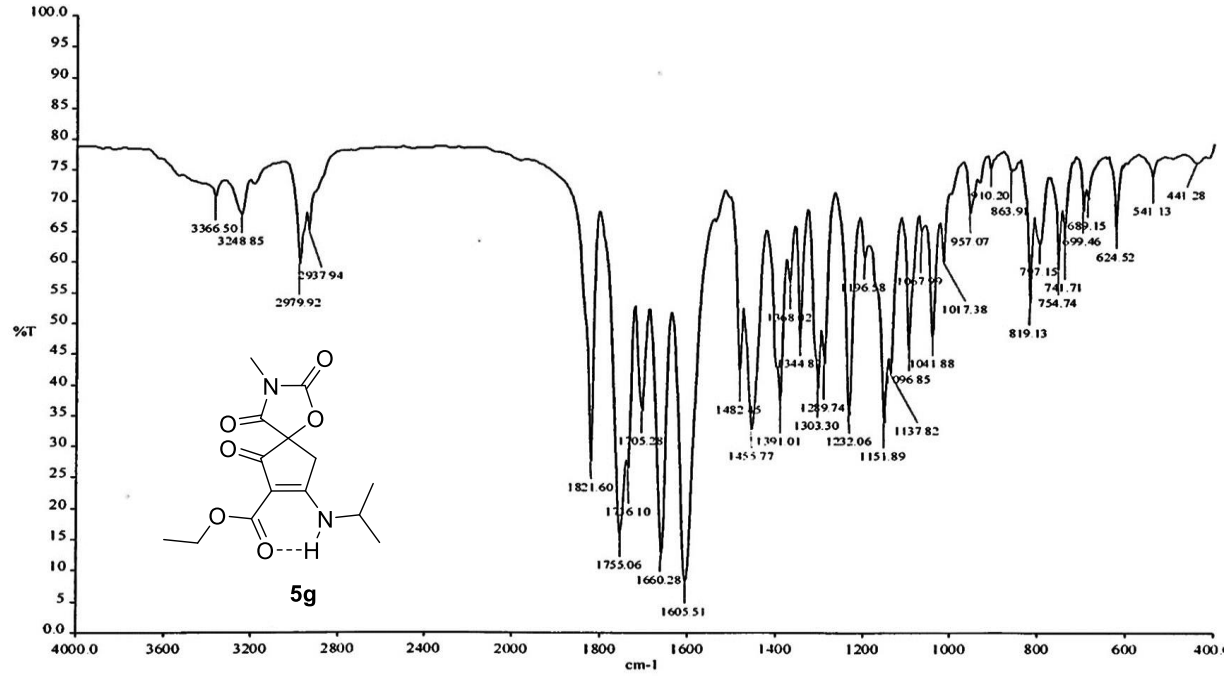
^{1}H NMR (300 MHz, $CDCl_3$) of (5f):



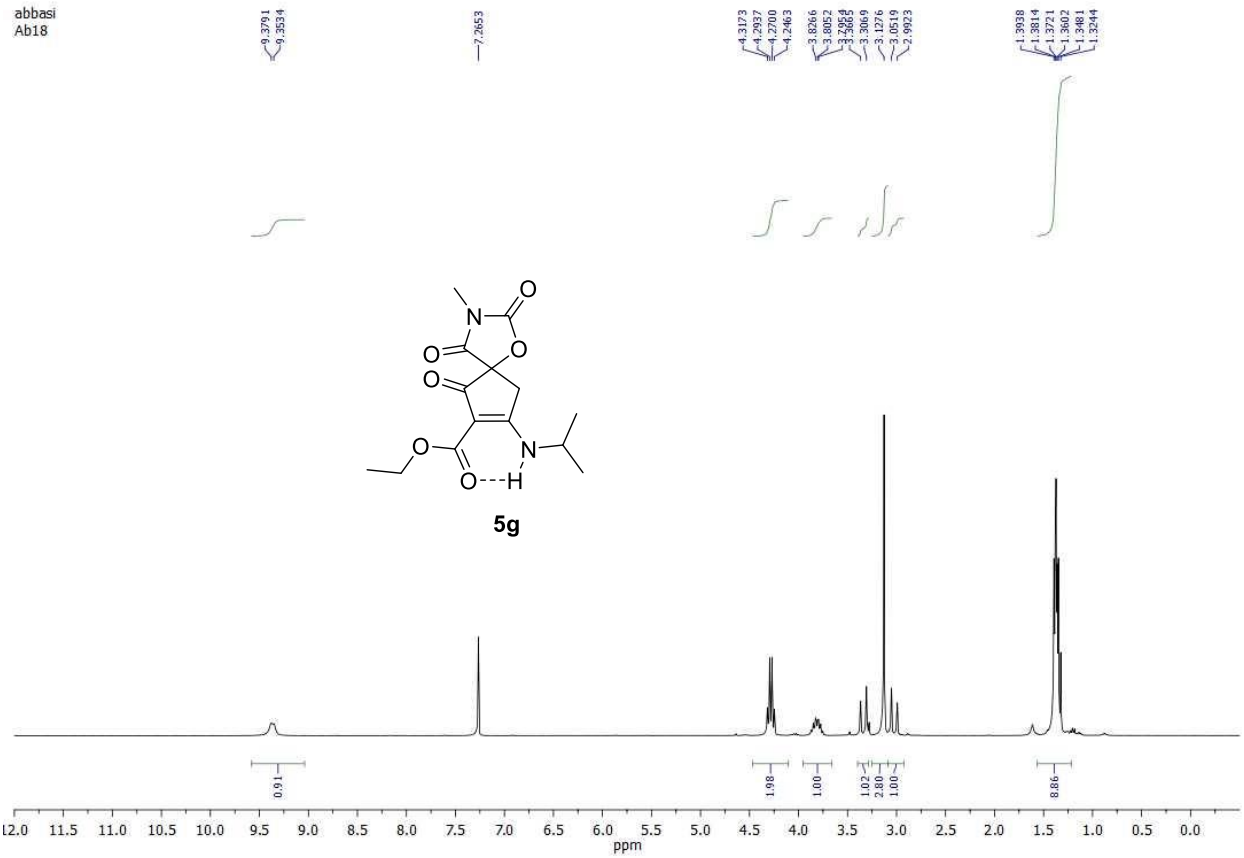
^{13}C NMR (75 MHz, $CDCl_3$) of (5f):



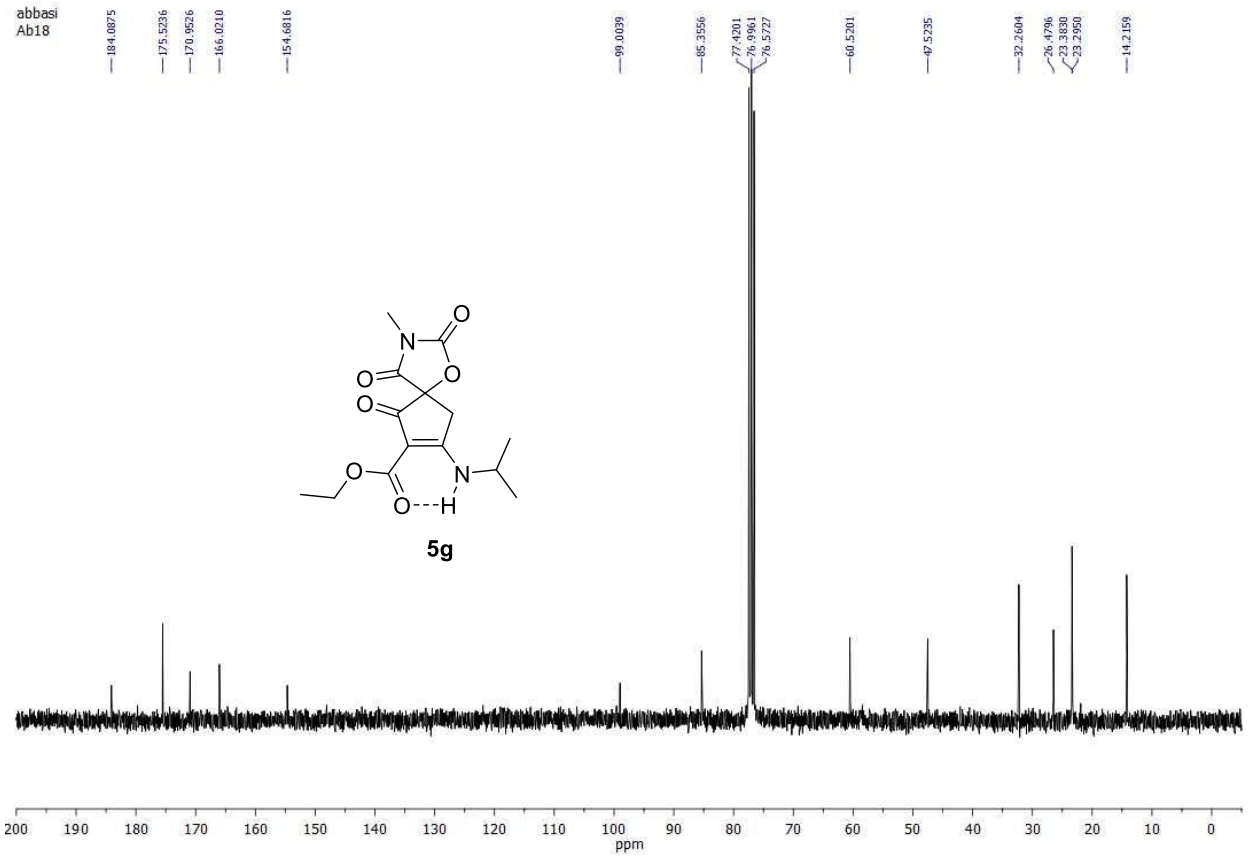
FT-IR of (5g):



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



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



*Details of single crystal X-ray analysis of **4a**:*

Suitable single crystals of compound **4a** were obtained by dissolving the compound in methanol and slow solvent evaporating method during three days at room temperature. The data collection was performed on a STOE IPDS-2T diffractometer with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) at 298 K. A high quality colorless crystal of **4a** was selected and mounted on a glass fiber as a data collector. Orientation matrices and cell constants for collecting data were attained by least-squares refinement of the diffraction data from 3158 unique reflections. Data were obtained in the range of θ = 2.4–29.4° in a series of ω scans in 1° oscillations and integrated using Stoe X-AREA [i] software. A numerical absorption correction was used with X-RED [ii] and X-SHAPE [iii] software. The data were refined for Lorentz and Polarizing effects. Solving the structure was done by direct methods and subsequent difference Fourier maps, and finally, refinement on F^2 was carried out by a full-matrix least-squares procedure using anisotropic displacement parameters [iv]. X-STEP32 crystallographic software [v] was applied for the refinements. A summary of the crystal data and refinement details for **4a** are given in Table S1. Crystallographic data (excluding structural factors) for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, no. 2034055 for **4a**.

Table S1. Crystallographic data of **4a**

Compound	**4a**
Net formula	$C_{11}H_{12}N_2O_6$
M_r/g mol^{-1}	268.23
Crystal size/mm	0.5 × 0.4 × 0.3
Crystal shape/color	Plate, Colorless
T/K	298
Radiation	Mo $K\alpha$ radiation, λ = 0.71073 Å
Diffractometer	STOE IPDS 2T diffractometer
Crystal system	Monoclinic
Space group	$P2_1/n$

a/Å	10.204(2)
b/Å	8.3564(17)
c/Å	13.753(3)
β/°	93.39(3)
V/Å^3	1170.7(4)
Z	4
Calc. density/g cm^{-3}	1.522
μ/mm^{-1}	0.13
Refls. Measured	12773
R_{int}	0.125
h, k, l	-13→13, -9→11, -18→18
Θ range	2.4–29.4
Observed refls.	3158
Refls in refinement	2196
Parameters/Restraints	175/0
F(000)	560
$R[F^2 > 2\sigma(F^2)]$	0.062
$wR(F^2)$	0.177
S	1.10
Shift/error$_{max}$	<0.001
Max/Min electron density/e Å^{-3}	0.31/-0.27

[i] Stoe & Cie, X–AREA: Program for the Acquisition and Analysis of Data, Version 1. 30; Stoe & Cie GmbH: Darmatadt, Germany, 2005.
[ii] Stoe & Cie, X–AREA: Program for the Acquisition and Analysis of Data, Version 1. 30; Stoe & Cie GmbH: Darmatadt, Germany, 2005.
[iii] Stoe & Cie, X–SHAPE: Program for Crystal Optimization for Numerical Absorption Correction, Version 2.05; Stoe & Cie GmbH: Darmatadt, Germany, 2004.

[iv] G.M. Sheldrick, SHELX97, University of Göttingen, Germany, Program for Crystal Structure Refinement, 1997.
[v] Stoe & Cie, X-STEP32: Crystallographic Package, Version 1.07b; Stoe & Cie, GmbH:, Darmstadt, Germany, 2000.