Supporting Information

Stereoselective tandem synthesis of thiazolo fused naphthyridines and thienopyridines from *o*-alkynylaldehydes via Au(III)-catalyzed regioselective 6-*endo-dig* ring closure

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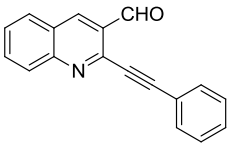
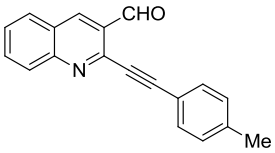
General Method: ^{1}H NMR (300 MHz, 400 MHz) and ^{13}C NMR (75 MHz, 100 MHz) spectra were recorded in $CDCl_3$. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd = doublet of doublet), coupling constants in Hertz, and integration. High-resolution mass spectra were recorded on electrospray mass spectrometer. Crystal structure analysis was accomplished on single crystal X-ray diffractometer. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates and visualized by either UV irradiation or by staining with I_2. All purchased chemicals were used as received. All melting points are uncorrected. The specific rotations were measured with Rudolph autopol II automatic polarimeter using light of 546 nm wavelength.

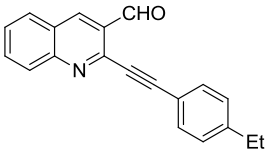
General Procedure for the Synthesis of *o*-Alkanylaldehyde 1a–o, 2, 3a–e. The *o*-alkanyl aldehyde **1a–o, 2a–e** was readily prepared by coupling reaction of corresponding *o*-halo aldehyde with terminal alkynes using reported procedures.[1] The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS) with those reported in literature.



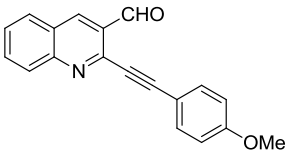
2-(Phenylethynyl)quinoline-3-carbaldehyde (1a).[1a] The product was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 10.8 (s, 1H), 8.75 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 797 (d, *J* = 8.1 Hz, 1H), 7.87 (td, *J* = 1.5 Hz, 1H), 7.72–7.61 (m, 3H), 7.48–7.42 (m, 3H); ^{13}C NMR ($CDCl_3$) δ: 190.81, 150.18, 143.91, 137.17, 133.07, 132.33, 129.88, 129.68, 129.34, 128.84, 128.62, 128.26, 126.44, 121.35, 95.55, 85.55. HRMS Calcd for $C_{18}H_{11}NO$ ($M+H^+$): 257.0841, found: 257.0852.



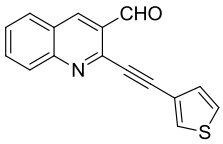
2-(*p*-Tolylethynyl)quinoline-3-carbaldehyde(1b).[1a] The product was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 8.71 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.85–7.79 (d, *J* = 8.4 Hz, 1H), 7.60–7.53 (m, 3H), 7.19–7.15 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.9, 150.2, 144.1, 140.4, 137.1, 133.0, 132.3, 129.7, 129.4, 129.3, 128.8, 128.1, 126.4, 118.3, 96.0, 85.1, 21.7. HRMS Calcd for $C_{19}H_{13}NO$ ($M+H^+$): 271.0997, found: 271.0979.



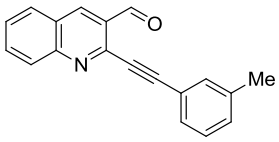
2-((4-Ethylphenyl)ethynyl)quinoline-3-carbaldehyde(1c).[1a] This compound was obtained as a light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 8.71 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 7.3 Hz, 1H), 7.61–7.57 (m, 3H), 7.25–7.21 (m, 2H), 2.67 (q, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.9, 150.1, 146.5, 144.1, 137.0, 132.9, 132.3, 129.6, 129.2, 128.7, 128.1, 128.1, 126.3, 118.4, 96.0, 85.0, 28.9, 15.2. HRMS Calcd for $C_{20}H_{15}NO$ ($M+H^+$): 285.1154, found: 285.1154.



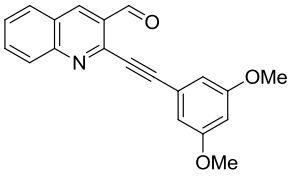
2-((4-Methoxyphenyl)ethynyl)quinoline-3-carbaldehyde (1d).[1a] The product was obtained as a orange solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.80 (s, 1H), 8.73 (s, 1H), 8.16 (d, *J* = 8.4Hz, 1H), 7.96–7.83 (m, 2H), 7.66–7.59 (m, 3H), 6.95–6.83 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.9, 160.9, 150.2, 144.2, 137.0, 134.0, 132.9, 129.6, 129.2, 128.7, 128.0, 126.3, 114.3, 113.3, 96.1, 84.2, 55.4. HRMS Calcd for $C_{19}H_{13}NO_2$ ($M+H^+$): 287.0946, found: 287.0951.



2-(Thiophen-3-ylethynyl)quinoline-3-carbaldehyde(1e).[1a] The product was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 1.5 Hz, 1H), 7.79–7.78 (m, 1H), 7.63 (t, *J* = 0.9 Hz, 1H), 7.39–7.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.8, 150.2, 143.9, 137.2, 133.1, 131.6, 130.0, 129.7, 129.3, 128.8, 128.2, 126.4, 126.0, 120.5, 90.8, 85.4. HRMS Calcd for $C_{16}H_9NOS$ ($M+H^+$): 263.0405, found: 263.0450.

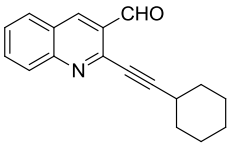


2-(*m*-Tolylethynyl)quinoline-3-carbaldehyde(1f).[1a] The product was obtained as a orange solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ :10.81 (s, 1H), 8.74 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.33–7.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.9, 150.2, 144.0, 138.4, 137.1, 133.0, 132.9, 130.8, 129.7, 129.4, 129.3, 128.8, 128.5, 128.2, 126.4, 121.1, 95.9, 85.2, 21.2. HRMS Calcd for $C_{19}H_{13}NO$ ($M+H^+$): 271.0997, found: 271.0970.

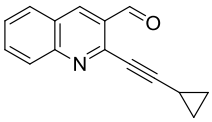


2-((3,5-Dimethoxyphenyl)ethynyl)quinoline-3-carbaldehyde(1g).[1b]

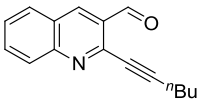
The product was obtained as a orange solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.8 (s, 1H), 8.76 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.99–7.86 (m, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 6.85 (s, 2H), 6.56 (s, 1H), 3.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.9, 160.8, 150.3, 143.9, 137.3, 133.2, 129.8, 129.4, 128.9, 128.4, 126.6, 122.6, 110.1, 103.6, 95.6, 85.1, 55.7. HRMS (ESI) Calcd for $C_{20}H_{15}NO_3$ ($M+H^+$) 317.1052, found 317.1060.



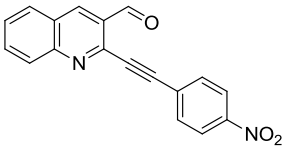
2-(Cyclohexylethynyl)quinoline-3-carbaldehyde (1h). [1b] The product was obtained as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.70 (s, 1H), 8.69 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.86–7.80 (m, 1H), 7.58 (td, *J* = 0.9 and 7.9 Hz, 1H), 2.80–2.75 (m, 1H), 2.02–1.97 (m, 2H), 1.82–1.55 (m, 5H), 1.47–1.36 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.4, 150.1, 144.6, 136.8, 132.8, 129.6, 129.2, 128.8, 127.9, 126.2, 102.0, 77.5, 32.1, 29.9, 25.7, 24.9. HRMS (ESI) Calcd for $C_{18}H_{17}NO$ ($M+H^+$) 263.1310, found 263.1311.



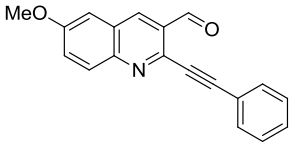
2-(Cyclopropylethynyl)quinoline-3-carbaldehyde (1i). [1c] The product was obtained as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.65 (s, 1H), 8.67 (s, 1H), 8.10 (s, 1H), 7.92–7.73 (m, 2H), 7.59 (s, 1H), 1.63–1.62 (m, 1H), 1.14–1.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.2, 150.1, 144.4, 136.8, 132.8, 129.6, 129.1, 128.8, 127.8, 126.2, 101.4, 72.8, 9.2, 0.4. HRMS (ESI) Calcd for $C_{15}H_{11}NO$ ($M+H^+$) 221.0841, found 221.0842.



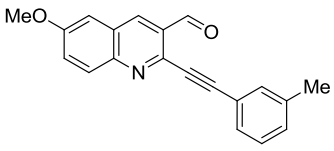
2-(Hex-1-yn-1-yl)quinoline-3-carbaldehyde (1j). [1b] The product was obtained as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.68 (s, 1H), 8.68 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.93–7.80 (m, 2H), 7.61–7.56 (m, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.73–1.66 (m, 2H), 1.57–1.47 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.0, 150.1, 144.5, 136.8, 131.8, 129.6, 129.2, 128.7, 127.9, 126.2, 98.1, 87.8, 30.2, 22.2, 19.4, 13.6. HRMS (ESI) Calcd for $C_{16}H_{15}NO$ ($M+H^+$) 237.1154, found 237.1162.



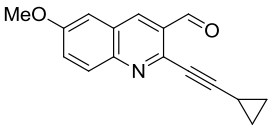
2-((4-Nitrophenyl)ethynyl)quinoline-3-carbaldehyde (1k).[1a] The product was obtained as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.71 (s, 1H), 8.76 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91–7.87 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.9, 150.0, 147.9, 142.4, 137.9, 133.4, 133.1, 132.6, 129.6, 129.4, 128.9, 128.8, 128.1, 126.6, 123.8, 92.3, 89.8. HRMS (ESI) Calcd for $C_{18}H_{10}N_2O_3$ ($M+H^+$) 302.0691, found 302.0692.



6-Methoxy-2-(phenylethynyl)quinoline-3-carbaldehyde (1l).[1a] The product was obtained as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 8.61 (s, 1H), 8.06 (d, *J* = 9.3 Hz, 1H), 7.70–7.67 (m, 2H), 7.52–7.41 (m, 4H), 7.17 (d, *J* = 2.7 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 191.0, 159.0, 146.6, 141.5, 135.3, 132.2, 130.8, 129.7, 129.1, 128.6, 127.7, 126.3, 121.6, 106.2, 94.7, 85.6, 55.8. HRMS (ESI) Calcd for $C_{19}H_{13}NO_2$ ($M+H^+$) 287.0946, found 287.0947.

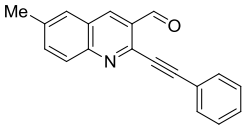


6-Methoxy-2-(*m*-tolylethynyl)quinoline-3-carbaldehyde (1m).[1a] This compound was obtained as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 8.61 (s, 1H), 8.07 (d, *J* = 9.5 Hz, 1H), 7.51–7.47 (m, 3H), 7.30–7.24 (m, 2H), 7.16 (d, *J* = 2.2 Hz, 1H), 3.95 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.0, 159.5, 146.4, 141.5, 138.3, 135.4, 132.8, 130.6, 129.3, 128.4, 127.8, 126.4, 121.1, 106.2, 85.1, 55.8, 21.2. HRMS (ESI) Calcd for $C_{20}H_{15}NO_2$ ($M+H^+$) 301.1103, found: 301.1103.

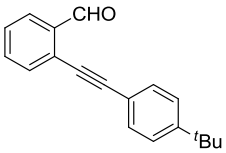


2-(Cyclopropylethynyl)-6-methoxyquinoline-3-carbaldehyde (1n).

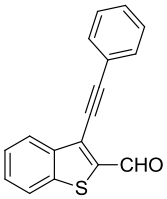
The product was obtained as a yellow needles (DCM/Ether), mp: 181–182 °C : ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.6 (s, 1H), 8.45 (s, 1H), 7.91 (d, *J* = 9.16 Hz, 1H), 7.39 (d, *J* = 8.24 Hz, 1H), 7.04 (s, 1H), 3.88 (s, 3H), 1.57–1.53 (m, 1H), 0.95–0.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 158.5, 146.3, 141.8, 134.9, 130.4, 128.8, 127.2, 126.0, 106.0, 100.2, 55.6, 9.0, 0.2. HRMS Calcd for $C_{16}H_{13}NO_2$ ($M+H^+$): 251.0946, found 251.0947



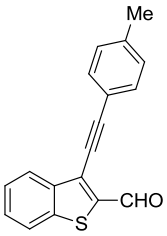
6-Methyl-2-(phenylethynyl)quinoline-3-carbaldehyde (1o). [1d] The product was obtained as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.80 (s, 1H), 8.65 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.71–7.70 (m, 4H), 7.51–7.41 (m, 4H), 7.37–7.24 (m, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.9, 148.9, 143.0, 138.6, 136.3, 135.5, 132.3, 129.7, 129.0, 128.9, 128.6, 128.3, 126.5, 121.5, 95.1, 85.6, 21.7. HRMS Calcd for $C_{19}H_{13}NO$ ($M+H^+$): 271.0997, found 271.0998.



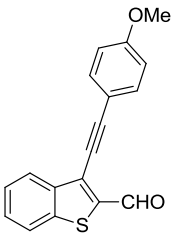
2-((4-(*tert*-Butyl)phenyl)ethynyl)benzaldehyde (2). [1e] This compound was obtained as a off white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.65 (s, 1H), 7.93 (d, *J* = 6.84 Hz, 1H), 7.63–7.61 (m, 1H), 7.55 (t, *J* = 6.88 Hz, 1H), 7.51–7.49 (m, 2H), 7.43–7.38 (m, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.6, 152.4, 135.7, 133.7, 133.1, 128.3, 127.1, 127.0, 125.5, 119.2, 96.6, 84.2, 34.8, 31.0. HRMS Calcd for $C_{19}H_{18}O$ ($M+H^+$): 262.1358, found: 262.1359.



3-(Phenylethynyl)benzo[*b*]thiophene-2-carbaldehyde(3a).[1a] This compound was obtained as a yellow brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.40 (s, 1H), 8.10–8.08 (m, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.59–7.56 (m, 2H), 7.51–7.43 (m, 2H), 7.37–7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 180.9, 139.9, 137.5, 135.8, 128.4, 126.0, 125.3, 125.1, 124.2, 122.1, 121.5, 119.8, 118.3, 95.5, 77.0. HRMS Calcd for $C_{17}H_{10}OS$ ($M+H^+$): 262.0452, found: 262.0451

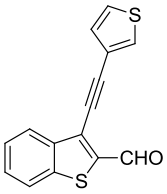


3-(*p*-Tolylethynyl)benzo[*b*]thiophene-2-carbaldehyde (3b). The product was obtained as a yellow needles (DCM/Ether), mp: 177–179 °C : ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.4 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.87–7.85 (m, 1H), 7.56–7.48 (m, 4H), 7.23 (d, *J*= 8.24 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.6, 143.0, 140.7, 139.6, 139.2, 131.8, 129.3, 128.8, 125.5, 125.1, 123.2, 118.7, 99.4, 80.0, 21.5. HRMS Calcd for $C_{18}H_{12}OS$ ($M+H^+$): 276.0609, found 276.0608.

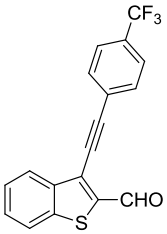


3-((4-Methoxyphenyl)ethynyl)benzo[*b*]thiophene-2-carbaldehyde (3c):[1f] The product was obtained as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (s, 1H), 8.12 (dd, *J* = 2.2, 8.1 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.57–7.49 (m, 4H), 6.93–6.91 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.6, 160.6, 142.7, 141.1, 139.4, 133.5,

128.8, 128.3, 125.5, 125.1, 123.3, 114.3, 113.8, 99.4, 79.6, 55.4. HRMS Calcd for $C_{18}H_{12}O_2SNa$ ($M+Na^+$): 315.0456, found: 315.0457.



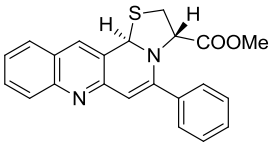
3-(Thiophen-3-ylethynyl)benzo[*b*]thiophene-2-carbaldehyde (3d).[1a] This compound was obtained as yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.12–8.10 (m, 1H), 7.86–7.84 (m, 1H), 7.69–7.67 (m, 1H), 7.53–7.48 (m, 2H), 7.37–7.35 (m, 1H), 7.28–7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 143.0, 140.5, 138.9, 130.2, 129.3, 128.3, 127.0, 125.6, 125.1, 124.5, 122.8, 120.5, 93.6, 79.7. HRMS Calcd for $C_{15}H_8OS_2$ ($M+H^+$): 268.0017, found 268.0017.



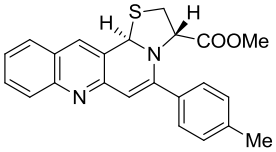
3-((4-(Trifluoromethyl)phenyl)ethynyl)benzo[*b*]thiophene-2-carbaldehyde (3e).[1a] This compound was obtained as a dark brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.40 (s, 1H), 8.09–8.07 (m, 1H), 7.84 (d, J = 7.3 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.53–7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.1, 144.2, 141.0, 139.2, 132.2, 129.0, 126.6, 125.8, 125.60, 125.57, 124.9, 123.4, 97.1, 82.6. HRMS Calcd for $C_{18}H_9F_3OS$ ($M+H^+$): 330.0326, found 330.0326.

General procedure for the synthesis of Benzo[*b*] thiazolo[2,3-*f*][1,6]naphthyridine 5a–o. An oven-dried Schlenk tube with a Teflon screw valve was charged with 1.1 equiv of *L*(-) Cysteine methyl ester hydrochloride **4,** EDC (2.0 mL), 0.5 mmol of the 2-alkanylaldehyde **1a–o**, **2**, **3a–e**, and $AuCl_3$ (10 mol %). The reaction mixture was heated to 80 °C until 2-alkanylaldehyde **1a–o**, **2**, **3a–e** had been completely consumed (as determined by TLC) and was allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate

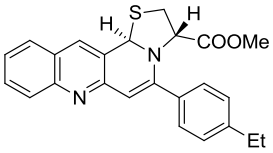
(10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel.



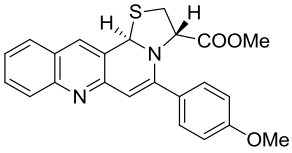
(3S,12*b*R)-methyl 5-phenyl-3,12*b*-dihydro-2H-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5a). The product was obtained as a yellow needles (DCM/Ether), mp: 177–179 °C; $[\alpha]_D^{27.5}$ = -357.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.74–7.71 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.39–7.37 (m, 4H), 6.39 (s, 1H), 4.29–4.27 (m, 1H), 3.82 (s, 3H), 3.36–3.32 (m, 1H), 3.12–3.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 147.1, 142.5, 137.8, 132.2, 131.1, 129.8, 129.3, 128.9, 128.4, 127.7, 127.3, 126.9, 121.9, 96.4, 87.4, 67.4, 64.9, 52.7, 37.7. HRMS Calcd for $C_{22}H_{18}N_2O_2S$ ($M+H^+$): 374.1089, found 374.1088.



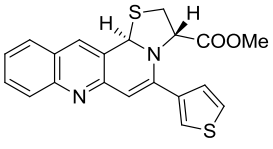
(3S,12*b*R)-methyl5-(*p*-tolyl)-3,12*b*-dihydro-2H-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5b). The product was obtained as a yellow needles (DCM/Ether), mp: 173–175 °C; $[\alpha]_D^{27}$ = -317.1 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.80 (td, *J* = 6.6 and 1.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 6.88–6.83 (m, 4H), 6.51 (s, 1H), 5.84 (s, 1H), 5.55 (td, *J* = 5.1 and 1.5 Hz, 1H), 3.69 (s, 3H), 3.54–3.49 (m, 1H), 3.32–3.27 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.3, 162.8, 161.9, 149.8, 136.5, 135.3, 134.8, 132.4, 131.7, 129.9, 129.8, 129.3, 129.2, 128.9, 127.8, 127.3, 127.2, 70.0, 52.6, 37.3, 21.0. HRMS Calcd for $C_{23}H_{20}N_2O_2S$ ($M+H^+$): 388.1245, found 388.1244.



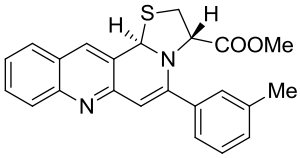
(3S,12*b*R)-Methyl-5-(4-ethylphenyl)-3,12*b*-dihydro-2H-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5c). The product was obtained as a yellow needles (DCM/Ether), mp: 155–157 °C; $[\alpha]_D^{27}$ = -289.6 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.11–8.09 (m, 1H), 7.81–7.76 (m, 1H), 7.72–7.68 (m, 1H), 7.66–7.63 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.55–7.48 (m, 1H), 7.21–7.18 (m, 2H), 6.37 (s, 1H), 4.27 (t, *J* = 6.9 Hz, 1H), 3.81 (s, 3H), 3.33–3.31 (m, 1H), 3.11–3.07 (m, 1H), 2.66 (q, *J* = 6.9 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 146.1, 146.0, 137.8, 134.0, 132.2, 131.2, 130.4, 129.8, 128.8, 128.7, 127.5, 128.0, 127.7, 127.3, 126.9, 119.0, 67.4, 64.9, 52.7, 37.8, 28.9, 15.2. HRMS Calcd for $C_{24}H_{22}N_2O_2S$ ($M+H^+$): 402.1402, found 402.1403.



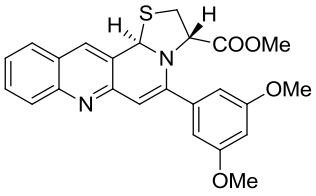
(3S,12*b*R)-Methyl-5-(4-methoxyphenyl)-3,12b-dihydro-2H-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5d). The product was obtained as a yellow needles (DCM/Ether), mp: 171–172 °C; $[\alpha]_D^{27}$ = -319.4 (c 0.1, MeOH): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.75 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.68–6.60 (m, 3H), 5.93 (s, 1H), 5.60 (t, *J* = 5.4 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.58–3.52 (m, 1H), 3.40–3.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.3, 162.8, 161.9, 158.5, 149.8, 135.4, 134.7, 131.7, 130.5, 130.0, 129.8, 129.2, 127.9, 127.4, 127.1, 113.6, 70.0, 55.1, 52.6, 36.8. HRMS Calcd for $C_{23}H_{20}N_2O_3S$ ($M+H^+$): 404.1195, found 404.1195.



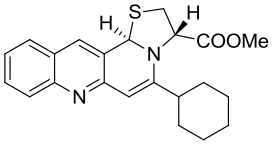
(3S,12*b*R)-Methyl-5-(thiophen-3-yl)-3,12*b*-dihydro-2*H*-benzo[b]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5e). The product was obtained as a yellow needles (DCM/Ether), mp: 159–161 °C; $[\alpha]_D^{30}$ = -276.7 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 3.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.77–7.74 (m, 2H), 7.66–7.63 (m, 1H), 7.51–7.48 (m, 1H), 7.36–7.34 (m, 1H), 7.31–7.28 (m, 1H), 6.36–6.33 (m, 1H), 4.27–4.25 (m, 1H), 3.79 (s, 3H), 3.34–3.30 (m, 1H), 3.24–3.22 (m, 1H), 3.11–3.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 147.1, 142.6, 137.6, 131.2, 131.0, 129.9, 129.8, 128.8, 127.6, 127.3, 126.9, 125.5, 121.1, 91.8, 87.1, 67.4, 64.8, 52.7, 37.7. HRMS Calcd for $C_{20}H_{16}N_2O_2S_2$ ($M+H^+$): 380.0653, found 380.0654.



(3S,12bR)-Methyl-5-(*m*-tolyl)-3,12*b*-dihydro-2H benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5f). The product was obtained as a yellow needles (DCM/Ether), mp: 172–174 °C; $[\alpha]_D^{27}$ = -319.1 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 8.10 (d, *J* = 7.68 Hz, 1H), 7.83–7.78 (m, 1H), 7.73–7.67 (m, 1H), 7.56–7.49 (m, 4H), 7.30–7.26 (m, 1H), 7.22–7.20 (m, 1H), 6.41 (s, 1H), 4.30 (t, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 3.38–3.34 (m, 1H), 3.14–3.09 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 147.1, 142.6, 138.1, 137.8, 134.0, 132.6, 131.1, 130.3, 129.7, 129.3, 128.8, 128.2, 127.6, 127.3, 126.9, 121.7, 96.7, 87.1, 67.4, 64.9, 52.7, 37.8, 21.0. HRMS Calcd for $C_{23}H_{20}N_2O_2S$ ($M+H^+$): 388.1245, found 388.1247.

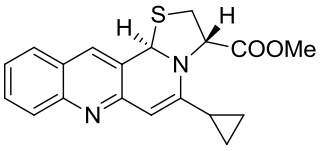


(3S,12*b*R)-Methyl-5-(3,5-dimethoxyphenyl)-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5g). The product was obtained as a yellow needles (DCM/Ether), mp: 179–182 °C; $[\alpha]_D^{27}$ = -325.1 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (s, 1H), 7.99–7.97 (m, 1H), 7.68–7.66 (m, 1H), 7.59–7.55 (m, 1H), 7.44–7.40 (m, 2H), 6.80 (t, *J* = 2.28Hz, 1H), 6.74 (t, *J* = 2.28Hz, , 1H), 6.40 (d, *J* = 2.28Hz, 1H),6.28 (s, 1H), 4.19 (t, *J* = 5.96 Hz, 1H), 3.68 (s, 9H), 3.27–3.23 (m, 1H), 3.09–2.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 156.49, 156.46, 143.1, 133.7, 127.3, 125.8, 124.7, 123.6, 123.4, 123.0, 119.1, 105.9, 98.2, 92.3, 82.9, 63.4, 60.8, 51.4, 48.6, 33.7, 25.6. HRMS Calcd for $C_{24}H_{22}N_2O_4S$ ($M+H^+$): 434.1300, found 434.1302

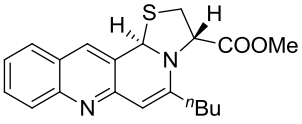


(3S,12*b*R)-Methyl-5-cyclohexyl-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate(67:33)(Mixture) (dr=68:32) (5h). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -301.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 0.5H)(minor), 8.13 (s, 1H)(major), 8.05–8.00 (m, 1.7H)(major + minor), 7.77–7.72 (m, 1.7H) (major + minor), 7.67–7.60 (m, 1.7H) (major + minor), 7.50–7.44 (m, 1.8H) (major + minor), 6.26 (s, 1H) (major), 6.08 (s, 0.5H) (minor), 4.27–4.23 (m, 1H) (major), 4.04–4.02 (m, 0.5H) (minor), 3.81 (s, 3H) (major), 3.79 (s, 1.5H) (minor), 3.48–3.43 (m, 0.5H)(minor), 3.31–3.27 (m, 1H) (major), 3.15–3.10 (m, 0.6H) (minor), 3.08–3.05 (m, 1H) (major), 2.74–2.69 (m, 1.6H) (major + minor), 1.98–1.92 (m, 3H) (major + minor), 1.79–1.76 (m, 3H) (major + minor), 1.67–1.62 (m, 3H) (major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 171.5, 147.5, 146.9, 143.2, 143.1, 137.6, 133.8, 133.2, 133.2, 130.8, 130.1, 129.5, 128.8, 128.7, 127.6, 127.1, 126.9, 126.7, 102.7,

100.7, 79.1, 78.7, 68.6, 67.5, 65.7, 64.8, 52.7, 52.6, 38.7, 37.5, 32.0, 30.0, 29.9, 25.7, 25.0, 24.9. HRMS Calcd for $C_{22}H_{24}N_2O_2S$ ($M+H^+$): 380.1558, found 380.1559.

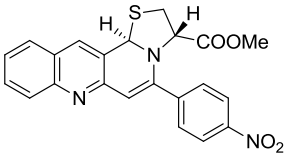


(3S,12*b*R)-Methyl-5-cyclopropyl-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5i). The product was obtained as a yellow needles (DCM/Ether), mp: 162–165 °C; $[\alpha]_D^{27.5}$ = -275.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 8.02 (d, *J* = 8.76 Hz, 1H), 7.75 (d, *J* = 8.04 Hz, 1H), 7.67–7.63 (m, 1H), 7.51–7.47 (m, 1H), 6.25 (s, 1H), 4.27 (t, *J* = 6.62 Hz, 1H), 3.84 (s, 3H), 3.33–3.30 (m, 1H), 3.10–3.06 (m, 1H), 1.60–1.58 (m, 1H), 1.04–0.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.4, 147.5, 146.8, 142.9, 137.4, 134.0, 133.0, 132.9, 130.9, 130.2, 129.5, 128.6, 128.57, 127.6, 127.55, 127.1, 126.9, 126.6, 102.1, 100.2, 74.4, 74.0, 68.7, 67.4, 65.7, 64.8, 52.6, 52.57, 38.8, 37.6, 9.15, 9.1, 9.0, 8.8, 8.7, 0.4. HRMS Calcd for $C_{19}H_{18}N_2O_2S$ ($M+H^+$): 338.1089, found 388.1089

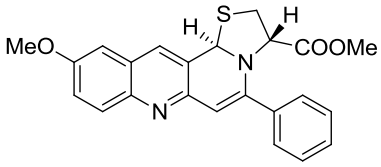


(3S,12*b*R)-Methyl-5-butyl-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (dr=67:33) (5j). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -301.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 0.5H)(minor), 8.08 (s, 1H)(major), 7.98–7.93 (m, 1.5H)(major + minor), 7.83–7.79 (d, J = 12.84, 0.3H) (minor), 7.69–7.63 (m, 1.9H) (major + minor), 7.59–7.53 (m, 1.9H) (major + minor), 7.51–7.45 (m, 0.5H) (minor), 7.41–7.35 (m, 1.5H) (major + minor), 7.26–7.21 (m, 0.5H) (minor) 6.18 (s, 1H) (major), 5.97 (s, 0.4H) (minor), 4.19–4.16 (m, 1H) (major), 3.98–3.95 (m, 0.6H) (minor), 3.72–3.70 (m, 4.6H) (major + minor), 3.41–3.31 (m, 1H) (major), 3.24–3.19 (m, 1H) (major), 3.08–2.96 (m, 2H) (major + minor), 2.47–2.42 (q, *J* = 14.2 Hz, 7.32 Hz 2.8H) (major + minor) 1.61–1.53(m, 2.42H) (major + minor),

1.45–1.34 (m, 2.5H) (major + minor), 0.87–0.84 (m, 4H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.3, 147.3, 146.7, 142.8, 137.4, 134.0, 132.8, 132.4, 130.9, 130.1, 129.4, 128.4, 127.4, 127.0, 126.8, 126.5, 124.8, 102.6, 98.8, 97.0, 78.9, 68.6, 67.2, 65.6, 64.6, 52.8, 52.5, 52.4, 38.7, 37.4, 30.0, 21.8, 19.3, 13.7, 13.4, 0.8. HRMS Calcd for $C_{20}H_{22}N_2O_2S$ ($M+H^+$): 354.1402, found 354.1401.

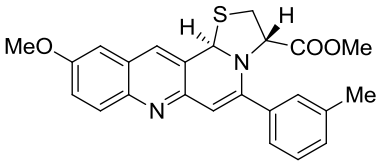


(3S,12*b*R)-Methyl-5-(4-nitrophenyl)-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5k). The product was obtained as a yellow needles (DCM/Ether), mp: 178–180 °C ; $[\alpha]_D^{27.5}$ = -345.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16–8.11 (m, 4H), 7.84 (d, *J* = 8.04 Hz, 1H), 7.75–7.69 (m, 3H), 7.55 (t, *J* = 7.32 Hz, 1H), 6.91 (s, 1H), 6.38 (s, 1H), 4.83 (d, *J* = 5.88 Hz, 1H), 3.86 (s, 3H), 3.29–3.26 (m, 1H), 2.98–2.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 154.0, 149.1, 147.0, 145.2, 143.3, 132.1, 130.6, 130.5, 130.3, 129.5, 128.8, 128.2, 127.2, 99.9, 70.3, 68.1, 53.1, 37.2, 35.9. HRMS Calcd for $C_{22}H_{17}N_3O_4S$ ($M+H^+$): 419.0940, found 419.0943.

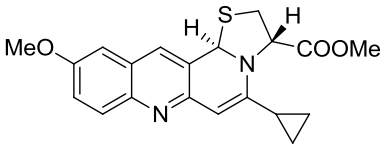


(3S,12*b*R)-Methyl-10-methoxy-5-phenyl-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (dr=67:33) (5l). The product was obtained as a yellow needles (DCM/Ether), mp: 179–181 °C; $[\alpha]_D^{27.5}$ = -355.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 0.5H)) (minor), 8.07 (s, 1H)) (major),, 7.92 (t, *J* = 9.16 Hz, 1.64H)) (major + minor), 7.66–7.64 (m, 2H))(major + minor), 7.60–7.58 (m, 1.2H) (major + minor), 7.33–7.29 (m, 5H) (major + minor),, 7.28–7.24 (m, 1H))(major + minor),, 6.99–6.96 (m, 1.5H))(major + minor),, 6.30 (s, 1H))(major),6.07(s, 0.4H) (minor), 4.22 (t, *J* = 7.08 Hz, 1H)) (major), 4.06–4.02 (m, 0.5H)) (minor),, 3.84 (s, 1.5H)) (minor),, 3.82 (m,

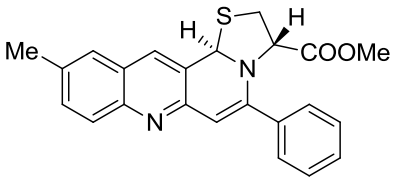
3H) (major), 3.75(s, 3H) (major), 3.72(s, 1.4H) (minor), 3.45–3.41 (m, 1H))(major + minor), 3.45–3.41 (m, 1H))(major + minor), 3.31–3.26 (m, 1H))(major + minor), 3.11–3.00 (m, 2H) (major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.2, 168.8, 155.73, 155.70, 141.2, 140.3, 137.0, 135.4, 131.0, 130.0, 129.4, 127.6, 127.4, 126.5, 125.5, 120.6, 120.0, 119.3, 102.4, 102.2, 93.0, 84.7, 65.8, 64.7, 63.0, 62.2, 58.9, 52.8, 49.9, 36.1, 35.1. HRMS Calcd for $C_{23}H_{20}N_2O_3S$ ($M+H^+$): 404.1195, found 404.1195.



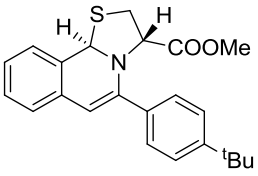
(3S,12*b*R)-Methyl-10-methoxy-5-(*m*-tolyl)-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (dr=62:38) (5m). The product was obtained as a yellow needles (DCM/Ether), mp: 173–175 °C; $[\alpha]_D^{27.5}$ = -319.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 0.6H)(minor), 8.12 (s, 1H)(major), 7.97 (t, *J*=9.16Hz 2H)(major + minor), 7.52–7.44 (m, 3.8H) (major + minor), 7.32–7.21 (m, 4.1H) (major + minor), 7.18–7.16 (m, 1.8H) (major + minor), 7.03–7.02 (m, 2H) (major + minor), 6.35 (s, 0.9H) (major), 6.13 (s, 0.6H) (minor), 4.27 (t, *J*=6.62Hz 1H) (major), 4.09 (t, *J*=5.8Hz 0.8H) (minor), 3.96–3.88 (m, 5.3H) (major + minor), 3.81–3.78 (m, 3.1H) (major + minor), 3.51–3.46 (m, 0.7H) (major), 3.36–3.32 (m, 1H) (major), 3.17–3.06 (m, 2.2H) (major + minor) 2.35–2.34(m, 5.4H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ:171.9, 171.5, 158.5, 158.3, 143.8, 43.1, 139.84, 139.82, 138.0, 137.97, 137.95, 133.7, 132.7, 132.5, 130.3, 130.2, 130.0, 129.9, 129.1, 128.2, 128.17, 128.1, 123.3, 122.5, 121.9, 121,8, 105.1, 104.9, 95.9, 94.1, 87.1, 86.6, 68.5, 67.4, 65.6, 64.9, 55.5, 55.4, 52.6, 52.5, 38.7, 37.8, 21.1. HRMS Calcd for $C_{24}H_{22}N_2O_3S$ ($M+H^+$): 418.1351, found 418.1350.



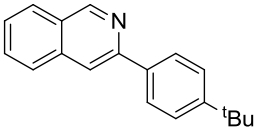
(3S,12*b*R)-Methyl-5-cyclopropyl-10-methoxy-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (dr=68:32) (5n). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -275.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (s, 0.5H)(minor), 7.97 (s, 1H)(major), 7.82 (t, *J*=9.52Hz 1.8H)(major + minor), 7.24–7.18 (m, 1.8H) (major + minor), 6.90 (s, 2H) (major + minor), 6.13 (s, 1H) (major) 5.91 (s, 0.5H) (minor), 4.17 (t, *J*=6.6Hz 1H) (major), 3.99 (t, J=6.2Hz 0.4H) (minor), 3.78–3.73 (m, 9H) (major + minor),3.22–3.21(m, 1H), 3.07–2.95 (m, 2H) (major + minor), 1.16–1.08 (m, 1.5H) (major + minor), 0.94–0.78 (m, 6.2H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 171.4, 158.1, 157.9, 143.6, 142.8, 140.1, 140.0, 137.6, 133.2, 132.6, 130.0, 129.9, 129.6, 127.6, 122.9, 122.1, 105.0, 104.7, 100.9, 99.1, 74.2, 73.8, 68.6, 67.3, 65.6, 64.7, 55.3, 55.28, 53.3, 52.5, 52.4, 38.7, 37.5, 15.0, 8.8, 8.7, 8.6, 8.4, 0.3. HRMS Calcd for $C_{20}H_{20}N_2O_3S$ ($M+H^+$): 368.1195, found 368.1196.



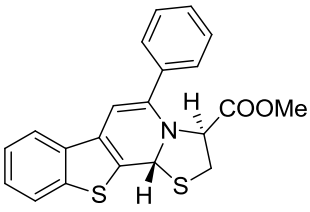
(3S,12*b*R)-Methyl-10-methyl-5-phenyl-3,12*b*-dihydro-2*H*-benzo[*b*]thiazolo[2,3-*f*][1,6]naphthyridine-3-carboxylate (5o). The product was obtained as a yellow needles (DCM/Ether), mp: 177–179 °C; $[\alpha]_D^{29}$ = -357.0 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (s, 1H), 8.17 (d, *J* = 8.72 Hz, 1H), 7.84 (s, 1H), 7.77 (dd, *J*=6.8 and 1.84 Hz, 1H), 7.24–7.22 (m, 3H), 7.14–7.12 (m, 2H),6.61 (s, 1H), 5.96 (s, 1H), 5.72–5.70 (m, 1H), 3.83 (s, 3H), 3.75–3.70 (m, 1H), 3.47–3.41 (m, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.6, 162.8, 161.0, 137.3, 135.7, 135.4, 134.2, 134.0, 129.4, 128.7, 128.4, 128.2, 127.9, 127.0, 126.8, 69.8, 52.6, 37.8, 29.6, 21.5. HRMS Calcd for $C_{23}H_{20}N_2O_2S$ ($M+H^+$): 388.1245, found 388.1244.



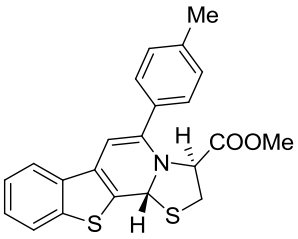
(3S,10*b*R)-Methyl-5-(4-(tert-butyl)phenyl)-3,10*b*-dihydro-2*H*-thiazolo[2,3-*a*]isoquinoline-3-carboxylate (dr=55:45) (6).The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -299.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.39 (m, 1.1H)(major + minor), 7.31–7.27 (m, 0.7H) (major + minor), 7.24–7.13 (m, 0.5H) (major + minor), 6.18 (s, 0.12H) (major), 5.96–5.92 (m, 0.2H) (major + minor), 4.20–4.17 (m, 0.18H) (major), 3.94–3.85 (m, 0.16H) (minor), 3.72–3.69 (m, 1H) (major), 3.42–3.35 (m, 0.4H) (major + minor), 3.28–3.24 (m, 0.24H)(minor), 3.07–2.99 (m, 0.52H) (major + minor), 1.24 (s, 2.1H) (major + minor), 1.17–1.09 (m, 0.7H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.1, 171.0, 170.6, 170.5, 150.8, 150.7, 143,4, 140.4, 140.6, 138.6, 136.6, 132.1, 132.0 131.4, 130.3, 130.2, 129.0, 127.9, 127.6, 127.4, 127.3, 127.2, 127.0, 126.5, 126.2, 125.9, 124.4, 124.3, 123.7, 123.0, 122.2, 121.7, 120.8, 119.1, 119.0, 96.1, 94.5, 85.6, 85.1, 69.1, 69.2, 68.5, 67.7, 64.9, 64.8, 64.5, 64.4, 64.1, 64.0,39.2, 38.2, 37.9, 36.9, 36.4, 33.8, 30.9, 30.2, 28.7, 27.3, 14.2 . HRMS Calcd for $C_{23}H_{25}NO_2S$ ($M+H^+$): 379.1606, found 379.1606.



3-(4-(*tert*-Butyl)phenyl)isoquinoline (7).[2] This compound was obtained as a off white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.25 (s, 1H), 8.00–7.97 (m, 3H), 7.90 (d, J = 8.10 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.52–7.45 (m, 3H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.3, 150.6, 150.3, 135.8, 135.7, 129.4, 126.6, 126.5, 125.8 (2C), 125.6, 124.7, 115.0, 33.6, 30.3. HRMS Calcd for $C_{19}H_{19}N$ ($M+H^+$): 261.1517, found: 261.1519.

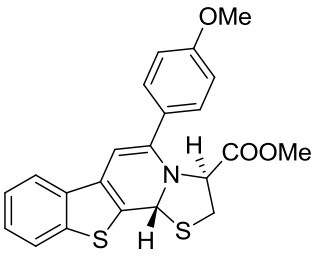


(3S,11*b*R)-Methyl-5-phenyl-3,11*b*-dihydro-2*H*-benzo[4,5]thieno [2,3-*c*]thiazolo[3,2-*a*]pyridine-3-carboxylate (66:34) (8a). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{31}$ = -301.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89–7.84 (m, 1.8H)(major + minor), 7.71–7.66 (m, 1.8H) (major + minor), 7.56–7.53 (m, 4.0H) (major + minor), 7.36–7.24 (m, 9.2H) (major + minor), 6.32 (s, 1H) (major), 6.12 (s, 0.6H) (minor), 4.29 (t, *J*=6.64Hz, 1H) (major), 3.97 (t, *J*=3.64Hz, 0.5H) (minor), 3.71–3.70 (m 5.04H) (major + minor), 3.43–3.39 (m, 1.1H) (major + minor), 3.16–3.06 (m, 2.03H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 170.8, 152.7, 146.0, 139.9, 139.4, 137.5, 137.2, 131.5, 131.4, 128.5, 128.4, 128.2, 125.5, 124,9, 124.6, 123.1, 122.9, 122.7, 122.4, 122.3, 117.1, 114.6, 97.2, 96.8, 81.8, 81.2, 66.0, 65.6, 64.5, 64.3, 52.54, 52.50, 39.0, 37.5 . HRMS Calcd for $C_{21}H_{17}NO_2S_2$ ($M+H^+$): 379.0701, found 379.0703.

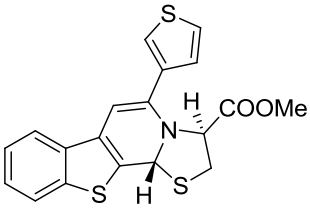


(3S,11*b*R)-Methyl-5-(*p*-tolyl)-3,11*b*-dihydro-2*H*-benzo[4,5] thieno[2,3-*c*]thiazolo[3,2-*a*]pyridine-3-carboxylate (dr=59:41) (8b). The product was obtained as a yellow needles, mp: 162–164 °C; $[\alpha]_D^{31}$ = -312.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03–7.98 (m, 1.9H)(major + minor), 7.84–7.79 (m, 1.9H) (major + minor), 7.60–7.57 (m, 3.9H) (major + minor), 7.49–7.38 (m, 3.8H) (major + minor), 7.23 (d, *J* = 7.32 Hz, 4H) (major + minor), 6.46 (s, 1H) (major), 6.26 (s, 0.7H) (minor), 4.42 (t, *J*=6.6Hz, 1H) (major), 4.09 (t, *J*=8.04Hz 0.7H) (minor), 3.82 (s, 5.8H) (major + minor),3.54 –3.52 (m, 1.44H) (major + minor), 3.27–3.19 (m, 1.8H) (major + minor), 2.41 (s, 5.4H) (major + minor); 13C NMR (100 MHz, CDCl3) δ: 171.6, 170.8, 152.2, 145.6, 139.8, 138.5, 138.4,

137.4, 137.1, 131.3, 131.2, 128.9, 125.4, 124.7, 122.9, 122.5, 122.3, 122.1, 119.7, 119.5, 117.1, 114.7, 97.3, 97.0, 81.1, 80.5, 65.9, 65.5, 64.4, 64.2, 52.3, 38.8, 37.4, 21.2, 20.7.. HRMS Calcd for C22H19NO2S2 (M+H+): 393.0857, found 393.0855.

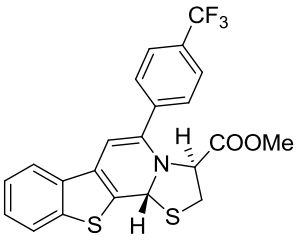


(3S,11*b*R)-Methyl-5-(4-methoxyphenyl)-3,11*b*-dihydro-2*H*-benzo[4,5]thieno[2,3-*c*]thiazolo[3,2-*a*]pyridine-3-carboxylate (dr=60:40) (8c). The product was obtained as a yellow needles, mp: 167–169 °C; $[\alpha]_D^{27}$ = -311.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.90 (m, 1H)(major + minor), 7.81–7.74 (m, 1.1H) (major + minor), 7.57–7.53 (m, 1.9H) (major + minor), 7.46–7.26 (m, 2.2H) (major + minor), 6.93–6.90 (m, 2H) (major + minor), 6.40 (s, 0.5H) (major), 6.19 (s, 0.34H) (minor), 4.41–4.37 (m, 0.5H) (major + minor), 4.08–4.03 (m, 0.56H) (major + minor) 3.84–3.81 (m, 5.95H) (major + minor), 3.53–3.44 (m, 1.2H) (major + minor), 3.24–3.14 (m, 1.1H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.0, 159.9, 159.8, 151.9, 145.3, 140.0, 139.6, 137.7, 137.4, 133.2, 133.1, 125.6, 125.0, 124.95, 124.7, 123.3, 122.9, 122.6, 122.4, 117.7, 115.2, 115.0, 114.1, 97.4, 97.0, 85.6, 80.1, 66.3, 65.9, 64.7, 64.6, 55.3, 52.7, 52.6, 39.2, 37.7 . HRMS Calcd for $C_{22}H_{19}NO_3S_2$ ($M+H^+$): 409.0806, found 409.0806.



(3S,11*b*R)-Methyl-5-(thiophen-3-yl)-3,11*b*-dihydro-2*H*-benzo[4,5]thieno[2,3-*c*]thiazolo[3,2-*a*]pyridine-3-carboxylate (dr=75:25) (8d). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -290.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95–7.89 (m, 1.9H)(major + minor), 7.78–7.74 (m, 2H) (major + minor),

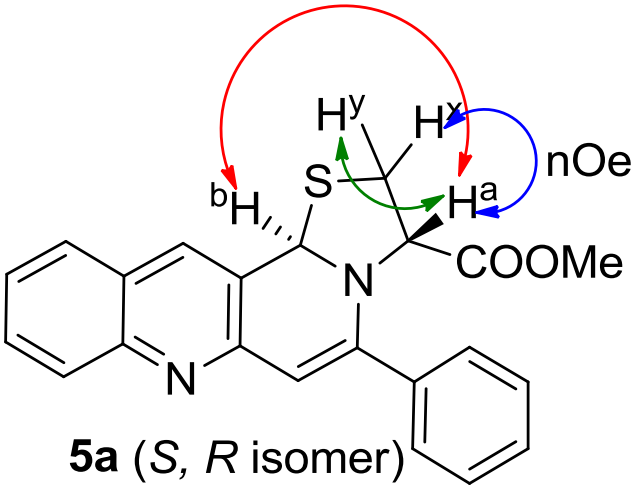
7.43–7.40 (m, 4H) (major + minor), 7.34–7.31 (m, 1H) (major + minor), 7.27–7.24 (m, 1H) (major + minor),7.16 (d, J=5.84Hz, 1H) (major + minor), 6.38 (s, 1H) (major), 6.17 (s, 0.35H) (minor), 4.38–4.36 (m, 1H) (major + minor), 4.06–4.02 (m, 0.4H) (major + minor), 3.80–3.79 (m, 4.2H) (major + minor), 3.50–3.47 (m, 1.4H) (major + minor), 3.23–3.14 (m, 1.4H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.1, 152.5, 145.9, 140.0, 139.6, 139.2, 138.1, 137.7, 137.4, 132.5, 132.2, 132.1, 130.5, 129.5, 129.4, 129.0, 128.8, 128.7, 128.5, 128.3, 125.6, 125.5, 125.0, 124.8, 123.3, 122.9, 122.8, 122.6, 122.4, 117.3, 114.8, 114.0, 97.5, 97.1, 81.5, 81.0, 66.2, 65.8, 64.6, 64.5, 52.7, 52.6, 39.2, 37.7 . HRMS Calcd for $C_{19}H_{15}NO_2S_3$ ($M+H^+$): 385.0265, found 385.0266.



(3S,11*b*R)-Methyl-5-(4-(trifluoromethyl)phenyl)-3,11*b*-dihydro-2*H*-benzo[4,5]thieno[2,3-*c*]thiazolo[3,2-*a*]pyridine-3-carboxylate (dr=50:50) (8e). The product was obtained as a yellow needles, mp: 161–163 °C; $[\alpha]_D^{27}$ = -301.3 (c 0.1, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86–7.81 (m, 1.9H)(major + minor), 7.71–7.66 (m, 1.9H) (major + minor), 7.63–7.61 (m, 3H) (major + minor), 7.55–7.53 (m, 3H) (major + minor), 7.38–7.24 (m, 4H) (major + minor), 6.31 (s, 1H) (major), 6.11(s, 0.5H) (minor), 4.29 (t, J=5.92Hz, 1H) (major + minor), 3.99 (t, J=7.8Hz, 0.5H) (minor), 3.72 (m, 4.5H) (major + minor), 3.42–3.41 (m, 1.2H) (major + minor), 3.17–3.07 (m, 1.9H) (major + minor) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 170.9, 154.2, 147.4, 139.7, 139.2, 137.5, 137.2, 131.7, 131.6, 126.8, 126.4, 125.6, 125.2, 125.1, 125.0, 124.8, 122.9, 122.52, 122.50, 122.3, 116.3, 113.9, 95.8, 95.3, 84.3, 83.7, 66.0, 65.7, 64.5, 64.2, 52.5, 39.0, 37.5. HRMS Calcd for $C_{22}H_{16}F_3NO_2S_2$ ($M+H^+$): 447.0575, found 447.0574

NOESY Experiment

NOESY Experiment of 5a:



Results: The relative configuration of the new stereogenic center at H^b in product **5a** was determined by NOESY experiments.^{1}H NMR spectra of **5a** show that H^b appears at 6.39 as a singlet and H^a at 4.29–4.27 as multiplet. No distinct NOE effect was observed between H^b and H^a in compound **5a**. This suggested that H^b and H^a are located in *trans*-orientation.

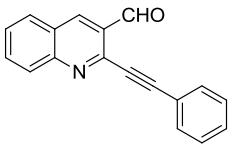
References:

1. (a) A. K. Verma; S. K. R. Kotla; D. Choudhary; M. Patel; R. K. Tiwari, *J. Org. Chem.* 2013, **78**, 4386; (b) A. K. Verma; V. Rustagi; T. Aggarwal; A. P. Singh, *J. Org. Chem.* 2010, **75**, 7691; (c) M. Zahid; V. O. Iaroshenko; A. S. Saghyan; C. Fischer; P. Langer *Tetrahedron* 2013, **69**, 3451; (d) A. Chandra; B. Singh; S. Upadhyay; R. M. Singh, *Tetrahedron* 2008, **64**, 11680; (e) V. Rustagi; T. Aggarwal; A. K. Verma, *Green Chem.* 2011, **13**, 1640; (f) V. Rustagi; R. K. Tiwari; A. K. Verma, *Eur. J. Org. Chem.* 2012, **24**, 4590.

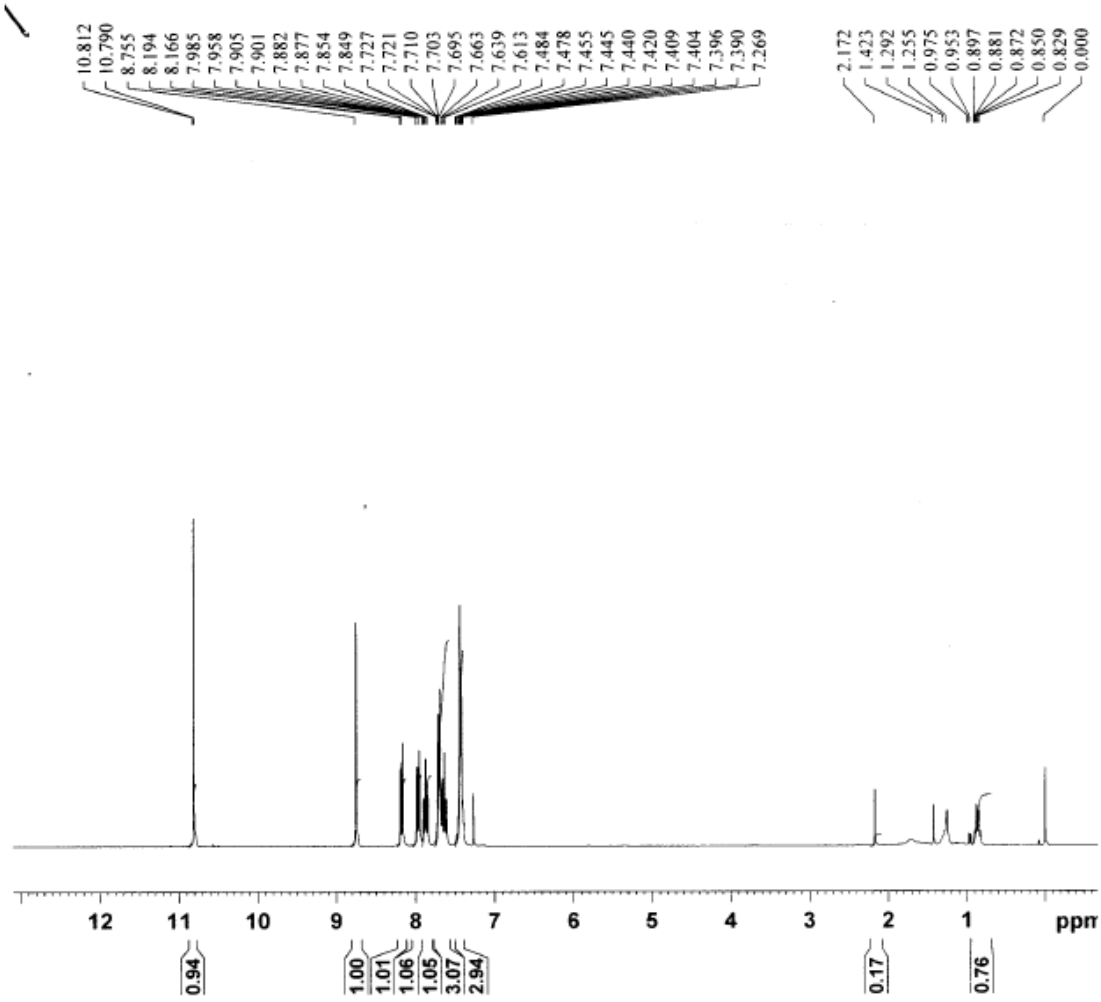
2. D. Yang, S. Burugupalli, D. Daniel, Y. Chen *J. Org. Chem.* 2012, **77**, 4466

Copies of ^{1}H NMR, ^{13}C NMR

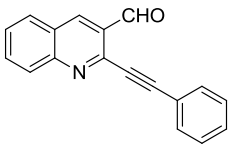
^{1}H NMR



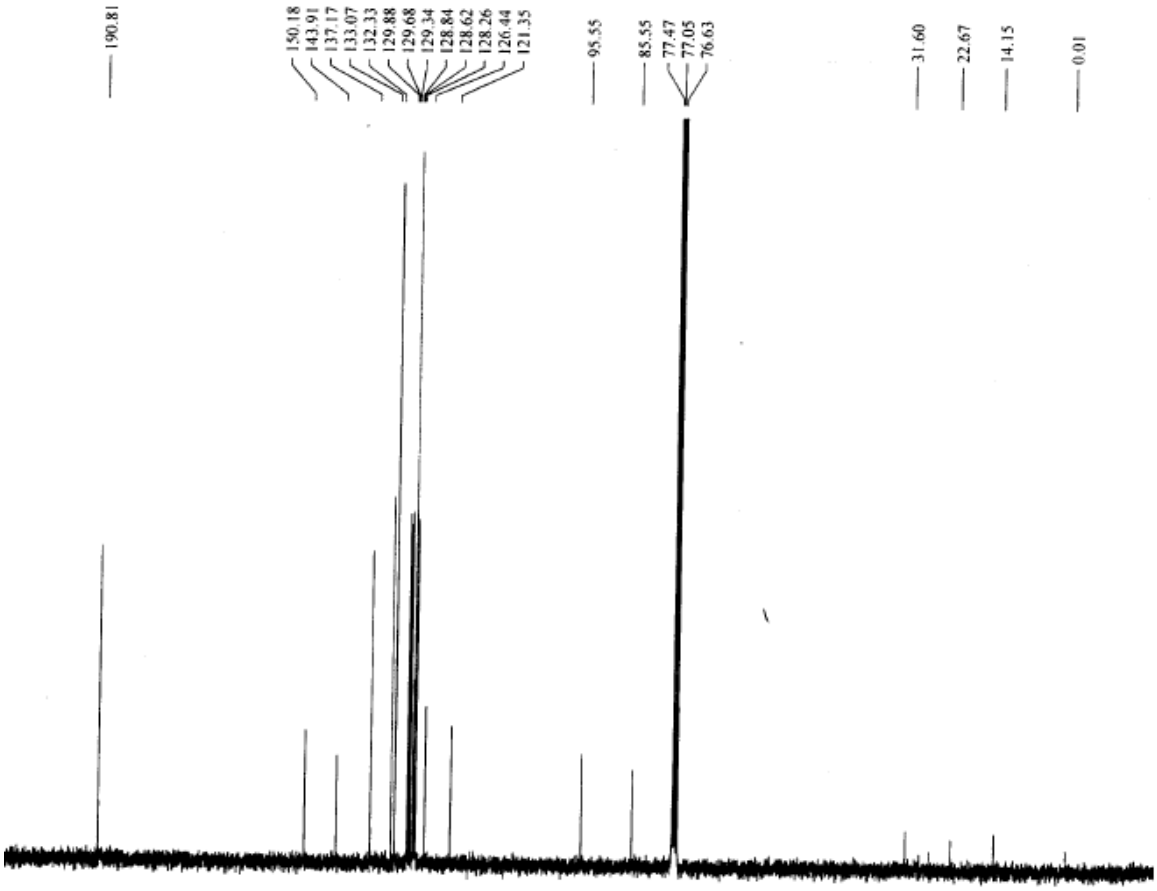
1a



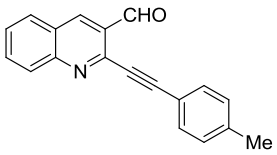
^{13}C NMR



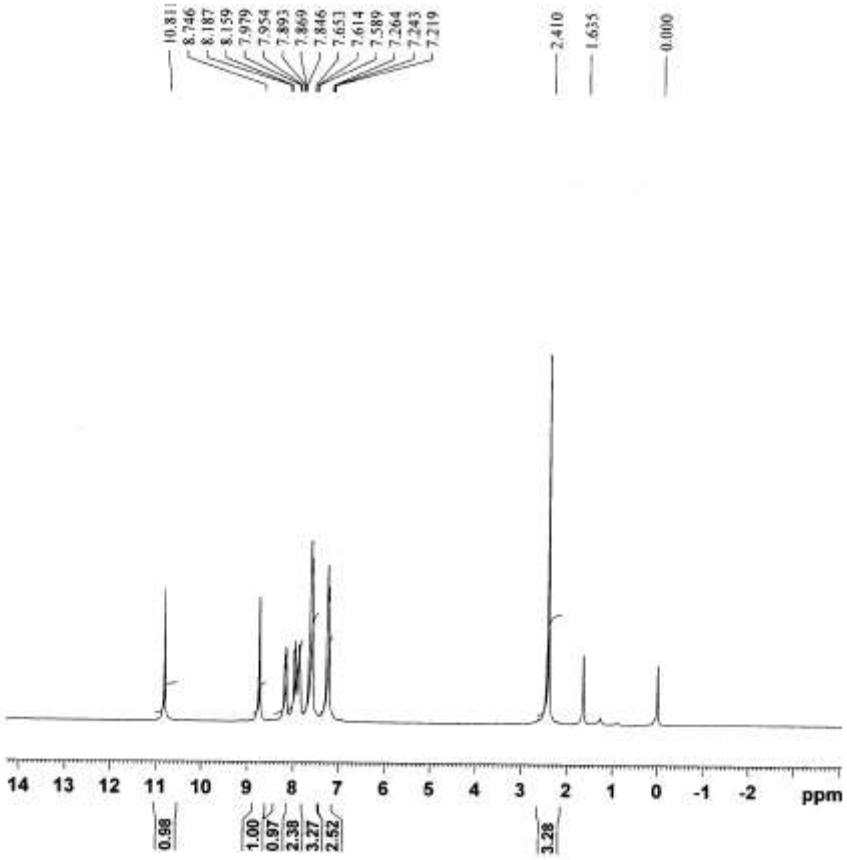
1a



^{1}H NMR


CHO
N
Me

1b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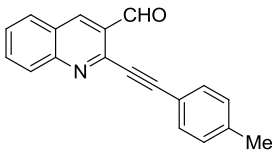
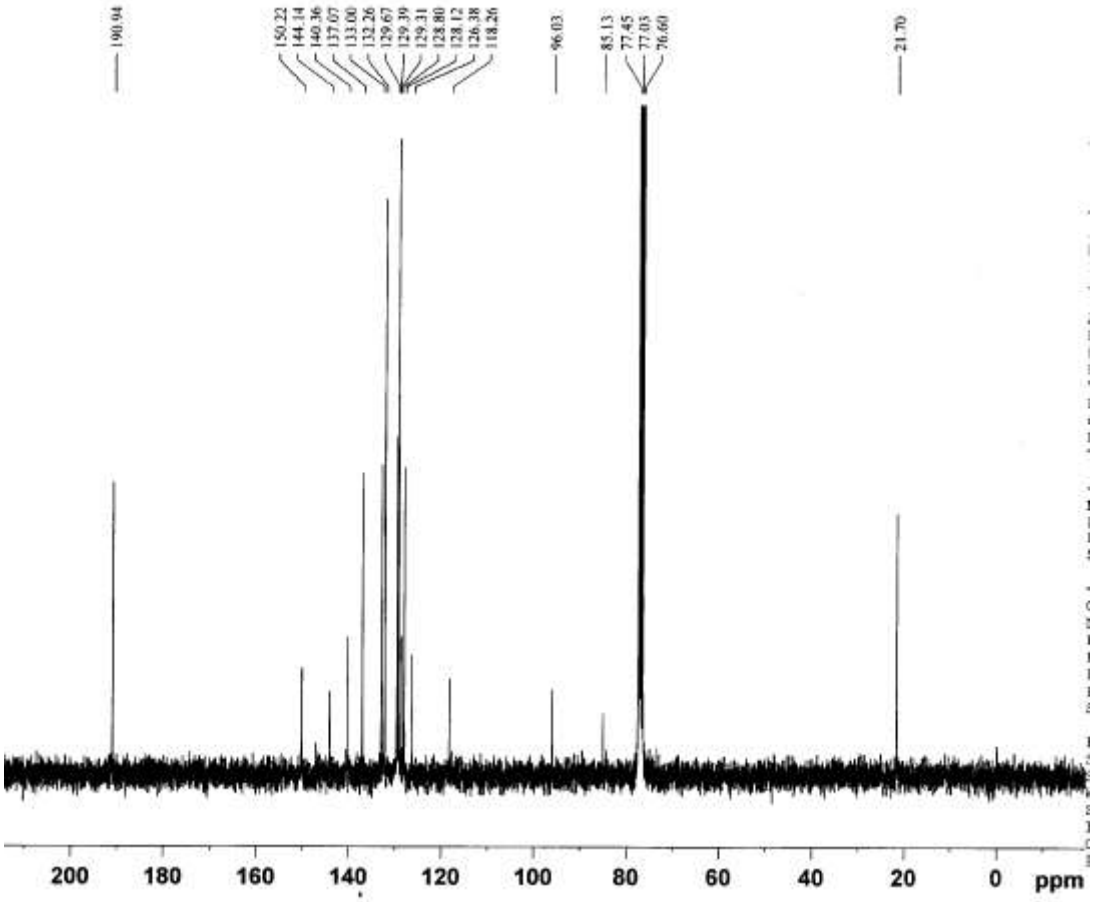
8.746
8.187
8.159
7.979
7.954
7.893
7.869
7.846
7.651
7.614
7.589
7.264
7.243
7.219
2.410
1.635
0.000
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
0.98
1.00
0.97
2.38
3.27
2.52
3.28

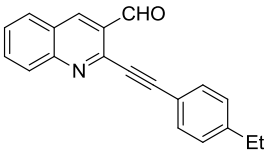
^{13}C NMR



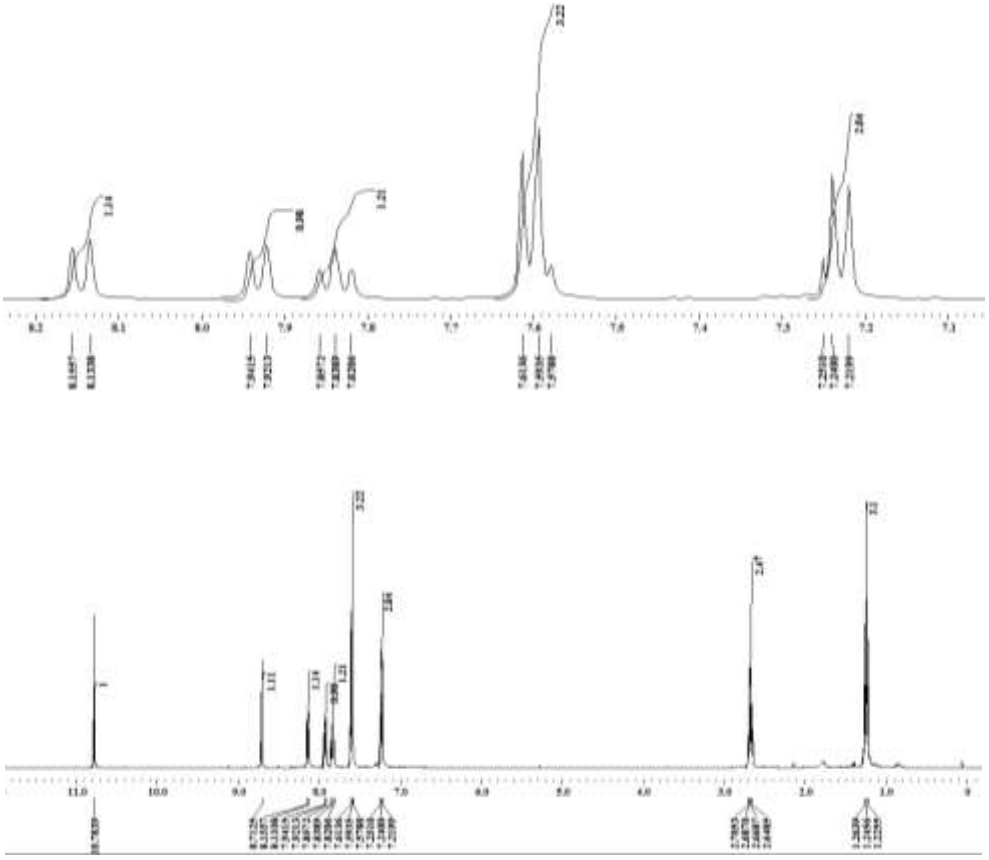
1b



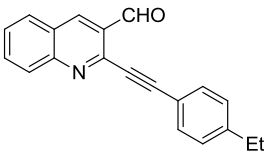
^{1}H NMR



1c



^{13}C NMR



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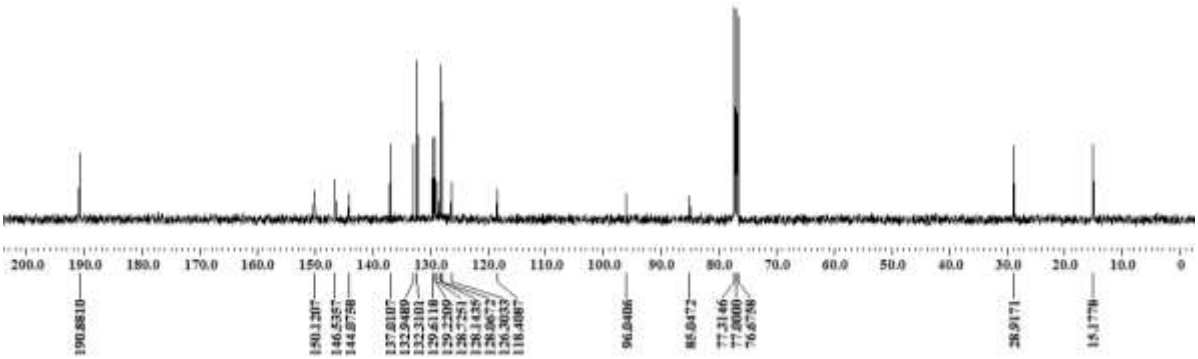
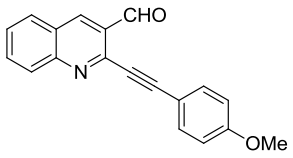
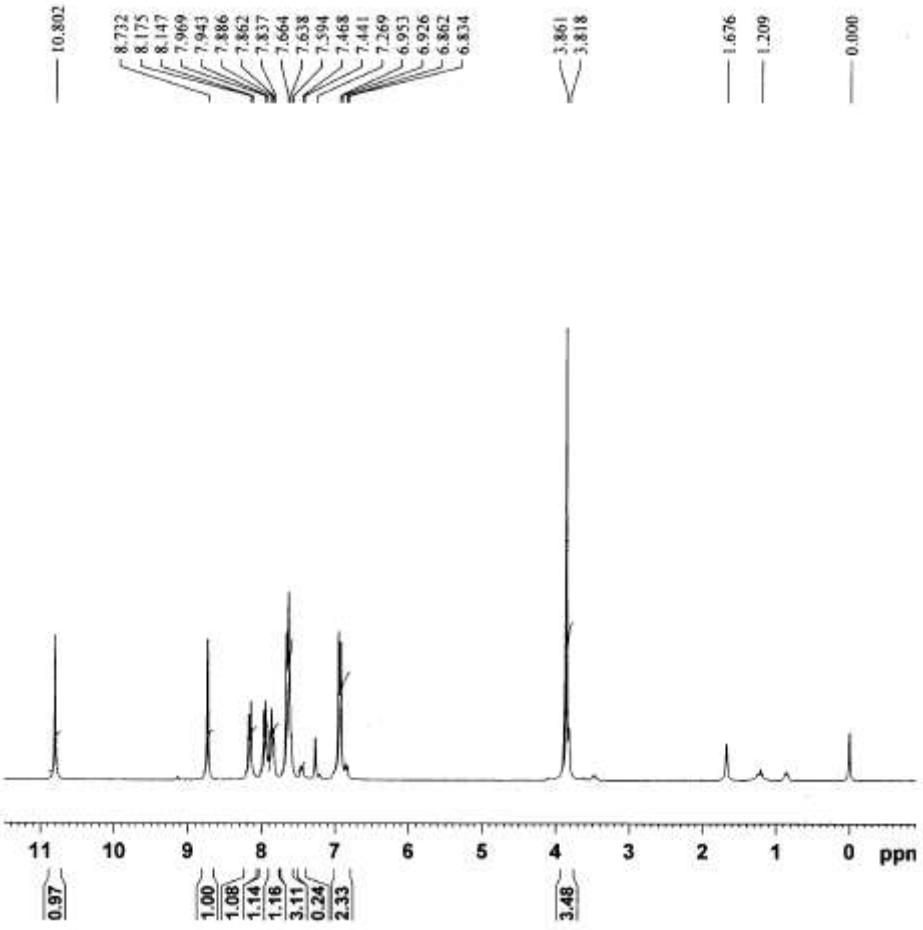


^{1}H NMR


CHO
N
OMe

1d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8.732
8.175
8.147
7.969
7.943
7.886
7.862
7.837
7.664
7.638
7.594
7.468
7.441
7.269
6.953
6.926
6.862
6.834
3.861
3.818
1.676
1.209
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppn
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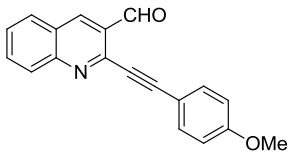
1.00
1.08
1.14
1.16
3.11
0.24
2.33
3.48

^{13}C NMR



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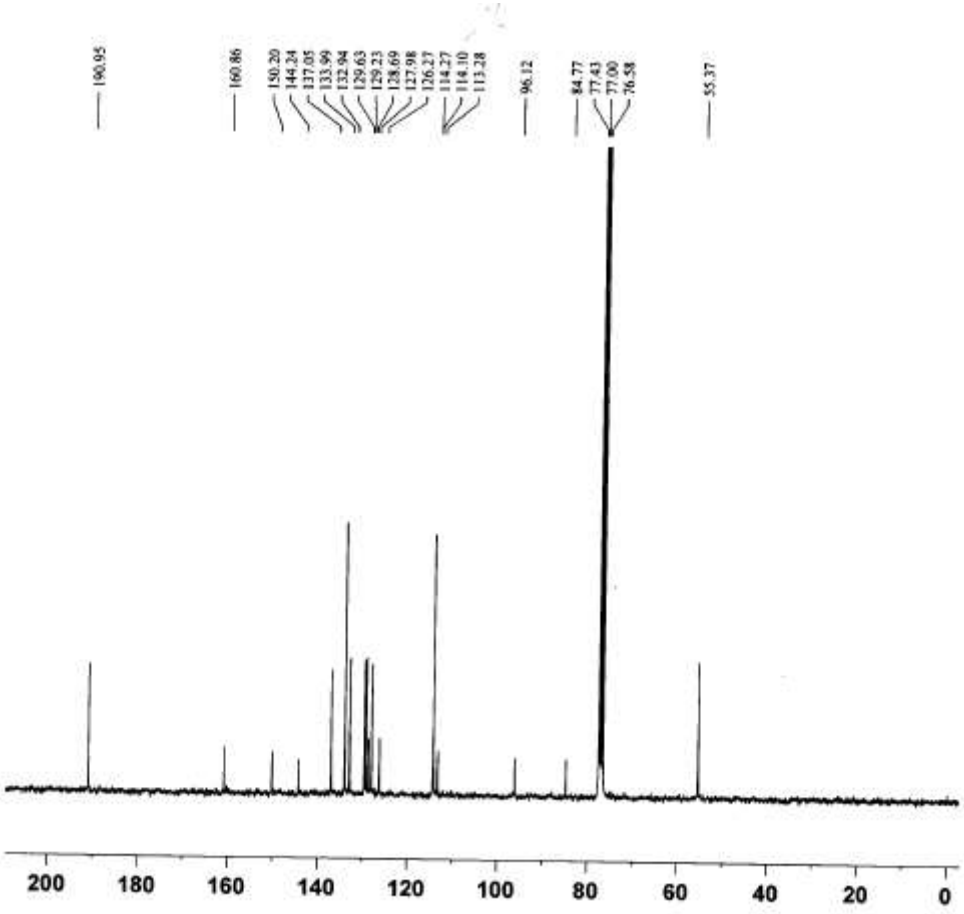
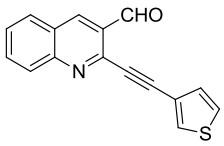
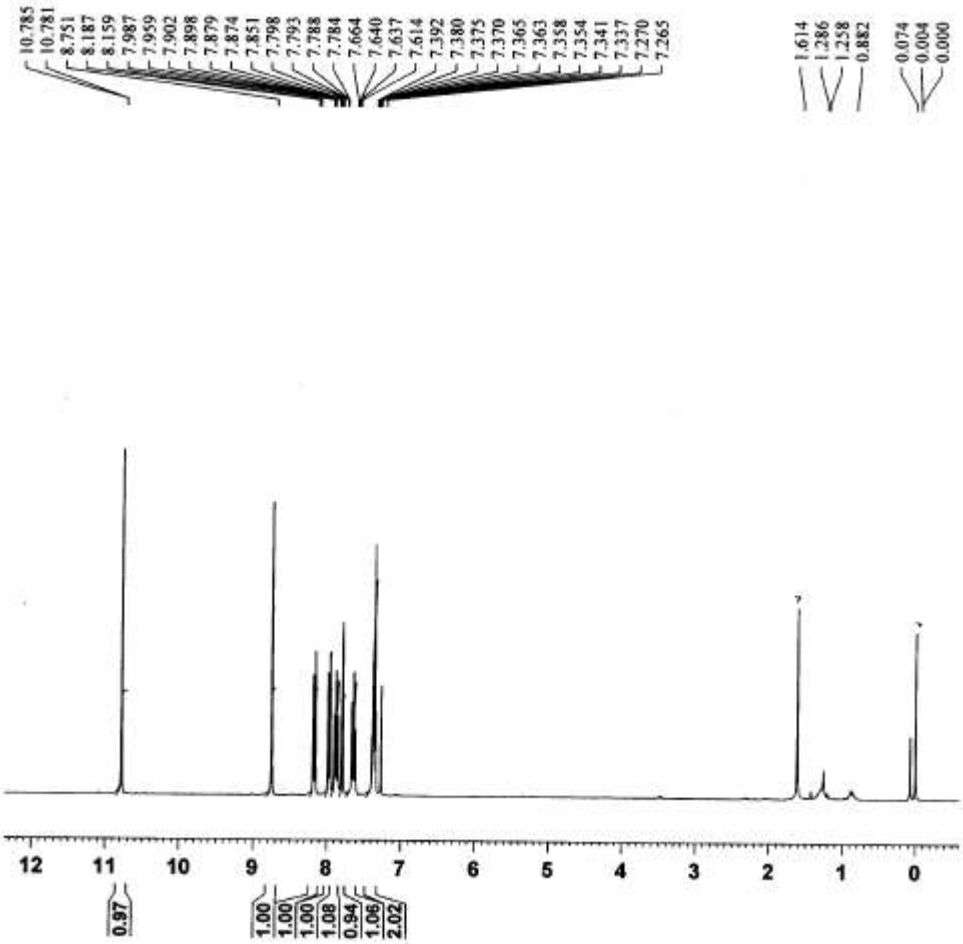


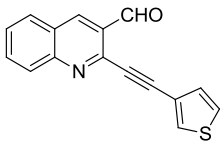
^{1}H NMR



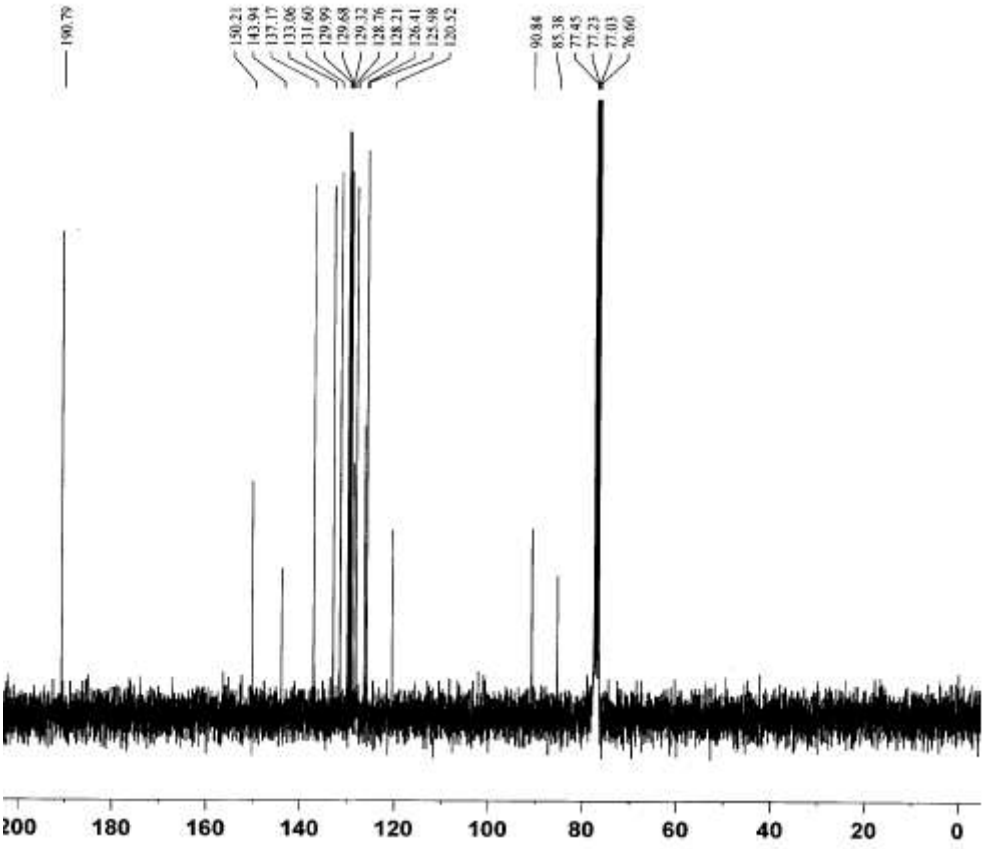
1e



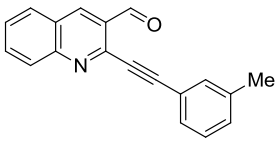
^{13}C NMR



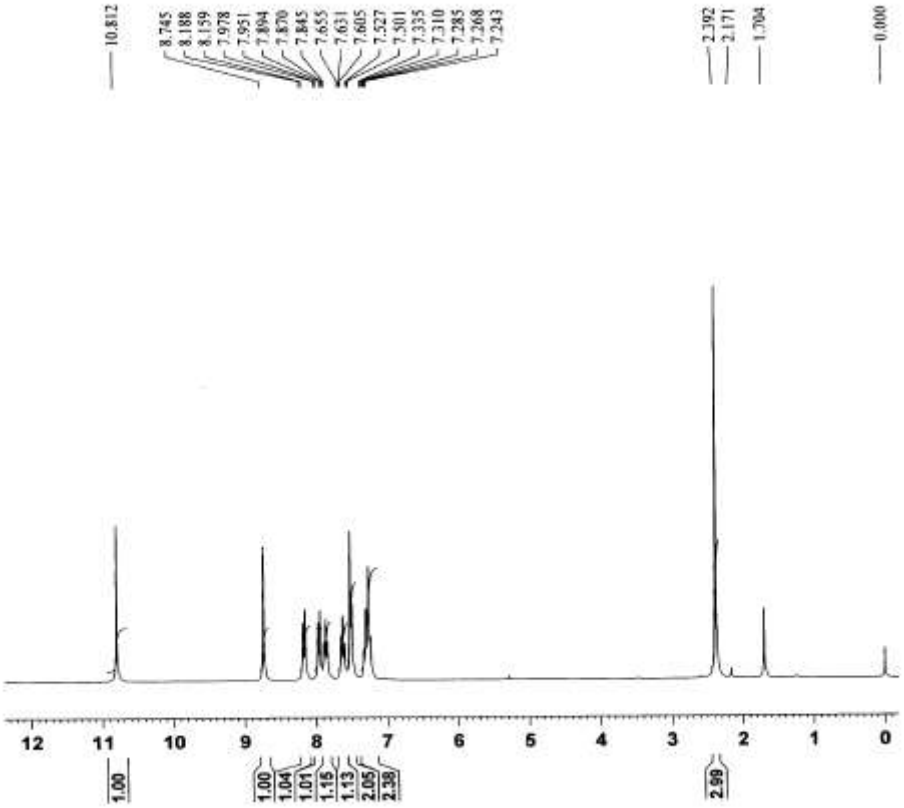
1e



^{1}H NMR


O
N
Me

1f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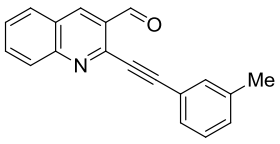
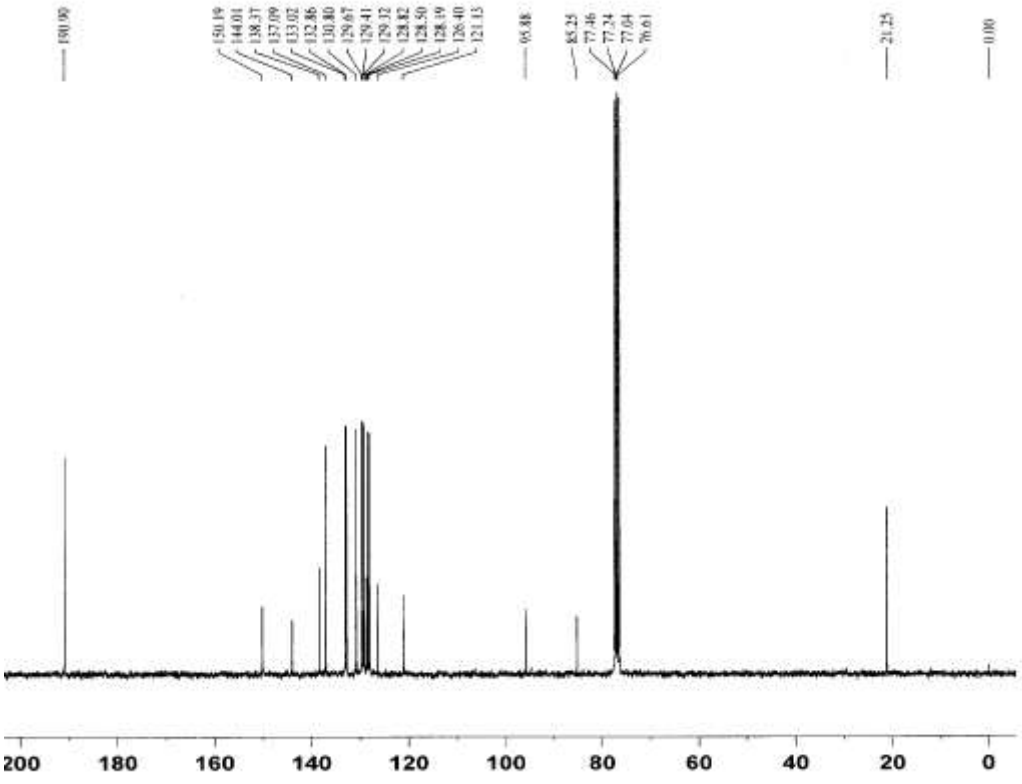
8.159
7.978
7.951
7.894
7.870
7.845
7.655
7.631
7.605
7.527
7.501
7.335
7.310
7.285
7.268
7.243
2.392
2.171
1.704
0.000
12
11
10
9
8
7
6
5
4
3
2
1
0
1.00
1.00
1.04
1.01
1.15
1.13
2.05
2.38
2.99

^{13}C NMR


O
N
Me

1f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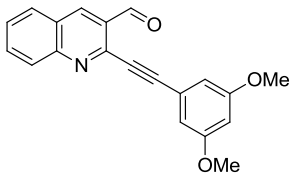
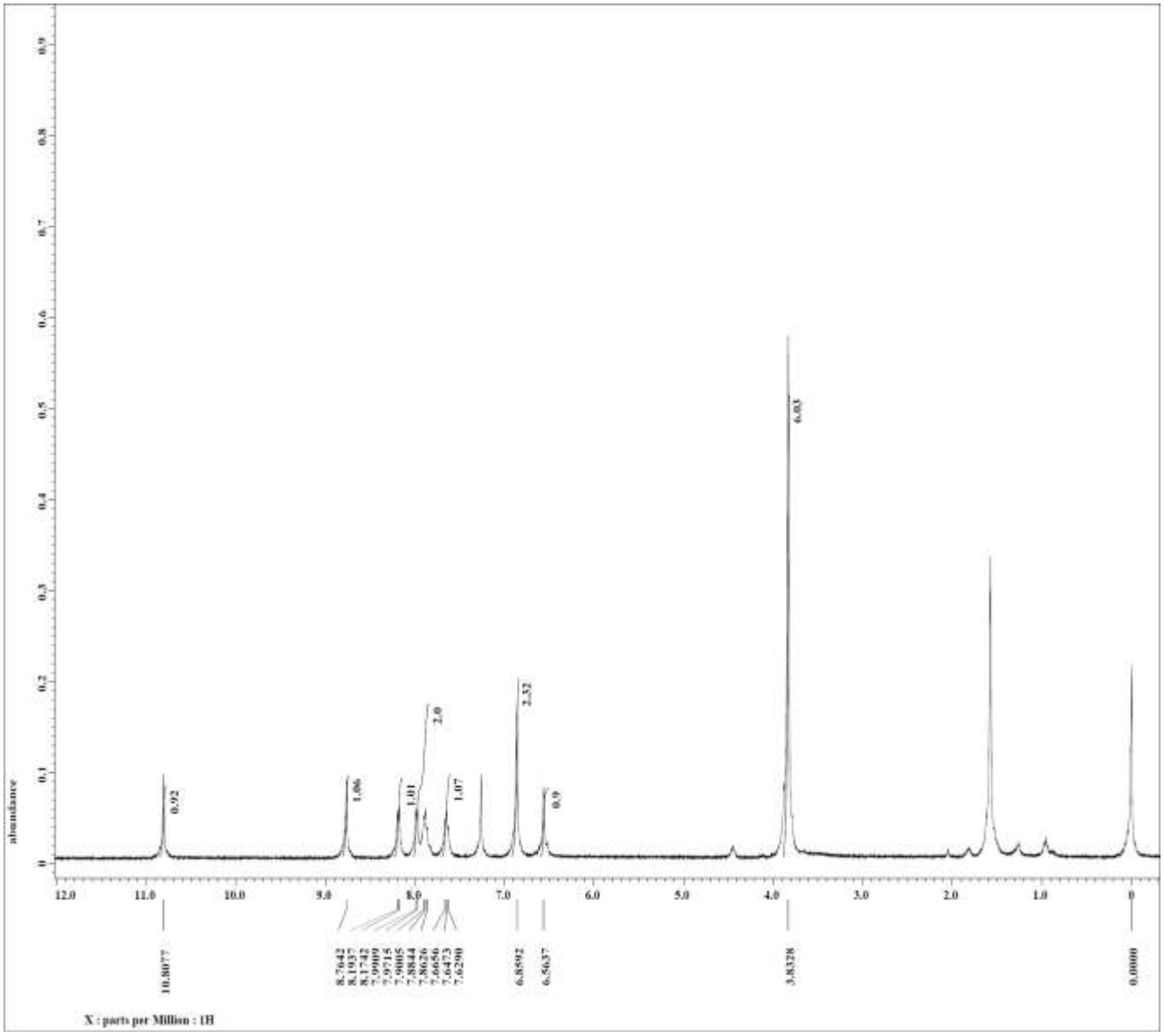
150.19
144.01
138.37
137.09
133.02
132.86
130.80
129.67
129.41
129.32
128.82
128.50
128.19
126.40
121.15
95.88
85.25
77.46
77.24
77.04
76.61
21.25
0.00
200
180
160
140
120
100
80
60
40
20
0

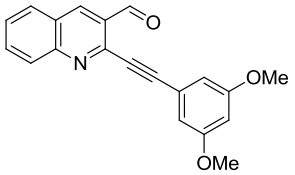
^{1}H NMR


O
N
OMe
OMe

1g


abundance
0.92
1.06
1.01
2.0
1.07
2.32
0.9
6.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.8077
8.7642
8.1937
8.1742
7.9989
7.9715
7.9005
7.8844
7.8626
7.6456
7.6473
7.6290
6.8592
6.5637
3.8328
0.0000
X : parts per Million : 1H

^{13}C NMR



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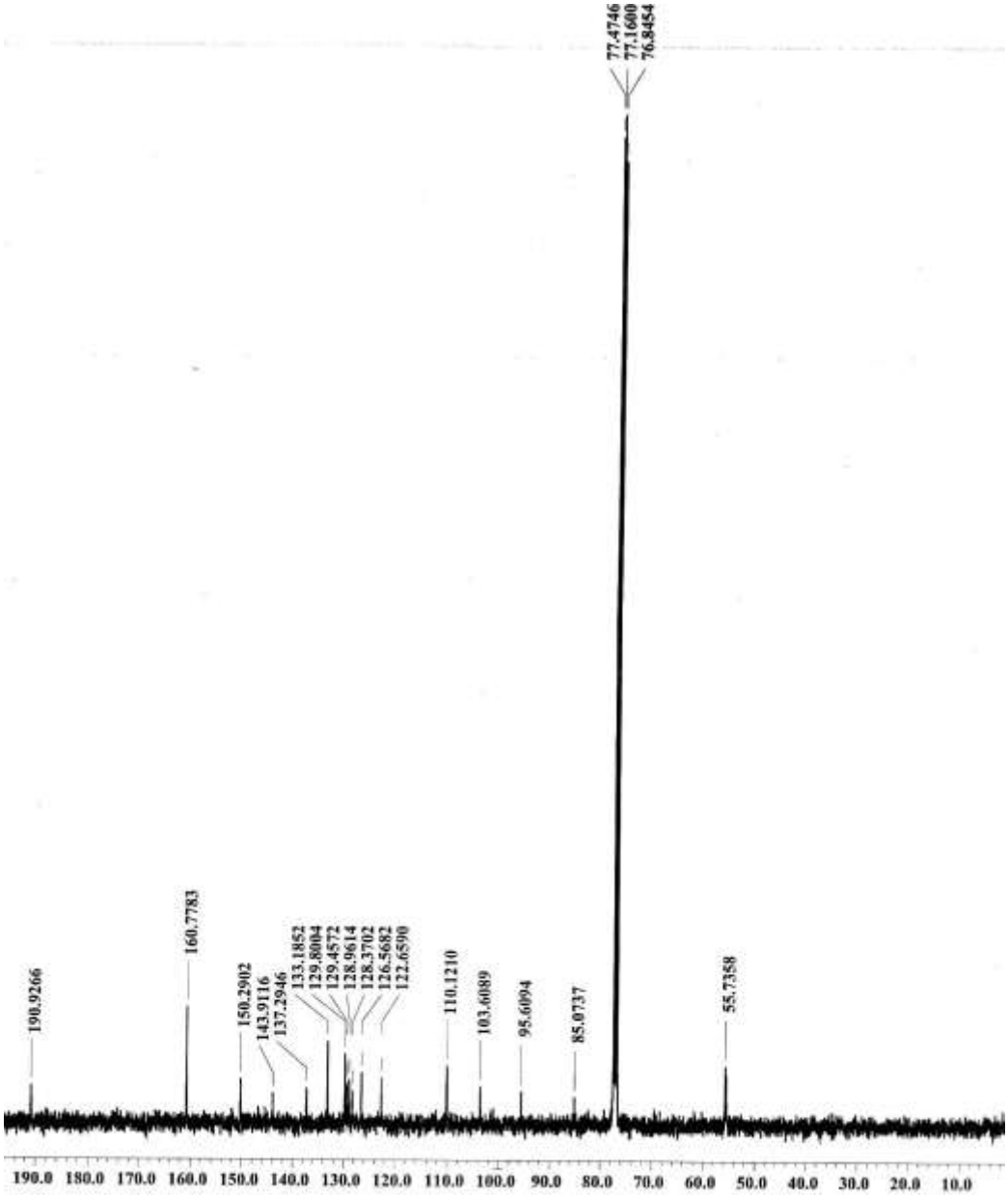
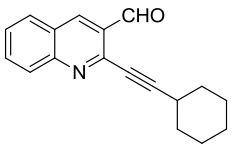
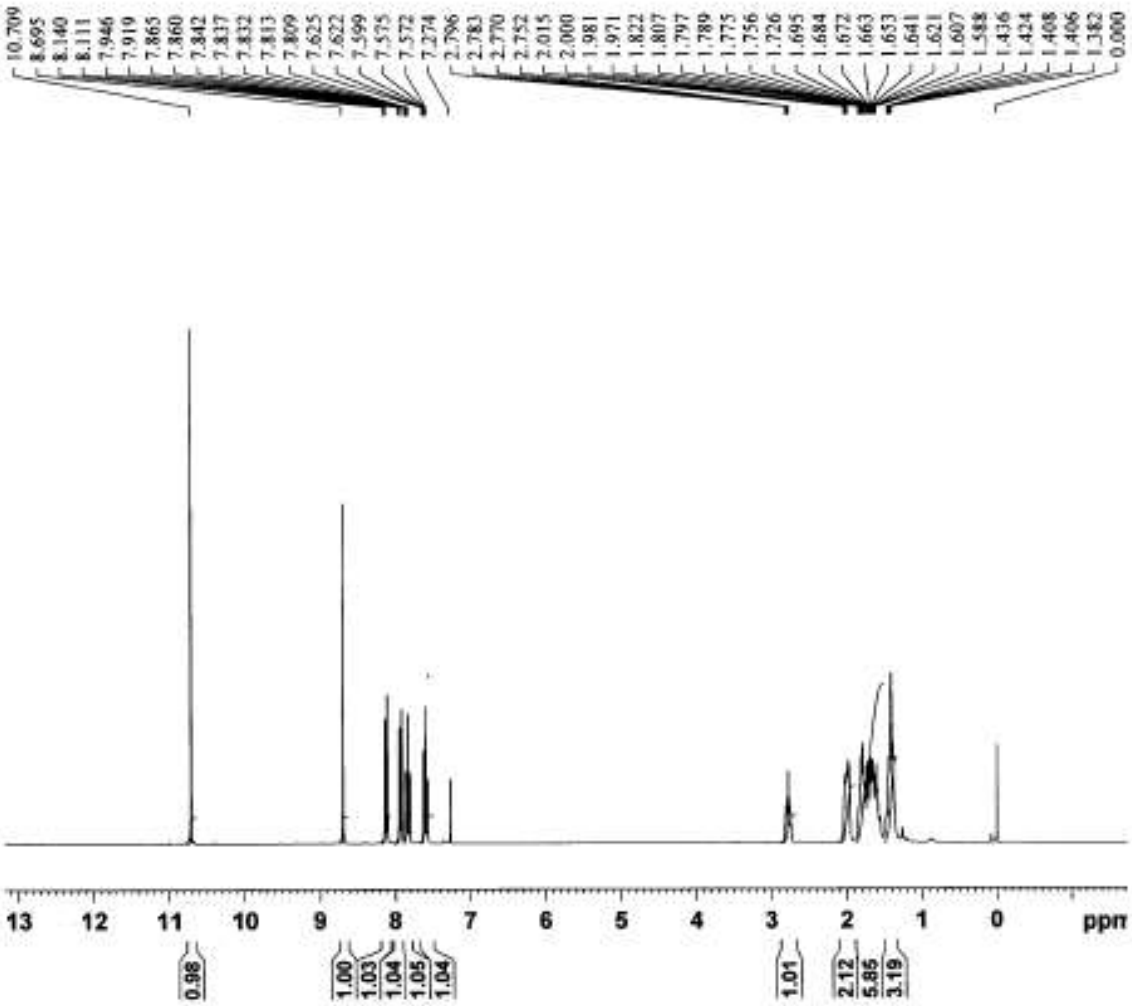


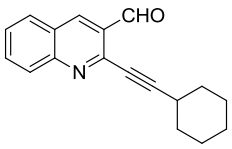
^{1}H NMR



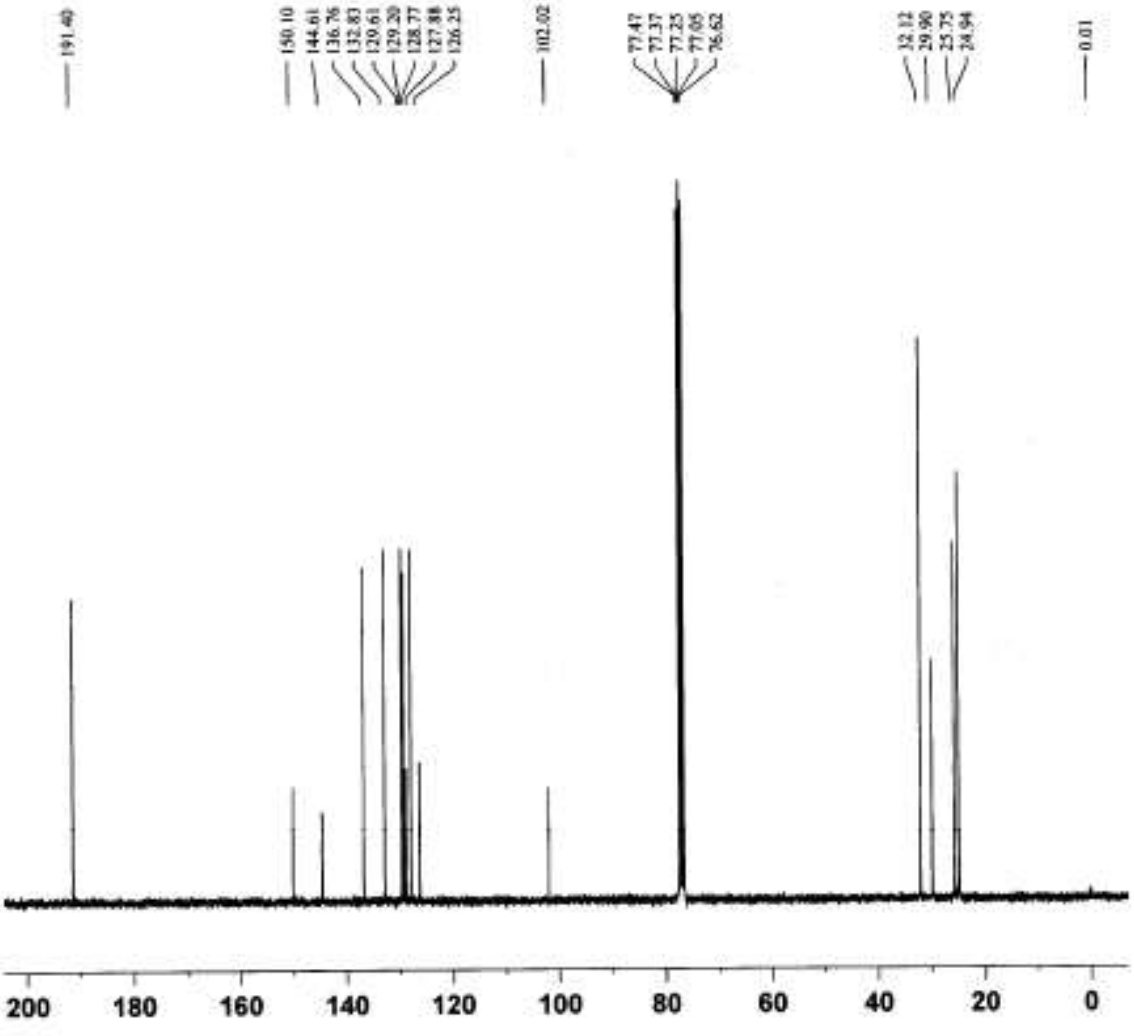
1h



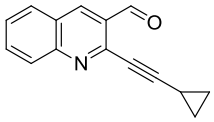
^{13}C NMR


CHO
N

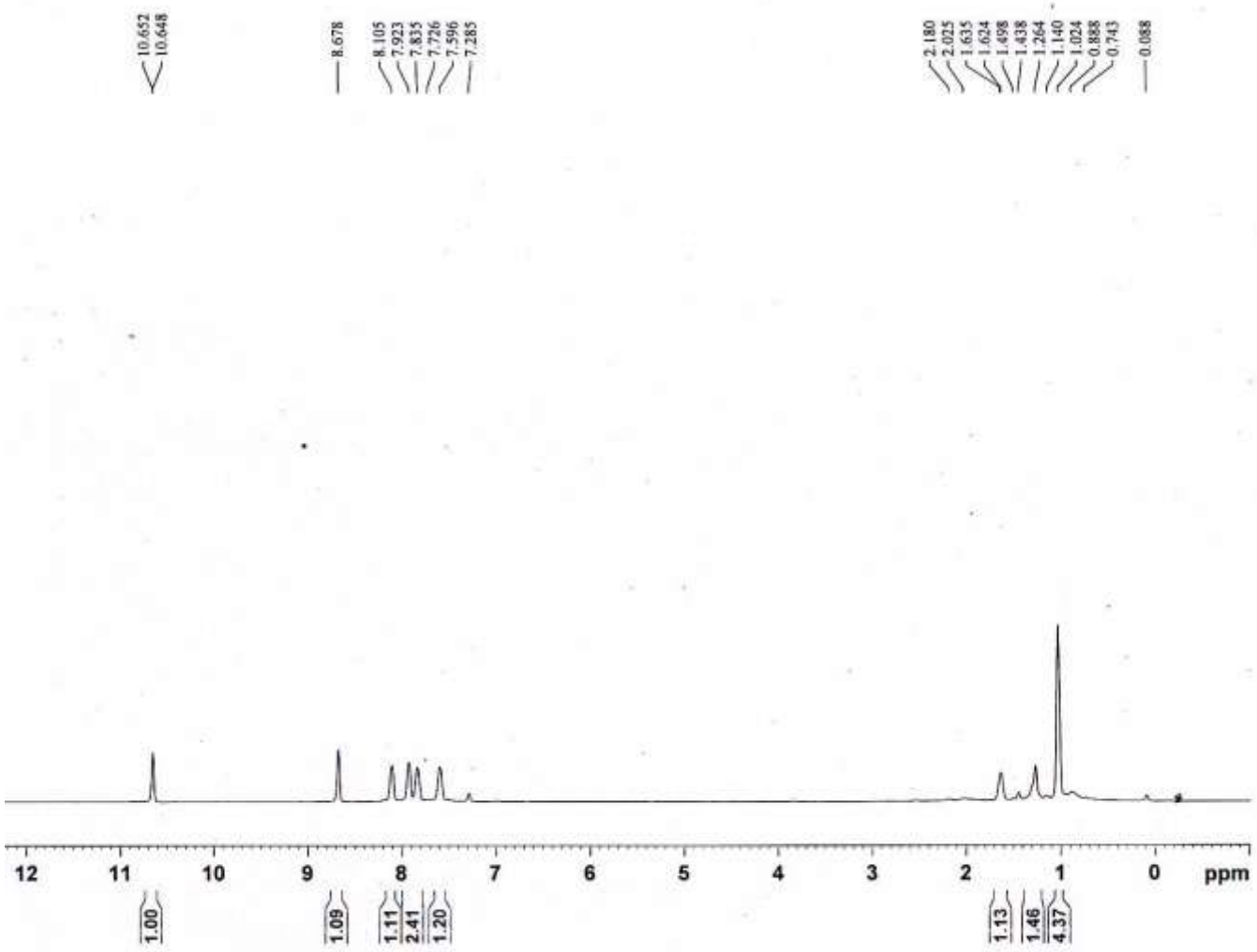
1h


191.40
150.10
144.61
136.76
132.83
129.61
129.20
128.77
127.38
126.25
102.02
77.47
77.37
77.23
77.05
76.62
32.12
29.90
23.75
14.94
0.01
200
180
160
140
120
100
80
60
40
20
0

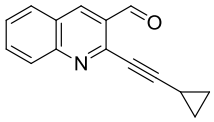
^{1}H NMR


O
N

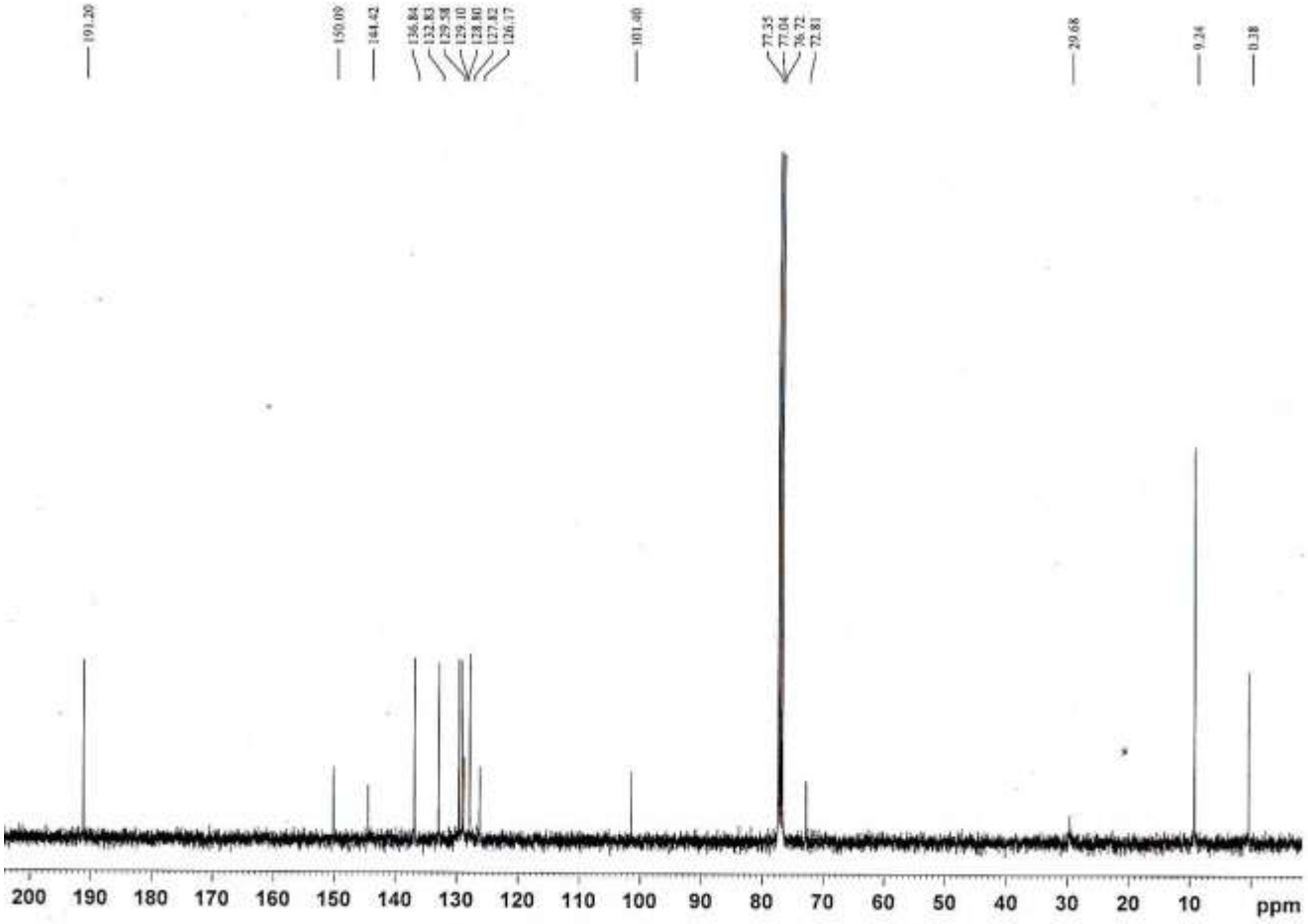
1i


10.652
10.648
8.678
8.105
7.923
7.835
7.726
7.596
7.285
2.180
2.025
1.635
1.624
1.498
1.438
1.264
1.140
1.024
0.888
0.743
0.088
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.09
1.11
2.41
1.20
1.13
1.46
4.37

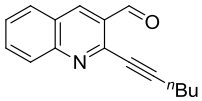
^{13}C NMR


O
N

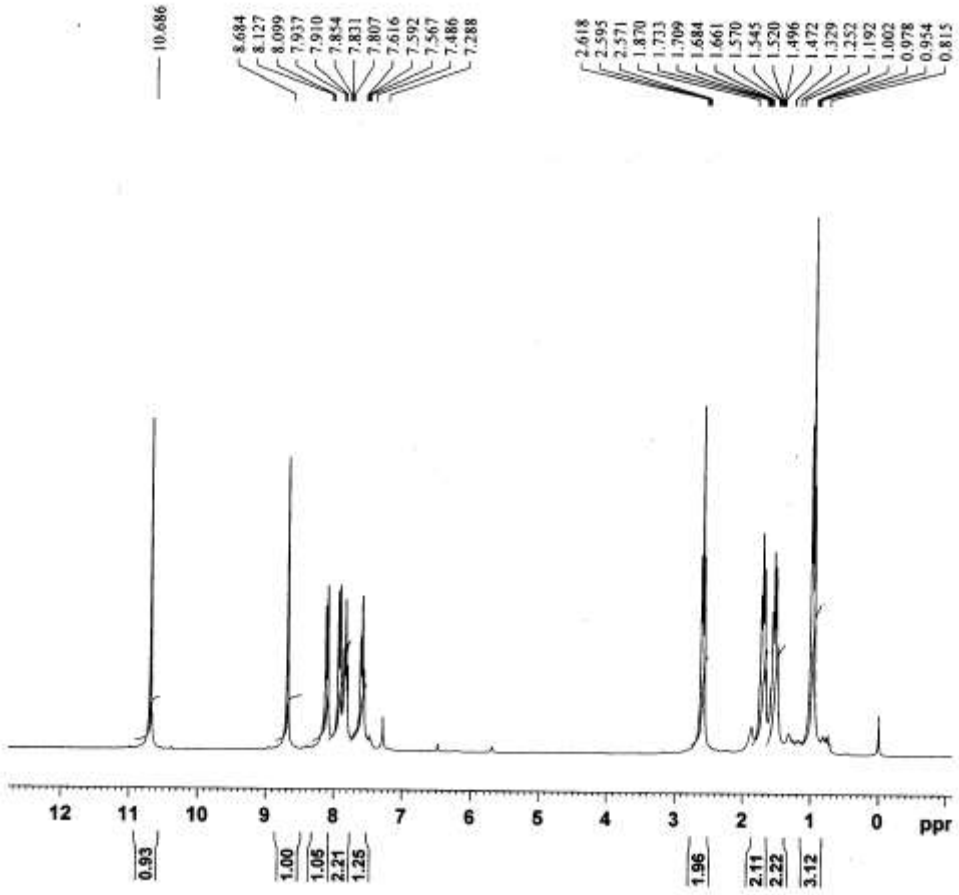
1i


191.20
150.09
144.42
136.84
132.83
129.58
129.10
128.80
127.82
126.77
101.40
77.35
77.04
76.72
72.81
29.68
9.24
0.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H NMR


O
N
nBu

1j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8.099
7.937
7.910
7.854
7.831
7.807
7.616
7.592
7.567
7.486
7.288
2.618
2.595
2.571
1.870
1.733
1.709
1.684
1.661
1.570
1.545
1.520
1.496
1.472
1.329
1.252
1.192
1.002
0.978
0.954
0.815
12
11
10
9
8
7
6
5
4
3
2
1
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ppr
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1.00
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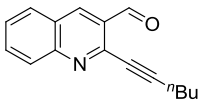
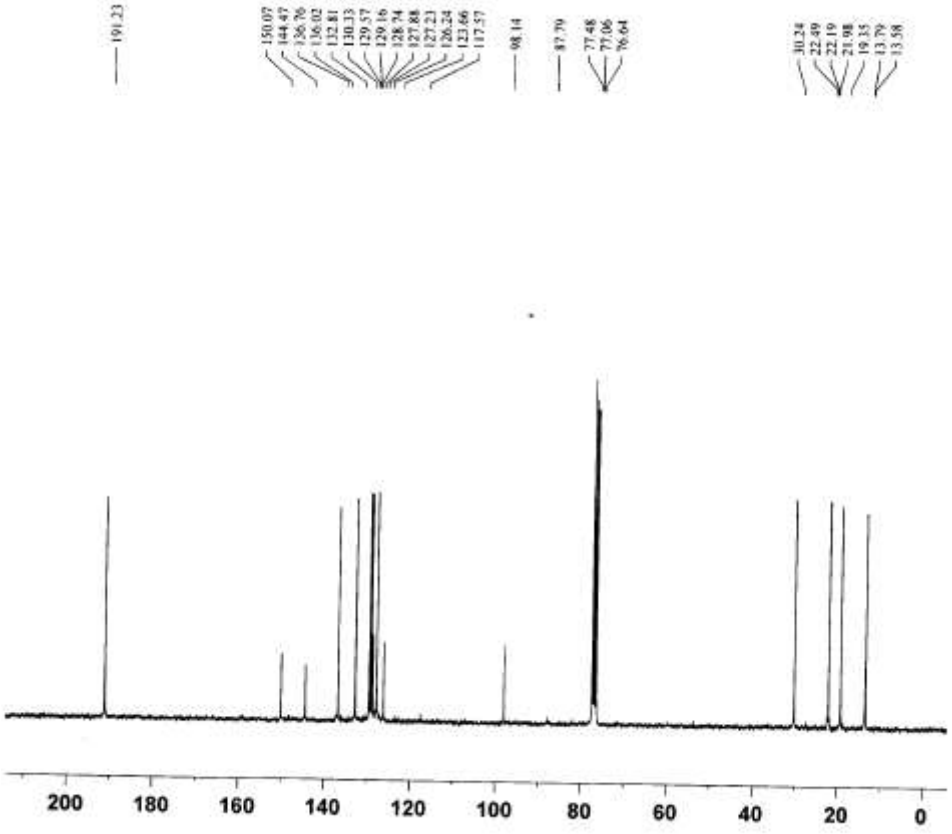
2.21
1.25
1.96
2.11
2.22
3.12

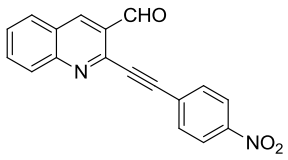
^{13}C NMR



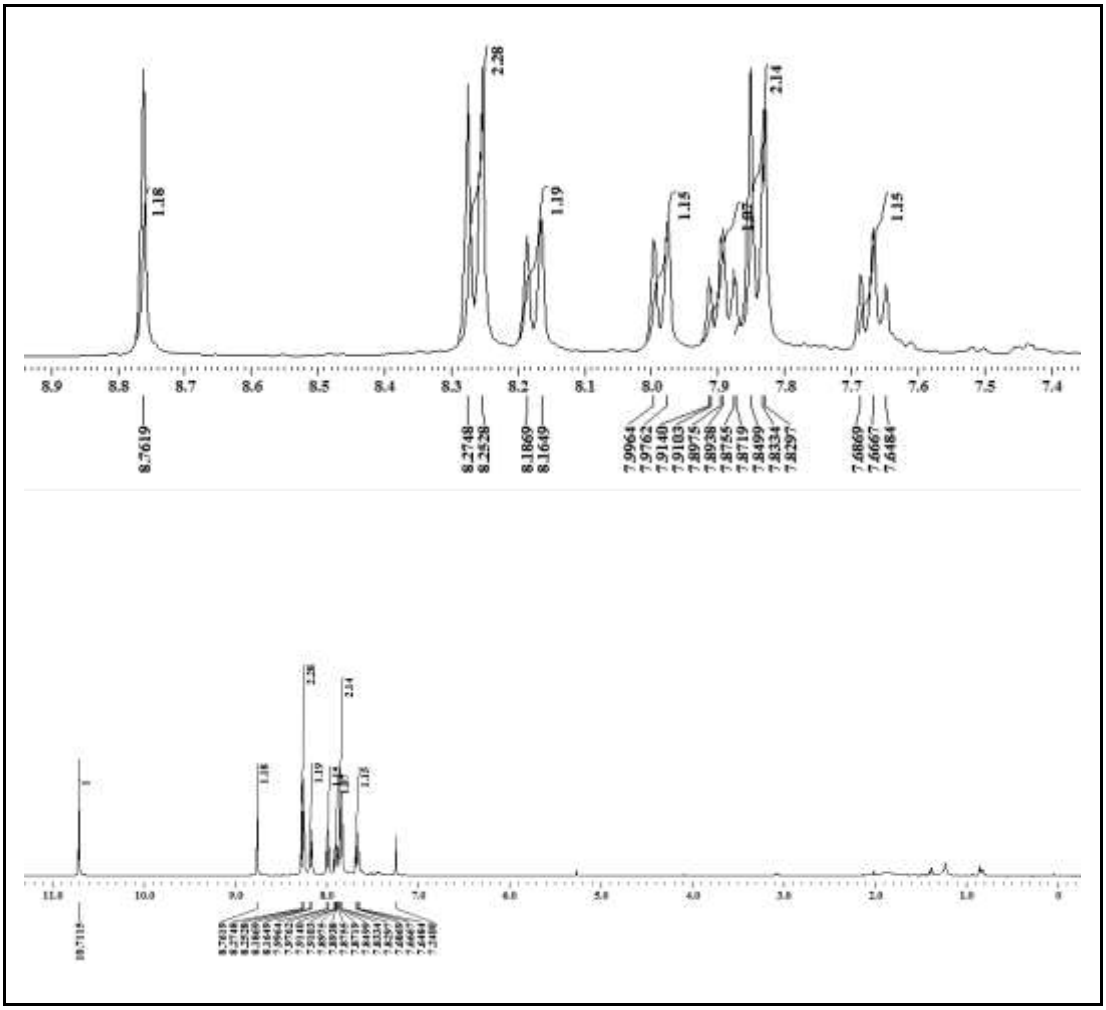
1j



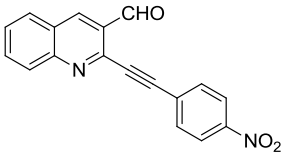
^{1}H NMR



1k



^{13}C NMR



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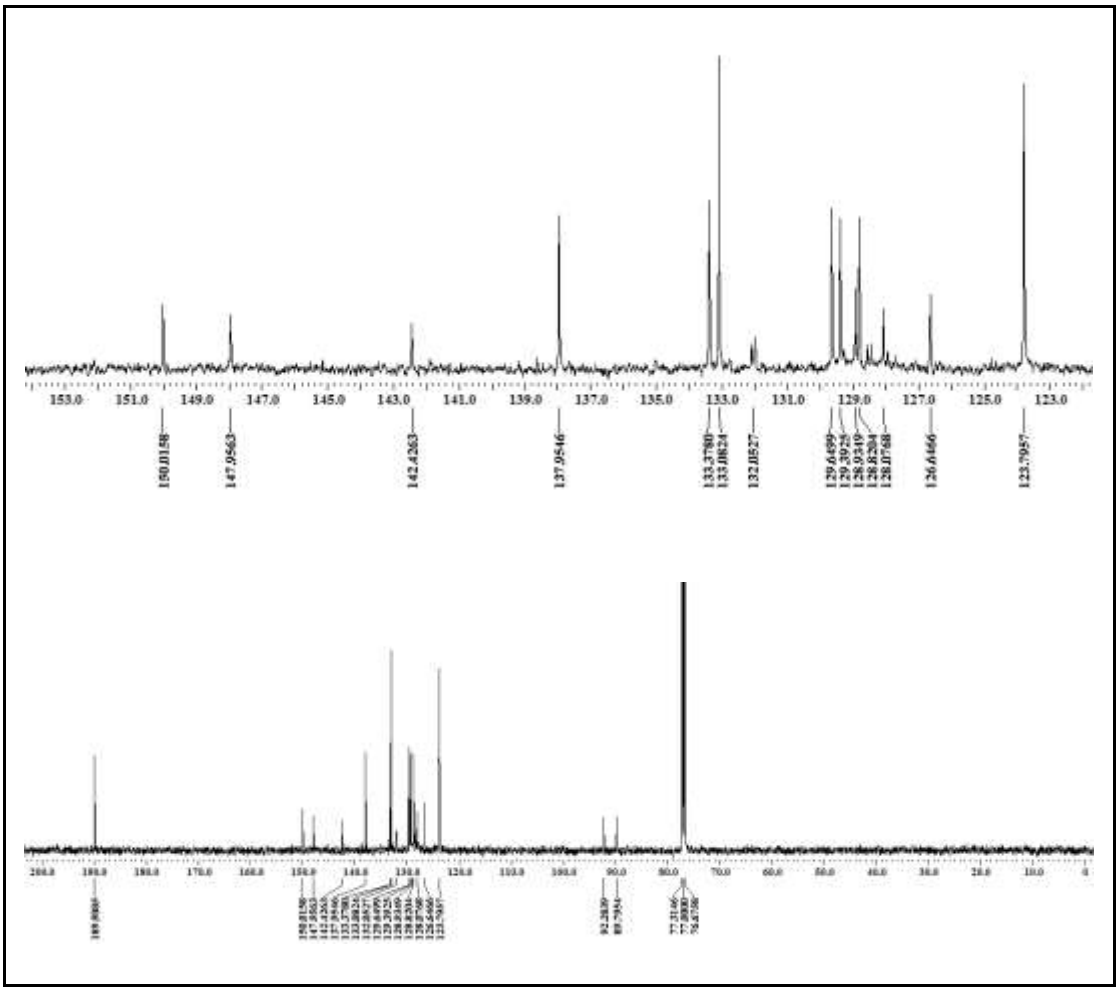
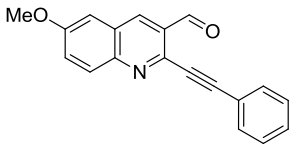
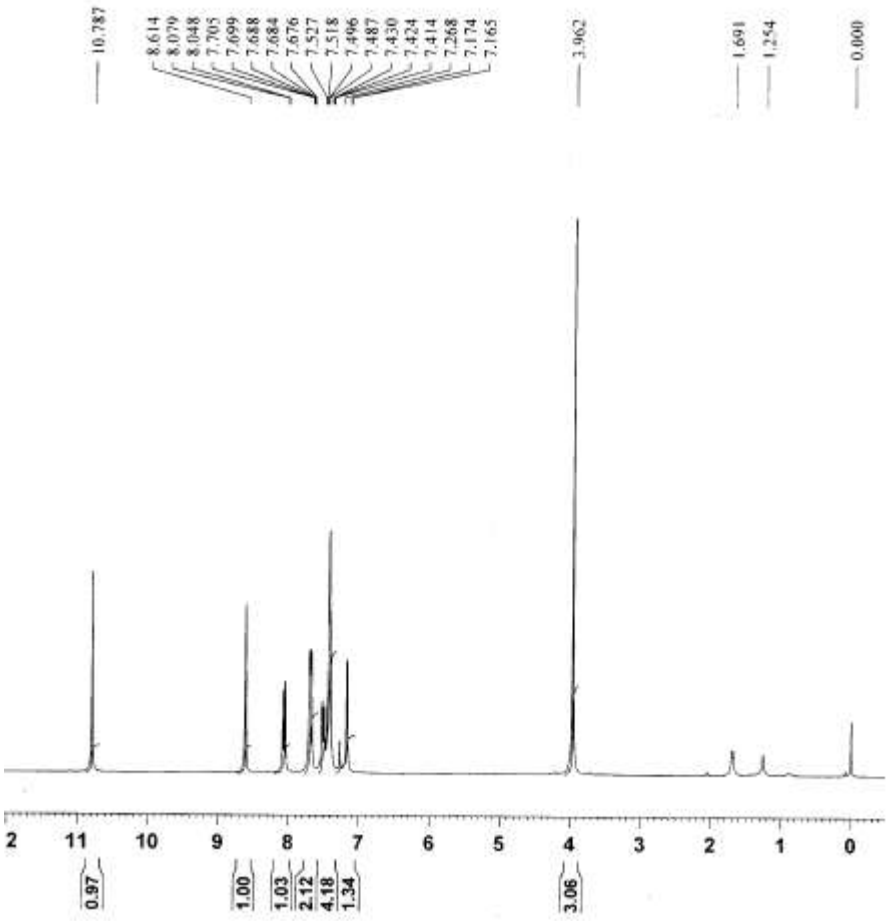


^{1}H NMR


MeO
O
N

1l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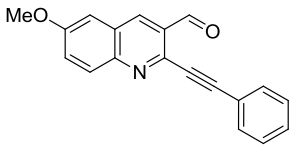
8.079
8.048
7.705
7.699
7.688
7.684
7.676
7.527
7.518
7.496
7.487
7.430
7.424
7.414
7.268
7.174
7.165
3.962
1.691
1.254
0.000
2 11 10 9 8 7 6 5 4 3 2 1 0
0.97
1.00
1.03
2.12
4.18
1.34
3.06

^{13}C NMR



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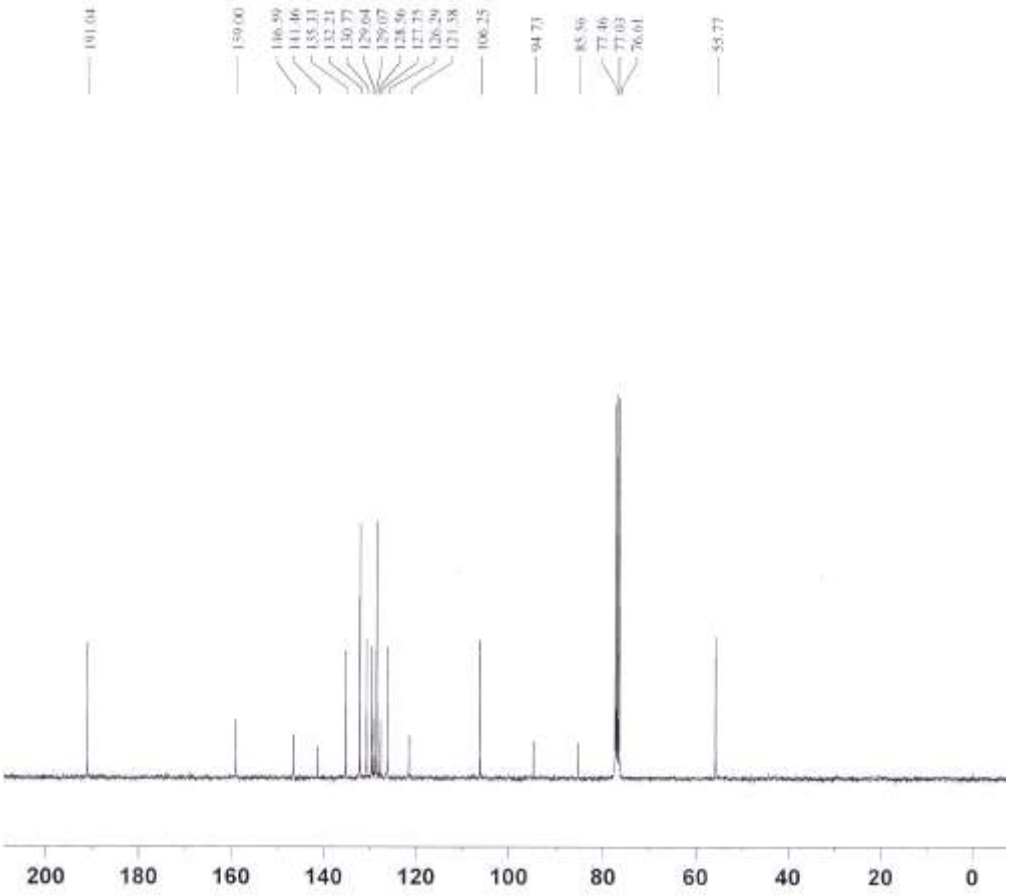
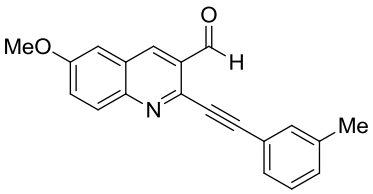
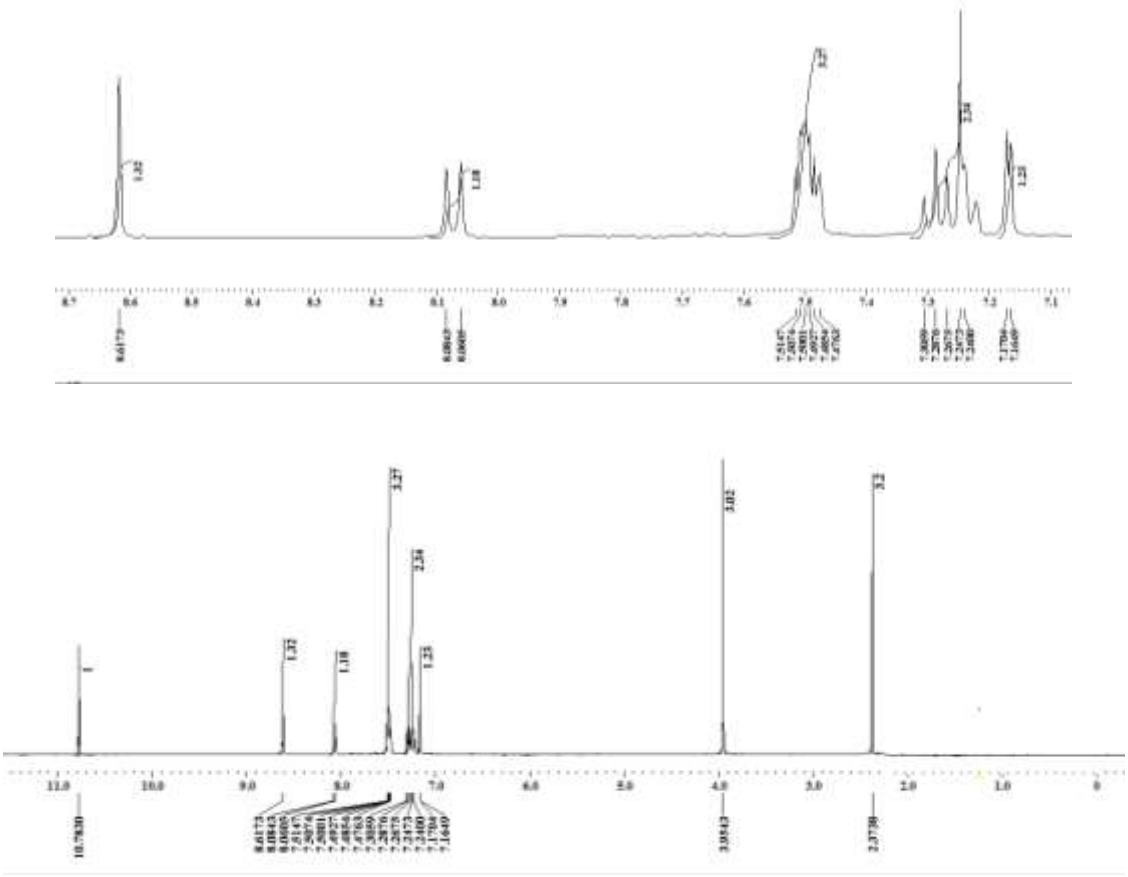


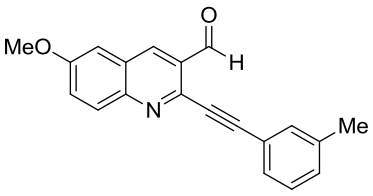
^{1}H NMR



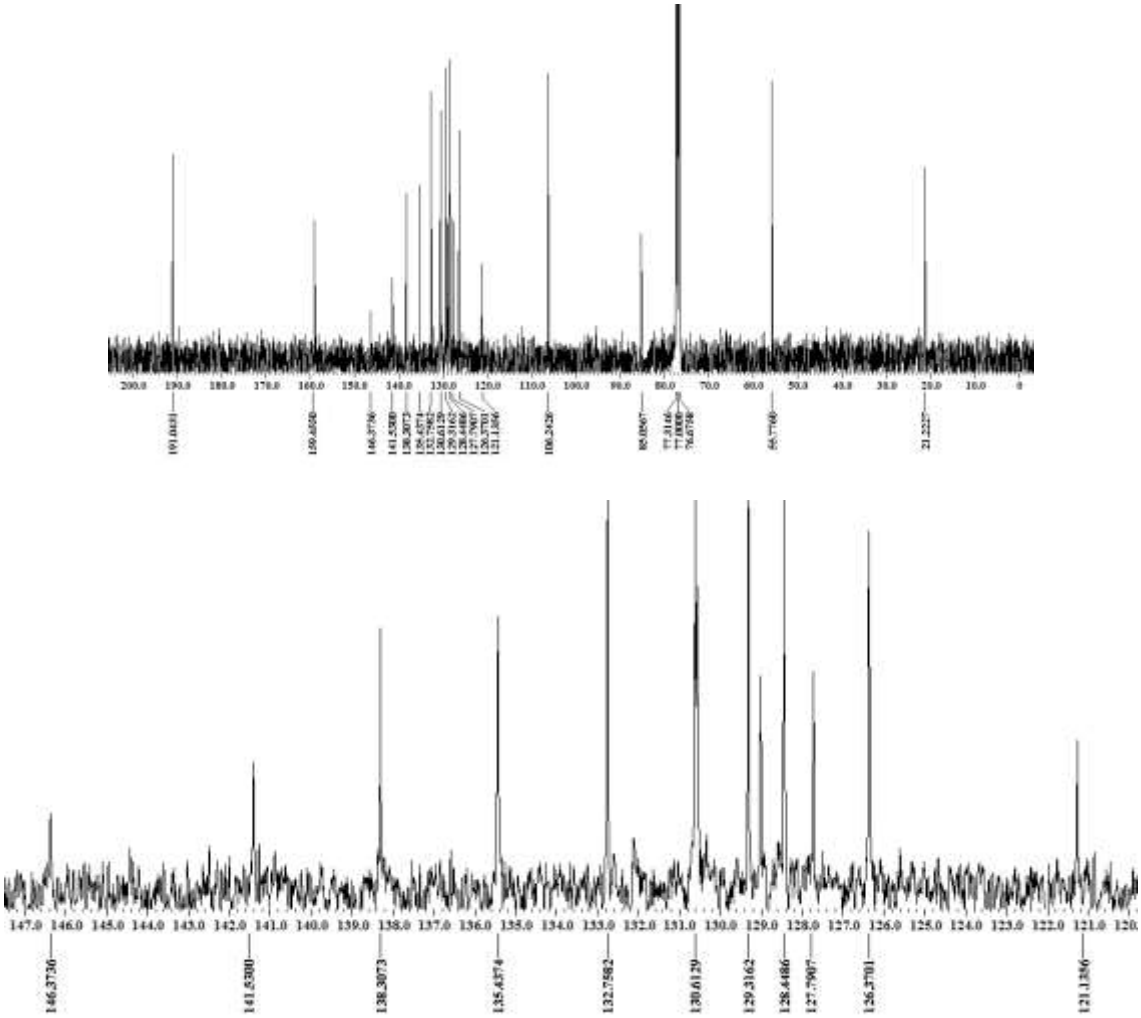
1m



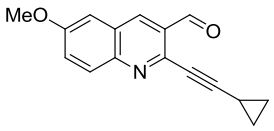
^{13}C NMR



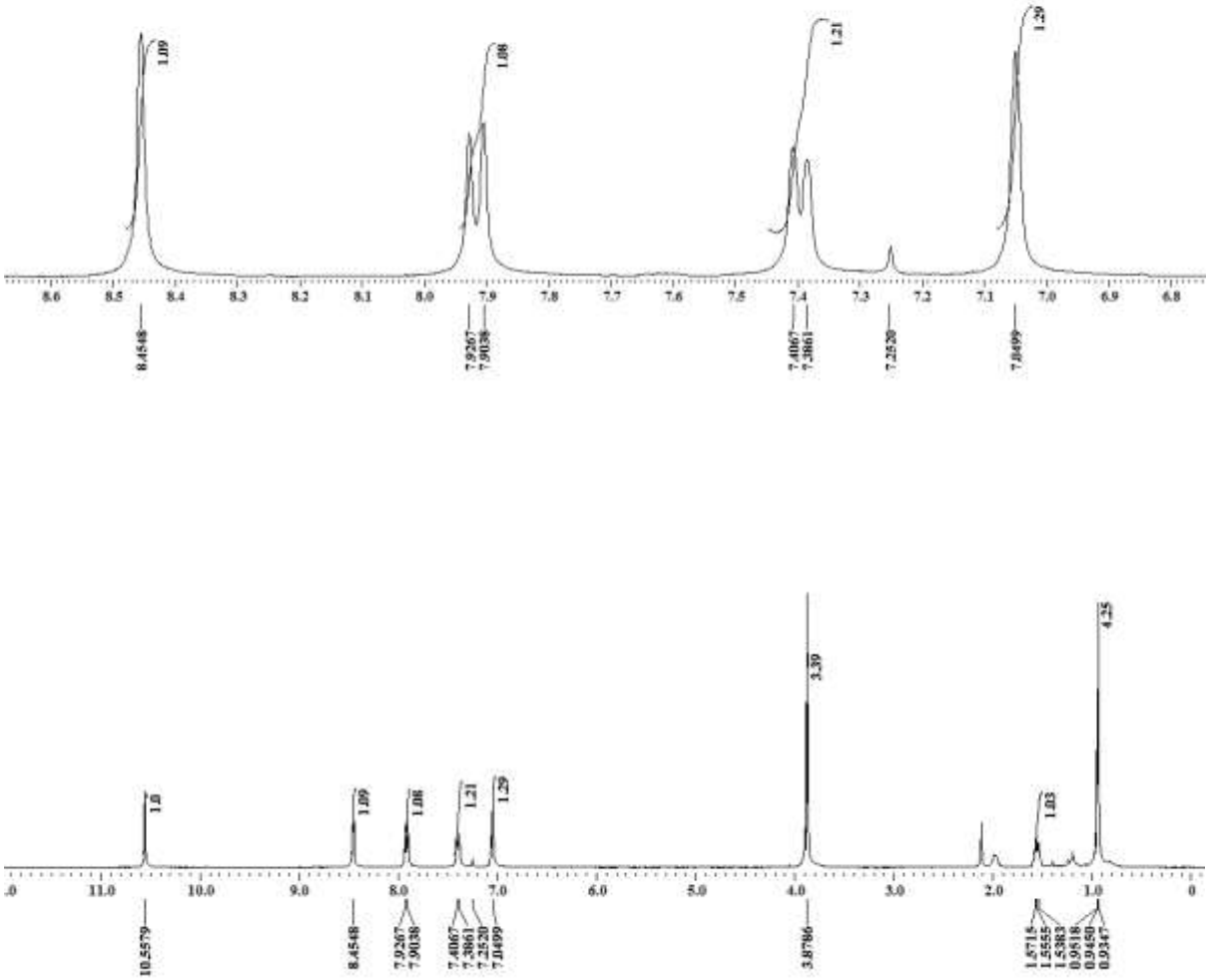
1m



^{1}H NMR


MeO
O
N

1n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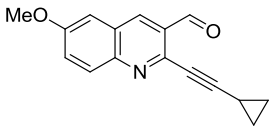
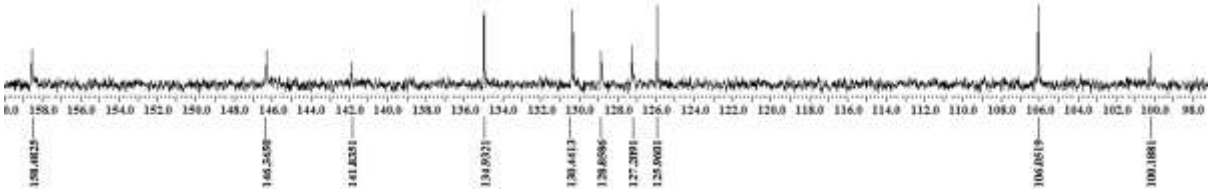
1.08
1.21
1.29
8.4548
7.9267
7.9038
7.4067
7.3861
7.2520
7.0499

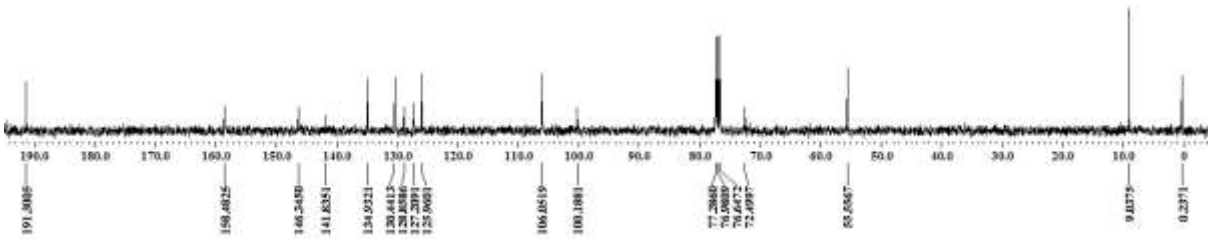
1.0
1.09
1.08
1.21
1.29
3.39
1.03
4.25
10.5579
8.4548
7.9267
7.9038
7.4067
7.3861
7.2520
7.0499
3.8786
1.6715
1.5555
1.5383
0.9618
0.9450
0.9347

^{13}C NMR

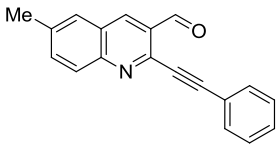


1n

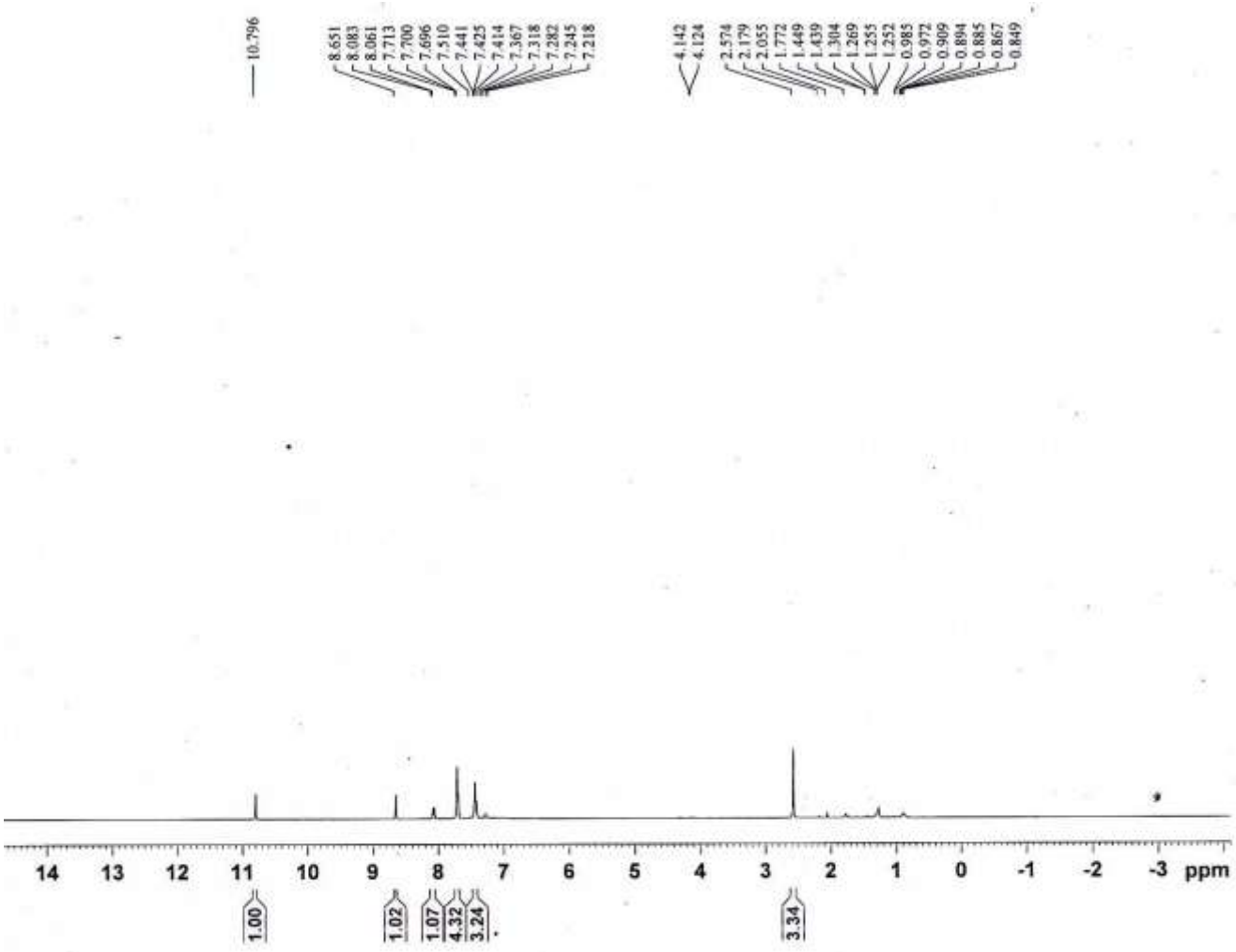




^{1}H NMR


Me
O
N

1o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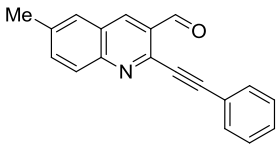
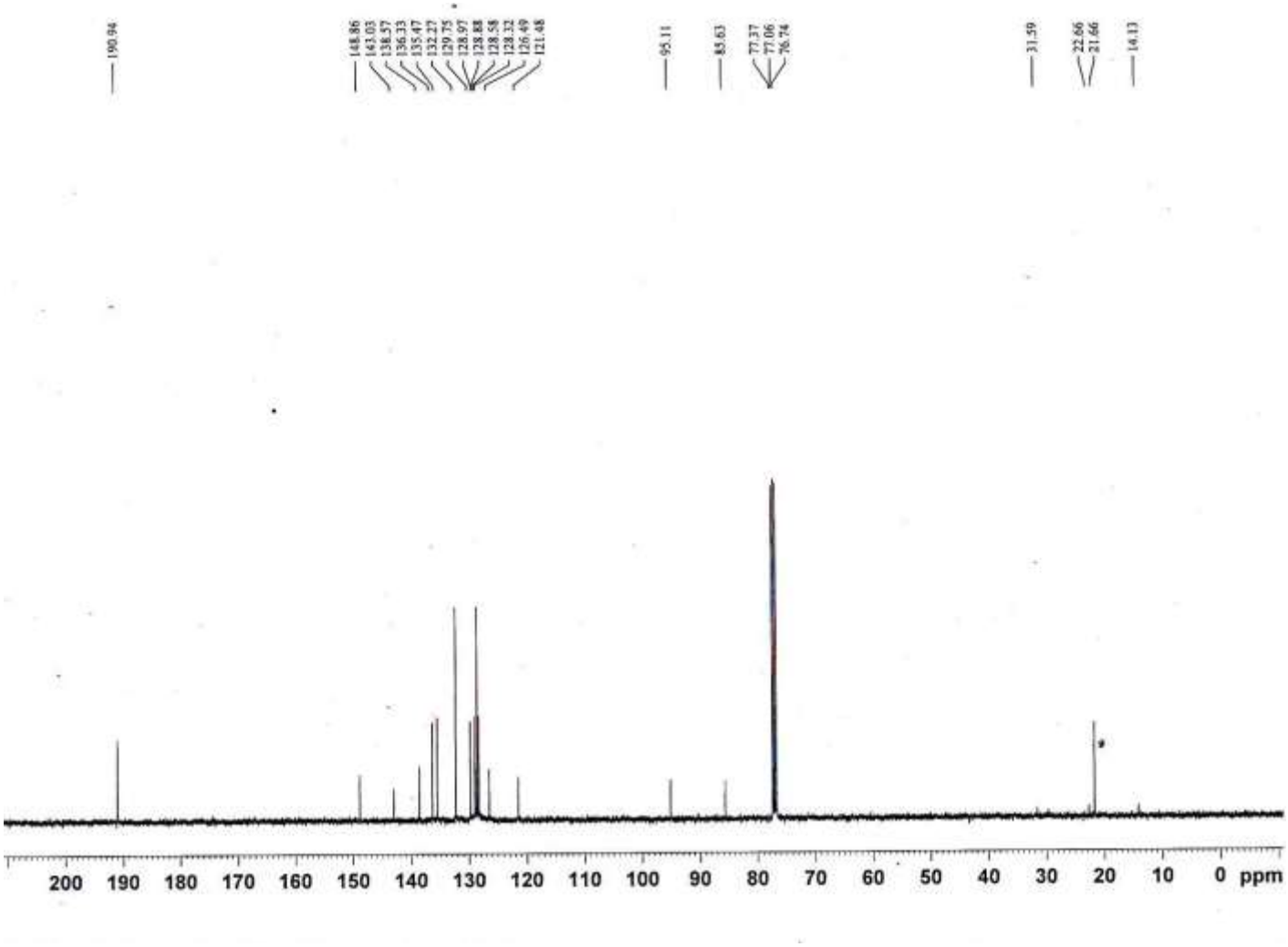
8.061
7.713
7.700
7.696
7.510
7.441
7.425
7.414
7.367
7.318
7.282
7.245
7.218
4.142
4.124
2.574
2.179
2.055
1.772
1.449
1.439
1.304
1.269
1.255
1.252
0.985
0.972
0.909
0.894
0.885
0.867
0.849
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
1.00
1.02
1.07
4.32
3.24
3.34

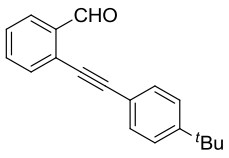
^{13}C NMR



1o



^{1}H NMR



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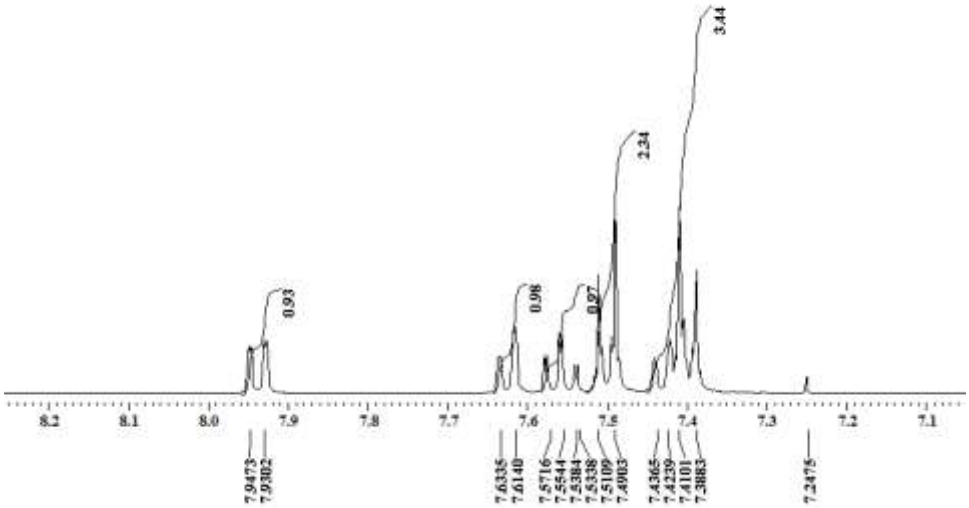
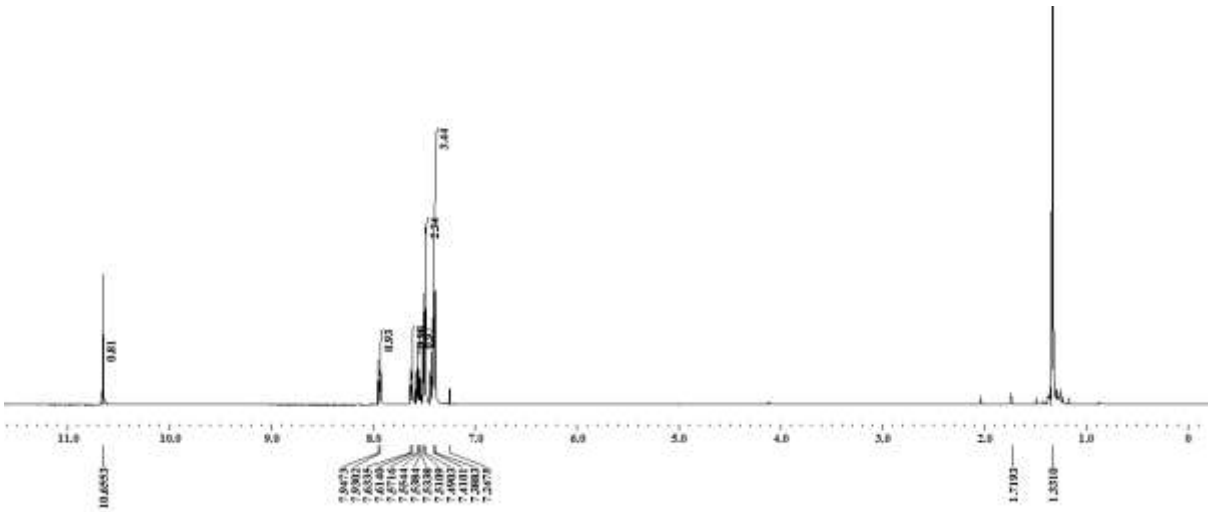
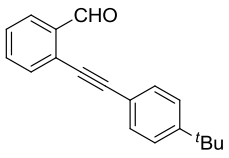




^{13}C NMR



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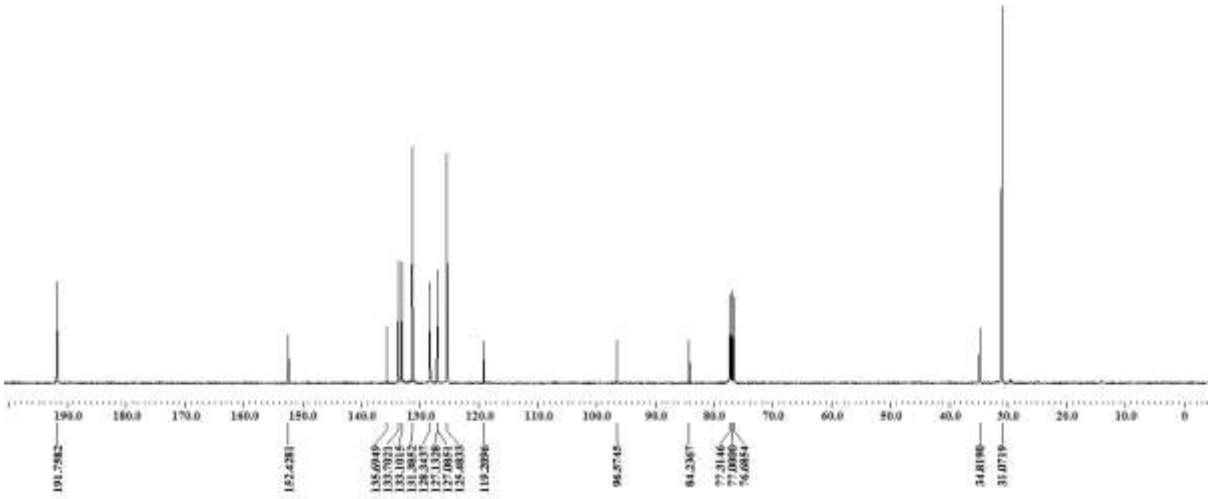
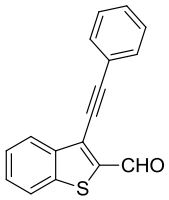
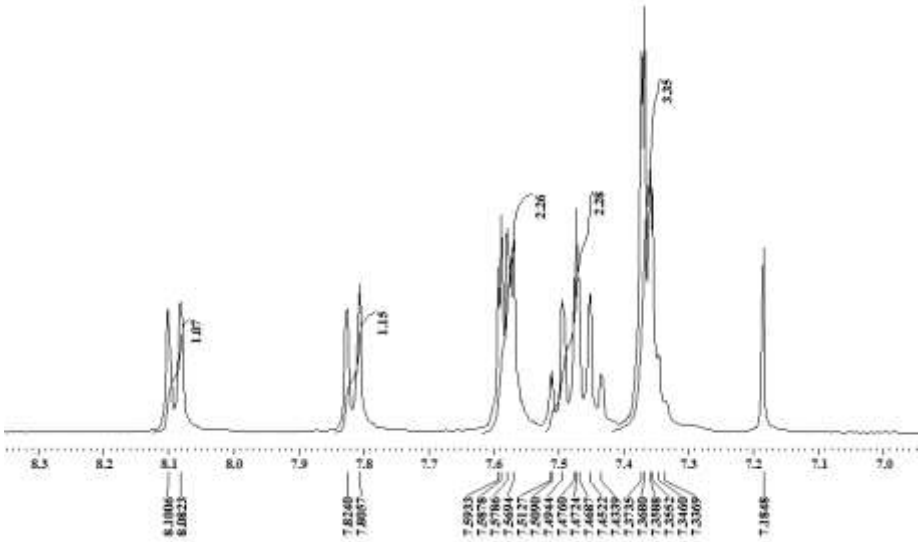
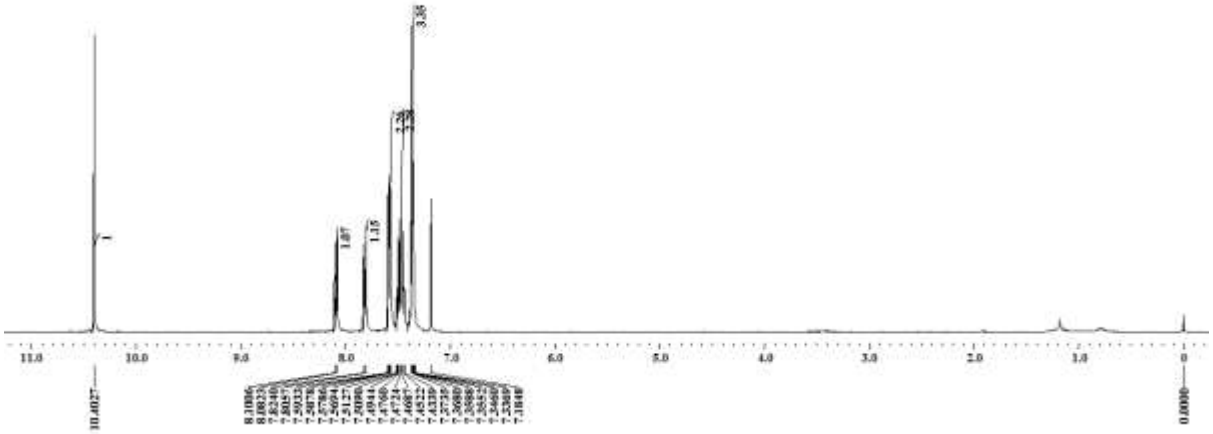


^{1}H NMR

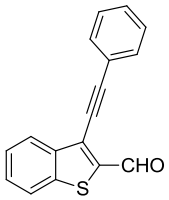


3a

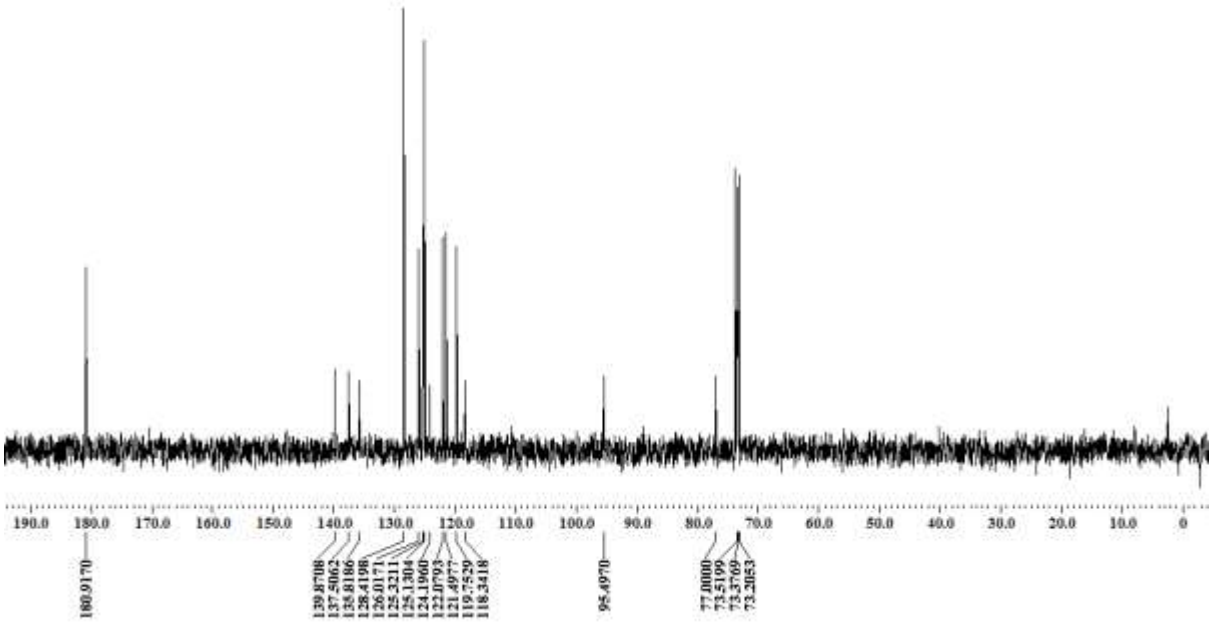




^{13}C NMR


CHO
S

3a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70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.9170
139.8708
137.5062
135.8186
128.4198
126.0171
125.3211
125.1304
124.1960
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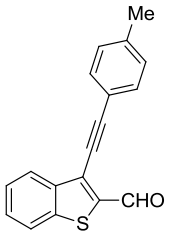
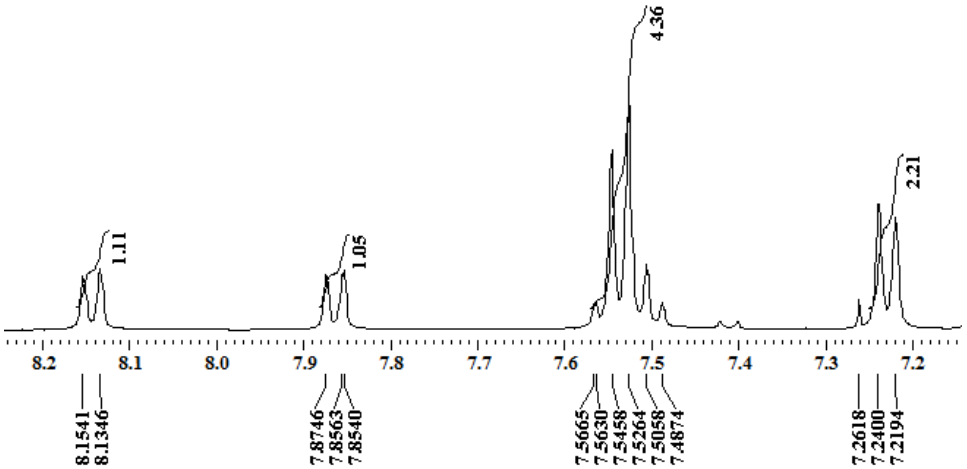
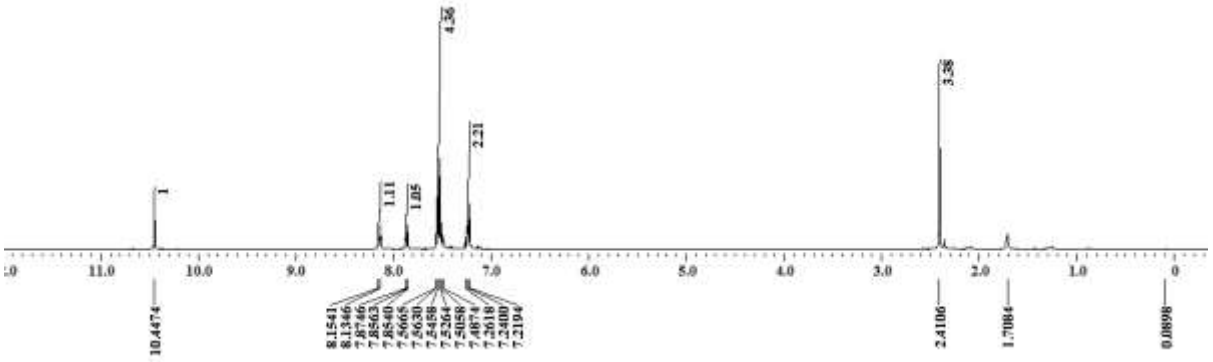
119.7529
118.3418
95.4970
77.0000
73.5199
73.3769
73.2053

^{1}H NMR

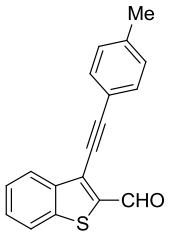


3b





^{13}C NMR



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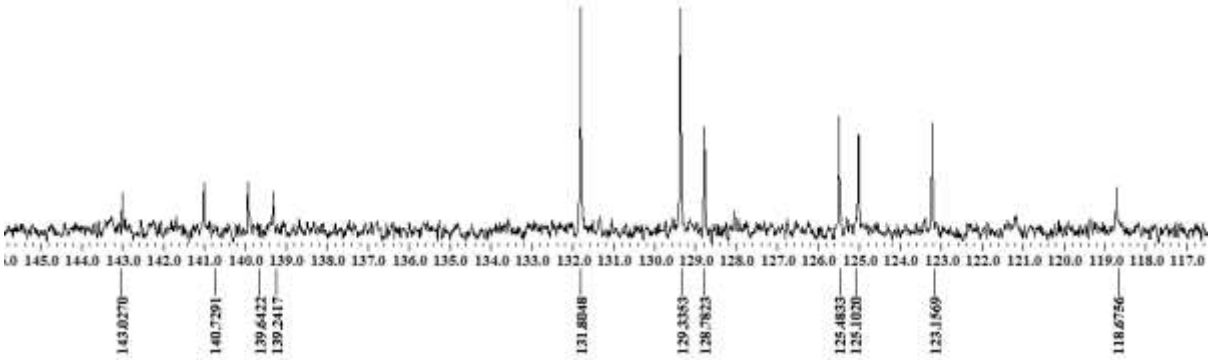
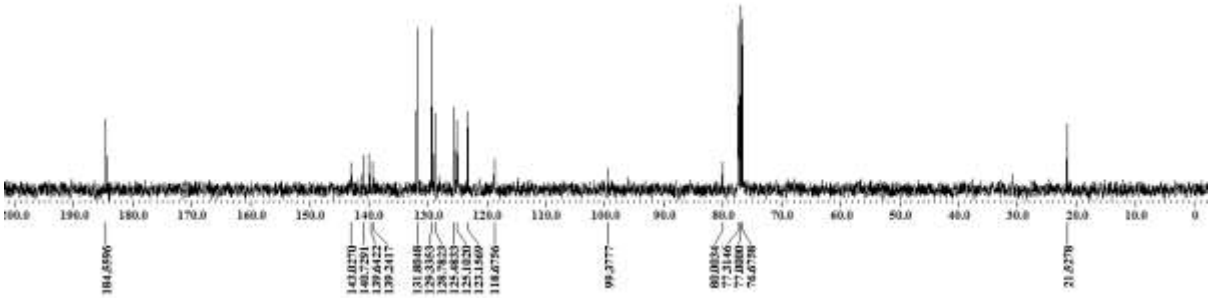
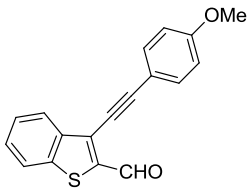
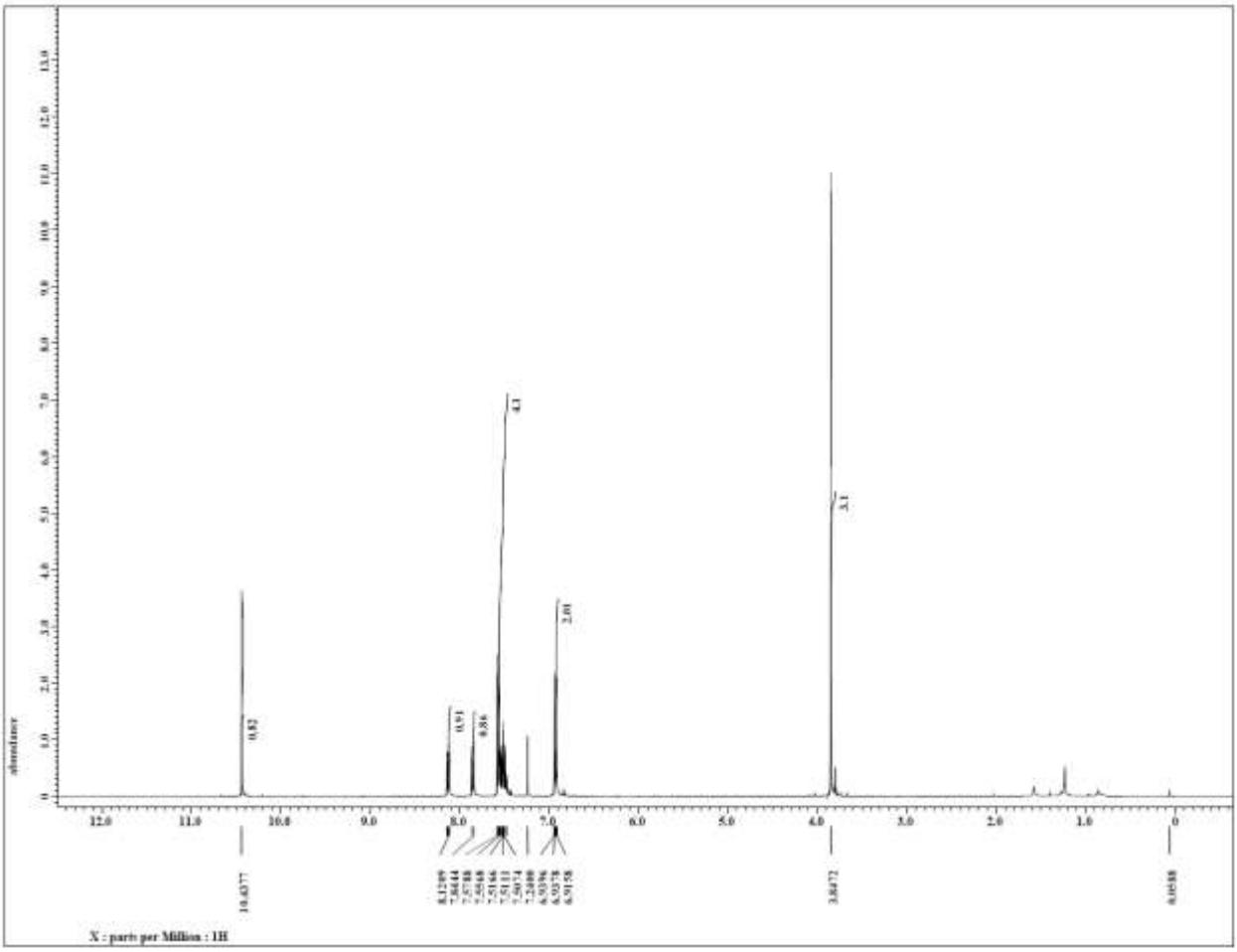




^{1}H NMR


OMe
S
CHO

3c


abundance
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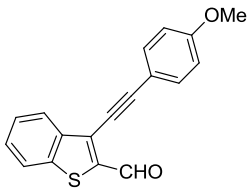
0.91
0.86
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

^{13}C NMR



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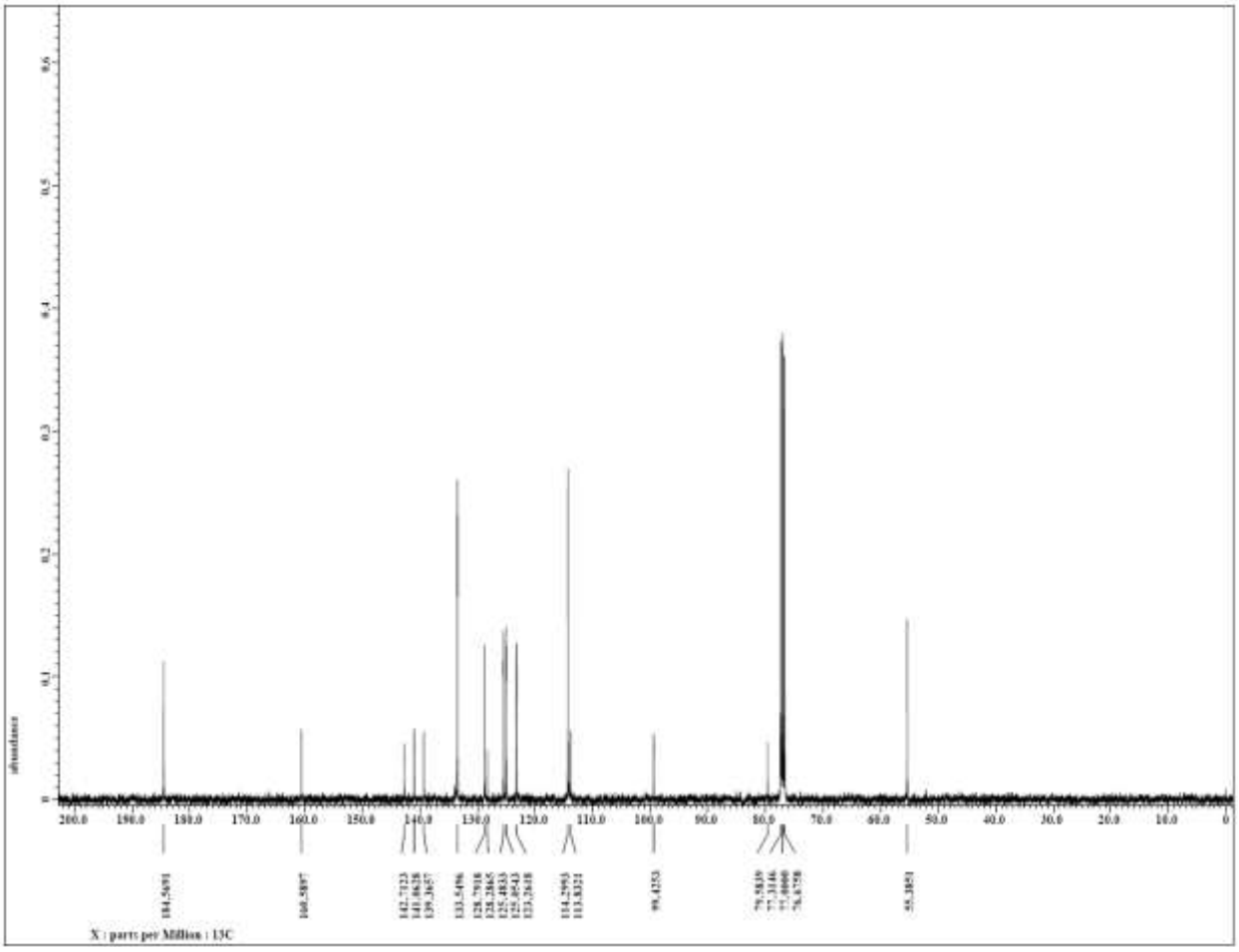
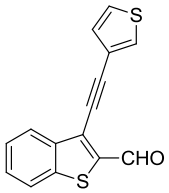
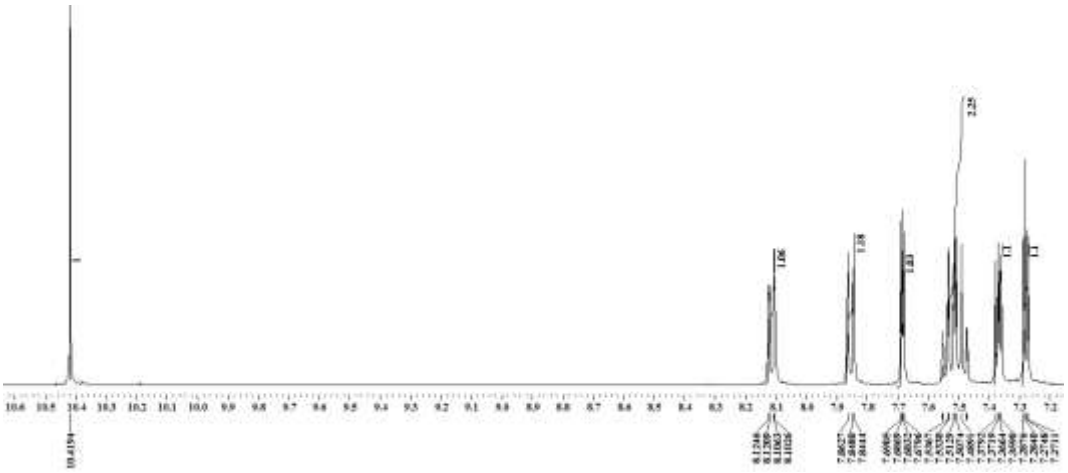
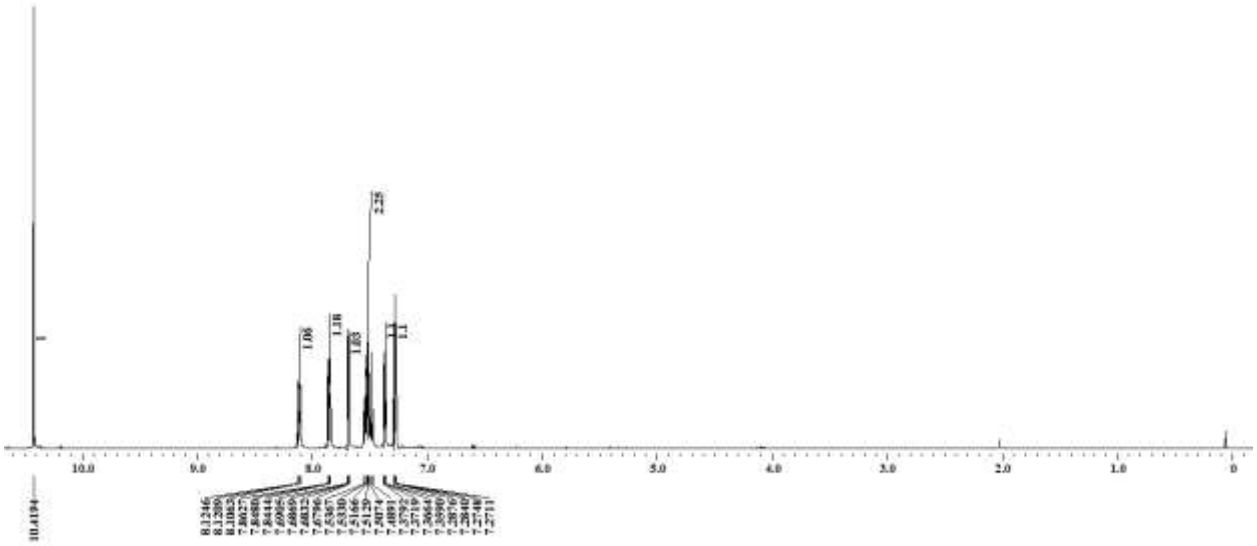


^{1}H NMR

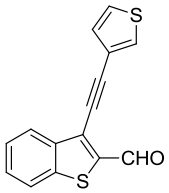


3d

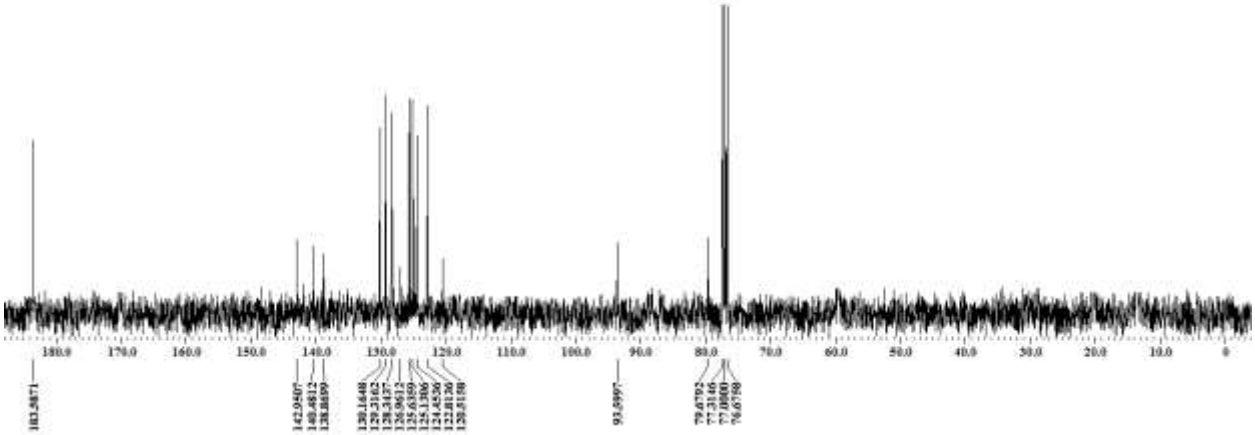




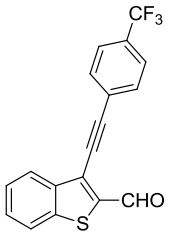
^{13}C NMR



3d



^{1}H NMR



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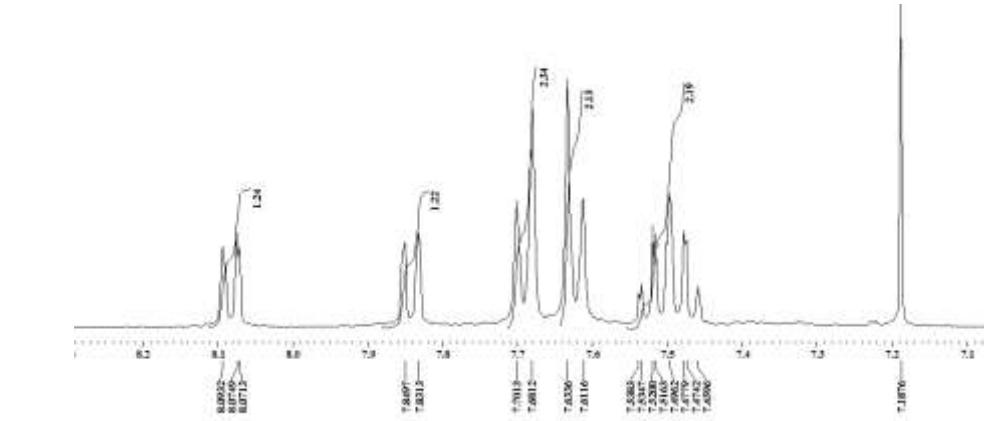
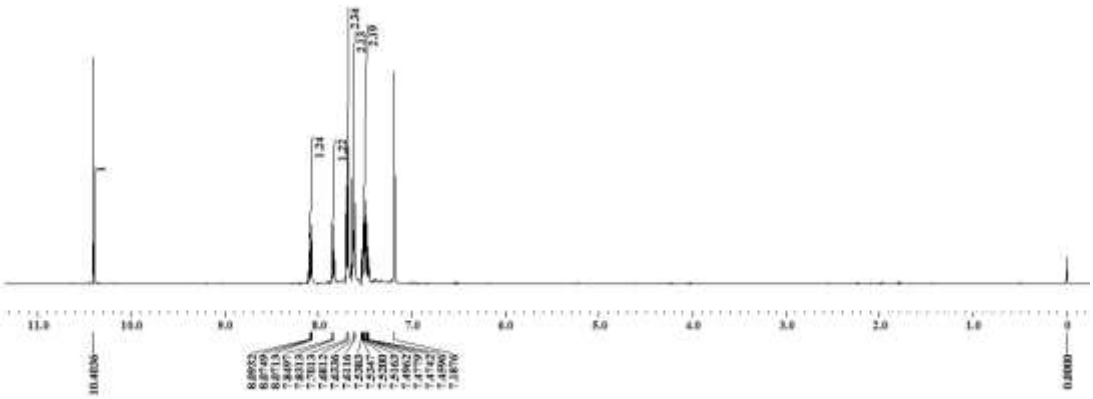
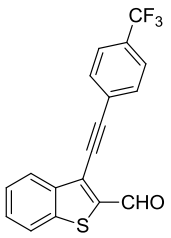
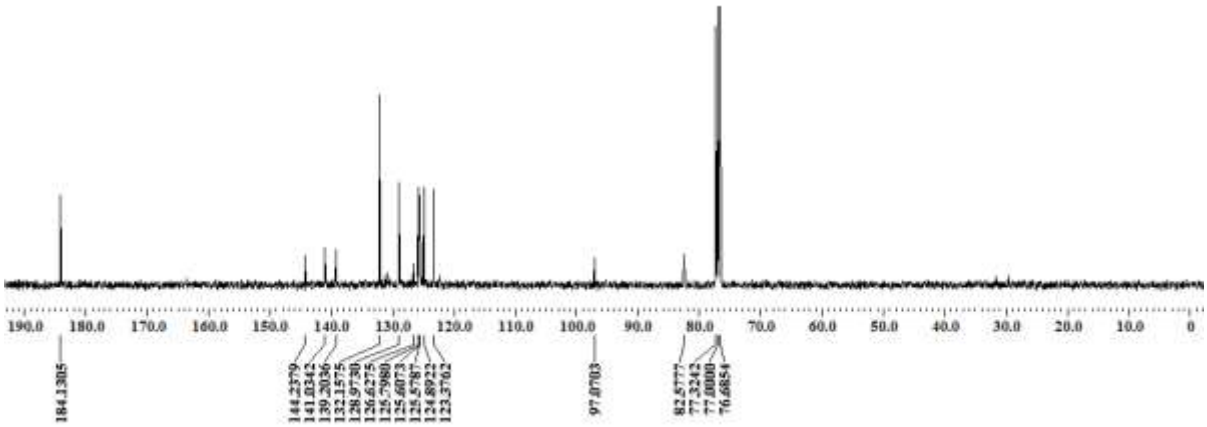




^{13}C NMR


CF3
CHO
S

3e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50.0
40.0
30.0
20.0
10.0
0
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144.2579
141.0342
139.2036
132.1575
128.9730
126.4275
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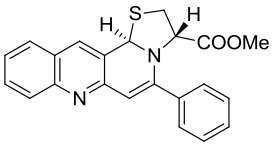
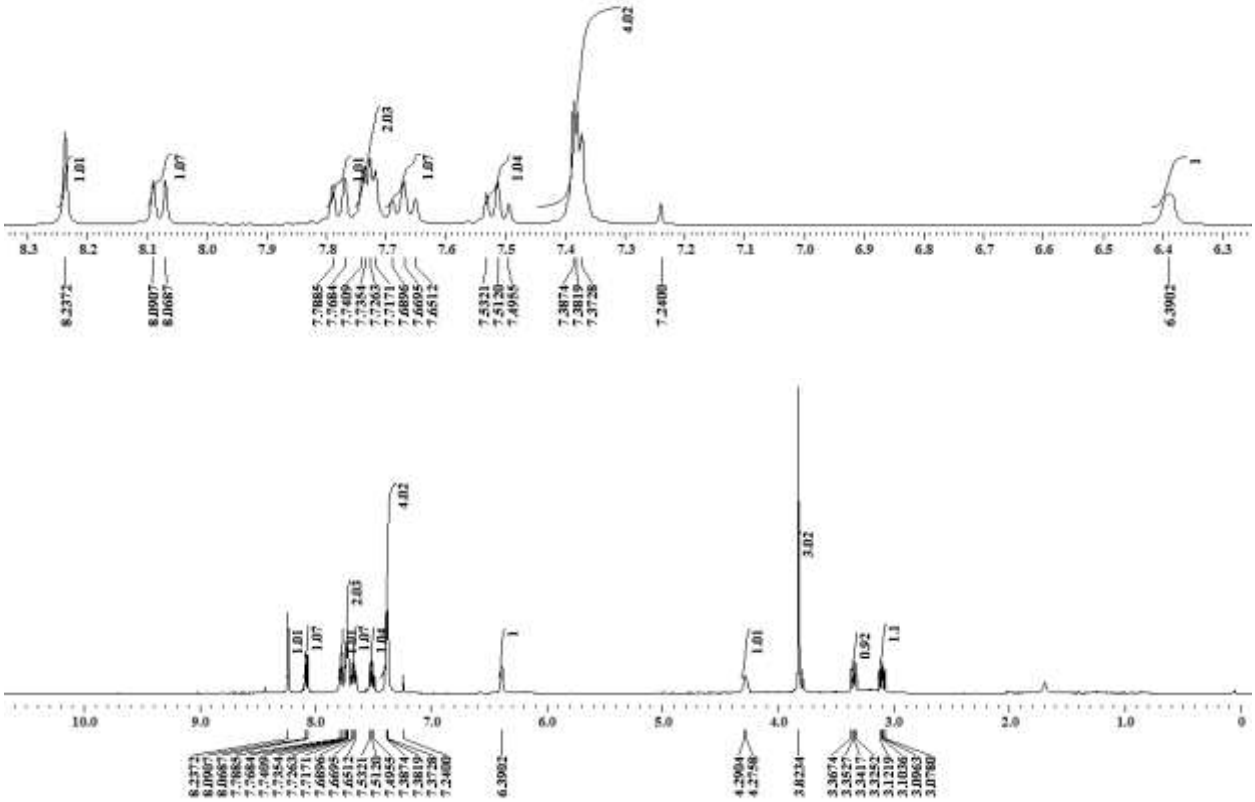
76.6854

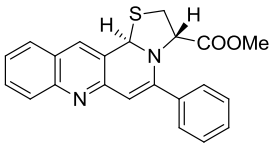
^{1}H NMR



5a



^{13}C NMR



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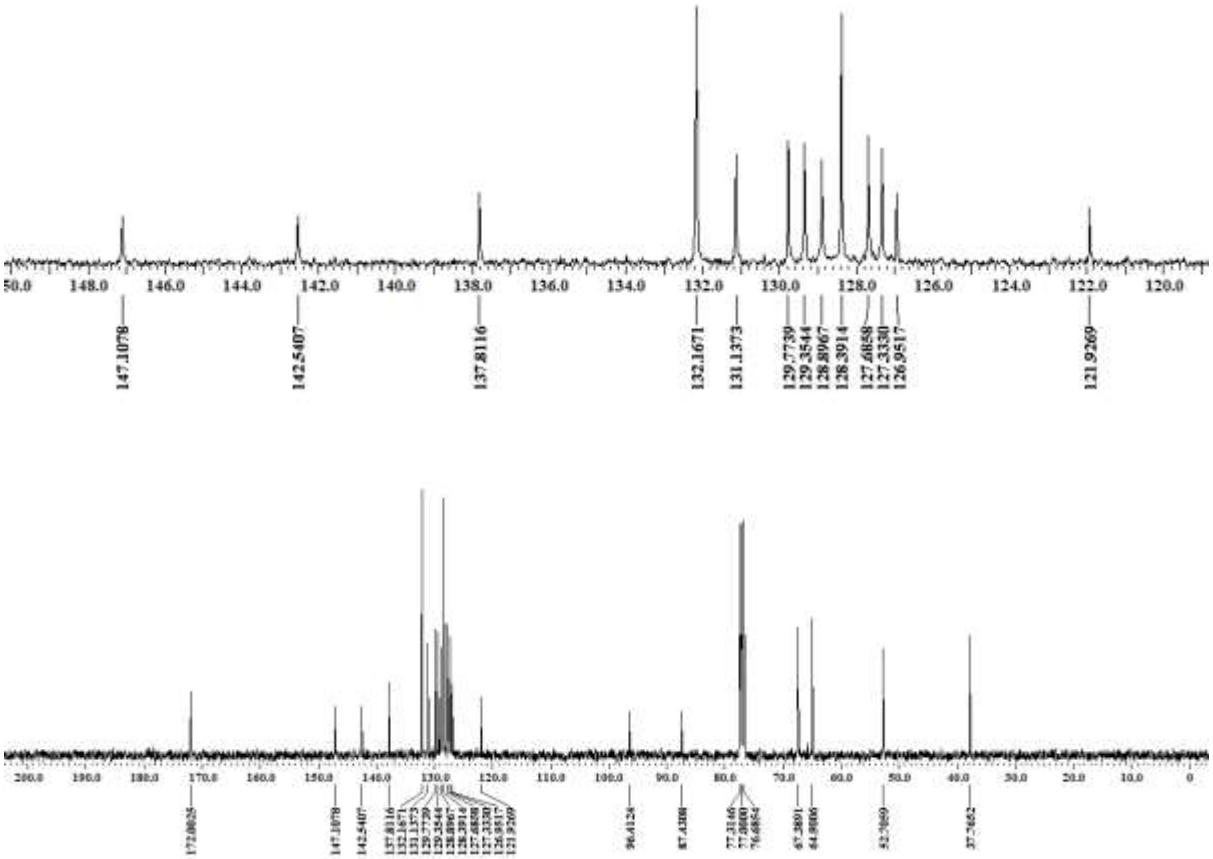

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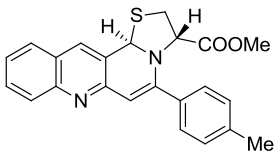

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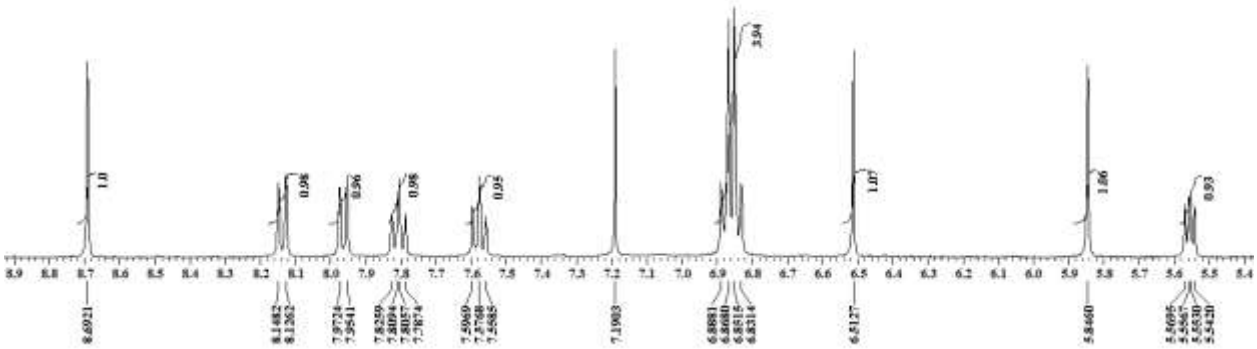

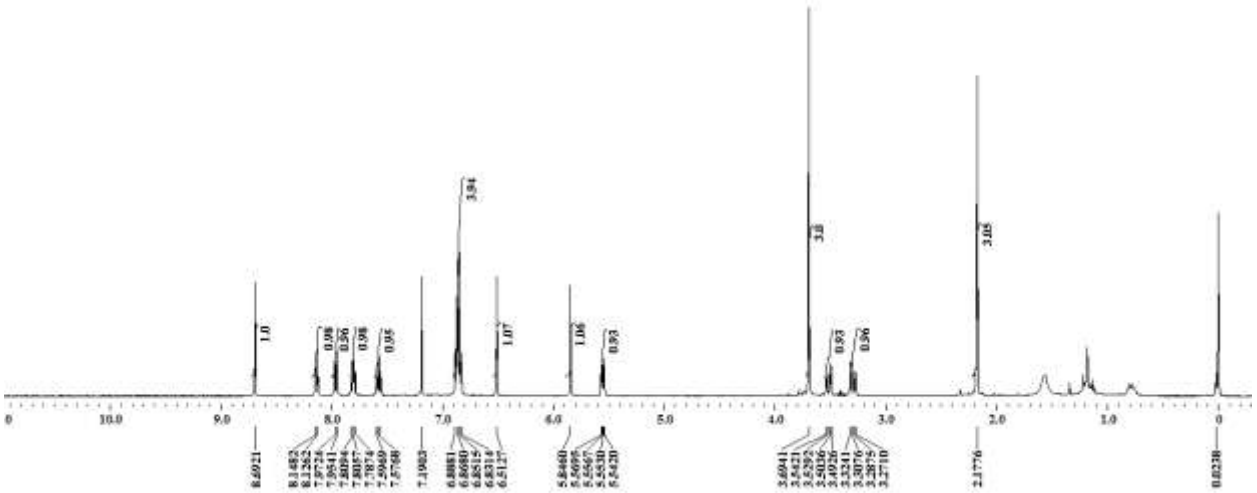

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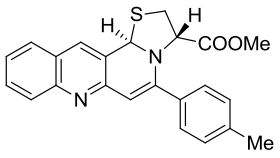

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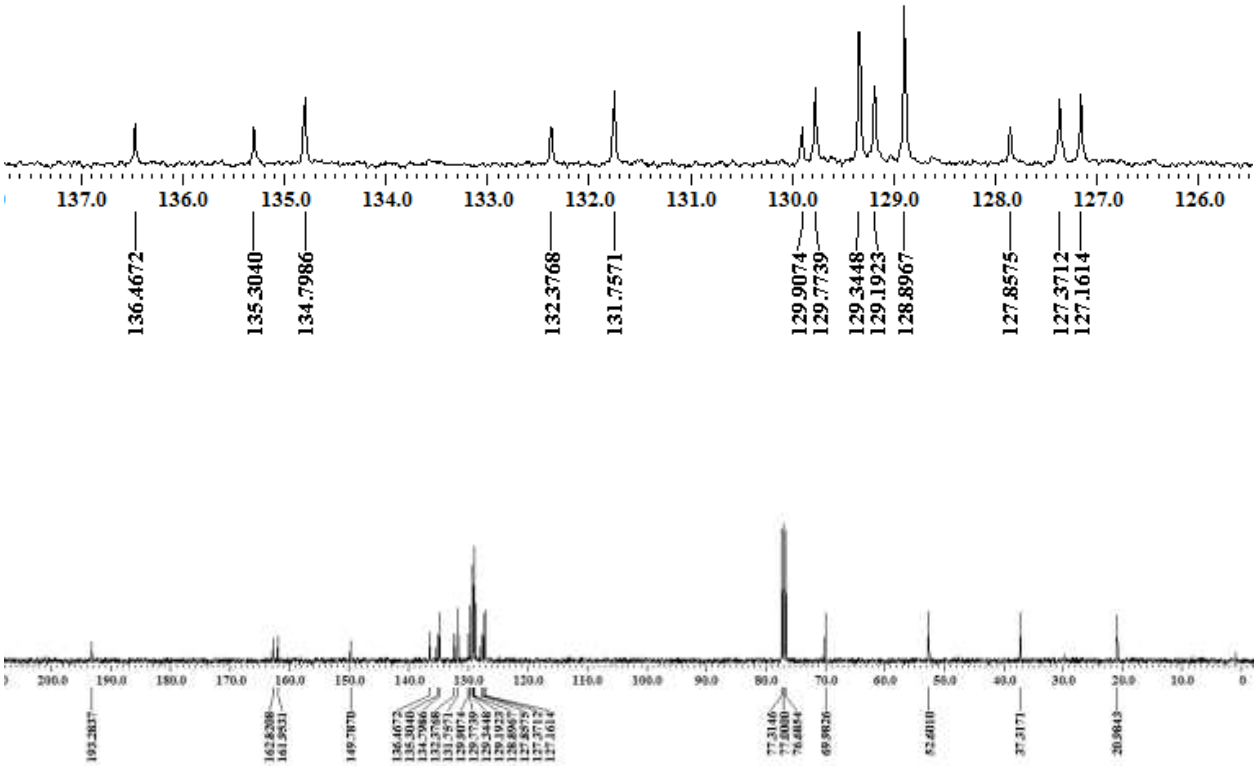

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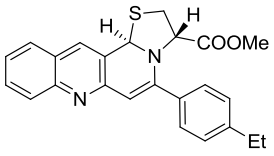

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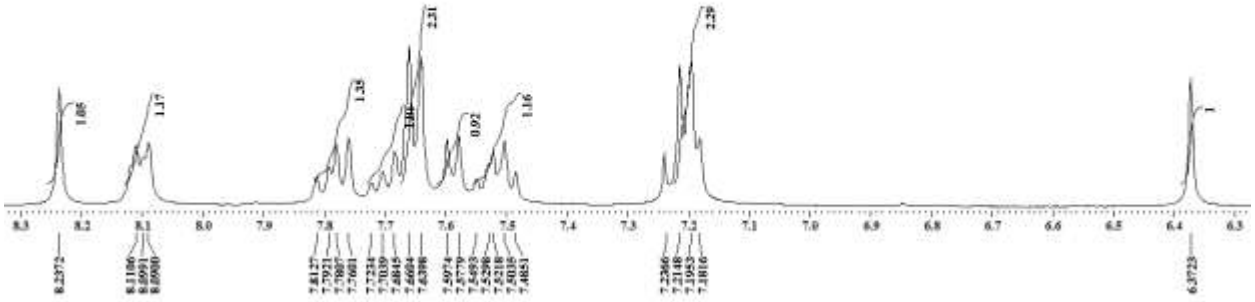

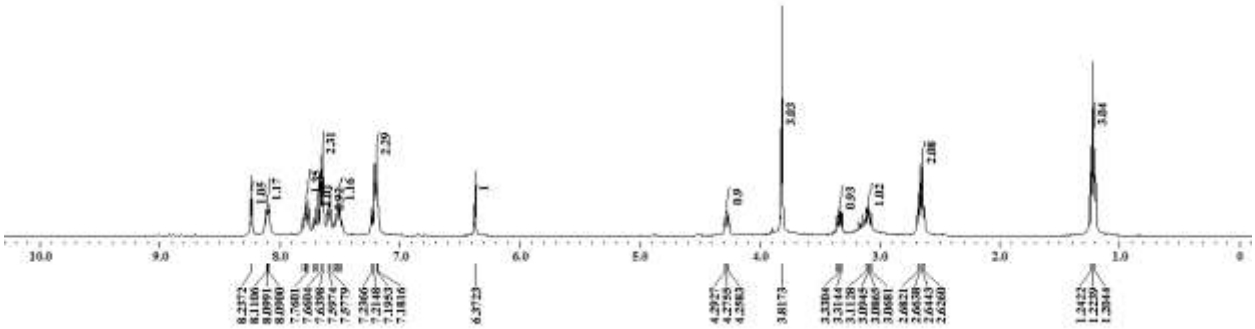

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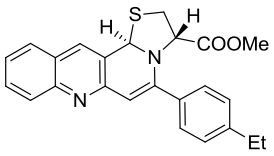

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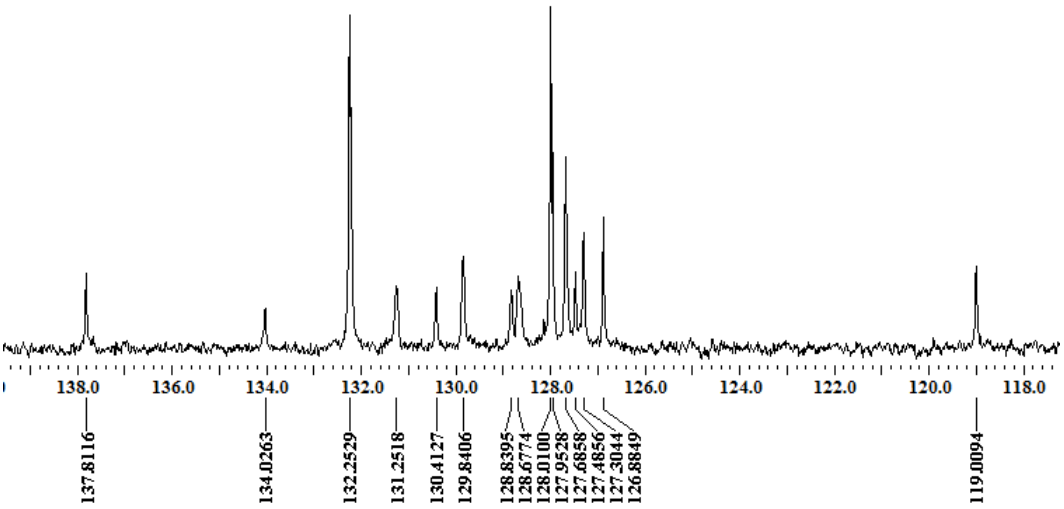

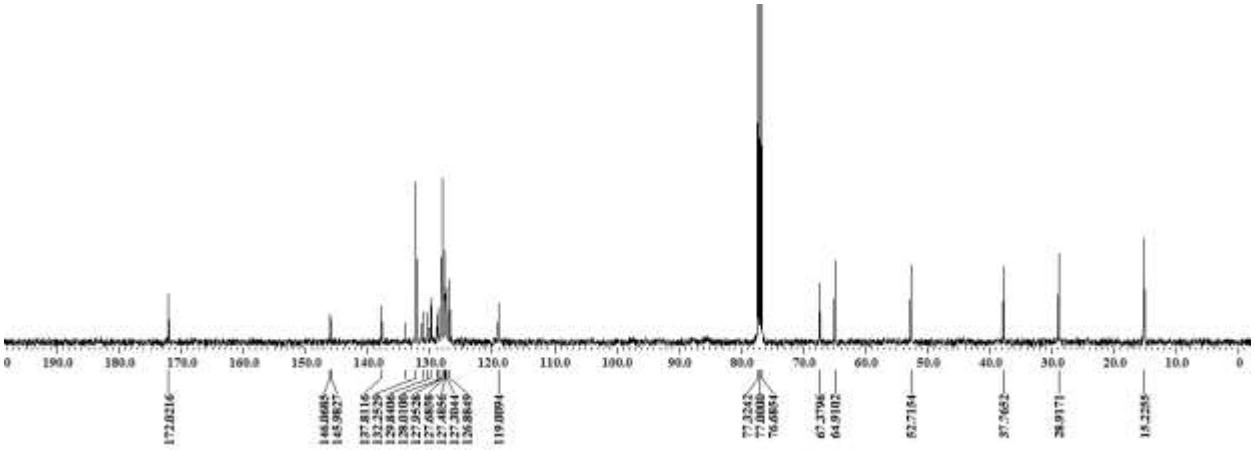

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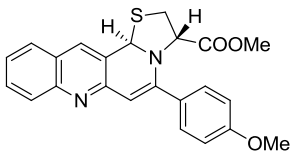

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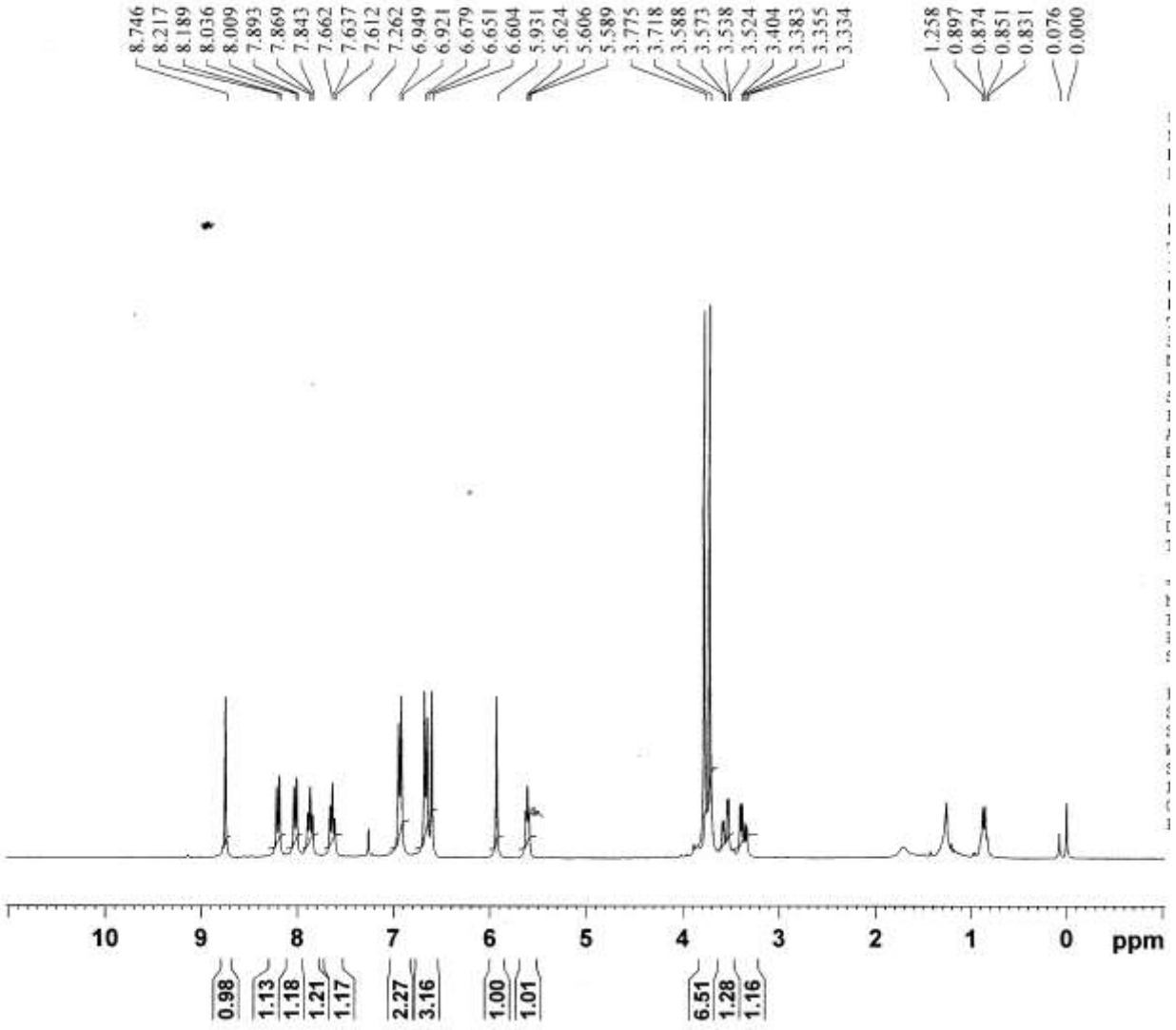

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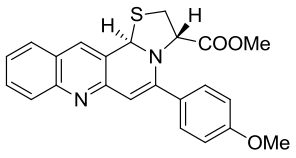
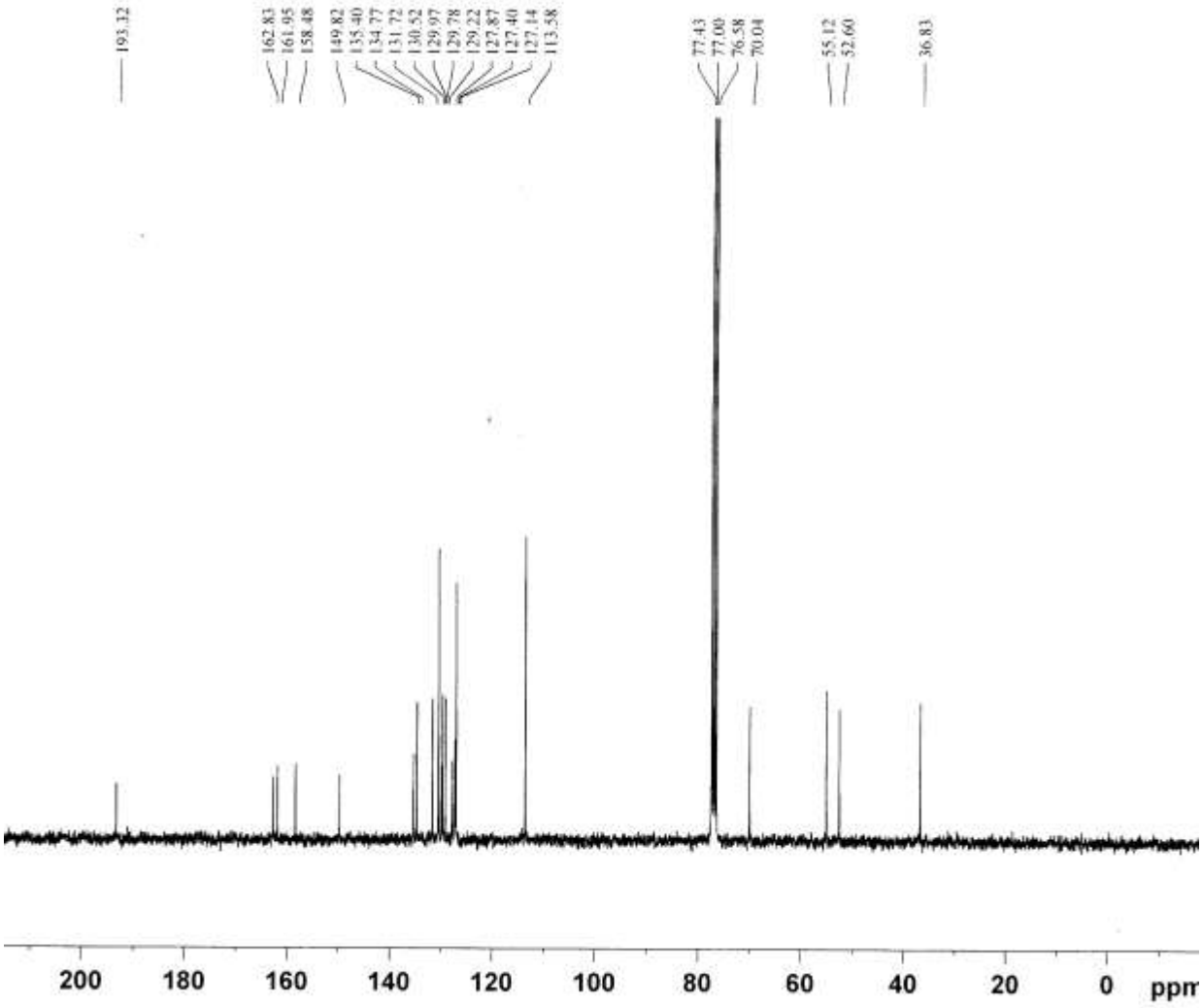

S
H
H
COOMe
N
N
OMe

5d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135.40
134.77
131.72
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127.87
127.40
127.14
113.58
77.43
77.00
76.58
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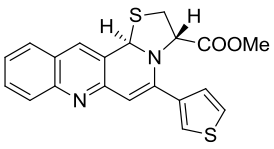
^{1}H NMR



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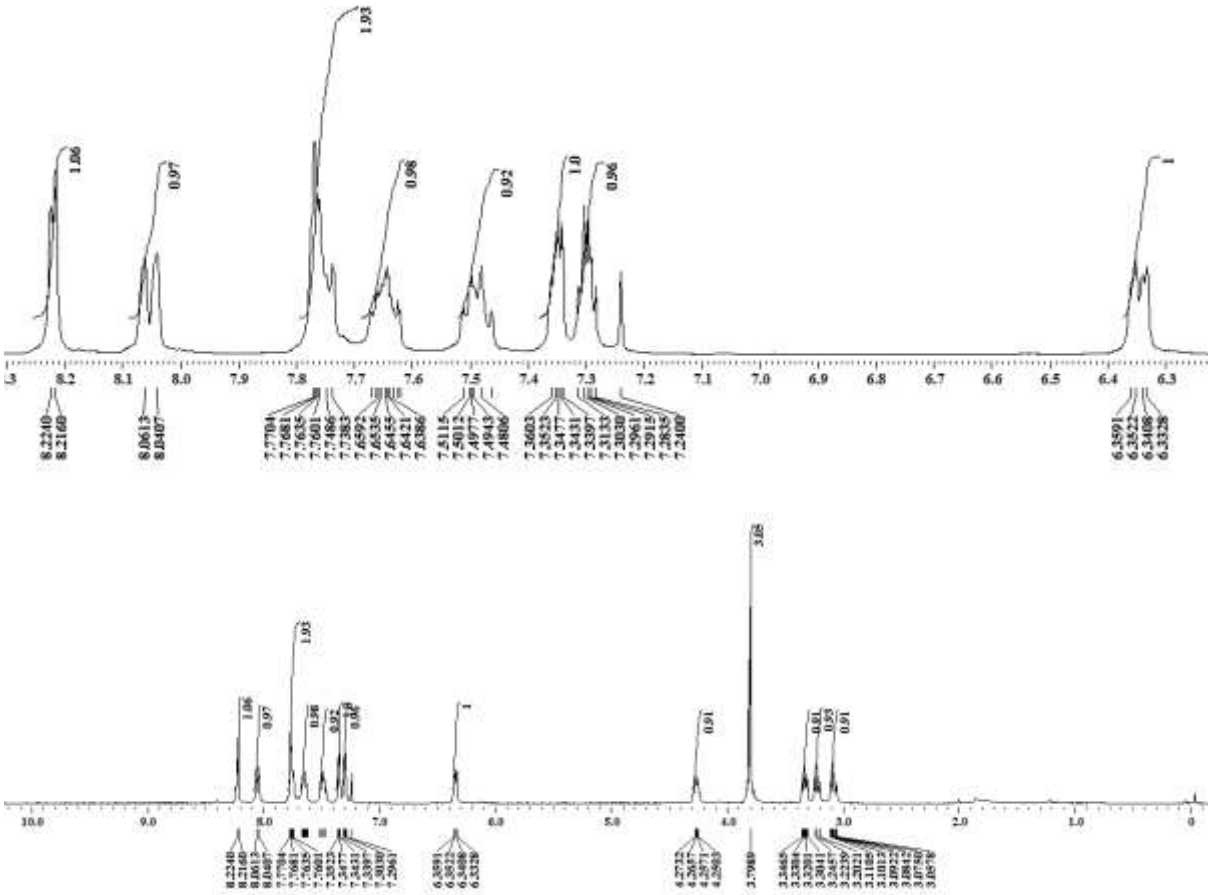

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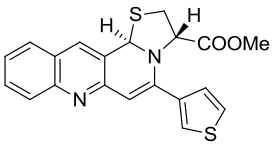

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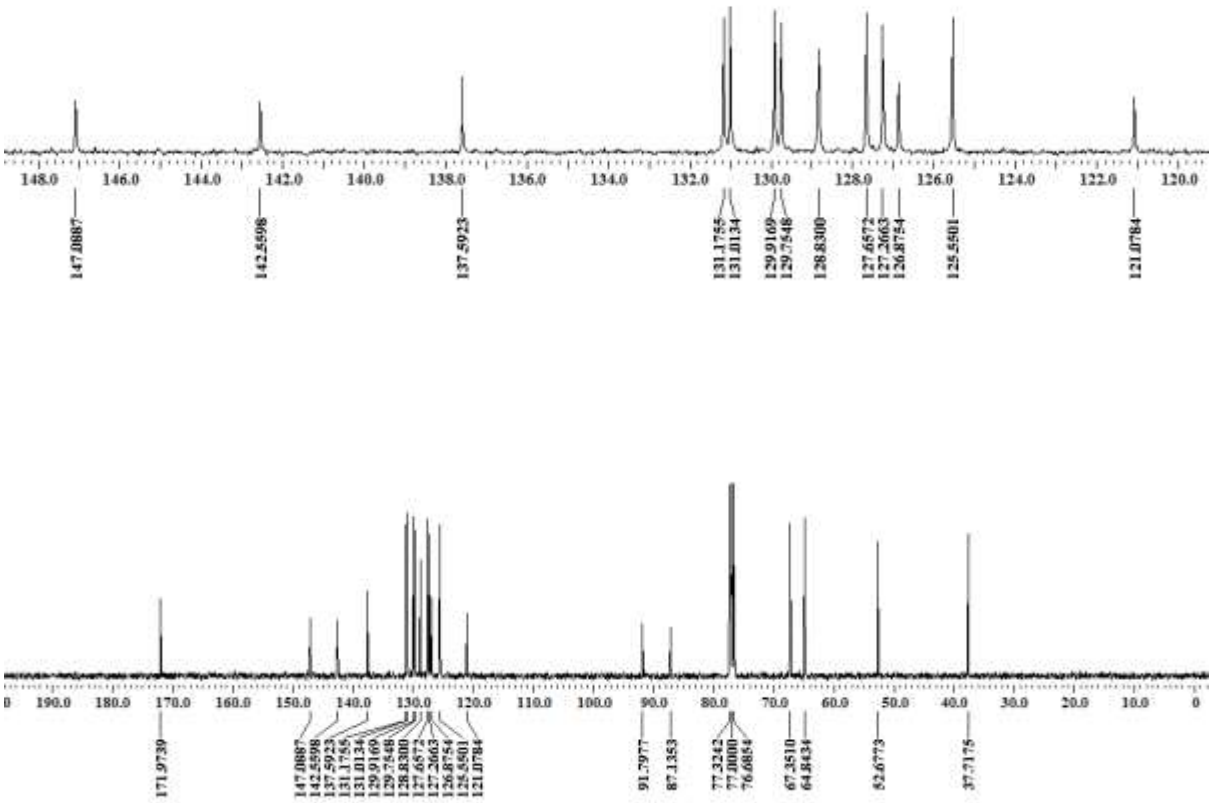

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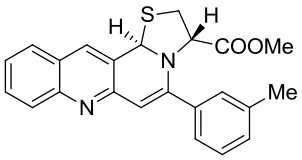

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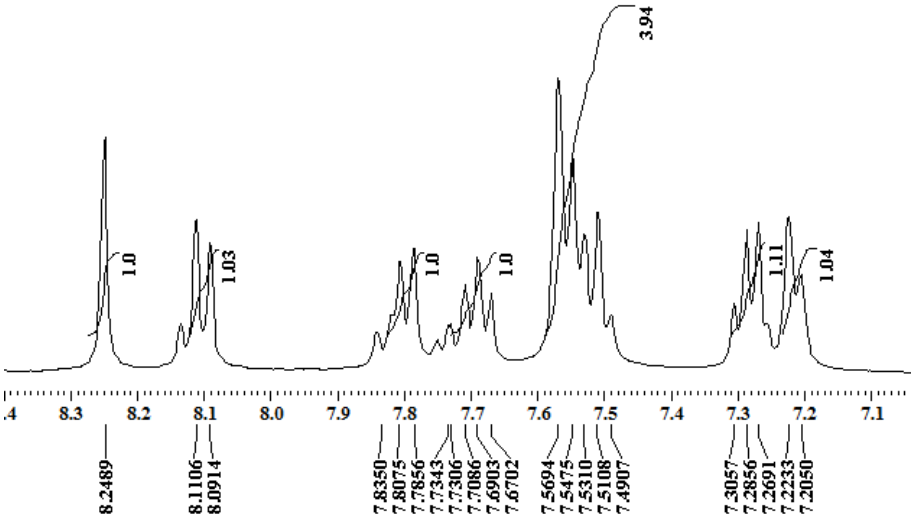

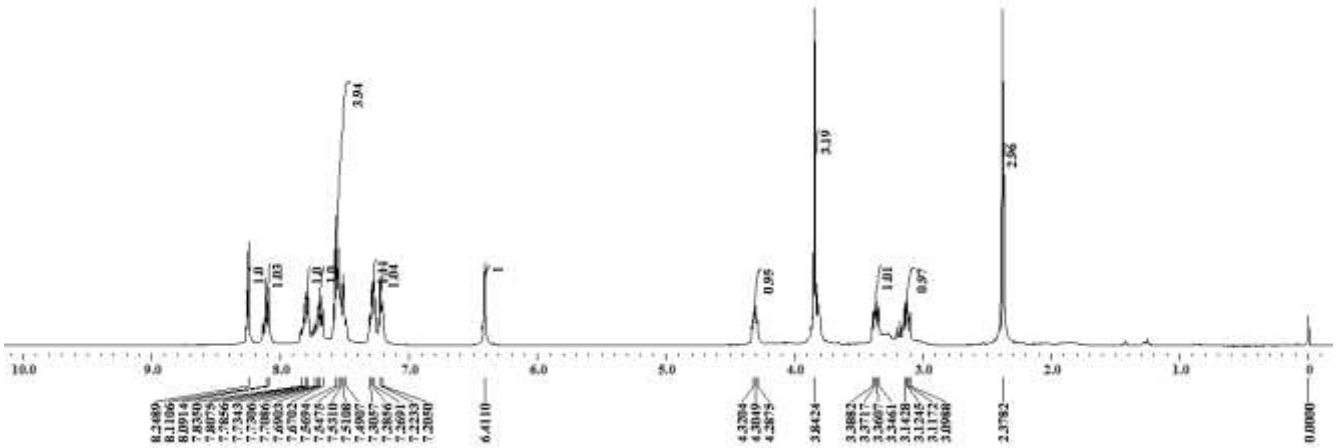

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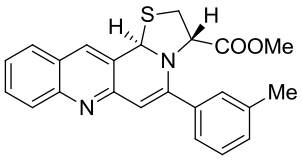
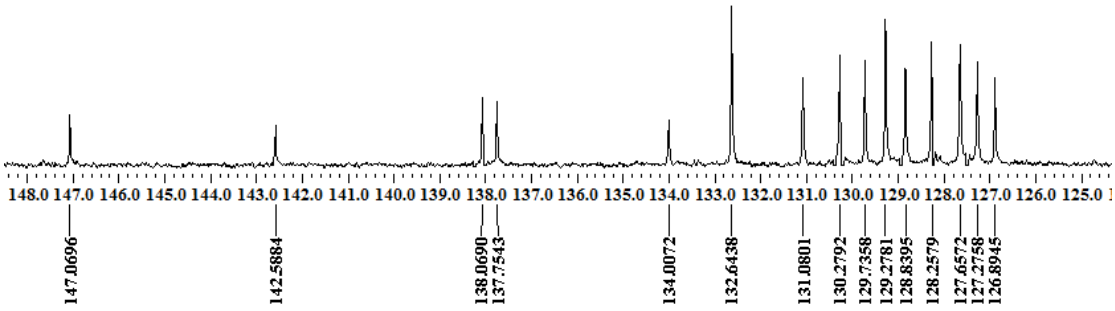

H
S
H
COOMe
N
N
Me

5f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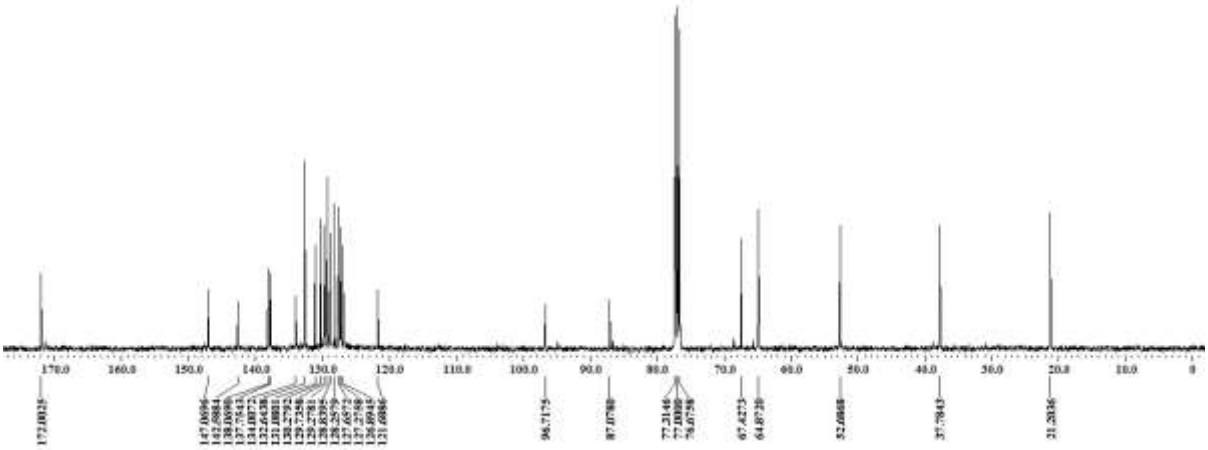

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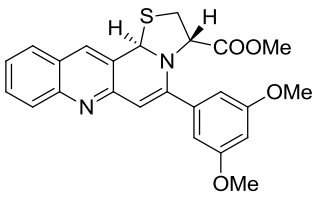

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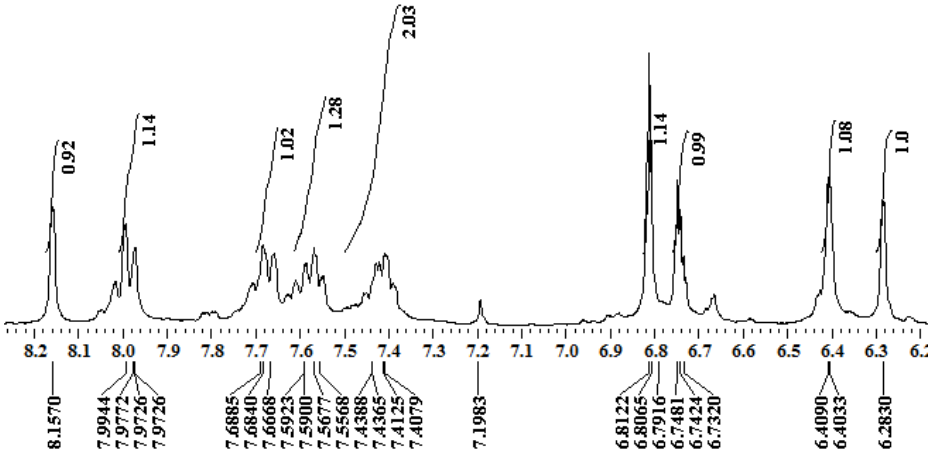
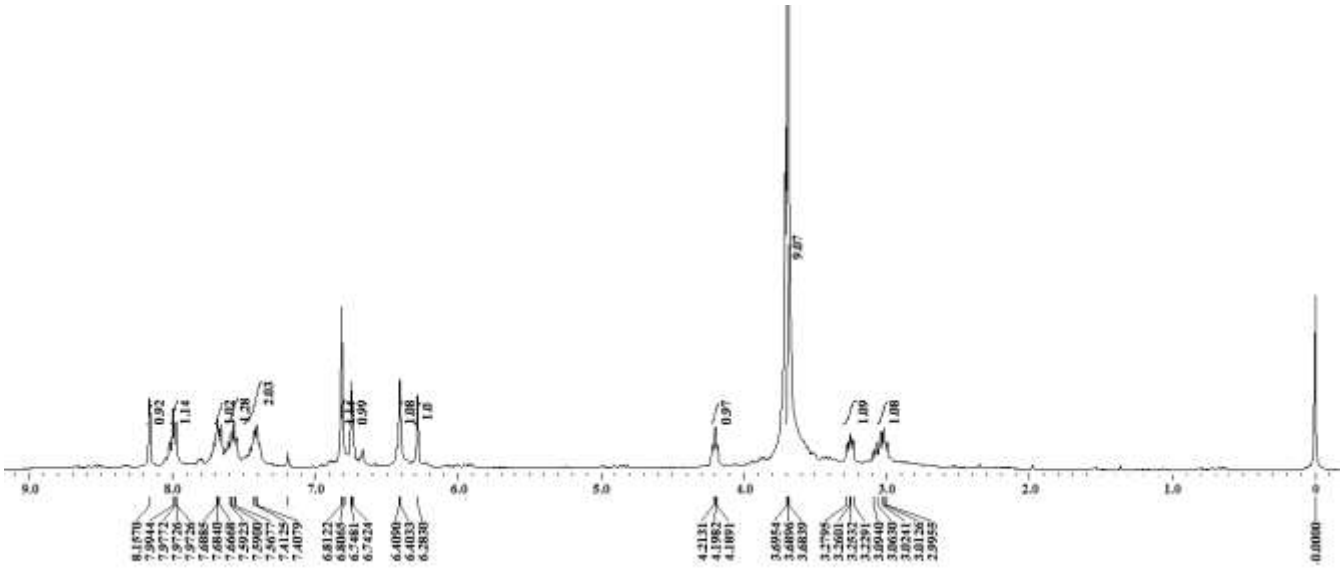
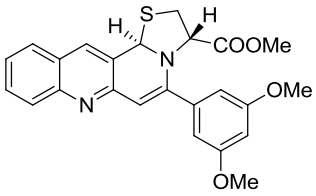




^{13}C NMR



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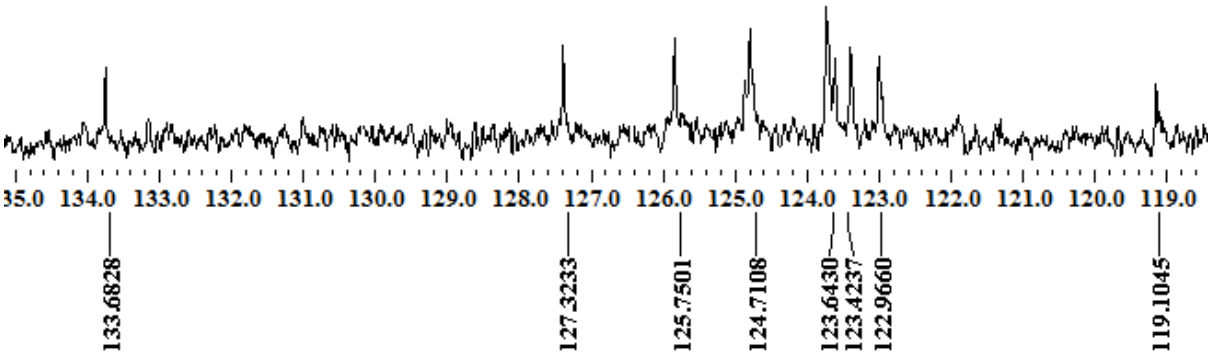

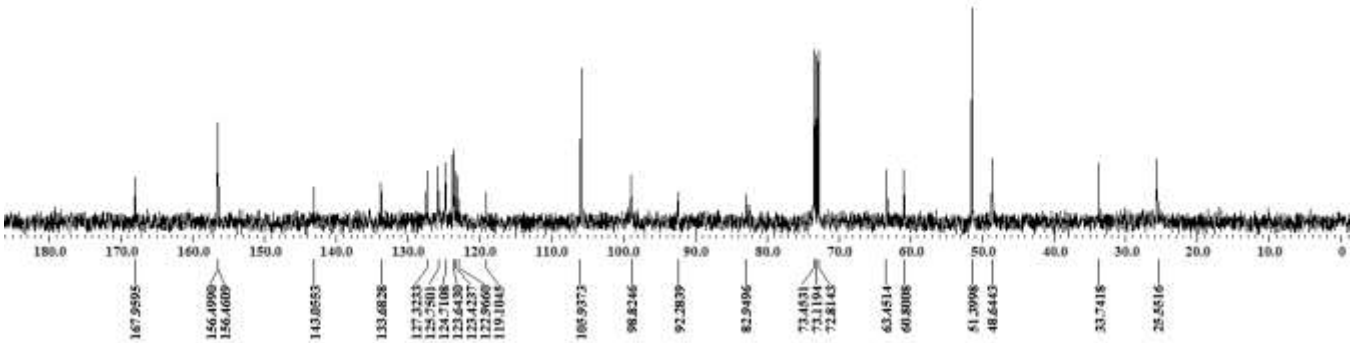

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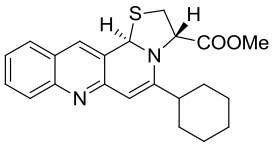

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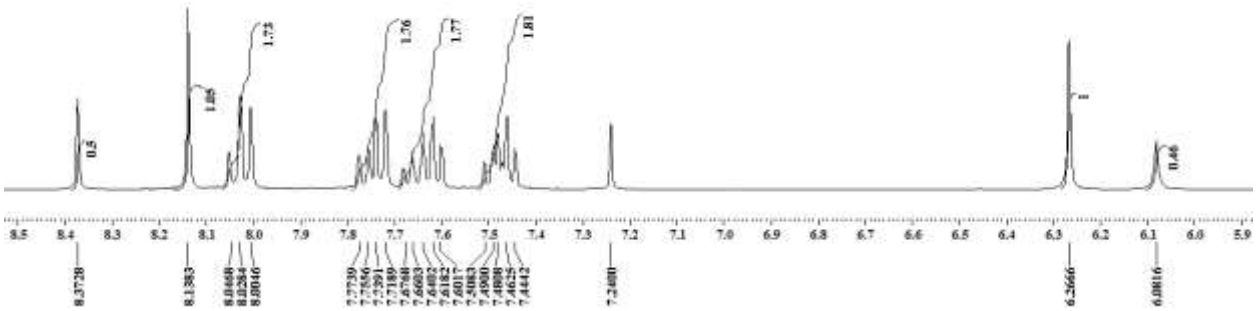

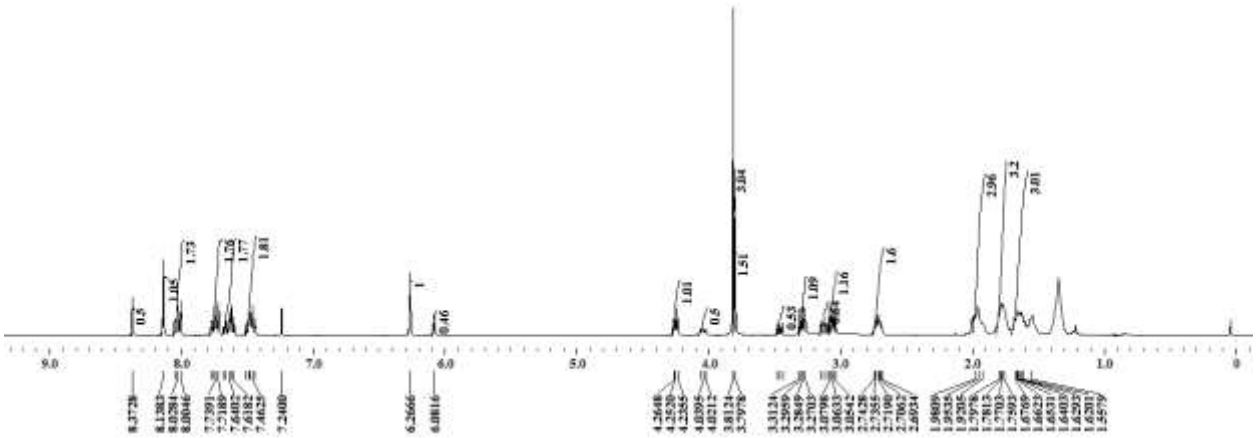

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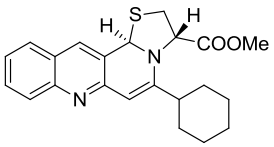

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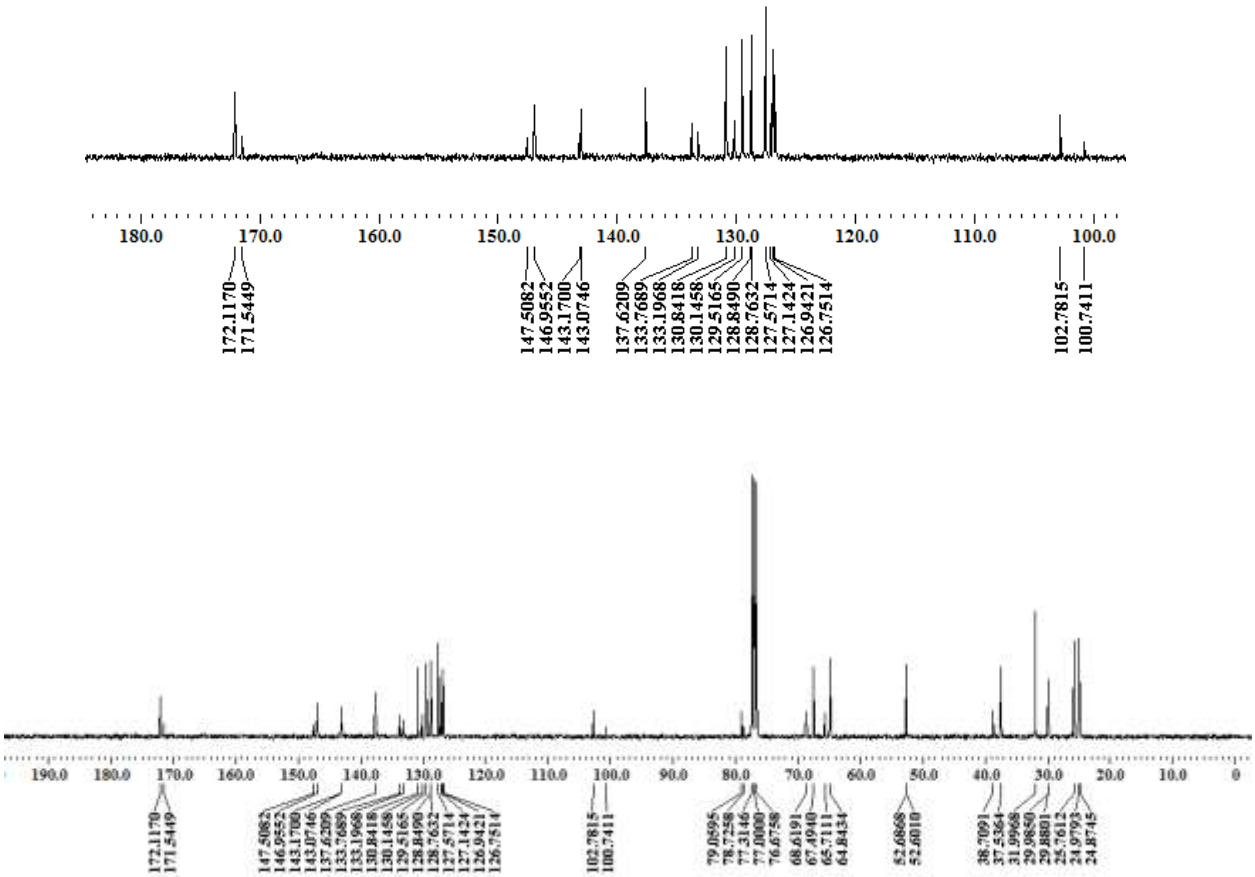

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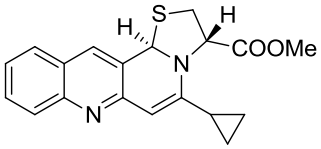

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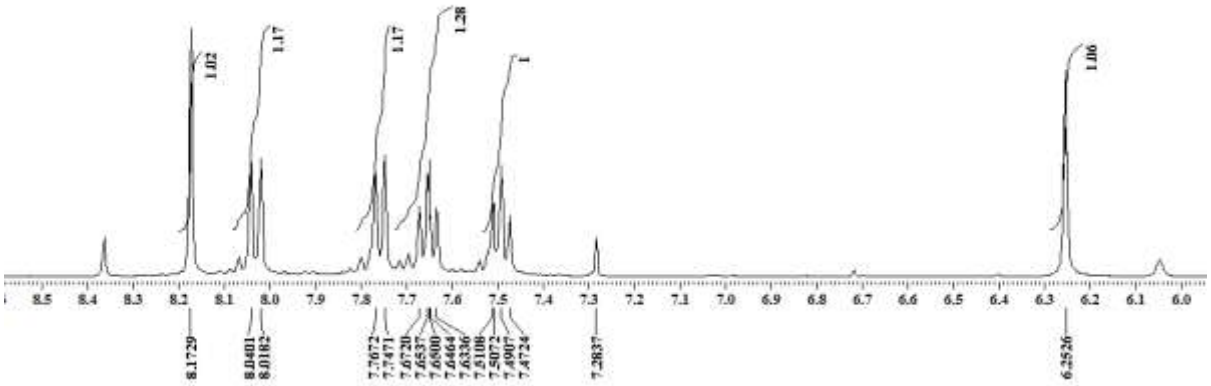

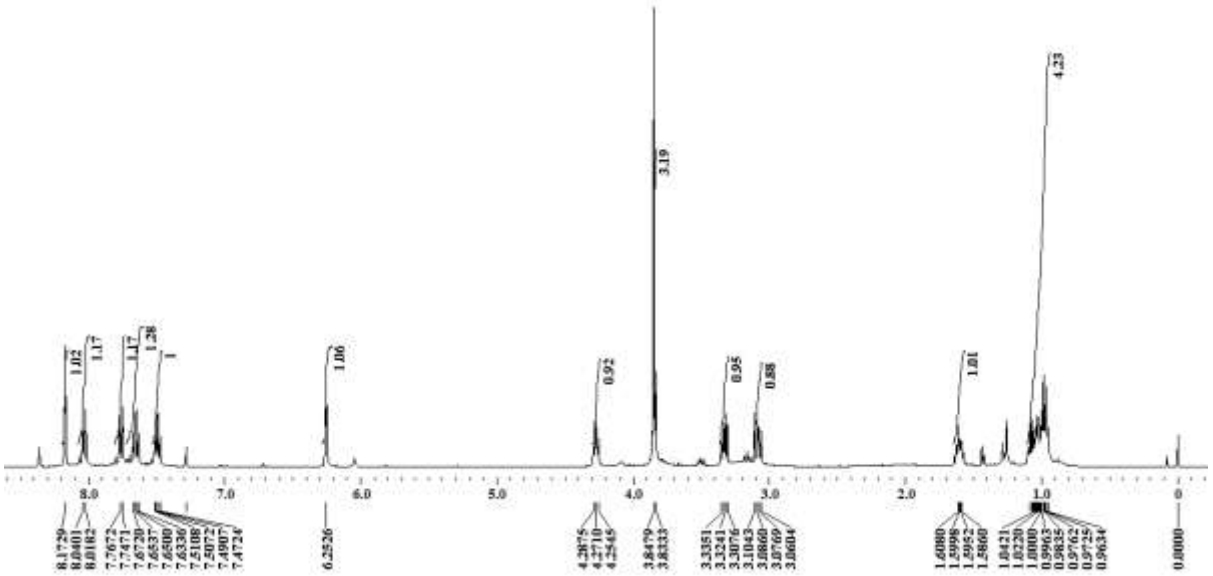

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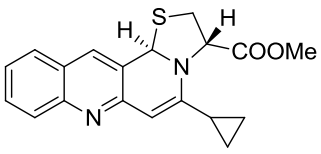

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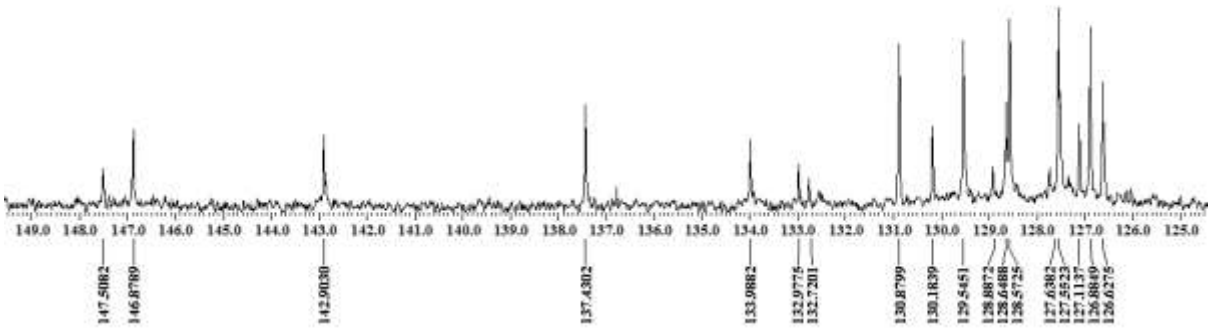

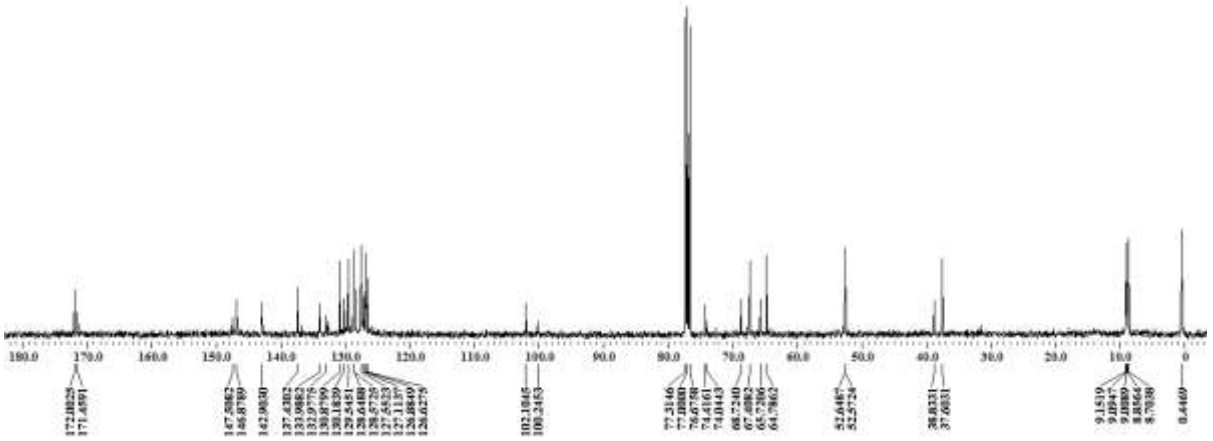

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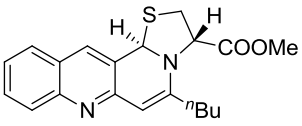

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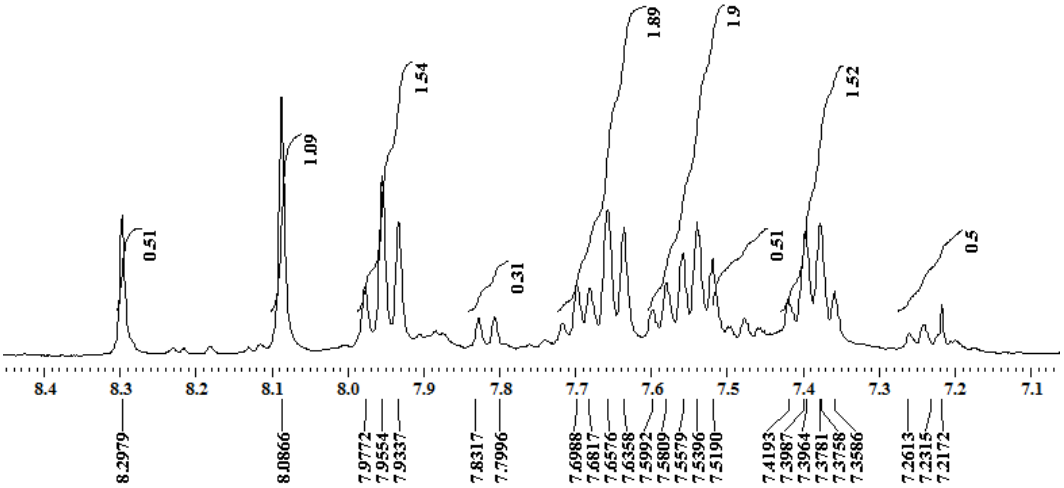

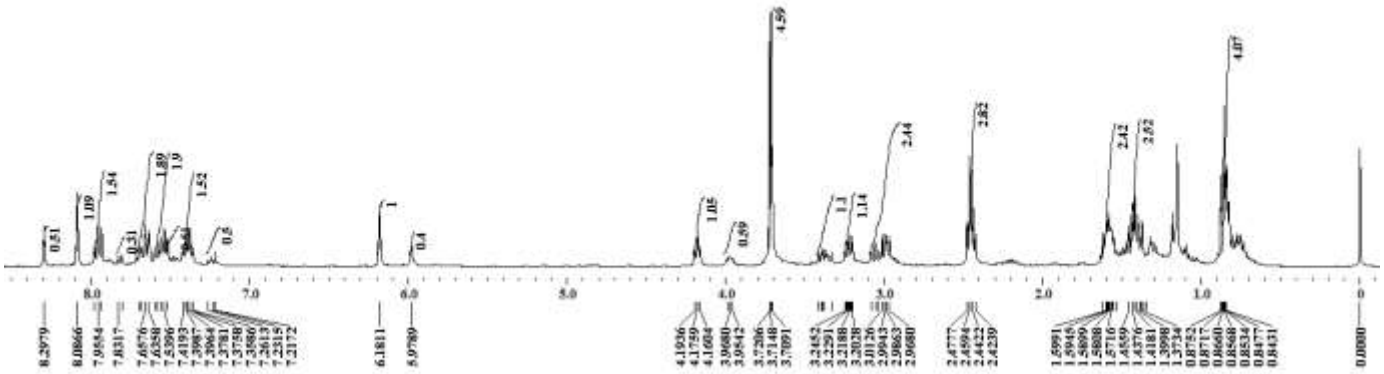

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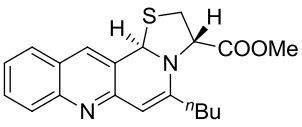

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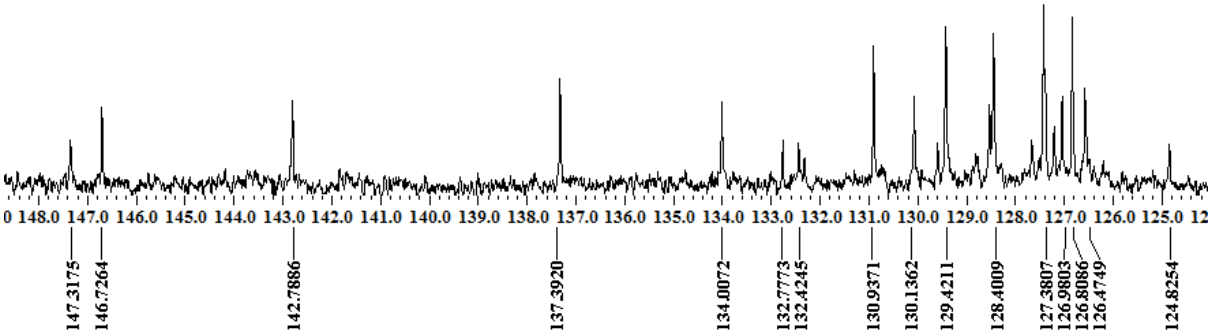

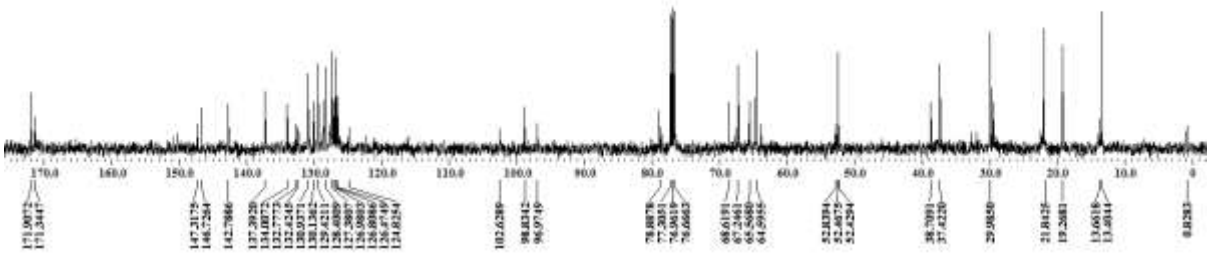

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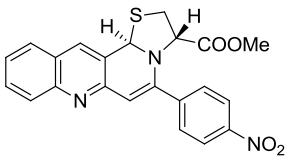

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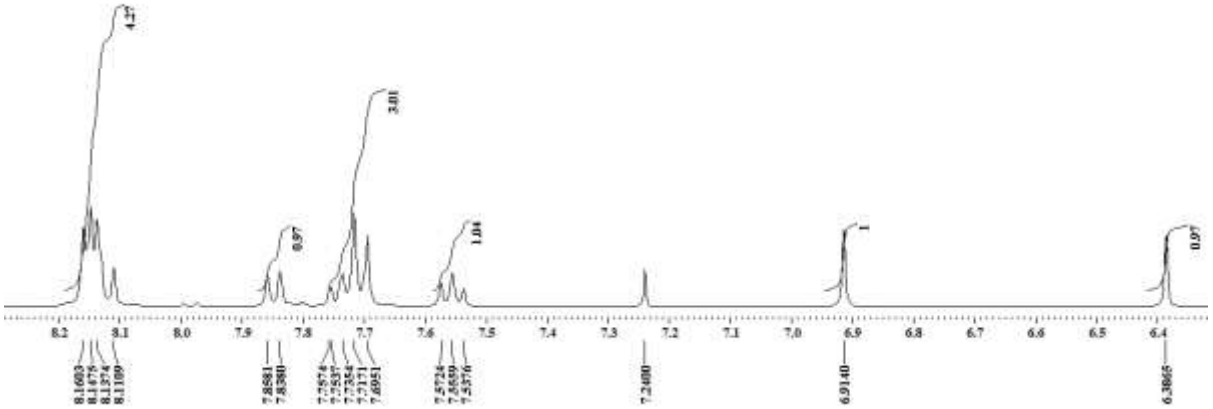

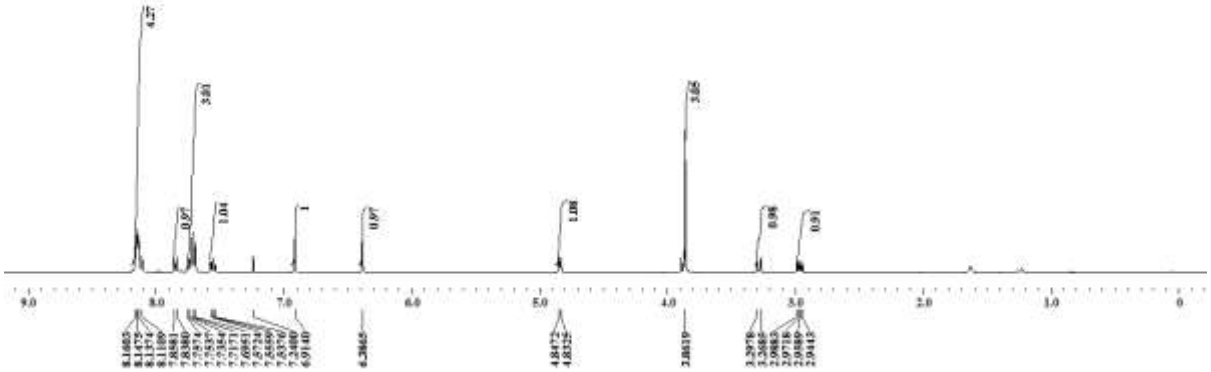

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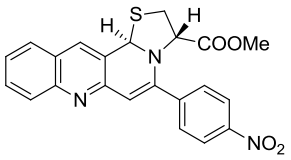

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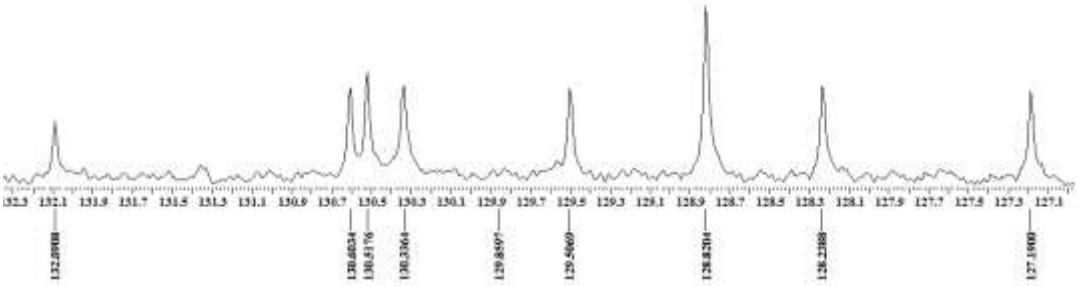

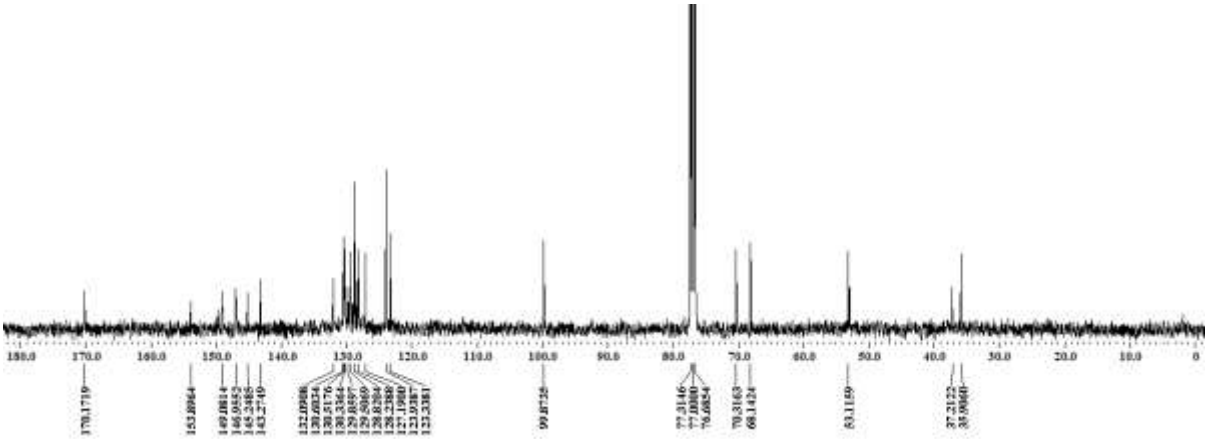

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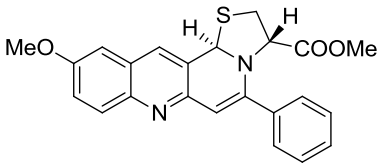

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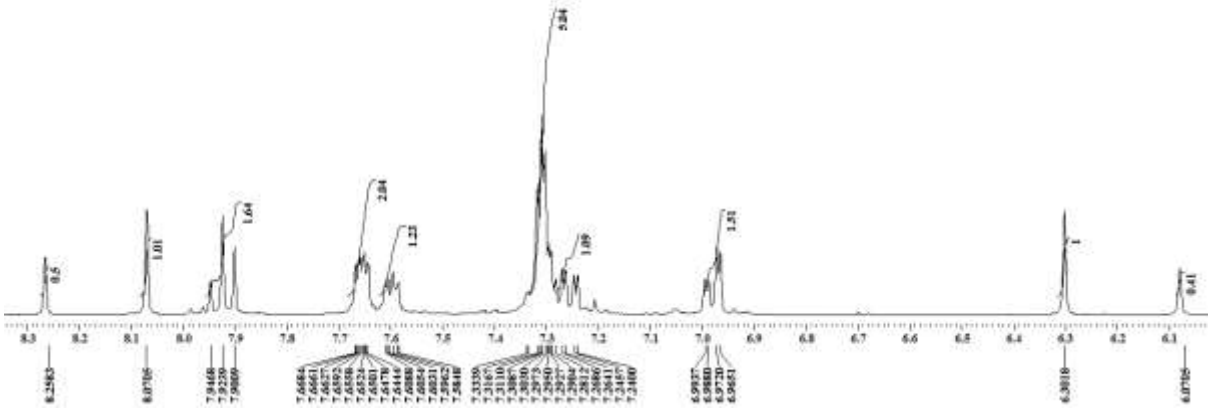

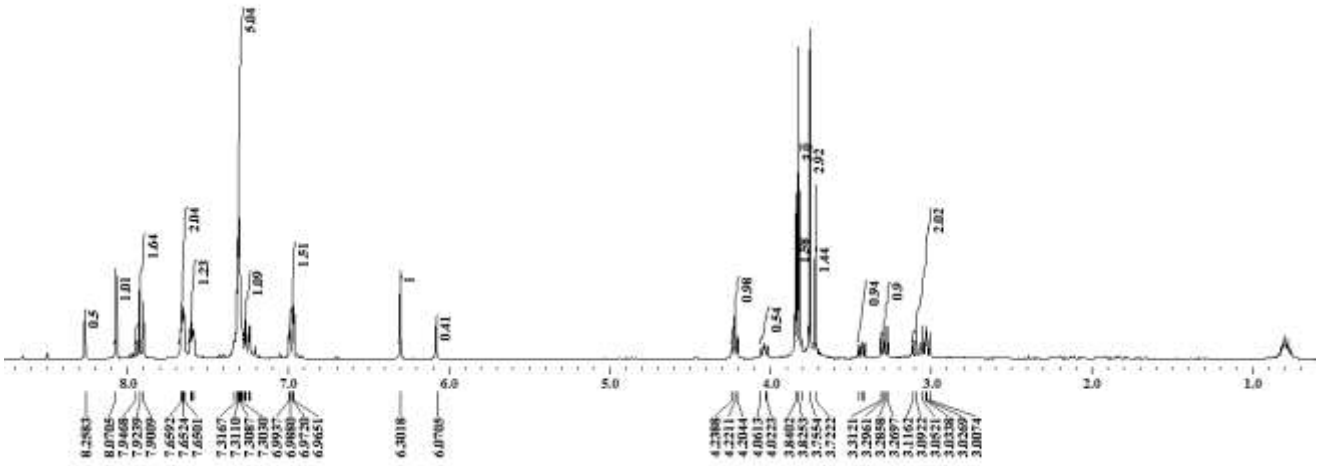

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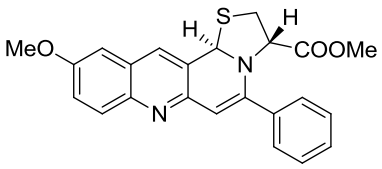

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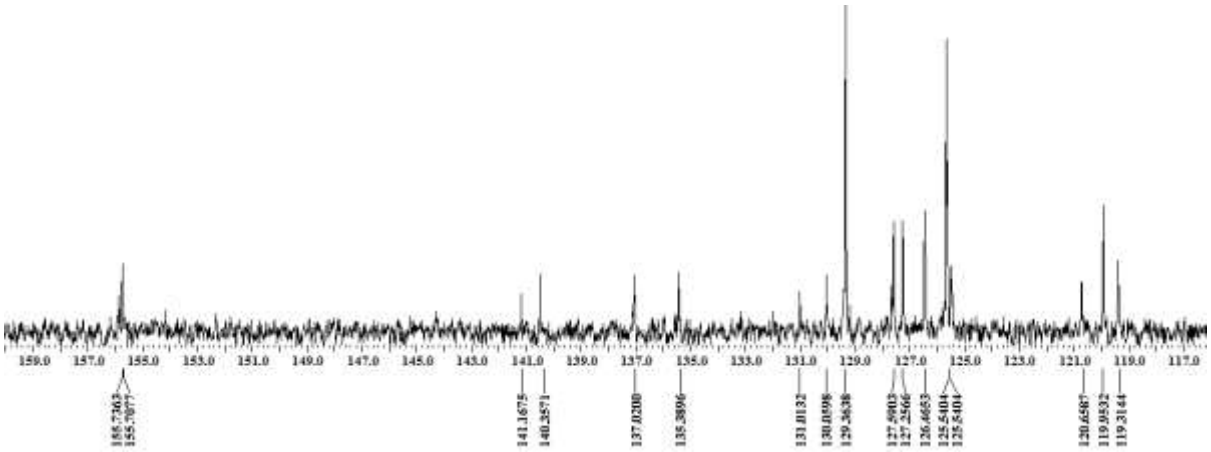

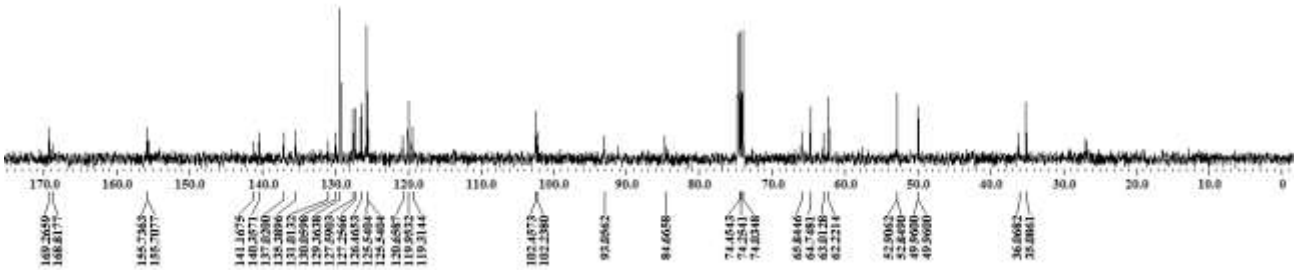

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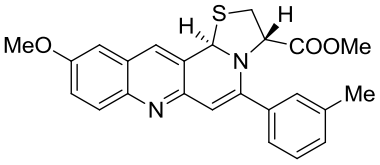

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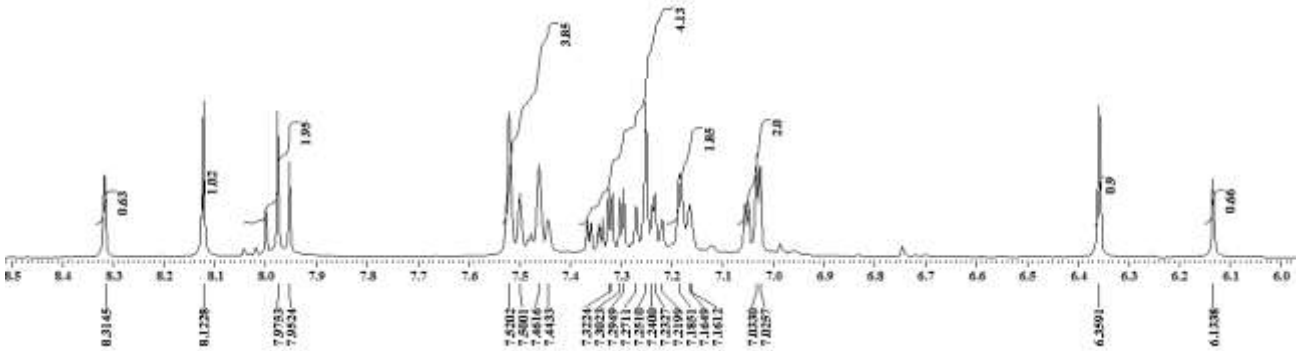

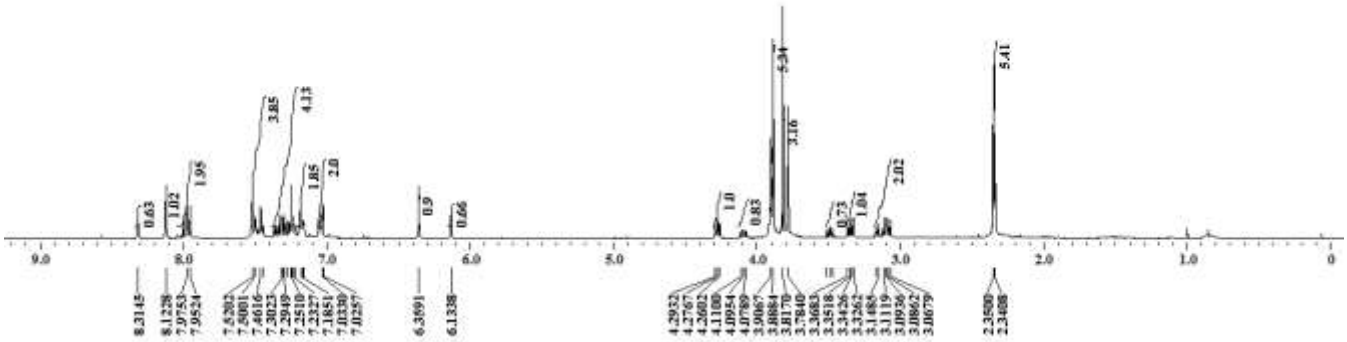

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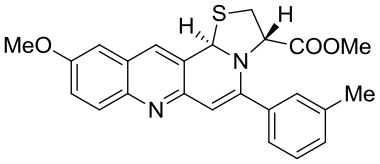

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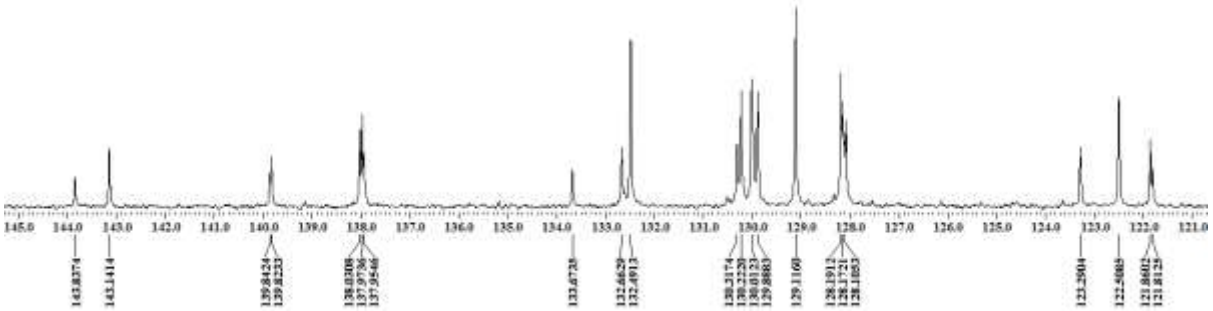

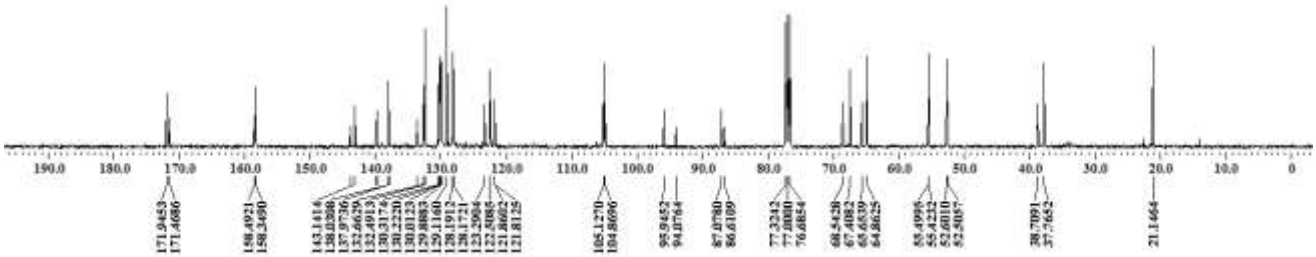

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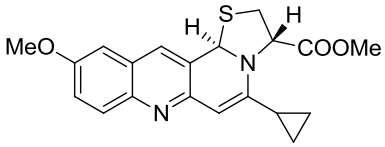

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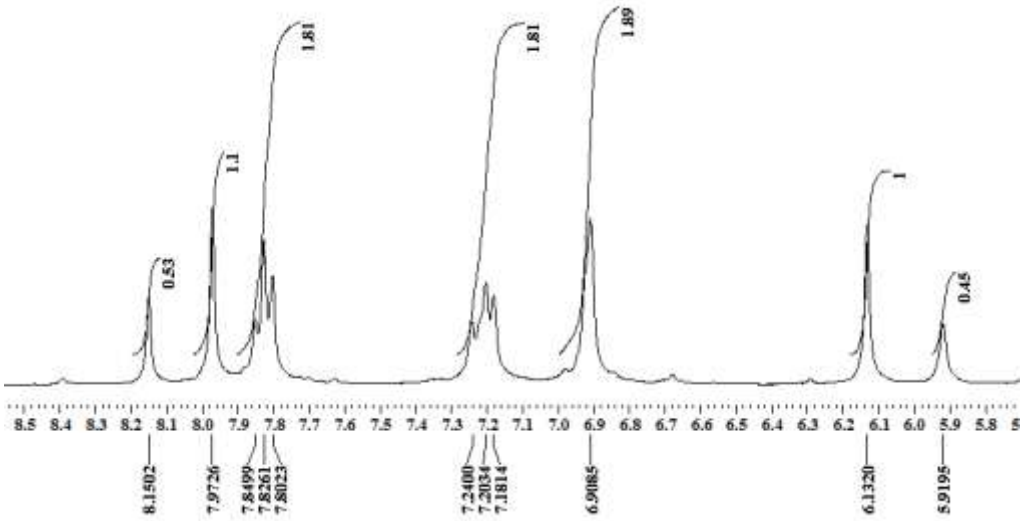

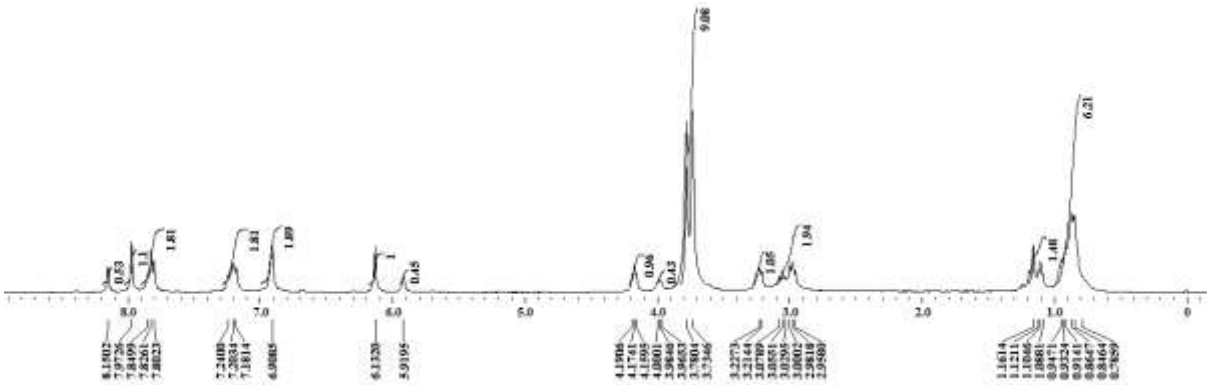

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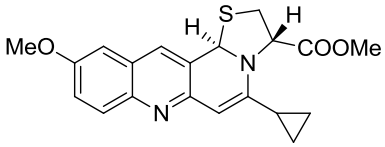

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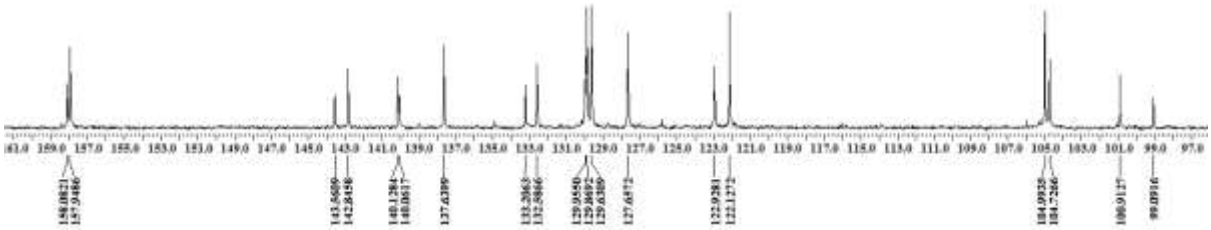

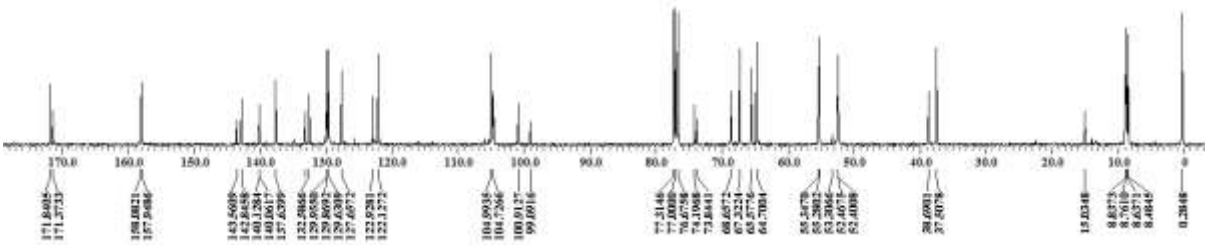

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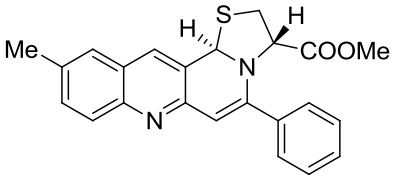

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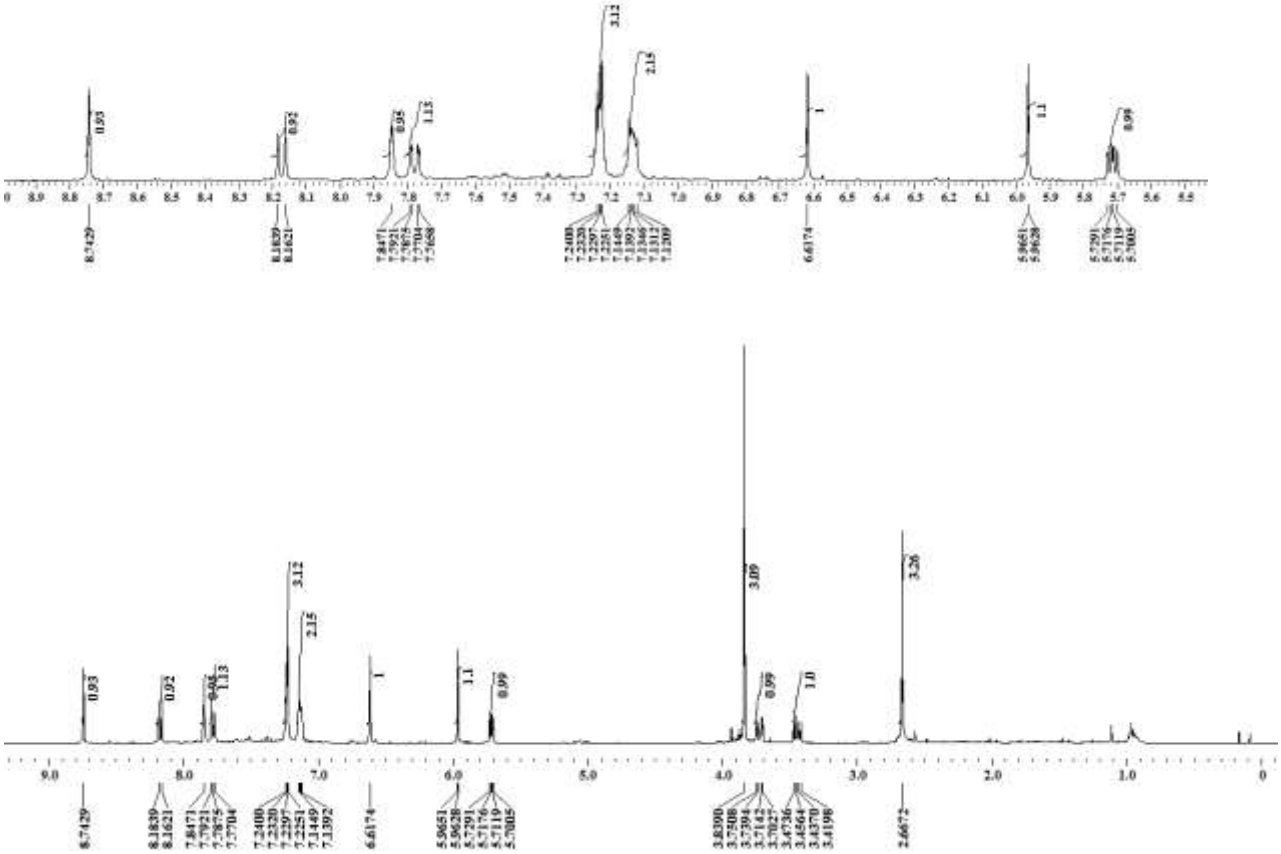

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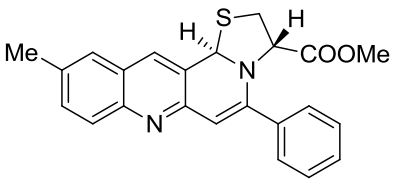

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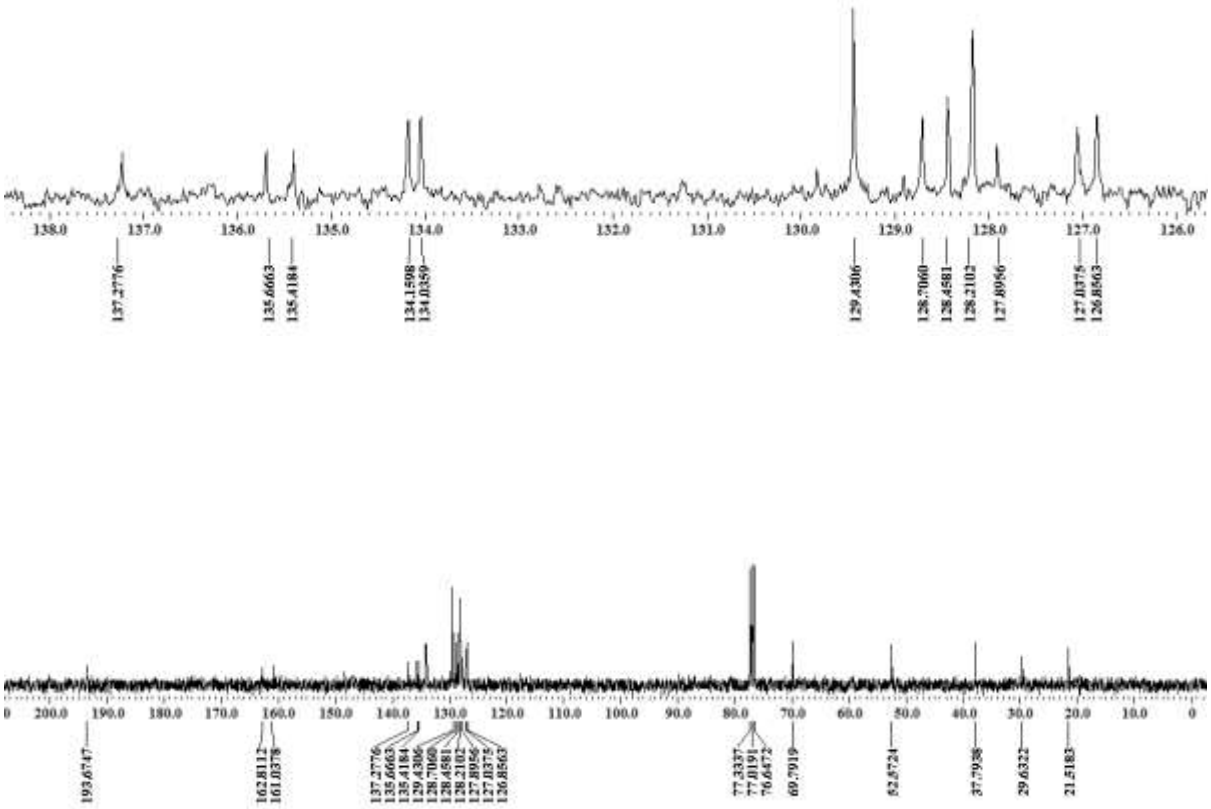

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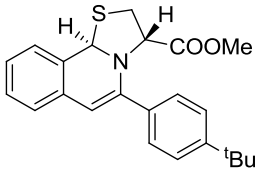

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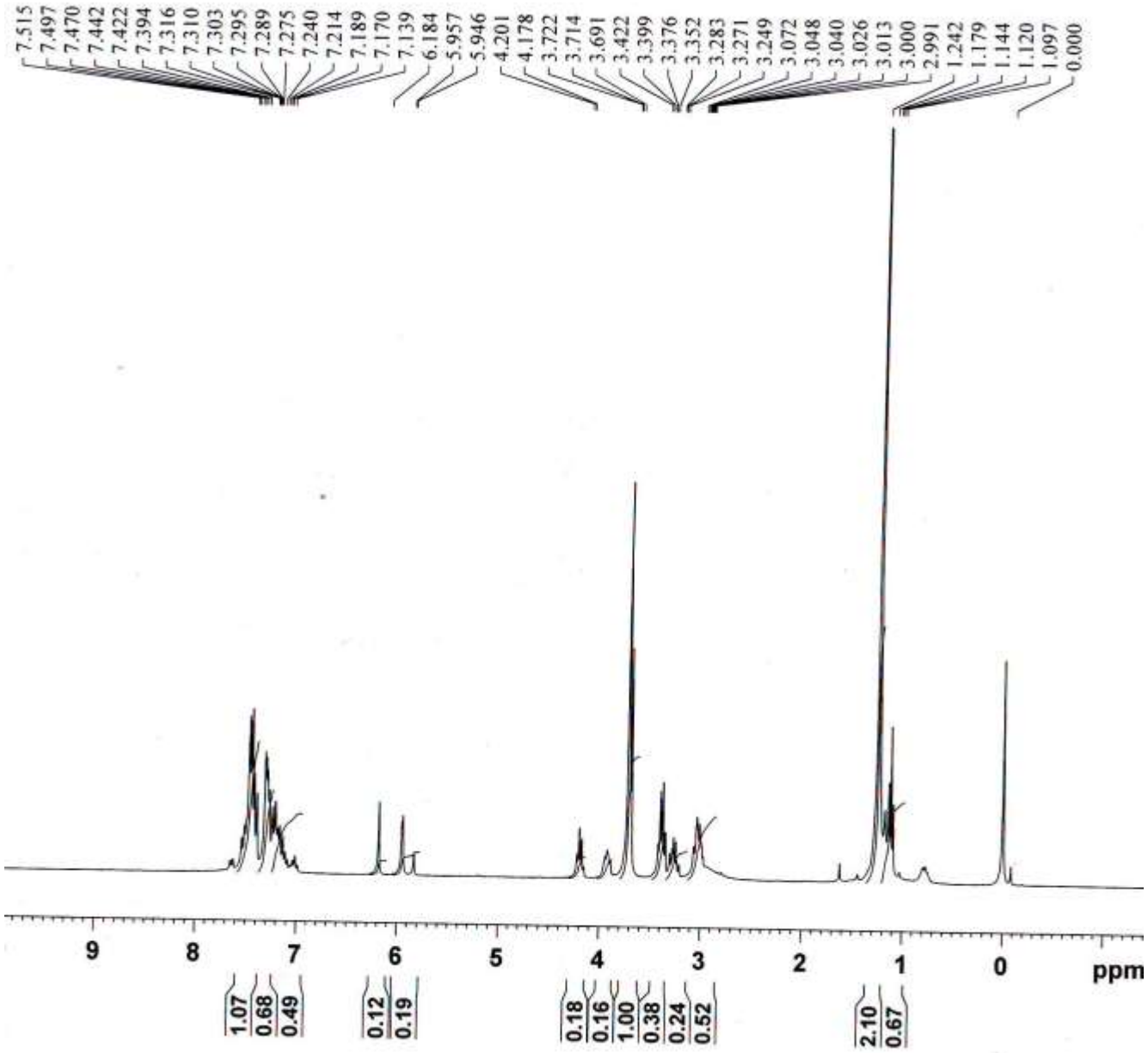

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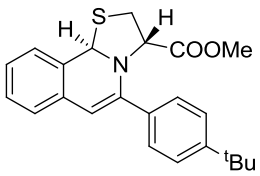

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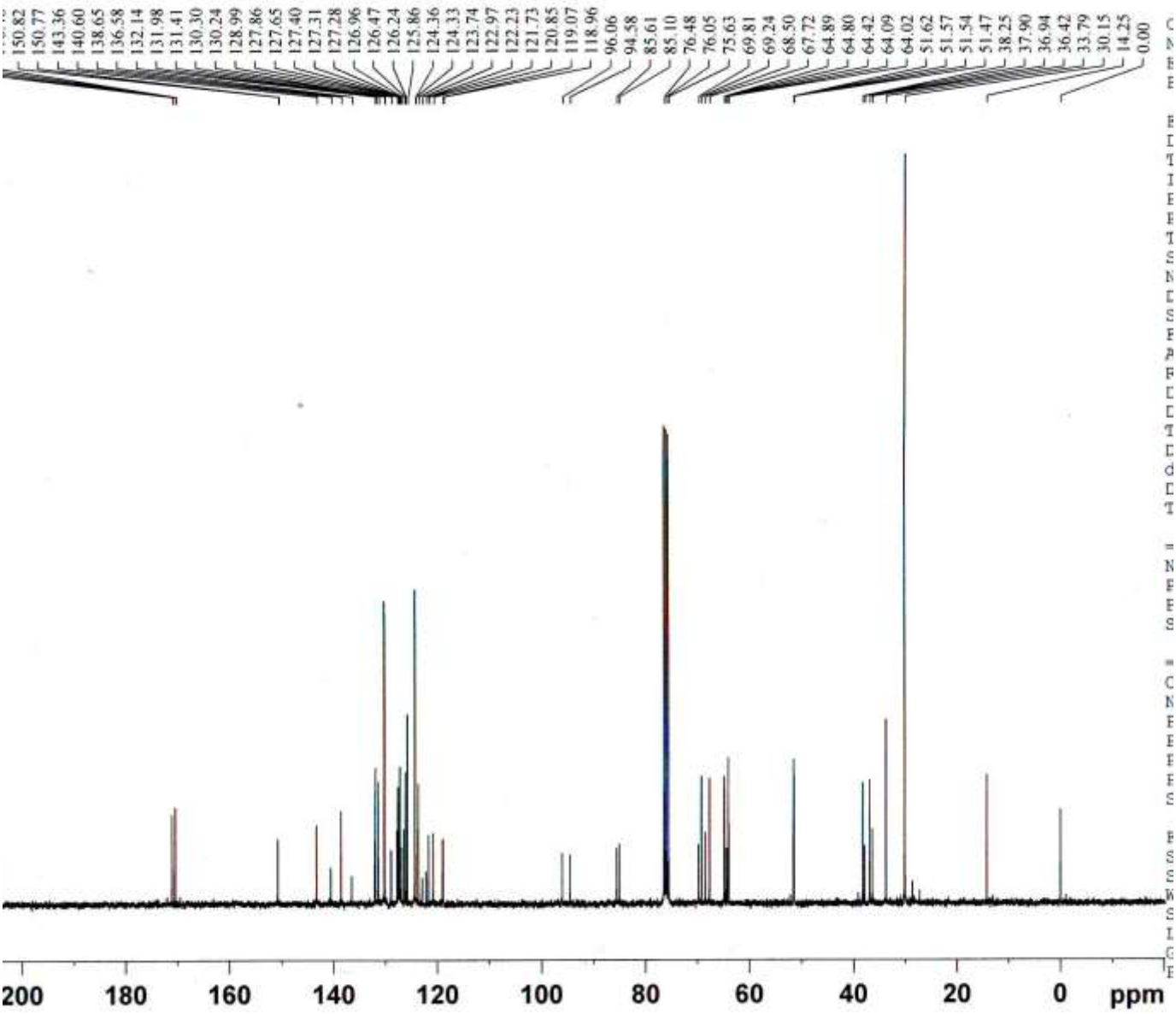

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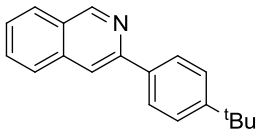
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tBu

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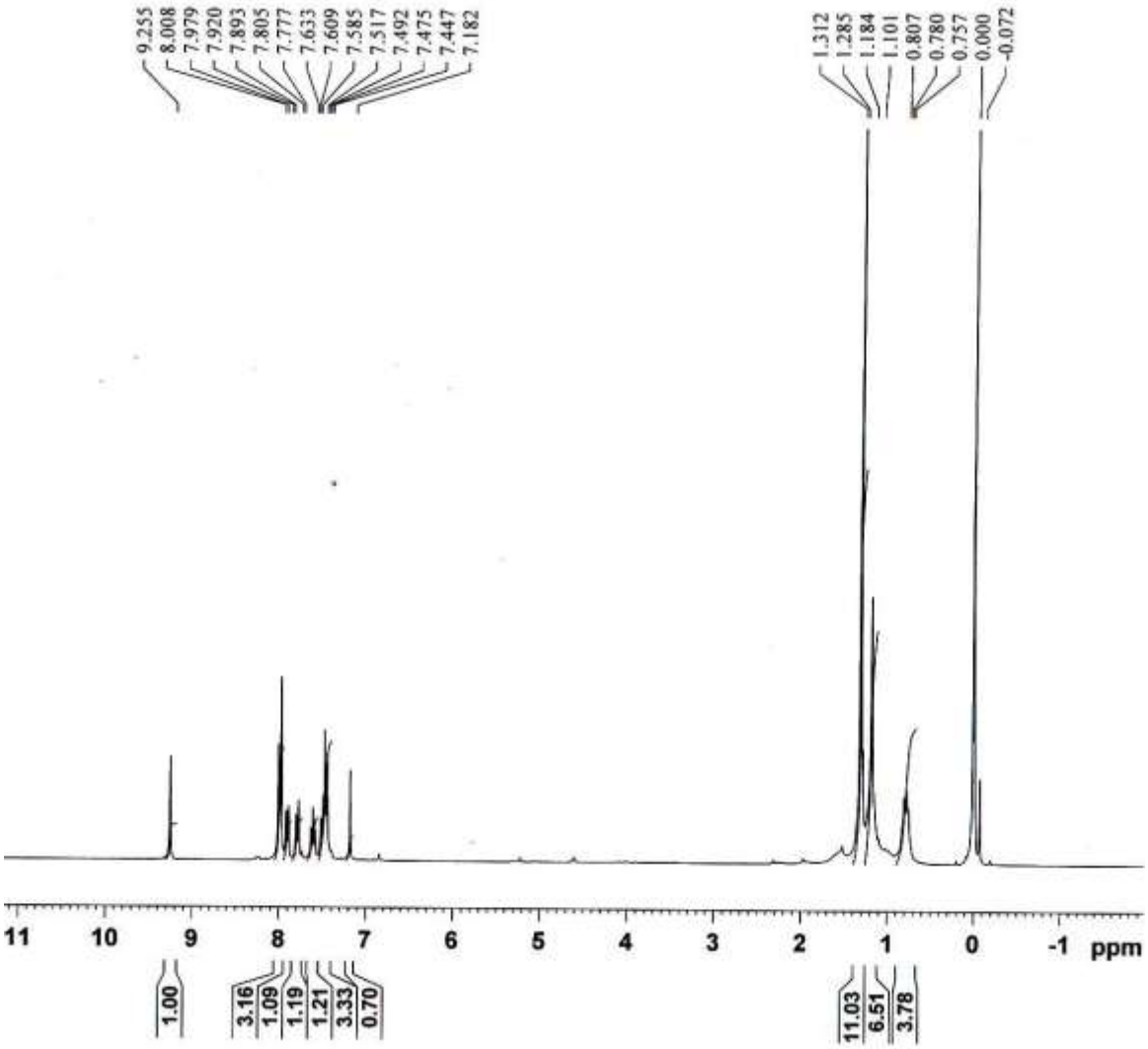
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7.447
7.182
1.312
1.285
1.184
1.101
0.807
0.780
0.757
0.000
-0.072
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.19
1.21
3.33
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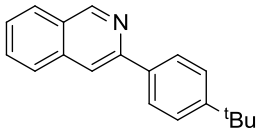
6.51
3.78

^{13}C NMR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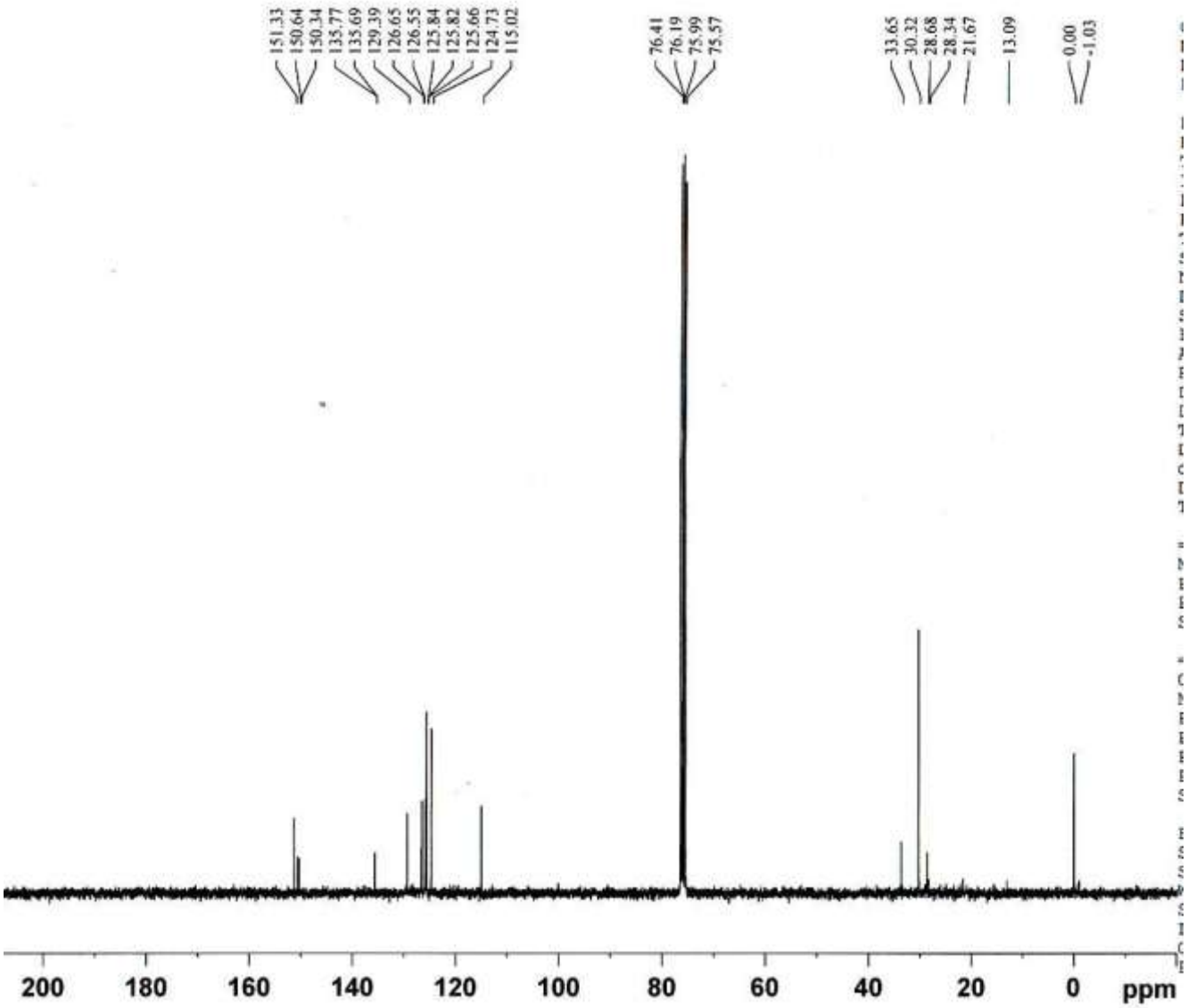
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76.41
76.19
75.99
75.57
33.65
30.32
28.68
28.34
21.67
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40
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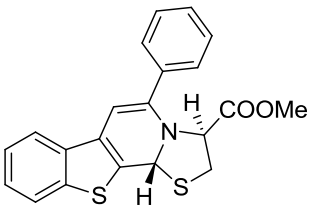
ppm

^{1}H NMR



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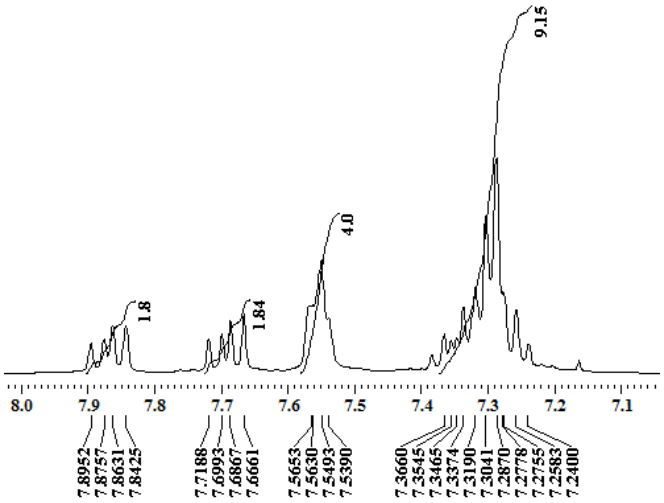

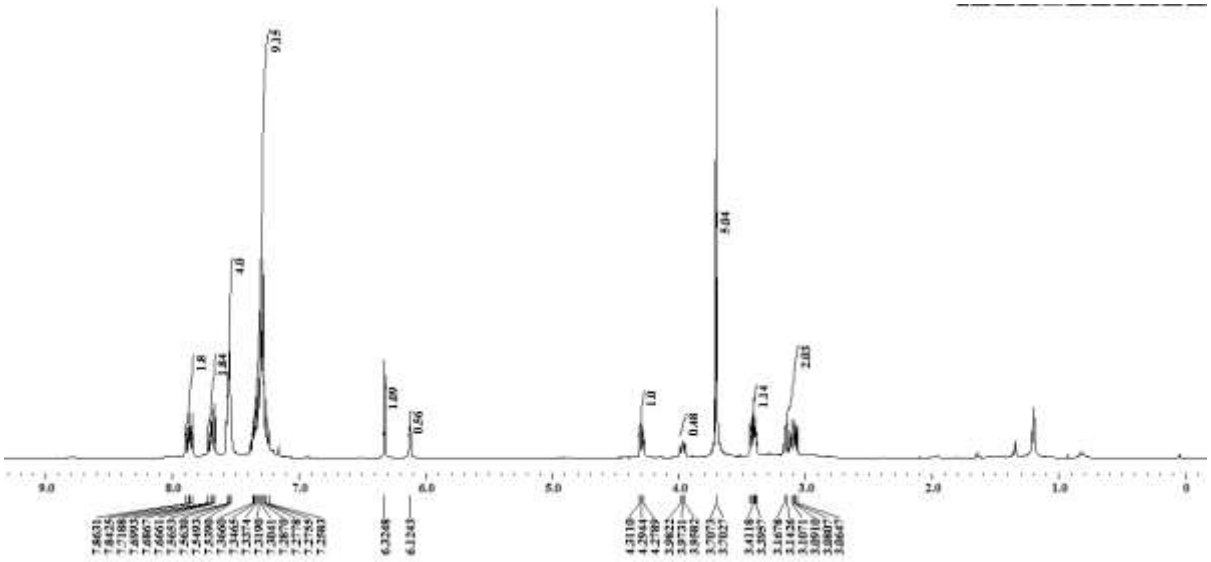

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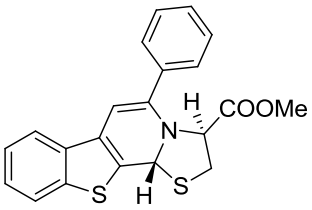

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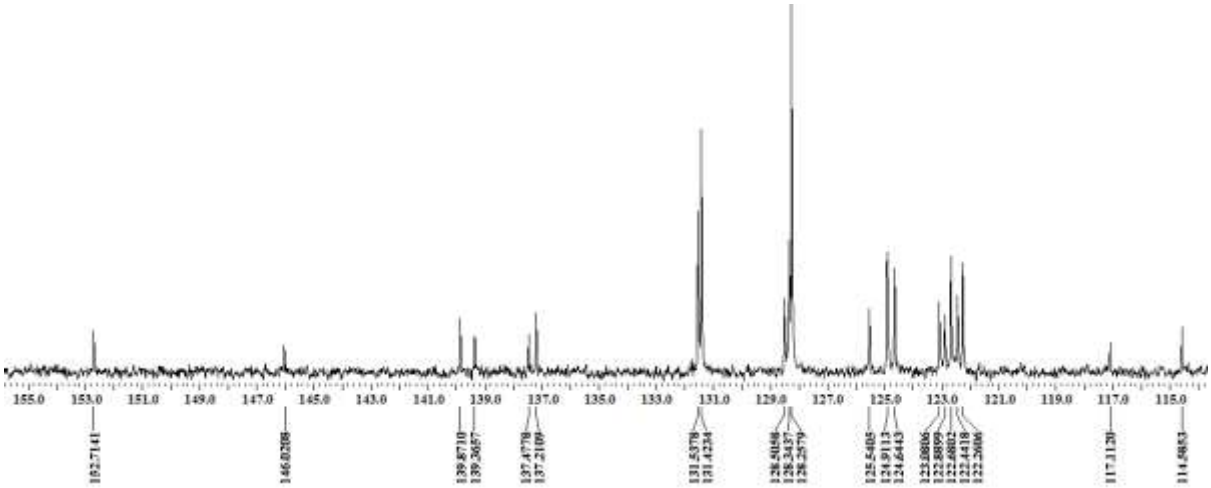

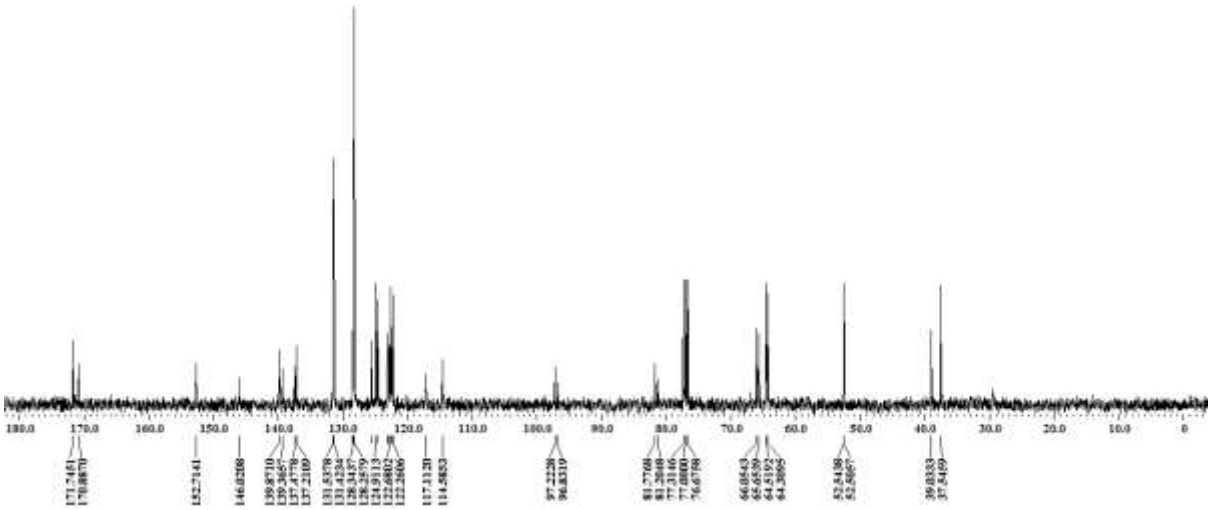

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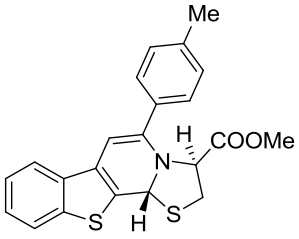

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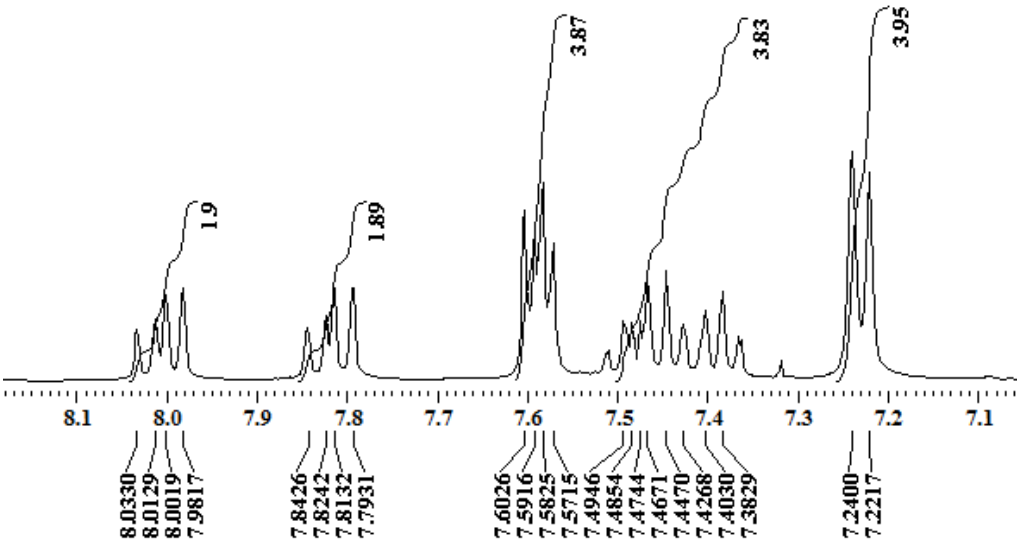

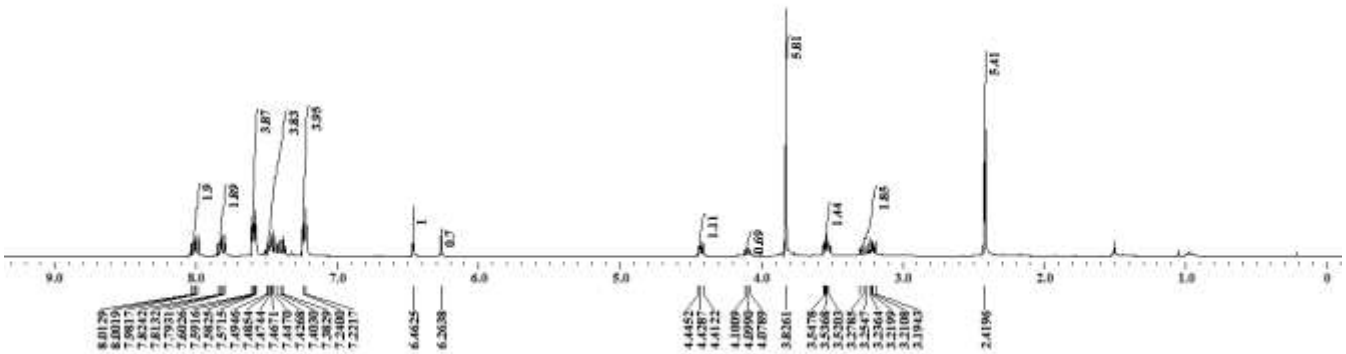

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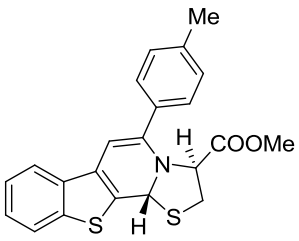

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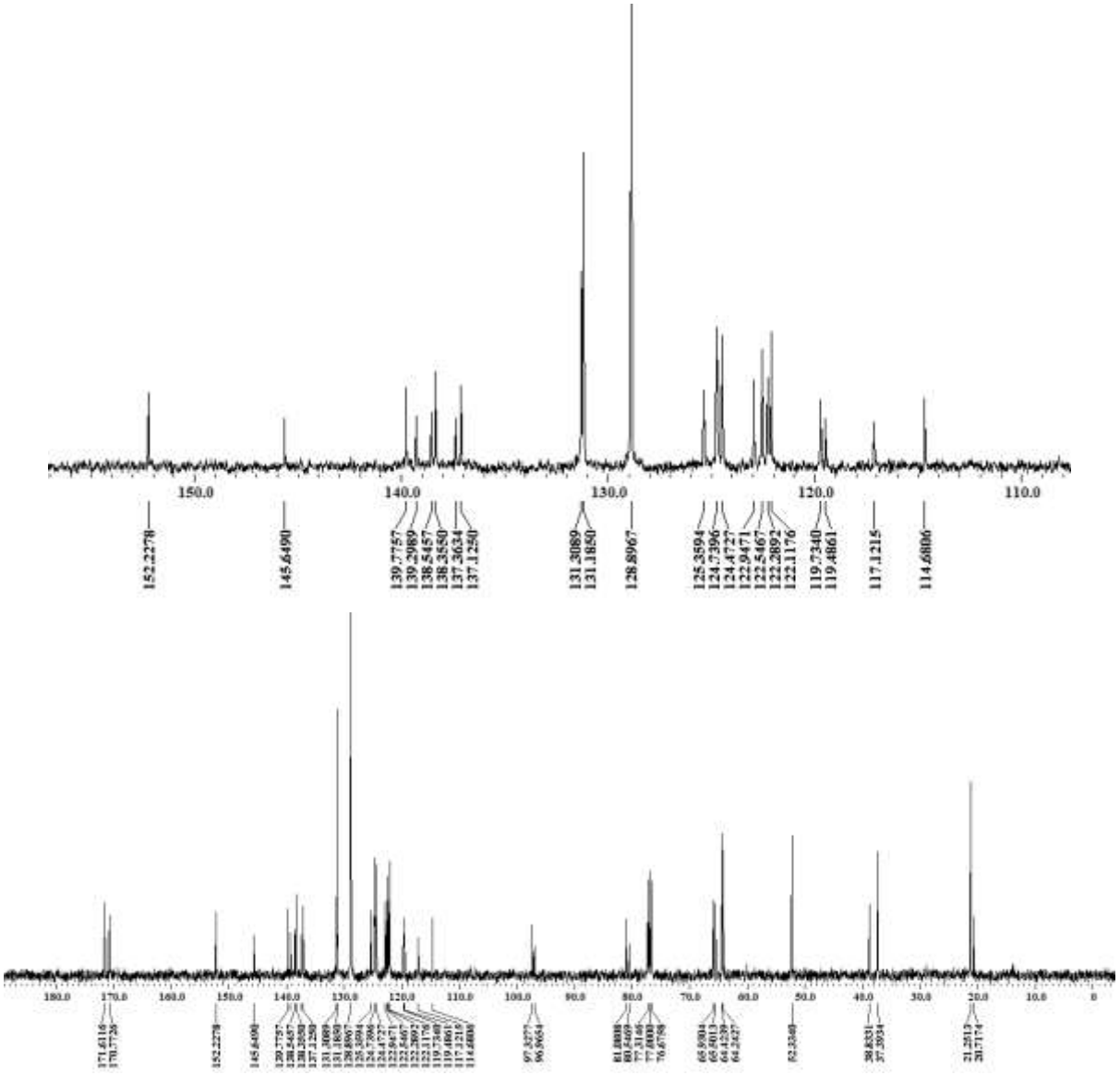

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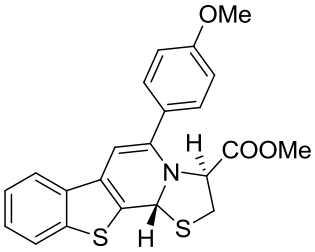

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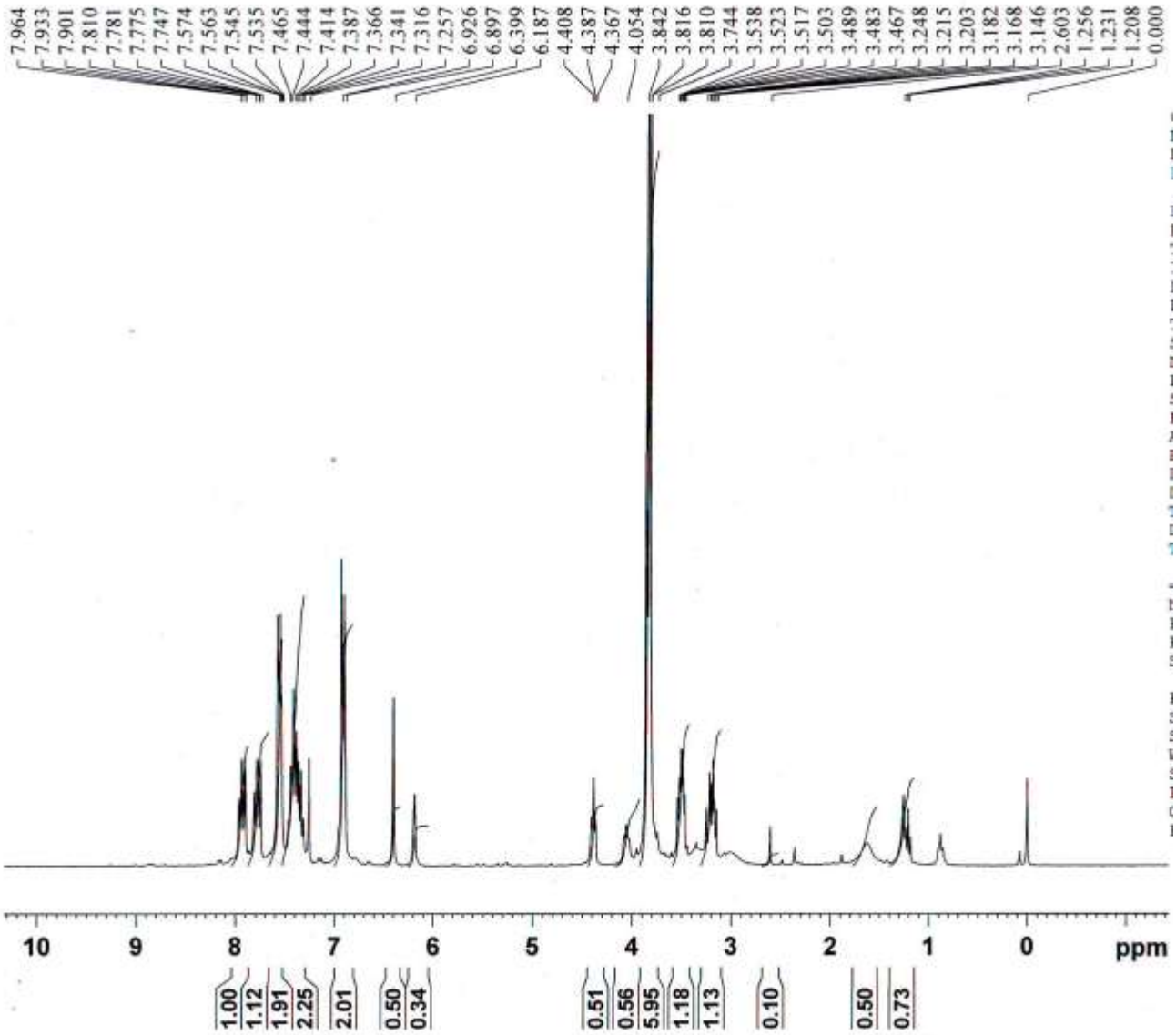

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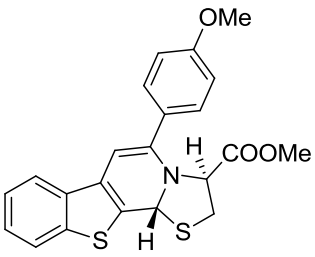

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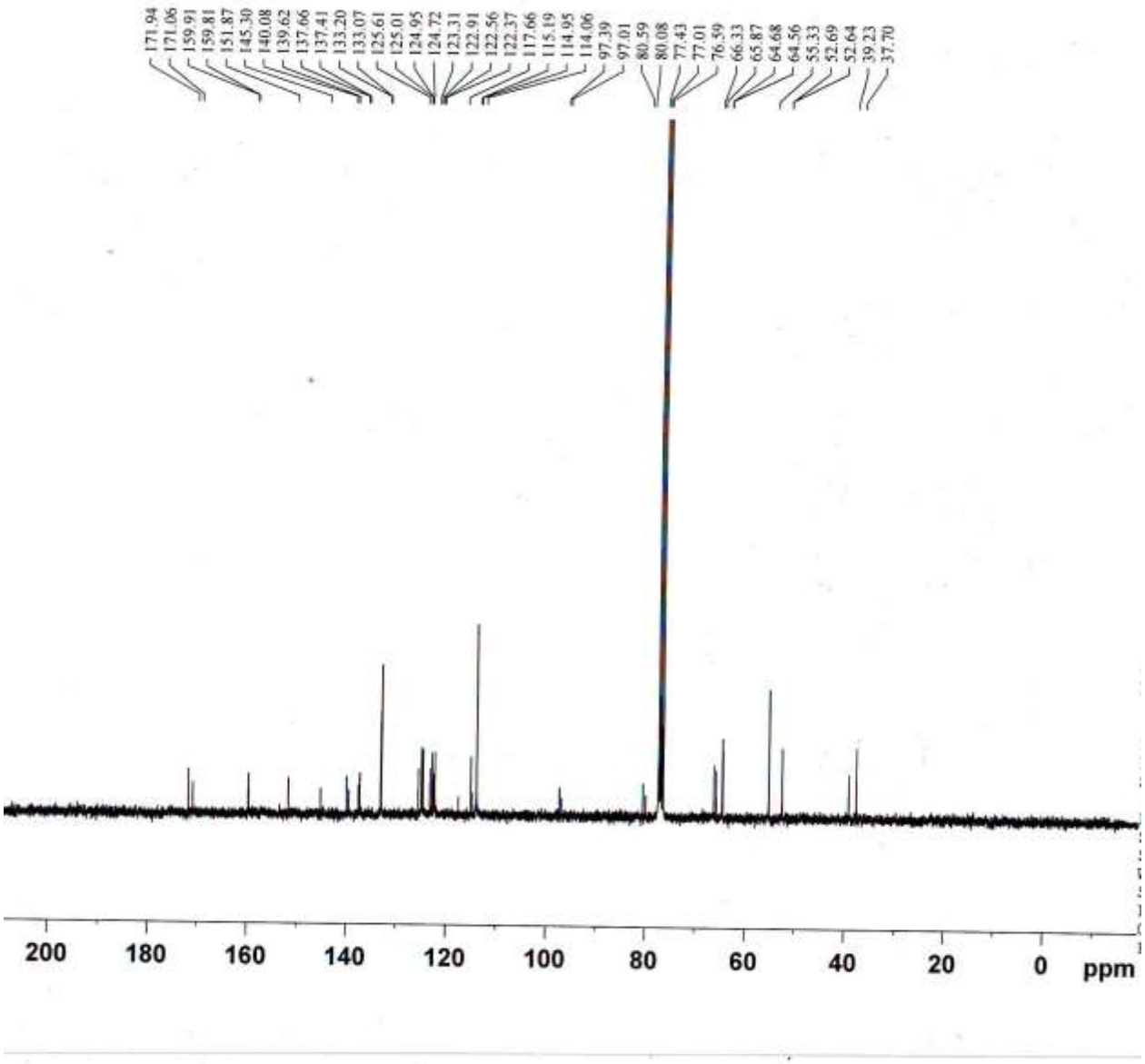

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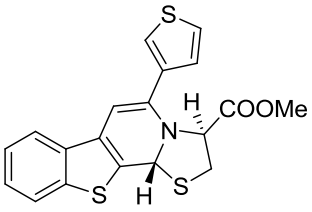

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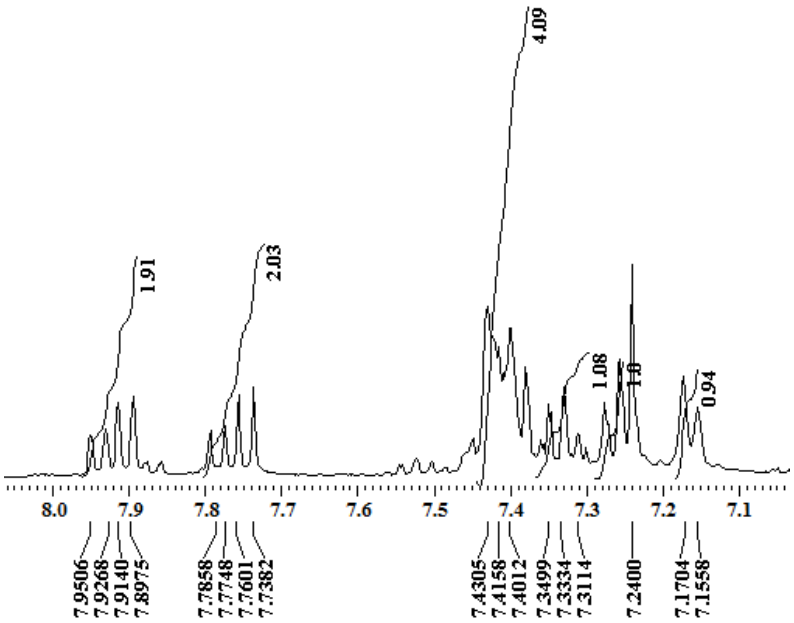

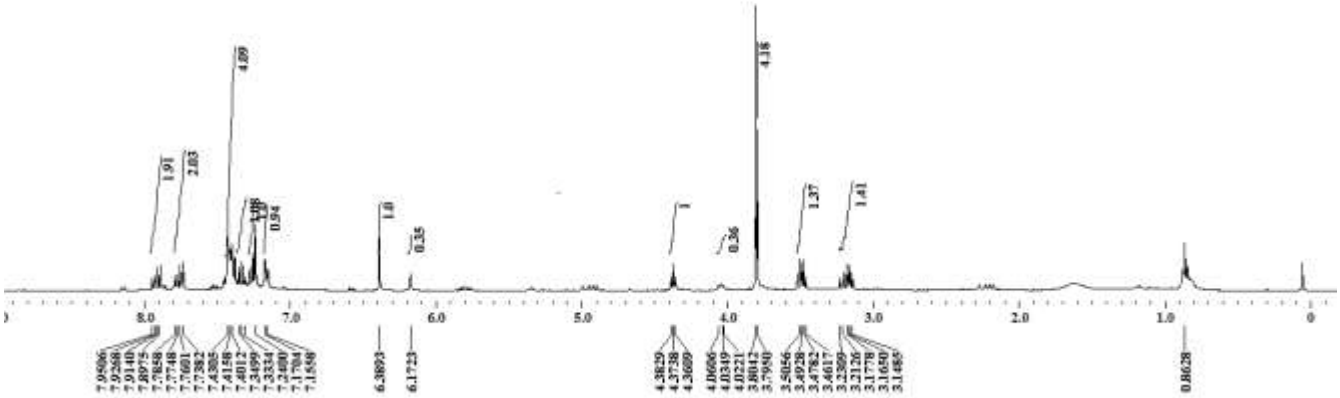

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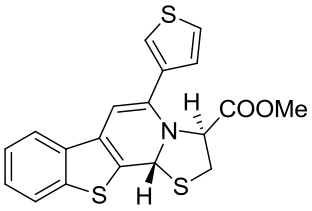

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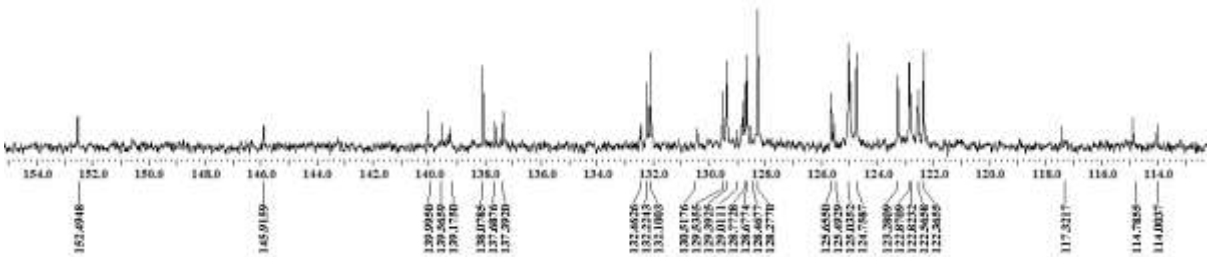

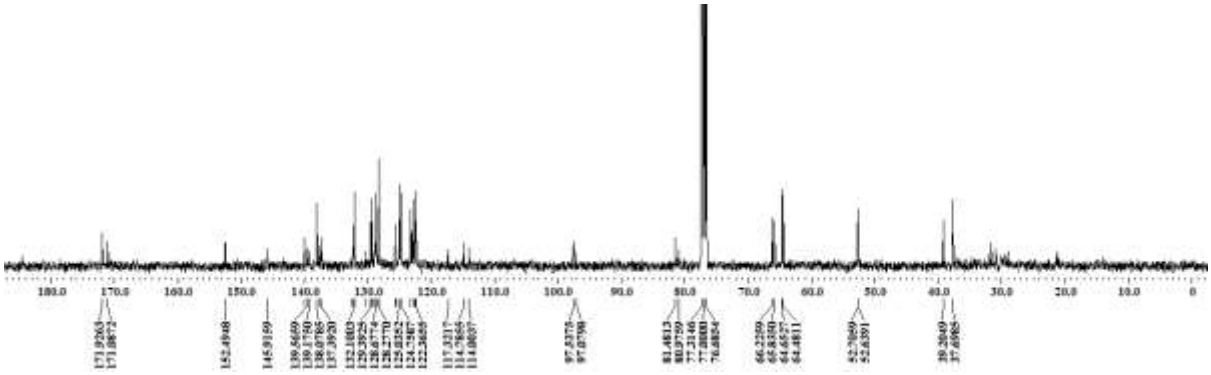

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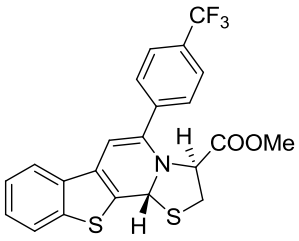

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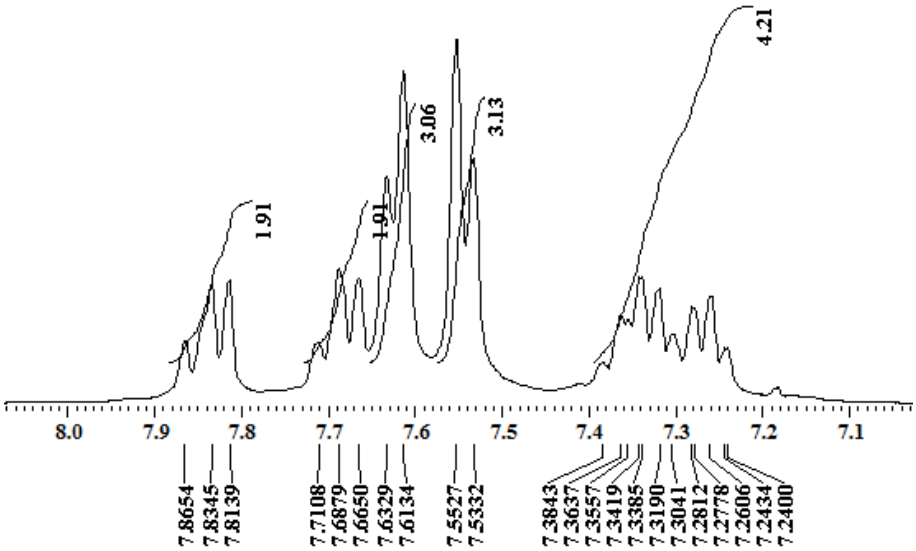

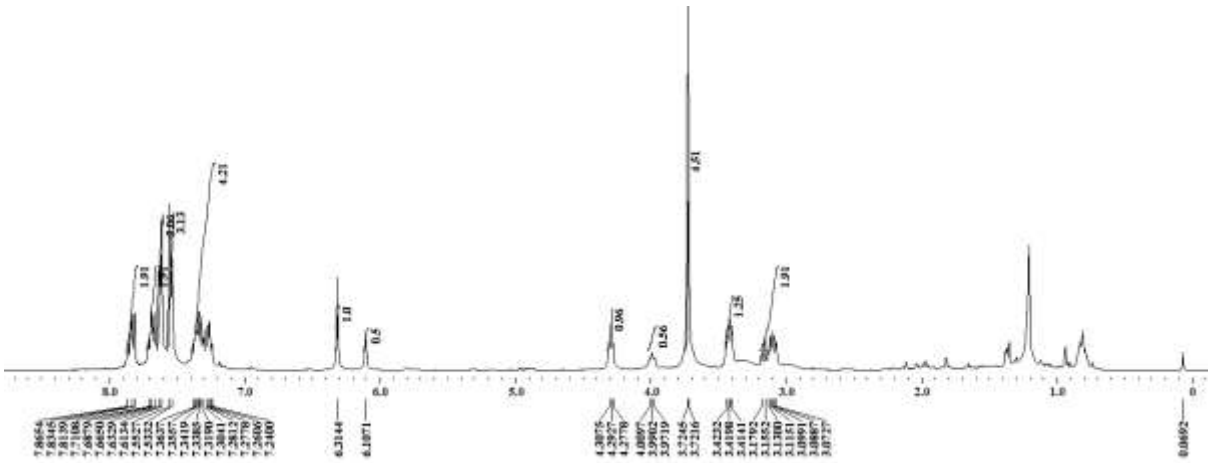

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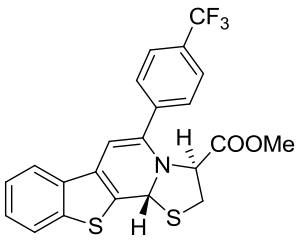

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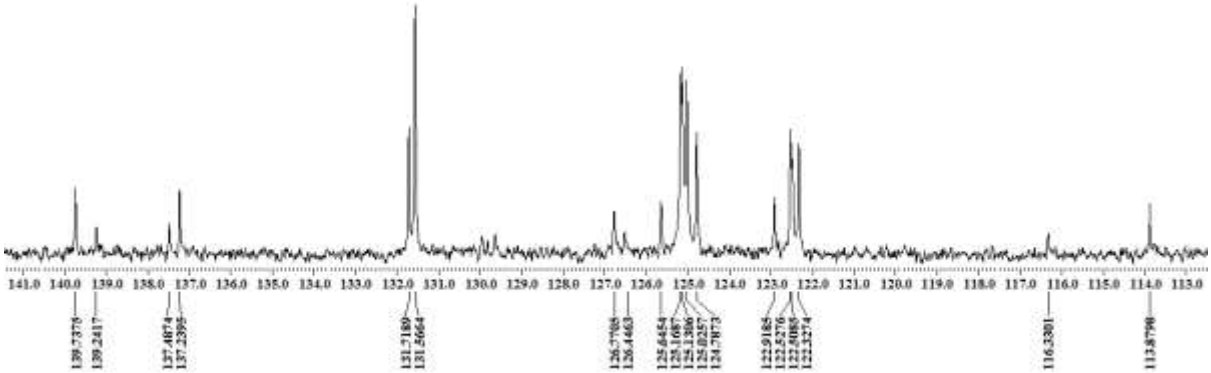
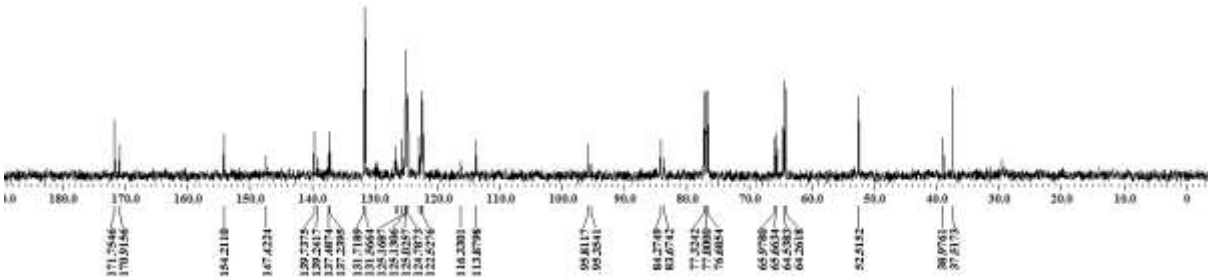
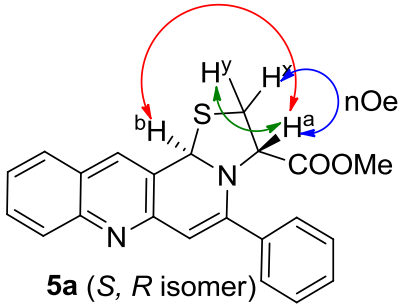


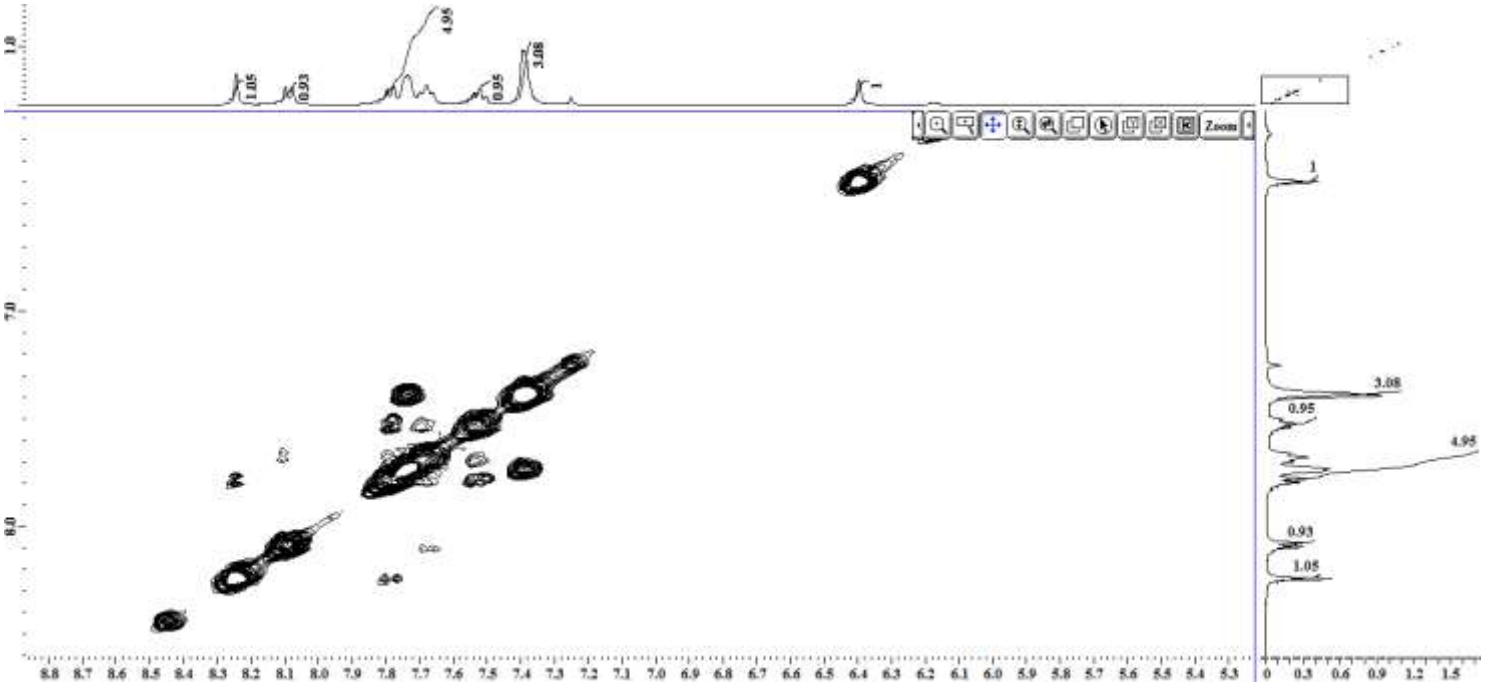


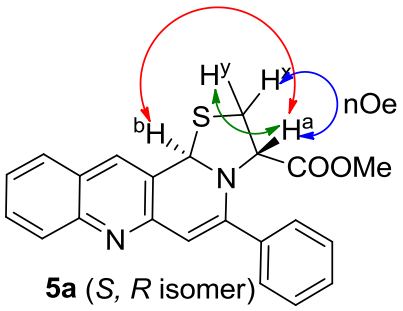
NOESY



5a (*S, R* isomer)

5a (expanded form)





5a (*S, R* isomer)

(Full View of NOESY Spectra of Compound **5a**)